# SUPPORTING INFORMATION

## 1,4-Palladium Shift/C($sp^3$)-H Activation Strategy for the Remote Construction of 5-Membered Rings

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## 1- General information:

### Techniques

All reactions involving air-sensitive material were carried out in pre-dried glassware under an argon atmosphere by using Schlenk techniques employing double-line argon-vacuum lines and working in an argon-filled glove box. Analytical thin layer chromatography (TLC) was performed using pre-coated *Merck silica gel 60 F254* plates (0.25 mm). Visualization of the developed chromatogram was performed by UV absorbance (254 nm) or TLC stains (KMnO4 and Phosphomolybdic acid). Flash chromatography was performed using *Silicycle SiliaFlash P60* (230-400 mesh) with the indicated solvent system, using gradients of increasing polarity in most cases.

### Chemicals

Anhydrous THF, DME, DMF, toluene were purchased from Acros Organics or Sigma-Aldrich. The solvents were degassed by three cycles of freeze-pump-thaw and storing in single-necked flasks equipped with a J-Young PTFE valve when necessary. $Pd(PCy_3)_2$ was purchased from Strem. All other chemical reagents were purchased from Sigma-Aldrich, Acros Organics, Fisher, and Fluorochem and used as received without further purification unless otherwise stated.

### Instrumentation

Preparative HPLC was performed using a preparative Shimadzu HPLC system with a Gemini 10 μm NX-C18, LC Column 150 × 30mm.

Melting points were obtained on a Büchi B-565, and are uncorrected. IR spectra were recorded on an ATR Varian Scimitar 800 and are reported in reciprocal centimeters (cm-1).

Nuclear magnetic resonance spectra were recorded on a Bruker Advance 400 (400 MHz), on a Bruker Advance 500 (500 MHz) or a Bruker Advance 600 (600 MHz) in deuterated chloroform S4 (residual peaks 1H δ 7.26 ppm, 13C δ 77.16 ppm) unless otherwise noted. 19F NMR spectra were referenced to external CFCl3. 31P NMR spectra were referenced to external 85% phosphoric acid. Data are reported in parts per million (ppm) as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, sept = septuplet, m = multiplet and brs = broad singlet), coupling constant in Hz and integration. High resolution

mass spectra were recorded by Dr. H. Nadig (Department of Chemistry, University of Basel) on a Bruker maXis 4G QTOF ESI mass spectrometer. X-ray crystallographic analysis was performed by Dr. M. Neuburger of the University of Basel.

## 2- General procedures:

### General procedure for Knoevenagel condensations:

In a round bottom flask was stirred the *ortho*-bromobenzaldehyde derivatives (1 equiv), malonic acid (1.1 equiv), piperidine (1.1 equiv) in pyridine (2.5 M) at 90 °C for 15h. Pyridine was removed under vacuum, the crude mixture was acidified with HCl (2 M) and extracted with AcOEt (3 times). The crude mixture was dried over sodium sulfate, filtered and evaporated under vacuum. The acid was purified by precipitated in $Et_2O$ or used without further purifications for next step.

### General procedure for aldolisation reaction:

Aldehyde (1 equiv) and ketone (1 equiv) were dissolved in EtOH (1 M), followed by addition of NaOH (1 equiv) in water (1 M). The reaction was stirred at 45°C until completion and evaporated under vacuum. The crude was dissolved in dichloromethane and the organic phase was washed with water. The crude was dried over sodium sulfate, filtered and evaporated under vacuum. The desired chalcones were purified by chromatography on silica gel using cyclohexane/AcOEt as solvent.

### General procedure for amide synthesis:

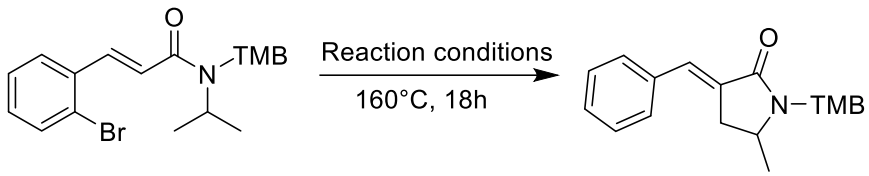
The carboxylic acid (1 equiv) was suspended in dichloromethane (0.05 M) with DMF (0.01 equiv). Oxalyl chloride (1.5 equiv) was carefully added to the resulting mixture, which was then stirred for 2h. The solvent and excess of oxalyl chloride were removed under vacuum, and the crude was dissolved in dichloromethane (0.05 M). Then, a solution of amine (1 equiv) and $Et_3N$ (2 equiv) in dichloromethane (0.05 M) was carefully added. The reaction was followed by TLC (cyclohexane/AcOEt). After completion, the solvent was removed and the crude was purified by chromatography on silica gel, using cyclohexane/AcOEt as solvent.

### General procedure for the 1,4-Pd shift/C($sp^3$)-H activation:

In a 10 mL screw cap charged with amide (0.1 mmol, 1 equiv) was weighted in a glovebox $Pd(PCy_3)_2$ (0.01 mmol, 10 mol %), $PCy_3$ (when mentioned) (2.8 mg, 0.01 mmol, 10 mol%), pivalic acid (0.03 mmol, 30 mol %) and $Rb_2CO_3$ (0.15 mmol, 1.5 equiv). The vial was charged with mesitylene (4 mL) and stirred under argon in a previously heated heating block at 160 °C for 16 h. The reaction was cooled to room temperature, filtered over celite, and evaporated under vacuum. The crude was purified by preparative HPLC using gradient of solvent ($H_2O$:

MeCN) [90:10] to [10:90]. The collected fractions were evaporated under vacuum to afford the desired product.

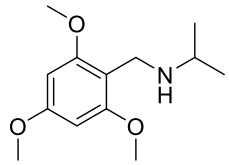
## 3- Table S1: 1,4-Pd shift/C($sp^3$)-H activation reaction optimization:




| Pd source | Additive (30 mol%) | Base | Solvent | NMR yield (Isolated) |
|---|---|---|---|---|
| $Pd(P\textit{t}\text{-}Bu_3)_2$ (10 mol%) | PivOH | $Rb_2CO_3$ (1.5 equiv.) | Mesitylene [0.05M] | 0% |
| $Pd(PPh_3)_4$ (10 mol%) | PivOH | $Rb_2CO_3$ (1.5 equiv.) | Mesitylene [0.05M] | 8% |
| $[Pd(\eta^3\text{-allyl})Cl_2]/PPh_3$ (10 mol%) | PivOH | $Cs_2CO_3$ (2 equiv.) | Mesitylene [0.05M] | 0% |
| $Pd_2dba_3/PCy_3$ (10 mol%) | PivOH | $Rb_2CO_3$ (1.5 equiv.) | Mesitylene [0.05M] | 31% |
| $Pd(PCy_3)_2$ (10 mol%) | PivOH | $Rb_2CO_3$ (1.5 equiv.) | Mesitylene [0.05M] | 65% |
| $Pd(PCy_3)_2$ (10 mol%) | PivOH | $Rb_2CO_3$ (1.5 equiv.) | Mesitylene [0.025M] | 100% (94%) |
| $Pd(PCy_3)_2$ (5 mol%) | PivOH | $Rb_2CO_3$ (1.5 equiv.) | Mesitylene [0.025M] | 51% |

## 4- Amines:

### *N*-(2,4,6-Trimethoxybenzyl)propan-2-amine $S_a$:

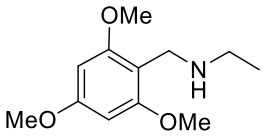


Chemical Formula: $C_{13}H_{21}NO_3$
Exact Mass: 239.1521

*N*-(2,4,6-trimethoxybenzyl)propan-2-amine was obtained according to a known procedure.

The physical and spectroscopic properties matched those described in the literature.[1]

### *N*-(2,4,6-trimethoxybenzyl)ethanamine $S_b$:

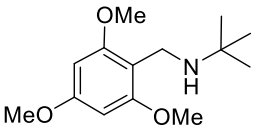


Chemical Formula: $C_{12}H_{19}NO_3$
Exact Mass: 225.1365

N-(2,4,6-trimethoxybenzyl)ethanamine was obtained according to a known procedure.

The physical and spectroscopic properties matched those described in the literature. [1]

### 2-Methyl-*N*-(2,4,6-trimethoxybenzyl)propan-2-amine $S_c$:

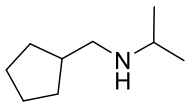


Chemical Formula: $C_{14}H_{23}NO_3$
Exact Mass: 253.1678

2-Methyl-N-(2,4,6-trimethoxybenzyl)propan-2-amine was obtained according to a known procedure.

The physical and spectroscopic properties matched those described in the literature. [1]

**_N_-(Cyclopentylmethyl)propan-2-amine $S_i$:**



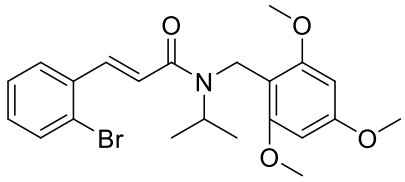
Chemical Formula: $C_9H_{19}N$
Exact Mass: 141.1517

N-(Cyclopentylmethyl)propan-2-amine was obtained according to a known procedure.

The physical and spectroscopic properties matched those described in the literature. [1]

## 5- Synthesis of reaction substrates:

### (E)-3-(2-bromophenyl)-N-isopropyl-N-(2,4,6-trimethoxybenzyl)acrylamide 1a:




Chemical Formula: $C_{22}H_{26}BrNO_4$
Exact Mass: 447.1045

Following the general procedure for amide synthesis, 2-bromocinnamic acid (411 mg, 1.81 mmol, 1 equiv) was reacted with oxalyl chloride (0.26 mL, 2.72 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with **$S_a$** (433 mg, 1.81 mmol, 1 equiv) and $Et_3N$ (0.51 mL, 3.62 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1a** was obtained as a white solid (720 mg, 1.6 mmol, 89 %).

**$^1$H NMR (400 MHz, Chloroform-*d*) δ** = 7.88 (d, J = 15.4 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.31 – 7.28 (m, 1H), 7.24 – 7.18 (m, 1H), 7.18 – 7.10 (m, 1H), 6.10 (s, 2H), 4.60 (s, 2H), 4.14 – 4.05 (sept, J = 7.0 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 6H), 1.17 (d, J = 6.9 Hz, 6H).

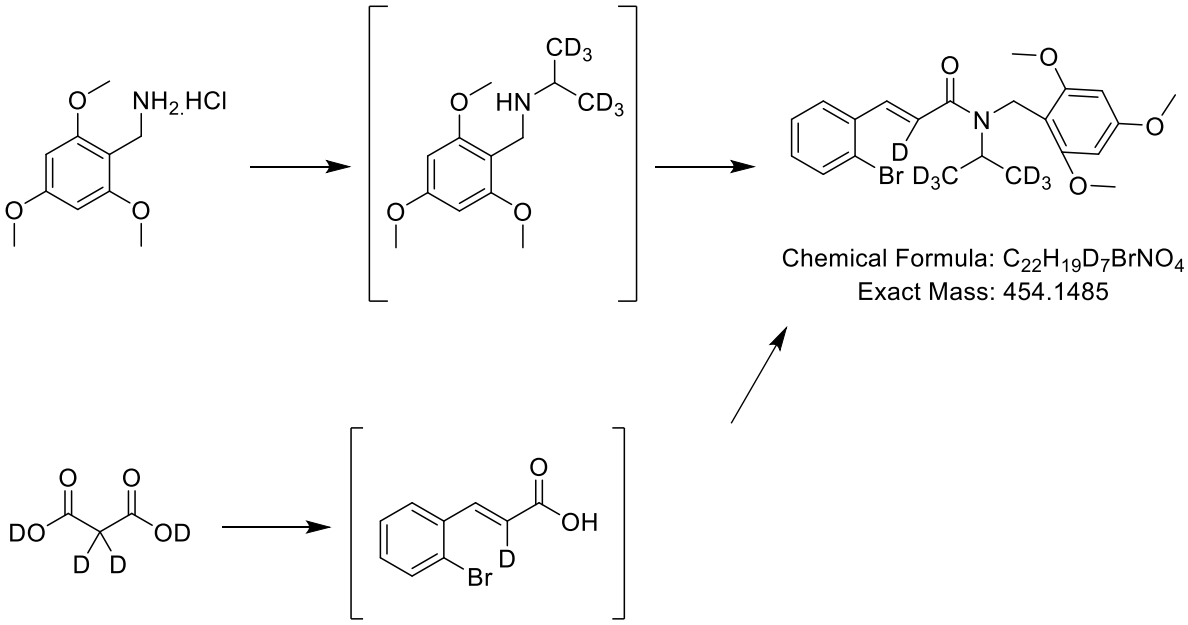
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ** = 166.7, 161.2, 159.7, 138.1, 136.6, 133.4, 130.0, 127.6, 127.5, 125.0, 124.9, 106.4, 90.5, 55.6, 55.4, 49.1, 39.7, 19.9.

**HRMS** (ESI): Calculated for $C_{22}H_{26}BrNaNO_4$ ($[M+Na]^+$): 470.0943; found: 470.0937

**IR** (neat) : $\nu$ = 2362, 1596, 1467 $cm^{-1}$

**m.p.:** 86 - 88°C

## (E)-3-(2-bromophenyl)-N-(propan-2-yl-1,1,1,3,3,3-d6)-N-(2,4,6)trimethoxybenzyl)acrylamide-2-d 1a-$d_7$:




(2,4,6-trimethoxyphenyl)methanamine hydrochloride (500 mg, 2.14 mmol, 1 equiv) was exchanged with methanol-$D_4$ (10 mL) by stirring at room temperature overnight. After evaporation of the volatiles, the free amine was reacted with acetone- $D_6$ (2.4 mL, 32 mmol, 15 equiv) in dry benzene (20 mL) and refluxed in a Dean-Stark apparatus overnight. The volatiles were removed under vacuum, and the imine was then dissolved in diglyme (15 mL) and cooled to 0°C with an ice batch. $NaBD_4$ (4.28 mmol, 179 mg, 2 equiv) was carefully added to the solution, which was slowly warmed to room temperature. After completion, the reaction was quenched with 2M NaOH (20 mL) and extracted with DCM (3 x 15 mL). The combined organic phases were dried over sodium sulfate, filtered and evaporated under vacuum. The desired amine was obtained without further purification. (508 mg, 2.12 mmol, 99%).

Malonic acid-$D_4$ (3 g, 27.8 mmol, 1 equiv), 2-Bromobenzaldehyde (5.14 g, 27.8 mmol, 1 equiv), piperidine (2 drops) were refluxed in pyridine (50 mL) for 3h. Solvent were removed, and the reaction was quenched with 2M HCl (50 mL) and extracted with DCM (3 x 25 mL). The combined organic layers were dried over sodium sulfate, filtered and evaporated under vacuum to afford the deuterated cinnamic acid derivative (6.26 g, 27.45 mmol, 99%).

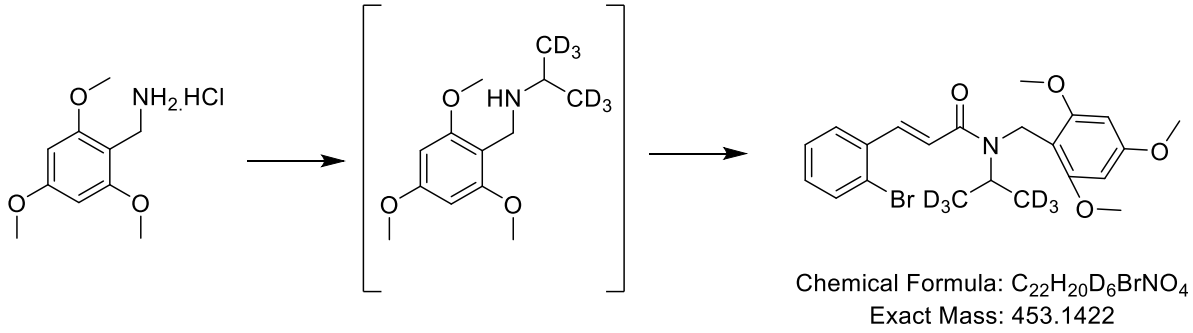
The deuterated cinnamic acid derivative (274 mg, 1.2 mmol, 1 equiv) was reacted with oxalyl chloride (0.17 mL, 1.8 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with the deuterated amine (294 mg, 1.2 mmol, 1 equiv) and $Et_3N$ (0.33 mL, 2.4 mmol, 2

equiv) in dichloromethane. After evaporation and purification, **1a-d$_7$** was obtained as a white solid (412 mg, 0.9 mmol, 75 %).

**$^1$H NMR (400 MHz, Chloroform-*d*) δ** = 7.91 – 7.86 (m, 1H), 7.60 – 7.55 (m, 2H), 7.31 – 7.28 (m, 1H), 7.18 – 7.12 (m, 1H), 6.11 (s, 2H), 4.59 (s, 2H), 4.12 – 4.04 (m, 1H), 3.81 (s, 3H), 3.78 (s, 6H).

**$^{13}$C NMR (101 MHz, CDCl$_3$) δ =** 166.7, 161.1, 159.7, 138.0, 136.6, 133.4, 129.9, 127.6, 127.5, 124.9, 106.4, 90.5, 55.5, 55.4, 49.0, 39.7.

## (E)-3-(2-bromophenyl)-N-(propan-2-yl-1,1,1,3,3,3-d6)-N-(2,4,6-trimethoxybenzyl)acrylamide 1a-d$_6$:

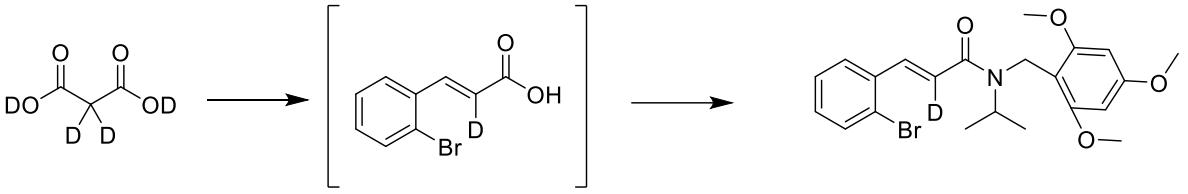



Following the general procedure for amide synthesis, 2-bromocinnamic acid (182 mg, 0.8 mmol, 1 equiv) was reacted with oxalyl chloride (0.11 mL, 1.2 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with the deuterated amine (195 mg, 0.8 mmol, 1 equiv) and $Et_3N$ (0.22 mL, 1.6 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1a-d$_6$** was obtained as a white solid (302 mg, 0.66 mmol, 83 %).

**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.87 (d, J = 15.5 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.30 – 7.27 (m, 1H), 7.21 (d, J = 15.4 Hz, 1H), 7.17 – 7.11 (m, 1H), 6.10 (s, 2H), 4.59 (s, 2H), 4.12 – 4.03 (m, 1H), 3.80 (s, 3H), 3.77 (s, 6H).

**$^{13}$C NMR (101 MHz, CDCl$_3$) δ =** 166.8, 161.1, 159.7, 138.0, 136.6, 133.4, 129.9, 127.6, 127.5, 124.9, 124.9, 106.4, 90.6, 55.5, 55.4, 39.7.

## (E)-3-(2-bromophenyl)-N-isopropyl-N-(2,4,6-trimethoxybenzyl)acrylamide-2-d 1a-$d_1$:



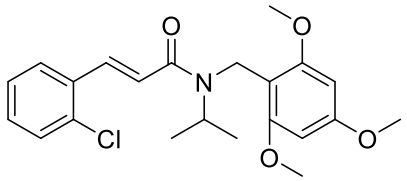

Chemical Formula: $C_{22}H_{25}DBrNO_4$
Exact Mass: 448.1108

The deuterated cinnamic acid derivative (251 mg, 1.1 mmol, 1 equiv) was reacted with oxalyl chloride (0.15 mL, 1.65 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with **$S_a$** (261 mg, 1.1 mmol, 1 equiv) and $Et_3N$ (0.31 mL, 2.2 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1a-$d_1$** was obtained as a white solid (451 mg, 1.0 mmol, 91 %).

**$^1$H NMR (400 MHz, Chloroform-*d*) δ** = 7.91 – 7.83 (m, 1H), 7.59 – 7.54 (m, 2H), 7.30 – 7.25 (m, 1H), 7.17 – 7.10 (m, 1H), 6.10 (s, 2H), 4.58 (s, 2H), 4.08 (sept, J = 6.9 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 6H), 1.16 (d, J = 6.9 Hz, 6H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 166.7, 161.1, 159.7, 138.0, 136.5, 133.4, 129.9, 127.6, 127.5, 124.9, 106.4, 90.5, 55.5, 55.4, 49.1, 39.6, 19.9.

## (E)-3-(2-chlorophenyl)-N-isopropyl-N-(2,4,6-trimethoxybenzyl)acrylamide 1a':




Chemical Formula: $C_{22}H_{26}ClNO_4$
Exact Mass: 403.1550

Following the general procedure for amide synthesis, 2-chlorocinnamic acid (139 mg, 0.76 mmol, 1 equiv) was reacted with oxalyl chloride (0.1 mL, 1.14 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with **$S_a$** (182 mg, 0.76 mmol, 1 equiv) and $Et_3N$ (0.21 mL, 1.52 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1a'** was obtained as a white solid (210 mg, 0.52 mmol, 68 %).

**$^1$H NMR (400 MHz, Chloroform-*d*) δ** = 7.93 (d, J = 15.6 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.41 – 7.37 (m, 1H), 7.30 – 7.20 (m, 3H), 6.10 (s, 2H), 4.59 (s, 2H), 4.08 (sept, J = 6.9 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 6H), 1.17 (d, J = 6.9 Hz, 6H).

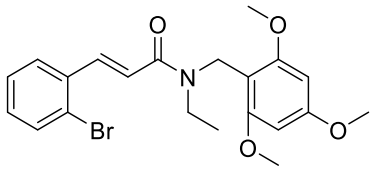
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 166.8, 161.1, 159.7, 135.6, 134.8, 134.5, 130.1, 129.7, 127.5, 126.9, 124.8, 106.4, 90.5, 55.5, 55.4, 49.1, 39.7, 19.9.

**HRMS** (ESI): Calculated for $C_{22}H_{26}ClNaNO_4$ ($[M+Na]^+$): 426.1448; found: 426.1451

**IR** (neat) : ν = 2362, 1592, 1463 $cm^{-1}$

**m.p.:** 67 - 69°C

## (E)-3-(2-bromophenyl)-N-ethyl-N-(2,4,6-trimethoxybenzyl)acrylamide 1b:



Chemical Formula: $C_{21}H_{24}BrNO_4$
Exact Mass: 433.0889

Following the general procedure for amide synthesis, 2-bromocinnamic acid (300 mg, 1.32 mmol, 1 equiv) was reacted with oxalyl chloride (0.17 mL, 1.98 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with **$S_b$** (297mg, 1.32 mmol, 1 equiv) and $Et_3N$ (0.37 mL, 2.64 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1b** was obtained as a yellowish oil (487 mg, 1.12 mmol, 85 %).

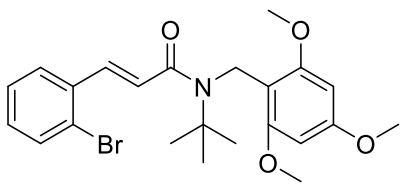
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 8.04 – 7.90 (m, 1H), 7.66 – 7.54 (m, 2H), 7.36 – 7.28 (m, 1.8H), 7.20 – 7.14 (m, 1H), 6.80 (d, J = 15.4 Hz, 0.2H), 6.15 – 6.09 (m, 2H), 4.78 (s, 0.4H), 4.61 (s, 1.6H), 3.83 – 3.76 (m, 9H), 3.38 (q, J = 7.0 Hz, 1.6H), 3.27 (q, J = 7.0 Hz, 0.4H), 1.07 (t, J = 6.9 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 165.8, 161.2, 159.8, 138.8, 136.4, 133.3, 129.9, 127.5, 127.4, 124.9, 123.3, 105.5, 90.3, 55.5, 55.3, 39.6, 12.6.

**HRMS** (ESI): Calculated for $C_{21}H_{25}BrNO_4$ ($[M+H]^+$): 434.0967; found: 434.0961

**IR** (neat) : ν = 1597, 1468 $cm^{-1}$

## (E)-3-(2-bromophenyl)-N-(tert-butyl)-N-(2,4,6 trimethoxybenzyl)acrylamide 1c:



Chemical Formula: $C_{23}H_{28}BrNO_4$
Exact Mass: 461.1202

Following the general procedure for amide synthesis, 2-bromocinnamic acid (1 g, 4.4 mmol, 1 equiv) was reacted with oxalyl chloride (0.62 mL, 6.6 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The

acid chloride was then reacted with **S$_c$** (1.11 g, 4.4 mmol, 1 equiv) and $Et_3N$ (1.24 mL, 8.8 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1c** was obtained as a colorless oil (1.45 g, 3.13 mmol, 72 %).

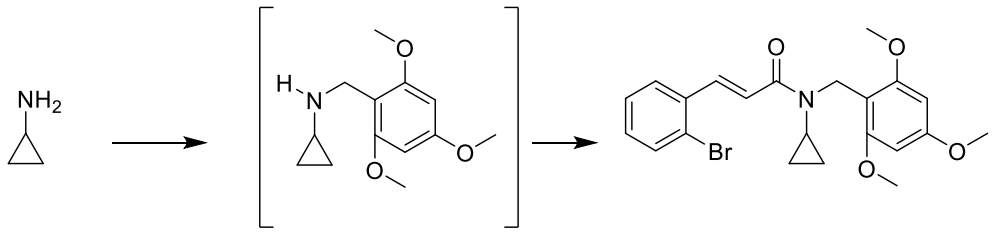
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.73 (d, *J* = 15.5 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.52 – 7.48 (m, 1H), 7.26 – 7.22 (m, 1H), 7.14 – 7.09 (m, 1H), 6.08 (s, 2H), 4.70 (s, 2H), 3.79 (s, 3H), 3.76 (s, 6H), 1.37 (s, 9H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ** = 169.3, 160.7, 159.3, 136.6, 136.6, 133.2, 129.8, 128.0, 127.6, 127.5, 124.7, 107.5, 90.6, 57.5, 55.4, 55.4, 40.5, 28.5.

**HRMS** (ESI): Calculated for $C_{23}H_{28}BrNNaO_4$ ($[M+Na]^+$): 484.1099; found: 484.1094

**IR** (neat) : ν = 1605, 1465, 1402, 1128 $cm^{-1}$

## (E)-3-(2-bromophenyl)-N-cyclopropyl-N-(2,4,6-trimethoxybenzyl)acrylamide 1d:




Chemical Formula: $C_{22}H_{24}BrNO_4$
Exact Mass: 445.0889

In a 250 mL round bottom flask equipped with stirring bar, cyclopropanamine (0.22 mL, 3.16 mmol, 1.2 equiv), 2,4,6-trimethoxybenzaldehyde (496 mg, 2.53 mmol, 1 equiv) and AcOH (0.29 mL, 5.06 mmol, 2 equiv) were stirred for 2 h in 1,2-dichloroethane (50 mL) at room temperature. Then, $NaBH(OAc)_3$ (1.07 g, 5.06 mmol, 2 equiv) was added to the mixture which was stirred overnight. The crude was quenched with NaOH (2 M, 50 mL) and the crude was extracted with DCM (3 x 50 mL). The combined organic layers were dried over sodium sulfate, filtered and evaporated under vacuum. The intermediate amine (592 mg, 2.50 mmol, 99 %) was obtained as a clear oil and directly used for next step.

Following the general procedure for amide synthesis, 2-bromocinnamic acid (143 mg, 0.632 mmol, 1 equiv) was reacted with oxalyl chloride (0.09 mL, 0.948 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with *N*-protected cyclopropanamine intermediate (150 mg, 0.632 mmol, 1 equiv) and $Et_3N$ (0.180 mL, 1.26 mmol, 2 equiv) in

dichloromethane. After evaporation and purification, **1d** was obtained as a yellowish oil (236 mg, 0.529 mmol, 84 %).

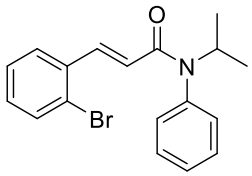
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.96 (d, J = 15.5 Hz, 1H), 7.63 – 7.53 (m, 2H), 7.31 – 7.26 (m, 1H), 7.18 – 7.10 (m, 2H), 6.11 (s, 2H), 4.72 (s, 2H), 3.80 (s, 3H), 3.78 (s, 6H), 2.35 – 2.25 (m, 1H), 0.81 – 0.64 (m, 4H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 167.7, 160.8, 160.0, 139.2, 136.2, 133.4, 130.2, 127.8, 127.5, 125.0, 123.7, 105.9, 90.3, 55.8, 55.4, 38.4, 28.0, 9.2.

**HRMS** (ESI): Calculated for $C_{22}H_{25}BrNO_4$ ($[M+H]^+$): 446.0967; found: 446.0961

**IR** (neat) : ν = 2361, 1646, 1132 $cm^{-1}$

## (E)-3-(2-bromophenyl)-N-isopropyl-N-phenylacrylamide 1e:




Chemical Formula: $C_{18}H_{18}BrNO$
Exact Mass: 343.0572

Following the general procedure for amide synthesis, 2-bromocinnamic acid (143 mg, 0.63 mmol, 1 equiv) was reacted with oxalyl chloride (0.1 mL, 0.95 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with *N*-isopropylaniline (86 mg, 0.63 mmol, 1 equiv) and $Et_3N$ (0.18 mL, 1.26 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1e** was obtained as a white solid (151 mg, 0.44 mmol, 69 %).

**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.97 (d, J = 15.4 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.48 – 7.39 (m, 3H), 7.18 – 7.04 (m, 5H), 6.04 (d, J = 15.4 Hz, 1H), 5.12 (sept, J = 6.8 Hz, 1H), 1.13 (d, J = 6.8 Hz, 6H).

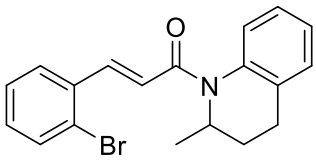
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ** = 165.0, 140.0, 138.4, 135.6, 133.3, 130.7, 130.3, 129.4, 128.5, 127.8, 127.4, 125.1, 122.9, 46.7, 21.1.

**HRMS** (ESI): Calculated for $C_{18}H_{18}BrNaNO$ ($[M+Na]^+$): 366.0469; found: 366.0464

**IR** (neat) : ν = 2363, 1650 $cm^{-1}$

**m.p.:** 80 - 82°C

## (E)-3-(2-bromophenyl)-1-(2-methyl-3,4-dihydroquinolin-1(2H)-yl)prop-2-en-1-one 1f:




Chemical Formula: $C_{19}H_{18}BrNO$
Exact Mass: 355.0572

Following the general procedure for amide synthesis, 2-bromocinnamic acid (568 mg, 2.5 mmol, 1 equiv) was reacted with oxalyl chloride (0.35 mL, 3.75 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with 2-methyl-1,2,3,4-tetrahydroquinoline (368 mg, 2.5 mmol, 1 equiv) and $Et_3N$ (0.69 mL, 5 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1f** was obtained as a white solid (720 mg, 2.02 mmol, 81 %).

**$^1$H NMR (400 MHz, Chloroform-*d*) δ** = 8.06 (d, J = 15.5 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.38 – 7.34 (m, 1H), 7.24 – 7.07 (m, 6H), 6.66 (d, J = 15.5 Hz, 1H), 4.95 – 4.86 (m, 1H), 2.68 (dt, J = 14.9, 5.1 Hz, 1H), 2.63 – 2.54 (m, 1H), 2.45 – 2.36 (m, 1H), 1.48 – 1.38 (m, 1H), 1.22 (d, J = 6.4 Hz, 3H).

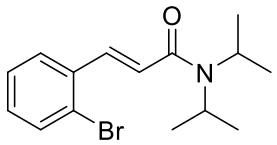
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 165.1, 140.2, 137.2, 135.7, 133.5, 130.5, 127.8, 127.8, 127.6, 126.5, 126.4, 125.9, 125.2, 123.3, 49.2, 32.7, 26.2, 20.4.

**HRMS** (ESI): Calculated for $C_{19}H_{18}BrNNaO$ ($[M+Na]^+$): 378.0469; found: 378.0464

**IR** (neat) : ν = 2361, 1650, 1354 $cm^{-1}$

**m.p.:** 97 - 99°C

## (E)-3-(2-bromophenyl)-N,N-diisopropylacrylamide 1g:




Chemical Formula: $C_{15}H_{20}BrNO$
Exact Mass: 309.0728

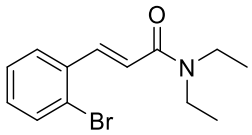
Following the general procedure for amide synthesis, 2-bromocinnamic acid (1.5 g, 6.61 mmol, 1 equiv) was reacted with oxalyl chloride (0.94 mL, 9.92 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with diisopropylamine (0.94 mL, 6.61 mmol, 1 equiv) and $Et_3N$ (1.9 mL, 13.2 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1g** was obtained as a colorless oil (1.76 g, 5.68 mmol, 86 %).

**$^1$H NMR (400 MHz, Chloroform-*d*) δ** = 7.83 (d, *J* = 15.5 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.33 – 7.27 (m, 1H), 7.20 – 7.15 (m, 1H), 6.76 (d, *J* = 15.5 Hz, 1H), 4.10 (br s, 1H), 3.83 (br s, 1H), 1.47 – 1.23 (m, 12H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 165.9, 139.0, 136.1, 133.5, 130.3, 127.7, 127.6, 125.0, 124.2.
**HRMS** (ESI): Calculated for $C_{15}H_{20}BrNaNO$ ($[M+Na]^+$): 332.0626; found: 332.0621

**IR** (neat) : ν = 2362, 1598 $cm^{-1}$

## (E)-3-(2-bromophenyl)-N,N-diethylacrylamide 1h:




Chemical Formula: $C_{13}H_{16}BrNO$
Exact Mass: 281.0415

Following the general procedure for amide synthesis, 2-bromocinnamic acid (232 mg, 1.02 mmol, 1 equiv) was reacted with oxalyl chloride (0.15 mL, 1.53 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with diethylamine (0.1 mL, 1.02 mmol, 1 equiv) and $Et_3N$ (0.29 mL, 2.04 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1h** was obtained as a yellowish oil (187 mg, 0.663 mmol, 65 %).

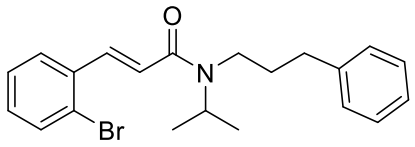
**$^1$H NMR (400 MHz, Chloroform-*d*) δ** = 7.99 (d, *J* = 15.4 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.58 – 7.54 (m, 1H), 7.33 – 7.27 (m, 1H), 7.22 – 7.15 (m, 1H), 6.76 (d, *J* = 15.4 Hz, 1H), 3.56 – 3.40 (m, 4H), 1.29 – 1.16 (m, 6H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 165.4, 140.8, 135.9, 133.5, 130.5, 127.9, 127.6, 125.1, 121.3, 42.5, 41.2, 15.2, 13.3.

**HRMS** (ESI): Calculated for $C_{13}H_{17}BrNO$ ($[M+H]^+$): 282.0494; found: 282.0488

**IR** (neat) : ν = 2363, 1649 $cm^{-1}$

## (E)-3-(2-bromophenyl)-N-isopropyl-N-(3-phenylpropyl)acrylamide 1i:




Chemical Formula: $C_{21}H_{24}BrNO$
Exact Mass: 385.1041

In a 250 mL round bottom flask equipped with stirring bar, hydrocinnamaldehyde (0.72 mL, 5.43 mmol, 1 equiv), isopropylamine (0.93 mL, 10.9 mmol, 2 equiv) and AcOH (0.62 mL, 10.9 mmol, 2 equiv) were stirred for 2 h in 1,2-dichloroethane (30 mL) at room temperature. Then, $NaBH(OAc)_3$ (2.3 g, 10.9 mmol, 2 equiv) was added to the mixture which was stirred overnight. The crude was quenched with NaOH (2 M, 30 mL) and the crude was extracted with DCM (3 x 30 mL). The combined organic layers were dried over sodium sulfate, filtered and evaporated under vacuum. The intermediate amine (956 mg, 10.8 mmol, 99 %) was obtained as a clear oil and directly used for next step.

Following the general procedure for amide synthesis, 2-bromocinnamic acid (136 mg, 0.6 mmol, 1 equiv) was reacted with oxalyl chloride (0.08 mL, 0.9 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with the intermediate amine (106 mg, 0.6 mmol, 1 equiv) and $Et_3N$ (0.17 mL, 1.2 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1i** was obtained as a colorless oil (187 mg, 0.484 mmol, 81 %).

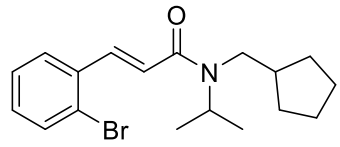
**$^1$H NMR (500 MHz, Chloroform-*d*) δ** = 8.00 – 7.88 (m, 1H), 7.61 – 7.55 (m, 1H), 7.31 – 7.26 (m, 3H), 7.25 – 7.15 (m, 5H), 6.84 – 6.78 (m, 0.4H), 6.50 – 6.44 (m, 0.6H), 4.86 – 4.75 (m, 0.6H), 4.31 – 4.22 (m, 0.4H), 3.36 – 3.22 (m, 2H), 2.68 (t, J = 7.2 Hz, 2H), 2.04 – 1.95 (m, 2H), 1.23 – 1.15 (m, 6H).

**$^{13}$C NMR (126 MHz, $CDCl_3$) δ =** 166.2, 165.6, 141.8, 140.9, 140.8, 140.1, 135.7, 133.5, 130.4, 128.8, 128.6, 127.9, 127.8, 127.6, 126.4, 126.0, 125.2, 122.1, 121.7, 49.0, 45.9, 42.4, 41.4, 33.9, 33.4, 33.3, 31.1, 21.7, 20.7.

**HRMS** (ESI): Calculated for $C_{21}H_{24}BrNaNO$ ($[M+Na]^+$): 408.0939; found: 408.0933

**IR** (neat) : ν = 2363, 1647, 1420 $cm^{-1}$

## (E)-3-(2-bromophenyl)-N-(cyclopentylmethyl)-N-isopropylacrylamide 1j:




Chemical Formula: $C_{18}H_{24}BrNO$
Exact Mass: 349.1041

Following the general procedure for amide synthesis, 2-bromocinnamic acid (82 mg, 0.363 mmol, 1 equiv) was reacted with oxalyl chloride (0.047 mL, 0.543 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with **S$_j$** (51 mg, 0.363 mmol, 1 equiv) and $Et_3N$ (0.1 mL, 0.72 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1j** was obtained as a colorless oil (74 mg, 0.211 mmol, 58 %).

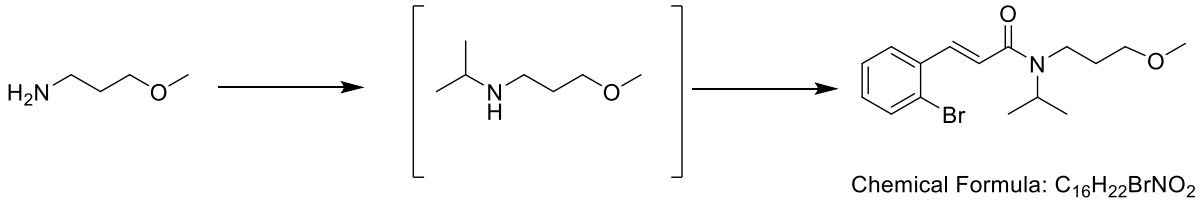
**$^1$H NMR (500 MHz, Chloroform-*d*) δ** = 7.99 – 7.86 (m, 1H), 7.63 – 7.49 (m, 2H), 7.33 – 7.28 (m, 1H), 7.20 – 7.14 (m, 1H), 6.88 – 6.77 (m, 1H), 4.44 – 4.20 (m, 1H), 3.35 – 3.28 (m, 2H), 2.33 – 2.11 (m, 1H), 1.84 – 1.71 (m, 2H), 1.68 – 1.63 (m, 2H), 1.60 – 1.53 (m, 2H), 1.31 – 1.21 (m, 8H).

**$^{13}$C NMR (126 MHz, $CDCl_3$) δ** = 180.4, 166.1, 145.1, 140.1, 139.8, 135.9, 133.4, 130.2, 127.7, 127.5, 124.9, 122.7, 49.8, 49.1, 48.9, 46.1, 43.5, 41.7, 40.1, 35.6, 31.0, 30.8, 30.0, 27.0, 25.8, 24.9, 23.7, 21.9, 20.5.

**HRMS** (ESI): Calculated for $C_{18}H_{24}BrNaNO$ ($[M+Na]^+$): 372.0939; found: 372.0931

**IR** (neat) : ν = 2361, 1648, 1423 $cm^{-1}$

## (E)-3-(2-bromophenyl)-N-isopropyl-N-(3-methoxypropyl)acrylamide 1k:




Chemical Formula: $C_{16}H_{22}BrNO_2$
Exact Mass: 339.0834

In a 250 mL round bottom flask equipped with stirring bar, 3-methyloxypropylamine (0.92 mL, 9.05 mmol, 1 equiv), acetone (2.7 mL, 36.2 mmol, 4 equiv) and AcOH (1.0 mL, 18.1 mmol, 2 equiv) were stirred for 2 h in 1,2-dichloroethane (50 mL) at room temperature. Then, $NaBH(OAc)_3$ (3.8 g, 18.1 mmol, 2 equiv) was added to the mixture which was stirred overnight.

The crude was quenched with NaOH (2 M, 50 mL) and the crude was extracted with DCM (3 x 50 mL). The combined organic layers were dried over sodium sulfate, filtered and evaporated under vacuum. The intermediate amine (976 mg, 8.33 mmol, 92 %) was obtained as a clear oil and directly used for next step.

Following the general procedure for amide synthesis, 2-bromocinnamic acid (227 mg, 1 mmol, 1 equiv) was reacted with oxalyl chloride (0.13 mL, 1 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with the intermediate amine (117 mg, 1 mmol, 1 equiv) and $Et_3N$ (0.28 mL, 2 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1k** was obtained as a colorless oil (267 mg, 0.82 mmol, 81 %).

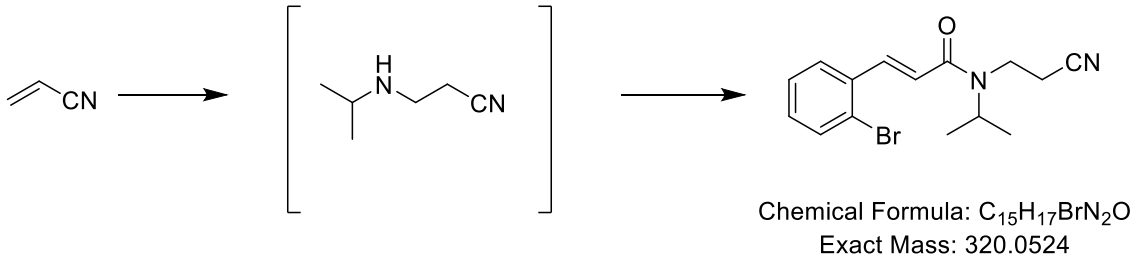
**$^1$H NMR (400 MHz, Chloroform-*d*) δ** = 8.03 (d, J = 15.3 Hz, 0.6H), 7.91 (d, J = 15.4 Hz, 0.4H), 7.66 – 7.55 (m, 2H), 7.32 – 7.30 (m, 1H), 7.20 – 7.17 (m, 1H), 6.94 (d, J = 15.3 Hz, 0.6H), 6.83 (d, J = 15.4 Hz, 0.4H), 4.85 – 4.75 (m, 0.6H), 4.34 – 4.25 (m, 0.4H), 3.50 – 3.37 (m, 4H), 3.37 – 3.32 (m, 3H), 1.96 – 1.85 (m, 2H), 1.29 – 1.19 (m, 6H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 166.2, 165.9, 140.8, 140.0, 135.9, 133.5, 130.4, 127.9, 127.7, 127.6, 125.2, 125.0, 122.2, 122.1, 71.1, 69.8, 58.9, 58.7, 49.1, 46.0, 40.4, 39.2, 32.3, 29.7, 21.6, 20.6.

**HRMS** (ESI): Calculated for $C_{16}H_{22}BrNaNO_2$ ($[M+Na]^+$): 362.0732; found: 362.0726

**IR** (neat) : $\nu$ = 2361, 1642 $cm^{-1}$

## (E)-3-(2-bromophenyl)-N-(2-cyanoethyl)-N-isopropylacrylamide 1l:




Chemical Formula: $C_{15}H_{17}BrN_2O$
Exact Mass: 320.0524

In a 25 mL double-neck flask charged with isopropylamine (1.1 mL, 12.6 mmol, 2 equiv ) in EtOH (6 mL) and cooled to 0°C was added via dropping funnel, a solution of acrylonitrile (0.41 mL, 6.32 mmol, 1 equiv) in EtOH (6 mL). The reaction was allowed to reach room temperature, and the volatiles were removed under vacuum. The desired amine was pure enough to react in next step (454 mg, 4.04 mmol, 64%).

Following the general procedure for amide synthesis, 2-bromocinnamic acid (143 mg, 0.63 mmol, 1 equiv) was reacted with oxalyl chloride (0.1 mL, 0.95 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with the intermediate amine (70 mg, 0.63 mmol, 1 equiv) and $Et_3N$ (0.18 mL, 1.26 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1l** was obtained as a yellowish oil (134 mg, 0.42 mmol, 66 %).

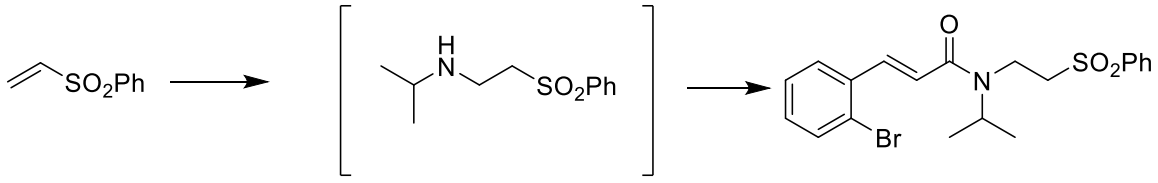
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.95 (d, J = 15.2 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.35 – 7.30 (m, 1H), 7.24 – 7.18 (m, 1H), 6.80 (d, J = 15.3 Hz, 1H), 4.37 – 4.27 (m, 1H), 3.57 (t, J = 7.0 Hz, 2H), 2.82 (t, J = 7.0 Hz, 2H), 1.30 (d, J = 6.7 Hz, 6H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 167.0, 141.5, 135.4, 133.6, 130.9, 127.8, 127.7, 125.2, 120.8, 118.5, 49.1, 37.8, 21.7, 17.2.

**HRMS** (ESI): Calculated for $C_{15}H_{17}BrNaN_2O_4$ ($[M+Na]^+$): 343.0422; found: 343.0416

**IR** (neat) : ν = 2363, 1646, 1418 $cm^{-1}$

## (E)-3-(2-bromophenyl)-N-isopropyl-N-(3 (phenylsulfonyl)propyl)acrylamide 1m:




Chemical Formula: $C_{21}H_{24}BrNO_3S$
Exact Mass: 449.0660

In a 25 mL double-neck flask charged with isopropylamine (1.1 mL, 12.6 mmol, 2 equiv ) in EtOH (6 mL) and cooled to 0°C was added via dropping funnel, a solution of phenyl vinyl sulfone (1.06 g, 6.32 mmol, 1 equiv) in EtOH (6 mL). The reaction was allowed to reach room temperature, and the volatiles were removed under vacuum. The desired amine was pure enough to react in next step (1.4 g, 6.31 mmol, 99%).

Following the general procedure for amide synthesis, 2-bromocinnamic acid (143 mg, 0.63 mmol, 1 equiv) was reacted with oxalyl chloride (0.1 mL, 0.95 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with the intermediate amine (144 mg, 0.63 mmol,

1 equiv) and $Et_3N$ (0.18 mL, 1.26 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1m** was obtained as a colorless oil (202 mg, 0.46 mmol, 73 %).

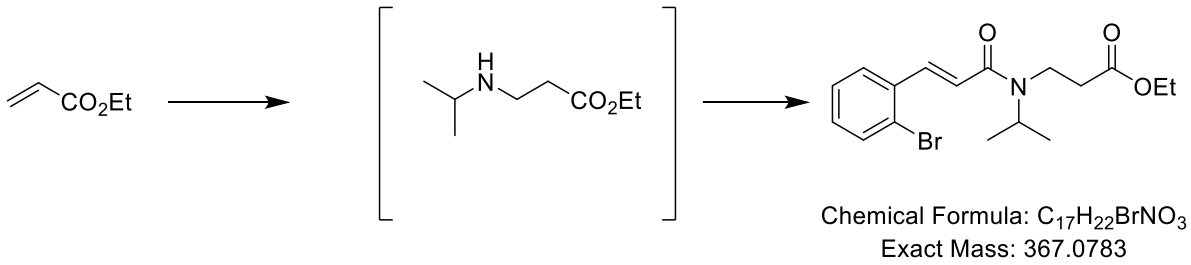
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 8.00 – 7.82 (m, 3H), 7.70 – 7.64 (m, 1H), 7.63 – 7.43 (m, 4H), 7.31 – 7.27 (m, 1H), 7.22 – 7.12 (m, 1H), 6.78 – 6.57 (m, 1H), 4.91 – 4.66 (m, 0.3H), 4.33 – 4.21 (m, 0.7H), 3.81 – 3.71 (m, 0.7H), 3.68 – 3.43 (m, 3H), 3.40 – 3.26 (m, 0.4H), 1.25 (d, J = 6.5 Hz, 5H), 1.17 – 1.06 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 166.5, 141.3, 139.1, 135.4, 134.0, 133.5, 130.8, 129.5, 128.0, 127.8, 127.7, 125.1, 120.6, 54.5, 49.3, 35.6, 29.8, 21.4, 20.4.

**HRMS** (ESI): Calculated for $C_{21}H_{24}BrNaNO_3S$ ($[M+Na]^+$): 458.0401; found: 458.0396

**IR** (neat) : ν = 2362, 904 $cm^{-1}$

## ethyl (E)-3-(3-(2-bromophenyl)-N-isopropylacrylamido)propanoate 1n:




Chemical Formula: $C_{17}H_{22}BrNO_3$
Exact Mass: 367.0783

In a 25 mL double-neck flask charged with isopropylamine (1.1 mL, 12.6 mmol, 2 equiv ) in EtOH (6 mL) and cooled to 0°C was added via dropping funnel, a solution of ethyl acrylate (633 mg, 6.32 mmol, 1 equiv) in EtOH (6 mL). The reaction was allowed to reach room temperature, and the volatiles were removed under vacuum. The desired amine was pure enough to react in next step (876 mg, 5.5 mmol, 87%).

Following the general procedure for amide synthesis, 2-bromocinnamic acid (143 mg, 0.63 mmol, 1 equiv) was reacted with oxalyl chloride (0.1 mL, 0.95 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with the intermediate amine (101 mg, 0.63 mmol, 1 equiv) and $Et_3N$ (0.18 mL, 1.26 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1n** was obtained as a yellowish oil (152 mg, 0.41 mmol, 65 %).

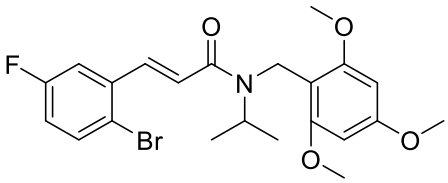
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 8.07 – 7.85 (m, 1H), 7.61 – 7.53 (m, 2H), 7.33 – 7.27 (m, 1H), 7.22 – 7.14 (m, 1H), 6.80 (d, J = 15.4 Hz, 1H), 4.88 – 4.74 (m, 0.4H), 4.33 – 4.23 (m, 0.6H), 4.15 (q, J = 7.2 Hz, 2H), 3.70 – 3.55 (m, 2H), 2.75 – 2.58 (m, 2H), 1.31 – 1.13 (m, 10H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 172.2, 171.2, 166.3, 165.7, 141.7, 140.5, 135.7, 133.5, 130.6, 127.8, 127.7, 125.0, 121.6, 121.3, 61.1, 60.6, 49.1, 46.0, 38.7, 37.3, 36.8, 34.1, 21.5, 20.5, 14.3.

**HRMS** (ESI): Calculated for $C_{17}H_{22}BrNaNO_3$ ($[M+Na]^+$): 390.0681; found: 390.0677

**IR** (neat) : ν = 2362, 1624, 1423 $cm^{-1}$

## (E)-3-(2-bromo-5-fluorophenyl)-N-isopropyl-N-(2,4,6-trimethoxybenzyl)acrylamide 1o:




Chemical Formula: $C_{22}H_{25}BrFNO_4$
Exact Mass: 465.0951

Following the general procedure for amide synthesis, 2-Bromo-5-fluorocinnamic acid (186 mg, 0.76 mmol, 1 equiv) was reacted with oxalyl chloride (0.1 mL, 1.14 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with **$S_a$** (182 mg, 0.76 mmol, 1 equiv) and $Et_3N$ (0.22 mL, 1.52 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1o** was obtained as a white solid (302 mg, 0.65 mmol, 85 %).

**$^{1}$H NMR (400 MHz, Chloroform-*d*) δ =** 7.80 (d, *J* = 15.4, 1H), 7.56 – 7.50 (m, 1H), 7.27 – 7.23 (m, 1H), 7.18 (d, *J* = 15.4 Hz, 1H), 6.92 – 6.87 (m, 1H), 6.11 (s, 2H), 4.57 (s, 2H), 4.15 – 4.07 (m, 1H), 3.81 (s, 3H), 3.78 (s, 6H), 1.18 (d, *J* = 6.9 Hz, 6H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ** = 166.2, 163.1, 161.1, 160.7, 159.5, 137.0, 134.4 (d, J = 9.3 Hz), 125.9, 118.9 (d, J = 3.9 Hz), 117.0 (d, J = 22.1 Hz), 114.1 (d, J = 21.4 Hz), 106.2, 90.5, 55.4, 55.3, 49.3, 39.6, 19.8.

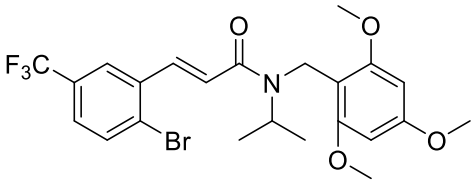
**$^{19}$F NMR (376 MHz, $CDCl_3$) δ =** -114.9.

**HRMS** (ESI): Calculated for $C_{22}H_{26}BrFNO_4$ ($[M+H]^+$): 466.1029; found: 466.1026

**IR** (neat) : ν = 2360, 1597, 1464 $cm^{-1}$

**m.p.:** 92 - 94°C

## (E)-3-(2-bromo-5-(trifluoromethyl)phenyl)-N-isopropyl-N-(2,4,6-trimethoxybenzyl)acrylamide 1p:



Chemical Formula: $C_{23}H_{25}BrF_3NO_4$
Exact Mass: 515.0919

Following the general procedure for Knoevenagel condensation, 2-bromo-5-(trifluoromethyl)benzaldehyde (500 mg, 1.98 mmol, 1 equiv) was reacted with malonic acid (227 mg, 2.18 mmol, 1.1 equiv), piperidine (0.22 mL, 2.18 mmol, 1.1 equiv) in pyridine at 90 °C for 15h. After evaporation and purification, the intermediate carboxylic acid (584 mg, 1.98 mmol, 1 equiv) was reacted with oxalyl chloride (0.28 mL, 2.97 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with **$S_a$** (474 mg, 1.98 mmol, 1 equiv) and $Et_3N$ (0.55 mL, 3.96 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1p** was obtained as a colorless oil (896 mg, 1.73 mmol, 88 %).

**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.88 – 7.82 (m, 1H), 7.76 – 7.74 (m, 1H), 7.74 – 7.70 (m, 1H), 7.41 – 7.37 (m, 1H), 7.27 – 7.20 (m, 1H), 6.11 (s, 2H), 4.58 (s, 2H), 4.15 (sept, J = 6.9 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 6H), 1.21 (d, J = 6.9 Hz, 6H).

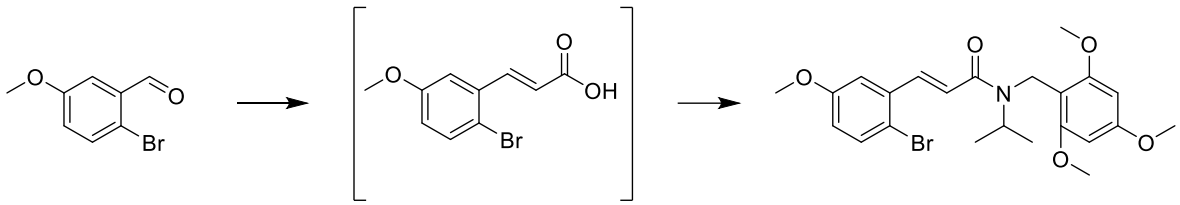
**$^{13}$C NMR (126 MHz, $CDCl_3$) δ =** 166.1, 161.3, 159.7, 137.6, 136.7, 134.0, 130.1 (q, J = 32.6 Hz), 128.5, 126.6, 126.1, 124.3 (q, J = 2.9 Hz), 123.9 (q, J = 271.9 Hz), 106.4, 90.6, 55.5, 55.4, 49.4, 39.7, 19.9.

**$^{19}$F NMR (471 MHz, $CDCl_3$) δ =** -62.7.

**HRMS** (ESI): Calculated for $C_{23}H_{25}BrF_3NaNO_4$ ($[M+Na]^+$): 538.0817; found: 538.0812

**IR** (neat) : ν = 2362, 1648 $cm^{-1}$

## (E)-3-(2-bromo-5-methoxyphenyl)-N-isopropyl-N-(2,4,6-trimethoxybenzyl)acrylamide 1q:



Chemical Formula: $C_{23}H_{28}BrNO_5$
Exact Mass: 477.1151

Following the general procedure for Knoevenagel condensation, 2-bromo-5-methoxybenzaldehyde (2 g, 9.02 mmol, 1 equiv) was reacted with malonic acid (1.03 g, 9.92 mmol, 1.1 equiv), piperidine (0.98 mL, 9.92 mmol, 1.1 equiv) in pyridine at 90 °C for 15h. After evaporation and purification, the intermediate carboxylic acid (195 mg, 0.76 mmol, 1 equiv) was reacted with oxalyl chloride (0.1 mL, 1.14 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with **$S_a$** (182 mg, 0.76 mmol, 1 equiv) and $Et_3N$ (0.214 mL, 1.52 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1q** was obtained as a white solid (284 mg, 0.594 mmol, 78 %).

**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.82 (d, J = 15.4 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.18 (d, J = 15.4 Hz, 1H), 7.12 – 7.07 (m, 1H), 6.76 – 7.70 (m, 1H), 6.10 (s, 2H), 4.58 (s, 2H), 4.09 (sept, J = 6.9 Hz, 1H), 3.80 (s, 3H), 3.80 (s, 6H), 3.77 (s, 6H), 1.16 (d, J = 6.8 Hz, 6H).

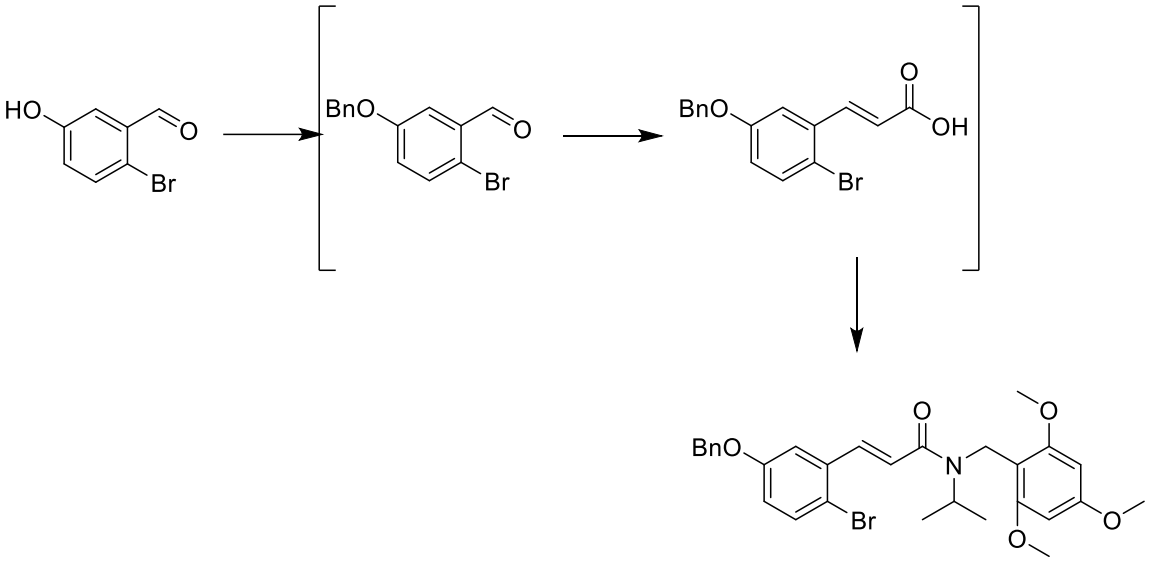
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ** = 166.7, 161.2, 159.7, 159.0, 138.1, 137.3, 133.9, 125.1, 115.7, 115.6, 113.2, 106.4, 90.5, 55.6, 55.6, 55.4, 49.1, 39.7, 19.9.

**HRMS** (ESI): Calculated for $C_{23}H_{28}BrNaNO_5$ ($[M+Na]^+$): 500.1049; found: 500.1043

**IR** (neat) : ν = 2364 $cm^{-1}$

**m.p.:** 104 - 106°C

## (E)-3-(5-(benzyloxy)-2-bromophenyl)-N-isopropyl-N-(2,4,6-trimethoxybenzyl)acrylamide 1r:




Chemical Formula: $C_{29}H_{32}BrNO_5$
Exact Mass: 553.1464

In a 100 mL flask charged with 2-bromo-5-hydroxybenzaldehyde (500 mg, 2.48 mmol, 1 equiv) and $K_2CO_3$ (1.02 g, 7.44 mmol, 3 equiv) in DMF (10 mL) was added benzyl bromide (0.45 mL, 3.72 mmol, 1.5 equiv). The reaction was stirred to room temperature and monitored by TLC using Cyclohexane/AcOEt as solvent. After completion, the reaction was quenched with water (10 mL) and extracted with AcOEt (3 x 10 mL). The combined organic phases were washed with 10% LiCl solution (3 x 10 mL) and the crude was dried over sodium sulfate, filtered and evaporated under vacuum. The crude was used in next step without further purification (720 mg, 2.48 mmol, 99 %).

Following the general procedure for Knoevenagel condensation, 5-(benzyloxy)-2-bromobenzaldehyde (720 mg, 2.48 mmol, 1 equiv) was reacted with malonic acid (284 mg, 2.73 mmol, 1.1 equiv), piperidine (0.25 mL, 2.73 mmol, 1.1 equiv) in pyridine at 90 °C for 15h. After evaporation and purification, the intermediate carboxylic acid (333 mg, 1.0 mmol, 1 equiv) was reacted with oxalyl chloride (0.14 mL, 1.5 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with $\mathbf{S_a}$ (239 mg, 1.0 mmol, 1 equiv) and $Et_3N$ (0.28 mL, 2 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1r** was obtained as a yellowish solid (387 mg, 0.7 mmol, 70 %).

**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.85 – 7.79 (m, 1H), 7.48 – 7.45 (m, 1H), 7.42 – 7.29 (m, 5H), 7.18 – 7.11 (m, 2H), 6.82 – 6.78 (m, 1H), 6.11 (s, 2H), 5.05 (s, 2H), 4.58 (s, 2H), 4.16 – 4.07 (m, 1H), 3.79 (s, 3H), 3.76 (s, 6H), 1.17 (d, J = 6.9 Hz, 6H).

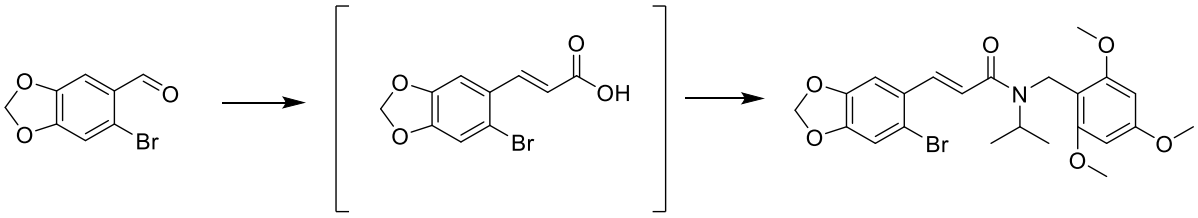
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 166.6, 161.1, 159.7, 158.1, 137.9, 137.3, 136.5, 133.9, 128.8, 128.3, 127.6, 125.1, 116.6, 115.8, 114.2, 106.4, 90.6, 70.5, 55.4, 49.1, 39.6, 19.9.

**HRMS** (ESI): Calculated for $C_{29}H_{33}BrNO_5$ ($[M+H]^+$): 554.1542; found: 554.1537

**IR** (neat) : ν = 1594, 1464, 905 $cm^{-1}$

**m.p.:** 115 - 117°C

## (E)-3-(6-bromobenzo[d][1,3]dioxol-5-yl)-N-isopropyl-N-(2,4,6-trimethoxybenzyl)acrylamide 1s:




Following the general procedure for Knoevenagel condensation, 6-Bromopiperonal (2.29 g, 10 mmol, 1 equiv) was reacted with malonic acid (1.15 g, 11 mmol, 1.1 equiv), piperidine (1.1 mL, 11 mmol, 1.1 equiv) in pyridine at 90 °C for 15h. After evaporation and purification, the intermediate carboxylic acid (148 mg, 0.547 mmol, 1 equiv) was reacted with oxalyl chloride (0.07 mL, 0.821 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with **$S_a$** (131 mg, 0.547 mmol, 1 equiv) and $Et_3N$ (0.154 mL, 1.09 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1s** was obtained as a yellowish solid (202 mg, 0.41 mmol, 75 %).

**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.83 (d, J = 15.4 Hz, 1H), 7.11 – 6.99 (m, 3H), 6.11 (s, 2H), 5.99 (s, 2H), 4.57 (s, 2H), 4.09 (sept, J = 6.8 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 6H), 1.17 (d, J = 6.9 Hz, 6H).

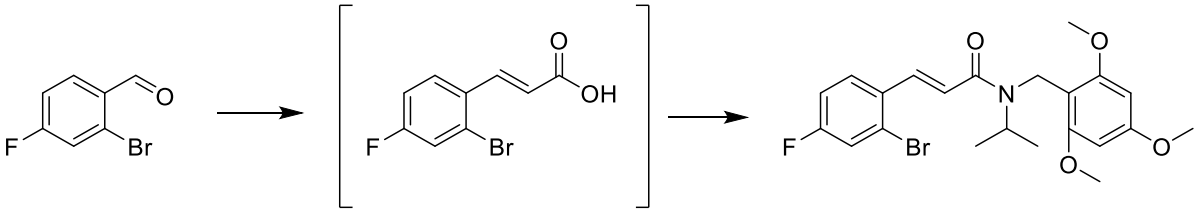
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 166.9, 161.2, 159.7, 149.0, 147.8, 138.0, 129.8, 123.1, 116.8, 113.2, 106.5, 102.1, 90.6, 55.6, 55.4, 49.3, 39.7, 19.9.

**HRMS** (ESI): Calculated for $C_{23}H_{26}BrNaNO_6$ ($[M+Na]^+$): 514.0841; found: 514.0836

**IR** (neat) : ν = 2362, 1596, 1474 $cm^{-1}$

**m.p.:** 115- 117°C

## (E)-3-(2-bromo-4-fluorophenyl)-N-isopropyl-N-(2,4,6-trimethoxybenzyl)acrylamide 1t:




Chemical Formula: $C_{22}H_{25}BrFNO_4$
Exact Mass: 465.0951

Following the general procedure for Knoevenagel condensation, 2-bromo-4-fluorobenzaldehyde (812 mg, 4 mmol, 1 equiv) was reacted with malonic acid (458 mg, 4.4 mmol, 1.1 equiv), piperidine (0.44 mL, 4.4 mmol,1.1 equiv) in pyridine at 90 °C for 15h. After evaporation and purification, the intermediate carboxylic acid (155 mg, 0.63 mmol, 1 equiv) was reacted with oxalyl chloride (0.08 mL, 0.95 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with **$S_a$** (151 mg, 0.63 mmol, 1 equiv) and $Et_3N$ (0.18 mL, 1.26 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1t** was obtained as a yellowish solid (236 mg, 0.506 mmol, 80 %).

**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.82 (d, J = 15.4 Hz, 1H), 7.56 – 7.54 (m, 1H), 7.36 – 7.32 (m, 1H), 7.15 (d, J = 15.4 Hz, 1H), 7.05 – 7.00 (m, 1H), 6.10 (s, 2H), 4.58 (s, 2H), 4.08 (sept, J = 6.9 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 6H), 1.16 (d, J = 6.9 Hz, 6H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ** = 166.6, 162.7 (d, J = 257 Hz) , 161.1, 159.7, 137.0, 132.9, 132.9, 128.6 (d, J = 8.2 Hz), , 125.0, 124.9, 124.8, 120.4 (d, J = 24.7 Hz), 114.9 (d, J = 21.2 Hz), 106.4, 55.6, 55.4, 49.2, 39.7, 19.9.

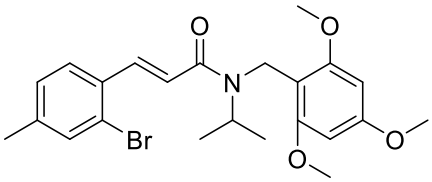
**$^{19}$F NMR (376 MHz, $CDCl_3$) δ =** -111.1

**HRMS** (ESI): Calculated for $C_{22}H_{26}BrFNO_4$ ($[M+H]^+$): 466.1029; found: 466.1024

**IR** (neat) : ν = 2361, 159, 1460 $cm^{-1}$

**m.p.:** 95 - 97°C

## (E)-3-(2-bromo-4-methylphenyl)-N-isopropyl-N-(2,4,6-trimethoxybenzyl)acrylamide 1u:




Chemical Formula: $C_{23}H_{28}BrNO_4$
Exact Mass: 461.1202

Following the general procedure for Knoevenagel condensation, 2-bromo-4-methylbenzaldehyde (500 mg, 2.51 mmol, 1 equiv) was reacted with malonic acid (287 mg, 2.76 mmol, 1.1 equiv), piperidine (0.27 mL, 2.76 mmol, 1.1 equiv) in pyridine at 90 °C for 15h. After evaporation and purification, the intermediate carboxylic acid (605 mg, 2.51 mmol, 1 equiv) was reacted with oxalyl chloride (0.35 mL, 3.76 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with **$S_a$** (601 mg, 2.51 mmol, 1 equiv) and $Et_3N$ (0.70 mL, 5.0 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1u** was obtained as a white solid (812 mg, 1.75 mmol, 70 %).

**$^1$H NMR (400 MHz, Chloroform-*d*) δ** = 7.90 – 7.80 (m, 1H), 7.49 – 7.45 (m, 1H), 7.43 – 7.41 (m, 1H), 7.23 – 7.16 (m, 1H), 7.11 – 7.07 (m, 1H), 6.10 (s, 2H), 4.59 (s, 2H), 4.08 (sept, J = 6.8 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 6H), 2.33 (s, 3H), 1.16 (d, J = 6.9 Hz, 6H).

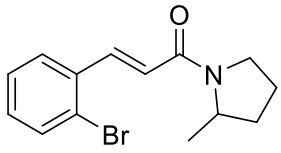
**$^{13}$C NMR (126 MHz, $CDCl_3$) δ =** 166.9, 161.1, 159.7, 140.5, 138.0, 133.8, 133.6, 128.5, 127.3, 124.8, 123.9, 106.5, 90.6, 55.6, 55.4, 49.1, 39.7, 21.0, 19.9.

**HRMS** (ESI): Calculated for $C_{23}H_{29}BrNO_4$ ($[M+H]^+$): 462.1280; found: 462.1274

**IR** (neat) : ν = 1598, 1458, 1130 $cm^{-1}$

**m.p.:** 94 - 96°C

## (E)-3-(2-bromophenyl)-1-(2-methylpyrrolidin-1-yl)prop-2-en-1-one 1v:




Chemical Formula: $C_{14}H_{16}BrNO$
Exact Mass: 293.0415

Following the general procedure for amide synthesis, 2-bromocinnamic acid (330 mg, 1.45 mmol, 1 equiv) was reacted with oxalyl chloride (0.20 mL, 2.18 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with 2-methylpyrrolidine (0.14 mL, 1.45 mmol, 1 equiv) and $Et_3N$ (0.41 mL, 2.90 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1v** was obtained as a yellowish solid (369 mg, 1.25 mmol, 86 %).

**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 8.06 – 7.95 (m, 1H), 7.62 – 7.52 (m, 2H), 7.32 – 7.26 (m, 1H), 7.19 – 7.12 (m, 1H), 6.72 – 6.61 (m, 1H), 4.39 – 4.14 (m, 1H), 3.74 – 3.51 (m, 2H), 2.13 – 1.87 (m, 3H), 1.76 – 1.59 (m, 1H), 1.28 – 1.23 (m, 3H).

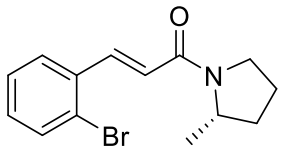
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 164.1, 164.0, 140.3, 140.2, 135.9, 135.8, 133.5, 133.5, 130.5, 127.9, 127.9, 127.6, 125.2, 125.1, 122.7, 122.2, 53.4, 53.1, 47.1, 46.1, 33.4, 32.1, 24.1, 22.3, 22.0, 19.7.

**HRMS** (ESI): Calculated for $C_{14}H_{16}BrNNaO$ ($[M+Na]^+$): 316.0313; found: 316.0307

**IR** (neat) : ν = 1649, 1603, 1407 $cm^{-1}$

**m.p.:** 78 - 80°C

## (S,E)-3-(2-bromophenyl)-1-(2-methylpyrrolidin-1-yl)prop-2-en-1-one (S)-1v:




Chemical Formula: $C_{14}H_{16}BrNO$
Exact Mass: 293.0415

Following the general procedure for amide synthesis, 2-bromocinnamic acid (2.65 g, 11.7 mmol, 1 equiv) was reacted with oxalyl chloride (1.66 mL, 17.6 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with (S)-2-methylpyrrolidine (1 g, 11.7 mmol, 1 equiv) and $Et_3N$

(3.25 mL, 23.4 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **(S)-1v** was obtained as a yellowish oil (3.44 g, 11.7 mmol, 100 %).

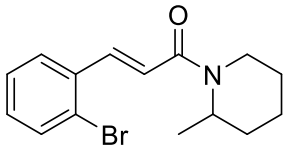
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 8.04 – 7.95 (m, 1H), 7.61 – 7.50 (m, 2H), 7.33 – 7.27 (m, 1H), 7.21 – 7.13 (m, 1H), 6.73 – 6.62 (m, 1H), 4.38 – 4.15 (m, 1H), 3.73 – 3.54 (m, 2H), 2.15 – 1.90 (m, 3H), 1.77 – 1.58 (m, 1H), 1.29 – 1.23 (m, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 164.1, 164.0, 140.3, 140.1, 135.9, 135.8, 133.5, 133.5, 130.5, 127.9, 127.9, 127.6, 125.2, 125.1, 122.7, 122.2, 53.4, 53.1, 47.1, 46.1, 33.4, 32.1, 24.1, 22.3, 22.0, 19.7.

**HRMS** (ESI): Calculated for $C_{14}H_{16}BrNNaO$ ($[M+Na]^+$): 316.0313; found: 316.0306

**IR** (neat) : ν = 1649, 1407 $cm^{-1}$

## (E)-3-(2-bromophenyl)-1-(2-methylpiperidin-1-yl)prop-2-en-1-one 1w:




Chemical Formula: $C_{15}H_{18}BrNO$
Exact Mass: 307.0572

Following the general procedure for amide synthesis, 2-bromocinnamic acid (232 mg, 1.02 mmol, 1 equiv) was reacted with oxalyl chloride (0.14 mL, 1.53 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with 2-methylpiperidine (0.12 mL, 1.02 mmol, 1 equiv) and $Et_3N$ (0.28 mL, 2.04 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1w** was obtained as a yellowish oil (292 mg, 0.95 mmol, 93 %).

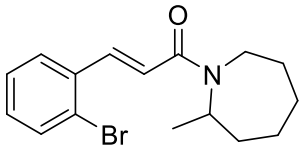
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.88 (d, J = 15.5 Hz, 1H), 7.58 (ddd, J = 8.9, 7.9, 1.5 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.19 – 7.15 (m, 1H), 6.80 (d, J = 15.5 Hz, 1H), 4.47 (br s, 1H), 3.25 – 2.74 (m, 1H), 1.76 – 1.54 (m, 6H), 1.54 – 1.42 (m, 1H), 1.30 – 1.18 (m, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 165.2, 140.0, 135.9, 133.3, 130.2, 127.6, 127.5, 124.8, 121.8, 18.9.

**HRMS** (ESI): Calculated for $C_{15}H_{19}BrNO$ ($[M+H]^+$): 308.0650; found: 308.0645

**IR** (neat) : ν = 2362, 2157, 1644 $cm^{-1}$

## (E)-3-(2-bromophenyl)-1-(2-methylazepan-1-yl)prop-2-en-1-one 1x:




Chemical Formula: $C_{16}H_{20}BrNO$
Exact Mass: 321.0728

Following the general procedure for amide synthesis, 2-bromocinnamic acid (300 mg, 1.32 mmol, 1 equiv) was reacted with oxalyl chloride (0.17 mL, 1.98 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with 2-methylazepane hydrochloride (198 mg, 1.32 mmol, 1 equiv) and $Et_3N$ (0.37 mL, 2.64 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1x** was obtained as a colorless oil (205 mg, 0.64 mmol, 48 %).

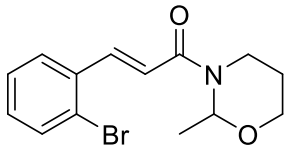
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 8.06 – 7.94 (m, 1H), 7.62 – 7.58 (m, 1H), 7.57 – 7.53 (m, 1H), 7.33 – 7.28 (m, 1H), 7.20 – 7.14 (m, 1H), 6.86 – 6.79 (m, 1H), 4.68 – 4.56 (m, 0.6H), 4.23 – 4.15 (m, 0.4H), 4.10 – 3.97 (m, 0.4H), 3.78 – 3.67 (m, 0.6H), 3.14 – 3.04 (m, 0.5H), 2.79 – 2.67 (m, 0.5H), 2.14 – 2.02 (m, 1H), 1.94 – 1.72 (m, 3H), 1.71 – 1.62 (m, 0.5H), 1.57 – 1.49 (m, 0.5H), 1.47 – 1.36 (m, 1H), 1.34 – 1.23 (m, 2H), 1.21 (d, J = 6.4 Hz, 1.5H), 1.12 (d, J = 6.4 Hz, 1.5H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 165.7, 165.6, 140.8, 140.4, 135.9, 135.9, 133.4, 133.4, 130.3, 130.3, 127.8, 127.7, 127.5, 125.0, 124.9, 121.6, 121.5, 53.0, 50.1, 41.7, 40.4, 36.4, 35.6, 30.7, 29.9, 29.4, 28.3, 25.2, 25.0, 21.2, 19.4.

**HRMS** (ESI): Calculated for $C_{16}H_{21}BrNO$ ($[M+H]^+$): 322.0807; found: 322.0801

**IR** (neat) : ν = 2362, 1623 $cm^{-1}$

## (E)-3-(2-bromophenyl)-1-(2-methyl-1,3-oxazinan-3-yl)prop-2-en-1-one 1y:




Chemical Formula: $C_{14}H_{16}BrNO_2$
Exact Mass: 309.0364

Following the general procedure for amide synthesis, 2-bromocinnamic acid (350 mg, 1.54 mmol, 1 equiv) was reacted with oxalyl chloride (0.20 mL, 2.31 mmol, 1.5 equiv) with DMF (1 drop) in

dichloromethane. The acid chloride was then reacted with 2-methyl-1,3-oxazinane (156 mg, 1.54 mmol, 1 equiv) and $Et_3N$ (0.43 mL, 3.08 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1y** was obtained as a yellowish oil (361 mg, 1.16 mmol, 76 %).

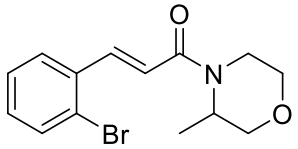
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.94 – 7.85 (m, 1H), 7.60 – 7.53 (m, 2H), 7.32 – 7.27 (m, 1H), 7.20 – 7.15 (m, 1H), 6.75 – 6.66 (m, 1H), 5.92 – 5.85 (m, 1H), 4.27 (br. s, 1H), 3.99 (ddd, J = 11.9, 10.3, 4.2 Hz, 1H), 3.75 – 3.68 (m, 1H), 3.35 – 3.23 (m, 1H), 2.00 – 1.86 (m, 1H), 1.73 – 1.65 (m, 1H), 1.52 (d, J = 6.2 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 164.6, 141.1, 135.4, 133.4, 130.6, 127.7, 127.6, 124.9, 120.7, 79.5, 59.7, 25.7, 16.5.

**HRMS** (ESI): Calculated for $C_{14}H_{17}BrNO_2$ ($[M+H]^+$): 310.0443; found: 310.0437

**IR** (neat) : ν = 1625, 1424, 1107 $cm^{-1}$

## (E)-3-(2-bromophenyl)-1-(3-methylmorpholino)prop-2-en-1-one 1z:




Chemical Formula: $C_{14}H_{16}BrNO_2$
Exact Mass: 309.0364

Following the general procedure for amide synthesis, 2-bromocinnamic acid (568 mg, 2.5 mmol, 1 equiv) was reacted with oxalyl chloride (0.35 mL, 3.75 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with 3-methylmorpholine (253 mg, 2.5 mmol, 1 equiv) and $Et_3N$ (0.69 mL, 5 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1z** was obtained as a colorless oil (580 mg, 1.87 mmol, 75 %).

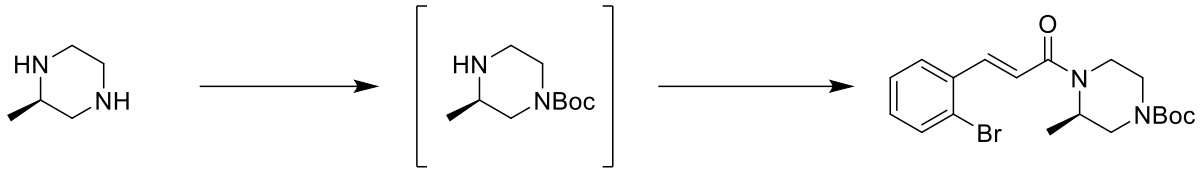
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.96 (d, J = 15.4 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.57 – 7.54 (m, 1H), 7.32 – 7.27 (m, 1H), 7.21 – 7.16 (m, 1H), 6.74 (d, J = 15.4 Hz, 1H), 4.80 – 4.00 (m, 2H), 3.97 – 3.91 (m, 1H), 3.76 – 3.70 (m, 1H), 3.67 – 3.61 (m, 1H), 3.52 – 3.46 (m, 1H), 3.30 (br. s, 1H), 1.37 (d, J = 7.0 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 165.3, 141.4, 135.6, 133.5, 130.7, 127.8, 127.7, 125.0, 120.4, 71.0, 67.1.

**HRMS** (ESI): Calculated for $C_{14}H_{17}BrNO_2$ ($[M+H]^+$): 310.0443; found: 310.0438

**IR** (neat) : ν = 1625, 1425, 1106 $cm^{-1}$

**tert-butyl (E)-4-(3-(2-bromophenyl)acryloyl)-3-methylpiperazine-1-carboxylate 1aa:**




Chemical Formula:
$C_{19}H_{25}BrN_2O_3$
Exact Mass: 408.1049

(R)-2-methylpiperazine (600 mg, 6 mmol, 1 equiv) was dissolved in dry dichloromethane (80 mL) and cooled to 0°C. A solution of the $Boc_2O$ (1.31 g, 6 mmol, 1 equiv) in 20 mL of dry dichloromethanewas added dropwise in 30 min and then pyridine (0.73 mL, 9 mmol, 1.5 equiv). The reaction mixture was allowed to reach room temperature and was stirred overnight. The crude was quenched with NaOH (1M, 60 mL) and the aqueous phase was extracted with DCM (3 x 20 mL). The combined organic layers were dried over sodium sulfate, filtered and evaporated under vacuum. The *N*-Boc protected piperazine was then used without further purification for next step.

Following the general procedure for amide synthesis, 2-bromocinnamic acid (568 mg, 2.5 mmol, 1 equiv) was reacted with oxalyl chloride (0.35 mL, 3.75 mmol, 1.5 equiv) with DMF (1 drop) in dichloromethane. The acid chloride was then reacted with *N*-Boc protected piperazine (500 mg, 2.5 mmol, 1 equiv) and $Et_3N$ (0.69 mL, 5 mmol, 2 equiv) in dichloromethane. After evaporation and purification, **1aa** was obtained as a yellowish oil (684 mg, 1.67 mmol, 67 %).

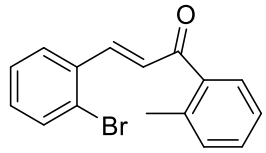
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.94 (d, J = 15.4 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.33 – 7.28 (m, 1H), 7.22 – 7.16 (m, 1H), 6.75 (d, J = 15.5 Hz, 1H), 4.98 – 3.74 (m, 4H), 3.46 – 2.79 (m, 3H), 1.48 (s, 9H), 1.26 (d, J = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 165.4, 155.1, 141.4, 135.6, 133.5, 130.7, 127.8, 127.7, 125.1, 120.7, 80.4, 28.5.

**HRMS** (ESI): Calculated for $C_{19}H_{25}BrNaN_2O_3$ ($[M+Na]^+$): 431.0946; found: 431.0941

**IR** (neat) : ν = 2362, 1690, 1423 $cm^{-1}$

## (E)-3-(2-bromophenyl)-1-(o-tolyl)prop-2-en-1-one 3a:




Chemical Formula: $C_{16}H_{13}BrO$
Exact Mass: 300.0150

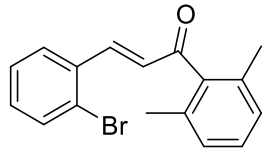
Following the general procedure for aldolisation reaction, 2-bromobenzaldehyde (1.11 g, 6 mmol, 1 equiv), 1-(o-tolyl)ethan-1-one (805 mg, 6 mmol, 1 equiv), and NaOH (240 mg, 6 mmol, 1 equiv) were reacted in EtOH/water at 45 °C. After completion, the crude was extracted and purified by chromatography on silica gel to afford **3a** as a yellowish solid (1.8 g, 6 mmol, 100%).

The physical and spectroscopic properties matched those described in the literature. [2]

**$^{1}$H NMR (400 MHz, Chloroform-*d*) δ =** 7.84 (d, *J* = 16.0 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.62 – 7.59 (m, 1H), 7.55 – 7.52 (m, 1H), 7.42 – 7.32 (m, 2H), 7.31 – 7.26 (m, 2H), 7.26 – 7.21 (m, 1H), 7.06 (d, *J* = 16.0 Hz, 1H), 2.48 (s, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 196.2, 144.4, 138.7, 137.3, 134.9, 133.6, 131.5, 130.8, 129.4, 129.3, 128.5, 128.0, 127.9, 125.9, 125.6, 20.5.

## (E)-3-(2-bromophenyl)-1-(2,6-dimethylphenyl)prop-2-en-1-one 3b:




Chemical Formula: $C_{17}H_{15}BrO$
Exact Mass: 314.0306

Following the general procedure for aldolisation reaction, 2-bromobenzaldehyde (1.11 g, 6 mmol, 1 equiv), 1-(2,6-dimethylphenyl)ethan-1-one (889 mg, 6 mmol, 1 equiv), and NaOH (240 mg, 6 mmol, 1 equiv) were reacted in EtOH/water at 45 °C. After completion, the crude was extracted and purified by chromatography on silica gel to afford **3b** as a colorless oil (1.89 g, 6 mmol, 99%).

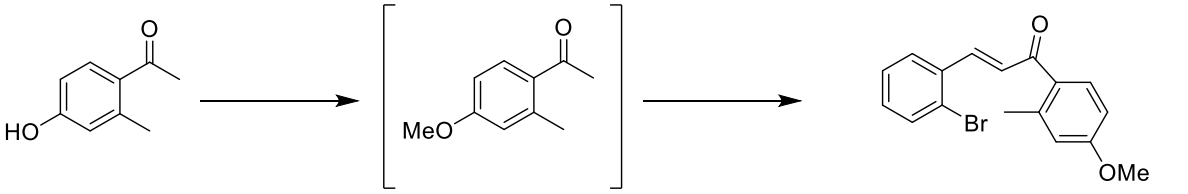
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.68 – 7.64 (m, 1H), 7.62 – 7.58 (m, 1H), 7.58 – 7.56 (m, 1H), 7.37 – 7.32 (m, 1H), 7.25 – 7.19 (m, 2H), 7.10 – 7.06 (m, 2H), 6.83 (d, J = 16.2 Hz, 1H), 2.25 (s, 6H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 201.2, 145.9, 139.6, 134.7, 134.2, 133.5, 131.8, 130.7, 129.0, 128.1, 128.0, 127.8, 125.8, 19.6, 19.6.

