Supporting Information

Polyfunctional Imidazolium Aryloxide Betaine / Lewis Acid Catalysts as Tool for the Asymmetric Synthesis of Disfavored Diastereomers

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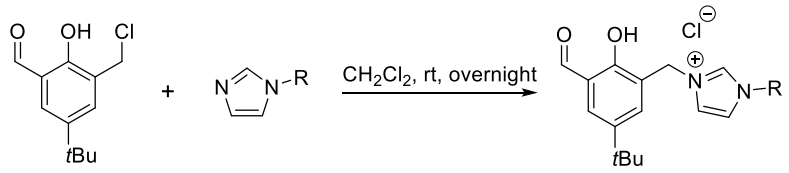
General Remarks

All air and moisture sensitive reactions were performed in oven-dried glassware (150 °C and heated to 630 °C for several min under high vacuum) and under a positive pressure of nitrogen (ca. 0.2 bar). Liquids were added *via* syringe, solids were added neat against a nitrogen flow. Solvents were removed using a rotary evaporator (40 °C water bath). Non-volatile compounds were dried *in vacuo* at 0.03 mbar and freeze-dried using liquid nitrogen. Technical grade solvents (dichloromethane, petroleum ether, diethyl ether, tetrahydrofuran and toluene) were distilled before use. Anhydrous solvents (acetonitrile, tetrahydrofuran, toluene, dichloromethane) were dried in a solvent purification system (*MBraun MB SPS-800*). Purchased chemicals were used without further purification. For catalytic enantioselective reactions were carried out in a parallel synthesizer (*Heidolph Synthesis 1*, shaking at 450 rpm) in some cases and are annotated. $Ni(acac)_2$ was dried in a Kugelrohr distilliation apparatus under reduced pressure (0.01 mbar) at 100 °C for 1 h. The aldehyde **7** was synthesized according to the literature of *Nayak et al.*[1] *Trans*-β-nitrostyrene **2A,** *trans*-3-methoxy-β-nitrosytrene **2O**, *trans*-2-methoxy-β-nitrostyrene **2P**, *trans*-4-methoxy-β-nitrostyrene **2N**, 3,4-methylenedioxy-β-nitrosytrene **2Q** were purchased from commercial suppliers (Sigma-Aldrich, Fluorochem) and were used without further purification. 1-Nitro-4-phenylbutadiene **2T** was synthesized according to a procedure of *Lautens et al*.,[2] benzyl (*E*)-β-nitroacrylate **2Z** was synthesized according to the literature,[3] (*E*)-(2-nitrovinyl)cyclopropane **2W** was synthesized according to literature[4] and all other nitroolefins were synthesized according to literature known procedures.[5,6] Ethyl 2-oxocyclopentanecarboxylate **1a**, methyl 2-oxocyclopentanecarboxylate **1b**, dimethyl malonate **1i** and ethyl 2-oxocyclohexanecarboxylate **1e** were purchased from commercial suppliers (Sigma-Aldrich, Alfa Aesar). According to the literature the ketoesters, isopropyl 2-oxocyclohexanecarboxylate **1c**,[7] methyl 2-methylacetoacetate **1h**,[8] ethyl 2-oxocycloheptanecarboxylate **1f**,[9] ethyl 2-oxocyclooctanecarboxylate **1g**,[9] ethyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate **1d**,[10] ethyl 1-methyl-2-oxopyrrolidine-3-carboxylate **1j**[11]**,** ethyl 1-methyl-2,5-dioxopyrrolidine-3-carboxylate **1k**[12] and ethyl 2-oxocyclohex-3-ene-1-carboxylate **1l**[13] were synthesized. The α,β-disubstituted nitroolefins **3A-Me**, **3B-Me**, **3C-Me**, **3E-Me**, **3I-Me** and **3K-Me** were synthesized according to the Literature.[14] Yields refer to purified compounds. Except as indicated otherwise, reactions were magnetically stirred and monitored by NMR-spectroscopy or thin layer-chromatography (TLC) using silica gel plates (silica gel 60 F_{254}). Visualization occurred by fluorescence quenching under UV light and/or by staining with $KMnO_4$/NaOH. Purification by flash-chromatography was performed on silica gel 60 (40-63 µm particle size), using a forced flow of eluent at 0.2-0.4 bar overpressure. NMR spectra were recorded at room temperature on spectrometers (*Bruker Avance*) operating at 700, 500, 400 or 300 *MHz* (^{1}H), 176,

125, 100 or 75 MHz (^{13}C) and 376 *MHz* (^{19}F). Chemical shifts δ are referred in terms of ppm, coupling constants *J* are given in Hz. The following abbreviations classify the multiplicity: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *quint* = quintet, *sept* = septet, *m* = multiplet (denotes a complex pattern), *dd* = doublet of doublets, *dt* = doublet of triplets, *td* = triplet of doublets and *br* = broad signal. Infrared spectra were recorded by the IR service of the University of Stuttgart on an FT-IR spectrometer (*Bruker Alpha FT-IR*) with an ATR unit and the signals are given by wavenumbers (cm^{-1}). Optical rotation was measured on a polarimeter operating at the sodium D line with a 100 mm path cell length. Melting points were measured using a melting point apparatus (*Büchi 535*) in open glass capillaries and are uncorrected. Mass spectra (*Finnigan MAT95* for EI- or CI-measurements, *Bruker Daltonics micrOTOF-Q* for ESI-measurements) were obtained from the MS service of the University of Stuttgart. Ionization methods are stated in parentheses. The UV-Vis spectra were recorded with a Lambda 365-Spectrometer (PerkinElmer). EPR spectra in the X band were recorded with a Bruker System EMX at 108 K in THF. Enantiomeric excesses (*ee*) were determined by high performance liquid chromatography (HPLC) using an *Elite LaChrom* System with *HITACHI*-modules and chiral stationary phase HPLC columns (*Daicel Chiralpak ODH, ADH, ASH*). Single crystal X-ray analysis was performed by Dr. Wolfgang Frey (University of Stuttgart).

General Procedures

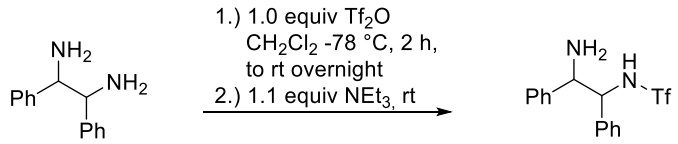
General Procedure for the Imidazolium Synthesis (GP1)



7 **Im** **AId**

To a solution of the corresponding imidazole **Im** (1.0 equiv) in dichloromethane or acetonitrile (*c* = 0.2 to 0.1 mol/L) was added the chloromethylated aldehyde **7** (1.0 equiv) and the reaction mixture was stirred at room temperature overnight. The reaction mixture was concentrated under reduced pressure, the residue redissolved in a small amount of dichloromethane (10 mL/mmol) and the solution was added to a stirred solution of diethylether (80-100 ml/mmol) to cause precipitation. The precipitate was filtered, washed with diethylether and the resulting solid was dried *in vacuo*.

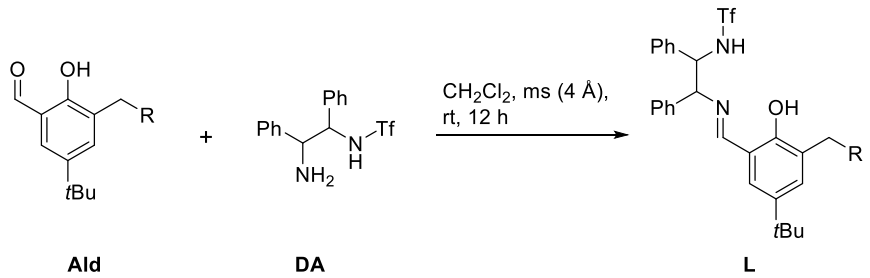
General Procedure for the Synthesis of Trifluoromethylsulfonamides (GP2)



DA **9**

The 1,2-diphenylethane-1,2-diamine **DA** (1.0 equiv) was dissolved in anhydrous dichloromethane (*c* = 0.10-0.15 mol/L) and cooled to -78 °C under N_2-atmosphere. Afterwards trifluoromethanesulfonic anhydride (1.0 equiv, 1 M in dichloromethane) was added *via* a syringe pump (1 mL/h). The reaction mixture was stirred for 1 h at -78 °C and was warmed to room temperature overnight. The reaction was quenched by adding water (2 mL/mmol) and triethylamine (1.1 equiv). The layers were separated, the aqueous layer was extracted with dichloromethane (2x10 mL/mmol), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified *via* column chromatography with CH_2Cl_2/MeOH as eluent (30/1 → 15/1, R_f(10/1) = 0.2) and was isolated as a white solid.

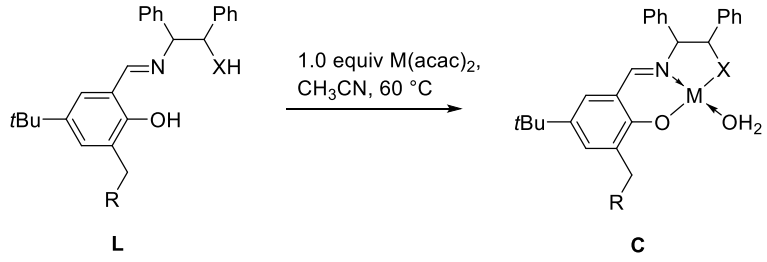
General procedure for the Imine-Synthesis (GP3)



Ald **DA** **L**

A mixture of the corresponding aldehyde **Ald** (1.0 equiv) and the corresponding amine **9** (1.0 equiv) was dissolved in anhydrous dichloromethane (*c* = 0.02-0.05 mol/L) under nitrogen atmosphere. To the reaction mixture was added molecular sieves (4Å) and the mixture was stirred for 12 h at ambient temperature. The molecular sieves were removed *via* filtration through a pad of celite®, they were washed with dichloromethane and the solvent of the solution was removed under reduced pressure. The residue was dissolved again in dichloromethane (1 to 2 mL/mmol) and the product was precipitated by adding this solution to a stirred solution of diethylether (150 mL/g crude product). The solid was filtered off, washed with diethylether (50 mL/g crude product) and dried *in vacuo* to yield a yellow solid, which was used in the following steps without further purification.

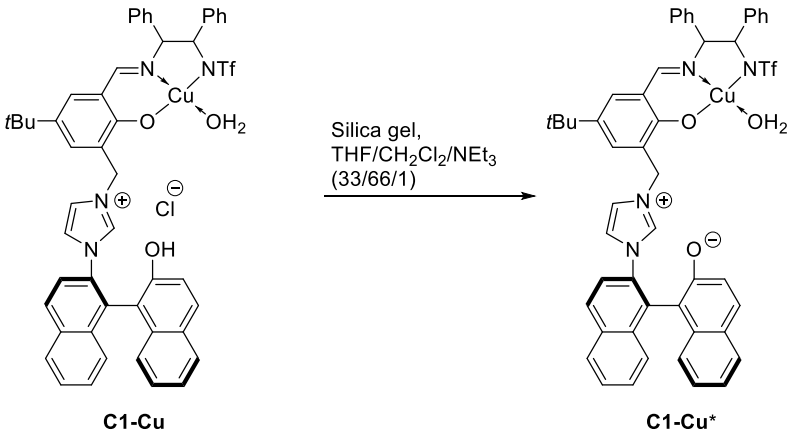
General Procedure for the Complexation (GP4)



L **C**

The ligand **L** (1.0 equiv) was dissolved in anhydrous acetonitrile (*c* = 0.02-0.05 mol/L) and the corresponding metal source (1.0 equiv) was added in one portion to the stirred solution under nitrogen atmosphere at room temperature. The reaction mixture was heated to 60 °C and stirred for 12-14 h. Afterwards the solution was filtered over a small pad of celite®, the filter cake was washed with dichlormethane (20 mL/mmol) and the solvent was removed under reduced pressure. The residue was dissolved in a small amount of dichloromethane and the product was precipitated by adding this solution to pentane (100 mL/g crude product). The solid was filtered off, washed with pentane (20 mL/g crude product) and dried *in vacuo*.

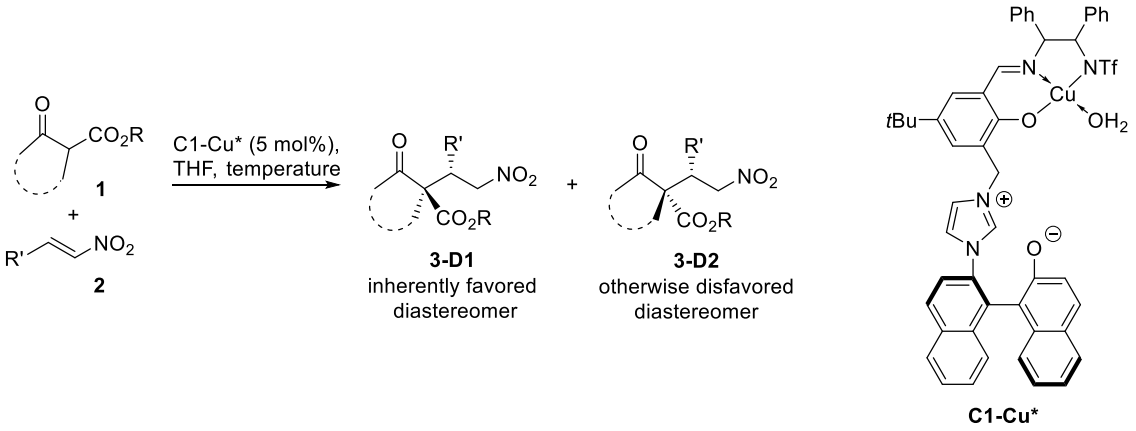
General Procedure for the Activation of the Complexes (GP5)



C1-Cu **C1-Cu***

The complexes **C1-Cu** were dissolved in a solvent mixture of THF/ CH_2Cl_2/NEt_3 (33/66/1, 1 mL/50 mg complex) and the solution was filtered over to a small silica pad (5 cm, Ø 2.5 cm) in a glass frit. The activated complex was eluted by the THF/ CH_2Cl_2/NEt_3 mixture (33/66/1, 30 to 50 mL/50 mg complex). The volatiles were removed under reduced pressure and the product **C1-Cu*** was dried under high vacuum for 1 hour. The activated catalyst could be used without further purification in the catalytic Michael additions.

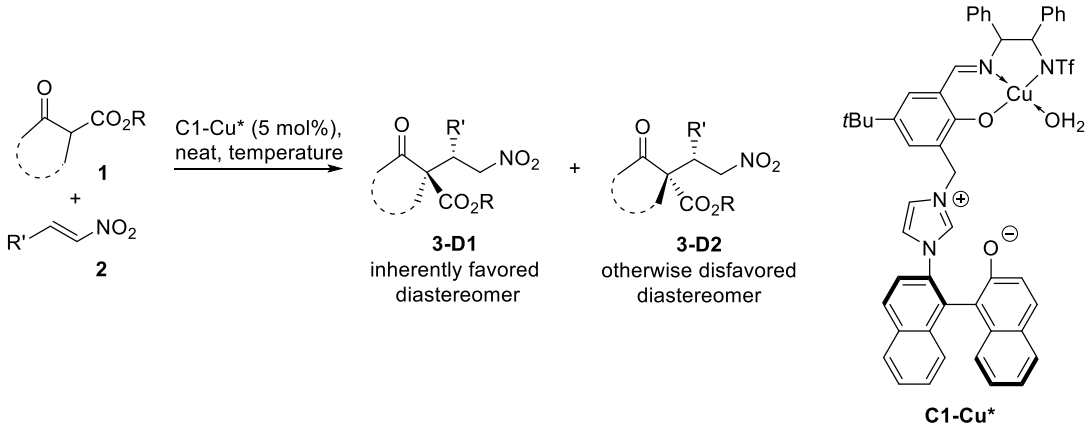
General Procedure for the Catalytic Reaction under Standard Conditions (GP6-standard)



In a synthesizer tube was added a solution of the corresponding nitroolefin **2** (0.20 mmol, 1.0 equiv) in THF (0.1 mL) at -20 °C under a nitrogen atmosphere. The activated catalyst **C1-Cu*** (9.32 mg, 0.01 mmol, 5 mol%) was added as a stock solution (0.1 mL) in THF and the reactions mixture was shaken for 5 min (450 rpm). The corresponding Michael-donor **1** (0.22 mmol, 1.1 equiv) was added plus additional solvent (0.2 mL) to avoid loss of material at the glass wall. The reaction mixture was shaken at -20 °C for the appropriate time using a parallel synthesizer system (*Heidolph Synthesis 1*, shaking at 450 rpm). Afterwards the reaction mixture was diluted with a solvent mixture of petroleum ether/ethyl acetate (1/1,

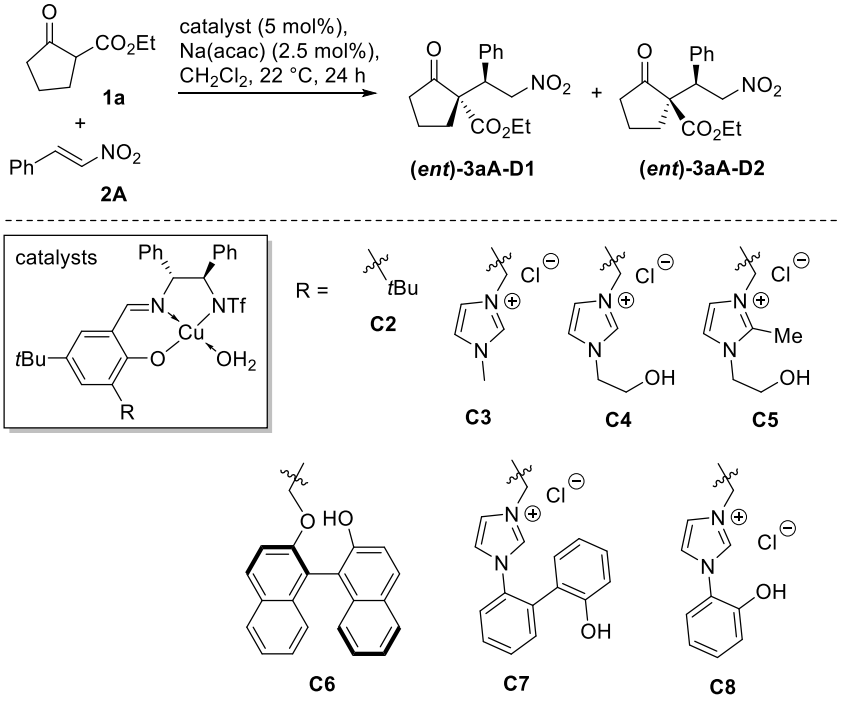
1-2 mL), filtered through a small pad of silica to separate the catalyst from the reaction mixture and the crude product was eluted with additional petroleum ether/ethyl acetate (1/1, 5 mL). After the removal of the solvent under reduced pressure the crude product was purified *via* column chromatography with petroleum ether/ethyl acetate as eluent (10/1→ 5/1) to yield the pure product.

General Procedure for Catalytic Reaction under Neat Conditions (GP6-neat)



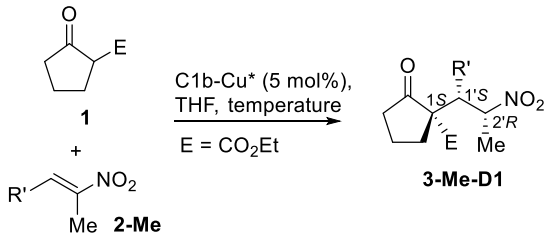
The corresponding nitroolefin **2** (0.2 mmol, 1.0 equiv) and the activated catalyst **C1-Cu*** (9.32 mg, 0.01 mmol, 5 mol%) were added to the liquid Michael-Donor **1** (0.4 mmol, 2.0 equiv) in a catalysis vial fitted with a magnetic stir bar at the corresponding temperature under nitrogen atmosphere. The reaction mixture was stirred at the corresponding temperature for the given time in a catalysis tube. Afterwards the reaction mixture was diluted with a solvent mixture of petroleum ether/ethyl acetate (1/1, 1-2 mL), filtered through a small pad of silica to remove the catalyst from the reaction mixture and the crude product was eluted with additional petroleum ether/ethyl acetate (1/1, 5 mL). After the removal of the solvent under reduced pressure the crude product was purified *via* column chromatography with petroleum ether/ethyl acetate as eluent (10/1→ 5/1) to yield the pure product.

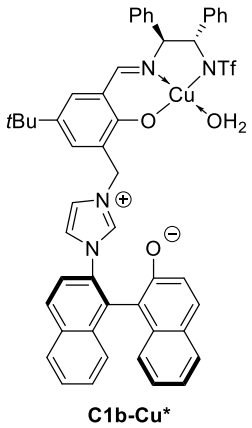
General Procedure for the Catalytic Reaction with External Base (GP6-control)



The corresponding catalyst **C3-C9** (5 mol%) and the corresponding base (2.5 mol%) was added to a catalysis tube with CH_2Cl_2 (0.05 mL) at room temperature. Afterwards the *trans*-β-nitrostyrene **2A** (7.46 mg, 0.050 mmol, 1.0 equiv) and the β-ketoester **1a** (8.59 mg, 0.055 mmol, 1.1 equiv) were added as separate stock solutions in CH_2Cl_2 (each 0.1 mL) and the reaction mixture was stirred 24 h at room temperature. Then the reaction mixture was diluted with a solvent mixture of petroleum ether/ethyl acetate (1/1, 1 mL), filtered through a small pad of silica and the crude product was eluted with additional petroleum ether/ethyl acetate (1/1, 5 mL). After the removal of the solvent under reduced pressure, the crude product was purified *via* preparative TLC (petroleum ether/ethyl acetate, 5/1).

General Procedure for the Catalytic Reaction with α,β-Substituted Nitroolefins (GP7)

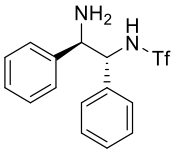




The activated catalyst **C1b-Cu*** (9.32 mg, 0.01 mmol, 5 mol%) was added as a stock solution (0.1 mL) in anhydrous THF to a catalysis tube fitted with a magnetic stirring bar under nitrogen atmosphere. Afterwards the corresponding nitroolefin **2-Me** (0.20 mmol, 1.0 equiv) was added and the reaction mixture was cooled to 0 °C. The corresponding Michael-donor **1** (0.40 mmol, 2.0 equiv) was added plus additional solvent (0.1 mL) to avoid loss of material at the glass wall and the reaction mixture was stirred at 0 °C for the appropriate time. Afterwards the reaction mixture was diluted with a solvent mixture of petroleum ether/ethyl acetate (1/1, 1-2 mL), filtered through a small pad of silica to separate the catalyst from the reaction mixture and the crude product was eluted with additional petroleum ether/ethyl acetate (1/1, 5 mL). After the removal of the solvent under reduced pressure the crude product was purified *via* column chromatography with petroleum ether/ethyl acetate as eluent (10/1→ 5/1) to yield the pure product (possible impurities of remaining **1** can be removed using high vacuum at 100 °C in a Kugelrohr apparatus for 1 h).

Synthesis of Sulfonamides

***N*-((1*R*,2*R*)-2-Amino-1,2-diphenylethyl)-1,1,1-trifluoromethanesulfonamide (9a)**

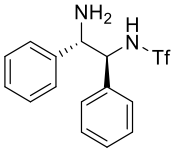


9a

9a was prepared according to **GP2**, using (1*R*,2*R*)-1,2-diphenylethylenediamine (0.178 g, 0.838 mmol, 1.0 equiv) and trifluoromethanesulfonic anhydride (0.838 mL, 0.670 g, 0.838 mmol, 1 M in dichloromethane) in anhydrous dichloromethane (8 mL). The reaction was quenched with water (2 mL) and triethylamine (0.128 mL, 0.093 g, 1.1 equiv). After purification *via* column chromatography, the product **9a** was isolated as a white solid (0.226 g, 0.656 mmol, 78%)

$C_{15}H_{15}F_3N_2O_2S$. MW: 344.35 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.44-7.28 (*m*, 10H, Ar*H*), 4.71 (*d*, 1H, *J* = 3.0 Hz, C*H*NHTf), 4.41 (*d*, 1H, *J* = 3.0 Hz, C*H*NH_2), 3.05 (*br*, 3H, NH_2 and N*H*Tf).
The analytical data of **9a** is in agreement with the literature.[15]

***N*-((1*S*,2*S*)-2-Amino-1,2-diphenylethyl)-1,1,1-trifluoromethanesulfonamide (9b)**



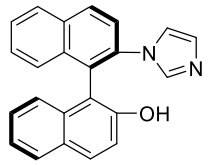
9b

9b was prepared according to **GP2**, using (1*S*,2*S*)-1,2-diphenylethylenediamine (0.504 g, 2.37 mmol, 1.0 equiv) and trifluoromethanesulfonic anhydride (2.37 mL, 0.670 g, 2.37 mmol, 1 M in dichloromethane) in anhydrous dichloromethane (25 mL). The reaction was quenched with water (5 mL) and triethylamine (0.36 mL, 0.264 g, 1.1 equiv). After purification *via* column chromatography, the product **9b** was isolated as a white solid (0.623 g, 1.81 mmol, 76%).

$C_{15}H_{15}F_3N_2O_2S$. MW: 344.35 g/mol.**^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.44-7.28 (*m*, 10H, Ar*H*), 4.71 (*d*, 1H, *J* = 3.0 Hz, C*H*NHTf), 4.41 (*d*, 1H, *J* = 3.0 Hz, C*H*NH_2), 3.07 (*br*, 3H, NH_2 and N*H*Tf).
The analytical data of **9b** is in agreement with the literature. [16]

Synthesis of the Imidazols

(*R*)-2-(Imidazol-1-yl)-2'-hydroxy-1,1'-binaphthyl (6)



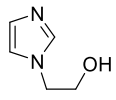
6

Imidazole derivative **6** was synthesized according to procedure by *Crabtree et al.*[17] (*R*)-2,2- Diamino-1,1'-binaphthyl **5** (0.807 g, 2,84 mmol, 1.0 equiv) was added to 20 mL of demineralized water, followed by two drops of concentrated H_3PO_4 and the reaction mixture was stirred for 5 min at room temperature. Afterwards 40% aqueous glyoxal solution (1.62 mL, 2.058 g, 14.18 mmol, 5.0 equiv), paraformaldehyde (0.426 g, 14.18 mmol, 5 equiv) and dioxane (20 mL) were added. The reaction mixture was heated to 80 °C, ammonium chloride (0.759 g, 14.2 mmol, 5.0 equiv) was added and refluxing was continued for 5 h. After cooling to room temperature, the mixture was treated with 20 mL of saturated K_2CO_3-solution and the product was extracted with dichloromethane (3x20 mL). The combined organic fractions were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude product was purified *via* column chromatography on silica gel (acetone/MeOH, 10/1) to yield the pure product **6** as a slightly yellow solid (0.529 g, 1.57 mmol, 55%).

$C_{23}H_{16}N_2O$. MW: 336.39 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 11.46 (*br*, 1H, O*H*), 8,06 (*d*, 1H, *J* = 8.5 Hz, Ar*H*), 7.99 (*d*, 1H, *J* = 8.1 Hz, Ar*H*), 7.87-7.79 (*m*, 2H, NC*H*N and Ar*H*), 7.60-7.49 (*m*, 3H, Ar*H*), 7.45-7.33 (*m*, 2H, Ar*H*), 7.32-7.24 (*m*, 1H, Ar*H*), 7.22-7.14 (*m*, 1H, Ar*H*), 6.89 (*d*, 1H, *J* = 8.0 Hz, Ar*H*), 6.86 (*m*, 1H, C*H*N), 6.83 (*m*, 1H, C*H*N), 6.74 (*d*, *J* = 8.58 Hz, 1H, Ar*H*).

The analytical data of **6** is in agreement with the literature.[17]

2-(1H-Imidazol-1-yl)ethan-1-ol (15)



15

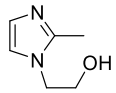
Imidazole (0.60 g, 8.81 mmol, 1.0 equiv) was added to a solution of NaOEt (1.44 g, 21.15 mmol, 2.4 equiv) in absolute ethanol (10 mL) and heated for 30 min to reflux. Subsequently, 2-chloroethanol (1.18 mL, 1.42 g, 17.63 mmol, 2.0 equiv) was added dropwise to the reaction mixture and refluxing was continued for 12 h. The resulting suspension was filtered and the solvent was removed under reduced pressure to

yield a sticky oil. The crude product was purified *via* column chromatography on silica (EE/MeOH 10/1 to 5/1) to yield product **15** as slightly yellow oil (0.298 g, 2.64 mmol, 30%).

$C_5H_8N_2O$. MW: 112.13 g/mol. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.33 (*s*, 1H, NC*H*N), 6.92-6.84 (*m*, 2H, NC*HCH*N), 4.38 (*br*, 1H, O*H*), 4.02 (*t*, 2H, *J* = 5.3 Hz, CH_2), 3.85 ((*t*, 2H, *J* = 5.3 Hz, CH_2).

The analytical data of **15** is in agreement with the literature.[18]

2-(2-Methyl-1H-imidazol-1-yl)ethan-1-ol (16)

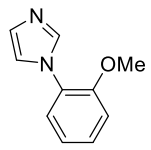


16

2-Methyl-1H-imidazole (0.852 g, 10.37 mmol, 1.0 equiv), dissolved in anhydrous DMF (2 mL), was added dropwise to a suspension of NaH (0.453 g, 10.37 mmol, 1.0 eq) in anhydrous DMF (10 mL). The mixture was stirred for 60 min at 90 °C, then cooled to 0 °C. 2-chloroethanol (0.696 mL, 0.835 g, 10.37 mmol, 1.0 equiv), dissolved in anhydrous DMF (2 mL), was added dropwise and the mixture was heated again to 90 °C for 12 h. The resulting suspension was filtered, the filter cake was washed with 10 mL ethanol and the solvent was removed under reduced pressure. The crude product was purified *via* column chromatography on silica (EE/MeOH 15/1 to 5/1). The isolated material still contained 5% starting material as an impurity which was removed *via* Kugelrohr distillation (100 °C, 3.5x10^{-1} mbar). The analytically pure product **16** (0.943 g, 8.42 mmol, 81%) was isolated as a slightly yellow solid.

$C_6H_{10}N_2O$. MW: 126.16 g/mol. **MP** = 80-81 °C. **^{1}H NMR (400 MHz, CD_3OD)**: δ = 7.01 (*d*, 1H, *J* = 1.5 Hz, NC*H*), 6.80 (*d*, 1H, *J* = 1.5 Hz, NC*H*), 4.01 (*t*, 2H, *J* = 5.2 Hz, CH_2N), 3.78 (*t*, 2H, *J* = 5.2 Hz, CH_2OH), 2.37 (*s*, 3H, CH_3). **^{13}C NMR (100 MHz, CD_3OD)**: δ = 146.3, 126.7, 121.1, 62.4, 12.6. **IR (solid)**: $\tilde{\nu}$ = 3127, 3106, 2963, 2932, 2828, 1530, 1501, 1425, 1352, 1291, 1073, 761, 682 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_6H_{11}N_2O]^+$ 127.0866, measured 127.0858.

1-(2-Methoxyphenyl)-1H-imidazole (17)



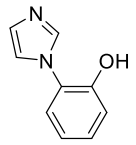
17

An aqueous solution of formaldehyde (2.11 mL, 28.4 mmol, 1.0 equiv, 37% in water) and an aqueous solution of glyoxal (3.25 mL, 28.4 mmol, 1.0 equiv, 40% in water) were dissolved in acetic acid (10 mL) and the resulting solution was heated to 70 °C. *o*-Anisidine (3.20 mL, 28.4 mmol, 1.0 equiv), ammonium acetate (2.19 g, 28.4 mmol, 1.0 equiv) and acetic acid (10 mL) were suspended in a beaker and added to the reaction. The beaker was rinsed with a mixture of water (1 mL) and acetic acid (3 mL) transferring all material to the reaction mixture, which was stirred at 70 °C overnight. The mixture was cooled to room temperature and was poured in a saturated aqueous $NaHCO_3$ (200 mL). A small amount of potassium hydroxide was added to raise the pH over 8 and the suspension was extracted with THF (3x100 mL), the combined organic layers were washed with brine and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified *via* column chromatography on silica (CH_2Cl_2/MeOH 60/1 to 40/1) to yield **17** as a brownish oil (2.50 g, 14.35 mmol, 51%).

$C_{10}H_{10}N_2O$. MW: 174.20 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.78 (*t*, 1H, *J* = 1.1 Hz, NC*H*N), 7.39-7.31 (*m*, 1H, Ar*H*), 7.28 (*dd*, 1H, *J* = 7.8 Hz, 1.6 Hz, Ar*H*), 7.20 (*t*, 1H, *J* = 1.1 Hz, NC*H*), 7.16 (*t*, 1H, *J* = 1.1 Hz, NC*H*), 7.07-7.00 (*m*, 2H, Ar*H*), 3.84 (*s*, 3H, OCH_3).

The analytical data of **17** is in agreement with the literature.[19]

2-(1H-Imidazol-1-yl)phenol (18)



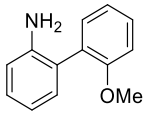
18

To 1-(2-methoxyphenyl)-1H-imidazole **17** (2.50 g, 14.35 mmol, 1.0 equiv) was added 47% aqueous hydrobromic acid (16.7 mL, 24.71 g, 143.51 mmol, 10.0 equiv) and the mixture was refluxed for 48 h under N_2-atmosphere. After 24 h additional 47% aqueous hydrobromic acid (16.7 mL, 24.71 g, 143.51 mmol, 10 equiv) was added. Afterwards the reaction mixture was neutralized by adding saturated aqueous $NaHCO_3$ (300 mL), the product precipitated as a beige solid and was collected by filtration. The crude product was purified *via* Soxhlet extraction using chloroform (100 mL) as solvent. The pure product precipitated in the still pot, was filtered off, washed with chloroform (50 mL) and dried *in vacuo*. The product **18** was isolated as a greyish solid (0.851 g, 5.31 mmol, 37%).

$C_9H_8N_2O$. MW: 160.17 g/mol. **^{1}H NMR (300 MHz, DMSO)**: δ = 10.24 (*s*, 1H, O*H*), 7.92 (*t*, 1H, *J* = 1.1 Hz, NC*H*N), 7.44 (*t*, 1H, *J* = 1.1 Hz, NC*H*), 7.32 (*dd*, 1H, *J* = 7.9 Hz, 1.6 Hz, Ar*H*), 7.25-7.18 (*m*, 1H, Ar*H*), 7.08-7.02 (*m*, 2H, Ar*H* and NC*H*), 6.94-6.87 (*m*, 1H, Ar*H*).

The analytical data of **18** is in agreement with the literature.[20]

2'-Methoxy-[1,1'-biphenyl]-2-amine (19)



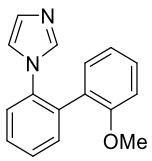
19

The preparation of **19** was performed as described in the literature.[21] To a 50 mL round bottom flask was added K_2CO_3 (1.96 g, 14.2 mmol, 2.0 equiv), $Pd(PPh_3)_4$ (0.164 g, 0.142 mmol, 2 mol%), 2-bromoaniline (0.80 mL, 1.22 g, 0.709 mmol, 1.0 equiv), 2-methoxyphenylboronic acid (1.62 g, 1.06 mmol, 1.5 equiv), demineralized water (2 mL), THF (14 mL), and toluene (3.5 mL). The reaction mixture was stirred for 12 h at 80 °C. Afterwards the reaction mixture was concentrated under reduced pressure and the residue was extracted with ethyl acetate (3x30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified *via* column chromatography (petroleum ether/ethyl acetate, 5/1 to 3/1) to yield the product **19** as a white solid (0.784 g, 3.93 mmol, 56%).

$C_{13}H_{13}NO$. MW: 199.25 g/mol. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.36 (*m*, 1H, Ar*H*), 7.27 (*d,* 1H, *J* = 8.3 Hz, Ar*H*), 7.18 (*t,* 1H, *J* = 7.8 Hz, Ar*H*), 7.11 (*d,* 1H, *J* = 7.5 Hz, Ar*H*), 7.05 (*t,* 1H, *J* = 7.4 Hz, Ar*H*), 7.01 (*d,* 1H, *J* = 8.2 Hz, Ar*H*), 6.84 (*t,* 1H, *J* = 7.5 Hz, Ar*H*), 6.78 (*d,* 1H, *J* = 8.0 Hz, Ar*H*), 3.81 7.01 (*s,* 3H, ArOCH_3), 3.68 (*s,* 2H, Ar-NH_2).

The analytical data of **14** is in agreement with the literature.[21]

1-(2'-Methoxy-[1,1'-biphenyl]-2-yl)-1H-imidazole (20)



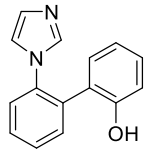
20

Amine **19** (559 mg, 2.80 mmol, 1.0 equiv) was dissolved in methanol (5.0 mL) in a 50 mL round-bottomed flask, then glyoxal (322 mL, 407 mg, 2.80 mmol, 1.0 equiv, 40% in water) was added and the reaction

mixture was stirred for 2 h at room temperature. Afterwards ammonium chloride (300 mg, 5.61 mmol, 2.0 equiv) followed by paraformaldehyde (417 mL, 455 mg, 5.61 mmol, 2.0 equiv, 37% in water) were added and the reaction mixture was refluxed for one hour. Then phosphoric acid (3.78 mL, 646 mg, 0.561 mmol, 2.0 equiv 85% in water) was added and refluxing was continued for 12 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was basicified with 40% aqueous potassium hydroxide. The aqueous mixture was extracted with CH_2Cl_2 (3x30 mL), the combined organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified *via* column chromatography (CH_2Cl_2/MeOH, 30/1 to 20/1) and the product **20** was isolated as yellowish oil (0.139 g, 0.555 mmol, 20%).

$C_{16}H_{14}N_2O$. MW: 250.30 g/mol. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.49-7.41 (*m*, 3H, Ar*H*), 7.40-7.34 (*m*, 2H, NC*H*N and Ar*H*), 7.31-7.27 (*m*, 1H, Ar*H*), 7.17 (*dd,* 1H, *J* = 7.5, 1.7 Hz, Ar*H*), 6.97 (*t,* 1H, *J* = 7.5 Hz, Ar*H*), 6.92 (*s*, 1H, NC*H*CHN), 6.80-6.76 (*m*, 2H, NCHC*H*N and Ar*H*), 3.49 (*s,* 3H, ArOCH_3). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 156.5, 137.4, 136.6, 134.5, 132.2, 130.9, 129.8, 128.69, 128.67, 128.2, 127.1, 125.4, 120.9., 120.1, 110.7, 55.3. **IR (solid)**: $\tilde{\nu}$ = 3394, 3115, 3067, 2927, 2836, 2156, 1596, 1508, 1461, 1434, 1296, 1275, 1245, 1118, 1059, 1025, 757 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{16}H_{15}N_2O]^+$ 251.1179, measured 251.1185.

2'-(1H-Imidazol-1-yl)-[1,1'-biphenyl]-2-ol (21)



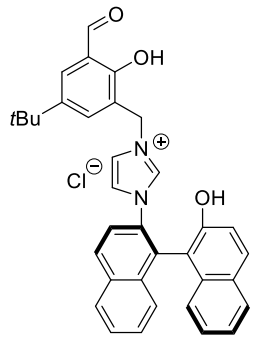
21

Imidazole **20** (139 mg, 0.543 mg, 1.0 equiv) and hydrobromic acid (1.0 mL, 1.50 g, 16.0 equiv, 47% in water) were refluxed for 48 h. The reaction mixture was neutralized with saturated aqueous $NaHCO_3$-solution (5 mL) and the aqueous suspension was extracted with CH_2Cl_2 (3x5 mL). After drying over $MgSO_4$, the solvent was removed under reduced pressure to yield the pure product **21** as a slightly brown solid (126 mg, 0.533 mmol, 98%).

$C_{15}H_{12}N_2O$. MW: 236.27 g/mol. **MP** = 190-191 °C. **^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 10.63 (br, 1H, ArO*H*), 7.61 (*s*, 1H, NC*H*N), 7.52-7.46 (*m*, 3H, Ar*H*), 7.36 (*d,* 1H, *J* = 7.8 Hz, Ar*H*), 7.18-712 (*m*, 2H, Ar*H*), 6.88-6.81 (*m*, 3H, NC*H*CHN and Ar*H*), 6.69 (*s*, 1H, NC*H*CHN). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 155.3, 137.5, 136.4, 135.9, 132.1, 130.7, 129.7, 128.9, 128.5, 126.9, 125.8, 125.7, 120.7, 119.4, 116.2. **IR (solid)**: $\tilde{\nu}$ = 3061, 2926, 2854, 2692, 2590, 1730, 1594, 1506, 1444, 1400, 1290, 1240, 1107, 1063, 755, 733 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{15}H_{13}N_2O]^+$ 237.1022, measured 237.1011.

Synthesis of the Aldehydes

(*R*)-3-(5-(*tert*-Butyl)-3-formyl-2-hydroxybenzyl)-1-(2'-hydroxy-[1,1'-binaphthalen]-2-yl)-1H-imidazol-3-ium chloride (8)

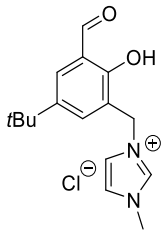


8

Aldehyde **8** was prepared according to **GP1**, using 3-(chloromethyl)-5-(*tert*-butyl)-2-hydroxybenzaldehyde **7** (0.318 g, 1.41 mmol, 1.0 equiv) and (*R*)-2-(imidazol-1-yl)-2'-hydroxy-1,1'-binaphthyl **6** (0.473 g, 1.41 mmol, 1.0 equiv) in dichloromethane (10 mL). The imidazolium salt **8** was isolated as a beige solid (0.789 g, 1.40 mmol, >99%).

$C_{35}H_{31}ClN_2O_3$. MW: 563.09 g/mol. **MP** = 194-195 °C. $[\alpha_D^{20}] = 14.9$ (c = 0.12 g/dl, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 11.06 (*s*, 1H, ArO*H*), 10.13 (*b*, 1H, ArO*H*), 9.86 (*s*, 1H, C*H*O), 9.64 (*s*, 1H, NC*H*N), 8.21 (*d*, 1H, *J* = 2.2 Hz, Ar*H*), 8.03 (*d*, 1H, *J* = 8.2 Hz, Ar*H*), 7.95 (*d*, 1H, *J* = 8.3 Hz, Ar*H*), 7.71 (*t*, 1H, *J* = 3.2 Hz, Ar*H*), 7.59-7.51 (*m*, 3H, Ar*H*), 7.41-7.32 (*m*, 2H, Ar*H*), 7.19 (*t*, 1H, *J* = 7.1 Hz, Ar*H*), 7.13-7.07 (*m*, 1H, Ar*H*), 7.12 (*s*, 1H, NC*H*CHN), 6.80 (*s*, 1H, NCHC*H*N), 6.75 (*d*, 1H, *J* = 8.4 Hz, Ar*H*), 5.56 (*d*, 1H, *J* = 14.0 Hz, ArC*H*H), 5.47 (*d*, 1H, *J* = 14.0 Hz, ArC*H*H), 1.33 (s, 9H, C(CH_3)$_3$). **^{13}C NMR (176 MHz, $CDCl_3$)**: δ = 196.6, 157.4, 153.8, 144.2, 137.7, 137.1, 134.1, 133.5, 133.2, 132.5, 1311.4, 131.3, 130.8, 130.2, 128.5, 128.45, 128.38, 128.1, 127.8, 126.9, 123.4, 123.2, 122.7, 122.4, 121.9, 121.4, 120.4, 120.3, 113.6, 47.9, 34.6, 31.4. **IR (solid)**: $\tilde{\nu}$ = 3053, 2958, 2869, 1651, 1622, 1507, 1478, 1433, 1344, 1274, 1207, 1099, 817, 748, 723, 627 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{35}H_{31}N_2O_3]^+$ 527.2329, measured 527.2332.

3-(5-(*tert*-Butyl)-3-formyl-2-hydroxybenzyl)-1-methyl-1H-imidazol-3-ium chloride (22)



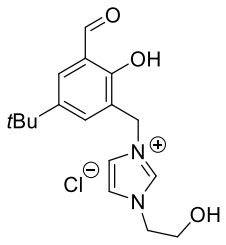
22

Aldehyde **22** was prepared according to **GP1**, using 3-(chloromethyl)-5-(*tert*-butyl)-2-hydroxybenzaldehyde **7** (0.626 g, 2.76 mmol, 1.0 equiv) and 1-methylimidazole (0.228 g, 2.76 mmol, 1.0 equiv) in acetonitrile (10 mL). The imidazolium salt **22** was isolated as a beige solid (0.663 g, 2.15 mmol, 78**%**).

$C_{16}H_{21}ClN_2O_2$. MW: 308.81 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 11.45 (br, 1H, O*H*), 11.24 (s, 1H, NC*H*N), 9.91 (s, 1H, C*H*O), 8.38 (d, 1H, *J* = 2.5 Hz, Ar*H*), 7.61 (d, 1H, *J* = 2.5 Hz, Ar*H*), 7.53 (s, 1H, C*H*N), 7.07 (s, 1H, C*H*N), 5.69 (s, 2H, CH_2), 4.01 (s, 3H, CH_3), 1.37 (s, 9H, C(CH_3)$_3$).

The analytical data of **17** is in agreement with the literature.[22]

3-(5-(*tert*-Butyl)-3-formyl-2-hydroxybenzyl)-1-(2-hydroxyethyl)-1H-imidazol-3-ium chloride (23)



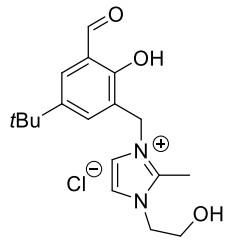
23

Aldehyde **23** was prepared according to **GP1**, using 3-(chloromethyl)-5-(*tert*-butyl)-2-hydroxybenzaldehyde **7** (0.307 g, 1.35 mmol, 1.0 equiv) and 2-(1H-imidazol-1-yl)ethan-1-ol **15** (0.152 g, 1.35 mmol, 1.0 equiv) in acetonitrile (5 mL). The crude product was dissolved in acetone (1 mL) and precipitated in diethylether (30 mL). The product **23** was isolated as a beige solid (0.355 g, 1.04 mmol, 77%).

$C_{17}H_{23}ClN_2O_3$. MW: 338.83 g/mol. **MP** = 207-208 °C. **^{1}H NMR (400 MHz, MeOD)**: δ = 9.97 (*s*, 1H, C*H*O), 9.07 (*s*, 1H, NC*H*N), 7.91-7.84 (*m*, 2H, Ar*H*), 7.65 (s, 1H, NC*H*CHN), 7.61 (s, 1H, NC*H*CHN), 5.47 (s, 2H, ArCH_2), 4.29 (*t*, 2H, *J* = 4.9 Hz, CH_2OH), 3.85 (*t*, 2H, *J* = 4.9 Hz, CH_2CH$_2$OH), 1.37 (s, 9H, C(CH_3)$_3$). **^{13}C NMR (75 MHz,**

$CDCl_3$): δ = 198.9, 158.4, 144.9, 138.1, 136.7, 133.2, 124.1, 123.7, 122.7, 122.1, 61.0, 53.30, 53.28, 35.2, 31.6. **IR (solid)**: $\tilde{\nu}$ = 3130, 3067, 2953, 2861, 1650, 1560, 1469, 1440, 1383, 1270, 1223, 1152, 1063, 1008, 763, 720, 632 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{17}H_{23}N_2O_3]^+$ 303.1703, measured 303.1709

3-(5-(*tert*-Butyl)-3-formyl-2-hydroxybenzyl)-1-(2-hydroxyethyl)-2-methyl-1H-imidazol-3-ium chloride (24)

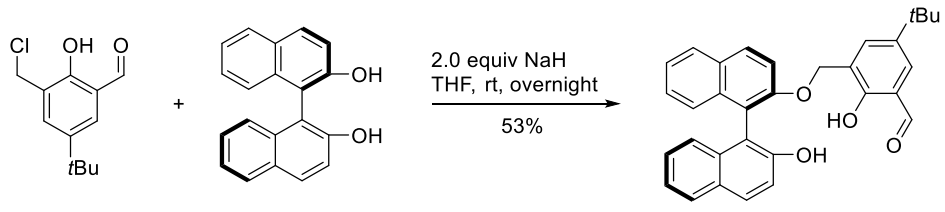


24

Aldehyde **24** was prepared according to **GP1**, using 3-(chloromethyl)-5-(*tert*-butyl)-2-hydroxybenzaldehyde **7** (0.243 g, 1.07 mmol, 1.0 equiv) and 2-(2-methyl-1H-imidazol-1-yl)ethan-1-ol **16** (0.135 g, 1.07 mmol, 1.0 equiv) in acetonitrile (5 mL). The imidazolium salt **24** was isolated as yellow oil (0.275 g, 0.78 mmol, 73%).

$C_{18}H_{25}ClN_2O_3$. MW: 352.86 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 11.19 (*br*, 1H, ArO*H*), 9.88 (*s*, 1H, C*H*O), 7.88 (*d*, 1H, *J* = 2.4 Hz, Ar*H*), 7.58 (*d*, 1H, *J* = 2.4 Hz, Ar*H*), 7.53 (*d*, 1H, *J* = 2.1 Hz, NC*H*CHN), 7.30 (*d*, 1H, *J* = 2.1 Hz, NC*H*CHN), 5.36 (s, 2H, ArCH_2), 4.29 (*t*, 2H, *J* = 5.0 Hz, CH_2OH), 3.87 (*t*, 2H, *J* = 5.0 Hz, C$H_2$$CH_2$OH), 2.85 (*s*, 3H, CC$H_3$), 1.30 (s, 9H, C(C$H_3$)$_3$). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 196.7, 157.5, 144.8, 143.8, 136.4, 131.3, 122.0, 121.5, 121.2, 120.5, 60.3, 51.5, 47.3, 34.4, 31.3, 11.0. **IR (solid)**: $\tilde{\nu}$ = 3280, 2958, 2870, 1651, 1478, 1426, 1385, 1274, 1219, 1075, 1008, 733, 673 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{18}H_{25}N_2O_5]^+$ 317.1860, measured 317.1846.

(*R*)-5-(*tert*-Butyl)-2-hydroxy-3-(((2'-hydroxy-[1,1'-binaphthalen]-2-yl)oxy)methyl)benzaldehyde (25)

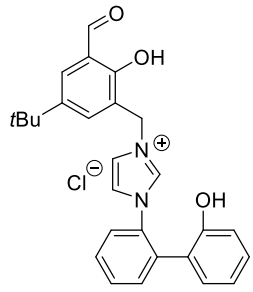


7 **(*R*)-BINOL** **25**

To a stirred suspension of NaH (0.155 g, 3.56 mmol, 2.0 equiv) in anhydrous THF (2.5 mL) in a Schlenk-flask was added a solution of **(*R*)-BINOL** (0.509 g, 1.78 mmol, 1.0 equiv) dissolved in anhydrous THF (3.0 mL). After stirring the reaction mixture for 30 min, a solution of the aldehyde **7** (0.403 g, 1.78 mmol, 1.0 equiv) in anhydrous THF (3.0 mL) was added dropwise and stirring was continued for 12 h at room temperature. Afterwards the solvent was removed under reduced pressure and the residue was redissolved in CH_2Cl_2 (10 mL). The organic layer was washed with aqueous 1 M HCl (2x5 mL), water (5 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified *via* column chromatography on silica with petroleum ether/ethyl acetate (15/1 to 10/1, R_f(6/1) = 0.35) as eluent and the product **25** was isolated as slightly beige foam (0.451 g, 0.95 mmol, 53%).

$C_{32}H_{28}O_4$. MW: 476.56 g/mol. **MP** = 147-148 °C. $[\alpha_D^{20}] = 4.5$ (c = 0.13 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 11.10 (*br*, 1H, O*H*), 9.82 (*s*, 1H, C*H*O), 8:07 (*d*, 1H, *J* = 9.1 Hz, Ar*H*), 7.95-7.82 (*m*, 3H, Ar*H*), 7.62 (*d*, 1H, *J* = 9.1 Hz, Ar*H*), 7.43-7.26 (*m*, 5H, Ar*H*), 7.25-7.08 (*m*, 4H, Ar*H*), 5.52 (*d*, 1H, *J* = 13.2 Hz, ArC*H*H), 5.16 (*d*, 1H, *J* = 13.2 Hz, ArCH*H*), 4.94 (s, 1H, $_{Naphtyl}$O*H*), 1.01 (s, 9H, C(CH_3)$_3$). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 197.0, 156.2, 154.9, 151.4, 142.8, 134.2, 133.9, 132.9, 131.3, 130.0, 129.8, 129.3, 128.6, 128.34, 128.31, 127.5, 126.7, 125.11, 125.07, 125.0, 124.5, 123.4, 119.4, 117.7, 116.1, 115.2, 114.9, 64.7, 34.1, 31.1. **IR (solid)**: $\tilde{\nu}$ = 3428, 3056, 2962, 2868, 1651, 1620, 1592, 1463, 1381, 1265, 1215, 1090, 814, 747, 732 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{32}H_{28}O_4]^+$ 499.1880, measured 499.1872.

3-(5-(*tert*-Butyl)-3-formyl-2-hydroxybenzyl)-1-(2'-hydroxy-[1,1'-biphenyl]-2-yl)-1H-imidazol-3-ium chloride (26)

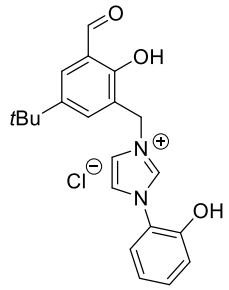


26

Aldehyde **26** was prepared according to **GP1**, using 3-(chloromethyl)-5-(*tert*-butyl)-2-hydroxybenzaldehyde **7** (96.2 mg, 0.424 mmol, 1.0 equiv) and 2'-(1H-Imidazol-1-yl)-[1,1'-biphenyl]-2-ol **21** (100.3 mg, 0.424 mmol, 1.0 equiv) in a solvent mixture of acetonitrile (1 mL) and CH_2Cl_2 (3 mL). The imidazolium salt **26** was isolated as a beige solid (0.105 g, 0.227 mmol, 53%).

$C_{27}H_{27}ClN_2O_3$. MW: 462.97 g/mol. **MP** = 251 °C (decomp.). **^{1}H NMR (400 MHz, MeOD)**: δ = 9.99 (*s*, 1H, C*H*O), 8.84 (*s*, 1H, NC*H*N), 7.87-7.81 (*m*, 2H, Ar*H*), 7.69-7.57 (*m*, 4H, Ar*H*), 7.63 (*t*, 1H, *J* = 1.7 Hz, NC*H*CHN), 7.50 (*d*, 1H, *J* = 7.3 Hz, NCHC*H*N), 7.14 (*d*, *J* = 7.5 Hz, Ar*H*), 7.08 (*t*, *J* = 8.1 Hz, Ar*H*), 6.81 (*t*, *J* = 7.5 Hz, Ar*H*), 6.58 (*d*, *J* = 8.1 Hz, Ar*H*), 5.37 (s, 2H, ArCH_2), 1.38 (s, 9H, C(CH_3)$_3$). **^{13}C NMR (100 MHz, MeOD)**: δ = 199.0, 158.3, 155.3, 144.8, 138.3, 136.7, 136.6, 135.5, 133.4, 133.3, 132.0, 131.8, 131.4, 130.1, 126.6, 125.1, 124.6, 123.1, 122.3,122.1, 121.0,116.3, 49.3, 35.2, 31.6. **IR (solid)**: $\tilde{\nu}$ = 3064, 2959, 1651, 1481, 1445, 1365, 1273, 1219, 1104, 1073, 834, 758, 632 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{27}H_{27}N_2O_3]^+$ 427.2016, measured 427.2030.

3-(5-(*tert*-Butyl)-3-formyl-2-hydroxybenzyl)-1-(2-hydroxyphenyl)-1H-imidazol-3-ium chloride (27)



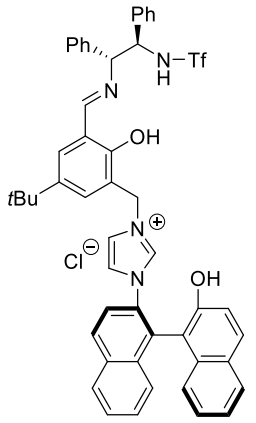
27

Aldehyde **27** was prepared according to **GP1**, using 3-(chloromethyl)-5-(*tert*-butyl)-2-hydroxybenzaldehyde **7** (0.182 g, 0.803 mmol, 1.0 equiv) and 2-(1H-imidazol-1-yl)phenol **18** (0.129 g, 0.803 mmol, 1.0 equiv) in a solvent mixture of CH_2Cl_2 and methanol (10/1, 1.5 mL). The reaction mixture was washed with aqueous 1 M HCl (2x5 mL), the organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. Afterwards the purification of the crude product was continued as described in **GP1** to yield a beige solid (0.171 g, 0.442 mmol, 73%)

$C_{21}H_{23}ClN_2O_3$. MW: 386.88 g/mol. **MP =** 137 °C (decomp.). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 11.39 (*br*, 1H, O*H*), 9.90 (*s*, 1H, C*H*O and *s*, 1H, NC*H*N); 8:35 (*d*, 1H, *J* = 2.1 Hz, Ar*H*), 7.76 (*s*, 1H, C*H*N), 7.63-7.54 (*m*, 2H, Ar*H*), 7.41 (*s*, 1H, C*H*N), 7.22 (*d*, 1H, *J* = 8.4 Hz, Ar*H*), 7.12 (*t*, 1H, *J* = 8.0 Hz, Ar*H*), 6.76 (*t*, 1H, *J* = 8.0 Hz, Ar*H*), 5.72 (*s*, 2H, CH_2), 1.33 (s, 9H, C(CH_3)$_3$). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 196.9, 157.6, 150.8, 144.4, 137.5, 136.3, 131.7, 131.3, 124.1, 123.0, 122.4, 121.8, 121.7, 120.4, 119.9, 119.1, 48.0, 34.6, 31.4 **IR (solid)**: $\tilde{\nu}$ = 3057, 2963, 2868, 1655, 1623, 1456, 1509, 1478, 1433, 1345, 1275, 1216, 1099, 819, 729 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{21}H_{23}N_2O_3]^+$ 351.1703, measured 351.1693.

Synthesis of Imine-Ligands

3-(5-(*tert*-Butyl)-3-((*E*)-(((1*R*,2*R*)-1,2-diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-hydroxybenzyl)-1-((*R*)-2'-hydroxy-[1,1'-binaphthalen]-2-yl)-1H-imidazol-3-ium chloride (L1a)

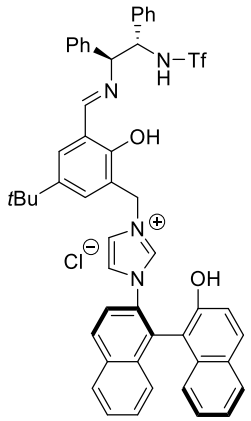


L1a

Imine **L1a** was prepared according to **GP3**, using aldehyde **8** (44.59 mg, 0.0792 mmol, 1.0 equiv), amine **9a** (27.27 mg, 0.0792 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (4 mL). The product **L1a** was isolated as a yellow solid (58.1 mg, 0.0653 mmol, 82%).

$C_{50}H_{44}ClF_3N_4O_4S$. MW: 889.43 g/mol. **MP** = 224-225 °C. $[\alpha_D^{20}] = 120.8$ (c = 0.15 g/dl, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 14.08 (*br*, 1H, ArO*H*), 10.58 (*br*, 1H, N*H*Tf), 9.81 (*br*, 1H, ArO*H*), 9.39 (*s*, 1H, NC*H*N), 8.21 (*s*, 1H, C*H*N), 8.05 (*d*, 1H, *J* = 8.8 Hz, Ar*H*), 7.95 (*d*, 1H, *J* = 8.2 Hz, Ar*H*), 7.87 (*s*, 1H, Ar*H*), 7.65-7.49 (*m*, 5H, Ar*H*), 7.40-7.31 (*m*, 5H, Ar*H*), 7.19-7.04 (*m*, 8H, Ar*H*), 7.01-6.97 (*m*, 2H, Ar*H*), 6.85 (*s*, 1H, NHCC*H*N), 6.79 (*s*, 1H, N*H*CCHN), 6.77 (*d*, 1H, *J* = 8.2 Hz, Ar*H*), 5.64 (*d*, 1H, *J* = 13.8 Hz, ArCH*H*), 5.42 (*d*, 1H, *J* = 10.6 Hz, CNC*H*Ar), 5.29 (*d*, 1H, *J* = 13.8 Hz, ArCH*H*), 4.93 (*d*, 1H, *J* = 10.6 Hz, ArC*H*NHTf), 1.16 (s, 9H, C(C*H*$_3$)$_3$). **^{19}F NMR (376 MHz, $CDCl_3$)**: δ = 78.0. **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 167.8, 157.1, 153.4, 141.7, 140.4, 139.5, 138.3, 136.8, 134.2, 133.6, 133.2, 132.9, 132.4, 131.6, 130.7, 130.1, 129.5, 129.0, 128.6, 128.4, 128.19, 128.17, 128.08, 128.05, 128.0, 127.8, 127.61, 127.60, 126.9, 123.6, 123.1, 122.62, 122.59, 122.4, 120.8., 119.9, 119.5 (*q*, J = 321.8 Hz, *C*F_3), 118.2, 113.8, 73.6, 65.7, 48.3, 34.2, 31.5.**IR (solid)**: $\tilde{\nu}$ = 3143, 3060, 3032, 2962, 2870, 1628, 1509, 1479, 1371, 1275, 1226, 1193, 1147, 1050, 817, 750, 732, 699 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{50}H_{44}F_3N_4O_4S]^+$ 853.3030, measured 853.3032.

3-(5-(*tert*-Butyl)-3-((*E*)-(((1*S*,2*S*)-1,2-diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)-methyl)-2-hydroxybenzyl)-1-((*R*)-2'-hydroxy-[1,1'-binaphthalen]-2-yl)-1H-imidazol-3-ium chloride (L1b)

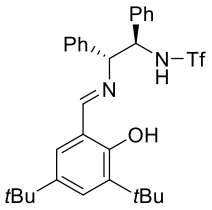


L1b

Imine **L1b** was prepared according to **GP3**, using aldehyde **8** (239.6 mg, 0.425 mmol, 1.0 equiv), amine **9b** (146.5 mg, 0.425 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (20 mL). The product **L1b** was isolated as a yellow solid (360.1 mg, 0.405 mmol, 95%).

$C_{50}H_{44}ClF_3N_4O_4S$. MW: 889.43 g/mol **MP** = 192 °C (decomp.). $[\alpha_D^{20}]$ = 41.8 (c = 0.15 g/dl, CH_2Cl_2). **^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 14.00 (*br*, 1H, ArO*H*), 9.17 (*s*, 1H, NC*H*N), 8.27 (*s*, 1H, C*H*N), 8.01 (*d*, 1H, *J* = 8.7 Hz, Ar*H*), 7.90 (*d*, 1H, *J* = 8.2 Hz, Ar*H*), 7.74-7.63 (*m*, 4H, Ar*H*), 7.54 (*t*, 1H, *J* = 7.2 Hz, Ar*H*), 7.49 (*d*, 1H, *J* = 8.8 Hz, Ar*H*), 7.45-7.31 (*m*, 4H, Ar*H*), 7.22 (*t*, 1H, *J* = 7.2 Hz, Ar*H*), 7.19 (*s*, 1H, N*H*CCHN), 7.16-7.07 (*m*, 7H, Ar*H*), 7.05-7.01 (*m*, 2H, Ar*H*), 6.92 (*s*, 1H, Ar*H*), 6.76 (*d*, 1H, *J* = 8.4 Hz, Ar*H*), 6.69 (*s*, 1H, NHCC*H*N), 5.69 (*d*, 1H, *J* = 13.7 Hz, ArCH*H*), 5.32 (*d*, 1H, *J* = 9.8 Hz, CNC*H*Ar), 5.19 (*d*, 1H, *J* = 13.7 Hz, ArCH*H*), 5.32 (*d*, 1H, *J* = 10.0 Hz, ArC*H*NHTf), 1.08 (s, 9H, C(CH_3)$_3$). **^{19}F NMR (376 MHz, $CDCl_3$)**: δ = 77.6. **^{13}C NMR (176 MHz, $CDCl_3$)**: δ = 167.5, 157.5, 153.3, 141.5, 138.8, 138.2, 136.2, 134.2, 133.5, 133.2, 132.6, 131.8, 131.6, 131.0, 130.1, 130.0, 129.0, 128.8, 128.7, 128.63, 128.56, 128.4, 128.3, 128.2, 128.14, 128.09, 127.9, 127.7, 127.1, 123.5, 123.4, 122.5, 122.42, 122.37, 120.7, 119.8, 119.6 (*q*, J = 321.5 Hz, *C*F_3), 118.7, 118.2, 116.9, 113.3, 74.9, 65.8, 49.1, 34.1, 31.4. **IR (solid)**: $\tilde{\nu}$ = 3058, 3031, 2958, 2866, 1626, 1600, 1478, 1434, 1369, 1345, 1225, 1187, 1145, 1048, 937, 816, 749, 698, 598 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{50}H_{44}F_3N_4O_4S]^+$ 853.3030, measured 853.3008.

***N*-((1*R*,2*R*)-2-(((*E*)-3,5-Di-*tert*-butyl-2-hydroxybenzylidene)amino)-1,2-diphenylethyl)-1,1,1-trifluoromethanesulfonamide (L2)**

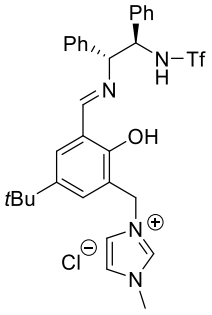


L2

Imine **L2** was prepared according to **GP3**, using 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (42.29 mg, 0.181 mmol, 1.0 equiv), amine **9a** (27.27 mg, 0.181 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (3 mL). The product **L2** was purified *via* column chromatography (petroleum ether/ethyl acetate 20/1 to 10/1) and was isolated as a slightly yellow solid (64.0 mg, 0.114 mmol, 63%).

$C_{30}H_{35}F_3N_2O_3S$. MW: 560.68 g/mol. **MP** = 114-115 °C. $[\alpha_D^{20}] = 18.4$ (c = 0.22 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 12.85 (*br*, 1H, ArO*H*), 8.16 (*s*, 1H, C*H*N), 7.41 (*d*, 1H, *J* = 2.5 Hz, Ar*H*), 7.36-7.22 (*m*, 8H, Ar*H*), 7.13-7.08 (*m*, 2H, Ar*H*), 6.93 (*d*, 1H, *J* = 2.4 Hz, Ar*H*), 5.86 (*br*, 1H, N*H*Tf), 5.04 (*d*, 1H, *J* = 5.0 Hz, CNC*H*Ar), 4.63 (*d*, 1H, *J* = 5.1 Hz, ArC*H*NHTf), 1.47 (s, 9H, C(CH_3)$_3$), 1.25 (s, 9H, C(CH_3)$_3$). **^{19}F NMR (376 MHz, $CDCl_3$)**: δ = 77.5. **^{13}C NMR (176 MHz, $CDCl_3$)**: δ = 169.5, 157.9, 140.8, 138.3, 137.5, 137.1, 129.0, 128.8, 128.5, 128.4, 127.7, 127.0, 126.8, 119.6 (*q*, J = 336.5 Hz, *C*F_3), 117.6, 78.4, 64.8, 35.3, 34.3, 31.5, 29.6. **IR (Solid)**: $\tilde{\nu}$ = 3270, 2958, 1619, 1596, 1455, 1436, 1371, 1228, 1196, 1141, 1048, 1027, 757, 696 cm^{-1}, **HRMS (ESI)** *m/z*: calculated $[C_{30}H_{35}F_3N_2O_3SNa]^+$ 583.2213, measured 583.2301.

3-(5-(*tert*-Butyl)-3-((*E*)-(((1*R*,2*R*)-1,2-diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-hydroxybenzyl)-1-methyl-1H-imidazol-3-ium chloride (L3)

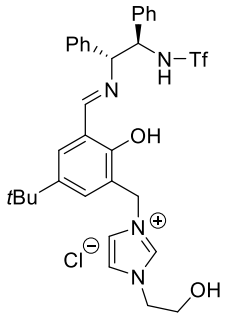


L3

Imine **L3** was prepared according to **GP3**, using 3-(5-(*tert*-butyl)-3-formyl-2-hydroxybenzyl)-1-methyl-1*H*-imidazol-3-ium chloride (31.70 mg, 0.1037 mmol, 1.0 equiv), amine **9a** (35.70 mg, 0.1037 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (3 mL). The product **L3** was isolated as a yellow solid (42.1 mg, 0.0663 mmol, 64%).

$C_{31}H_{34}ClF_3N_4O_3S$. MW: 635.14 g/mol. **MP** = 188-189 °C. $[\alpha_D^{20}] = 114$ (c = 0.15 g/dl, CH_2Cl_2). **^{1}H NMR (400 MHz, MeOD)**: δ = 8.99 (*s*, 1H, NC*H*N), 8.60 (*s*, 1H, C*H*N), 7.68-7.64 (*m*, 2H, Ar*H* and NHCC*H*N), 7.54-7.51 (*m*, 2H, Ar*H* and N*H*CCHN), 7.23-7.14 (*m*, 8H, Ar*H*), 7.12-7.08 (*m*, 2H, Ar*H*), 5.53 (*d*, 1H, *J* = 13.9 Hz, ArCH*H*), 5.38 (*d*, 1H, *J* = 14.0 Hz, ArCH*H*), 4.96 (*d*, 1H, *J* = 9.9 Hz, CNC*H*Ar), 4.62 (*d*, 1H, *J* = 9.8 Hz, ArC*H*NHTf), 3.91 (s, 3H, NCH_3). 1.34 (s, 9H, C(CH_3)$_3$). **^{19}F NMR (376 MHz, MeOD)**: δ = 80.1. **^{13}C NMR (176 MHz, MeOD)**: δ = 168.3, 158.3, 143.5, 140.4, 139.3, 132.5, 131.5, 129.6, 129.4, 129.1, 129.0, 128.7, 124.7, 124.6, 123.9, 123.8, 122.1, 120.9 (*q*, J = 320.6 Hz, *C*F_3), 120.0, 79.6, 66.6, 36.45, 36.42, 35.1, 31.7. **IR (Solid)**: $\tilde{\nu}$ = 2957, 1628, 1455, 1367, 1281, 1225, 1188, 1147, 1049, 955, 758, 699, 598 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{31}H_{34}F_3N_4O_3S]^+$ 599.2298, measured 599.2281.

3-(5-(*tert*-Butyl)-3-((*E*)-(((1*R*,2*R*)-1,2-diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-hydroxybenzyl)-1-(2-hydroxyethyl)-1H-imidazol-3-ium chloride (L4)



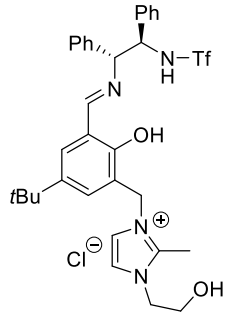
L4

Imine **L4** was prepared according to **GP3**, using aldehyde **23** (31.52 mg, 0.0930 mmol, 1.0 equiv), amine **9a** (32.03 mg, 0.0930 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (2.5 mL). The product **L4** was isolated as a yellow solid (38.8 mg, 0.0583 mmol, 63%).

$C_{32}H_{36}ClF_3N_4O_4S$. MW: 665.17 g/mol. **MP** = 250-251 °C. $[\alpha_D^{20}] = 20.2$ (c = 0.15 g/dl, CH_2Cl_2). **^{1}H NMR (500 MHz, MeOD)**: δ = 9.08 (*s*, 1H, NC*H*N), 8.61 (*s*, 1H, C*H*N), 7.69 (*t*, 1H, *J* = 1.7 Hz, N*H*CCHN), 7.65 (*d*, 1H, *J* = 2.4 Hz, Ar*H*), 7.62 (*t*, 1H, *J* = 1.7 Hz, NHCC*H*N), 7.54 (*d*, 1H, *J* = 2.4 Hz, Ar*H*), 7.25-7.15 (*m*, 8H, Ar*H*), 7.13-7.08 (*m*, 2H, Ar*H*), 5.55 (*d*, 1H, *J* = 14.0 Hz, ArCH*H*), 5.44 (*d*, 1H, *J* = 14.0 Hz, ArCH*H*), 4.96 (*d*, 1H, *J* = 9.7 Hz, CNC*H*Ar), 4.64 (*d*, 1H, *J* = 10.0 Hz, ArC*H*NHTf), 4.31-4.27 (*m*, 2H, CH_2CH$_2$OH), 3.89-3.85 (*m*, 2H, CH$_2$CH_2OH), 1.36 (s, 9H, C(CH_3)$_3$). **^{19}F NMR (376 MHz, MeOD)**: δ = 79.9. **^{13}C NMR (100 MHz, MeOD)**: δ = 168.2, 158.6,

143.4, 140.5, 139.8, 132.5, 131.5, 129.6, 129.3, 129.0, 128.9, 128.9, 128.7, 123.9, 123.9, 123.7, 122.1, 121.4 (*q*, J = 322.5 Hz, *C*F_3), 120.0, 79.7, 66.7, 61.1, 53.3, 49.8, 35.0, 31.7. **IR (Solid)**: $\tilde{\nu}$ = 2959, 2666, 1628, 1600, 1469, 1367, 1282, 1224, 1186, 1147, 1047, 1027, 954, 759, 699, 598 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{32}H_{36}F_3N_4O_4S]^+$ 629.2404, measured 629.2401.

3-(5-(*tert*-Butyl)-3-((*E*)-(((1*R*,2*R*)-1,2-diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-hydroxybenzyl)-1-(2-hydroxyethyl)-2-methyl-1H-imidazol-3-ium chloride (L5)

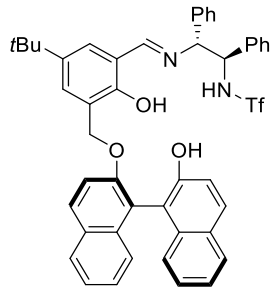


L5

Imine **L5** was prepared according to **GP3**, using aldehyde **24** (33.03 mg, 0.0975 mmol, 1.0 equiv), amine **9a** (34.40 mg, 0.0975 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (4 mL). The product **L5** was isolated as a yellow solid (43.0 mg, 0.0633 mmol, 65%).

$C_{33}H_{38}ClF_3N_4O_4S$. MW: 679.20 g/mol. **MP** = 150 °C (decomp.). $[\boldsymbol{\alpha}_{\boldsymbol{D}}^{\boldsymbol{20}}]$ = 18.2 (c = 0.11 g/dl, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 14.29 (*b*, 1H, ArO*H*), 8.65 (*s*, 1H, C*H*N), 7.37-7.35 (*m*, 2H, Ar*H*), 7.33-7.29 (*m*, 2H, Ar*H* and N*H*CCHN), 7.17-7.05 (*m*, 9H, Ar*H*), 6.76 (*t*, 1H, *J* = 1.3 Hz, NHCC*H*N), 5.33 (*d*, 1H, *J* = 14.2 Hz, ArCH*H*), 5.12 (*d*, 1H, *J* = 10.0 Hz, CNC*H*Ar), 4.93-4.88 (*m*, 2H, ArCH*H* and ArC*H*NHTf), 4.22-4.09 (*m*, 2H, C$H_2$$CH_2$OH), 3.90-3.77 (*m*, 2H, CH_2CH_2OH), 2.80 (*s*, 3H, CH_3), 1.26 (*s*, 9H, C(CH_3)$_3$). **^{19}F NMR (376 MHz, $CDCl_3$)**: δ = 78.3. **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 167.5, 158.2, 144.8, 141.4, 139.3, 138.6, 130.6, 130.3, 128.6, 128.35, 128.28, 128.2, 127.9, 127.7, 122.3, 120.5, 120.2, 119.0, 75.7, 65.9, 59.9, 51.1, 48.5, 34.2, 31.6, 10.8. **IR (solid)**: $\tilde{\nu}$ = 3300, 3033, 2962, 2872, 1630, 1601, 1456, 1370, 1226, 1191, 1147, 1049, 732, 699, 600 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{33}H_{38}F_3N_4O_4S]^+$ 643.2560, measured 643.2556.

***N*-((1*R*,2*R*)-2-(((*E*)-5-(tert-butyl)-2-hydroxy-3-(((2'-hydroxy-[(*R*)-1,1'-binaphthalen]-2-yl)oxy)methyl)benzylidene)amino)-1,2-diphenylethyl)-1,1,1-trifluoromethanesulfonamide (L6)**

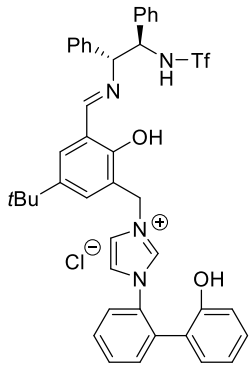


L6

Imine **L6** was prepared according to **GP3**, using aldehyde **25** (51.04 mg, 0.107 mmol, 1.0 equiv), amine **9a** (36.88 mg, 0.107 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (4 mL). The crude product was purified *via* crystallization. The received solid was dissolved in CH_2Cl_2 (1 mL), overlaid with n-hexane (10 mL) and the mixture cooled to -20 °C overnight. The crystalline product **L6** was separated, dried under reduced pressure and isolated as a yellow solid (63.1 mg, 0.0786 mmol, 73%).

$C_{47}H_{41}F_3N_2O_5S$. MW: 802.91 g/mol. **MP** = 133 °C (decomp.). $[\alpha_D^{20}] = 46.6$ (c = 0.19 g/dl, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 12.75 (*b*, 1H, ArO*H*), 8.11 (*s*, 1H, C*H*N), 8.09 (*d*, 1H, *J* = 9.8 Hz, Ar*H*), 7.96-7.89 (*m*, 2H, Ar*H*), 7.86 (*d*, 1H, *J* = 8.0 Hz, Ar*H*), 7.69 (*d*, 1H, *J* = 9.0 Hz, Ar*H*), 7.42-7.18 (*m*, 14H, Ar*H*), 7.16-7.08 (*m*, 3H, Ar*H*), 7.03 (*d*, 1H, *J* = 1.9 Hz, Ar*H*), 6.93 (*d*, 1H, *J* = 2.1 Hz, Ar*H*), 5.71 (*b*, 1H, ArO*H*), 5.37 (*d*, 1H, *J* = 12.8 Hz, ArCH*H*), 5.19 (*d*, 1H, *J* = 12.8 Hz, ArC*H*H), 5.07 (*d*, 1H, *J* = 4.6 Hz, CNC*H*Ar), 4.64 (*d*, 1H, *J* = 4.6 Hz, ArC*H*NHTf), 1.00 (*s*, 9H, C(C*H*$_3$)$_3$). **^{19}F NMR (376 MHz, $CDCl_3$)**: δ = 77.4. **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 168.6, 155.5, 155.2, 151.4, 141.9, 138.2, 137.4, 134.3, 134.0, 131.2, 129.9, 129.7, 129.4, 129.4, 129.0, 128.8, 128.6, 128.5, 128.3, 128.3, 127.6, 127.6, 127.4, 127.0, 126.6, 125.1, 125.1, 124.4, 124.4, 123.4, 119.6 (*q*, *J* = 303.2 Hz, *C*F$_3$), 117.8, 117.0, 116.0, 115.5, 115.1, 75.4, 65.5, 64.8, 34.0, 31.2. **IR (solid)**: $\tilde{\nu}$ = 3529, 3313, 3063, 2962, 1623, 1597, 1457, 1378, 1265, 1228, 1201, 1145, 1055, 734, 700 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{47}H_{41}F_3N_2O_5S]^+$ 803.2761, measured 803.2750.

3-(5-(*tert*-Butyl)-3-((*E*)-(((1*R*,2*R*)-1,2-diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-hydroxybenzyl)-1-(2'-hydroxy-[1,1'-biphenyl]-2-yl)-1H-imidazol-3-ium chloride (L7)

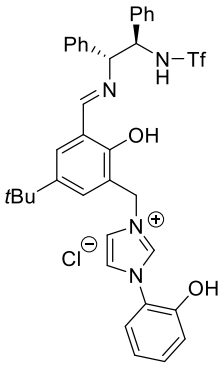


L7

Imine **L7** was prepared according to **GP3**, using aldehyde **26** (42.58 mg, 0.0893 mmol, 1.0 equiv), amine **9a** (30.77 mg, 0.0893 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (4 mL). The formed yellow solid was dissolved by addition of methanol (1 mL) and the resulting solution was the filtered over a small pad of celite®. After removal of the solvent, the received solid was dissolved in chloroform (0.5 mL), overlaid with diethylether (3 mL) and the mixture cooled to -20 °C overnight. The crystalline product **L7** was separated, dried under reduced pressure and isolated as a yellow solid (34.6 mg, 0.0438 mmol, 67%).

$C_{42}H_{40}ClF_3N_4O_4S$. MW: 789.31 g/mol. **MP** = 235 °C (decomp.). $[\alpha_D^{20}] = \ldots 40.2$ (c = 0.15 g/dl, CH_2Cl_2). **^{1}H NMR (400 MHz, MeOD)**: δ = 8.93 (*s*, 1H, NC*H*N), 8.65 (*s*, 1H, C*H*N), 7.71-7.55 (*m*, 6H, Ar*H*), 7.53-7.47 (*m*, 2H, Ar*H* and N*H*CCHN), 7.25-7.13 (*m*, 10H, Ar*H*), 7.09 (*d*, 1H, *J* = 7.3 Hz, Ar*H*), 7.04-6.98 (*m*, 1H, Ar*H*), 6.67 (*b*, 1H, NHCC*H*N), 6.61 (*d*, 1H, *J* = 8.3 Hz, Ar*H*), 5.42 (*s*, 2H, ArCH_2), 5.00 (*d*, 1H, *J* = 9.7 Hz, CNC*H*Ar), 4.70 (*d*, 1H, *J* = 9.7 Hz, ArC*H*NHTf), 1.36 (*s*, 9H, C(CH_3)$_3$). **^{19}F NMR (376 MHz, $CDCl_3$)**: δ = 79.8. **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 168.4, 158.3, 155.3, 143.5, 140.5, 139.4, 138.0, 136.6, 135.4, 133.4, 132.5, 132.0, 131.8, 131.7, 131.3, 130.1, 129.6, 129.4, 129.1, 129.0, 128.7, 126.6, 125.0, 124.9, 124.6, 123.1, 123.0, 121.6, 121.1, 120.9 (*q*, *J* = 320.6 Hz, *C*F$_3$), 120.1, 116.3, 79.7, 66.5, 49.8, 35.0, 31.8. **IR (solid)**: $\tilde{\nu}$ = 2966, 1631, 1602, 1444, 1363, 1224, 1191, 1146, 1047, 957, 760, 729 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{42}H_{40}F_3N_4O_4S]^+$ 753.2717, measured 753.2744.

3-(5-(*tert*-Butyl)-3-((*E*)-(((1*R*,2*R*)-1,2-diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-hydroxybenzyl)-1-(2-hydroxyphenyl)-1H-imidazol-3-ium chloride (L8)



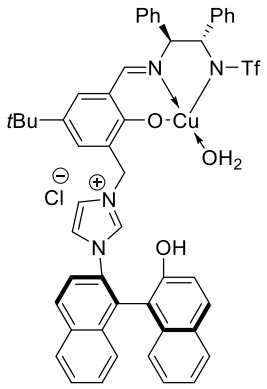
L8

Imine **L8** was prepared according to **GP3**, using aldehyde **27** (45.00 mg, 0.116 mmol, 1.0 equiv), amine **9a** (40.05 mg, 0.116 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (4 mL). After removing the solvent, the received solid was dissolved in chloroform (1 mL), overlaid with diethylether (10 mL) and cooled to -20 °C overnight. The precipitated solid was separated, dried under reduced pressure and the product **L8** was isolated as a yellow solid (52.5 mg, 0.0736 mmol, 63%).

$C_{36}H_{36}ClF_3N_4O_4S$. MW: 713.21 g/mol. **MP** = 186 °C (decomp.). $[\alpha_D^{20}] = 123.0$ (c = 0.21 g/dl, CH_2Cl_2). **^{1}H NMR (700 MHz, $CDCl_3$)**: δ = 14.51 (*br*, 1H, ArO*H*), 9.25 (*s*, 1H, NC*H*N), 8.61 (*s*, 1H, C*H*N), 7.62 (*s*, 1H, Ar*H*), 7.57 (*s*, 1H, Ar*H*), 7.47 (*d*, 1H, *J* = 6.5 Hz, Ar*H*), 7.42-7.38 (*m*, 2H, Ar*H*), 7.17-7.07 (*m*, 10H, Ar*H*), 7.02 (*d*, 1H, *J* = 6.8 Hz, N*H*CCHN), 6.72 (*d*, 1H, *J* = 7.1 Hz, NHCC*H*N), 5.52 (*d*, 1H, *J* = 13.3 Hz, ArCH*H*), 5.25 (*d*, 1H, *J* = 10.1 Hz, CNC*H*Ar), 5.20 (*d*, 1H, *J* = 13.3 Hz, ArCH*H*), 5.32 (*d*, 1H, *J* = 10.1 Hz, ArC*H*NHTf), 1.11 (s, 9H, C(C*H*$_3$)$_3$). **^{19}F NMR (376 MHz, $CDCl_3$)**: δ = 78.0. **^{13}C NMR (176 MHz, $CDCl_3$)**: δ = 167.7, 158.1, 150.4, 141.9, 139.0, 138.4, 036.2, 131.5, 131.1, 130.8, 128.7, 128.5, 128.3, 128.2, 128.0, 127.8, 123.5, 122.3, 122.0, 121.8, 120.4, 119.9, 119.6 (*q*, *J* = 321.7 Hz, *C*F$_3$), 119.0, 118.9, 75.2, 65.8, 49.5, 34.1, 31.3.**IR (Solid)**: $\tilde{\nu}$ = 3148, 3032, 2961, 2869, 2696, 1630, 1601, 1465, 1370, 1226, 1191, 1147, 1049, 909, 756, 731, 699, 598 cm^{-1}, **HRMS (ESI)** *m/z*: calculated $[C_{36}H_{36}F_3N_4O_4S]^+$ 677.2404, measured 677.2431.

Synthesis of the Complexes

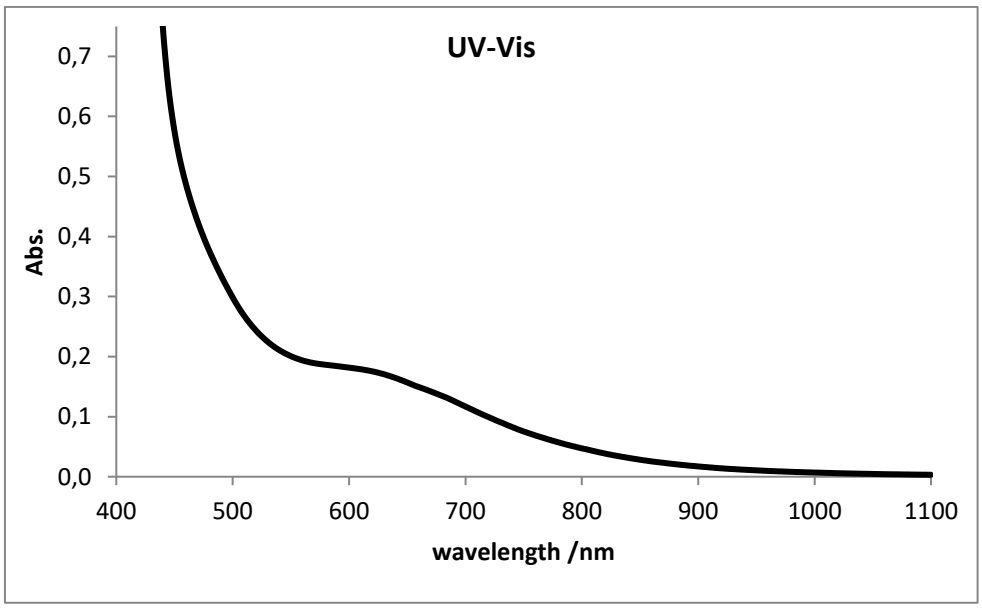
Cu(II)-Phenoxyimine-Complex (*S,S*)(*R*) (C1b-Cu)



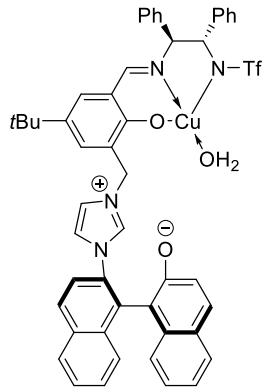
C1b-Cu

Complex **C1b-Cu** was prepared according to **GP4**, using ligand **L1b** (281.2 mg,0.316 mmol, 1.0 equiv) and copper(II) acetylacetonate (82.8 mg, 0.316 mmol, 1.0 equiv) and anhydrous acetonitrile (20 mL). The complex **C1b-Cu** was isolated as a green solid (299.4 mg, 0.309 mmol, 98%).

$C_{50}H_{44}ClCuF_3N_4O_5S$. MW: 968.98 g/mol. **MP** = 228 °C (decomp.). $[\alpha_D^{20}]$ = -79.7 (c = 0.21 g/dl, CH_2Cl_2). **^{1}H NMR:** paramagnetic species. **^{13}C NMR:** paramagnetic species. **IR (solid)**: $\tilde{\nu}$ = 3393, 3139, 3058, 3025, 2952, 2865, 1623, 1541, 1451, 1434, 1318, 1272, 1173, 1094, 1071, 814, 748, 700, 627 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{50}H_{42}CuF_3N_4O_4S]^+$ 914.2169, measured 914.2167. **Elemental Analysis** calculated for $[C_{50}H_{42}ClCuF_3N_4O_4S \times 1H_2O]$: C 61.98, H 4.58, N 5.78, found: C 61.88, H 4.65, N 5.59.



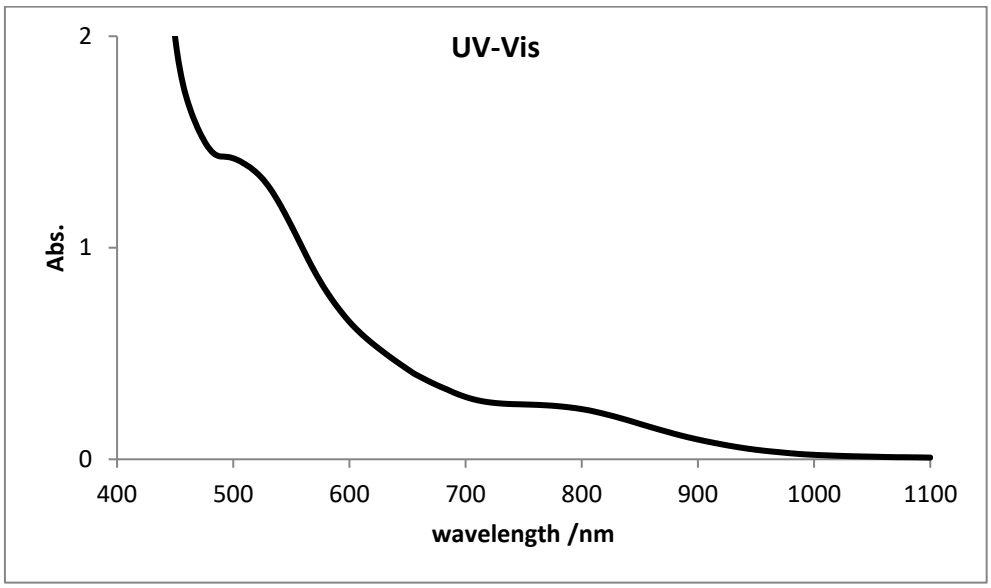
Activated Cu(II)-Phenoxyimine-Complex (*S,S*)(*R*) (C1b-Cu*)



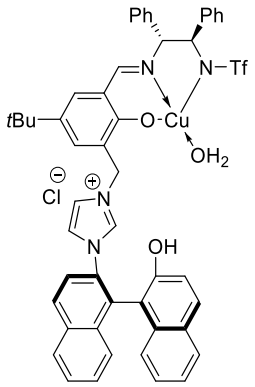
C1b-Cu*

The deprotonation of the complex **C1b-Cu** (40.0 mg, 0.0413 mmol, 1.0 equiv) was performed according to **GP5.** The complex **C1b-Cu*** was isolated as a red brown solid (38.7 mg, 0.414 mmol, >99%).

$C_{50}H_{43}CuF_3N_4O_5S$. MW: 932.52 g/mol. **MP** = 201 °C (decomp.). $[\alpha_D^{20}]$ = -867.4 (c = 0.16 g/dl, CH_2Cl_2). **^{1}H NMR:** paramagnetic species. **^{13}C NMR:** paramagnetic species. **IR (solid)**: $\tilde{\nu}$ = 3138, 3057, 3026, 2962, 2864, 1624, 1591, 1542, 1450, 1438, 1367, 1346, 1319, 1260, 1175, 1093, 1060, 1023, 798, 747, 700 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{50}H_{42}CuF_3N_4O_4S]^+$ 914.2169, measured 914.2157. **Elemental Analysis** calculated for [$C_{50}H_{42}CuF_3N_4O_4S$ x 1H_2O x 1THF]: C 64.58, H 5.12, N 5.58, found: C 64.55, H 5.11, N 5.30.



Cu(II)-Phenoxyimine-Complex (*R*,*R*)(*R*) (C1a-Cu)

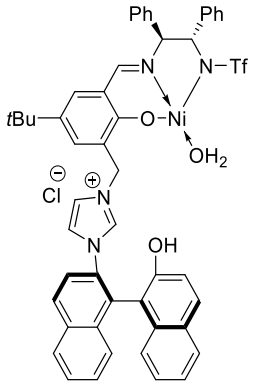


C1a-Cu

Complex **C1a-Cu** was prepared according to **GP4**, using ligand **L1a** (18.66 mg, 0.0210 mmol, 1.0 equiv) and copper(II) acetylacetonate (5.49 mg, 0.0210 mmol, 1.0 equiv) and anhydrous acetonitrile (3 mL). The complex **C1a-Cu** was isolated as a green solid (14.8 mg, 0.0153 mmol, 73%).

$C_{50}H_{44}ClCuF_3N_4O_5S$. MW: 968.98 g/mol. **MP** = 225 °C (decomp.). $[\alpha_D^{20}] = 629.2$ (c = 0.15 g/dl, CH_2Cl_2). **^{1}H NMR:** paramagnetic species. **^{13}C NMR:** paramagnetic species. **IR (solid)**: $\tilde{\nu}$ = 3060, 2961, 1625, 1543, 1451, 1434, 1320, 1274, 1211, 1186, 1095, 1073, 909, 731, 702 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{50}H_{42}CuF_3N_4O_4S]^+$ 914.2169, measured 914.2170. **Elemental Analysis** calculated for [$C_{50}H_{42}CuF_3N_4O_4S$ x $1H_2O$]: C 61.98, H 4.58, N 5.78, found: C 61.69, H 4.55, N 5.77.

Ni(II)-Phenoxyimine-Complex (*S*,*S*)(*R*) (C1b-Ni)

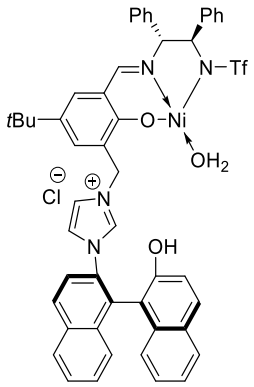


C1b-Ni

Complex **C1b-Ni** was prepared according to **GP4**, using ligand **L1b** (44.30 mg, 0.0498 mmol, 1.0 equiv) and nickel(II) acetylacetonate (12.79 mg, 0.0498 mmol, 1.0 equiv) and anhydrous acetonitrile (4 mL). The complex **C1b-Ni** was isolated as a brown solid (44.1 mg, 0.0457 mmol, 92%).

$C_{50}H_{44}ClF_3N_4NiO_5S$. MW: 964.12 g/mol. **MP** = 235 °C (decomp.). $[\alpha_D^{20}] = -203.8$ (c = 0.15 g/dl, CH_2Cl_2). **^{1}H NMR:** paramagnetic species. **^{13}C NMR:** paramagnetic species. **IR (solid)**: $\tilde{\nu}$ = 3142, 3056, 3025, 2955, 1622, 1600, 1544, 1510, 1451, 1434, 1323, 1274, 1210, 1180, 1095, 1067, 1002, 957, 815, 749, 699 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{50}H_{42}NiF_3N_4O_4S]^+$ 909.2227, measured 909.2220. **Elemental Analysis** calculated for $[C_{50}H_{42}ClNiF_3N_4O_4S \times 1H_2O]$: C 62.29, H 4.60, N 5.81, found: C 61.90, H 4.67, N 5.47.

Ni(II)-Phenoxyimine-Complex (*R,R*)(*R*) (C1a-Ni)



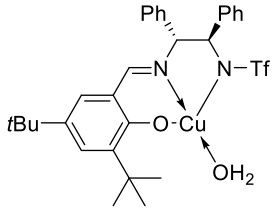
C1a-Ni

Complex **C1a-Ni** was prepared according to **GP4**, using ligand **L1a** (25.92 mg, 0.029 mmol, 1.0 equiv) and nickel(II) acetylacetonate (7.49 mg, 0.029 mmol, 1.0 equiv) and anhydrous acetonitrile (3 mL). The complex **C1a-Ni** was isolated as a brown solid (26.6 mg, 0.0276 mmol, 95%).

$C_{50}H_{44}ClF_3N_4NiO_5S$. MW: 964.12 g/mol. **MP** = 234 °C (decomp.). $[\alpha_D^{20}] = 53.7$ (c = 0.15 g/dl, CH_2Cl_2). **^{1}H NMR:** paramagnetic species. **^{13}C NMR:** paramagnetic species. **IR (solid)**: $\tilde{\nu}$ = 3361, 3060, 2960, 1622, 1603, 1545, 1510, 1451, 1435, 1323, 1275, 1210, 1184, 1147, 910, 732 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{50}H_{42}NiF_3N_4O_4S]^+$ 909.2227, measured 909.2244.

Control Systems

Cu(II)-Phenoxyimine-Complex (*R,R*) (C2)

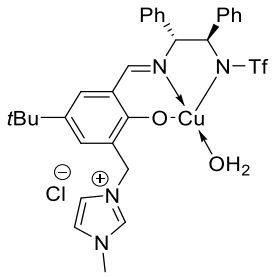


C2

Complex **C2** was prepared according to **GP4**, using ligand **L2** (19.5 mg, 0.0348 mmol, 1.0 equiv) and copper(II) acetylacetonate (9.56 mg, 0.037 mmol, 1.05 equiv) and anhydrous acetonitrile (2 mL). The complex **C2** was isolated as a green solid (19.1 mg, 0.0298 mmol, 85%).

$C_{30}H_{35}CuF_3N_2O_4S$. MW: 640.22 g/mol. **MP** = 120 °C (decomp.). $[\alpha_D^{20}] = 19.7$ (c = 0.15 g/dl, CH_2Cl_2). **^{1}H NMR:** paramagnetic species. **^{13}C NMR:** paramagnetic species. **IR (solid)**: $\tilde{\nu}$ = 2955, 1617, 1576, 1526, 1450, 1429, 1387, 1360, 1319, 1172, 1146, 1070, 1009, 939, 778, 698 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{30}H_{33}CuF_3N_2NaO_3S]^+$ 644.1352, measured 644.1347.

Cu(II)-Phenoxyimine-Complex (*R,R*) (C3)

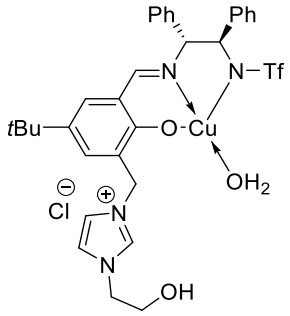


C3

Complex **C3** was prepared according to **GP4**, using ligand **L3** (16.45 mg, 0.0259 mmol, 1.0 equiv) and copper(II) acetylacetonate (7.12 mg, 0.0272 mmol, 1.05 equiv) and anhydrous acetonitrile (2 mL). The complex **C3** was isolated as a green solid (15.2 mg, 0,0212 mmol, 82%).

$C_{31}H_{34}ClCuF_3N_4O_4S$. MW: 714.69 g/mol. **MP** = 168 °C (decomp.). $[\alpha_D^{20}] = 603.8$ (c = 0.15 g/dl, CH_2Cl_2). **^{1}H NMR:** paramagnetic species. **^{13}C NMR:** paramagnetic species. **IR (solid)**: $\tilde{\nu}$ = 2955, 1625, 1544, 1451, 1393, 1321, 1212, 1180, 1073, 996, 942, 766, 702 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{31}H_{32}CuF_3N_4O_3S]^+$ 660.1438, measured 660.1427. **Elemental Analysis** calculated for $[C_{31}H_{32}ClCuF_3N_4O3S \times 1H_2O]$: C 52.09, H 4.79, N 7.84, found: C 51.68, H 4.72, N 7.45.

Cu(II)-Phenoxyimine-Complex (*R,R*) (C4)

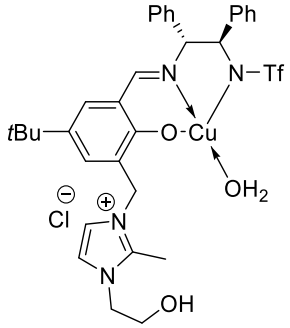


C4

Complex **C4** was prepared according to **GP4**, using ligand **L4** (16.4 mg, 0.0247 mmol, 1.0 equiv) and copper(II) acetylacetonate (6.78 mg, 0.0259 mmol, 1.05 equiv) and anhydrous acetonitrile (2 mL). The complex **C4** was isolated as a green solid (12.1 mg, 0.0163 mmol, 66%).

$C_{32}H_{36}ClCuF_3N_4O_5S$. MW: 744.71 g/mol. **MP** = 180 °C (decomp.). $[\alpha_D^{20}] = 399.4$ (c = 0.15 g/dl, CH_2Cl_2). **^{1}H NMR:** paramagnetic species. **^{13}C NMR:** paramagnetic species. **IR (solid)**: $\tilde{\nu}$ = 3423, 3062, 2959, 1625, 1545, 1451, 1320, 1211, 1176, 1072, 996, 766, 701 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{32}H_{34}CuF_3N_4O_4S]^+$ 690.1543, measured 690.1556. **Elemental Analysis** calculated for $[C_{32}H_{34}ClCuF_3N_4O_4S \times 1H_2O]$: C 51.61, H 4.87, N 7.52, found: C 51.73, H 4.84, N 7.38.

Cu(II)-Phenoxyimine-Complex (*R,R*) (C5)



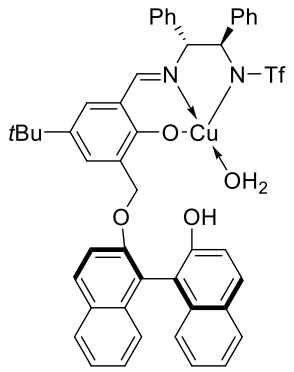
C5

Complex **C5** was prepared according to **GP4**, using ligand **L5** (15.8 mg, 0.0232 mmol, 1.0 equiv) and copper(II) acetylacetonate (6.38 mg, 0.02 mmol, 1.0 equiv) and anhydrous acetonitrile (2 mL). The complex **C5** was isolated as a green solid (15.7 mg, 0.0206 mmol, 89%).

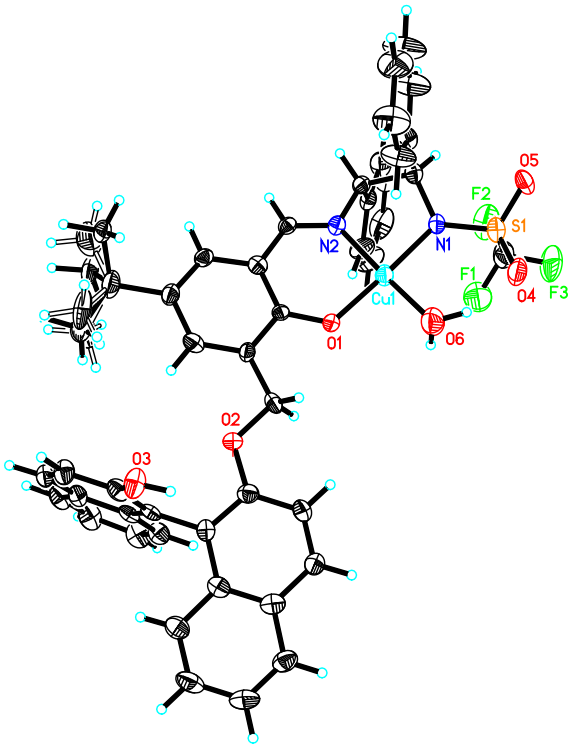
$C_{33}H_{38}ClCuF_3N_4O_5S$. MW: 758.74 g/mol. **MP** = 160 °C (decomp.). $[\alpha_D^{20}] = 586.8$ (c = 0.15 g/dl, CH_2Cl_2). **^{1}H NMR:** paramagnetic species. **^{13}C NMR:** paramagnetic species. **IR (solid)**: $\tilde{\nu}$ = 3387, 2962, 1626, 1544,

1451, 1395, 1366, 1320, 1212, 1186, 1073, 733, 702 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{33}H_{36}CuF_3N_4O_4S]^+$ 704.1700, measured 704.1733.

Cu(II)-Phenoxyimine-Complex (*R,R*)(*R*) (C6)



C6

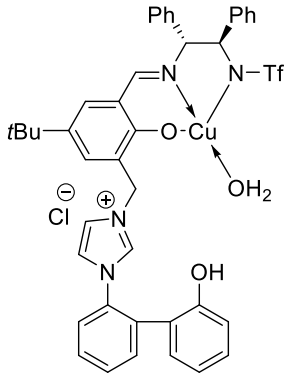


Complex **C6** was prepared according to **GP4**, using ligand **L6** (15.91 mg, 0.0198 mmol, 1.0 equiv) and copper(II) acetylacetonate (5.19 mg, 0.0198 mmol, 1.0 equiv) and anhydrous acetonitrile (2 mL). The crude product was recrystallized in the freezer by dissolving in CH_2Cl_2 (0.2 mL) and overlaying with *n*-hexane (5 mL). The complex **C6** was isolated as a green solid (8.1 mg, 0.00918 mmol, 46%).

$C_{47}H_{41}CuF_3N_2O_6S$. MW: 882.45 g/mol. **MP** = 200 °C (decomp.). $[\alpha_D^{20}] = 53.1$ (c = 0.15 g/dl, CH_2Cl_2). **^{1}H NMR:** paramagnetic species. **^{13}C NMR:** paramagnetic species. **IR (solid)**: $\tilde{\nu}$ = 3405, 3060, 2961, 1622, 1592, 1545, 1507, 1438, 1317, 1262, 1210, 1178, 1146, 1071, 1013, 908, 811, 731, 699 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{47}H_{39}CuF_3N_2NaO_5S]^+$ 886.1720, measured 886.1699.

CCDC 1872223 contains the supplementary crystallographic data for compound **C6**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Cu(II)-Phenoxyimine-Complex (*R,R*) (C7)

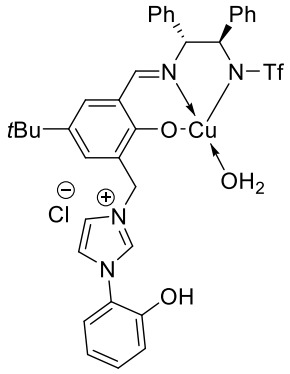


C7

Complex **C7** was prepared according to **GP4**, using ligand **L7** (24.9 mg, 0.0315 mmol, 1.0 equiv) and copper(II) acetylacetonate (8.26 mg, 0.0315 mmol, 1.0 equiv) and anhydrous acetonitrile (2 mL). The complex **C7** is isolated as a green solid (23.2 mg, 0.0267 mmol, 85%).

$C_{42}H_{40}ClCuF_3N_4O_5S$. MW: 868.85 g/mol. **MP** = 112 °C (decomp.). $[\boldsymbol{\alpha_D^{20}}] = 67.2$ (c = 0.15 g/dl, CH_2Cl_2). **^{1}H NMR:** paramagnetic species. **^{13}C NMR:** paramagnetic species. **IR (solid)**: $\tilde{\nu}$ = 3062, 2960, 2925, 2854, 2251, 1655, 1625, 1547, 1489, 1451, 1403, 1318, 1273, 1187, 1144, 1072, 908, 761, 729, 699 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{42}H_{38}CuF_3N_2O_4S]^+$ 814.1856, measured 814.1866.

Cu(II)-Phenoxyimine-Complex (*R,R*) (C8)



C8

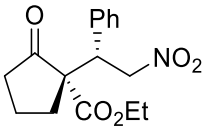
Complex **C8** was prepared according to **GP4**, using ligand **L8** (37.5 mg, 0.0526 mmol, 1.0 equiv) and copper(II) acetylacetonate (13.8 mg, 0.0526 mmol, 1.0 equiv) and anhydrous acetonitrile (3 mL). The complex **C8** is isolated as a green solid (39.0 mg, 0.0492 mmol, 93%).

$C_{36}H_{36}ClCuF_3N_4O_5S$. MW: 792.76 g/mol. **MP** = 199 °C (decomp.). $[\boldsymbol{\alpha_D^{20}}] = 126.9$ (c = 0.15 g/dl, CH_2Cl_2). **^{1}H NMR:** paramagnetic species. **^{13}C NMR:** paramagnetic species. **IR (solid)**: $\tilde{\nu}$ = 3061, 2961, 1724, 1625, 1547,

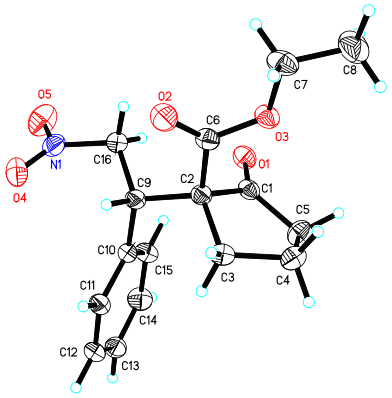
1452, 1366, 1318, 1275, 1212, 1185, 910, 765, 732, 702 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{36}H_{34}CuF_3N_4O_4S]^+$ 738.1543, measured 738.1525. **Elemental Analysis** calculated for $[C_{36}H_{34}ClCuF_3N_4O_4S$ x $2H_2O]$: C 53.33, H 4.72, N 6.91, found: C 53.49, H 4.66, N 6.66.

Catalytic Products

Ethyl (*S*)-1-((*S*)-2-Nitro-1-phenylethyl)-2-oxocyclopentane-1-carboxylate (3aA)



3aA

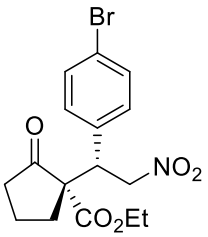


The product **3aA** was synthesized as described in **GP6-standard**. **3aA** was isolated as a white solid (60.8 mg, 0.199 mmol, 99%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 94:6, $ee_{(S,S)}$ = 99%). Diastereomerically pure substance **3aA** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (90/10), 0.7 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 22.2 min, $t_{(R,S)}$ = 15.9 min.

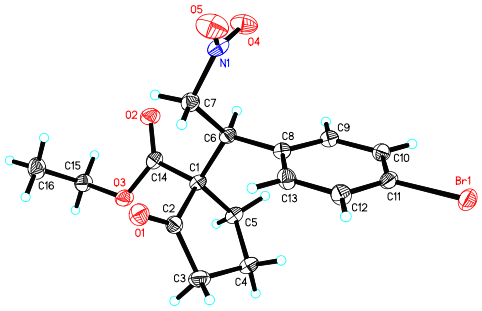
$C_{16}H_{19}NO_5$. MW: 305.33 g/mol. **MP** = 86-87 °C. $[\alpha_D^{20}]$ = 13,7 (c = 0.15 g/dl, CH_2Cl_2). **^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 7.33-7.27 (*m*, 3H, Ar*H*), 7.21-7.17 (*m*, 2H, Ar*H*), 5.29 (*dd*, 1H, *J* = 13.3, 11.3 Hz, CH*H*NO_2), 4.83 (*dd*, 1H, *J* = 13.3, 3.5 Hz, C*H*HNO_2), 4.29-4.15 (*m*, 3H, OCH_2CH_3 and C*H*Ph), 2.46-2.38 (*m*, 1H, $CH_{cyclopentane}$), 2.35-2.28 (*m*, 1H, $CH_{cyclopentane}$), 2.03-1.92 (*m*, 2H, $CH_{cyclopentane}$), 1.86-1.75 (*m*, 1H, $CH_{cyclopentane}$), 1.47-1.37 (*m*, 1H, $CH_{cyclopentane}$), 1.27 (*t*, 3H, *J* = 7.1 Hz, OCH_2CH_3). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 215.7, 171.2, 135.7, 129.3, 129.2, 128.6, 77.1, 62.41, 62.37, 47.4, 39.7, 33.7, 19.7, 14.2. **IR (solid)**: $\tilde{\nu}$ = 2980, 1726, 1554, 1378, 1229, 1149, 1229, 1111, 704 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{16}H_{19}NNaO_5]^+$ 328.1155, measured 328.1158.

CCDC 1872231 contains the supplementary crystallographic data for compound **3aA**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Ethyl (*S*)-1-((*S*)-1-(4-Bromophenyl)-2-nitroethyl)-2-oxocyclopentane-1-carboxylate (3aB)



3aB

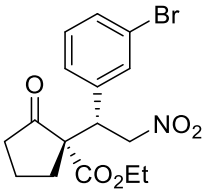


The product **3aB** was synthesized as described in **GP6-standard**. **3aB** was isolated as a white solid (70.3 mg, 0.183 mmol, 92%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 94:6, $ee_{(S,S)}$ = 99%). Diastereomerically pure substance **3aB** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (90/10), 0.7 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 32.9 min, $t_{(R,S)}$ = 20.5 min.

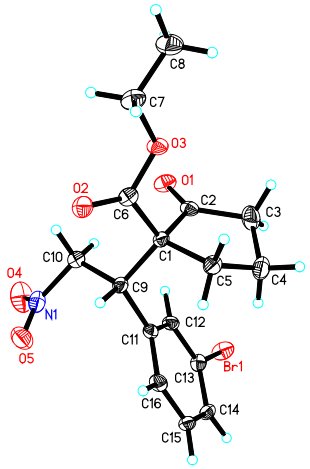
$C_{16}H_{18}BrNO_5$. MW: 384.23 g/mol. **MP** = 115-116 °C. $[\alpha_D^{20}]$ = 38.5 (c = 0.14 g/dl, CH_2Cl_2). **^{1}H NMR (700 MHz, $CDCl_3$)**: δ = 7.44 (*d*, 2H, *J* = 8.5 Hz, Ar*H*), 7.08 (*d*, 2H, *J* = 8.5 Hz, Ar*H*), 5.25 (*dd*, 1H, *J* = 13.6, 11.2 Hz, CH*H*NO_2), 4.83 (*dd*, 1H, *J* = 13.6, 3.5 Hz, C*H*HNO_2), 4.28-4.15 (*m*, 3H, O$CH_2$$CH_3$ and C*H*Ar), 2.47-2.41 (*m*, 1H, C$H_{cyclopentane}$), 2.33-2.29 (*m*, 1H, C$H_{cyclopentane}$), 2.02-1.94 (*m*, 1H, C$H_{cyclopentane}$), 1.93-1.80 (*m*, 2H, C$H_{cyclopentane}$), 1.56-1.49 (*m*, 1H, C$H_{cyclopentane}$), 1.27 (*t*, 3H, *J* = 7.2 Hz, OCH_2CH_3). **^{13}C NMR (176 MHz, $CDCl_3$)**: δ = 215.3, 170.9, 134.8, 132.3, 131.0, 122.8, 76.8, 62.6, 62.3, 46.8, 39.6, 33.6, 19.7, 14.2. **IR (solid)**: $\tilde{\nu}$ = 2978, 1725, 1533, 1490, 1378, 1228, 1149, 1115, 1076, 1011, 827 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{16}H_{18}BrNNaO_5]^+$ 406.0261, measured 406.0257.

CCDC 1872225 contains the supplementary crystallographic data for compound **3aB**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Ethyl (*S*)-1-((*S*)-1-(3-Bromophenyl)-2-nitroethyl)-2-oxocyclopentane-1-carboxylate (3aC)



3aC

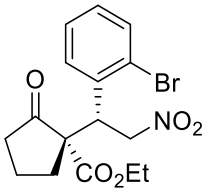


The product **3aC** was synthesized as described in **GP6-standard**. **3aC** was isolated as a white solid (74.1 mg, 0.193 mmol, 96%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 96:4, $ee_{(S,S)}$ = 99%). Diastereomerically pure substance **3aC** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel AS-H, *n*-hexane/*i*PrOH (91/9), 0.7 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 57.8 min, $t_{(R,S)}$ = 21.8 min.

$C_{16}H_{18}BrNO_5$. MW: 384.23 g/mol. **MP =** 100 °C. $[\alpha_D^{20}]$ = 21.5 (c = 0.19 g/dl, CH_2Cl_2). **^{1}H NMR (700 MHz, $CDCl_3$)**: δ = 7.43 (*d*, 1H, *J* = 7.9 Hz, Ar*H*), 7.35 (s, 1H, Ar*H*), 7.19 (*t*, 1H, *J* = 7.9 Hz, Ar*H*), 7.13 (*d*, 1H, *J* = 7.9 Hz, Ar*H*), 5.23 (*dd*, 1H, *J* = 13.7, 11.2 Hz, CH*H*NO_2), 4.79 (*dd*, 1H, *J* = 13.7, 3.4 Hz, C*H*HNO_2), 4.27-4.15 (*m*, 3H, OCH_2CH_3 and C*H*Ar), 2.48-2.42 (*m*, 1H, $CH_{cyclopentane}$), 2.36-2.31 (*m*, 1H, $CH_{cyclopentane}$), 2.04-1.98 (*m*, 1H, $CH_{cyclopentane}$), 1.94-1.81 (*m*, 2H, $CH_{cyclopentane}$), 1.57-1.51 (*m*, 1H, $CH_{cyclopentane}$), 1.27 (*t*, 3H, *J* = 7.2 Hz, OCH_2CH_3). **^{13}C NMR (176 MHz, $CDCl_3$)**: δ = 215.1, 170.7, 138.2, 132.6, 131.8, 130.7, 127.7, 123.2, 76.8, 62.6, 62.5, 46.8, 39.5, 33.4, 19.7, 14.2. **IR (solid)**: $\tilde{\nu}$ = 2980, 1723, 1551, 1476, 1432, 1377, 1317, 1226, 1147, 1111, 1076, 1014, 998, 822, 794, 699 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{16}H_{18}BrNNaO_5]^+$ 406.0261, measured 406.0271.

CCDC 1872232 contains the supplementary crystallographic data for compound **3aC**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Ethyl (*S*)-1-((*R*)-1-(2-Bromophenyl)-2-nitroethyl)-2-oxocyclopentane-1-carboxylate (3aD)

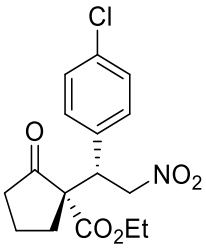


3aD

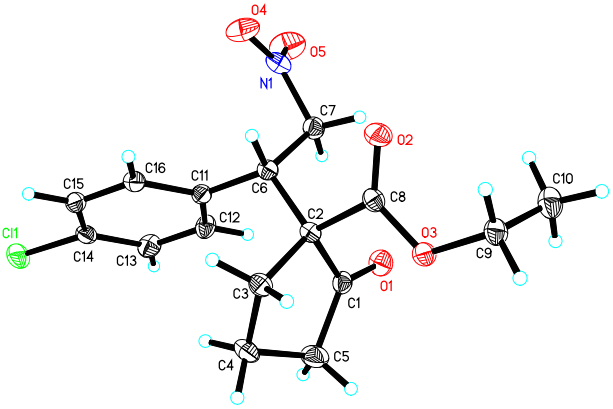
The product **3aD** was synthesized as described in **GP6-standard**. **3aD** was isolated as a white solid (64.0 mg, 0.167 mmol, 83%, $dr_{(S,R+R,S):(R,R+S,S)}$ = 90:10, $ee_{(S,R)}$ = 99%). Diastereomerically pure substance **3aD** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (91/9), 0.7 mL min^{-1}, detection at 214 nm, $t_{(S,R)}$ = 23.6 min, $t_{(R,R)}$ = 16.3 min.

$C_{16}H_{18}BrNO_5$. MW: 384.23 g/mol. **MP** = 84-85 °C. $[\alpha_D^{20}]$ = 54.1 (c = 0.16 g/dl, CH_2Cl_2). **^{1}H NMR (700 MHz, $CDCl_3$)**: δ = 7.61 (*dd*, 1H, *J* = 8.0, 1.1 Hz, Ar*H*), 7.27 (*t*, 1H, *J* = 8.0 Hz, Ar*H*), 7.21 (*dd*, 1H, *J* = 7.8, 1.6 Hz, Ar*H*), 7.14 (*td*, 1H, *J* = 7.8, 1.6 Hz, Ar*H*), 5.36 (*dd*, 1H, *J* = 14.0, 10.8 Hz, C*H*NO_2), 5.01 (*dd*, 1H, *J* = 10.7, 3.3 Hz, *CH*Ar), 4.90 (*dd*, 1H, *J* = 13.9, 3.3 Hz, *CH*HNO_2), 4.33-4.20 (*m*, 2H, O*CH*$_2$CH$_3$), 2.46-2.39 (*m*, 2H, *CH*$_{cyclopentane}$), 1.97-1.81 (*m*, 3H, *CH*$_{cyclopentane}$), 1.57-1.51 (*m*, 1H, *CH*$_{cyclopentane}$), 1.29 (*t*, 3H, *J* = 7.2 Hz, OCH$_2$*CH*$_3$). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 216.0, 171.2, 135.7, 133.9, 129.9, 128.4, 128.3, 128.0, 76.8, 62.5, 44.5, 39.7, 33.4, 20.0, 14.2. **IR (solid)**: $\tilde{\nu}$ = 2979, 1724, 1552, 147, 1434, 1377, 1274, 1228, 1147, 1025, 859, 757, 660 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{16}H_{18}BrNNaO_5]^+$ 406.0261, measured 406.0268.

Ethyl (*S*)-1-((*S*)-1-(4-Chlorophenyl)-2-nitroethyl)-2-oxocyclopentane-1-carboxylate (3aE)



3aE



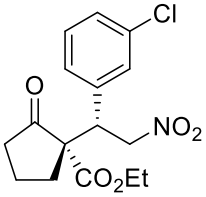
The product **3aE** was synthesized as described in **GP6-standard**. **3aE** was isolated as a white solid (66.8 mg, 0.197 mmol, 98%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 95:5, $ee_{(S,S)}$ = 99%). Diastereomerically pure substance **3aE** was

obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (90/10), 0.7 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 26.0 min, $t_{(R,S)}$ = 16.4 min.

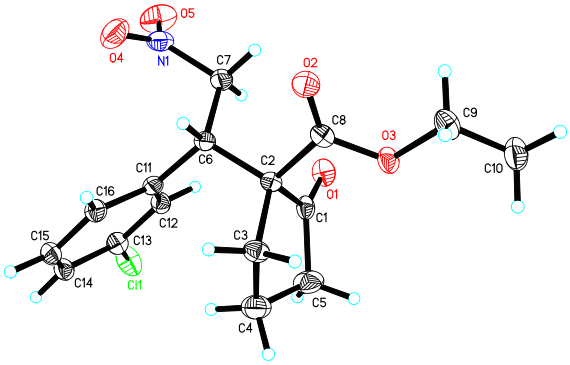
$C_{16}H_{18}ClNO_5$. MW: 339.77 g/mol. **MP** = 124-125 °C. $[\alpha_D^{20}]$ = 32.8 (c = 0.15 g/dl, CH_2Cl_2 CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.32-7.26 (*m*, 2H, Ar*H*), 7.17-7.11 (*m*, 2H, Ar*H*), 5.26 (*dd*, 1H, *J* = 13.6, 11.1 Hz, CH*H*NO_2), 4.83 (*dd*, 1H, *J* = 13.6, 3.4 Hz, C*H*HNO_2), 4.32-4.12 (*m*, 3H, OC*H*$_2$CH$_3$ and C*H*Ar), 2.51-2.25 (*m*, 2H, C*H*$_{cyclopentane}$), 2.06-1.75 (*m*, 3H, C*H*$_{cyclopentane}$), 1.59-1.45 (*m*, 1H, C*H*$_{cyclopentane}$), 1.27 (*t*, 3H, *J* = 7.3 Hz, OCH$_2$C*H*$_3$). **^{13}C NMR (176 MHz, $CDCl_3$)**: δ = 215.3, 170.9, 134.6, 134.2, 130.7, 129.4, 76.9, 62.5, 62.4, 46.7, 39.5, 33.5, 19.7, 14.2. **IR (solid)**: $\tilde{\nu}$ = 2980, 1724, 1552, 1493, 1445, 1377, 1296, 1274, 1226, 1147, 1115, 1093, 1013, 910, 827, 730 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{16}H_{18}ClNNaO_5]^+$ 362.0766, measured 362.0737.

CCDC 1872234 contains the supplementary crystallographic data for compound **3aE**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Ethyl (*S*)-1-((*S*)-1-(3-Chlorophenyl)-2-nitroethyl)-2-oxocyclopentane-1-carboxylate (3aF)



3aF



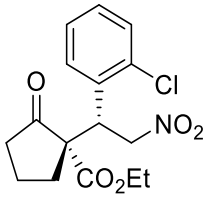
The product **3aF** was synthesized as described in **GP6-standard**. **3aF** was isolated as a white solid (65.1 mg, 0.192 mmol, 96%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 97:3, $ee_{(S,S)}$ = 99%). Diastereomerically pure substance **3aF** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (90/10), 0.7 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 23.1 min, $t_{(R,S)}$ = 16.7 min.

$C_{16}H_{18}ClNO_5$. MW: 339.77 g/mol. **MP** = 98-99 °C. $[\alpha_D^{20}]$ = 24.6 (c = 0.31 g/dl, CH_2Cl_2), **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.30-7.18 (*m*, 3H, Ar*H*), 7.12-7.06 (m, 1H, Ar*H*), 5.24 (*dd*, 1H, *J* = 13.6, 11.0 Hz, CH*H*NO_2), 4.79 (*dd*, 1H, *J* = 13.6, 3.4 Hz, C*H*HNO_2), 4.32-4.12 (*m*, 3H, OC*H*$_2$CH$_3$ and C*H*Ar), 2.52-2.26 (*m*, 2H, C*H*$_{cyclopentane}$),

2.09-1.76 (*m*, 3H, C*H*$_{cyclopentane}$), 1.61-1.47 (*m*, 1H, C*H*$_{cyclopentane}$), 1.27 (*t*, 3H, *J* = 7.2 Hz, OCH$_2$C*H*$_3$). **^{13}C NMR (176 MHz, CDCl$_3$)**: δ = 215.1, 170.8, 137.9, 135.0, 130.4, 129.7, 128.9, 127.3, 76.8, 62.6, 62.4, 46.9, 39.5, 33.4, 19.7, 14.1. **IR (solid)**: $\tilde{\nu}$ = 3068, 2980, 2896, 1723, 1596, 1552, 1477, 1435, 1377, 1317, 1225, 1147, 1111, 1014, 912, 838, 790, 699 cm^{-1}. **HRMS (ESI)** *m/z*: calculated [$C_{16}H_{18}ClNNaO_5$]$^+$ 362.0766, measured 362.0740.

CCDC 1872233 contains the supplementary crystallographic data for compound **3aF**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Ethyl (*S*)-1-((*R*)-1-(2-Chlorophenyl)-2-nitroethyl)-2-oxocyclopentane-1-carboxylate (3aG)

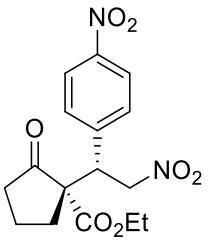


3aG

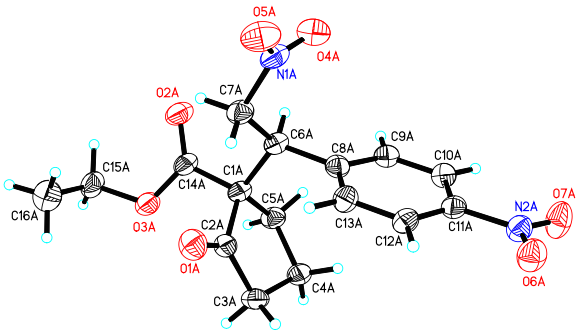
The product **3aG** was synthesized as described in **GP6-standard** within 72 h reaction time. **3aG** was isolated as a white solid (56.3 mg, 0.166 mmol, 83%, $dr_{(S,R+R,S):(R,R+S,S)}$ = 93:7, $ee_{(S,R)}$ = 99%). Diastereomerically pure substance **3aG** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (90/10), 0.7 mL min^{-1}, detection at 214 nm, $t_{(S,R)}$ = 22.3 min, $t_{(R,R)}$ = 15.1 min.

$C_{16}H_{18}ClNO_5$. MW: 339.77 g/mol. **MP** = 89-90 °C. $[\alpha_D^{20}]$ = 21.8 (c = 0.23 g/dl, CH_2Cl_2), **^{1}H NMR (300 MHz, CDCl$_3$)**: δ = 7.46-7.38 (*m*, 1H, Ar*H*), 7.25-7.19 (*m*, 3H, Ar*H*), 5.37 (*dd*, 1H, *J* = 14.0, 10.9 Hz, CH*H*NO$_2$), 5.01 (*dd*, 1H, *J* = 10.9, 3.3 Hz, C*H*Ar), 4.90 (*dd*, 1H, *J* = 14.0, 3.3 Hz, C*H*HNO$_2$), 4.36-4.16 (*m*, 2H, OC*H*$_2$CH$_3$), 2.50-2.32 (*m*, 2H, C*H*$_{cyclopentane}$), 2.00-1.76 (*m*, 3H, C*H*$_{cyclopentane}$), 1.61-1.47 (*m*, 1H, C*H*$_{cyclopentane}$), 1.29 (*t*, 3H, *J* = 7.4 Hz, OCH$_2$C*H*$_3$). **^{13}C NMR (176 MHz, CDCl$_3$)**: δ = 215.9, 171.3, 136.7, 134.0, 130.5, 129.6, 128.3, 127.7, 76.6, 62.51, 62.50, 41.7, 39.6, 33.4, 19.9, 14.2. **IR (solid)**: $\tilde{\nu}$ = 2979, 2922, 1724, 1552, 1476, 1438, 1377, 1275, 1228, 1147, 1110, 1038, 1014, 859, 758 cm^{-1}. **HRMS (ESI)** *m/z*: calculated [$C_{16}H_{18}ClNNaO_5$]$^+$ 362.0766, measured 362.0788.

Ethyl (*S*)-1-((*S*)-2-Nitro-1-(4-nitrophenyl)ethyl)-2-oxocyclopentane-1-carboxylate (3aH)



3aH

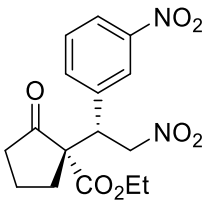


The product **3aH** was synthesized as described in **GP6-standard**. **3aH** was isolated as a white solid (69.5 mg, 0.198 mmol, 99%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 94:6, $ee_{(S,S)}$ = 96%). Diastereomerically pure substance **3aH** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (90/10), 0.7 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 98.5 min, $t_{(R,S)}$ = 57.8 min.

$C_{16}H_{18}N_2O_7$. MW: 350.33 g/mol. **MP** = 124-125 C. $[\alpha_D^{20}]$ = 37.8 (c = 0.18 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 8.23-8.14 (*m*, 2H, Ar*H*), 7.46-7.38 (*m*, 2H, Ar*H*), 5.32 (*dd*, 1H, *J* = 14.1, 11.9 Hz, CH*H*NO_2), 4.82 (*dd*, 1H, *J* = 14.1, 3.3 Hz, C*H*HNO_2), 4.38-4.14 (*m*, 3H, OCH_2CH_3 and C*H*Ar), 2.57-2.31 (*m*, 2H, $CH_{cyclopentane}$), 2.08-1.78 (*m*, 3H, $CH_{cyclopentane}$), 1.67-1.52 (*m*, 1H, $CH_{cyclopentane}$), 1.28 (*t*, 3H, *J* = 7.2 Hz, OCH_2CH_3). **^{13}C NMR (176 MHz, $CDCl_3$)**: δ = 214.6, 170.4, 148.0, 143.4, 130.5, 124.2, 76.5, 62.8, 62.5, 46.8, 39.3, 33.4, 19.7, 14.2. **IR (solid)**: $\tilde{\nu}$ = 2980, 2259, 1724, 1605, 1554, 1522, 1447, 1377, 1347, 1318, 1227, 1148, 1111, 1014, 909, 857, 727, 700 cm^{-1}. **HRMS (EI)** *m/z*: calculated $[C_{16}H_{18}N_2O_7]^+$ 350.1114, measured 350.1105.

CCDC 1872227 contains the supplementary crystallographic data for compound **3aH**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Ethyl (*S*)-1-((*S*)-2-Nitro-1-(3-nitrophenyl)ethyl)-2-oxocyclopentane-1-carboxylate (3aI)

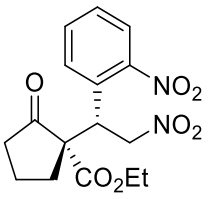


3aI

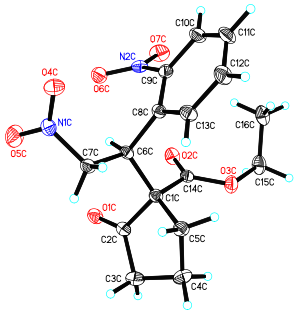
The product **3aI** was synthesized as described in **GP6-standard**. **3aI** was isolated as a colorless oil (70.1 mg, 0.199 mmol, 99%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 97:3, $ee_{(S,S)}$ = 99%). Diastereomerically pure substance **3aI** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (90/10), 0.7 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 59.7 min, $t_{(R,S)}$ = 45.2 min.

$C_{16}H_{18}N_2O_7$. MW: 350.33 g/mol. $[\alpha_D^{20}]$ = 18.3 (c = 0.16 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 8.20-8.14 (*m*, 1H, Ar*H*), 8.11 (*t*, 1H, *J* = 1.9 Hz, Ar*H*),7.60-7.49 (*m*, 2H, Ar*H*), 5.28 (*dd*, 1H, *J* = 14.0, 11.3 Hz, CH*H*NO_2), 4.80 (*dd*, 1H, *J* = 13.8, 3.3 Hz, C*H*HNO_2), 4.35 (*dd*, 1H, *J* = 11.2, 3.3 Hz, C*H*Ar),4.30-4.13 (*m*, 2H, OCH_2CH_3), 2.57-2.34 (*m*, 2H, $CH_{cyclopentane}$), 2.11-1.81 (*m*, 3H, $CH_{cyclopentane}$), 1.72-1.56 (*m*, 1H, $CH_{cyclopentane}$), 1.27 (*t*, 3H, *J* = 7.2 Hz, OCH_2CH_3). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 214.2, 170.2, 148.6, 138.2, 135.1, 130.2, 124.5, 123.6, 76.5, 62.8, 62.7, 46.7, 39.0, 33.1, 19.6, 14.1. **IR (solid)**: $\tilde{\nu}$ = 3091, 2980, 1723, 1553, 1529, 1467, 1446, 1378, 1349, 1317, 1279, 1228, 1149, 1108, 1015, 909, 859, 811, 737, 693 cm^{-1}. **HRMS (EI)** *m/z*: calculated $[C_{16}H_{18}N_2O_7]^+$ 350.1114, measured 350.1107.

Ethyl (*S*)-1-((*S*)-2-Nitro-1-(2-nitrophenyl)ethyl)-2-oxocyclopentane-1-carboxylate (3aJ)



3aJ

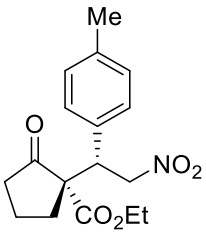


The product **3aJ** was synthesized as described in **GP6-standard**. **3aJ** was isolated in diastereomerically pure form as a white solid (68.0 mg, 0.194 mmol, 97%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 99:1, $ee_{(S,S)}$ = 99%). The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (90/10), 0.7 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 101.9 min, $t_{(R,S)}$ = 37.4 min.

