Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Au- and Pd-Catalyzed Cyclization Processes: Synthesis of Polyfunctionalized Cyclopropanes

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1. General Information

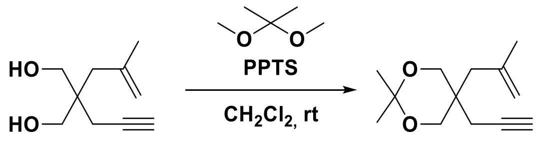
Unless otherwise stated, commercial reagents and solvents were used without further purification. Solvents for chromatography [petroleum ether (PE), ethyl acetate (EtOAc), diethyl ether (Et_2O) and Toluene (Tol) were used as received without further purification. Reactions were monitored by analytical thin layer chromatography (TLC), which was performed on 0.20-mm pre-coated silica plates (Kieselgel 60, F254; Macherey-Nagel GmbH & Co. KG, Düren, Germany). Products were purified by flash chromatography on 200–300 mesh silica gels, SiO_2. Some solvents for use in reactions were freshly distilled [tetrahydrofuran (THF) and toluene (Tol) were distilled from sodium/benzophenone ketyl]. Some solvents for use in reactions were placed in 4Å MS over 24h. [Dichloromethane (DCM) and Dichloroethane (DCE)] NMR spectra (^1H, ^{13}C, and ^{19}F NMR spectra, and COSY, DEPT135, HSQC, HMBC, NOESY) were recorded on a Bruker Avance 400 MHz spectrometer (Bruker, Rheinstetten, Germany). All NMR spectra were recorded in $CDCl_3$, CD_2Cl_2, $(CD_3)SO$ or $(CD_3)_2CO$ at room temperature (20 ± 3 °C). All chemical shifts are quoted in parts per million downfield from tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz [Hz] and result from averaging the experimentally found values. Analytical GC/MS analyses were performed on a Shimadzu QP2010S- MS chromatograph (EI, 70 eV), equipped with an SLB-5ms capillary column (thickness 0.25 mm, length 30 m, and inside diameter 0.25 mm). High resolution mass spectroscopy (HRMS) analyses for new compounds were performed by Institut de Chimie de Nice using a Thermo Vanquish UHPLC-Q-Exactive Focus Mass Spectrometer equipped with H-ESI source operated in a positive mode and by Plateforme Bernard Rossi, CEA TIRO, on a LTQ Orbitrap hybrid mass spectrometer with an electrospray-ionization (ESI) probe (Thermoscientific; San Jose, CA, USA) by direct infusion. The following products were prepared by the reported procedures: diisopropyl-2-(2-methylallyl)-2-(prop-2-yn-1-yl)malonate (**1a**)[1], dimethyl-2-(2-methylallyl)-2-(prop-2-yn-1-yl)malonate (**1b**)[1], diisopropyl-2-allyl-2-(prop-2-yn-1-yl)malonate (**1c**)[1], diisopropyl3-(2-bromophenyl)-3a-methyltetrahydro-3*H*-cyclopenta[c]cyclopropa[b]furan-5,5(6*H*)-dicarboxylate (**2a**)[1], dimethyl3-(2-bromophenyl)-3a-methyltetrahydro-3*H*-cyclopenta[c] cyclopropa[b]furan-5,5(6*H*)-dicarboxylate (**2b**)[1], diisopropyl3-(2-bromophenyl)tetrahydro-3H-cyclopenta[c]-cyclopropa[b]furan-5,5(6*H*)-dicarboxylate (**2c**)[1], 2-propenyl-1-ethynylbenzenes (**1d**)[2], 2-(2-methylallyl)-2-(prop-2-yn-1-yl)propane-1,3-diol[3].

Spectral data were consistent with data reported in the literature.

2. Experimental Procedures and Characterization Data

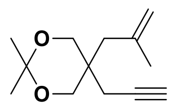
2.1 General Procedure for the preparation of 1,6-enynes

2.1.1 Synthesis of 2-(2-methylallyl)-2-(prop-2-yn-1-yl) propane-1,3-diol (1e)



77%, 1e

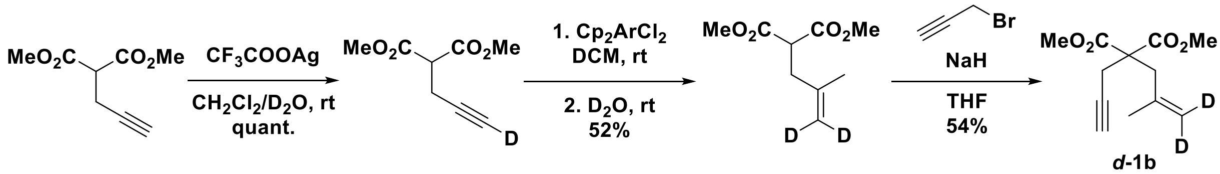
A round-bottomed flask, equipped with a magnetic stirring bar, was charged with pyridinium *p*-toluene sulfonate (291.10 mg, 1.69 mmol, 0.2 eq.), 2-(2-methylallyl)-2-(prop-2-yn-1-yl) ropane-1,3-diol (1.41 g, 8.4 mmol, 1 eq.), 2,2-dimethoxypropane (5.27 g, 50.61 mmol, 6 eq.), and CH_2Cl_2 (28.0 mL, 0.3 M). The resulting mixture was stirred at room temperature for 12 h. Then an aqueous saturated solution of $NaHCO_3$ and H_2O were added to the flask. The organic materials were extracted with CH_2Cl_2. The combined organic layer was washed with H_2O and brine, dried over $MgSO_4$, and concentrated removed under reduced pressure. The crude was purified by flash column chromatography on silica gel. (6.53 mmol, 1.36g, 77% yield)



Chemical Formula: $C_{13}H_{20}O_2$
Exact Mass: 208,1463

2-(2-methylallyl)-2-(prop-2-yn-1-yl) propane-1,3-diol (1e)
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.93 (dd, *J* = 2.2, 1.4 Hz, 1H), 4.79 (dd, *J* = 2.2, 1.0 Hz, 1H), 3.71 – 3.66 (m, 4H), 2.45 (d, *J* = 2.7 Hz, 2H), 2.12 (d, *J* = 0.8 Hz, 2H), 2.04 (t, *J* = 2.7 Hz, 1H), 1.79 (dd, *J* = 1.4, 0.8 Hz, 3H), 1.42 (s, 3H), 1.41 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.8, 115.5, 98.1, 81.2, 71.2, 67.0, 39.8, 35.9, 26.3, 25.2, 22.4, 21.3.
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{13}H_{21}O_2$ 209.1536, found 209.1536.

1.1.1 Synthesis of dimethyl-2-(2-methylallyl-3,3-d2)-2-(prop-2-yn-1-yl) malonate (*d*-1b)



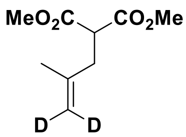
d-1b

Dimethyl 2-(prop-2-yn-1-yl)malonate (1.0 g, 5.8 mmol, 1 eq.) was added to a vigorously stirred solution of CF_3COOAg (64.9 mg, 0.294 mmol, 5 mol%) and D_2O (2.35 g, 117.5 mmol, 20 eq.) in CH_2Cl_2 (12 mL, 0.5 M) under air. The reaction mixture was stirred at 25°C for 16 h. The product was extracted with DCM (3 x 20 mL). The combined organic layer passed through celite and the solution was dried over $MgSO_4$. The volatiles were removed under vacuum and the product was used in the next step without further purification (1g, 5,84 mmol, >99%). Spectral data were consistent with data reported in the literature.[4]

To a suspension of Cp_2ZrCl_2 (1.77 g, 5.84 mmol, 1.0 eq.) and $AlMe_3$ (8.76 mL, 17.53 mmol, 3.0 eq.) in DCE (60 mL) was added dimethyl-2-(prop-2-yn-1-yl-3-d)malonate (1.0 g, 5.84 mmol, 1.0 eq) in DCE (50 mL) dropwise at 0°C. After the reaction mixture is stirred for 12 h at room temperature, it was treated with D_2O (3.0 mL) and then with saturated aqueous Na_2CO_3 at 0°C. The heterogeneous mixture was extracted with Et_2O. The organic layers were combined, dried over $MgSO_4$, and concentrated in vacuo. Flash column chromatography (Et_2O/petroleum ether=30/70) provided the corresponding allyl malonate (570 mg, 52%) as a colorless oil.

Dimethyl 2-(2-methylallyl-3,3-d_2)malonate (570 mg, 3.03 mmol, 1 eq.) in THF (5 mL) was added slowly to a suspension of NaH (98 %) (145 mg, 6.06 mmol, 2 eq.) in THF (5 mL) under N_2, and the mixture was stirred at room temperature for 1 h. Then, a solution of propargyl bromide (900 mg, 6.06 mmol, 2 eq.) in THF (5 mL) was added dropwise in the mixture at 0°C and the resulting mixture was stirred at room temperature for 2 h. Water was added slowly to quench the reaction, and the reaction mixture was extracted with Et_2O. The combined organic extracts were washed three times with H_2O and brine, dried over Na_2SO_4, filtered and concentrated. The crude product ***d*-1b** was purified by silica gel flash chromatography. (365 mg, 1.61 mmol, 54%)

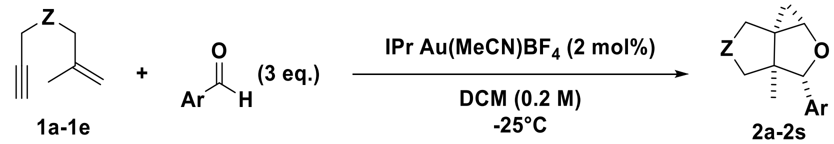
Spectral data were consistent with data reported in the literature.[5]



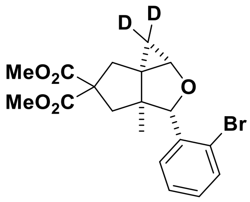
Chemical Formula: $C_9H_{12}D_2O_4$
Exact Mass: 188,1018

Dimethyl 2-(2-methylallyl-3,3-d$_2$)malonate
(0.075 g, 0.184 mmol, 69%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 6H), 2.61 (d, J = 1.4 Hz, 2H), 1.74 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.6, 141.5, 52.7, 50.5, 36.5, 22.3.
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_9H_{13}D_2O_4$ 189.1090, found 189.1090.

2.1.2 General procedure A for Gold(I)-Catalyzed Prins-Type Cyclization

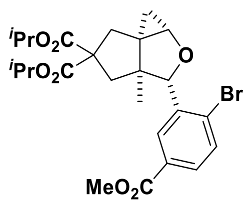


General procedure A: a solution of 1,6-enyne (0.446-3.360 mmol, 1 eq.) and the corresponding commercially available aldehyde (3 eq.) in dry CH_2Cl_2(0.2 M) was cooled to -25°C, and the gold complex (2 mol %) was added after 15 min. The solution was kept at -25°C for 8h and then the cooling device was switched off, which initiated slow warming to RT. After TLC monitoring, the mixture was filtered through a short pad of silica with a 1:1 petroleum ether/EtOAc mixture as the eluting solvent, and the solvents were evaporated under reduced pressure. The crude product was purified by silica gel flash chromatography using an EtOAc/petroleum ether mixture as the eluant.



Chemical Formula: $C_{19}H_{19}D_2BrO_5$
Exact Mass: 410,0698

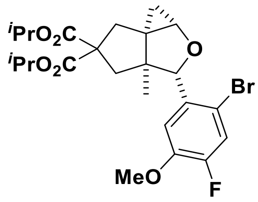
Dimethyl-3-(2-bromophenyl)-3a-methyltetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate-1,1-d$_2$ (2b-D)
Prepared according to GP A using 1.61 mmol of **1b-*d*** (0.455 g, 1.11 mmol, 69%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.41 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.08 (td, *J* = 7.6, 1.8 Hz, 1H), 5.71 (s, 1H), 3.85 (s, 3H), 3.81 (s, 1H), 3.74 (s, 3H), 3.55 (dd, *J* = 14.4, 1.6 Hz, 1H), 2.45 (dd, *J* = 13.4, 0.8 Hz, 1H), 2.27 – 2.17 (m, 2H), 0.68 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.4, 172.1, 139.6, 132.8, 129.0, 128.9, 127.1, 122.0, 96.7, 64.5, 60.4, 53.0, 53.0, 52.9, 47.9, 41.3, 38.0, 22.2.
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{20}D_2BrO_5$ 411.0771 found 411.0772.



Chemical Formula: $C_{25}H_{31}BrO_7$
Exact Mass: 522,1253

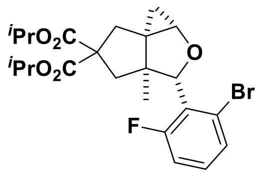
Diisopropyl-3-(2-bromo-5-(methoxycarbonyl)phenyl)-3a-methyltetrahydro-3*H* cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate (2d)
Prepared according to GP A using 0.713 mmol of **1a** (0.059 g, 0.113 mmol, 16%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 2.2 Hz, 1H), 7.74 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 1H), 5.82 (s, 1H), 5.18 (p, *J* = 6.3 Hz, 1H), 5.04 (p, *J* = 6.2 Hz, 1H), 3.90 (s, 3H),

3.85 (dd, J = 4.9, 1.6 Hz, 1H), 3.53 (dd, J = 14.3, 1.5 Hz, 1H), 2.45 (d, J = 13.4 Hz, 1H), 2.28 – 2.08 (m, 2H), 1.32 (dd, J = 6.3, 5.2 Hz, 6H), 1.24 (dd, J = 6.3, 3.4 Hz, 6H), 1.11 (dd, J = 6.7, 1.7 Hz, 1H), 0.86 (dd, J = 6.7, 4.9 Hz, 1H), 0.66 (s, 3H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.5, 171.2, 166.6, 140.7, 133.0, 129.9, 129.7, 129.3, 127.3, 96.5, 69.5, 69.3, 65.0, 60.8, 53.1, 52.4, 47.9, 41.7, 37.8, 22.5, 21.8, 21.8, 21.7, 21.7, 19.5.
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{32}BrO_7$ 523.1326, found 523.1326.



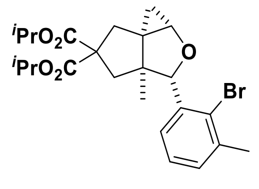
Chemical Formula: $C_{24}H_{30}BrFO_6$
Exact Mass: 512,1210

Diisopropyl-3-(2-bromo-4-fluoro-5-methoxyphenyl)-3a-methyltetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate (2e)
Prepared according to GP A using 0.713 mmol of **1a** (0.061 g, 0.119 mmol, 17%)
^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 10.4 Hz, 1H), 7.04 (d, J = 9.1 Hz, 1H), 5.71 (s, 1H), 5.17 (p, J = 6.3 Hz, 1H), 5.04 (p, J = 6.3 Hz, 1H), 3.86 (s, 3H), 3.82 (dd, J = 4.9, 1.6 Hz, 1H), 3.50 (dd, J = 14.3, 1.5 Hz, 1H), 2.44 (d, J = 13.4 Hz, 1H), 2.21 – 2.09 (m, 2H), 1.31 (t, J = 6.3 Hz, 6H), 1.26 – 1.20 (m, 6H), 0.99 (dd, J = 6.5, 1.7 Hz, 1H), 0.84 (dd, J = 6.6, 4.9 Hz, 1H), 0.67 (s, 3H).
$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -134.5.
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.4, 171.1, 146.9 (d, J = 10.3 Hz), 136.2 (d, J = 3.7 Hz), 120.2 (d, J = 21.3 Hz), 113.3 (d, J = 2.1 Hz), 111.0 (d, J = 8.2 Hz), 96.5, 69.5, 69.3, 64.8, 60.8, 56.5, 53.0, 47.9, 41.6, 37.8, 22.3, 21.8 (d, J = 4.3 Hz), 21.7 (d, J = 2.2 Hz), 19.5.
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{31}BrFO_6$ 513.1283, found 513.1287.



Chemical Formula: $C_{23}H_{28}BrFO_5$
Exact Mass: 482,1104

Diisopropyl-3-(2-bromo-6-fluorophenyl)-3a-methyltetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate (2f)
Prepared according to GP A using 0.713 mmol of **1a** (0.093 g, 0.258 mmol, 36%)
^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (dt, J = 7.9, 1.1 Hz, 1H), 7.07 (td, J = 8.1, 5.5 Hz, 1H), 6.97 (ddd, J = 11.4, 8.3, 1.3 Hz, 1H), 5.98 (d, J = 1.5 Hz, 1H), 5.19 (p, J = 6.3 Hz, 1H), 5.05 (dq, J = 12.5, 6.2 Hz, 1H), 3.81 (dd, J = 5.1, 1.7 Hz, 1H), 3.42 (dd, J = 14.3, 1.6 Hz, 1H), 2.46 (d, J = 13.3 Hz, 1H), 2.18 (dd, J = 13.3, 1.6 Hz, 1H), 2.05 (d, J = 14.3 Hz, 1H), 1.38 (dt, J = 6.4, 1.4 Hz, 1H), 1.32 (t, J = 6.1 Hz, 6H), 1.24 (dd, J = 6.3, 2.5 Hz, 6H), 0.91 (d, J = 1.1 Hz, 3H), 0.80 (dd, J = 6.5, 5.0 Hz, 1H).
$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -104.6.
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.4, 171.2, 162.9, 160.4, 129.74 (d, J = 10.1 Hz), 129.22 (d, J = 3.4 Hz), 126.65 (d, J = 11.9 Hz), 123.66 (d, J = 5.9 Hz), 116.18 (d, J = 24.4 Hz), 96.7, 69.5, 69.3, 65.7, 60.8, 54.0, 47.5, 41.7, 38.1, 21.8, 21.8, 21.7, 21.7, 21.7, 19.1, 19.1.
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{29}BrFO_5$ 483.1177, found 483.1181.



Chemical Formula: $C_{24}H_{31}BrO_5$
Exact Mass: 478,1355

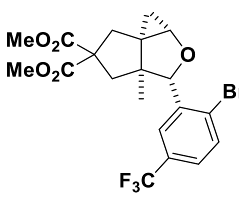
Diisopropyl-3-(2-bromo-3-methylphenyl)-3a-methyltetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate (2g)

Prepared according to GP A using 0.713 mmol of **1a** (0.139 g, 0.290 mmol, 41%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 2.0 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 11H), 7.11 (dd, *J* = 7.5, 2.0 Hz, 1H), 5.87 (s, 1H), 5.30 (s, 1H), 5.18 (hept, *J* = 6.2 Hz, 1H), 5.03 (h, *J* = 6.3 Hz, 1H), 3.81 (dd, *J* = 5.0, 1.7 Hz, 1H), 3.56 (dd, *J* = 14.3, 1.5 Hz, 1H), 2.47 – 2.42 (m, 1H), 2.40 (s, 3H), 2.22 – 2.13 (m, 2H), 1.32 (dd, *J* = 7.3, 6.3 Hz, 6H), 1.24 (dd, *J* = 6.3, 4.0 Hz, 6H), 1.04 (dd, *J* = 6.5, 1.8 Hz, 1H), 0.80 (dd, *J* = 6.6, 4.9 Hz, 1H), 0.66 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.5, 171.3, 140.6, 138.2, 129.7, 126.7, 126.3, 124.7, 97.3, 69.4, 69.2, 64.8, 60.9, 52.9, 48.3, 41.6, 37.9, 24.0, 22.4, 21.8, 21.8, 21.7, 21.7, 21.7, 19.0.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{32}BrO_5$ 479.1428, found 479.1431.



Chemical Formula: $C_{20}H_{20}BrF_3O_5$
Exact Mass: 476,0446

Dimethyl-3-(2-bromo-5-(trifluoromethyl)phenyl)-3a-methyltetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate (2i)

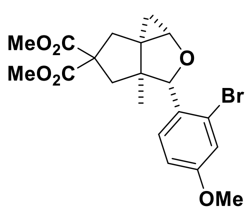
Prepared according to GP A using 1.11 mmol of **1b** (0.164 g, 0.344 mmol, 31%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 2.3 Hz, 1H), 7.62 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.34 (dd, *J* = 8.3, 2.3 Hz, 1H), 5.75 (s, 1H), 3.85 (s, 4H), 3.75 (s, 3H), 3.56 (dd, *J* = 14.4, 1.6 Hz, 1H), 2.56 – 2.41 (m, 1H), 2.27 – 2.16 (m, 2H), 1.14 – 1.06 (m, 1H), 0.87 (dd, *J* = 6.8, 4.9 Hz, 1H), 0.66 (s, 3H).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -62.7.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.3, 171.9, 141.0, 133.4, 129.74 (q, *J* = 32.8 Hz), 125.85 (q, *J* = 3.9 Hz), 125.63 (d, *J* = 1.5 Hz), 125.49 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 272.9 Hz), 96.2, 64.8, 60.3, 53.1, 53.1, 53.0, 47.9, 41.6, 37.9, 22.3, 19.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{21}BrF_3O_5$ 477.0519, found 477.0518.

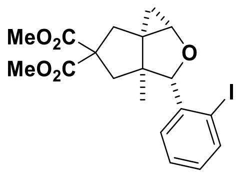


Chemical Formula: $C_{20}H_{23}BrO_6$
Exact Mass: 438,0678

Dimethyl-3-(2-bromo-4-methoxyphenyl)-3a-methyltetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate (2j)

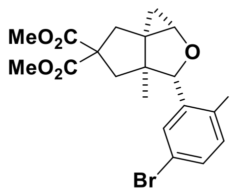
Prepared according to GP A using 0.446 mmol of **1b** (0.079 g, 0.222 mmol, 50%)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.29 (d, *J* = 8.8 Hz, 1H), 7.03 (d, *J* = 2.7 Hz, 1H), 6.81 (dd, *J* = 8.7, 2.6 Hz, 1H), 5.63 (s, 1H), 3.85 (s, 3H), 3.82 – 3.78 (m, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.50 (dd, *J* = 14.3, 1.6 Hz, 1H), 2.42 (d, *J* = 13.3 Hz, 1H), 2.23 (dd, *J* = 13.3, 1.5 Hz, 1H), 2.18 (d, *J* = 14.3 Hz, 1H), 1.05 (dd, *J* = 6.6, 1.7 Hz, 1H), 0.83 (dd, *J* = 6.6, 4.9 Hz, 1H), 0.67 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 172.4, 172.1, 159.2, 131.3, 129.6, 122.1, 117.7, 113.3, 96.5, 64.4, 60.3, 55.6, 53.0, 53.0, 52.9, 47.6, 41.4, 38.1, 22.1, 19.7.
HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{20}H_{24}BrO_6$ 439.0751, found 439.0753.



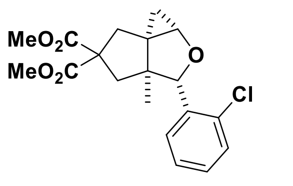
Chemical Formula: $C_{19}H_{21}IO_5$
Exact Mass: 456,0434

Dimethyl-3-(2-iodophenyl)-3a-methyltetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate (2k)
Prepared according to GP A using 1.11 mmol of **1b** (0.232 g, 0.508 mmol, 46%)
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.78 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.37 – 7.27 (m, 2H), 6.92 (ddd, *J* = 7.9, 6.9, 2.0 Hz, 1H), 5.62 (s, 1H), 3.86 (s, 3H), 3.82 (dd, *J* = 5.0, 1.7 Hz, 1H), 3.75 (s, 3H), 3.69 (dd, *J* = 14.4, 1.5 Hz, 1H), 2.47 (dd, *J* = 13.5, 0.7 Hz, 1H), 2.29 – 2.12 (m, 2H), 1.09 (dd, *J* = 6.6, 1.8 Hz, 1H), 0.83 (dd, *J* = 6.7, 4.9 Hz, 1H), 0.69 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 172.2, 171.7, 138.3, 129.9, 124.8, 106.6, 94.3, 64.8, 60.1, 53.1, 53.0, 52.9, 46.9, 41.6, 38.0, 21.2, 20.6
HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{19}H_{22}IO_5$ 457.0506, found 457.0508.



Chemical Formula: $C_{19}H_{20}BrIO_5$
Exact Mass: 533,9539

Dimethyl-3-(5-bromo-2-iodophenyl)-3a-methyltetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate (2l)
Prepared according to GP A using 0.713 mmol of **1b** (0.097 g, 0.182 mmol, 20%)
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.62 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 2.5 Hz, 1H), 7.06 (dd, *J* = 8.4, 2.5 Hz, 1H), 5.57 (s, 1H), 3.86 (s, 3H), 3.81 (dd, *J* = 5.0, 1.7 Hz, 1H), 3.75 (s, 3H), 3.68 (dd, *J* = 14.4, 1.5 Hz, 1H), 2.48 (dd, *J* = 13.4, 0.7 Hz, 1H), 2.31 – 2.13 (m, 2H), 1.08 (dd, *J* = 6.8, 1.8 Hz, 1H), 0.85 (dd, *J* = 6.8, 5.0 Hz, 1H), 0.71 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 172.4, 172.0, 145.3, 140.9, 132.4, 131.9, 122.7, 99.8, 95.0, 64.9, 60.5, 53.3, 53.1, 53.1, 48.9, 41.7, 37.9, 22.8, 19.2
HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{19}H_{21}BrIO_5$ 534.9612, found 534.9617



Chemical Formula: $C_{19}H_{21}ClO_5$
Exact Mass: 364,1078

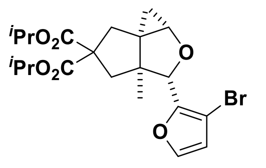
Dimethyl-3-(2-chlorophenyl)-3a-methyltetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate (2m)

Prepared according to GP A using 1.11 mmol of **1b** (0.328 g, 0.899 mmol, 81%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.7 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.18 – 7.13 (m, 1H), 5.72 (s, 1H), 3.85 (d, *J* = 1.0 Hz, 3H), 3.83 (d, *J* = 5.0 Hz, 1H), 3.75 (d, *J* = 1.0 Hz, 3H), 3.45 (d, *J* = 14.3 Hz, 1H), 2.44 (d, *J* = 13.3 Hz, 1H), 2.25 (d, *J* = 13.3 Hz, 1H), 2.18 (d, *J* = 14.3 Hz, 1H), 1.07 (dt, *J* = 6.6, 1.3 Hz, 1H), 0.88 – 0.82 (m, 1H), 0.67 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.4, 172.1, 137.7, 131.9, 129.4, 128.6, 128.5, 126.5, 94.9, 64.6, 60.3, 53.0, 53.0, 52.8, 47.3, 41.4, 38.1, 21.9, 19.8.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{21}BrIO_5$ 365.1150, found 365.1151



Chemical Formula: $C_{21}H_{27}BrO_6$
Exact Mass: 454,0991

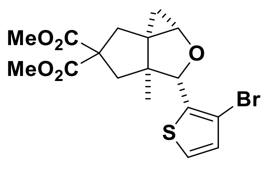
Diisopropyl-3-(3-bromofuran-2-yl)-3a-methyltetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate (2n)

Prepared according to GP A using 0.713 mmol of **1a** (0.240 g, 0.666 mmol, 94%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 2.0 Hz, 1H), 6.36 (d, *J* = 1.9 Hz, 1H), 5.43 (s, 1H), 5.15 (p, *J* = 6.2 Hz, 1H), 5.03 (p, *J* = 6.3 Hz, 1H), 3.82 (dd, *J* = 5.0, 1.7 Hz, 1H), 2.92 (dd, *J* = 14.2, 1.4 Hz, 1H), 2.49 – 2.38 (m, 1H), 2.21 (dd, *J* = 13.5, 1.4 Hz, 1H), 2.16 (d, *J* = 14.2 Hz, 1H), 1.37 – 1.28 (m, 7H), 1.22 (dd, *J* = 6.3, 2.6 Hz, 6H), 0.89 – 0.77 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.4, 171.1, 148.6, 142.7, 113.9, 98.4, 89.8, 69.5, 69.3, 65.1, 60.3, 54.0, 46.5, 40.5, 37.8, 21.8, 21.7, 21.7, 20.7, 19.4.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{28}BrO_6$ 455.1064, found 455.1067.



Chemical Formula: $C_{17}H_{19}BrO_5S$
Exact Mass: 414,0137

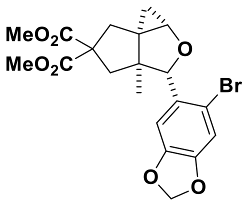
Dimethyl-3-(3-bromothiophen-2-yl)-3a-methyltetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate (2o)

Prepared according to GP A using 1.11 mmol of **1b** (0.340 g, 0.819 mmol, 73%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 5.3 Hz, 1H), 6.87 (d, *J* = 5.3 Hz, 1H), 5.57 (s, 1H), 3.83 (s, 3H), 3.82 – 3.75 (m, 1H), 3.72 (s, 3H), 3.38 (dd, *J* = 14.4, 1.6 Hz, 1H), 2.48 – 2.35 (m, 1H), 2.22 (dd, *J* = 13.4, 1.6 Hz, 1H), 2.16 (d, *J* = 14.4 Hz, 1H), 1.08 (dd, *J* = 6.7, 1.7 Hz, 1H), 0.85 (dd, *J* = 6.6, 4.9 Hz, 1H), 0.79 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.4, 172.1, 142.9, 139.7, 129.2, 128.9, 127.8, 100.3, 97.3, 64.8, 60.5, 53.2, 53.0, 53.0, 48.9, 41.7, 38.0, 22.8, 19.1.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{20}BrO_5S$ 415.0209, found 415.0210.



Chemical Formula: $C_{20}H_{21}BrO_7$
Exact Mass: 452,0471

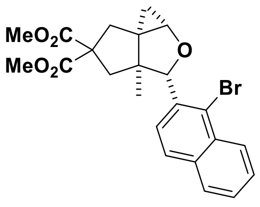
Dimethyl-3-(6-bromobenzo[d][1,3]dioxol-5-yl)-3a-methyltetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate (2p)

Prepared according to GP A using 1.11 mmol of **1b** (0.100 g, 0.221 mmol, 20%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (d, *J* = 15.3 Hz, 2H), 5.95 (s, 2H), 5.62 (s, 1H), 3.84 (s, 3H), 3.79 (dd, *J* = 4.9, 1.6 Hz, 1H), 3.74 (s, 3H), 3.50 (dd, *J* = 14.4, 1.6 Hz, 1H), 2.43 (dd, *J* = 13.3, 0.7 Hz, 1H), 2.24 – 2.14 (m, 2H), 1.04 (dd, *J* = 6.6, 1.7 Hz, 1H), 0.83 (dd, *J* = 6.7, 4.9 Hz, 1H), 0.71 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.2, 171.9, 147.4, 147.2, 132.8, 112.5, 112.1, 108.7, 101.7, 96.5, 64.4, 60.2, 52.9, 52.9, 52.9, 47.6, 41.2, 37.9, 22.0, 19.4.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{22}BrO_7$ 453.0543, found 453.0545.



Chemical Formula: $C_{23}H_{23}BrO_5$
Exact Mass: 458,0729

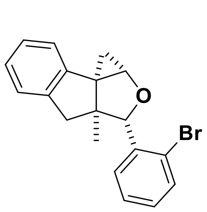
Dimethyl-3-(1-bromonaphthalen-2-yl)-3a-methyltetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate (2q)

Prepared according to GP A using 1.11 mmol of **1b** (0.181 g, 0.394 mmol, 35%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.5 Hz, 1H), 7.78 (dd, *J* = 17.2, 8.3 Hz, 2H), 7.64 – 7.47 (m, 3H), 6.05 (s, 1H), 3.90 (d, *J* = 1.3 Hz, 3H), 3.76 (d, *J* = 1.4 Hz, 3H), 3.68 (d, *J* = 14.3 Hz, 1H), 2.49 (d, *J* = 13.3 Hz, 1H), 2.31 – 2.13 (m, 2H), 1.18 (d, *J* = 6.3 Hz, 1H), 0.89 (t, *J* = 5.8 Hz, 1H), 0.70 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.4, 172.1, 137.8, 134.2, 132.2, 128.2, 127.6, 127.5, 127.3, 126.6, 126.0, 122.1, 97.4, 65.0, 60.4, 53.5, 53.1, 53.0, 48.0, 41.4, 38.0, 22.4, 19.4.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{24}BrO_5$ 459.0802, found 459.0803.

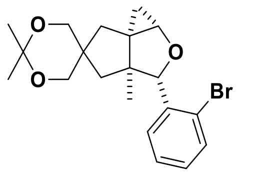


Chemical Formula: $C_{19}H_{17}BrO$
Exact Mass: 340,0463

3-(2-bromophenyl)-3a-methyl-1,1a,3a,4-tetrahydro-3*H*-cyclopropa[*b*]indeno[1,2-*c*]furan (2r)

Prepared according to GP A using 1.75 mmol of **1d** (0.338 g, 0.938 mmol, 54%)

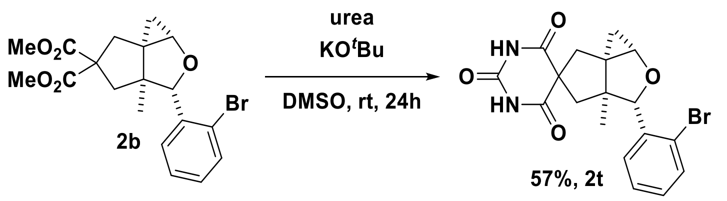
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (ddd, *J* = 7.9, 6.3, 1.5 Hz, 2H), 7.33 (td, *J* = 7.6, 1.3 Hz, 1H), 7.25 – 7.10 (m, 4H), 6.76 (dd, *J* = 6.4, 2.0 Hz, 1H), 5.83 (s, 1H), 4.05 (dd, *J* = 4.9, 2.0 Hz, 1H), 3.90 (d, *J* = 16.9 Hz, 1H), 3.07 (d, *J* = 16.9 Hz, 1H), 1.57 (dd, *J* = 6.8, 2.0 Hz, 1H), 1.43 (dd, *J* = 6.8, 5.0 Hz, 1H), 0.79 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.0, 141.8, 139.6, 132.8, 128.9, 128.9, 127.2, 126.9, 126.8, 124.9, 122.1, 119.3, 97.6, 65.4, 55.6, 48.8, 47.5, 21.4, 20.8.
HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{19}H_{18}BrO$ 341.0536, found 341.0535



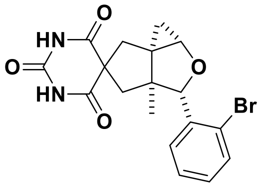
Chemical Formula: $C_{20}H_{25}BrO_3$
Exact Mass: 392,0987

3-(2-bromophenyl)-2',2',3a-trimethyltetrahydro-3*H*,6*H*-spiro[cyclopenta[*c*]cyclopropa[*b*]furan-5,5'-[1,3]dioxane] (2s)
Prepared according to GP A using 3.36 mmol of **1e** (0.263 g, 0.669 mmol, 20%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.41 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.08 (td, *J* = 7.5, 1.6 Hz, 1H), 5.65 (s, 1H), 4.11 (dd, *J* = 11.4, 2.0 Hz, 1H), 4.00 – 3.91 (m, 2H), 3.82 (d, *J* = 11.3 Hz, 1H), 3.54 (dd, *J* = 11.4, 2.0 Hz, 1H), 2.54 (d, *J* = 14.4 Hz, 1H), 2.01 – 1.77 (m, 2H), 1.46 (d, *J* = 11.1 Hz, 4H), 1.42 (s, 3H), 1.01 (dd, *J* = 6.5, 1.6 Hz, 1H), 0.73 (dd, *J* = 6.5, 5.0 Hz, 1H), 0.66 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.8, 131.7, 127.8, 127.8, 126.1, 121.1, 97.0, 96.7, 69.3, 67.8, 64.3, 52.0, 47.2, 42.3, 40.5, 37.2, 26.1, 21.6, 19.9, 17.2.
HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{20}H_{26}BrO_3$ 393.1060, found 393.1059

2.1.3 Synthesis of 3-(2-bromophenyl)-3a-methyltetrahydro-2'*H*,3*H*,6*H*-spiro[cyclopenta[*c*]cyclopropa[b]furan-5,5'-pyrimidine]-2',4',6'(1'*H*,3'*H*)-trione (2t):



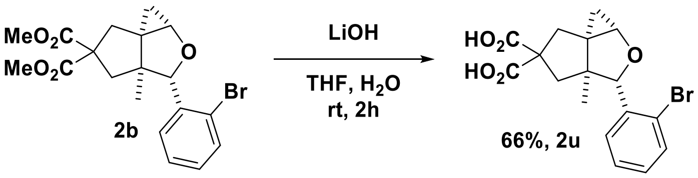
To a solution of **2b** (200.0 mg, 0.488 mmol, 1.0 eq.) in DMSO (0.5 mL, 1.0 M), urea (2.930 mmol, 6 eq.) and KO*^{t}*Bu (1.080 mmol, 2.2 eq.) were added and the mixture was stirred at room temperature for 2 h. Afterwards, the mixture was diluted with EtOAc and washed with HCl (0.1 M). The aqueous phase was extracted with EtOAc, the combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The crude mixture was purified by silica gel chromatography. (112 mg, 0.276 mmol, 57% yield)



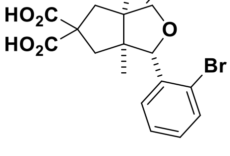
Chemical Formula: $C_{18}H_{17}BrN_2O_4$
Exact Mass: 404,0372

(2-bromophenyl)-3a-methyltetrahydro-2'*H*,3*H*,6*H*-spiro[cyclopenta[*c*]cyclopropa[*b*]furan-5,5'-pyrimidine]-2',4',6'(1'*H*,3'*H*)-trione (2t)
^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 10.09 (s, 2H), 7.54 (ddd, *J* = 14.4, 7.9, 1.5 Hz, 2H), 7.38 (ddd, *J* = 8.3, 7.4, 1.3 Hz, 1H), 7.20 (td, *J* = 7.7, 1.8 Hz, 1H), 6.08 (s, 1H), 3.97 (dd, *J* = 4.9, 1.7 Hz, 1H), 3.28 (d, *J* = 14.3 Hz, 1H), 2.83 (d, *J* = 13.4 Hz, 1H), 2.63 (d, *J* = 13.5 Hz, 1H), 2.51 (d, *J* = 14.3 Hz, 1H), 2.21 (d, *J* = 13.6 Hz, 1H), 1.08 (dd, *J* = 6.5, 1.8 Hz, 1H), 0.81 (dd, *J* = 6.5, 4.8 Hz, 1H), 0.78 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, Acetone-*d*$_6$) δ 178.9, 178.0, 154.9, 145.7, 137.6, 134.2, 134.1, 132.4, 126.8, 101.8, 70.2, 62.8, 59.5, 55.2, 47.6, 46.6, 26.7, 23.2.
HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{18}H_{18}BrN_2O_4$ 405.0444, found 405.0445.

2.1.4 Synthesis of 3-(2-bromophenyl)-3a-methyltetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylic acid (2u)



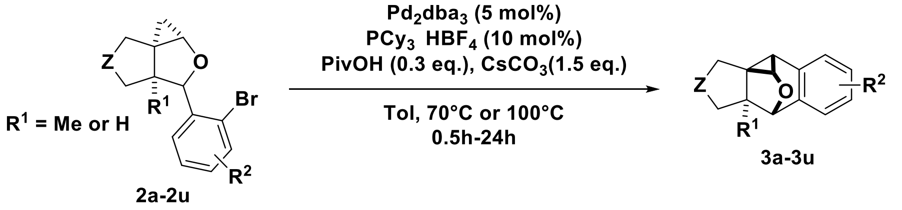
To a solution of **2b** (500.0 mg, 1.22 mmol, 1.0 eq.) in THF (20.0 mL) and H_2O (6.0 mL) was added LiOH (4.9 mmol, 4 eq.). The mixture was stirred at 25 °C for 5 h and then poured into water (25 mL). After acidifying with diluted aqueous HCl solution, the precipitate was collected by filtration and washed with H_2O to give **2u** (306 mg, 0.803 mmol, 66%)



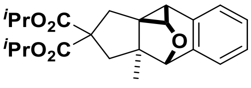
Chemical Formula: $C_{17}H_{17}BrO_5$
Exact Mass: 380,0259

3-(2-bromophenyl)-3a-methyltetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylic acid (2u)
^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 11.37 (s, 2H), 7.56 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.48 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.35 (td, *J* = 7.6, 1.3 Hz, 1H), 7.18 (td, *J* = 7.6, 1.8 Hz, 1H), 5.84 (s, 1H), 3.90 – 3.77 (m, 1H), 3.64 – 3.54 (m, 1H), 2.48 (dd, *J* = 13.3, 0.8 Hz, 1H), 2.24 (dd, *J* = 13.3, 1.5 Hz, 1H), 2.20 (d, *J* = 14.2 Hz, 1H), 1.08 (dd, *J* = 6.4, 1.7 Hz, 1H), 0.86 (dd, *J* = 6.4, 4.8 Hz, 1H), 0.68 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, Acetone-*d*$_6$) δ 173.5, 172.9, 141.0, 133.5, 130.2, 129.9, 128.0, 122.4, 97.5, 65.5, 60.8, 53.8, 48.9, 42.4, 38.5, 22.6, 19.5.
HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{17}H_{18}BrO_5$ 381.0332, found 381.0331.

2.2 General procedure for Pd-catalyzed C-H Activation

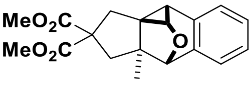


General procedure B: To a Schlenk tube was successively added the Pd complex (4.58 mg, 0.005 mmol, 5 mol%), the phosphine ligand (7.4 mg, 0.020 mmol, 10 mol%), PivOH (3.1 mg, 0.030 mmol, 0.3 eq.), the base (48.9 mg, 0.150 mmol, 1.5 eq.) and the cyclopropane derivative (0.1 mmol, 1.0 eq.). The tube was then placed under Argon (3 times vacuum/argon exchange). Then Tol. (1 mL, 0.1 M) was added, and the tube was placed in a pre-heated oil bath at the indicated temperature. After TLC monitoring, the reaction mixture was filtered through a short pad of silica with a 1:1 petroleum ether/EtOAc mixture as the eluting solvent. The desired product was obtained using an Tol/Et_2O mixture as the eluant.



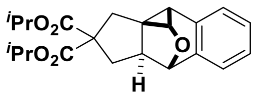
Chemical Formula: $C_{23}H_{28}O_5$
Exact Mass: 384,1937

Diisopropyl-4a-methyl-4,4a,5,9b-tetrahydro-1*H*-1,5-epoxycyclopenta[*b*]cyclopropa[*a*]naphthalene-3,3(2*H*)-dicarboxylate (3a)
Prepared according to GP B (70°C) using 0.1 mmol of **2a** (0.037 g, 0.096 mmol, 96%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 2H), 7.16 (td, *J* = 7.1, 1.9 Hz, 1H), 7.07 (dd, *J* = 7.2, 1.3 Hz, 1H), 5.07 (heptd, *J* = 6.3, 4.5 Hz, 2H), 4.71 (s, 1H), 3.80 (d, *J* = 5.3 Hz, 1H), 2.57 – 2.44 (m, 3H), 2.37 (d, *J* = 13.3 Hz, 1H), 2.19 (d, *J* = 13.3 Hz, 1H), 1.30 – 1.21 (m, 12H), 0.49 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.0, 171.8, 134.2, 132.7, 127.7, 126.7, 125.0, 124.3, 82.9, 69.2, 69.1, 61.4, 59.0, 47.9, 40.4, 35.7, 32.5, 22.2, 21.7, 21.6, 21.6, 15.9.
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{29}O_5$ 385.2010, found 385.2012.