**HRMS** (ESI): Calculated for $C_{17}H_{16}BrO$ ($[M+H]^+$): 315.0385; found: 315.0379

**IR** (neat) : ν = 1650, 1462 $cm^{-1}$

## (E)-3-(2-bromophenyl)-1-(4-methoxy-2-methylphenyl)prop-2-en-1-one 3c:




Chemical Formula: $C_{17}H_{15}BrO_2$
Exact Mass: 330.0255

A solution of 1-(4-hydroxy-2-methylphenyl)ethan-1-one (1.0 g, 6.66 mmol, 1 equiv), $K_2CO_3$ (1.2 g, 8.66 mmol, 1.3 equiv) and iodomethane (0.62 ml, 10 mmol, 1.5 equiv) in acetone (25 ml) was heated to 70 °C for 6 h. After cooling to room temperature, the crude was evaporated under vacuum, dissolved in DCM (30 mL) and washed with water (3 x 10 mL). The organic phase was dried over sodium sulfate, filtered and evaporated under vacuum. The desired product was used without further purification (6.65 mmol, 1.09 g, 99%).

Following the general procedure for aldolisation reaction, 2-bromobenzaldehyde (555 mg, 3 mmol, 1 equiv), 1-(4-methoxy-2-methylphenyl)ethan-1-one (493 mg, 3 mmol, 1 equiv), and NaOH (120 mg, 3 mmol, 1 equiv) were reacted in EtOH/water at 45 °C. After completion, the crude was extracted and purified by chromatography on silica gel to afford **3c** as a yellowish oil (992 mg, 3 mmol, 99%).

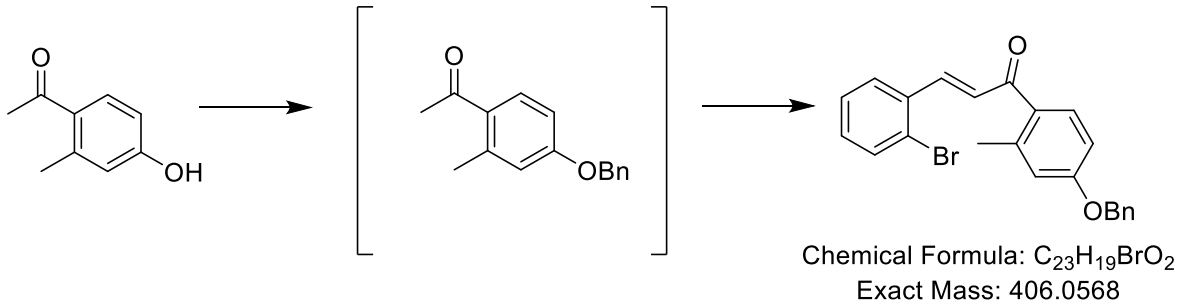
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.89 (d, J = 15.9 Hz, 1H), 7.70 – 7.60 (m, 3H), 7.37 – 7.32 (m, 1H), 7.26 – 7.20 (m, 1H), 7.14 (d, J = 15.9 Hz, 1H), 6.82 – 6.73 (m, 2H), 3.86 (s, 3H), 2.54 (s, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 193.8, 161.8, 143.0, 141.4, 135.3, 133.6, 131.6, 131.3, 131.1, 129.1, 128.0, 127.8, 125.8, 117.3, 110.7, 55.5, 21.5.

**HRMS** (ESI): Calculated for $C_{17}H_{16}BrO_2$ ($[M+H]^+$): 331.0334; found: 331.0330

**IR** (neat) : ν = 1652, 1465 $cm^{-1}$

## (E)-1-(4-(benzyloxy)-2-methylphenyl)-3-(2-bromophenyl)prop-2-en-1-one 3d:




Chemical Formula: $C_{23}H_{19}BrO_2$
Exact Mass: 406.0568

1-(4-hydroxy-2-methylphenyl)ethan-1-one (1.0 g, 6.66 mmol, 1 equiv) and $K_2CO_3$ (1.2 g, 8.66 mmol, 1.3 equiv) were stirred in DMF (25 mL). Benzyl bromide (0.96 mL, 8 mmol, 1.2 equiv) was added and the mixture was stirred at 70°C for 6 h . After cooling to room temperature, the crude was quenched with water (25 mL) and extracted with Et2O (3 x 30 mL). The combined organic layers were then washed with LiCl (10 %, 50 mL), dried over sodium sulfate, filtered and evaporated under vacuum. The crude was used in the next step without further purification (1.6 g, 6.66 mmol, 100%).

Following the general procedure for aldolisation reaction, 2-bromobenzaldehyde (1.23 g, 6.66 mmol, 1 equiv), 1-(4-benzyl-2-methylphenyl)ethan-1-one (1.6 g, 6.66 mmol, 1 equiv), and NaOH (270 mg, 6.66 mmol, 1 equiv) were reacted in EtOH/water at 45 °C. After completion, the crude was extracted and purified by chromatography on silica gel to afford **3d** as a yellowish oil (2.7 g, 6.65 mmol, 99%).

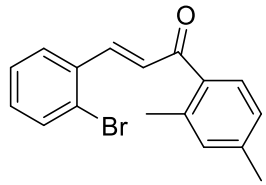
**$^{1}$H NMR (400 MHz, Chloroform-*d*) δ** = 7.90 (d, J = 15.9 Hz, 1H), 7.70 – 7.61 (m, 3H), 7.46 – 7.38 (m, 4H), 7.37 – 7.31 (m, 2H), 7.25 – 7.21 (m, 1H), 7.14 (d, J = 15.9 Hz, 1H), 6.91 – 6.84 (m, 2H), 5.13 (s, 2H), 2.53 (s, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 193.8, 160.9, 143.0, 141.4, 136.6, 135.2, 133.6, 131.6, 131.3, 131.3, 129.1, 128.8, 128.3, 128.0, 127.9, 127.6, 125.9, 118.2, 111.5, 70.1, 21.5.

**HRMS** (ESI): Calculated for $C_{23}H_{20}BrO_2$ ($[M+H]^+$): 407.0647; found: 407.0641

**IR** (neat) : ν = 1620, 1455 $cm^{-1}$

## (E)-3-(2-bromophenyl)-1-(2,4-dimethylphenyl)prop-2-en-1-one 3e:




Chemical Formula: $C_{17}H_{15}BrO$
Exact Mass: 314.0306

Following the general procedure for aldolisation reaction, 2-bromobenzaldehyde (555 g, 3 mmol, 1 equiv), 1-(2,4-dimethylphenyl)ethan-1-one (445 mg, 3 mmol, 1 equiv), and NaOH (120 mg, 3 mmol, 1 equiv) were reacted in EtOH/water at 45 °C. After completion, the crude was extracted and purified by chromatography on silica gel to afford **3e** as a yellowish oil (941 mg, 2.99 mmol, 99%).

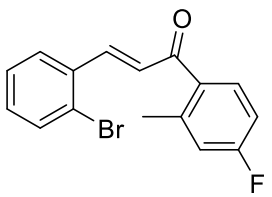
**$^{1}$H NMR (500 MHz, Chloroform-*d*) δ** = 7.86 (d, J = 16.0 Hz, 1H), 7.69 – 7.66 (m, 1H), 7.63 – 7.60 (m, 1H), 7.50 – 7.47 (m, 1H), 7.36 – 7.32 (m, 1H), 7.25 – 7.21 (m, 1H), 7.11 – 7.05 (m, 3H), 2.47 (s, 3H), 2.38 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$) δ =** 195.5, 143.7, 141.4, 138.0, 135.8, 135.1, 133.6, 132.5, 131.4, 129.4, 129.1, 128.0, 127.9, 126.3, 125.9, 21.6, 20.7.

**HRMS** (ESI): Calculated for $C_{17}H_{16}BrO$ ($[M+H]^+$): 315.0385; found: 315.0378

**IR** (neat) : ν = 1650, 1464 $cm^{-1}$

## (E)-3-(2-bromophenyl)-1-(4-fluoro-2-methylphenyl)prop-2-en-1-one 3f:




Chemical Formula: $C_{16}H_{12}BrFO$
Exact Mass: 318.0056

Following the general procedure for aldolisation reaction, 2-bromobenzaldehyde (555 mg, 3 mmol, 1 equiv), 1-(4-fluoro-2-methylphenyl)ethan-1-one (457 mg, 3 mmol, 1 equiv), and NaOH (120 mg, 3 mmol, 1 equiv) were reacted in EtOH/water at 45 °C. After completion, the crude was extracted and purified by chromatography on silica gel to afford **3f** as a colorless oil (812 mg, 2.54 mmol, 85%).

**$^{1}$H NMR (500 MHz, Chloroform-*d*) δ =** 7.84 (d, J = 16.0 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.64 – 7.60 (m, 1H), 7.59 – 7.55 (m, 1H), 7.37 – 7.33 (m, 1H), 7.27 – 7.23 (m, 1H), 7.05 (d, J = 16.0 Hz, 1H), 7.01 – 6.95 (m, 2H), 2.49 (s, 3H).

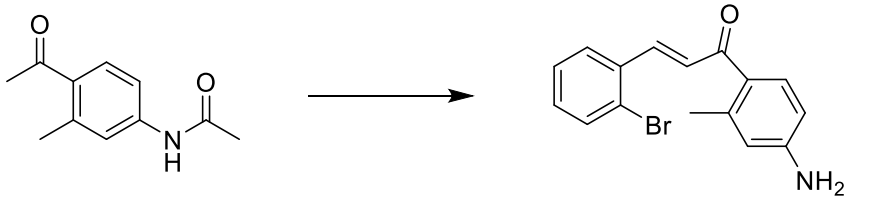
**$^{13}$C NMR (126 MHz, $CDCl_3$) δ** = 194.8, 163.9 (d, J = 251.8 Hz), 144.4, 141.2 (d, J = 8.5 Hz), 134.8, 133.7, 131.6, 131.0 (d, J = 8.9 Hz), 129.1, 128.0 (d, J = 6.1 Hz), 126.0, 118.4 (d, J = 22.4 Hz), 112.6 (d, J = 21.6 Hz), 20.8 (d, J = 1.3 Hz).

**$^{19}$F NMR (376 MHz, $CDCl_3$) δ** = -109.1.

**HRMS** (ESI): Calculated for $C_{16}H_{12}BrNaFO$ ($[M+Na]^+$): 340.9953; found: 340.9948

**IR** (neat) : ν = 1625, 1456 $cm^{-1}$

## (E)-1-(4-amino-2-methylphenyl)-3-(2-bromophenyl)prop-2-en-1-one 3g:




Chemical Formula: $C_{16}H_{14}BrNO$
Exact Mass: 315.0259

Following the general procedure for aldolisation reaction, 2-bromobenzaldehyde (555 mg, 3 mmol, 1 equiv), *N*-(4-acetyl-3-methylphenyl)acetamide (574 mg, 3 mmol, 1 equiv), and NaOH (120 mg, 3 mmol, 1 equiv) were reacted in EtOH/water at 45 °C. After completion, the crude was extracted and purified by chromatography on silica gel to afford **3g** as a yellowish oil (178 mg, 0.56 mmol, 19%).

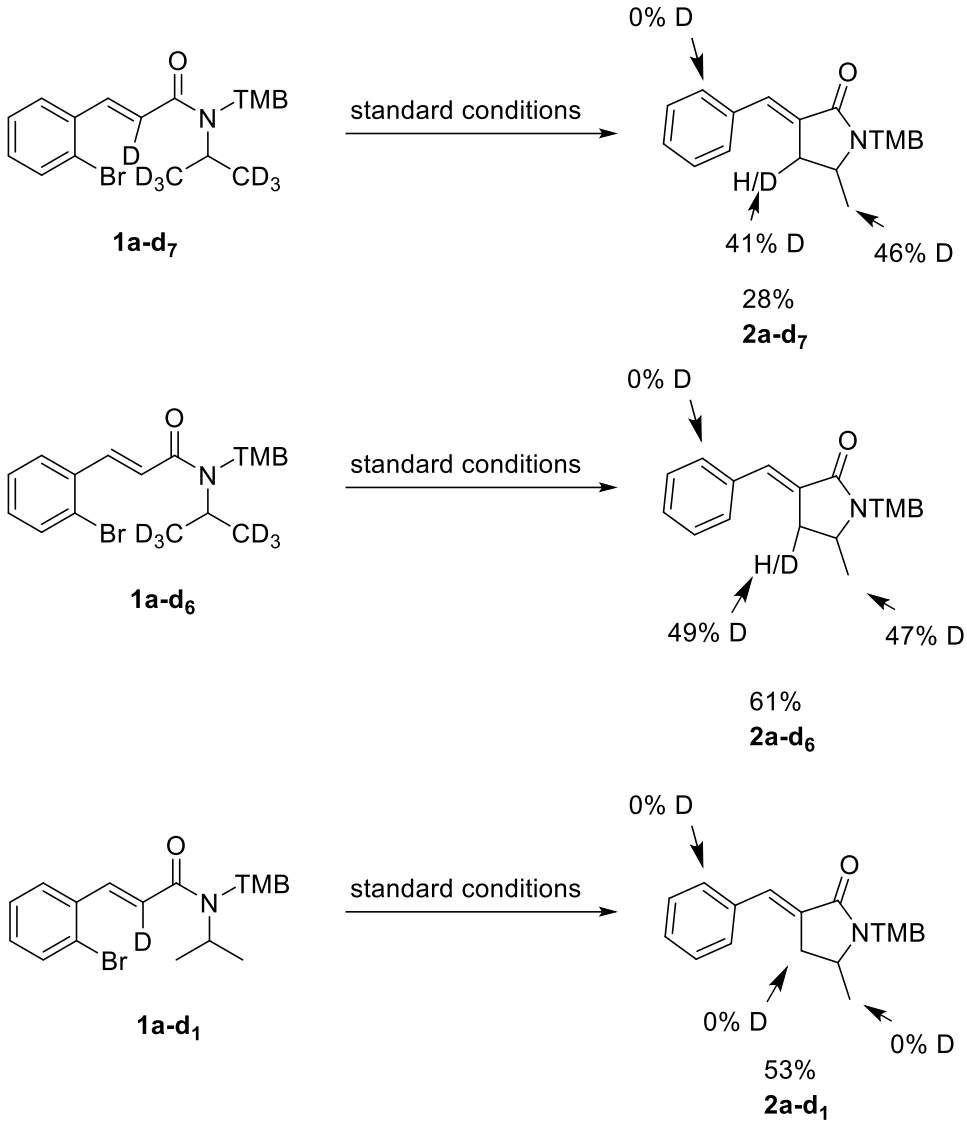
**$^{1}$H NMR (400 MHz, Chloroform-*d*) δ** = 7.91 (d, J = 15.7 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.65 – 7.59 (m, 2H), 7.36 – 7.28 (m, 1H), 7.24 – 7.18 (m, 2H), 6.55 – 6.45 (m, 2H), 4.01 (br. s, 2H), 2.52 (s, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 192.4, 149.7, 142.2, 141.8, 135.6, 133.6, 132.5, 131.0, 129.0, 128.3, 127.9, 127.8, 125.7, 117.8, 111.2, 22.0.

**HRMS** (ESI): Calculated for $C_{16}H_{15}BrNO$ ($[M+H]^+$): 316.0337; found: 316.0334

**IR** (neat) : ν = 1652, 1449 $cm^{-1}$

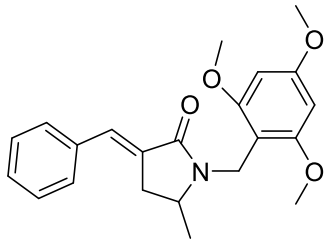
## 6- Scheme S1: Experiments with deuterated substrates:




The deuteration experiments were run in standard conditions. Starting from **1a-d$_7$**, no deuterium incorporation was observed on the aromatic ring. Proton incorporation on the γ-lactam brings evidence for the reversibility of the C($sp^3$)-H activation step, This H/D exchange can be assigned to an external proton source (presumably from mesitylene or traces of water) exchanging with the deuterium atom on the Pd-bound pivalate, consistent with previous observations.[3] Similar H/D exchanges were observed from partially deuterated substrates **1a-d$_6$** and **1a-d$_1$** .

## 7- 1,4-Pd shift/C($sp^3$)-H activation products:

### (E)-3-benzylidene-5-methyl-1-(2,4,6-trimethoxybenzyl)pyrrolidin-2-one 2a:



Chemical Formula: $C_{22}H_{25}NO_4$
Exact Mass: 367.1784

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1a** (45 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2a** was obtained as a yellowish oil (36.5 mg, 0.099 mmol, 100%).

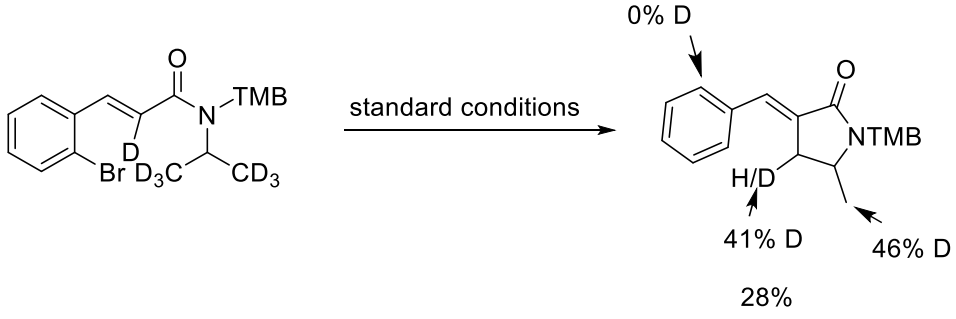
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.49 – 7.42 (m, 2H), 7.42 – 7.33 (m, 3H), 7.33 – 7.23 (m, 1H), 6.12 (s, 2H), 5.12 (d, J = 14.1, 1H), 4.28 (d, J = 14.2, 1H), 3.81 (s, 3H), 3.79 (s, 6H), 3.48 – 3.39 (m, 1H), 3.08 (dd, J = 17.0 Hz, 7.6 Hz, 1H), 2.58 – 2.47 (m, 1H), 1.20 (d, J = 6.3, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 168.1, 161.1, 160.1, 136.5, 132.1, 129.5, 129.4, 128.7, 128.1, 104.7, 90.5, 55.9, 55.4, 50.2, 33.7, 33.3, 20.9.

**HRMS** (ESI): Calculated for $C_{22}H_{25}NaNO_4$ ($[M+Na]^+$): 390.1681; found: 390.1676

**IR** (neat) : ν = 2362, 1682, 1607, 1417 $cm^{-1}$

### (E)-3-benzylidene-5-methyl-1-(2,4,6-trimethoxybenzyl)pyrrolidin-2-one 2a-d:

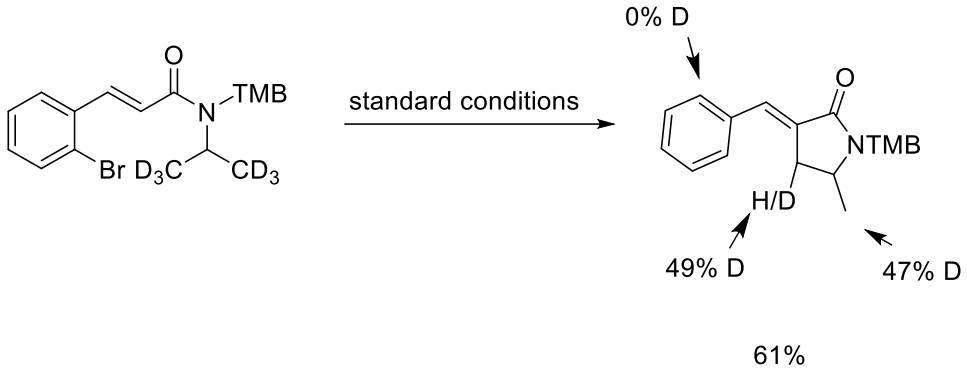



**$^1$H NMR (400 MHz, Chloroform-*d*) δ** = 7.47 – 7.43 (m, 2H), 7.40 – 7.35 (m, 3H), 7.31 – 7.28 (m, 1H), 6.12 (s, 2H), 5.12 (d, J = 14.2 Hz, 1H), 4.28 (d, J = 14.1 Hz, 1H), 3.82 (s, 3H), 3.79

(s, 6H), 3.46 – 3.41 (m, 1H), 3.12 – 3.02 (m, 0.59H), 2.57 – 2.50 (m, 0.58H), 1.22 – 1.15 (m, 1.63H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 168.2, 161.2, 160.2, 136.5, 129.5, 128.7, 128.1, 104.7, 90.5, 55.9, 55.5, 33.3, 26.5.

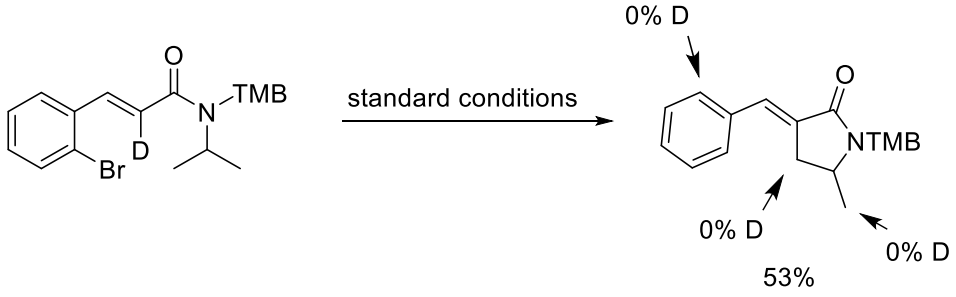
## (E)-3-benzylidene-5-methyl-1-(2,4,6-trimethoxybenzyl)pyrrolidin-2-one 2a-d:




**$^{1}$H NMR (400 MHz, Chloroform-*d*) δ** = 7.47 – 7.43 (m, 2H), 7.40 – 7.35 (m, 3H), 7.31 – 7.26 (m, 1H), 6.12 (s, 2H), 5.12 (d, J = 14.1 Hz, 1H), 4.30 – 4.25 (m, 1H), 3.82 (s, 3H), 3.79 (s, 6H), 3.47 – 3.41 (m, 1H), 3.11 – 3.03 (m, 0.51H), 2.57 – 2.49 (m, 0.50H), 1.22 – 1.18 (m, 1.59H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 168.2, 161.2, 160.2, 136.5, 129.5, 128.7, 128.1, 104.7, 90.5, 55.9, 55.5, 33.3, 26.5.

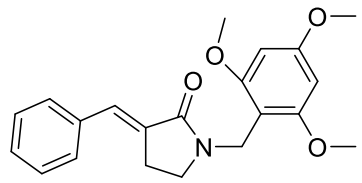
## (E)-3-benzylidene-5-methyl-1-(2,4,6-trimethoxybenzyl)pyrrolidin-2-one 2a-d:




**$^{1}$H NMR (400 MHz, Chloroform-*d*) δ =** 7.47 – 7.44 (m, 2H), 7.40 – 7.35 (m, 3H), 7.31 – 7.28 (m, 1H), 6.12 (s, 2H), 5.12 (d, J = 14.1 Hz, 1H), 4.28 (d, J = 14.2 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 6H), 3.50 – 3.40 (m, 1H), 3.08 (ddd, J = 17.4, 8.1, 3.0 Hz, 1H), 2.57 – 2.51 (m, 1H), 1.21 (d, J = 6.2 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 168.2, 161.2, 160.2, 136.5, 132.1, 129.6, 129.4, 128.7, 128.1, 104.7, 90.5, 55.9, 55.5, 50.2, 33.7, 33.3, 21.0.

## (E)-3-benzylidene-1-(2,4,6-trimethoxybenzyl)pyrrolidin-2-one 2b:



Chemical Formula: $C_{21}H_{23}NO_4$
Exact Mass: 353.1627

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1b** (43.4 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%), $PCy_3$ (2.8 mg, 0.01 mmol, 10 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2b** was obtained as a yellow oil (16 mg, 0.045 mmol, 45%).

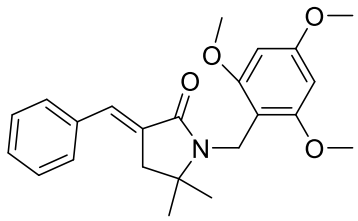
**$^1$H NMR (500 MHz, Chloroform-*d*) δ =** 7.47 – 7.44 (m, 2H), 7.39 – 7.34 (m, 3H), 7.30 – 7.28 (m, 1H), 6.13 (s, 2H), 4.66 (s, 2H), 3.82 (s, 3H), 3.81 (s, 6H), 3.26 (dd, J = 7.1, 5.9 Hz, 2H), 2.92 (ddd, J = 8.9, 5.9, 2.9 Hz, 2H).

**$^{13}$C NMR (126 MHz, $CDCl_3$) δ =** 168.4, 161.2, 160.0, 136.3, 132.2, 129.4, 129.0, 128.6, 128.0, 104.4, 90.3, 55.8, 55.3, 43.5, 35.3, 24.3.

**HRMS** (ESI): Calculated for $C_{21}H_{23}NaNO_4$ ($[M+Na]^+$): 376.1525; found: 376.1519

**IR** (neat) : ν = 2362, 1604 $cm^{-1}$

## (E)-3-benzylidene-5,5-dimethyl-1-(2,4,6-trimethoxybenzyl)pyrrolidin-2-one 2c:



Chemical Formula: $C_{23}H_{27}NO_4$
Exact Mass: 381.1940

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1c** (46.2 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2c** was obtained as a colorless oil (19.5 mg, 0.051 mmol, 51%).

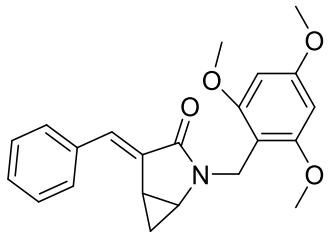
**$^1$H NMR (500 MHz, Chloroform-*d*) δ =** 7.47 – 7.43 (m, 2H), 7.42 – 7.36 (m, 3H), 7.31 – 7.27 (m, 1H), 6.10 (s, 2H), 4.71 (s, 2H), 3.81 (s, 9H), 2.80 (s, 2H), 1.13 (s, 6H).

**$^{13}$C NMR (126 MHz, $CDCl_3$) δ =** 168.3, 161.0, 159.8, 136.6, 131.7, 129.6, 129.4, 128.7, 128.1, 107.0, 90.5, 59.3, 55.9, 55.4, 42.5, 32.3, 27.7.

**HRMS** (ESI): Calculated for $C_{23}H_{28}NO_4$ ($[M+H]^+$): 382.2018; found: 382.2013

**IR** (neat) : ν = 2363, 912 $cm^{-1}$

## (E)-4-benzylidene-2-(2,4,6-trimethoxybenzyl)-2-azabicyclo[3.1.0]hexan-3-one 2d:



Chemical Formula: $C_{22}H_{23}NO_4$
Exact Mass: 365.1627

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1d** (44.6 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%)

and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2d** was obtained as a colorless oil (25.5 mg, 0.070 mmol, 70%).

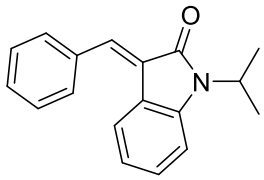
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.55 – 7.52 (m, 2H), 7.32 – 7.25 (m, 3H), 7.23 – 7.18 (m, 1H), 6.04 (s, 2H), 4.54 (d, *J* = 1.9 Hz, 2H), 3.73 (s, 3H), 3.72 (s, 6H), 3.01 – 2.92 (m, 1H), 2.22 – 2.14 (m, 1H), 0.93 (dt, *J* = 8.5, 5.1 Hz, 1H), 0.49 – 0.44 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 168.0, 161.3, 160.1, 136.2, 134.6, 130.0, 129.6, 129.4, 128.7, 128.5, 128.3, 104.9, 90.4, 55.9, 55.5, 35.2, 35.2, 20.4, 13.1.

**HRMS** (ESI): Calculated for $C_{22}H_{23}NaNO_4$ ($[M+Na]^+$): 388.1525; found: 388.1519

**IR** (neat) : ν = 1681, 1612, 1419 $cm^{-1}$

## (E)-3-benzylidene-1-isopropylindolin-2-one 2e:




Chemical Formula: $C_{18}H_{17}NO$
Exact Mass: 263.1310

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1e** (34.4 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2e** was obtained as a yellow oil (12.5 mg, 0.048 mmol, 48%).

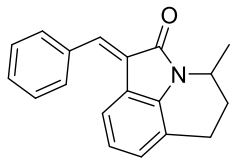
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.83 (s, 1H), 7.65 – 7.60 (m, 3H), 7.49 – 7.41 (m, 3H), 7.25 – 7.19 (m, 1H), 7.02 – 6.97 (m, 1H), 6.87 – 6.81 (m, 1H), 4.72 (sept, J = 7.0 Hz, 1H), 1.53 (d, J = 7.0 Hz, 6H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 168.0, 142.9, 136.9, 135.1, 129.5, 129.4, 129.2, 128.6, 127.5, 122.9, 121.7, 121.2, 109.8, 43.8, 19.5.

**HRMS** (ESI): Calculated for $C_{18}H_{17}NaNO$ ($[M+Na]^+$): 286.1208; found: 286.1202

**IR** (neat) : ν = 2361, 1701, 1463 $cm^{-1}$

## (E)-1-benzylidene-4-methyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one 2f:



Chemical Formula: $C_{19}H_{17}NO$
Exact Mass: 275.1310

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1f** (36 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2f** was obtained as a yellow oil (24 mg, 0.088 mmol, 88%).

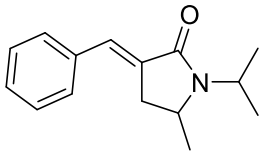
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.82 (s, 1H), 7.68 – 7.64 (m, 2H), 7.49 – 7.38 (m, 4H), 7.05 – 6.99 (m, 1H), 6.82 – 6.76 (m, 1H), 4.56 – 4.47 (m, 1H), 2.91 – 2.80 (m, 1H), 2.71 (dt, J = 16.6, 3.8 Hz, 1H), 1.98 – 1.92 (m, 3H), 1.34 (d, J = 6.7 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 167.3, 139.9, 137.0, 135.3, 129.6, 129.5, 128.7, 128.7, 128.5, 121.2, 120.8, 120.0, 119.9, 44.2, 27.0, 20.8, 18.5.

**HRMS** (ESI): Calculated for $C_{19}H_{17}NaNO$ ($[M+Na]^+$): 298.1208; found: 298.1202

**IR** (neat) : ν = 2363, 1701, 1460 $cm^{-1}$

## (E)-3-benzylidene-1-isopropyl-5-methylpyrrolidin-2-one 2g:



Chemical Formula: $C_{15}H_{19}NO$
Exact Mass: 229.1467

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1g** (31 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2g** was obtained as a colorless oil (21 mg, 0.097 mmol, 97%).

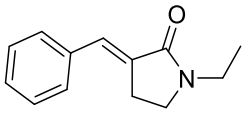
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.47 – 7.43 (m, 2H), 7.41 – 7.36 (m, 2H), 7.34 – 7.29 (m, 1H), 4.23 (sept, J = 7.0 Hz, 1H), 3.95 – 3.86 (m, 1H), 3.23 (ddd, J = 17.4, 8.1, 3.1 Hz, 1H), 2.62 – 2.59 (m, 1H), 1.35 (t, J = 8.1 Hz, 6H), 1.31 (d, J = 6.4 Hz, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$) δ =** 168.8, 136.2, 131.6, 129.6, 129.6, 128.7, 128.3, 50.9, 45.2, 34.4, 23.8, 21.8, 19.6.

**HRMS** (ESI): Calculated for $C_{15}H_{19}NaNO$ ($[M+Na]^+$): 252.1364; found:252.1360

**IR** (neat) : ν = 2363, 1682, 1423 $cm^{-1}$

## (E)-3-benzylidene-1-ethylpyrrolidin-2-one 2h:




Chemical Formula: $C_{13}H_{15}NO$
Exact Mass: 201.1154

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1h** (28.2 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2h** was obtained as a yellow oil (6.3 mg, 0.031 mmol, 31%).

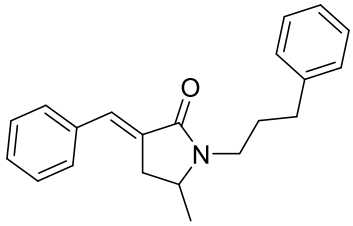
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.50 – 7.46 (m, 2H), 7.43 – 7.38 (m, 2H), 7.36 – 7.28 (m, 2H), 3.55 – 3.47 (m, 4H), 3.10 – 3.02 (m, 2H), 1.20 (t, *J* = 7.3 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 168.9, 136.1, 131.5, 129.8, 129.6, 128.8, 128.4, 44.1, 37.9, 24.5, 12.7.

**HRMS** (ESI): Calculated for $C_{13}H_{15}NaNO$ ($[M+Na]^+$): 224.1051; found: 224.1046

**IR** (neat) : ν = 2364, 1679, 1608, 1419 $cm^{-1}$

## (E)-3-benzylidene-5-methyl-1-(3-phenylpropyl)pyrrolidin-2-one 2i:




Chemical Formula: $C_{21}H_{23}NO$
Exact Mass: 305.1780

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1i** (39 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), $PCy_3$ (2.8 mg, 0.01 mmol, 10 %), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2i** was obtained as a yellowish oil (25 mg, 0.082 mmol, 82%).

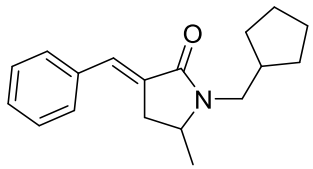
**$^1$H NMR (400 MHz, Chloroform-*d*) δ** = 7.48 – 7.44 (m, 2H), 7.42 – 7.34 (m, 3H), 7.34 – 7.28 (m, 3H), 7.23 – 7.15 (m, 3H), 3.86 – 3.74 (m, 2H), 3.26 – 3.11 (m, 2H), 2.67 (t, J = 7.8 Hz, 2H), 2.61 – 2.57 (m, 1H), 2.02 – 1.81 (m, 2H), 1.24 (d, J = 6.3 Hz, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$) δ =** 169.1, 141.6, 136.1, 131.0, 130.0, 129.6, 128.8, 128.6, 128.5, 128.4, 126.1, 51.1, 40.6, 33.8, 33.5, 29.2, 20.9.

**HRMS** (ESI): Calculated for $C_{21}H_{24}NO$ ($[M+H]^+$): 306.1858; found: 306.1852

**IR** (neat) : ν = 1679, 1423 $cm^{-1}$

## (E)-3-benzylidene-1-(cyclopentylmethyl)-5-methylpyrrolidin-2-one 2j:




Chemical Formula: $C_{18}H_{23}NO$
Exact Mass: 269.1780

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1j** (35 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), $PCy_3$ (2.8 mg, 0.01 mmol, 10 %), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2j** was obtained as a colorless oil (18 mg, 0.067 mmol, 67%).

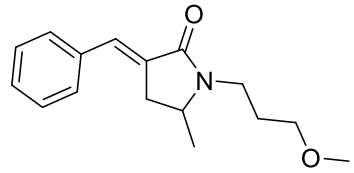
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.48 – 7.44 (m, 2H), 7.42 – 7.34 (m, 3H), 7.33 – 7.28 (m, 1H), 3.90 – 3.81 (m, 1H), 3.76 (dd, *J* = 13.7, 9.5 Hz, 1H), 3.26 (ddd, *J* = 17.4, 7.8, 2.8 Hz, 1H), 3.02 (dd, *J* = 13.7, 6.2 Hz, 1H), 2.63 – 2.60 (m, 1H), 2.29 – 2.18 (m, 1H), 1.83 – 1.73 (m, 1H), 1.71 – 1.62 (m, 3H), 1.57 – 1.50 (m, 2H), 1.32 – 1.24 (m, 5H).

**$^{13}$C NMR (126 MHz, $CDCl_3$) δ =** 169.2, 136.2, 131.2, 129.9, 129.6, 128.8, 128.4, 51.1, 45.3, 38.1, 33.9, 31.0, 30.4, 25.4, 25.1, 20.8.

**HRMS** (ESI): Calculated for $C_{18}H_{24}NO$ ($[M+H]^+$): 270.1858; found: 270.1852

**IR** (neat) : ν = 1685, 1419 $cm^{-1}$

## (E)-3-benzylidene-1-(3-methoxypropyl)-5-methylpyrrolidin-2-one 2k:



Chemical Formula: $C_{15}H_{19}NO_2$
Exact Mass: 245.1416

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1k** (34 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2k** was obtained as a yellowish oil (15.5 mg, 0.060 mmol, 60%).

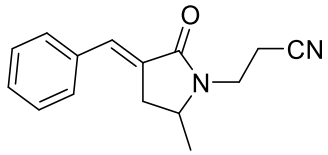
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.49 – 7.44 (m, 2H), 7.43 – 7.39 (m, 2H), 7.36 – 7.29 (m, 2H), 3.87 – 3.72 (m, 2H), 3.44 (t, J = 6.3 Hz, 2H), 3.34 (s, 3H), 3.31 – 3.20 (m, 2H), 2.64 – 2.59 (m, 1H), 1.99 – 1.77 (m, 2H), 1.29 (d, J = 6.3 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 169.1, 136.0, 130.9, 129.7, 129.5, 128.6, 128.3, 70.4, 58.7, 51.3, 38.2, 33.7, 27.8, 20.9.

**HRMS** (ESI): Calculated for $C_{15}H_{19}NaNO_2$ ($[M+Na]^+$): 282.1470; found: 282.1465

**IR** (neat) : ν = 1681, 1421, 1115 $cm^{-1}$

## (E)-3-(3-benzylidene-5-methyl-2-oxopyrrolidin-1-yl)propanenitrile 2l:



Chemical Formula: $C_{15}H_{16}N_2O$
Exact Mass: 240.1263

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1l** (32 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2l** was obtained as a colorless oil (12 mg, 0.051 mmol, 51%).

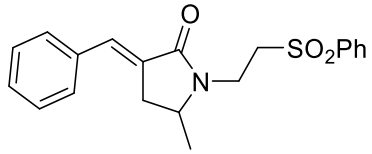
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.49 – 7.45 (m, 2H), 7.44 – 7.41 (m, 1H), 7.40 – 7.33 (m, 2H), 4.03 – 3.94 (m, 1H), 3.88 (dt, J = 13.9, 6.3 Hz, 1H), 3.54 – 3.45 (m, 1H), 3.34 (ddd, J = 17.5, 7.9, 2.8 Hz, 1H), 2.85 – 2.76 (m, 1H), 2.74 – 2.64 (m, 2H), 1.36 (d, J = 6.3 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 169.6, 135.5, 131.1, 129.6, 129.4, 128.7, 118.1, 52.0, 37.4, 33.8, 20.9, 16.6.

**HRMS** (ESI): Calculated for $C_{15}H_{16}NaN_2O$ ($[M+Na]^+$): 263.1160; found: 263.1155

**IR** (neat) : ν = 2362, 1682, 1615 $cm^{-1}$

## (E)-3-benzylidene-5-methyl-1-(2-(phenylsulfonyl)ethyl)pyrrolidin-2-one 2m:




Chemical Formula: $C_{20}H_{21}NO_3S$
Exact Mass: 355.1242

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1m** (43.6 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2m** was obtained as a colorless oil (14.5 mg, 0.040 mmol, 40%).

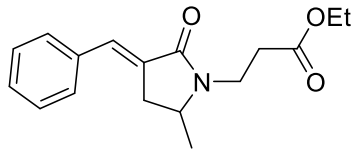
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.96 – 7.92 (m, 2H), 7.69 – 7.63 (m, 1H), 7.61 – 7.55 (m, 2H), 7.45 – 7.37 (m, 4H), 7.35 – 7.30 (m, 1H), 7.29 – 7.27 (m, 1H), 4.01 – 3.92 (m, 1H), 3.92 – 3.83 (m, 1H), 3.68 – 3.56 (m, 2H), 3.42 – 3.31 (m, 1H), 3.23 – 3.13 (m, 1H), 2.63 – 2.59 (m, 1H), 1.28 (d, J = 6.3 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 169.5, 139.2, 135.7, 134.1, 130.8, 129.8, 129.7, 129.6, 128.8, 128.8, 128.0, 53.3, 52.0, 35.5, 33.8, 21.0.

**HRMS** (ESI): Calculated for $C_{20}H_{21}NaNO_3S$ ($[M+Na]^+$): 378.1140; found: 378.1137

**IR** (neat) : ν = 1681, 1614, 1419 $cm^{-1}$

## ethyl (E)-3-(3-benzylidene-5-methyl-2-oxopyrrolidin-1-yl)propanoate 2n:



Chemical Formula: $C_{17}H_{21}NO_3$
Exact Mass: 287.1521

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1n** (37 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2n** was obtained as a yellowish oil (18 mg, 0.062 mmol, 62%).

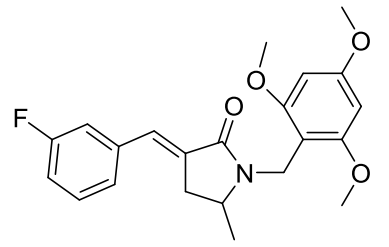
**$^1$H NMR (400 MHz, Chloroform-*d*) δ** = 7.48 – 7.44 (m, 2H), 7.42 – 7.37 (m, 2H), 7.37 – 7.29 (m, 2H), 4.15 (q, J = 7.2 Hz, 2H), 4.00 – 3.91 (m, 1H), 3.90 – 3.81 (m, 1H), 3.47 (dt, J = 14.3, 7.2 Hz, 1H), 3.26 (ddd, J = 17.4, 7.9, 2.9 Hz, 1H), 2.73 (dt, J = 16.2, 7.3 Hz, 1H), 2.66 – 2.54 (m, 2H), 1.30 (d, J = 6.3 Hz, 3H), 1.26 (t, J = 7.2 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ** = 171.8, 169.1, 135.8, 130.4, 130.1, 129.5, 128.7, 128.4, 60.8, 51.6, 36.8, 33.7, 32.8, 20.9, 14.2.

**HRMS** (ESI): Calculated for $C_{17}H_{21}NaNO_3$ ($[M+Na]^+$): 310.1419; found: 310.1414

**IR** (neat) : ν = 2361, 1978, 1732, 1419 $cm^{-1}$

## (E)-3-(3-fluorobenzylidene)-5-methyl-1-(2,4,6-trimethoxybenzyl)pyrrolidin-2-one 2o:



Chemical Formula: $C_{22}H_{24}FNO_4$
Exact Mass: 385.1689

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1o** (46.6 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2o** was obtained as a colorless oil (19.5 mg, 0.051 mmol, 51%).

**$^{1}$H NMR (400 MHz, Chloroform-*d*) δ =** 7.37 – 7.29 (m, 2H), 7.24 – 7.20 (m, 1H), 7.16 – 7.11 (m, 1H), 7.01 – 6.95 (m, 1H), 6.12 (s, 2H), 5.11 (d, J = 14.2, 1H), 4.28 (d, J = 14.2 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 6H), 3.49 – 3.42 (m, 1H), 3.10 – 3.00 (m, 1H), 2.54 – 2.48 (m, 1H), 1.21 (d, J = 6.2 Hz, 3H).

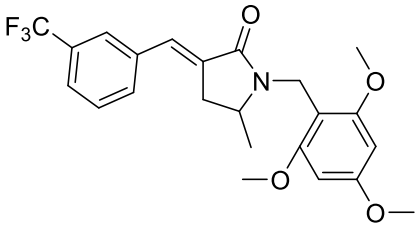
**$^{13}$C NMR (101 MHz, Chloroform-*d*) δ** = 167.7, 162.9 (d, J = 245.5 Hz), 161.2, 160.1, 138.6 (d, J = 7.7 Hz), 133.5, 130.1 (d, J = 8.4 Hz), 128.2 (d, J = 2.6 Hz), 125.5 (d, J = 2.9 Hz), 115.7 (d, J = 21.7 Hz), 115.0 (d, J = 21.4 Hz), 104.5, 90.4, 55.9, 55.4, 50.2, 33.6, 33.3, 20.9.

**$^{19}$F NMR (376 MHz, $CDCl_3$) δ =** -113.01.

**HRMS** (ESI): Calculated for $C_{22}H_{24}FNaNO_4$ ($[M+Na]^+$): 408.1587; found: 408.1582

**IR** (neat) : ν = 1679, 1608, 1419 $cm^{-1}$

## (E)-5-methyl-3-(4-(trifluoromethyl)benzylidene)-1-(2,4,6-trimethoxybenzyl)pyrrolidin-2-one 2p:




Chemical Formula: $C_{23}H_{24}F_3NO_4$
Exact Mass: 435.1657

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1p** (51.6 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2p** was obtained as a colorless oil (33.5 mg, 0.077 mmol, 77%).

**$^{1}$H NMR (400 MHz, Chloroform-*d*) δ** = 7.68 (m, 1H), 7.62 – 7.60 (m, 1H), 7.56 – 7.46 (m, 2H), 7.40 – 7.38 (m, 1H), 6.12 (s, 2H), 5.12 (d, J = 14.2 Hz, 1H), 4.29 (d, J = 14.1 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 6H), 3.53 – 3.44 (m, 1H), 3.09 (ddd, J = 17.4, 8.1, 3.1 Hz, 1H), 2.56 – 2.48 (m, 1H), 1.23 (d, J = 6.3 Hz, 3H).

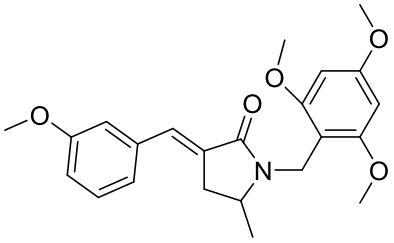
**$^{13}$C NMR (126 MHz, $CDCl_3$) δ =** 167.6, 161.2, 160.1, 137.2, 134.2, 132.7, 131.3, 131.0, 129.2, 127.8, 125.6 (q, J = 3.9 Hz), 124.6 (q, J = 3.1 Hz), 124.3 (q, J = 271.3 Hz), 104.5, 90.5, 55.9, 55.5, 50.2, 33.6, 33.4, 20.9.

**$^{19}$F NMR (471 MHz, $CDCl_3$) δ** = -62.8.

**HRMS** (ESI): Calculated for $C_{23}H_{25}F_3NO_4$ ($[M+H]^+$): 436.1736; found: 436.1730

**IR** (neat) : ν = 1681, 1609, 1329, 1132 $cm^{-1}$

## (E)-3-(3-methoxybenzylidene)-5-methyl-1-(2,4,6-trimethoxybenzyl)pyrrolidin-2-one 2q:



Chemical Formula: $C_{23}H_{27}NO_5$
Exact Mass: 397.1889

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1q** (47.8 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2q** was obtained as a yellowish oil (40 mg, 0.039 mmol, 100%).

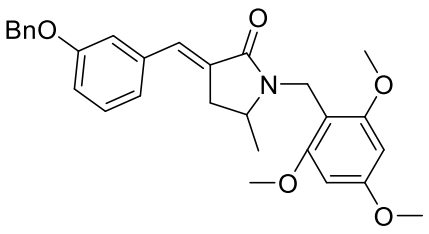
**$^1$H NMR (400 MHz, Chloroform-*d*) δ** = 7.35 – 7.33 (m, 1H), 7.29 (t, J = 7.9 Hz, 1H), 7.07 – 7.03 (m, 1H), 7.00 – 6.96 (m, 1H), 6.87 – 6.81 (m, 1H), 6.11 (s, 2H), 5.11 (d, J = 14.1 Hz, 1H), 4.27 (d, J = 14.1 Hz, 1H), 3.81 (s, 6H), 3.78 (s, 6H), 3.49 – 3.38 (m, 1H), 3.07 (ddd, J = 17.4, 8.2, 3.0 Hz, 1H), 2.56 – 2.47 (m, 1H), 1.20 (d, J = 6.2 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 168.0, 161.1, 160.1, 159.7, 137.8, 132.4, 129.6, 129.3, 122.1, 115.0, 113.6, 104.6, 90.4, 55.9, 55.4, 55.4, 55.4, 50.2, 33.6, 33.3, 20.9.

**HRMS** (ESI): Calculated for $C_{23}H_{27}NaNO_5$ ($[M+Na]^+$): 420.1787; found: 420.1781

**IR** (neat) : ν = 1690, 1423 $cm^{-1}$

## (E)-3-(3-(benzyloxy)benzylidene)-5-methyl-1-(2,4,6-trimethoxybenzyl)pyrrolidin-2-one 2r:



Chemical Formula: $C_{29}H_{31}NO_5$
Exact Mass: 473.2202

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1r** (55 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2r** was obtained as a yellowish oil (34.5 mg, 0.073 mmol, 73%).

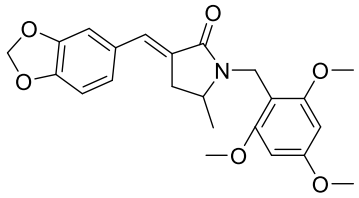
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.45 – 7.41 (m, 2H), 7.39 – 7.36 (m, 2H), 7.35 – 7.26 (m, 3H), 7.08 – 7.03 (m, 2H), 6.95 – 6.90 (m, 1H), 6.12 (s, 2H), 5.13 – 5.06 (m, 3H), 4.27 (d, J = 14.1 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 6H), 3.46 – 3.37 (m, 1H), 3.00 (ddd, J = 17.4, 8.1, 3.0 Hz, 1H), 2.51 – 2.40 (m, 1H), 1.18 (d, J = 6.8 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 167.9, 161.0, 160.0, 158.8, 137.7, 136.9, 132.4, 129.5, 129.1, 128.6, 128.0, 127.4, 122.4, 115.7, 114.6, 104.6, 90.3, 70.1, 55.8, 55.7, 50.1, 33.5, 33.2, 20.8.

**HRMS** (ESI): Calculated for $C_{23}H_{29}BrNaNO_4$ ($[M+Na]^+$): 496.2100; found: 496.2094

**IR** (neat) : ν = 1681, 1596, 1416 $cm^{-1}$

## (E)-3-(benzo[d][1,3]dioxol-5-ylmethylene)-5-methyl-1-(2,4,6-trimethoxybenzyl)pyrrolidin-2-one 2s:



Chemical Formula: $C_{23}H_{25}NO_6$
Exact Mass: 411.1682

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1s** (49 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2s** was obtained as a yellowish solid (29 mg, 0.071 mmol, 71%).

**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.29 – 7.27 (m, 1H), 6.98 – 6.93 (m, 2H), 6.84 – 6.80 (m, 1H), 6.11 (s, 2H), 5.97 (s, 2H), 5.10 (d, J = 14.2 Hz, 1H), 4.26 (d, J = 14.1 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 6H), 3.48 – 3.38 (m, 1H), 3.02 (ddd, J = 17.2, 8.2, 3.0 Hz, 1H), 2.52 – 2.42 (m, 1H), 1.20 (d, J = 6.2 Hz, 3H).

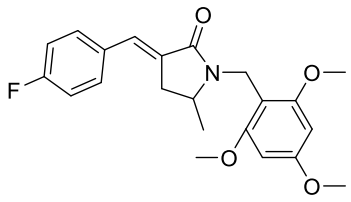
**$^{13}$C NMR (126 MHz, $CDCl_3$) δ** = 168.3, 161.1, 160.1, 148.0, 147.6, 130.8, 130.1, 129.2, 124.6, 109.0, 108.7, 104.8, 101.4, 90.5, 55.9, 55.4, 50.2, 33.6, 33.3, 21.0.

**HRMS** (ESI): Calculated for $C_{23}H_{25}NaNO_6$ ($[M+Na]^+$): 434.1580; found: 434.1574

**IR** (neat) : ν = 1679, 1608, 1416 $cm^{-1}$

**m.p.** : 58 – 60 °C

## (E)-3-(4-fluorobenzylidene)-5-methyl-1-(2,4,6-trimethoxybenzyl)pyrrolidin-2-one 2t:




Chemical Formula: $C_{22}H_{24}FNO_4$
Exact Mass: 385.1689

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1t** (47 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2t** was obtained as a yellowish oil (25 mg, 0.064 mmol, 64%).

**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.45 – 7.39 (m, 2H), 7.34 – 7.32 (m, 1H), 7.09 – 7.02 (m, 2H), 6.12 (s, 2H), 5.11 (d, *J* = 14.1 Hz, 1H), 4.27 (d, *J* = 14.1 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 6H), 3.50 – 3.40 (m, 1H), 3.04 (ddd, *J* = 17.3, 8.1, 3.1 Hz, 1H), 2.55 – 2.45 (m, 1H), 1.21 (d, *J* = 6.3 Hz, 3H).

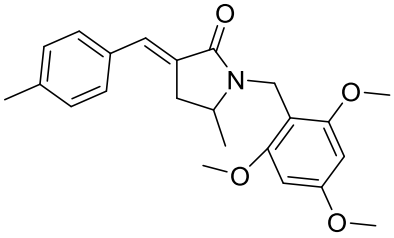
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 168.0, 163.6, 161.1, 160.1, 132.67 (d, J = 3.5 Hz) 131.6 (d, J = 2.4 Hz), 131.2 (d, J = 8.0 Hz), 128.2, 115.7 (d, J = 22.0 Hz), 104.6, 90.4, 55.9, 55.5, 50.2, 33.5, 33.3, 21.0.

**$^{19}$F NMR (376 MHz, $CDCl_3$) δ =** -112.8.

**HRMS** (ESI): Calculated for $C_{22}H_{24}FNaNO_4$ ($[M+Na]^+$): 408.1587; found: 408.1583

**IR** (neat) : ν = 1677, 1608, 1422 $cm^{-1}$

## (E)-5-methyl-3-(4-methylbenzylidene)-1-(2,4,6-trimethoxybenzyl)pyrrolidin-2-one 2u:



Chemical Formula: $C_{23}H_{27}NO_4$
Exact Mass: 381.1940

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1u** (46 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), $PCy_3$ (2.8 mg, 0.01 mmol, 10 %), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2u** was obtained as a colorless oil (25 mg, 0.076 mmol, 76%).

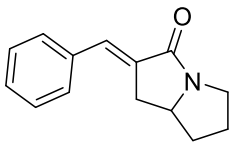
**$^1$H NMR (500 MHz, Chloroform-*d*) δ =** 7.36 – 7.33 (m, 3H), 7.19 – 7.16 (m, 2H), 6.12 (s, 2H), 5.11 (d, *J* = 14.1 Hz, 1H), 4.26 (d, *J* = 14.1 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 6H), 3.44 (ddt, *J* = 8.3, 6.2, 3.1 Hz, 1H), 3.06 (ddd, *J* = 17.2, 8.1, 3.0 Hz, 1H), 2.56 – 2.48 (m, 1H), 2.36 (s, 3H), 1.20 (d, *J* = 6.3 Hz, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$) δ =** 168.2, 161.0, 160.0, 138.1, 133.6, 130.9, 129.4, 129.3, 129.2, 104.7, 90.3, 55.8, 55.3, 50.1, 33.6, 33.1, 21.3, 20.8.

**HRMS** (ESI): Calculated for $C_{23}H_{28}NO_4$ ($[M+H]^+$): 382.2018; found: 382.2013

**IR** (neat) : ν = 2361, 1680, 1608, 1416 $cm^{-1}$

## (E)-2-benzylidenehexahydro-3H-pyrrolizin-3-one 2v:



Chemical Formula: $C_{14}H_{15}NO$
Exact Mass: 213.1154

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1v** (29.4 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), $PCy_3$ (2.8 mg, 0.01 mmol, 10 mol%), pivalic

acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2v** was obtained as a yellowish oil (11 mg, 0.051 mmol, 51%).

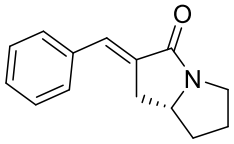
**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.49 – 7.45 (m, 2H), 7.43 – 7.37 (m, 2H), 7.34 – 7.29 (m, 2H), 3.89 – 3.86 (m, 1H), 3.75 (dt, J = 12.0, 8.2 Hz, 1H), 3.34 – 3.22 (m, 2H), 2.86 – 2.78 (m, 1H), 2.22 – 2.00 (m, 3H), 1.33 – 1.19 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 170.4, 136.0, 133.9, 130.5, 129.7, 128.8, 128.6, 59.3, 42.2, 32.4, 31.4, 26.3.

**HRMS** (ESI): Calculated for $C_{14}H_{15}NaNO$ ($[M+Na]^+$): 236.1051; found: 236.1046

**IR** (neat) : ν = 2361, 1681, 1419 $cm^{-1}$

## (*R*,*E*)-2-benzylidenehexahydro-3H-pyrrolizin-3-one (*R*)-2v:



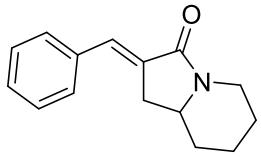

Chemical Formula: $C_{14}H_{15}NO$
Exact Mass: 213.1154

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, ***( S )*** **- 1v** (29.4 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), $PCy_3$ (2.8 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, ***( R )*****-2v** was obtained as a yellowish oil (10.5 mg, 0.050 mmol, 50%).

**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.49 – 7.45 (m, 2H), 7.42 – 7.37 (m, 2H), 7.34 – 7.29 (m, 2H), 3.91 – 3.82 (m, 1H), 3.79 – 3.72 (m, 1H), 3.34 – 3.22 (m, 2H), 2.82 (dt, J = 17.6, 3.3 Hz, 1H), 2.21 – 1.97 (m, 3H), 1.33 – 1.21 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$) δ =** 170.4, 136.0, 133.9, 130.6, 129.7, 128.8, 128.6, 59.3, 42.2, 32.4, 31.5, 26.3.

## (E)-2-benzylidenehexahydroindolizin-3(2H)-one 2w:



Chemical Formula: $C_{15}H_{17}NO$
Exact Mass: 227.1310

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1w** (30.8 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2w** was obtained as a colorless oil (22.2 mg, 0.098 mmol, 98%).

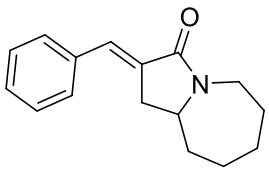
**$^1$H NMR (500 MHz, Chloroform-*d*) δ =** 7.49 – 7.44 (m, 2H), 7.42 – 7.37 (m, 2H), 7.36 – 7.34 (m, 1H), 7.33 – 7.28 (m, 1H), 4.35 – 4.28 (m, 1H), 3.58 – 3.51 (m, 1H), 3.24 (ddd, J = 17.5, 7.8, 2.7 Hz, 1H), 2.81 – 2.77 (m, 1H), 2.66 – 2.58 (m, 1H), 2.01 – 1.86 (m, 2H), 1.77 – 1.70 (m, 1H), 1.57 – 1.36 (m, 2H), 1.27 – 1.13 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$) δ =** 167.7, 136.2, 131.0, 129.9, 129.6, 128.8, 128.4, 55.2, 40.9, 34.1, 32.3, 24.8, 24.1.

**HRMS** (ESI): Calculated for $C_{15}H_{17}NaNO$ ($[M+Na]^+$): 250.1208; found: 250.1202

**IR** (neat) : ν = 2937, 1632, 1444 $cm^{-1}$

## (E)-2-benzylideneoctahydro-3H-pyrrolo[1,2-a]azepin-3-one 2x:



Chemical Formula: $C_{16}H_{19}NO$
Exact Mass: 241.1467

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1x** (32.2 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2x** was obtained as a yellowish oil (9.5 mg, 0.039 mmol, 40%).

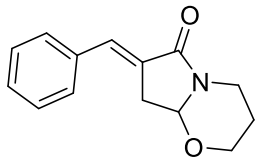
**$^{1}$H NMR (400 MHz, Chloroform-*d*) δ** = 7.48 – 7.44 (m, 2H), 7.42 – 7.36 (m, 2H), 7.34 – 7.28 (m, 2H), 3.94 – 3.81 (m, 2H), 3.29 – 3.15 (m, 2H), 2.64 – 2.57 (m, 1H), 1.98 – 1.89 (m, 1H), 1.85 – 1.75 (m, 1H), 1.75 – 1.62 (m, 4H), 1.60 – 1.51 (m, 2H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 169.4, 136.2, 131.8, 129.6, 129.1, 128.8, 128.3, 57.0, 43.5, 36.8, 33.6, 29.6, 27.4, 25.3.

**HRMS** (ESI): Calculated for $C_{16}H_{19}NaNO$ ($[M+Na]^+$): 264.1364; found: 264.1359

**IR** (neat) : ν = 1650, 1421 $cm^{-1}$

## (E)-7-benzylidenetetrahydro-2H-pyrrolo[2,1-b][1,3]oxazin-6(7H)-one 2y:




Chemical Formula: $C_{14}H_{15}NO_2$
Exact Mass: 229.1103

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1y** (31 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2y** was obtained as a colorless oil (20.5 mg, 0.090 mmol, 90%).

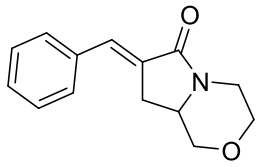
**$^{1}$H NMR (400 MHz, Chloroform-*d*) δ** = 7.48 – 7.45 (m, 2H), 7.42 – 7.37 (m, 3H), 7.35 – 7.30 (m, 1H), 5.06 (dd, J = 6.7, 1.8 Hz, 1H), 4.36 (ddt, J = 13.3, 5.4, 1.7 Hz, 1H), 4.12 (ddt, J = 11.6, 4.5, 1.7 Hz, 1H), 3.78 (ddd, J = 12.6, 11.8, 2.3 Hz, 1H), 3.26 (ddd, J = 17.9, 6.6, 2.7 Hz, 1H), 3.17 – 3.08 (m, 1H), 2.88 (dt, J = 17.9, 2.3 Hz, 1H), 1.93 – 1.80 (m, 1H), 1.58 – 1.51 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 167.6, 135.6, 131.4, 129.7, 128.8, 128.4, 127.9, 85.4, 67.2, 39.0, 32.7, 24.8.

**HRMS** (ESI): Calculated for $C_{14}H_{16}NO_2$ ($[M+H]^+$): 230.1181; found: 230.1178

**IR** (neat) : ν = 2364, 1685, 1449 $cm^{-1}$

## (E)-7-benzylidenehexahydro-6H-pyrrolo[2,1-c][1,4]oxazin-6-one 2z:



Chemical Formula: $C_{14}H_{15}NO_2$
Exact Mass: 229.1103

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1z** (31 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), $PCy_3$ (2.8 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2z** was obtained as a colorless oil (16 mg, 0.069 mmol, 69%).

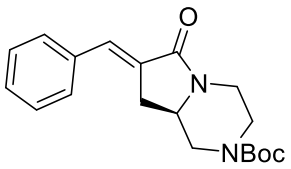
**$^1$H NMR (500 MHz, Chloroform-*d*) δ =** 7.51 – 7.48 (m, 2H), 7.45 – 7.41 (m, 3H), 7.38 – 7.34 (m, 1H), 4.18 (dd, J = 13.3, 3.0 Hz, 1H), 4.08 (dd, J = 11.1, 3.9 Hz, 1H), 4.00 – 3.96 (m, 1H), 3.91 – 3.84 (m, 1H), 3.48 – 3.42 (m, 1H), 3.24 – 3.12 (m, 3H), 2.60 – 2.52 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$) δ =** 167.6, 135.7, 131.1, 129.7, 129.4, 128.9, 128.8, 72.6, 66.5, 53.2, 41.1, 27.5.

**HRMS** (ESI): Calculated for $C_{14}H_{16}NO_2$ ($[M+H]^+$): 230.1181; found: 230.1176

**IR** (neat) : ν = 2361, 1682, 1447 $cm^{-1}$

## tert-butyl (E)-7-benzylidene-6-oxohexahydropyrrolo[1,2-a]pyrazine-2(1H)-carboxylate 2aa:



Chemical Formula: $C_{19}H_{24}N_2O_3$
Exact Mass: 328.1787

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **1aa** (41 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **2aa** was obtained as a colorless oil (17 mg, 0.052 mmol, 52%).

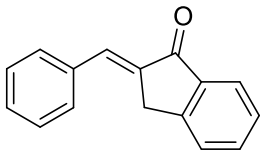
**$^1$H NMR (500 MHz, Chloroform-*d*) δ** = 7.49 – 7.45 (m, 2H), 7.43 – 7.39 (m, 3H), 7.36 – 7.32 (m, 1H), 4.35 (br. s, 1H), 4.25 – 4.19 (m, 1H), 4.15 (br. s, 1H), 3.72 – 3.65 (m, 1H), 3.22 (ddd, J = 17.7, 7.9, 2.7 Hz, 1H), 2.99 – 2.93 (m, 1H), 2.77 (br. s, 1H), 2.64 – 2.57 (m, 1H), 2.47 (br. s, 1H), 1.49 (s, 9H).

**$^{13}$C NMR (126 MHz, $CDCl_3$) δ =** 167.7, 154.5, 135.7, 131.1, 129.7, 129.5, 129.0, 128.9, 128.8, 127.9, 80.8, 53.4, 40.3, 28.8, 28.5.

**HRMS** (ESI): Calculated for $C_{19}H_{24}NaN_2O_3$ ($[M+Na]^+$): 351.1685; found: 351.1679

**IR** (neat) : ν = 2361, 1688, 1422 $cm^{-1}$

## (E)-2-benzylidene-2,3-dihydro-1H-inden-1-one 4a:




Chemical Formula: $C_{16}H_{12}O$
Exact Mass: 220.0888

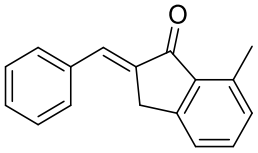
Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **3a** (30 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), $PCy_3$ (2.8 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **4a** was obtained as a white solid (14.5 mg, 0.066 mmol, 66%).

The physical and spectroscopic properties matched those described in the literature. [4]

**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.94 – 7.91 (m, 1H), 7.70 – 7.67 (m, 3H), 7.64 – 7.60 (m, 1H), 7.58 – 7.55 (m, 1H), 7.49 – 7.38 (m, 4H), 4.06 (d, *J* = 2.1 Hz, 2H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 194.5, 149.8, 138.2, 135.6, 134.9, 134.8, 134.1, 130.9, 129.8, 129.1, 127.8, 126.3, 124.6, 32.6.

## (E)-2-benzylidene-7-methyl-2,3-dihydro-1H-inden-1-one 4b:



Chemical Formula: $C_{17}H_{14}O$
Exact Mass: 234.1045

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **3b** (31.5 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), $PCy_3$ (2.8 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **4b** was obtained as a white solid (16.5 mg, 0.070 mmol, 70%).

**$^1$H NMR (400 MHz, Chloroform-*d*) δ** = 7.69 – 7.65 (m, 2H), 7.62 – 7.60 (m, 1H), 7.48 – 7.43 (m, 3H), 7.42 – 7.38 (m, 1H), 7.38 – 7.34 (m, 1H), 7.18 – 7.14 (m, 1H), 4.01 (d, J = 2.2 Hz, 2H), 2.75 (s, 3H).

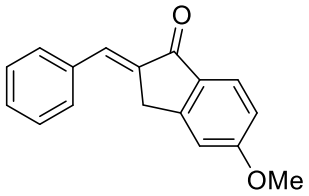
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 195.4, 150.4, 139.7, 135.7, 135.6, 135.4, 134.1, 133.1, 130.8, 129.7, 129.8, 129.0, 123.6, 32.3, 18.7.

**HRMS** (ESI): Calculated for $C_{17}H_{15}O$ ($[M+H]^+$): 235.1123; found: 235.1118

**IR** (neat) : ν = 1693, 1629 $cm^{-1}$

**m.p**.: 230 - 232°C (decomp.)

## (E)-2-benzylidene-5-methoxy-2,3-dihydro-1H-inden-1-one 4c:



Chemical Formula: $C_{17}H_{14}O_2$
Exact Mass: 250.0994

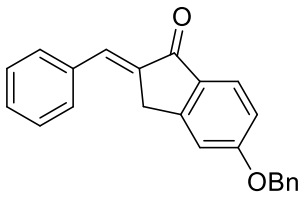
Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **3c** (33 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), $PCy_3$ (2.8 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **4c** was obtained as a white solid (20 mg, 0.081 mmol, 81%).

The physical and spectroscopic properties matched those described in the literature. [5]

**$^1$H NMR (500 MHz, Chloroform-*d*) δ =** 7.88 – 7.85 (m, 1H), 7.68 – 7.66 (m, 2H), 7.63 – 7.61 (m, 1H), 7.48 – 7.44 (m, 2H), 7.41 – 7.37 (m, 1H), 7.01 – 6.99 (m, 1H), 6.98 – 6.95 (m, 1H), 4.02 (d, J = 1.7 Hz, 2H), 3.92 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$) δ =** 192.9, 165.4, 152.7, 135.8, 135.4, 132.8, 131.6, 130.7, 129.5, 129.0, 126.4, 115.4, 109.9, 55.9, 32.7.

## (E)-2-benzylidene-5-(benzyloxy)-2,3-dihydro-1H-inden-1-one 4d:




Chemical Formula: $C_{23}H_{18}O_2$
Exact Mass: 326.1307

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **3d** (41 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), $PCy_3$ (2.8 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **4d** was obtained as a white solid (26 mg, 0.080 mmol, 80%).

**$^1$H NMR (500 MHz, Chloroform-*d*) δ =** 7.87 – 7.85 (m, 1H), 7.67 – 7.65 (m, 2H), 7.63 – 7.61 (m, 1H), 7.47 – 7.42 (m, 4H), 7.42 – 7.35 (m, 4H), 7.07 – 7.03 (m, 2H), 5.18 (s, 2H), 4.00 (d, J = 1.6 Hz, 2H).

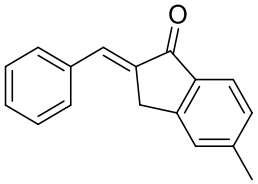
**$^{13}$C NMR (126 MHz, $CDCl_3$) δ =** 192.9, 164.5, 152.6, 136.2, 135.7, 135.4, 132.9, 131.8, 130.7, 129.5, 129.0, 128.9, 128.5, 127.6, 126.4, 116.1, 110.9, 70.6, 32.7.

**HRMS** (ESI): Calculated for $C_{23}H_{19}O_2$ ($[M+H]^+$): 327.1385; found: 327.1380

**IR** (neat) : ν = 1682 $cm^{-1}$

**m.p**.: 256 - 258°C (decomp.)

## (E)-2-benzylidene-5-methyl-2,3-dihydro-1H-inden-1-one 4e:




Chemical Formula: $C_{17}H_{14}O$
Exact Mass: 234.1045

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **3e** (31.5 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **4e** was obtained as a white solid (11.5 mg, 0.050 mmol, 50%).

**$^1$H NMR (400 MHz, Chloroform-*d*) δ =** 7.81 (d, J = 7.8 Hz, 1H), 7.71 – 7.63 (m, 3H), 7.51 – 7.42 (m, 2H), 7.44 – 7.37 (m, 1H), 7.37 – 7.33 (m, 1H), 7.28 – 7.20 (m, 1H), 4.01 (s, 2H), 2.48 (s, 3H).

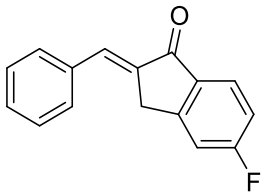
**$^{13}$C NMR (126 MHz, $CDCl_3$) δ** = 193.9, 150.1, 145.9, 135.8, 135.5, 135.2, 133.4, 130.6, 129.5, 128.9, 128.9, 126.5, 124.3, 32.3, 22.3.

**HRMS** (ESI): Calculated for $C_{17}H_{15}O$ ($[M+H]^+$): 235.1123; found: 235.1117

**IR** (neat) : ν = 1692, 1631, 1273 $cm^{-1}$

**m.p**.: 222 - 224°C (decomp.)

## (E)-2-benzylidene-5-fluoro-2,3-dihydro-1H-inden-1-one 4f:




Chemical Formula: $C_{16}H_{11}FO$
Exact Mass: 238.0794

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **3f** (32 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), $PCy_3$ (2.8 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **4f** was obtained as a white solid (21 mg, 0.089 mmol, 89%).

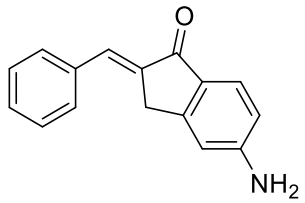
The physical and spectroscopic properties matched those described in the literature. [6]

**$^{1}$H NMR (400 MHz, Chloroform-*d*) δ =** 7.94 – 7.90 (m, 1H), 7.69 – 7.64 (m, 3H), 7.50 – 7.38 (m, 3H), 7.24 – 7.20 (m, 1H), 7.16 – 7.10 (m, 1H), 4.05 (s, 2H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 192.7, 167.2 (d, J = 256.2 Hz), 152.5 (d, J = 10.1 Hz), 135.3, 134.6 (d, J = 1.9 Hz), 134.4, 134.2, 130.8, 129.9, 129.1, 126.9 (d, J = 10.2 Hz), 116.1 (d, J = 23.8 Hz), 113.1 (d, J = 22.9 Hz), 32.6 (d, J = 2.2 Hz).

**$^{19}$F NMR (376 MHz, $CDCl_3$) δ** = -102.5.

## (E)-5-amino-2-benzylidene-2,3-dihydro-1H-inden-1-one 4g:




Chemical Formula: $C_{16}H_{13}NO$
Exact Mass: 235.0997

Following the general procedure for the 1,4-Pd shift/C($sp^3$)-H activation, **3g** (31.5 mg, 0.1 mmol, 1 equiv) was reacted with $Pd(PCy_3)_2$ (6.7 mg, 0.01 mmol, 10 mol%), $PCy_3$ (2.8 mg, 0.01 mmol, 10 mol%), pivalic acid (3.1 mg, 0.03 mmol, 30 mol%) and $Rb_2CO_3$ (35 mg, 0.15 mmol, 1.5 equiv) in mesitylene (4 mL) at 160°C for 16h. After purification, **4g** was obtained as a white solid (14 mg, 0.060 mmol, 60%).

The physical and spectroscopic properties matched those described in the literature. [7]

**$^{1}$H NMR (400 MHz, Chloroform-*d*) δ** = 7.76 – 7.72 (m, 1H), 7.66 – 7.62 (m, 2H), 7.58 – 7.55 (m, 1H), 7.47 – 7.41 (m, 2H), 7.39 – 7.34 (m, 1H), 6.70 – 6.68 (m, 1H), 6.67 – 6.63 (m, 1H), 4.30 (br. s, 2H), 3.91 (d, J = 2.1 Hz, 2H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ =** 192.3, 152.9, 152.8, 135.9, 135.9, 131.7, 130.4, 129.2, 129.1, 128.8, 126.6, 114.9, 109.5, 32.3.