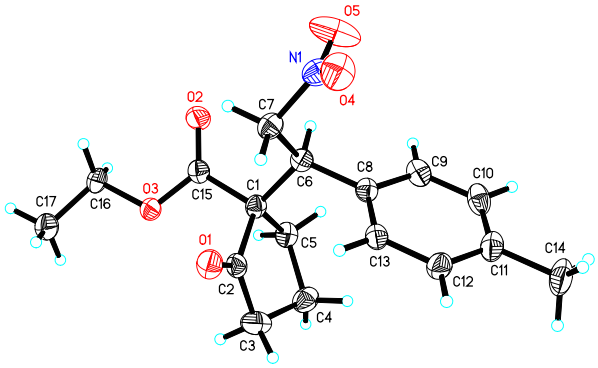
$C_{16}H_{18}N_2O_7$. MW: 350.33 g/mol. **MP** = 85-86 C. $[\alpha_D^{20}]$ = -135.3 (c = 0.25 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.89-7.83 (*m*, 1H, Ar*H*), 7.60-7.52 (*m*, 1H, Ar*H*), 7.50-7.41 (*m*, 1H, Ar*H*), 5.37 (*dd*, 1H, *J* = 14.4, 10.8 Hz, CH*H*NO_2), 5.02 (*dd*, 1H, *J* = 10.9, 3.3 Hz, C*H*Ar), 4.89 (*dd*, 1H, *J* = 14.4, 3.3 Hz, C*H*HNO_2), 4.35-4.14 (*m*, 2H, OC$H_2$$CH_3$), 2.60-2.42 (*m*, 2H, C$H_{cyclopentane}$), 2.16-1.72 (*m*, 4H, C$H_{cyclopentane}$), 1.27 (*t*, 3H, *J* = 7.0 Hz, OCH_2CH_3). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 215.6, 170.8, 151.6, 133.3, 131.5, 129.3, 128.6, 125.4, 77.1, 62.7, 62.6, 40.0, 39.5, 34.2, 19.9, 14.1. **IR (solid)**: $\tilde{\nu}$ = 2982, 1725, 1609, 1554, 1527, 1447, 1377, 1356, 1318, 1276, 1229, 1148, 1014, 855, 788, 711 cm^{-1}. **HRMS (EI)** *m/z*: calculated $[C_{16}H_{18}N_2O_7]^+$ 350.1114, measured 350.1103.

CCDC 1872224 contains the supplementary crystallographic data for compound **3aJ**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Ethyl (*S*)-1-((*S*)-2-Nitro-1-(*p*-tolyl)ethyl)-2-oxocyclopentane-1-carboxylate (3aK)



3aK



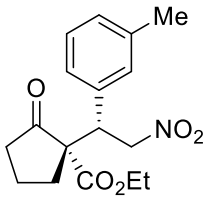
The product **3aK** was synthesized as described in **GP6-standard**. **3aK** was isolated as a white solid (59.1 mg, 0.185 mmol, 92%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 93:7, $ee_{(S,S)}$ = 99%). Diastereomerically pure substance **3aK** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel AS-H, *n*-hexane/*i*PrOH (95/5), 0.7 mL min^{-1}, detection at 220 nm, $t_{(S,S)}$ = 37.9 min, $t_{(R,S)}$ = 17.0 min.

$C_{17}H_{21}NO_5$. MW: 319.36 g/mol. **MP** = 107-108 °C. $[\alpha_D^{20}]$ = 43.1 (c = 0.21 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.15-7.02 (*m*, 4H, Ar*H*), 5.26 (*dd*, 1H, *J* = 13.5, 11.1 Hz, CH*H*NO_2), 4.81 (*dd*, 1H, *J* = 13.5, 3.7 Hz, C*H*HNO_2), 4.32-4.10 (*m*, 3H, C*H*Ar and OC$H_2$$CH_3$), 2.48-2.24 (*m*, 2H, C$H_{cyclopentane}$), 2.30 (*s*, 3H, Ar$CH_3$), 2.06-1.90 (*m*, 2H, C$H_{cyclopentane}$), 1.89-1.72 (*m*, 1H, C$H_{cyclopentane}$), 1.51-1.36 (*m*, 1H, C$H_{cyclopentane}$), 1.27 (*t*, 3H, *J* = 7.1 Hz, OCH_2CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ =215.8, 171.3, 138.4, 132.5, 129.8, 129.2, 77.2, 62.4, 62.3, 47.1, 39.7, 33.8, 21.2, 19.8, 14.2. **IR (solid)**: $\tilde{\nu}$ = 2980, 2924, 1724, 1552, 1516, 1446, 1378, 1275,

1226, 1147, 1120, 1107, 1019 822 cm^{-1}. **HRMS (EI)** *m/z*: calculated $[C_{17}H_{21}NO_5]^+$ 319.1420, measured 319.1416.

CCDC 1872235 contains the supplementary crystallographic data for compound **3aK**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Ethyl (*S*)-1-((*S*)-2-Nitro-1-(*m*-tolyl)ethyl)-2-oxocyclopentane-1-carboxylate (3aL)

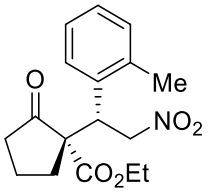


3aL

The product **3aL** was synthesized as described in **GP6-standard**. **3aL** was isolated as a colorless oil (62.0 mg, 0.194 mmol, 97%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 96:4, $ee_{(S,S)}$ = 99%). Diastereomerically pure substance **3aL** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (90/10), 0.7 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 16.6 min, $t_{(R,S)}$ = 12.7 min.

$C_{17}H_{21}NO_5$. MW: 319.36 g/mol. $[\alpha_D^{20}]$ = 38.4 (c = 0.24 g/dl, CH_2Cl_2). **^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 7.18 (*t*, 1H, *J* = 7.8 Hz, Ar*H*), 7.08 (*d*, 1H, *J* = 7.8 Hz, Ar*H*),6.99-6.95 (*m*, 2H, Ar*H*), 5.26 (*dd*, 1H, *J* = 13.6, 11.4 Hz, CH*H*NO_2), 4.80 (*dd*, 1H, *J* = 13.6, 3.8 Hz, C*H*HNO_2),4.28-4.12 (*m*, 3H, C*H*Ar and OCH_2CH_3), 2.46-2.37 (*m*, 1H, $CH_{cyclopentane}$), 2.31 (*s*, 3H, ArCH_3), 2.33-2.26 (*m*, 1H, $CH_{cyclopentane}$), 2.03-1.93 (*m*, 2H, $CH_{cyclopentane}$),), 1.86-1.75 (*m*, 1H, $CH_{cyclopentane}$), 1.48-1.39 (*m*, 1H, $CH_{cyclopentaen}$), 1.27 (*t*, 3H, *J* = 7.1 Hz, OCH_2CH_3). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 215.8, 171.3, 138.8, 135.6, 130.2, 129.3, 129.0, 126.1, 77.2, 62.4, 62.3, 47.4, 39.7, 33.7, 21.6, 19.8, 14.3. **IR (solid)**: $\tilde{\nu}$ = 2979, 1726, 1554, 1446, 1378, 1226, 1147, 1112, 1019, 708cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{17}H_{21}NNaO_5]^+$ 342.1312, measured 342.1306.

Ethyl (*S*)-1-((*S*)-2-Nitro-1-(*o*-tolyl)ethyl)-2-oxocyclopentane-1-carboxylate (3aM)

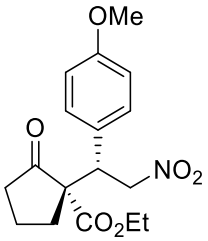


3aM

The product **3aM** was synthesized as described in **GP6-standard**. **3aM** was isolated as a colorless oil (54.1 mg, 0.169 mmol, 85%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 96:4, $ee_{(S,S)}$ = 99%). Diastereomerically pure substance **3aM** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (91/9), 0.7 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 17.6 min, $t_{(R,S)}$ = 15.6 min.

$C_{17}H_{21}NO_5$. MW: 319.36 g/mol. $[\alpha_D^{20}]$ = 60.1 (c = 0.24 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.20-7.05 (*m*, 4H, Ar*H*), 5.32 (*dd*, 1H, *J* = 13.8, 10.9 Hz, CH*H*NO_2), 4.87 (*dd*, 1H, *J* = 13.8, 3.6 Hz, C*H*HNO_2), 4.63 (*dd*, 1H, *J* = 10.9, 3.5 Hz, C*H*Ar),4.34-4.13 (*m*, 2H, OCH_2CH_3), 2.49-2.25 (*m*, 2H, $CH_{cyclopentane}$), 2.42 (*s*, 3H, ArCH_3), 2.02-1.74 (*m*, 3H, $CH_{cyclopentane}$), 1.66-1.55 (*m*, 1H, $CH_{cyclopentane}$), 1.27 (*t*, 3H, *J* = 7.2 Hz, OCH_2CH_3). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 216.2, 171.6, 138.6, 134.7, 131.3, 128.2, 127.0, 126.4, 77.4, 62.6, 62.4, 41.3, 39.7, 33.0, 20.3, 20.0, 14.2. **IR (solid)**: $\tilde{\nu}$ = 2978, 1725, 1552, 1465, 1446, 1378, 1275, 1228, 1146, 1123, 1084, 1030, 1014, 751, 727cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{17}H_{21}NNaO_5]^+$ 342.1312, measured 342.1310.

Ethyl (*S*)-1-((*S*)-1-(4-Methoxyphenyl)-2-nitroethyl)-2-oxocyclopentane-1-carboxylate (3aN)

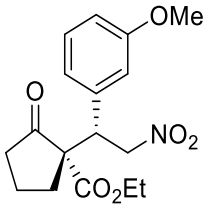


3aN

The product **3aN** was synthesized as described in **GP6-standard**. **3aN** was isolated as a colorless oil and as a mixture of diastereomers, which could not be separated (60.4 mg, 0.192 mmol, 90%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 93:7, $ee_{(S,S)}$ = 99%). The *ee* values were determined by chiral column HPLC: Chiracel 2xOD-H in series, *n*-hexane/*i*PrOH (85/15), 0.3 mL min^{-1}, detection at 213 nm, $t_{(S,S)}$ = 102.4 min, $t_{(R,S)}$ = 72.6 min.

$C_{17}H_{21}NO_6$. MW: 335.36 g/mol. $[\alpha_D^{20}]$ = 46.5 (c = 0.12 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ =7.21-7.06 (*m*, 2H, Ar*H*), 6.84-6.77 (*m*, 2H, Ar*H*), 5.23 (*dd*, 1H, *J* = 13.2, 11.2 Hz, CH*H*NO_2), 4.79 (*dd*, 1H, *J* = 13.3, 3.6 Hz, C*H*HNO_2),4.30-4.08 (*m*, 3H, O$CH_2$$CH_3$ and C*H*Ar), 3.76 (*s*, 3H, OCH_3), 2.47-2.23 (*m*, 2H, $CH_{cyclopentane}$), 2.05-1.71 (*m*, 3H, $CH_{cyclopentane}$), 1.51-1.37 (*m*, 1H, $CH_{cyclopentane}$), 1.25 (*t*, 3H, *J* = 7.2 Hz, OCH_2CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 215.8, 171.3, 159.6, 130.4, 127.3, 114.5, 77.2, 62.4, 62.3, 55.3, 46.8, 39.7, 33.7, 19.7, 14.1. **IR (solid)**: $\tilde{\nu}$ = 2961, 1726, 1612, 1554, 1515, 1349, 1253, 1230, 1182, 1148, 1120, 1033, 838, 732 cm^{-1}. **HRMS (EI)** *m/z*: calculated $[C_{17}H_{21}N_1O_6]^+$ 335.1369, measured 335.1368.

Ethyl (*S*)-1-((*S*)-1-(3-Methoxyphenyl)-2-nitroethyl)-2-oxocyclopentane-1-carboxylate (3aO)

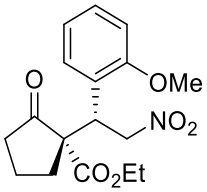


3aO

The product **3aO** was synthesized as described in **GP6-standard**. **3aO** was isolated as a colorless oil (63.8 mg, 0.190 mmol, 95%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 96:4, $ee_{(S,S)}$ = 99%). Diastereomerically pure substance **3aO** was obtained by trituration of the mixture of diastereomers with a solvent mixture of n-hexane/diethyleteher (10/1)for analytic purposes. The *ee* values were determined by chiral column HPLC: Chiracel AS-H, *n*-hexane/*i*PrOH (80/20), 1.0 mL min^{-1}, detection at 220 nm, $t_{(S,S)}$ = 133.3 min, $t_{(R,S)}$ = 14.0 min.

$C_{17}H_{21}NO_6$. MW: 335.36 g/mol. $[\alpha_D^{20}]$ = 33.1 (c = 0.28 g/dl, CH_2Cl_2). **^{1}H NMR (500 MHz, $CDCl_3$)**: δ =7.21 (*t*, 1H, *J* = 7.9 Hz Ar*H*), 6.81 (*dd*, 1H, *J* = 8.2, 4.2 Hz Ar*H*), 6.76 (*d*, 1H, *J* = 7.8 Hz Ar*H*), 6.72 (*t*, 1H, *J* = 1.9 Hz Ar*H*), 5.26 (*dd*, 1H, *J* = 13.4, 11.0 Hz, CH*H*NO_2), 4.82 (*dd*, 1H, *J* = 13.5, 3.5 Hz, C*H*HNO_2),4.29-4.13 (*m*, 3H, O$CH_2$$CH_3$ and C*H*Ar), 3.77 (*s*, 3H, OCH_3), 2.47-2.37 (*m*, 1H, $CH_{cyclopentane}$), 2.34-2.26 (*m*, 1H, $CH_{cyclopentane}$), 2.06-1.94 (*m*, 2H, $CH_{cyclopentane}$), 1.87-1.77 (*m*, 1H, $CH_{cyclopentane}$),1.51-1.42 (*m*, 1H, $CH_{cyclopentane}$), 1.27 (*t*, 3H, *J* = 7.0 Hz, OCH_2CH_3). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 215.7, 171.2, 160.0, 137.2, 130.2, 121.3, 115.5, 113.7, 77.1, 62.4, 62.3, 55.4, 47.4, 39.7, 33.8, 19.8, 14.2. **IR (solid)**: $\tilde{\nu}$ = 2979, 1226, 1553, 1466, 1446, 1378, 1317, 1275, 1229, 1147, 1123, 1031, 1014, 751, 727 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{17}H_{21}NNaO_6]^+$ 358.1261, measured 358.1262.

Ethyl (*S*)-1-((*S*)-1-(2-Methoxyphenyl)-2-nitroethyl)-2-oxocyclopentane-1-carboxylate (3aP)

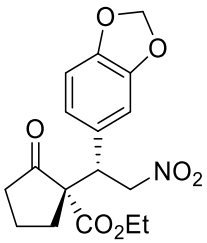


3aP

The product **3aP** was synthesized as described in **GP6-standard** within 72 h reaction time. **3aP** was isolated as a white solid (52.9 mg, 0.158 mmol, 79%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 95:5, $ee_{(S,S)}$ = 99%). Diastereomerically pure substance **3aP** was obtained by trituration of the mixture of diastereomers with a solvent mixture of n-hexane/diethyleteher (10/1) for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (95/5), 0.5 mL min^{-1}, detection at 220 nm, $t_{(S,S)}$ = 45.0 min, $t_{(R,S)}$ = 34.3 min.

$C_{17}H_{21}NO_6$. MW: 335.36 g/mol. **MP** = 85-86 °C. $[\alpha_D^{20}]$ = 52.0 (c = 0.27 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.26 (*dt*, 1H, *J* = 7.8, 1.6 Hz, Ar*H*), 7.13 (*dd*, 1H, *J* = 7.5, 1.6 Hz, Ar*H*), 6.93-6.84 (*m*, 2H, Ar*H*), 5.25 (*dd*, 1H, *J* = 13.4, 11.0 Hz, CH*H*NO_2), 4.91 (*dd*, 1H, *J* = 13.4, 3.6 Hz, C*H*HNO_2), 4.73 (*dd*, 1H, *J* = 11.0, 3.3 Hz, C*H*Ar),4.31-4.14 (*m*, 2H, OCH_2CH_3), 3.82 (*s*, 3H, OCH_3), 2.46-2.24 (*m*, 2H, $CH_{cyclopentane}$), 2.09-1.72 (*m*, 3H, $CH_{cyclopentane}$), 1.49-1.34 (*m*, 1H, $CH_{cyclopentane}$), 1.26 (*t*, 3H, *J* = 7.1 Hz, OCH_2CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 215.4, 171.8, 158.0, 129.7, 124.3, 121.2, 111.3, 76.5, 62.2, 61.6, 55.3, 39.4, 33.7, 20.0, 14.1. **IR (solid)**: $\tilde{\nu}$ = 2967, 2841, 1724, 1551, 1494, 1463, 1440, 1378, 1289, 1275, 1246, 1226, 1147, 1123, 1025, 757 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{17}H_{21}NNaO_6]^+$ 358.1261, measured 358.1272.

Ethyl (*S*)-1-((*S*)-1-(Benzo[d][1,3]dioxol-5-yl)-2-nitroethyl)-2-oxocyclopentane-1-carboxylate (3aQ)



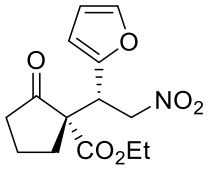
3aQ

The product **3aQ** was synthesized as described in **GP6-standard** within 72 h reaction time. **3aQ** was isolated as a colorless oil and as a mixture of diastereomers, which could not be separated (65.3 mg, 0.187 mmol, 94%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 95:5, $ee_{(S,S)}$ = 99%). The *ee* values were determined by chiral column

HPLC: Chiracel AS-H, *n*-hexane/*i*PrOH (70/30), 1.0 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 73.3 min, $t_{(R,S)}$ = 19.3 min.

$C_{17}H_{19}NO_7$. MW: 349.34 g/mol. $[\alpha_D^{20}]$ = 39.7 (c = 0.19 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 6.79-6.61 (*m*, 3H, Ar*H*), 5.93 (*s*, 2H, OC*H*$_2$O), 5.20 (*dd*, 1H, *J* = 13.3, 11.3 Hz, CH*H*NO_2), 4.76 (*dd*, 1H, *J* = 13.3, 3.5 Hz, C*H*HNO_2), 4.30-4.06 (*m*, 3H, OC*H*$_2$$CH_3$ and C*H*Ar), 2.49-2.24 (*m*, 2H, C*H*$_{cyclopentane}$), 2.09-1.74 (*m*, 3H, C*H*$_{cyclopentane}$), 1.60-1.46 (*m*, 1H, C*H*$_{cyclopentane}$), 1.26 (*t*, 3H, *J* = 7.1 Hz, OCH_2CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 215.7, 171.1, 148.2, 147.7, 129.1, 123.0, 109.2, 108.7, 101.4, 77.2, 62.5, 62.3, 47.2, 39.6, 33.6, 19.7, 14.1. **IR (solid)**: $\tilde{\nu}$ = 2979, 2898, 2780, 1722, 1552, 1504, 1489, 1445, 1377, 1244, 1225, 1150, 1107, 1036, 933, 905, 816, 730 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{17}H_{19}NNaO_7]^+$ 372.1054, measured 372.1037.

Ethyl (*S*)-1-((*S*)-1-(Furan-2-yl)-2-nitroethyl)-2-oxocyclopentane-1-carboxylate (3aR)

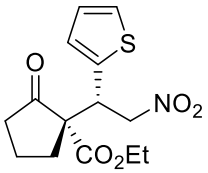


3aR

The product **3aR** was synthesized as described in **GP6-standard**. **3aR** was isolated as a colorless oil and as a mixture of diastereomers, which could not be separated (52.9 mg, 0.179 mmol, 89%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 90:10, $ee_{(S,S)}$ = 99%) . The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (91/9), 0.7 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 25.1 min, $t_{(R,S)}$ = 13.5 min.

$C_{14}H_{17}NO_6$. MW: 295.29 g/mol. $[\alpha_D^{20}]$ = 71.7 (c = 0.12 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.31 (*d*, 1H, *J* = 1.5, Ar*H*), 6.30-6.26 (*m*, 1H, Ar*H*), 6.24-6.20 (*m*, 1H, Ar*H*) 5.10 (*dd*, 1H, *J* = 13.4, 11.0 Hz, CH*H*NO_2), 4.77 (*dd*, 1H, *J* = 13.5, 3.2 Hz, C*H*HNO_2), 4.32 (*dd*, 1H, *J* = 11.0, 3.2 Hz, C*H*Ar),4.27-4.11 (*m*, 2H, OC*H*$_2$$CH_3$), 2.49-2.28 (*m*, 2H, C*H*$_{cyclopentane}$), 2.25-2.10 (*m*, 1H, C*H*$_{cyclopentane}$), 2.06-1.80 (*m*, 2H, C*H*$_{cyclopentane}$), 1.48-1.33 (*m*, 1H, C*H*$_{cyclopentane}$), 1.25 (*t*, 3H, *J* = 7.2 Hz, OCH_2CH_3). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 214.5, 171.0, 149.4, 143.0, 110.9, 110.4, 75.7, 62.4, 60.8, 41.4, 39.2, 34.2, 19.7, 14.1. **IR (solid)**: $\tilde{\nu}$ = 3127, 2979, 1726, 1555, 1505, 1467, 1447, 1403, 1377, 1317, 1230, 1147, 1111, 1074, 1015, 917, 822, 744 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{14}H_{17}NNaO_6]^+$ 318.0948, measured 318.0951.

Ethyl (*S*)-1-((*S*)-2-Nitro-1-(thiophen-2-yl)ethyl)-2-oxocyclopentane-1-carboxylate (3aS)

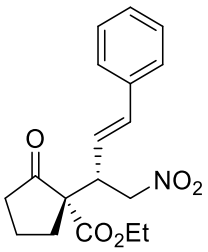


3aS

The product **3aS** was synthesized as described in **GP6-standard**. **3aS** was isolated as a white solid (60.1 mg, 0.193 mmol, 97%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 96:4, $ee_{(S,S)}$ = 98%). Diastereomerically pure substance **3aS** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes**.** The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (91/9), 0.7 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 26.8 min, $t_{(R,S)}$ = 16.5 min.

$C_{14}H_{17}NO_5S$. MW: 311.35 g/mol. **MP** = 76-77 °C. $[\alpha_D^{20}]$ = 30.3 (c = 015 g/dl, CH_2Cl_2). **^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 7.22 (*d*, 1H, *J* = 4.9, Ar*H*), 6.95-6.90 (*m*, 2H, Ar*H*), 5.22 (*dd*, 1H, *J* = 13.3, 10.8 Hz, CH*H*NO_2), 4.78 (*dd*, 1H, *J* = 13.3, 3.4 Hz, C*H*HNO_2), 4.52 (*dd*, 1H, *J* = 10.9, 3.3 Hz, C*H*Ar),4.31-4.16 (*m*, 2H, OCH_2CH_3), 2.51-2.42 (*m*, 1H, C$H_{cyclopentane}$), 2.38-2.32 (*m*, 1H, C$H_{cyclopentane}$), 2.17-2.04 (*m*, 2H, C$H_{cyclopentane}$), 1.95-1.84 (*m*, 1H, C$H_{cyclopentane}$), 1.65-1.56 (*m*, 1H, C$H_{cyclopentane}$), 1.28 (*t*, 3H, *J* = 7.2 Hz, OCH_2CH_3). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 215.3, 170.9, 137.9, 128.4, 127.3, 126.1, 78.3, 62.7, 62.5, 42.9, 39.5, 33.8, 19.7, 14.2. **IR (solid)**: $\tilde{\nu}$ = 3115, 2962, 2921, 2853, 1741, 1724, 1556, 1549, 1437, 1378, 1322, 1248, 1234, 1188, 1144, 1113, 1013, 999, 854, 714 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{14}H_{17}NNaO_5S]^+$ 334.0720, measured 334.0706.

Ethyl (*S*)-1-((*S,E*)-1-Nitro-4-phenylbut-3-en-2-yl)-2-oxocyclopentane-1-carboxylate (3aT)

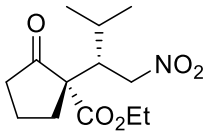


3aT

The product **3aT** was synthesized as described in **GP6-standard**. **3aT** was isolated as a colorless oil and as a mixture of diastereomers, which could not be separated (56.6 mg, 0.171 mmol, 85%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 91:9, $ee_{(S,S)}$ = 97%). The *ee* values were determined by chiral column HPLC: Chiracel 2xOD-H in series, *n*-hexane/*i*PrOH (85/15), 0.3 mL min^{-1}, detection at 213 nm, $t_{(S,S)}$ = 92.2 min, $t_{(R,S)}$ = 66.1 min.

$C_{18}H_{21}NO_5$. MW: 331.37 g/mol. $[\alpha_D^{20}]$ = 20.4 (c = 0.10 g/dl, CH_2Cl_2). **^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 7.30-7.18 (*m*, 5H, Ar*H*), 6.52 (*d*, *J* = 15.7, PhC*H*=CHC), 5.78 (*dd*, 1H, *J* = 15.8, 10.1 Hz, PhCH=C*H*CH), 4.88 (*dd*, 1H, *J* = 12.5, 11.0 Hz, C*H*HNO_2), 4.53 (*dd*, 1H, *J* = 12.5, 3.2 Hz, CH*H*NO_2), 4.24-4.12 (*m*, 2H, OC*H*$_2$CH$_3$), 3.64 (*dt*, 1H, *J* = 10.2, 3.1 Hz, PhCH=C*H*CH), 2.51-2.32 (*m*, 2H, C*H*$_{cyclopentane}$), 2.18-2.09 (*m*, 2H, C*H*$_{cyclopentane}$), 1.95-1.87 (*m*, 2H, C*H*$_{cyclopentane}$), 1.23 (*t*, 3H, *J* = 7.2 Hz, OCH$_2$C*H*$_3$). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 214.3, 170.7, 137.2, 135.8, 128.7, 126.7, 122.7, 76.7, 62.3, 61.7, 45.9, 39.1, 33.4, 19.8, 14.1. **IR (solid)**: $\tilde{\nu}$ = 3061, 3027, 2978, 2923, 1745, 1722, 1551, 1448, 1378, 1316, 1224, 1151, 1112, 1031, 971, 915, 748, 694 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{18}H_{21}NNaO_5]^+$ 354.1312, measured 354.1306.

Ethyl (*S*)-1-((*S*)-3-Methyl-1-nitrobutan-2-yl)-2-oxocyclopentane-1-carboxylate (3aU)

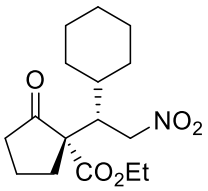


3aU

The product **3aU** was synthesized as described in **GP6-standard** within72 h reaction time. **3aU** was isolated as a colorless oil (49.8 mg, 0.184 mmol, 92%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 98:2, $ee_{(S,S)}$ = 99%). Diastereomerically pure substance **3aU** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel AS-H, *n*-hexane/*i*PrOH (91/9), 0.7 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 13.0 min, $t_{(R,S)}$ = 15.3 min.

$C_{13}H_{21}NO_5$. MW: 271.31 g/mol. $[\alpha_D^{20}]$ = -2.9 (c = 0.25 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 4.50 (*dd*, 1H, *J* = 13.7, 6.3 Hz, CH*H*NO_2), 4.42 (*dd*, 1H, *J* = 13.7, 5.1 Hz, C*H*HNO_2), 4.25-4.09 (*m*, 2H, OC*H*$_2$CH$_3$), 3.18-3.10 (*m*, 1H, C*Hi*Pr), 2.62-2.35 (*m*, 2H, Alkyl*H*), 2.30-2.14 (*m*, 1H, Alkyl*H*), 2.10-1.84 (*m*, 4H, Alkyl*H*), 1.25 (*t*, 3H, *J* = 7.2 Hz, OCH$_2$C*H*$_3$), 0.97 (*d*, 3H, *J* = 7.0 Hz, CHC*H*$_3$), 0.82 (*d*, 3H, *J* = 6.9 Hz, CHC*H*$_3$). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 213.4, 170.0, 73.8, 64.0, 62.3, 45.3, 37.7, 31.2, 28.3, 22.4, 19.5, 17.8, 14.1. **IR (solid)**: $\tilde{\nu}$ = 2967, 1751, 1719, 1553, 1467, 1384, 1365, 1221, 1179, 1154, 1126, 1095, 1025, 857 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{13}H_{21}NNaO_5]^+$ 294.1312, measured 294.1301.

Ethyl (*S*)-1-((*S*)-1-Cyclohexyl-2-nitroethyl)-2-oxocyclopentane-1-carboxylate (3aV)

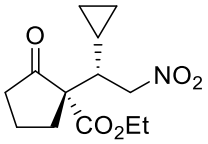


3aV

The product **3aV** was synthesized as described in **GP6-neat** within 72 h reaction time. Diastereomerically pure **3aV** was isolated as a colorless oil (56.1 mg, 0.180 mmol, 90%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 97:3, $ee_{(S,S)}$ = 99%). The *ee* values were determined by chiral column HPLC: Chiracel AS-H, *n*-hexane/*i*PrOH (91/9), 0.7 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 13.9 min, $t_{(R,S)}$ = 15.4 min.

$C_{16}H_{25}NO_5$. MW: 311.38 g/mol. $[\alpha_D^{20}]$ = -9.2 (c = 0.21 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 4.57 (*dd*, 1H, *J* = 13.7, 6.8 Hz, CH*H*NO_2), 4.38 (*dd*, 1H, *J* = 13.7, 4.7 Hz, C*H*HNO_2), 4.26-4.09 (*m*, 2H, OC*H*$_2$CH$_3$), 3.13-3.06 (*m*, 1H, C*H*CH_2NO_2), 2.60-2.35 (*m*, 2H, Alkyl*H*), 2.29-2.14 (*m*, 1H, Alkyl*H*), 2.06-1.84 (*m*, 3H, Alkyl*H*), 1.77-1.66 (*m*, 2H, Alkyl*H*), 1.66-1.53 (*m*, 3H, Alkyl*H*), 1.53-1.43 (*m*, 1H, Alkyl*H*), 1.25 (*t*, 3H, *J* = 7.1 Hz, OCH_2CH_3), 1.21-0.86 (*m*, 5H, Alkyl*H*). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 213.6, 170.2, 74.4, 63.9, 62.2, 45.3, 38.9, 37.7, 32.6, 31.4, 28.5, 26.9, 26.5, 26.0, 19.5, 14.1. **IR (solid)**: $\tilde{\nu}$ = 2927, 2854, 1750, 1719, 1552, 1448, 1373, 1220, 1176, 1153, 1140, 1111, 1016 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{16}H_{25}NNaO_5]^+$ 334.1625, measured 334.1629.

Ethyl (*S*)-1-((*S*)-1-Cyclopropyl-2-nitroethyl)-2-oxocyclopentane-1-carboxylate (3aW)



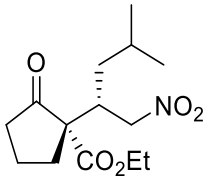
3aW

The product **3aW** was synthesized as described in **GP6-neat** within 72 h reaction time. **3aW** was isolated as a colorless oil and mixture of diastereomeres, which could not be separated (51.6 mg, 0.192 mmol, 96%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 88:12, $ee_{(S,S)}$ = 98%). The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (97/3), 0.5 mL min^{-1}, detection at 220 nm, $t_{(S,S)}$ = 45.4 min, $t_{(R,S)}$ = 40.2 min.

$C_{13}H_{19}NO_5$. MW: 269.30 g/mol. $[\alpha_D^{20}]$ = -0.06 (c = 0.15 g/dl, CH_2Cl_2).**^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 4.72 (*dd*, 1H, *J* = 12.5, 8.3 Hz, CH*H*NO_2), 4.50 (*dd*, 1H, *J* = 12.7, 3.9 Hz, C*H*HNO_2), 4.27-4.12 (*m*, 2H, OC*H*$_2$CH$_3$), 2.56-2.27 (*m*, 4H, Alkyl*H*), 2.26-1.86 (*m*, 1H, C*H*CH_2NO_2), 1.89-1.65 (*m*, 2H, Alkyl*H*), 1.26 (*t*, 3H, *J* = 7.1 Hz,

OCH_2CH_3), 0.74-0.43 (*m*, 3H, Alkyl*H*), 0.35-0.17 (*m*, 1H, Alkyl*H*). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 213.9, 170.3, 78.2, 64.0, 62.2, 45.0, 38.6, 31.6, 19.6, 14.1, 11.9, 5.7, 2.4. **IR (solid)**: $\tilde{\nu}$ = 2981, 2923, 2258, 1748, 1723, 1552., 1464, 1434, 1380, 1298, 1225, 1160, 1112, 1030, 910, 728, 648 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{13}H_{20}NO_5]^+$ 270.1336, measured 270.1323.

Ethyl (*S*)-1-((*S*)-4-Methyl-1-nitropentan-2-yl)-2-oxocyclopentane-1-carboxylate (3aX)

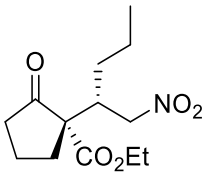


3aX

The product **3aX** was synthesized as described in **GP6-neat** within 72 h reaction time. **3aX** was isolated as a colorless oil (49.0 mg, 0.172 mmol, 86%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 90:10, $ee_{(S,S)}$ = 99%). The purification of the diastereomerical mixture *via* preparative TLC (petroleum ether/ethyl acetate, 10/1) led to 5% impurity of minor diastereomer and was used for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel 2xOD-H in series, *n*-hexane/*i*PrOH (90/10), 0.3 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 46.8 min, $t_{(R,S)}$ = 42.2 min.

$C_{14}H_{23}NO_5$. MW: 285.34 g/mol. $[\alpha_D^{20}]$ = -2.6 (c = 0.11 g/dl, CH_2Cl_2). **^{1}H NMR (700 MHz, $CDCl_3$)**: δ = 4.57 (*dd*, 1H, *J* = 13.2, 5.0 Hz, $CHHNO_2$), 4.39 (*dd*, 1H, *J* = 13.3, 5.6 Hz, $CHHNO_2$), 4.18 (*q*, 2H, *J* = 7.2 Hz, OCH_2CH_3), 3.02-2.97 (*m*, 1H, $CHCH_2NO_2$), 2.50-2.41 (*m*, 2H, Alkyl*H*), 2.28-2.21 (*m*, 1H, Alkyl*H*), 2.05-1.89 (*m*, 3H, Alkyl*H*), 1.58-1.52 (*m*, 1H, Alkyl*H*), 1.35-1.29 (*m*, 1H, Alkyl*H*), 1.29-1.24 (*m*, 1H, Alkyl*H*), 1.26 (*t*, 3H, *J* = 7.1 Hz, OCH_2CH_3), 0.90 (*dd*, 6H, *J* = 11.7, 6.4 Hz, $CH(CH_3)_2$).**^{13}C NMR (176 MHz, $CDCl_3$)**: δ = 213.6, 170.4, 77.5, 63.5, 62.2, 39.0, 38.4, 38.3, 31.6, 25.8,23.8, 21.3, 19.4, 14.1. **IR (solid)**: $\tilde{\nu}$ = 2959, 2872, 1749, 1719, 1551, 1468, 1381, 1368, 1221, 1157, 1131, 1106, 1020 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{14}H_{23}NNaO_5]^+$ 308.1468, measured 308.1467.

Ethyl (*S*)-1-((*S*)-1-Nitropentan-2-yl)-2-oxocyclopentane-1-carboxylate (3aY)

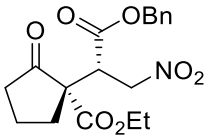


3aY

The product **3aY** was synthesized as described in **GP6-neat** within 72 h reaction time. **3aY** was isolated as a colorless oil (52.1 mg, 0.192 mmol, 96%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 87:13, $ee_{(S,S)}$ = 98%). Diastereomerically pure substance **3aY** was obtained by purification of diastereomerical mixture *via* preparative TLC (petroleum ether/ethyl acetate, 10/1) for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (97/3), 0.3 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 47.5 min, $t_{(R,S)}$ = 40.7 min.

$C_{13}H_{21}NO_5$. MW: 271.31 g/mol. $[\alpha_D^{20}]$ = -8.2 (c = 0.23 g/dl, CH_2Cl_2). **^{1}H NMR (700 MHz, $CDCl_3$)**: δ = 4.53 (*dd*, 1H, *J* = 13.3, 4.6 Hz, CH*H*NO_2), 4.46 (*dd*, 1H, *J* = 13.3, 6.5 Hz, C*H*HNO_2), 4.19 (*q*, 2H, *J* = 7.1 Hz, OCH_2CH_3), 2.96-2.90 (*m*, 1H, C*H*CH_2NO_2), 2.51-2.43 (*m*, 2H, Alkyl*H*), 2.28-2.21 (*m*, 1H, Alkyl*H*), 2.04-1.91 (*m*, 3H, Alkyl*H*), 1.60-1.53 (*m*, 1H, Alkyl*H*), 1.42-1.34 (*m*, 1H, Alkyl*H*), 1.33-1.24 (*m*, 2H, Alkyl*H*), 1.26 (*t*, 3H, *J* = 7.1 Hz, OCH_2CH_3), 0.90 (*t*, 3H, *J* = 7.0 Hz, $CH_2CH_2CH_3$). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 213.7, 170.5, 77.3, 63.3, 62.1, 40.2, 38.3, 32.0, 31.9, 20.7, 19.4, 14.1. **IR (solid)**: $\tilde{\nu}$ = 2963, 2875, 1749, 1720, 1552, 1466, 1381, 1223, 1175, 1157, 1126, 1028, 822 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{13}H_{21}NNaO_5]^+$ 294.1312, measured 294.1301.

Ethyl (*S*)-1-((*S*)-1-(Benzyloxy)-3-nitro-1-oxopropan-2-yl)-2-oxocyclopentane-1-carboxylate (3aZ)

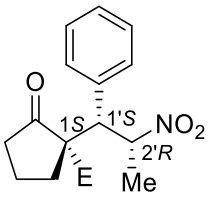


3aZ

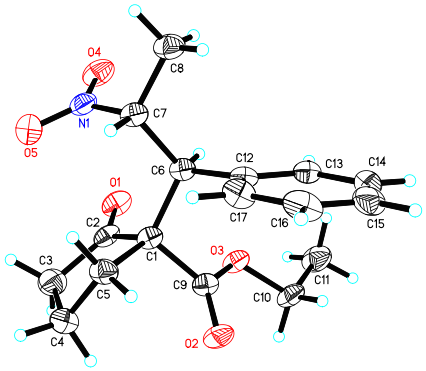
The product **3aZ** was synthesized as described in **GP6-standard** within 48 h reaction time. **3aZ** was isolated as a colorless oil as mixture of diastereomers, which could not be separated (40.8 mg, 0.112 mmol, 56%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 74:26, $ee_{(S,S)}$ = 96%). The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (95/5), 0.7 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 44.6 min, $t_{(R,S)}$ = 37.8 min.

$C_{18}H_{21}NO_7$. MW: 363.37 g/mol. $[\alpha_D^{20}]$ = 2.0 (c = 0.13 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.41-7.28 (m, 5H, Ar*H*), 5.15 (*d*, 2H, *J* = 1.5 Hz, OCH_2Ar), 4.94 (*dd*, 1H, *J* = 14.4, 9.9 Hz, CH*H*NO_2), 4.59 (*dd*, 1H, *J* = 14.5, 3.2 Hz, C*H*HNO_2), 4.20-4.06 (*m*, 2H, OC$H_2$$CH_3$), 4.01 (*dd*, 1H, *J* = 10.0, 3.2 Hz,C*H*CO_2Bn), 2.51-2.37 (*m*, 2H, C$H_{cyclopentane}$), 2.26-1.80 (*m*, 4H, C$H_{cyclopentane}$), 1.20 (*t*, 3H, *J* = 7.2 Hz, OCH$_2$CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 212.4, 170.1, 169.4, 134.7, 128.8, 128.7, 128.6, 73.5, 68.0, 62.6, 60.0, 46.5, 38.1, 32.3, 19.4, 13.9. **IR (solid)**: $\tilde{\nu}$ = 2963, 2924, 1725, 1557, 1455, 1378, 1221, 1153, 1110, 949, 915, 751, 698 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{18}H_{21}NNaO_7]^+$ 386.1210, measured 386.1211.

Ethyl (1*S*)-1-((1*S*,2*R*)-2-Nitro-1-phenylpropyl)-2-oxocyclopentane-1-carboxylate (3aA-Me)



3aA-Me
E = CO_2Et

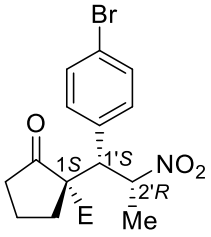


The product **3aA-Me** was synthesized as described in **GP7** within 120 h reaction time. **3aA-Me** was isolated as a white solid as mixture of diastereomers (57.9 mg, 0.181 mmol, 91%, $dr_{(S,S,R+R,R,S):D2:D3:D4}$ = 94:3:2:1, $ee_{(S,S,R)}$ = >99%). Diastereomerically pure substance **3aA-Me** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* and *dr* values were determined by chiral column HPLC of the crude reaction mixture: Chiracel IB, *n*-heptane/*i*PrOH (98/2), 0.3 mL min^{-1}, detection at 210 nm, $t_{(S,S,R)}$ = 69.1 min, $t_{(R,R,S)}$ = 67.3 min.

$C_{17}H_{21}NO_5$. MW: 319.36 g/mol. **MP** = 96-97 °C. $[\alpha_D^{20}]$ = -12.0 (c = 0.13 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.34-7.26 (*m*, 3H, Ar*H*), 7.16-7.13 (*m*, 2H, Ar*H*), 5.35-5.25 (*m*, 1H, C*H*CH_3NO_2), 4.06 (*d*, 1H, *J* = 10.1 Hz, C*H*Ar), 4.00-3.81 (*m*, 2H, OC$H_2$$CH_3$), 2.66-2.59 (*m*, 1H, C$H_{cyclopentane}$), 2.43-2.14 (*m*, 3H, C$H_{cyclopentane}$), 2.01-1.74 (*m*, 2H, C$H_{cyclopentane}$), 1.20 (*d*, 3H, *J* = 6.7 Hz, CHC$H_3$$NO_2$), 1.10 (*t*, 3H, *J* = 7.1 Hz, OCH$_2$CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 212.2, 168.4, 136.2, 129.5, 128.9, 128.2, 82.5, 64.9, 62.1, 52.5, 37.4, 30.4, 19.5, 19.1, 13.7. **IR (solid)**: $\tilde{\nu}$ = 2983, 1753, 1728, 1553, 1454, 1388, 1361, 1225, 1123, 705. **HRMS (ESI)** *m/z*: calculated $[C_{17}H_{21}NNaO_5]^+$ 342.1312, measured 342.1310.

CCDC 1908072 contains the supplementary crystallographic data for compound **3aA-Me**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Ethyl (1*S*)-1-((1*S,2R*)-1-(4-Bromophenyl)-2-nitropropyl)-2-oxocyclopentane-1-carboxylate (3aB-Me)

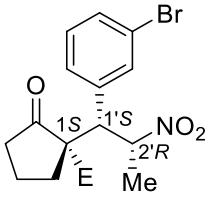


3aB-Me
E = CO_2Et

The product **3aB-Me** was synthesized as described in **GP7** within 120 h reaction time. **3aB-Me** was isolated as a white solid as mixture of diastereomers (73.4 mg, 0.184 mmol, 92%, $dr_{(S,S,R+R,R,S):D2:D3:D4}$ = 94:3:2:1, $ee_{(S,S,R)}$ = >99%). Diastereomerically pure substance **3aB-Me** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* and *dr* values were determined by chiral column HPLC of the crude reaction mixture: Chiracel IB, *n*-heptane/*i*PrOH (98/2), 0.5 mL min^{-1}, detection at 210 nm, $t_{(S,S,R)}$ = 60.9 min, $t_{(R,R,S)}$ = 56.9 min.

$C_{17}H_{20}BrNO_5$. MW: 398.25 g/mol. **MP** = 93-94 °C. $[\alpha_D^{20}]$ = -11.3 (c = 0.21 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.47-7.43 (*m*, 2H, Ar*H*), 7.06-7.02 (*m*, 2H, Ar*H*), 5.30-5.21 (*m*, 1H, C*H*CH_3NO_2), 4.05 (*d*, 1H, *J* = 9.7 Hz, C*H*Ar), 4.00-3.84 (*m*, 2H, OCH_2CH_3), 2.62-2.55 (*m*, 1H, $CH_{cyclopentane}$), 2.43-2.13 (*m*, 3H, $CH_{cyclopentane}$), 2.03-1.76 (*m*, 2H, $CH_{cyclopentane}$), 1.21 (*d*, 3H, *J* = 6.6 Hz, CHCH_3NO_2), 1.12 (*t*, 3H, *J* = 7.2 Hz, OCH_2CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ =211.9, 168.3, 135.3, 132.1, 131.1, 122.3, 82.2, 64.7, 62.3, 51.9, 37.3, 30.5, 19.5, 19.0, 13.7. **IR (solid)**: $\tilde{\nu}$ = 2981, 1753, 1727, 1553, 1490, 1451, 1407, 1389, 1360, 1225, 1124, 1011, 838. **HRMS (ESI)** *m/z*: calculated $[C_{17}H_{20}BrNNaO_5]^+$ 420.0417, measured 420.0415.

Ethyl (1*S*)-1-((1*S,2R*)-1-(3-Bromophenyl)-2-nitropropyl)-2-oxocyclopentane-1-carboxylate (3aC-Me)



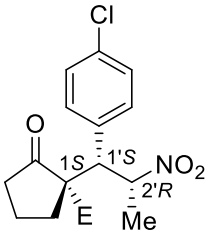
3aC-Me
E = CO_2Et

The product **3aC-Me** was synthesized as described in **GP7** within 120 h reaction time. **3aC-Me** was isolated as a white solid as mixture of diastereomers (68.2 mg, 0.171 mmol, 86%, $dr_{(S,S,R+R,R,S):D2:D3:D4}$ = 97:2:1:0.2, $ee_{(S,S,R)}$ = 99%). Diastereomerically pure substance **3aC-Me** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* and *dr* values were determined by chiral

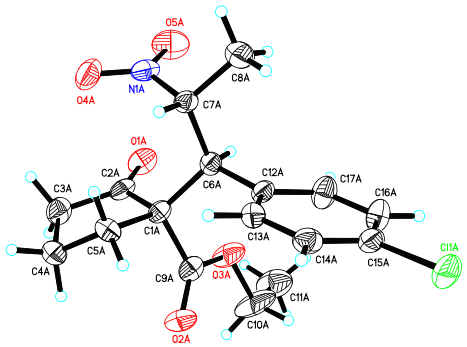
column HPLC of the crude reaction mixture: Chiracel ADH, *n*-heptane/*i*PrOH (97/3), 0.3 mL min^{-1}, detection at 210 nm, $t_{(S,S,R)}$ = 61.1 min, $t_{(R,R,S)}$ = 57.9 min.

$C_{17}H_{20}BrNO_5$. MW: 398.25 g/mol. **MP** = 117-118 °C. $[\alpha_D^{20}]$ = -16.0 (c = 0.13 g/dl, CH_2Cl_2). **^{1}H NMR (700 MHz, $CDCl_3$)**: δ = 7.45-7.41 (*m*, 1H, Ar*H*), 7.33 (*t*, 1H, *J* = 1.7 Hz, Ar*H*), 7.19 (*t*, 1H, *J* = 7.8 Hz, Ar*H*), 7.10-7.08 (*m*, 1H, Ar*H*), 5.28-5.18 (*m*, 1H, C*H*CH_3NO_2), 4.04 (*d*, 1H, *J* = 9.9 Hz, C*H*Ar), 4.02-3.85 (*m*, 2H, OCH_2CH_3), 2.66-2.58 (*m*, 1H, $CH_{cyclopentane}$), 2.44-2.15 (*m*, 3H, $CH_{cyclopentane}$), 2.03-1.76 (*m*, 2H, $CH_{cyclopentane}$), 1.22 (*d*, 3H, *J* = 6.6 Hz, CHCH_3NO_2), 1.12 (*t*, 3H, *J* = 7.2 Hz, OCH_2CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 211.6, 168.1, 138.6, 132.7, 131.4, 130.5, 127.8, 122.9, 82.2, 64.9, 62.3, 52.0, 37.2, 30.1, 19.5, 16.0, 13.7. **IR (solid)**: $\tilde{\nu}$ = 2981, 1753, 1725, 1552, 1475, 1450, 1387, 1360, 1223, 1193, 1175, 1153, 1121, 1093, 1021, 866, 792, 705. **HRMS (ESI)** *m/z*: calculated $[C_{17}H_{20}BrNNaO_5]^+$ 420.0417, measured 420.0421.

Ethyl (1*S*)-1-((1*S*,2*R*)-1-(4-Chlorophenyl)-2-nitropropyl)-2-oxocyclopentane-1-carboxylate (3aE-Me)



3aE-Me
E = CO_2Et

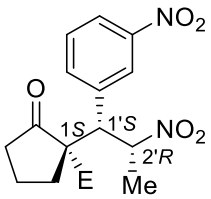


The product **3aE-Me** was synthesized as described in **GP7** within 120 h reaction time. **3aE-Me** was isolated as a white solid as mixture of diastereomers (69.9 mg, 0.198 mmol, 99%, $dr_{(S,S,R+R,R,S):(S,S,S+R,R,R):D3:D4}$ = 94:3:3:0.4, $ee_{(S,S,R)}$ = >99%). Diastereomerically pure substance **3aE-Me** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* and *dr* values were determined by chiral column HPLC of the crude reaction mixture: Chiracel IB, *n*-heptane/*i*PrOH (95/5), 0.3 mL min^{-1}, detection at 210 nm, $t_{(S,S,R)}$ = 31.8 min, $t_{(R,R,S)}$ = 30.7 min.

$C_{17}H_{20}ClNO_5$. MW: 353.80 g/mol. **MP** = 83-84 °C. $[\alpha_D^{20}]$ = -18.3 (c = 0.13 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.32-7.28 (*m*, 2H, Ar*H*), 7.12-7.08 (*m*, 2H, Ar*H*), 5.31-5.21 (*m*, 1H, C*H*CH_3NO_2), 4.06 (*d*, 1H, *J* = 9.7 Hz, C*H*Ar), 4.00-3.84 (*m*, 2H, OCH_2CH_3), 2.64-2.56 (*m*, 1H, $CH_{cyclopentane}$), 2.43-2.14 (*m*, 3H, $CH_{cyclopentane}$), 2.03-1.76 (*m*, 2H, $CH_{cyclopentane}$), 1.21 (*d*, 3H, *J* = 6.5 Hz, CHCH_3NO_2), 1.13 (*t*, 3H, *J* = 7.2 Hz, OCH_2CH_3). **^{13}C NMR (176 MHz, $CDCl_3$)**: δ = 211.9, 168.3, 134.8, 134.2, 130.8, 129.2, 82.3, 64.8, 62.3, 51.8, 37.3, 30.5, 19.5, 19.0, 13.7. **IR (solid)**: $\tilde{\nu}$ = 2982, 1753, 1727, 1553, 1493, 1451, 1389, 1360, 1225, 1193, 1152, 1124, 1094, 1015 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{17}H_{20}ClNNaO_5]^+$ 376.0922, measured 376.0921.

CCDC 1908073 contains the supplementary crystallographic data for compound **3aE-Me**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Ethyl (1*S*)-1-((1*S*,2*R*)-1-(3-Nitroophenyl)-2-nitropropyl)-2-oxocyclopentane-1-carboxylate (3aI-Me)

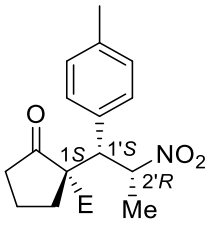


3aI-Me
E = CO_2Et

The product **3aI-Me** was synthesized as described in **GP7** within 120 h reaction time. **3aI-Me** was isolated as a white solid as mixture of diastereomers (64.4 mg, 0.177 mmol, 88%, $dr_{(S,S,R+R,R,S):D2:D3:D4}$ = 92:5:2:1, $ee_{(S,S,R)}$ = >99%). Diastereomerically pure substance **3aI-Me** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* and *dr* values were determined by chiral column HPLC of the crude reaction mixture: Chiracel ADH, *n*-heptane/*i*PrOH (95/5), 0.7 mL min^{-1}, detection at 210 nm, $t_{(S,S,R)}$ = 58.7 min, $t_{(R,R,S)}$ = 70.5 min.

$C_{17}H_{20}N_2O_7$. MW: 364.35 g/mol. **MP** = 98-99 °C. $[\alpha_D^{20}]$ = -33.1 (c = 0.15 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 8.19-8.16 (*m*, 1H, Ar*H*), 8.07 (*s*, 1H, Ar*H*), 7.56-7.52 (*m*, 2H, Ar*H*), 5.30-5.21 (*m*, 1H, C*H*CH_3NO_2), 4.25 (*d*, 1H, *J* = 9.5 Hz, C*H*Ar), 4.02-3.83 (*m*, 2H, OCH_2CH_3), 2.71-2.63 (*m*, 1H, $CH_{cyclopentane}$), 2.47-2.18 (*m*, 3H, $CH_{cyclopentane}$), 2.11-1.81 (*m*, 2H, $CH_{cyclopentane}$), 1.23 (*d*, 3H, *J* = 6.7 Hz, CHCH_3NO_2), 1.11 (*t*, 3H, *J* = 7.2 Hz, OCH_2CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 211.1, 167.9, 148.4, 138.5, 135.6, 130.0, 124.3, 123.3, 82.0, 65.0, 62.5, 51.9, 37.0, 29.9, 19.4, 19.0, 13.7. **IR (solid)**: $\tilde{\nu}$ = 3090, 2983, 1752, 1724, 1553, 1528, 1449, 1389, 1348, 1224, 1175, 1120, 1020, 911, 869, 811. **HRMS (ESI)** *m/z*: calculated $[C_{17}H_{20}N_2NaO_7]^+$ 387.1163, measured 387.1163.

Ethyl (1*S*)-1-((1*S*,2*R*)-2-nitro-1-*p*-tolylpropyl)-2-oxocyclopentane-1-carboxylate (3aK-Me)

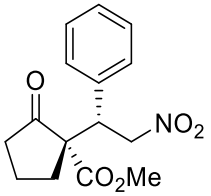


3aK-Me
E = CO_2Et

The product **3aK-Me** was synthesized as described in **GP7** within 120 h reaction time. **3aK-Me** was isolated as a white solid as mixture of diastereomers (49.4 mg, 0.148 mmol, 74%, $dr_{(S,S,R+R,R,S):D2:D3:D4}$ = 93:4:2:0.1, $ee_{(S,S,R)}$ = >98%). Diastereomerically pure substance **3aK-Me** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* and *dr* values were determined by chiral column and reversed phase HPLC of the crude reaction mixture: Chiracel IB, *n*-heptane/*i*PrOH (98/2), 0.5 mL min^{-1}, detection at 210 nm, $t_{(S,S,R)}$ = 63.7 min, $t_{(R,R,S)}$ = 58.8 min.

$C_{18}H_{23}NO_5$. MW: 333.38 g/mol. **MP** = 96-97 °C. $[\alpha_D^{20}]$ = -8.2 (c = 0.14 g/dl, CH_2Cl_2). **^{1}H NMR (700 MHz, $CDCl_3$)**: δ = 7.11-7.07 (*m*, 2H, Ar*H*), 7.03-7.00 (*m*, 2H, Ar*H*), 5.34-5.24 (*m*, 1H, C*H*CH_3NO_2), 4.03-3.82 (*m*, 3H, C*H*Ar and OC*H*$_2CH_3$), 2.63-2.55 (*m*, 1H, C*H*$_{cyclopentane}$), 2.41-2.14 (*m*, 3H, C*H*$_{cyclopentane}$), 2.31 (*s*, 3H, Ar-C*H*$_3$), 1.99-1.75 (*m*, 2H, C*H*$_{cyclopentane}$), 1.19 (*d*, 3H, *J* = 6.4 Hz, CHC*H*$_3NO_2$), 1.12 (*t*, 3H, *J* = 6.9 Hz, OCH_2CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ =212.4, 168.6, 137.9, 133.1, 129.6, 129.3, 82.6, 64.9, 62.1, 52.2, 37.5, 30.5, 21.0, 19.5, 19.1, 13.7. **IR (solid)**: $\tilde{\nu}$ = 2980, 1750, 1725, 1547, 1515, 1446, 1403, 1387, 1359, 1220, 1187, 1153, 1126, 1108, 1022, 870, 832, 812. **HRMS (ESI)** *m/z*: calculated $[C_{18}H_{23}NNaO_5]^+$ 356.1468, measured 356.1464.

Methyl (*S*)-1-((*S*)-2-Nitro-1-phenylethyl)-2-oxocyclopentane-1-carboxylate (3bA)



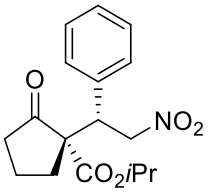
3bA

The product **3bA** was synthesized as described in **GP6-standard**. **3bA** was isolated as colorless oil (53.8 mg, 0.185 mmol, 92%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 95:5, $ee_{(S,S)}$ = 99%). Diastereomerically pure substance **3bA** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee*

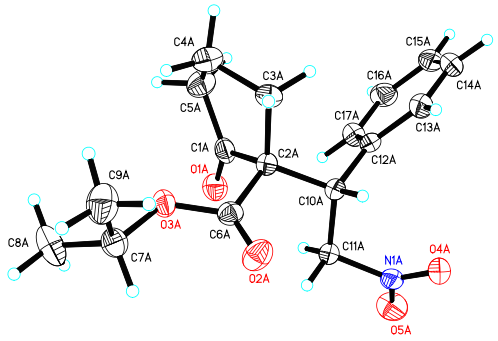
values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (90/10), 1.0 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 23.3 min, $t_{(R,S)}$ = 16.2 min.

$C_{15}H_{17}NO_5$. MW: 291.30 g/mol. $[\alpha_D^{20}]$ = 29.2 (c = 0.15 g/dl, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.34-7.27 (*m*, 3H, Ar*H*), 7.21-7.14 (*m*, 2H, Ar*H*), 5.26 (*dd*, 1H, *J* = 13.5, 11.2 Hz, CH*H*NO_2), 4.83 (*dd*, 1H, *J* = 13.5, 3.7 Hz, C*H*HNO_2), 4.20 (*dd*, 1H, *J* = 11.1, 3.6 Hz, C*H*Ph), 3.75 (*s*, 3H, OCH_3), 2.48-2.28 (*m*, 2H, $CH_{cyclopentane}$), 2.06-1.92 (*m*, 2H, $CH_{cyclopentane}$), 1.87-1.74 (*m*, 1H, $CH_{cyclopentane}$), 1.47-1.36 (*m*, 1H, $CH_{cyclopentane}$). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 215.5, 171.6, 135.6, 129.3, 129.2, 128.6, 77.0, 62.4, 53.2, 47.5, 39.7, 33.6, 19.7. **IR (solid)**: $\tilde{\nu}$ = 2957, 2923, 1726, 1550, 1433, 1378, 1229, 1147, 1111, 703 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{15}H_{17}NNaO_5]^+$ 314.0999, measured 314.1011.

Isopropyl (*S*)-1-((*S*)-2-Nitro-1-phenylethyl)-2-oxocyclopentane-1-carboxylate (3cA)



3cA

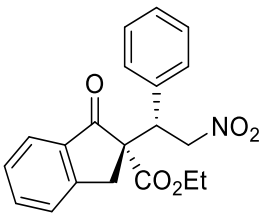


The product **3cA** was synthesized as described in **GP6-standard**. **3cA** was isolated as white solid (58.8 mg, 0.184 mmol, 92%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 97:3, $ee_{(S,S)}$ = 99%). Diastereomerically pure substance **3cA** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (95/5), 0.3 mL min^{-1}, detection at 220 nm, $t_{(S,S)}$ = 19.6 min, $t_{(R,S)}$ = 18.3 min.

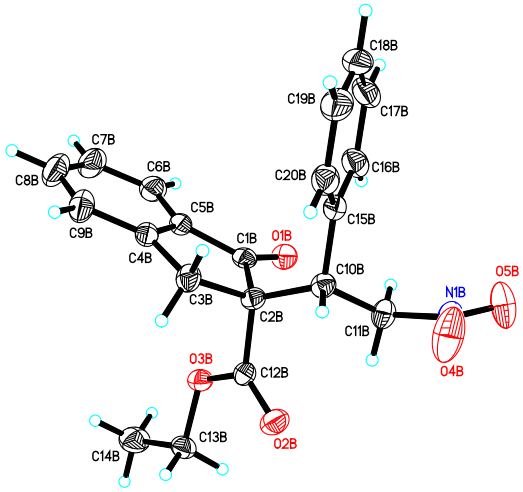
$C_{17}H_{21}NO_5$. MW: 319.36 g/mol. **MP** = 84-85 °C. $[\alpha_D^{20}]$ = 16.2 (c = 0.15 g/dl, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.34-7.27 (*m*, 3H, Ar*H*), 7.22-7.16 (*m*, 2H, Ar*H*), 5.30 (*dd*, 1H, *J* = 13.3, 11.1 Hz, CH*H*NO_2), 5.07 (*sept,* 1H, *J* = 6.3 Hz, OC*H*$(CH_3)_2$), 4.83 (*dd*, 1H, *J* = 13.5, 3.3 Hz, C*H*HNO_2), 4.18 (*dd*, 1H, *J* = 11.0, 3.3 Hz, C*H*Ph), 2.45-2.34 (*m*, 1H, $CH_{cyclopentane}$), 2.33-2.24 (*m*, 1H, $CH_{cyclopentane}$), 2.04-1.89 (*m*, 2H, $CH_{cyclopentane}$), 1.87-1.74 (*m*, 1H, $CH_{cyclopentane}$), 1.48-1.37 (*m*, 1H, $CH_{cyclopentane}$), 1.25 (*d*, 6H, *J* = 6.3 Hz, OCH$(CH_3)_2$). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 215.6, 170.8, 135.8, 129.4, 129.1, 128.5, 77.2, 70.3, 62.5, 47.4, 39.6, 33.7, 21.7, 21.6, 19.7. **IR (solid)**: $\tilde{\nu}$ = 3.034, 2981, 1742, 1720, 1553, 1455, 1377, 1231, 1148, 1100, 907, 729, 702 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{17}H_{21}NNaO_5]^+$ 342.1312, measured 342.1312.

CCDC 1872236 contains the supplementary crystallographic data for compound **3cA**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Ethyl (*S*)-2-((*S*)-2-Nitro-1-phenylethyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3dA)



3dA

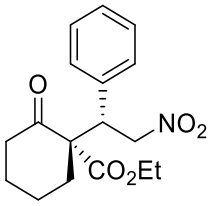


The product **3dA** was synthesized as described in **GP6-standard**. **3dA** was isolated as colorless oil (63.1 mg, 0.179 mmol, 89%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 93:7, $ee_{(S,S)}$ = 99%). Diastereomerically pure substance **3dA** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (80/20), 1.0 mL min^{-1}, detection at 220 nm, $t_{(S,S)}$ = 29.3 min, $t_{(R,S)}$ = 11.8 min.

$C_{20}H_{19}NO_5$. MW: 353.37 g/mol. **MP** = 90-91 °C. $[\alpha_D^{20}]$ = 24.0 (c = 0.12 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.75 (*d*, 1H, *J* = 7.8 Hz, Ar*H*), 7.49 (*dt*, *J* = 7.5, 1.3 Hz, Ar*H*), 7.34 (*t*, 1H, *J* = 7.2 Hz, Ar*H*), 7.23 (*d*, 1H, *J* = 7.8 Hz, Ar*H*), 7.17-7.09 (*m*, 5H, Ar*H*), 5.19 (*dd*, 1H, *J* = 13.5, 11.0 Hz, C*H*NO_2), 5.06 (*dd*, 1H, *J* = 13.5, 3.6 Hz, C*H*NO_2), 4.48 (*dd*, 1H, *J* = 11.0, 3.5 Hz, C*H*Ph), 4.15 (*q*, 2H, *J* = 7.1 Hz, O$CH_2$$CH_3$), 3.49 (*d*, 1H, *J* = 17.6 Hz, C$H_{cyclopentane}$), 3.16 (*d*, 1H, *J* = 17.6 Hz, C$H_{cyclopentane}$), 1.16 (*t*, 3H, *J* = 7.1 Hz, OCH_2CH_3). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 202.2, 170.7, 152.5, 136.3, 135.8, 135.0, 129.1, 128.7, 128.4, 128.0, 126.1, 124.5, 77.3, 62.4, 61.9, 47.6, 36.7. **IR (solid)**: $\tilde{\nu}$ = 3063, 3034, 2982, 2926, 1731, 1704, 1605, 1551, 1378, 1240, 1213, 1182, 1009, 909, 754, 730, 702 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{20}H_{19}NNaO_5]^+$ 376.1155, measured 376.1151.

CCDC 1872229 contains the supplementary crystallographic data for compound **3dA**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Ethyl (*S*)-1-((*S*)-2-Nitro-1-phenylethyl)-2-oxocyclohexane-1-carboxylate (3eA)

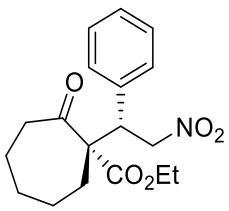


3eA

The product **3eA** was synthesized as described in **GP6-neat** at 0°C within 72 h reaction time. **3eA** was isolated as a colorless oil and as a mixture of diastereomers, which could not be separated (61.6 mg, 0.193 mmol, 96%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 80:20, $ee_{(S,S)}$ = 97%). The *ee* values were determined by chiral column HPLC: Chiracel AS-H, *n*-hexane/*i*PrOH (95/5), 0.5 mL min^{-1}, detection at 220 nm, $t_{(S,S)}$ = 71.3 min, $t_{(R,S)}$ = 33.5 min.

$C_{17}H_{21}NO_5$. MW: 319.36 g/mol. $[\alpha_D^{20}]$ = -40.9 (c = 0.15 g/dl, CH_2Cl_2). **Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 7.32-7.21 (*m*, 5H, Ar*H*), 5.16 (*dd*, 1H, *J* = 13.6, 11.0 Hz, CH*H*NO_2), 4.76 (*dd*, 1H, *J* = 13.6, 3.3 Hz, C*H*HNO_2), 4.25-4.08 (*m*, 3H, OCH_2CH_3 and C*H*Ph), 2.53-2.39 (*m*, 3H, $CH_{cyclohexane}$), 1.99-1.92 (*m*, 1H, $CH_{cyclohexane}$), 1.79-1.69 (*m*, 1H,$CH_{cyclohexane}$), 1.65-1.59 (*m*, 1H, $CH_{cyclohexane}$), 1.54-1.43 (*m*, 1H, $CH_{cyclohexane}$), 1.41-1.34 (*m*, 1H, $CH_{cyclohexane}$),1.24 (*t*, 3H, *J* = 7.0 Hz, OCH_2CH_3). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 206.7, 170.4, 135.9, 129.7, 128.8, 128.3, 77.4, 64.4, 62.3, 48.0, 41.5, 33.5, 26.3, 22.3, 14.1. **Minor Diastereomer :[23] ^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.32-7.21 (*m*, 3H, Ar*H*), 7.17-7.13 (*m*, 2H, Ar*H*), 5.06 (*dd*, 1H, *J* = 13.2, 3.1 Hz, CH*H*NO_2), 4.79 (*dd*, 1H, *J* = 13.2, 11.3 Hz, C*H*HNO_2), 4.25-4.08 (*m*, 2H, OCH_2CH_3), 4.00 (*dd*, 1H, *J* = 11.3, 3.1 Hz, C*H*Ph), 2.55-2.39 (*m*, 3H, $CH_{cyclohexane}$), 2.13-2.06 (*m*, 1H, $CH_{cyclohexane}$), 2.05-1.99 (*m*, 1H,$CH_{cyclohexane}$), 1.72-1.64 (*m*, 1H, $CH_{cyclohexane}$), 1.64-1.60 (*m*, 1H, $CH_{cyclohexane}$), 1.54-1.43 (*m*, 1H, $CH_{cyclohexane}$), 1.25 (*t*, 3H, *J* = 6.8 Hz, OCH_2CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 207.2, 169.8, 135.5, 129.6, 128.8, 128.6, 77.7, 63.1, 62.1, 47.9, 37.2, 33.5, 28.8, 22.5, 14.1. **IR (solid)**: $\tilde{\nu}$ = 3032, 2944, 2870, 1709, 1552, 1435, 1378, 1235, 1203, 1095, 1019, 703 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{17}H_{22}NO_5]^+$ 320.1492, measured 320.1485.

Ethyl (*S*)-1-((*S*)-2-Nitro-1-phenylethyl)-2-oxocycloheptane-1-carboxylate (3fA)

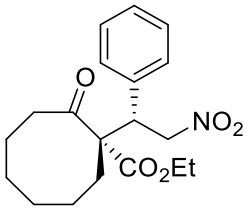


3fA

The product **3fA** was synthesized as described in **GP6-standard**. **3fA** was isolated as colorless oil (63.7 mg, 0.191 mmol, 96%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 91:9, $ee_{(S,S)}$ = 99%). Diastereomerically pure substance **3fA** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (95/5), 1.0 mL min^{-1}, detection at 220 nm, $t_{(S,S)}$ = 20.3 min, $t_{(R,S)}$ = 11.6 min.

$C_{18}H_{23}NO_5$. MW: 333.38 g/mol. **MP** = 85-86 °C. $[\alpha_D^{20}]$ = 10.9 (c = 0.15 g/dl, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.34-7.27 (*m*, 3H, Ar*H*), 7.22-7.16 (*m*, 2H, Ar*H*), 5.14 (*dd*, 1H, *J* = 13.6, 11.1 Hz, CH*H*NO_2), 4.81 (*dd*, 1H, *J* = 13.6, 3.0 Hz, C*H*HNO_2), 4.33-4.17 (*m*, 2H, OC$H_2$$CH_3$), 4.06 (*dd*, 1H, *J* = 11.0, 3.0 Hz, C*H*Ph), 2.59-2.48 (*m*, 1H, C$H_{cycloheptane}$), 2.18-2.00 (*m*, 2H, C$H_{cycloheptane}$), 1.86-1.76 (*m*, 1H, C$H_{cycloheptane}$), 1.71-1.57 (*m*, 3H, C$H_{cycloheptane}$), 1.52-1.37 (*m*, 2H, C$H_{cycloheptane}$), 1.35-1.23 (*m*, 1H, C$H_{cycloheptane}$), 1.30 (*t*, 3H, *J* = 7.1 Hz, OCH_2CH_3). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 210.6, 171.8, 135.2, 129.5, 128.8, 128.4, 78.2, 65.6, 62.1, 50.9, 45.3, 34.2, 30.2, 25.1, 24.3, 14.1. **IR (solid)**: $\tilde{\nu}$ = 3032, 2934, 2862, 1698, 1551, 1454, 1378, 1226, 1152, 1021, 702 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{18}H_{24}NO_5]^+$ 334.1649, measured 334.1636.

Ethyl (*S*)-1-((*S*)-2-Nitro-1-phenylethyl)-2-oxocyclooctane-1-carboxylate (3gA)



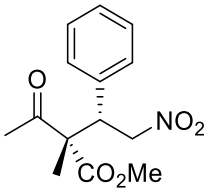
3gA

The product **3gA** was synthesized as described in **GP6-standard** using 0.1 mL THF (instead of 0.4 mL) at 0°C within 72 h reaction time. **3gA** was isolated as a colorless oil and as a mixture of diastereomeres, which could not be separated (37.4 mg, 0.108 mmol, 54%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 69:31, $ee_{(S,S)}$ = 92%). The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (95/5), 0.7 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 24.4 min, $t_{(R,S)}$ = 17.7 min.

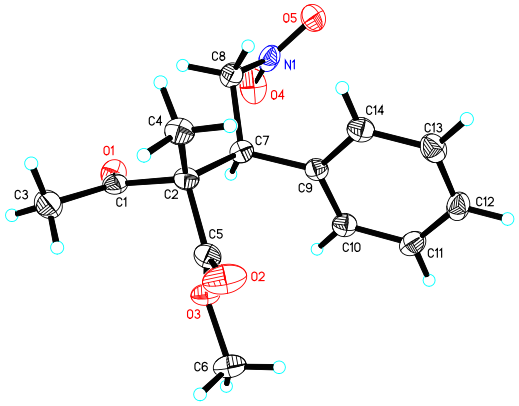
$C_{19}H_{25}NO_5$. MW: 347.41 g/mol. $[\alpha_D^{20}]$ = 10.2 (c = 0.23 g/dl, CH_2Cl_2). **Major Diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.30-7.22 (*m*, 5H, Ar*H*), 5.03-4.2 (*m*, 2H, C$H_2$$NO_2$), 4.34-3.95 (*m*, 3H, OC$H_2$$CH_3$ and C*H*Ph), 2.68-2.11 (*m*, 3H, C$H_{cyclooctane}$), 2.04-1.93 (*m*, 1H, C$H_{cyclooctane}$), 1.85-1.54 (*m*, 6H, C$H_{cyclooctane}$), 1.43-1.69 (*m*, 2H, C$H_{cyclooctane}$), 1.18 (*t*, 3H, *J* = 7.1 Hz, OCH_2CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 211.2, 170.6, 135.9, 129.6, 128.6, 128.3, 77.4, 65.6, 62.0, 47.4, 40.7, 29.8, 28.2 25.7, 25.5, 24.4, 14.0. **Minor Diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.30-7.22 (*m*, 3H, Ar*H*), 7.13-7.08 (*m*, 2H, Ar*H*), 5.01 (*dd*, 1H,

J = 13.3, 3.1 Hz, CH*H*NO_2), 4.71 (*dd*, 1H, *J* = 13.3, 11.3 Hz, C*H*HNO_2), 4.34-3.95 (*m*, 3H, OCH_2CH_3 and C*H*Ph), 2.68-2.11 (*m*, 4H, $CH_{cyclooctane}$), 1.85-1.54 (*m*, 6H, $CH_{cyclooctane}$), 1.43-1.69 (*m*, 2H, $CH_{cyclooctane}$), 1.31 (*t*, 3H, *J* = 7.1 Hz, OCH_2CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 210.9, 170.7, 136.1, 129.6, 128.8, 128.4, 78.7, 64.6, 62.1, 46.2, 40.1, 31.8, 27.4, 26.4, 24.9, 22.6, 14.2. **IR (solid)**: $\tilde{\nu}$ = 2931, 2859, 1742, 1705, 1553, 1455, 1378, 1281, 1220, 1183, 1093, 1022, 703 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{19}H_{25}NO_5Na]^+$ 370.1625, measured 370.1627.

Methyl (2*S*,3*S*)-2-Acetyl-2-methyl-4-nitro-3-phenylbutanoate (3hA)



3hA

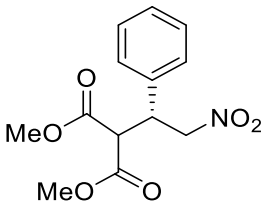


The product **3hA** was synthesized as described in **GP6-standard** using 0.125 mL THF (*n*(**2A**) = 0.25 mmol, *n*(**1h**) = 0.50 mmol, *n*(**C1b-Cu***) = 0.0125 mmol) within 72 h reaction time. **3hA** was isolated as a white solid (57.2 mg, 0.205 mmol, 80%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 84:16, $ee_{(S,S)}$ = 75%). Diastereomerically pure substance **3hA** was obtained by trituration of the mixture of diastereomers with *n*-hexane for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (91/9), 0.7 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 30.1 min, $t_{(R,S)}$ = 22.1 min.

$C_{14}H_{17}NO_5$. MW: 279.29 g/mol. MP = 71-72 °C. $[\alpha_D^{20}]$ = −17.7 (c = 0.24 g/dl, CH_2Cl_2), **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.33-7.27 (m, 3H, Ar*H*), 7.23-7.18 (m, 2H, Ar*H*), 4.93 (*m*, 2H, CH_2NO_2), 4.24 (*dd*, 1H, *J* = 8.0, 6.6 Hz, C*H*Ar), 3.64 (*s*, 3H,OCH_3), 2.11 (s, 3H, $COCH_3$), 1.44 (s, 3H, CH_3)..**^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 205.4, 171.4, 135.5, 129.3, 128.9, 128.5, 76.9, 62.1, 52.9, 47.4, 27.8, 18.1. **IR (solid)**: $\tilde{\nu}$ = 3000, 2954, 1711, 1603, 1552, 1497, 1455, 1434, 1379, 1359, 1307, 1238, 1198, 1118, 1096, 976, 832, 704 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{14}H_{18}NO_5]^+$ 280.1179, measured 280.1169.

CCDC 1872230 contains the supplementary crystallographic data for compound **3hA**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Dimethyl (*R*)-2-(2-Nitro-1-phenylethyl)malonate (3iA)



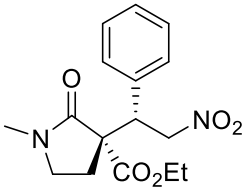
3iA

The product **3iA** was synthesized as described in **GP6-standard,** using 0.1 mL THF (instead of 0.4 mL) within 72 h reaction time. **3iA** was isolated as colorless oil (32.4 mg, 0.115 mmol, 58%, $ee_{(R)}$ = 80%). The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (70/30), 0.5 mL min^{-1}, detection at 254 nm, $t_{(R)}$ = 26.5 min, $t_{(S)}$ = 24.3 min.

$C_{13}H_{15}NO_6$. MW: 281.26 g/mol. $[\alpha_D^{20}] = -4.3$ (c = 0.37 g/dl, $CHCl_3$), **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.36-7.27 (m, 3H, Ar*H*), 7.25-7.19 (m, 2H, Ar*H*), 4.93 (*dd*, 1H, *J* = 13.2, 5.4 Hz, CH*H*NO_2), 4.86 (*dd*, 1H, *J* = 13.2, 8.6 Hz, C*H*HNO_2), 4.25 (*td*, 1H, *J* = 8.6, 5.4 Hz, C*H*Ar), 3.86 (*d*, 1H, *J* = 9.0 Hz, C*H*$(CO_2Me)_2$), 3.75 (s, 3H, CO_2CH_3), 3.55 (s, 3H, CO_2CH_3).**^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 168.0, 167.4, 136.2, 129.1, 128.5, 128.0, 77.5, 54.9, 53.1, 52.9, 43.0. **IR (solid)**: $\tilde{\nu}$ = 3033, 2956, 1731, 1551, 1434, 1379, 1290, 1256, 1236, 1196, 1152, 1018, 700 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{13}H_{15}NNaO_6]^+$ 304.0792, measured 304.0793.

The absolute configuration of (-)- was determined to be (R)-isomer by comparing the specific optical rotation with literature value.[24] [lit. for the (*S*)-enantiomere (93% *ee*): $[\alpha_D^{20}] = +4.40$ (c = 1.02 g/dL, $CHCl_3$)]

Ethyl (*S*)-1-Methyl-3-((*S*)-2-nitro-1-phenylethyl)-2-oxopyrrolidine-3-carboxylate (3jA)

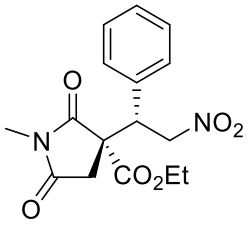


3jA

The product **3jA** was synthesized as described in **GP6-standard** using 0.1 mL THF (instead of 0.4 mL) at -30°C within 72 h reaction time. **3jA** was isolated as colorless oil and as a mixture of diastereomeres, which could not be separated (45.4 mg, 0.142 mmol, 71%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 84:16, $ee_{(S,S)}$ = 91%). The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (90/10), 0.5 mL min^{-1}, detection at 214 nm, $t_{(S,S)}$ = 57.7 min, $t_{(R,S)}$ = 49.5 min.

$C_{16}H_{20}N_2O_5$. MW: 320.35 g/mol. $[\alpha_D^{20}] = 62.4$ (c = 0.16 g/dl, CH_2Cl_2). **Major Diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.32-7.23 (*m*, 5H, Ar*H*), 5.29 (*dd*, 1H, *J* = 13.7, 11.0 Hz, CH*H*NO_2), 5.02 (*dd*, 1H, *J* = 13.7, 3.4 Hz, C*H*HNO_2), 4.34-4.15 (*m*, 3H, *J* = 7.1 Hz, OCH_2CH$_3$ and C*H*CH_2NO_2), 3.15-3.05 (*m*, 1H, Alkyl*H*), 2.76 (*s,* 3H, NCH_3), 2.32-2.17 (*m*, 2H, Alkyl*H*), 2.07-1.96 (*m*, 1H, Alkyl*H*), 1.29 (*t*, 3H, *J* = 7.1 Hz, OCH_2CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 171.5, 170.9, 135.5, 129.3, 128.9, 128.6, 77.4, 62.4, 58.0, 47.4, 46.8, 30.2, 28.6, 14.2. **Minor Diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.32-7.23 (*m*, 5H, Ar*H*), 5.51 (*dd*, 1H, *J* = 13.6, 3.6 Hz, CH*H*NO_2), 5.11 (*dd*, 1H, *J* = 13.6, 11.1 Hz, C*H*HNO_2), 4.34-4.15 (*m*, 2H, *J* = 7.1 Hz, OCH_2CH$_3$), 4.11 (*dd*, 1H, *J* = 11.1, 3.6 Hz, C*H*CH_2NO_2), 3.35-3.25 (*m*, 1H, Alkyl*H*), 3.30-2.91 (*m*, 1H, Alkyl*H*), 2.75 (*s,* 3H, NCH_3), 2.46-2.36 (*m*, 1H, Alkyl*H*), 2.07-1.96 (*m*, 1H, Alkyl*H*), 1.30 (*t*, 3H, *J* = 7.2 Hz, OCH_2CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ =170.3, 170.0, 135.9, 129.1, 128.9, 128.4, 77.4, 62.4, 58.2, 47.4, 46.7, 30.4, 27.0, 14.17. **IR (solid)**: $\tilde{\nu}$ = 3032, 2983, 2935, 2887, 1730, 1686, 1551, 1498, 1455, 1433, 1404, 1379, 1307, 1270, 1230, 1197, 1099, 705 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{16}H_{20}N_2NaO_5]^+$ 343.1264, measured 343.1248.

Ethyl (*S*)-1-Methyl-3-((*S*)-2-nitro-1-phenylethyl)-2,5-dioxopyrrolidine-3-carboxylate (3kA)

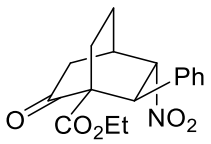


3kA

The product **3kA** was synthesized as described in **GP6-standard** using 0.1 mL THF (instead of 0.4 mL). **3kA** was isolated as colorless oil and as a mixture of diastereomeres, which could not be separated (63.4 mg, 0.189 mmol, 95%, $dr_{(S,S+R,R):(R,S+S,R)}$ = 83:17, $ee_{(S,S)}$ = 98%). The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (80/20), 1.0 mL min^{-1}, detection at 220 nm, $t_{(S,S)}$ = 55.6 min, $t_{(R,S)}$ = 20.6 min.

$C_{16}H_{18}N_2O_6$. MW: 334.33 g/mol. $[\alpha_D^{20}] = 60.5$ (c = 0.36 g/dl, CH_2Cl_2). **Major Diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.34-7.28 (*m*, 3H, Ar*H*), 7.16-7.13 (*m*, 2H, Ar*H*), 5.25 (*dd*, 1H, *J* = 13.7, 10.6 Hz, CH*H*NO_2), 5.12 (*dd*, 1H, *J* = 13.8, 3.6 Hz, C*H*HNO_2), 4.34-4.15 (*m*, 3H, *J* = 7.1 Hz, OCH_2CH_3 and C*H*CH_2NO_2), 2.92 (*s,* 3H, NCH_3), 2.86 (*d*, *J* = 18.2 Hz, COC*H*H), 2.66 (*d*, *J* = 18.2 Hz, COCH*H*), 1.29 (*t*, 3H, *J* = 7.1 Hz, OCH_2CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 174.8, 173.4, 169.1, 133.7, 129.6, 129.4, 128.9, 76.8, 63.4, 56.7, 46.8, 38.4, 25.4, 14.0. **Minor Diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.34-7.28 (*m*, 3H, Ar*H*), 7.25-7.20 (*m*, 2H, Ar*H*), 5.19 (*dd*, 1H, *J* = 13.4, 4.1 Hz, CH*H*NO_2), 5.12 (*dd*, 1H, *J* = 13.4, 10.5 Hz, C*H*HNO_2), 4.42 (*dd*, 1H, *J* = 10.5, 4.1 Hz, C*H*CH_2NO_2), 4.34-4.15 (*m*, 2H, *J* = 7.1 Hz, OCH_2CH_3) 3.19 (*d*, *J* = 18.1 Hz, COC*H*H), 2.66 (*d*, *J* = 18.1 Hz, COCH*H*), 2.74 (*s,* 3H, NCH_3), 1.33 (*t*, 3H, *J* = 7.2 Hz, OCH_2CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ =173.8, 173.6, 170.5, 133.7, 129.4, 129.2, 128.7, 76.0, 63.6, 58.1, 46.3, 35.7, 25.4, 14.2. **IR (solid)**: $\tilde{\nu}$ = 2984, 1785, 1736, 1699, 1553, 1497, 1435, 1379, 1341, 1284, 1245, 1187, 1128, 1076, 1011, 913, 732, 704 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{16}H_{18}N_2NaO_6]^+$ 357.1057, measured 357.1050.

Ethyl (1S,2S,3S,4R)-3-Nitro-6-oxo-2-phenylbicyclo[2.2.2]octane-1-carboxylate (4-D2)



4-D2

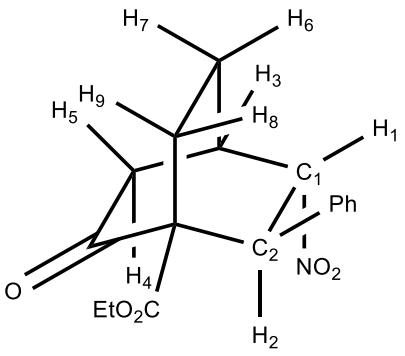
The product **4-D2** was synthesized as described in **GP6-standard** using 0.1 mL THF (instead of 0.4 mL) at 22°C. After completing 71 h of reaction time, *tetra-n*-butylammonium fluoride (60 µL, 0.3 equiv, 1 M in

THF) was added and the reaction mixture was stirred an additional hour at room temperature. The work up was proceeded as described in **GP6 Standard** and **4-D2** was isolated as colorless oil (59.6 mg, 0.189 mmol, 92%, $dr_{(S,S,S,R+R,R,R,S):(R,S,S,S+S,R,R,R)}$ = 93:7, $ee_{(S,S,S,R)}$ = 97%). Diastereomerically pure substance **4-D2** was obtained by purification *via* preparative TLC (petroleum ether/ethyl acetate, 8/1) for analytical purposes. The *ee* values were determined by chiral column HPLC: Chiracel OD-H, *n*-hexane/*i*PrOH (95/5), 0.7 mL min^{-1}, detection at 220 nm, $t_{(S,S,S,R)}$ = 46.1 min, $t_{(R,R,R,S)}$ = 43.7 min.

$C_{17}H_{19}NO_5$. MW: 317.34 g/mol. $[\alpha_D^{20}] = 25.3$ (c = 0.34 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.36-7.26 (*m*, 5H, Ar*H*), 5.04-4.99 (*m*, 1H, CH*H*NO_2), 5.04-4.99 (*m*, 1H, C*H*NO_2), 4.49-4.45 (*m*, 1H, C*H*Ph), 4.13-3.90 (*m*, 2H, OCH_2CH_3), 3.05 (*sext*, 1H, *J* = 2.8 Hz, $(CH_2)_2CH$CHNO_2), 2.70 (*dt*, 1H, *J* = 19.5, 2.4 Hz, COC*H*HCH), 2.50-2.37 (*m*, 2H, COCH*H*CH and $(C)_3CH$HCH_2), 2.20-1.94 (*m*, 3H, $(C)_3$CH*H*CH_2CH), 1.11 (*t*, 3H, *J* = 7.2 Hz, OCH_2CH_3). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 205.7, 168.7, 136.5, 129.2, 129.0, 128.5, 90.3, 61.4, 59.2, 44.4, 38.3, 34.8, 23.8, 20.1, 14.0. **IR (solid)**: $\tilde{\nu}$ = 2977, 1726, 1550, 1497, 1471, 1455, 1406, 1368, 1306, 1267, 1242, 1171, 1076, 1047, 705 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{17}H_{19}NO_5Na]^+$ 340.1155, measured 340.1164.

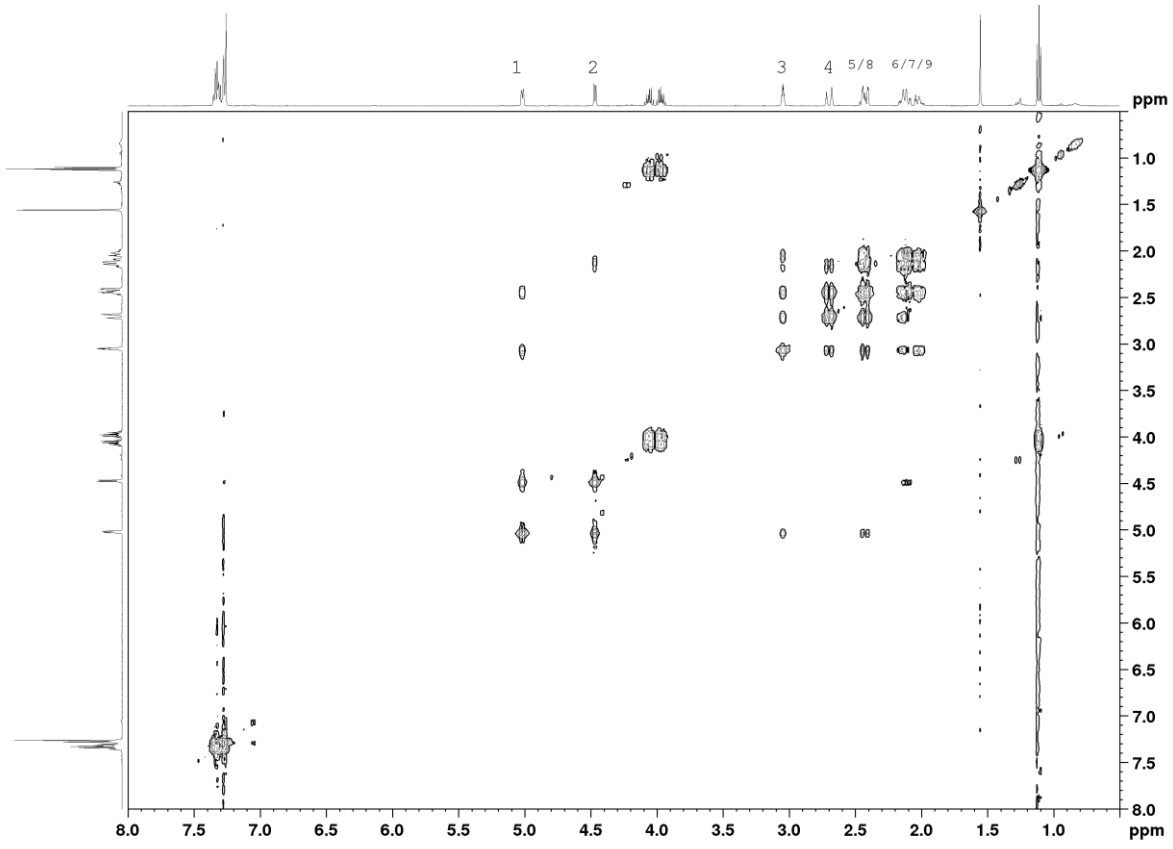
Confirming the Configurational Outcome with 2D-NMR Experiments of Compound 4-D2.

To confirm the structure of the major diastereomer of compound **4-D2**, several NMR-Experiments were performed (COSY, HSQC, HMBC and NOESY) and the different 2D-NMR spectra are shown in the next chapters.

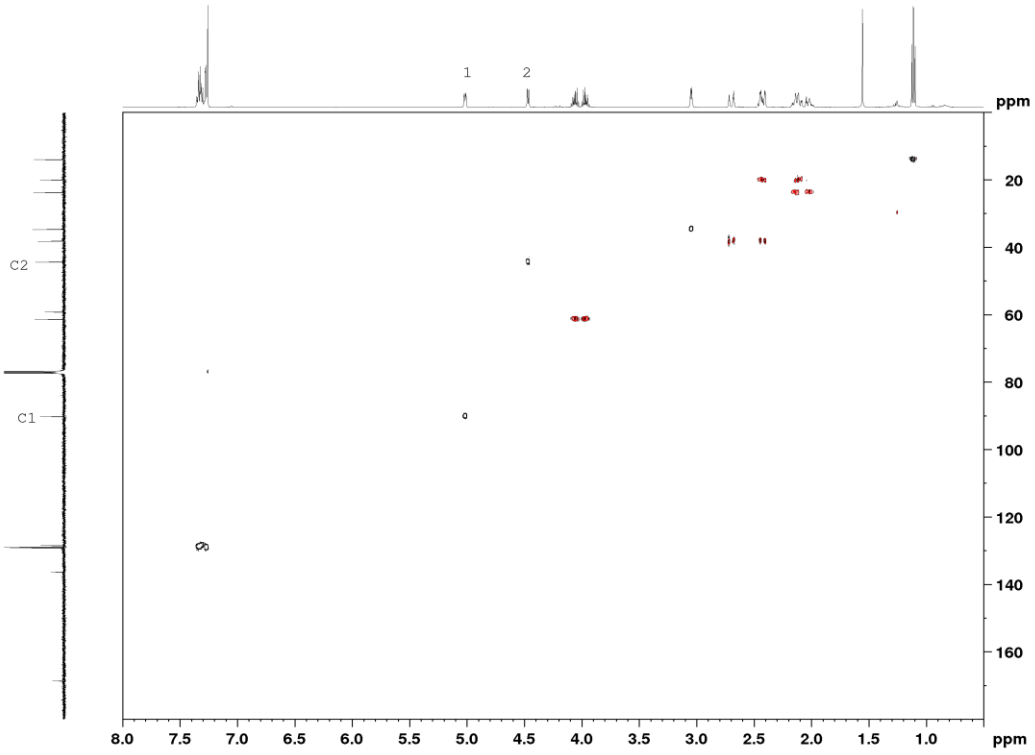


4-D2

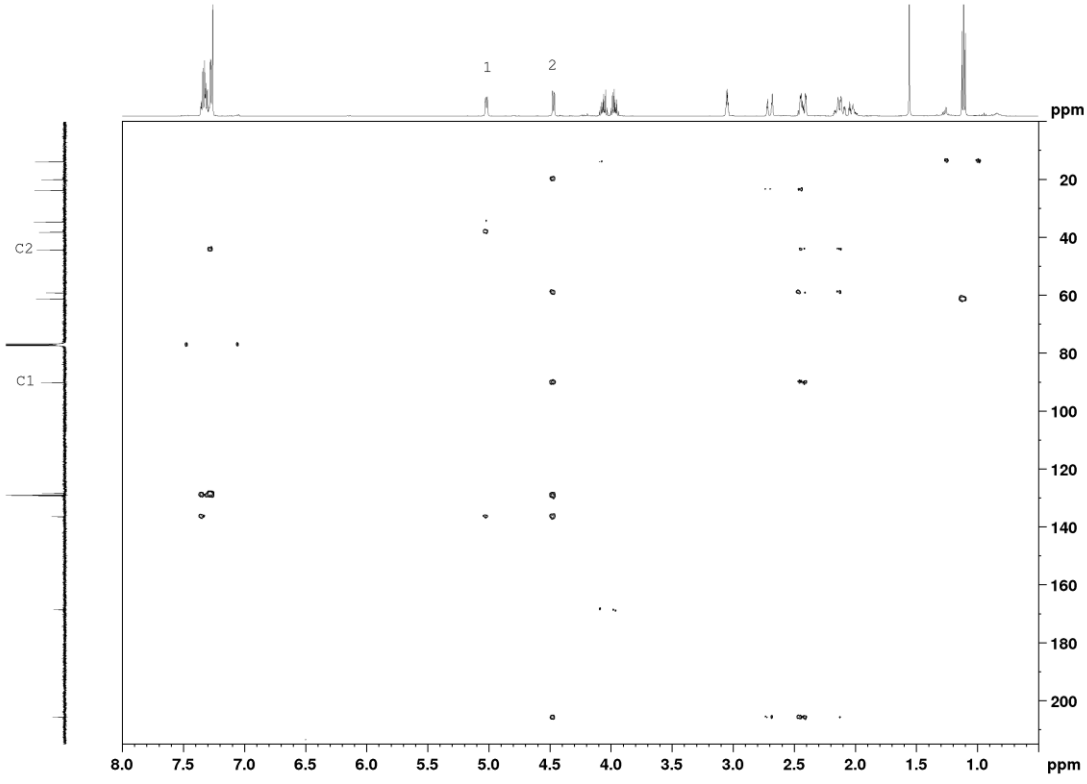
COSY-Experiment



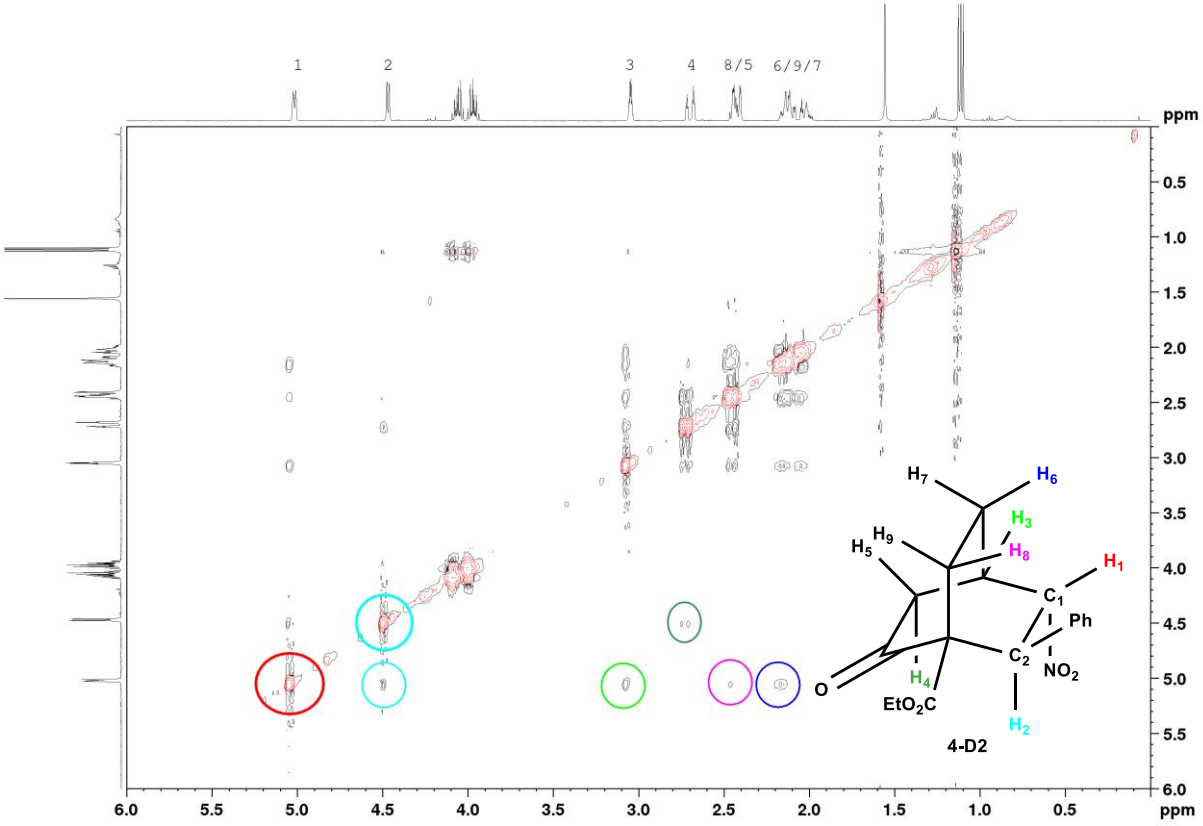
HSQC-Experiment



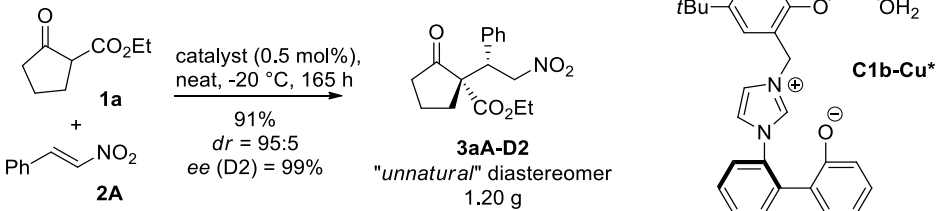
HMBC-Experiment



NOESY-Experiment



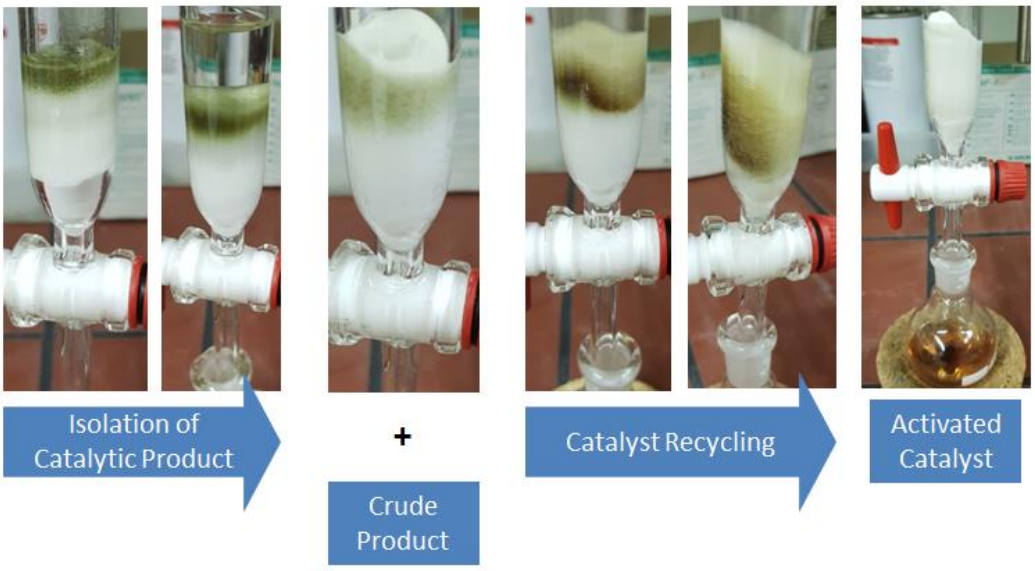
Upscaling Experiment for the Synthesis of Ethyl (*S*)-1-((*S*)-2-Nitro-1-phenylethyl)-2-oxocyclopentane-1-carboxylate 3aA



The product **3aA-D2** was synthesized as described in **GP6 neat**. Using 1.27 mL **1a** (1.34 g, 8.60 mmol, 2.0 equiv), 0.64 g **2A** (4.30 mmol, 1.0 equiv) and 19.7 mg of the catalyst **C1b-Cu*** (0.0215 mmol, 0.5 mol%) for 165 h at -20 °C. The product **3aA-D2** was isolated as a white solid (1.20 g, 3.904 mmol, 91%, *dr* = 95:5, ee = 99%). The analytical data are in agreement with the published data in this supporting information.

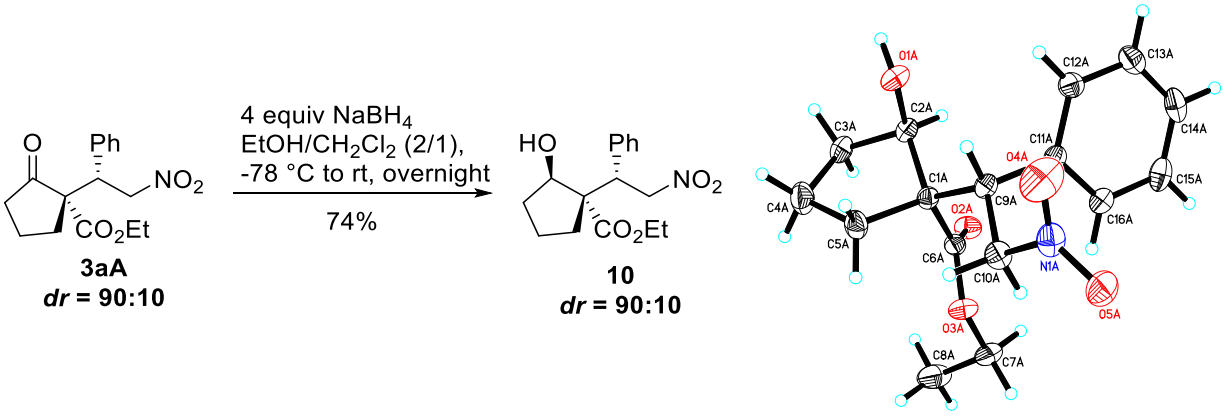
Catalyst Recycling:

The catalytic reaction was performed as described in **GP6-standard**. Upon filtration of the reaction mixture the catalyst **C1b-Cu*** turned green on the silica and stuck on the top end of the silica pad (see pictures left), while isolating the crude product with a solvent mixture of petroleum ether/ethyl acetate (1/1, 5 to 10 mL). The residual solvent was then completely pressed through the silica pad (to dryness) to allow for a solvent exchange. Then the silica pad was rinsed using a solvent mixture of CH_2Cl_2/THF/NEt_3 (66/33/1). By that the catalyst turned brown again and the activated catalyst was collected using approximately 10 mL of the solvent mixture (see pictures right). The solvent was removed under reduced pressure, the resulting brown solid was dried in high *vacuo* and the activated catalyst could be used without further purification in the next catalytic transformation. For that purpose the reisolated catalyst **C1b-Cu*** was dissolved in THF (0.05 mL) and transferred to a reaction vessel. Additional THF (0.05 mL) was used to allow for a complete catalyst transfer. Afterwards the substrates were added as described in **GP6-standard**.



Derivatisation of the Catalytic Product 3aA

Ethyl (1*S*,2*R*)-2-hydroxy-1-((*S*)-2-nitro-1-phenylethyl)cyclopentane-1-carboxylate (10)

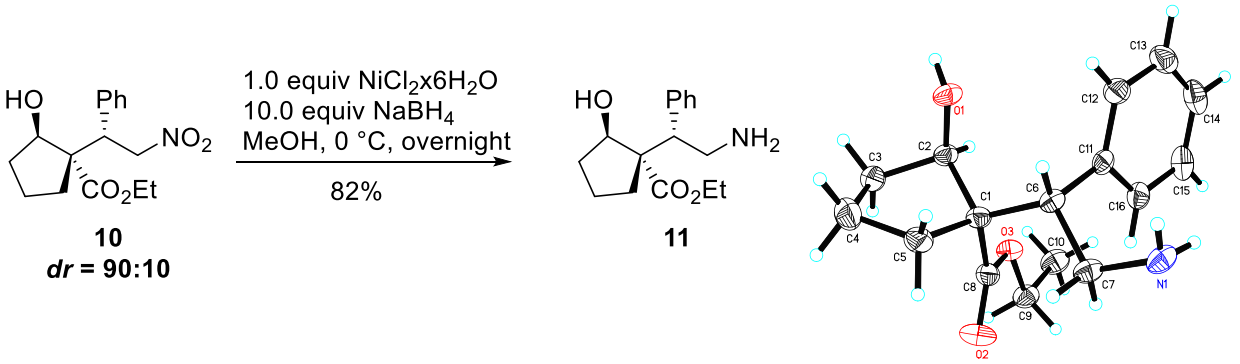


3aA (71.5 mg, 0.234 mmol, 1.0 equiv, $dr_{(S,S+R,R):(R,S+S,R)}$ = 90:10, $ee_{(S,S)}$ = 99%) was dissolved in a solvent mixture of ethanol/dichloromethane (1.0 mL/0.5 mL) and cooled to −78 °C under nitrogen atmosphere. $NaBH_4$ (35.4 mg, 0.937 mmol, 4.0 equiv) was added in portions to the reaction mixture at −78 °C which was then slowly warmed to room temperature overnight. Afterwards saturated aqueous ammonium chloride (5 mL) was added and the crude product was extracted with CH_2Cl_2 (3x10 mL). The combined organic fraction was washed with water (5 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified via column chromatography on silica gel (petroleum ether/ethyl acetate, 5/1 to 2/1) to yield the pure product **10** as a colorless solid and as a mixture of diastereomers, which could not be separated (52.9 mg, 0.172 mmol, *dr* = 90:10, 74%).

$C_{16}H_{21}NO_5$. MW: 307.35 g/mol. **MP =** 139-140 °C. $[\alpha_D^{20}]$ = 31.8 (c = 0.28 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.33-7.27 (*m*, 3H, Ar*H*), 7.25-7.21 (*m*, 2H, Ar*H*), 5.06 (*dd*, 1H, *J* = 13.2, 11.6 Hz, CH*H*NO_2), 4.83 (*dd*, 1H, *J* = 13.2, 4.2 Hz, C*H*HNO_2), 4.28-4.21 (*m*, 2H, C*H*OH and C*H*Ph), 4.16-3.97 (*m*, 2H, OCH_2CH_3), 2.34-2.26 (*m*, 1H, $CH_{cyclopentane}$), 2.05-1.87 (*m*, 3H, $CH_{cyclopentane}$), 1.66-1.52 (*m*, 3H, $CH_{cyclopentane}$ and CHO*H*), 1.17 (*t*, 3H, *J* = 7.1 Hz, OCH_2CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 174.0, 137.3, 128.7, 128.3, 128.0, 78.5, 75.1, 62.7, 61.2, 45.9, 33.8, 32.2, 21.1, 14.0. **IR (solid)**: $\tilde{\nu}$ = 3500, 3034, 2978, 2934, 2877, 1707, 1555, 1543, 1443, 1378, 1316, 1217, 1189, 1084, 1070, 1013, 701 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{16}H_{20}NO_5]^-$ 306.1336, measured 306.1340.

CCDC 1872237 contains the supplementary crystallographic data for compound **10**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Ethyl (1*S*,2*R*)-2-hydroxy-1-((*S*)-2-nitro-1-phenylethyl)cyclopentane-1-carboxylate (11)

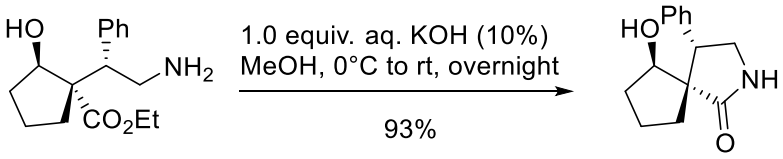


The reaction was performed in analogy to a literature procedure.[25] **10** (24.7 mg, 0.0804 mmol, 1.0 equiv) was dissolved in MeOH (1 mL) under nitrogen atmosphere and $NiCl_2x6H_2O$ (19.12 mg, 0.0804 mmol, 1.0 equiv) was added. The reaction mixture was cooled to 0 °C and $NaBH_4$ (30.42 mg, 0.8042 mmol, 10 equiv) was added in several portions. The reaction mixture was slowly warmed to room temperature overnight. Afterwards, a saturated aqueous NH_4Cl-solution (5 mL) was added and the aqueous phase was extracted using dichloromethane (3x5 mL). The combined organic fraction was dried over $MgSO_4$ and the solvents were removed under reduced pressure to yield the product **11** (18.2 mg, 0.0656 mmol, 82%) as a colorless solid. Product **11** slowly cyclizes to the corresponding spiro-compound by storage for longer time, whereby also decomposition was observed.

$C_{16}H_{23}NO_5$. MW: 277.36 g/mol. **MP =** 127-128°C. $[\alpha_D^{20}]$ = 29.8 (c = 0.25 g/dl, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.28-7.12 (*m*, 5H, Ar*H*), 4.30-4.25 (*m*, 1H, C*H*Ph), 3.97-3.85 (*m*, 2H, OCH_2CH$_3$) 3.34-3.29 (*m*, 1H, C*H*OH), 3.25-3.09 (*m*, 2H, CH_2NH$_2$), 2.55 (*br*, 3H, NH_2 and O*H*) 2.33-2-26 (*m*, 1H, C$H_{cyclopentane}$), 1.98-1.70 (*m*, 3H, C$H_{cyclopentane}$), 1.62-1.56 (*m*, 2H, C$H_{cyclopentane}$), 1.08 (*t*, 3H, *J* = 7.1 Hz, OCH$_2$CH_3). **^{13}C NMR (176 MHz, $CDCl_3$)**: δ = 175.1, 141.4, 128.7, 128.3, 126.9, 77.3, 63.5, 60.5, 51.4, 43.3, 33.4, 28.5, 20.9, 14.0. **IR (solid)**: $\tilde{\nu}$ = 3296, 3030, 2923, 2872, 2853, 2244, 1684, 1454, 1375, 1261, 1089, 1064, 1025, 908 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{16}H_{23}NO_3Na]^-$ 300.1570, measured 300.1556.

CCDC 1908074 contains the supplementary crystallographic data for compound **11**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(4*S*,5*S*,6*R*)-6-hydroxy-4-phenyl-2-azaspiro[4.4]nonan-1-one (15)

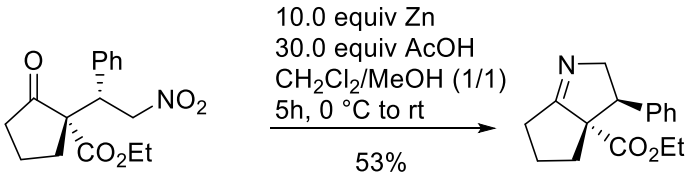


11 **15**

11 (30.7 mg, 0.111 mmol, 1.0 equiv) was dissolved in methanol (60 µL), cooled to 0°C and 10% aqueous KOH solution (71 µL, 0.111 mmol, 1.0 equiv) was added dropwise. The reaction mixture was slowly warmed to room temperature overnight. After removing the solvent under reduced pressure, the residue was dissolved in dichloromethane (1.5 mL) and washed with saturated aqueous NH_4Cl solution (0.2 mL). The organic layer was separated, washed with brine (1 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure to yield the product **15** (23.8 mg, 0.103 mmol, 93%) as a colorless oil.

$C_{14}H_{17}NO_2$. MW: 231.29 g/mol. $[\alpha_D^{20}]$ = -101.7 (c = 0.21 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.35-7.19 (*m*, 5H, Ar*H*), 6.57 (*b*, 1H, N*H*CO)4.10-4.06 (*m*, 1H, C*H*Ph), 3.74-3.68 (*dd*, 1H, *J* = 7.0, 10.0 Hz, C*H*OH), 3.33-3.29 (*m*, 2H, CH_2NH$_2$), 2.26-2.12 (*m*, 1H, C$H_{cyclopentane}$), 2.09-1.94 (*m*, 2H, C$H_{cyclopentane}$), 1.89-1.62 (*m*, 3H, O*H* and C$H_{cyclopentane}$), 1.51-1.40 (*m*, 1H, C$H_{cyclopentane}$). **^{13}C NMR (176 MHz, $CDCl_3$)**: δ = 181.3, 142.3, 129.2, 127.7, 127.5, 77.3, 75.9, 50.9, 47.6, 35.6, 33.5, 21.4. **IR (solid)**: $\tilde{\nu}$ = 3266, 3029, 2948, 2875, 2244, 1680, 1494, 1485, 1454, 1433, 1370, 1263, 1083, 1063, 1025, 909 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{14}H_{17}NO_2Na]^+$ 254.1451, measured 254.1166.

Ethyl (3*S*,3a*S*)-3-phenyl-2,4,5,6-tetrahydrocyclopenta[b]pyrrole-3a(3H)-carboxylate (12)



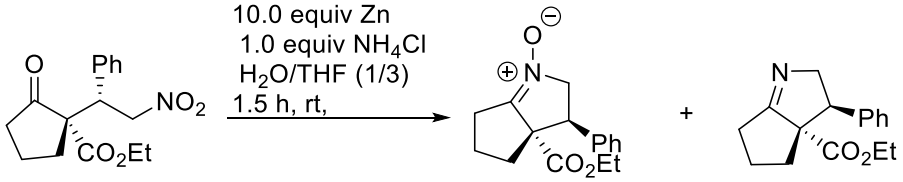
3aA **12**
***dr* = 94:6** ***dr* = 94:6**

3aA (67.8 mg, 0.222 mmol, 1.0 equiv, $dr_{(S,S+R,R):(R,S+S,R)}$ = 94:6, $ee_{(S,S)}$ = 99%) was dissolved in a solvent mixture of methanol/dichloromethane (0.4 mL/0.4 mL) and cooled to 0 °C. Zinc powder (145.1 mg, 2.220 mmol, 10 equiv), followed by glacial acetic acid (0.38 ml, 6.662 mmol, 30 equiv) were added to the reaction mixture at 0 °C. After 30 minutes the ice bath was removed and stirring was continued 4.5 h at room temperature. The reaction mixture was filtrated and the residue was washed with dichloromethane (2 mL). After evaporating the solvents, the reaction mixture was redissolved in dichloromethane (5 mL) and washed with saturated aqueous $NaHCO_3$ (5 mL). The water phase was extracted twice with

dichloromethane (5 mL) and the combined organic fractions were dried over Na_2SO_4. After removing the solvent under reduced pressure, the crude product was purified via column chromatography on silica gel (CH_2Cl_2/MeOH, 40/1 to 20/1) to yield the pure product **12** as a yellowish oil and as a mixture of diastereomers, which could not be separated (30.1 mg, 0.117 mmol, dr = 94:6, 53%).

$C_{16}H_{19}NO_2$. MW: 257.33 g/mol. $[\alpha_D^{20}] = -50.0$ (c = 0.19 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.32-7.21 (*m*, 3H, Ar*H*), 7.09-704 (*m*, 2H, Ar*H*), 4.66-4.53 (*m*, 1H, C*H*Ph), 4.44 (*d*, 1H, *J* = 14.9 Hz, C*H*HNC), 4.25 (*q*, 2H, *J* = 7.0 Hz, OCH_2CH$_3$), 3.85 (*d*, 1H, *J* = 6.2 Hz, CH*H*NC), 2.55-2.39 (*m*, 1H, C$H_{cyclopentane}$), 2.32-2.1.99 (*m*, 2H, C$H_{cyclopentane}$), 1.88-1.74(*m*, 2H, C$H_{cyclopentane}$), 1.30 (*t*, 3H, *J* = 7.1 Hz, OCH$_2$CH_3), 0.99-0.0.86(*m*, 1H, C$H_{cyclopentane}$). **^{13}C NMR (176 MHz, $CDCl_3$)**: δ = 185.6, 173.1, 140.9, 128.7, 128.1, 127.1, 72.6, 61.5, 52.4, 33.6, 27.7, 25.8, 25.6, 14.3. **IR (solid)**: $\tilde{\nu}$ = 3028, 2955, 2873, 1719, 1673, 1494, 1449, 1298, 1226, 1174, 1144, 1129, 1055, 1026, 766, 701 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{16}H_{20}NO_2]^+$ 258.1489, measured 258.1478.

(3*S*,3a*S*)-3a-(Ethoxycarbonyl)-3-phenyl-2,3,3a,4,5,6-hexahydro-1l4-cyclopenta[b]pyrrol-1-olate (13)



3aA
***dr* = 94:6**

13
62%

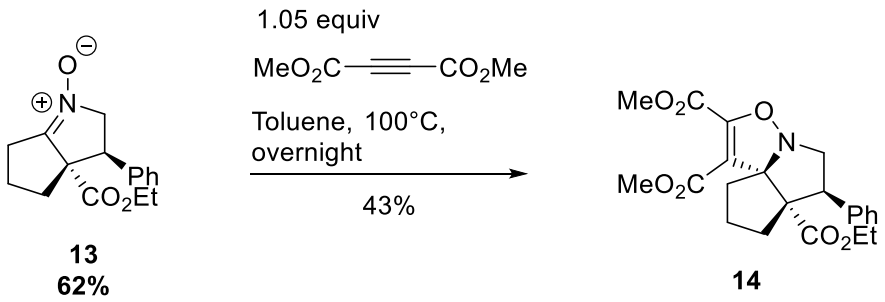
12
***dr* = 94:6**
28%

3aA (207.0 mg, 0.678 mmol, 1.0 equiv, $dr_{(S,S+R,R):(R,S+S,R)}$ = 94:6, $ee_{(S,S)}$ = 99%) was dissolved in THF (3 mL) and a solution of ammonium chloride (36.3 mg, 0.678 mmol, 1.0 equiv) in H_2O (1 mL) was added. Afterwards zinc powder (443.25 mg, 6.780 mmol, 10 equiv) was added in portions and the reaction mixture was stirred for 3 h at room temperature. The reaction mixture was filtrated and the residue was washed with THF (2 mL). After evaporating the solvents, the reaction mixture was redissolved in chloroform (5 mL) and washed with H_2O (5 mL). The water phase was extracted twice with chloroform (5 mL) and the combined organic fractions were dried over $MgSO_4$. After removing the solvent under reduced pressure, the crude product was purified via column chromatography on silica gel (CH_2Cl_2/MeOH, 40/1 to 20/1) to yield the pure product **13** as colorless oil (115.2 mg, 0.422 mmol, 62%) and the side product **12** was isolated as yellowish oil (48.9 mg, 0.190 mmol, 28%).

$C_{16}H_{19}NO_3$. MW: 273.33 g/mol. $[\alpha_D^{20}] = 28.4$ (c = 0.29 g/dl, CH_2Cl_2). **^{1}H NMR (700 MHz, $CDCl_3$)**: δ = 7.36 (*t*, 2H, *J* = 7.6 Hz, Ar*H*), 7.30 (*t*, 1H, *J* = 7.5 Hz, Ar*H*), 7.14 (*d*, 2H, *J* = 7.7 Hz, Ar*H*), 5.06-5.01 (*m*, 1H, C*H*Ph), 4.29 (*q*, 2H, *J* = 7.1 Hz, OCH_2CH$_3$), 4.25 (*d*, 1H, *J* = 13.8 Hz, C*H*HNO), 3.99 (*d*, 1H, *J* = 6.8 Hz, CH*H*NO), 2.63-2.56

(*m*, 1H, C*H*$_{cyclopentane}$), 2.47-2.41 (*m*, 1H, C*H*$_{cyclopentane}$), 2.13-2.05(*m*, 1H, C*H*$_{cyclopentane}$), 1.97-1.91 (*m*, 1H, C*H*$_{cyclopentane}$), 1.80-1.75 (*m*, 1H, C*H*$_{cyclopentane}$), 1.34 (*t*, 3H, *J* = 7.1 Hz, OCH$_2$C*H*$_3$), 1.01-0.95(*m*, 1H, C*H*$_{cyclopentane}$). **^{13}C NMR (176 MHz, CDCl$_3$)**: δ = 172.9, 152.6, 139.0, 129.3, 128.0, 127.6, 73.3, 67.4, 62.3, 46.7, 29.8, 26.7, 22.9, 14.4. **IR (solid)**: $\tilde{\nu}$ = 3416, 3030, 2975, 1722, 1637, 1497, 1458, 1352, 1285, 1252, 1229, 1207, 1142, 1019, 756, 703 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{16}H_{19}NO_3]^+$ 274.1438, measured 274.1434.

6a-ethyl 2,3-dimethyl (3a*R*,6a*S*,7*S*)-7-Phenyl-5,6,7,8-tetrahydrocyclopenta[2,3]pyrrolo[1,2-*b*][1,2] oxazole-2,3,6a(4*H*)-tricarboxylate (14)



13
62%

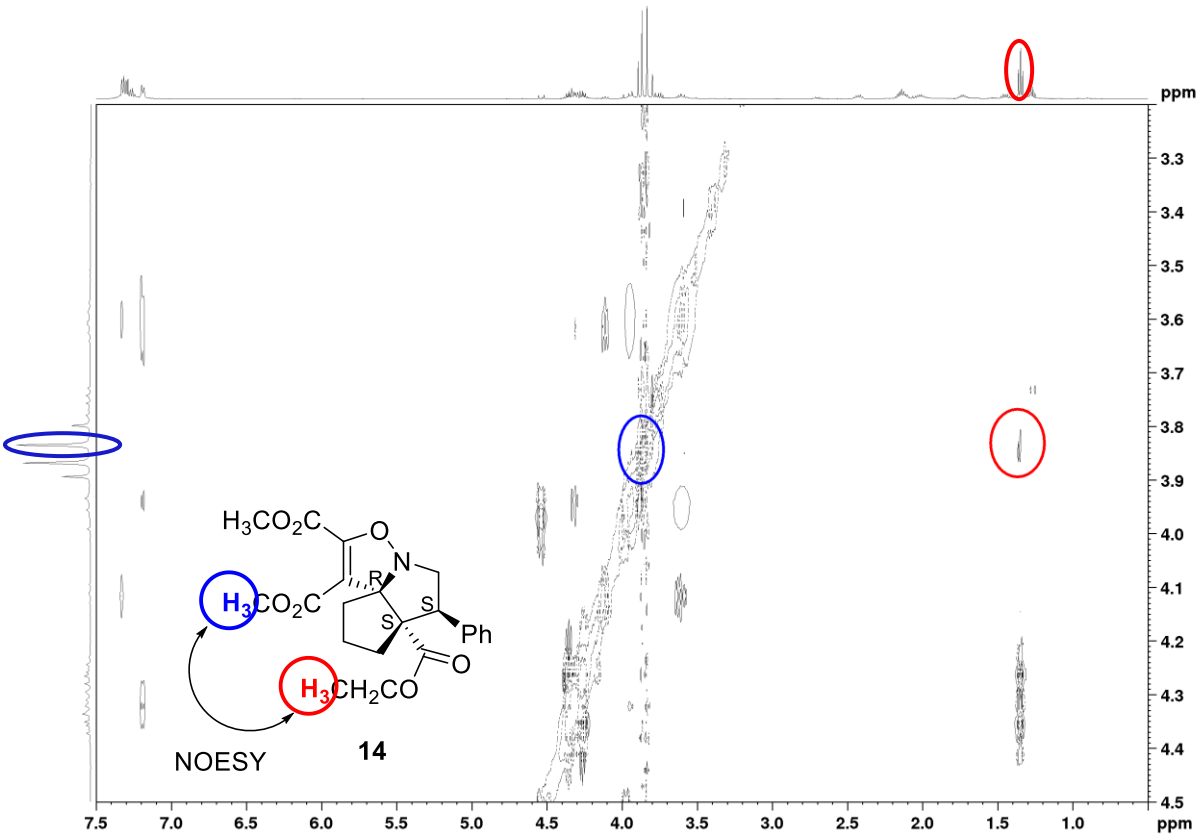
14

13 (40.2 mg, 0.147 mmol, 1.0 equiv) was dissolved in toluene (0.5 mL), dimethyl acetylenedicarboxylate (19.0 µL, 21.95 mg, 0.154 mmol, 1.05 equiv) was added and the reaction mixture was stirred overnight at 100 °C. After evaporating all volatiles under reduced pressure, the crude product was purified via column chromatography on silica gel (petroleum ether/ethyl acetate, 5/1 to 2/1) to yield the pure product **14** as yellowish oil (26.8 mg, 0.0645 mmol, 43%).

$C_{22}H_{25}NO_7$. MW: 415.44 g/mol. $[\alpha_D^{20}] = 106.5$ (c = 0.27 g/dl, CH_2Cl_2). **^{1}H NMR (300 MHz, CDCl$_3$)**: δ = 7.33-7-14 (*m*, 5H, Ar*H*), 4.39-4.17 (*m*, 3H, C*H*Ph and OC*H*$_2$CH$_3$), 3.93-3.73 (*m*, 1H, C*H*HNO), 3.84 (*s*, 3H, OC*H*$_3$) 3.81 (*s*, 3H, OC*H*$_3$), 3.62-3.48 (*m*, 1H, *J* = 6.8 Hz, CH*H*NO), 2.45-2.33 (*m*, 1H, C*H*$_{cyclopentane}$), 2.47-2.41 (*m*, 1H, C*H*$_{cyclopentane}$), 2.17-1.84 (*m*, 4H, C*H*$_{cyclopentane}$), 1.78-1.62 (*m*, 1H, C*H*$_{cyclopentane}$), 1.47-1.39 (*m*, 1H, C*H*$_{cyclopentane}$), 1.32 (*t*, 3H, *J* = 7.1 Hz, OCH$_2$C*H*$_3$). **^{13}C NMR (75 MHz, CDCl$_3$)**: δ =172.5, 161.5, 159.7, 137.3, 128.5, 128.32, 128.29, 127.9, 127.1, 72.6, 68.7, 61.8, 52.43, 52.29, 52.1, 47.3, 39.0, 30.3, 24.0, 14.1. **IR (solid)**: $\tilde{\nu}$ = 3061, 2954, 2852, 1719, 1631, 1437, 1312, 1280, 1238, 1205, 1149, 1096, 1034, 762, 702 cm^{-1}. **HRMS (ESI)** *m/z*: calculated $[C_{22}H_{25}NO_7]^+$ 416.1704, measured 416.1708.

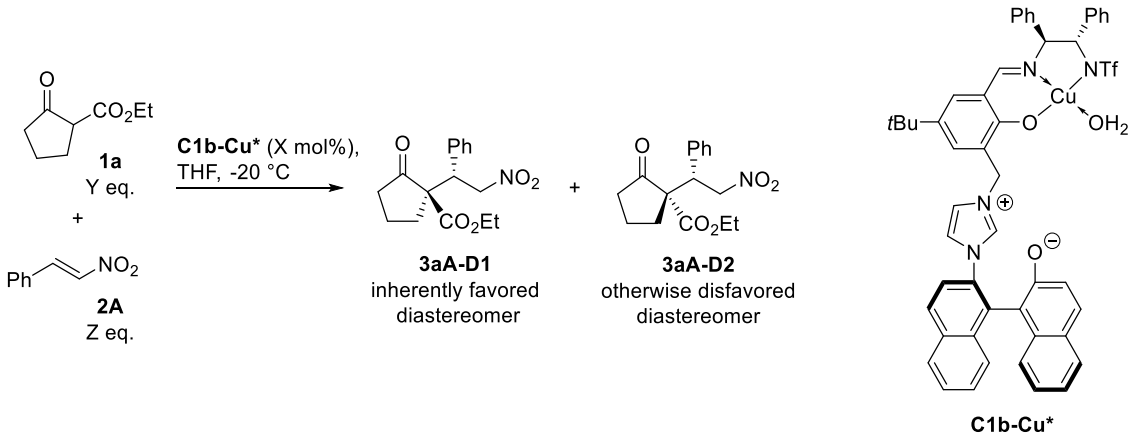
Confirming the Configurational Outcome with 2D-NOESY-NMR Experiments of Compound 14.

To confirm the structure of the major diastereomer of compound **14**, a NOESY NMR-Experiment was performed and is shown in the following 2D-NMR spectra.



Kinetic Experiments

Kinetic Experiments – Initial Rate Kinetic Analysis



Determining the Partial Reaction Order for the Catalyst C1b-Cu*

For varying initial concentrations of the activated Cu(II)-catalyst **C1b-Cu*** (5.1 mol%-1.0 mol%): To a NMR sample tube were added a solution of catalyst **C1b-Cu*** (0.00254 mmol, 0.00200 mmol, 0.00151 mmol, 0.00103 mmol, 0.000503 mmol), 1,2-diphenylethane (internal standard, 0.05 mmol), ketoester **1a** (8.15 µl, 8.59 mg, 0.055 mmol, 1.1 equiv), nitroolefin **2A** (7.46 mg, 0.05 mmol, 1.0 equiv) in tetrahydrofuran-d8 (0.5 mL). The reaction mixture was analyzed by ^{1}H NMR spectroscopy at room temperature to monitor the yield / time dependence of **3aA-D2**.

Concentration of **3aA-D2** in mol/L versus time in the reactions with different catalyst loadings are summarized in **Table S1** and are plotted in **Figure S1**. The partial reaction order for the catalyst **C1b-Cu***was determined in **Figure S2** as 0.93 (ref.26) using the differential method.[27, 28, 29]

Table S1: Varying initial concentrations of the activated Cu(II)-catalyst **C1b-Cu*** (5.1 mol%-1.0 mol%)

Entry	[**C1b-Cu***] in mol/L	*d* [**3aA-D2**]/*dt* in mol/L min	ln ([**C1b-Cu***])	ln(d[**3aA**]/dt)
1	0,005074	1,48399E-04	-5,28	-8,82
2	0,004002	1,38750E-04	-5,52	-8,88
3	0,003020	1,02244E-04	-5,80	-9,19
4	0,002056	6,62626E-05	-6,19	-9,62
5	0,001006	3,57237E-05	-6,90	-10,24

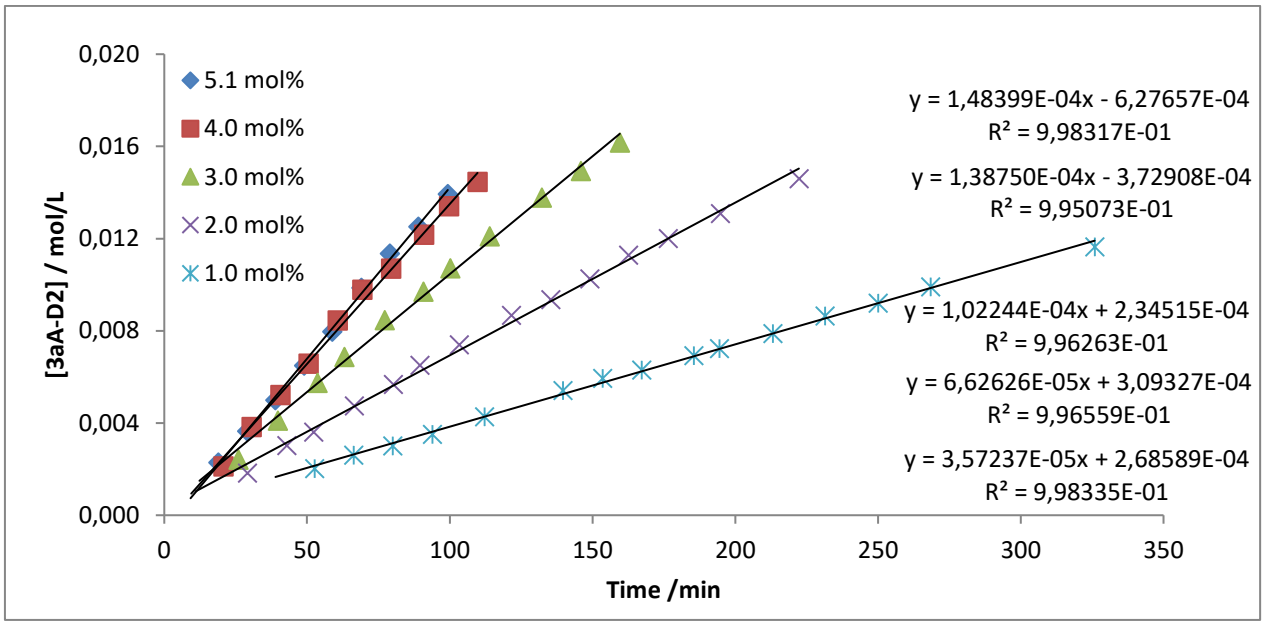


Figure S1: Plots of the Yields of 3aA -D2 in mol/L versus time with different catalyst loadings.

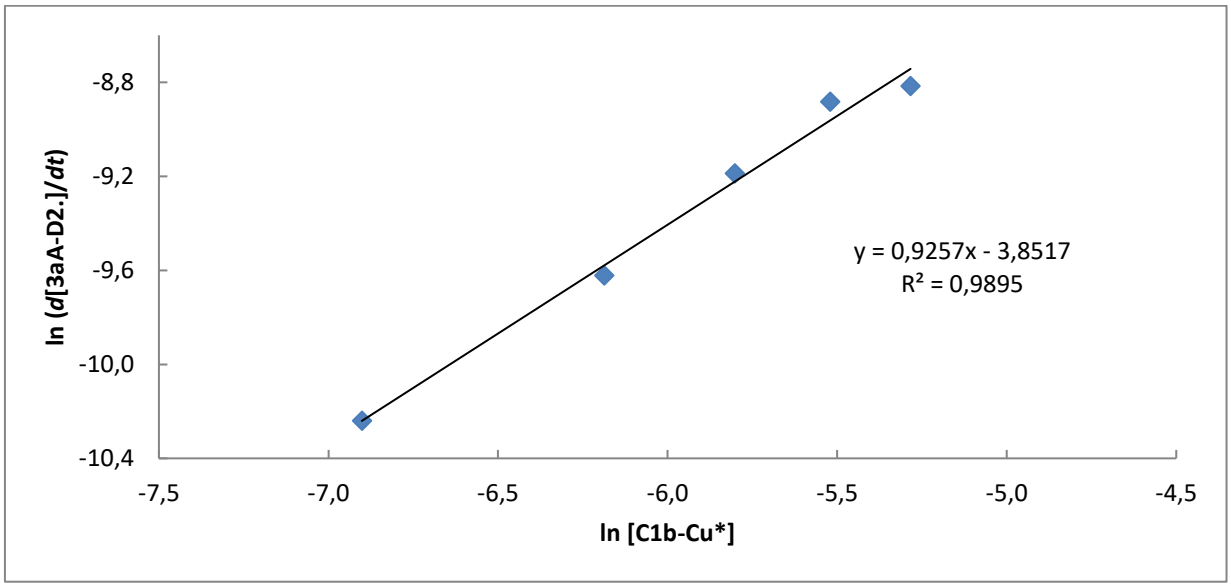


Figure S2: Plot for determining the partial reaction order of the catalyst C1b-Cu* (*c* in mol/L).