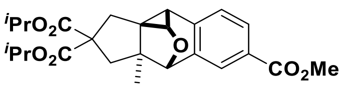
Chemical Formula: $C_{19}H_{20}O_5$
Exact Mass: 328,1311

Dimethyl-4a-methyl-4,4a,5,9b-tetrahydro-1*H*-1,5-epoxycyclopenta[*b*]cyclopropa[*a*]naphthalene-3,3(2*H*)-dicarboxylate (3b)
Prepared according to GP B (70°C) using 0.1 mmol of **2b** (0.032 g, 0.097 mmol, 97%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 2H), 7.16 (td, *J* = 7.1, 1.9 Hz, 1H), 7.10 – 7.03 (m, 1H), 4.71 (s, 1H), 3.80 (d, *J* = 5.3 Hz, 1H), 3.76 (d, *J* = 7.1 Hz, 6H), 2.58 (d, *J* = 13.5 Hz, 1H), 2.54 – 2.48 (m, 2H), 2.40 (d, *J* = 13.3 Hz, 1H), 2.23 (d, *J* = 13.4 Hz, 1H), 0.48 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.4, 172.0, 137.7, 131.8, 129.4, 128.5, 128.5, 126.5, 94.8, 64.5, 60.3, 53.0, 52.9, 52.8, 47.3, 41.4, 38.1, 21.9, 19.7.
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{21}O_5$ 329.1384, found 329.1383.



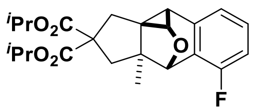
Chemical Formula: $C_{22}H_{26}O_5$
Exact Mass: 370,1780

Diisopropyl-4,4a,5,9b-tetrahydro-1*H*-1,5-epoxycyclopenta[*b*]cyclopropa[*a*]naphthalene-3,3(2*H*)-dicarboxylate (3c)
Prepared according to GP B (70°C) using 0.1 mmol of **2c** (0.027 g, 0.072 mmol, 72%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.20 (m, 2H), 7.14 (td, *J* = 7.1, 1.9 Hz, 1H), 7.08 – 7.04 (m, 1H), 5.04 (dp, *J* = 23.4, 6.3 Hz, 2H), 4.86 (s, 1H), 3.84 (d, *J* = 5.3 Hz, 1H), 2.59 (d, *J* = 13.8 Hz, 1H), 2.55 – 2.50 (m, 2H), 2.47 (d, *J* = 13.7 Hz, 1H), 1.91 – 1.75 (m, 2H), 1.27 – 1.18 (m, 12H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.8, 170.4, 134.6, 131.8, 126.9, 125.8, 124.1, 121.8, 78.2, 68.1, 68.1, 61.6, 57.2, 45.3, 33.1, 32.4, 32.2, 21.2, 20.7, 20.7, 20.6.
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{27}O_5$ 371.1853, found 371.1855.



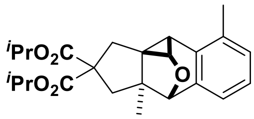
Chemical Formula: $C_{25}H_{30}O_7$
Exact Mass: 442,1992

3,3-diisopropyl-7-methyl-4a-methyl-4,4a,5,9b-tetrahydro-1*H*-1,5-epoxycyclopenta[*b*]cyclopropa[*a*]naphthalene-3,3,7(2*H*)-tricarboxylate (3d)
Prepared according to GP B (70°C) using 0.1 mmol of **2d** (0.035 g, 0.079 mmol, 79%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.75 (d, *J* = 1.7 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 5.05 (pd, *J* = 6.3, 5.2 Hz, 2H), 4.76 (s, 1H), 3.89 (s, 3H), 3.86 (d, *J* = 5.2 Hz, 1H), 2.57 – 2.42 (m, 3H), 2.39 – 2.30 (m, 1H), 2.17 (d, *J* = 13.4 Hz, 1H), 1.29 – 1.16 (m, 12H), 0.46 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.8, 171.5, 167.2, 138.5, 134.0, 129.1, 126.8, 126.7, 125.3, 82.5, 69.1, 69.1, 61.1, 59.7, 52.0, 47.7, 40.1, 36.5, 32.2, 22.7, 21.5, 21.5, 21.5, 15.8.
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{31}O_7$ 443.2064, found 443.2066.



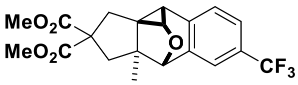
Chemical Formula: $C_{23}H_{27}FO_5$
Exact Mass: 402,1843

Diisopropyl-6-fluoro-4a-methyl-4,4a,5,9b-tetrahydro-1*H*-1,5-epoxycyclopenta[*b*]cyclopropa[*a*]naphthalene-3,3(2*H*)-dicarboxylate (3f)
Prepared according to GP B (100°C) using 0.1 mmol of **2f** (0.024 g, 0.060 mmol, 60%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (ddd, *J* = 8.3, 7.5, 5.6 Hz, 1H), 7.04 (d, *J* = 7.4 Hz, 1H), 6.92 – 6.82 (m, 1H), 5.16 (s, 1H), 5.06 (pd, *J* = 6.2, 3.3 Hz, 2H), 3.81 (d, *J* = 5.3 Hz, 1H), 2.53 – 2.44 (m, 3H), 2.38 (d, *J* = 13.4 Hz, 1H), 2.18 (d, *J* = 13.4 Hz, 1H), 1.28 – 1.20 (m, 12H), 0.54 (s, 3H).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -127.2
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.0, 171.7, 159.2, 156.8, 135.58 (d, *J* = 6.0 Hz), 128.63 (d, *J* = 8.1 Hz), 122.41 (d, *J* = 3.1 Hz), 120.99 (d, *J* = 18.7 Hz), 112.04 (d, *J* = 21.6 Hz), 75.9, 75.9, 69.3, 69.2, 61.3, 59.3, 47.6, 40.2, 36.0, 32.3, 22.1, 22.1, 21.7, 21.7, 21.6, 15.6.
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{28}FO_5$ 403.1915, found 403.1916.



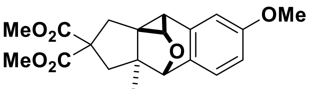
Chemical Formula: $C_{24}H_{30}O_5$
Exact Mass: 398,2093

Diisopropyl-4a,9-dimethyl-4,4a,5,9b-tetrahydro-1*H*-1,5-epoxycyclopenta[*b*]cyclopropa[*a*]naphthalene-3,3(2*H*)-dicarboxylate (3g)
Prepared according to GP B (100°C) using 0.1 mmol of **2g** (0.024 g, 0.060 mmol, 60%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.07 (m, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.90 (dd, *J* = 7.3, 1.4 Hz, 1H), 5.05 (hd, *J* = 6.2, 4.7 Hz, 2H), 4.67 (s, 1H), 3.80 (d, *J* = 5.3 Hz, 1H), 2.60 (d, *J* = 5.4 Hz, 1H), 2.56 – 2.42 (m, 2H), 2.35 (d, *J* = 16.2 Hz, 4H), 2.18 (d, *J* = 13.3 Hz, 1H), 1.28 – 1.20 (m, 12H), 0.47 (s, 3H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 172.1, 171.9, 134.5, 133.9, 130.6, 129.4, 124.5, 122.3, 83.1, 69.1, 69.1, 61.4, 59.3, 47.6, 40.3, 35.7, 32.7, 21.7, 21.7, 21.6, 18.9, 18.5, 16.0.
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{31}O_5$ 399.2166, found 399.2163.



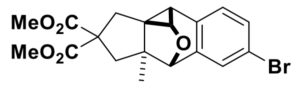
Chemical Formula: $C_{20}H_{19}F_3O_5$
Exact Mass: 396,1185

Dimethyl-4a-methyl-7-(trifluoromethyl)-4,4a,5,9b-tetrahydro-1*H*-1,5-epoxycyclopenta[*b*]cyclopropa[*a*]naphthalene-3,3(2*H*)-dicarboxylate (3i)
Prepared according to GP B (100°C) using 0.1 mmol of **2i** (0.028 g, 0.072 mmol, 72%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.33 (s, 1H), 4.77 (s, 1H), 3.87 (d, *J* = 5.2 Hz, 1H), 3.80 – 3.72 (m, 5H), 2.61 – 2.54 (m, 2H), 2.50 (d, *J* = 13.5 Hz, 1H), 2.42 (d, *J* = 13.5 Hz, 1H), 2.23 (d, *J* = 13.4 Hz, 1H), 0.48 (s, 2H).
$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -61.88.
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 172.8, 172.6, 137.0, 136.9, 134.4, 127.39 (q, *J* = 32.3 Hz), 127.1, 124.77 (q, *J* = 3.9 Hz), 124.5 (q, *J* =272.8 Hz), 121.16 (q, *J* = 3.8 Hz), 82.5, 61.0, 59.4, 53.2, 53.1, 47.7, 40.3, 36.3, 32.4, 22.4, 15.9.
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{20}F_3O_5$ 397.1257, found 397.1257.



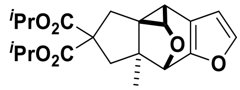
Chemical Formula: $C_{20}H_{22}O_6$
Exact Mass: 358,1416

Dimethyl-8-methoxy-4a-methyl-4,4a,5,9b-tetrahydro-1*H*-1,5-epoxycyclopenta[*b*]cyclopropa[*a*]naphthalene-3,3(2*H*)-dicarboxylate (3j)
Prepared according to GP B (100°C) using 0.1 mmol of **2j** (0.011 g, 0.030 mmol, 53%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.1 Hz, 1H), 6.84 (d, *J* = 2.5 Hz, 1H), 6.68 (dd, *J* = 8.1, 2.5 Hz, 1H), 4.66 (s, 1H), 3.79 (s, 3H), 3.76 (s, 4H), 3.75 (s, 3H), 2.60 – 2.46 (m, 2H), 2.45 (d, *J* = 5.3 Hz, 1H), 2.36 (d, *J* = 5.2 Hz, 1H), 2.20 (d, *J* = 13.3 Hz, 1H), 0.49 (s, 3H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 173.0, 172.8, 159.5, 134.0, 129.2, 128.4, 126.8, 125.3, 112.9, 110.0, 82.5, 61.0, 58.8, 55.4, 53.1, 53.1, 48.4, 40.6, 36.0, 32.7, 22.6, 16.1.
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{23}O_6$ 359.1489, found 359.1490.



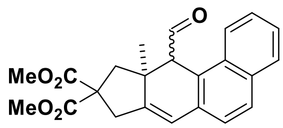
Chemical Formula: $C_{19}H_{19}BrO_5$
Exact Mass: 406,0416

Dimethyl-7-bromo-4a-methyl-4,4a,5,9b-tetrahydro-1*H*-1,5-epoxycyclopenta[*b*]cyclopropa[*a*]naphthalene-3,3(2*H*)-dicarboxylate (3l)
Prepared according to GP B (100°C) using 0.1 mmol of **2l** (0.019 g, 0.047 mmol, 47%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.22 (d, *J* = 2.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 4.66 (s, 1H), 3.81 (d, *J* = 5.3 Hz, 1H), 3.76 (d, *J* = 5.3 Hz, 6H), 2.63 – 2.44 (m, 3H), 2.39 (d, *J* = 13.3 Hz, 1H), 2.20 (d, *J* = 13.4 Hz, 1H), 0.49 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.9, 172.6, 135.9, 131.7, 130.7, 128.4, 127.5, 118.8, 82.3, 61.0, 59.1, 53.2, 53.1, 47.9, 40.4, 35.9, 32.5, 21.9, 16.0.
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{20}BrO_5$ 407.0489, found 407.0490.



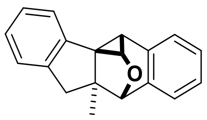
Chemical Formula: $C_{21}H_{26}O_6$
Exact Mass: 374,1729

Dimethyl-4a-methyl-4,4a,5,8b-tetrahydro-1*H*-1,5-epoxycyclopropa[7,7*a*]indeno[5,6-*b*]furan-3,3(2*H*)-dicarboxylate (3n)
Prepared according to GP B (100°C) using 0.1 mmol of **2n** (0.009 g, 0.024 mmol, 24%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.28 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.17 (d, *J* = 3.2 Hz, 1H), 5.19 (s, 1H), 5.14 (p, *J* = 6.2 Hz, 1H), 5.04 (p, *J* = 6.2 Hz, 1H), 3.81 (dd, *J* = 5.1, 1.7 Hz, 1H), 2.82 (dd, *J* = 14.2, 1.4 Hz, 1H), 2.40 (d, *J* = 13.5 Hz, 1H), 2.24 (dd, *J* = 13.6, 1.4 Hz, 1H), 2.18 (d, *J* = 14.1 Hz, 1H), 1.33 – 1.17 (m, 12H), 0.81 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.4, 171.1, 152.4, 142.0, 110.0, 107.3, 92.0, 69.3, 64.8, 60.3, 52.9, 46.0, 40.6, 37.9, 21.7, 21.7, 21.6, 20.2, 19.8.
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{28}O_6$ 377.1959, found 377.1952



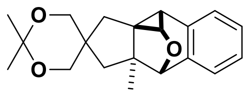
Chemical Formula: $C_{23}H_{22}O_5$
Exact Mass: 378,1467

Dimethyl-7-formyl-7a-methyl-7,7a,8,10-tetrahydro-9*H*-cyclopenta[*b*]phenanthrene-9,9-dicarboxylate (4q)
Prepared according to GP B (100°C) using 0.1 mmol of **2q** (0.009 mg, 0.024 mmol, 24%)
Only major diastereomers is described here (cis:trans 1:5).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (d, *J* = 5.1 Hz, 1H), 8.11 (d, *J* = 8.6 Hz, 1H), 7.81 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.51 (dddd, *J* = 19.9, 8.0, 6.8, 1.4 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 1H), 7.09 (t, *J* = 2.1 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.45 (dd, *J* = 17.6, 2.7 Hz, 1H), 3.38 (d, *J* = 5.1 Hz, 1H), 3.30 – 3.22 (m, 1H), 2.73 – 2.51 (m, 2H), 1.10 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 200.4, 172.3, 172.1, 149.0, 133.9, 129.8, 129.4, 128.6, 127.8, 127.7, 126.5, 126.0, 125.6, 122.9, 114.2, 62.9, 59.5, 53.1, 43.6, 43.3, 38.8, 24.8.
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{23}O_5$ 379.1540, found 379.1541.



Chemical Formula: $C_{19}H_{16}O$
Exact Mass: 260,1201

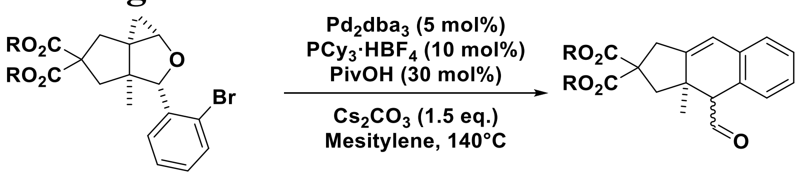
6a-methyl-1a,6,6a,7-tetrahydro-1*H*-1,6-epoxybenzo[*b*]cyclopropa[*d*]fluorene (3r)
Prepared according to GP B (100°C) using 0.1 mmol of **2r** (0.008 g, 0.032 mmol, 45%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.31 (td, *J* = 7.5, 1.4 Hz, 1H), 7.21 (qd, *J* = 7.7, 1.2 Hz, 2H), 7.18 – 7.10 (m, 3H), 7.00 (dd, *J* = 6.7, 1.7 Hz, 1H), 4.97 (s, 1H), 3.87 (d, *J* = 5.3 Hz, 1H), 3.23 (d, *J* = 14.4 Hz, 1H), 3.15 (d, *J* = 5.3 Hz, 1H), 2.48 (d, *J* = 14.4 Hz, 1H), 0.54 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) 145.1, 139.4, 135.0, 131.5, 128.0, 126.9, 126.7, 126.2, 125.5, 125.4, 124.2, 120.1, 82.6, 62.0, 54.7, 40.6, 39.5, 23.5, 17.0.
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{17}O$ 261.1274, found 261.1275.



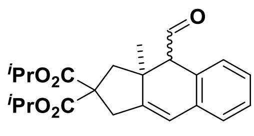
Chemical Formula: $C_{20}H_{24}O_3$
Exact Mass: 312,1725

2,2,4a'-trimethyl-4',4a',5',9b'-tetrahydro-1'*H*,2'*H*-spiro[[1,3]dioxane-5,3'-[1,5]epoxycyclopenta[*b*]cyclopropa[a]naphthalene] (3s)
Prepared according to GP B (70°C) using 0.1 mmol of **2s** (0.015 g, 0.048 mmol, 68% (71%))
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.19 (m, 2H), 7.15 (td, *J* = 7.2, 1.6 Hz, 1H), 7.05 (dd, *J* = 7.3, 1.3 Hz, 1H), 4.66 (s, 1H), 3.82 (d, *J* = 11.3 Hz, 1H), 3.78 – 3.70 (m, 3H), 3.65 (dd, *J* = 11.3, 2.0 Hz, 1H), 2.41 (d, *J* = 5.3 Hz, 1H), 2.01 (d, *J* = 1.9 Hz, 2H), 1.49 (d, *J* = 13.3 Hz, 1H), 1.43 (d, *J* = 14.5 Hz, 6H), 1.27 (d, *J* = 13.2 Hz, 1H), 0.46 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 134.3, 132.9, 127.7, 126.9, 124.9, 124.3, 97.8, 83.3, 71.1, 70.4, 59.2, 46.7, 44.1, 39.4, 34.9, 32.7, 27.0, 21.3, 21.0, 17.9.
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{25}O_3$ 313.1798, found 313.1799.

2.3 General procedure for One Pot C-H Activation/Thermal rearrangement.



General procedure C: A 4 mL screw-cap vial equipped with a magnetic stir bar was charged with the starting material (0.195 mmol, 1.0 eq.), Pd complex (5 mol%), $PCy_3{\cdot}HBF_4$ (10 mol%), Cs_2CO_3 (1.5 eq.) and PivOH (0.3 eq.). The vial was purged with argon, then dry and degassed mesitylene (0.2 M) was added. The resulting mixture was placed in a preheated bath at 140°C and stirred overnight. The reaction was then cooled to room temperature and filtered through a pad of silica. The crude product was purified by silica gel flash chromatography using an Tol/Et_2O mixture as the eluant.



Chemical Formula: $C_{23}H_{28}O_5$
Exact Mass: 384,1937

Diisopropyl-4-formyl-3a-methyl-1,3,3a,4-tetrahydro-2*H*-cyclopenta[*b*]naphthalene-2,2-dicarboxylate (4a)

Prepared according to GP C using 0.195 mmol of **2a** (0.052 mg, 0.135 mmol, 79%)

cis (minor product):

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (d, *J* = 4.1 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.16 (td, *J* = 7.4, 1.5 Hz, 1H), 7.08 (dd, *J* = 7.3, 1.5 Hz, 2H), 6.25 (dd, *J* = 2.6, 1.4 Hz, 1H), 5.04 (dp, *J* = 14.8, 6.3 Hz, 2H), 3.70 (d, *J* = 4.1 Hz, 1H), 3.37 (dd, *J* = 17.2, 2.7 Hz, 1H), 2.94 (d, *J* = 17.3 Hz, 1H), 2.72 (d, *J* = 14.1 Hz, 1H), 2.28 (d, *J* = 14.0 Hz, 1H), 1.25 (s, 4H), 1.23 (t, *J* = 1.4 Hz, 7H), 1.22 (d, *J* = 2.7 Hz, 3H), 1.08 (s, 3H).

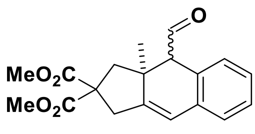
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 204.3, 171.2, 171.1, 149.1, 134.0, 130.0, 127.7, 127.0, 126.5, 126.4, 118.6, 69.3, 69.3, 60.3, 59.7, 45.6, 44.6, 37.7, 21.6, 21.6, 21.5, 19.6.

trans (major product):

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (d, *J* = 5.3 Hz, 1H), 7.25 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.18 – 7.14 (m, 1H), 7.13 – 7.09 (m, 2H), 6.31 (dd, *J* = 2.7, 1.4 Hz, 1H), 5.07 (dp, *J* = 20.7, 6.3 Hz, 2H), 3.36 (dd, *J* = 17.7, 2.6 Hz, 1H), 3.29 (d, *J* = 5.3 Hz, 1H), 3.07 (dd, *J* = 17.6, 1.4 Hz, 1H), 2.61 (d, *J* = 14.6 Hz, 1H), 2.45 (d, *J* = 14.6 Hz, 1H), 1.28 (d, *J* = 1.5 Hz, 3H), 1.26 (t, *J* = 1.8 Hz, 6H), 1.25 (d, *J* = 2.2 Hz, 3H), 1.09 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 200.6, 171.4, 171.2, 148.1, 133.9, 130.1, 129.0, 128.7, 128.3, 128.2, 127.5, 126.4, 118.3, 69.5, 69.3, 62.3, 59.5, 43.8, 43.1, 38.0, 25.3, 21.5, 21.5, 21.4

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{29}O_5$ 385.2010, found 385.2010.



Chemical Formula: $C_{19}H_{20}O_5$
Exact Mass: 328,1311

Dimethyl(*trans*)-4-formyl-3a-methyl-1,3,3a,4-tetrahydro-2*H*-cyclopenta[*b*]naphthalene-2,2- dicarboxylate (4b)

Prepared according to GP C using 0.195 mmol of **2b** (0.043 mg, 0.134 mmol, 83%)

cis (minor product):

^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.08 (d, *J* = 4.0 Hz, 1H), 7.18 – 7.12 (m, 1H), 7.09 (td, *J* = 7.6, 1.5 Hz, 1H), 7.02 (dd, *J* = 7.4, 1.5 Hz, 2H), 6.19 (dd, *J* = 2.6, 1.4 Hz, 1H), 3.65 (s, 3H), 3.63 (s, 3H), 3.56 (d, *J* = 4.0 Hz, 1H), 3.31 – 3.25 (m, 1H), 2.92 (d, *J* = 17.3 Hz, 1H), 2.62 (d, *J* = 14.1 Hz, 1H), 2.26 (d, *J* = 14.1 Hz, 1H), 0.97 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 203.9, 172.0, 148.9, 134.0, 130.0, 127.7, 126.9, 126.4, 126.4, 118.6, 60.3, 59.5, 45.6, 44.5, 37.6, 19.3.

trans (major product):

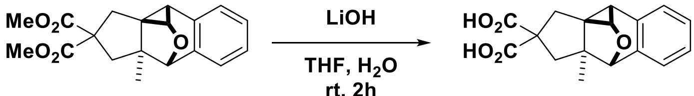
^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.21 (d, *J* = 5.0 Hz, 1H), 7.16 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.10 – 7.05 (m, 1H), 7.02 (dd, *J* = 7.3, 1.5 Hz, 2H), 6.21 (dd, *J* = 2.7, 1.5 Hz, 1H), 3.66 (s, 3H), 3.62 (s, 3H), 3.26 (dd, *J* = 17.7, 2.7 Hz, 1H), 3.18 (d, *J* = 4.9 Hz, 1H), 3.03 – 2.95 (m, 1H), 2.53 (d, *J* = 14.5 Hz, 1H), 2.35 (d, *J* = 14.6 Hz, 1H), 0.95 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 200.0, 172.2, 172.0, 148.0, 134.0, 130.0, 128.7, 128.5, 127.5, 126.4, 118.3, 62.1, 59.3, 43.7, 43.0, 38.0, 25.0.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{21}O_5$ 329.1384, found 329.1023.

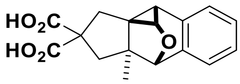
2.4 Post-Functionalization Procedure

2.4.1 Synthesis of 4a-methyl-4,4a,5,9b-tetrahydro-1*H*-1,5-epoxycyclopenta[*b*]cyclopropa[*a*]naphthalene-3,3(2*H*)-dicarboxylic acid (5)



3b quant., 5

To a solution of **3b** (32.8 mg, 0.1 mmol, 1.0 eq.) in THF (1.5 mL) and H_2O (0.5 mL) was added LiOH (9.6 mg, 0.4 mmol, 4 eq.). The mixture was stirred at 25 °C for 5 h and then poured into water (5mL). After acidifying with diluted aqueous HCl solution, the precipitate was collected by filtration and washed with H_2O to give **5** (29.8 mg, 0.099 mmol, >99%).



Chemical Formula: $C_{17}H_{16}O_5$
Exact Mass: 300,0998

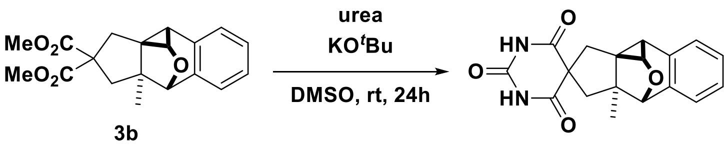
4a-methyl-4,4a,5,9b-tetrahydro-1*H*-1,5-epoxycyclopenta[*b*]cyclopropa[*a*]naphthalene-3,3(2*H*)-dicarboxylic acid (5)

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 7.31 (d, *J* = 7.4 Hz, 1H), 7.23 (td, *J* = 7.2, 2.0 Hz, 1H), 7.17 – 7.09 (m, 2H), 4.75 (s, 1H), 3.71 (d, *J* = 5.3 Hz, 1H), 2.62 – 2.49 (m, 3H), 2.36 – 2.27 (m, 2H), 0.47 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, Acetone-*d*$_6$) δ 173.8, 173.6, 135.6, 134.0, 128.2, 127.3, 125.5, 125.0, 83.3, 61.4, 59.7, 48.5, 41.2, 36.3, 33.1, 22.6, 16.2.

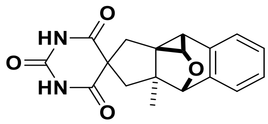
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{17}O_5$ 301.1071, found 301.1071.

2.4.2 Synthesis of 4a'-methyl-4',4a',5',9b'-tetrahydro-1'*H*,2*H*,2'*H*-spiro[pyrimidine-5,3'-[1,5]epoxycyclopenta[*b*]cyclopropa[*a*]naphthalene]-2,4,6(1*H*,3*H*)-trione (6)



3b 81%, 6

To a solution of **3b** (32,8 mg, 0.1 mmol, 1.0 eq.) in DMSO (0.2 mL, 1.0 M), urea (36.3 mg, 0.6mmol, 6 eq.) and KO*ᵗ*Bu (25.0 mg, 0.220 mmol, 2.2 eq.) were added and the mixture was stirred at room temperature for 2 h. Afterwards, the mixture was diluted with EtOAc and washed with HCl (0.1 M). The aqueous phase was extracted with EtOAc, the combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The crude mixture was purified by recrystallization (Acetone/Heptane). (26.4 mg, 0.081 mmol, 81% yield)



Chemical Formula: $C_{18}H_{16}N_2O_4$
Exact Mass: 324,1110

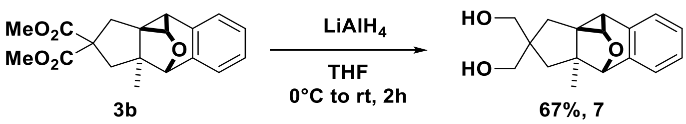
4a'-methyl-4',4a',5',9b'-tetrahydro-1'*H*,2*H*,2'*H*-spiro[pyrimidine-5,3'-[1,5]epoxycyclopenta[*b*]cyclopropa[a]naphthalene]-2,4,6(1*H*,3*H*)-trione (6)

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.09 (s, 1H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.22 (td, *J* = 7.3, 2.0 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 2H), 4.75 (s, 1H), 3.82 (d, *J* = 5.3 Hz, 1H), 3.30 (d, *J* = 9.2 Hz, 1H), 2.62 (s, 1H), 2.57 (d, *J* = 12.9 Hz, 1H), 2.16 (d, *J* = 12.9 Hz, 2H), 1.89 (d, *J* = 12.8 Hz, 1H), 0.51 (s, 3H).

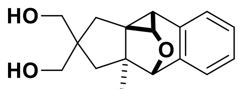
^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 173.7, 173.6, 173.4, 173.3, 150.4, 134.4, 132.8, 127.2, 126.3, 124.5, 124.1, 81.8, 58.8, 57.5, 48.2, 42.9, 35.8, 32.6, 21.5, 15.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{17}N_2O_4$ 325.1183, found 325.1182.

2.4.3 Synthesis of (4a-methyl-2,3,4,4a,5,9b-hexahydro-1*H*-1,5-epoxycyclopenta[*b*]cyclopropa[*a*]naphthalene-3,3-diyl)dimethanol (7)



Lithium aluminum hydride (8.35 mg, 0.220 mmol, 2.2 equiv.) was stirred in dry THF (0.4 M) at 0°C. Then **3b** (32.84 mg, 0.1 mmol, 1 equiv.) was dissolved in THF (0.4 M) and added dropwise at 0°C. Then, the mixture was slowly warmed to room temperature until the completion of the reaction. It was then cooled to 0°C, and the reaction was worked up using the Fieser procedure.[6] Then crude was concentrated in vacuo and purified by flash column chromatography.



Chemical Formula: $C_{17}H_{20}O_3$
Exact Mass: 272,1412

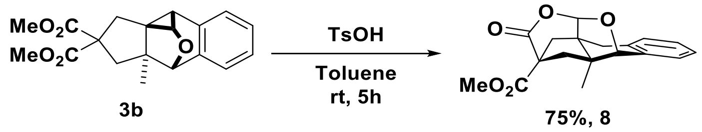
(4a-methyl-2,3,4,4a,5,9b-hexahydro-1*H*-1,5-epoxycyclopenta[*b*]cyclopropa[*a*]naphthalene-3,3-diyl)dimethanol (7)

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 7.28 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.20 (td, *J* = 7.3, 1.7 Hz, 1H), 7.12 (td, *J* = 7.3, 1.3 Hz, 1H), 7.08 (dd, *J* = 7.3, 1.7 Hz, 1H), 4.64 (s, 1H), 3.88 (d, *J* = 5.4 Hz, 2H), 3.72 (d, *J* = 5.3 Hz, 1H), 3.67 – 3.60 (m, 4H), 2.84 (s, 1H), 2.42 (d, *J* = 5.3 Hz, 1H), 1.87 (d, *J* = 13.0 Hz, 1H), 1.69 (d, *J* = 13.0 Hz, 1H), 1.50 (d, *J* = 13.1 Hz, 1H), 1.38 (d, *J* = 13.1 Hz, 1H), 0.48 (s, 3H).

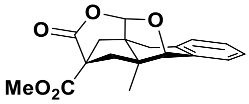
^{13}C{^{1}H} NMR (101 MHz, Acetone-*d*$_6$) δ 136.1, 134.6, 128.0, 127.3, 125.2, 124.9, 84.1, 69.6, 69.2, 60.3, 52.2, 47.7, 38.9, 35.5, 22.0, 18.0.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{21}O_3$ 273.1485, found 273.14852.

2.4.4 Synthesis of methyl-12-methyl-2-oxo-7,11b-dihydro-2H,5H-4a,7,3-(epiethane[1,1,2]triyl)benzo[c]pyrano[2,3-e]oxepine-3(4H)-carboxylate (8)



In a 4 mL screw-cap tube equipped with a magnetic stir bar was charged with **3b** (32.84 mg, 0.1 mmol, 1.0 eq) and TsOH (5.17 mg, 0.030 mmol, 0.3 eq.). The vial was purged with argon, then dry toluene (1 mL, 0.1 M) was added. The resulting mixture was placed in a preheated bath at 100°C and stirred for 2h. After TLC monitoring, the reaction was then cooled to room temperature and concentrated under vacuum. The crude mixture was purified by silica gel chromatography using an Tol/Et_2O mixture as the eluant. (23.7 mg, 0.075 mmol, 76% yield)



Chemical Formula: $C_{18}H_{18}O_5$
Molecular Weight: 314,3370

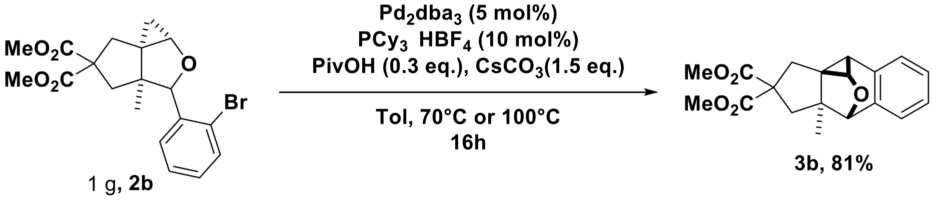
Methyl-5a-methyl-3-oxo-5,5a,6,11-tetrahydro-1H-1,6-epoxy-4,11a-methanonaphtho[2,3-c]oxepine-4(3H)-carboxylate (8)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 1H), 7.23 – 7.14 (m, 1H), 5.40 (s, 1H), 4.80 (s, 1H), 3.82 (s, 3H), 3.07 – 2.93 (m, 2H), 2.51 – 2.39 (m, 3H), 2.24 (d, J = 12.7 Hz, 1H), 0.99 (s, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) 170.6, 170.2, 137.7, 132.2, 129.6, 129.0, 128.9, 127.2, 107.4, 85.4, 56.6, 53.0, 52.8, 47.8, 41.1, 36.5, 34.0, 18.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{19}O_5$ 315.1227, found 315.1228.

2.5 Gram scale Reaction

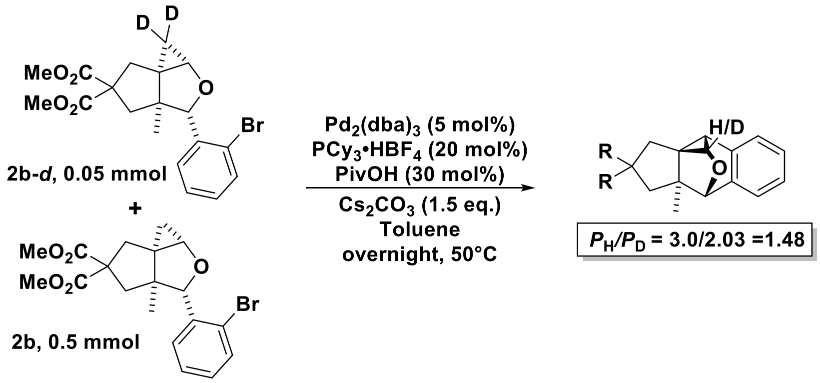


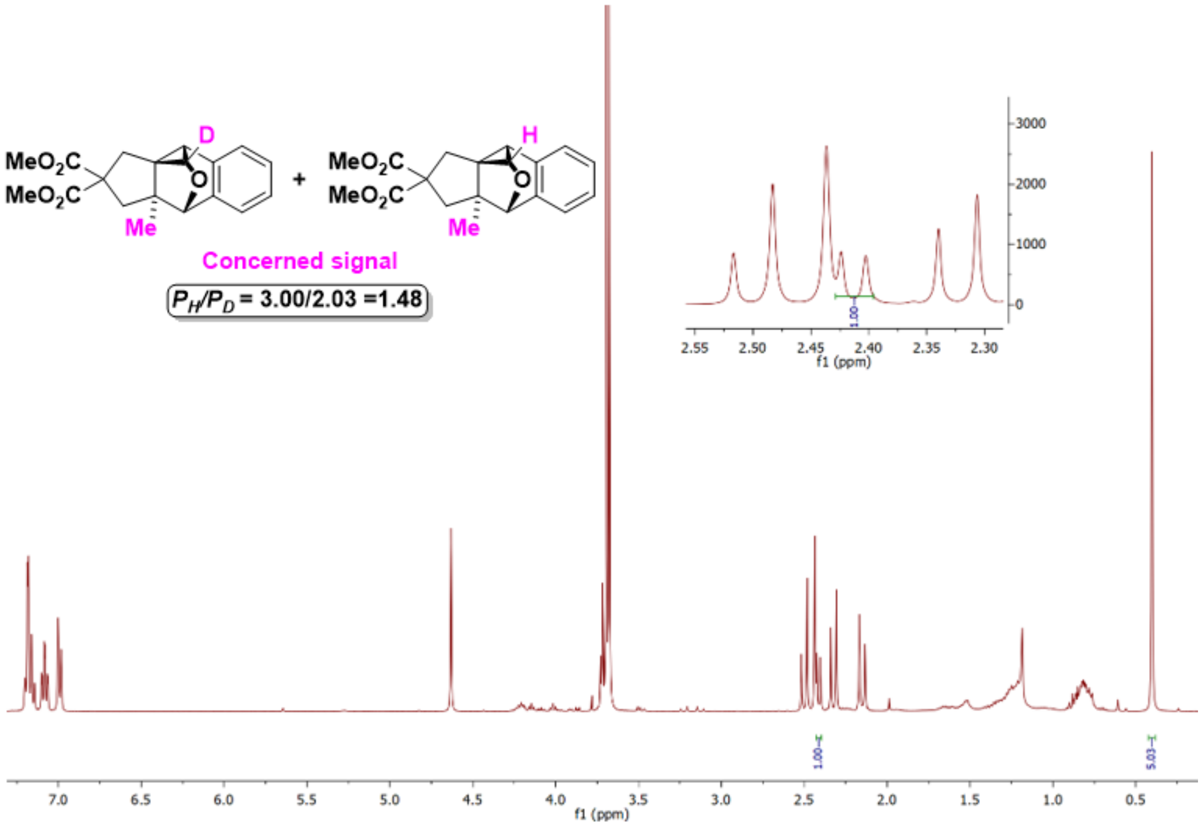
To a Schlenk tube was successively added the Pd complex (4.58 mg, 0.005 mmol, 5 mol%), the phosphine ligand (7.4 mg, 0.020 mmol, 10 mol%), PivOH (3.1 mg, 0.030 mmol, 0.3 eq.), the base (48.9 mg, 0.150 mmol, 1.5 eq.) and the cyclopropane derivative (0.1 mmol, 1.0 eq.). After, the tube was placed under Argon (3 times to vacuum argon exchange). Then Tol. (1 mL, 0.1 M) was added, and the tube was placed in a pre-heated oil bath at the indicated temperature. After TLC monitoring, the reaction mixture was filtered through a short pad of silica with a 1:1 petroleum ether/EtOAc mixture as the eluting solvent. The desired product was obtained using an Tol/Et_2O mixture as the eluant (650.0 mg, 1.98 mmol, 81%).

3. Kinetic Isotope Effect (KIE) Experiments

Intramolecular Competition Experiment:

Following the general procedure B at 50°C, C-H Activation was done on a mixture of model substrate and d^2-model substrate. The distribution of the product was calculated from the ^{1}H-NMR signal.





KIE Determination from Parallel Reactions

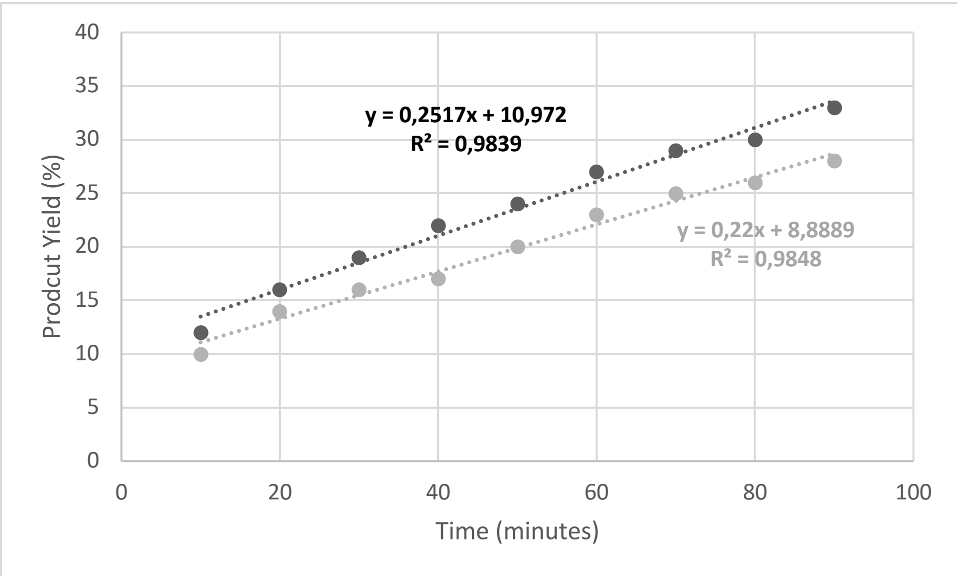
Reactions performed on a 0.1 mmol scale. To a screw cap NMR tube was successively added the Pd complex (4.58 mg, 0.005 mmol, 5 mol%), the phosphine ligand (7.4 mg, 0.020 mmol, 10 mol%), PivOH (3.1 mg, 0.030 mmol, 0.3 eq.), the base (48.9 mg, 0.150 mmol, 1.5 eq.) and 1,3,5-Trimethoxybenzene (0.033 mmol, 5.56 mg, 0.3 eq) as an internal standard. The tube was then placed under Argon (3 times vacuum/argon exchange) and Tol. (0.5 mL, 0.2 M) was added. A solution of **2b** or **2b-D** in Tol. (0.5 mL, 0.2 M) was charged on a syringe. After 5min, the solution is added in the tube and vigorously shaken before placing it in a 500 MHz NMR spectrometer for 1.5 hours at 70°C. An analysis is run every 10 minutes during this reaction time. The tables below summarize the results obtained.

Table S1. a. yields determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as internal standard.

Time (minutes)	Yields **3b** (%)[a]	Yields **3b-*d*** (%)[a]
10	12	10
20	16	14
30	19	16
40	22	17
50	24	20
60	27	23
70	29	25
80	30	26
90	33	28

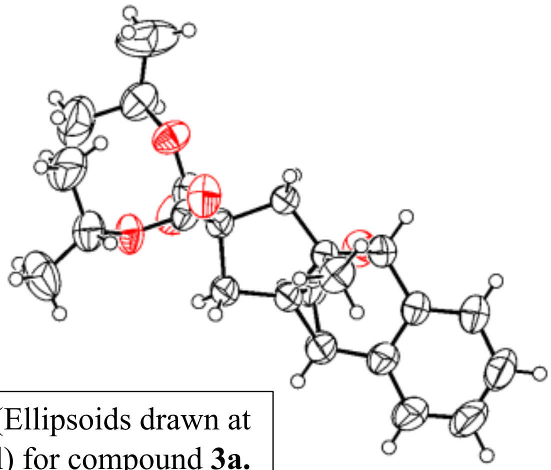
In this mechanistic study, the ratio of k_H/k_D was determined from initial slope method.
KIE = k_H/k_D = 0.2517/0.2200 = 1.14

Figure 1. Product Yield vs Time for Product 3a and 3a-D



4. X-ray Data

- Single suitable crystal of $C_{23}H_{28}O_5$ **3a** was selected and were on a SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer. The crystal was kept at 295 K during data collection. Using Olex2[7], the structure was solved with the SHELXT[8] structure solution program using Intrinsic Phasing and refined with the SHELXL[9] refinement package using Least Squares minimization.