## 8- Checkcif for compound 2y:

### checkCIF/PLATON report

Structure factors have been supplied for datablock(s) RR2369_130K_0m

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

### Datablock: RR2369_130K_0m

---

```
Bond precision:  C-C = 0.0020 A          Wavelength=1.54178

Cell:           a=11.7451(8)    b=9.8812(7)        c=19.5125(14)
                alpha=90        beta=95.463(3)     gamma=90
Temperature:    130 K

                Calculated                Reported
Volume          2254.3(3)                 2254.2(3)
Space group     C 2/c                     C 1 2/c 1
Hall group      -C 2yc                    -C 2yc
Moiety formula  C14 H15 N O2              C14 H15 N O2
Sum formula     C14 H15 N O2              C14 H15 N O2
Mr              229.27                    229.28
Dx,g cm-3       1.351                     1.351
Z               8                         8
Mu (mm-1)       0.727                     0.727
F000            976.0                     979.1
F000'           978.92
h,k,lmax        14,12,23                  14,11,23
Nref            2152                      2084
Tmin,Tmax       0.890,0.971               0.860,0.970
Tmin'           0.890

Correction method= # Reported T Limits: Tmin=0.860 Tmax=0.970
AbsCorr = MULTI-SCAN

Data completeness= 0.968          Theta(max)= 70.240

R(reflections)= 0.0400( 1939)     wR2(reflections)= 0.1016( 2084)

S = 1.054                 Npar= 154
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---

The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

**Alert level C**

| | | | |
|---|---|---|---|
| PLAT029_ALERT_3_C | _diffrn_measured_fraction_theta_full value Low . | 0.968 | Wh |
| PLAT094_ALERT_2_C | Ratio of Maximum / Minimum Residual Density .... | 2.14 | Re |
| PLAT906_ALERT_3_C | Large K Value in the Analysis of Variance ..... | 2.341 | Ch |
| PLAT911_ALERT_3_C | Missing FCF Refl Between Thmin & STh/L= 0.600 | 6 | Re |

**Alert level G**

| | | | |
|---|---|---|---|
| PLAT068_ALERT_1_G | Reported F000 Differs from Calcd (or Missing)... | Please | Ch |
| PLAT073_ALERT_1_G | H-atoms ref, but _hydrogen_treatment Reported as | constr | Ch |
| PLAT398_ALERT_2_G | Deviating C-O-C Angle From 120 for O1 | 109.5 | De |
| PLAT793_ALERT_4_G | Model has Chirality at C8 (Centro SPGR) | R | Ve |
| PLAT912_ALERT_4_G | Missing # of FCF Reflections Above STh/L= 0.600 | 60 | No |
| PLAT960_ALERT_3_G | Number of Intensities with I < - 2*sig(I) ... | 1 | Ch |
| PLAT978_ALERT_2_G | Number C-C Bonds with Positive Residual Density. | 8 | In |
| PLAT982_ALERT_1_G | The C-f'= 0.019 Deviates from IT-value = | 0.018 | C |
| PLAT982_ALERT_1_G | The N-f'= 0.033 Deviates from IT-value = | 0.031 | C |
| PLAT982_ALERT_1_G | The O-f'= 0.052 Deviates from IT-value = | 0.049 | C |

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
10 **ALERT level G** = General information/check it is not something unexpected

5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

### Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
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;
PROBLEM: _diffrn_measured_fraction_theta_full value Low .      0.968 Why?
RESPONSE: ...
;
_vrf_PLAT094_RR2369_130K_0m
;
PROBLEM: Ratio of Maximum / Minimum Residual Density ....       2.14 Report
RESPONSE: ...
;
_vrf_PLAT906_RR2369_130K_0m
;
PROBLEM: Large K Value in the Analysis of Variance ......      2.341 Check
RESPONSE: ...
;
_vrf_PLAT911_RR2369_130K_0m
;
PROBLEM: Missing FCF Refl Between Thmin & STh/L=    0.600          6 Report
RESPONSE: ...
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

**Publication of your CIF in IUCr journals**

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

**Publication of your CIF in other journals**

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

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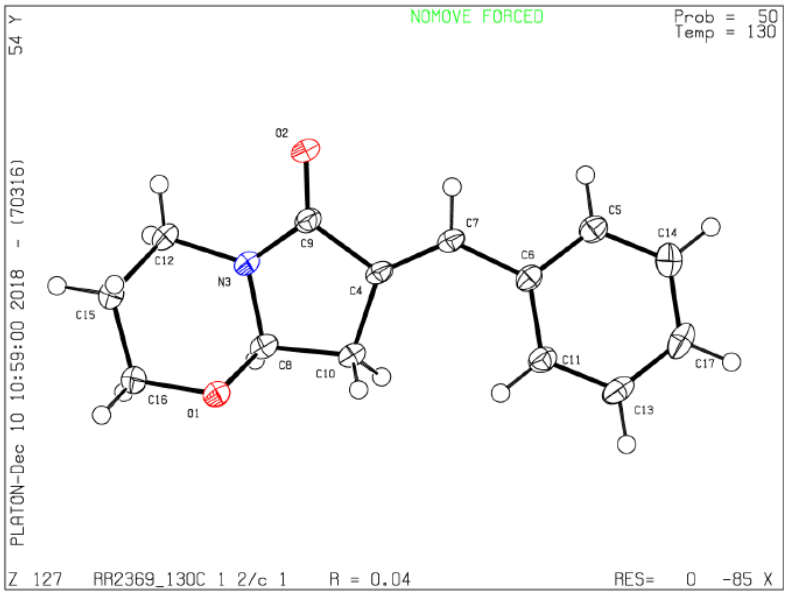
**PLATON version of 19/10/2018; check.def file version of 15/10/2018**

**Datablock RR2369_130K_0m** - ellipsoid plot



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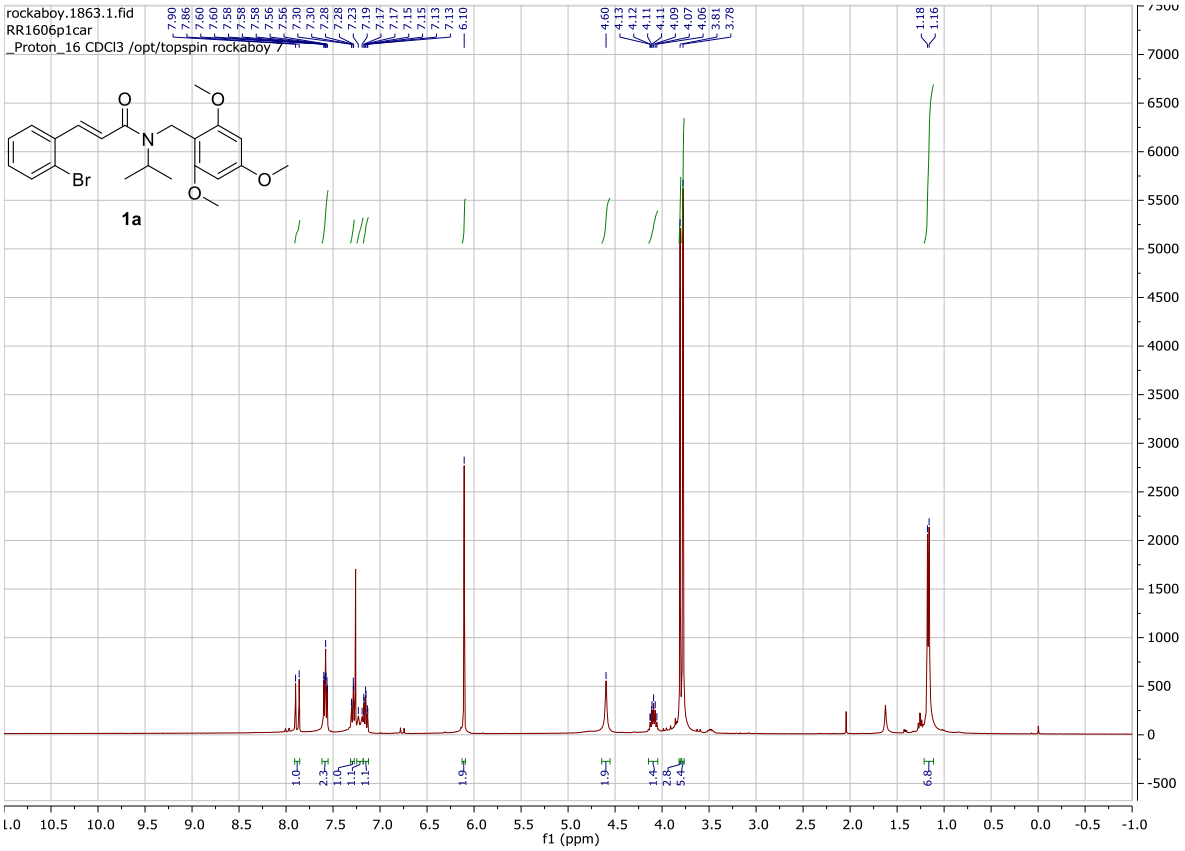


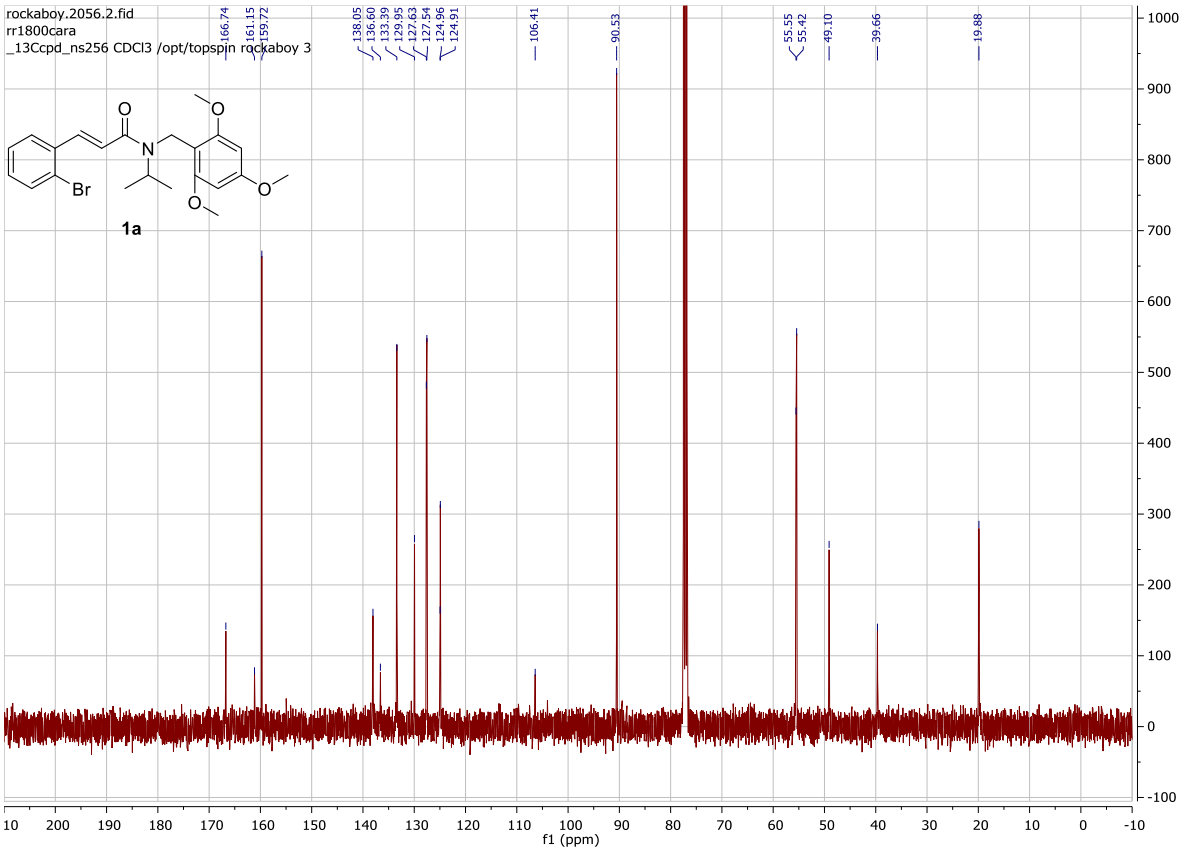

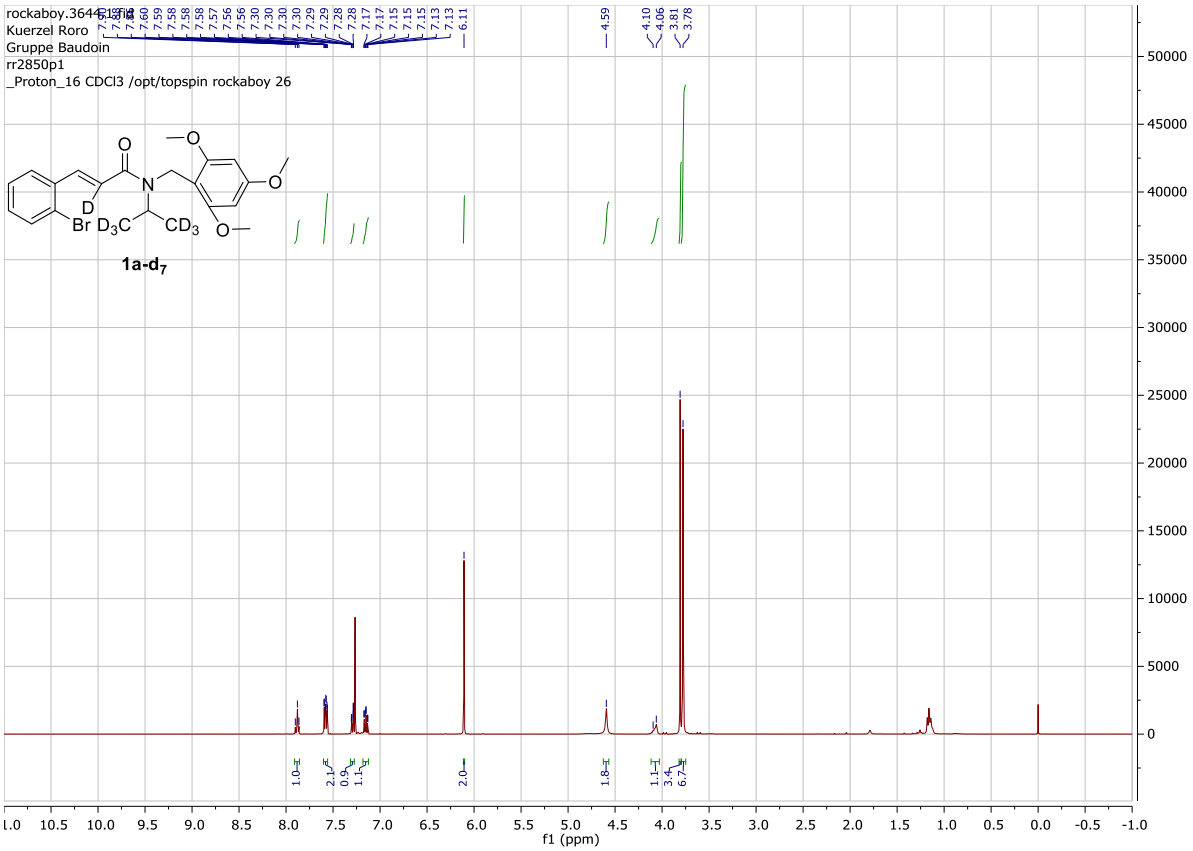
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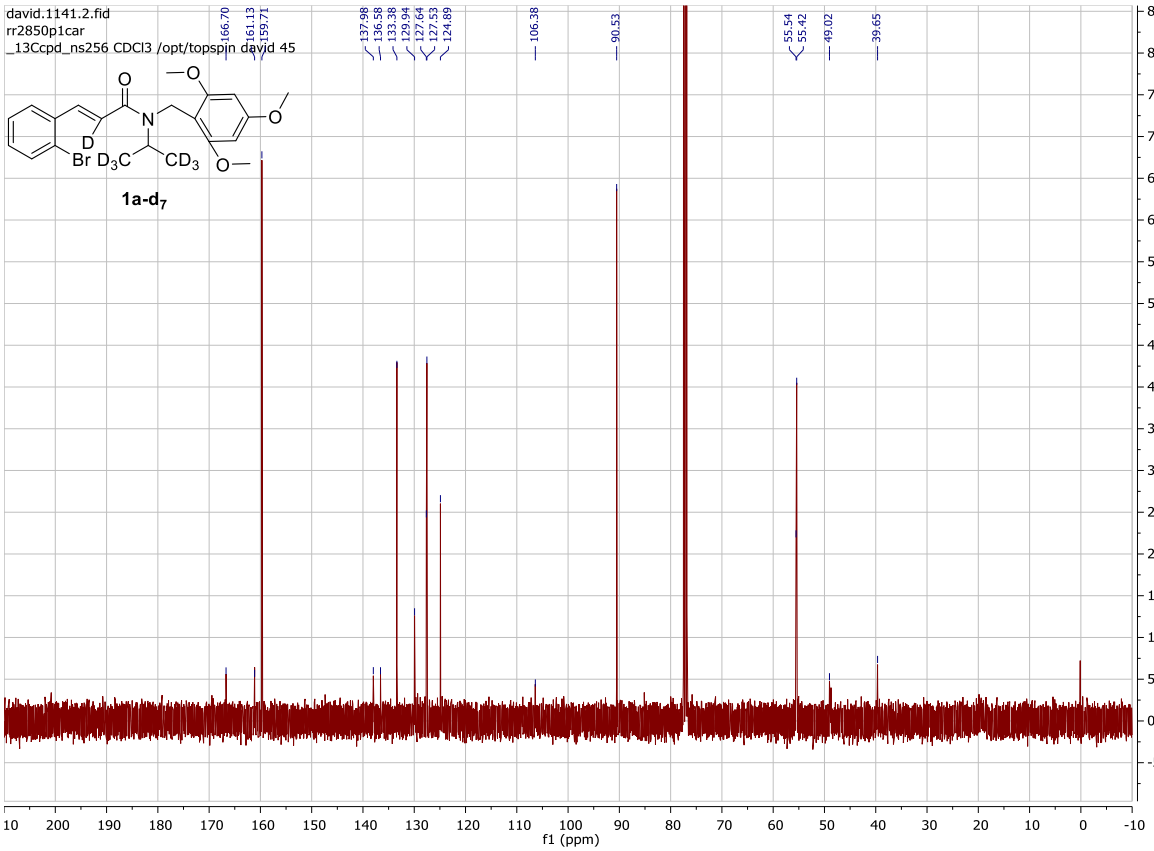
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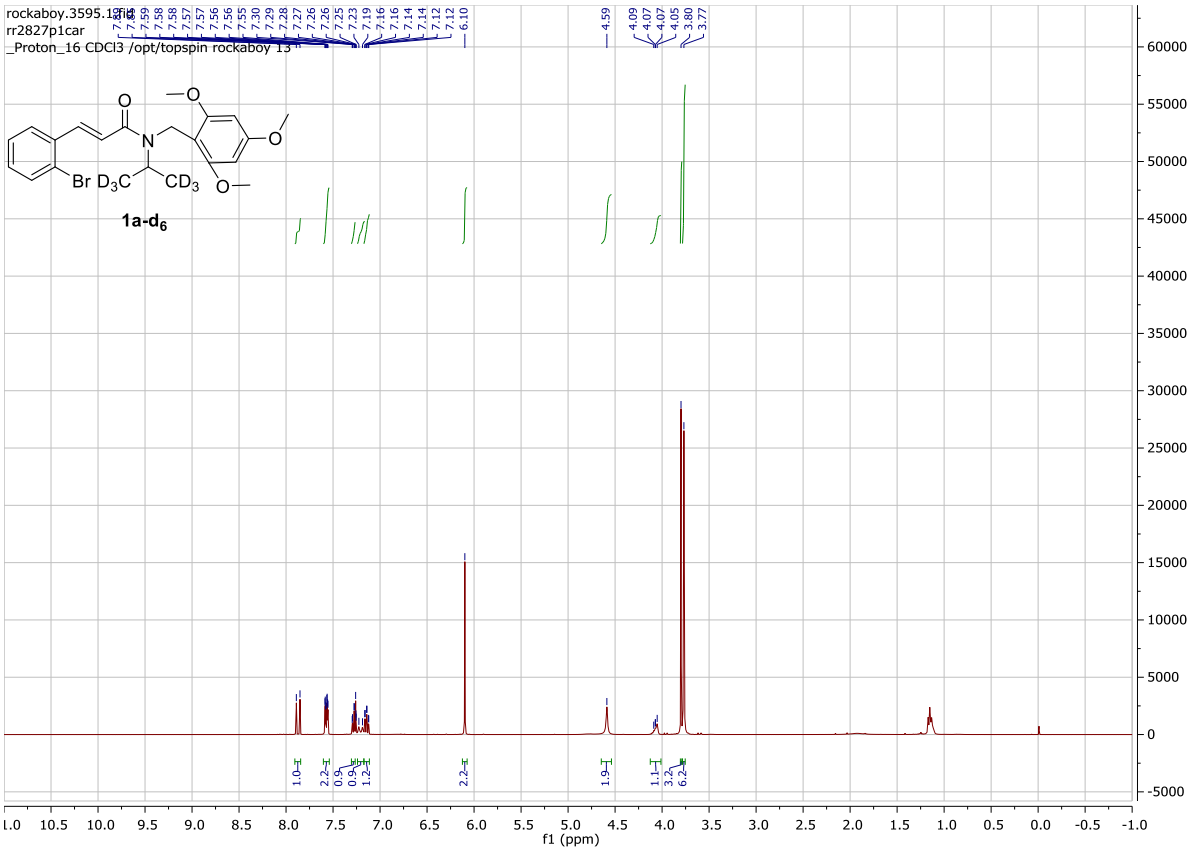
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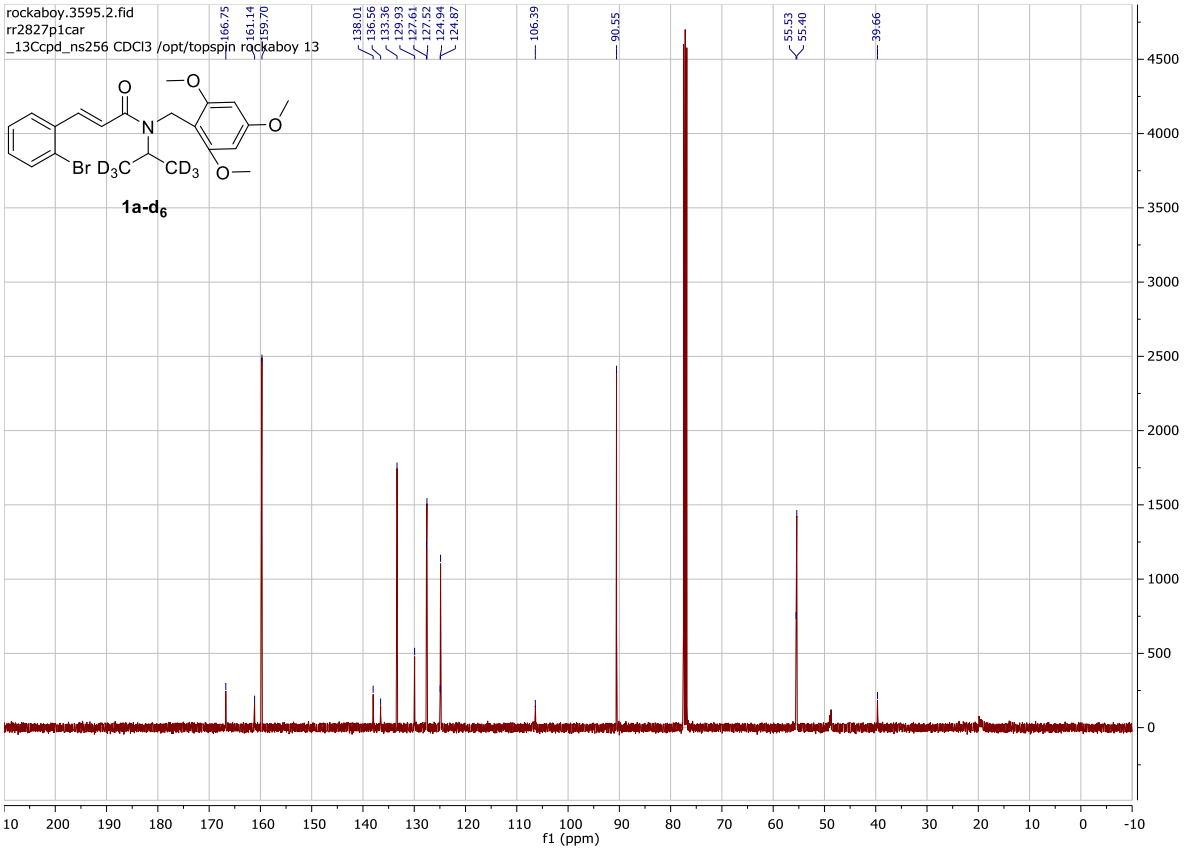
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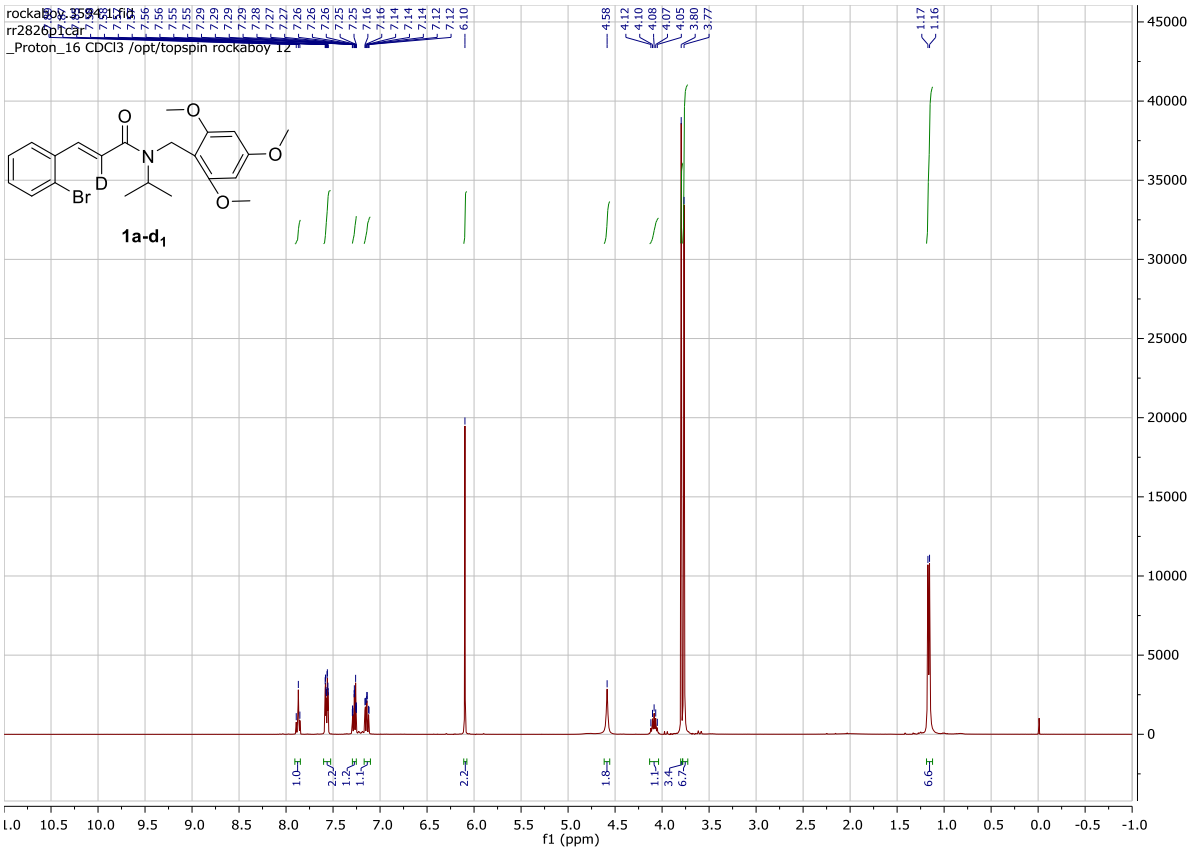
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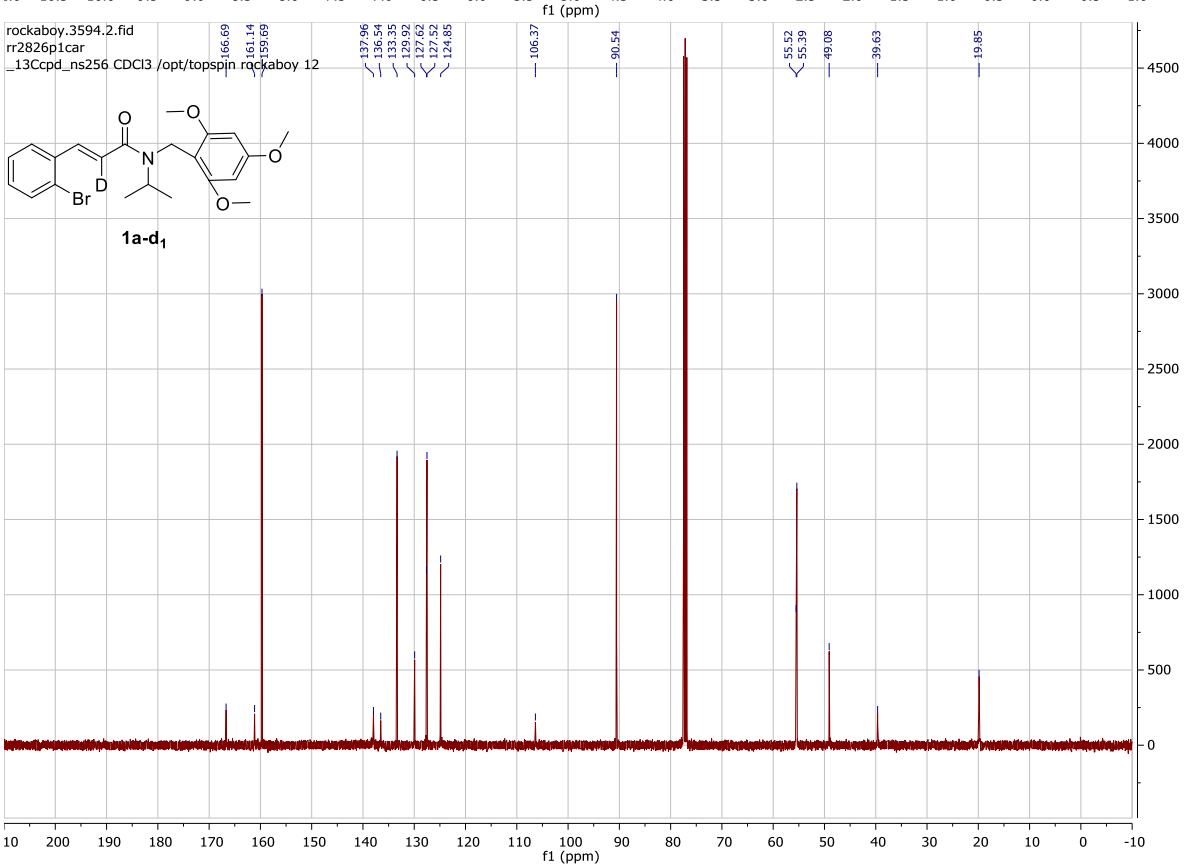
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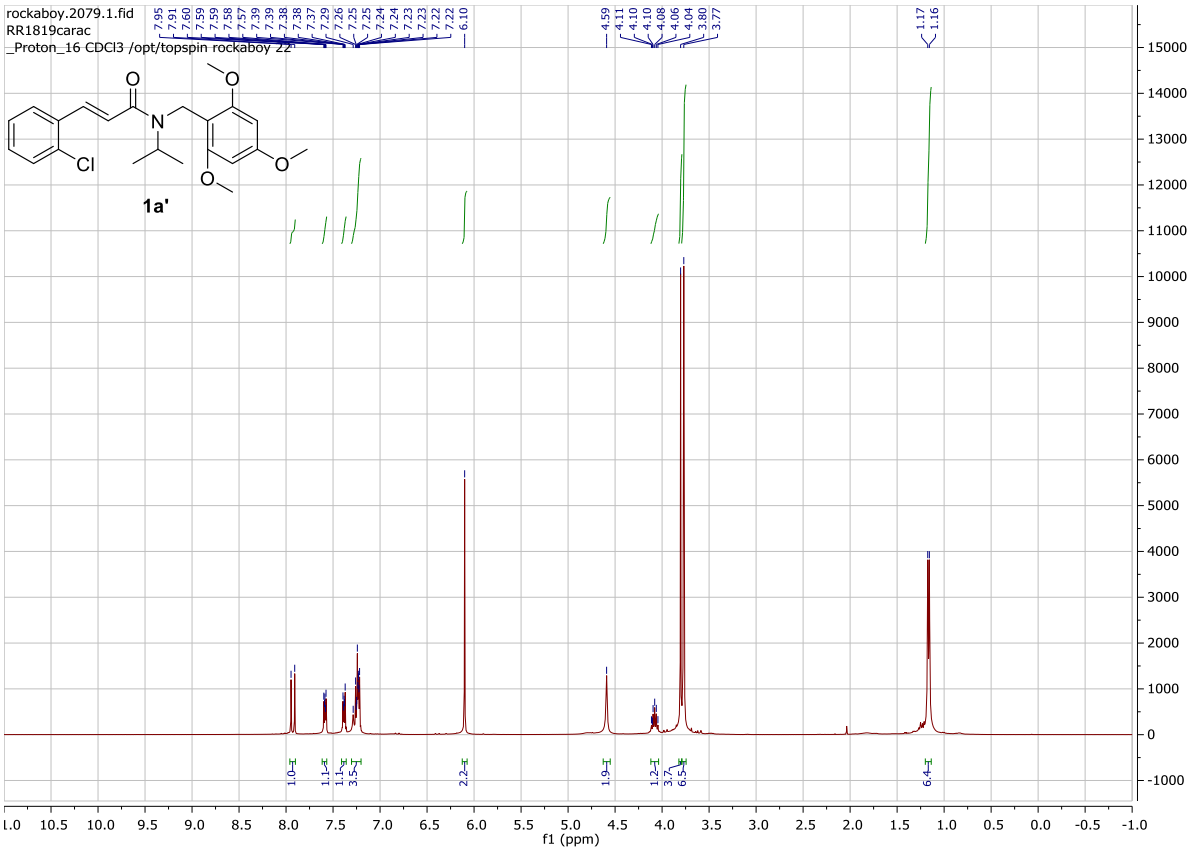
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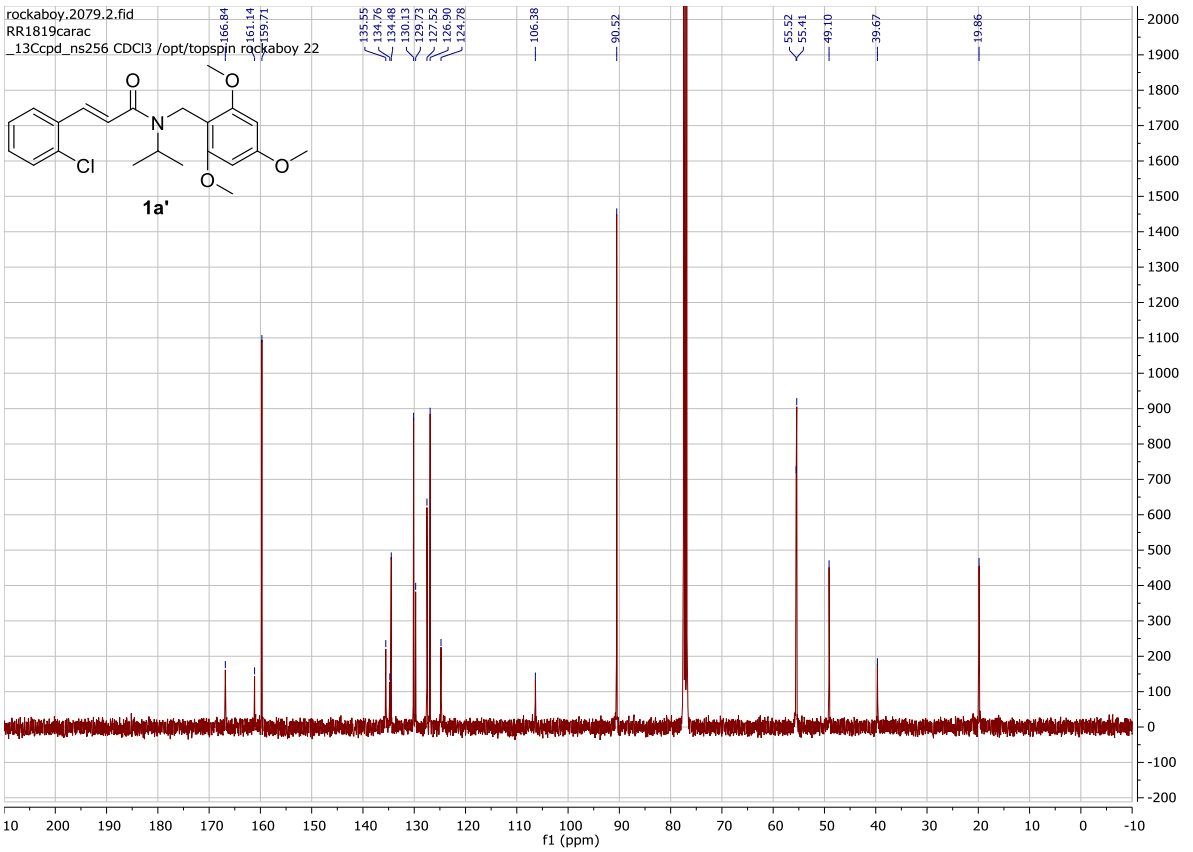
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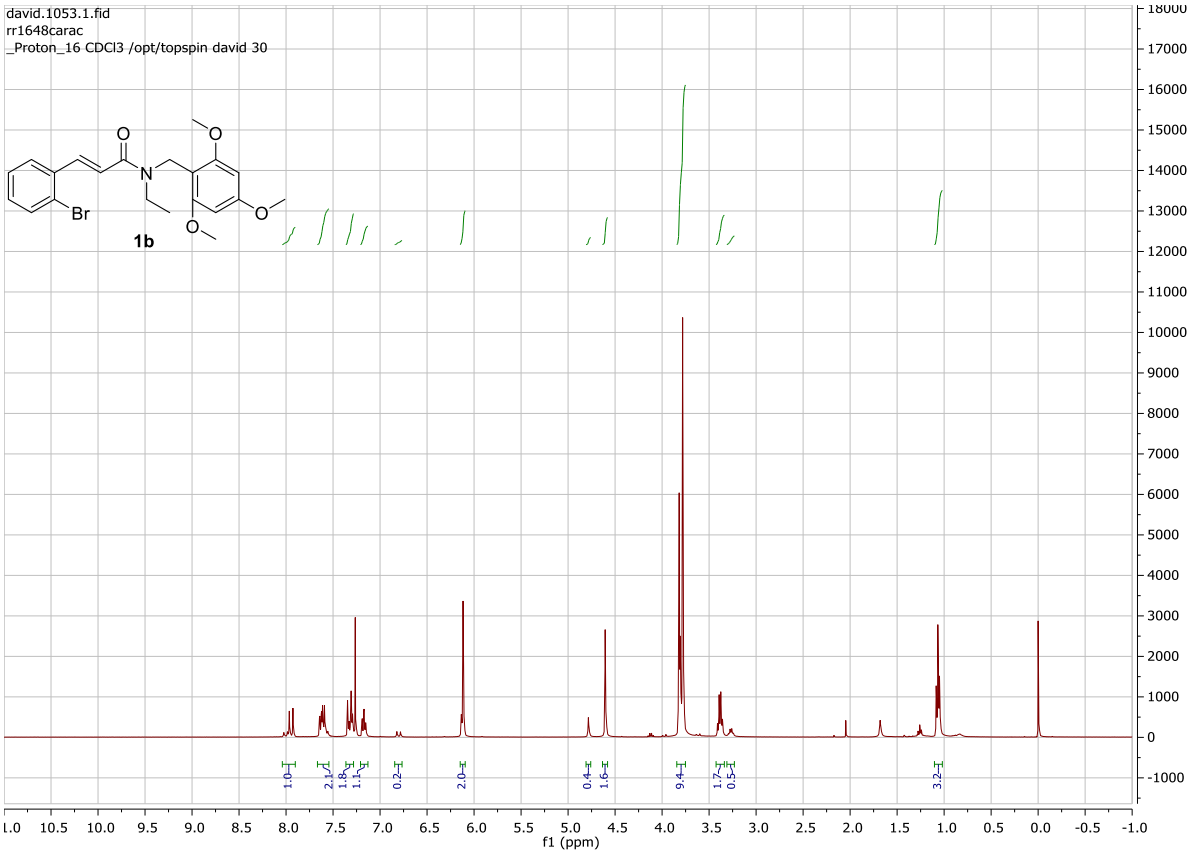
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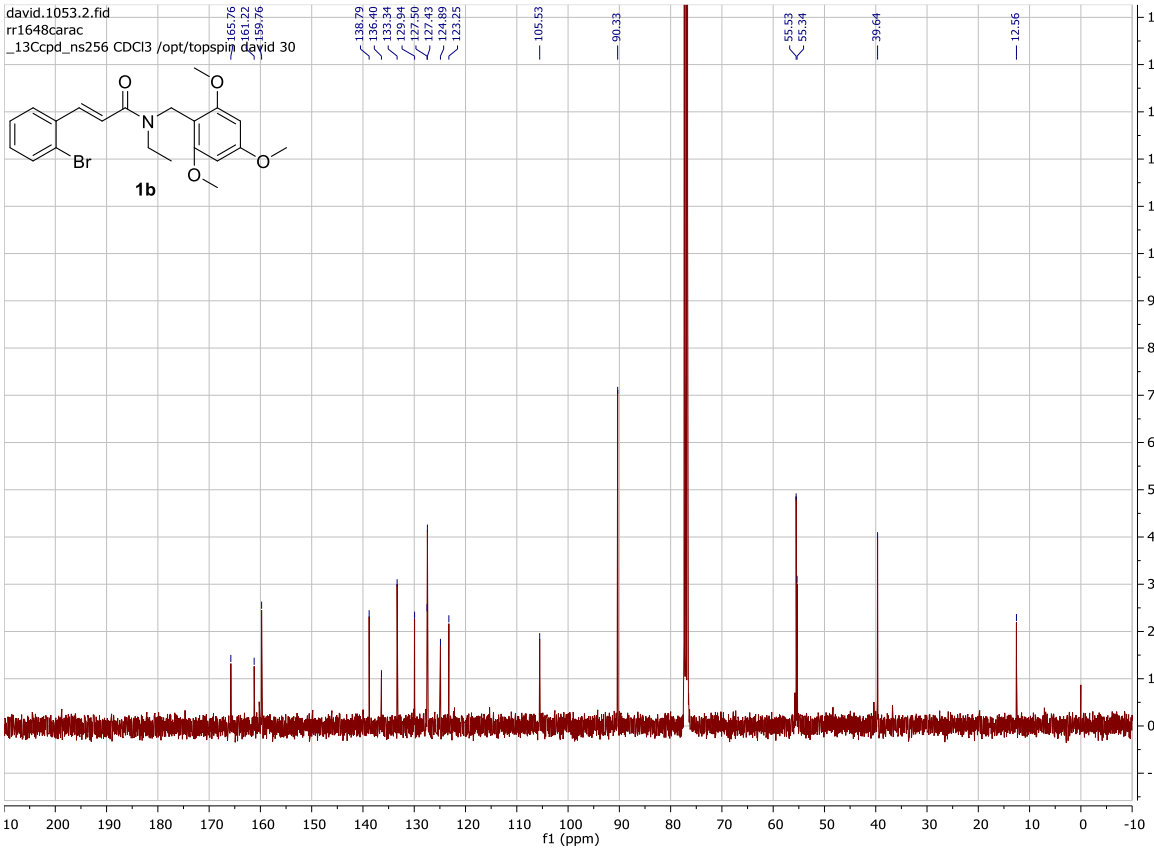
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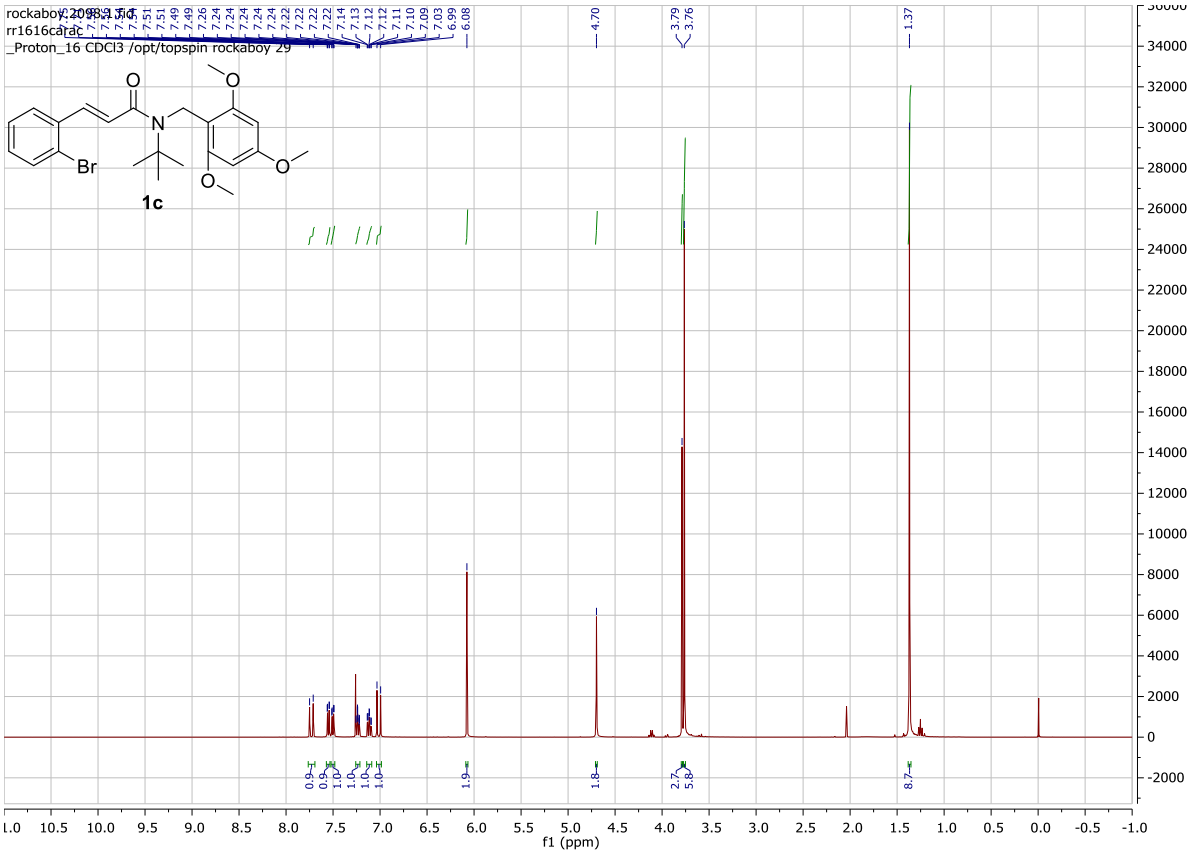
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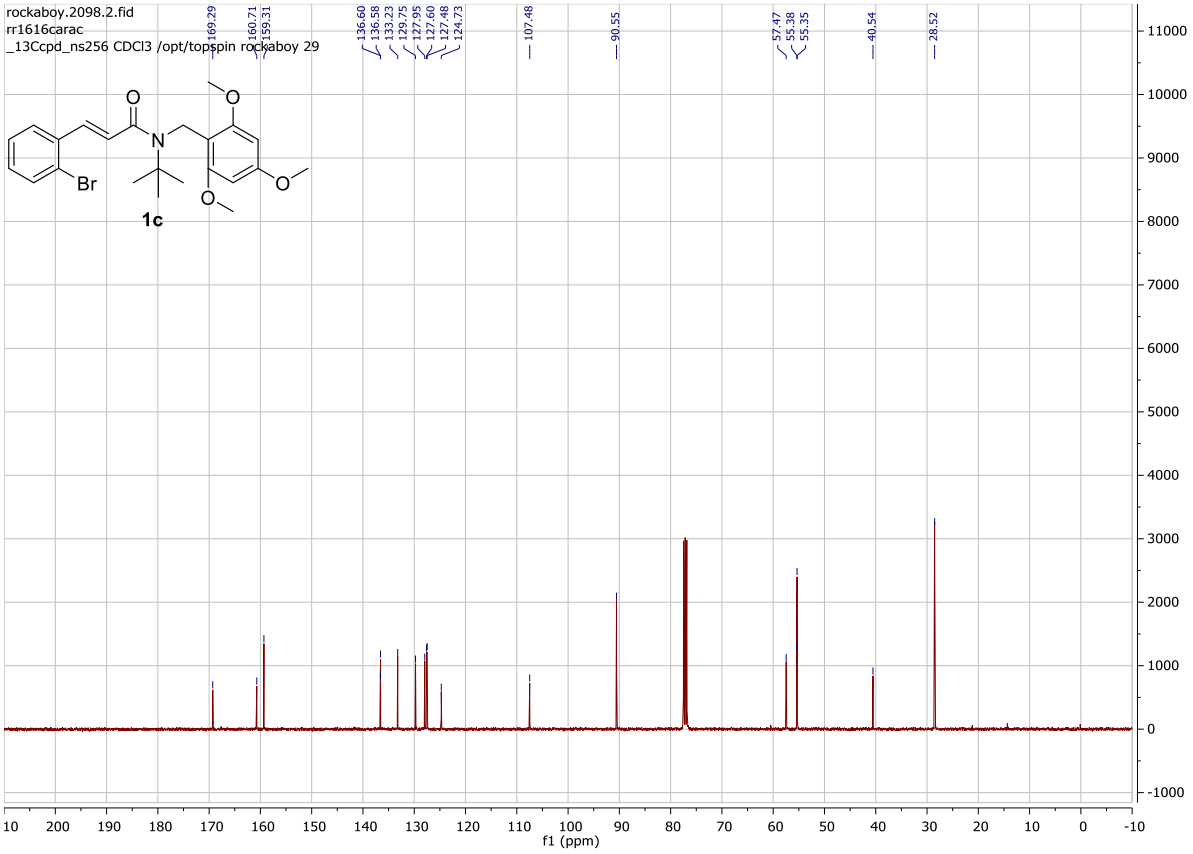
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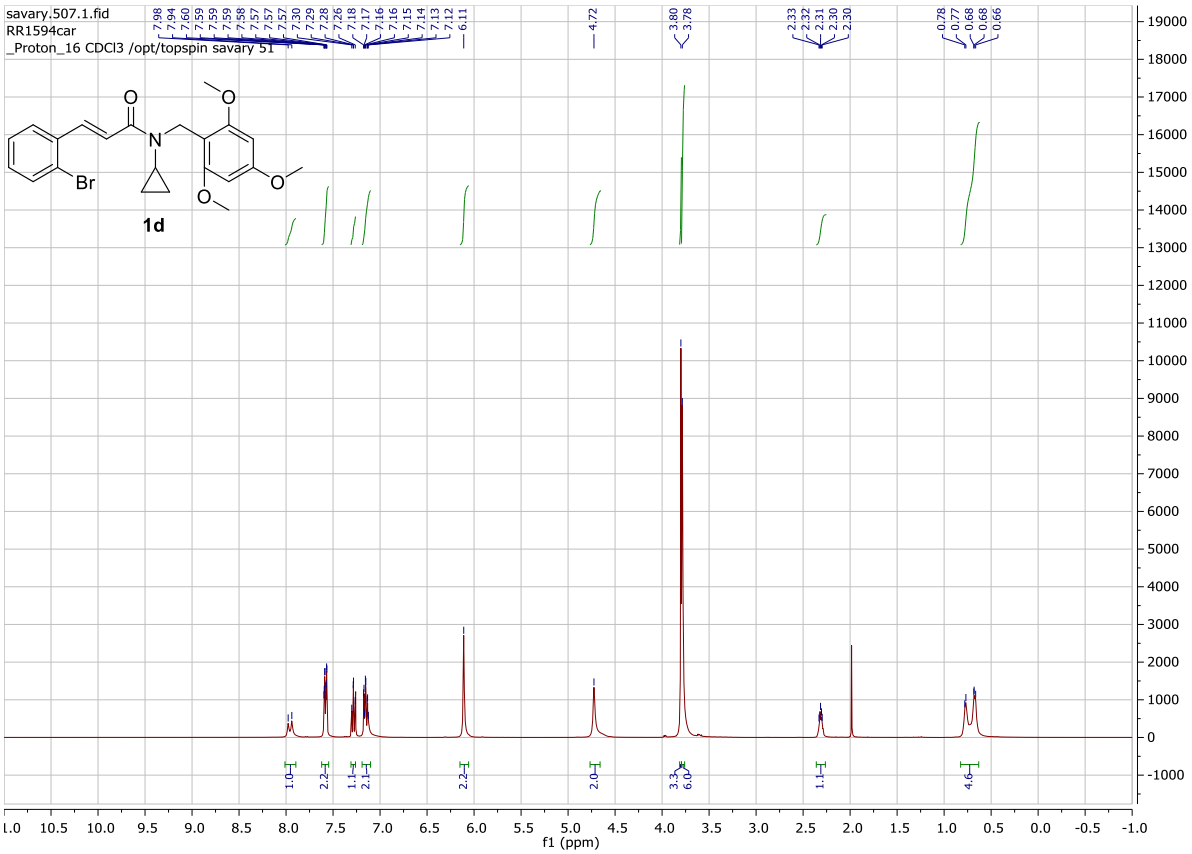
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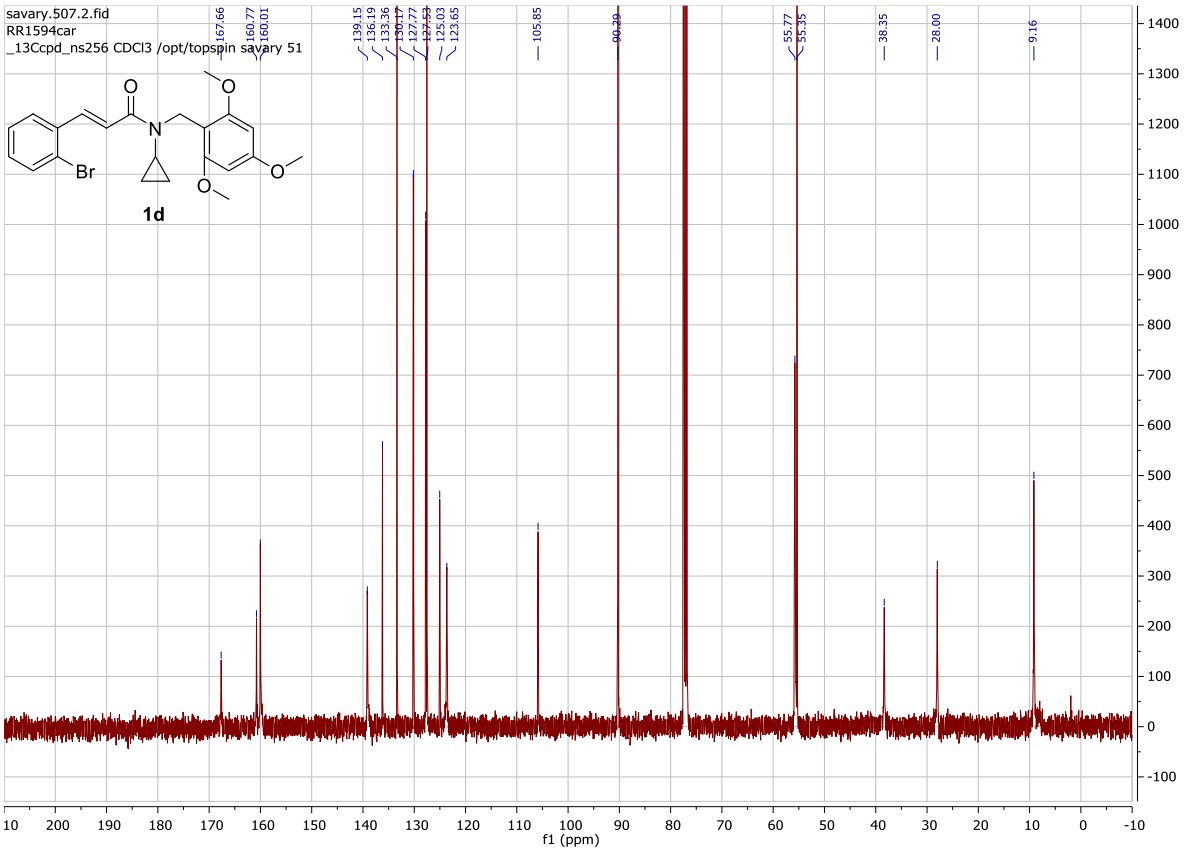
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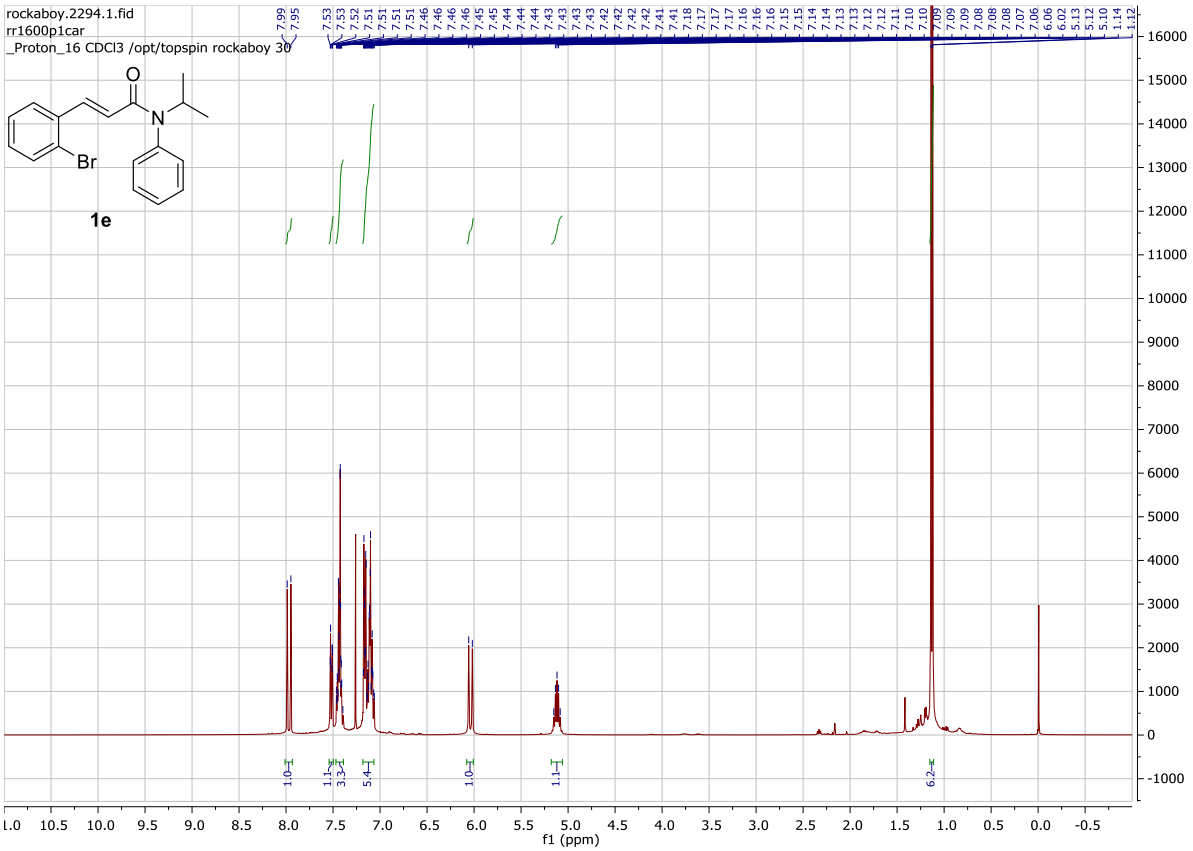
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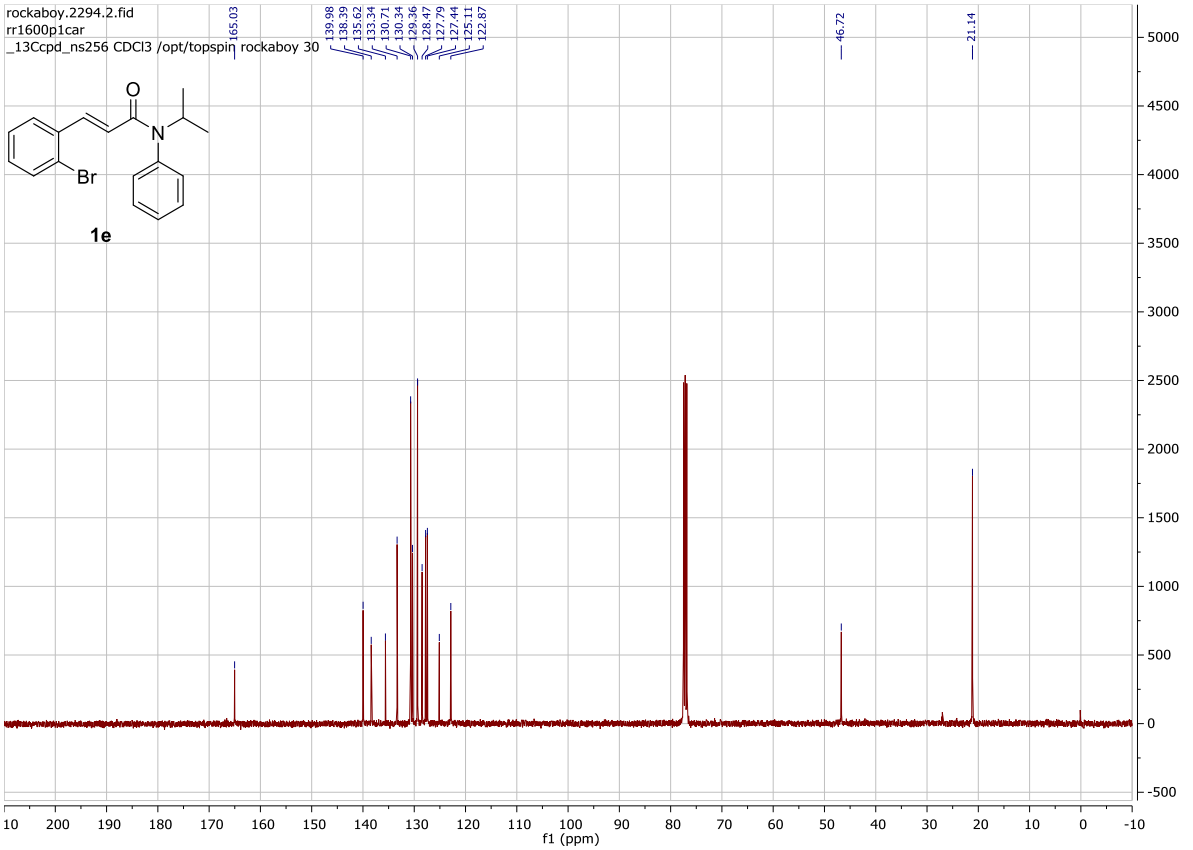
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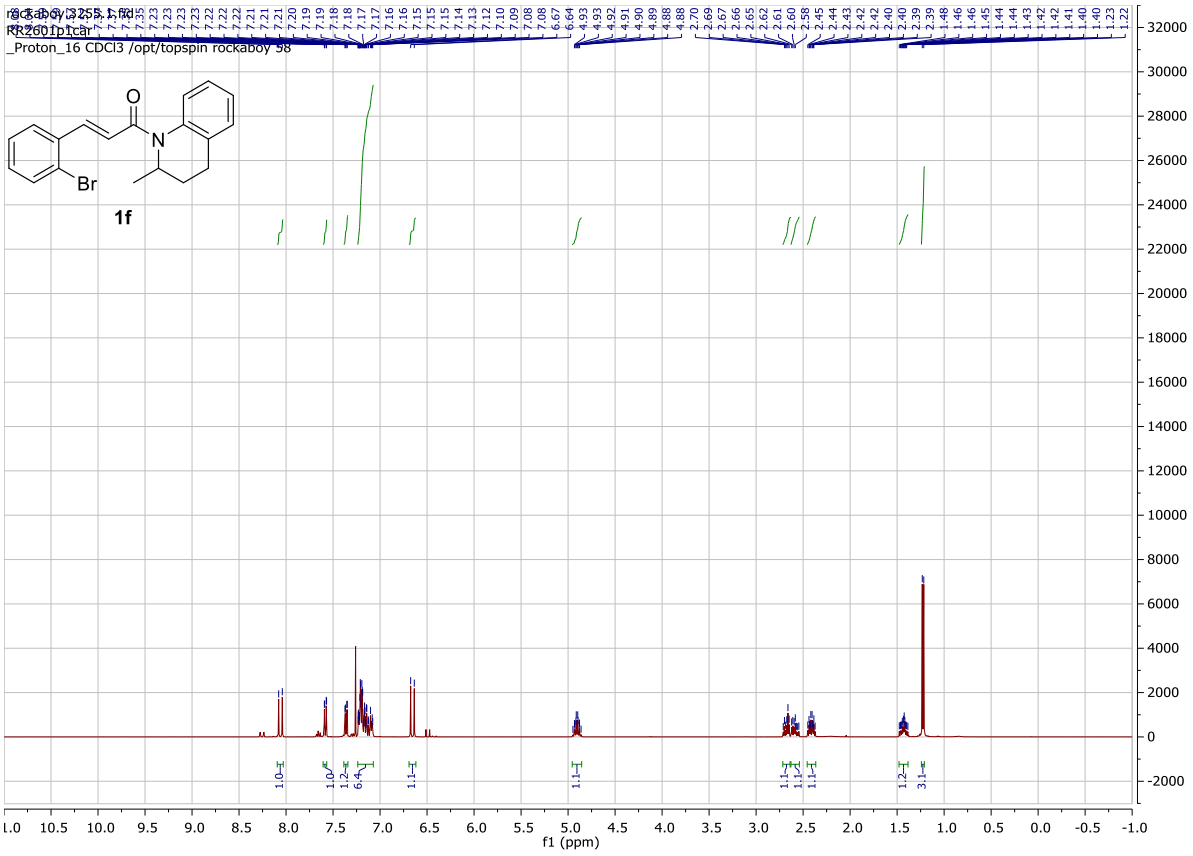
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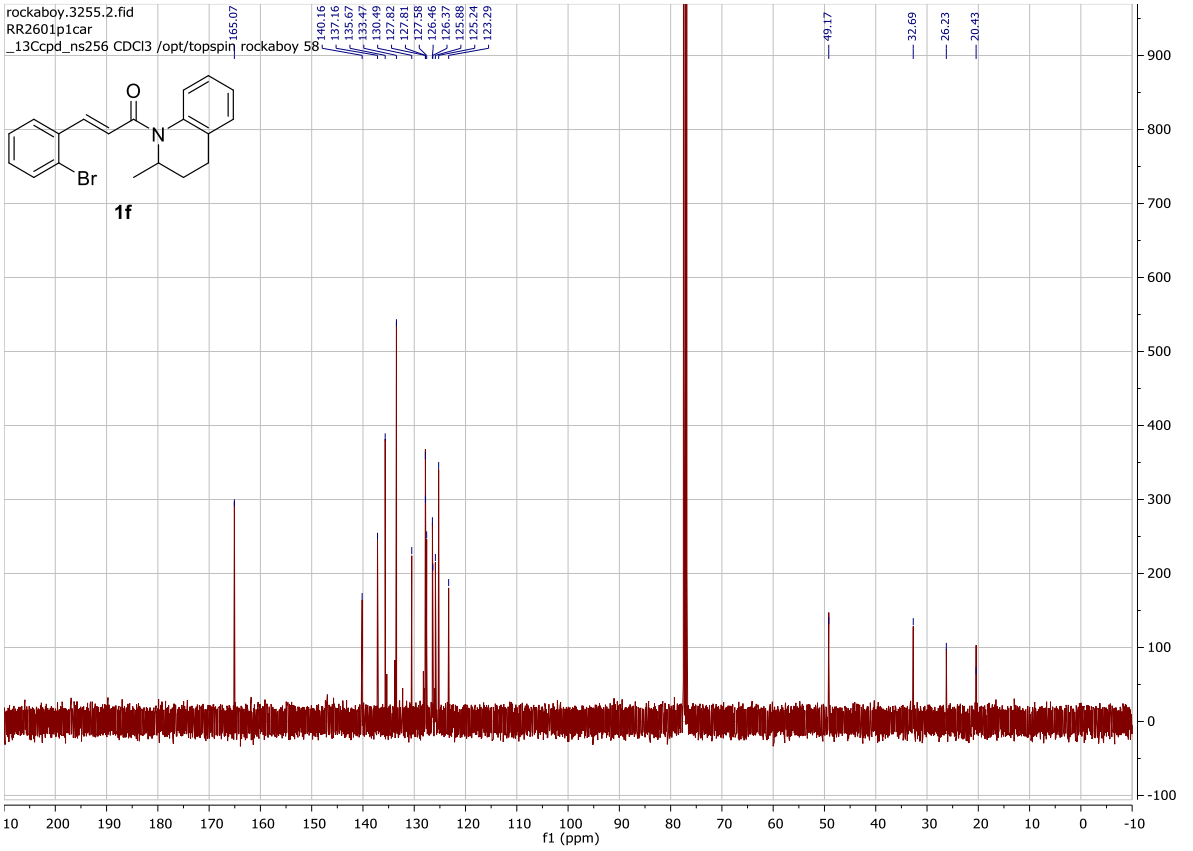
