Supplementary Information for

Asymmetric Photocatalytic C-H Functionalization of Toluene and Derivatives

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A. General Information

The NMR spectra were recorded at 400 MHz and 500 MHz for ^{1}H, at 101 MHz and 125.8 MHz for ^{13}C, at 376 MHz for ^{19}F and at 47 MHz for ^{11}B. The chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvents ($CHCl_3$ @ 7.26 ppm ^{1}H NMR, 77.00 ppm ^{13}C NMR). Coupling constants are given in Hz and are quoted to the nearest 0.5 Hz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet; br s, broad signal;, app t, apparent triplet.

High-resolution mass spectra (HRMS) were obtained from the ICIQ High Resolution Mass Spectrometry Unit on MicroTOF Focus and Maxis Impact (Bruker Daltonics) with electrospray ionizationOptical rotations were measured on a Polarimeter Jasco P-1030 and are reported as follows: $[\alpha]_D$ rt (c in g per 100 mL, solvent).

*The authors are indebted to the team of the Research Support Area at ICIQ, particularly to the NMR and the High Resolution Mass Spectrometry Units. Grace Fox is thanked for proofreading the manuscript. The authors are grateful to Pablo Bonilla for the synthesis and provision of the organic catalyst (S)-**B**.*

General Procedures. All reactions were set up under an argon atmosphere in oven-dried glassware using standard Schlenk techniques, unless otherwise stated. Synthesis grade solvents were used as purchased. Anhydrous solvents were taken from a commercial SPS solvent dispenser. Chromatographic purification of products was accomplished using force-flow chromatography (FC) on silica gel (35-70 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used, using UV light as the visualizing agent and either phosphomolybdic acid in EtOH or basic aqueous potassium permangante ($KMnO_4$), and heat as developing agents. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator (in vacuo at 40 ºC, ~5 mbar).

Determination of Diastereomeric Ratio. The diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture through integration of diagnostic signals.

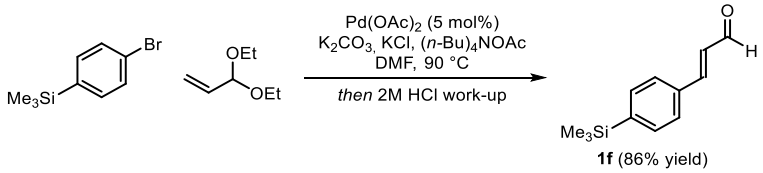
Determination of Enantiomeric Purity: HPLC analysis on chiral stationary phase was performed on an Agilient 1200 series HPLC, using a Daicel Chiralpak IC-3 column with *i*-PrOH:hexane as the eluent. UPC^2 analysis on chiral stationary phase was performed on an Waters Acquity instrument using a CEL1, ID3 or IE3 chiral colums. The exact conditions for the analyses are specified within the characterization section. HPLC/UPC^2 traces were compared to racemic samples prepared by running the reactions in the presence of a catalytic amount (20 mol%) of racemic catalyst **A**. This was prepared by mixing equimolar amounts of amine catalysts (*S*)-**A** and its enantiomer (*R*)-**A**, both synthetized according to literature procedures.[1,2]

Materials: Commercial grade reagents and solvents were purchased at the highest commercial quality from Sigma Aldrich, Fluka, Acros Organics, Tokyo Chemical Industry, Fluorochem or Alfa Aesar and used as received, unless otherwise stated. Organic catalysts (*S*)-**A**, (*R*)-**A** and (*S*)-**B** were synthesized according to previously reported procedures.[1,2] The majority of enals **1** and toluene derivatives are commercially available. Cinnamaldehyde **1a** was distilled prior to use. Enals **1d** and **1e** were prepared according to the literature procedure,[2] whereas the synthetic procedures for

compounds **1f**, **1g**, **3** and for the benzylic derivatives employed in the synthesis of products **2m** and **2q** are reported in section B of the Supporting Information.

B. Substrate Synthesis

Synthesis of (*E*)-3-(4-(trimethylsilyl)phenyl)acrylaldehyde (1f):



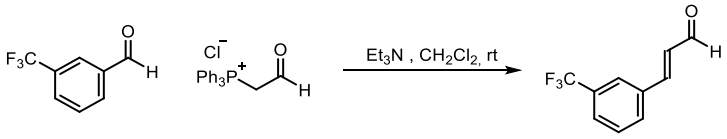
1f (86% yield)

Compound **1f** was prepared according to a reported literature procedure.[2] An oven-dried two-necked flask, fitted with a condenser, was charged with $Pd(OAc)_2$ (29.0 mg, 131 μmol), K_2CO_3 (905 mg, 6.54 mmol), KCl (325 mg, 4.36 mmol), $(n\text{-}Bu)_4NOAc$ (2.63 g, 8.73 mmol), (4-bromophenyl)trimethylsilane (853 μL, 4.36 mmol) and 3,3-diethoxyprop-1-ene (2.00 mL, 13.1 mmol) in anhydorus DMF (45 mL). The resulting mixture was heated to 90 ºC and stirred for 18 hours. The reaction was allowed to cool to room temperature and quenched by dropwise addition of 2M *aq.* HCl solution (30 mL). The resulting mixture was stirred at room temperature for further 15 minutes. Water (100 mL) was added and the crude mixture was extracted with Et_2O (3 x 150 mL). The organic phase were collected, dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification of the crude material by column chromatography on silica gel (gradient from 5% EtOAc in hexane to 10% EtOAc in hexane) gave product **1f** (766 mg, 86% yield) as an off-white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.73 (d, *J* = 7.5 Hz, 1H), 7.65 – 7.43 (m, 5H), 6.76 (dd, *J* = 16.0, 7.5 Hz, 1H), 0.31 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.8, 152.9, 145.2, 134.2, 134.0, 128.7, 127.6, -1.3.

Synthesis of (*E*)-3-(3-(trifluoromethyl)phenyl)acrylaldehyde (1g):



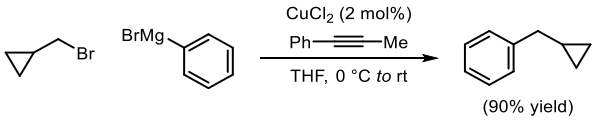
1g (30% yield)

Compound **1g** was prepared according to a reported literature procedure.[2] To a solution of (formylmethyl)triphenylphosphonium chloride (3.55 g, 10.4 mmol) in anhydrous CH_2Cl_2 (50 mL) was added Et_3N (2.18 mL, 15.6 mmol) and, succesively, 3-(trifluoromethyl)benzaldehyde (1.39 mL, 10.4 mmol) dropwise. The reaction was stirred for 48 hours at room temperature and, then, concentrated under reduced pressure. Purification of the crude material by column chromatography on silica gel (gradient from 5% EtOAc in hexane to 10% EtOAc in hexane) gave product **1g** (630 mg, 30% yield) as a yellow oil. The spectroscopic properties of this compound were consistent with the data available in the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.77 (d, *J* = 7.5 Hz, 1H), 7.83 (br. s, 1H), 7.78 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.60 (dd, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 16.0 Hz, 1H), 6.80 (dd, *J* = 16.0, 7.5 Hz, 1H).

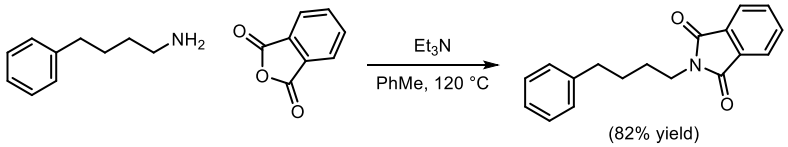
^{13}C NMR (101 MHz, $CDCl_3$): δ 193.1, 150.3, 134.8, 131.8 (q, $^2J_{C\text{-}F}$ = 33.0 Hz), 131.2 (q, $^4J_{C\text{-}F}$ = 1.5 Hz), 130.0, 129.7, 127.6 (q, $^3J_{C\text{-}F}$ = 3.5 Hz), 125.2 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 123.6 (q, $^1J_{C\text{-}F}$ = 272.5 Hz).
^{19}F NMR (376 MHz, $CDCl_3$): δ -63.09 (s, 3F).

Synthesis of (cyclopropylmethyl)benzene:



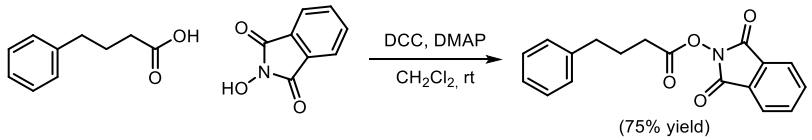
This compound was prepared according to a reported literature procedure.[4] To a mixture of (bromomethyl)cyclopropane (1.94 mL, 20.0 mmol), $CuCl_2$ (54.0 mg, 0.40 mmol) and 1-phenyl-1-propyne (0.25 mL, 2.00 mmol) in anhydorus THF (25 mL) at 0 °C was added a 3M solution of phenylmagnesium bromide (10.0 mL, 30.0 mmol) in Et_2O. The mixture was stirred at 0 °C for 20 minutes, then, warmed up to room temperature and stirred overnight. The reaction was quenched by slow addition of 1M *aq.* HCl solution (25 mL) and *sat. aq.* NH_4Cl solution (25 mL). The resulting mixture was extracted with Et_2O (3 x 100 mL). The organic phase were collected, dried over Na_2SO_4 and the solvent was removed under reduced pressure to deliver the crude material. Purification by column chromatography on silica gel (hexane) provided the desired copuling product (2.38 g, 90% yield) as a colourless liquid. The spectroscopic properties of this compound were consistent with the data available in the literature.[5]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.31 (m, 4H), 7.32 – 7.23 (m, 1H), 2.63 (d, *J* = 7.0 Hz, 2H), 1.14 – 1.01 (m, 1H), 0.63 – 0.58 (m, 2H), 0.38 – 0.21 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 142.2, 128.4, 128.3, 125.9, 40.4, 11.9, 4.7.

Synthesis of 2-(4-phenylbutyl)isoindoline-1,3-dione:



A solution of 4-phenylbutylamine (0.79 mL, 5.00 mmol), phthalic anhydride (741 mg, 5.00 mmol) and triethylamine (2.79 mL, 20.0 mmol) in toluene (50 mL) was refluxed (120 °C) with a Dean–Stark apparatus for 16 hours. The reaction mixture was allowed to cool down to room temperature and concentrated under reduced pressure. The residue was re-dissolved in EtOAc (50 mL) and washed, first, with *sat. aq.* $NaHCO_3$ solution (2 x 25 mL) and, then, with water (25 mL). The organic phase were combined, dried over Na_2SO_4 and the solvent was removed *in vacuo*. Purification by column chromatography on silica gel support (*gradient from* hexane *to* 20% EtOAc in hexane) gave the desired amide (1.14 g, 82% yield) as a colourless solid. The spectroscopic properties of this compound were consistent with the data available in the literature.[6]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.35 – 7.24 (m, 2H), 7.23 – 7.13 (m, 3H), 3.74 (t, *J* = 7.0 Hz, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 1.82 – 1.62 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 168.4, 142.0, 133.9, 132.2, 128.4, 128.3, 125.8, 123.2, 37.8, 35.4, 28.6, 28.2.

Synthesis of 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate:

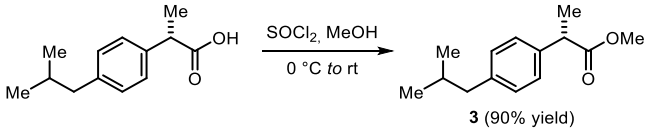


This compound was prepared according to a reported literature procedure.[7] To a stirring solution of 4-phenylbutirric acid (1.07 g, 6.50 mmol), *N*-hydroxyphthalimide (1.17 g, 7.15 mmol) and DMAP (79.0 mg, 0.65 mmol) in CH_2Cl_2 (30 mL) was added DCC (1.48 g, 7.15 mmol). The reaction was stirred at room temperature for 6 hours and then placed in a freezer at -20 °C for 2 hours observing the precipitation of the urea by-product, which was filtered and rinsed with cold Et_2O. The filtrate was concentrated under reduced pressure to provide the crude material. Purification by column chromatography on silica gel (*gradient from* hexane *to* 20% EtOAc in hexane) gave the desired ester (1.50 g, 75% yield) as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 – 7.87 (m, 2H), 7.86 – 7.77 (m, 2H), 7.37 – 7.30 (m, 2H), 7.31 – 7.20 (m, 3H), 2.80 (t, *J* = 7.5 Hz, 2H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.14 (tt, *J* = 7.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.4, 162.0, 140.7, 134.8, 129.0, 128.6, 128.5, 126.2, 124.0, 34.6, 30.2, 26.3.

Synthesis of methyl (*S*)-2-(4-isobutylphenyl)propanoate (3):



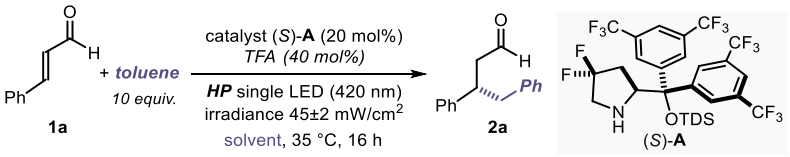
This compound was prepared according to a reported literature procedure.[8] To a solution of (*S*)-2-(4-isobutylphenyl)propanoic acid (0.775 g, 5.00 mmol) in MeOH (50 mL) at 0 °C was added dropwise thionyl chloride (2.4 g, 20.0 mmol). Completed the addition, the reaction was warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography on silica gel (*gradient from* hexane *to* 10% Et_2O in hexane) to give ester **3** (0.828 g, 90% yield) as a colourless liquid. The spectroscopic properties of this compound were consistent with the data available in the literature.[8] $[\alpha]_D^{26}$ = +69.4 (c = 0.95, $CHCl_3$); Lit: $[\alpha]_D^{26}$ = +64.6 (c = 1.00, $CHCl_3$, for (*S*)-enantiomer).[9]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.70 (q, *J* = 7.0 Hz, 1H), 3.66 (s, 3H), 2.44 (d, *J* = 7.0 Hz, 2H), 1.85 (dp, *J* = 13.6, 7.0 Hz, 1H), 1.49 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 7.0 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.4, 140.7, 137.9, 129.5, 127.3, 52.1, 45.2, 31.9, 30.3, 22.5, 18.8.

C. Optimization Studies and Control Experiments

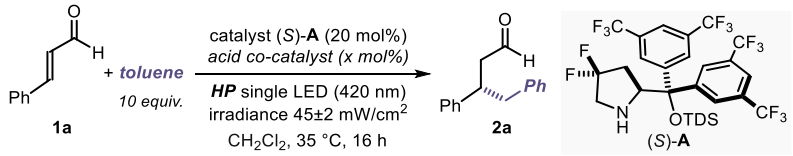
Table S1. *Evaluation of different solvents*



entry	Solvent	Yield (%)[a]	*ee* (%)
1	Cyclohexane	6	-
2	Benzene	28	68
3	Toluene	19	60
4	Chlorobenzene	40	68
5	Dichloroethane	57	83
6	**Dichloromethane**	**57**	**83**
7	Methyl *t*-butyl ether	-	-
8	Acetonitrile	-	-
9	Dimethylsulfoxide	-	-
10	Hexafluoroisopropanol	-	-

[a] Yield of **2a** determined by ^{1}H NMR analysis of the crude mixture using trichloroethylene as the internal standard.

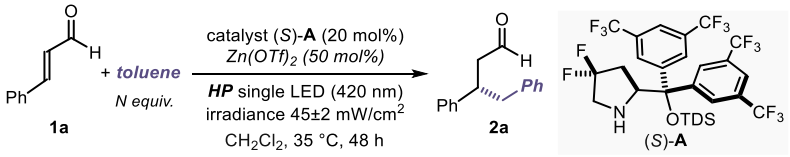
Table S2. *Screening of acid co-catalysts*



entry	Acid	Yield (%)[a]	*ee* (%)
1	Trifluoroacetic acid (40 mol%)	19	60
2	Diphenyl phosphate (40 mol%)	-	-
3	Trifluoromethansulfonic acid (40 mol%)	-	-
4	Methansulfonic acid (40 mol%)	34	78
5	Trichloroacetic acid (40 mol%)	7	-
6	$Zn(CF_3CO_2)_2$ (40 mol%)	5<	-
7	$Zn(MeSO_3)_2$ (40 mol%)	8	-
8	$Zn(ClO_4)_2$ (40 mol%)	10	-
9	$Zn(BF_4)_2$ (40 mol%)	5<	-
10	$ZnBr_2$ (40 mol%)	5<	-
11	$Zn(CF_3SO_3)_2$ (40 mol%)	52	83
12	**$Zn(CF_3SO_3)_2$ (50 mol%)**	**57**	**83**
13	$Mg(CF_3SO_3)_2$ (50 mol%)	40	80
14	$Ca(CF_3SO_3)_2$ (50 mol%)	39	78

[a] Yield of **2a** determined by ^{1}H NMR analysis of the crude mixture using trichloroethylene as the internal standard.

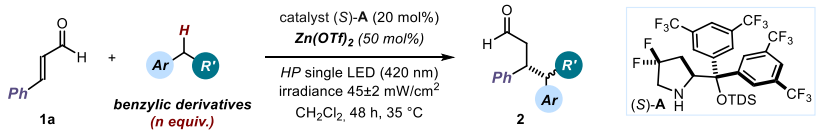
Table S3. *Evaluation of toluene stoichiometry*

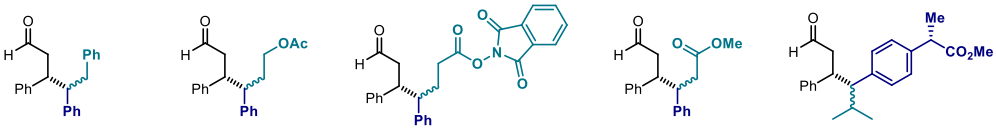


entry	Equiv.	Yield (%)[a]	*ee* (%)
1	1	28	82
2	3	42	81
3	5	53	82
4	**10**	**63**	**83**

[a] Yield of **2a** determined by ^{1}H NMR analysis of the crude mixture using trichloroethylene as the internal standard.

Table S4. *Evaluation of the stoichiometry for elaborated substrates*





for 2o

3 equiv.
36% *in situ* yield, 1.6:1 dr

4 equiv.
49% *in situ* yield, 1.7:1 dr

5 equiv.
53% yield, 1.8:1 dr
85% ee_{major}/83% ee_{minor}
92% of recovered starting material after FCC

10 equiv.
61% yield, 1.8:1 dr
88% ee_{major}/83% ee_{minor}

for 2p

3 equiv.
36% *in situ* yield, 1.6:1 dr

4 equiv.
33% *in situ* yield, 1.5:1 dr

5 equiv.
55% yield, 1.6:1 dr
83% ee_{major}/78% ee_{minor}
92% of recovered starting material after FCC

10 equiv.
55% yield, 1.5:1 dr
81% ee_{major}/77% ee_{minor}

for 2t

3 equiv.
26% *in situ* yield, 1.6:1 dr

4 equiv.
36% *in situ* yield, 1.6:1 dr

5 equiv.
51% yield, 1.5:1 dr
80% ee_{major}/83% ee_{minor}
92% of recovered starting material after FCC

10 equiv.
52% yield, 1.4:1 dr
75% ee_{major}/82% ee_{minor}

for 2u

3 equiv.
26% *in situ* yield, 1:1 dr

4 equiv.
36% *in situ* yield, 1.1:1 dr

5 equiv.
45% *yield*, 1.1:1 dr
82% ee_{major}/82% ee_{minor}
93% of recovered starting material after FCC

10 equiv.
51% yield, 1:1 dr
80% ee/78% ee

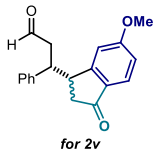
for 4

3 equiv.
28% *in situ* yield

4 equiv.
35% *in situ* yield

5 equiv.
50% *isolated* yield
1:1.3:8.2:10 dr
75% of recovered starting material after FCC

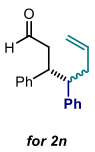
10 equiv.
51% yield
1:1.3:8.2:10 dr



for 2v

5 equiv.
35% *in situ* yield, 1.6:1 dr

10 equiv.
58% yield, 1.9:1 dr
91% ee/86% ee
85% of recovered starting material after FCC



for 2n

5 equiv.
26% yield, 2.5:1 dr
86% ee_{major}/79% ee_{minor}
unrecoverable benzylic derivative (volatile)

10 equiv.
30% yield, 4 :1 dr
81% ee_{major}/75% ee_{minor}

In most of the cases, such as for products **2o-v** and **4**, the unreacted benzylic substrates can be completely recovered in high purity during the purification procedure *via* flash column chromatography.

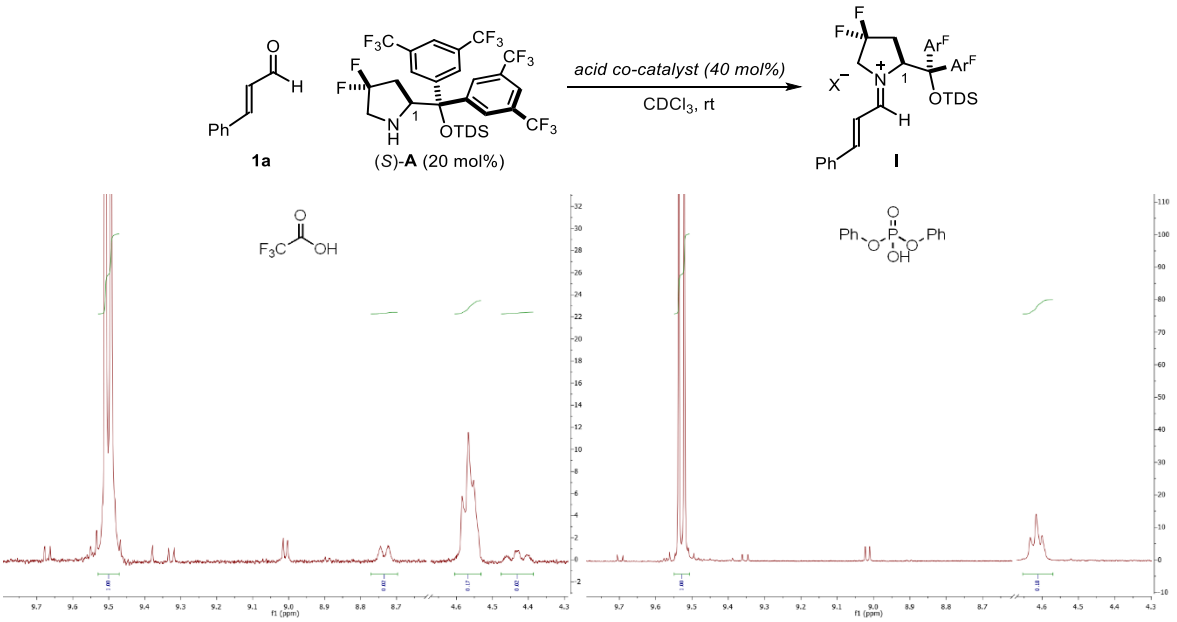
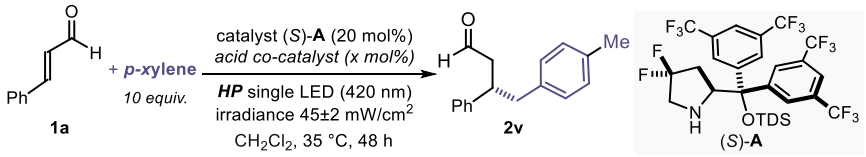


Figure S1. *Evaluating the ability of different Brønsted acids to promote the iminium ion formation.* Characteristic ^{1}H NMR signals of the species involved (400 MHz, $CDCl_3$): 9.50 (d, *J* = 7.5 Hz, C*H*O of 1a), 8.73 (d, *J* = 11.0 Hz, C*H*N of iminium ion I), 4.57 (t, *J* = 8.0 Hz, C1-*H* of (*S*)-A), 4.43 (br. t, J = 14.0 Hz, C1-*H* of iminium ion I).[2] The spectrum on the left conerns the experiment performed with trifluoroacetic acid (TFA), while the spectrum on the right refers to the experiment performed with diphenyl phosphate (DPP) as acid co-catalyst. The presence of a doublet and broad triplet at 8.73 ppm and 4.43 ppm, respectively, is diagnostic of the iminium ion formation occurring. Accordingly, this study showes that DPP is not acidic enough to promote the condensation step, whereas TFA elicits the formation of iminium ion I.

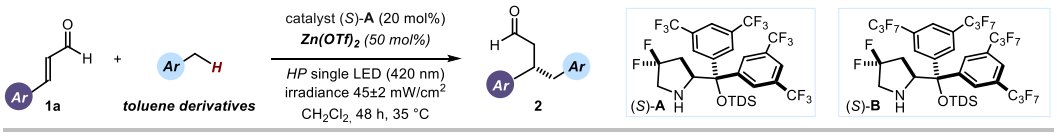
Table S5. *Reaction conditions re-optimization for adduct* ***2v***

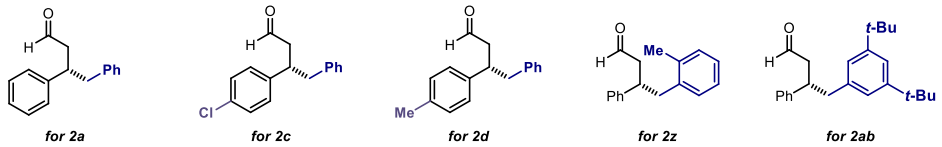


entry	Acid	Yield (%)[a]	*ee* (%)
1	$Zn(CF_3SO_3)_2$ (50 mol%)	15	-
2	Trifluoroacetic acid (40 mol%)	57	80
3	Trifluoroacetic acid (60 mol%)	58	77
4	Trifluoroacetic acid (80 mol%)	60	75
5	Trifluoroacetic acid (100 mol%)	62	71
6	**Trichloroacetic acid (100 mol%)**	**62**	**83**

[a] Yield of **2v** determined by ^{1}H NMR analysis of the crude mixture using trichloroethylene as the internal standard.

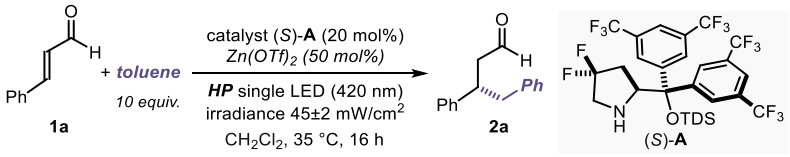
Table S6. *Effect of (S)-**B** vs (S)-**A** on enantioselectivity*





for 2a	for 2c	for 2d	for 2z	for 2ab
***(S)*-A** 63% yield, 83% *ee*	***(S)*-A** 59% yield, 67% *ee*	***(S)*-A** 48% yield, 60% *ee*	***(S)*-A** 47% yield, 77% *ee*	***(S)*-A** 59% yield, 74% *ee*
***(S)*-B** 61% yield, 83% *ee*	***(S)*-B** 46% yield, 67% *ee*	***(S)*-B** 35% yield, 60% *ee*	***(S)*-B** 46% yield, 80% *ee*	***(S)*-B** 53% yield, 75% *ee*

Table S7. Control Experiments



entry	$Zn(OTf)_2$	Catalyst	Light	Yield **2a** (%)[a]
1	✗	✓	✓	<5
2	✓	✗	✓	<5
3	✓	✓	✗	<5

[a] Yield of **2a** determined by ^{1}H NMR analysis of the crude mixture using trichloroethylene as the internal standard - no diagnostic signals for **2a** formation were detcted.

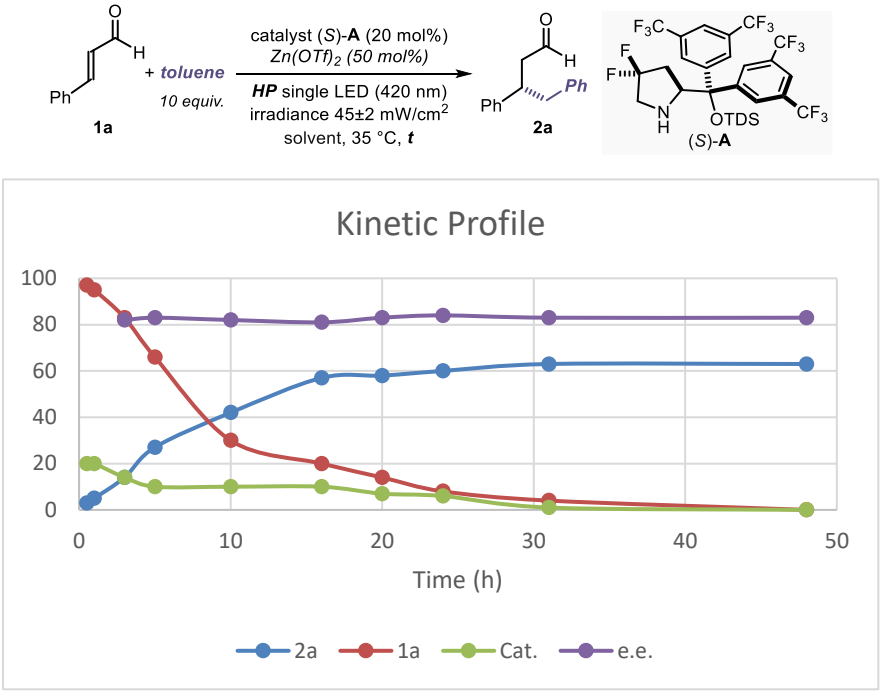
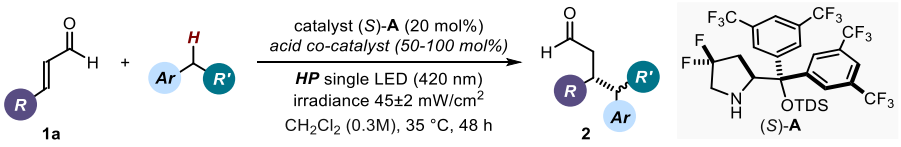


Figure S2. *Determination of the reaction kinetic profile*. The kinetic profile was studied monitoring the progression in time of a benchmark reaction between cinnamaldehyde **1a** and toluene, under optimized catalytic conditions. The reaction mantained a constant level of enantioinduction (81-83% *ee*), while complete consumption of enal **1a** was observed after more than 40 hours. Accordingly, we decided to evaluate the scope of the methodology running each reaction for 48 hours.

D. Experimental Procedures

D.1 General Procedure for the photochemical C-H functionalization of toluene and derivatives



General Procedure: A 15 mL Schlenk tube was charged with a mixture of amine catalyst (*S*)-**A** (0.02 mmol, 20 mol%, 14 mg), acid co-catalst (0.05-0.1 mmol, depending on the substrate) and enal **1** (0.1 mmol, 1 equiv.) in CH_2Cl_2 (300 µL). The corresponding toluene derivative (1 mmol, 10 equiv.) was added to the reaction vessel. This was placed under an atmosphere of argon, cooled to –78 °C, degassed *via* vacuum evacuation (5 minutes), backfilled with argon and, ultimately, warmed to room temperature. The freeze-pump-thaw cycle was repeated four times, and then the Schlenk tube was sealed with Parafilm and placed into a 3D-printed plastic support mounted on an aluminium block fitted with a 420 nm high-power single LED (λ = 420 nm, irradiance = 45 mW/cm^2, as controlled by

an external power supply; the setup is detailed in Figure S3). This setup secured a reliable irradiation while keeping a distance of 1 cm between the reaction vessel and the light source. The reaction was stirred at ambient temperature for 48 hours. The solvent was removed *in vacuo* and the crude mixture was purified by column chromatography on silica gel to give the corresponding product **2** in the stated yield and enantiomeric purity. If not otherwise stated, full consumption of the limiting enal (**1**) was observed by ^{1}H NMR analysis on the crude mixture at the end of the reaction.

In the case of the reactions delivering products **2o-v** and **4**, it was possible to fully recover the unreacted starting material (~90% recovered yield), as the first eluting compound, after purification procedure *via* flash column chromatography.

N.B. The internal temperature of the reaction was detected to be ~35 °C, as measured with a thermometer. In all cases, when the photochemical reaction was run carefully controlling and mantaining the temperature at 35 °C by means of a chiller connected to the irradiation plate, it proceeded with analogous efficiency.

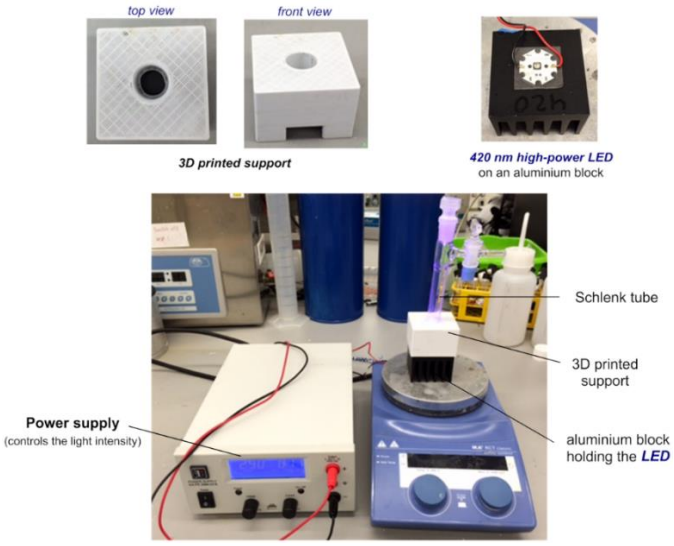
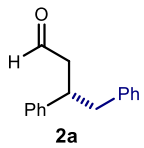


Figure S3. Detailed set-up and illumination system. The light source for illuminating the reaction vessel consisted in a 420 nm high-power single LED (OCU-440 UE420-X-T) purchased from OSA OPTO.*

D.2 Characterization of Products 2

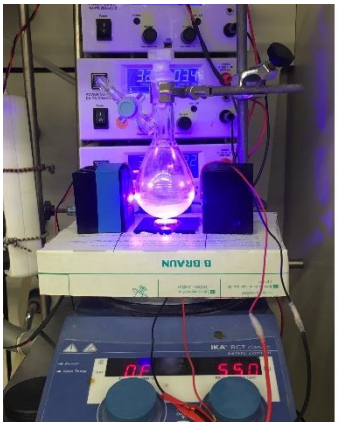


2a

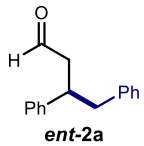
(*S*)-3,4-diphenylbutanal (2a). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), toluene (92.0 mg, 1 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The crude mixture was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **2a** (14.6 mg, 63% yield, 83% ee, average of two runs) as a colourless oil that displayed spectroscopic data consistent with those reported previously.[2] The enantiomeric excess was determined to be 83% by HPLC analysis on a Daicel Chiralpak IC-3 column: 90:10 hexane/*i*-PrOH, flow rate 0.6 mL/min, λ = 215 nm: τ_{major} = 12.4 min, τ_{minor} = 13.5 min. $[\alpha]_D^{26}$ = -47.5 (c = 0.44, $CHCl_3$, 83% ee); Lit: $[\alpha]_D^{26}$ = -45.8 (c = 0.49, $CHCl_3$, 88% ee for (*S*)-enantiomer).[2] The

*For more information on the LED used, visit https://www.osa-opto.com/tl_files/osa_opto/inhalte/files/datasheets/ocl-440/440_UE420.pdf

absolute configuration for compound **2a** was determined in comparison to the data available in the literature.[2] Accordingly, the absolute configuration for all of the products **2** was assigned likewise.
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.59 (t, *J* = 2.0 Hz, 1H), 7.31 – 7.14 (m, 8H), 7.08 – 7.04 (app d, *J* = 5.0 Hz 2H), 3.49 (p, *J* = 7.5 Hz, 1H), 2.96 (dd, *J* = 13.5, 7.1 Hz, 1H), 2.88 (dd, *J* = 13.5, 7.9 Hz, 1H), 2.81 – 2.70 (m, 2H);
^{13}C NMR (125.8 MHz, $CDCl_3$): δ 201.7, 143.4, 139.4, 129.3, 128.7, 128.5, 127.7, 126.9, 126.5, 49.1, 43.5, 42.2.

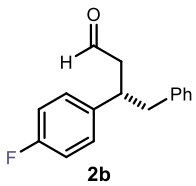


1 mmol scale reaction. The model reaction was repeated on a more synthetically useful scale using three high power single LEDs and a 50 mL round-bottom Schlenk flask to increase the surface-area-to-volume ratio, which secured a more efficient irradiation of the reaction mixture (see pictures to the left). To a 50 mL round-bottom Schlenk flask containing aminocatalyst (*S*)-**A** (0.2 mmol, 20 mol%, 141 mg), zinc(II) triflate (0,5 mmol, 181 mg) and cynnamaldehyde **1a** (1 mmol, 1 equiv., 132 mg) in dichloromethane (3 mL) was added toluene (10 mmol, 921 mg). The reaction vessel was placed under an atmosphere of argon, cooled to – 78 °C, degassed via vacuum evacuation (5 min), backfilled with argon and, ultimately, warmed to room temperature. The freeze-pump-thaw cycle was repeated five times, and then three 420 nm high-power single LEDs (λ = 420 nm, irradiance = 45 mW/cm^2, as controlled by an external power supply) were placed at 1 cm distance from the sides and the bottom of the Schlenk flask. The reaction was stirred under visible light irradiation at ambient temperature (~35 °C) for 60 hours. The solvent was removed under reduced pressure and the crude mixture was purified by column chromatography on silica gel (hexane/diethyl ether 92:8) to afford product **2a** as a pale yellow oil (111 mg, 51% yield, 83% ee).



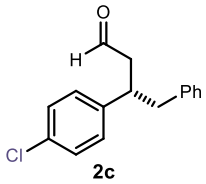
***ent*-2a**

(*R*)-3,4-diphenylbutanal (*ent*-2a). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*R*)-**A** (14.1 mg, 20 mol%), toluene (92.0 mg, 1 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The crude mixture was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product *ent*-**2a** (14.6 mg, 63% yield, 82% ee, average of two runs) as a colourless oil that displayed spectroscopic data consistent with those reported previously.[2] The enantiomeric excess was determined to be 82% by HPLC analysis on a Daicel Chiralpak IC-3 column: 90:10 hexane/*i*-PrOH, flow rate 0.6 mL/min, λ = 215 nm: τ_{major} = 13.5 min, τ_{minor} = 12.4 min. $[\alpha]_D^{26}$ = +55.3 (c = 0.067, $CHCl_3$, 82% ee).



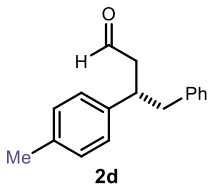
2b

(*S*)-3-(4-fluorophenyl)-4-phenylbutanal (2b). Prepared according to the general procedure using enal **1b** (15.0 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), toluene (92.0 mg, 1 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The crude mixture was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **2b** (17.0 mg, 70% yield, 80% ee, average of two runs) as a colourless oil that displayed spectroscopic data consistent with those reported previously.[2] The enantiomeric excess was determined to be 80% by UPC[2] analysis on a Daicel Chiralpak ID-3 column: gradient CO_2/MeCN from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 275 nm: τ_{major} = 2.49 min, τ_{minor} = 2.57 min. $[\alpha]_D^{26}$ = -38.4 (c = 0.71, $CHCl_3$, 80% ee); Lit: $[\alpha]_D^{26}$ = -45.3 (c = 0.69, $CHCl_3$, 85% ee for (*S*)-enantiomer).[2]
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.61 (t, *J* = 2.0 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.20 – 7.15 (m, 1H), 7.12 – 7.07 (m, 2H), 7.04 – 7.01 (m, 2H), 6.96 (t, *J* = 9.0 Hz, 2H), 3.49 (p, *J* = 7.5 Hz, 1H), 2.89 (d, *J* = 7.5 Hz, 2H), 2.75 (dd, *J* = 7.5, 2.0 Hz, 2H);
^{13}C NMR (125.8 MHz, $CDCl_3$): δ 201.7, 161.7 (d, $^1J_{C\text{-}F}$ = 245.0 Hz), 139.1, 139.0 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 129.3, 129.1 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 128.5, 126.6, 115.5 (d, $^2J_{C\text{-}F}$ = 21.0 Hz), 49.3, 43.5, 41.3.



2c

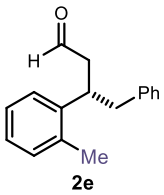
(*S*)-3-(4-Chlorophenyl)-4-phenylbutanal (2c). Prepared according to the general procedure using enal **1c** (16.7 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), toluene (92.0 mg, 1 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The crude mixture was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **2c** (15.3 mg, 59% yield, 67% ee, average of two runs) as a colourless oil that displayed spectroscopic data consistent with those reported previously.[2] The enantiomeric excess was determined to be 67% by UPC[2] analysis on a Daicel Chiralpak IE-3 column: gradient CO_2/MeCN from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 220 nm: τ_{major} = 4.2 min, τ_{minor} = 4.41 min. $[\alpha]_D^{26}$ = -46.5 (c = 0.49, $CHCl_3$, 67% ee); Lit: $[\alpha]_D^{26}$ = -56.8 (c = 0.69, $CHCl_3$, 86% ee for (*S*)-enantiomer).[2]
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.61 (t, *J* = 2.0 Hz, 1H), 7.32 – 7.11 (m, 5H), 7.10 – 7.00 (m, 4H), 3.48 (p, *J* = 7.5 Hz, 1H), 2.89 (d, *J* = 7.5 Hz, 2H), 2.75 (dd, *J* = 7.5, 2 Hz, 2H);
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.1, 141.8, 139.0, 132.6, 129.3, 128.9, 128.6, 126.6, 49.1, 43.3, 41.4.



2d

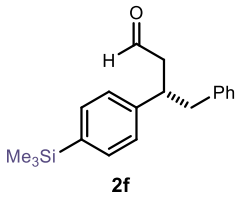
(*S*)-4-phenyl-3-(p-tolyl)butanal (2d). Prepared according to the general procedure using enal **1d** (14.6 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), toluene (92 mg, 1 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The crude mixture was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **2d** (11.3 mg, 48% yield, 60% ee, average of two runs) as a colourless oil that displayed spectroscopic data consistent with those reported previously.[2] The enantiomeric excess was determined to be 60% by UPC[2] analysis on a Daicel Chiralpak ID-3 column: gradient CO_2/MeCN from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 220 nm: τ_{major} = 3.01 min, τ_{minor} = 3.28 min. $[\alpha]_D^{26}$ = -19.3 (c = 0.25, $CHCl_3$, 60% ee); Lit: $[\alpha]_D^{26}$ = -42.5 (c = 0.50, $CHCl_3$, 78% ee for (*S*)-enantiomer).[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.57 (t, *J* = 2.0 Hz, 1H), 7.28 – 7.15 (m, 3H), 7.11 – 7.02 (m 6H), 3.45 (p, *J* = 7.5 Hz, 1H), 2.95 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.85 (dd, *J* = 13.5, 8.0 Hz, 1H), 2.77 – 2.66 (m, 2H), 2.31 (s, 3H);
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.9, 140.3, 139.6, 136.4, 129.4, 128.5, 127.5, 126.5, 49.1, 43.5, 41.8, 21,2.



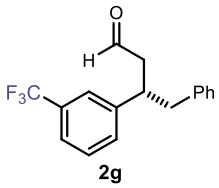
2e

(*S*)-4-phenyl-3-(o-tolyl)butanal (2e). Prepared according to the general procedure using enal **1e** (14.6 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), toluene (92 mg, 1 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The crude mixture was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **2e** (11.5 mg, 48% yield, 72% ee, average of two runs) as a colourless oil that displayed spectroscopic data consistent with those reported previously.[2] The enantiomeric excess was determined to be 72% by UPC[2] analysis on a Daicel Chiralpak IE-3 column: gradient CO_2/MeCN from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 220 nm: τ_{major} = 3.58 min, τ_{minor} = 3.75 min. $[\alpha]_D^{26}$ = -26.4 (c = 0.37, $CHCl_3$, 72% ee).
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.56 (t, *J* = 2.0 Hz, 1H), 7.25 – 7.14 (m, 5H), 7.12 – 7.07 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 2H) 3.76 (p, *J* = 7.5 Hz, 1H), 2.91 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.85 – 2.70 (m, 3H), 2.21 (s, 3H);
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.7, 141.6, 139.5, 136.0, 130.6, 129.3, 128.4, 126.51, 126.0, 49.0, 43.2, 36.9, 19,7.



2f

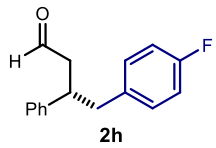
(*S*)-4-phenyl-3-(4-(trimethylsilyl)phenyl)butanal (2f). Prepared according to the general procedure using enal **1f** (20.4 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), toluene (92 mg, 1 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The crude mixture was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **2f** (14.8 mg, 50% yield, 70% ee, average of two runs) as an off-white solid. The enantiomeric excess was determined to be 70% by UPC[2] analysis on a Daicel Chiralpak IE-3 column: gradient CO_2/MeCN from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 2 mL/min, λ = 210 nm: τ_{major} = 3.97 min, τ_{minor} = 4.79 min. $[\alpha]_D^{26}$ = -19.8 (c = 0.14, $CHCl_3$, 70% ee).
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.59 (t, *J* = 2.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.24 – 7.18 (m, 3H), 7.15 – 7.10 (m, 2H), 3.51 (tt, *J* = 8.5, 6.5 Hz, 1H), 3.03 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.88 (dd, *J* = 13.5, 8.5 Hz, 1H), 2.82 – 2.69 (m, 2H), 0.28 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.6, 143.9, 139.3, 138.7, 133.7, 129.2, 128.4, 126.9, 126.4, 48.7, 43.2, 41.9, -1.10.
HRMS (ESI) Exact mass calculated for $C_{19}H_{24}NaOSi$ $[M+Na]^+$: 319.1489, found: 319.1488.



2g

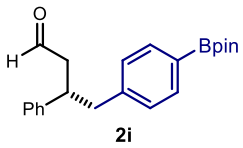
(*S*)-4-phenyl-3-(3-(trifluoromethyl)phenyl)butanal (2g). Prepared according to the general procedure using enal **1g** (20.0 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), toluene (92 mg, 1 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The crude mixture was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **2g** (9.6 mg, 33% yield, 84% ee, average of two runs) as a pale yellow oil. The enantiomeric excess was determined, upon sodium borohydride reduction of the isolated aldehyde to

afford the corresponding alcohol, to be 84% by UPC[2] analysis on a Daicel Chiralpak IE-3 column: gradient CO_2/MeOH from 100% CO_2 to 80:20 over 4 minutes, curve 6, flow rate 2 mL/min, λ = 215 nm: τ_{major} = 3.97 min, τ_{minor} = 4.06 min. $[\alpha]_D^{26}$ = -25.8 (c = 0.21, $CHCl_3$, 84% ee).
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.64 (t, *J* = 1.5 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.17 (m, 3H), 7.07 – 7.01 (m, 2H), 3.60 (tt, *J* = 7.5 Hz, 1H), 2.94 (d, *J* = 7.5 Hz, 2H), 2.83 (dd, *J* = 7.5, 1.5 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 200.5, 144.3, 138.6, 131.13 (q, $^4J_{C\text{-}F}$ = 1.0 Hz), 130.9 (q, $^2J_{C\text{-}F}$ = 32.0 Hz), 129.2, 129.0, 128.4, 126.6, 124.2 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 124.1 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 123.6 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 48.7, 43.0, 41.6.
^{19}F NMR (376 MHz, $CDCl_3$): δ -62.70 (s, 3F).
HRMS (ESI) Exact mass calculated for $C_{18}H_{19}F_3NaO_2$ $[M+CH_3OH+Na]^+$: 347.1229, found: 347.1245.



2h

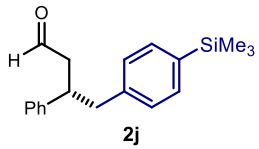
(*S*)-4-(4-fluorophenyl)-3-phenylbutanal (2h). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), 4-fluorotoluene (110 mg, 1 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The crude mixture was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **2h** (16.2 mg, 67% yield, 80% ee, average of two runs) as a pale yellow oil that displayed spectroscopic data consistent with those reported previously.[2] The enantiomeric excess was determined, upon sodium borohydride reduction of the isolated aldehyde to afford the corresponding alcohol, to be 80% by HPLC analysis on a Daicel Chiralpak IC-3 column: 90:10 hexane/*i*-PrOH, flow rate 0.5 mL/min, λ = 215 nm. τ_{Major} = 16.0 min, τ_{minor} = 15.1 min. $[\alpha]_D^{26}$ = -49.1 (c = 0.18, $CHCl_3$); Lit: $[\alpha]_D^{26}$ = -46.0 (c = 0.63, $CHCl_3$, 92% ee for (*S*)-enantiomer).[2]
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.65 (t, *J* = 2.0 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.26 – 7.19 (m, 1H), 7.18 – 7.11 (m, 2H), 7.03 – 6.96 (m, 2H), 6.96 – 6.88 (m, 2H), 3.47 (tt, *J* = 7.5 Hz, 1H), 2.92 (d, *J* = 7.5 Hz, 2H), 2.85 – 2.72 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.3, 161.5 (d, $^1J_{C\text{-}F}$ = 244.5 Hz), 142.8, 134.9 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 130.6 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 128.6, 127.5, 126.8, 115.1 (d, $^2J_{C\text{-}F}$ = 21.0 Hz), 49.0, 42.4, 42.0.
^{19}F NMR (376 MHz, $CDCl_3$): δ -116.92 (tt, $^3J_{H\text{-}F}$ = 8.5 Hz, $^4J_{H\text{-}F}$ = 5.5 Hz, 1F).



2i

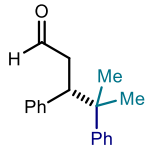
(*S*)-3-phenyl-4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-yl)phenyl)butanal (2i). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), 4,4,5,5-tetramethyl-2-(*p*-tolyl)-1,3,2-dioxaborolane (218 mg, 1 mmol), zinc(II) triflate (18.2 mg, 0.05 mmol) and dichloromethane (300 µL). The crude mixture was purified by flash column chromatography (hextane/diethyl ether 92:8) to afford product **2i** (19.0 mg, 54% yield, 80% ee, average of two runs) as a pale yellow oil. The enantiomeric excess was determined to be 80% by UPC[2] analysis on a Daicel Chiralpak IE-3 column: gradient CO_2/MeCN from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 2 mL/min, λ = 229 nm: τ_{major} = 1.74 min, τ_{minor} = 2.00 min. $[\alpha]_D^{26}$ = -29.7 (c= 0.37, $CHCl_3$, 80% ee).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (t, *J* = 1.9 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.30 – 7.24 (m, 3H), 7.22 – 7.13 (m, 3H), 7.06 (d, *J* = 7.9 Hz, 2H), 3.50 (p, *J* = 7.5 Hz, 1H), 2.93 (qd, *J* = 13.5, 7.5 Hz, 2H), 2.82 – 2.67 (m, 2H), 1.33 (s, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.6, 143.2, 142.7, 135.0, 128.8, 128.8, 128.7, 127.7, 126.9, 83.9, 49.1, 43.6, 42.0, 29.9, 25.0;
^{11}B NMR (47 MHz, $CDCl_3$) δ 30.8;
HRMS (ESI) Exact mass calculated for $C_{22}H_{27}NaO_3B$ $[M+Na]^+$: 372.1982, found: 372.1973.