Standard Displacement Ellipsoid Plot (Ellipsoids drawn at 50% probability level) for compound **3a.**

Table S2. Crystal data and structure refinement for **3a.**

Identification code	**3a**
Empirical formula	$C_{23}H_{28}O_5$
Formula weight	768.90
Temperature/K	295
Crystal system	triclinic
Space group	P-1
a/Å	11.5105(3)
b/Å	14.1983(4)
c/Å	14.3748(4)
α/°	70.403(2)
β/°	77.993(2)
γ/°	80.425(2)
Volume/Å^3	2152.85(11)
Z	2
ρ_{calc}g/cm^3	1.186
μ/mm^{-1}	0.670
F(000)	824.0
Crystal size/mm^3	0.26 × 0.26 × 0.06
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.644 to 145.828
Index ranges	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -16 ≤ l ≤ 17
Reflections collected	40354
Independent reflections	8384 [R_{int} = 0.0321, R_{sigma} = 0.0192]
Data/restraints/parameters	8384/9/515
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0550, wR_2 = 0.1508
Final R indexes [all data]	R_1 = 0.0729, wR_2 = 0.1661

Largest diff. peak/hole / e Å^{-3}	0.32/-0.19

Table S3. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **3a**. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	6516.9(12)	716.5(11)	1761.3(11)	61.9(4)
O2	9631(2)	-1073.4(13)	2404.9(17)	101.1(7)
O3	10193.3(14)	-496.7(10)	3481.7(11)	60.8(4)
O4	10859.1(13)	1927.6(11)	2166.5(13)	68.4(4)
O5	11857.5(11)	644.8(10)	1660.9(12)	58.6(4)
C1	8424.4(16)	1112.4(16)	808.1(14)	50.9(4)
C2	7470.4(18)	418.2(17)	1100.9(17)	60.2(5)
C3	7683.7(18)	1146.4(18)	33.7(17)	62.1(5)
C4	6740.3(18)	1990.9(18)	-198.2(16)	61.8(5)
C5	6365(2)	2420(2)	-1121.3(19)	78.5(7)
C6	5447(2)	3184(3)	-1243(2)	91.7(9)
C7	4902(2)	3536(2)	-462(2)	88.6(8)
C8	5255.8(19)	3114.7(19)	465.6(19)	71.1(6)
C9	6170.2(17)	2338.2(17)	603.3(16)	57.9(5)
C10	6617.8(16)	1775.8(16)	1572.1(15)	54.0(5)
C11	7977.0(15)	1813.3(14)	1424.9(13)	46.0(4)
C12	8576.9(16)	1255.6(14)	2346.4(14)	47.7(4)
C13	9776.1(15)	700.5(13)	1963.9(13)	44.7(4)
C14	9712.7(16)	772.6(17)	871.4(15)	54.7(5)
C15	8334(2)	2887.3(16)	934.4(18)	64.5(5)
C16	9870.3(17)	-393.8(15)	2622.9(16)	54.4(5)
C17	10333(2)	-1518.1(16)	4190.3(19)	71.7(6)
C18	11492(3)	-2057(3)	3858(3)	114.5(11)
C19	10204(5)	-1398(2)	5193(2)	137.3(17)
C20	10869.7(16)	1175.2(14)	1966.2(14)	47.4(4)
C21	13014.7(17)	993.4(18)	1588.1(19)	65.4(6)
C22	13867(2)	555(3)	869(3)	100.6(10)
C23	13336(2)	702(3)	2610(2)	100.4(10)
O6	-358.3(13)	4038.2(11)	3432.6(12)	65.5(4)
O7	4758.2(15)	3616.8(19)	2583.2(15)	98.2(7)
O8	4776.3(12)	4329.9(13)	3732.3(12)	69.9(4)
O9	1942.0(18)	3329.5(17)	5366.1(14)	102.8(7)
O10	3529.0(17)	2431.3(15)	4850.1(14)	98.0(7)
C24	1210.8(17)	5045.6(14)	3187.2(16)	52.7(5)
C25	34.1(19)	4694.1(17)	3811.4(17)	62.1(5)
C26	87.3(18)	5782.1(16)	3132.0(17)	58.6(5)
C27	-488.1(17)	6032.5(15)	2242.9(17)	56.9(5)
C28	-1107(2)	6956.2(17)	1821(2)	71.4(6)
C29	-1663(2)	7091.6(19)	1022(2)	80.3(7)
C30	-1602(2)	6327(2)	622(2)	80.4(7)

Table S3. Fractional Atomic Coordinates (×10[4]) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **3a**. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C31	-990.0(19)	5401.6(18)	1033.9(18)	64.9(6)
C32	-426.0(17)	5254.5(15)	1833.4(16)	54.7(5)
C33	225.2(17)	4285.8(15)	2390.0(16)	55.0(5)
C34	1484.5(17)	4463.3(14)	2454.4(15)	50.9(4)
C35	2242.1(17)	3540.1(14)	3025.1(16)	54.5(5)
C36	2910.8(16)	3917.1(15)	3653.2(15)	50.9(4)
C37	2307.7(17)	4994.4(15)	3608.5(16)	52.8(5)
C38	2182(2)	5011.9(18)	1423.9(17)	65.8(6)
C39	4246.3(18)	3921.3(17)	3252.8(16)	58.7(5)
C40	6079.5(19)	4357(2)	3455(2)	81.3(7)
C41	6676(3)	3352(3)	3924(4)	151.5(19)
C42	6362(3)	5189(4)	3749(4)	137.9(16)
C43	2734.7(18)	3215.7(18)	4724.9(17)	63.1(5)
C44	3438(3)	1638(2)	5823(2)	107.1(10)
C45	4164(5)	1852(4)	6445(4)	179(2)
C46	3855(6)	695(3)	5605(4)	189(2)

Table S4. Anisotropic Displacement Parameters (Å^2×10^3) for ad628p. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	50.2(8)	66.4(9)	67.6(9)	-15.2(7)	-9.2(7)	-15.1(6)
O2	146.7(18)	58.0(10)	123.8(16)	-28.6(10)	-71.9(14)	-16.7(10)
O3	79.3(10)	47.5(7)	57.0(8)	-10.2(6)	-23.4(7)	-7.5(7)
O4	58.4(8)	59.6(9)	102.3(12)	-39.7(8)	-23.8(8)	-3.6(7)
O5	36.2(6)	62.2(8)	85.1(10)	-31.5(7)	-13.5(6)	-4.3(6)
C1	41.7(9)	67.1(12)	48.2(10)	-24.0(9)	-11.4(8)	0.4(8)
C2	51.2(11)	61.7(12)	75.4(14)	-26.5(11)	-20.3(10)	-3.8(9)
C3	50.1(11)	85.0(15)	62.6(13)	-36.3(12)	-18.1(9)	0.6(10)
C4	48.9(11)	82.9(15)	56.9(12)	-21.4(11)	-17.9(9)	-5.0(10)
C5	64.6(14)	113(2)	61.7(14)	-25.6(14)	-24.7(11)	-4.4(13)
C6	69.8(16)	126(2)	71.8(17)	-8.3(16)	-37.0(14)	-4.5(16)
C7	62.1(15)	102(2)	91(2)	-12.5(16)	-33.5(14)	11.9(14)
C8	48.8(11)	84.9(16)	77.2(16)	-22.7(13)	-19.3(11)	5.7(11)
C9	41.6(10)	73.2(13)	59.6(12)	-20.1(10)	-15.2(9)	0.1(9)
C10	41.0(9)	66.6(12)	54.0(11)	-20.4(9)	-7.4(8)	-1.7(8)
C11	38.4(9)	56.0(10)	43.1(10)	-15.1(8)	-8.1(7)	-2.8(7)
C12	41.9(9)	57.3(10)	45.9(10)	-18.8(8)	-9.8(7)	-2.0(8)
C13	39.4(9)	51.6(10)	47.6(10)	-19.7(8)	-12.0(7)	-2.1(7)
C14	41.4(9)	77.5(13)	52.6(11)	-31.2(10)	-12.1(8)	2.3(9)
C15	64.5(13)	60.2(12)	68.4(14)	-11.4(10)	-18.1(11)	-14.4(10)

Table S4. Anisotropic Displacement Parameters ($Å^2×10^3$) for ad628p. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a*^2U_{11}+2hka*b*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C16	48.4(10)	51.4(10)	69.8(13)	-22.9(10)	-18.2(9)	-3.5(8)
C17	85.1(16)	48.0(11)	74.9(16)	-4.7(10)	-23.1(13)	-5.3(11)
C18	100(2)	90(2)	131(3)	-11(2)	-37(2)	23.3(18)
C19	254(5)	76.1(19)	68(2)	-1.1(15)	-38(3)	-11(3)
C20	43.3(9)	48.8(10)	52.9(11)	-15.8(8)	-16.4(8)	-2.0(8)
C21	40.3(10)	74.9(14)	87.9(16)	-28.1(12)	-15.4(10)	-12.6(9)
C22	45.0(13)	141(3)	135(3)	-74(2)	1.3(14)	-17.4(15)
C23	60.8(15)	142(3)	105(2)	-33(2)	-34.5(15)	-13.9(16)
O6	54.1(8)	61.3(8)	74.9(10)	-15.8(7)	-1.8(7)	-11.9(7)
O7	52.9(9)	164(2)	97.9(14)	-80.0(14)	2.1(9)	-1.8(11)
O8	39.0(7)	105.4(12)	70.4(10)	-36.0(9)	-7.1(6)	-5.9(7)
O9	86.7(13)	116.1(15)	64.3(11)	-6.6(10)	11.4(9)	27.0(11)
O10	73.4(11)	89.1(12)	81.5(12)	11.3(10)	5.3(9)	25.8(9)
C24	47.7(10)	51.1(10)	64.4(12)	-25.1(9)	-15.1(9)	3.3(8)
C25	54.5(12)	70.5(13)	58.9(13)	-20.2(11)	-5.0(9)	-6.0(10)
C26	49.3(11)	59.2(12)	75.0(14)	-33.7(11)	-13.9(9)	4.9(9)
C27	46.1(10)	53.0(11)	75.2(14)	-23.8(10)	-16.4(9)	1.2(8)
C28	61.2(13)	53.6(12)	104.7(19)	-27.7(12)	-29.4(13)	6.3(10)
C29	65.4(14)	62.0(14)	108(2)	-10.2(13)	-39.5(14)	5.8(11)
C30	70.2(15)	83.6(17)	92.1(19)	-17.7(14)	-41.4(14)	-5.6(13)
C31	56.6(12)	69.3(13)	77.9(15)	-26.4(11)	-22.9(11)	-9.4(10)
C32	46.0(10)	52.4(11)	70.6(13)	-22.2(9)	-17.0(9)	-3.2(8)
C33	51.6(11)	50.5(10)	68.6(13)	-24.2(9)	-12.5(9)	-5.4(8)
C34	46.3(10)	47.9(10)	63.1(12)	-22.8(9)	-14.3(8)	1.1(8)
C35	47.0(10)	49.3(10)	67.8(13)	-20.8(9)	-11.5(9)	1.4(8)
C36	39.6(9)	58.1(11)	52.5(11)	-17.2(9)	-8.2(8)	2.3(8)
C37	46.0(10)	59.8(11)	58.5(12)	-25.4(9)	-14.0(8)	0.0(8)
C38	55.9(12)	75.0(14)	61.5(13)	-18.3(11)	-1.9(10)	-9.7(10)
C39	44.0(10)	73.3(13)	56.1(12)	-20.6(10)	-9.0(9)	3.1(9)
C40	39.8(11)	117(2)	86.0(18)	-31.7(16)	-6.8(11)	-9.5(12)
C41	57.1(17)	155(4)	203(5)	1(3)	-45(2)	5(2)
C42	68.6(19)	192(4)	185(4)	-92(4)	-12(2)	-42(2)
C43	45.6(10)	73.5(14)	61.0(13)	-14.6(11)	-7.7(9)	4.8(10)
C44	82.6(19)	100.2(19)	88(2)	19.7(15)	-5.2(14)	15.6(15)
C45	214(6)	150(4)	141(4)	39(3)	-81(4)	-41(4)
C46	268(7)	92(2)	141(4)	13(2)	0(4)	13(3)

Table S5. Bond Lengths for **3a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C2	1.402(3)	O6	C25	1.396(3)

Table S5. Bond Lengths for **3a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C10	1.456(2)	O6	C33	1.458(3)
O2	C16	1.197(2)	O7	C39	1.191(3)
O3	C16	1.317(2)	O8	C39	1.321(3)
O3	C17	1.472(2)	O8	C40	1.473(3)
O4	C20	1.194(2)	O9	C43	1.187(3)
O5	C20	1.335(2)	O10	C43	1.305(3)
O5	C21	1.469(2)	O10	C44	1.469(3)
C1	C2	1.498(3)	C24	C25	1.519(3)
C1	C3	1.521(3)	C24	C26	1.520(3)
C1	C11	1.508(3)	C24	C34	1.501(3)
C1	C14	1.493(3)	C24	C37	1.491(3)
C2	C3	1.532(3)	C25	C26	1.529(3)
C3	C4	1.476(3)	C26	C27	1.472(3)
C4	C5	1.388(3)	C27	C28	1.390(3)
C4	C9	1.400(3)	C27	C32	1.402(3)
C5	C6	1.375(4)	C28	C29	1.373(4)
C6	C7	1.372(4)	C29	C30	1.375(4)
C7	C8	1.382(4)	C30	C31	1.384(3)
C8	C9	1.384(3)	C31	C32	1.375(3)
C9	C10	1.503(3)	C32	C33	1.504(3)
C10	C11	1.542(2)	C33	C34	1.538(3)
C11	C12	1.534(3)	C34	C35	1.532(3)
C11	C15	1.535(3)	C34	C38	1.544(3)
C12	C13	1.563(2)	C35	C36	1.564(3)
C13	C14	1.555(3)	C36	C37	1.557(3)
C13	C16	1.524(3)	C36	C39	1.525(3)
C13	C20	1.525(2)	C36	C43	1.521(3)
C17	C18	1.495(4)	C40	C41	1.478(5)
C17	C19	1.481(4)	C40	C42	1.484(5)
C21	C22	1.492(4)	C44	C45	1.473(6)
C21	C23	1.494(4)	C44	C46	1.457(6)

Table S6. Bond Angles for **3a.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	O1	C10	104.47(15)	C25	O6	C33	104.90(15)
C16	O3	C17	117.83(16)	C39	O8	C40	117.79(18)
C20	O5	C21	118.05(15)	C43	O10	C44	119.0(2)
C2	C1	C3	60.98(14)	C25	C24	C26	60.43(14)
C2	C1	C11	103.83(16)	C34	C24	C25	103.08(16)
C11	C1	C3	116.98(16)	C34	C24	C26	116.71(17)
C14	C1	C2	124.25(19)	C37	C24	C25	124.31(19)

Table S6. Bond Angles for **3a.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C14	C1	C3	130.90(17)	C37	C24	C26	131.14(17)
C14	C1	C11	108.80(15)	C37	C24	C34	109.22(16)
O1	C2	C1	110.13(17)	O6	C25	C24	109.70(17)
O1	C2	C3	116.22(18)	O6	C25	C26	116.48(19)
C1	C2	C3	60.26(14)	C24	C25	C26	59.80(13)
C1	C3	C2	58.77(13)	C24	C26	C25	59.76(13)
C4	C3	C1	117.42(18)	C27	C26	C24	117.55(17)
C4	C3	C2	114.68(18)	C27	C26	C25	114.39(18)
C5	C4	C3	125.0(2)	C28	C27	C26	124.71(19)
C5	C4	C9	119.4(2)	C28	C27	C32	119.3(2)
C9	C4	C3	115.62(19)	C32	C27	C26	115.98(18)
C6	C5	C4	119.9(3)	C29	C28	C27	119.8(2)
C7	C6	C5	120.7(2)	C28	C29	C30	120.8(2)
C6	C7	C8	120.3(2)	C29	C30	C31	120.1(2)
C7	C8	C9	119.7(2)	C32	C31	C30	119.8(2)
C4	C9	C10	114.04(18)	C27	C32	C33	113.57(18)
C8	C9	C4	120.0(2)	C31	C32	C27	120.16(19)
C8	C9	C10	126.0(2)	C31	C32	C33	126.16(18)
O1	C10	C9	106.65(16)	O6	C33	C32	106.56(16)
O1	C10	C11	103.04(15)	O6	C33	C34	102.39(16)
C9	C10	C11	109.61(16)	C32	C33	C34	110.08(16)
C1	C11	C10	100.64(15)	C24	C34	C33	101.54(15)
C1	C11	C12	100.09(15)	C24	C34	C35	100.12(16)
C1	C11	C15	115.25(17)	C24	C34	C38	114.53(17)
C12	C11	C10	116.04(15)	C33	C34	C38	112.57(17)
C12	C11	C15	111.41(16)	C35	C34	C33	115.72(16)
C15	C11	C10	112.48(16)	C35	C34	C38	111.43(17)
C11	C12	C13	106.32(14)	C34	C35	C36	106.13(15)
C14	C13	C12	105.97(14)	C37	C36	C35	106.01(14)
C16	C13	C12	109.07(15)	C39	C36	C35	112.15(16)
C16	C13	C14	110.57(16)	C39	C36	C37	111.31(17)
C16	C13	C20	109.10(14)	C43	C36	C35	108.12(17)
C20	C13	C12	112.87(14)	C43	C36	C37	110.41(16)
C20	C13	C14	109.23(15)	C43	C36	C39	108.77(16)
C1	C14	C13	102.39(14)	C24	C37	C36	102.16(15)
O2	C16	O3	123.9(2)	O7	C39	O8	123.4(2)
O2	C16	C13	124.07(19)	O7	C39	C36	125.3(2)
O3	C16	C13	111.91(15)	O8	C39	C36	111.25(17)
O3	C17	C18	109.5(2)	O8	C40	C41	109.0(2)
O3	C17	C19	106.3(2)	O8	C40	C42	106.3(2)
C19	C17	C18	115.2(3)	C41	C40	C42	115.7(3)
O4	C20	O5	124.47(17)	O9	C43	O10	123.2(2)
O4	C20	C13	126.00(17)	O9	C43	C36	124.9(2)

Table S6. Bond Angles for **3a.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O5	C20	C13	109.46(15)	O10	C43	C36	111.78(18)
O5	C21	C22	105.69(18)	O10	C44	C45	108.5(3)
O5	C21	C23	109.4(2)	C46	C44	O10	106.0(3)
C22	C21	C23	115.1(2)	C46	C44	C45	113.2(4)

Table S7. Torsion Angles for **3a.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C2	C3	C1	99.23(19)	O6	C25	C26	C24	-98.39(19)
O1	C2	C3	C4	-9.1(3)	O6	C25	C26	C27	10.5(3)
O1	C10	C11	C1	41.07(18)	O6	C33	C34	C24	-41.62(18)
O1	C10	C11	C12	-65.8(2)	O6	C33	C34	C35	65.7(2)
O1	C10	C11	C15	164.26(16)	O6	C33	C34	C38	-164.57(16)
C1	C2	C3	C4	-108.3(2)	C24	C25	C26	C27	108.88(19)
C1	C3	C4	C5	148.8(2)	C24	C26	C27	C28	-148.1(2)
C1	C3	C4	C9	-33.8(3)	C24	C26	C27	C32	34.3(3)
C1	C11	C12	C13	31.05(18)	C24	C34	C35	C36	-31.47(19)
C2	O1	C10	C9	75.83(18)	C25	O6	C33	C32	-75.45(18)
C2	O1	C10	C11	-39.56(18)	C25	O6	C33	C34	40.15(19)
C2	C1	C3	C4	103.6(2)	C25	C24	C26	C27	-103.6(2)
C2	C1	C11	C10	-26.95(19)	C25	C24	C34	C33	27.17(19)
C2	C1	C11	C12	92.20(17)	C25	C24	C34	C35	-91.94(17)
C2	C1	C11	C15	-148.20(17)	C25	C24	C34	C38	148.76(18)
C2	C1	C14	C13	-87.4(2)	C25	C24	C37	C36	87.3(2)
C2	C3	C4	C5	-145.1(2)	C25	C26	C27	C28	144.7(2)
C2	C3	C4	C9	32.3(3)	C25	C26	C27	C32	-32.9(3)
C3	C1	C2	O1	-109.43(19)	C26	C24	C25	O6	109.9(2)
C3	C1	C11	C10	37.2(2)	C26	C24	C34	C33	-36.1(2)
C3	C1	C11	C12	156.39(18)	C26	C24	C34	C35	-155.19(18)
C3	C1	C11	C15	-84.0(2)	C26	C24	C34	C38	85.5(2)
C3	C1	C14	C13	-166.7(2)	C26	C24	C37	C36	166.0(2)
C3	C4	C5	C6	177.8(2)	C26	C27	C28	C29	-176.6(2)
C3	C4	C9	C8	-178.7(2)	C26	C27	C32	C31	176.7(2)
C3	C4	C9	C10	-0.6(3)	C26	C27	C32	C33	0.2(3)
C4	C5	C6	C7	0.7(5)	C27	C28	C29	C30	-0.9(4)
C4	C9	C10	O1	-54.5(2)	C27	C32	C33	O6	54.7(2)
C4	C9	C10	C11	56.4(2)	C27	C32	C33	C34	-55.6(2)
C5	C4	C9	C8	-1.1(3)	C28	C27	C32	C31	-1.1(3)
C5	C4	C9	C10	177.0(2)	C28	C27	C32	C33	-177.5(2)

Table S7. Torsion Angles for **3a.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C5	C6	C7	C8	-1.2(5)	C28	C29	C30	C31	1.0(4)
C6	C7	C8	C9	0.5(4)	C29	C30	C31	C32	-1.1(4)
C7	C8	C9	C4	0.7(4)	C30	C31	C32	C27	1.2(3)
C7	C8	C9	C10	-177.2(2)	C30	C31	C32	C33	177.1(2)
C8	C9	C10	O1	123.5(2)	C31	C32	C33	O6	-121.4(2)
C8	C9	C10	C11	-125.6(2)	C31	C32	C33	C34	128.3(2)
C9	C4	C5	C6	0.5(4)	C32	C27	C28	C29	1.0(4)
C9	C10	C11	C1	-72.18(19)	C32	C33	C34	C24	71.4(2)
C9	C10	C11	C12	-179.05(16)	C32	C33	C34	C35	178.70(17)
C9	C10	C11	C15	51.0(2)	C32	C33	C34	C38	-51.5(2)
C10	O1	C2	C1	22.6(2)	C33	O6	C25	C24	-23.2(2)
C10	O1	C2	C3	-43.3(2)	C33	O6	C25	C26	42.1(2)
C10	C11	C12	C13	138.25(16)	C33	C34	C35	C36	-139.62(17)
C11	C1	C2	O1	4.0(2)	C34	C24	C25	O6	-3.6(2)
C11	C1	C2	C3	113.44(17)	C34	C24	C25	C26	-113.50(18)
C11	C1	C3	C2	-91.39(19)	C34	C24	C26	C25	90.3(2)
C11	C1	C3	C4	12.2(3)	C34	C24	C26	C27	-13.3(3)
C11	C1	C14	C13	35.1(2)	C34	C24	C37	C36	-34.5(2)
C11	C12	C13	C14	-11.42(19)	C34	C35	C36	C37	12.2(2)
C11	C12	C13	C16	-130.48(16)	C34	C35	C36	C39	-109.50(19)
C11	C12	C13	C20	108.08(17)	C34	C35	C36	C43	130.58(17)
C12	C13	C14	C1	-13.4(2)	C35	C36	C37	C24	12.5(2)
C12	C13	C16	O2	98.9(3)	C35	C36	C39	O7	-4.6(3)
C12	C13	C16	O3	-78.13(19)	C35	C36	C39	O8	174.07(17)
C12	C13	C20	O4	-4.8(3)	C35	C36	C43	O9	-90.6(3)
C12	C13	C20	O5	178.11(15)	C35	C36	C43	O10	85.8(2)
C14	C1	C2	O1	128.70(19)	C37	C24	C25	O6	-128.2(2)
C14	C1	C2	C3	-121.9(2)	C37	C24	C25	C26	121.9(2)
C14	C1	C3	C2	111.8(3)	C37	C24	C26	C25	-111.4(3)
C14	C1	C3	C4	-144.6(2)	C37	C24	C26	C27	145.0(2)
C14	C1	C11	C10	-161.07(17)	C37	C24	C34	C33	161.10(17)
C14	C1	C11	C12	-41.9(2)	C37	C24	C34	C35	42.0(2)
C14	C1	C11	C15	77.7(2)	C37	C24	C34	C38	-77.3(2)
C14	C13	C16	O2	-17.2(3)	C37	C36	C39	O7	-123.2(3)
C14	C13	C16	O3	165.72(16)	C37	C36	C39	O8	55.5(2)
C14	C13	C20	O4	112.8(2)	C37	C36	C43	O9	24.9(3)
C14	C13	C20	O5	-64.28(19)	C37	C36	C43	O10	-158.6(2)
C15	C11	C12	C13	-91.31(18)	C38	C34	C35	C36	90.08(19)
C16	O3	C17	C18	77.5(3)	C39	O8	C40	C41	-78.2(3)
C16	O3	C17	C19	-157.5(3)	C39	O8	C40	C42	156.5(3)

Table S7. Torsion Angles for **3a.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C16	C13	C14	C1	104.66(18)	C39	C36	C37	C24	134.73(18)
C16	C13	C20	O4	-126.3(2)	C39	C36	C43	O9	147.3(3)
C16	C13	C20	O5	56.7(2)	C39	C36	C43	O10	-36.2(3)
C17	O3	C16	O2	3.6(3)	C40	O8	C39	O7	-3.4(4)
C17	O3	C16	C13	-179.34(17)	C40	O8	C39	C36	177.89(19)
C20	O5	C21	C22	-157.5(2)	C43	O10	C44	C45	-92.4(4)
C20	O5	C21	C23	78.0(3)	C43	O10	C44	C46	145.7(4)
C20	C13	C14	C1	-135.27(16)	C43	C36	C37	C24	-104.36(19)
C20	C13	C16	O2	-137.3(2)	C43	C36	C39	O7	114.9(3)
C20	C13	C16	O3	45.6(2)	C43	C36	C39	O8	-66.4(2)
C21	O5	C20	O4	1.5(3)	C44	O10	C43	O9	1.0(4)
C21	O5	C20	C13	178.65(17)	C44	O10	C43	C36	-175.5(3)

Table S8. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3a.**

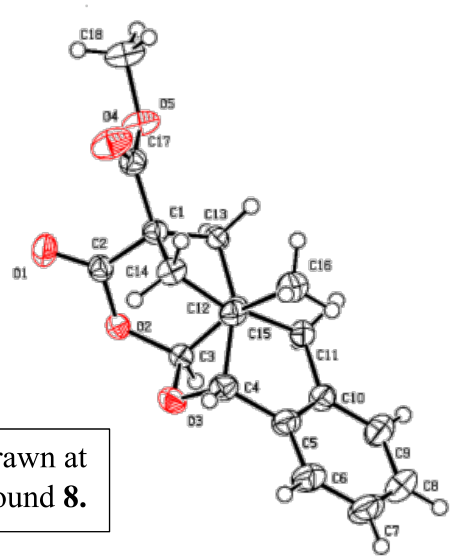
Atom	*x*	*y*	*z*	U(eq)
H2	7707.2	-301.35	1209.9	72
H3	8071.32	863.46	-502.86	74
H5	6734.25	2191.43	-1657.15	94
H6	5193.28	3464.47	-1860.3	110
H7	4292.32	4061.53	-556.99	106
H8	4880.92	3351.45	994.93	85
H10	6184.6	2018.08	2125.09	65
H12A	8069.38	776.7	2837.79	57
H12B	8729.35	1726.81	2652.69	57
H14A	10220.85	1257.8	390.57	66
H14B	9941.86	124.92	760.51	66
H15A	9188.21	2868.66	817.7	97
H15B	7993.25	3282.92	1369.85	97
H15C	8043.22	3181.79	308.88	97
H17	9681.03	-1882.08	4189.15	86
H18A	11586.3	-2721.45	4323.12	172
H18B	12137.86	-1694.76	3831.56	172
H18C	11495.94	-2101.64	3205.34	172
H19A	10848.49	-1056.13	5209.5	206
H19B	10222.88	-2048.16	5690.93	206
H19C	9457.37	-1012.27	5327.34	206
H21	12946.48	1727.82	1305.91	79
H22A	13969.71	-163.47	1152.26	151
H22B	14623.82	814.92	736.53	151

Table S8. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3a.**

Atom	*x*	*y*	*z*	U(eq)
H22C	13556.94	731.38	255.3	151
H23A	12726.88	996.04	3027.52	151
H23B	14085.85	939.37	2564.14	151
H23C	13400.95	-16.74	2894.72	151
H25	-82.12	4554.52	4538.15	74
H26	17.15	6302.45	3453.93	70
H28	-1144.28	7481.52	2079.51	86
H29	-2086.25	7707.79	747.08	96
H30	-1973.05	6431.05	74.18	97
H31	-960.24	4881.03	770.37	78
H33	238.75	3745.42	2105.26	66
H35A	2809.17	3258.01	2561.81	65
H35B	1737.99	3028.21	3460.71	65
H37A	2109.57	5073.79	4269.56	63
H37B	2817.22	5502.81	3174.38	63
H38A	2179.12	4660	958.97	99
H38B	2990.36	5031.07	1488.57	99
H38C	1809.63	5685.63	1183.41	99
H40	6291.2	4519.56	2726.09	98
H41A	6520.12	3201.57	4638.08	227
H41B	7521.28	3343.98	3692.6	227
H41C	6373.91	2856.28	3744.7	227
H42A	5822.71	5777.52	3515.89	207
H42B	7167.53	5333.34	3457.15	207
H42C	6278.16	4995.25	4465.12	207
H44	2602.5	1628.33	6152.94	129
H45A	3865.7	2489.56	6544.02	269
H45B	4979.7	1870.72	6114.27	269
H45C	4120.92	1334.26	7081.09	269
H46A	3363.13	605.42	5183.86	283
H46B	3807.6	147.28	6219.47	283
H46C	4667.64	712.69	5268.79	283

- Single suitable crystal of $C_{18}H_{18}O_5$ **8** was selected and were on a SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer. The crystal was kept at 295 K during data collection. Using Olex2[7], the structure was solved with the SHELXT[8] structure solution program using Intrinsic Phasing and refined with the SHELXL[9] refinement package using Least Squares minimization.

CDCC Deposit Number: 2339538



Standard Displacement Ellipsoid Plot (Ellipsoids drawn at 50% probability level) for compound **8.**

Table S9. Crystal data and structure refinement for **8.**

Identification code	**8**
Empirical formula	$C_{18}H_{18}O_5$
Formula weight	628.65
Temperature/K	240.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.7560(2)
b/Å	12.0801(2)
c/Å	12.2130(3)
α/°	63.904(2)
β/°	78.660(2)
γ/°	85.123(2)
Volume/Å^3	1527.19(6)
Z	2
ρ_{calc}g/cm^3	1.367
μ/mm^{-1}	0.825
F(000)	664.0
Crystal size/mm^3	0.24 × 0.14 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.67 to 144.764
Index ranges	$-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $-15 \leq l \leq 15$
Reflections collected	31992
Independent reflections	5950 [R_{int} = 0.0249, R_{sigma} = 0.0153]
Data/restraints/parameters	5950/0/420
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0349, wR_2 = 0.0926
Final R indexes [all data]	R_1 = 0.0377, wR_2 = 0.0953
Largest diff. peak/hole / e Å^{-3}	0.28/-0.18

Table S10. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **8**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	616.1(9)	3712.2(8)	6748.2(8)	41.1(2)
O2	1319.5(7)	4628.1(7)	4759.0(7)	29.89(19)
O3	3192.8(7)	4964.9(8)	3677.3(8)	33.7(2)
O4	1631.8(9)	5202.8(11)	8123.5(9)	50.7(3)
O5	89.9(8)	6123.0(9)	7269.3(8)	40.2(2)
C1	1628.1(10)	5644.1(10)	5998.1(10)	25.9(2)
C2	1139.9(10)	4575.5(10)	5907.9(11)	28.0(2)
C3	2097.9(10)	5528.3(10)	3744.5(10)	26.4(2)
C4	4047.6(10)	5807.4(11)	3602.2(11)	31.5(3)
C5	4374.8(11)	6765.4(12)	2275.0(11)	33.1(3)
C6	5446.3(12)	6745.4(14)	1554.7(13)	42.7(3)
C7	5721.8(13)	7630.1(16)	341.3(14)	50.8(4)
C8	4924.9(15)	8530.4(15)	-163.2(14)	53.2(4)
C9	3857.5(13)	8560.1(14)	549.9(13)	44.6(3)
C10	3573.8(11)	7693.9(11)	1774.0(11)	32.4(3)
C11	2439.8(10)	7801.4(11)	2571.9(11)	29.6(2)
C12	2270.9(9)	6726.7(10)	3859.1(10)	24.0(2)
C13	1355.2(9)	6822.0(10)	4877.3(10)	24.7(2)
C14	2977.0(10)	5528.7(12)	5777.0(11)	30.5(3)
C15	3402.6(10)	6416.5(11)	4403.6(11)	28.0(2)
C16	4044.9(11)	7502.3(13)	4324.1(13)	38.9(3)
C17	1139.7(10)	5616.0(11)	7260.8(11)	30.7(3)
C18	-437.7(13)	6212.5(16)	8406.1(13)	49.0(4)
O6	3027.0(11)	623.3(10)	2703.3(10)	57.9(3)
O7	1720.3(8)	-172.8(8)	4401.5(8)	36.9(2)
O8	2057.5(8)	-1408.1(7)	6372.1(8)	35.5(2)
O9	4734.4(10)	2569.5(12)	3105.7(12)	65.7(3)
O10	3101.3(9)	3259.1(9)	2349.4(9)	46.5(2)
C19	2959.2(10)	1434.2(11)	4207.2(11)	30.4(3)
C20	2610.2(12)	616.3(11)	3679.7(12)	35.5(3)
C21	1381.2(10)	-420.7(11)	5690.9(11)	29.3(2)
C22	2468.0(11)	-1078.3(11)	7240.2(12)	34.2(3)
C23	1501.8(11)	-1330.0(11)	8338.4(11)	33.6(3)
C24	1527.0(13)	-2362.4(13)	9457.8(13)	42.9(3)
C25	599.0(15)	-2638.4(14)	10427.0(13)	48.8(4)
C26	-365.3(16)	-1886.6(15)	10279.6(13)	52.7(4)
C27	-392.7(14)	-845.9(14)	9172.8(13)	47.4(3)
C28	541.5(11)	-542.1(11)	8196.5(11)	33.7(3)
C29	524.3(11)	637.7(11)	7009.0(11)	33.1(3)
C30	1534.8(10)	664.9(10)	5998.9(10)	26.6(2)

Table S10. Fractional Atomic Coordinates (×10[4]) and Equivalent Isotropic Displacement Parameters (Å[2]×10[3]) for **8**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C31	1821.8(10)	1840.3(10)	4814.4(11)	30.0(2)
C32	3598.6(10)	643.0(12)	5302.6(12)	35.7(3)
C33	2687.3(10)	300.7(11)	6498.1(11)	31.0(3)
C34	2943.2(14)	941.6(14)	7257.7(14)	46.9(3)
C35	3716.5(12)	2475.2(12)	3168.1(12)	38.4(3)
C36	3741.1(18)	4270.5(15)	1306.0(15)	62.5(5)

Table S11. Anisotropic Displacement Parameters (Å[2]×10[3]) for **8**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	51.8(6)	30.3(5)	33.7(5)	-7.9(4)	-1.1(4)	-11.4(4)
O2	34.1(4)	26.1(4)	31.0(4)	-14.8(3)	-0.7(3)	-6.5(3)
O3	32.8(4)	28.3(4)	41.1(5)	-18.9(4)	-0.8(4)	2.8(3)
O4	47.6(6)	73.2(7)	30.7(5)	-21.7(5)	-12.2(4)	10.9(5)
O5	33.8(5)	59.4(6)	31.9(5)	-25.8(4)	-3.8(4)	6.4(4)
C1	25.7(5)	27.1(6)	26.0(5)	-12.4(5)	-4.6(4)	-0.1(4)
C2	28.5(6)	24.7(6)	29.3(6)	-10.5(5)	-5.3(4)	1.1(4)
C3	28.6(6)	24.7(5)	25.9(5)	-12.1(4)	-1.8(4)	-1.8(4)
C4	24.8(6)	35.1(6)	34.2(6)	-15.7(5)	-3.9(5)	2.8(5)
C5	30.6(6)	37.9(7)	32.5(6)	-18.3(5)	-0.6(5)	-3.2(5)
C6	34.0(7)	52.8(8)	41.6(7)	-24.3(7)	1.8(6)	-0.3(6)
C7	42.3(8)	64.2(10)	42.4(8)	-26.6(7)	12.3(6)	-8.9(7)
C8	57.9(9)	54.7(9)	32.8(7)	-11.8(7)	9.3(6)	-9.5(7)
C9	47.9(8)	42.8(8)	33.5(7)	-10.5(6)	1.0(6)	-2.9(6)
C10	34.1(6)	32.7(6)	30.2(6)	-14.6(5)	-0.5(5)	-5.2(5)
C11	30.8(6)	26.0(6)	29.3(6)	-10.1(5)	-3.5(5)	-0.5(4)
C12	23.8(5)	22.9(5)	26.4(5)	-11.8(4)	-3.5(4)	-1.2(4)
C13	25.2(5)	22.3(5)	27.9(5)	-12.4(4)	-3.4(4)	-0.1(4)
C14	25.4(6)	37.6(6)	29.4(6)	-14.7(5)	-6.9(5)	1.6(5)
C15	23.6(5)	32.2(6)	29.4(6)	-14.4(5)	-4.1(4)	-1.4(4)
C16	32.5(6)	47.2(8)	42.5(7)	-24.0(6)	-3.2(5)	-11.1(6)
C17	32.3(6)	32.1(6)	28.6(6)	-13.7(5)	-4.5(5)	-3.0(5)
C18	46.1(8)	69.1(10)	37.7(7)	-32.5(7)	0.5(6)	4.4(7)
O6	81.5(8)	50.6(6)	43.4(6)	-30.2(5)	17.7(5)	-21.9(6)
O7	45.8(5)	35.4(5)	32.5(4)	-17.7(4)	-0.8(4)	-12.9(4)
O8	43.1(5)	24.2(4)	38.8(5)	-14.9(4)	-4.5(4)	3.3(4)
O9	38.5(6)	71.8(8)	63.9(7)	-11.9(6)	7.4(5)	-20.5(5)
O10	54.3(6)	36.4(5)	37.3(5)	-6.9(4)	1.5(4)	-15.3(4)
C19	28.7(6)	27.6(6)	34.2(6)	-15.2(5)	2.6(5)	-4.3(5)
C20	41.4(7)	29.7(6)	35.0(6)	-16.5(5)	3.0(5)	-5.4(5)
C21	30.1(6)	27.3(6)	29.6(6)	-12.2(5)	-1.6(5)	-4.0(5)

Table S11. Anisotropic Displacement Parameters (Å^2×10^3) for **8**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C22	30.8(6)	30.8(6)	37.8(7)	-11.2(5)	-8.9(5)	3.3(5)
C23	38.3(7)	30.4(6)	31.1(6)	-11.3(5)	-7.2(5)	-4.4(5)
C24	52.3(8)	36.3(7)	36.5(7)	-9.2(6)	-14.4(6)	-3.4(6)
C25	73.1(11)	40.0(8)	27.8(6)	-8.0(6)	-7.9(6)	-11.6(7)
C26	69.0(10)	47.5(8)	32.7(7)	-15.5(6)	11.2(7)	-12.1(7)
C27	52.6(9)	42.1(8)	39.4(7)	-16.8(6)	8.7(6)	-1.8(6)
C28	40.2(7)	29.4(6)	30.4(6)	-13.7(5)	-0.7(5)	-4.0(5)
C29	32.7(6)	28.7(6)	33.4(6)	-12.7(5)	1.5(5)	2.0(5)
C30	25.6(5)	23.4(5)	30.0(6)	-12.2(5)	-2.2(4)	0.3(4)
C31	31.4(6)	23.7(5)	32.4(6)	-12.2(5)	-0.2(5)	0.3(4)
C32	25.5(6)	35.6(7)	43.3(7)	-15.5(6)	-2.3(5)	-2.9(5)
C33	27.7(6)	30.3(6)	33.9(6)	-12.7(5)	-4.7(5)	-2.4(5)
C34	51.3(8)	50.7(8)	43.8(8)	-21.8(7)	-9.6(6)	-15.4(7)
C35	39.9(7)	36.8(7)	37.8(7)	-19.3(6)	6.8(6)	-10.7(6)
C36	88.1(13)	44.3(9)	39.9(8)	-8.8(7)	10.8(8)	-26.9(8)

Table S12. Bond Lengths for **8**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C2	1.1996(15)	O6	C20	1.1933(16)
O2	C2	1.3508(14)	O7	C20	1.3593(15)
O2	C3	1.4468(13)	O7	C21	1.4447(14)
O3	C3	1.4091(14)	O8	C21	1.4046(15)
O3	C4	1.4525(15)	O8	C22	1.4564(15)
O4	C17	1.1925(15)	O9	C35	1.1959(18)
O5	C17	1.3305(15)	O10	C35	1.3246(18)
O5	C18	1.4512(15)	O10	C36	1.4464(17)
C1	C2	1.5113(16)	C19	C20	1.5141(17)
C1	C13	1.5437(15)	C19	C31	1.5483(16)
C1	C14	1.5602(15)	C19	C32	1.5546(18)
C1	C17	1.5225(15)	C19	C35	1.5253(17)
C3	C12	1.5480(15)	C21	C30	1.5475(15)
C4	C5	1.5149(17)	C22	C23	1.5107(18)
C4	C15	1.5235(16)	C22	C33	1.5218(17)
C5	C6	1.3925(18)	C23	C24	1.3910(18)
C5	C10	1.4008(18)	C23	C28	1.3998(18)
C6	C7	1.386(2)	C24	C25	1.382(2)
C7	C8	1.380(2)	C25	C26	1.380(2)
C8	C9	1.387(2)	C26	C27	1.387(2)
C9	C10	1.3885(18)	C27	C28	1.3896(19)
C10	C11	1.5214(16)	C28	C29	1.5242(17)

Table S12. Bond Lengths for **8**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C11	C12	1.5237(15)	C29	C30	1.5260(15)
C12	C13	1.5156(14)	C30	C31	1.5183(16)
C12	C15	1.5481(15)	C30	C33	1.5455(16)
C14	C15	1.5469(16)	C32	C33	1.5427(17)
C15	C16	1.5257(17)	C33	C34	1.5270(18)

Table S13. Bond Angles for **8.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	O2	C3	121.31(9)	C20	O7	C21	119.94(9)
C3	O3	C4	107.43(8)	C21	O8	C22	107.13(8)
C17	O5	C18	115.75(10)	C35	O10	C36	115.93(13)
C2	C1	C13	106.60(9)	C20	C19	C31	106.62(10)
C2	C1	C14	107.56(9)	C20	C19	C32	109.08(10)
C2	C1	C17	109.48(9)	C20	C19	C35	108.28(10)
C13	C1	C14	105.33(9)	C31	C19	C32	104.61(9)
C17	C1	C13	115.20(9)	C35	C19	C31	115.60(10)
C17	C1	C14	112.24(9)	C35	C19	C32	112.36(10)
O1	C2	O2	118.51(11)	O6	C20	O7	118.69(12)
O1	C2	C1	126.19(11)	O6	C20	C19	126.20(12)
O2	C2	C1	115.30(9)	O7	C20	C19	115.09(10)
O2	C3	C12	115.72(9)	O7	C21	C30	115.54(9)
O3	C3	O2	107.38(9)	O8	C21	O7	107.66(9)
O3	C3	C12	107.34(9)	O8	C21	C30	107.86(9)
O3	C4	C5	109.80(10)	O8	C22	C23	108.16(10)
O3	C4	C15	103.32(9)	O8	C22	C33	102.77(9)
C5	C4	C15	109.96(10)	C23	C22	C33	110.57(10)
C6	C5	C4	121.65(12)	C24	C23	C22	121.01(12)
C6	C5	C10	119.79(12)	C24	C23	C28	119.96(12)
C10	C5	C4	118.56(11)	C28	C23	C22	118.94(11)
C7	C6	C5	120.48(14)	C25	C24	C23	120.67(14)
C8	C7	C6	119.86(13)	C26	C25	C24	119.64(13)
C7	C8	C9	120.01(14)	C25	C26	C27	120.14(14)
C8	C9	C10	120.94(14)	C26	C27	C28	120.98(15)
C5	C10	C11	120.85(11)	C23	C28	C29	121.00(11)
C9	C10	C5	118.90(12)	C27	C28	C23	118.57(12)
C9	C10	C11	120.16(12)	C27	C28	C29	120.42(12)
C10	C11	C12	111.67(10)	C28	C29	C30	110.85(10)
C3	C12	C15	100.63(9)	C29	C30	C21	108.15(9)
C11	C12	C3	109.01(9)	C29	C30	C33	111.48(10)
C11	C12	C15	111.74(9)	C31	C30	C21	110.23(9)
C13	C12	C3	110.21(9)	C31	C30	C29	120.20(9)