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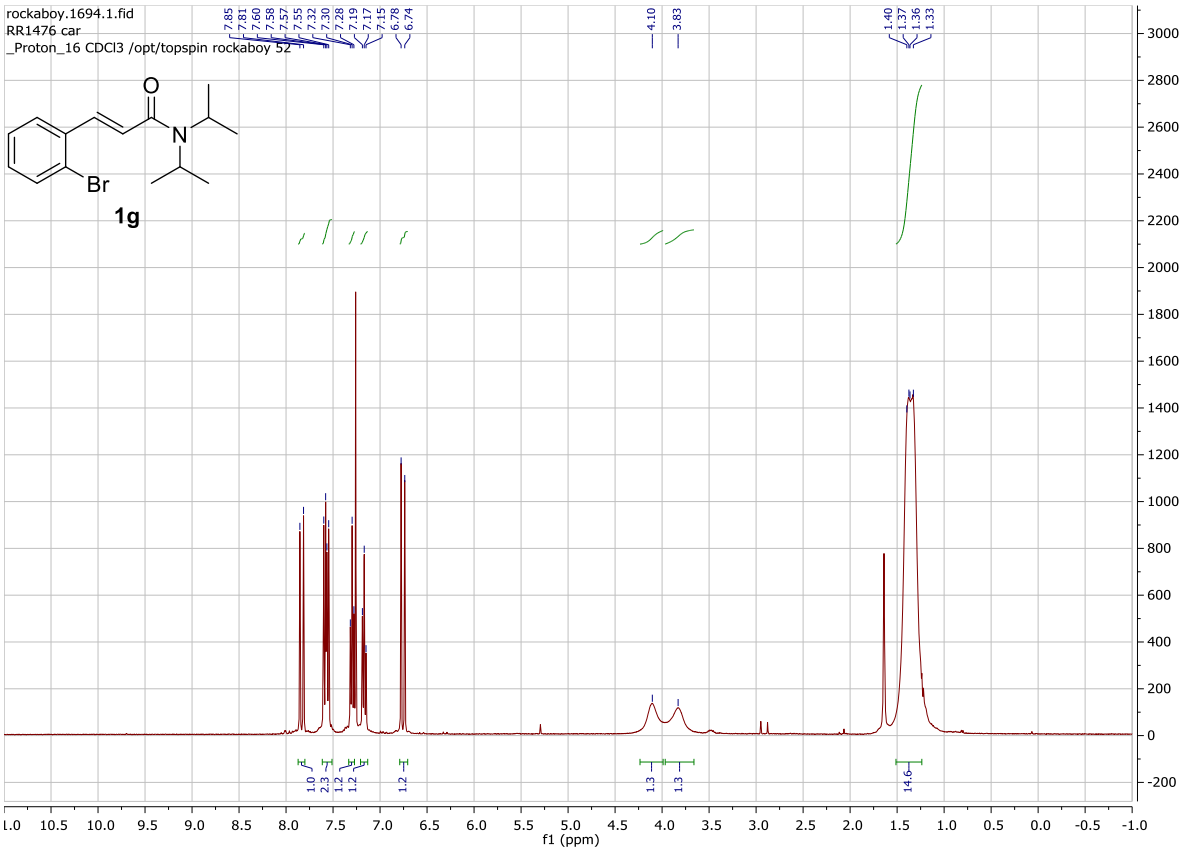
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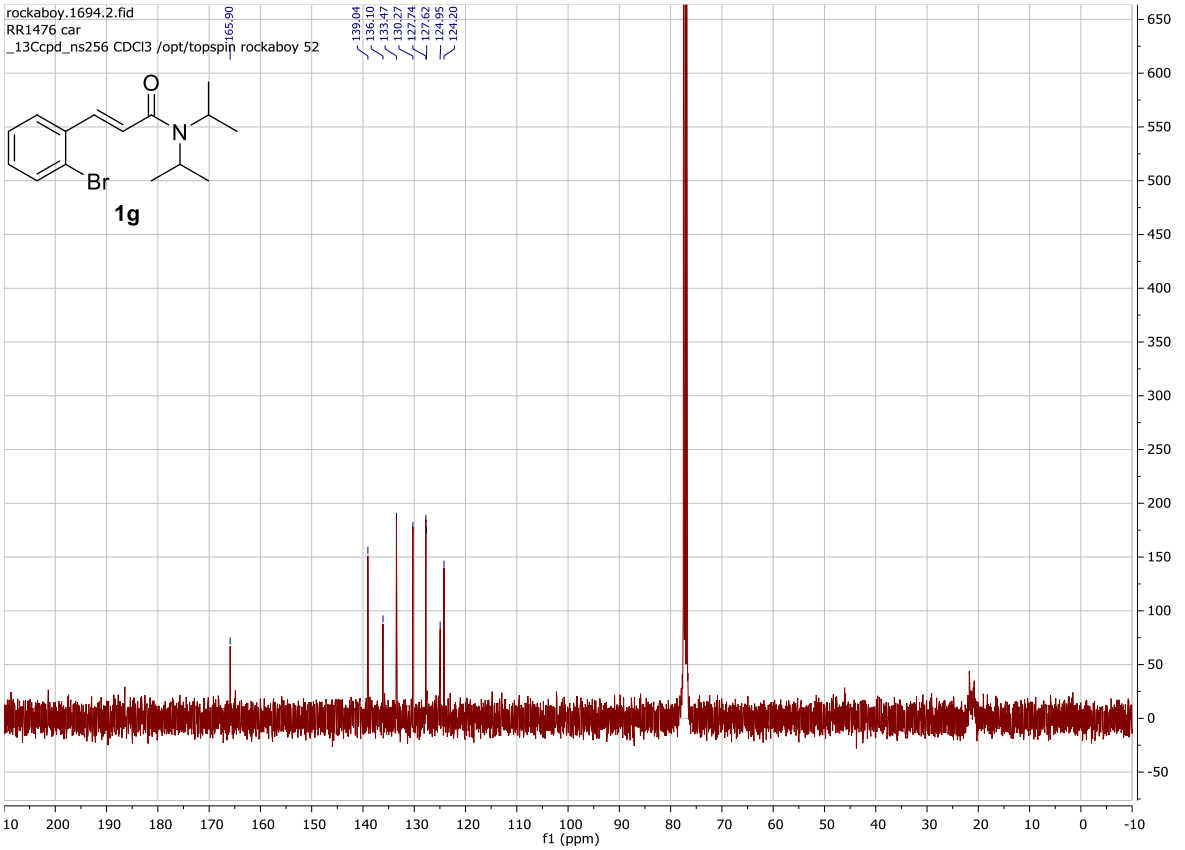
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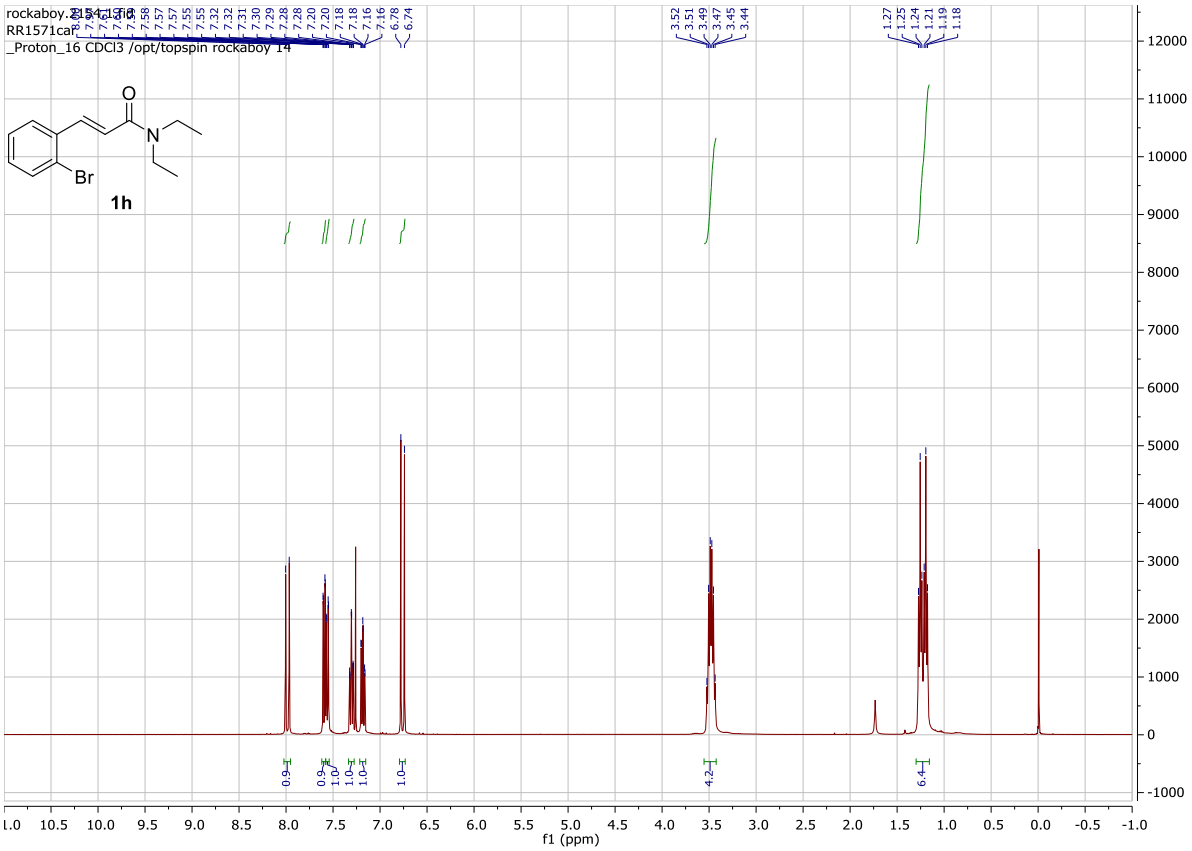
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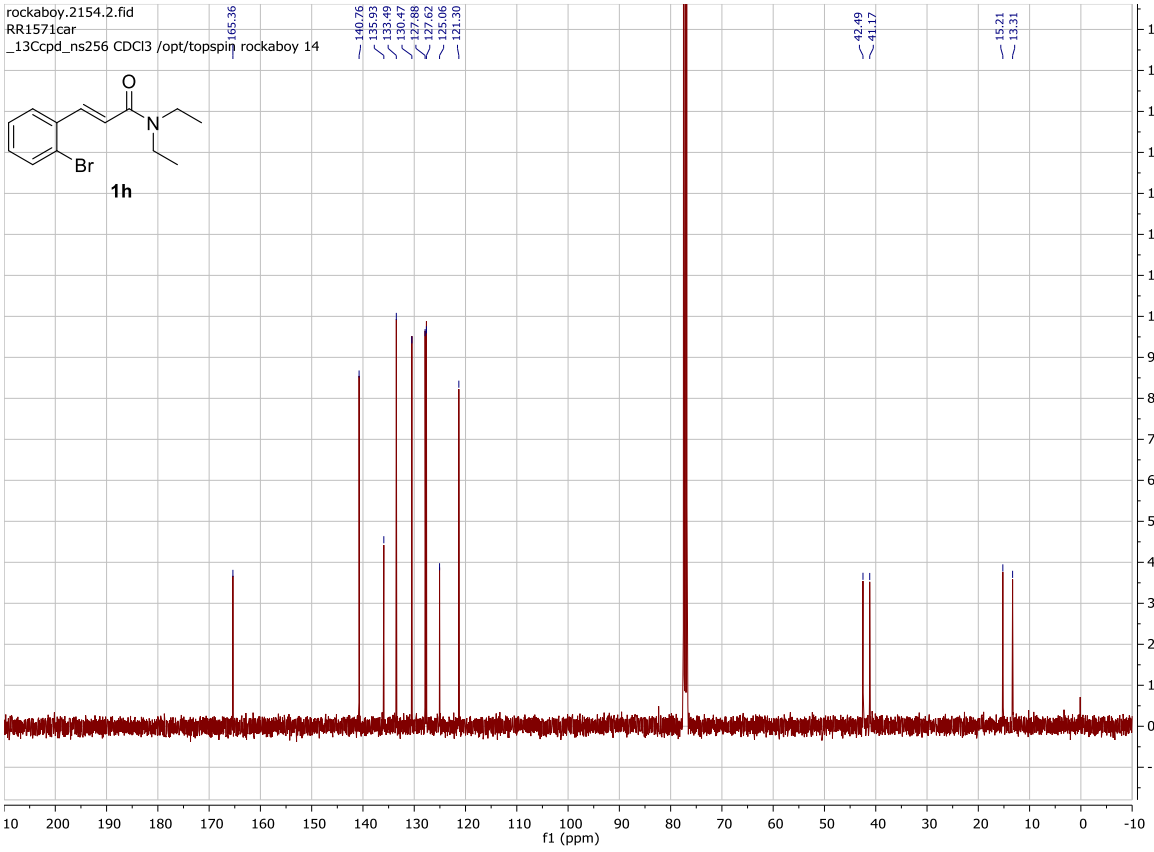
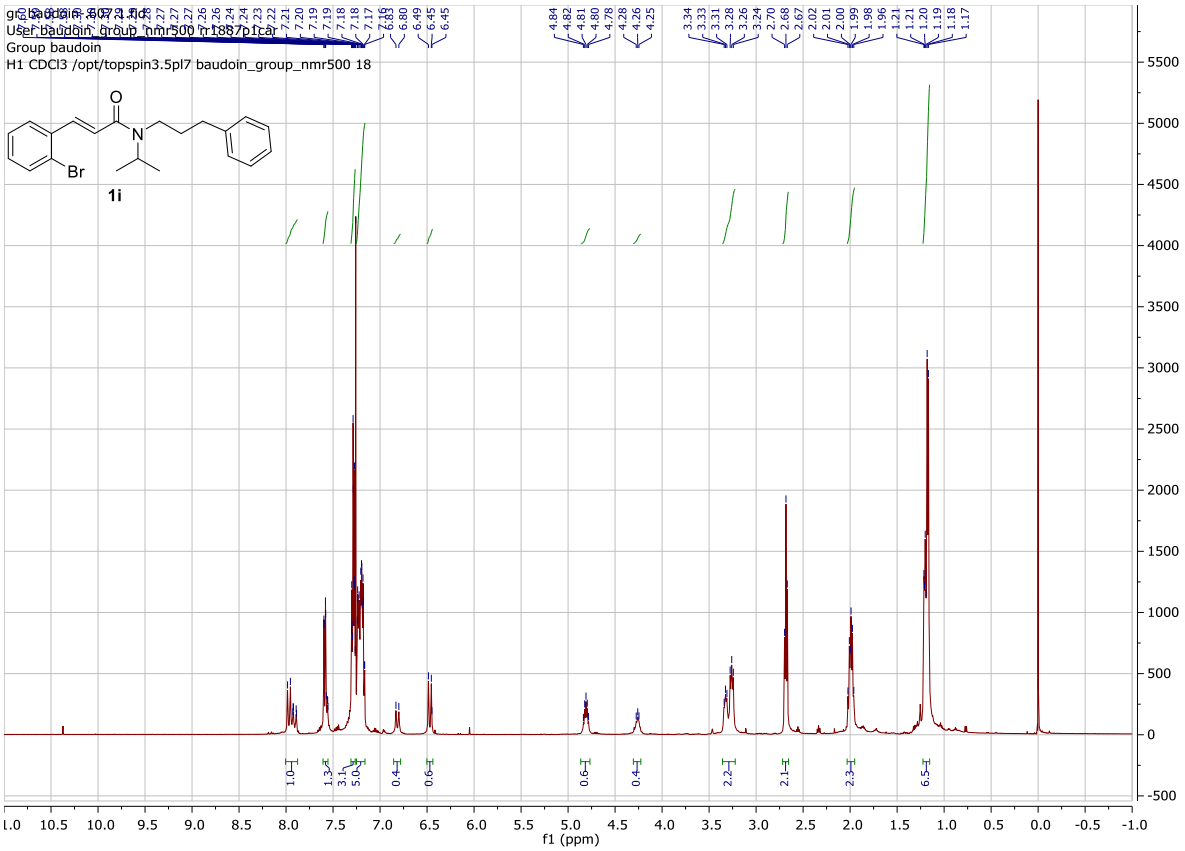
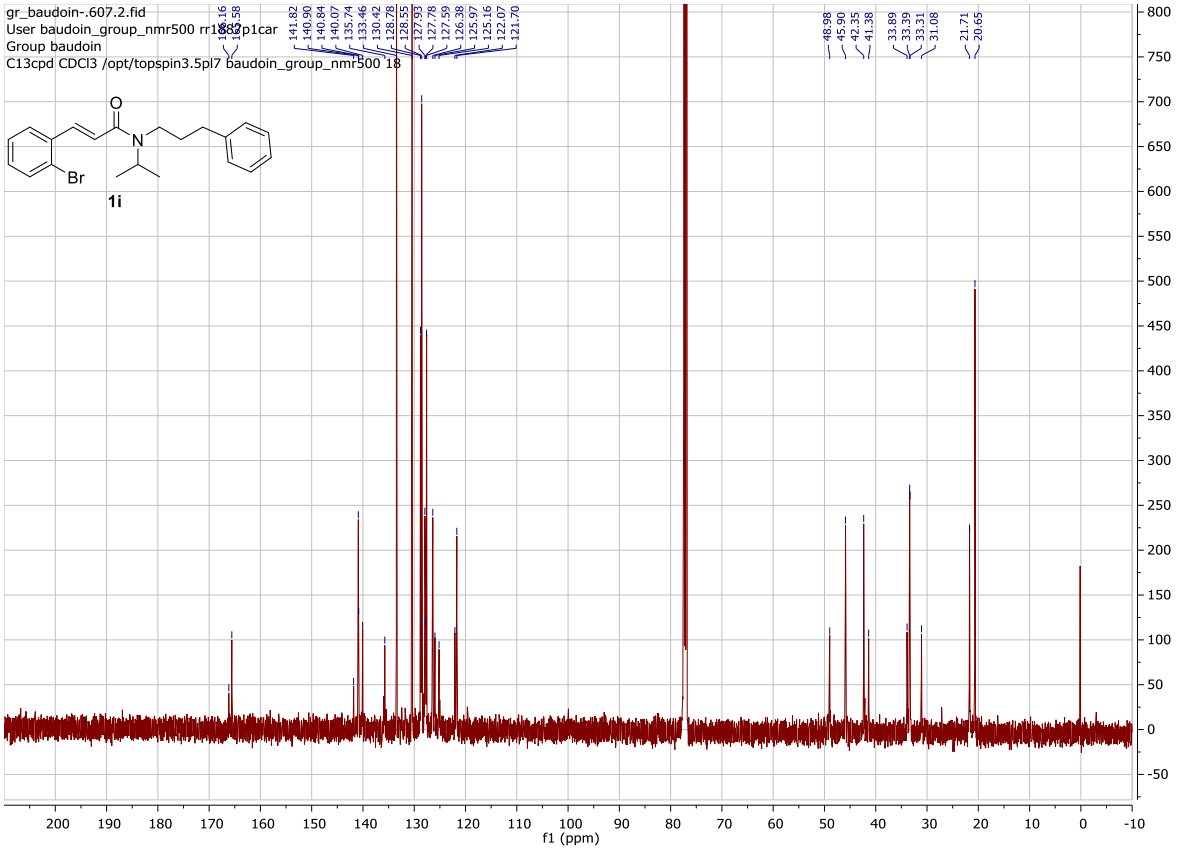
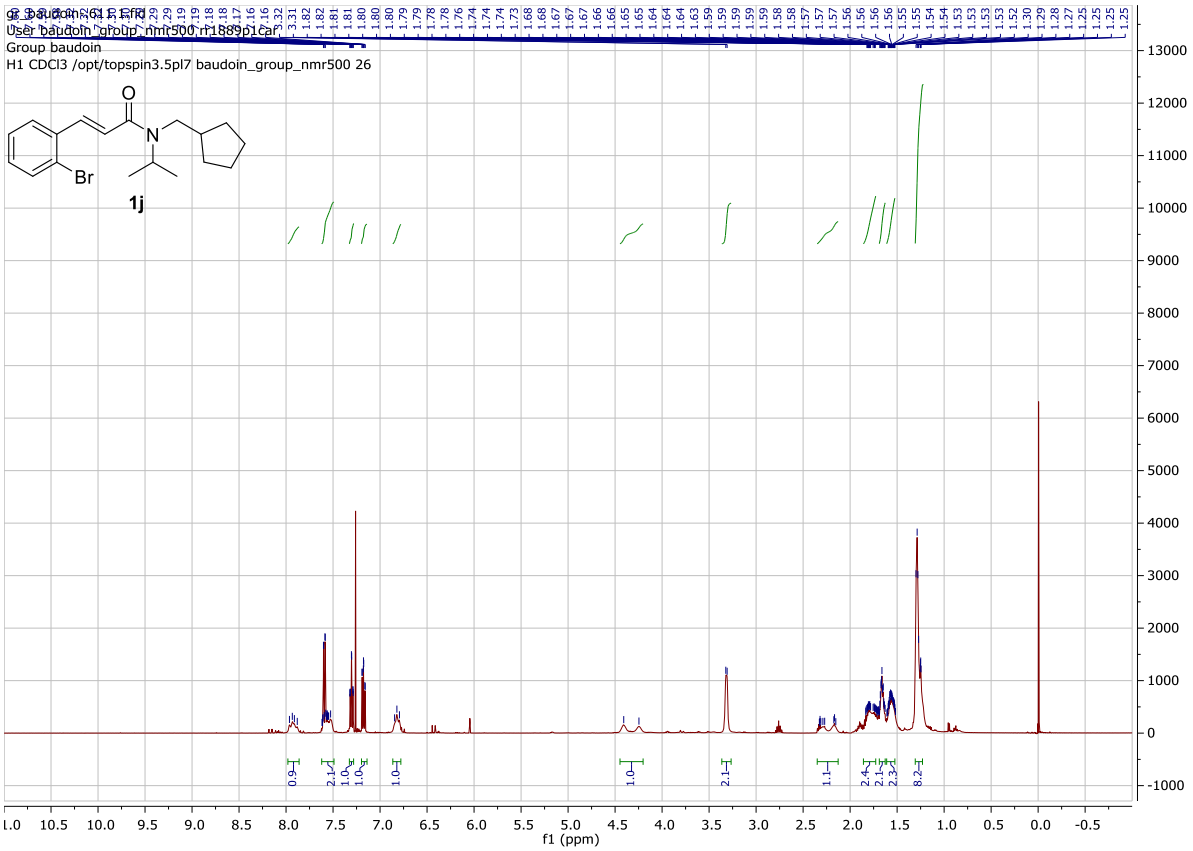
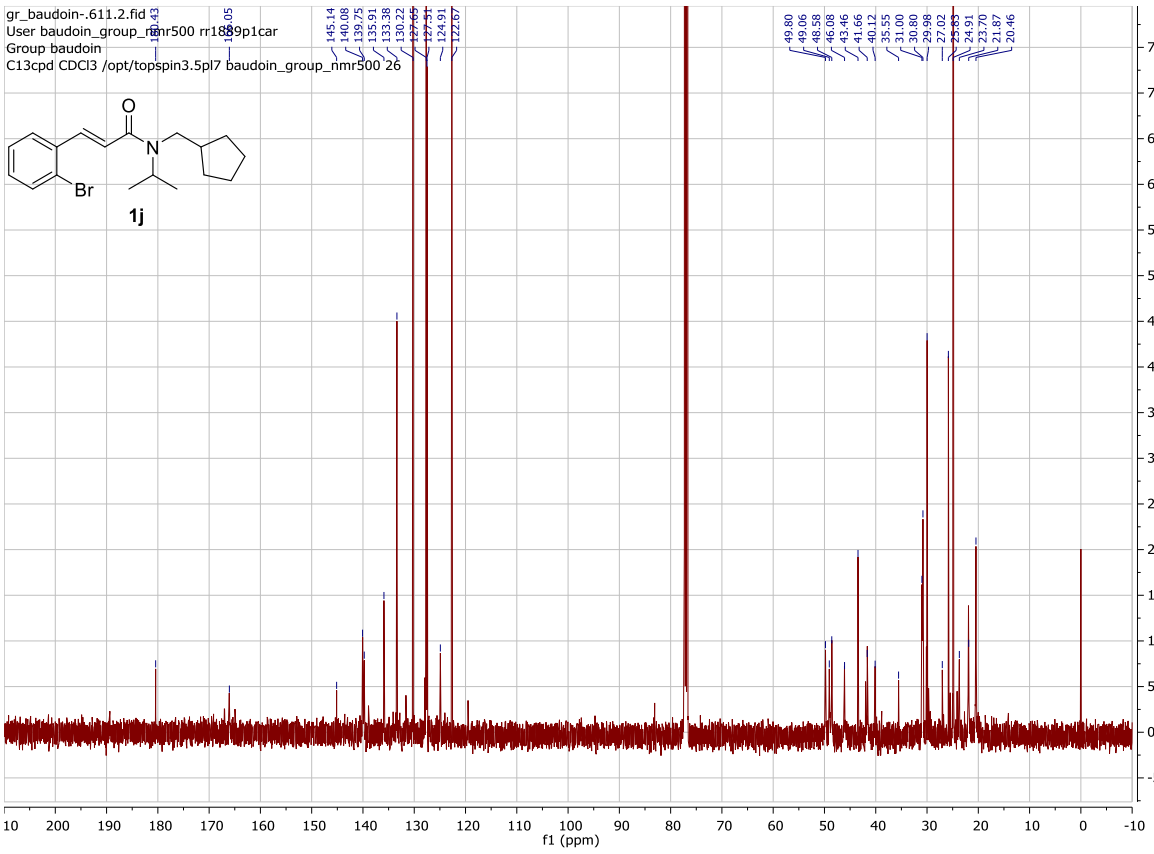
1h
f1 (ppm)


rockaboy.2154.2.fid
RR1571car
_13Ccpd_ns256 CDCl3 /opt/topspin rockaboy 14
1h
f1 (ppm)


User baudoin_group_nmr500 rr1887p1car
Group baudoin
H1 CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 18
1i
f1 (ppm)


gr_baudoin-.607.2.fid
User baudoin_group_nmr500 rr1887p1car
Group baudoin
C13cpd CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 18
1i
f1 (ppm)


gr_baudoin-.611.1.fid
User baudoin_group_nmr500 rr1889p1car
Group baudoin
H1 CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 26
O
N
Br
1j
f1 (ppm)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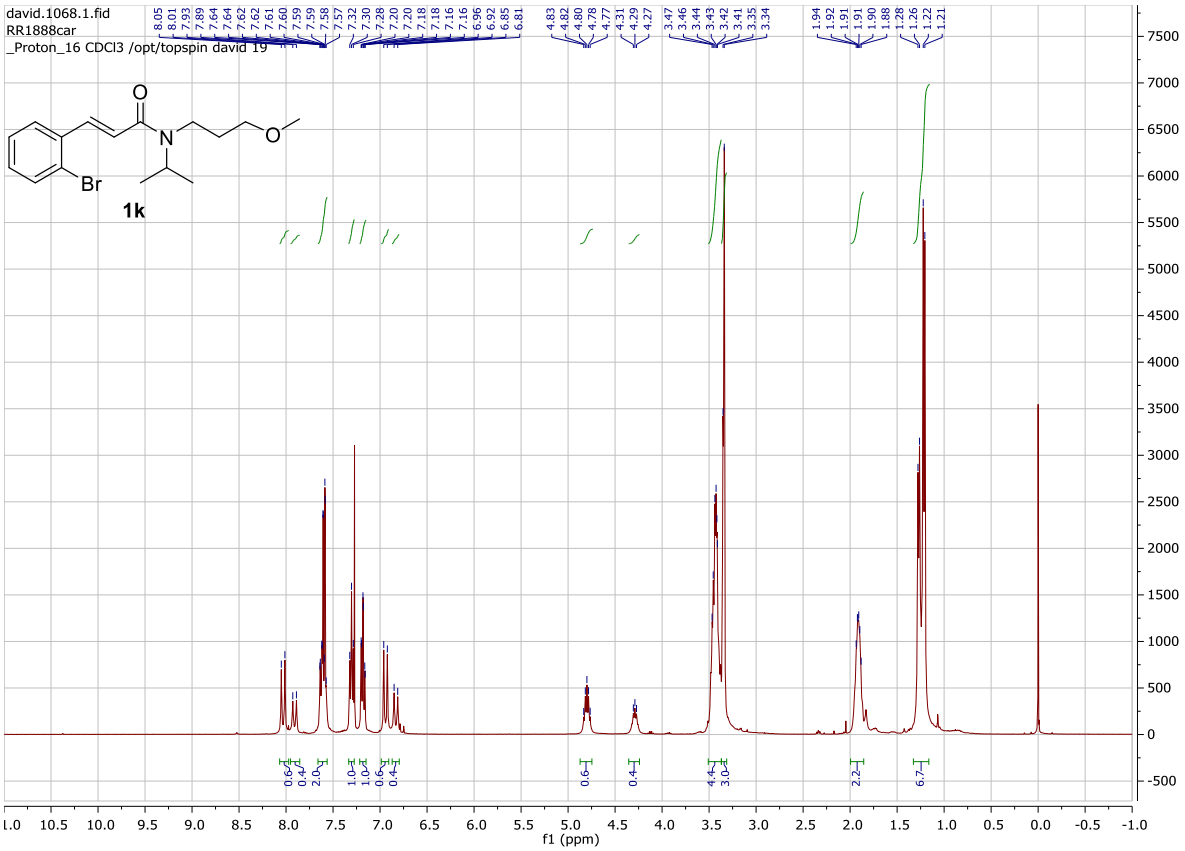
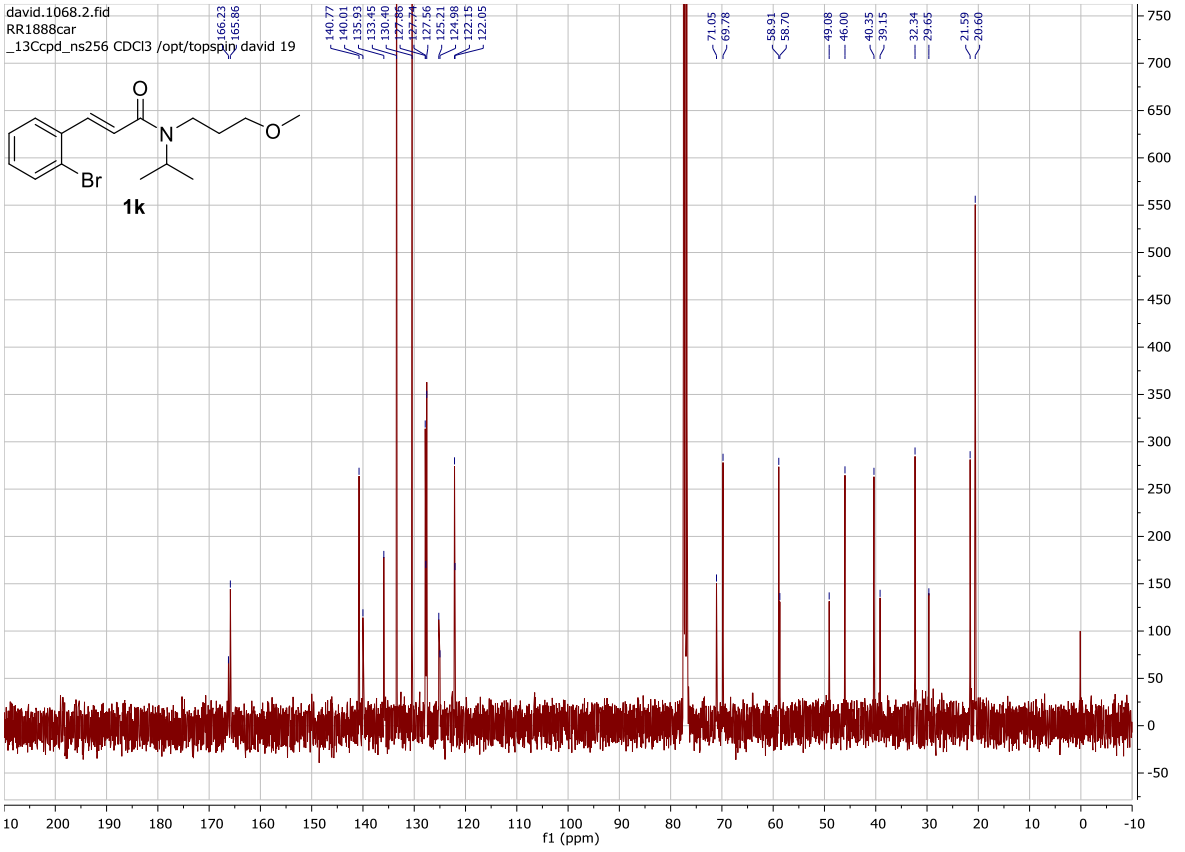
User baudoin_group_nmr500 rr1889p1car
Group baudoin
C13cpd CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 26
O
N
Br
1j
f1 (ppm)


david.1068.1.fid
RR1888car
_Proton_16 CDCl3 /opt/topspin david 19
1k
f1 (ppm)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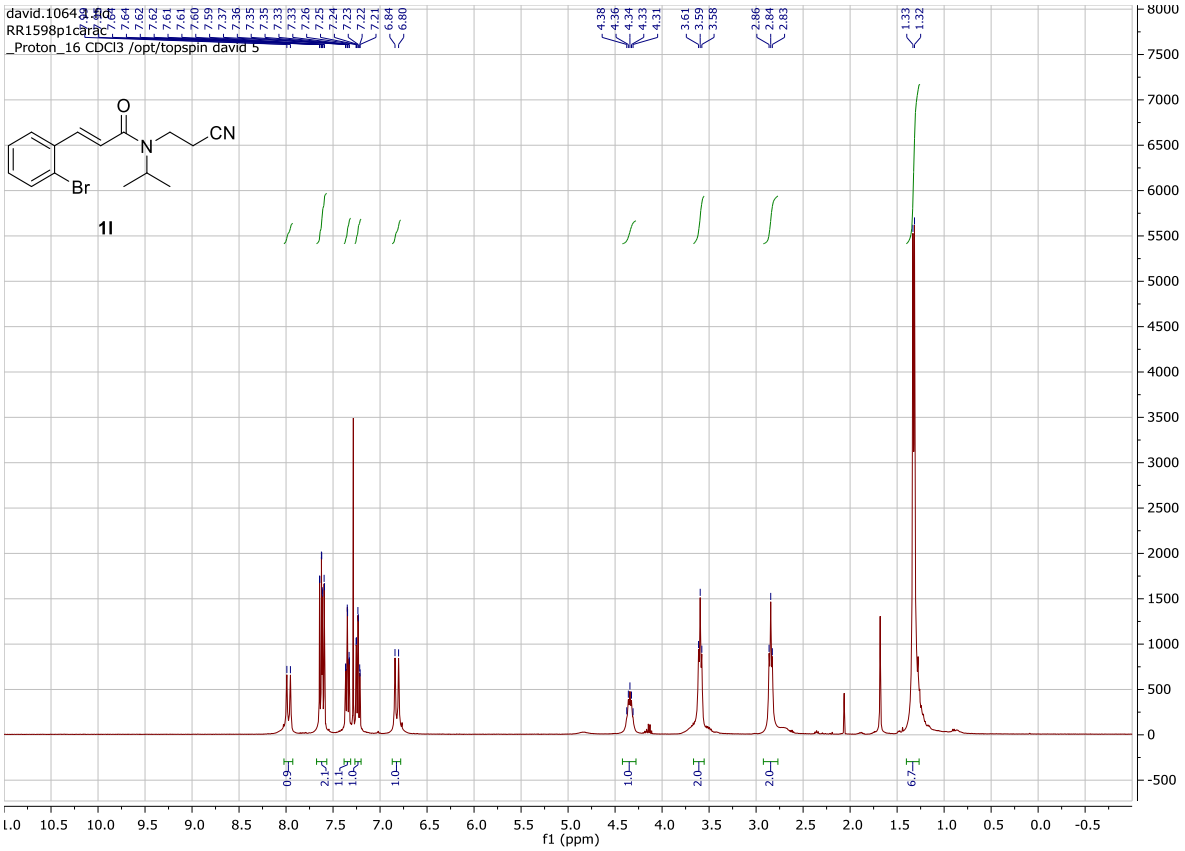
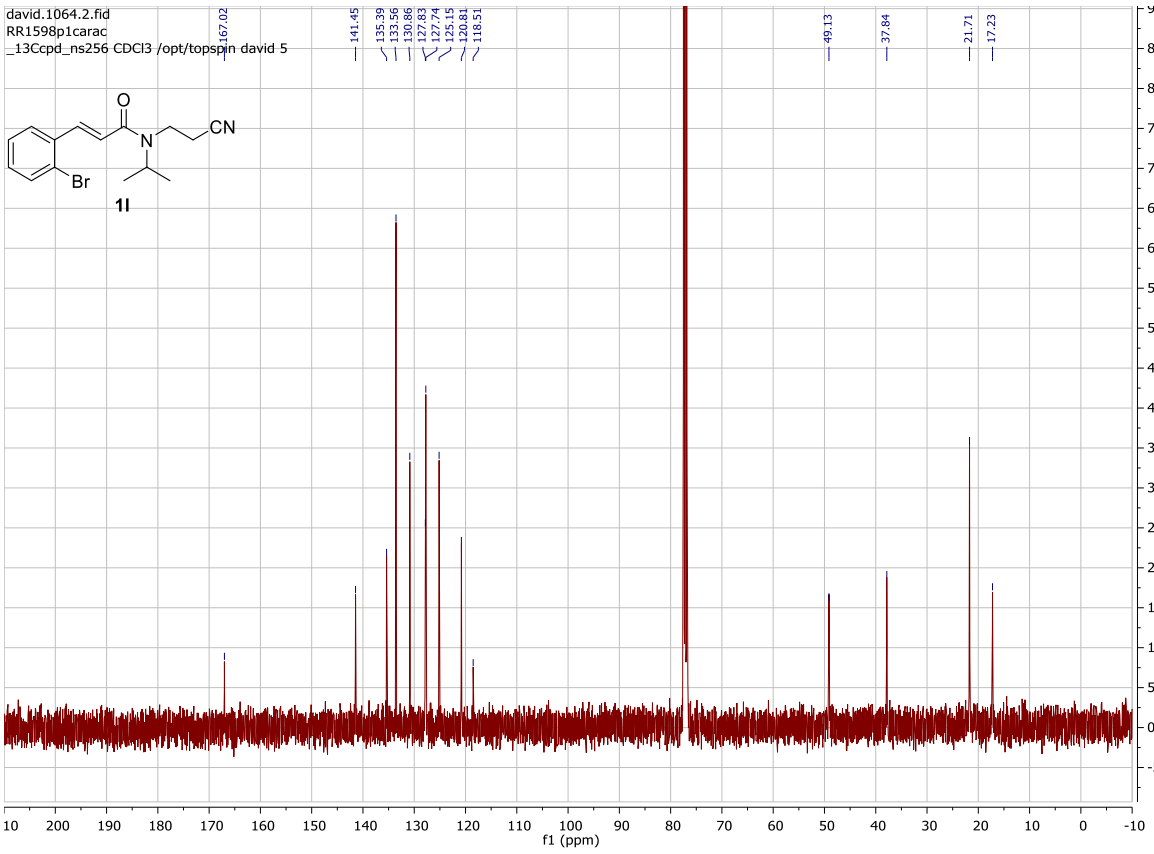
RR1888car
_13Ccpd_ns256 CDCl3 /opt/topspin david 19
1k
f1 (ppm)


david.1064.1.fid
RR1598p1carac
_Proton_16 CDCl3 /opt/topspin david 5
1l
f1 (ppm)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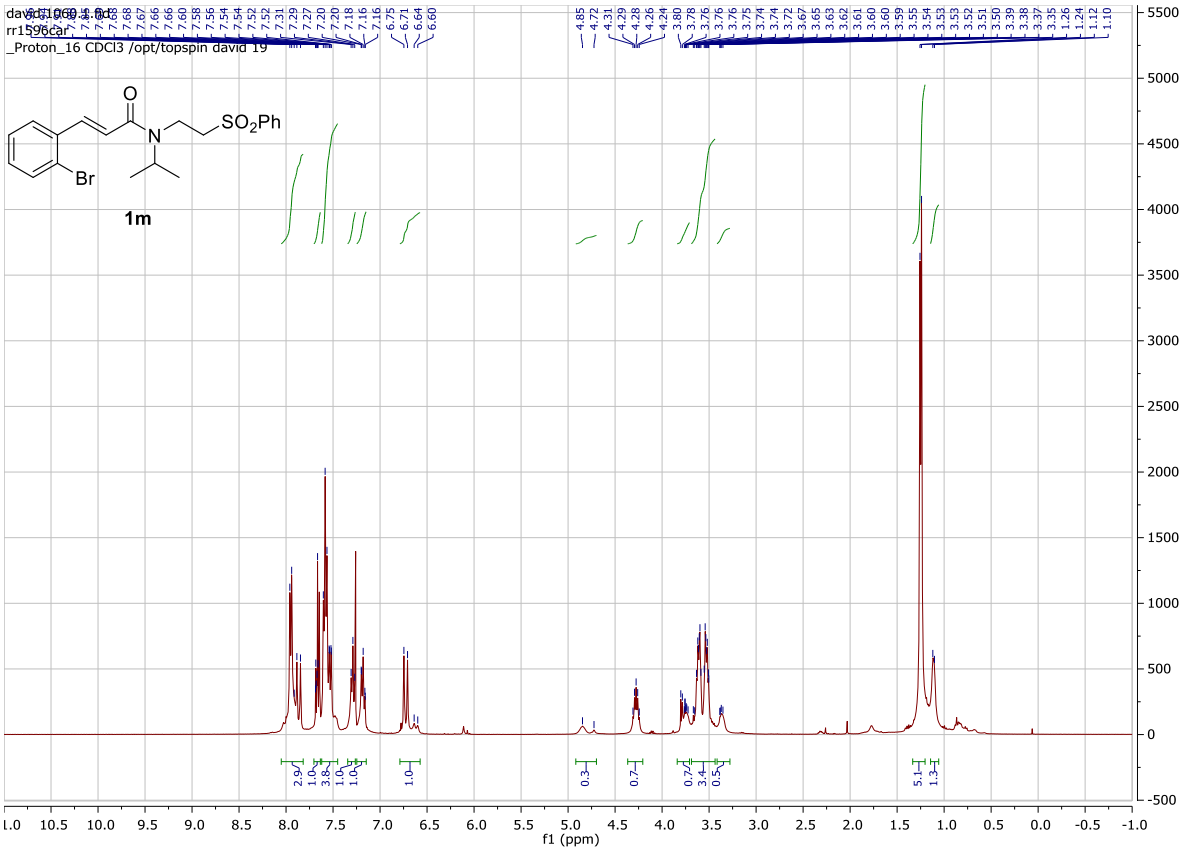
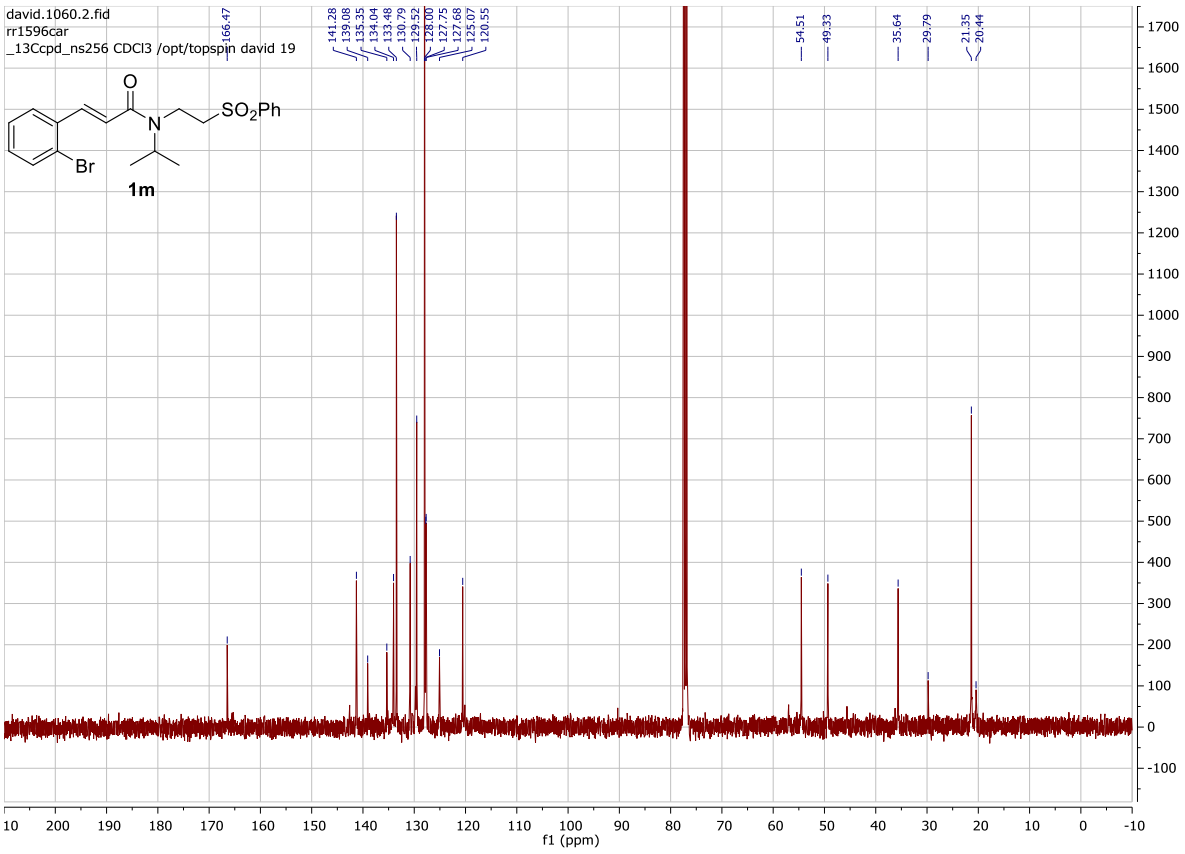
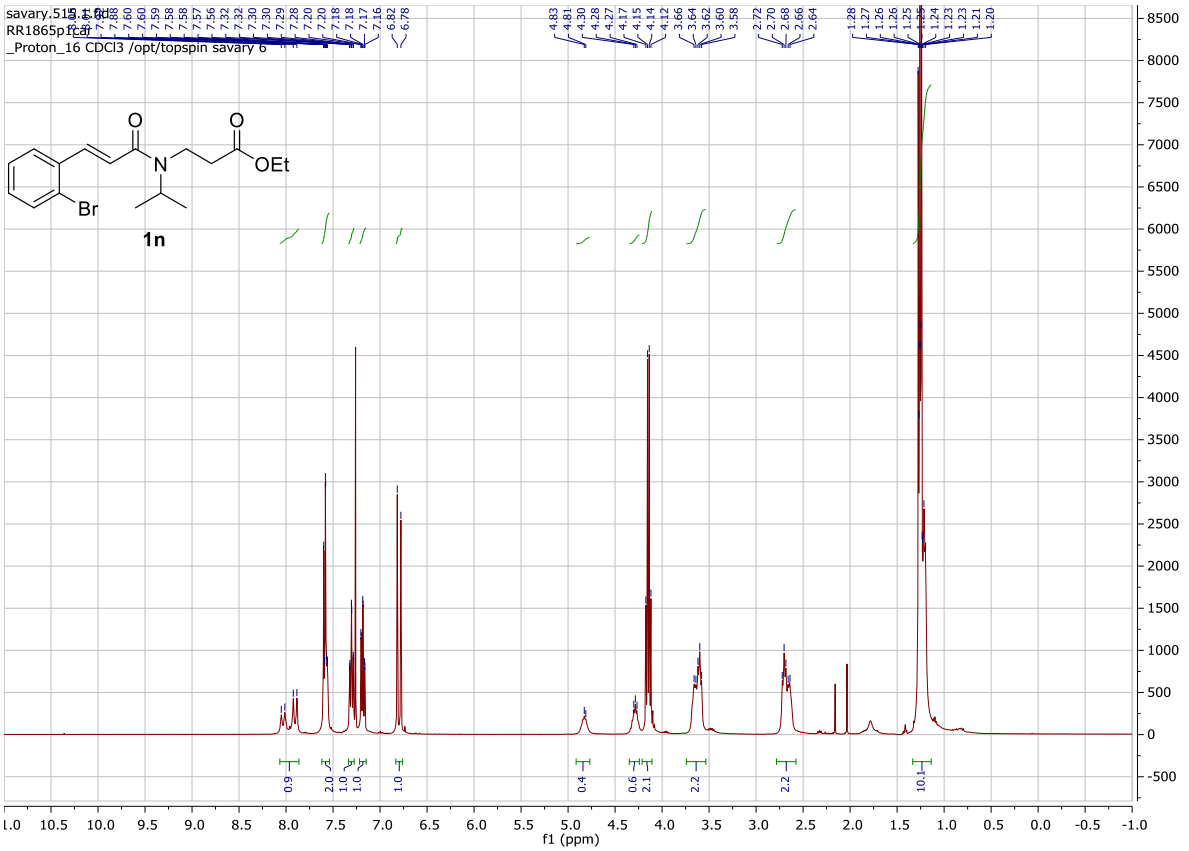
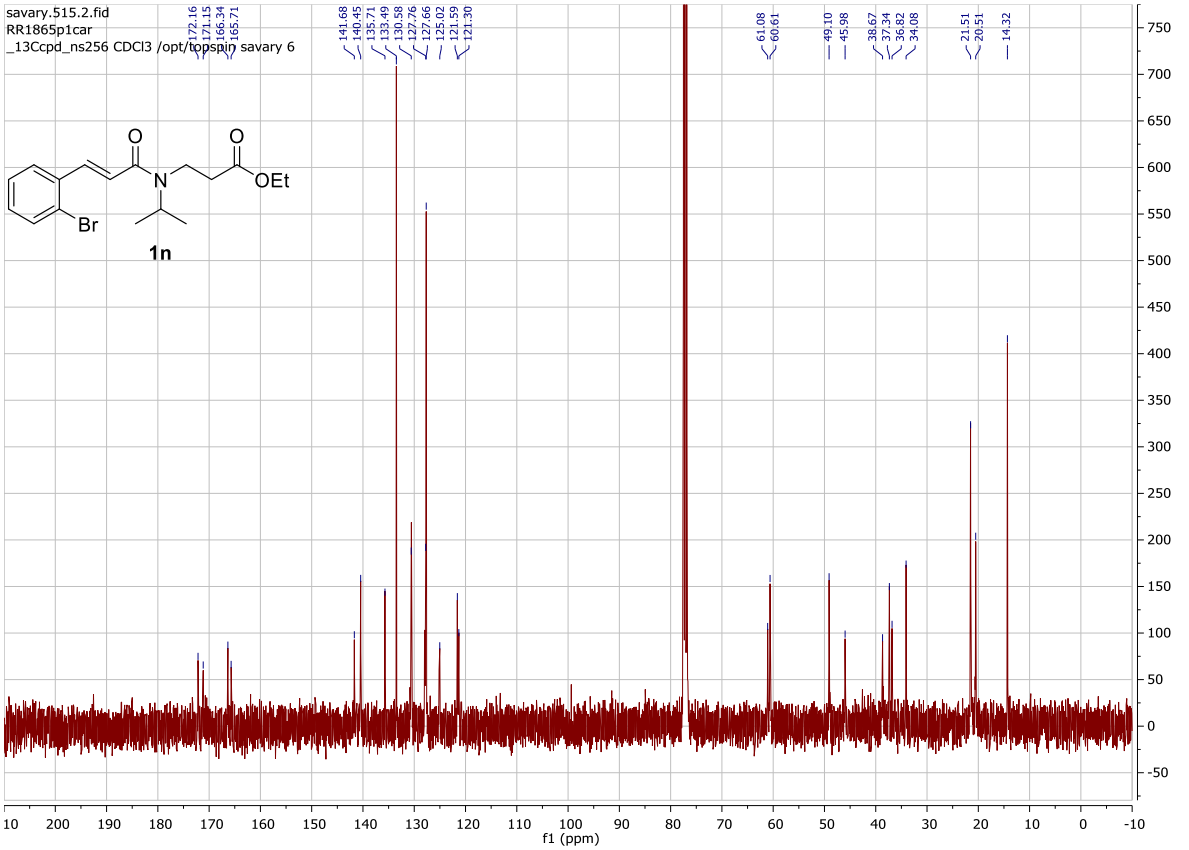
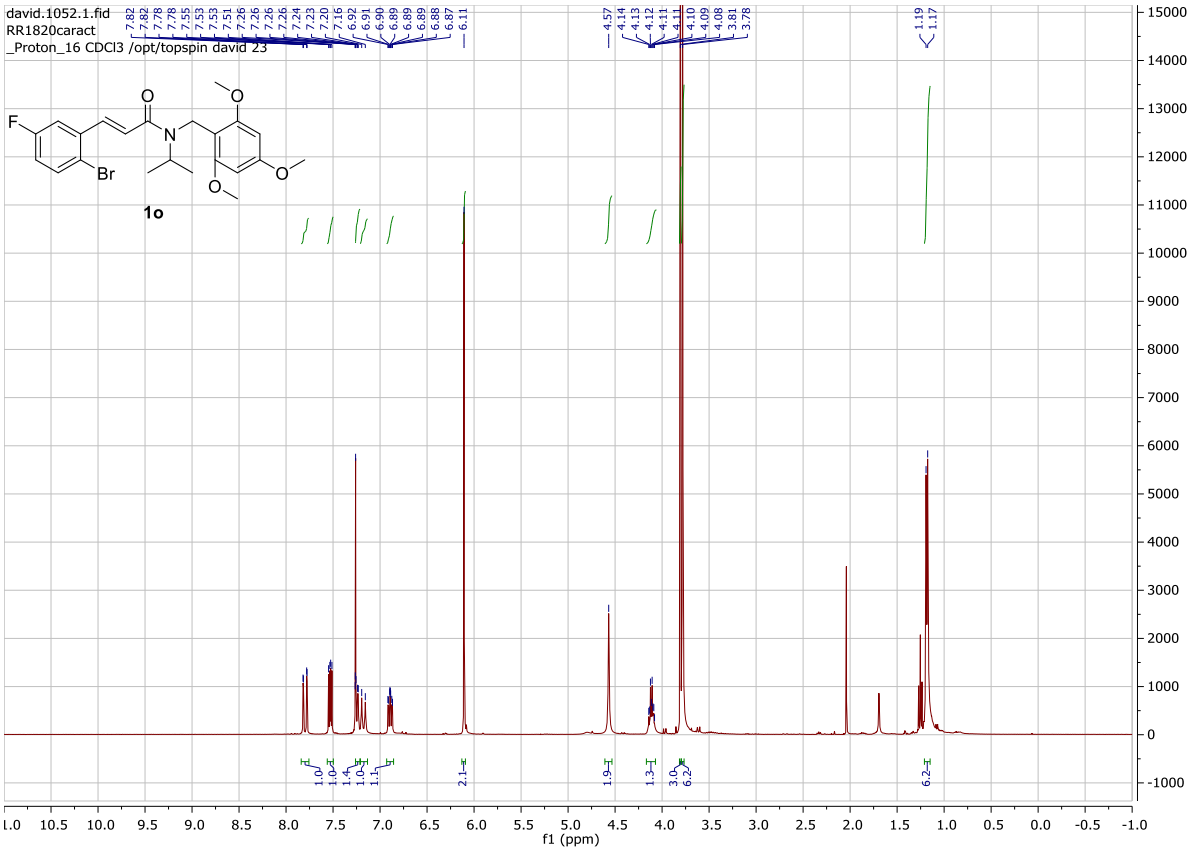
_13Ccpd_ns256 CDCl3 /opt/topspin david 5
1l
f1 (ppm)


david.1060.1.fid
rr1596car
_Proton_16 CDCl3 /opt/topspin david 19
O
N
SO2Ph
Br
1m
f1 (ppm)


david.1060.2.fid
rr1596car
_13Ccpd_ns256 CDCl3 /opt/topspin david 19
O
N
SO2Ph
Br
1m
f1 (ppm)


savary.515.1.fid
RR1865p1car
_Proton_16 CDCl3 /opt/topspin savary 6
O
O
N
OEt
Br
1n
f1 (ppm)


savary.515.2.fid
RR1865p1car
_13Ccpd_ns256 CDCl3 /opt/topspin savary 6
O
O
N
OEt
Br
1n
f1 (ppm)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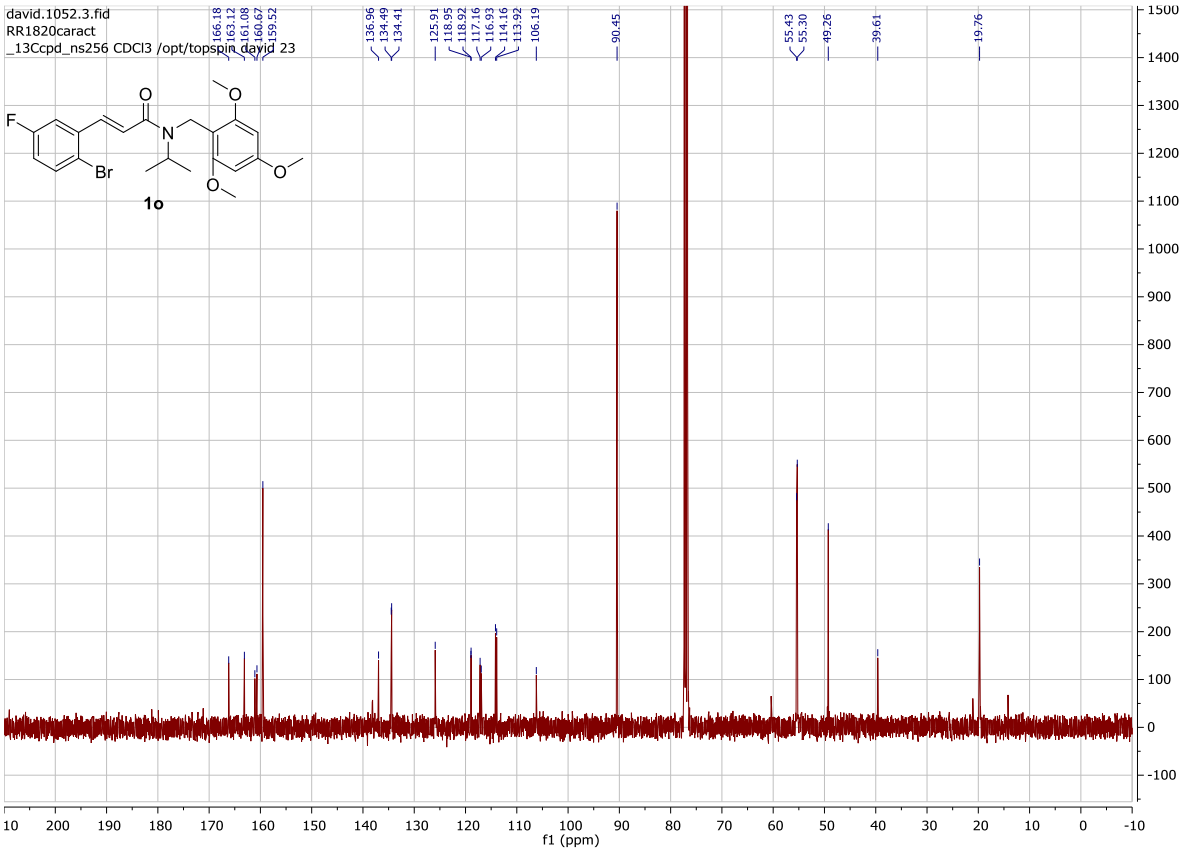
RR1820caract
_Proton_16 CDCl3 /opt/topspin david 23
1o
f1 (ppm)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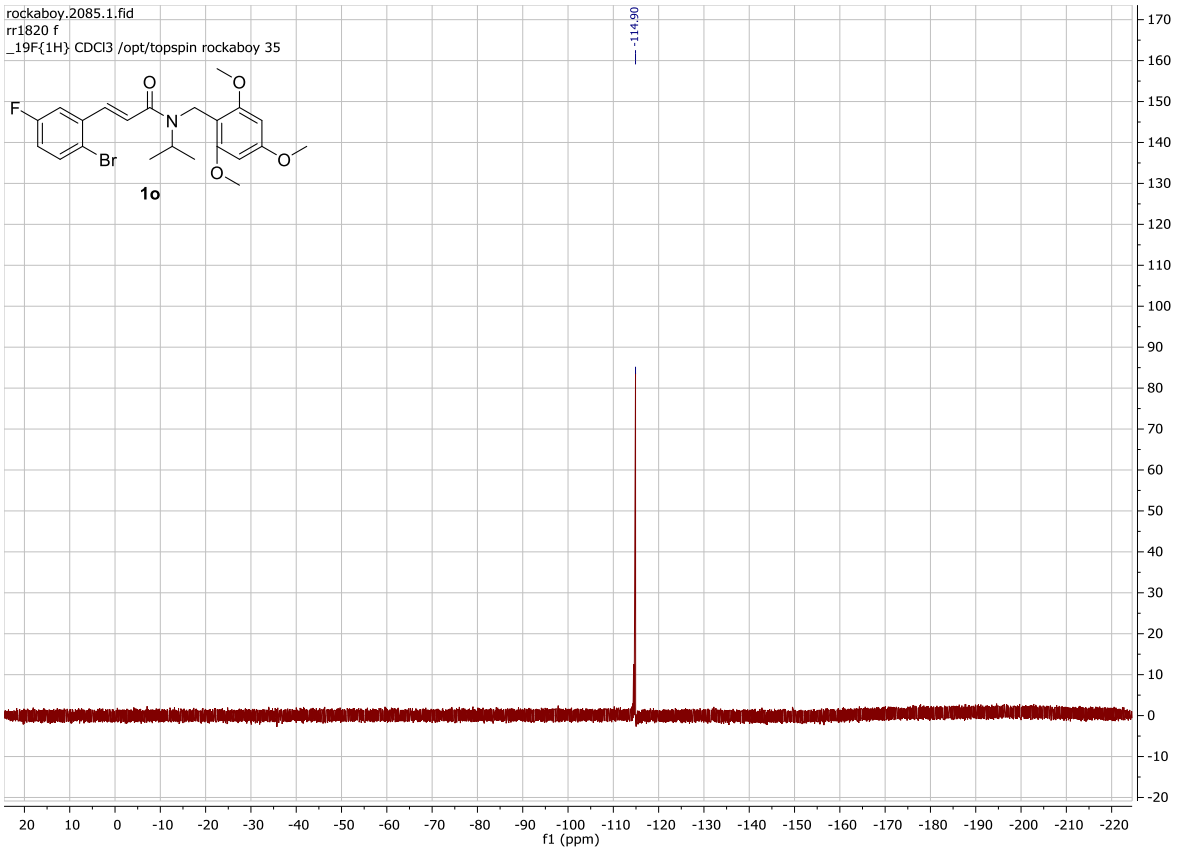
RR1820caract
_13Ccpd_ns256 CDCl3 /opt/topspin david 23
1o
f1 (ppm)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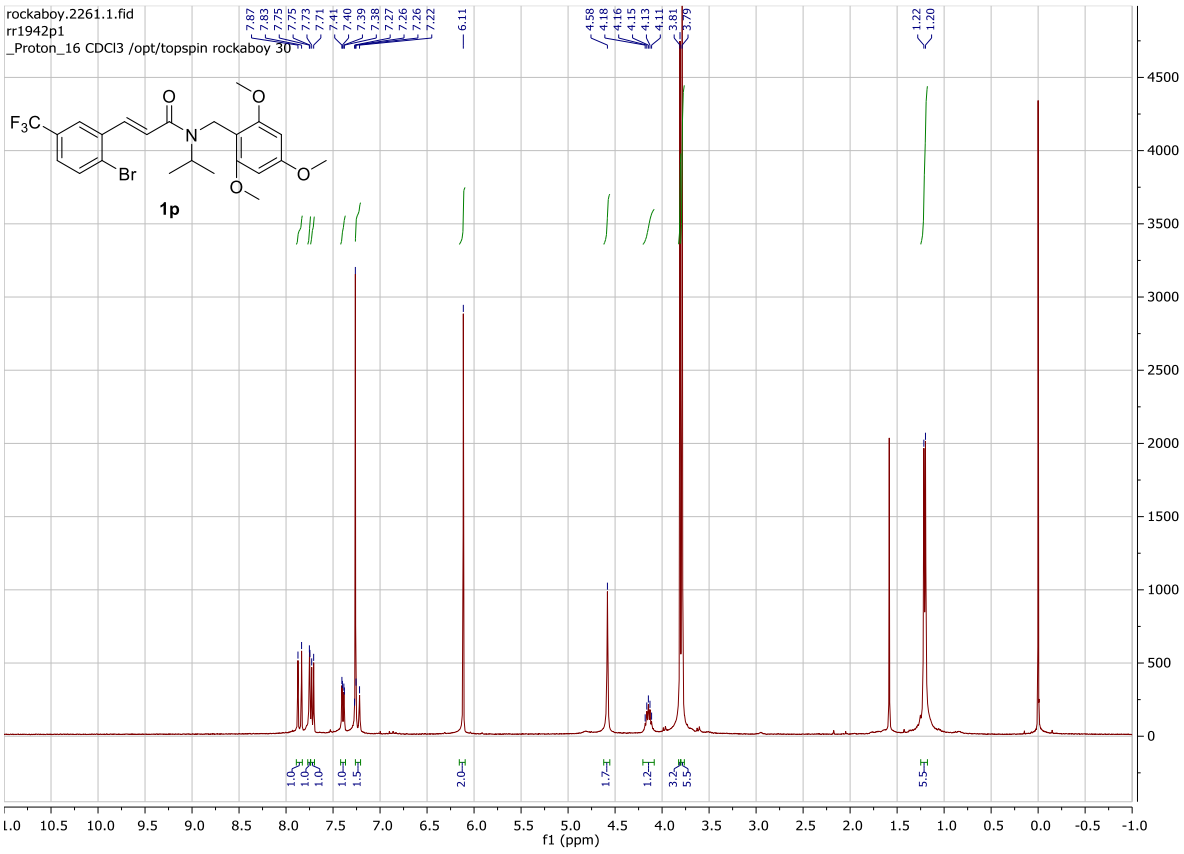
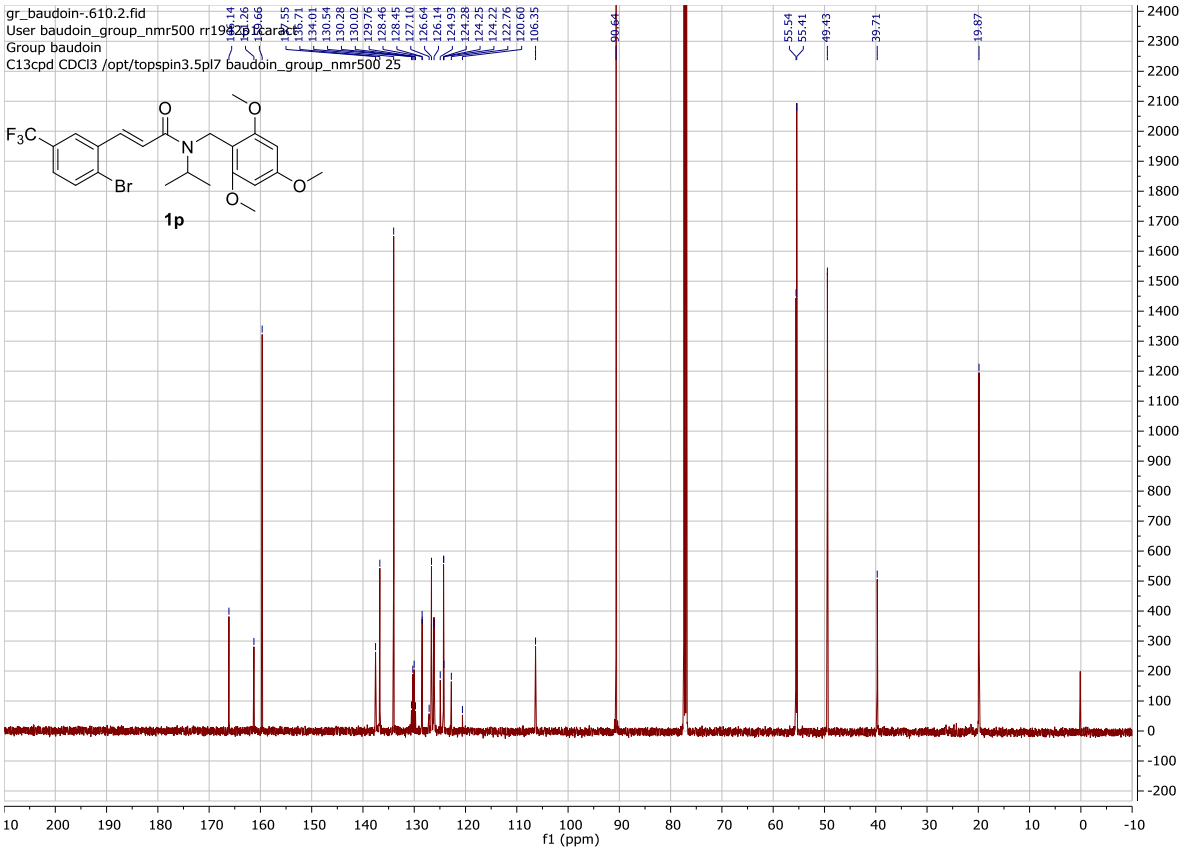
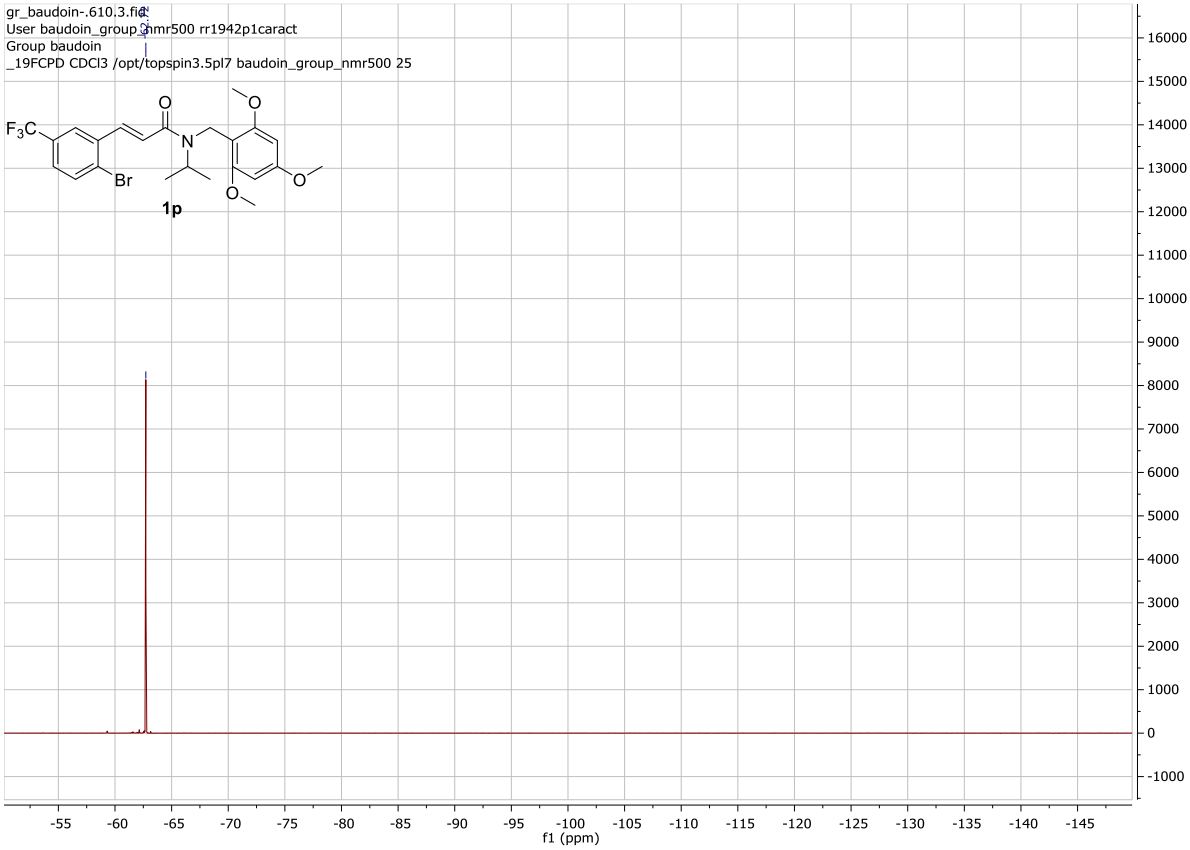
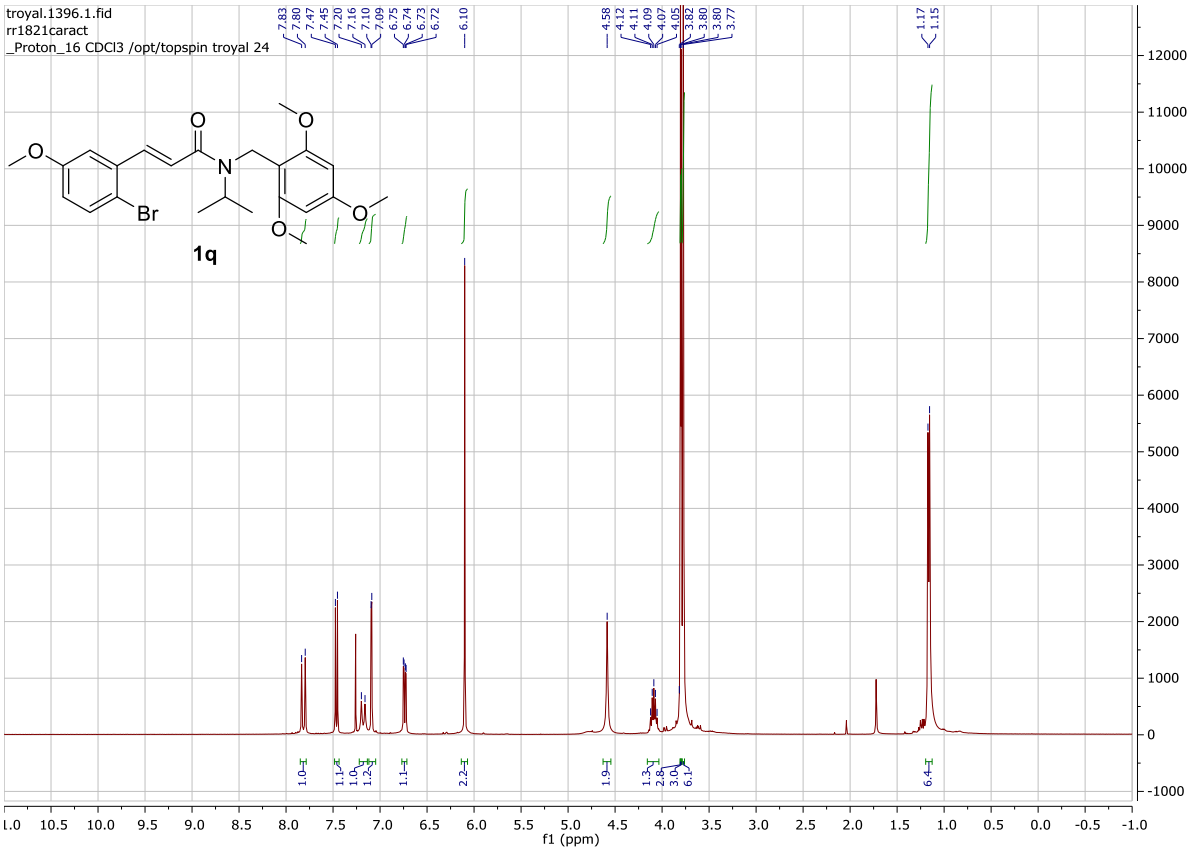
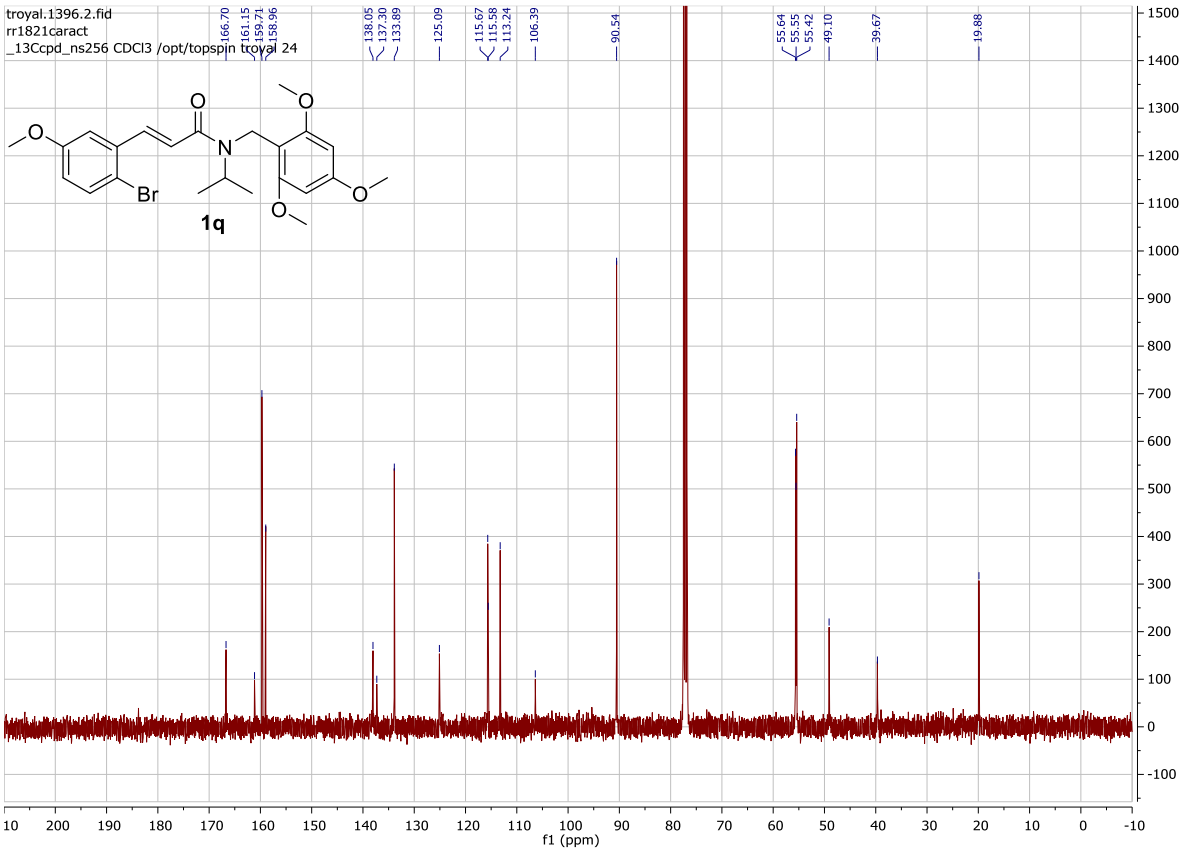
rr1820 f
_19F{1H} CDCl3 /opt/topspin rockaboy 35
-114.90
1o
f1 (ppm)

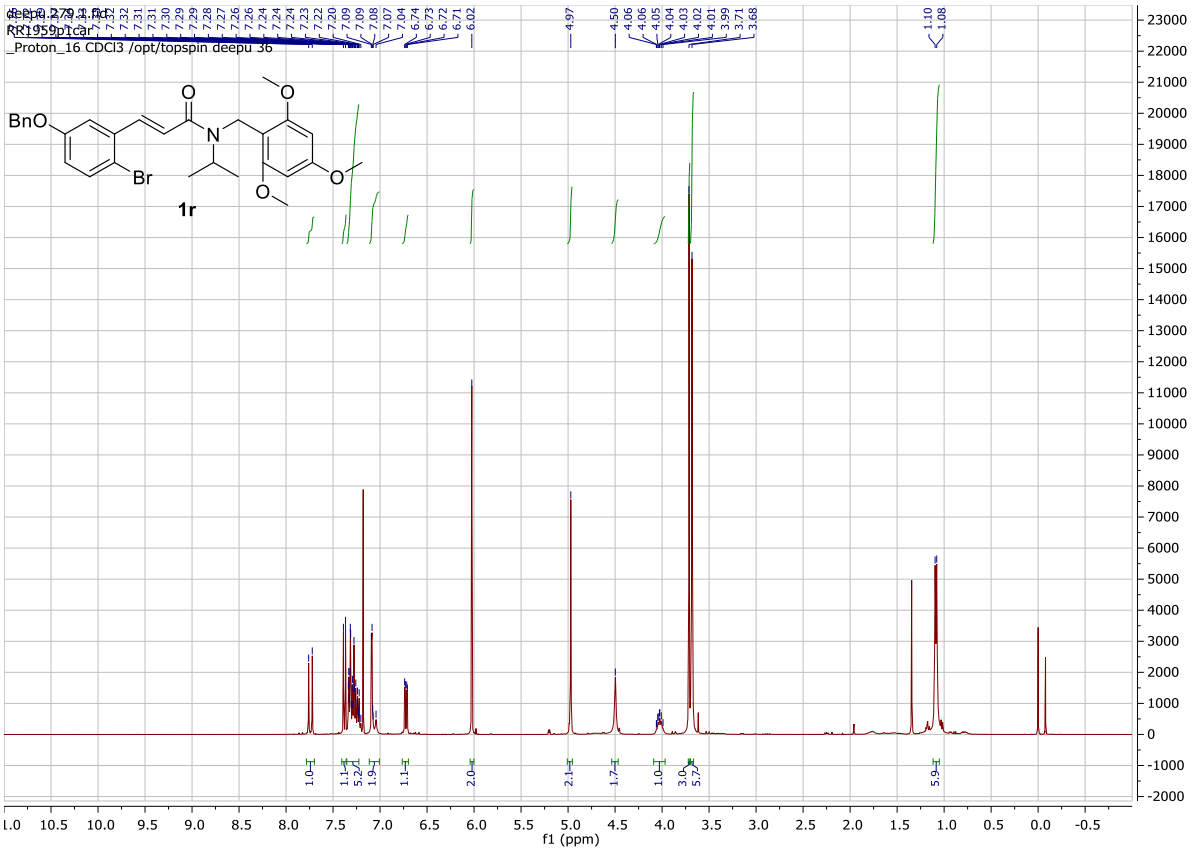

rockaboy.2261.1.fid
rr1942p1
_Proton_16 CDCl3 /opt/topspin rockaboy 30
7.87
7.83
7.75
7.75
7.73
7.71
7.41
7.40
7.39
7.38
7.27
7.26
7.26
7.22
6.11
4.58
4.18
4.16
4.15
4.13
4.11
3.81
3.79
1.22
1.20
1p
f1 (ppm)

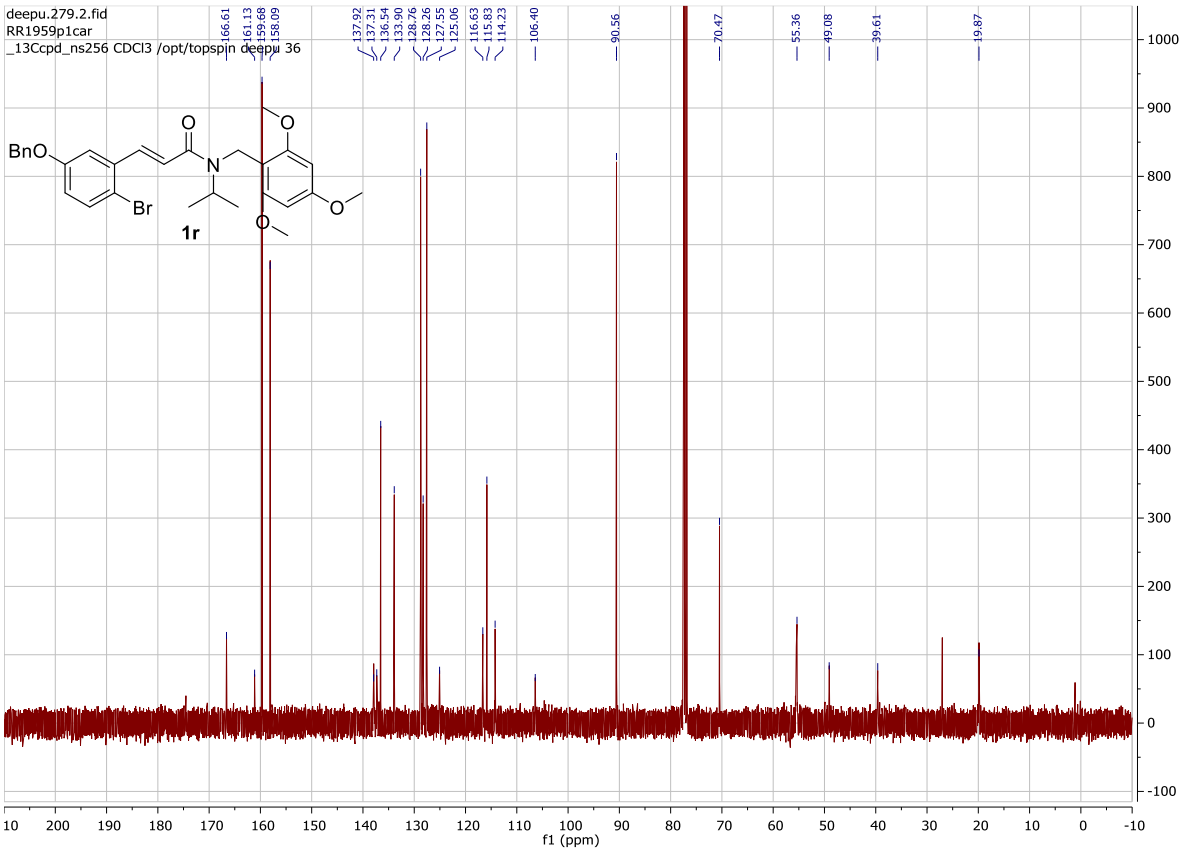

gr_baudoin-.610.2.fid
User baudoin_group_nmr500 rr1942p1caract
Group baudoin
C13cpd CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 25
1p
f1 (ppm)

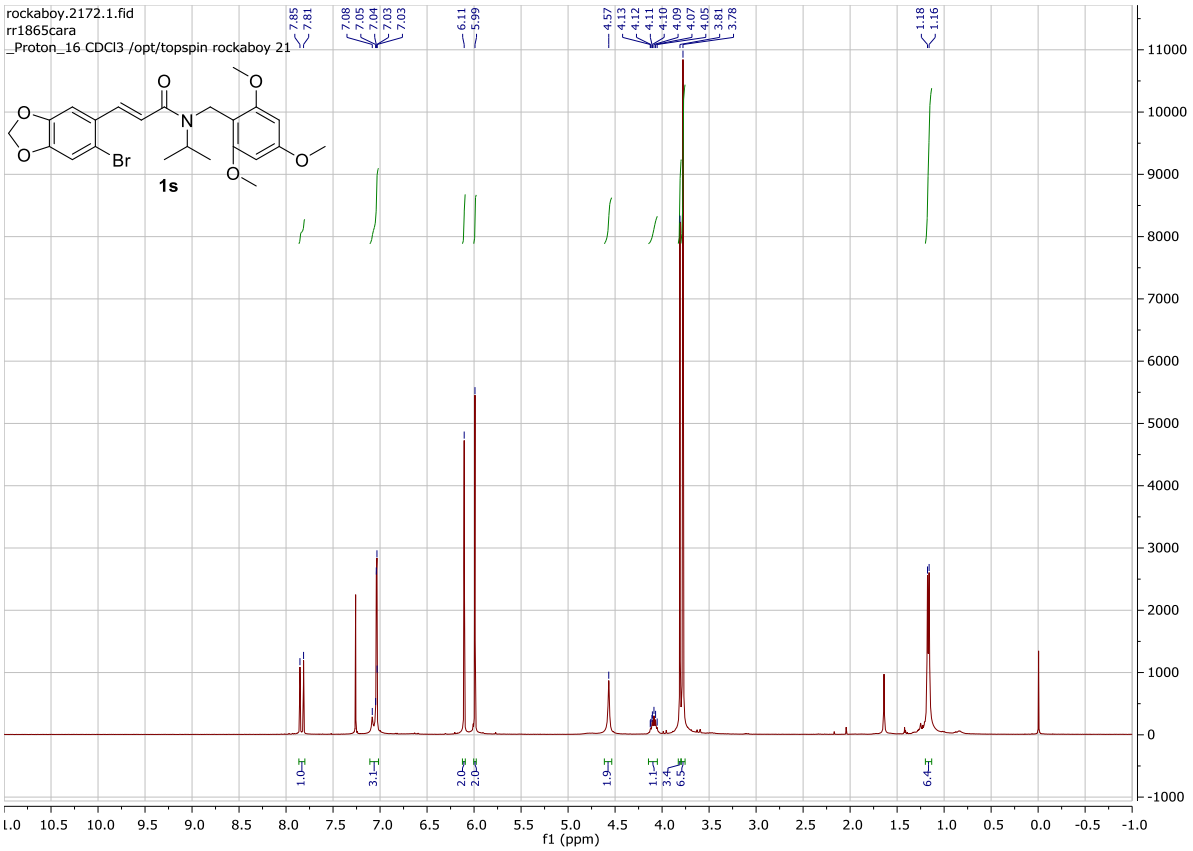

gr_baudoin-.610.3.fid
User baudoin_group_nmr500 rr1942p1caract
Group baudoin
_19FCPD CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 25
1p
f1 (ppm)

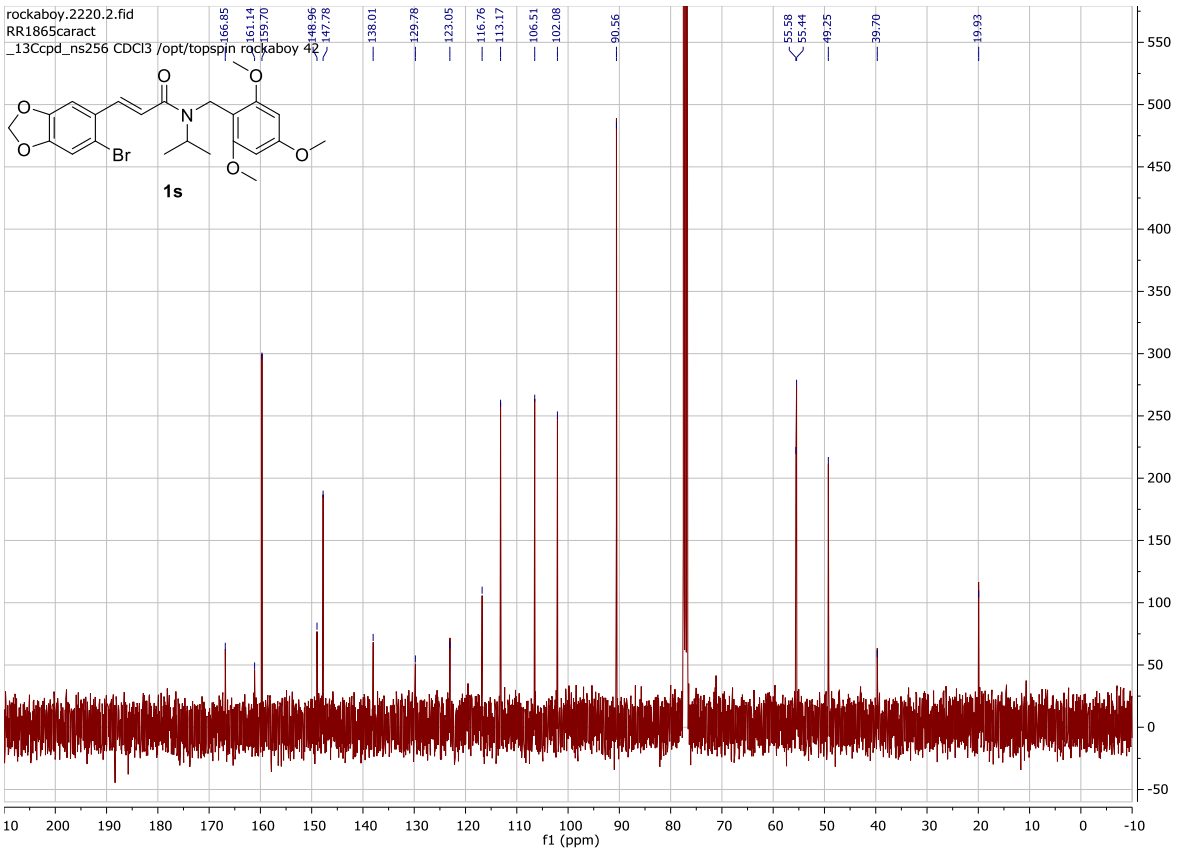

troyal.1396.1.fid
rr1821caract
_Proton_16 CDCl3 /opt/topspin troyal 24
7.83
7.80
7.47
7.45
7.20
7.16
7.10
7.09
6.75
6.74
6.73
6.72
6.10
4.58
4.12
4.11
4.09
4.07
4.05
3.82
3.80
3.80
3.77
1.17
1.15
1q
f1 (ppm)

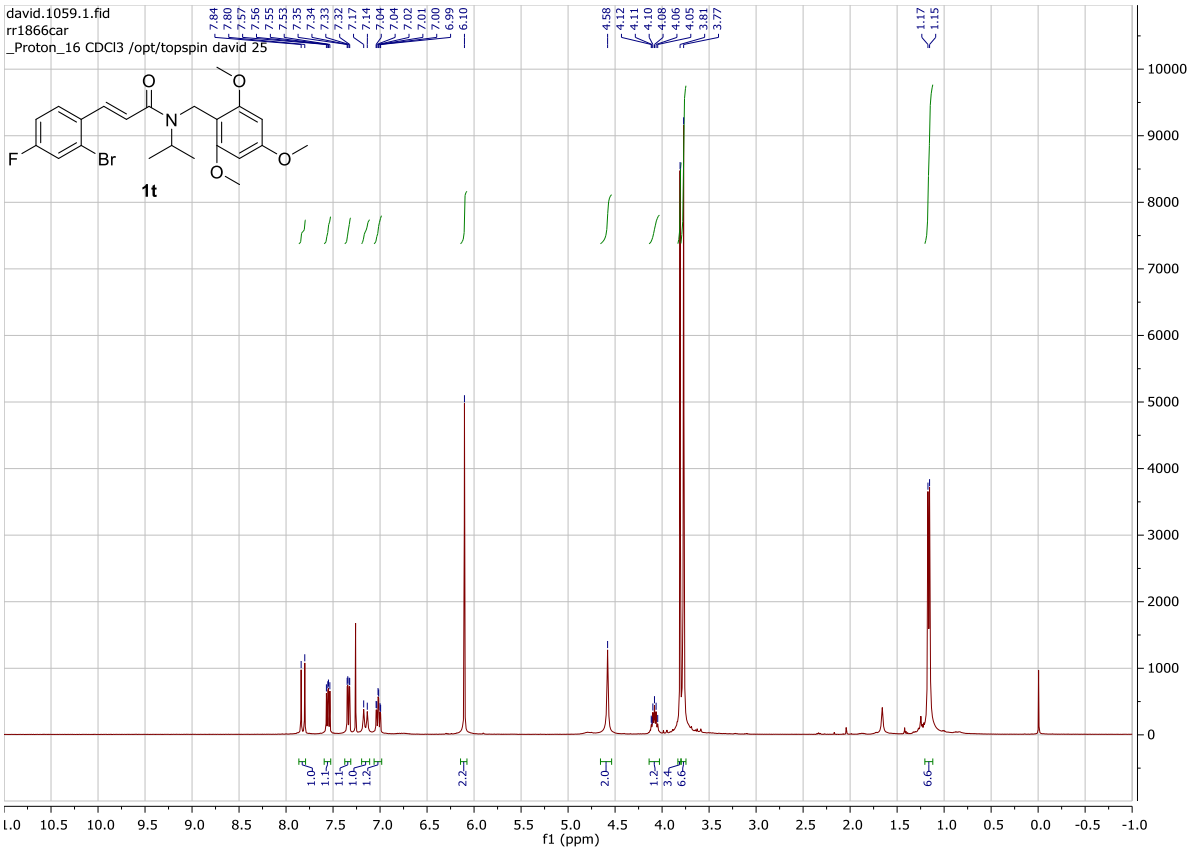

troyal.1396.2.fid
rr1821caract
_13Ccpd_ns256 CDCl3 /opt/topspin troyal 24
166.70
161.15
159.71
158.96
138.05
137.30
133.89
125.09
115.67
115.58
113.24
106.39
90.54
55.64
55.55
55.42
49.10
39.67
19.88
1q
f1 (ppm)


deepu.279.1.fid
RR1959p1car
_Proton_16 CDCl3 /opt/topspin deepu 36
BnO
Br
1r
f1 (ppm)


deepu.279.2.fid
RR1959p1car
_13Ccpd_ns256 CDCl3 /opt/topspin deepu 36
BnO
Br
1r
f1 (ppm)


rockaboy.2172.1.fid
rr1865cara
_Proton_16 CDCl3 /opt/topspin rockaboy 21
7.85
7.81
7.08
7.05
7.04
7.03
7.03
6.11
5.99
4.57
4.13
4.12
4.11
4.10
4.09
4.07
4.05
3.81
3.78
1.18
1.16
1s
1.0
3.1
2.0
2.0
1.9
1.1
3.4
6.5
6.4
f1 (ppm)


rockaboy.2220.2.fid
RR1865caract
_13Ccpd_ns256 CDCl3 /opt/topspin rockaboy 42
166.85
161.14
159.70
148.96
147.78
138.01
129.78
123.05
116.76
113.17
106.51
102.08
90.56
55.58
55.44
49.25
39.70
19.93
1s
f1 (ppm)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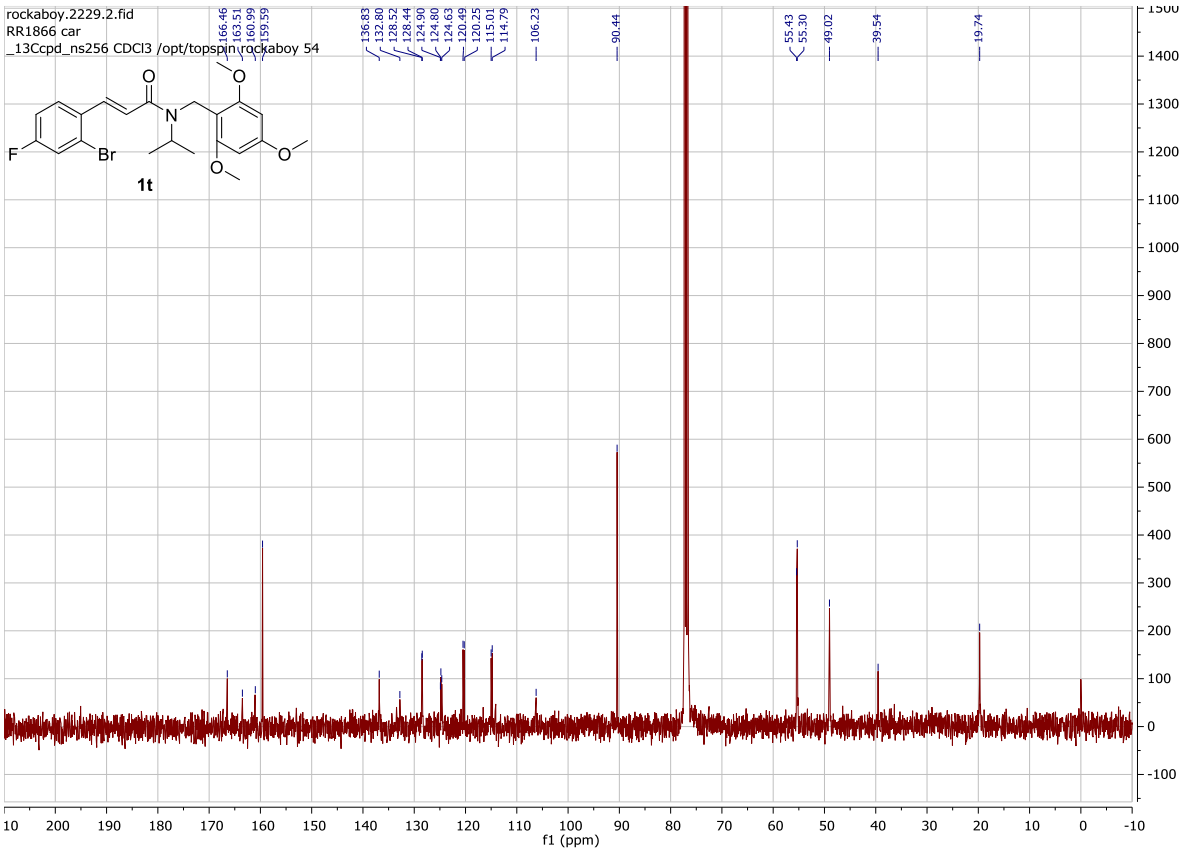
rr1866car
_Proton_16 CDCl3 /opt/topspin david 25
1t
f1 (ppm)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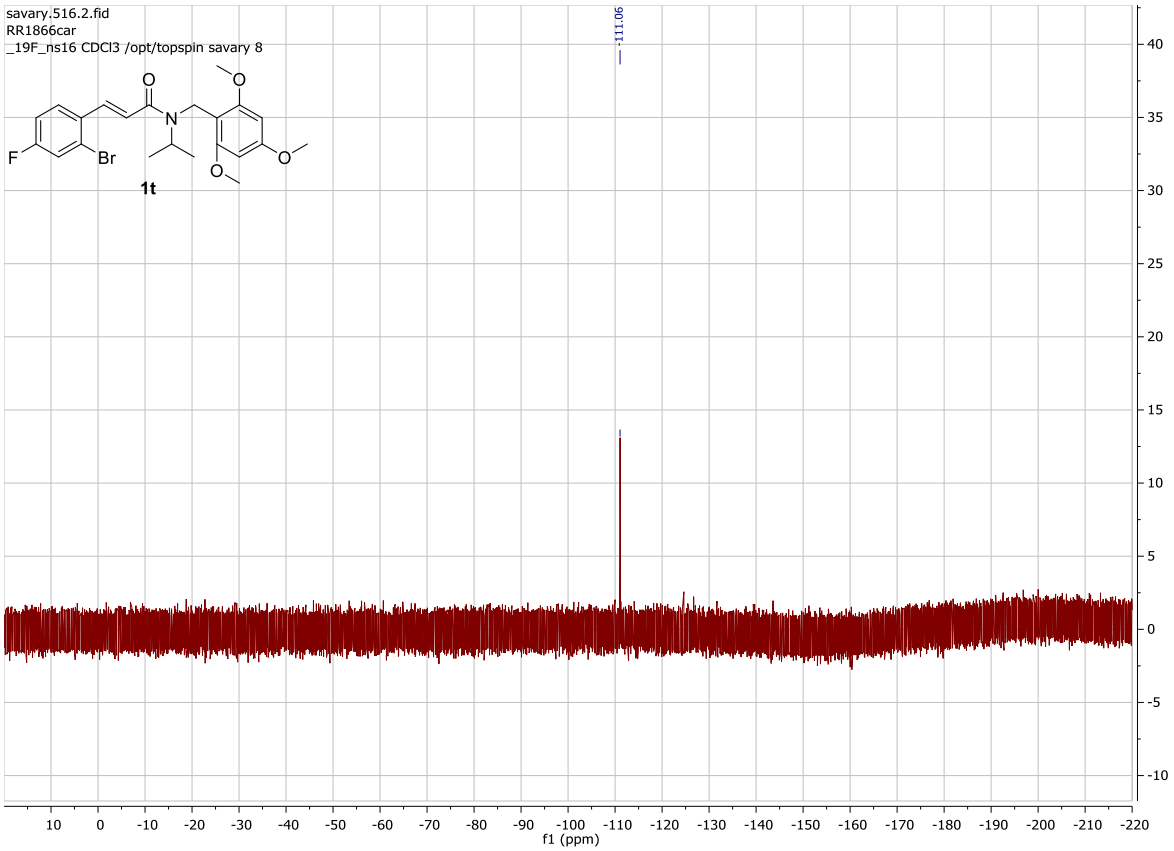
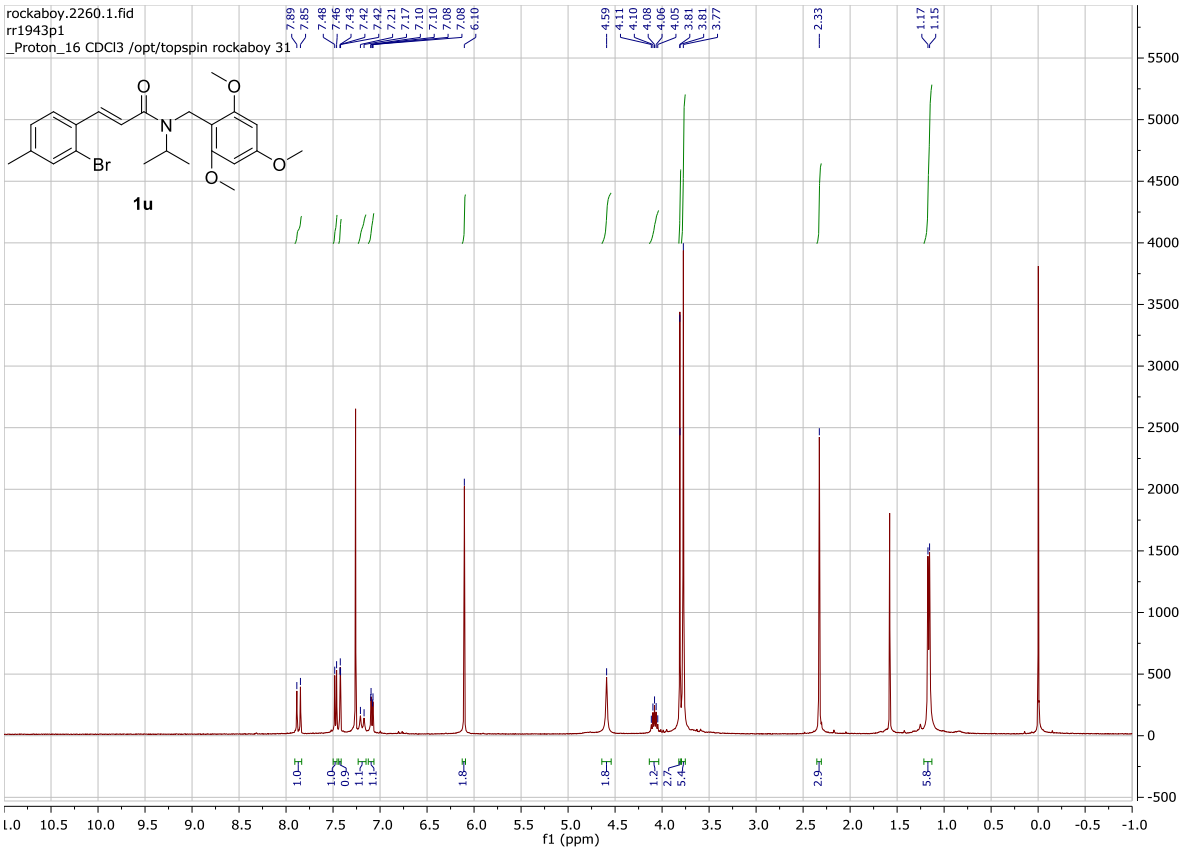
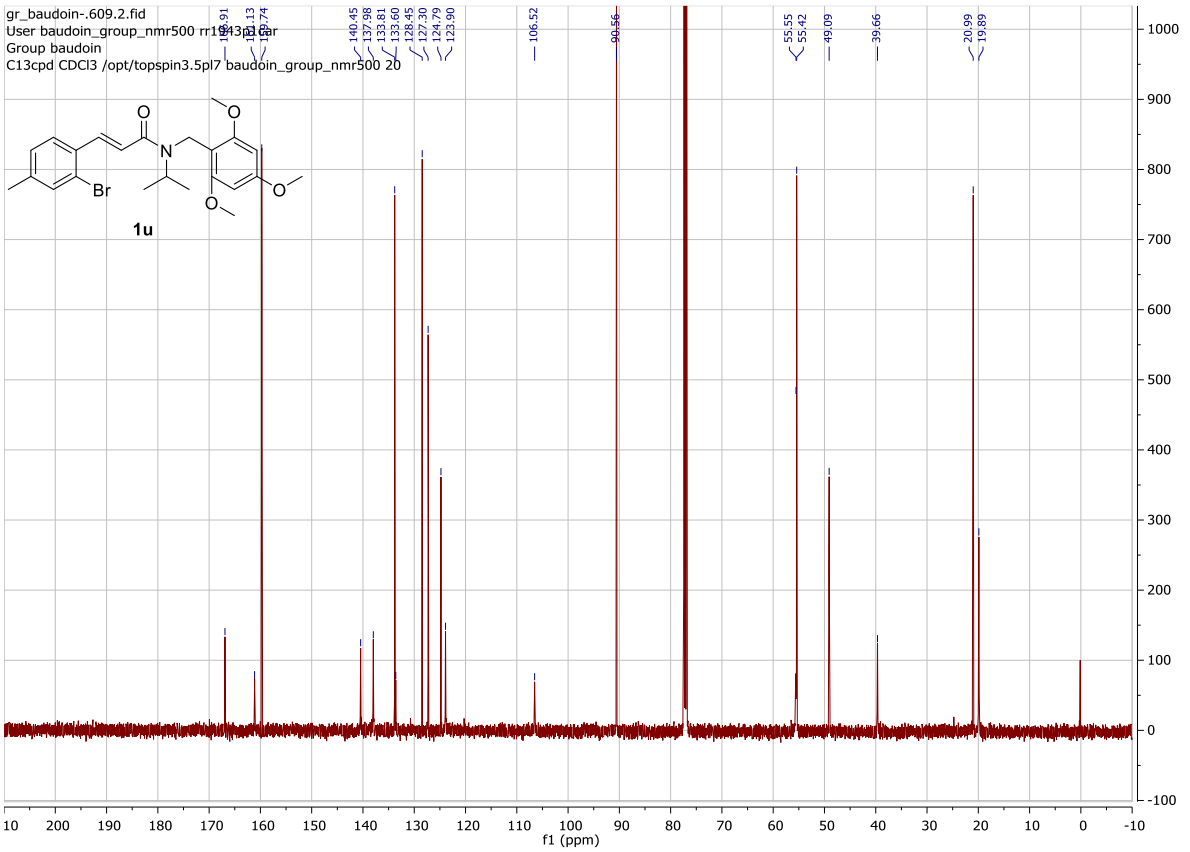
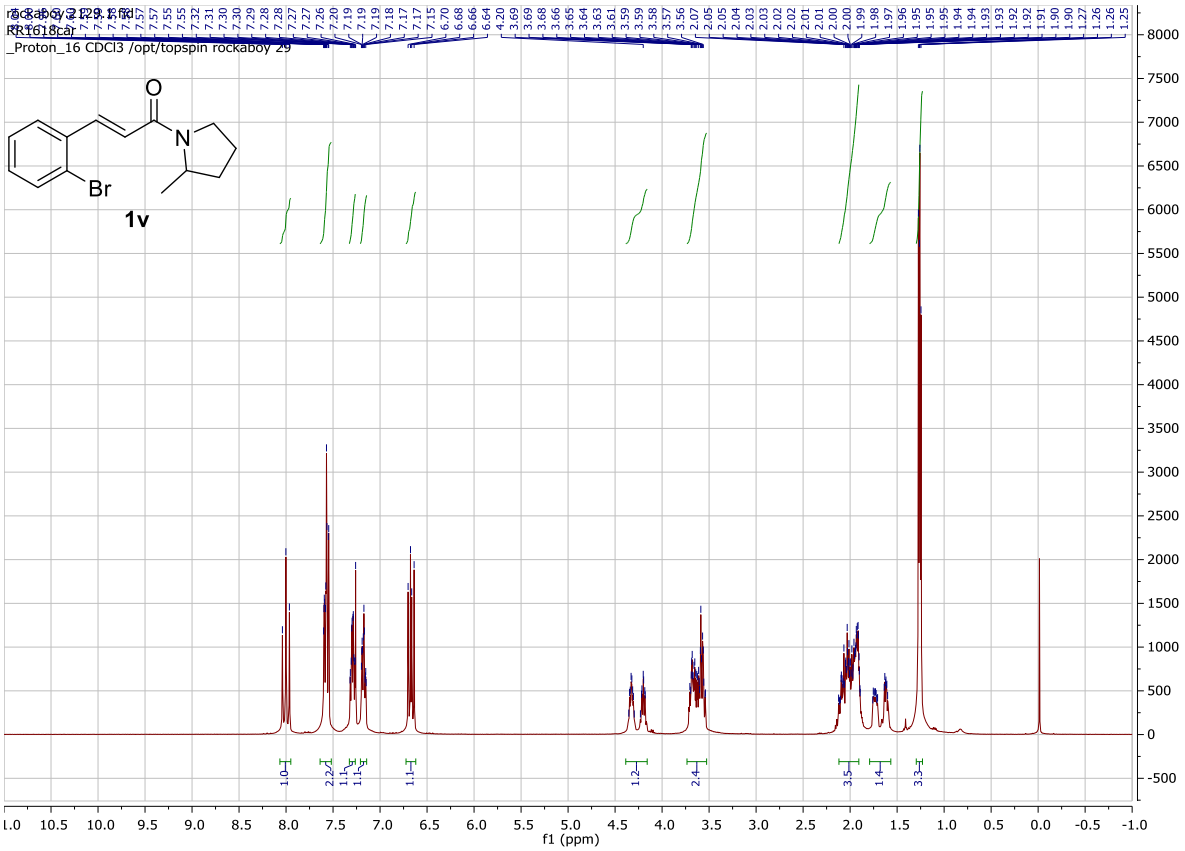
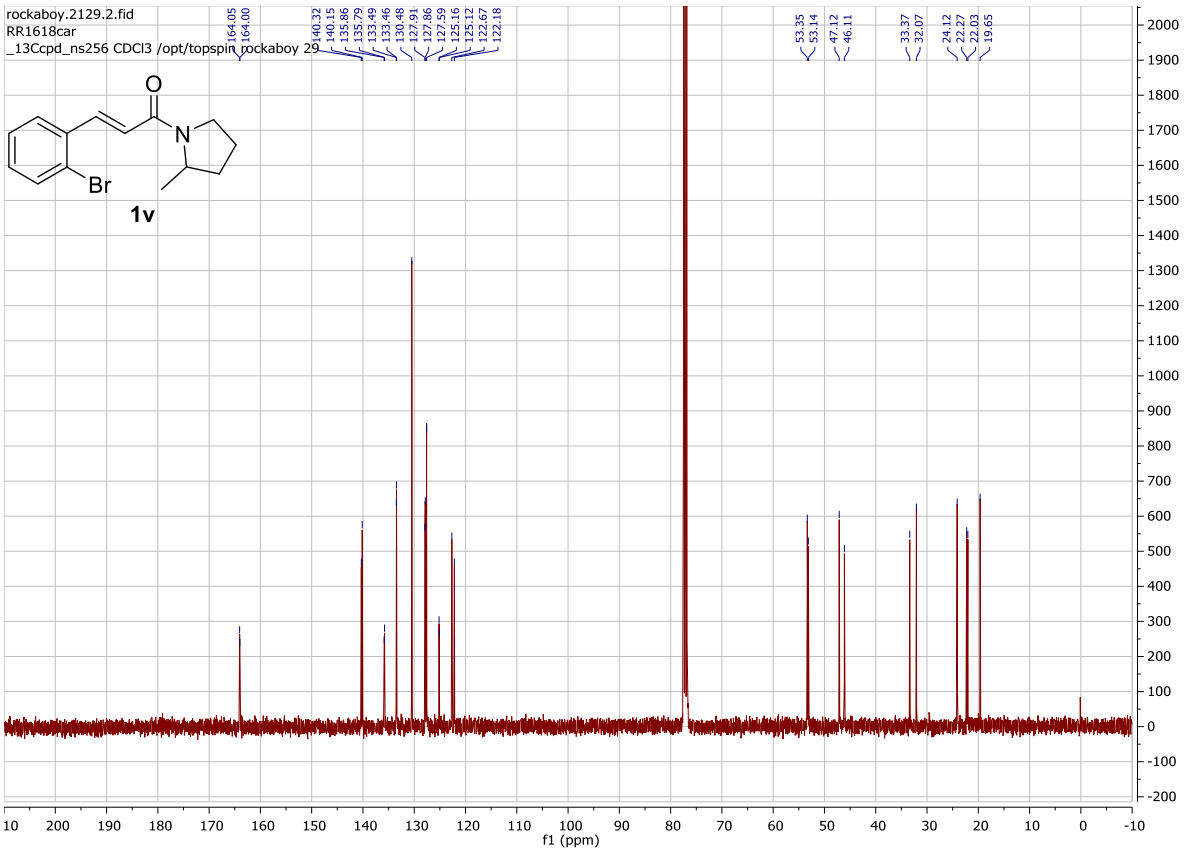
RR1866 car
_13Ccpd_ns256 CDCl3 /opt/topspin rockaboy 54
1t
f1 (ppm)

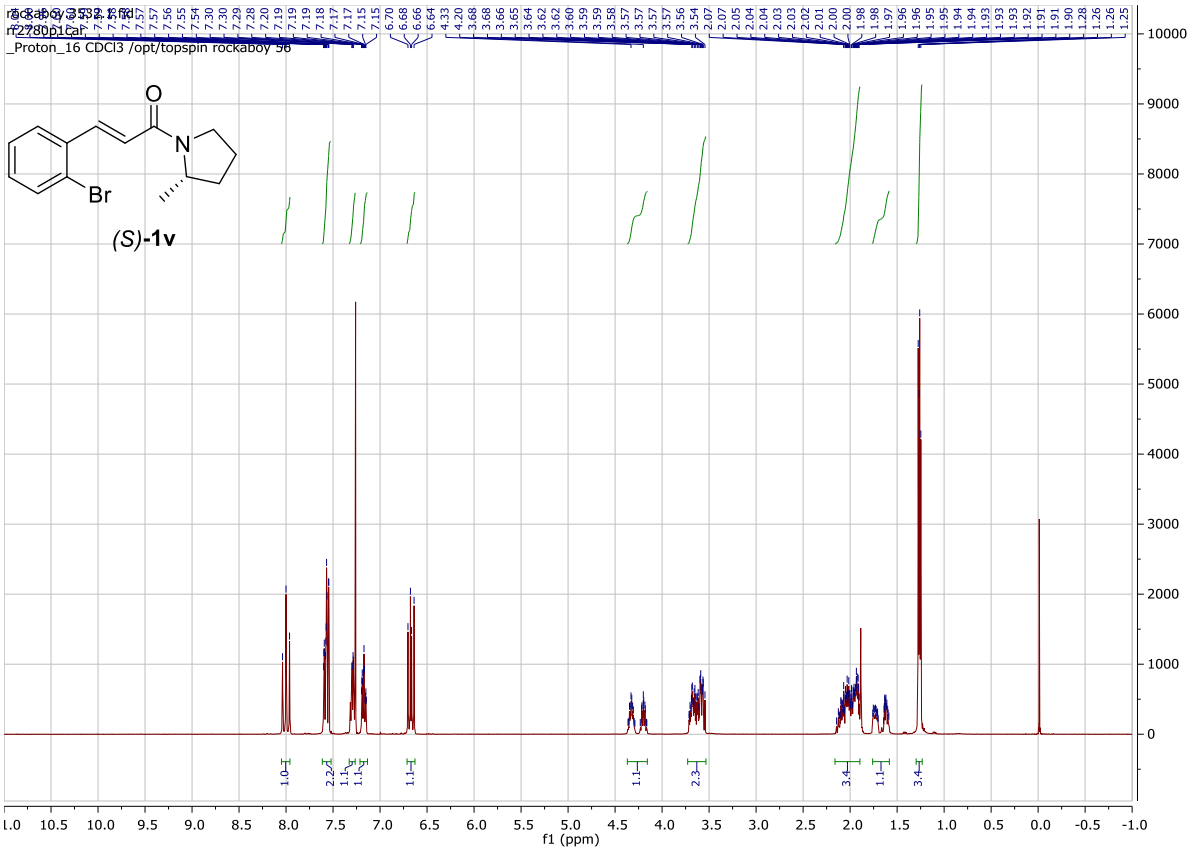

savary.516.2.fid
RR1866car
_19F_ns16 CDCl3 /opt/topspin savary 8
-111.06
F
Br
O
N
O
O
O
1t
40
35
30
25
20
15
10
5
0
-5
-10
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

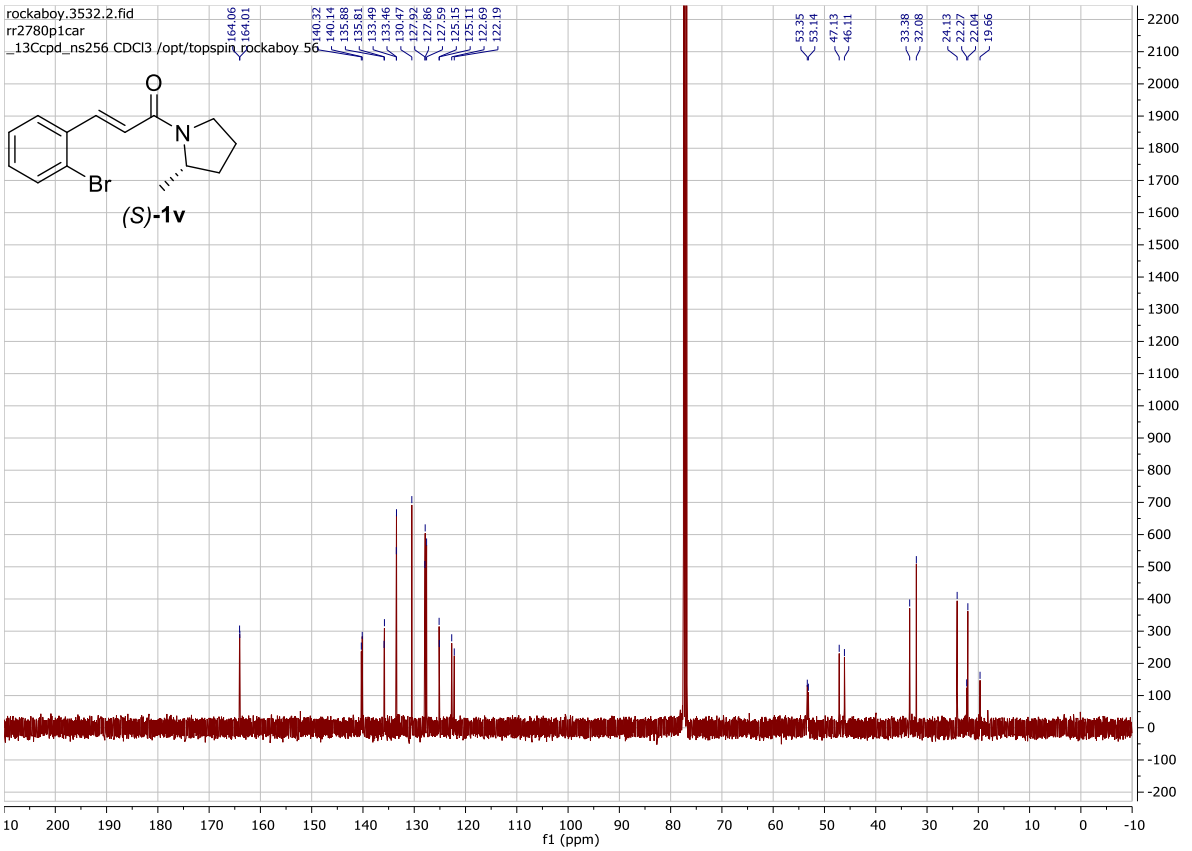

rockaboy.2260.1.fid
rr1943p1
_Proton_16 CDCl3 /opt/topspin rockaboy 31
7.89
7.85
7.48
7.46
7.43
7.42
7.42
7.21
7.17
7.10
7.10
7.08
7.08
6.10
4.59
4.11
4.10
4.08
4.06
4.05
3.81
3.81
3.77
2.33
1.17
1.15
1.0
1.0
0.9
1.1
1.1
1.8
1.8
1.2
2.7
5.4
2.9
5.8