Determining the Partial Reaction Order for the Ketoester 1a

For varying initial concentrations of the ketoester **1a** (1.7 equiv – 0.3 equiv): To a NMR sample tube were added a solution of catalyst **C1b-Cu*** (1.16 mg, 0.00125 mmol, 2.5 mol%), 1,2-diphenylethane (internal standard, 0.05 mmol), ketoester **1a** (0.0839 mmol, 0.0642 mmol, 0.0456 mmol, 0.0348 mmol, 0.0227 mmol, 0.0163 mmol), nitroolefin **2A** (7.46 mg, 0.05 mmol, 1.0 equiv) in tetrahydrofuran-d8 (0.5 mL). The reaction mixture was analyzed by ^{1}H NMR spectroscopy at room temperature to monitor the yield / time dependence of **3aA-D2**.

Concentration of **3aA-D2** in mol/L versus time in the reactions for varying initial concentrations of the ketoester **1a** are summarized in the **Table S2** and are plotted in **Figure S3**. The partial reaction order for the ketoester **1a** was determined in **Figure S4** as 0.67 (ref. 30) using the differential method. [27, 28, 29]

Table S2: Varying initial concentrations of the ketoester **1a** (1.7 equiv – 0.3 equiv).

Entry	[**1a**] in mol/L	*d* [**3aA-D2**]/*dt* in mol/L min	ln ([**1a**])	ln(d[**3aA-D2**]/dt)
1	0,16782	1,34285E-04	-1,78	-8,92
2	0,12844	1,21685E-04	-2,05	-9,01
3	0,09120	9,06893E-05	-2,39	-9,31
4	0,06966	7,88032E-05	-2,66	-9,45
5	0,04548	5,83488E-05	-3,09	-9,75
6	0,03266	4,57819E-05	-3,42	-9,99

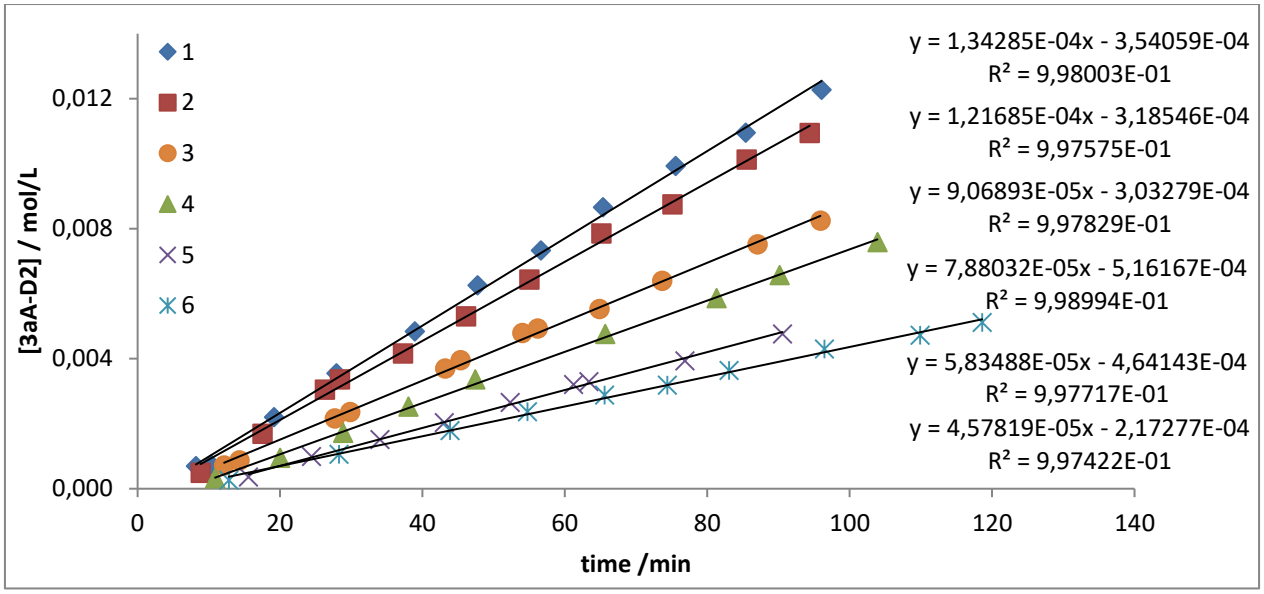


Figure S3. Plots of the Yields of 3aA-D2 in mol/L versus time with different equivalents of the ketoester 1a.

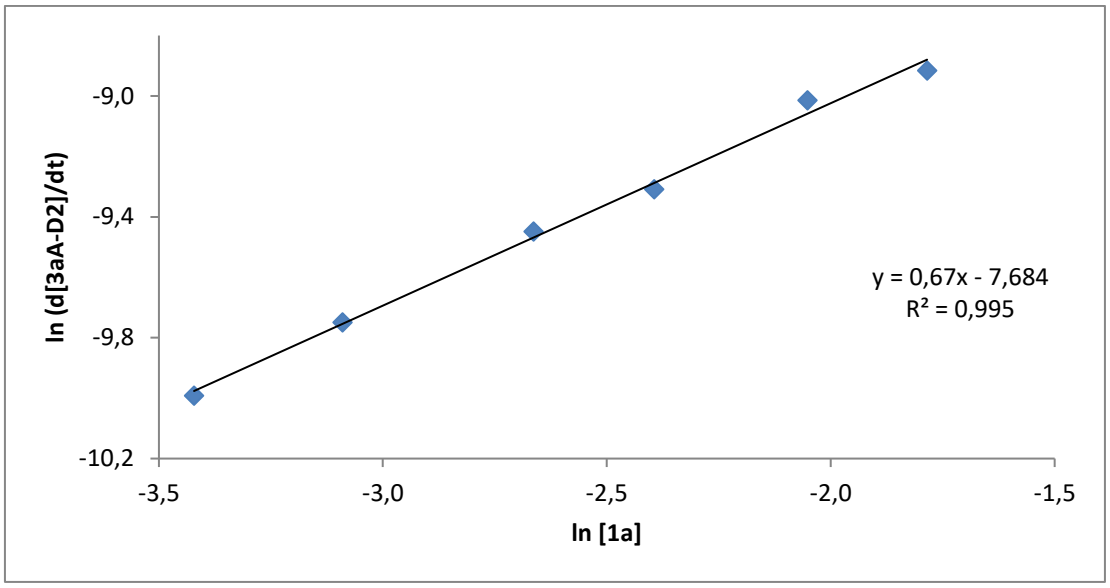


Figure S4. Plot for determining the partial reaction order for the ketoester 1a (*c* in mol/L).

Determining the Partial Reaction Order for the Nitroolefin 2A

For varying initial concentrations of the nitroolefin **2A** (1.5 equiv – 0.5 equiv): To a NMR sample tube were added a solution of catalyst **C1b-Cu*** (2.33 mg, 0.0025 mmol, 5 mol%), 1,2-diphenylethane (internal standard, 0.05 mmol), ketoester **1a** (7.41 µl, 7.81 mg, 0.05 mmol, 1.0 equiv), nitroolefin **2A** (0.0750 mmol, 0.0625 mmol, 0.0502 mmol, 0.0371 mmol, 0.0252 mmol) in tetrahydrofuran-d8 (0.5 mL). The reaction mixture was analyzed by ^{1}H NMR spectroscopy at room temperature to monitor the yield / time dependence of **3aA-D2**.

Concentration of **3aA-D2** in mol/L versus time in the reactions for varying initial concentrations of the nitroolefin **2A** are summarized in the **Table S3** and are plotted in **Figure S5**. The partial reaction order for the nitroolefin **2A** was determined in **Figure S6** as 0.96 [ref. 31] using the differential method. [27, 28, 29]

Table S3: Varying initial concentrations of the nitroolefin **2A** (1.5 equiv – 0.5 equiv).

Entry	Equiv.	[**2A**] in mol/L	*d* [**3aA-D2**]/*dt* in mol/L min	ln ([**2A**])	ln(d[**3aA-D2**]/dt)
1	1.50	0,149916	2,51365E-04	-1,90	-8,29
2	1.25	0,124974	2,16457E-04	-2,08	-8,44
3	1.00	0,100302	1,61663E-04	-2,30	-8,73
4	0.75	0,074154	1,33278E-04	-2,60	-8,92
5	0.50	0,050420	8,79391E-05	-2,99	-9,34

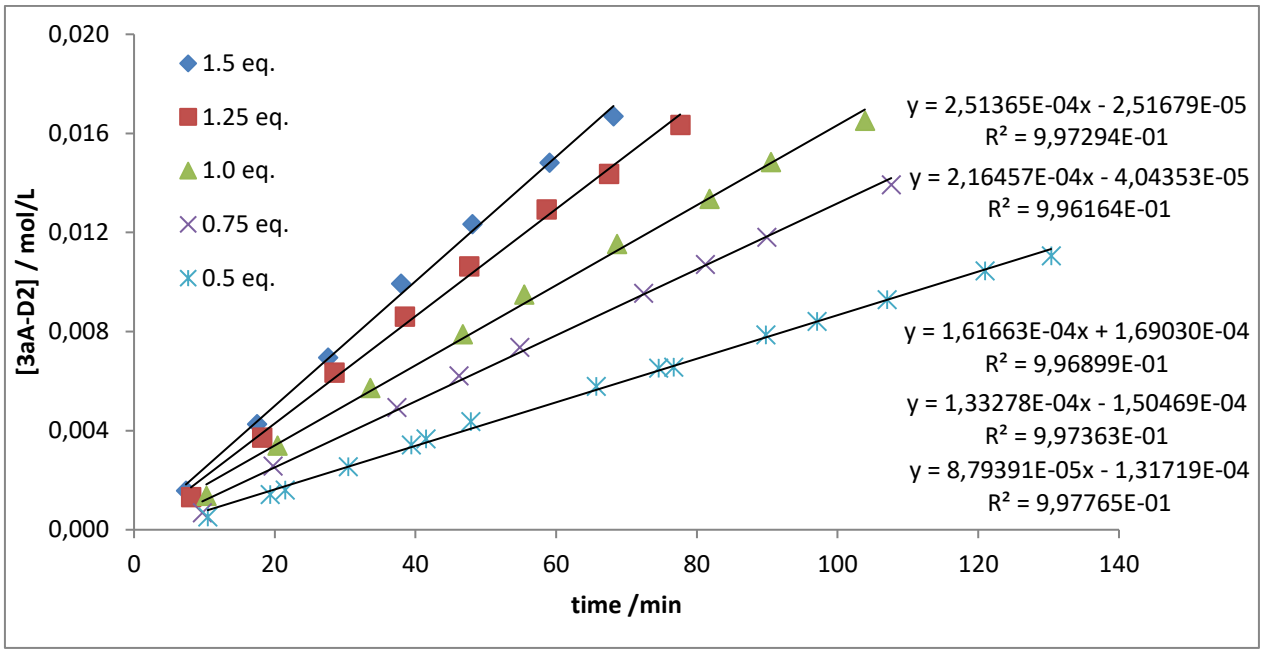


Figure S5: Plots of the Yields of 3aA-D2 in mol/L versus time with different equivalents of the nitroolefin 2A.

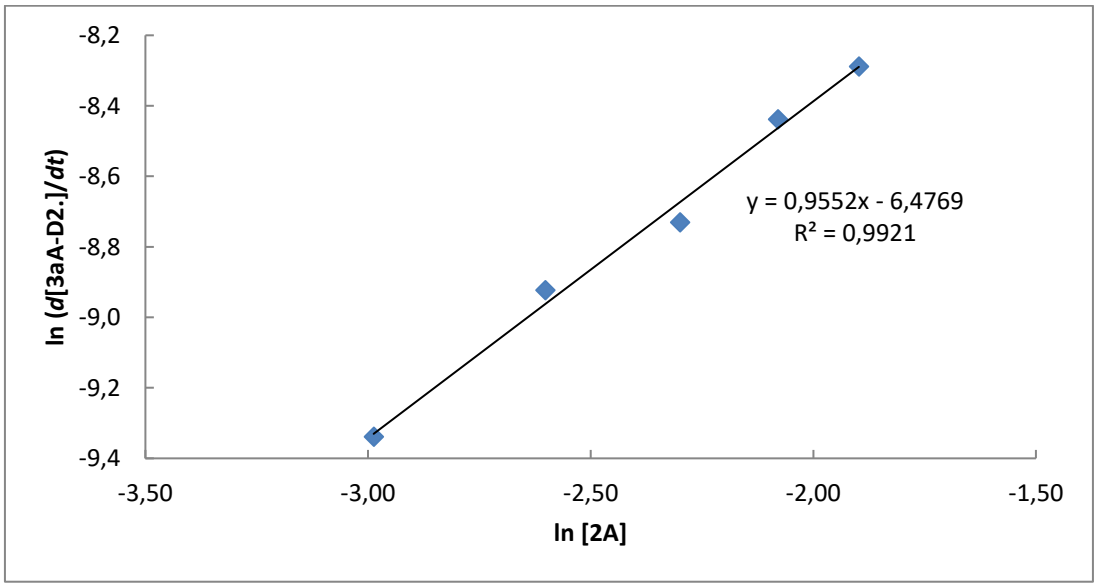


Figure S6: Plot for determining the partial reaction order for the nitroolefin 2A (c in mol/L).

Kinetic Experiments – Probing Catalyst Robustness and Product Influence

For probing the catalyst stability/robustness and product influence during the catalytic reaction three kinetic experiments were performed under the "same-excess" conditions of the reactants **1a** and **2A** in analogy to *Blackmond*.[32,33] The different initial concentrations for the reactants **1a** and **2A** and the catalyst for the kinetic experiments are summarized in **Table S4**.

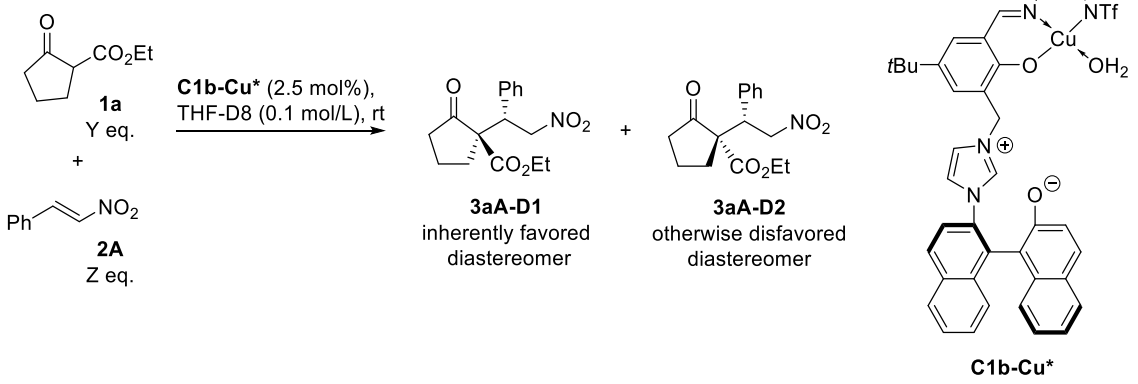


Table S4: Different initial concentrations of β-ketoester **1a**, nitroolefin **2A** and product **3aA** in "same-excess"-experiments and "product addition" for investigation of possible product inhibition and catalyst stability.

#	Experiment	[**1a**] /mol/L	Equiv of **1a**	[**2A**] /mol/L	Equiv of **2A**	[**C1b-Cu***] /mol/L	Equiv. of **C1b-Cu***	**[3aA]** /mol/L	Equiv. of **3aA**
B1	Standard	0.11	1.1	0.10	1.0	0.0025	0.025	0.00	0.0
B2	Same Excess	0.06	0.6	0.05	0.5	0.0025	0.025	0.00	0.0
B3	Product Addition	0.06	0.6	0.05	0.5	0.0025	0.025	0.05	0.5

The corresponding experiments **B1-B3** were performed by adding a solution of the catalyst **C1b-Cu***, 1,2-diphenylethane (internal standard, 0.05 mmol), ketoester **1a** (freshly distilled), and nitroolefin **2A** in tetrahydrofuran-d8 (0.5 mL, degassed via "freeze-pump-thaw"-method) to an NMR sample tube under vigorous exclusion of air (**Table S4**). The reaction mixture was analysed by ^{1}H NMR spectroscopy at room temperature to monitor the time dependence of the conversion of **2A**.

In **Figure S7** the concentration profiles of the "same-excess"- and "product-addition"-experiments are illustrated. The "same excess" experiment **B2** starts at the point, where the "standard"-experiment **B1** has reached 50% conversion. In the "standard" reaction **B1**, the catalyst already promoted ca. 10 turnovers, but in **B2** the catalyst is fresh and therefore the catalyst stability can be investigated. To compare the

concentration profiles **B1** and **B2**, the curve of **B2** is shifted by adjusting the starting time to the point where **B1** reaches the same conversion. Both profiles overlay when the time adjustment is performed (**Figure S7**, ○ with □) thus demonstrating that the catalyst is not affected by several catalyst turnovers and nearly no catalyst deactivation takes place during the catalytic reaction.

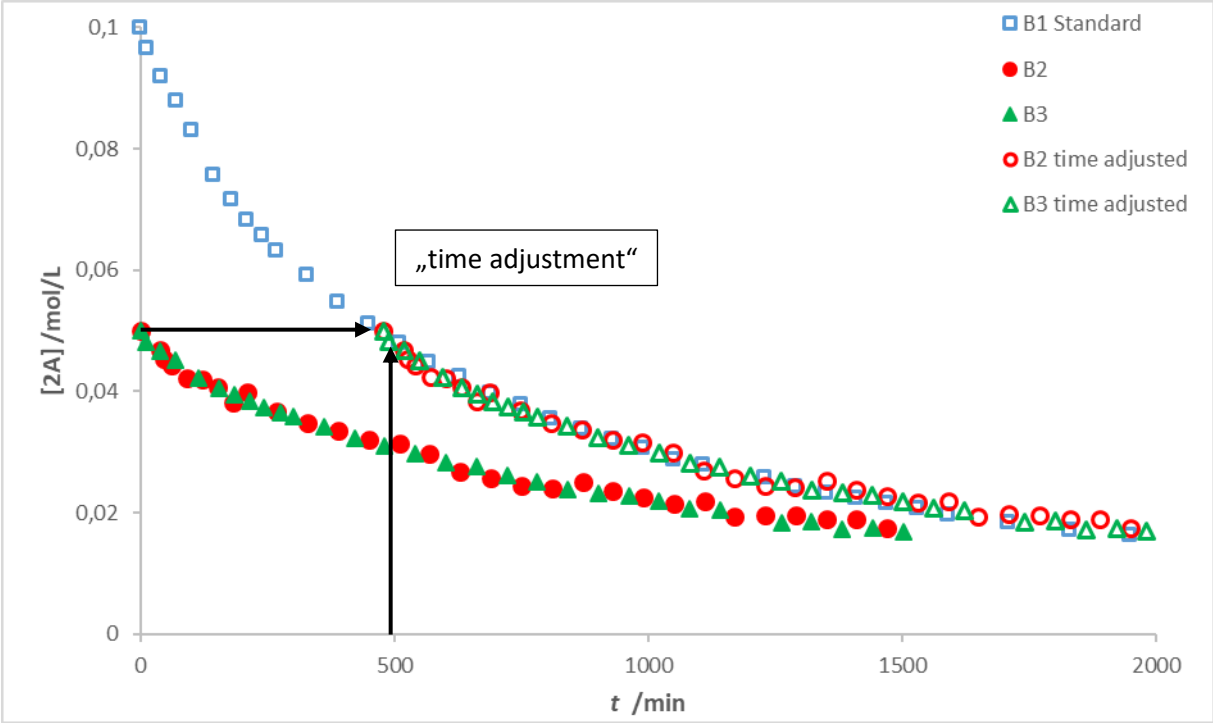


Figure S7. Probing catalyst stability and product influence on the catalytic reaction.

In a third experiment **B3**, 50 mol% of product **3aA** was added to the same initial conditions as in reaction **B2** to provide an identical concentration of substrates **1a** and **2A** but also of product **3aA** in the time-adjusted point of **B1**. This experiment enables investigation of the effect of product **3aA** on the catalyst's behaviour. Overlaying the concentration profile **B3** (**Figure S7**, △ with □) by adjusting the starting time to the point where the concentrations of curve **B3** is equal to **B1** leads to nearly complete overlay of both profiles. This nearly identical curve progression shows that the product **3aA** is not influencing the catalyst in the catalytic reaction.

Raw Data and Calculated Concentrations for the "Same-Excess"- and "Product Addition"-Experiments.

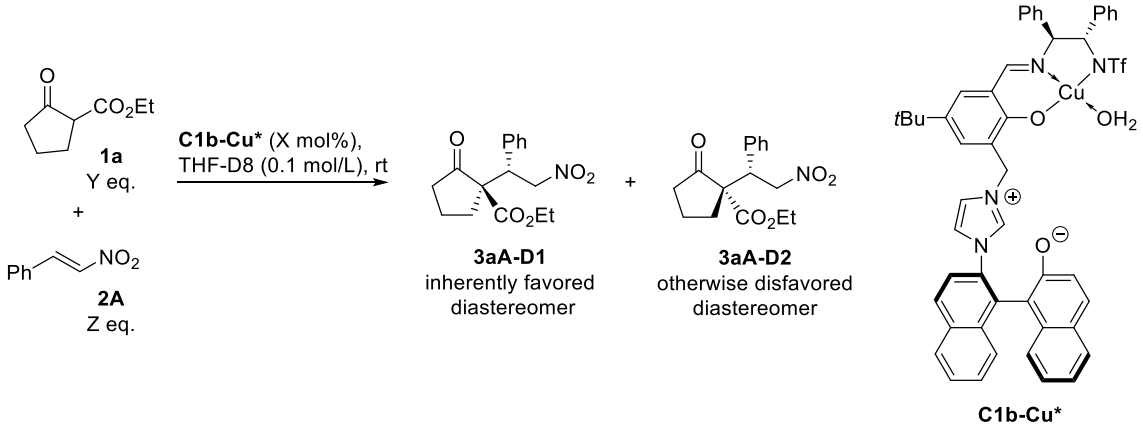
Table S5. Raw data of the "same-excess"-experiments **B1-B3**, calculated concentration of nitroolefin **2A** and time adjustment.

B1 - Standard		**B2 -50%**			**B3 - 50% + 50% 3aA**		
Time /min	**[2A] /mol/L**	**Time /min**	**Time adjustment /min**	**[2A] /mol/L**	**Time /min**	**Time adjustment /min**	**[2A] /mol/L**
0	0,1000	0	480	0,0500	0	480	0,0500
13	0,0965	39	519	0,0468	10	490	0,0481
41	0,0920	48	528	0,0454	39	519	0,0467
71	0,0878	62	542	0,0443	69	549	0,0451
101	0,0831	92	572	0,0422	115	595	0,0422
143	0,0758	123	603	0,0421	154	634	0,0405
178	0,0716	152	632	0,0407	184	664	0,0395
208	0,0683	183	663	0,0383	214	694	0,0383
240	0,0657	209	689	0,0399	244	724	0,0374
268	0,0632	269	749	0,0368	275	755	0,0366
328	0,0592	329	809	0,0348	301	781	0,0358
388	0,0548	390	870	0,0336	361	841	0,0342
448	0,0512	449	929	0,0320	421	901	0,0324
509	0,0481	509	989	0,0315	481	961	0,0310
568	0,0449	569	1049	0,0298	541	1021	0,0298
628	0,0424	630	1110	0,0268	601	1081	0,0282
688	0,0398	690	1170	0,0257	661	1141	0,0276
748	0,0378	750	1230	0,0244	721	1201	0,0261
808	0,0355	810	1290	0,0241	781	1261	0,0251
868	0,0339	871	1351	0,0251	842	1322	0,0237
928	0,0321	930	1410	0,0237	901	1381	0,0233
989	0,0308	990	1470	0,0226	961	1441	0,0228
1048	0,0288	1051	1531	0,0215	1021	1501	0,0219
1108	0,0279	1111	1591	0,0219	1081	1561	0,0207
1228	0,0258	1170	1650	0,0193	1141	1621	0,0204
1288	0,0243	1230	1710	0,0196	1261	1741	0,0184
1348	0,0234	1290	1770	0,0195	1322	1802	0,0186
1408	0,0226	1351	1831	0,0189	1381	1861	0,0173
1469	0,0217	1410	1890	0,0189	1441	1921	0,0174
1528	0,0209	1470	1950	0,0175	1501	1981	0,0169

1588	0,0198						
1708	0,0185						
1828	0,0172						
1948	0,0163						

Kinetic Experiments – Determination of reaction orders using variable time normalization graphical analysis (VTNA)

The orders of the reaction of all reaction components were determined using the variable time normalization graphical analysis method (VTNA) described by Burés.[34,35]



Four reactions **K1-K4** with different initial concentrations of each component, catalyst **C1b-Cu***, β-ketoester **1a** and nitroolefin **2A**, were performed and monitored via ^{1}H NMR. The different initial concentrations for the components used in the kinetic experiments are summarized in the T**able S6**.

Table S6: Variation of the initial concentrations of catalyst **C1b-Cu***, β-ketoester **1a** and nitroolefin **2A**.

#	Experiment	[**1a**] / mol/L	Equiv. of **1a**	[**2A**] / mol/L	Equiv. of **2A**	[**C1b-Cu***] / mol/L	Equiv. of **C1b-Cu***
K1	Standard	0.11	1.1	0.10	1.0	0.0050	0.050
K2	Dif. [**C1b-Cu***]	0.11	1.1	0.10	1.0	0.0025	0.025
K3	Dif. [**1a**]	0.15	1.5	0.10	1.0	0.0050	0.050
K4	Dif. [**2A**]	0.11	1.1	0.15	1.5	0.0050	0.050

The corresponding experiments **K1-K4** were performed by adding a solution of the catalyst **C1b-Cu***, 1,2-diphenylethane (internal standard, 0.05 mmol), ketoester **1a**, nitroolefin **2A** in tetrahydrofuran-d8 (0.5 mL) to an NMR sample tube as shown in table **S6**. The reaction mixture was analyzed by ^{1}H NMR spectroscopy at room temperature to monitor the conversion of **1a** and **2A** and the yield of **3aA** in dependence of time (**Figure S8**).

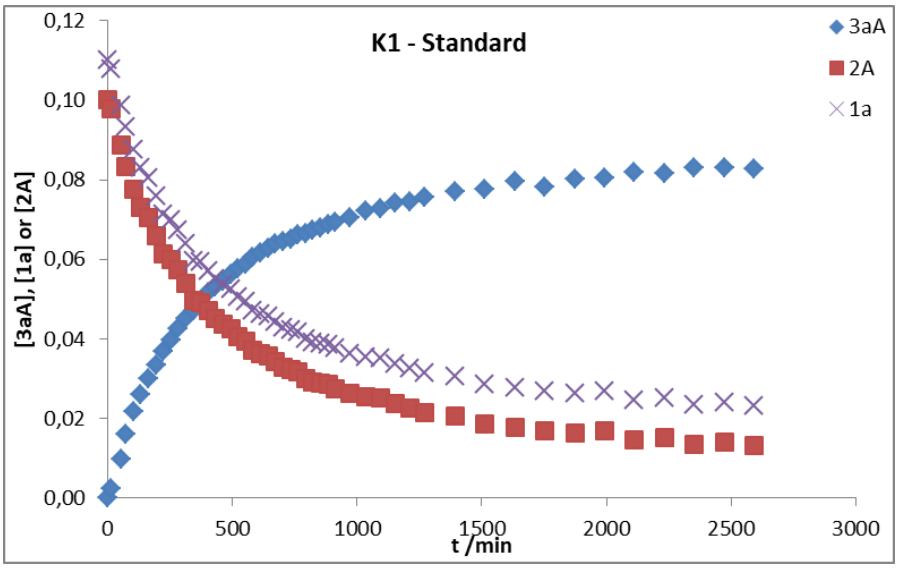


Figure S8. Conversion of 1a and 2A and the yield of 3aA in dependence of time.

The reaction progress profiles of all four reactions **K1-K4** are plotted in **Figure S9** and were investigated using VTNA.[34,35,36] VTNA makes use of a variable normalization of the time scale for a visual comparison of entire concentration reaction profiles. The normalization of the time axis enables the comparison of the progress reaction profiles of the series of reactions where different initial concentrations of each reaction component were used. For each component variables with different exponents were added to this normalized time axis. The order in each component can be determined visually by systematically changing each exponent of the normalized time axis, with the intention to obtain a linear overlay of all reaction profiles in the plot. The normalized time axis equation used for the investigation of the catalytic reaction is described as:

$$\sum_{i=1}^{n} [C1b\text{-}Cu^*]^{\alpha}[1a]^{\beta}[2A]^{\gamma}\Delta t =$$

$$\sum_{i=1}^{n}\left(\frac{[C1b\text{-}Cu^*]_i + [C1b\text{-}Cu^*]_{i-1}}{2}\right)^{\alpha}\left(\frac{[1a]_i + [1a]_{i-1}}{2}\right)^{\beta}\left(\frac{[2A]_i + [2A]_{i-1}}{2}\right)^{\gamma}(t_i - t_{i-1})$$

The equation can be simplified by substituting the term of the catalyst with $[C1b\text{-}Cu^*]_0^{\alpha}t$, because the concentration of active catalyst is constant and no deactivation of the catalyst during the reaction takes place, as shown by the "Same-Excess"-experiments in the previous section (**Kinetic Experiments – Probing Catalyst Robustness and Product Influence**). The simplified equation can be described as followed, whereby $[C1b\text{-}Cu^*]_0$ the initial concentration of the catalyst is.

$$\sum_{i=1}^{n}([C1b\text{-}Cu^{*}]_0)^{\alpha}\left(\frac{[1a]_i+[1a]_{i-1}}{2}\right)^{\beta}\left(\frac{[2A]_i+[2A]_{i-1}}{2}\right)^{\gamma}(t_i-t_{i-1})$$

In **Figure S9** the original reaction progress profiles of the conversion in nitroolefin **2A** and the time were plotted. The VTNA cannot be applied on reaction profiles with different starting coordinates (**K4**, **[2A]** = 0.15 mol/L), therefore the profile of **K4** has to be shifted vertically to the starting point of the other reaction progress profiles (**[2A]** = 0.10 mol/L, **Figure S9**).[35] Application of the normalization to all components displaying a kinetic effect in the reaction should result in a plot with a straight line with the slope equaling the rate constant k_{obs}. The reaction profiles overlay in a straight line (**Figure S10**), when all the driving forces, which change during the catalytic reaction, were raised to orders of 0.90 in **C1b-Cu***, 0.85 in **1a** and 1.15 in **2A**. The slope, k_{obs} of the reaction and was found to be 2.9 $L^{2.9}mol^{-2.9}s^{-1}$. The plot of this time normalized reaction profiles is shown in **Figure S10**.

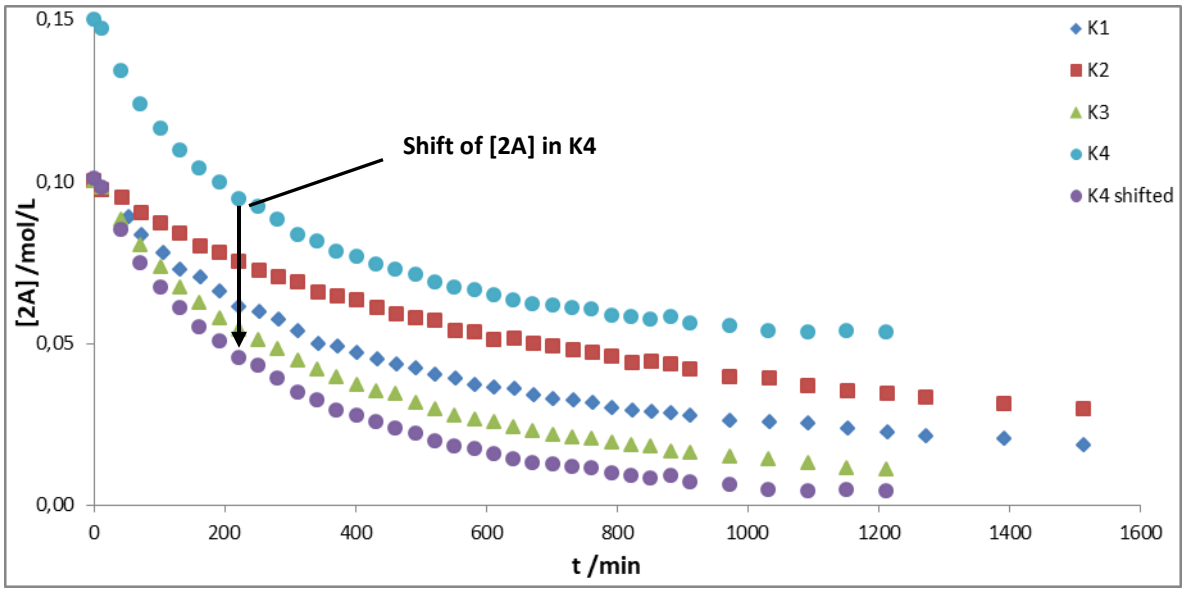


Figure S9. Original reaction progress profile of the conversion of nitroolefin 2A for the four reactions (α, β, γ = 0).

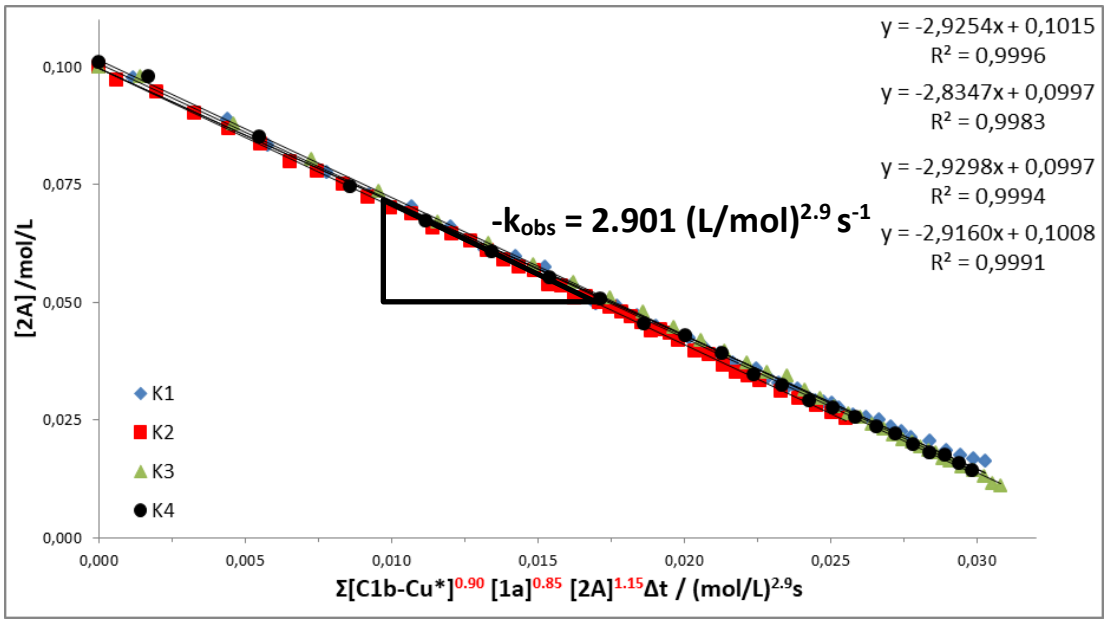


Figure S10. Best overlay of all four reaction progress profiles with orders 0.90 in C1b-Cu*, 0.85 in 1a and 1.15 in 2A. Unit of x-axis in s(mol/L) $^{2.9}$ (k_{obs} = 2.9 $L^{2.9}mol^{-2.9}s^{-1}$)

Modifying any of the orders in the reaction components to other values did not lead to overlaying (non-linear profiles). In the following **Figure S11-S13** the correct orders were systematically modified by ±0.3 to evaluate the divergences of the corresponding normalized reaction profiles. In all cases (**Figure S11-S13**), the manipulated profiles of the different initial concentration's diverge from the other profiles with the correct orders.

Evaluation of the order in catalyst [C1b-Cu*]

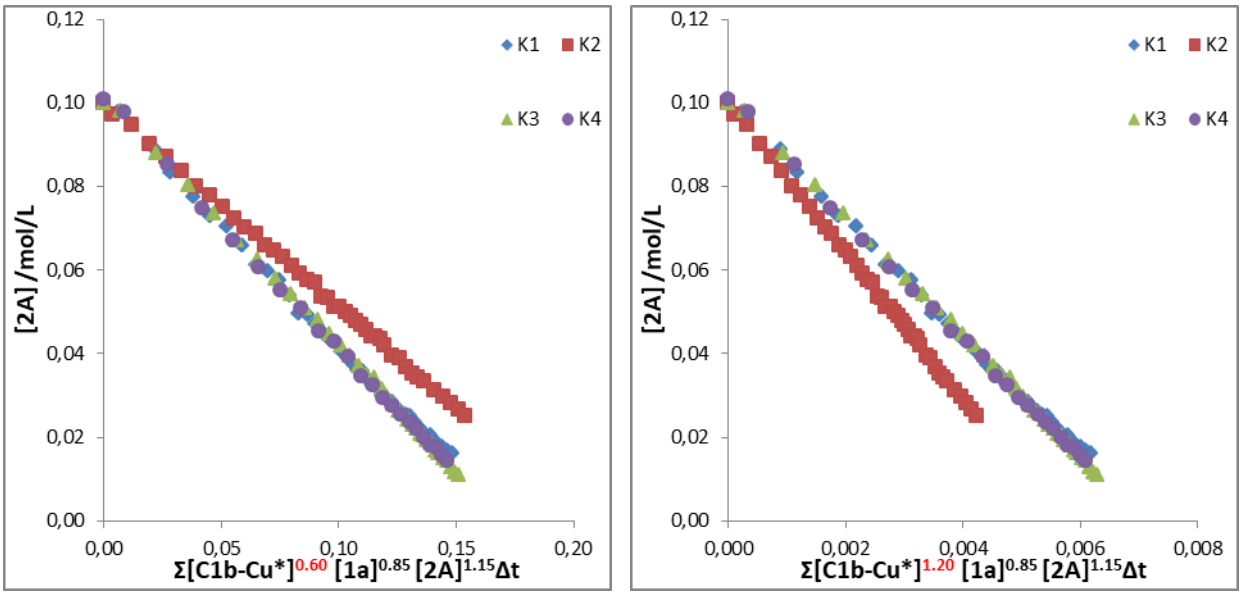


Figure S11. Divergence of the reaction profiles when the order in [C1b-Cu*] is modified ±0.3 from 0.90.

Evaluation of the order in [1a]

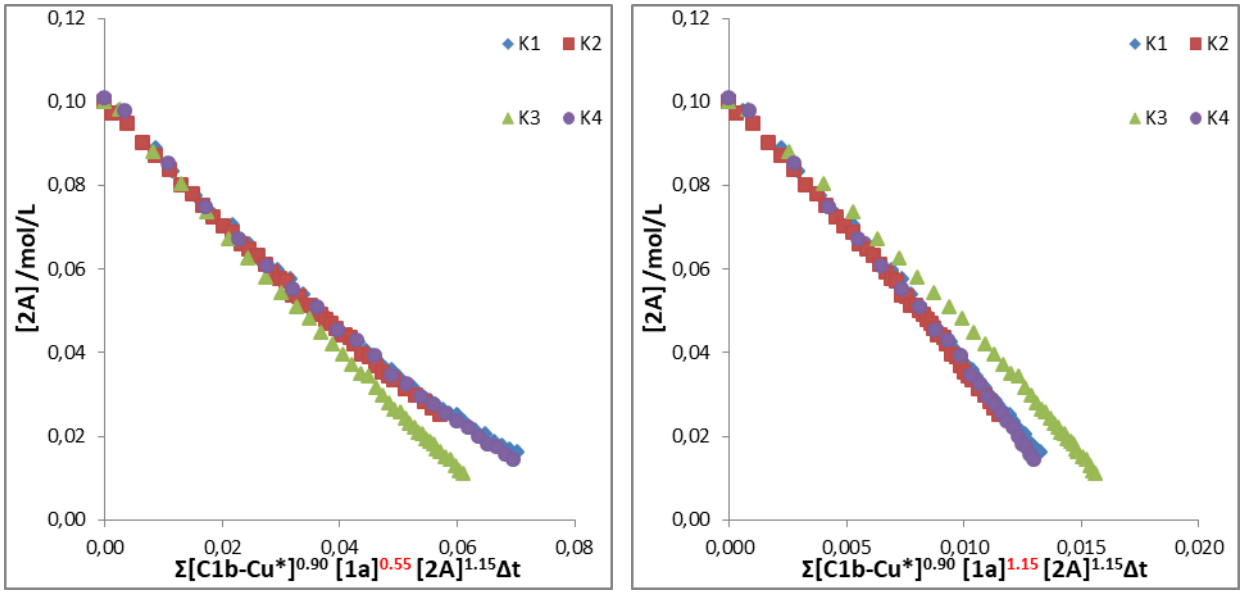


Figure S12. Divergence of the reaction profiles when the order in [1a] is modified by ±0.3 from 0.85.

Evaluation of the order in [2A]

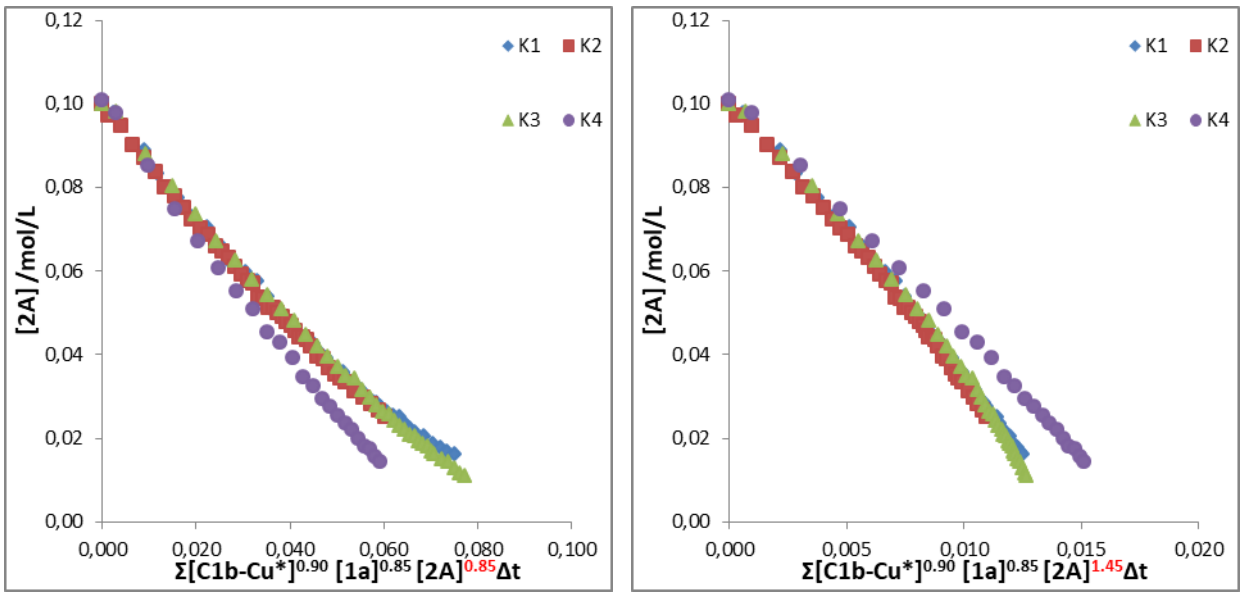


Figure S13. Divergence of the reaction profiles when the order in [2A] is modified by ±0.3 from 1.15.

Raw Data, Calculated Concentrations and Processed Data for the VTNA.

All processed data are given in α = 0.90, β = 0.85, γ = 1.15.

K1, Standard				
Time /min	**[C1b-Cu*]$_0$ /mol/L**	**[1a]$^{a)}$ /mol/L**	**[2A] /mol/L**	$\sum [\boldsymbol{C1b\text{-}Cu^*}]^{\alpha}[\boldsymbol{1a}]^{\beta}[\boldsymbol{2A}]^{\gamma}\Delta\boldsymbol{t}$
0	0,005	0,110	0,100	0,0000
13	0,005	0,108	0,098	0,0010
53	0,005	0,099	0,089	0,0039
73	0,005	0,093	0,083	0,0051
106	0,005	0,088	0,078	0,0069
133	0,005	0,083	0,073	0,0082
163	0,005	0,080	0,070	0,0094
193	0,005	0,076	0,066	0,0106
223	0,005	0,071	0,061	0,0116
253	0,005	0,070	0,060	0,0126
283	0,005	0,067	0,057	0,0134
313	0,005	0,064	0,054	0,0142
343	0,005	0,060	0,050	0,0149
373	0,005	0,059	0,049	0,0155
403	0,005	0,057	0,047	0,0161
433	0,005	0,055	0,045	0,0167
463	0,005	0,054	0,044	0,0172
493	0,005	0,052	0,042	0,0177
523	0,005	0,050	0,040	0,0181
553	0,005	0,049	0,039	0,0185
583	0,005	0,047	0,037	0,0189
613	0,005	0,046	0,036	0,0193
643	0,005	0,046	0,036	0,0196
673	0,005	0,044	0,034	0,0199
703	0,005	0,043	0,033	0,0202
733	0,005	0,042	0,032	0,0205
763	0,005	0,042	0,032	0,0208
793	0,005	0,040	0,030	0,0211
823	0,005	0,039	0,029	0,0213

853	0,005	0,039	0,029	0,0215
883	0,005	0,039	0,029	0,0217
913	0,005	0,038	0,028	0,0220
973	0,005	0,036	0,026	0,0224
1033	0,005	0,036	0,026	0,0227
1093	0,005	0,035	0,025	0,0231
1153	0,005	0,034	0,024	0,0234
1213	0,005	0,032	0,022	0,0237
1273	0,005	0,031	0,021	0,0240
1393	0,005	0,030	0,020	0,0245
1513	0,005	0,029	0,019	0,0250
1633	0,005	0,028	0,018	0,0254
1753	0,005	0,027	0,017	0,0257
1873	0,005	0,026	0,016	0,0261

a) Due to inaccuracy in the integration of the signals of **1a** in the ^{1}H-NMR, **[1a]** was calculated using Blackmond's "excess" method ([1a] = [2a]–[e]).[32,33]

[e] is defined as the difference of concentration of the two reactants, which can be seen as the stoichiometry of the reactants and remains constant during the reaction.

K2, Difference in [C1b-Cu*]				
Time /min	**[C1b-Cu*]$_0$ /mol/L**	**[1a] a) /mol/L**	**[2A] /mol/L**	$\sum[\boldsymbol{C1b\text{-}Cu}^*]^{\alpha}[\boldsymbol{1a}]^{\beta}[\boldsymbol{2A}]^{\gamma}\Delta\boldsymbol{t}$
0	0,0025	0,110	0,100	0,0000
13	0,0025	0,107	0,097	0,0006
43	0,0025	0,105	0,095	0,0018
73	0,0025	0,100	0,090	0,0029
103	0,0025	0,097	0,087	0,0039
133	0,0025	0,094	0,084	0,0049
163	0,0025	0,090	0,080	0,0058
193	0,0025	0,088	0,078	0,0066
223	0,0025	0,085	0,075	0,0074
253	0,0025	0,082	0,072	0,0081
283	0,0025	0,080	0,070	0,0088
313	0,0025	0,079	0,069	0,0095

343	0,0025	0,076	0,066	0,0101
373	0,0025	0,075	0,065	0,0106
403	0,0025	0,073	0,063	0,0112
433	0,0025	0,071	0,061	0,0117
463	0,0025	0,069	0,059	0,0122
493	0,0025	0,068	0,058	0,0127
523	0,0025	0,067	0,057	0,0131
553	0,0025	0,064	0,054	0,0135
583	0,0025	0,063	0,053	0,0139
613	0,0025	0,061	0,051	0,0143
643	0,0025	0,061	0,051	0,0146
673	0,0025	0,060	0,050	0,0150
703	0,0025	0,059	0,049	0,0153
733	0,0025	0,058	0,048	0,0156
763	0,0025	0,057	0,047	0,0160
793	0,0025	0,056	0,046	0,0163
823	0,0025	0,054	0,044	0,0165
853	0,0025	0,054	0,044	0,0168
883	0,0025	0,054	0,044	0,0171
913	0,0025	0,052	0,042	0,0173
973	0,0025	0,050	0,040	0,0178
1033	0,0025	0,049	0,039	0,0182
1093	0,0025	0,047	0,037	0,0186
1153	0,0025	0,045	0,035	0,0190
1213	0,0025	0,044	0,034	0,0193
1273	0,0025	0,043	0,033	0,0197
1393	0,0025	0,041	0,031	0,0203
1513	0,0025	0,040	0,030	0,0208
1633	0,0025	0,038	0,028	0,0213
1753	0,0025	0,037	0,027	0,0217
1873	0,0025	0,035	0,025	0,0221

a) Due to inaccuracy in the integration of the signals of **1a** in the ^{1}H-NMR, **[1a]** was calculated using Blackmond's "excess" method ([1a] = [2a]–[e]).[32, 33] [e] is defined as the difference of concentration of the two reactants, which can be seen as the stoichiometry of the reactants and remains constant during the reaction.

K3, Difference in [1a]				
Time /min	**$[C1b\text{-}Cu^*]_0$ /mol/L**	**[1a] [a)] /mol/L**	**[2A] /mol/L**	$\sum [C1b\text{-}Cu^*]^{\alpha}[1a]^{\beta}[2A]^{\gamma}\Delta t$
0	0,005	0,150	0,100	0,0000
12	0,005	0,148	0,098	0,0013
42	0,005	0,138	0,088	0,0041
72	0,005	0,130	0,080	0,0065
102	0,005	0,124	0,074	0,0085
132	0,005	0,117	0,067	0,0102
162	0,005	0,113	0,063	0,0117
192	0,005	0,108	0,058	0,0131
222	0,005	0,104	0,054	0,0143
252	0,005	0,101	0,051	0,0153
282	0,005	0,098	0,048	0,0163
312	0,005	0,095	0,045	0,0172
342	0,005	0,092	0,042	0,0180
372	0,005	0,090	0,040	0,0187
402	0,005	0,087	0,037	0,0193
432	0,005	0,085	0,035	0,0199
462	0,005	0,084	0,034	0,0205
492	0,005	0,081	0,031	0,0210
522	0,005	0,080	0,030	0,0214
552	0,005	0,078	0,028	0,0219
582	0,005	0,076	0,026	0,0222
612	0,005	0,076	0,026	0,0226
642	0,005	0,074	0,024	0,0229
672	0,005	0,073	0,023	0,0232
702	0,005	0,072	0,022	0,0235
732	0,005	0,071	0,021	0,0238
762	0,005	0,070	0,020	0,0240
792	0,005	0,069	0,019	0,0243
822	0,005	0,069	0,019	0,0245
852	0,005	0,068	0,018	0,0247
882	0,005	0,067	0,017	0,0249
912	0,005	0,066	0,016	0,0251

972	0,005	0,065	0,015	0,0254
1032	0,005	0,064	0,014	0,0258
1092	0,005	0,063	0,013	0,0260
1152	0,005	0,062	0,012	0,0263
1212	0,005	0,061	0,011	0,0265

a) Due to inaccuracy in the integration of the signals of **1a** in the ^{1}H-NMR, **[1a]** was calculated using Blackmond's "excess" method ([1a] = [2a]–[e]).[32, 33] [e] is defined as the difference of concentration of the two reactants, which can be seen as the stoichiometry of the reactants and remains constant during the reaction.

K4, Difference in [2A]					
Time /min	**[C1b-Cu*]$_0$ /mol/L**	**[1a] a) /mol/L**	**[2A] /mol/L**	**[2A] (vertical shifted) /mol/L**	$\sum[\boldsymbol{C1b\text{-}Cu^*}]^{\alpha}[\boldsymbol{1a}]^{\beta}[\boldsymbol{2A}]^{\gamma}\Delta\boldsymbol{t}$
0	0,005	0,110	0,150	0,101	0,0000
12	0,005	0,107	0,147	0,098	0,0016
42	0,005	0,094	0,134	0,085	0,0050
72	0,005	0,084	0,124	0,075	0,0078
102	0,005	0,076	0,116	0,067	0,0101
132	0,005	0,070	0,110	0,061	0,0121
162	0,005	0,064	0,104	0,055	0,0139
192	0,005	0,060	0,100	0,051	0,0154
222	0,005	0,054	0,094	0,045	0,0168
252	0,005	0,052	0,092	0,043	0,0180
282	0,005	0,048	0,088	0,039	0,0191
312	0,005	0,044	0,084	0,035	0,0201
342	0,005	0,041	0,081	0,032	0,0210
372	0,005	0,038	0,078	0,029	0,0217
402	0,005	0,037	0,077	0,028	0,0225
432	0,005	0,034	0,074	0,025	0,0231
462	0,005	0,033	0,073	0,024	0,0238
492	0,005	0,031	0,071	0,022	0,0243
522	0,005	0,029	0,069	0,020	0,0249
552	0,005	0,027	0,067	0,018	0,0253

582	0,005	0,027	0,067	0,018	0,0258
612	0,005	0,025	0,065	0,016	0,0262
642	0,005	0,023	0,063	0,014	0,0266

a) Due to inaccuracy in the integration of the signals of **1a** in the ^{1}H-NMR, **[1a]** was calculated using Blackmond's "excess" method ([1a] = [2a]–[e]).[32, 33] [e] is defined as the difference of concentration of the two reactants, which can be seen as the stoichiometry of the reactants and remains constant during the reaction.

Investigation of Possible Non-Linear-Effects

For determining the linear-effect behavior of the reaction, catalytic reactions were performed as described in **GP6-standard**, on a 0.050 mmol scale (0.050 mmol trans-β-nitrostyrene **2A,** 0.055 mmol ethyl 2-oxocyclopentanecarboxylate **1a**, 5 mol% catalyst **C1b-Cu***). Catalysts **C1b-Cu*** with 6 different enantiomeric excesses were used (see **Table S7**), which were prepared by mixing the corresponding amounts of pure enantiomers of the catalysts **C1b-Cu*.**

Table S7: Enantiomeric excess of the catalyst and the different product diastereomers **3aA-D1** and **3aA-D2**.

ee **(C1b-Cu*) /%** **catalyst**	***ee*** **(3aA-D2) /%** **product**	***ee*** **(3aA-D1) /%** **product**
0	2	2
19	19	13
38	39	25
58	58	39
79	75	52
100	99	69

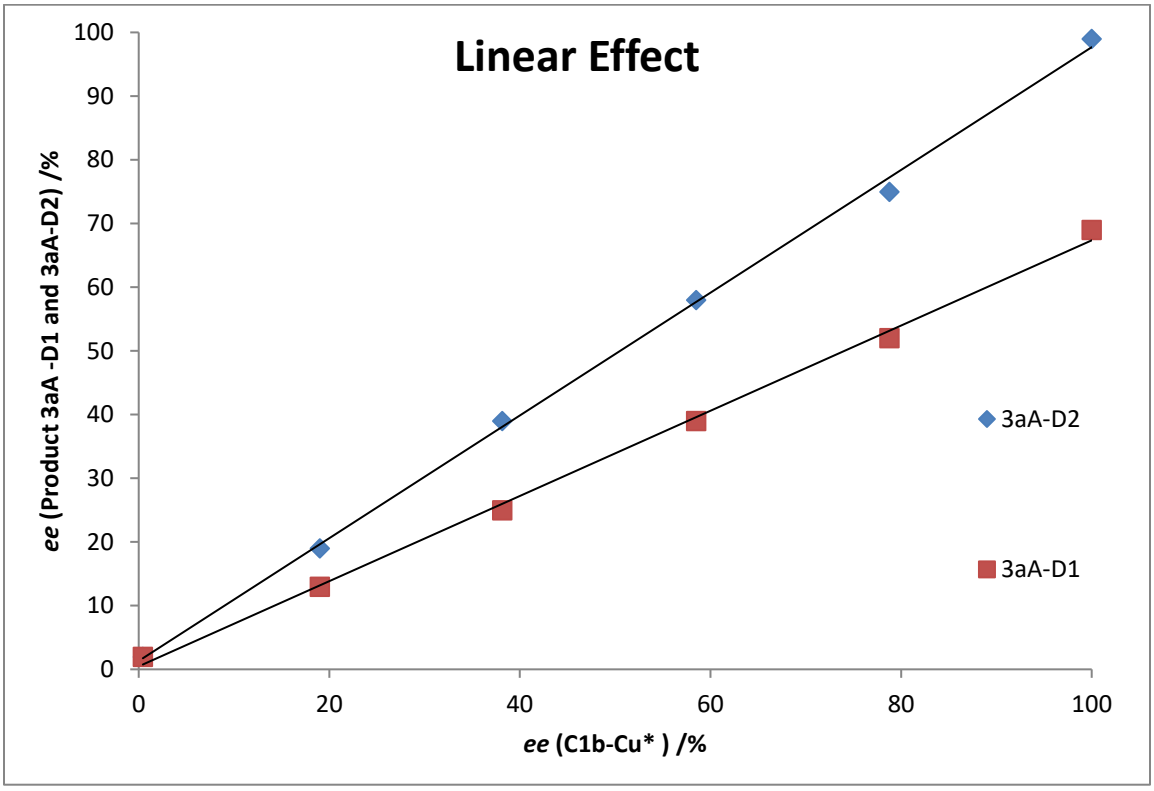


Figure S14: Linear effect plot of the catalytic reaction with different *ee*-values of the catalyst C1b-Cu*.

Beer's Law Plot

The UV-Vis measurements for the concentration dependence of the highly colored complex **C1b-Cu*** (12.9 mg, 0.0138 mmol) were performed in a cuvette (b = 1.0 mm, Quartz SUPRASIL® from HellmaAnalytics). Initially, the solid was dissolved in THF (0.3 mL) and the stock solution diluted by defined amounts of THF to measure the concentration-absorbance dependence of complex **C1b-Cu***. The measured and calculated data is shown in **Table S8**. Plotting the absorbance vs. concentration leads to an overall linear curve in the relevant concentrations range of up to 0.05 mol/L of the complex **C1b-Cu*** (**Figure S15**). The catalytic reactions in THF were performed at a concentration of 0.025 mol/L in the linear region of the Beer's law plot in **Figure S15**. This represents that no aggregation to dimers or oligomers at the concentration of the catalytic reaction takes place and supports the monomeric nature of the active catalyst in the catalyzed reactions.

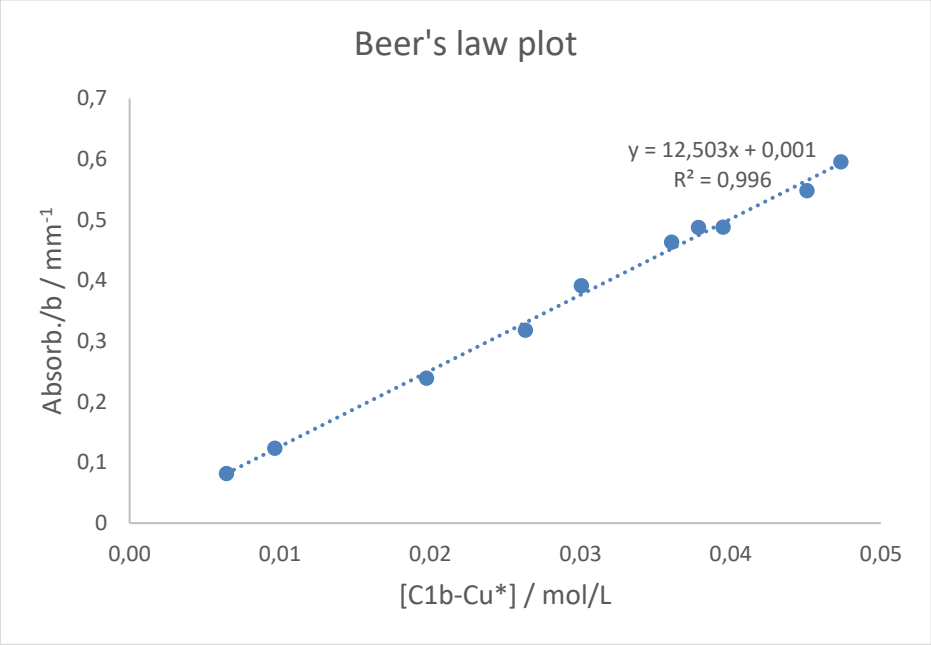


Figure S15.Beer's law plot of absorbance vs. concentration of the complex C1b-Cu*.

Table S8. Measured and calculated data for the concentration and UV-Vis absorbance dependence of complex **C1b-Cu***.

[**C1b-Cu***] / mol/L	Absorb. at 780 nm	Absorb/b / mm^{-1}
0,04732	0,05955832	0,59558321
0,03785	0,04878504	0,48785038
0,04506	0,05480639	0,54806389

0,03605	0,04632853	0,46328532
0,03004	0,03918400	0,39184002
0,03948	0,04880679	0,48806787
0,02632	0,03182365	0,31823647
0,01974	0,02392687	0,23926868
0,00966	0,01236153	0,12361533
0,00644	0,00820574	0,08205741

Titration Experiments in the UV-Vis

Catalyst **C1b-Cu*** (9.55 mg, 0.0104 mmol, 1 equiv) was dissolved in THF (3 mL) and filled in a cuvette (d = 10 mm, Quartz SUPRASIL® from HellmaAnalytics). The β-ketoester **1a** was added directly to the cuvette and after shaking the cuvette, the UV-Vis spectra was measured of the reaction mixtures at room temperature. In the titration experiment different equivalents (0, 20, 50, 100, 150, 200, 300 and 350 equiv) of **1a** were used.

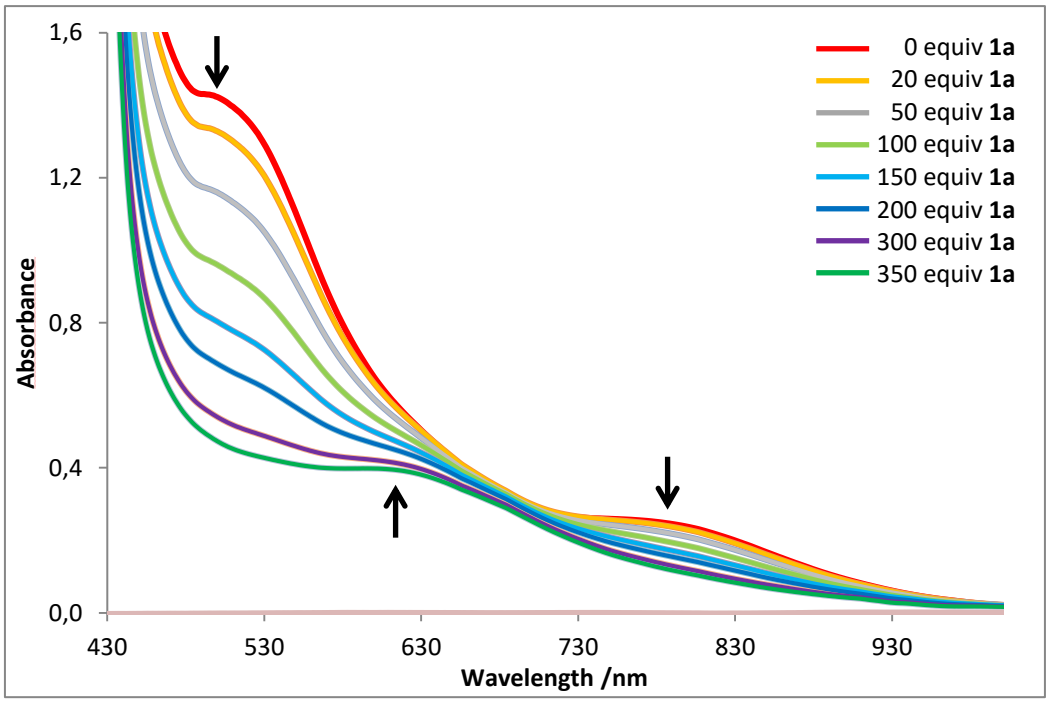


Figure S16. UV-Vis spectra of the titration experiment using β-ketoester 1a.

Titration Experiments in the EPR

Catalyst **C1b-Cu*** (4.99 mg, 0.00535 mmol, 1 equiv) was dissolved in THF (0.2 mL) and filled in an EPR-tube. The β-ketoester **1a** (0, 100 and 400 equiv) was added directly to the tube and after shaking for 1 minute at room temperature, the reaction mixture in the tube was frozen in liquid nitrogen. The EPR-measurement was performed at 108 K.

Spectra were fitted using the "Pepper" model in a least-squares fitting of EPR spectra using EasySpin.[37]

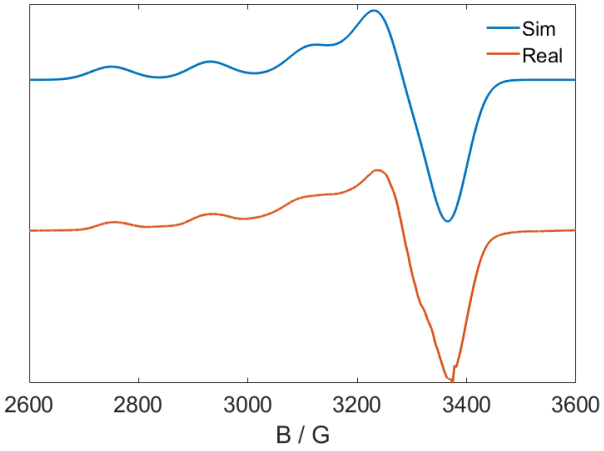


Figure S17. EPR-spectra of C1b-Cu

Lw = 8.1970

g_{II} = 2.1303 A_{II} (63,65Cu) = 523.26 MHz

$g_{\perp}$ = 1.9692 $A_{\perp}$ (63,65Cu) = 32.63 MHz

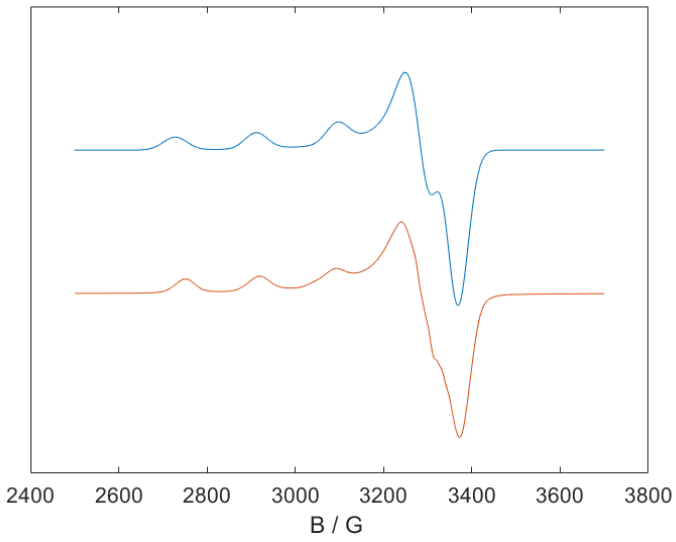


Figure S18. EPR-spectra of C1b-Cu*

LW = 5.93

g_{II} = 2.257 A_{II} (63,65Cu) = 526.52 MHz

$g_{\perp}$ = 2.0592 $A_{\perp}$ (63,65Cu) = 38.063 MHz

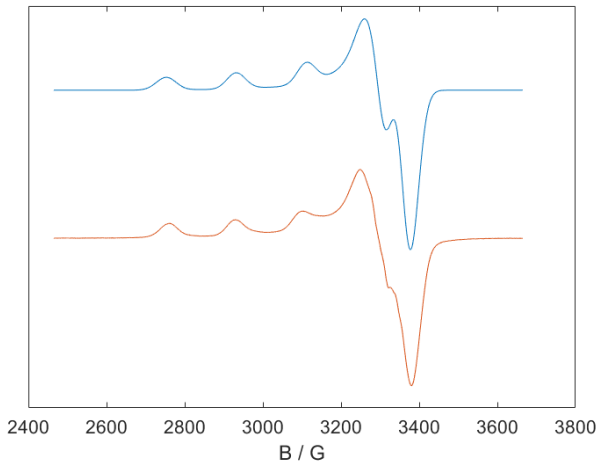


Figure S19. EPR-spectra of C1b-Cu* + 20 equiv nitrolefin 2A

LW = 5.5

g_{II} = 2.264 A_{II} (63,65Cu) = 549.97 MHz

$g_{\perp}$ = 2.0504 $A_{\perp}$ (63,65Cu) = 41.96 MHz

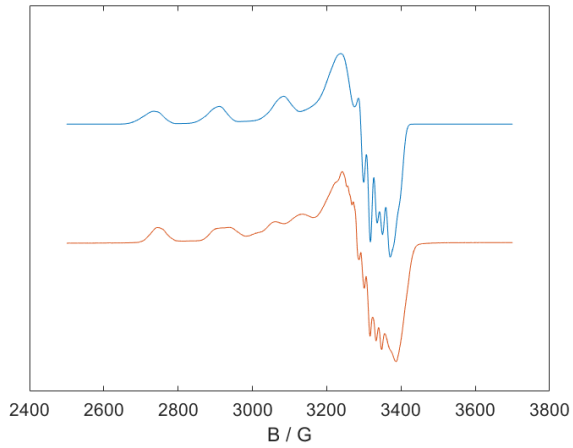


Figure S20. EPR-spectra of C1b-Cu* + 100 equiv β-ketoester 1a

A suitable fit could not be generated.

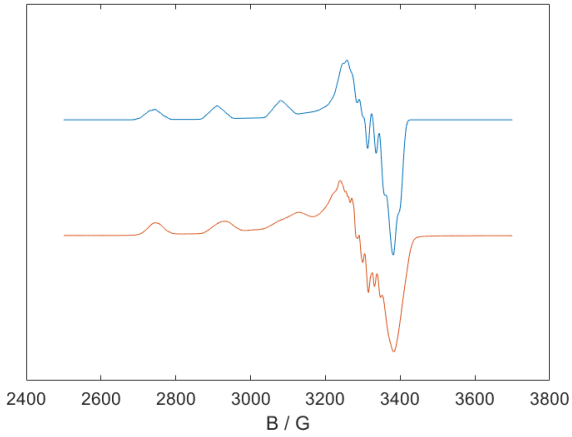


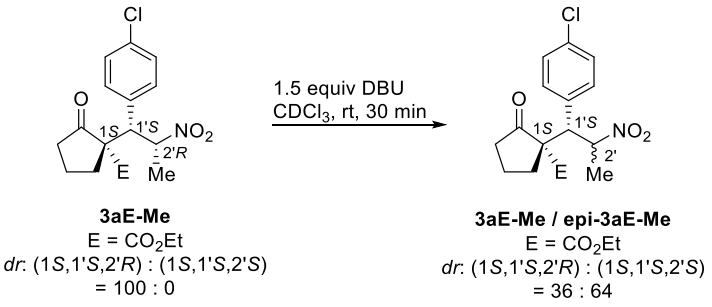
Figure S21. EPR-spectra of C1b-Cu* + 400 equiv β-ketoester 1a

LW = 1.7

g_{II} = 2.2406 A_{II} (63,65Cu) = 589.93 MHz 14N 42, 29

$g_{\perp}$ = 2.0432 $A_{\perp}$ (63,65Cu) = 46.3445 MHz 14 N 47, 34

Epimerization Experiment of Third Stereocenter with Base



3aE-Me
E = CO_2Et
dr: (1*S*,1'*S*,2'*R*) : (1*S*,1'*S*,2'*S*)
= 100 : 0

3aE-Me / epi-3aE-Me
E = CO_2Et
dr: (1*S*,1'*S*,2'*R*) : (1*S*,1'*S*,2'*S*)
= 36 : 64

3aE-Me (10.2 mg, 0.029 mmol, 1.0 equiv) was dissolved in 0.4 mL $CDCl_3$, added to an NMR-tube and treated with DBU (6.45 µL, 6.6 mg, 0.043 mmol, 1.5 equiv). The reaction mixture was analyzed by ^{1}H-NMR and then filtrated over silica gel after reaching the equilibria (at 30 minutes reaction time at room temperature). The silica pad was washed with 5.0 ml dichloromethane and the solvent was removed under reduced pressure to yield epimerized **epi-3aE-Me** (9.6 mg, 0.027 mmol, 94%).

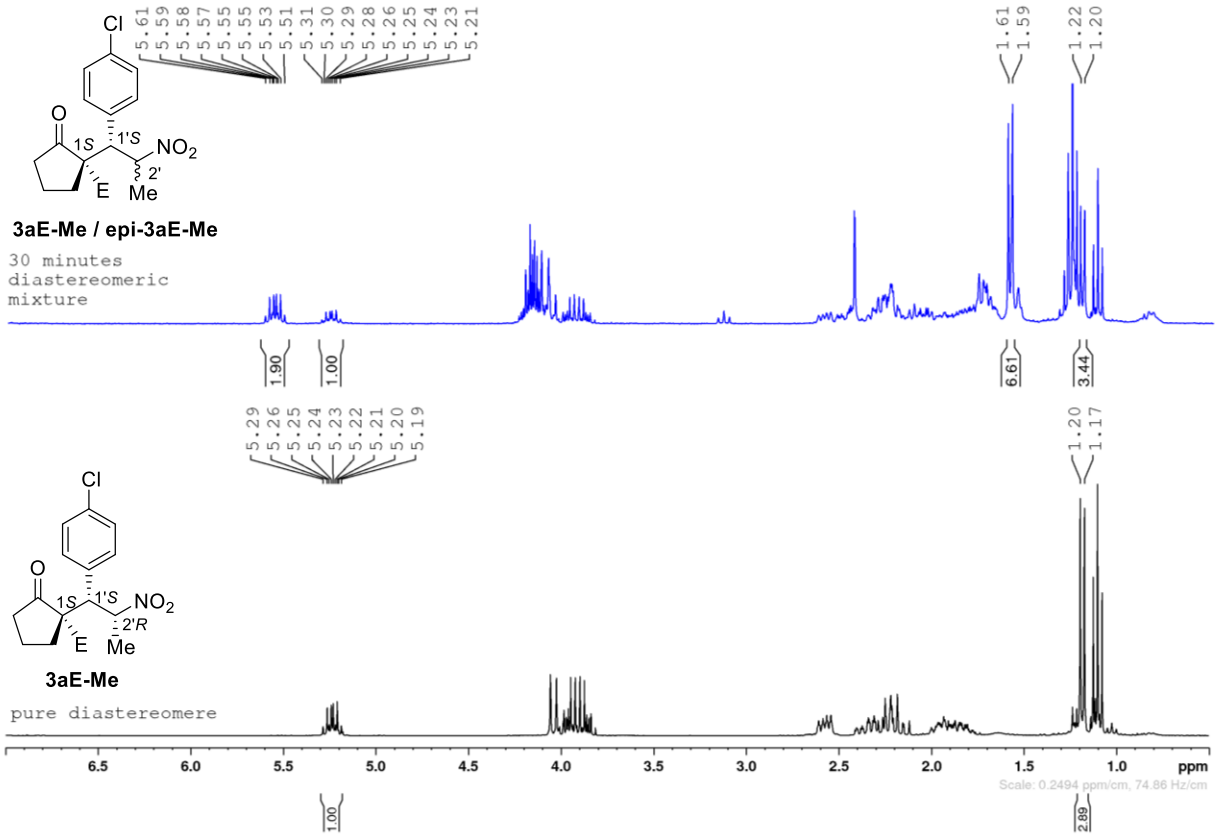
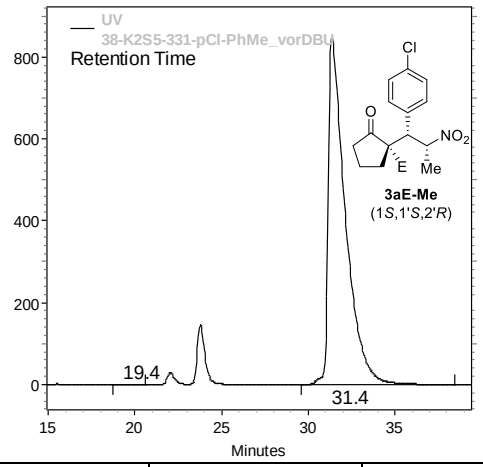
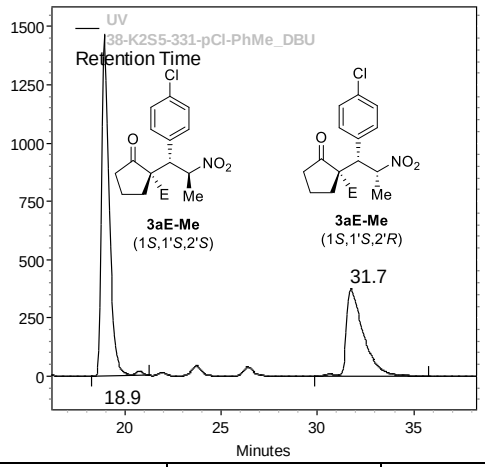


Figure S22. ^{1}H-NMR-Spectra of an epimerization experiment of 3aE-Me with an equilibrium ratio of 36 : 64 of the diastereomers (1*S*,1'*S*,2'*R*) : (1*S*,1'*S*,2'*S*).

Before epimerization

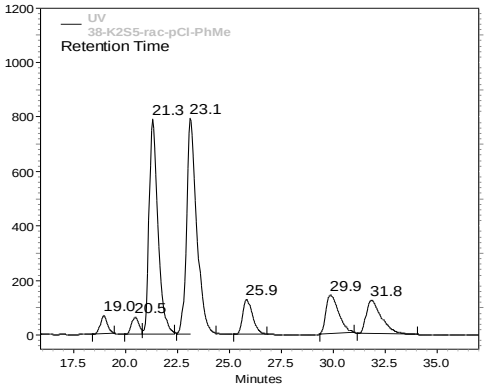


After 30 minutes epimerization



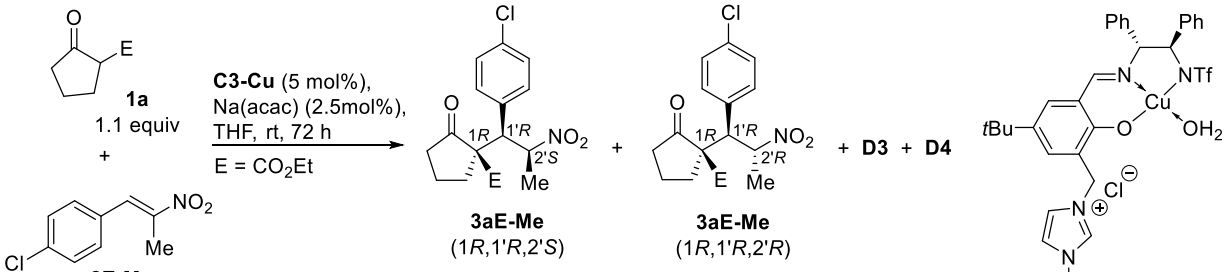
Retention Time	Area	Area %	Retention Time	Area	Area %
19.4	54893	0.02	18.9	163329876	64.30
31.4	233275559	99.98	31.7	90665329	35.70

Racemic mixture



Retention Time	Area	Area %
19.0	6267947	2.25
20.5	6135987	2.20
21.3	92560009	33.19
23.1	109689136	39.34
25.9	16424042	5.89
29.9	23282247	8.35
31.8	24489484	8.78
Column: IB, *n*-heptane/*i*PrOH (95/5), 0.5 mL/min, 210 nm		

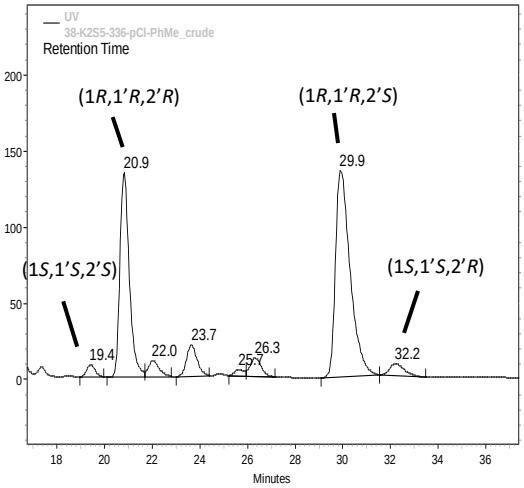
Control Experiments Regarding the Formation of the Third Stereocenter



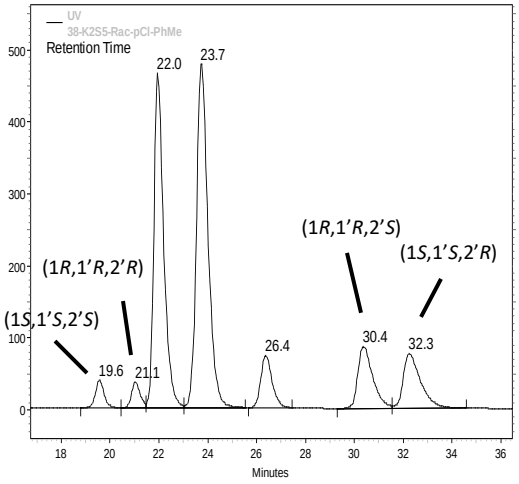
yield = 12 %
dr (1*R*,1'*R*,2'*S*) : (1*R*,1'*R*,2'*R*) : D3 : D4 = 53 : 34 : 4 : 9
ee (1*R*,1'*R*,2'*S*) = 89%
ee (1*R*,1'*R*,2'*R*) = 90%

C2 (1.65 mg, 5.0 mol%) and sodium acetylacetonate (0.18 mg, 2.5 mol%) was added to a catalysis tube and dissolved in THF (0.05 mL). Afterwards the nitroolefin **2E-Me** (9.88 mg, 0.050 mmol, 1.0 equiv), the β-ketoester **1a** (8.59 mg, 8.15 µL, 0.055 mmol, 1.1 equiv) and THF (0.05 ml) were added. The reaction mixture was stirred for 3 days at room temperature. Then the reaction mixture was diluted with a solvent mixture of petroleum ether/ethyl acetate (1/1, 1 mL), filtered through a small pad of silica and the crude product was eluted with additional petroleum ether/ethyl acetate (1/1, 5 mL). After the removal of the solvent under reduced pressure the crude product (12%, determined with ^{1}H NMR with mesitylene as internal standard) was analyzed using HPLC and ^{1}H NMR spectroscopy.

Control experiment



Racemic mixture



Retention Time	Area	Area %	Retention Time	Area	Area %
19.4	776461	1.69	19.6	3888410	2.41
20.9	14645991	31.90	21.1	3579281	2.22
22.0	1406762	3.06	22.0	52228352	32.34
23.7	2510058	5.47	23.7	62726132	38.84
25.7	486468	1.06	26.4	9378557	5.81
26.3	1545785	3.37	30.4	14631829	9.06
29.9	23178736	50.49	32.3	15046706	9.32
32.2	1355296	2.95			
Column: IB, *n*-heptane/*i*PrOH (95/5), 0.5 mL/min, 210 nm					

Computational Methods

The crystal structure of **C6** (Figure 3, see manuscript) served as a starting point to calculate optimized minimum energy structures of **C6** and the betaine catalyst in its naphthol form **C1b-Cu** (Figure 6. see manuscript). Having identified these structures, we explored the reaction mechanism of the catalytic cycle (Scheme 4, see manuscript) by calculating stationary points along the reaction pathway (minima as well as transition state structures; Figures 7, see manuscript). The density functional theory (DFT) calculations were performed at the B3LYP[38] level of theory using the cc-pVDZ[39] basis set as implemented in the Gaussian 16 program package[40]. All Structures were preoptimized in the gas phase and confirmed to be either true minima or true transition states structures by frequency calculations (zero or one imaginary frequency, respectively). We searched for the most stable conformers as a function of the binding motifs and torsion angles of the ligand. The structures were reoptimized using the IEF-PCM model[41] to include the self-consistent reaction field of the solvent (tetrahydrofurane, THF). We extracted and compared relative free Gibbs energies at 250 K. The presented structures are neutral (except **C1b-Cu**, which is a cation) and exhibit a multiplicity of 2. All calculations were performed in the electronic ground states.

Control System C6:

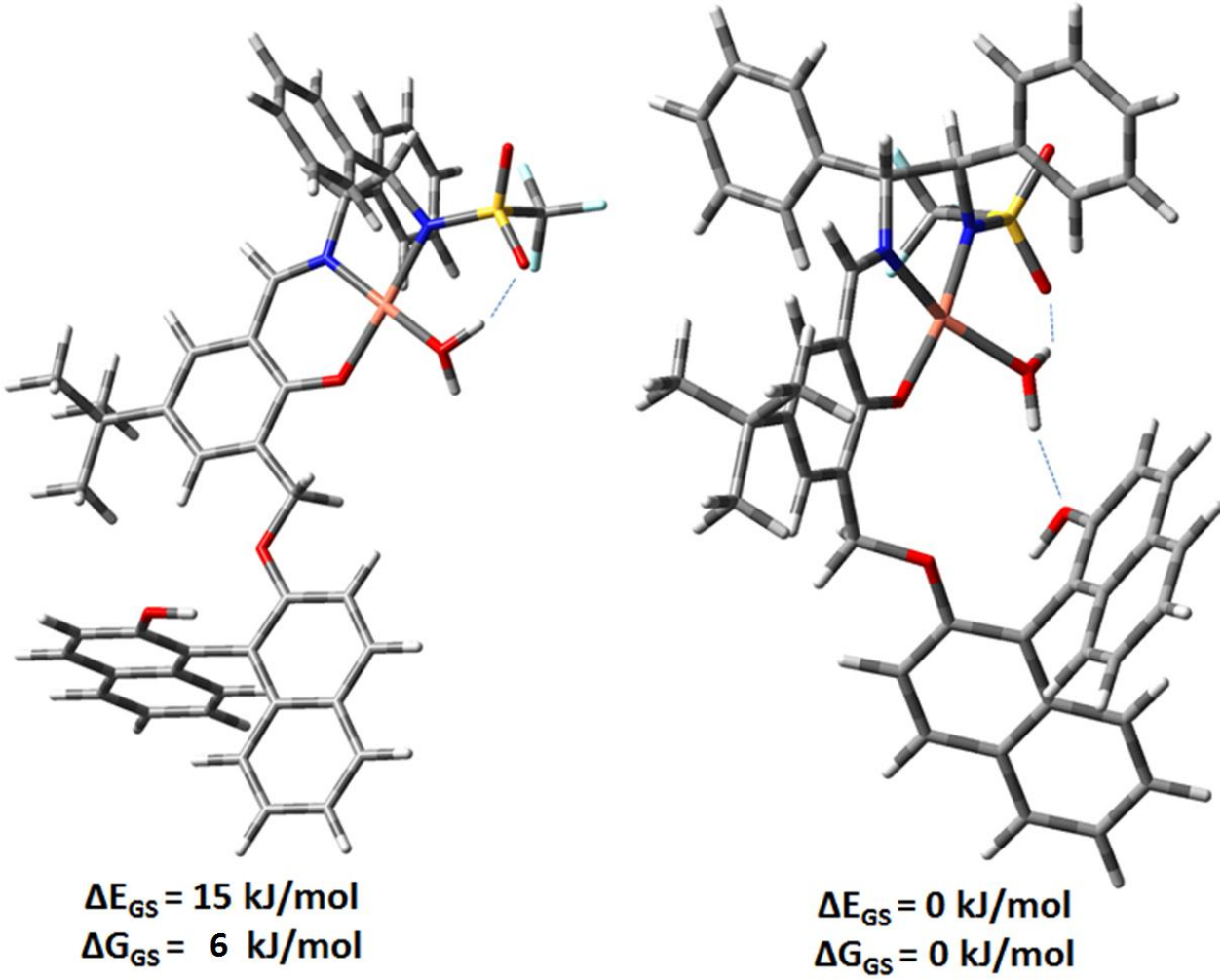


Figure S23: Optimized structures of C6 by DFT calculations at the B3LYP/cc-pVDZ/IEF-PCM (THF) level of theory. ΔEGS is the relative electronic energy in the ground state at 0 K. ΔGGS is the relative electronic energy corrected for the free energy in the ground state at 250 K. The dotted blue lines indicate hydrogen bonding. Light gray: H; dark gray: C; dark blue: N; orange: P; orange: Cu; light blue F; yellow: S.

The most stable structure of **C6** (Figure S23, right) exhibits two stabilizing hydrogen bonds: 1) between the naphthol OH and the water ligand on the and 2) between the water ligand and the sulfonyl moiety. A rotation of the binaphthol moiety results in the breaking of one hydrogen bond a destabilization of 6 kJ/mol (Figure S23, left).

Precatalyst C1b-Cu

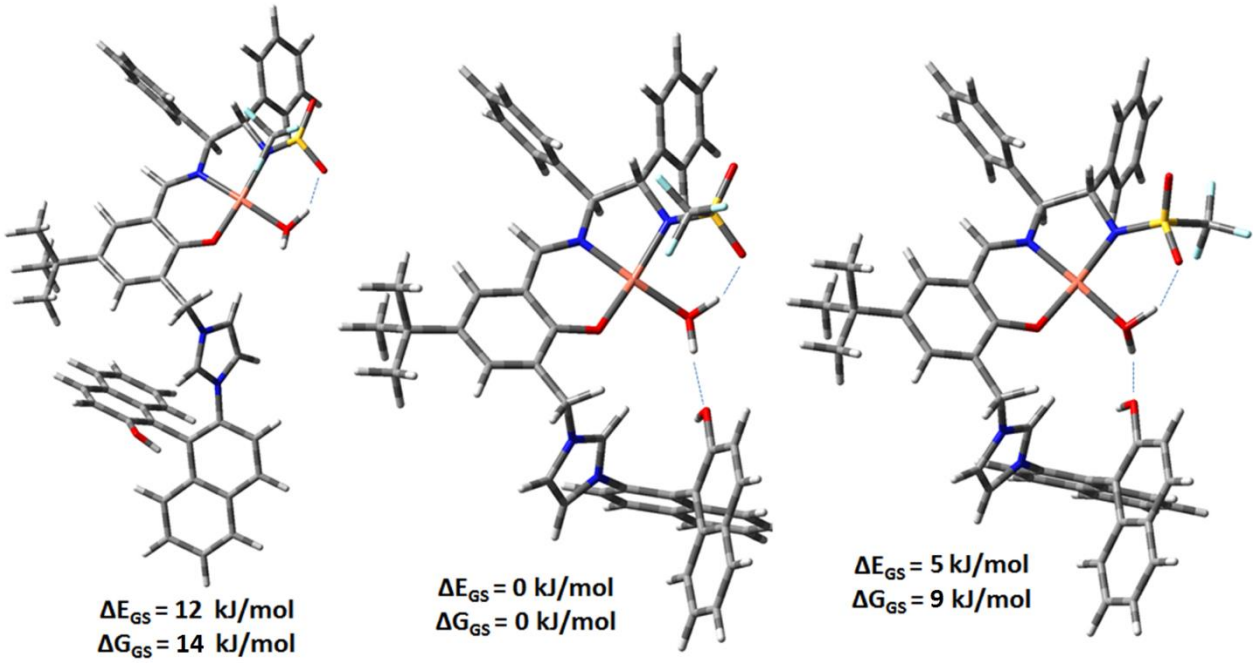


Figure S24: Optimized structures of C1b-Cu by DFT calculations at the B3LYP/cc-pVDZ/IEF-PCM (THF) level of theory. ΔEGS is the relative electronic energy in the ground state at 0 K. ΔGGS is the relative electronic energy corrected for the free energy in the ground state at 250 K. The dotted blue lines indicate hydrogen bonding. Same color code as in Figure S23.

The most stable structure of **C1b-Cu** (Figure S24, middle) exhibits two stabilizing hydrogen bonds: 1) between the naphthol OH and the water ligand on the and 2) between the water ligand and the sulfonyl moiety. Similar to **C6**, a rotation of the binaphthol moiety results in the breaking of one hydrogen bond a destabilization of 14 kJ/mol (Figure S24, left). Furthermore, rotating the sulfonyl moiety also destabilizes the complexes (9 kJ/mol, Figure S24, left). While the hydrogen bonding is intact, the H_2O ligand is pulled away from the planar coordination sphere of the copper center.

Intermediate structure II within the catalytic cycle

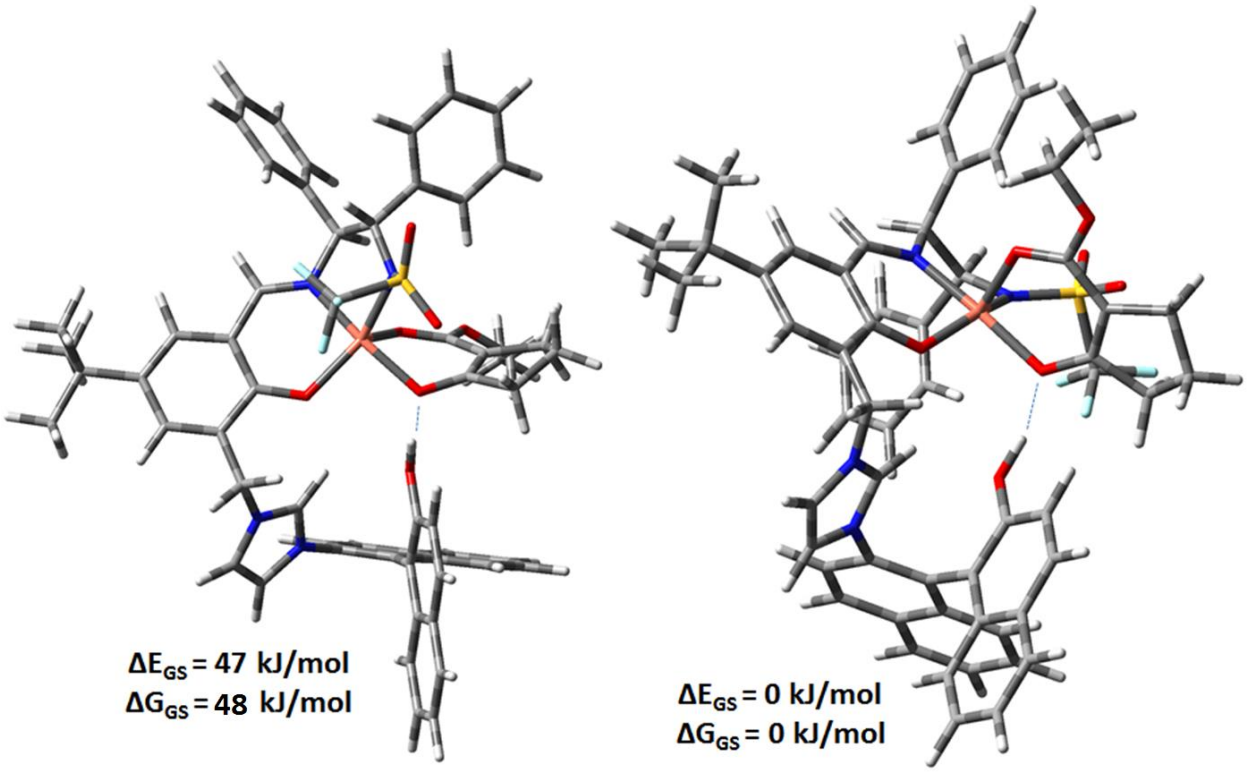


Figure S25: Optimized structures of II within the catalytic cycle (see Scheme 4): optimized structures by DFT calculations at the B3LYP/cc-pVDZ/IEF-PCM (THF) level of theory. ΔEGS is the relative electronic energy in the ground state at 0 K. ΔGGS is the relative electronic energy corrected for the free energy in the ground state at 300 K. The dotted blue lines indicate hydrogen bonding. Same color code as in Figure S23.

The most stable structure of **II** (Figure S25, right) exhibits intramolecular hydrogen bonding between the naphthol OH and the coordinated ketoester. Note that the copper center adopts a square pyramidal coordination sphere (coordination number of 5). A rotation of the bidentate ketoester distorts and destabilizes the complex significantly leading to a trigonal bipyramidal coordination sphere (48 kJ/mol, Figure S25, left).

TS I(keto) / II

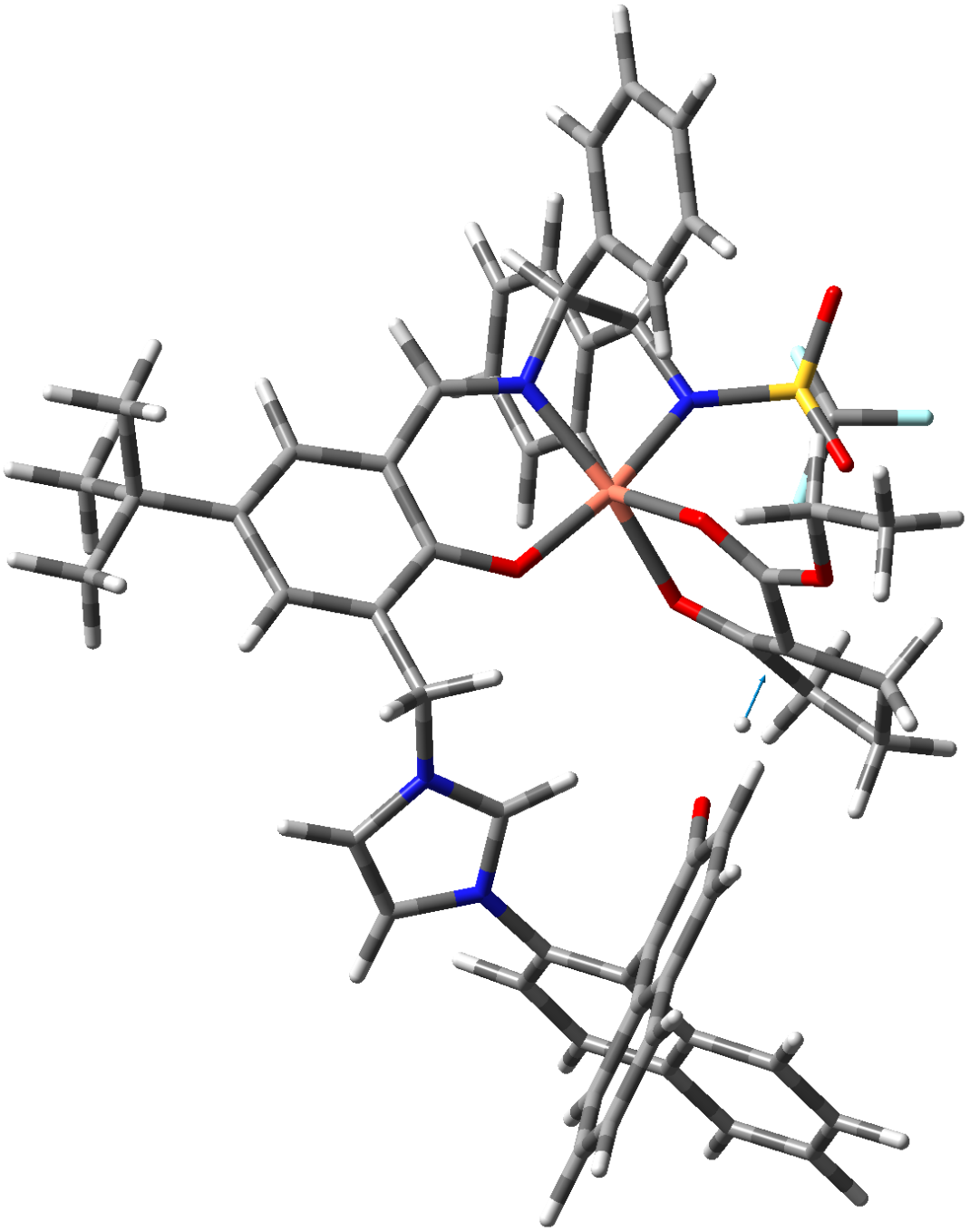


Figure S26: Optimized structures of the intermediate structure TS I(keto) / II within the catalytic cycle (see Scheme 4 of the main manuscript): optimized structures by DFT calculations at the B3LYP/cc-pVDZ/IEF-PCM (THF) level of theory. Same color code as in Figure S23. The blue arrow is the displacement vector of the virtual frequency vibration.

TS III / III.1

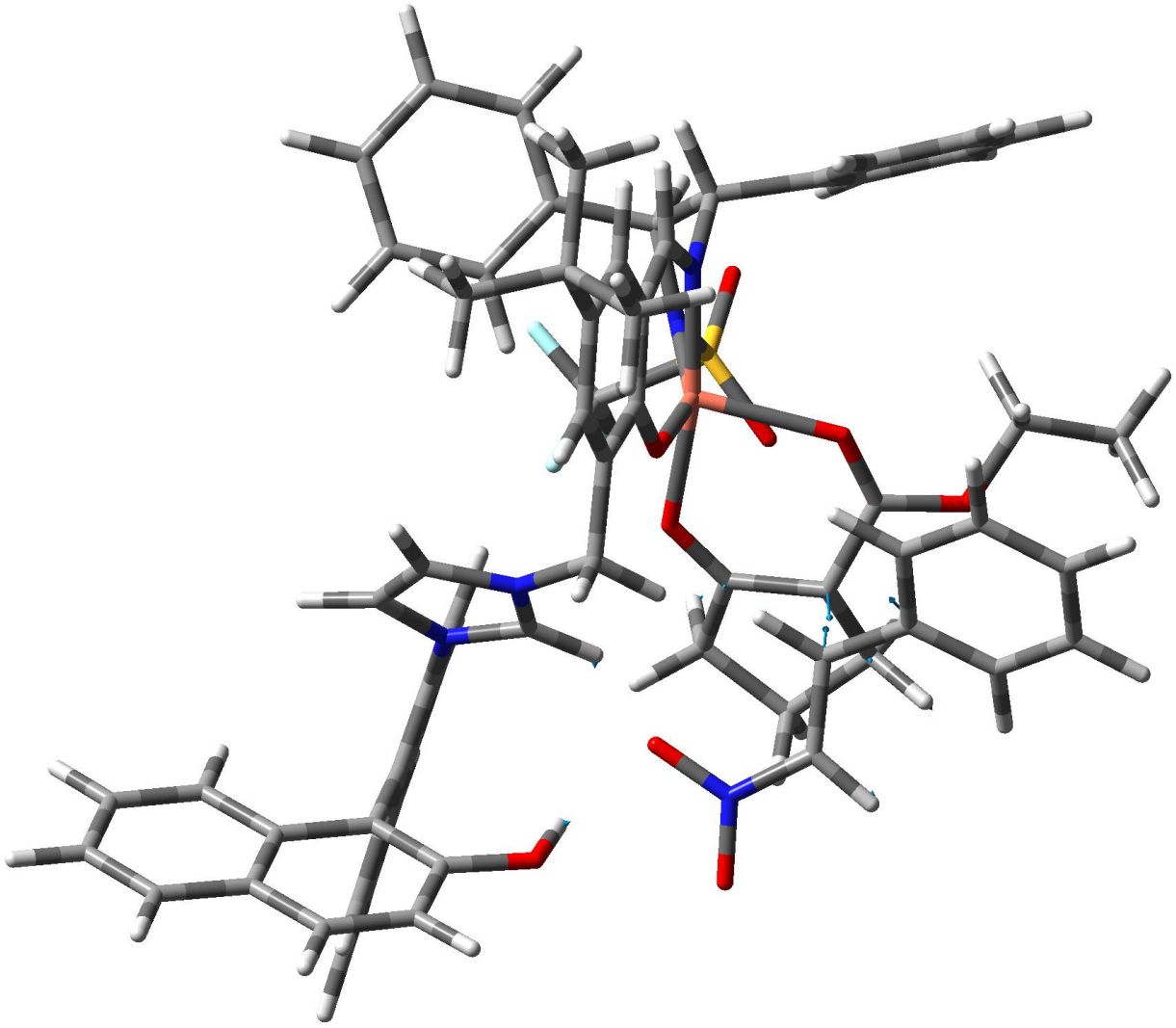


Figure S27: Optimized structures of the intermediate structure TS III / III.1 within the catalytic cycle (see Scheme 4 of the main manuscript): optimized structures by DFT calculations at the B3LYP/cc-pVDZ/IEF-PCM (THF) level of theory. Same color code as in Figure S23. The blue arrow is the displacement vector of the virtual frequency vibration.

Overview of the Optimized Minimum and Transition State Structures of the Catalytic Cycle

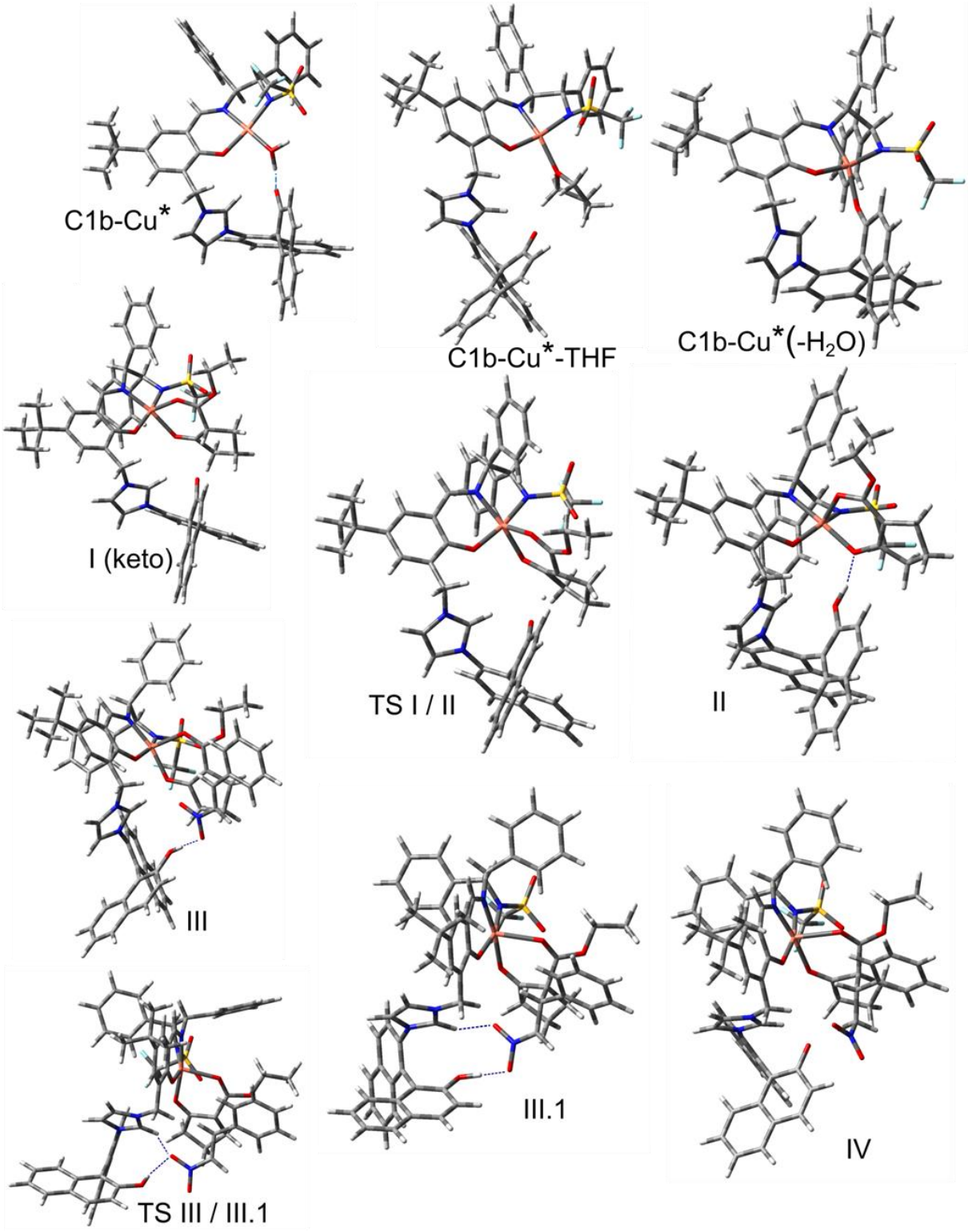
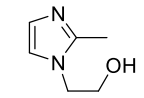


Figure S28. Optimized minimum and transition state structures of the proposed catalytic cycle (cf. Scheme 4, see manuscript). The structures arise from DFT calculations at the B3LYP/cc-pVDZ/IEF-PCM (THF) level of theory. The dotted blue lines indicate hydrogen bonding. Same color code as in Figure S23. For energetics refer to Figure 7, see manuscript.

NMR-Data



16

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FIDRES 0.122266 Hz
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RG 139.45
DW 62.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

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NUC1 1H
P1 13.70 usec
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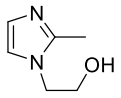

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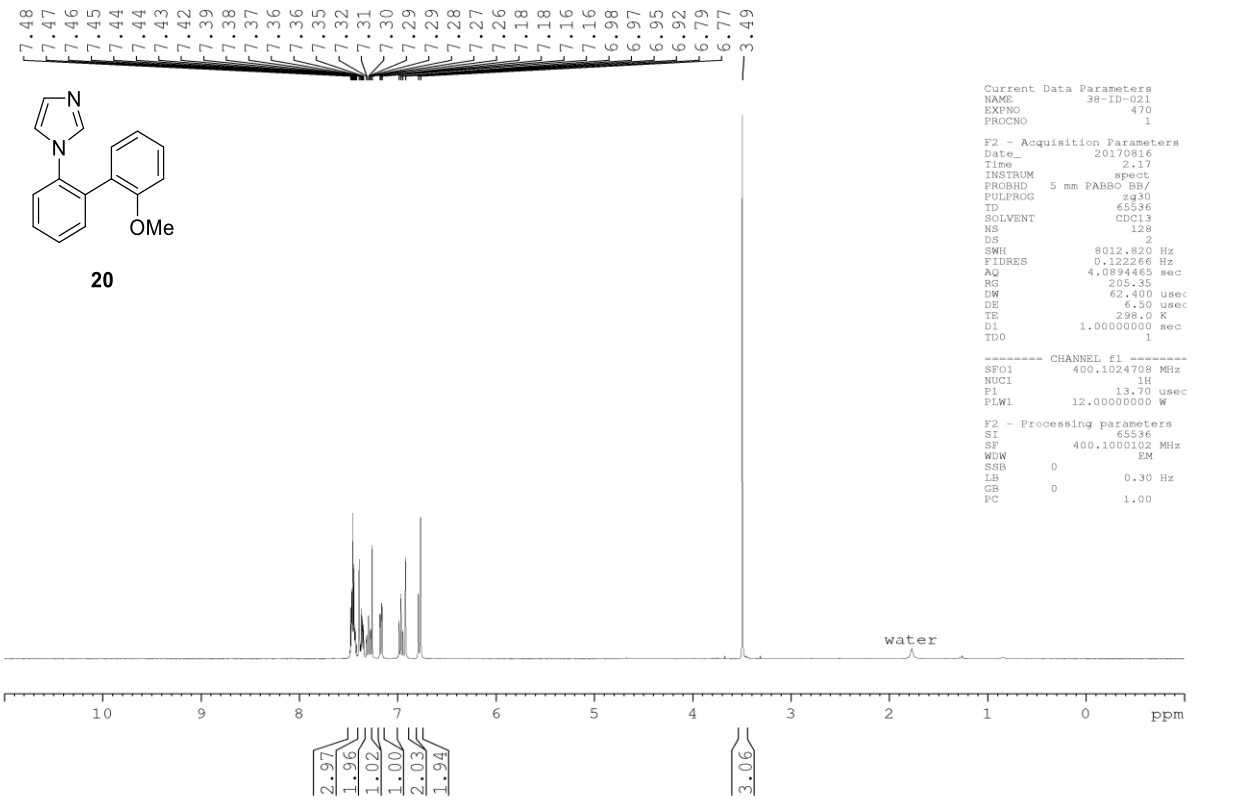
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TD0 1
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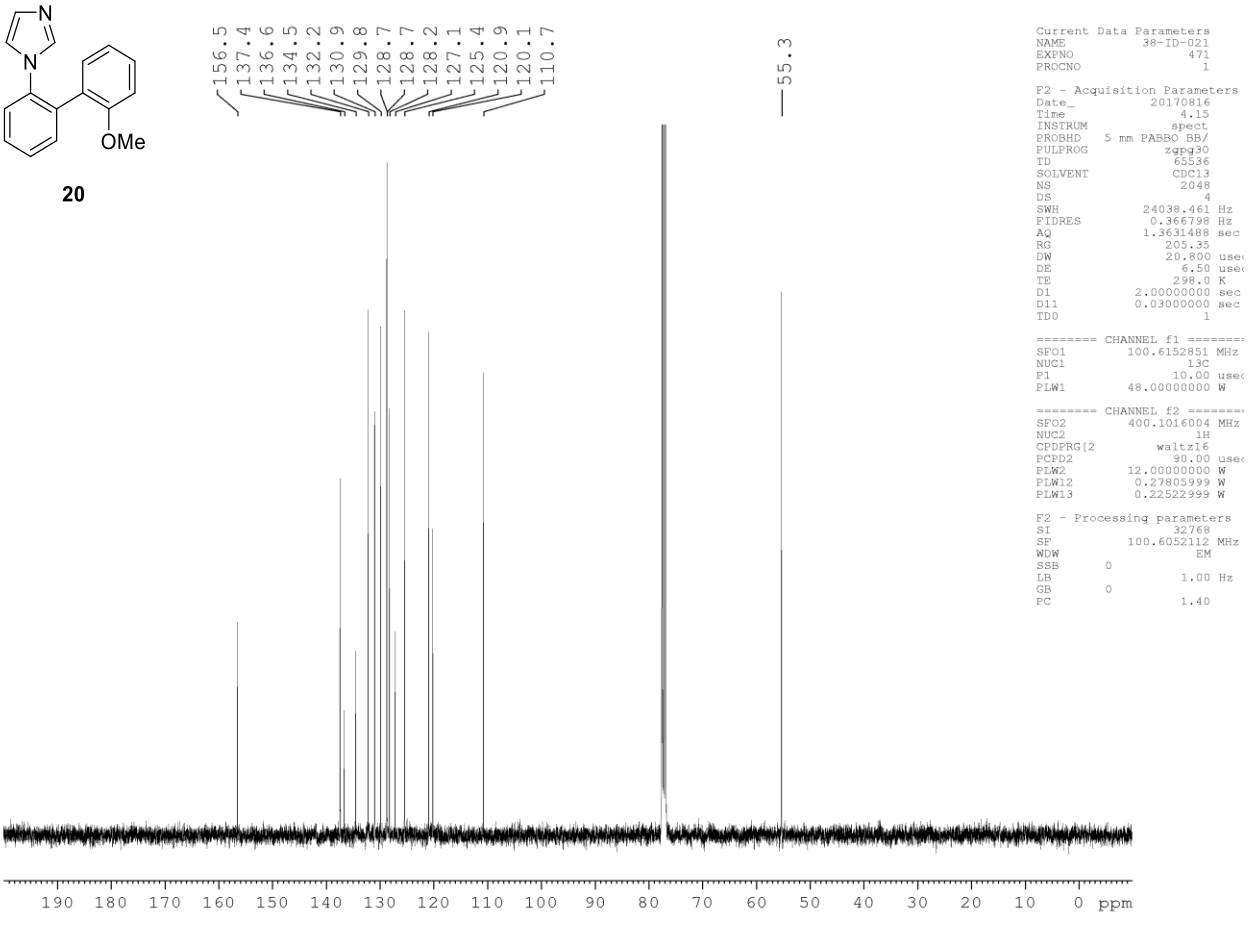
3.06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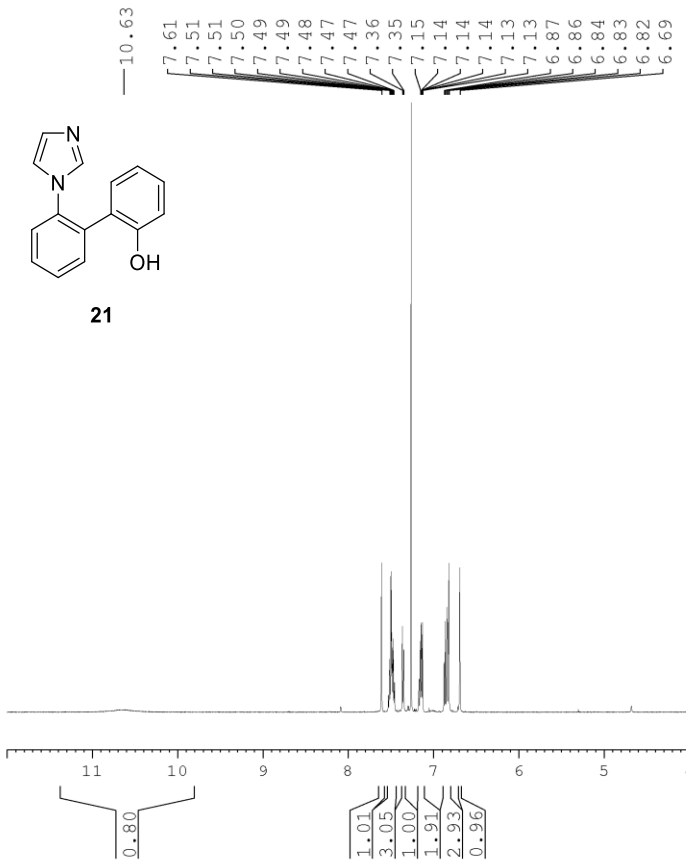
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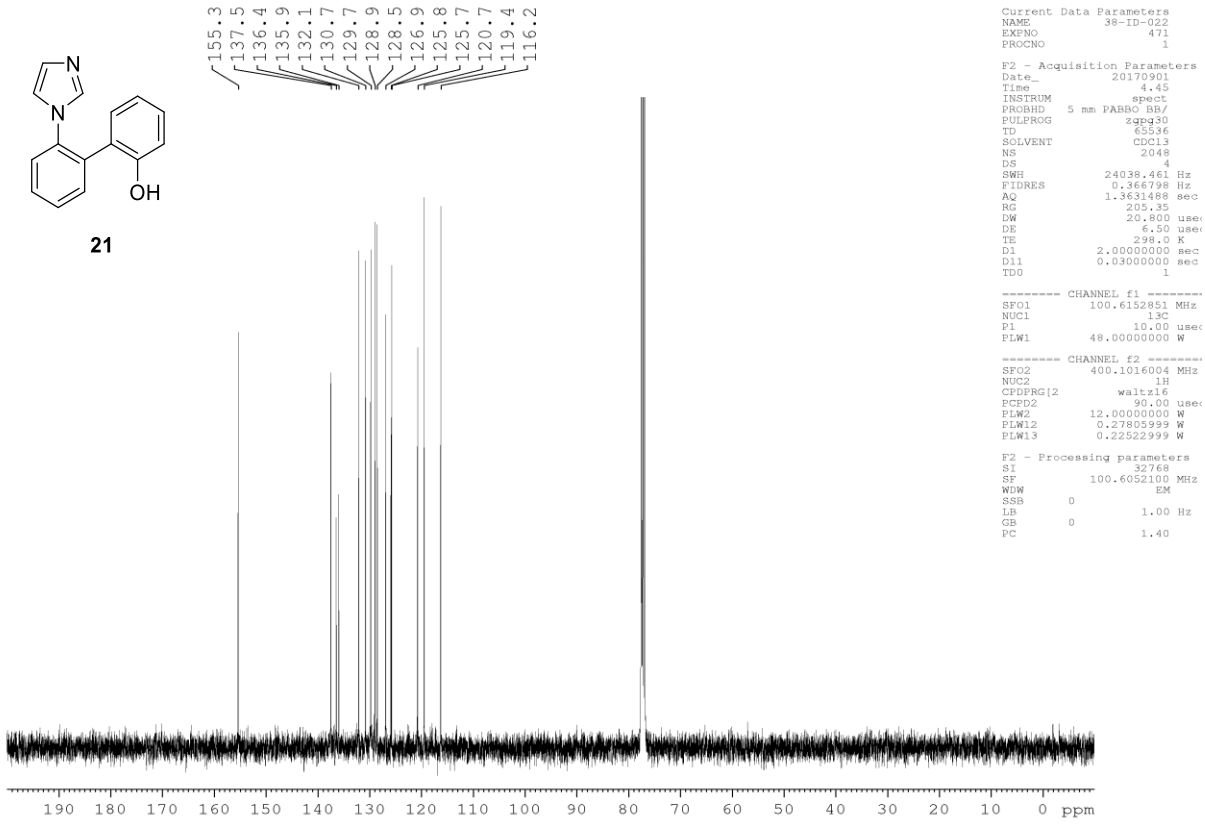
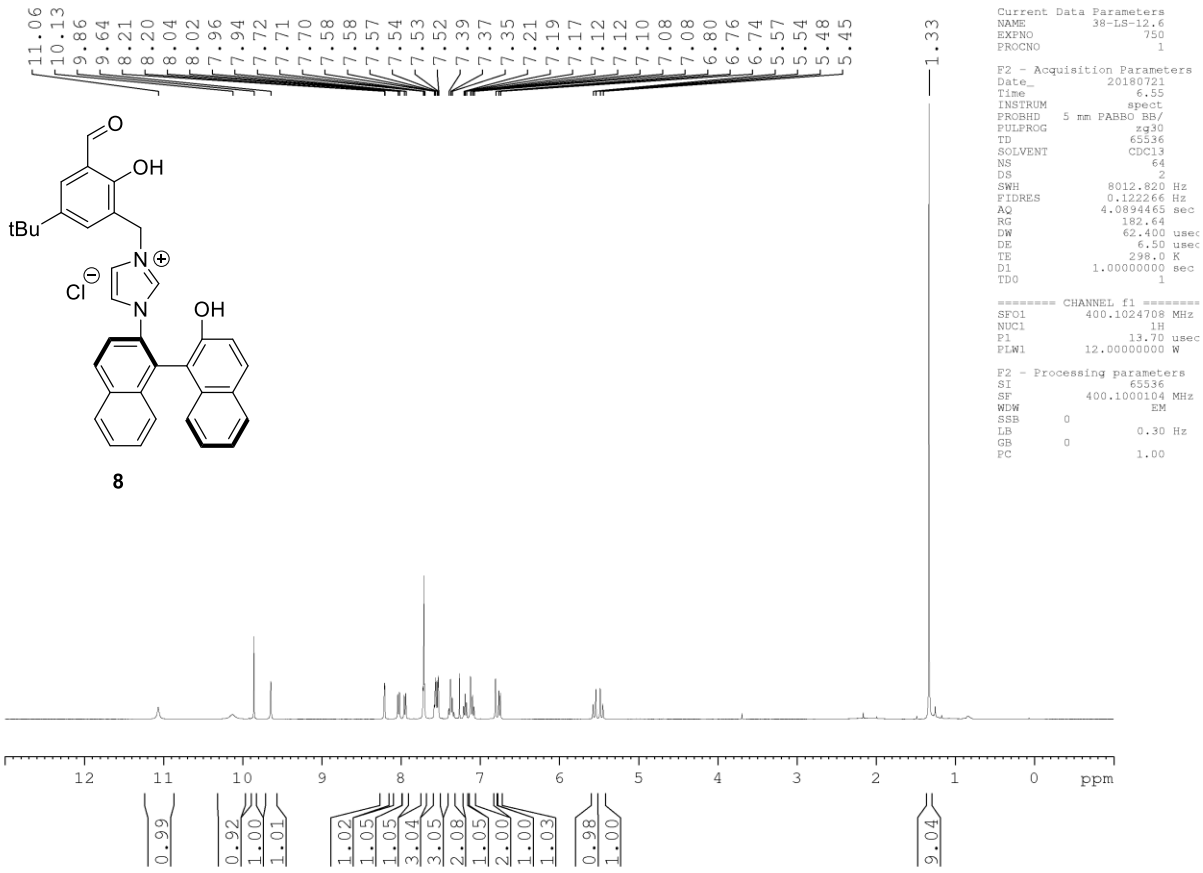
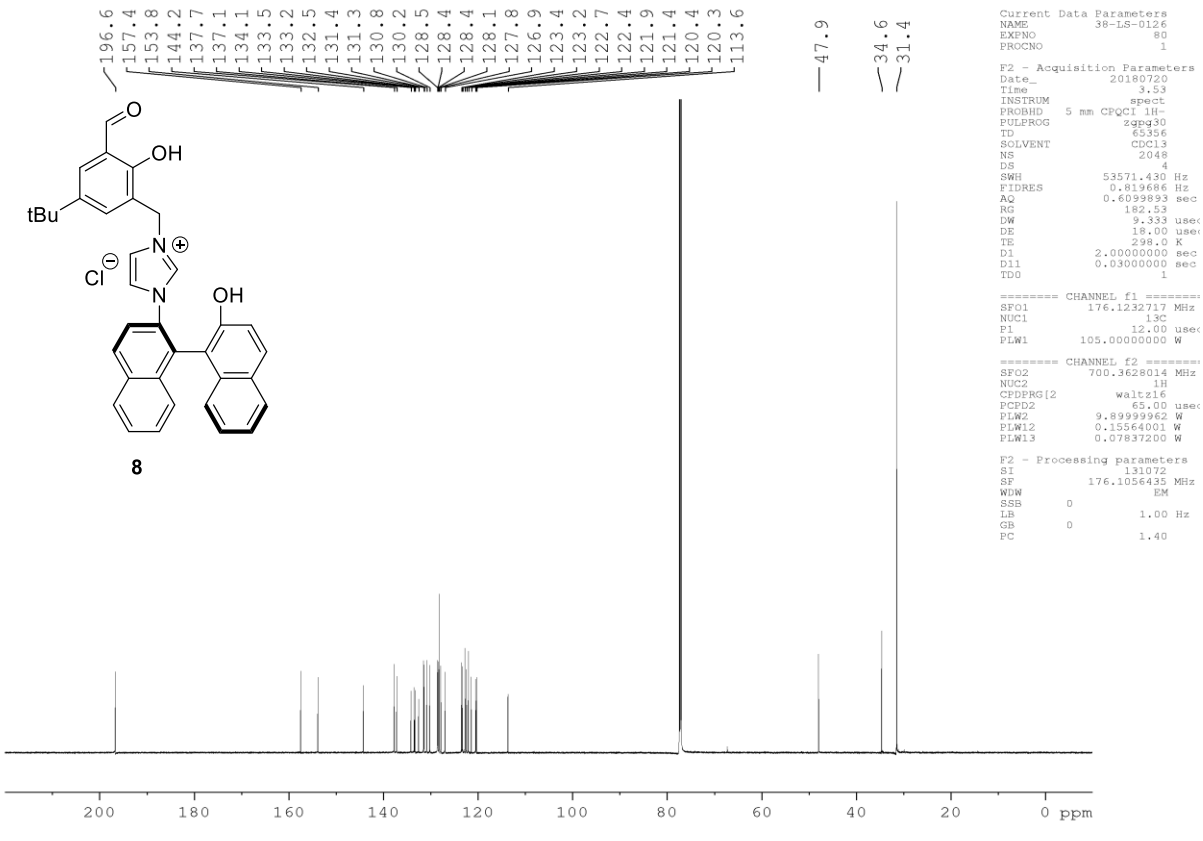
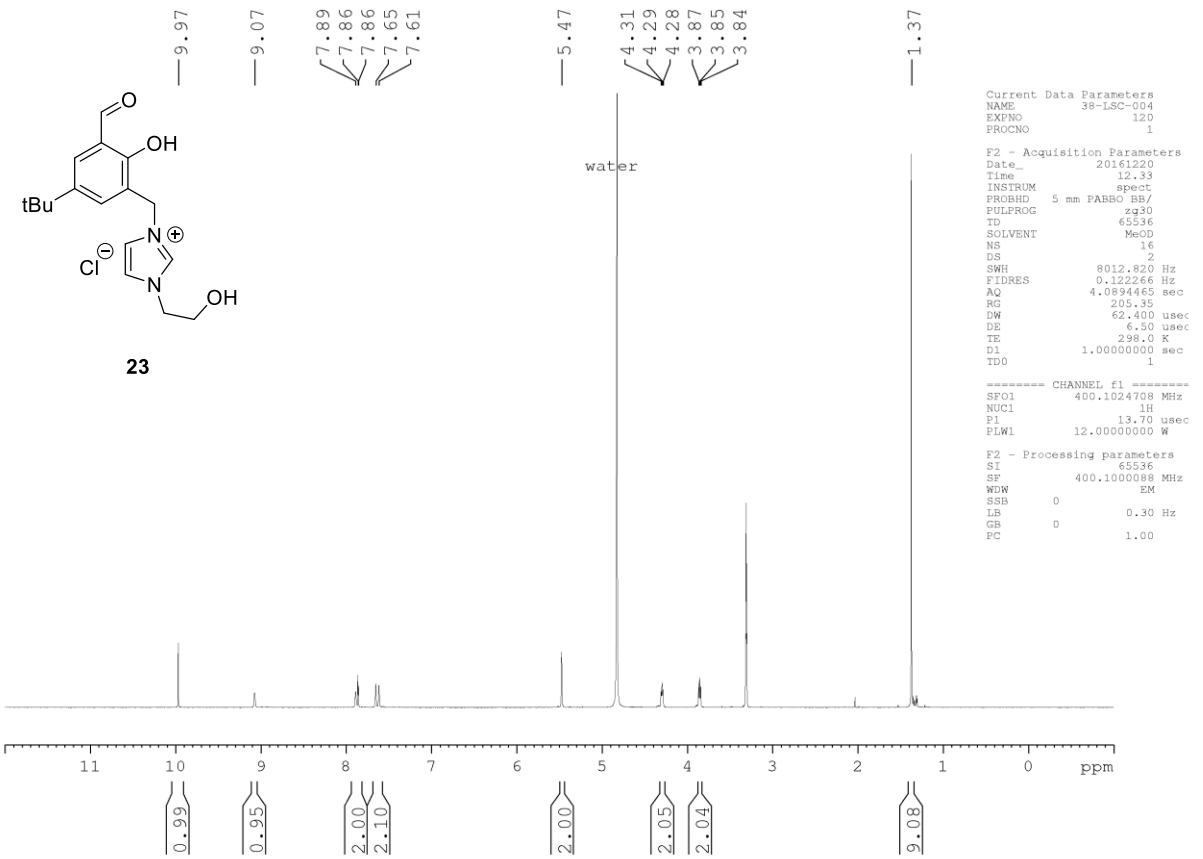
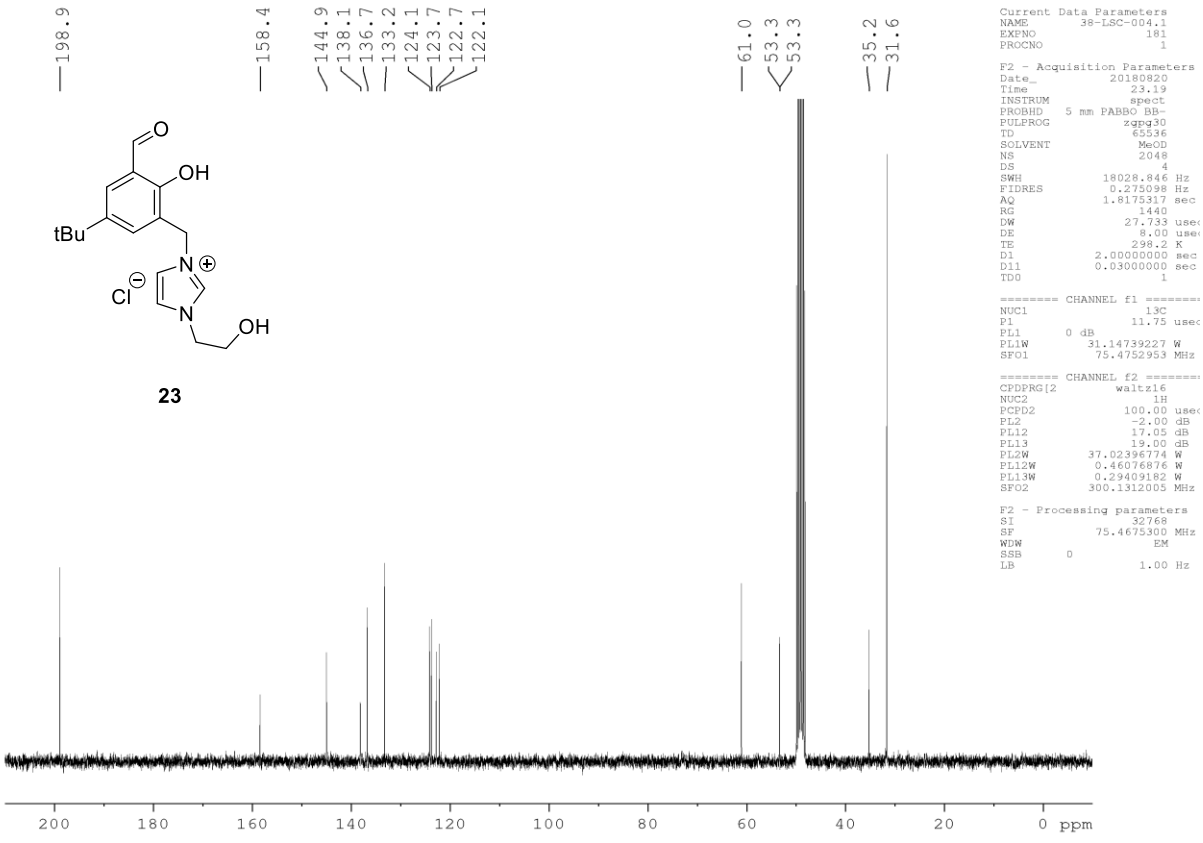
NS 32
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5859712 sec
RG 724
DW 48.400 usec
DE 10.00 usec
TE 296.8 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.23 usec
PL1 1.00 dB
PL1W 19.75309753 W
SFO1 500.1560886 MHz
F2 - Processing parameters
SI 16384
SF 500.1530154 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.80
1.01
3.05
1.00
1.91
2.93
0.96

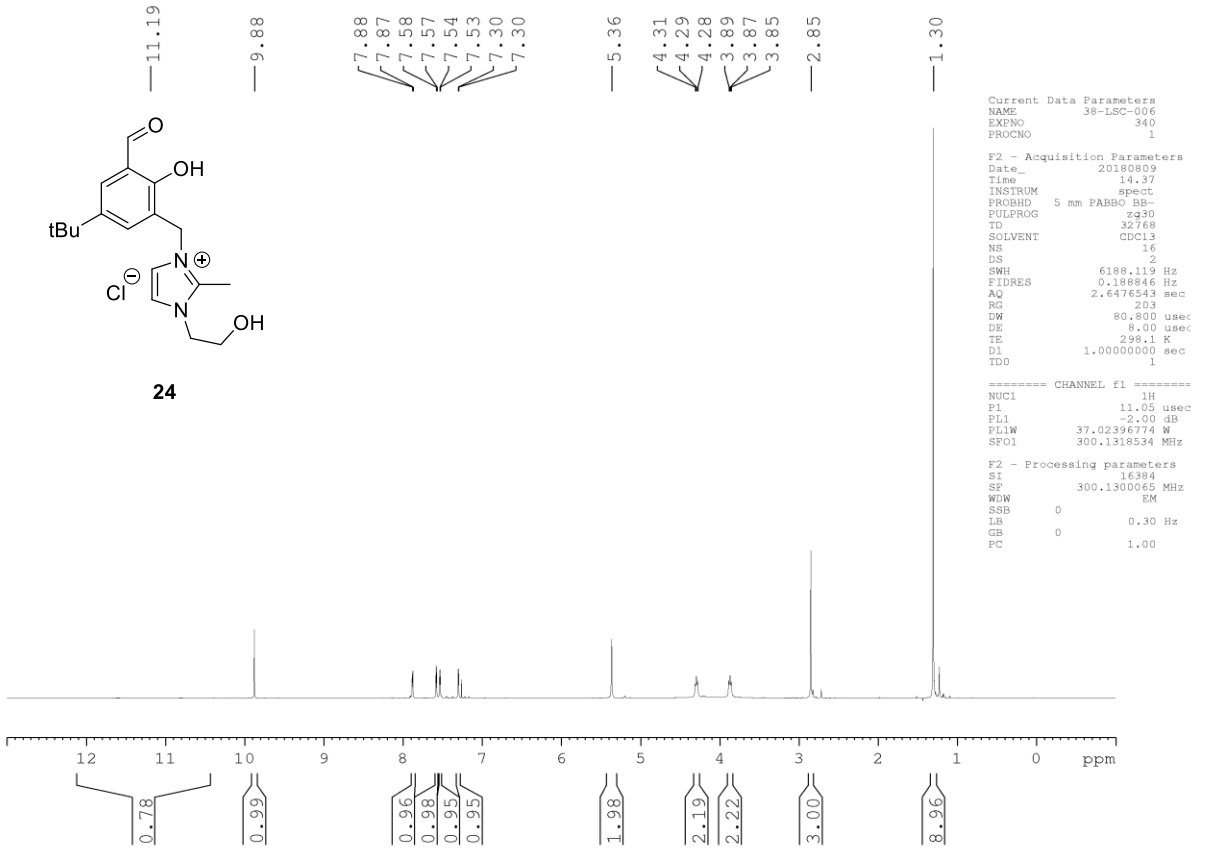

155.3
137.5
136.4
135.9
132.1
130.7
129.7
128.9
128.5
126.9
125.8
125.7
120.7
119.4
116.2
N
N
OH
21
Current Data Parameters
NAME 38-ID-022
EXPNO 471
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170901
Time 4.45
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 205.35
DW 20.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6152851 MHz
NUC1 13C
P1 10.00 usec
PLW1 48.00000000 W
======== CHANNEL f2 ========
SFO2 400.1016004 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 12.00000000 W
PLW12 0.27805999 W
PLW13 0.22522999 W
F2 - Processing parameters
SI 32768
SF 100.6052100 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