Table S13. Bond Angles for **8.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C13	C12	C11	119.13(9)	C31	C30	C33	104.38(9)
C13	C12	C15	104.51(9)	C33	C30	C21	100.65(9)
C12	C13	C1	100.00(8)	C30	C31	C19	99.65(9)
C15	C14	C1	105.90(9)	C33	C32	C19	106.49(9)
C4	C15	C12	97.69(9)	C22	C33	C30	98.37(9)
C4	C15	C14	115.23(10)	C22	C33	C32	113.86(10)
C4	C15	C16	114.21(10)	C22	C33	C34	114.15(11)
C14	C15	C12	102.78(9)	C32	C33	C30	102.60(9)
C16	C15	C12	116.28(10)	C34	C33	C30	115.66(11)
C16	C15	C14	109.81(10)	C34	C33	C32	111.16(10)
O4	C17	O5	124.52(11)	O9	C35	O10	124.55(13)
O4	C17	C1	124.73(11)	O9	C35	C19	124.15(13)
O5	C17	C1	110.74(10)	O10	C35	C19	111.30(11)

Table S14. Torsion Angles for **8**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O2	C3	C12	C11	-146.09(9)	O7	C21	C30	C29	143.10(10)
O2	C3	C12	C13	-13.60(13)	O7	C21	C30	C31	9.87(14)
O2	C3	C12	C15	96.32(10)	O7	C21	C30	C33	-99.92(11)
O3	C3	C12	C11	94.06(10)	O8	C21	C30	C29	-96.42(11)
O3	C3	C12	C13	-133.45(9)	O8	C21	C30	C31	130.36(10)
O3	C3	C12	C15	-23.53(11)	O8	C21	C30	C33	20.57(11)
O3	C4	C5	C6	-107.23(13)	O8	C22	C23	C24	103.51(13)
O3	C4	C5	C10	73.17(13)	O8	C22	C23	C28	-73.05(14)
O3	C4	C15	C12	-47.42(10)	O8	C22	C33	C30	47.50(11)
O3	C4	C15	C14	60.67(12)	O8	C22	C33	C32	-60.32(12)
O3	C4	C15	C16	-170.82(10)	O8	C22	C33	C34	170.57(10)
C1	C14	C15	C4	-118.46(10)	C19	C32	C33	C22	117.52(11)
C1	C14	C15	C12	-13.48(11)	C19	C32	C33	C30	12.34(12)
C1	C14	C15	C16	110.87(11)	C19	C32	C33	C34	-111.88(12)
C2	O2	C3	O3	93.77(11)	C20	O7	C21	O8	-88.06(12)
C2	O2	C3	C12	-26.06(14)	C20	O7	C21	C30	32.54(15)
C2	C1	C13	C12	-76.69(10)	C20	C19	C31	C30	76.76(11)
C2	C1	C14	C15	98.63(10)	C20	C19	C32	C33	-97.35(11)
C2	C1	C17	O4	98.49(15)	C20	C19	C35	O9	-109.91(16)
C2	C1	C17	O5	-81.91(12)	C20	C19	C35	O10	70.23(13)
C3	O2	C2	O1	-169.88(10)	C21	O7	C20	O6	165.24(13)

Table S14. Torsion Angles for **8**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C3	O2	C2	C1	10.46(14)	C21	O7	C20	C19	-15.99(16)
C3	O3	C4	C5	-82.66(11)	C21	O8	C22	C23	80.56(11)
C3	O3	C4	C15	34.60(11)	C21	O8	C22	C33	-36.41(12)
C3	C12	C13	C1	60.61(10)	C21	C30	C31	C19	-59.80(11)
C3	C12	C15	C4	41.80(10)	C21	C30	C33	C22	-40.25(11)
C3	C12	C15	C14	-76.34(10)	C21	C30	C33	C32	76.60(10)
C3	C12	C15	C16	163.69(10)	C21	C30	C33	C34	-162.22(10)
C4	O3	C3	O2	-131.35(9)	C22	O8	C21	O7	134.67(9)
C4	O3	C3	C12	-6.31(11)	C22	O8	C21	C30	9.35(12)
C4	C5	C6	C7	179.74(13)	C22	C23	C24	C25	-174.93(12)
C4	C5	C10	C9	-178.65(12)	C22	C23	C28	C27	173.87(12)
C4	C5	C10	C11	4.80(17)	C22	C23	C28	C29	-7.28(18)
C5	C4	C15	C12	69.74(11)	C23	C22	C33	C30	-67.74(11)
C5	C4	C15	C14	177.82(9)	C23	C22	C33	C32	-175.56(10)
C5	C4	C15	C16	-53.67(13)	C23	C22	C33	C34	55.33(14)
C5	C6	C7	C8	-0.7(2)	C23	C24	C25	C26	0.4(2)
C5	C10	C11	C12	-6.34(16)	C23	C28	C29	C30	10.92(16)
C6	C5	C10	C9	1.74(19)	C24	C23	C28	C27	-2.72(19)
C6	C5	C10	C11	-174.81(12)	C24	C23	C28	C29	176.12(12)
C6	C7	C8	C9	1.0(2)	C24	C25	C26	C27	-1.3(2)
C7	C8	C9	C10	0.1(2)	C25	C26	C27	C28	0.1(2)
C8	C9	C10	C5	-1.5(2)	C26	C27	C28	C23	1.9(2)
C8	C9	C10	C11	175.10(13)	C26	C27	C28	C29	-176.96(14)
C9	C10	C11	C12	177.16(11)	C27	C28	C29	C30	-170.26(12)
C10	C5	C6	C7	-0.7(2)	C28	C23	C24	C25	1.6(2)
C10	C11	C12	C3	-67.09(12)	C28	C29	C30	C21	63.12(13)
C10	C11	C12	C13	165.30(10)	C28	C29	C30	C31	-169.17(10)
C10	C11	C12	C15	43.24(12)	C28	C29	C30	C33	-46.63(13)
C11	C12	C13	C1	-172.35(9)	C29	C30	C31	C19	173.43(10)
C11	C12	C15	C4	-73.77(11)	C29	C30	C33	C22	74.24(11)
C11	C12	C15	C14	168.09(9)	C29	C30	C33	C32	-168.90(9)
C11	C12	C15	C16	48.12(13)	C29	C30	C33	C34	-47.72(14)
C13	C1	C2	O1	-137.36(12)	C31	C19	C20	O6	138.70(15)
C13	C1	C2	O2	42.26(12)	C31	C19	C20	O7	-39.97(14)
C13	C1	C14	C15	-14.78(11)	C31	C19	C32	C33	16.41(12)
C13	C1	C17	O4	-141.42(13)	C31	C19	C35	O9	130.61(15)

Table S14. Torsion Angles for **8**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C13	C1	C17	O5	38.18(14)	C31	C19	C35	O10	-49.25(15)
C13	C12	C15	C4	156.11(9)	C31	C30	C33	C22	-154.54(9)
C13	C12	C15	C14	37.96(11)	C31	C30	C33	C32	-37.69(11)
C13	C12	C15	C16	-82.01(12)	C31	C30	C33	C34	83.49(12)
C14	C1	C2	O1	110.08(13)	C32	C19	C20	O6	-108.85(16)
C14	C1	C2	O2	-70.30(12)	C32	C19	C20	O7	72.47(13)
C14	C1	C13	C12	37.40(10)	C32	C19	C31	C30	-38.73(11)
C14	C1	C17	O4	-20.88(17)	C32	C19	C35	O9	10.64(18)
C14	C1	C17	O5	158.72(10)	C32	C19	C35	O10	-169.22(10)
C15	C4	C5	C6	139.73(12)	C33	C22	C23	C24	-144.68(12)
C15	C4	C5	C10	-39.87(15)	C33	C22	C23	C28	38.77(15)
C15	C12	C13	C1	-46.74(10)	C33	C30	C31	C19	47.52(11)
C17	C1	C2	O1	-12.14(16)	C35	C19	C20	O6	13.71(19)
C17	C1	C2	O2	167.49(9)	C35	C19	C20	O7	-164.96(11)
C17	C1	C13	C12	161.65(9)	C35	C19	C31	C30	-162.85(10)
C17	C1	C14	C15	-140.88(10)	C35	C19	C32	C33	142.57(10)
C18	O5	C17	O4	2.98(19)	C36	O10	C35	O9	1.5(2)
C18	O5	C17	C1	-176.63(11)	C36	O10	C35	C19	-178.63(11)

Table S15. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **8**.

Atom	*x*	*y*	*z*	U(eq)
H3	1810.94	5747.92	2964.6	32
H4	4740.01	5358.06	3931.12	38
H6	5986.73	6127.23	1894.12	51
H7	6449.95	7617.12	-137.16	61
H8	5105.38	9123.6	-990.26	64
H9	3318.66	9175.35	199.53	54
H11A	1791.45	7823.53	2166.36	36
H11B	2436.96	8575.77	2648.73	36
H13A	569.06	6803.07	4729.17	30
H13B	1454.31	7567.55	4977.74	30
H14A	3304.14	5763.19	6324.01	37
H14B	3208.67	4680.02	5937.42	37
H16A	4755.17	7212.02	4654.05	58
H16B	3556.68	7882.85	4802.08	58

Table S15. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **8**.

Atom	*x*	*y*	*z*	U(eq)
H16C	4231.06	8102.56	3465.56	58
H18A	-1153.19	6678.44	8287.63	74
H18B	91.62	6626.99	8621.81	74
H18C	-604.35	5391.85	9068.71	74
H21	556.45	-676.67	5963.73	35
H22	3184.27	-1530.21	7496.26	41
H24	2181.95	-2877.44	9555.87	51
H25	624.5	-3334.6	11182.59	59
H26	-1004.94	-2080.02	10930.66	63
H27	-1053.04	-338.62	9081.73	57
H29A	574.8	1352.56	7176.66	40
H29B	-209.36	689.76	6722.39	40
H31A	1948.46	2537.35	4983.61	36
H31B	1217.27	2051.4	4305.16	36
H32A	3919.92	-102.51	5230.35	43
H32B	4234.61	1114.23	5307.66	43
H34A	2343.96	733.49	7988.16	70
H34B	2957.51	1826.98	6759.67	70
H34C	3690.55	671.45	7507.84	70
H36A	3248.49	4702.8	694.85	94
H36B	4417.22	3952.67	937.85	94
H36C	3986.67	4834.43	1585.69	94

5. References

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[6] **Fieser work-up**: To work up a reaction containing x g lithium aluminum hydride: 1) Dilute with ether and cool to 0°C, 2) Slowly add x mL water, 3) Add x mL 15 % aqueous sodium hydroxide, 4) Add 3x mL water, 5) Warm to RT and stir 15 min, 6) Add some anhydrous magnesium sulfate, 7) Stir 15 min and filter to remove salt.
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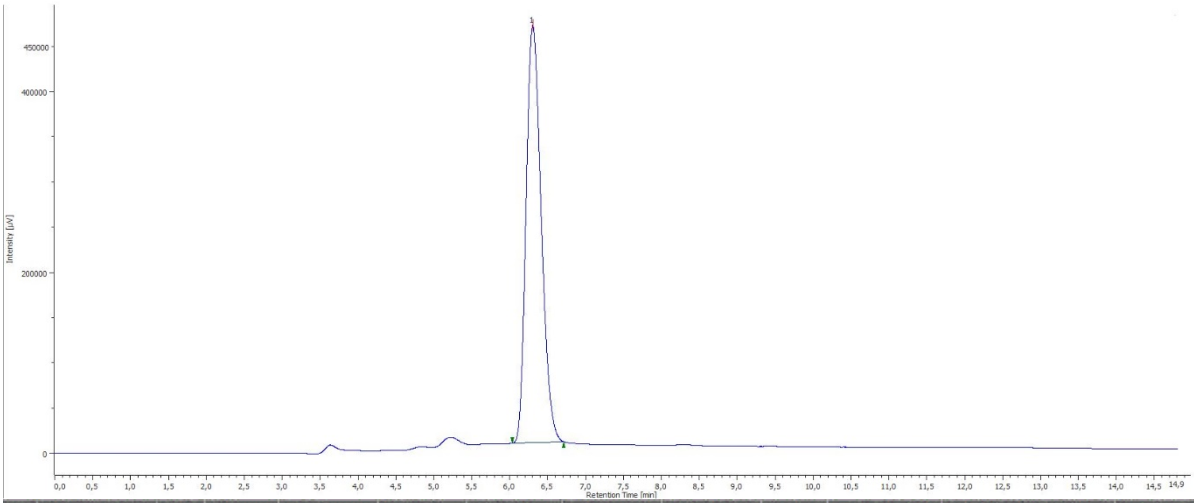
[9] G. M. Sheldrick, *Acta Cryst.*, 2015, ***C71***, 3-8.

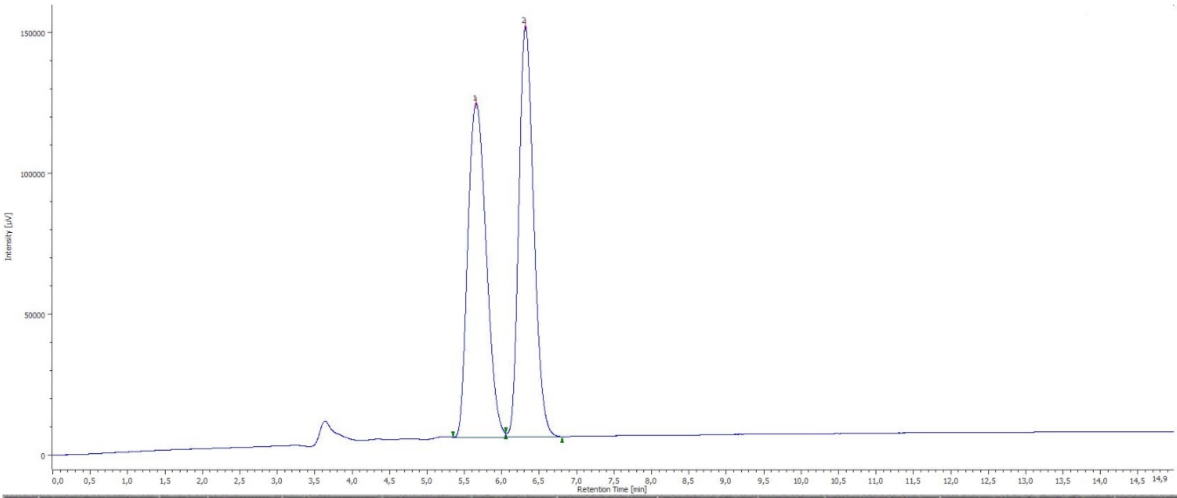
6. HPLC Spectra

- Dimethyl-4a-methyl-4,4a,5,9b-tetrahydro-1*H*-1,5-epoxycyclopenta[*b*]cyclopropa[*a*]naphthalene-3,3(2*H*)-dicarboxylate (**3b)**

HPLC: (OD-H, ^{i}PrOH/n-hexane = 70/30, flow rate = 1.0 mL/min, I = 225 nm) tR =6.3

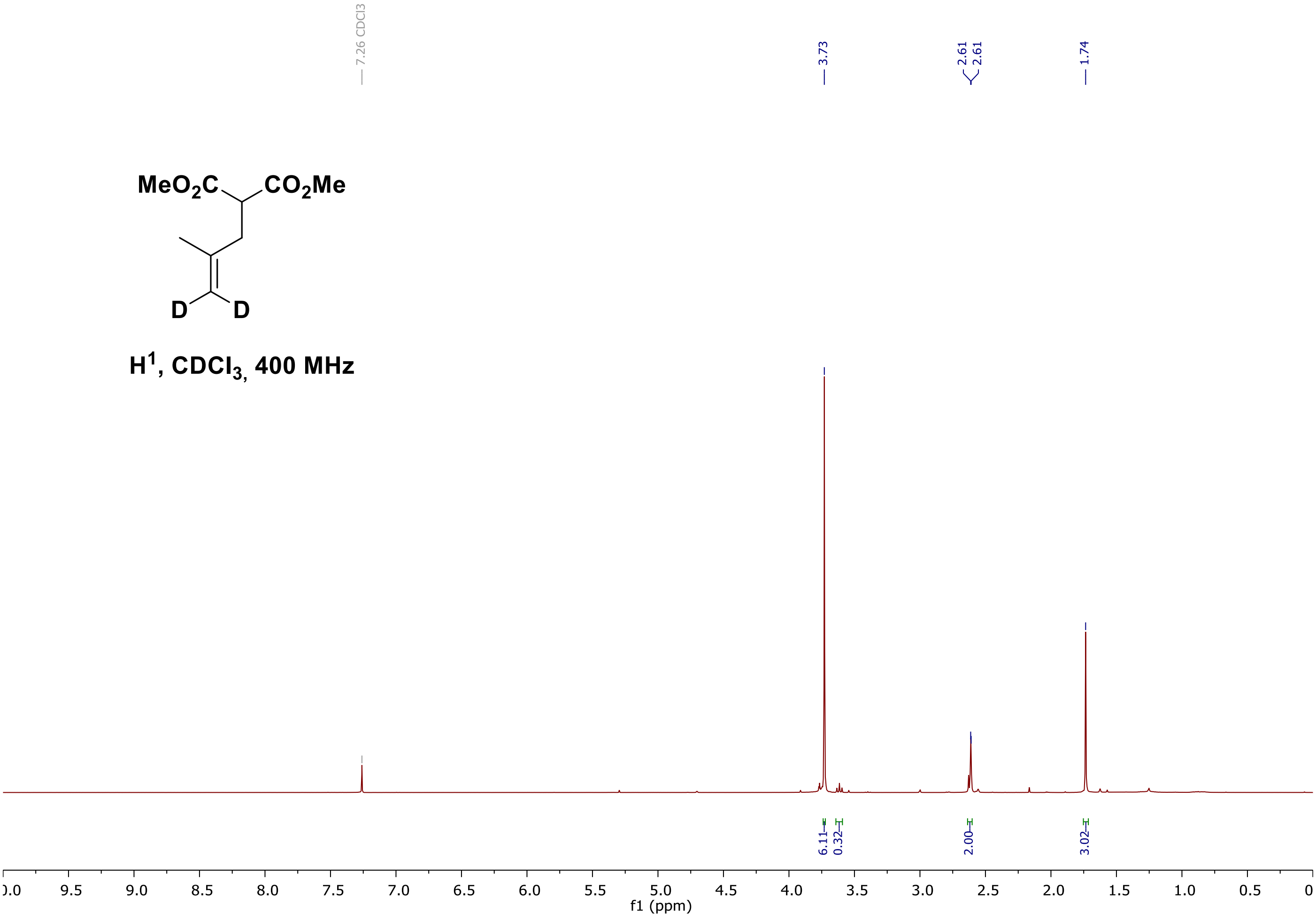


#	Peak Name	CH	tR	Area	Height	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	13	6,300	6390192	460968	100,000	100,000	N/A	4692	N/A	1,253	

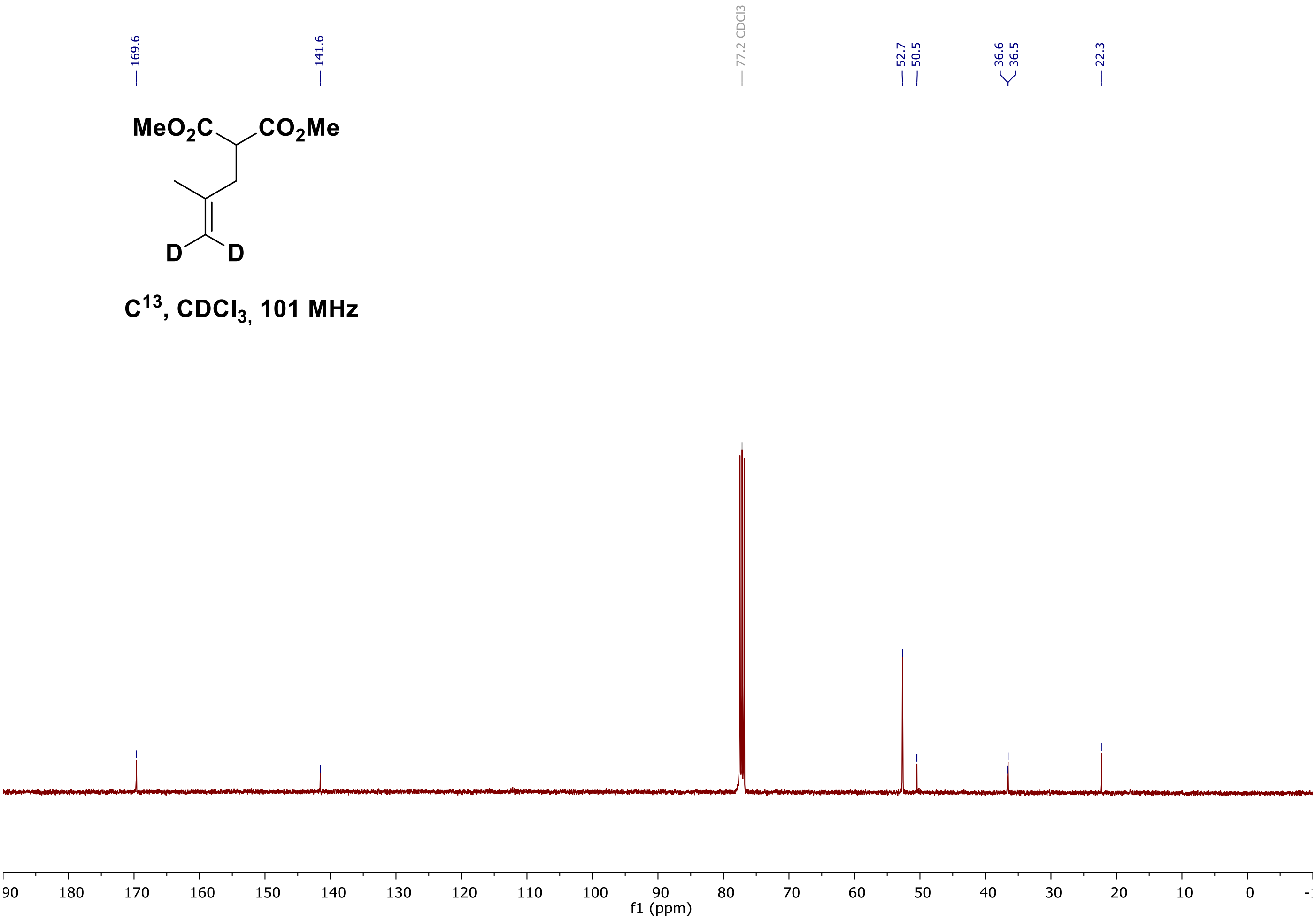


#	Peak Name	CH	tR	Area	Height	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	13	5,653	2023973	118605	50,109	44,854	N/A	2376	1,597	1,228	
2	Unknown	13	6,313	2015198	145818	49,891	55,146	N/A	4792	N/A	1,230	

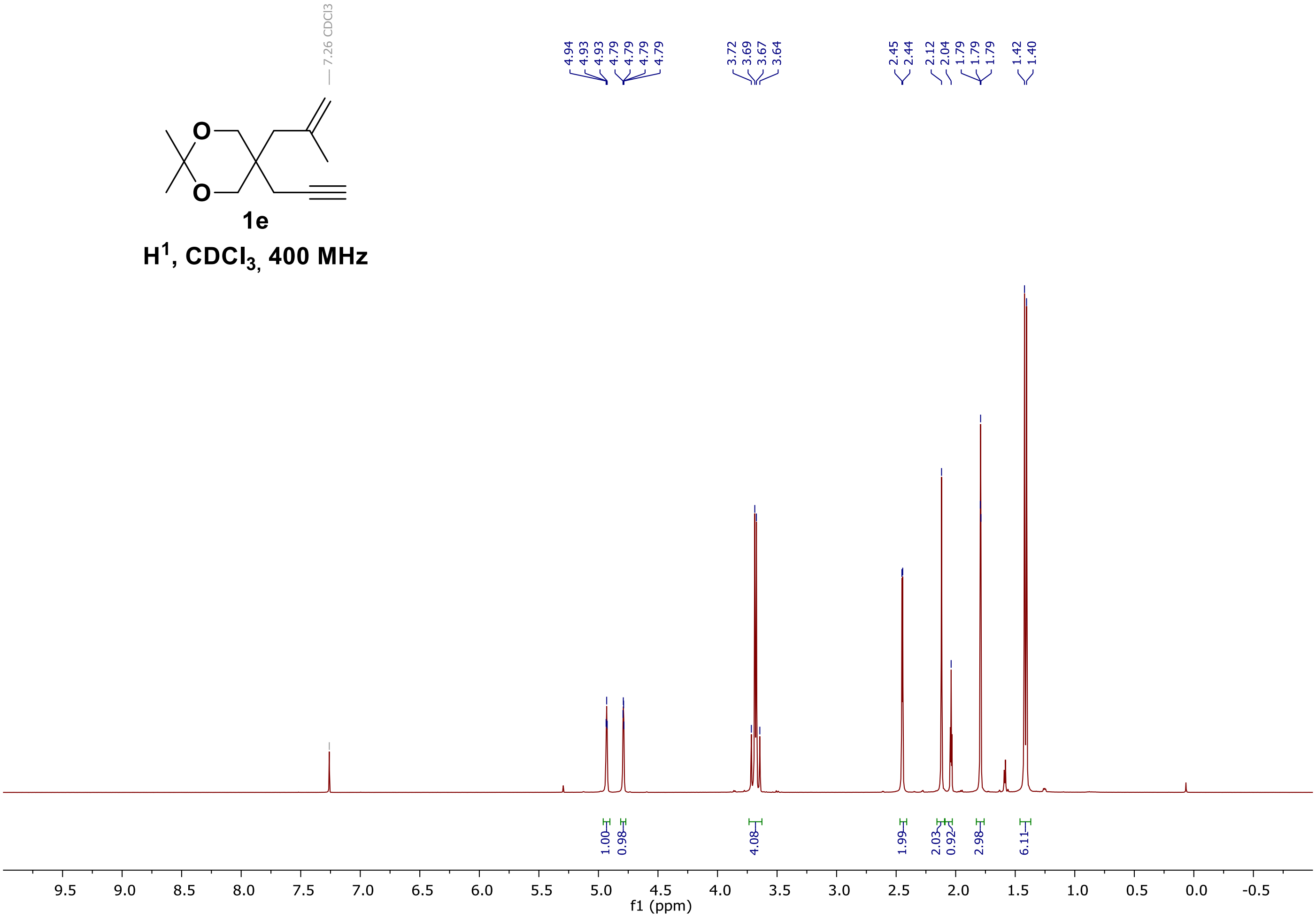
7. NMR Spectra

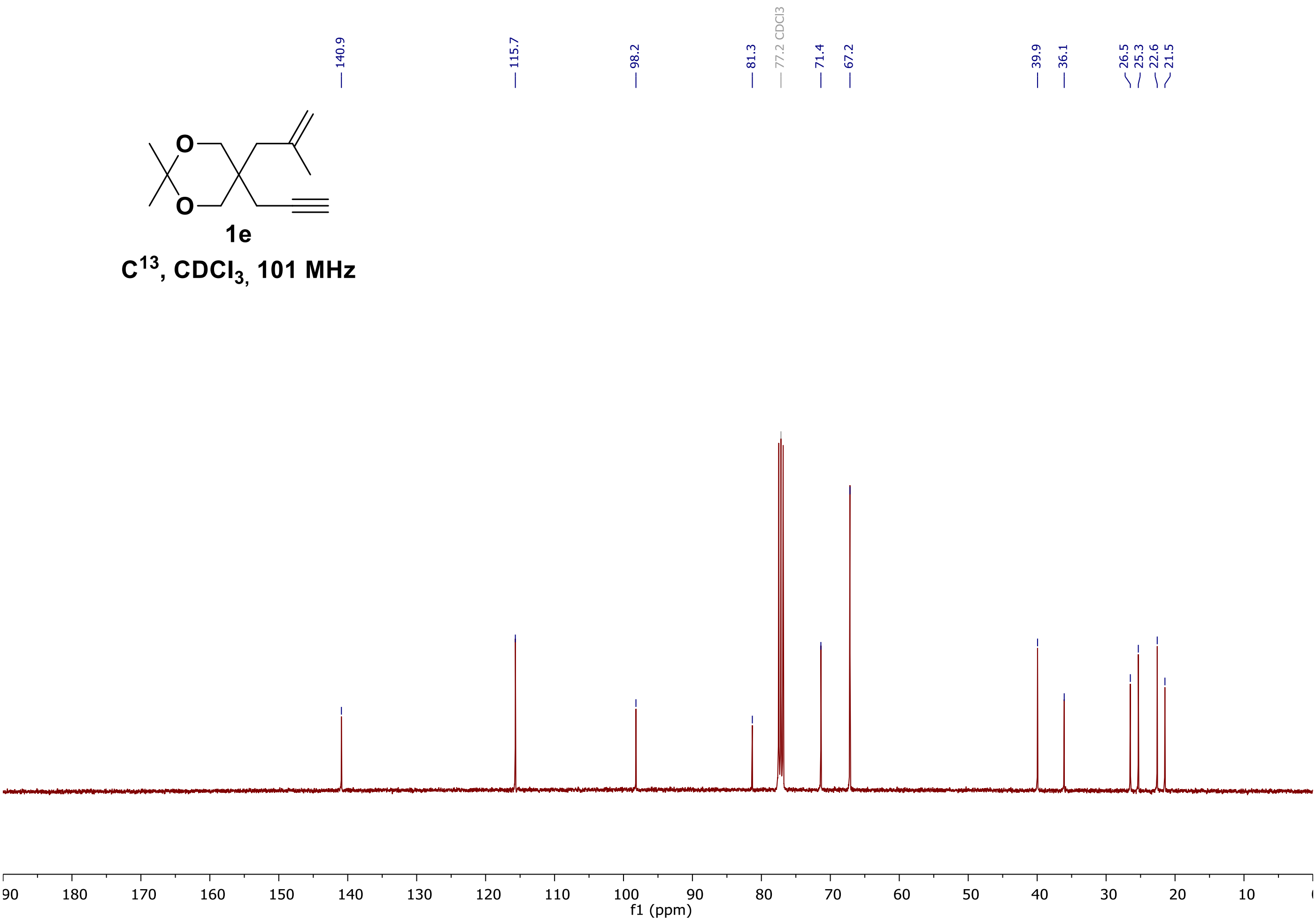


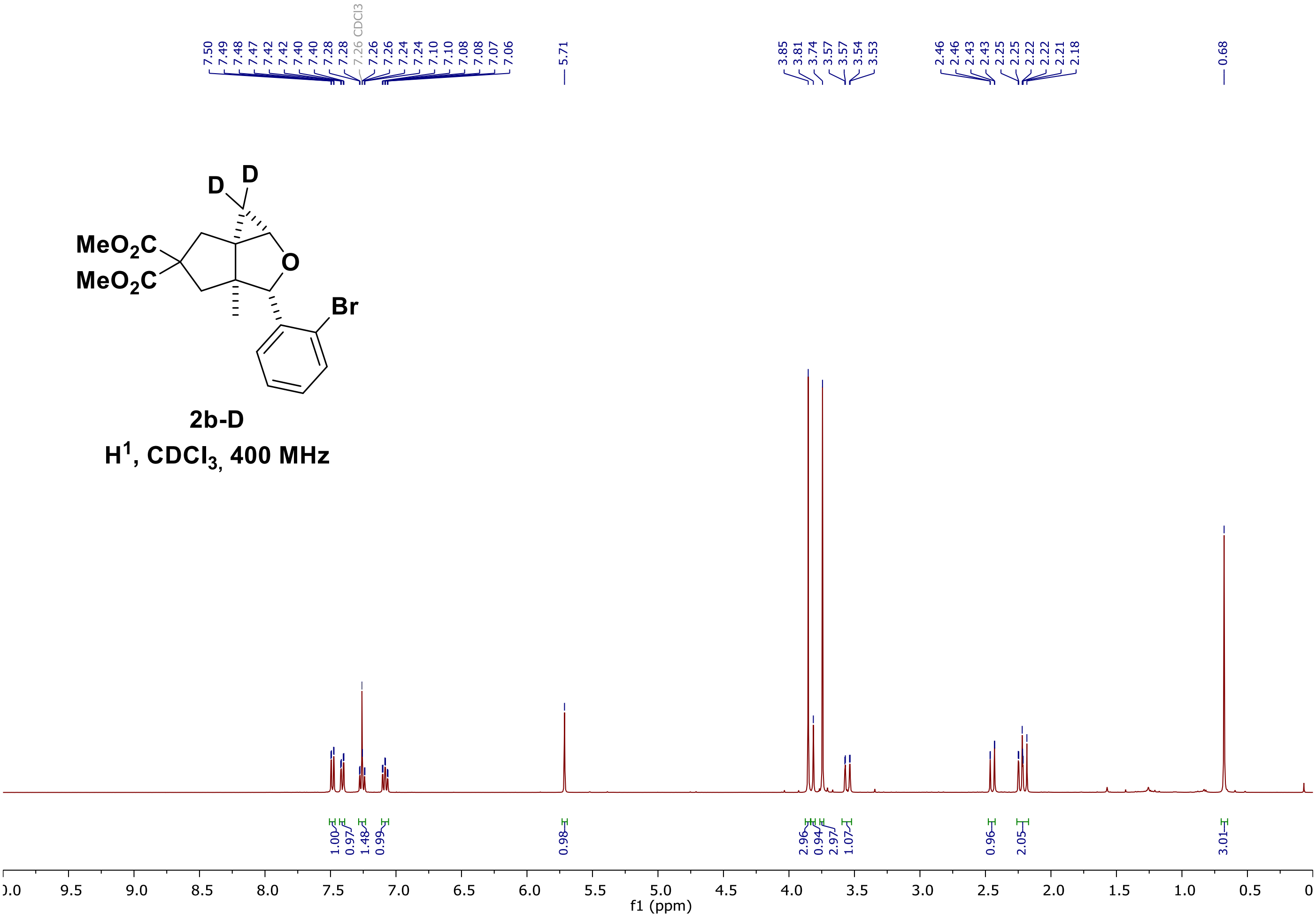
7.26 CDCl3
3.73
2.61
2.61
1.74
MeO2C
CO2Me
D
D
H1, CDCl3, 400 MHz
6.11
0.32
2.00
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)



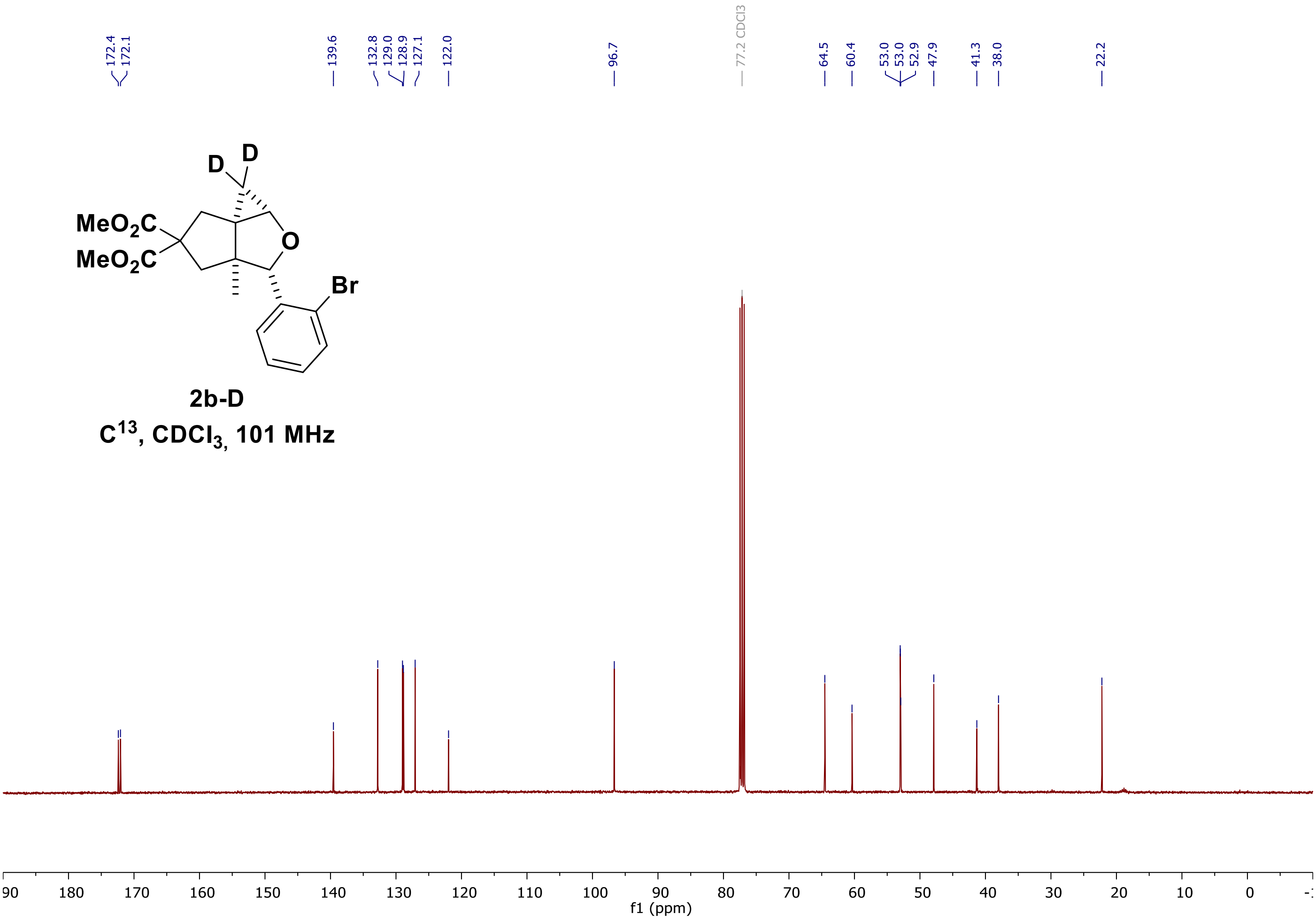
169.6
141.6
77.2 CDCl3
52.7
50.5
36.6
36.5
22.3
MeO2C
CO2Me
D
D
C13, CDCl3, 101 MHz
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26 CDCl3
4.94
4.93
4.93
4.79
4.79
4.79
4.79
3.72
3.69
3.67
3.64
2.45
2.44
2.12
2.04
1.79
1.79
1.79
1.42
1.40
1e
H1, CDCl3, 400 MHz
1.00
0.98
4.08
1.99
2.03
0.92
2.98
6.11
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)


140.9
115.7
98.2
81.3
77.2 CDCl3
71.4
67.2
39.9
36.1
26.5
25.3
22.6
21.5
1e
C13, CDCl3, 101 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



