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Chiral Cyclopentadienyl Rh^{III}-Catalyzed Enantioselective Cyclopropanation of Electron-Deficient Olefins Enable Rapid Access to UPF-648 and Oxypilin Natural Products

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Supplementary Information

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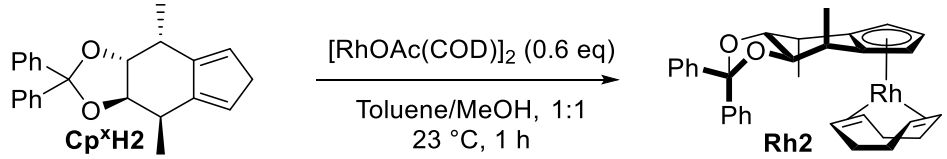
General Methods

Toluene, dichloromethane, tetrahydrofuran, acetonitrile and diethyl ether were purified by an Innovative Technology Solvent Delivery System. Chemicals and other solvents were used as obtained from the suppliers. Flash chromatography was performed with Silicycle silica gel 60 (0.040-0.063 μm grade) or acidic alumina (C. Roth, Aluminium oxide 90 acidic). Analytical thin-layer chromatography was performed with commercial glass plates coated with 0.25 mm silica gel (E. Merck, Kieselgel 60 F254). Compounds were either visualised under UV-light at 254 nm or by dipping the plates in an aqueous potassium permanganate solution followed by heating. Proton nuclear magnetic resonance (^{1}H-NMR) data were acquired on a Bruker *AV400* (400 MHz). Chemical shifts (δ) are reported in parts per million (ppm) relative to incompletely deuterated $CDCl_3$ (s, 7.26 ppm), C_6D_6 (s, 7.16 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; dd, doublet of doublets; qd, quadruplet of dublets; m, multiplet; br, broad. Proton decoupled Carbon-13 nuclear magnetic resonance (^{13}C-NMR) data were acquired on a Bruker *AV400* (101 MHz) spectrometer. Chemical shifts are reported in ppm relative to $CDCl_3$ (77.16 ppm), C_6D_6 (128.06 ppm). Proton decoupled Fluorine-19 nuclear magnetic resonance (^{19}F-NMR) were acquired at 376 MHz on a Bruker *AV400* spectrometer. Infrared (IR) data were recorded on an Alpha-P Bruker FT-IR Spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). HRMS measurements were performed by an Agilent LC-MS TOF. High resolution mass are given in *m/z*. Enantiomeric excesses were measured on an Agilent or Waters HPLC, or on a Thar SFC Investigator system using chiral stationary phase columns. Optical rotations were measured on a Polartronic M polarimeter using a 0.5 cm cell with a Na 589 nm filter.

Catalyst synthesis

Catalysts **Rh1**, **Rh3**, **Rh4**, **Rh5**, **Rh6**, **Rh7**, **Rh8** and **Rh9** were prepared following the literature procedures.[1-3] Ligands **Cp^{x}H1** and **Cp^{x}H2** were prepared following the literature procedure.[2]

Complex **Rh2** was prepared following the complexation method published.[1]



Without any precautions from air and moisture, in a test tube were dissolved [Rh(cod)OAc]$_2$ (4.7 mg, 8.7 μg, 0.6 Equiv.), and **Cp^{x}H2** (5 mg, 15 μmol) in a mixture of MeOH/Toluene (1/1) (0.05 M) stirred at 23 °C for 1h. The solvents were evaporated *in vacuo*. The crude was filtrated on a pad of silica with toluene to afforded **Rh2** as a yellow solid (6.0 mg, 10.8 μmol, 72% yield). **^{1}H NMR** : (400 MHz, C_6D_6) δ 7.90 – 7.77 (m, 4H), 7.19 (d, *J* = 8.0 Hz, 4H), 7.07 (dd, *J* = 9.6, 7.4 Hz, 2H), 5.09 (t, *J* = 2.4 Hz, 1H), 4.77 (s, 1H), 4.51 (dd, *J* = 10.2, 6.0 Hz, 1H), 4.14 (dd, *J* = 10.1, 6.7 Hz, 1H), 4.08 – 3.99 (m, 1H), 3.87 – 3.76 (m, 2H), 3.50 – 3.33 (m, 2H), 3.03 (p, *J* = 6.9 Hz, 1H), 2.53 (p, *J* = 7.0 Hz, 1H), 2.20 – 2.02 (m, 4H), 1.92 – 1.79 (m, 4H), 1.63 (d, *J* = 7.0 Hz, 3H), 1.16 (d, *J* = 7.1 Hz, 3H); **^{13}C NMR** : (101 MHz, C_6D_6) δ 144.9 , 126.6 , 126.5 , 110.8 , 105.4 , 86.9 (d, *J* = 4.0 Hz), 83.9 (d, *J* = 3.6 Hz), 82.6 (d, *J* = 3.8 Hz), 76.2 (d, *J* = 23.6 Hz), 67.4 (d, *J* = 14.1 Hz), 64.0 (d, *J* = 14.1 Hz), 32.8 , 32.7 , 31.9 (d, *J* = 26.5 Hz), 21.9 , 16.6; **IR (ATR)** : $\tilde{\nu}$ = 2971, 2930, 2875, 2825, 1449, 1208, 1174, 1082, 1046, 700 cm^{-1} ; **HRMS (ESI)** : calculated for $[C_{32}H_{35}O_2Rh]^+$: 554.1687, found: 554.1634 ; **$[\alpha]_D^{20}$** : -48.3 (c = 0.2, CH_2Cl_2) ; **m.p. :** 114 °C ; **R_f [Toluene]** : 0.89.

Substrate synthesis

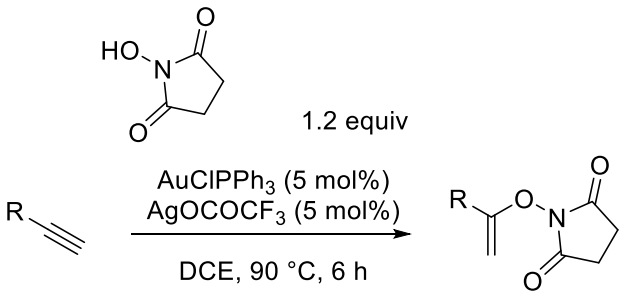
Compound **1** was prepared following the literature procedure.[4a]

N-enoxysuccinimides **2a, 2b, 2c, 2d, 2f, 2g, 2j, 2l, 2m** are known and were prepared following a procedure developed in our group. [4b]

N-Methoxy-*N*-methylacrylamide **3g** was prepared according to published procedure.[5]

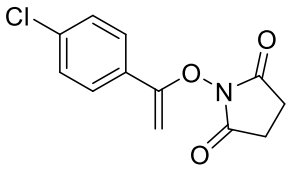
7-(tert-butyldimethylsilyloxy)hept-1-en-3-one **3j** was prepared following literature procedure.[6]

Typical procedure for N-Enoxysuccinimide substrates preparation:



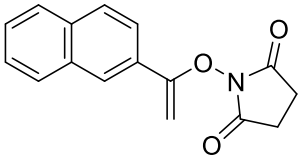
Following known procedure,[4b] PPh_3AuCl (5 mol %) and silver trifluoroacetate (5 mol %) were premixed in 1,2-DCE (1ml) for 10 mins at rt and filtered over a short plug of celite before use. In a sealed tube, the cationic gold complex was added to alkyne (10 mmol) in 1,2-DCE (4ml) and *N*-hydroxysuccinimide (11 mmol) was then added. The tube was sealed and the reaction was stirred for 6 h at reflux. The reaction was diluted with DCM and passed through a short plug of celite. The filtrate was concentrated and the residue purified by column chromatography.

1-((1-(4-chlorophenyl)vinyl)oxy)pyrrolidine-2,5-dione 2e:



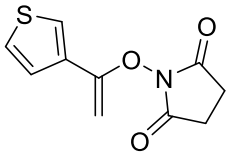
The product **2e** was obtained as a white solid in 18 % yield using 10 mol% catalyst. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 4.84 (d, *J* = 4.3 Hz, 1H), 4.41 (d, *J* = 4.3 Hz, 1H), 2.86 (s, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.8, 158.5, 135.9, 130.6, 128.8, 127.8, 87.3, 25.8; **IR (ATR, cm^{-1}):** ν_{max} = 1723, 1643, 1491, 1202, 1105, 817, 648; **HRMS (APPI/LTQ-Orbitrap) m/z:** $[M + H]^+$ Calcd for $C_{12}H_{11}ClNO_3^+$ 252.0422; Found 252.0431; **Rf:** 0.43 (Pentane: EtOAc, 1:1); **m.p.:** 200 °C.

1-((1-(naphthalen-2-yl)vinyl)oxy)pyrrolidine-2,5-dione 2h:



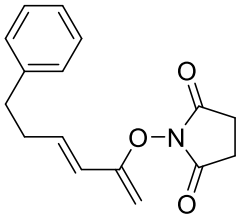
The product **2h** was obtained as a white solid in 23 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.90 – 7.82 (m, 3H), 7.73 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.54 – 7.47 (m, 2H), 4.99 (d, *J* = 4.2 Hz, 1H), 4.49 (d, *J* = 4.2 Hz, 1H), 2.89 (s, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.0, 159.4, 134.0, 133.1, 129.3, 128.8, 128.3, 127.8, 127.0, 126.6, 126.1, 123.8, 87.2, 25.8; **IR (ATR**, **cm^{-1}):** ν_{max} = 1731, 1644, 1368, 1197, 1090, 819, 646; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{16}H_{13}NNaO_3^+$ 290.0788; Found 290.0789; **Rf:** 0.46 (Pentane: EtOAc, 1:1); **m.p.:** 206 °C.

1-((1-(thiophen-3-yl)vinyl)oxy)pyrrolidine-2,5-dione 2i:



The product **2i** was obtained as a white solid in 24 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 2.9, 1.1 Hz, 1H), 7.31 (dd, *J* = 5.1, 3.0 Hz, 1H), 7.26 (m, 1H), 4.79 (d, *J* = 4.2 Hz, 1H), 4.34 (d, *J* = 4.2 Hz, 1H), 2.86 (s, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.8, 155.3, 133.3, 126.2, 125.6, 123.8, 85.7, 25.8; **IR (ATR, cm^{-1}):** ν_{max} = 1727, 1648, 1372, 1269, 1204, 1101, 1064, 805, 658, 645; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{10}H_9NNaO_3S^+$ 246.0195; Found 246.0202; **Rf:** 0.42 (Pentane: EtOAc, 1:1); **m.p.:** 179 °C.

(E)-1-((6-phenylhexa-1,3-dien-2-yl)oxy)pyrrolidine-2,5-dione 2k:



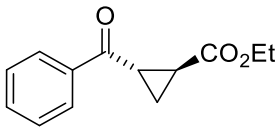
The product **2k** was obtained as a white solid in 15 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.22 – 7.15 (m, 3H), 6.33 (dt, *J* = 15.8, 6.9 Hz, 1H), 5.94 (d, *J* = 15.9 Hz, 1H), 4.33 (d, *J* = 3.6 Hz, 1H), 4.13 (d, *J* = 3.6 Hz, 1H), 2.82 (s, 4H), 2.78 – 2.71 (m, 2H), 2.47 (q, *J* = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.9, 156.8, 141.6, 133.9, 128.5, 126.1, 121.8, 87.5, 35.2, 34.7, 25.7; **IR (ATR, cm^{-1}):** ν_{max} = 1732, 1609, 1367, 1274, 1197, 1076, 701, 646; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{16}H_{17}NNaO_3^+$ 294.1101; Found 294.1106; **Rf:** 0.44 (Pentane: EtOAc, 1:1); **m.p.:** 74 °C.

General Procedures for the Enantioselective Rh-Catalyzed cyclopropanation

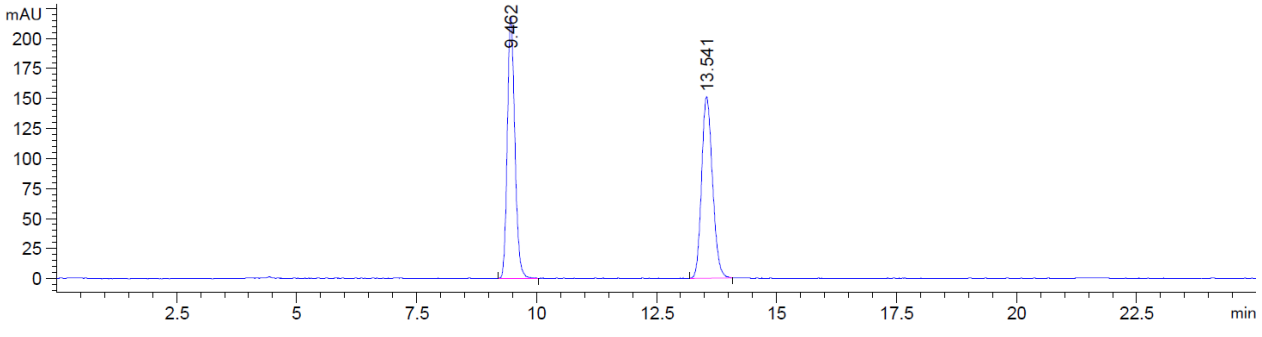
Representative procedure:

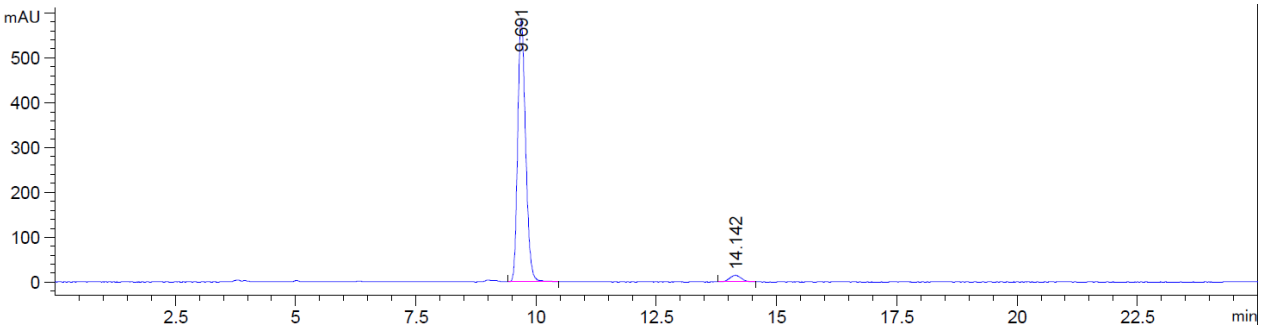
Without protection from oxygen and moisture, **Rh1** (2.15 mg, 5.00 µmol), dibenzoylperoxide (1.20 mg, 5.00 µmol) and CsOAc (38.0 mg, 0.12 mmol, 2.0 equiv.) were weighed into a vial equipped with a magnetic stir bar and sealed with a rubber septum. 200 µL of TFE was added and the mixture was stirred at 23°C for 2 mins. The substrate (0.10 mmol, 1.00 equiv.) and 300 µL of TFE were added followed by alkene (0.12mmol, 1.20 equiv.). The reaction mixture was stirred for 16 hours. The mixture was concentrated under reduced pressure and the residue was purified further by silica gel column (pentane/EtOAc).

ethyl (1*S*,2*S*)-2-benzoylcyclopropane-1-carboxylate 4aa:



Obtained as a colorless oil in 66 % yield. All spectroscopic data were in agreement with those reported previously in the literature.[7] **R_f:** 0.71 (Pentane: EtOAc, 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.4 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.19 (ddd, *J* = 8.7, 5.8, 3.9 Hz, 1H), 2.38 (ddd, *J* = 8.7, 5.9, 3.8 Hz, 1H), 1.57-1.31 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.2, 172.5, 137.2, 133.5, 128.8, 128.4, 61.3, 26.1, 24.9, 18.1, 14.4; **$[\alpha]_D^{20}$**= 186.7 (c = 0.43, $CHCl_3$); **Chiral HPLC:** (Chiralpak IC; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 14.2 min, t_R (major) = 9.7 min, 96.5 : 3.5 er.)

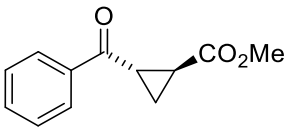




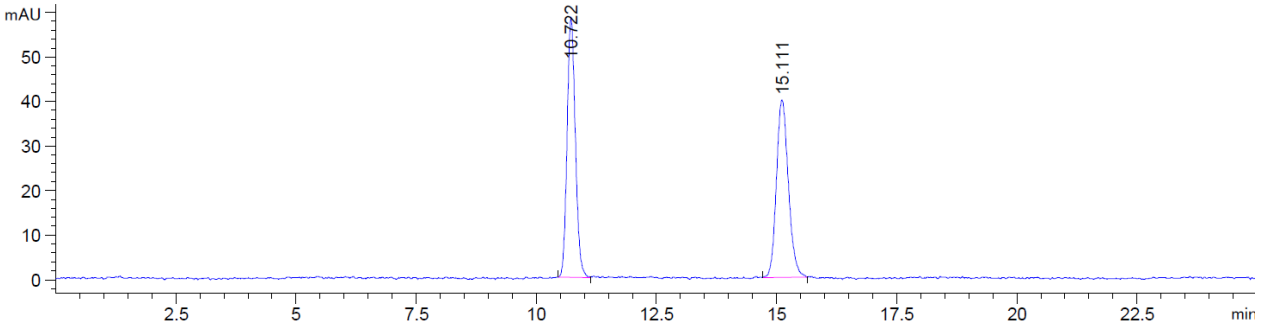
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.462	BB	0.1696	2381.61670	217.68115	49.9121
2	13.541	BB	0.2424	2390.00317	151.20357	50.0879

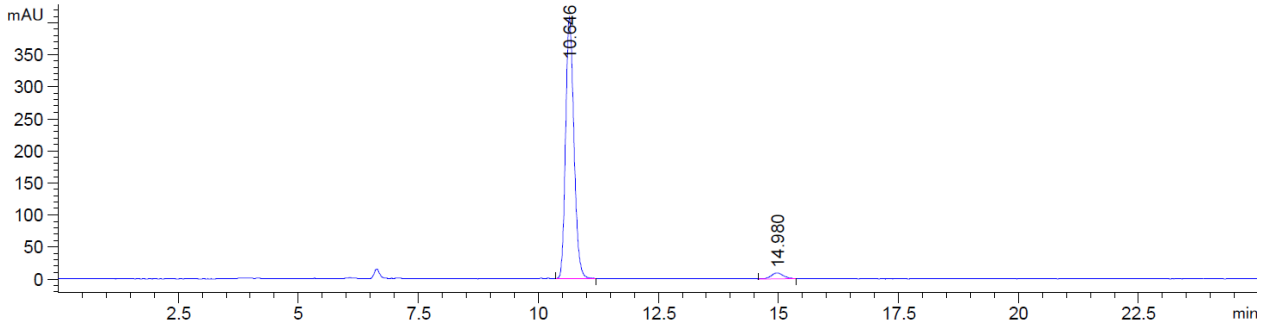
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.691	VB	0.1784	6725.15186	583.97089	96.4283
2	14.142	BB	0.2625	249.09724	14.78963	3.5717

methyl (1*S*,2*S*)-2-benzoylcyclopropane-1-carboxylate 4ab:



Obtained as a colorless oil in 70 % yield. All spectroscopic data were in agreement with those reported previously in the literature.[8] **R_f:** 0.54 (Pentane: EtOAc, 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.1 Hz, 2H), 7.67 – 7.54 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 3.74 (s, 3H), 3.20 (ddd, *J* = 8.7, 5.8, 3.9 Hz, 1H), 2.40 (ddd, *J* = 8.7, 5.9, 3.8 Hz, 1H), 1.69 – 1.51 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.2, 172.9, 137.1, 133.6, 128.8, 128.4, 52.4, 26.1, 24.6, 18.1; **$[\alpha]_D^{20}$**= 202.2 (c = 1.0, $CHCl_3$); **Chiral HPLC:** (Chiralpak IC; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 15.0 min, t_R (major) = 10.7 min, 97:3 er.).





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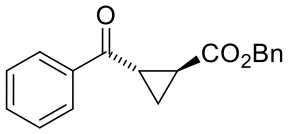
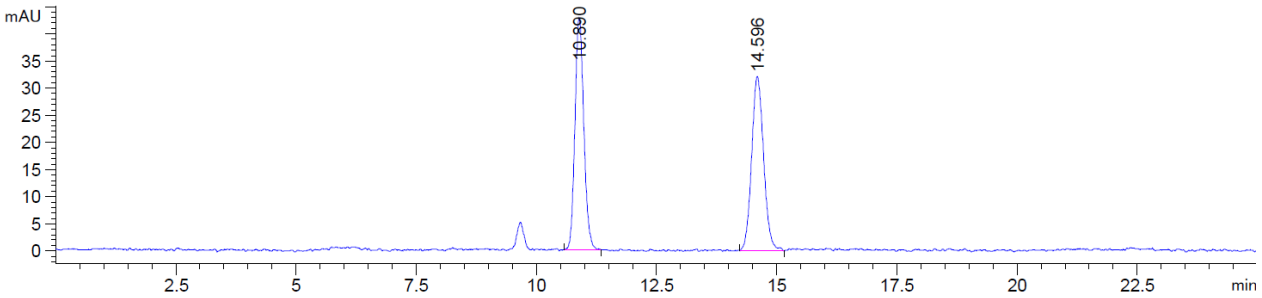
1	10.722	BV	0.1850	694.96338	58.33838	50.2123
2	15.111	BB	0.2614	689.08789	39.91840	49.7877

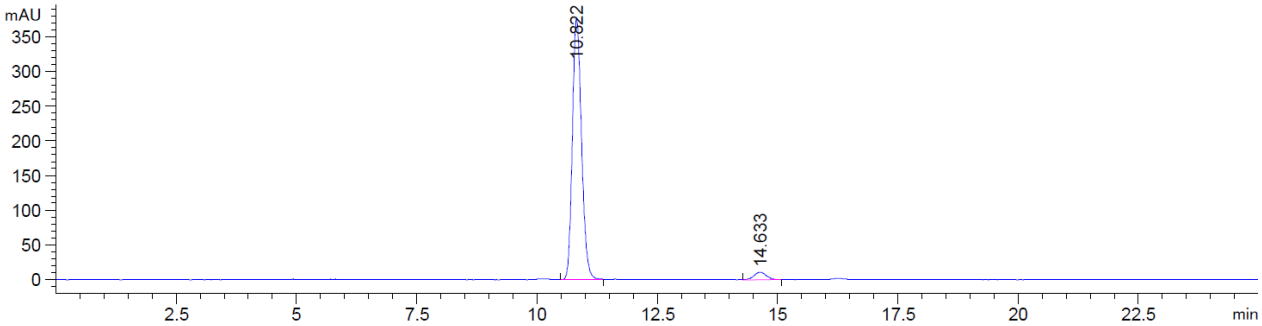
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.646	BB	0.1868	4912.49854	407.16922	96.7384
2	14.980	BV	0.2516	165.62936	9.13227	3.2616

benzyl (1*S*,2*S*)-2-benzoylcyclopropane-1-carboxylate 4ac:



Obtained as a colorless oil in 67 % yield. All spectroscopic data were in agreement with those reported previously in the literature.[9] **R_f:** 0.60 (Pentane: EtOAc, 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d , *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.37 (m, 5H), 5.17 (s, 2H), 3.25 (ddd, *J* = 9.5, 5.8, 3.9 Hz, 1H), 2.45 (ddd, *J* = 8.7, 5.9, 3.9 Hz, 1H), 1.64 (dddt, *J* = 11.3, 9.3, 5.9, 2.9 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.1, 172.3, 137.1, 135.7, 133.5, 128.8, 128.8, 128.5, 128.4, 128.4, 67.1, 26.3, 24.8, 18.2; **$[\alpha]_D^{20}$**= 159.3 (c = 1.0, $CHCl_3$); **Chiral HPLC:** (Chiralpak IC; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 14.6 min, t_R (major) = 10.8 min, 96:4 er.).





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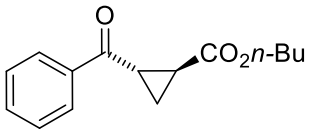
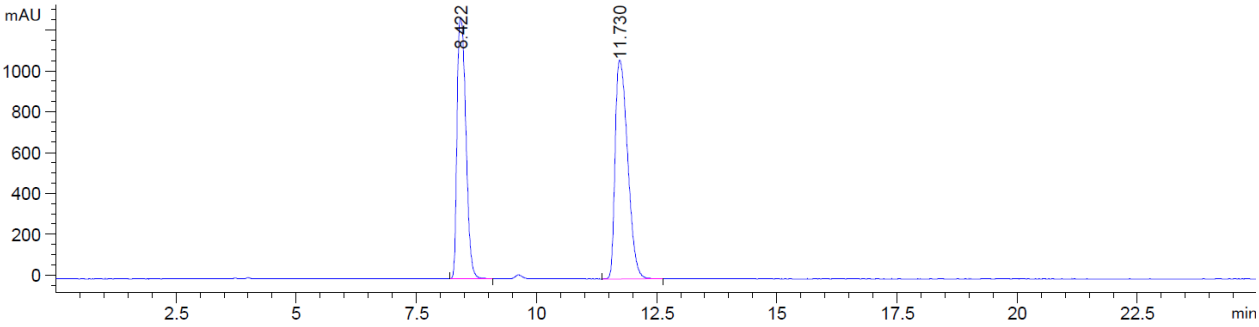
1	10.890	BB	0.1995	547.46198	42.71715	49.5853
2	14.596	BB	0.2680	556.61914	32.14916	50.4147

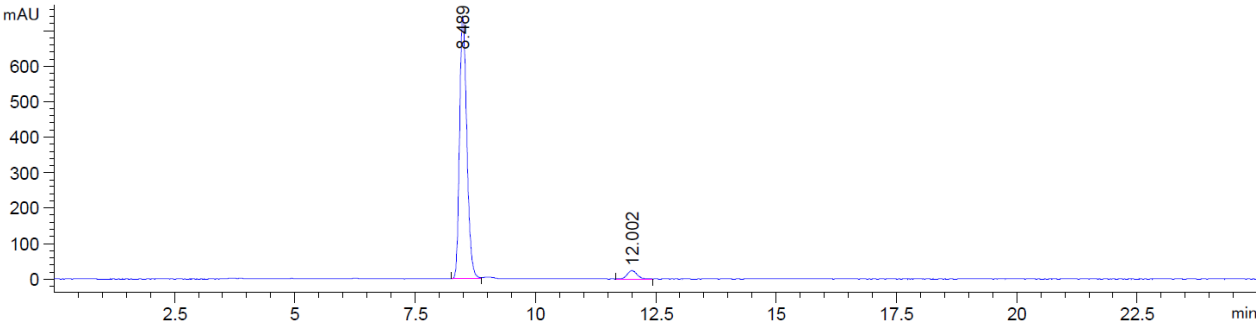
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.822	BV	0.2044	4988.96973	376.94653	96.2305
2	14.633	VB	0.2599	195.42775	10.96457	3.7695

butyl (1*S*,2*S*)-2-benzoylcyclopropane-1-carboxylate 4ad:



Obtained as a colorless oil in 75 % yield. All spectroscopic data were in agreement with those reported previously in the literature.[10] **R_f:** 0.79 (Pentane: EtOAc, 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.4 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 4.13 (t, *J* = 6.7 Hz, 2H), 3.19 (ddd, *J* = 8.8, 5.8, 3.9 Hz, 1H), 2.39 (ddd, *J* = 8.7, 5.9, 3.9 Hz, 1H), 1.67-1.58 (m, 4H), 1.40 (dq, *J* = 14.6, 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.3, 172.6, 137.2, 133.5, 128.8, 128.4, 65.2, 30.8, 26.1, 24.8, 19.3, 18.1, 13.9; **$[\alpha]_D^{20}$**= 159.3 (c = 1.0, $CHCl_3$); **Chiral HPLC:** (Chiralpak IC; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 12.0 min, t_R (major) = 8.5 min, 96:4 er.).

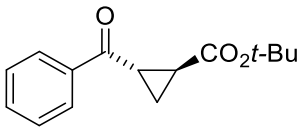




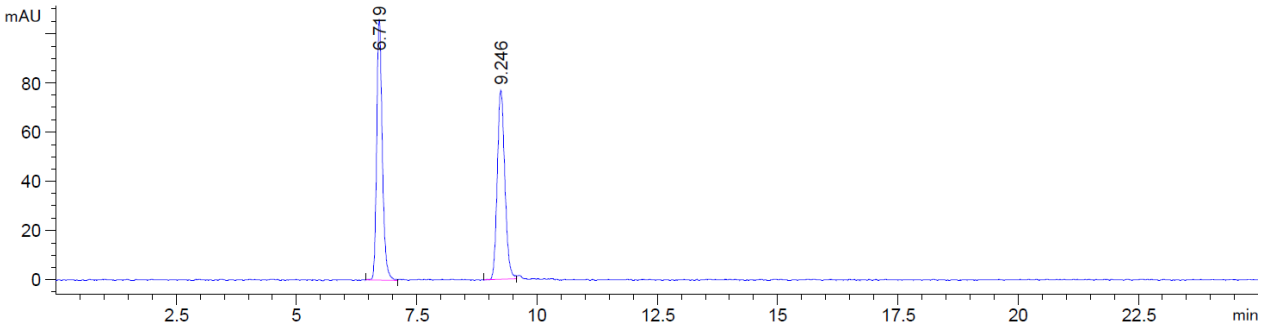
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.422	BV	0.2072	1.63134e4	1275.70947	45.7711
2	11.730	BB	0.2884	1.93279e4	1071.84656	54.2289

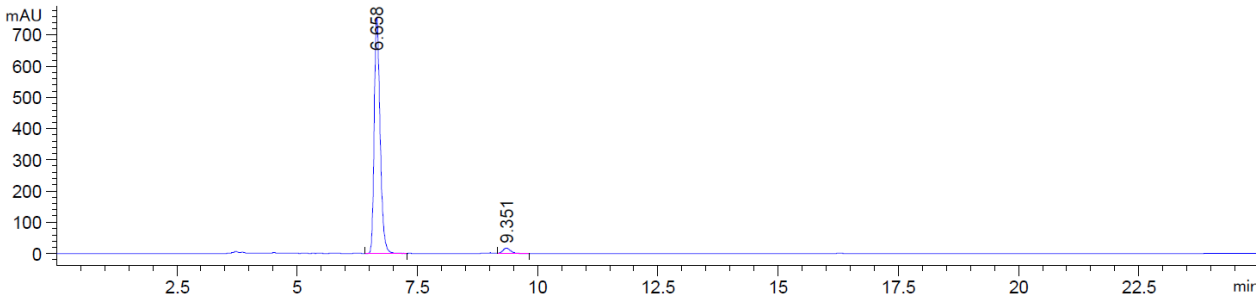
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.489	BV	0.1653	7778.25195	735.77301	95.8551
2	12.002	BB	0.2174	336.34171	23.71722	4.1449

***tert*-butyl (1*S*,2*S*)-2-benzoylcyclopropane-1-carboxylate 4ae:**



Obtained as a colorless oil in 85 % yield. All spectroscopic data were in agreement with those reported previously in the literature.[9] **R_f:** 0.88 (Pentane: EtOAc, 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 3.12 (ddd, *J* = 8.6, 5.7, 3.8 Hz, 1H), 2.31 (ddd, *J* = 8.6, 5.7, 3.8 Hz, 1H), 1.60 – 1.50 (m, 2H), 1.47 (s,9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.5, 171.6, 137.3, 133.4, 128.8, 128.4, 81.4, 28.2, 26.0, 25.9, 18.0; **$[\alpha]_D^{20}$**= 160.7 (c = 1.0, $CHCl_3$); **Chiral HPLC:** (Chiralpak IC; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 9.3 min, t_R (major) = 6.7 min, 97:3 er.).

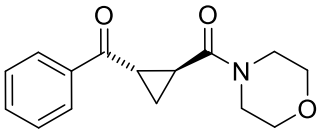




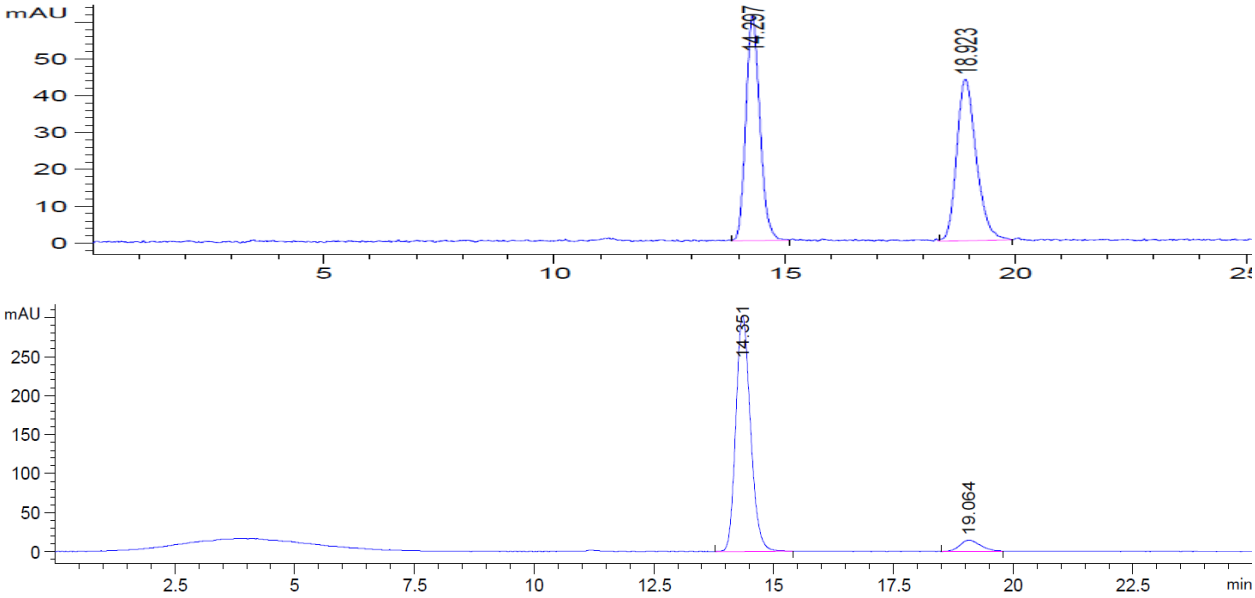
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.719	BV	0.1222	857.39441	106.24300	50.3225
2	9.246	BV	0.1704	846.40399	76.91145	49.6775

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.658	BB	0.1310	6420.25635	756.64691	96.9352
2	9.351	VB	0.1808	202.99185	17.57105	3.0648

((1*S*,2*S*)-2-benzoylcyclopropyl)(morpholino)methanone 4af:



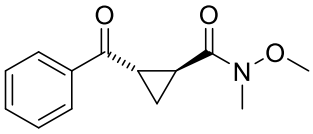
Obtained as a white solid in 63 % yield. All spectroscopic data were in agreement with those reported previously in the literature.[10] **Rf:** 0.5 (EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 – 8.00 (m, 2H), 7.65 – 7.55 (m, 1H), 7.49 (ddd, *J* = 8.1, 6.7, 1.3 Hz, 2H), 3.70 (s, 8H), 3.28 (ddd, *J* = 8.7, 5.5, 3.9 Hz, 1H), 2.55 (ddd, *J* = 8.7, 5.9, 3.9 Hz, 1H), 1.64 (ddd, *J* = 8.7, 5.9, 3.1 Hz, 1H), 1.57 (ddd, *J* = 8.7, 5.9, 3.1 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.3, 169.5, 137.1, 133.6, 128.8, 128.5, 66.9, 46.2, 42.8, 25.9, 23.1, 18.4; **IR (ATR, cm^{-1}):** ν_{max} 2973, 2856, 1670, 1637, 1448, 1388, 1222, 1068, 703; **HRMS (ESI)** calc'd. for $[M+H]^+$ = $[C15H18NO3]^+$: 260.1287, found: 260.1181; ; **m.p.:** 142 °C; **$[\alpha]_D^{20}$**= 129.2 (c = 1.0, $CHCl_3$); **Chiral HPLC:** (Chiralpak IC; hexane:*i*-PrOH 70:30, 1.0 mL/min, 254 nm; t_R (minor) = 19.1 min, t_R (major) = 14.3 min, 93.5:6.5er.)



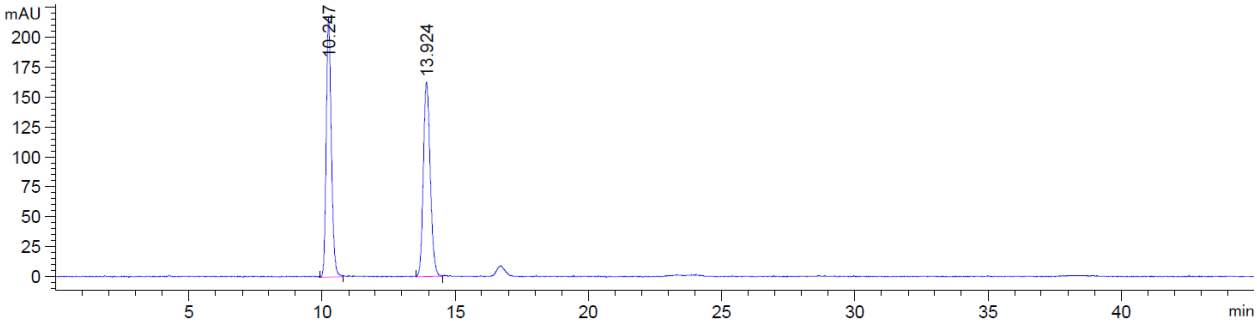
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.297	BB	0.3228	1288.94336	60.94218	49.8885
2	18.923	VB	0.4369	1294.70605	43.79892	50.1115

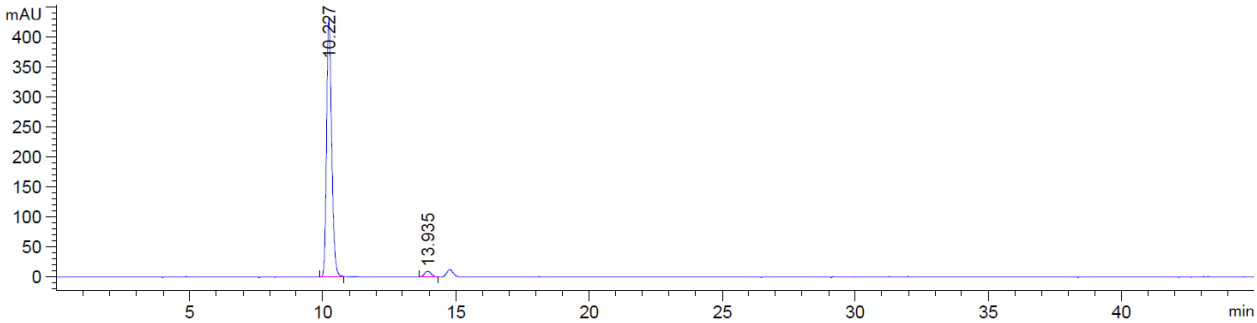
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.351	BB	0.3303	6427.68359	302.01569	93.4928
2	19.064	BV	0.3790	447.37286	14.61927	6.5072

(1*S*,2*S*)-2-benzoyl-*N*-methoxy-*N*-methylcyclopropane-1-carboxamide 4ag:



Obtained as a colorless oil 75 % yield. **Rf:** 0.29 (Pentane: EtOAc, 7:3); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 3.69 (s, 3H), 3.21 - 3.16 (m, 4H), 2.87 (br, 1H), 1.62 - 1.53 (d, *J* = 37.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.1, 171.9, 137.2, 133.5, 128.8, 128.5, 62.0, 32.7, 25.9, 22.5, 17.9; **IR (ATR, cm^{-1}):** $\tilde{\nu}$ 2937, 1654, 1449, 1394, 1372, 1223, 1176, 1013, 991, 703; **HRMS (ESI)** calc'd. for $[M+H]^+$ = $[C13H16NO3]^+$: 234.1125, found: 234.115; **$[\alpha]_D^{20}$**= 136.7 (c = 1.0, $CHCl_3$); **Chiral HPLC:** (Chiralpak IC; hexane:*i*-PrOH 80:20, 1.0 mL/min, 254 nm; t_R (minor) = 14.0 min, t_R (major) = 10.2 min, 97:3 er.).

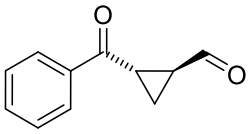




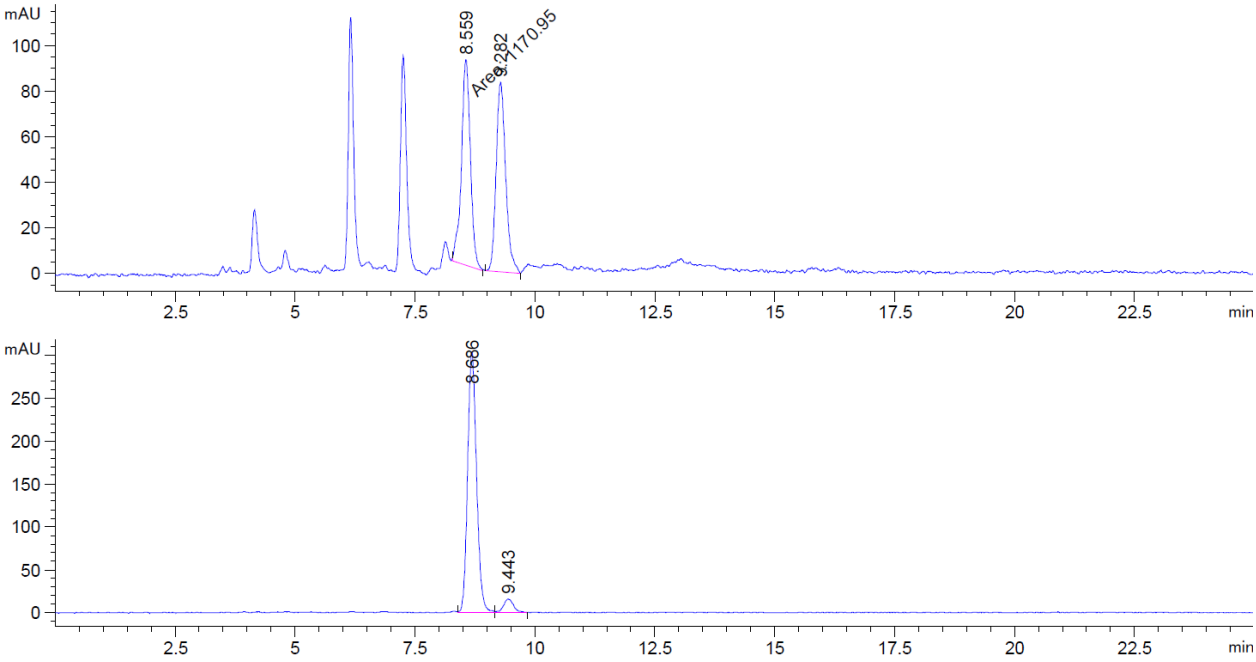
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.247	BV	0.2038	2898.03027	216.99194	49.9151
2	13.924	BB	0.2715	2907.89429	161.90630	50.0849

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.227	BV	0.2055	5756.75049	432.02039	97.1009
2	13.935	BB	0.2218	171.87520	9.55851	2.8991

(1*S*,2*S*)-2-benzoylcyclopropane-1-carbaldehyde 4ah:



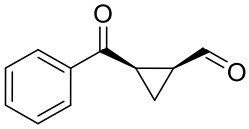
Obtained as a colorless oil in 49 % yield. All spectroscopic data were in agreement with those reported previously in the literature.[9] *er* was measured upon reduction of aldehyde to alcohol by $NaBH_4$ in MeOH. **Rf:** 0.42 (Pentane: EtOAc, 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.55 (d, *J* = 3.6 Hz, 1H), 8.06 – 7.95 (m, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 3.31 (ddd, *J* = 8.7, 5.9, 3.8 Hz, 1H), 2.67 (ddt, *J* = 7.4, 5.7, 3.7 Hz, 1H), 1.80 (ddd, *J* = 8.6, 5.9, 3.7 Hz, 1H), 1.73 – 1.62 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.9, 196.3, 137.0, 133.7, 128.9, 128.4, 33.0, 26.2, 17.8; **$[\alpha]_D^{20}$**= 220.4 (c = 0.39, $CHCl_3$); **Chiral HPLC:** (Chiralpak IC; hexane:*i*-PrOH 70:30, 1.0 mL/min, 254 nm; t_R (minor) = 9.4 min, t_R (major) = 8.7 min, 94.5:5.5 er.).