11.06
10.13
9.86
9.64
8.21
8.20
8.04
8.02
7.96
7.94
7.72
7.71
7.70
7.58
7.58
7.57
7.54
7.53
7.52
7.39
7.37
7.35
7.21
7.19
7.17
7.12
7.12
7.10
7.08
7.08
6.80
6.76
6.74
5.57
5.54
5.48
5.45
1.33
O
OH
tBu
N
Cl
N
OH
8
Current Data Parameters
NAME 38-LS-12.6
EXPNO 750
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180721
Time 6.55
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 182.64
DW 62.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1024708 MHz
NUC1 1H
P1 13.70 usec
PLW1 12.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1000104 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.99 0.92 1.00 1.01 1.02 1.05 1.05 3.04 3.05 2.08 1.05 2.00 1.00 1.03 0.98 1.00 9.04

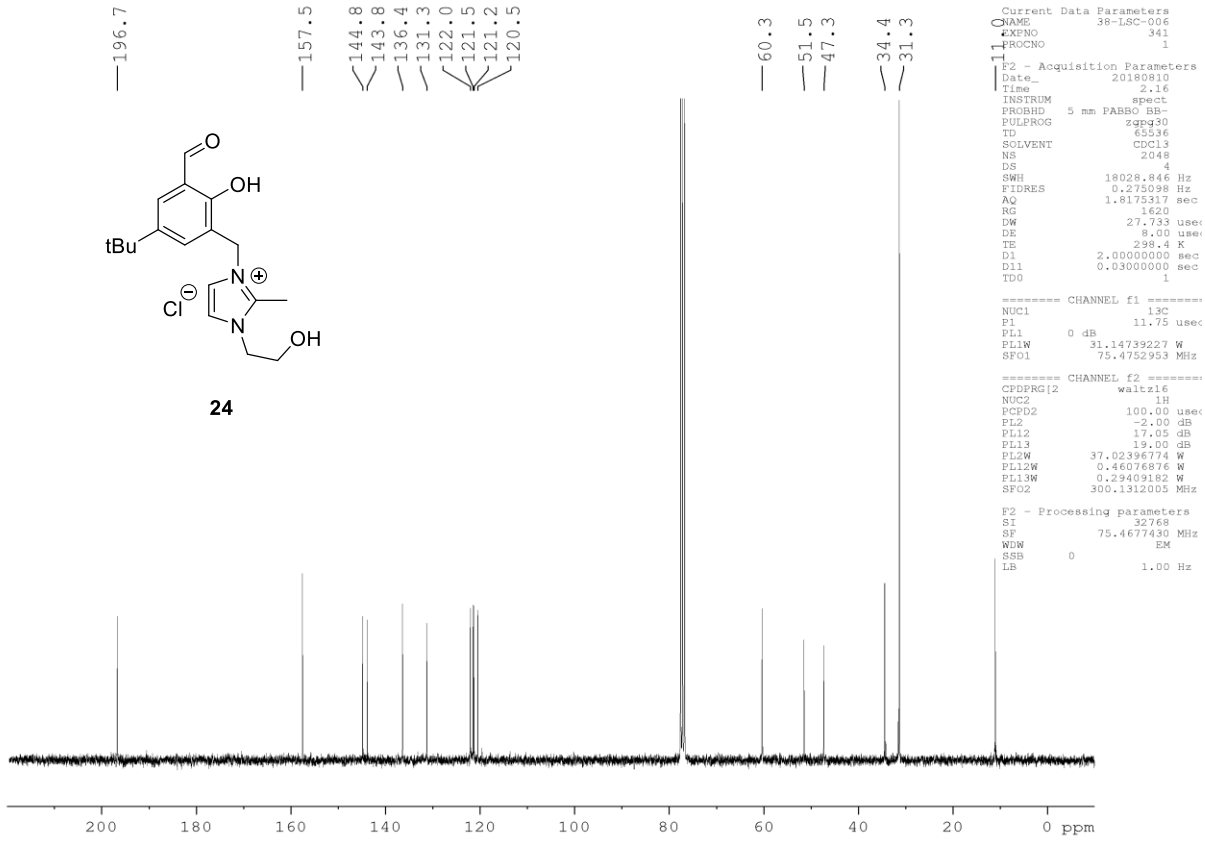

196.6
157.4
153.8
144.2
137.7
137.1
134.1
133.5
133.2
132.5
131.4
131.3
130.8
130.2
128.5
128.4
128.4
128.1
127.8
126.9
123.4
123.2
122.7
122.4
121.9
121.4
120.4
120.3
113.6
47.9
34.6
31.4
O
OH
tBu
N
Cl
N
OH
8
Current Data Parameters
NAME 38-LS-0126
EXPNO 80
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180720
Time 3.53
INSTRUM spect
PROBHD 5 mm CPQCI 1H-
PULPROG zgpg30
TD 65356
SOLVENT CDCl3
NS 2048
DS 4
SWH 53571.430 Hz
FIDRES 0.819686 Hz
AQ 0.6099893 sec
RG 182.53
DW 9.333 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 176.1232717 MHz
NUC1 13C
P1 12.00 usec
PLW1 105.00000000 W
======== CHANNEL f2 ========
SFO2 700.3628014 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 65.00 usec
PLW2 9.89999962 W
PLW12 0.15564001 W
PLW13 0.07837200 W
F2 - Processing parameters
SI 131072
SF 176.1056435 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm


9.97
9.07
7.89
7.86
7.86
7.65
7.61
5.47
4.31
4.29
4.28
3.87
3.85
3.84
1.37
water
O
OH
tBu
N
Cl
N
OH
23
Current Data Parameters
NAME 38-LSC-004
EXPNO 120
PROCNO 1
F2 - Acquisition Parameters
Date_ 20161220
Time 12.33
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 205.35
DW 62.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1024708 MHz
NUC1 1H
P1 13.70 usec
PLW1 12.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1000088 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.99
0.95
2.00
2.10
2.00
2.05
2.04
9.08

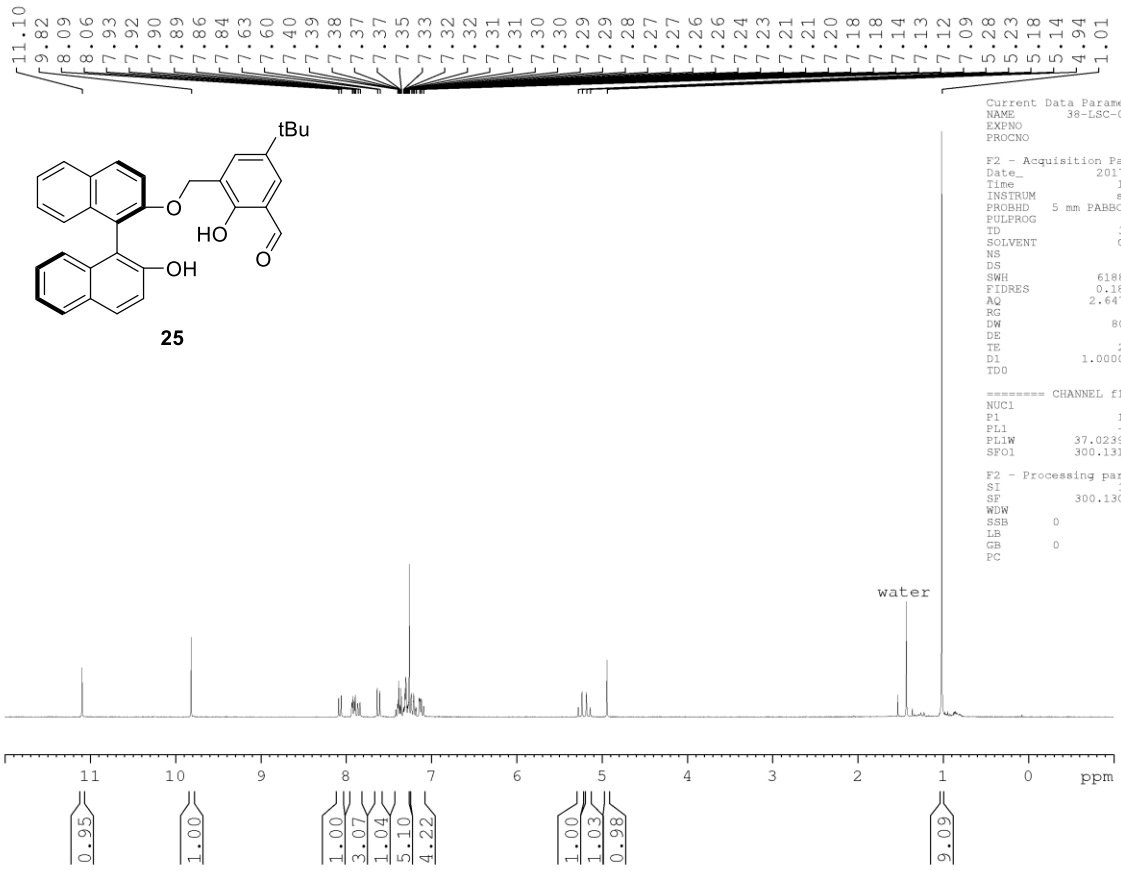

198.9
158.4
144.9
138.1
136.7
133.2
124.1
123.7
122.7
122.1
61.0
53.3
53.3
35.2
31.6
O
OH
tBu
N
Cl
N
OH
23
Current Data Parameters
NAME 38-LSC-004.1
EXPNO 181
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180820
Time 23.19
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 2048
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 1440
DW 27.733 usec
DE 8.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.75 usec
PL1 0 dB
PL1W 31.14739227 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -2.00 dB
PL12 17.05 dB
PL13 19.00 dB
PL2W 37.02396774 W
PL12W 0.46076876 W
PL13W 0.29409182 W
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4675300 MHz
WDW EM
SSB 0
LB 1.00 Hz
200
180
160
140
120
100
80
60
40
20
0 ppm

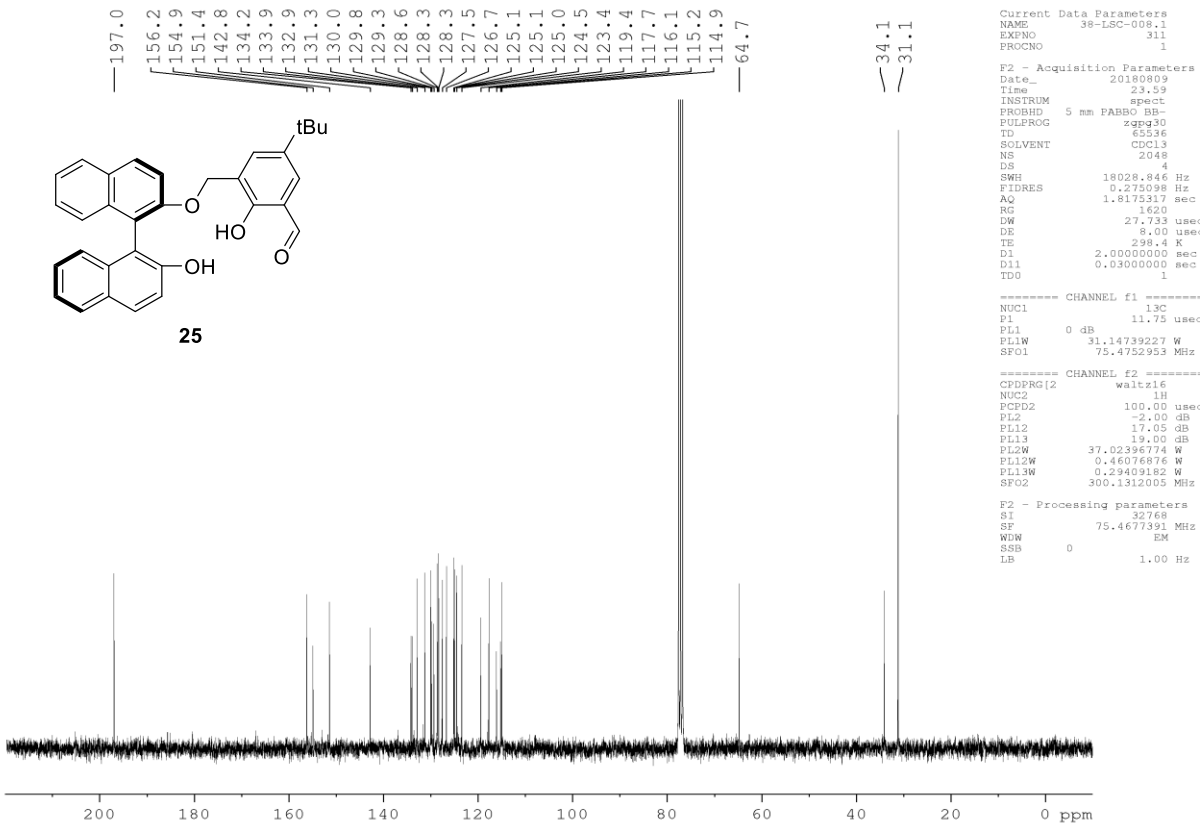

11.19
9.88
7.88
7.87
7.58
7.57
7.54
7.53
7.30
7.30
5.36
4.31
4.29
4.28
3.89
3.87
3.85
2.85
1.30
O
OH
tBu
N
Cl
N
OH
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.78
0.99
0.96
0.98
0.95
0.95
1.98
2.19
2.22
3.00
8.96

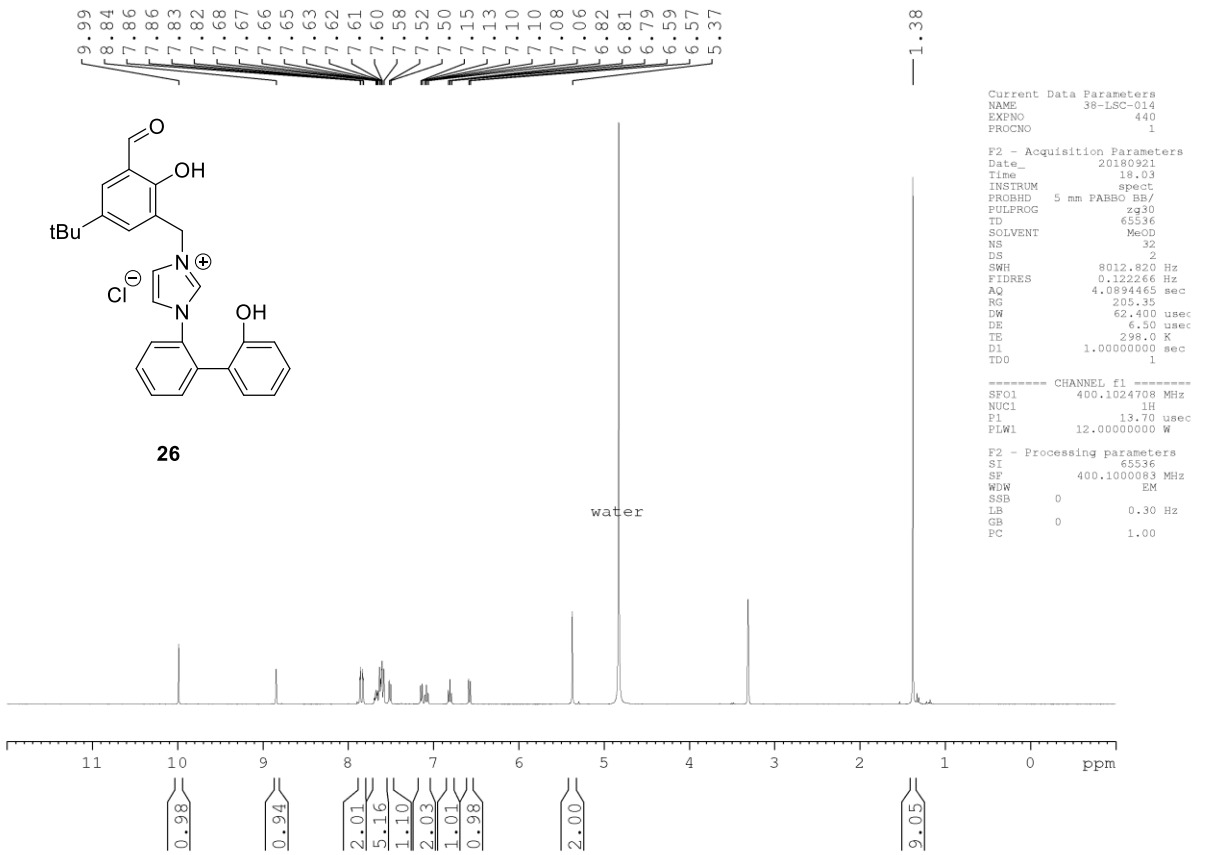
24


196.7
157.5
144.8
143.8
136.4
131.3
122.0
121.5
121.2
120.5
60.3
51.5
47.3
34.4
31.3
O
OH
tBu
N
Cl
N
OH
200
180
160
140
120
100
80
60
40
20
0 ppm

24


11.10
9.82
8.09
8.06
7.93
7.92
7.90
7.89
7.86
7.84
7.63
7.60
7.40
7.39
7.38
7.37
7.37
7.35
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.27
7.27
7.26
7.26
7.24
7.23
7.21
7.21
7.20
7.18
7.18
7.14
7.13
7.12
7.09
5.28
5.23
5.18
5.14
4.94
1.01
tBu
O
HO
O
OH
25
Current Data Parameters
NAME 38-LSC-008.1
EXPNO 440
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170428
Time 14.31
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 456
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
water
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.95
1.00
1.00
3.07
1.04
5.10
4.22
1.00
1.03
0.98
9.09


197.0
156.2
154.9
151.4
142.8
134.2
133.9
132.9
131.3
130.0
129.8
129.3
128.6
128.3
128.3
127.5
126.7
125.1
125.1
125.0
124.5
123.4
119.4
117.7
116.1
115.2
114.9
64.7
34.1
31.1
tBu
O
HO
O
OH
25
Current Data Parameters
NAME 38-LSC-008.1
EXPNO 311
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180809
Time 23.59
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 1620
DW 27.733 usec
DE 8.00 usec
TE 298.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.75 usec
PL1 0 dB
PL1W 91.14739227 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -2.00 dB
PL12 17.05 dB
PL13 19.00 dB
PL2W 37.02396774 W
PL12W 0.46076876 W
PL13W 0.29409182 W
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677391 MHz
WDW EM
SSB 0
LB 1.00 Hz
200
180
160
140
120
100
80
60
40
20
0 ppm



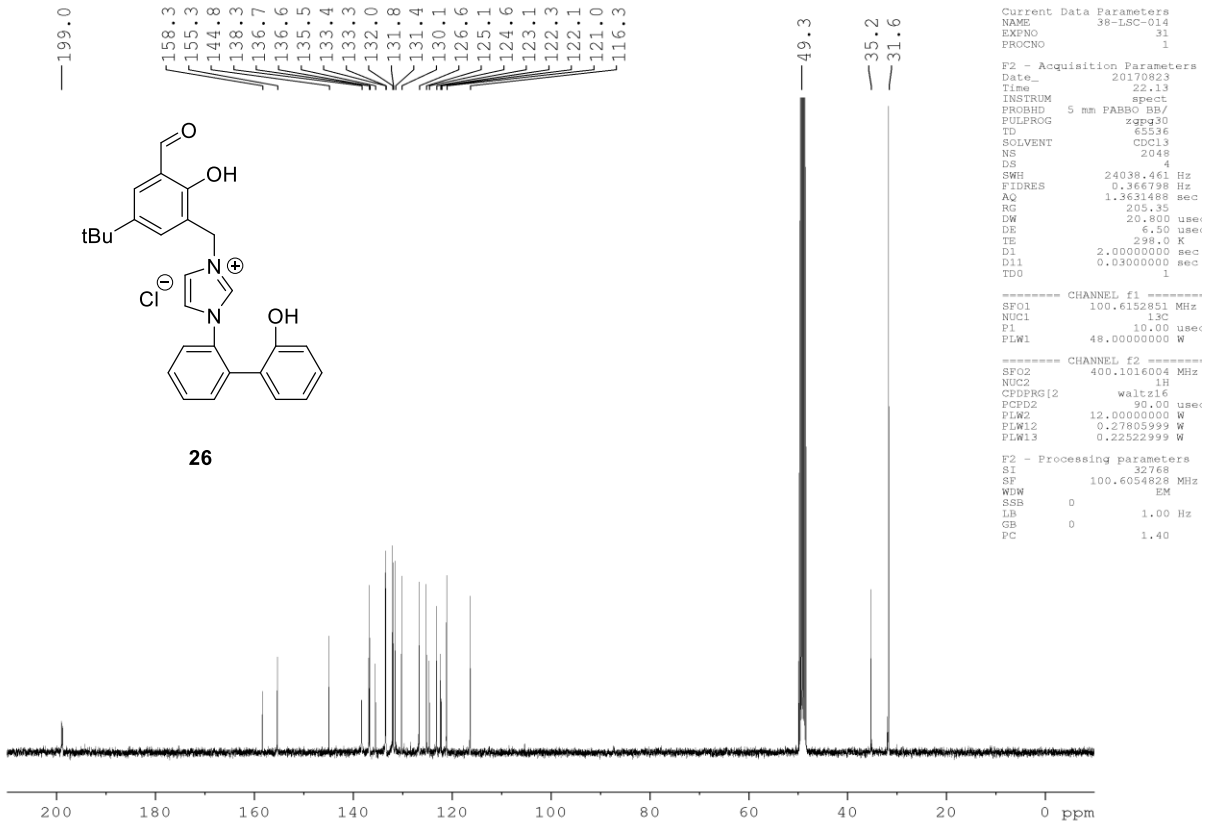
26

Current Data Parameters
NAME 38-LSC-014
EXPNO 440
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180921
Time 18.03
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 32
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 205.35
DW 62.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1024708 MHz
NUC1 1H
P1 13.70 usec
PLW1 12.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1000083 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



26

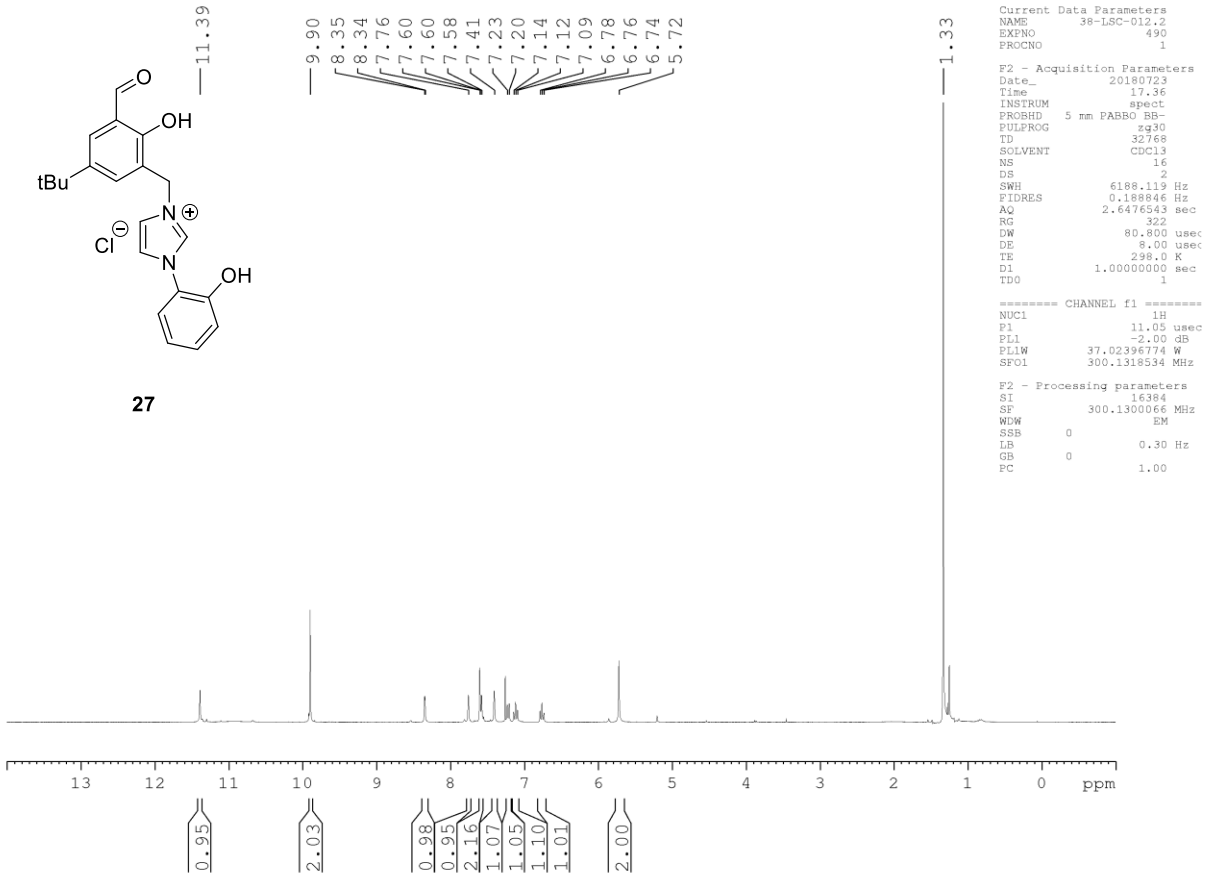
Current Data Parameters
NAME 38-LSC-014
EXPNO 31
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170823
Time 22.13
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 205.35
DW 20.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 100.6152851 MHz
NUC1 13C
P1 10.00 usec
PLW1 48.00000000 W

======== CHANNEL f2 ========
SFO2 400.1016004 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 12.00000000 W
PLW12 0.27805999 W
PLW13 0.22522999 W

F2 - Processing parameters
SI 32768
SF 100.6054828 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



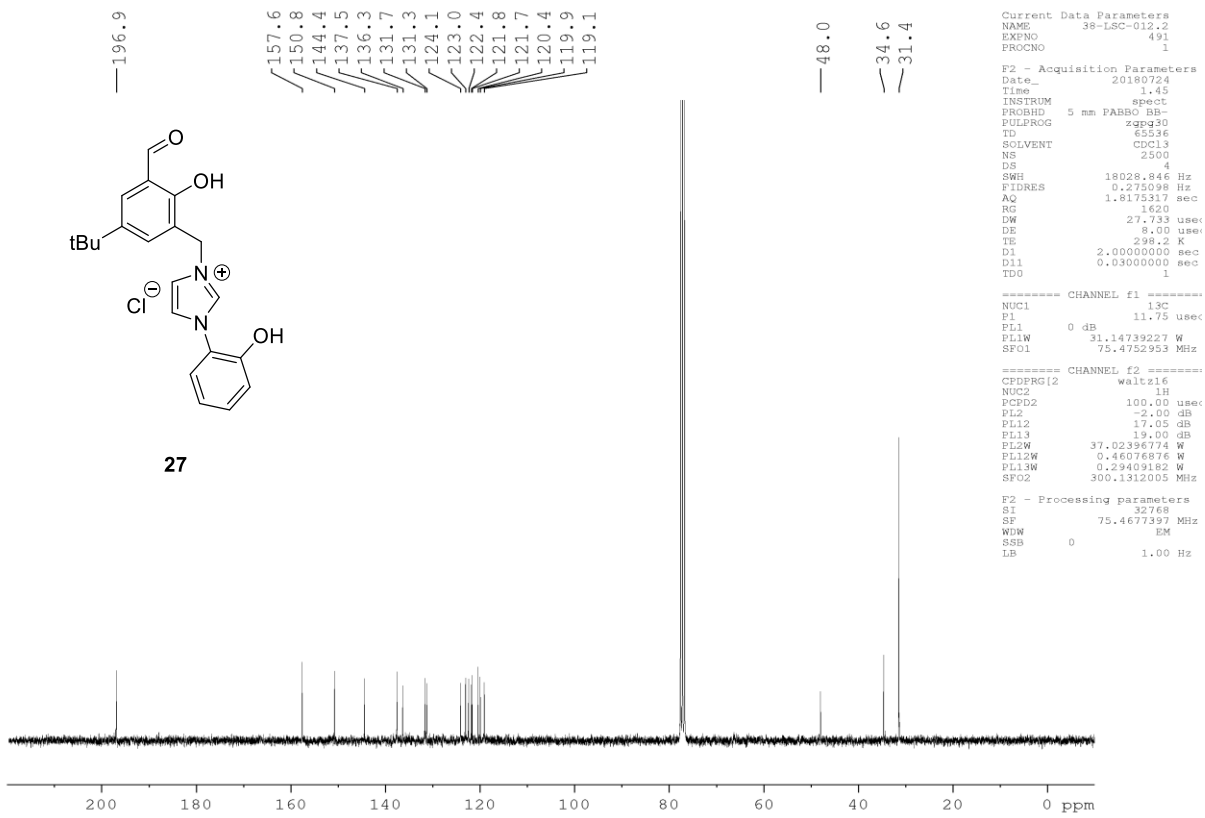
27

```
Current Data Parameters
NAME                 38-LSC-012.2
EXPNO                         490
PROCNO                          1

F2 - Acquisition Parameters
Date_               20180723
Time                      17.36
INSTRUM                   spect
PROBHD    5 mm PABBO BB-
PULPROG                   zg30
TD                       32768
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                 6188.119 Hz
FIDRES              0.188846 Hz
AQ                  2.6476543 sec
RG                         322
DW                    80.800 usec
DE                     8.00 usec
TE                     298.0 K
D1                 1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                      11.05 usec
PL1                     -2.00 dB
PL1W               37.02396774 W
SFO1               300.1318534 MHz

F2 - Processing parameters
SI                       16384
SF                 300.1300066 MHz
WDW                         EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```



27

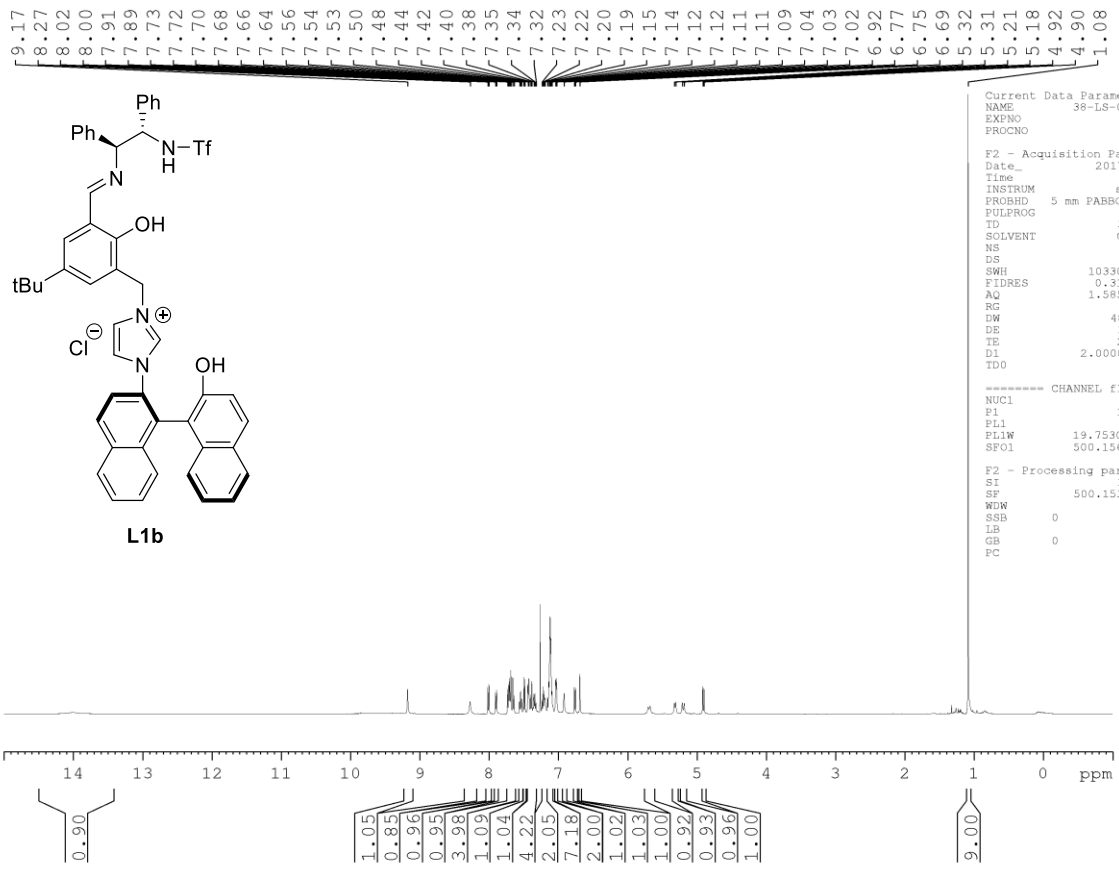
```
Current Data Parameters
NAME                 38-LSC-012.2
EXPNO                         491
PROCNO                          1

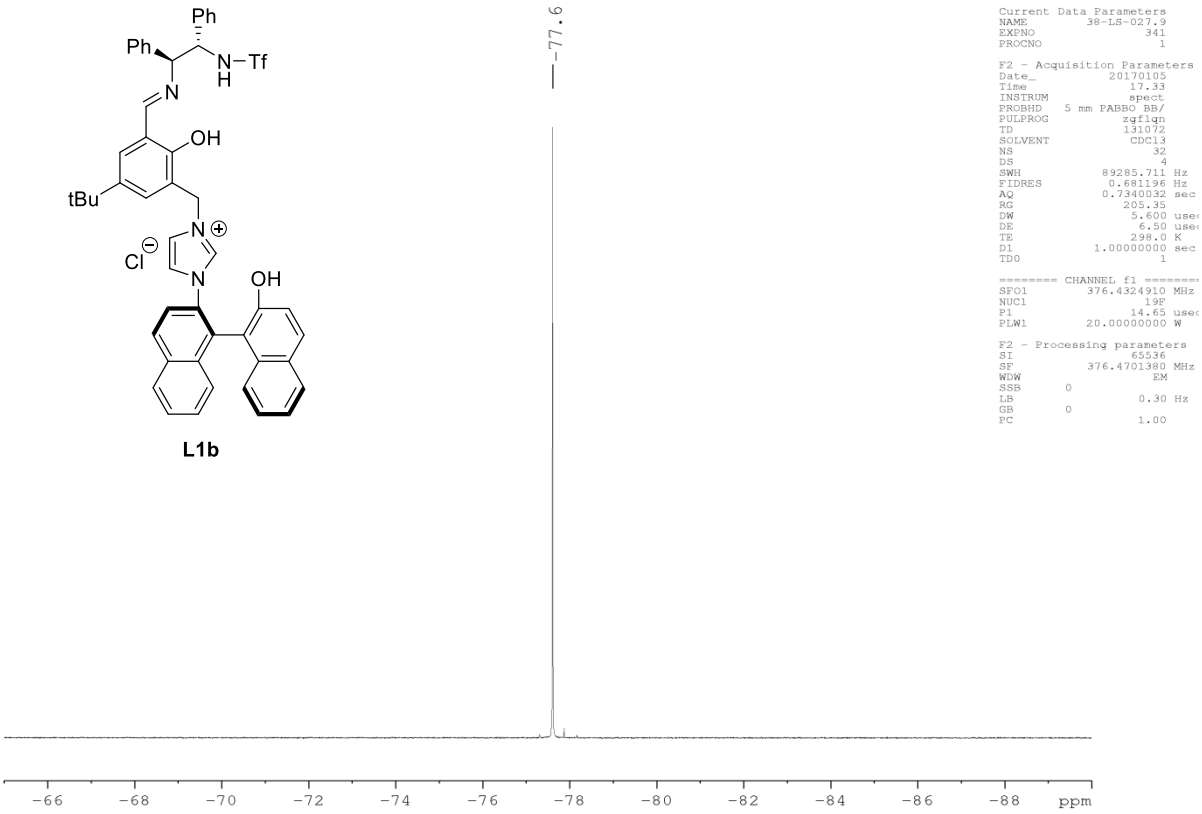
F2 - Acquisition Parameters
Date_               20180724
Time                       1.45
INSTRUM                   spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        2500
DS                           4
SWH                18028.846 Hz
FIDRES              0.275098 Hz
AQ                  1.8175317 sec
RG                        1620
DW                    27.733 usec
DE                     8.00 usec
TE                     298.2 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                          1

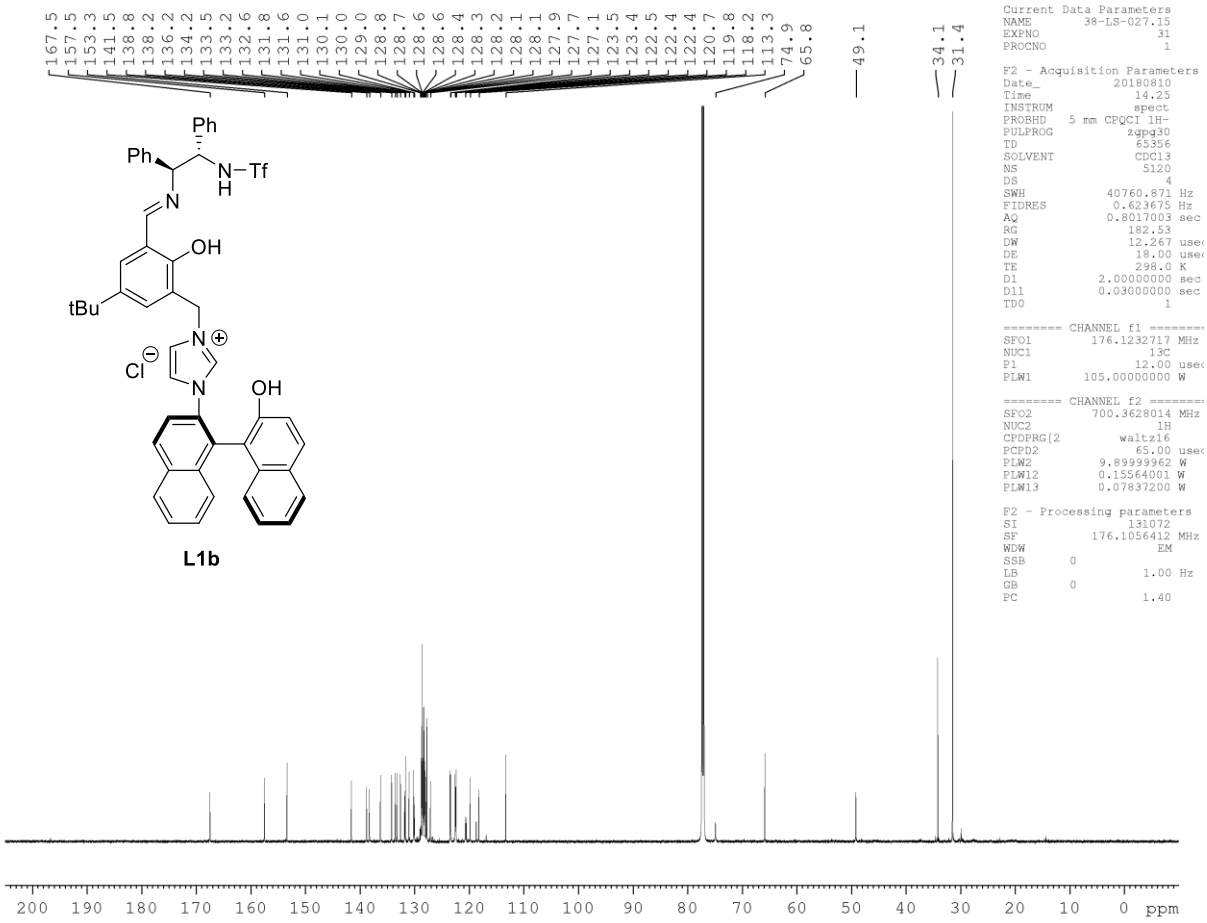
======== CHANNEL f1 ========
NUC1                       13C
P1                      11.75 usec
PL1          0 dB
PL1W               31.14739227 W
SFO1               75.4752953 MHz

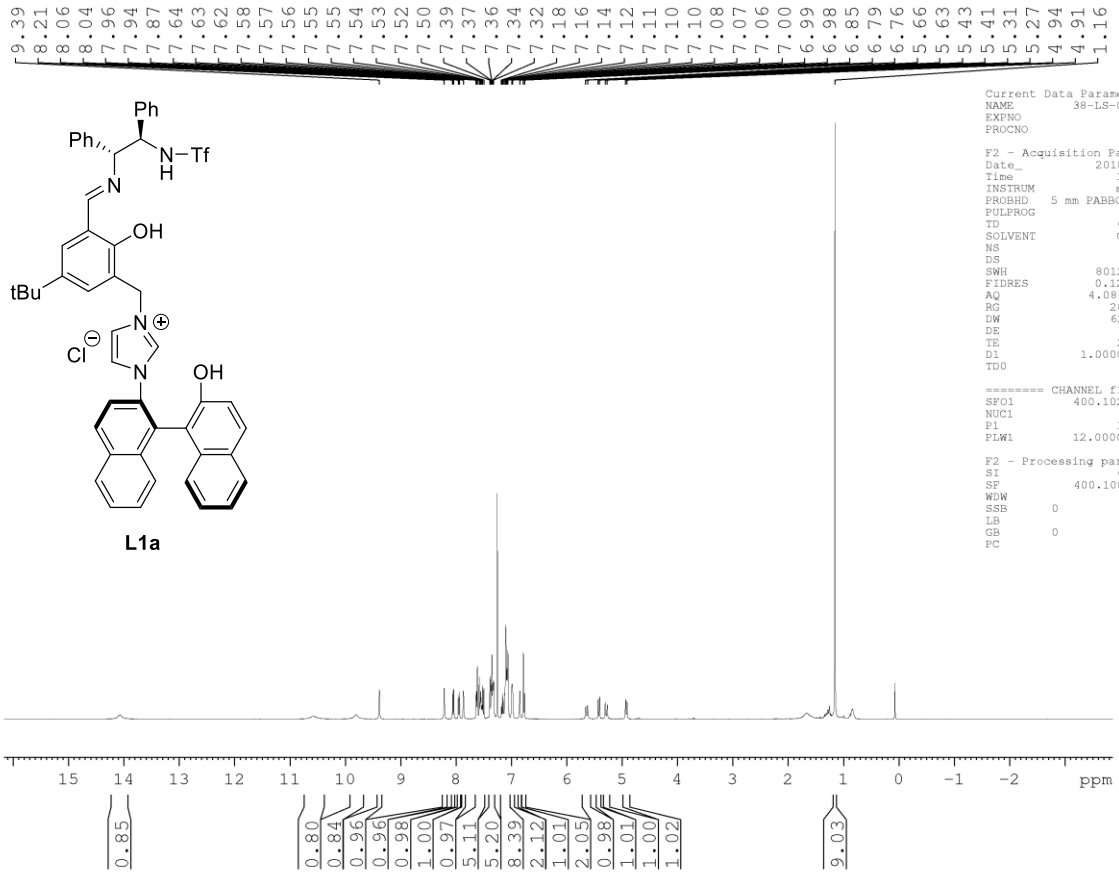
======== CHANNEL f2 ========
CPDPRG[2                waltz16
NUC2                        1H
PCPD2                  100.00 usec
PL2                     -2.00 dB
PL12                    17.05 dB
PL13                    19.00 dB
PL2W               37.02396774 W
PL12W               0.46076876 W
PL13W               0.29409182 W
SFO2               300.1312005 MHz

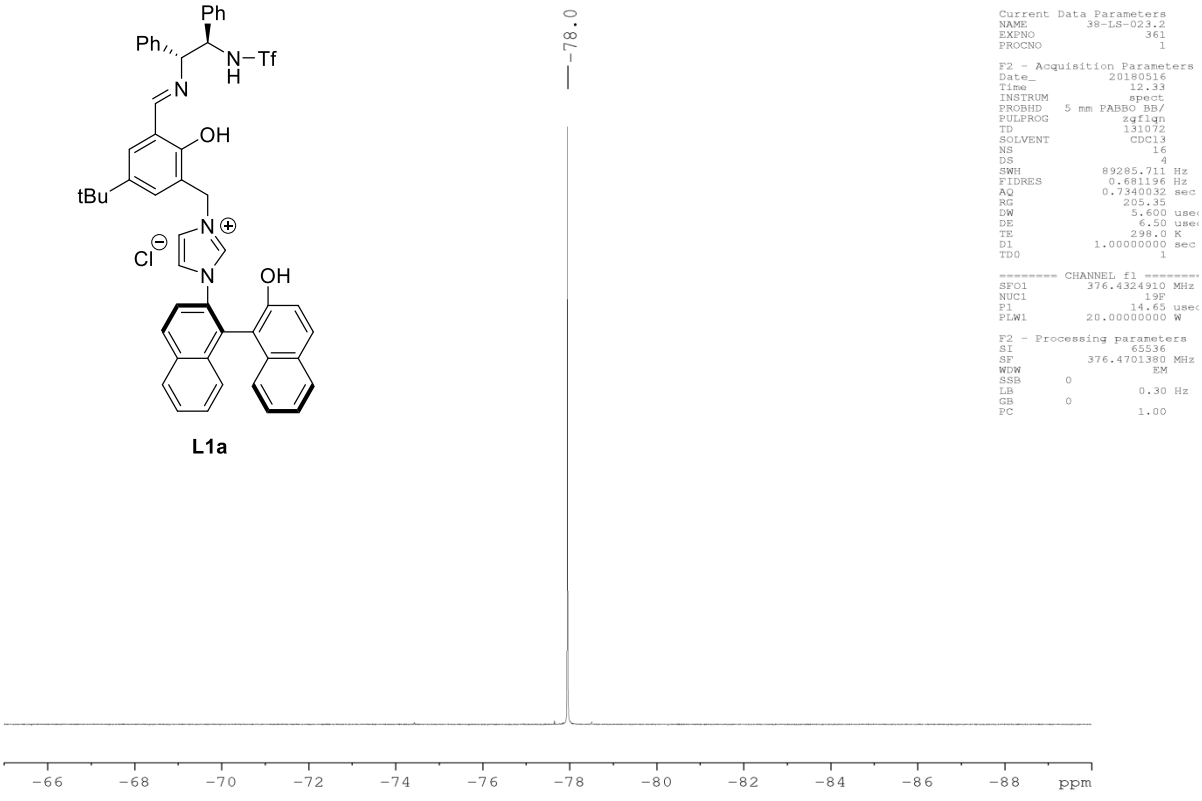
F2 - Processing parameters
SI                       32768
SF                 75.4677397 MHz
WDW                         EM
SSB          0
LB                      1.00 Hz
```

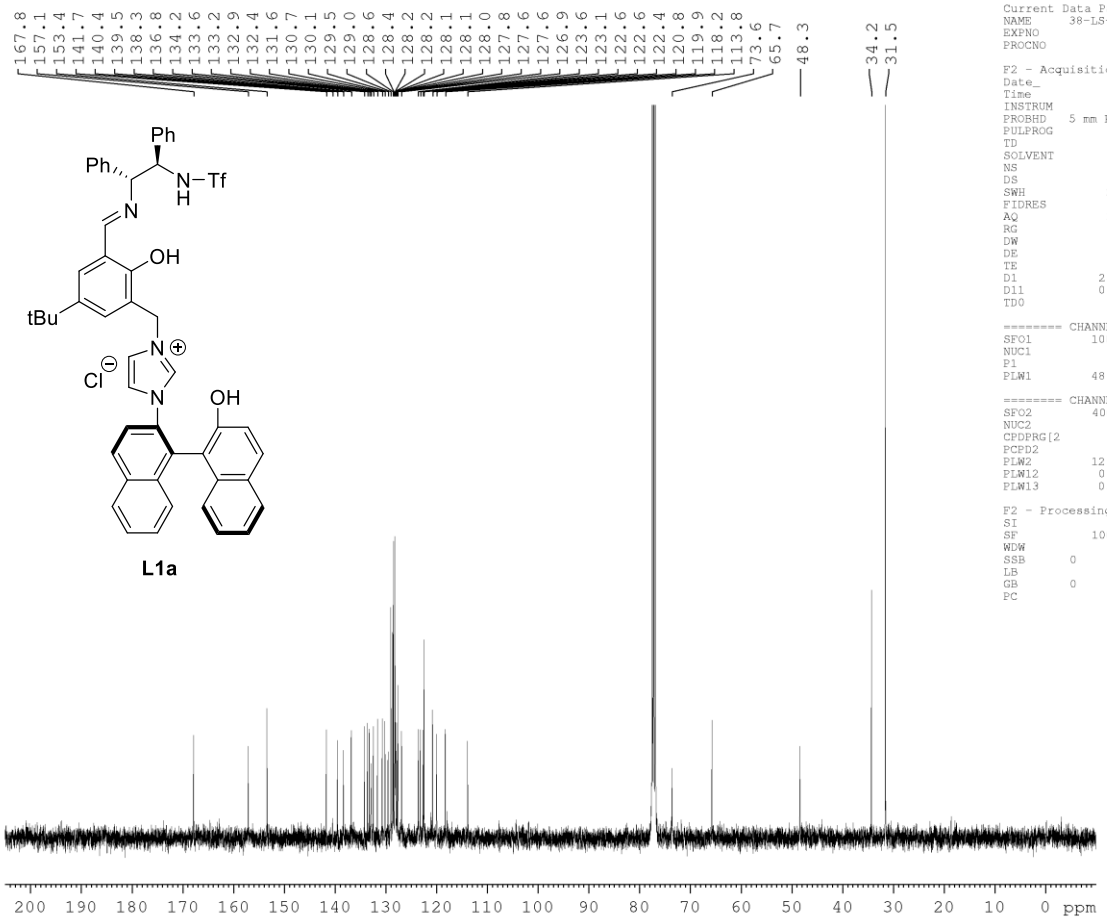

9.17 8.27 8.02 8.00 7.91 7.89 7.73 7.72 7.70 7.68 7.66 7.64 7.56 7.54 7.53 7.50 7.48 7.44 7.42 7.40 7.38 7.35 7.34 7.32 7.23 7.22 7.20 7.19 7.15 7.14 7.12 7.12 7.11 7.11 7.09 7.04 7.03 7.02 6.92 6.77 6.75 6.69 5.32 5.31 5.21 5.18 4.92 4.90 1.08
Ph
Ph
N–Tf
H
N
OH
tBu
N⊕
Cl⊖
N
OH
L1b
Current Data Parameters
NAME 38-LS-027.9
EXPNO 70
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170110
Time 0.37
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5859712 sec
RG 362
DW 48.400 usec
DE 10.00 usec
TE 296.8 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.23 usec
PL1 1.00 dB
PL1W 19.75309753 W
SFO1 500.1560886 MHz
F2 - Processing parameters
SI 16384
SF 500.1530155 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.90
1.05 0.85 0.96 0.95 3.98 1.09 1.04 4.22 2.05 7.18 2.00 1.02 1.03 1.00 0.92 0.93 0.96 1.00
9.00


−77.6
Ph
Ph
N–Tf
H
N
OH
tBu
N⊕
Cl⊖
N
OH
L1b
Current Data Parameters
NAME 38-LS-027.9
EXPNO 341
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170105
Time 17.33
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgflqn
TD 131072
SOLVENT CDCl3
NS 32
DS 4
SWH 89285.711 Hz
FIDRES 0.681196 Hz
AQ 0.7340032 sec
RG 205.35
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 376.4324910 MHz
NUC1 19F
P1 14.65 usec
PLW1 20.00000000 W
F2 - Processing parameters
SI 65536
SF 376.4701380 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
−66 −68 −70 −72 −74 −76 −78 −80 −82 −84 −86 −88 ppm


167.5
157.5
153.3
141.5
138.8
138.2
136.2
134.2
133.5
133.2
132.6
131.8
131.6
131.0
130.1
130.0
129.0
128.8
128.7
128.6
128.6
128.4
128.3
128.2
128.1
128.1
127.9
127.7
127.1
123.5
123.4
122.5
122.4
122.4
120.7
119.8
118.2
113.3
74.9
65.8
49.1
34.1
31.4
Ph
Ph
N–Tf
H
N
OH
tBu
N⊕
Cl⊖
N
OH
L1b
Current Data Parameters
NAME 38-LS-027.15
EXPNO 31
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180810
Time 14.25
INSTRUM spect
PROBHD 5 mm CPQCI 1H-
PULPROG zgpg30
TD 65356
SOLVENT CDCl3
NS 5120
DS 4
SWH 40760.871 Hz
FIDRES 0.623675 Hz
AQ 0.8017003 sec
RG 182.53
DW 12.267 use
DE 18.00 use
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 176.1232717 MHz
NUC1 13C
P1 12.00 use
PLW1 105.00000000 W
======== CHANNEL f2 ========
SFO2 700.3628014 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 65.00 use
PLW2 9.89999962 W
PLW12 0.15564001 W
PLW13 0.07837200 W
F2 - Processing parameters
SI 131072
SF 176.1056412 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


9.39 8.21 8.06 8.04 7.96 7.94 7.87 7.64 7.63 7.62 7.58 7.57 7.56 7.55 7.55 7.54 7.53 7.52 7.50 7.39 7.37 7.36 7.34 7.32 7.18 7.16 7.14 7.12 7.11 7.10 7.10 7.08 7.07 7.06 7.00 6.99 6.98 6.85 6.79 6.76 5.66 5.63 5.43 5.41 5.31 5.27 4.94 4.91 1.16
Ph
Ph
N–Tf
H
N
OH
tBu
N
Cl
N
OH
L1a
Current Data Parameters
NAME 38-LS-023.2
EXPNO 360
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180516
Time 12.32
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 205.35
DW 62.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1024708 MHz
NUC1 1H
P1 13.70 usec
PLW1 12.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1000103 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 ppm
0.85 0.80 0.84 0.96 0.96 0.98 1.00 0.97 5.11 5.20 8.39 2.12 1.01 2.05 0.98 1.01 1.00 1.02 9.03


Ph
Ph
N–Tf
H
N
OH
tBu
N
Cl
N
OH
L1a
−78.0
Current Data Parameters
NAME 38-LS-023.2
EXPNO 361
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180516
Time 12.33
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgflqn
TD 131072
SOLVENT CDCl3
NS 16
DS 4
SWH 89285.711 Hz
FIDRES 0.681196 Hz
AQ 0.7340032 sec
RG 205.35
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 376.4324910 MHz
NUC1 19F
P1 14.65 usec
PLW1 20.00000000 W
F2 - Processing parameters
SI 65536
SF 376.4701380 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
−66 −68 −70 −72 −74 −76 −78 −80 −82 −84 −86 −88 ppm



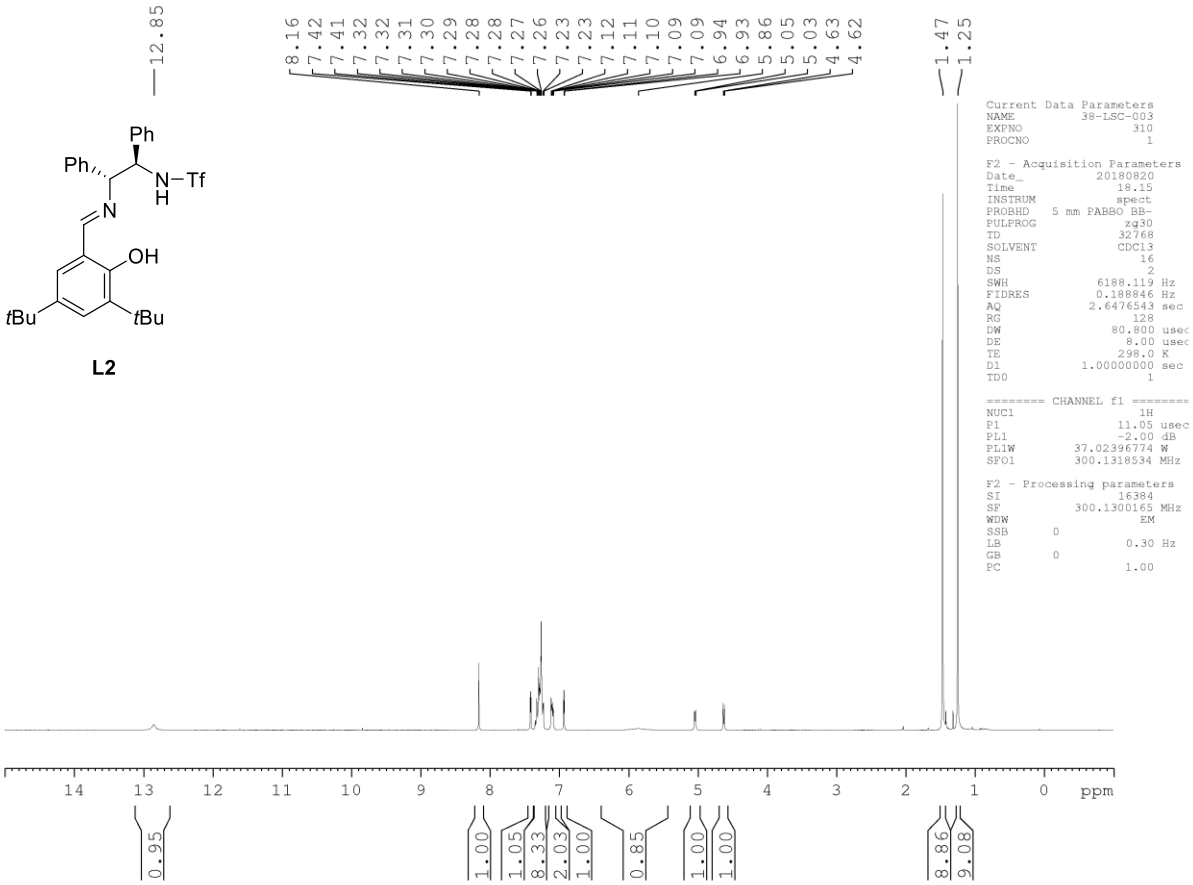

```
Current Data Parameters
NAME      38-LS-023.3_AUg
EXPNO                 314
PROCNO                  1

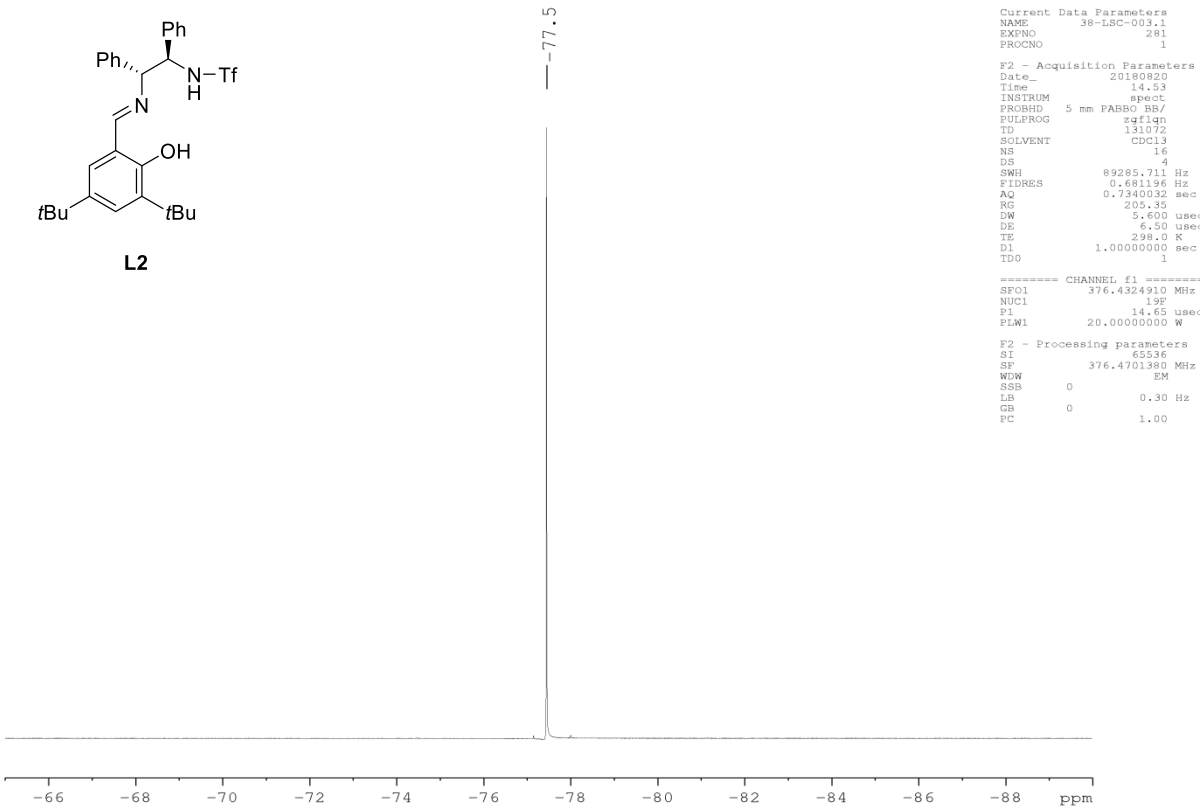
F2 - Acquisition Parameters
Date_           20180823
Time              3.50
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                 2048
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                205.35
DW                20.800 use
DE                 6.50 use
TE               298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

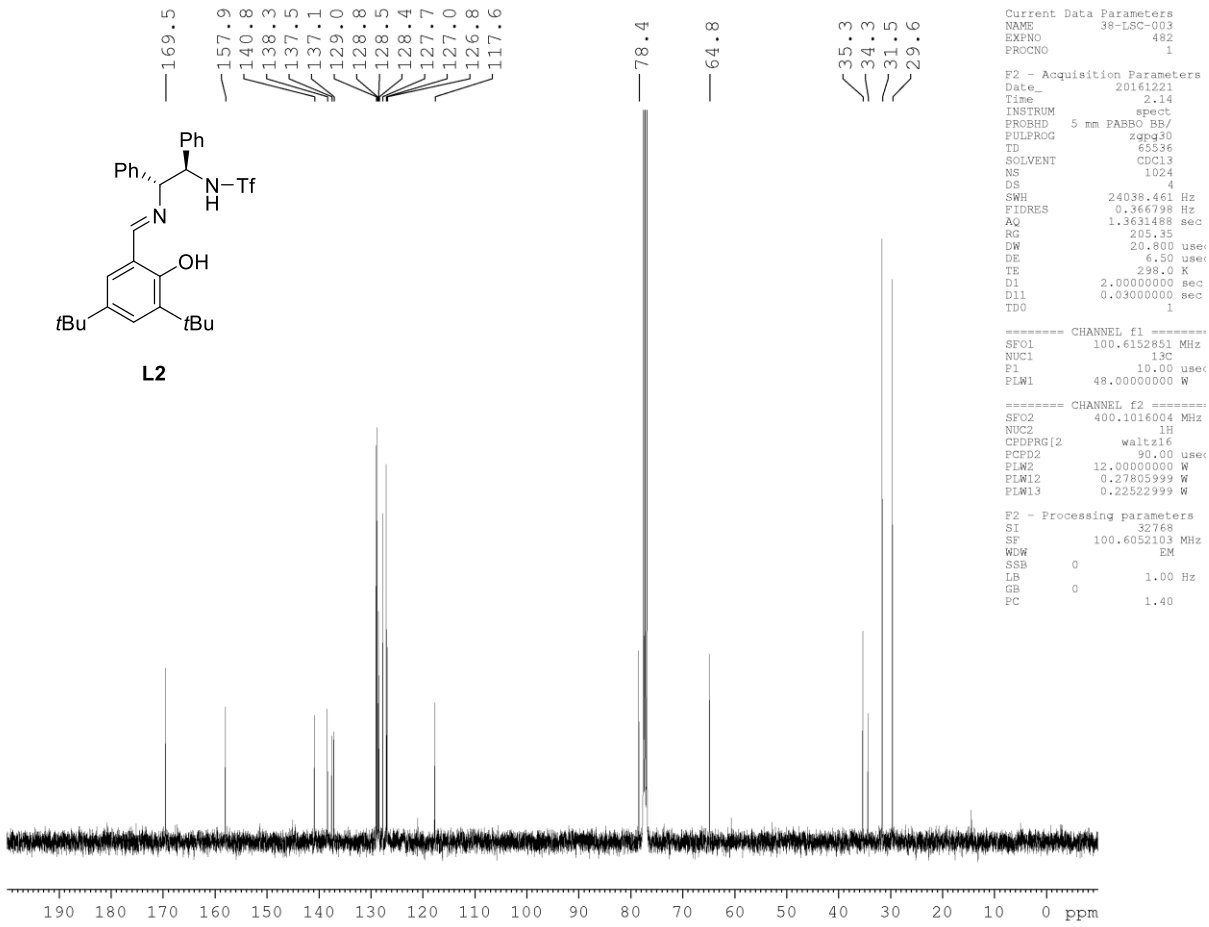
======== CHANNEL f1 ========
SFO1         100.6152851 MHz
NUC1               13C
P1                10.00 use
PLW1         48.00000000 W

======== CHANNEL f2 ========
SFO2         400.1016004 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2             90.00 use
PLW2         12.00000000 W
PLW12         0.27805999 W
PLW13         0.22522999 W

F2 - Processing parameters
SI                32768
SF           100.6052124 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```


12.85
8.16
7.42
7.41
7.32
7.32
7.31
7.30
7.29
7.28
7.28
7.27
7.26
7.23
7.23
7.12
7.11
7.10
7.09
7.09
6.94
6.93
5.86
5.05
5.03
4.63
4.62
1.47
1.25
Ph
Ph
N–Tf
H
N
OH
tBu
tBu
L2
Current Data Parameters
NAME 38-LSC-003
EXPNO 310
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180820
Time 18.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 128
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300165 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.95
1.00
1.05
8.33
2.03
1.00
0.85
1.00
1.00
8.86
9.08


-77.5
Ph
Ph
N–Tf
H
N
OH
tBu
tBu
L2
Current Data Parameters
NAME 38-LSC-003.1
EXPNO 281
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180820
Time 14.53
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgflqn
TD 131072
SOLVENT CDCl3
NS 16
DS 4
SWH 89285.711 Hz
FIDRES 0.681196 Hz
AQ 0.7340032 sec
RG 205.35
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 376.4324910 MHz
NUC1 19F
P1 14.65 usec
PLW1 20.00000000 W
F2 - Processing parameters
SI 65536
SF 376.4701380 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
-66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 ppm



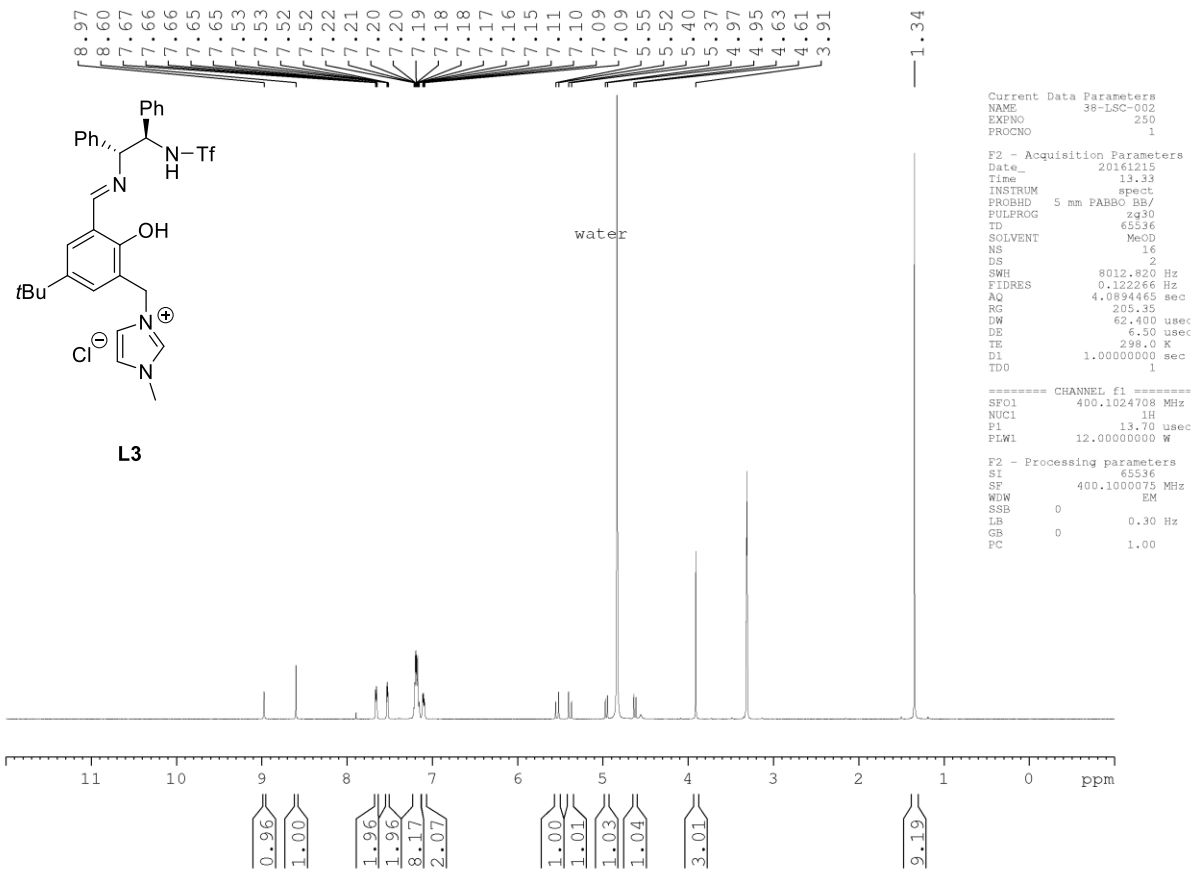

```
Current Data Parameters
NAME            38-LSC-003
EXPNO                  482
PROCNO                   1

F2 - Acquisition Parameters
Date_           20161221
Time                2.14
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                205.35
DW                20.800 usec
DE                 6.50 usec
TE               298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6152851 MHz
NUC1                13C
P1                10.00 usec
PLW1         48.00000000 W

======== CHANNEL f2 ========
SFO2         400.1016004 MHz
NUC2                1H
CPDPRG[2          waltz16
PCPD2              90.00 usec
PLW2         12.00000000 W
PLW12         0.27805999 W
PLW13         0.22522999 W

F2 - Processing parameters
SI                 32768
SF           100.6052103 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```



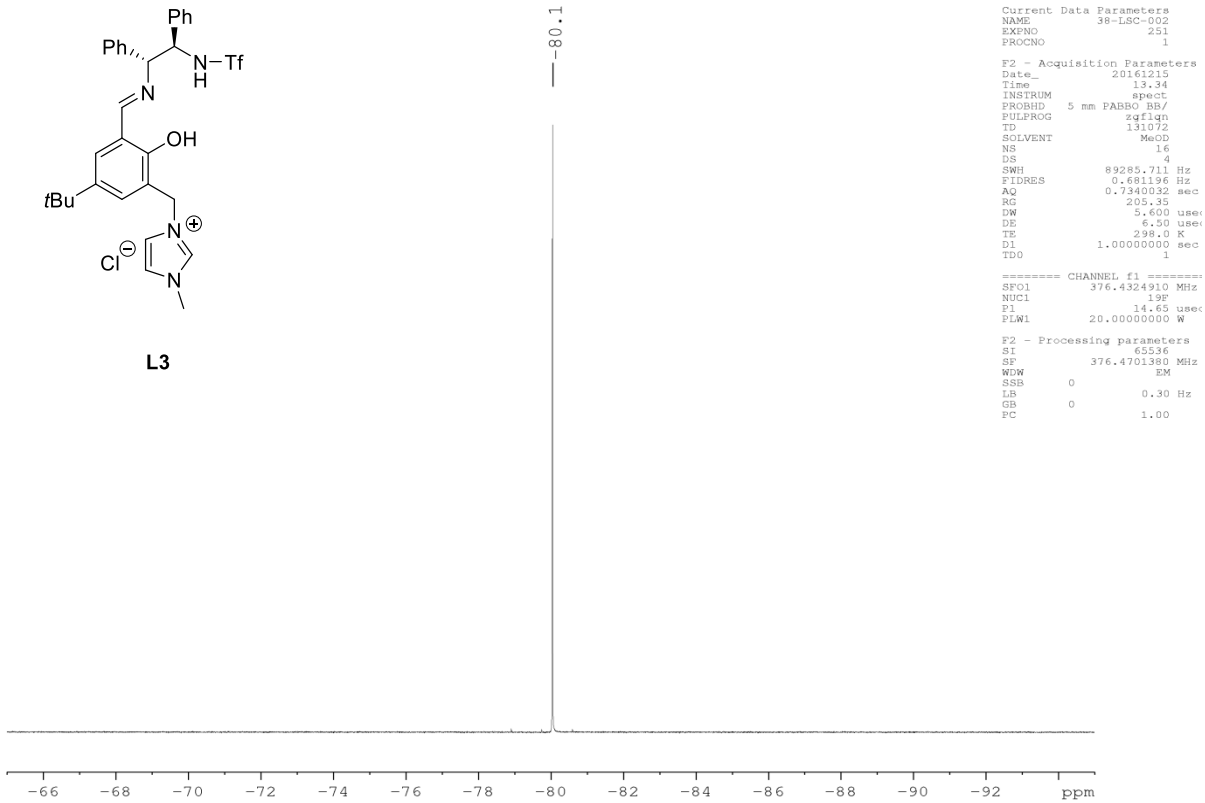
L3

```
Current Data Parameters
NAME          38-LSC-002
EXPNO                250
PROCNO                 1

F2 - Acquisition Parameters
Date_           20161215
Time               13.33
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT            MeOD
NS                   16
DS                    2
SWH           8012.820 Hz
FIDRES        0.122266 Hz
AQ            4.0894465 sec
RG               205.35
DW               62.400 usec
DE                6.50 usec
TE               298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        400.1024708 MHz
NUC1                1H
P1                13.70 usec
PLW1        12.00000000 W

F2 - Processing parameters
SI                65536
SF          400.1000075 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



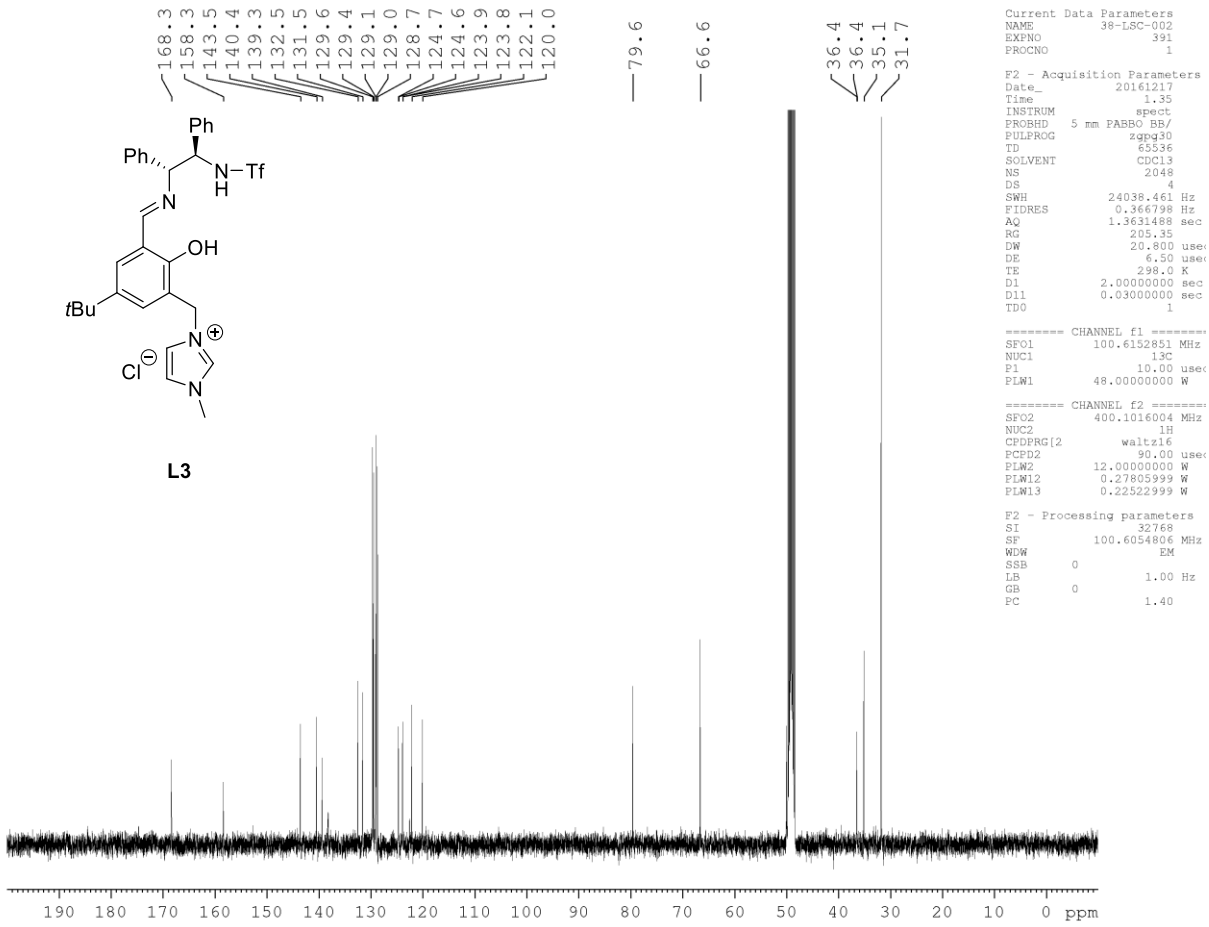
L3

```
Current Data Parameters
NAME          38-LSC-002
EXPNO                251
PROCNO                 1

F2 - Acquisition Parameters
Date_           20161215
Time               13.34
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgflqn
TD               131072
SOLVENT            MeOD
NS                   16
DS                    4
SWH           89285.711 Hz
FIDRES        0.681196 Hz
AQ            0.7340032 sec
RG               205.35
DW               5.600 usec
DE                6.50 usec
TE               298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        376.4324910 MHz
NUC1                19F
P1                14.65 usec
PLW1        20.00000000 W

F2 - Processing parameters
SI                65536
SF          376.4701380 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



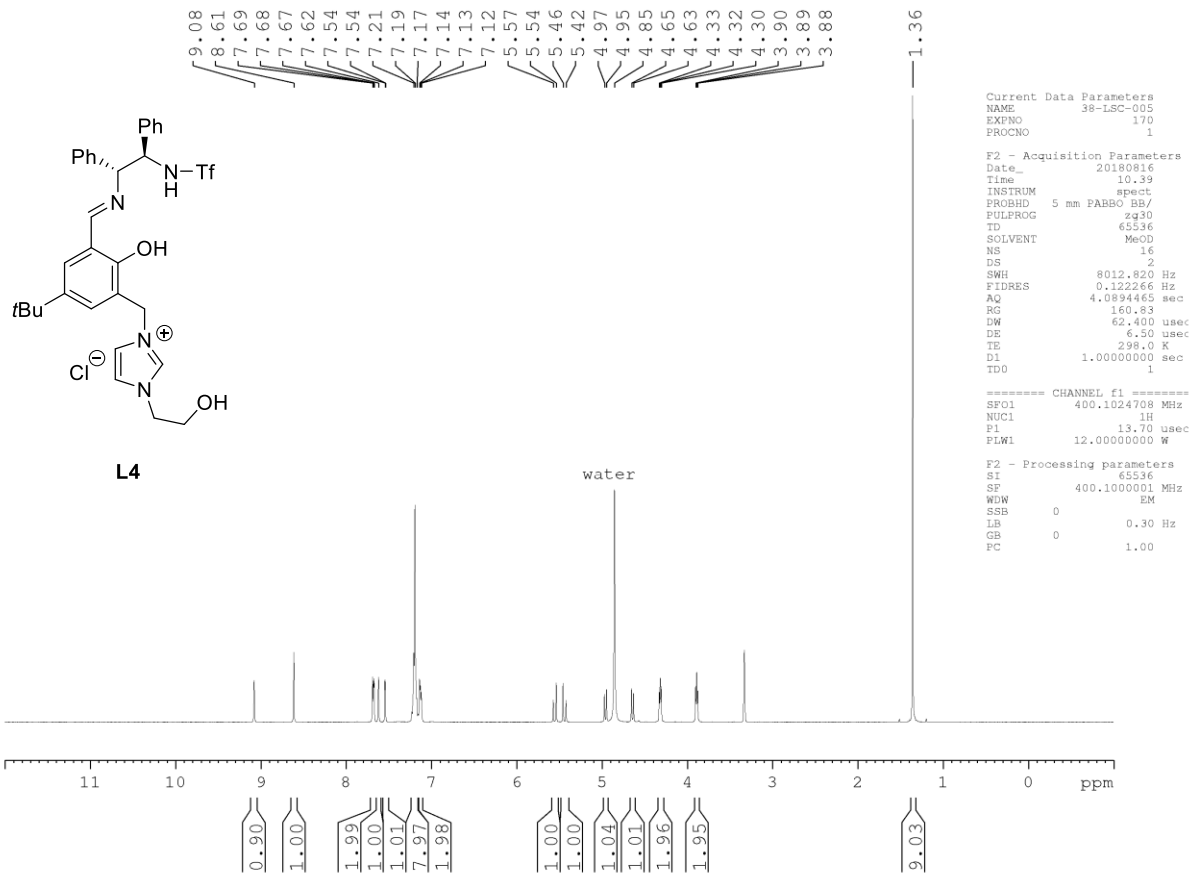

```
Current Data Parameters
NAME          38-LSC-002
EXPNO                391
PROCNO                 1

F2 - Acquisition Parameters
Date_           20161217
Time                1.35
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 2048
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                205.35
DW                20.800 use
DE                 6.50 use
TE               298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6152851 MHz
NUC1                  13C
P1                  10.00 use
PLW1         48.00000000 W

======== CHANNEL f2 ========
SFO2         400.1016004 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2               90.00 use
PLW2         12.00000000 W
PLW12         0.27805999 W
PLW13         0.22522999 W

F2 - Processing parameters
SI                 32768
SF           100.6054806 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

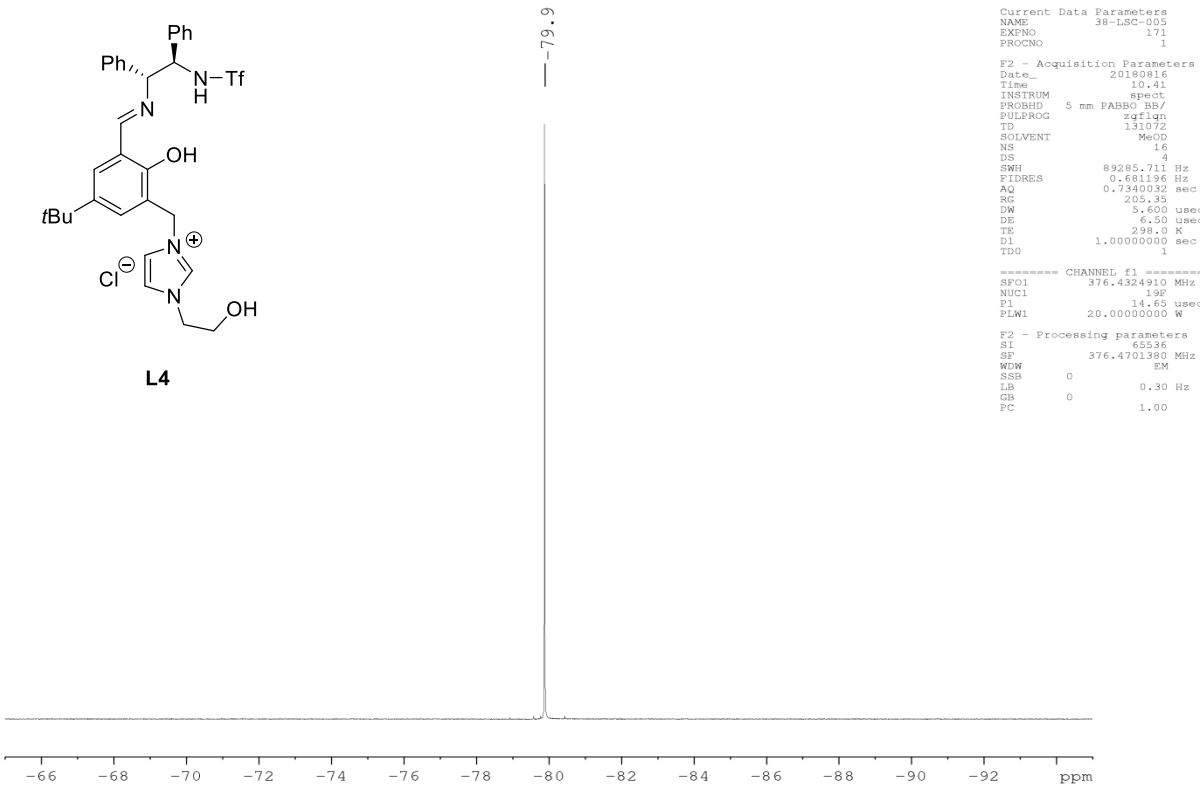



```
Current Data Parameters
NAME          38-LSC-005
EXPNO                170
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180816
Time               10.39
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT            MeOD
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894465 sec
RG                160.83
DW                62.400 usec
DE                 6.50 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          400.1024708 MHz
NUC1                  1H
P1                13.70 usec
PLW1         12.00000000 W

F2 - Processing parameters
SI                65536
SF          400.1000001 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

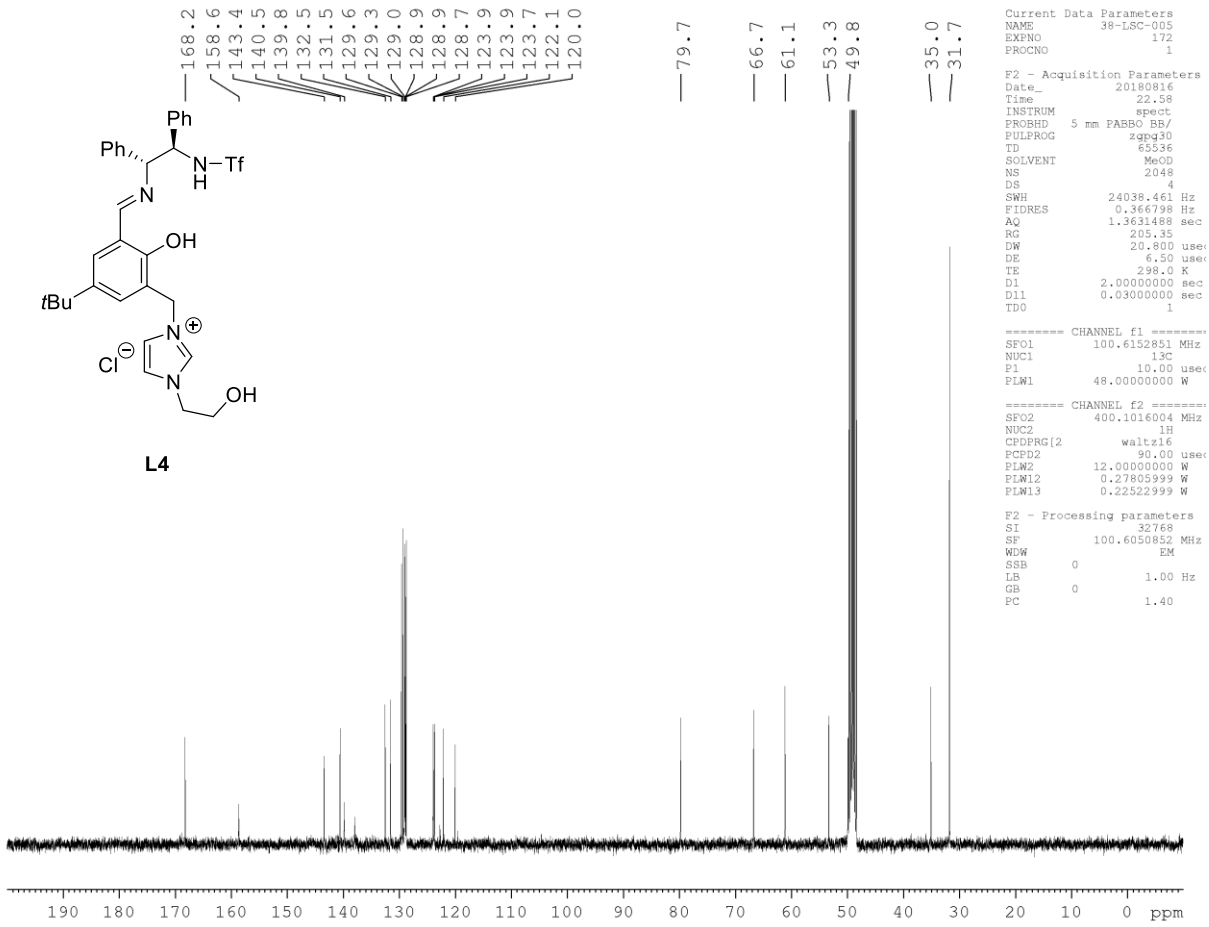


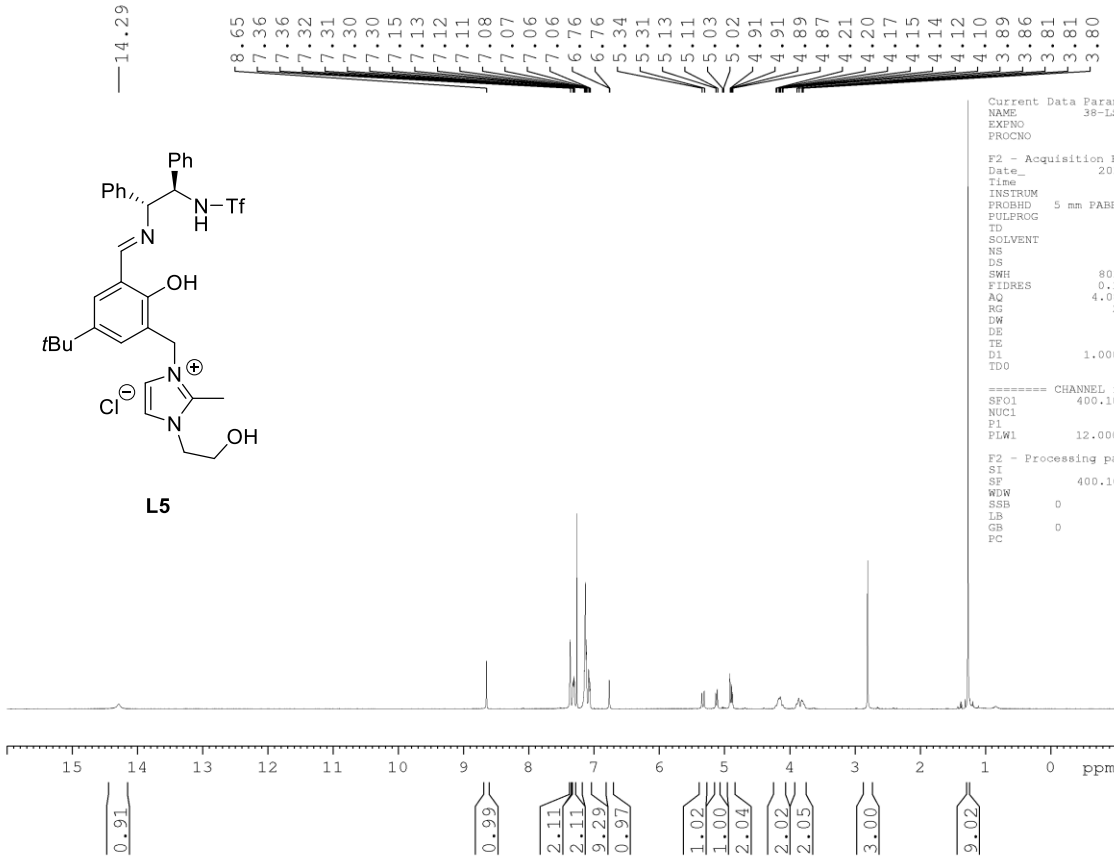

```
Current Data Parameters
NAME          38-LSC-005
EXPNO                171
PROCNO                 1

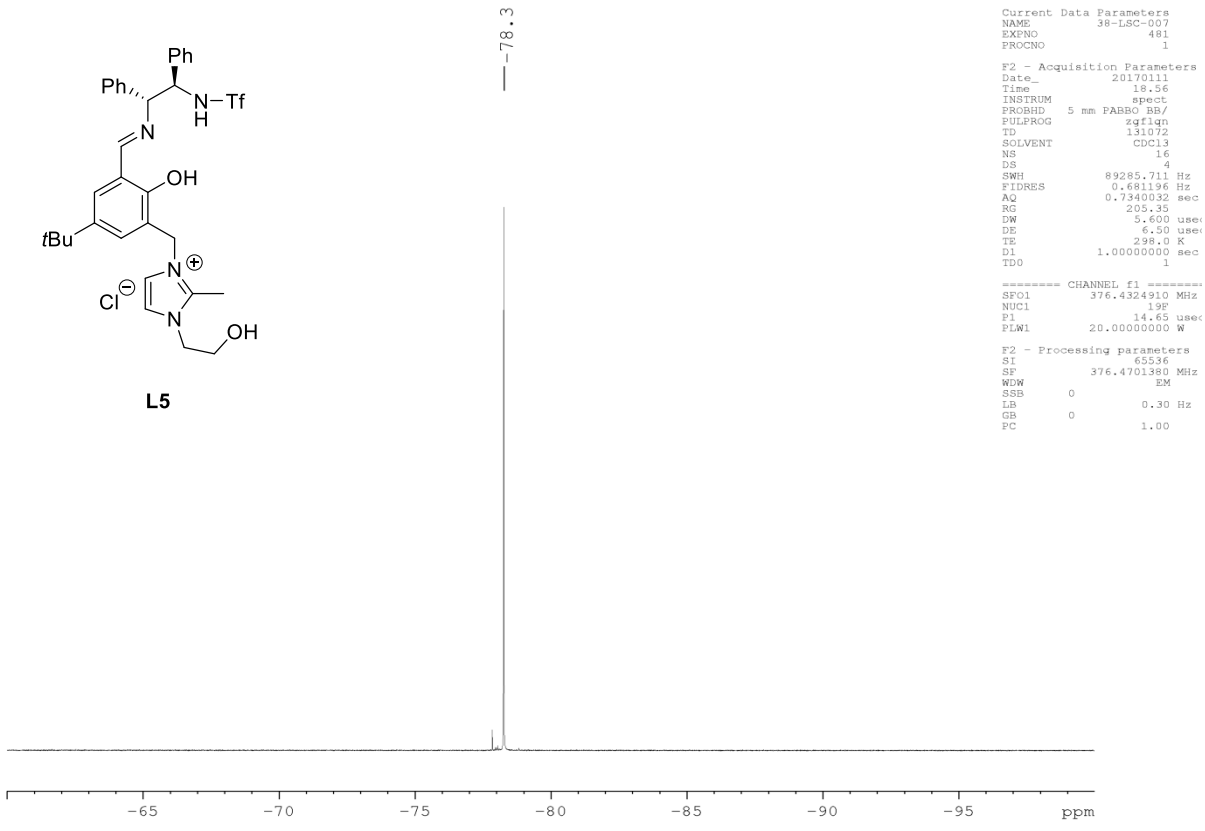
F2 - Acquisition Parameters
Date_           20180816
Time               10.41
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgflqn
TD               131072
SOLVENT            MeOD
NS                    16
DS                     4
SWH            89285.711 Hz
FIDRES          0.681196 Hz
AQ              0.7340032 sec
RG                205.35
DW                5.600 usec
DE                 6.50 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

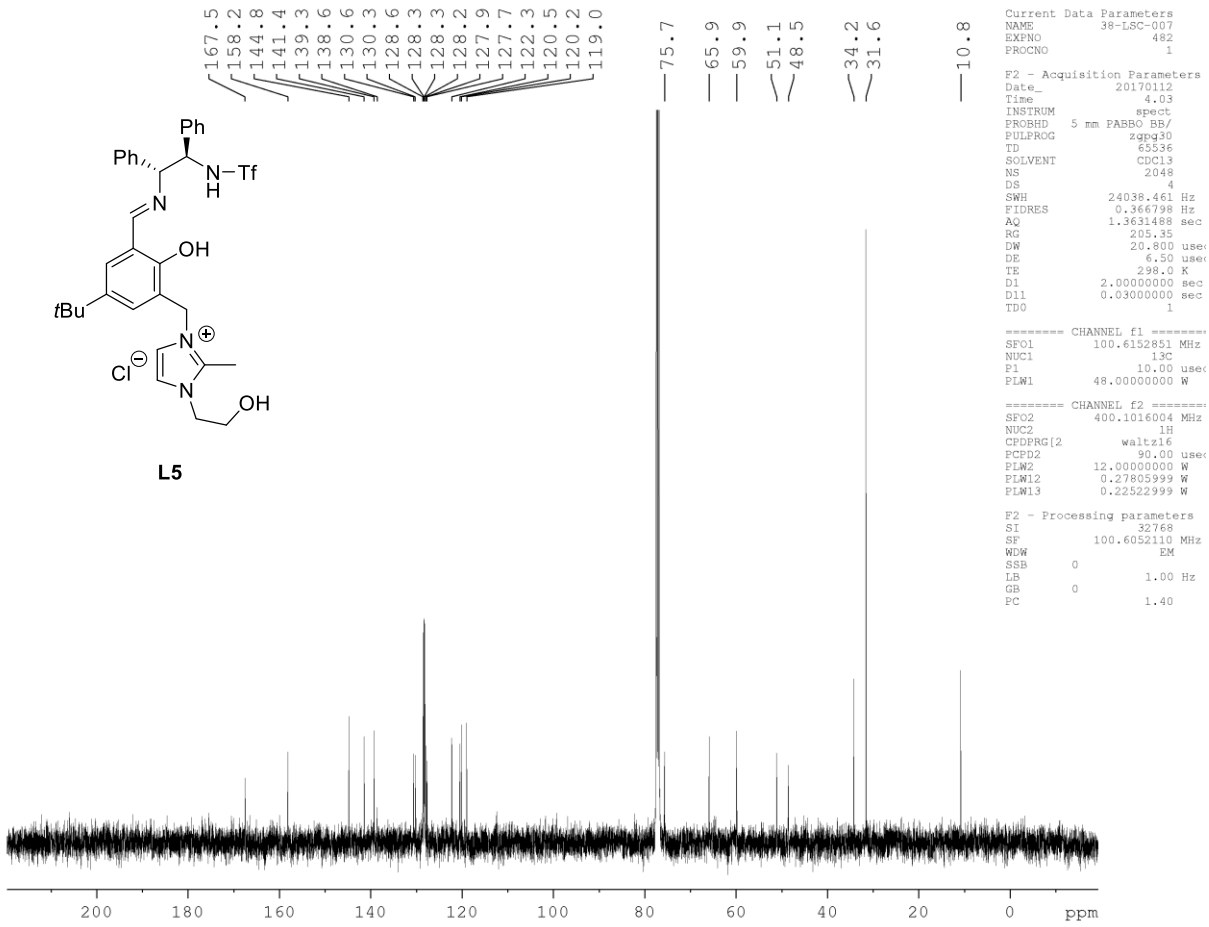
======== CHANNEL f1 ========
SFO1          376.4324910 MHz
NUC1                 19F
P1                14.65 usec
PLW1         20.00000000 W

F2 - Processing parameters
SI                65536
SF          376.4701380 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```


168.2
158.6
143.4
140.5
139.8
132.5
131.5
129.6
129.3
129.0
128.9
128.9
128.7
123.9
123.9
123.7
122.1
120.0
79.7
66.7
61.1
53.3
49.8
35.0
31.7
Ph
Ph
N–Tf
H
N
OH
tBu
N
Cl
N
OH
L4
Current Data Parameters
NAME 38-LSC-005
EXPNO 172
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180816
Time 22.58
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 2048
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 205.35
DW 20.800 use
DE 6.50 use
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6152851 MHz
NUC1 13C
P1 10.00 use
PLW1 48.00000000 W
======== CHANNEL f2 ========
SFO2 400.1016004 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 use
PLW2 12.00000000 W
PLW12 0.27805999 W
PLW13 0.22522999 W
F2 - Processing parameters
SI 32768
SF 100.6050852 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


14.29
8.65
7.36
7.36
7.32
7.31
7.30
7.30
7.15
7.13
7.12
7.11
7.08
7.07
7.06
7.06
6.76
6.76
5.34
5.31
5.13
5.11
5.03
5.02
4.91
4.91
4.89
4.87
4.21
4.20
4.17
4.15
4.14
4.12
4.10
3.89
3.86
3.81
3.81
3.80
Ph
Ph
N–Tf
H
N
OH
tBu
N
Cl
N
OH
L5
Current Data Parameters
NAME 38-LSC-007
EXPNO 480
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170111
Time 18.54
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 205.35
DW 62.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1024708 MHz
NUC1 1H
P1 13.70 usec
PLW1 12.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1000100 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.91
0.99
2.11
2.11
9.29
0.97
1.02
1.00
2.04
2.02
2.05
3.00
9.02


-78.3
Ph
Ph
N–Tf
H
N
OH
tBu
N
Cl
N
OH
L5
Current Data Parameters
NAME 38-LSC-007
EXPNO 481
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170111
Time 18.56
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgflqn
TD 131072
SOLVENT CDCl3
NS 16
DS 4
SWH 89285.711 Hz
FIDRES 0.681196 Hz
AQ 0.7340032 sec
RG 205.35
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 376.4324910 MHz
NUC1 19F
P1 14.65 usec
PLW1 20.00000000 W
F2 - Processing parameters
SI 65536
SF 376.4701380 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
-65 -70 -75 -80 -85 -90 -95 ppm



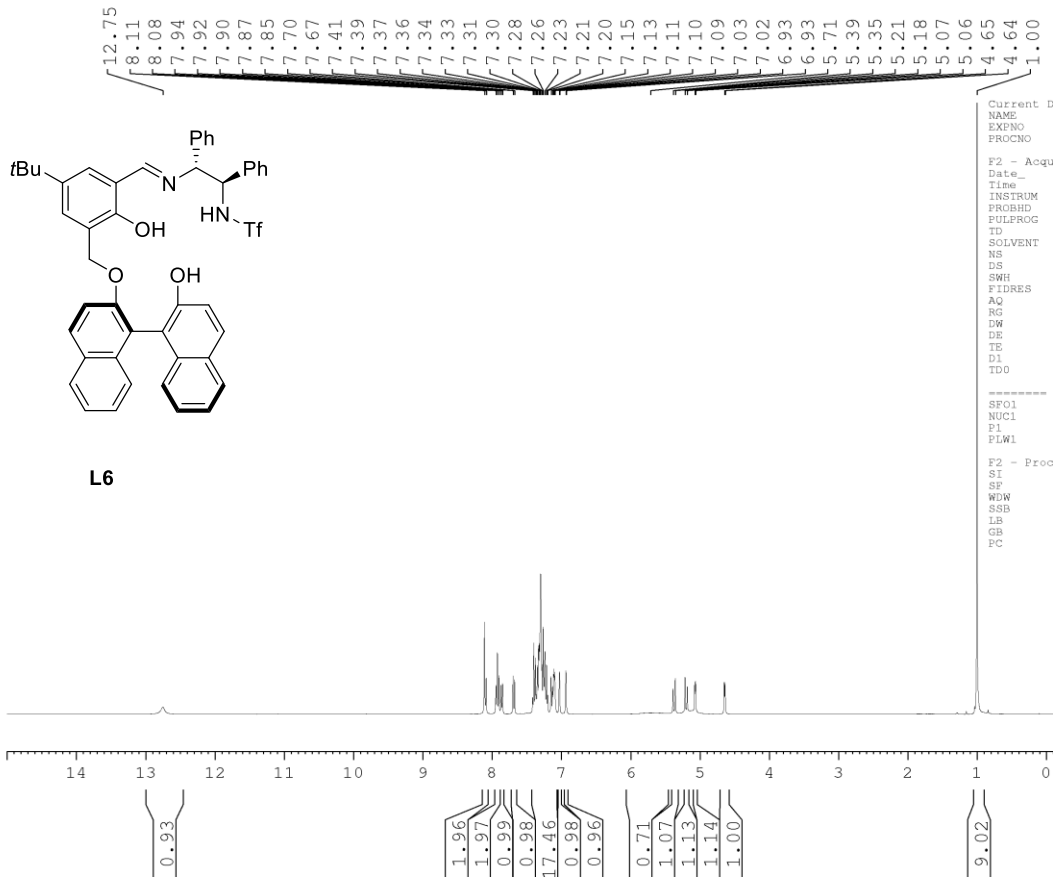
Current Data Parameters
NAME 38-LSC-007
EXPNO 482
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170112
Time 4.03
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 205.35
DW 20.800 use
DE 6.50 use
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

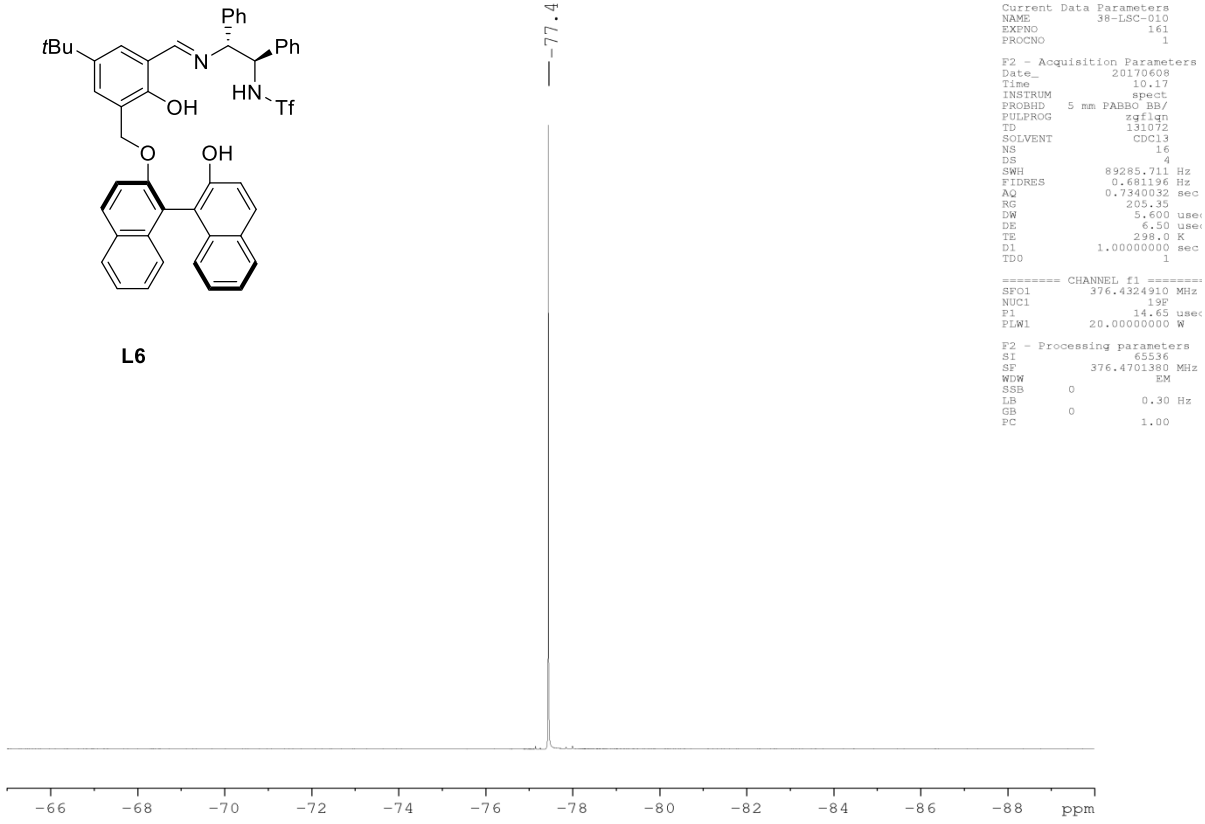
======== CHANNEL f1 ========
SFO1 100.6152851 MHz
NUC1 13C
P1 10.00 use
PLW1 48.00000000 W

======== CHANNEL f2 ========
SFO2 400.1016004 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 use
PLW2 12.00000000 W
PLW12 0.27805999 W
PLW13 0.22522999 W

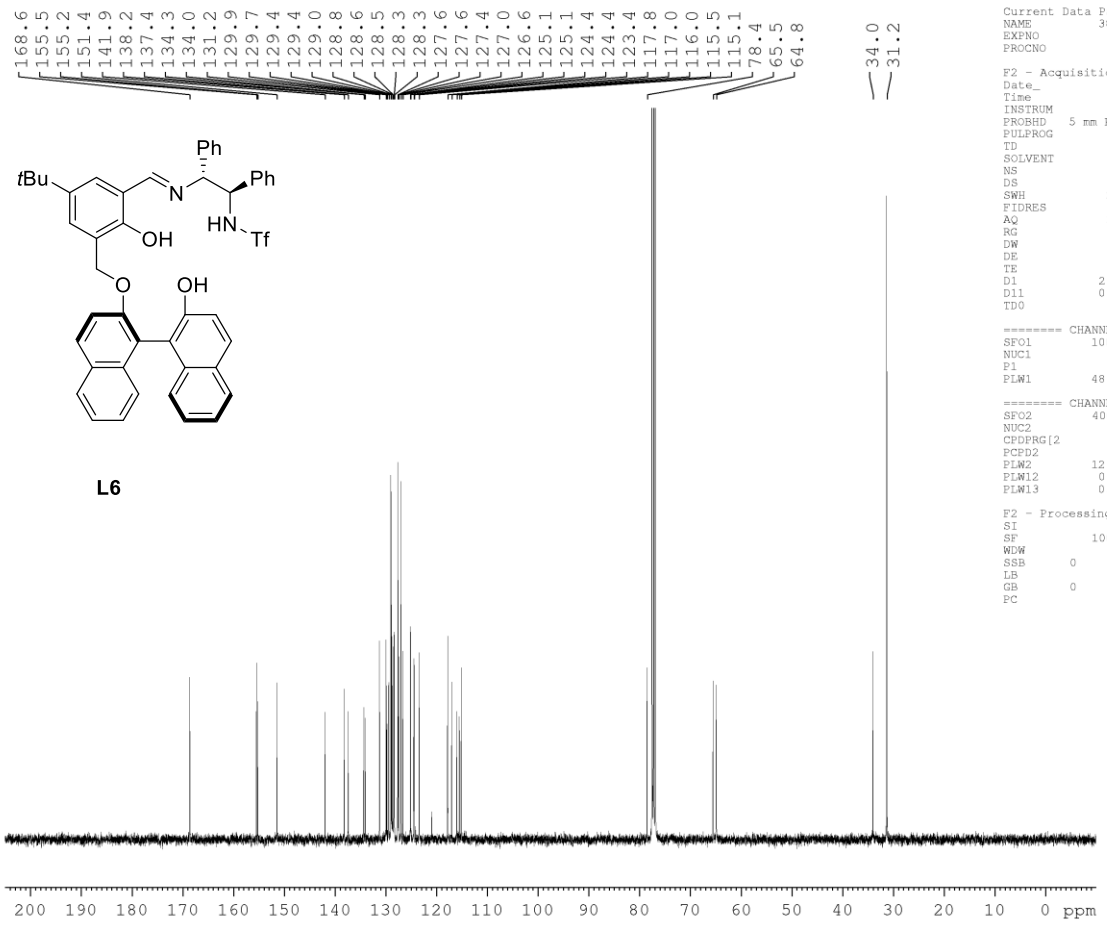
F2 - Processing parameters
SI 32768
SF 100.6052110 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


12.75
8.11
8.08
7.94
7.92
7.90
7.87
7.85
7.70
7.67
7.41
7.39
7.37
7.36
7.34
7.33
7.31
7.30
7.28
7.26
7.23
7.21
7.20
7.15
7.13
7.11
7.10
7.09
7.03
7.02
6.93
6.93
5.71
5.39
5.35
5.21
5.18
5.07
5.06
4.65
4.64
1.00
tBu
Ph
N
Ph
HN
Tf
OH
O
OH
Current Data Parameters
NAME 38-LSC-010
EXPNO 160
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170608
Time 10.16
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 114.36
DW 62.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1024708 MHz
NUC1 1H
P1 13.70 usec
PLW1 12.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1000087 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.93
1.96
1.97
0.99
0.98
17.46
0.98
0.96
0.71
1.07
1.13
1.14
1.00
9.02

L6


tBu
Ph
N
Ph
HN
Tf
OH
O
OH
−77.4
Current Data Parameters
NAME 38-LSC-010
EXPNO 161
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170608
Time 10.17
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgflqn
TD 131072
SOLVENT CDCl3
NS 16
DS 4
SWH 89285.711 Hz
FIDRES 0.681196 Hz
AQ 0.7340032 sec
RG 205.35
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 376.4324910 MHz
NUC1 19F
P1 14.65 usec
PLW1 20.00000000 W
F2 - Processing parameters
SI 65536
SF 376.4701380 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
−66
−68
−70
−72
−74
−76
−78
−80
−82
−84
−86
−88
ppm

L6



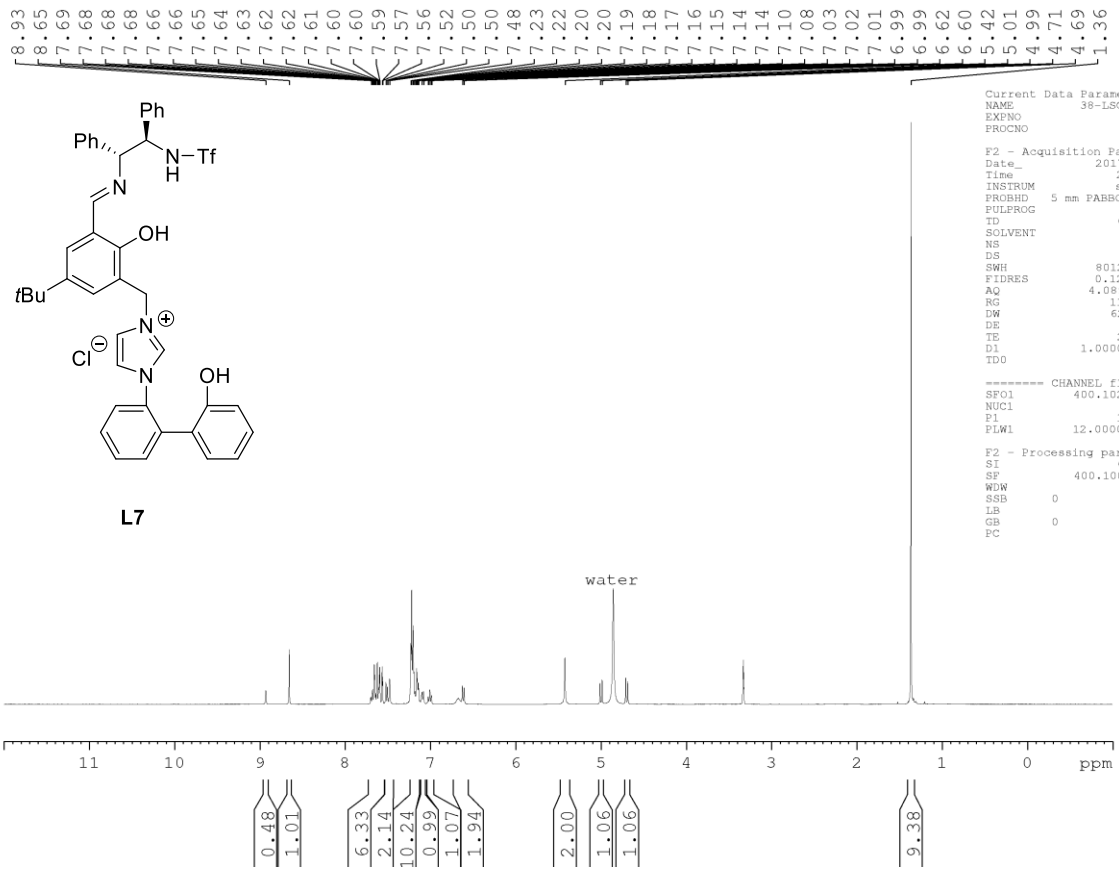

```
Current Data Parameters
NAME            38-LSC-010
EXPNO                  162
PROCNO                   1

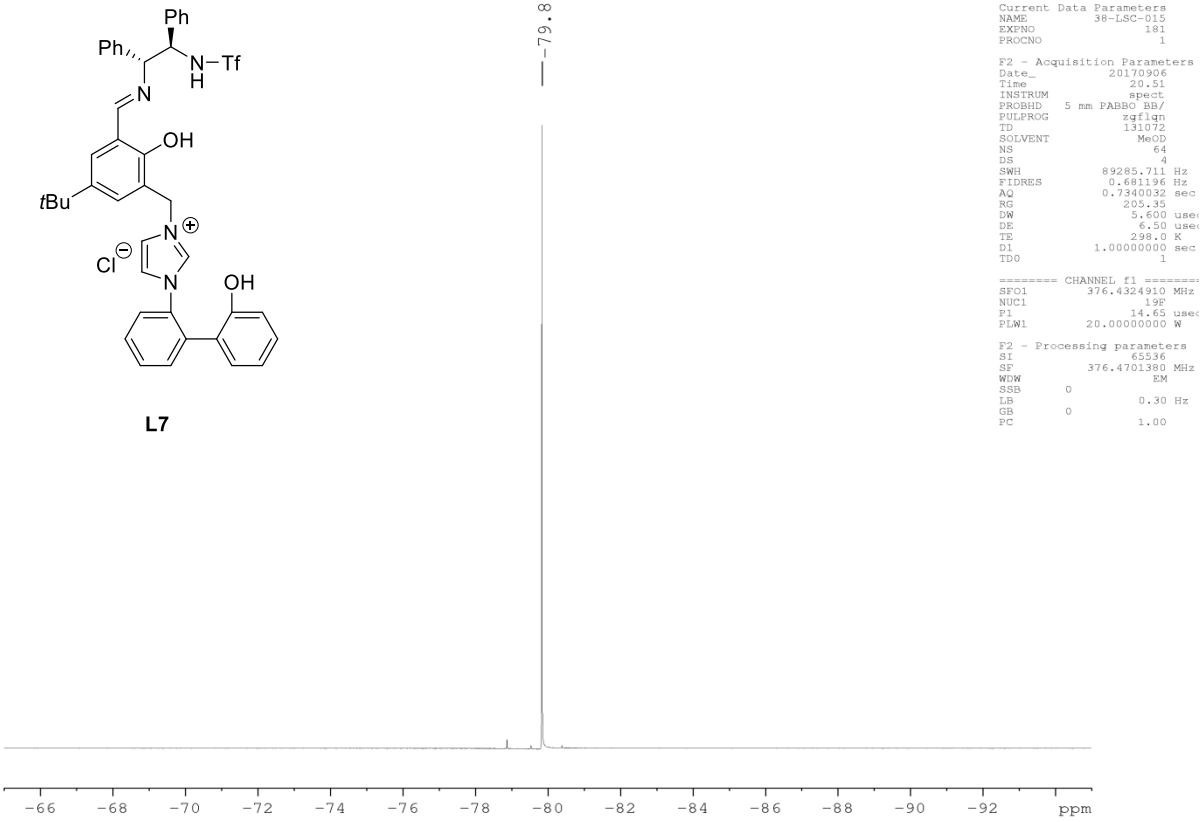
F2 - Acquisition Parameters
Date_           20170609
Time               1.13
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                205.35
DW                20.800 use
DE                 6.50 use
TE               298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

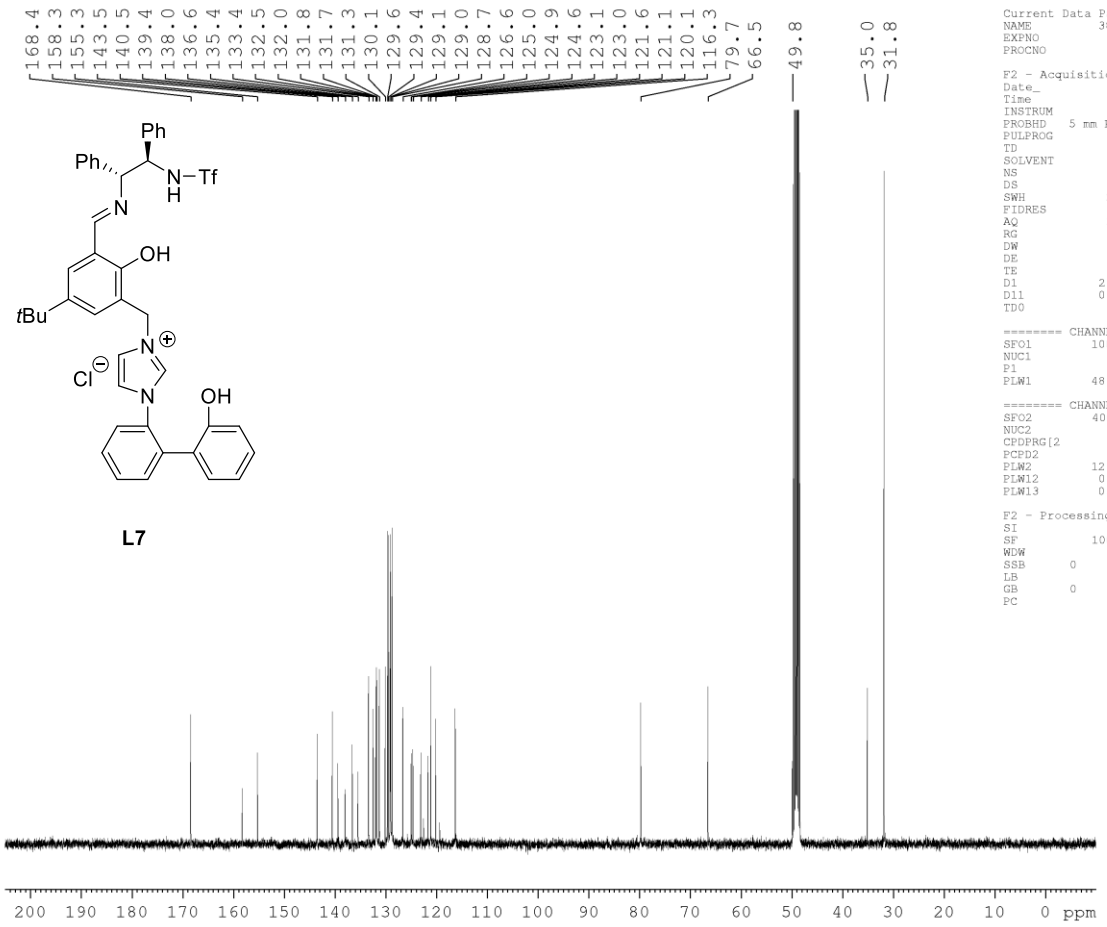
======== CHANNEL f1 ========
SFO1         100.6152851 MHz
NUC1               13C
P1                10.00 use
PLW1         48.00000000 W

======== CHANNEL f2 ========
SFO2         400.1016004 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2             90.00 use
PLW2         12.00000000 W
PLW12         0.27805999 W
PLW13         0.22522999 W

F2 - Processing parameters
SI                 32768
SF           100.6052133 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```


8.93 8.65 7.69 7.68 7.68 7.68 7.66 7.66 7.65 7.64 7.63 7.62 7.62 7.61 7.60 7.60 7.59 7.57 7.56 7.52 7.50 7.50 7.48 7.23 7.22 7.20 7.20 7.19 7.18 7.17 7.16 7.15 7.14 7.14 7.10 7.08 7.03 7.02 7.01 6.99 6.99 6.62 6.60 5.42 5.01 4.99 4.71 4.69 1.36
Ph
Ph
N–Tf
H
N
OH
tBu
N
Cl
N
OH
L7
Current Data Parameters
NAME 38-LSC-015
EXPNO 180
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170906
Time 20.48
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 128
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 114.36
DW 62.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1024708 MHz
NUC1 1H
P1 13.70 usec
PLW1 12.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1000000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
water
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.48 1.01 6.33 2.14 10.24 0.99 1.07 1.94 2.00 1.06 1.06 9.38


Ph
Ph
N–Tf
H
N
OH
tBu
N
Cl
N
OH
L7
-79.8
Current Data Parameters
NAME 38-LSC-015
EXPNO 181
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170906
Time 20.51
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgflqn
TD 131072
SOLVENT MeOD
NS 64
DS 4
SWH 89285.711 Hz
FIDRES 0.681196 Hz
AQ 0.7340032 sec
RG 205.35
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 376.4324910 MHz
NUC1 19F
P1 14.65 usec
PLW1 20.00000000 W
F2 - Processing parameters
SI 65536
SF 376.4701380 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
-66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 ppm



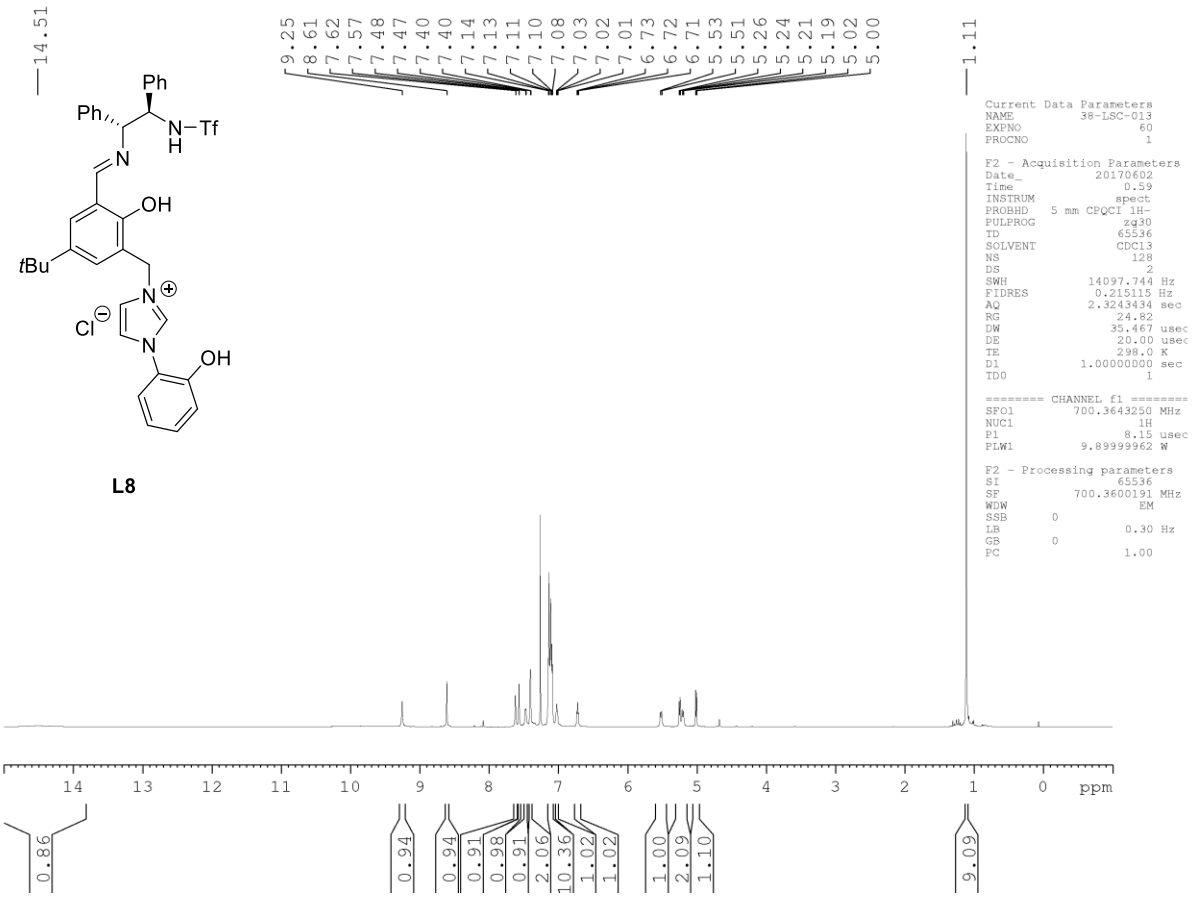

```
Current Data Parameters
NAME            38-LSC-015
EXPNO                182
PROCNO                 1

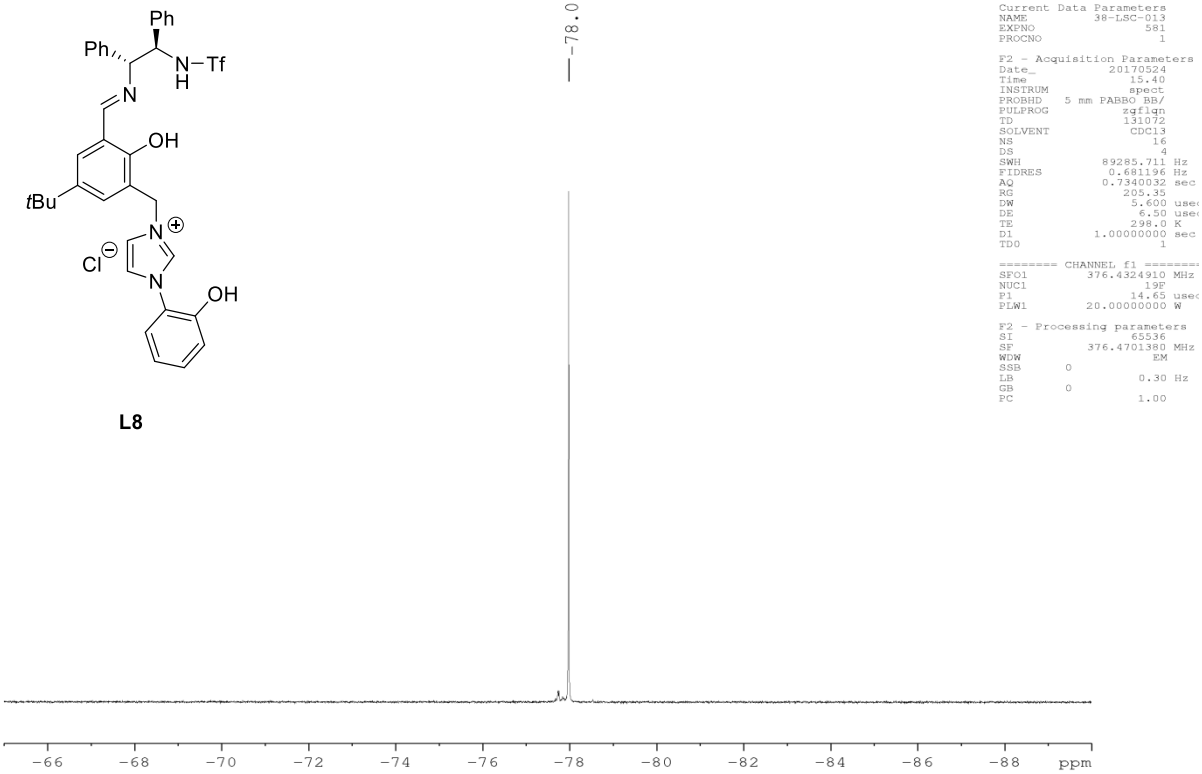
F2 - Acquisition Parameters
Date_           20170906
Time               22.50
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT             MeOD
NS                  2048
DS                     4
SWH            24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                   205.35
DW                  20.800 use
DE                   6.50 use
TE                 298.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                    1

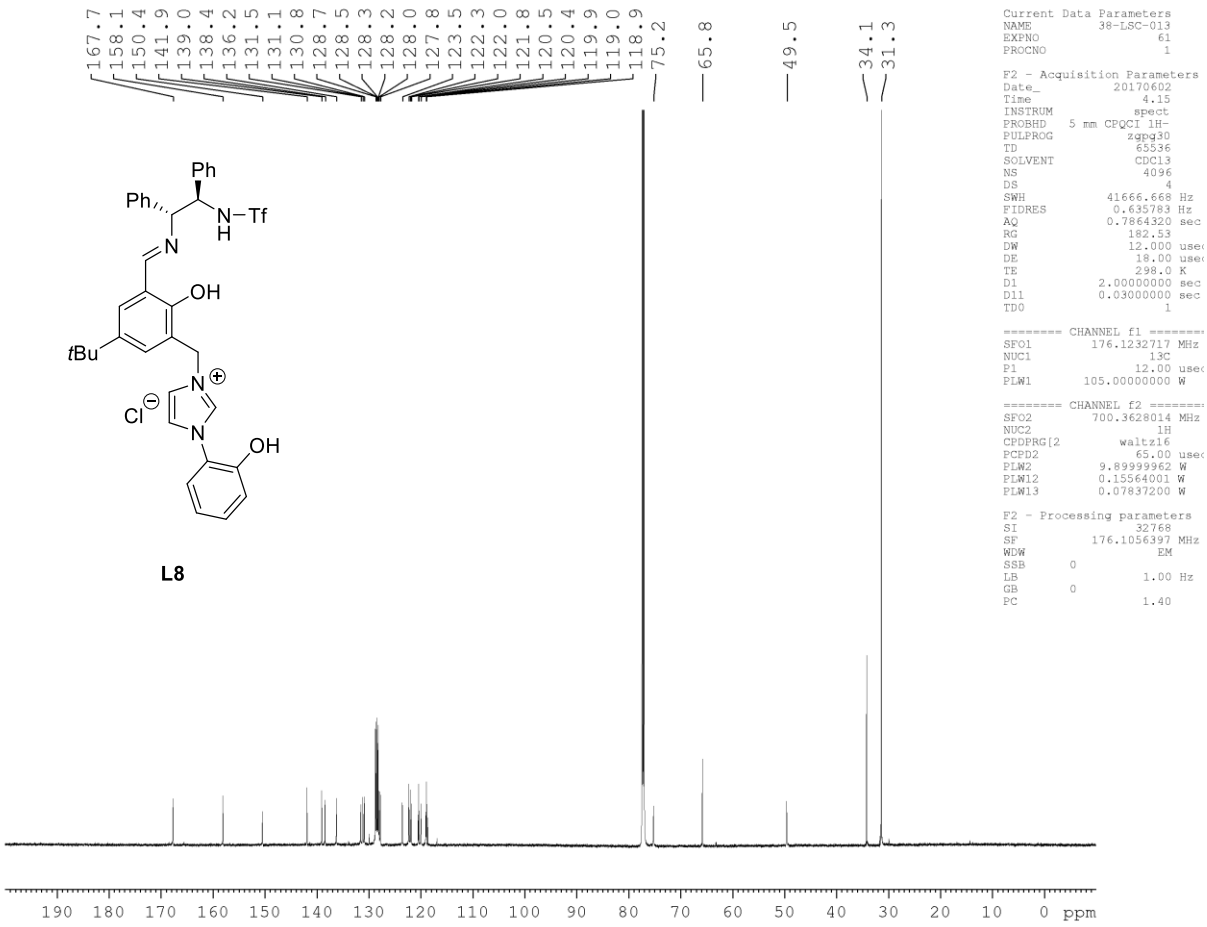
======== CHANNEL f1 ========
SFO1          100.6152851 MHz
NUC1                 13C
P1                  10.00 use
PLW1          48.00000000 W

======== CHANNEL f2 ========
SFO2          400.1016004 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2               90.00 use
PLW2          12.00000000 W
PLW12          0.27805999 W
PLW13          0.22522999 W

F2 - Processing parameters
SI                  32768
SF            100.6050865 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```


14.51
9.25
8.61
7.62
7.57
7.48
7.47
7.40
7.40
7.14
7.13
7.11
7.10
7.08
7.03
7.02
7.01
6.73
6.72
6.71
5.53
5.51
5.26
5.24
5.21
5.19
5.02
5.00
1.11
Ph
Ph
N−Tf
H
N
OH
tBu
N
Cl
N
OH
L8
Current Data Parameters
NAME 38-LSC-013
EXPNO 60
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170602
Time 0.59
INSTRUM spect
PROBHD 5 mm CPQCI 1H-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 128
DS 2
SWH 14097.744 Hz
FIDRES 0.215115 Hz
AQ 2.3243434 sec
RG 24.82
DW 35.467 usec
DE 20.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 700.3643250 MHz
NUC1 1H
P1 8.15 usec
PLW1 9.89999962 W
F2 - Processing parameters
SI 65536
SF 700.3600191 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.86
0.94
0.94
0.91
0.98
0.91
2.06
10.36
1.02
1.02
1.00
2.09
1.10
9.09


-78.0
Ph
Ph
N−Tf
H
N
OH
tBu
N
Cl
N
OH
L8
Current Data Parameters
NAME 38-LSC-013
EXPNO 581
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170524
Time 15.40
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgflqn
TD 131072
SOLVENT CDCl3
NS 16
DS 4
SWH 89285.711 Hz
FIDRES 0.681196 Hz
AQ 0.7340032 sec
RG 205.35
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 376.4324910 MHz
NUC1 19F
P1 14.65 usec
PLW1 20.00000000 W
F2 - Processing parameters
SI 65536
SF 376.4701380 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
-66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 ppm