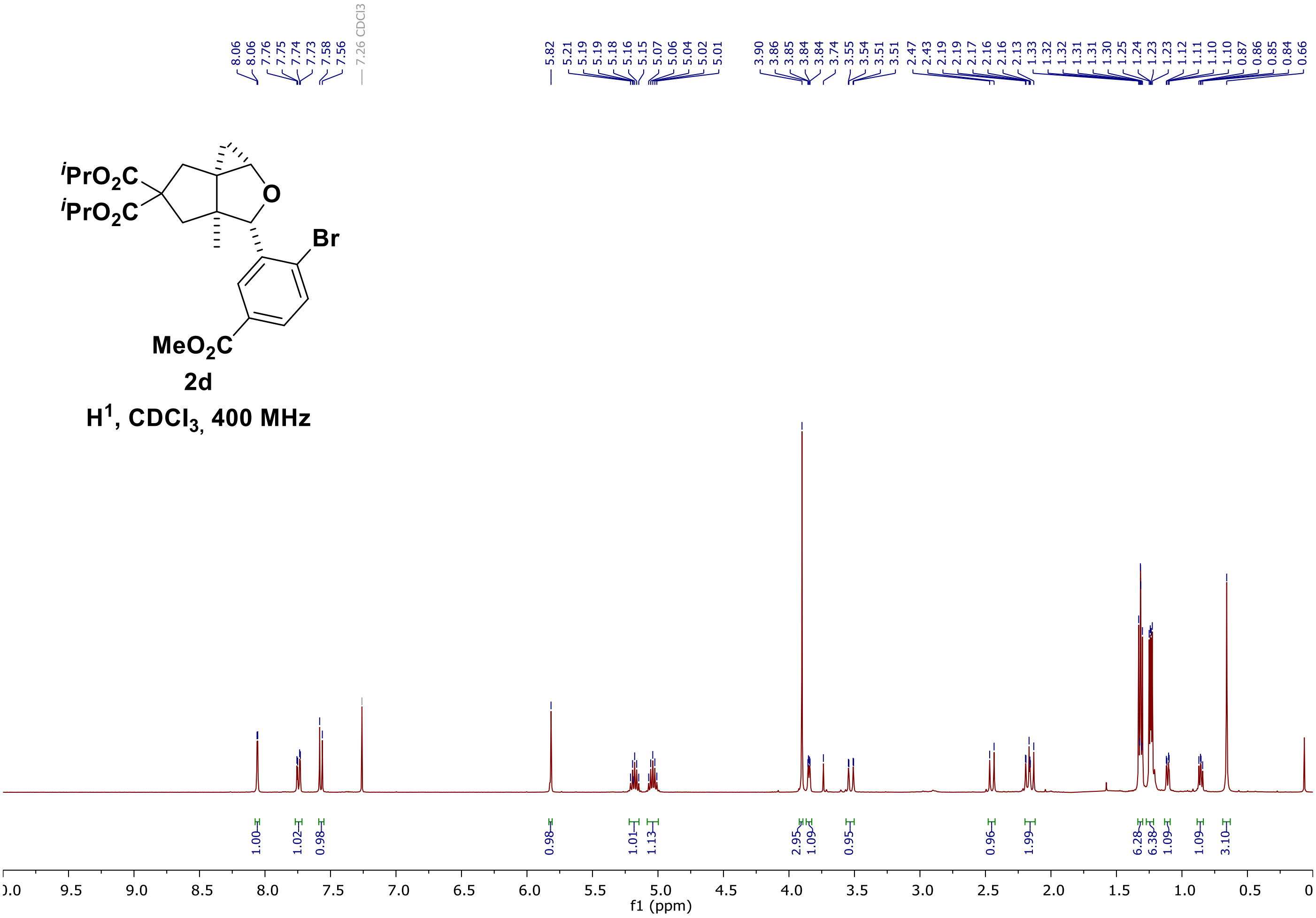
2b-D
H[1], $CDCl_3$, 400 MHz



2b-D
C[13], $CDCl_3$, 101 MHz

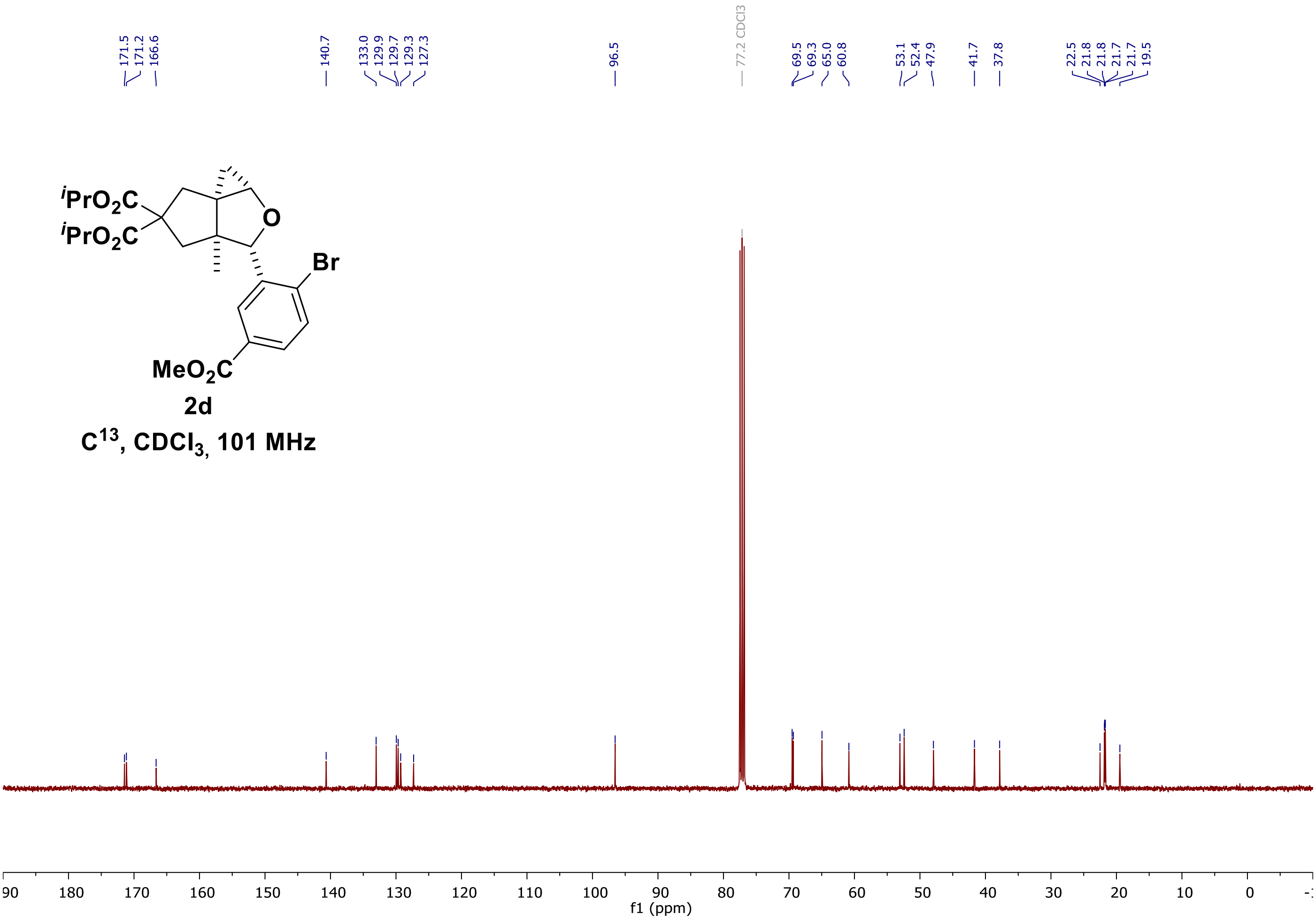
2d

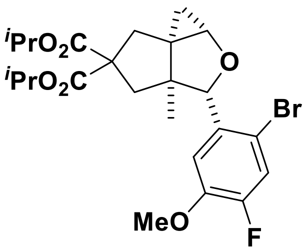
H^1, $CDCl_3$, 400 MHz



2d

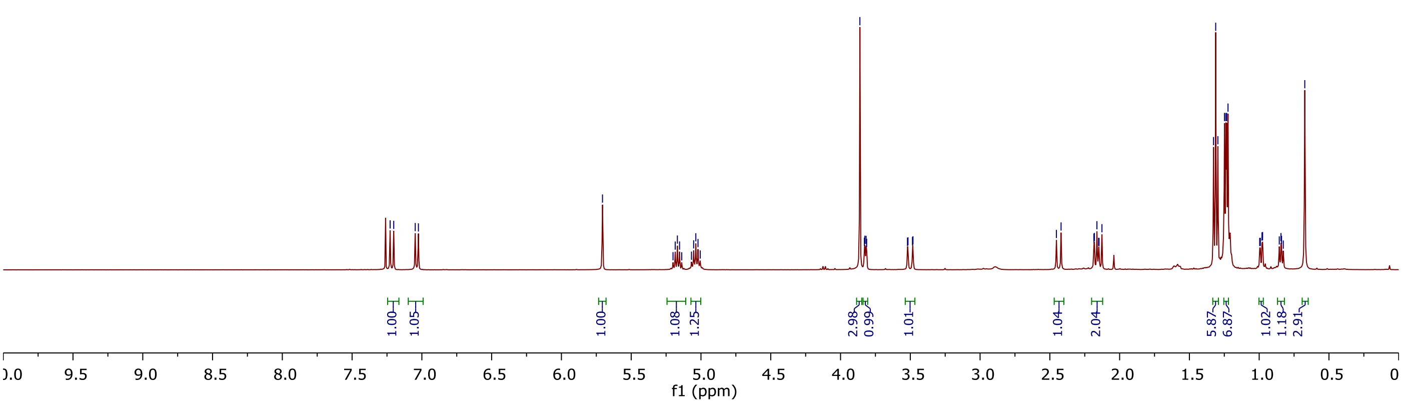
C^{13}, $CDCl_3$, 101 MHz

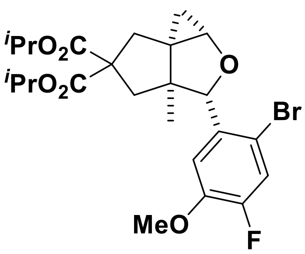




2e

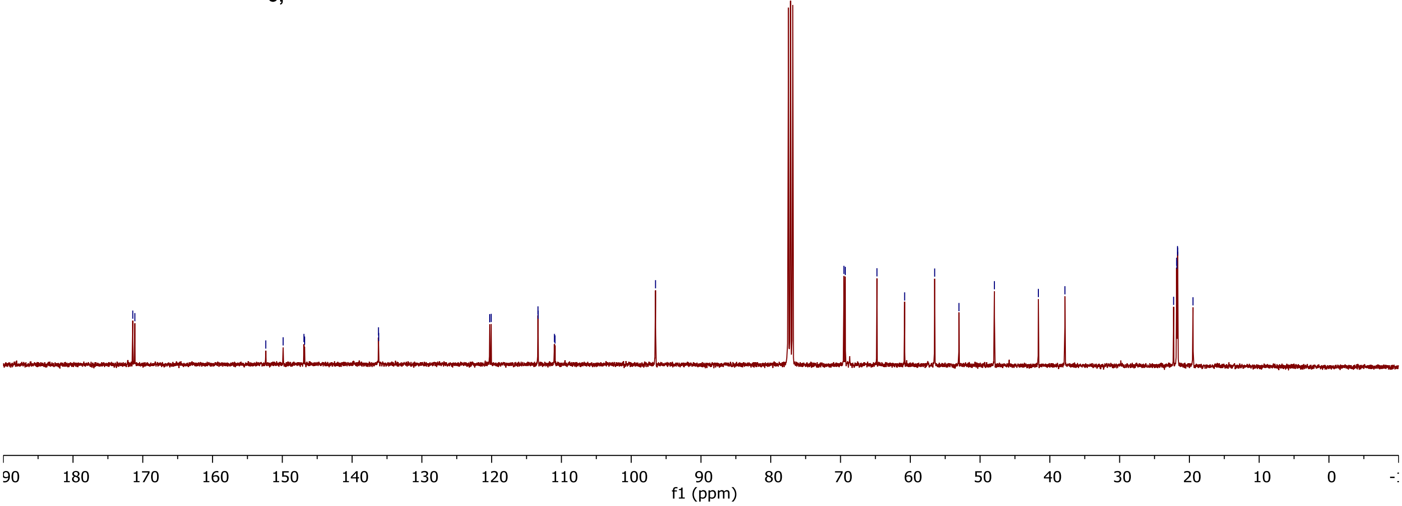
H[1], $CDCl_3$, 400 MHz

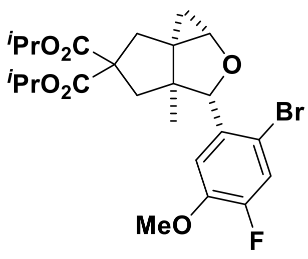




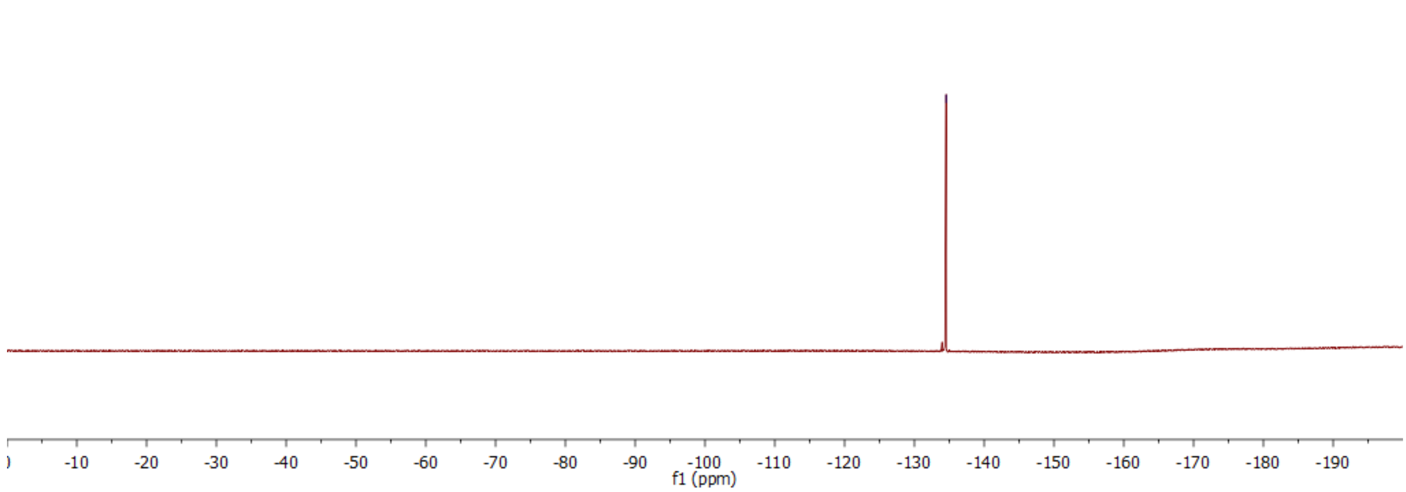
2e

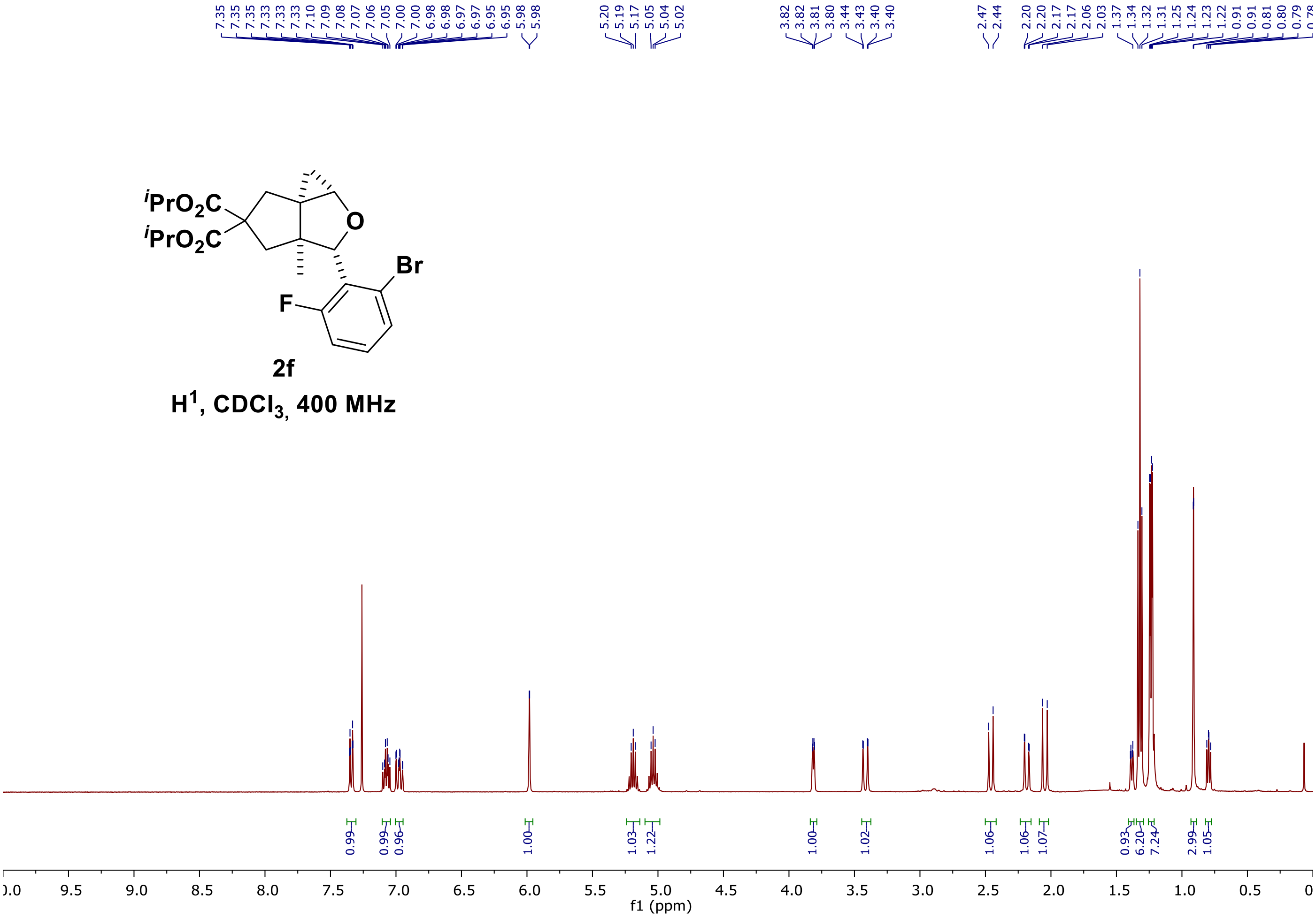
C[13], $CDCl_3$, 101 MHz

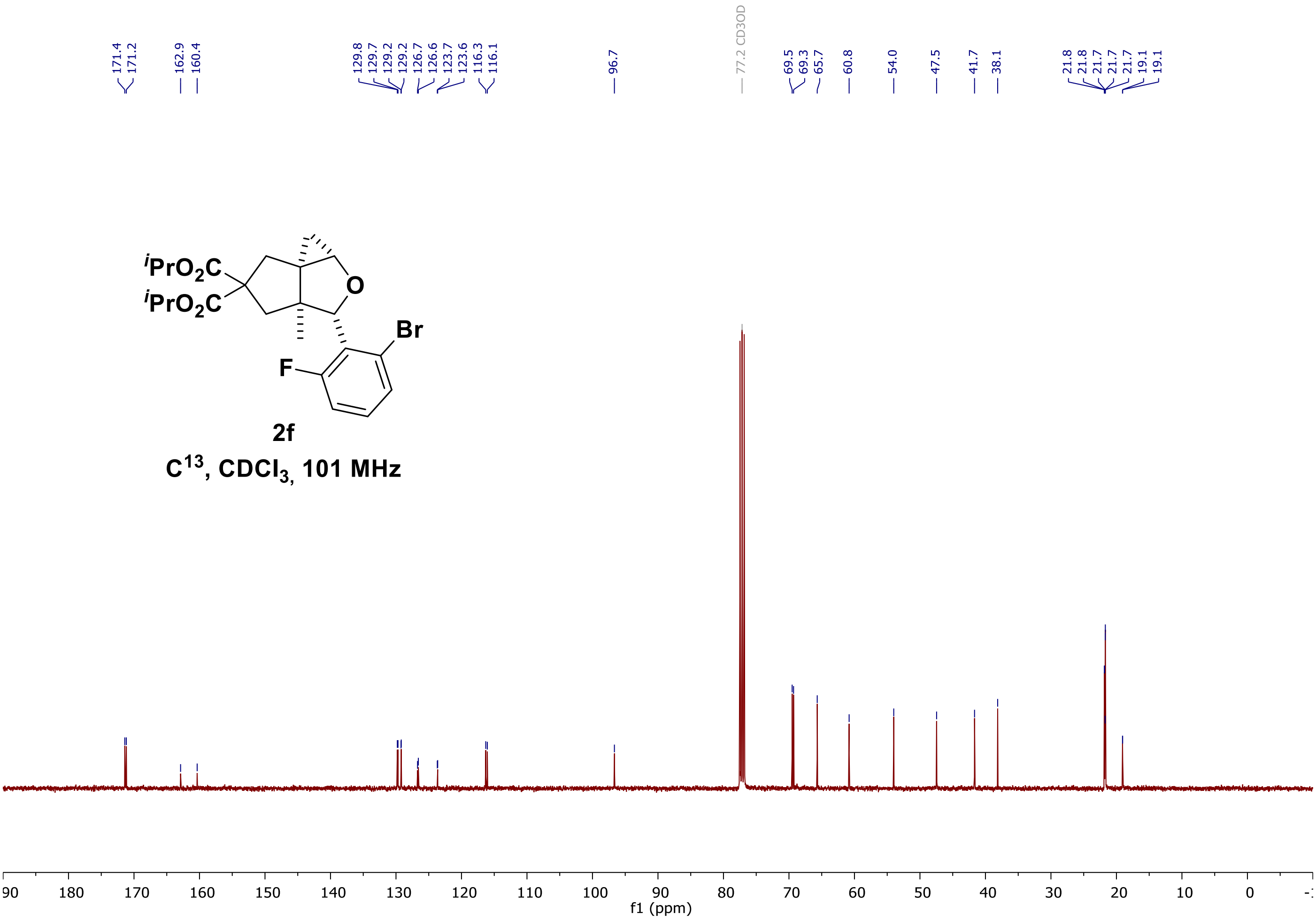


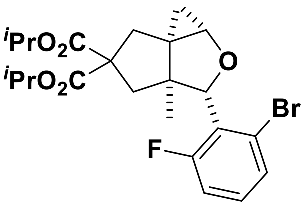


2e
F19, $CDCl_3$, 376 MHz



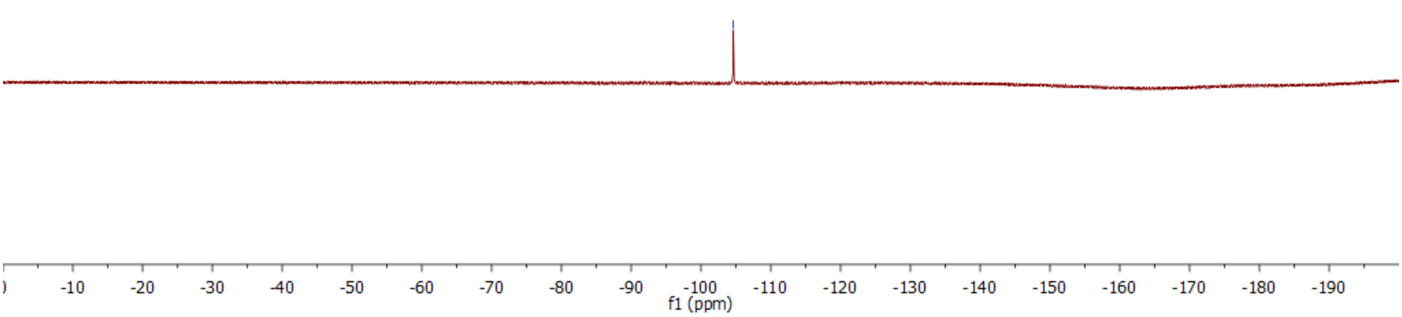

7.35 7.35 7.35 7.33 7.33 7.33 7.10 7.09 7.08 7.07 7.06 7.05 7.00 7.00 6.98 6.98 6.97 6.97 6.95 6.95 5.98 5.98 5.20 5.19 5.17 5.05 5.04 5.02 3.82 3.82 3.81 3.80 3.44 3.43 3.40 3.40 2.47 2.44 2.20 2.20 2.17 2.17 2.06 2.03 1.37 1.34 1.32 1.31 1.25 1.24 1.23 1.22 0.91 0.91 0.81 0.80 0.79
$^{i}PrO_2C$
$^{i}PrO_2C$
O
Br
F
2f
H^1, $CDCl_3$, 400 MHz
0.99 0.99 0.96 1.00 1.03 1.22 1.00 1.02 1.06 1.06 1.07 0.93 6.20 7.24 2.99 1.05
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
f1 (ppm)

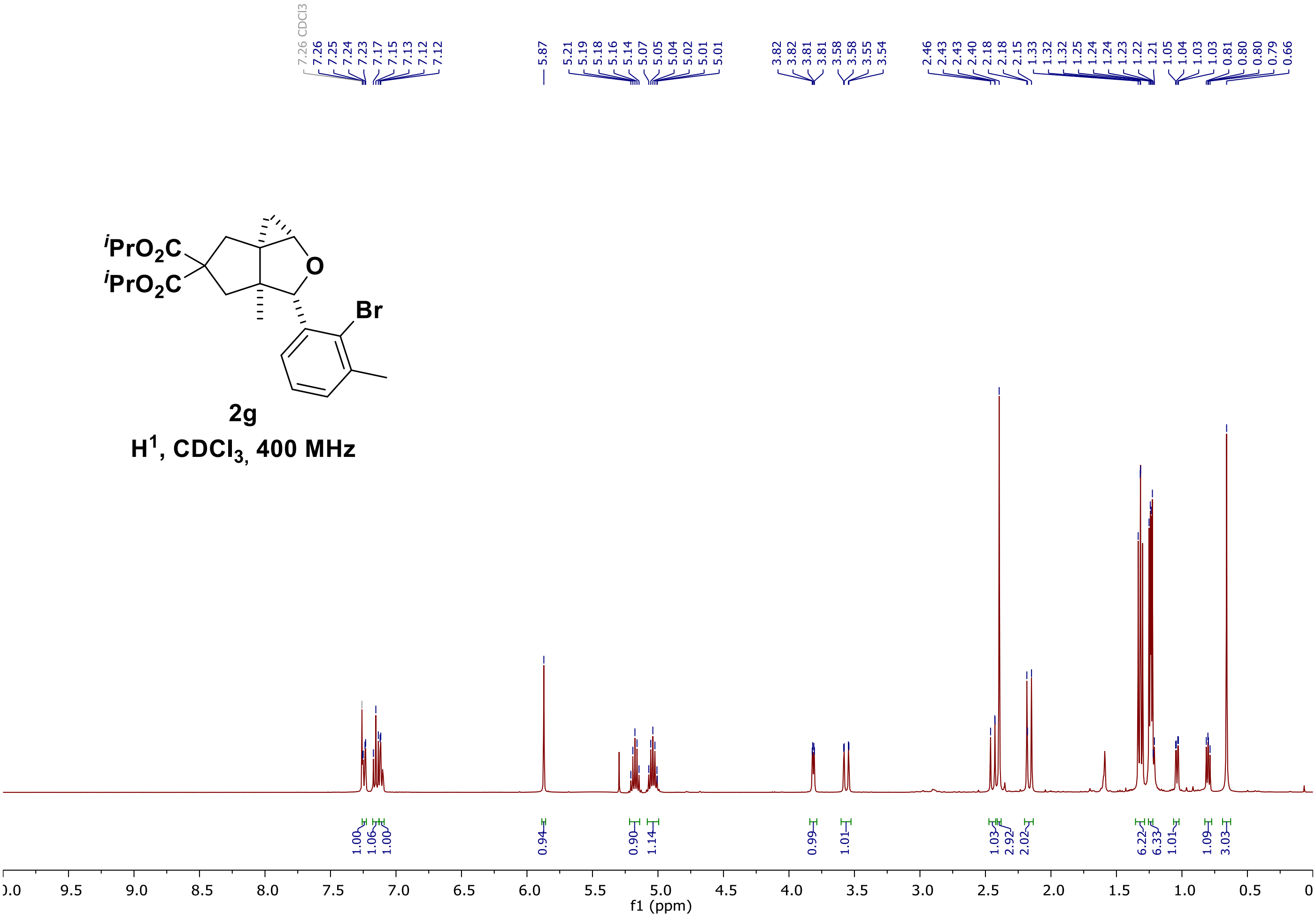

171.4 171.2 162.9 160.4 129.8 129.7 129.2 129.2 126.7 126.6 123.7 123.6 116.3 116.1 96.7 77.2 CD3OD 69.5 69.3 65.7 60.8 54.0 47.5 41.7 38.1 21.8 21.8 21.7 21.7 21.7 19.1 19.1
$^{i}PrO_2C$
$^{i}PrO_2C$
O
Br
F
2f
C^{13}, $CDCl_3$, 101 MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



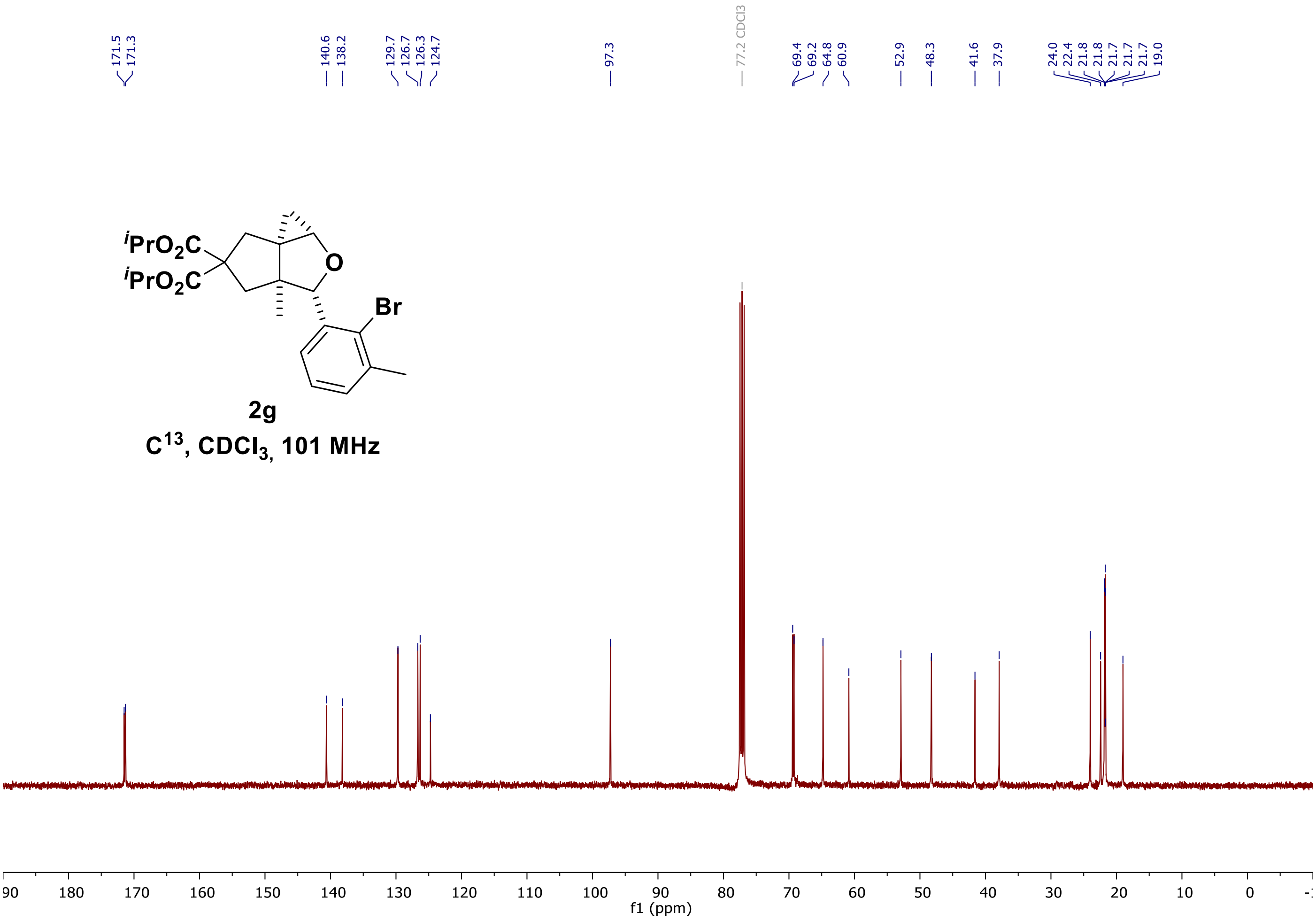
2f

F[19], CDCl$_3$, 376 MHz

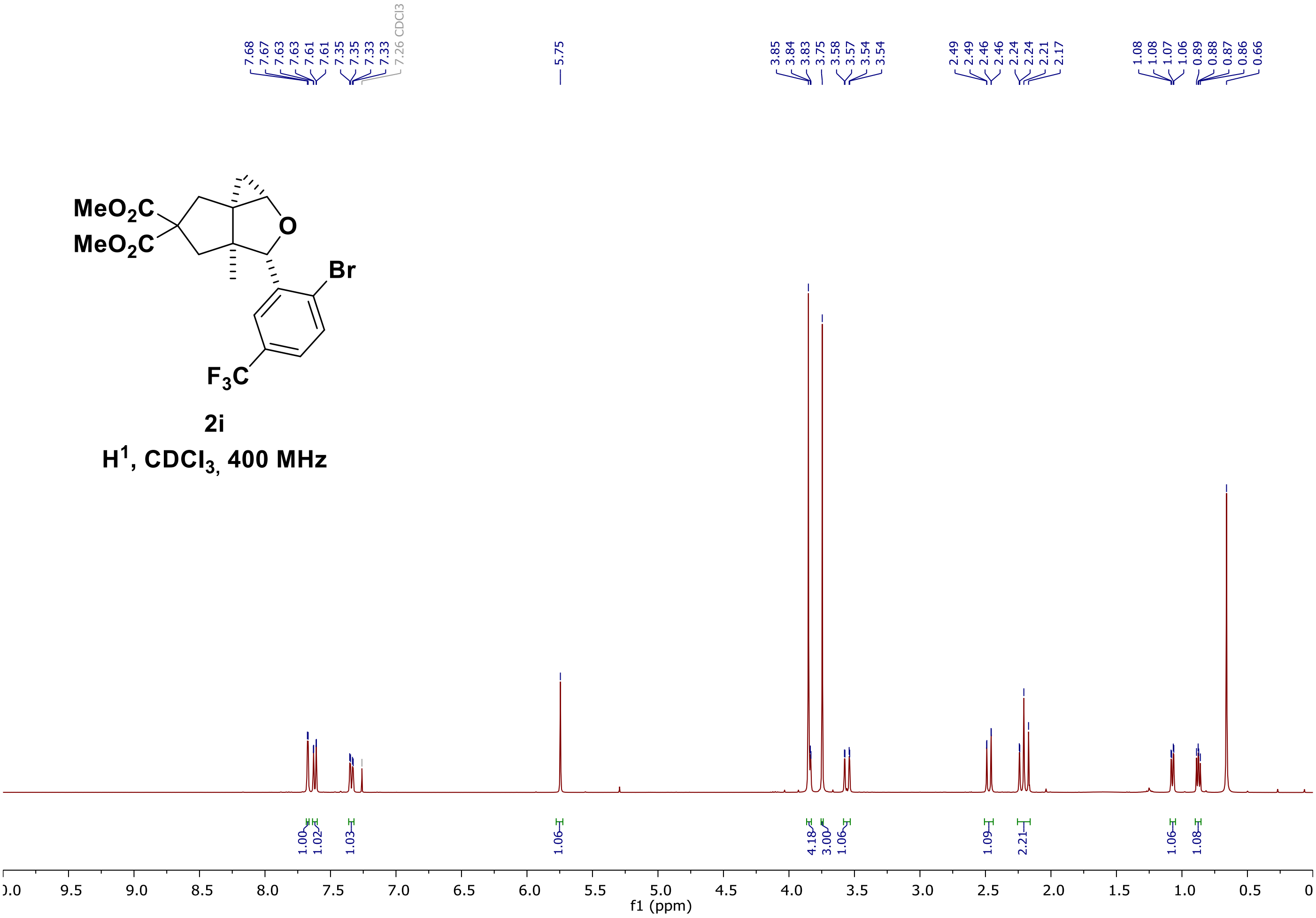


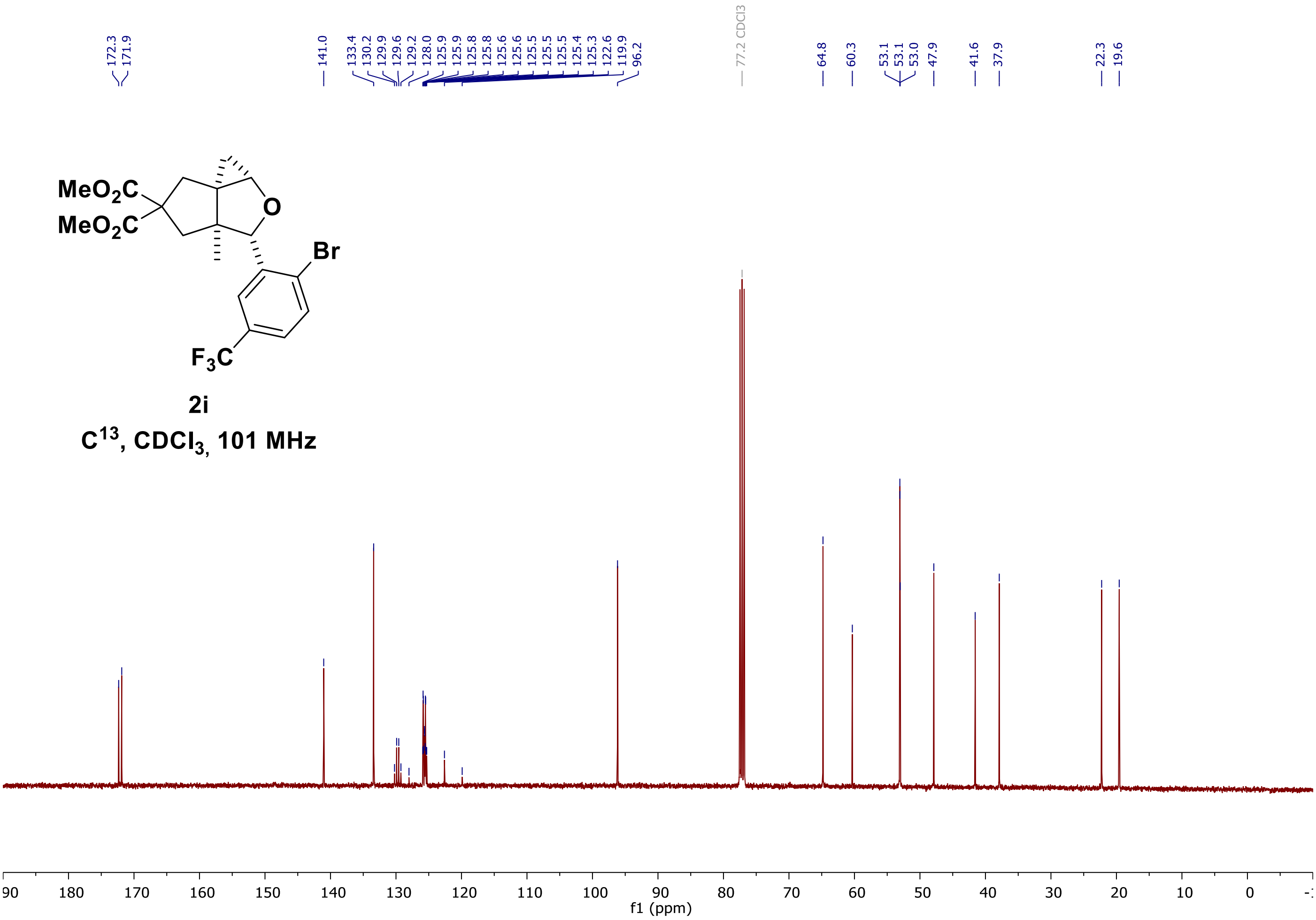


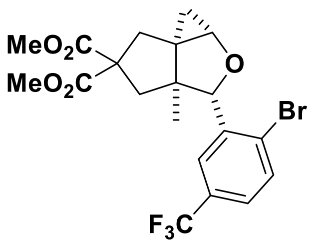
7.26 CDCl3
7.26 7.25 7.24 7.23 7.17 7.15 7.13 7.12 7.12
5.87
5.21 5.19 5.18 5.16 5.14 5.07 5.05 5.04 5.02 5.01 5.01
3.82 3.82 3.81 3.81 3.58 3.58 3.55 3.54
2.46 2.43 2.43 2.40 2.18 2.18 2.15 1.33 1.32 1.25 1.24 1.24 1.23 1.22 1.21 1.05 1.04 1.03 1.03 0.81 0.80 0.80 0.79 0.66
iPrO2C
iPrO2C
O
Br
2g
H1, CDCl3, 400 MHz
1.00 1.06 1.00
0.94
0.90 1.14
0.99
1.01
1.03 2.92 2.02
6.22 6.33 1.01
1.09 3.03
f1 (ppm)



171.5 171.3
140.6 138.2
129.7 126.7 126.3 124.7
97.3
77.2 CDCl3
69.4 69.2 64.8 60.9
52.9
48.3
41.6
37.9
24.0 22.4 21.8 21.7 21.7 21.7 19.0
iPrO2C
iPrO2C
O
Br
2g
C13, CDCl3, 101 MHz
f1 (ppm)

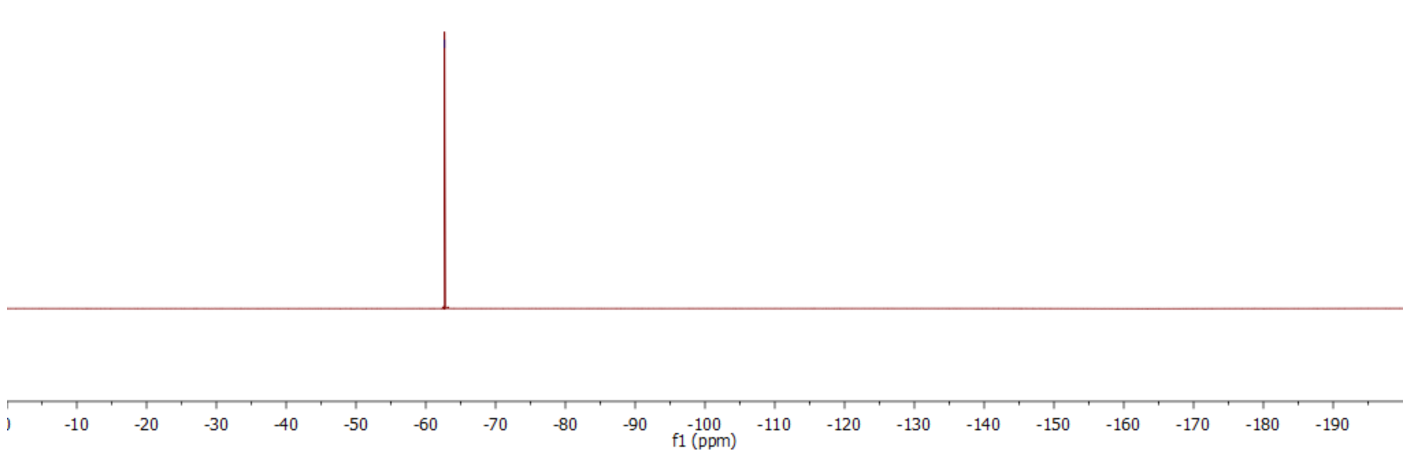

7.68
7.67
7.63
7.63
7.61
7.61
7.35
7.35
7.33
7.33
7.26 CDCl3
5.75
3.85
3.84
3.83
3.75
3.58
3.57
3.54
3.54
2.49
2.49
2.46
2.46
2.24
2.24
2.21
2.17
1.08
1.08
1.07
1.06
0.89
0.88
0.87
0.86
0.66
MeO2C
MeO2C
O
Br
F3C
2i
H1, CDCl3, 400 MHz
1.00
1.02
1.03
1.06
4.18
3.00
1.06
1.09
2.21
1.06
1.08
f1 (ppm)

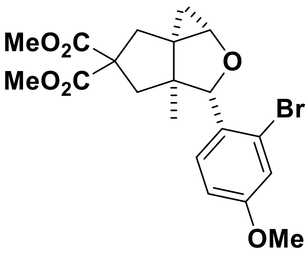

172.3
171.9
141.0
133.4
130.2
129.9
129.6
129.2
128.0
125.9
125.9
125.8
125.8
125.6
125.6
125.5
125.5
125.4
125.3
122.6
119.9
96.2
77.2 CDCl3
64.8
60.3
53.1
53.1
53.0
47.9
41.6
37.9
22.3
19.6
MeO2C
MeO2C
O
Br
F3C
2i
C13, CDCl3, 101 MHz
f1 (ppm)