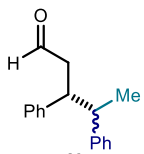
2j

(*S*)-3-phenyl-4-(4-(trimethylsilyl)phenyl)butanal (2j). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), trimethyl(*p*-tolyl)silane (164 mg, 1 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The crude mixture was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **2j** (16.5 mg, 56% yield, 80% ee, average of two runs) as a colourless oil. The enantiomeric excess was determined, upon sodium borohydride reduction of the isolated aldehyde to afford the corresponding alcohol, to be 80% by HPLC analysis on a Daicel Chiralpak IC-3 column: 90:10 hexane/*i*-PrOH, flow rate 0.6 mL/min, λ = 215 nm: τ_{Major} = 10.0 min, τ_{minor} = 11.0 min. $[\alpha]_D^{26}$ = -40.1 (c = 0.67, $CHCl_3$, 80% ee).
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.58 (t, *J* = 2.0 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 7.07 (d, *J* = 7.9 Hz, 2H), 3.55-3.44 (m, 1H), 2.99 (dd, *J* = 13.5, 6.7 Hz, 1H), 2.85 (dd, *J* = 13.6, 8.3 Hz, 1H), 2.80 – 2.67 (m, 2H), 0.24 (s, 9H);
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.8, 143.5, 140.0, 138.3, 133.6, 128.8 (2 signals), 127.7, 126.9, 49.0, 43.4, 42.0, -0.9.
HRMS (ESI) Exact mass calculated for $C_{19}H_{24}NaOSi$ $[M+Na]^+$: 319.1484, found: 319.1489.



2k

(*S*)-4-methyl-3,4-diphenylpentanal (2k). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), cumene (120 mg, 1 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The crude mixture was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **2k** (9.6 mg, 38% yield, 53% ee, average of two runs) as a pale yellow oil that displayed spectroscopic data consistent with those reported previously.[2] The enantiomeric excess was determined to be 53% by HPLC analysis on a Daicel Chiralpak IC-3 column: 90:10 hexane/*i*-PrOH, flow rate 1.0 mL/min, λ = 215 nm: τ_{Major} = 8.4 min, τ_{minor} = 12.2 min. $[\alpha]_D^{26}$ = -35.2 (c = 0.11, $CHCl_3$, 53% ee); Lit: $[\alpha]_D^{26}$ = -33.0 (c = 0.37, $CHCl_3$, 71% ee for (*S*)-enantiomer).[2]
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.34 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.41 – 7.31 (m, 4H), 7.31 – 7.21 (m, 4H), 7.15 – 7.09 (m, 2H), 3.53 (dd, *J* = 11.0, 4.0 Hz, 1H), 2.81 (ddd, *J* = 16.5, 11.0, 3.0 Hz, 1H), 2.46 (ddd, *J* = 16.5, 4.0, 1.5 Hz, 1H), 1.33 (s, 3H), 1.24 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 202.0, 147.9, 140.2, 130.0, 128.3, 128.0, 127.0, 126.6, 126.3, 51.2, 45.0, 41.2, 28.8, 23.2.



2l

(*3R*)-3,4-diphenylpentanal (2l). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), ethylbenzene (106 mg, 1 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The d.r. was determined to be 1.5:1 by ^{1}H NMR analysis of the crude mixture, which was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **2l** (15.9 mg, 67% yield, average of two runs) as an off-white solid that displayed

spectroscopic data consistent with those reported previously.[2] The enantiomeric excess of both diastereoisomers was determined, upon sodium borohydride reduction of the isolated aldehydes to afford the corresponding alcohols, by HPLC analysis on a Daicel Chiralpak IC-3 column, 97:3 hexane/*i*-PrOH, flow rate 1.2 mL/min, λ = 215 nm. *Major diastereomer:* τ_{Major} = 24.9 min, τ_{minor} = 20.4 min. *Minor diastereomer:* τ_{Major} = 18.0 min, τ_{minor} = 19.1 min. $[\alpha]_D^{26}$ = –19.4 (c = 0.087, $CHCl_3$, 1.5:1 *d.r.*, 80% ee_{major}, 77% ee_{minor}); Lit: $[\alpha]_D^{26}$ = -40.4 (c = 0.42, $CHCl_3$, 1.2:1 *d.r.*, 92% ee_{major}, 92% ee_{minor} for (3*R*)-enantiomer).[2]

Spectroscopic data for ***major diastereoisomer****:*

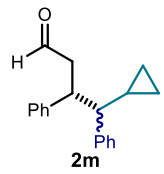
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.43 – 7.12 (m, 8H), 7.05 – 6.97 (m, 2H), 3.33 (td, *J* = 10.5, 4.5 Hz, 1H), 2.92 (dq, *J* = 10.5, 7.0 Hz, 1H, *A*), 2.65 (ddd, *J* = 16.5, 10.5, 2.5 Hz, 1H), 2.49 (ddd, *J* = 16.5, 4.5, 1.5 Hz, 1H), 1.07 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (125.8 MHz, $CDCl_3$) δ 201.6, 145.1, 142.6, 128.7, 128.7, 128.1, 127.6, 126.8, 126.7, 49.0, 47.5, 46.0, 20.5.

Spectroscopic data for ***minor diastereoisomer****:*

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (t, *J* = 2.0 Hz, 1H), 7.43 – 7.12 (m, 8H), 7.05 – 6.97 (m, 2H), 3.49 (td, *J* = 7.5, 7.5 Hz, 1H), 3.09 (dq, *J* = 7.0, 7.0 Hz, 1H), 2.83 (dd, *J* = 7.5, 2.0 Hz, 2H), 1.31 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (125.8 MHz, $CDCl_3$) δ 202.0, 143.8, 141.5, 128.5, 128.1 (*2 signals*), 128.0, 126.6, 126.3, 46.6, 46.1, 45.0, 18.0.



2m

(3*R*)-4-cyclopropyl-3,4-diphenylbutanal (2m). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), (cyclopropylmethyl)benzene (132 mg, 1 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The d.r. was determined to be 1:1 by ^{1}H NMR analysis of the crude mixture, which was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **2m** (10.3 mg, 39% yield, average of two runs) as an off-white solid. The enantiomeric excess of both diastereoisomers was determined, upon sodium borohydride reduction of the isolated aldehydes to afford the corresponding alcohols, by UPC[2] analysis on a Daicel Chiralpak CEL-1 column: gradient CO_2/*i*-PrOH from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 220 nm. *Diastereomer A:* τ_{Major} = 4.07 min, τ_{minor} = 3.96 min. *Diastereomer B:* τ_{Major} = 4.42 min, τ_{minor} = 4.13 min. $[\alpha]_D^{26}$ = –15.4 (c = 0.15, $CHCl_3$, 1:1 *d.r.*, 82% ee_A, 85% ee_B).

Spectroscopic data for ***diastereoisomer A****:*

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.69 (t, *J* = 2.0 Hz, 1H), 7.38 – 7.11 (m, 10H), 3.71 (ddd, *J* = 9.0, 8.0, 6.0 Hz, 1H), 3.10 (ddd, *J* = 17.0, 6.0, 2.0 Hz, 1H), 2.84 (ddd, *J* = 17.0, 9.0, 2.0 Hz, 1H), 2.01 (dd, *J* = 10.5, 8.0 Hz, 1H), 1.07 (dddd, *J* = 13.0, 10.5, 8.0, 5.0 Hz, 1H), 0.76 (dddd, *J* = 9.0, 7.5, 6.0, 4.5 Hz, 1H), 0.44 (dddd, *J* = 9.0, 8.0, 5.5, 4.5 Hz, 1H), 0.34 (ddd, *J* = 10.5, 9.0, 5.0 Hz, 1H), 0.03 (ddd, *J* = 9.0, 5.5, 4.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, *aromatic C-H signals were not assigned and reported for both diastereoisomers*): δ 201.7, 142.8, 141.5, 128.6 (C_{Ar}-H), 128.5 (*2 signals*, C_{Ar}-H), 128.4 (C_{Ar}-H), 128.3 (C_{Ar}-H), 128.2 (C_{Ar}-H), 128.0 (C_{Ar}-H), 127.8 (C_{Ar}-H), 56.9, 47.4, 46.3, 14.9, 7.7, 1.0.

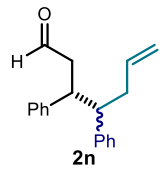
Spectroscopic data for ***diastereoisomer B****:*

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.46 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.38 – 7.11 (m, 6H), 7.00 – 6.96 (m, 2H), 6.95 – 6.92 (m, 2H), 3.62 (ddd, *J* = 9.5, 9.5, 5.0 Hz, 1H), 2.75 (ddd, *J* = 17.0, 9.5, 2.5 Hz, 1H),

2.61 (ddd, *J* = 17.0, 5.0, 1.5 Hz, 1H), 2.09 (dd, *J* = 9.5, 9.5 Hz, 1H), 0.98 – 0.88 (m, 1H), 0.31 – 0.21 (m, 2H), -0.08 – -0.15 (m, 1H), -0.21 – -0.27 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, *aromatic C-H signals were not assigned and reported for both diastereoisomers*): δ 202.1, 143.4, 142.3, 128.6 (C_{Ar}-H), 128.5 (*2 signals*, C_{Ar}-H), 128.4 (C_{Ar}-H), 128.3 (C_{Ar}-H), 128.2 (C_{Ar}-H), 128.0 (C_{Ar}-H), 127.8 (C_{Ar}-H), 56.7, 48.2, 46.7, 15.3, 7.2, 2.8.

HRMS (ESI) Exact mass calculated for $C_{19}H_{20}NaO$ $[M+Na]^+$: 287.1406, found: 287.1403.



2n

(*3R*)-3,4-diphenylhept-6-enal (2n). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), 4-phenyl-1-butene (66.1 mg, 0.5 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and CH_2Cl_2 (300 µL). The d.r. was determined to be 2.5:1 by ^{1}H NMR analysis of the crude mixture, which was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **2n** (6.8 mg, 26% yield, average of two runs) as a colourless solid that displayed spectroscopic data consistent with those reported previously.[2] The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC-3 column: 95:5 hexane/*i*-PrOH, flow rate 0.5 mL/min, λ = 215 nm. *Major diastereomer:* τ_{Major} = 19.9 min, τ_{minor} = 26.4 min. *Minor diastereomer:* τ_{Major} = 15.9 min, τ_{minor} = 16.7 min. $[\alpha]_D^{26}$ = –1.3 (c = 0.11, $CHCl_3$, 4:1 *d.r.*, 86% ee_{major}, 79% ee_{minor}); Lit: $[\alpha]_D^{26}$ = -1.7 (c = 0.48, $CHCl_3$, 1.5:1 *d.r.*, 92% ee_{major}, 90% ee_{minor} for (3*R*)-enantiomer).[2]

*Spectroscopic data for **major diastereoisomer**:*

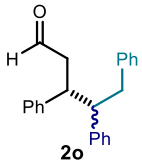
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.36 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.41 – 7.16 (m, 10H), 5.43 (ddt, *J* = 17.0, 10.5, 7.0 Hz, 1H), 4.84 – 4.69 (m, 2H), 3.42 (td, *J* = 10.5, 4.5 Hz, 1H), 2.93 – 2.75 (m, 1H), 2.62 (ddd, *J* = 17.0, 10.5, 2.5 Hz, 1H), 2.57 – 2.37 (m, 1H), 2.27 – 2.14 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 201.5, 142.7, 142.4, 136.5, 128.9, 128.8, 128.6, 128.3, 127.1, 127.0, 116.2, 52.1, 49.0, 46.3, 38.5.

*Spectroscopic data for **minor diastereoisomer**:*

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.64 (t, *J* = 2.0 Hz, 1H), 7.41 – 7.16 (m, 8H), 6.95 – 6.85 (m, 2H), 5.64 (ddt, *J* = 17.0, 10.0, 6.5 Hz, 1H), 5.08 – 4.92 (m, 2H), 3.61 (dt, *J* = 9.0, 6.0 Hz, 1H), 3.01 (dt, *J* = 9.6, 6.0 Hz, 1H), 2.93 – 2.75 (m, 2H), 2.57 – 2.37 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 202.0, 142.8, 142.4, 136.8, 129.4, 129.1, 128.1, 127.9, 126.8, 126.6, 116.7, 50.6, 47.2, 44.5, 37.0.

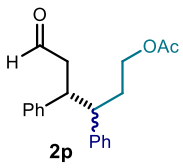


2o

(*3R*)-3,4,5-triphenylpentanal (2o). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), 1,2-diphenylethane (91 mg, 0.5 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The d.r. was determined to be 1.8:1 by ^{1}H NMR analysis of the crude mixture, which was purified by flash column chromatography (hexane/diethyl ether 97:3) to afford product **2o** (16.7 mg, 53% yield, average of two runs) as an off-white solid. The enantiomeric excess of both diastereoisomers was determined, upon sodium borohydride reduction of the isolated aldehydes to afford the corresponding alcohols, by UPC[2] analysis on a Daicel Chiralpak CEL-1 column: gradient CO_2/MeOH from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 210 nm. *Major diastereomer:* τ_{Major} = 4.13 min, τ_{minor} = 4.00 min. *Minor diastereomer:* τ_{Major} = 4.41 min, τ_{minor} = 4.27 min. $[\alpha]_D^{26}$ = –20.4 (c = 0.11, $CHCl_3$, 1.8:1 *d.r.*, 85% ee_{major}, 83% ee_{minor}).

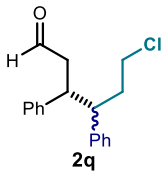
*Spectroscopic data for **major diastereoisomer**:*

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.39 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.46 – 6.82 (m, 13H), 6.70 (dd, *J* = 7.5, 2.0 Hz, 2H), 3.54 (td, *J* = 10.5, 4.5 Hz, 1H), 3.15 – 2.99 (m, 1H), 2.97 – 2.87 (m, 1H), 2.87 – 2.74 (m, 1H), 2.71 – 2.54 (m, 1H), 2.49 (ddd, *J* = 17.0, 4.5, 1.5 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.3, 142.8, 142.0, 140.2, 128.9, 128.8, 128.6, 128.5, 128.2, 127.8, 127.1, 126.8, 125.6, 54.5, 49.0, 46.2, 40.7.
Spectroscopic data for ***minor diastereoisomer****:*
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.62 (t, *J* = 2.0 Hz, 1H), 7.46 – 6.82 (m, 15H), 3.65 (dt, *J* = 9.0, 6.0 Hz, 1H), 3.30 (dt, *J* = 9.0, 6.0 Hz, 1H), 3.15 – 2.99 (m, 1H), 2.87 – 2.74 (m, 1H), 2.71 – 2.54 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.8, 140.5, 140.4, 140.0, 129.3, 129.1, 129.0, 128.2, 128.0, 127.7, 126.7, 126.5, 125.9, 52.2, 47.4, 44.3, 38.9.
HRMS (ESI) Exact mass calculated for $C_{24}H_{26}NaO_2$ $[M+CH_3OH+Na]^+$: 369.1825, found: 369.1841.



2p

(*4R*)-6-oxo-3,4-diphenylhexyl acetate (2p). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), 3-phenylpropyl acetate (89 mg, 0.5 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 μL). The d.r. was determined to be 1.6:1 by ^{1}H NMR analysis of the crude mixture, which was purified by flash column chromatography (*gradient from* hexane/diethyl ether 90:10 *to* hexane/diethyl ether 50:50) to afford the *major diastereoisomer* of product **2p** (10.4 mg) as a pale yellow oil. Continued elution delivered the *minor diastereoisomer* of **2p** (6.9 mg) as a yellow oil (55% overall yield, average of two runs). The enantiomeric excess of both diastereoisomers was determined, upon sodium borohydride reduction of the isolated aldehydes to afford the corresponding alcohols, by HPLC analysis on a Daicel Chiralpak IC-3 column: 90:10 hexane/*i*-PrOH, flow rate 1.2 mL/min, λ = 215 nm. *Major diastereomer:* τ_{Major} = 26.4 min, τ_{minor} = 32.0 min. *Minor diastereomer:* τ_{Major} = 26.7 min, τ_{minor} = 24.8 min.
Characterization for ***major diastereoisomer****:*
$[\alpha]_D^{26}$ = –8.8 (c = 0.15, $CHCl_3$, 83% ee_{major}).
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.35 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.41 – 7.33 (m, 4H), 7.32 – 7.22 (m, 6H), 3.78 (ddd, *J* = 11.0, 7.0, 5.5 Hz, 1H), 3.64 (dt, *J* = 11.0, 7.5 Hz, 1H), 3.39 (ddd, *J* = 10.5, 10.5, 4.5 Hz, 1H), 2.89 (ddd, *J* = 10.5, 10.5, 5.0 Hz, 1H), 2.62 (ddd, *J* = 17.0, 10.5, 2.5 Hz, 1H), 2.44 (ddd, *J* = 17.0, 4.5, 1.5 Hz, 1H), 1.90 (s, 3H), 1.82 – 1.70 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.1, 170.8, 142.3, 141.8, 129.0, 128.9, 128.2, 128.1, 127.2, 127.1, 62.8, 49.0, 48.7, 46.6, 32.8, 20.8.
HRMS (ESI) Exact mass calculated for $C_{20}H_{22}NaO_3$ $[M+Na]^+$: 333.1461, found: 333.1461.
Characterization for ***minor diastereoisomer****:*
$[\alpha]_D^{26}$ = +6.2 (c = 0.26, $CHCl_3$, 78% ee_{minor}).
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.64 (t, *J* = 2.0 Hz, 1H), 7.24 – 7.14 (m, 6H), 6.95 – 6.91 (m, 2H), 6.91 – 6.86 (m, 2H), 3.96 (ddd, *J* = 11.0, 7.5, 5.0 Hz, 1H), 3.81 (dt, *J* = 11.0, 7.5 Hz, 1H), 3.55 (ddd, *J* = 9.0, 6.5, 6.5 Hz, 1H), 3.03 (ddd, *J* = 11.0, 6.5, 4.0 Hz, 1H), 2.88 (ddd, *J* = 17.0, 6.5, 2.0 Hz, 1H), 2.79 (ddd, *J* = 17.0, 9.0, 2.0 Hz, 1H), 2.19 – 2.06 (m, 1H), 2.05 – 1.90 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.5, 170.9, 140.5, 139.9, 128.9, 128.8, 128.1, 128.0, 126.8, 126.8, 62.9, 47.5, 46.9, 45.1, 31.6, 20.9.
HRMS (ESI) Exact mass calculated for $C_{20}H_{22}NaO_3$ $[M+Na]^+$: 333.1461, found: 333.1473.



2q

(*R*)-6-chloro-3,4-diphenylhexanal (2q). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), (3-chloropropyl)benzene (77 mg, 0.5 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The d.r. was determined to be 1.4:1 by ^{1}H NMR analysis of the crude mixture, which was purified by flash column chromatography (hexane/diethyl ether 97:3) to afford product **2q** (14.5 mg, 51% yield, average of two runs) as an off-white solid. The enantiomeric excess of both diastereoisomers was determined, upon sodium borohydride reduction of the isolated aldehydes to afford the corresponding alcohols, by UPC^2 analysis on a Daicel Chiralpak CEL-1 column: isocratic CO_2/*i*-90:10, flow rate 3 mL/min, λ = 220 nm. *Major diastereomer:* τ_{Major} = 3.89 min, τ_{minor} = 3.01 min. *Minor diastereomer:* τ_{Major} = 3.36 min, τ_{minor} = 2.82 min. $[\alpha]_D^{26}$ = –64.7 (c = 0.43, $CHCl_3$, 1.4:1 *d.r.*, 77% ee_{major}, 76% ee_{minor}).

*Spectroscopic data for **major diastereoisomer**:*

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.63 (t, *J* = 2.0 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.33 – 7.25 (m, 5H), 7.24 – 7.15 (m, 2H), 6.92 (ddd, *J* = 14.0, 8.0, 2.0 Hz, 1H), 3.47 – 3.37 (m, 1H), 3.30 – 3.13 (m, 1H), 3.12 – 2.97 (m, 2H), 2.64 (ddd, *J* = 17.0, 10.0, 2.5 Hz, 1H), 2.44 (ddd, *J* = 17.0, 4.5, 1.5 Hz, 1H), 1.93 – 1.77 (m, 2H).

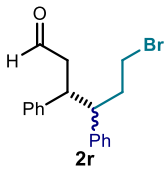
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.2, 142.3, 141.4, 129.2, 129.1, 128.2, 128.2, 127.5, 127.3, 49.4, 48.8, 46.6, 43.2, 36.9.

*Spectroscopic data for **minor diastereoisomer**:*

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.33 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.33 – 7.25 (m, 5H), 7.24 – 7.15 (m, 2H), 6.92 (ddd, *J* = 14.0, 8.0, 2.0 Hz, 1H), 3.60 – 3.51 (m, 1H), 3.47 – 3.37 (m, 1H), 3.30 – 3.13 (m, 2H), 2.95 – 2.74 (m, 2H), 2.28 – 2.06 (m, 2H) .

^{13}C NMR (101 MHz, $CDCl_3$): δ 201.6, 140.7, 139.6, 129.1, 128.9, 128.4, 128.3, 127.0, 126.9, 48.1, 47.3, 46.4, 36.0, 29.8.

HRMS (ESI) Exact mass calculated for $C_{19}H_{23}ClNaO_2$ $[M+CH_3OH+Na]^+$: 341.1279, found: 341.1268.



2r

(*R*)-6-bromo-3,4-diphenylhexanal (2r). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), (3-bromopropyl)benzene (100 mg, 0.5 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The d.r. was determined to be 1.5:1 by ^{1}H NMR analysis of the crude mixture, which was purified by flash column chromatography (hexane/diethyl ether 97:3) to afford product **2r** (13.5 mg, 41% yield, average of two runs) as an off-white solid. The enantiomeric excess of both diastereoisomers was determined, upon sodium borohydride reduction of the isolated aldehydes to afford the corresponding alcohols, by UPC^2 analysis on a Daicel Chiralpak CEL-1 column: isocratic CO_2/*i*-PrOH 90:10, flow rate 3 mL/min, λ = 205 nm. *Major diastereomer:* τ_{Major} = 4.69 min, τ_{minor} = 3.59 min. *Minor diastereomer:* τ_{Major} = 4.02 min, τ_{minor} = 3.38 min. $[\alpha]_D^{26}$ = –38.8 (c = 0.49, $CHCl_3$, 1.5:1 *d.r.*, 80% ee_{major}, 74% ee_{minor}).

*Spectroscopic data for **major diastereoisomer**:*

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.35 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.34 – 7.25 (m, 5H), 7.24 – 7.13 (m, 2H), 6.92 (ddd, *J* = 12.0, 8.0, 2.0 Hz, 1H), 3.42 (td, *J* = 10.5, 4.5 Hz, 1H), 3.20 – 2.98 (m, 2H), 2.95 – 2.76 (m, 1H), 2.64 (ddd, *J* = 17.0, 10.0, 2.5 Hz, 1H), 2.44 (ddd, *J* = 17.0, 4.5, 1.5 Hz, 1H), 2.03 – 1.83 (m, 2H).

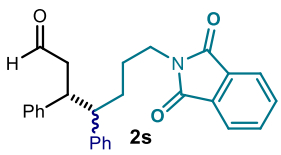
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.2, 142.2, 141.3, 129.2, 129.0, 128.2, 128.2, 127.5, 127.3, 49.8, 49.4, 46.3, 36.9, 32.1.

*Spectroscopic data for **minor diastereoisomer**:*

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.65 (t, *J* = 2.0 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.34 – 7.25 (m, 5H), 7.24 – 7.13 (m, 2H), 6.92 (ddd, *J* = 12.0, 8.0, 2.0 Hz, 1H), 3.60 – 3.51 (m, 1H), 3.34 – 3.26 (m, 1H), 3.20 – 2.98 (m, 2H), 2.95 – 2.76 (m, 2H), 2.35 – 2.15 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 201.5, 140.7, 139.4, 129.1, 128.9, 128.4, 128.3, 127.0, 126.9, 49.4, 47.3, 45.0, 36.1, 31.9.

HRMS (ESI) Exact mass calculated for $C_{19}H_{23}BrNaO_2$ $[M+CH_3OH+Na]^+$: 385.0774, found: 385.0768.



(*R*)-7-(1,3-dioxoisoindolin-2-yl)-3,4-diphenylheptanal (2s). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), 2-(4-phenylbutyl)isoindoline-1,3-dione (140 mg, 0.5 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 μL). The d.r. was determined to be 1.6:1 by ^{1}H NMR analysis of the crude mixture, which was purified by flash column chromatography on silica gel support (*gradient from* hexane/diethyl ether 95:5 *to* hexane/diethyl ether 70:30) to afford the *major diastereoisomer* of product **2s** (15.0 mg) as an off-white solid. Continued elution delivered the *minor diastereoisomer* of **2s** (8.7 mg) as a pale yellow solid (57% overall yield, average of two runs). The enantiomeric excess for both diastereoisomer was determined by UPC^2 analysis on a Daicel Chiralpak IC-3 column: gradient CO_2/*i*-PrOH from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 210 nm: *Major diastereomer:* τ_{major} = 3.92 min, τ_{minor} = 4.04 min; *Minor diastereomer:* τ_{major} = 4.13 min, τ_{minor} = 4.23 min.

*Characterization for **major diastereoisomer**:*

$[\alpha]_D^{26}$ = –191.0 (c = 0.18, $CHCl_3$, 83% ee_{major}).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.33 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.78 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.34 (ddd, *J* = 7.0, 7.0, 1.0 Hz, 2H), 7.28 – 7.20 (m, 7H), 7.16 – 7.08 (m, 1H), 3.52 – 3.39 (m, 2H), 3.34 (ddd, *J* = 10.5, 10.0, 4.5 Hz, 1H), 2.79 (ddd, *J* = 10.5, 10.5, 2.5 Hz, 1H), 2.59 (ddd, *J* = 17.0, 10.0, 2.5 Hz, 1H), 2.41 (ddd, *J* = 17.0, 4.5, 1.5 Hz, 1H), 1.54 – 1.43 (m, 2H), 1.41 – 1.33 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 201.4, 168.2, 142.5, 142.3, 133.8, 132.0, 128.8, 128.6, 128.2, 128.0, 127.0, 126.8, 123.1, 51.2, 49.0, 46.6, 37.4, 30.7, 26.1.

HRMS (ESI) Exact mass calculated for $C_{27}H_{25}NNaO_3$ $[M+Na]^+$: 434.1727, found: 434.1716.

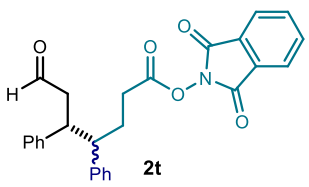
*Characterization for **minor diastereoisomer**:*

$[\alpha]_D^{26}$ = +62.7 (c = 0.21, $CHCl_3$, 80% ee_{minor}).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.61 (t, *J* = 2.0 Hz, 1H), 7.84 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.21 – 7.10 (m, 6H), 6.94 – 6.83 (m, 4H), 3.70 – 3.56 (m, 2H), 3.50 (ddd, *J* = 9.0, 6.5, 6.0 Hz, 1H), 2.94 (ddd, *J* = 11.0, 6.5, 4.5 Hz, 1H), 2.86 (ddd, *J* = 17.0, 6.0, 2.0 Hz, 1H), 2.77 (ddd, *J* = 17.0, 9.0, 2.0 Hz, 1H), 1.85 – 1.75 (m, 1H), 1.75 – 1.65 (m, 1H), 1.58 – 1.47 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 201.9, 168.4, 140.8, 140.7, 133.9, 132.1, 128.9, 128.8, 128.0 (*2 signals*), 126.6, 126.5, 123.2, 50.5, 47.0, 45.4, 37.7, 29.6, 26.7.

HRMS (ESI) Exact mass calculated for $C_{27}H_{25}NNaO_3$ $[M+Na]^+$: 434.1727, found: 434.1722.



1,3-dioxoisoindolin-2-yl (*5R*)-7-oxo-4,5-diphenylheptanoate (2t). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate (155 mg, 0.5 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The d.r. was determined to be 1.5:1 by ^{1}H NMR analysis of the crude mixture, which was purified by flash column chromatography on *neutral* silica gel support in order to prevent hydrolization of the product (*gradient from* hexane/diethyl ether 90:10 *to* hexane/diethyl ether 40:60) to afford the *major diastereoisomer* of product **2t** (14.3 mg) as an off-white solid. Continued elution delivered the *minor diastereoisomer* of **2t** (8.3 mg) as an amber wax (51% overall yield, average of two runs). The enantiomeric excess for both diastereoisomer was determined, upon sodium borohydride reduction of the isolated aldehydes to afford the corresponding diols, by UPC^2 analysis on a Daicel Chiralpak CEL-1 column: gradient CO_2/EtOH from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 215 nm: *Major diastereomer:* τ_{major} = 4.43 min, τ_{minor} = 4.29 min; *Minor diastereomer:* τ_{major} = 4.43 min, τ_{minor} = 4.34 min.

*Characterization for **major diastereoisomer**:*

$[\alpha]_D^{26}$ = –11.2 (c = 0.12, $CHCl_3$, 80% ee_{major}).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.32 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.86 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.77 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.38 (dd, *J* = 8.5, 6.5 Hz, 2H), 7.34 – 7.26 (m, 7H), 7.24 – 7.20 (m, 1H), 3.38 (td, *J* = 11.0, 4.5 Hz, 1H), 2.95 (td, *J* = 11.0, 3.5 Hz, 1H), 2.65 – 2.58 (m, 2H), 2.42 (ddd, *J* = 17.0, 4.5, 1.5 Hz, 1H), 2.34 (ddd, *J* = 16.5, 8.0, 5.0 Hz, 1H), 2.25 – 2.18 (m, 1H), 1.94 – 1.84 (m, 1H), 1.81 – 1.72 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 201.5, 169.5, 162.3, 142.4, 141.7, 135.1, 129.5, 129.3, 128.7, 128.4, 127.9, 127.5, 125.9, 124.3, 50.6, 49.7, 47.0, 29.4, 29.2.

HRMS (ESI) Exact mass calculated for $C_{27}H_{23}NNaO_5$ $[M+Na]^+$: 464.1468, found: 464.1481.

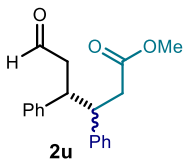
*Characterization for **minor diastereoisomer**:*

$[\alpha]_D^{26}$ = +10.2 (c = 0.09, $CHCl_3$, 83% ee_{minor}).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.62 (t, *J* = 2.0 Hz, 1H), 7.88 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.21 – 7.09 (m, 6H), 6.95 – 6.88 (m, 4H), 3.57 – 3.51 (m, 1H), 3.03 (ddd, *J* = 11.0, 7.0, 3.5 Hz, 1H), 2.93 (ddd, *J* = 17.0, 6.0, 2.0 Hz, 1H), 2.82 (ddd, *J* = 17.0, 9.0, 2.0 Hz, 1H), 2.54 – 2.45 (m, 1H), 2.41 – 2.25 (m, 3H), 2.08 – 1.98 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 201.5, 169.4, 161.9, 140.7, 139.6, 134.8, 128.9 (*2 signals*), 128.7, 128.3, 128.1, 126.9, 126.7, 124.0, 49.9, 47.3, 45.2, 29.3, 28.1.

HRMS (ESI) Exact mass calculated for $C_{27}H_{23}NNaO_5$ $[M+Na]^+$: 464.1468, found: 464.1464.



methyl (*4R*)-6-oxo-3,4-diphenylhexanoate (2u). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), methyl 3-phenylpropionate (82 mg, 0.5 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The d.r. was determined to be 1.1:1 by ^{1}H NMR analysis of the crude mixture, which was purified by flash column chromatography (*gradient from* hexane/diethyl ether 95:5 *to* hexane/diethyl ether 75:25) to afford the *major diastereoisomer* of product **2u** (7.3 mg) as a colourless solid. Continued elution delivered the *minor diastereoisomer* of **2u** (5.9 mg) as a colourless oil (45% overall yield, average of two runs). The enantiomeric excess of both diastereoisomers was determined by HPLC analysis on a Daicel

Chiralpak IC-3 column: 80:20 hexane/*i*-PrOH, flow rate 1.0 mL/min, λ = 215 nm. *Major diastereomer:* τ_{Major} = 11.1 min, τ_{minor} = 14.3 min. *Minor diastereomer:* τ_{Major} = 16.0 min, τ_{minor} = 14.4 min.

Characterization for ***major diastereoisomer****:*

$[\alpha]_D^{26}$ = +18.3 (c = 0.04, $CHCl_3$, 82% *ee*).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.35 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.41 – 7.24 (m, 10H), 3.46 – 3.31 (m, 2H), 3.40 (s, 3H), 2.67 (ddd, *J* = 17.0, 9.5, 2.5 Hz, 1H), 2.55 – 2.38 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.8, 172.3, 141.7, 141.6, 129.0, 128.8, 128.2, 128.1, 127.3 (*2 signals*), 51.3, 48.7, 47.9, 45.9, 39.5.

HRMS (ESI) Exact mass calculated for $C_{19}H_{20}NaO_3$ $[M+Na]^+$: 319.1305, found: 319.1307.

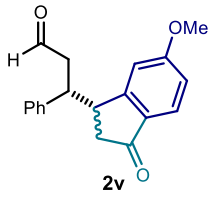
Characterization for ***minor diastereoisomer****:*

$[\alpha]_D^{26}$ = +18.3 (c = 0.07, $CHCl_3$, 82% *ee*).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.61 (t, *J* = 2.0 Hz, 1H), 7.26 – 7.16 (m, 6H), 6.95 – 6.87 (m, 4H), 3.66 – 3.59 (m, 1H), 3.59 (s, 3H), 3.56 – 3.51 (m, 1H), 2.83 – 2.79 (m, 2H), 2.76 (dd, *J* = 16.0, 6.5 Hz, 1H), 2.65 (dd, *J* = 16.0, 8.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 201.3, 172.5, 139.9, 139.7, 128.9, 128.7, 128.1, 128.0, 127.0, 126.9, 51.7, 46.5, 46.5, 44.2, 37.4.

HRMS (ESI) Exact mass calculated for $C_{19}H_{20}NaO_3$ $[M+Na]^+$: 319.1305, found: 319.1295.



2v

(*R*)-3-(6-methoxy-3-oxo-2,3-dihydro-1H-inden-1-yl)-3-phenylpropanal (2v) Prepared according to the general procedure using cinnamaldehyde (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), 5-methoxy-2,3-dihydro-1H-inden-1-one (162 mg, 1 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The d.r. was determined to be 1.9:1 by ^{1}H NMR analysis of the crude mixture, which was purified by flash column chromatography (*gradient from* hexane/diethyl ether 90:10 *to* hexane/diethyl ether 80:20, two consecutive purifications) to afford the *minor diastereoisomer* of product **2v** (7.6 mg) as an off-white solid. Continued elution delivered the *major diastereoisomer* of **2v** (9..4 mg) as an off-white solid (58% overall yield, average of two runs). The enantiomeric excess was determined UPC^2 analysis on a Daicel Chiralpak IC-3 column: gradient CO_2/*i*-PrOH from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 220 nm. *Major diastereomer:* τ_{major} = 4.67 min, τ_{minor} = 4.82 min. *Minor diastereomer:* τ_{major} = 4.58 min, τ_{minor} = 4.42 min. UPC^2 (Daicel Chiralpak IC-3 column, 20 °C, gradient CO_2/ *i*-PrOH from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 220 nm).

Characterization for ***major diastereoisomer****:*

$[\alpha]_D^{26}$ = –5.41 (c = 0.21 $CHCl_3$, 91% ee_{major}).

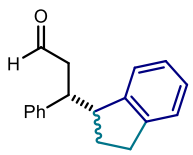
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.70 (dd, *J* = 2.0, 1.5 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.31 – 7.17 (m, 5H), 6.87 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.74 (d, *J* = 2.0 Hz, 1H), 3,83 (s, 3H), 3.62 – 3.69 (m, 1H), 3.56 (ddd, *J* = 17.5, 5.5, 1.5 Hz, 1H), 3.04 – 2.91 (m, 3H), 2.69 (d, *J* = 13.5 Hz, 1H);

^{13}C NMR (128 MHz, $CDCl_3$) δ 205.1, 200.1, 165.5, 156.0, 141.9, 130.0, 128.7, 128.2, 127.0, 125.7, 115.5, 109.4, 55.6, 51.2, 48.2, 41.0, 29.7;

Characterization data for ***minor diastereoisomer***

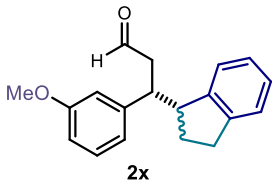
$[\alpha]_D^{26}$ = –23.85 (c = 0.08, $CHCl_3$, 86% ee_{minor}).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.71 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.30 – 7.14 (m, 5H), 6.87 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.79 (bs, 1H), 3.97 (ddd, *J* = 9.5, 6.0, 4.0 Hz, 1H), 3,85 (s, 3H), 3.08 (qd, *J* = 8.0, 4.5 Hz, 2H), 3.03 – 2.87 (m, 3H);
^{13}C NMR (128 MHz, $CDCl_3$) δ 205.4, 201.5, 165.6, 156.6, 141.2, 130.8, 128.8, 128.2, 127.2, 125.7, 115.7, 109.6, 55.8, 51.2, 44.8, 40.1, 29.8;
HRMS (ESI) Exact mass calculated for $C_{19}H_{18}NaO_3$ $[M+Na]^+$: 317.1148, found: 317.1148.



2w

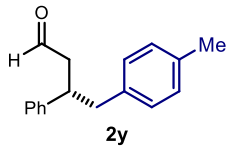
(3*R*)-3-(2,3-dihydro-1H-inden-1-yl)-3-phenylpropanal (2w). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), indane (118 mg, 1 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The d.r. was determined to be 1.1:1 by ^{1}H NMR analysis of the crude mixture, which was purified by flash column chromatography (hexane/diethyl ether 95:5) to afford product **2w** (23.7 mg, 91% yield, 1.1:1 mixture of diastereoisomers, average of two runs) as a pale yellow oil. The enantiomeric excess of both diastereoisomers was determined, upon sodium borohydride reduction of the isolated aldehydes to afford the corresponding alcohols, by HPLC analysis on a Daicel Chiralpak IC-3 column, 98.5:1.5 hexane/*i*-PrOH, flow rate 1.2 mL/min, T = 30 °C, λ = 215 nm. *Major diastereomer:* τ_{minor} = 45.9 min, τ_{major} = 62.2 min. *Minor diastereomer:* τ_{major} = 43.7 min, τ_{minor} = 52.1 min. $[\alpha]_D^{26}$ = –28.8 (c = 0.80, $CHCl_3$, 1.1:1 *d.r.*, 80% ee_{major}, 77% ee_{minor}).
*The spectroscopic data for compound **2w** were not assigned and are reported as a mixture of diastereoisomers:*
^{1}H NMR (400 MHz, $CDCl_3$, isolated as a 1.1:1 mixture of diastereoisomers) δ 9.60 (dd, *J* = 2.5, 1.7 Hz, 1H), 9.57 (t, *J* = 2.1 Hz, 1H), 7.33 – 7.11 (m, 16H), 7.07 (app t, *J* = 7.2 Hz, 1H), 6.88 (d, *J* = 7.5 Hz, 1H), 3.65 – 3.58 (m, 1H), 3.53 (q, *J* = 6.4 Hz, 1H), 3.43 – 3.35 (m, 2H), 2.96 – 2.83 (m, 3H), 2.80 – 2.60 (m, 5H), 2.20 – 2.11 (m, 1H), 2.10 – 1.99 (m, 1H), 1.97 – 1.88 (m, 1H), 1.87 – 1.79 (m, 1H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 201.8, 144.9, 144.8, 144.7, 144.3, 142.4, 142.0, 128.5, 128.4, 128.3, 128.2, 127.0, 126.9, 126.8, 126.7, 126.0, 125.9, 125.3, 124.8, 124.6, 124.5, 50.4, 47.6, 46.1, 43.8, 43.6, 31.2, 30,7, 29.3, 29.1;
HRMS (ESI) Exact mass calculated for $C_{19}H_{22}NaO_2$ $[M+CH_3OH+Na]^+$: 305.1512, found: 305.1516.



2x

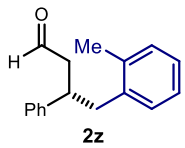
(3*R*)-3-(2,3-dihydro-1H-inden-1-yl)-3-(3-methoxyphenyl)propanal (2x). Prepared according to the general procedure using enal **1u** (16.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), indane (118 mg, 1 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The d.r. was determined to be 1.4:1 by ^{1}H NMR analysis of the crude mixture, was purified by flash column chromatography (hexane/diethyl ether 95:5) to afford product **2x** (18.0 mg, 64% yield, 1.4:1 mixture of diastereoisomers, average of two runs) as a pale yellow oil. The enantiomeric excess of both diastereoisomers was determined, upon sodium borohydride reduction of the isolated aldehydes to afford the corresponding alcohols, by UPC^2 analysis on a Daicel Chiralpak ID-3 column: gradient CO_2/*i*PrOH from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 273 nm: *Minor diastereomer:* τ_{major} = 3.35 min, τ_{minor} = 3.48 min; *Major diastereomer:* τ_{major} = 3.40 min, τ_{minor} = 3.67 min. $[\alpha]_D^{26}$ = –24.0 (c = 0.55, $CHCl_3$, 1.4:1 *d.r.*, 86% ee_{Major}, 82% ee_{minor}).
*Spectroscopic data for **major diastereoisomer**:*

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (dd, *J* = 2.5, 1.5 Hz, 1H, *A*), 7.30 – 7.25 (m, 1H), 7.23 – 7.12 (m, 3H,), 7.11 – 7.04 (m, 1H), 6.81 – 6.73 (m, 2H), 6.66 (t, *J* = 2.0 Hz, 1H), 3.74 (s, 3H), 3.63 – 3.47 (m, 1H), 3.41 – 3.32 (m, 1H), 2.93 – 2.60 (m, 4H), 2.23 – 1.99 (m, 1H), 1.97 – 1.90 (m, 1H);
Spectroscopic data for ***minor diastereoisomer****:*
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (t, *J* = 2.0 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.23 – 7.12 (m, 3H), 7.11 – 6.93 (d, 7.07 *J* = 7.5 Hz, 1H), 6.81 – 6.73 (m, 2H), 6.62 (t, *J* = 2.0 Hz, 1H), 3.72 (s, 3H), 3.63 – 3.47 (m, 1H), 3.41 – 3.32 (m, 1H), 2.93 – 2.60 (m, 4H), 2.23 – 1.99 (m, 1H), 1.97 – 1.90 (m, 1H);
The signals relative to ^{13}C NMR analysis were not assigned and are reported as a mixture of diastereoisomers:
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 202.0, 159.8, 159.6, 145.1, 145.0, 144.9, 144.4, 144.1, 143.7, 129.6, 129.5, 127.2, 127.1, 126.2, 126.0, 125.4, 125.0, 124.7, 124.7, 120.8, 120.6, 114.4, 114.1, 112.3, 112.1, 55.3, 50.4, 47.7, 46.2, 44.0, 43.7, 31.7, 30.9, 29.3.
HRMS (ESI) Exact mass calculated for $C_{19}H_{20}NaO_2$ $[M+Na]^+$: 303.1356, found: 303.1368.



2y

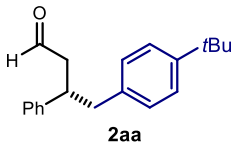
(*S*)-3-phenyl-4-(*p*-tolyl)butanal (2y). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), *p*-xylene (134 mg, 1 mmol), trichloroacetic acid (16.3 mg, 100 mol%) and dichloromethane (300 µL). The crude mixture was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **2y** (15.0 mg, 63% yield, 83% ee, average of two runs) as a colourless oil that displayed spectroscopic data consistent with those reported previously.[2] The enantiomeric excess was determined to be 83% by HPLC analysis on a Daicel Chiralpak IC-3 column: 96:4 hexane/*i*-PrOH, flow rate 0.8 mL/min, λ = 215 nm: τ_{major} = 12.1 min, τ_{minor} = 13.1 min. $[\alpha]_D^{26}$ = -17.3 (c = 0.45, $CHCl_3$, 83% ee); Lit: $[\alpha]_D^{26}$ = -50.8 (c = 0.69, $CHCl_3$, 91% ee for (*S*)-enantiomer).[2]
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.58 (t, *J* = 2.0 Hz, 1H), 7.31–7.26 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 3.46 (p, 7.04 (d, *J* = 7.5 Hz, 1H) 2.94 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.83 (dd, *J* = 13.5, 8.0 Hz, 1H), 2.78 – 2.68 (m, 2H), 2.29 (s, 3H);
^{13}C NMR (125.8 MHz, $CDCl_3$): δ 201.8, 143.5, 136.3, 136.0, 129.2, 129.2, 128.7, 127.7, 126.8, 49.1, 43.0, 42.2, 21.2.



2z

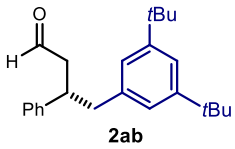
(*S*)-3-phenyl-4-(*o*-tolyl)butanal (2z). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), *o*-xylene (134 mg, 1 mmol), trichloroacetic acid (16.3 mg, 100 mol%) and dichloromethane (300 µL). The crude mixture was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **2z** (11.0 mg, 47% yield, 77% ee, average of two runs) as a colourless oil that displayed spectroscopic data consistent with those reported previously.[2] The enantiomeric excess was determined to be 77% by HPLC analysis on a Daicel Chiralpak IC-3 column: 90:10 hexane/*i*-PrOH, flow rate 0.7 mL/min, λ = 215 nm: τ_{major} = 10.5 min, τ_{minor} = 11.9 min. $[\alpha]_D^{26}$ = -40.7 (c = 0.23, $CHCl_3$, 77% ee); Lit: $[\alpha]_D^{26}$ = -22.2 (c = 0.59, $CHCl_3$, 90% ee for (*S*)-enantiomer).[2]
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.57 (t, *J* = 1.9 Hz, 1H), 7.32–7.25 (m, 2H), 7.23–7.03 (m, 6H), 6.97 (d, *J* = 7.0 Hz, 1H), 6.78 (s, 1H), 3.47 (p, *J* = 7.4 Hz, 1H), 2.97 – 2.86 (m, *2*H), 2.85 – 2.72 (m, 2H), 2.26 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 201.7, 143.6, 137.7, 136.5, 130.6, 130.3, 128.8, 127.6, 126.9, 126.7, 125.9, 49.0, 41.0, 19.6.



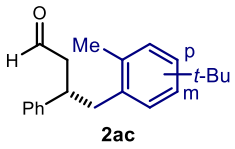
2aa

(*S*)-4-(4-(tert-butyl)phenyl)-3-phenylbutanal (2aa). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), 1-(*t*-butyl)-4-methylbenzene (148 mg, 1 mmol), trichloroacetic acid (16.3 mg, 100 mol%) and dichloromethane (300 µL). The crude mixture was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **2aa** (15.0 mg, 53% yield, 77% ee, average of two runs) as a colourless oil. The enantiomeric excess was determined, upon sodium borohydride reduction of the isolated aldehyde to afford the corresponding alcohol, to be 77% by HPLC analysis on a Daicel Chiralpak IC-3 column: 90:10 hexane/*i*-PrOH, flow rate 0.6 mL/min, λ = 215 nm: τ_{Major} = 10.9 min, τ_{minor} = 12.2 min. $[\alpha]_D^{26}$ = -33.4 (c = 0.63, $CHCl_3$, 78% ee).
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.57 (t, *J* = 2.0 Hz, 1H), 7.33–7.22 (m, 4H), 7.24–7.18 (m, 3H), 7.02 (d, *J* = 8.2 Hz, 2H), 3.54 – 3.47 (m, 1H), 3.00 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.85 (dd, *J* = 13.6, 8.6 Hz, 1H) 2.81 – 2.69 (m, 2H), 1.32 (s, 9H);
^{13}C NMR (125.8 MHz, $CDCl_3$): δ 202.0, 149.4, 143.7, 136.3, 129.0, 128.8, 127.6, 126.9, 125.4, 48.9, 42.9, 42.1, 34.5, 31.5.
HRMS (ESI) Exact mass calculated for $C_{21}H_{28}NaO_2$ $[M+CH_3OH+Na]^+$: 335.1980, found: 335.1982.



2ab

(*S*)-4-(3,5-di-tert-butylphenyl)-3-phenylbutanal (2ab). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), 1,3-di-*t*-butyl-5-methylbenzene (204 mg, 1 mmol), trichloroacetic acid (16.3 mg, 100 mol%) and dichloromethane (300 µL). The crude mixture was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **2ab** (20.0 mg, 59% yield, 74% ee, average of two runs) as a colourless oil. The enantiomeric excess was determined to be 74% by HPLC analysis on a Daicel Chiralpak IC-3 column: 98:2 hexane/*i*-PrOH, flow rate 0.6 mL/min, λ = 215 nm: τ_{Major} = 10.9 min, τ_{minor} = 12.2 min. $[\alpha]_D^{26}$ = -19.1 (c = 0.73, $CHCl_3$, 74% ee).
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.59 (t, *J* = 2.0 Hz, 1H), 7.30–7.25 (m, 2H), 7.23–7.17 (m, 2H), 7.14 (d, *J* = 6.8 Hz, 2H), 6.82 (d, *J* = 1.8 Hz, 2H), 3.45 (p, *J* = 7.4 Hz, 1H), 2.95 (dd, *J* = 13.4, 7.2 Hz, 1H), 2.87 (dd, *J* = 13.4, 7.6 Hz, 1H) 2.81 – 2.72 (m, 2H), 1.26 (s, 18H);
^{13}C NMR (125.8 MHz, $CDCl_3$): δ 202.0, 150.7, 143.5, 138.2, 128.7, 127.8, 126.8, 123.7, 120.2, 49.0, 44.1, 42.4, 34.8, 31.5.
HRMS (ESI) Exact mass calculated for $C_{24}H_{32}NaO$ $[M+Na]^+$: 359.2348, found: 359.2345.