L8

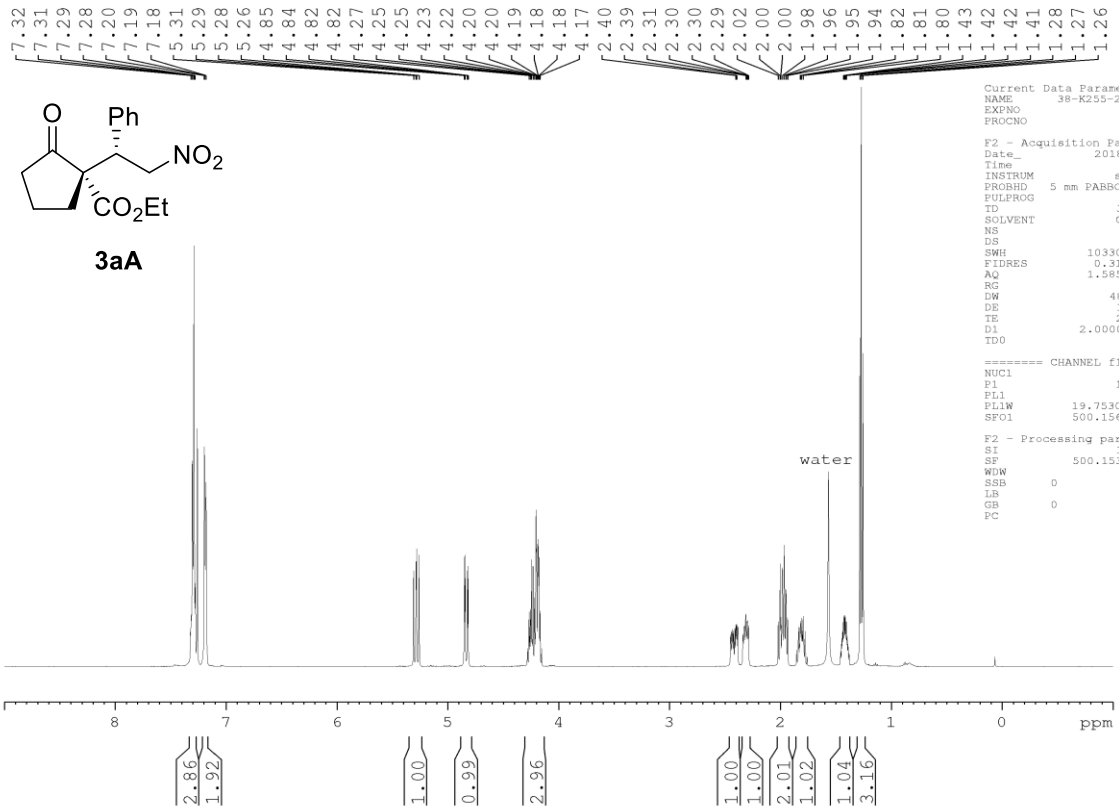
```
Current Data Parameters
NAME            38-LSC-013
EXPNO                   61
PROCNO                   1

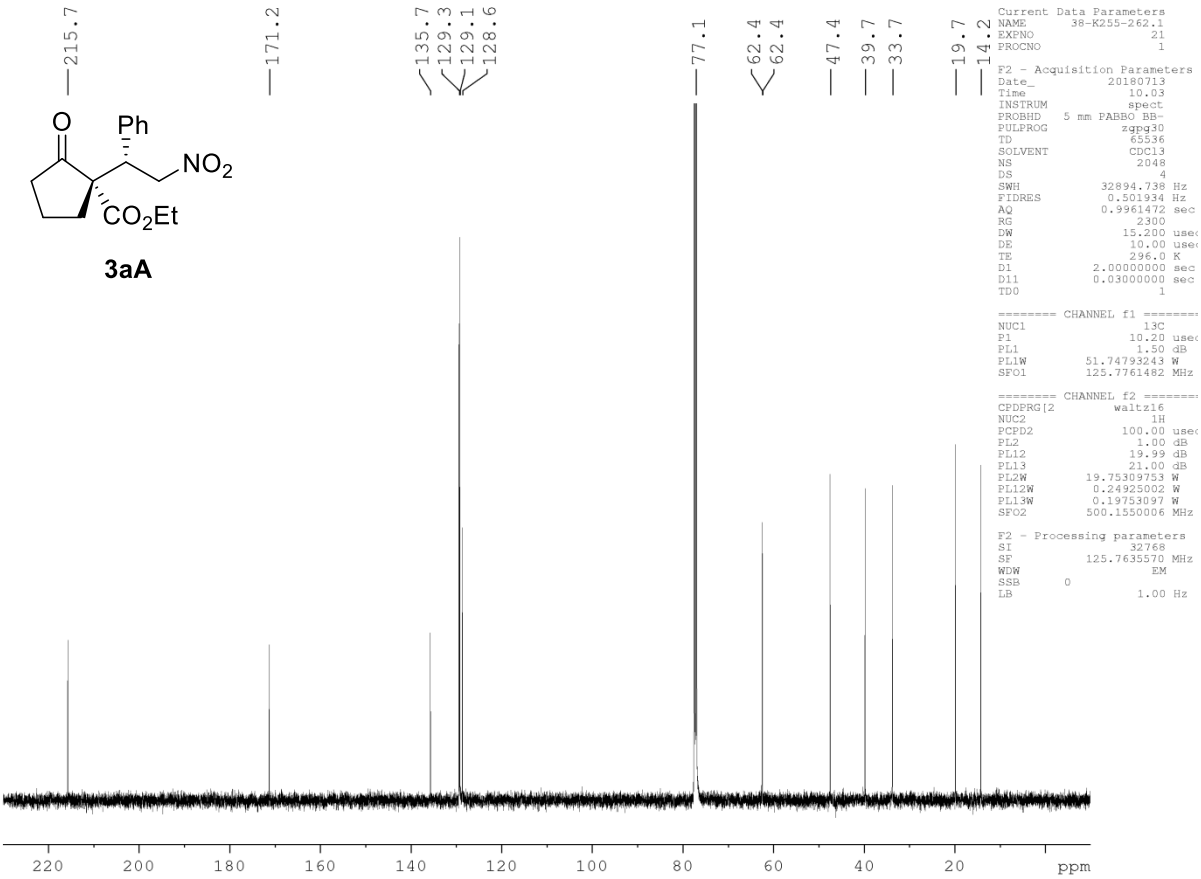
F2 - Acquisition Parameters
Date_             20170602
Time                  4.15
INSTRUM              spect
PROBHD   5 mm CPQCI 1H-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    4096
DS                       4
SWH              41666.668 Hz
FIDRES           0.635783 Hz
AQ               0.7864320 sec
RG                   182.53
DW                12.000 use
DE                 18.00 use
TE                 298.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

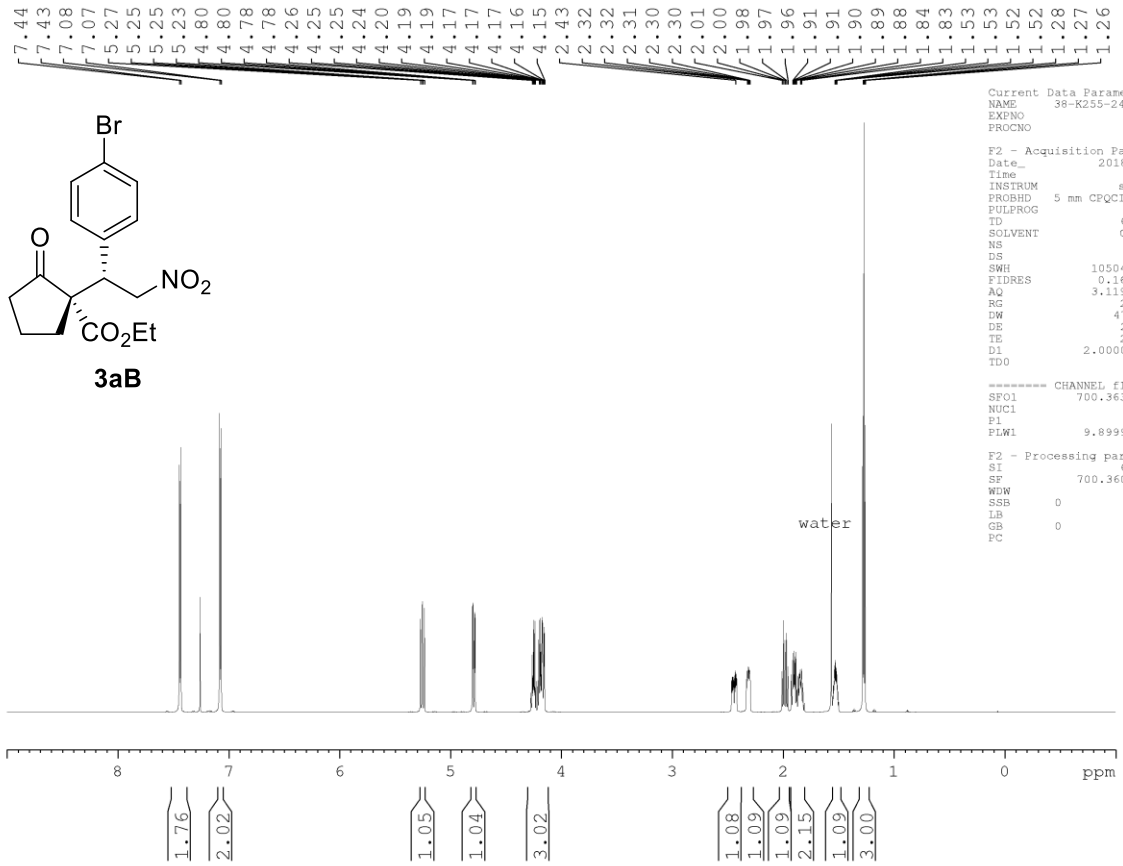
======== CHANNEL f1 ========
SFO1          176.1232717 MHz
NUC1                    13C
P1                   12.00 use
PLW1        105.00000000 W

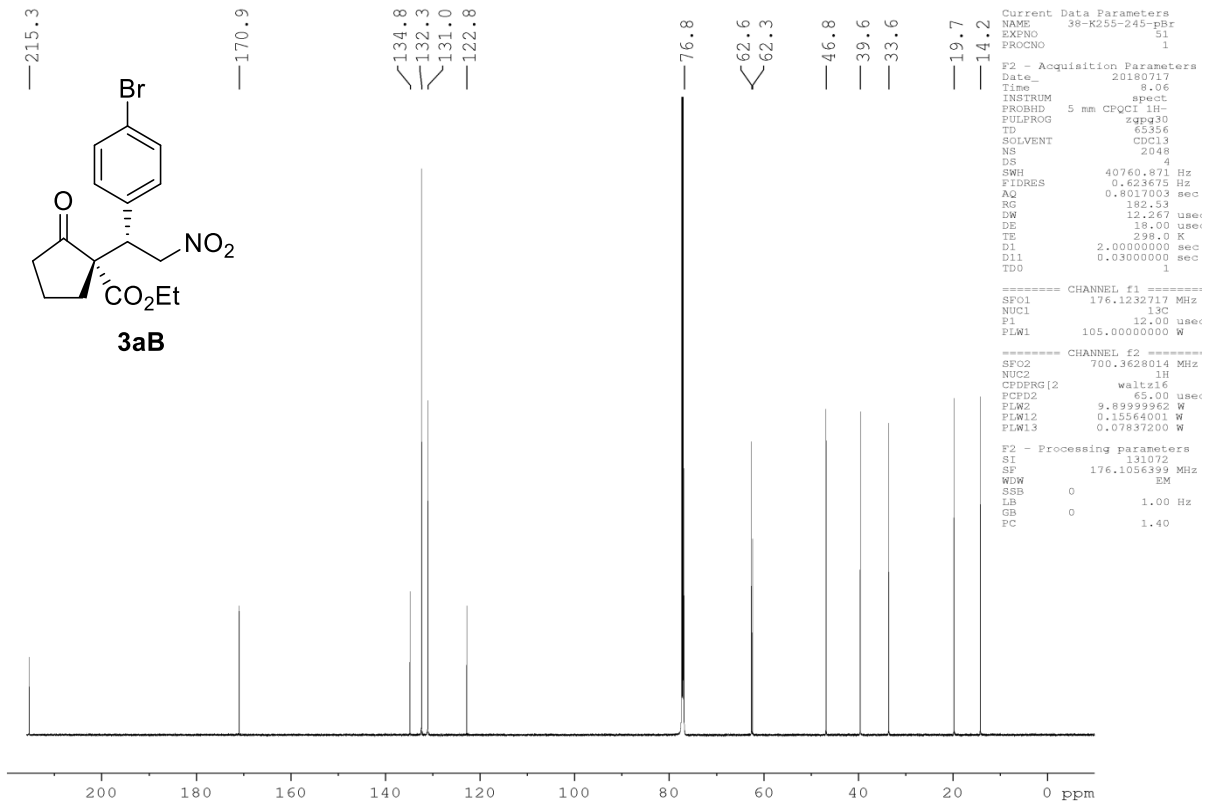
======== CHANNEL f2 ========
SFO2          700.3628014 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                65.00 use
PLW2           9.89999962 W
PLW12          0.15564001 W
PLW13          0.07837200 W

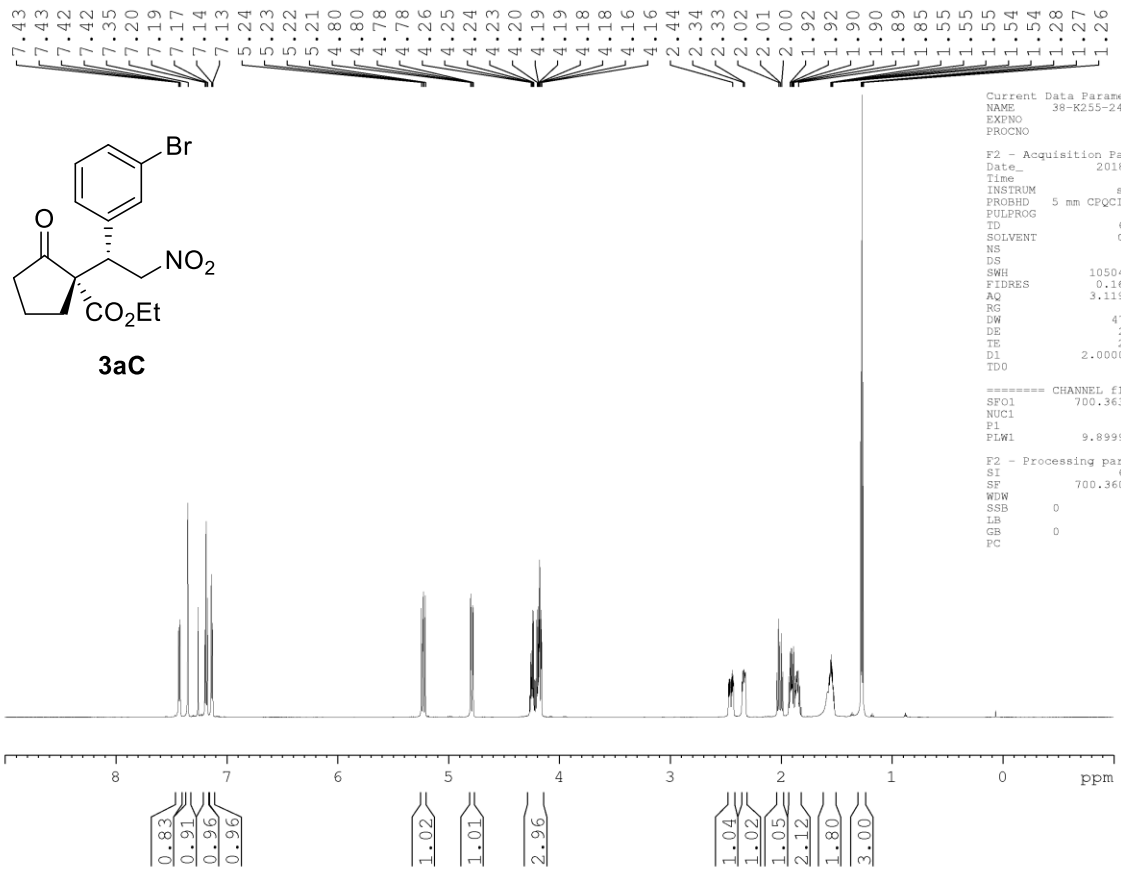
F2 - Processing parameters
SI                    32768
SF           176.1056397 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

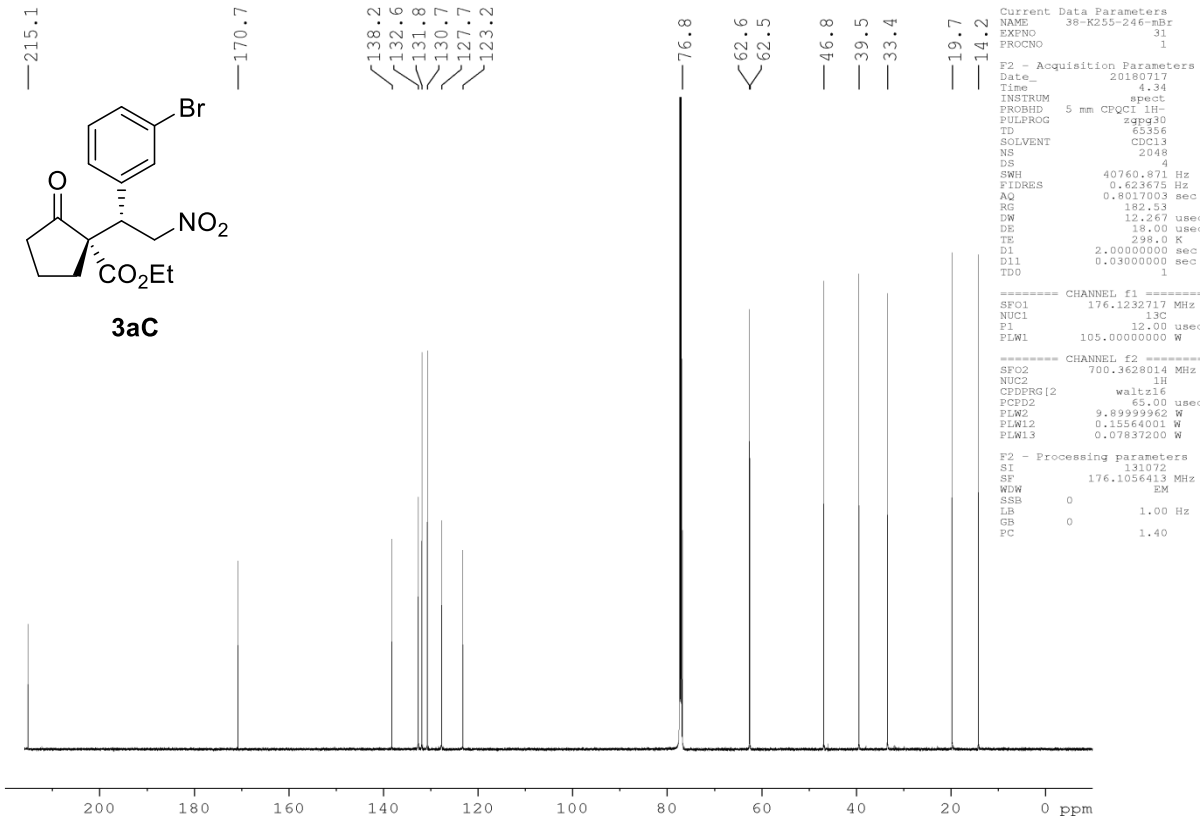

7.32 7.31 7.29 7.28 7.20 7.19 7.18 5.31 5.29 5.28 5.26 4.85 4.84 4.82 4.82 4.27 4.25 4.25 4.23 4.22 4.20 4.20 4.19 4.18 4.18 4.17 2.40 2.39 2.31 2.30 2.30 2.29 2.02 2.00 2.00 1.98 1.96 1.95 1.94 1.82 1.81 1.80 1.43 1.42 1.42 1.41 1.28 1.27 1.26
O
Ph
NO2
CO2Et
3aA
water
8 7 6 5 4 3 2 1 0 ppm
2.86 1.92 1.00 0.99 2.96 1.00 1.00 2.01 1.02 1.04 3.16
Current Data Parameters
NAME 38-K255-262.1
EXPNO 20
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180713
Time 9.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5859712 sec
RG 362
DW 48.400 usec
DE 10.00 usec
TE 296.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.23 usec
PL1 1.00 dB
PL1W 19.75309753 W
SFO1 500.1560886 MHz
F2 - Processing parameters
SI 16384
SF 500.1530162 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

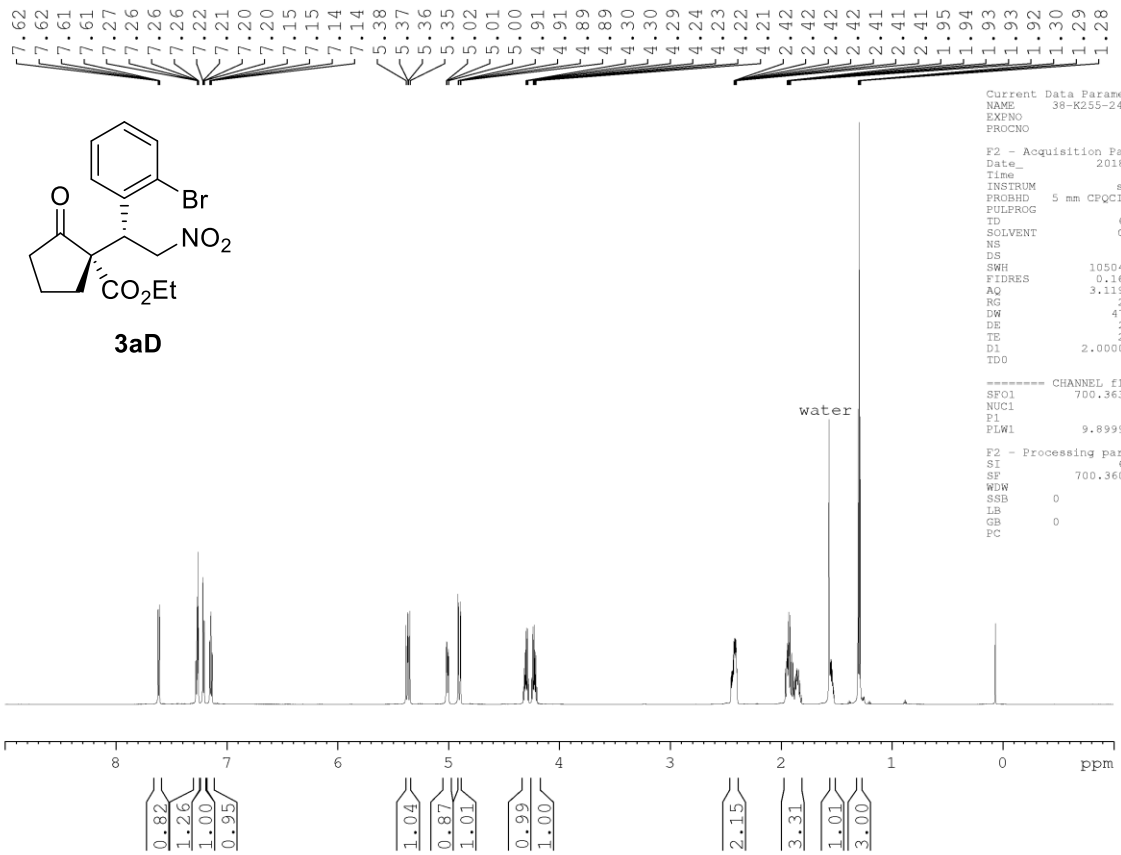

215.7 171.2 135.7 129.3 129.1 128.6 77.1 62.4 62.4 47.4 39.7 33.7 19.7 14.2
O
Ph
NO2
CO2Et
3aA
220 200 180 160 140 120 100 80 60 40 20 ppm
Current Data Parameters
NAME 38-K255-262.1
EXPNO 21
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180713
Time 10.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 32894.738 Hz
FIDRES 0.501934 Hz
AQ 0.9961472 sec
RG 2300
DW 15.200 usec
DE 10.00 usec
TE 296.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.20 usec
PL1 1.50 dB
PL1W 51.74793243 W
SFO1 125.7761482 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.00 dB
PL12 19.99 dB
PL13 21.00 dB
PL2W 19.75309753 W
PL12W 0.24925002 W
PL13W 0.19753097 W
SFO2 500.1550006 MHz
F2 - Processing parameters
SI 32768
SF 125.7635570 MHz
WDW EM
SSB 0
LB 1.00 Hz

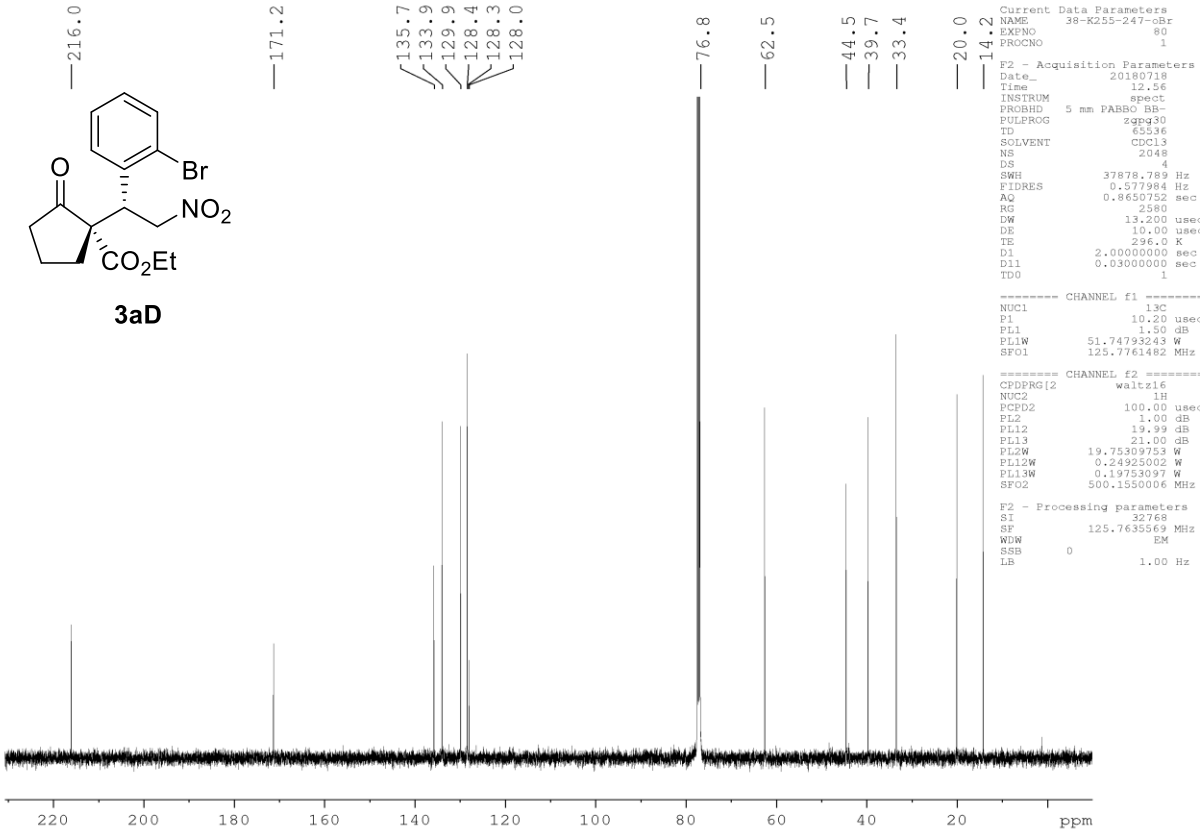

7.44 7.43 7.08 7.07 5.27 5.25 5.25 5.23 4.80 4.80 4.78 4.78 4.26 4.25 4.25 4.24 4.20 4.19 4.19 4.17 4.17 4.17 4.16 4.15
2.43 2.32 2.32 2.31 2.30 2.30 2.01 2.00 1.98 1.97 1.96 1.91 1.91 1.90 1.89 1.88 1.84 1.83 1.53 1.53 1.52 1.52 1.28 1.27 1.26
Br
O
NO2
CO2Et
3aB
water
ppm
1.76
2.02
1.05
1.04
3.02
1.08
1.09
1.09
2.15
1.09
3.00

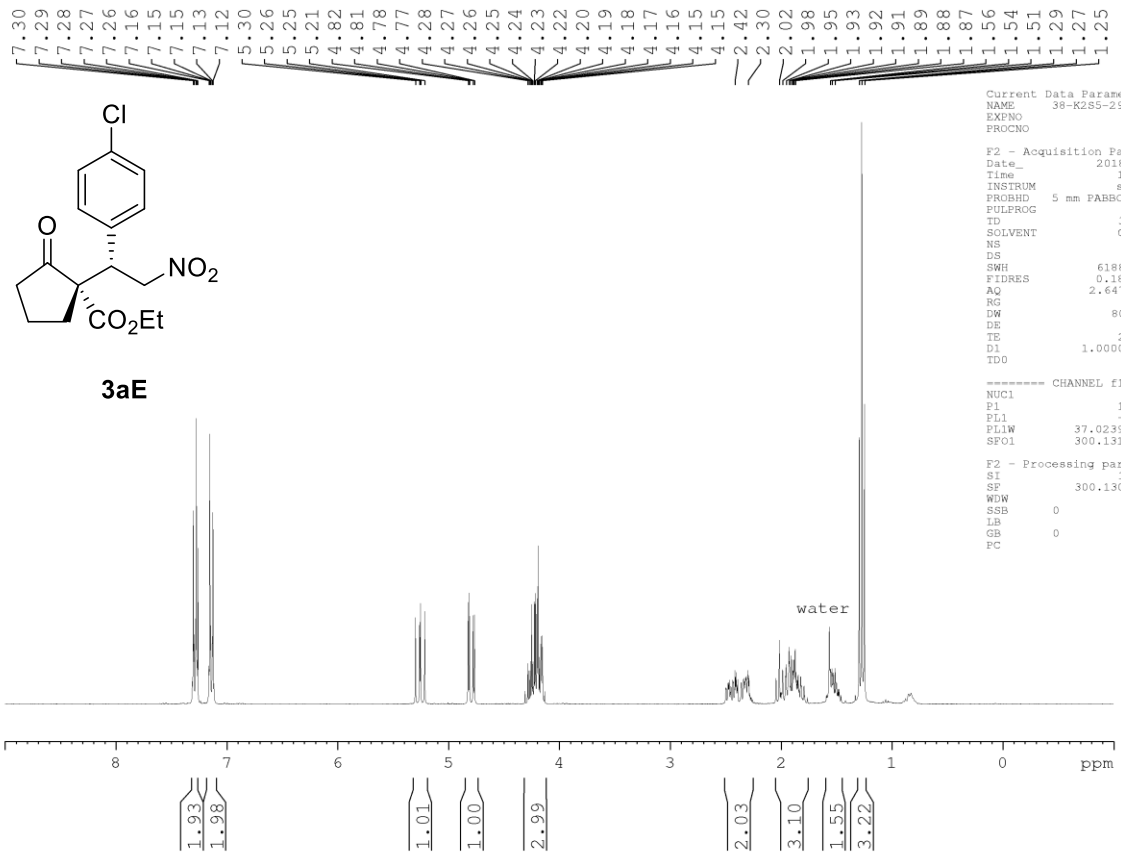

215.3
170.9
134.8
132.3
131.0
122.8
76.8
62.6
62.3
46.8
39.6
33.6
19.7
14.2
Br
O
NO2
CO2Et
3aB
ppm

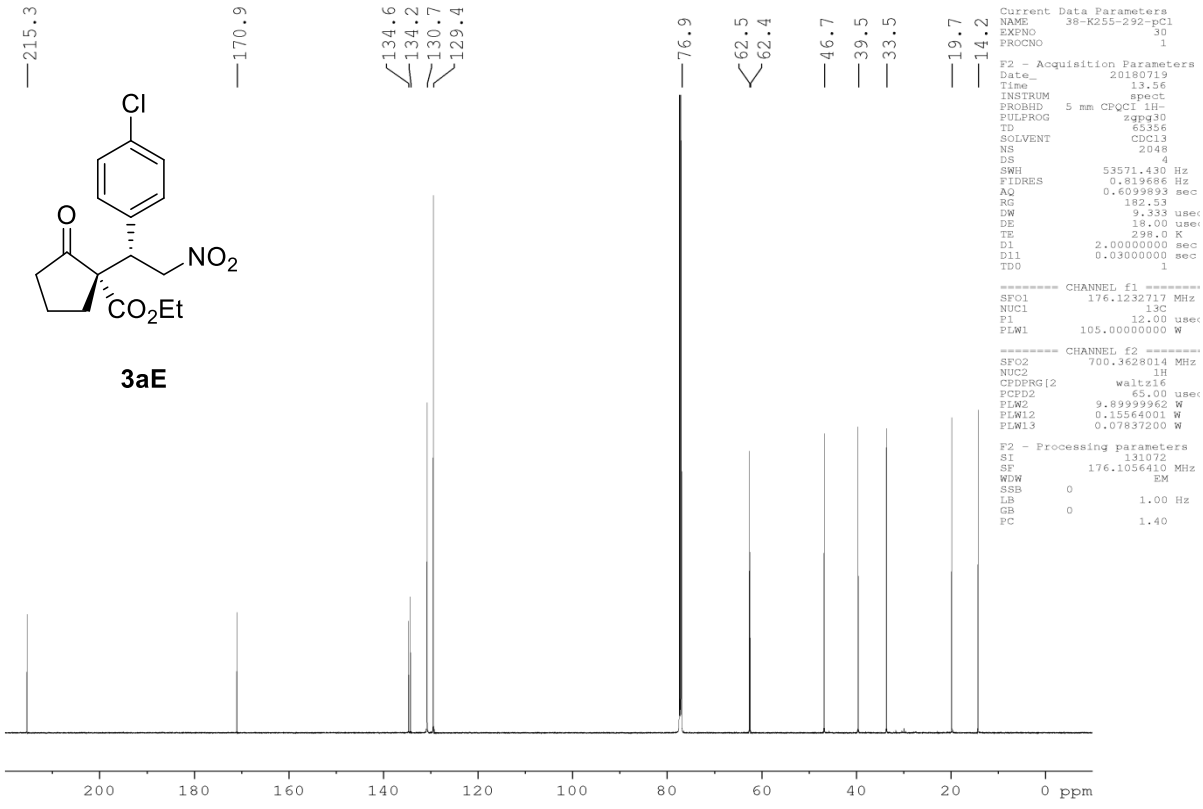

7.43 7.43 7.42 7.42 7.35 7.20 7.19 7.17 7.14 7.13
5.24 5.23 5.22 5.21 4.80 4.80 4.78 4.78 4.26 4.25 4.24 4.23 4.20 4.19 4.19 4.18 4.18 4.16 4.16
2.44 2.34 2.33 2.02 2.01 2.00 1.92 1.92 1.90 1.90 1.89 1.85 1.55 1.55 1.55 1.54 1.54 1.28 1.27 1.26
Br
O
NO2
CO2Et
3aC
Current Data Parameters
NAME 38-K255-246-mBr
EXPNO 30
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180717
Time 2.55
INSTRUM spect
PROBHD 5 mm CPQCI 1H-
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 10504.202 Hz
FIDRES 0.160281 Hz
AQ 3.1195135 sec
RG 20.5
DW 47.600 usec
DE 20.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 700.3632917 MHz
NUC1 1H
P1 8.15 usec
PLW1 9.89999962 W
F2 - Processing parameters
SI 65536
SF 700.3600193 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
0.83 0.91 0.96 0.96 1.02 1.01 2.96 1.04 1.02 1.05 2.12 1.80 3.00

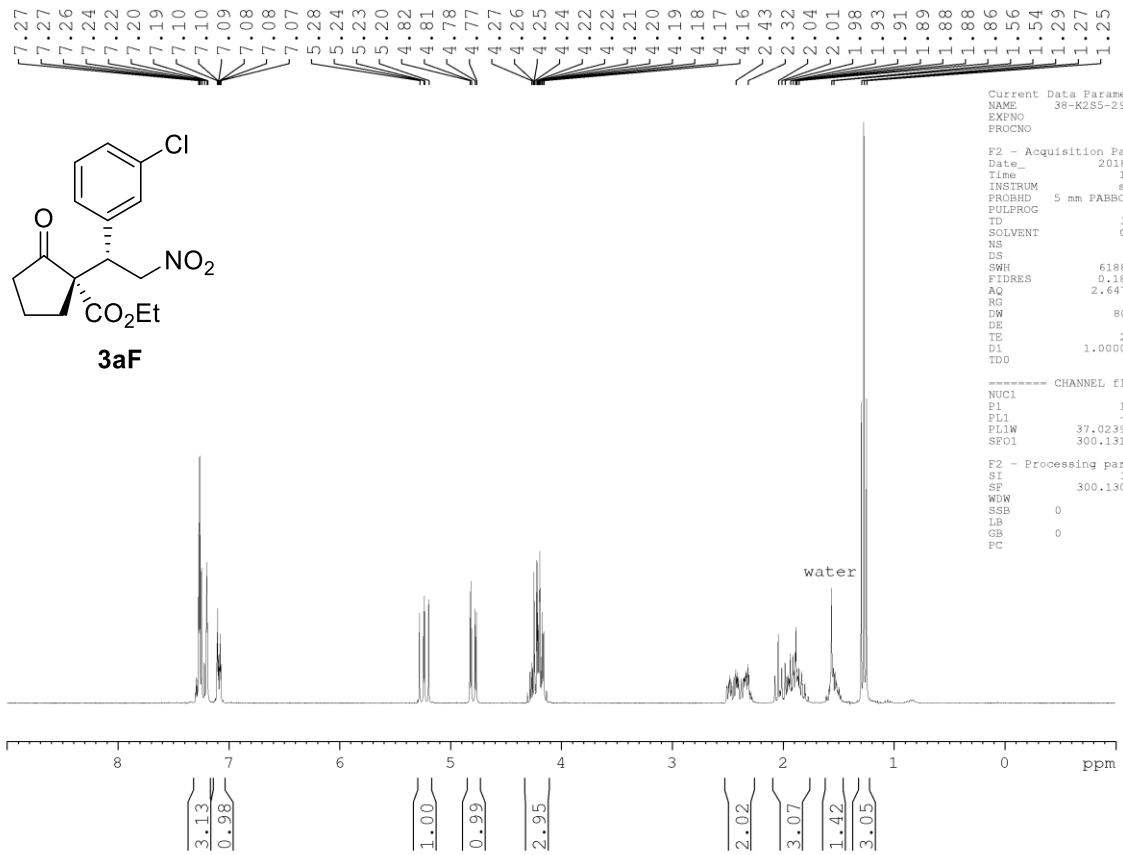

215.1 170.7 138.2 132.6 131.8 130.7 127.7 123.2 76.8 62.6 62.5 46.8 39.5 33.4 19.7 14.2
Br
O
NO2
CO2Et
3aC
Current Data Parameters
NAME 38-K255-246-mBr
EXPNO 31
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180717
Time 4.34
INSTRUM spect
PROBHD 5 mm CPQCI 1H-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 40760.871 Hz
FIDRES 0.623675 Hz
AQ 0.8017003 sec
RG 182.53
DW 12.267 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 176.1232717 MHz
NUC1 13C
P1 12.00 usec
PLW1 105.00000000 W
======== CHANNEL f2 ========
SFO2 700.3628014 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 65.00 usec
PLW2 9.89999962 W
PLW12 0.15564001 W
PLW13 0.07837200 W
F2 - Processing parameters
SI 131072
SF 176.1056413 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm

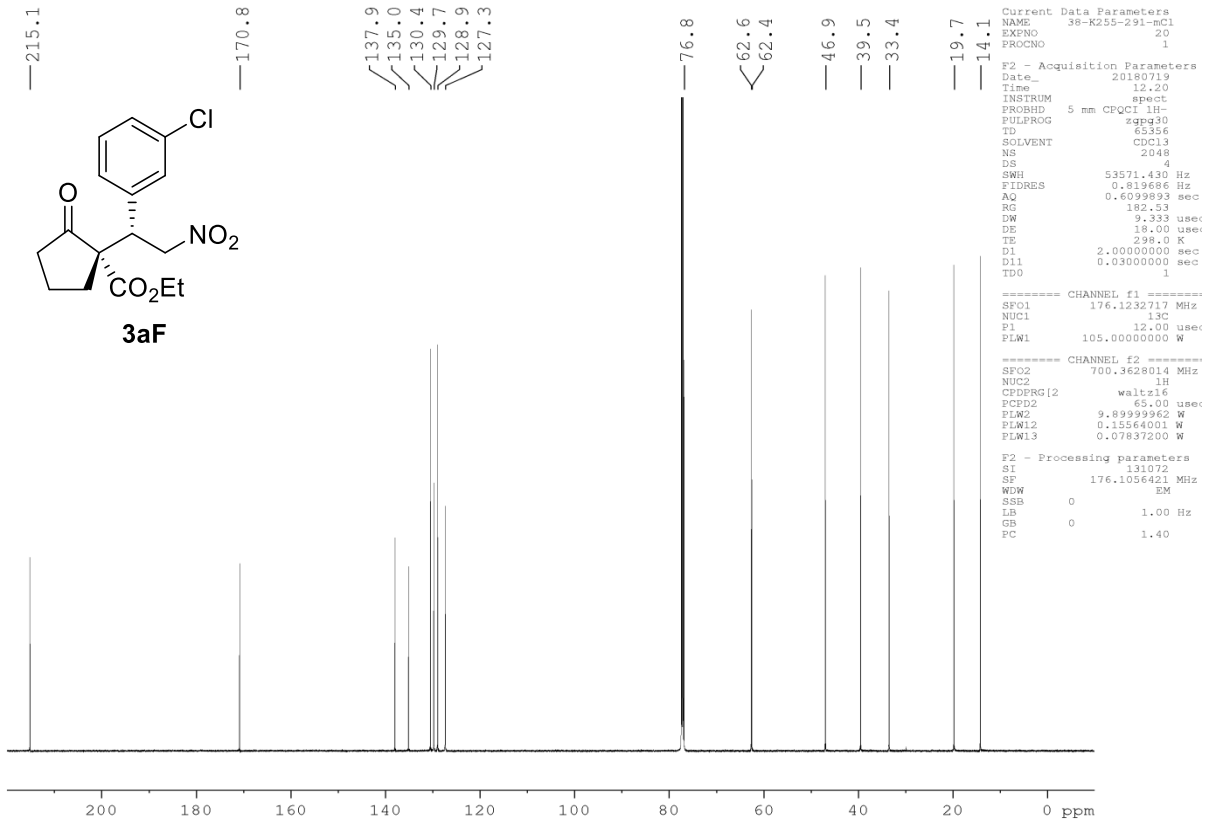

7.62 7.62 7.61 7.61 7.27 7.26 7.26 7.26 7.22 7.21 7.20 7.20 7.15 7.14 7.14
5.38 5.37 5.36 5.35 5.02 5.01 5.00 4.91 4.89 4.89 4.30 4.30 4.29 4.24 4.23 4.22 4.21
2.42 2.42 2.42 2.42 2.41 2.41 2.41 1.95 1.94 1.93 1.93 1.92 1.30 1.29 1.28
Br
O
NO2
CO2Et
3aD
water
Current Data Parameters
NAME 38-K255-247-oBr
EXPNO 40
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180717
Time 4.41
INSTRUM spect
PROBHD 5 mm CPQCI 1H-
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 10504.202 Hz
FIDRES 0.160281 Hz
AQ 3.1195135 sec
RG 21.86
DW 47.600 usec
DE 20.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 700.3632917 MHz
NUC1 1H
P1 8.15 usec
PLW1 9.89999962 W
F2 - Processing parameters
SI 65536
SF 700.3600176 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
0.82 1.26 1.00 0.95 1.04 0.87 1.01 0.99 1.00 2.15 3.31 1.01 3.00

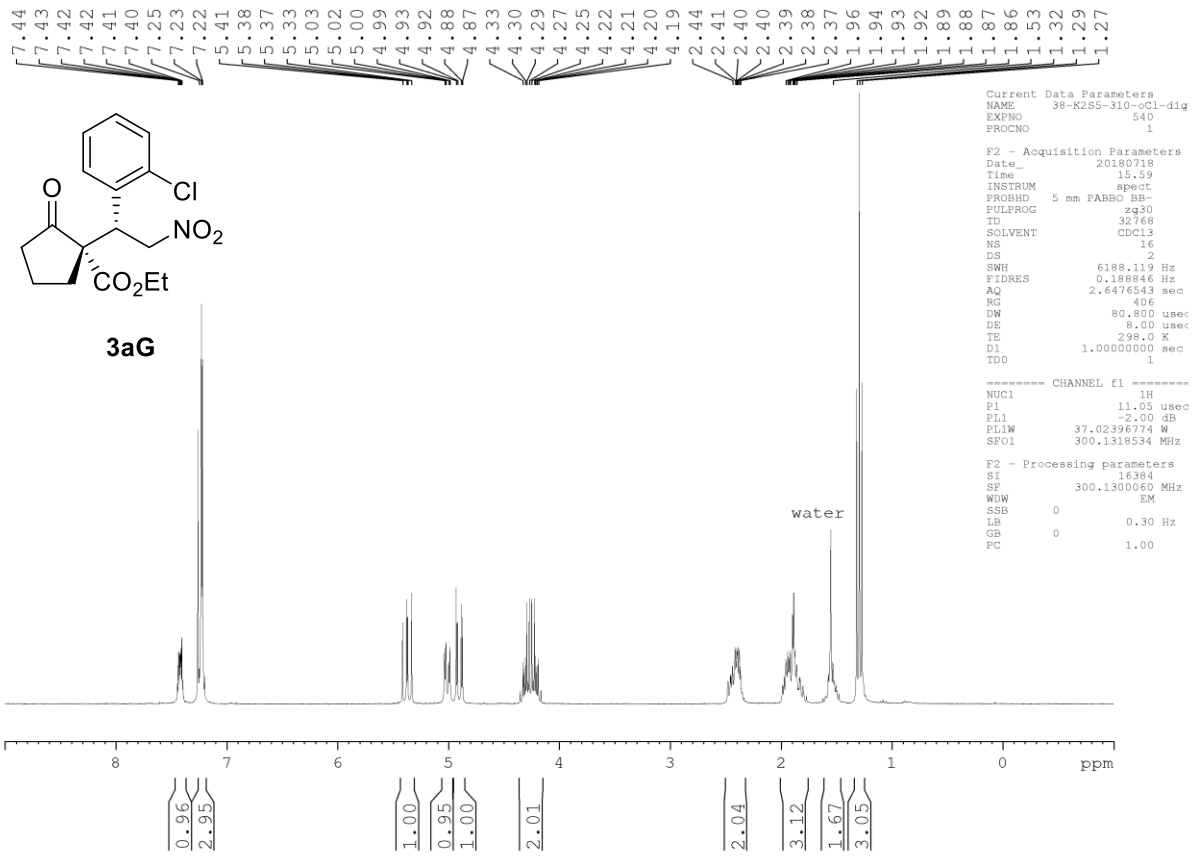

216.0 171.2 135.7 133.9 129.9 128.4 128.3 128.0 76.8 62.5 44.5 39.7 33.4 20.0 14.2
Br
O
NO2
CO2Et
3aD
Current Data Parameters
NAME 38-K255-247-oBr
EXPNO 80
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180718
Time 12.56
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 37878.789 Hz
FIDRES 0.577984 Hz
AQ 0.8650752 sec
RG 2580
DW 13.200 usec
DE 10.00 usec
TE 296.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.20 usec
PL1 1.50 dB
PL1W 51.74793243 W
SFO1 125.7761482 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.00 dB
PL12 19.99 dB
PL13 21.00 dB
PL2W 19.75309753 W
PL12W 0.24925002 W
PL13W 0.19753097 W
SFO2 500.1550006 MHz
F2 - Processing parameters
SI 32768
SF 125.7635569 MHz
WDW EM
SSB 0
LB 1.00 Hz
220 200 180 160 140 120 100 80 60 40 20 ppm

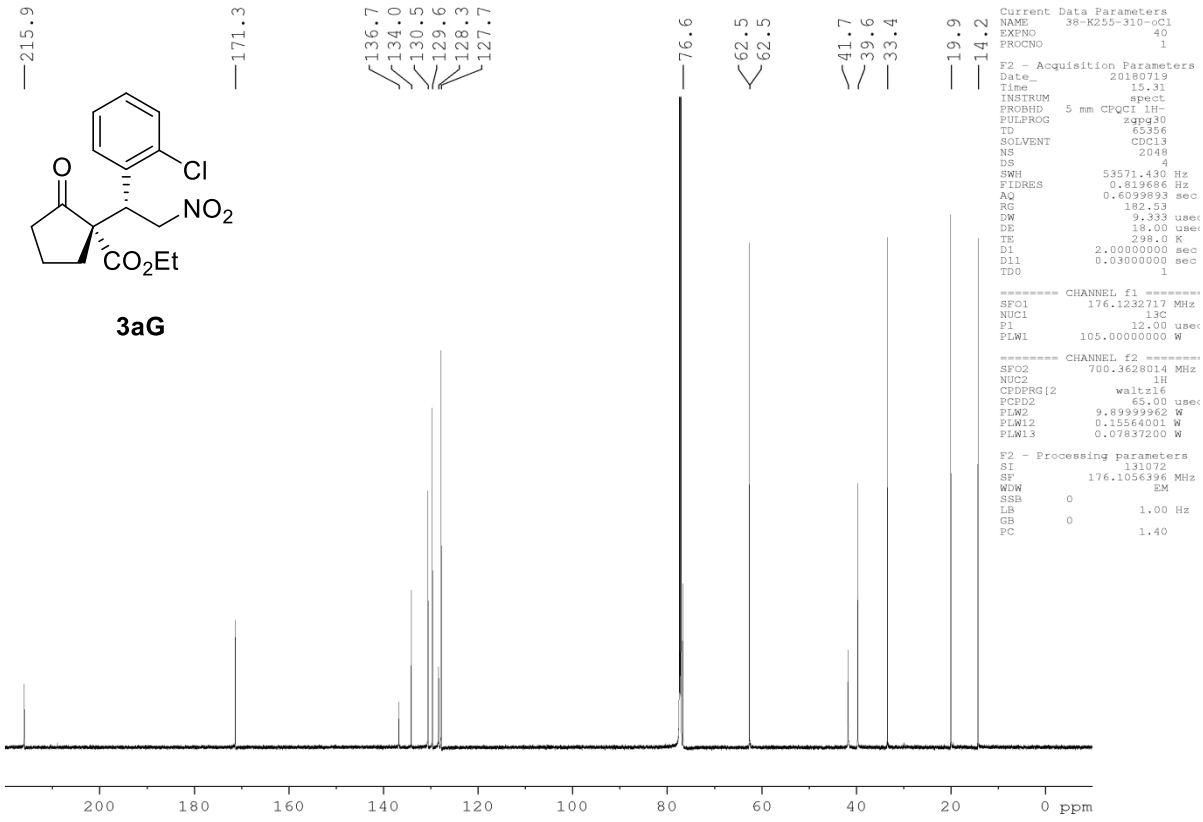

7.30 7.29 7.28 7.27 7.26 7.16 7.15 7.15 7.13 7.12 5.30 5.26 5.25 5.21 4.82 4.81 4.78 4.77 4.28 4.27 4.26 4.25 4.24 4.23 4.22 4.20 4.19 4.18 4.17 4.16 4.15 2.42 2.30 2.02 1.98 1.95 1.93 1.92 1.91 1.89 1.88 1.87 1.56 1.54 1.51 1.29 1.27 1.25
Cl
O
NO2
CO2Et
3aE
water
8 7 6 5 4 3 2 1 0 ppm
1.93 1.98 1.01 1.00 2.99 2.03 3.10 1.55 3.22
Current Data Parameters
NAME 38-K2S5-292-pC1_dig
EXPNO 440
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180718
Time 14.54
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 322
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300060 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

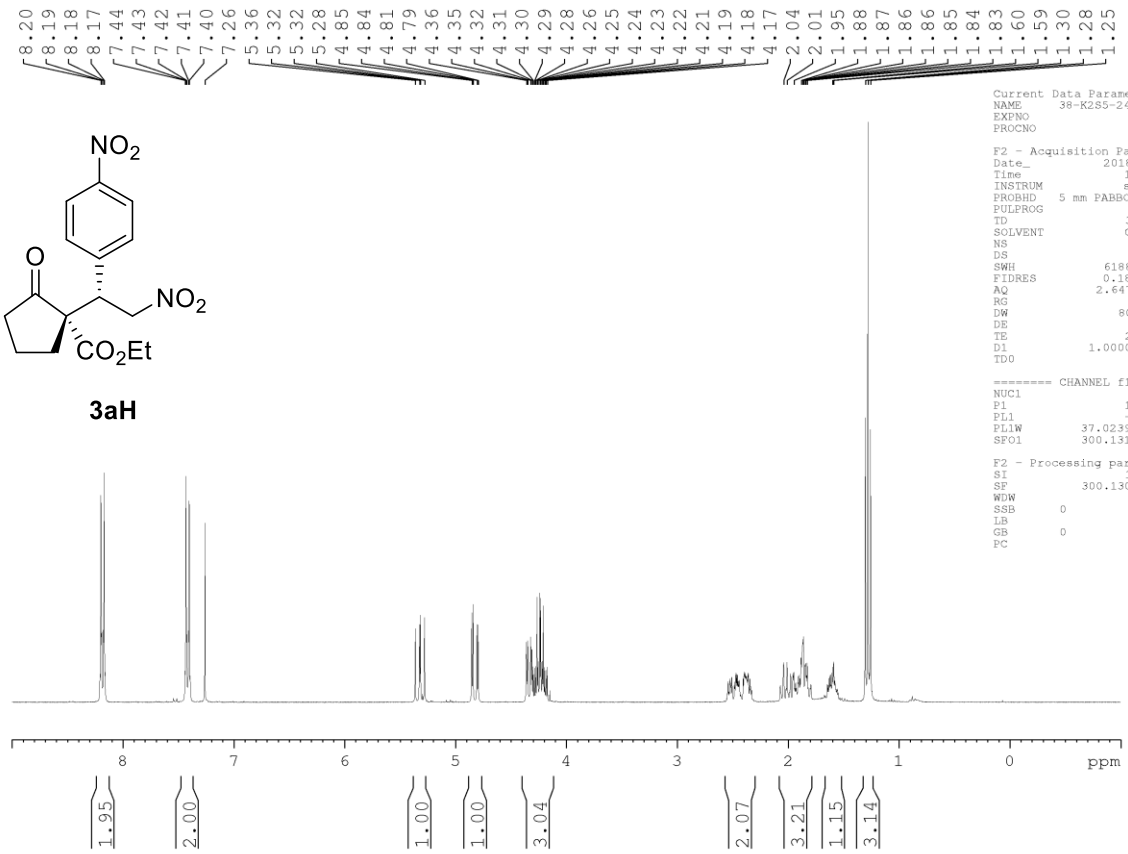

215.3 170.9 134.6 134.2 130.7 129.4 76.9 62.5 62.4 46.7 39.5 33.5 19.7 14.2
Cl
O
NO2
CO2Et
3aE
200 180 160 140 120 100 80 60 40 20 0 ppm
Current Data Parameters
NAME 38-K2S5-292-pC1
EXPNO 30
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180719
Time 13.56
INSTRUM spect
PROBHD 5 mm CPQCI 1H-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 53571.430 Hz
FIDRES 0.819686 Hz
AQ 0.6099893 sec
RG 182.53
DW 9.333 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 176.1232717 MHz
NUC1 13C
P1 12.00 usec
PLW1 105.00000000 W
======== CHANNEL f2 ========
SFO2 700.3628014 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 65.00 usec
PLW2 9.89999962 W
PLW12 0.15564001 W
PLW13 0.07837200 W
F2 - Processing parameters
SI 131072
SF 176.1056410 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

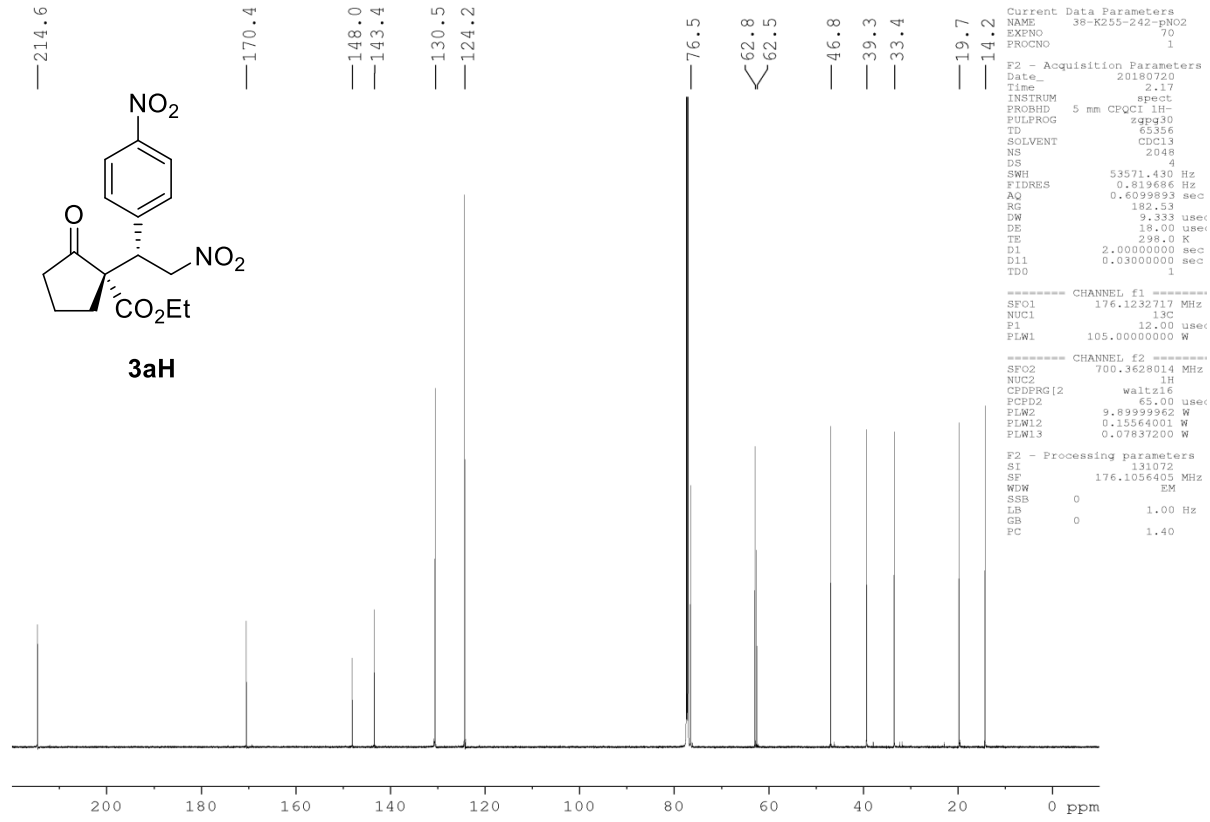

7.27 7.27 7.26 7.24 7.22 7.20 7.19 7.10 7.10 7.09 7.08 7.08 7.07
5.28 5.24 5.23 5.20 4.82 4.81 4.78 4.77
4.27 4.26 4.25 4.24 4.22 4.22 4.21 4.20 4.19 4.18 4.17 4.16
2.43 2.32 2.04 2.01 1.98 1.93 1.91 1.89 1.88 1.88 1.86 1.56 1.54 1.29 1.27 1.25
Cl
O
NO2
CO2Et
3aF
water
8 7 6 5 4 3 2 1 0 ppm
3.13 0.98 1.00 0.99 2.95 2.02 3.07 1.42 3.05
Current Data Parameters
NAME 38-K2S5-291-mC1-dig
EXPNO 530
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180718
Time 15.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 322
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

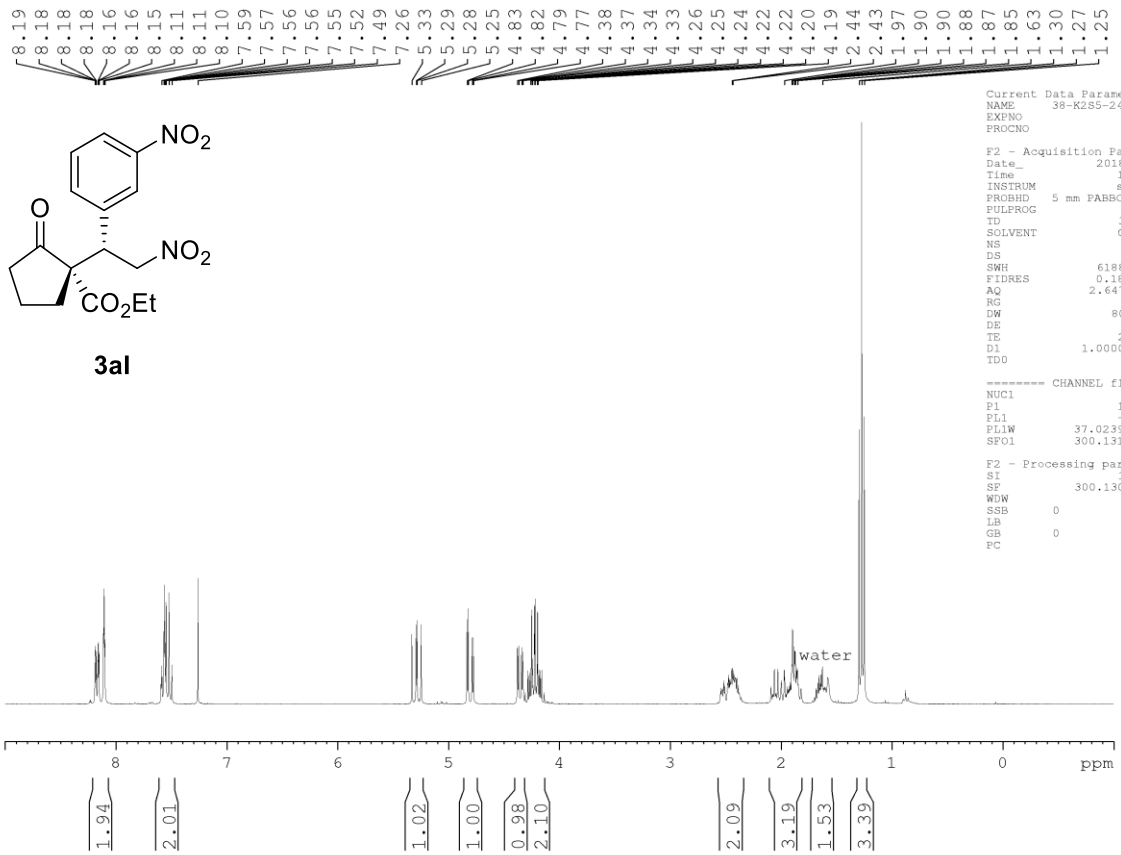

215.1
170.8
137.9 135.0 130.4 129.7 128.9 127.3
76.8
62.6 62.4
46.9
39.5
33.4
19.7
14.1
Cl
O
NO2
CO2Et
3aF
200 180 160 140 120 100 80 60 40 20 0 ppm
Current Data Parameters
NAME 38-K2S5-291-mC1
EXPNO 20
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180719
Time 12.20
INSTRUM spect
PROBHD 5 mm CPQCI 1H-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 53571.430 Hz
FIDRES 0.819686 Hz
AQ 0.6099893 sec
RG 182.53
DW 9.333 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 176.1232717 MHz
NUC1 13C
P1 12.00 usec
PLW1 105.00000000 W
======== CHANNEL f2 ========
SFO2 700.3628014 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 65.00 usec
PLW2 9.89999962 W
PLW12 0.15564001 W
PLW13 0.07837200 W
F2 - Processing parameters
SI 131072
SF 176.1056421 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

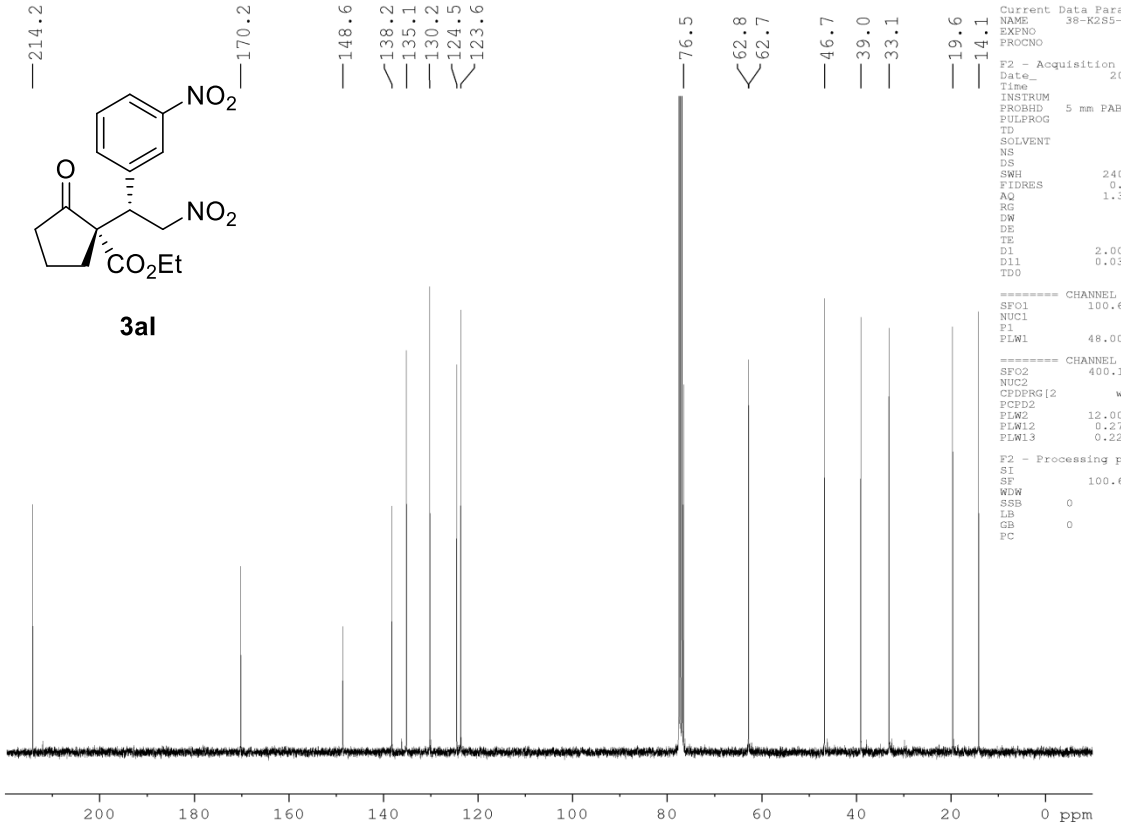

7.44 7.43 7.42 7.42 7.41 7.40 7.25 7.23 7.22
5.41 5.38 5.37 5.33 5.03 5.02 5.00 4.99 4.93 4.92 4.88 4.87
4.33 4.30 4.29 4.27 4.25 4.22 4.21 4.20 4.19
2.44 2.41 2.40 2.40 2.39 2.38 2.37 1.96 1.94 1.93 1.92 1.89 1.88 1.87 1.86 1.53 1.32 1.29 1.27
Cl
O
NO2
CO2Et
3aG
water
Current Data Parameters
NAME 38-K2S5-310-oCl-dig
EXPNO 540
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180718
Time 15.59
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 406
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300060 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
0.96 2.95 1.00 0.95 1.00 2.01 2.04 3.12 1.67 3.05

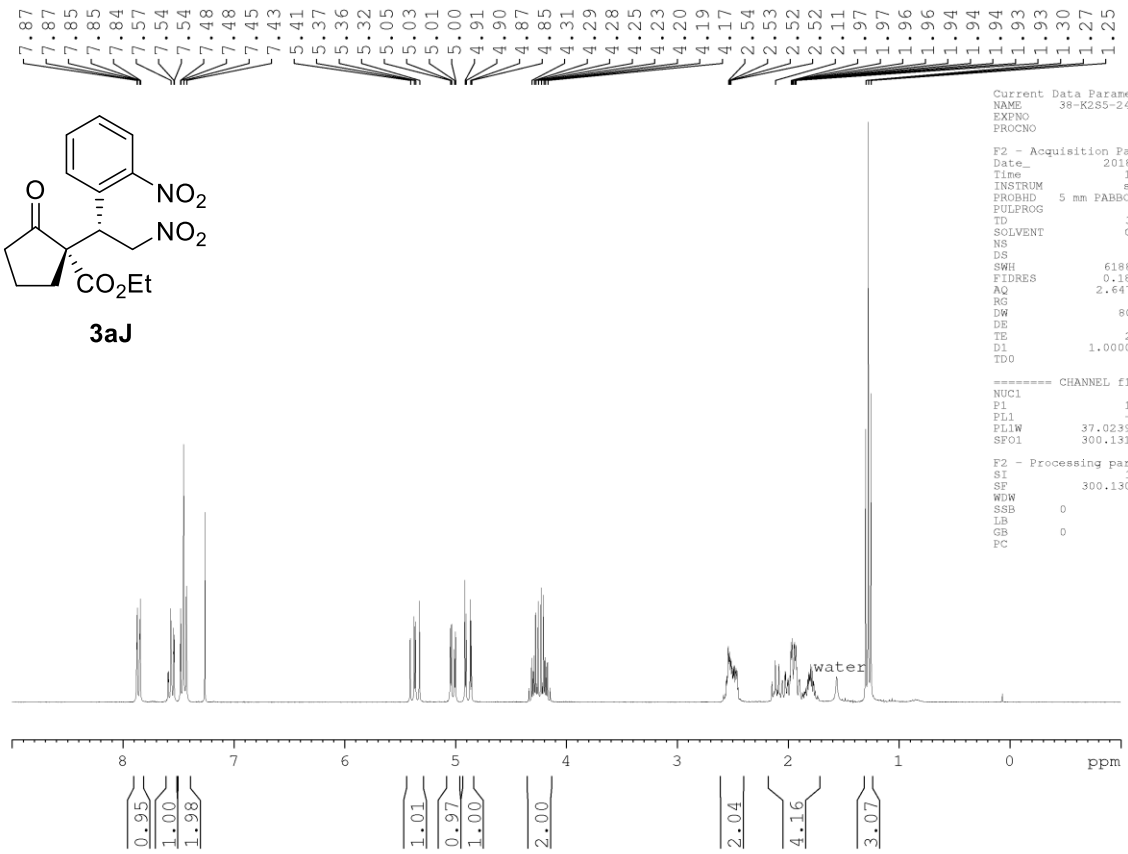

215.9
171.3
136.7
134.0
130.5
129.6
128.3
127.7
76.6
62.5
62.5
41.7
39.6
33.4
19.9
14.2
Cl
O
NO2
CO2Et
3aG
Current Data Parameters
NAME 38-K2S5-310-oC1
EXPNO 40
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180719
Time 15.31
INSTRUM spect
PROBHD 5 mm CPQCI 1H-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 53571.430 Hz
FIDRES 0.819686 Hz
AQ 0.6099893 sec
RG 182.53
DW 9.333 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 176.1232717 MHz
NUC1 13C
P1 12.00 usec
PLW1 105.00000000 W
======== CHANNEL f2 ========
SFO2 700.3628014 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 65.00 usec
PLW2 9.89999962 W
PLW12 0.15564001 W
PLW13 0.07837200 W
F2 - Processing parameters
SI 131072
SF 176.1056396 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm


8.20
8.19
8.18
8.17
7.44
7.43
7.42
7.41
7.40
7.26
5.36
5.32
5.32
5.28
4.85
4.84
4.81
4.79
4.36
4.35
4.32
4.31
4.30
4.29
4.28
4.26
4.25
4.24
4.23
4.22
4.21
4.19
4.18
4.17
2.04
2.01
1.95
1.88
1.87
1.86
1.86
1.85
1.84
1.83
1.60
1.59
1.30
1.28
1.25
NO2
O
NO2
CO2Et
3aH
Current Data Parameters
NAME 38-K2S5-242-pNO2_di
EXPNO 710
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180718
Time 18.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 362
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
0
ppm
1.95
2.00
1.00
1.00
3.04
2.07
3.21
1.15
3.14


214.6
170.4
148.0
143.4
130.5
124.2
76.5
62.8
62.5
46.8
39.3
33.4
19.7
14.2
NO2
O
NO2
CO2Et
3aH
Current Data Parameters
NAME 38-K2S5-242-pNO2
EXPNO 70
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180720
Time 2.17
INSTRUM spect
PROBHD 5 mm CPQCI 1H-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 53571.430 Hz
FIDRES 0.819686 Hz
AQ 0.6099893 sec
RG 182.53
DW 9.333 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 176.1232717 MHz
NUC1 13C
P1 12.00 usec
PLW1 105.00000000 W
======== CHANNEL f2 ========
SFO2 700.3628014 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 65.00 usec
PLW2 9.89999962 W
PLW12 0.15564001 W
PLW13 0.07837200 W
F2 - Processing parameters
SI 131072
SF 176.1056405 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0 ppm


8.19 8.18 8.18 8.18 8.16 8.16 8.15 8.11 8.11 8.10 7.59 7.57 7.56 7.56 7.55 7.52 7.49 7.26 5.33 5.29 5.28 5.25 4.83 4.82 4.79 4.77 4.38 4.37 4.34 4.33 4.26 4.25 4.24 4.22 4.22 4.20 4.19 2.44 2.43 1.97 1.90 1.90 1.88 1.87 1.85 1.63 1.30 1.27 1.25
NO2
NO2
O
CO2Et
3al
water
ppm
1.94
2.01
1.02
1.00
0.98
2.10
2.09
3.19
1.53
3.39


214.2
170.2
148.6
138.2
135.1
130.2
124.5
123.6
76.5
62.8
62.7
46.7
39.0
33.1
19.6
14.1
NO2
NO2
O
CO2Et
3al
ppm

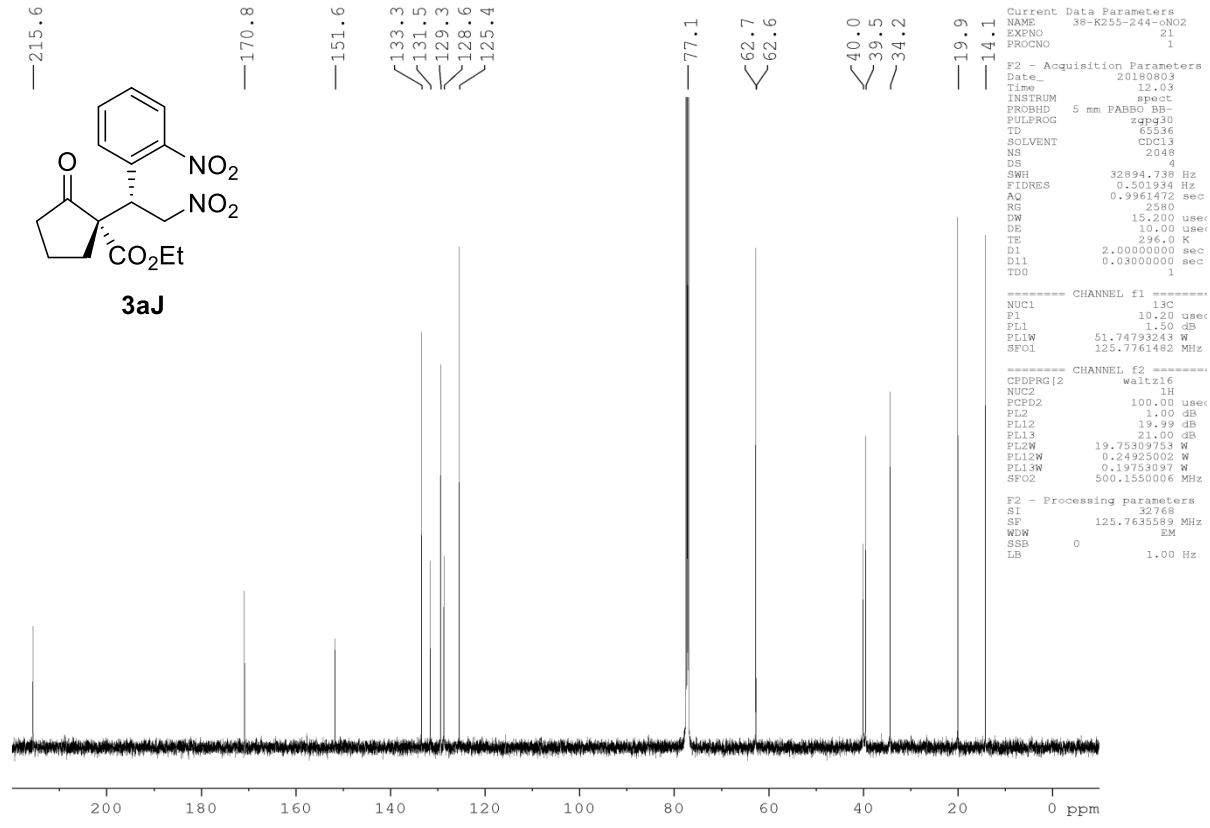



```
Current Data Parameters
NAME      38-K2S5-244-oNO2
EXPNO                  290
PROCNO                   1

F2 - Acquisition Parameters
Date_           20180802
Time              13.43
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           6188.119 Hz
FIDRES        0.188846 Hz
AQ            2.6476543 sec
RG                 322
DW              80.800 usec
DE               8.00 usec
TE              298.1 K
D1            1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1              11.05 usec
PL1             -2.00 dB
PL1W        37.02396774 W
SFO1        300.1318534 MHz

F2 - Processing parameters
SI               16384
SF          300.1300062 MHz
WDW                 EM
SSB       0
LB              0.30 Hz
GB        0
PC              1.00
```

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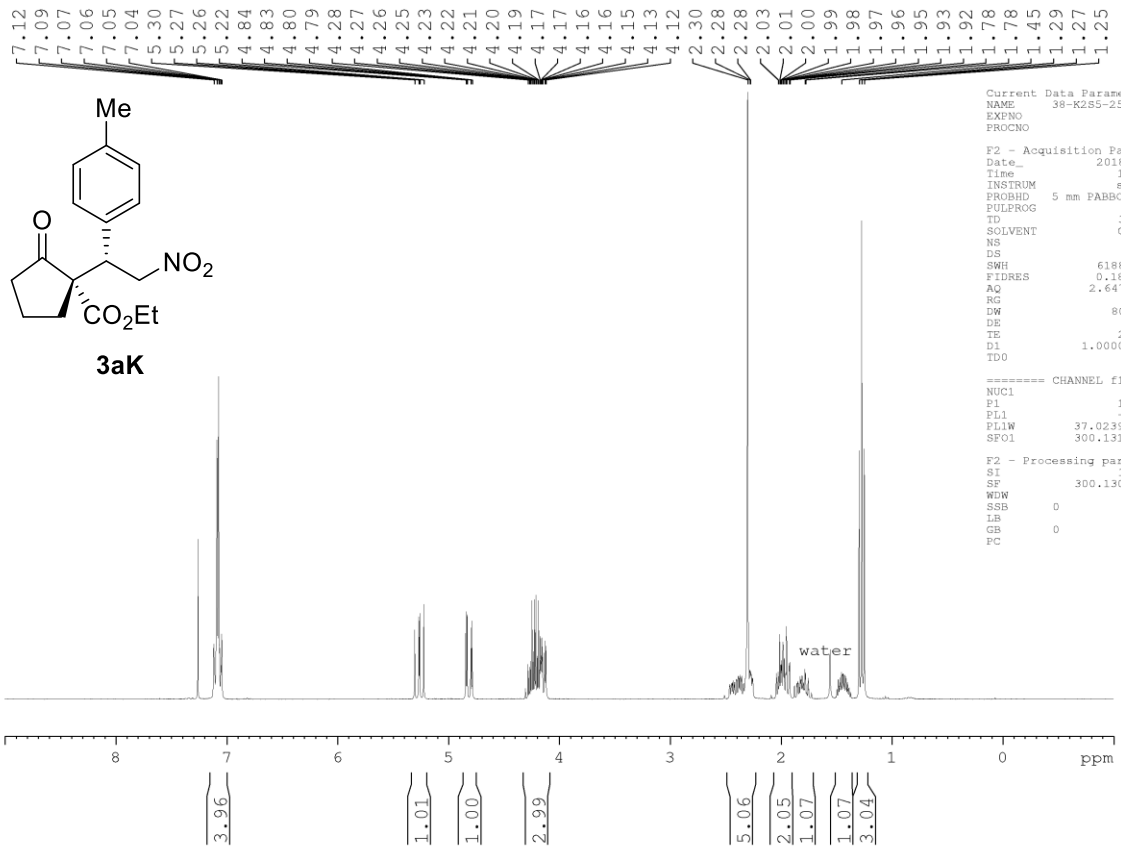
Current Data Parameters
NAME      38-K2S5-244-oNO2
EXPNO                  21
PROCNO                  1

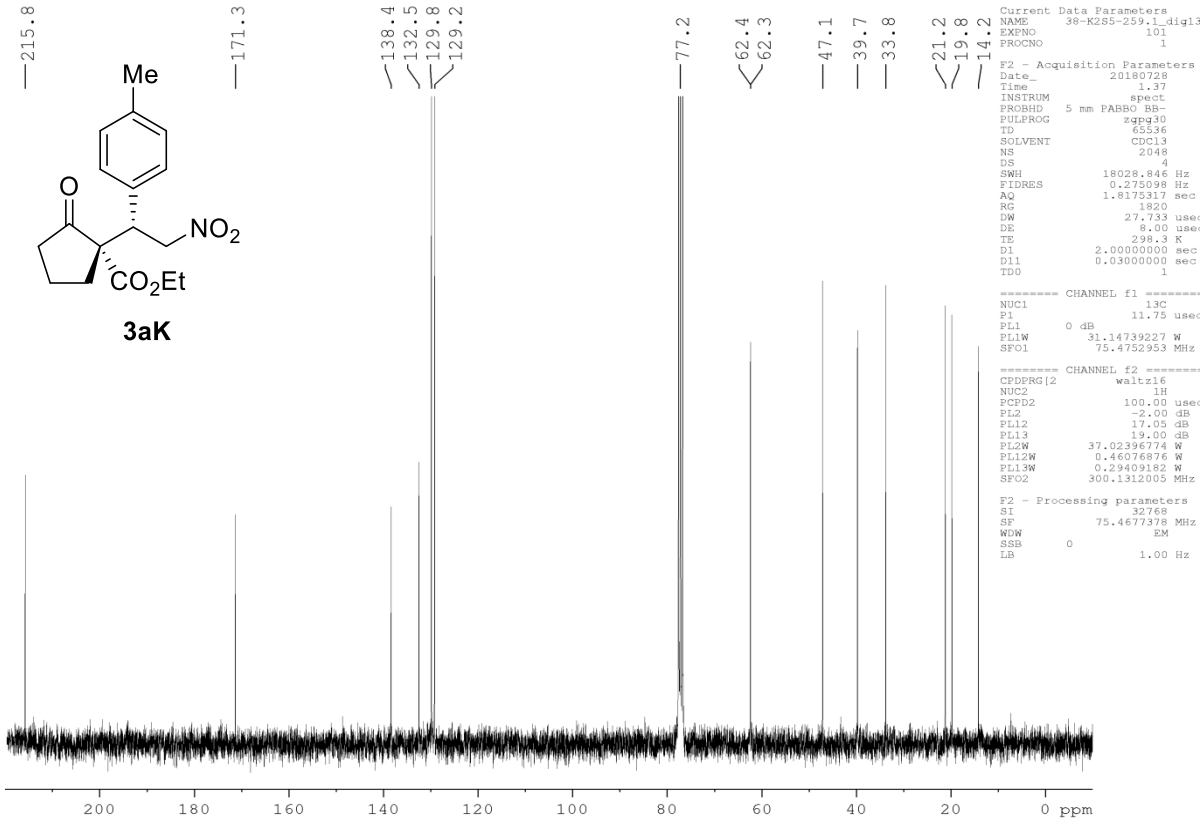
F2 - Acquisition Parameters
Date_           20180803
Time              12.03
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                2048
DS                   4
SWH          32894.738 Hz
FIDRES        0.501934 Hz
AQ            0.9961472 sec
RG                2580
DW              15.200 usec
DE              10.00 usec
TE              296.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                  1

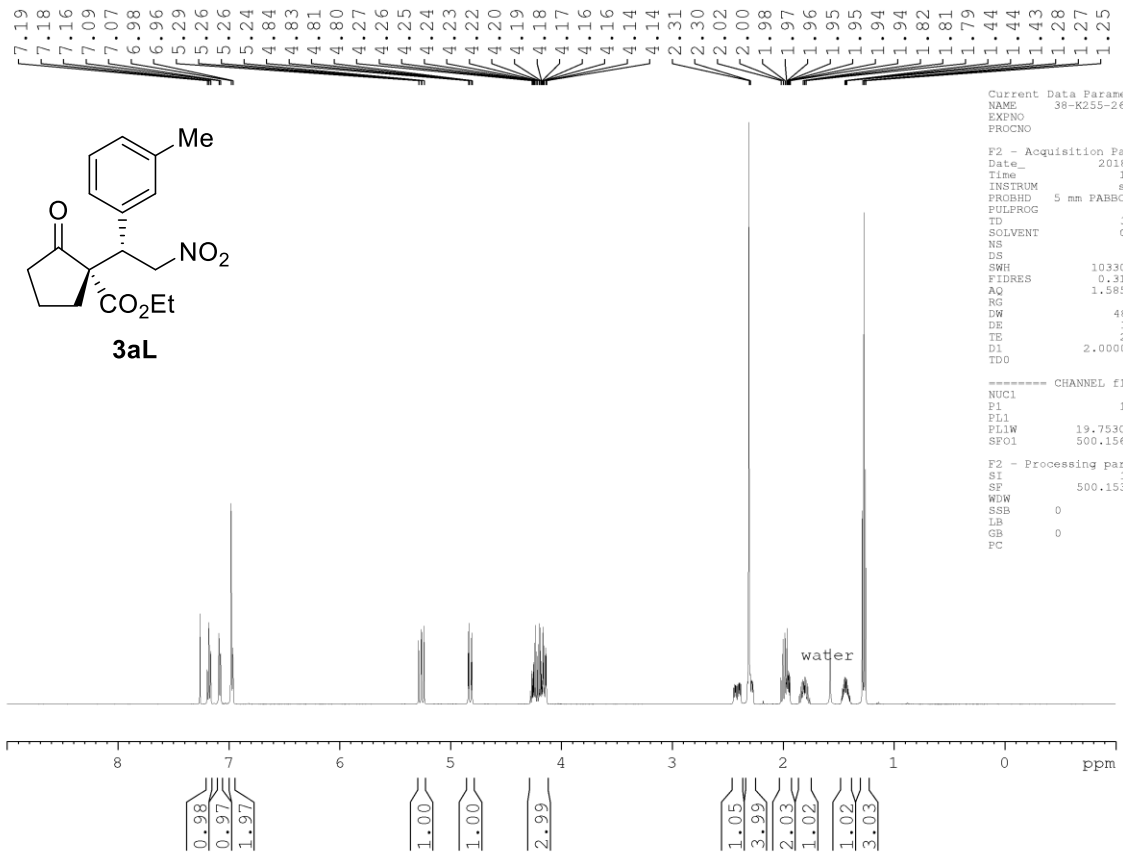
======== CHANNEL f1 ========
NUC1                13C
P1              10.20 usec
PL1              1.50 dB
PL1W        51.74793243 W
SFO1        125.7761482 MHz

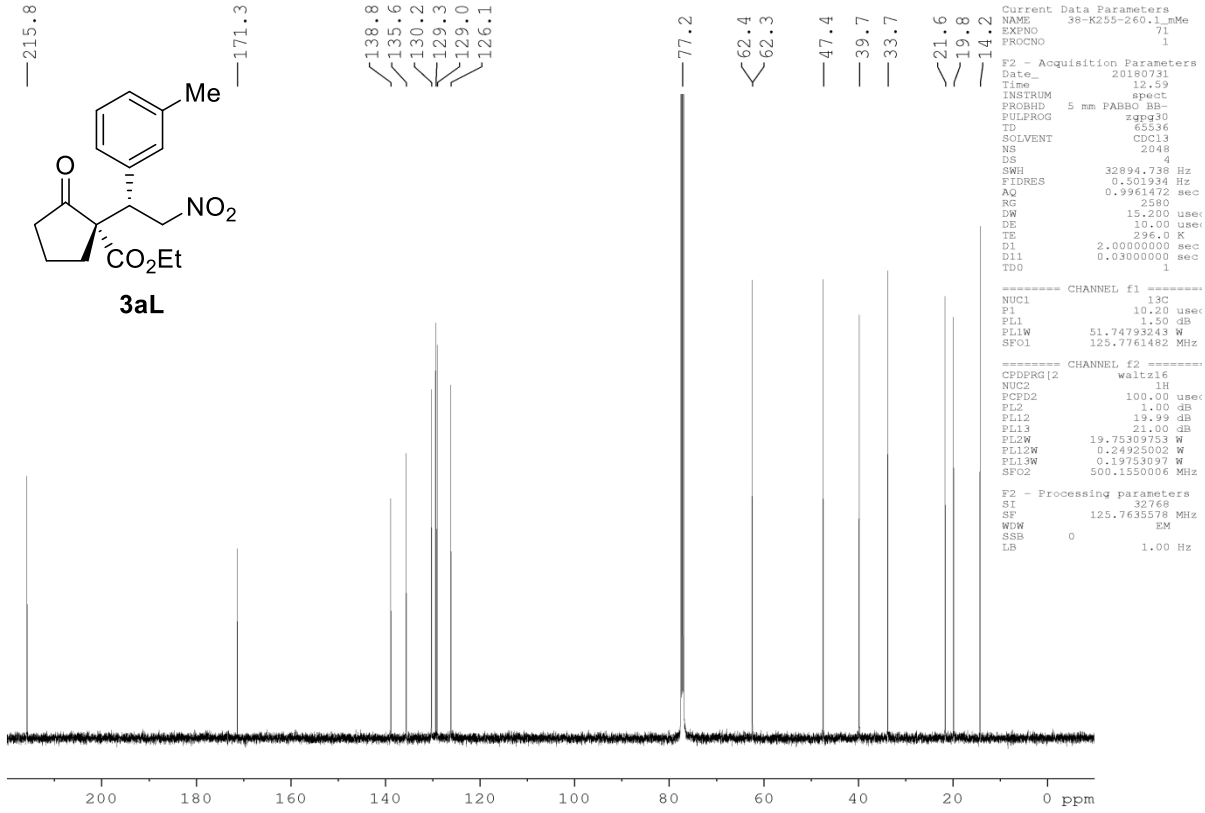
======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                1H
PCPD2           100.00 usec
PL2              1.00 dB
PL12            19.99 dB
PL13            21.00 dB
PL2W        19.75309753 W
PL12W        0.24925002 W
PL13W        0.19753097 W
SFO2        500.1550006 MHz

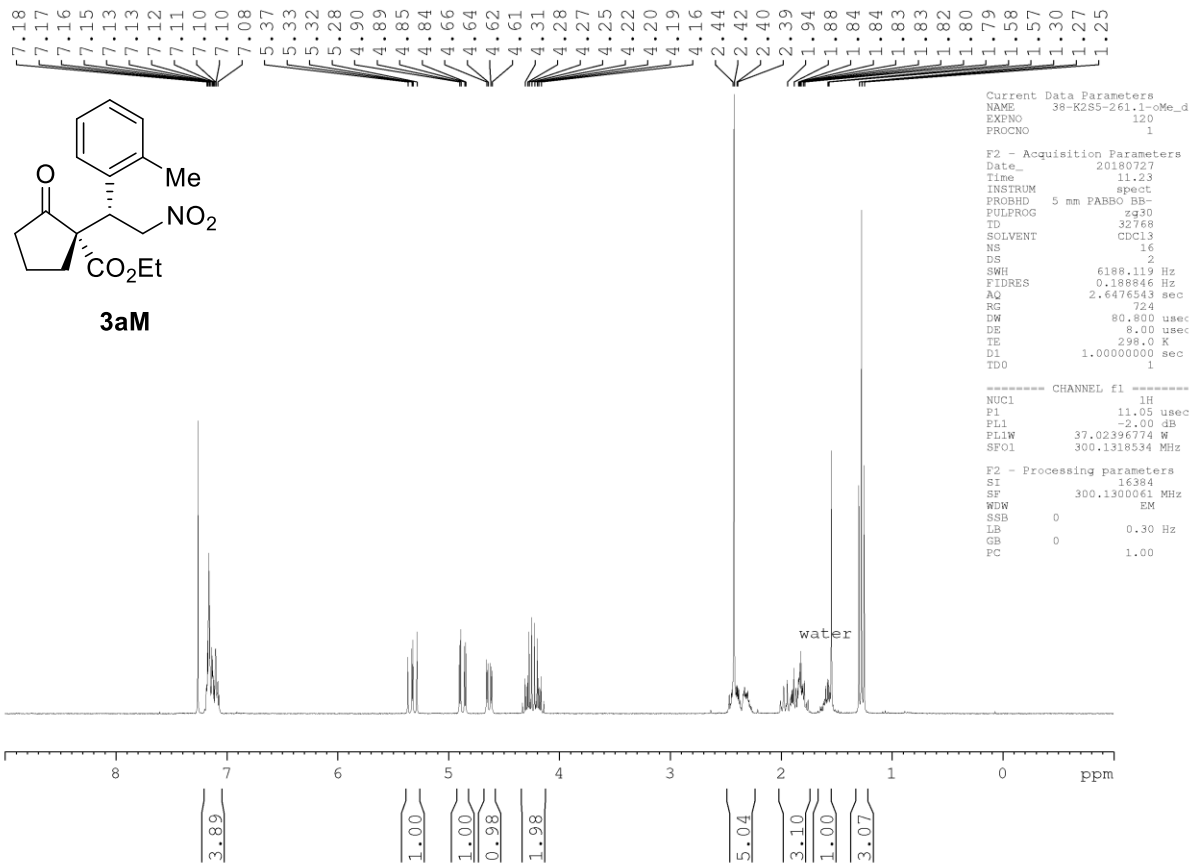
F2 - Processing parameters
SI               32768
SF          125.7635589 MHz
WDW                 EM
SSB       0
LB              1.00 Hz
```

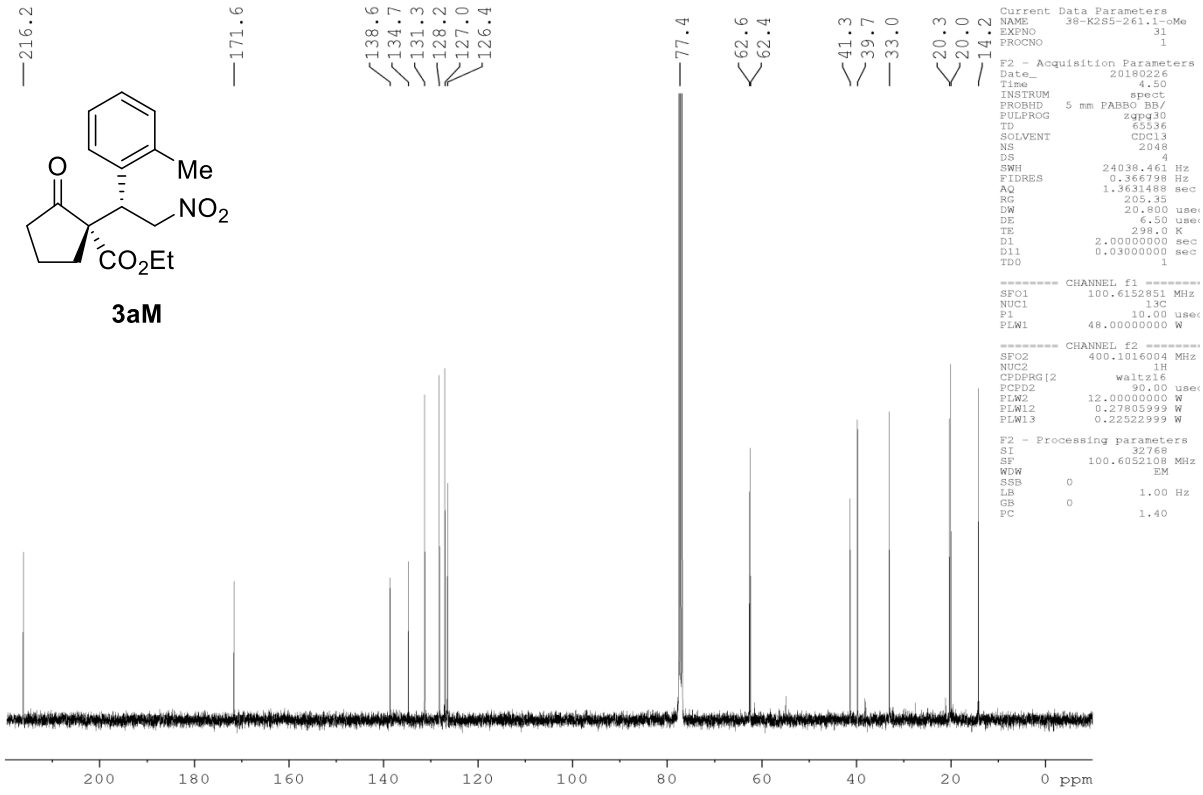

7.12 7.09 7.07 7.06 7.05 7.04 5.30 5.27 5.26 5.22 4.84 4.83 4.80 4.79 4.28 4.27 4.26 4.25 4.23 4.22 4.21 4.20 4.19 4.17 4.17 4.16 4.16 4.15 4.13 4.12 2.30 2.28 2.28 2.03 2.01 2.00 1.99 1.98 1.97 1.96 1.95 1.93 1.92 1.78 1.78 1.45 1.29 1.27 1.25
Me
O
NO2
CO2Et
3aK
water
8 7 6 5 4 3 2 1 0 ppm
3.96 1.01 1.00 2.99 5.06 2.05 1.07 1.07 3.04

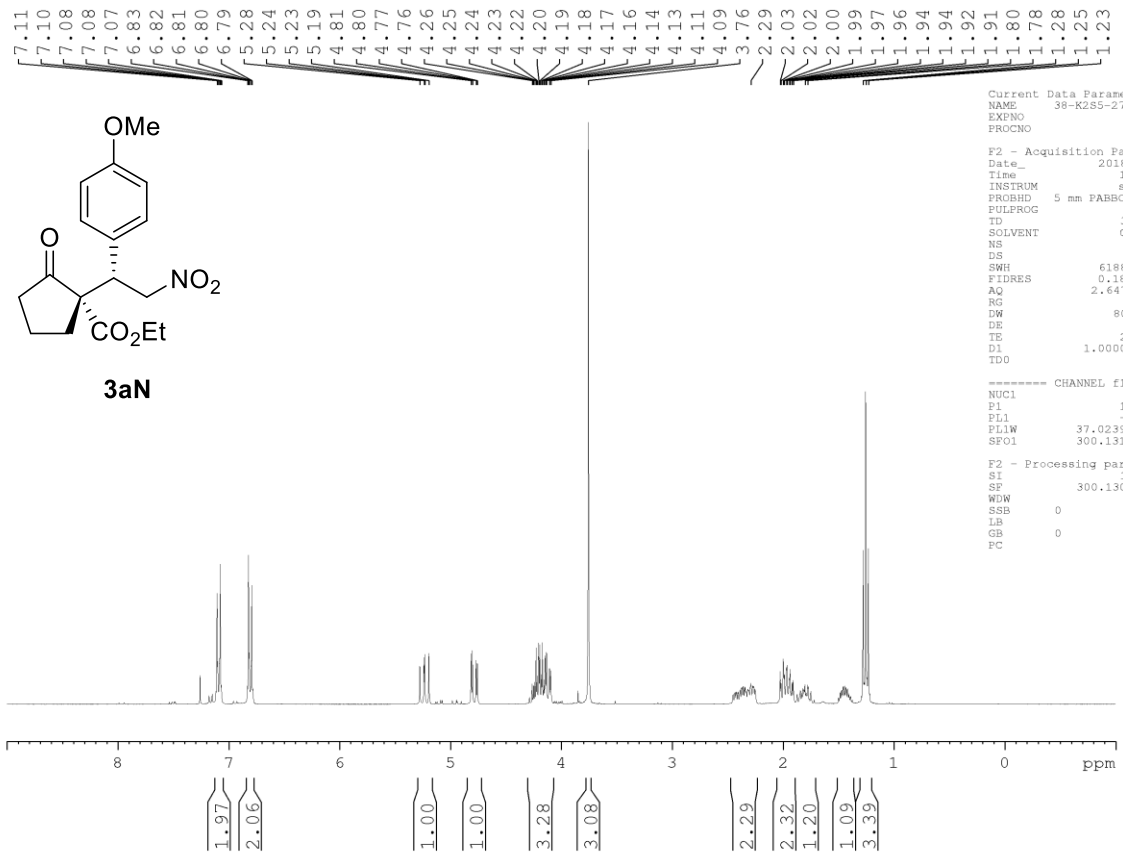

215.8 171.3 138.4 132.5 129.8 129.2 77.2 62.4 62.3 47.1 39.7 33.8 21.2 19.8 14.2
Me
O
NO2
CO2Et
3aK
200 180 160 140 120 100 80 60 40 20 0 ppm

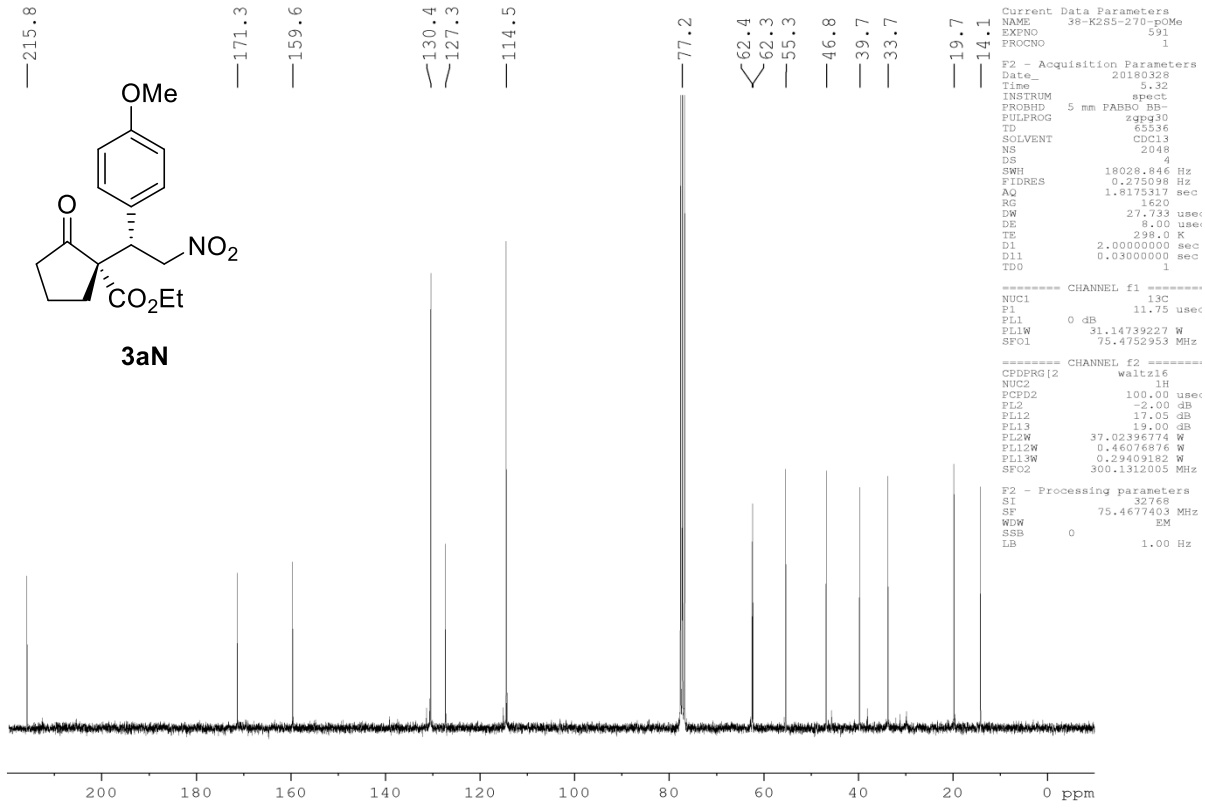

7.19 7.18 7.16 7.09 7.07 6.98 6.96 5.29 5.26 5.24 4.84 4.83 4.81 4.80 4.27 4.26 4.25 4.24 4.23 4.22 4.20 4.19 4.18 4.17 4.16 4.16 4.14 4.14 2.31 2.30 2.02 2.00 1.98 1.97 1.96 1.95 1.95 1.94 1.82 1.81 1.79 1.44 1.44 1.43 1.28 1.27 1.25
Me
O
NO2
CO2Et
3aL
water
8 7 6 5 4 3 2 1 0 ppm
0.98 0.97 1.97 1.00 1.00 2.99 1.05 3.99 2.03 1.02 1.02 3.03

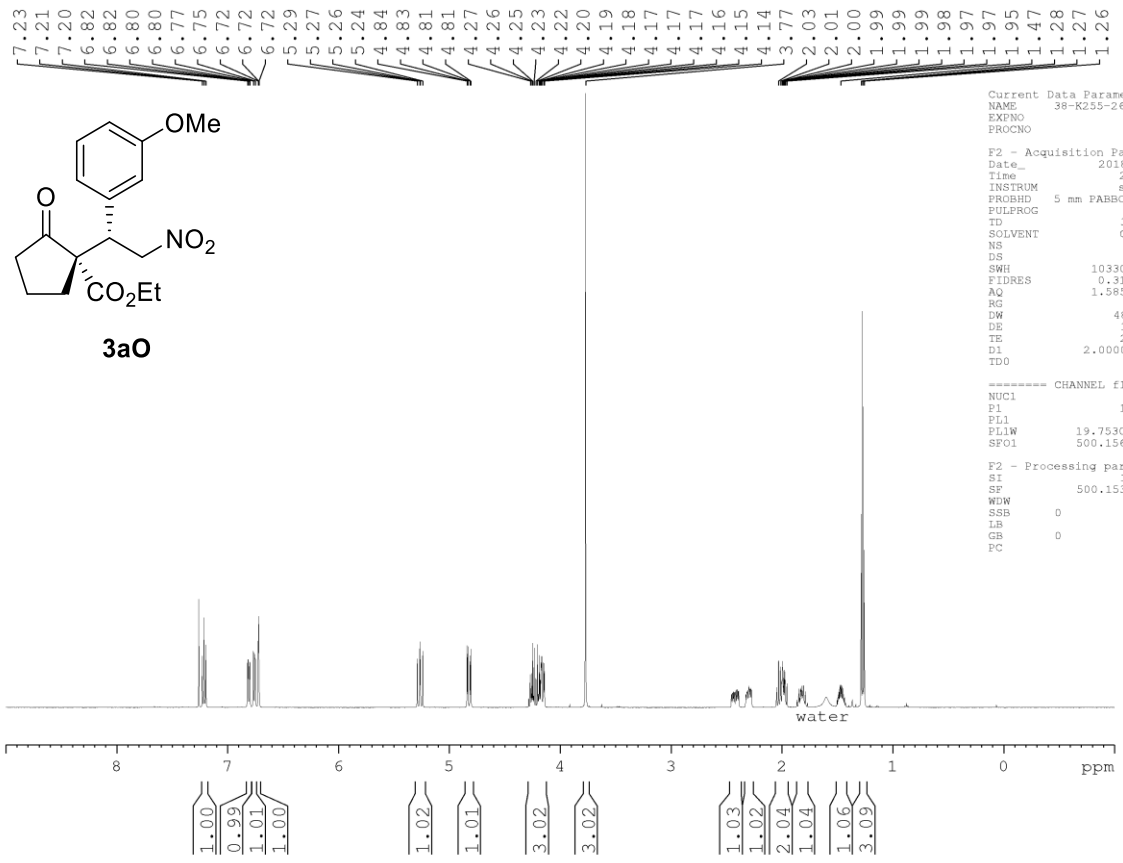

215.8 171.3 138.8 135.6 130.2 129.3 129.0 126.1 77.2 62.4 62.3 47.4 39.7 33.7 21.6 19.8 14.2
Me
O
NO2
CO2Et
3aL
200 180 160 140 120 100 80 60 40 20 0 ppm


7.18 7.17 7.16 7.15 7.13 7.13 7.12 7.11 7.10 7.10 7.08
5.37 5.33 5.32 5.28 4.90 4.89 4.85 4.84 4.66 4.64 4.62 4.61
4.31 4.28 4.27 4.25 4.22 4.20 4.19 4.16
2.44 2.42 2.40 2.39 1.94 1.88 1.84 1.84 1.83 1.82 1.80 1.79 1.58 1.57 1.30 1.27 1.25
O
Me
NO2
CO2Et
3aM
water
8 7 6 5 4 3 2 1 0 ppm
3.89 1.00 1.00 0.98 1.98 5.04 3.10 1.00 3.07
Current Data Parameters
NAME 38-K2S5-261.1-oMe_d
EXPNO 120
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180727
Time 11.23
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 724
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


216.2 171.6 138.6 134.7 131.3 128.2 127.0 126.4 77.4 62.6 62.4 41.3 39.7 33.0 20.3 20.0 14.2
O
Me
NO2
CO2Et
3aM
200 180 160 140 120 100 80 60 40 20 0 ppm
Current Data Parameters
NAME 38-K2S5-261.1-oMe
EXPNO 31
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180226
Time 4.50
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 205.35
DW 20.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6152851 MHz
NUC1 13C
P1 10.00 usec
PLW1 48.00000000 W
======== CHANNEL f2 ========
SFO2 400.1016004 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 12.00000000 W
PLW12 0.27805999 W
PLW13 0.22522999 W
F2 - Processing parameters
SI 32768
SF 100.6052108 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


7.11 7.10 7.08 7.08 7.07 6.83 6.82 6.81 6.80 6.79 5.28 5.24 5.23 5.19 4.81 4.80 4.77 4.76 4.26 4.25 4.24 4.23 4.22 4.20 4.19 4.18 4.17 4.16 4.14 4.13 4.11 4.09 3.76 2.29 2.03 2.02 2.00 1.99 1.97 1.96 1.94 1.94 1.92 1.91 1.80 1.78 1.28 1.25 1.23
OMe
O
NO2
CO2Et
3aN
Current Data Parameters
NAME 38-K2S5-270-pOMe
EXPNO 350
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180321
Time 14.04
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 161
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
1.97 2.06 1.00 1.00 3.28 3.08 2.29 2.32 1.20 1.09 3.39


215.8 171.3 159.6 130.4 127.3 114.5 77.2 62.4 62.3 55.3 46.8 39.7 33.7 19.7 14.1
OMe
O
NO2
CO2Et
3aN
Current Data Parameters
NAME 38-K2S5-270-pOMe
EXPNO 591
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180328
Time 5.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 1620
DW 27.733 usec
DE 8.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.75 usec
PL1 0 dB
PL1W 31.14739227 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -2.00 dB
PL12 17.05 dB
PL13 19.00 dB
PL2W 37.02396774 W
PL12W 0.46076876 W
PL13W 0.29409182 W
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677403 MHz
WDW EM
SSB 0
LB 1.00 Hz
200 180 160 140 120 100 80 60 40 20 0 ppm

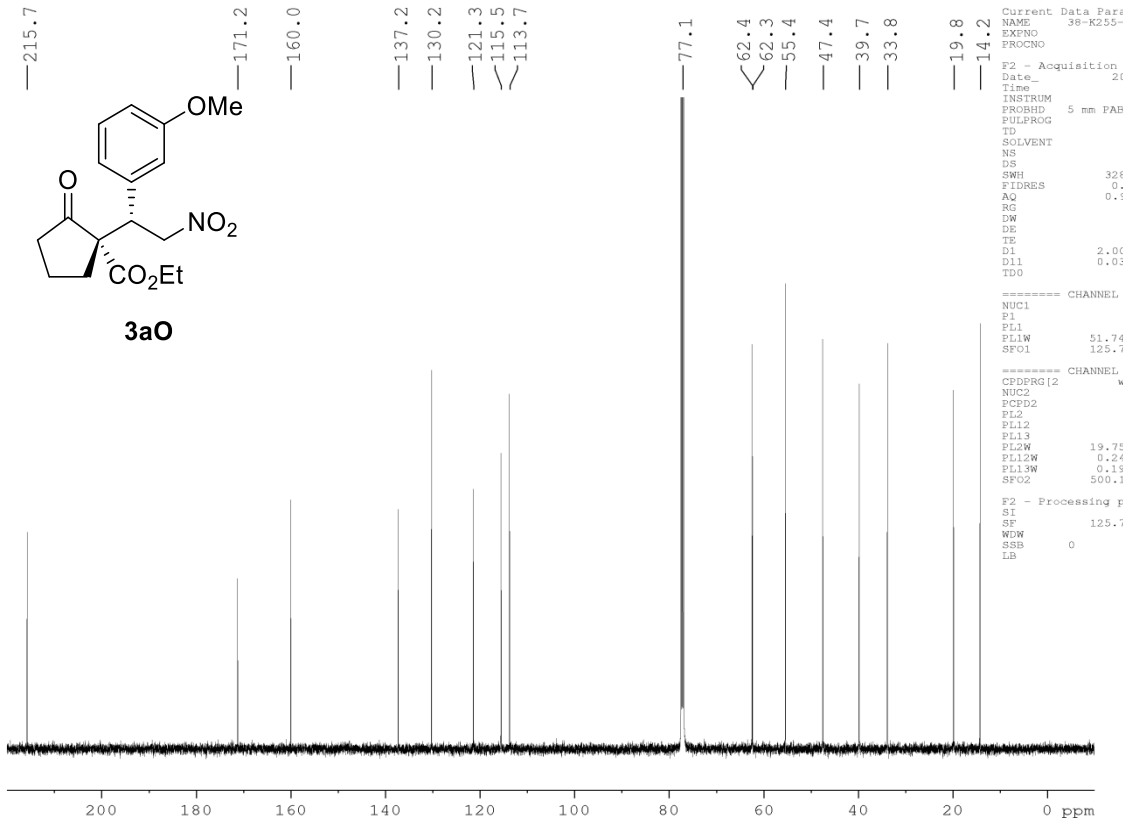



```
Current Data Parameters
NAME      38-K255-266-oOMe-di
EXPNO                     50
PROCNO                     1

F2 - Acquisition Parameters
Date_               20180802
Time                   20.41
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       32
DS                        0
SWH               10330.578 Hz
FIDRES             0.315264 Hz
AQ                 1.5859712 sec
RG                      256
DW                   48.400 usec
DE                   10.00 usec
TE                   296.0 K
D1                2.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                     11.23 usec
PL1                     1.00 dB
PL1W             19.75309753 W
SFO1            500.1560886 MHz

F2 - Processing parameters
SI                        16384
SF                500.1530160 MHz
WDW                          EM
SSB                       0
LB                        0.30 Hz
GB                        0
PC                        1.00
```



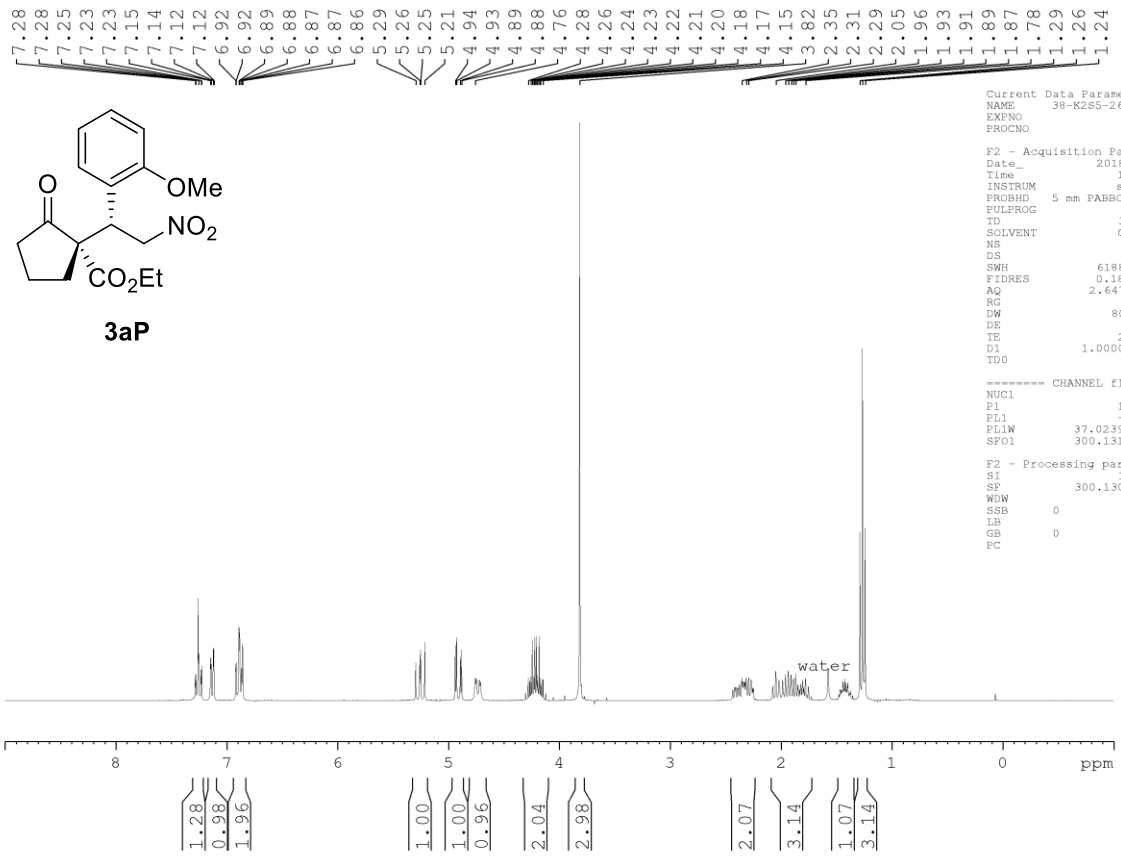

```
Current Data Parameters
NAME      38-K255-266-oOMe-di
EXPNO                     51
PROCNO                     1

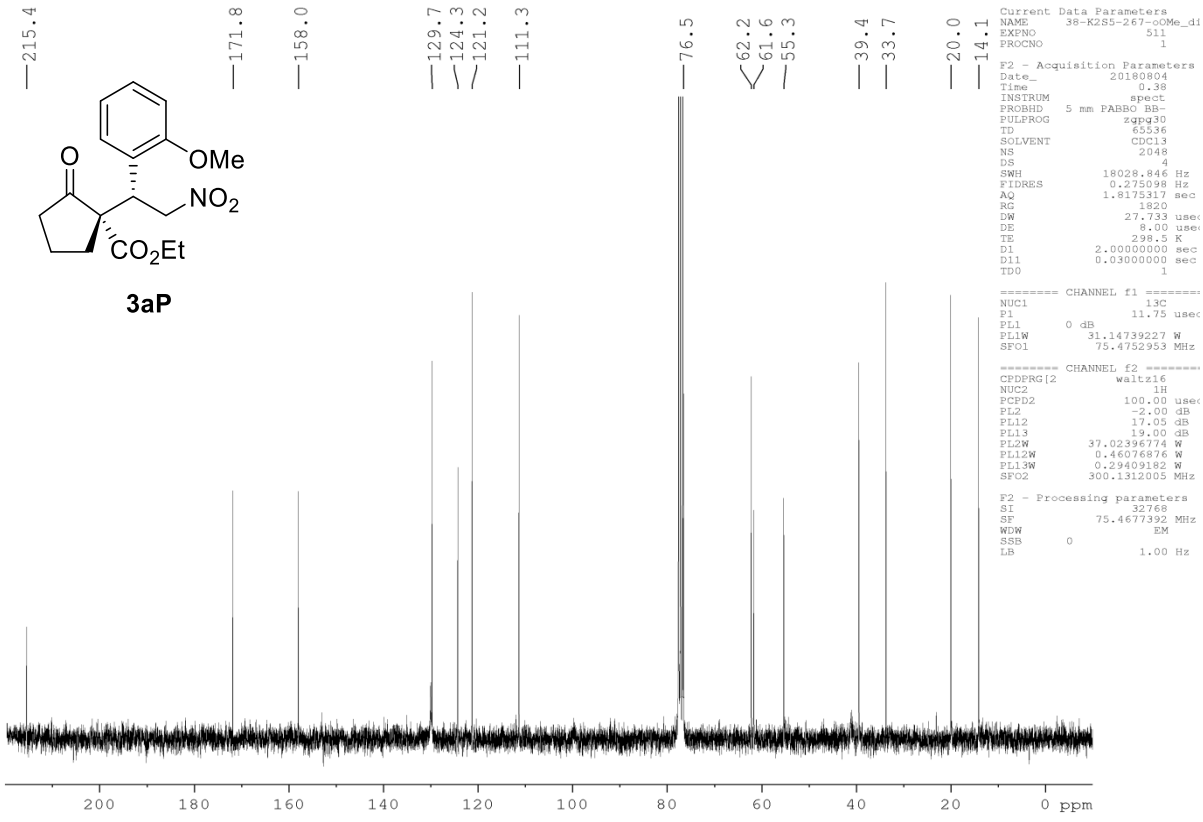
F2 - Acquisition Parameters
Date_               20180802
Time                   22.27
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     2048
DS                        4
SWH               32894.738 Hz
FIDRES             0.501934 Hz
AQ                 0.9961472 sec
RG                     2580
DW                   15.200 usec
DE                   10.00 usec
TE                   296.0 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

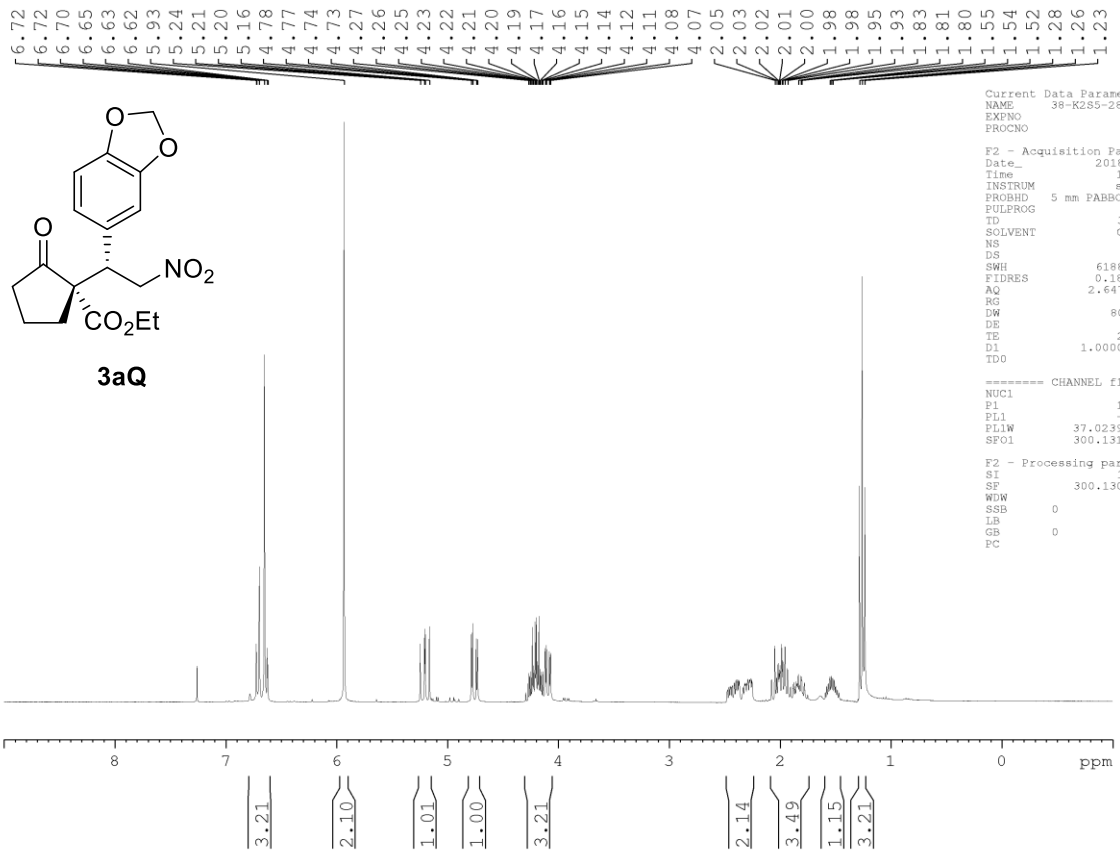
======== CHANNEL f1 ========
NUC1                     13C
P1                     10.20 usec
PL1                     1.50 dB
PL1W             51.74793243 W
SFO1            125.7761482 MHz

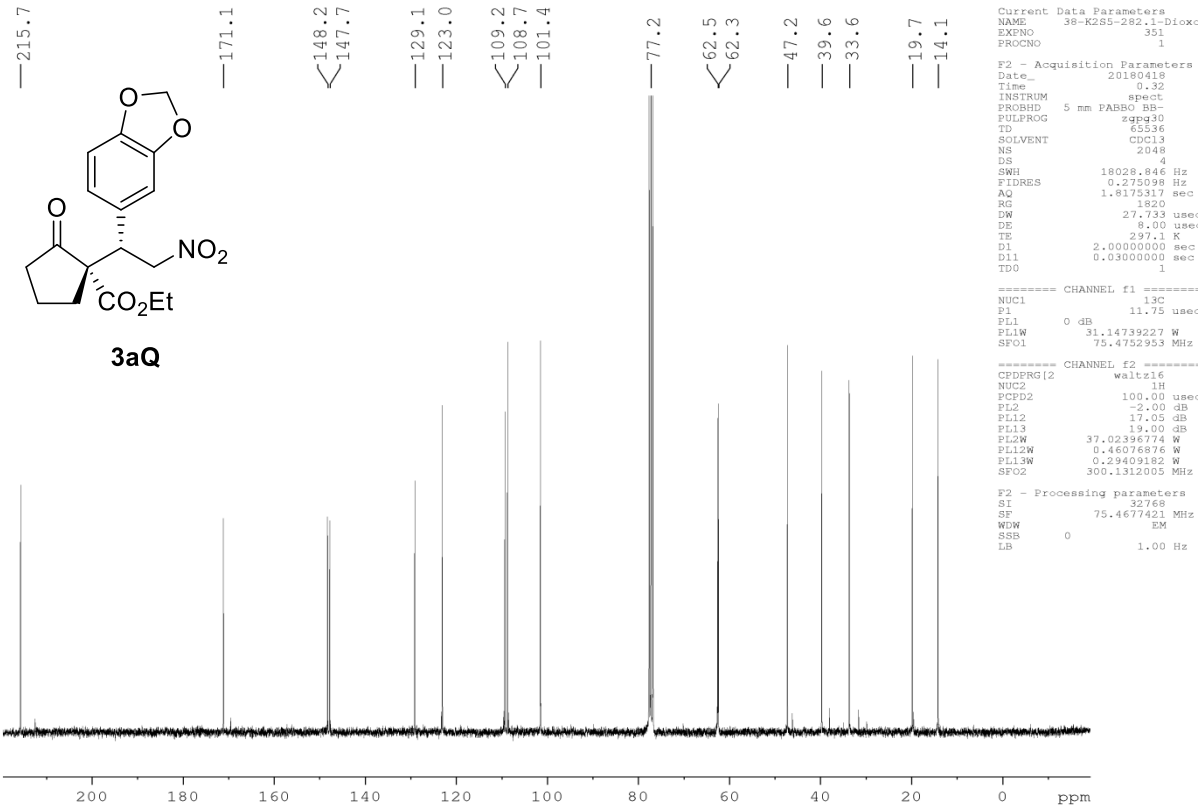
======== CHANNEL f2 ========
CPDPRG[2            waltz16
NUC2                      1H
PCPD2                100.00 usec
PL2                     1.00 dB
PL12                   19.99 dB
PL13                   21.00 dB
PL2W             19.75309753 W
PL12W             0.24925002 W
PL13W             0.19753097 W
SFO2            500.1550006 MHz

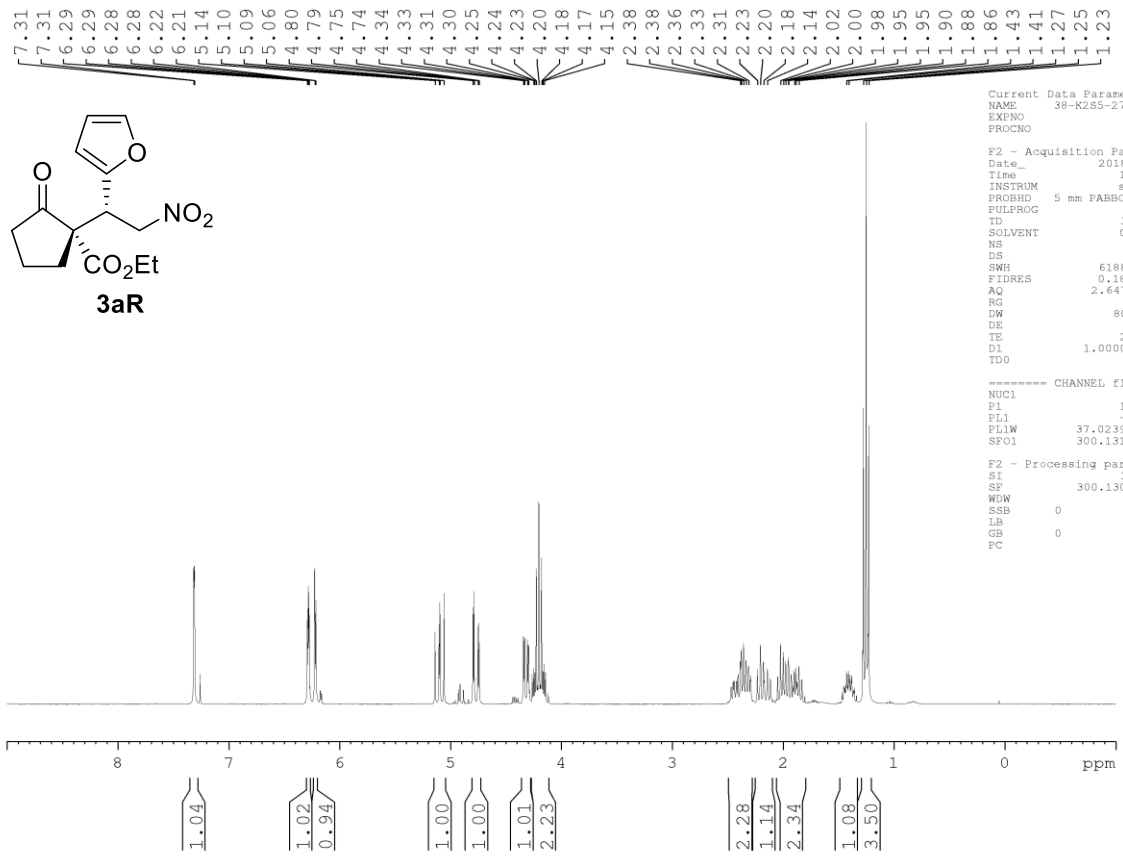
F2 - Processing parameters
SI                        32768
SF                125.7635576 MHz
WDW                          EM
SSB                       0
LB                     1.00 Hz
```

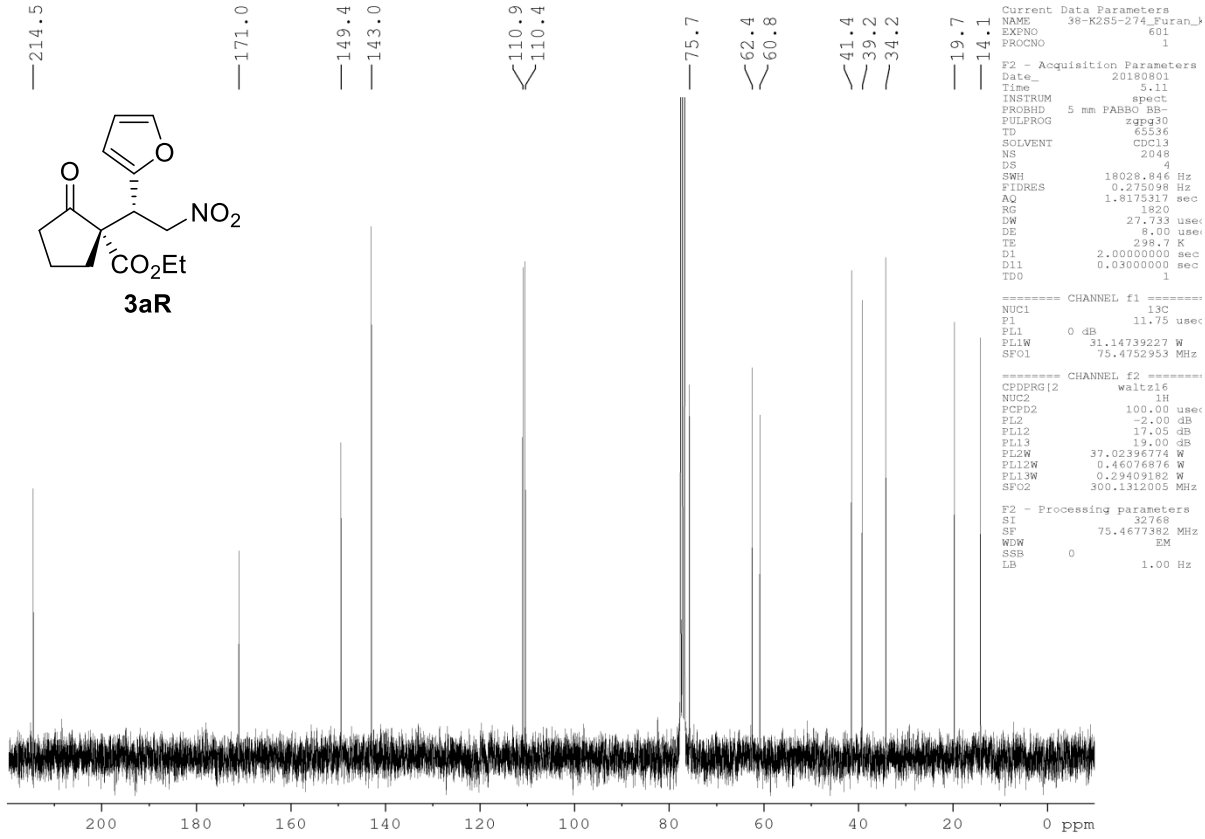

7.28 7.28 7.25 7.23 7.23 7.15 7.14 7.12 7.12 6.92 6.92 6.89 6.88 6.87 6.87 6.86 5.29 5.26 5.25 5.21 4.94 4.93 4.89 4.88 4.76 4.28 4.26 4.24 4.23 4.22 4.21 4.20 4.18 4.17 4.15 3.82 2.35 2.31 2.29 2.05 1.96 1.93 1.91 1.89 1.87 1.78 1.29 1.26 1.24
OMe
NO2
CO2Et
3aP
water
ppm
1.28 0.98 1.96 1.00 1.00 0.96 2.04 2.98 2.07 3.14 1.07 3.14

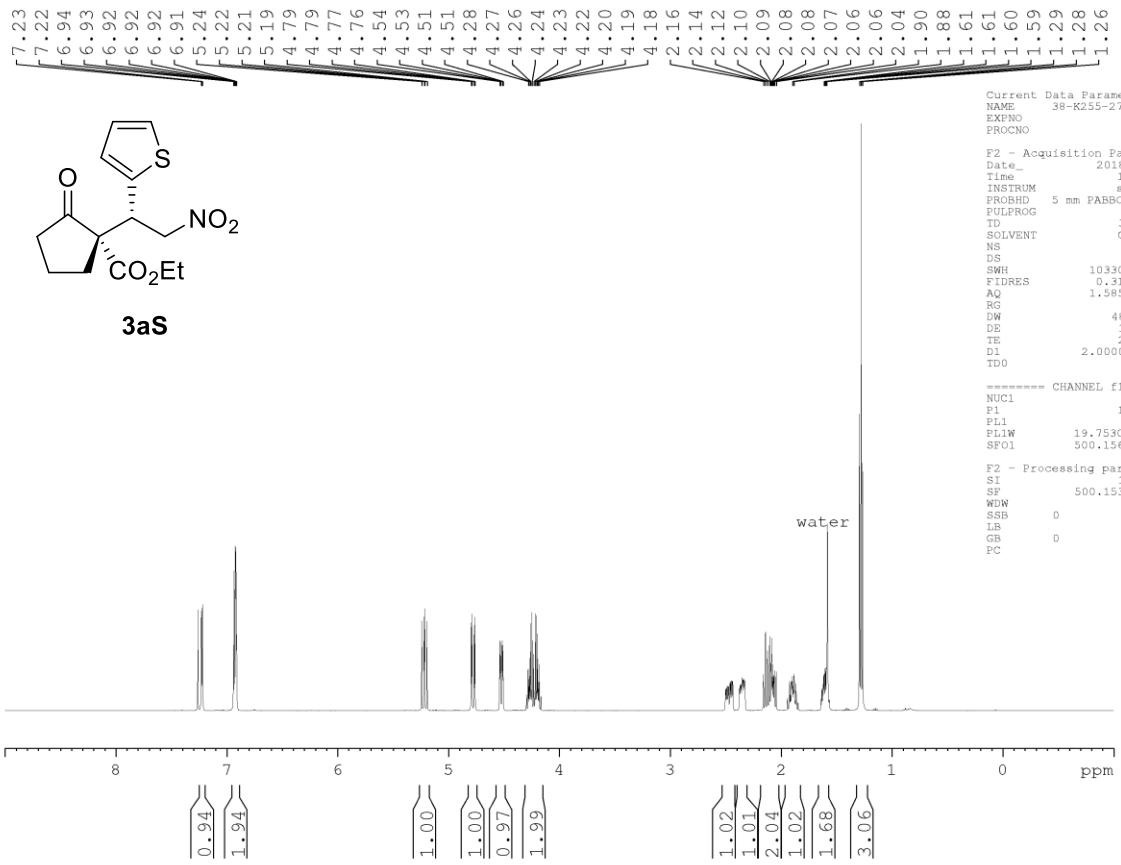

215.4 171.8 158.0 129.7 124.3 121.2 111.3 76.5 62.2 61.6 55.3 39.4 33.7 20.0 14.1
OMe
NO2
CO2Et
3aP
ppm