2i

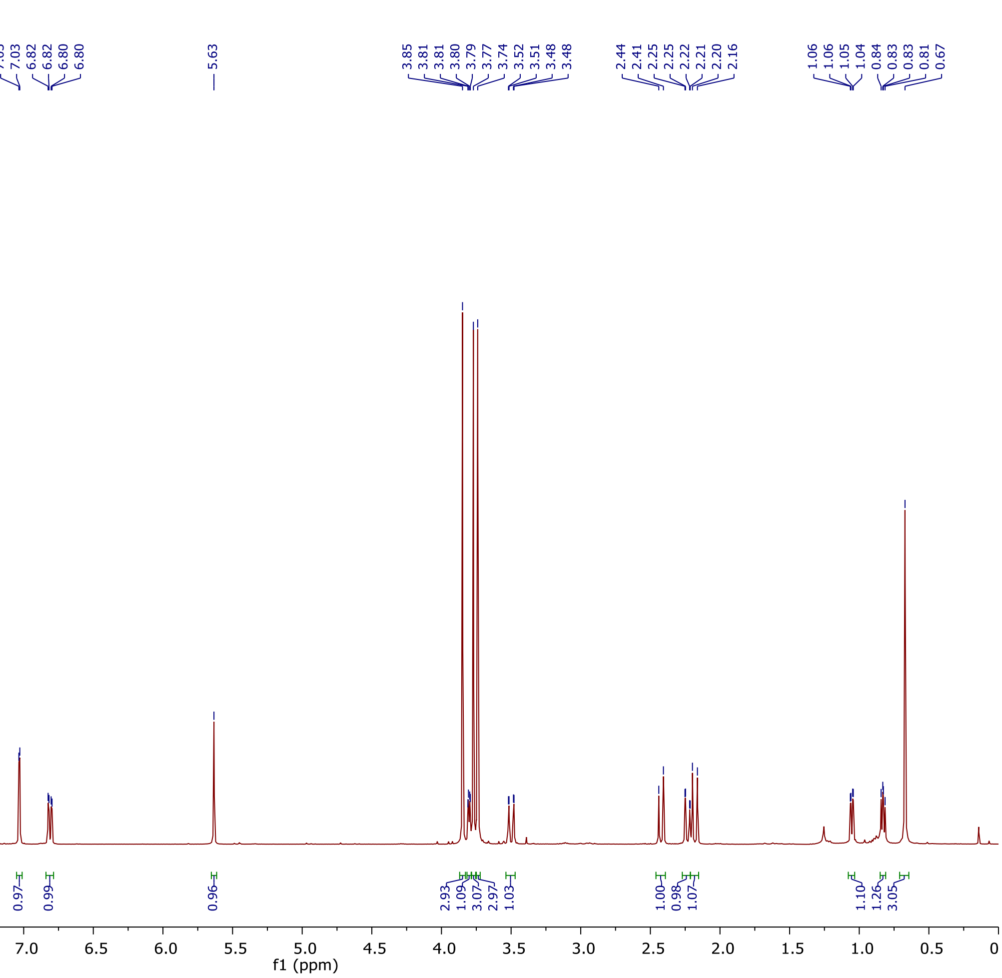
F^{19}, $CDCl_3$, 376 MHz

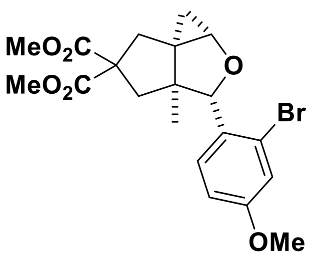




2j

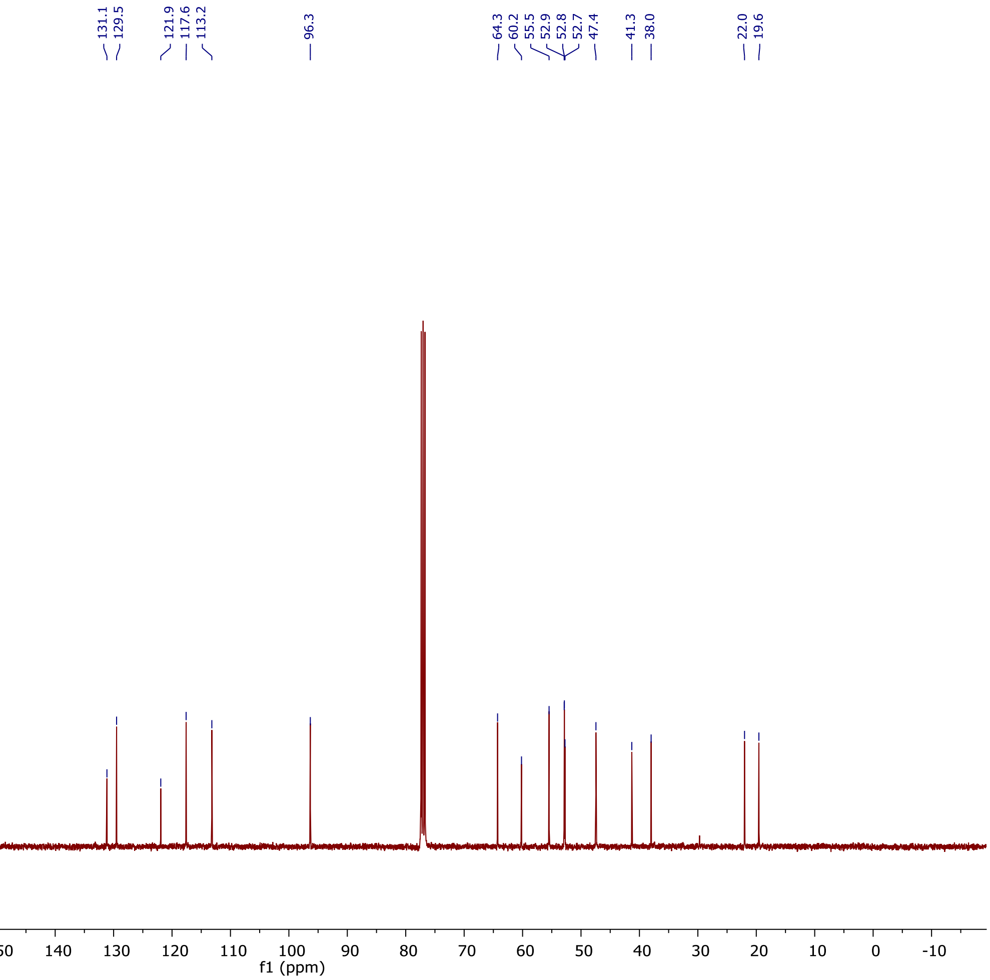
H[1], CDCl$_3$, 400 MHz

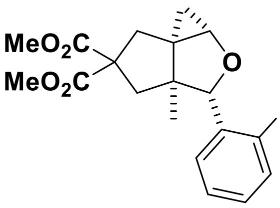




2j

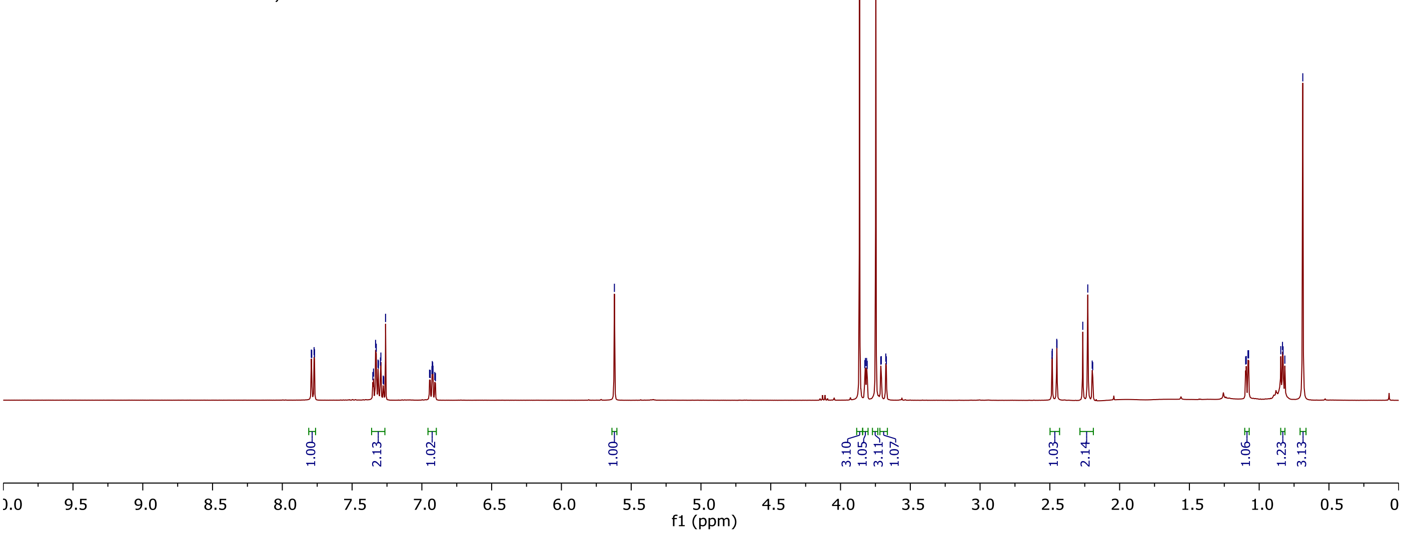
C[13], CDCl$_3$, 101 MHz

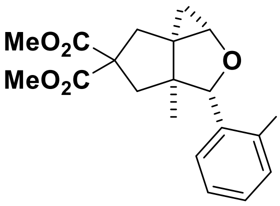




2k

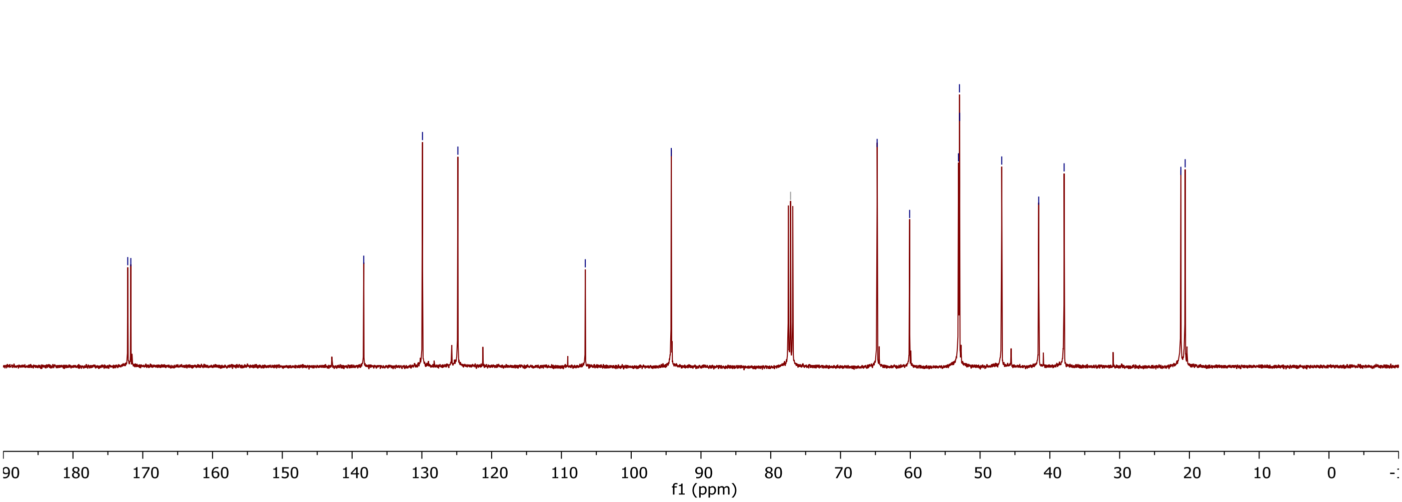
H^1, $CDCl_3$, 400 MHz

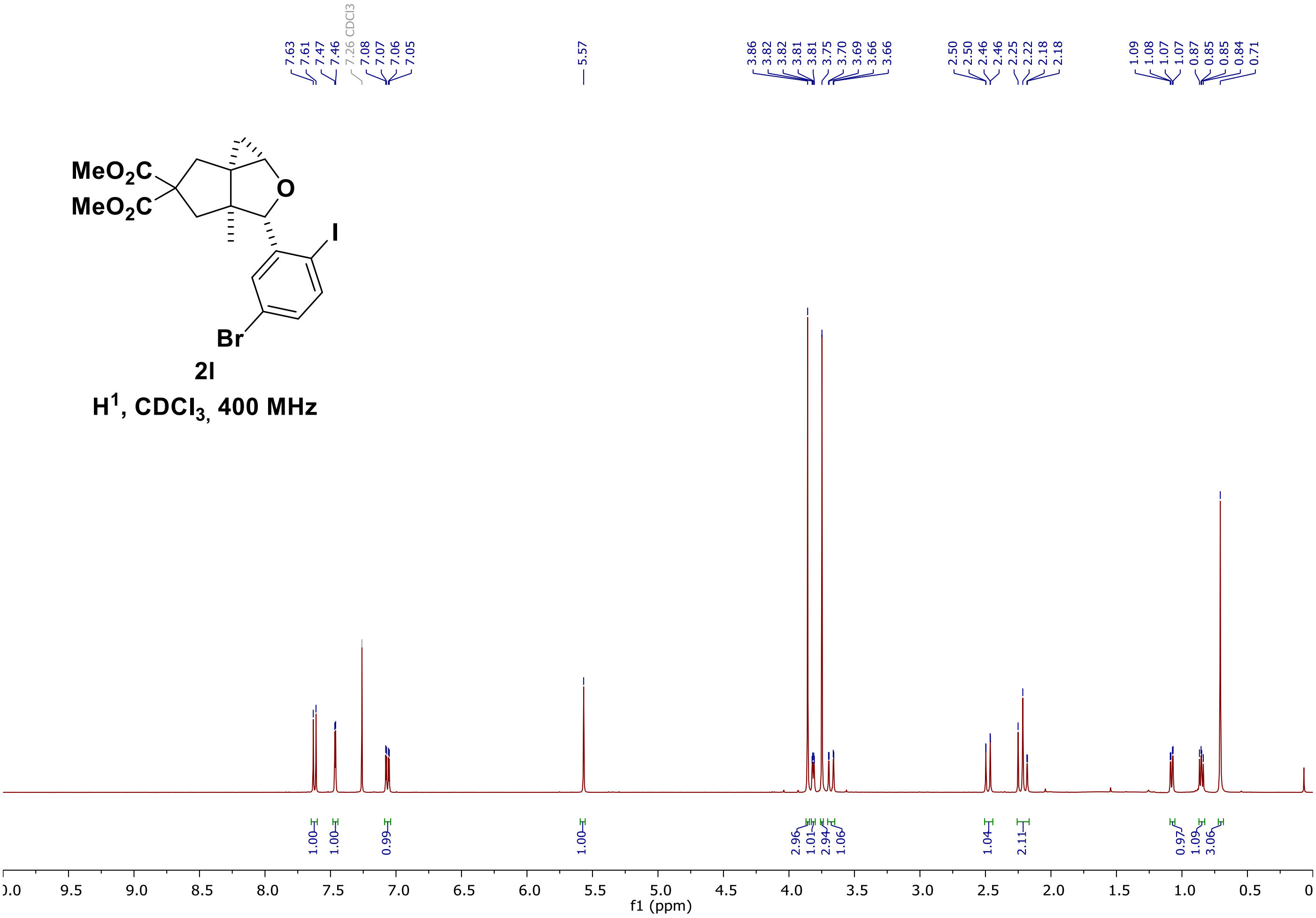




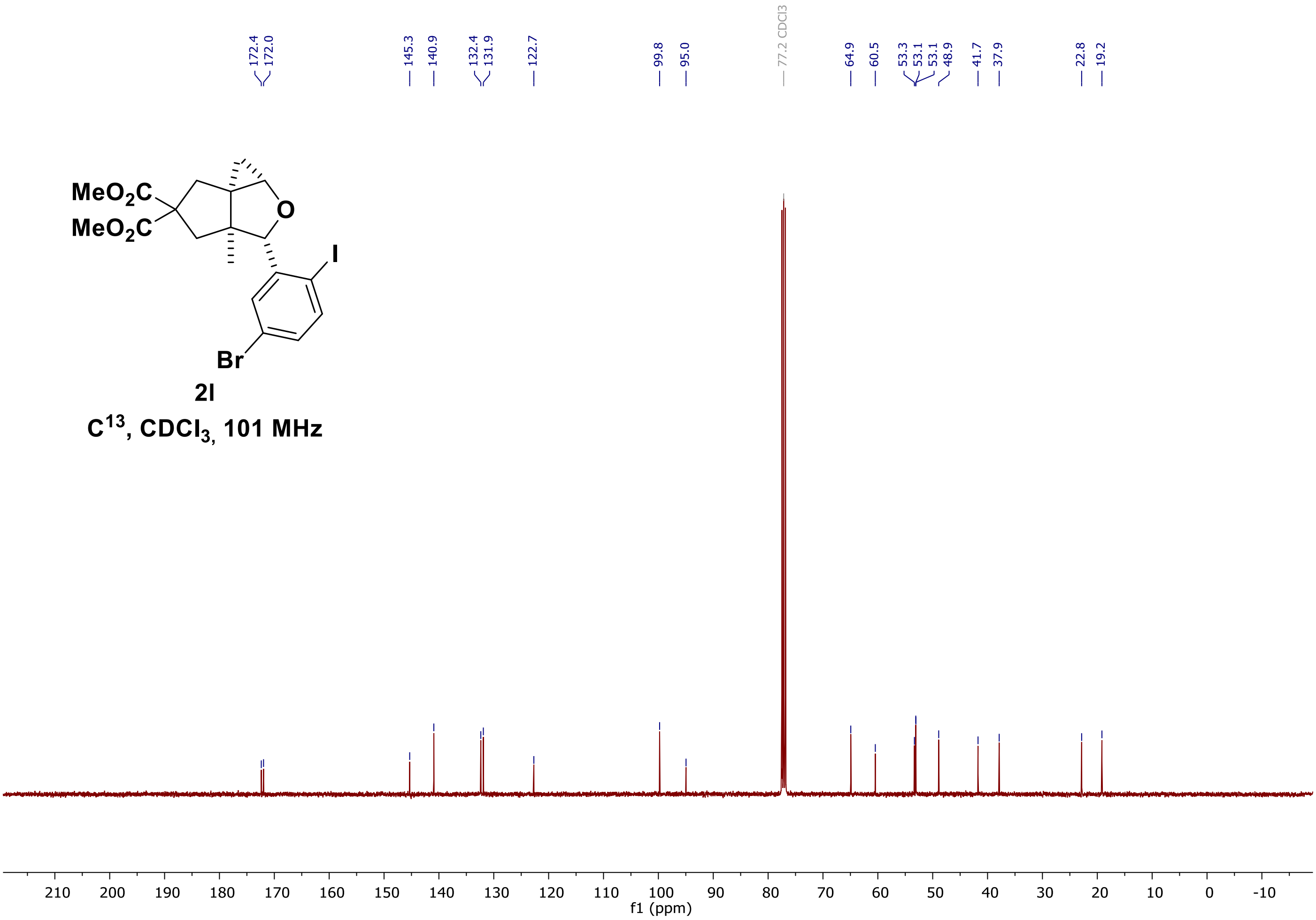
2k

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

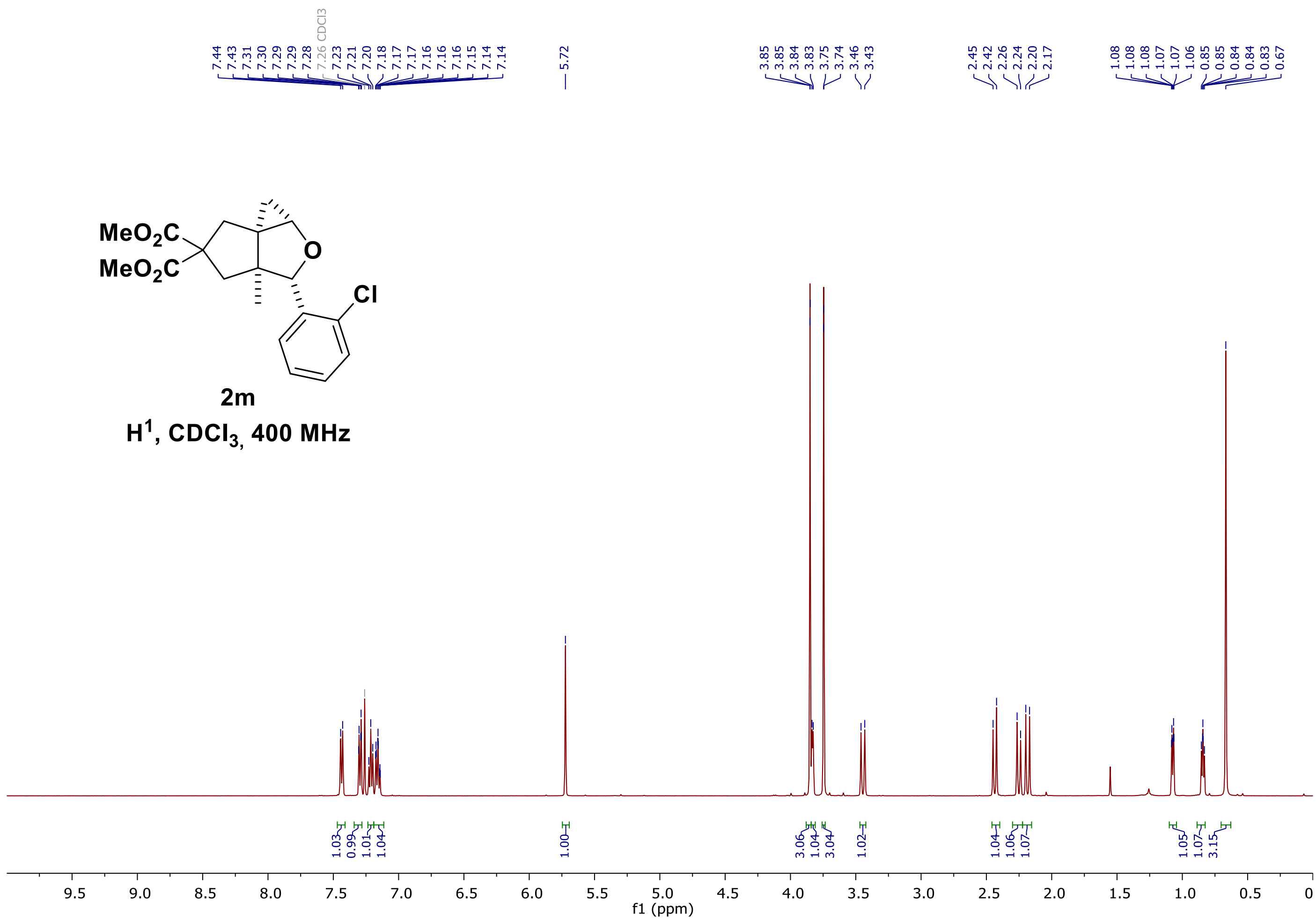


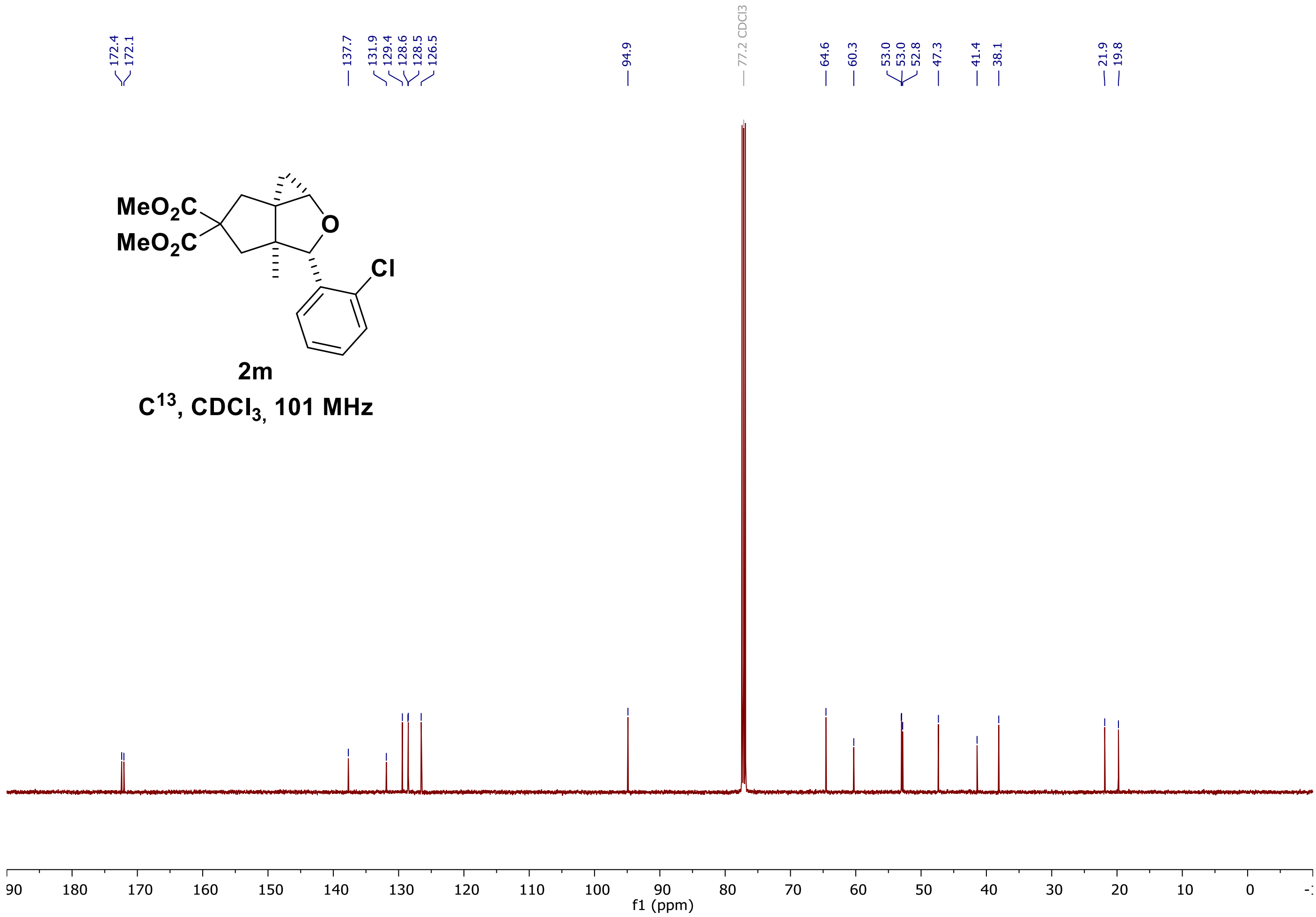


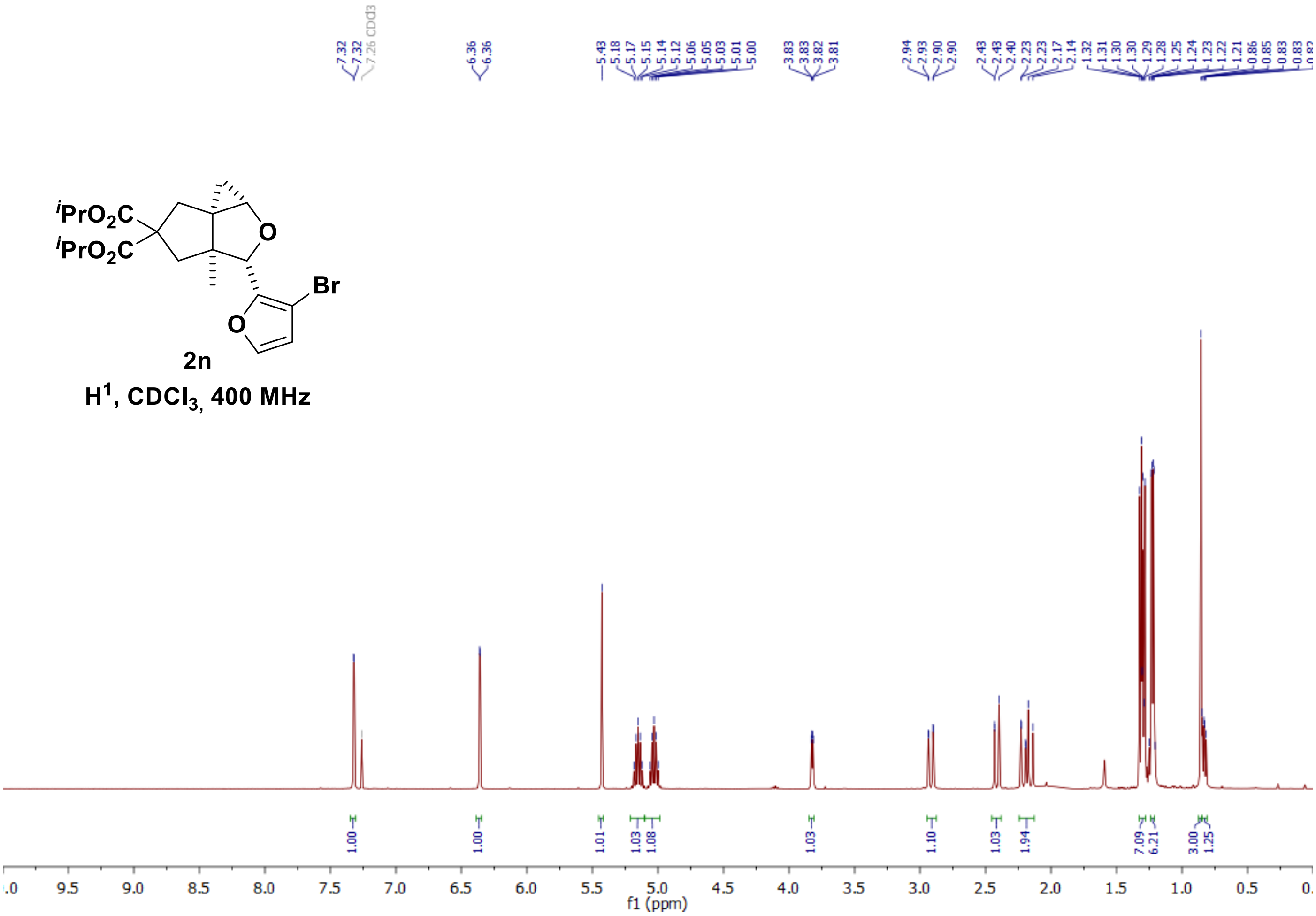
MeO2C
MeO2C
O
I
Br
2l
H1, CDCl3, 400 MHz
7.63
7.61
7.47
7.46
7.26 CDCl3
7.08
7.07
7.06
7.05
5.57
3.86
3.82
3.82
3.81
3.81
3.75
3.70
3.69
3.66
3.66
2.50
2.50
2.46
2.46
2.25
2.22
2.18
2.18
1.09
1.08
1.07
1.07
0.87
0.85
0.85
0.84
0.71
1.00
1.00
0.99
1.00
2.96
1.01
2.94
1.06
1.04
2.11
0.97
1.09
3.06
f1 (ppm)



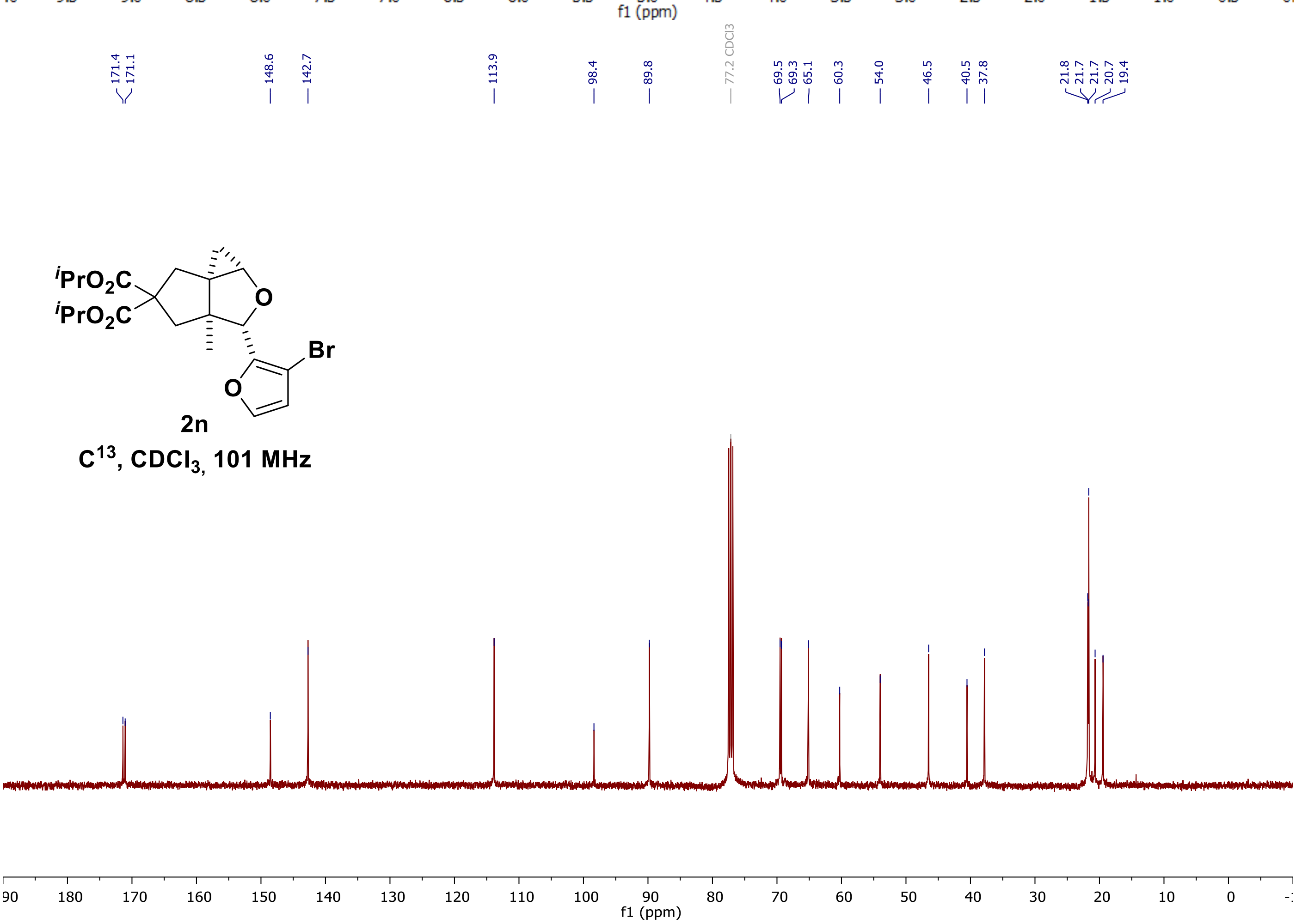
MeO2C
MeO2C
O
I
Br
2l
C13, CDCl3, 101 MHz
172.4
172.0
145.3
140.9
132.4
131.9
122.7
99.8
95.0
77.2 CDCl3
64.9
60.5
53.3
53.1
53.1
48.9
41.7
37.9
22.8
19.2
f1 (ppm)


7.44 7.43 7.31 7.30 7.29 7.29 7.28 7.26 CDCl3 7.23 7.21 7.20 7.18 7.17 7.17 7.16 7.16 7.16 7.15 7.14 7.14
5.72
3.85 3.85 3.84 3.83 3.75 3.74 3.46 3.43
2.45 2.42 2.26 2.24 2.20 2.17
1.08 1.08 1.08 1.07 1.07 1.06 0.85 0.85 0.84 0.84 0.83 0.67
MeO2C
MeO2C
O
Cl
2m
H1, CDCl3, 400 MHz
1.03 0.99 1.01 1.04
1.00
3.06 1.04 3.04
1.02
1.04 1.06 1.07
1.05 1.07 3.15
f1 (ppm)

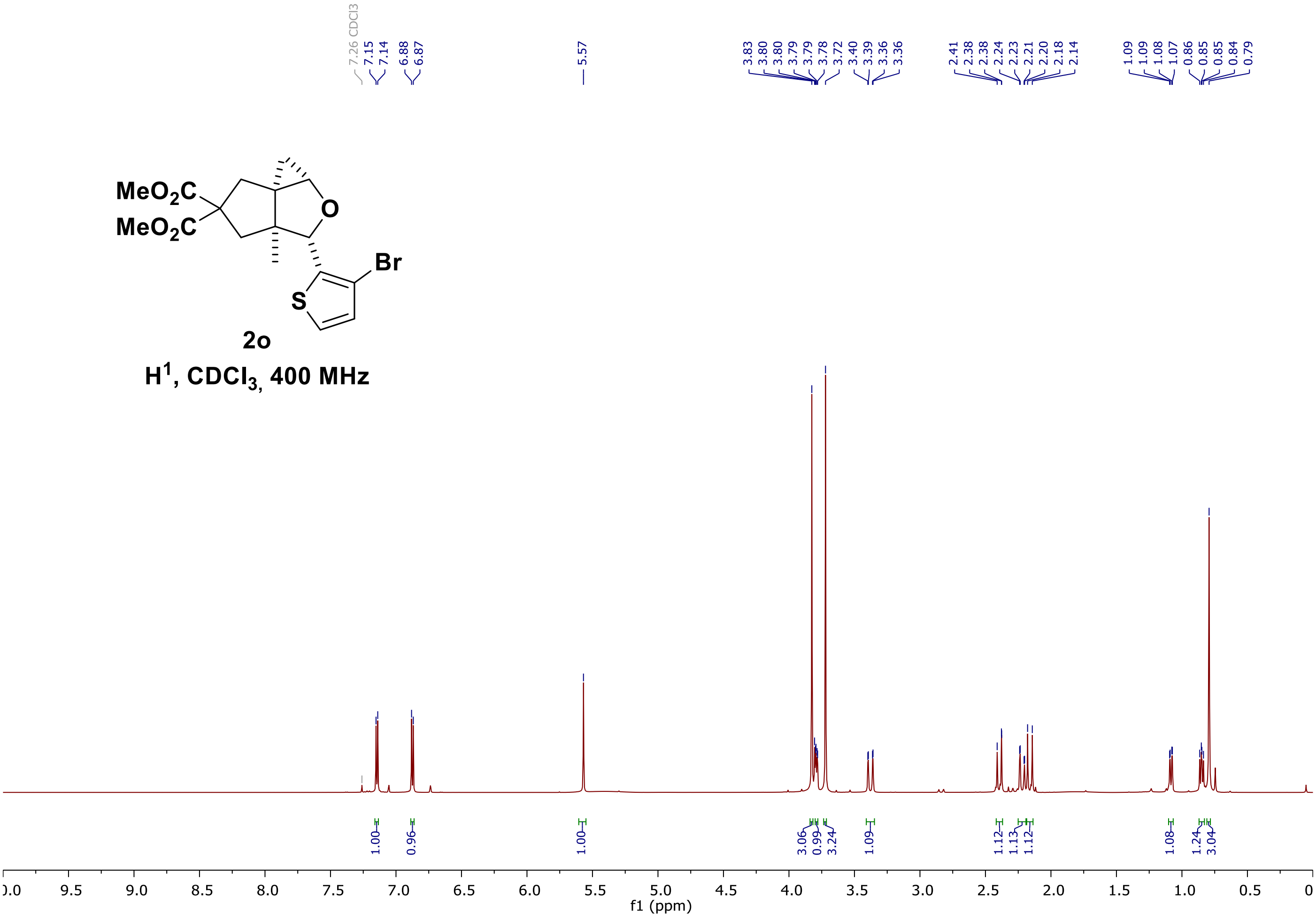

172.4 172.1
137.7
131.9 129.4 128.6 128.5 126.5
94.9
77.2 CDCl3
64.6
60.3
53.0 53.0 52.8
47.3
41.4
38.1
21.9
19.8
MeO2C
MeO2C
O
Cl
2m
C13, CDCl3, 101 MHz
f1 (ppm)

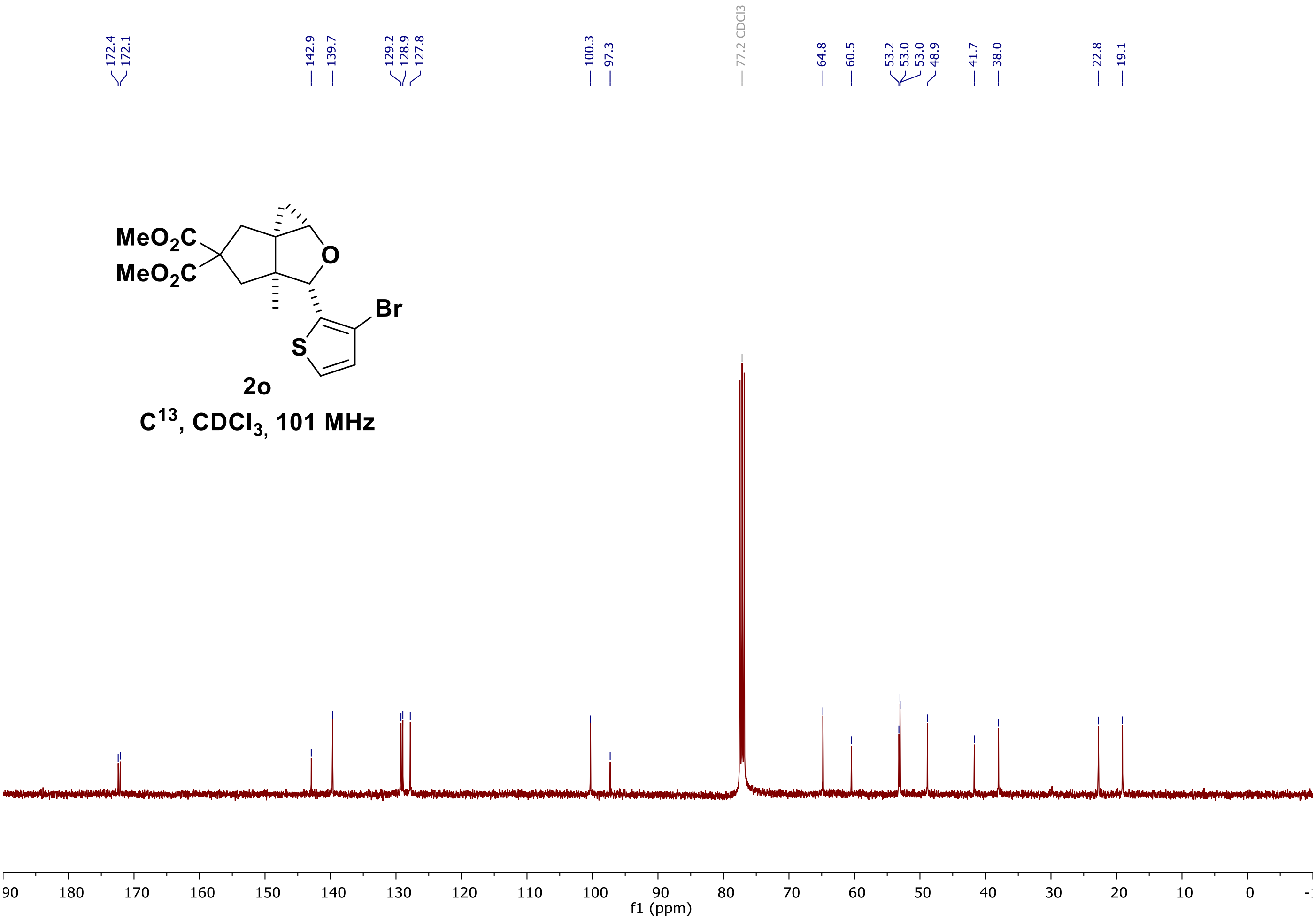


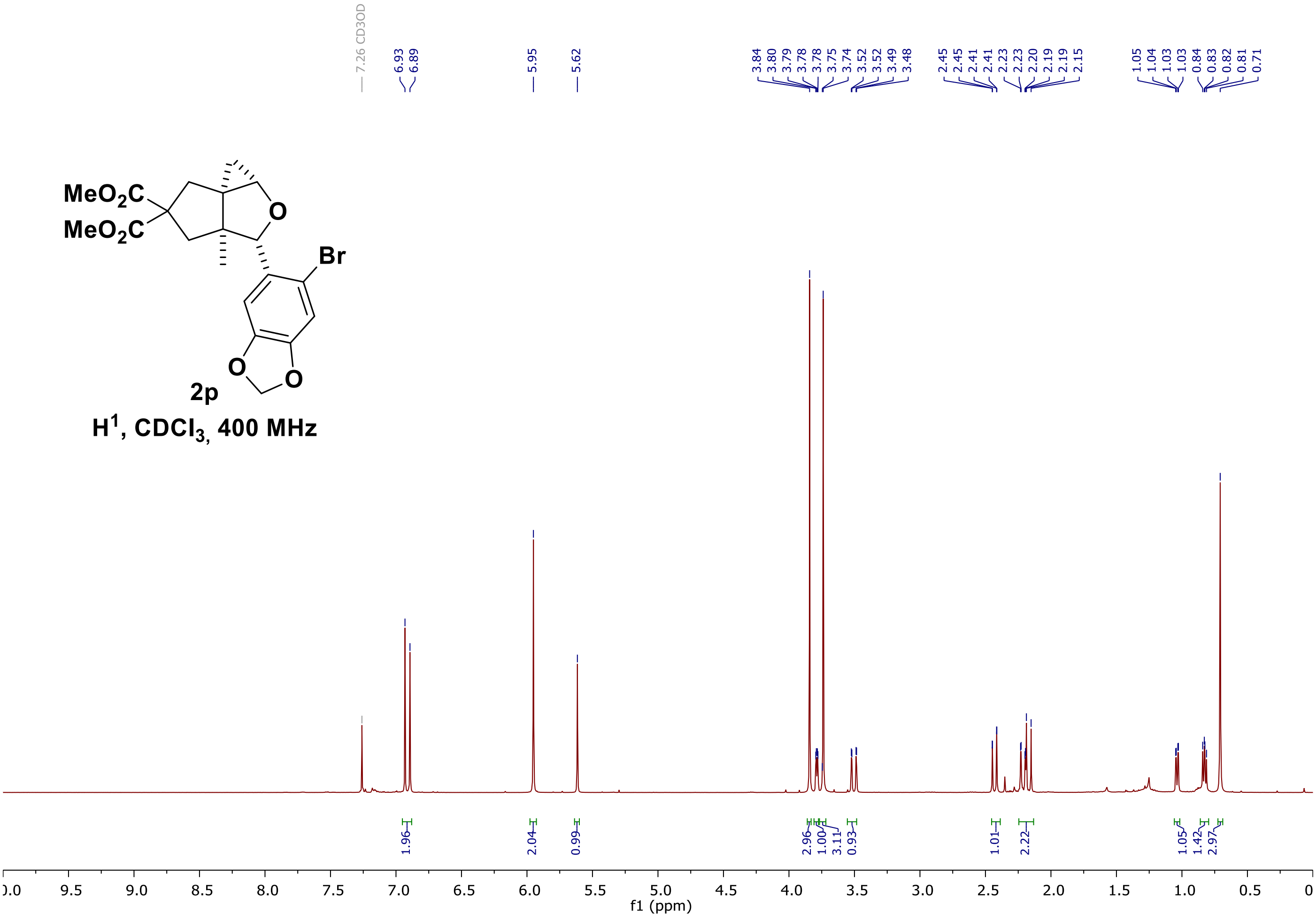
iPrO2C
iPrO2C
O
Br
O
2n
H1, CDCl3, 400 MHz
f1 (ppm)