f1 (ppm)

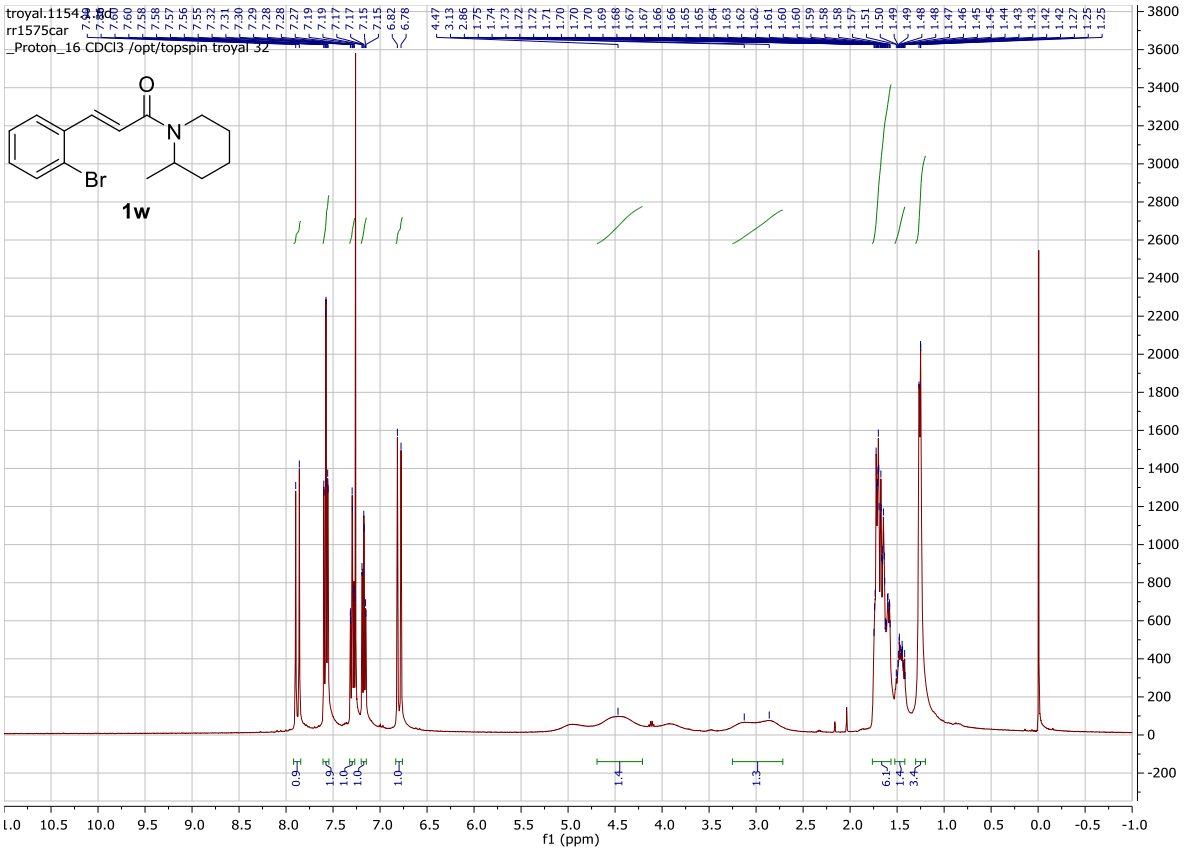

gr_baudoin-.609.2.fid
User baudoin_group_nmr500 rr1943p1.car
Group baudoin
C13cpd CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 20
140.45
137.98
133.81
133.60
128.45
127.30
124.79
123.90
106.52
90.56
55.55
55.42
49.09
39.66
20.99
19.89
f1 (ppm)

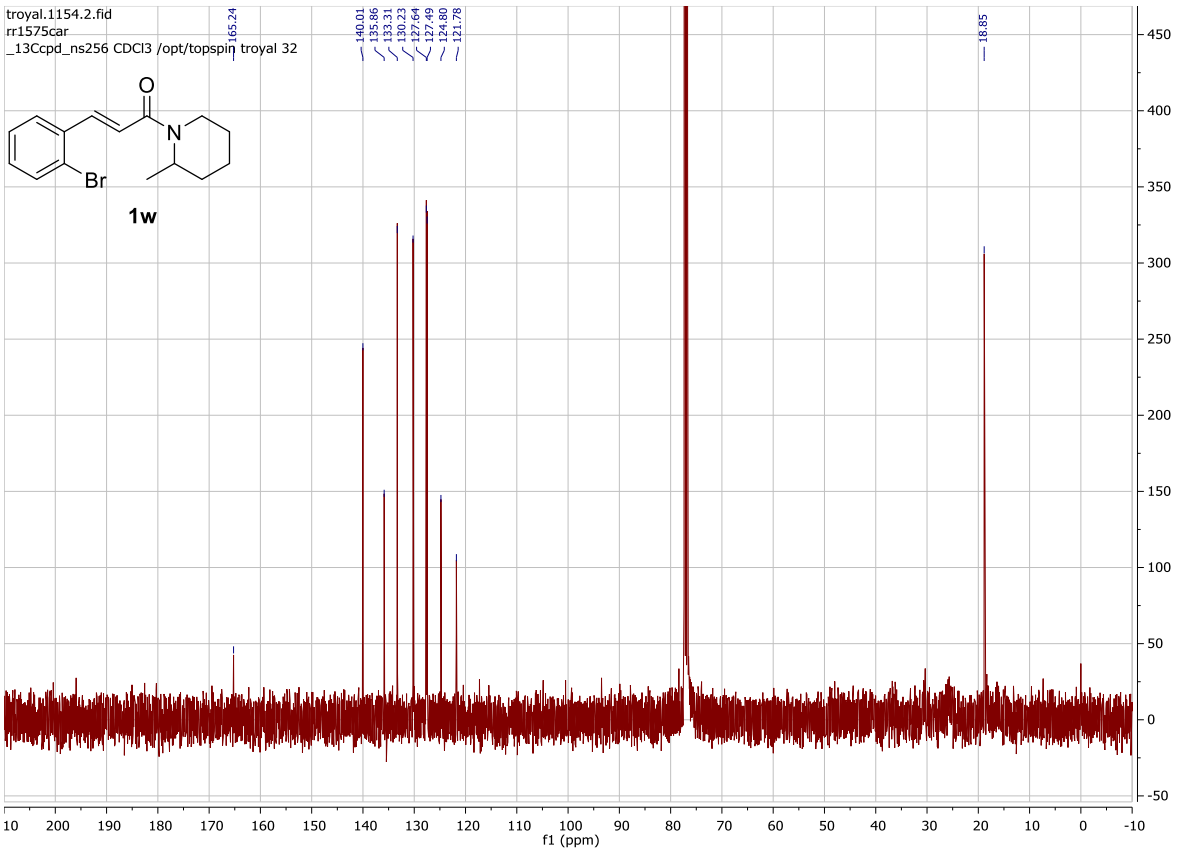

rockaboy.2129.1.fid
RR1618car
_Proton_16 CDCl3 /opt/topspin rockaboy 29
O
N
Br
1v
f1 (ppm)

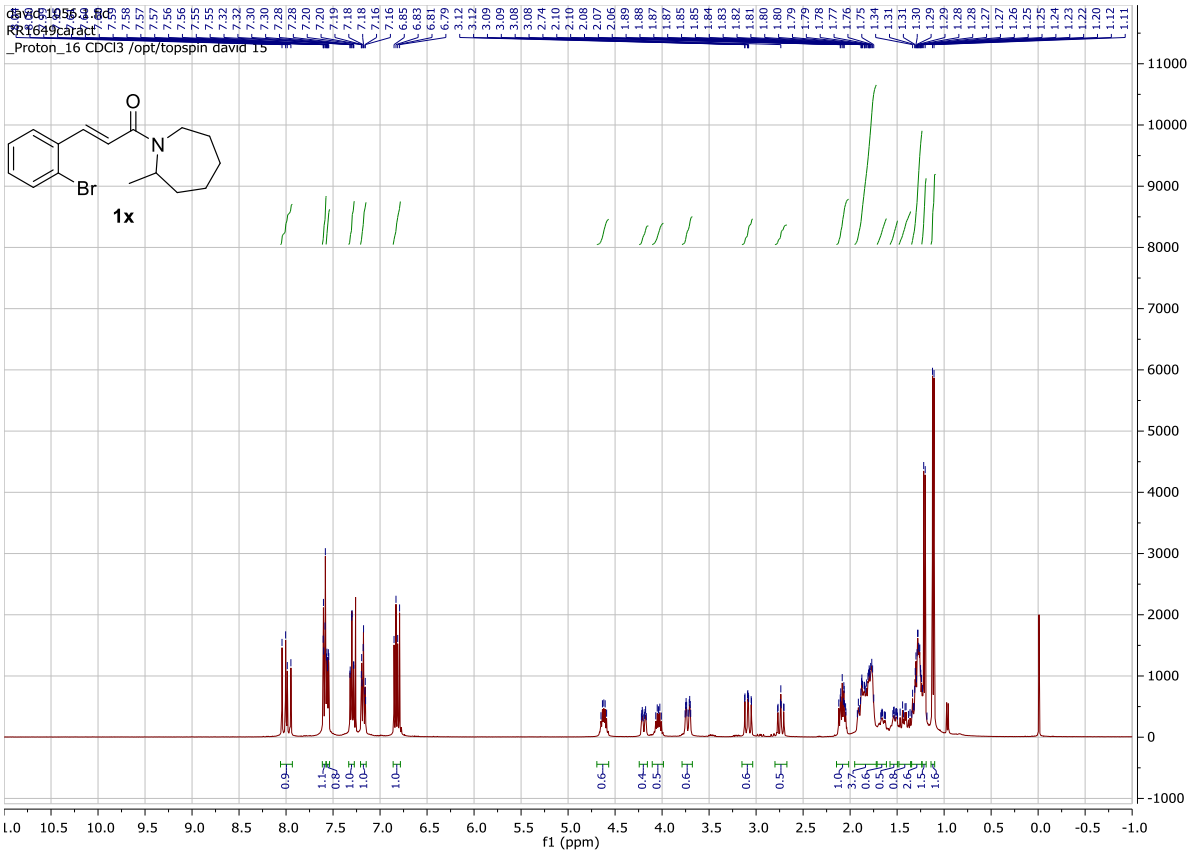

rockaboy.2129.2.fid
RR1618car
_13Ccpd_ns256 CDCl3 /opt/topspin rockaboy 29
164.05
164.00
140.32
140.15
135.86
135.79
133.49
133.46
130.48
127.91
127.86
127.59
125.16
125.12
122.67
122.18
53.35
53.14
47.12
46.11
33.37
32.07
24.12
22.27
22.03
19.65
O
N
Br
1v
f1 (ppm)


rockaboy.3532.1.fid
rr2780p1car
_Proton_16 CDCl3 /opt/topspin rockaboy 56
O
N
Br
(S)-1v
f1 (ppm)


rockaboy.3532.2.fid
rr2780p1car
_13Ccpd_ns256 CDCl3 /opt/topspin rockaboy 56
O
N
Br
(S)-1v
f1 (ppm)


troyal.1154.1.fid
rr1575car
_Proton_16 CDCl3 /opt/topspin troyal 32
O
N
Br
1w
f1 (ppm)


troyal.1154.2.fid
rr1575car
_13Ccpd_ns256 CDCl3 /opt/topspin troyal 32
165.24
140.01
135.86
133.31
130.23
127.64
127.49
124.80
121.78
18.85
O
N
Br
1w
f1 (ppm)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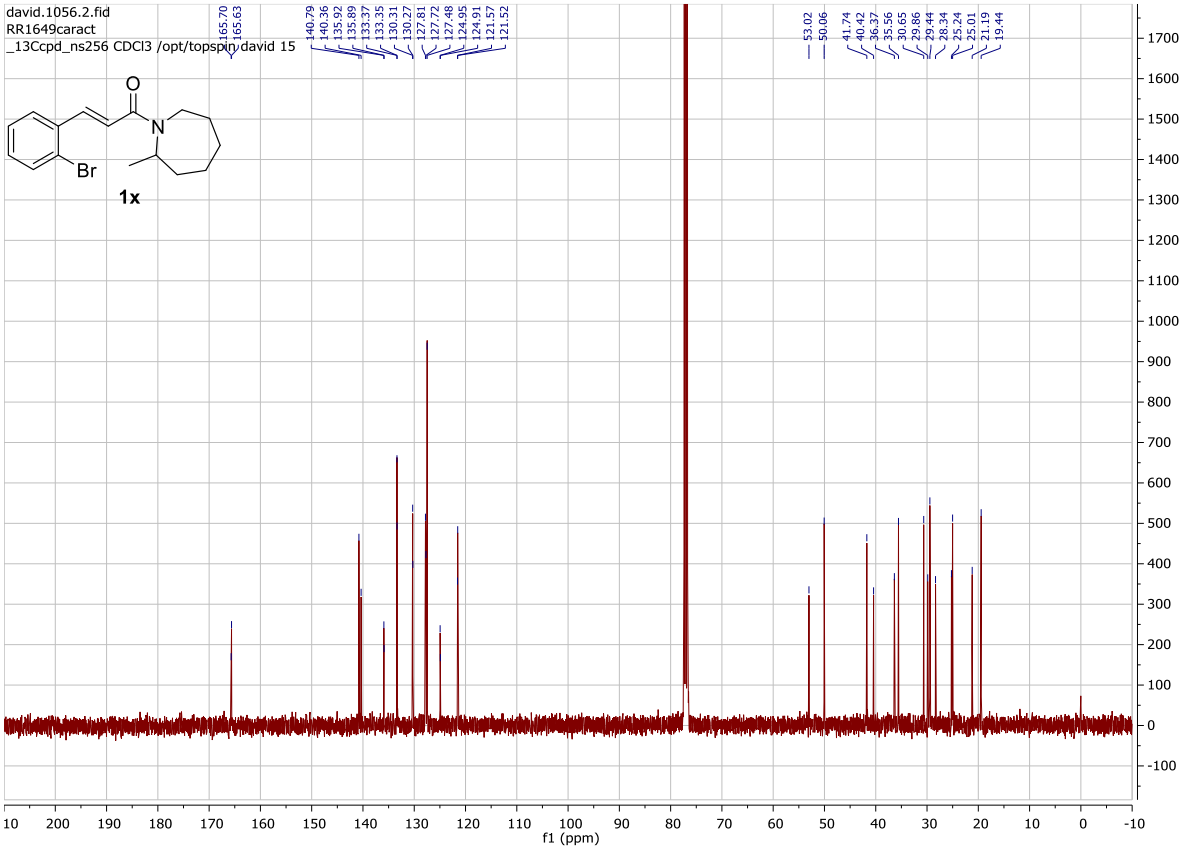
RR1649caract
_Proton_16 CDCl3 /opt/topspin david 15
O
N
Br
1x
f1 (ppm)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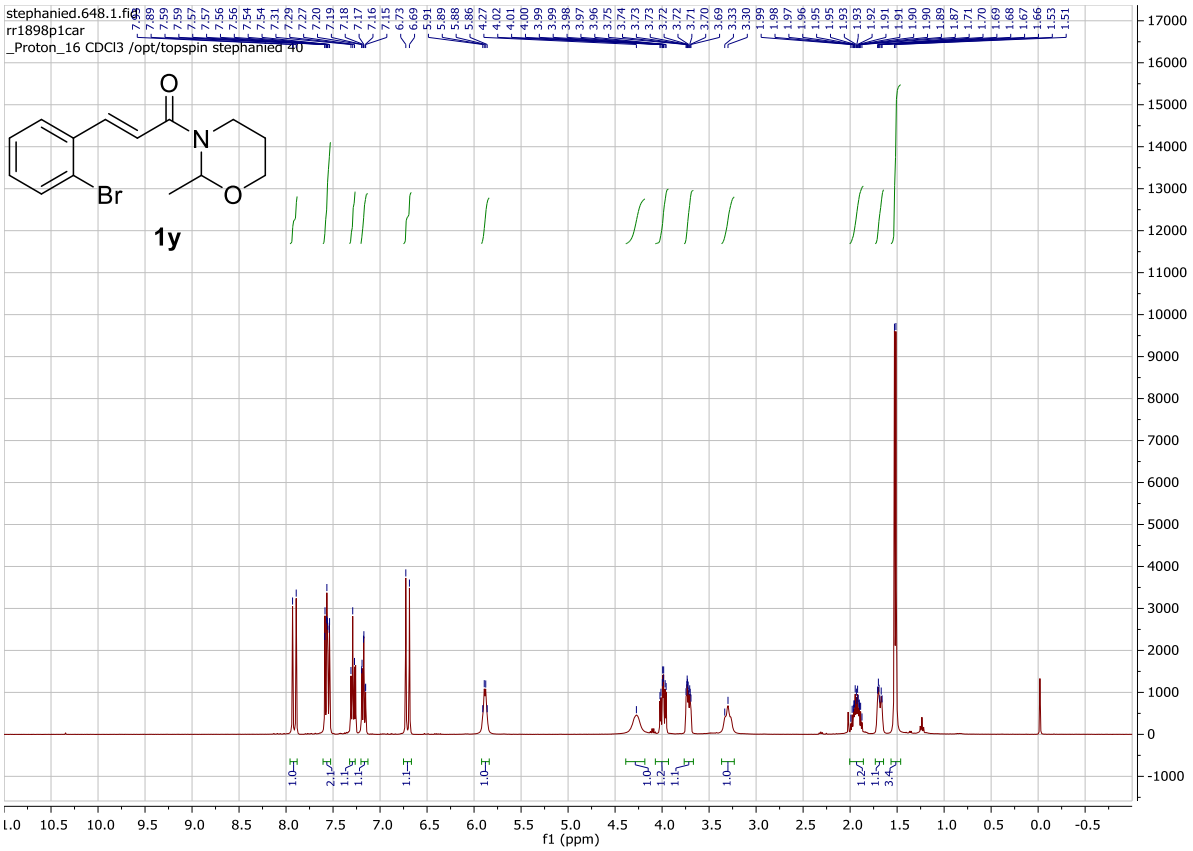
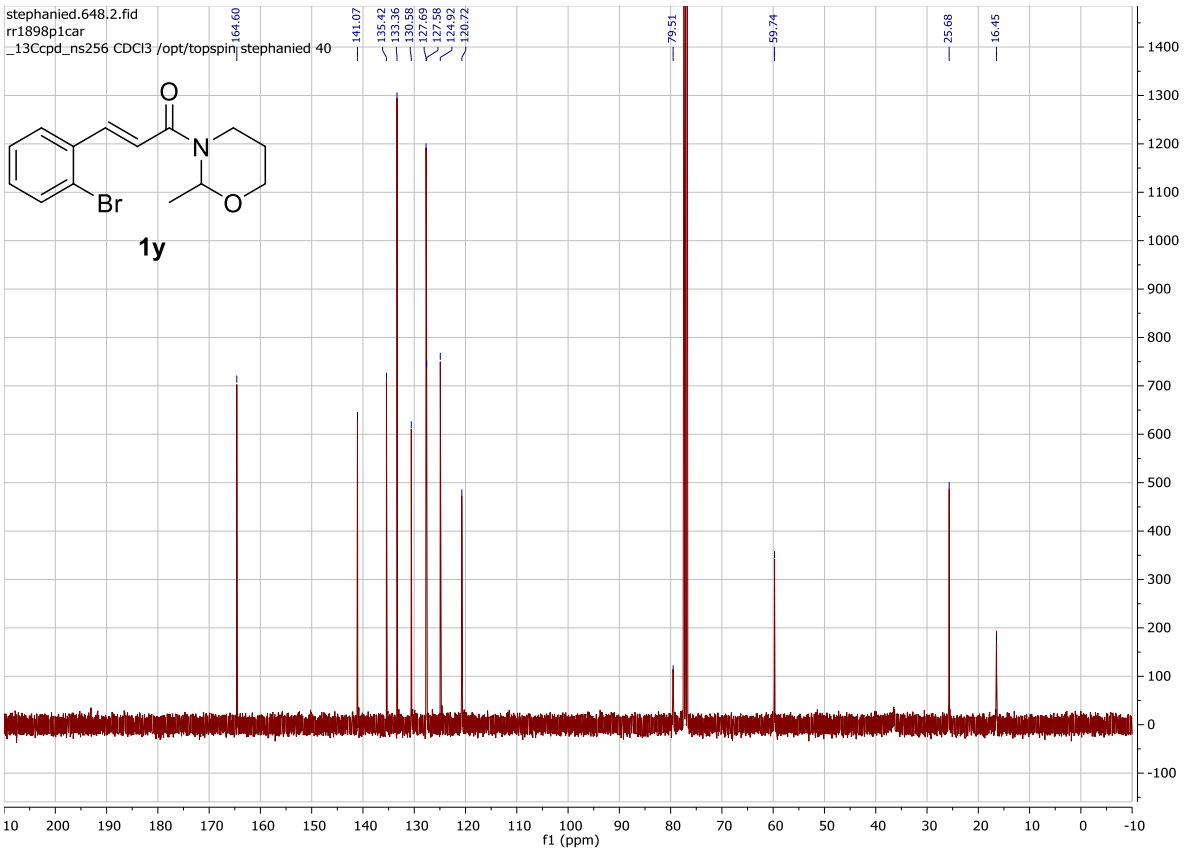
RR1649caract
_13Ccpd_ns256 CDCl3 /opt/topspin david 15
O
N
Br
1x
f1 (ppm)


stephanied.648.1.fid
rr1898p1car
_Proton_16 CDCl3 /opt/topspin stephanied 40
O
N
Br
O
1y
f1 (ppm)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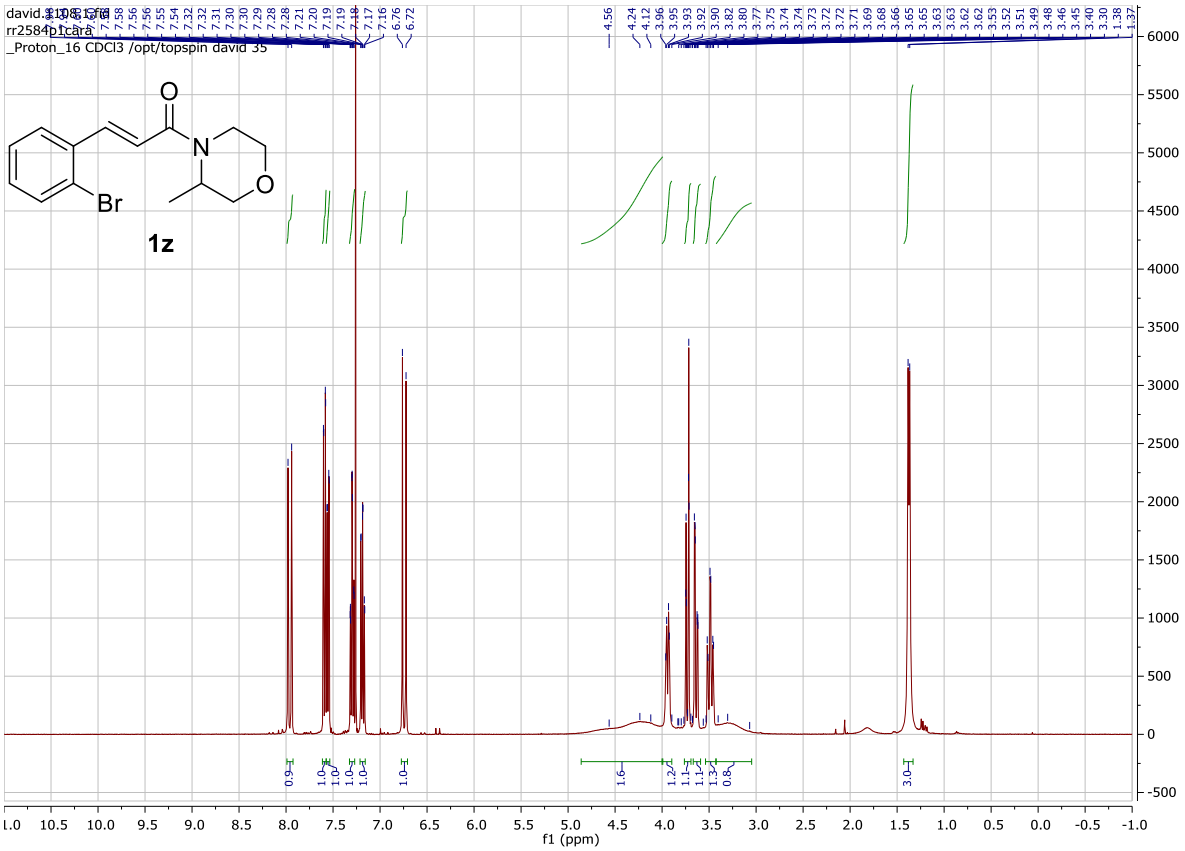
_13Ccpd_ns256 CDCl3 /opt/topspin stephanied 40
164.60
141.07
135.42
133.36
130.58
127.69
127.58
124.92
120.72
79.51
59.74
25.68
16.45
O
N
Br
O
1y
f1 (ppm)


david.1108.1.fid
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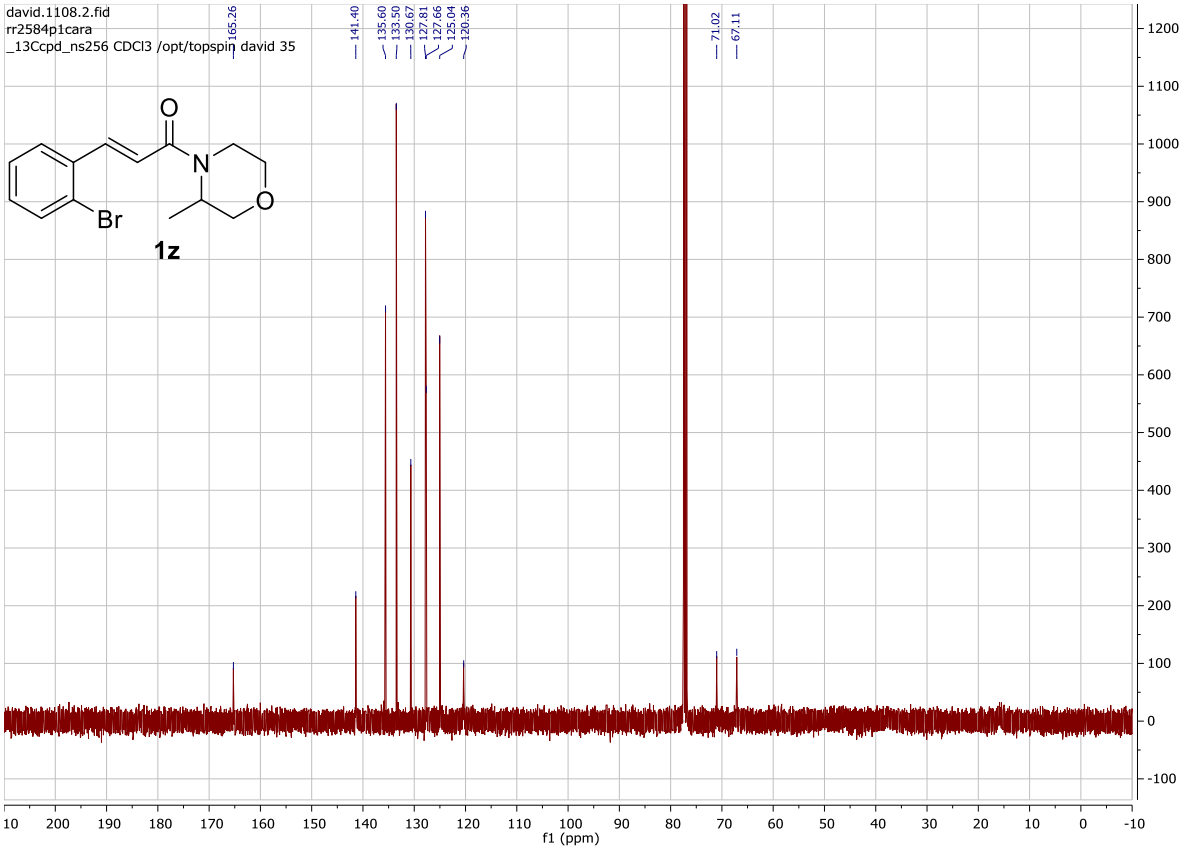
_Proton_16 CDCl3 /opt/topspin david 35
O
N
O
Br
1z
f1 (ppm)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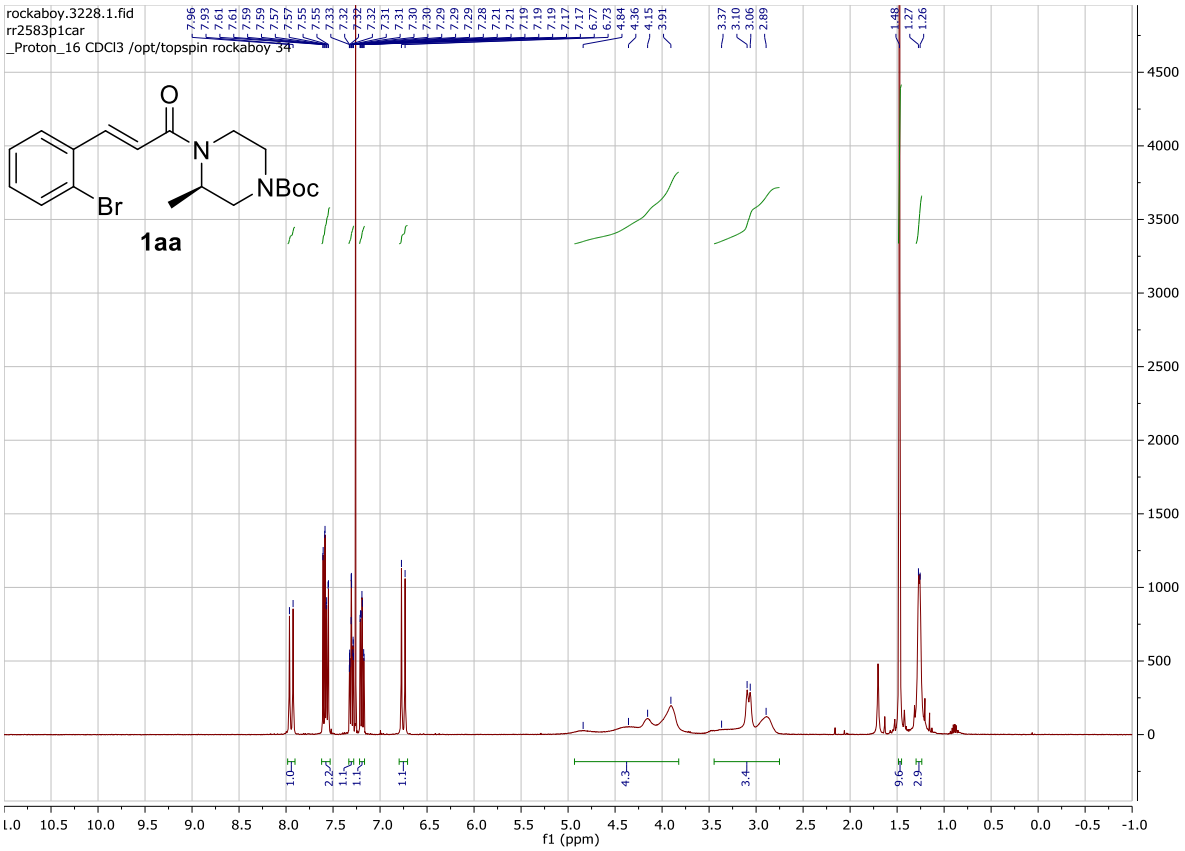
_13Ccpd_ns256 CDCl3 /opt/topspin david 35
165.26
141.40
135.60
133.50
130.67
127.81
127.66
125.04
120.36
71.02
67.11
O
N
O
Br
1z
f1 (ppm)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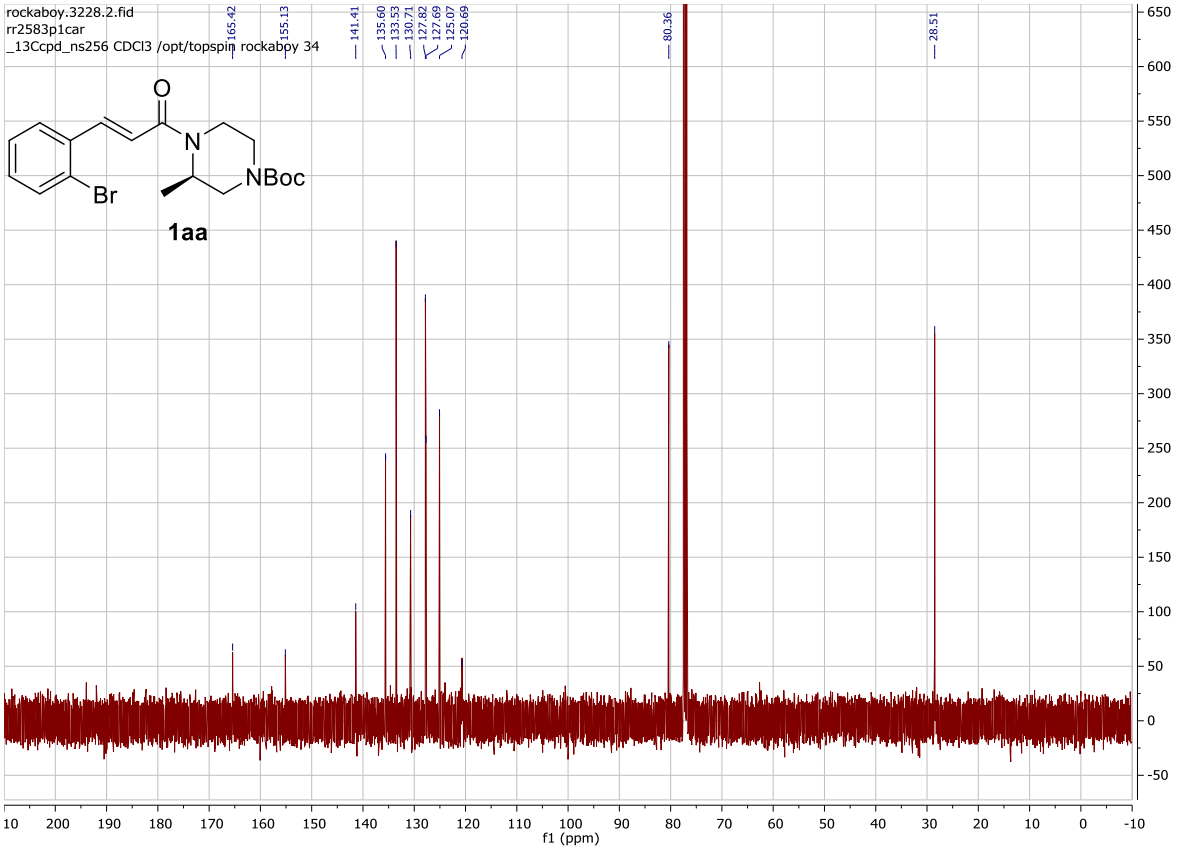
O
N
NBoc
Br
1aa
f1 (ppm)


rockaboy.3228.2.fid
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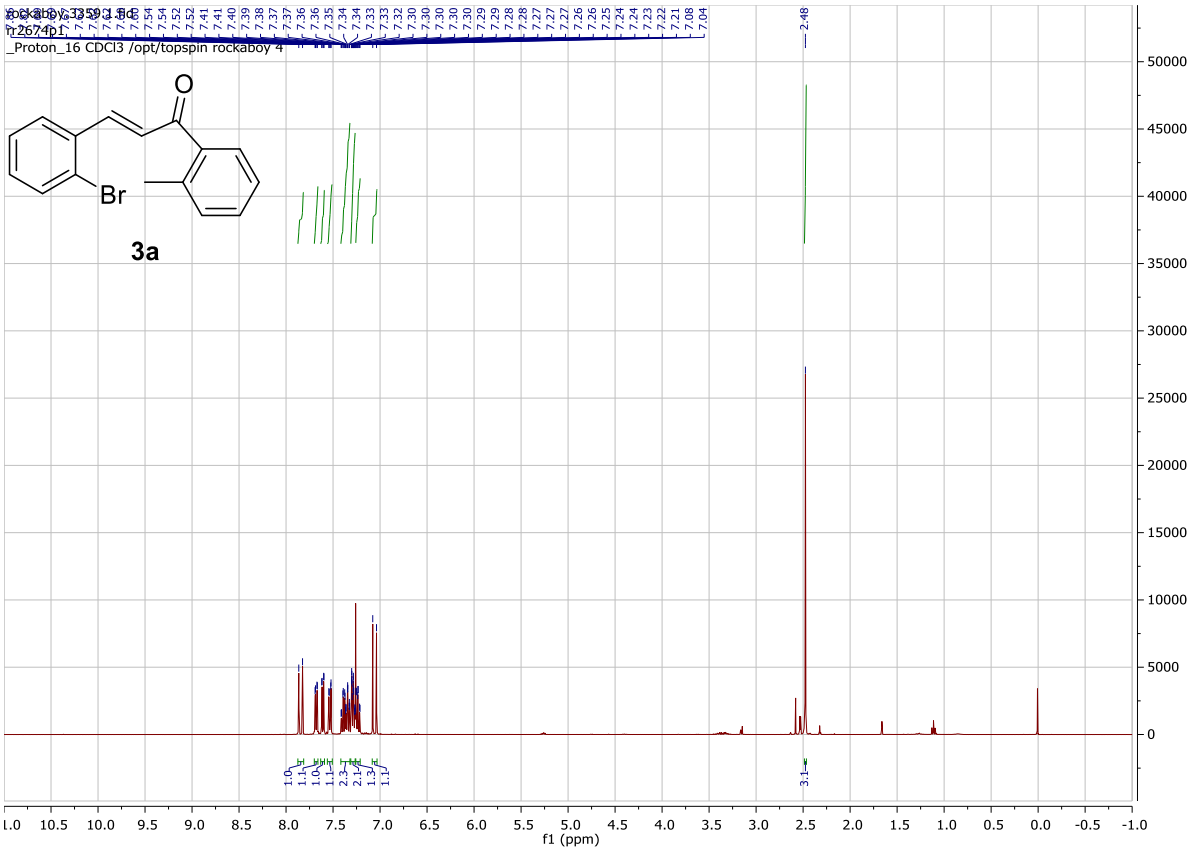
_13Ccpd_ns256 CDCl3 /opt/topspin rockaboy 34
O
N
NBoc
Br
1aa
f1 (ppm)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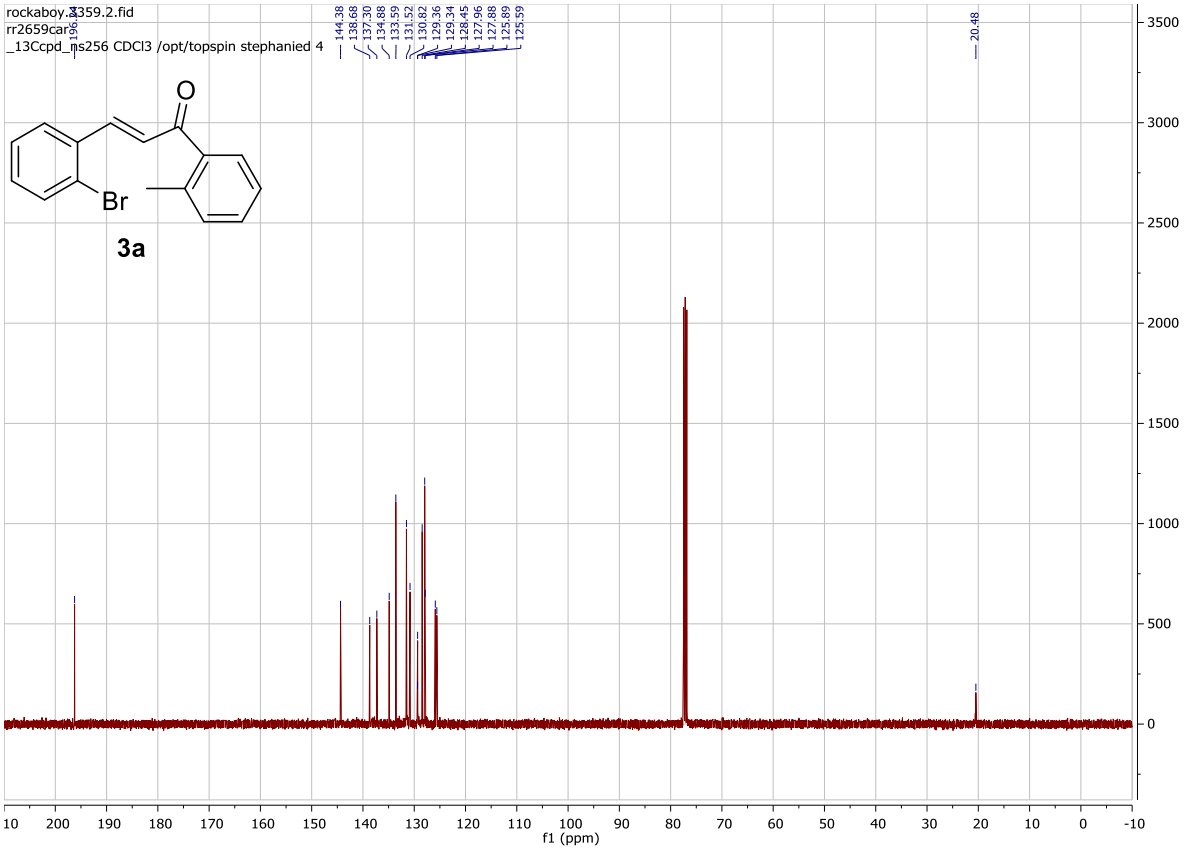
O
Br
3a
f1 (ppm)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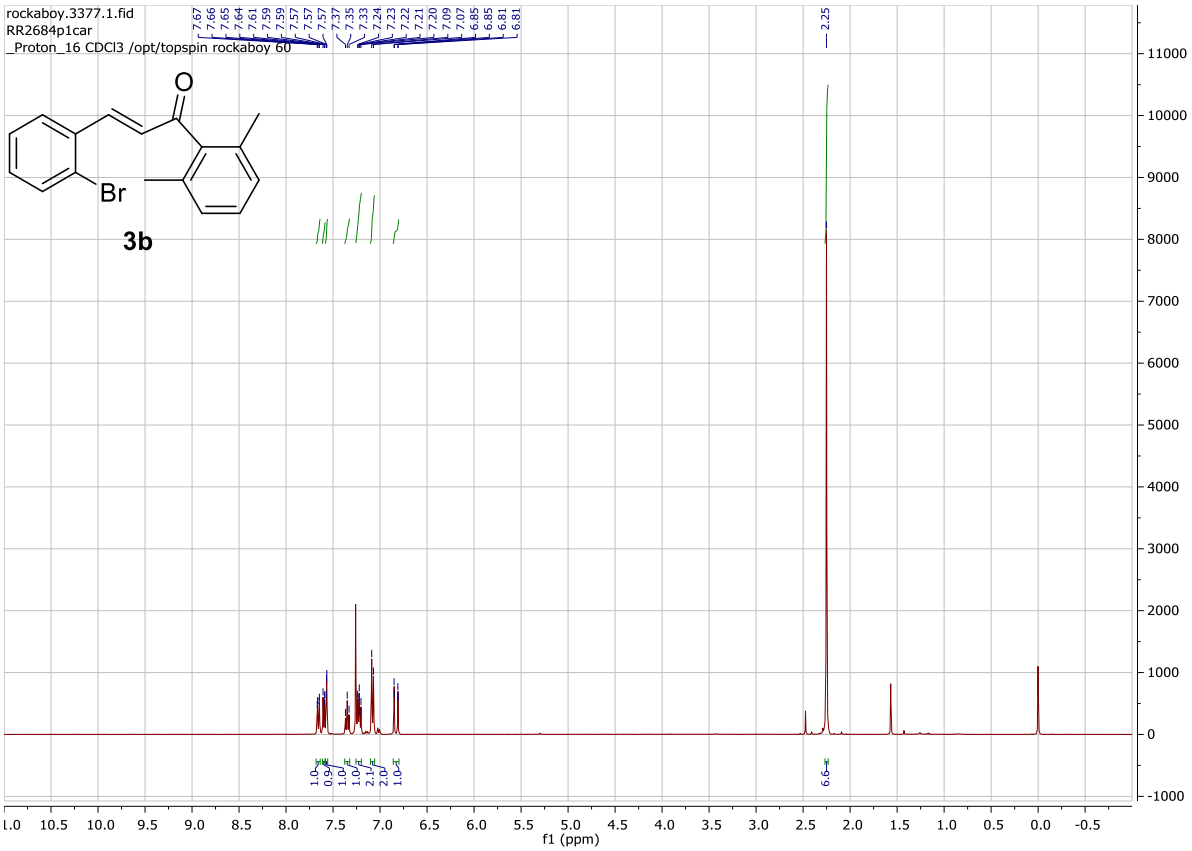
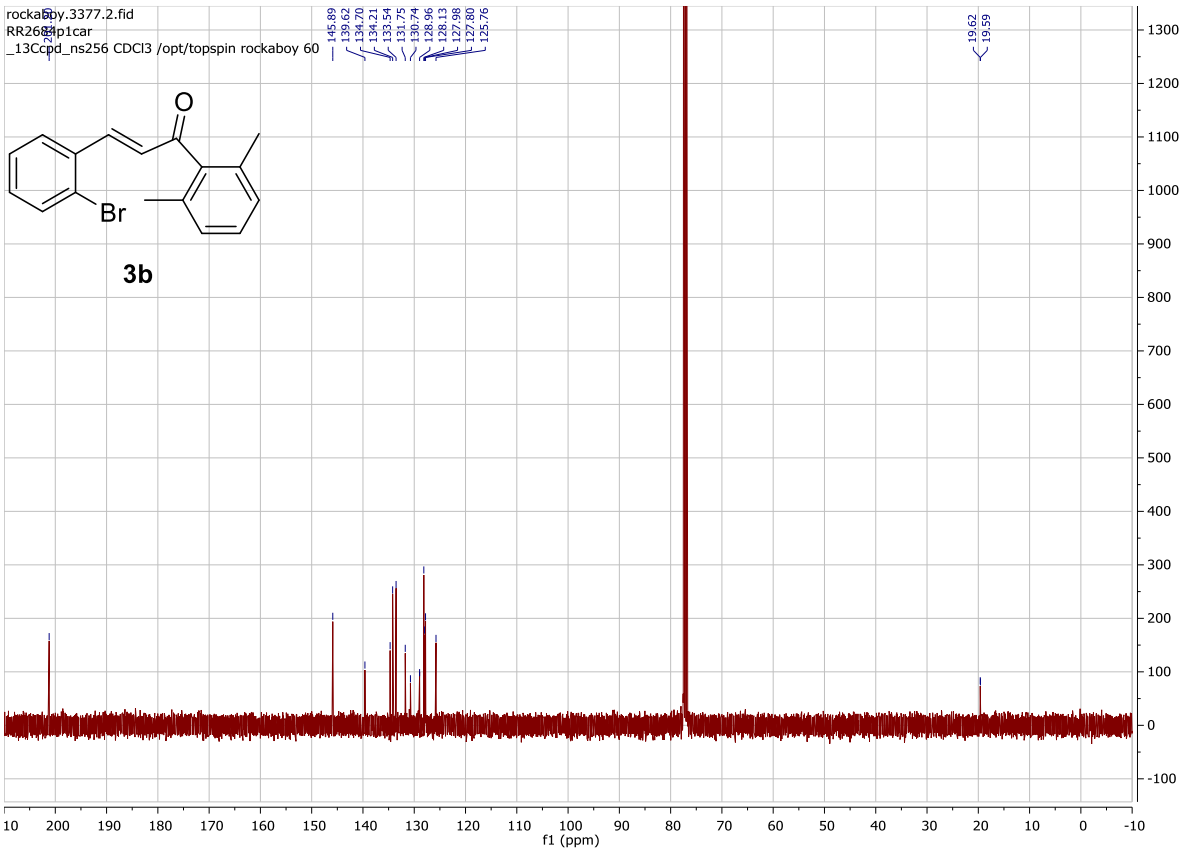
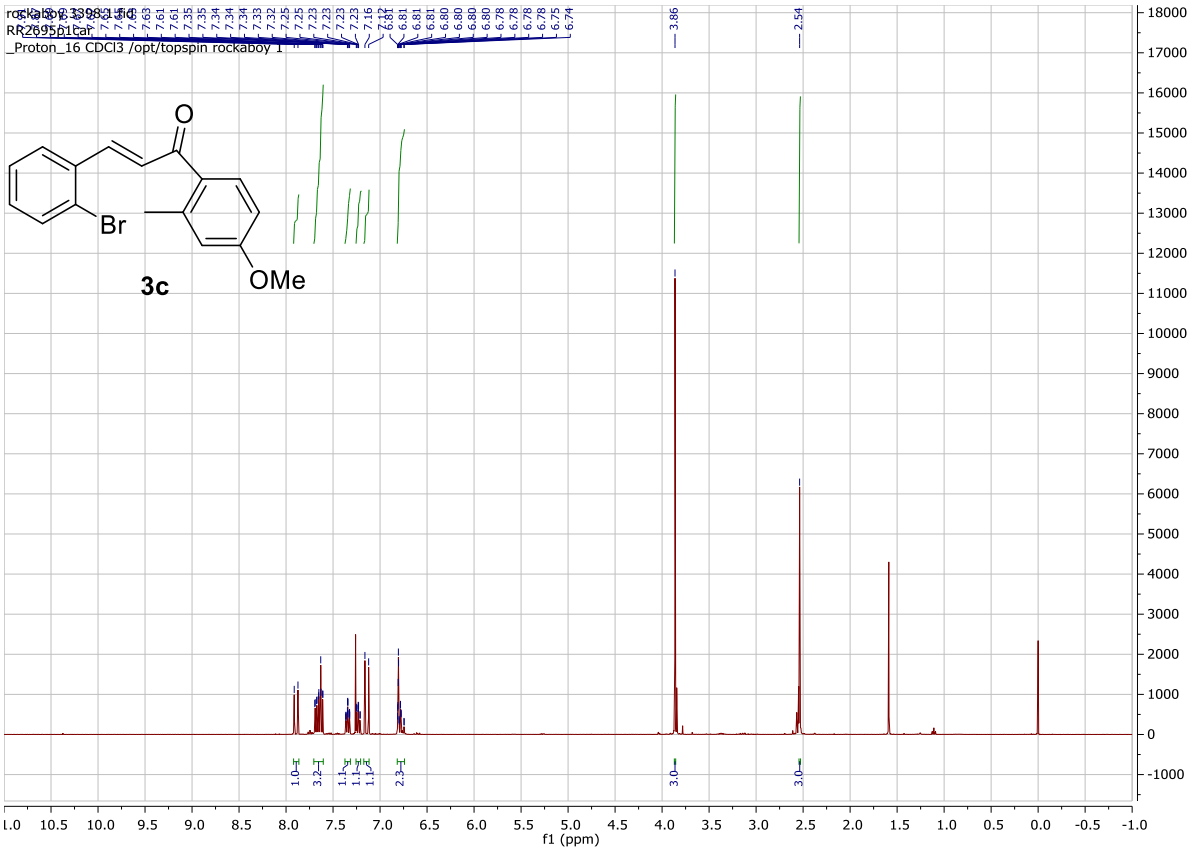
_13Ccpd_ns256 CDCl3 /opt/topspin stephanied 4
O
Br
3a
f1 (ppm)


rockaboy.3377.1.fid
RR2684p1car
_Proton_16 CDCl3 /opt/topspin rockaboy 60
7.67
7.66
7.65
7.64
7.61
7.59
7.59
7.57
7.57
7.57
7.37
7.35
7.33
7.24
7.23
7.22
7.21
7.20
7.09
7.07
6.85
6.85
6.81
6.81
2.25
O
Br
3b
1.0
0.9
1.0
1.0
2.1
2.0
1.0
6.6
f1 (ppm)


rockaboy.3377.2.fid
RR2684p1car
_13Cpnd_ns256 CDCl3 /opt/topspin rockaboy 60
145.89
139.62
134.70
134.21
133.54
131.75
130.74
128.96
128.13
127.98
127.80
125.76
77.48
77.16
76.84
19.62
19.59
O
Br
3b
f1 (ppm)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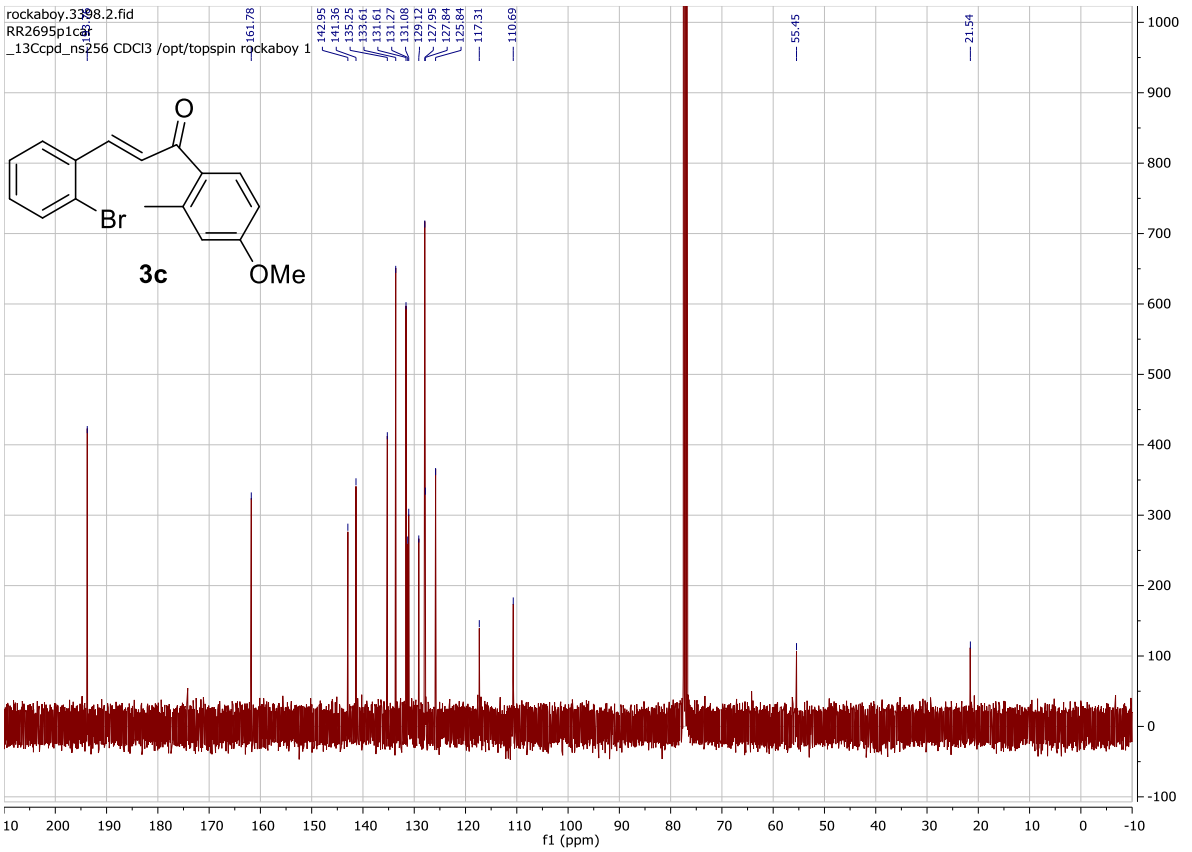
RR2695p1cal
_Proton_16 CDCl3 /opt/topspin rockaboy 1
3.86
2.54
Br
O
OMe
3c
f1 (ppm)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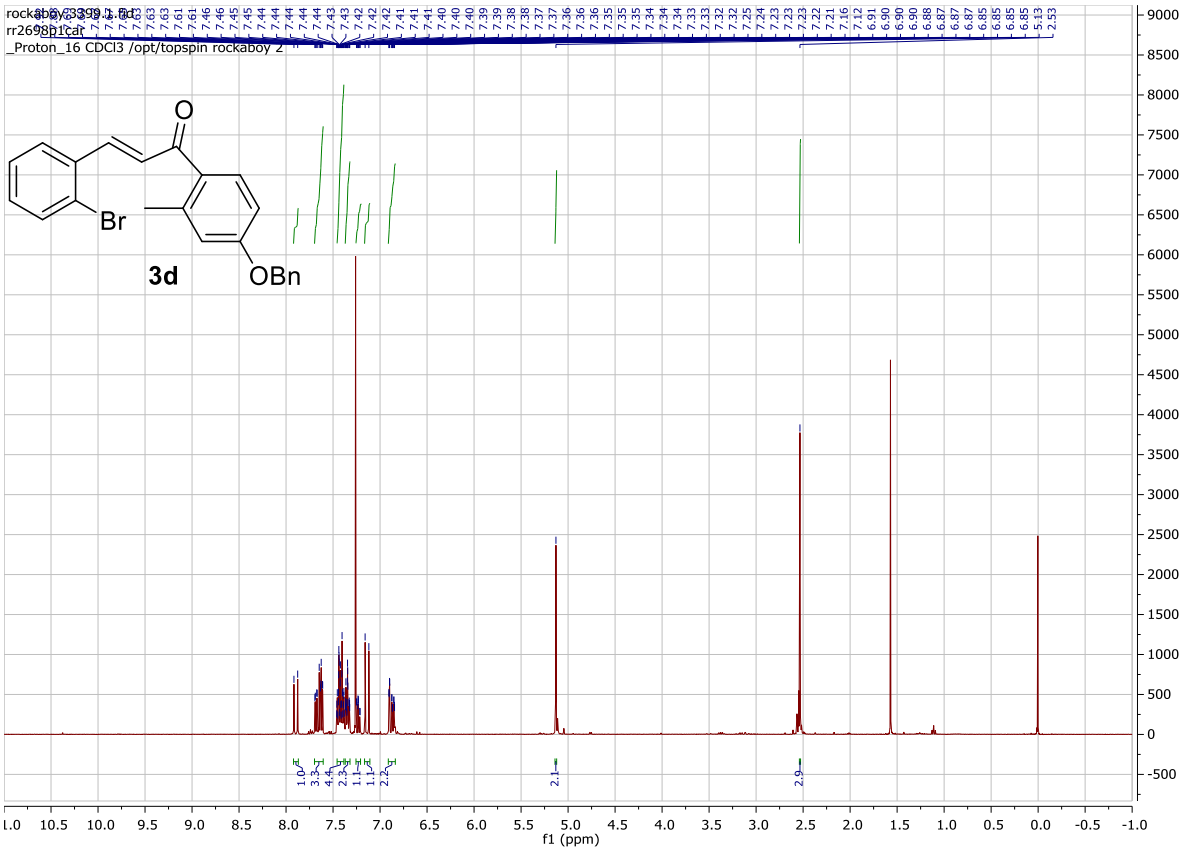
RR2695p1cal
_13Ccpd_ns256 CDCl3 /opt/topspin rockaboy 1
161.78
142.95
141.36
135.25
133.61
131.61
131.27
131.08
129.12
127.95
127.84
125.84
117.31
110.69
55.45
21.54
Br
O
OMe
3c
f1 (ppm)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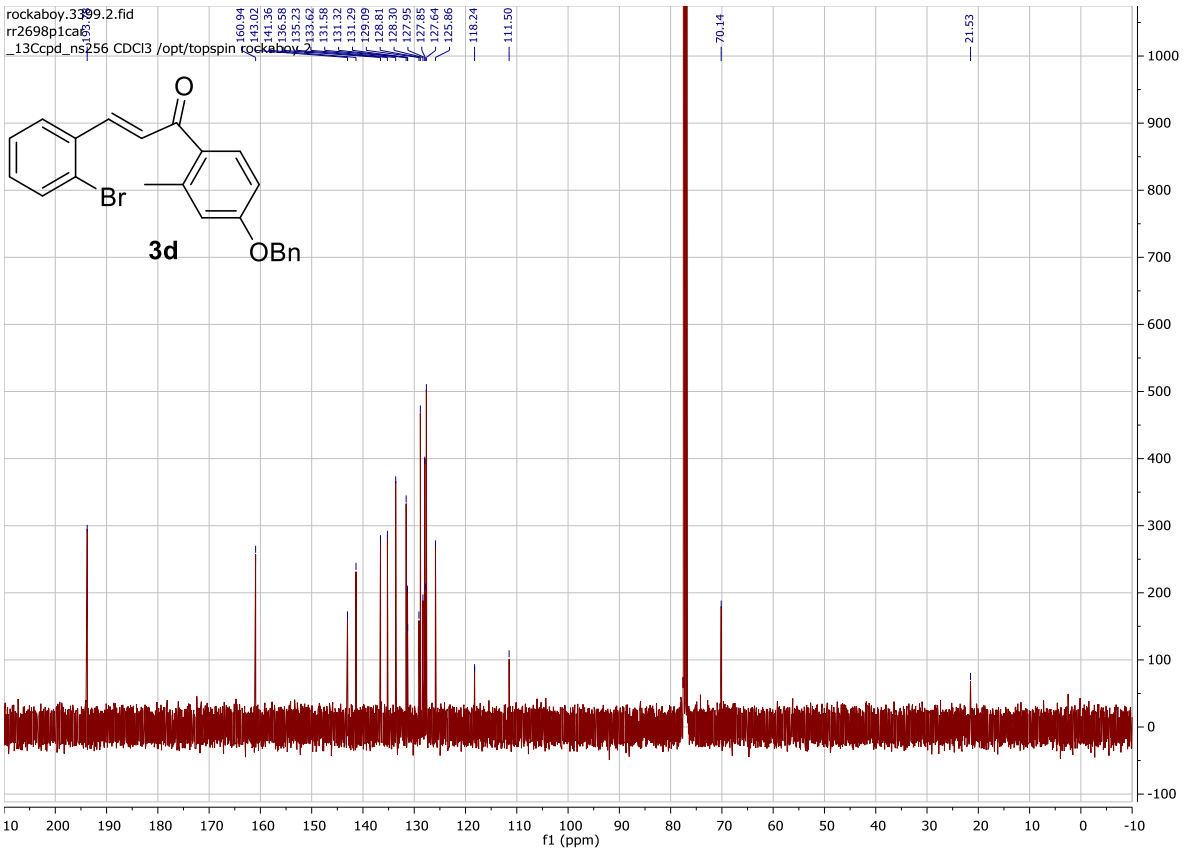
rr2698p1cal
_Proton_16 CDCl3 /opt/topspin rockaboy 2
O
Br
3d
OBn
f1 (ppm)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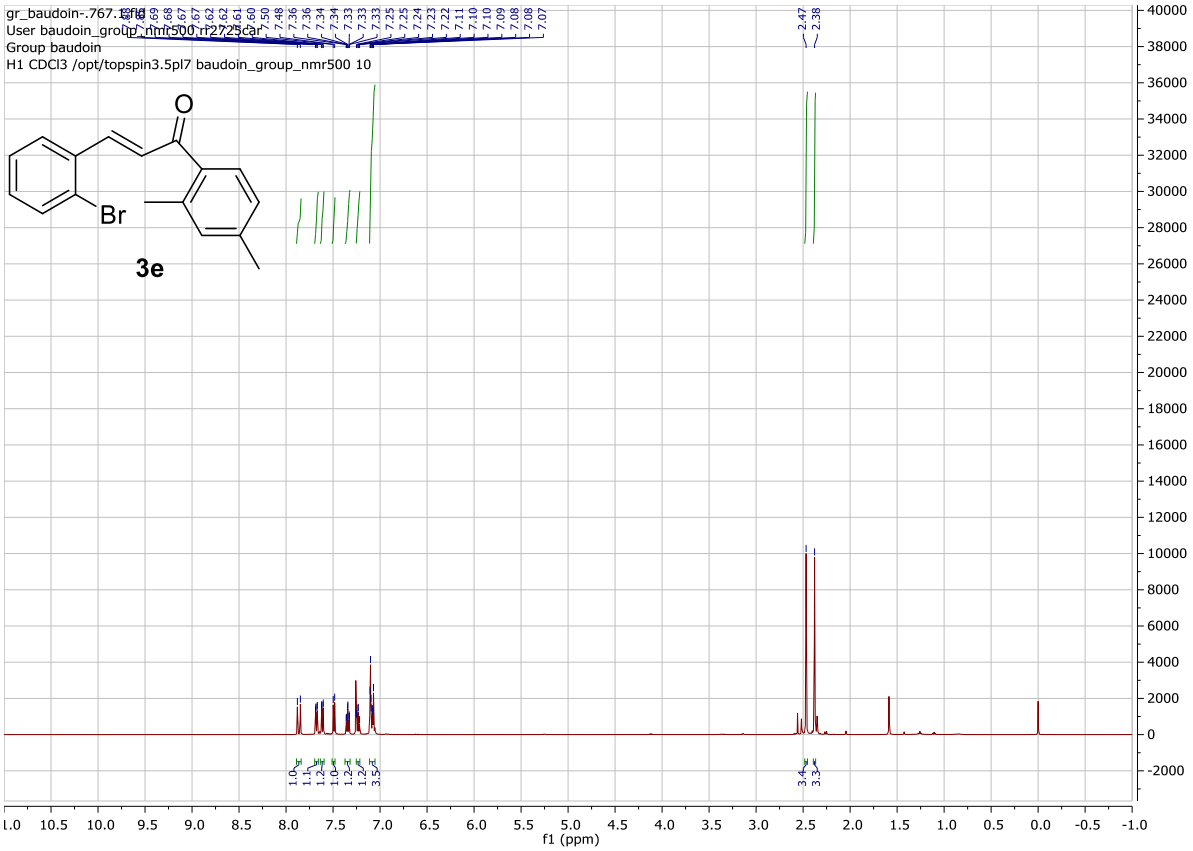
rr2698p1cal
_13Ccpd_ns256 CDCl3 /opt/topspin rockaboy
160.94
143.02
141.36
136.58
135.23
133.62
131.58
131.32
131.29
129.09
128.81
128.30
127.95
127.85
127.64
125.86
118.24
111.50
70.14
21.53
O
Br
3d
OBn
f1 (ppm)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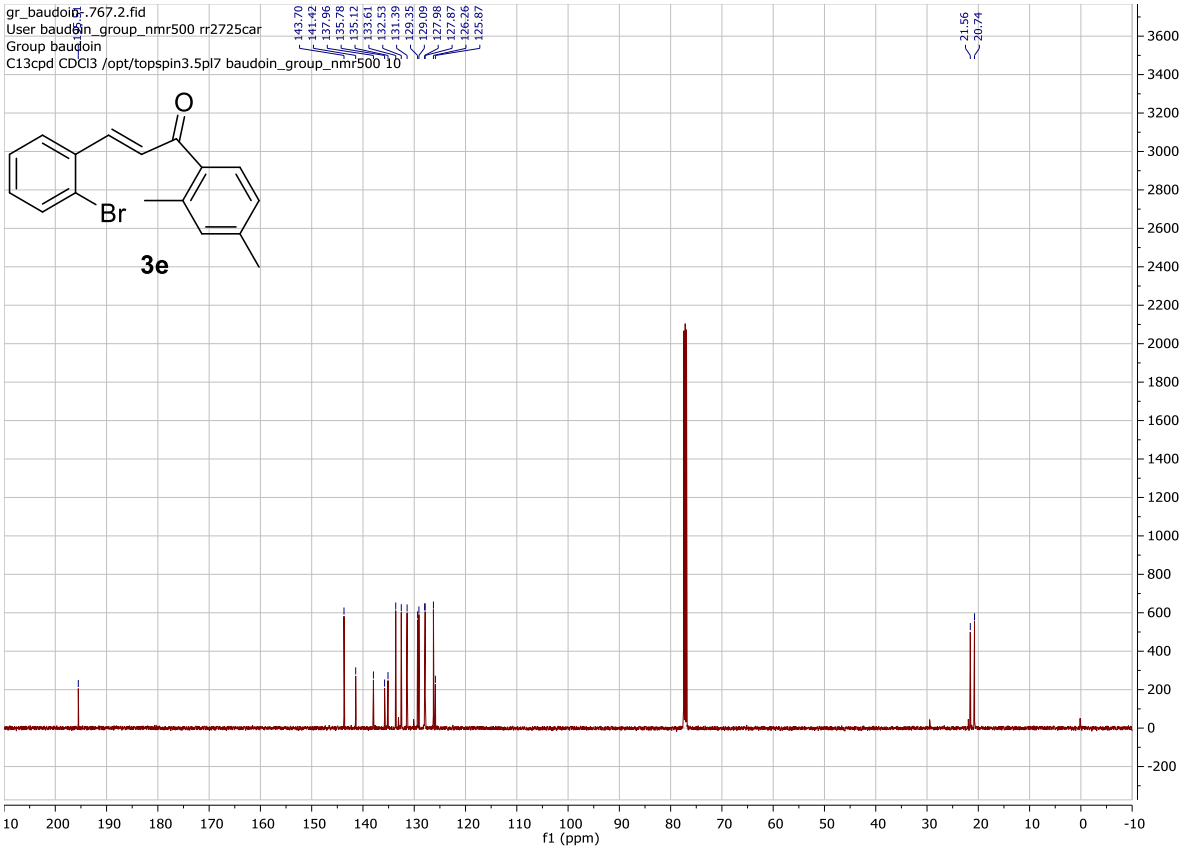
User baudoin_group_nmr500 rr2725car
Group baudoin
H1 CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 10
O
Br
3e
f1 (ppm)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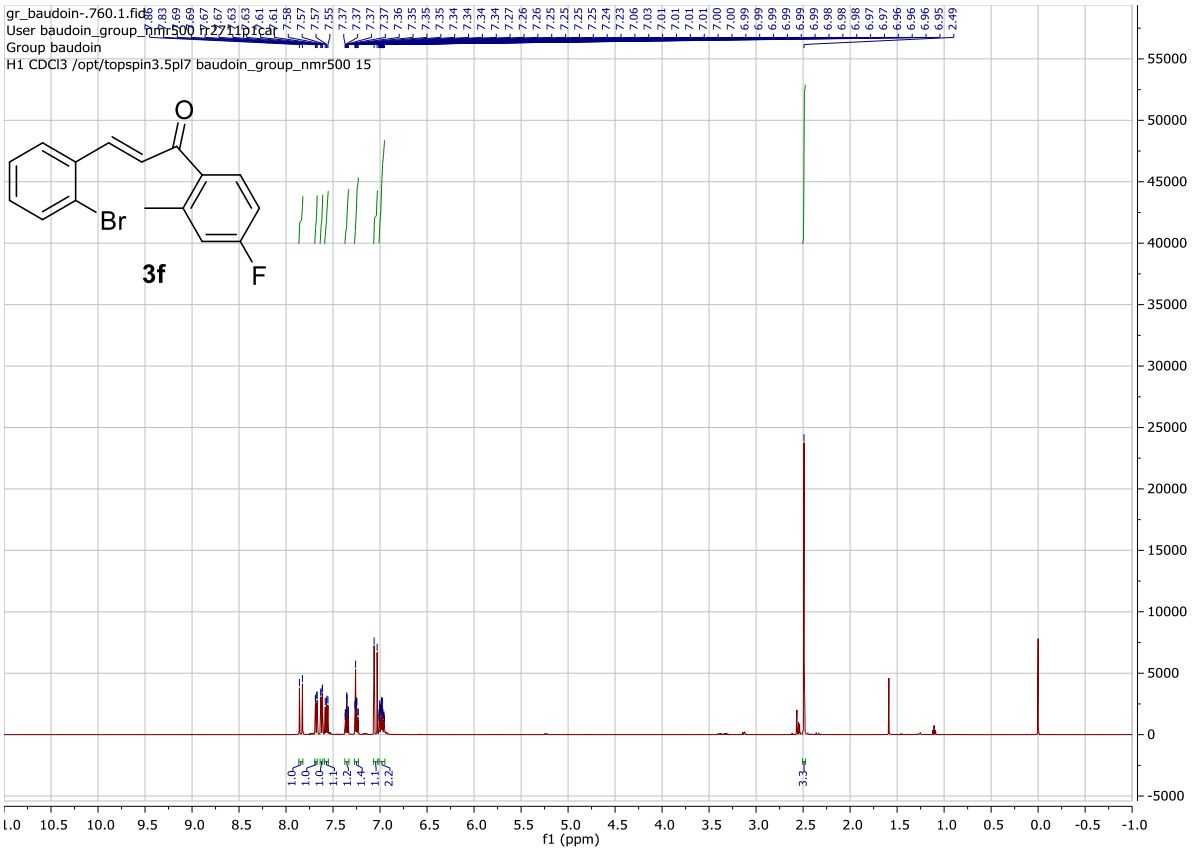
C13cpd CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 10
O
Br
3e
f1 (ppm)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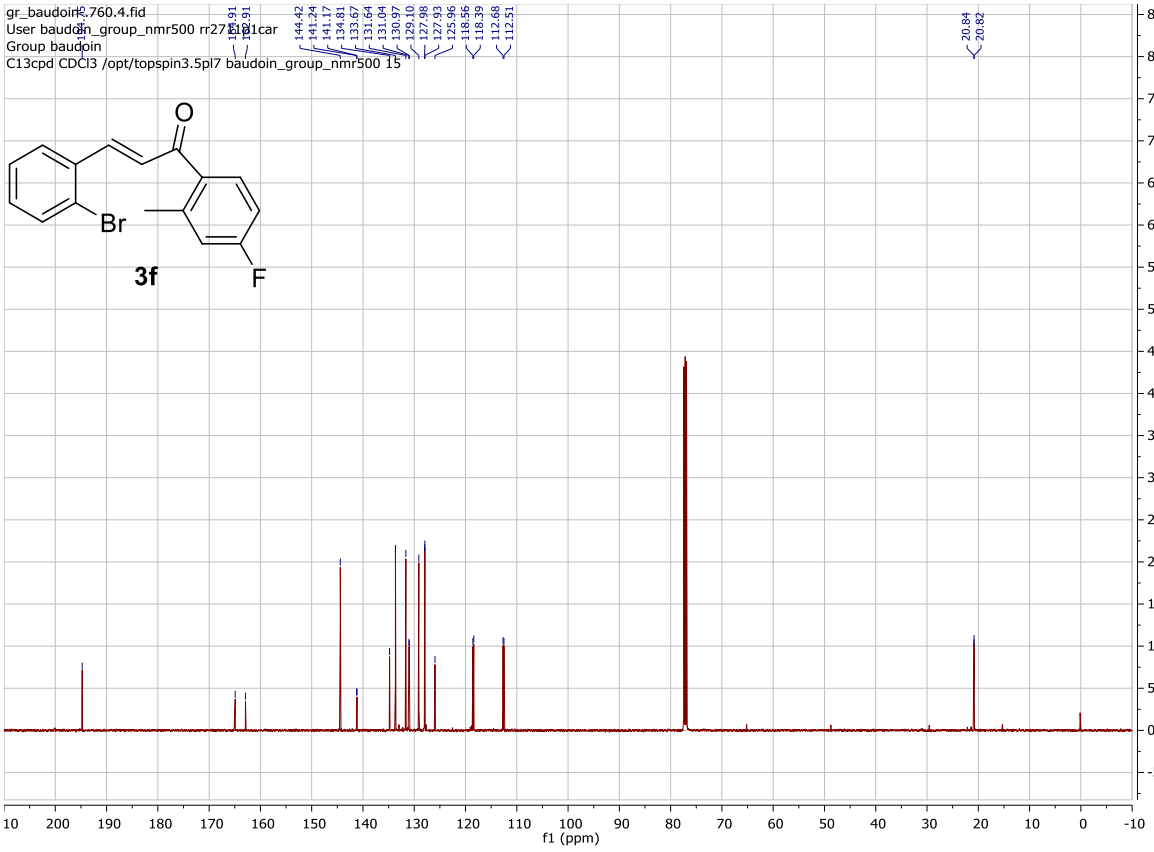
User baudoin_group_nmr500 rr2711p1car
Group baudoin
H1 CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 15
O
Br
F
3f
f1 (ppm)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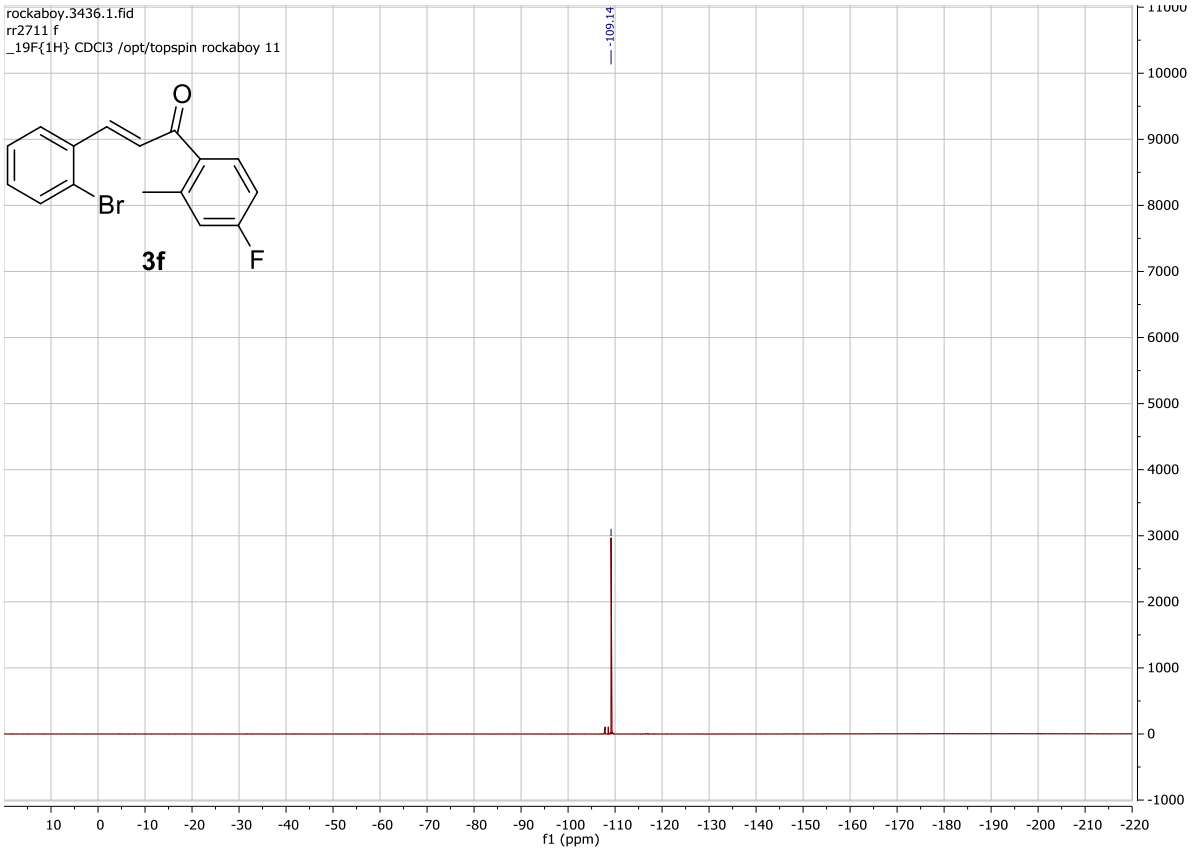
Group baudoin
C13cpd CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 15
O
Br
F
3f
f1 (ppm)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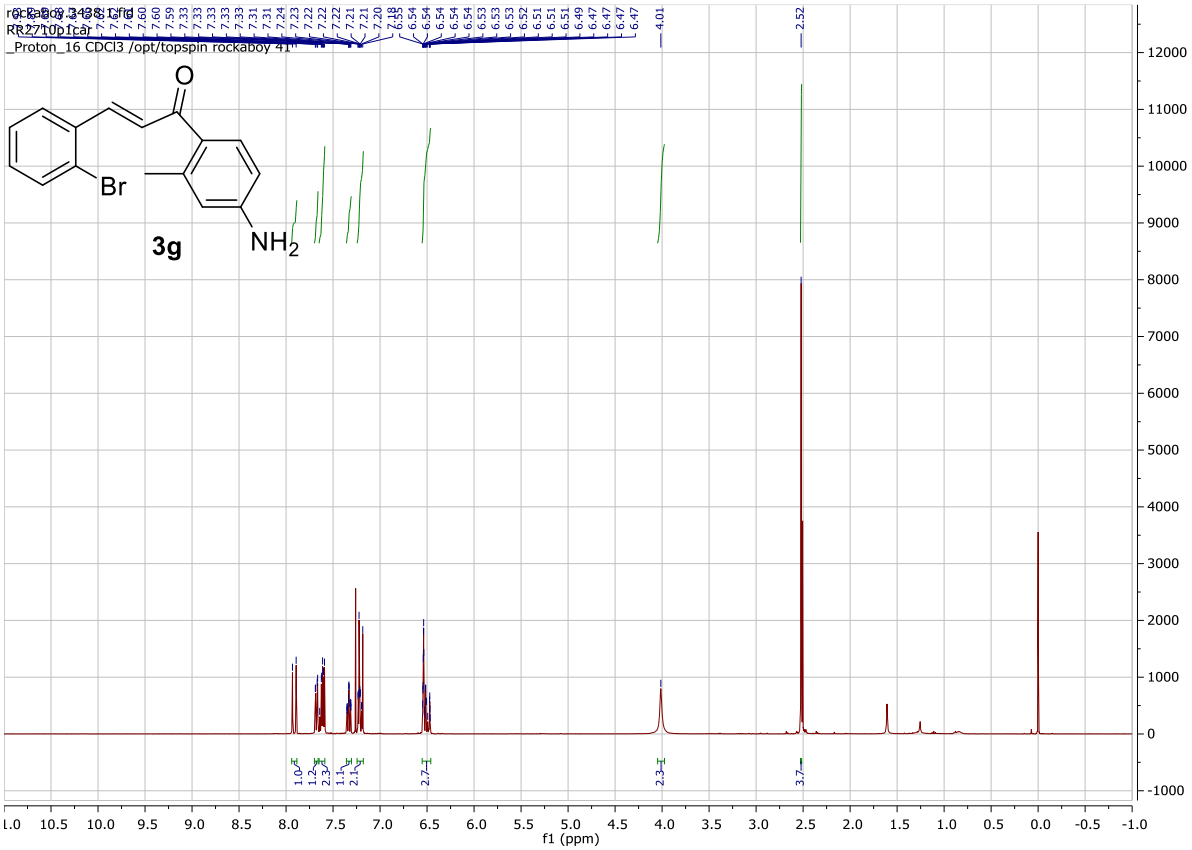
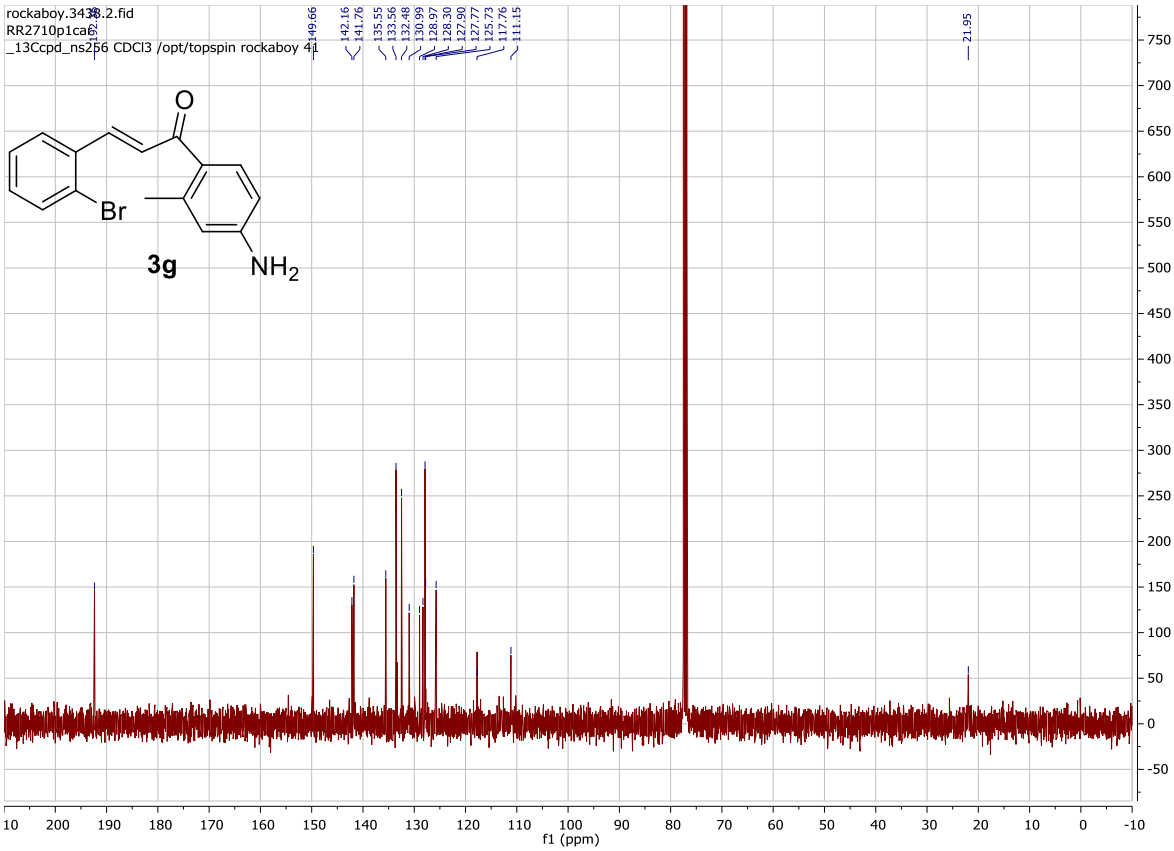
rr2711 f
_19F{1H} CDCl3 /opt/topspin rockaboy 11
-109.14
O
Br
F
3f
f1 (ppm)


RR2710p1.ra
_Proton_16 CDCl3 /opt/topspin rockaboy 41
4.01
2.52
O
Br
NH2
3g
f1 (ppm)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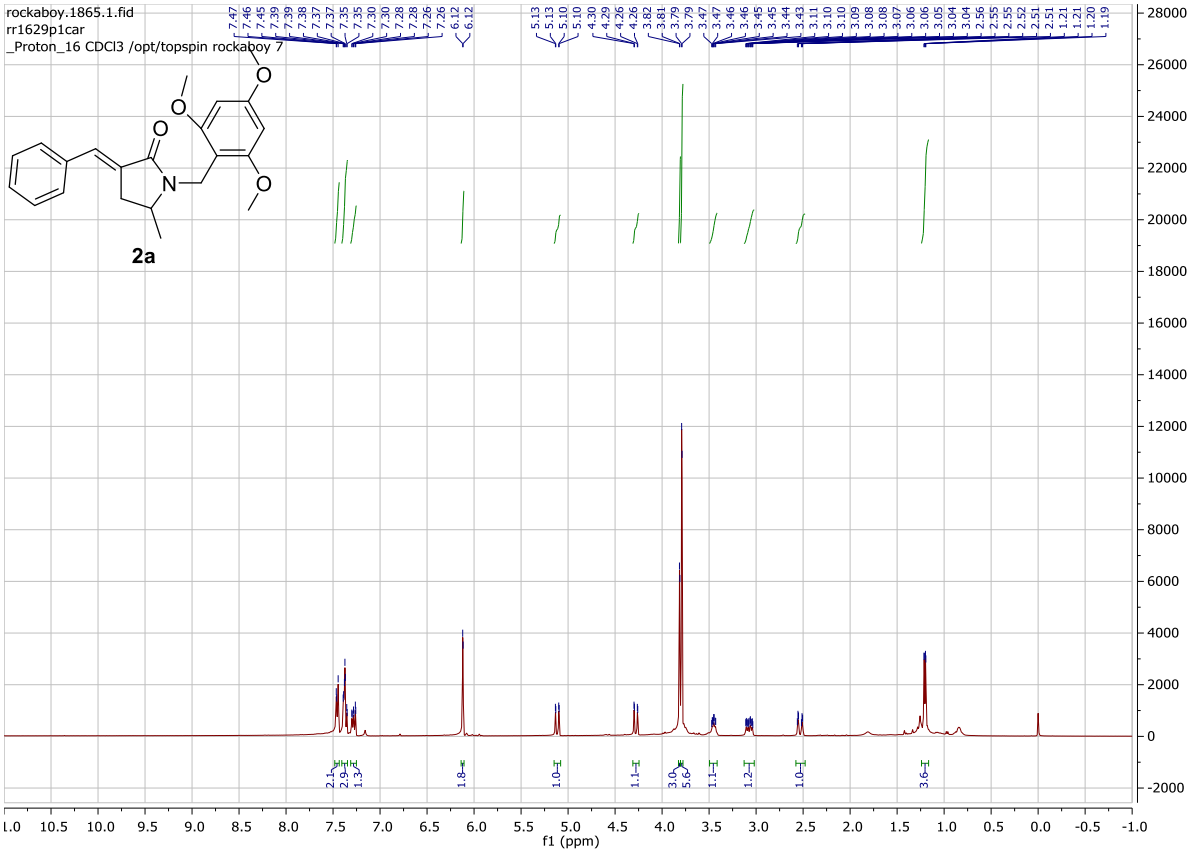
192.22
149.66
142.16
141.76
135.55
133.56
132.48
130.99
128.97
128.30
127.90
127.77
125.73
117.76
111.15
21.95
O
Br
NH2
3g
f1 (ppm)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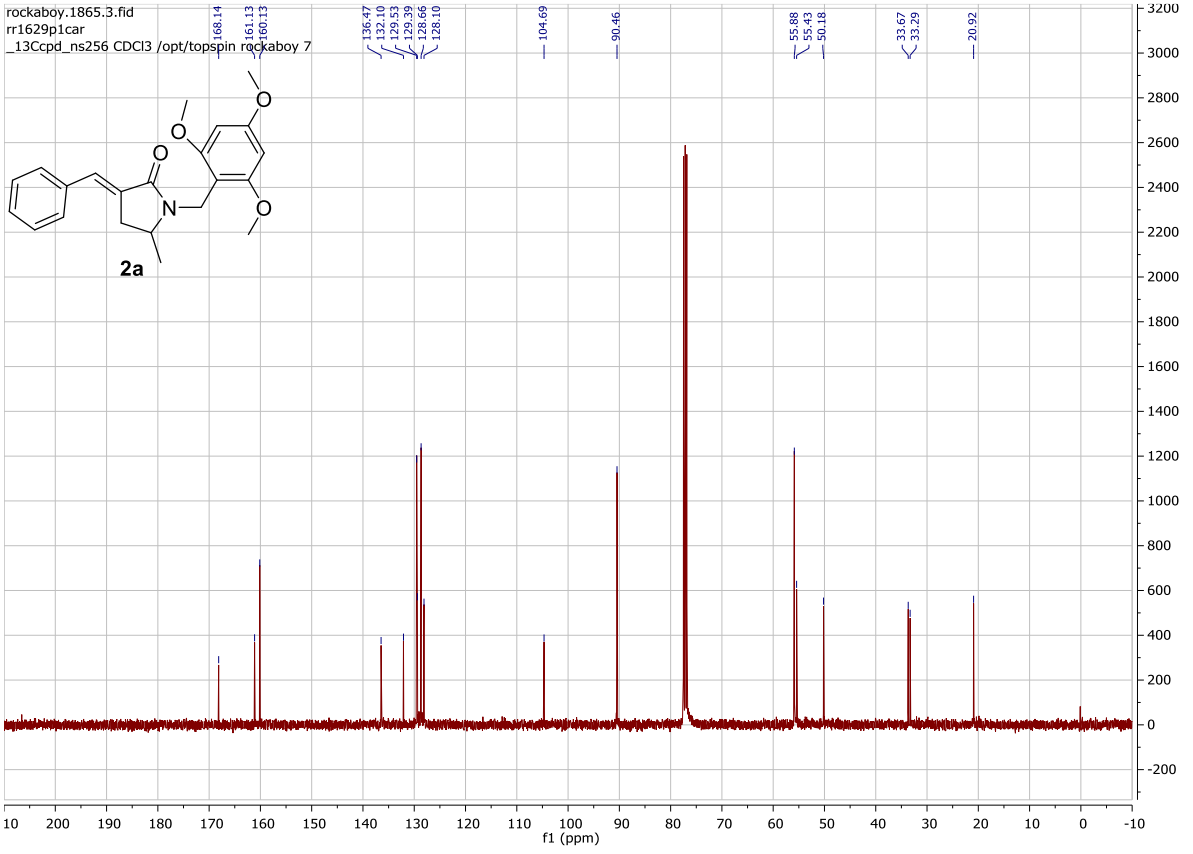