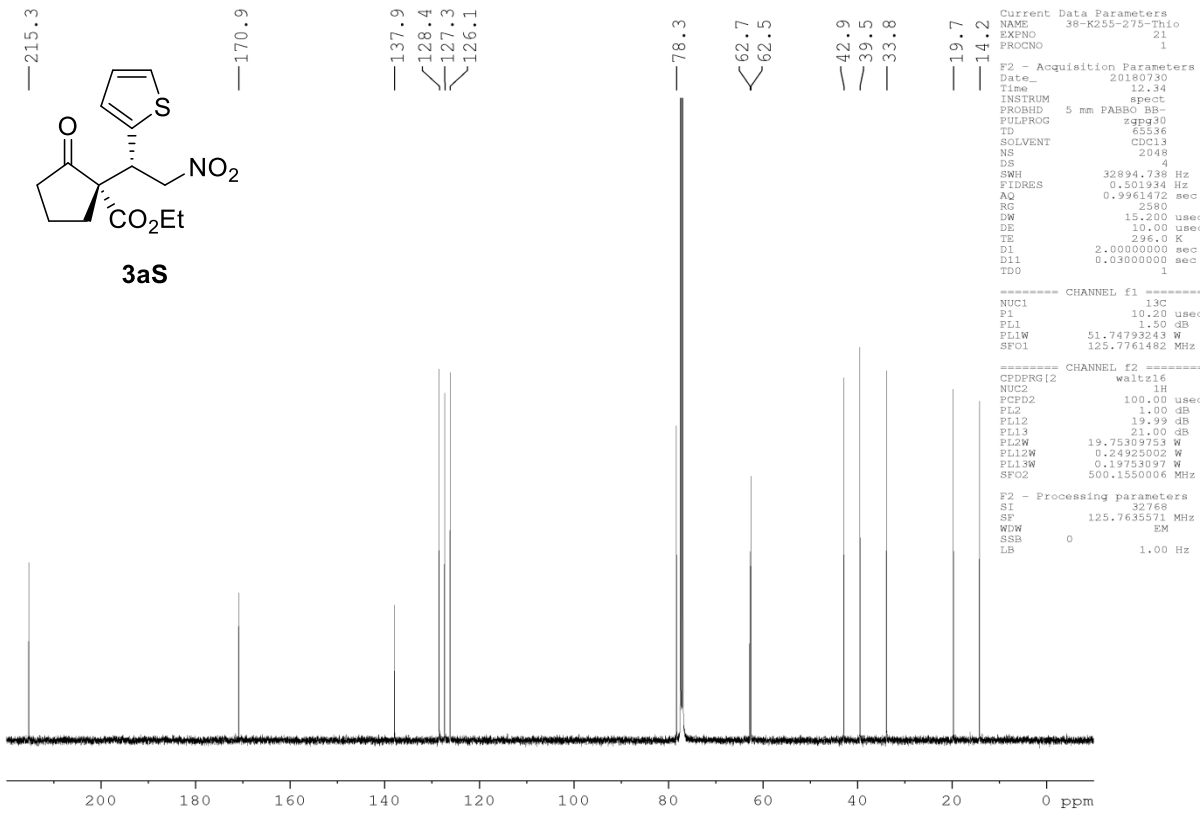

6.72 6.72 6.70 6.65 6.63 6.62 5.93 5.24 5.21 5.20 5.16 4.78 4.77 4.74 4.73 4.27 4.26 4.25 4.23 4.22 4.21 4.20 4.19 4.17 4.16 4.15 4.14 4.12 4.11 4.08 4.07 2.05 2.03 2.02 2.01 2.00 1.98 1.98 1.95 1.93 1.83 1.81 1.80 1.55 1.54 1.52 1.28 1.26 1.23
NO2
CO2Et
3aQ
Current Data Parameters
NAME 38-K2S5-282.1-Dioxo
EXPNO 350
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180417
Time 13.19
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 181
DW 80.800 usec
DE 8.00 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
3.21 2.10 1.01 1.00 3.21 2.14 3.49 1.15 3.21

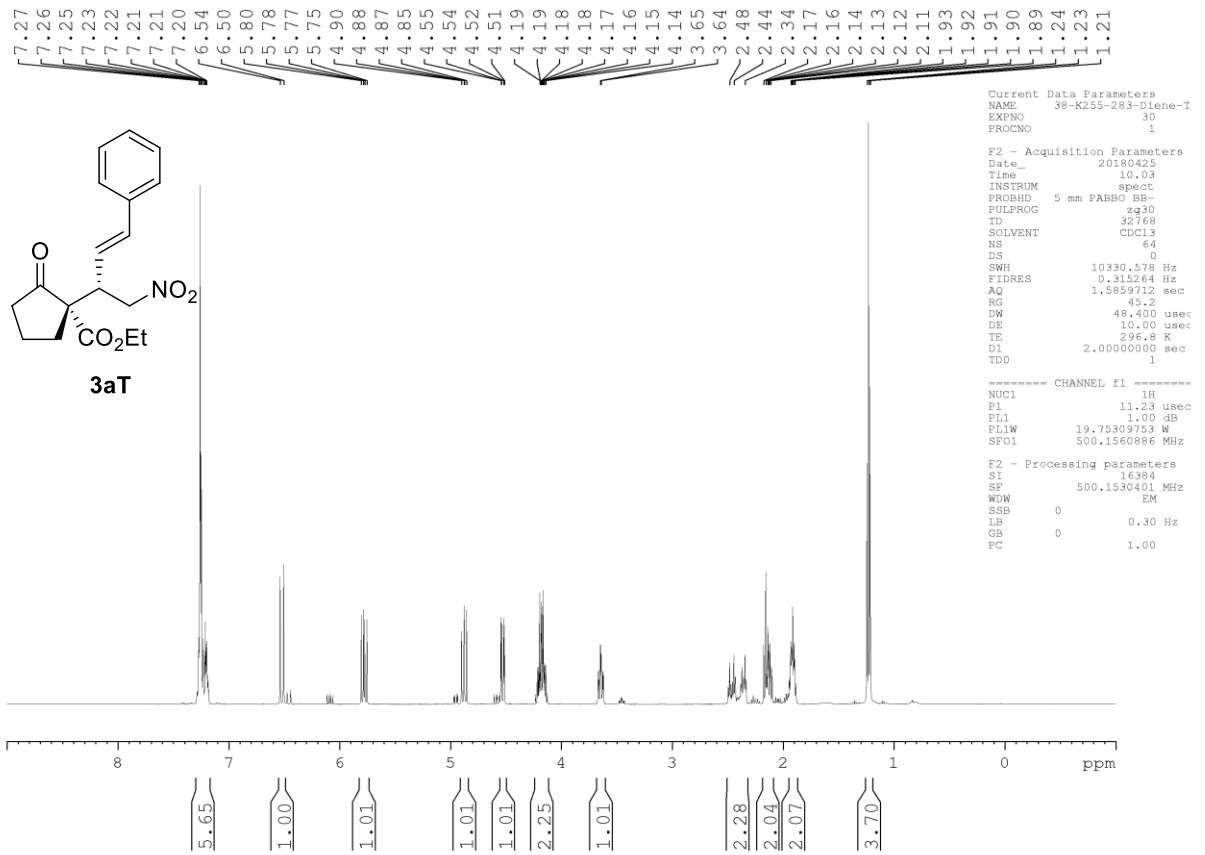

215.7 171.1 148.2 147.7 129.1 123.0 109.2 108.7 101.4 77.2 62.5 62.3 47.2 39.6 33.6 19.7 14.1
NO2
CO2Et
3aQ
Current Data Parameters
NAME 38-K2S5-282.1-Dioxo
EXPNO 351
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180418
Time 0.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 1820
DW 27.733 usec
DE 8.00 usec
TE 297.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.75 usec
PL1 0 dB
PL1W 31.14739227 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -2.00 dB
PL12 17.05 dB
PL13 19.00 dB
PL2W 37.02396774 W
PL12W 0.46076876 W
PL13W 0.29409182 W
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677421 MHz
WDW EM
SSB 0
LB 1.00 Hz
200 180 160 140 120 100 80 60 40 20 0 ppm

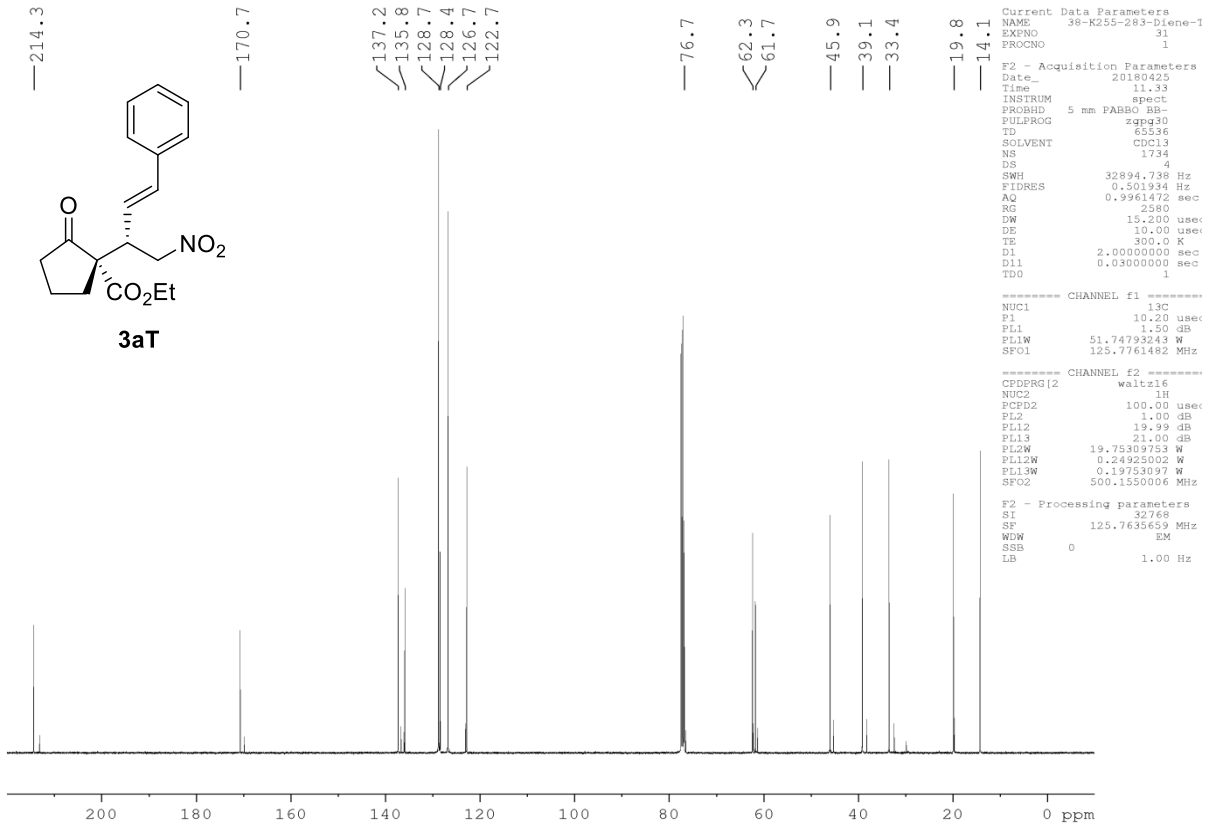

7.31 7.31 6.29 6.28 6.28 6.22 6.21 5.14 5.10 5.09 5.06 4.80 4.79 4.75 4.74 4.34 4.33 4.31 4.30 4.25 4.24 4.23 4.20 4.18 4.17 4.15 2.38 2.38 2.36 2.33 2.31 2.23 2.20 2.18 2.14 2.02 2.00 1.98 1.95 1.95 1.90 1.88 1.86 1.43 1.41 1.27 1.25 1.23
O
O
NO2
CO2Et
3aR
Current Data Parameters
NAME 38-K2S5-274-Furan
EXPNO 390
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180403
Time 17.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 161
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300062 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
1.04 1.02 0.94 1.00 1.00 1.01 2.23 2.28 1.14 2.34 1.08 3.50

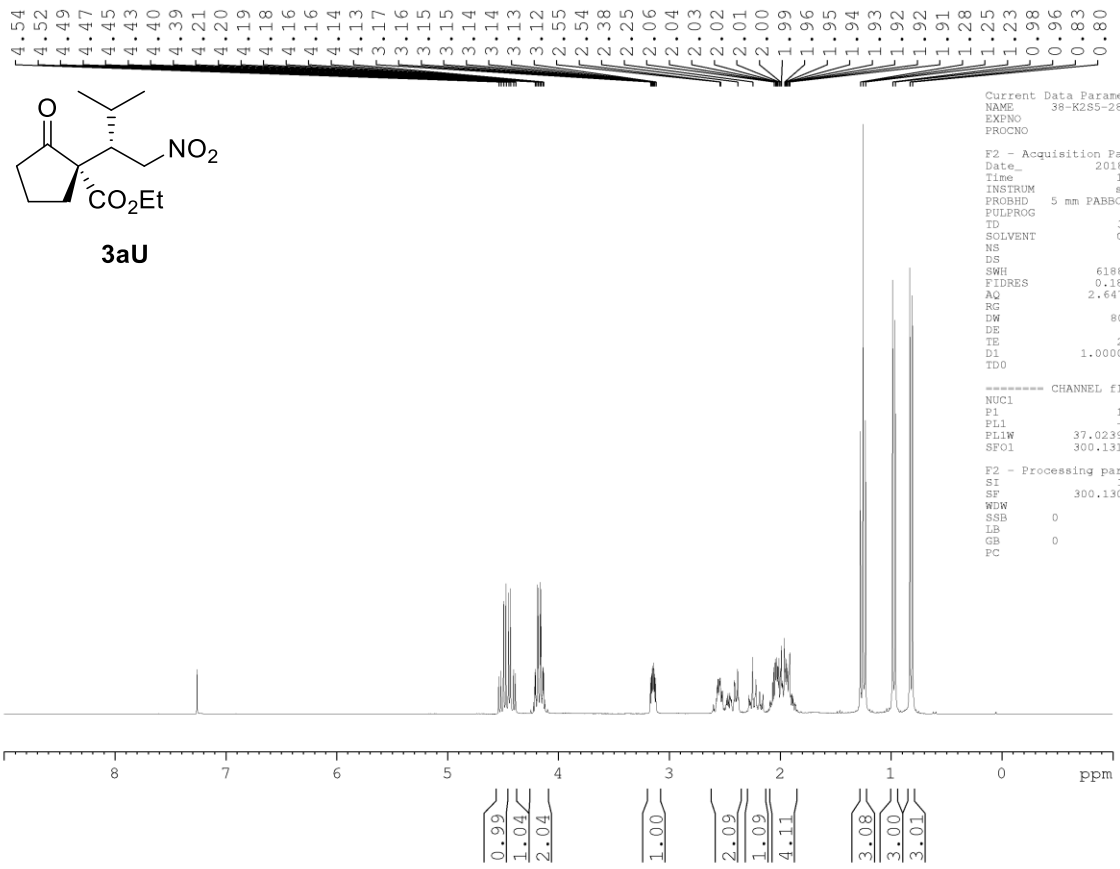

214.5 171.0 149.4 143.0 110.9 110.4 75.7 62.4 60.8 41.4 39.2 34.2 19.7 14.1
O
O
NO2
CO2Et
3aR
Current Data Parameters
NAME 38-K2S5-274_Furan_
EXPNO 601
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180801
Time 5.11
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 1820
DW 27.733 usec
DE 8.00 usec
TE 298.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.75 usec
PL1 0 dB
PL1W 31.14739227 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -2.00 dB
PL12 17.05 dB
PL13 19.00 dB
PL2W 37.02396774 W
PL12W 0.46076876 W
PL13W 0.29409182 W
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677382 MHz
WDW EM
SSB 0
LB 1.00 Hz
200 180 160 140 120 100 80 60 40 20 0 ppm

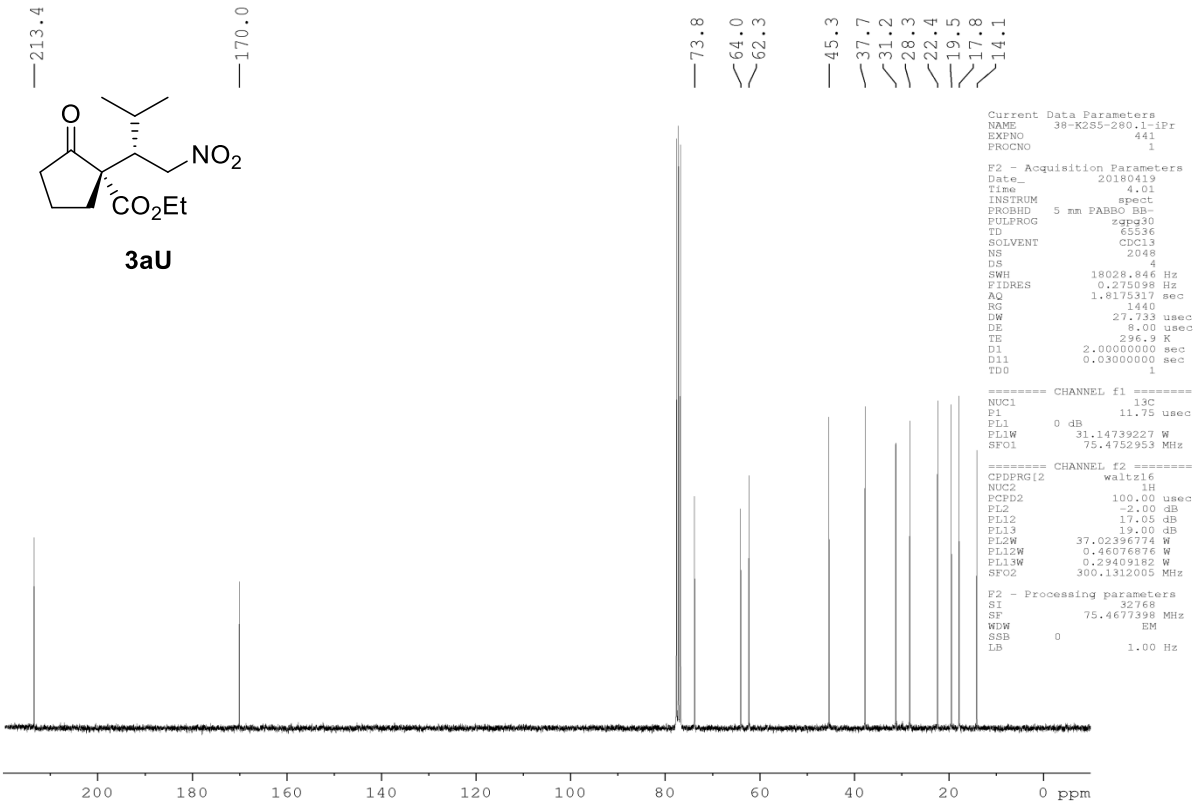

7.23 7.22 6.94 6.93 6.92 6.92 6.92 6.91 5.24 5.22 5.21 5.19 4.79 4.79 4.77 4.76 4.54 4.53 4.51 4.51 4.28 4.27 4.26 4.24 4.23 4.22 4.20 4.19 4.18 2.16 2.14 2.12 2.10 2.09 2.08 2.08 2.07 2.06 2.06 2.04 1.90 1.88 1.61 1.61 1.60 1.59 1.29 1.28 1.26
O
S
NO2
CO2Et
3aS
water
Current Data Parameters
NAME 38-K255-275-Thio
EXPNO 20
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180730
Time 10.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5859712 sec
RG 256
DW 48.400 usec
DE 10.00 usec
TE 296.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.23 usec
PL1 1.00 dB
PL1W 19.75309753 W
SFO1 500.1560886 MHz
F2 - Processing parameters
SI 16384
SF 500.1530158 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
0.94 1.94 1.00 1.00 0.97 1.99 1.02 1.01 2.04 1.02 1.68 3.06

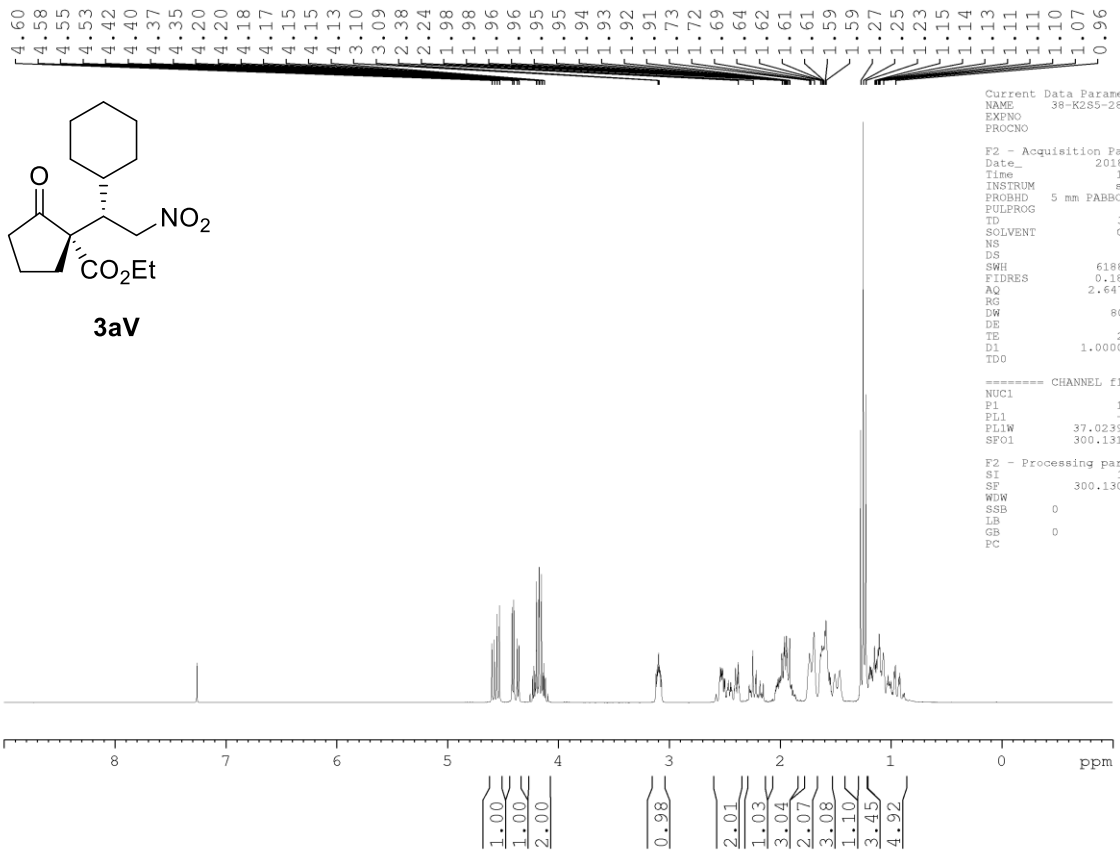

215.3 170.9 137.9 128.4 127.3 126.1 78.3 62.7 62.5 42.9 39.5 33.8 19.7 14.2
O
S
NO2
CO2Et
3aS
Current Data Parameters
NAME 38-K255-275-Thio
EXPNO 21
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180730
Time 12.34
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 32894.738 Hz
FIDRES 0.501934 Hz
AQ 0.9961472 sec
RG 2580
DW 15.200 usec
DE 10.00 usec
TE 296.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.20 usec
PL1 1.50 dB
PL1W 51.74793243 W
SFO1 125.7761482 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.00 dB
PL12 19.99 dB
PL13 21.00 dB
PL2W 19.75309753 W
PL12W 0.24925002 W
PL13W 0.19753097 W
SFO2 500.1550006 MHz
F2 - Processing parameters
SI 32768
SF 125.7635571 MHz
WDW EM
SSB 0
LB 1.00 Hz
200 180 160 140 120 100 80 60 40 20 0 ppm

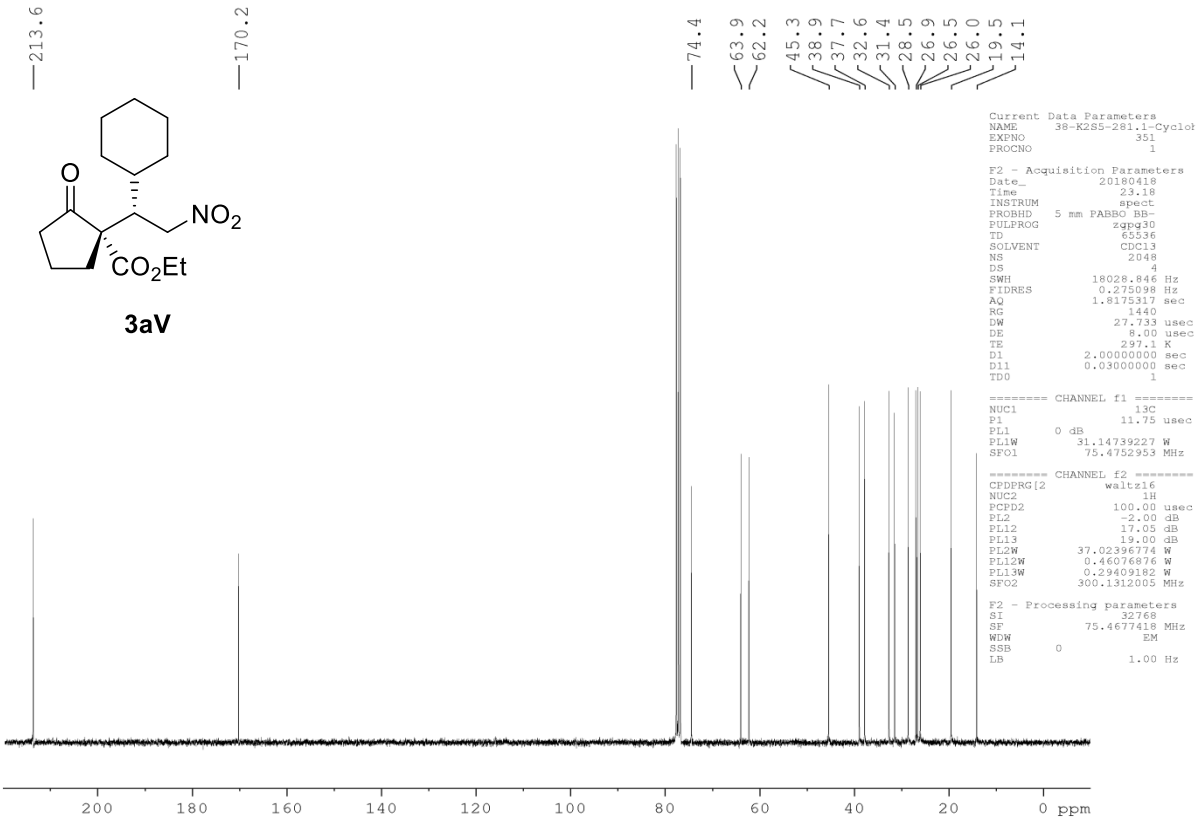

7.27
7.26
7.25
7.23
7.22
7.21
7.21
7.20
6.54
6.50
5.80
5.78
5.77
5.75
4.90
4.88
4.87
4.85
4.55
4.54
4.52
4.51
4.19
4.19
4.18
4.18
4.17
4.16
4.15
4.14
3.65
3.64
2.48
2.44
2.34
2.17
2.16
2.14
2.13
2.12
2.11
1.93
1.92
1.91
1.90
1.89
1.24
1.23
1.21
O
NO2
CO2Et
3aT
Current Data Parameters
NAME 38-K255-283-Diene-T
EXPNO 30
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180425
Time 10.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5859712 sec
RG 45.2
DW 48.400 usec
DE 10.00 usec
TE 296.8 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.23 usec
PL1 1.00 dB
PL1W 19.75309753 W
SFO1 500.1560886 MHz
F2 - Processing parameters
SI 16384
SF 500.1530401 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
0
ppm
5.65
1.00
1.01
1.01
1.01
2.25
1.01
2.28
2.04
2.07
3.70

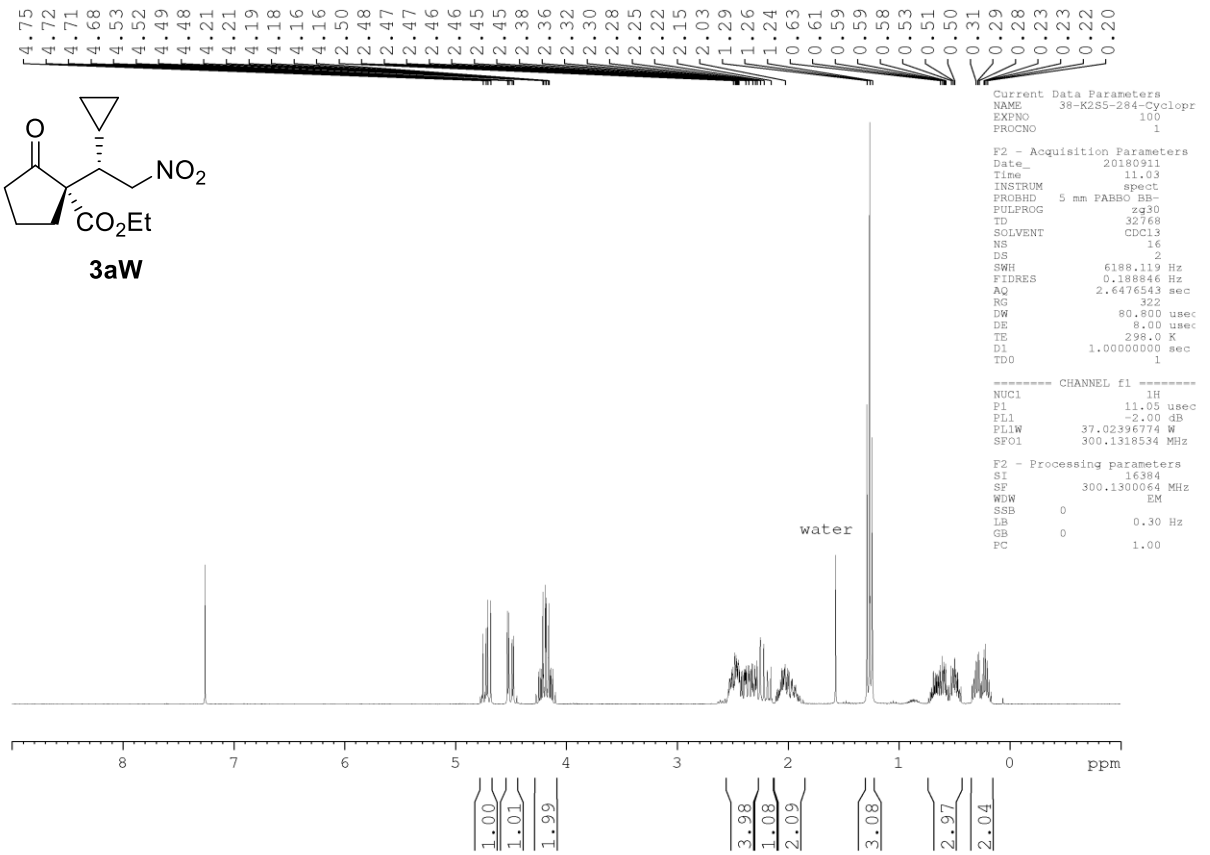

214.3
170.7
137.2
135.8
128.7
128.4
126.7
122.7
76.7
62.3
61.7
45.9
39.1
33.4
19.8
14.1
O
NO2
CO2Et
3aT
Current Data Parameters
NAME 38-K255-283-Diene-T
EXPNO 31
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180425
Time 11.33
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1734
DS 4
SWH 32894.738 Hz
FIDRES 0.501934 Hz
AQ 0.9961472 sec
RG 2580
DW 15.200 usec
DE 10.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.20 usec
PL1 1.50 dB
PL1W 51.74793243 W
SFO1 125.7761482 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.00 dB
PL12 19.99 dB
PL13 21.00 dB
PL2W 19.75309753 W
PL12W 0.24925002 W
PL13W 0.19753097 W
SFO2 500.1550006 MHz
F2 - Processing parameters
SI 32768
SF 125.7635659 MHz
WDW EM
SSB 0
LB 1.00 Hz
200
180
160
140
120
100
80
60
40
20
0 ppm

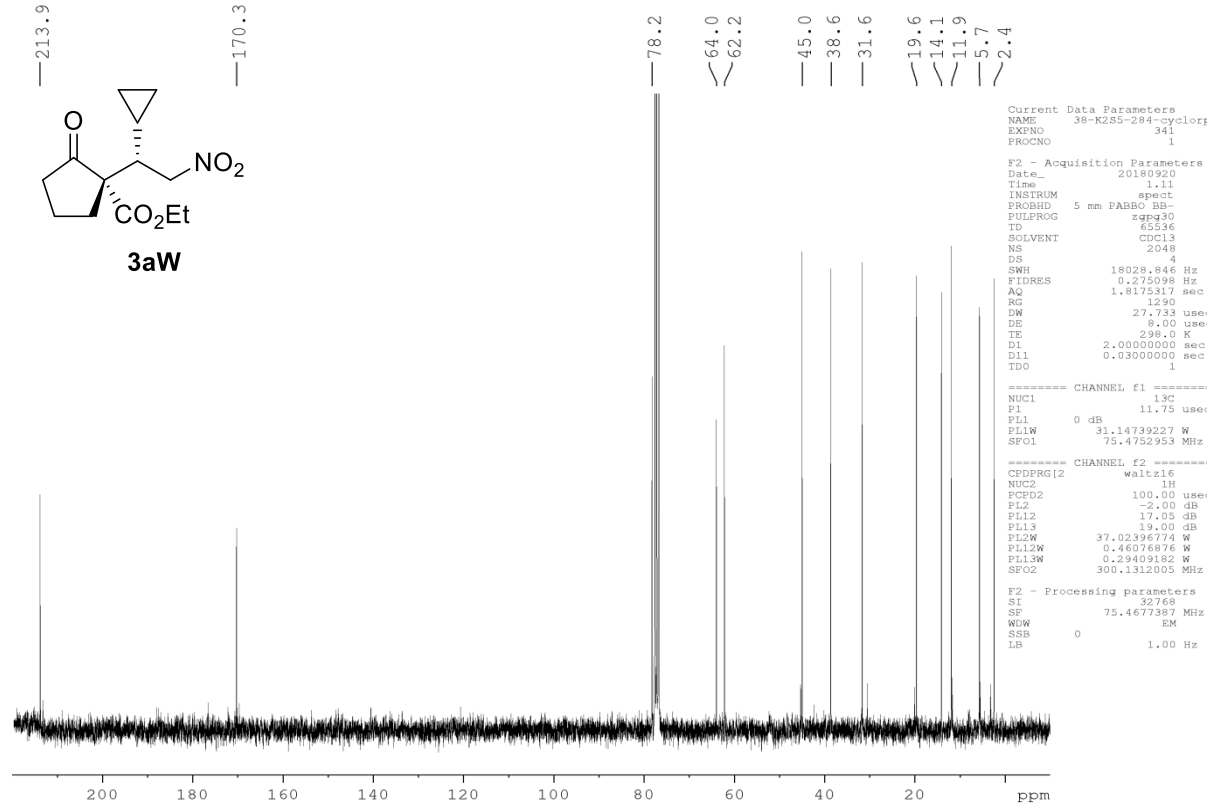

4.54 4.52 4.49 4.47 4.45 4.43 4.40 4.39 4.21 4.20 4.19 4.18 4.16 4.16 4.14 4.13 3.17 3.16 3.15 3.15 3.14 3.14 3.13 3.12 2.55 2.54 2.38 2.25 2.06 2.04 2.03 2.02 2.01 2.00 1.99 1.96 1.95 1.94 1.93 1.92 1.92 1.91 1.28 1.25 1.23 0.98 0.96 0.83 0.80
O
NO2
CO2Et
3aU
Current Data Parameters
NAME 38-K2S5-280.1-iPr
EXPNO 440
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180418
Time 12.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 181
DW 80.800 usec
DE 8.00 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300060 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
0.99 1.04 2.04 1.00 2.09 1.09 4.11 3.08 3.00 3.01

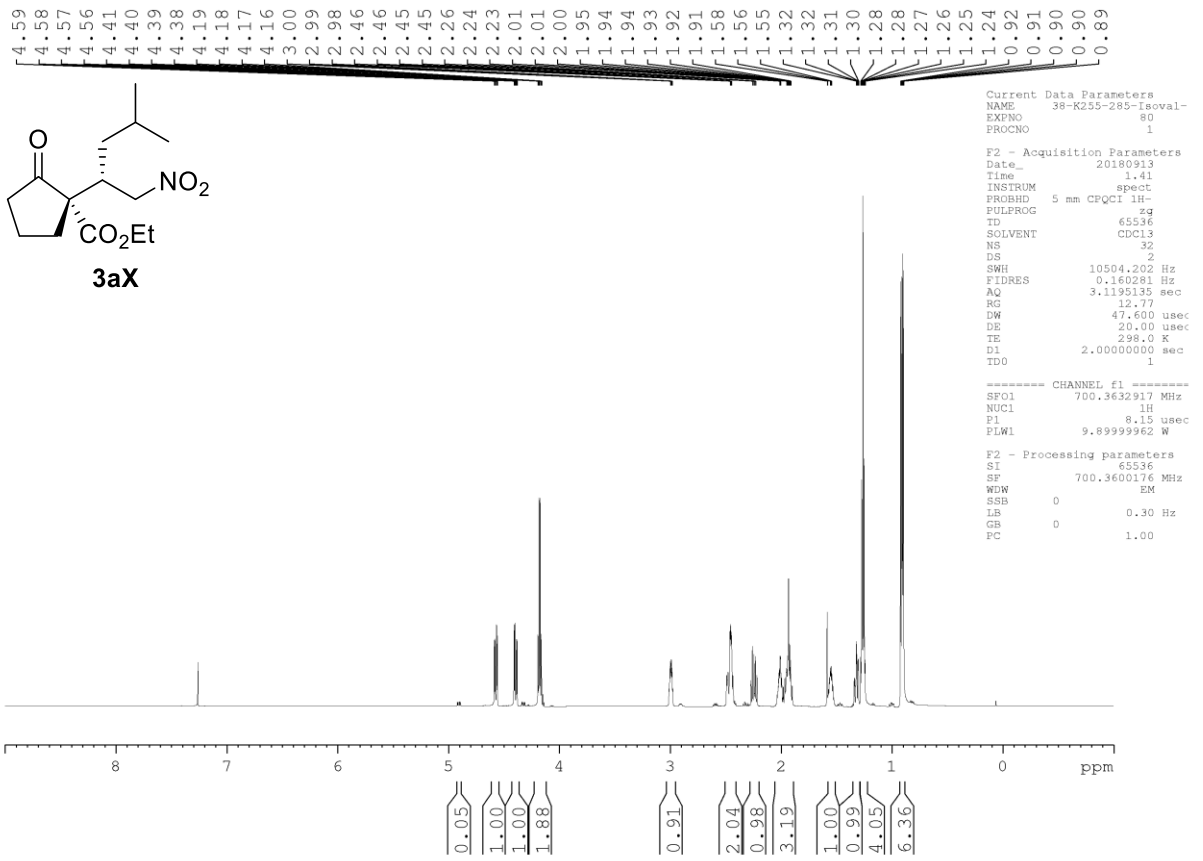

213.4
170.0
73.8
64.0
62.3
45.3
37.7
31.2
28.3
22.4
19.5
17.8
14.1
O
NO2
CO2Et
3aU
Current Data Parameters
NAME 38-K2S5-280.1-iPr
EXPNO 441
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180419
Time 4.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 1440
DW 27.733 usec
DE 8.00 usec
TE 296.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.75 usec
PL1 0 dB
PL1W 31.14739227 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -2.00 dB
PL12 17.05 dB
PL13 19.00 dB
PL2W 37.02396774 W
PL12W 0.46076876 W
PL13W 0.29409182 W
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677398 MHz
WDW EM
SSB 0
LB 1.00 Hz
200 180 160 140 120 100 80 60 40 20 0 ppm

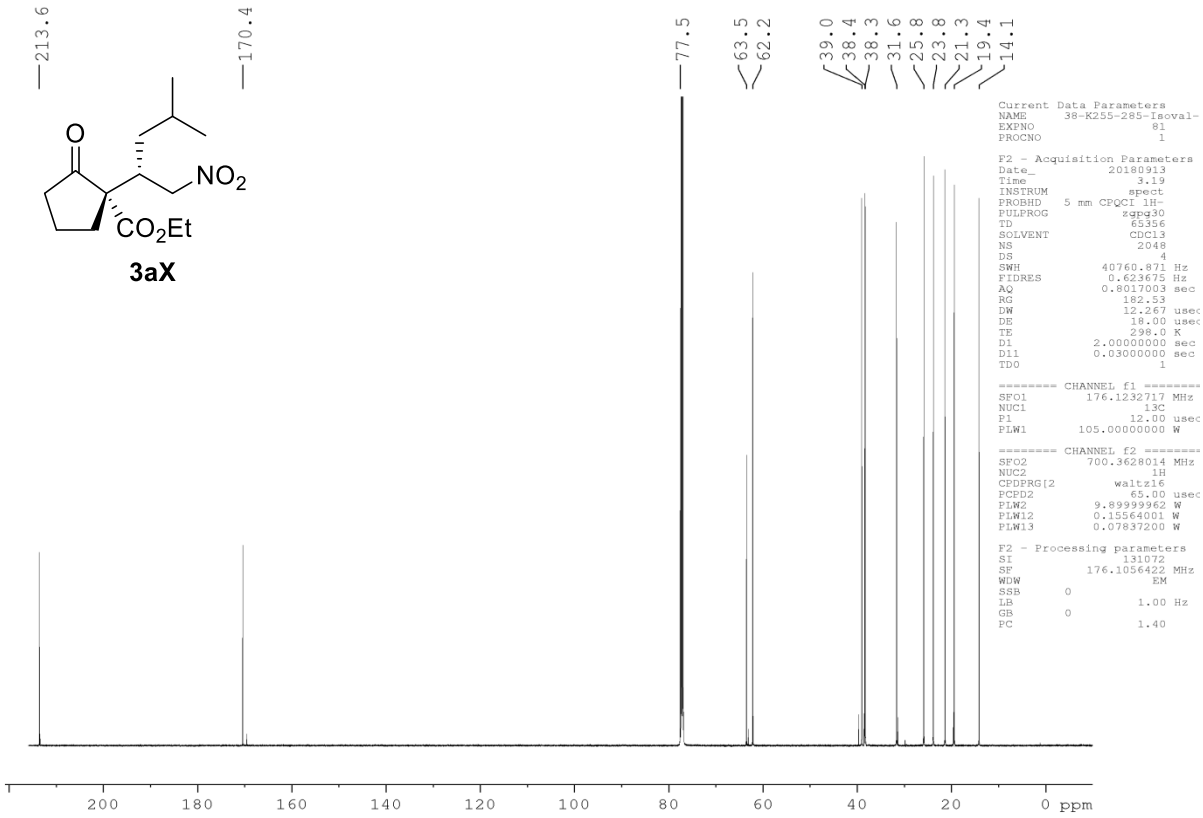

4.60 4.58 4.55 4.53 4.42 4.40 4.37 4.35 4.20 4.20 4.18 4.17 4.15 4.13 3.10 3.09 2.38 2.24 1.98 1.98 1.96 1.96 1.95 1.95 1.94 1.93 1.92 1.91 1.73 1.72 1.69 1.64 1.62 1.61 1.61 1.59 1.59 1.27 1.25 1.23 1.15 1.14 1.13 1.11 1.10 1.07 0.96
O
NO2
CO2Et
3aV
Current Data Parameters
NAME 38-K2S5-281.1-Cyclo
EXPNO 350
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180418
Time 11.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 144
DW 80.800 usec
DE 8.00 usec
TE 296.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300060 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
1.00 1.00 2.00 0.98 2.01 1.03 3.04 2.07 3.08 1.10 3.45 4.92

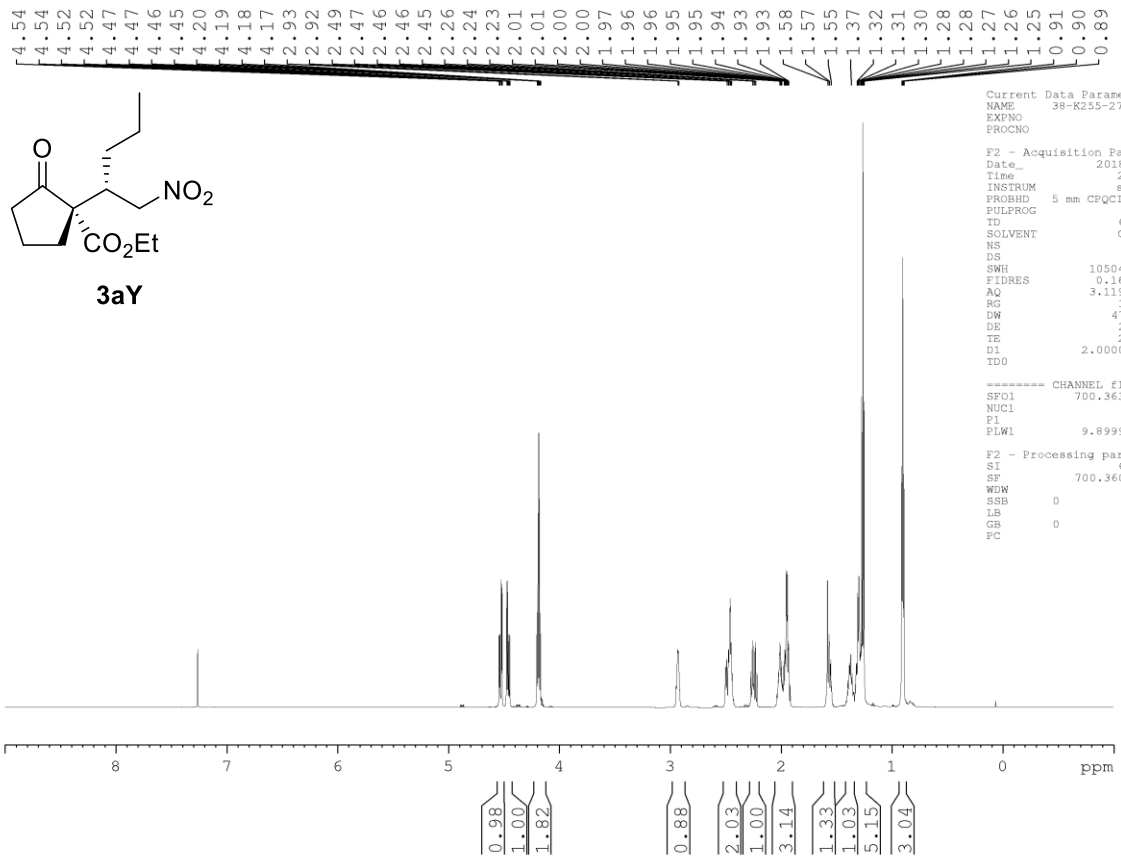

213.6
170.2
74.4
63.9
62.2
45.3
38.9
37.7
32.6
31.4
28.5
26.9
26.5
26.0
19.5
14.1
O
NO2
CO2Et
3aV
Current Data Parameters
NAME 38-K2S5-281.1-Cyclo
EXPNO 351
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180418
Time 23.18
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 1440
DW 27.733 usec
DE 8.00 usec
TE 297.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.75 usec
PL1 0 dB
PL1W 31.14739227 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -2.00 dB
PL12 17.05 dB
PL13 19.00 dB
PL2W 37.02396774 W
PL12W 0.46076876 W
PL13W 0.29409182 W
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677418 MHz
WDW EM
SSB 0
LB 1.00 Hz
200 180 160 140 120 100 80 60 40 20 0 ppm

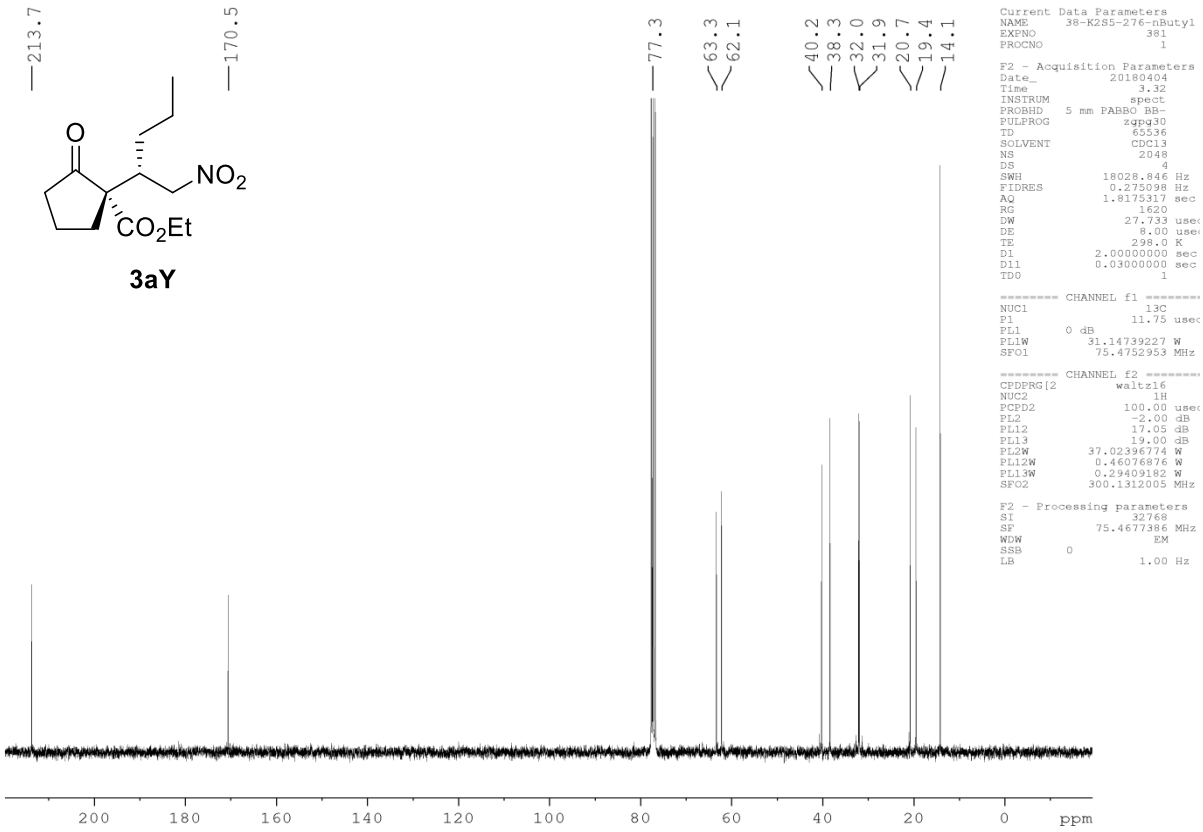

4.75 4.72 4.71 4.68 4.53 4.52 4.49 4.48 4.21 4.21 4.19 4.18 4.16 4.16 2.50 2.48 2.47 2.47 2.46 2.46 2.45 2.45 2.38 2.36 2.32 2.30 2.28 2.25 2.22 2.15 2.03 1.29 1.26 1.24 0.63 0.61 0.59 0.59 0.58 0.53 0.51 0.50 0.31 0.29 0.28 0.23 0.23 0.22 0.20
O
NO2
CO2Et
3aW
water
8 7 6 5 4 3 2 1 0 ppm
1.00 1.01 1.99 3.98 1.08 2.09 3.08 2.97 2.04

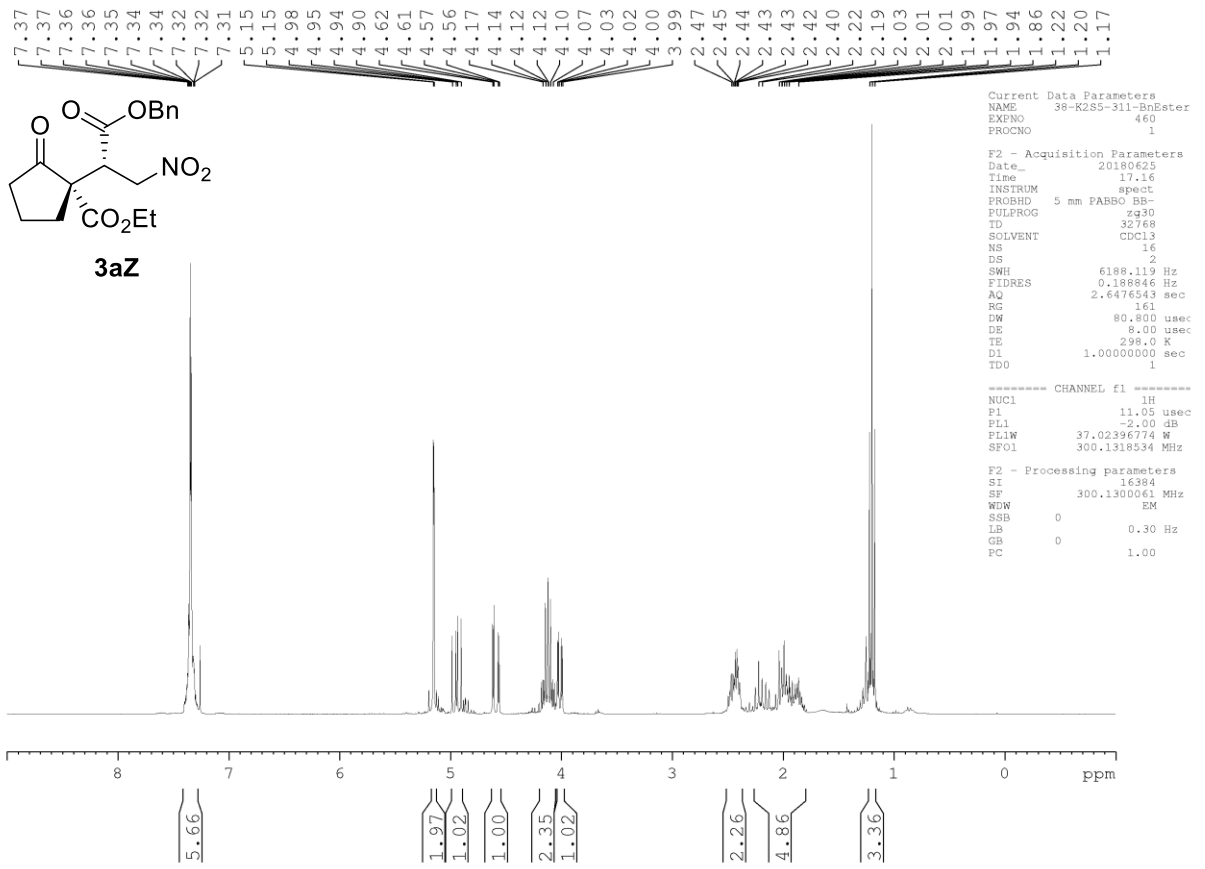

213.9
170.3
78.2
64.0
62.2
45.0
38.6
31.6
19.6
14.1
11.9
5.7
2.4
O
NO2
CO2Et
3aW
200 180 160 140 120 100 80 60 40 20 ppm

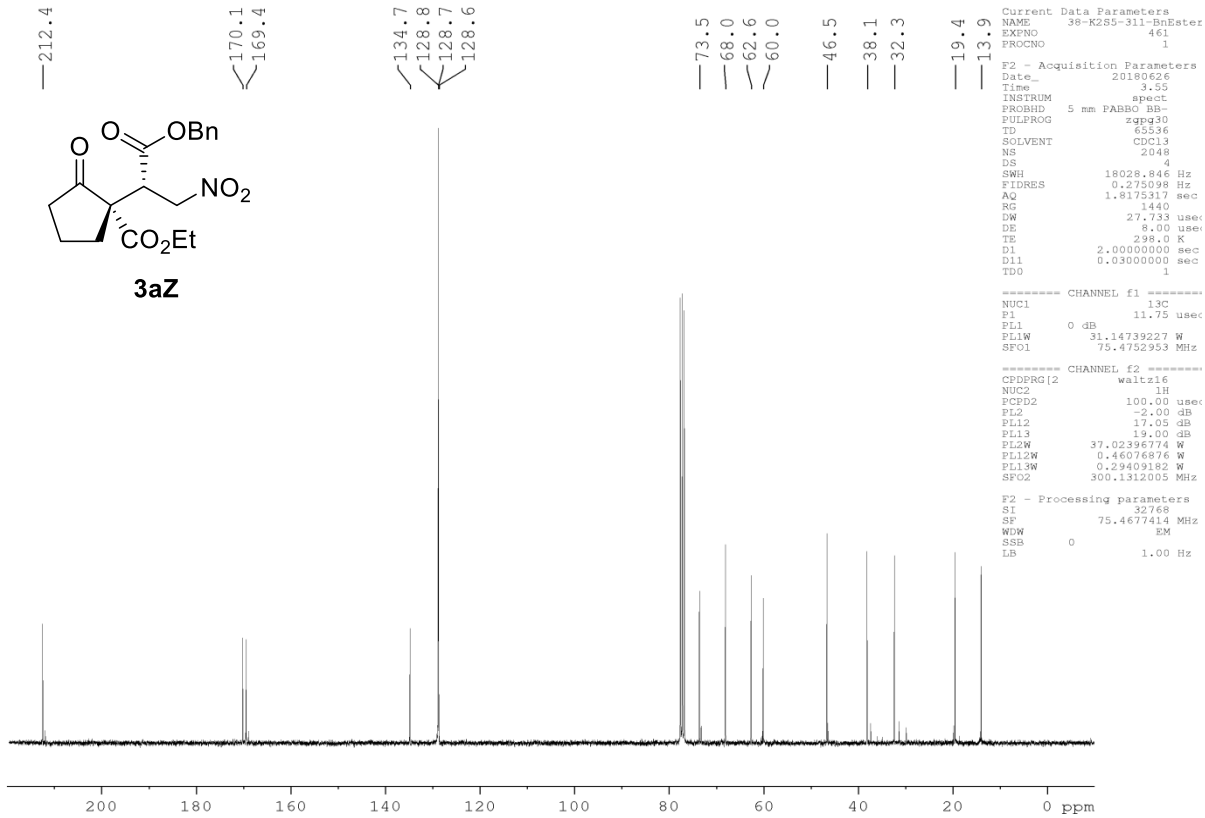

4.59 4.58 4.57 4.56 4.41 4.40 4.39 4.38 4.19 4.18 4.17 4.16 3.00 2.99 2.98 2.46 2.46 2.45 2.26 2.24 2.23 2.01 2.01 2.00 1.95 1.94 1.94 1.93 1.92 1.91 1.58 1.56 1.55 1.32 1.32 1.31 1.30 1.28 1.28 1.27 1.26 1.25 1.24 0.92 0.91 0.90 0.90 0.89
O
NO2
CO2Et
3aX
Current Data Parameters
NAME 38-K255-285-Isoval-
EXPNO 80
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180913
Time 1.41
INSTRUM spect
PROBHD 5 mm CPQCI 1H-
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 10504.202 Hz
FIDRES 0.160281 Hz
AQ 3.1195135 sec
RG 12.77
DW 47.600 usec
DE 20.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 700.3632917 MHz
NUC1 1H
P1 8.15 usec
PLW1 9.89999962 W
F2 - Processing parameters
SI 65536
SF 700.3600176 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
0.05 1.00 1.00 1.88 0.91 2.04 0.98 3.19 1.00 0.99 4.05 6.36

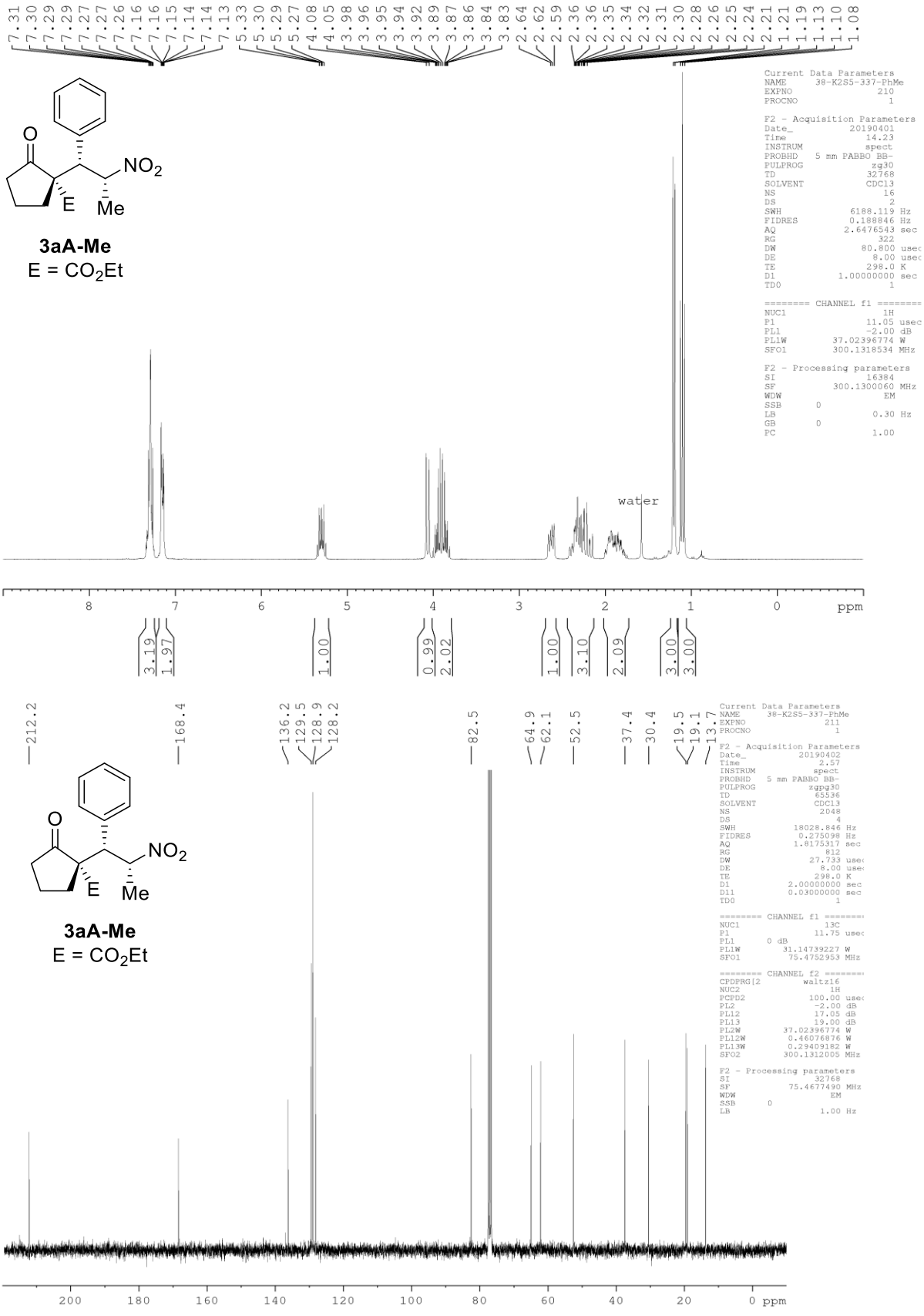

213.6 170.4 77.5 63.5 62.2 39.0 38.4 38.3 31.6 25.8 23.8 21.3 19.4 14.1
O
NO2
CO2Et
3aX
Current Data Parameters
NAME 38-K255-285-Isoval-
EXPNO 81
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180913
Time 3.19
INSTRUM spect
PROBHD 5 mm CPQCI 1H-
PULPROG zgpg30
TD 65356
SOLVENT CDCl3
NS 2048
DS 4
SWH 40760.871 Hz
FIDRES 0.623675 Hz
AQ 0.8017003 sec
RG 182.53
DW 12.267 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 176.1232717 MHz
NUC1 13C
P1 12.00 usec
PLW1 105.00000000 W
======== CHANNEL f2 ========
SFO2 700.3628014 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 65.00 usec
PLW2 9.89999962 W
PLW12 0.15564001 W
PLW13 0.07837200 W
F2 - Processing parameters
SI 131072
SF 176.1056422 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm

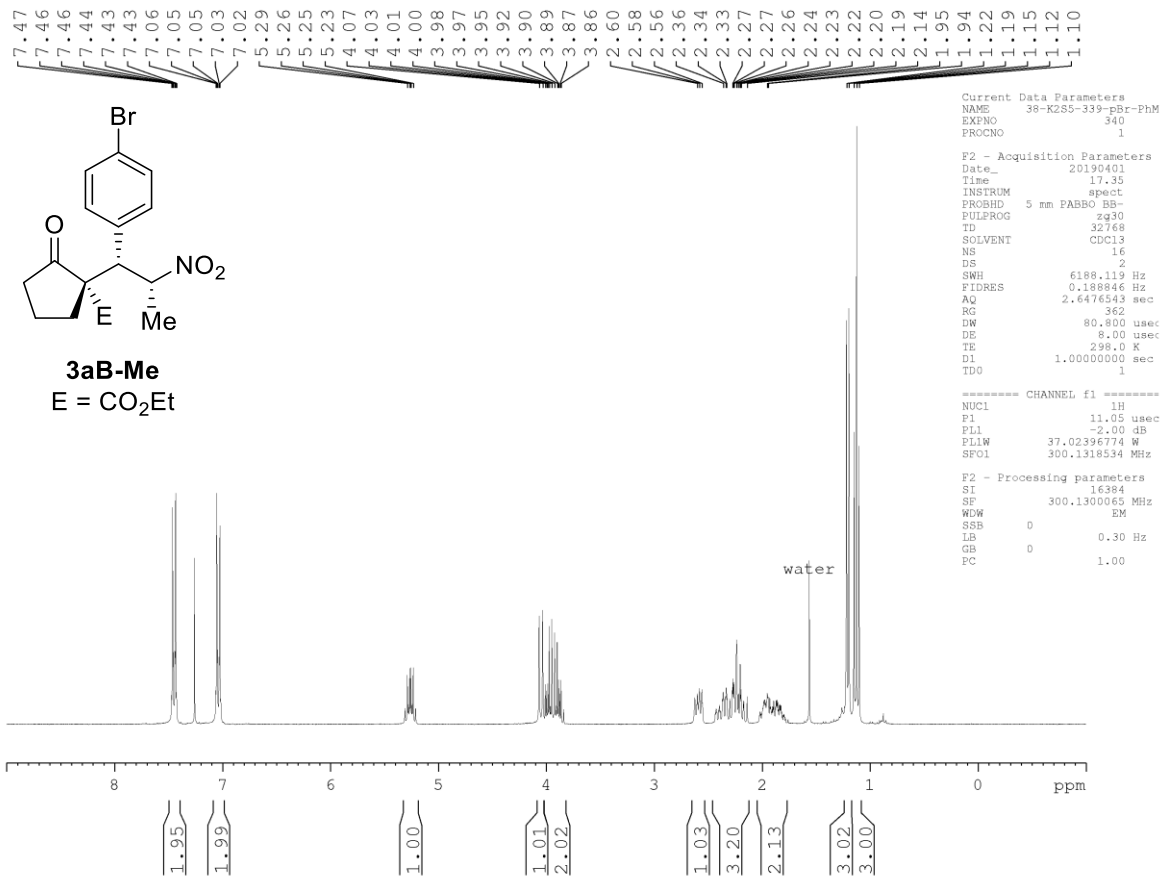

4.54 4.54 4.52 4.52 4.47 4.47 4.46 4.45 4.20 4.19 4.18 4.17 2.93 2.92 2.49 2.47 2.46 2.46 2.45 2.26 2.24 2.23 2.01 2.01 2.00 2.00 1.97 1.96 1.96 1.95 1.95 1.94 1.93 1.93 1.58 1.57 1.55 1.37 1.32 1.31 1.30 1.28 1.28 1.27 1.26 1.25 0.91 0.90 0.89
O
NO2
CO2Et
3aY
Current Data Parameters
NAME 38-K255-276.1-TK-F2
EXPNO 70
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180912
Time 23.55
INSTRUM spect
PROBHD 5 mm CPQCI 1H-
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 10504.202 Hz
FIDRES 0.160281 Hz
AQ 3.1195135 sec
RG 14.51
DW 47.600 usec
DE 20.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 700.3632917 MHz
NUC1 1H
P1 8.15 usec
PLW1 9.89999962 W
F2 - Processing parameters
SI 65536
SF 700.3600162 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
0.98 1.00 1.82 0.88 2.03 1.00 3.14 1.33 1.03 5.15 3.04

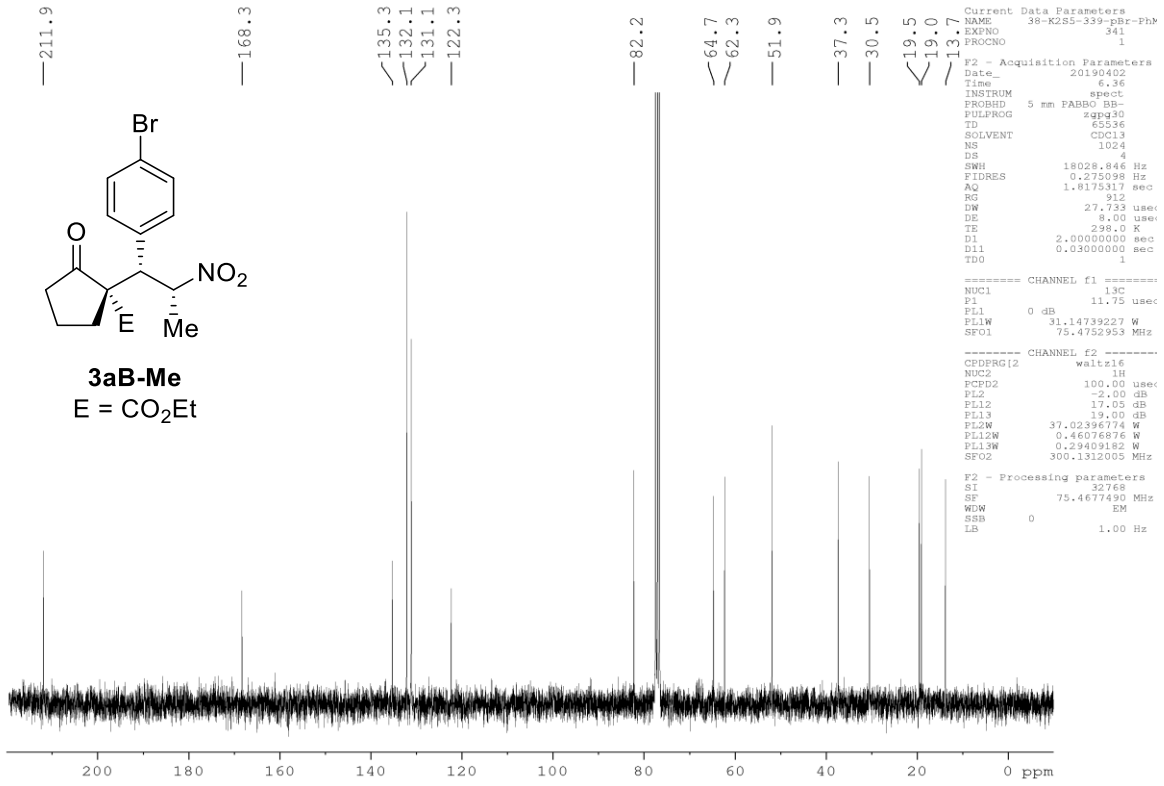

213.7
170.5
77.3
63.3
62.1
40.2
38.3
32.0
31.9
20.7
19.4
14.1
O
NO2
CO2Et
3aY
Current Data Parameters
NAME 38-K255-276-nButyl
EXPNO 381
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180404
Time 3.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 1620
DW 27.733 usec
DE 8.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.75 usec
PL1 0 dB
PL1W 31.14739227 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -2.00 dB
PL12 17.05 dB
PL13 19.00 dB
PL2W 37.02396774 W
PL12W 0.46076876 W
PL13W 0.29409182 W
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677386 MHz
WDW EM
SSB 0
LB 1.00 Hz
200 180 160 140 120 100 80 60 40 20 0 ppm

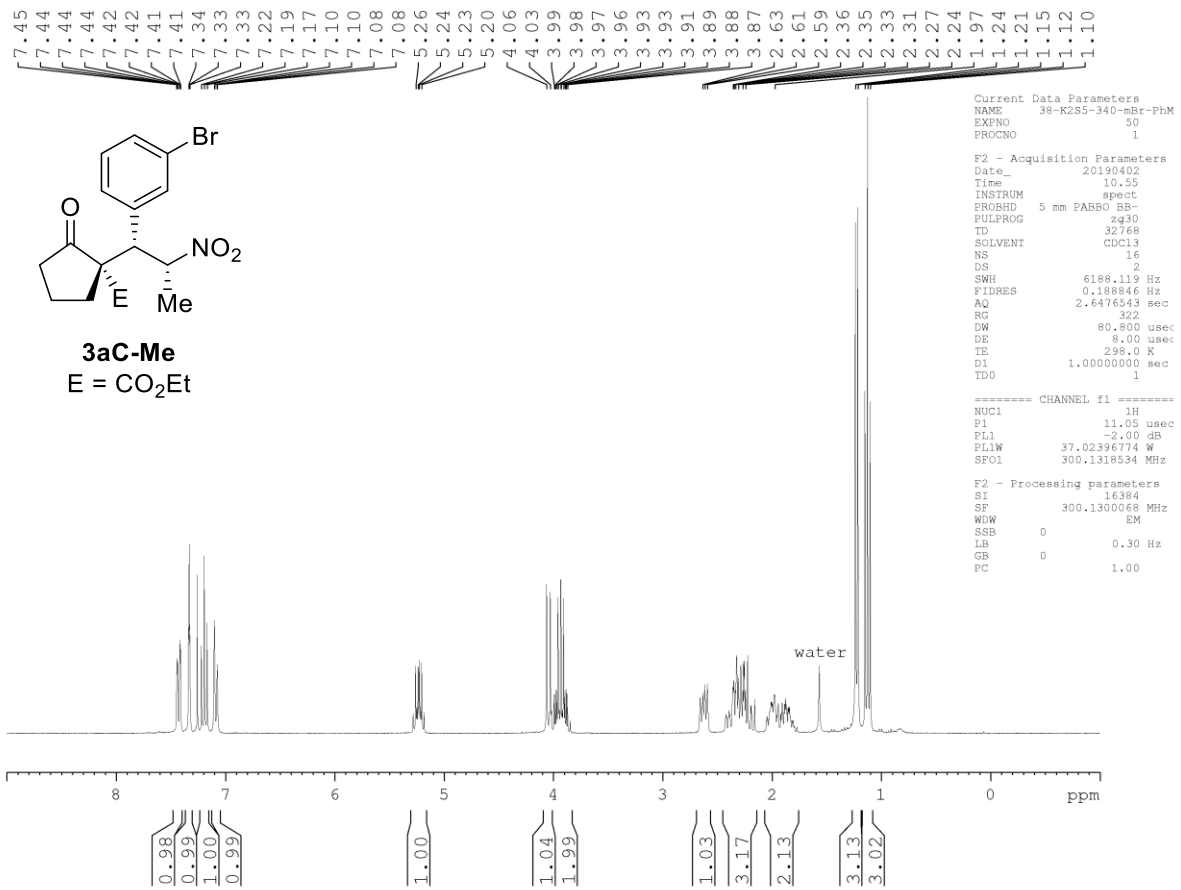

7.37 7.37 7.36 7.35 7.34 7.34 7.32 7.32 7.31
5.15 5.15 4.98 4.95 4.94 4.90 4.62 4.61 4.57 4.56 4.17 4.14 4.12 4.10 4.07 4.03 4.02 4.00 3.99
2.47 2.45 2.44 2.43 2.42 2.40 2.22 2.19 2.03 2.01 2.01 1.99 1.97 1.94 1.86 1.22 1.20 1.17
O
OBn
NO2
CO2Et
3aZ
Current Data Parameters
NAME 38-K2S5-311-BnEster
EXPNO 460
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180625
Time 17.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 161
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
5.66 1.97 1.02 1.00 2.35 1.02 2.26 4.86 3.36

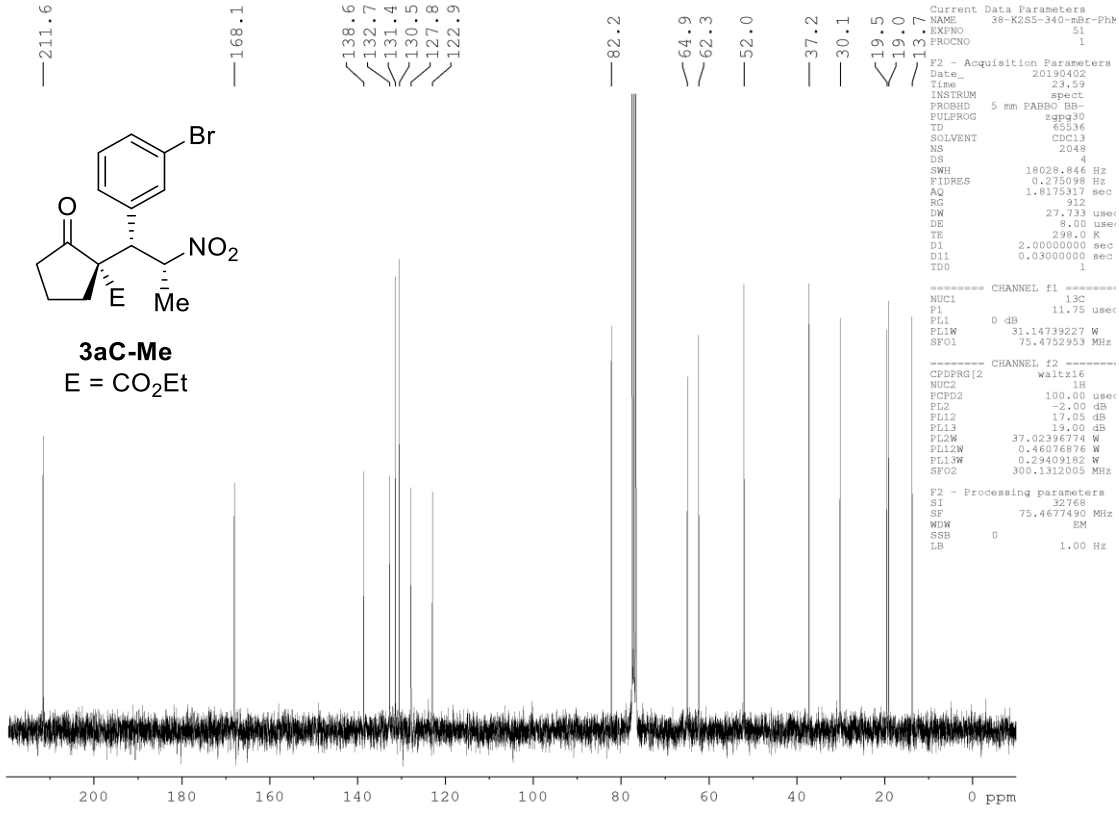

212.4
170.1 169.4
134.7 128.8 128.7 128.6
73.5 68.0 62.6 60.0 46.5 38.1 32.3 19.4 13.9
O
OBn
NO2
CO2Et
3aZ
Current Data Parameters
NAME 38-K2S5-311-BnEster
EXPNO 461
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180626
Time 3.55
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 1440
DW 27.733 usec
DE 8.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.75 usec
PL1 0 dB
PL1W 31.14739227 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -2.00 dB
PL12 17.05 dB
PL13 19.00 dB
PL2W 37.02396774 W
PL12W 0.46076876 W
PL13W 0.29409182 W
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677414 MHz
WDW EM
SSB 0
LB 1.00 Hz
200 180 160 140 120 100 80 60 40 20 0 ppm

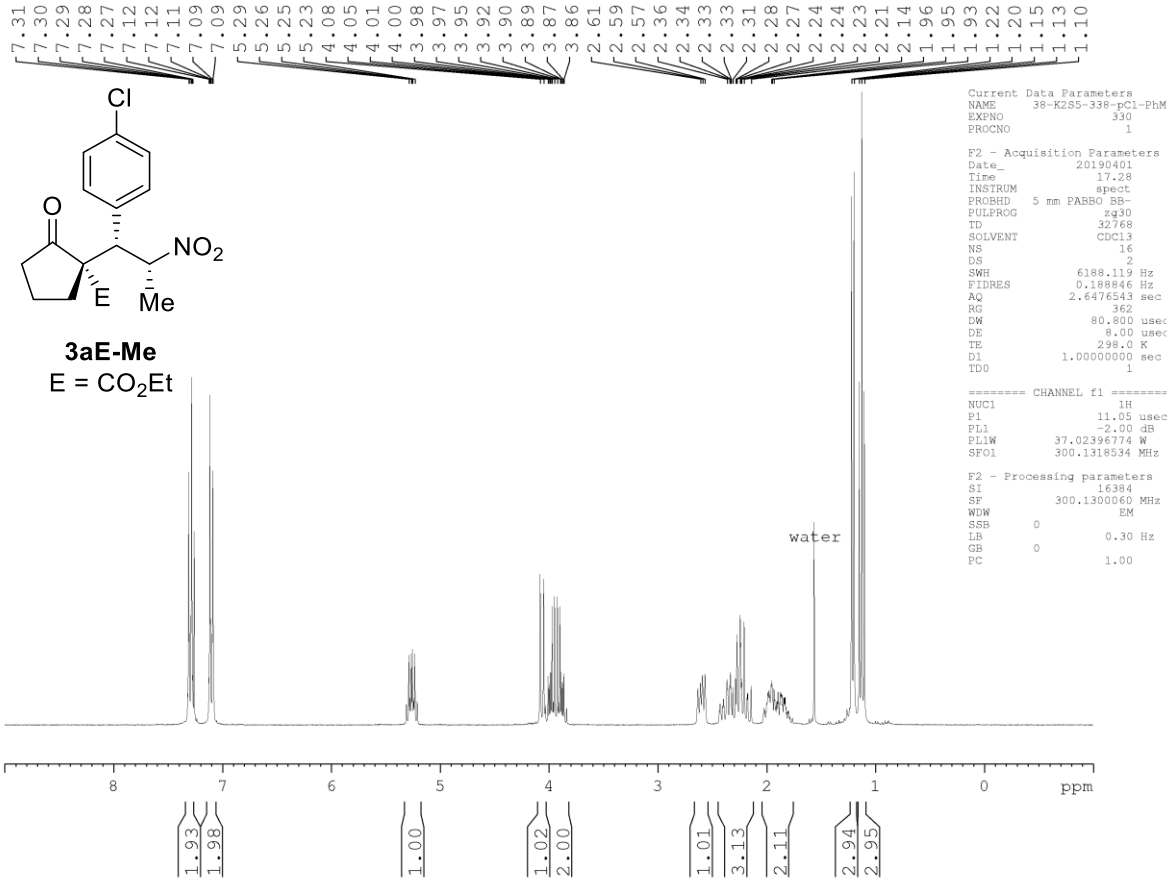

7.31 7.30 7.29 7.29 7.27 7.27 7.26 7.16 7.16 7.15 7.14 7.14 7.13
5.33 5.30 5.29 5.27 4.08 4.05 3.98 3.96 3.95 3.94 3.92 3.89 3.87 3.86 3.84 3.83
2.64 2.62 2.59 2.36 2.36 2.35 2.34 2.32 2.31 2.30 2.28 2.26 2.25 2.24 2.21 1.21 1.19 1.13 1.10 1.08
O
NO2
E
Me
3aA-Me
E = CO2Et
water
ppm
3.19 1.97 1.00 0.99 2.02 1.00 3.10 2.09 3.00 3.00
212.2 168.4 136.2 129.5 128.9 128.2 82.5 64.9 62.1 52.5 37.4 30.4 19.5 19.1 13.7
0 ppm

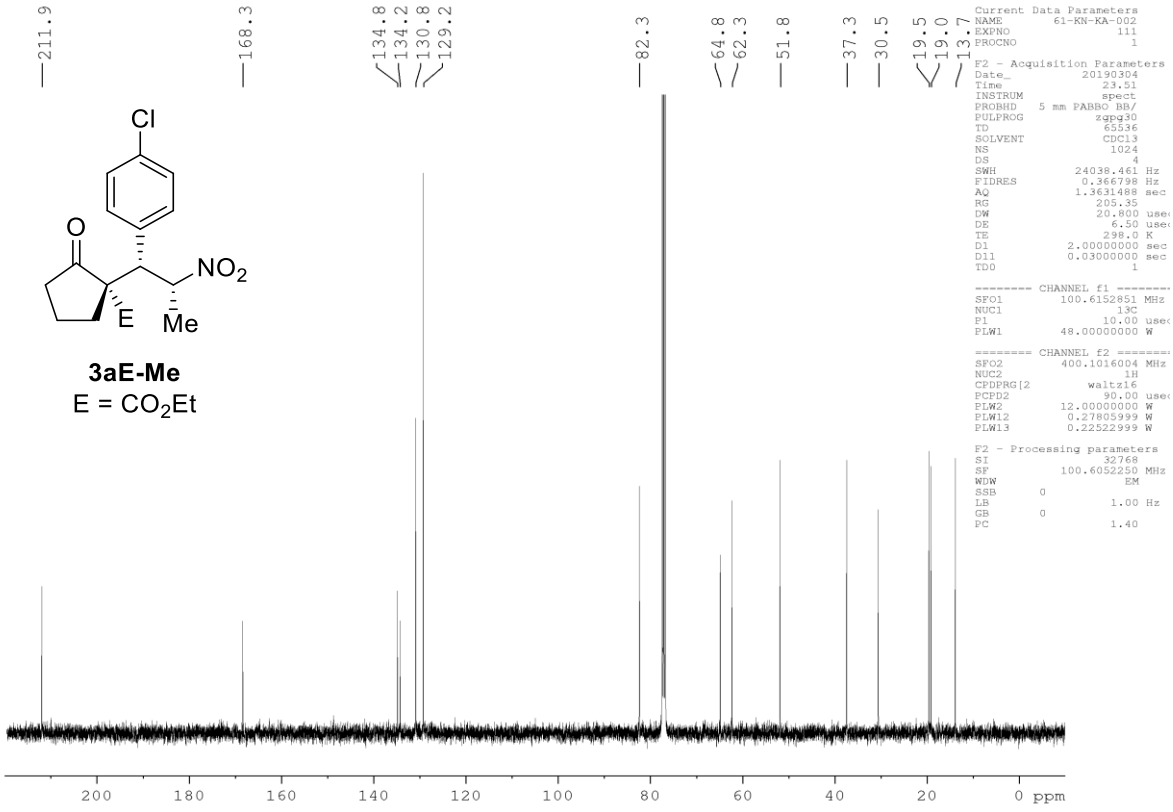

7.47 7.46 7.46 7.44 7.43 7.43 7.06 7.05 7.05 7.03 7.02
5.29 5.26 5.25 5.23 4.07 4.03 4.01 4.00 3.98 3.97 3.95 3.92 3.90 3.89 3.87 3.86
2.60 2.58 2.56 2.36 2.34 2.33 2.27 2.27 2.26 2.24 2.23 2.22 2.20 2.19 2.14 1.95 1.94 1.22 1.19 1.15 1.12 1.10
Br
O
NO2
E
Me
3aB-Me
E = CO2Et
water
ppm
1.95
1.99
1.00
1.01
2.02
1.03
3.20
2.13
3.02
3.00

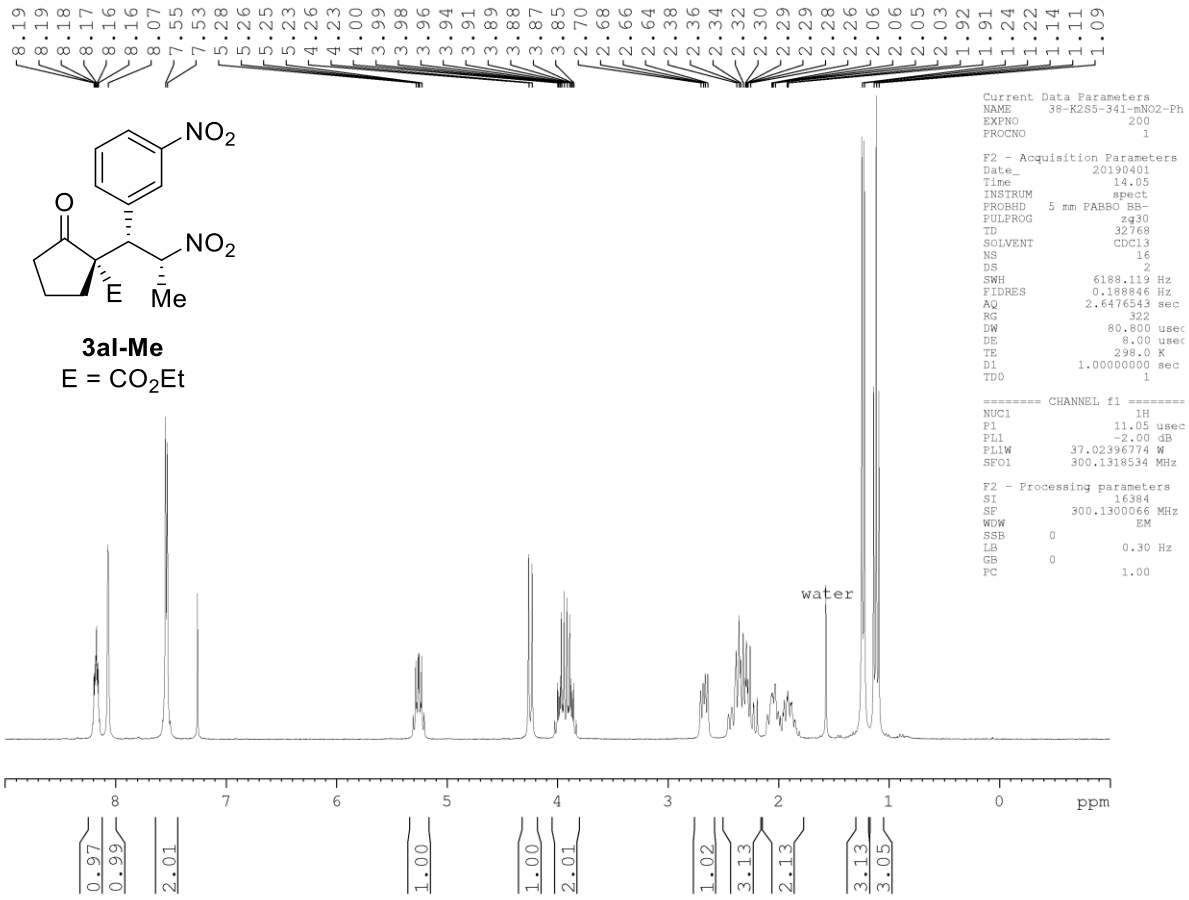

211.9
168.3
135.3
132.1
131.1
122.3
82.2
64.7
62.3
51.9
37.3
30.5
19.5
19.0
13.7
Br
O
NO2
E
Me
3aB-Me
E = CO2Et
ppm

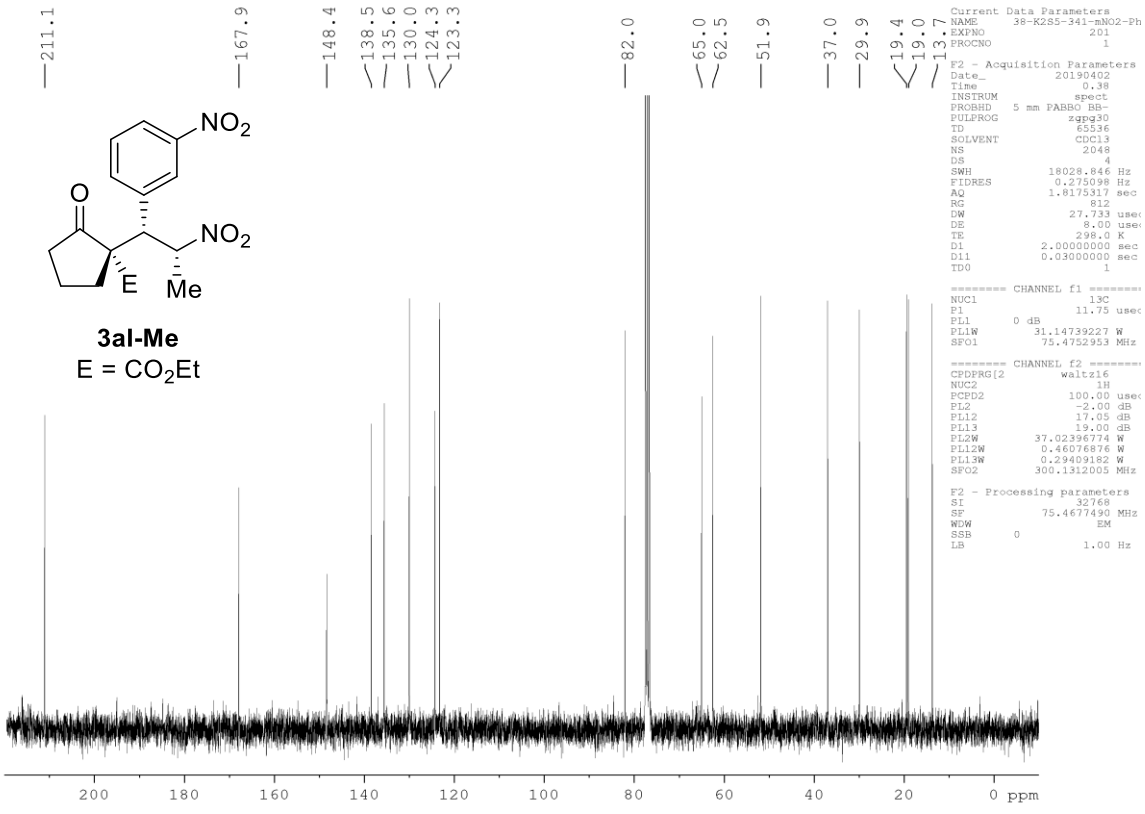

7.45 7.44 7.44 7.44 7.42 7.42 7.41 7.41 7.34 7.33 7.33 7.22 7.19 7.17 7.10 7.10 7.08 5.26 5.24 5.23 5.20 4.06 4.03 3.99 3.98 3.97 3.96 3.93 3.93 3.91 3.89 3.88 3.87 2.63 2.61 2.59 2.36 2.35 2.33 2.31 2.27 2.24 1.97 1.24 1.21 1.15 1.12 1.10
Br
O
NO2
E
Me
3aC-Me
E = CO2Et
water
ppm
0.98 0.99 1.00 0.99 1.00 1.04 1.99 1.03 3.17 2.13 3.13 3.02

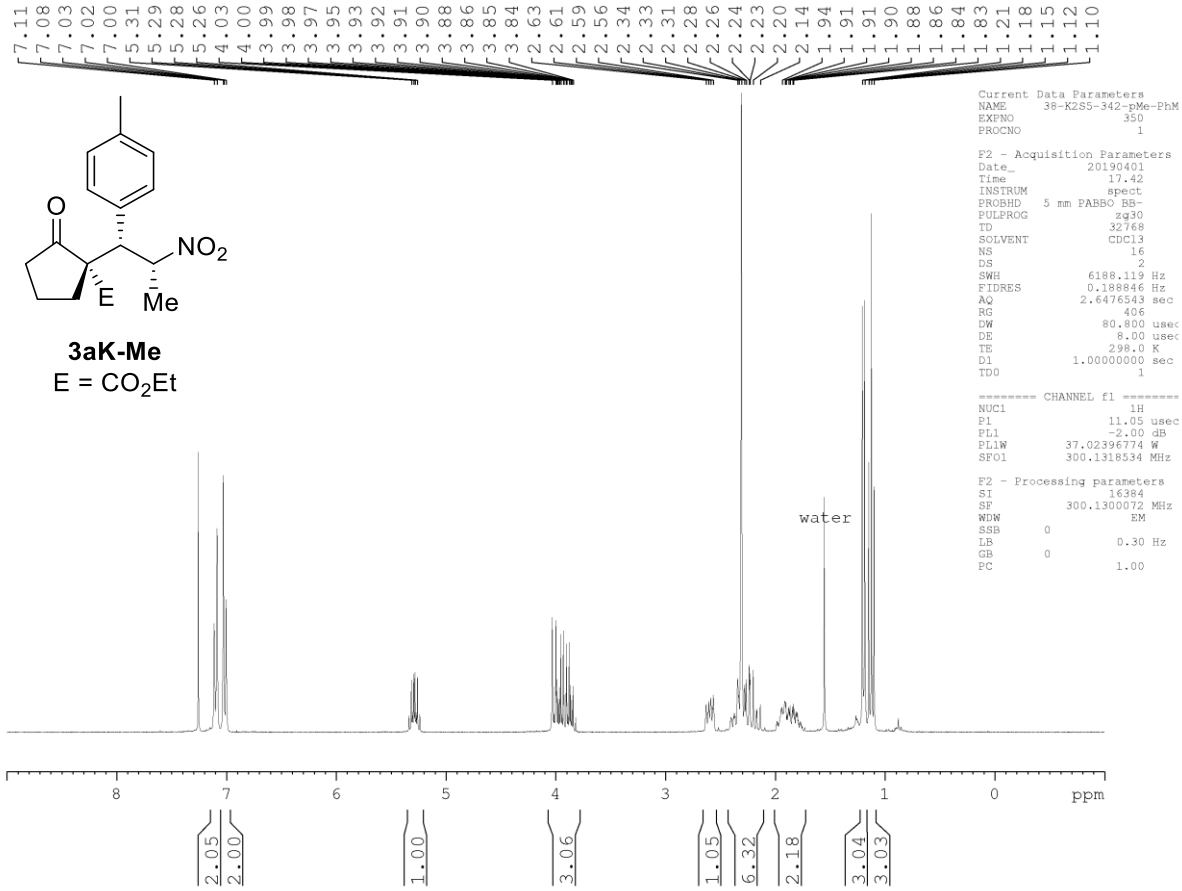

211.6 168.1 138.6 132.7 131.4 130.5 127.8 122.9 82.2 64.9 62.3 52.0 37.2 30.1 19.5 19.0 13.7
Br
O
NO2
E
Me
3aC-Me
E = CO2Et
ppm

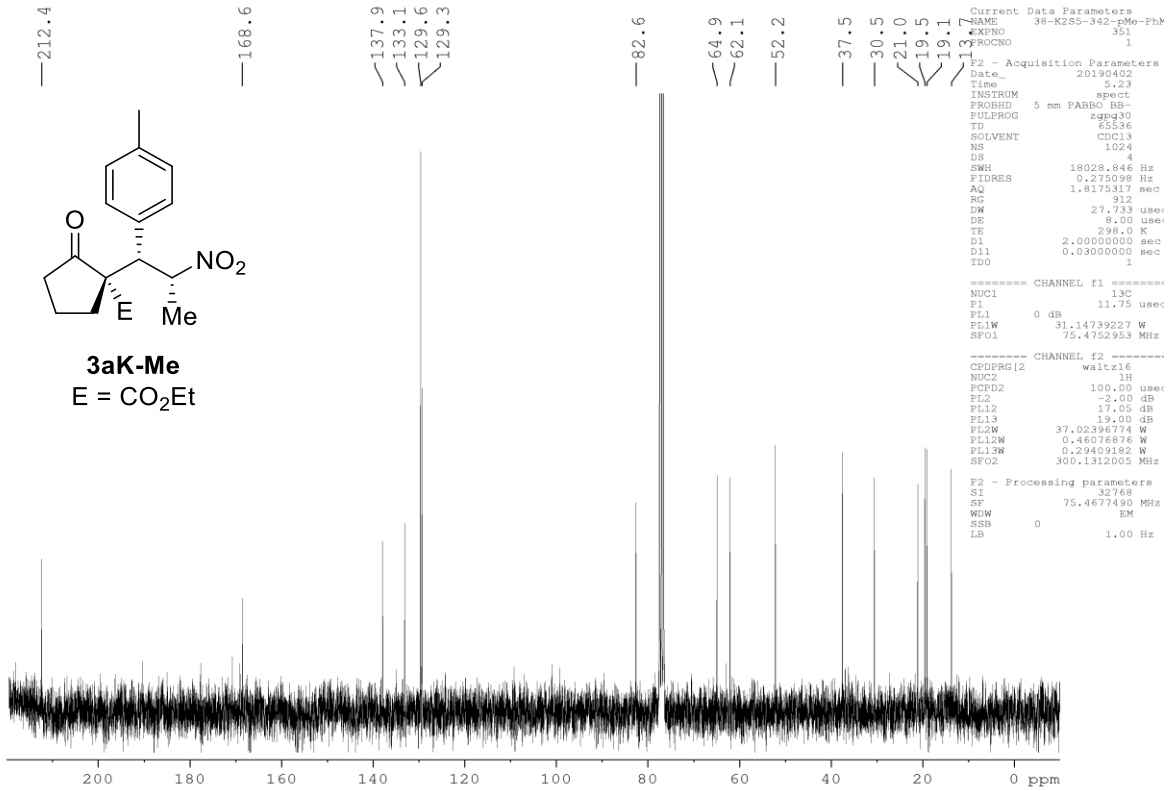

7.31 7.30 7.29 7.28 7.27 7.12 7.12 7.11 7.09 7.09
5.29 5.26 5.25 5.23 4.08 4.05 4.01 4.00 3.98 3.97 3.95 3.92 3.90 3.89 3.87 3.86
2.61 2.59 2.57 2.36 2.34 2.33 2.33 2.31 2.28 2.27 2.24 2.24 2.23 2.21 2.14 1.96 1.95 1.93 1.22 1.20 1.15 1.13 1.10
Cl
O
NO2
E
Me
3aE-Me
E = CO2Et
water
Current Data Parameters
NAME 38-K2S5-338-pCl-PhM
EXPNO 330
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190401
Time 17.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 362
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300060 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
1.93 1.98 1.00 1.02 2.00 1.01 3.13 2.11 2.94 2.95

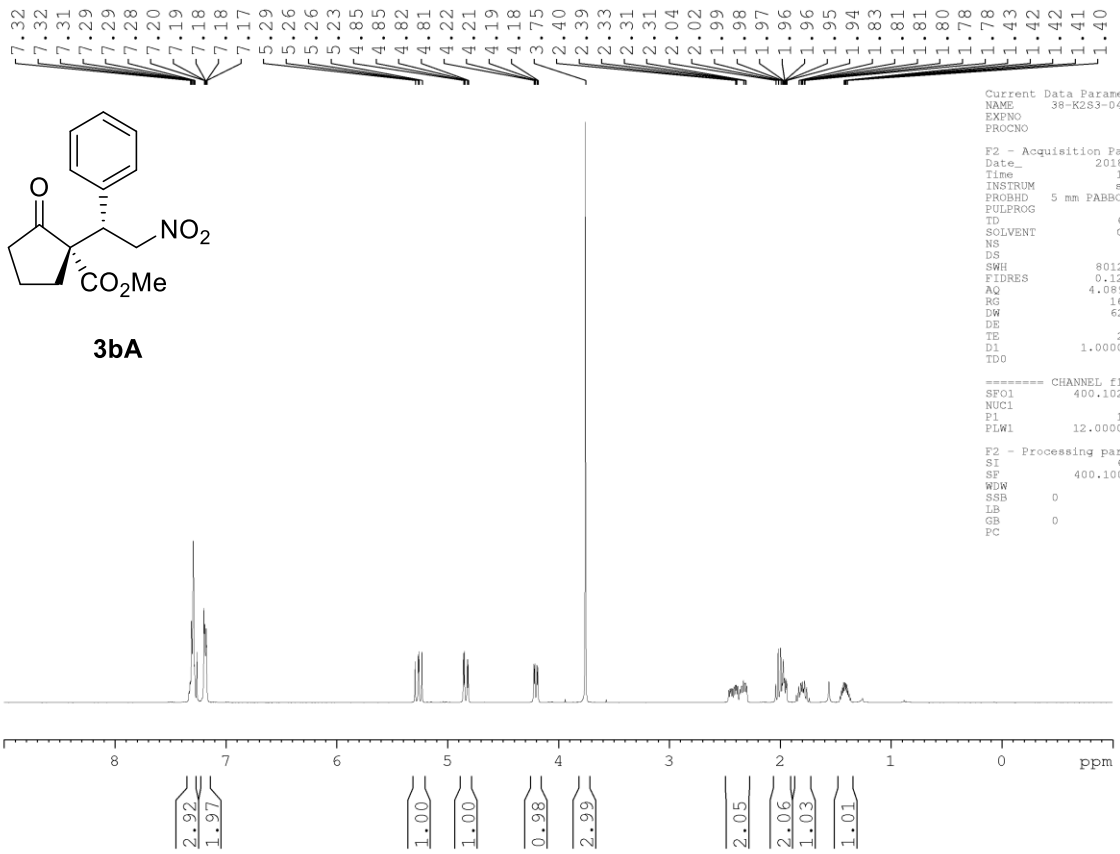

211.9 168.3 134.8 134.2 130.8 129.2 82.3 64.8 62.3 51.8 37.3 30.5 19.5 19.0 13.7
Cl
O
NO2
E
Me
3aE-Me
E = CO2Et
Current Data Parameters
NAME 61-KN-KA-002
EXPNO 111
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190304
Time 23.51
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 205.35
DW 20.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6152851 MHz
NUC1 13C
P1 10.00 usec
PLW1 48.00000000 W
======== CHANNEL f2 ========
SFO2 400.1016004 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 12.00000000 W
PLW12 0.27805999 W
PLW13 0.22522999 W
F2 - Processing parameters
SI 32768
SF 100.6052250 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm

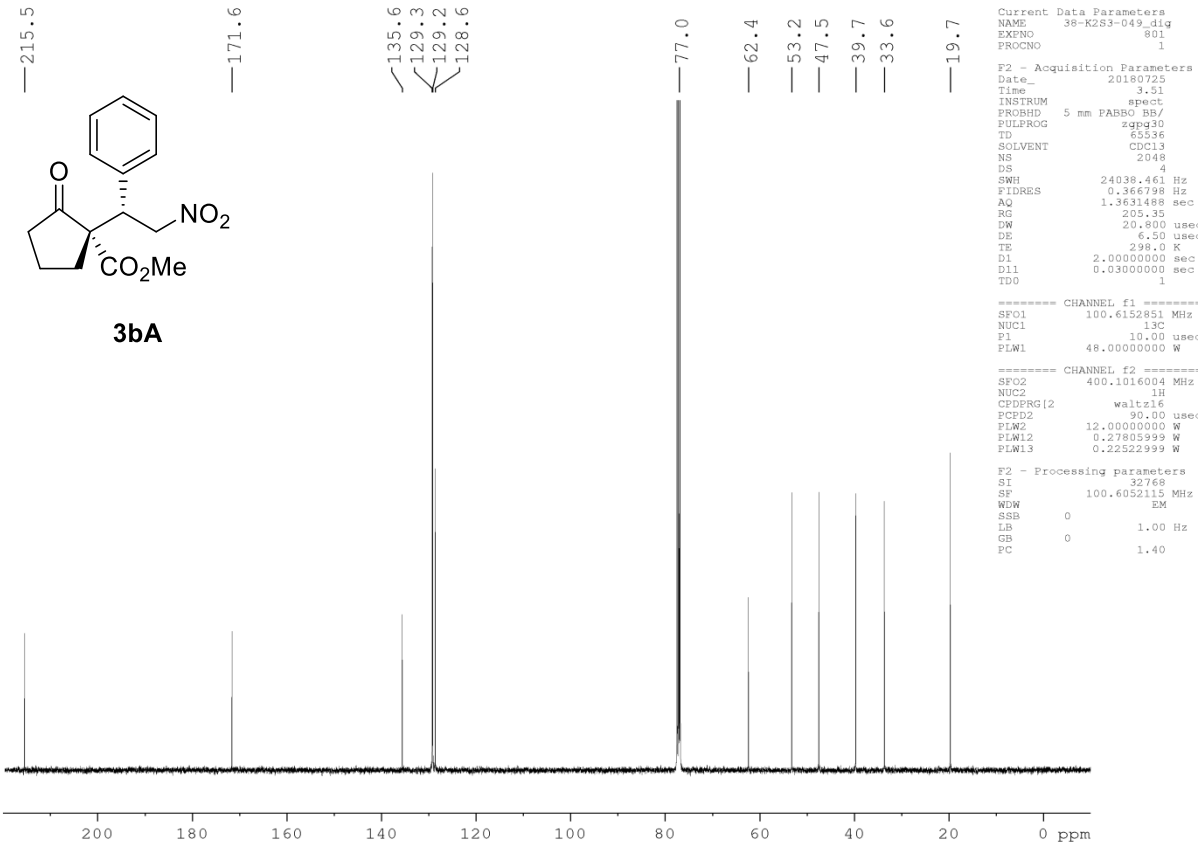

8.19
8.19
8.18
8.17
8.16
8.16
8.07
7.55
7.53
5.28
5.26
5.25
5.23
4.26
4.23
4.00
3.99
3.98
3.96
3.94
3.91
3.89
3.88
3.87
3.85
2.70
2.68
2.66
2.64
2.38
2.36
2.34
2.32
2.30
2.29
2.29
2.28
2.26
2.06
2.06
2.05
2.03
1.92
1.91
1.24
1.22
1.14
1.11
1.09
NO2
NO2
O
E
Me
3aI-Me
E = CO2Et
water
ppm
0.97
0.99
2.01
1.00
1.00
2.01
1.02
3.13
2.13
3.13
3.05

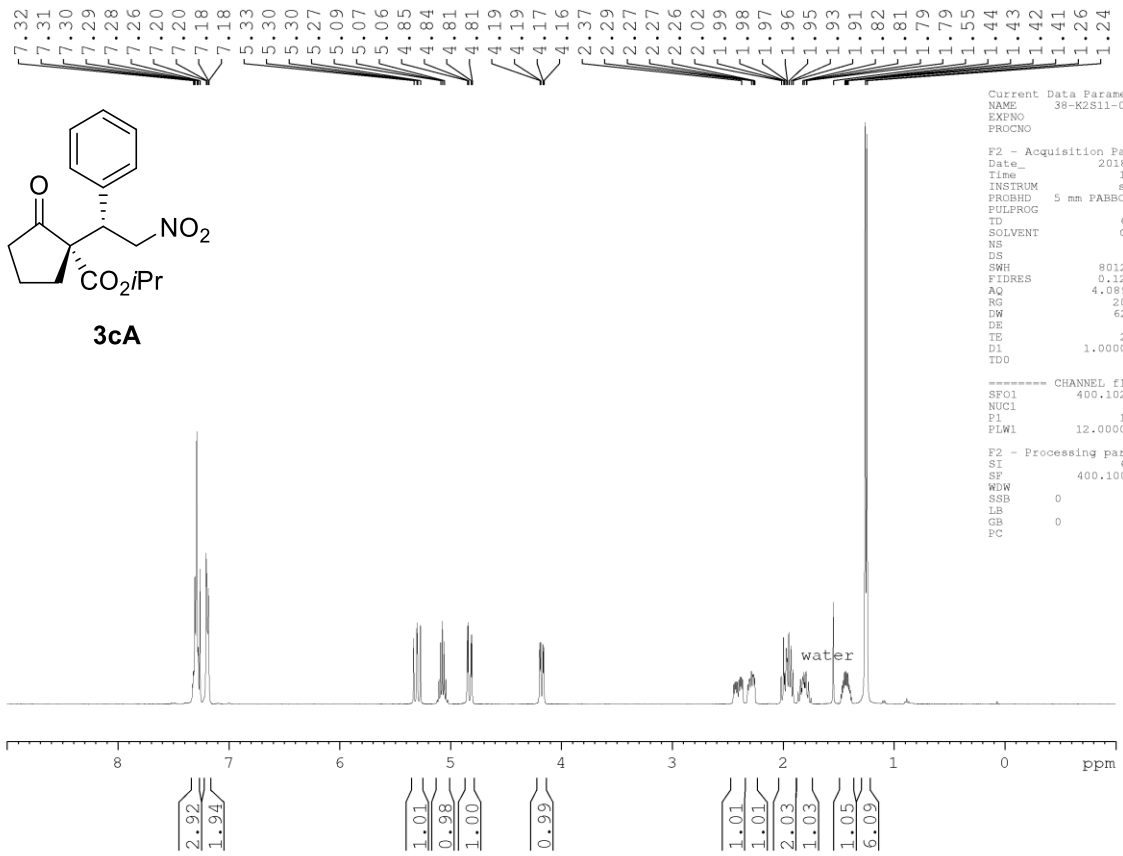

211.1
167.9
148.4
138.5
135.6
130.0
124.3
123.3
82.0
65.0
62.5
51.9
37.0
29.9
19.4
19.0
13.7
NO2
NO2
O
E
Me
3aI-Me
E = CO2Et
ppm

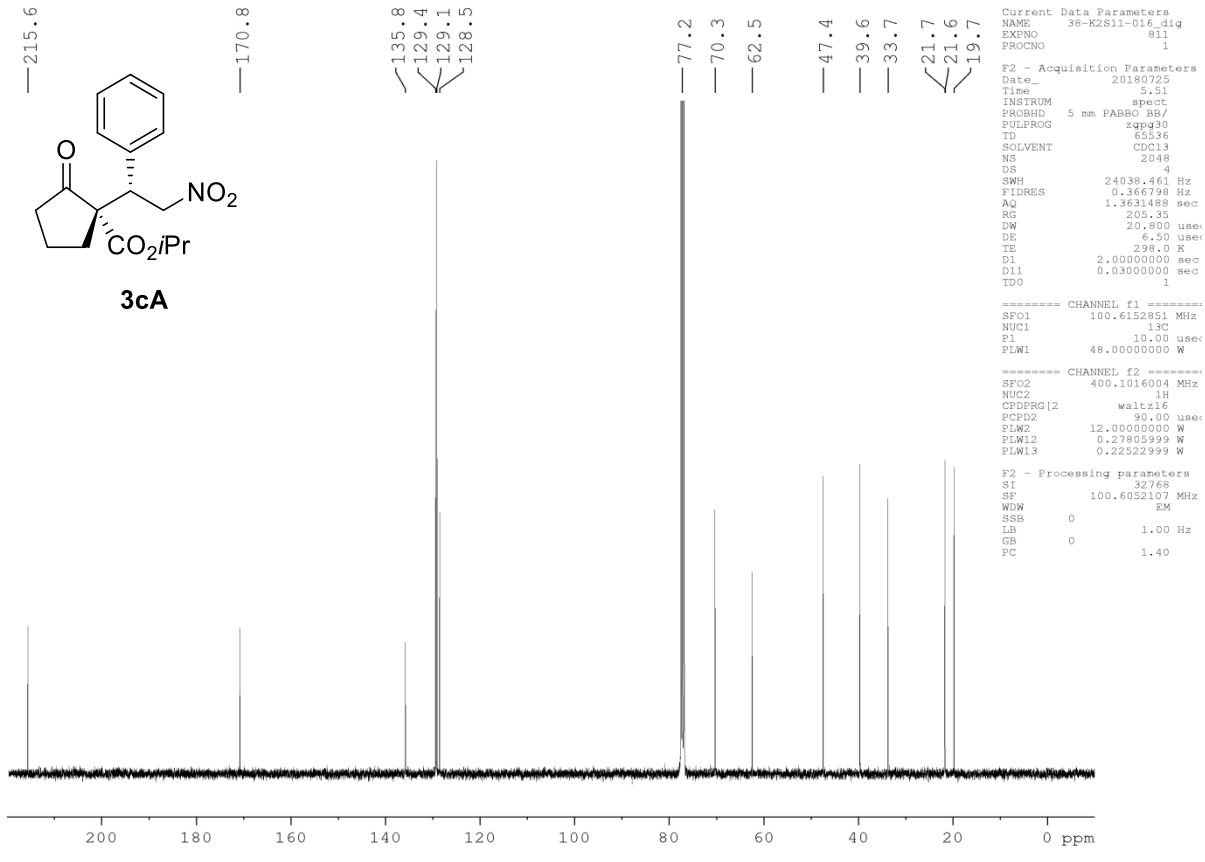

7.11 7.08 7.03 7.02 7.00 5.31 5.29 5.28 5.26 4.03 4.00 3.99 3.98 3.97 3.95 3.93 3.92 3.91 3.90 3.88 3.86 3.85 3.84 2.63 2.61 2.59 2.56 2.34 2.33 2.31 2.28 2.26 2.24 2.23 2.20 2.14 1.94 1.91 1.90 1.88 1.86 1.84 1.83 1.21 1.18 1.15 1.12 1.10
O
NO2
E
Me
3aK-Me
E = CO2Et
water
Current Data Parameters
NAME 38-K2S5-342-pMe-PhM
EXPNO 350
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190401
Time 17.42
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 406
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300072 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
2.05 2.00 1.00 3.06 1.05 6.32 2.18 3.04 3.03

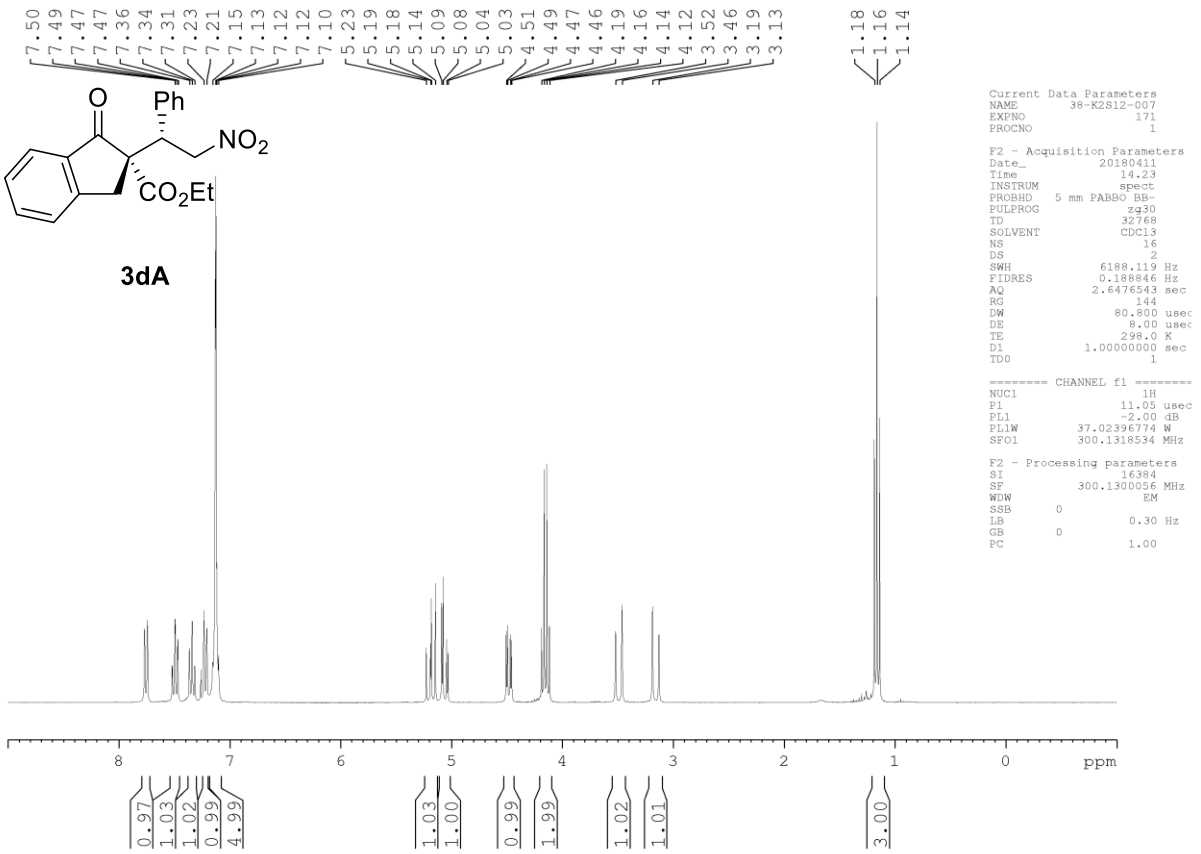

212.4 168.6 137.9 133.1 129.6 129.3 82.6 64.9 62.1 52.2 37.5 30.5 21.0 19.5 19.1 13.7
O
NO2
E
Me
3aK-Me
E = CO2Et
Current Data Parameters
NAME 38-K2S5-342-pMe-PhM
EXPNO 351
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190402
Time 5.23
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 912
DW 27.733 usec
DE 8.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.75 usec
PL1 0 dB
PL1W 31.14739227 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -2.00 dB
PL12 17.05 dB
PL13 19.00 dB
PL2W 37.02396774 W
PL12W 0.46076876 W
PL13W 0.29409182 W
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
200 180 160 140 120 100 80 60 40 20 0 ppm

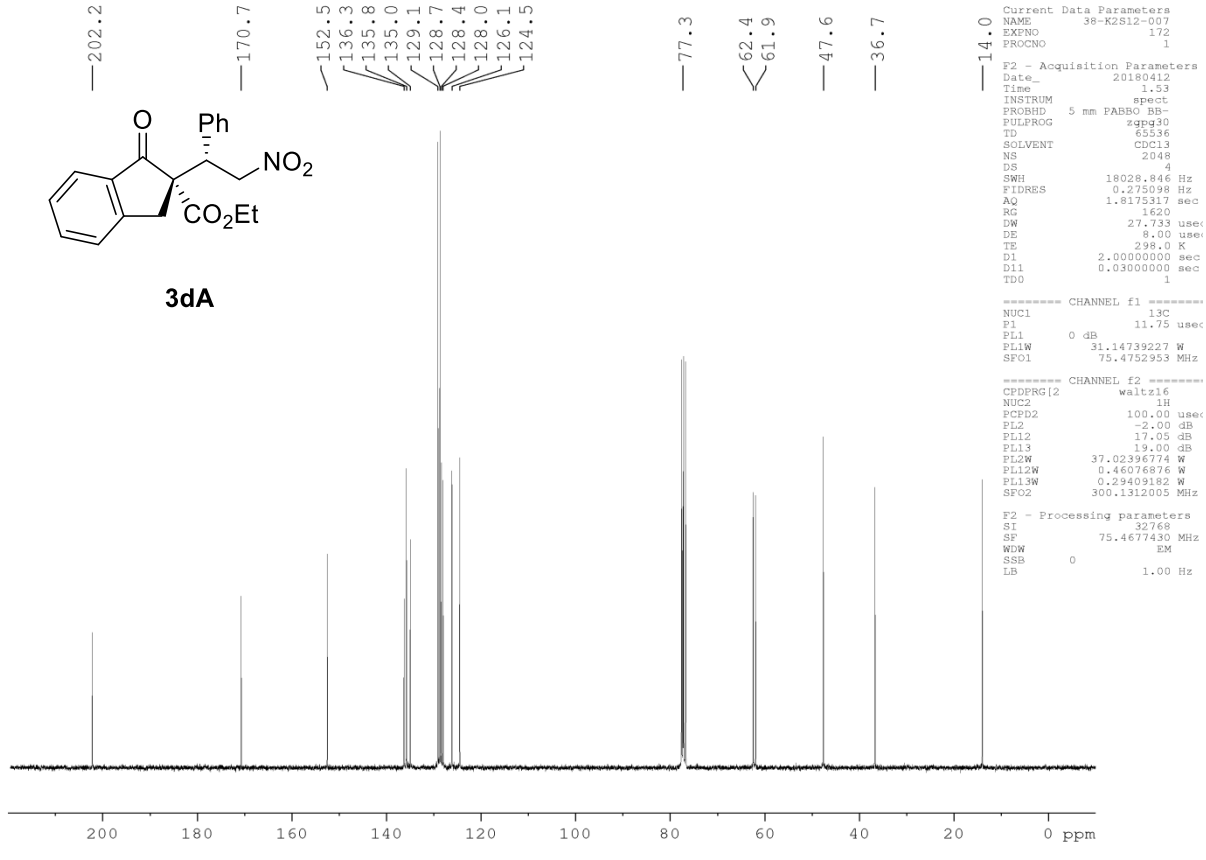

7.32 7.32 7.31 7.29 7.29 7.28 7.20 7.19 7.18 7.18 7.17
5.29 5.26 5.23 4.85 4.85 4.82 4.81 4.22 4.21 4.19 4.18 3.75
2.40 2.39 2.33 2.31 2.31 2.04 2.02 1.99 1.98 1.97 1.96 1.96 1.95 1.94 1.83 1.81 1.81 1.80 1.78 1.78 1.43 1.42 1.42 1.41 1.40
O
NO2
CO2Me
3bA
Current Data Parameters
NAME 38-KZS3-049_dig
EXPNO 800
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180724
Time 19.15
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 160.83
DW 62.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1024708 MHz
NUC1 1H
P1 13.70 usec
PLW1 12.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1000097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
2.92 1.97 1.00 1.00 0.98 2.99 2.05 2.06 1.03 1.01

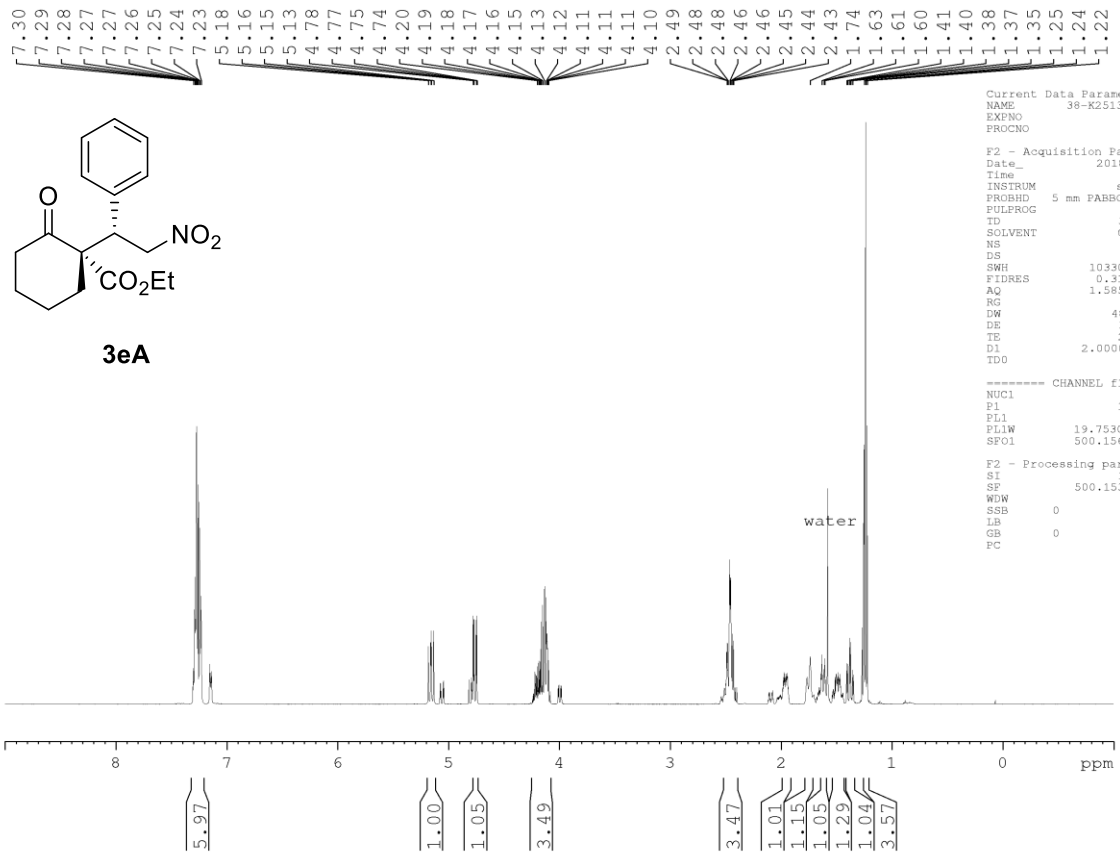

215.5 171.6 135.6 129.3 129.2 128.6 77.0 62.4 53.2 47.5 39.7 33.6 19.7
O
NO2
CO2Me
3bA
Current Data Parameters
NAME 38-KZS3-049_dig
EXPNO 801
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180725
Time 3.51
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 205.35
DW 20.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6152851 MHz
NUC1 13C
P1 10.00 usec
PLW1 48.00000000 W
======== CHANNEL f2 ========
SFO2 400.1016004 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 12.00000000 W
PLW12 0.27805999 W
PLW13 0.22522999 W
F2 - Processing parameters
SI 32768
SF 100.6052115 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm

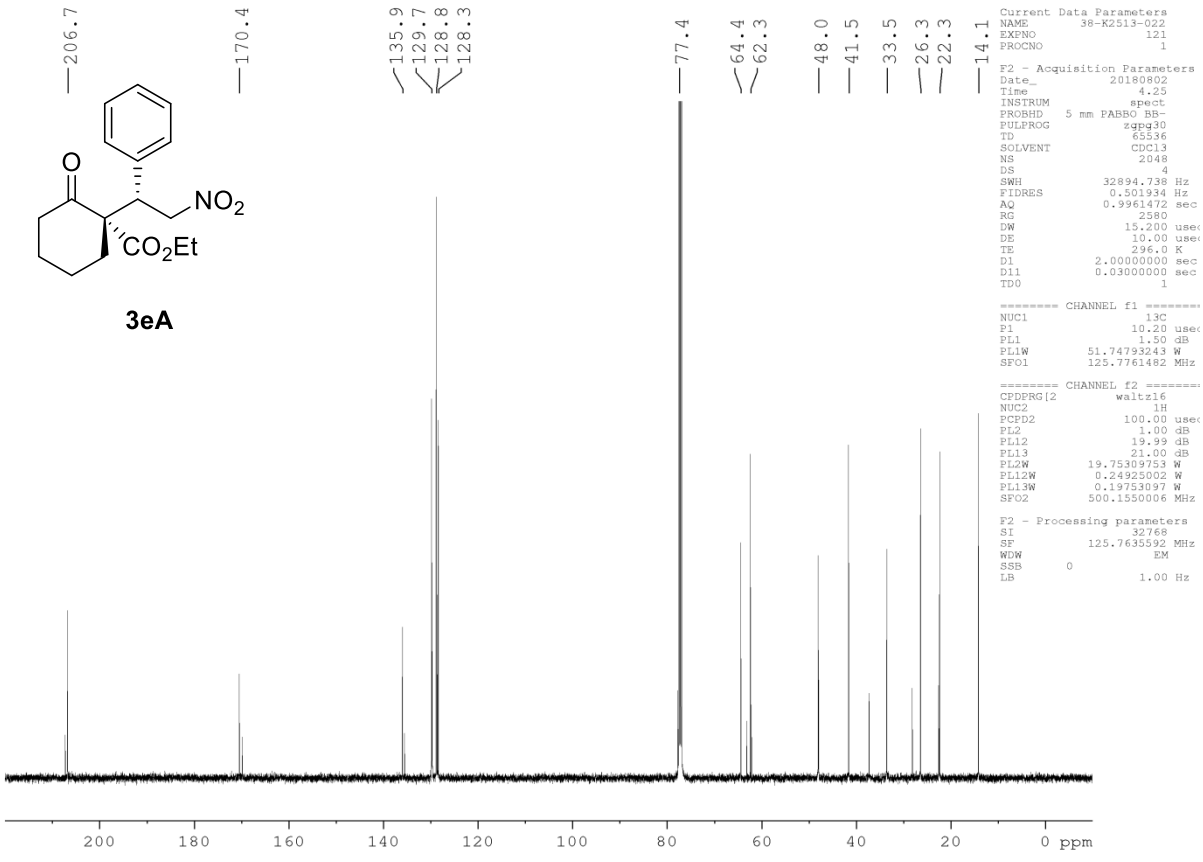

7.32 7.31 7.30 7.29 7.28 7.26 7.20 7.20 7.18 7.18
5.33 5.30 5.30 5.27 5.09 5.07 5.06 4.85 4.84 4.81 4.81
4.19 4.19 4.17 4.16
2.37 2.29 2.27 2.27 2.26 2.02 1.99 1.98 1.97 1.96 1.95 1.93 1.91 1.82 1.81 1.79 1.79 1.55 1.44 1.43 1.42 1.41 1.26 1.24
O
NO2
CO2iPr
3cA
water
8 7 6 5 4 3 2 1 0 ppm
2.92 1.94 1.01 0.98 1.00 0.99 1.01 1.01 2.03 1.03 1.05 6.09
Current Data Parameters
NAME 38-KZS11-016_dig
EXPNO 810
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180724
Time 19.20
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 205.35
DW 62.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1024708 MHz
NUC1 1H
P1 13.70 usec
PLW1 12.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1000099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

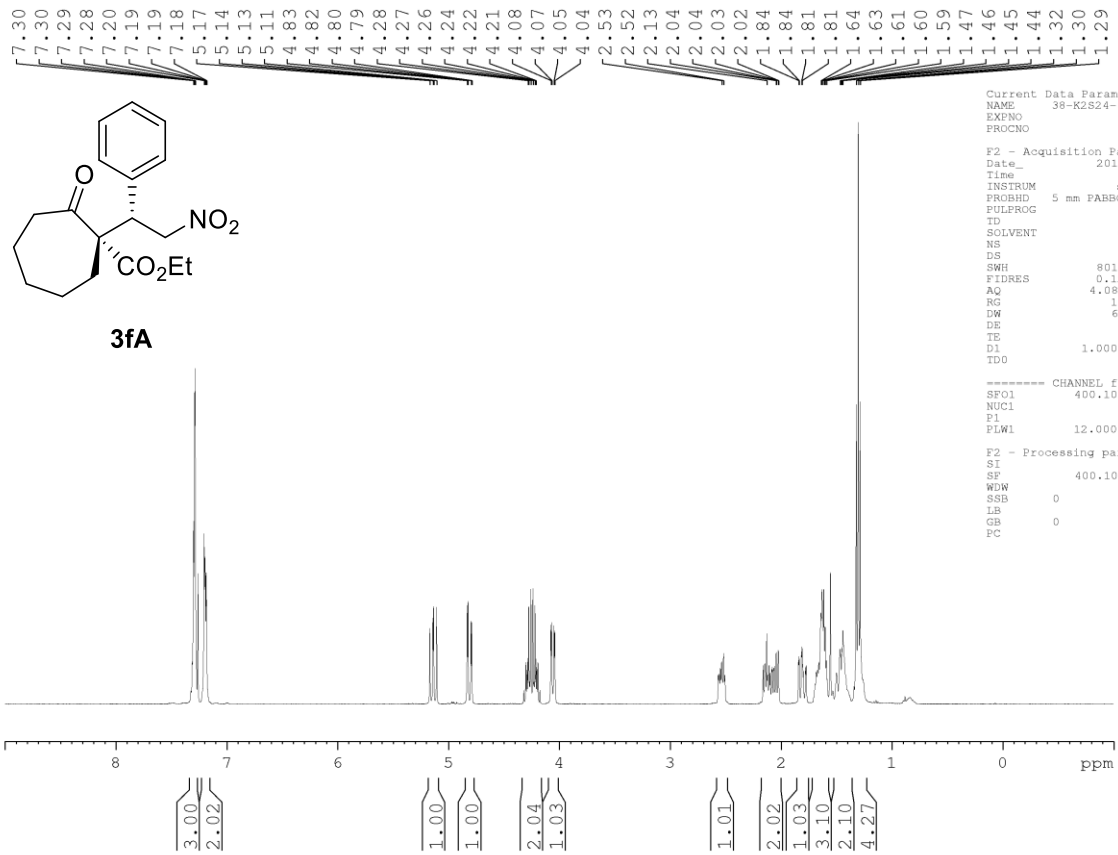

215.6 170.8 135.8 129.4 129.1 128.5 77.2 70.3 62.5 47.4 39.6 33.7 21.7 21.6 19.7
O
NO2
CO2iPr
3cA
200 180 160 140 120 100 80 60 40 20 0 ppm
Current Data Parameters
NAME 38-KZS11-016_dig
EXPNO 811
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180725
Time 5.51
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 205.35
DW 20.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6152851 MHz
NUC1 13C
P1 10.00 usec
PLW1 48.00000000 W
======== CHANNEL f2 ========
SFO2 400.1016004 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 12.00000000 W
PLW12 0.27805999 W
PLW13 0.22522999 W
F2 - Processing parameters
SI 32768
SF 100.6052107 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