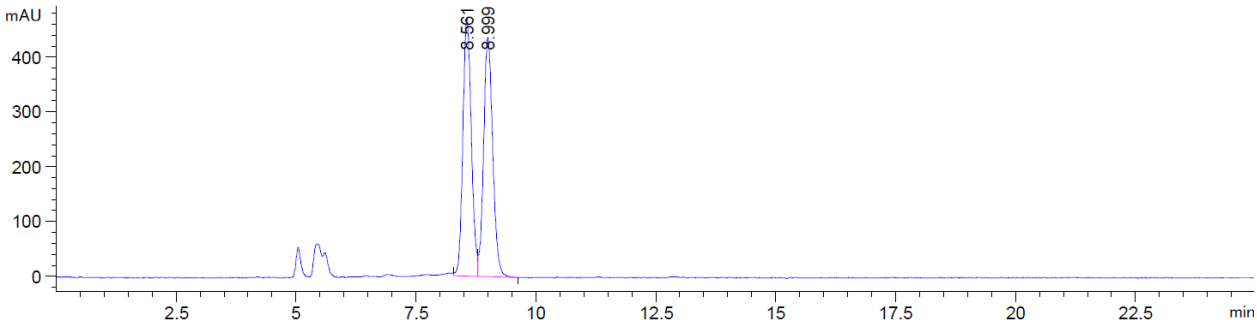
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.559	MM	0.2164	1170.95459	90.20403	50.4261
2	9.282	BB	0.2074	1151.16760	83.22108	49.5739

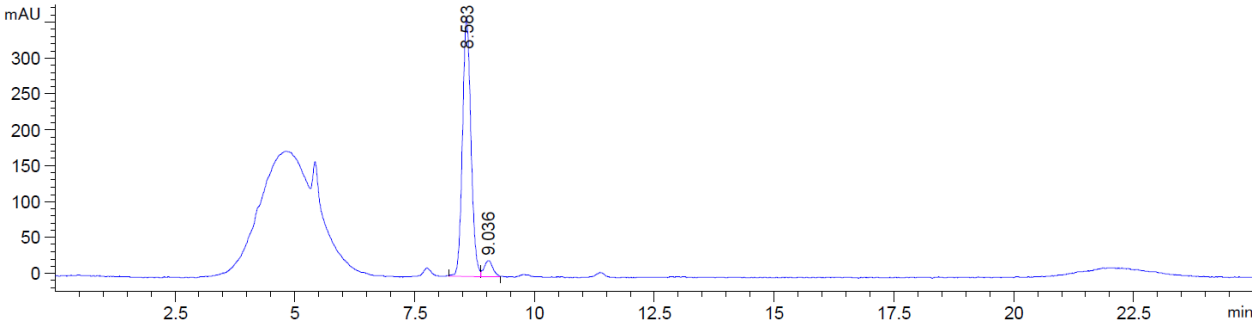
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.686	VV	0.2017	3949.10156	303.70782	94.4229
2	9.443	VB	0.1993	233.25214	15.70330	5.5771

(1*S*,2*R*)-2-benzoylcyclopropane-1-carbaldehyde 4ah':



Obtained as a colorless oil in 30 % yield. *er* was measured upon reduction of aldehyde to alcohol by $NaBH_4$ in MeOH. **Rf:** 0.27 (Pentane: EtOAc, 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.27 (d, *J* = 6.5 Hz, 1H), 8.00 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 3.27 – 3.13 (m, 1H), 2.29 (tt, *J* = 8.4, 6.5 Hz, 1H), 2.21 (td, *J* = 6.6, 4.8 Hz, 1H), 1.67 (td, *J* = 8.0, 4.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.8, 196.1, 137.1, 133.8, 128.9, 128.5, 32.5, 27.3, 14.1; **IR (ATR, cm^{-1}):** $\tilde{\nu}$ 1702, 1671, 1596, 1450, 1386, 1228, 1176, 988, 706; **HRMS (QTOF) m/z:** $[M + H]^+$ Calcd for $C_{11}H_{11}O_2^+$ 175.0754; Found 175.0754; **$[\alpha]_D^{20}$**= 56.5 (c = 0.31, $CHCl_3$); **Chiral HPLC:** (Chiralpak IA; hexane:*i*-PrOH 90:10, 1.0 mL/min, 254 nm; t_R (minor) = 9.0 min, t_R (major) = 8.6 min, 94:6 er.)

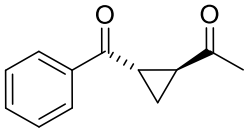




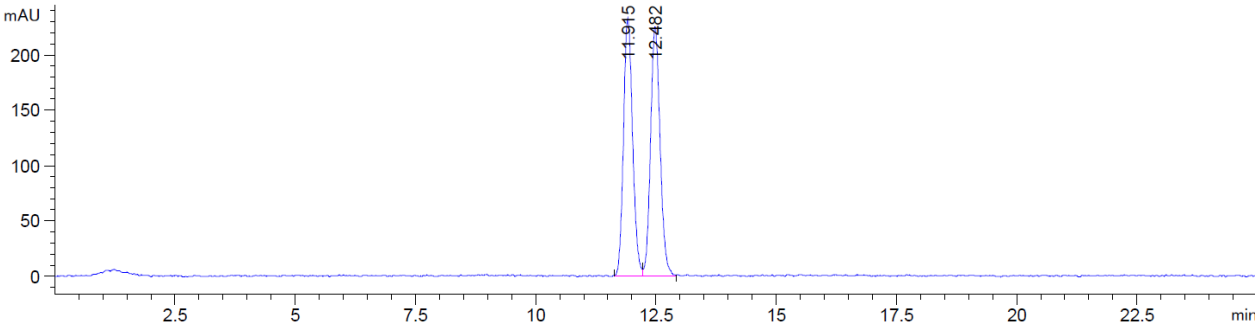
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.561	VV	0.1931	5766.48242	470.21170	49.8672
2	8.999	VB	0.2049	5797.20605	436.68414	50.1328

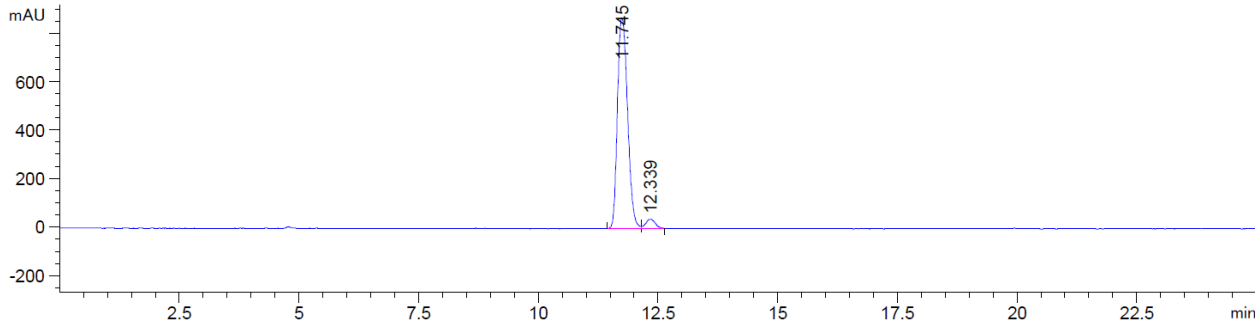
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.583	VV	0.1877	4451.32227	361.40985	93.8539
2	9.036	VV	0.1931	291.49725	22.51137	6.1461

1-((1*S*,2*S*)-2-benzoylcyclopropyl)ethan-1-one 4ai:



Obtained as a colorless oil 60 % yield. **Rf:** 0.60 (Pentane: EtOAc, 8:2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.1 Hz, 2H), 7.64 – 7.54 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 3.23 (ddd, *J* = 8.6, 5.8, 3.8 Hz, 1H), 2.74 – 2.63 (m, 1H), 2.34 (s, 3H), 1.61 (m, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.2, 197.4, 137.1, 133.6, 128.8, 128.4, 32.1, 31.2, 28.1, 20.0; **IR (ATR, cm^{-1}):** $\tilde{\nu}$ 1703, 1668, 1357, 1331, 1222, 1170, 995, 701; **HRMS (APPI/LTQ-Orbitrap) m/z:** $[M + H]^+$ Calcd for $C_{12}H_{13}O_2^+$ 189.0910; Found 189.0907; **$[\alpha]_D^{20}$**= 310.7 (c = 0.67, $CHCl_3$); **Chiral HPLC:** (Chiralpak IC; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 12.3 min, t_R (major) = 11.7 min, 96:4 er.)

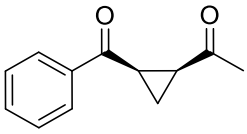




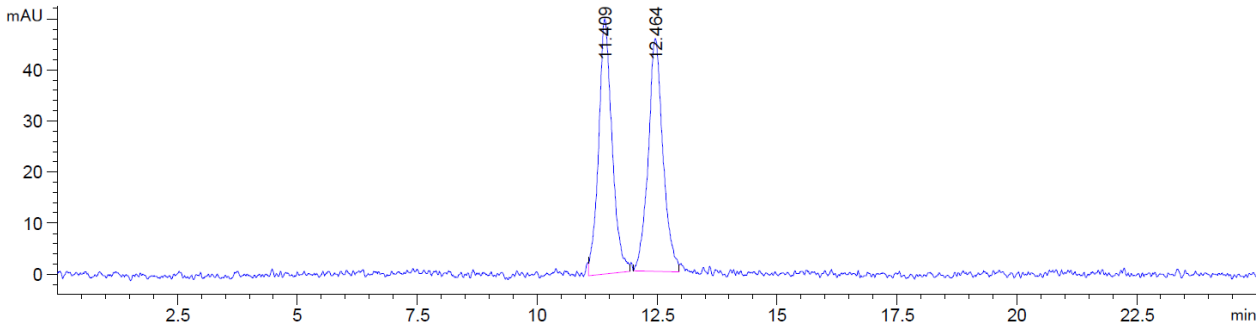
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.915	BV	0.2058	3065.06592	232.46843	49.6418
2	12.482	VV	0.2134	3109.29712	224.78831	50.3582

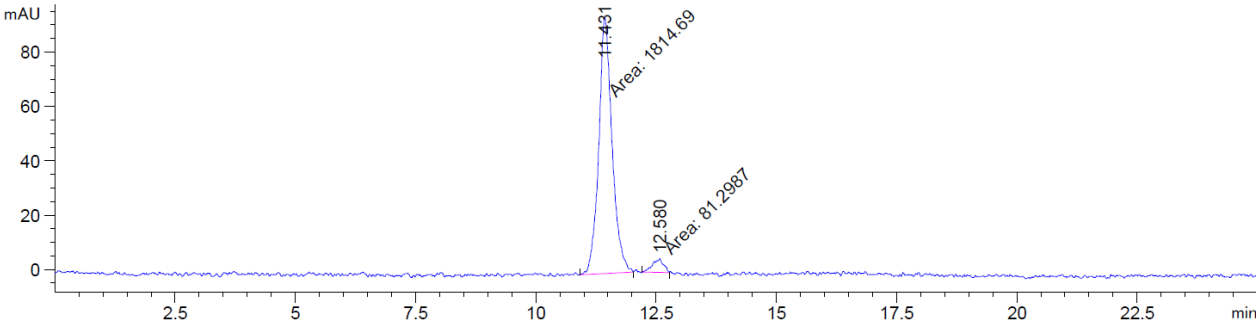
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.745	BV	0.2355	1.27865e4	869.72528	95.8231
2	12.339	VV	0.2105	557.35730	40.01844	4.1769

1-((1*S*,2*R*)-2-benzoylcyclopropyl)ethan-1-one 4ai':



Obtained as a colorless oil in 30 % yield. **Rf:** 0.20 (Pentane: EtOAc, 8:2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (m, 2H), 7.60 – 7.53 (m, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 2.91 (ddd, *J* = 9.2, 8.3, 6.8 Hz, 1H), 2.49 (ddd, *J* = 9.2, 8.1, 6.7 Hz, 1H), 2.20 (s, 3H), 1.96 (td, *J* = 6.7, 4.6 Hz, 1H), 1.39 (td, *J* = 8.2, 4.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.2, 195.3, 137.3, 133.4, 128.7, 128.4, 31.3, 30.7, 28.1, 13.3; **IR (ATR, cm^{-1}):** $\tilde{\nu}$ 1703, 1676, 1450, 1388, 1226, 1169, 1000, 698; **HRMS (APPI/LTQ-Orbitrap) m/z:** $[M + H]^+$ Calcd for $C_{12}H_{13}O_2^+$ 189.0910; Found 189.0905; **$[\alpha]_D^{20}$**= -40.9 (c = 0.33, $CHCl_3$); **Chiral HPLC:** (Chiralpak IA; hexane:*i*-PrOH 90:10, 1.0 mL/min, 254 nm; t_R (minor) = 12.6 min, t_R (major) = 11.4 min, 96:4 er.).

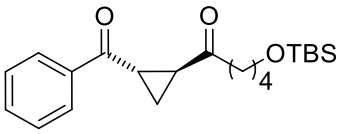




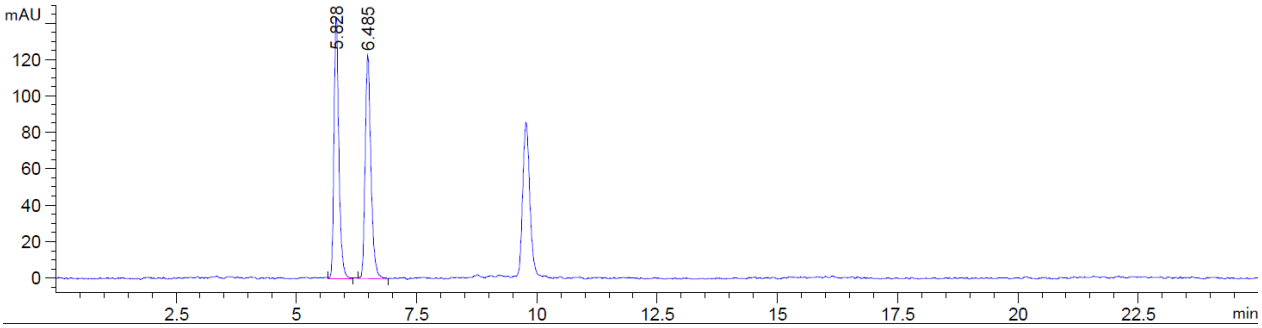
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.409	VV	0.2735	973.62109	49.93045	49.9523
2	12.464	BV	0.2934	975.48138	45.62514	50.0477

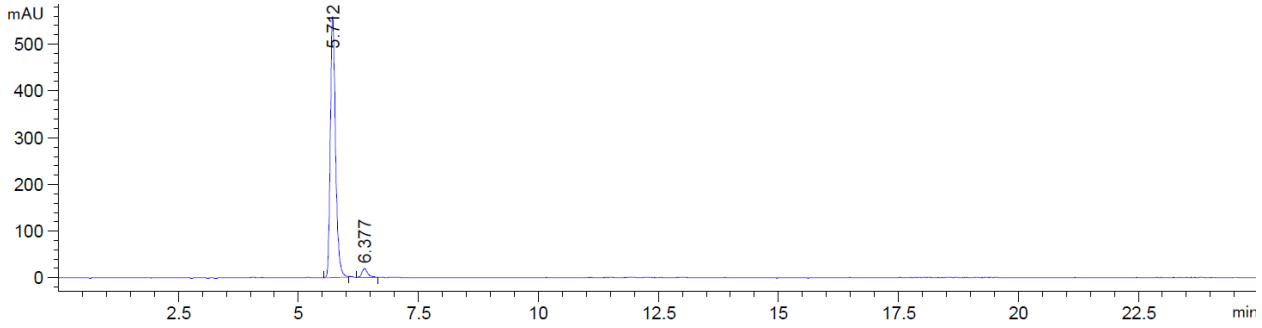
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.431	MM	0.3208	1814.69287	94.27563	95.7121
2	12.580	MM	0.2634	81.29866	5.14390	4.2879

1-((1*S*,2*S*)-2-benzoylcyclopropyl)-5-((*tert*-butyldimethylsilyl)oxy)pentan-1-one 4aj:



Obtained as a colorless oil 68 % yield. **Rf:** 0.73 (Pentane: EtOAc, 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 3.61 (t, *J* = 6.3 Hz, 2H), 3.24 - 3.19 (m, 1H), 2.72 - 2.59 (m, 3H), 1.72 - 1.49 (m, 6H), 0.87 (s, 9H), 0.03 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.3, 197.5, 137.1, 133.5, 128.8, 128.4, 62.9, 44.0, 32.3, 31.6, 27.9, 26.1, 20.4, 19.8, 18.5, -5.2; **IR (ATR, cm^{-1}):** $\tilde{\nu}$ 2953, 2929, 2857, 1705, 1672, 1450, 1360, 1337, 1254, 1222, 1100, 1003, 836, 776, 704; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{21}H_{32}NaO_3Si^+$ 383.2013; Found 383.2016; **$[\alpha]_D^{20}$**= 176.0 (c = 1.0, $CHCl_3$); **Chiral HPLC:** (Chiralpak IC; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 6.8 min, t_R (major) = 5.7 min, 96.5:3.5 er.)

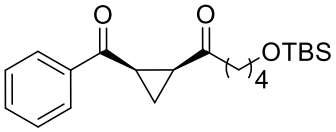




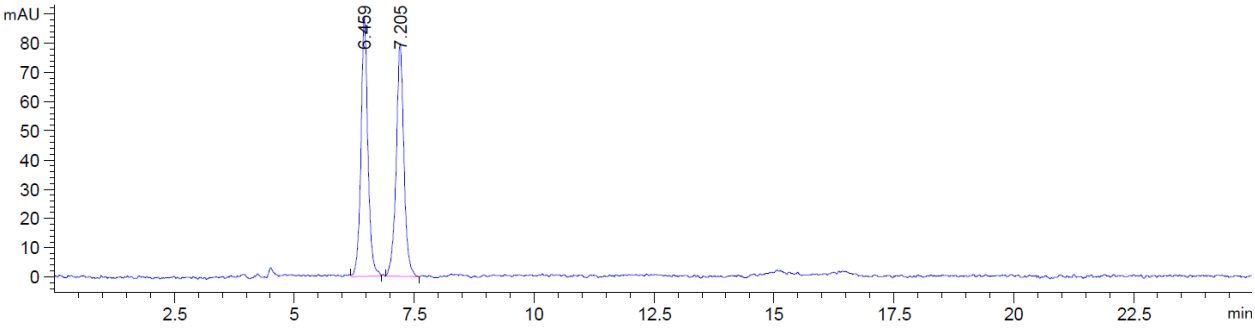
#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.828	VV	0.1057	1004.45374	143.46126	49.5105
2	6.485	VB	0.1275	1024.31726	122.50668	50.4895

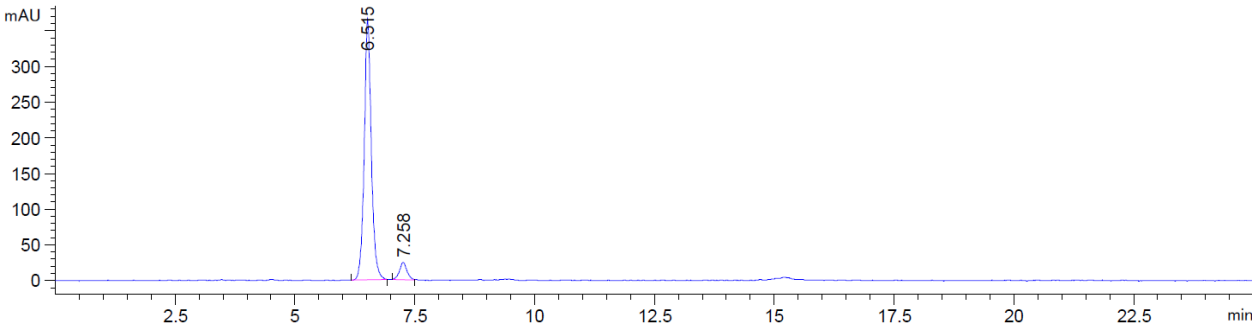
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.712	BV	0.1163	4227.96875	558.31421	96.5047
2	6.377	VB	0.1276	153.13438	18.67907	3.4953

1-((1*S*,2*R*)-2-benzoylcyclopropyl)-5-((*tert*-butyldimethylsilyl)oxy)pentan-1-one 4aj':



Obtained as a colorless oil in 27 % yield. **Rf:** 0.27 (Pentane: EtOAc, 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 3.59 – 3.45 (m, 2H), 2.86 (td, *J* = 8.4, 6.8 Hz, 1H), 2.60 - 2.43 (m, 3H), 1.94 (td, *J* = 6.7, 4.5 Hz, 1H), 1.57 - 1.52 (m, 2H), 1.43 - 1.34 (m, 3H), 0.87 (s, 9H), 0.01 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.1, 195.1, 137.4, 133.3, 128.7, 128.4, 62.9, 43.4, 32.2, 30.3, 28.0, 26.1, 20.2, 18.5, 13.0, -5.2; **IR (ATR, cm^{-1}):** $\tilde{\nu}$ 2952, 2929, 2857, 1704, 1679, 1450, 1389, 1254, 1225, 1100, 1003, 836, 776; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{21}H_{32}NaO_3Si^+$ 383.2013; Found 383.2025; **$[\alpha]_D^{20}$**= -23.2 (c = 0.46, $CHCl_3$); **Chiral HPLC:** (Chiralpak IA; hexane:*i*-PrOH 90:10, 1.0 mL/min, 254 nm; t_R (minor) = 7.2 min, t_R (major) = 6.5 min, 93:7 er.).

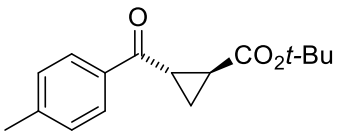




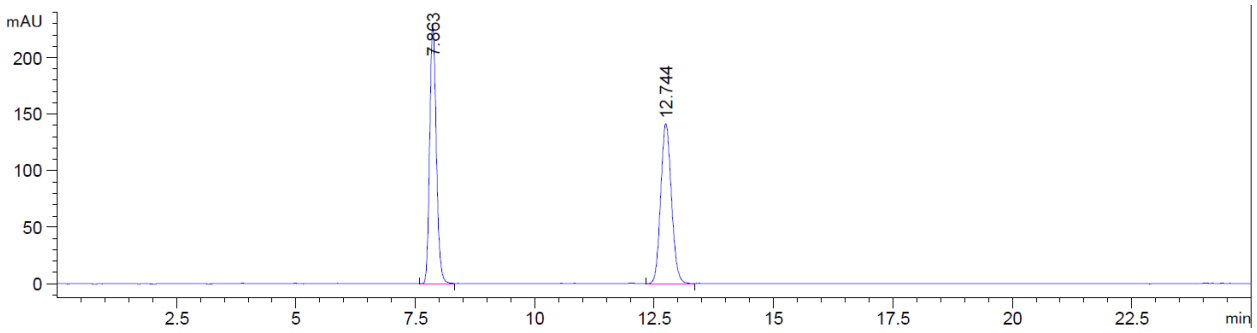
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.459	VV	0.1475	892.41779	88.61878	49.8903
2	7.205	BB	0.1670	896.34076	79.83986	50.1097

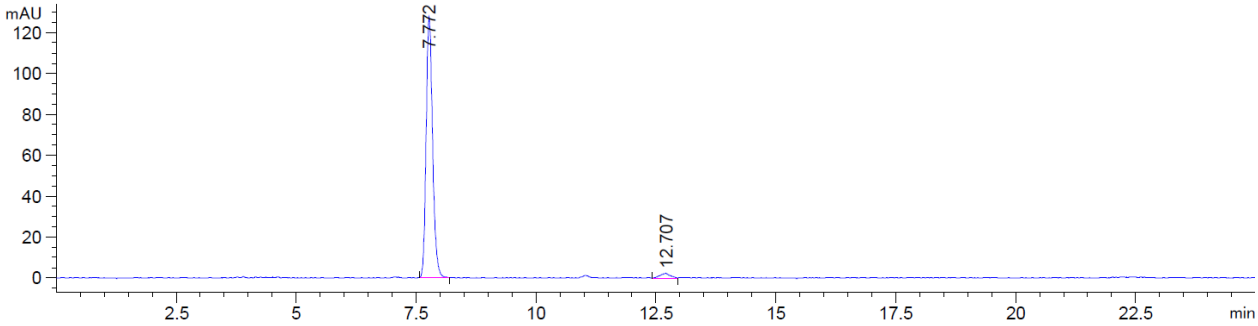
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.515	BB	0.1519	3762.48877	366.02954	93.3455
2	7.258	BV	0.1612	268.22464	24.60191	6.6545

***tert*-butyl (1*S*,2*S*)-2-(4-methylbenzoyl)cyclopropane-1-carboxylate 4be:**



Obtained as a white solid in 85 % yield. All spectroscopic data were in agreement with those reported previously in the literature.[11] **Rf:** 0.57 (Pentane: EtOAc, 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 3.09 (ddd, *J* = 8.7, 5.7, 3.9 Hz, 1H), 2.43 (s, 3H), 2.28 (ddd, *J* = 8.7, 5.7, 3.9 Hz, 1H), 1.57-1.48 (m, 2H), 1.47 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.0, 171.7, 144.3, 134.8, 129.5, 128.5, 81.4, 28.2, 25.8, 25.8, 21.8, 17.8; **$[\alpha]_D^{20}$**= 155.5 (c = 1.0, $CHCl_3$); **Chiral HPLC:** (Chiralpak IC; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 12.7 min, t_R (major) = 7.8 min, 97 : 3 er.).

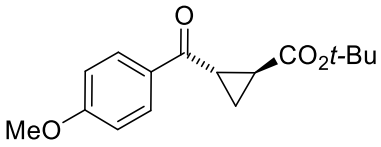




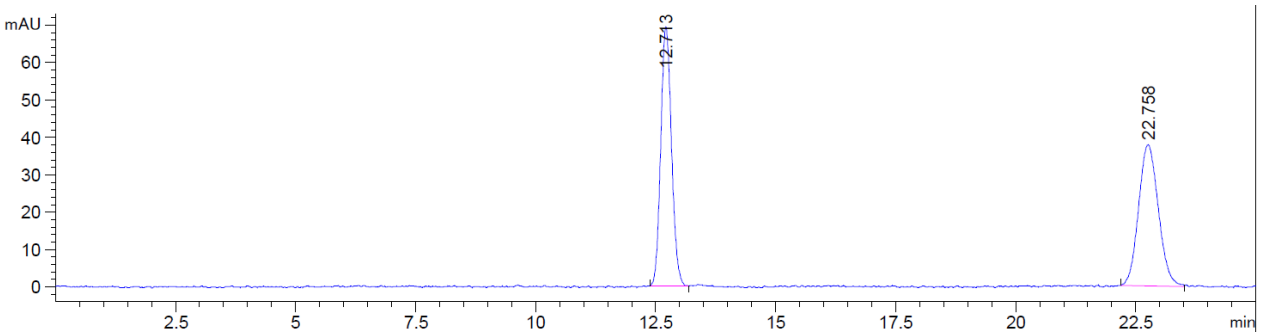
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.863	VB	0.1485	2210.44629	229.26483	49.9291
2	12.744	BB	0.2427	2216.72827	141.54912	50.0709

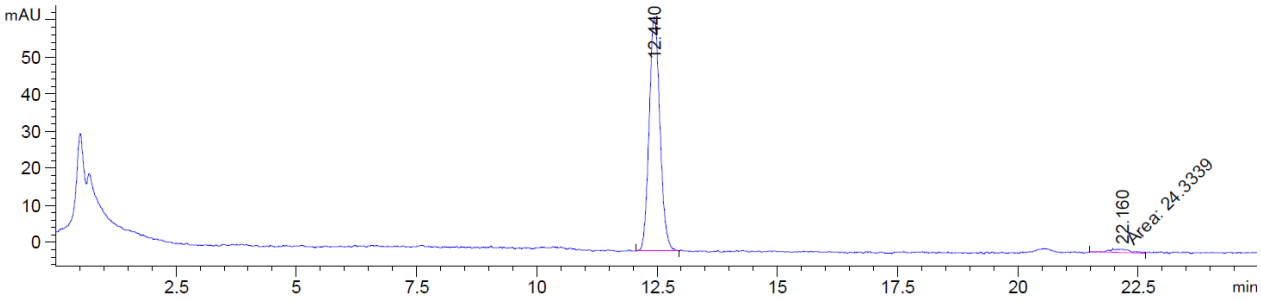
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.772	BV	0.1435	1198.18103	127.61766	97.3137
2	12.707	BB	0.1789	33.07463	2.31140	2.6863

***tert*-butyl (1*S*,2*S*)-2-(4-methoxybenzoyl)cyclopropane-1-carboxylate 4ce:**



Obtained as a white solid in 90 % yield. All spectroscopic data were in agreement with those reported previously in the literature.[11] **Rf:** 0.54 (Pentane: EtOAc, 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H), 3.07 (ddd, *J* = 8.7, 5.8, 3.9 Hz, 1H), 2.27 (ddd, *J* = 8.7, 5.8, 3.9 Hz, 1H), 1.56-1.48 (m, 2H), 1.47 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.8, 171.8, 163.8, 130.7, 130.4, 113.9, 81.3, 55.7, 28.2, 25.6, 17.7; **$[\alpha]_D^{20}$**= 136.7 (c = 1.0, $CHCl_3$); **Chiral HPLC:** (Chiralpak IC; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 22.2 min, t_R (major) = 12.4 min, 97.5 : 2.5 er.)

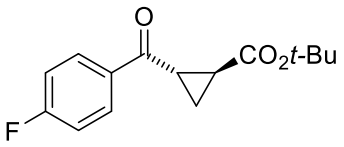




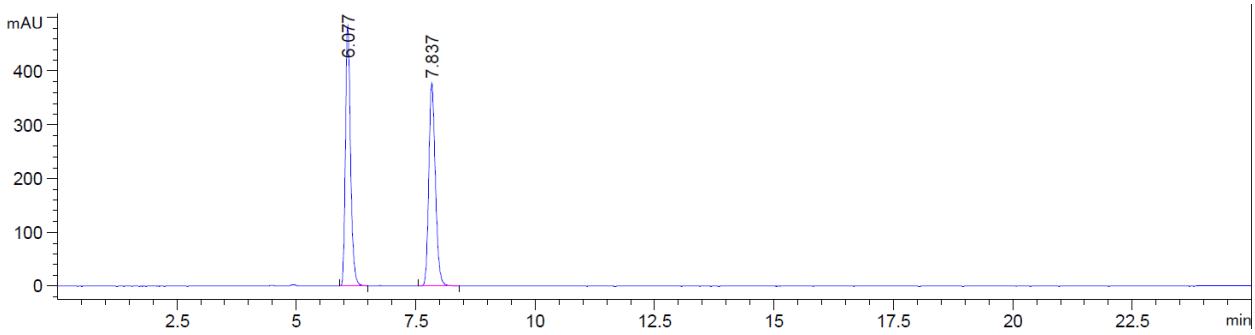
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.713	BB	0.2413	1076.41016	69.27698	49.8538
2	22.758	BV	0.4186	1082.72266	37.75511	50.1462

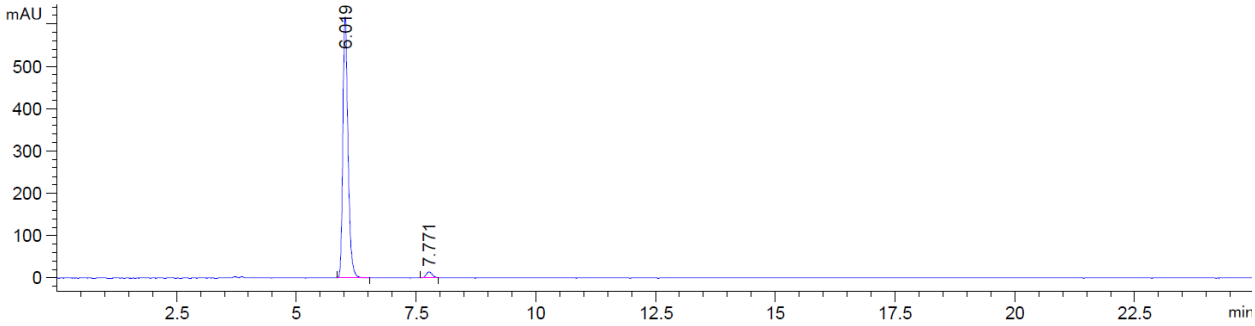
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.440	BV	0.2407	988.27277	63.12026	97.5969
2	22.160	MM	0.4497	24.33392	9.01837e-1	2.4031

***tert*-butyl (1*S*,2*S*)-2-(4-fluorobenzoyl)cyclopropane-1-carboxylate 4de:**



Obtained as a colorless oil in 81 % yield. **Rf :** 0.85 (Pentane: EtOAc, 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2H), 7.21 – 7.11 (m, 2H), 3.06 (ddd, *J* = 8.7, 5.7, 3.9 Hz, 1H), 2.30 (ddd, *J* = 8.7, 6.0, 3.9 Hz, 1H), 1.59 – 1.50 (m, 1H), 1.47 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.9, 171.5, 166.1 (d, *J* = 256.1 Hz), 133.7 (d, *J* = 2.9 Hz), 131.1 (d, *J* = 9.5 Hz), 115.9 (d, *J* = 22.0 Hz), 81.5, 28.2, 25.9, 25.8, 18.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.9; **IR (ATR, cm^{-1}):** $\tilde{\nu}$ 2979, 2934, 1723, 1673, 1597, 1397, 1369, 1336, 1215, 1152, 1013, 847, 595; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{15}H_{17}FNaO_3^+$ 287.1054; Found 287.1057; **$[\alpha]_D^{20}$**= 143.3 (c = 1.0, $CHCl_3$); **Chiral HPLC:** (Chiralpak IC; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 7.8 min, t_R (major) = 6.1 min, 97:2 er.).

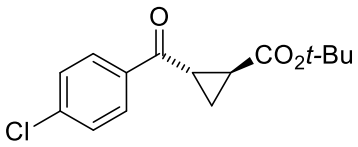




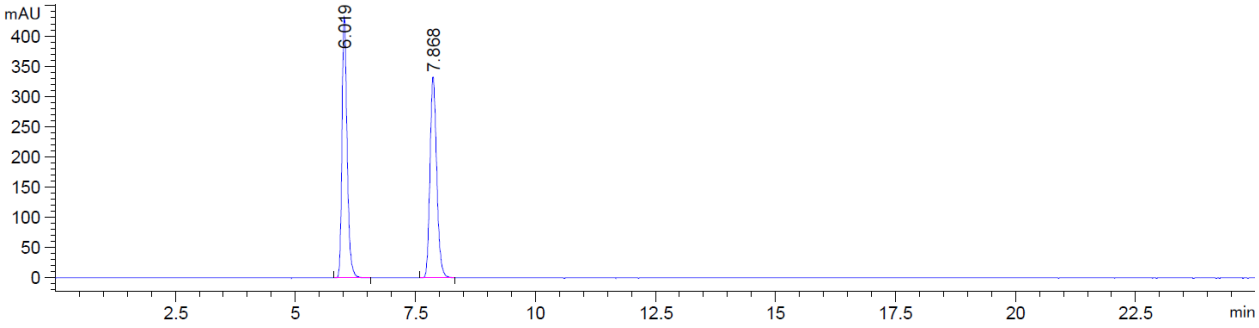
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.077	BV	0.1133	3613.45654	483.06952	49.9464
2	7.837	BB	0.1481	3621.21313	376.88516	50.0536

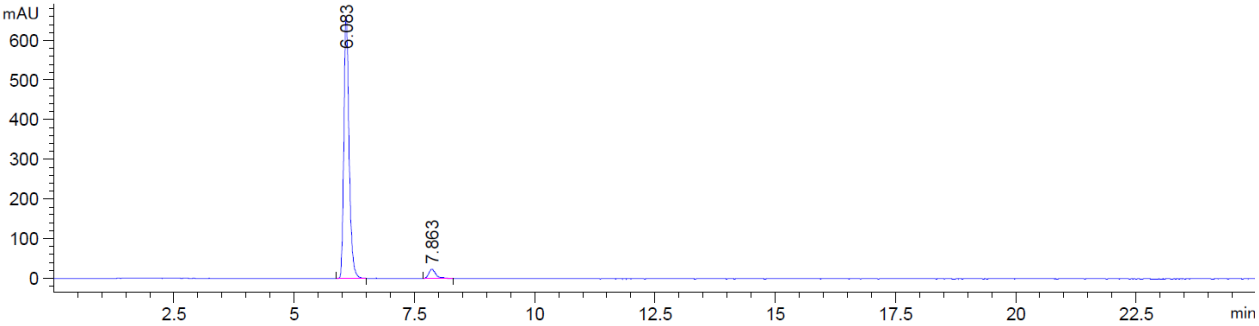
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.019	BB	0.1157	4640.17578	616.95508	97.2216
2	7.771	BV	0.1385	132.60632	14.53125	2.7784

***tert*-butyl (1*S*,2*S*)-2-(4-chlorobenzoyl)cyclopropane-1-carboxylate 4ee:**



Obtained as a white solid in 89 % yield after 40 hours. All spectroscopic data were in agreement with those reported previously in the literature.[11] **Rf:** 0.85 (Pentane: EtOAc, 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 – 7.88 (m, 2H), 7.54 – 7.39 (m, 2H), 3.05 (ddd, *J* = 8.6, 5.7, 3.9 Hz, 1H), 2.30 (ddd, *J* = 8.7, 6.0, 3.8 Hz, 1H), 1.58-1.51 (m 2H), 1.47 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.3, 171.4, 140.0, 135.6, 129.8, 129.1, 81.6, 28.2, 26.1, 25.8, 18.1; **m.p.:** 87 °C; **$[\alpha]_D^{20}$**= 132.2 (c = 1.0, $CHCl_3$); **Chiral HPLC:** (Chiralpak IC; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) 7.9 min, t_R (major) = 6.1min, 95:5 er.).

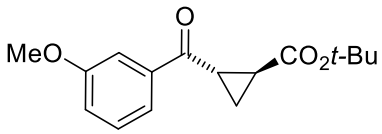




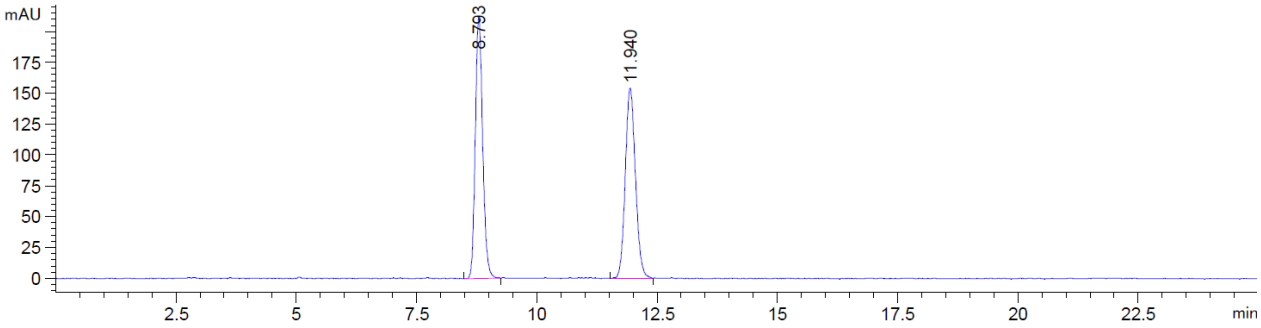
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.019	VB	0.1129	3221.86743	432.45953	49.9074
2	7.868	BV	0.1496	3233.82715	332.09854	50.0926

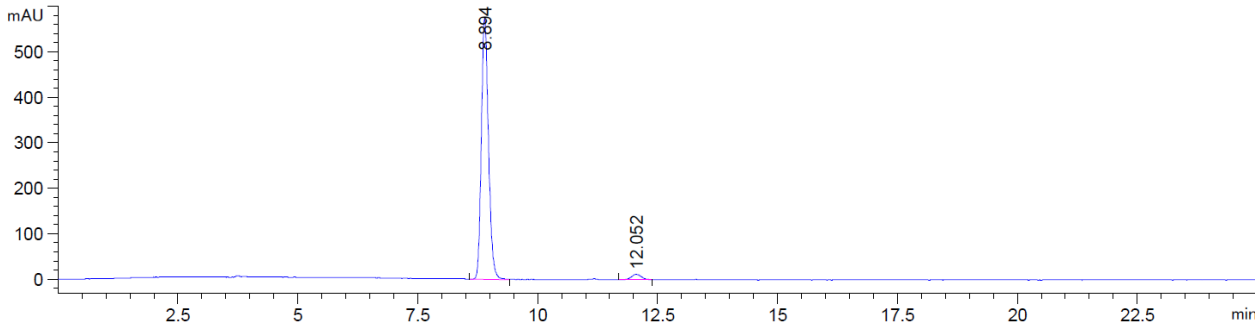
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.083	BV	0.1163	5010.05762	662.00177	95.1727
2	7.863	VV	0.1561	254.11627	24.28109	4.8273

***tert*-butyl (1*S*,2*S*)-2-(3-methoxybenzoyl)cyclopropane-1-carboxylate 4fe:**



Obtained as a colorless oil in 85 % yield. **Rf :** 0.73 (Pentane: EtOAc, 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.7 Hz, 1H), 7.57 – 7.47 (m, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.14 (ddd, *J* = 8.2, 2.6, 0.8 Hz, 1H), 3.86 (s, 3H), 3.09 (ddd, *J* = 8.7, 5.7, 3.9 Hz, 1H), 2.30 (ddd, *J* = 8.6, 5.9, 3.9 Hz, 1H), 1.58 - 1.51 (m, 2H), 1.47 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.3, 171.5, 160.0, 138.7, 129.8, 121.2, 120.0, 112.5, 81.4, 55.6, 28.2, 26.1, 26.0, 18.0; **IR (ATR, cm^{-1}):** $\tilde{\nu}$ 2978, 1722, 1673, 1597, 1582, 1368, 1333, 1261, 1215, 1151, 1023, 737; **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{16}H_{20}NaO_4^+$ 299.1254; Found 299.1262; **$[\alpha]_D^{20}$**= 152.2 (c = 1.0, $CHCl_3$); **Chiral HPLC:** (Chiralpak IC; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 12.1 min, t_R (major) = 8.9 min, 97:3 er.).

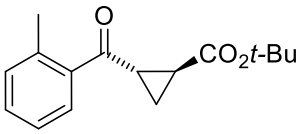




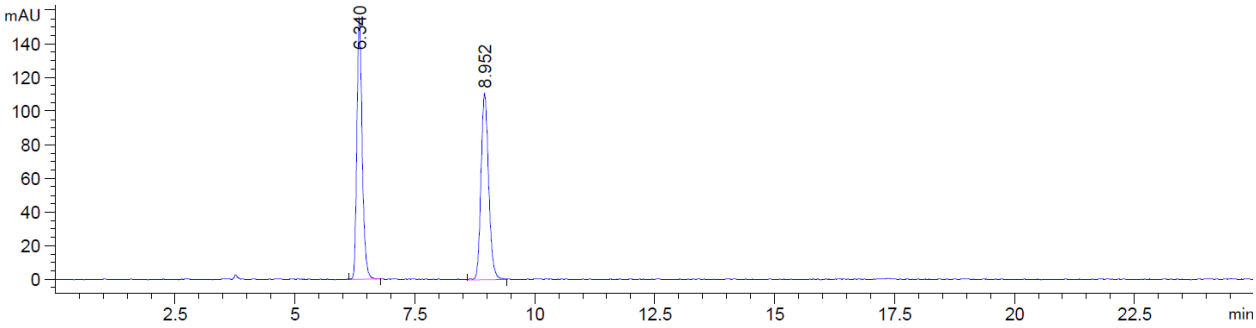
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.793	BV	0.1644	2258.33228	211.73732	49.9216
2	11.940	BV	0.2253	2265.42236	154.33229	50.0784

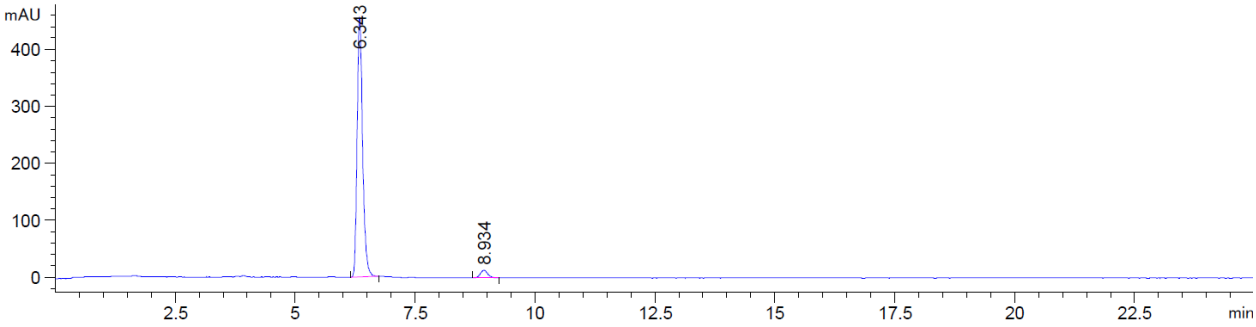
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.894	BV	0.1591	5958.15527	574.06329	97.0472
2	12.052	BV	0.2051	181.28375	11.94282	2.9528

***tert*-butyl (1*S*,2*S*)-2-(2-methylbenzoyl)cyclopropane-1-carboxylate 4ge:**



Obtained as a colorless oil in 73 % yield. All spectroscopic data were in agreement with those reported previously in the literature.[11] **Rf:** 0.81 (Pentane: EtOAc, 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 1H), 7.39 (td, *J* = 7.5, 1.3 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 6.3 Hz, 2H), 2.90 (ddd, *J* = 8.7, 5.7, 3.9 Hz, 1H), 2.50 (s, 3H), 2.29 (ddd, *J* = 8.7, 5.9, 3.9 Hz, 1H), 1.60-1.50 (m, 2H), 1.47 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$ δ 201.3, 171.4, 138.5, 137.8, 131.9, 131.6, 129.0, 125.9, 81.4, 29.1, 28.2, 26.3, 21.1, 18.1; **$[\alpha]_D^{20}$**= 163.7 (c = 1.0, $CHCl_3$); **Chiral HPLC:** (Chiralpak IC; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 8.9min, t_R (major) = 6.3 min, 96:4 er.).