2ac

(*S*)-4-(4-(tert-butyl)-2-methylphenyl)-3-phenylbutanal *and* **(S)-4-(5-(tert-butyl)-2-methylphenyl)-3-phenylbutanal (2ac).** Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), 4-(*t*-butyl)-1,2-dimethylbenzene (134 mg, 1 mmol), trichloroacetic acid (16.3 mg, 100 mol%) and dichloromethane (300 µL). The regioisomeric ratio was determined to be 6.5:1 by ^{1}H NMR analysis of the crude mixture, which was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **2ac** (18.0 mg, 60% yield, average of two runs) as a colourless oil. The enantiomeric excess was determined, upon

sodium borohydride reduction of the isolated aldehyde to afford the corresponding alcohol, to be 73% for the major regioisomer and 74% for the minor by UPC^2 analysis on CEL1 chiral column: 95:5 CO_2/EtOH, curve 6, flow rate 3 mL/min, λ = 203 nm. *Minor regioisomer:* τ_{minor} = 1.51 min, τ_{major} = 1.85 min; *major regioisomer:* τ_{minor} = 1.63 min, τ_{major} = 1.97 min. $[\alpha]_D^{26}$ = -15.6 (c = 0.25, $CHCl_3$, 6.5:1 *regioisomeric ratio*, 73% ee_{major}, 74% ee_{minor}).

*Spectroscopic data for **major regioisomer (2ac-p)**:*

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.55 (t, *J* = 2.0 Hz, 1H), 7.33–7.26 (m, 2H), 7.24–7.18 (m, 3H), 7.16–7.04 (m, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 3.50 – 3.41 (m, 1H), 2.94 (dd, *J* = 14.0, 6.0 Hz, 1H), 2.90 – 2.60 (m, 3H), 2.28 (s, 3H), 1.29 (s, 9H);

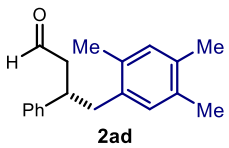
^{13}C NMR (101 MHz, $CDCl_3$): δ 202.0, 149.5, 143.9, 143.6, 135.9, 134.6, 129.9, 128.8, 127.5, 126.9, 122.9, 48.8, 40.9, 40.6, 34,4, 31.5, 19.9.

*Spectroscopic data for **minor regioisomer (2ac-m)**:*

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.60 (t, *J* = 2.0 Hz, 1H), 7.33–7.26 (m, 2H), 7.24–7.18 (m, 3H), 7.16–7.04 (m, 2H), 6.82 (d, *J* = 2.0 Hz, 1H), 3.50–3.41 (m, 1H), 2.94 (dd, *J* = 14.0, 6.0 Hz, 1H), 2.90–2.60 (m, 3H), 2.27 (s, 3H), 1.19 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 201.8, 148.6, 137.0, 133.3, 130.2, 128.7, 127.7, 126.8, 123.4, 49.2, 41.4, 40.9, 34.2, 31.4, 19.0.

HRMS (ESI) Exact mass calculated for $C_{22}H_{30}NaO_2$ $[M+CH_3OH+Na]^+$: 349.2154, found: 349.2138.



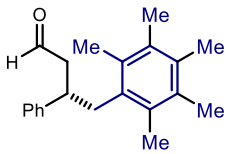
2ad

(*S*)-3-phenyl-4-(2,4,5-trimethylphenyl)butanal (2ad). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), 1,2,4,5-tetramethylbenzene (134 mg, 1 mmol), trichloroacetic acid (16.3 mg, 100 mol%) and dichloromethane (300 µL). The crude mixture was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **2ad** (18.0 mg, 68% yield, 82% ee, average of two runs) as a colourless oil. The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC-3 column: 90:10 hexane/*i*-PrOH, flow rate 0.6 mL/min, λ = 215 nm: τ_{Major} = 11.1 min, τ_{minor} = 12.0 min. $[\alpha]_D^{26}$ = -32.7 (c = 0.50, $CHCl_3$, 82% ee).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.54 (t, *J* = 2.0 Hz, 1H), 7.32–7.27 (m, 2H), 7.23 – 7.18 (m, 3H), 6.90 (s, 1H), 6.78 (s, 1H), 3.47 – 3.40 (m, 1H), 2.89 (dd, *J* = 13.7, 6.2 Hz, 1H), 2.82 – 2.71 (m, 3H), 2.19 (s, 6H), 2.17 (s, 6H);

^{13}C NMR (125.8 MHz, $CDCl_3$): δ 202.0, 144.0, 134.9, 134.7, 133.9, 133.6, 131.9, 131.6, 128.8, 127.5, 126.8, 48.8, 41.2, 40.6, 19.3, 19.0.

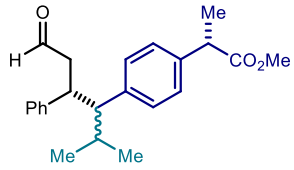
HRMS (ESI) Exact mass calculated for $C_{20}H_{26}NaO_2$ $[M+CH_3OH+Na]^+$: 321.1828, found: 321.1825.



2ae

(*S*)-4-(2,3,4,5,6-pentamethylphenyl)-3-phenylbutanal (2ae). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), hexamethylbenzene (162 mg, 1 mmol), trichloroacetic acid (16.3 mg, 100 mol%) and dichloromethane (300 µL). The crude mixture was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **2ae** (22.2 mg, 75% yield, 82% ee, average of two runs) as off-white solid. The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC-3 column: 90:10 hexane/*i*-PrOH, flow rate 0.6 mL/min, λ = 215 nm: τ_{major} = 11.1 min, τ_{minor} = 14.7 min. $[\alpha]_D^{26}$ = -23.6 (c = 0.50, $CHCl_3$, 82% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.47 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.35–7.30 (m, 2H), 7.30–7.20 (m, 3H), 3.42 (tt, *J* = 10.0, 5.5 Hz 1H), 3.11 (dd, *J* = 14.5, 9.5 Hz, 1H), 3.00 (dd, *J* = 14.5, 5.5 Hz, 1H), 2.86 (ddd, *J* = 16.5, 10.0, 2.5 Hz, 1H), (ddd, *J* = 16.5, 5.0, 2.0 Hz, 1H), 2.26 (s, 3H), 2.23 (s, 12H);
^{13}C NMR (101 MHz, $CDCl_3$): δ 202.2, 144.1, 133.4, 133.3, 132.9, 132.4, 128.8, 127.4, 126.9, 47.9, 41.3, 37.9, 17.3, 17.1, 17.1.
HRMS (ESI) Exact mass calculated for $C_{22}H_{30}NaO_2$ $[M+CH_3OH+Na]^+$: 349.2138, found: 349.2139



4

methyl (*S*)-2-(4-((*R*)-6-methyl-1-oxo-3-phenylheptan-4-yl)phenyl) propanoate (4). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), **3** (110 mg, 0.5 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The crude mixture, which was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford product **4** (34.5 mg, 50% yield) as a colorless oil. Due two the overlap of diagnostic signals in the ^{1}H NMR spectrum, the diastereomeric ratio of the product mixture was determined, upon sodium borohydride reduction of the isolated aldehydes to afford the corresponding alcohols, *via* UPC^2 analysis to be 1:1.3:8.2:10. $[\alpha]_D^{26}$ = 42.4 (c = 0.99, $CHCl_3$, 1:1.3:8.2:10 *d.r*).
*The spectroscopic data for compound **4** were not assigned and are reported as a mixture of diastereoisomers:*
^{1}H NMR (400 MHz, $CDCl_3$, *isolated as a 1.2:1 mixture of diastereoisomers*): δ 9.64 (t, *J* = 2.0, Hz, 1H), 9.41 (dd, *J* = 2.5, 1.0 Hz, 1H), 7.35–7.28 (m, 2H), 7.26–7.19 (m, 4H), 7.14–7.08 (m, 6H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.89–6.84 (m, 2H), 6.67 (d, *J* = 8.0 Hz, 2H), 3.85 (dt, *J* = 8.5, 6.0 Hz, 1H), 3.76 – 3.61 (m, 9H), 2.84 – 2.74 (m, 2H), 2.67 (ddd, *J* = 16.5, 8.5, 2.0 Hz, 1H), 2.61 – 2.52 (m, 2H), 2.44 (ddd, *J* = 17.0, 4.0, 1.5 Hz, 1H), 2.04 – 1.93 (m, 1H), 1.69 – 1.59 (m, 1H), 1.51 (d, *J* = 7.0 Hz, 3H), 1.44 (d, *J* = 7.0 Hz, 3H), 1.13 (d, *J* = 6.5 Hz, 3H), 0.74 (d, *J* = 7.0 Hz, 3H), 0.71 (d, *J* = 6.5 Hz, 2H), 0.65 (d, *J* = 7.0 Hz, 3H);
^{13}C NMR (101 MHz, $CDCl_3$): δ 202.3, 202.1, 175.3, 175.3, 143.0, 140.8, 138.9, 138.4, 138.3, 138.2, 130.7, 129.3, 128.9, 128.2, 127.9, 127.2, 126.9, 126.6, 126.4, 57.6, 57.0, 52.2, 52.1, 49.5, 48.4, 45.1, 45.1, 42.3, 40.6, 28.8, 28.4, 22.3, 20.1, 18.8, 16.6;
HRMS (ESI) Exact mass calculated for $C_{23}H_{28}NaO_3$ $[M+Na]^+$: 375.1923, found: 375.1931.

To gain further insight about the C-ζ selectivity for the reaction between **1a** and **3**, the recovered **3** after the photochemical protocol was submitted to HPLC analysis to determine the degree of its racemization. An analogous level of enantiopurity compared to the un-submitted starting material was inferred. The lack of racemization indicates that radical formation is not occurring at C-α position of **3**.

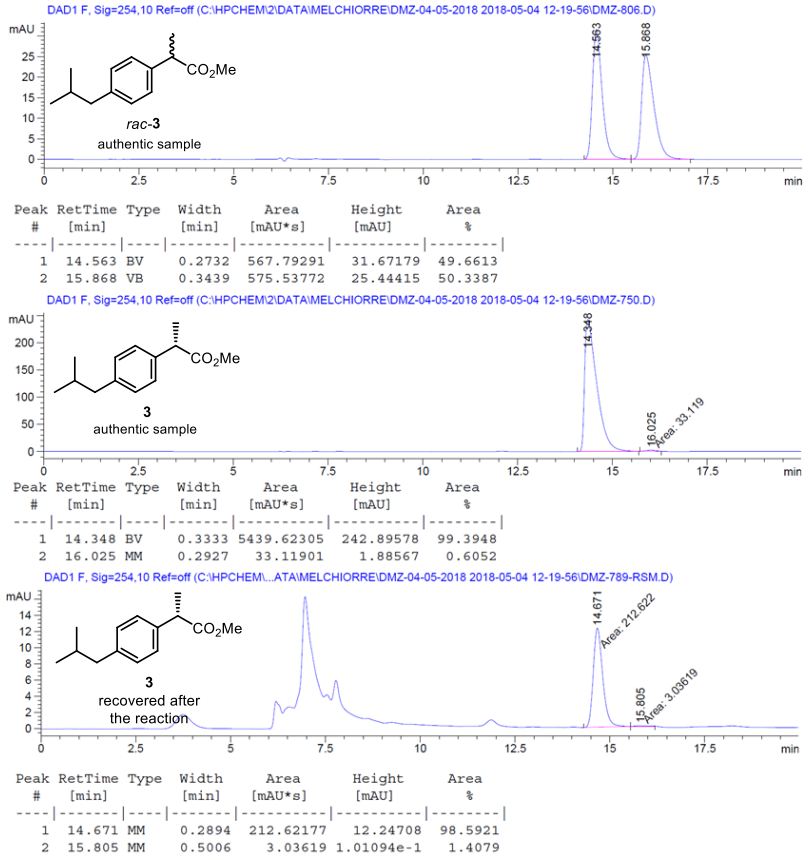
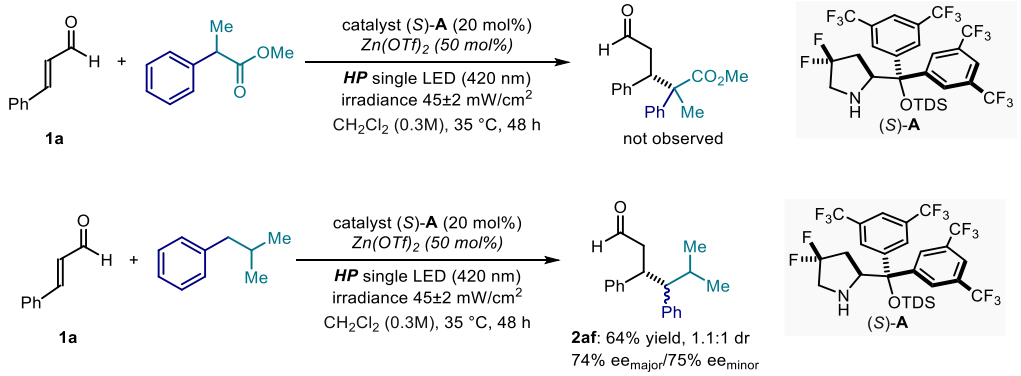
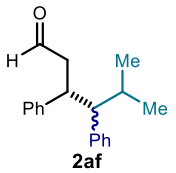


Figure S4. *HPLC analysis of an authentic sample of rac-**3**, (S)-**3** and the recovered starting material after the reaction to deliver **4**.*

We investigated the recativity of two substrates that, individually, could mimic both substitution patterns of (*S*)-ibuprofen methyl ester **3**. While methyl 2-phenylpropanoate remained completely unreacted, *iso*-butylbenzene (a secondary-carbon containing substrate) provided the corresponding product in good yield and enantioselectivity. The lack of reactivity of the former substrate is particularly informative since it mimics the tertiary carbon and the electronics of (*S*)-ibuprofen methyl ester **3**. Overall, these results indicate the difficulty to form a tertiary radical using the PCET mechanism operative in our system.





2af

(*R*)-5-methyl-3,4-diphenylhexanal (2af). Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), 1,2-diphenylethane (134 mg, 1 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The d.r. was determined to be 1.2:1 by ^{1}H NMR analysis of the crude mixture, which was purified by flash column chromatography (hexane/diethyl ether 97:3) to afford product **2af** (17 mg, 64% yield, average of two runs) as a pale-yellow oil. The enantiomeric excess of both diastereoisomers was determined, upon sodium borohydride reduction of the isolated aldehydes to afford the corresponding alcohols, by UPC^2 analysis on a Daicel Chiralpak IB column: gradient CO_2/EtOH from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 210 nm. *Major diastereomer:* τ_{Major} = 3.17 min, τ_{minor} = 2.71 min. *Minor diastereomer:* τ_{Major} = 3.51 min, τ_{minor} = 2.95 min. $[\alpha]_D^{26}$ = +53.5 (c = 0.57, $CHCl_3$, 1.2:1 *d.r.*, 74% ee_{major}, 75% ee_{minor}).

*Spectroscopic data for **major diastereoisomer**:*

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.66 (t, *J* = 2.0 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.29 – 7.20 (m, 2H), 7.19 – 7.10 (m, 4H), 6.76 – 6.71 (m, 2H), 3.87 (dt, *J* = 9.0, 6.5 Hz, 1H), 2.87 – 2.76 (m, 1H), 2.69 (ddd, *J* = 17.0, 9.0, 2.0 Hz, 1H), 2.63 – 2.54 (m, 1H), 2.03 (dp, *J* = 8.0, 7.0 Hz, 1H), 1.13 (d, *J* = 6.5 Hz, 3H), 0.76 (d, *J* = 7.0 Hz, 3H).

*Spectroscopic data for **minor diastereoisomer**:*

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.42 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.29 – 7.20 (m, 2H), 7.19 – 7.10 (m, 4H), 6.92 – 6.86 (m, 2H), 3.73 (td, *J* = 11.0, 4.0 Hz, 1H), 2.87 – 2.76 (m, 1H), 2.63 – 2.54 (m, 1H), 2.46 (ddd, *J* = 17.0, 4.0, 1.5 Hz, 1H), 1.67 (pd, *J* = 7.0, 4.0 Hz, 1H), 0.74 (d, *J* = 6.5 Hz, 3H), 0.67 (d, *J* = 7.0 Hz, 3H).

The signals relative to ^{13}C NMR analysis were not assigned and are reported as a mixture of diastereoisomers:

^{13}C NMR (125.8 MHz, $CDCl_3$) δ 202.3, 202.0, 143.1, 141.0, 139.5, 139.3, 130.6, 129.2, 128.9, 128.2, 128.1, 127.9, 127.4, 126.9, 126.8, 126.6, 126.3, 57.9, 57.4, 49.4, 48.5, 42.3, 40.6, 28.7, 28.4, 22.3, 19.8, 16.7.

D.3 Unreactive Substrates

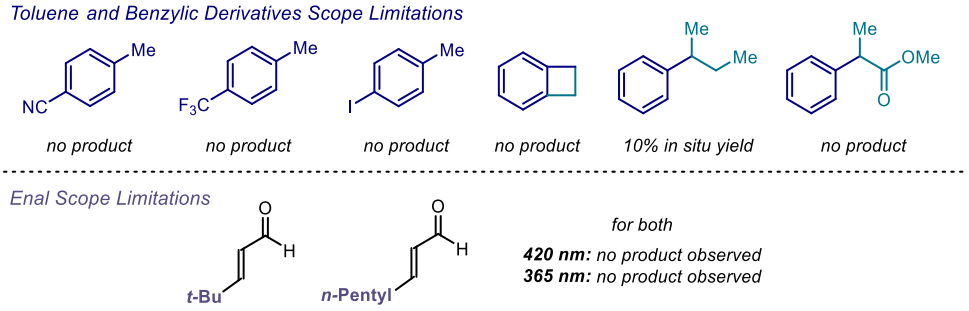
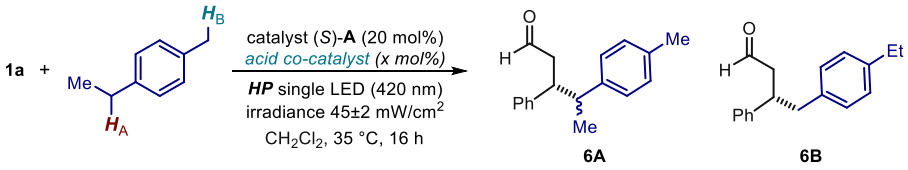


Figure S5. Survey of unreactive or scarcely reactive substrates.

E. Mechanistic Insights

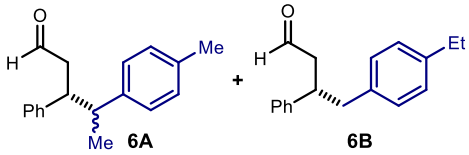
E.1. Site-selectivity study

Table S8. *Evaluating the influence of the strenght of the conjugate base on the regioselectivity*



entry	Acid	Yield (%)[a]	**6A** : **6B**[b]	dr **6A**[c]	ee **6A** (%) (major/minor)	ee **6B** (%)
1	$Zn(CF_3SO_3)_2$ (50 mol%)	63	1:6	1.7:1	76/75	77
2	TFA (100 mol%)	65	1:3.3	1.6:1	71/70	74
3	TCA (100 mol%)	62	1:3	1.5:1	73/77	71
4	DCA (100 mol%)	50	1:2.6	1.4:1	69/67	70
5	MCA (100 mol%)	-	-	-	-	-

[a] Overall isolated yields of mixtures of regioisomers **6A** and **6B.** [b] Regioisomeric ratio measured by ^{1}H NMR analysis of the crude mixture. [c] Diastereoisomeric ratio measured by ^{1}H NMR analysis of the crude mixture. TFA: trifluoroacetic acid; TCA: trichloroacetic acid; DCA: dichloroacetic acid; MCA: monochloroacetic acid.



(*3R*)-3-phenyl-4-(p-tolyl)pentanal (6A) *and* **(*S*)-4-(4-ethylphenyl)-3-phenylbutanal (6B).** Prepared according to the general procedure using enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), methyl 4-ethyltoluene (120 mg, 1 mmol), zinc(II) triflate (18.2 mg, 50 mol%) and dichloromethane (300 µL). The crude mixture was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford products **6** [16.0 mg, 63% yield, 6:1 mixture of regioisomers **6A** (1.7:1 d.r., 76% ee_{major}, 75% ee_{minor}) and **6B** (77% *ee*)] as a pale yellow oil. The enantiomeric excess of both regioisomers, and corresponding diastereoisomers for **6A**, was determined, upon sodium borohydride reduction of the isolated aldehydes to afford the corresponding alcohols, by UPC^2 analysis on a Daicel Chiralpak CEL-1 column: CO_2/MeOH 95:5, flow rate 3 mL/min, λ = 210 nm. For compound **6A**, *Major diastereomer:* τ_{Major} = 3.27 min, τ_{minor} = 2.59 min. *Minor diastereomer:* τ_{Major} = 3.47 min, τ_{minor} = 3.02 min. For compound **6B**: τ_{Major} = 4.46 min, τ_{minor} = 3.70 min.

*Spectroscopic data for compound **6A**, major diastereoisomer:*

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.47 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.48 – 7.23 (m, 7H), 7.16 – 7.10 (m, 2H), 3.40 (ddd, *J* = 10.0, 10.0, 4.5 Hz, 1H), 3.02 – 2.93 (m, 1H), 2.76 – 2.69 (m, 1H), 2.60 (ddd, *J* = 16.5, 4.5, 1.5 Hz, 1H), 2.47 (s, 3H), 1.15 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 201.8, 142.9, 142.2, 136.4, 129.5, 128.8, 128.3, 127.6, 126.9, 49.2, 47.7, 45.8, 21.2, 20.8.

*Spectroscopic data for compound **6A**, minor diastereoisomer:*

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.68 (t, *J* = 2.0 Hz, 1H), 7.48 – 7.23 (m, 7H), 7.03 – 6.99 (m, 2H), 3.64 – 3.57 (m, 1H), 3.17 (qd, *J* = 7.0, 7.0 Hz, 1H), 2.93 – 2.89 (m, 2H), 2.41 (s, 3H), 1.38 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 202.3, 141.7, 140.8, 135.9, 128.8, 128.7, 128.2, 128.1, 126.7, 46.6, 46.1, 44.6, 21.1, 18.0.

*Spectroscopic data for compound **6B**:*

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.70 (t, *J* = 2.0 Hz, 1H), 7.48 – 7.23 (m, 5H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.14 – 7.10 (m, 2H), 3.61 – 3.55 (m, 1H), 3.08 (dd, *J* = 13.5, 6.5 Hz, 1H), 3.01 – 2.93 (m, 1H), 2.88 – 2.84 (m, 2H), 2.76 – 2.69 (m, 2H), 1.34 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 201.9, 143.6, 142.4, 136.5, 129.3, 128.7, 128.0, 127.7, 126.8, 49.0, 43.1, 42.2, 28.6, 15.7.

HRMS (ESI) Exact mass calculated for $C_{19}H_{24}NaO_2$ $[M+CH_3OH+Na]^+$: 307.1669, found: 307.1665.

E.2 Determination of the Kinetic Isotope Effect (KIE)

E.2.1. Intermolecular competition experiment

A 15 mL Schlenk tube was charged with enal **1a** (13.2 mg, 0.1 mmol), aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%), zinc(II) triflate (18.2 mg, 50 mol%), and an equimolar solution of toluene (46.5 mg, 5 mmol) and toluene-d_8 (50 mg, 5 mmol) in dichloromethane (300 µL). The Schlenk tube was placed under an atmosphere of argon, cooled to – 78 °C, degassed *via* vacuum evacuation (5 min), backfilled with argon, and warmed to room temperature. The freeze-pump-thaw cycle was repeated five times, and then the Schlenk tube was sealed with Parafilm and placed into a 3D-printed plastic support mounted on an aluminium block fitted with a 420 nm high-power single LED (λ = 420 nm, irradiance = 45 mW/cm^2, as controlled by an external power supply). The reaction was stirred at ambient temperature (~35 °C) for 48 hours. The solvent was removed *in vacuo* and the crude mixture was purified by flash column chromatography (hexane/diethyl ether 92:8) to afford a mixture of product **2a** and **2a**-*d*. Integration of diagnostic peaks for **2a** in the ^{1}H NMR spectrum (specifically multiplets at 2.96 and 2.88, respectively) showed a deuterium incorporation at C**4** of 0.46D (over 2H, see figure below). Consequently, the magnitude of the kinetic isotope effect relative to the intermolecular competition was determined to be 3.3.

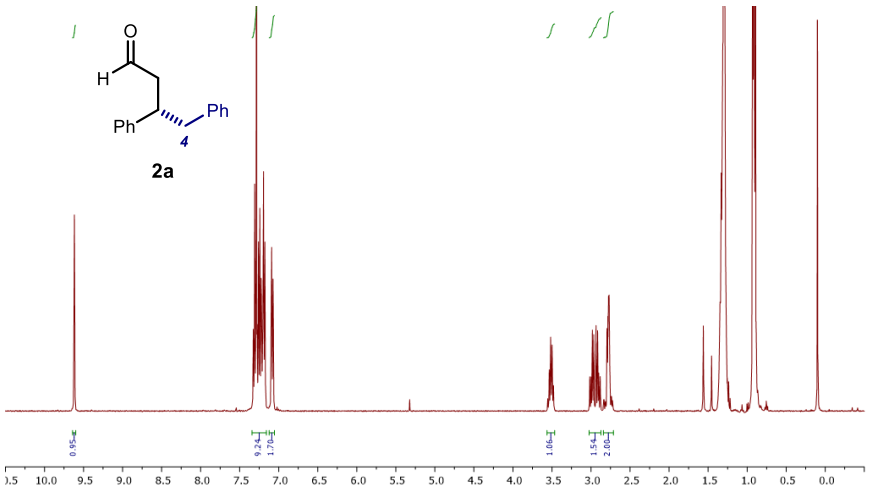
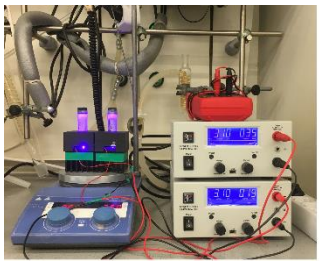
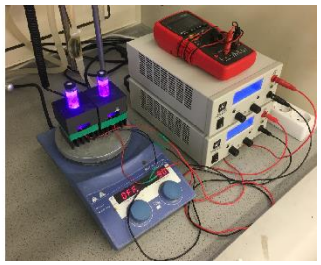


Figure S6. ^{1}H NMR analysis for the intermolecular competition experiment.

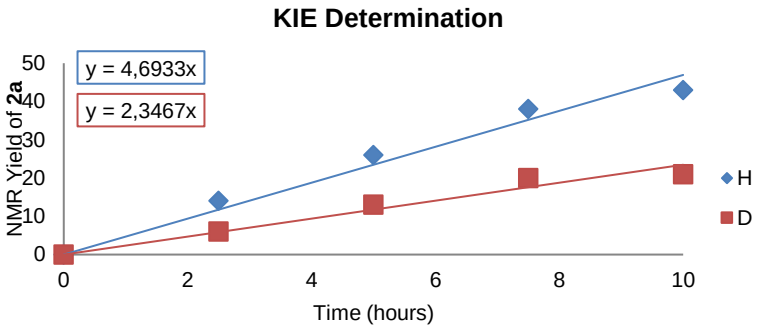
E.2.2. Parallel experiments





Two 5 mL argon-purged glass vials were charged with zinc(II) triflate (18.2 mg, 50 mol%), 300 µL of a stock solution of enal **1a** (13.2 mg, 0.1 mmol) and aminocatalyst (*S*)-**A** (14.1 mg, 20 mol%) in dichloromethane and either toluene (92.0 mg, 1 mmol) or toluene-d_8 (118 mg, 1 mmol). The vials were further flushed with argon, sealed with Parafilm, and then simoltaneously placed into two 3D-printed plastic supports mounted on an aluminium block fitted with a 420 nm high-power single LED (λ = 420 nm, irradiance = 45 mW/cm^2, as controlled by an external power supply, see figure above). The reactions were stirred under visible light irradiation at ambient temperature for the time stated for each experiment. Trichloroethylene (9 µL, 0.1 mmol) was added as the internal standard to the crude mixture and an aliquot of the resulting solution was taken to be directly analysed by ^{1}H NMR. The magnitude of the kinetic isotope effect, calculated plotting the kinetic profile of the two reactions (with toluene and toluene-d_8, respectively), was determined to be 2.00.

Time (h)	Toluene	Toluene-d_8
0	-	-
2.5	14	6
5	26	13
7.5	38	20
10	43	21



F. References

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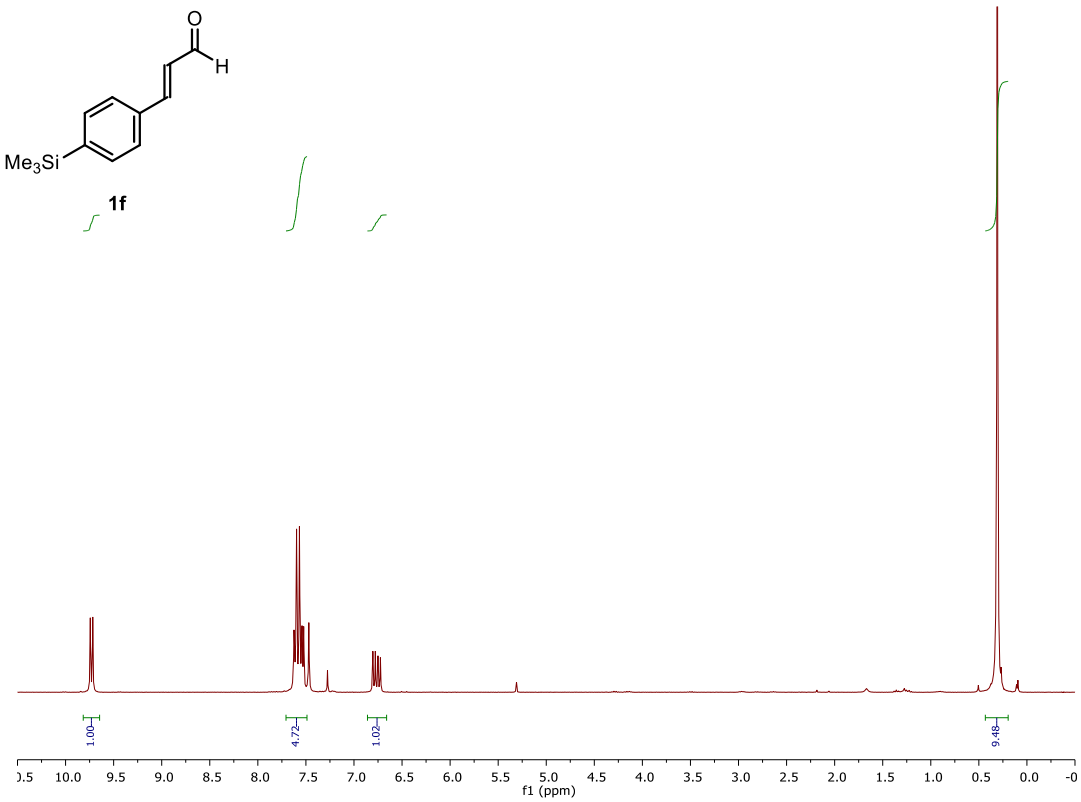
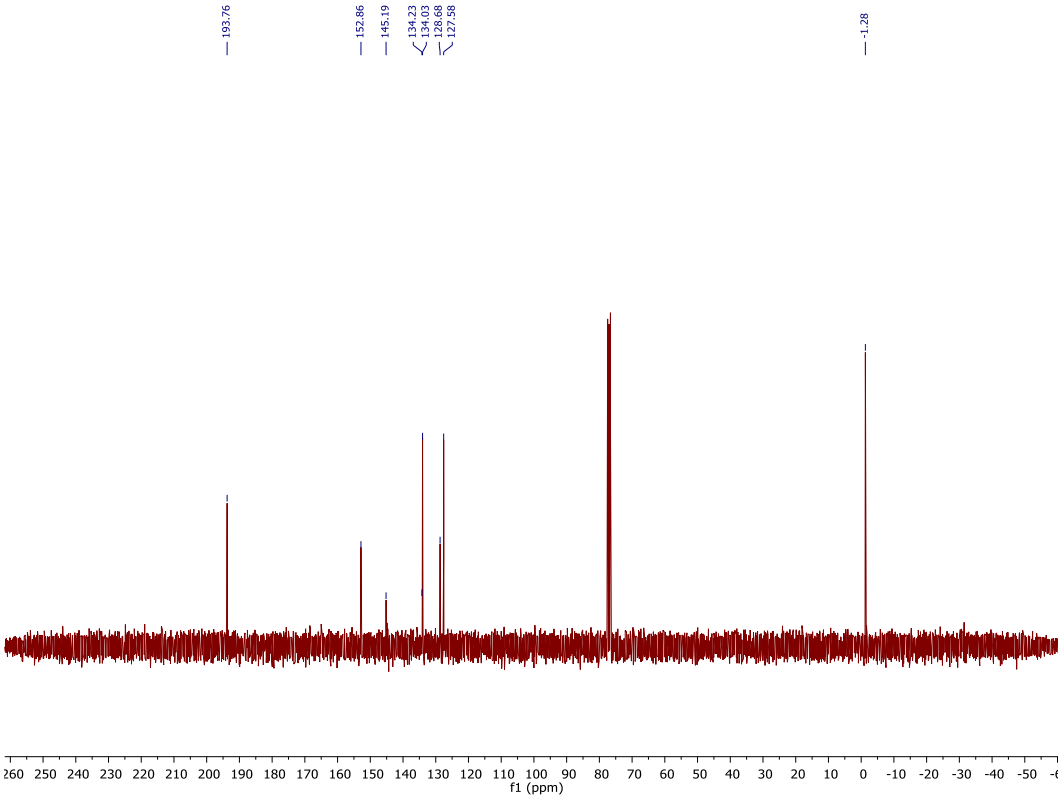
G. NMR Spectra