_Proton_16 CDCl3 /opt/topspin rockaboy 7
2a
f1 (ppm)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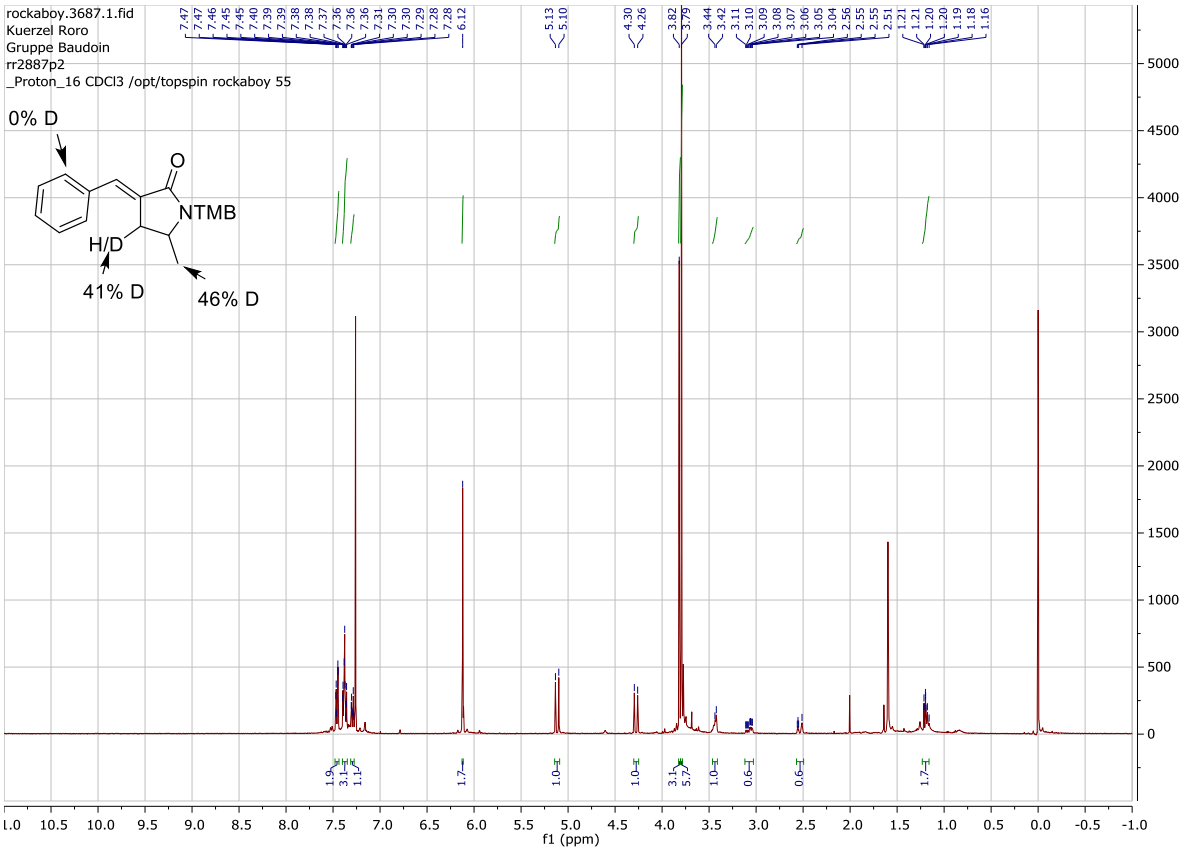
2a
f1 (ppm)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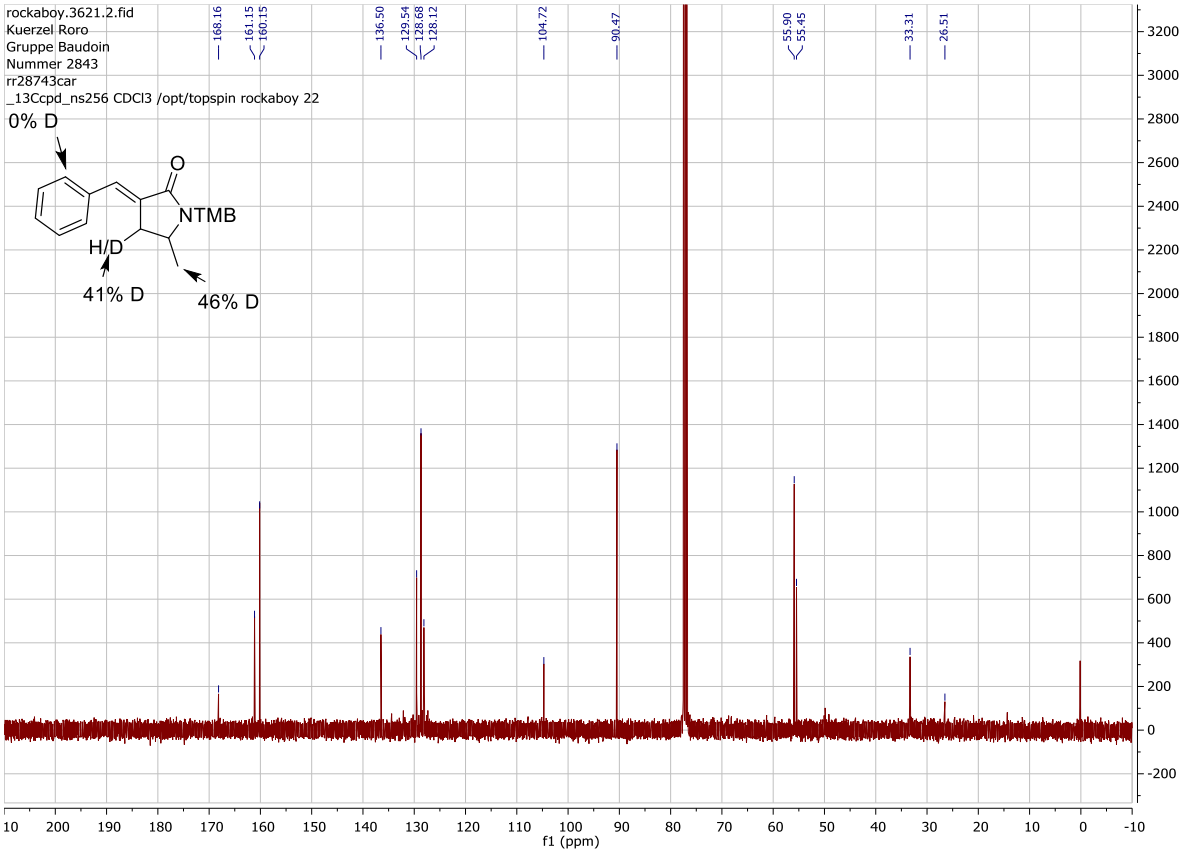
Kuerzel Roro
Gruppe Baudoin
rr2887p2
_Proton_16 CDCl3 /opt/topspin rockaboy 55
0% D
O
NTMB
H/D
41% D
46% D
f1 (ppm)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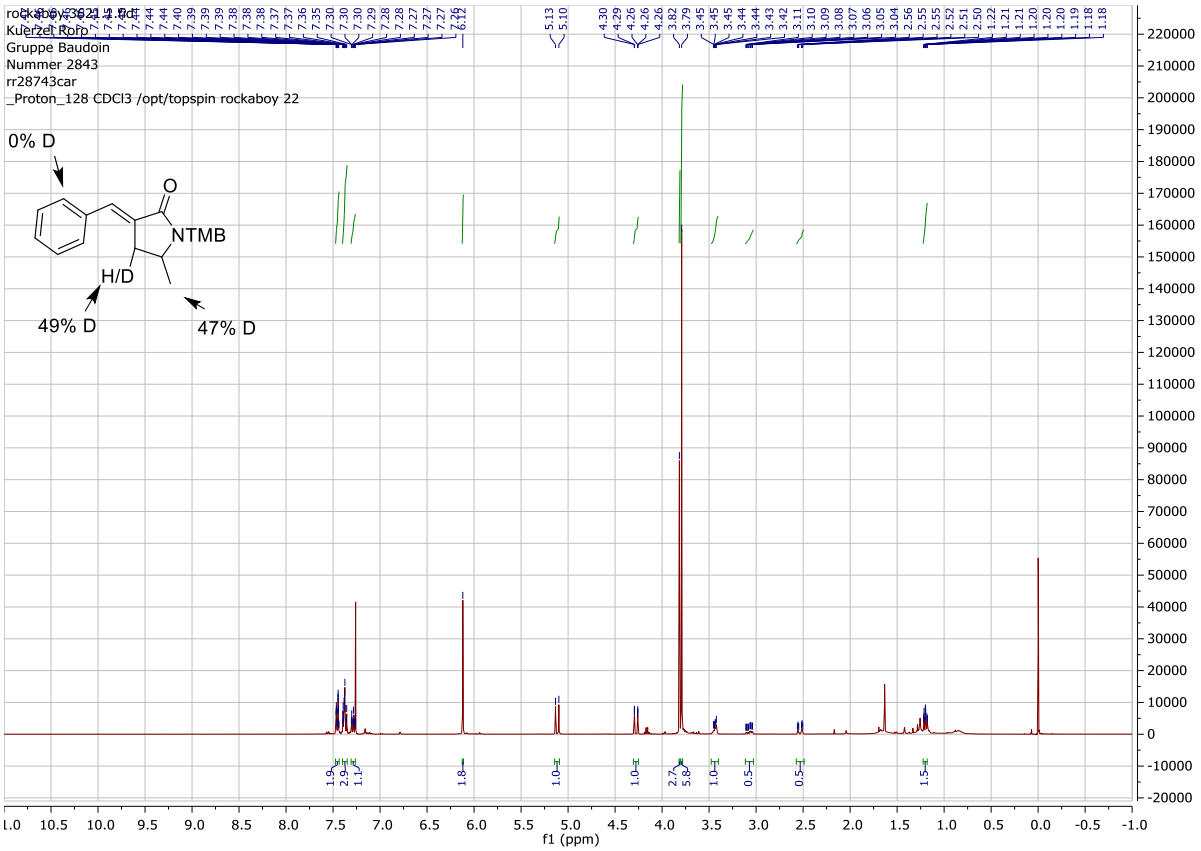
Kuerzel Roro
Gruppe Baudoin
Nummer 2843
rr28743car
_13Ccpd_ns256 CDCl3 /opt/topspin rockaboy 22
0% D
O
NTMB
H/D
41% D
46% D
f1 (ppm)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Kuerzel Roro
Gruppe Baudoin
Nummer 2843
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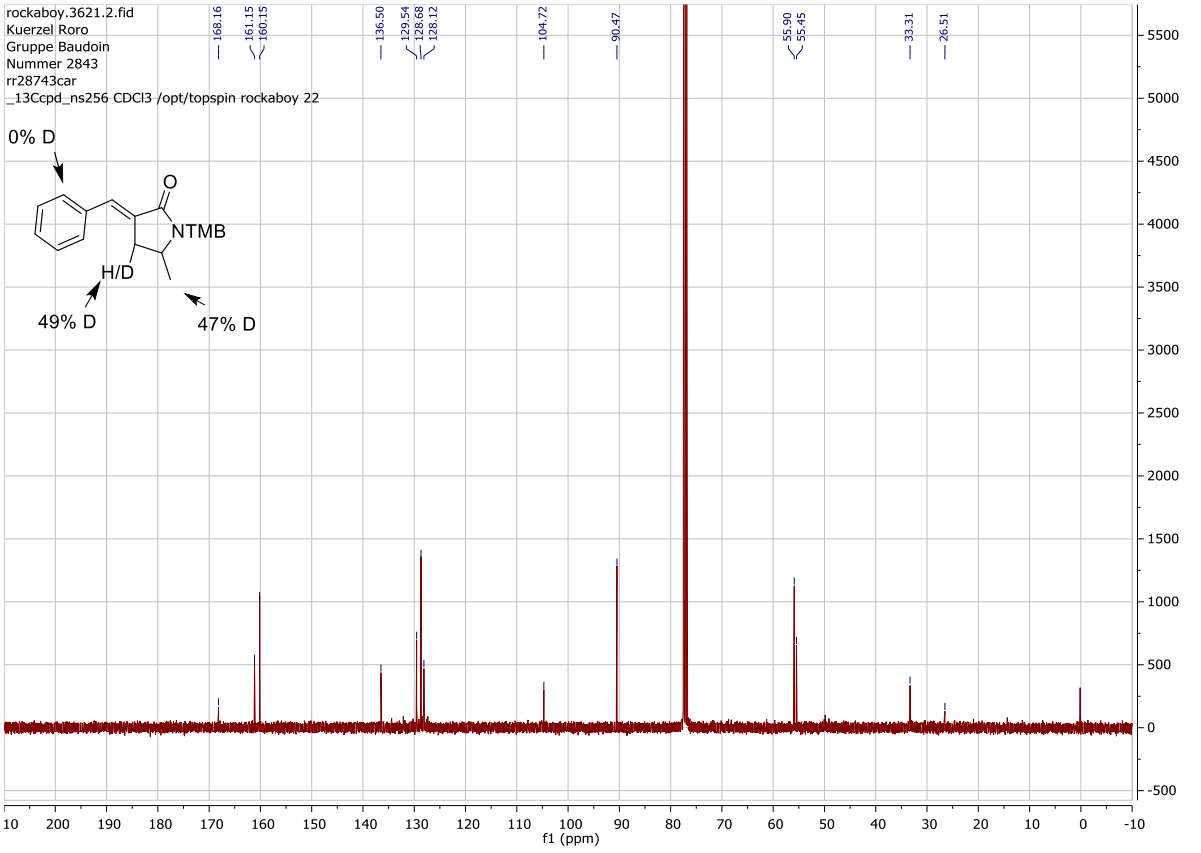
0% D
O
NTMB
H/D
49% D
47% D
f1 (ppm)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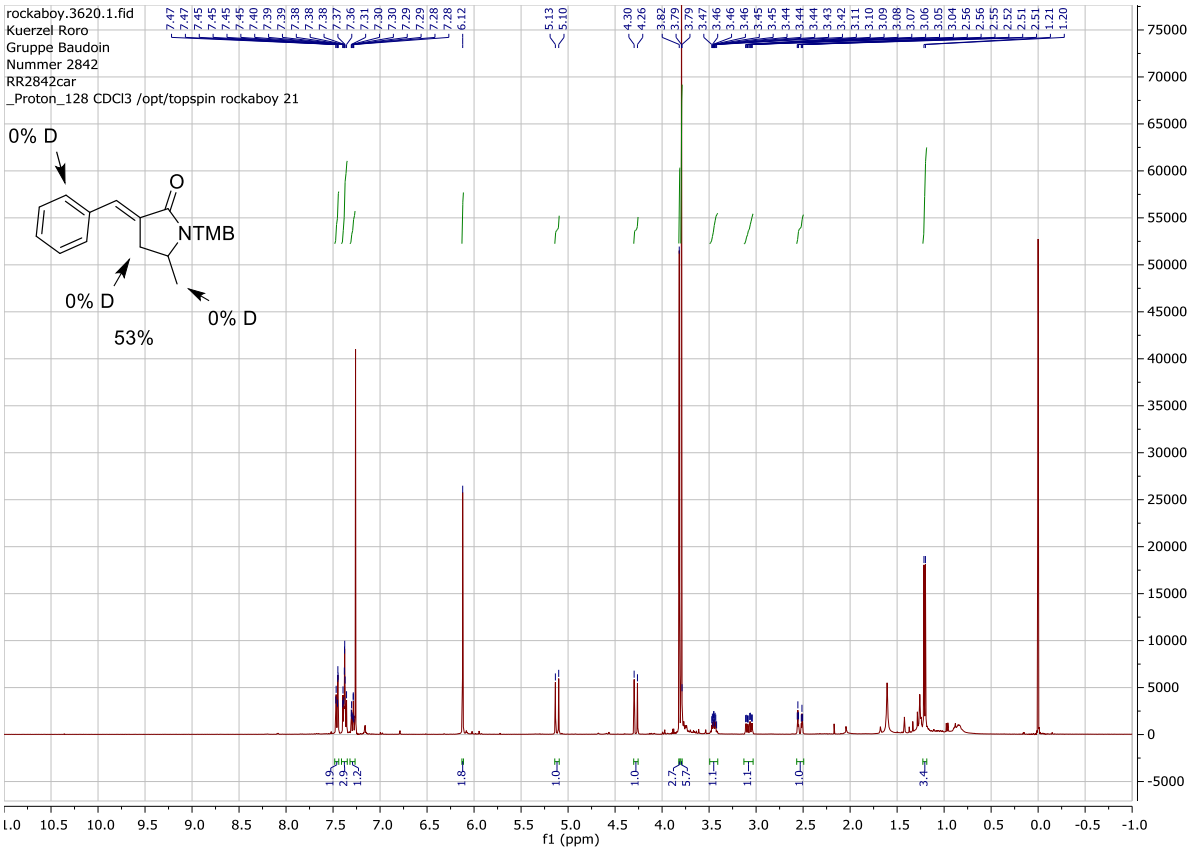
Kuerzel Roro
Gruppe Baudoin
Nummer 2843
rr28743car
_13Ccpd_ns256 CDCl3 /opt/topspin rockaboy 22
168.16
161.15
160.15
136.50
129.54
128.68
128.12
104.72
90.47
55.90
55.45
33.31
26.51
0% D
O
NTMB
H/D
49% D
47% D
f1 (ppm)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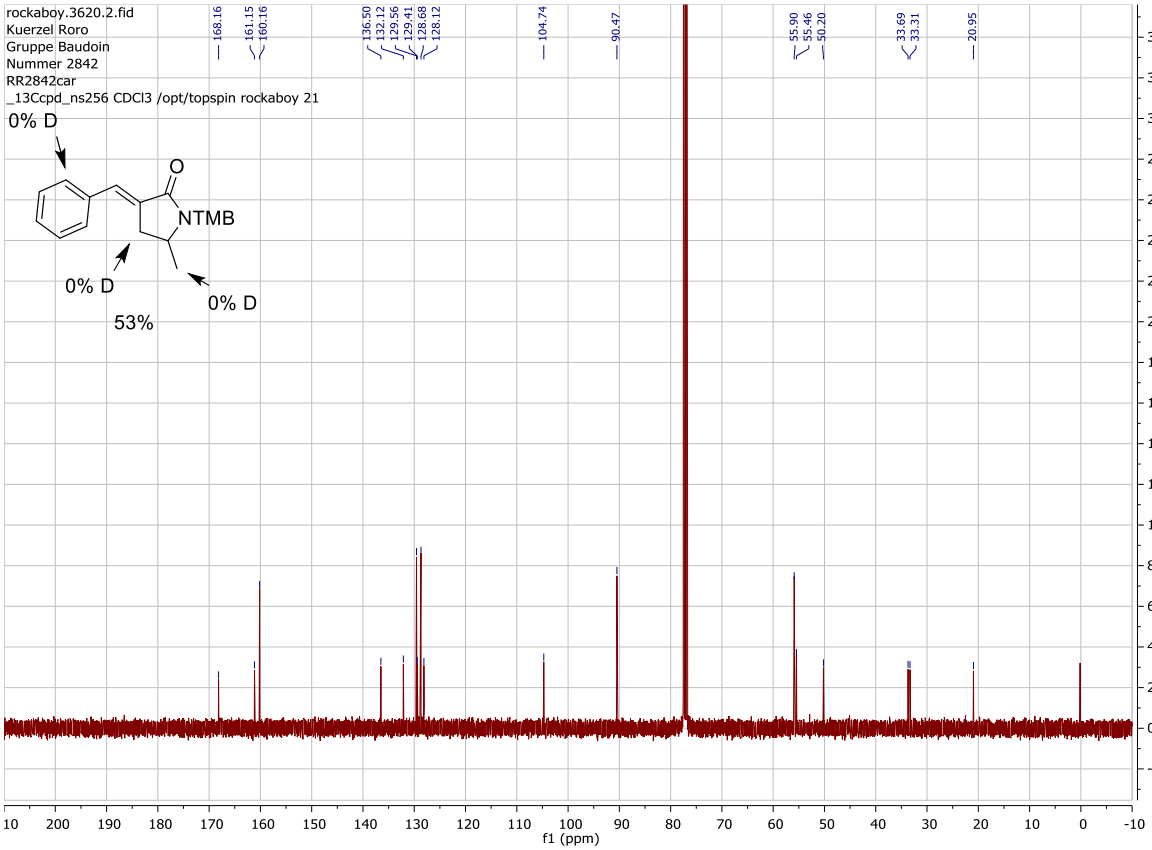
Gruppe Baudoin
Nummer 2842
RR2842car
_Proton_128 CDCl3 /opt/topspin rockaboy 21
0% D
O
NTMB
0% D
0% D
53%
f1 (ppm)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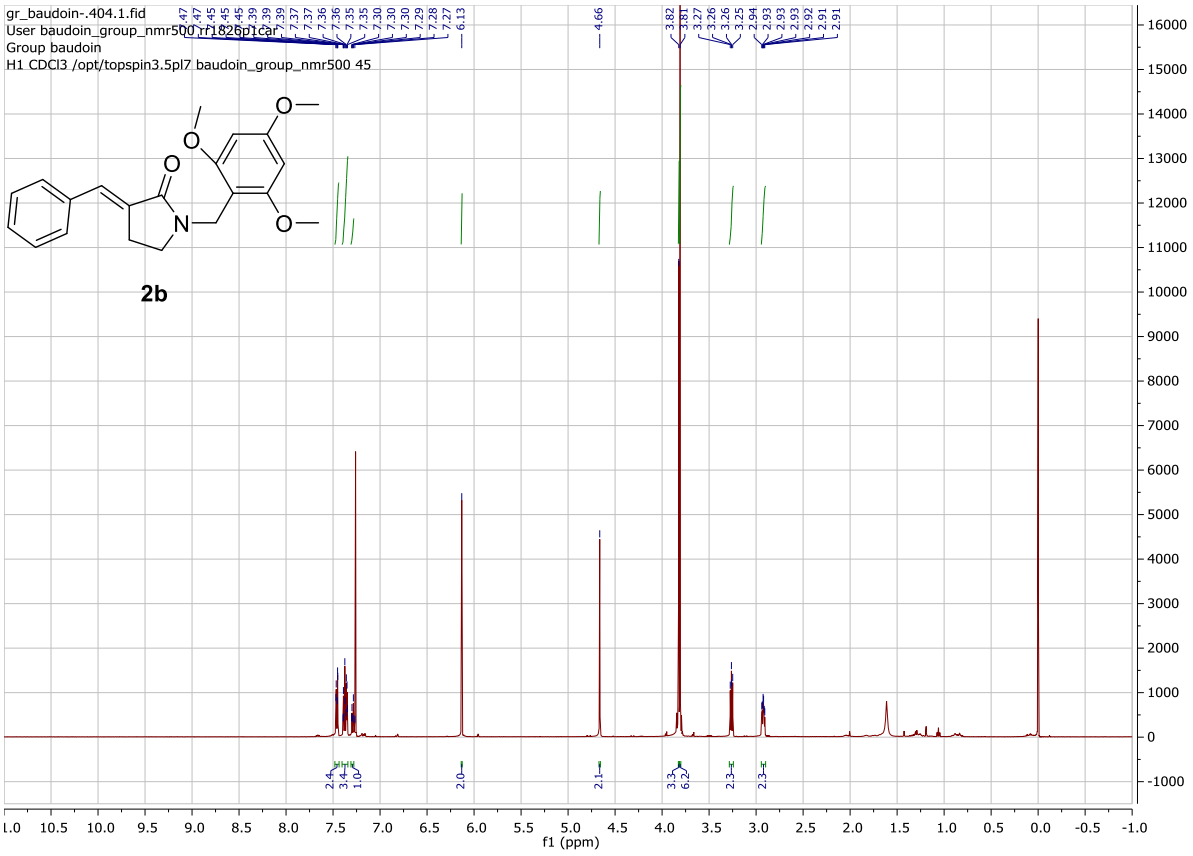
Kuerzel Roro
Gruppe Baudoin
Nummer 2842
RR2842car
_13Ccpd_ns256 CDCl3 /opt/topspin rockaboy 21
0% D
O
NTMB
0% D
0% D
53%
f1 (ppm)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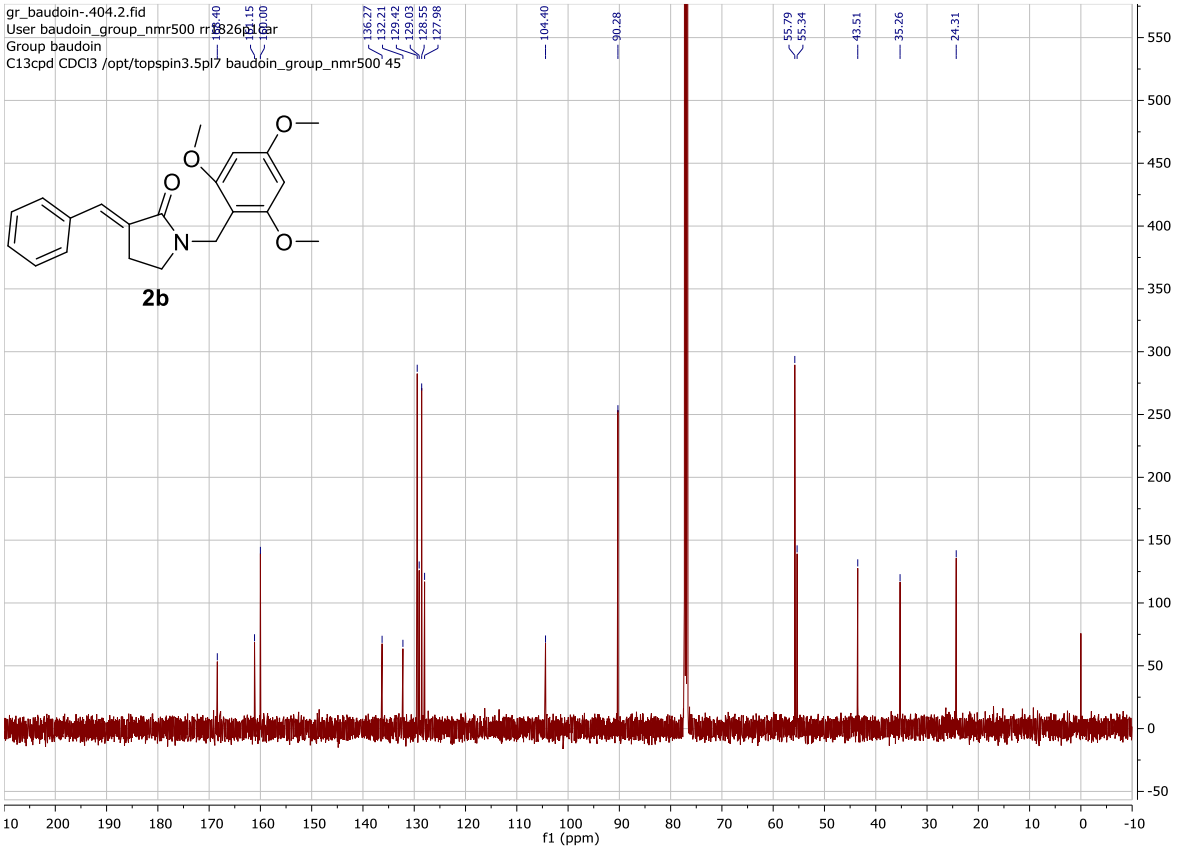
User baudoin_group_nmr500 rr1826p1car
Group baudoin
H1 CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 45
2b
f1 (ppm)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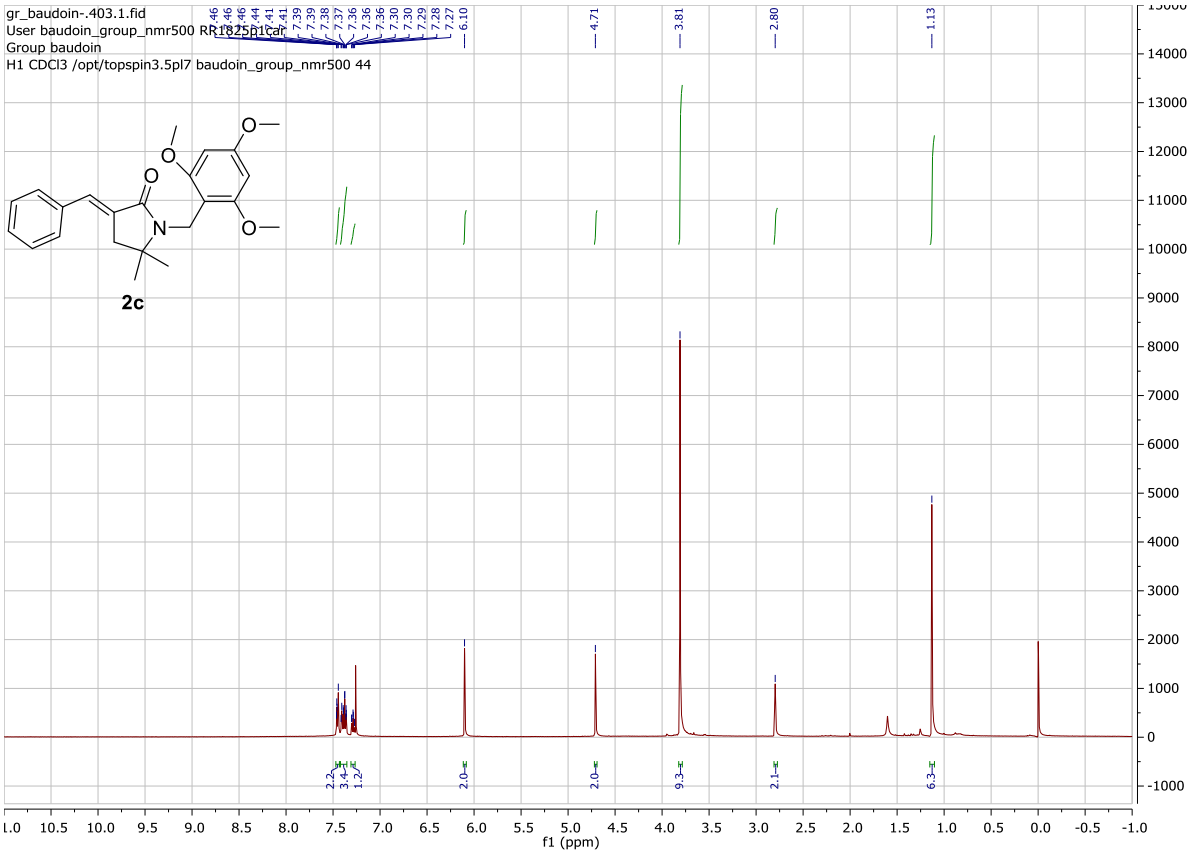
User baudoin_group_nmr500 rr1826p1car
Group baudoin
C13cpd CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 45
2b
f1 (ppm)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User baudoin_group_nmr500 RR1825p1car
Group baudoin
H1 CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 44
7.46
7.46
7.46
7.44
7.41
7.41
7.39
7.39
7.38
7.37
7.36
7.36
7.30
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7.29
7.28
7.27
6.10
4.71
3.81
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3.4
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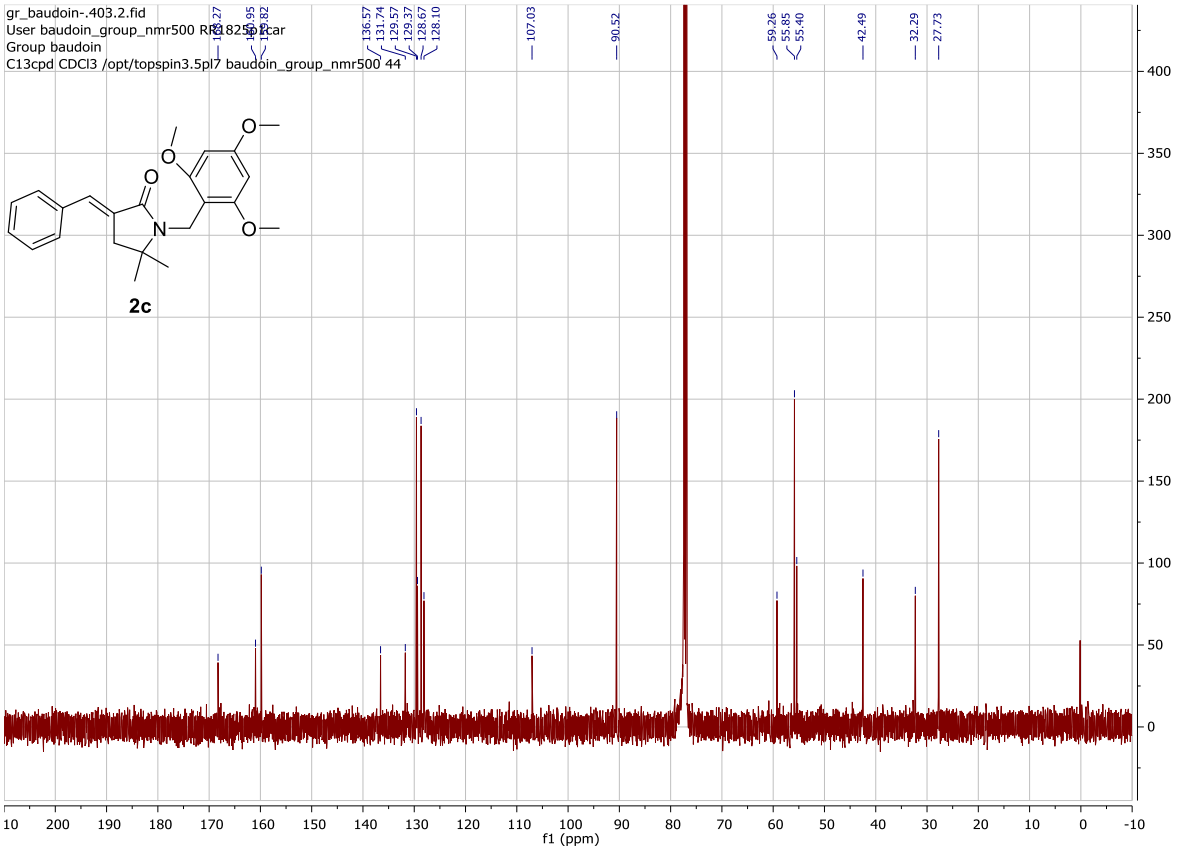
9.3
2.1
6.3
2c
f1 (ppm)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User baudoin_group_nmr500 RR1825p1car
Group baudoin
C13cpd CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 44
169.27
159.95
157.82
136.57
131.74
129.57
129.37
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90.52
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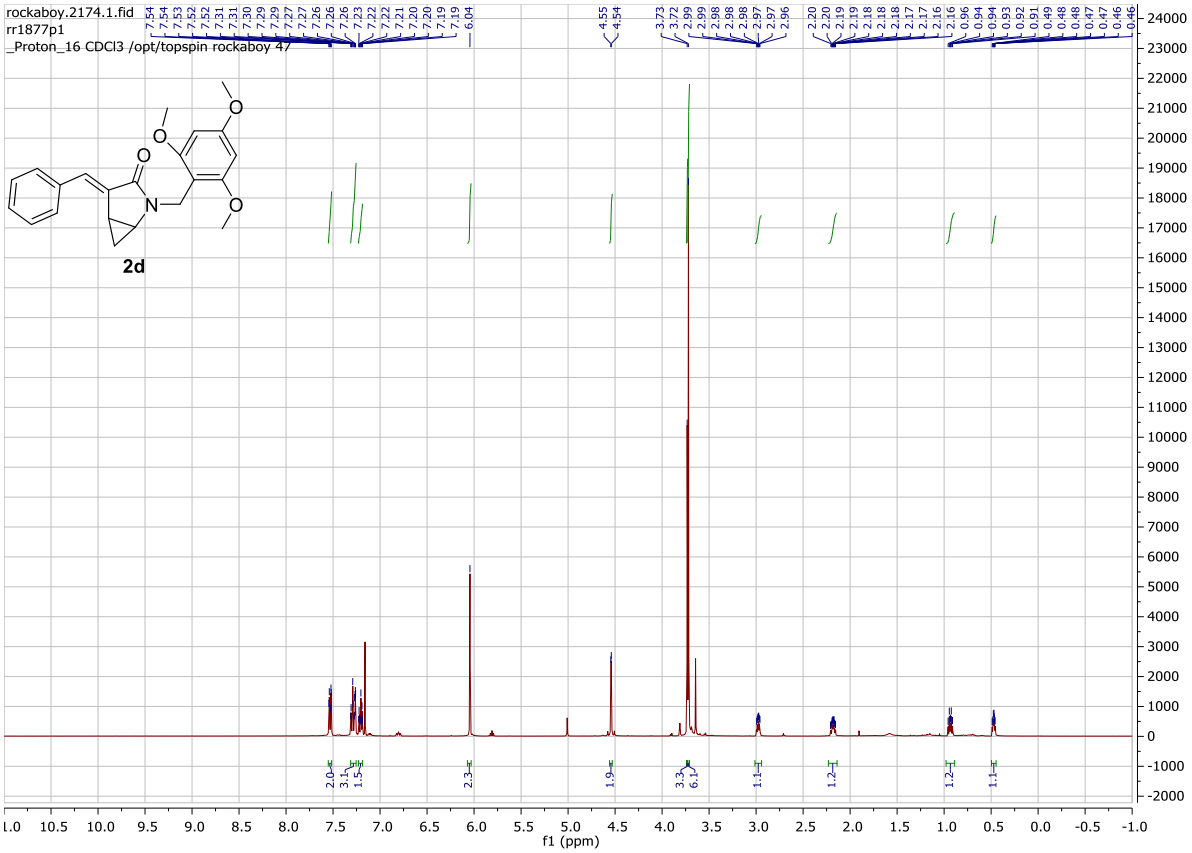
55.85
55.40
42.49
32.29
27.73
2c
f1 (ppm)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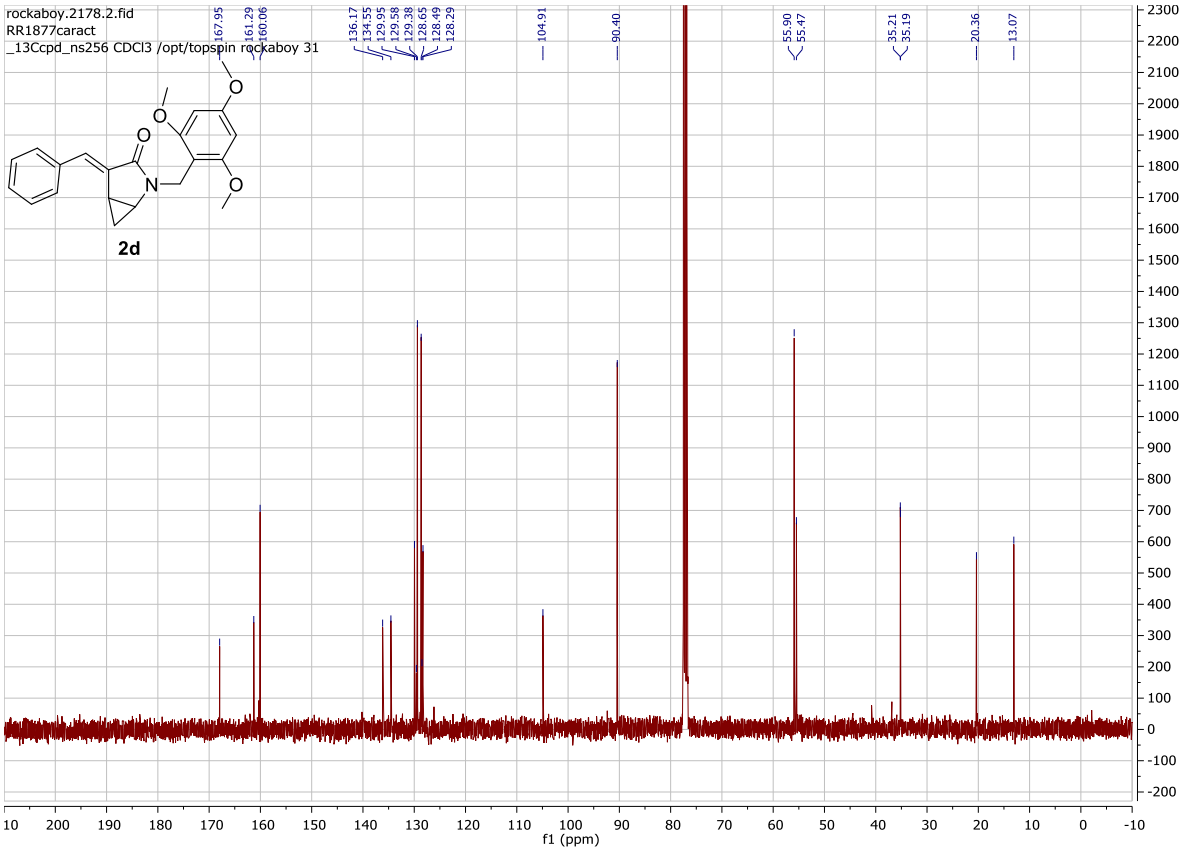
rr1877p1
_Proton_16 CDCl3 /opt/topspin rockaboy 47
2d
f1 (ppm)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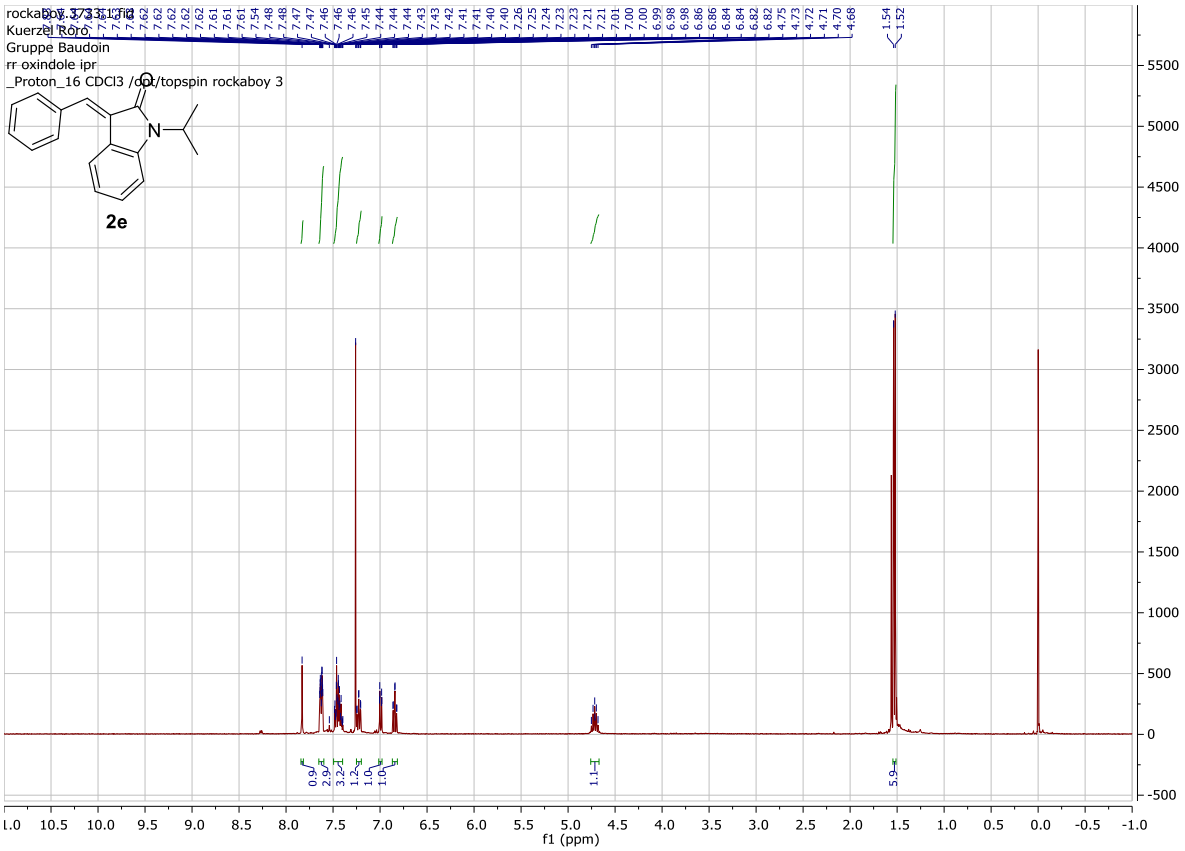
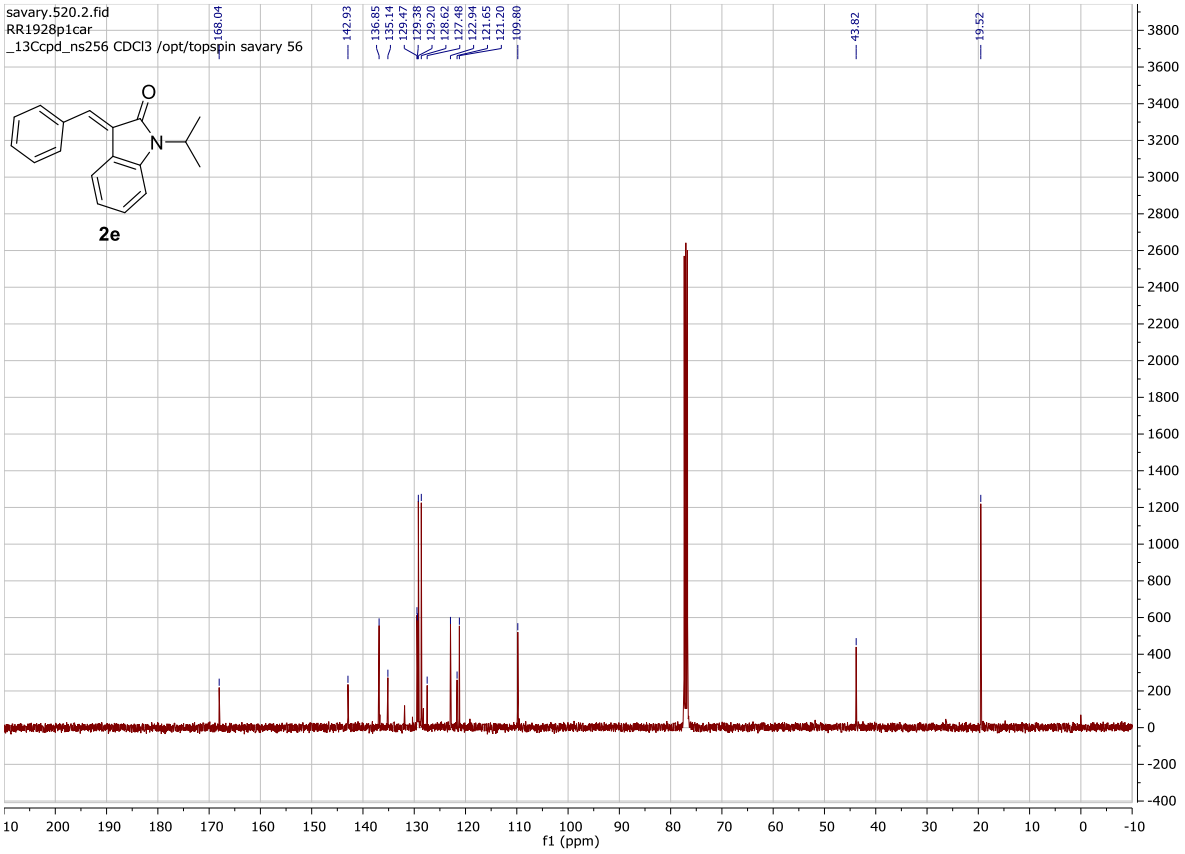
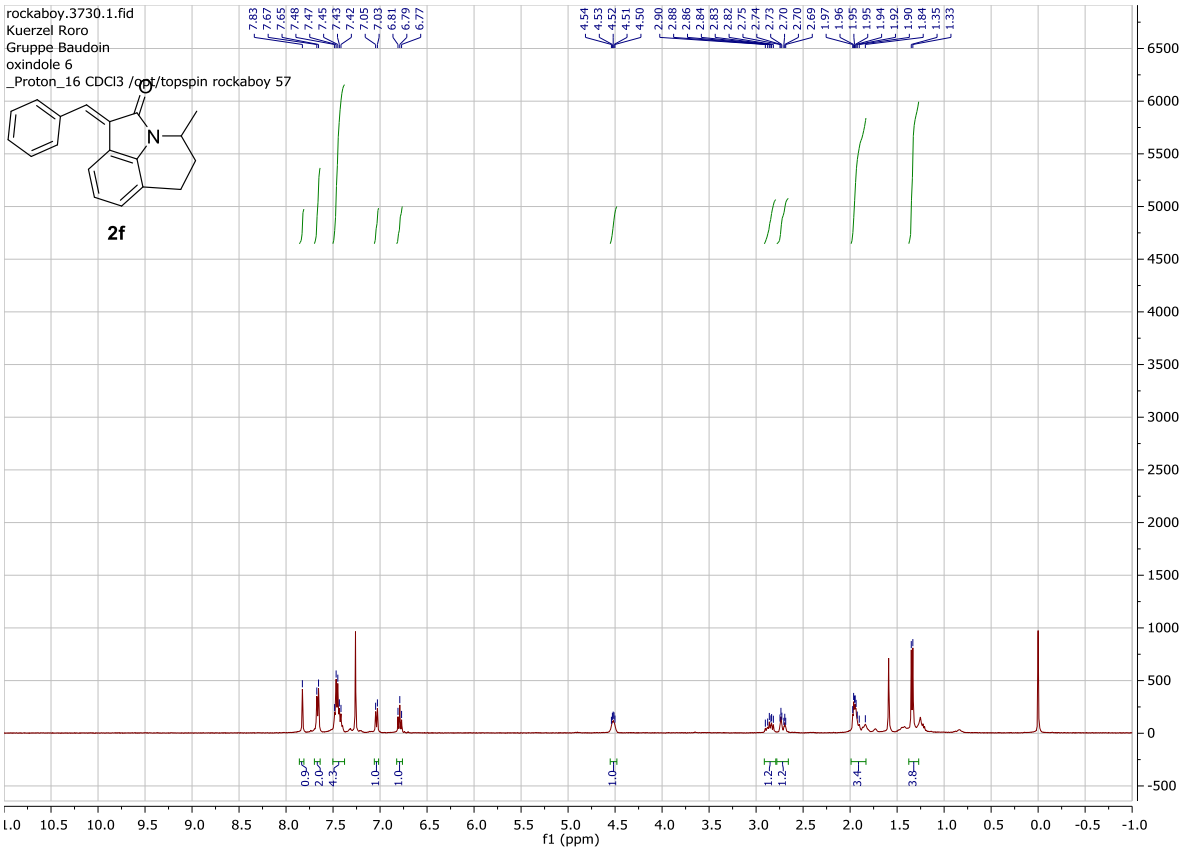
RR1877caract
_13Ccpd_ns256 CDCl3 /opt/topspin rockaboy 31
2d
f1 (ppm)


rockaboy.373.1.fid
Kuerzel RoRo
Gruppe Baudoin
rr oxindole ipr
_Proton_16 CDCl3 /opt/topspin rockaboy 3
O
N
2e
f1 (ppm)


savary.520.2.fid
RR1928p1car
_13Ccpd_ns256 CDCl3 /opt/topspin savary 56
168.04
142.93
136.85
135.14
129.47
129.38
129.20
128.62
127.46
122.94
121.65
121.20
109.80
43.82
19.52
O
N
2e
f1 (ppm)


rockaboy.3730.1.fid
Kuerzel Roro
Gruppe Baudoin
oxindole 6
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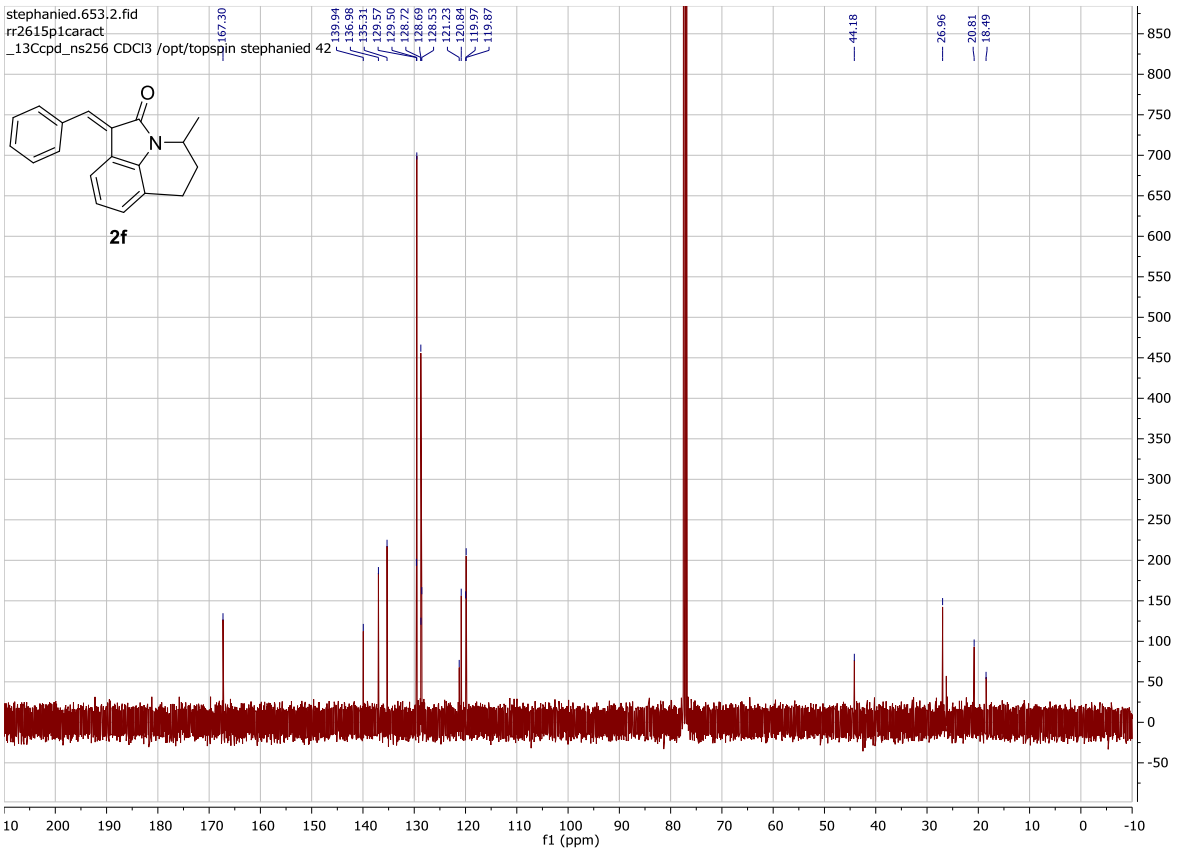
2f
f1 (ppm)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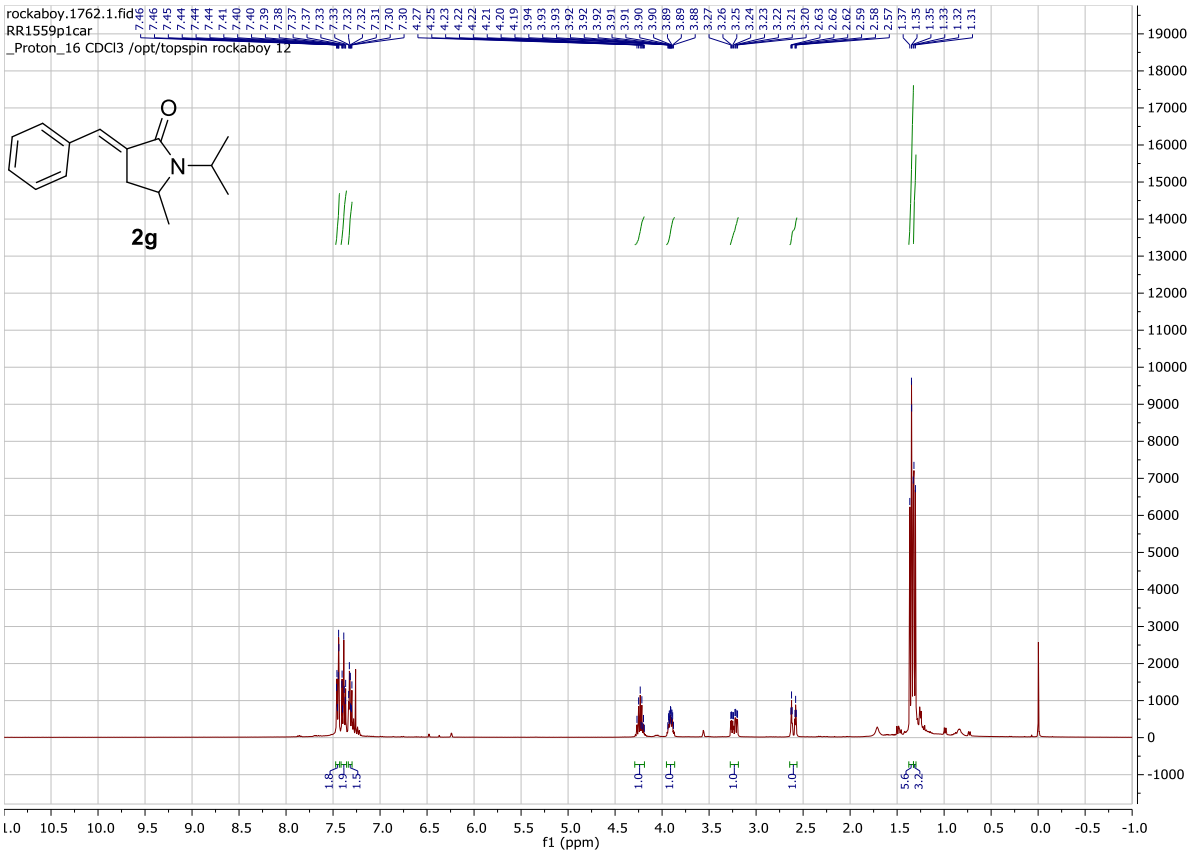
rr2615p1caract
_13Ccpd_ns256 CDCl3 /opt/topspin stephanied 42
2f
f1 (ppm)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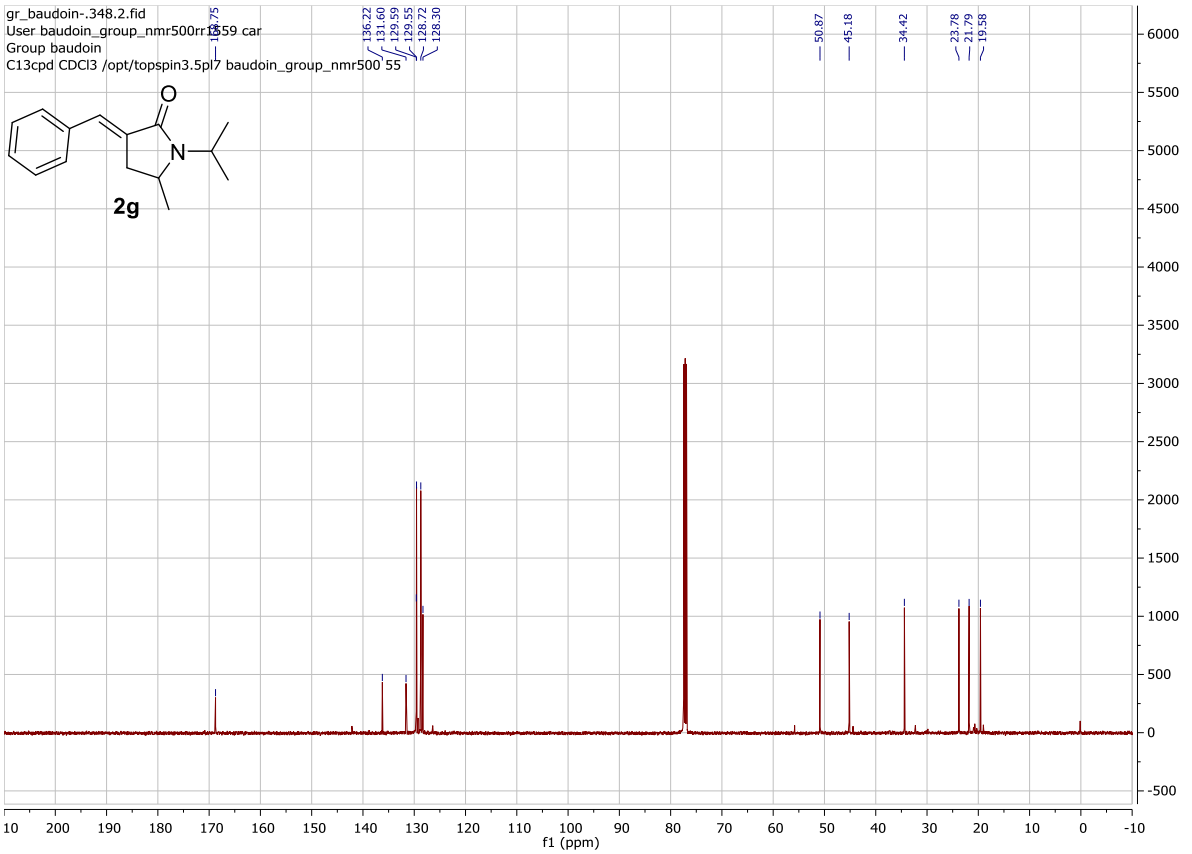
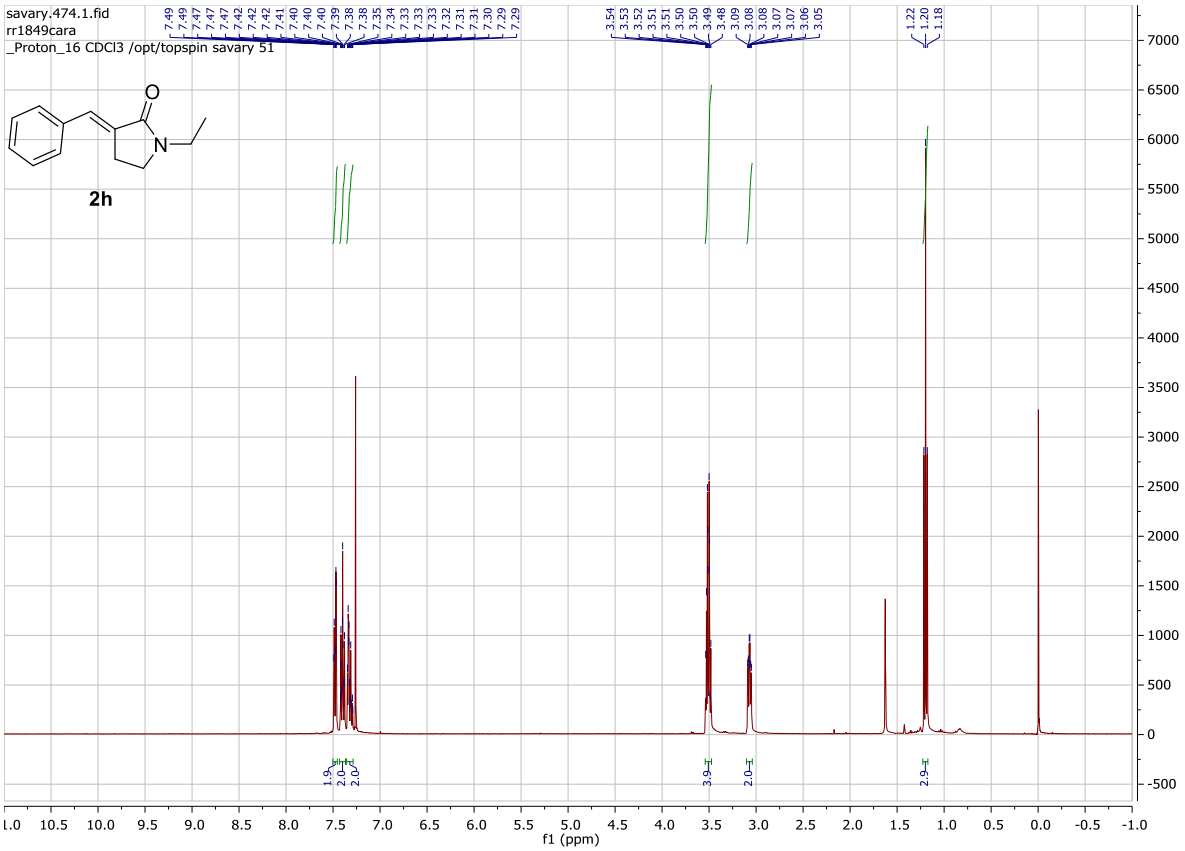
RR1559p1car
_Proton_16 CDCl3 /opt/topspin rockaboy 12
2g
f1 (ppm)


gr_baudoin-.348.2.fid
User baudoin_group_nmr500rr1559 car
Group baudoin
C13cpd CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 55
2g
f1 (ppm)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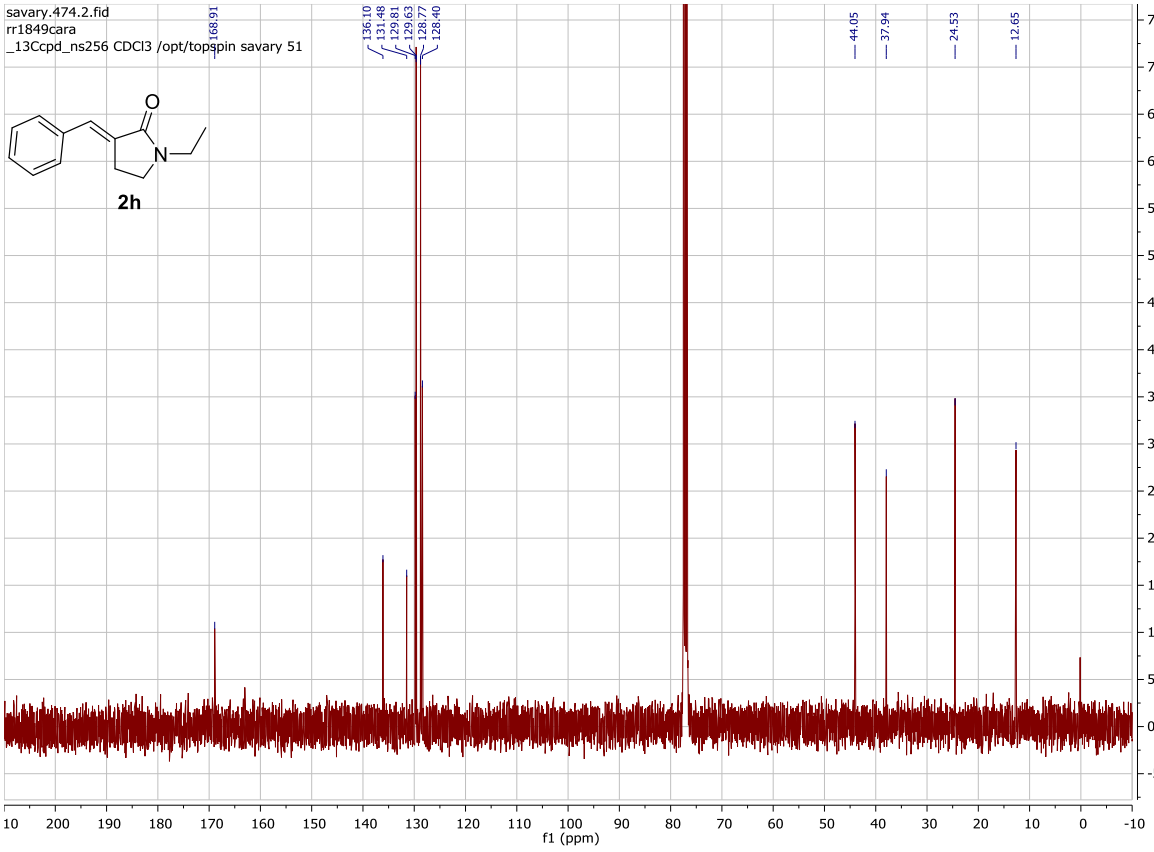
rr1849cara
_Proton_16 CDCl3 /opt/topspin savary 51
2h
f1 (ppm)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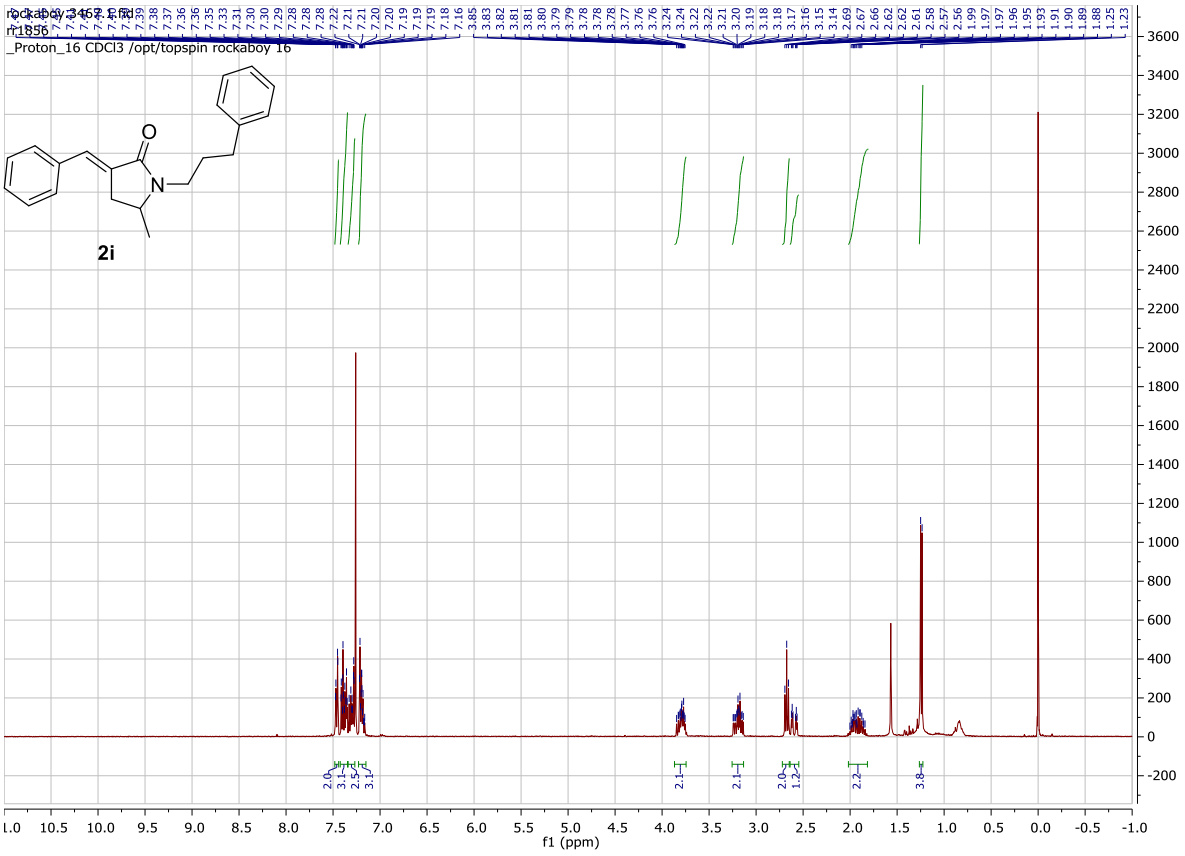
2h
f1 (ppm)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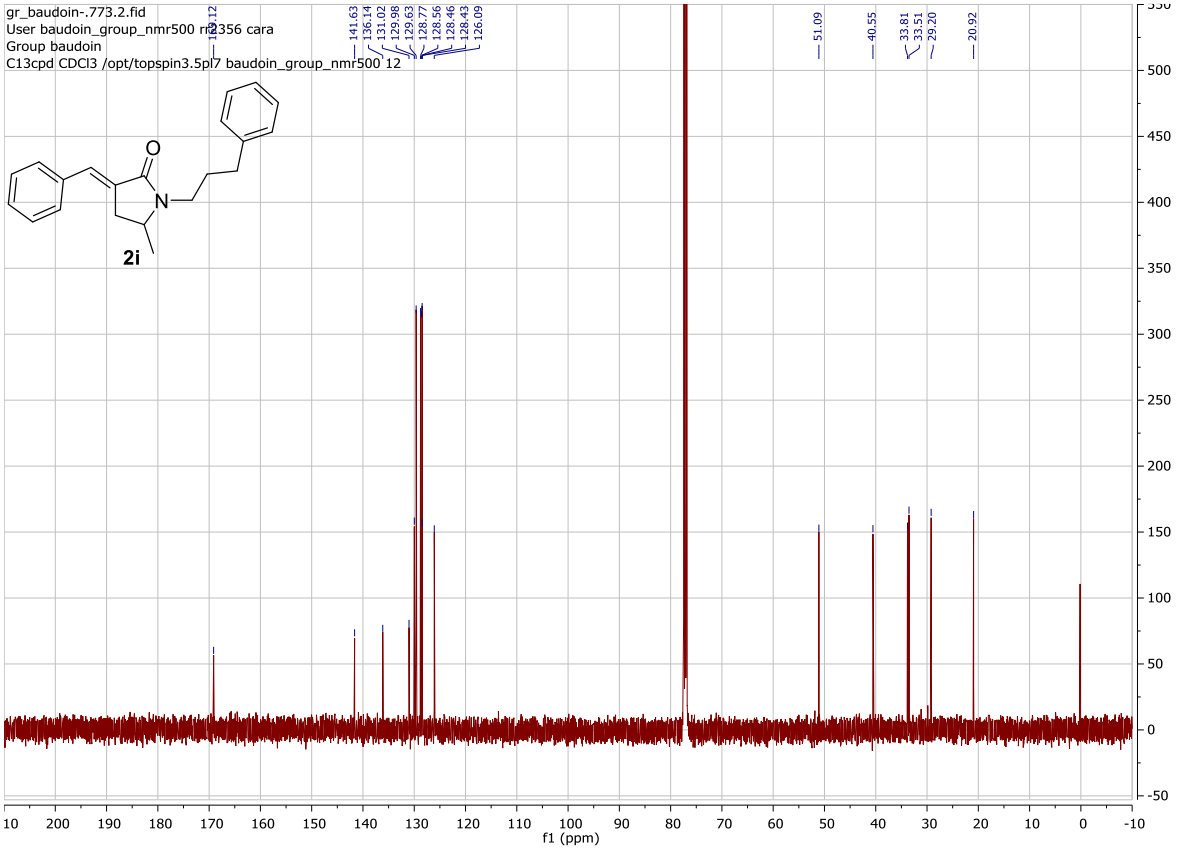
nr 1856
_Proton_16 CDCl3 /opt/topspin rockaboy 16
2i
f1 (ppm)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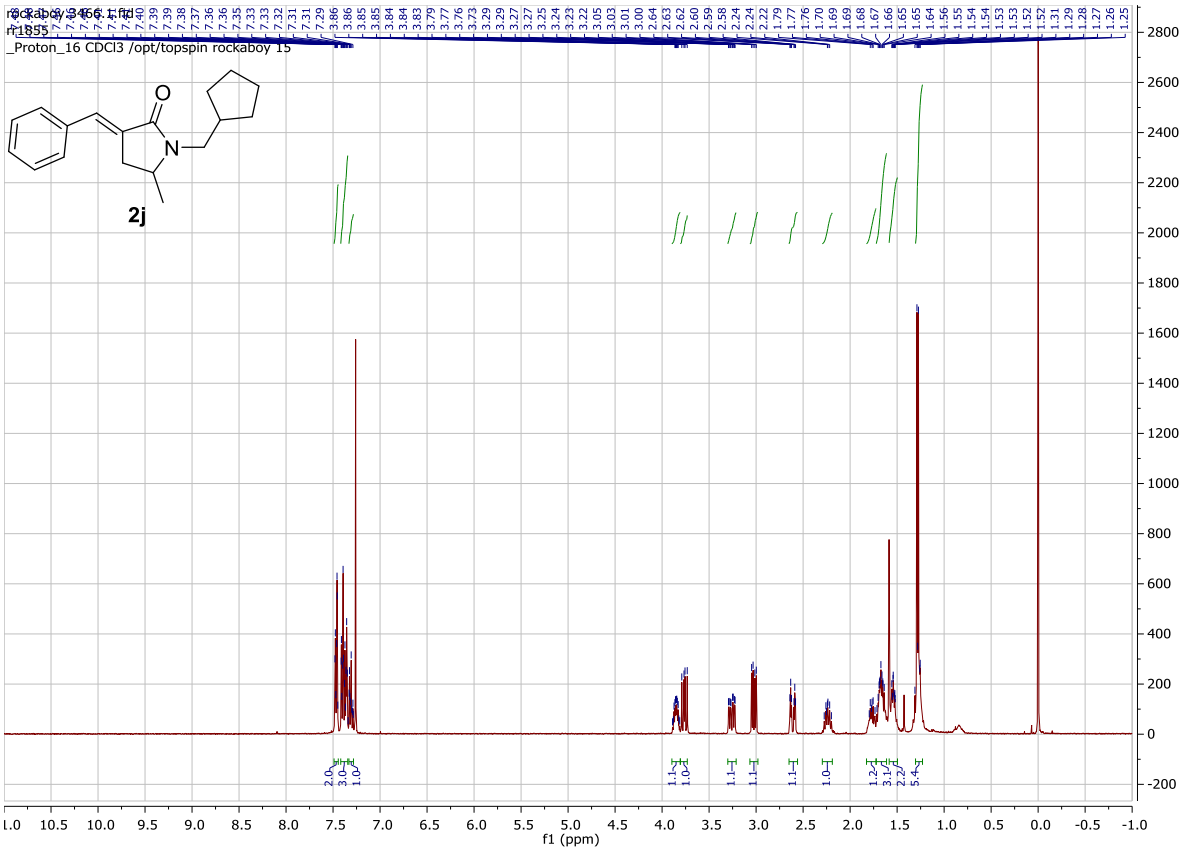
User baudoin_group_nmr500 nr 2356 cara
Group baudoin
C13cpd CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 12
170.12
141.63
136.14
131.02
129.98
129.63
128.77
128.56
128.46
128.43
126.09
51.09
40.55
33.81
33.51
29.20
20.92
2i
f1 (ppm)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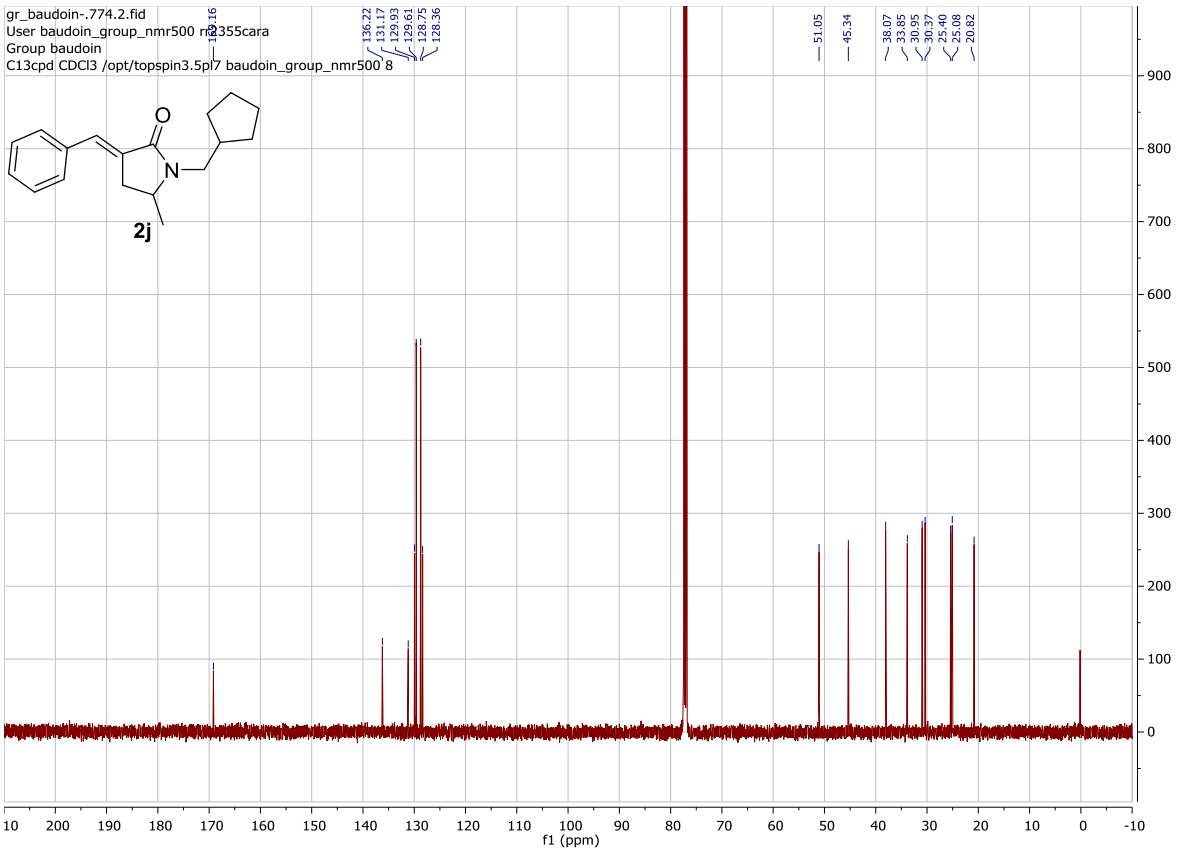
nr1855
_Proton_16 CDCl3 /opt/topspin rockaboy 15
2j
f1 (ppm)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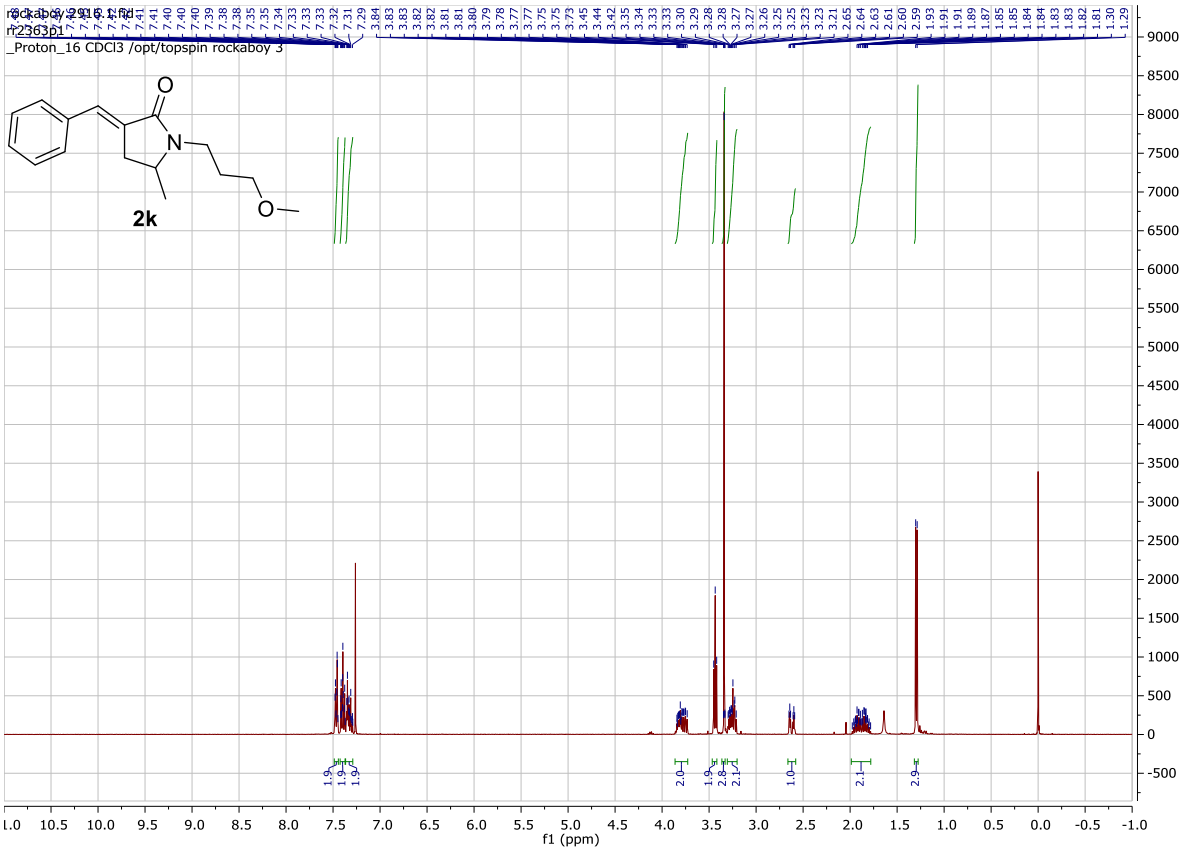
Group baudoin
C13cpd CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 8
2j
f1 (ppm)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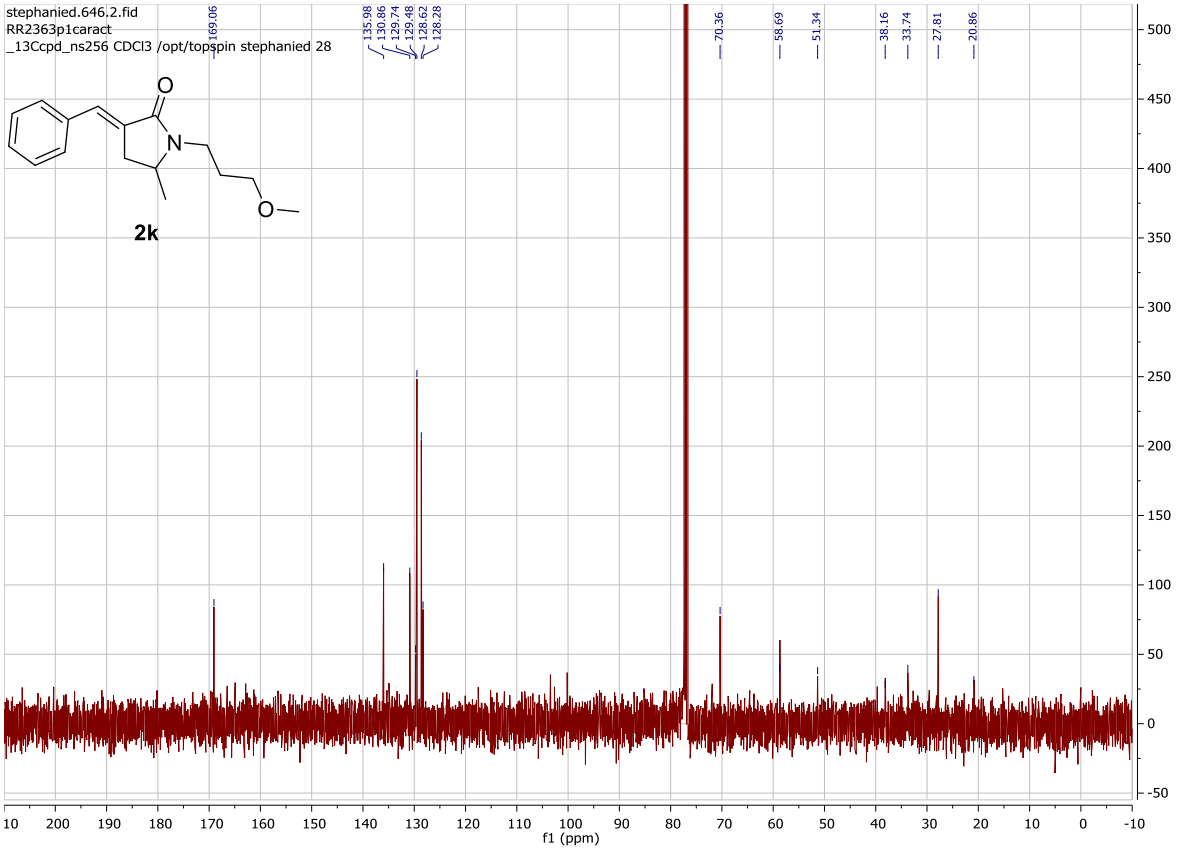
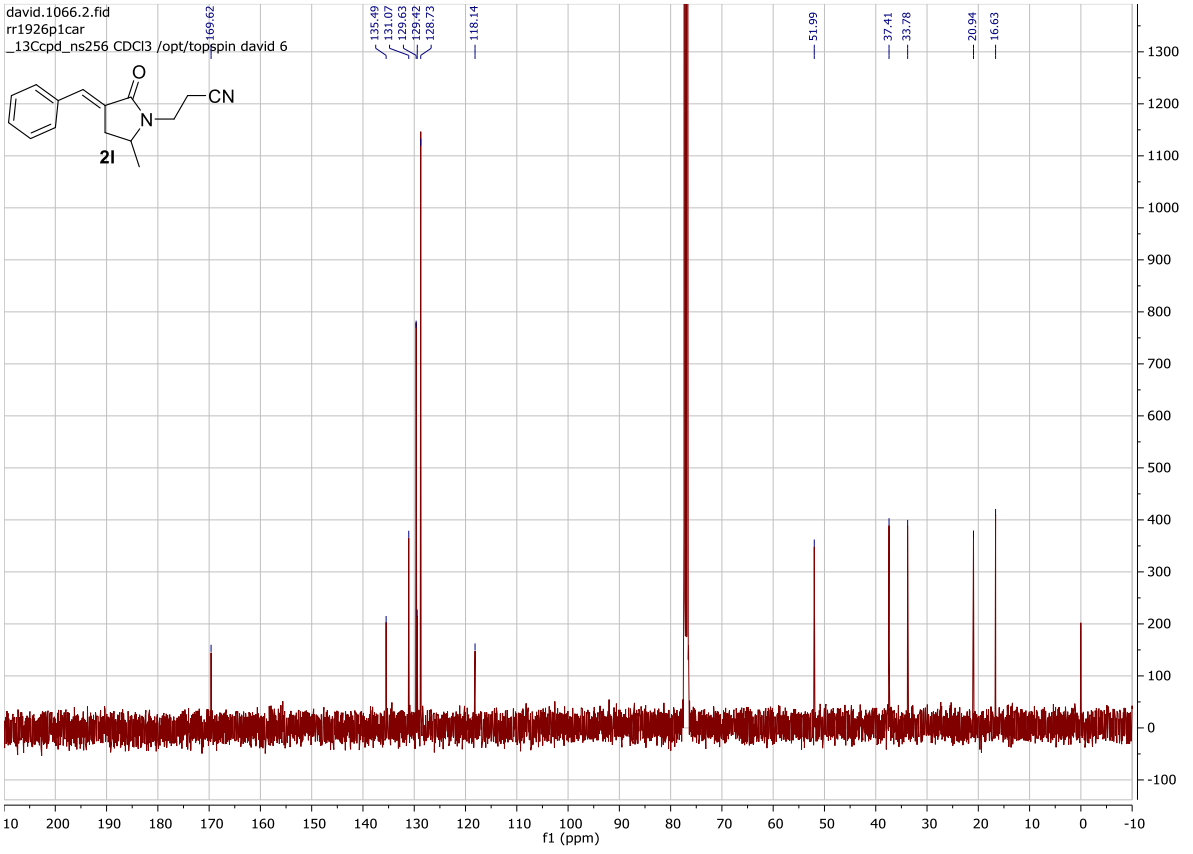
rr236361
_Proton_16 CDCl3 /opt/topspin rockaboy 3
O
N
O
2k
f1 (ppm)


stephanied.646.2.fid
RR2363p1caract
_13Ccpd_ns256 CDCl3 /opt/topspin stephanied 28
169.06
135.98
130.86
129.74
129.48
128.62
128.28
70.36
58.69
51.34
38.16
33.74
27.81
20.86
O
N
O
2k
f1 (ppm)


rr1926p1