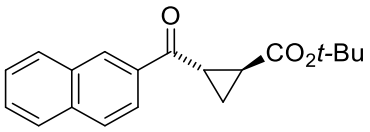




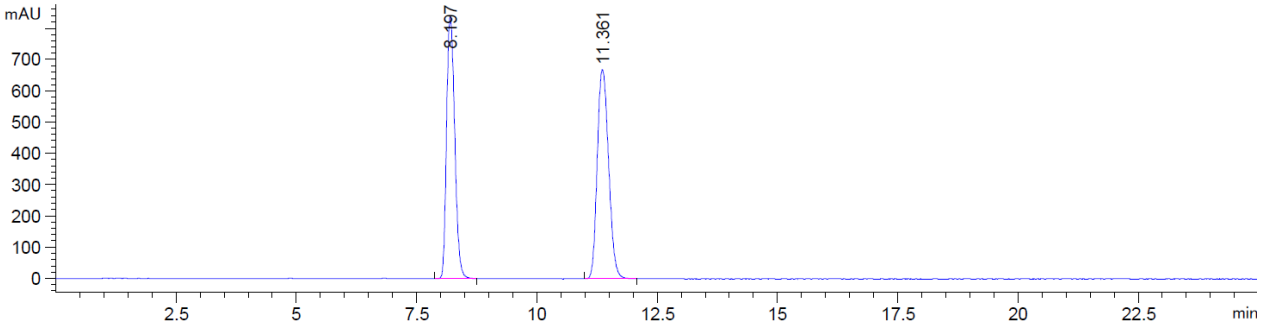
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.340	BB	0.1208	1206.90698	155.00461	49.6212
2	8.952	BV	0.1714	1225.33423	110.46253	50.3788

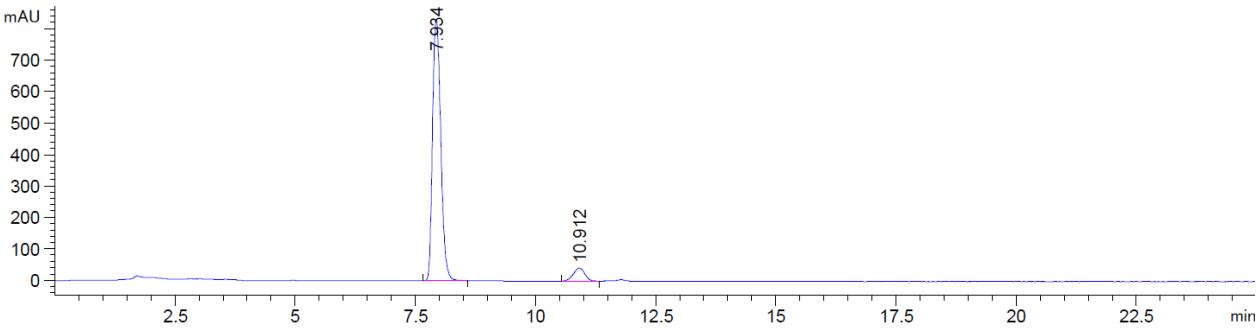
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.343	BB	0.1231	3633.08496	455.05917	96.0772
2	8.934	BB	0.1668	148.33574	13.64816	3.9228

***tert*-butyl (1*S*,2*S*)-2-(2-naphthoyl)cyclopropane-1-carboxylate 4he:**



Obtained as a white solid in 83 % yield after 56 hr. **Rf :** 0.70 (Pentane: EtOAc, 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.05 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.95 – 7.87 (m, 2H), 7.65 – 7.60 (m, 1H), 7.57 (td, *J* = 7.6, 7.0, 1.4 Hz, 1H), 3.32 – 3.25 (m, 1H), 2.38 (ddd, *J* = 8.7, 5.9, 3.9 Hz, 1H), 1.61 (m, 2H), 1.49 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.4, 171.7, 135.8, 134.6, 132.7, 130.4, 129.8, 128.8, 128.7, 127.9, 127.0, 124.0, 81.5, 28.3, 26.0, 26.0, 18.1; **IR (ATR, cm^{-1}):** $\tilde{\nu}$ 2978, 1722, 1668, 1467, 1394, 1368, 1329, 1153, 1125, 774; **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{19}H_{20}NaO_3^+$ 319.1305; Found 319.1304; **$[\alpha]_D^{20}$**= 72.7 (c = 1.0, $CHCl_3$); **m.p.:** 87 °C; **Chiral HPLC:** (Chiralpak IC; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 10.9 min, t_R (major) = 7.9 min, 96.5:3.5 er.).

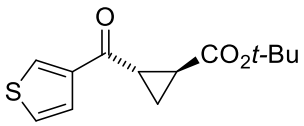




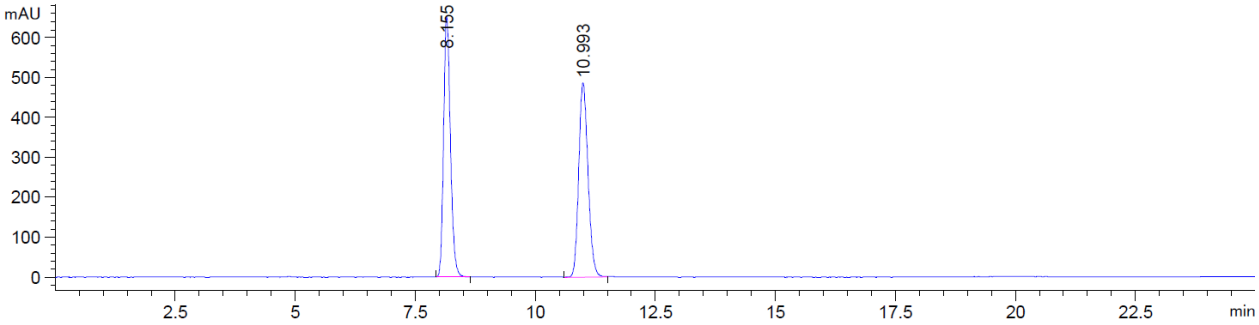
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.197	BV	0.1877	9884.07129	837.40527	47.3259
2	11.361	VV	0.2617	1.10010e4	669.35388	52.6741

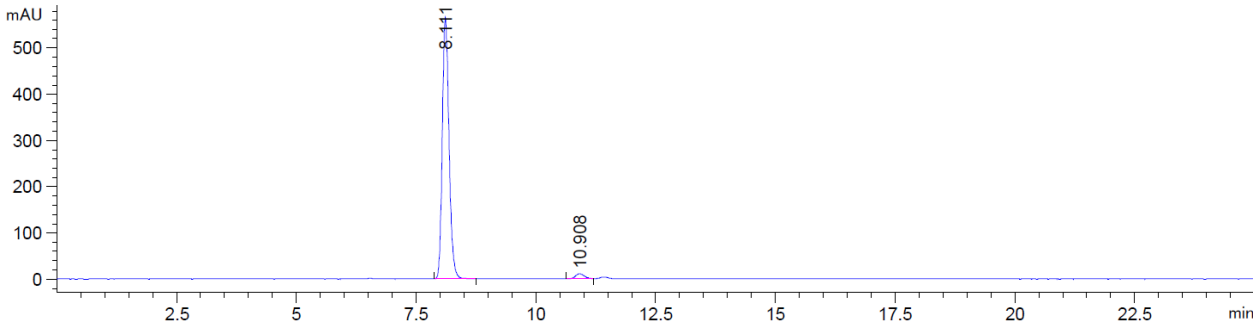
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.934	BB	0.1890	9900.57813	830.75073	93.4442
2	10.912	BB	0.2547	694.60229	42.05045	6.5558

***tert*-butyl (1*S*,2*S*)-2-(thiophene-3-carbonyl)cyclopropane-1-carboxylate 4ie:**



Obtained as a white solid in 69 % yield. **Rf :** 0.69 (Pentane: EtOAc, 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.59 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.35 (dd, *J* = 5.1, 2.9 Hz, 1H), 2.95 (ddd, *J* = 8.6, 5.7, 3.8 Hz, 1H), 2.28 (ddd, *J* = 8.7, 5.9, 3.8 Hz, 1H), 1.57 - 1.48 (m, 2H), 1.47 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.5, 171.6, 142.5, 132.7, 127.1, 126.7, 81.5, 28.2, 27.1, 25.7, 17.7; **IR (ATR, cm^{-1}):** $\tilde{\nu}$ 3105, 2978, 1720, 1663, 1511, 1415, 1385, 1367, 1326, 1233, 1215, 1153, 1023, 874, 841, 732; **HRMS (ESI/QTOF) m/z:** [M - O*t*-Bu]$^+$ Calcd for $C_9H_7O_2S^+$ 179.0161; Found 179.0171; **$[\alpha]_D^{20}$**= 148.3 (c = 1.0, $CHCl_3$); **m.p.:** 70 °C; **Chiral HPLC:** (Chiralpak IC; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 10.9 min, t_R (major) = 8.1 min, 97.5:2.5 er.).

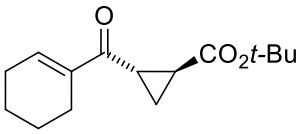




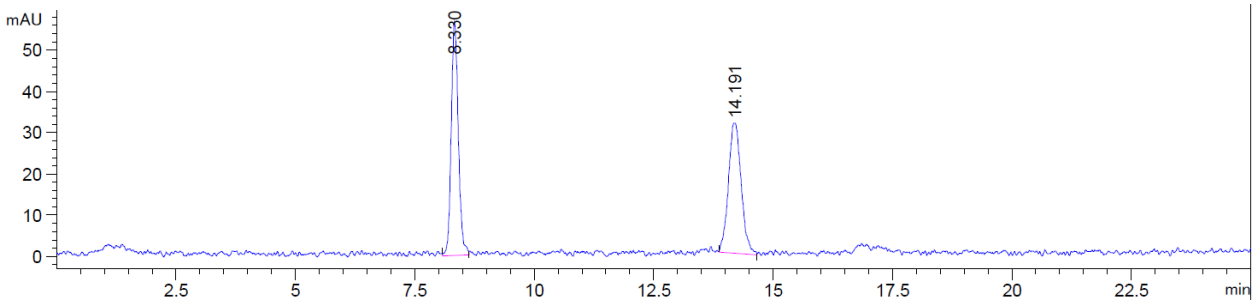
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.155	VB	0.1517	6466.68506	651.97577	49.6256
2	10.993	BV	0.2094	6564.25000	486.47342	50.3744

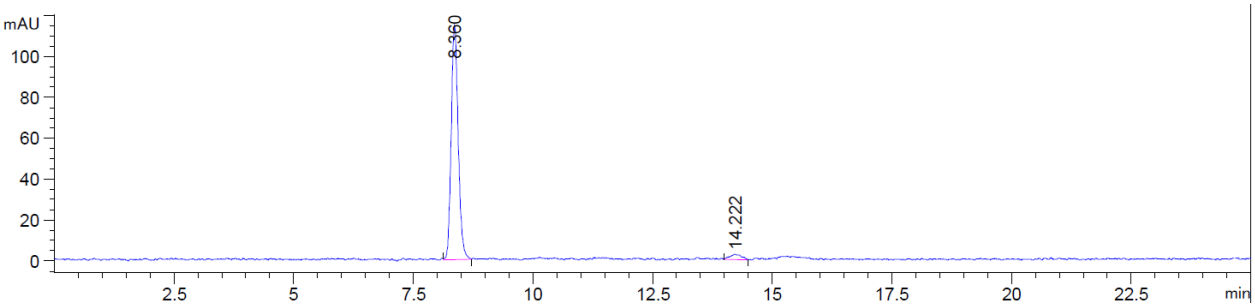
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.111	BV	0.1526	5541.05762	564.32837	97.5723
2	10.908	BB	0.1957	137.86838	10.74586	2.4277

***tert*-butyl (1*S*,2*S*)-2-(cyclohex-1-ene-1-carbonyl)cyclopropane-1-carboxylate 4je:**



Obtained as a white solid in 89 % yield. **Rf :** 0.57 (Pentane: EtOAc 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09 (m, 1H), 2.80 (ddd, *J* = 8.6, 5.8, 3.8 Hz, 1H), 2.32-2.22 (m, 4H), 2.11 (ddd, *J* = 8.6, 5.8, 3.8 Hz, 1H), 1.68-1.60 (m, 4H), 1.45 (s, 9H), 1.39-1.32 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.0, 141.3, 139.8, 81.1, 28.2, 26.4, 25.1, 24.5, 23.5, 22.0, 21.7, 17.3; **IR (ATR, cm^{-1}):** $\tilde{\nu}$ 2978, 2934, 1722, 1655, 1368, 0328, 1301, 1211, 1152, 1006, 850; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{15}H_{22}NaO_3^+$ 273.1461; Found 273.1470; **$[\alpha]_D^{20}$**= 148.8 (c = 1.0, $CHCl_3$); **m.p.:** 43°C; **Chiral HPLC:** (Chiralpak IC; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 14.2 min, t_R (major) = 8.3 min, 96:4 er.).

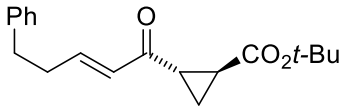




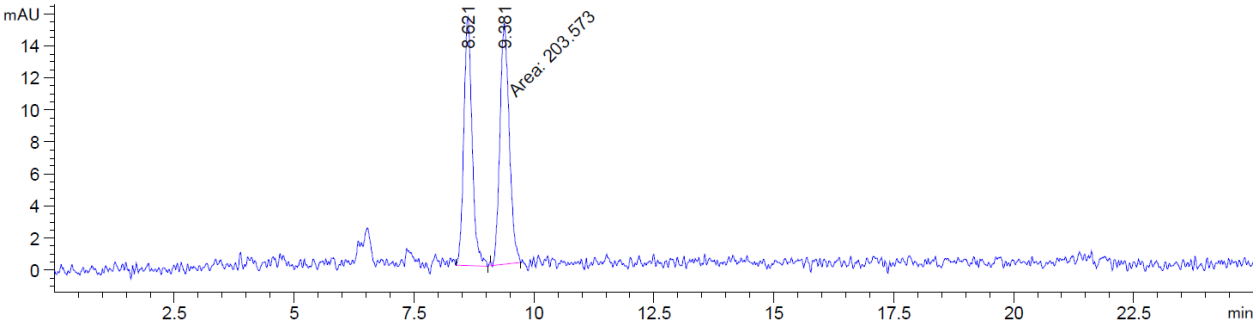
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.330	VV	0.1607	587.74585	56.80855	49.8653
2	14.191	VV	0.2357	590.92059	31.66677	50.1347

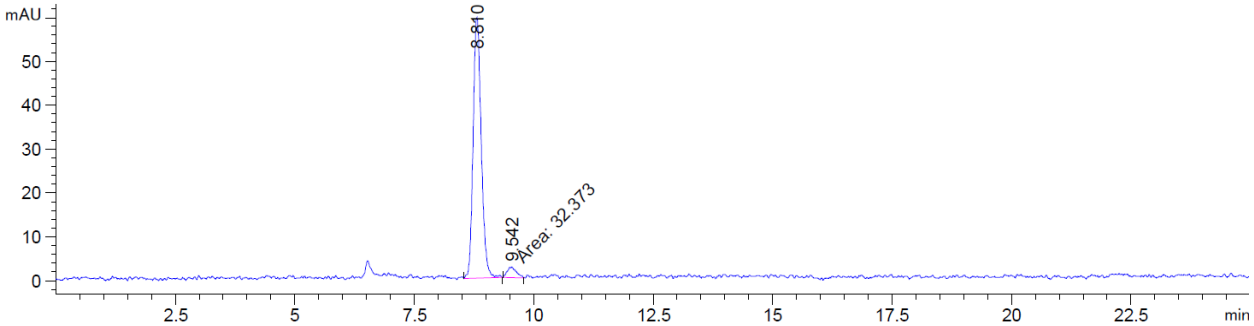
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.360	VV	0.1549	1166.70276	114.44882	96.1012
2	14.222	VB	0.2218	47.33260	2.63211	3.8988

***tert*-butyl (1*S*,2*S*)-2-((*E*)-5-phenylpent-2-enoyl)cyclopropane-1-carboxylate 4ke:**



Obtained as a colorless oil in 72 % yield. **Rf :** 0.73 (Pentane: EtOAc, 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.3 Hz, 2H), 7.24 – 7.15 (m, 3H), 6.97 (dt, *J* = 15.8, 6.8 Hz, 1H), 6.25 (dt, *J* = 15.8, 1.4 Hz, 1H), 2.85 – 2.77 (m, 2H), 2.63 – 2.50 (m, 3H), 2.13 (ddd, *J* = 8.6, 6.0, 3.8 Hz, 1H), 1.45 (s, 9H), 1.40 (ddd, *J* = 8.7, 5.7, 3.2 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.0, 171.6, 147.3, 140.8, 130.9, 128.7, 128.5, 126.4, 81.3, 34.5, 34.4, 28.2, 27.3, 25.5, 17.5; **IR (ATR, cm^{-1}):** $\tilde{\nu}$ 2978, 2932, 1720, 1684, 1661, 1625, 1368, 1337, 1214, 1150, 699; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{16}H_{17}NNaO_3^+$ 294.1101; Found 294.1106; **$[\alpha]_D^{20}$**= 112.2 (c = 0.89, $CHCl_3$); **Chiral HPLC:** (Chiralpak IG; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 9.5 min, t_R (major) = 8.8 min, 95.5:4.5 er.).

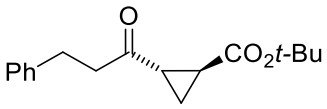




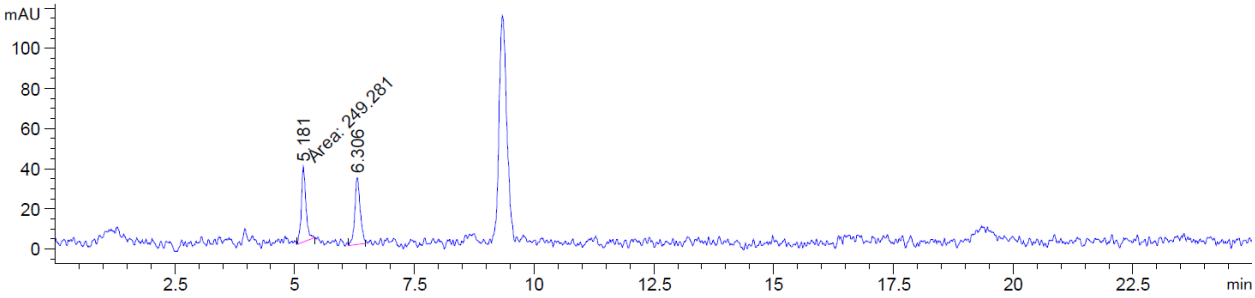
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.621	BB	0.1849	186.85617	15.46707	47.8592
2	9.381	MM	0.2255	203.57274	15.04730	52.1408

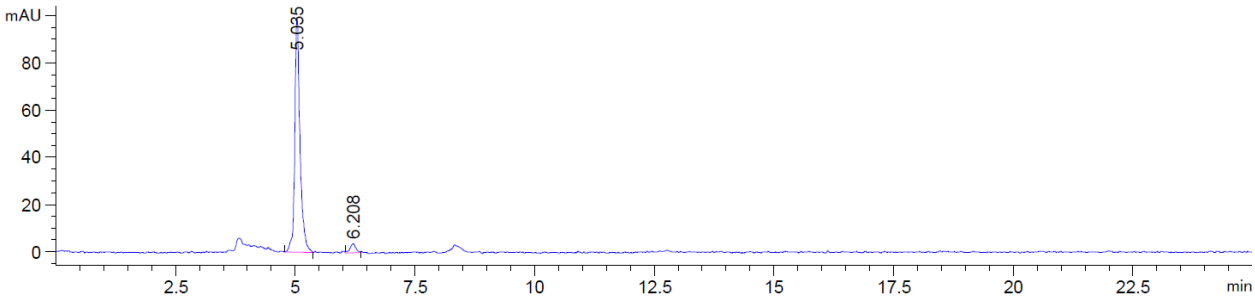
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.810	BB	0.1812	698.90253	59.41719	95.5731
2	9.542	MM	0.2249	32.37299	2.39918	4.4269

***tert*-butyl (1*S*,2*S*)-2-(3-phenylpropanoyl)cyclopropane-1-carboxylate 4le:**



Obtained as a colorless oil in 75 % yield. **Rf :** 0.80 (Pentane: EtOAc, 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.20 (t, *J* = 6.9 Hz, 3H), 2.93 (s, 4H), 2.40 – 2.33 (m, 1H), 2.12 – 2.03 (m, 1H), 1.44 (s, 9H), 1.37 – 1.30 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.0, 171.3, 140.9, 128.7, 128.5, 126.3, 81.4, 45.5, 29.8, 29.0, 28.2, 25.4, 17.2; **IR (ATR, cm^{-1}):** $\tilde{\nu}$ 2978, 1724, 1701, 1454, 1401, 1367, 1326, 1214, 1152, 1118, 1096, 840, 747, 699; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{17}H_{22}NaO_3^+$ 297.1461; Found 297.1470; **$[\alpha]_D^{20}$**= 159.6 (c = 1.0, $CHCl_3$); **Chiral HPLC:** (Chiralpak IB; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 6.2 min, t_R (major) = 5.0 min, 96:4 er.).

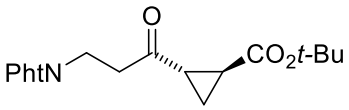




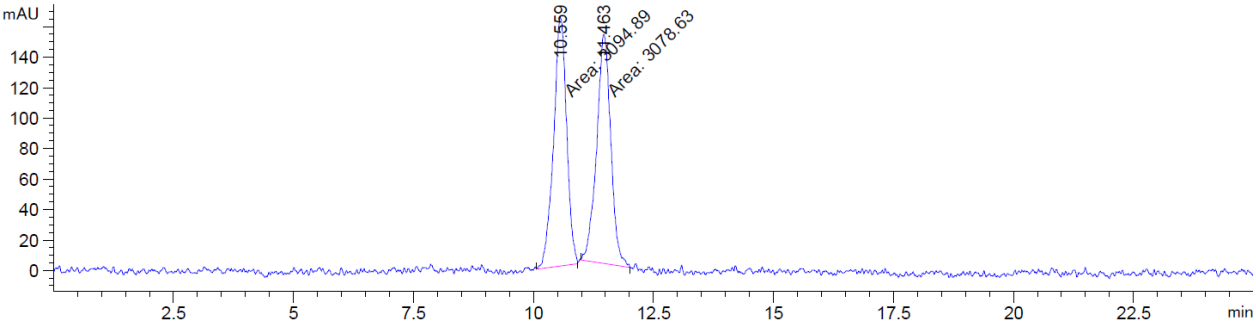
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.181	MM	0.1101	249.28102	37.73605	48.8097
2	6.306	VV	0.1155	261.43900	33.34191	51.1903

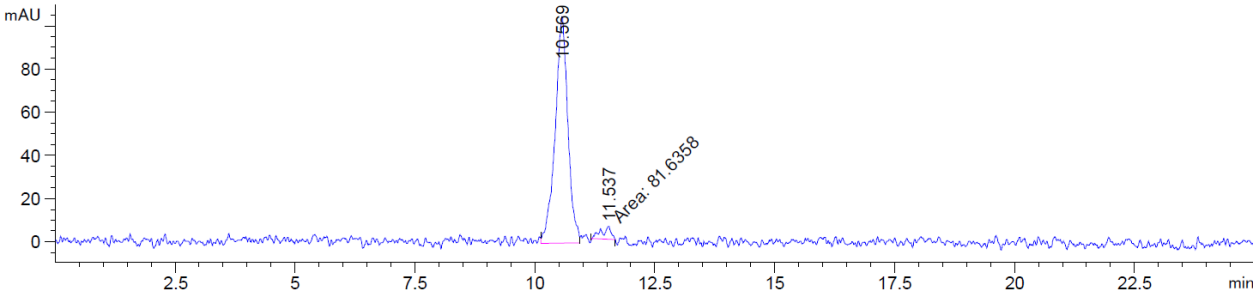
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.035	BB	0.1100	750.87933	99.58215	95.9004
2	6.208	VV	0.1182	32.09931	3.89445	4.0996

2-(((3-((1*S*,2*S*)-2-(*tert*-butoxycarbonyl)cyclopropyl)-3-oxopropyl)-□2-azaneyl)carbonyl)benzoic acid 4me:



Obtained as a white solid in 77 % yield. **Rf :** 0.18 (Pentane: EtOAc, 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dt, *J* = 6.9, 3.5 Hz, 2H), 7.72 (dd, *J* = 5.4, 3.1 Hz, 2H), 3.97 (t, *J* = 7.4 Hz, 2H), 3.06 (t, *J* = 7.4 Hz, 2H), 2.48 – 2.27 (m, 1H), 2.15 – 2.08 (m, 1H), 1.45 (s, 9H), 1.38 (t, *J* = 7.4 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.1, 171.1, 168.2, 134.2, 132.2, 123.5, 81.5, 41.8, 33.0, 29.0, 28.2, 25.7, 17.4; **IR (ATR, cm^{-1}):** $\tilde{\nu}$ 1773, 1714, 1396, 1369, 1337, 1216, 1155, 721; **HRMS (ESI/QTOF) m/z:** [M + Na]$^+$ Calcd for $C_{16}H_{14}N_2NaO_5^+$ 337.0795; Found 337.0787; **$[\alpha]_D^{20}$**= +127.2 (c = 1.0, $CHCl_3$); **m.p.:** 146 °C; **Chiral HPLC:** (Chiralpak IA; hexane:*i*-PrOH 90:10, 1.0 mL/min, 210 nm; t_R (minor) = 11.5 min, t_R (major) = 10.6 min, 96:4 er.).



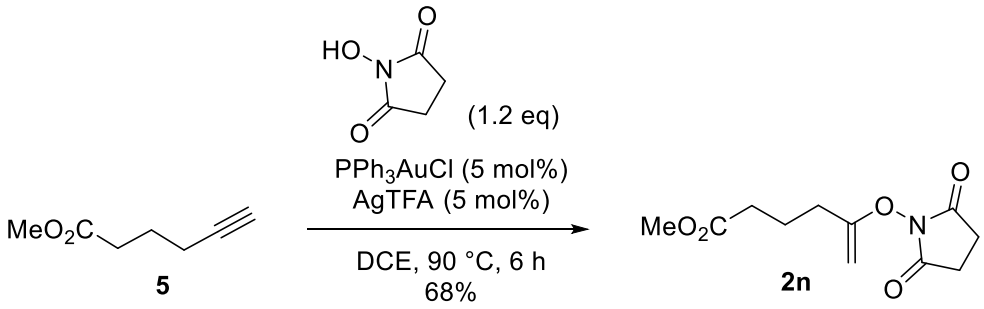


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.559	MM	0.3158	3094.88550	163.33197	50.1317
2	11.463	MM	0.3416	3078.62671	150.19917	49.8683

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.569	VV	0.2332	1934.82629	104.88237	95.9515
2	11.537	MM	0.2297	81.63585	5.92255	4.0485

Synthesis of aldehyde 7

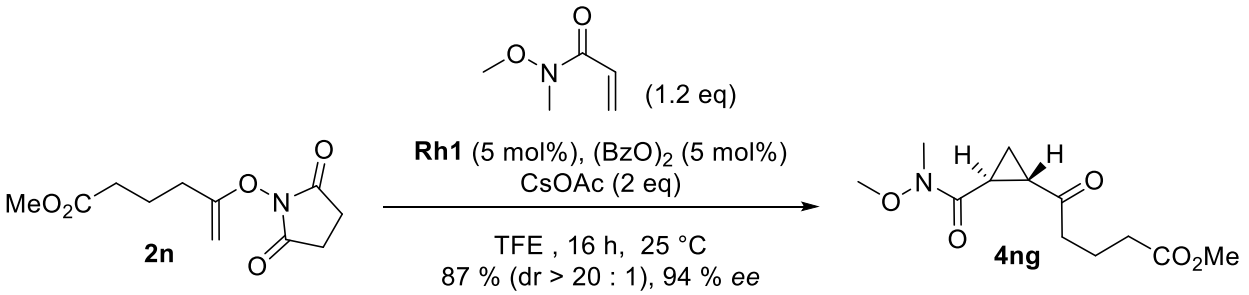
<u>*N*-Enoxysuccinimide 2n:</u>



PPh_3AuCl (49 mg, 0.3 mmol) and silver trifluoroacetate (22 mg, 0.3 mmol) were premixed in 1,2-DCE (1 mL) for 10 mins at rt and filtered over a short plug of celite before use. In a sealed tube, the cationic gold complex was added to **5** (0,757 g, 6 mmol) in 1,2-DCE (9 mL) and N-hydroxysuccinimide (253 mg, 2.2 mmol) was then added. The tube was sealed and the reaction was stirred for 6hr at reflux. The reaction was diluted with DCM and passed through a short plug of celite. The filtrate was concentrated and the residue purified by column chromatography (pentane/ethyl acetate, 7:3 to 1:1) to afford **2n** (0.33 g, 1.4 mmol, 68 % yield) as a white solid.

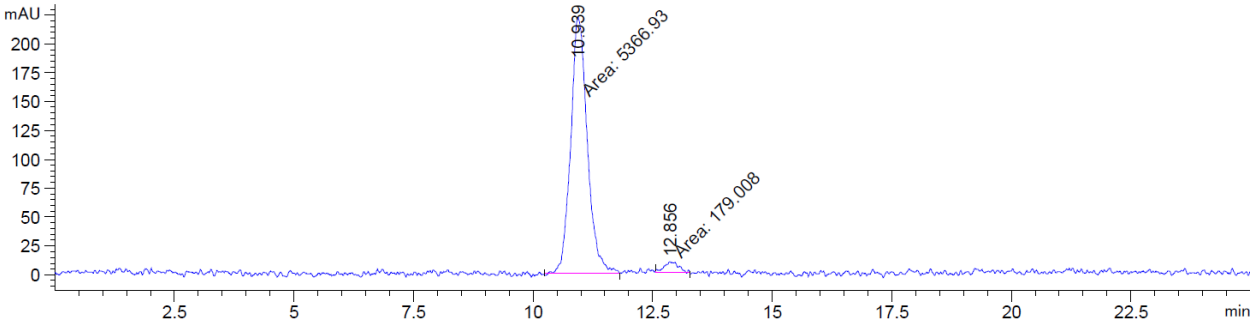
Rf : 0.37 (Pentane: EtOAc, 1:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.18 (d, *J* = 3.8 Hz, 1H), 4.04 (d, *J* = 3.8 Hz, 1H), 3.67 (s, 3H), 2.81 (s, 4H), 2.46 (t, *J* = 7.4 Hz, 2H), 2.36 (t, *J* = 7.3 Hz, 2H), 1.95 (p, *J* = 7.4 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 169.8, 160.5, 85.2, 51.7, 32.8, 30.7, 25.7, 22.1; **IR (ATR, cm^{-1}):** $\tilde{\nu}$ 1728, 1436, 1368, 1200, 1147; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{11}H_{15}NNaO_5^+$ 264.0842; Found 264.0848; **m.p.:** 69 °C.

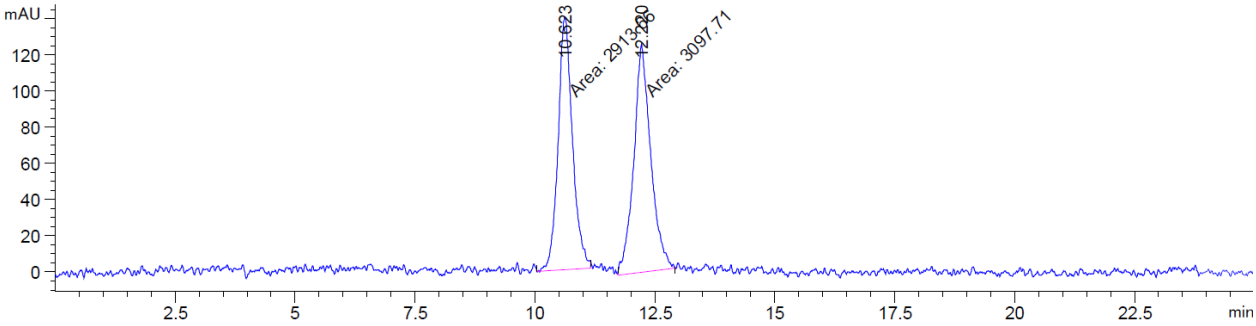
Cyclopropane 4ng:



Without protection from oxygen and moisture, **Rh1** (105 mg, 0.25 mmol), dibenzoylperoxide (59 mg, 0.25 mmol) and CsOAc (1.9 g, 9.8 mmol, 2.0 equiv.) were weighed into a 50 mL round bottom flask equipped with a magnetic stir bar and sealed with a rubber septum. 10 mL of TFE was added and the mixture was stirred at 23°C for 5 mins. **2n** (1.18 g, 4.9 mmol, 1.00 equiv.) and 15 mL of TFE were added followed by *N*-Methoxy-*N*-methylacrylamide (0.68 g, 5.9 mmol, 1.20 equiv.). The reaction mixture was stirred for 16 hours. The mixture was concentrated under reduced pressure and the residue was purified further by silica gel column (hexane/EtOAc, 7:3 then 1:1) to afford of cyclopropane **4ng** (1.09 g, 4.25 mmol, 87%) as a yellow oil.

Rf: 0.30 (Pentane: EtOAc, 1:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 3.73 (s, 3H), 3.67 (s, 3H), 3.20 (s, 3H), 2.76 – 2.63 (m, 3H), 2.51 – 2.42 (m, 1H), 2.35 (t, *J* = 7.3 Hz, 2H), 1.93 (p, *J* = 7.2 Hz, 2H), 1.41 (dddd, *J* = 10.0, 8.8, 5.8, 3.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.8, 173.6, 171.7, 61.9, 51.7, 43.0, 33.1, 32.7, 28.9, 21.8, 19.0, 17.3; **IR (ATR, cm^{-1}):** $\tilde{\nu}$ 2952, 1733, 1700, 1651, 1377, 1174, 1119, 996; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{12}H_{19}NNaO_5^+$ 280.1155; Found 280.1161; **$[\alpha]_D^{20}$**= 160.7 (c = 1.02, $CHCl_3$); **Chiral HPLC:** (Chiralpak IA; hexane:*i*-PrOH 70:30, 1.0 mL/min, 254 nm; t_R (minor) = 12.9 min, t_R (major) = 10.9 min, 97:3 er.).

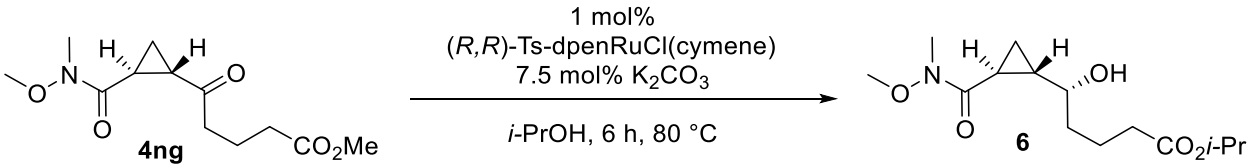




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.939	MM	0.4030	5366.93164	221.94817	96.7723
2	12.856	MM	0.3287	179.00833	9.07575	3.2277

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.599	MM	0.3374	189.72136	9.37037	50.1352
2	12.199	MM	0.3904	188.69820	8.05517	49.8648

Alcohol 6:

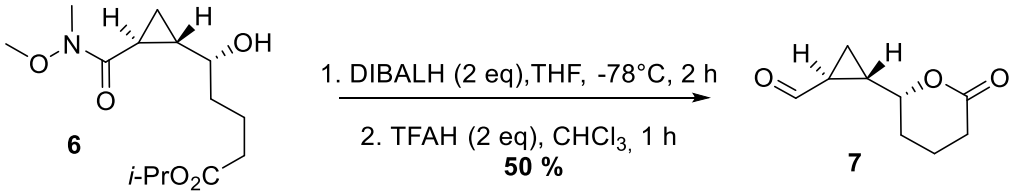


To a solution of **4ng** (257 mg, 1.0 mmol) and K_2CO_3 (10.4 mg, 0.075 mmol) in dry *i*-PrOH (10 mL) was added a solution of (*R,R*)-Ts-dpenRuCl(cymene) (6.3 mg, 10 □mol) in dry 1,2-DCE (1 mL). The solution was degassed and the reaction mixture was stirred at 80 °C under a N_2 atmosphere. After 6 h the solvent was removed under reduced pressure. The crude product was directly

purified by flash chromatography (pentane/ EtOAc 7:3 to 1:1) to afford alcohol **6** (255 mg, 0.89 mmol, 89 %, (*S,S,R*)/(*S,S,S*) = 8.5:1) as a pale yellow oil (dr was calculated upon conversion to compound **7**).

Rf: 0.27 (Pentane: EtOAc, 1:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.01 (p, *J* = 6.3 Hz, 1H), 3.78 (s, 3H), 3.24 – 3.12 (m, 4H), 2.31 (t, *J* = 7.2 Hz, 2H), 2.19-2.13 (br, 1H, -OH), 1.86 – 1.70 (m, 2H), 1.68 – 1.58 (m, 4H), 1.54 – 1.46 (m, 1H), 1.23 (d, *J* = 6.3 Hz, 6H), 0.84 (ddd, *J* = 8.4, 6.1, 4.1 Hz, 1H);**^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.8, 173.3, 73.8, 67.8, 61.8, 36.8, 34.6, 32.7, 28.4, 22.0 (2C), 21.1, 15.3, 12.4; **IR (ATR, cm^{-1}):** $\tilde{\nu}$ 3434, 2979, 2938, 1726, 1633, 1465, 1424, 1375, 1246, 1179, 1108, 1009, 980; **HRMS (ESI) m/z:** $[M + H]^+$ Calcd for $C_{14}H_{26}NO_5^+$ 288.1805; Found 288.1808; **$[\alpha]_D^{20}$**= + 11.0 (c = 1.0, $CHCl_3$).

Aldehyde 7:

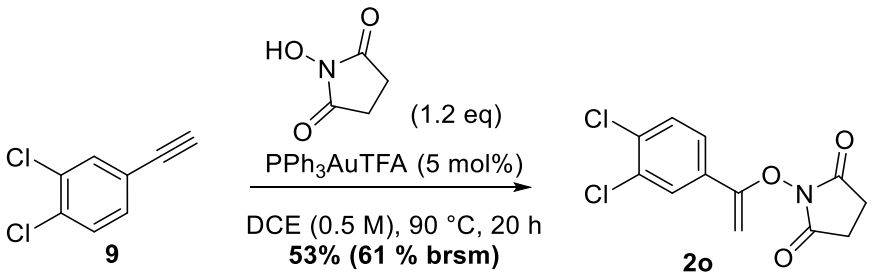


To a solution of **6** (100 mg, 0,35 mmol) in dry THF (3.5 mL) at -78°C, DIBAL-H (1,2 M in toluene, 0.58 ml, 0.70 mmol) was added dropwise. The solution was stirred at this temperature for 2.5h. The reaction was quenched with drops of water and acidified with 1N HCl solution. The solution was extracted with EtOAc, the combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude product was dissolved into $CHCl_3$ (2 ml) and TFAH (54 ml, 0.70 mmol) was added at 0°C. The reaction was run to completion (TLC) and then poured into a saturated solution of $NaHCO_3$. The mixture was extracted with EtOAc, the combined organic layers were dried over Na_2SO_4 and concentrated under vacuum to give aldehyde **7** (29 mg, 0172 mmol, 50 %, (*S,S,R*)/(*S,S,S*) = 8.5:1) as a colorless oil. All spectroscopic data were in agreement with those reported previously in the literature.[12]

Rf: 0.50 (EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.39 (d, *J* = 3.9 Hz, 1H), 3.92 (ddd, *J* = 10.5, 7.2, 3.2 Hz, 1H), 2.59 (dt, *J* = 18.4, 6.4 Hz, 1H), 2.47 (ddd, *J* = 17.8, 8.9, 7.0 Hz, 1H), 2.13 – 1.95 (m, 3H), 1.88 – 1.65 (m, 3H), 1.37 (dt, *J* = 9.4, 4.9 Hz, 1H), 1.14 (ddd, *J* = 8.4, 6.4, 4.9 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.0, 170.9, 81.0, 29.6, 28.2, 27.1, 26.9, 18.6, 12.0.**IR (ATR, cm^{-1}):** $\tilde{\nu}$ 1728, 1705, 1240, 1175, 1043; **HRMS (ESI) m/z:** $[M + H]^+$ Calcd for $C_9H_{12}O_3^+$ 191.0679; Found 191.0640; **$[\alpha]_D^{20}$**= + 39.7 (c = 1.0, $CHCl_3$).

Experimentals and datas – UPF-648

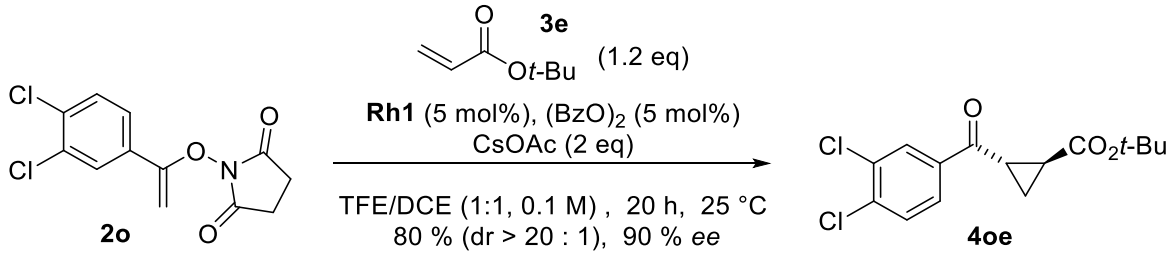
N-Enoxysuccinimide 2o:



PPh_3AuCl (12 mg, 0.025 mmol) and silver trifluoroacetate (5.5 mg, 0.025 mmol) were premixed in 1,2-DCE (0.5 mL) for 10 mins at rt and filtered over a short plug of celite before use. In a sealed tube, the cationic gold complex was added to 1,2-dichloro-4-ethynylbenzene **9** (86 mg, 0.5 mmol) in 1,2-DCE (0.5 mL) and N-hydroxysuccinimide (63 mg, 0.55 mmol) was then added. The tube was sealed and the reaction was stirred for 20 h at reflux. The reaction was diluted with DCM and passed through a short plug of celite. The filtrate was concentrated and the residue purified by column chromatography (pentane/ethyl acetate, 7:3 to 1:1) to afford **2o** (76 mg, 0.27 mmol, 53 % yield) as a white solid and **9** (10 mg, 0.06mmol, 12 % recovered) as a white solid.

Rf: 0.54 (Pentane: EtOAc, 1:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 2.0 Hz, 1H), 7.52 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 4.88 (d, *J* = 4.5 Hz, 1H), 4.47 (d, *J* = 4.5 Hz, 1H), 2.87 (s, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.7, 157.3, 134.0, 133.0, 132.0, 130.6, 128.3, 125.7, 88.2, 25.8; **IR (ATR, cm^{-1}):** $\tilde{\nu}$ 1725, 1652, 1203, 1110, 1070, 837, 647; **HRMS (APPI/LTQ-Orbitrap) m/z:** $[M + H]^+$ Calcd for $C_{12}H_{10}Cl_2NO_3^+$ 286.0032; Found 286.0044; **m.p.:** 213 °C.

Cyclopropane 4oe: (preformed catalyst)

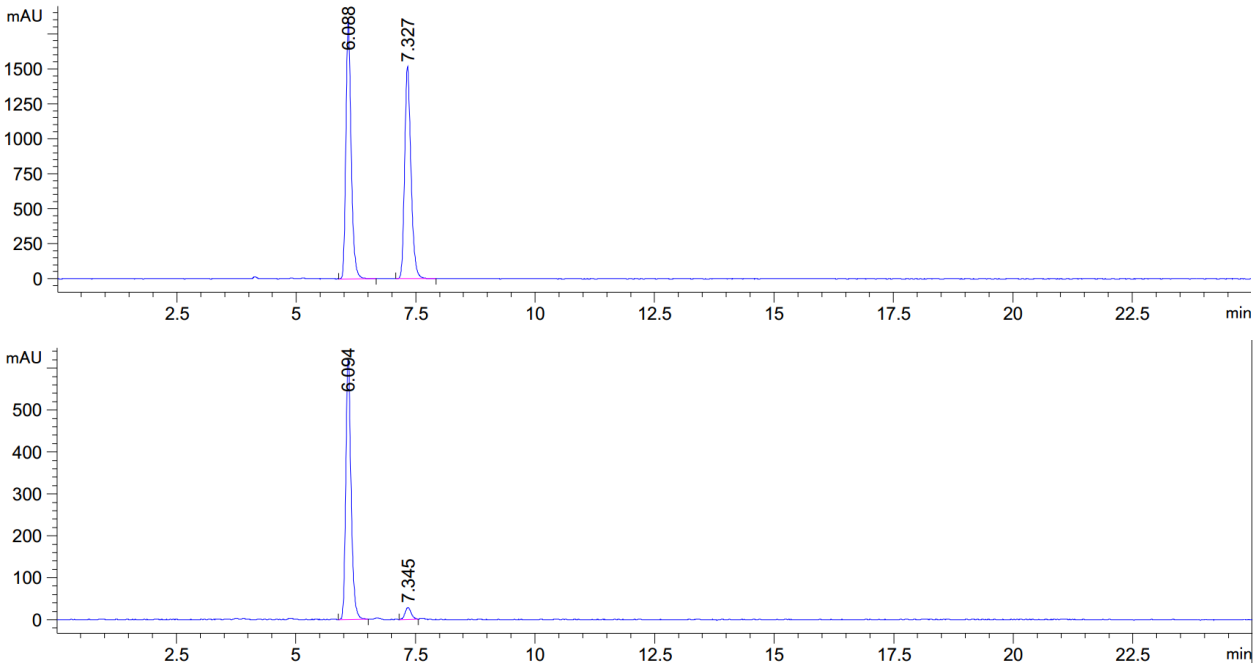


Without protection from oxygen and moisture, **Rh1** (2.15 mg, 5.00 µmol), dibenzoylperoxide (1.20 mg, 5.00 µmol) and CsOAc (38.0 mg, 0.12 mmol, 2.0 equiv.) were weighed into a vial equipped with a magnetic stir bar and sealed with a rubber septum. 500 µL of TFE was added

and the mixture was stirred at 23°C for 2 mins. **2o** (0.10 mmol, 1.00 equiv.) and 500 µL of 1,2-DCE were added followed by *tert*-butylacrylate **3e** (0.12mmol, 1.20 equiv.). The reaction mixture was stirred for 20 hours. The mixture was concentrated under reduced pressure and the residue was purified further by silica gel column (pentane/EtOAc, 20:1).to afford **2oe** (25.5 mg, 0.081 mmol, 81 % yield) with 90 % *ee*.as a colorless oil which solidified.