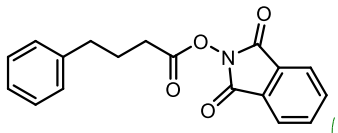
^{1}H NMR, 300 MHz, $CDCl_3$

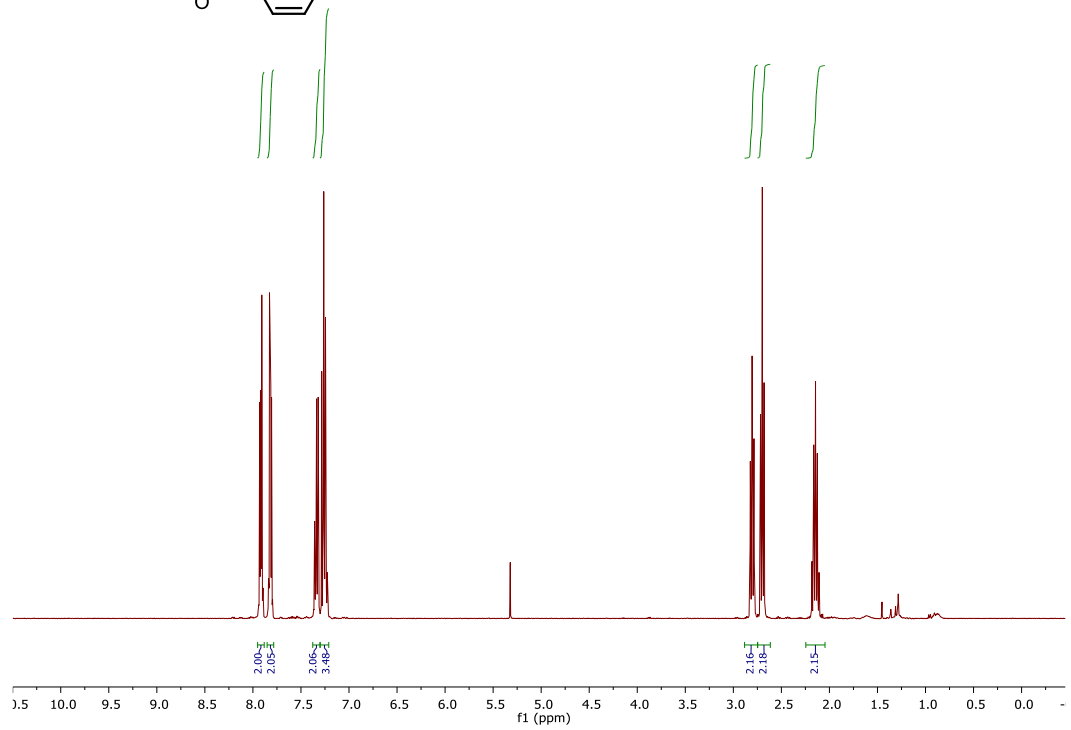


^{13}C NMR, 75 MHz, $CDCl_3$

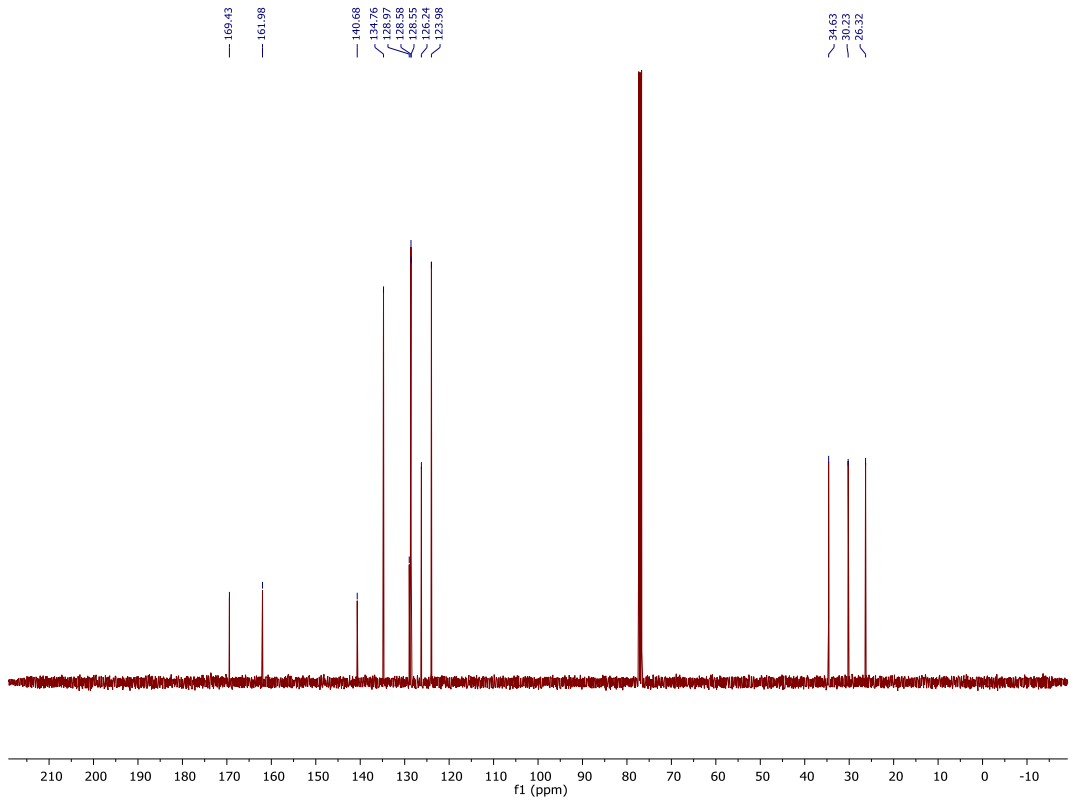


^{1}H NMR, 400 MHz, $CDCl_3$

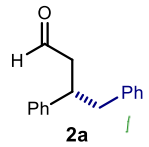




^{13}C NMR, 101 MHz, $CDCl_3$

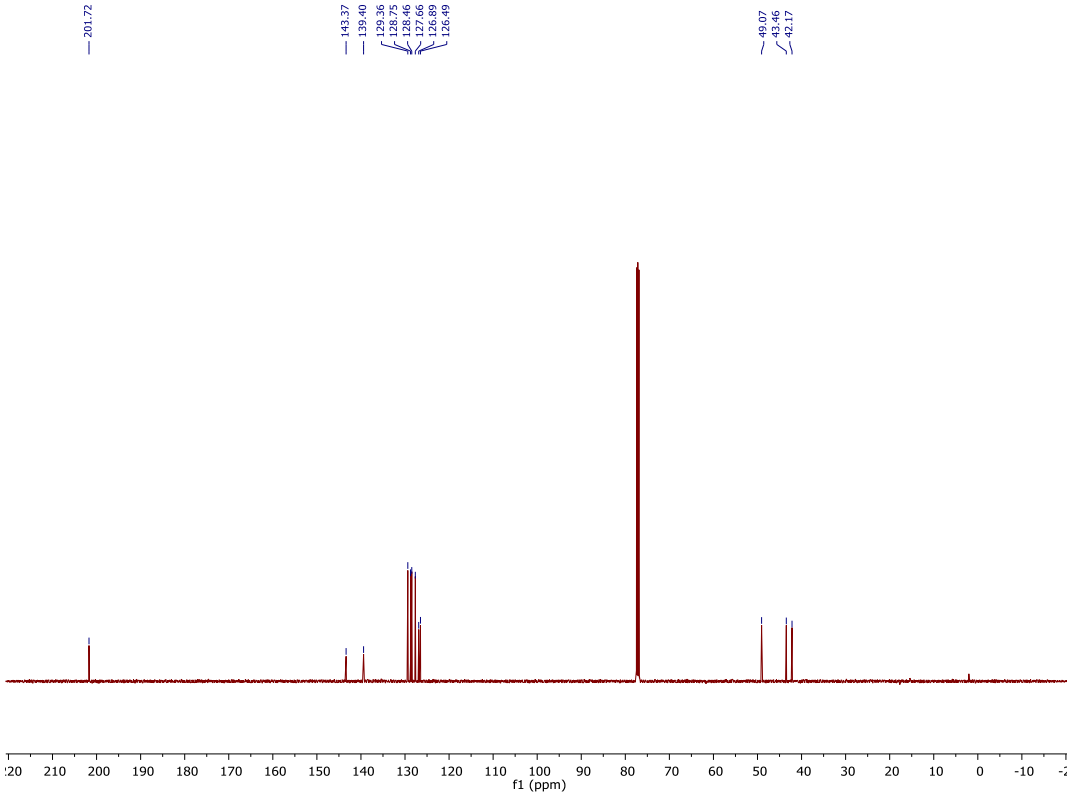


^{1}H NMR, 500 MHz, $CDCl_3$

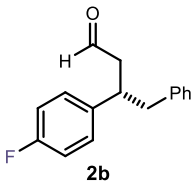


2a

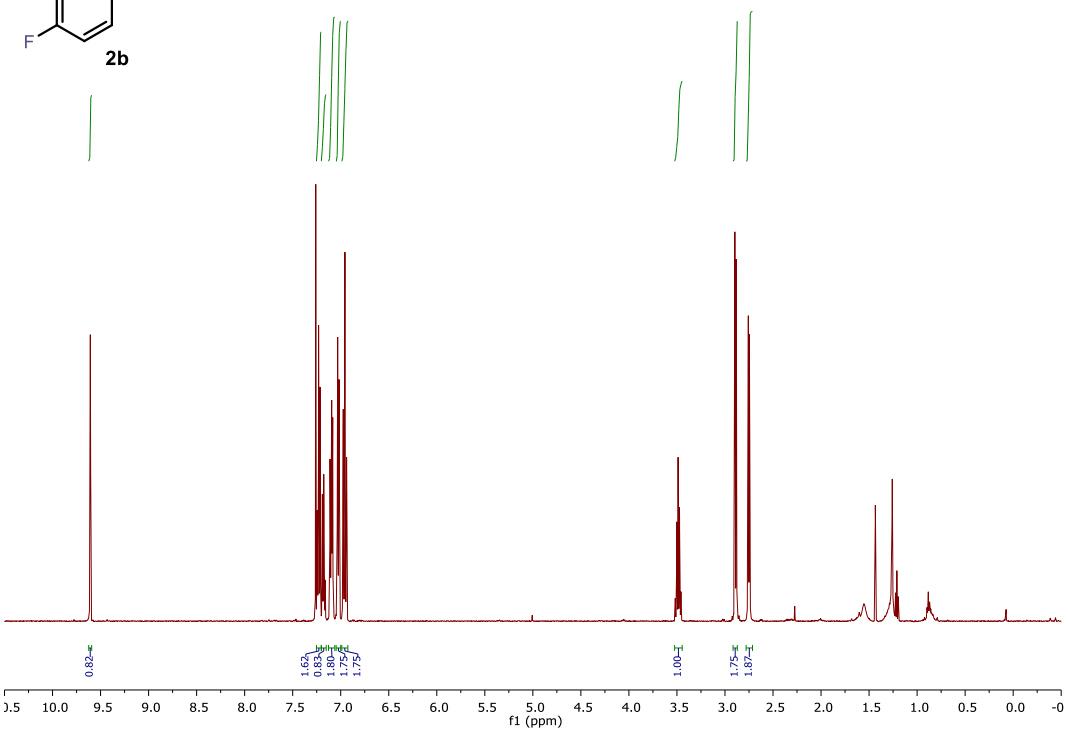
^{13}C NMR, 125.8 MHz, $CDCl_3$



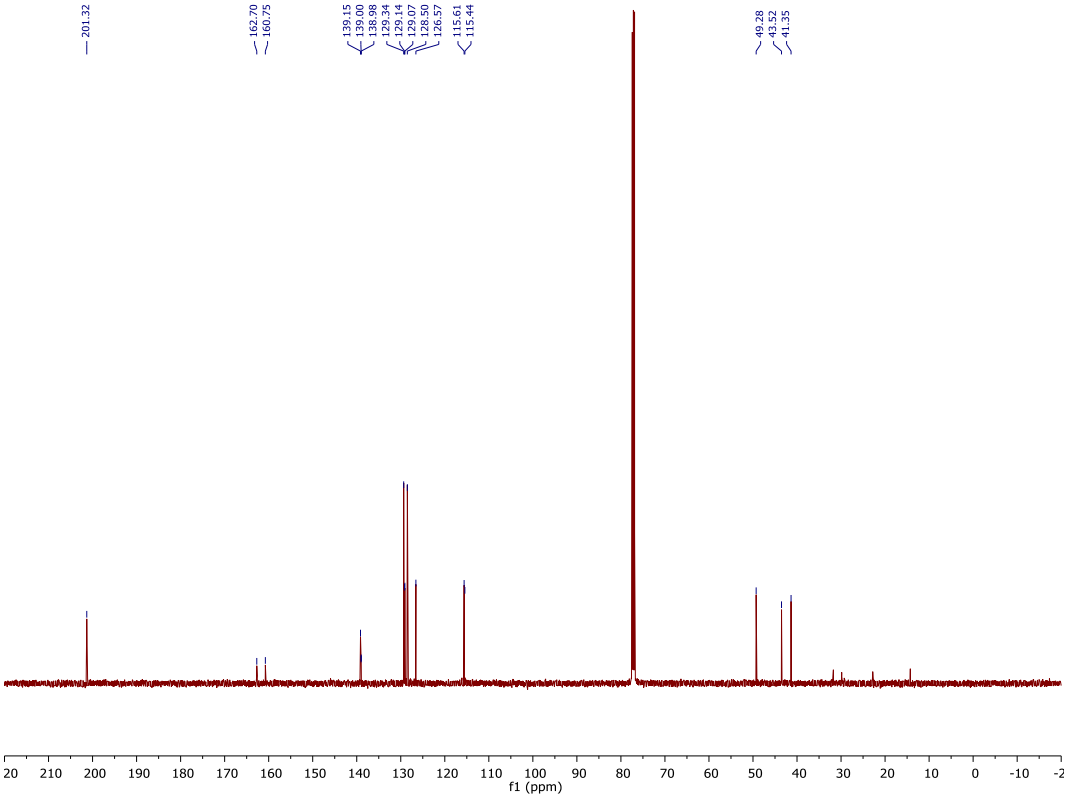
^{1}H NMR, 500 MHz, $CDCl_3$



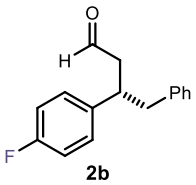
2b



^{13}C NMR, 125.8 MHz, $CDCl_3$

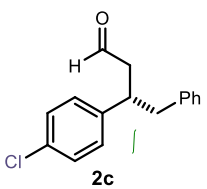


^{19}F NMR, 376 MHz, $CDCl_3$

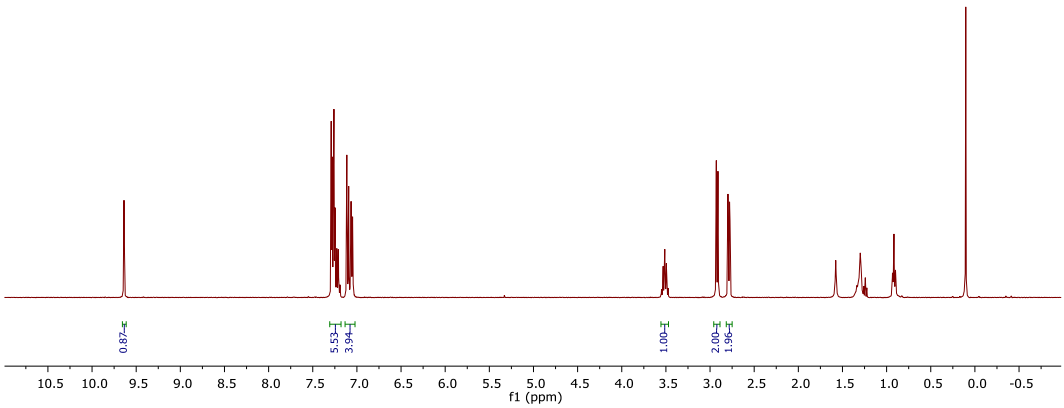


2b

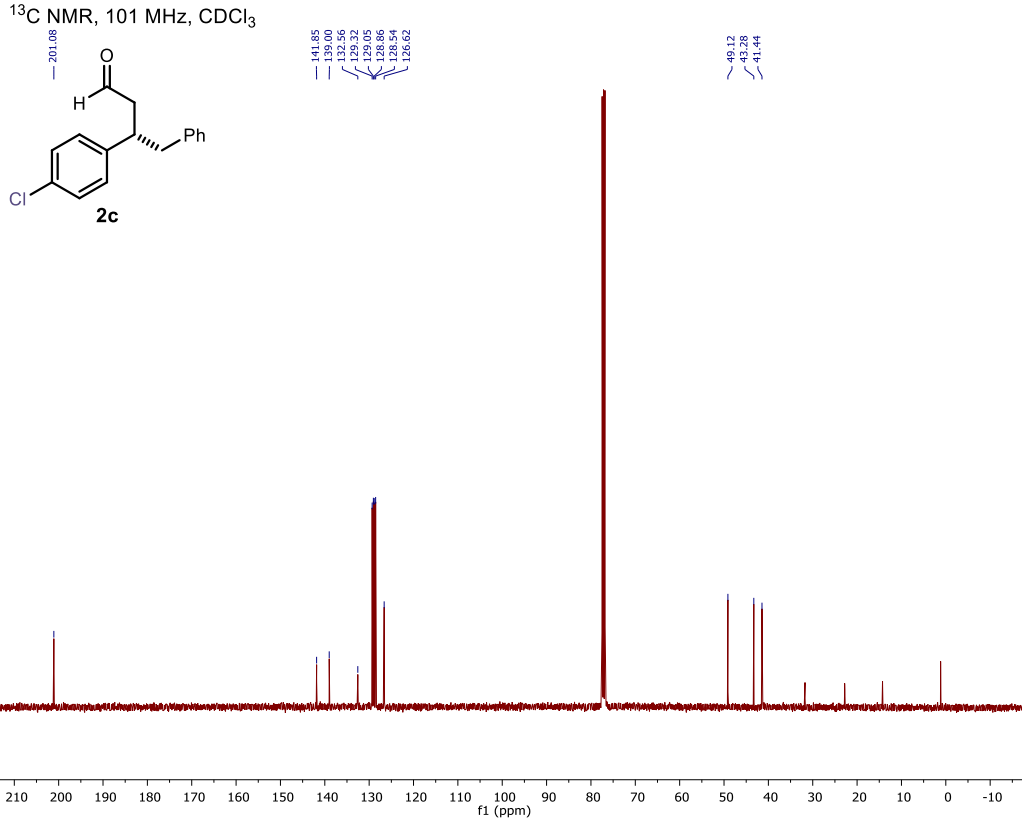
^{1}H NMR, 400 MHz, $CDCl_3$



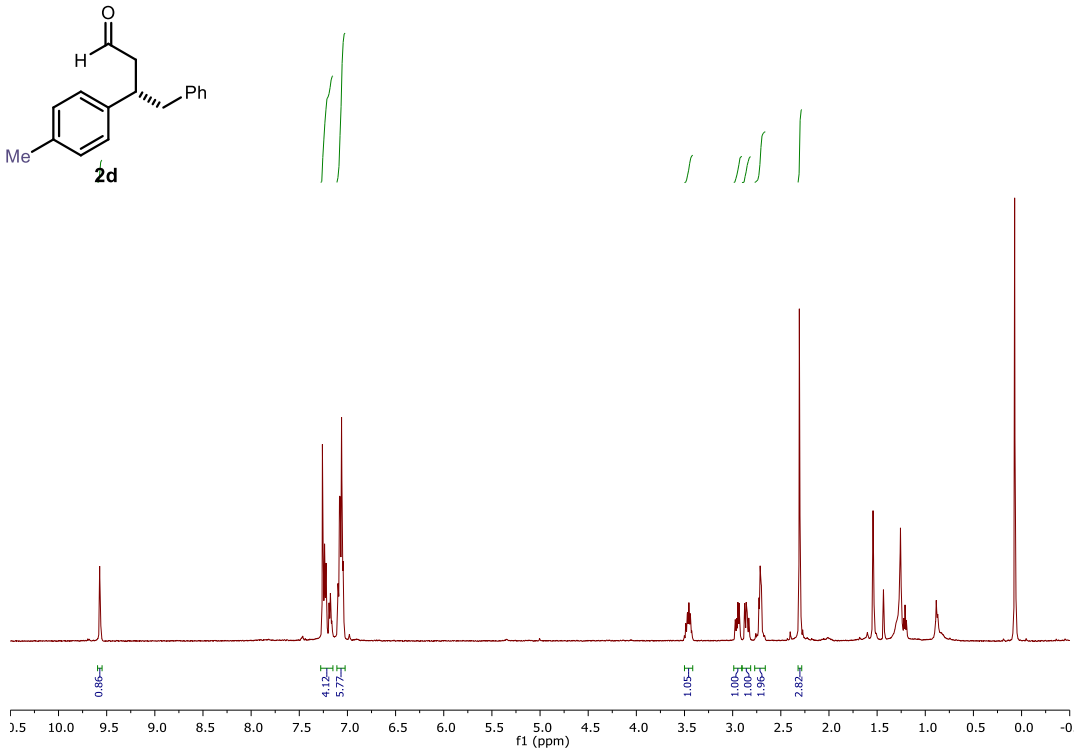
2c



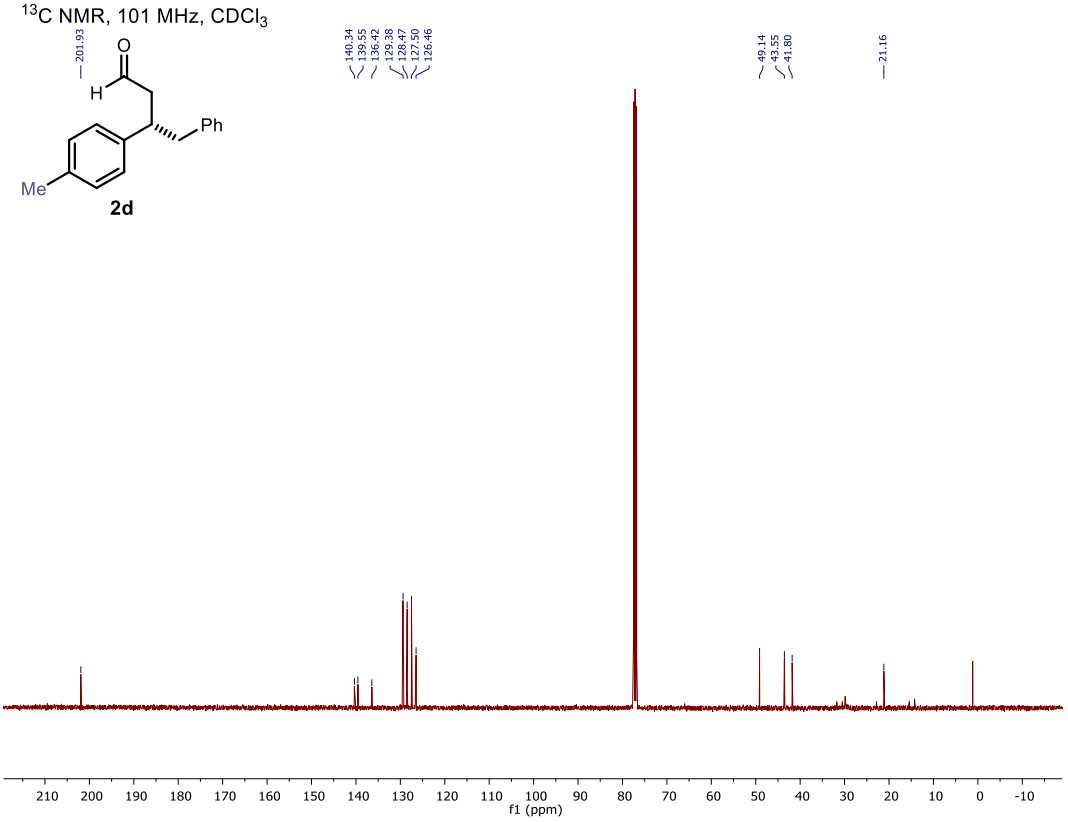
^{13}C NMR, 101 MHz, $CDCl_3$



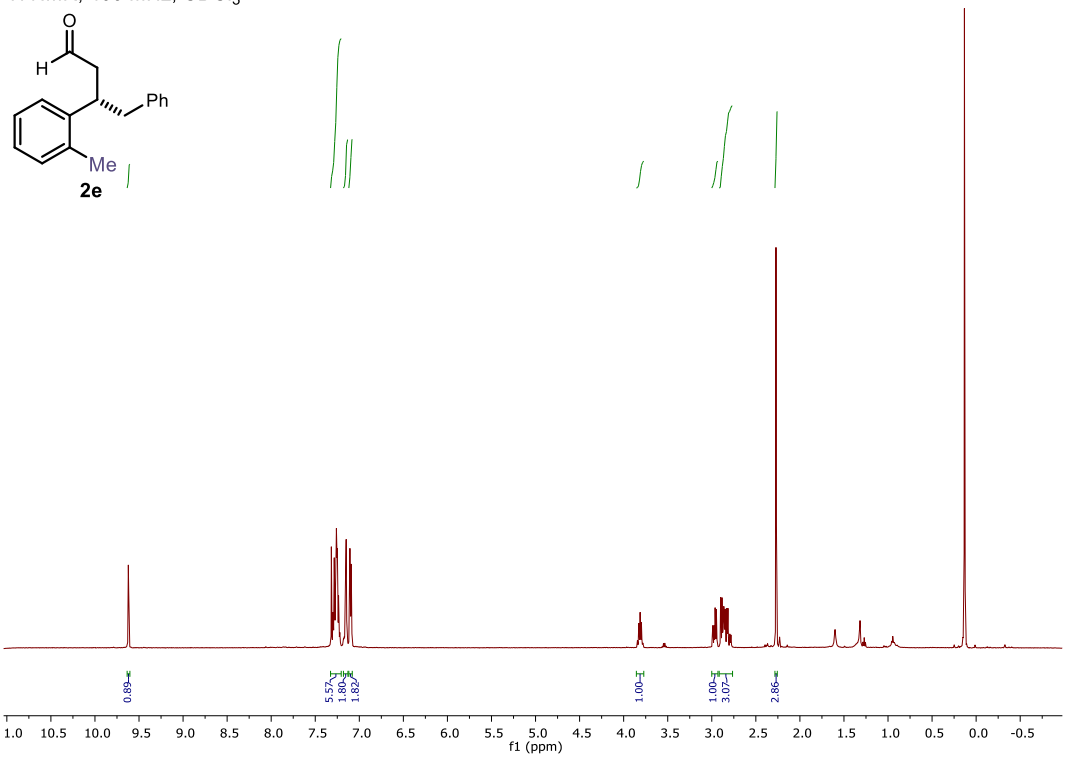
^{1}H NMR, 400 MHz, $CDCl_3$



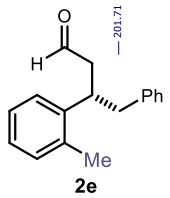
^{13}C NMR, 101 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$

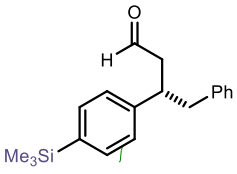


^{13}C NMR, 101 MHz, $CDCl_3$



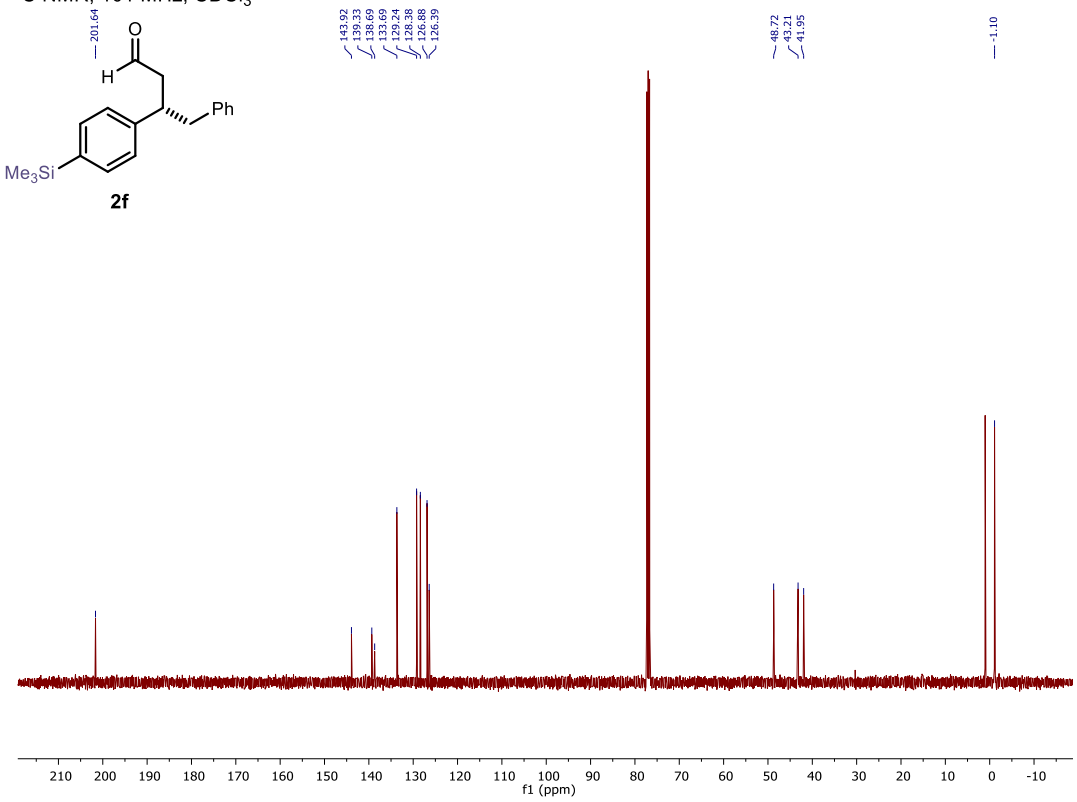
2e

^{1}H NMR, 400 MHz, $CDCl_3$

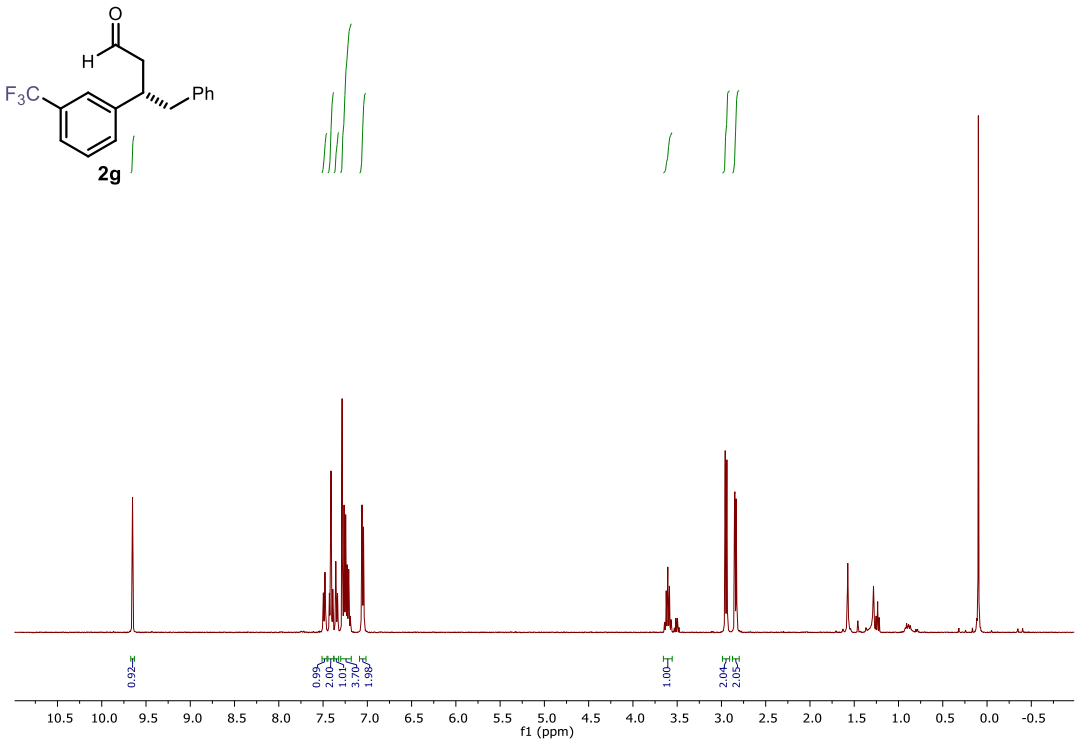


2f

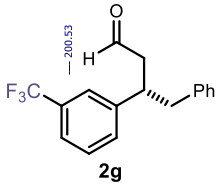
^{13}C NMR, 101 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$

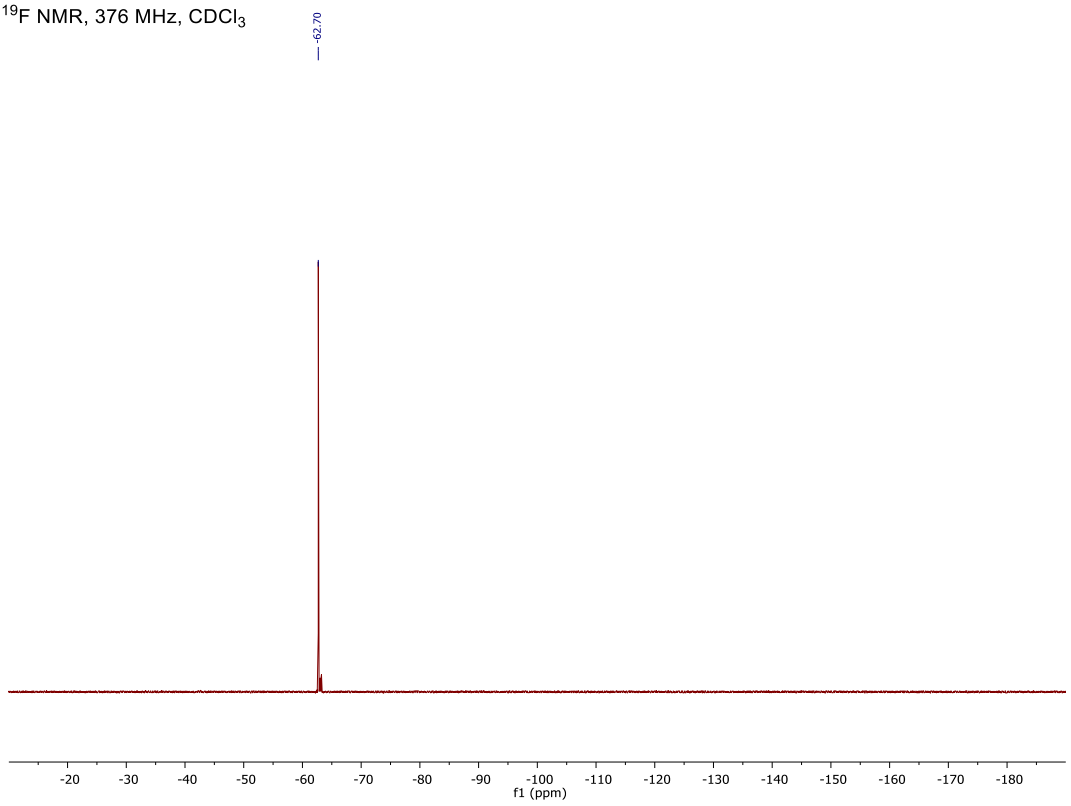


^{13}C NMR, 101 MHz, $CDCl_3$

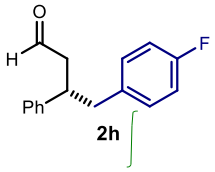


2g

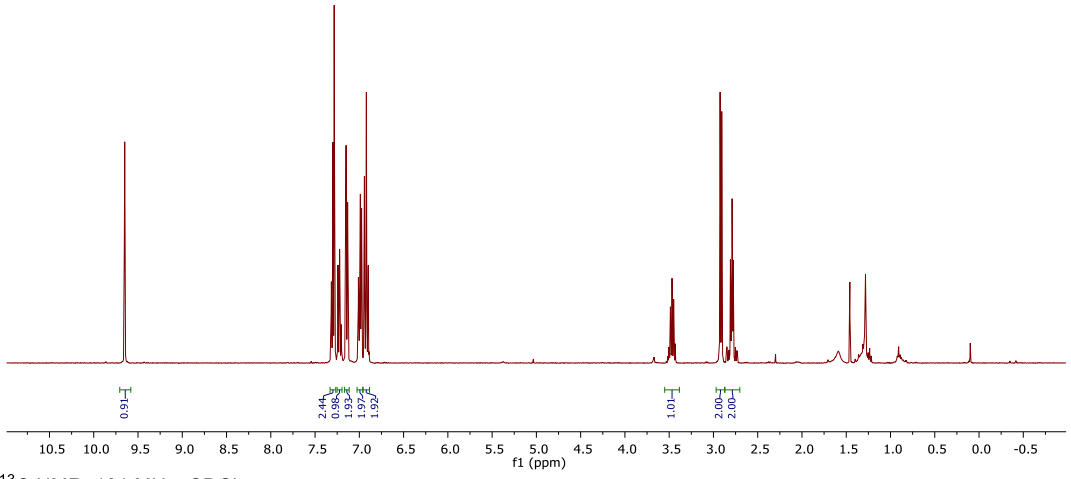
^{19}F NMR, 376 MHz, $CDCl_3$



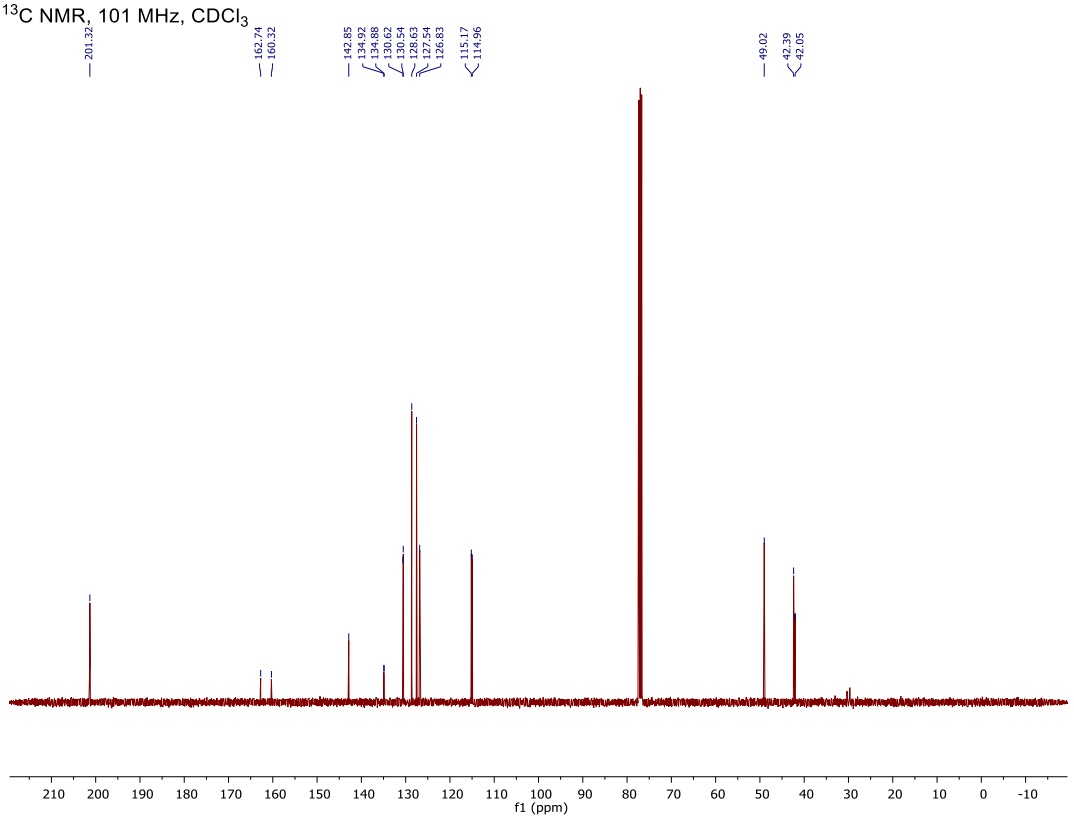
^{1}H NMR, 400 MHz, $CDCl_3$



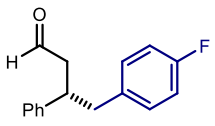
2h



^{13}C NMR, 101 MHz, $CDCl_3$

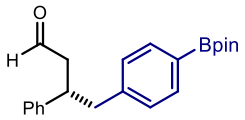


^{19}F NMR, 376 MHz, $CDCl_3$

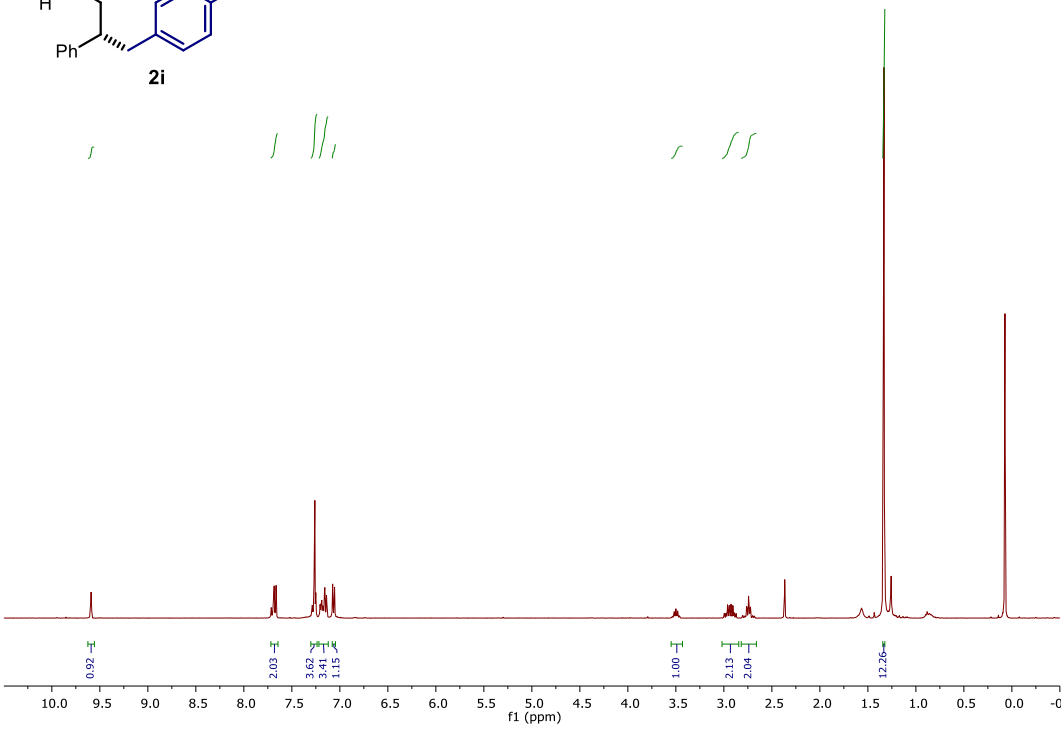


2h

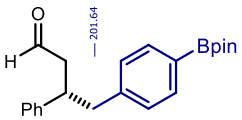
^{1}H NMR, 400 MHz, $CDCl_3$



2i

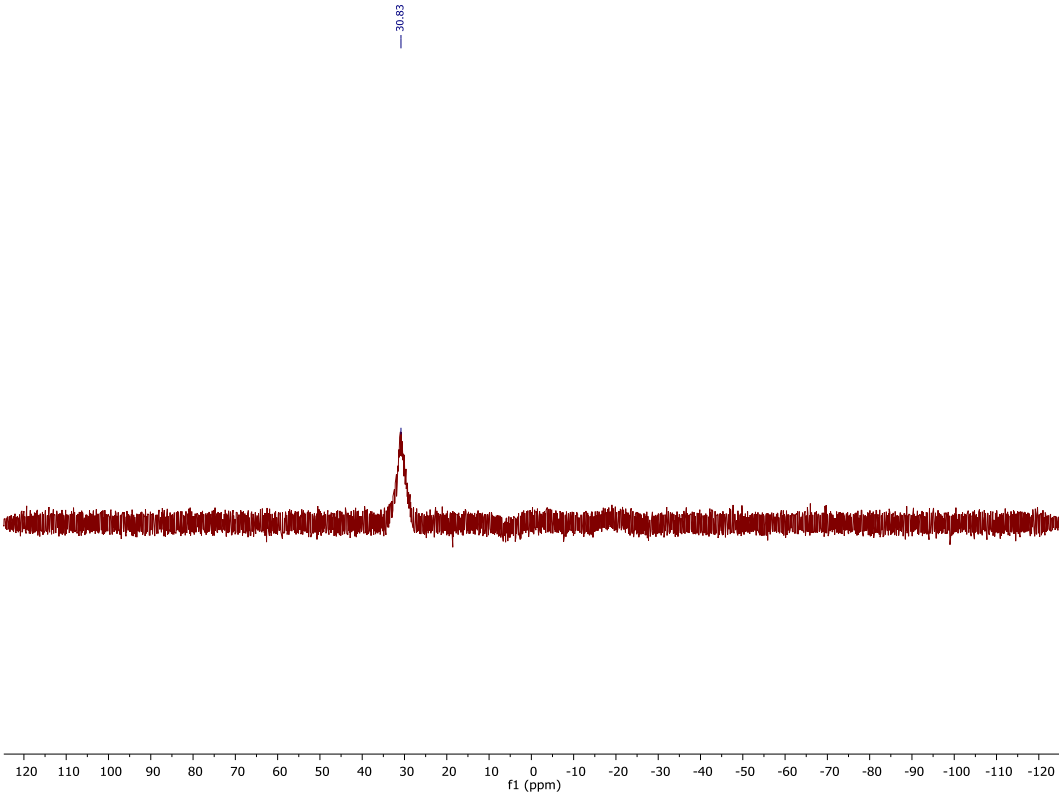


^{13}C NMR, 101 MHz, $CDCl_3$

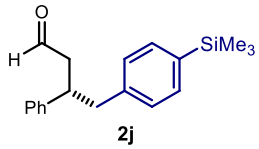


2i

^{11}B NMR, 47 MHz, $CDCl_3$

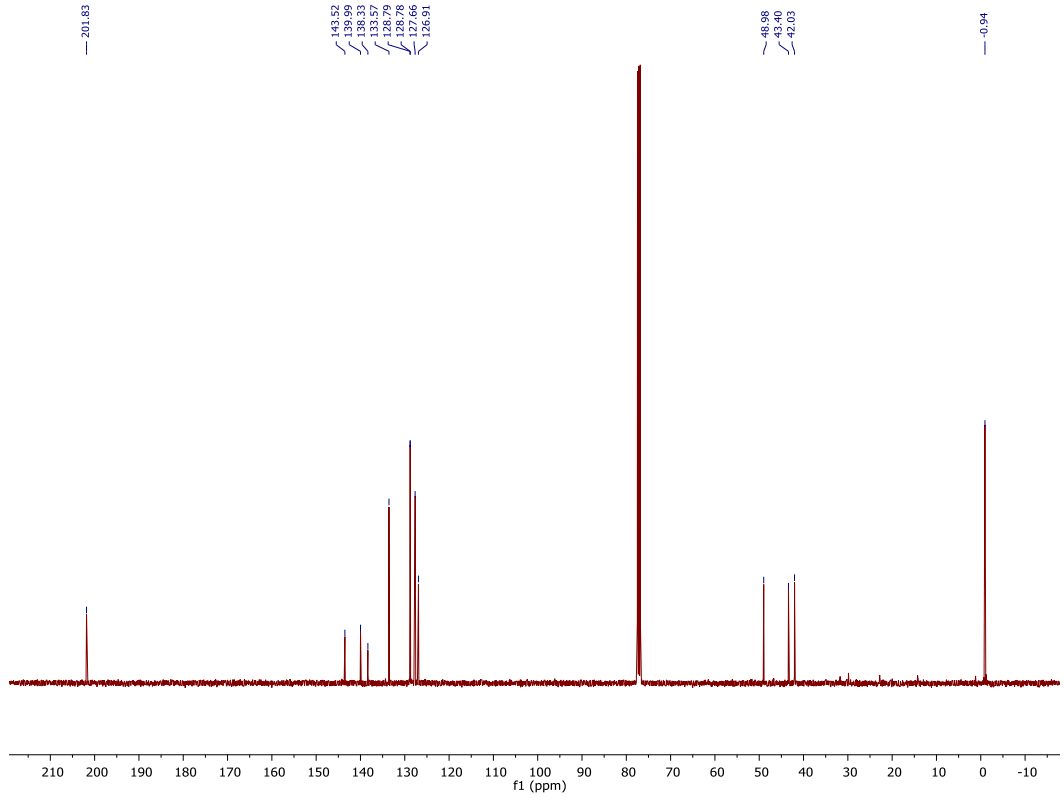


^{1}H NMR, 400 MHz, $CDCl_3$

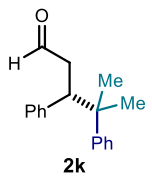


2j

^{13}C NMR, 101 MHz, $CDCl_3$

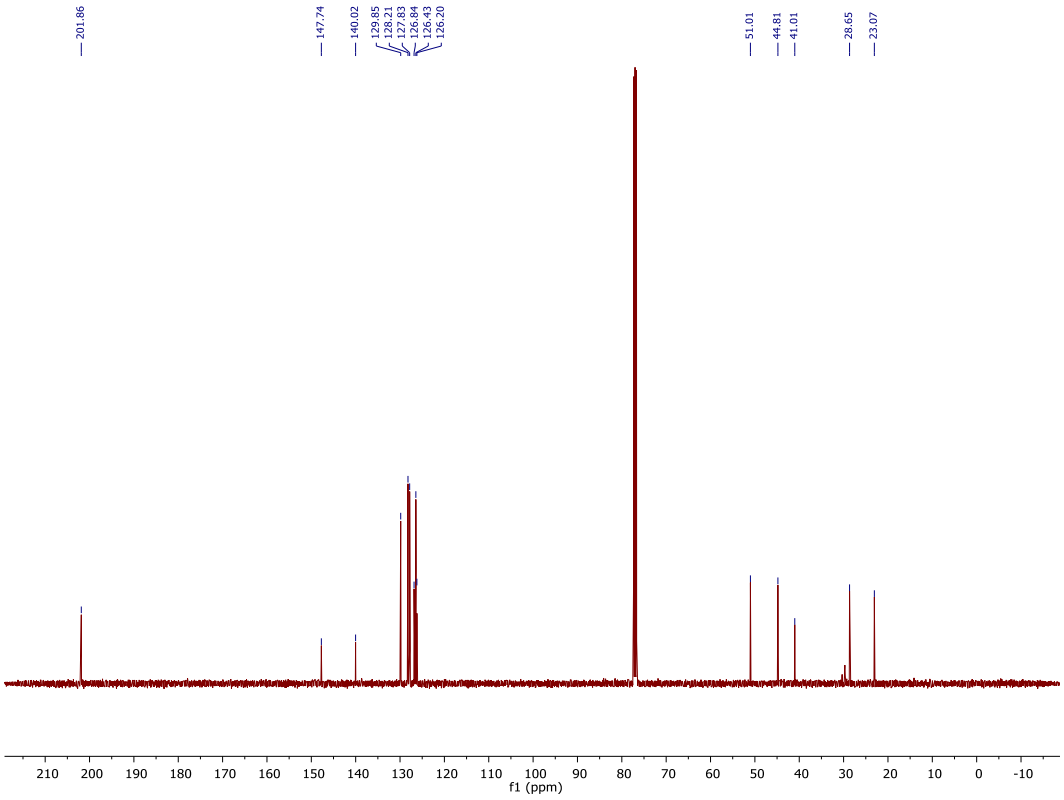


^{1}H NMR, 400 MHz, $CDCl_3$

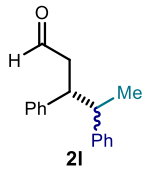


2k

^{13}C NMR, 101 MHz, $CDCl_3$

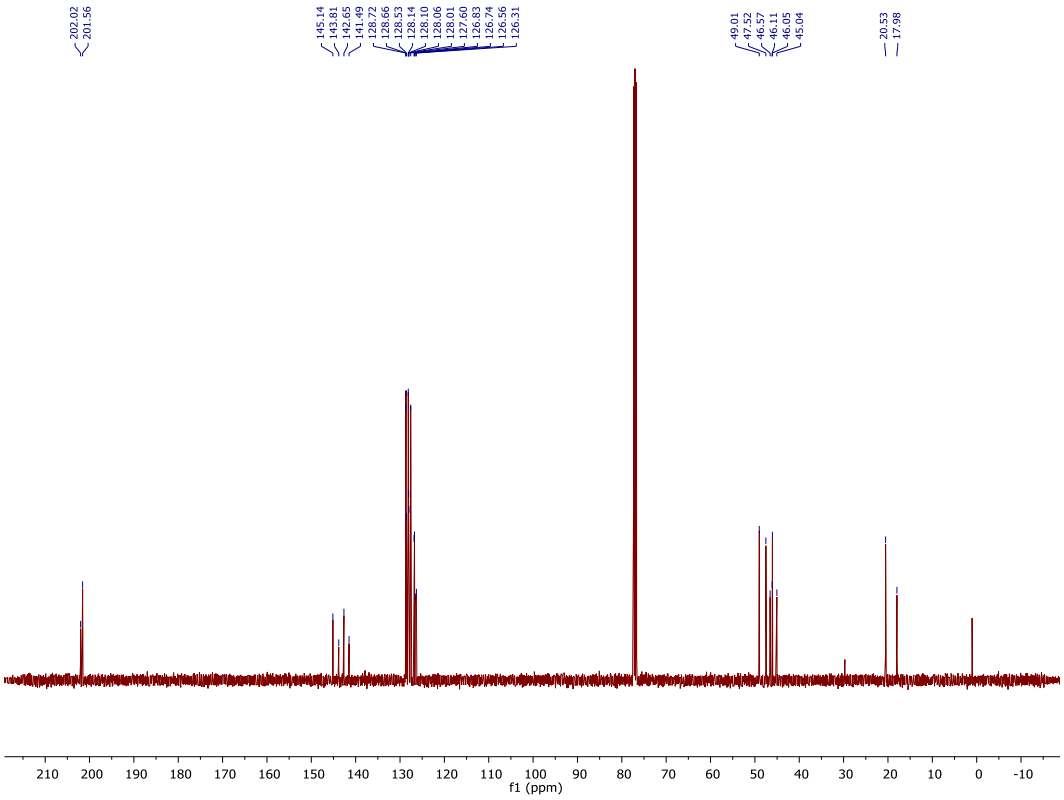


^{1}H NMR, 400 MHz, $CDCl_3$

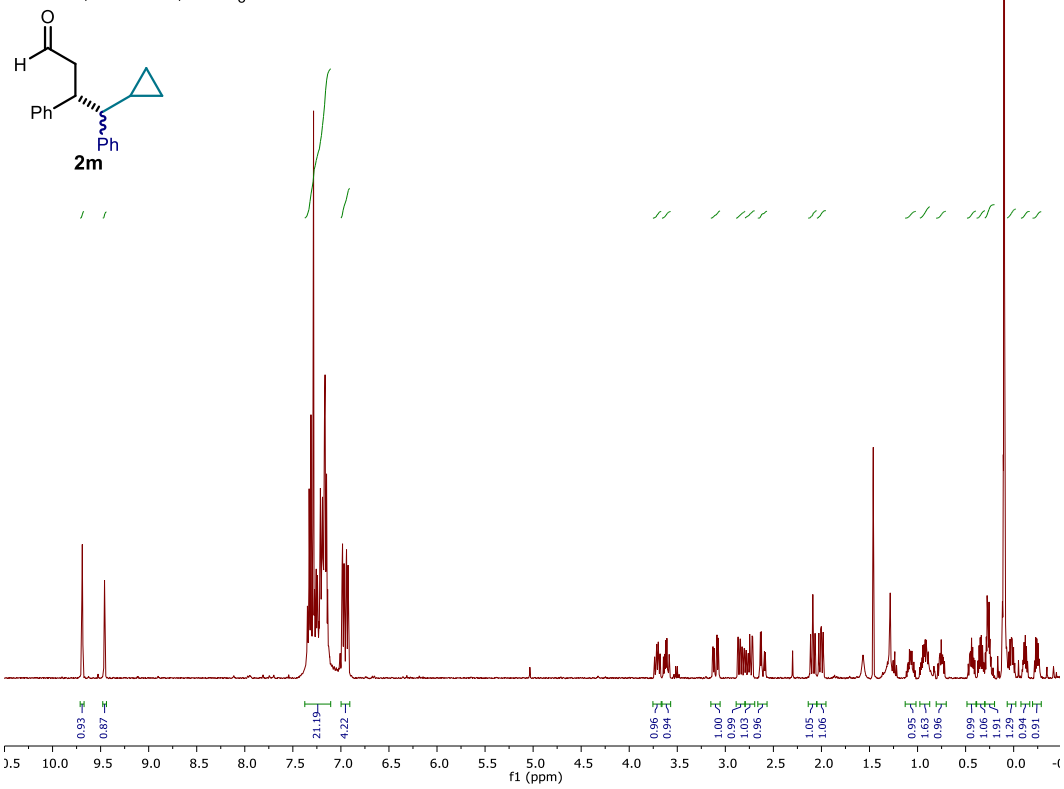


2l

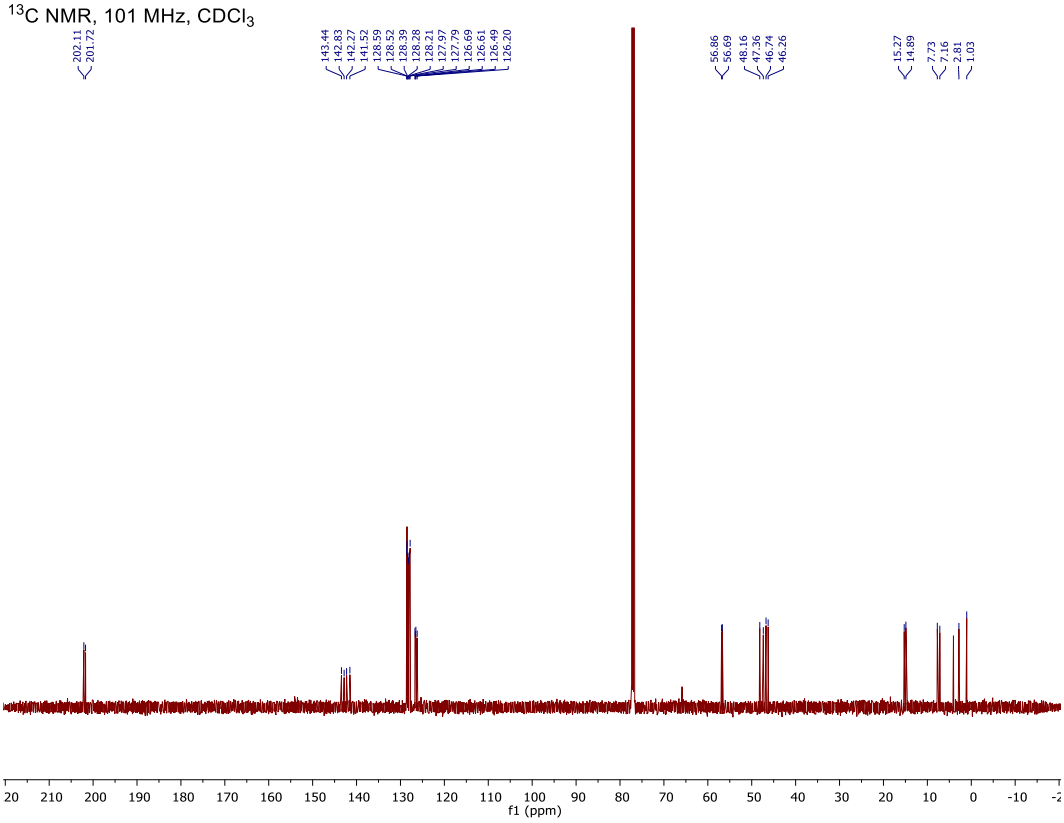
^{13}C NMR, 101 MHz, $CDCl_3$



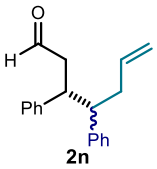
^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 101 MHz, $CDCl_3$

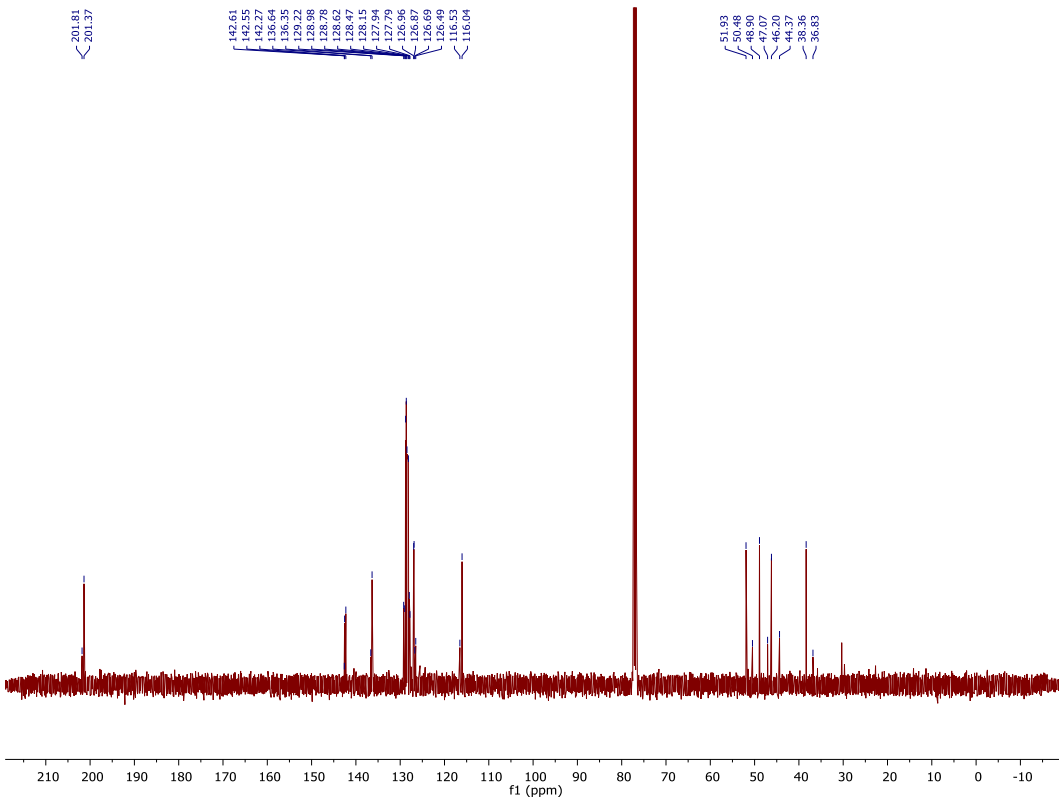


^{1}H NMR, 400 MHz, $CDCl_3$

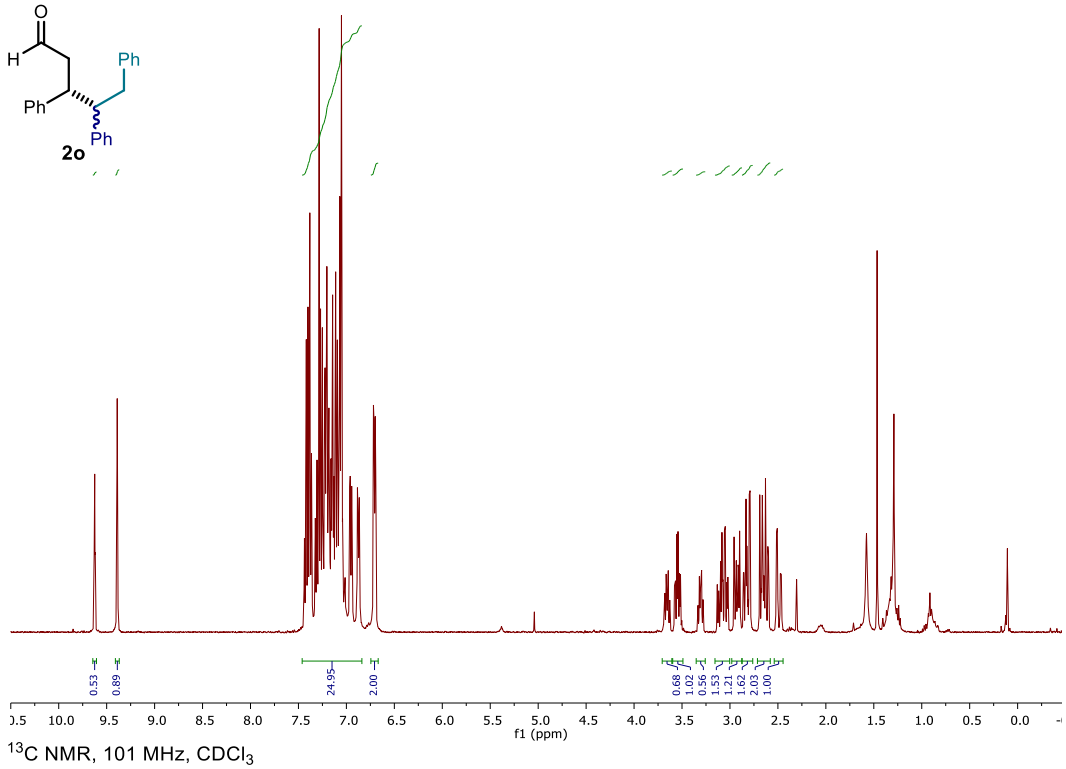


2n

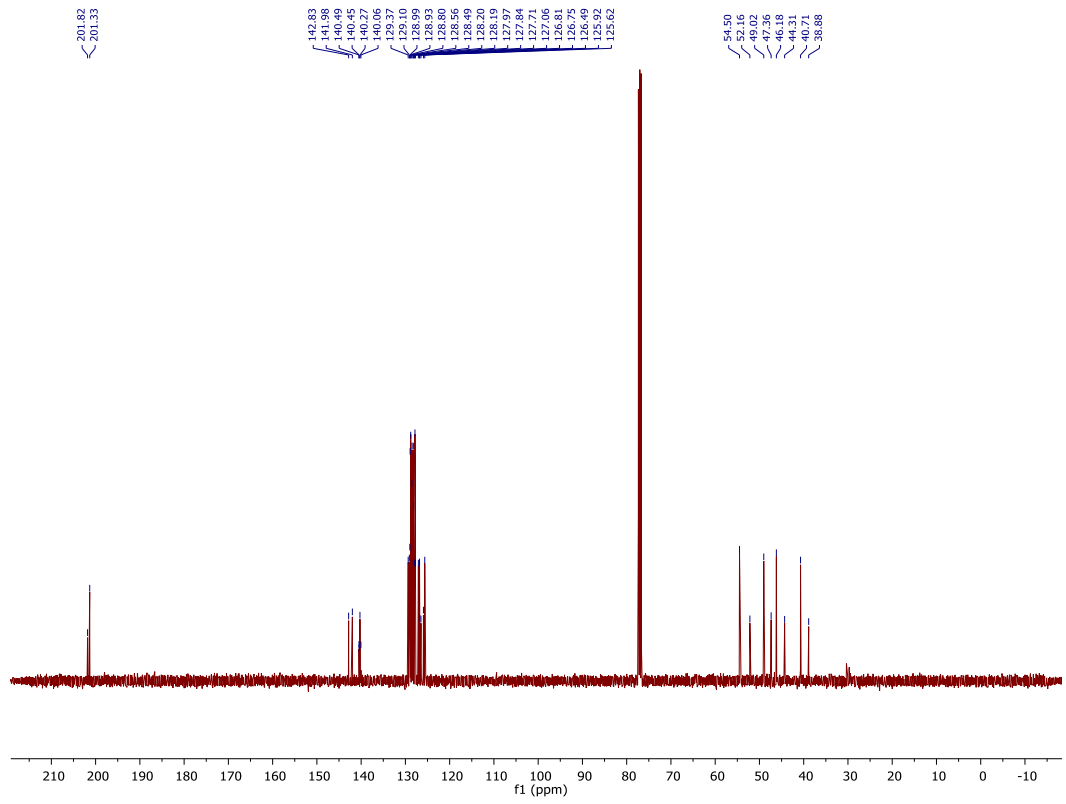
^{13}C NMR, 101 MHz, $CDCl_3$



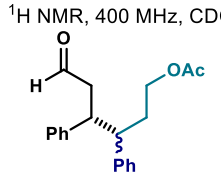
^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 101 MHz, $CDCl_3$