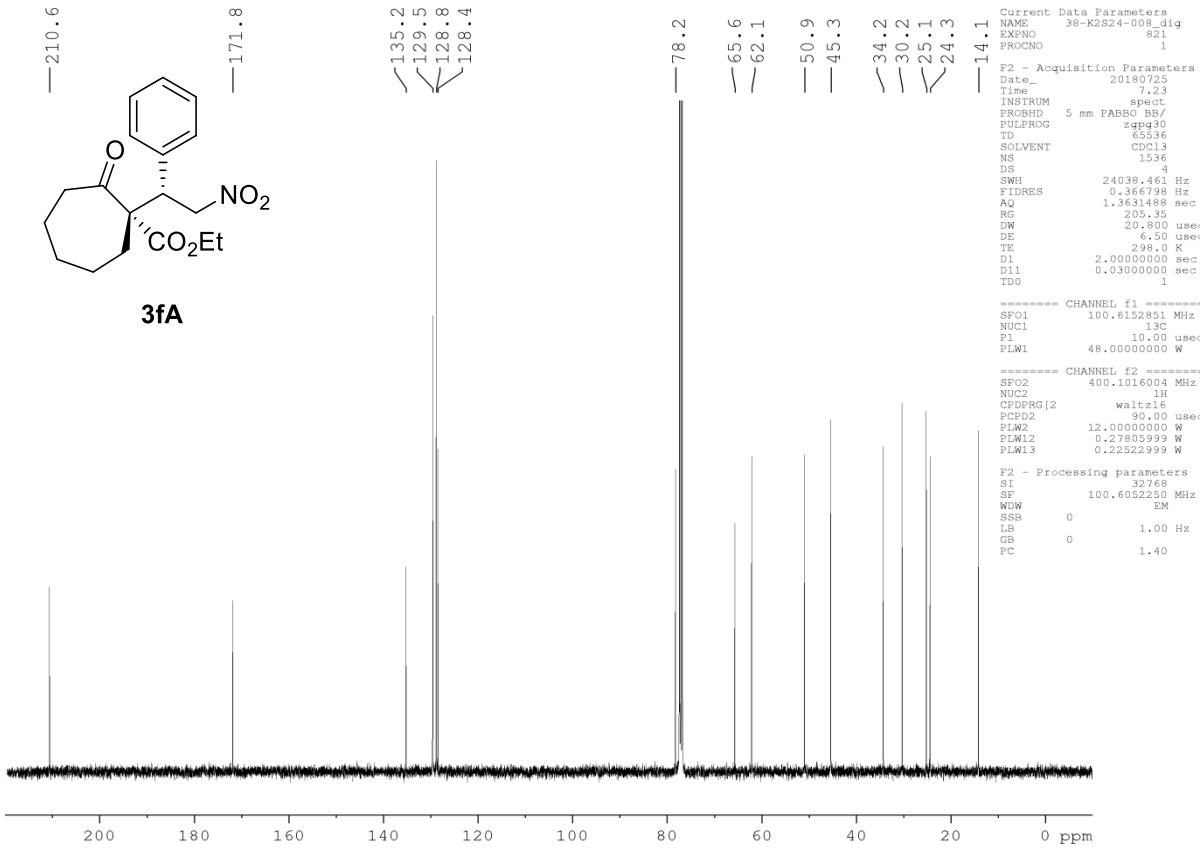

7.50
7.49
7.47
7.47
7.36
7.34
7.31
7.23
7.21
7.15
7.13
7.12
7.12
7.10
5.23
5.19
5.18
5.14
5.09
5.08
5.04
5.03
4.51
4.49
4.47
4.46
4.19
4.16
4.14
4.12
3.52
3.46
3.19
3.13
1.18
1.16
1.14
O
Ph
NO2
CO2Et
3dA
Current Data Parameters
NAME 38-KZS12-007
EXPNO 171
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180411
Time 14.23
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 144
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300056 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
0
ppm
0.97
1.03
1.02
0.99
4.99
1.03
1.00
0.99
1.99
1.02
1.01
3.00

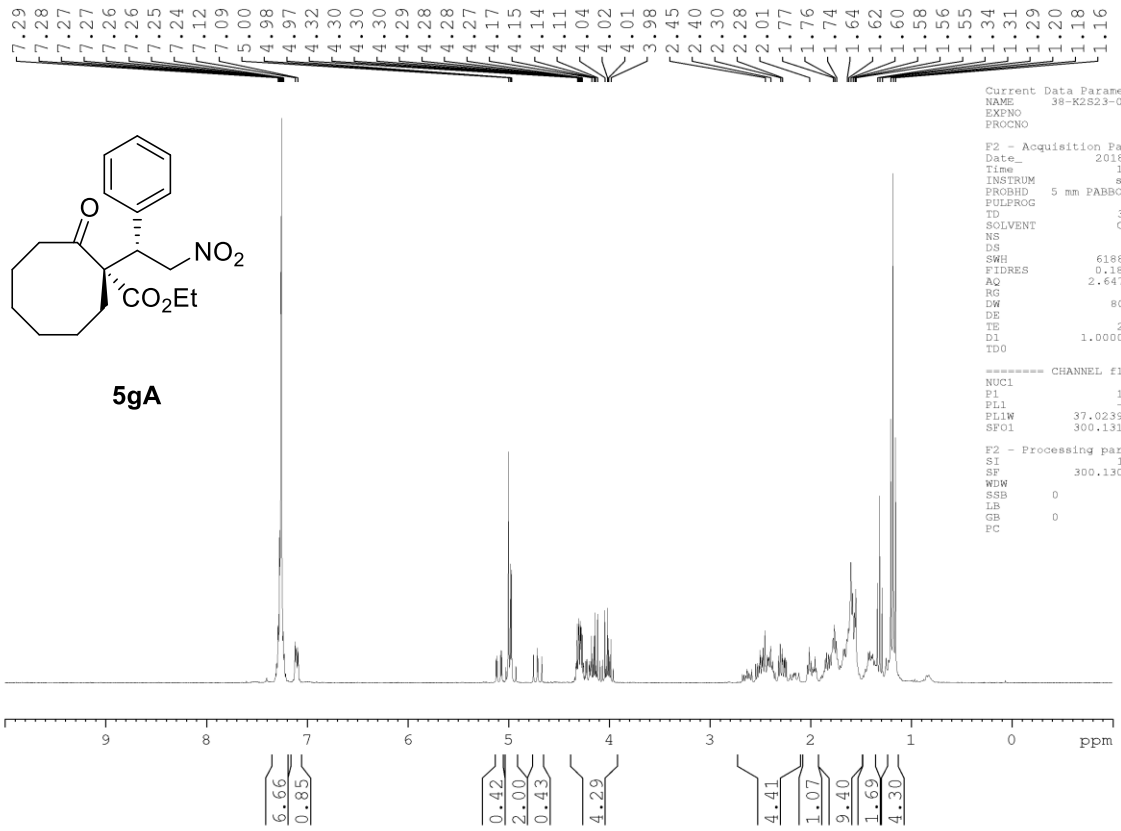

202.2
170.7
152.5
136.3
135.8
135.0
129.1
128.7
128.4
128.0
126.1
124.5
77.3
62.4
61.9
47.6
36.7
14.0
O
Ph
NO2
CO2Et
3dA
Current Data Parameters
NAME 38-KZS12-007
EXPNO 172
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180412
Time 1.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 1620
DW 27.733 usec
DE 8.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.75 usec
PL1 0 dB
PL1W 31.14739227 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -2.00 dB
PL12 17.05 dB
PL13 19.00 dB
PL2W 37.02396774 W
PL12W 0.46076876 W
PL13W 0.29409182 W
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677430 MHz
WDW EM
SSB 0
LB 1.00 Hz
200
180
160
140
120
100
80
60
40
20
0 ppm

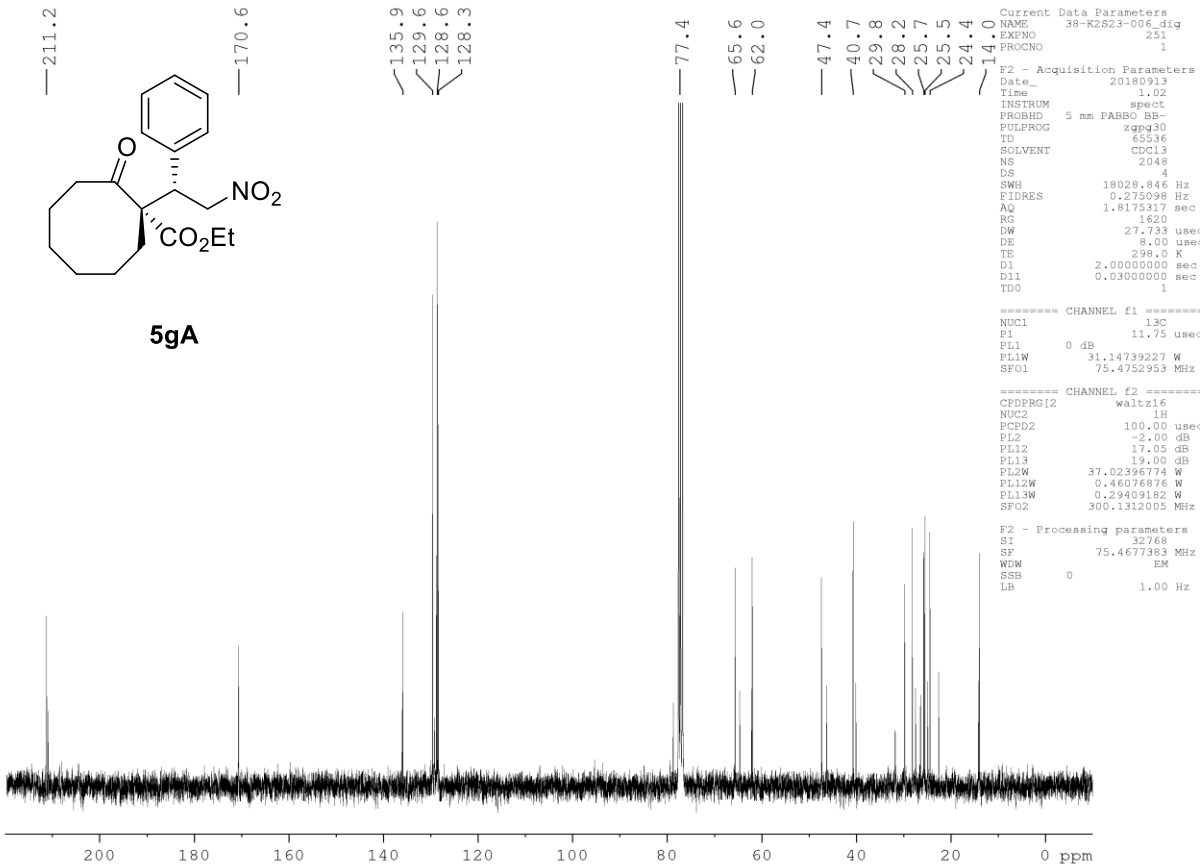

7.30 7.29 7.28 7.27 7.27 7.26 7.25 7.24 7.23 5.18 5.16 5.15 5.13 4.78 4.77 4.75 4.74 4.20 4.19 4.18 4.17 4.16 4.15 4.13 4.12 4.11 4.11 4.11 4.10 2.49 2.48 2.48 2.46 2.46 2.45 2.44 2.43 1.74 1.63 1.61 1.60 1.41 1.40 1.38 1.37 1.35 1.25 1.24 1.22
O
NO2
CO2Et
3eA
water
8 7 6 5 4 3 2 1 0 ppm
5.97 1.00 1.05 3.49 3.47 1.01 1.15 1.05 1.29 1.04 3.57
Current Data Parameters
NAME 38-K2513-022
EXPNO 120
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180802
Time 2.40
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5859712 sec
RG 203
DW 48.400 usec
DE 10.00 usec
TE 296.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.23 usec
PL1 1.00 dB
PL1W 19.75309753 W
SFO1 500.1560886 MHz
F2 - Processing parameters
SI 16384
SF 500.1530162 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

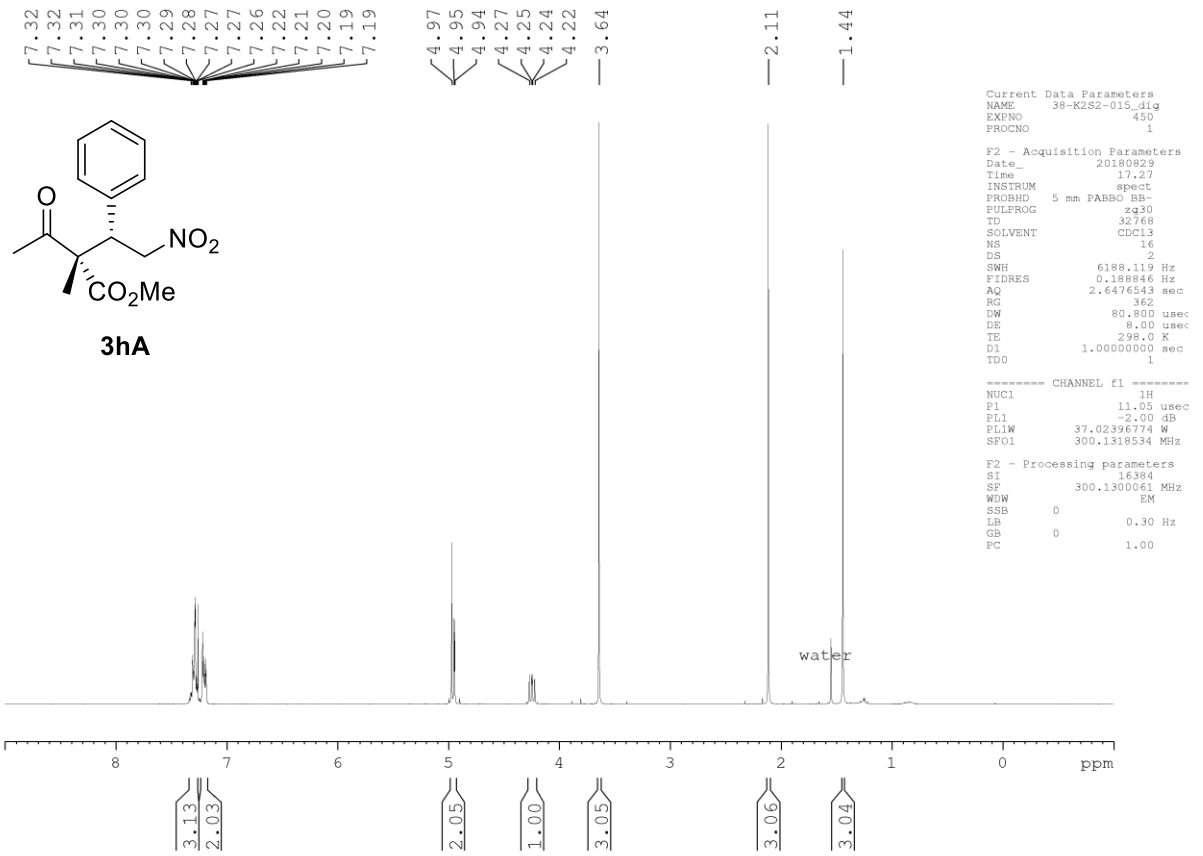

206.7 170.4 135.9 129.7 128.8 128.3 77.4 64.4 62.3 48.0 41.5 33.5 26.3 22.3 14.1
O
NO2
CO2Et
3eA
200 180 160 140 120 100 80 60 40 20 0 ppm
Current Data Parameters
NAME 38-K2513-022
EXPNO 121
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180802
Time 4.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 32894.738 Hz
FIDRES 0.501934 Hz
AQ 0.9961472 sec
RG 2580
DW 15.200 usec
DE 10.00 usec
TE 296.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.20 usec
PL1 1.50 dB
PL1W 51.74793243 W
SFO1 125.7761482 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.00 dB
PL12 19.99 dB
PL13 21.00 dB
PL2W 19.75309753 W
PL12W 0.24925002 W
PL13W 0.19753097 W
SFO2 500.1550006 MHz
F2 - Processing parameters
SI 32768
SF 125.7635592 MHz
WDW EM
SSB 0
LB 1.00 Hz

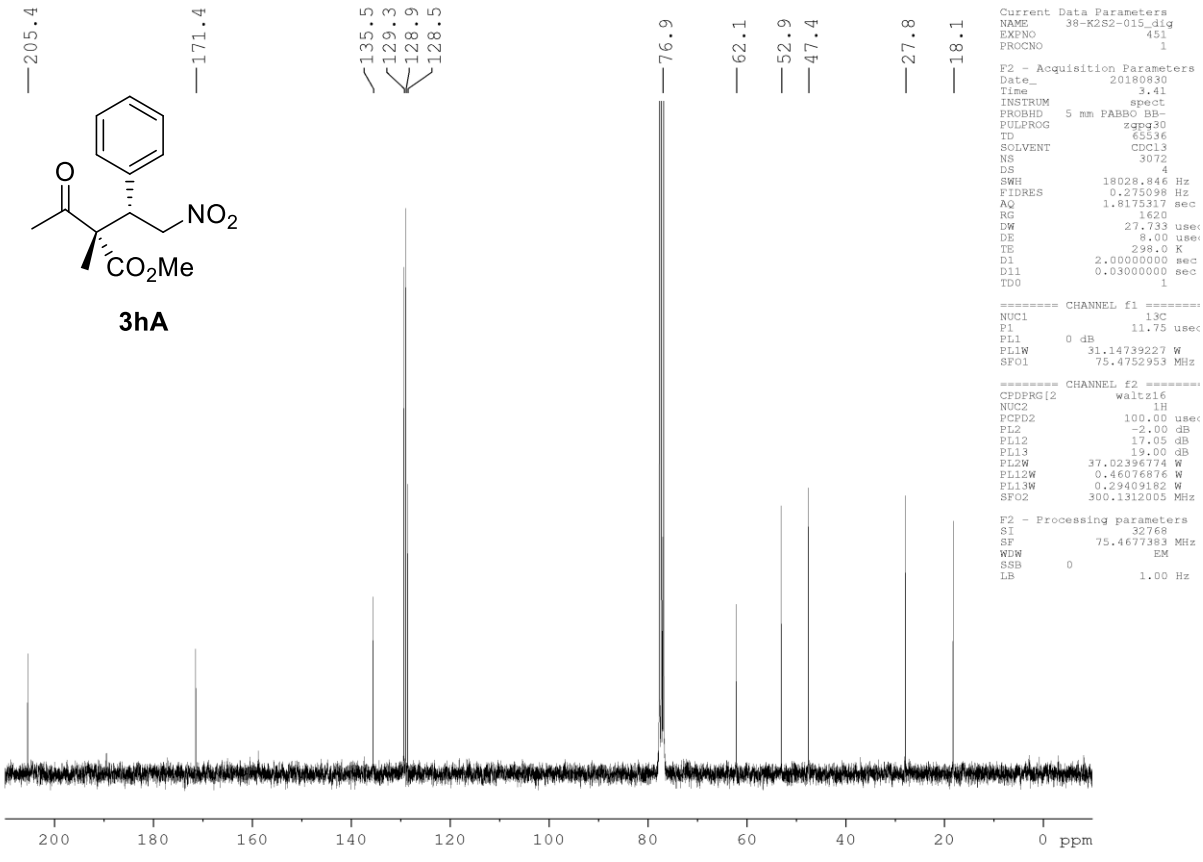

7.30 7.30 7.29 7.28 7.20 7.19 7.19 7.18 5.17 5.14 5.13 5.11 4.83 4.82 4.80 4.79 4.28 4.27 4.26 4.24 4.22 4.21 4.08 4.07 4.05 4.04 2.53 2.52 2.13 2.04 2.04 2.03 2.02 1.84 1.84 1.81 1.81 1.64 1.63 1.61 1.60 1.59 1.47 1.46 1.45 1.44 1.32 1.30 1.29
O
NO2
CO2Et
3fA
Current Data Parameters
NAME 38-K2S24-008_dig
EXPNO 820
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180724
Time 19.25
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 160.83
DW 62.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1024708 MHz
NUC1 1H
P1 13.70 usec
PLW1 12.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1000099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
3.00 2.02 1.00 1.00 2.04 1.03 1.01 2.02 1.03 3.10 2.10 4.27

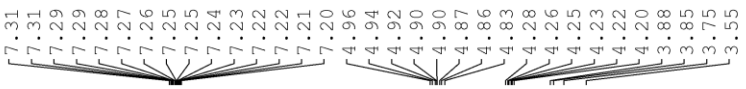

210.6 171.8 135.2 129.5 128.8 128.4 78.2 65.6 62.1 50.9 45.3 34.2 30.2 25.1 24.3 14.1
O
NO2
CO2Et
3fA
Current Data Parameters
NAME 38-K2S24-008_dig
EXPNO 821
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180725
Time 7.23
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1536
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 205.35
DW 20.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6152851 MHz
NUC1 13C
P1 10.00 usec
PLW1 48.00000000 W
======== CHANNEL f2 ========
SFO2 400.1016004 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 12.00000000 W
PLW12 0.27805999 W
PLW13 0.22522999 W
F2 - Processing parameters
SI 32768
SF 100.6052250 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm

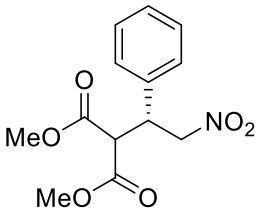

7.29 7.28 7.27 7.27 7.26 7.26 7.25 7.24 7.12 7.09 5.00 4.98 4.97 4.32 4.30 4.30 4.30 4.29 4.28 4.28 4.27 4.17 4.15 4.14 4.11 4.04 4.02 4.01 3.98 2.45 2.40 2.30 2.28 2.01 1.77 1.76 1.74 1.64 1.62 1.60 1.58 1.56 1.55 1.34 1.31 1.29 1.20 1.18 1.16
O
NO2
CO2Et
5gA
Current Data Parameters
NAME 38-K2S23-006_dig
EXPNO 250
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180912
Time 15.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 322
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300073 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9 8 7 6 5 4 3 2 1 0 ppm
6.66 0.85 0.42 2.00 0.43 4.29 4.41 1.07 9.40 1.69 4.30


211.2 170.6 135.9 129.6 128.6 128.3 77.4 65.6 62.0 47.4 40.7 29.8 28.2 25.7 25.5 24.4 14.0
O
NO2
CO2Et
5gA
Current Data Parameters
NAME 38-K2S23-006_dig
EXPNO 251
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180913
Time 1.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 1620
DW 27.733 usec
DE 8.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.75 usec
PL1 0 dB
PL1W 31.14739227 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -2.00 dB
PL12 17.05 dB
PL13 19.00 dB
PL2W 37.02396774 W
PL12W 0.46076876 W
PL13W 0.29409182 W
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677383 MHz
WDW EM
SSB 0
LB 1.00 Hz
200 180 160 140 120 100 80 60 40 20 0 ppm


7.32
7.32
7.31
7.30
7.30
7.30
7.29
7.28
7.27
7.27
7.26
7.22
7.21
7.20
7.19
7.19
4.97
4.95
4.94
4.27
4.25
4.24
4.22
3.64
2.11
1.44
O
NO2
CO2Me
3hA
water
8
7
6
5
4
3
2
1
0
ppm
3.13
2.03
2.05
1.00
3.05
3.06
3.04
Current Data Parameters
NAME 38-K2S2-015_dig
EXPNO 450
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180829
Time 17.27
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 362
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


205.4
171.4
135.5
129.3
128.9
128.5
76.9
62.1
52.9
47.4
27.8
18.1
O
NO2
CO2Me
3hA
200
180
160
140
120
100
80
60
40
20
0 ppm
Current Data Parameters
NAME 38-K2S2-015_dig
EXPNO 451
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180830
Time 3.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3072
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 1620
DW 27.733 usec
DE 8.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.75 usec
PL1 0 dB
PL1W 31.14739227 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -2.00 dB
PL12 17.05 dB
PL13 19.00 dB
PL2W 37.02396774 W
PL12W 0.46076876 W
PL13W 0.29409182 W
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677383 MHz
WDW EM
SSB 0
LB 1.00 Hz





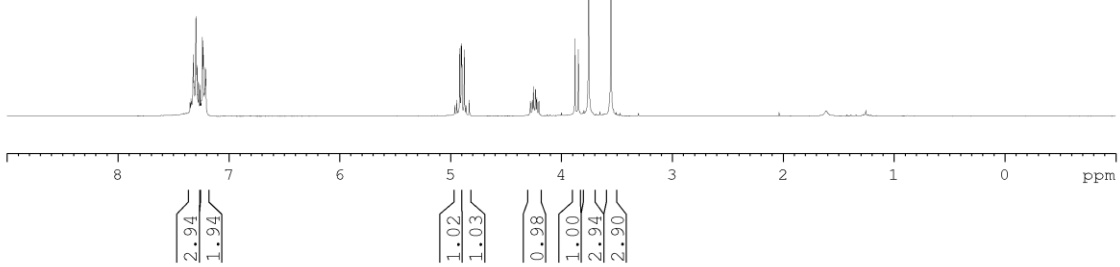
3iA

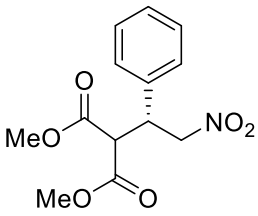
```
Current Data Parameters
NAME          38-K2S1-012
EXPNO                 500
PROCNO                  1

F2 - Acquisition Parameters
Date_           20180827
Time              19.26
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           6188.119 Hz
FIDRES        0.188846 Hz
AQ            2.6476543 sec
RG                 181
DW              80.800 usec
DE               8.00 usec
TE              298.0 K
D1          1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1                1H
P1              11.05 usec
PL1             -2.00 dB
PL1W       37.02396774 W
SFO1       300.1318534 MHz

F2 - Processing parameters
SI              16384
SF         300.1300061 MHz
WDW                EM
SSB       0
LB              0.30 Hz
GB        0
PC              1.00
```





3iA

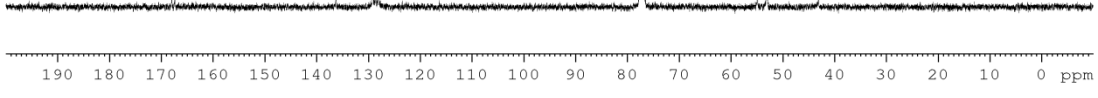
```
Current Data Parameters
NAME          38-K2S1-012
EXPNO                 501
PROCNO                  1

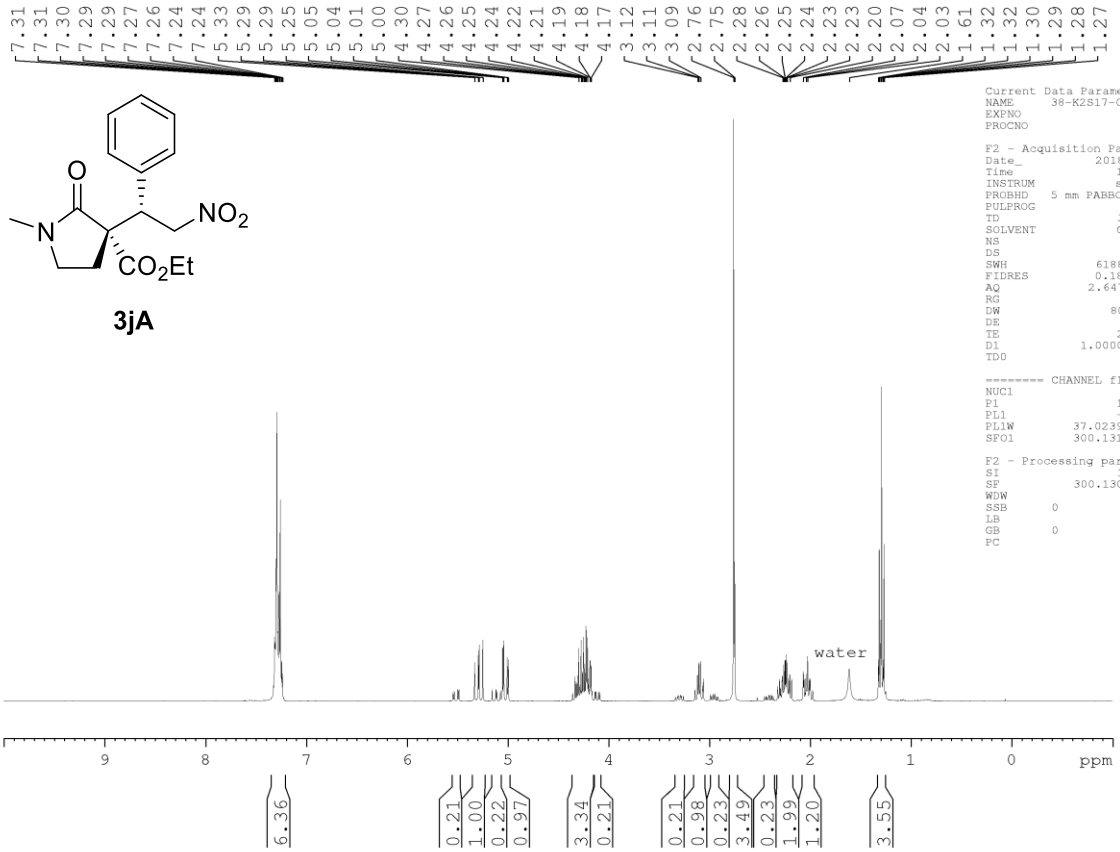
F2 - Acquisition Parameters
Date_           20180828
Time              1.39
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                2048
DS                   4
SWH          18028.846 Hz
FIDRES        0.275098 Hz
AQ            1.8175317 sec
RG                1620
DW              27.733 usec
DE               8.00 usec
TE              298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               13C
P1              11.75 usec
PL1       0 dB
PL1W       31.14739227 W
SFO1        75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                1H
PCPD2           100.00 usec
PL2             -2.00 dB
PL12            17.05 dB
PL13            19.00 dB
PL2W       37.02396774 W
PL12W       0.46076876 W
PL13W       0.29409182 W
SFO2       300.1312005 MHz

F2 - Processing parameters
SI              32768
SF         75.4677406 MHz
WDW                EM
SSB       0
LB              1.00 Hz
```



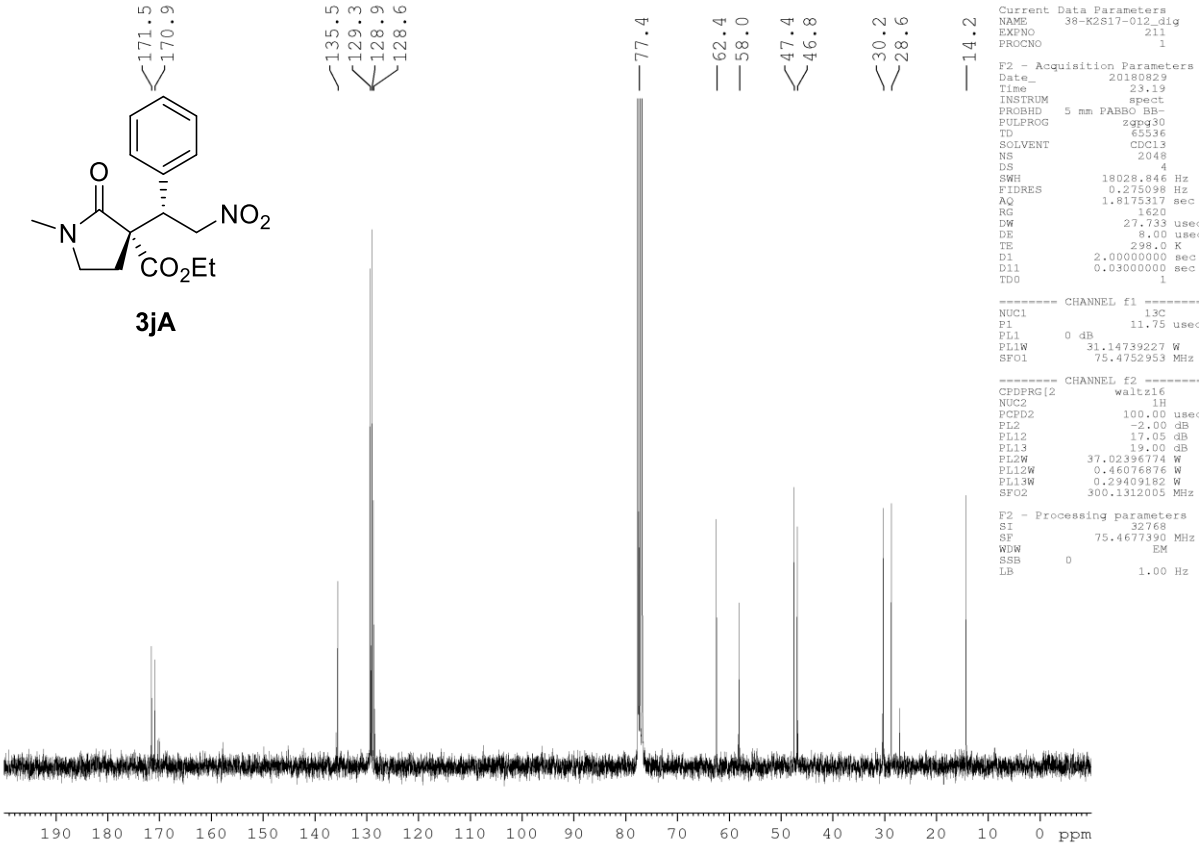



```
Current Data Parameters
NAME      38-K2S17-012_dig
EXPNO                  210
PROCNO                   1

F2 - Acquisition Parameters
Date_           20180829
Time              12.15
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           6188.119 Hz
FIDRES        0.188846 Hz
AQ            2.6476543 sec
RG                 322
DW              80.800 usec
DE               8.00 usec
TE              298.0 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1              11.05 usec
PL1             -2.00 dB
PL1W       37.02396774 W
SFO1       300.1318534 MHz

F2 - Processing parameters
SI               16384
SF          300.1300061 MHz
WDW                 EM
SSB      0
LB              0.30 Hz
GB       0
PC              1.00
```



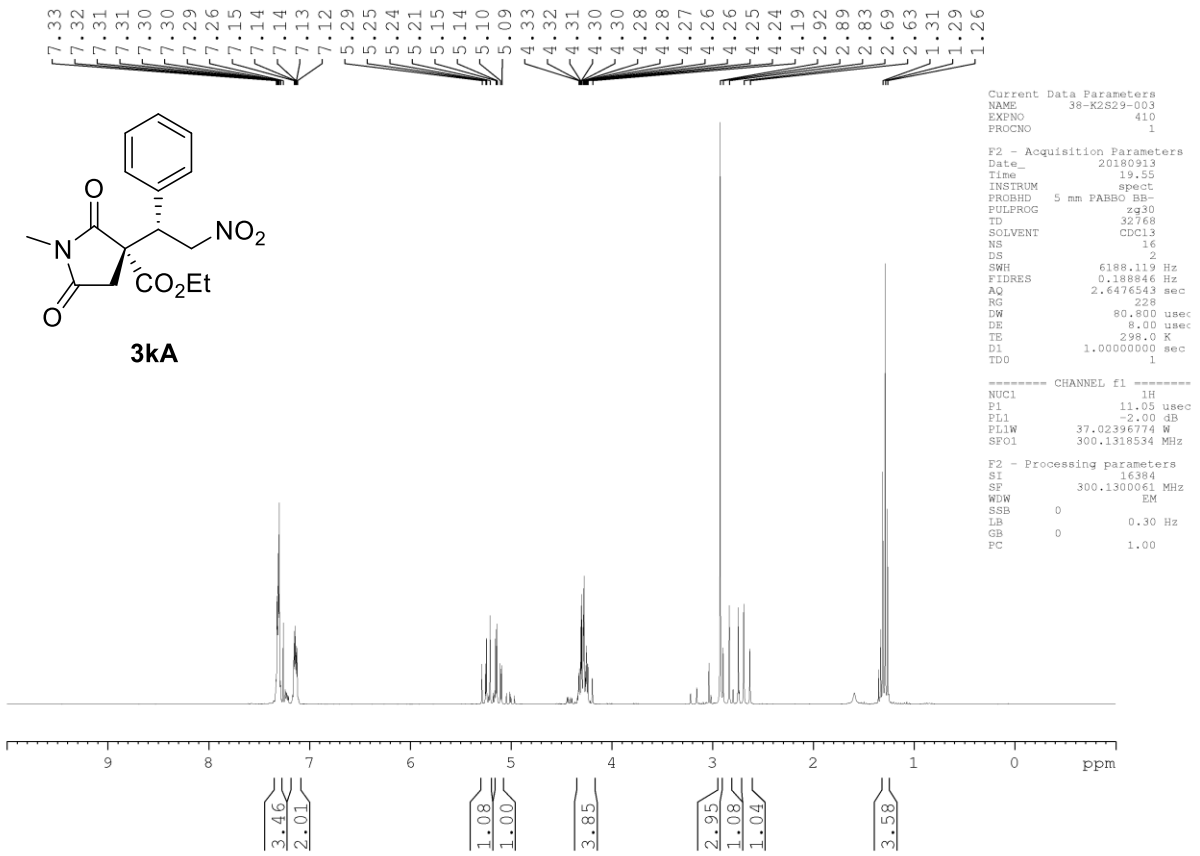

```
Current Data Parameters
NAME      38-K2S17-012_dig
EXPNO                  211
PROCNO                   1

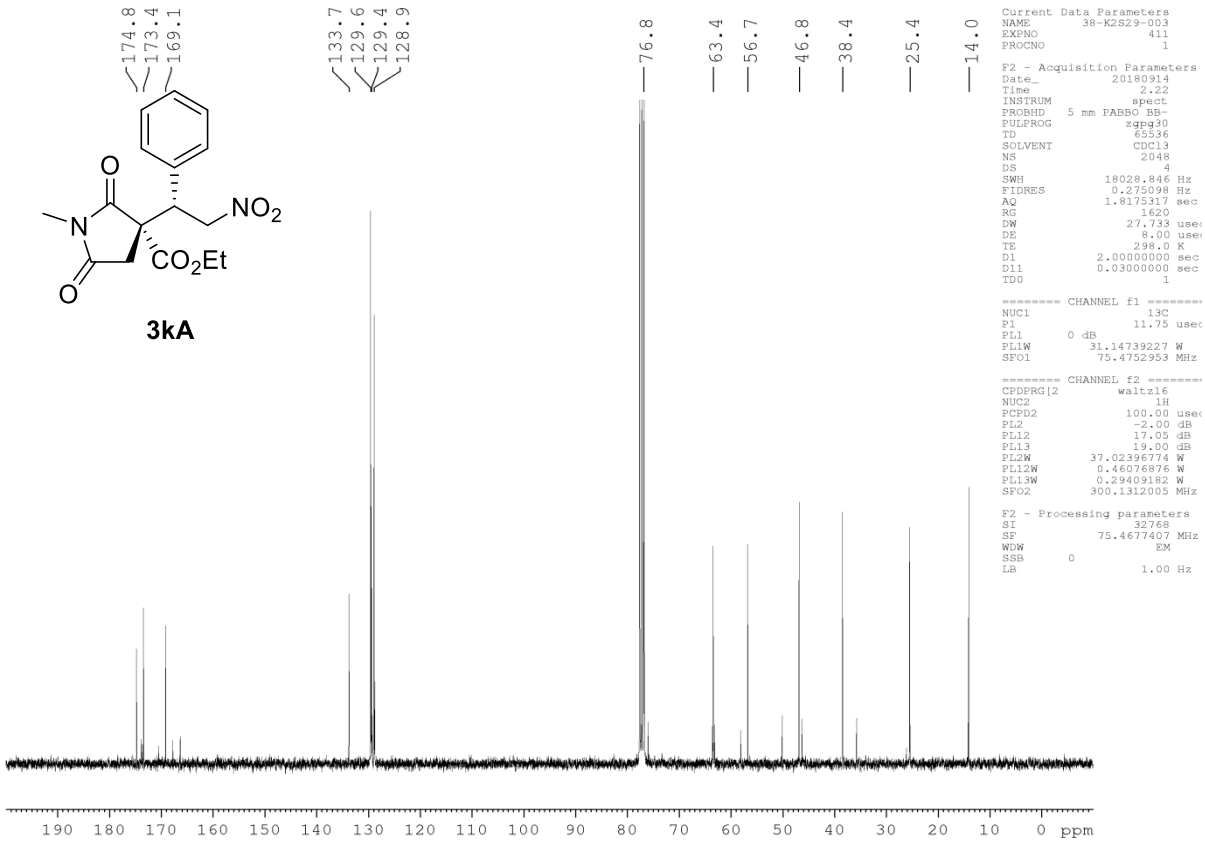
F2 - Acquisition Parameters
Date_           20180829
Time              23.19
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                2048
DS                   4
SWH          18028.846 Hz
FIDRES        0.275098 Hz
AQ            1.8175317 sec
RG                1620
DW             27.733 usec
DE               8.00 usec
TE              298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

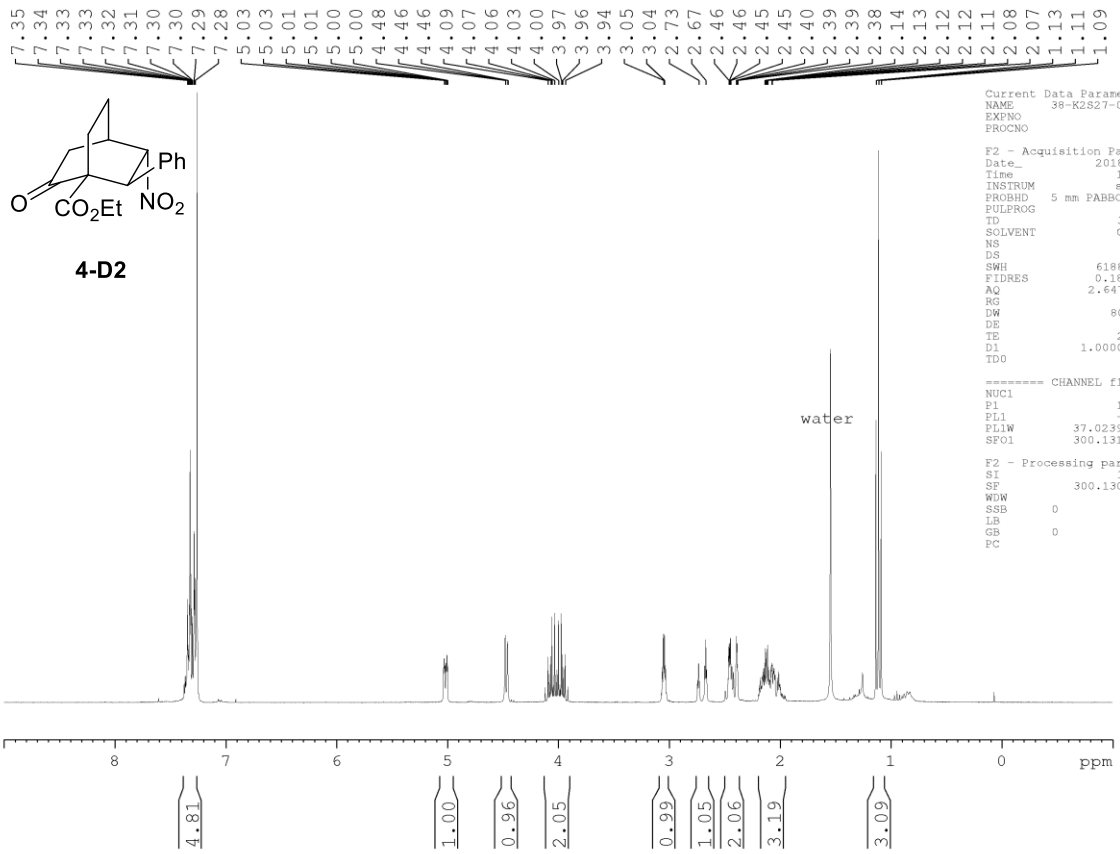
======== CHANNEL f1 ========
NUC1                13C
P1              11.75 usec
PL1        0 dB
PL1W       31.14739227 W
SFO1       75.4752953 MHz

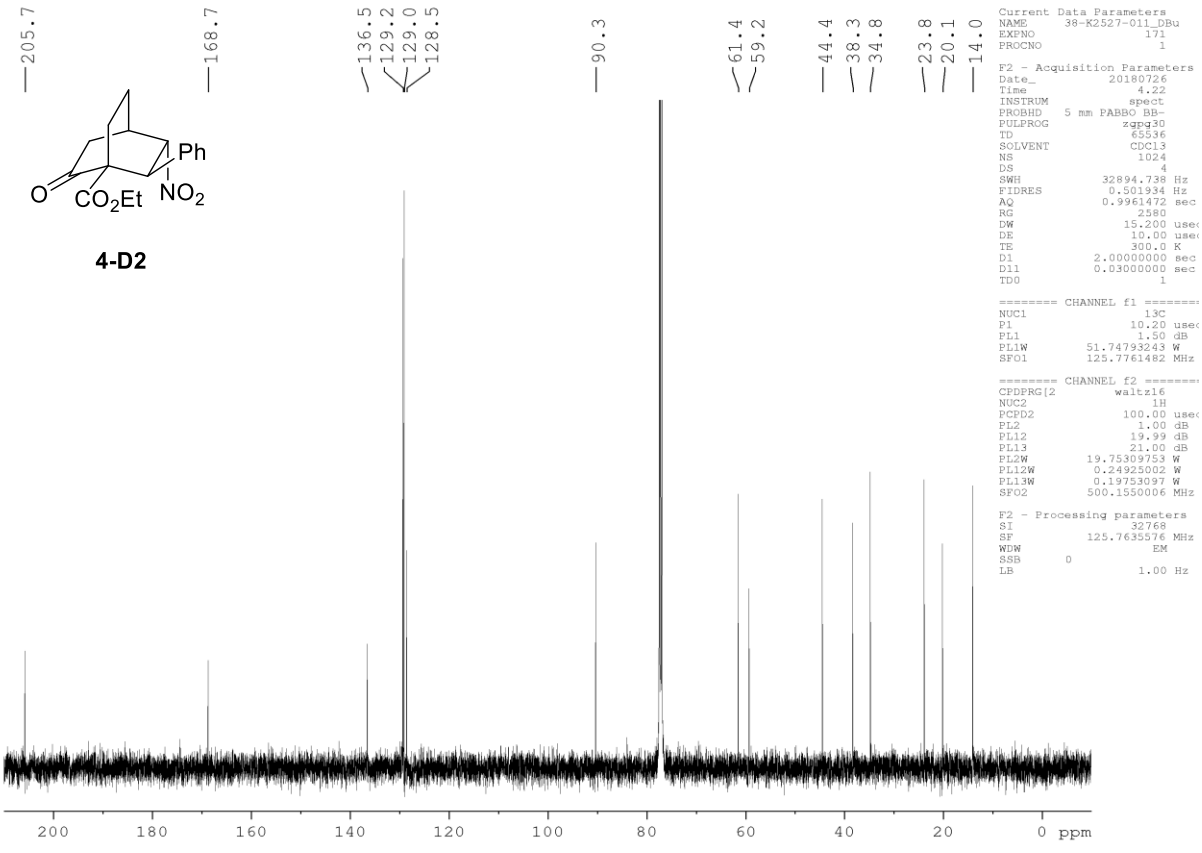
======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                1H
PCPD2          100.00 usec
PL2             -2.00 dB
PL12            17.05 dB
PL13            19.00 dB
PL2W       37.02396774 W
PL12W       0.46076876 W
PL13W       0.29409182 W
SFO2       300.1312005 MHz

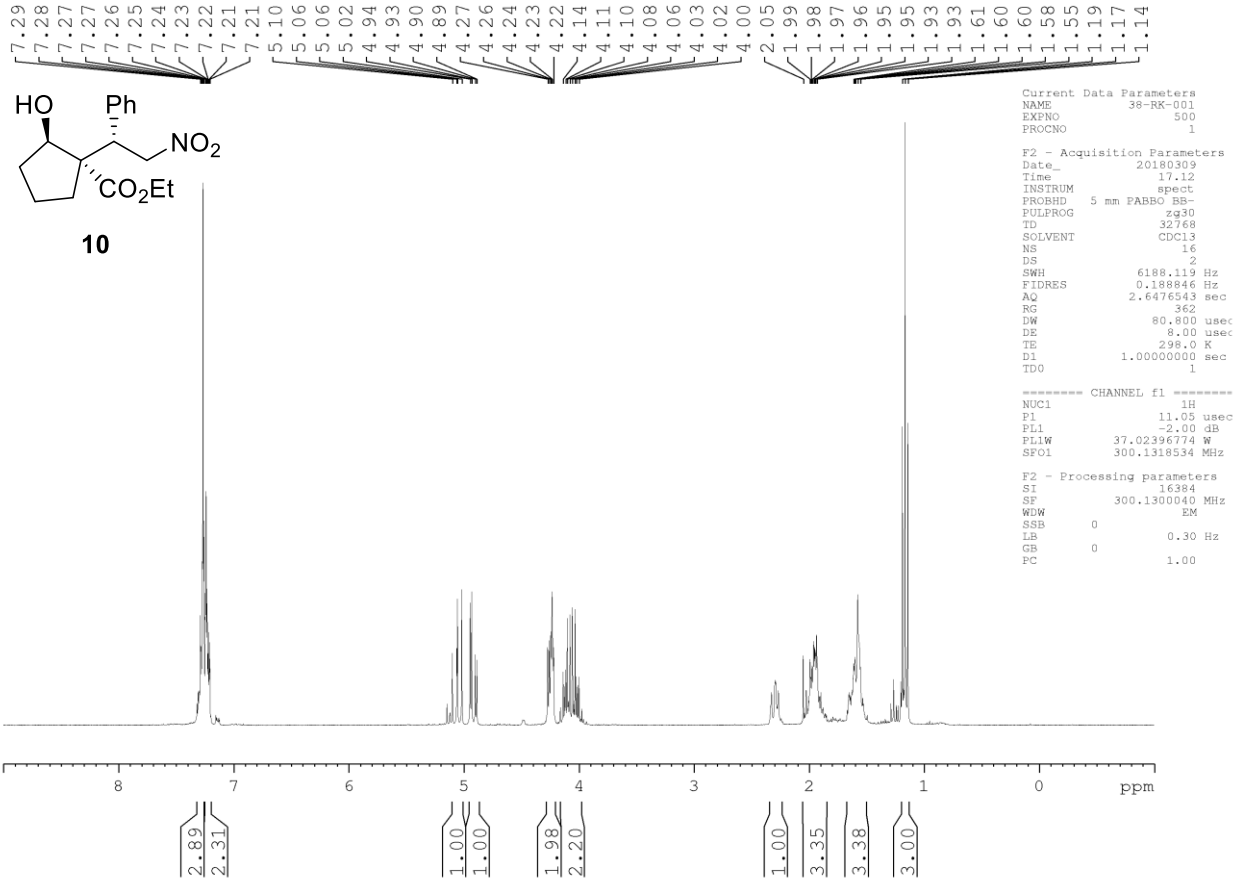
F2 - Processing parameters
SI               32768
SF          75.4677390 MHz
WDW                 EM
SSB      0
LB              1.00 Hz
```

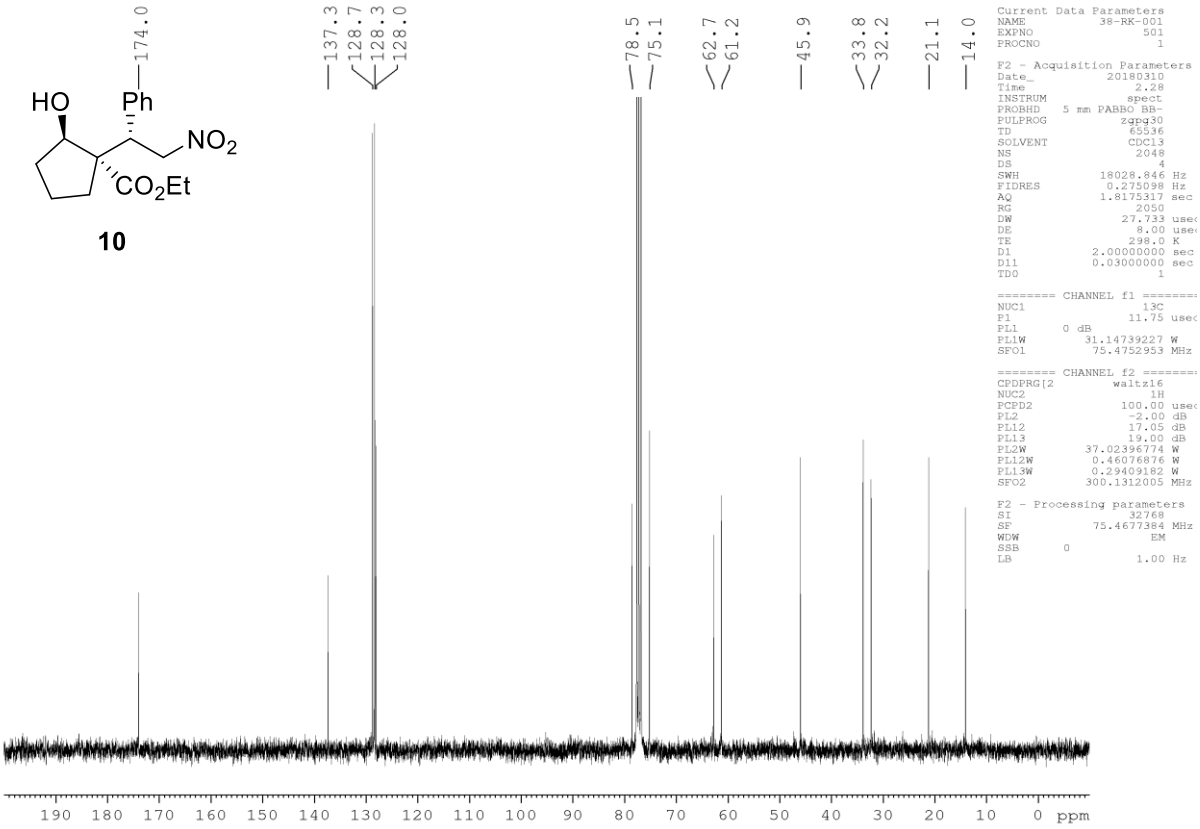

7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.26
7.15
7.14
7.14
7.13
7.12
5.29
5.25
5.24
5.21
5.15
5.14
5.10
5.09
4.33
4.32
4.31
4.30
4.28
4.28
4.27
4.26
4.26
4.25
4.24
4.19
2.92
2.89
2.83
2.69
2.63
1.31
1.29
1.26
O
N
O
NO2
CO2Et
3kA
Current Data Parameters
NAME 38-KZS29-003
EXPNO 410
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180913
Time 19.55
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 228
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9 8 7 6 5 4 3 2 1 0 ppm
3.46
2.01
1.08
1.00
3.85
2.95
1.08
1.04
3.58

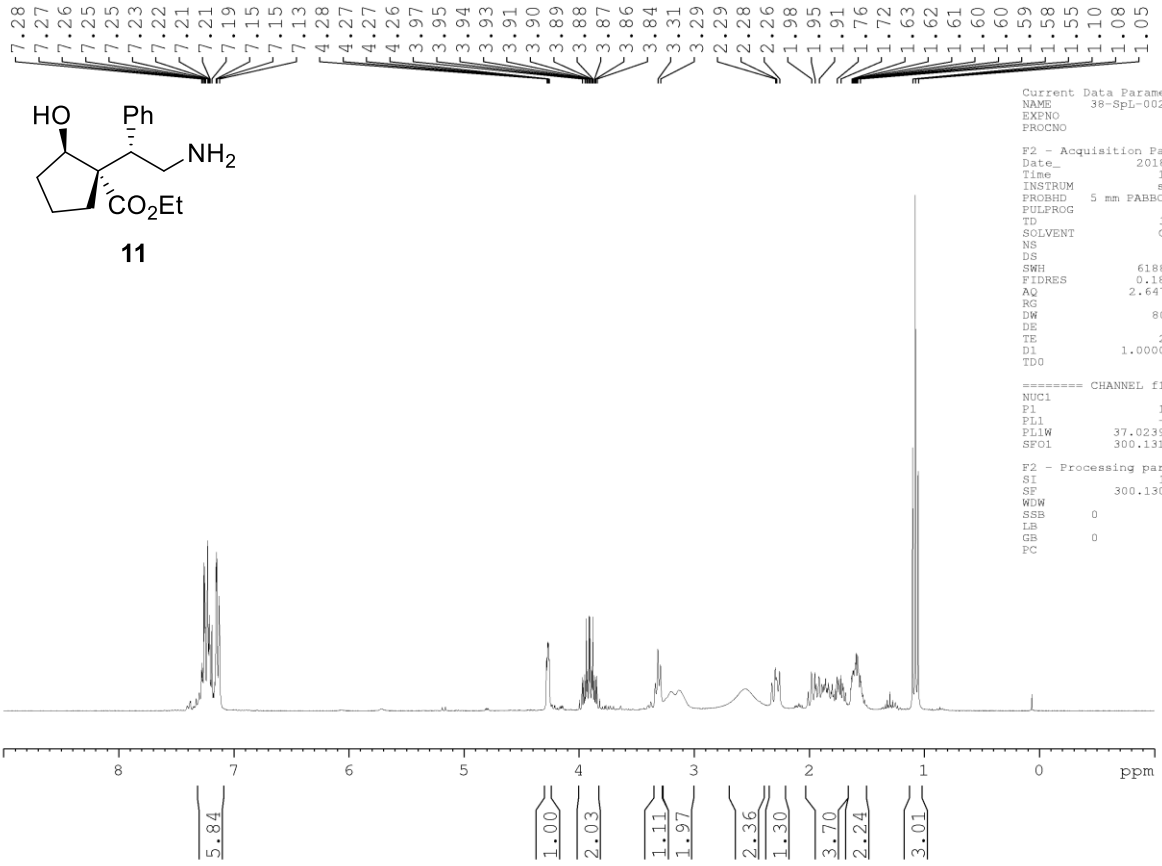

174.8
173.4
169.1
133.7
129.6
129.4
128.9
76.8
63.4
56.7
46.8
38.4
25.4
14.0
O
N
O
NO2
CO2Et
3kA
Current Data Parameters
NAME 38-KZS29-003
EXPNO 411
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180914
Time 2.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 1620
DW 27.733 usec
DE 8.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.75 usec
PL1 0 dB
PL1W 31.14739227 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -2.00 dB
PL12 17.05 dB
PL13 19.00 dB
PL2W 37.02396774 W
PL12W 0.46076876 W
PL13W 0.29409182 W
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677407 MHz
WDW EM
SSB 0
LB 1.00 Hz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

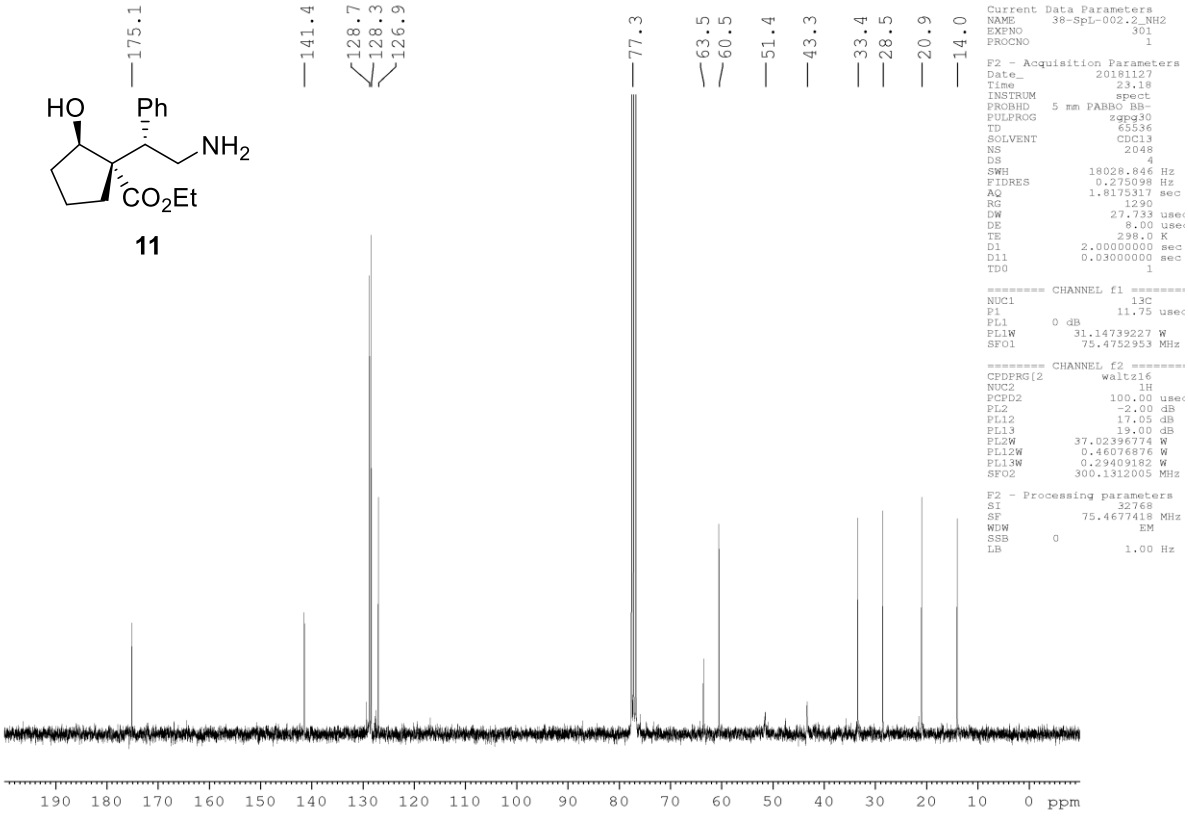

7.35 7.34 7.33 7.33 7.32 7.31 7.30 7.30 7.29 7.28
5.03 5.03 5.01 5.01 5.00 5.00 4.48 4.46 4.46 4.09 4.07 4.06 4.03 4.00 3.97 3.96 3.94
3.05 3.04 2.73 2.67 2.46 2.46 2.45 2.45 2.40 2.39 2.39 2.38 2.14 2.13 2.12 2.12 2.11 2.08 2.07 1.13 1.11 1.09
Ph
O
CO2Et
NO2
4-D2
water
Current Data Parameters
NAME 38-K2S27-011_DBU_di
EXPNO 431
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180920
Time 19.59
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 256
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 724
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300062 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
4.81 1.00 0.96 2.05 0.99 1.05 2.06 3.19 3.09

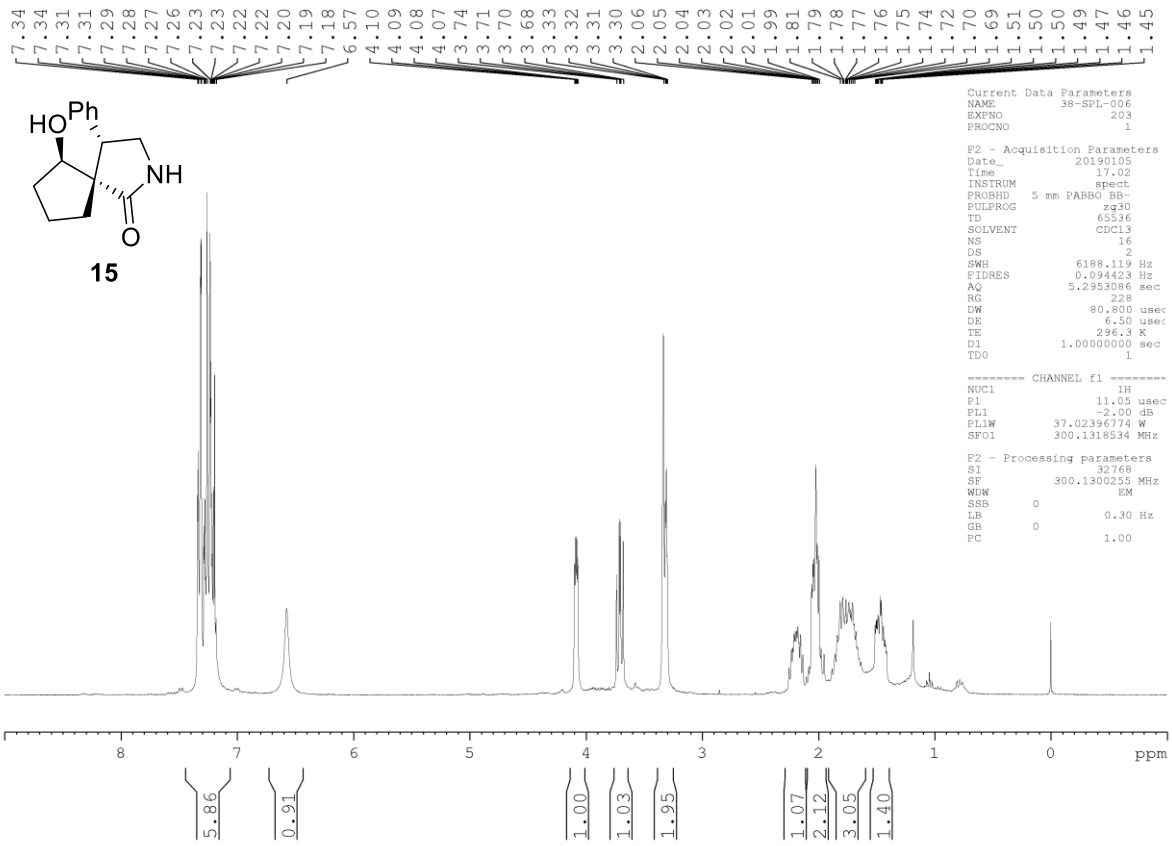

205.7 168.7 136.5 129.2 129.0 128.5 90.3 61.4 59.2 44.4 38.3 34.8 23.8 20.1 14.0
Ph
O
CO2Et
NO2
4-D2
Current Data Parameters
NAME 38-K2527-011_DBu
EXPNO 171
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180726
Time 4.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 32894.738 Hz
FIDRES 0.501934 Hz
AQ 0.9961472 sec
RG 2580
DW 15.200 usec
DE 10.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.20 usec
PL1 1.50 dB
PL1W 51.74793243 W
SFO1 125.7761482 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.00 dB
PL12 19.99 dB
PL13 21.00 dB
PL2W 19.75309753 W
PL12W 0.24925002 W
PL13W 0.19753097 W
SFO2 500.1550006 MHz
F2 - Processing parameters
SI 32768
SF 125.7635576 MHz
WDW EM
SSB 0
LB 1.00 Hz
200 180 160 140 120 100 80 60 40 20 0 ppm

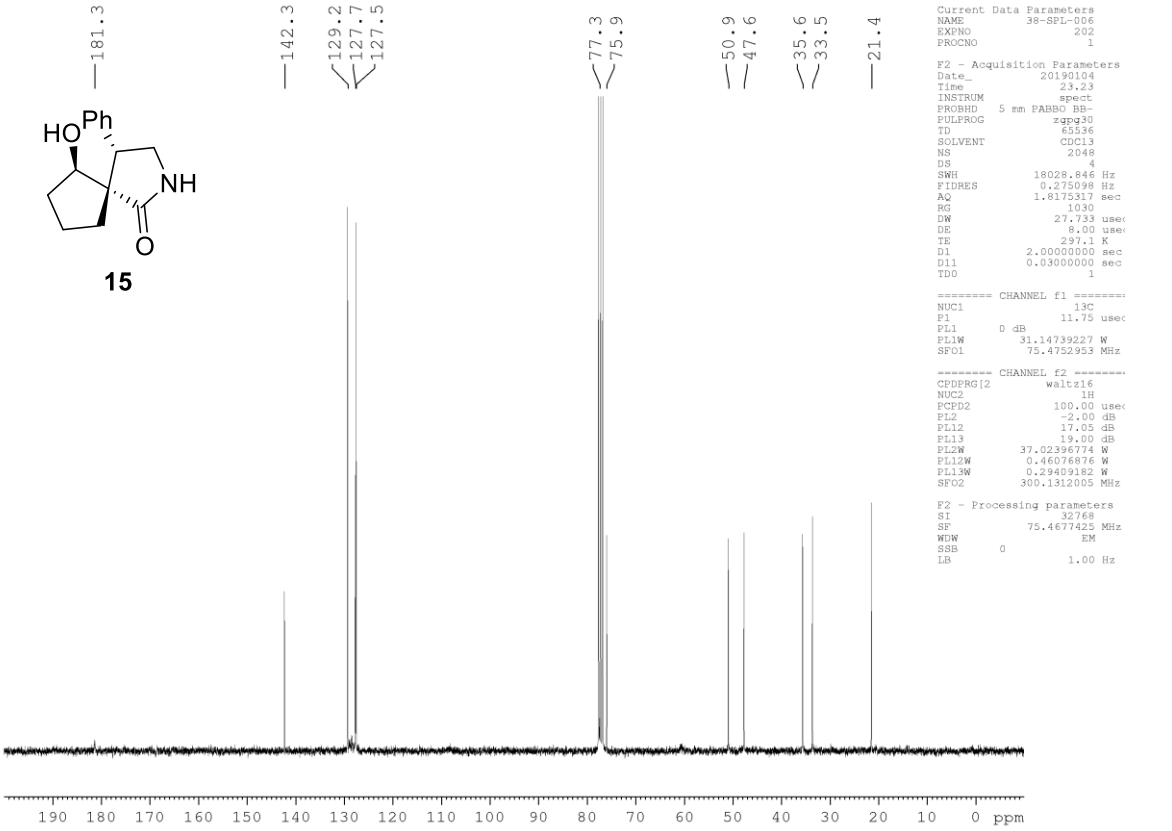

7.29 7.28 7.27 7.27 7.26 7.25 7.24 7.23 7.22 7.21 7.21
5.10 5.06 5.06 5.02 4.94 4.93 4.90 4.89 4.27 4.26 4.24 4.23 4.22 4.14 4.11 4.10 4.08 4.06 4.03 4.02 4.00
2.05 1.99 1.98 1.97 1.96 1.95 1.95 1.93 1.93 1.61 1.60 1.60 1.58 1.55 1.19 1.17 1.14
HO
Ph
NO2
CO2Et
10
Current Data Parameters
NAME 38-RK-001
EXPNO 500
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180309
Time 17.12
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 362
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300040 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
2.89 2.31 1.00 1.00 1.98 2.20 1.00 3.35 3.38 3.00

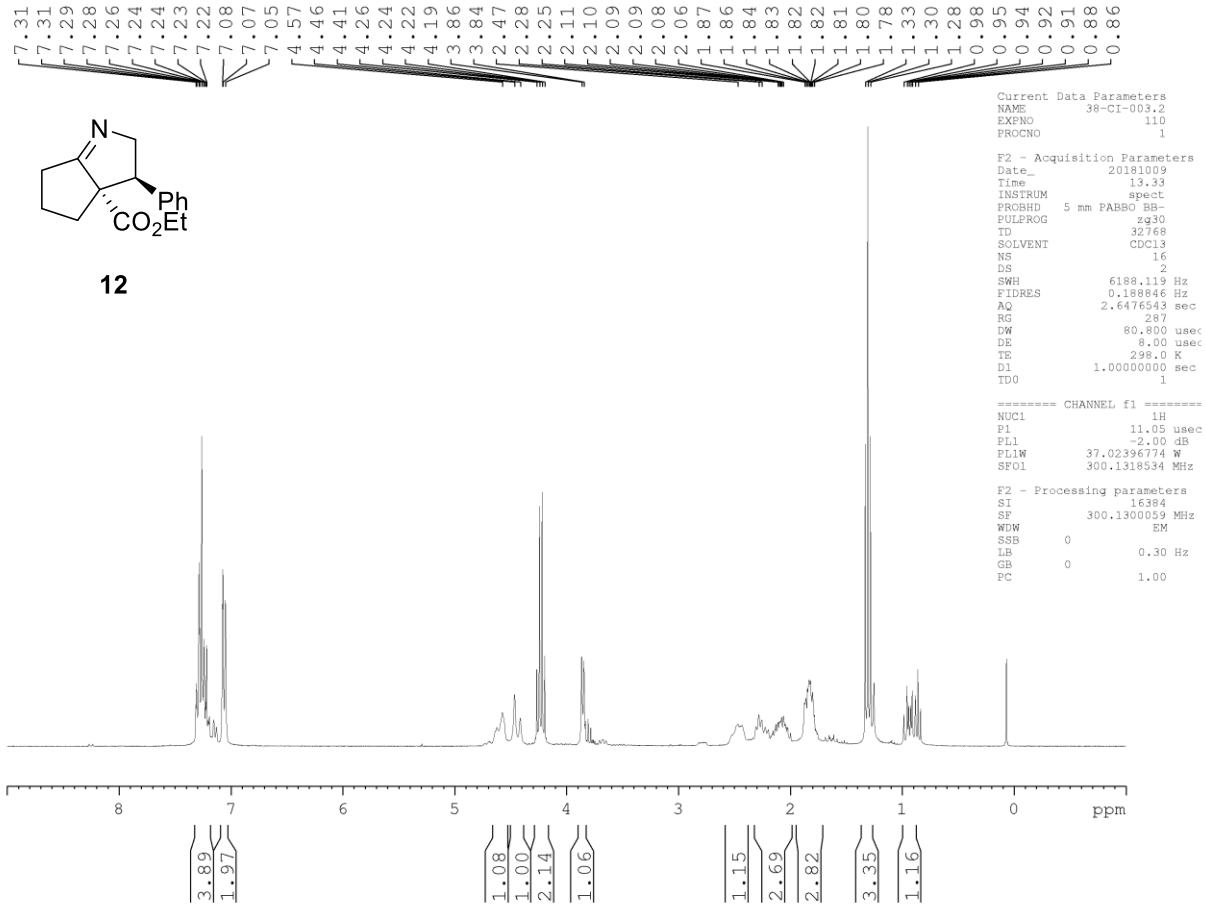

174.0
137.3 128.7 128.3 128.0
78.5 75.1
62.7 61.2
45.9
33.8 32.2
21.1
14.0
HO
Ph
NO2
CO2Et
10
Current Data Parameters
NAME 38-RK-001
EXPNO 501
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180310
Time 2.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 2050
DW 27.733 usec
DE 8.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.75 usec
PL1 0 dB
PL1W 31.14739227 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -2.00 dB
PL12 17.05 dB
PL13 19.00 dB
PL2W 37.02396774 W
PL12W 0.46076876 W
PL13W 0.29409182 W
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677384 MHz
WDW EM
SSB 0
LB 1.00 Hz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

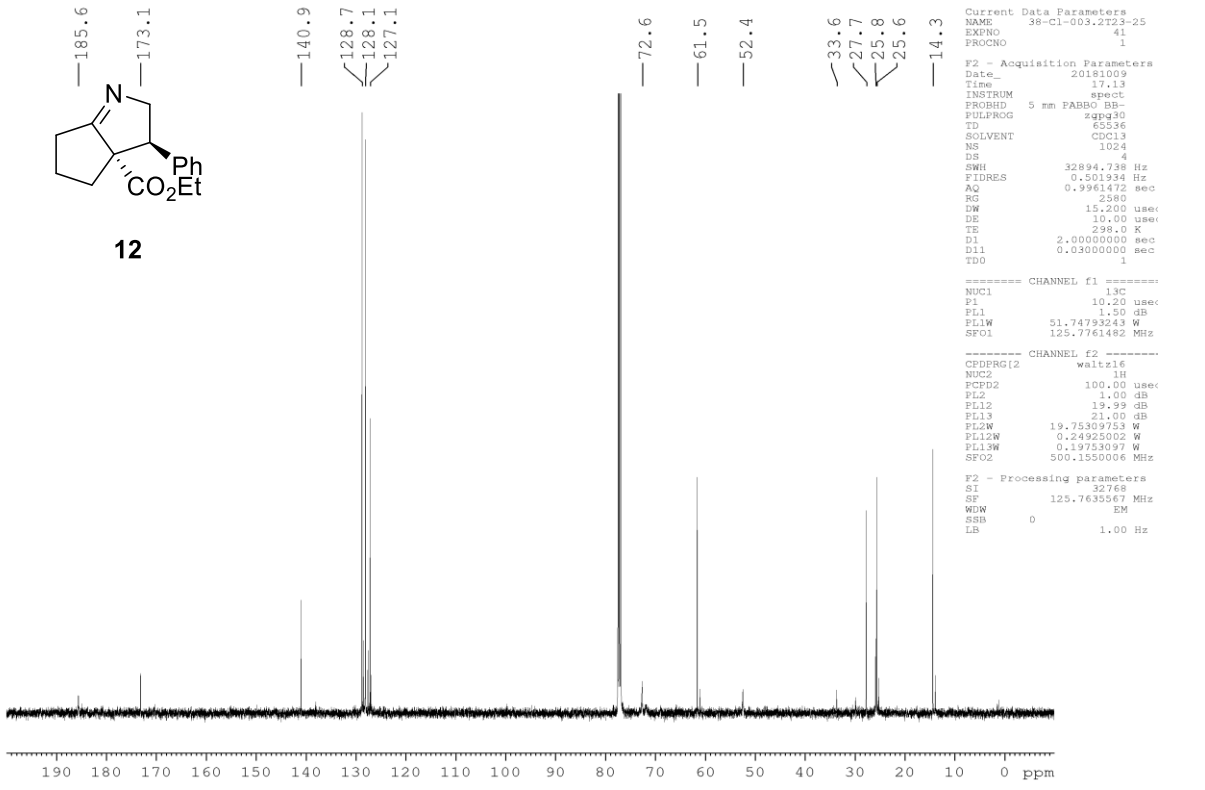

7.28 7.27 7.26 7.25 7.25 7.23 7.22 7.21 7.21 7.19 7.15 7.15 7.13
4.28 4.27 4.27 4.26 3.97 3.95 3.94 3.93 3.91 3.90 3.89 3.88 3.87 3.86 3.84 3.31 3.29 2.29 2.28 2.26 1.98 1.95 1.91 1.76 1.72 1.63 1.62 1.61 1.60 1.60 1.59 1.58 1.55 1.10 1.08 1.05
HO
Ph
NH2
CO2Et
11
Current Data Parameters
NAME 38-SpL-002.2_NH2
EXPNO 300
PROCNO 1
F2 - Acquisition Parameters
Date_ 20181127
Time 16.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 287
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
5.84 1.00 2.03 1.11 1.97 2.36 1.30 3.70 2.24 3.01

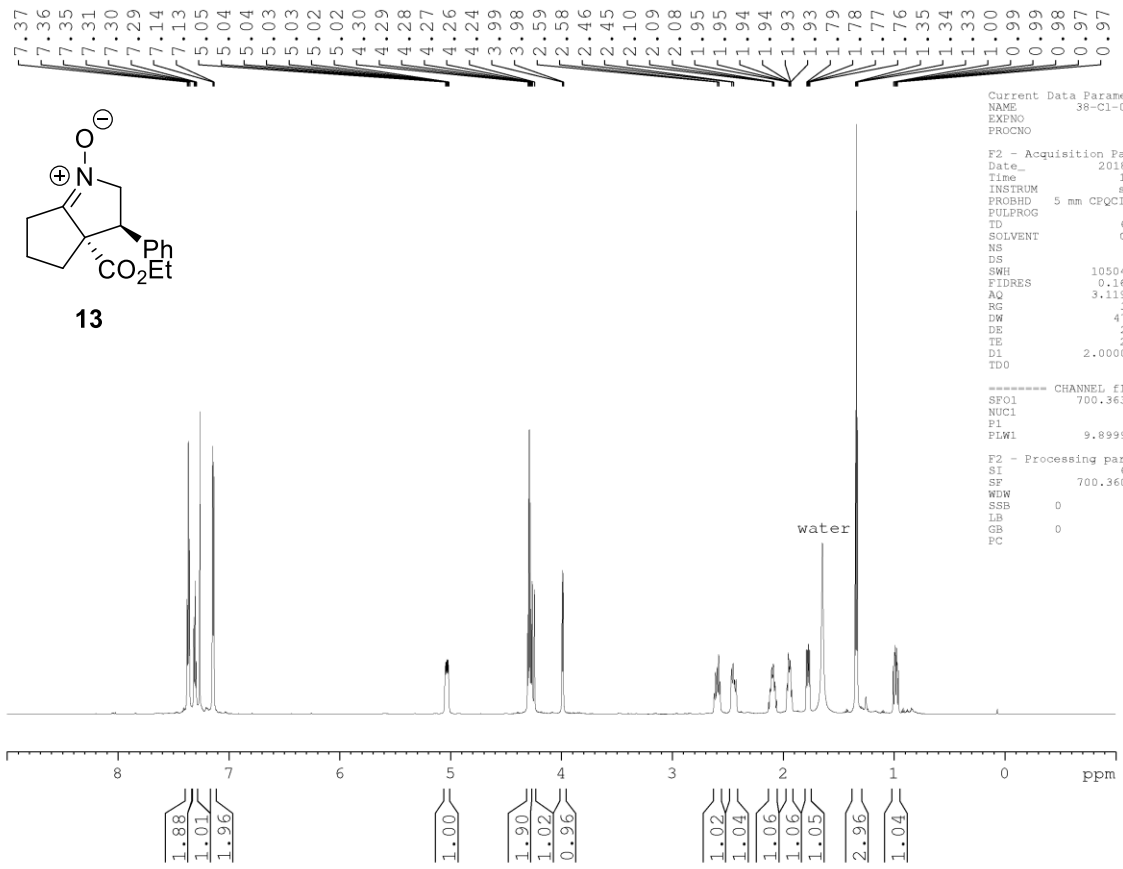

175.1
141.4
128.7
128.3
126.9
77.3
63.5
60.5
51.4
43.3
33.4
28.5
20.9
14.0
HO
Ph
NH2
CO2Et
11
Current Data Parameters
NAME 38-SpL-002.2_NH2
EXPNO 301
PROCNO 1
F2 - Acquisition Parameters
Date_ 20181127
Time 23.18
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 1290
DW 27.733 usec
DE 8.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.75 usec
PL1 0 dB
PL1W 31.14739227 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -2.00 dB
PL12 17.05 dB
PL13 19.00 dB
PL2W 37.02396774 W
PL12W 0.46076876 W
PL13W 0.29409182 W
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677418 MHz
WDW EM
SSB 0
LB 1.00 Hz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

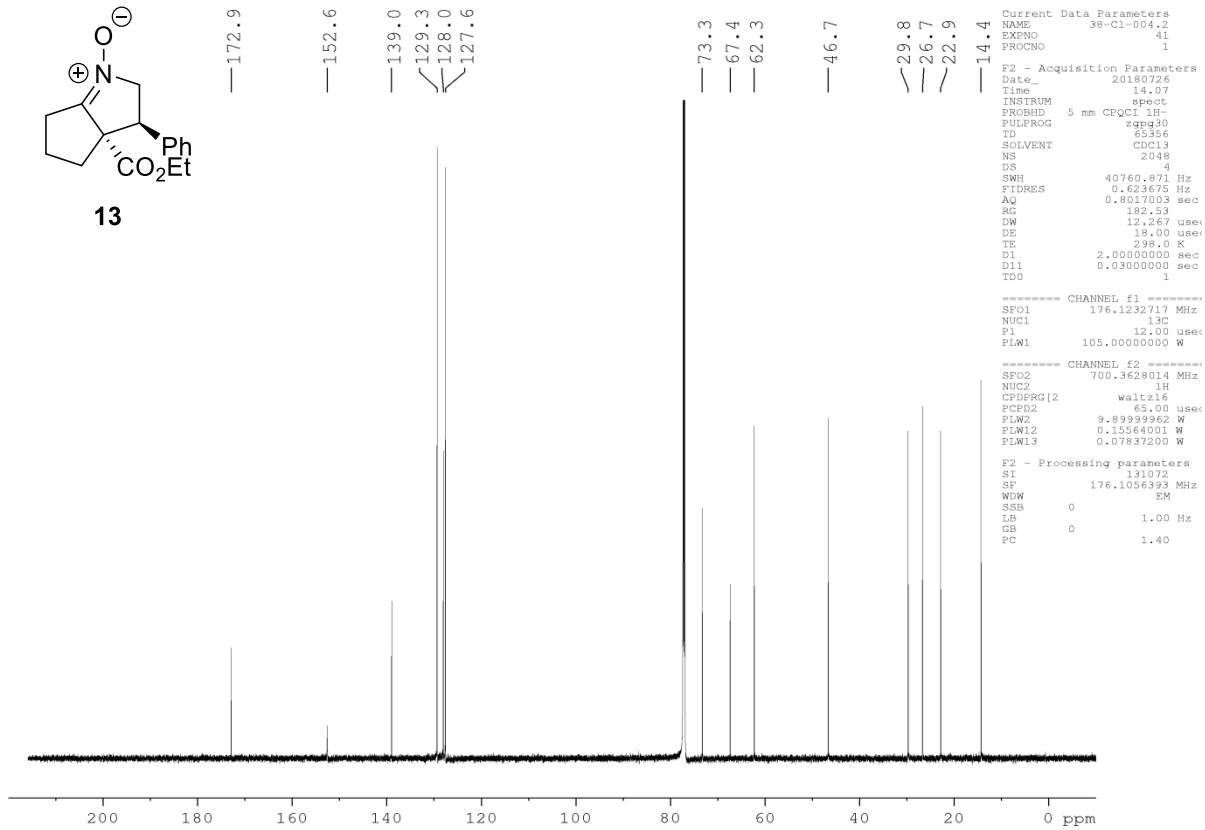

7.34 7.34 7.31 7.31 7.29 7.28 7.27 7.26 7.23 7.23 7.22 7.22 7.20 7.19 7.18 6.57 4.10 4.09 4.08 4.07 3.74 3.71 3.70 3.68 3.33 3.32 3.31 3.30 2.06 2.05 2.04 2.03 2.02 2.01 1.99 1.81 1.79 1.78 1.77 1.76 1.75 1.74 1.72 1.70 1.69 1.51 1.50 1.50 1.49 1.47 1.46 1.45
HO Ph NH O
15
Current Data Parameters
NAME 38-SPL-006
EXPNO 203
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190105
Time 17.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953086 sec
RG 228
DW 80.800 usec
DE 6.50 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300255 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
5.86 0.91 1.00 1.03 1.95 1.07 2.12 3.05 1.40

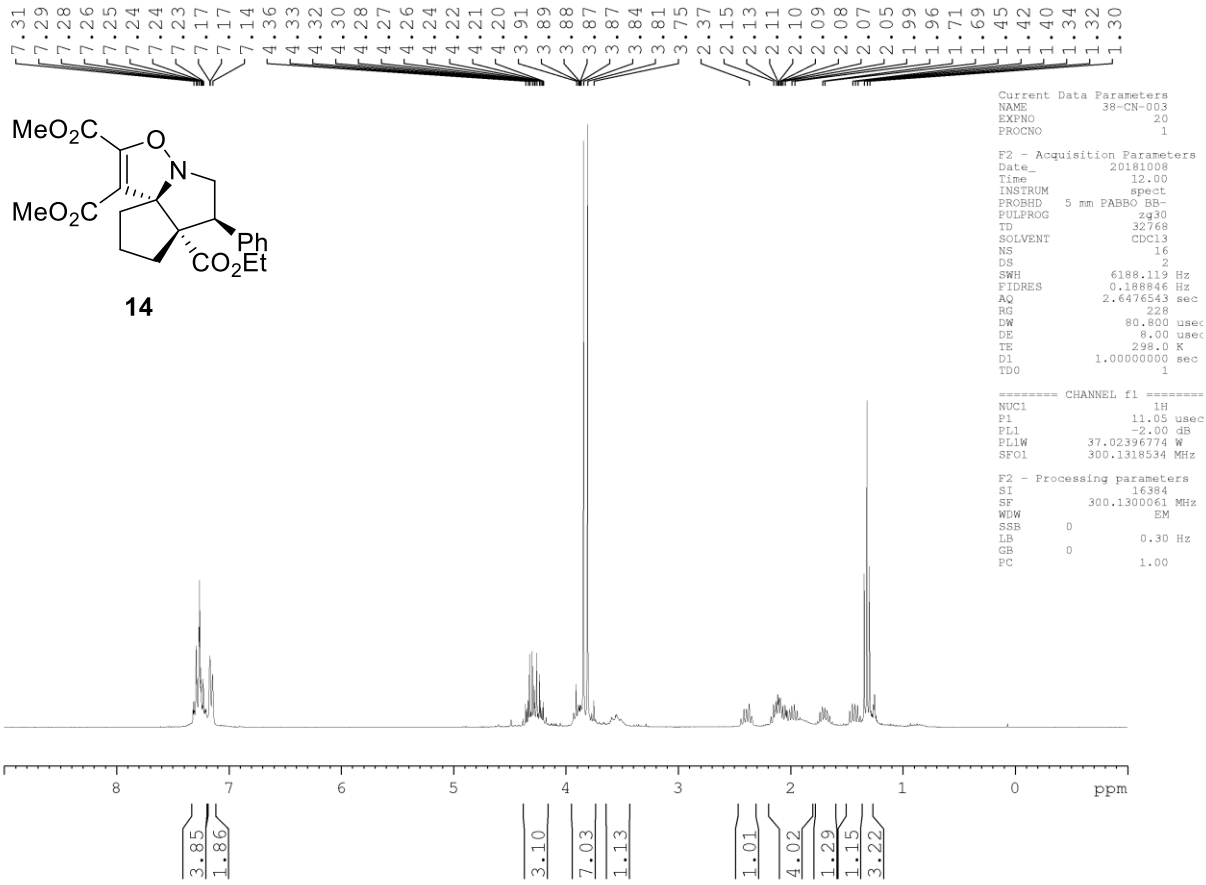

181.3 142.3 129.2 127.7 127.5 77.3 75.9 50.9 47.6 35.6 33.5 21.4
HO Ph NH O
15
Current Data Parameters
NAME 38-SPL-006
EXPNO 202
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190104
Time 23.23
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 1030
DW 27.733 usec
DE 8.00 usec
TE 297.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.75 usec
PL1 0 dB
PL1W 31.14739227 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -2.00 dB
PL12 17.05 dB
PL13 19.00 dB
PL2W 37.02396774 W
PL12W 0.46076876 W
PL13W 0.29409182 W
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677425 MHz
WDW EM
SSB 0
LB 1.00 Hz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

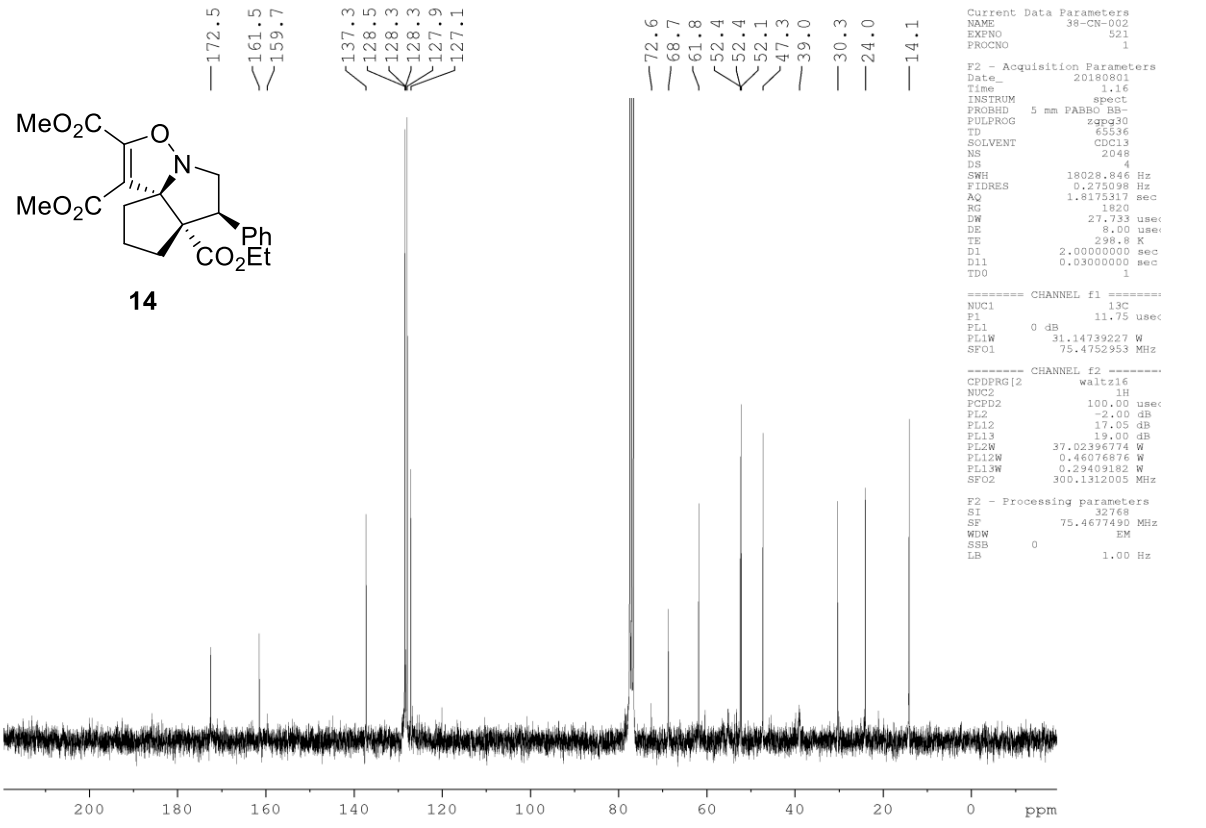

7.31 7.31 7.29 7.28 7.26 7.24 7.24 7.23 7.22 7.08 7.07 7.05 4.57 4.46 4.41 4.26 4.24 4.22 4.19 3.86 3.84 2.47 2.28 2.25 2.11 2.10 2.09 2.09 2.08 2.06 1.87 1.86 1.84 1.83 1.82 1.82 1.81 1.80 1.78 1.33 1.30 1.28 0.98 0.95 0.94 0.92 0.91 0.88 0.86
N
Ph
CO2Et
12
Current Data Parameters
NAME 38-CI-003.2
EXPNO 110
PROCNO 1
F2 - Acquisition Parameters
Date_ 20181009
Time 13.33
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 287
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300059 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
3.89 1.97 1.08 1.00 2.14 1.06 1.15 2.69 2.82 3.35 1.16


185.6 173.1 140.9 128.7 128.1 127.1 72.6 61.5 52.4 33.6 27.7 25.8 25.6 14.3
N
Ph
CO2Et
12
Current Data Parameters
NAME 38-CI-003.2T23-25
EXPNO 41
PROCNO 1
F2 - Acquisition Parameters
Date_ 20181009
Time 17.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 32894.738 Hz
FIDRES 0.501934 Hz
AQ 0.9961472 sec
RG 2580
DW 15.200 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.20 usec
PL1 1.50 dB
PL1W 51.74793243 W
SFO1 125.7761482 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.00 dB
PL12 19.99 dB
PL13 21.00 dB
PL2W 19.75309753 W
PL12W 0.24925002 W
PL13W 0.19753097 W
SFO2 500.1550006 MHz
F2 - Processing parameters
SI 32768
SF 125.7635567 MHz
WDW EM
SSB 0
LB 1.00 Hz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.37 7.36 7.35 7.31 7.30 7.29 7.14 7.13 5.05 5.04 5.04 5.03 5.03 5.02 5.02 4.30 4.29 4.28 4.27 4.26 4.24 3.99 3.98 2.59 2.58 2.46 2.45 2.10 2.09 2.08 1.95 1.95 1.94 1.94 1.93 1.93 1.79 1.78 1.77 1.76 1.35 1.34 1.33 1.00 0.99 0.99 0.98 0.97 0.97
Current Data Parameters
NAME 38-C1-004.2
EXPNO 40
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180726
Time 12.28
INSTRUM spect
PROBHD 5 mm CPQCI 1H-
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 10504.202 Hz
FIDRES 0.160281 Hz
AQ 3.1195135 sec
RG 31.36
DW 47.600 usec
DE 20.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
CHANNEL f1
SFO1 700.3632917 MHz
NUC1 1H
P1 8.15 usec
PLW1 9.89999962 W
F2 - Processing parameters
SI 65536
SF 700.3600168 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
N
Ph
CO2Et
13
water
8 7 6 5 4 3 2 1 0 ppm
1.88 1.01 1.96 1.00 1.90 1.02 0.96 1.02 1.04 1.06 1.06 1.05 2.96 1.04

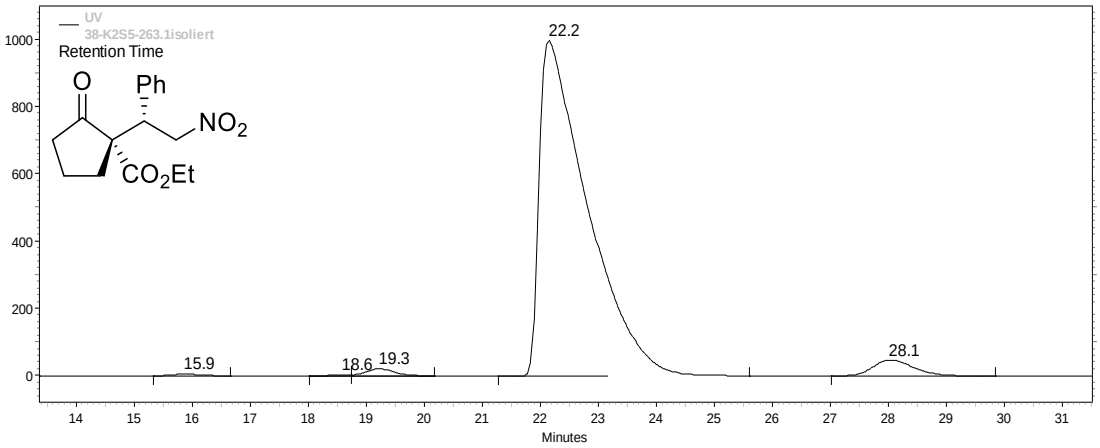

172.9 152.6 139.0 129.3 128.0 127.6 73.3 67.4 62.3 46.7 29.8 26.7 22.9 14.4
Current Data Parameters
NAME 38-C1-004.2
EXPNO 41
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180726
Time 14.07
INSTRUM spect
PROBHD 5 mm CPQCI 1H-
PULPROG zgpg30
TD 65356
SOLVENT CDCl3
NS 2048
DS 4
SWH 40760.871 Hz
FIDRES 0.623675 Hz
AQ 0.8017003 sec
RG 182.53
DW 12.267 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
SFO1 176.1232717 MHz
NUC1 13C
P1 12.00 usec
PLW1 105.00000000 W
CHANNEL f2
SFO2 700.3628014 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 65.00 usec
PLW2 9.89999962 W
PLW12 0.15564001 W
PLW13 0.07837200 W
F2 - Processing parameters
SI 131072
SF 176.1056393 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
N
Ph
CO2Et
13
200 180 160 140 120 100 80 60 40 20 0 ppm


7.31 7.29 7.28 7.26 7.25 7.24 7.24 7.23 7.17 7.17 7.14
4.36 4.33 4.32 4.30 4.28 4.27 4.26 4.24 4.22 4.21 4.20 3.91 3.89 3.88 3.87 3.87 3.84 3.81 3.75
2.37 2.15 2.13 2.11 2.10 2.09 2.08 2.07 2.05 1.99 1.96 1.71 1.69 1.45 1.42 1.40 1.34 1.32 1.30
MeO2C
O
N
MeO2C
Ph
CO2Et
14
Current Data Parameters
NAME 38-CN-003
EXPNO 20
PROCNO 1
F2 - Acquisition Parameters
Date_ 20181008
Time 12.00
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 228
DW 80.800 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -2.00 dB
PL1W 37.02396774 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
3.85 1.86 3.10 7.03 1.13 1.01 4.02 1.29 1.15 3.22


172.5 161.5 159.7 137.3 128.5 128.3 128.3 127.9 127.1 72.6 68.7 61.8 52.4 52.4 52.1 47.3 39.0 30.3 24.0 14.1
MeO2C
O
N
MeO2C
Ph
CO2Et
14
Current Data Parameters
NAME 38-CN-002
EXPNO 521
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180801
Time 1.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 1820
DW 27.733 usec
DE 8.00 usec
TE 298.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.75 usec
PL1 0 dB
PL1W 31.14739227 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -2.00 dB
PL12 17.05 dB
PL13 19.00 dB
PL2W 37.02396774 W
PL12W 0.46076876 W
PL13W 0.29409182 W
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
200 180 160 140 120 100 80 60 40 20 0 ppm

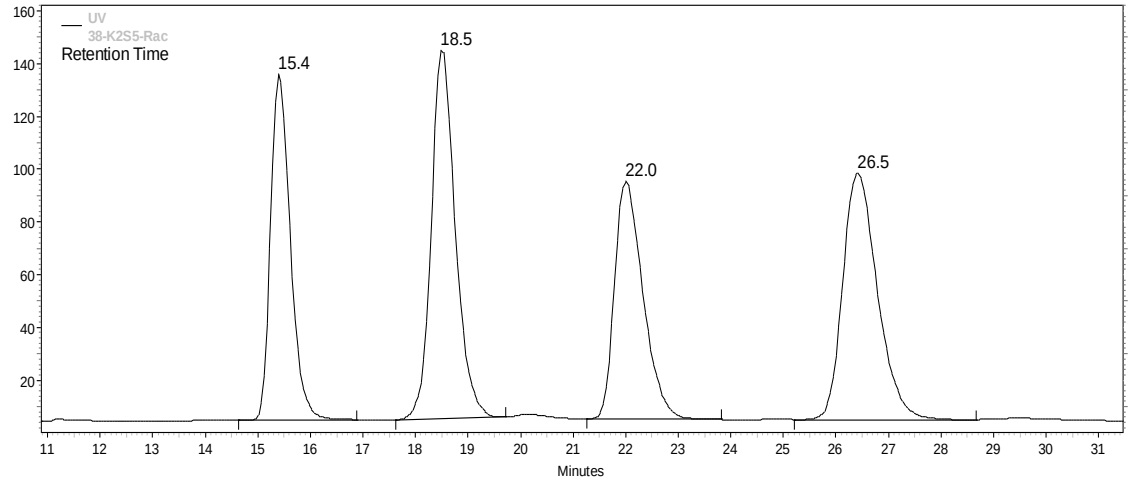
HPLC-Data

3aA, Column: ODH, *n*-hexane/*i*PrOH (90/10), 0.7 mL/min, 214 nm



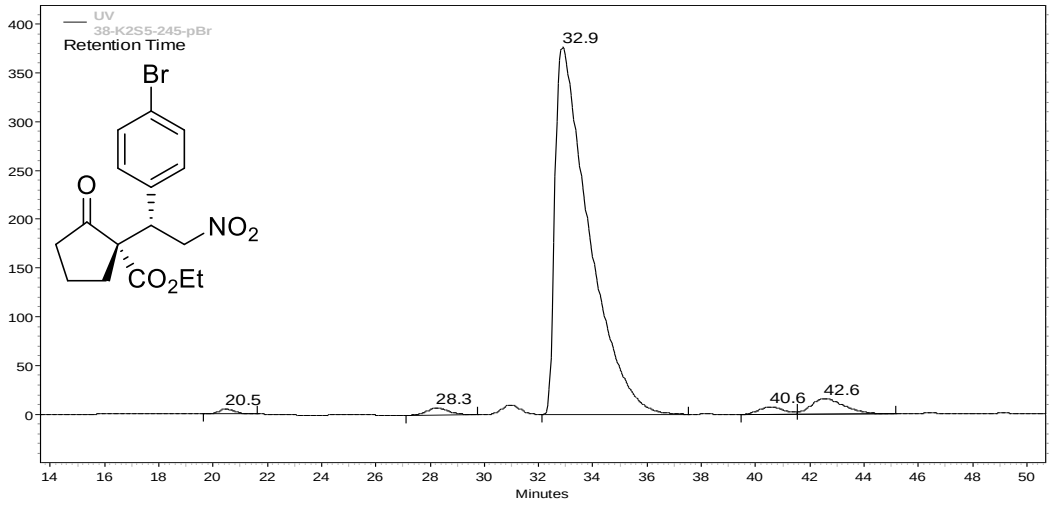
Retention Time	Area	Area %
15.9	559824	0.230
19.3	2854433	1.172
22.2	230427794	94.643
28.1	9384522	3.854

Racemic:



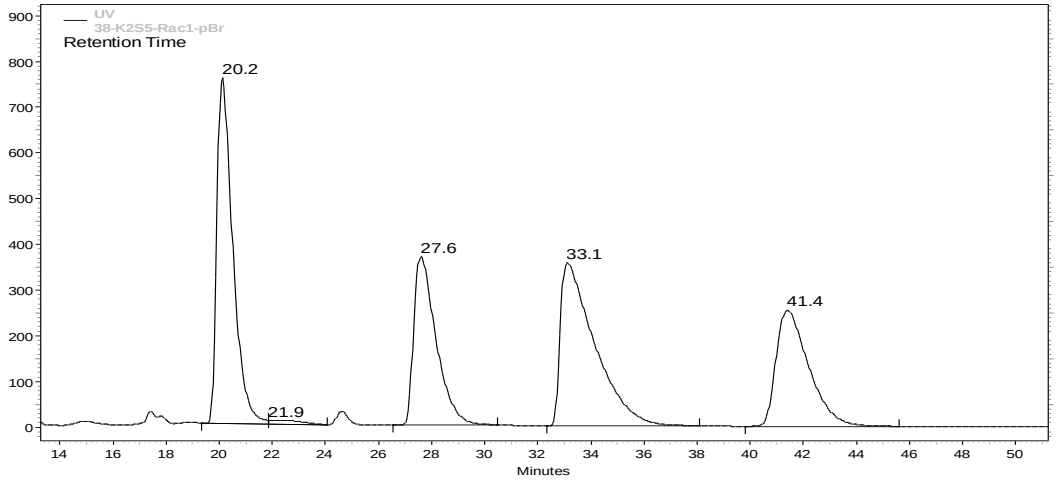
Retention Time	Area	Area %
15.4	13609290	21.9
18.5	17762810	28.6
22.0	13598914	21.9
26.5	17055328	27.5

3aB, Column: ODH, *n*-hexane/*i*PrOH (90/10), 0.7 mL/min, 214 nm



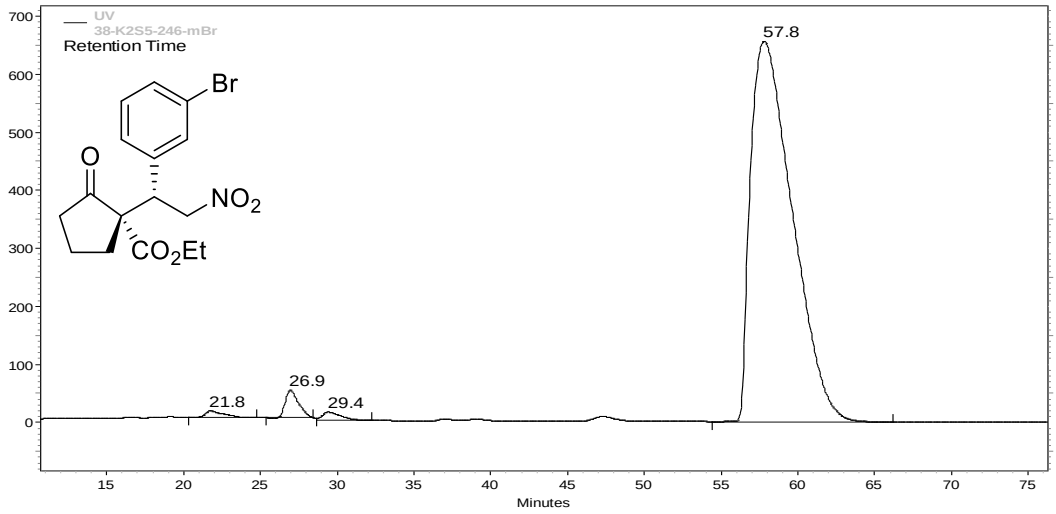
Retention Time	Area	Area %
20.5	802534	0.572
28.3	1609933	1.147
32.9	130879317	93.222
42.6	5165311	3.679

Racemic:



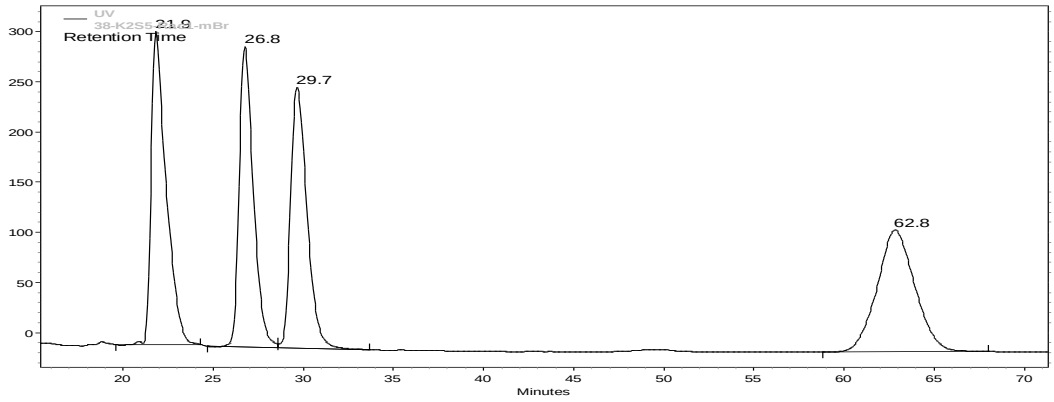
Retention Time	Area	Area %
20.2	125904894	29.408
27.6	85391052	19.945
33.1	127005792	29.665
41.4	86892779	20.296

3aC, Column: ASH, *n*-hexane/*i*PrOH (91/9), 0.7 mL/min, 214 nm



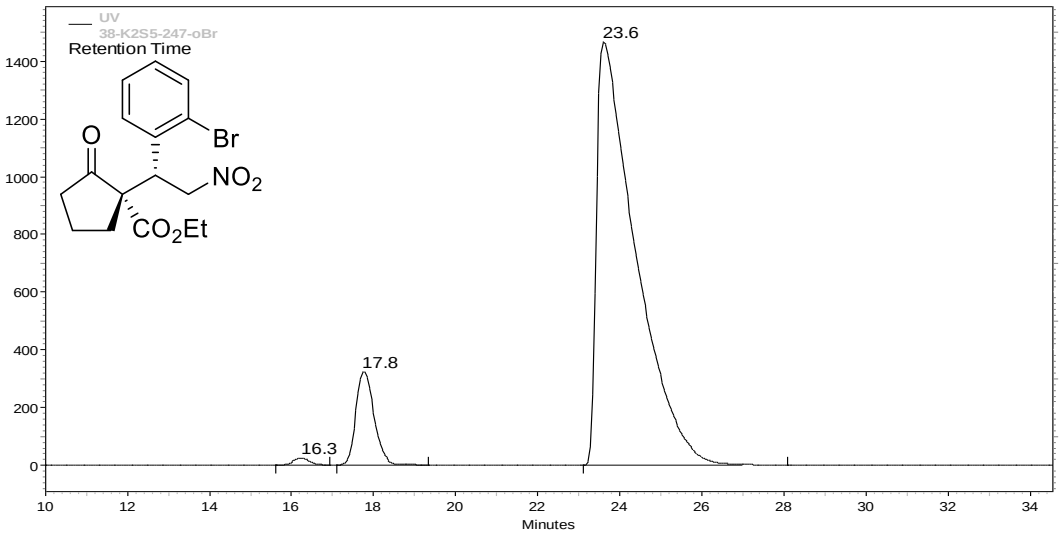
Retention Time	Area	Area %
21.8	3489283	0.676
26.9	11280693	2.185
29.4	4935539	0.956
57.8	496456523	96.182

Racemic:



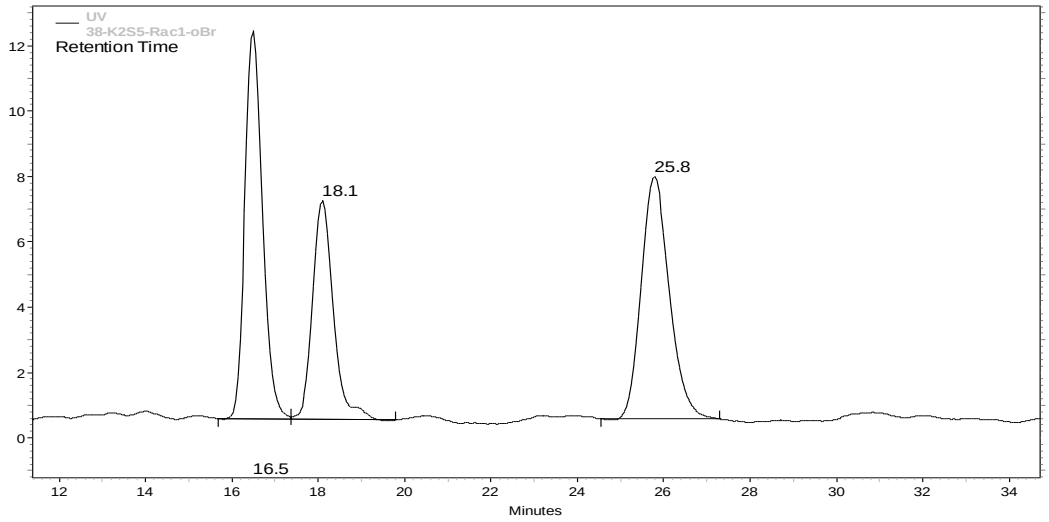
Retention Time	Area	Area %
21.9	71926238	26.209
26.8	65805111	23.978
29.7	66039477	24.064
62.8	70667364	25.750

3aD, Column: ODH, *n*-hexane/*i*PrOH (91/9), 0.7 mL/min, 214 nm



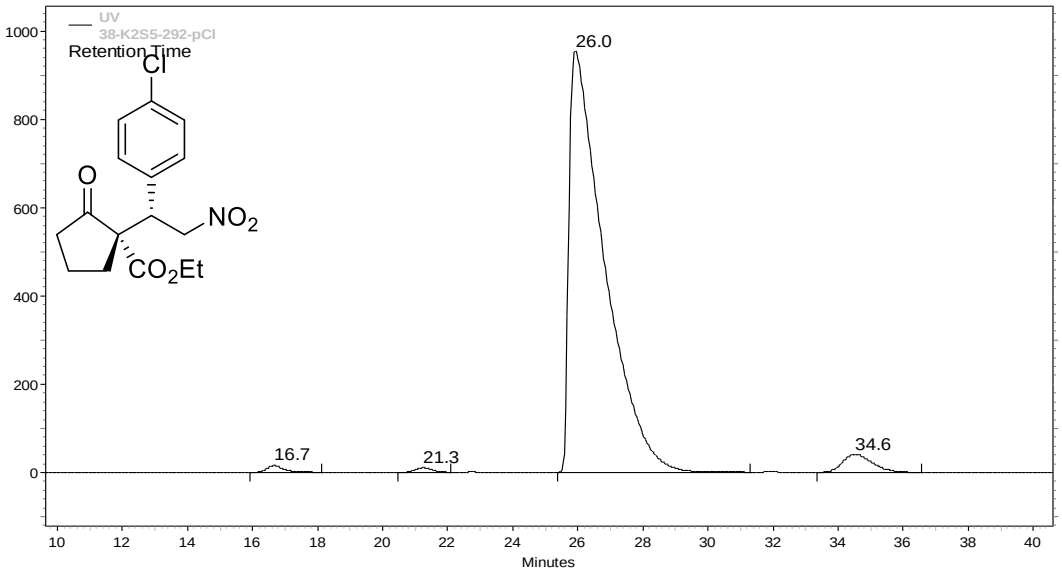
Retention Time	Area	Area %
16.3	2720733	0.629
17.8	39903578	9.232
23.6	389610198	90.139

Racemic:



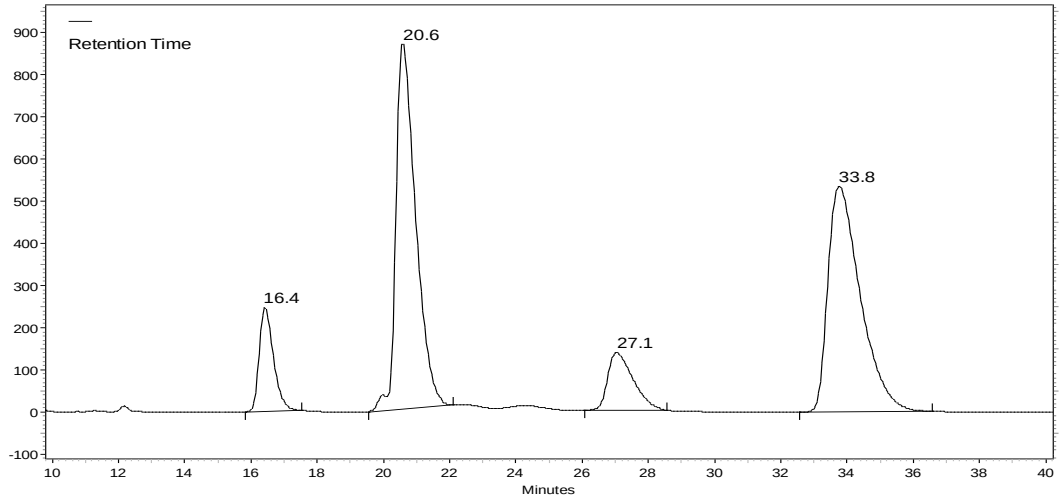
Retention Time	Area	Area %
16.5	1356510	37.675
18.1	888076	24.665
25.8	1355926	37.659

3aE, Column: ODH, *n*-hexane/*i*PrOH (90/10), 0.7 mL/min, 214 nm



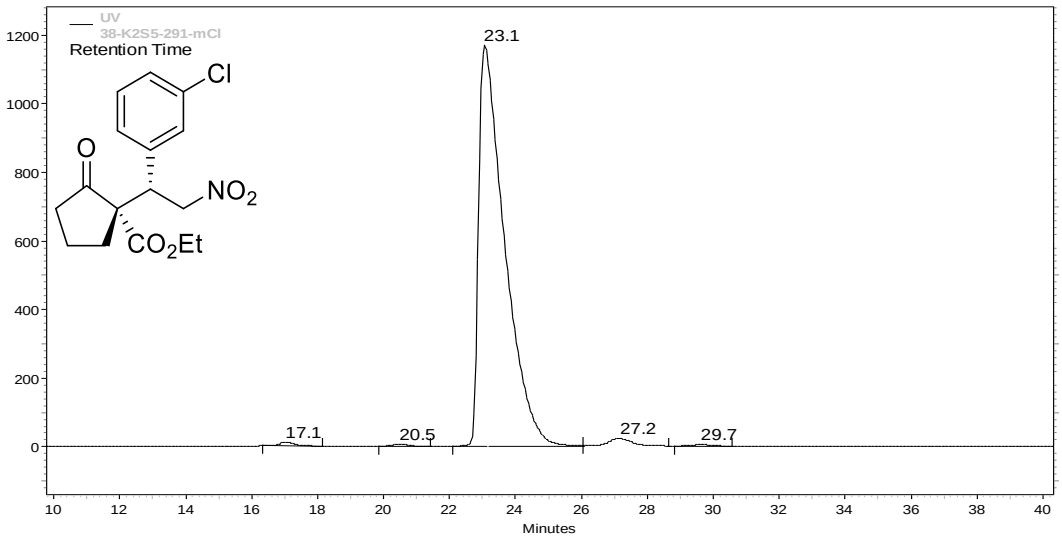
Retention Time	Area	Area %
16.7	2125923	0.710
21.3	1473526	0.492
26.0	285896436	95.425
34.6	10108656	3.374

Racemic:



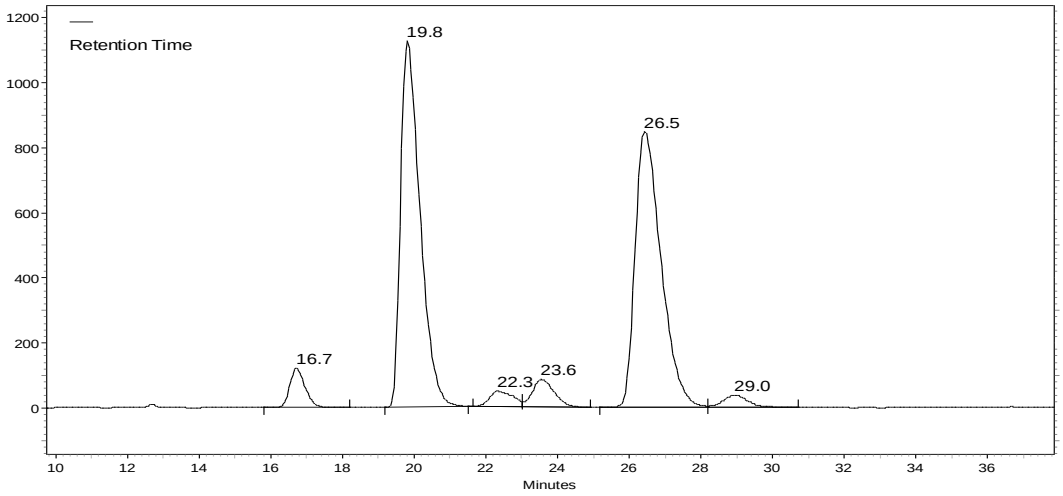
Retention Time	Area	Area %
16.4	29563216	8.491
20.6	144550786	41.516
27.1	29086629	8.354
33.8	144976316	41.639

3aF, Column: ODH, *n*-hexane/*i*PrOH (90/10), 0.7 mL/min, 214 nm



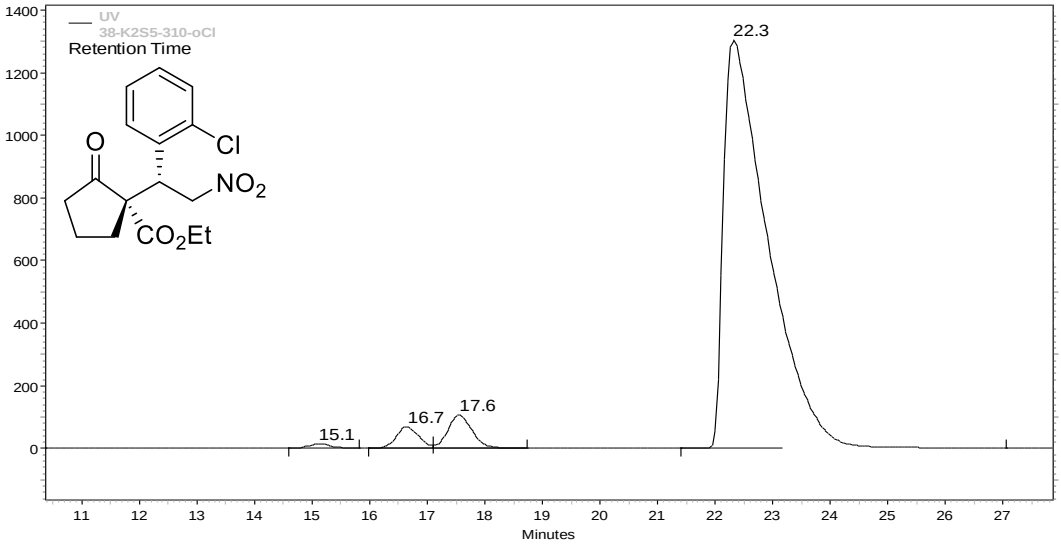
Retention Time	Area	Area %
17.1	1403245	0.534
20.5	805090	0.306
23.1	254975249	97.020
27.2	4935469	1.878

Racemic



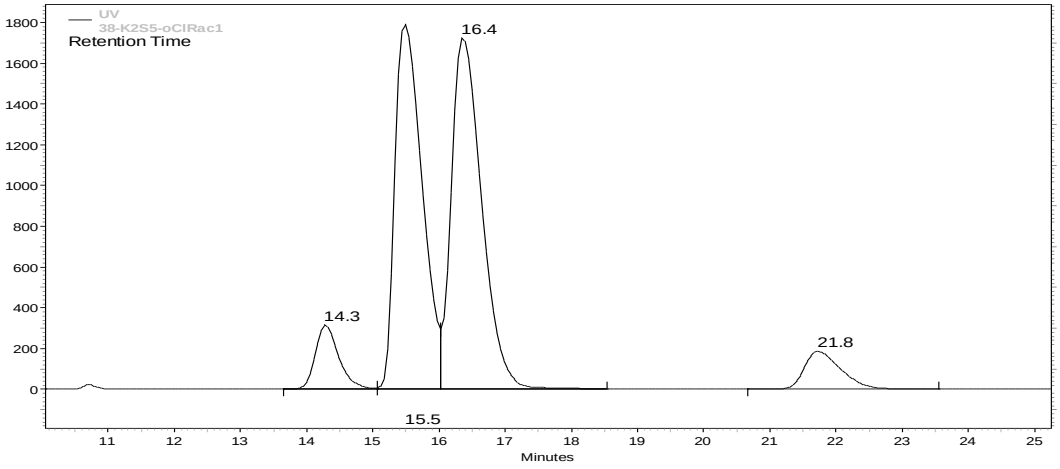
Retention Time	Area	Area %
16.7	14325587	3.715
19.8	170405921	44.191
23.6	14383879	3.730
26.5	170720491	44.273

3aG, Column: ODH, *n*-hexane/*i*PrOH (90/10), 0.7 mL/min, 214 nm



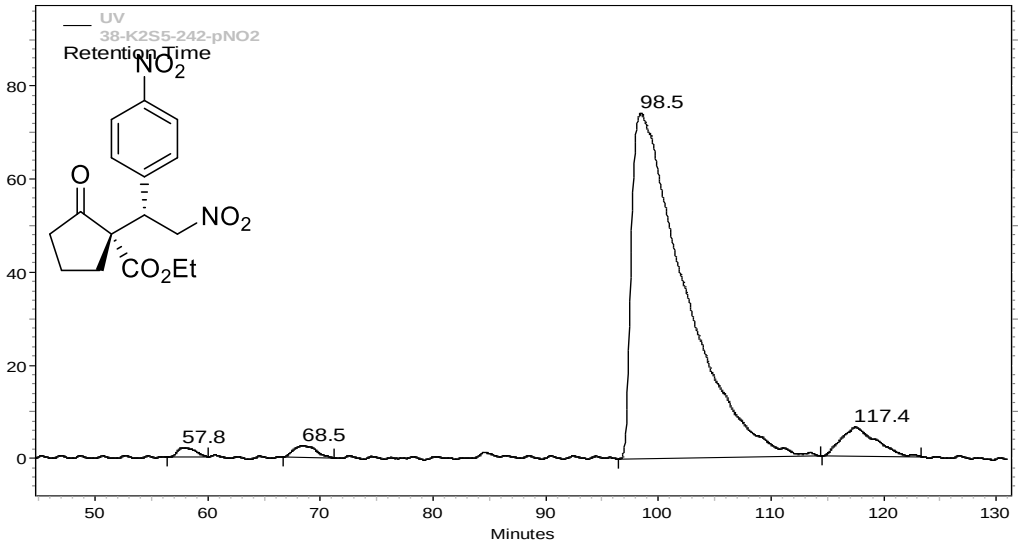
Retention Time	Area	Area %
15.1	1421475	0.475
16.7	7148087	2.388
17.6	12231275	4.086
22.3	278555313	93.051

Racemic:



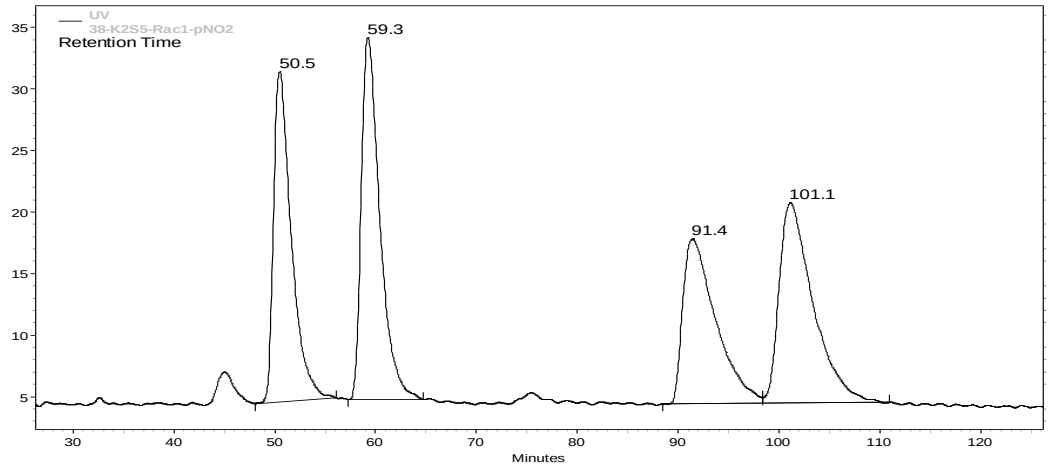
Retention Time	Area	Area %
14.3	31006198	6.379
15.5	206158507	42.414
16.4	220461047	45.357
21.8	28435541	5.850

3aH, Column: ODH, *n*-hexane/*i*PrOH (90/10), 0.7 mL/min, 214 nm



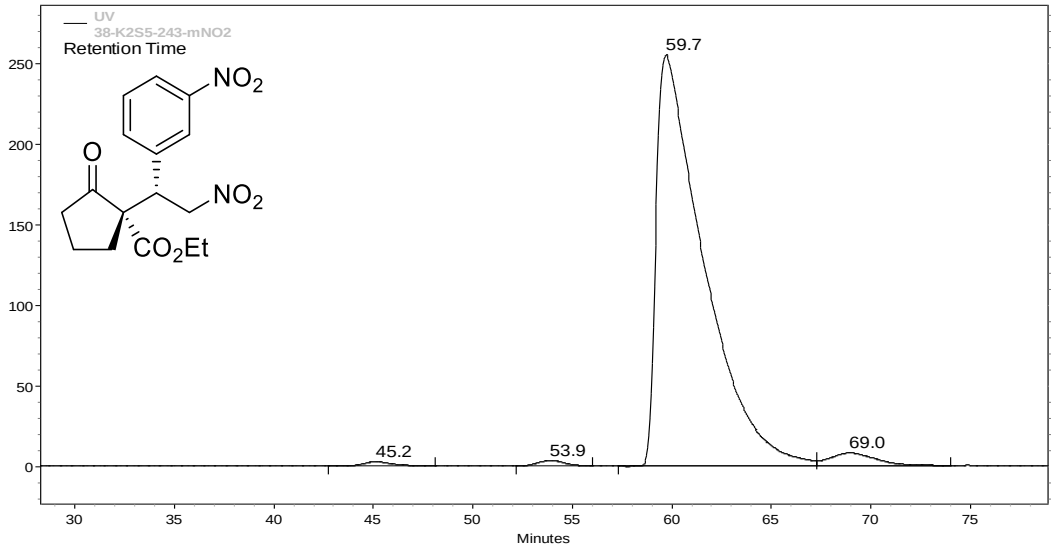
Retention Time	Area	Area %
57.8	898198	0.860
68.5	1416646	1.356
98.5	96746461	92.596
117.4	5421274	5.189

Racemic:



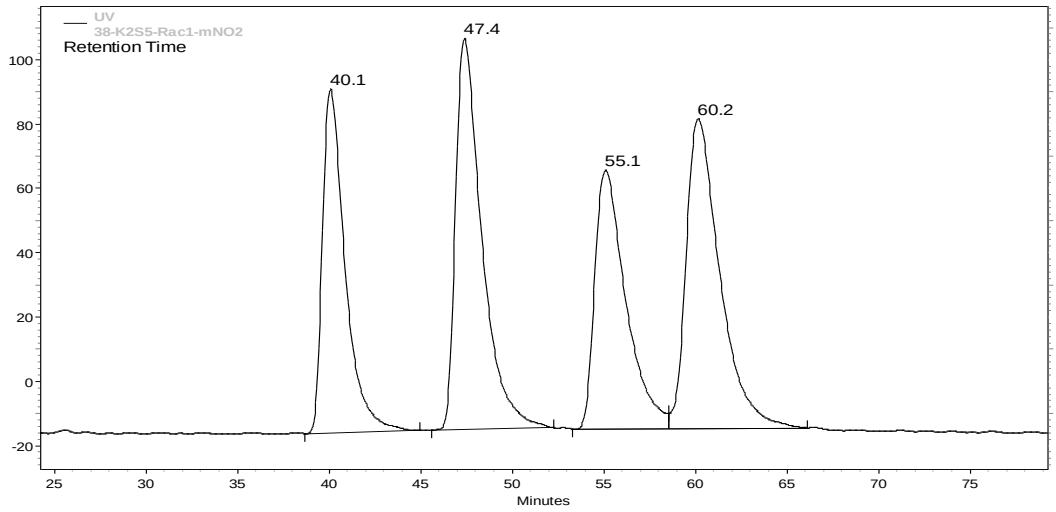
Retention Time	Area	Area %
50.5	13215248	23.740
59.3	15073085	27.077
91.4	12068267	21.679
101.1	15190034	27.287

3al, Column: ODH, *n*-hexane/*i*PrOH (90/10), 0.7 mL/min, 214 nm



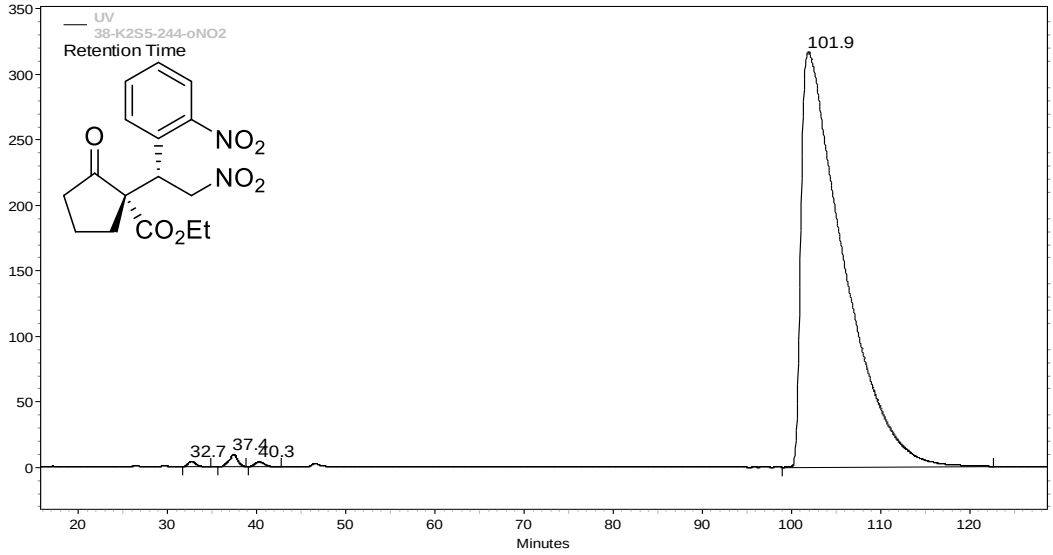
Retention Time	Area	Area %
45.2	1107792	0.629
53.9	1307038	0.742
59.7	168682761	95.720
69.0	5127635	2.910

Racemic:



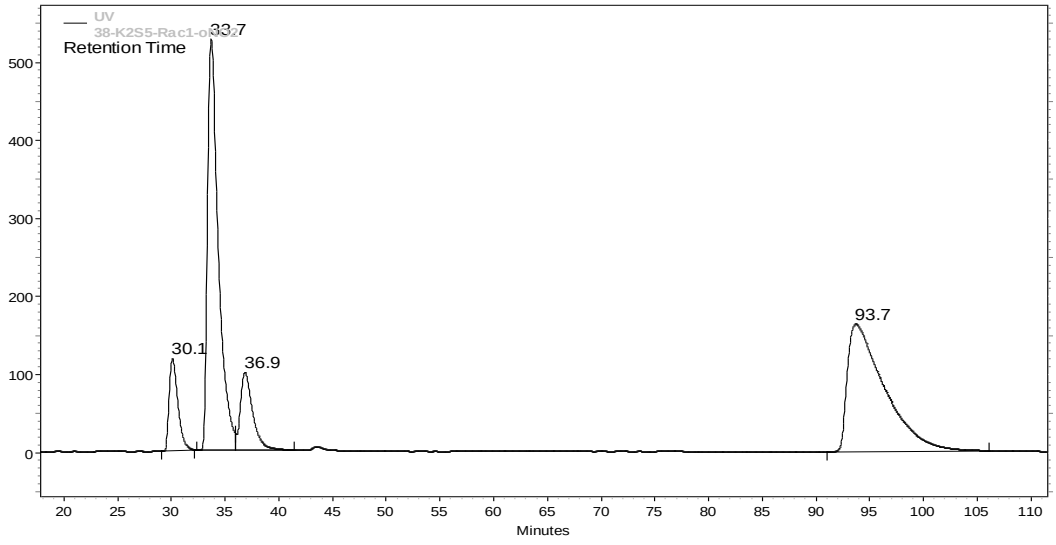
Retention Time	Area	Area %
40.1	36646767	21.248
47.4	48449422	28.091
55.1	37866240	21.955
60.2	49512853	28.707