_Proton_16 CDCl3 /opt/topspin rockaboy 37
O
N
CN
2l
f1 (ppm)


david.1066.2.fid
rr1926p1car
_13Ccpd_ns256 CDCl3 /opt/topspin david 6
169.62
135.49
131.07
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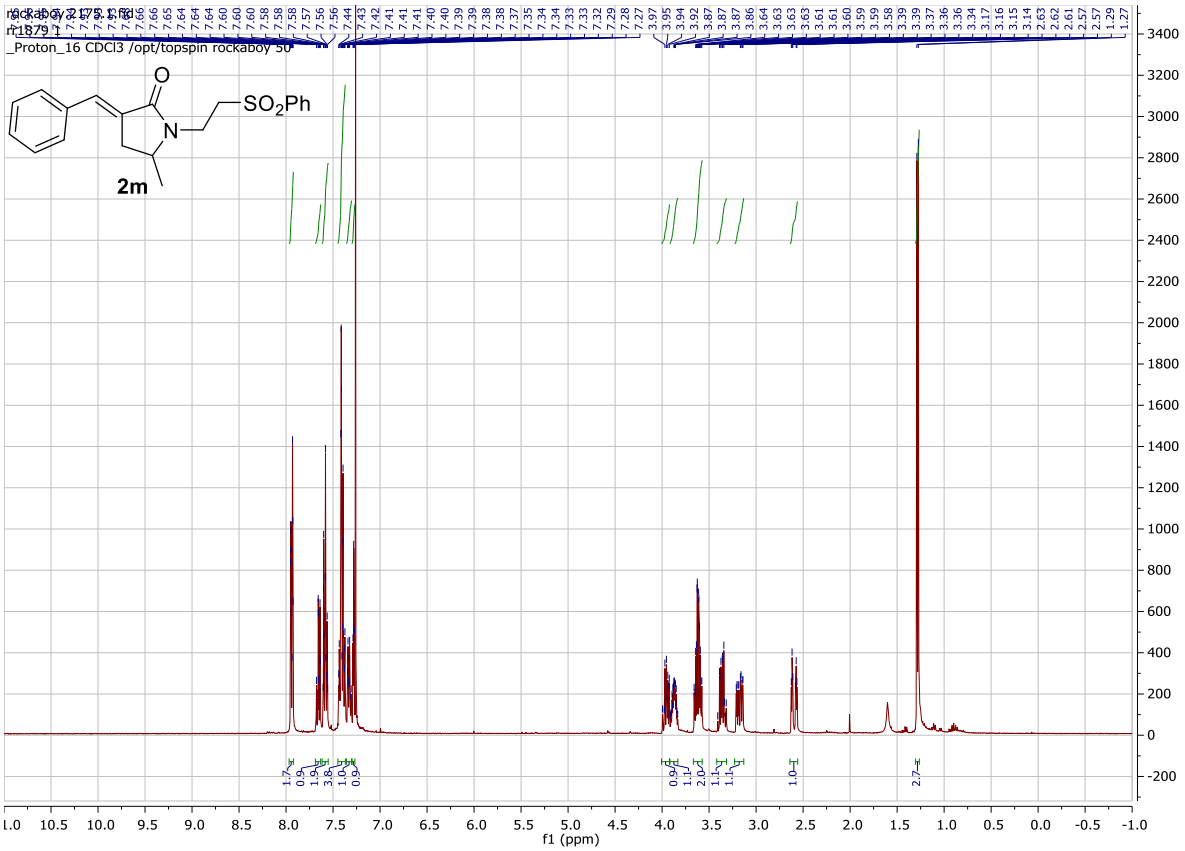
20.94
16.63
O
N
CN
2l
f1 (ppm)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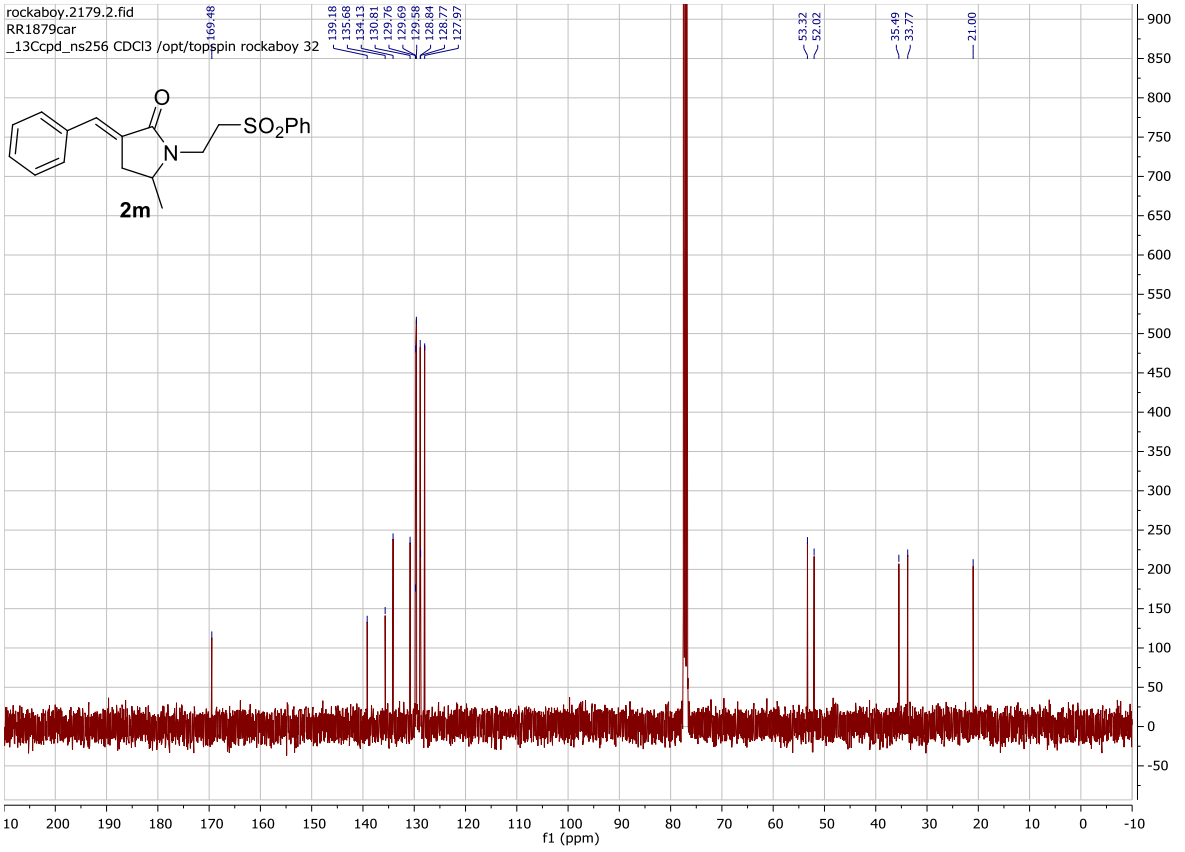
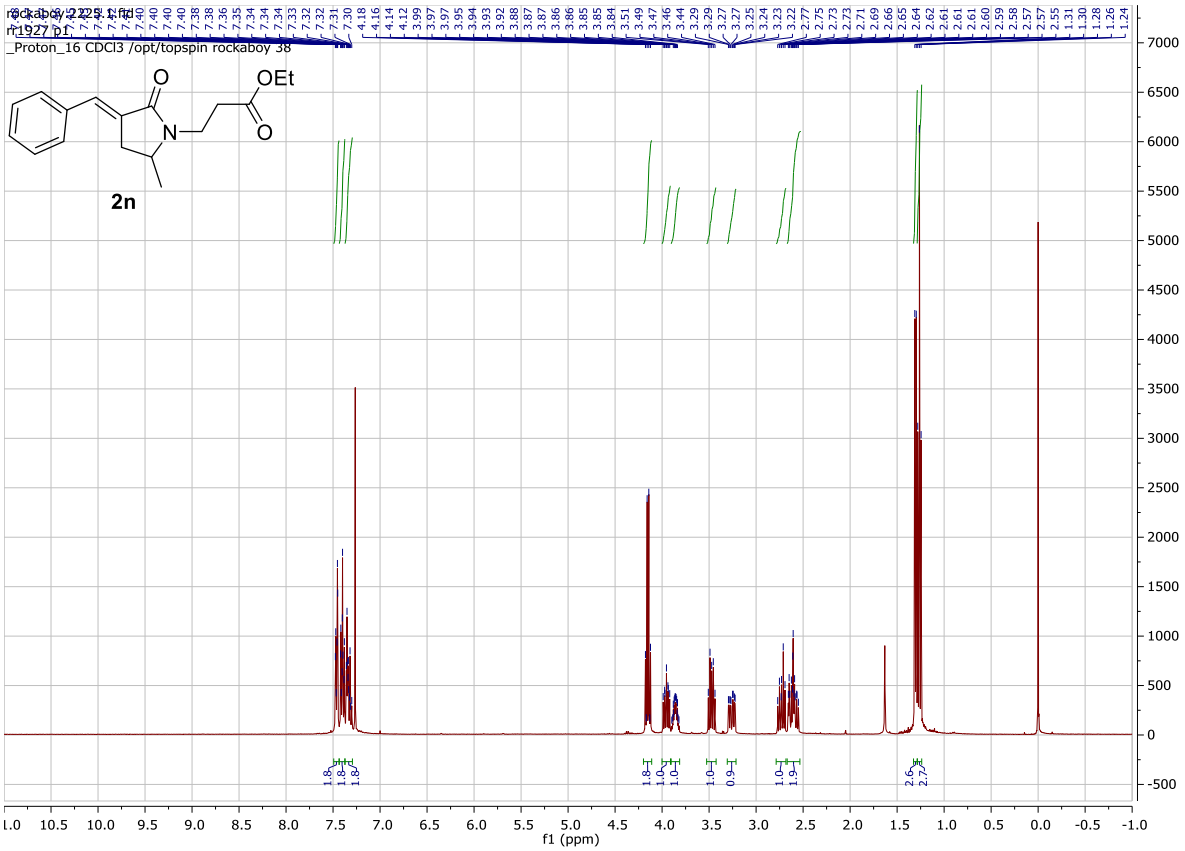
RR1879car
_Proton_16 CDCl3 /opt/topspin rockaboy 50
O
N
SO2Ph
2m
f1 (ppm)


rockaboy.2179.2.fid
RR1879car
_13Ccpd_ns256 CDCl3 /opt/topspin rockaboy 32
169.48
139.18
135.68
134.13
130.81
129.76
129.69
129.58
128.84
128.77
127.97
53.32
52.02
35.49
33.77
21.00
O
N
SO2Ph
2m
f1 (ppm)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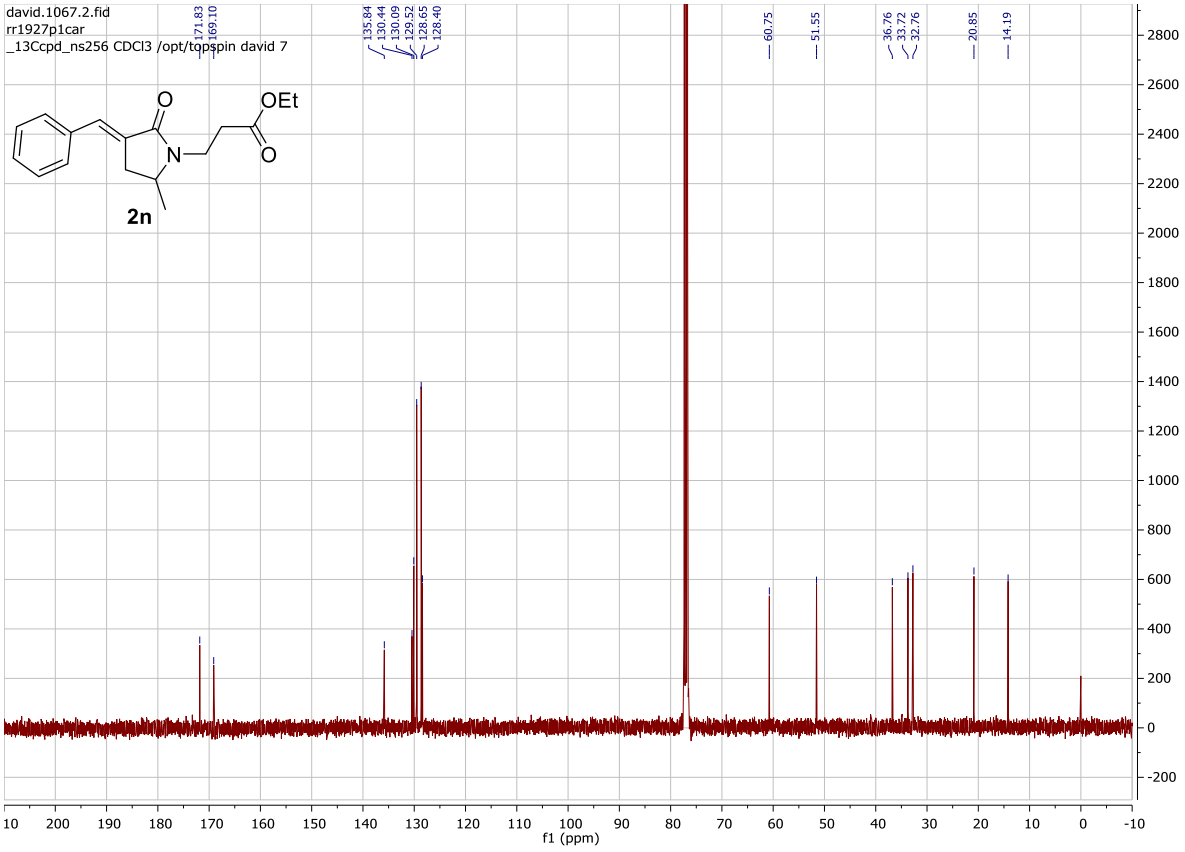
_Proton_16 CDCl3 /opt/topspin rockaboy 38
O
OEt
N
O
2n
f1 (ppm)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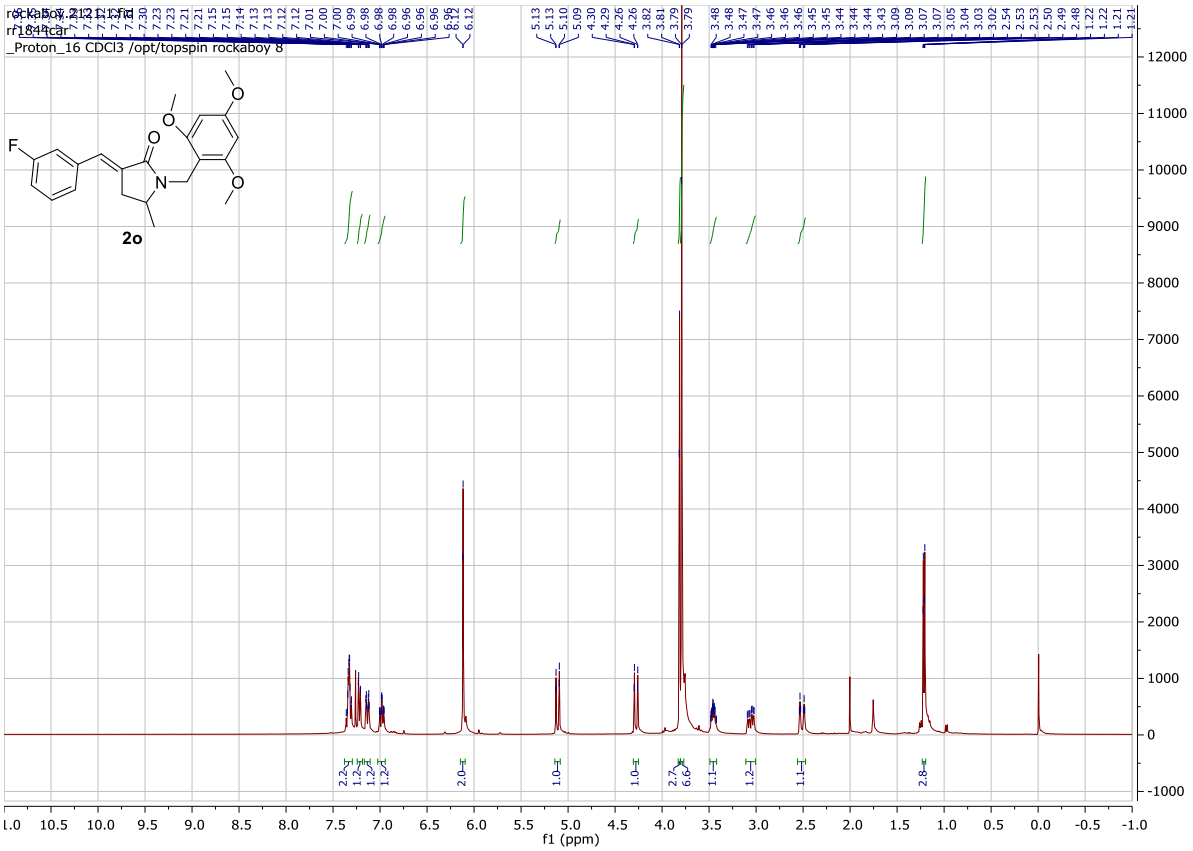
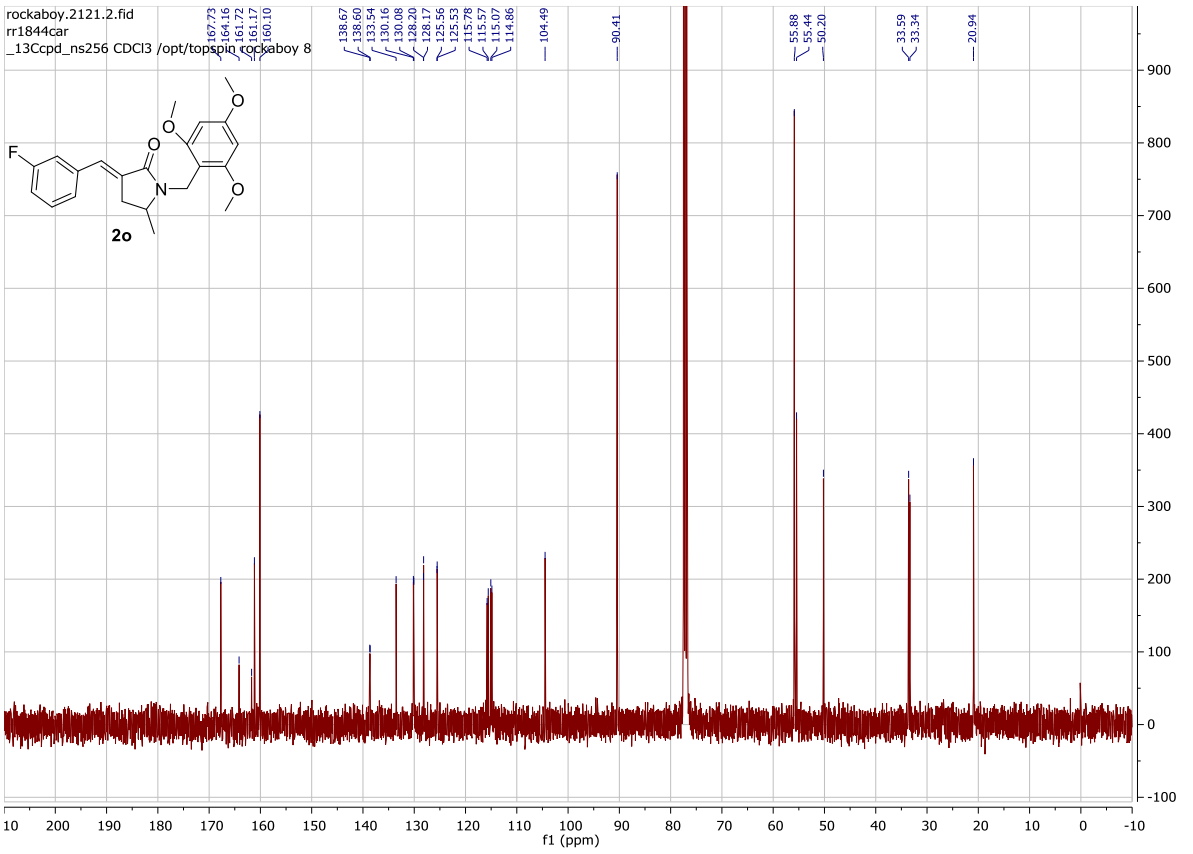
171.83
169.10
135.84
130.44
130.09
129.52
128.65
128.40
60.75
51.55
36.76
33.72
32.76
20.85
14.19
O
OEt
N
O
2n
f1 (ppm)


rockaboy.2121.1.fid
rr1844car
_Proton_16 CDCl3 /opt/topspin rockaboy 8
F
O
O
O
N
O
2o
f1 (ppm)


rockaboy.2121.2.fid
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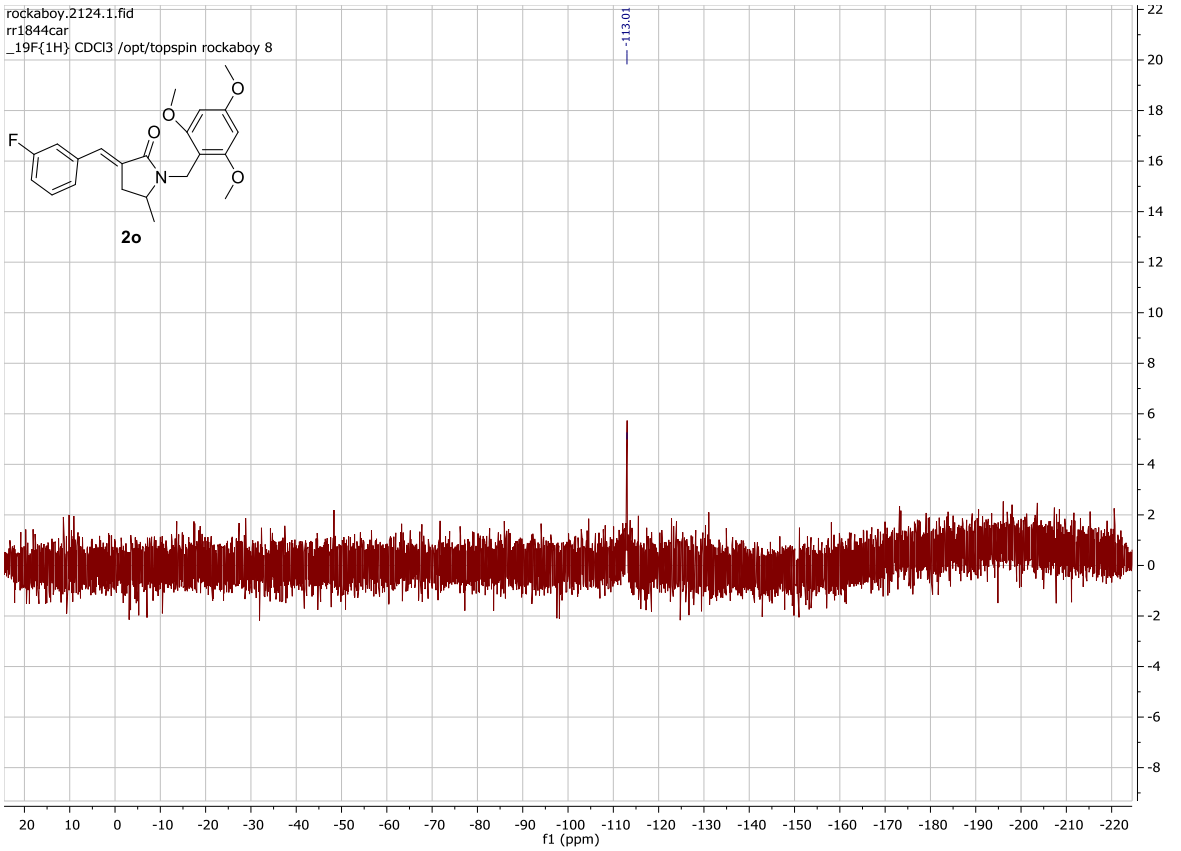
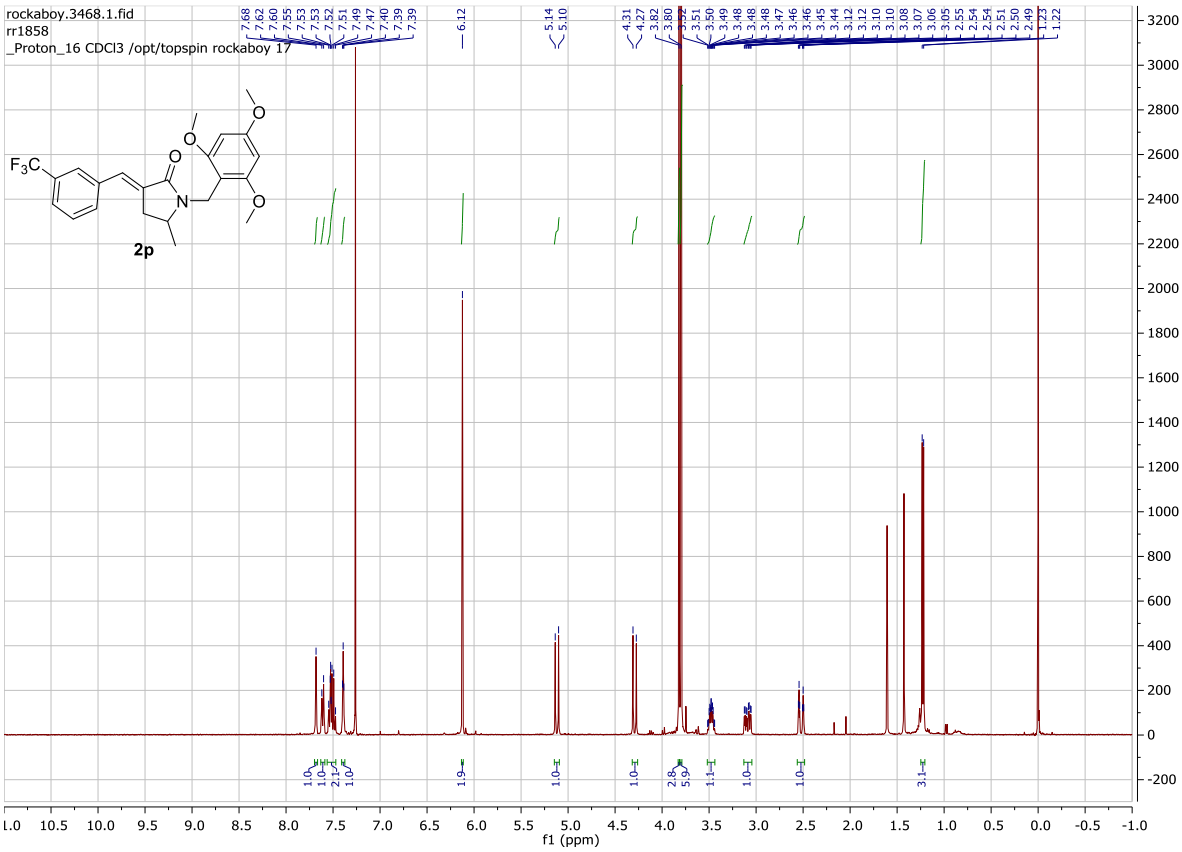
F
O
O
O
N
O
2o
f1 (ppm)


rockaboy.2124.1.fid
rr1844car
_19F{1H} CDCl3 /opt/topspin rockaboy 8
-113.01
F
O
O
O
O
N
2o
f1 (ppm)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rr1858
_Proton_16 CDCl3 /opt/topspin rockaboy 17
7.68
7.62
7.60
7.55
7.53
7.53
7.52
7.51
7.49
7.47
7.40
7.39
7.39
6.12
5.14
5.10
4.31
4.27
3.82
3.80
3.52
3.51
3.50
3.49
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3.48
3.47
3.46
3.45
3.44
3.12
3.12
3.10
3.10
3.08
3.07
3.06
3.05
2.55
2.54
2.54
2.51
2.50
2.49
1.23
1.22
F3C
O
O
O
O
N
2p
1.0
1.0
2.1
1.0
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1.0
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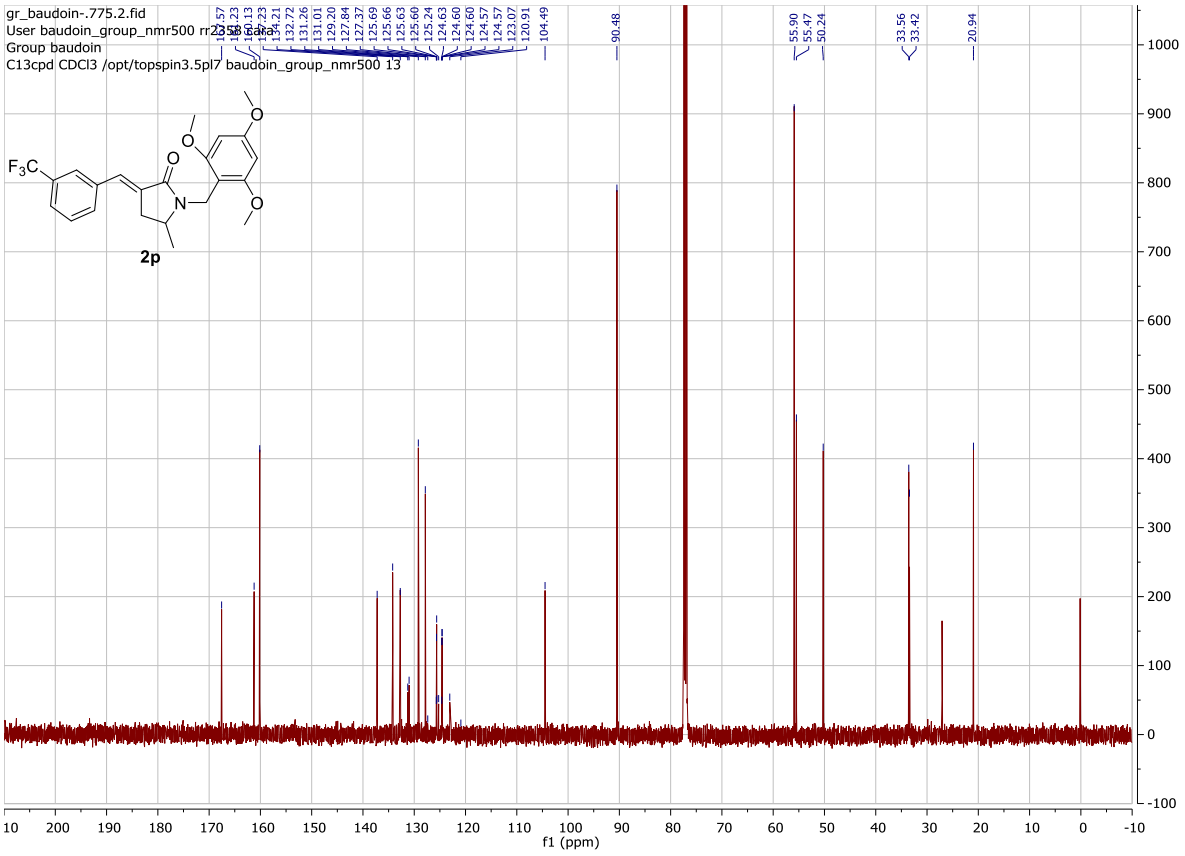
2.8
5.9
1.1
1.0
1.0
3.1
f1 (ppm)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User baudoin_group_nmr500 rr2358 cara
Group baudoin
C13cpd CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 13
157.57
147.23
146.13
137.23
134.21
132.72
131.26
131.01
129.20
127.84
127.37
125.69
125.66
125.63
125.60
125.24
124.63
124.60
124.60
124.57
124.57
123.07
120.91
104.49
90.48
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55.47
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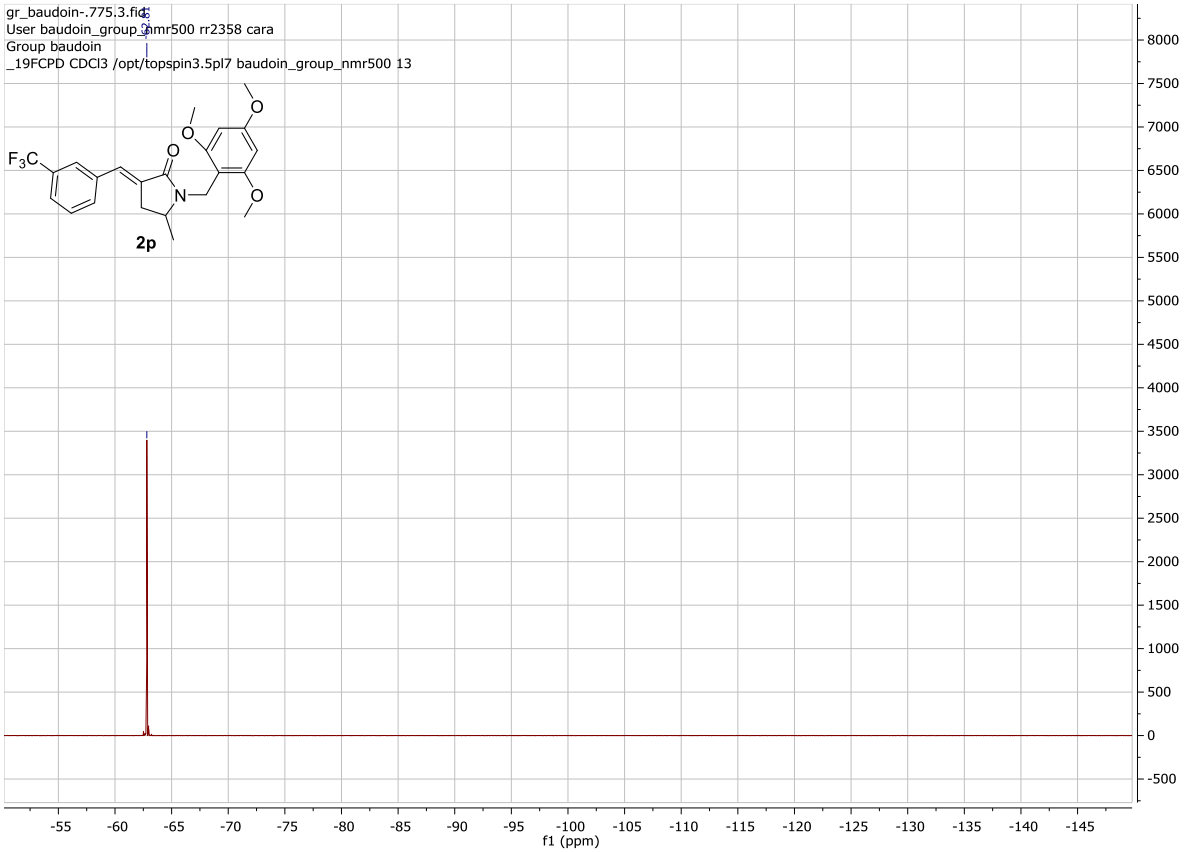
33.56
33.42
20.94
F3C
O
O
O
O
N
2p
f1 (ppm)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User baudoin_group_nmr500 rr2358 cara
Group baudoin
_19FCPD CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 13
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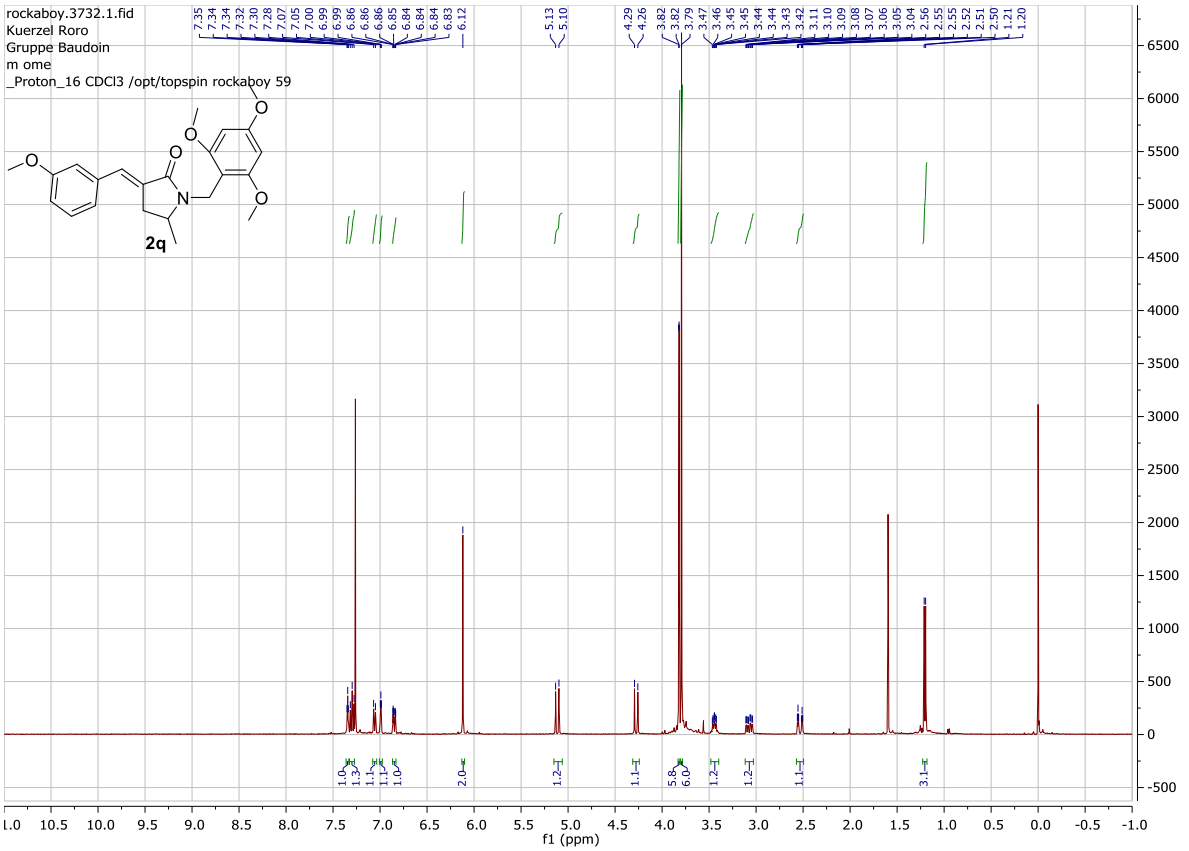
O
O
O
O
N
2p
f1 (ppm)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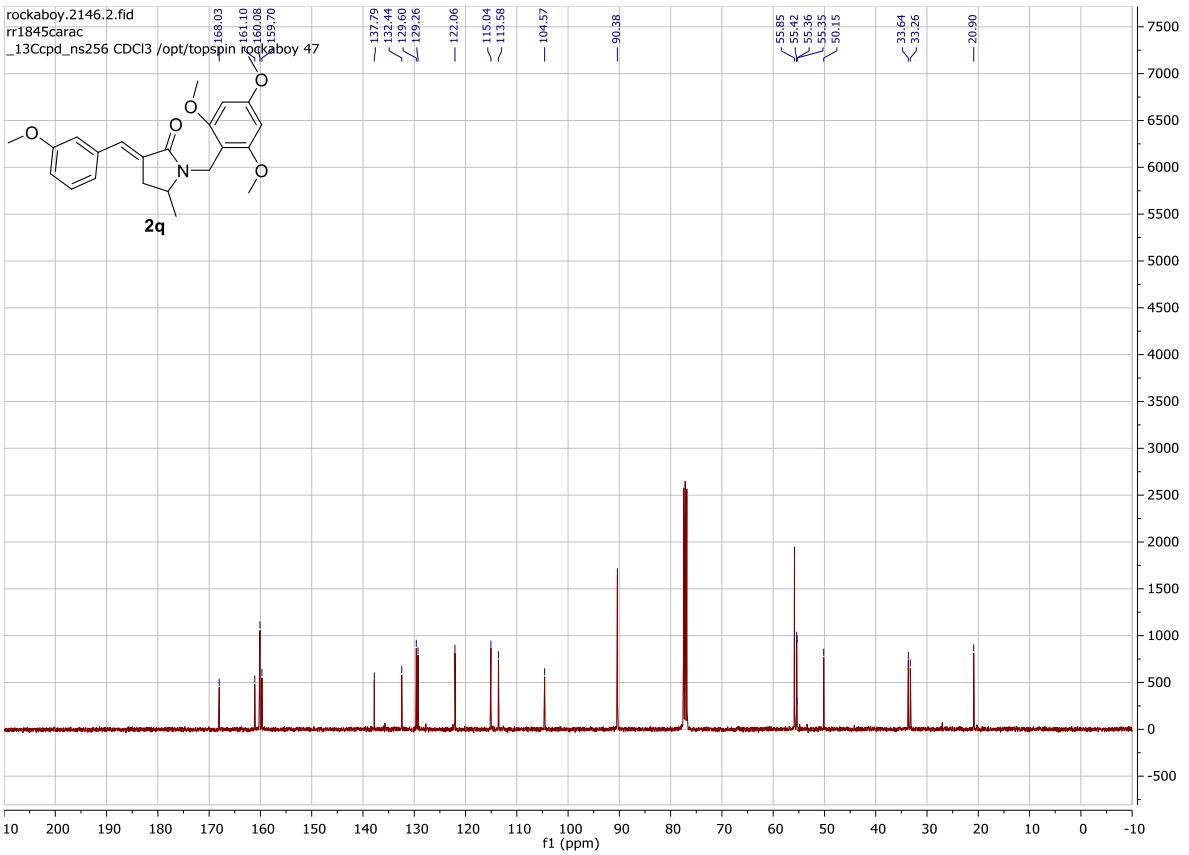
Kuerzel Roro
Gruppe Baudoin
m ome
_Proton_16 CDCl3 /opt/topspin rockaboy 59
2q
f1 (ppm)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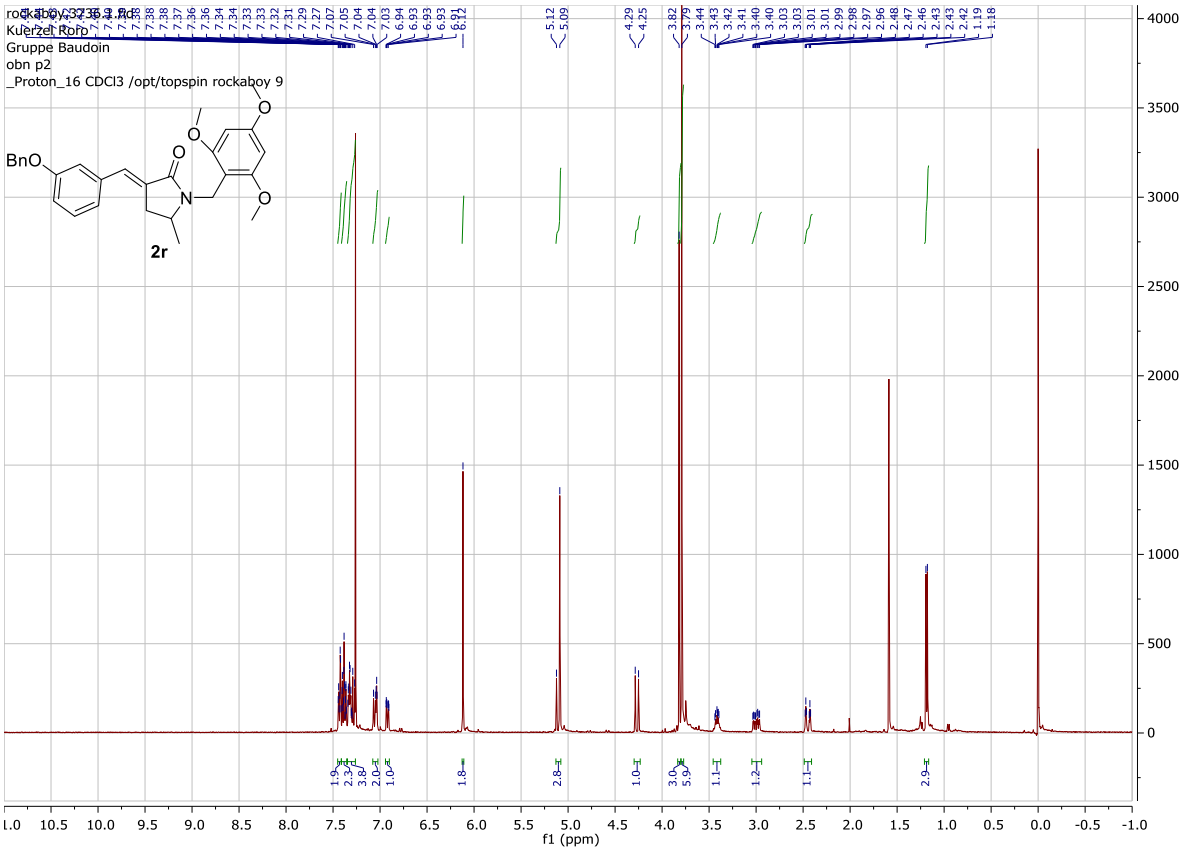
rr1845carac
_13Ccpd_ns256 CDCl3 /opt/topspin rockaboy 47
2q
f1 (ppm)


rockaboy.3235.3.fid
Kuerzel Rorb
Gruppe Baudoin
obn p2
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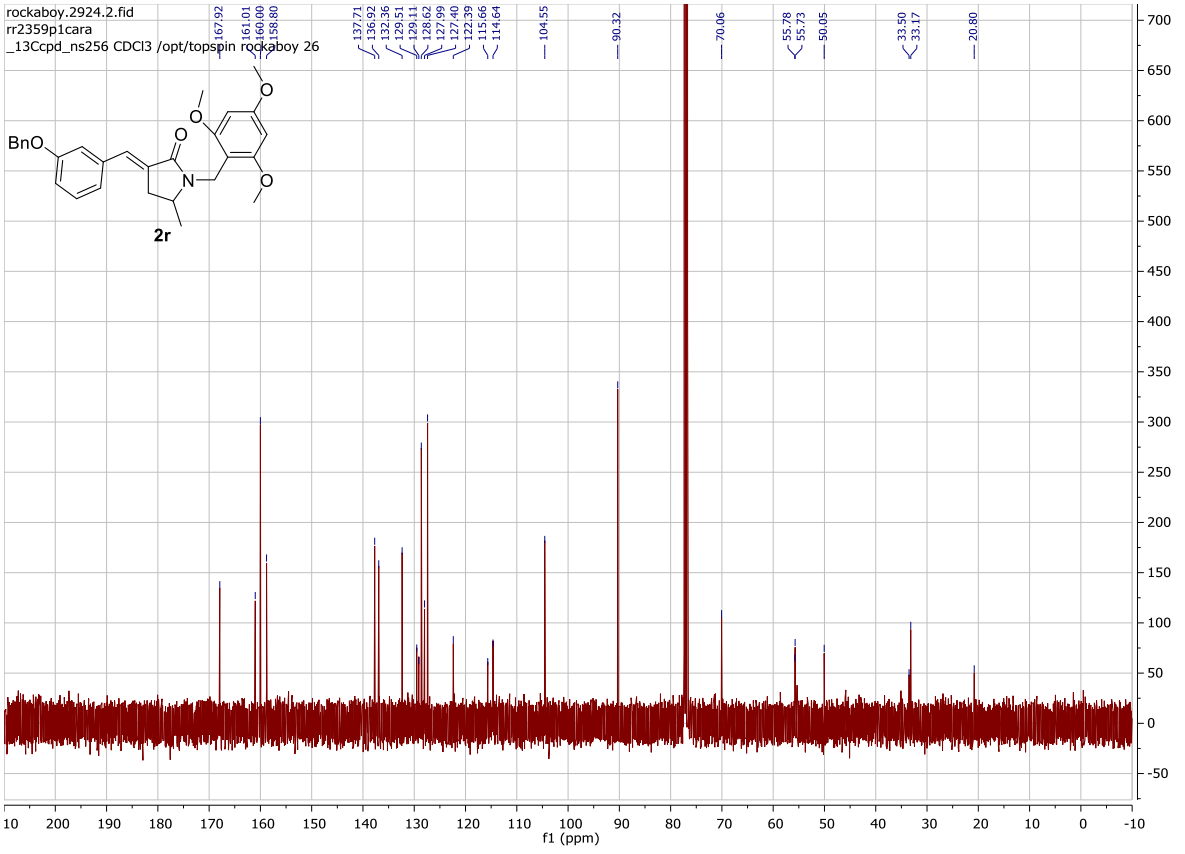
BnO
O
O
O
N
O
2r
f1 (ppm)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rr2359p1cara
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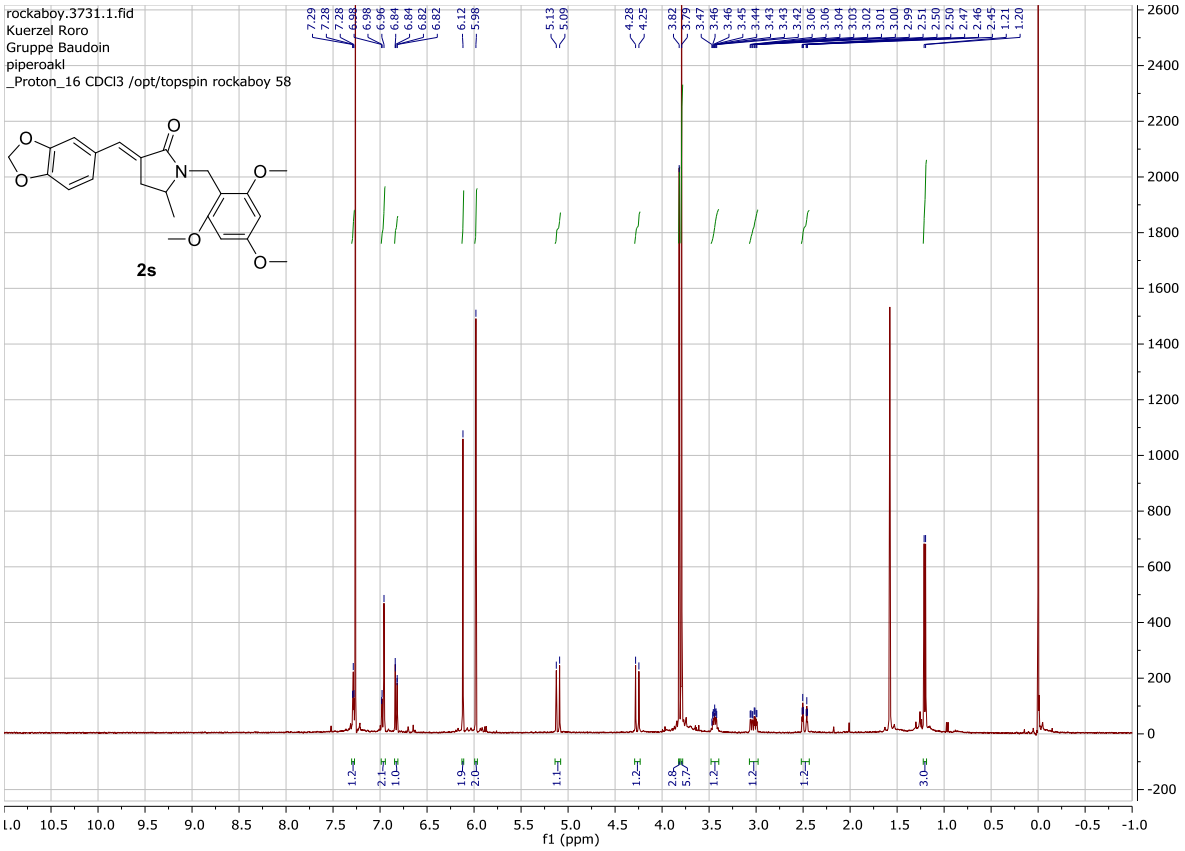
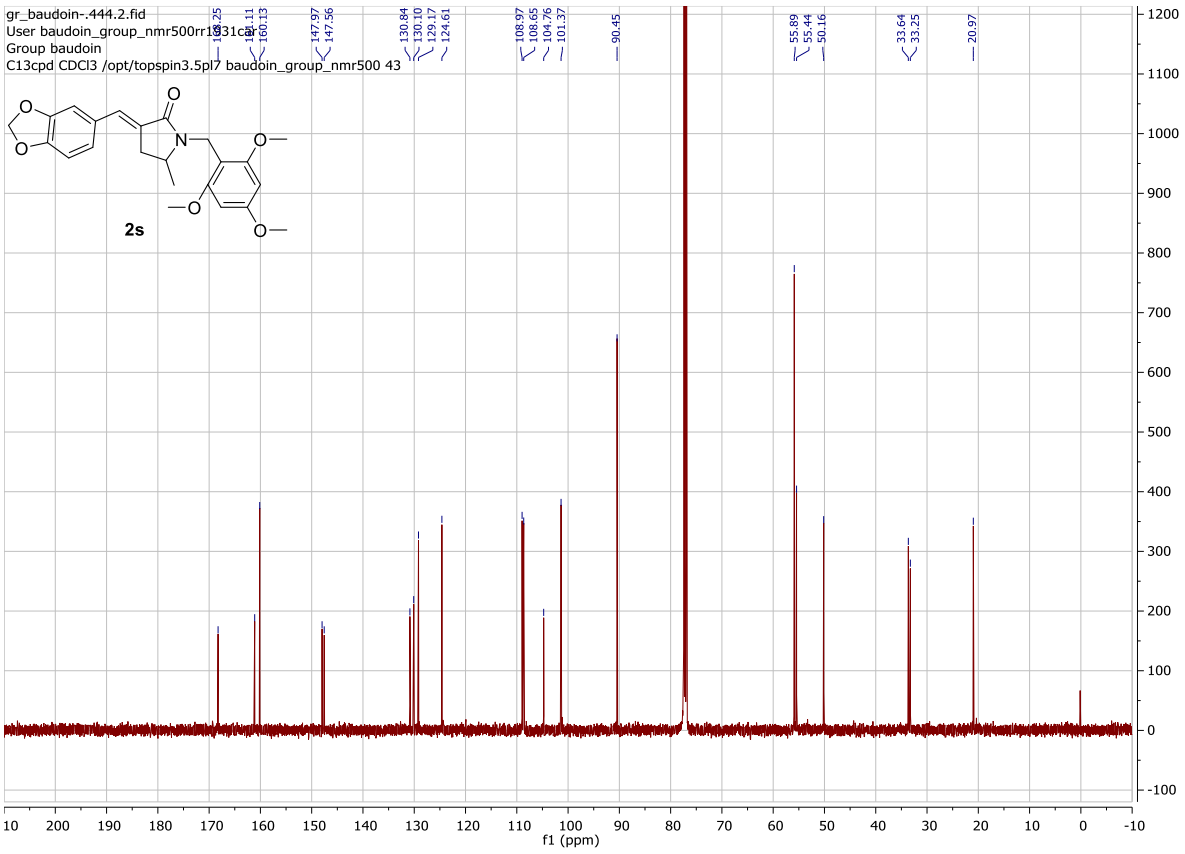
BnO
O
O
O
N
O
2r
f1 (ppm)


rockaboy.3731.1.fid
Kuerzel Roro
Gruppe Baudoin
piperoakl
_Proton_16 CDCl3 /opt/topspin rockaboy 58
2s
f1 (ppm)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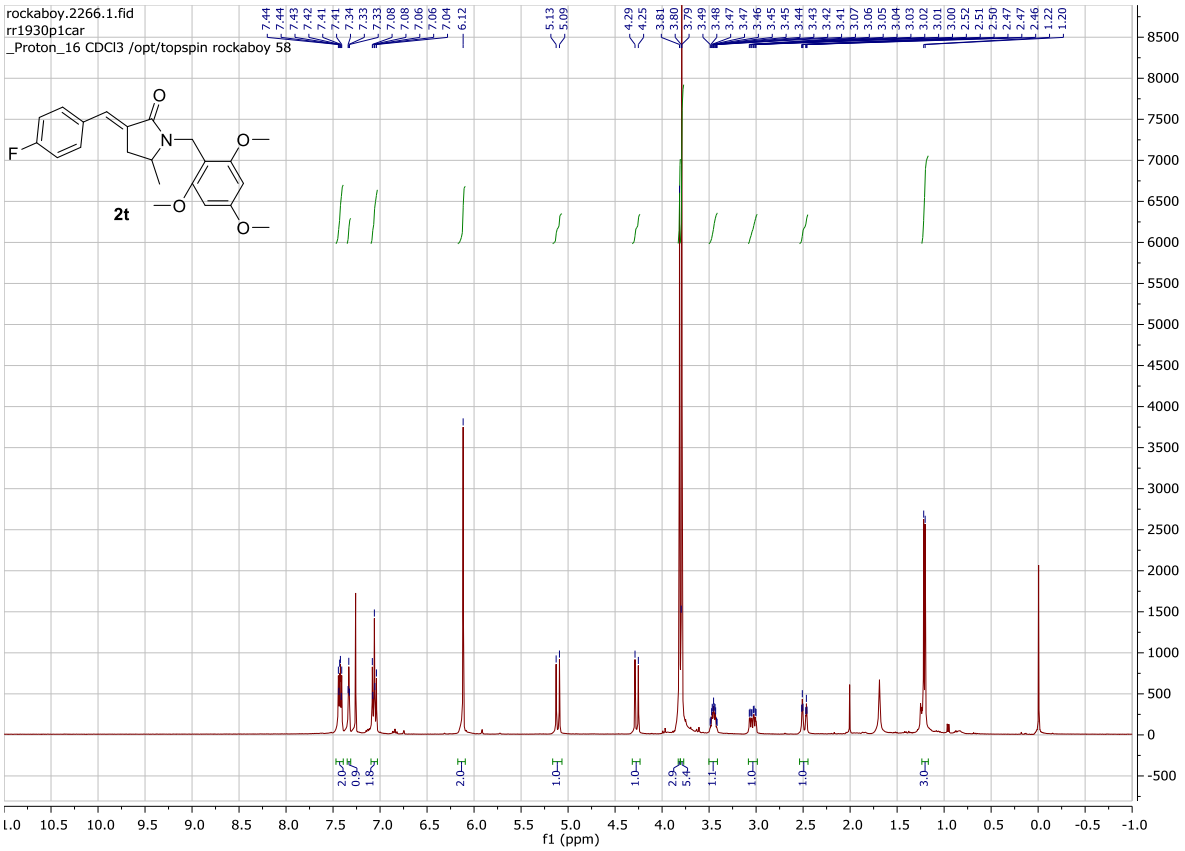
User baudoin_group_nmr500rr1331ca
Group baudoin
C13cpd CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 43
2s
f1 (ppm)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rr1930p1car
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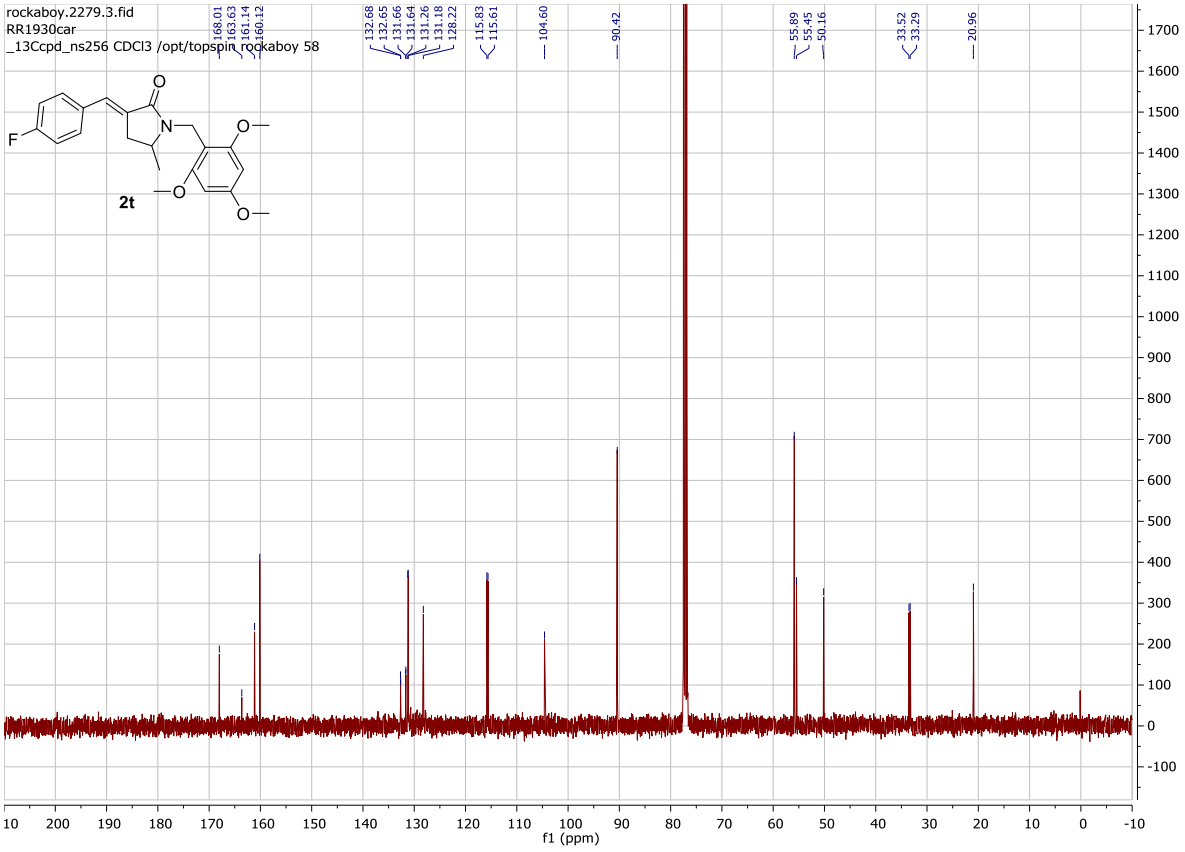
2t
f1 (ppm)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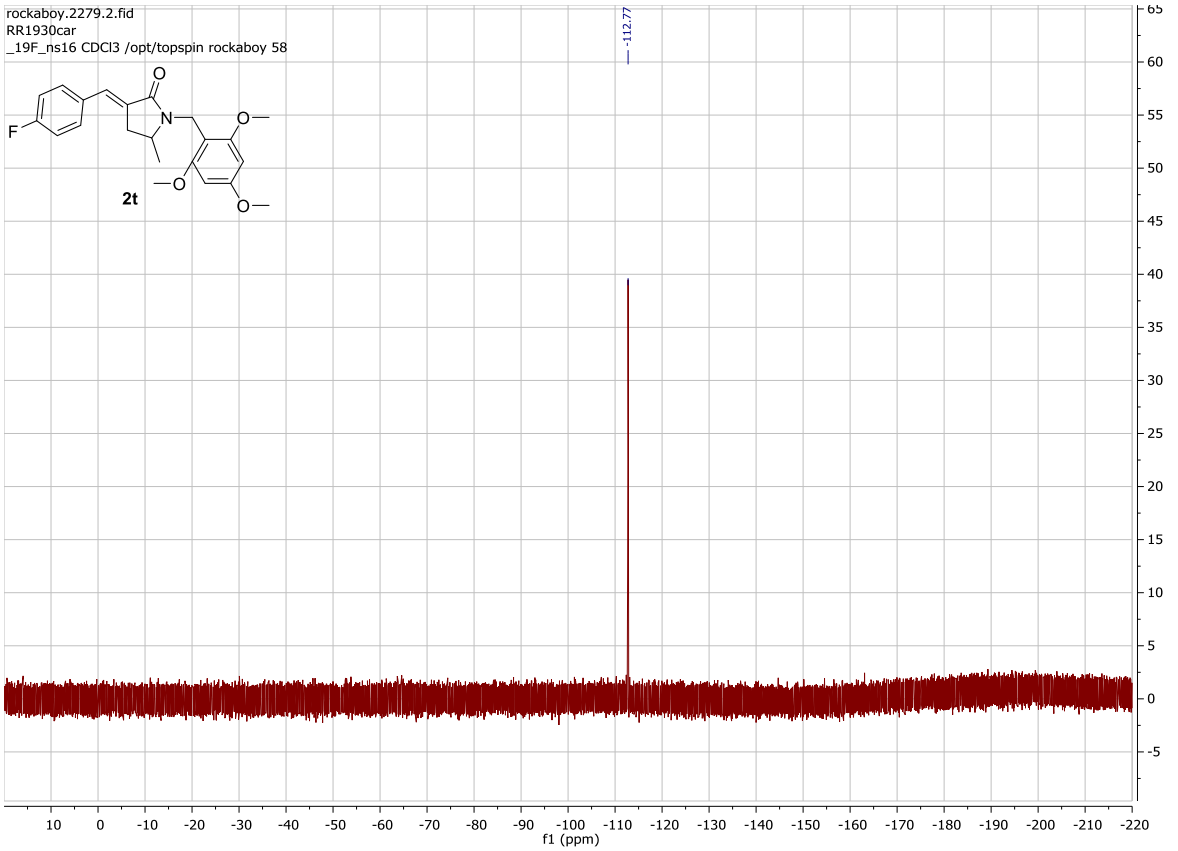
2t
f1 (ppm)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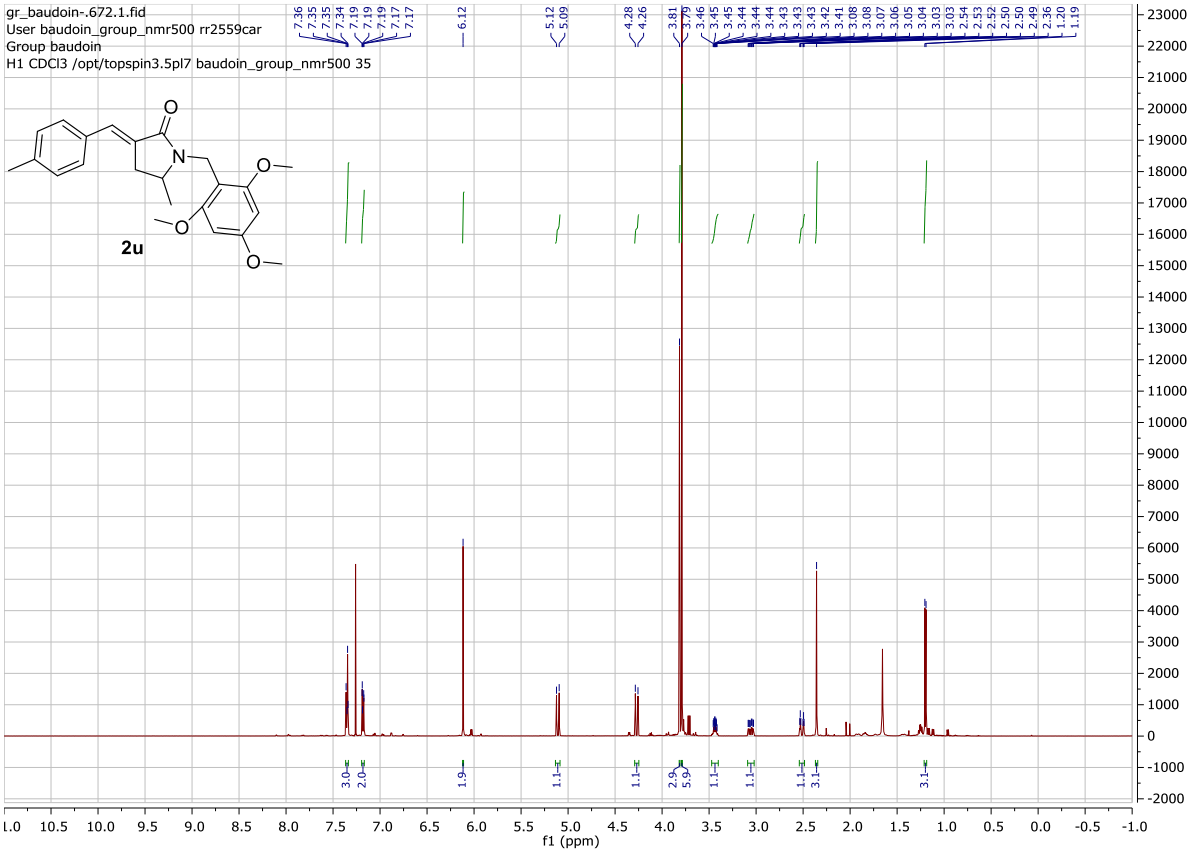
RR1930car
_19F_ns16 CDCl3 /opt/topspin rockaboy 58
-112.77
F
O
N
O
O
O
2t
f1 (ppm)


gr_baudoin-.672.1.fid
User baudoin_group_nmr500 rr2559car
Group baudoin
H1 CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 35
7.36
7.35
7.35
7.34
7.19
7.19
7.17
7.17
6.12
5.12
5.09
4.28
4.26
3.81
3.79
3.46
3.45
3.45
3.44
3.44
3.43
3.43
3.43
3.42
3.41
3.08
3.08
3.07
3.06
3.05
3.04
3.03
3.03
2.54
2.53
2.52
2.50
2.50
2.49
2.36
1.20
1.19
O
N
O
O
O
2u
3.0
2.0
1.9
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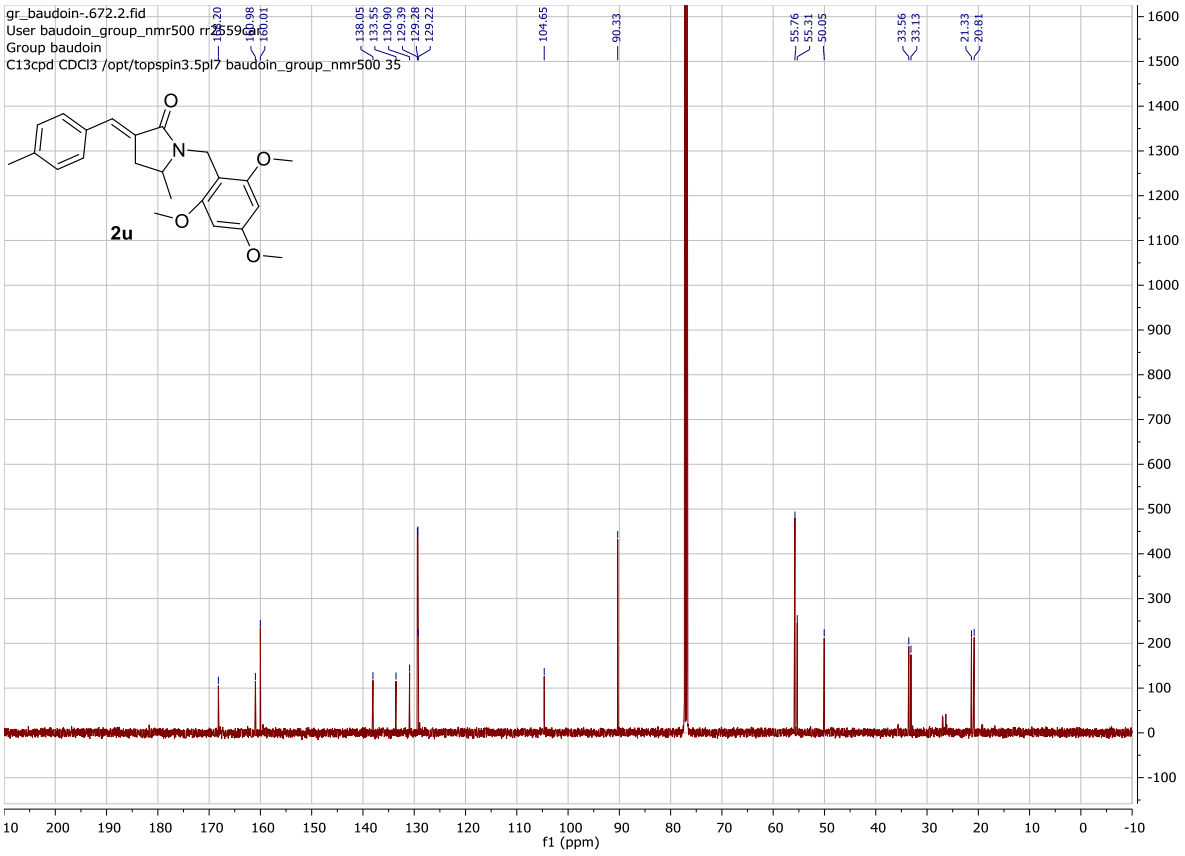
1.1
2.9
5.9
1.1
1.1
1.1
3.1
3.1
f1 (ppm)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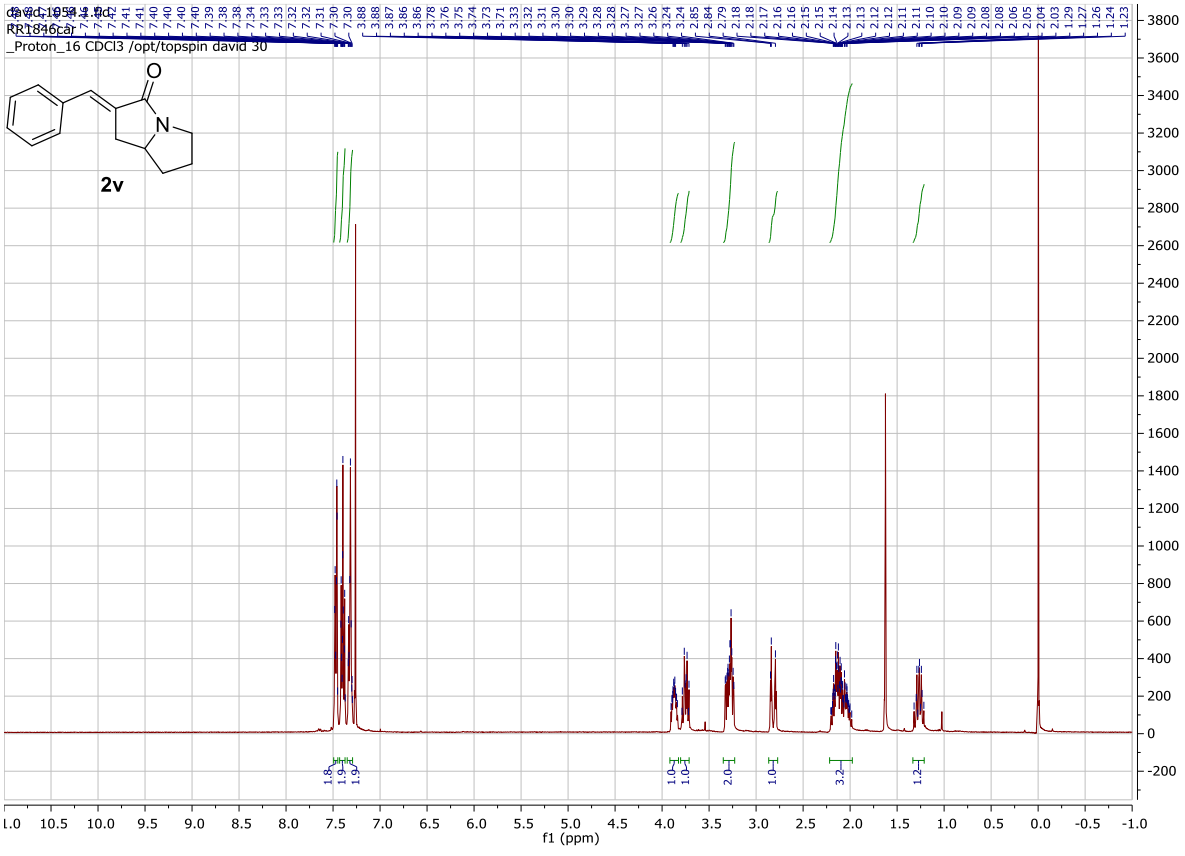
C13cpd CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 35
2u
f1 (ppm)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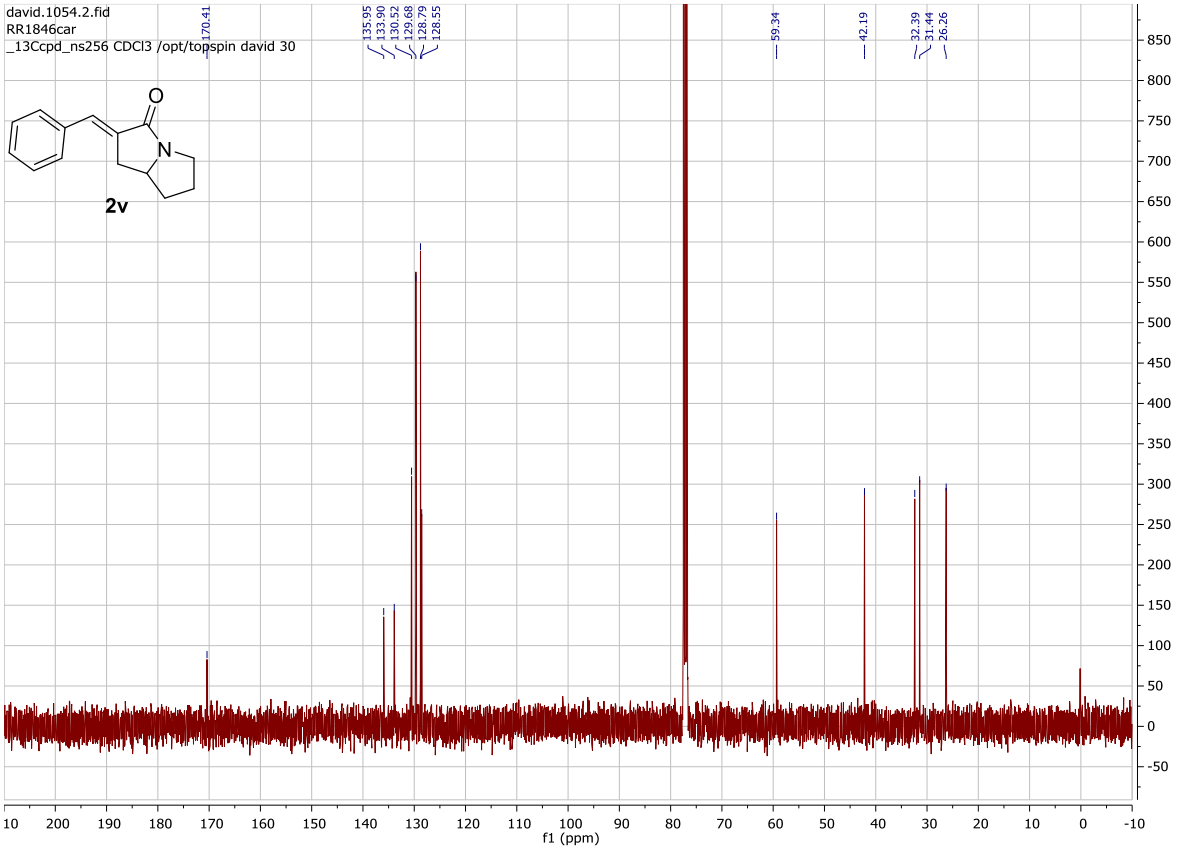
2v
f1 (ppm)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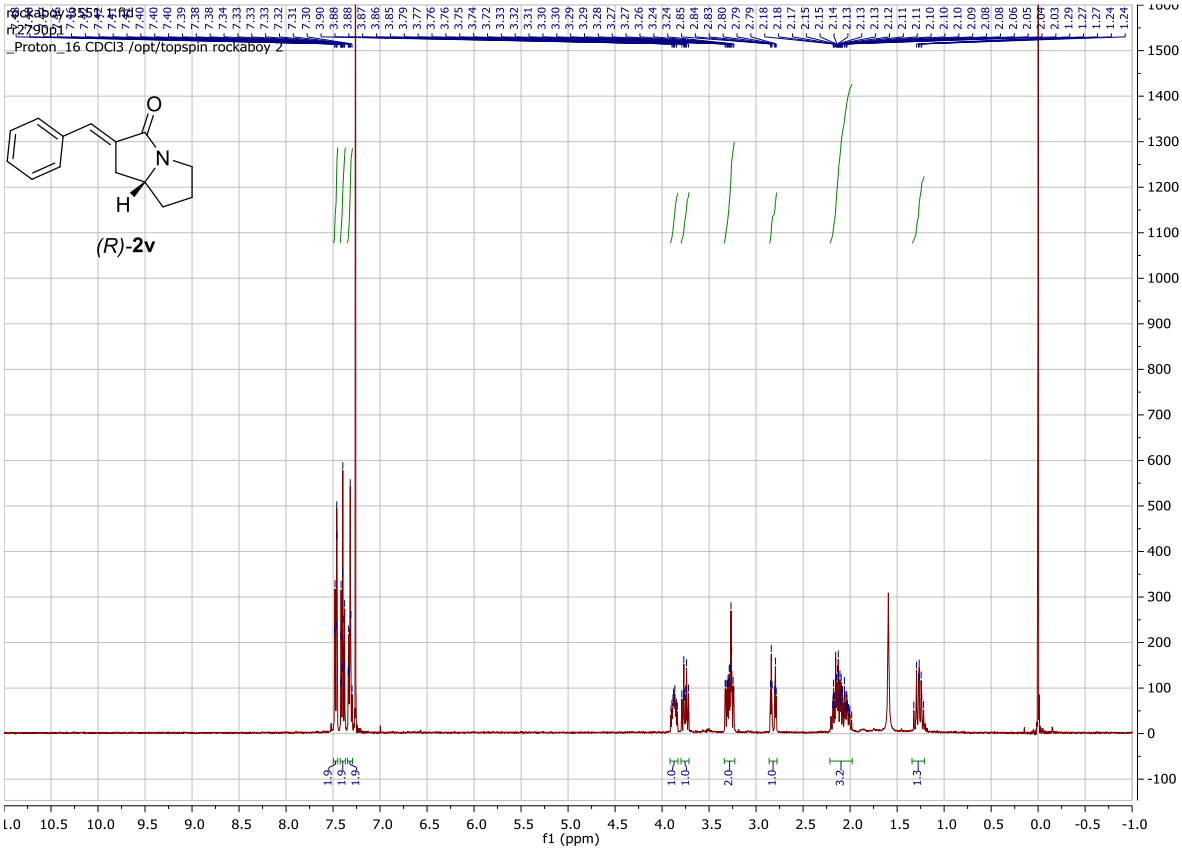
RR1846car
_13Ccpd_ns256 CDCl3 /opt/topspin david 30
170.41
135.95
133.90
130.52
129.68
128.79
128.55
59.34
42.19
32.39
31.44
26.26
O
N
2v
f1 (ppm)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n-2790p1
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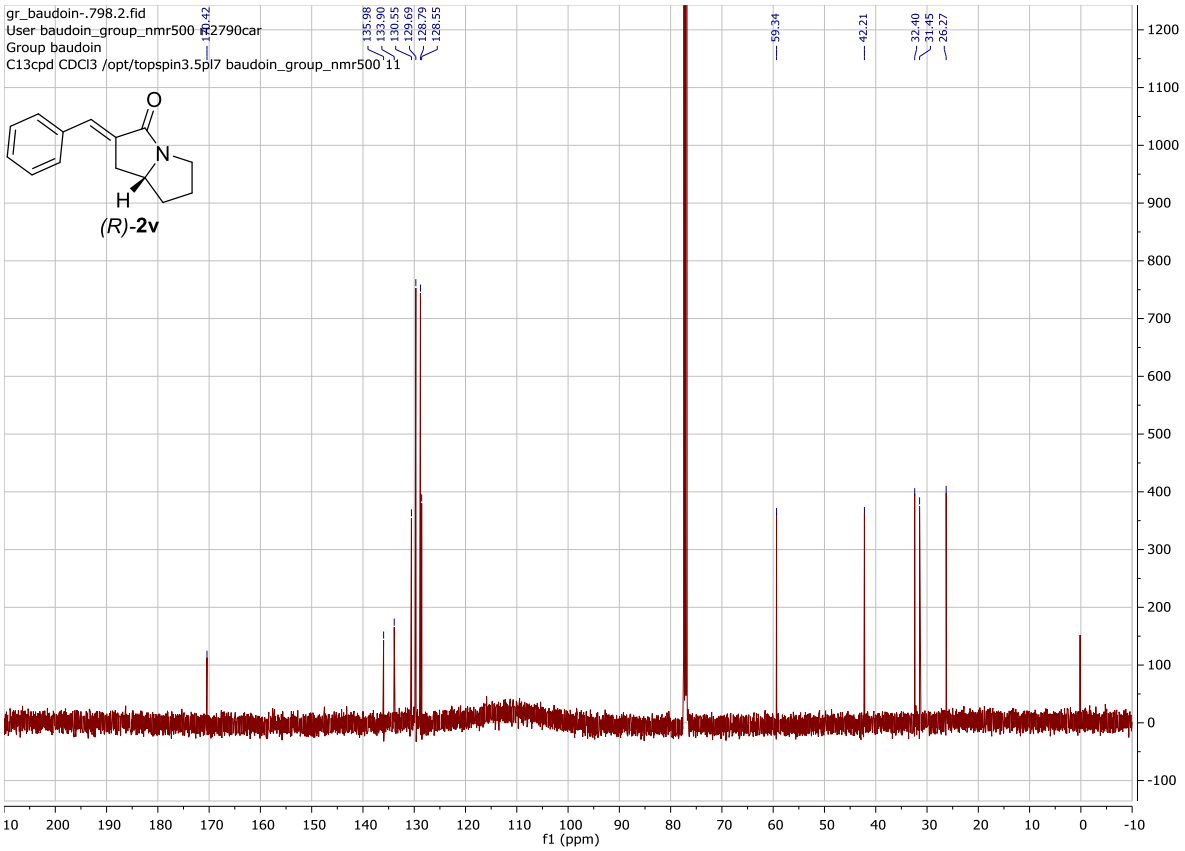
O
N
H
(R)-2v
f1 (ppm)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Group baudoin
C13cpd CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 11
169.42
135.98
133.90