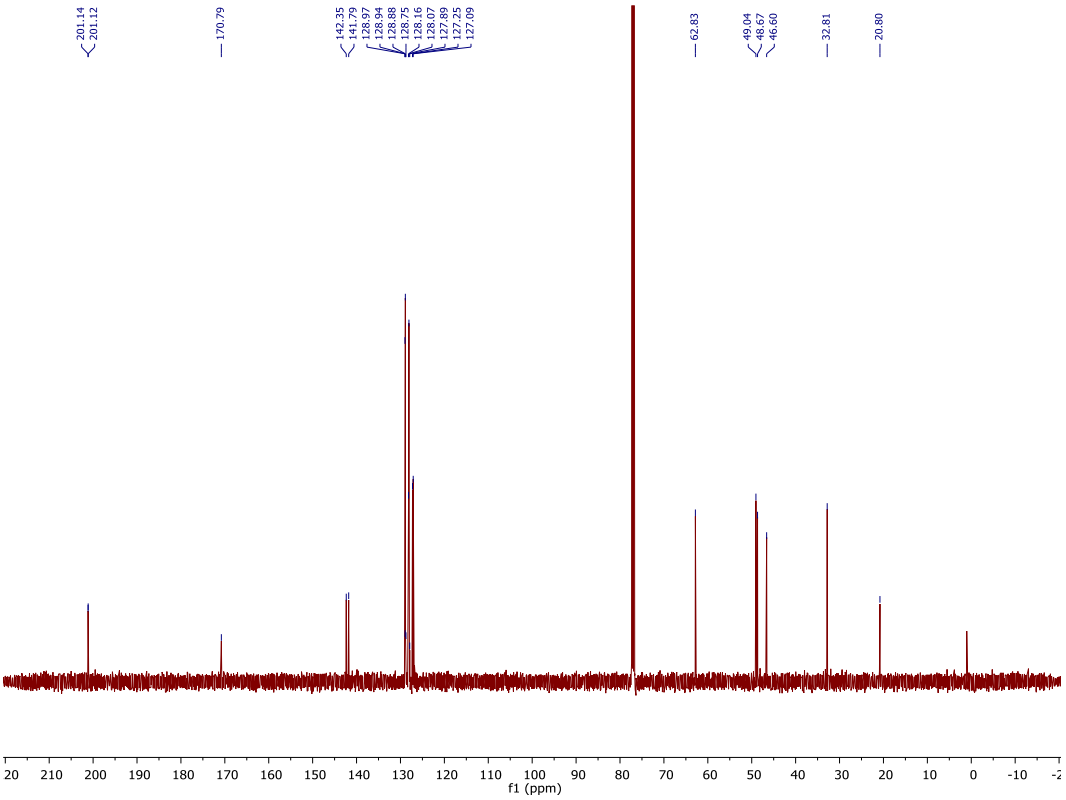
^{1}H NMR, 400 MHz, $CDCl_3$



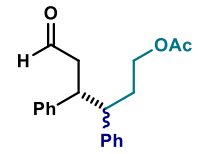
2p

major diastereoisomer

^{13}C NMR, 101 MHz, $CDCl_3$

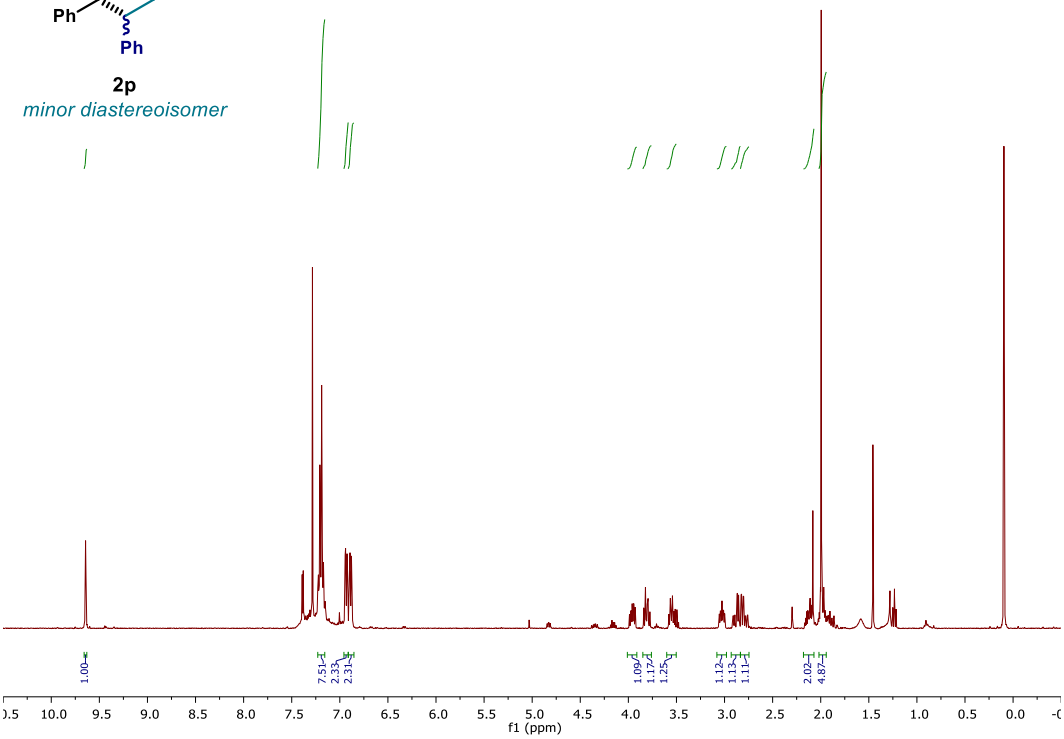


^{1}H NMR, 400 MHz, $CDCl_3$

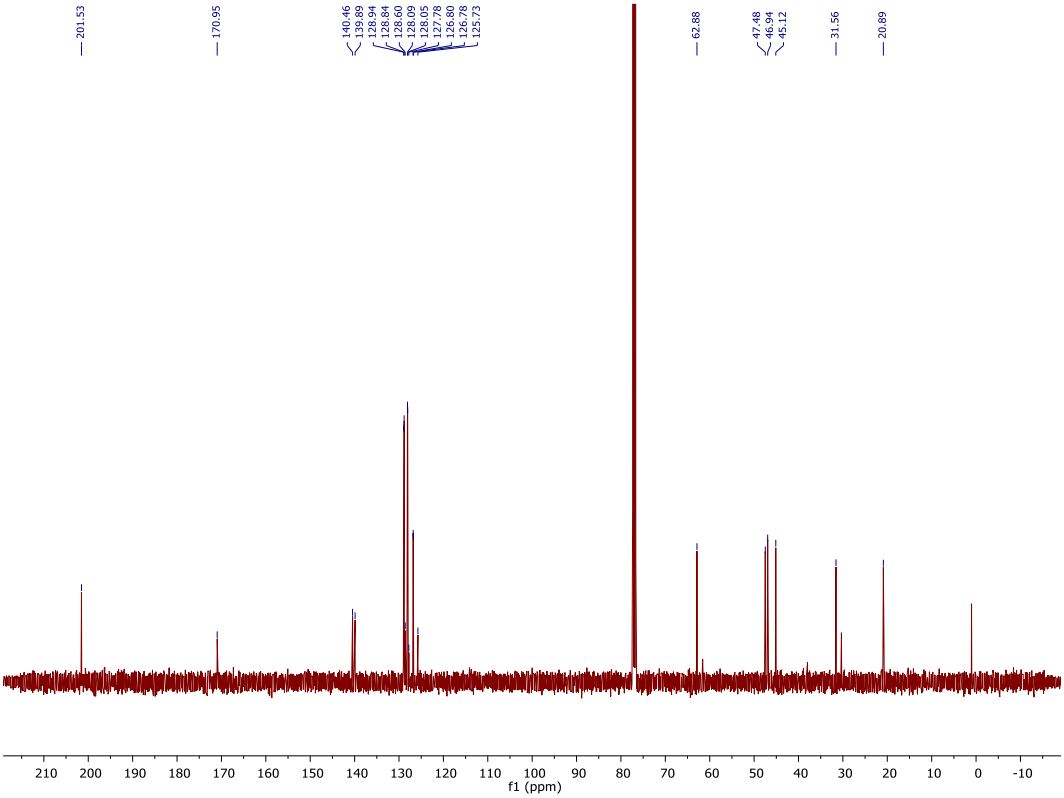


2p

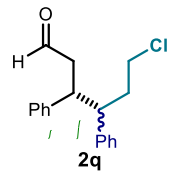
minor diastereoisomer



^{13}C NMR, 101 MHz, $CDCl_3$

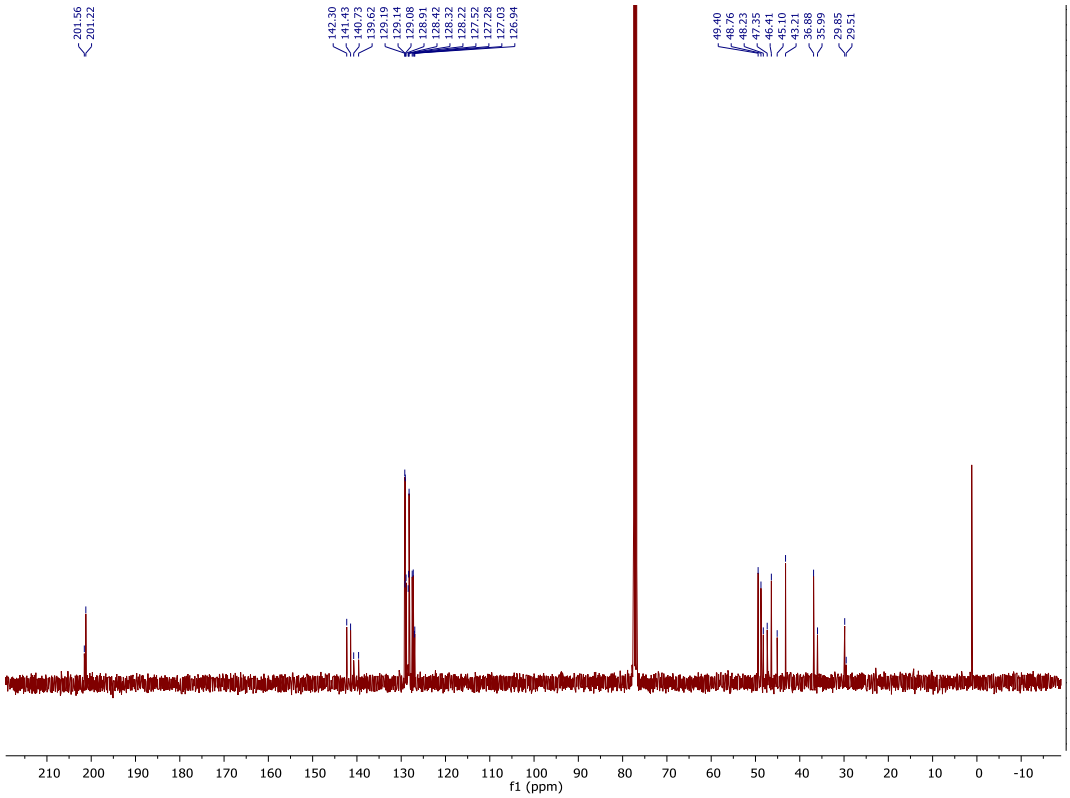


^{1}H NMR, 400 MHz, $CDCl_3$

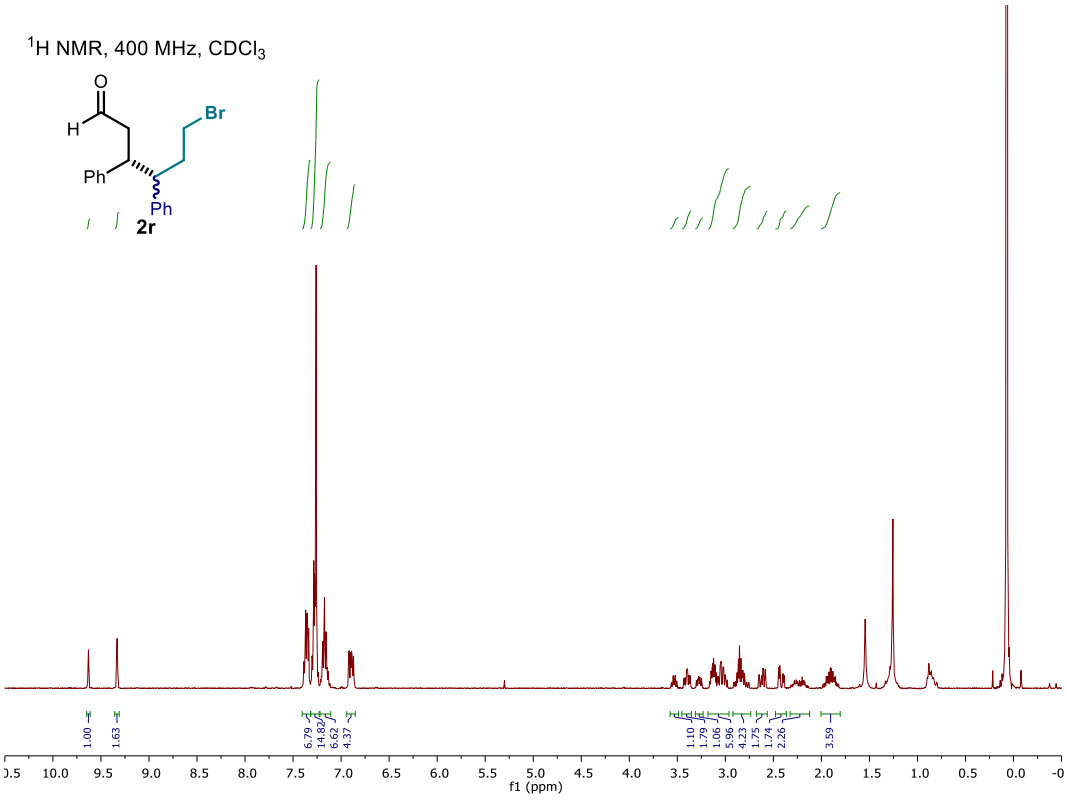


2q

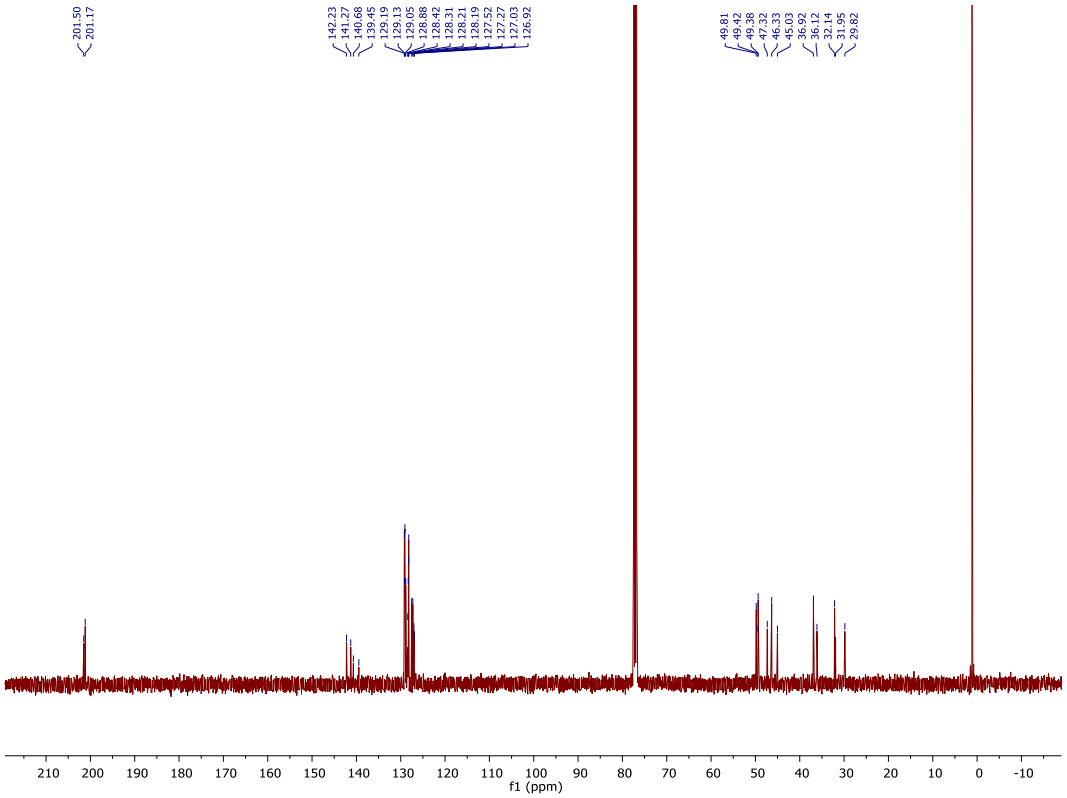
^{13}C NMR, 101 MHz, $CDCl_3$



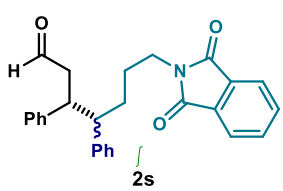
^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 101 MHz, $CDCl_3$