3aJ, Column: ODH, *n*-hexane/*i*PrOH (90/10), 0.7 mL/min, 220 nm



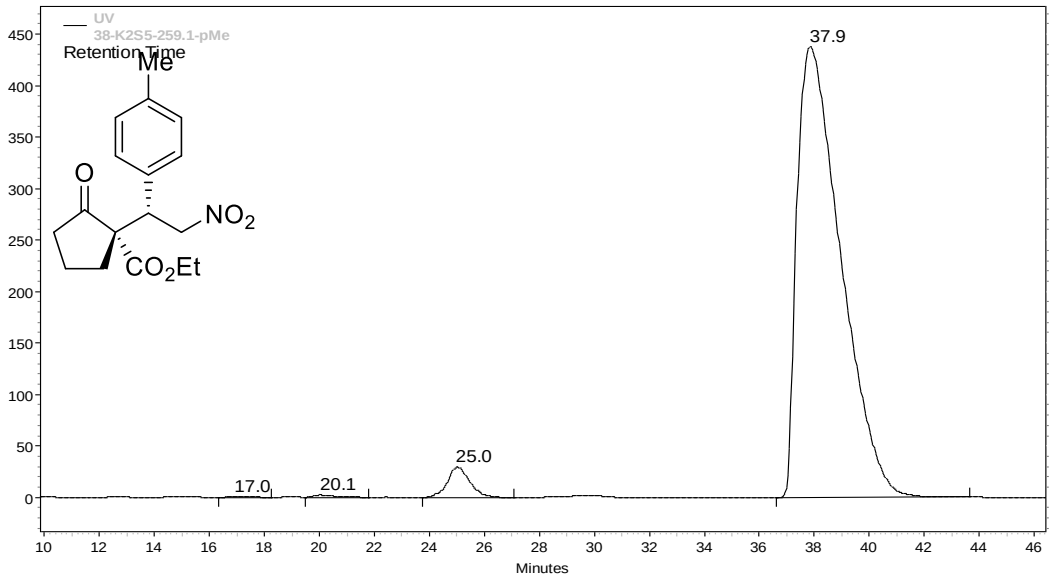
Retention Time	Area	Area %
32.7	1000035	0.237
37.4	2479248	0.588
40.3	1125962	0.267
101.9	416837520	98.907

Racemic:



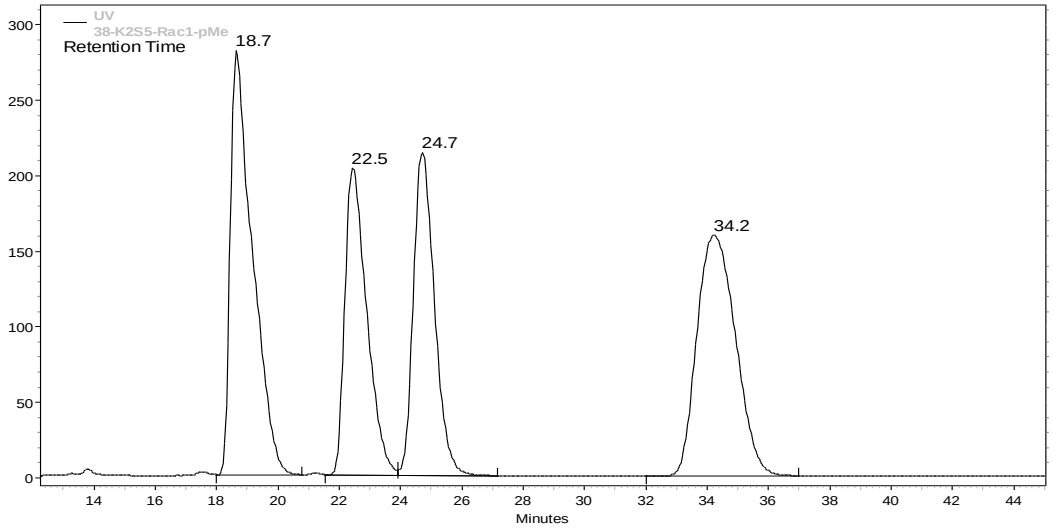
Retention Time	Area	Area %
30.1	26629613	7.283
33.7	151332492	41.388
36.9	31578801	8.637
93.7	156099978	42.692

3aK, Column: ASH, *n*-hexane/*i*PrOH (95/5), 0.7 mL/min, 220 nm



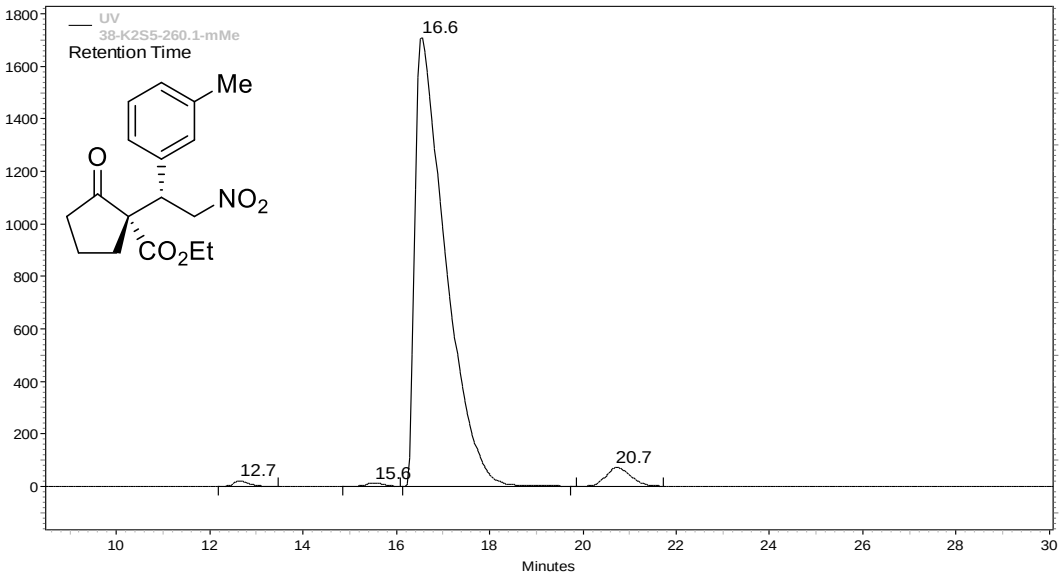
Retention Time	Area	Area %
17.0	197376	0.099
20.1	446691	0.223
25.0	6642493	3.316
37.9	193047444	96.363

Racemic:



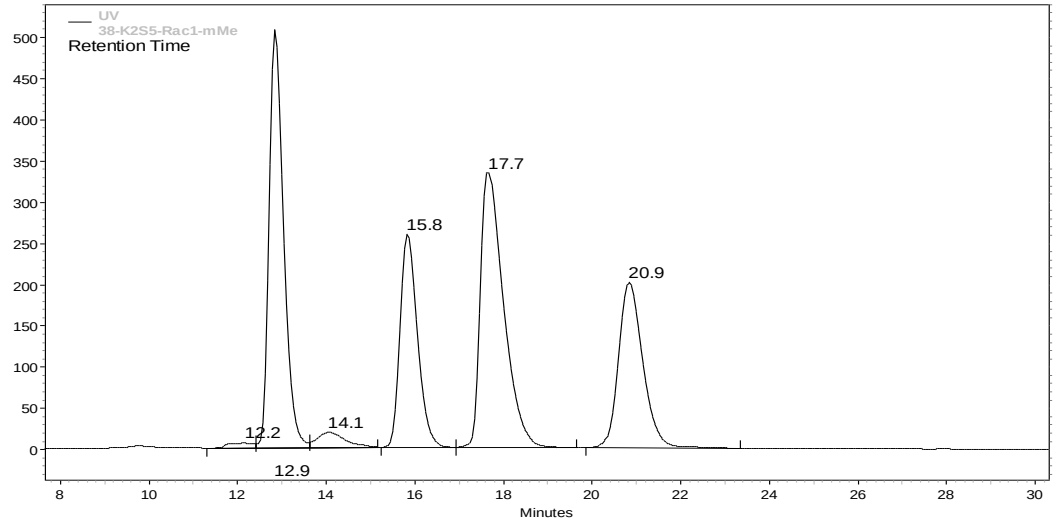
Retention Time	Area	Area %
18.7	56137823	29.016
22.5	40591137	20.981
24.7	40967862	21.175
34.2	55773130	28.828

3aL, Column: ODH, *n*-hexane/*i*PrOH (90/10), 0.7 mL/min, 214 nm



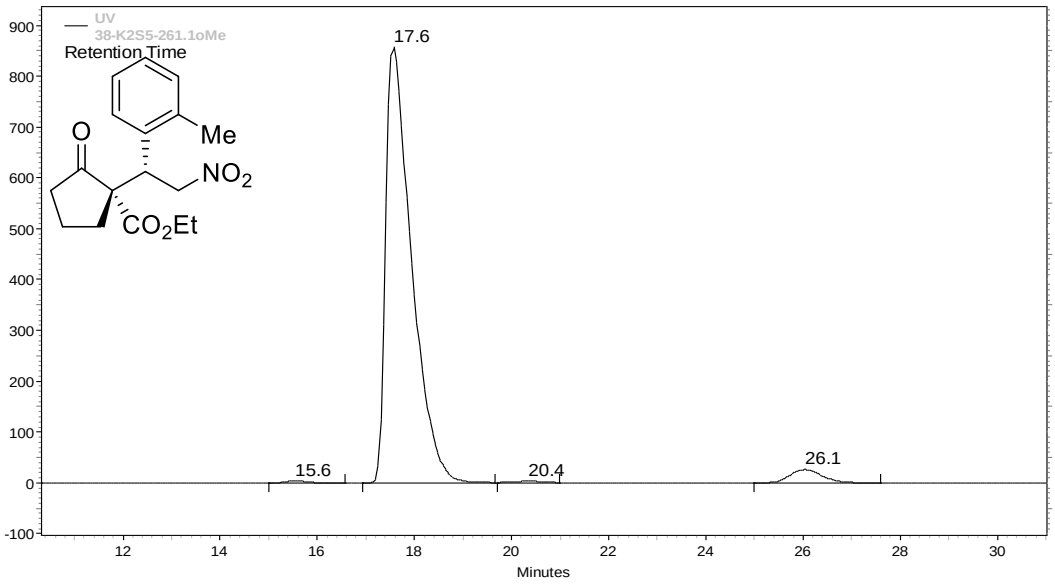
Retention Time	Area	Area %
12.7	1664907	0.516
15.6	1192160	0.369
16.6	309593085	95.891
20.7	10409043	3.224

Racemic:



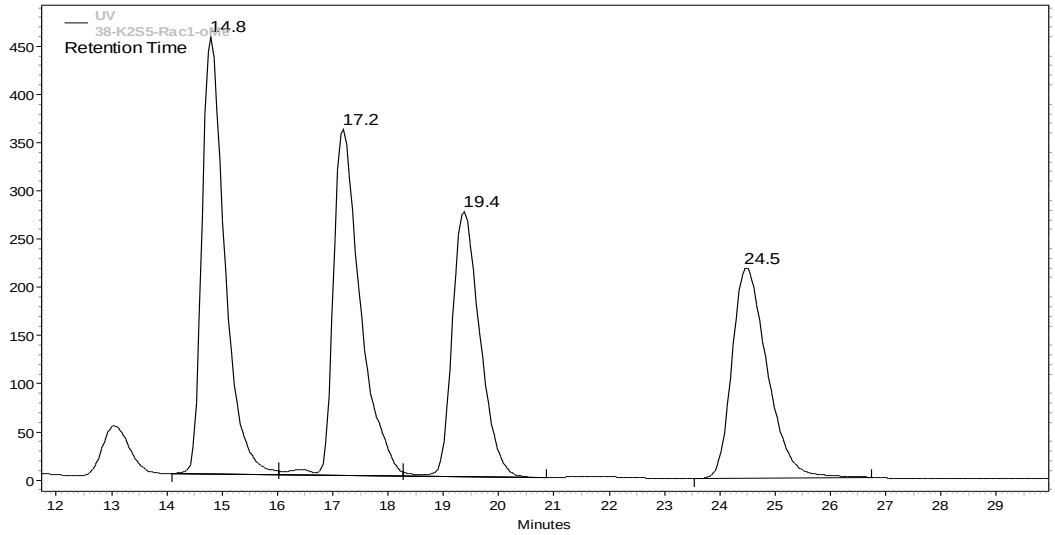
Retention Time	Area	Area %
12.9	46737154	29.680
15.8	28504447	18.101
17.7	47181287	29.962
20.9	30884682	19.613

3aM, Column: ODH, *n*-hexane/*i*PrOH (91/9), 0.7 mL/min, 214 nm



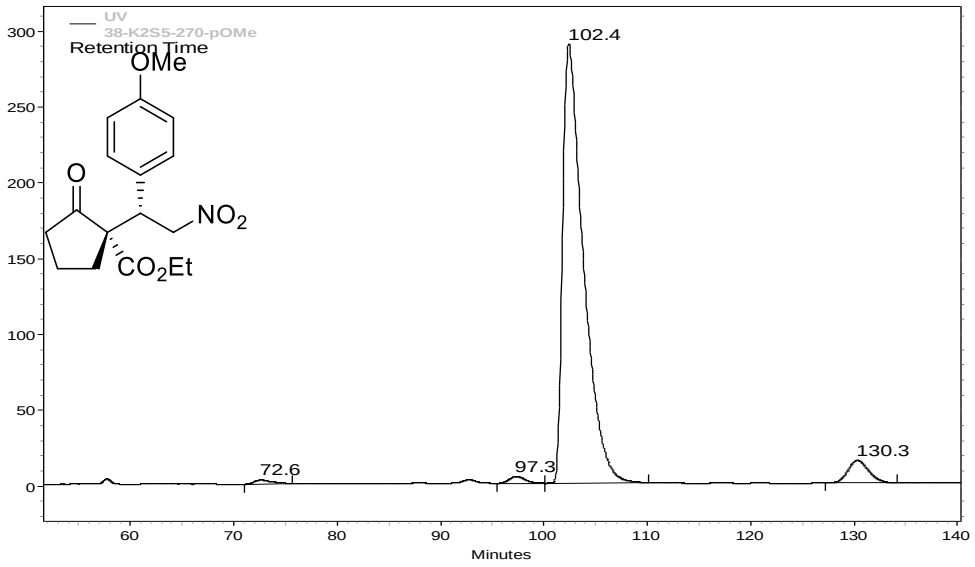
Retention Time	Area	Area %
15.6	524582	0.395
17.6	127020437	95.675
20.4	407083	0.307
26.1	4810230	3.623

Racemic:



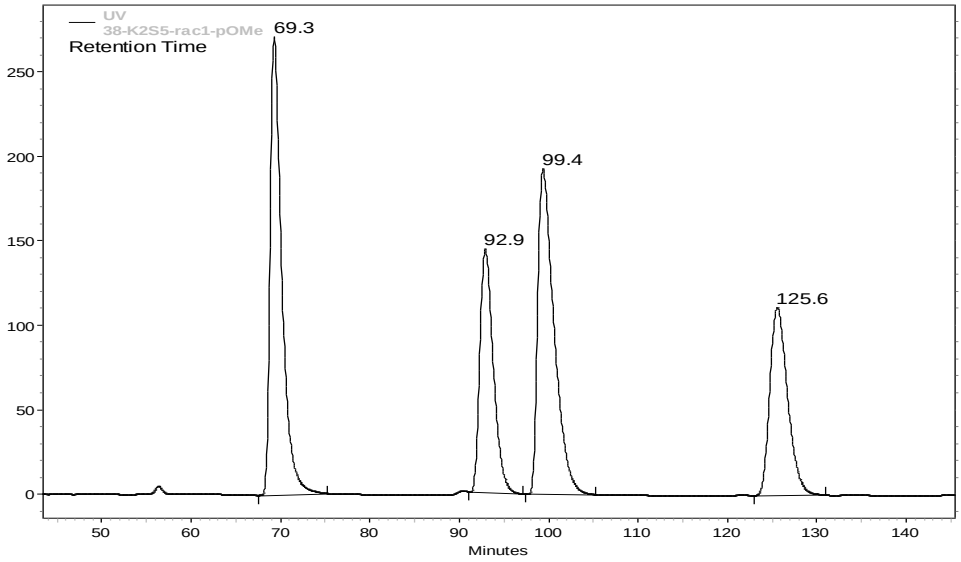
Retention Time	Area	Area %
14.8	52418912	29.412
17.2	48767349	27.363
19.4	38154279	21.408
24.5	38880554	21.816

3aN, 2xODH-Columns connected in series, *n*-hexane/*i*PrOH (85/15), 0.3 mL/min, 213 nm



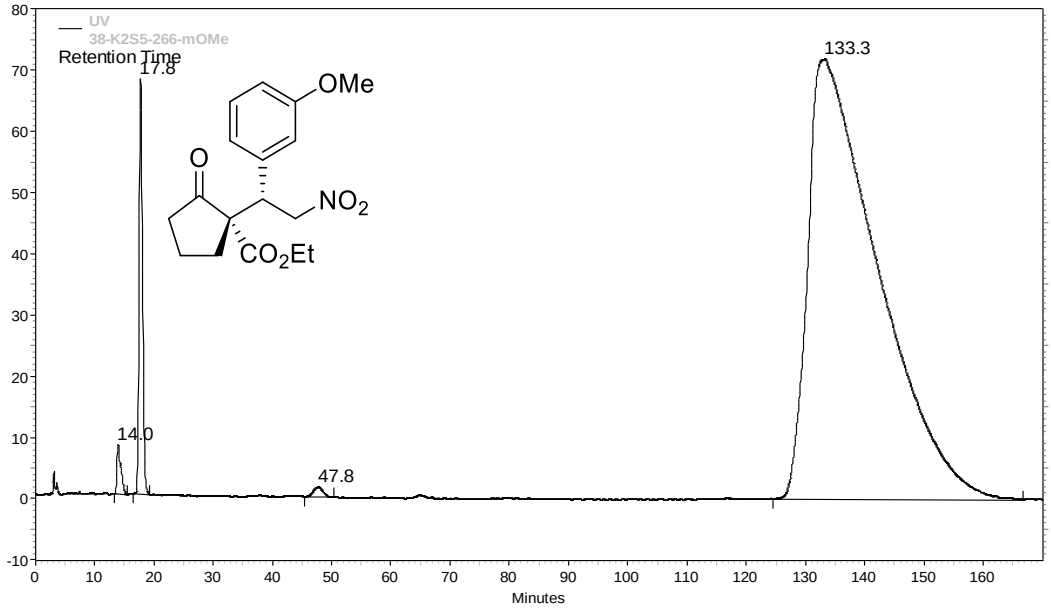
Retention Time	Area	Area %
72.6	1175286	0.681
97.3	1877974	1.088
102.4	161270962	93.411
130.3	8278989	4.795

Racemic:



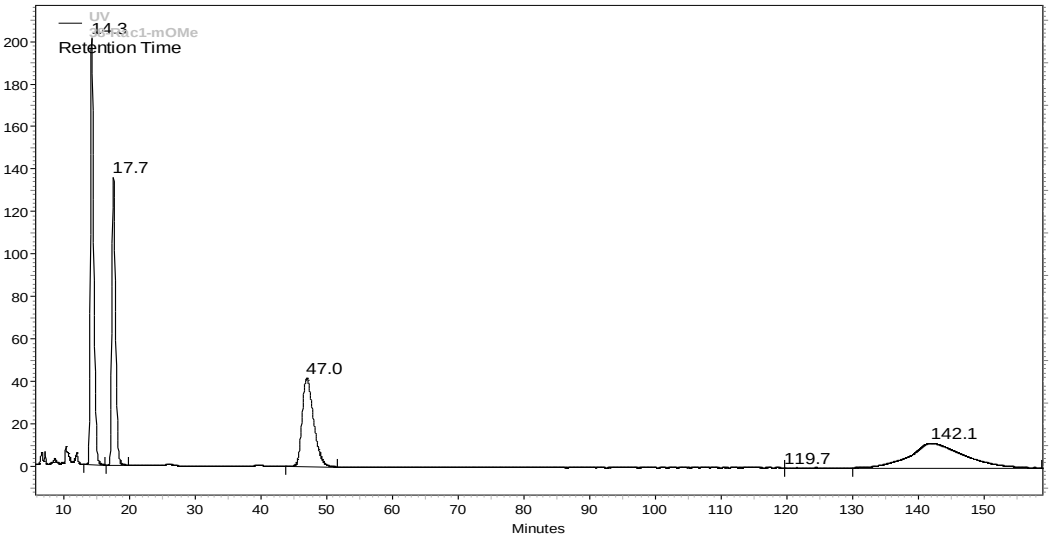
Retention Time	Area	Area %
69.3	97889825	30.798
92.9	60494423	19.033
99.4	97820152	30.776
125.6	61637665	19.393

3aO, Column: ASH, *n*-hexane/*i*PrOH (80/20), 1.0 mL/min, 220 nm



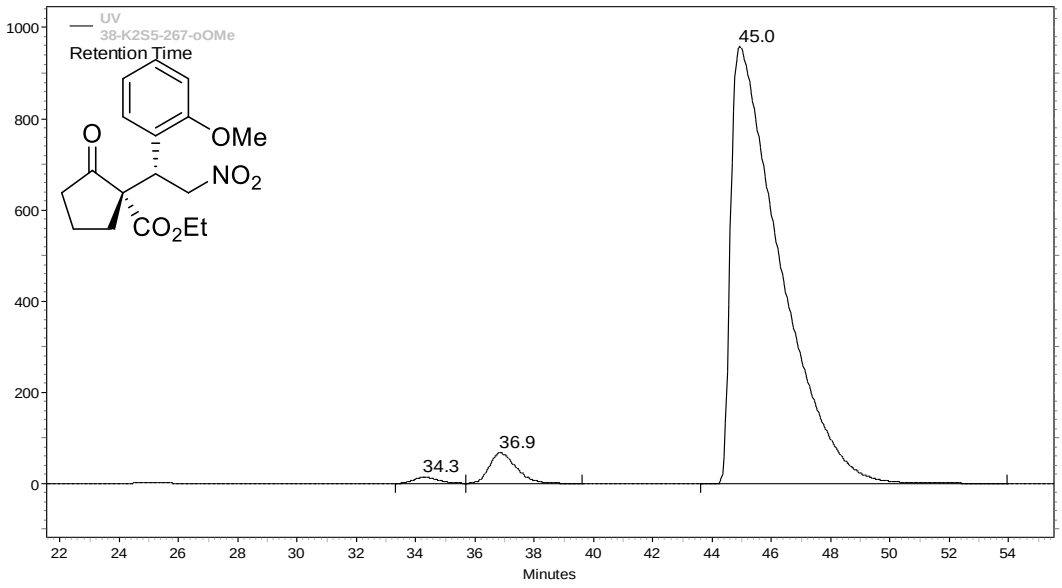
Retention Time	Area	Area %
14.0	1433421	0.577
17.8	11125941	4.476
47.8	760624	0.306
133.3	235250103	94.641

Racemic:



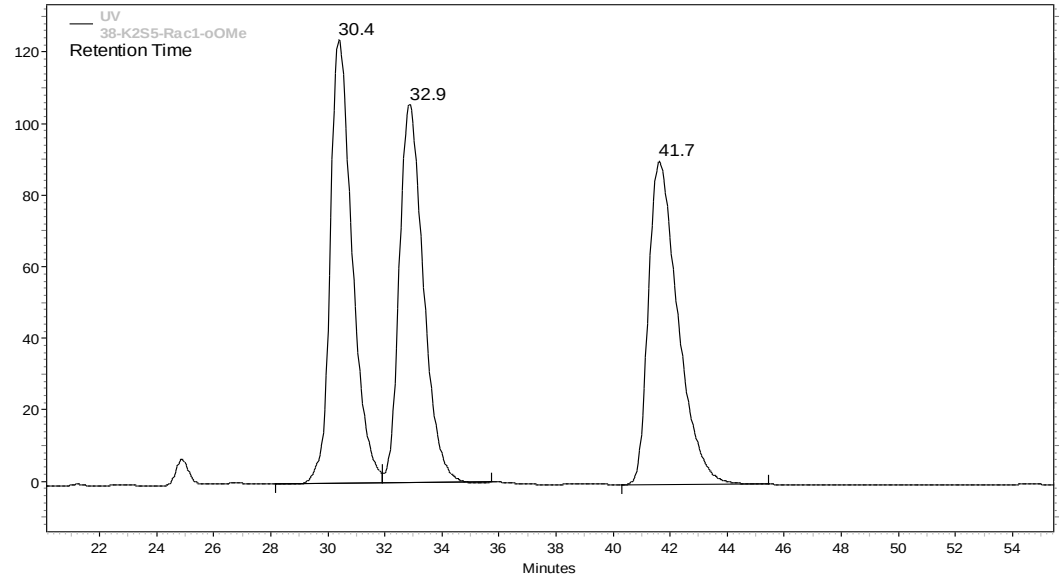
Retention Time	Area	Area %
14.3	29183194	30.097
17.7	20737927	21.388
47.0	20286679	20.922
142.1	26754656	27.593

3aP, Column: ODH, *n*-hexane/*i*PrOH (95/5), 0.5 mL/min, 220 nm



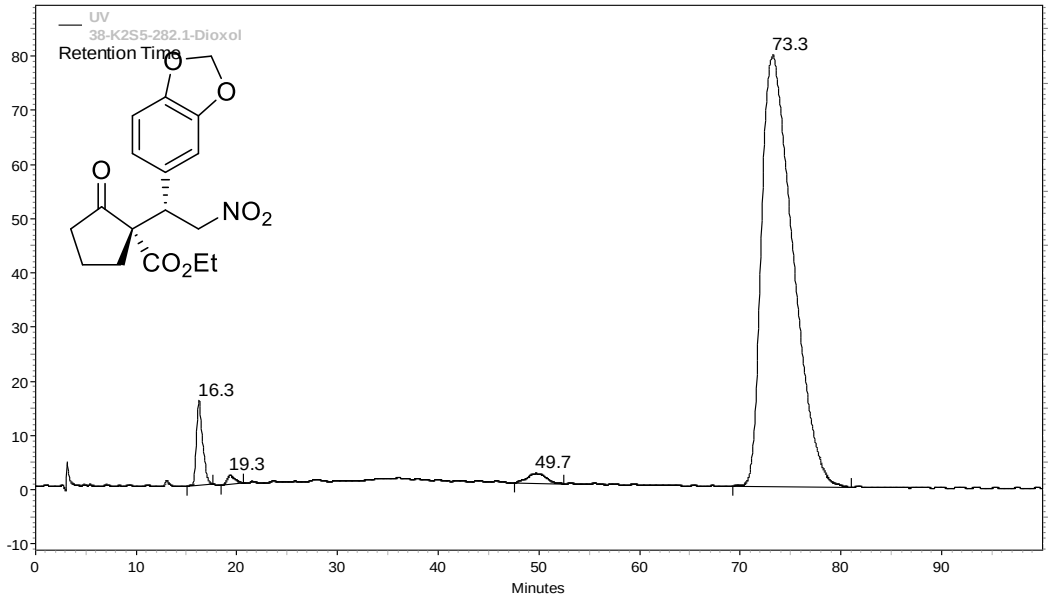
Retention Time	Area	Area %
34.3	2941699	0.637
36.9	16782941	3.636
45.0	441308797	95.613

Racemic:



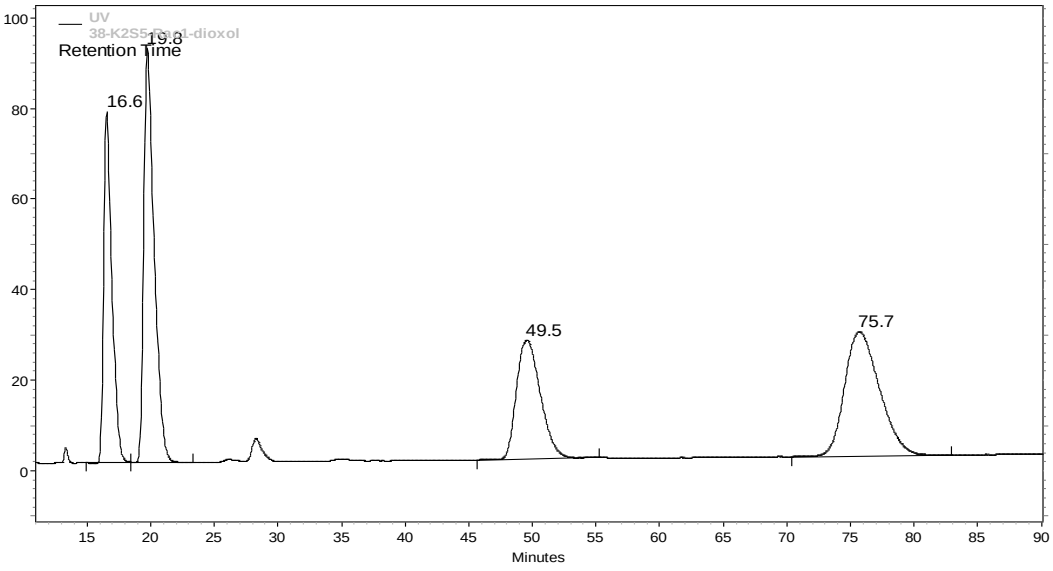
Retention Time	Area	Area %
30.4	26664725	34.412
32.9	24797161	32.001
41.7	26025719	33.587

3aQ, Column: ASH, *n*-hexane/*i*PrOH (70/30), 1.0 mL/min, 214 nm



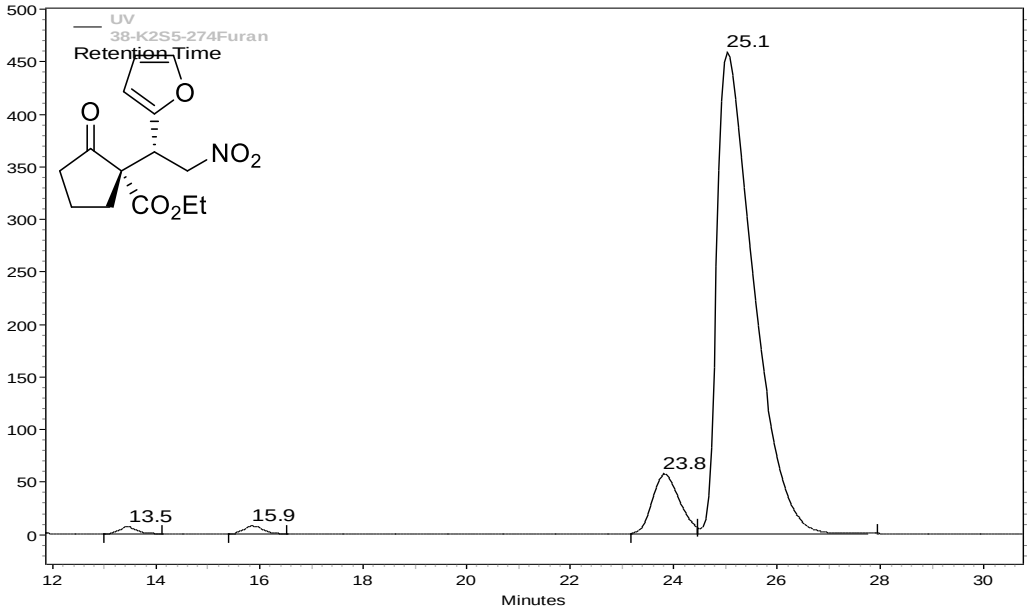
Retention Time	Area	Area %
16.3	2683901	3.682
19.3	360949	0.495
49.7	920038	1.262
73.3	68927526	94.561

Racemic:



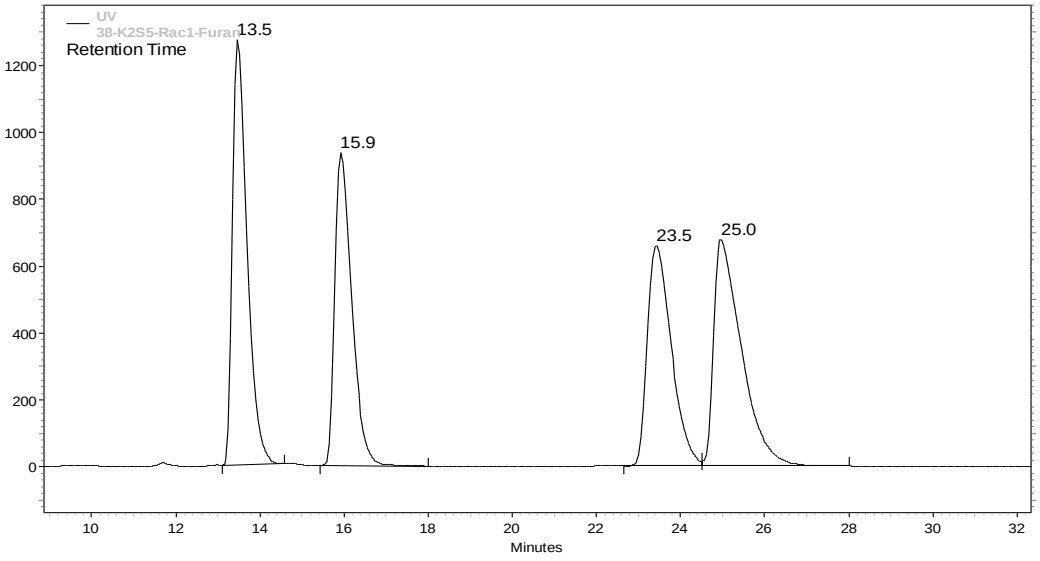
Retention Time	Area	Area %
16.6	13799817	19.973
19.8	20725156	29.996
49.5	13690333	19.814
75.7	20877722	30.217

3aR, Column: ODH, *n*-hexane/*i*PrOH (91/9), 0.7 mL/min, 214 nm



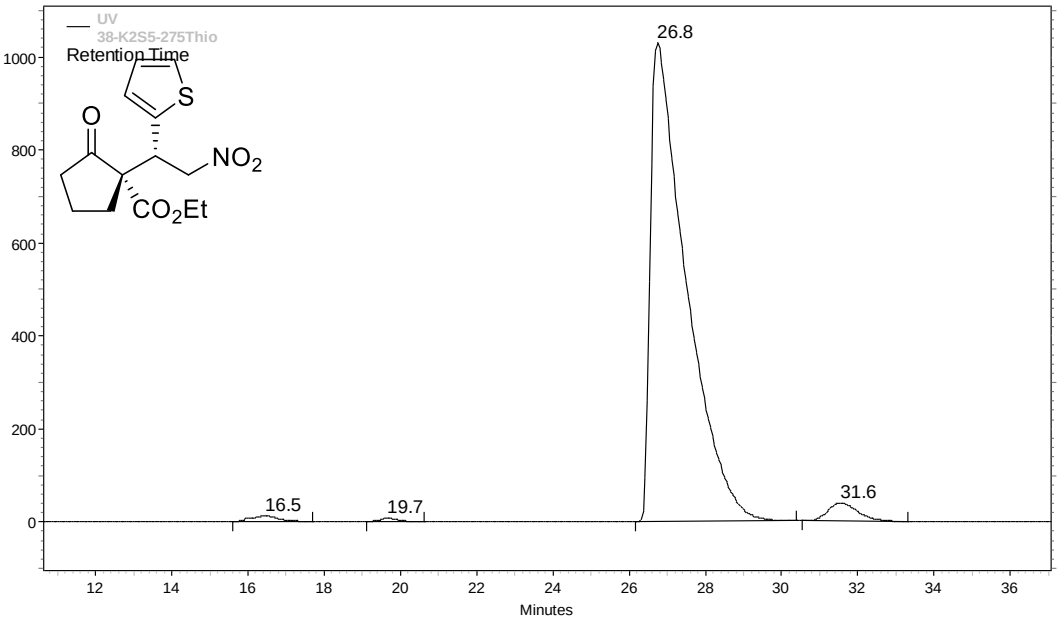
Retention Time	Area	Area %
13.5	619226	0.623
15.9	755680	0.761
23.8	8341691	8.399
25.1	89601893	90.217

Racemic:



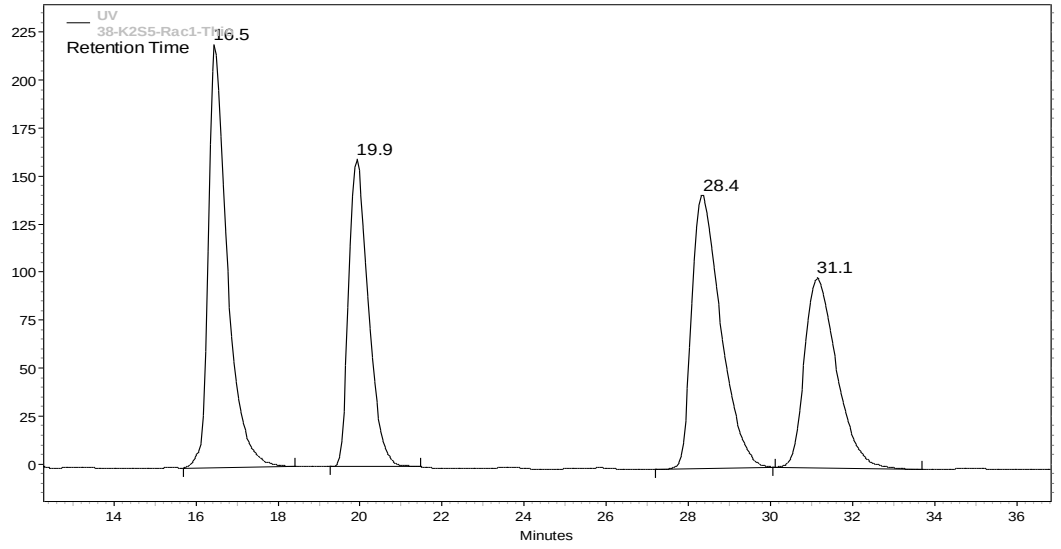
Retention Time	Area	Area %
13.5	120434791	26.497
15.9	104278968	22.943
23.5	103929591	22.866
25.0	125874162	27.694

3aS, Column: ODH, *n*-hexane/*i*PrOH (91/9), 0.7 mL/min, 214 nm



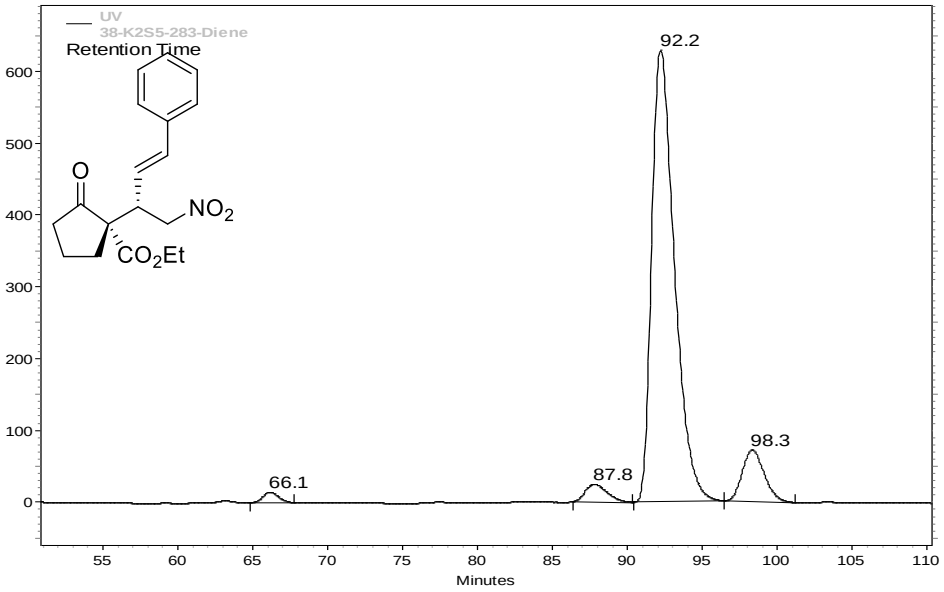
Retention Time	Area	Area %
16.5	2266083	0.814
19.7	860642	0.309
26.8	266830052	95.852
31.6	8420984	3.025

Racemic:



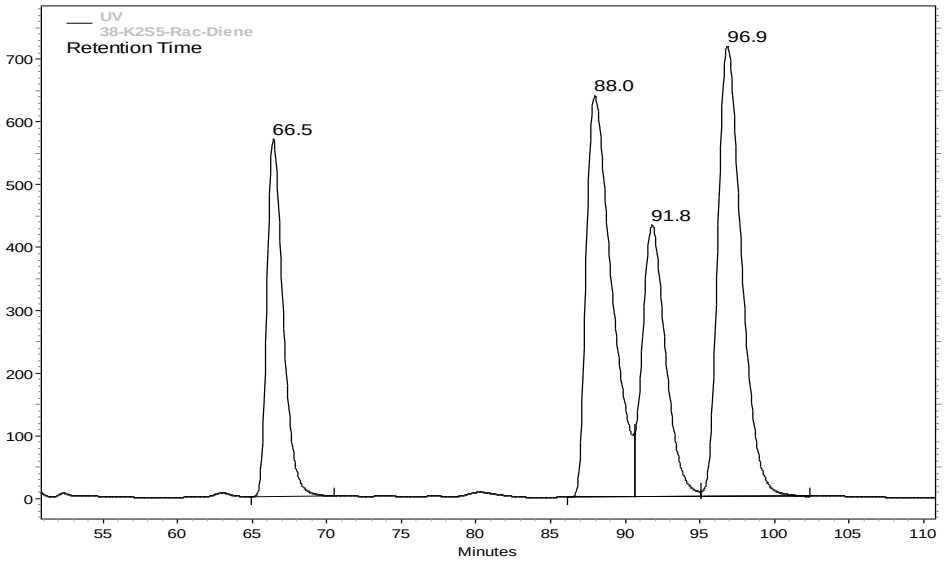
Retention Time	Area	Area %
16.5	28494813	28.682
19.9	21350084	21.490
28.4	28013658	28.197
31.1	21489805	21.631

3aT, Column: 2xODH-Columns connected in series, *n*-hexane/*i*PrOH (85/15), 0.3 mL/min, 213 nm



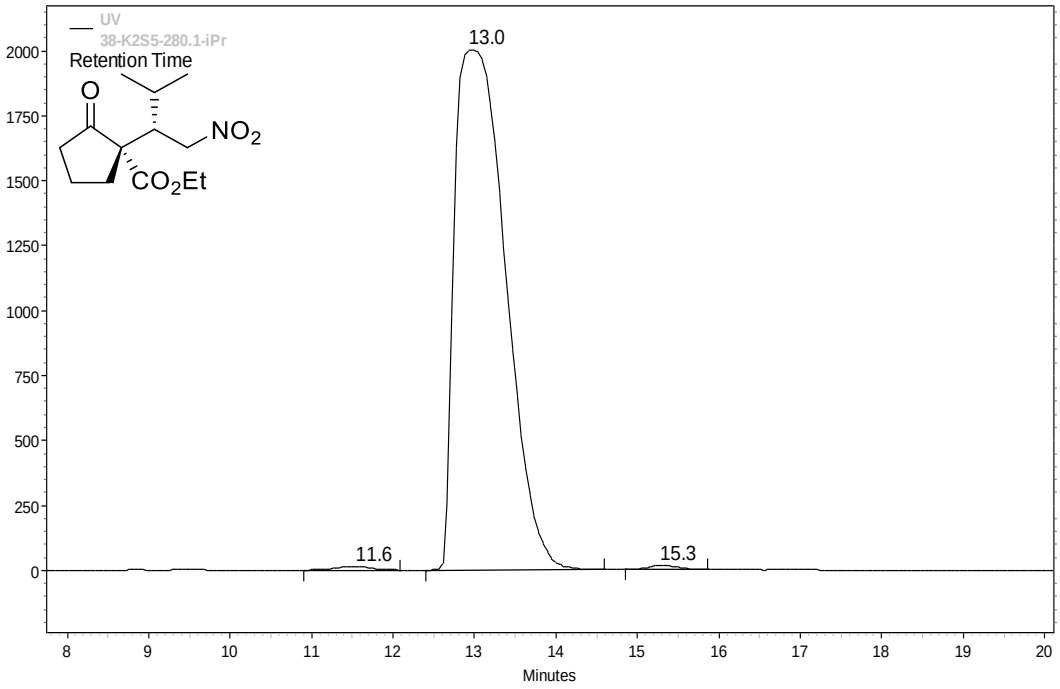
Retention Time	Area	Area %
66.1	4257618	1.379
87.8	10002128	3.239
92.2	265377030	85.929
98.3	29197549	9.454

Racemic:



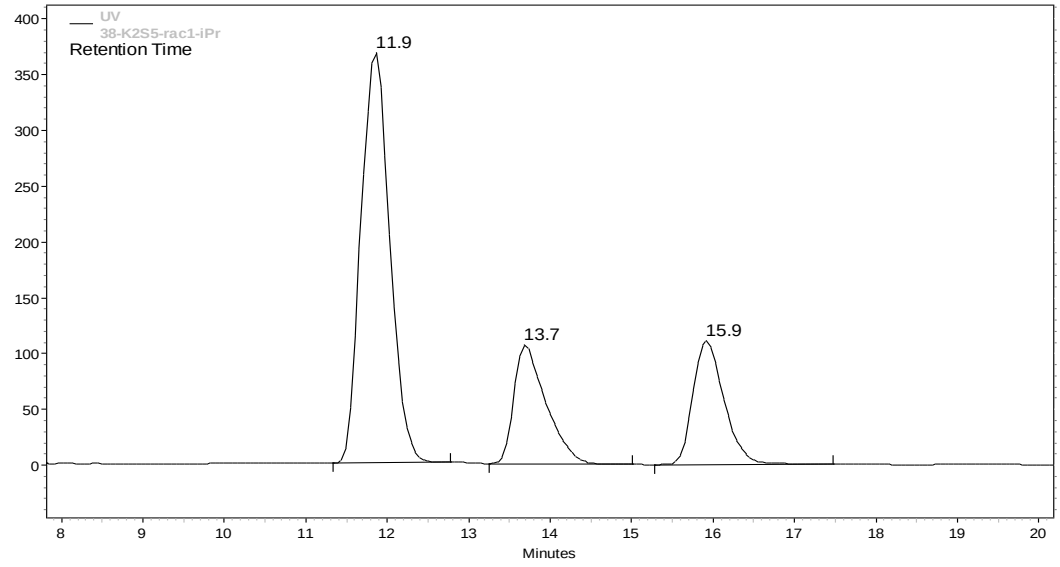
Retention Time	Area	Area %
66.5	172728948	17.541
88.0	304657581	30.938
91.8	188265952	19.119
96.9	319076021	32.402

3aU, Column: ASH, *n*-hexane/*i*PrOH (91/9), 0.7 mL/min, 214 nm



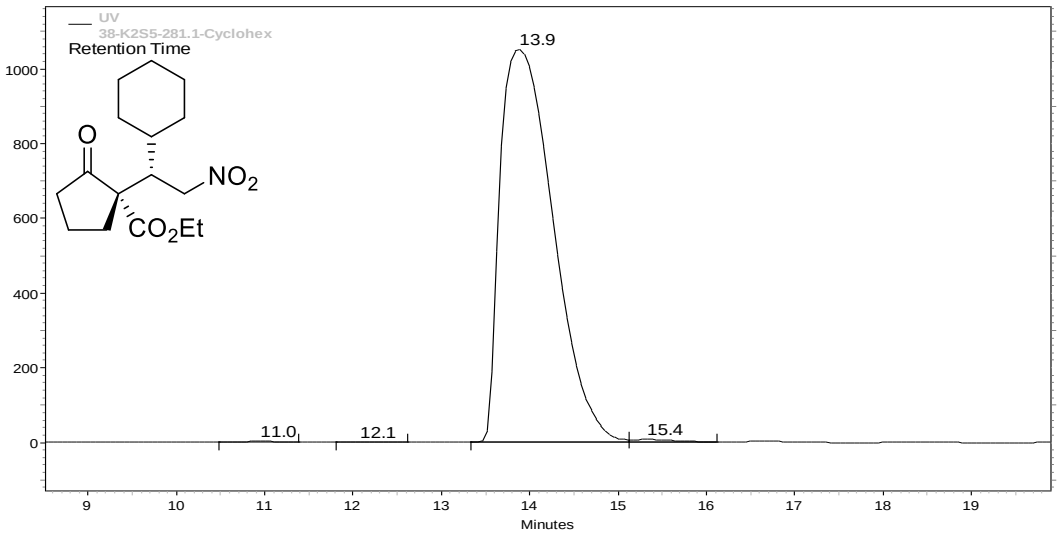
Retention Time	Area	Area %
11.6	1568707	0.448
13.0	347178584	99.099
15.3	1586922	0.453

Racemic:



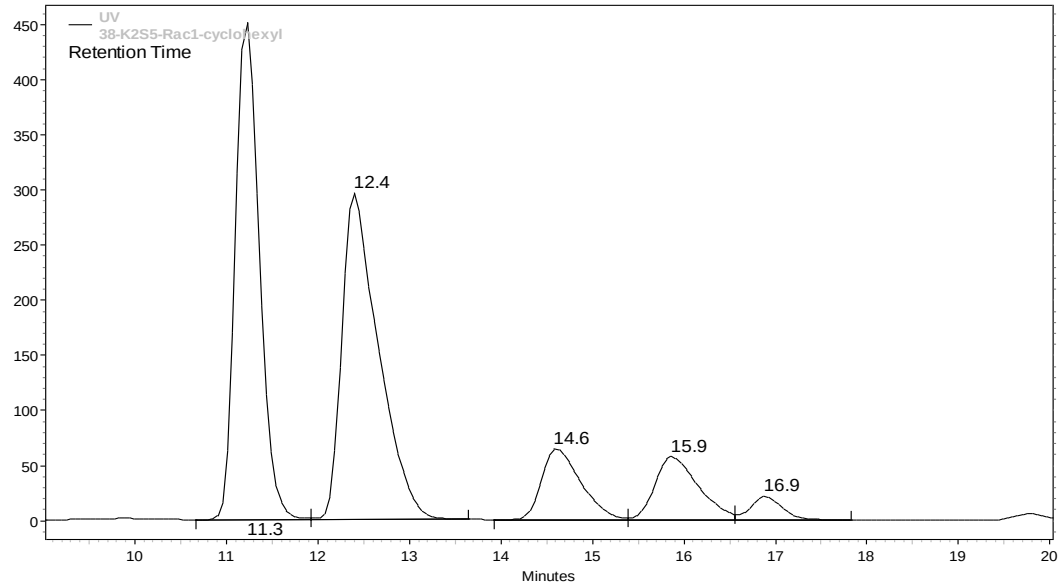
Retention Time	Area	Area %
11.9	36261277	60.814
13.7	11603885	19.461
15.9	11761328	19.725

3aV, Column: ASH, *n*-hexane/*i*PrOH (91/9), 0.7 mL/min, 214 nm



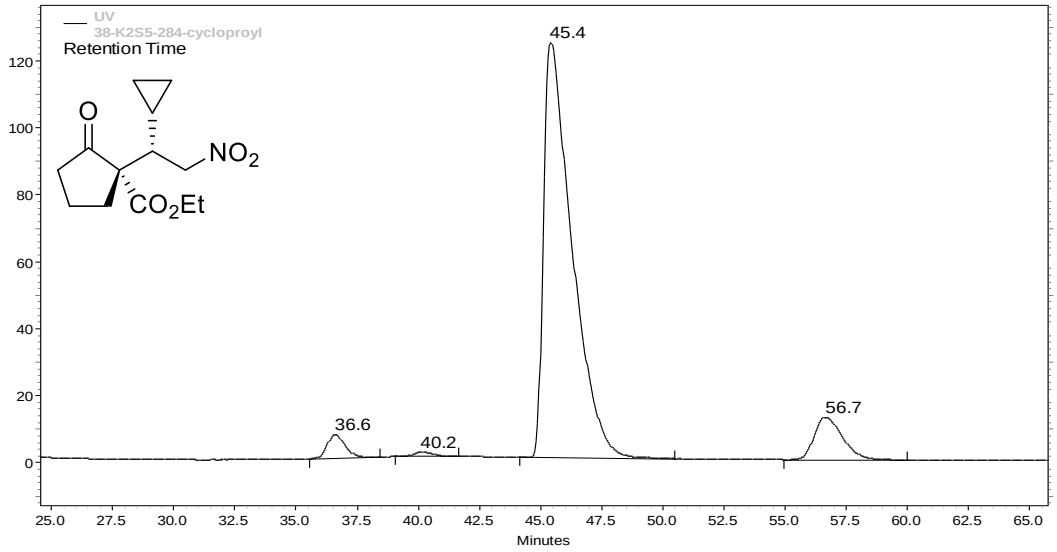
Retention Time	Area	Area %
11.0	296899	0.167
12.1	134864	0.076
13.9	176688596	99.234
15.4	931315	0.523

Racemic:



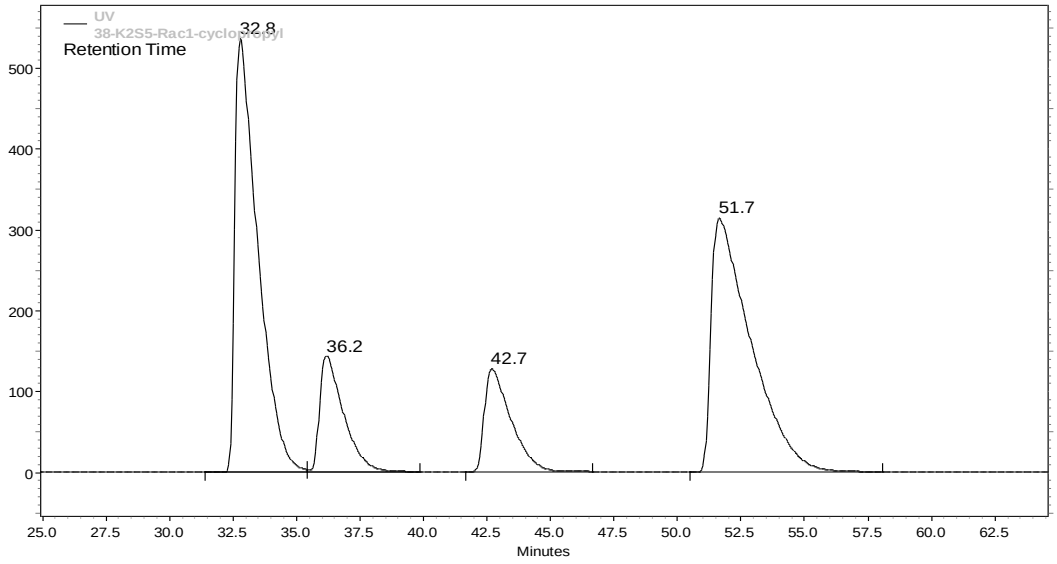
Retention Time	Area	Area %
11.3	32859087	39.515
12.4	33112210	39.819
14.6	7603102	9.143
15.9	7547649	9.076

3aW, Column: ODH, *n*-hexane/*i*PrOH (97/3), 0.5 mL/min, 220 nm



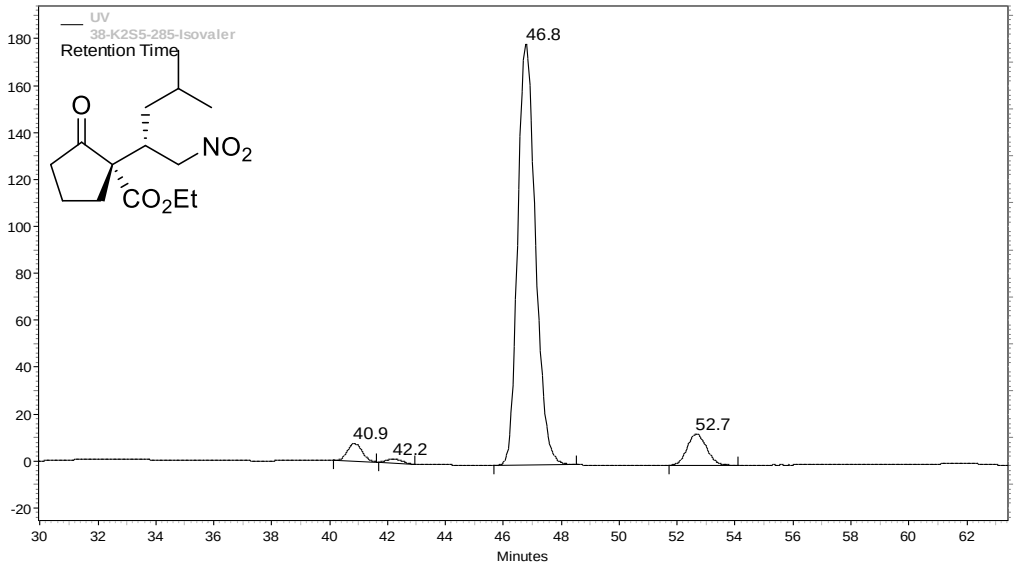
Retention Time	Area	Area %
36.6	1421139	3.109
40.2	302826	0.662
45.4	39925709	87.333
56.7	4067173	8.896

Racemic:



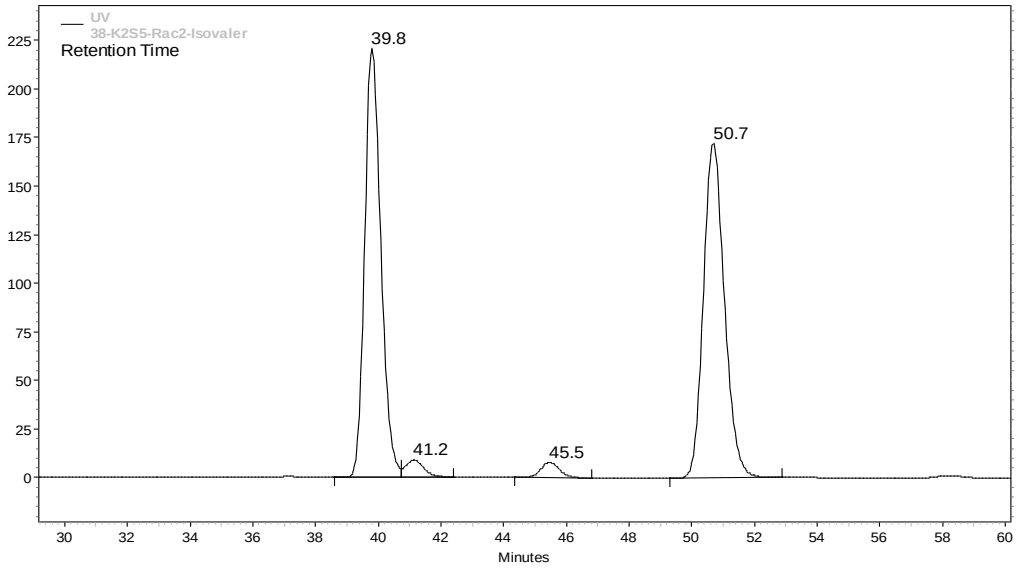
Retention Time	Area	Area %
32.8	134769253	39.085
36.2	37121588	10.766
42.7	36542765	10.598
51.7	136373328	39.551

3aX, 2xODH-Columns connected in series, *n*-hexane/*i*PrOH (90/10), 0.3 mL/min, 214 nm



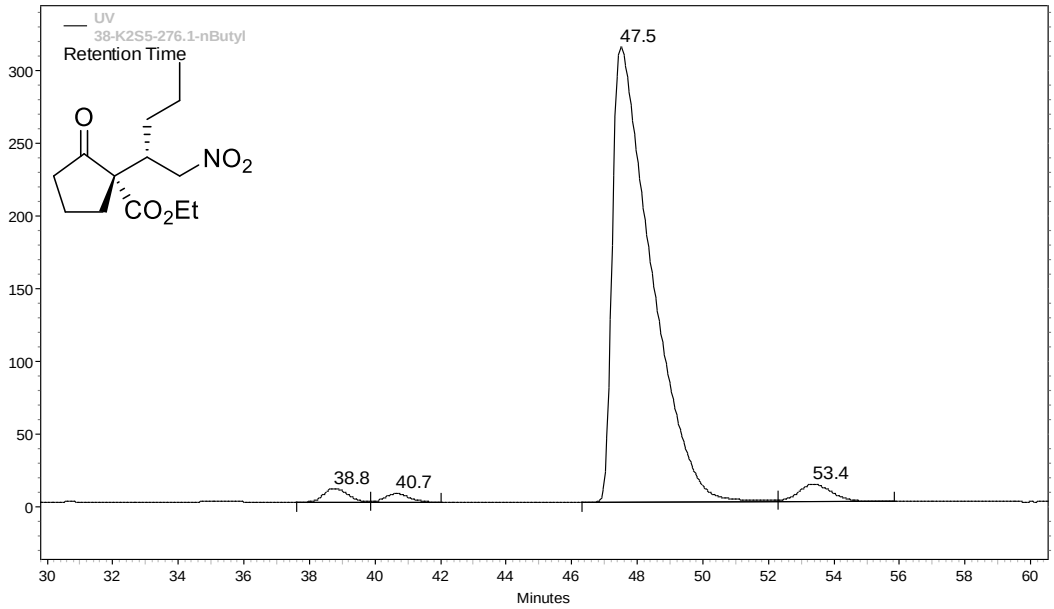
Retention Time	Area	Area %
40.9	1077336	3.120
42.2	231278	0.670
46.8	30759367	89.081
52.7	2461536	7.129

Racemic:



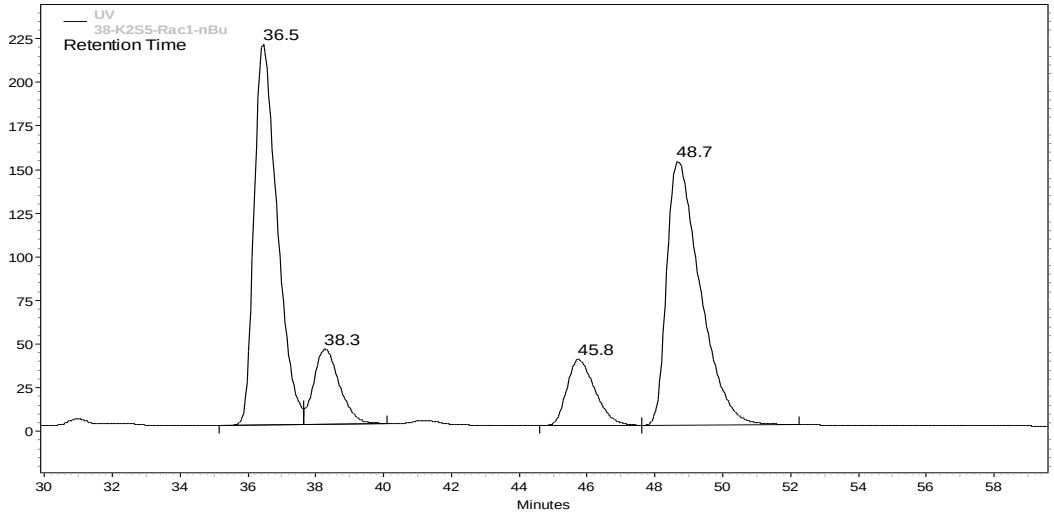
Retention Time	Area	Area %
39.8	31943671	47.842
41.2	1395155	2.090
45.5	1313109	1.967
50.7	32117383	48.102

3aY, Column: ODH, *n*-hexane/*i*PrOH (97/3), 0.3 mL/min, 214 nm



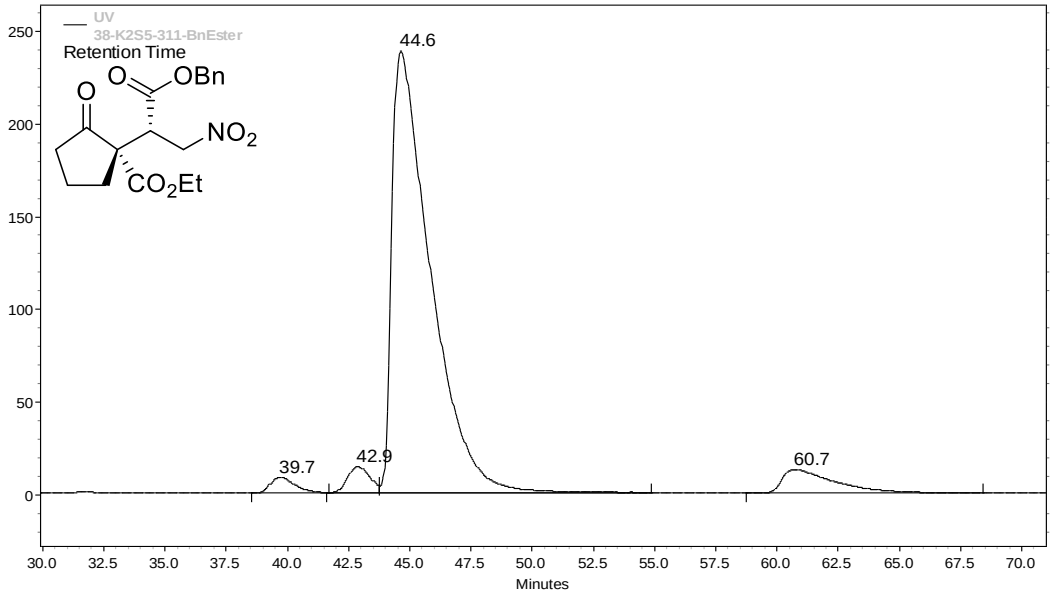
Retention Time	Area	Area %
38.8	1887934	1.719
40.7	1192600	1.086
47.5	103338422	94.075
53.4	3428038	3.121

Racemic:



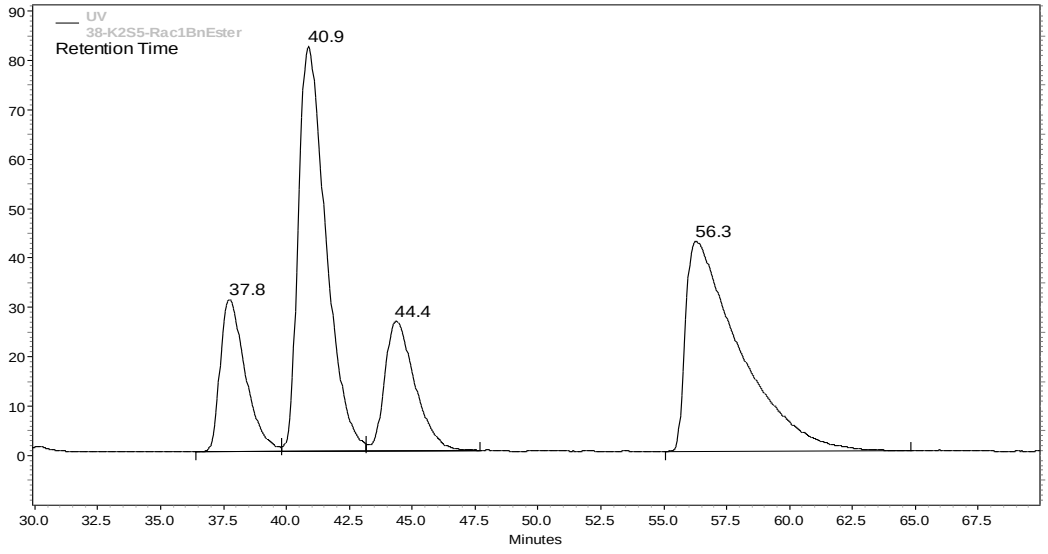
Retention Time	Area	Area %
36.5	41404117	41.164
38.3	9062764	9.010
45.8	8686224	8.636
48.7	41429025	41.189

3aZ, Column: ODH, *n*-hexane/*i*PrOH (95/5), 0.7 mL/min, 214 nm



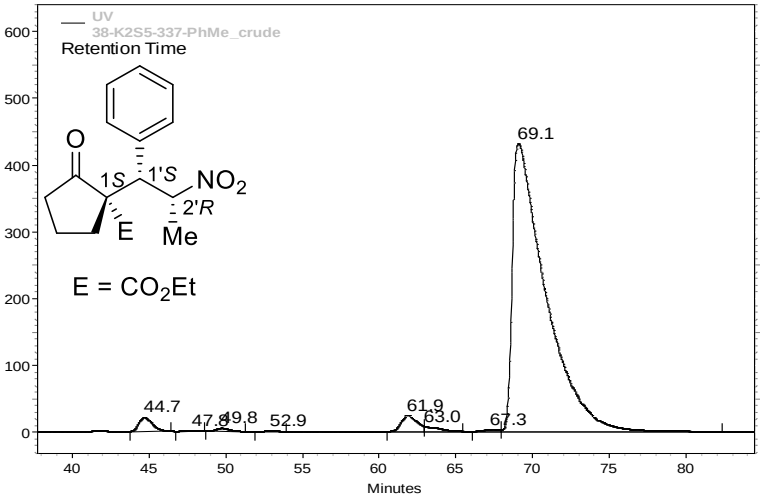
Retention Time	Area	Area %
39.7	2361018	2.001
42.9	3524355	2.987
44.6	104688917	88.716
60.7	7429738	6.296

Racemic:



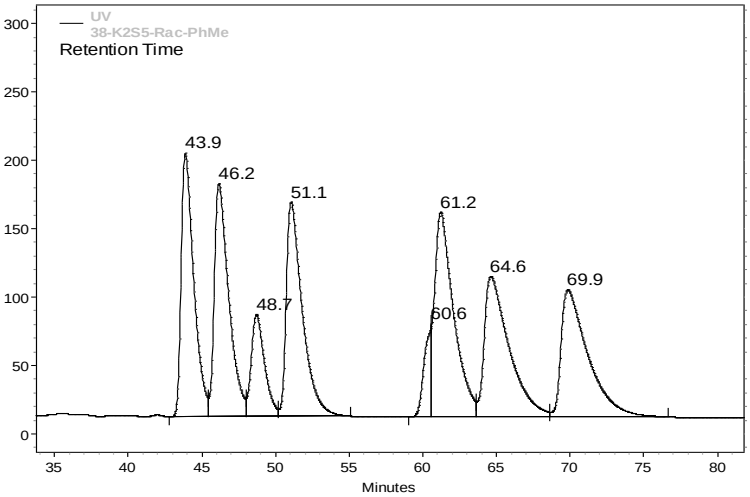
Retention Time	Area	Area %
37.8	8531261	12.602
40.9	25029049	36.971
44.4	8737328	12.906
56.3	25401927	37.522

3aA-Me, Column: IB, *n*-heptane/*i*PrOH (98/2), 0.3 mL/min, 210 nm, *dr* (D1:D2:D3:D4)*:* 94:3:2:1



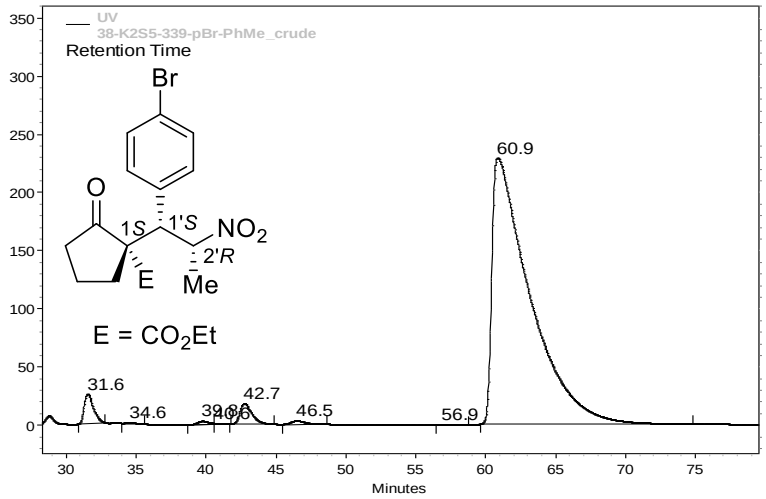
Diasteroemer	Retention Time	Area	Area %
D3	44.7	5158480	1.88
D3	47.8	293326	0.11
D2	49.8	1165160	0.42
D4	52.9	182071	0.07
D2	61.9	7084044	2.58
D4	63.0	1860482	0.68
D1 (1*R*,1'*R* 2'*S*)	67.3	720299	0.26
D1 (1*S*,1'*S*, 2'*R*)	69.1	258039188	94.00

Racemic:



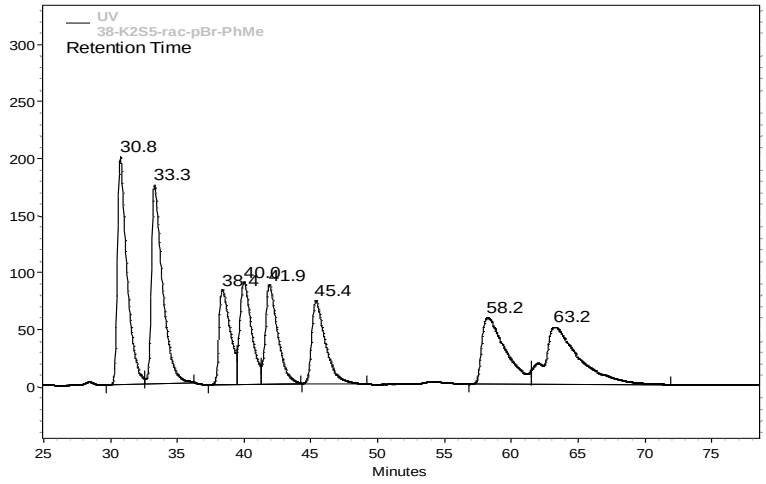
Diasteroemer	Retention Time	Area	Area %
D3	43.9	45364393	14.42
D3	46.2	46536697	14.79
D2	48.7	18639923	5.92
D4	51.1	47049378	14.95
D2	60.6	9341157	2.97
D4	61.2	53785410	17.09
D1 (1*R*,1'*R* 2'*S*)	64.6	47403752	15.06
D1 (1*S*,1'*S*, 2'*R*)	69.9	46577975	14.80

3aB-Me, Column: IB, *n*-heptane/*i*PrOH (98/2), 0.5 mL/min, 210 nm, *dr* (D1:D2:D3:D4)*:* 94:3:2:1



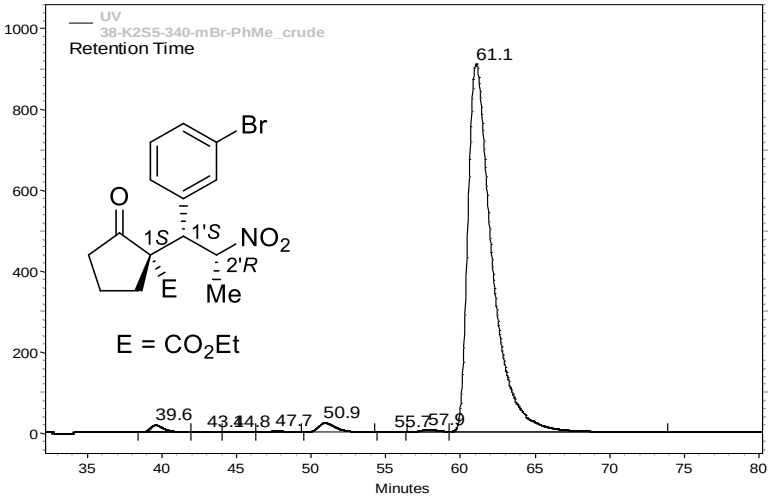
Diastereomer	Retention Time	Area	Area %
D2	31.6	4616552	2.53
D2	34.6	179480	0.10
D4	39.8	603820	0.33
D3	40.6	91902	0.05
D3	42.7	4228622	2.32
D4	46.6	895286	0.49
D1 (1*R*,1'*R* 2'*S*)	56.9	27570	0.02
D1 (1*S*,1'*S*, 2'*R*)	60.9	171937201	94.17

Racemic:



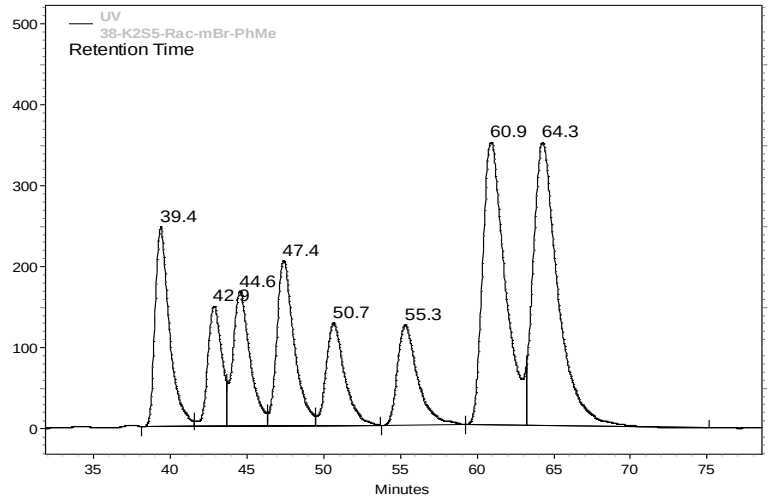
Diastereomer	Retention Time	Area	Area %
D2	30.8	40544282	17.51
D2	33.3	40839276	17.63
D4	38.4	19134108	8.26
D3	34.0	22280337	9.62
D3	41.9	22319279	9.64
D4	45.4	21054095	9.09
D1 (1*R*,1'*R* 2'*S*)	58.2	29096431	12.56
D1 (1*S*,1'*S*, 2'*R*)	63.2	36321463	15.68

3aC-Me, Column: ADH, *n*-heptane/*i*PrOH (97/3), 0.3 mL/min, 210 nm, *dr* (D1:D2:D3:D4)*:* 97:2:1:0.2



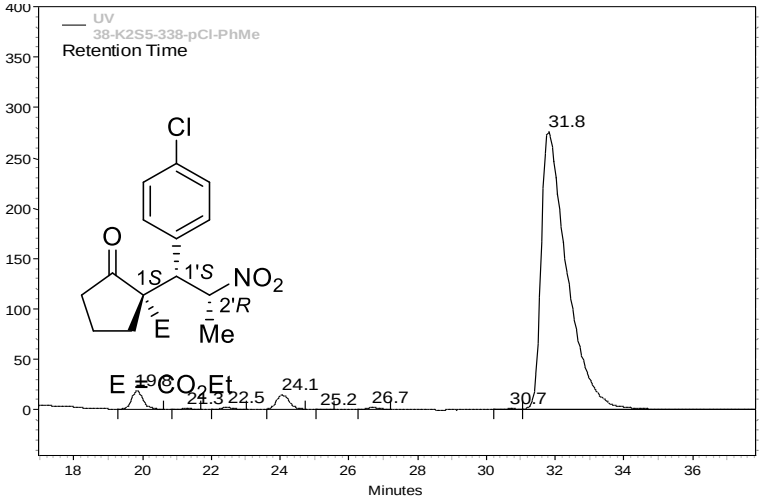
Diastereomer	Retention Time	Area	Area %
D3	39.6	4677800	1.09
D2	43.1	494718	0.12
D4	44.8	561076	0.13
D3	47.7	870391	0.20
D2	50.9	7633546	1.79
D4	55.7	93909	0.02
D1 (1*R*,1'*R* 2'*S*)	57.9	2120124	0.50
D1 (1*S*,1'*S*, 2'*R*)	61.1	410931984	96.15

Racemic:



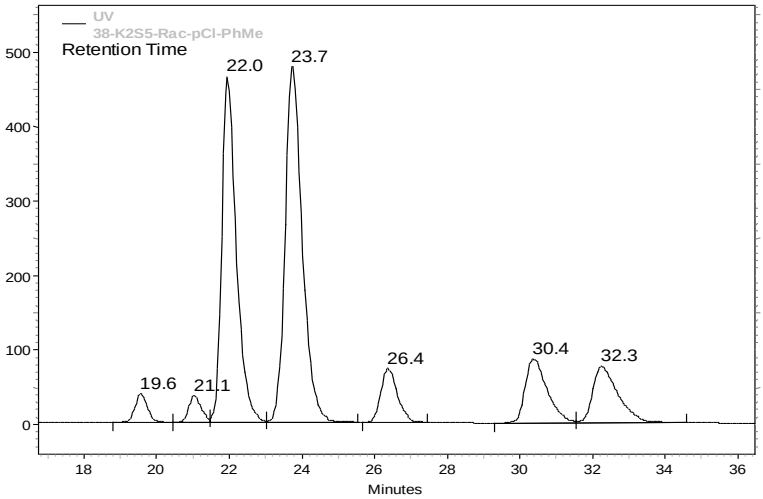
Diastereomer	Retention Time	Area	Area %
D3	39.4	64124237	10.57
D2	42.9	37625158	6.20
D4	44.6	51554322	8.49
D3	47.4	64268476	10.59
D2	50.7	42857466	7.06
D4	55.3	45705306	7.53
D1 (1*R*,1'*R* 2'*S*)	60.9	143770512	23.69
D1 (1*S*,1'*S*, 2'*R*)	64.3	156993971	25.87

3aE-Me, Column: IB, *n*-heptane/*i*PrOH (95/5), 0.3 mL/min, 210 nm, *dr* (D1:D2:D3:D4)*:* 94:3:3:0.4



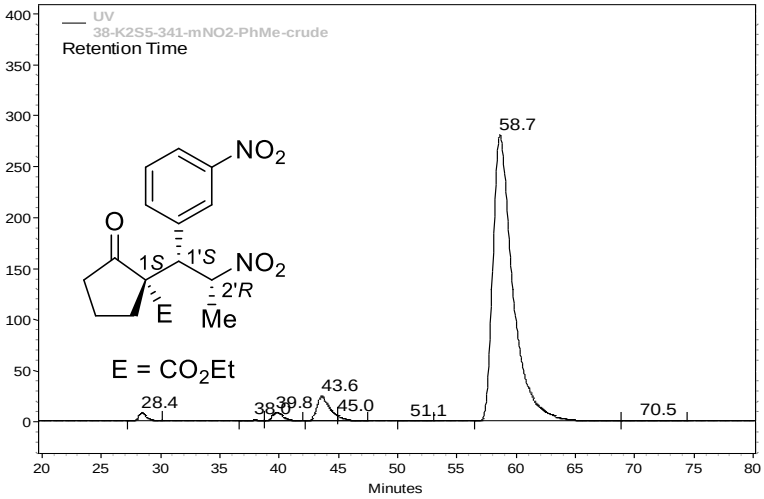
Diastereomer	Retention Time	Area	Area %
D2 (1*S*,1'S 2'*S*)	19.8	1779946	2.84
D2 (1*R*,1'*R*, 2'*R*)	21.3	70790	0.11
D3	22.5	229562	0.37
D3	24.1	1582400	2.52
D4	25.2	6154	0.01
D4	26.7	210488	0.34
D1 (1*R*,1'*R* 2'*S*)	30.7	124266	0.20
D1 (1*S*,1'*S*, 2'*R*)	31.8	58711258	93.62

Racemic:



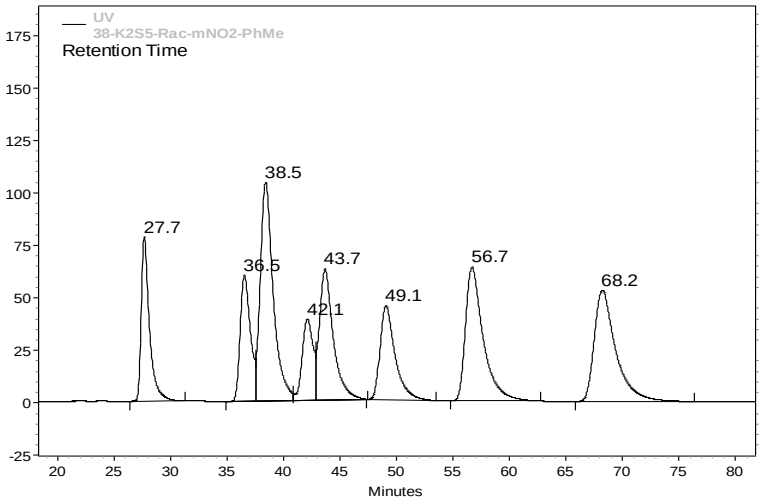
Diastereomer	Retention Time	Area	Area %
D2 (1*S*,1'S 2'*S*)	19.6	3888410	2.41
D2 (1*R*,1'*R*, 2'*R*)	21.1	3579281	2.22
D3	22.0	52228352	32.34
D3 + D4	23.7	62726132	38.84
D4	26.4	9378557	5.81
D1 (1*R*,1'*R* 2'*S*)	30.4	14631829	9.06
D1 (1*S*,1'*S*, 2'*R*)	32.3	15046706	9.32

3al-Me, Column: ADH, *n*-heptane/*i*PrOH (95/5), 0.7 mL/min, 220 nm, *dr* (D1:D2:D3:D4)*:* 92:5:2:1



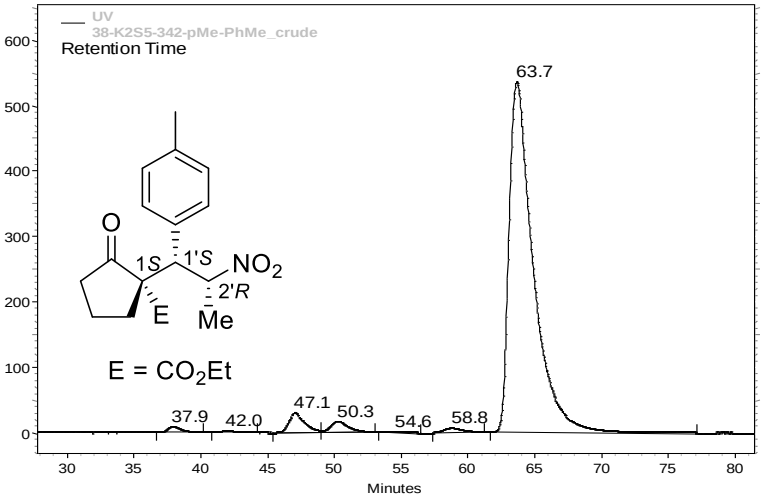
Diastereomer	Retention Time	Area	Area %
D4	28.4	1517130	1.05
D4	38.0	389136	0.27
D3	39.8	2264939	1.57
D2	43.6	7017561	4.88
D3	45.0	885332	0.62
D2	51.1	68266	0.05
D1 (1*S*,1'*S*, 2'*R*)	58.7	131375948	91.35
D1 (1*R*,1'*R* 2'*S*)	70.5	305494	0.21

Racemic:



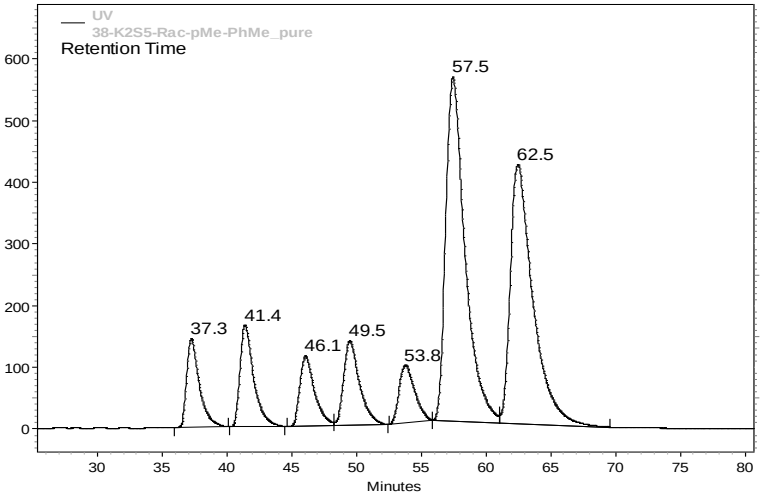
Diastereomer	Retention Time	Area	Area %
D4	27.7	15756445	9.38
D4	36.5	15042786	8.95
D3	38.5	33422375	19.89
D2	42.1	10632508	6.33
D3	43.7	21021615	12.51
D2	49.1	16261459	9.68
D1 (1*S*,1'*S*, 2'*R*)	56.7	27760058	16.52
D1 (1*R*,1'*R* 2'*S*)	68.2	28102240	16.73

3aK-Me, Column: ADH, *n*-heptane/*i*PrOH (98/2), 0.5 mL/min, 210 nm, *dr* (D1:D2:D3:D4)*:* 93:4:2:0.1



Diastereomer	Retention Time	Area	Area %
D2	37.9	2371664	0.82
D3	42.0	676255	0.23
D2	47.1	9629072	3.33
D3	50.3	6036439	2.09
D4	54.6	299967	0.10
D1 (1*R*,1′*R* 2′*S*) + D4	58.8	2494009	0.86
D1 (1*S*,1′*S*, 2′*R*)	63.7	267755287	92.56

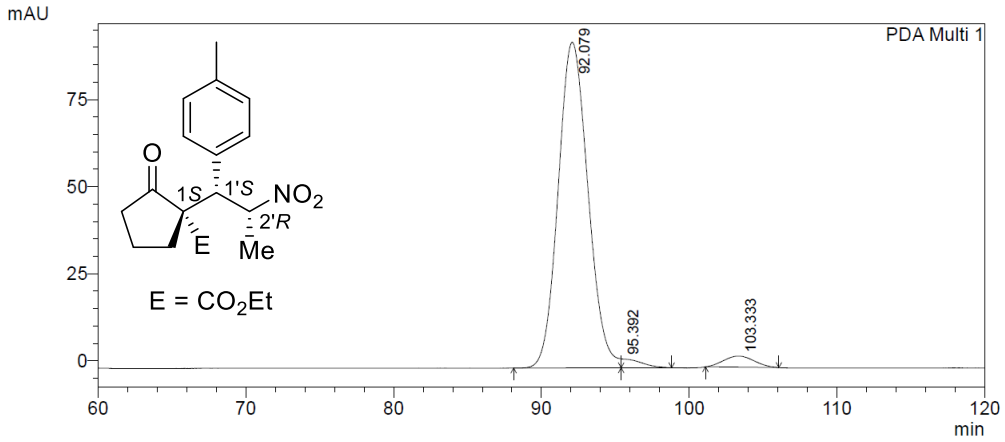
Racemic:



Diastereomer	Retention Time	Area	Area %
D2	37.3	38920184	6.12
D3	41.4	48292313	7.60
D2	46.1	35738361	5.62
D3	49.5	46528172	7.32
D4	53.8	31468096	4.95
D1 (1*R*,1′*R* 2′*S*) + D4	57.5	232056785	36.51
D1 (1*S*,1′*S*, 2′*R*)	62.5	202675029	31.88

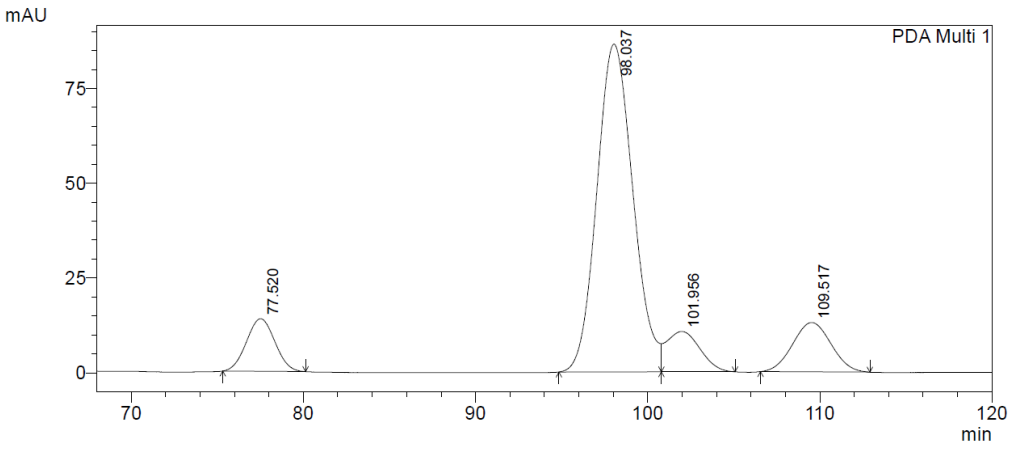
Confirming the *dr* of **3aK-Me** by reversed phase HPLC: Column (performed by Moritz Sinast, University of Stuttgart, Laschat Group): LiChrosorb® RP-18 (150 mm x 4.6 mm), Acetonitril/H_2O (40/60), 0.5 mL/min, 254 nm

Catalytic Reaction:



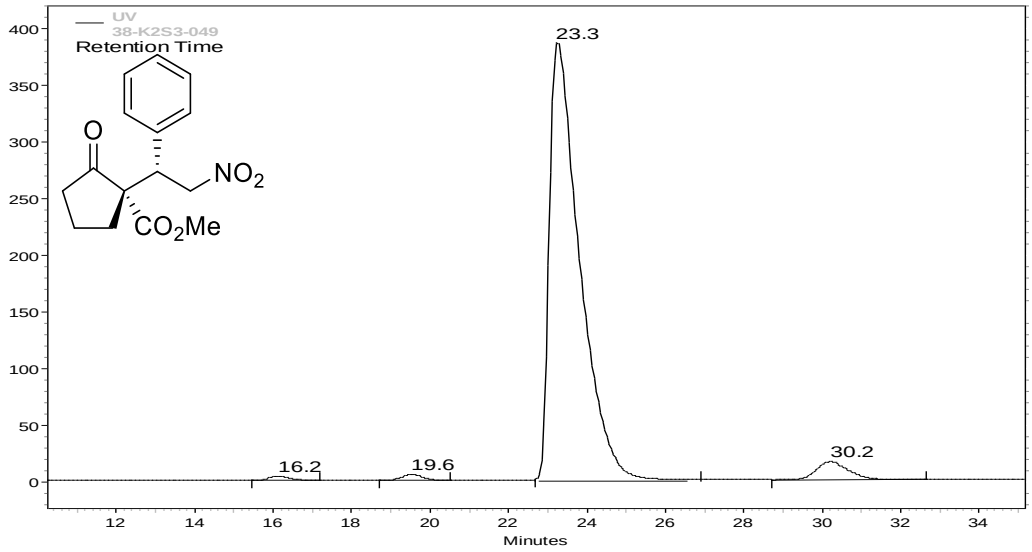
Diastereomer	Retention Time	Area	Area %
D4 (not found)	-	-	-
D1	92.1	13113320	94.960
D3	95.4	235596	1.706
D2	103.3	460394	3.334

Mixture of diastereoemers



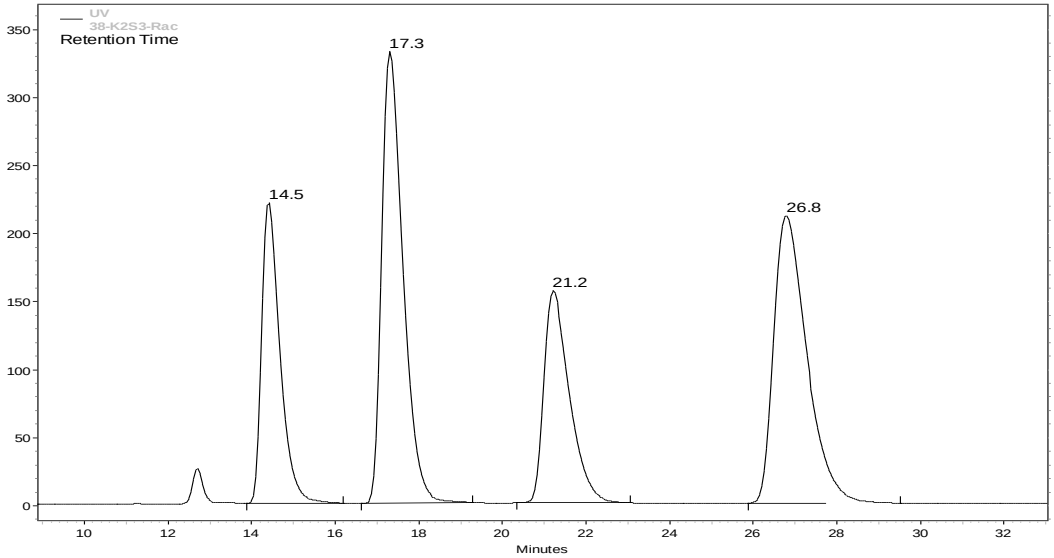
Diastereomer	Retention Time	Area	Area %
D4	77.5	1592754	9.030
D1	98.0	12591604	71.384
D3	102.0	1439914	8.163
D2	109.5	2014983	11.423

3bA, Column: ODH, *n*-hexane/*i*PrOH (90/10), 1.0 mL/min, 214 nm



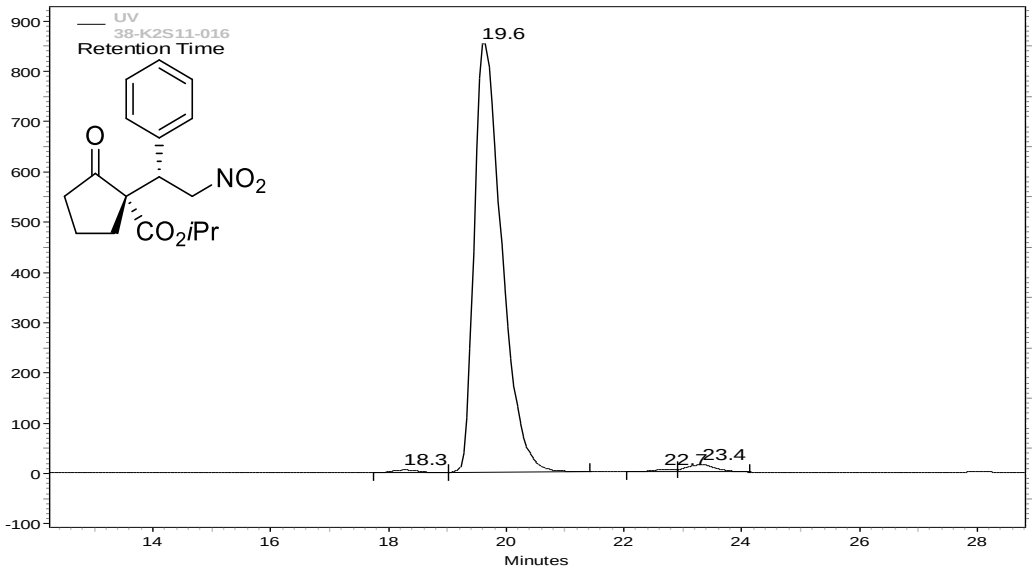
Retention Time	Area	Area %
16.2	525235	0.595
19.6	722493	0.818
23.3	83413435	94.471
30.2	3634382	4.116

Racemic:



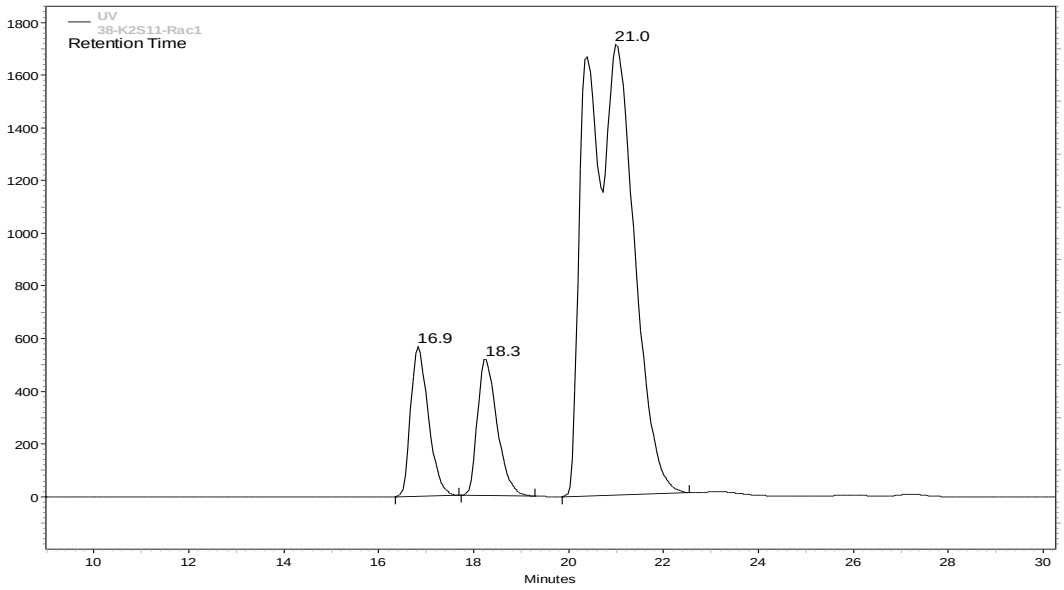
Retention Time	Area	Area %
14.5	26481236	18.183
17.3	46090247	31.647
21.2	26776669	18.386
26.8	46288836	31.784

3cA, Column: ODH, *n*-hexane/*i*PrOH (95/5), 0.3 mL/min, 220 nm



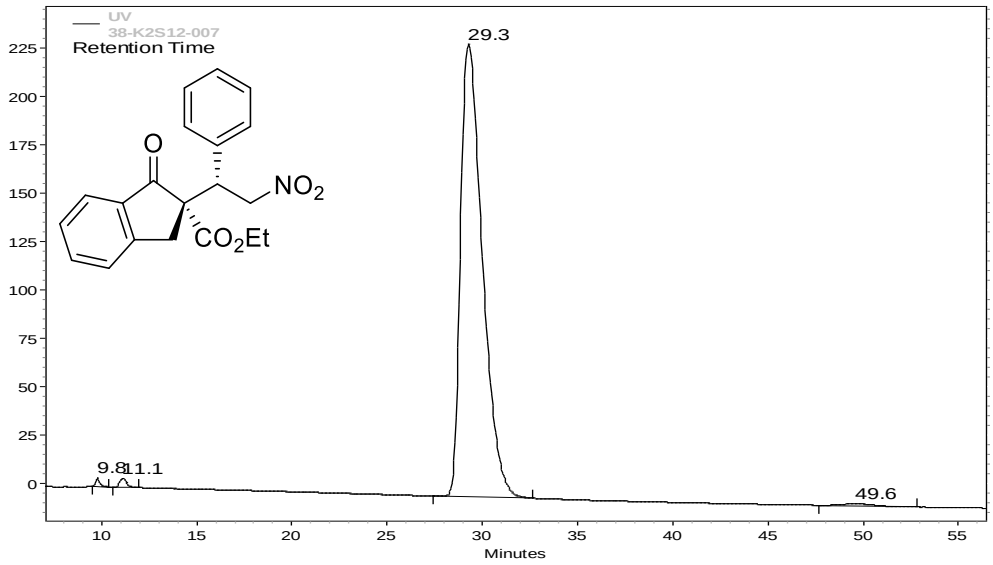
Retention Time	Area	Area %
18.3	529232	0.464
19.6	110884763	97.294
22.7	519506	0.456
23.4	2035139	1.786

Racemic:



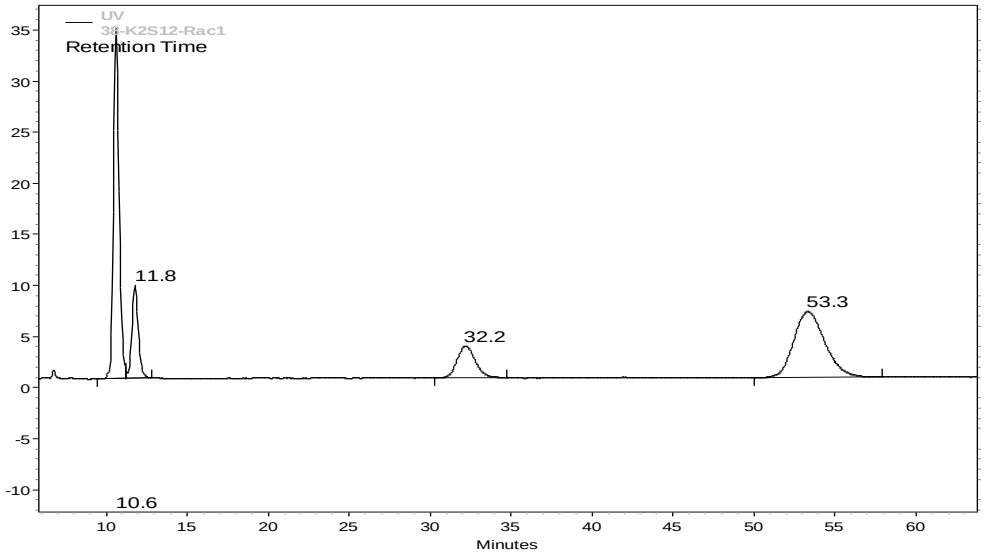
Retention Time	Area	Area %
16.9	59709582	9.960
18.3	60075770	10.021
21.0	479705940	80.019

3dA, Column: ODH, *n*-hexane/*i*PrOH (80/20), 1.0 mL/min, 220 nm



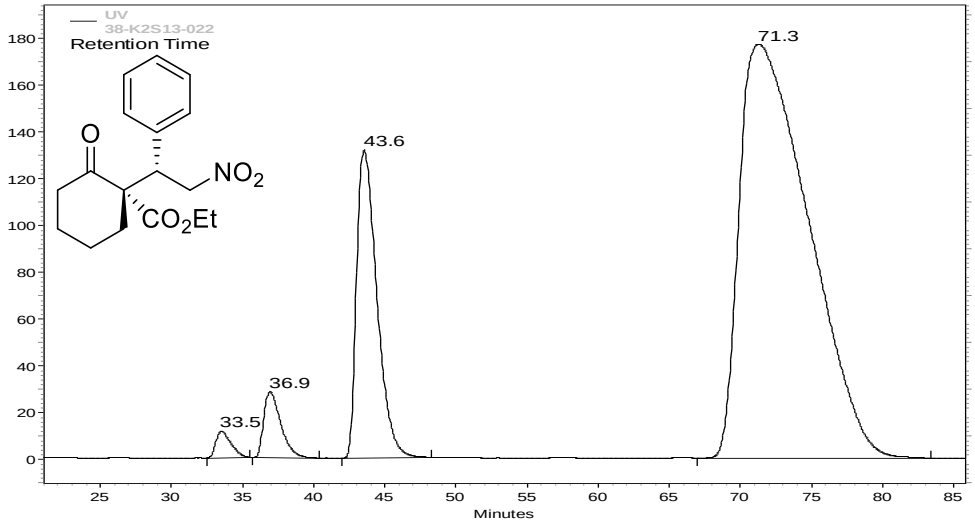
Retention Time	Area	Area %
9.8	266400	0.352
11.1	482120	0.638
29.3	74304622	98.302
49.6	534973	0.708

Racemic:



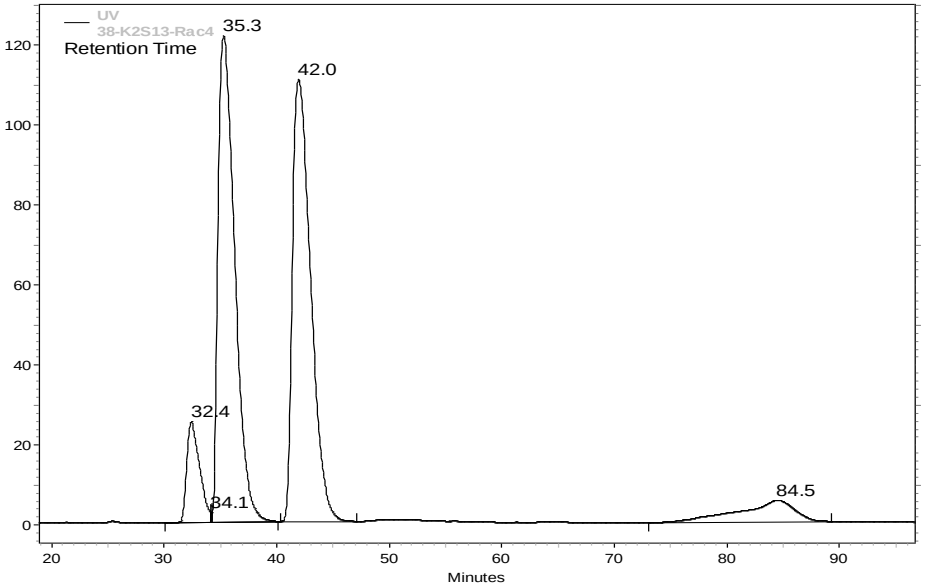
Retention Time	Area	Area %
10.6	3419186	38.670
11.8	1006147	11.379
32.2	982470	11.111
53.3	3434150	38.839

3eA, Column: ASH, *n*-hexane/*i*PrOH (95/5), 0.5 mL/min, 220 nm



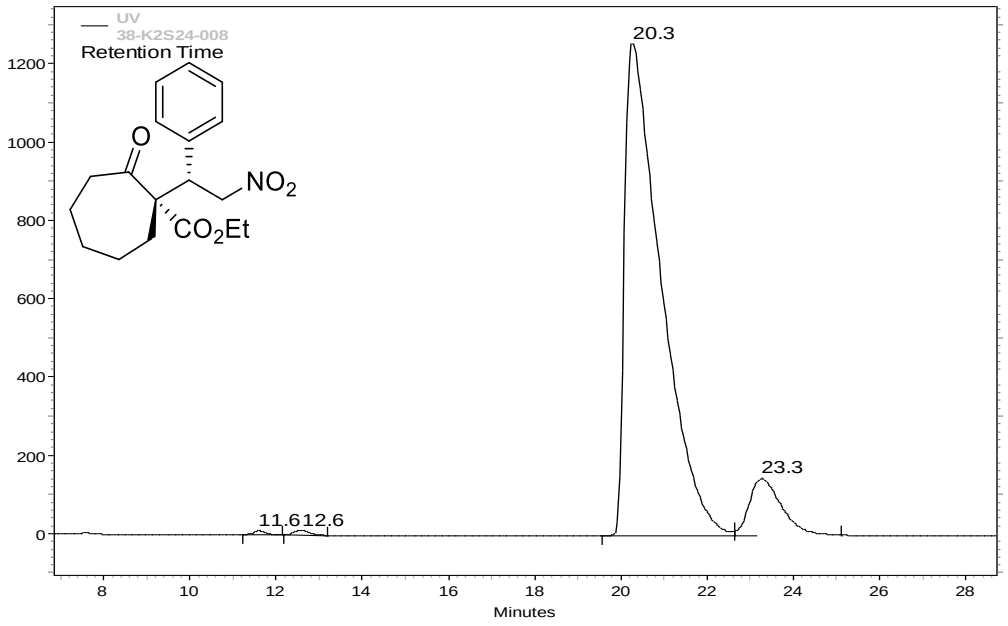
Retention Time	Area	Area %
9.8	266400	0.352
11.1	482120	0.638
29.3	74304622	98.302
49.6	534973	0.708

Racemic:



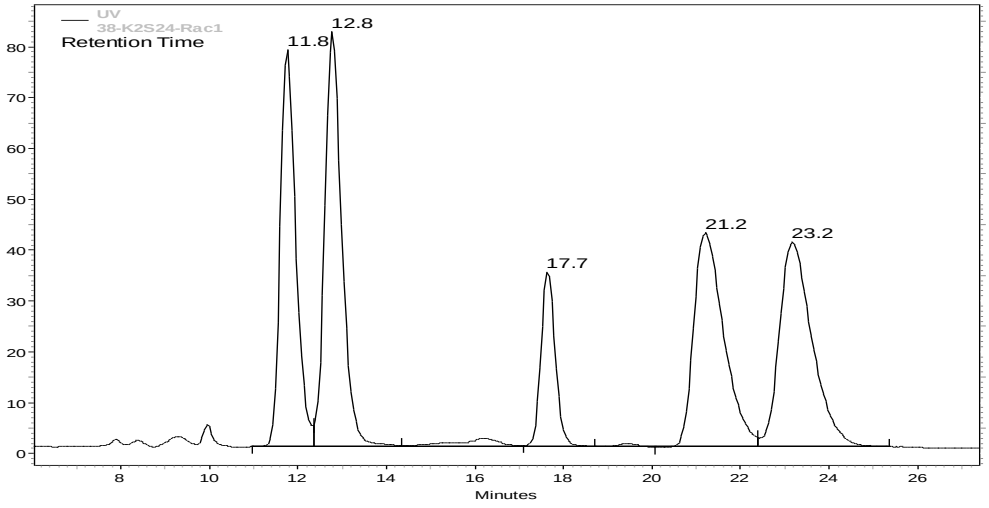
Retention Time	Area	Area %
32.4	7906791	6.860
35.3	49906879	43.298
42.0	49880106	43.275
84.5	7481259	6.491

3fA, Column: ODH, *n*-hexane/*i*PrOH (95/5), 1.0 mL/min, 220 nm



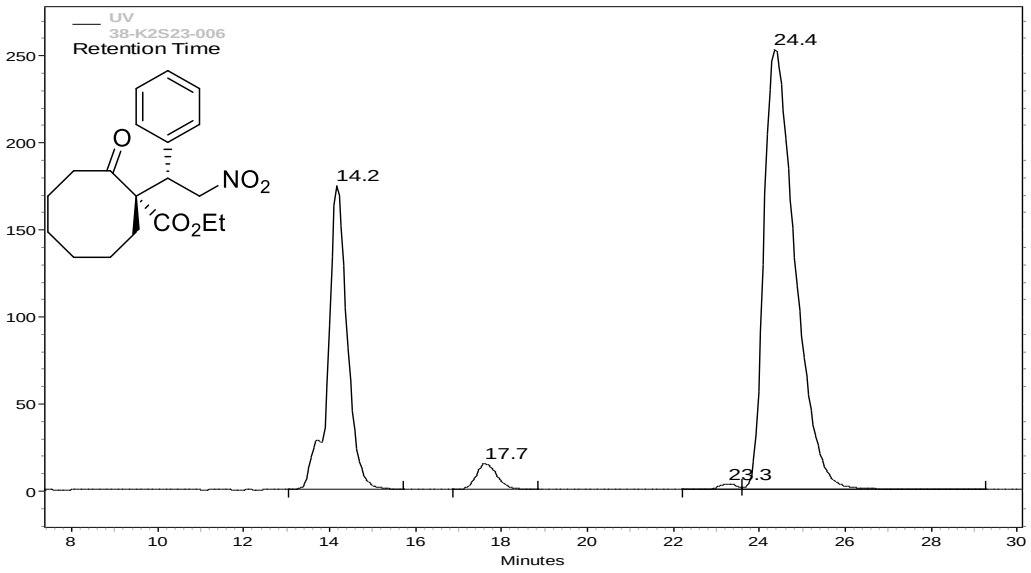
Retention Time	Area	Area %
11.6	948531	0.289
12.6	1229664	0.374
20.3	295890371	90.070
23.3	30443608	9.267

Racemic:



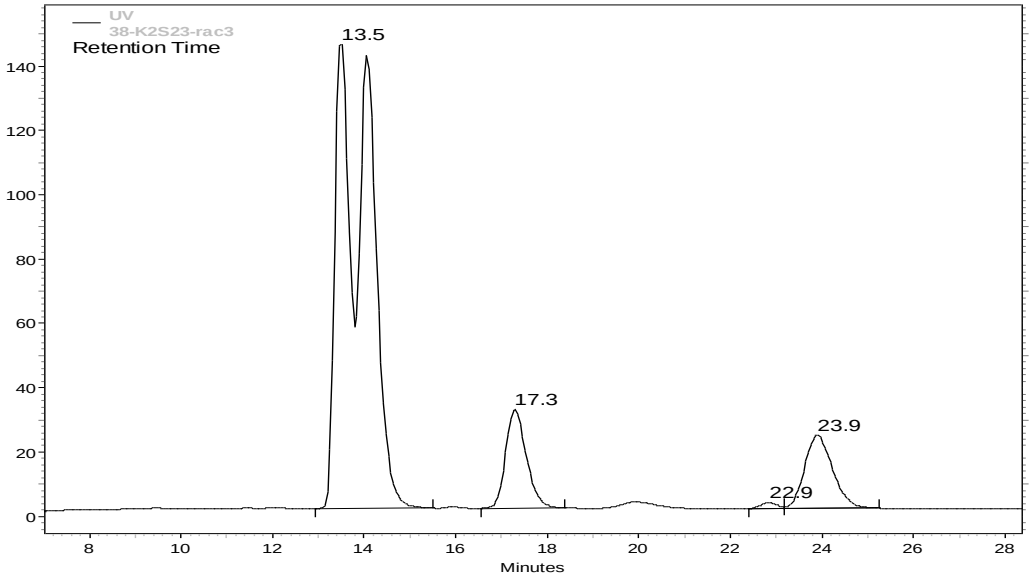
Retention Time	Area	Area %
11.8	7655415	21.314
12.8	8857724	24.662
21.2	7919225	22.049
23.2	8356322	23.266

3gA, Column: ODH, *n*-hexane/*i*PrOH (95/5), 0.7 mL/min, 214 nm



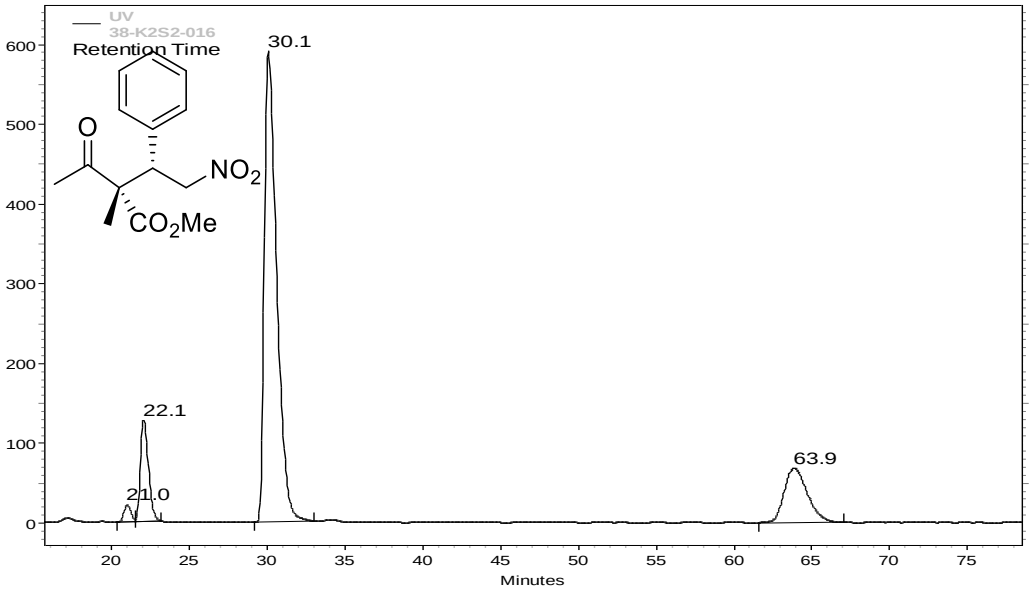
Retention Time	Area	Area %
14.2	21649320	28.932
17.7	1981626	2.648
23.3	349818	0.467
24.4	50847546	67.952

Racemic:



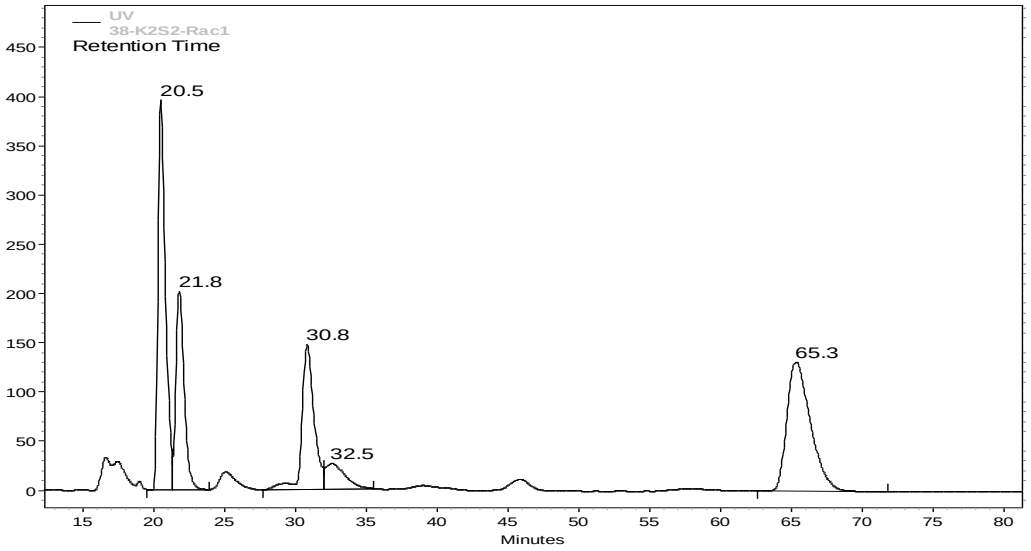
Retention Time	Area	Area %
13.5	28063820	78.036
17.3	3823218	10.631
23.9	3888332	10.812

3hA, Column: ODH, *n*-hexane/*i*PrOH (91/9), 0.7 mL/min, 214 nm



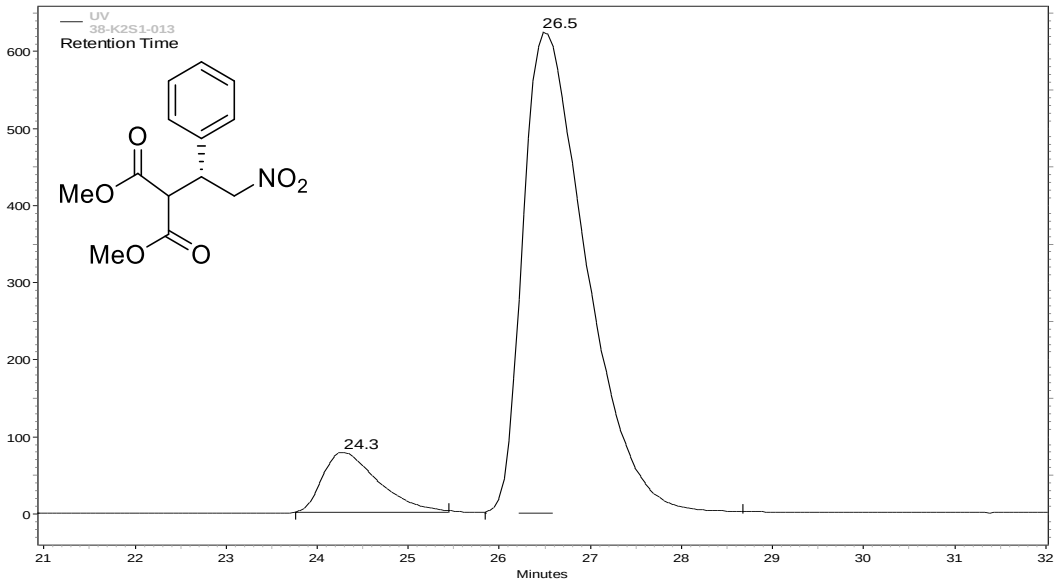
Retention Time	Area	Area %
21.0	2755638	1.521
22.1	18619044	10.278
30.1	131669829	72.683
63.9	28112032	15.518

Racemic:



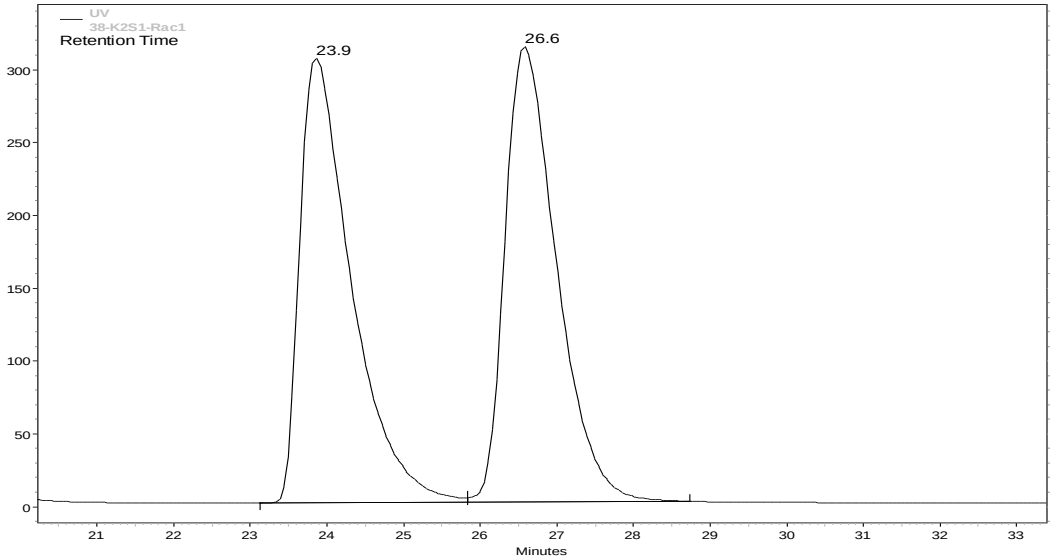
Retention Time	Area	Area %
20.5	58829776	29.825
21.8	32332725	16.392
30.8	35351487	17.922
65.3	61137668	30.995

3iA, Column: ODH, *n*-hexane/*i*PrOH (70/30), 0.5 mL/min, 254 nm



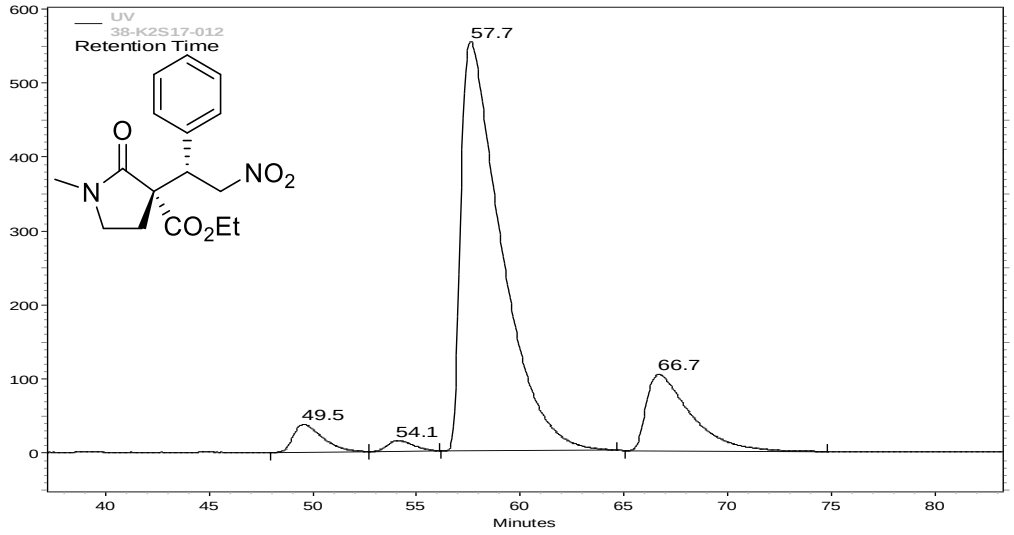
Retention Time	Area	Area %
24.3	13350467	9.898
26.5	121523624	90.102

Racemic:



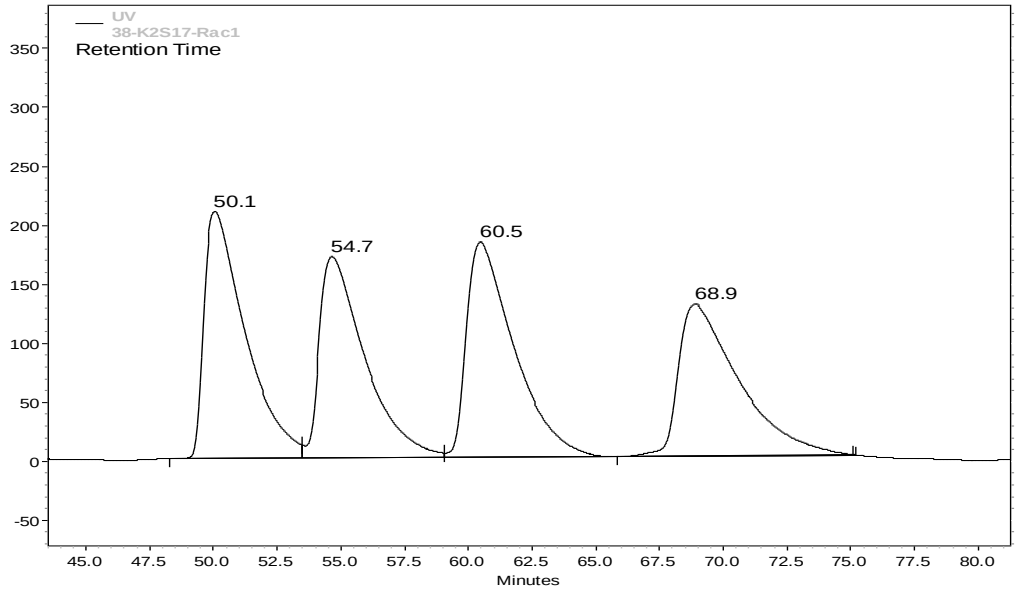
Retention Time	Area	Area %
23.9	57323510	49.453
26.6	58592092	50.547

3jA, Column: ODH, *n*-hexane/*i*PrOH (90/10), 0.5 mL/min, 214 nm



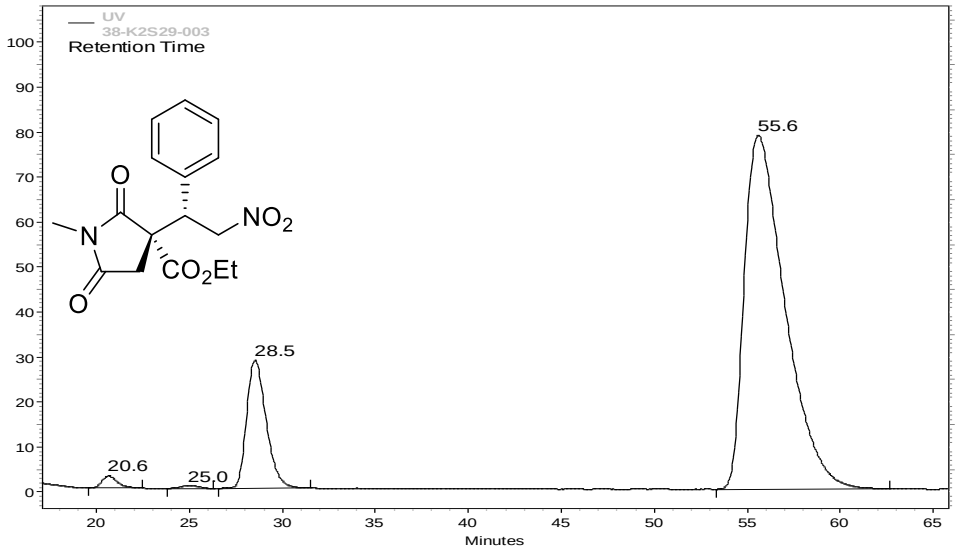
Retention Time	Area	Area %
49.5	14630631	3.853
54.1	5098928	1.343
57.7	298929307	78.723
66.7	61061857	16.081

Racemic:



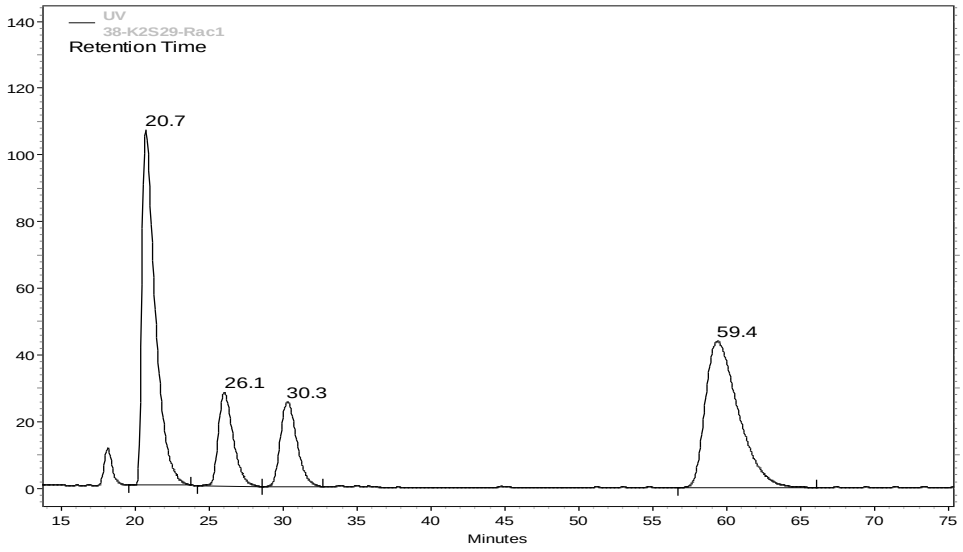
Retention Time	Area	Area %
50.1	94138173	26.369
54.7	83847562	23.486
60.5	94321912	26.420
68.9	84699156	23.725

3kA, Column: ODH, *n*-hexane/*i*PrOH (80/20), 1.0 mL/min, 220 nm



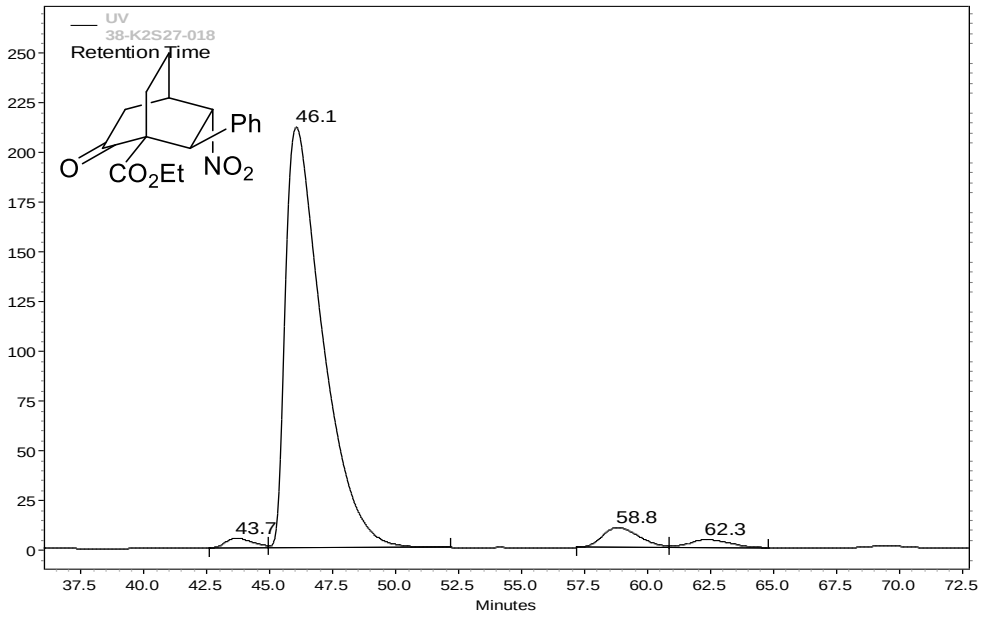
Retention Time	Area	Area %
20.6	596454	1.046
25.0	165302	0.290
28.5	8380907	14.694
55.6	47894271	83.971

Racemic:



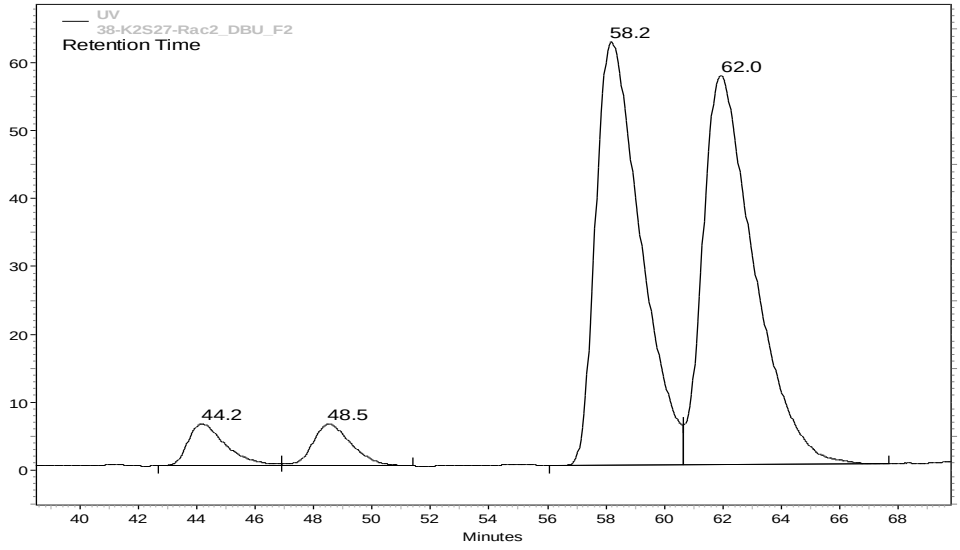
Retention Time	Area	Area %
20.7	26600079	38.309
26.1	7861077	11.321
30.3	7890896	11.364
59.4	27082916	39.005

4-D2, Column: ODH, *n*-hexane/*i*PrOH (95/5), 0.7 mL/min, 220 nm



Retention Time	Area	Area %
43.7	1515659	1.605
46.1	87093834	92.210
58.8	4082161	4.322
62.3	1760172	1.864

Racemic



Retention Time	Area	Area %
44.2	2222275	3.743
48.5	2266339	3.817
58.2	26837210	45.205
62.0	28042536	47.235

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