Characterization datas for 4oe : Rf: 0.75 (Pentane: EtOAc, 9:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 2.0 Hz, 1H), 7.83 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 3.04 – 2.97 (m, 1H), 2.35 – 2.27 (m, 1H), 1.58 – 1.53 (m, 2H), 1.47 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.4, 171.2, 138.1, 136.8, 133.5, 130.9, 130.4, 127.4, 81.7, 28.2, 26.2, 25.9, 18.4; **IR (ATR, cm^{-1}):** $\tilde{\nu}$ 2979, 1722, 1675, 1369, 1331, 1213, 1152, 1030, 844, 735; **HRMS (APPI/LTQ-Orbitrap) m/z:** [M - O*t*-Bu]$^{+}$ Calcd for $C_{11}H_7Cl_2O_2^{+}$ 240.9818; Found 240.9824; **$[\alpha]_D^{20}$**= 105.6 (c = 0.92, $CHCl_3$).

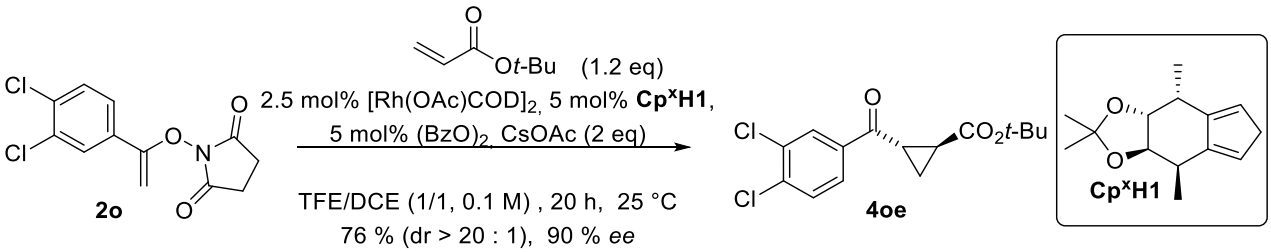
Chiral HPLC: (Chiralpak IC; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 7.3 min, t_R (major) = 6.1 min, 95:5 er.)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.088	BB	0.1171	1.41504e4	1852.73438	50.4341
2	7.327	BB	0.1392	1.39068e4	1513.02112	49.5659

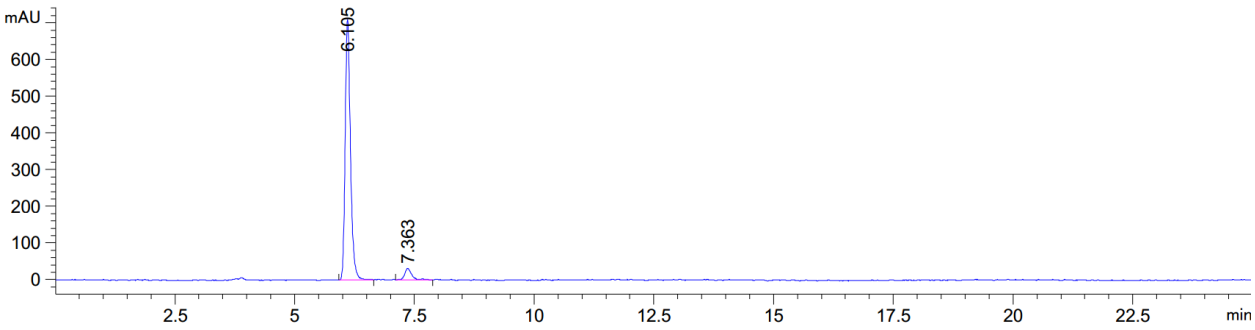
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.094	BB	0.1183	4765.27197	615.84705	95.0947
2	7.345	BB	0.1382	245.80739	28.07031	4.9053

Cyclopropane 4oe *: In situ* formation of catalyst[1] :



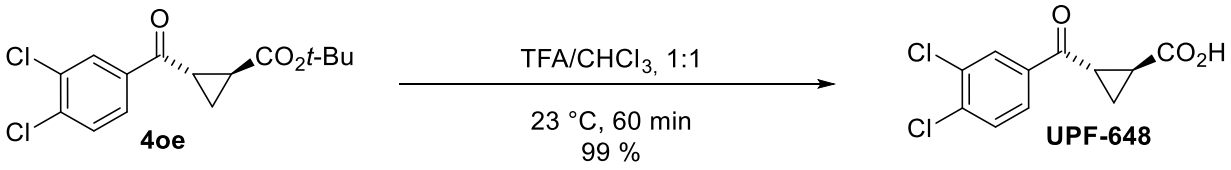
Without protection from oxygen and moisture, $[Rh(OAc)COD]_2$ (2.15 mg, 5.00 µmol) and **Cp^{X}H1** were weighed into a vial equipped with a magnetic stir bar and sealed with a rubber. 200 µL of TFE was added and the mixture was stirred at 25°C for 60 mins. Then dibenzoylperoxide (1.20 mg, 5.00 µmol) and CsOAc (38.0 mg, 0.12 mmol, 2.0 equiv.) were added followed by 300µL of TFE and the mixture was stirred at 25°C for 2 mins. **2o** (0.10 mmol, 1.00 equiv.) and 500 µL of 1,2-DCE were added followed by *tert*-butylacrylate (0.12mmol, 1.20 equiv.). The reaction mixture was stirred for 36 hours. The mixture was concentrated under reduced pressure and the residue was purified further by silica gel column (hexane/EtOAc, 20:1).to afford **4oe** (24.0 mg, 0.076 mmol, 76 % yield).with 89 % *ee* as a colorless oil which solidified.

Chiral HPLC: (Chiralpak IC; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 7.3 min, t_R (major) = 6.1 min, 94.5:5.5 er.)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.105	BB	0.1177	5434.71338	707.07800	94.5317
2	7.363	BB	0.1470	314.37787	30.82979	5.4683

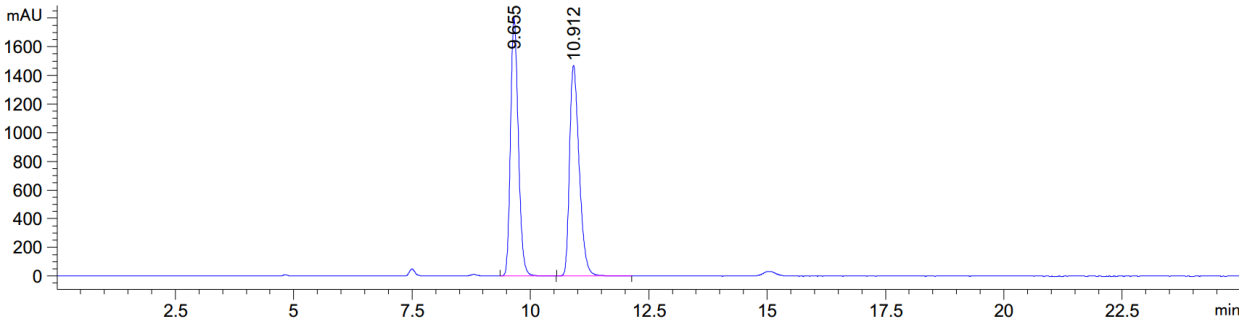
UPF-648

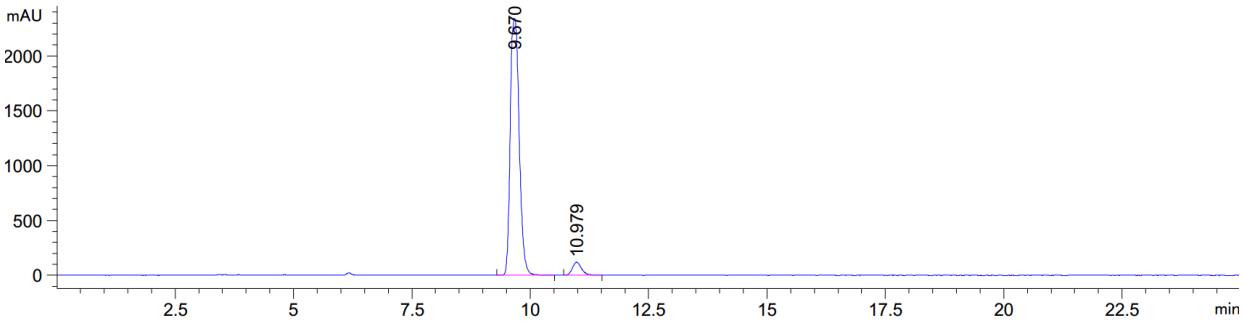


To a solution of **4oe** (43 mg, 0.136 mmol) in $CHCl_3$ (0.35 ml), TFA (0.35 ml) was added and the reaction was stirred at 23°C until completion (1 h, TLC). The mixture was quenched with a saturated solution of $NaHCO_3$ and washed with ethyl acetate. The aqueous layer was acidified with a 2N HCl solution and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and concentrated under vacuum to afford **UPF-648** (35 mg, 0.135 mmol, 99% yield) as a white solid. Recrystallization from toluene/hexanes (1:1) afforded **UPF-648** in 98 % *ee*.

Rf: 0.67 (EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 2.0 Hz, 1H), 7.85 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 3.15 (ddd, *J* = 8.7, 5.9, 3.8 Hz, 1H), 2.42 (ddd, *J* = 8.7, 6.0, 3.8 Hz, 1H), 1.69 (tdd, *J* = 9.5, 5.9, 3.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.6, 176.8, 138.4, 136.4, 133.7, 131.0, 130.4, 127.4, 26.4, 24.5, 18.7; **IR (ATR, cm^{-1}):** $\tilde{\nu}$ 3089 – 2856 (O-H, acid), 1703, 1676, 1395, 1324, 1214, 1031, 913; **HRMS (ESI) m/z:** $[M - H]^-$ Calcd for $C_{11}H_7Cl_2O_3^-$ 256.9778; Found 256.9783; ; **m.p.:** 88 °C; **$[\alpha]_D^{20}$**= 168.5 (c = 0.18, $CHCl_3$). The enantiomeric excess was measured upon conversion of acid to the methyl ester. All spectroscopic data were in agreement with those reported previously in the literature.[13]

Before recrystallization: **Chiral HPLC (methyl ester):** (Chiralpak IC; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 11.0 min, t_R (major) = 9.7 min, 95:5 er.)

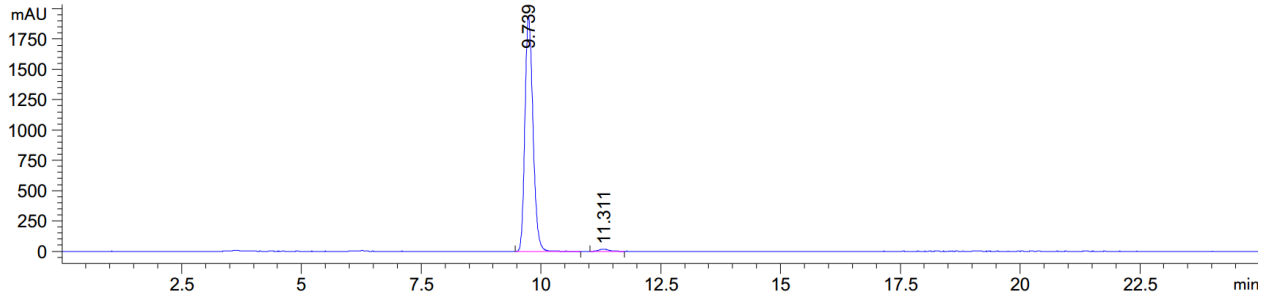




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.655	BB	0.1741	2.06741e4	1798.34314	49.8377
2	10.912	BB	0.2214	2.08087e4	1468.01111	50.1623

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.670	BB	0.2052	3.07410e4	2341.69653	95.0266
2	10.979	BB	0.2101	1608.90759	118.74154	4.9734

<u>After recrystallization:</u> **Chiral HPLC (methyl ester):** (Chiralpak IC; hexane:*i*-PrOH 95:05, 1.0 mL/min, 254 nm; t_R (minor) = 11.3 min, t_R (major) = 9.7 min, 99:1 er.)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.739	BB	0.1841	2.26463e4	1941.51099	98.8355
2	11.311	BB	0.2216	266.83533	18.35062	1.1645

Absolute configuration determination:

Absolute configuration was determined by comparison with optical rotations known in literature.[12,13]

References

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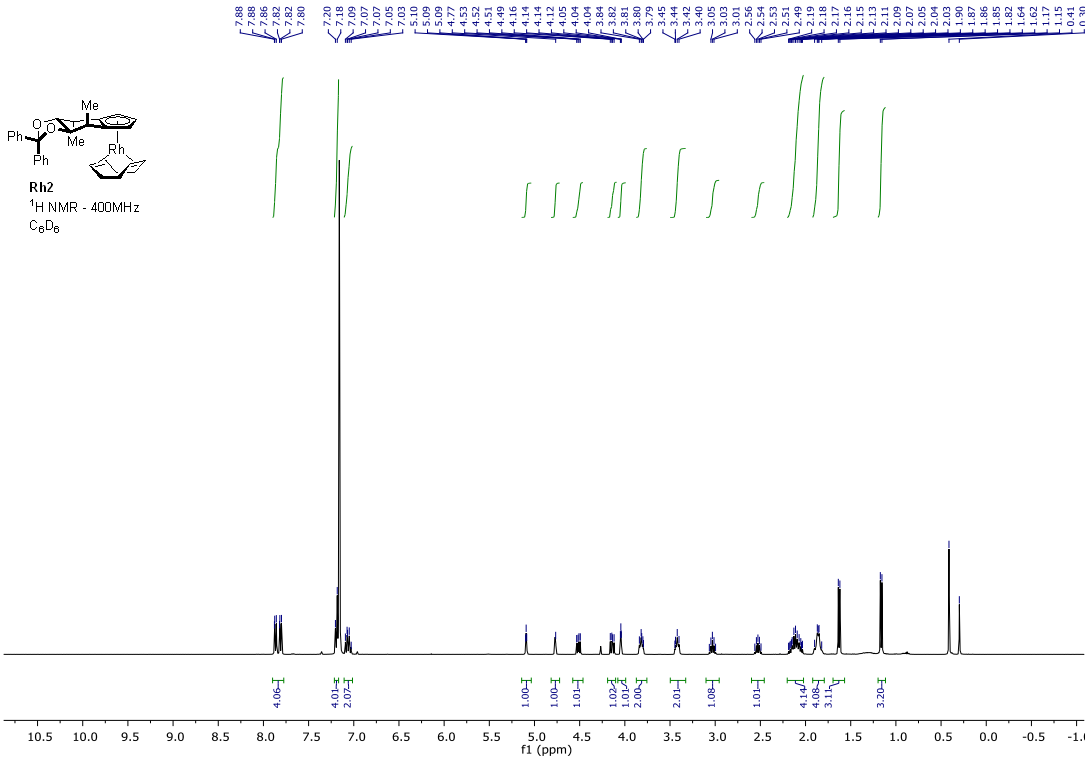
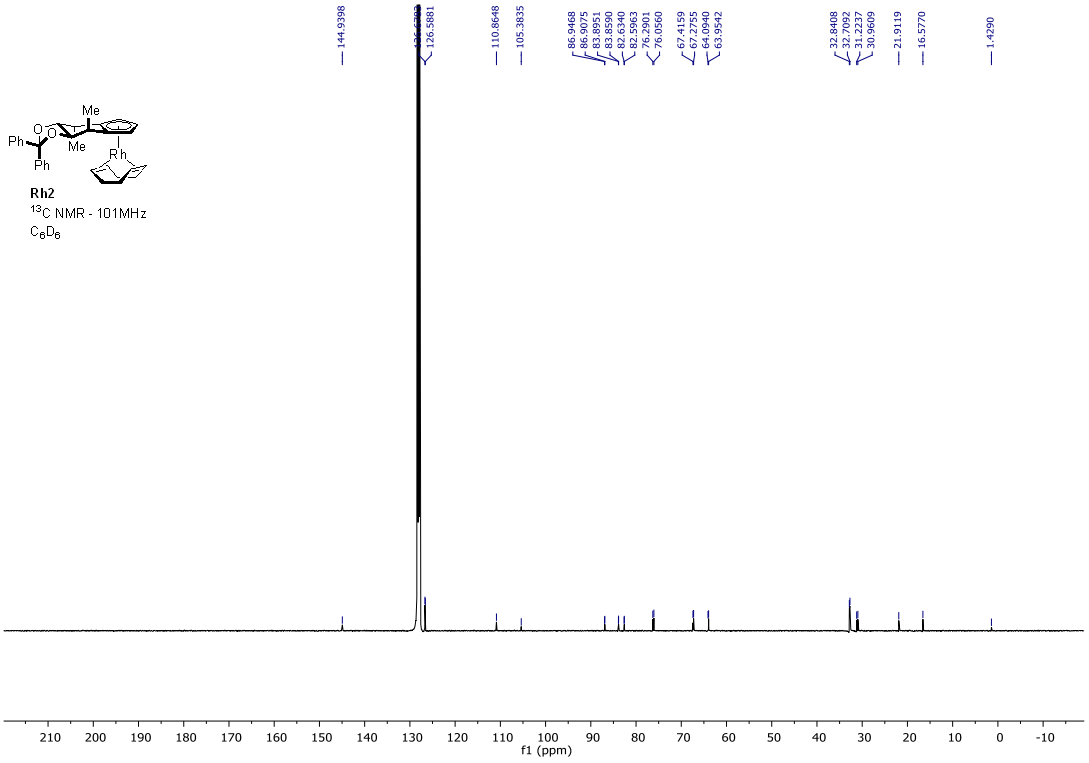
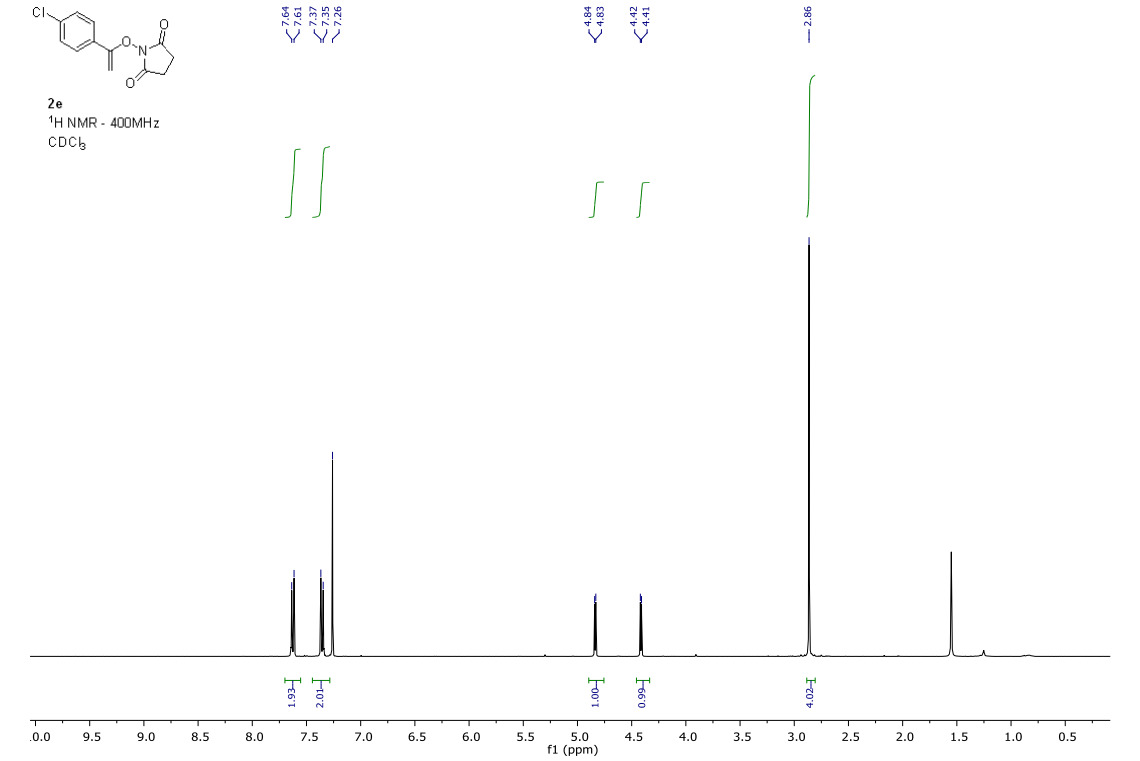
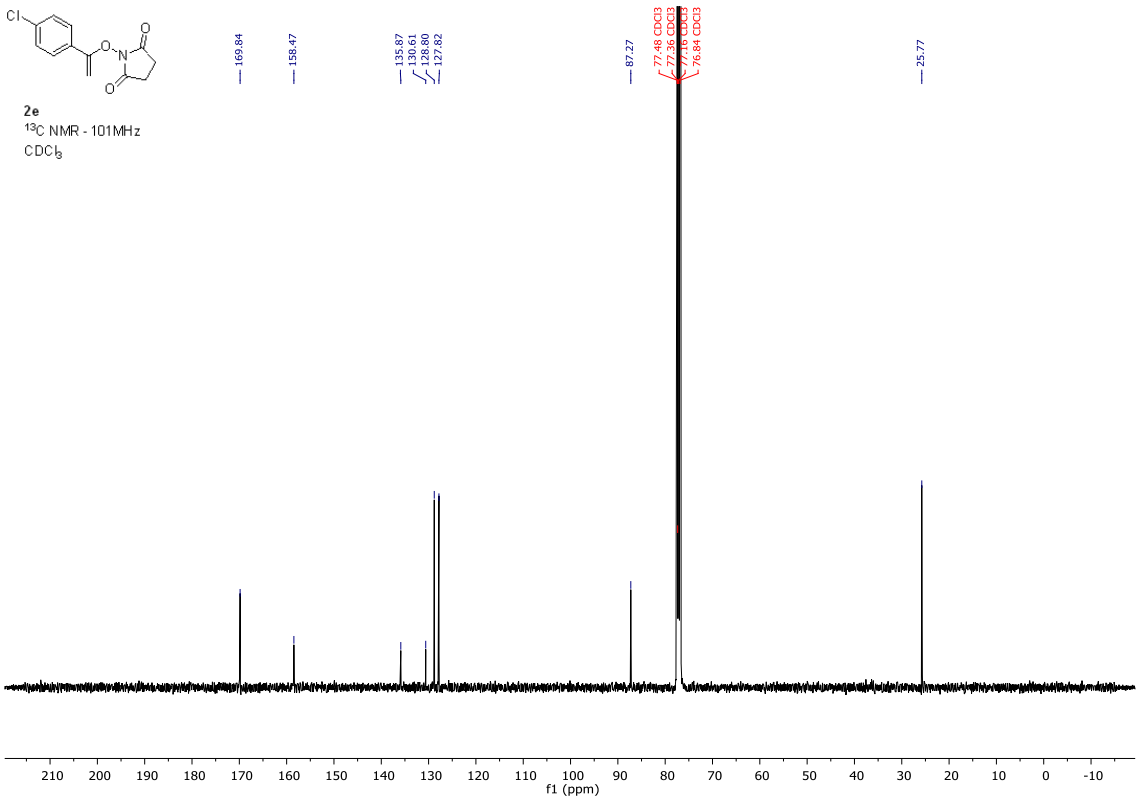

Rh2
^{1}H NMR - 400MHz
C_6D_6
f1 (ppm)


Rh2
^{13}C NMR - 101MHz
C_6D_6
f1 (ppm)


2e
1H NMR - 400MHz
CDCl3
7.64
7.61
7.37
7.35
7.26
4.84
4.83
4.42
4.41
2.86
1.93
2.01
1.00
0.99
4.02
f1 (ppm)


2e
13C NMR - 101MHz
CDCl3
169.84
158.47
135.87
136.61
129.80
127.82
87.27
77.48 CDCl3
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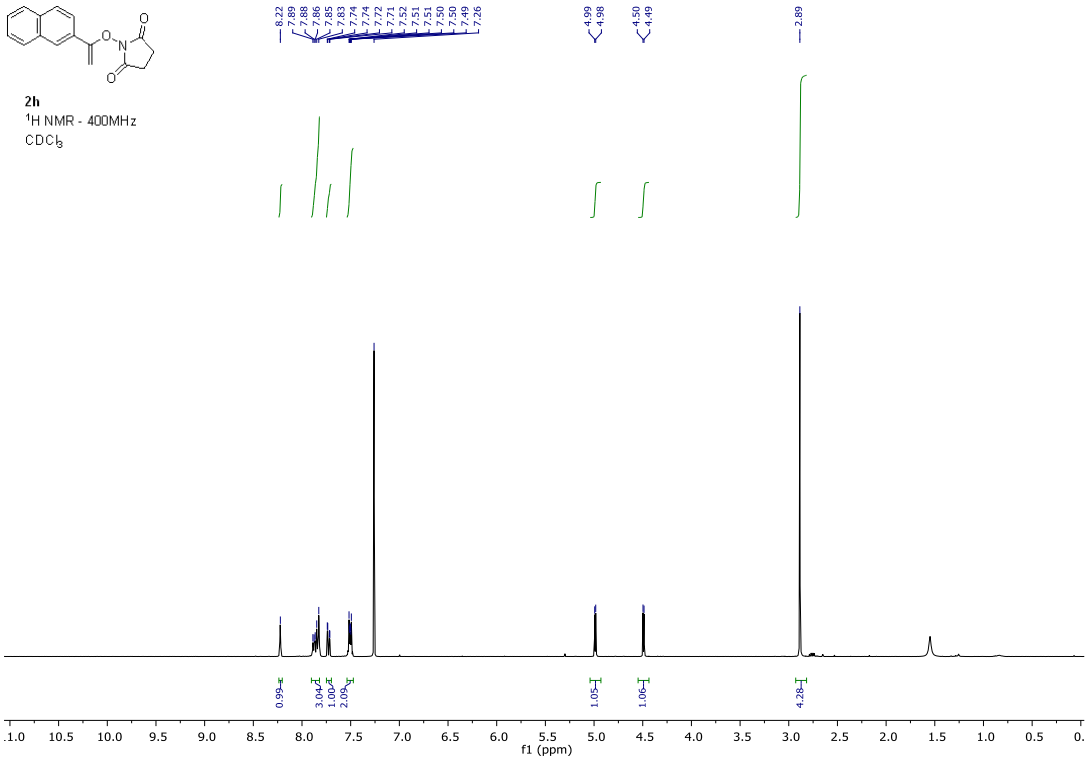
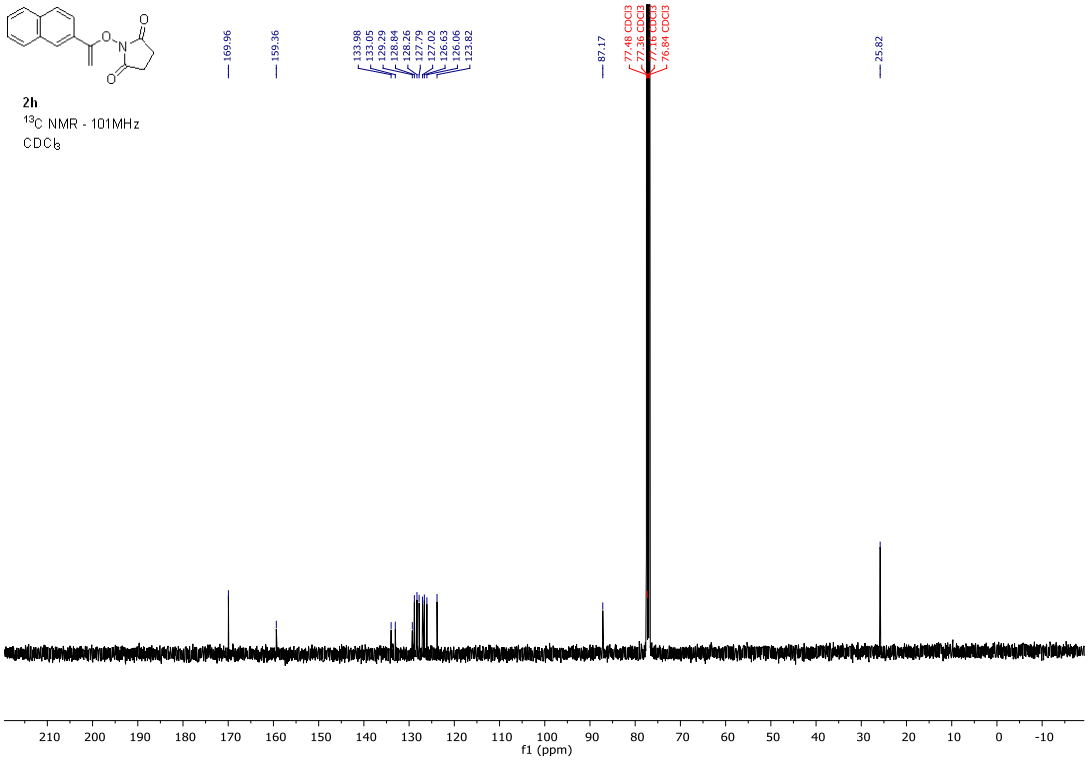
77.16 CDCl3
76.84 CDCl3
25.77
f1 (ppm)


2h
1H NMR - 400MHz
CDCl3
8.22
7.89
7.88
7.86
7.85
7.83
7.74
7.74
7.72
7.71
7.52
7.51
7.51
7.50
7.50
7.49
7.26
4.99
4.98
4.50
4.49
2.89
0.99
3.04
1.00
2.09
1.05
1.06
4.28
f1 (ppm)


2h
13C NMR - 101MHz
CDCl3
169.96
159.36
133.98
133.05
129.29
128.84
128.26
127.79
127.02
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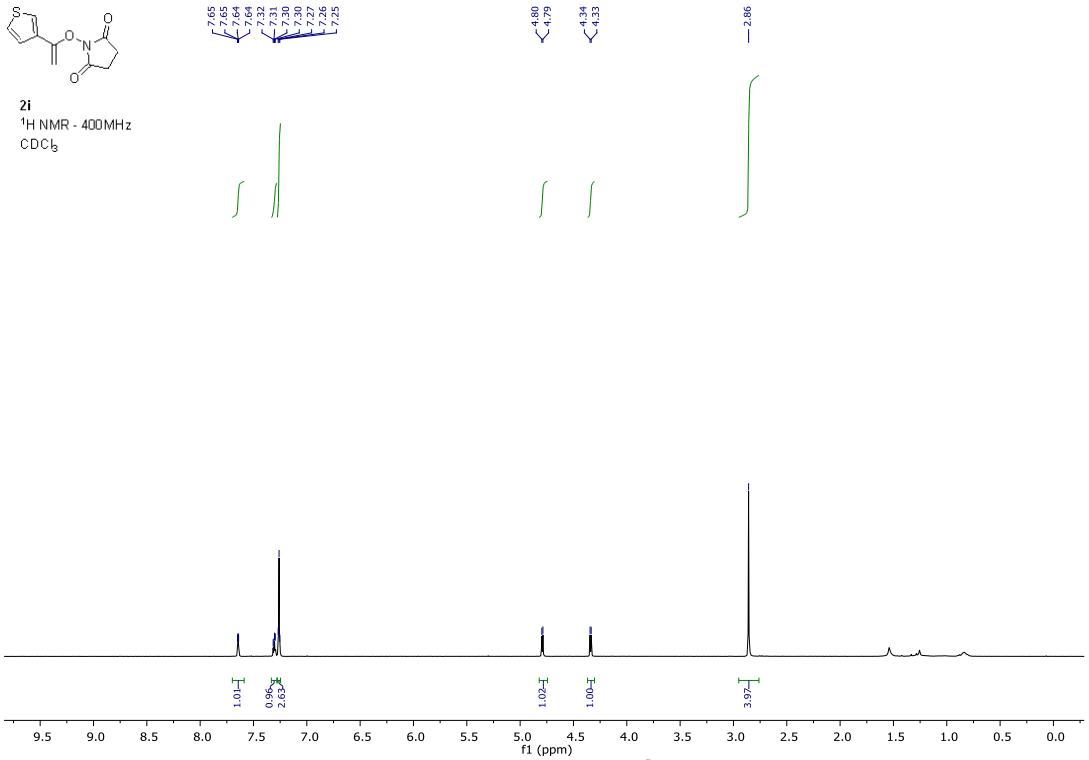
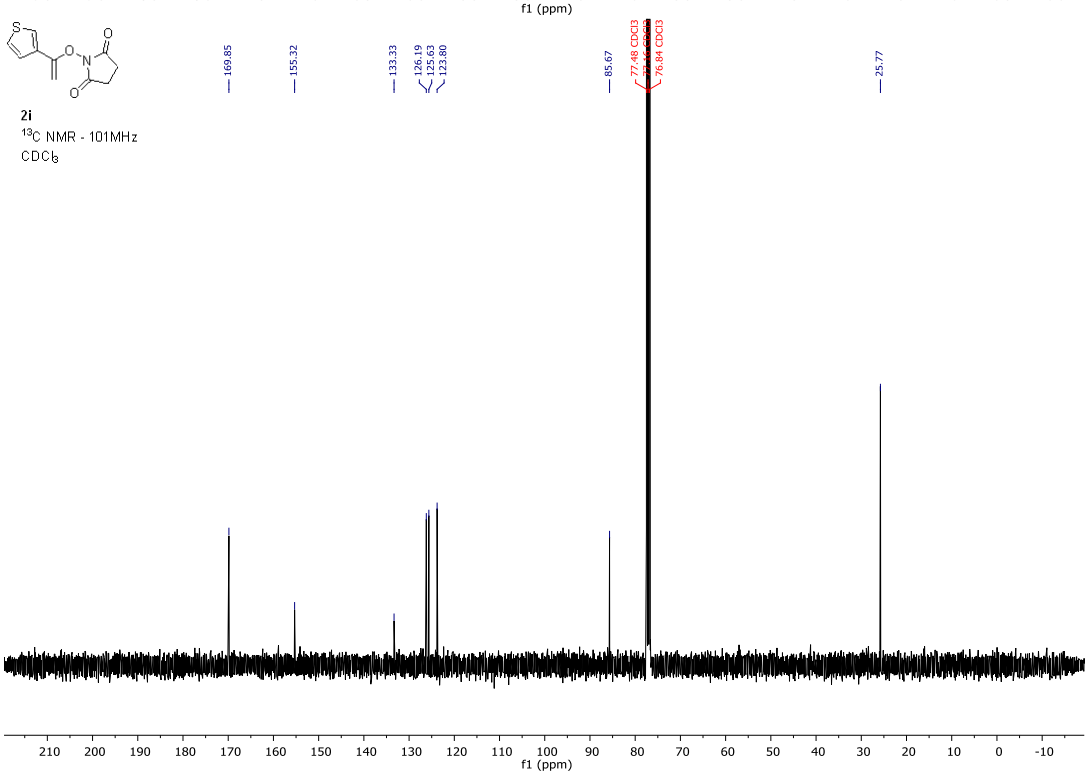
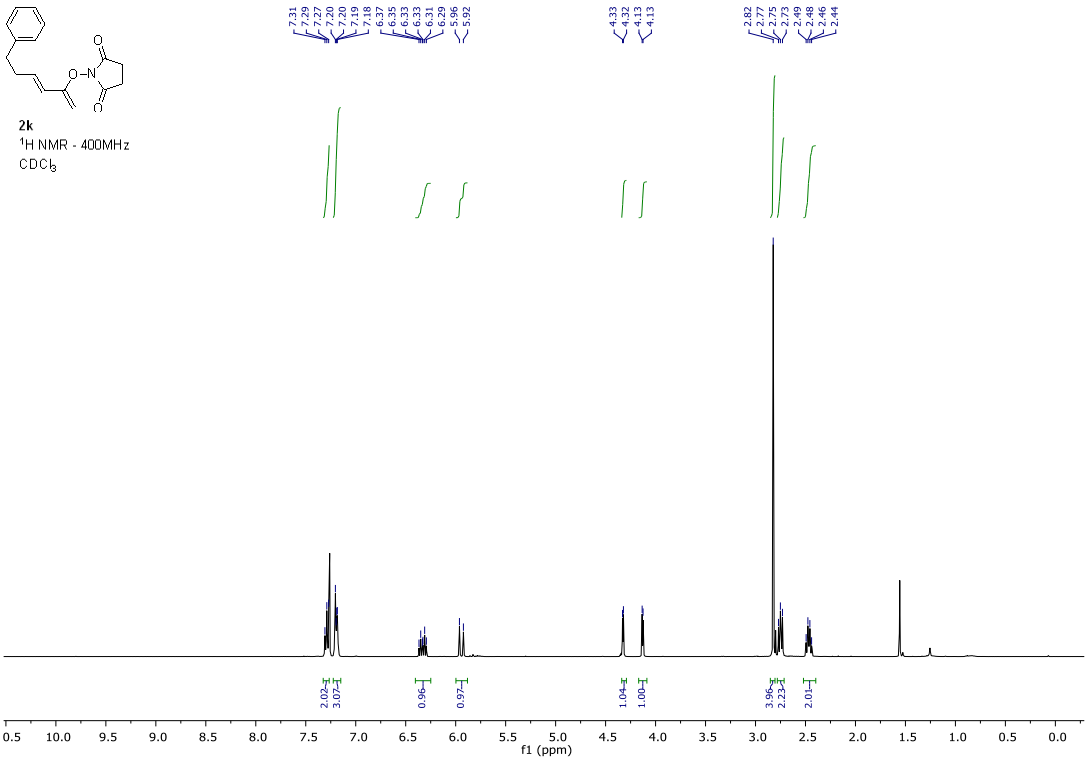
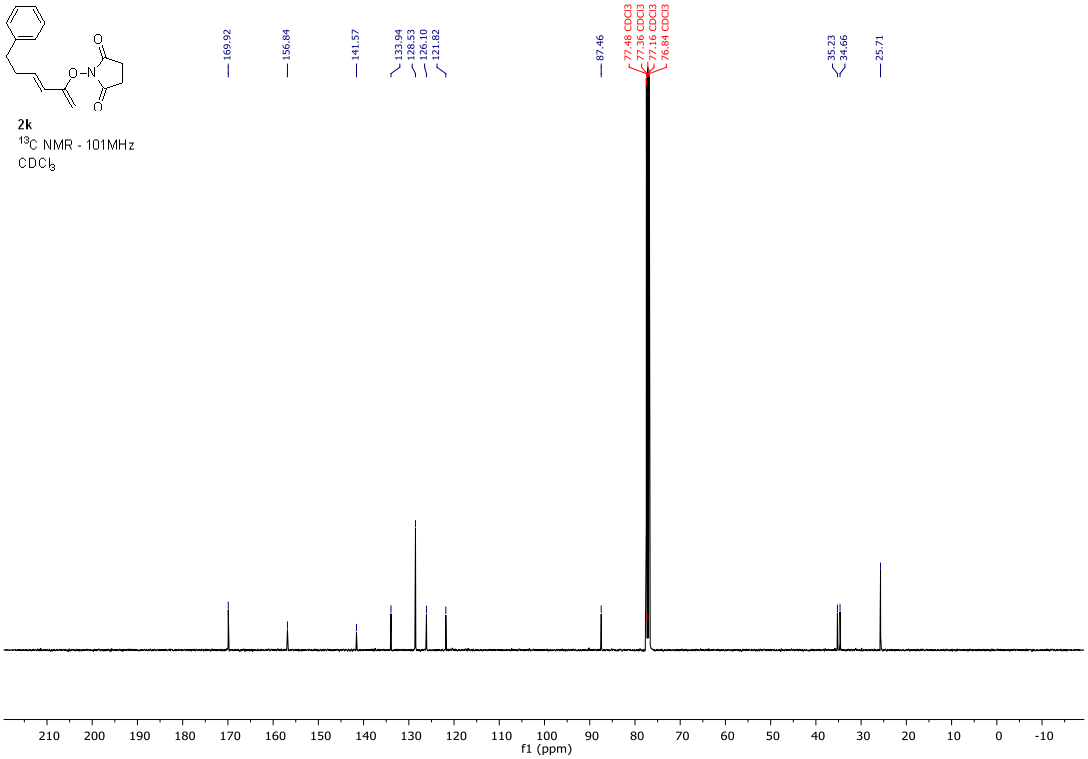
126.46
123.82
87.17
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
25.82
f1 (ppm)


2i
1H NMR - 400MHz
CDCl3
7.65
7.65
7.64
7.64
7.32
7.31
7.30
7.27
7.26
7.25
4.80
4.79
4.34
4.33
2.86
1.01
0.96
2.63
1.02
1.00
3.97
f1 (ppm)


2i
13C NMR - 101MHz
CDCl3
169.85
155.32
133.33
126.19
125.63
123.80
85.67
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
25.77
f1 (ppm)