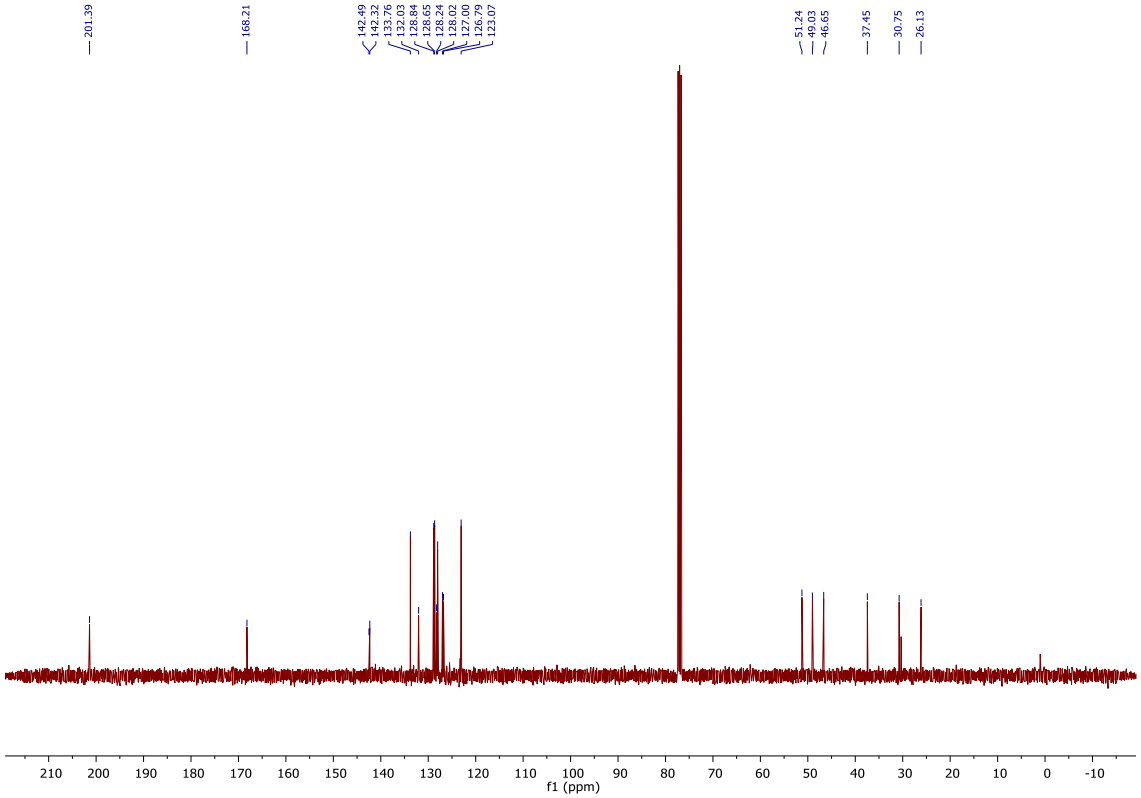
^{1}H NMR, 400 MHz, $CDCl_3$



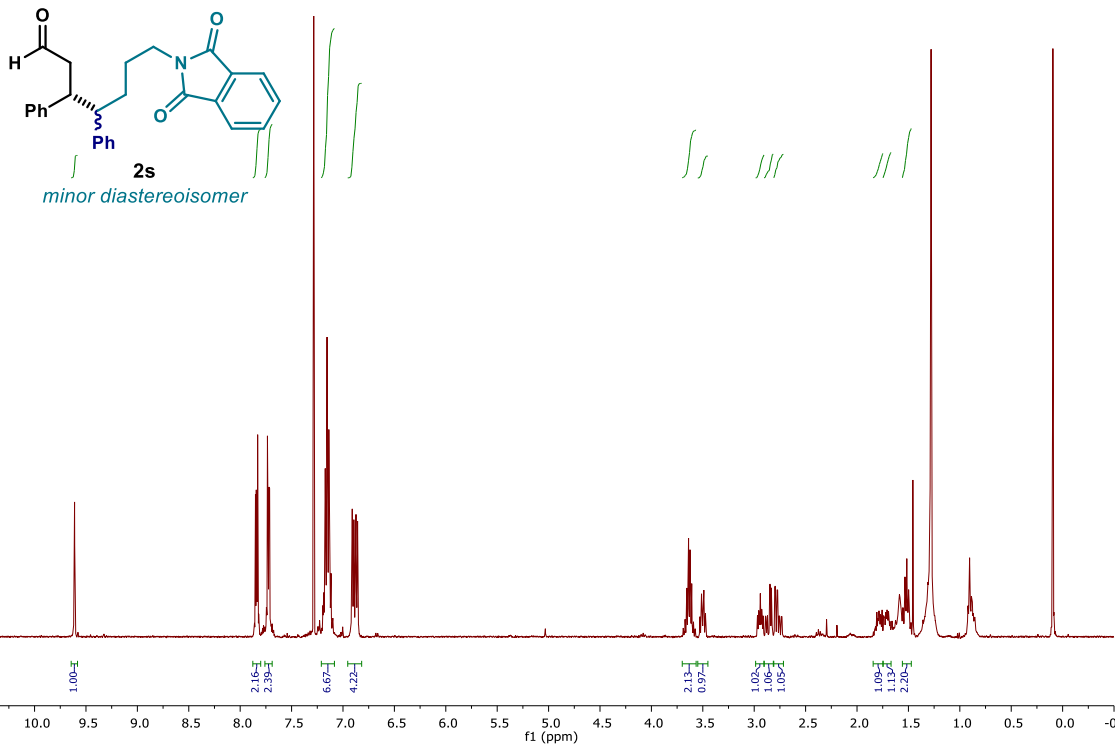
2s

major diastereoisomer

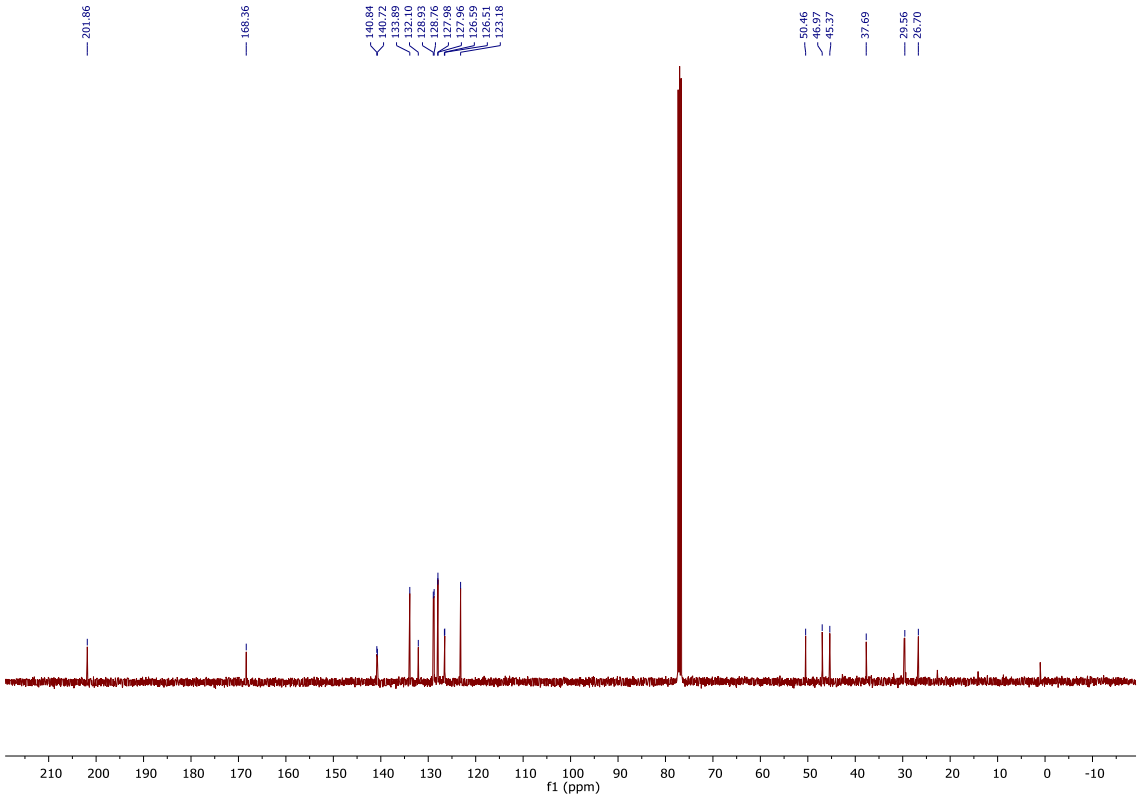
^{13}C NMR, 101 MHz, $CDCl_3$



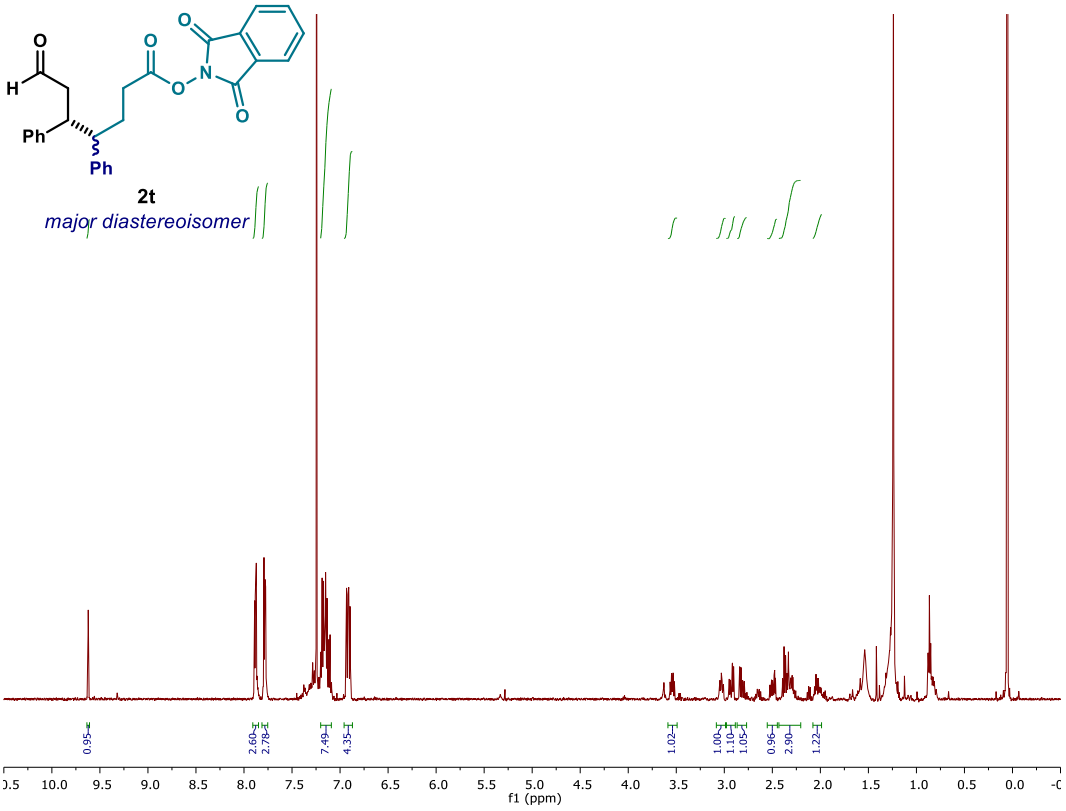
^{1}H NMR, 400 MHz, $CDCl_3$



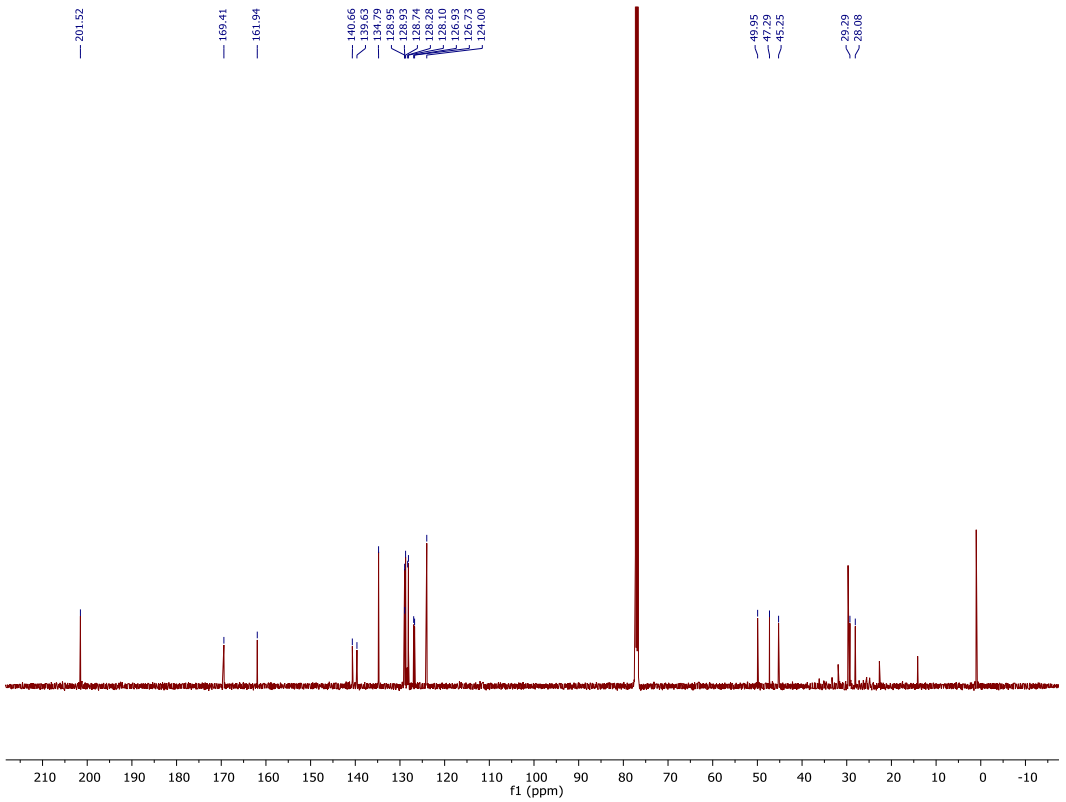
^{13}C NMR, 101 MHz, $CDCl_3$



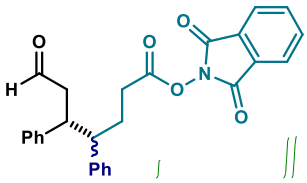
^{1}H NMR, 500 MHz, $CDCl_3$



^{13}C NMR, 125.8 MHz, $CDCl_3$



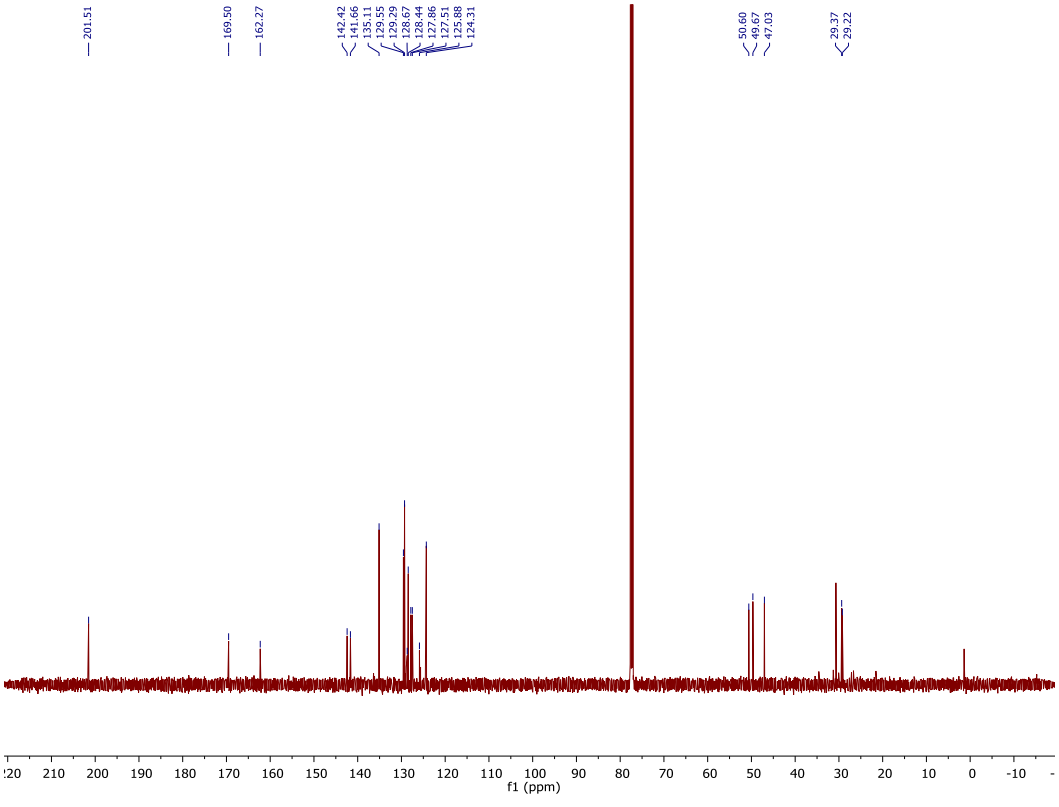
^{1}H NMR, 500 MHz, $CDCl_3$



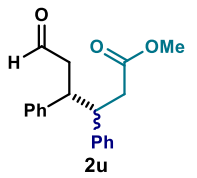
2t

minor diastereoisomer

^{13}C NMR, 125.8 MHz, $CDCl_3$



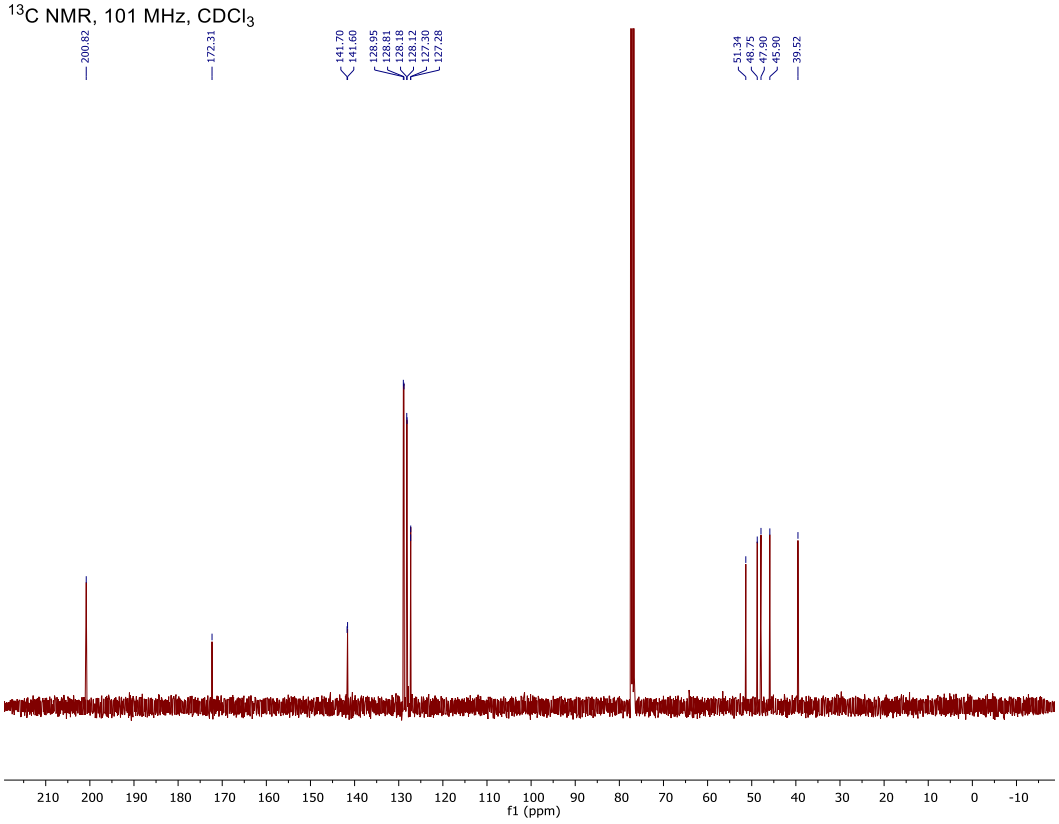
^{1}H NMR, 400 MHz, $CDCl_3$



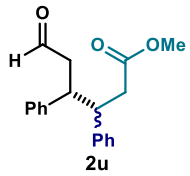
2u

diastereoisomer A

^{13}C NMR, 101 MHz, $CDCl_3$



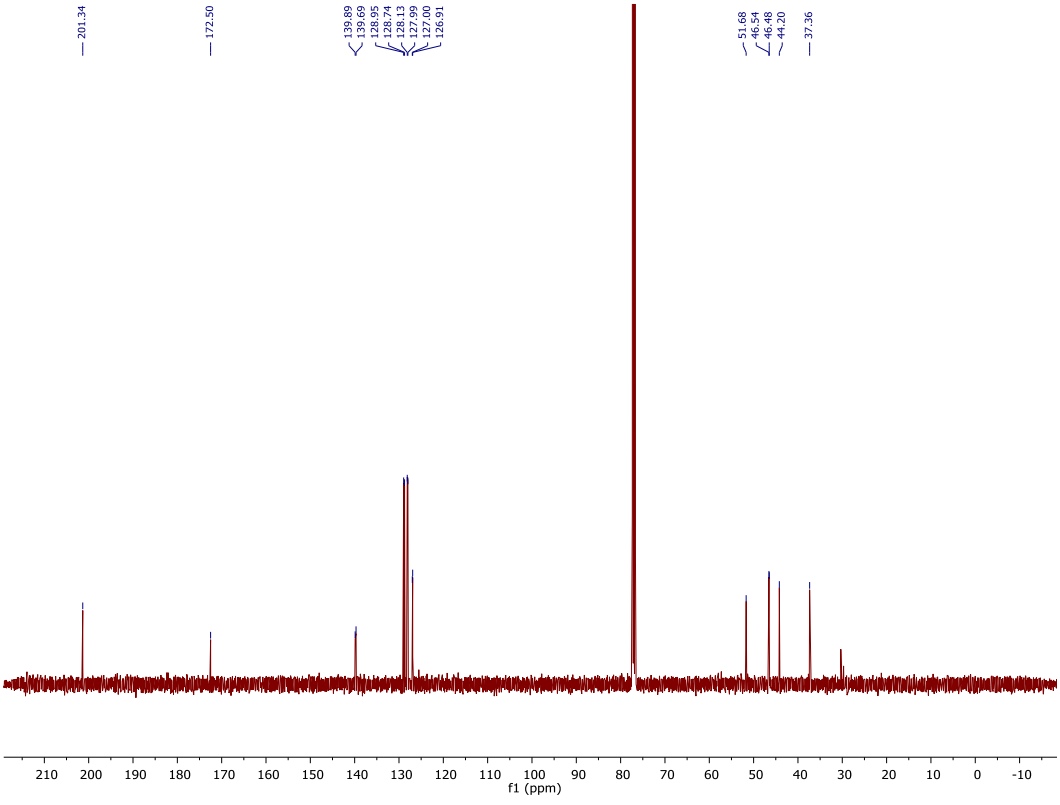
^{1}H NMR, 400 MHz, $CDCl_3$



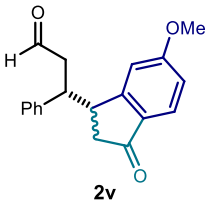
2u

diastereoisomer B

^{13}C NMR, 101 MHz, $CDCl_3$



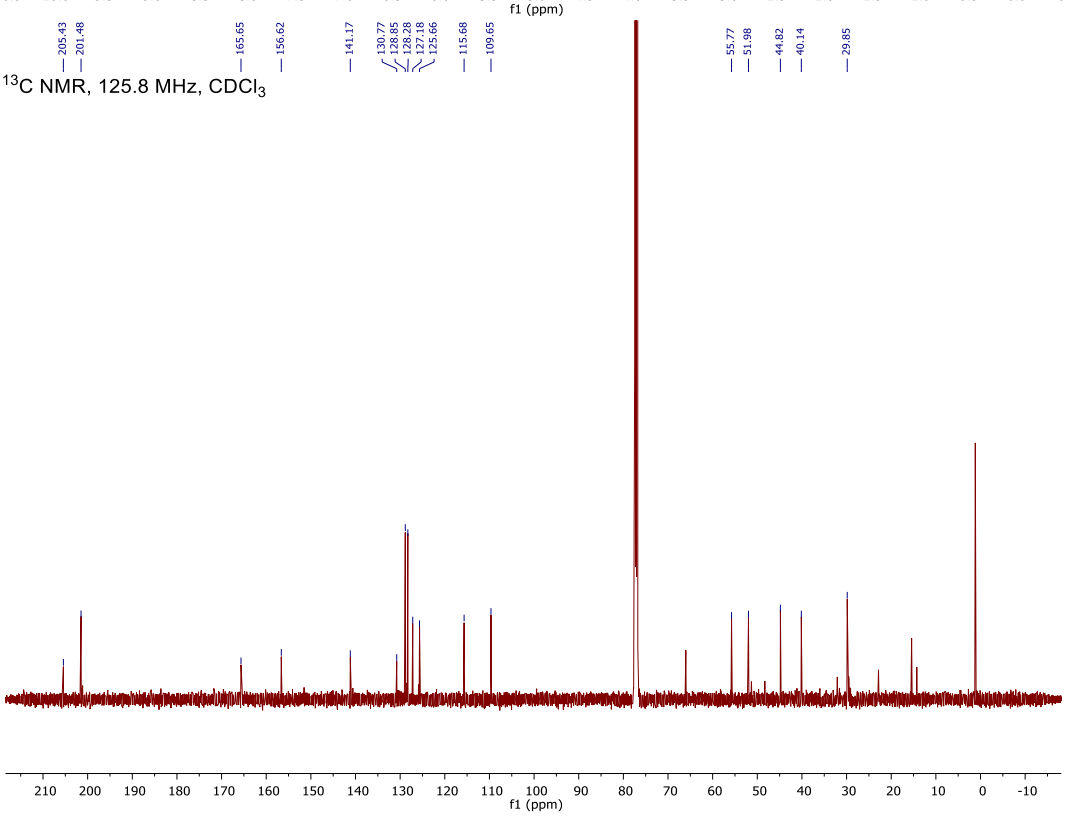
^{1}H NMR, 500 MHz, $CDCl_3$



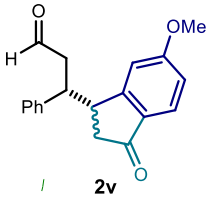
2v

minor diastereoisomer

^{13}C NMR, 125.8 MHz, $CDCl_3$



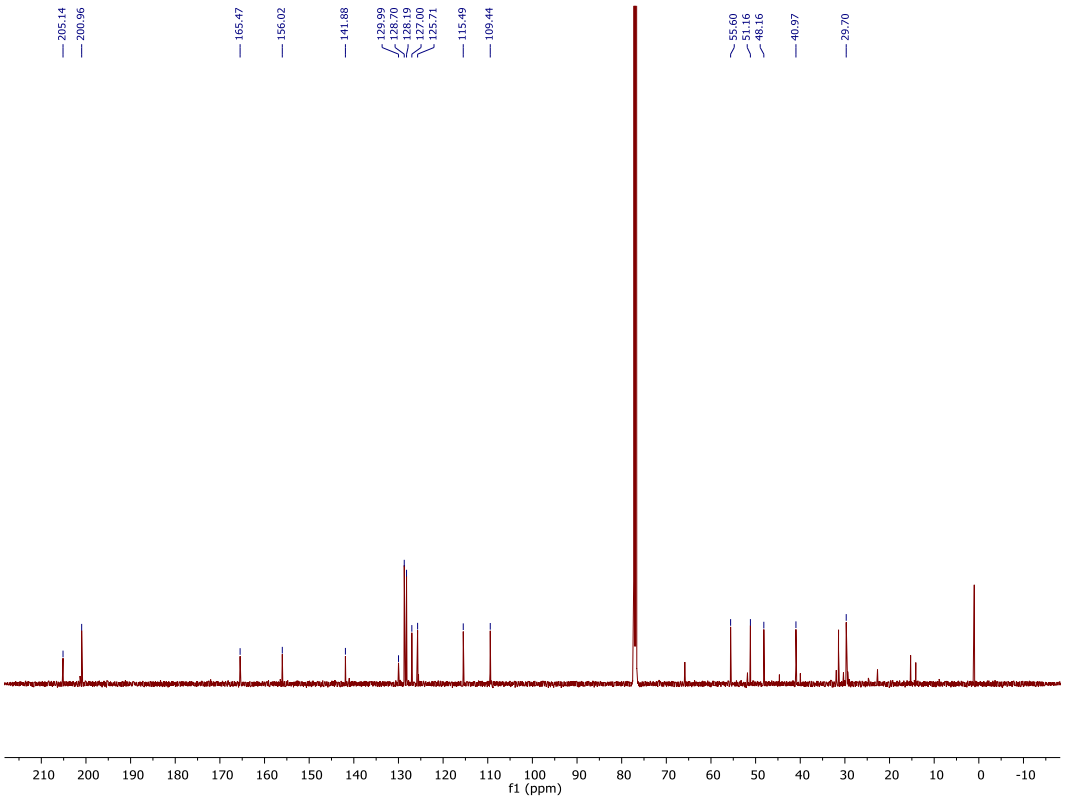
^{1}H NMR, 500 MHz, $CDCl_3$



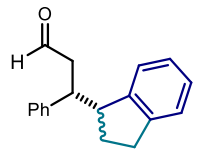
2v

major diastereoisomer

^{13}C NMR, 125.8 MHz, $CDCl_3$

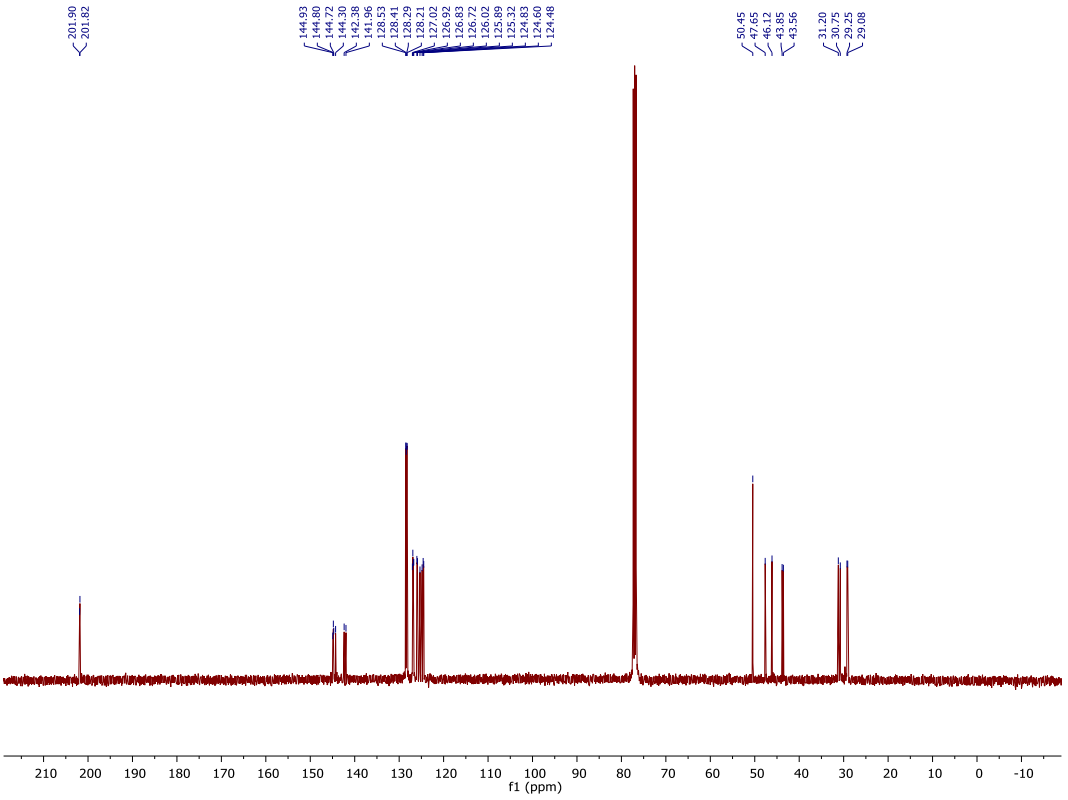


^{1}H NMR, 400 MHz, $CDCl_3$

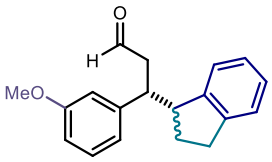


2w

^{13}C NMR, 101 MHz, $CDCl_3$



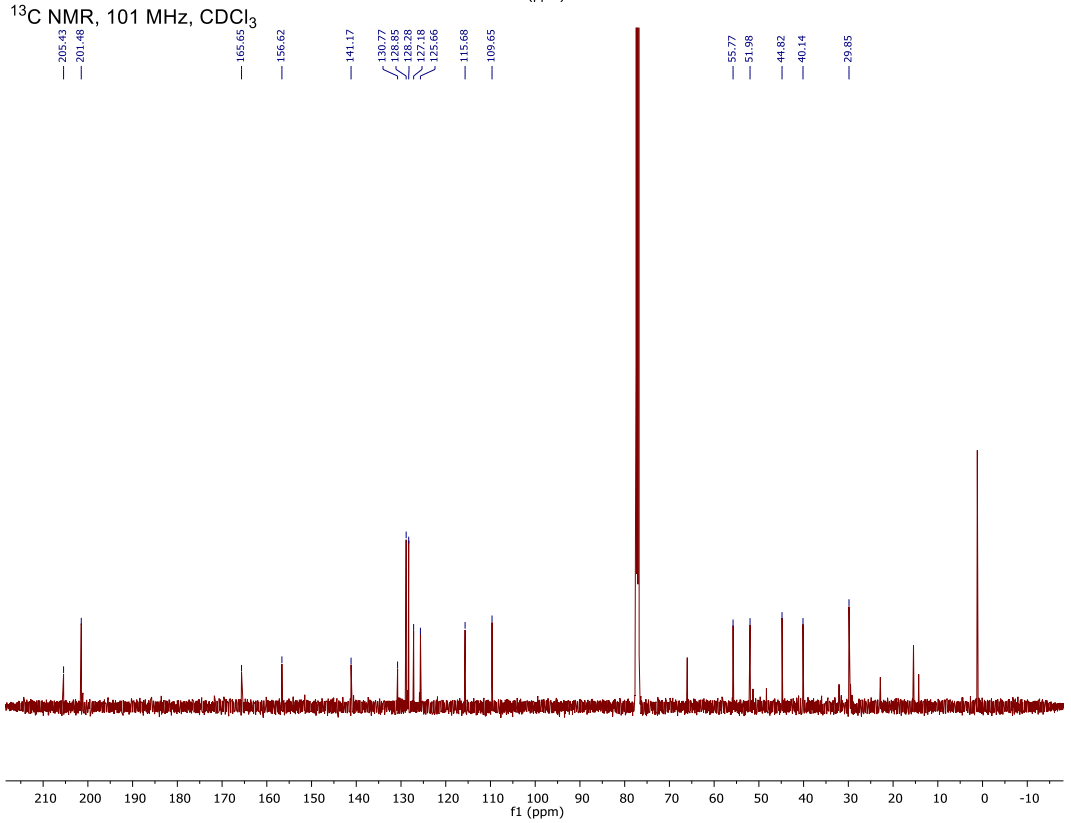
^{1}H NMR, 400 MHz, $CDCl_3$



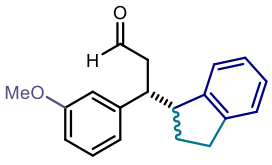
2x

minor diastereoisomer

^{13}C NMR, 101 MHz, $CDCl_3$

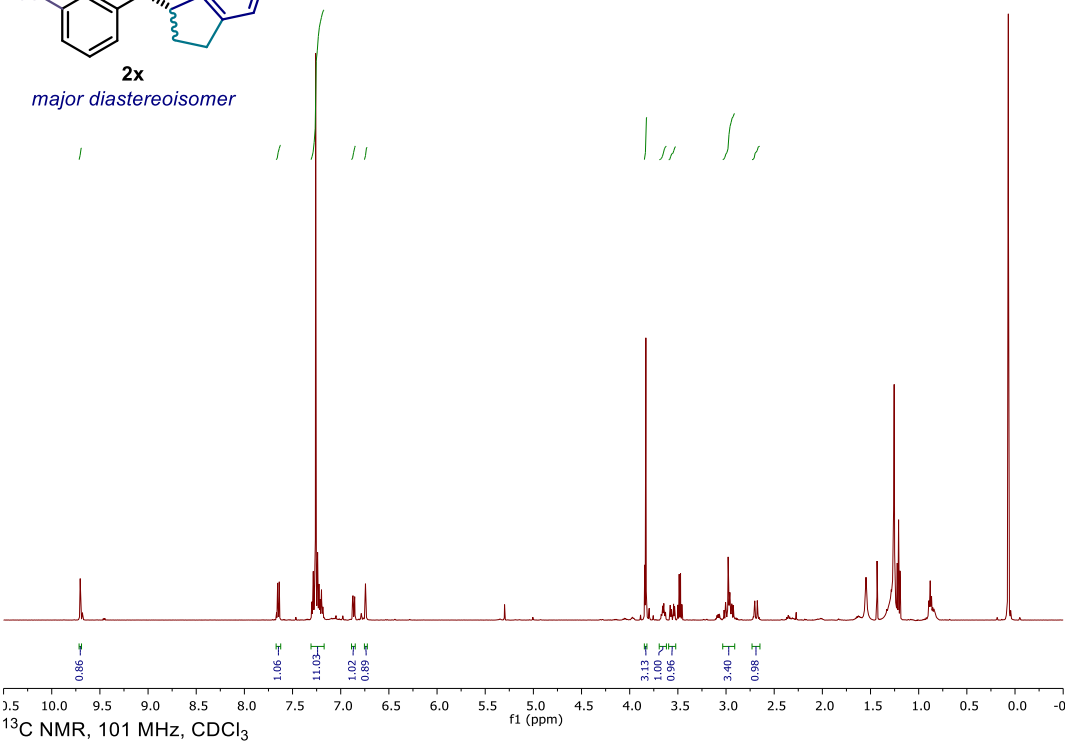


^{1}H NMR, 400 MHz, $CDCl_3$

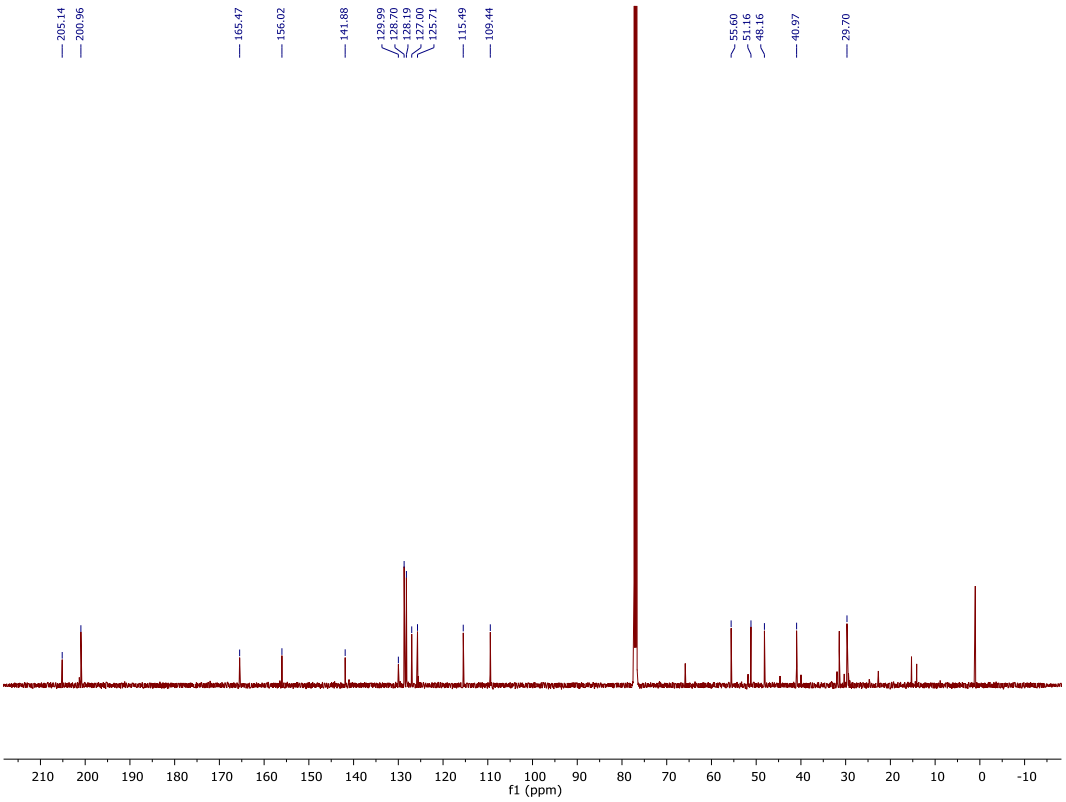


2x

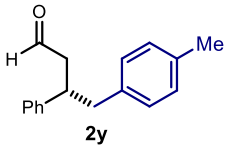
major diastereoisomer



^{13}C NMR, 101 MHz, $CDCl_3$

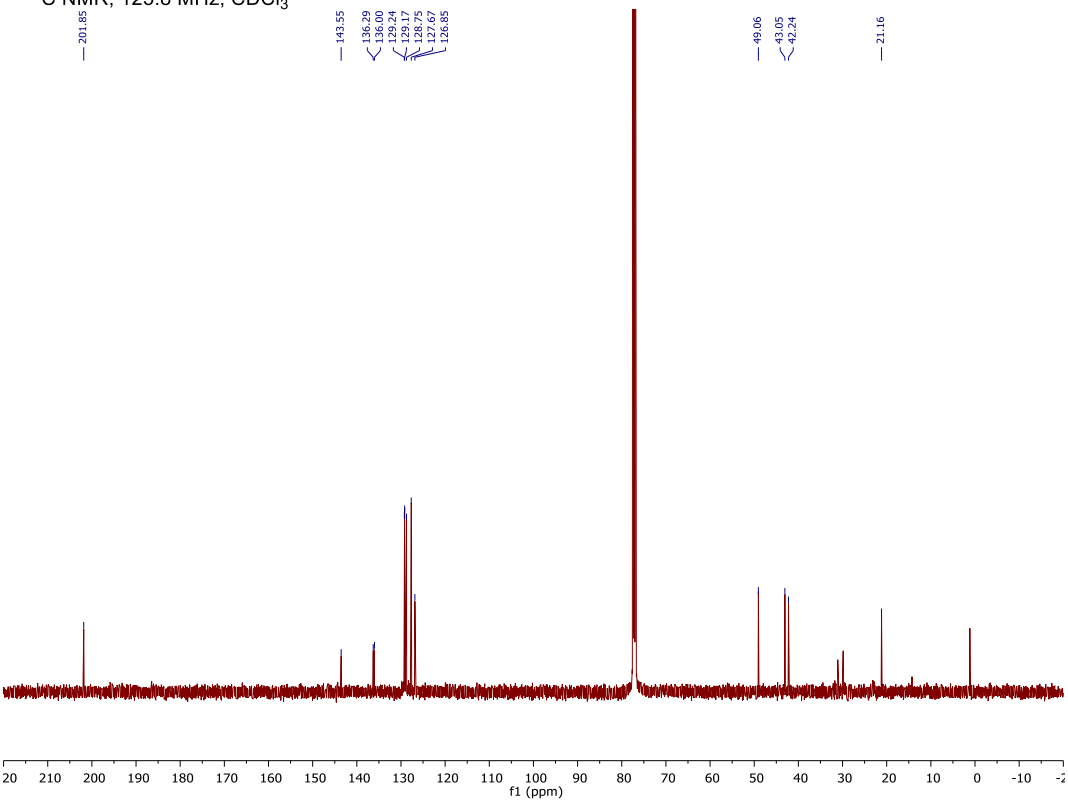


^{1}H NMR, 500 MHz, $CDCl_3$

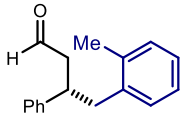


2y

^{13}C NMR, 125.8 MHz, $CDCl_3$

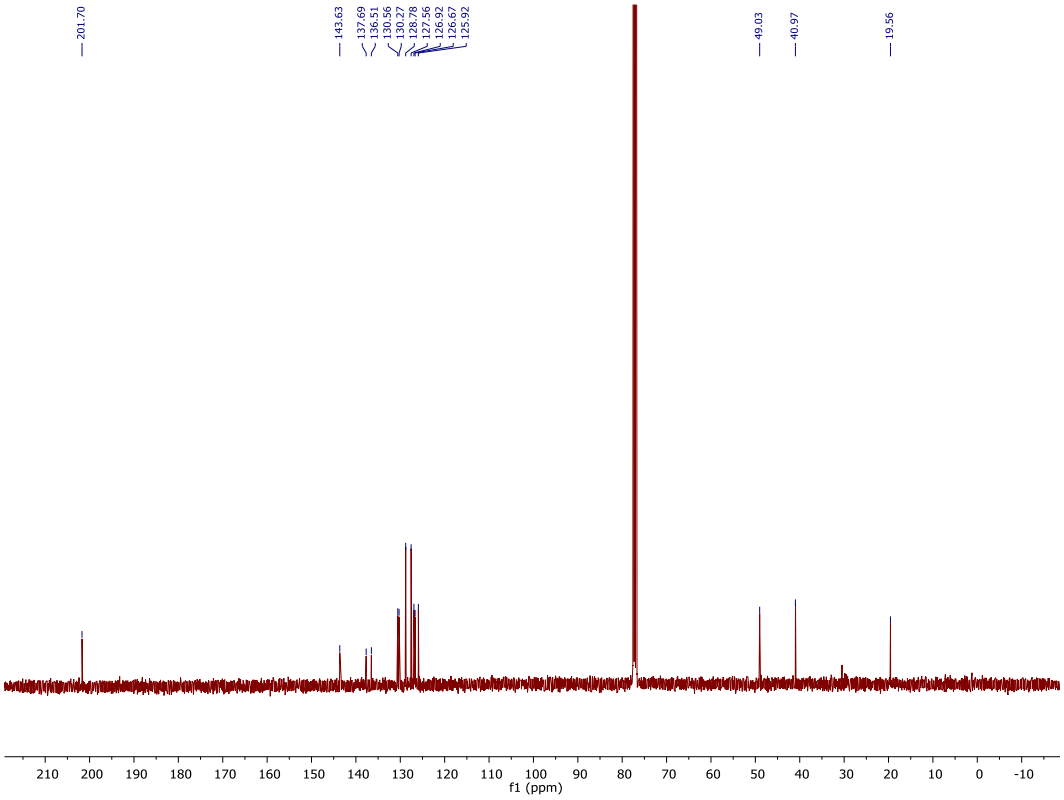


^{1}H NMR, 400 MHz, $CDCl_3$

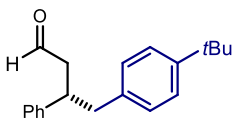


2z

^{13}C NMR, 101 MHz, $CDCl_3$

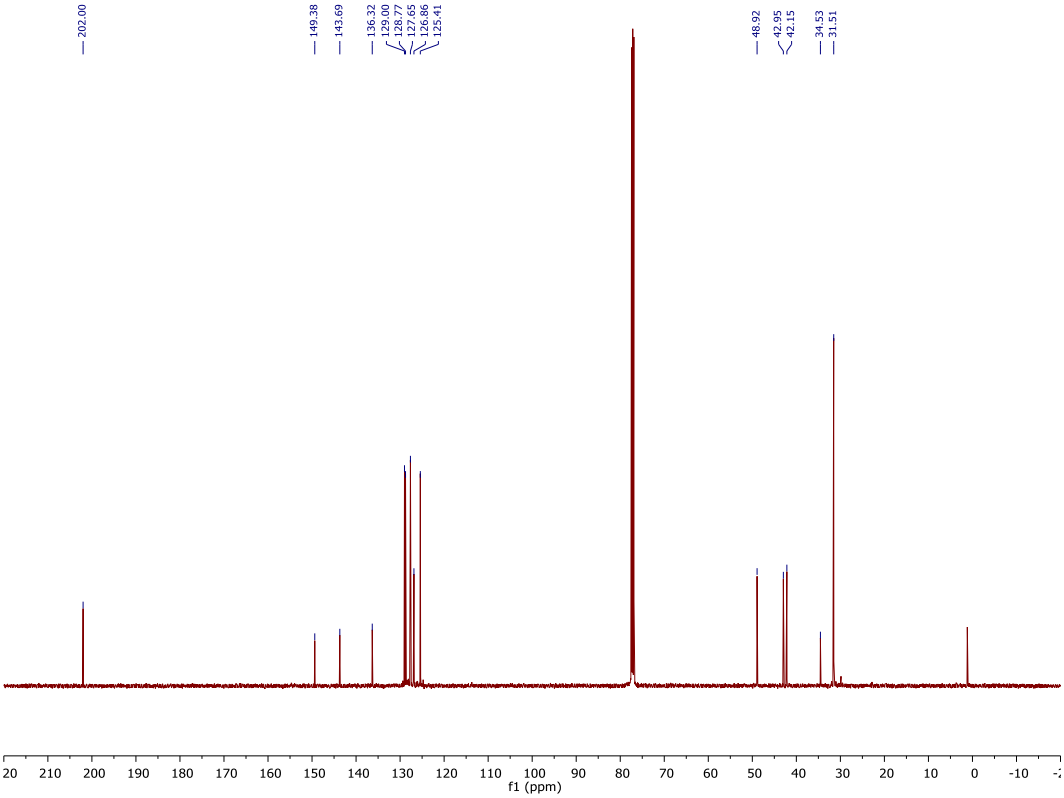


^{1}H NMR, 500 MHz, $CDCl_3$

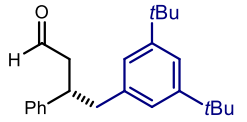


2aa

^{13}C NMR, 125.8 MHz, $CDCl_3$

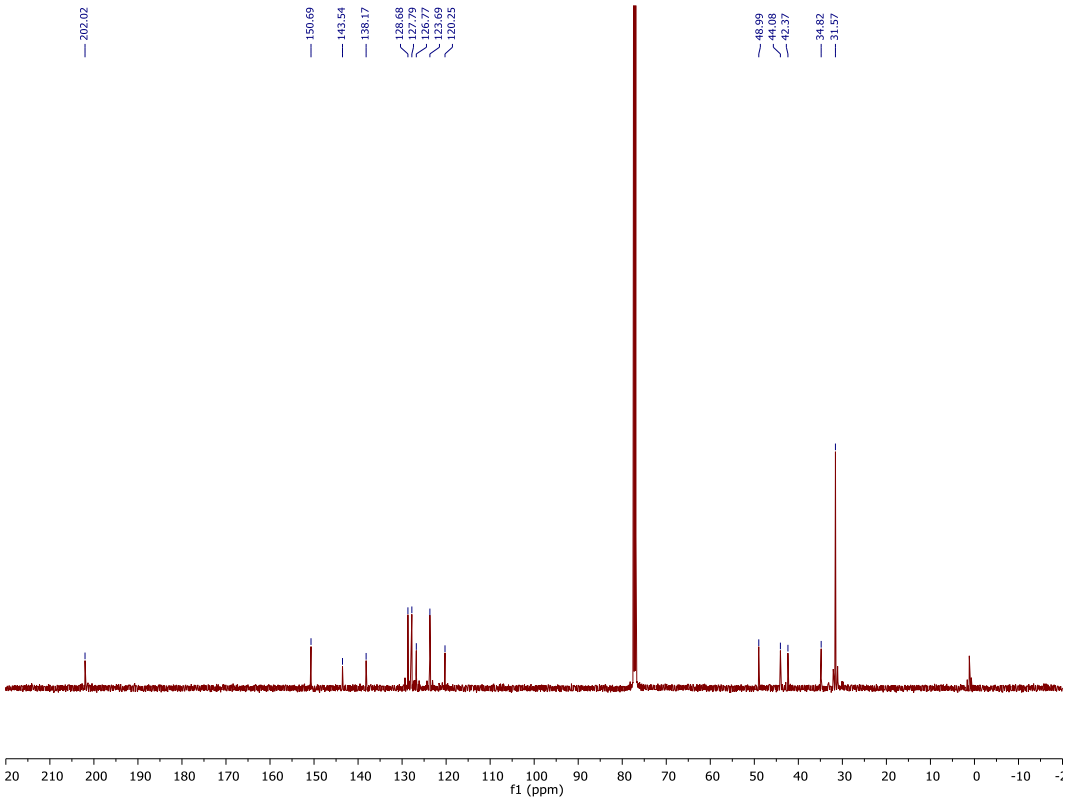


^{1}H NMR, 500 MHz, $CDCl_3$

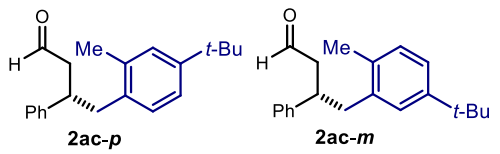


2ab

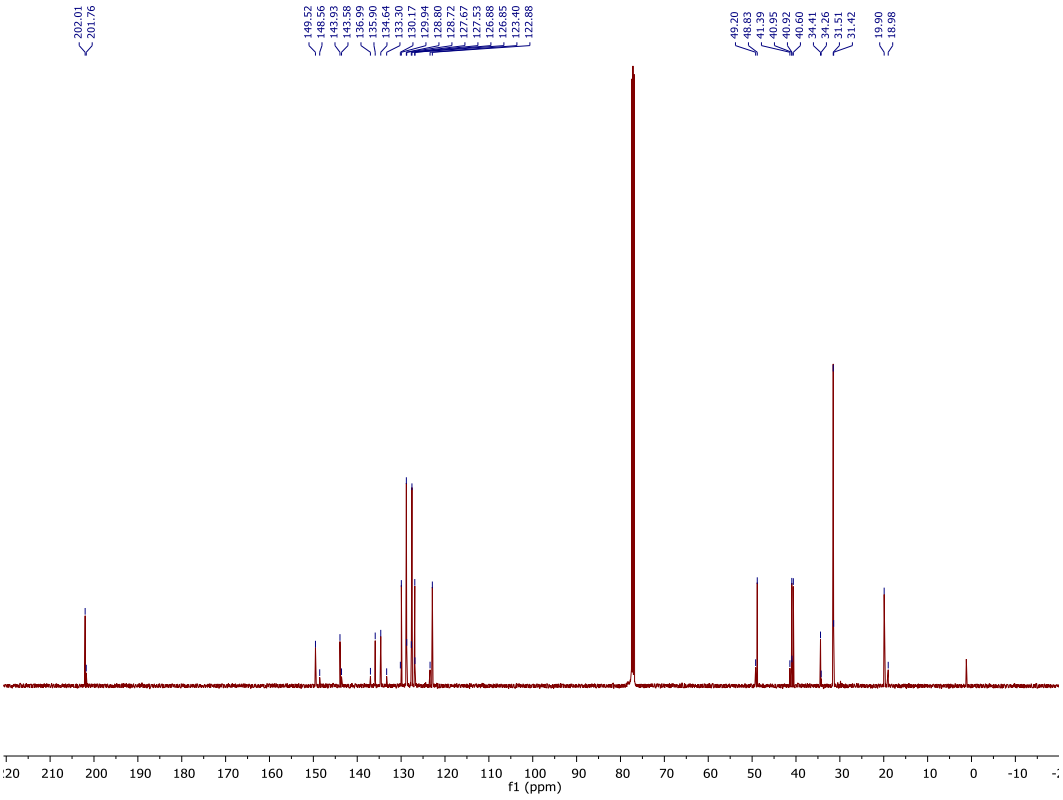
^{13}C NMR, 125.8 MHz, $CDCl_3$



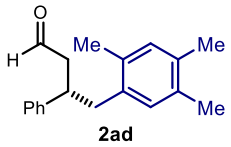
^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 101 MHz, $CDCl_3$

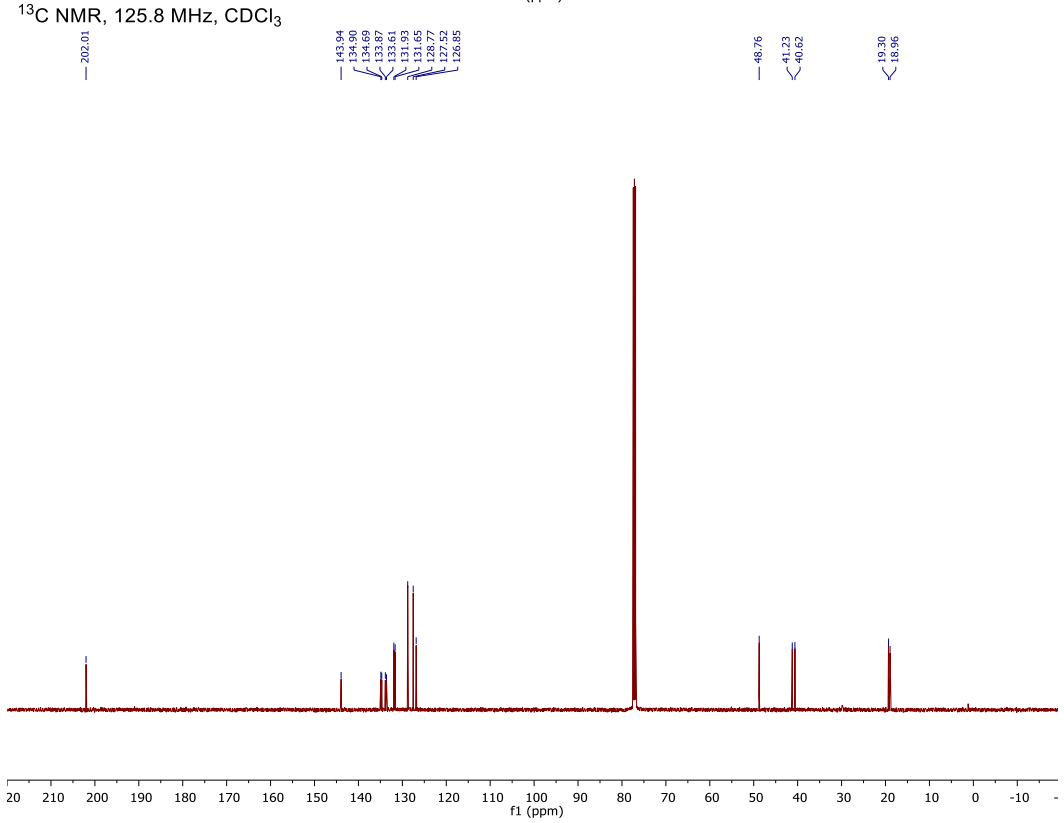


^{1}H NMR, 500 MHz, $CDCl_3$

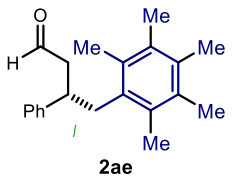


2ad

^{13}C NMR, 125.8 MHz, $CDCl_3$

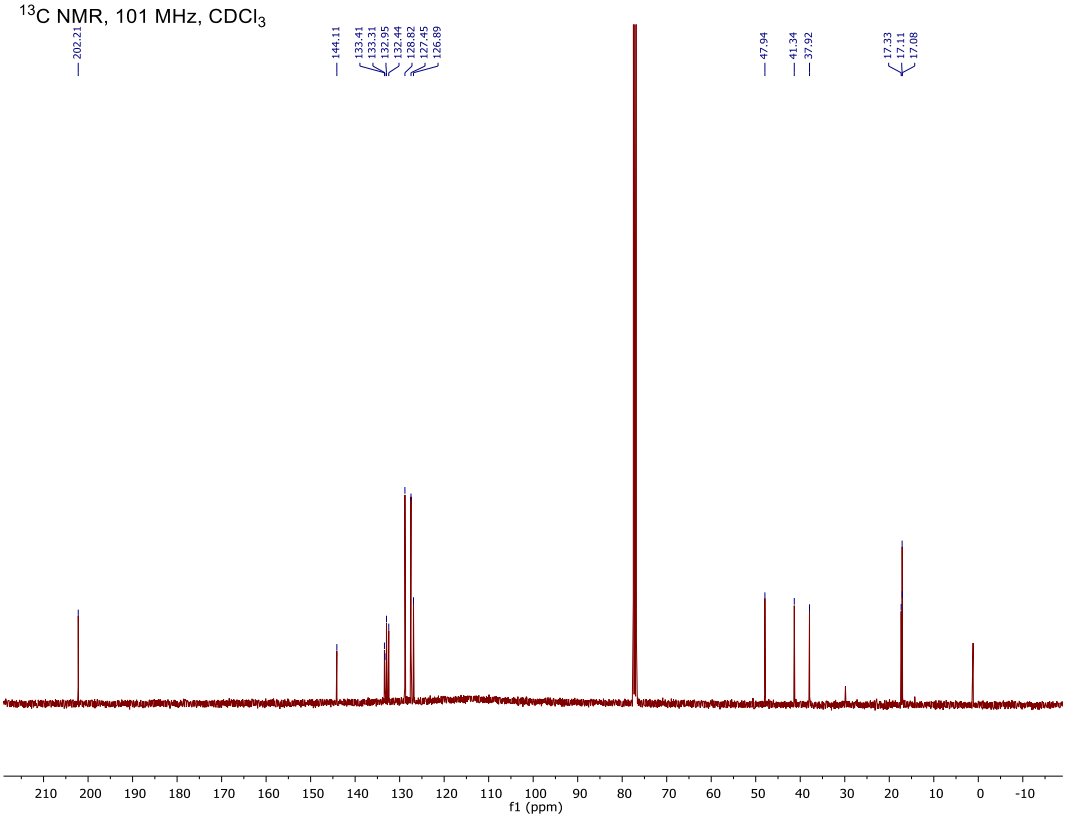


^{1}H NMR, 400 MHz, $CDCl_3$

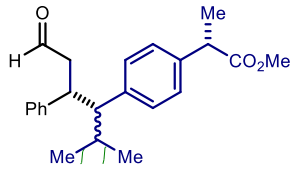


2ae

^{13}C NMR, 101 MHz, $CDCl_3$

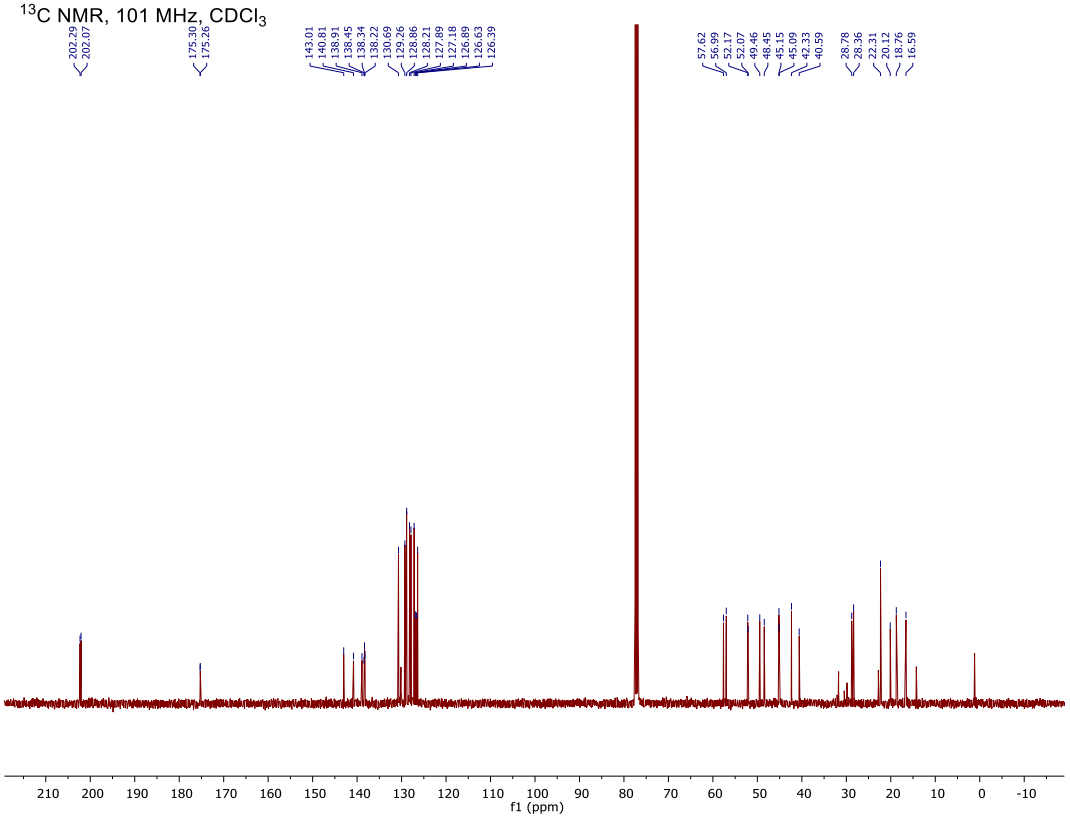


^{1}H NMR, 400 MHz, $CDCl_3$

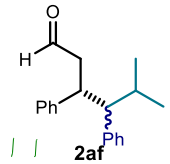


4

^{13}C NMR, 101 MHz, $CDCl_3$

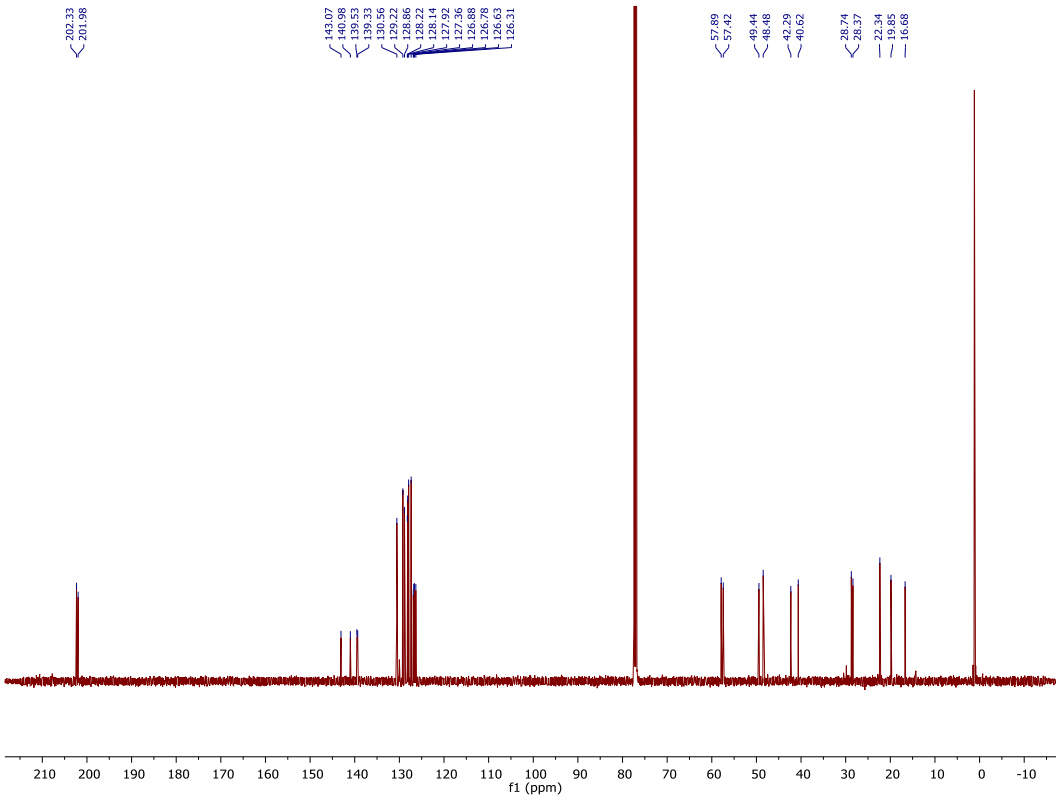


^{1}H NMR, 400 MHz, $CDCl_3$

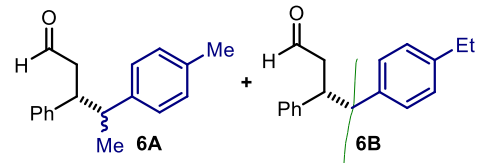


2af

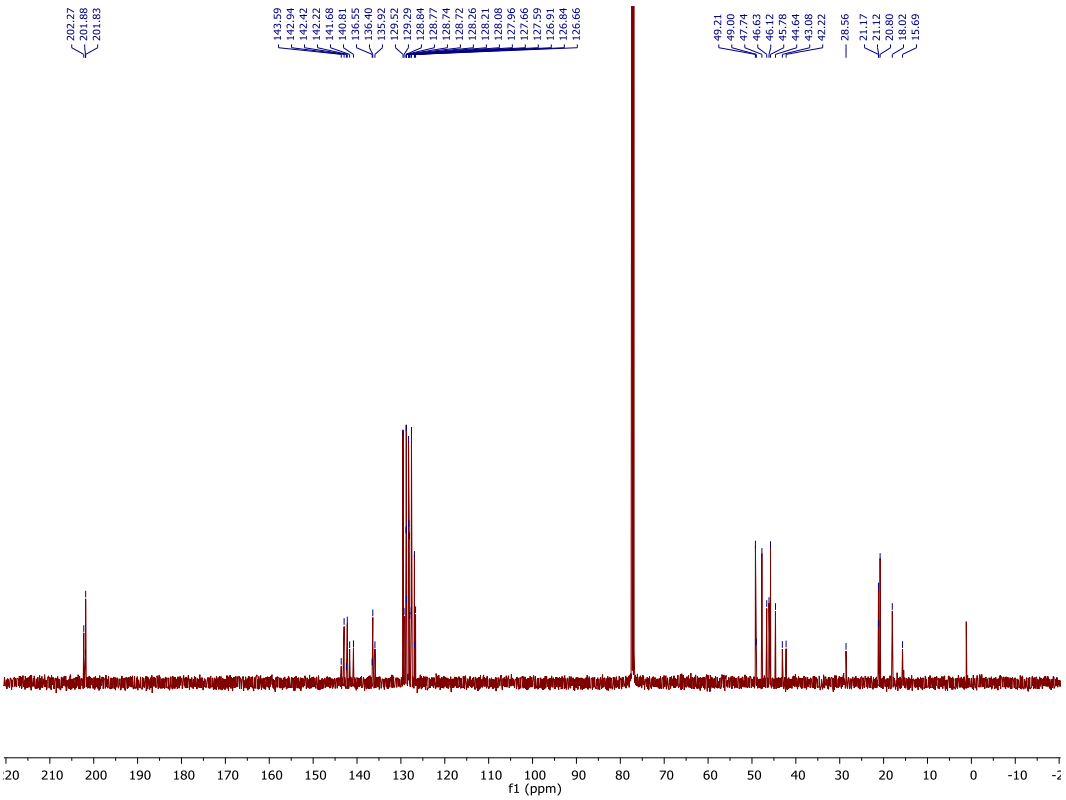
^{13}C NMR, 125.8 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$

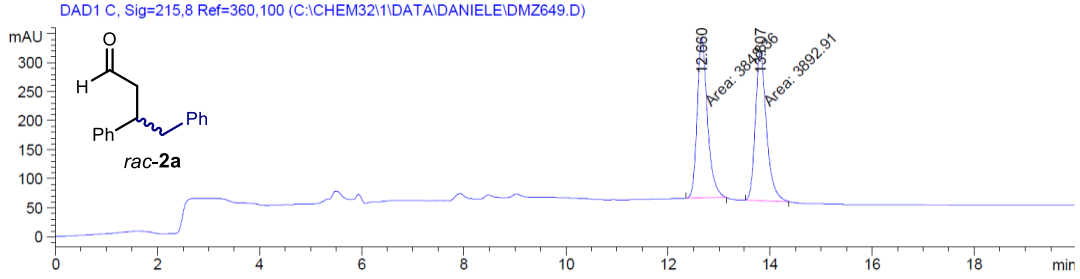


^{13}C NMR, 101 MHz, $CDCl_3$

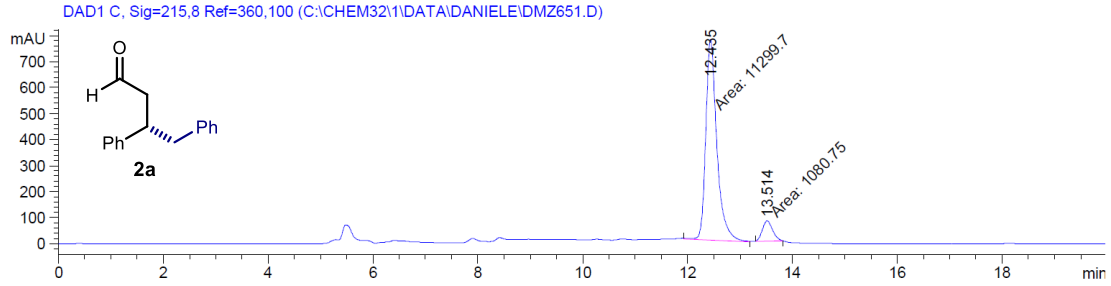


H. HPLC and UPC^2 Traces

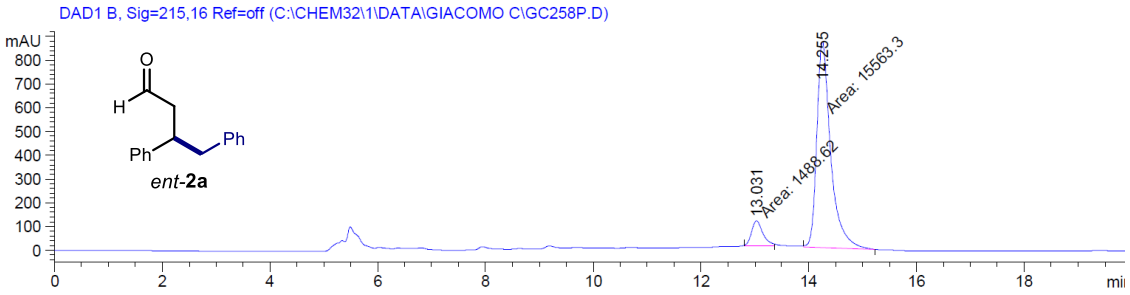
Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 °C, 90:10 hexane/*i*-PrOH, flow rate 0.6 mL/min, λ = 215 nm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.660	MM	0.2323	3848.36084	276.14331	49.7122
2	13.807	MM	0.2539	3892.91406	255.55632	50.2878

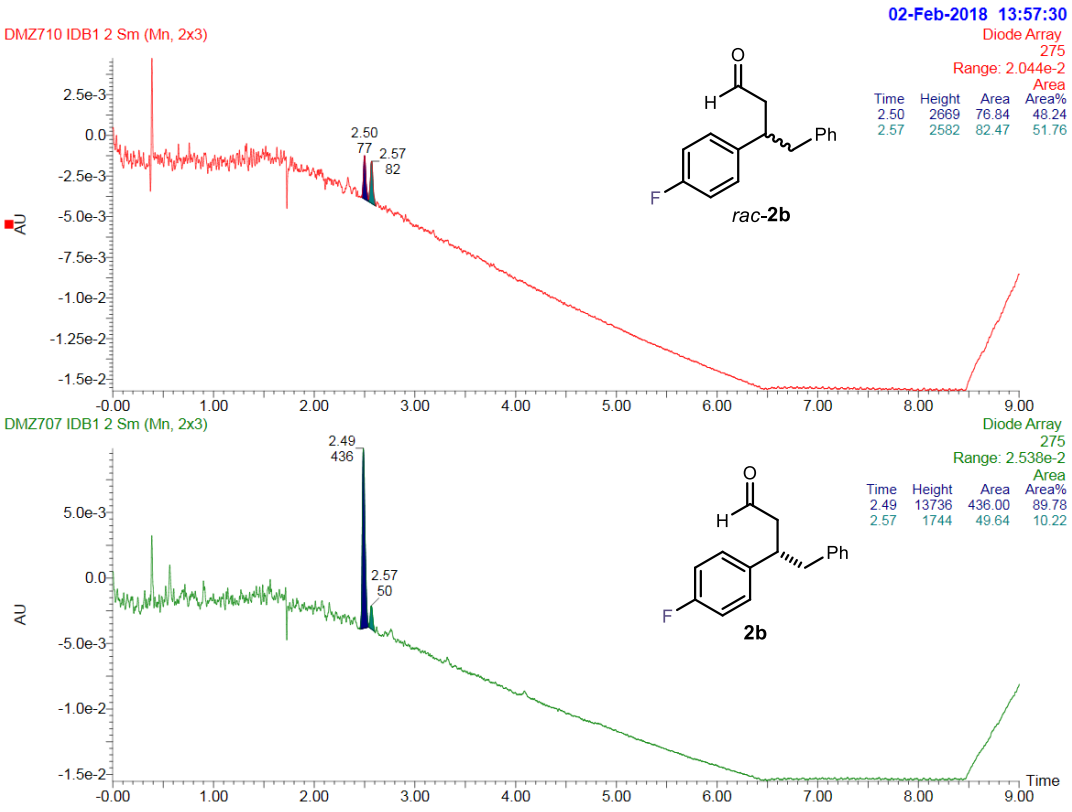


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.435	MM	0.2441	1.12997e4	771.47137	91.2705
2	13.514	MM	0.2287	1080.75391	78.77161	8.7295

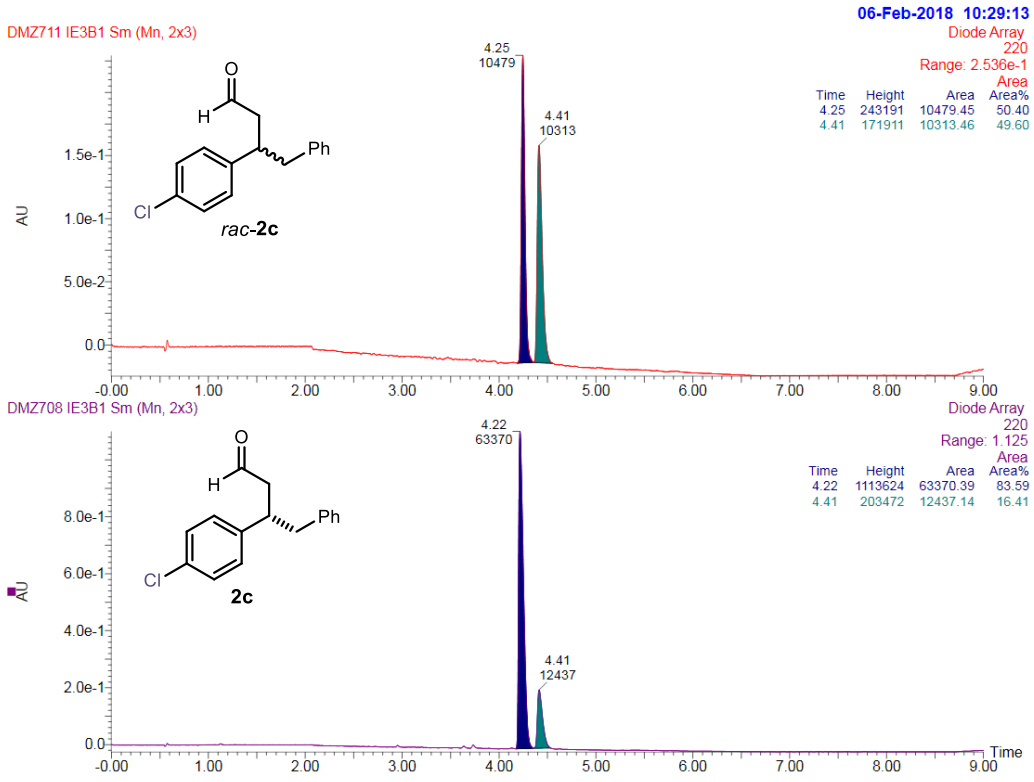


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.031	MM	0.2396	1488.62158	103.56684	8.7299
2	14.255	MM	0.2989	1.55633e4	867.88135	91.2701

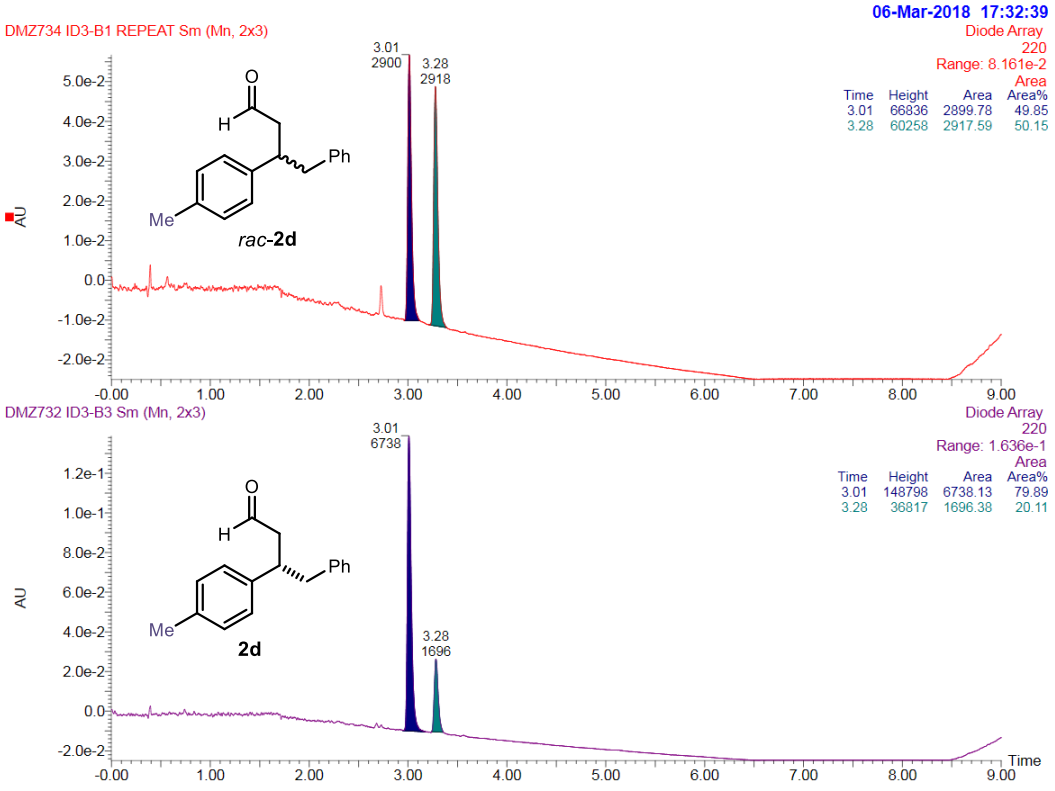
Conditions: UPC^2 (Daicel Chiralpak ID-3 column, 20 °C, gradient CO_2/MeCN from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 275 nm)



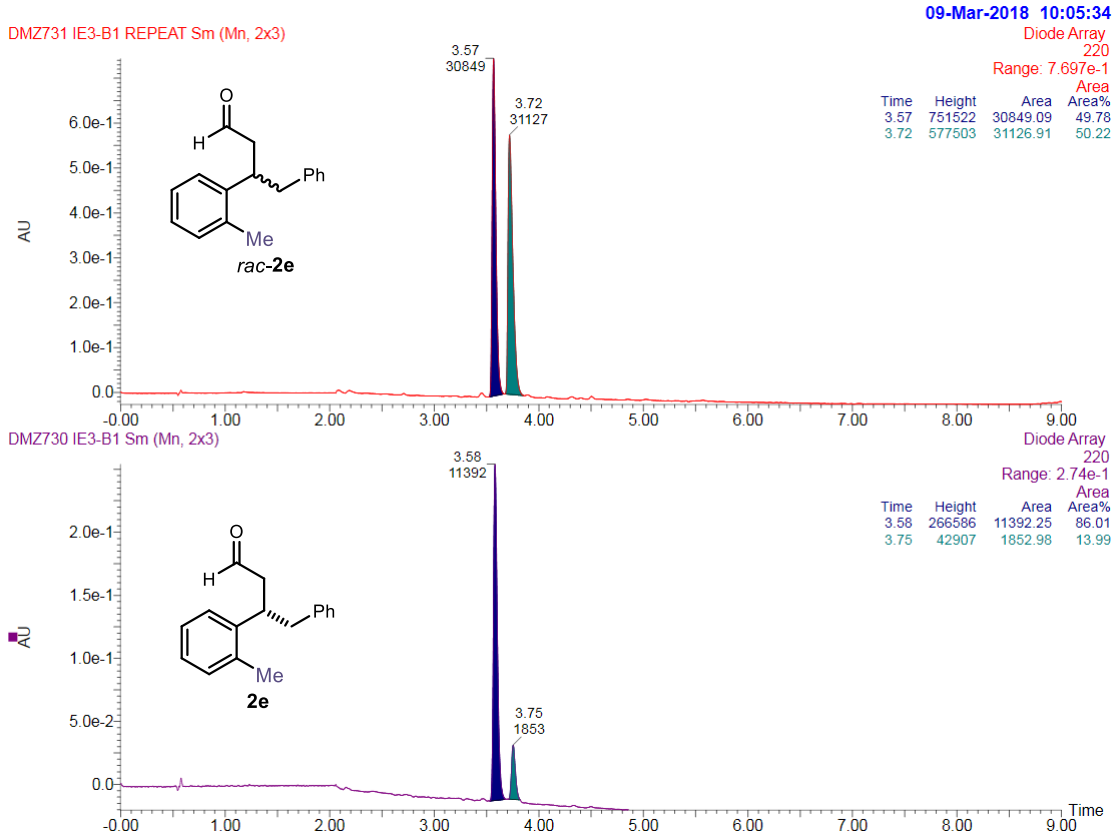
Conditions: UPC^2 (Daicel Chiralpak IE-3 column, 20 °C, gradient CO_2/MeCN from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 220 nm)