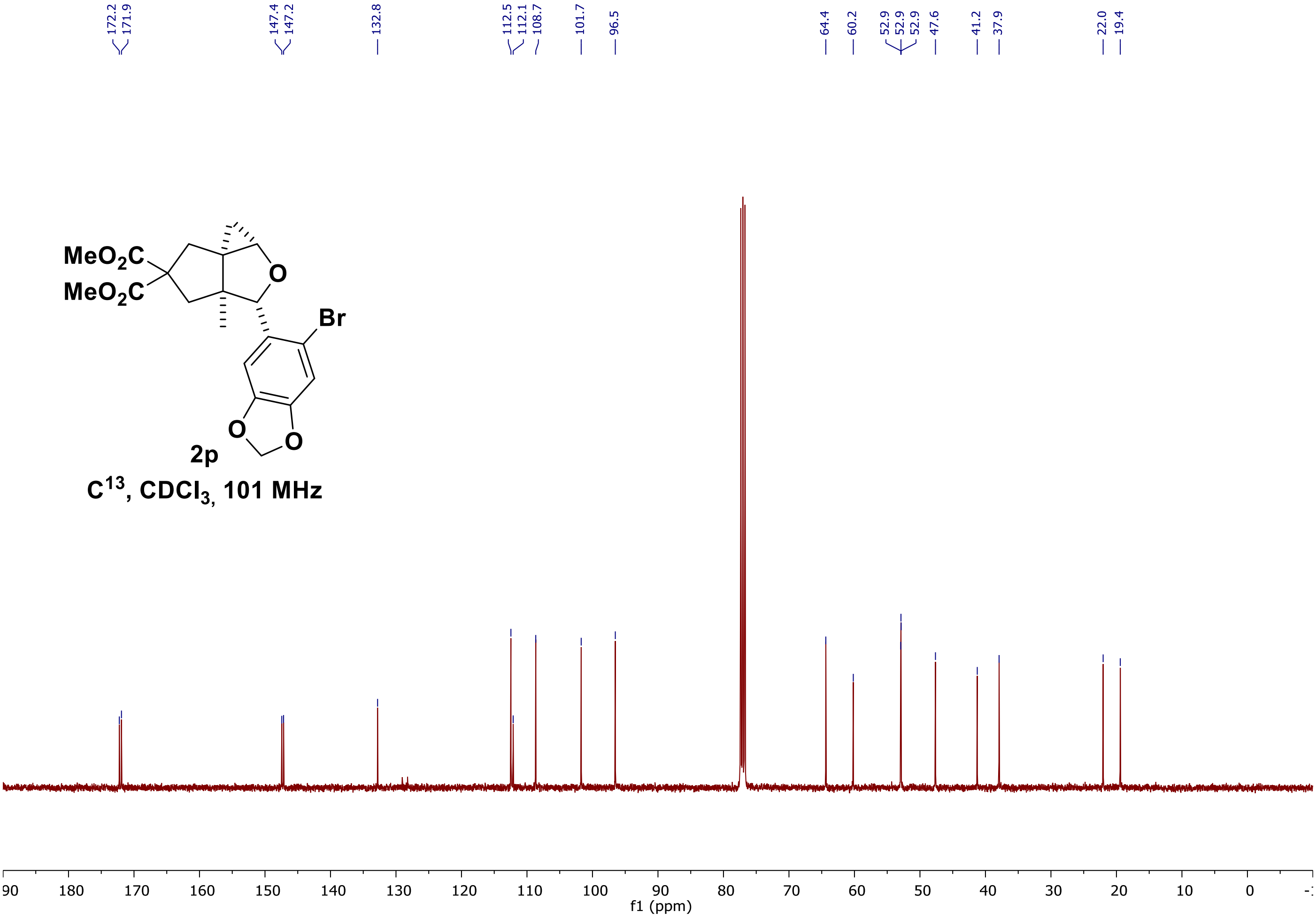


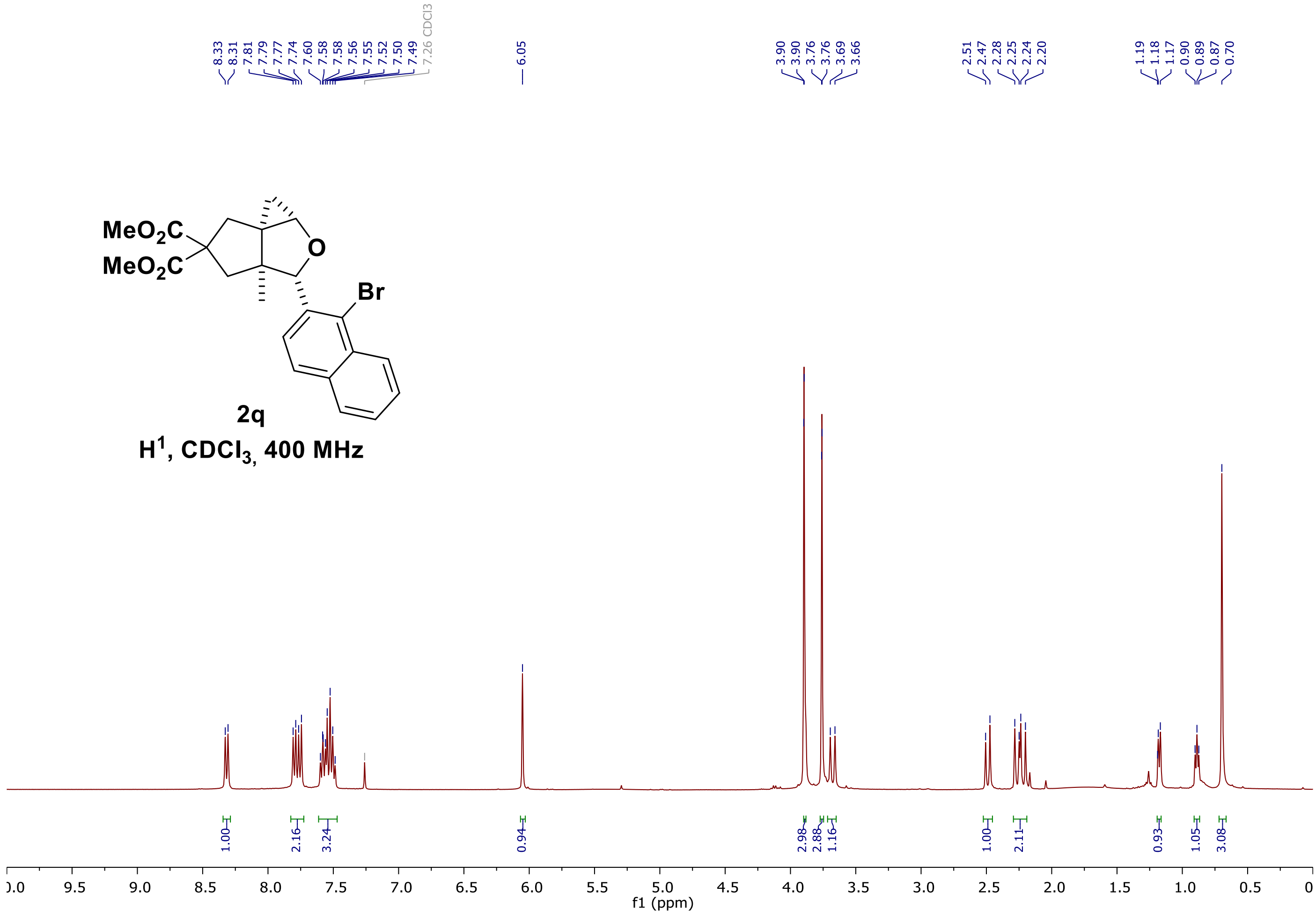
iPrO2C
iPrO2C
O
Br
O
2n
C13, CDCl3, 101 MHz
f1 (ppm)


MeO2C
MeO2C
O
Br
S
2o
H1, CDCl3, 400 MHz
7.26 CDCl3
7.15
7.14
6.88
6.87
5.57
3.83
3.80
3.80
3.79
3.79
3.78
3.72
3.40
3.39
3.36
3.36
2.41
2.38
2.38
2.24
2.23
2.21
2.20
2.18
2.14
1.09
1.09
1.08
1.07
0.86
0.85
0.85
0.84
0.79
1.00
0.96
1.00
3.06
0.99
3.24
1.09
1.12
1.13
1.12
1.08
1.24
3.04
f1 (ppm)

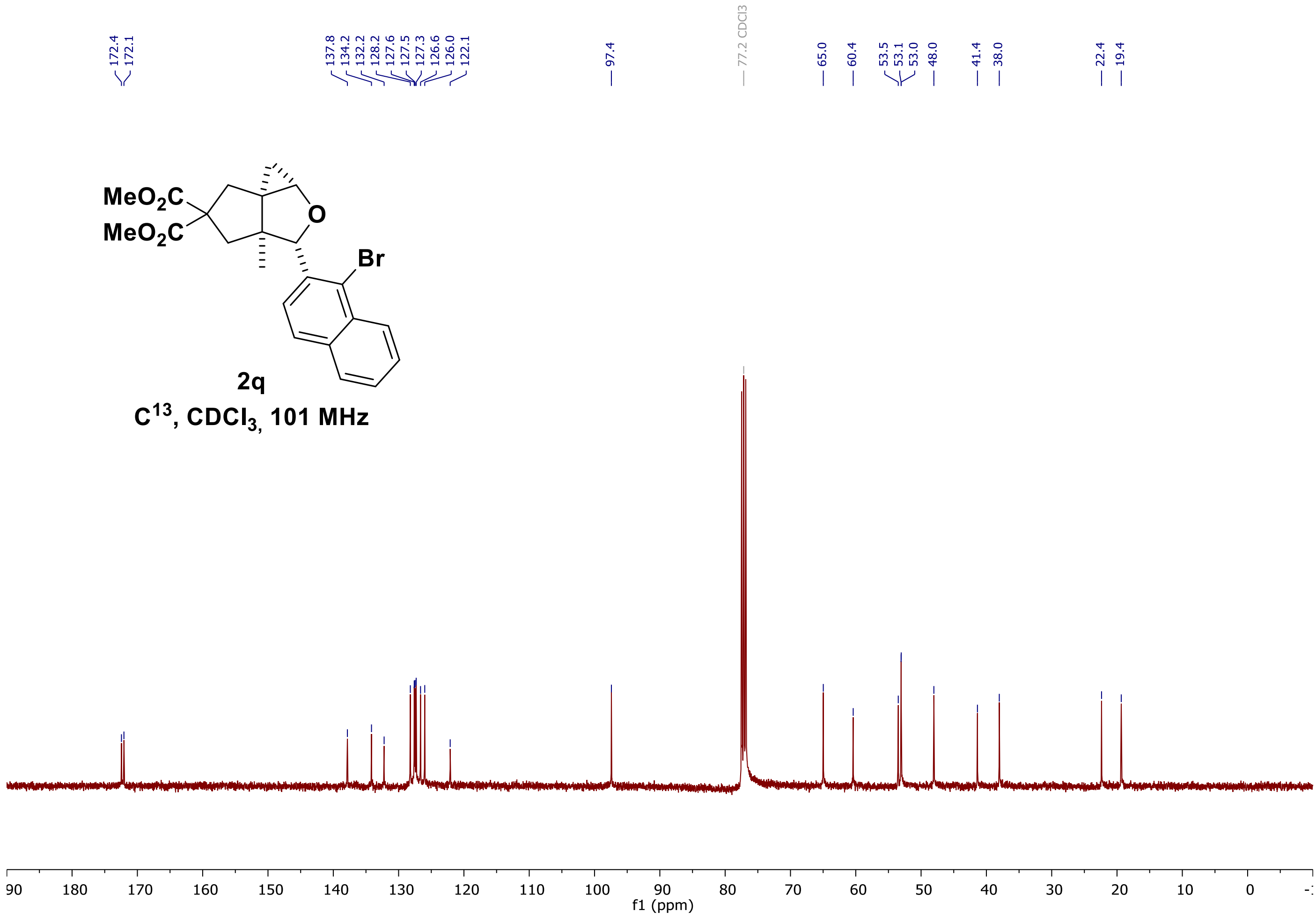

MeO2C
MeO2C
O
Br
S
2o
C13, CDCl3, 101 MHz
172.4
172.1
142.9
139.7
129.2
128.9
127.8
100.3
97.3
77.2 CDCl3
64.8
60.5
53.2
53.0
53.0
48.9
41.7
38.0
22.8
19.1
f1 (ppm)


7.26 CD3OD
6.93
6.89
5.95
5.62
3.84 3.80 3.79 3.78 3.78 3.75 3.74 3.52 3.52 3.49 3.48
2.45 2.45 2.41 2.41 2.23 2.23 2.20 2.19 2.19 2.15
1.05 1.04 1.03 1.03 0.84 0.83 0.82 0.81 0.71
MeO2C
MeO2C
O
Br
O
O
2p
H1, CDCl3, 400 MHz
1.96
2.04
0.99
2.96
1.00
3.11
0.93
1.01
2.22
1.05
1.42
2.97
f1 (ppm)

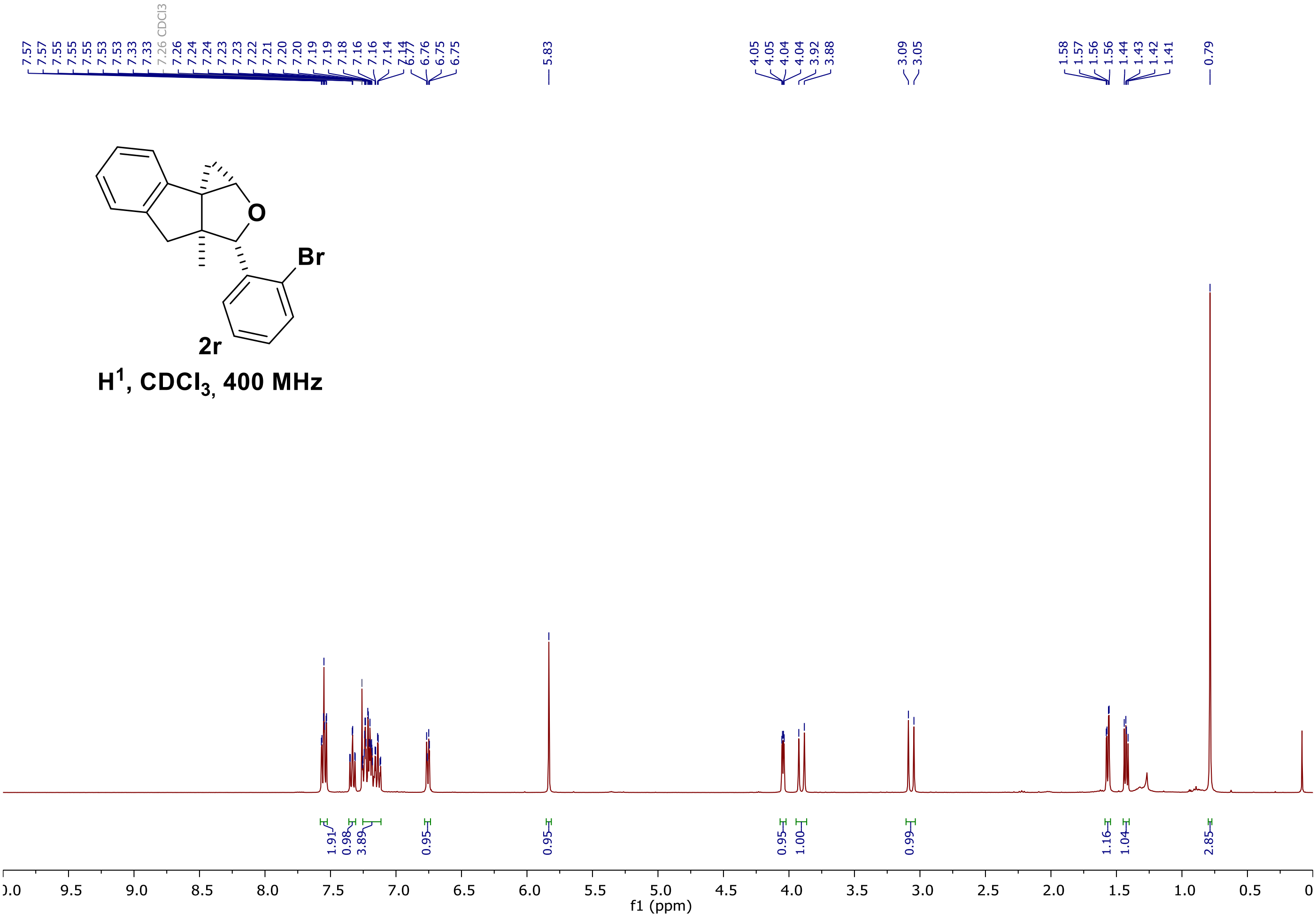

172.2
171.9
147.4
147.2
132.8
112.5
112.1
108.7
101.7
96.5
64.4
60.2
52.9
52.9
52.9
47.6
41.2
37.9
22.0
19.4
MeO2C
MeO2C
O
Br
O
O
2p
C13, CDCl3, 101 MHz
f1 (ppm)

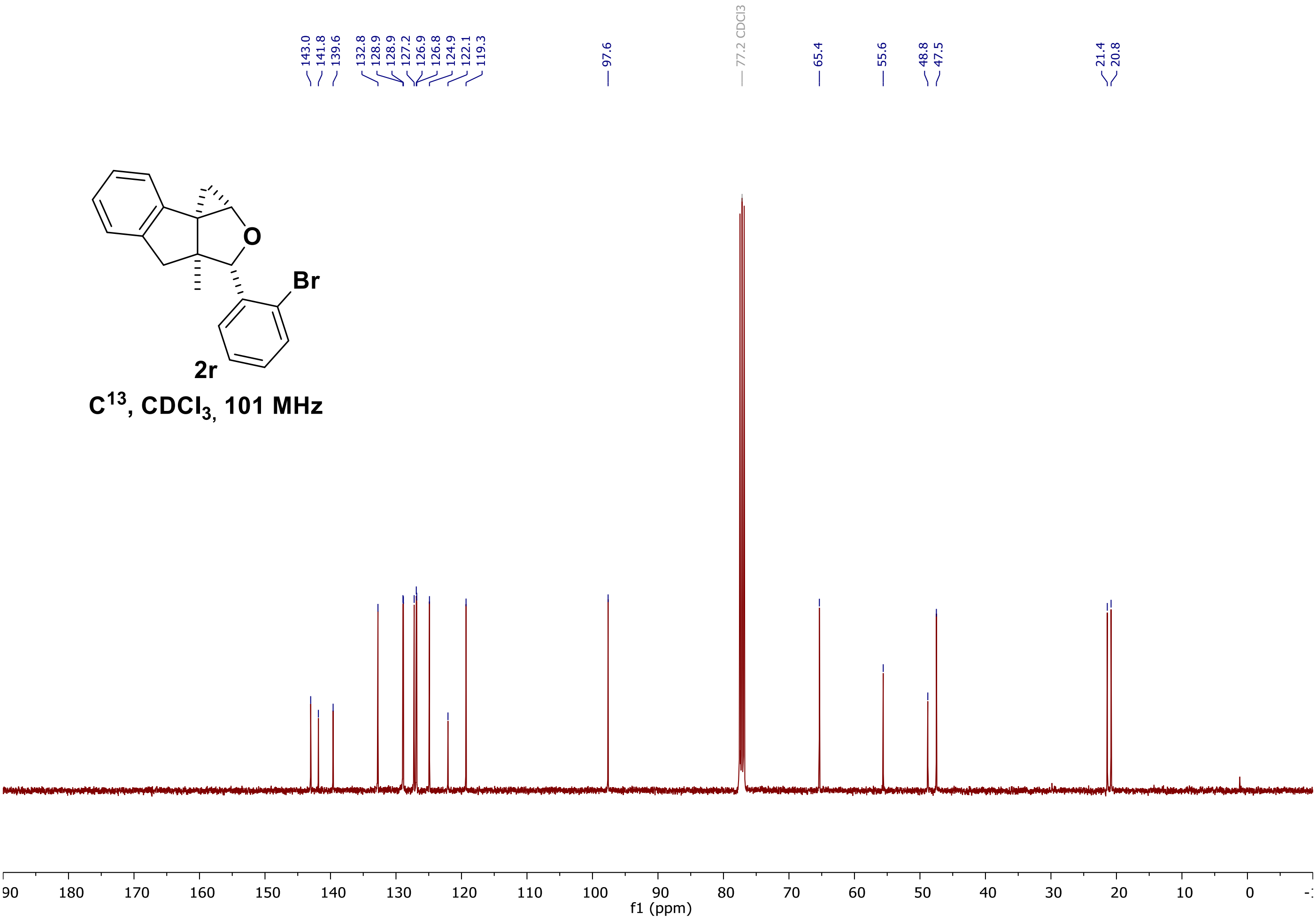


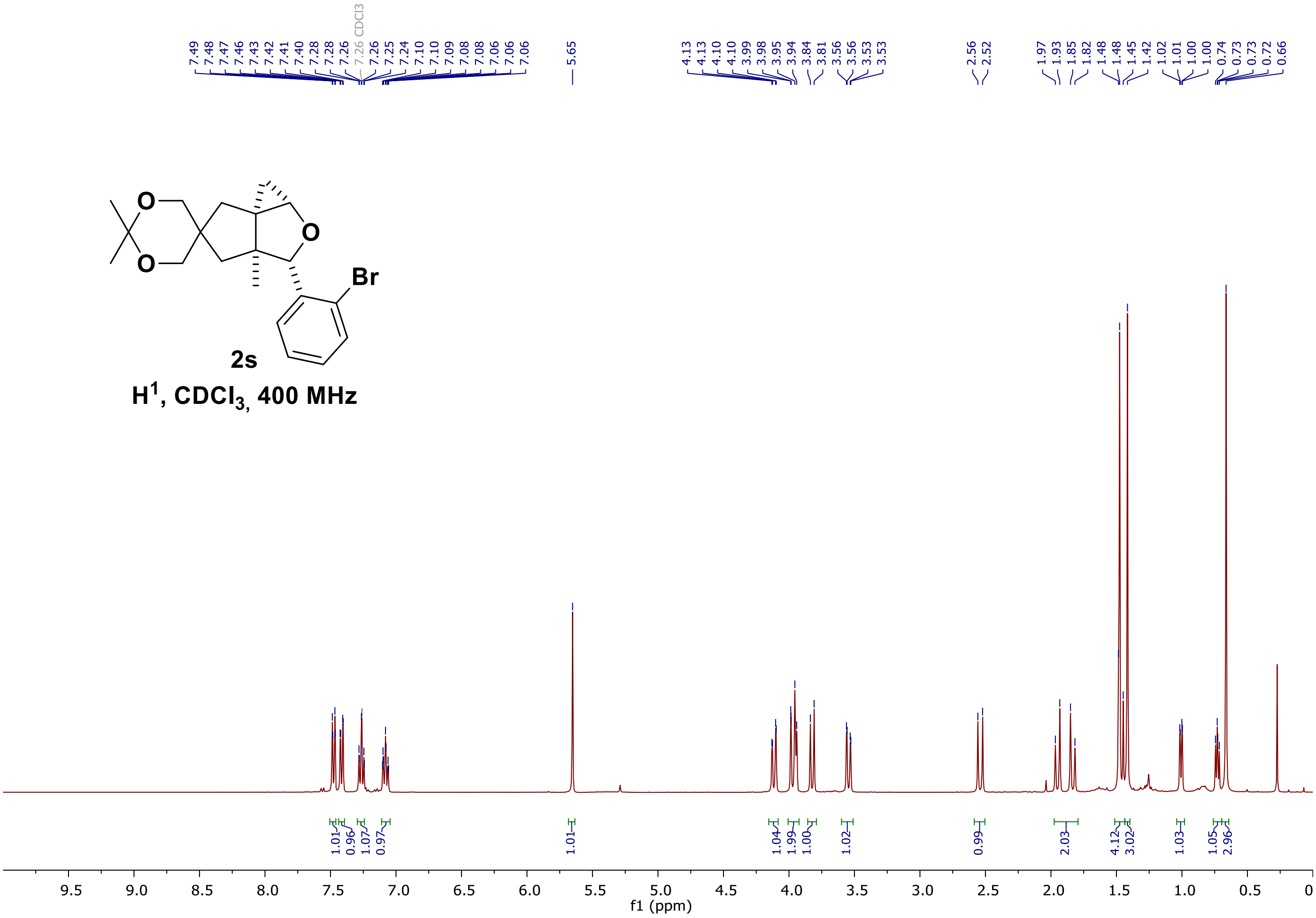
2q
H1, CDCl3, 400 MHz

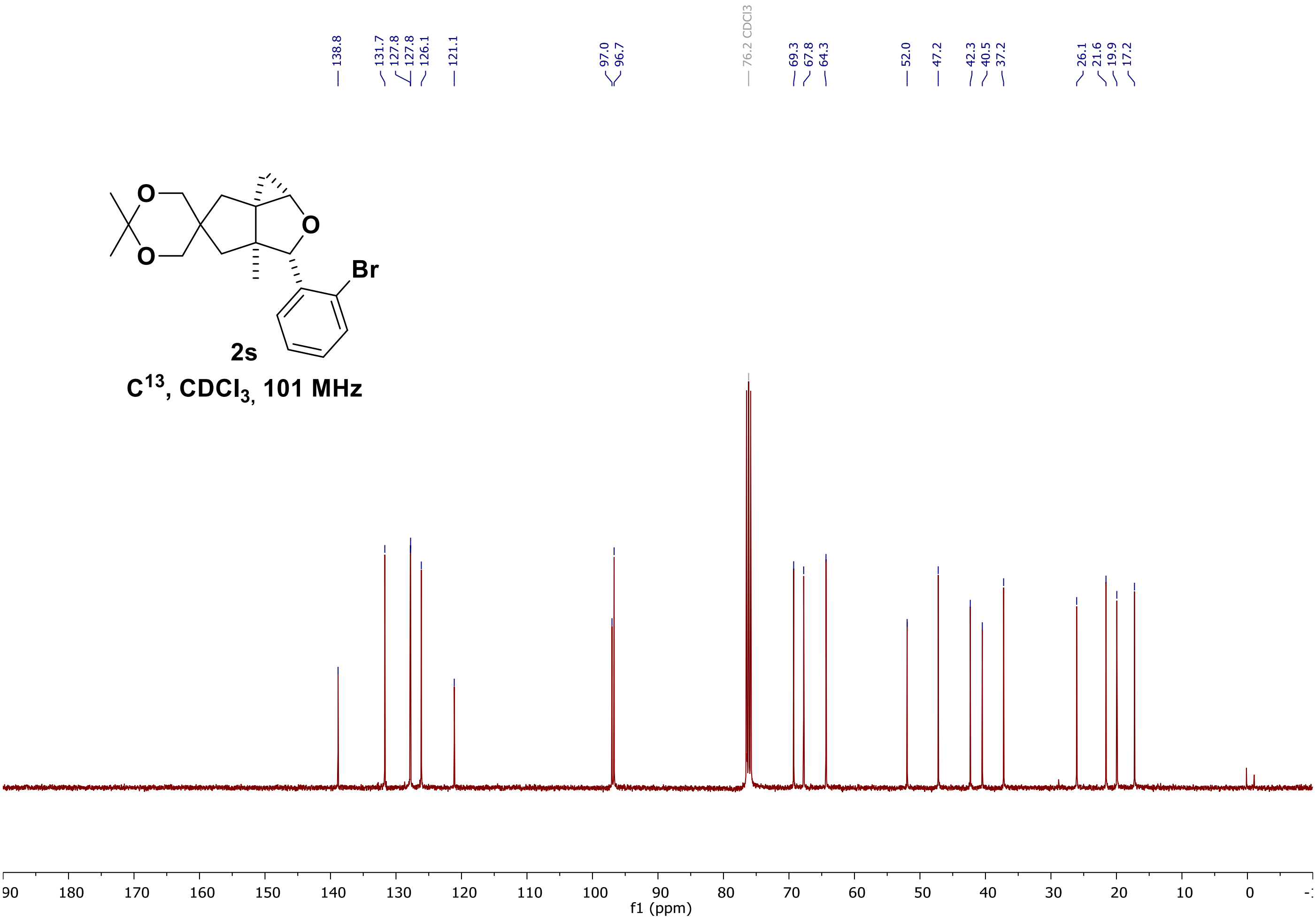


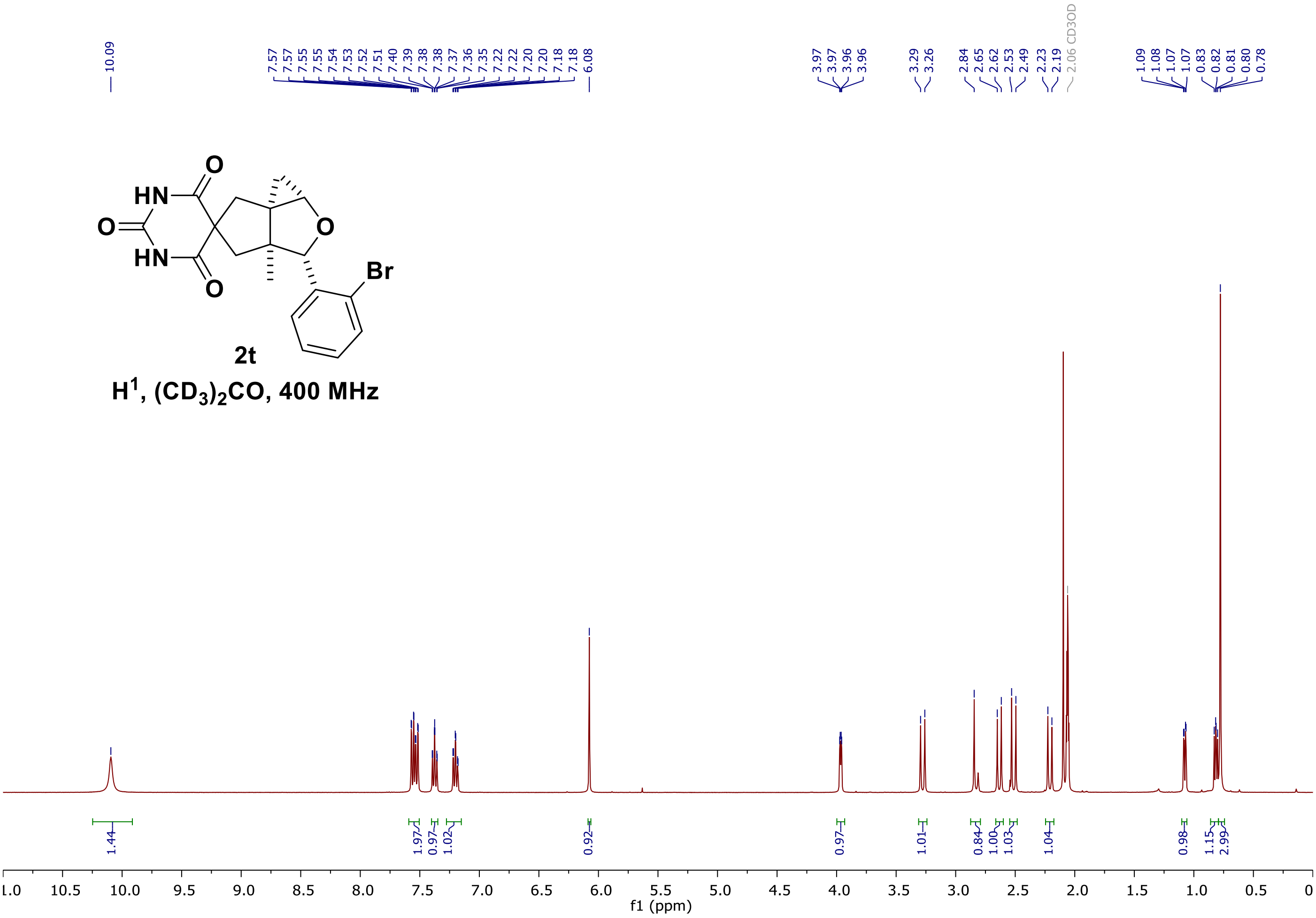
2q
C13, CDCl3, 101 MHz

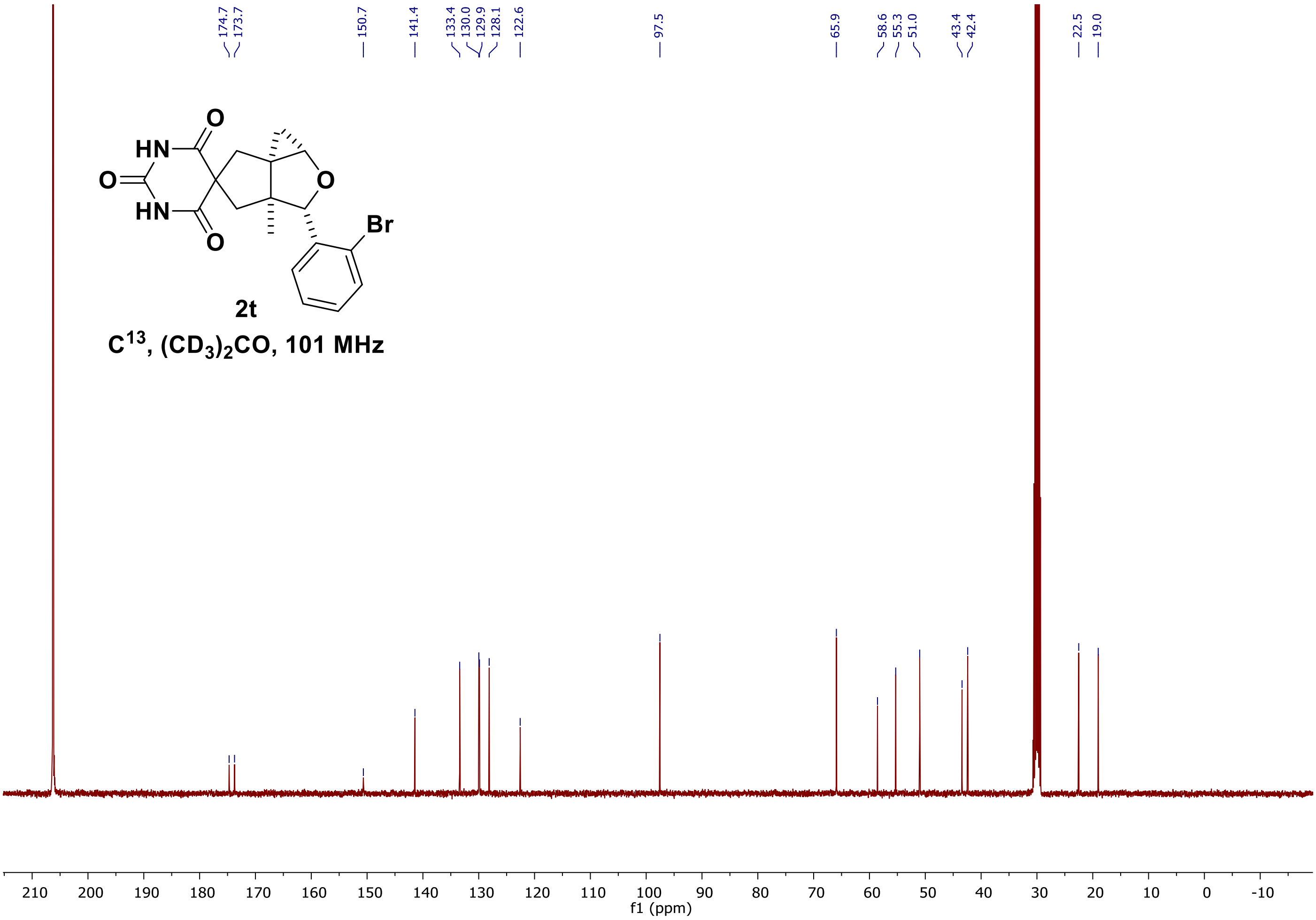

7.57 7.57 7.55 7.55 7.55 7.53 7.53 7.33 7.33 7.26 CDCl3 7.26 7.24 7.24 7.23 7.23 7.22 7.21 7.20 7.20 7.19 7.19 7.18 7.16 7.16 7.14 7.14 6.77 6.76 6.75 6.75
5.83
4.05 4.05 4.04 4.04 3.92 3.88
3.09 3.05
1.58 1.57 1.56 1.56 1.44 1.43 1.42 1.41
0.79
Br
O
2r
H1, CDCl3, 400 MHz
1.91 0.98 3.89 0.95 0.95 0.95 1.00 0.99 1.16 1.04 2.85
f1 (ppm)

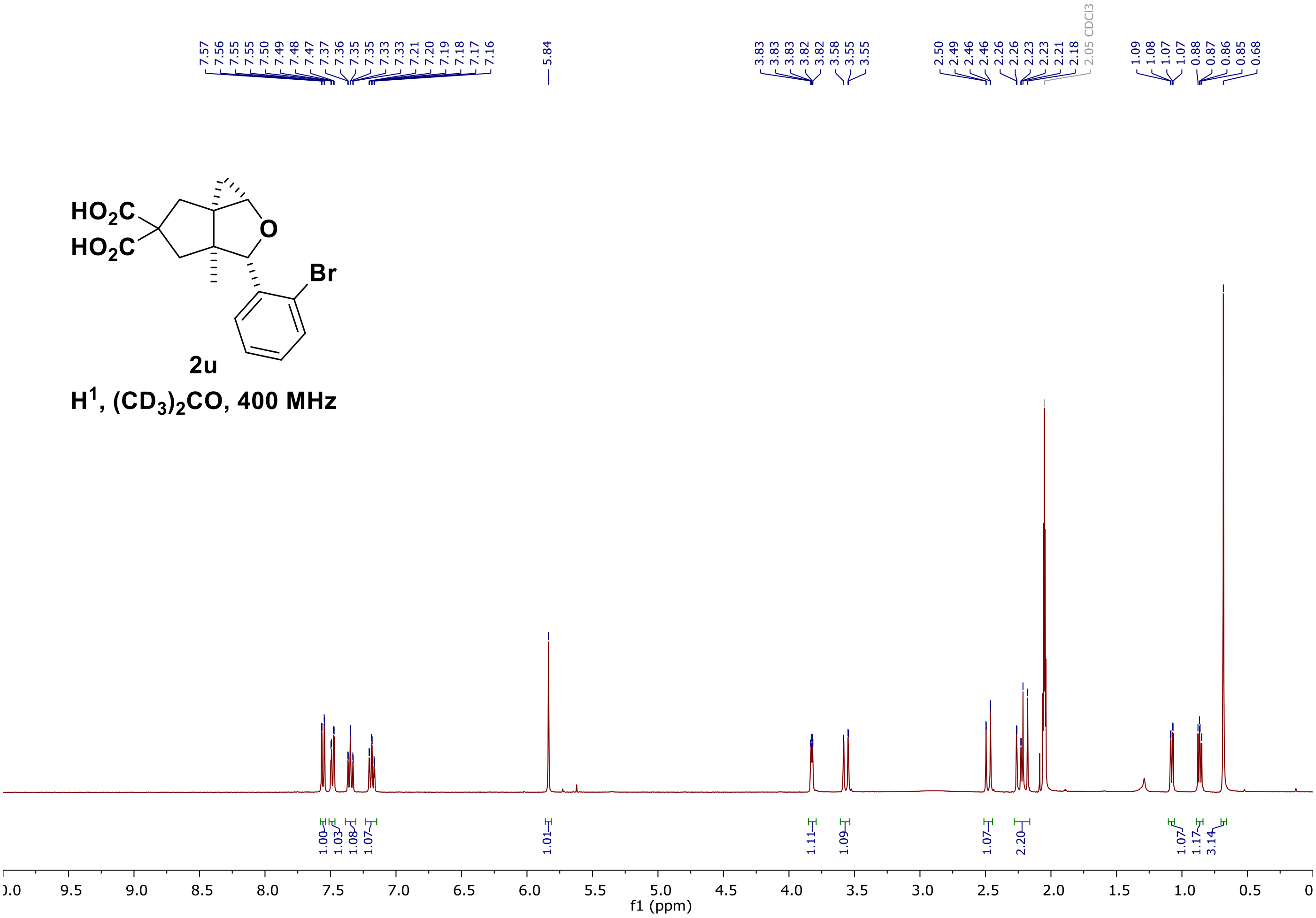

143.0 141.8 139.6 132.8 128.9 128.9 127.2 126.9 126.8 124.9 122.1 119.3
97.6
77.2 CDCl3
65.4
55.6
48.8 47.5
21.4 20.8
Br
O
2r
C13, CDCl3, 101 MHz
f1 (ppm)