2k
1H NMR - 400MHz
CDCl3
7.31
7.29
7.27
7.20
7.20
7.19
7.18
6.37
6.35
6.33
6.33
6.31
6.29
5.96
5.92
4.33
4.32
4.13
4.13
4.13
2.82
2.77
2.75
2.73
2.49
2.48
2.46
2.44
2.02
3.07
0.96
0.97
1.04
1.00
3.96
2.23
2.01
f1 (ppm)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141.57
133.94
128.53
126.10
121.82
87.46
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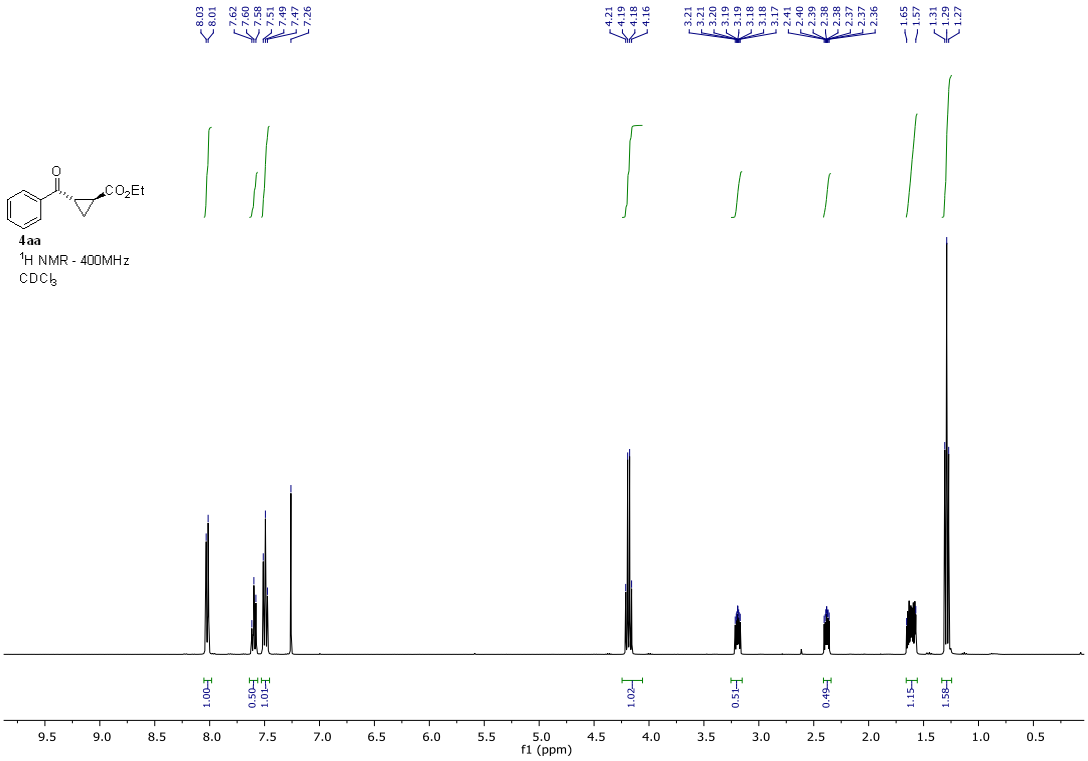
77.36 CDCl3
77.16 CDCl3
76.84 CDCl3
35.23
34.66
25.71
f1 (ppm)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8.01
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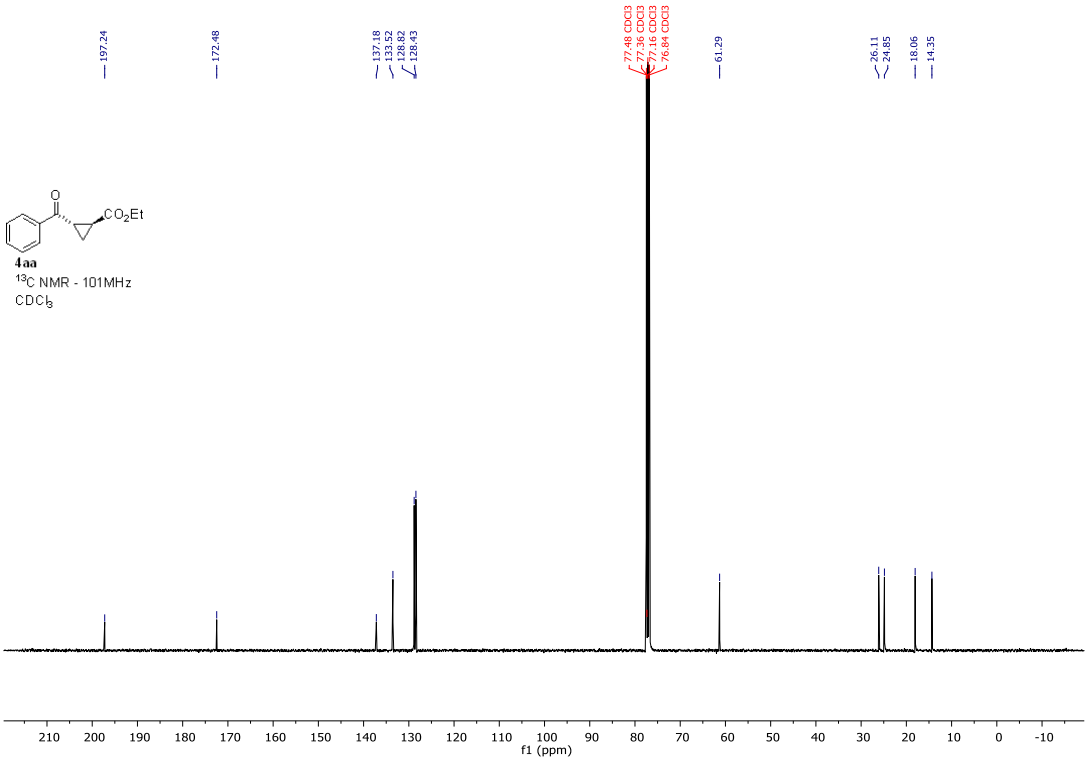
7.60
7.58
7.51
7.49
7.47
7.26
4.21
4.19
4.18
4.16
3.21
3.21
3.20
3.19
3.19
3.18
3.18
3.17
2.41
2.40
2.39
2.38
2.38
2.37
2.37
2.36
1.65
1.57
1.31
1.29
1.27
O
CO2Et
4aa
1H NMR - 400MHz
CDCl3
1.00
0.50
1.01
1.02
0.51
0.49
1.15
1.58
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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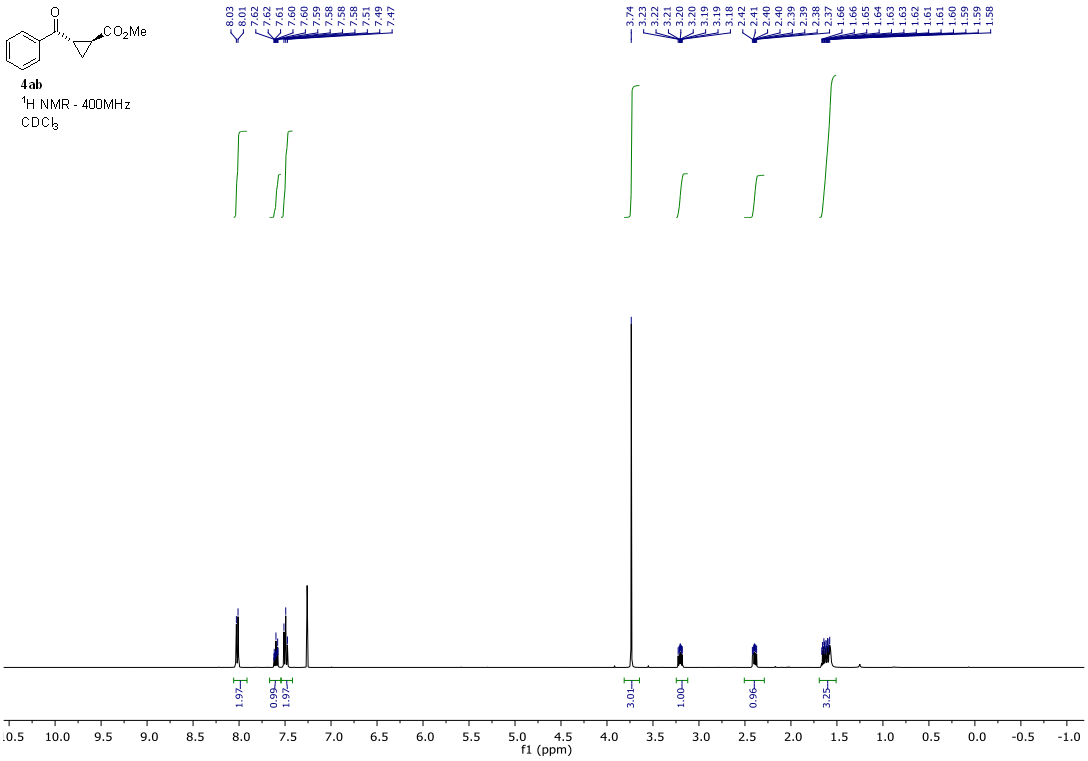
172.48
137.18
133.52
128.82
128.43
77.48 CDCl3
77.36 CDCl3
77.16 CDCl3
76.84 CDCl3
61.29
26.11
24.85
18.06
14.35
O
CO2Et
4aa
13C NMR - 101MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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1H NMR - 400MHz
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7.62
7.61
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7.60
7.59
7.58
7.58
7.58
7.51
7.49
7.47
3.74
3.23
3.22
3.21
3.20
3.20
3.19
3.19
3.18
2.42
2.41
2.40
2.40
2.39
2.38
2.38
2.37
1.66
1.66
1.65
1.64
1.63
1.63
1.62
1.61
1.61
1.60
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1.58
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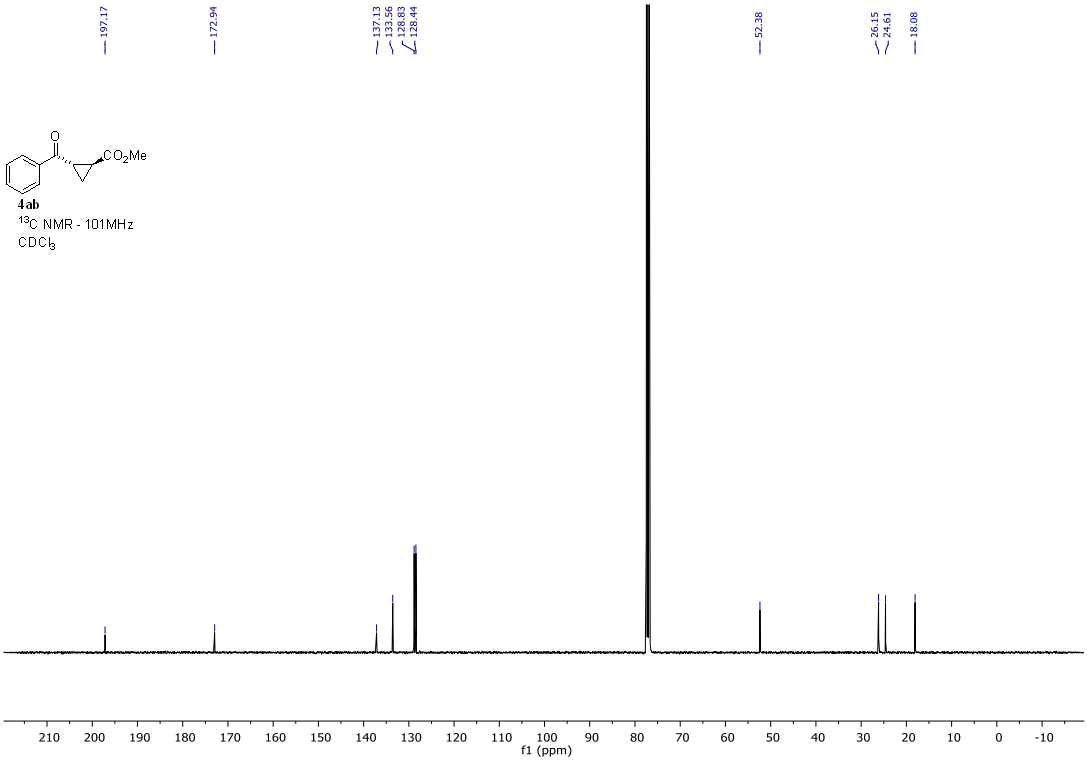
0.99
1.97
3.01
1.00
0.96
3.25
f1 (ppm)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13C NMR - 101MHz
CDCl3
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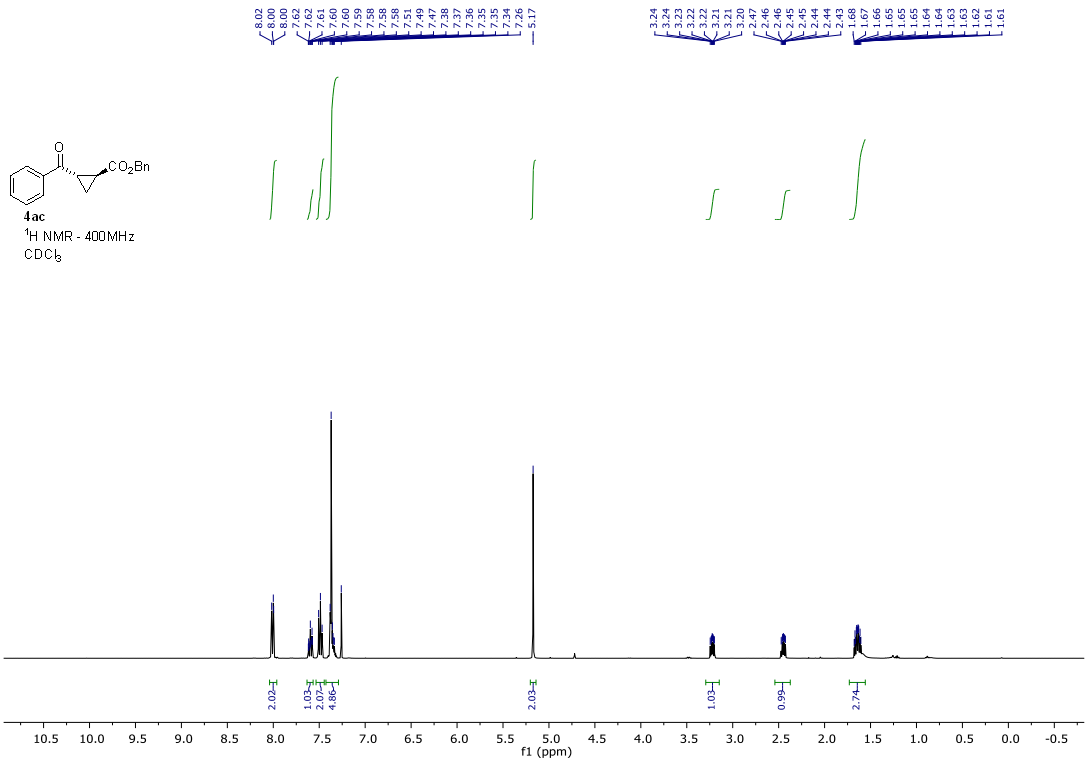
128.83
128.44
52.38
26.15
24.61
18.08
f1 (ppm)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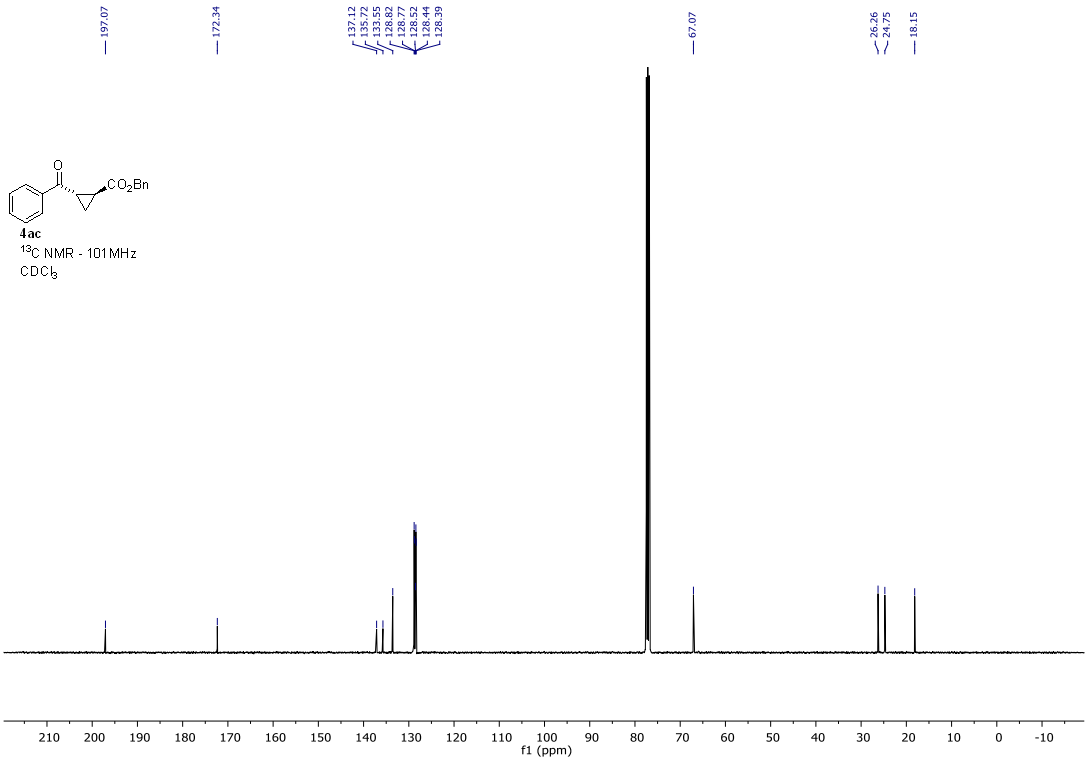
1H NMR - 400MHz
CDCl3
f1 (ppm)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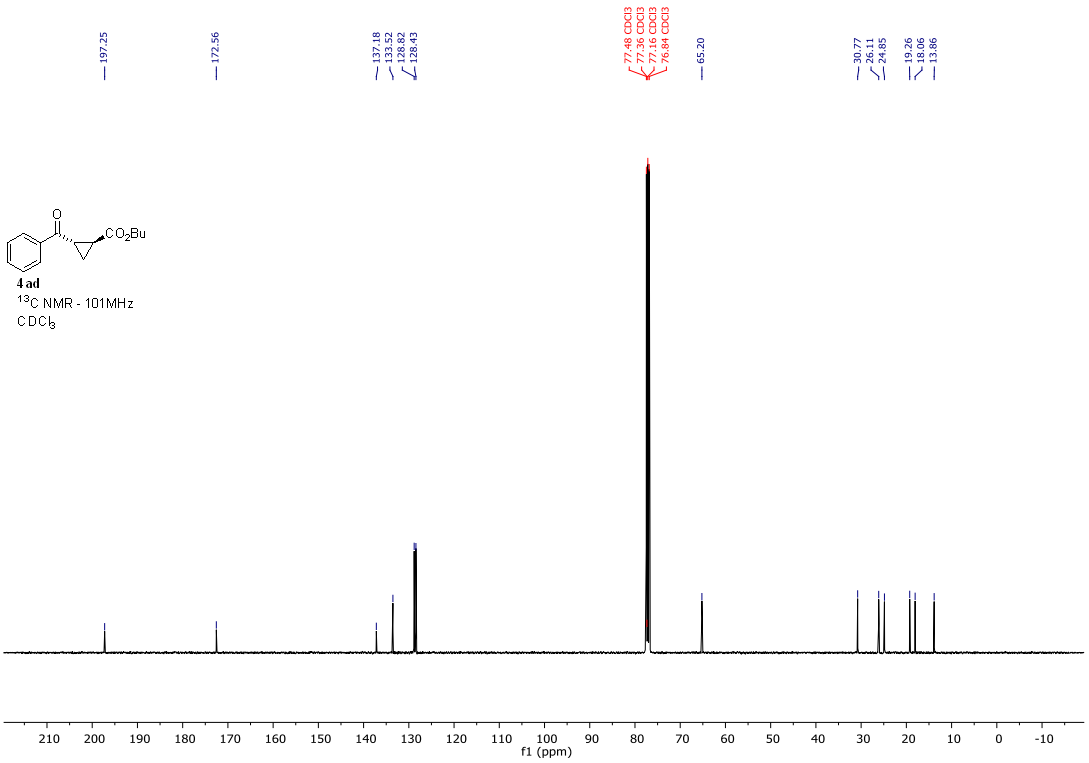
13C NMR - 101MHz
CDCl3
f1 (ppm)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172.56
137.18
133.52
128.82
128.43
77.48 CDCl3
77.36 CDCl3
77.16 CDCl3
76.84 CDCl3
65.20
30.77
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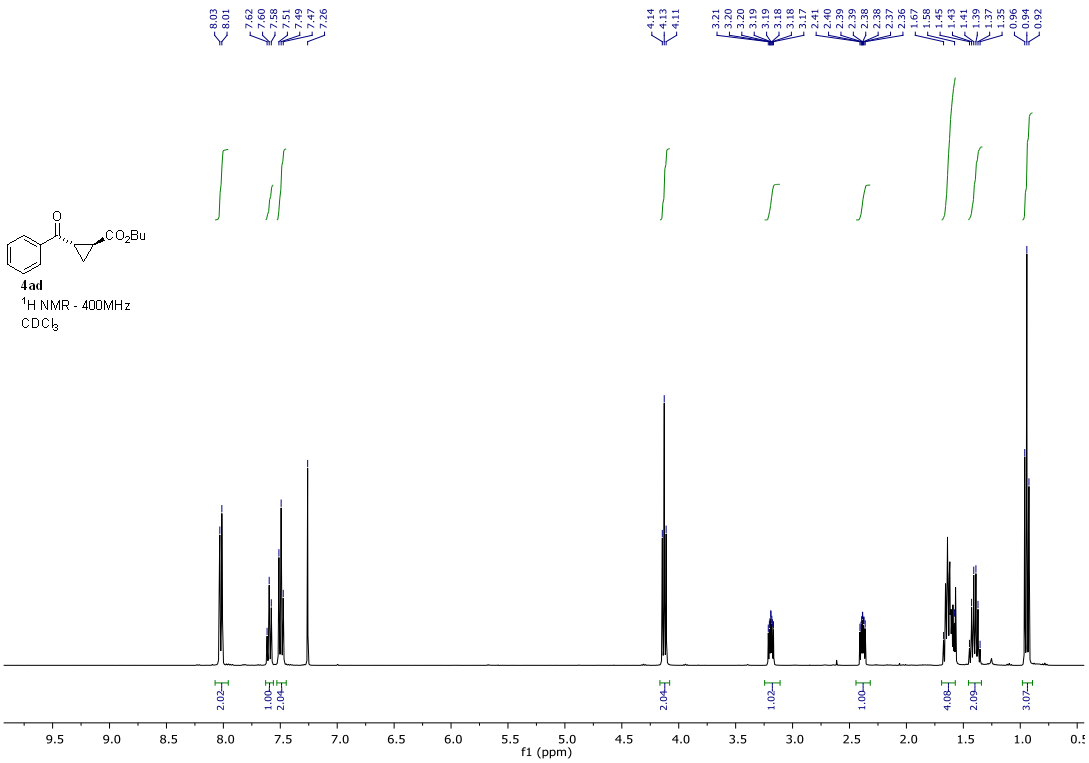
24.85
19.26
18.06
13.86
CO2Bu
4 ad
13C NMR - 101MHz
CDCl3
f1 (ppm)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8.01
7.62
7.60
7.58
7.51
7.49
7.47
7.26
4.14
4.13
4.11
3.21
3.20
3.20
3.19
3.19
3.18
3.18
3.17
2.41
2.40
2.39
2.39
2.38
2.38
2.37
2.36
1.67
1.58
1.45
1.43
1.41
1.39
1.37
1.35
0.96
0.94
0.92
CO2Bu
4 ad
1H NMR - 400MHz
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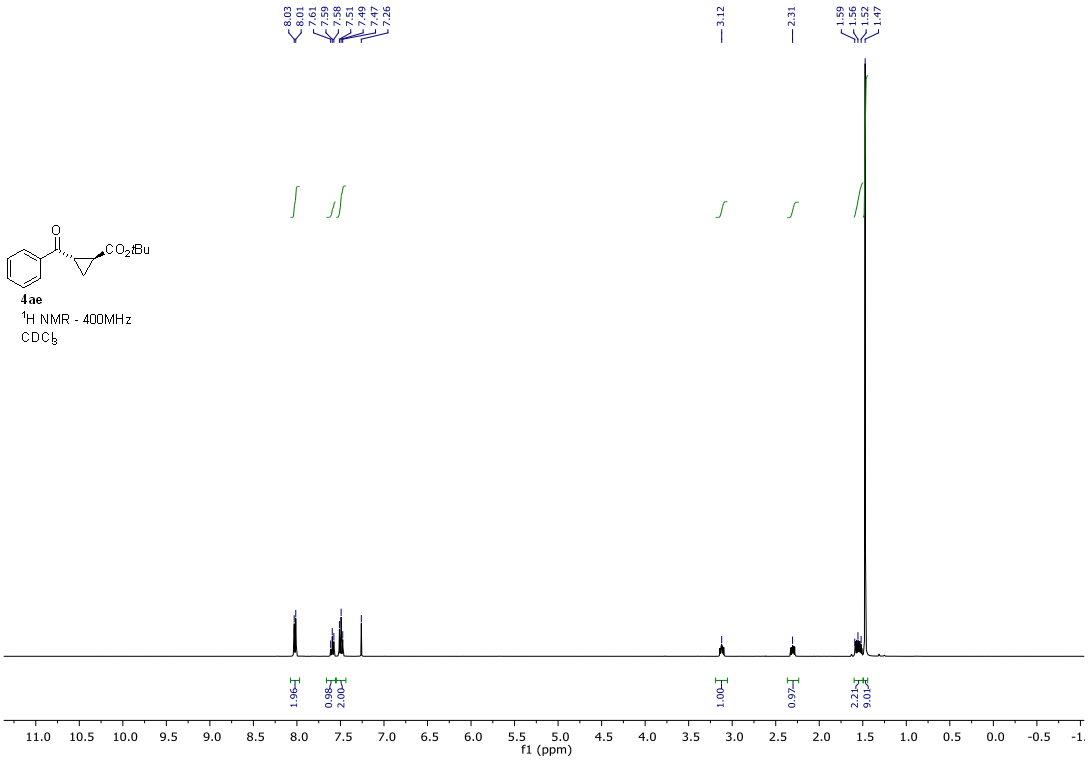
1.00
2.04
2.04
1.02
1.00
4.08
2.09
3.07
f1 (ppm)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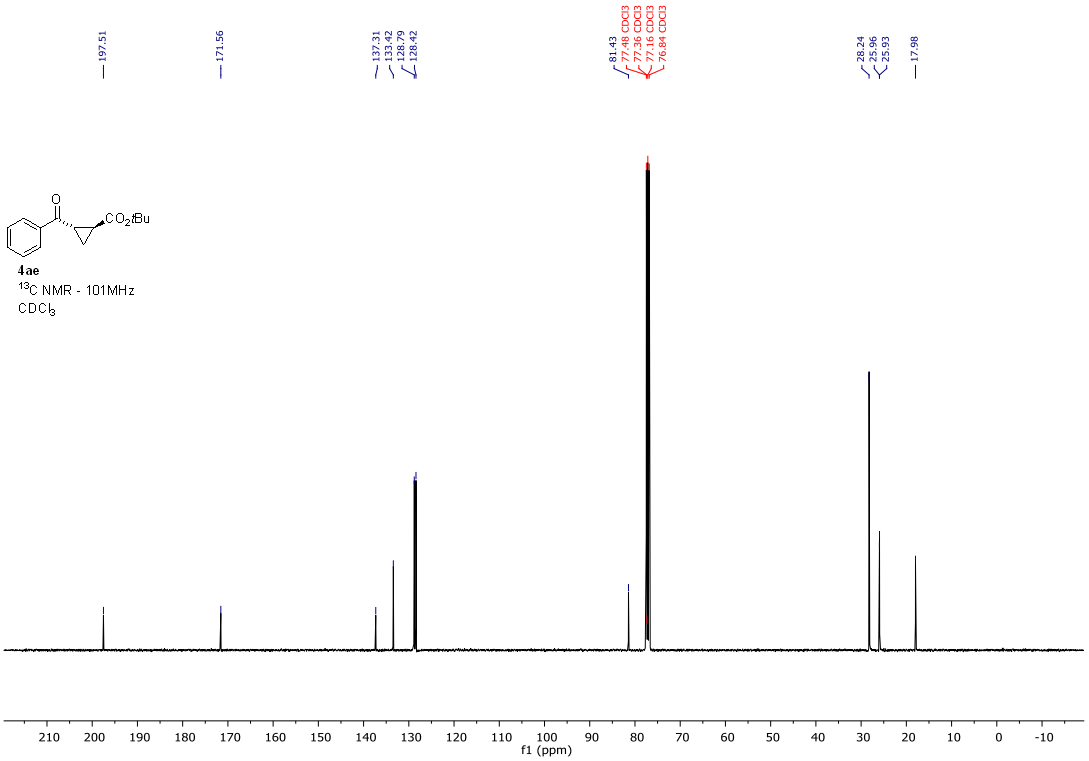
8.01
7.61
7.59
7.58
7.51
7.49
7.47
7.26
3.12
2.31
1.59
1.56
1.52
1.47
O
CO2tBu
4ae
1H NMR - 400MHz
CDCl3
1.96
0.98
2.00
1.00
0.97
2.21
9.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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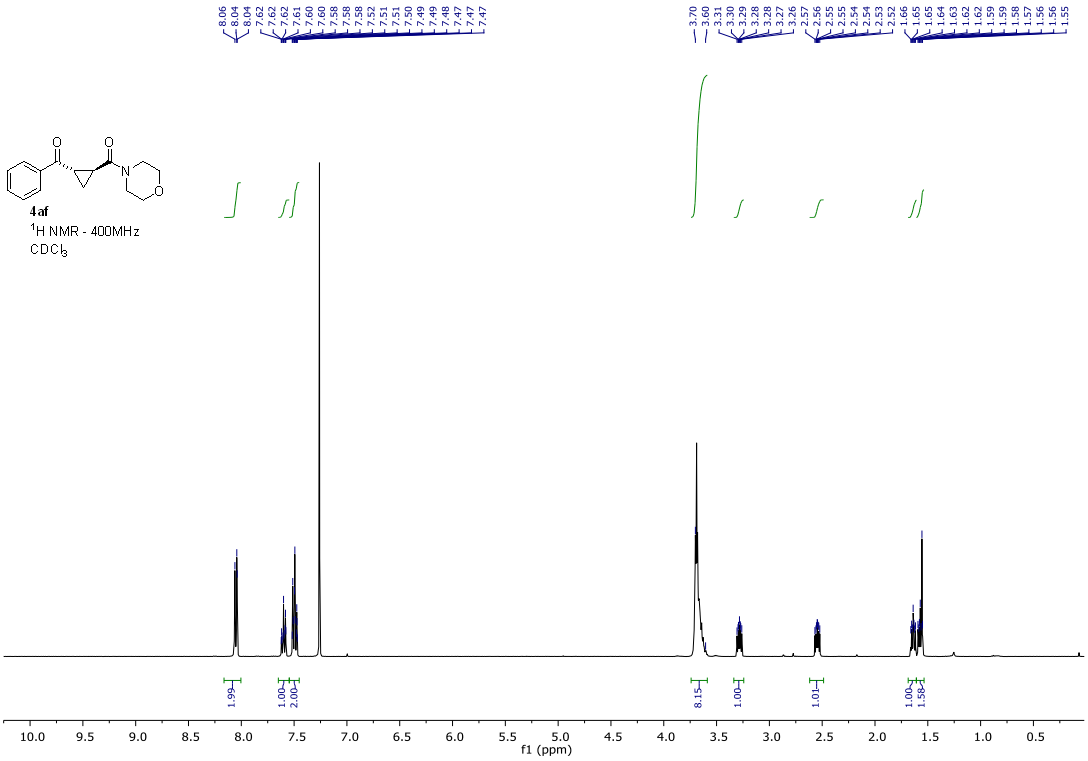
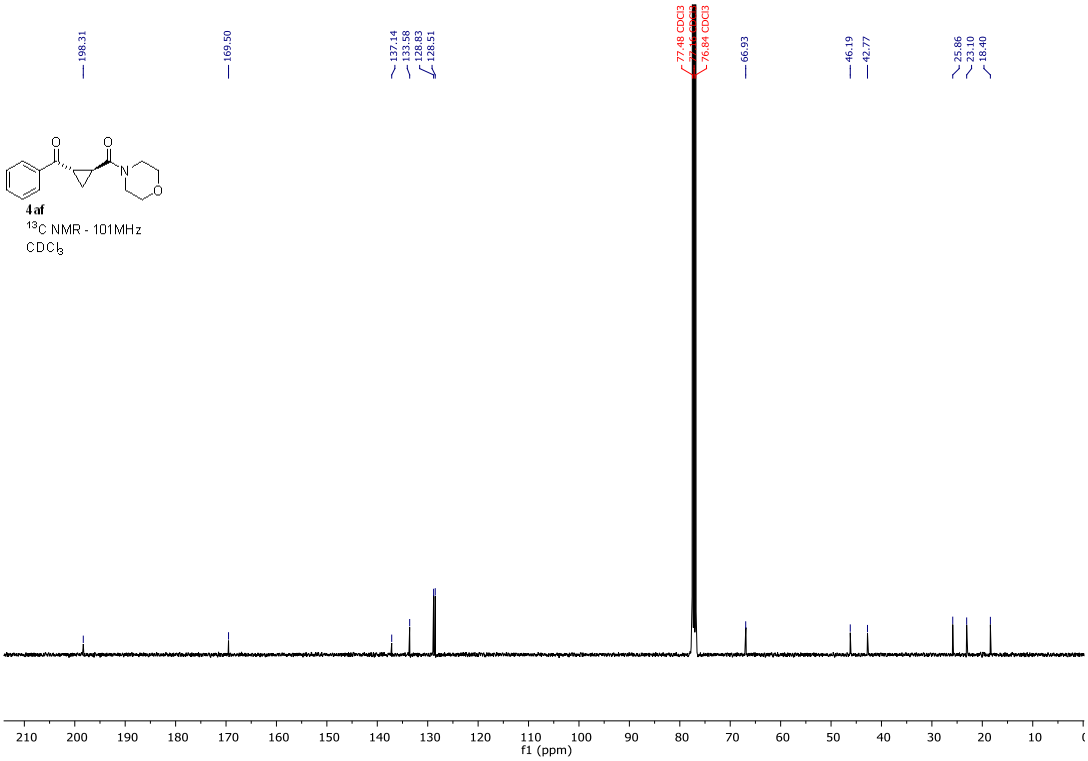
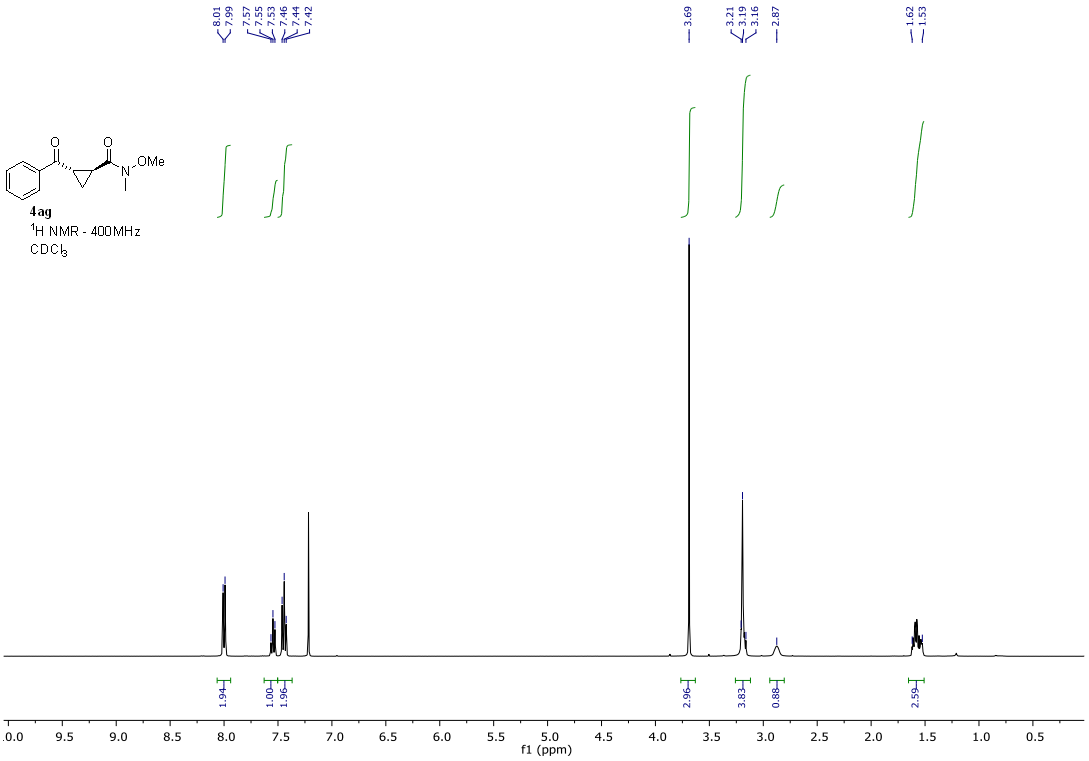
128.79
128.42
81.43
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
28.24
25.96
25.93
17.98
O
CO2tBu
4ae
13C NMR - 101MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


4af
^{1}H NMR - 400MHz
$CDCl_3$
f1 (ppm)


4af
^{13}C NMR - 101MHz
$CDCl_3$
f1 (ppm)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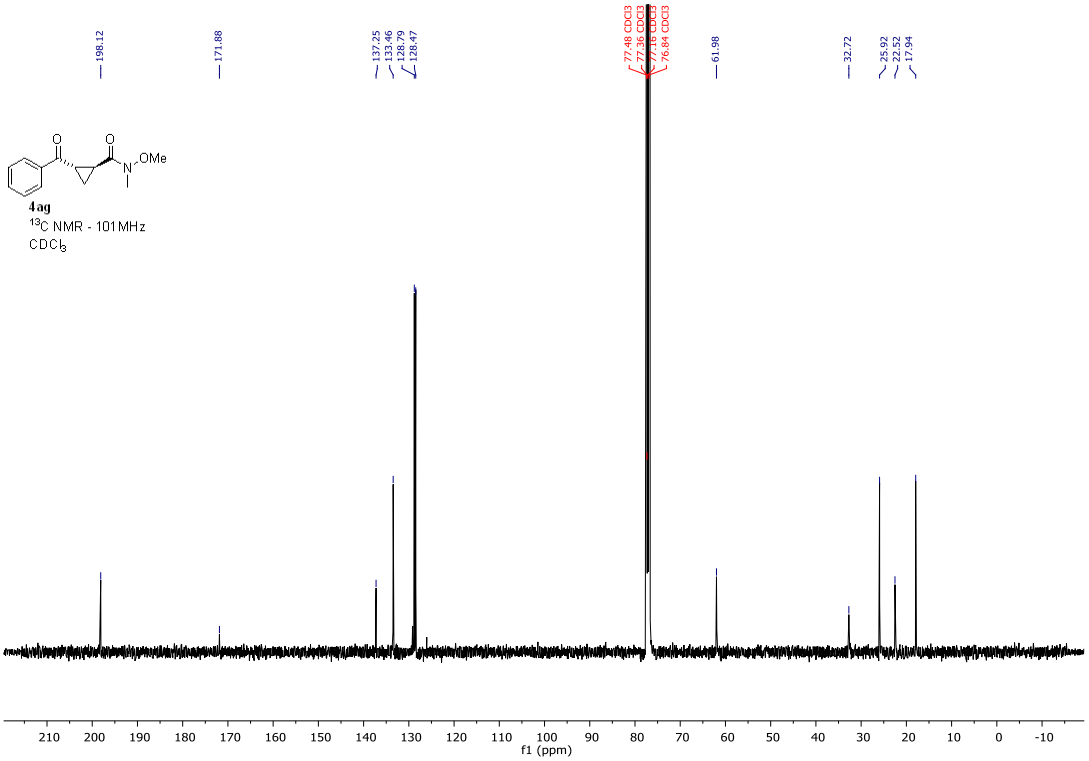
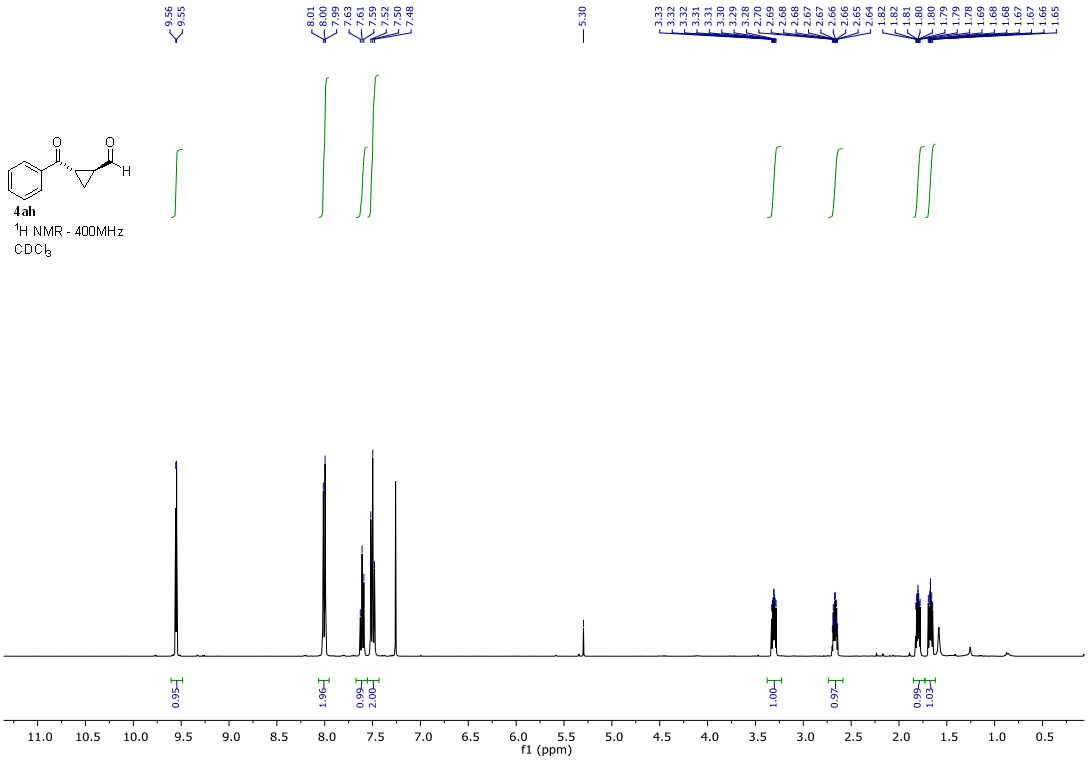
7.57
7.55
7.53
7.46
7.44
7.42
3.69
3.21
3.19
3.16
2.87
1.62
1.53
4ag
1H NMR - 400MHz
CDCl3
1.94
1.00
1.96
2.96
3.83
0.88
2.59
f1 (ppm)