130.55
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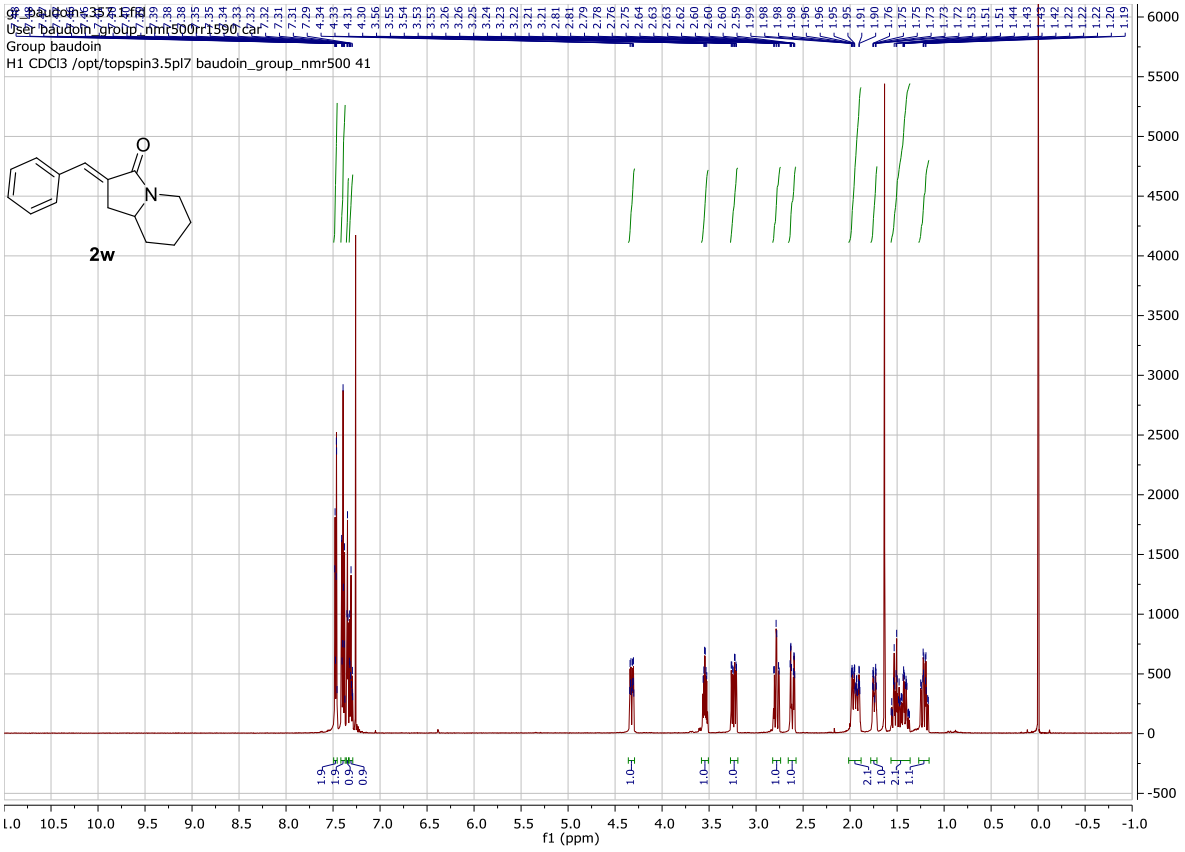
128.79
128.55
59.34
42.21
32.40
31.45
26.27
(R)-2v
f1 (ppm)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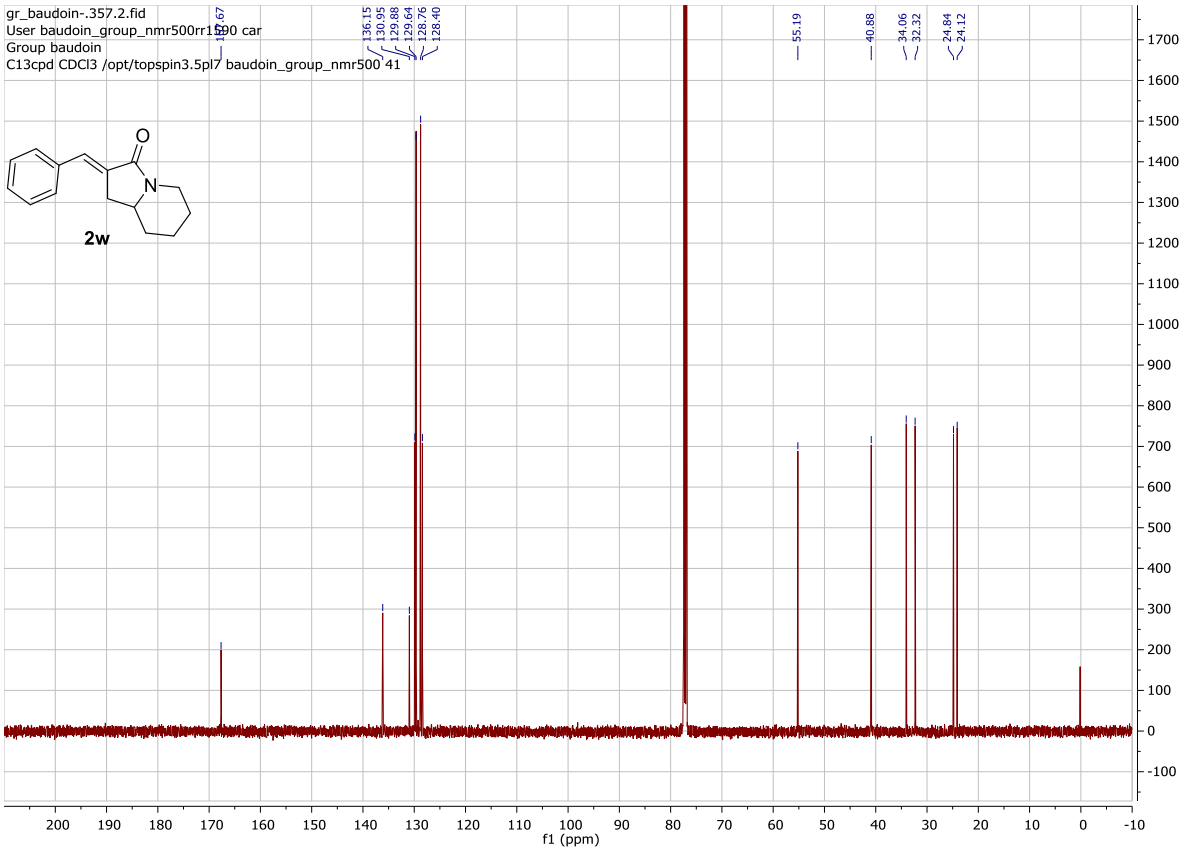
Group baudoin
H1 CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 41
2w
f1 (ppm)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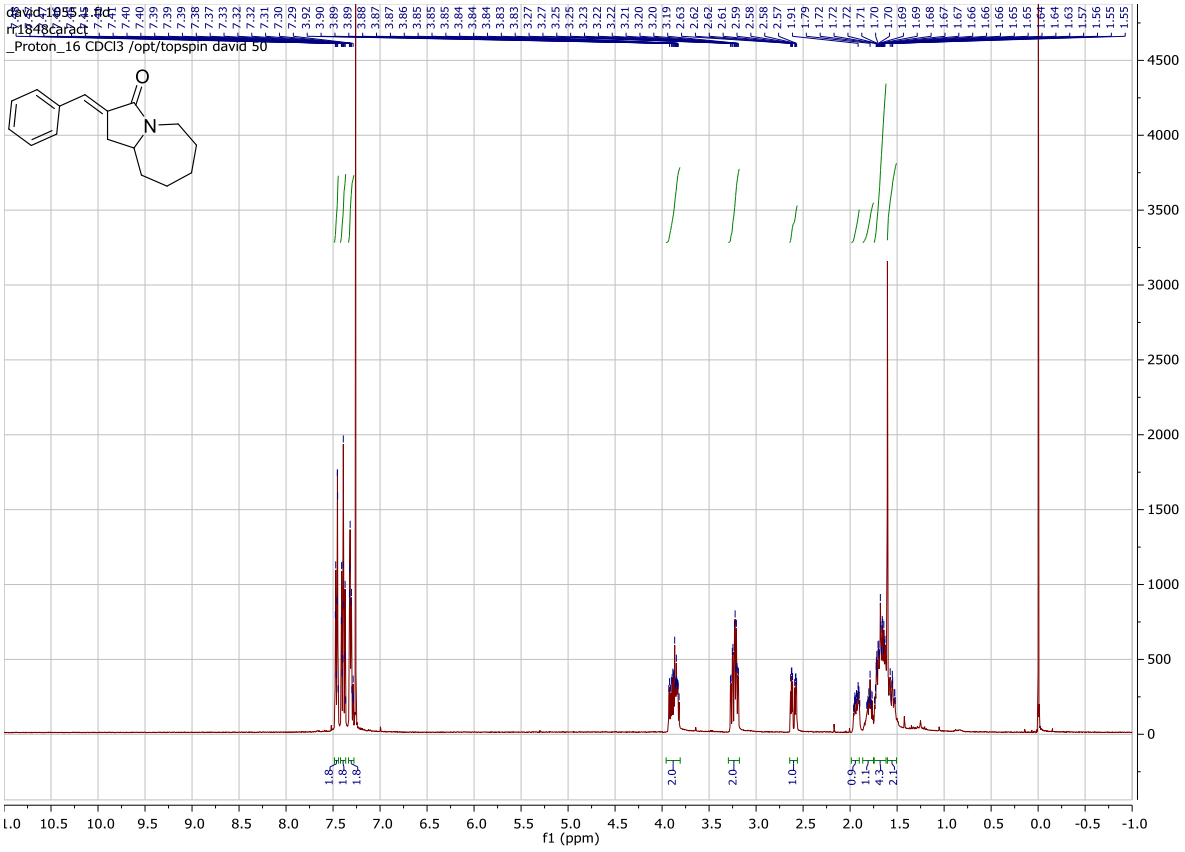
Group baudoin
C13cpd CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 41
171.67
136.15
130.95
129.88
129.64
128.76
128.40
55.19
40.88
34.06
32.32
24.84
24.12
O
N
2w
f1 (ppm)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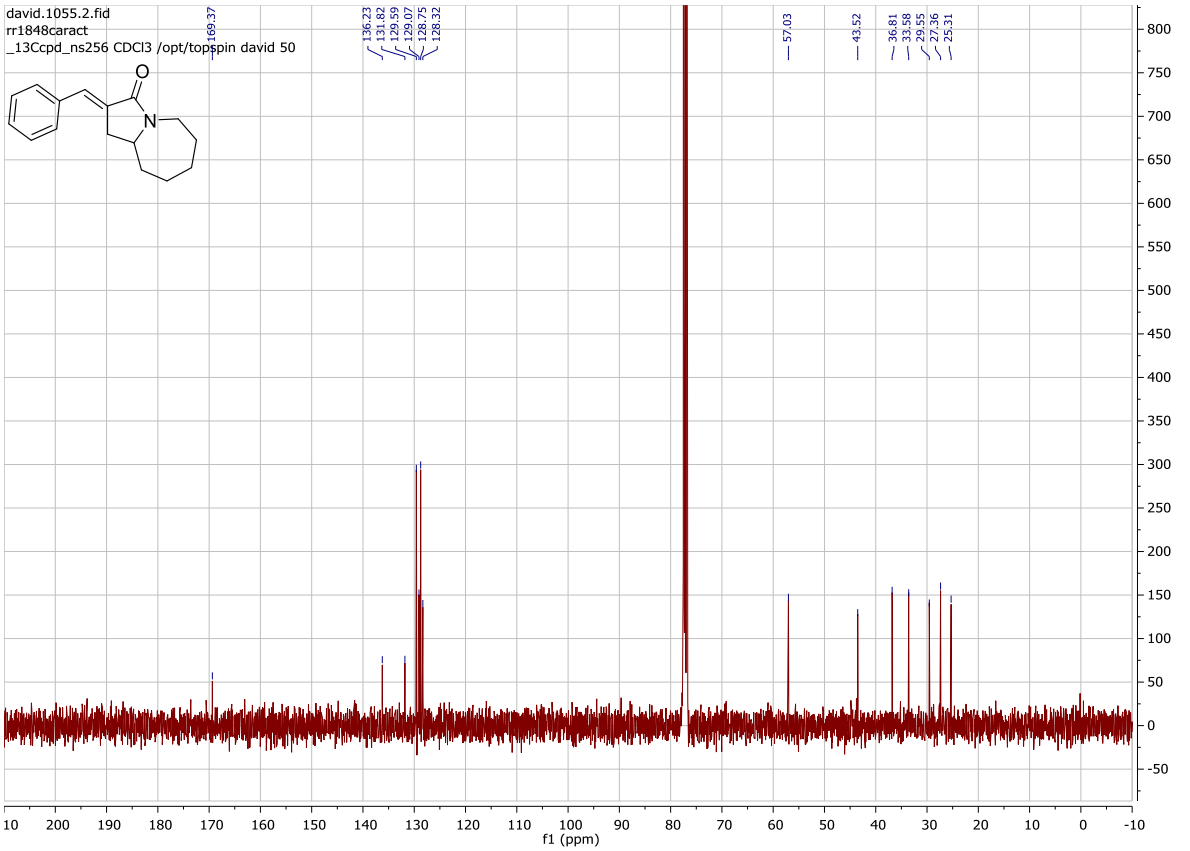
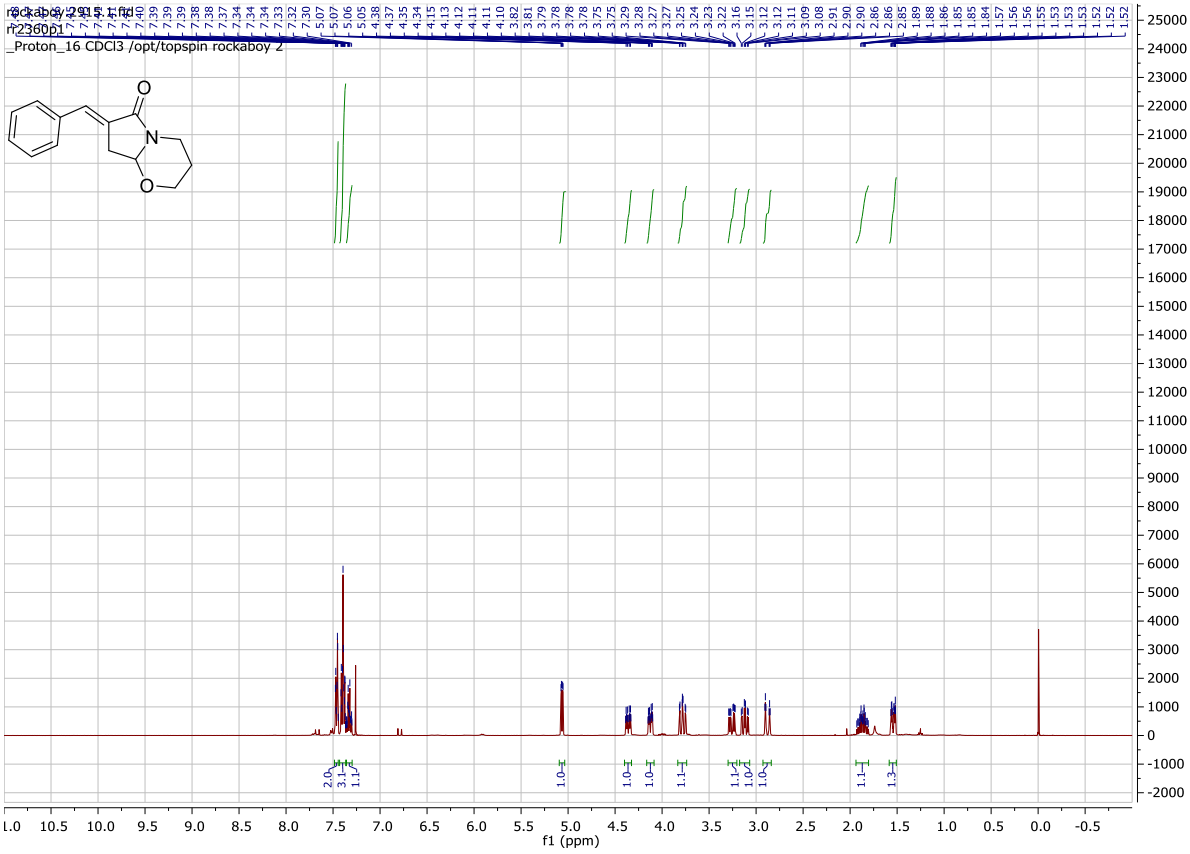
r_1848caract
_Proton_16 CDCl3 /opt/topspin david 50
O
N
1.8
1.8
1.8
2.0
2.0
1.0
0.9
1.1
4.3
2.1
f1 (ppm)


david.1055.2.fid
rr1848caract
_13Ccpd_ns256 CDCl3 /opt/topspin david 50
169.37
136.23
131.82
129.59
129.07
128.75
128.32
57.03
43.52
36.81
33.58
29.55
27.36
25.31
f1 (ppm)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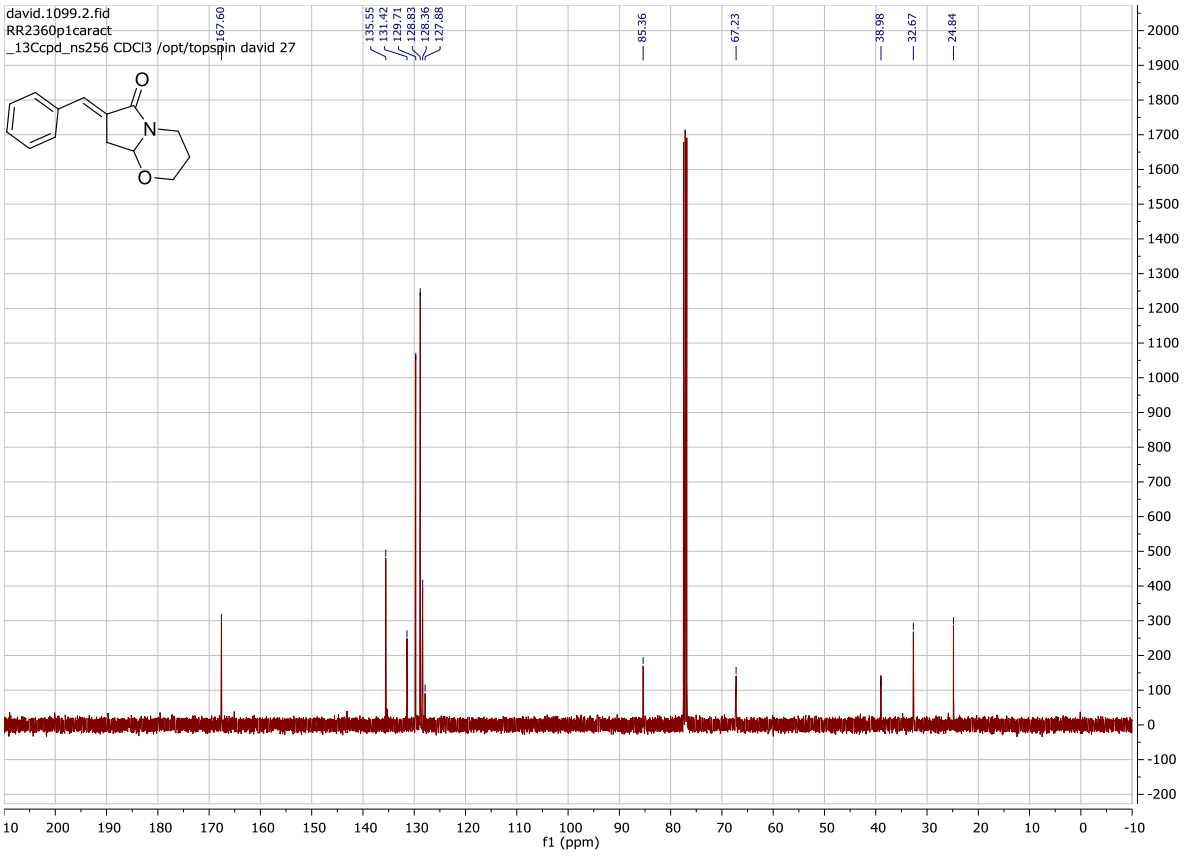
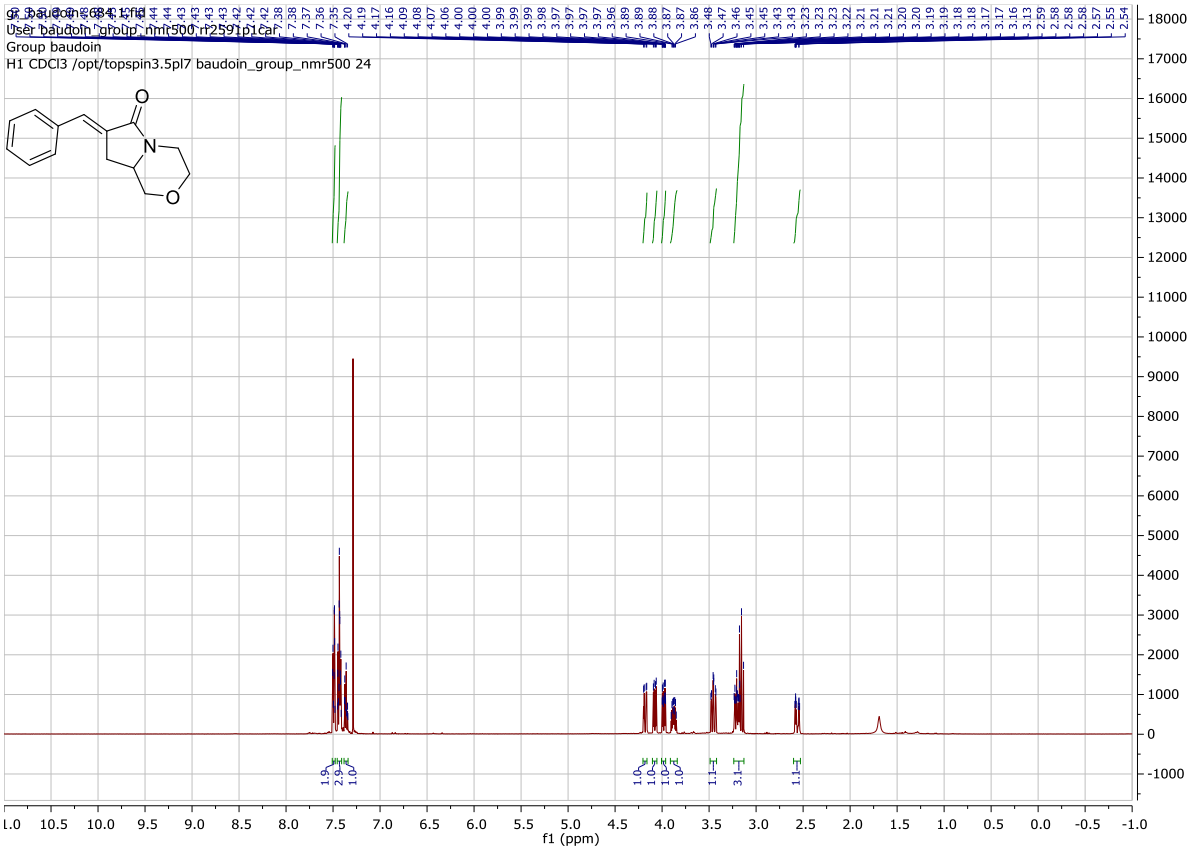
rr236001
_Proton_16 CDCl3 /opt/topspin rockaboy 2
f1 (ppm)


david.1099.2.fid
RR2360p1caract
_13Ccpd_ns256 CDCl3 /opt/topspin david 27
167.60
135.55
131.42
129.71
128.83
128.36
127.88
85.36
67.23
38.98
32.67
24.84
f1 (ppm)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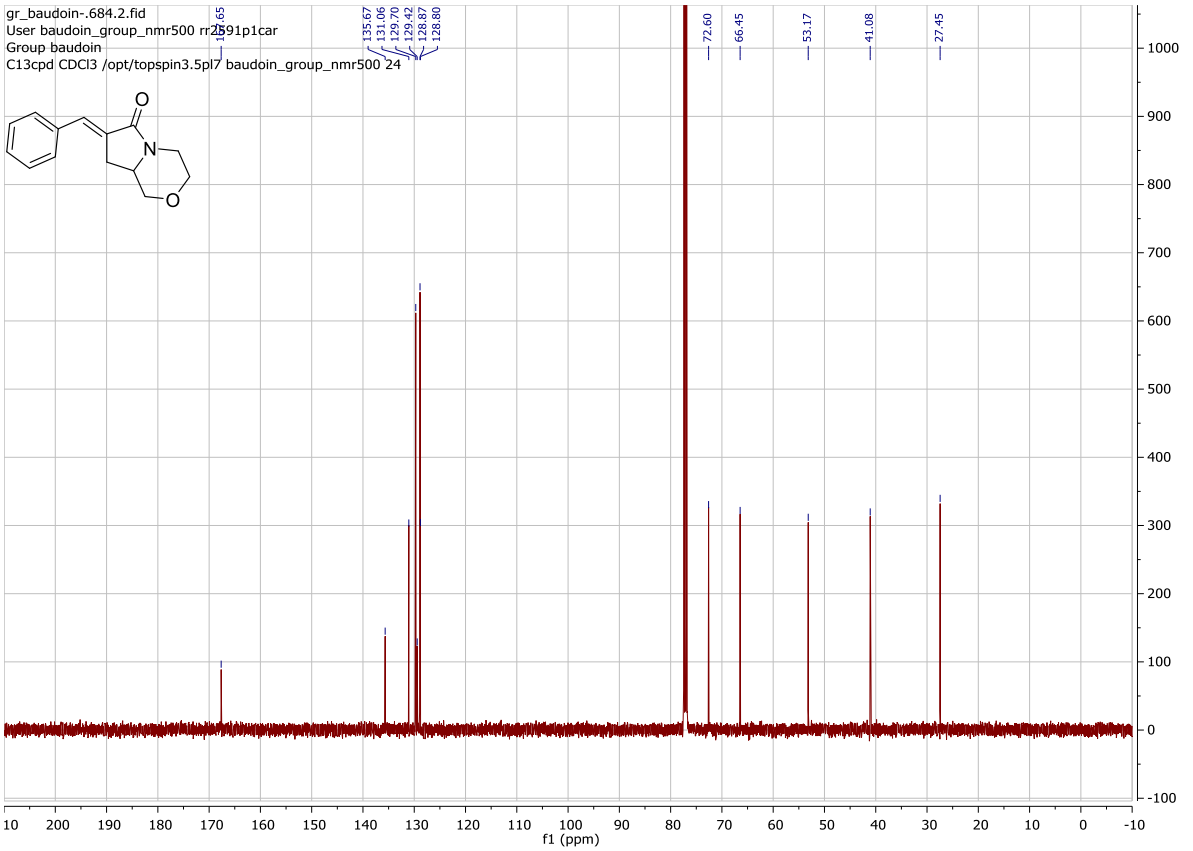
Group baudoin
H1 CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 24
f1 (ppm)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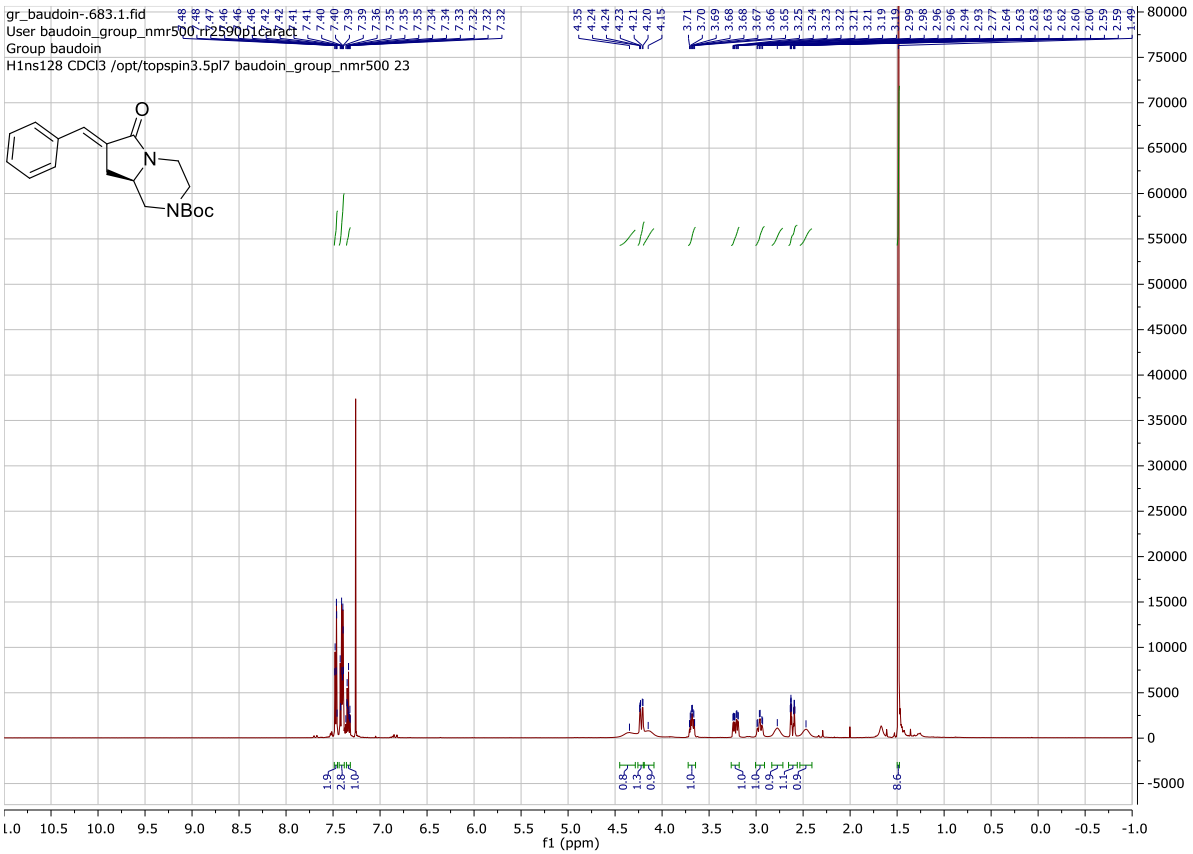
User baudoin_group_nmr500 rr2591p1car
Group baudoin
C13cpd CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 24
171.65
135.67
131.06
129.70
129.42
128.87
128.80
72.60
66.45
53.17
41.08
27.45
O
N
O
f1 (ppm)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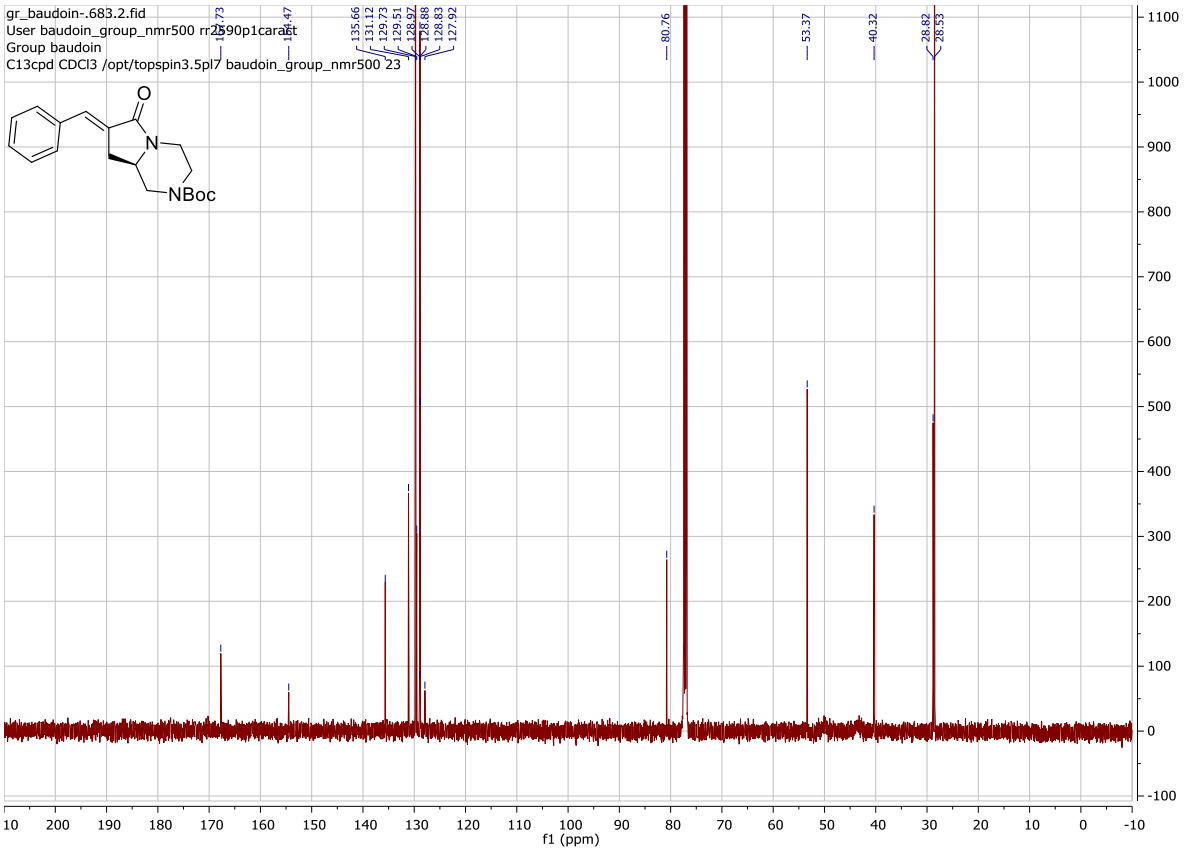
User baudoin_group_nmr500 rr2590p1caract
Group baudoin
H1ns128 CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 23
O
N
NBoc
1.9
2.8
1.0
0.8
1.3
0.9
1.0
1.0
1.0
0.9
1.1
0.9
8.6
f1 (ppm)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User baudoin_group_nmr500 rr2590p1caract
Group baudoin
C13cpd CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 23
O
N
NBoc
135.66
131.12
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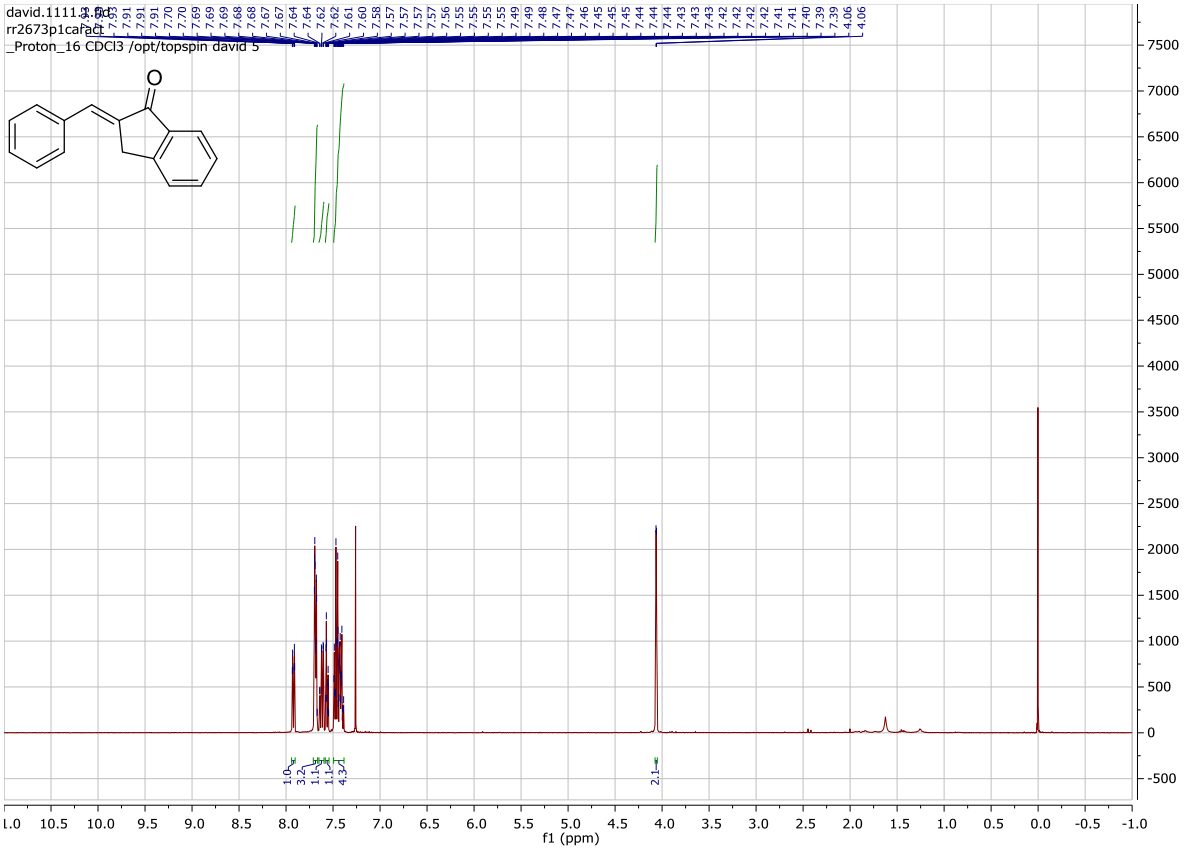
53.37
40.32
28.82
28.53
f1 (ppm)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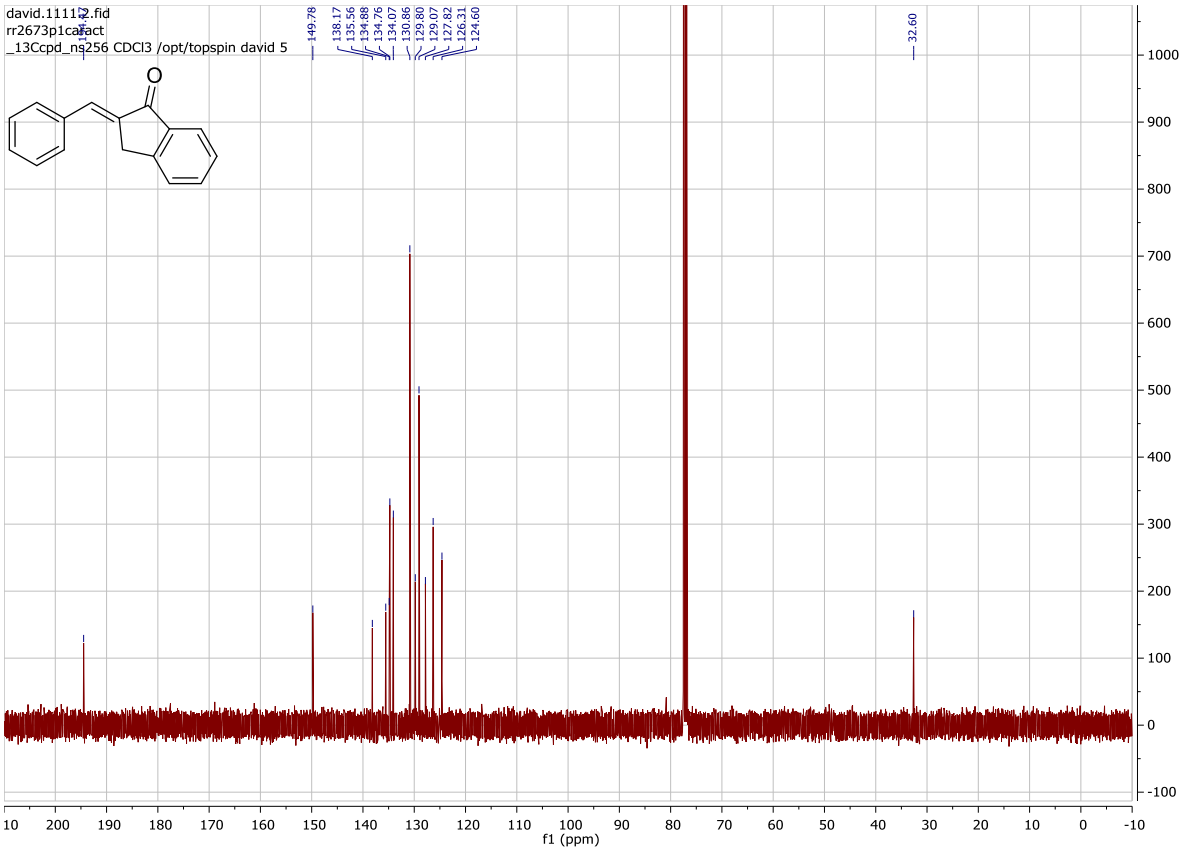
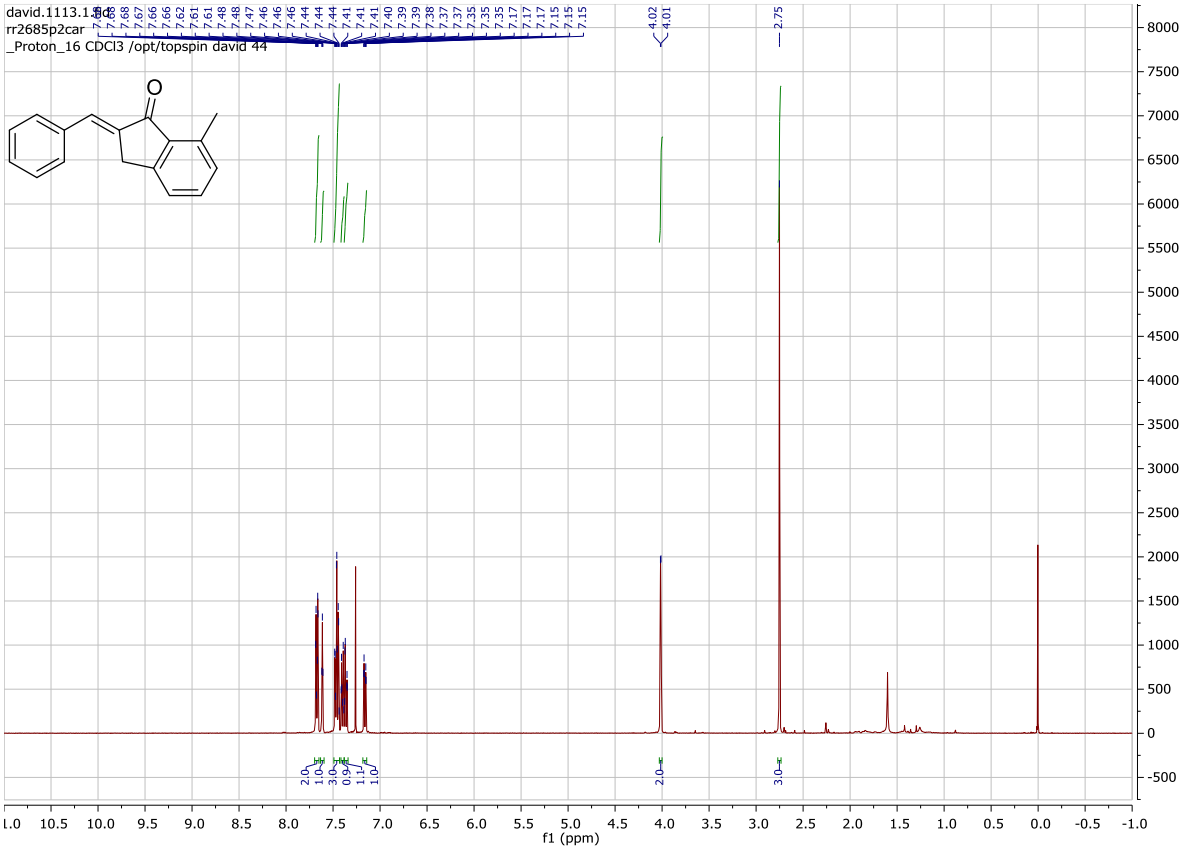
rr2673p1caract
_Proton_16 CDCl3 /opt/topspin david 5
O
f1 (ppm)


david.11112.fid
rr2673p1carfact
_13Ccpd_ns256 CDCl3 /opt/topspin david 5
149.78
138.17
135.56
134.88
134.76
134.07
130.86
129.80
129.07
127.82
126.31
124.60
32.60
f1 (ppm)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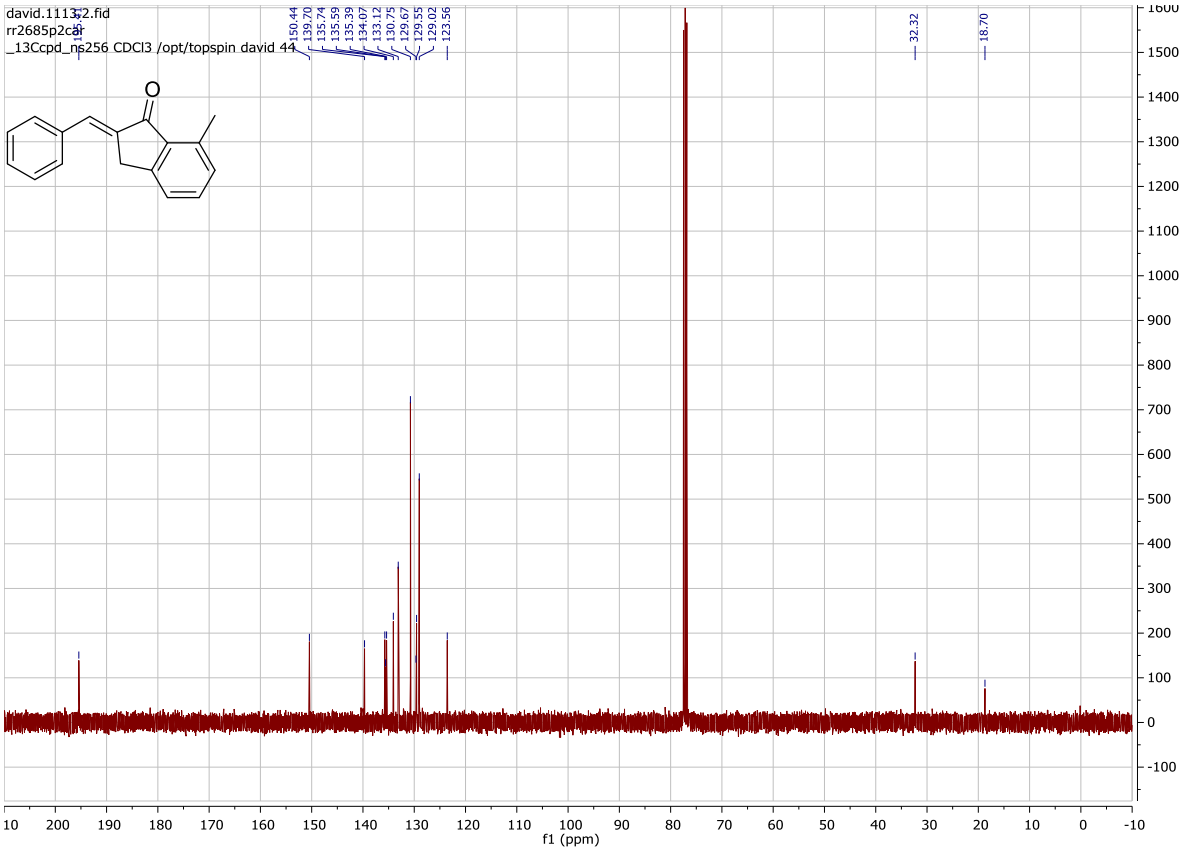
rr2685p2car
_Proton_16 CDCl3 /opt/topspin david 44
4.02
4.01
2.75
f1 (ppm)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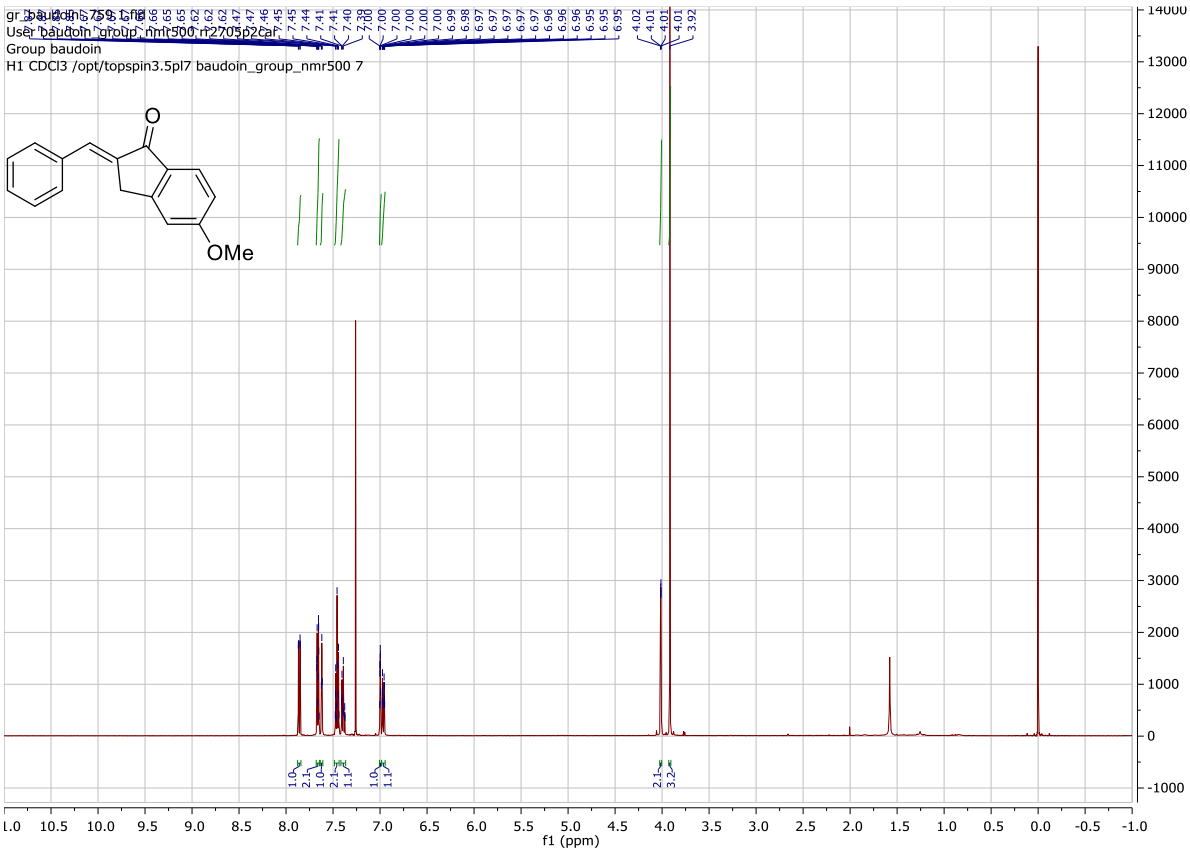
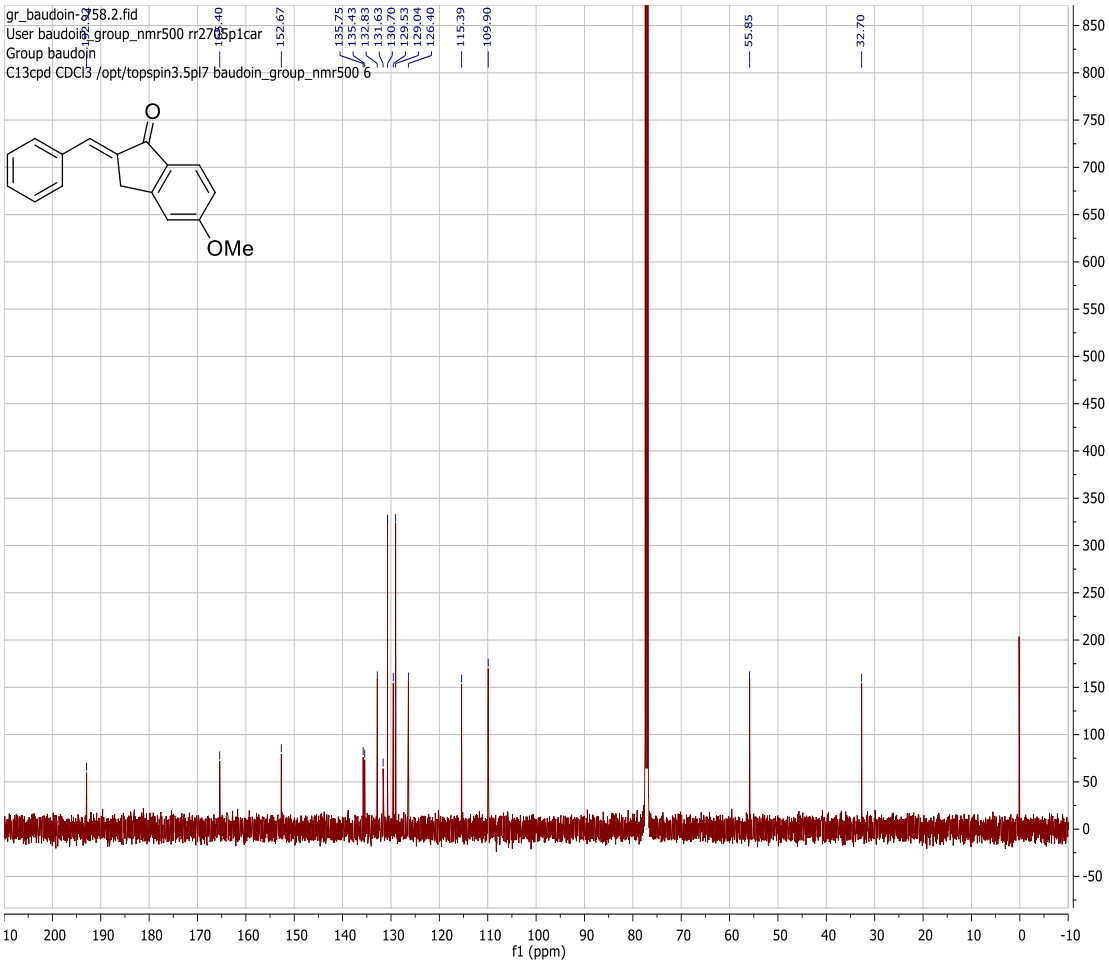
rr2685p2caf
_13Ccpd_ns256 CDCl3 /opt/topspin david 44
150.44
139.70
135.74
135.59
135.39
134.07
133.12
130.75
129.67
129.55
129.02
123.56
32.32
18.70
O
f1 (ppm)


Group baudoin
H1 CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 7
O
OMe
f1 (ppm)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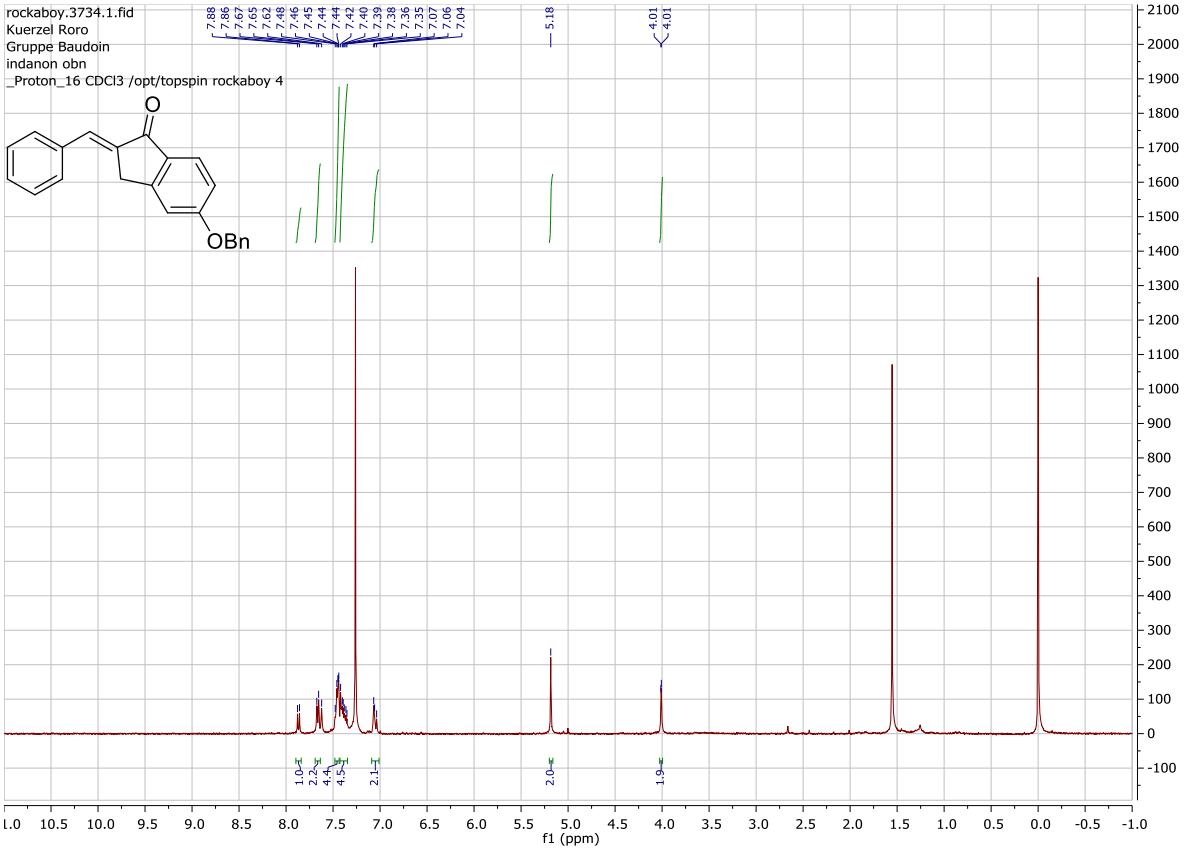
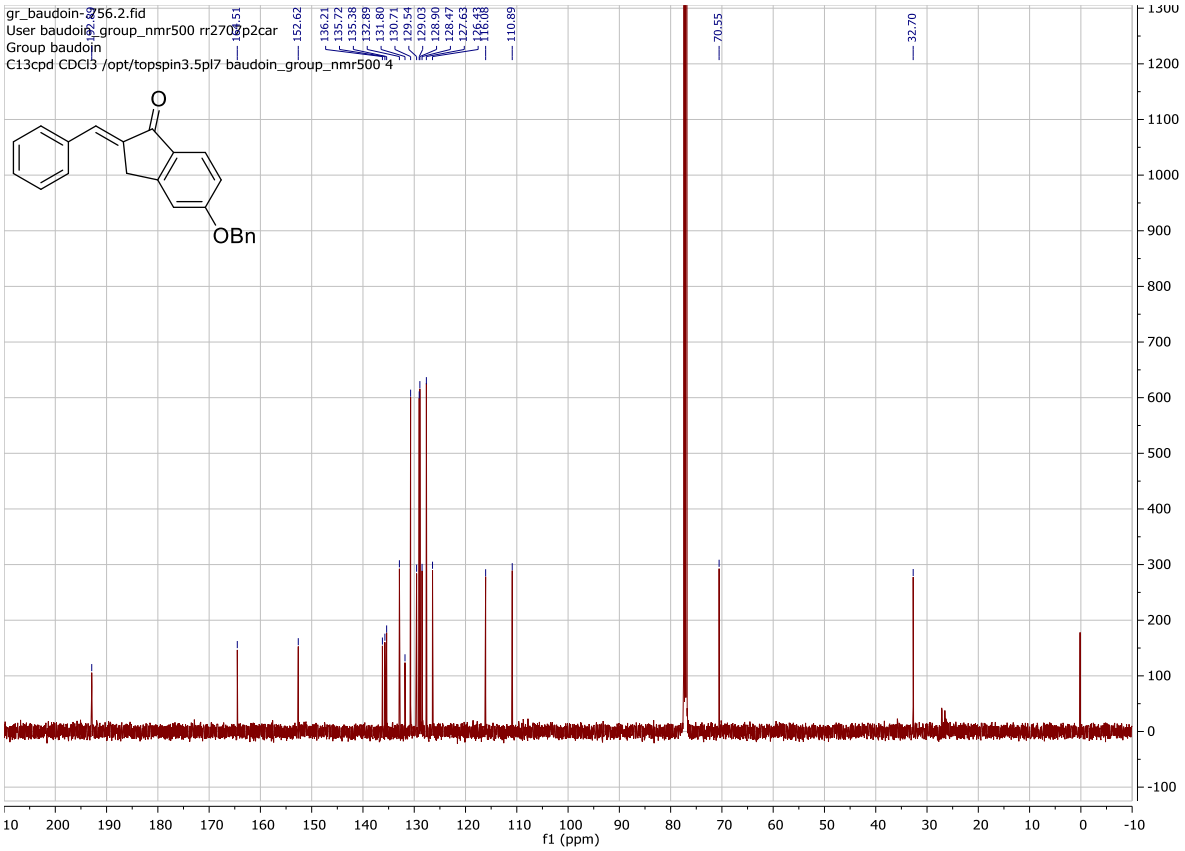
Group baudoin
C13cpd CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 6
192.42
166.40
152.67
135.75
135.43
132.83
131.63
130.70
129.53
129.04
126.40
115.39
109.90
55.85
32.70
O
OMe
f1 (ppm)


rockaboy.3734.1.fid
Kuerzel Roro
Gruppe Baudoin
indanon obn
_Proton_16 CDCl3 /opt/topspin rockaboy 4
7.88
7.86
7.67
7.65
7.62
7.48
7.46
7.45
7.44
7.44
7.42
7.40
7.39
7.38
7.36
7.35
7.07
7.06
7.04
5.18
4.01
4.01
O
OBn
1.0
2.2
4.4
4.5
2.1
2.0
1.9
f1 (ppm)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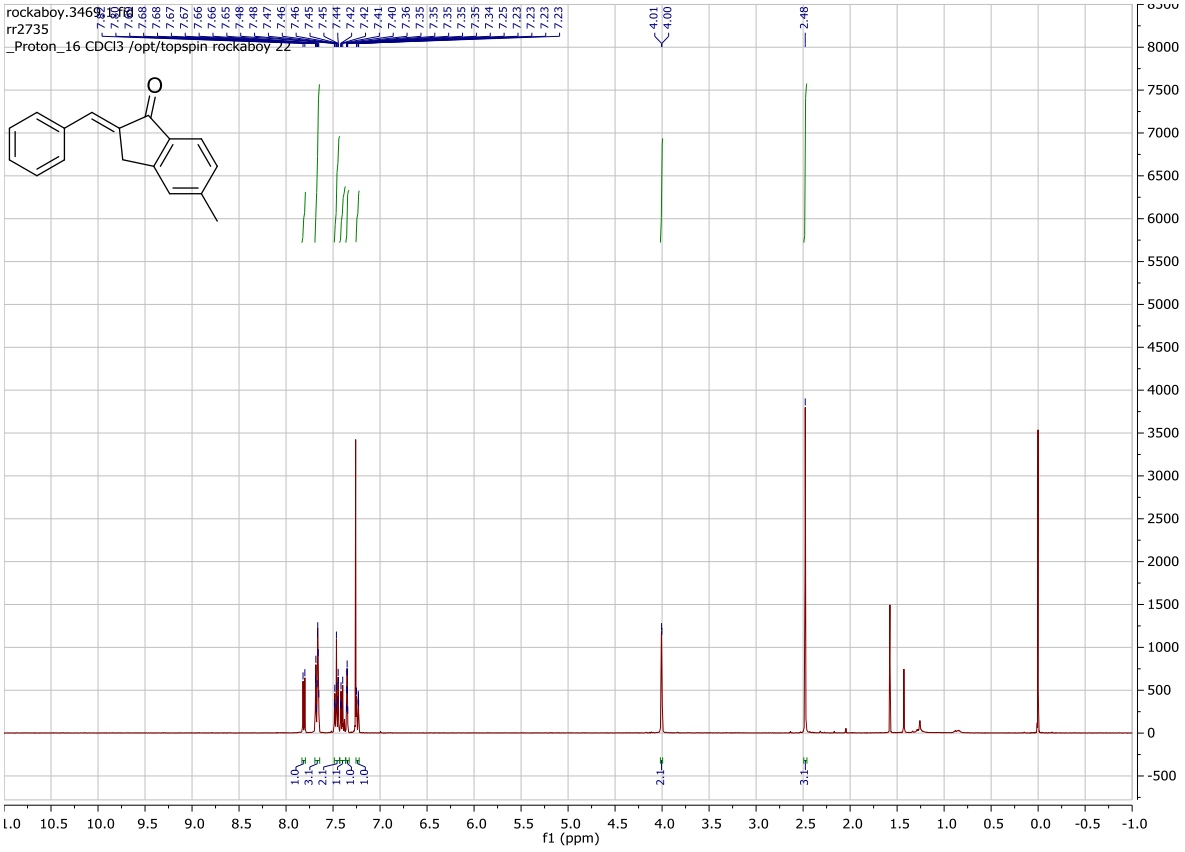
Group baudoin
C13cpd CDCl3 /opt/topspin3.5pl7 baudoin_group_nmr500 4
152.62
136.21
135.72
135.38
132.89
131.80
130.71
129.54
129.03
128.90
128.47
127.63
110.89
70.55
32.70
O
OBn
f1 (ppm)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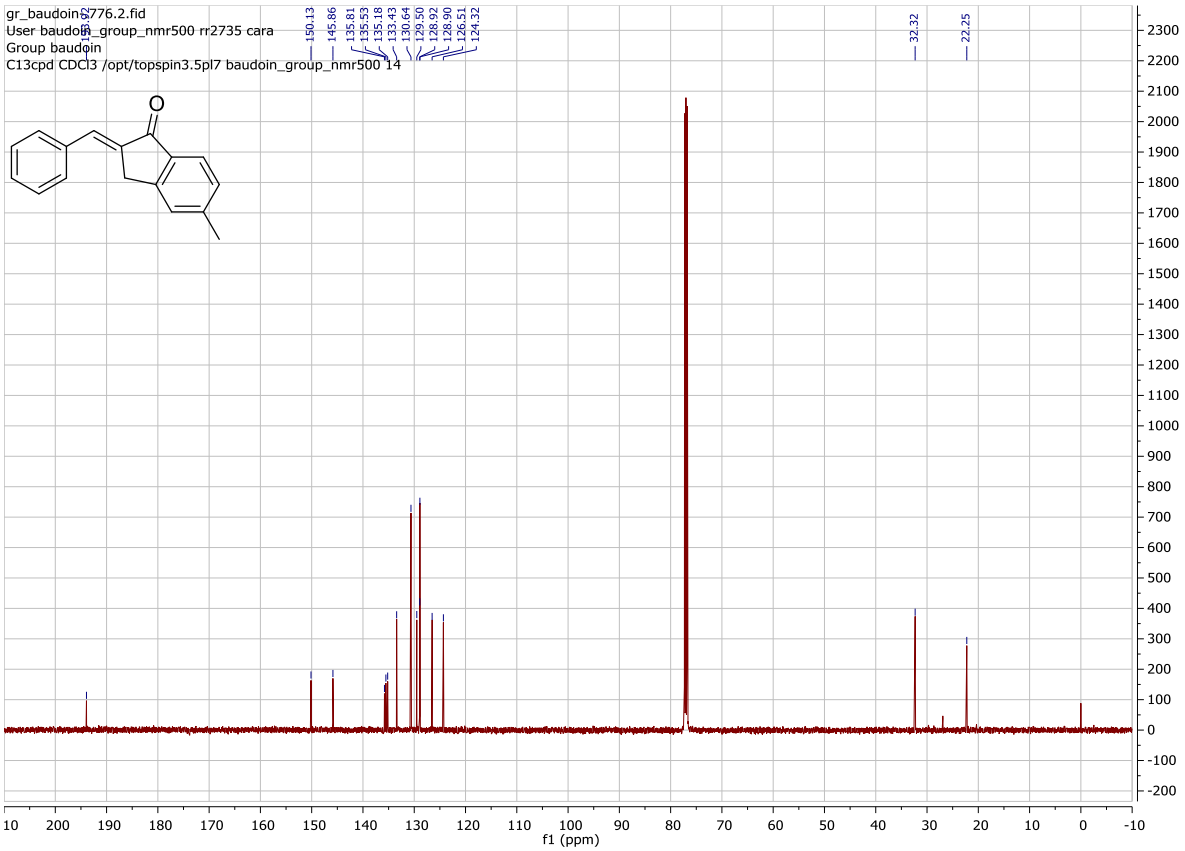
4.01
4.00
2.48
O
f1 (ppm)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Group baudoin
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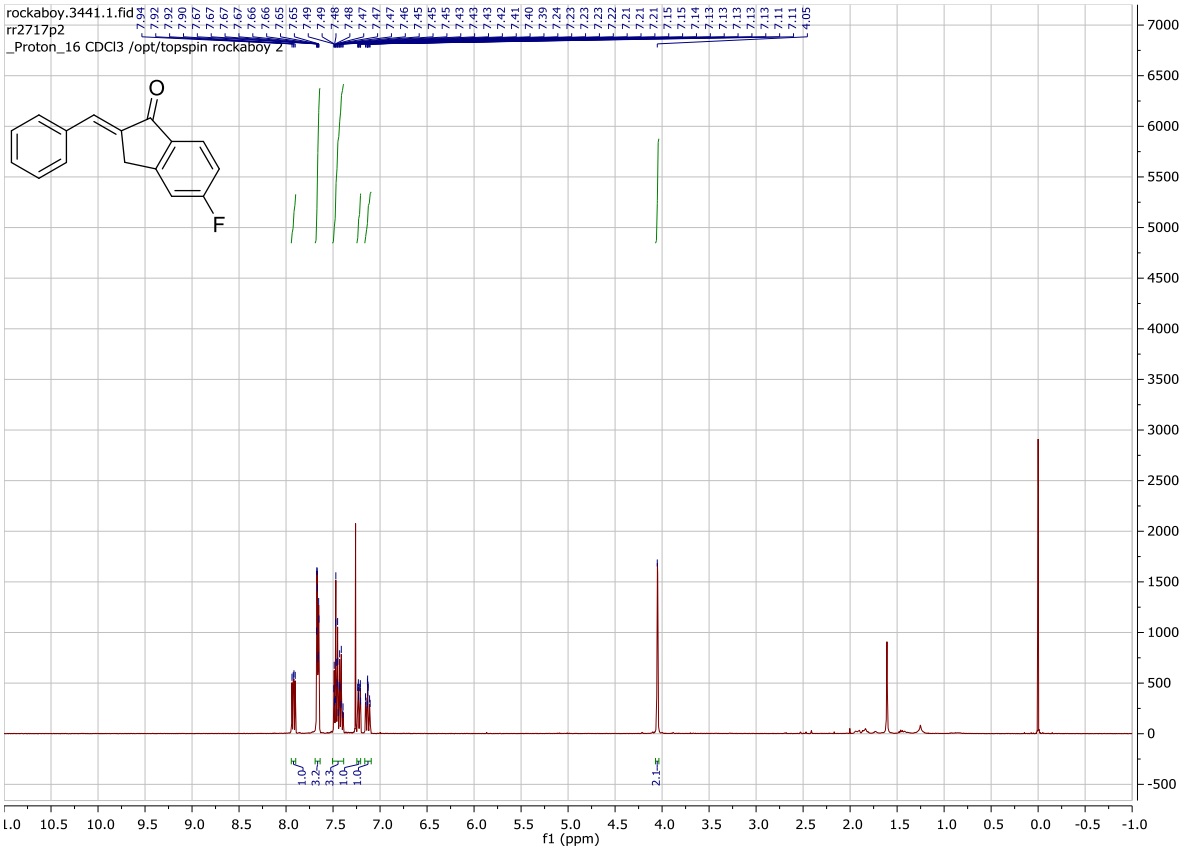
150.13
145.86
135.81
135.53
135.18
133.43
130.64
129.50
128.92
128.90
126.51
124.32
32.32
22.25
O
f1 (ppm)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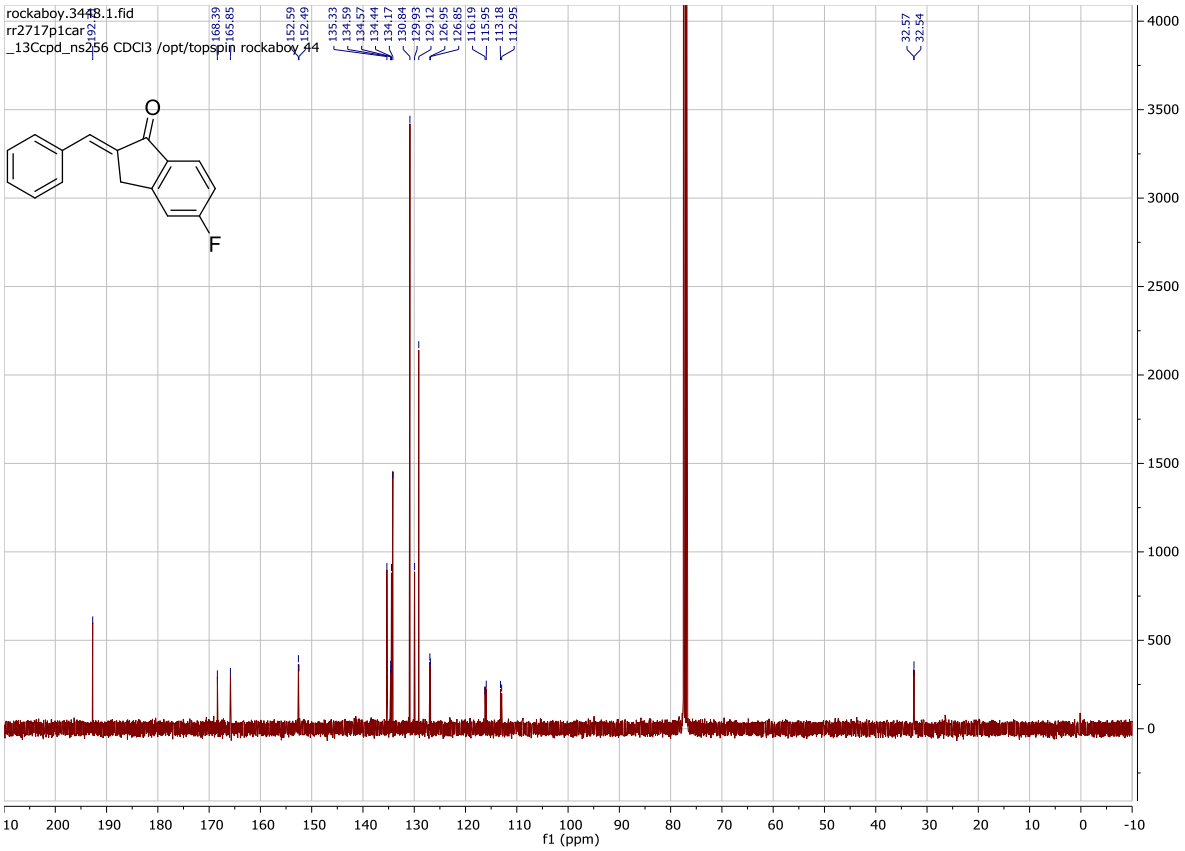
rr2717p2
_Proton_16 CDCl3 /opt/topspin rockaboy 2
O
F
1.0
3.2
3.3
2.1
1.0
1.0
1.0
2.1
f1 (ppm)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rr2717p1carr
_13Ccpd_ns256 CDCl3 /opt/topspin rockaboy 44
192.21
168.39
165.85
152.59
152.49
135.33
134.59
134.57
134.44
134.17
130.84
129.93
129.12
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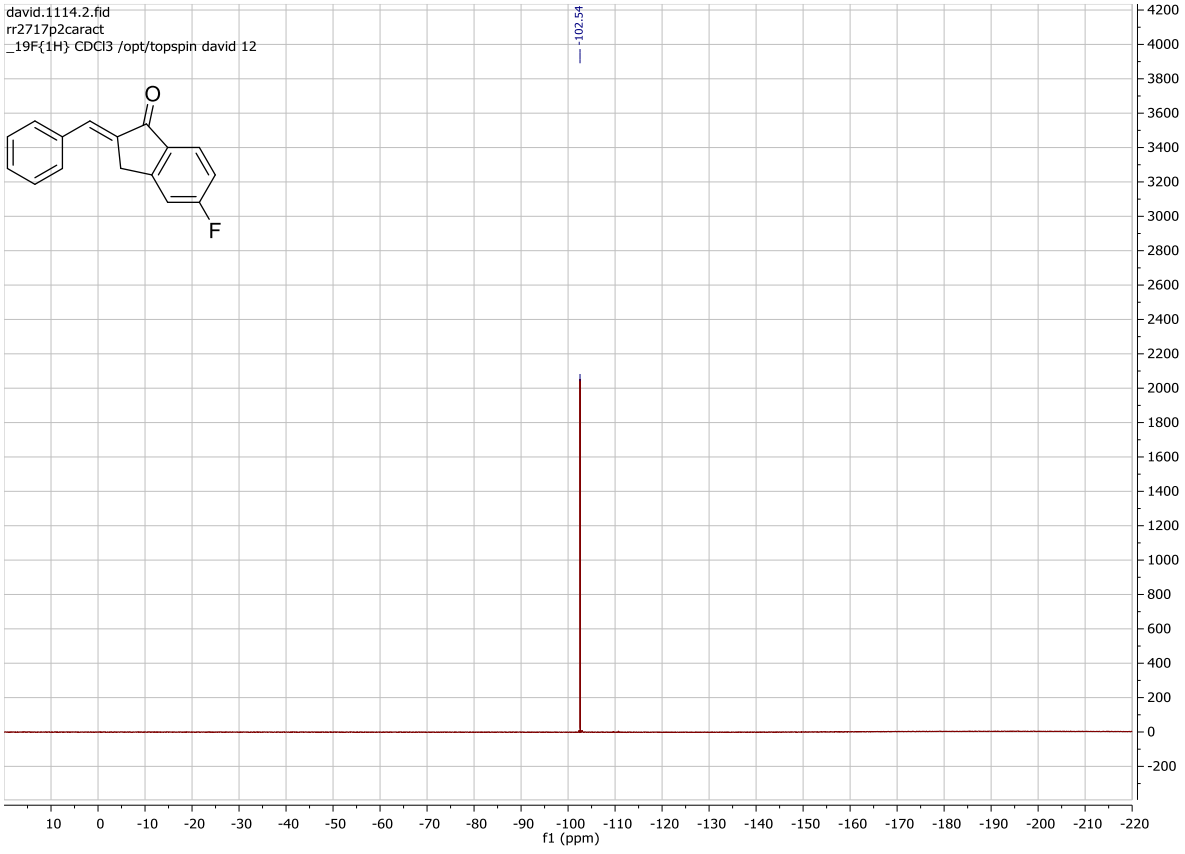
126.85
116.19
115.95
113.18
112.95
32.57
32.54
O
F
f1 (ppm)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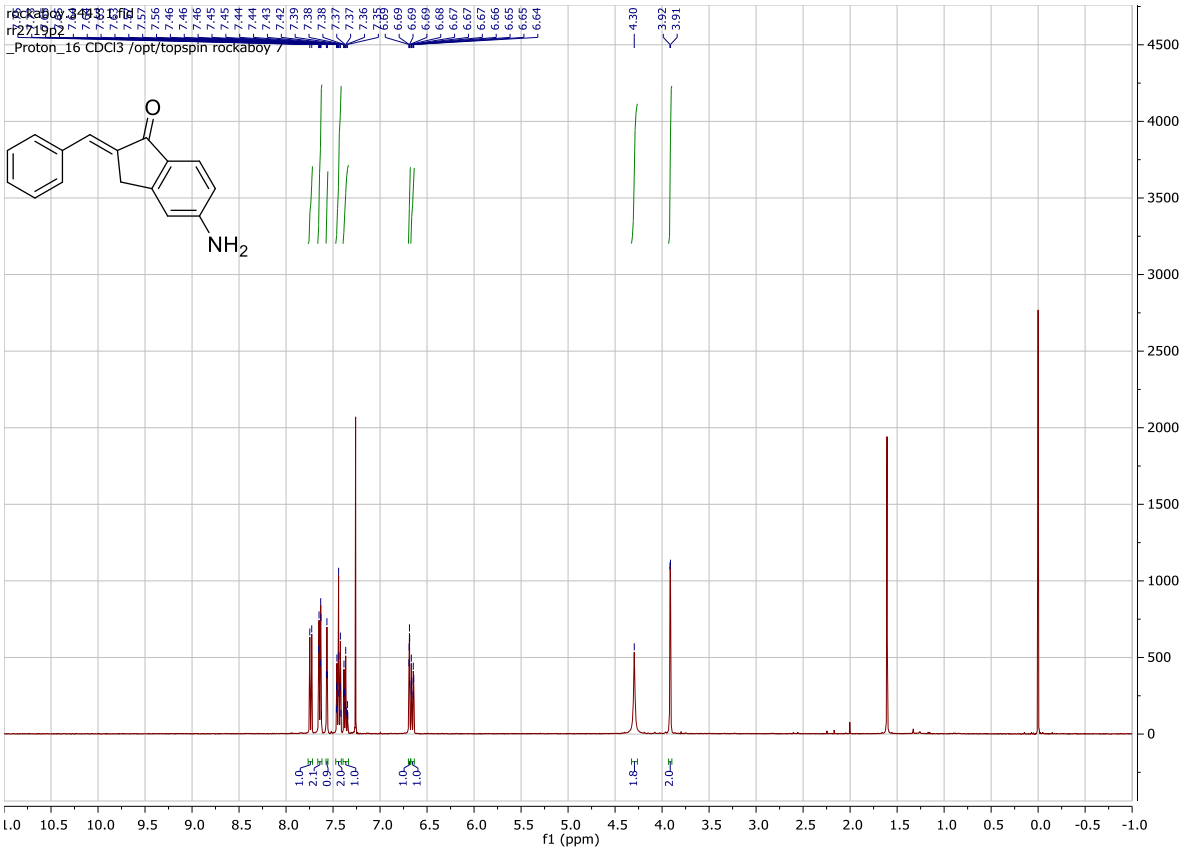
-102.54
O
F
f1 (ppm)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rr2719p1
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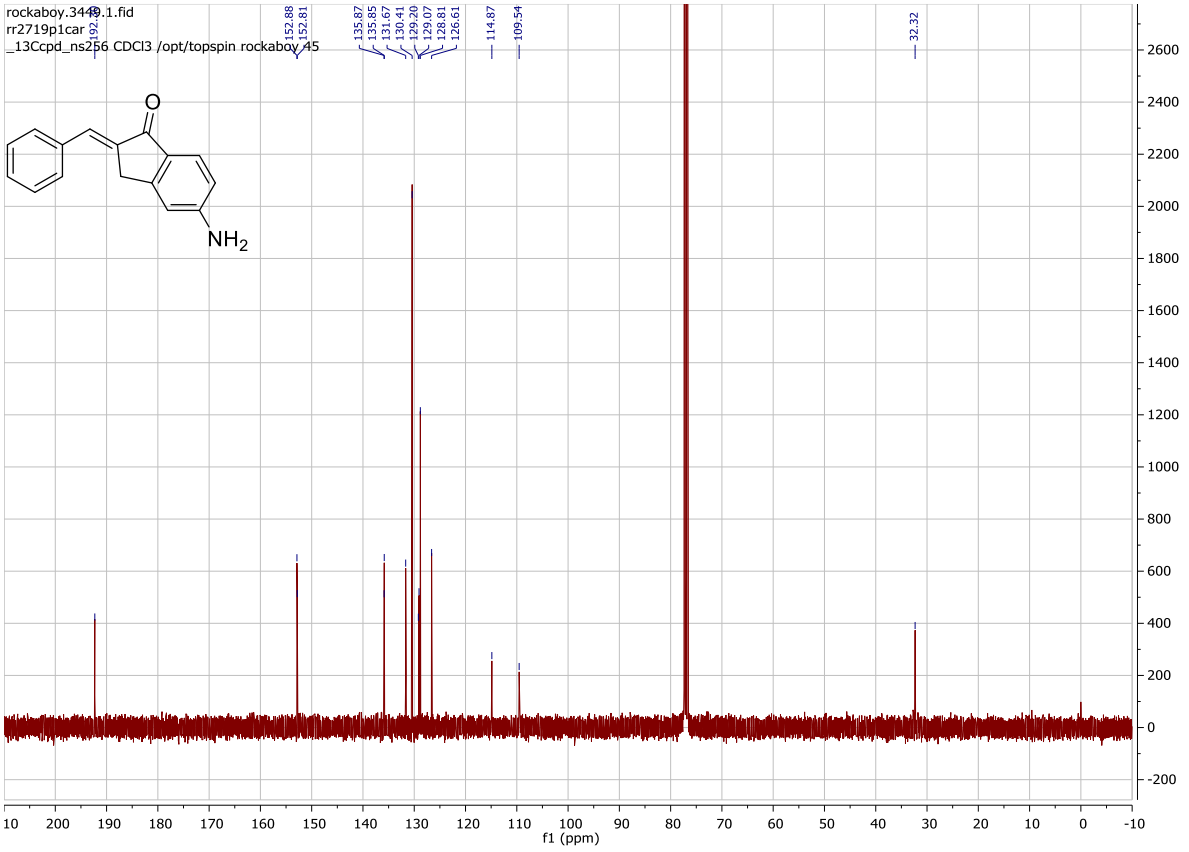
O
NH2
4.30
3.92
3.91
1.0
2.1
0.9
2.0
1.0
1.0
1.0
1.8
2.0
f1 (ppm)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rr2719p1car
_13Ccpd_ns256 CDCl3 /opt/topspin rockaboy 45
O
NH2
152.88
152.81
135.87
135.85
131.67
130.41
129.20
129.07
128.81
126.61
114.87
109.54
32.32
f1 (ppm)

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