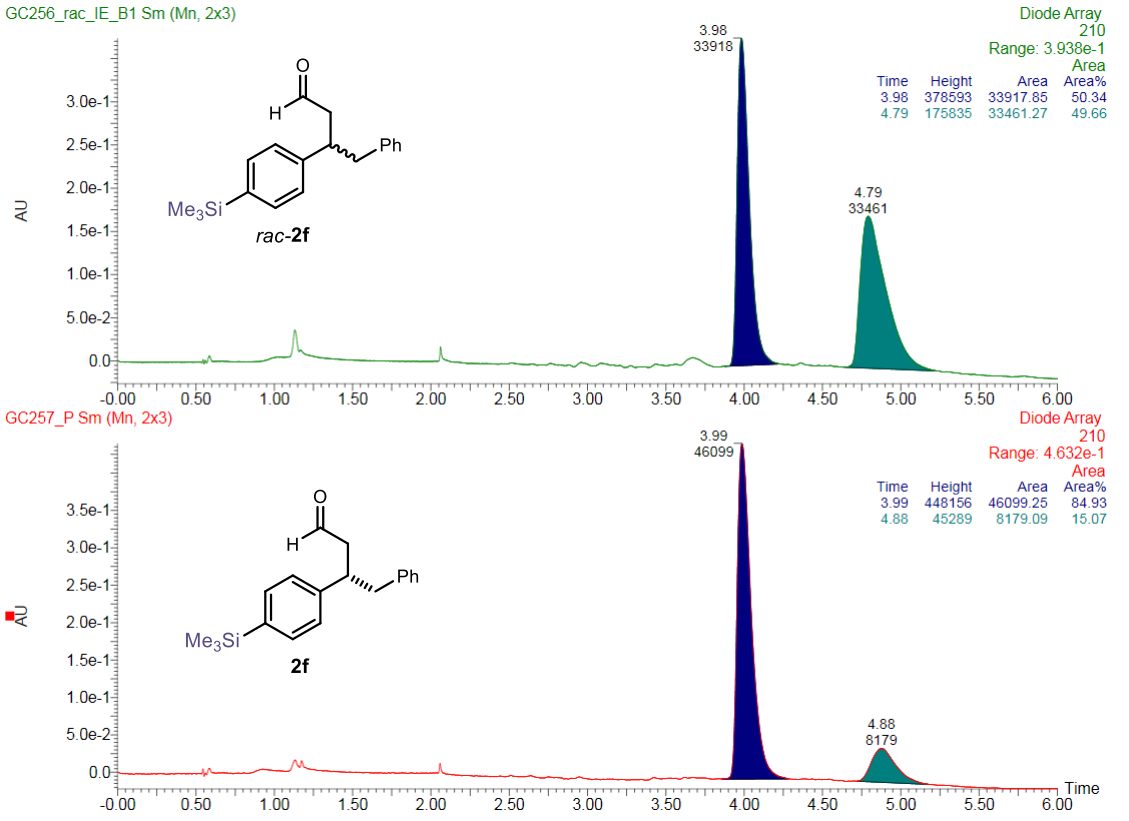
Conditions: UPC^2 (Daicel Chiralpak ID-3 column, 20 °C, gradient CO_2/MeCN from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 220 nm)



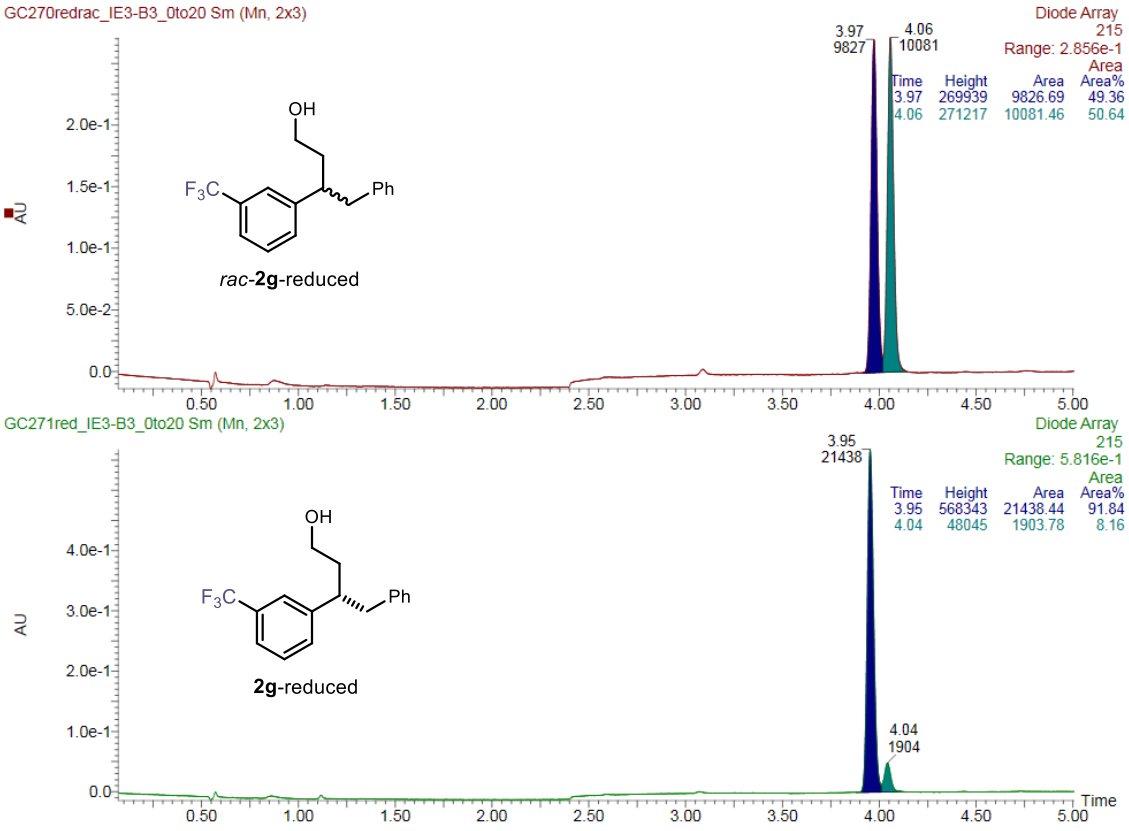
Conditions: UPC^2 (Daicel Chiralpak IE-3 column, 20 °C, gradient CO_2/MeCN from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 220 nm)



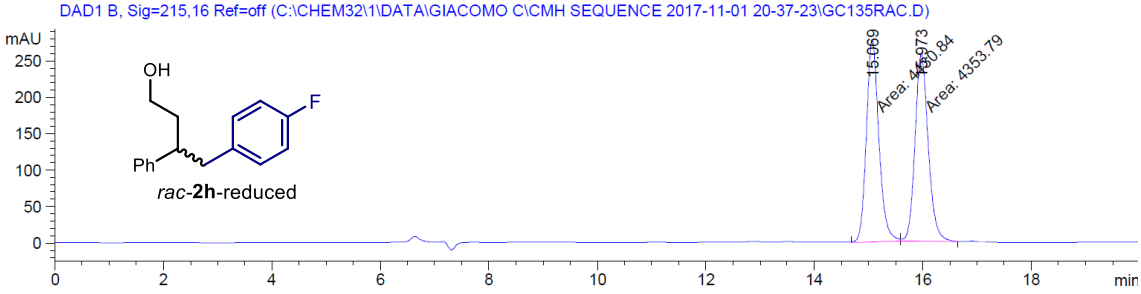
Conditions: UPC^2 (Daicel Chiralpak IE-3 column, 20 °C, gradient CO_2/MeCN from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 2 mL/min, λ = 210 nm)



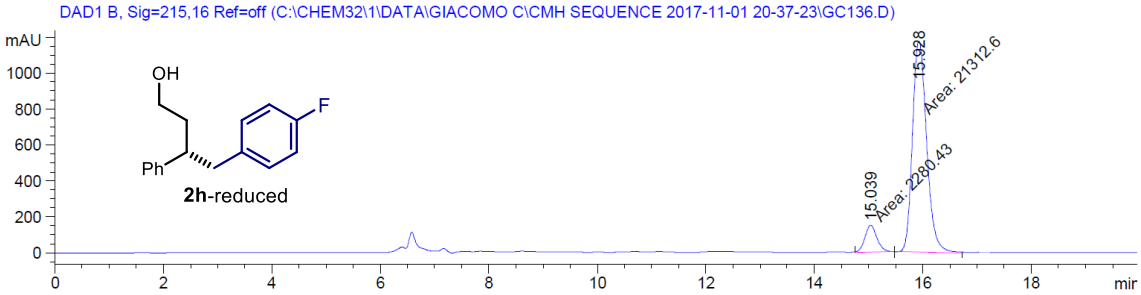
Conditions: UPC^2 (Daicel Chiralpak IE-3 column, 20 °C, gradient CO_2/MeOH from 100% CO_2 to 80:20 over 4 minutes, curve 6, flow rate 2 mL/min, λ = 215 nm)



Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 °C, 90:10 hexane/*i*-PrOH, flow rate 0.5 mL/min, λ = 215 nm)

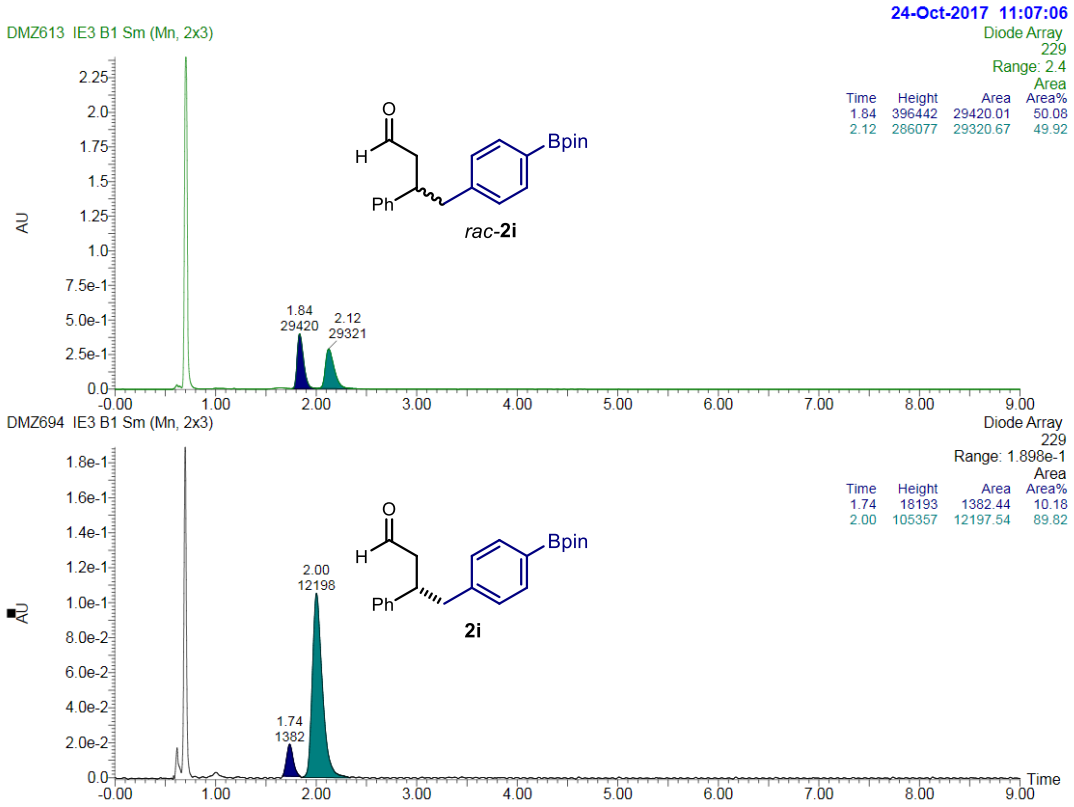


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.069	MM	0.2657	4430.84033	277.89716	50.4386
2	15.973	MM	0.2821	4353.78564	257.23444	49.5614

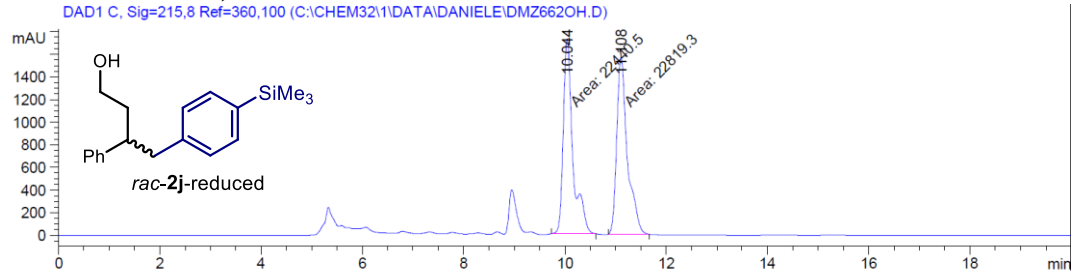


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.039	MM	0.2558	2280.43018	148.60152	9.6657
2	15.928	MM	0.3026	2.13126e4	1173.76208	90.3343

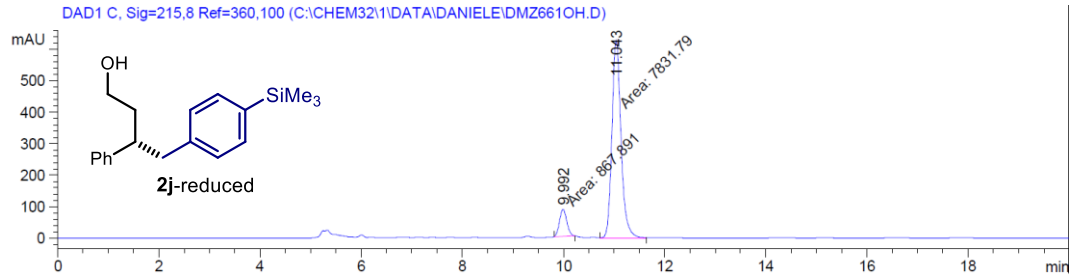
Conditions: UPC^2 (Daicel Chiralpak IE-3 column, 20 °C, gradient CO_2/MeCN from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 229 nm)



Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 °C, 90:10 hexane/*i*-PrOH, flow rate 0.6 mL/min, λ = 215 nm)

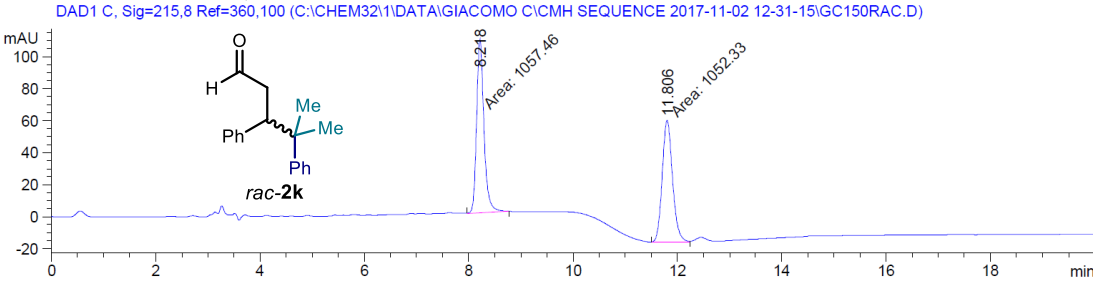


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.044	MM	0.2177	2.24405e4	1718.00415	49.5815
2	11.108	MM	0.2431	2.28193e4	1564.69275	50.4185

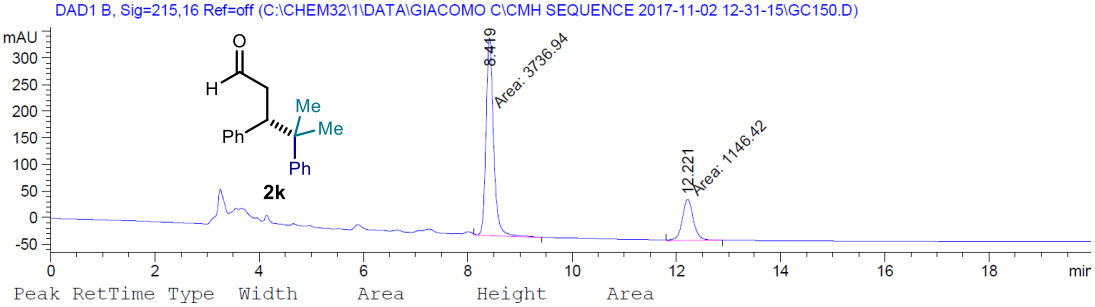


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.992	MM	0.1675	867.89099	86.35443	9.9761
2	11.043	MM	0.2078	7831.79150	628.06952	90.0239

Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 °C, 90:10 hexane/*i*-PrOH, flow rate 1.0 mL/min, λ = 215 nm)

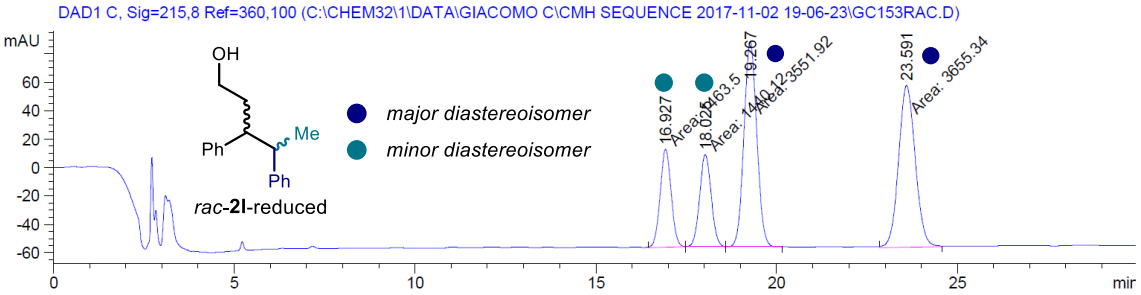


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.218	MM	0.1622	1057.45691	108.64613	50.1216
2	11.806	MM	0.2303	1052.32654	76.15945	49.8784

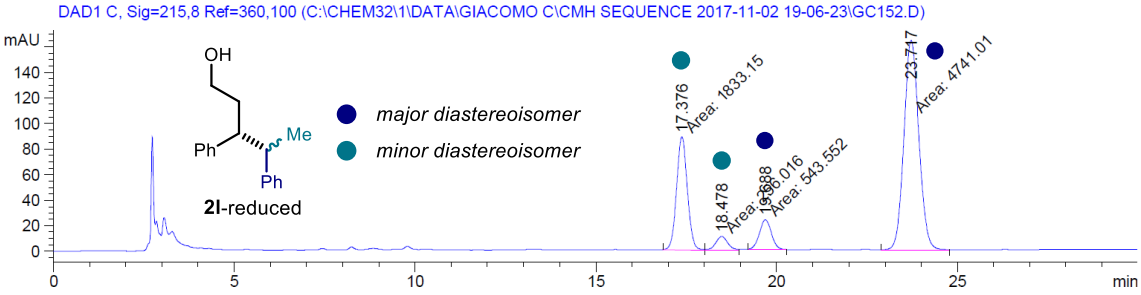


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.419	MM	0.1673	3736.94214	372.28320	76.5239
2	12.221	MM	0.2454	1146.42249	77.86103	23.4761

Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 °C, 97:3 hexane/*i*-PrOH, flow rate 1.2 mL/min, λ = 215 nm)

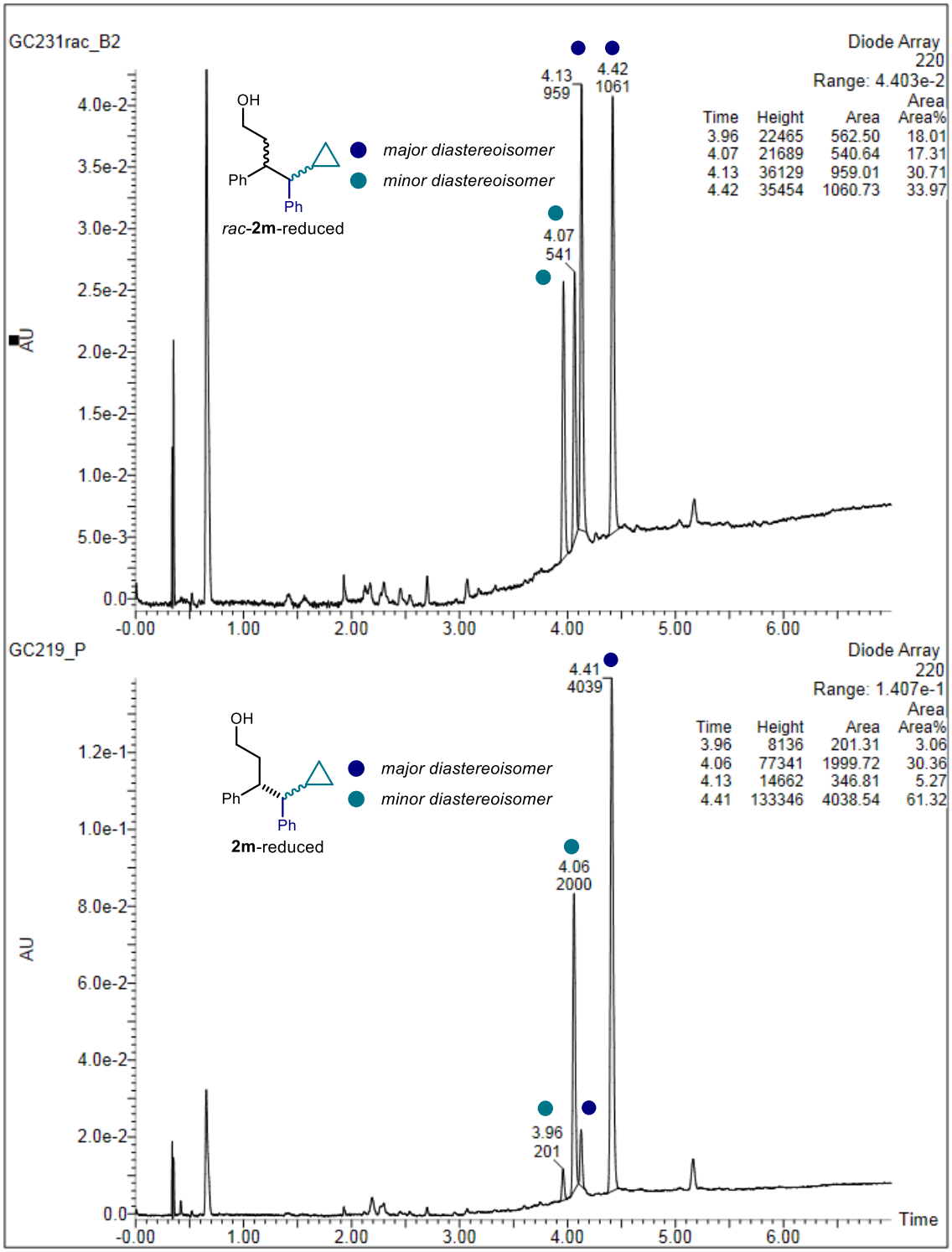


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.927	MM	0.3536	1463.49548	68.98871	14.4745
2	18.025	MM	0.3712	1440.12280	64.66197	14.2433
3	19.267	MM	0.4094	3551.92017	144.59261	35.1297
4	23.591	MM	0.5351	3655.34229	113.86221	36.1526

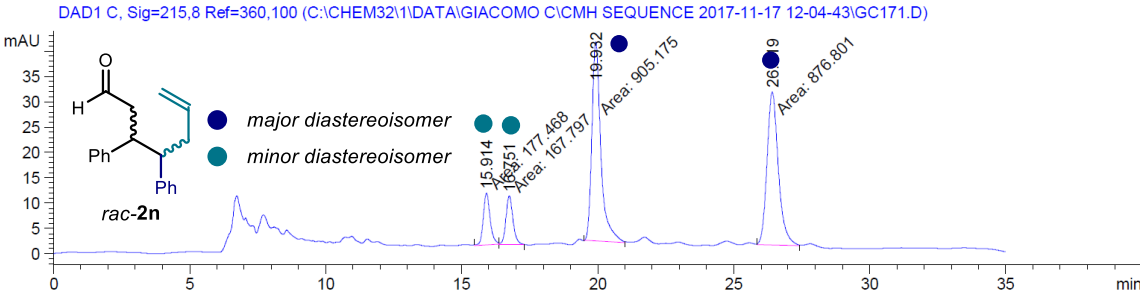


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.376	MM	0.3451	1833.14709	88.53117	24.8605
2	18.478	MM	0.3918	256.01578	10.89076	3.4720
3	19.688	MM	0.3880	543.55225	23.34823	7.3715
4	23.717	MM	0.4812	4741.00684	164.21342	64.2960

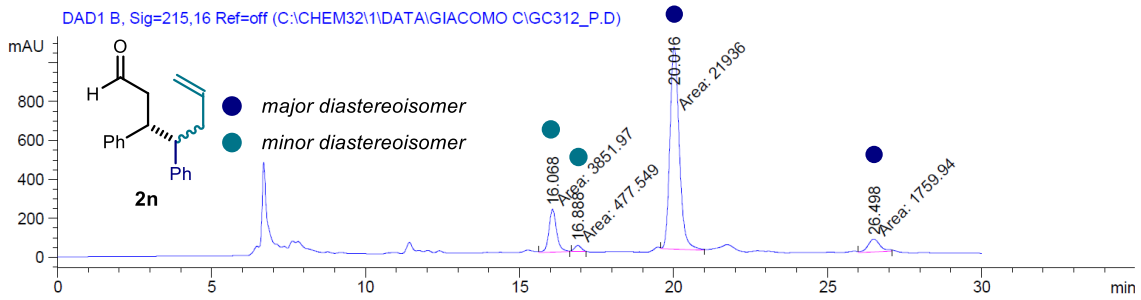
Conditions: UPC^2 (Daicel Chiralpak CEL-1 column, 20 °C, gradient CO_2/*i*-PrOH from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 220 nm)



Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 °C, 95:5 hexane/*i*-PrOH, flow rate 0.5 mL/min, λ = 215 nm)

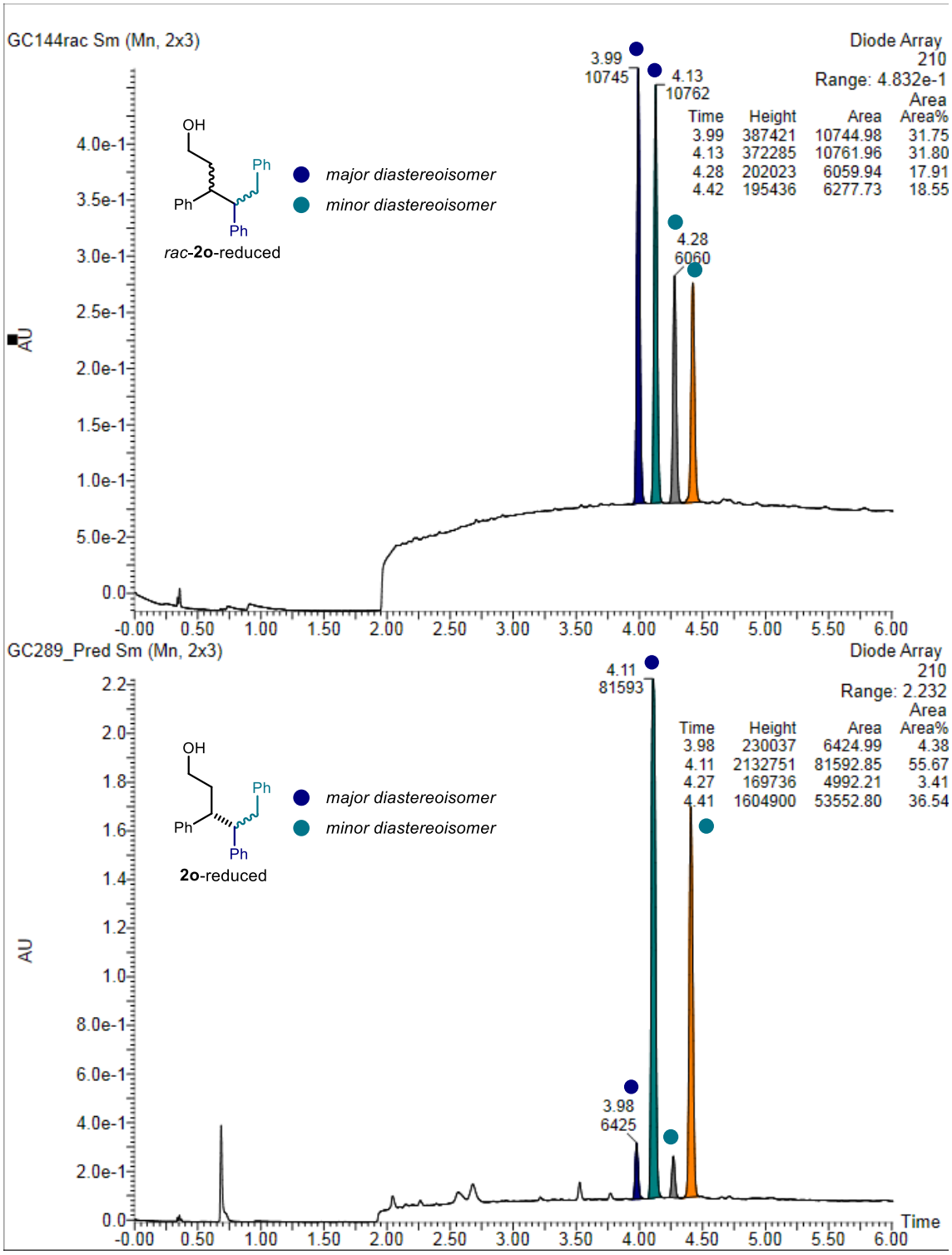


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.914	MM	0.2894	177.46751	10.21873	8.3426
2	16.751	MM	0.2934	167.79715	9.53161	7.8880
3	19.932	MM	0.3834	905.17523	39.35262	42.5516
4	26.419	MM	0.4836	876.80133	30.21835	41.2178

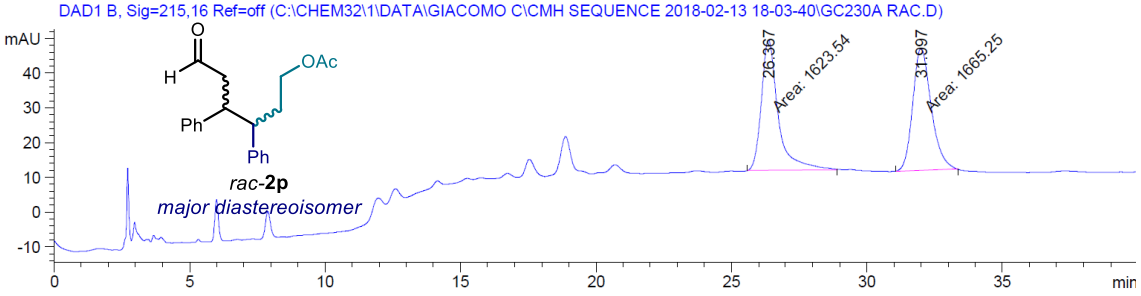


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.068	MM	0.2920	3851.97192	219.85869	13.7446
2	16.888	MM	0.2549	477.54913	31.22558	1.7040
3	20.016	MM	0.3517	2.19360e4	1039.63049	78.2716
4	26.498	MM	0.4493	1759.94153	65.28530	6.2798

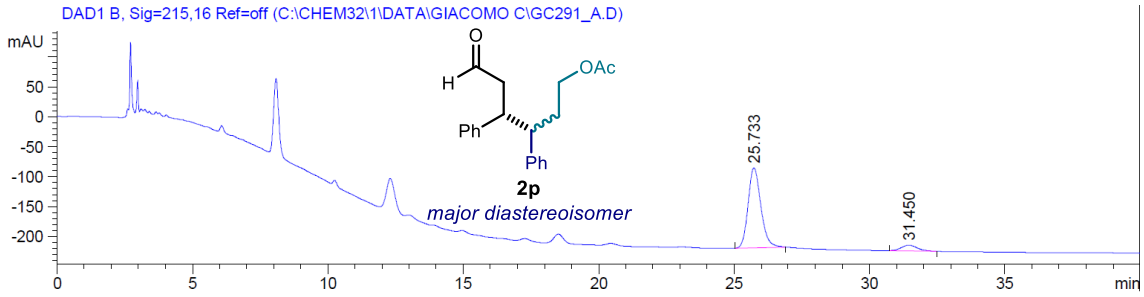
Conditions: UPC^2 (Daicel Chiralpak CEL-1 column, 20 °C, gradient CO_2/MeOH from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 210 nm)



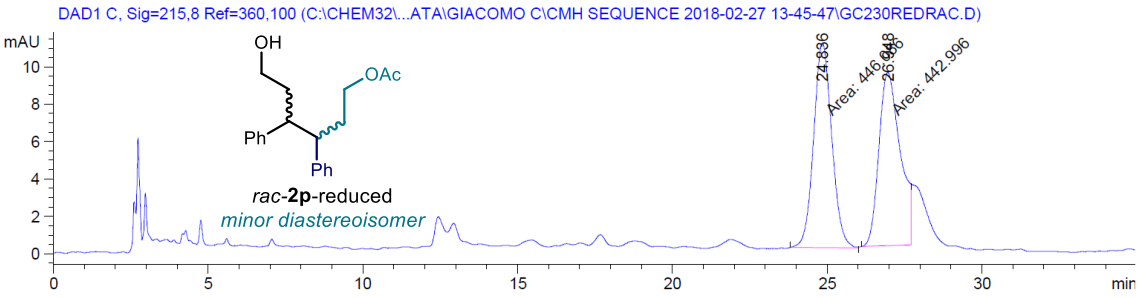
Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 °C, 90:10 hexane/*i*-PrOH, flow rate 1.2 mL/min, λ = 215 nm)



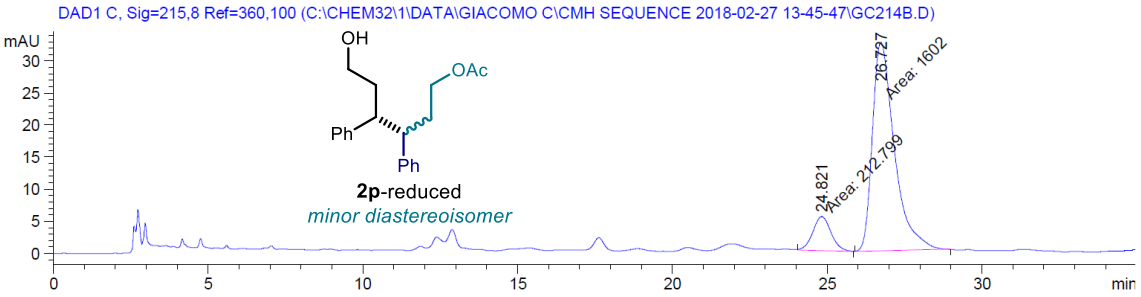
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.367	MM	0.7210	1623.53931	37.52808	49.3658
2	31.997	MM	0.7901	1665.25256	35.12791	50.6342



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.733	BB	0.5064	4409.52441	133.84396	91.6741
2	31.450	BB	0.6312	400.47531	9.62849	8.3259

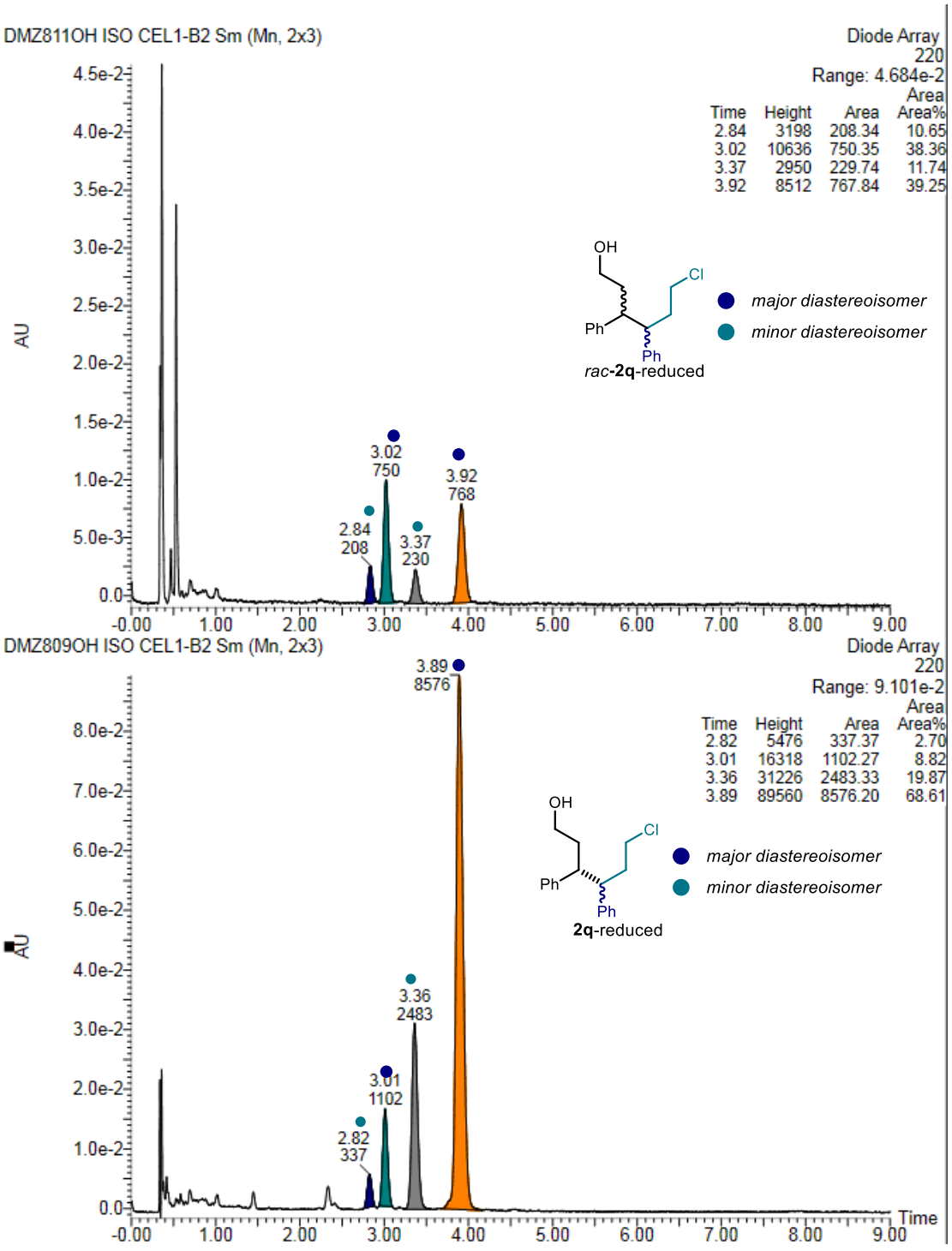


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.836	MM	0.6782	446.08609	10.96235	50.1738
2	26.948	MM	0.7973	442.99564	9.26019	49.8262

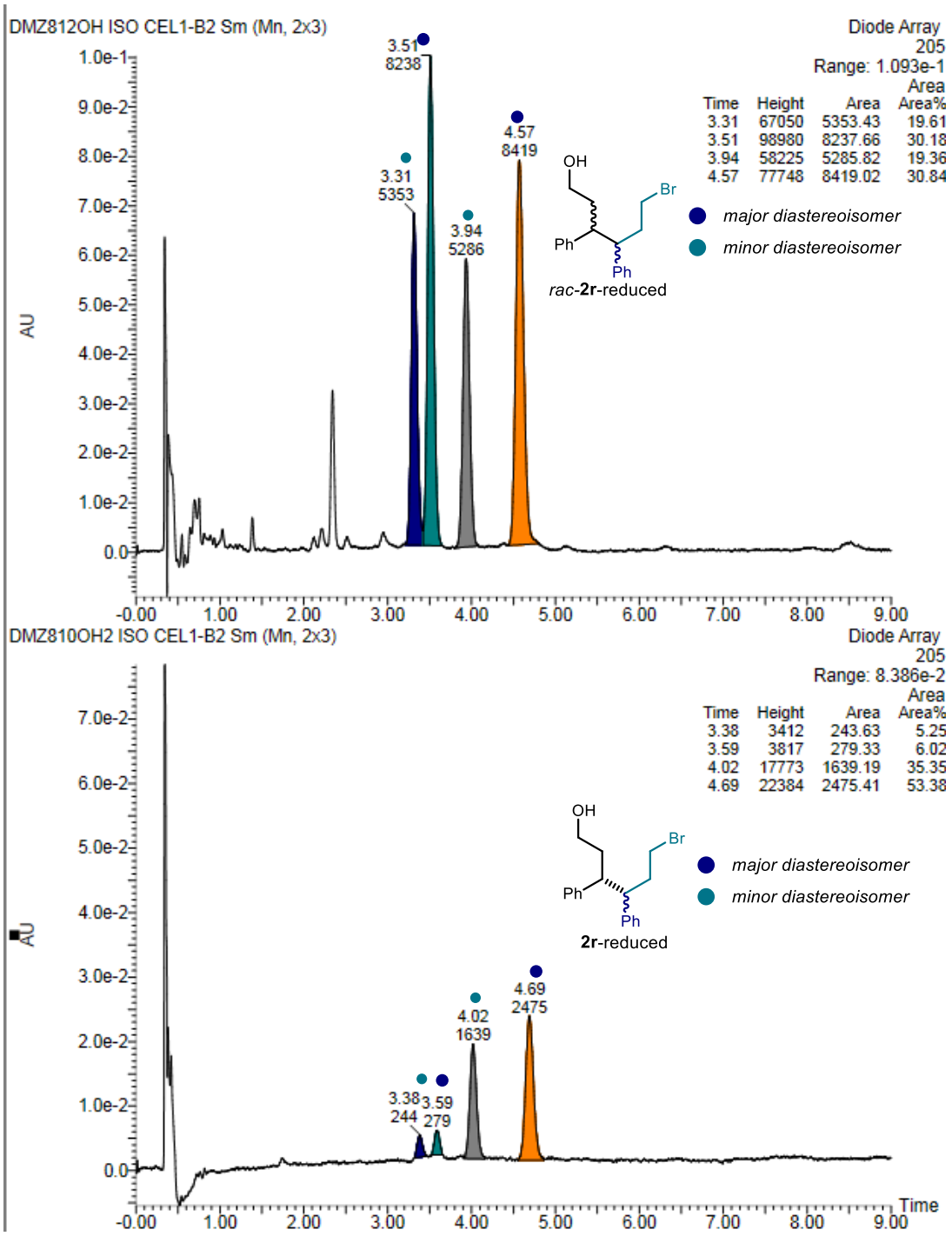


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.821	MM	0.6735	212.79890	5.26588	11.7257
2	26.727	MM	0.8229	1602.00220	32.44505	88.2743

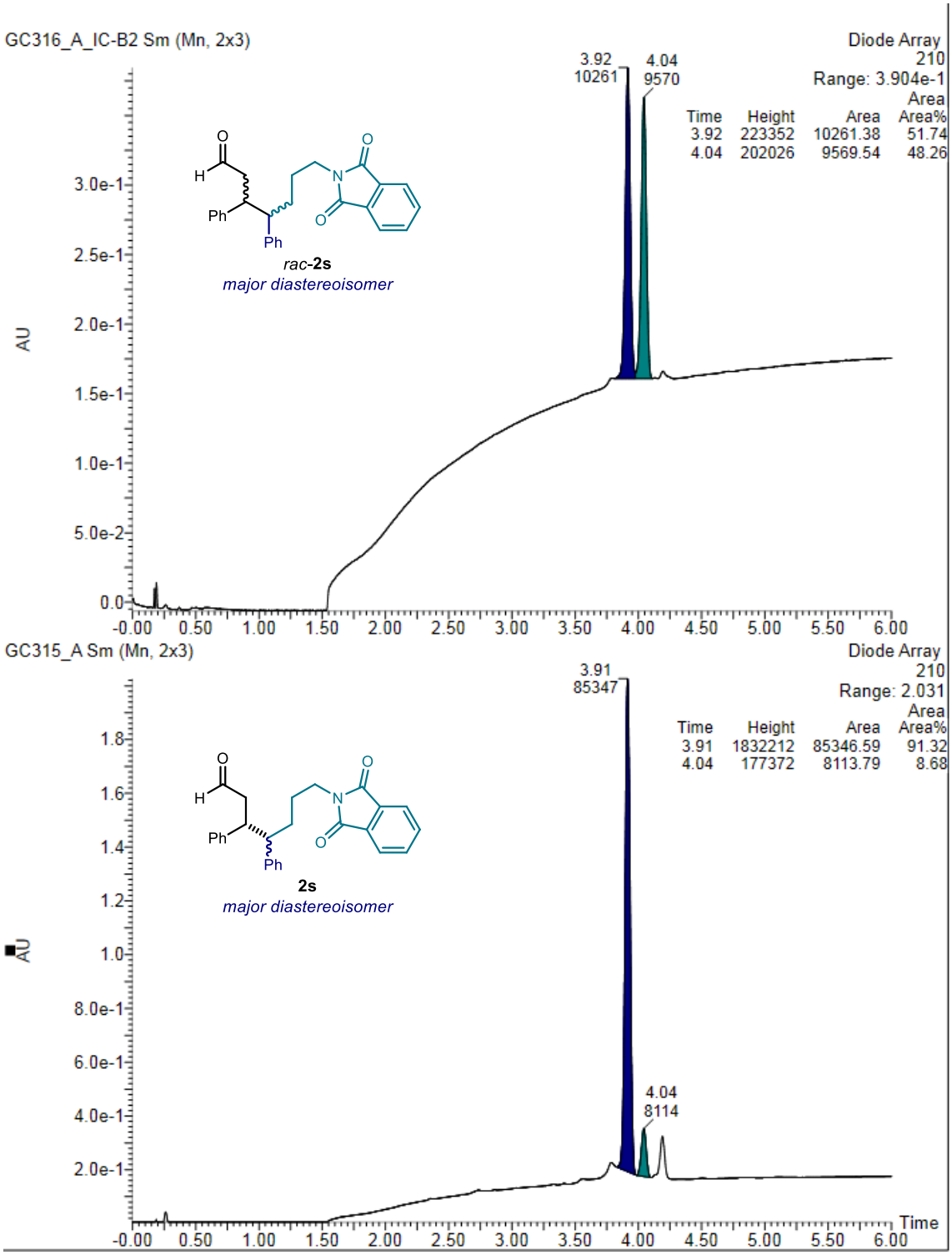
Conditions: UPC^2 (Daicel Chiralpak CEL-1 column, 20 °C, isocratic CO_2/*i*-PrOH 90:10 flow rate 3 mL/min, λ = 220 nm)



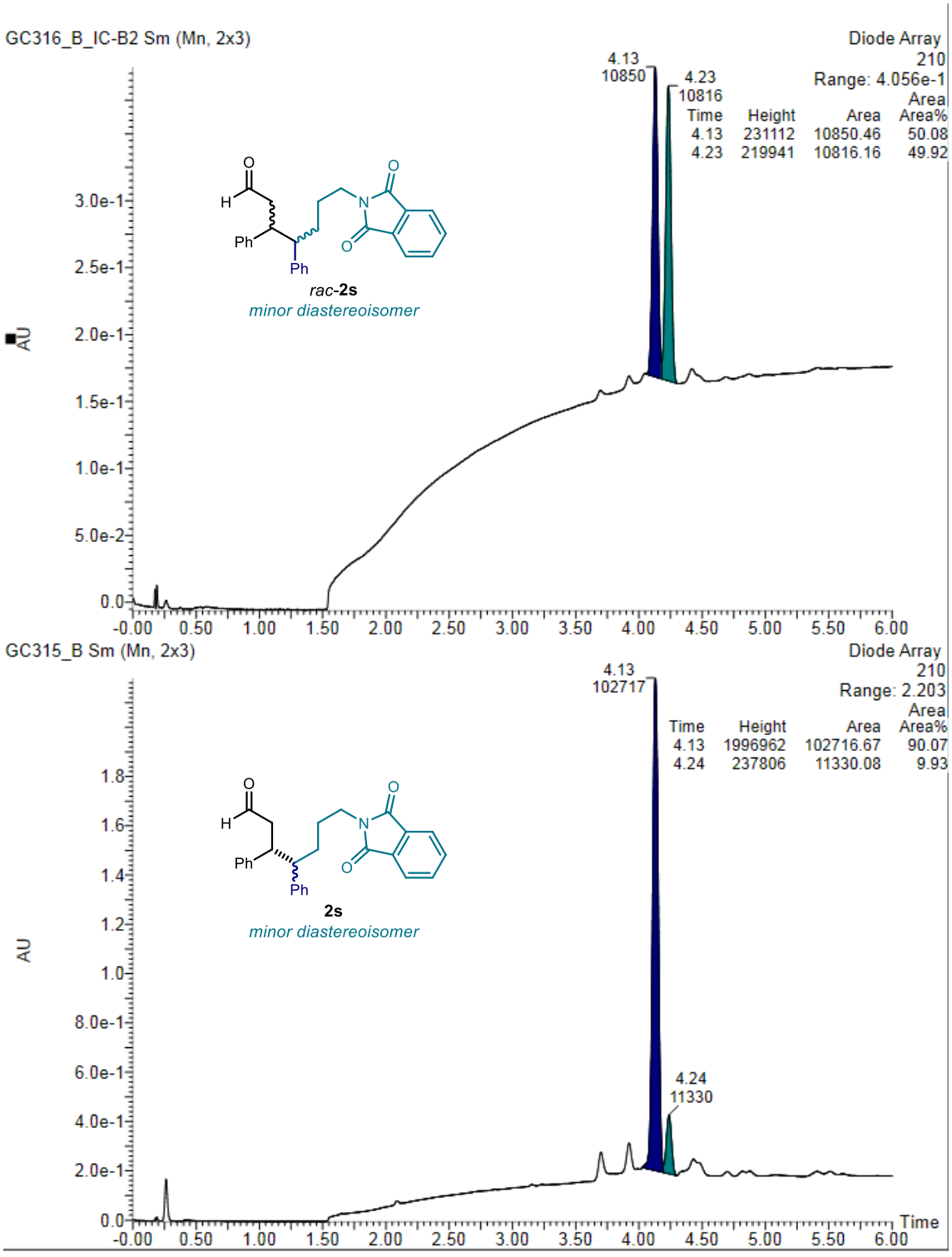
Conditions: UPC^2 (Daicel Chiralpak CEL-1 column, 20 °C, isocratic CO_2/*i*-PrOH 90:10 flow rate 3 mL/min, λ = 205 nm)