198.12
171.88
137.25
133.46
128.79
128.47
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.98
32.72
25.92
22.52
17.94
4ag
13C NMR - 101MHz
CDCl3
f1 (ppm)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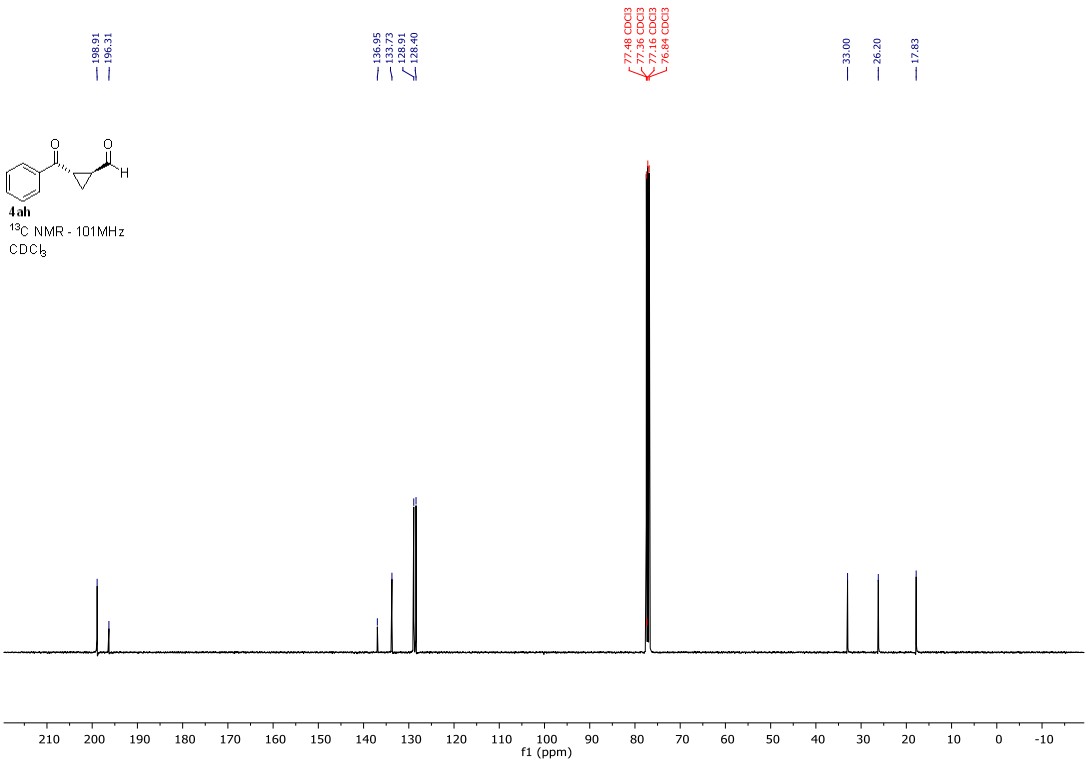
CDCl3
f1 (ppm)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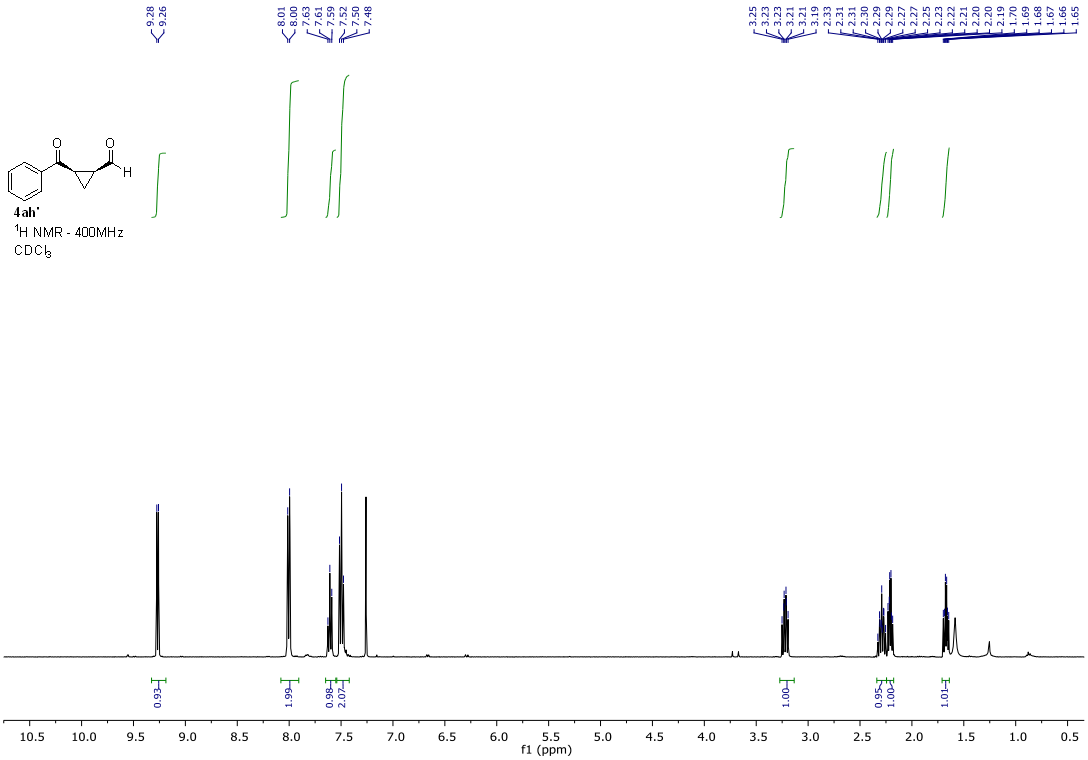
13C NMR - 101MHz
CDCl3
f1 (ppm)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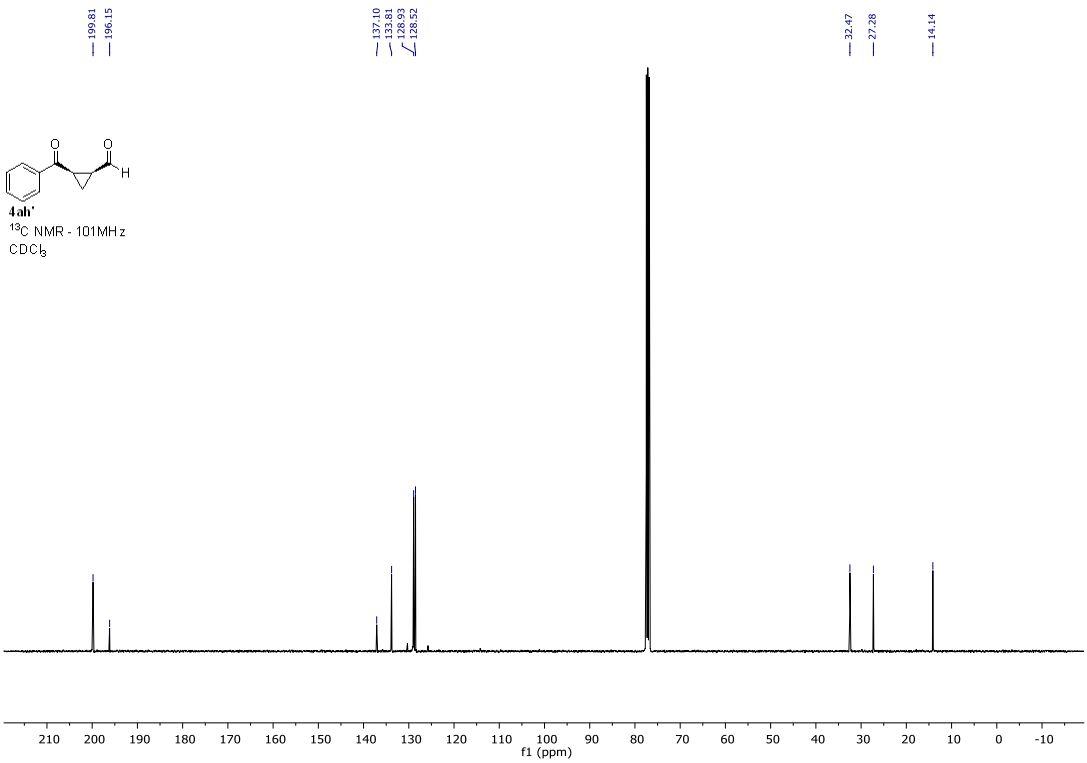
1H NMR - 400MHz
CDCl3
f1 (ppm)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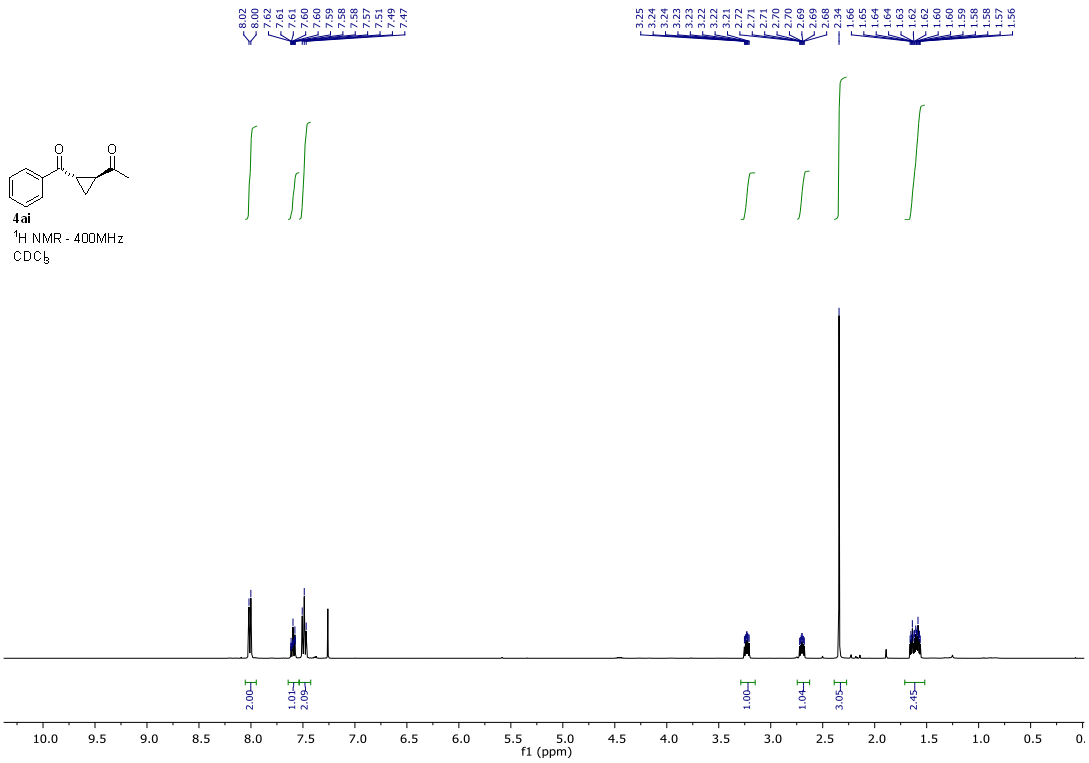
13C NMR - 101MHz
CDCl3
f1 (ppm)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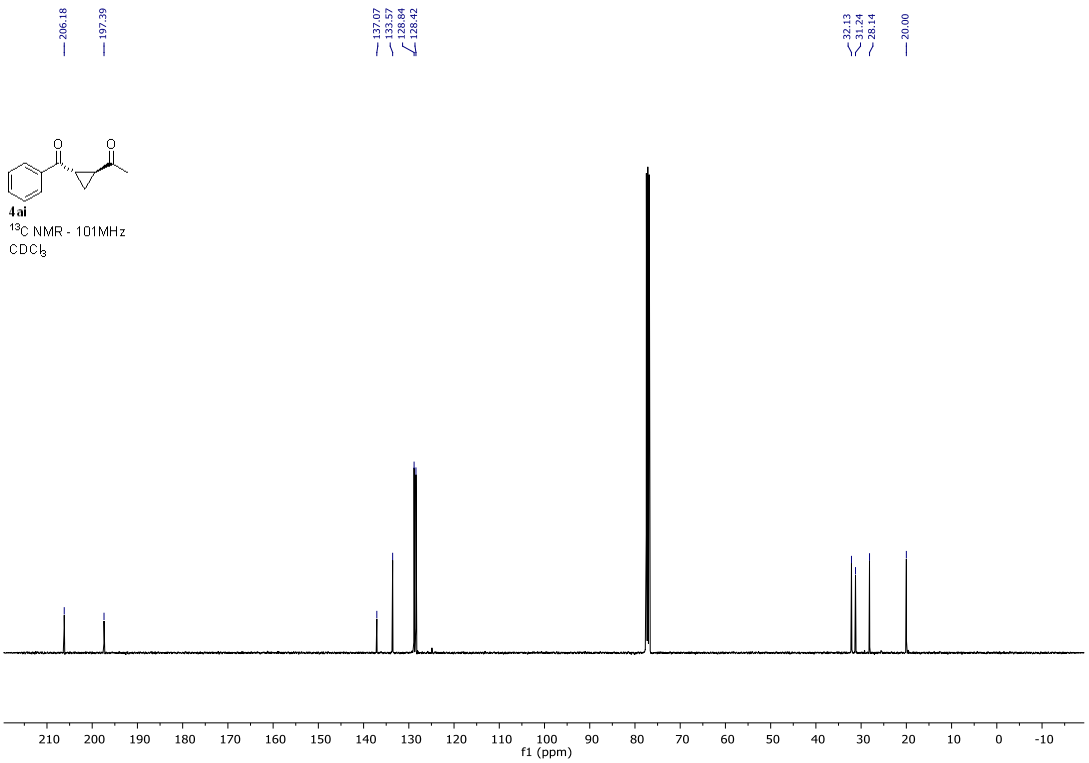
1H NMR - 400MHz
CDCl3
f1 (ppm)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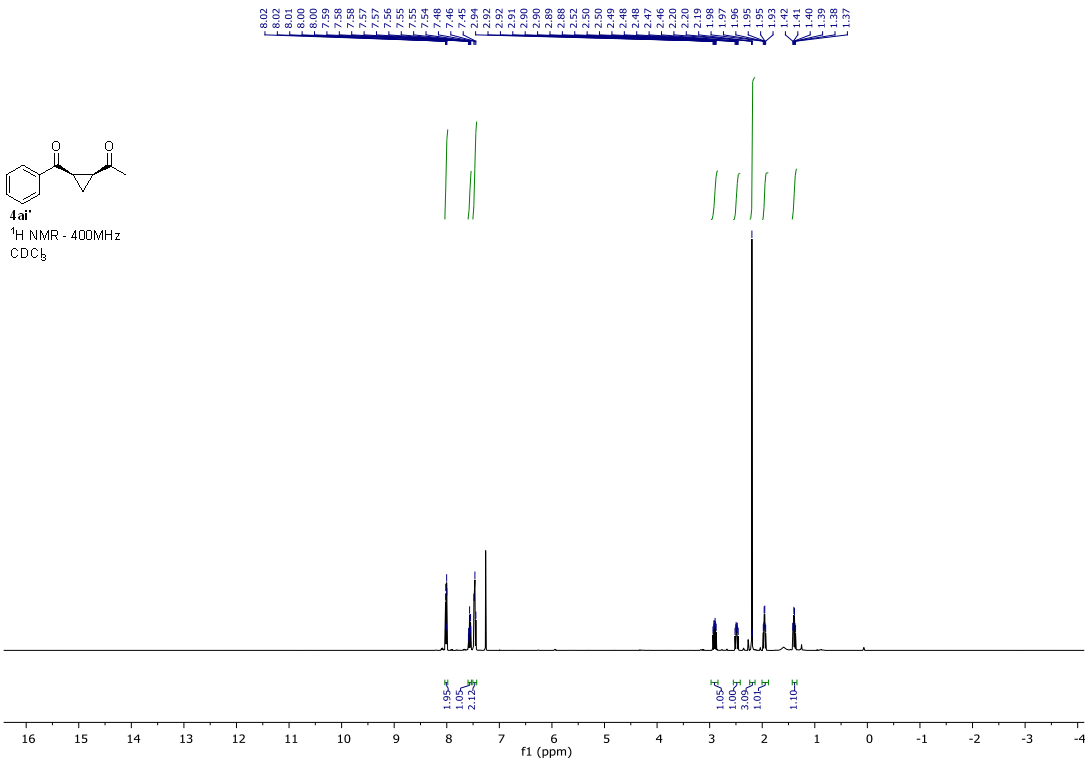
CDCl3
f1 (ppm)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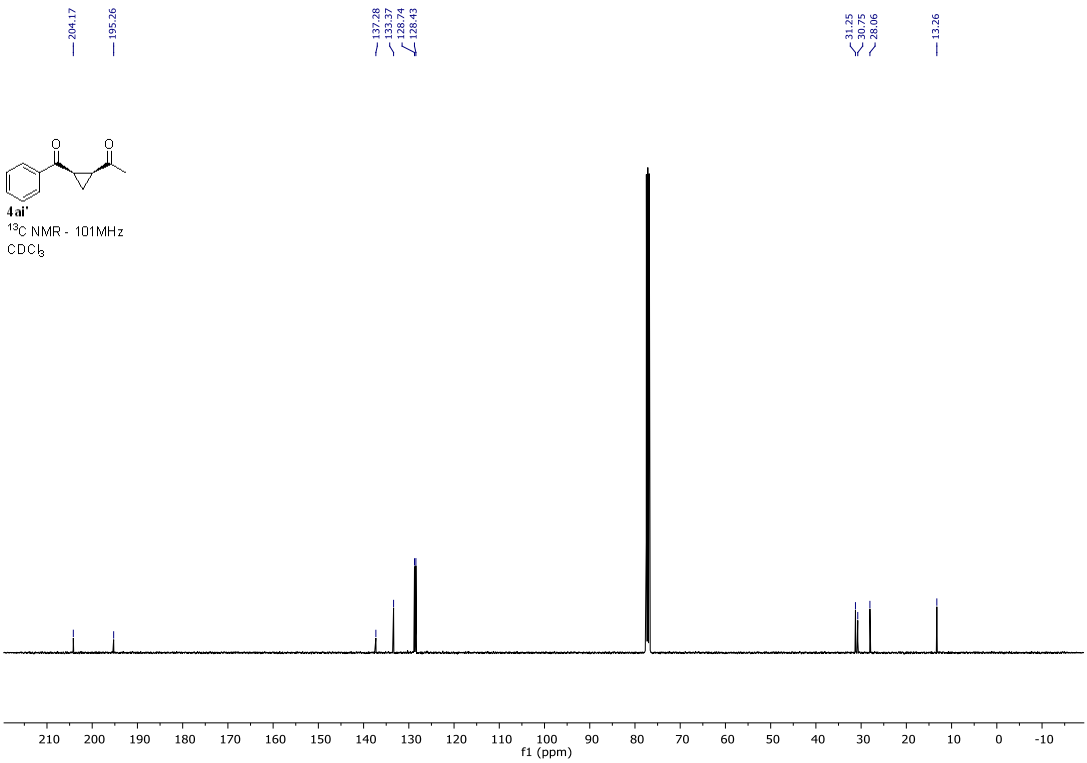
1H NMR - 400MHz
CDCl3
f1 (ppm)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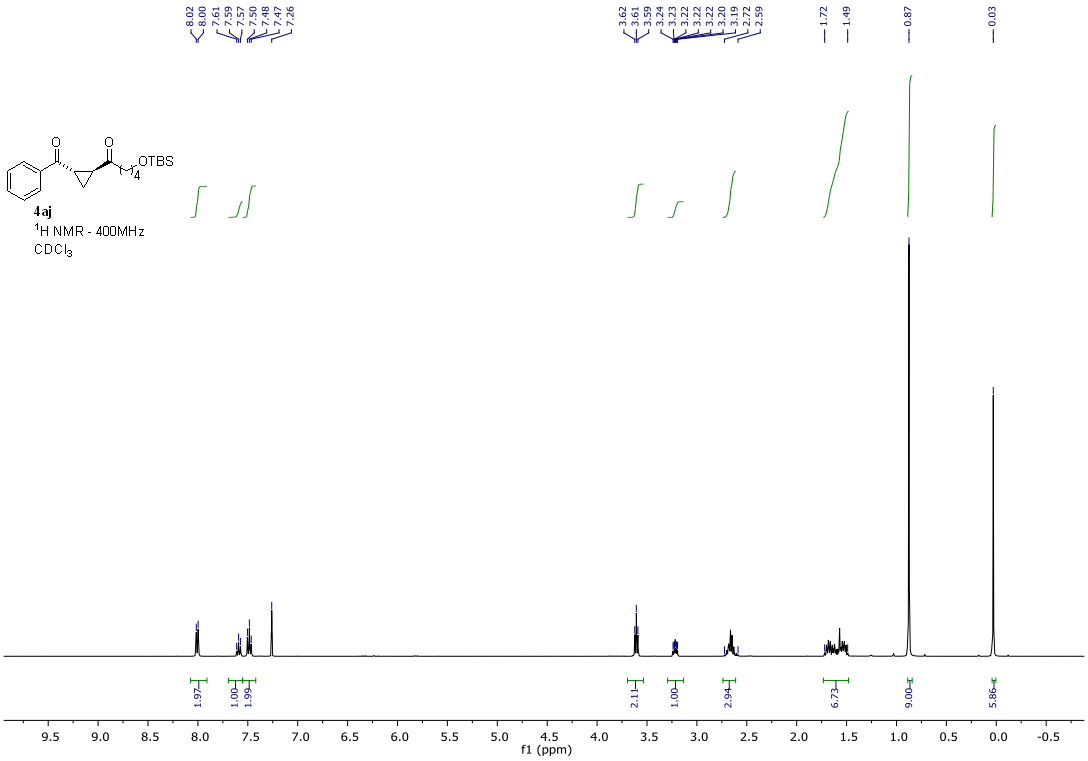
CDCl3
f1 (ppm)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3.59
3.24
3.23
3.22
3.22
3.22
3.20
3.19
2.72
2.59
1.72
1.49
0.87
0.03
OTBS
4
4aj
1H NMR - 400MHz
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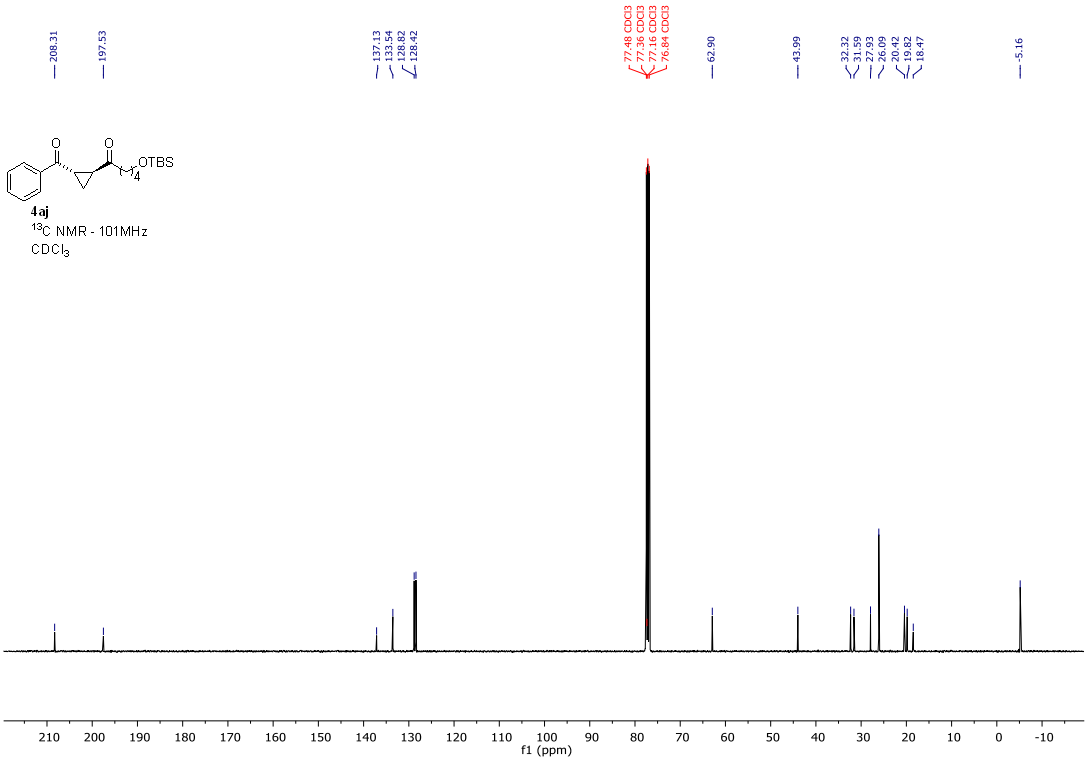
1.00
1.99
2.11
1.00
2.94
6.73
9.00
5.86
f1 (ppm)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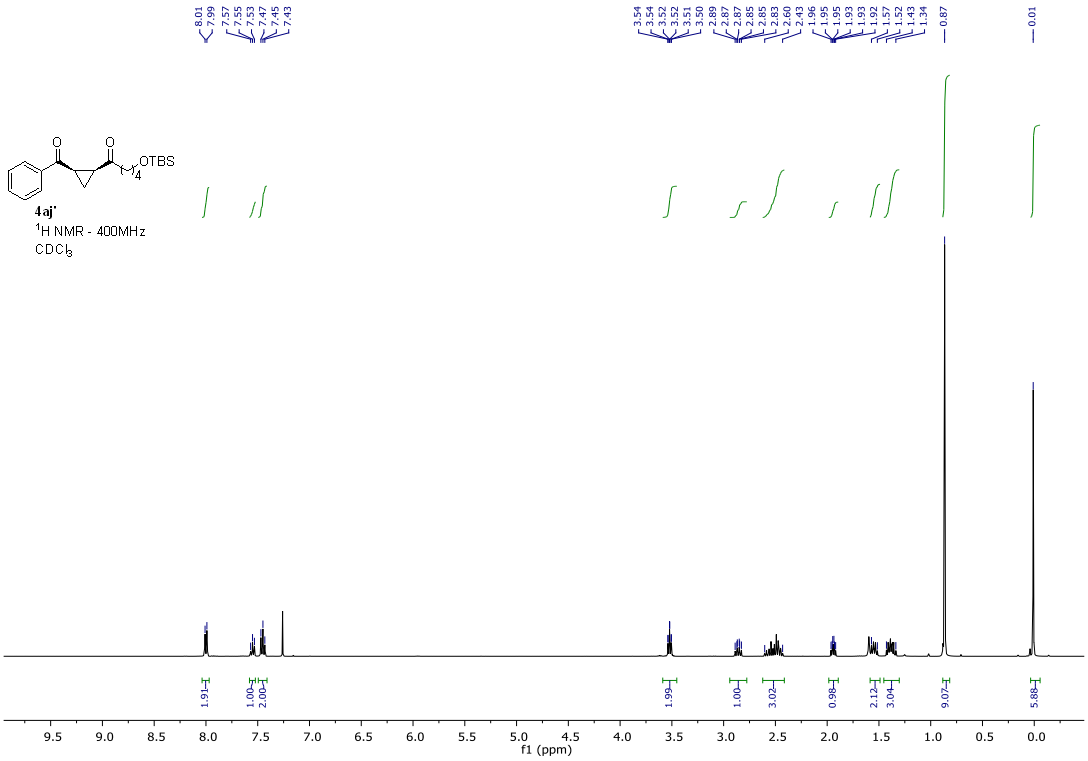
128.42
77.48 CDCl3
77.36 CDCl3
77.16 CDCl3
76.84 CDCl3
62.90
43.99
32.32
31.59
27.93
26.09
20.42
19.82
18.47
-5.16
OTBS
4
4aj
13C NMR - 101MHz
CDCl3
f1 (ppm)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2.60
2.43
1.96
1.95
1.95
1.93
1.93
1.92
1.57
1.52
1.43
1.34
0.87
0.01
OTBS
4
4aj'
1H NMR - 400MHz
CDCl3
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1.99
1.00
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2.12
3.04
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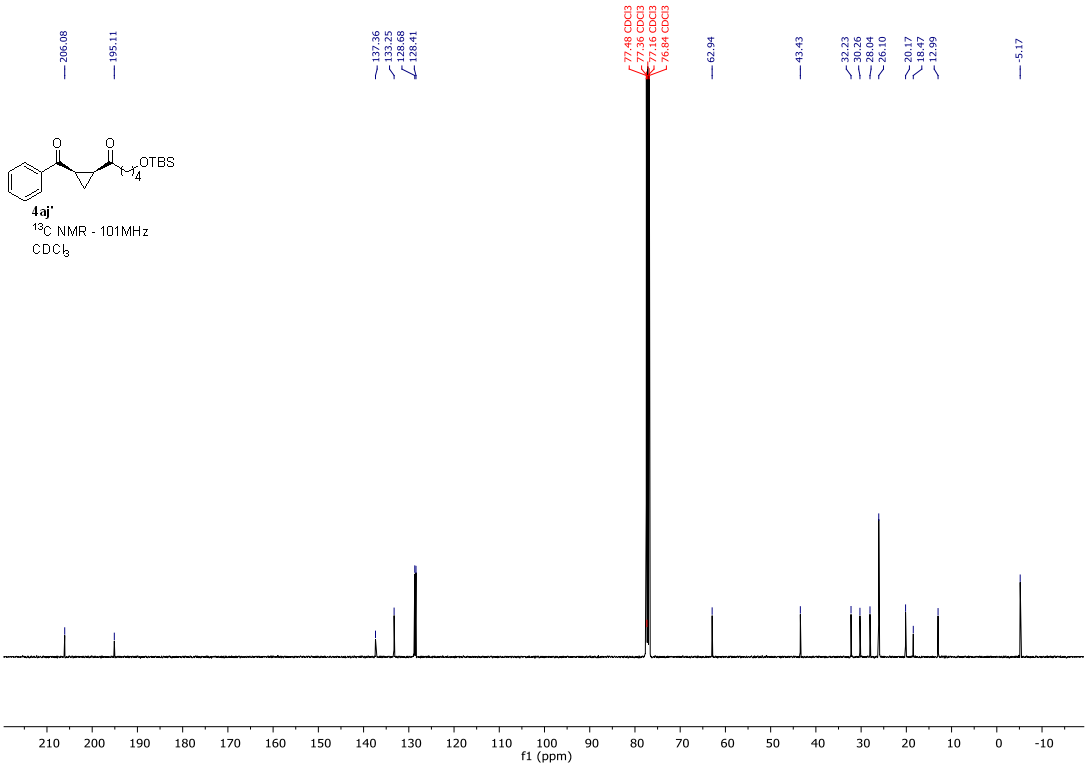
5.88
f1 (ppm)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77.36 CDCl3
77.16 CDCl3
76.84 CDCl3
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43.43
32.23
30.26
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12.99
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OTBS
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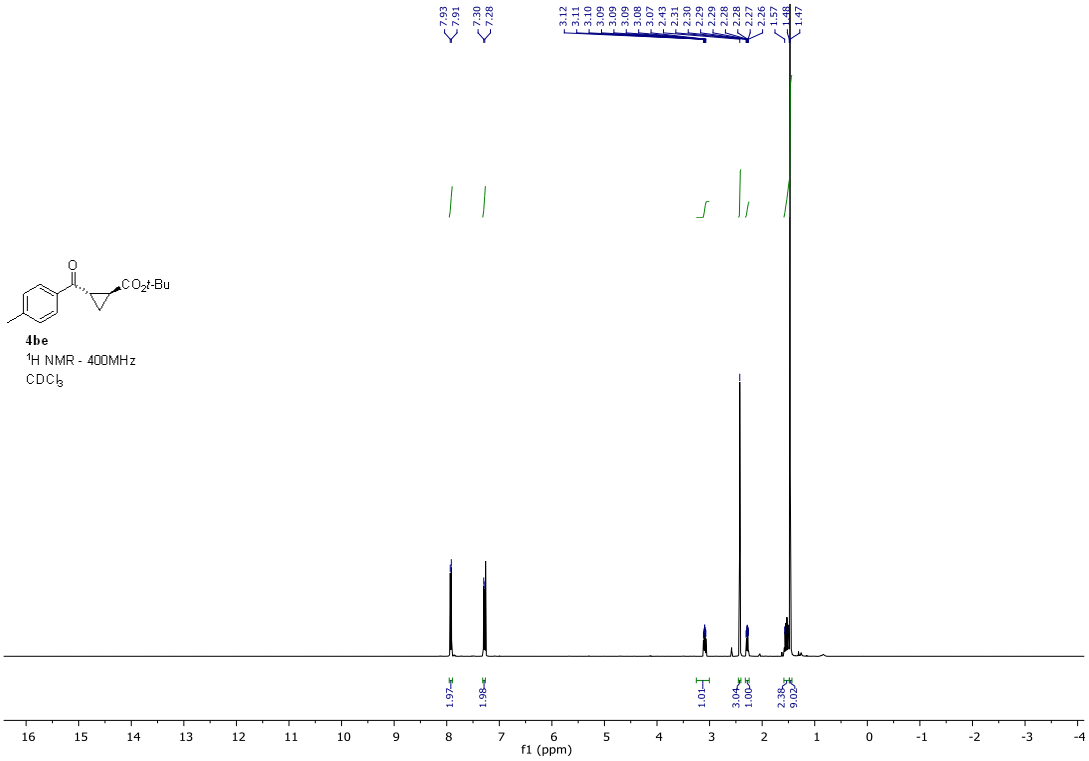
4aj'
13C NMR - 101MHz
CDCl3
f1 (ppm)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3.09
3.09
3.08
3.07
2.43
2.31
2.30
2.29
2.29
2.28
2.28
2.27
2.26
1.57
1.48
1.47
O
CO2t-Bu
4be
1H NMR - 400MHz
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1.98
1.01
3.04
1.00
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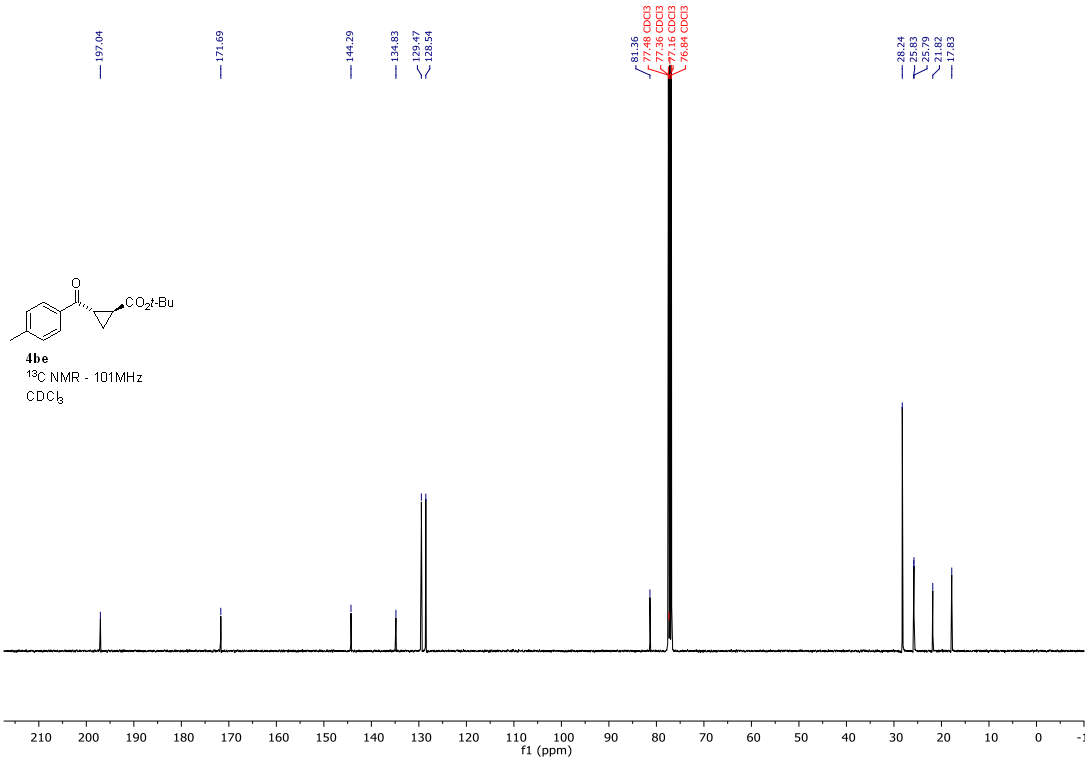
f1 (ppm)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128.54
81.36
77.48 CDCl3
77.36 CDCl3
77.16 CDCl3
76.84 CDCl3
28.24
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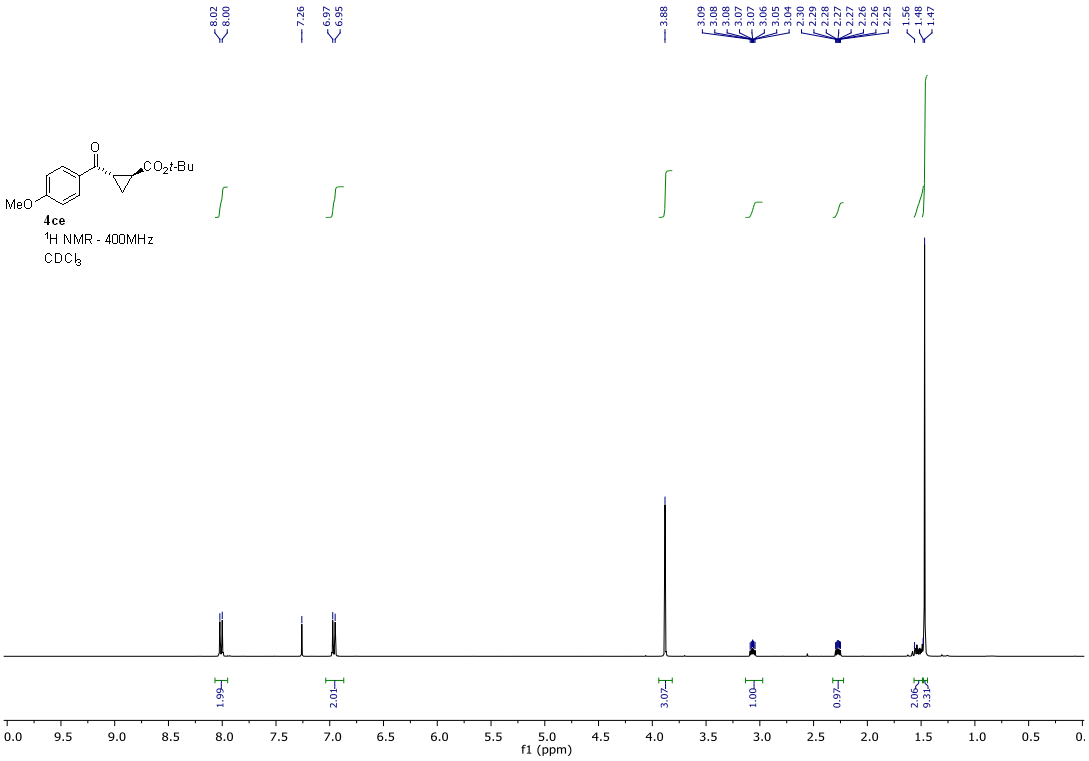
25.79
21.82
17.83
O
CO2t-Bu
4be
13C NMR - 101MHz
CDCl3
f1 (ppm)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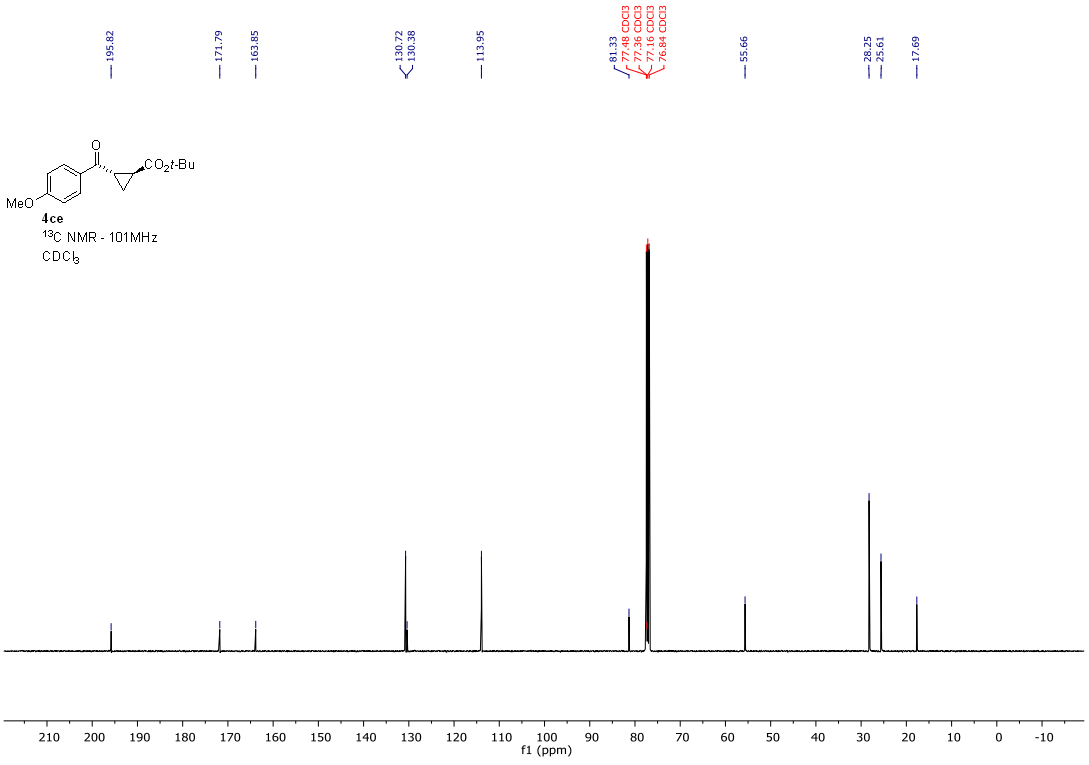
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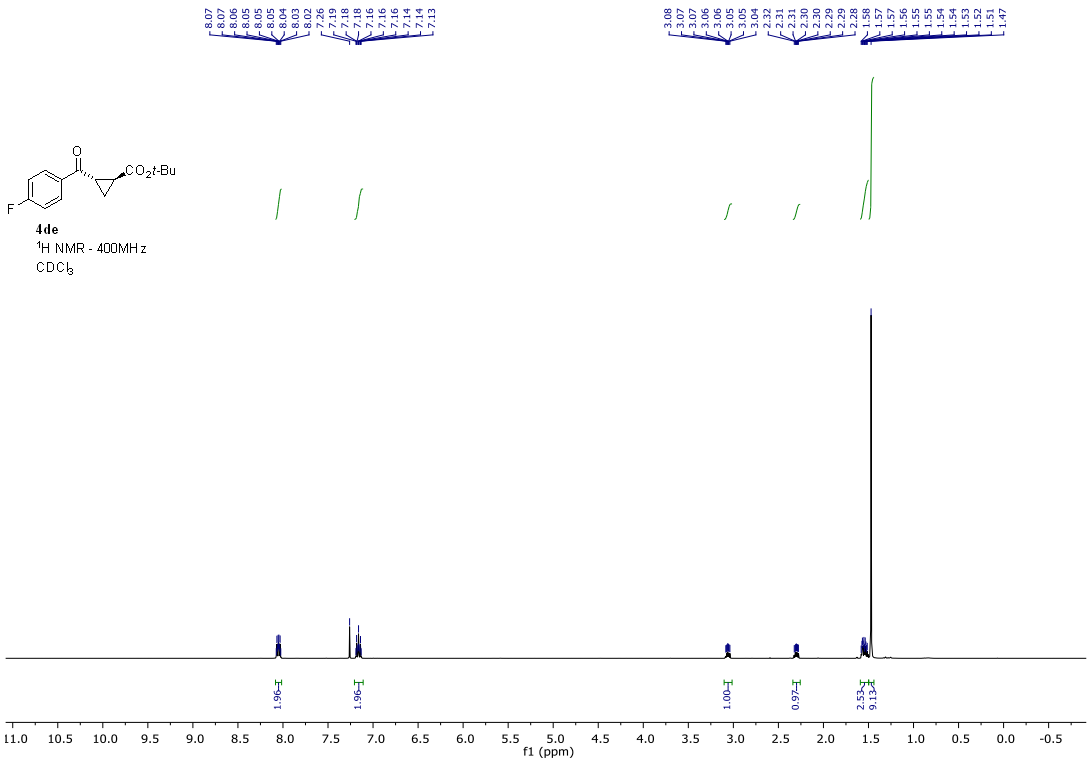
13C NMR - 101MHz
CDCl3
f1 (ppm)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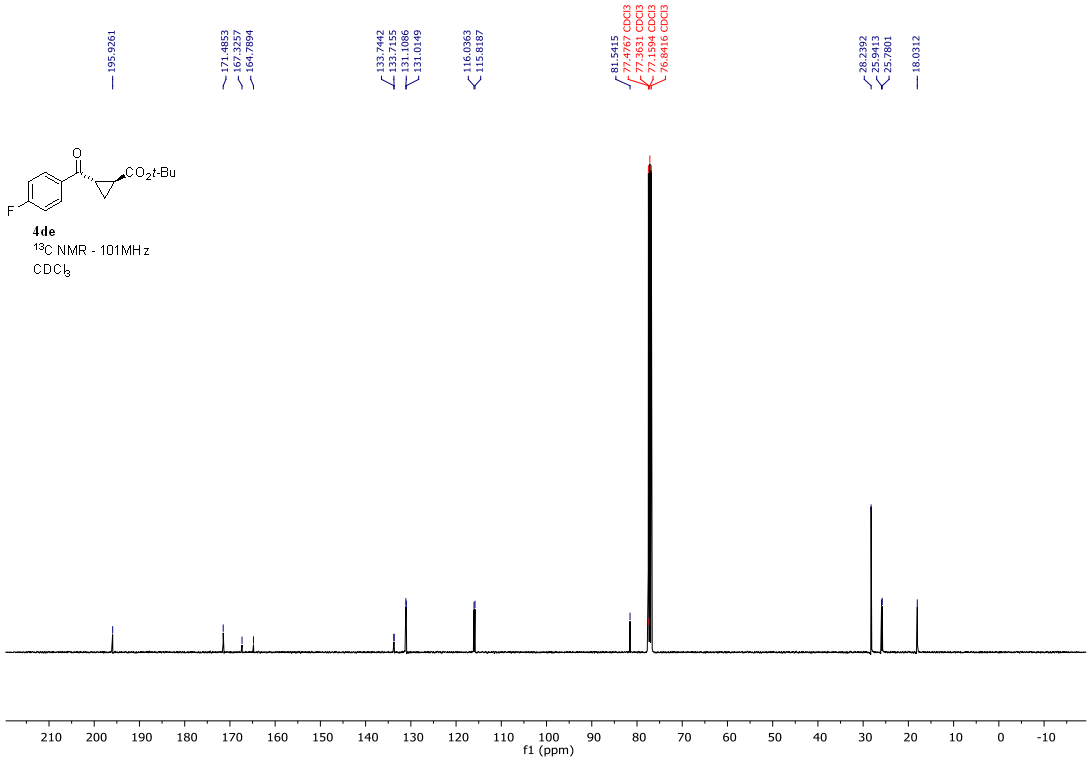
1.52
1.51
1.47
O
CO2t-Bu
F
4de
1H NMR - 400MHz
CDCl3
1.96
1.96
1.00
0.97
2.53
9.13
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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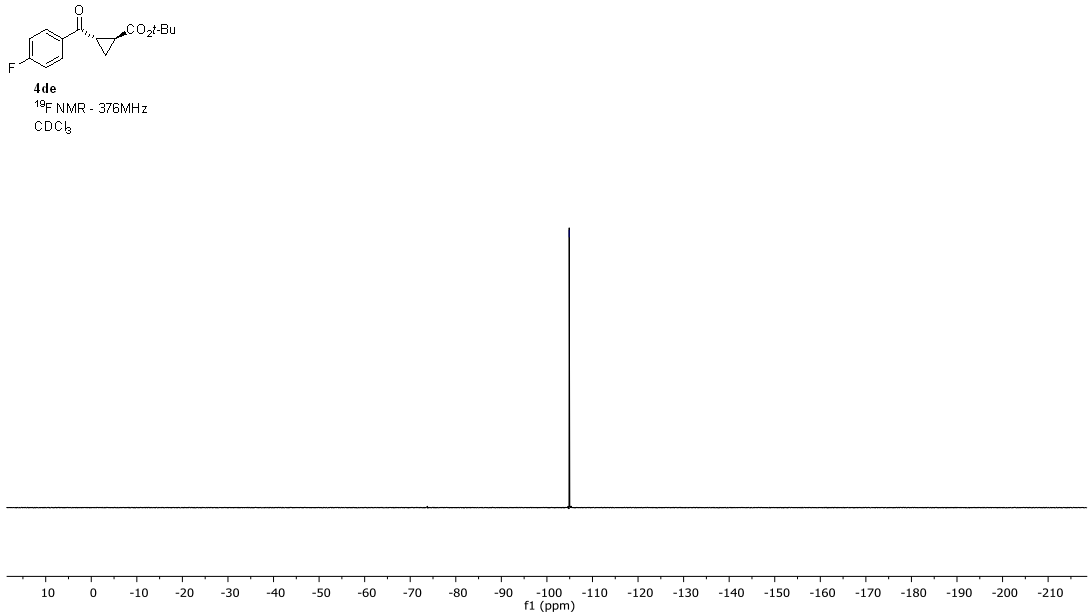
77.4767 CDCl3
77.1951 CDCl3
77.1594 CDCl3
76.8416 CDCl3
28.2392
25.9413
25.7801
18.0312
O
CO2t-Bu
F
4de
13C NMR - 101MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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F
4de
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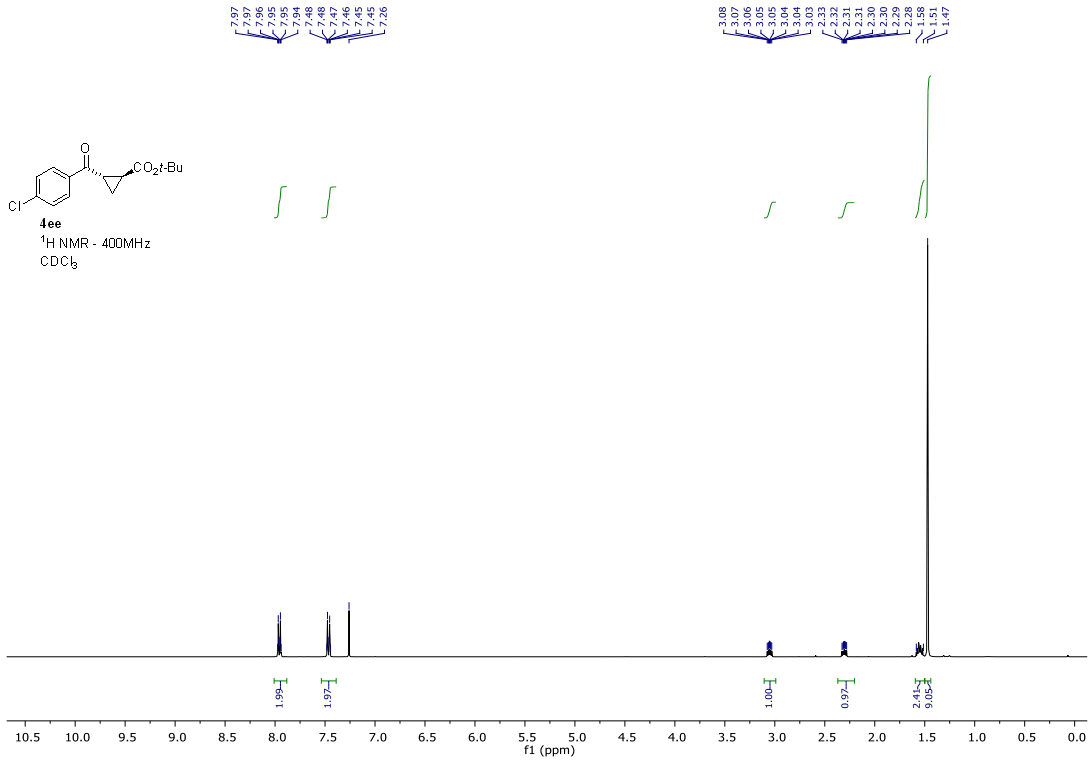
f1 (ppm)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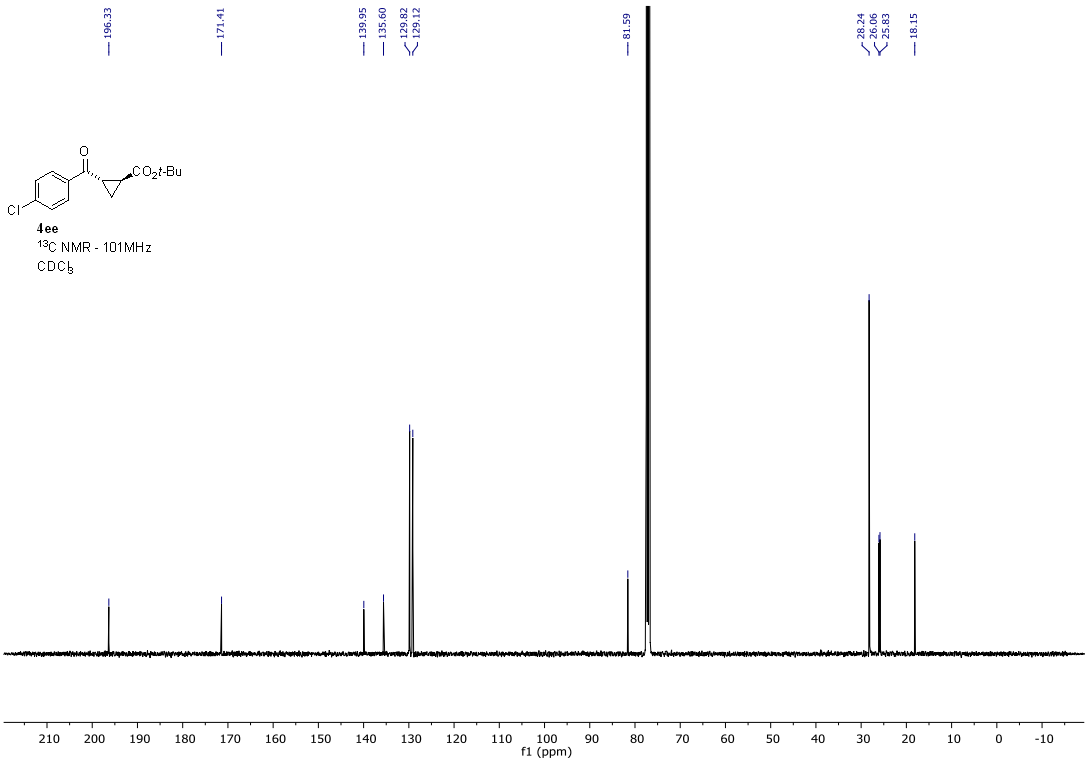
3.08 3.07 3.06 3.05 3.05 3.04 3.04 3.03 3.03 2.32 2.31 2.31 2.30 2.29 2.28 1.58 1.51 1.47
O
CO2t-Bu
Cl
4ee
1H NMR - 400MHz
CDCl3
1.99 1.97 1.00 0.97 2.41 9.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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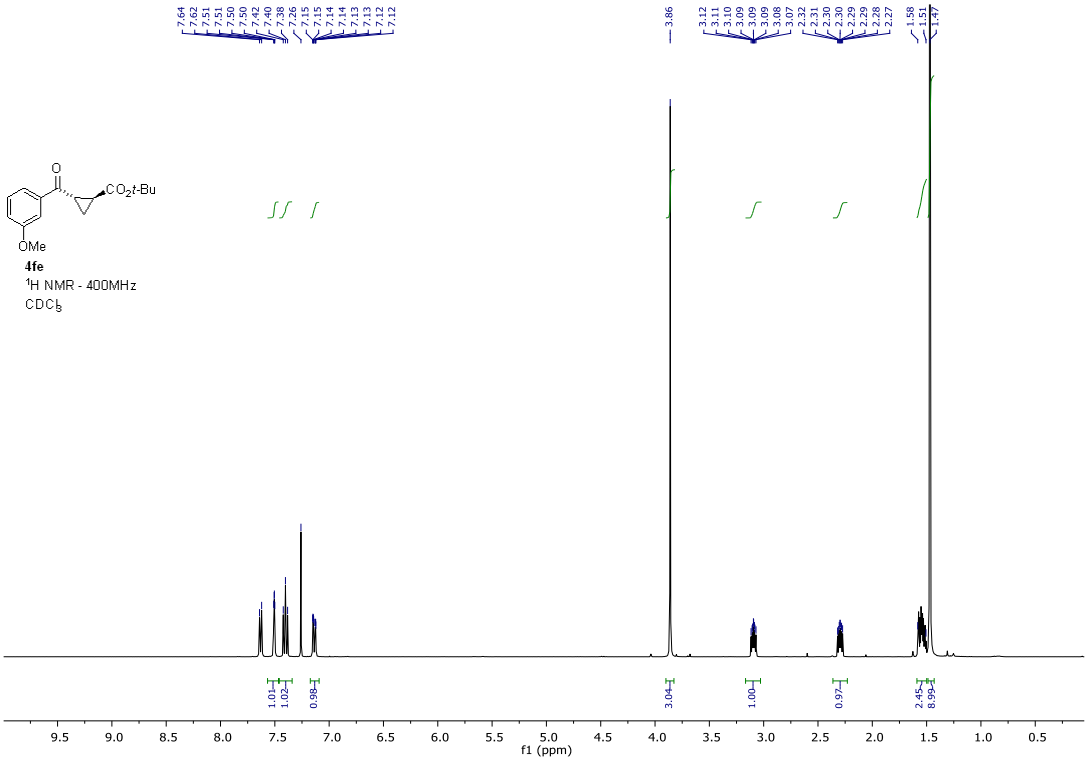
26.06
25.83
18.15
CO2t-Bu
Cl
4ee
13C NMR - 101MHz
CDCl3
f1 (ppm)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7.14
7.13
7.13
7.12
7.12
3.86
3.12
3.11
3.10
3.09
3.09
3.09
3.08
3.07
2.32
2.31
2.30
2.30
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2.29
2.28
2.27
1.58
1.51
1.47
CO2t-Bu
OMe
4fe
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0.98
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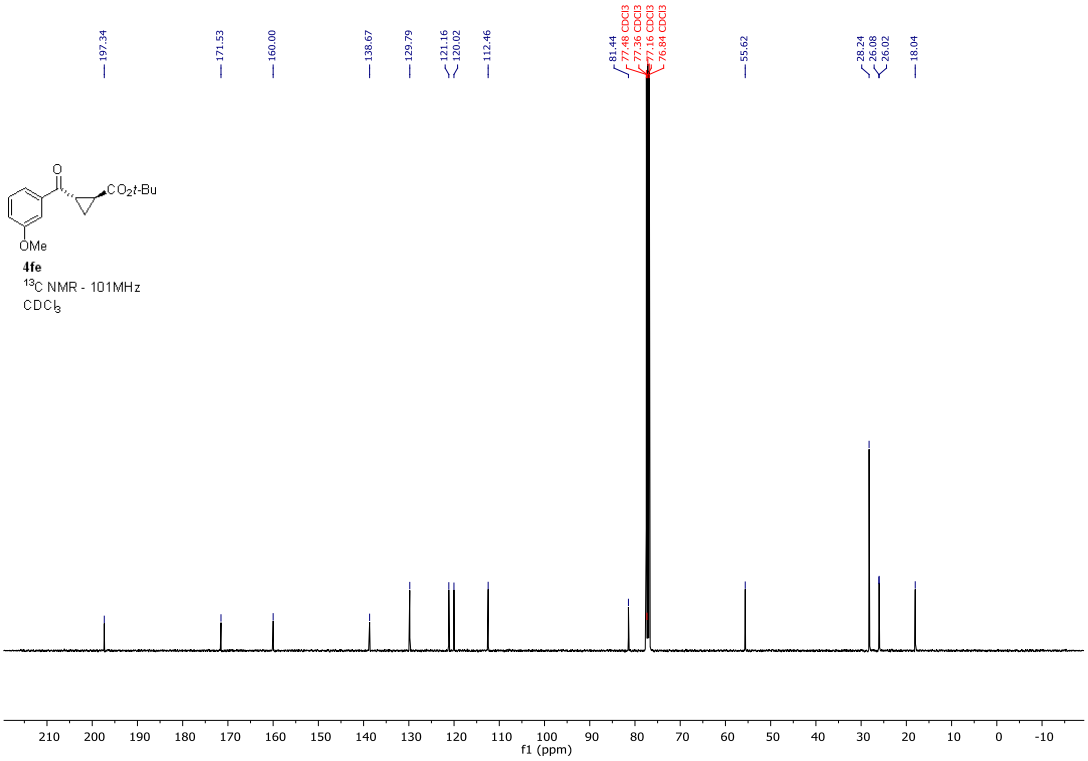
6.99
f1 (ppm)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112.46
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77.46 CDCl3
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77.16 CDCl3
76.84 CDCl3
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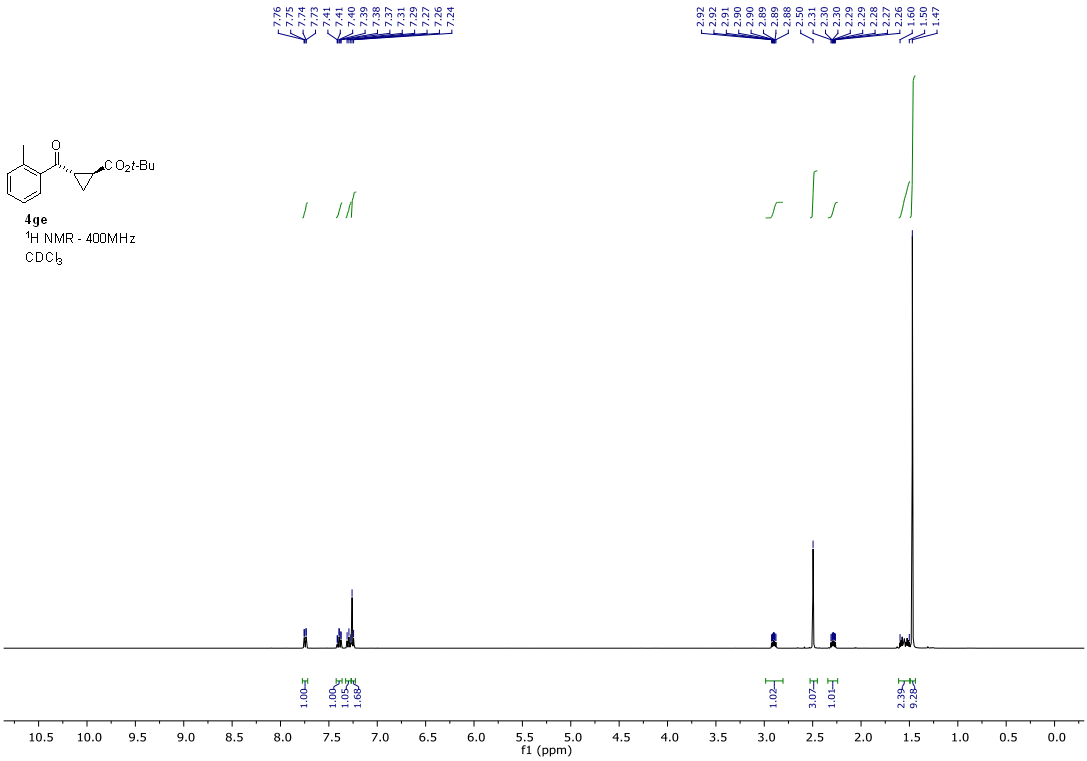
OMe
4fe
13C NMR - 101MHz
CDCl3
f1 (ppm)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7.39
7.38
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7.29
7.27
7.26
7.24
2.92
2.91
2.90
2.89
2.88
2.50
2.31
2.30
2.29
2.28
2.27
2.26
1.60
1.50
1.47
CO2t-Bu
4ge
1H NMR - 400MHz
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1.01
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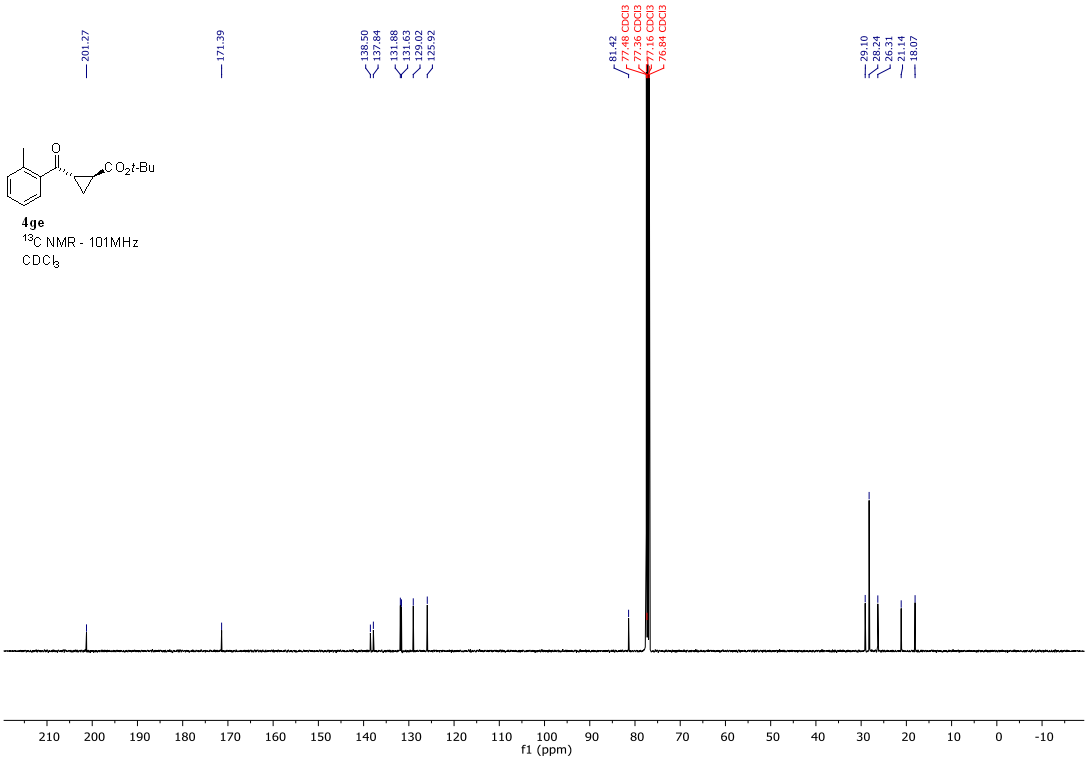
9.28
f1 (ppm)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81.42
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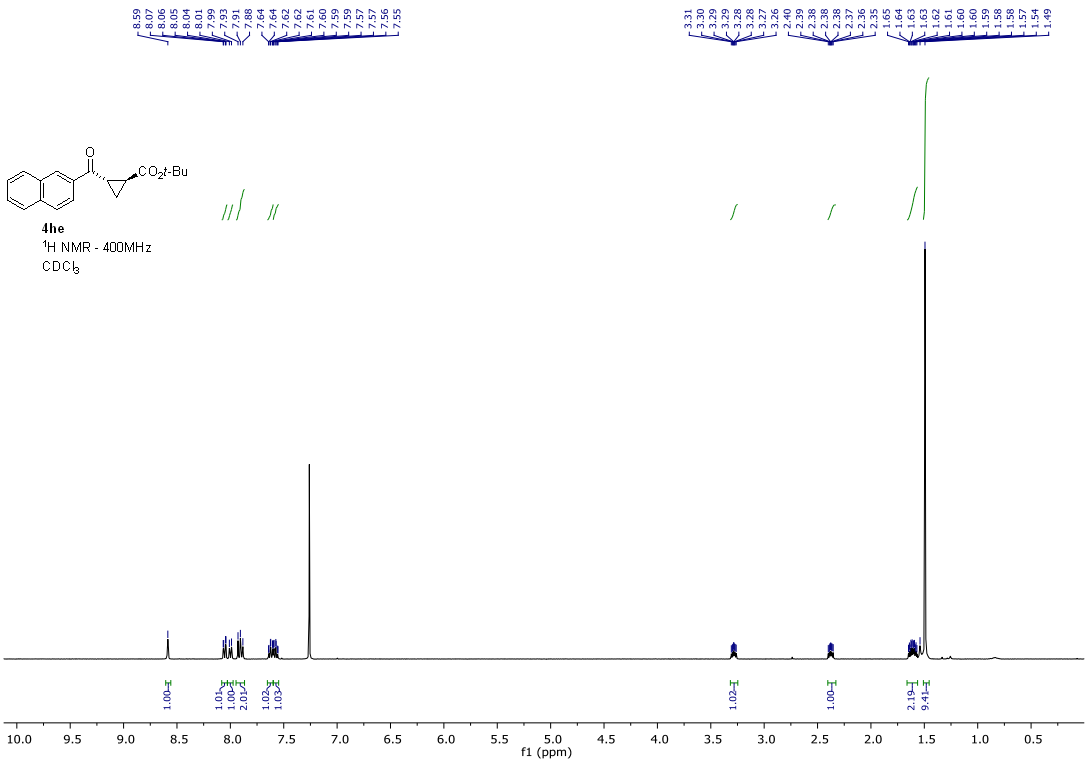
77.16 CDCl3
76.84 CDCl3
29.10
28.24
26.31
21.14
18.07
O
CO2t-Bu
4ge
13C NMR - 101MHz
CDCl3
f1 (ppm)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8.07
8.06
8.05
8.04
8.01
7.99
7.93
7.91
7.88
7.64
7.64
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7.62
7.61
7.60
7.59
7.59
7.57
7.57
7.56
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3.29
3.29
3.28
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3.27
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1.64
1.63
1.63
1.62
1.61
1.60
1.60
1.59
1.58
1.58
1.57
1.54
1.49
O
CO2t-Bu
4he
1H NMR - 400MHz
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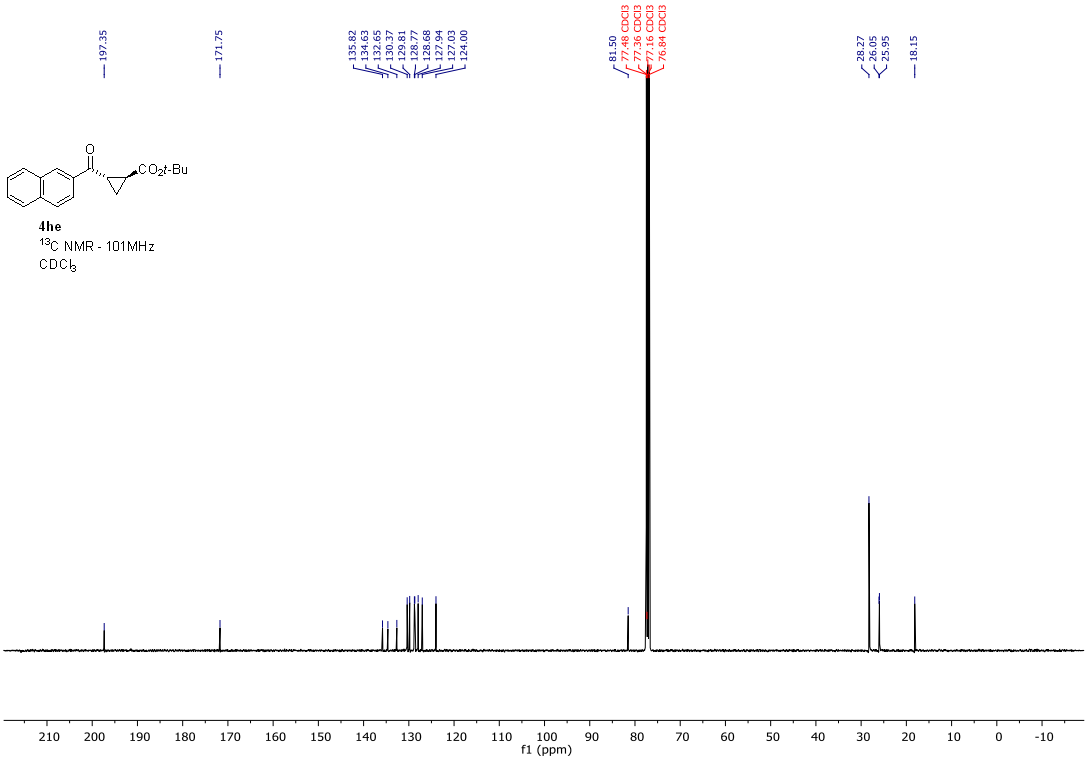
1.00
2.01
1.02
1.03
1.02
1.00
2.19
9.41
f1 (ppm)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130.37
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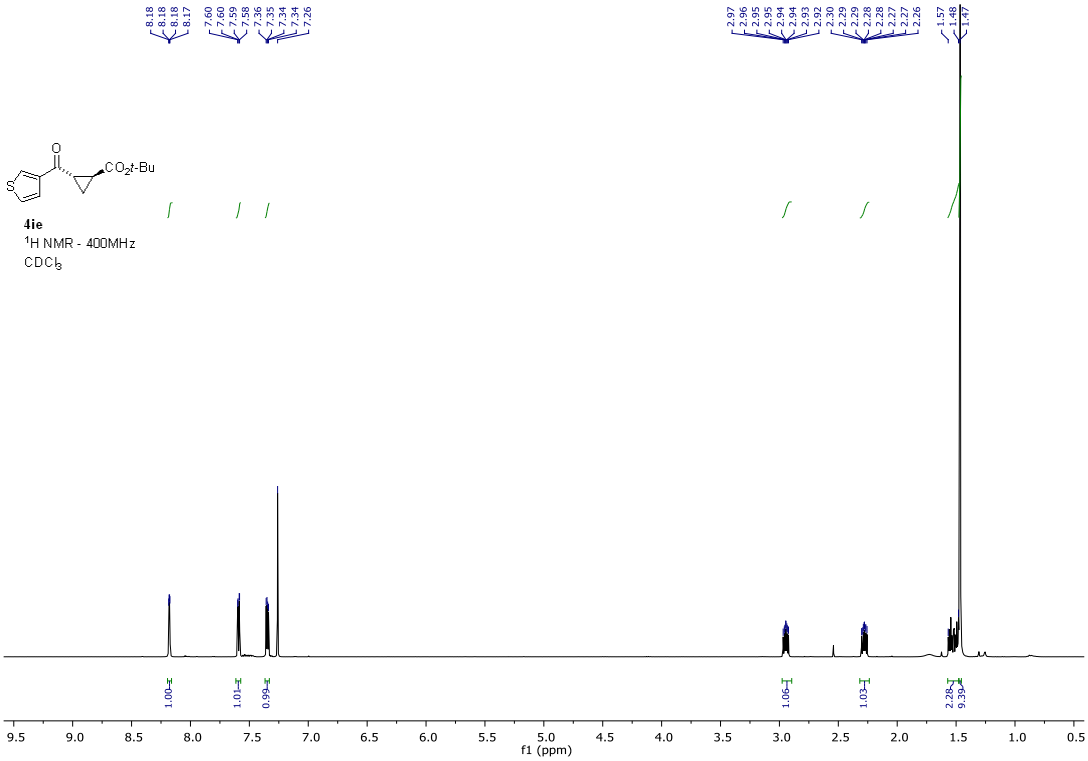
127.03
124.00
81.50
77.46 CDCl3
77.28 CDCl3
77.16 CDCl3
76.84 CDCl3
28.27
26.05
25.95
18.15
O
CO2t-Bu
4he
13C NMR - 101MHz
CDCl3
f1 (ppm)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8.18
8.18
8.17
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7.60
7.59
7.58
7.36
7.35
7.34
7.34
7.26
2.97
2.96
2.95
2.95
2.94
2.94
2.93
2.92
2.30
2.29
2.29
2.28
2.28
2.27
2.27
2.26
1.57
1.48
1.47
O
S
CO2t-Bu
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1H NMR - 400MHz
CDCl3
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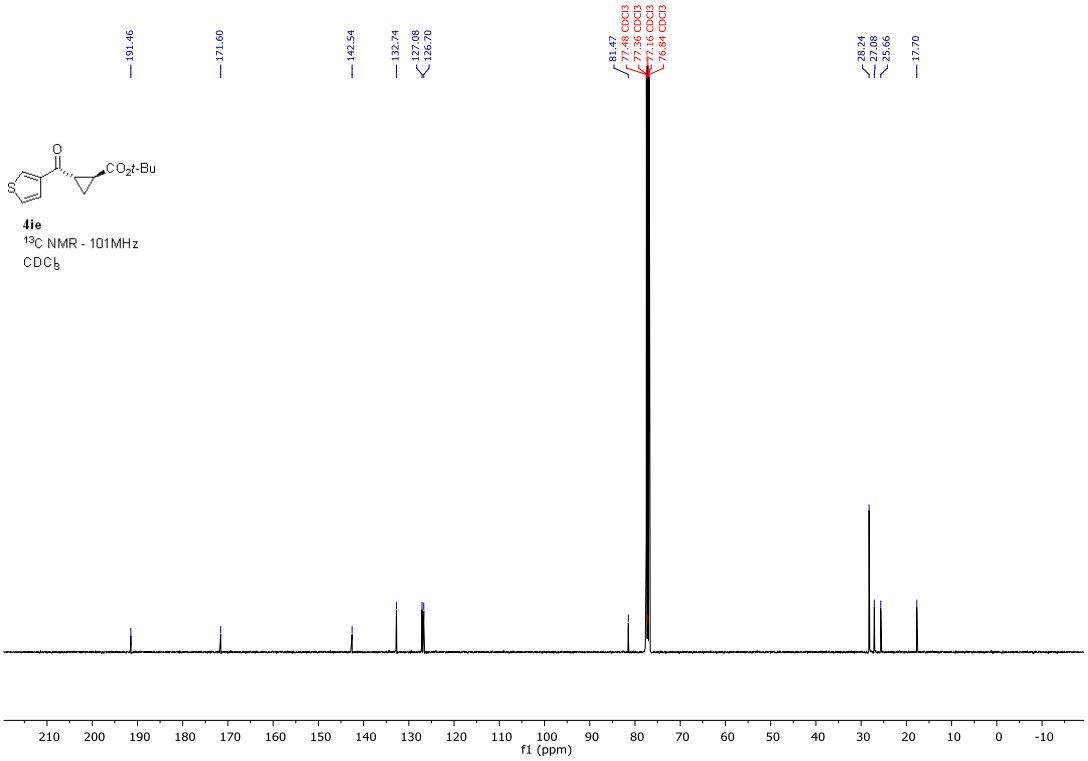
1.01
0.99
1.06
1.03
2.28
9.39
f1 (ppm)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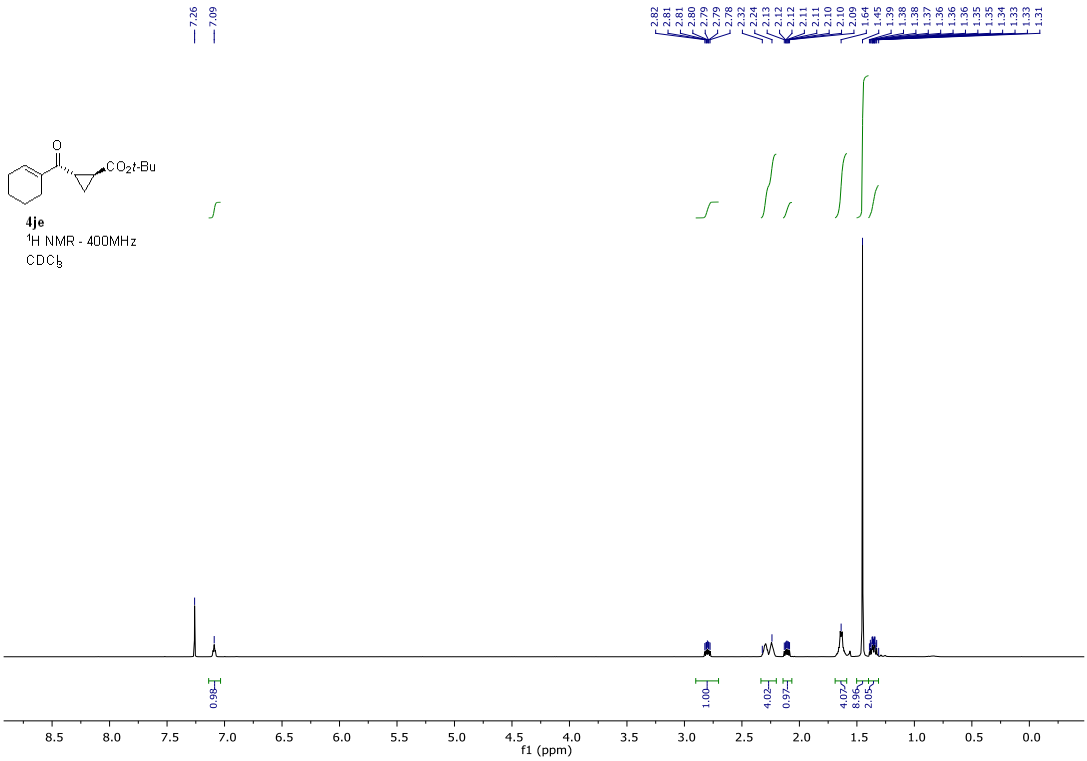
127.08
126.70
81.47
77.48 CDCl3
77.32 CDCl3
77.16 CDCl3
76.84 CDCl3
28.24
27.08
25.66
17.70
O
CO2t-Bu
S
4ie
13C NMR - 101MHz
CDCl3
f1 (ppm)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2.13
2.12
2.12
2.11
2.11
2.10
2.10
2.09
1.64
1.45
1.39
1.38
1.38
1.37
1.36
1.36
1.35
1.35
1.34
1.33
1.33
1.31
O
CO2t-Bu
4je
1H NMR - 400MHz
CDCl3
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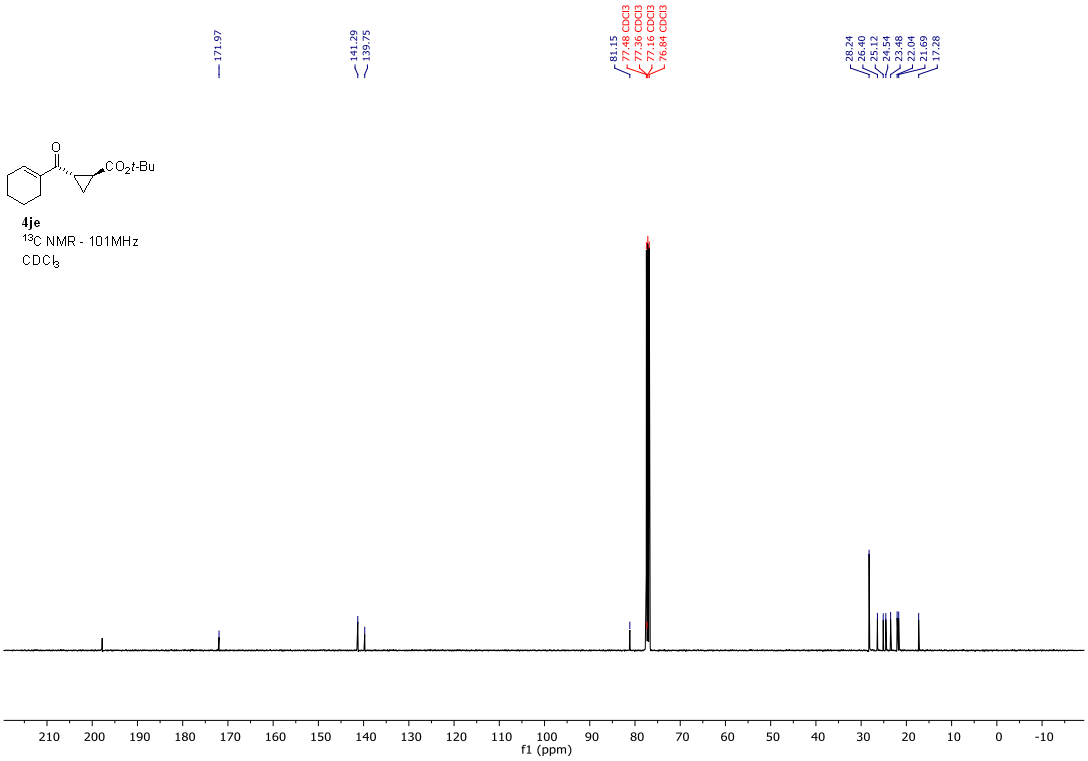
1.00
4.02
0.97
4.07
8.96
2.05
f1 (ppm)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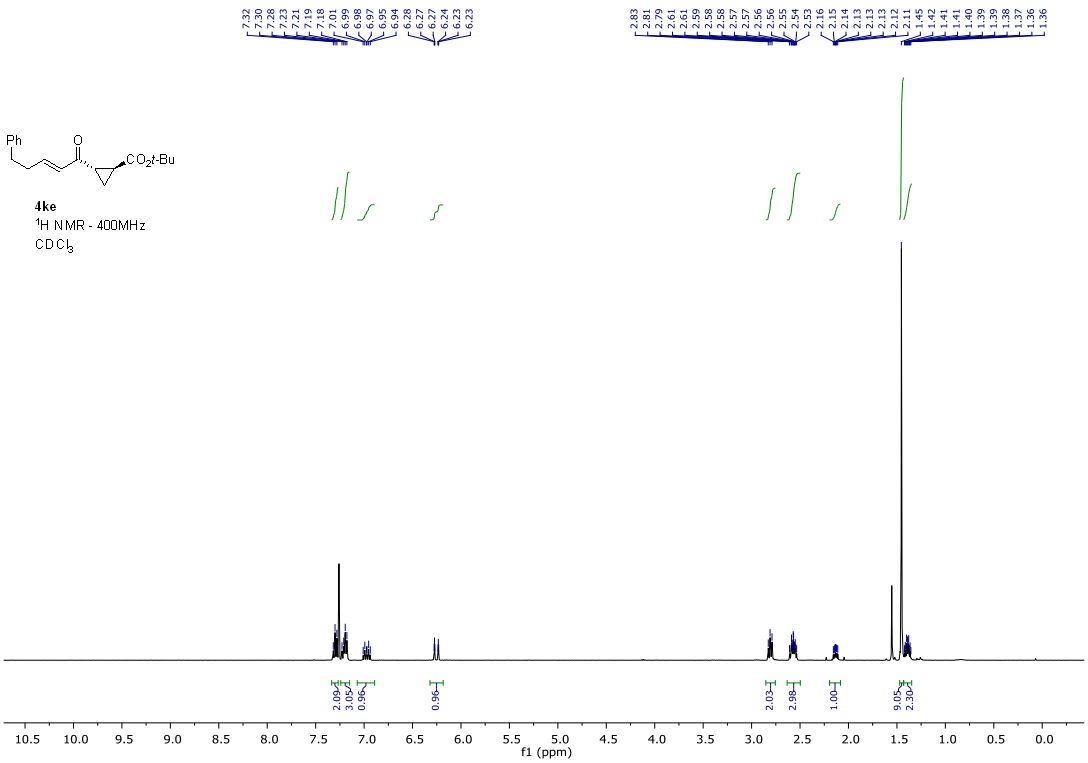
141.29
139.75
81.15
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
28.24
28.40
25.12
24.54
23.48
22.04
21.69
17.28
O
CO2t-Bu
4je
13C NMR - 101MHz
CDCl3
f1 (ppm)


Ph
O
CO2t-Bu
4ke
1H NMR - 400MHz
CDCl3
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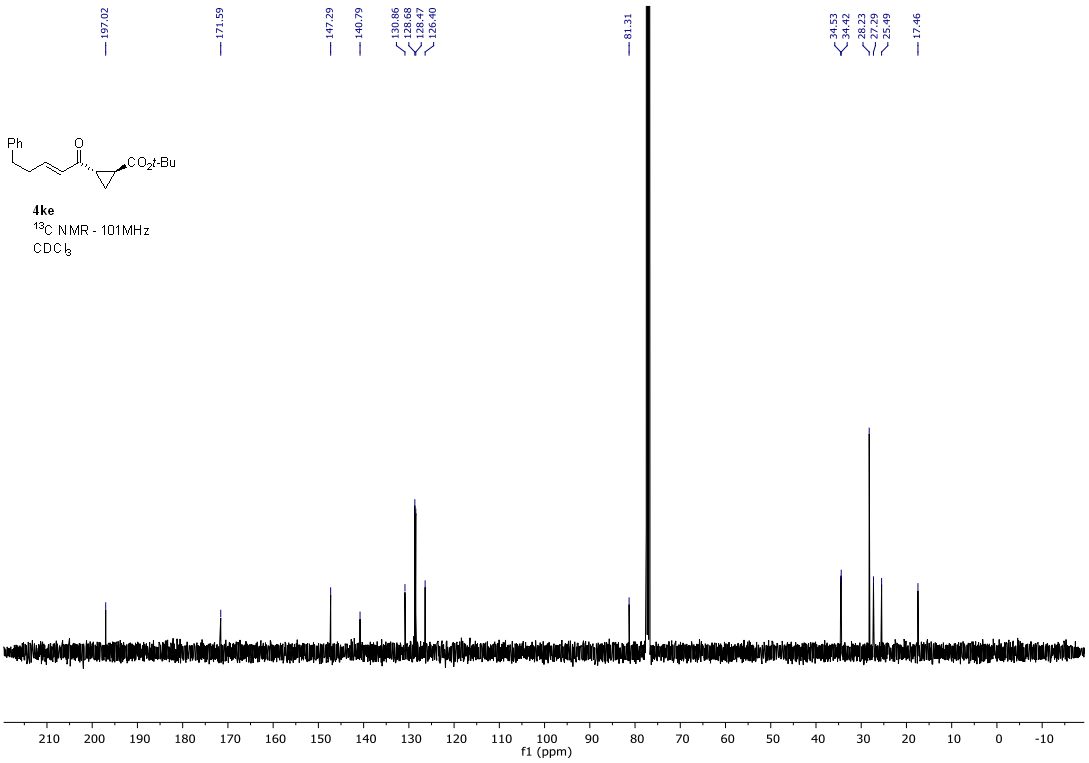
3.05
0.96
0.96
2.03
2.98
1.00
9.05
2.30
f1 (ppm)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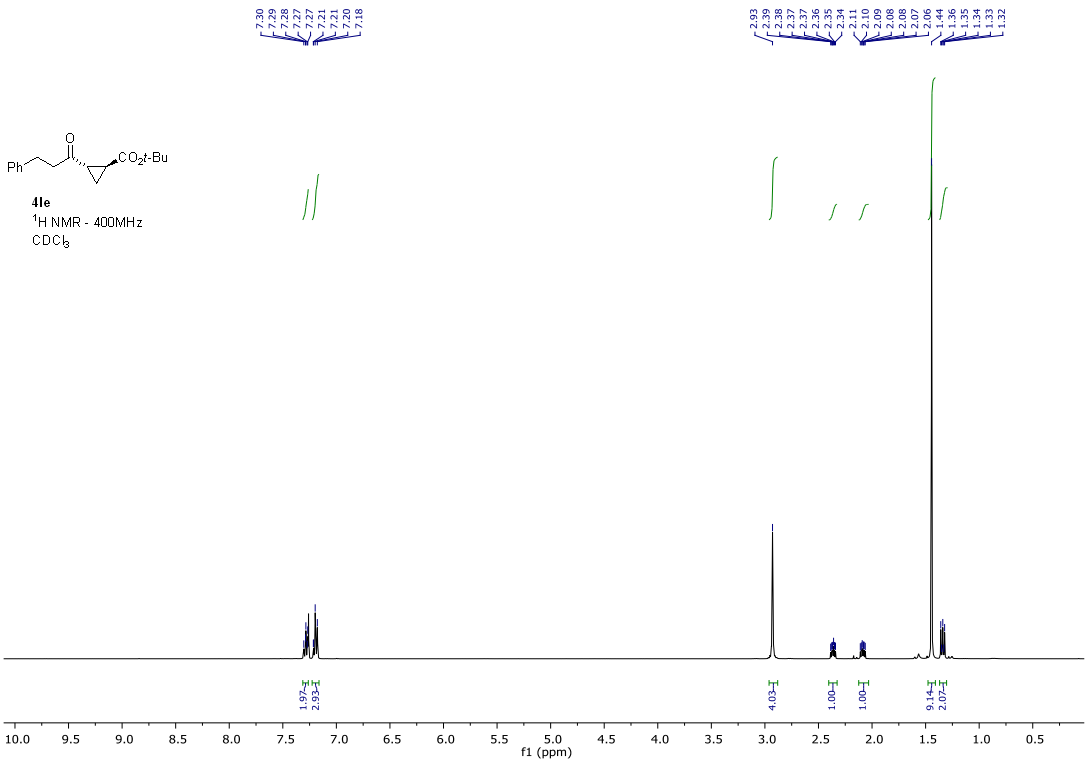
126.40
81.31
34.53
34.42
28.23
27.29
25.49
17.46
Ph
O
CO2t-Bu
4ke
13C NMR - 101MHz
CDCl3
f1 (ppm)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7.20
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2.39
2.38
2.37
2.37
2.36
2.35
2.34
2.11
2.10
2.09
2.09
2.08
2.07
2.06
1.44
1.36
1.35
1.34
1.33
1.32
Ph
O
CO2t-Bu
4le
1H NMR - 400MHz
CDCl3
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4.03
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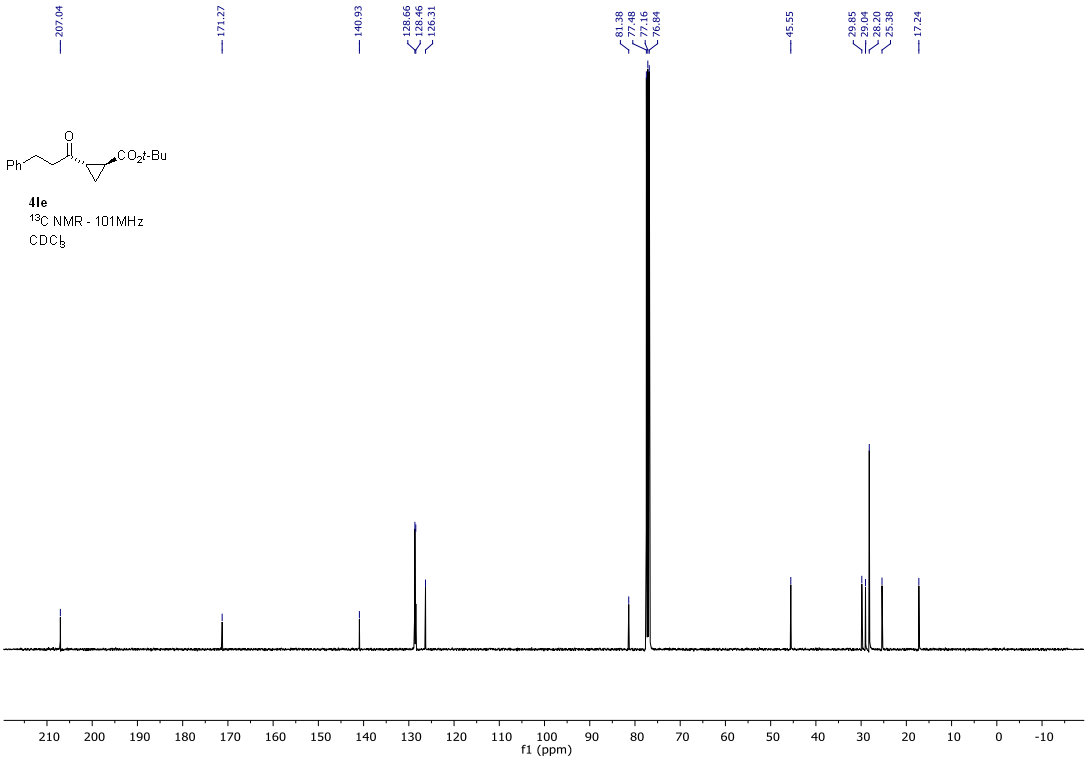
1.00
9.14
2.07
f1 (ppm)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81.38
77.48
77.16
76.84
45.55
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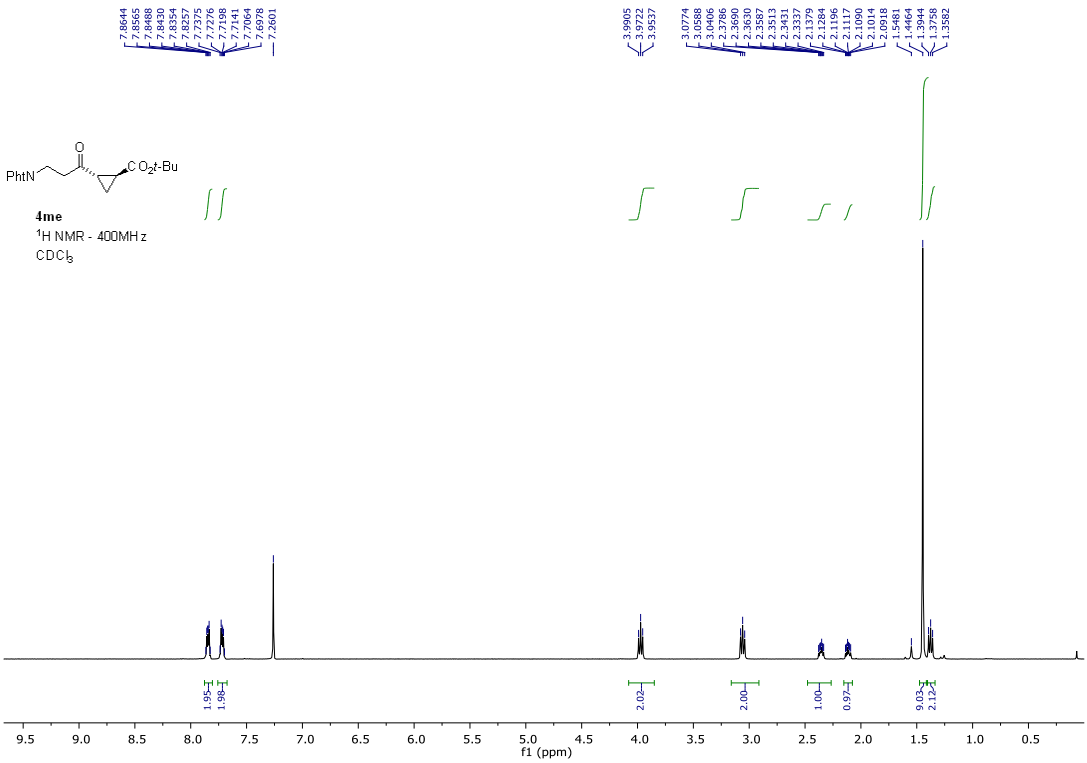
28.20
25.38
17.24
Ph
CO2t-Bu
4le
13C NMR - 101MHz
CDCl3
f1 (ppm)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7.6978
7.2601
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3.9722
3.9557
3.0774
3.0588
3.0406
2.3786
2.3690
2.3630
2.3587
2.3513
2.3431
2.3337
2.1379
2.1284
2.1165
2.1117
2.1090
2.1014
2.0918
1.5481
1.4464
1.3944
1.3758
1.3582
PhtN
CO2t-Bu
4me
1H NMR - 400MHz
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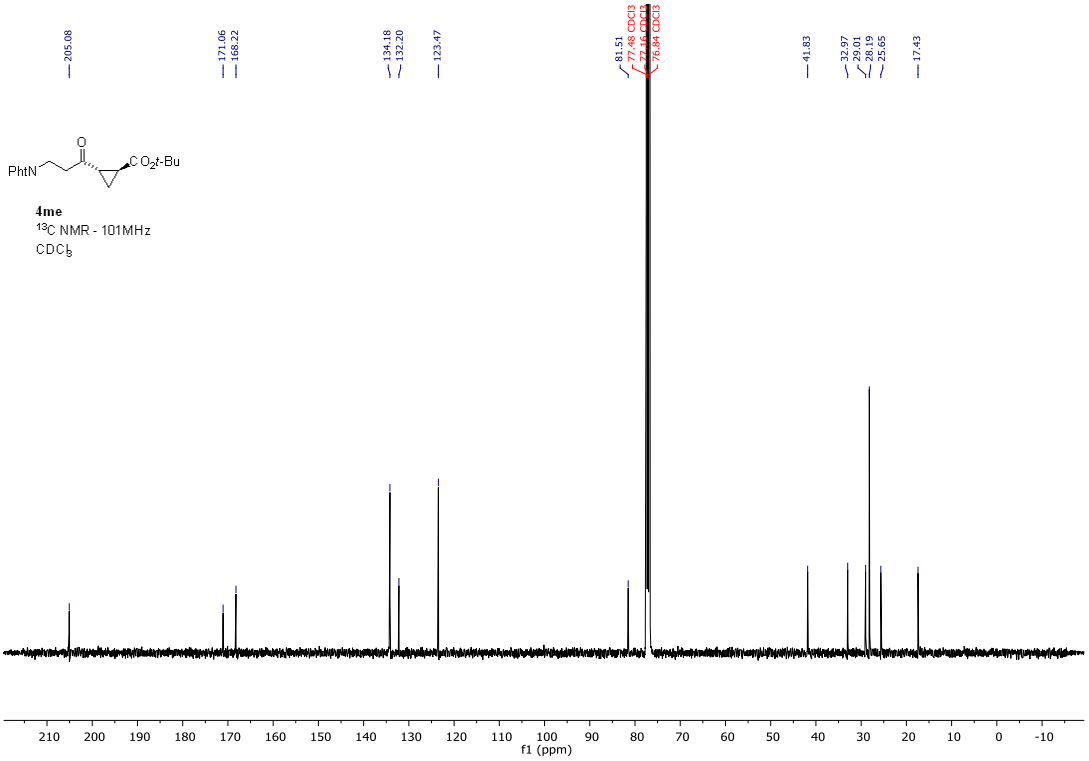
1.00
0.97
9.03
2.12
f1 (ppm)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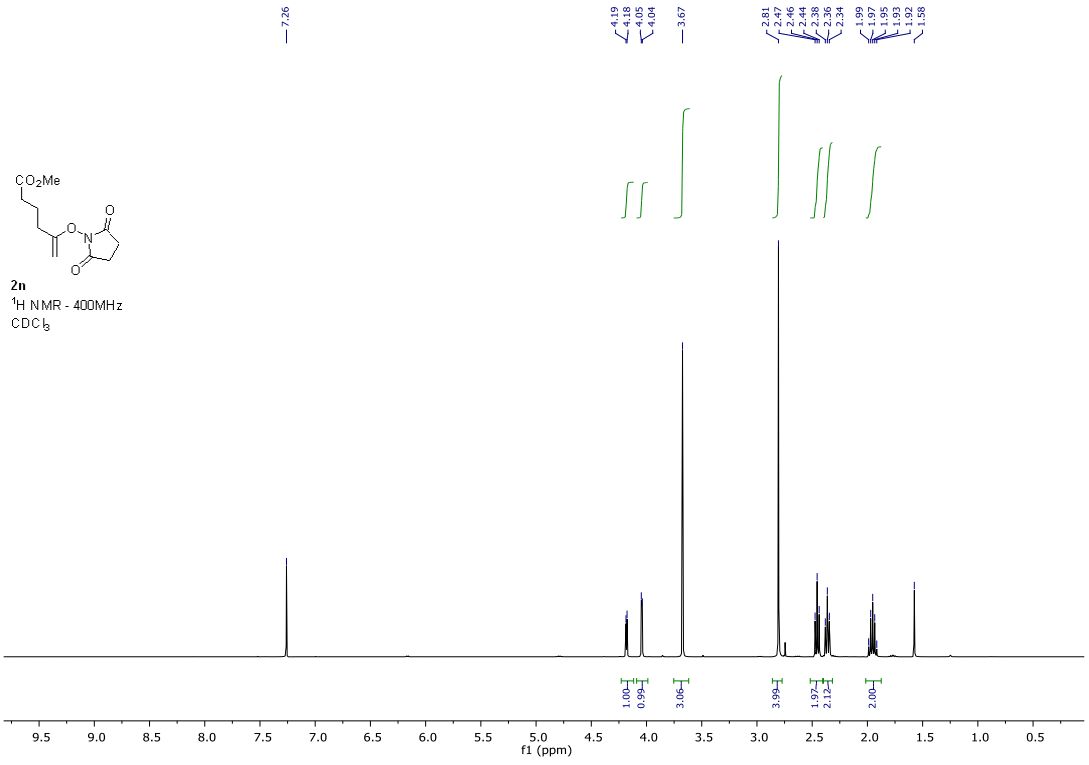
132.20
123.47
81.51
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
41.83
32.97
29.01
28.19
25.65
17.43
PhtN
CO2t-Bu
4me
13C NMR - 101MHz
CDCl3
f1 (ppm)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3.67
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2.47
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2.44
2.38
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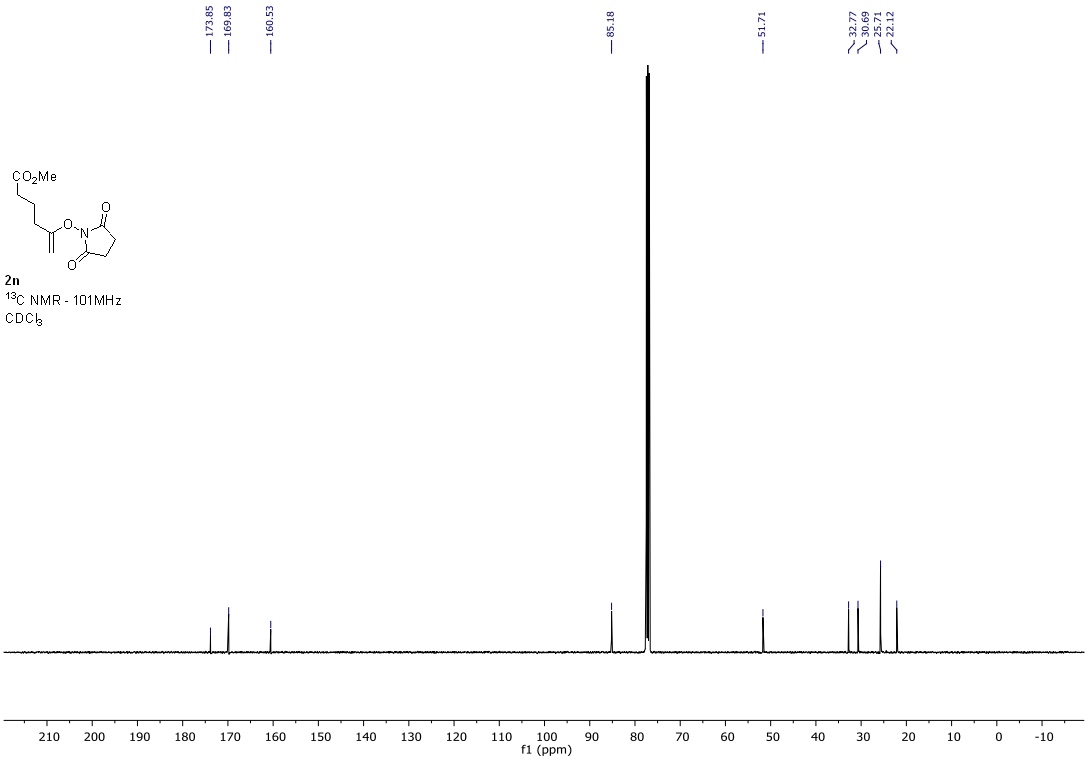
2.34
1.99
1.97
1.95
1.93
1.92
1.58
CO2Me
2n
1H NMR - 400MHz
CDCl3
1.00
0.99
3.06
3.99
1.97
2.12
2.00
f1 (ppm)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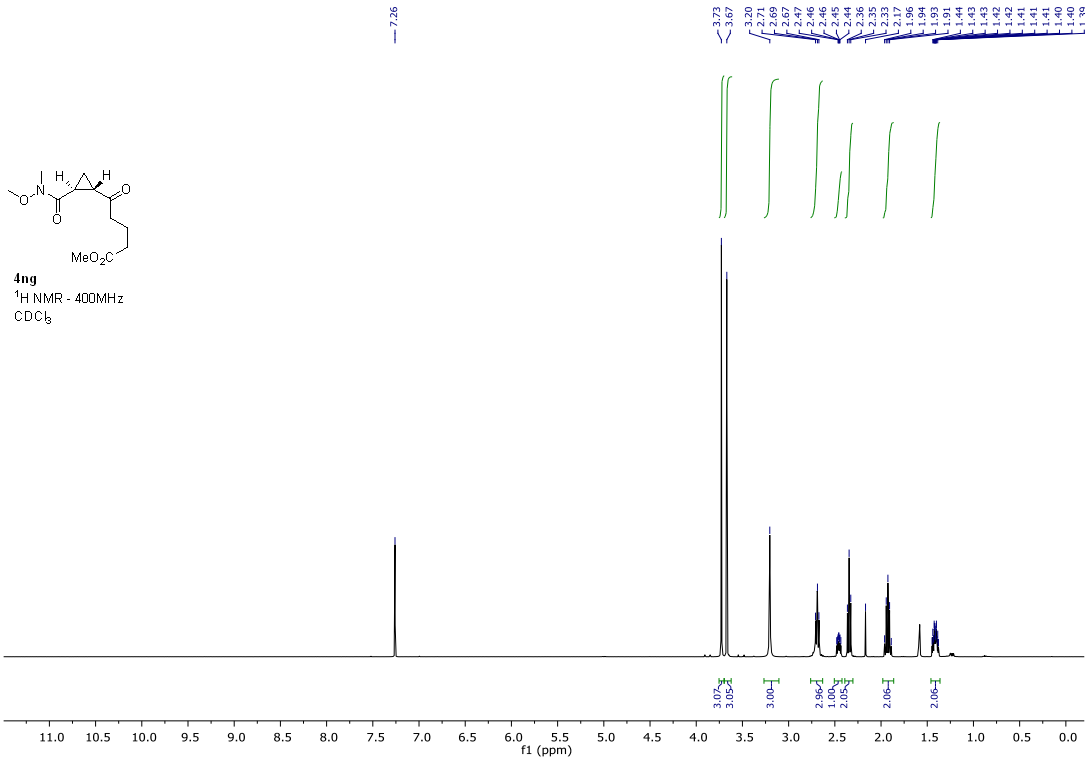
85.18
51.71
32.77
30.69
25.71
22.12
CO2Me
O
O
N
O
2n
13C NMR - 101MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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2.47
2.46
2.46
2.45
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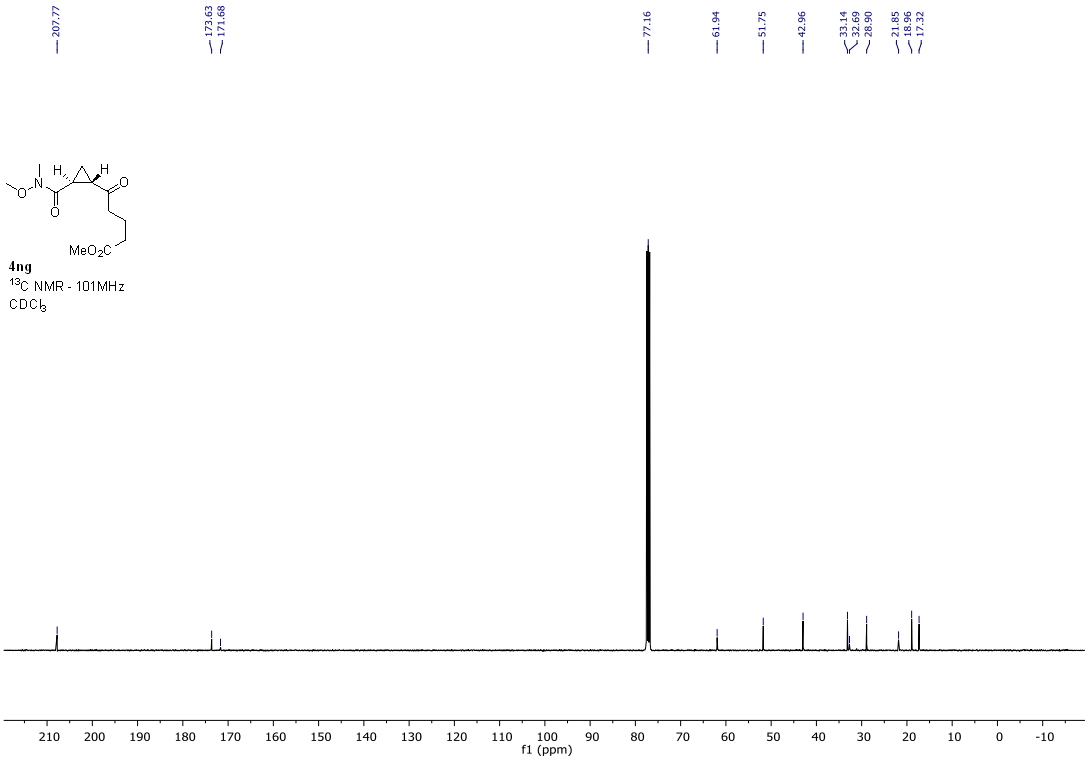
2.36
2.35
2.33
2.17
1.96
1.94
1.93
1.91
1.44
1.43
1.43
1.42
1.42
1.41
1.41
1.41
1.40
1.40
H
H
N
O
O
O
MeO2C
4ng
1H NMR - 400MHz
CDCl3
3.07
3.05
3.00
2.96
1.00
2.05
2.06
2.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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51.75
42.96
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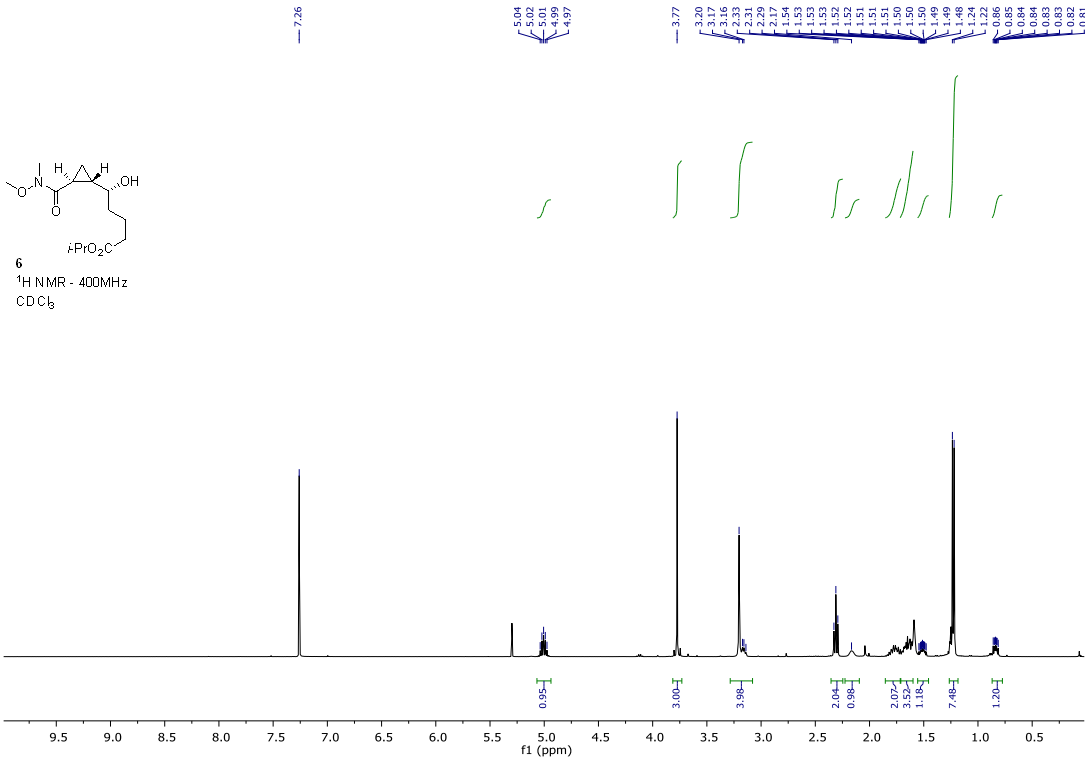
32.69
28.90
21.85
18.96
17.32
MeO2C
4ng
13C NMR - 101MHz
CDCl3
f1 (ppm)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5.01
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4.97
3.77
3.20
3.17
3.16
2.33
2.31
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2.17
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1.51
1.51
1.51
1.50
1.50
1.50
1.49
1.49
1.48
1.24
1.22
0.86
0.85
0.84
0.84
0.83
0.83
0.82
0.81
OH
i-PrO2C
6
1H NMR - 400MHz
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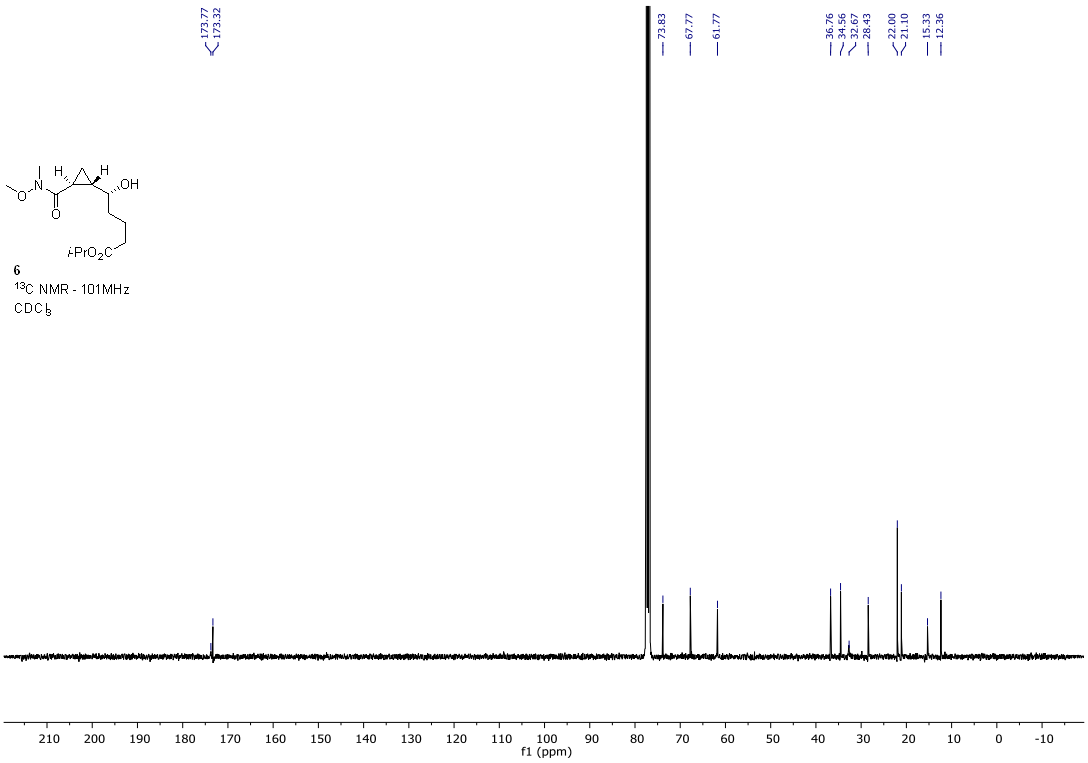
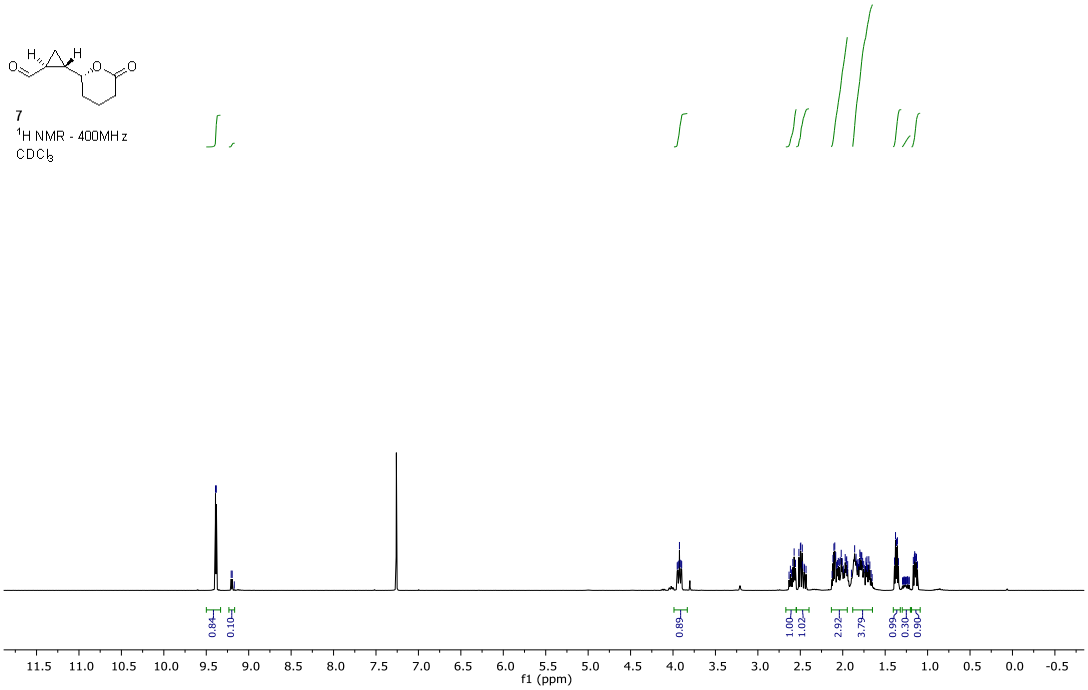
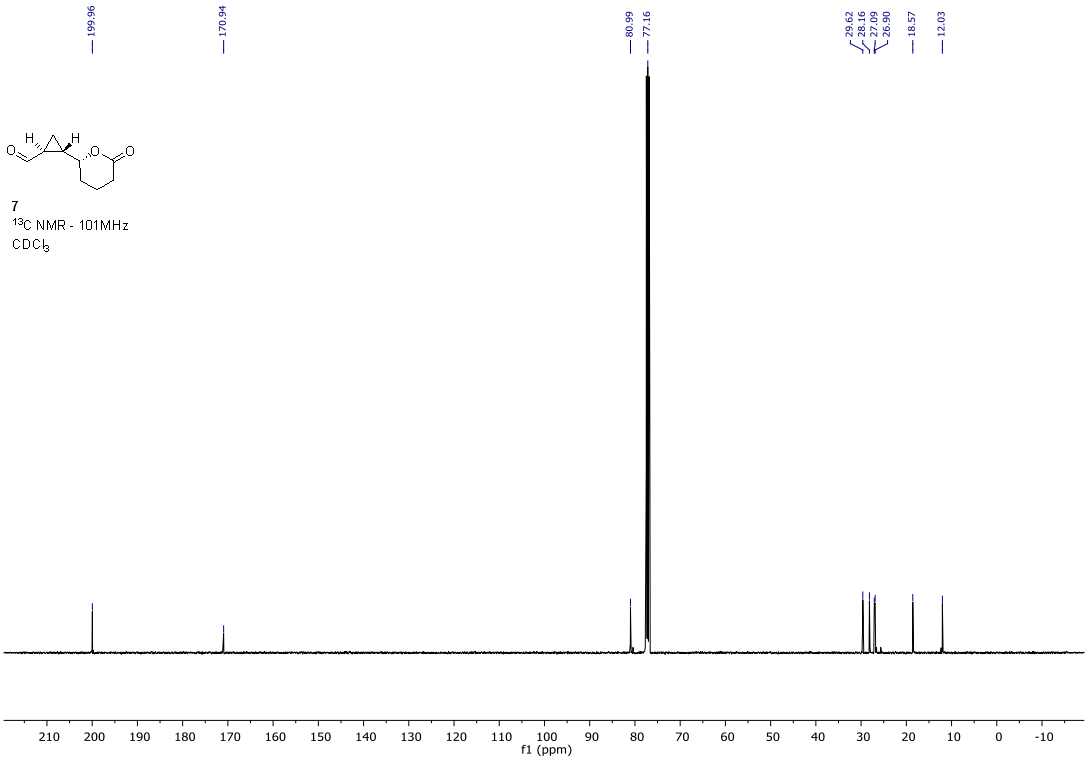
3.98
2.04
0.98
2.07
3.52
1.18
7.48
1.20
f1 (ppm)