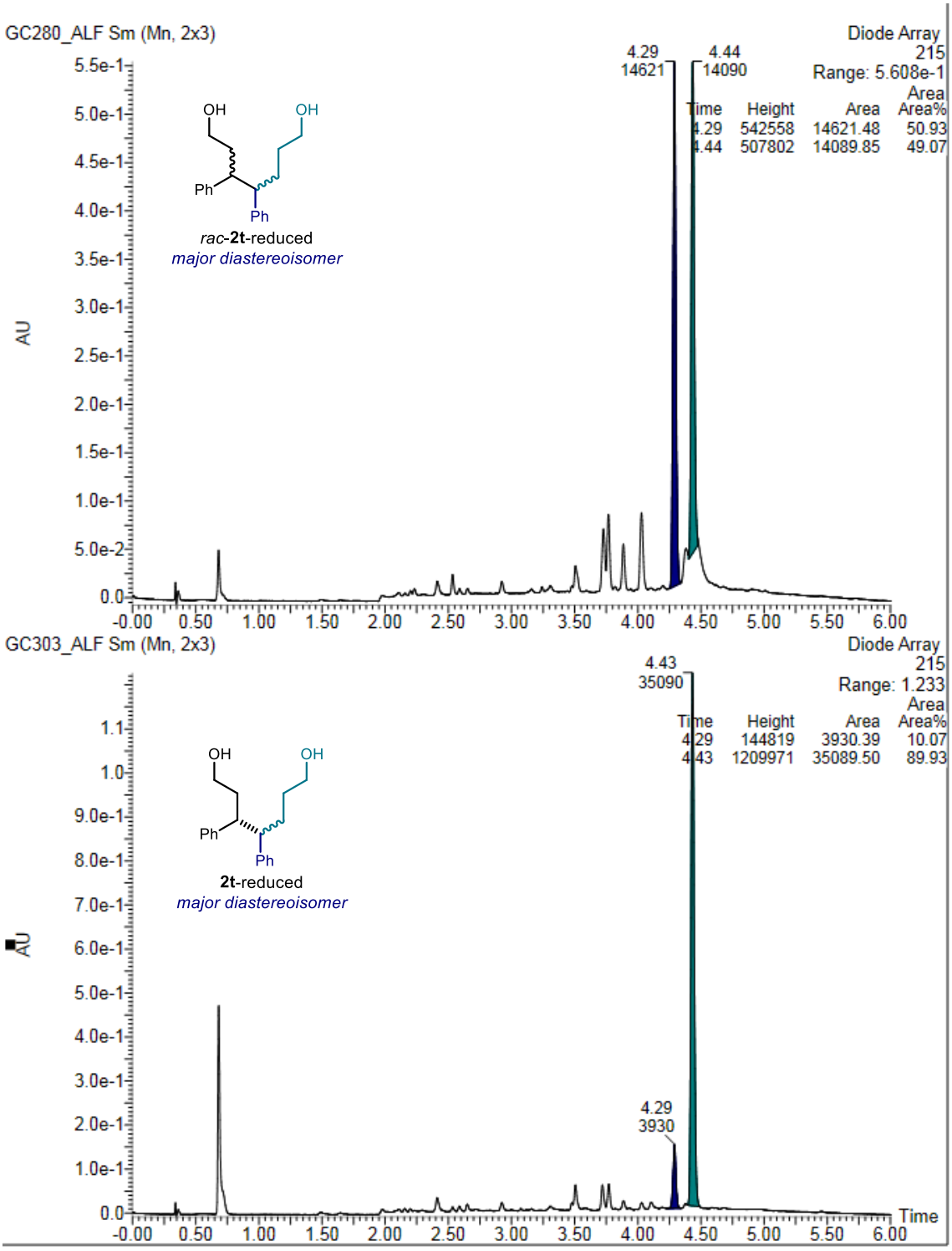
Conditions: UPC^2 (Daicel Chiralpak IC-3 column, 20 °C, gradient CO_2/*i*-PrOH from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 210 nm)



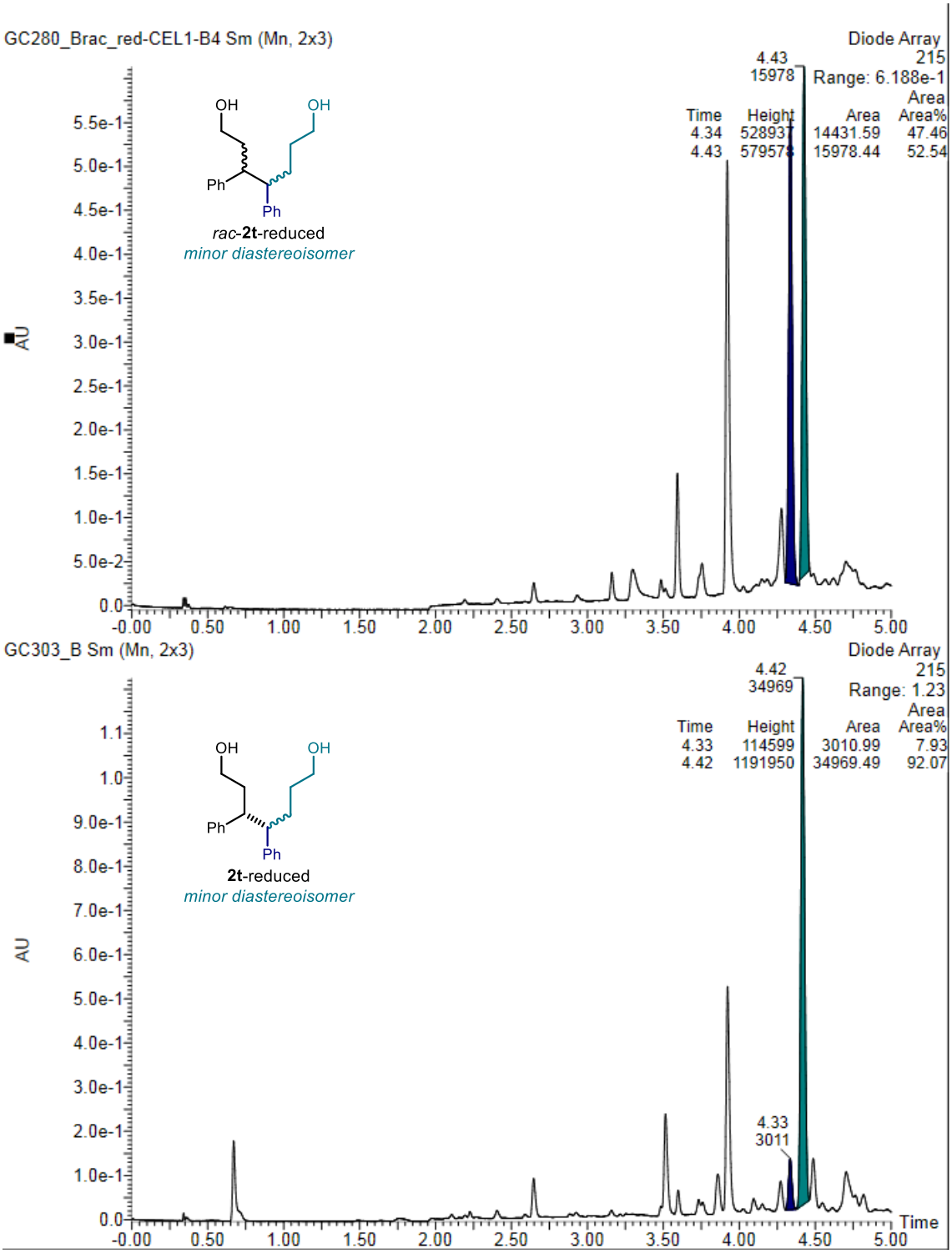
Conditions: UPC^2 (Daicel Chiralpak IC-3 column, 20 °C, gradient CO_2/*i*-PrOH from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 210 nm)



Conditions: UPC^2 (Daicel Chiralpak CEL-1 column, 20 °C, gradient CO_2/EtOH from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 215 nm)

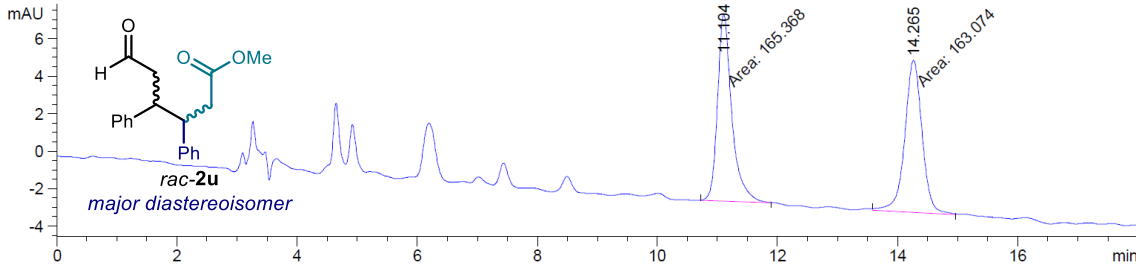


Conditions: UPC^2 (Daicel Chiralpak CEL-1 column, 20 °C, gradient CO_2/EtOH from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 215 nm)



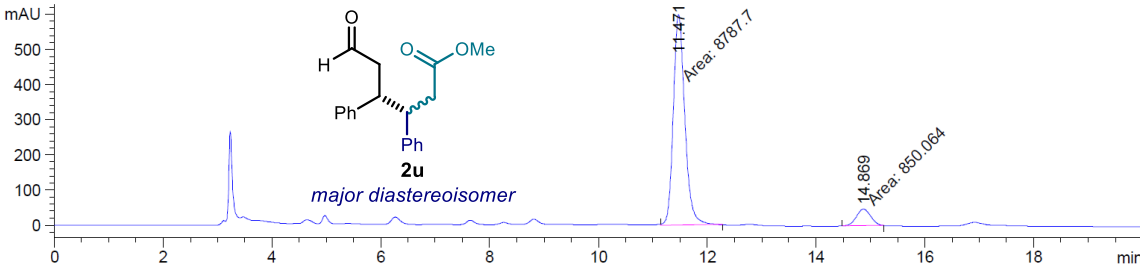
Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 °C, 80:20 hexane/*i*-PrOH, flow rate 1.0 mL/min, λ = 215 nm)

DAD1 C, Sig=215,8 Ref=360,100 (C:\CHEM32\1\DATA\GIACOMO C\CMH SEQUENCE 2017-11-14 10-56-12\GC166A.D)



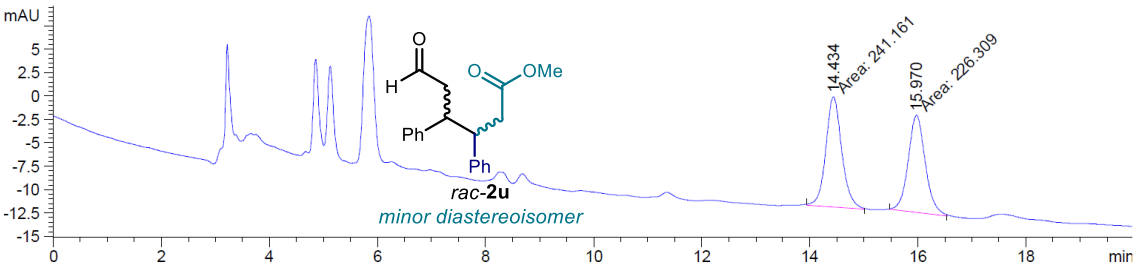
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.104	MM	0.2763	165.36761	9.97381	50.3492
2	14.265	MM	0.3351	163.07391	8.11038	49.6508

DAD1 B, Sig=215,16 Ref=off (C:\CHEM32\1\DATA\GIACOMO C\CMH SEQUENCE 2018-05-06 21-20-54\GC304_A.D)



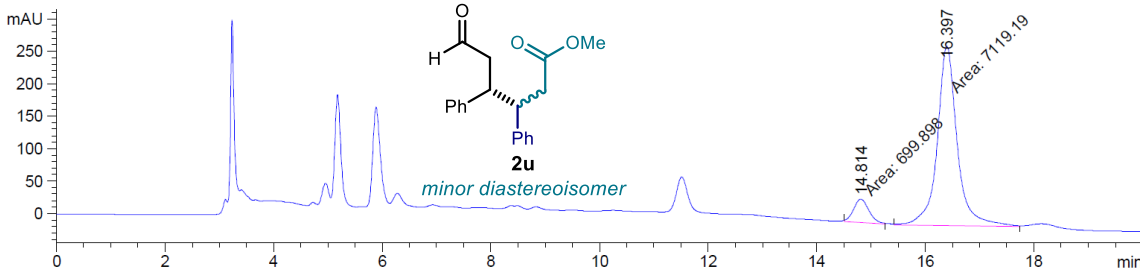
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.471	MM	0.2445	8787.70117	599.11578	91.1799
2	14.869	MM	0.3009	850.06439	47.08404	8.8201

DAD1 C, Sig=215,8 Ref=360,100 (C:\CHEM32\1\DATA\GIACOMO C\CMH SEQUENCE 2017-11-14 10-56-12\GC166B.D)



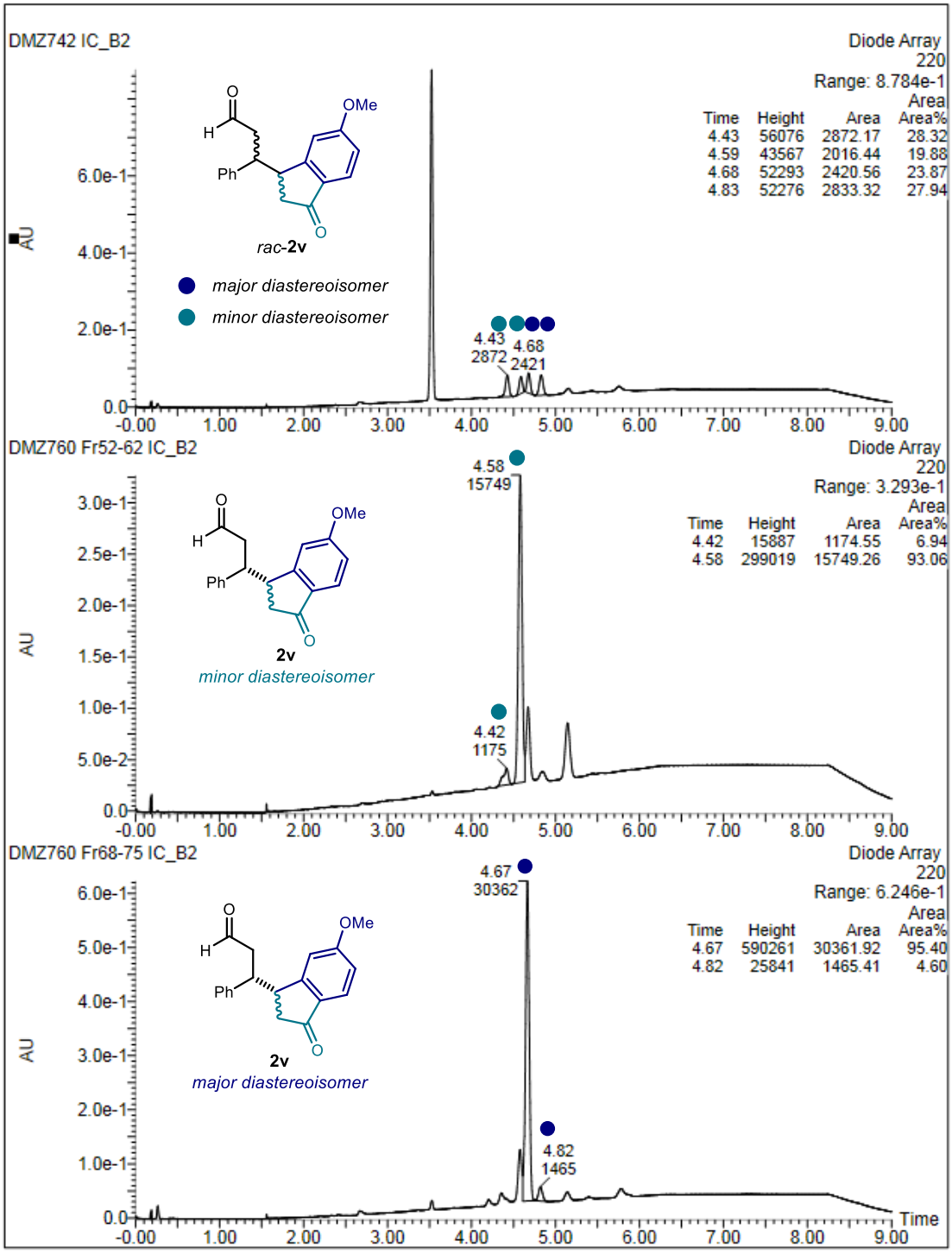
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.434	MM	0.3415	241.16136	11.77041	51.5886
2	15.970	MM	0.3647	226.30862	10.34327	48.4114

DAD1 C, Sig=215,8 Ref=360,100 (C:\CHEM32\1\DATA\GIACOMO C\CMH SEQUENCE 2018-05-06 21-20-54\GC304_B.D)

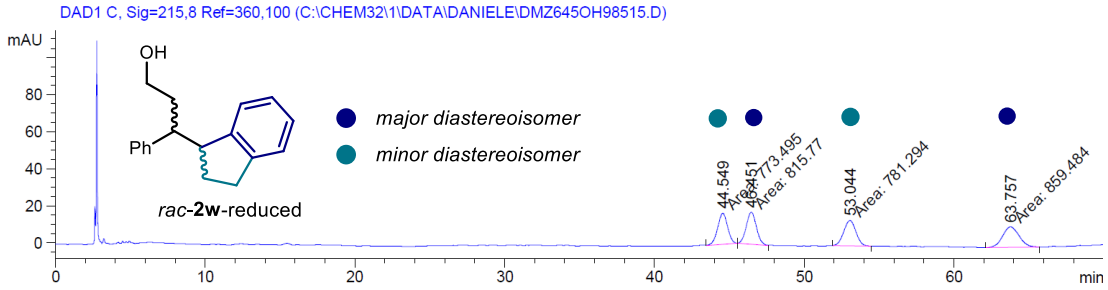


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.814	MM	0.3256	699.89795	35.83067	8.9511
2	16.397	MM	0.4289	7119.19482	276.66876	91.0489

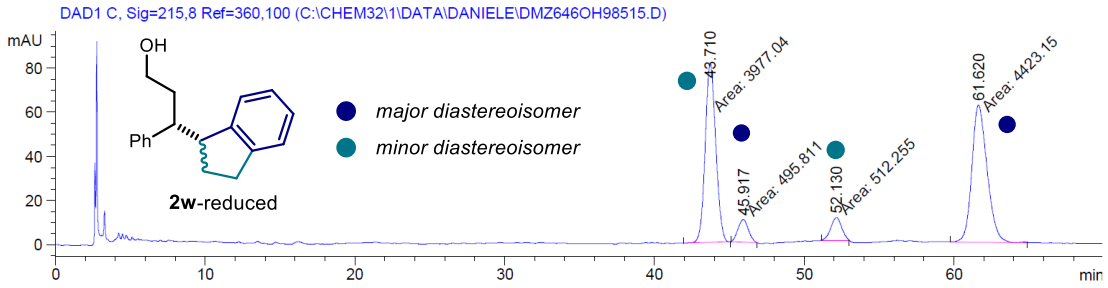
Conditions: UPC^2 (Daicel Chiralpak IC-3 column, 20 °C, gradient CO_2/*i*-PrOH from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 220 nm)



Conditions: HPLC (Daicel Chiralpak IC-3 column, 30 °C, 98.5:1.5 hexane/*i*-PrOH, flow rate 1.2 mL/min, λ = 215 nm)

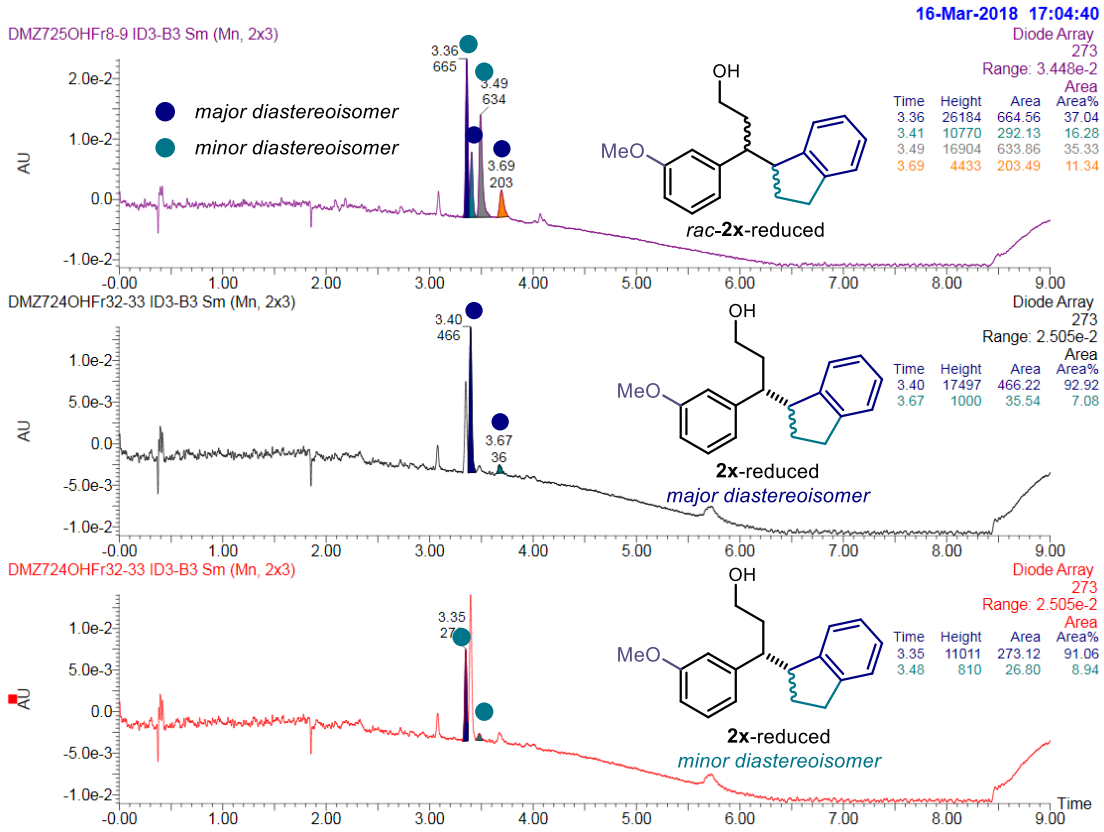


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.549	MM	0.7680	773.49457	16.78517	23.9469
2	46.451	MM	0.7868	815.77020	17.27946	25.2557
3	53.044	MM	0.9511	781.29395	13.69146	24.1883
4	63.757	MM	1.2824	859.48444	11.17007	26.6091

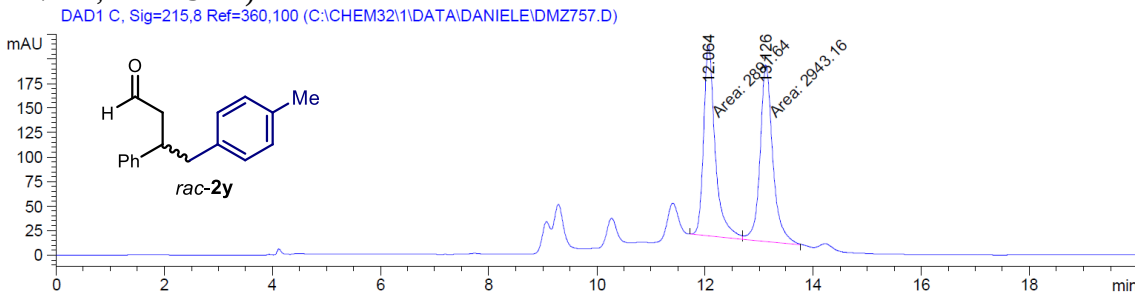


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.710	MM	0.8175	3977.03516	81.08303	42.2718
2	45.917	MM	0.8046	495.81079	10.27045	5.2700
3	52.130	MM	0.8338	512.25488	10.23955	5.4447
4	61.620	MM	1.1849	4423.15430	62.21484	47.0135

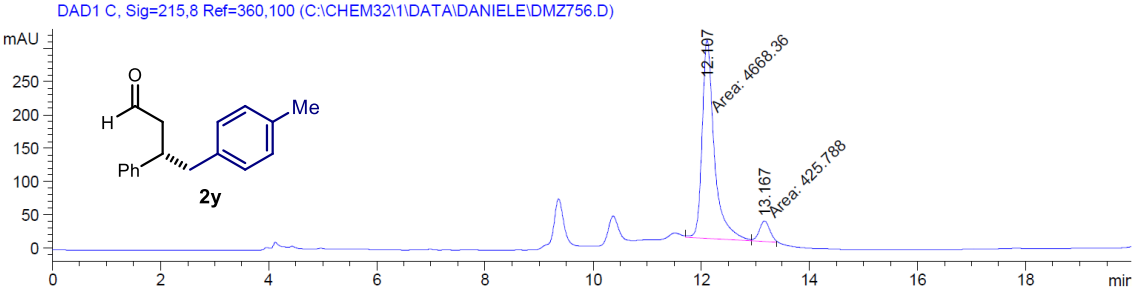
Conditions: UPC^2 (Daicel Chiralpak ID-3 column, 20 °C, gradient CO_2/*i*-PrOH from 100% CO_2 to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, λ = 273 nm)



Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 °C, 96:4 hexane/*i*-PrOH, flow rate 0.8 mL/min, λ = 215 nm)

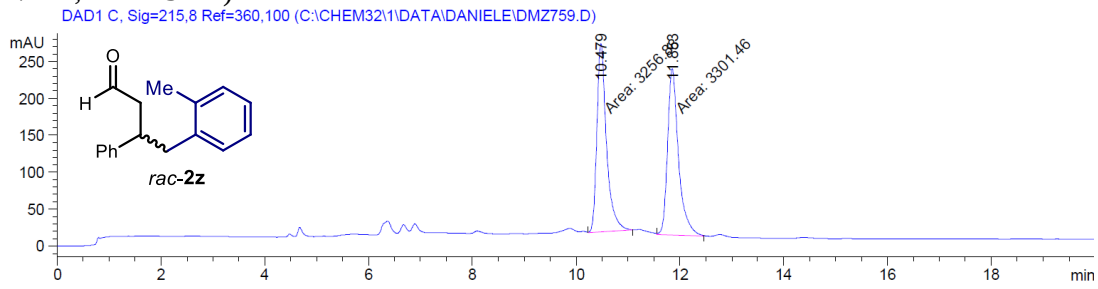


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.064	MF	0.2472	2891.63940	194.95476	49.5585
2	13.126	FM	0.2726	2943.15698	179.92612	50.4415

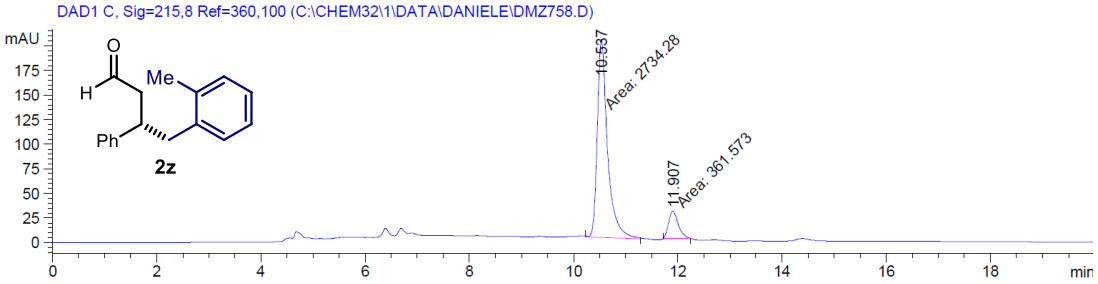


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.107	MF	0.2603	4668.36328	298.88525	91.6416
2	13.167	FM	0.2266	425.78842	31.31336	8.3584

Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 °C, 96:4 hexane/*i*-PrOH, flow rate 0.8 mL/min, λ = 215 nm)

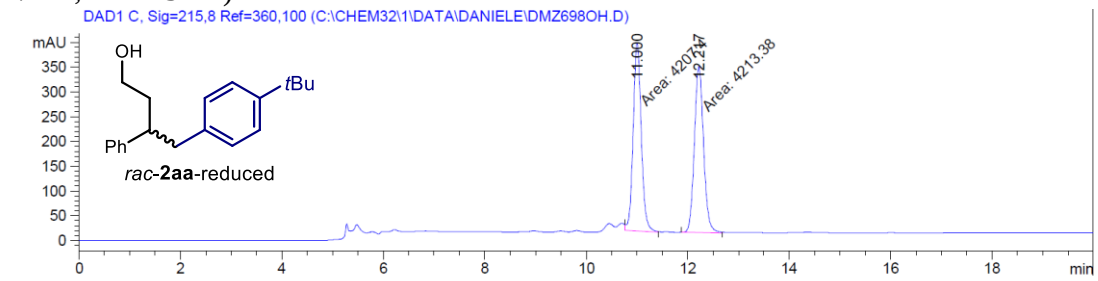


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.479	MM	0.2129	3256.88477	254.99597	49.6602
2	11.853	MM	0.2442	3301.45630	225.36890	50.3398

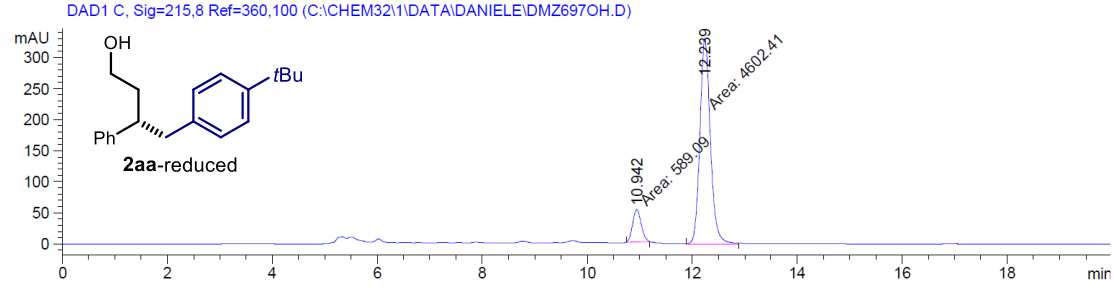


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.537	MM	0.2264	2734.28369	201.32080	88.3208
2	11.907	MM	0.2160	361.57263	27.90025	11.6792

Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 °C, 90:10 hexane/*i*-PrOH, flow rate 0.6 mL/min, λ = 215 nm)

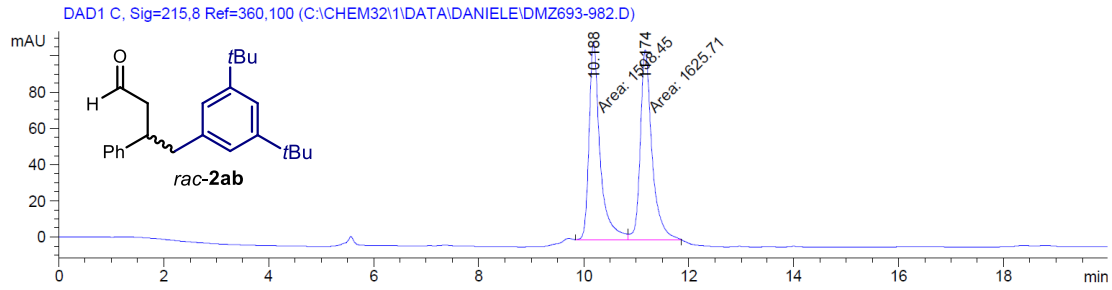


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.000	MM	0.1849	4207.39795	379.18771	49.9645
2	12.217	MM	0.2094	4213.38379	335.39847	50.0355

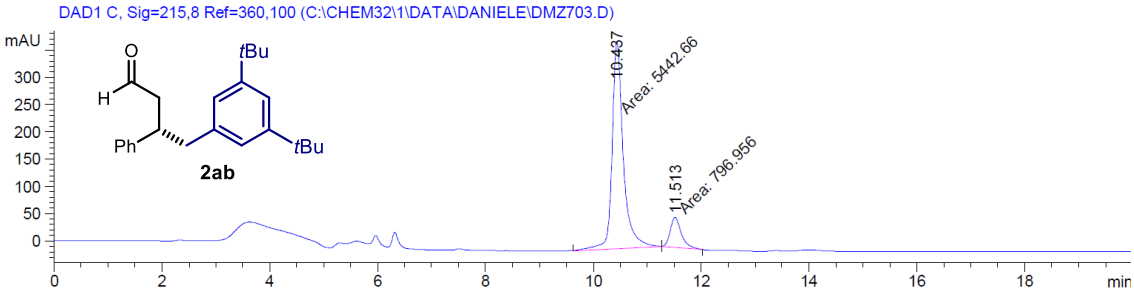


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.942	MM	0.1882	589.09033	52.17299	11.3472
2	12.239	MM	0.2318	4602.40918	330.96783	88.6528

Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 °C, 98:2 hexane/*i*-PrOH, flow rate 0.6 mL/min, λ = 215 nm)

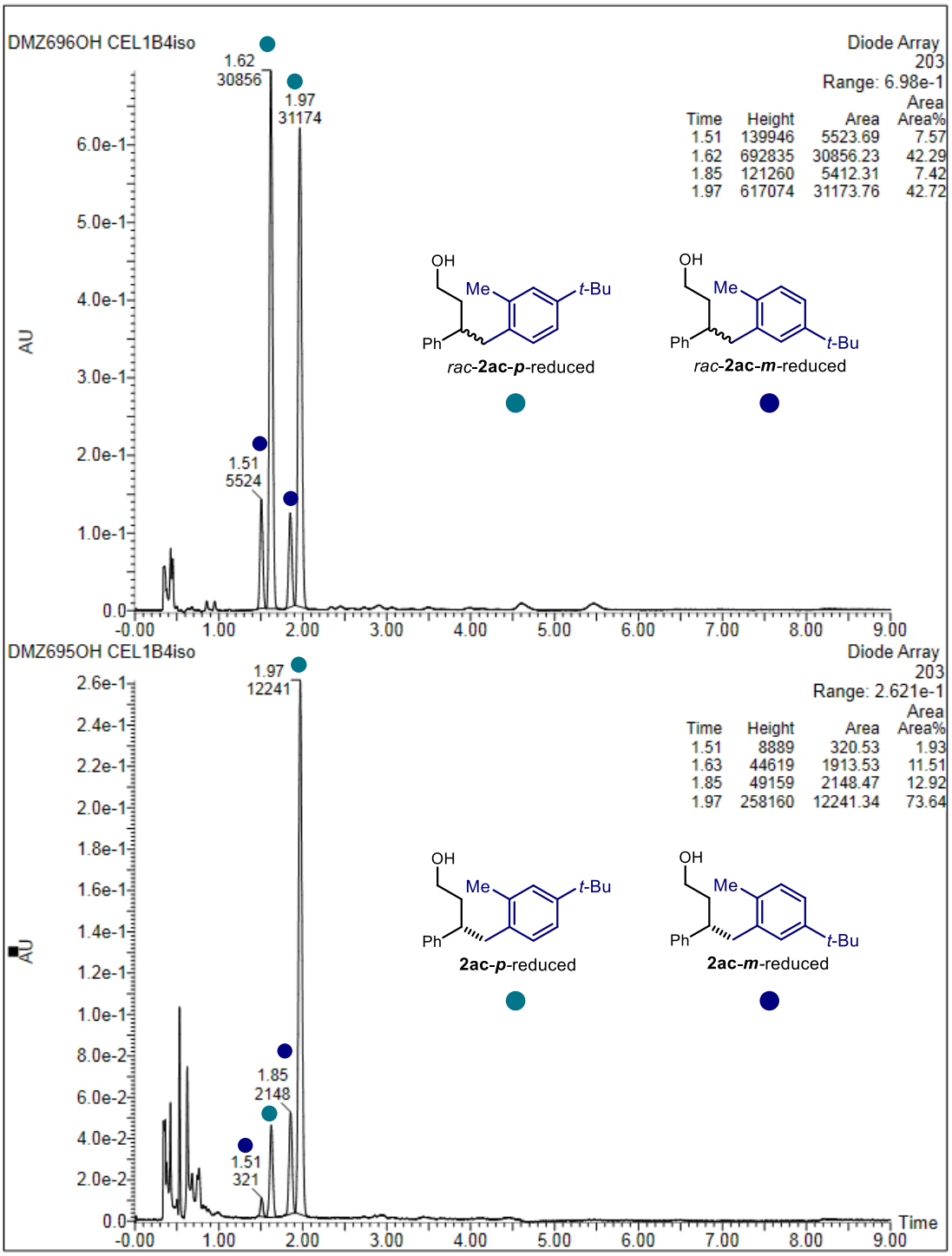


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.188	MF	0.2433	1598.44775	109.49973	49.5772
2	11.174	FM	0.2582	1625.70923	104.95632	50.4228

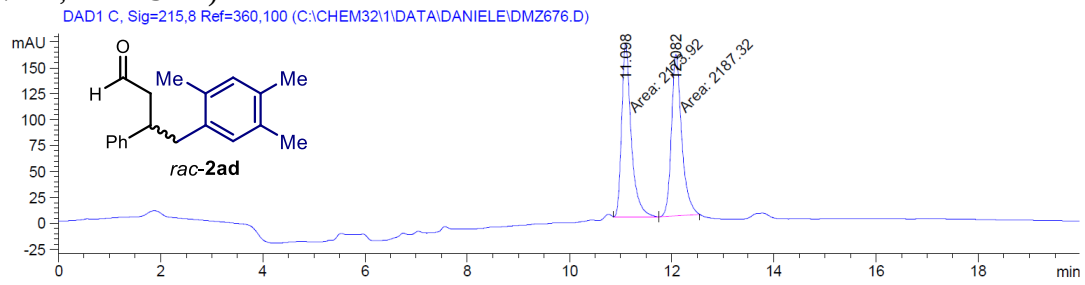


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.437	MM	0.2386	5442.66357	380.21954	87.2275
2	11.513	MM	0.2383	796.95605	55.74033	12.7725

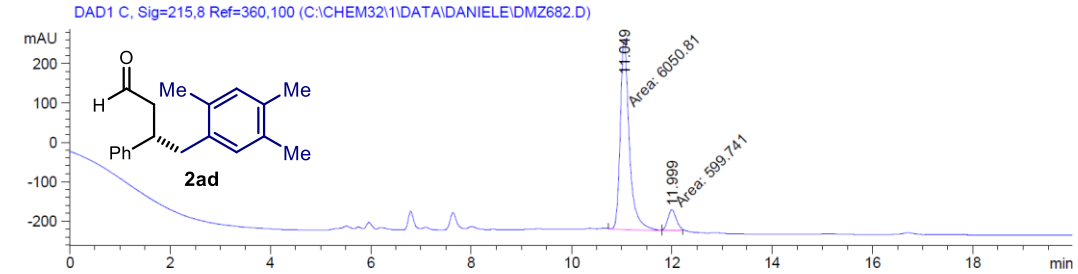
Conditions: UPC^2 (Daicel Chiralpak CEL1 column, 20 °C, isocratic CO_2/EtOH 95:5, flow rate 3 mL/min, λ = 203 nm)



Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 °C, 90:10 hexane/*i*-PrOH, flow rate 0.6 mL/min, λ = 215 nm)

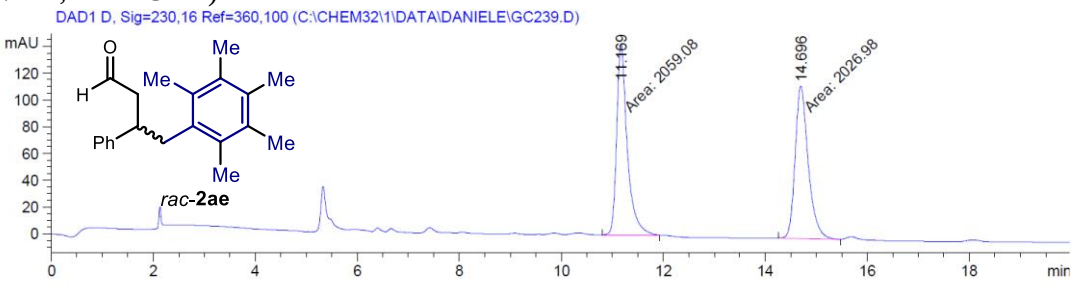


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.098	MM	0.2168	2173.91943	167.14604	49.8463
2	12.082	MM	0.2341	2187.32397	155.72803	50.1537

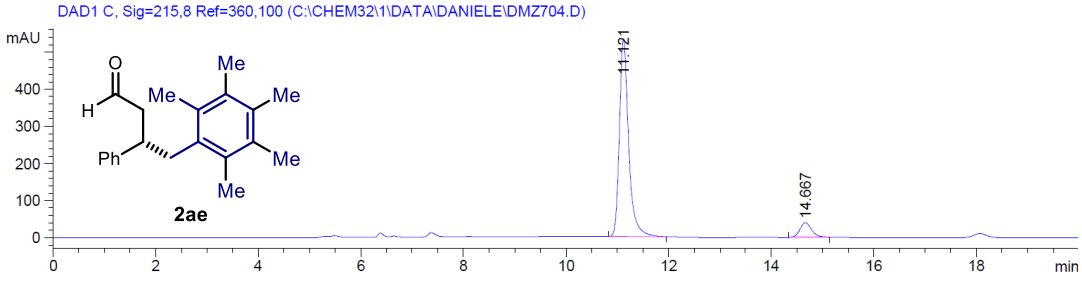


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.049	MM	0.2084	6050.81396	483.95087	90.9821
2	11.999	MM	0.1929	599.74091	51.81993	9.0179

Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 °C, 90:10 hexane/*i*-PrOH, flow rate 0.6 mL/min, λ = 215 nm)

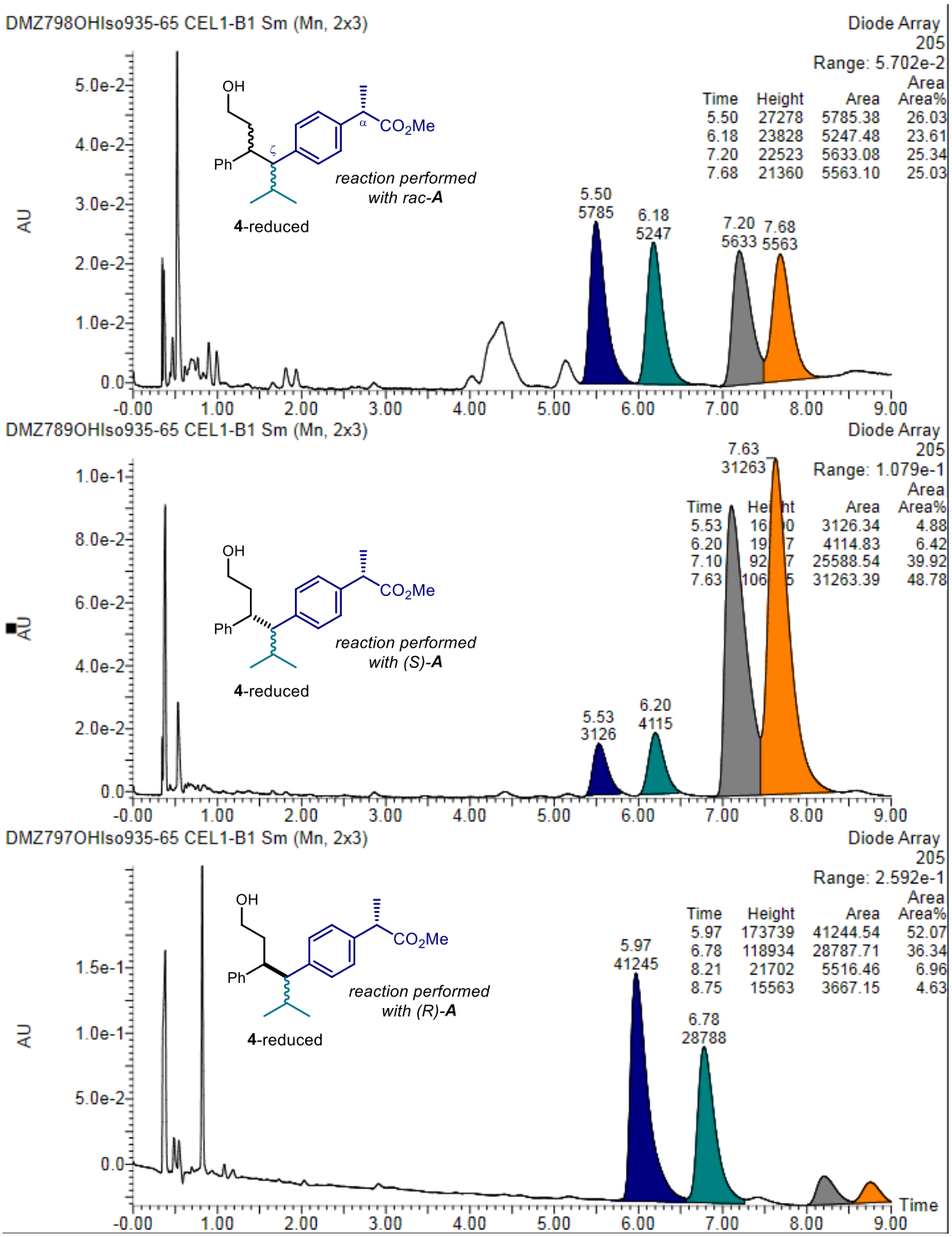


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.169	MM	0.2398	2059.08374	143.11581	50.3928
2	14.696	MM	0.2963	2026.98047	114.01085	49.6072

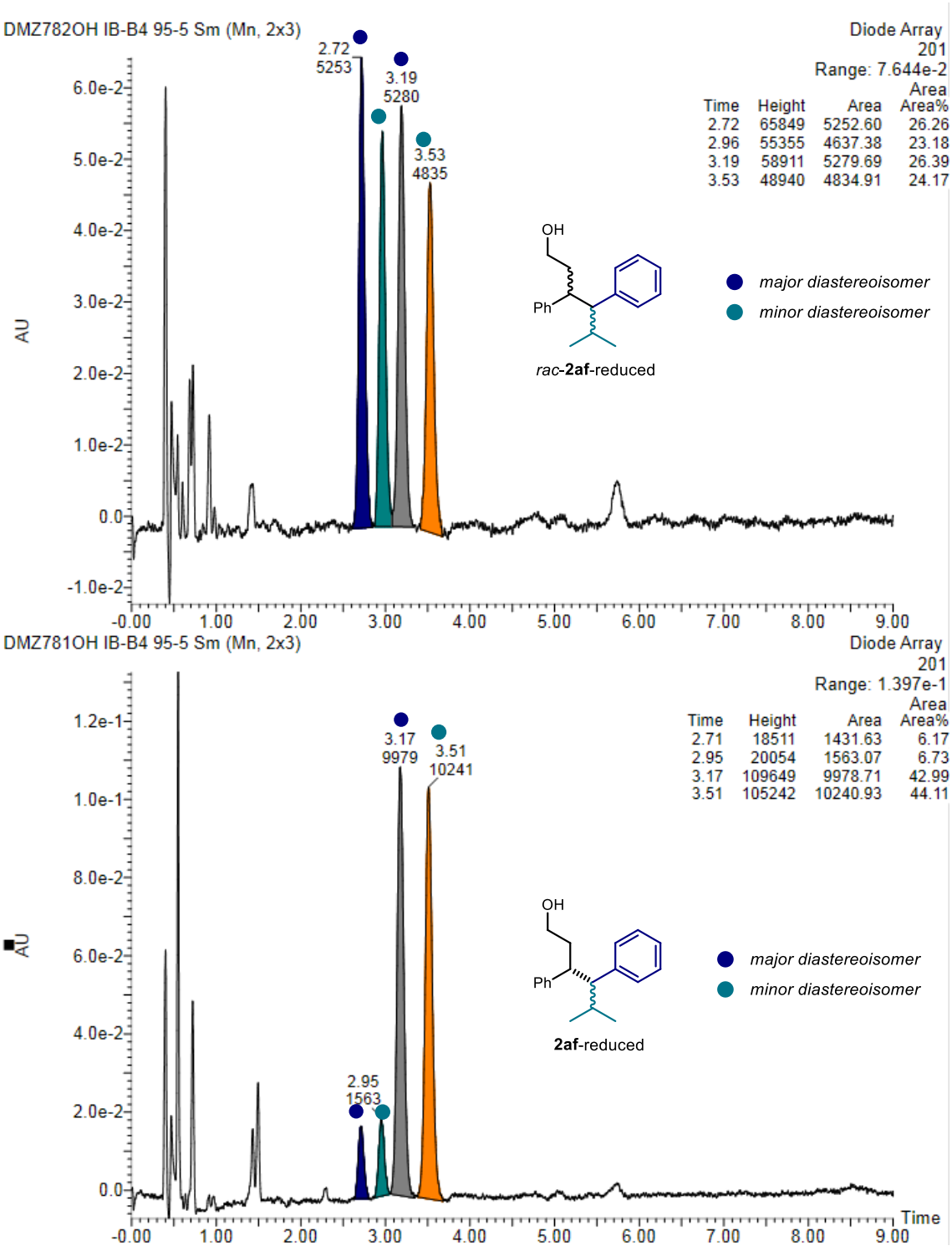


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.121	BB	0.1875	6646.23682	532.89545	91.3387
2	14.667	BB	0.2434	630.23785	39.65545	8.6613

Conditions: UPC^2 (Daicel Chiralpak CEL1 column, 20 °C, isocratic CO_2/MeCN 93.5:6.5, flow rate 3 mL/min, λ = 205 nm)



Conditions: UPC^2 (Daicel Chiralpak IB column, 20 °C, isocratic CO_2/EtOH 95:5, flow rate 3 mL/min, λ = 201 nm)



Conditions: UPC^2 (Daicel Chiralpak CEL-1 column, 20 °C, isocratic CO_2/MeOH 95:5, flow rate 3 mL/min, λ = 210 nm)