6
13C NMR - 101MHz
CDCl3
f1 (ppm)


7
1H NMR - 400MHz
CDCl3
f1 (ppm)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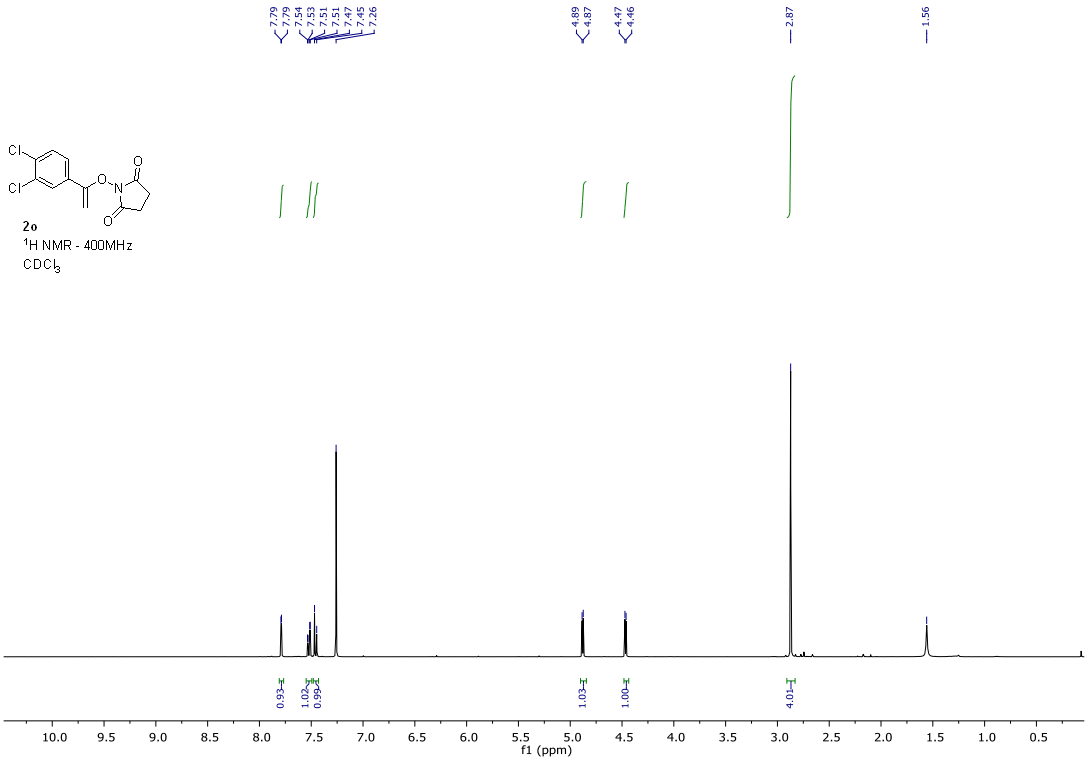
28.15
27.09
26.90
18.57
12.03
7
13C NMR - 101MHz
CDCl3
f1 (ppm)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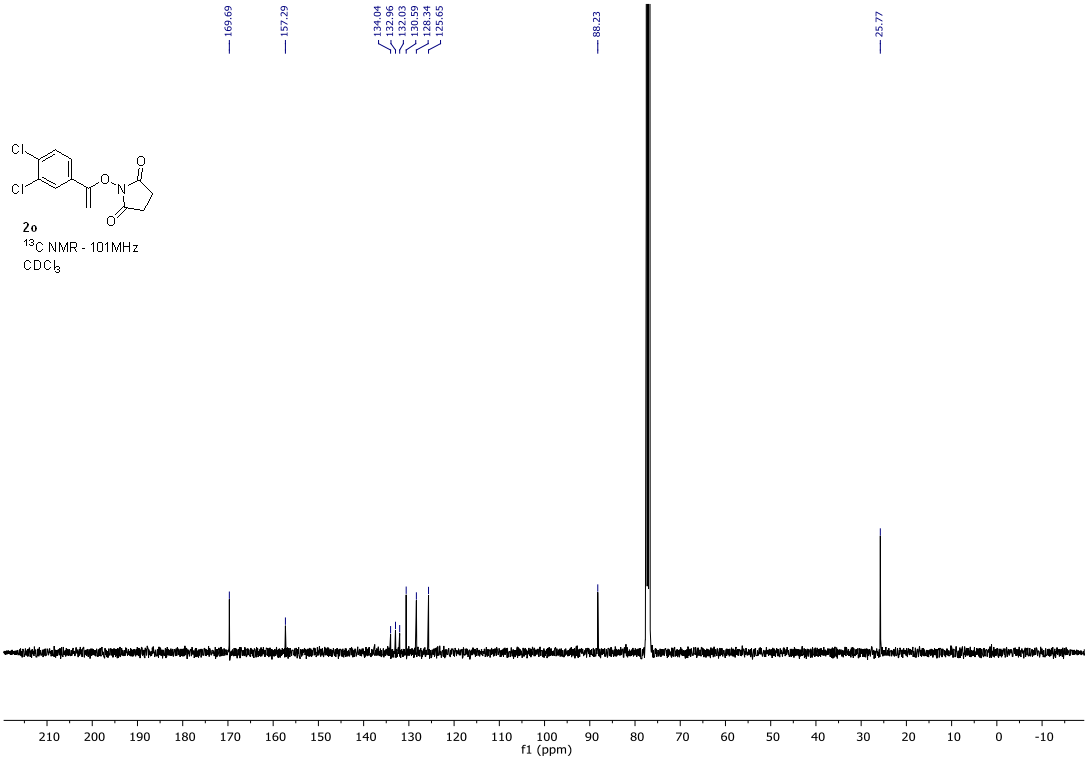
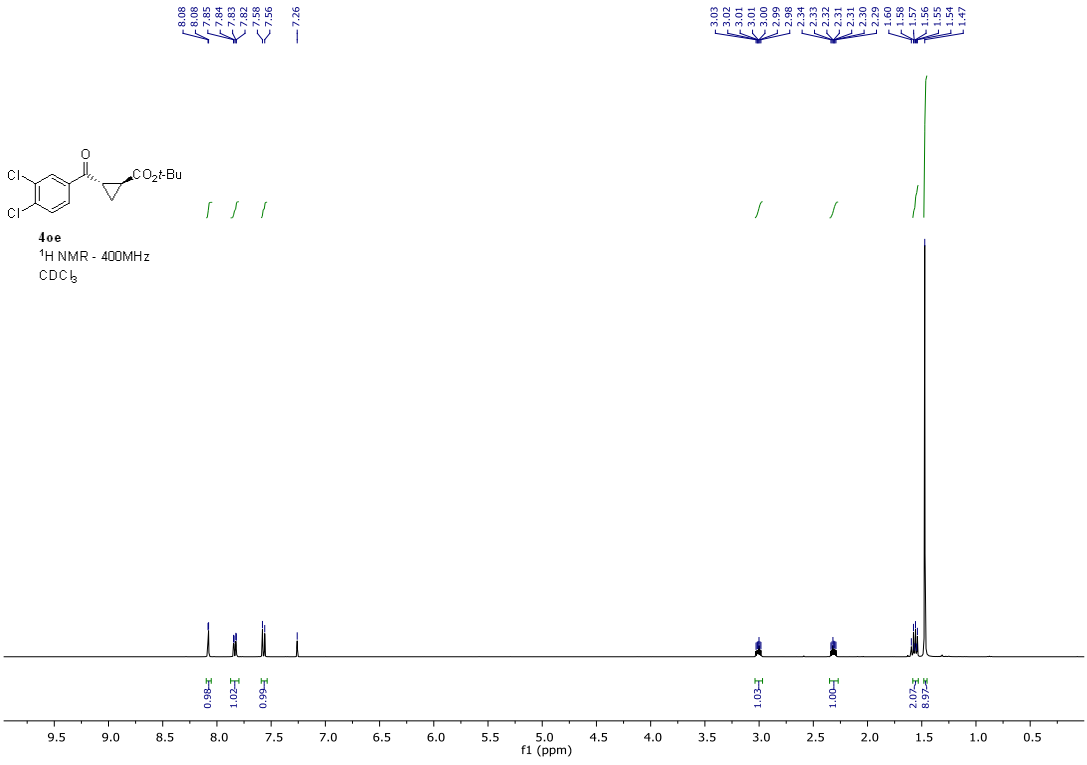
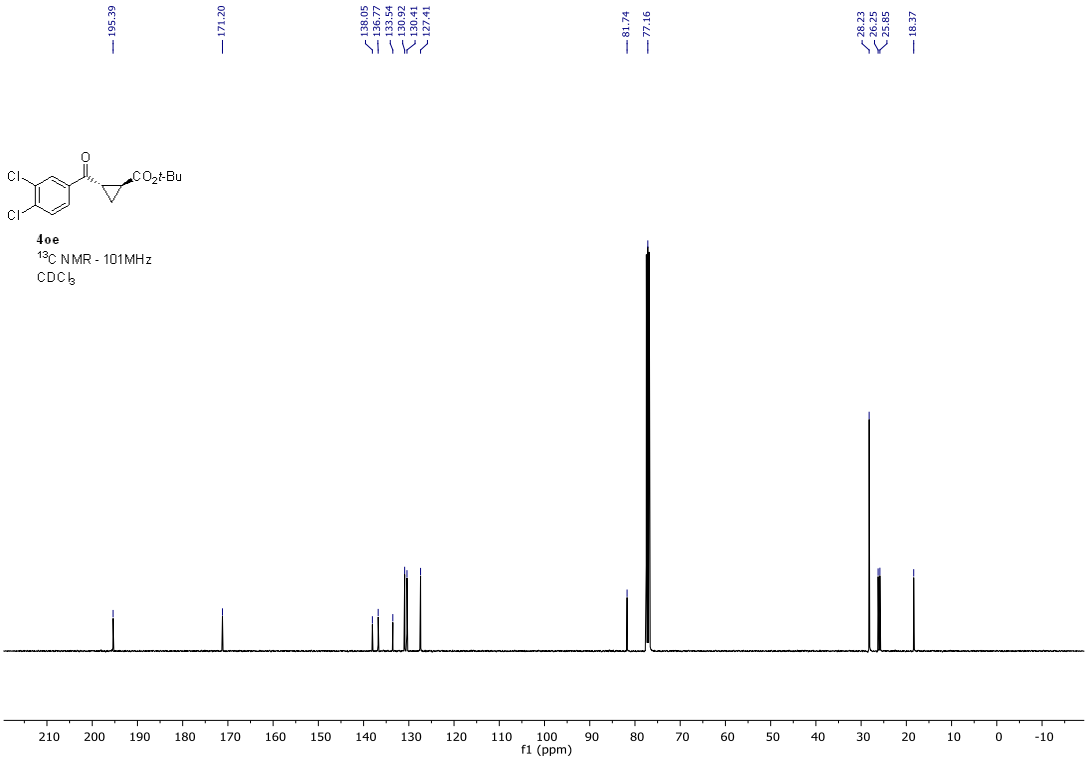
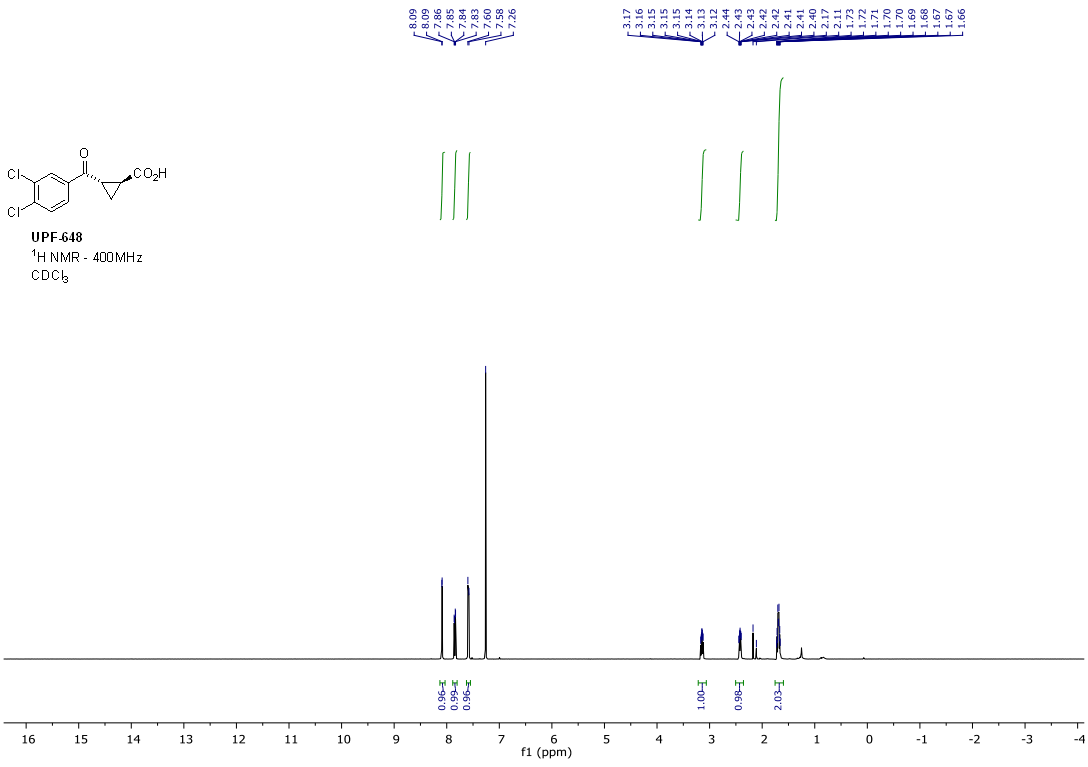
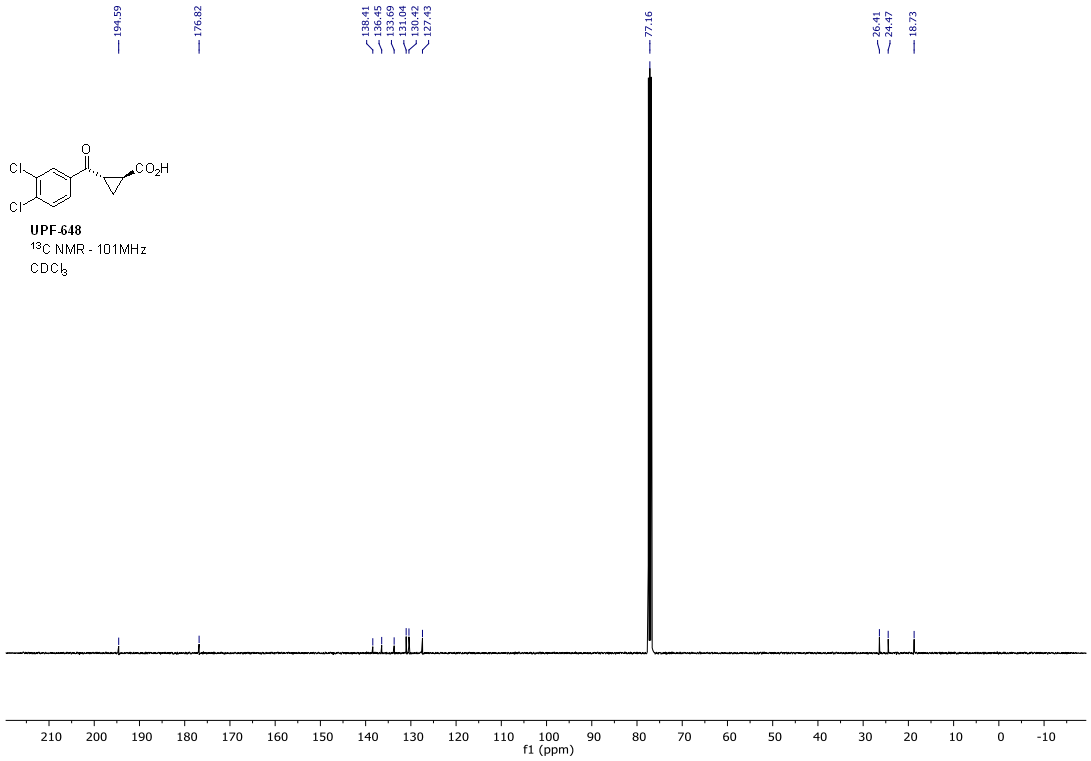
7.51
7.47
7.45
7.26
4.89
4.87
4.47
4.46
2.87
1.56
2o
1H NMR - 400MHz
CDCl3
0.93
1.02
0.99
1.03
1.00
4.01
f1 (ppm)


169.69
157.29
134.04
132.96
132.03
130.59
128.34
125.65
88.23
25.77
Cl
Cl
O
O
N
O
O
2o
13C NMR - 101MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.08
8.08
7.85
7.84
7.83
7.82
7.58
7.56
7.26
3.03
3.02
3.01
3.01
3.00
2.99
2.98
2.34
2.33
2.32
2.31
2.31
2.30
2.29
1.60
1.58
1.57
1.56
1.55
1.54
1.47
O
CO2t-Bu
Cl
Cl
4oe
1H NMR - 400MHz
CDCl3
0.98
1.02
0.99
1.03
1.00
2.07
8.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


195.39
171.20
138.05
136.77
133.54
130.92
130.41
127.41
81.74
77.16
28.23
26.25
25.85
18.37
O
Cl
Cl
CO2t-Bu
4oe
13C NMR - 101MHz
CDCl3
f1 (ppm)


8.09
8.09
7.86
7.85
7.84
7.83
7.60
7.58
7.26
3.17
3.16
3.15
3.15
3.15
3.14
3.13
3.12
2.44
2.43
2.43
2.42
2.42
2.41
2.41
2.40
2.17
2.11
1.73
1.72
1.71
1.70
1.70
1.69
1.68
1.67
1.67
1.66
O
Cl
Cl
CO2H
UPF-648
1H NMR - 400MHz
CDCl3
0.96
0.99
0.96
1.00
0.98
2.03
f1 (ppm)


194.59
176.82
138.41
136.45
133.69
131.04
130.42
127.43
77.16
26.41
24.47
18.73
Cl
Cl
O
CO2H
UPF-648
13C NMR - 101MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)