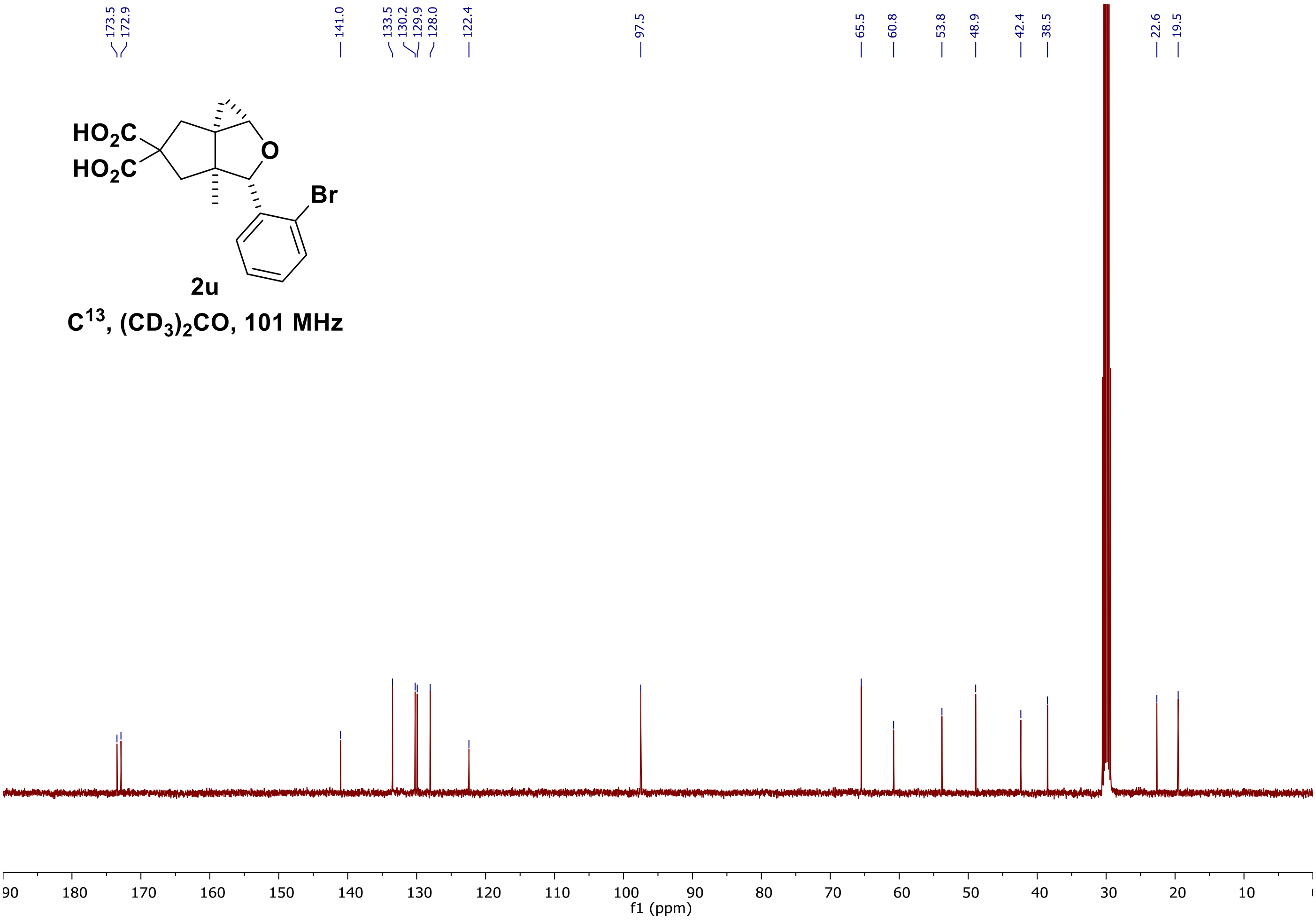

7.49 7.48 7.47 7.46 7.43 7.42 7.41 7.40 7.28 7.28 7.26 7.26 CDCl3 7.26 7.25 7.24 7.10 7.10 7.09 7.08 7.08 7.06 7.06 7.06
5.65
4.13 4.13 4.10 4.10 3.99 3.98 3.95 3.95 3.94 3.84 3.81 3.56 3.56 3.53 3.53
2.56 2.52
1.97 1.93 1.85 1.82 1.48 1.48 1.45 1.42 1.02 1.01 1.00 1.00 0.74 0.73 0.73 0.72 0.66
Br
O
O
O
2s
H1, CDCl3, 400 MHz
1.01 0.96 1.07 0.97 1.01 1.04 1.99 1.00 1.02 0.99 2.03 4.12 3.02 1.03 1.05 2.96
f1 (ppm)


138.8
131.7 127.8 127.8 126.1
121.1
97.0 96.7
76.2 CDCl3
69.3 67.8 64.3
52.0
47.2
42.3 40.5 37.2
26.1 21.6 19.9 17.2
Br
O
O
O
2s
C13, CDCl3, 101 MHz
f1 (ppm)


10.09
7.57
7.57
7.55
7.54
7.53
7.52
7.51
7.40
7.39
7.38
7.38
7.37
7.36
7.35
7.22
7.22
7.20
7.20
7.18
6.08
3.97
3.97
3.96
3.96
3.29
3.26
2.84
2.65
2.62
2.53
2.49
2.23
2.19
2.06 CD3OD
1.09
1.08
1.07
1.07
0.83
0.82
0.81
0.80
0.78
HN
O
O
HN
O
O
Br
2t
H1, (CD3)2CO, 400 MHz
1.44
1.97
0.97
1.02
0.92
0.97
1.01
0.84
1.00
1.03
1.04
0.98
1.15
2.99
f1 (ppm)

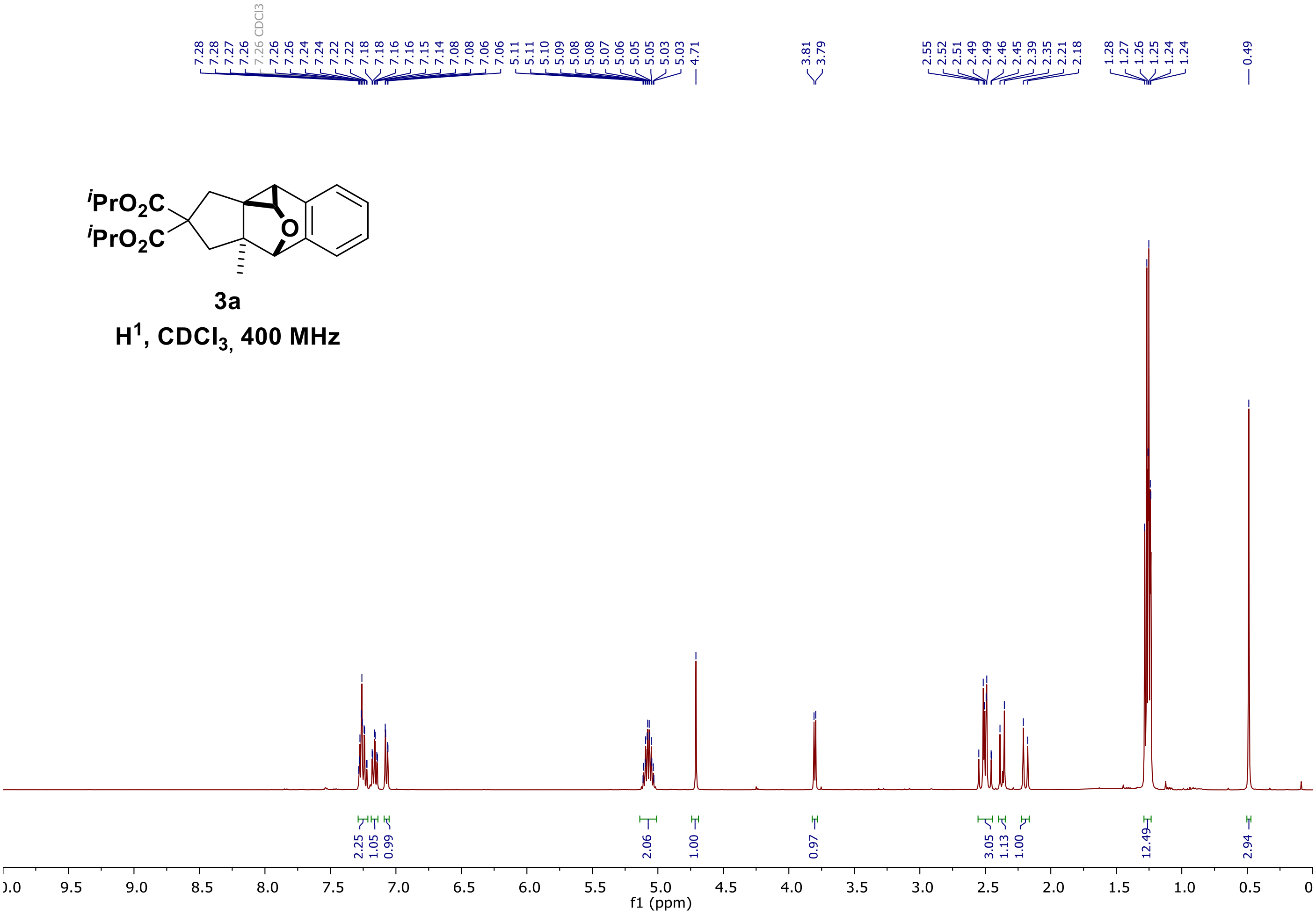

174.7
173.7
150.7
141.4
133.4
130.0
129.9
128.1
122.6
97.5
65.9
58.6
55.3
51.0
43.4
42.4
22.5
19.0
HN
O
O
HN
O
O
Br
2t
C13, (CD3)2CO, 101 MHz
f1 (ppm)


7.57 7.56 7.55 7.55 7.50 7.49 7.48 7.47 7.37 7.36 7.35 7.35 7.33 7.33 7.21 7.20 7.19 7.18 7.17 7.16
5.84
3.83 3.83 3.83 3.82 3.82 3.58 3.55 3.55
2.50 2.49 2.46 2.46 2.26 2.26 2.23 2.23 2.21 2.18
2.05 CDCl3
1.09 1.08 1.07 1.07 0.88 0.87 0.86 0.85 0.68
HO2C
HO2C
O
Br
2u
H1, (CD3)2CO, 400 MHz
1.00 1.03 1.08 1.07
1.01
1.11
1.09
1.07
2.20
1.07 1.17 3.14
f1 (ppm)


173.5 172.9
141.0
133.5 130.2 129.9 128.0
122.4
97.5
65.5
60.8
53.8
48.9
42.4
38.5
22.6
19.5
HO2C
HO2C
O
Br
2u
C13, (CD3)2CO, 101 MHz
f1 (ppm)

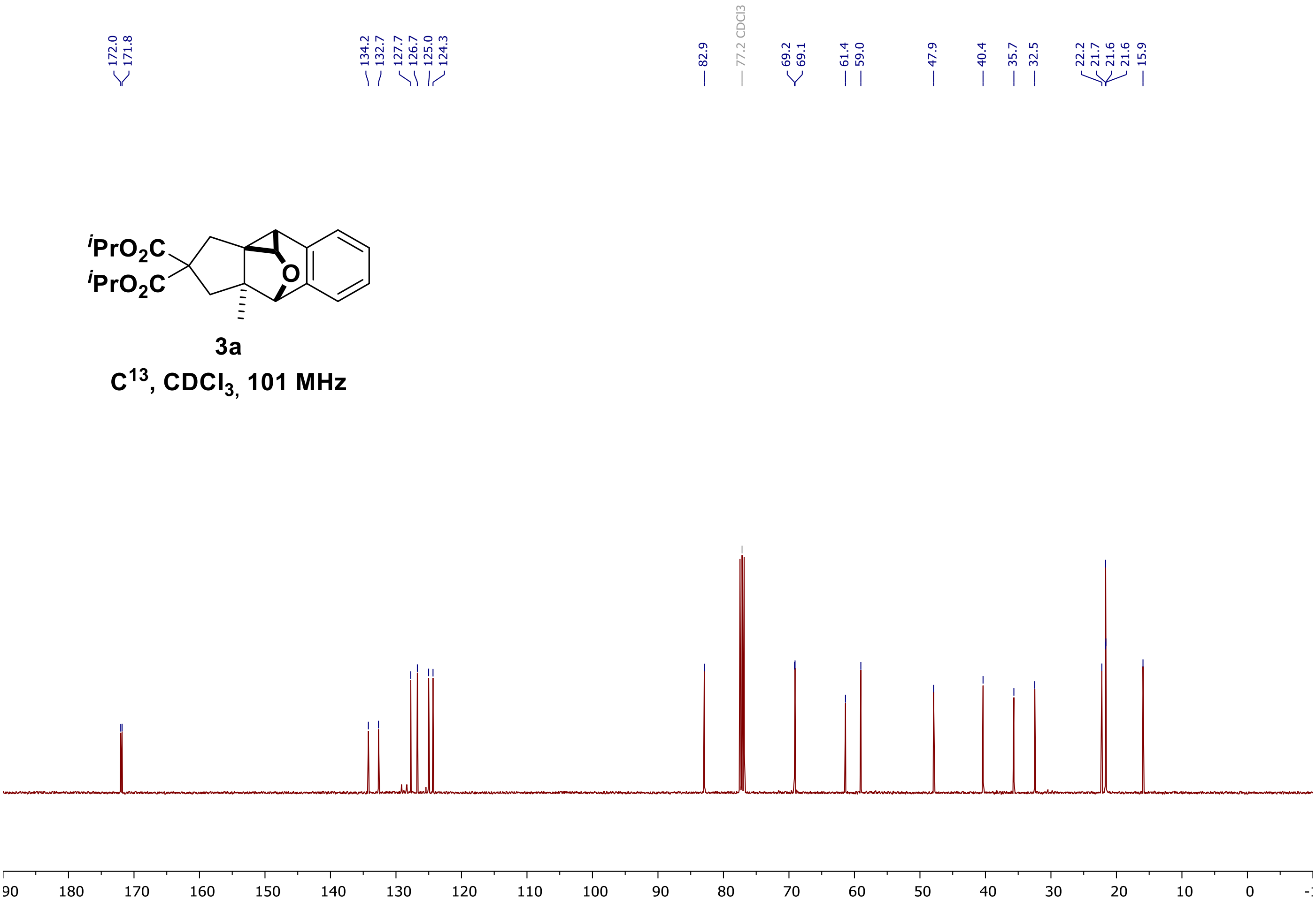
3a

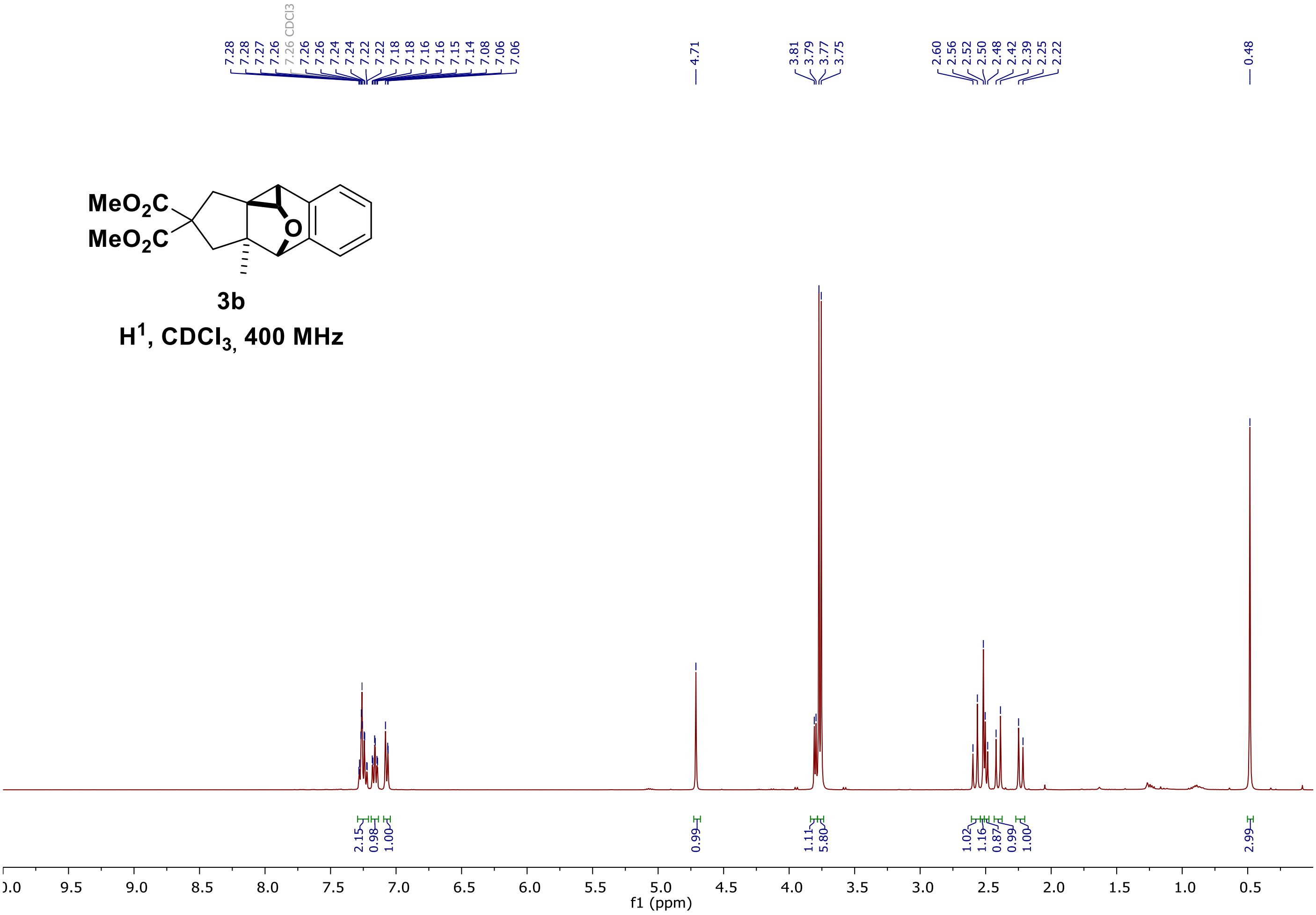
H[1], $CDCl_3$, 400 MHz

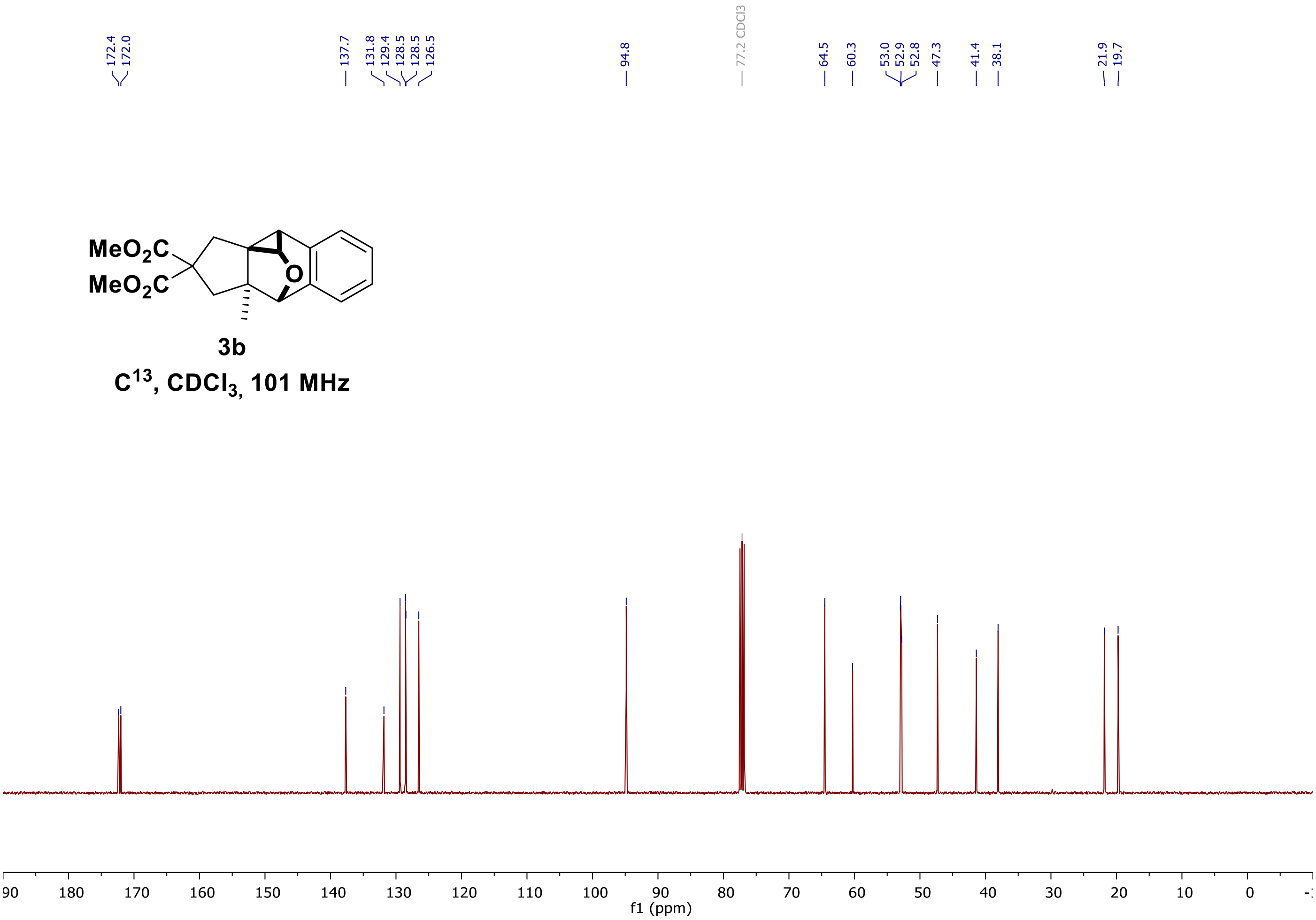


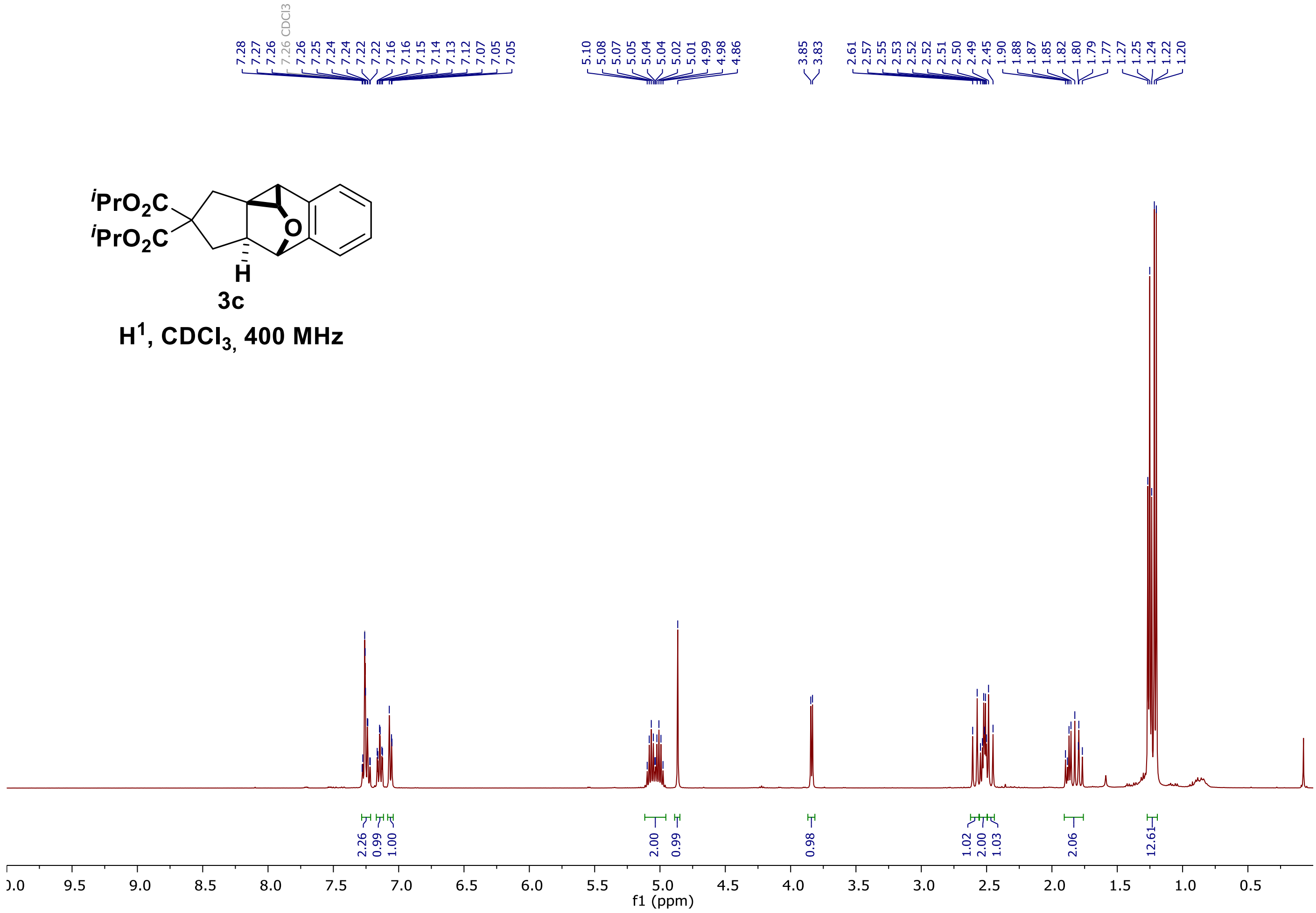
3a

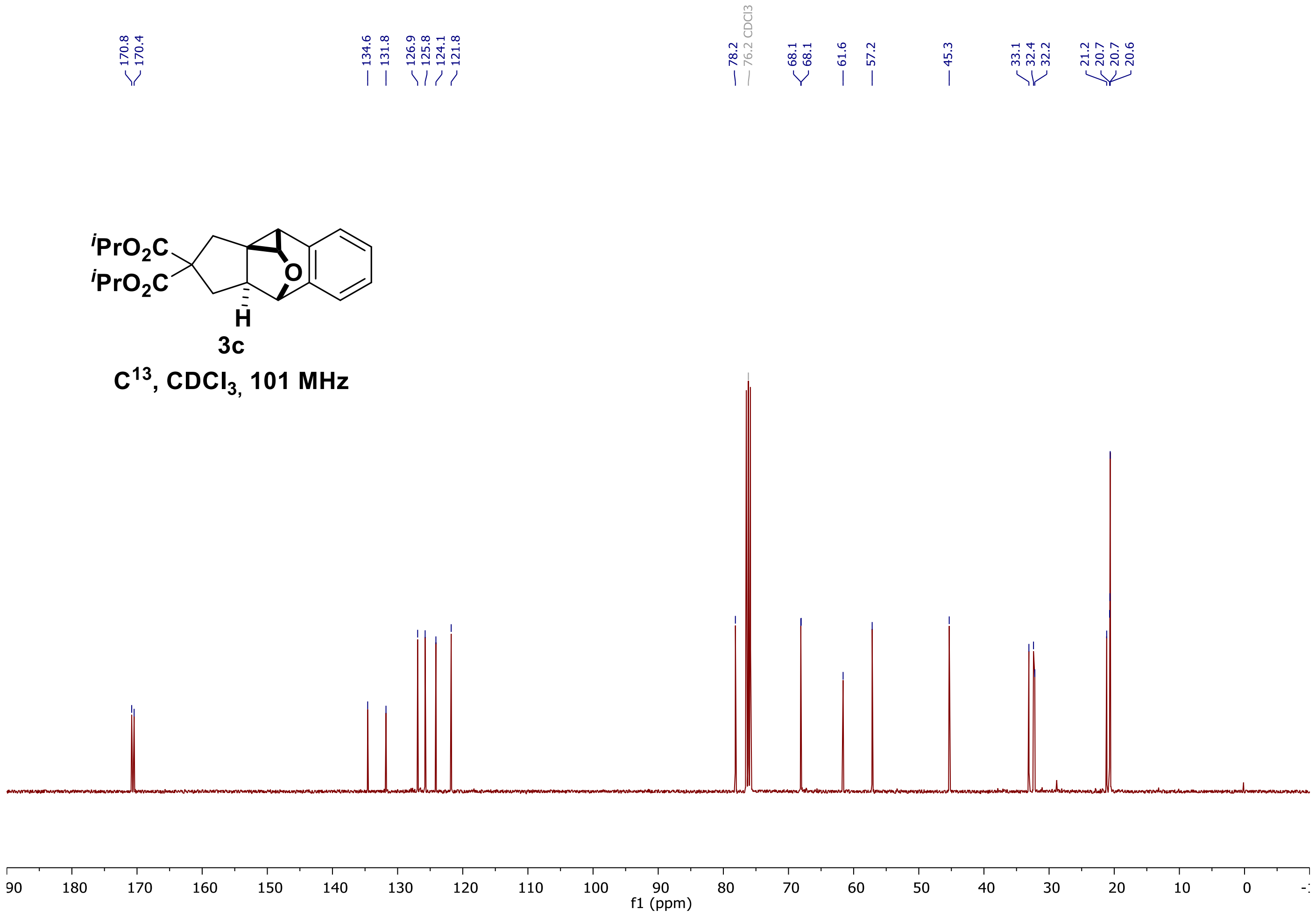
C[13], $CDCl_3$, 101 MHz

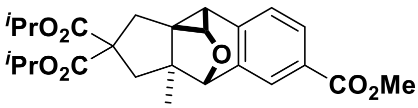



7.28 7.28 7.27 7.26 7.26 CDCl3 7.26 7.26 7.24 7.24 7.22 7.22 7.18 7.18 7.16 7.16 7.15 7.14 7.08 7.06
4.71
3.81 3.79 3.77 3.75
2.60 2.56 2.52 2.50 2.48 2.42 2.39 2.25 2.22
0.48
MeO2C
MeO2C
O
3b
H1, CDCl3, 400 MHz
2.15 0.98 1.00
0.99
1.11 5.80
1.02 1.16 0.87 0.99 1.00
2.99
f1 (ppm)


172.4 172.0
137.7
131.8 129.4 128.5 128.5 126.5
94.8
77.2 CDCl3
64.5
60.3
53.0 52.9 52.8
47.3
41.4
38.1
21.9
19.7
MeO2C
MeO2C
O
3b
C13, CDCl3, 101 MHz
f1 (ppm)

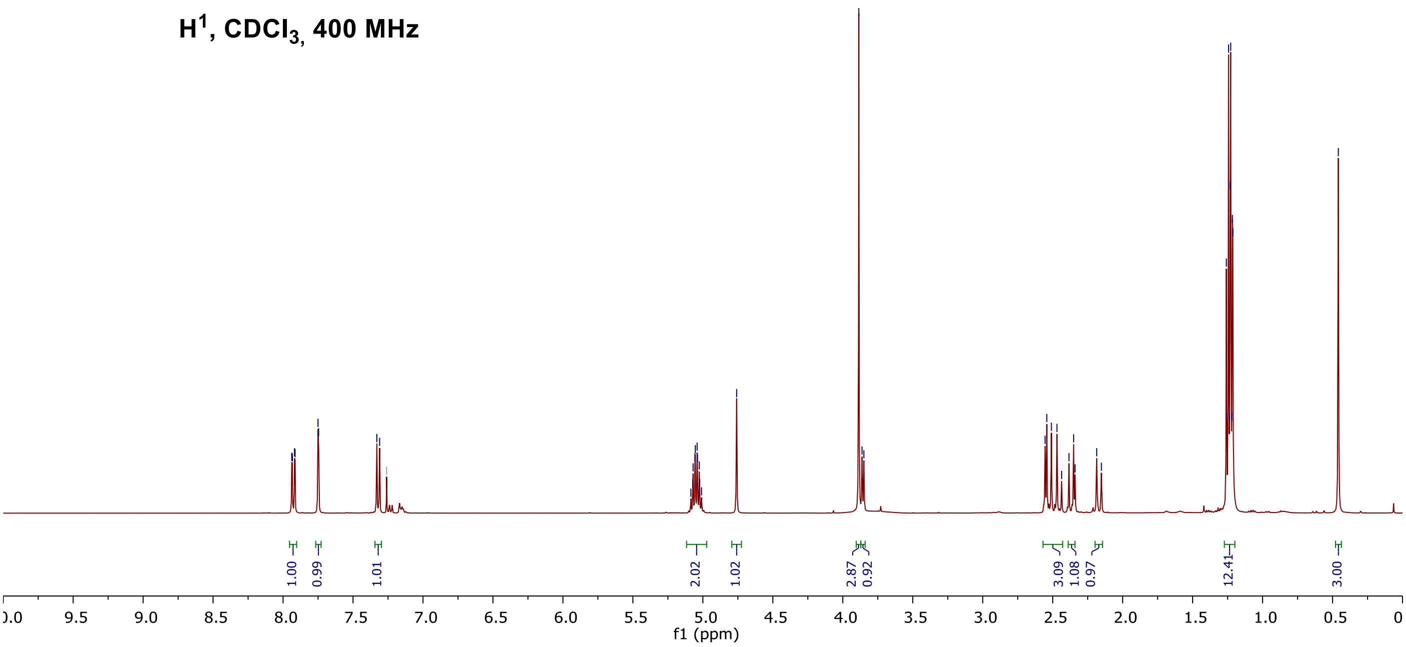

7.28 7.27 7.26 7.26 CDCl3 7.26 7.25 7.24 7.24 7.22 7.22 7.16 7.16 7.15 7.14 7.13 7.12 7.07 7.05 7.05
5.10 5.08 5.07 5.05 5.04 5.04 5.02 5.01 4.99 4.98 4.86
3.85 3.83
2.61 2.57 2.55 2.53 2.52 2.52 2.51 2.50 2.49 2.45 1.90 1.88 1.87 1.85 1.82 1.80 1.79 1.77 1.27 1.25 1.24 1.22 1.20
iPrO2C
iPrO2C
O
H
3c
H1, CDCl3, 400 MHz
2.26 0.99 1.00 2.00 0.99 0.98 1.02 2.00 1.03 2.06 12.61
f1 (ppm)

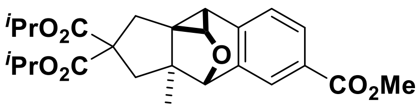

170.8 170.4 134.6 131.8 126.9 125.8 124.1 121.8 78.2 76.2 CDCl3 68.1 68.1 61.6 57.2 45.3 33.1 32.4 32.2 21.2 20.7 20.7 20.6
iPrO2C
iPrO2C
O
H
3c
C13, CDCl3, 101 MHz
f1 (ppm)



3d

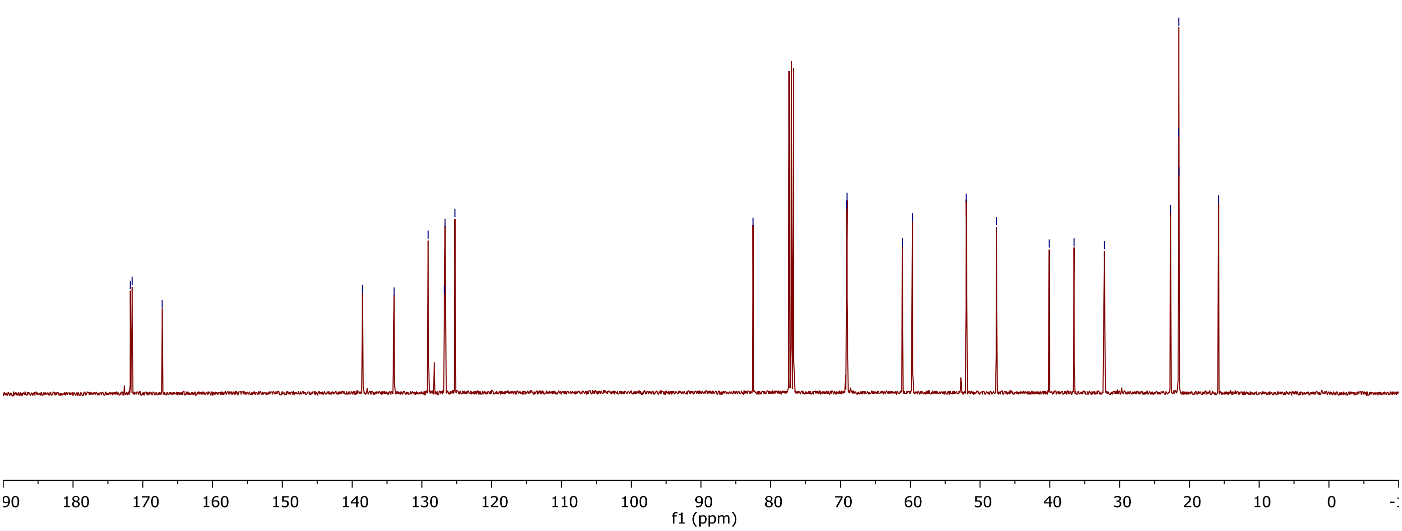
H[1], $CDCl_3$, 400 MHz

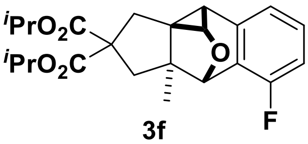




3d

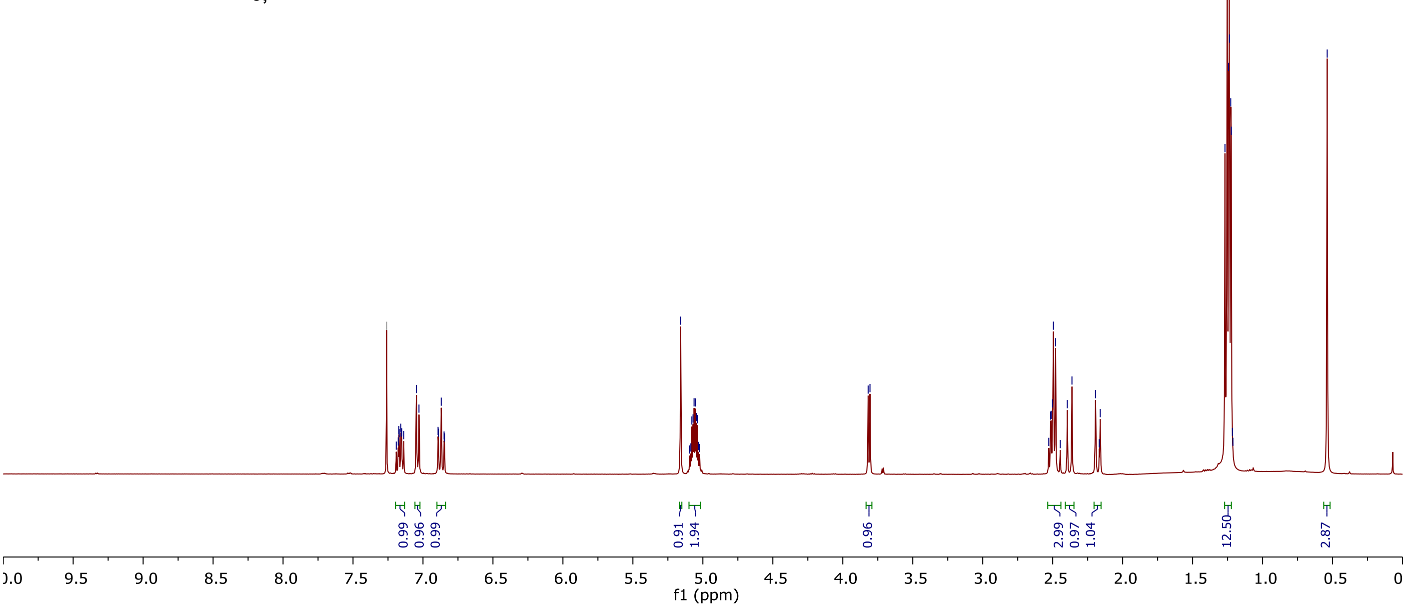
C[13], $CDCl_3$, 101 MHz

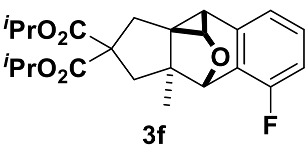




3f

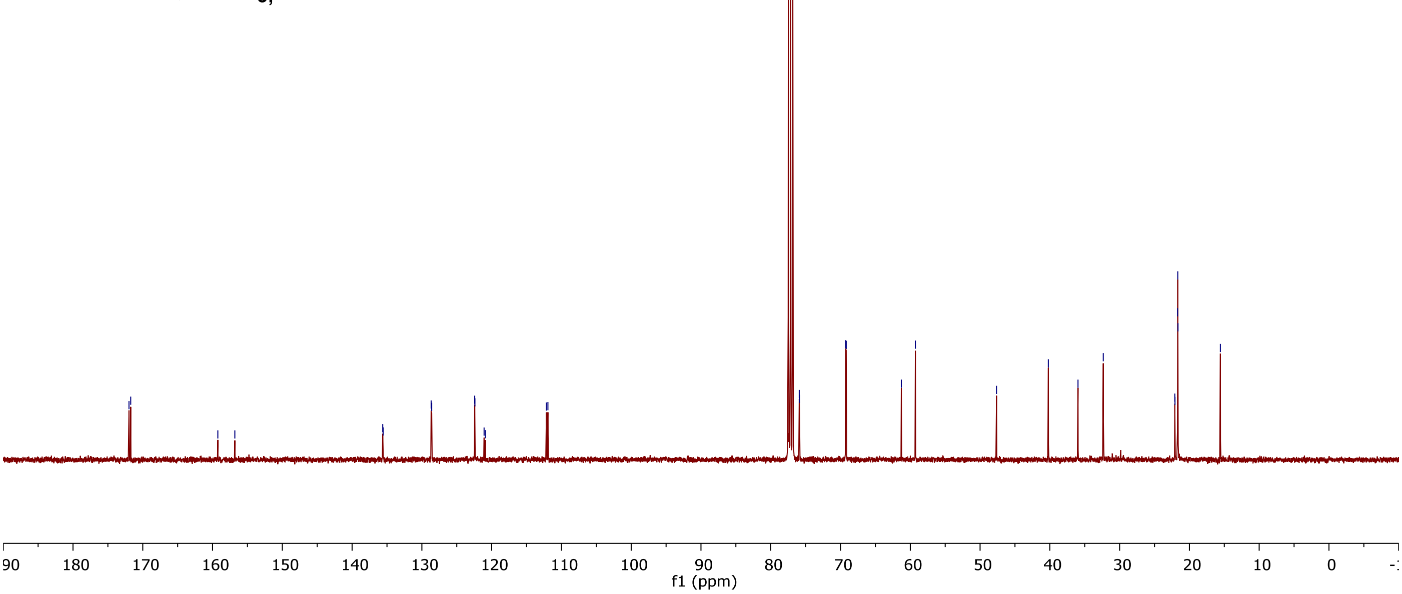
H^1, $CDCl_3$, 400 MHz

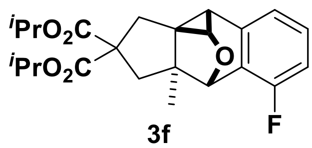




3f

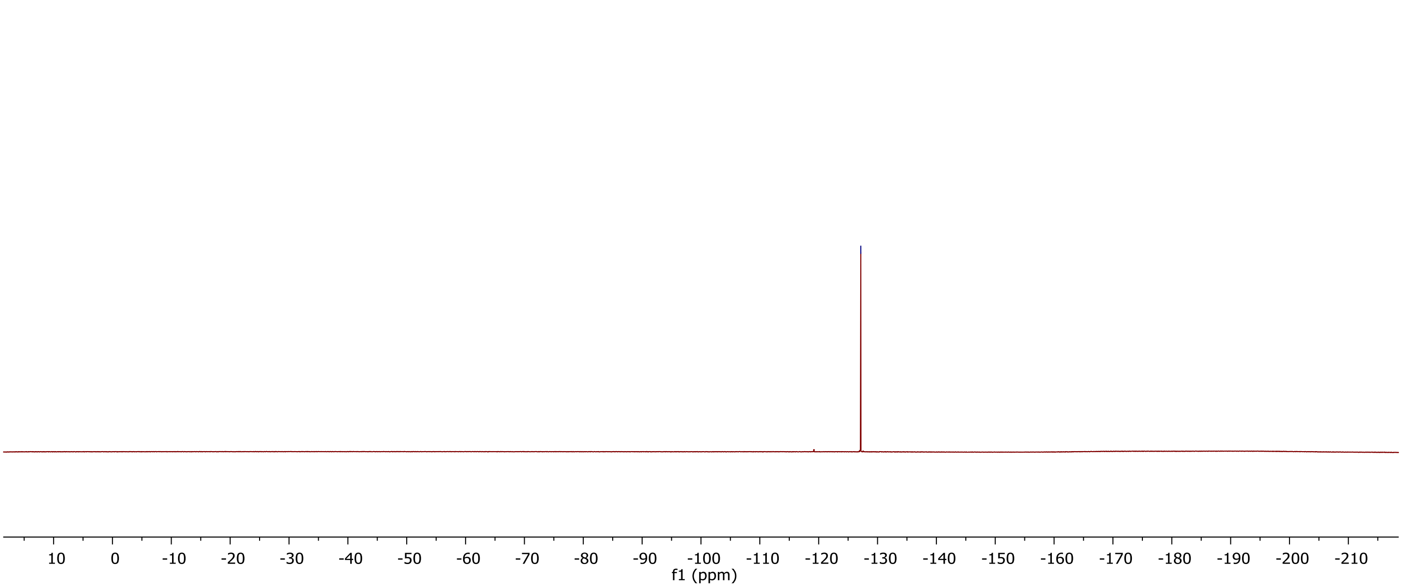
C^{13}, $CDCl_3$, 101 MHz

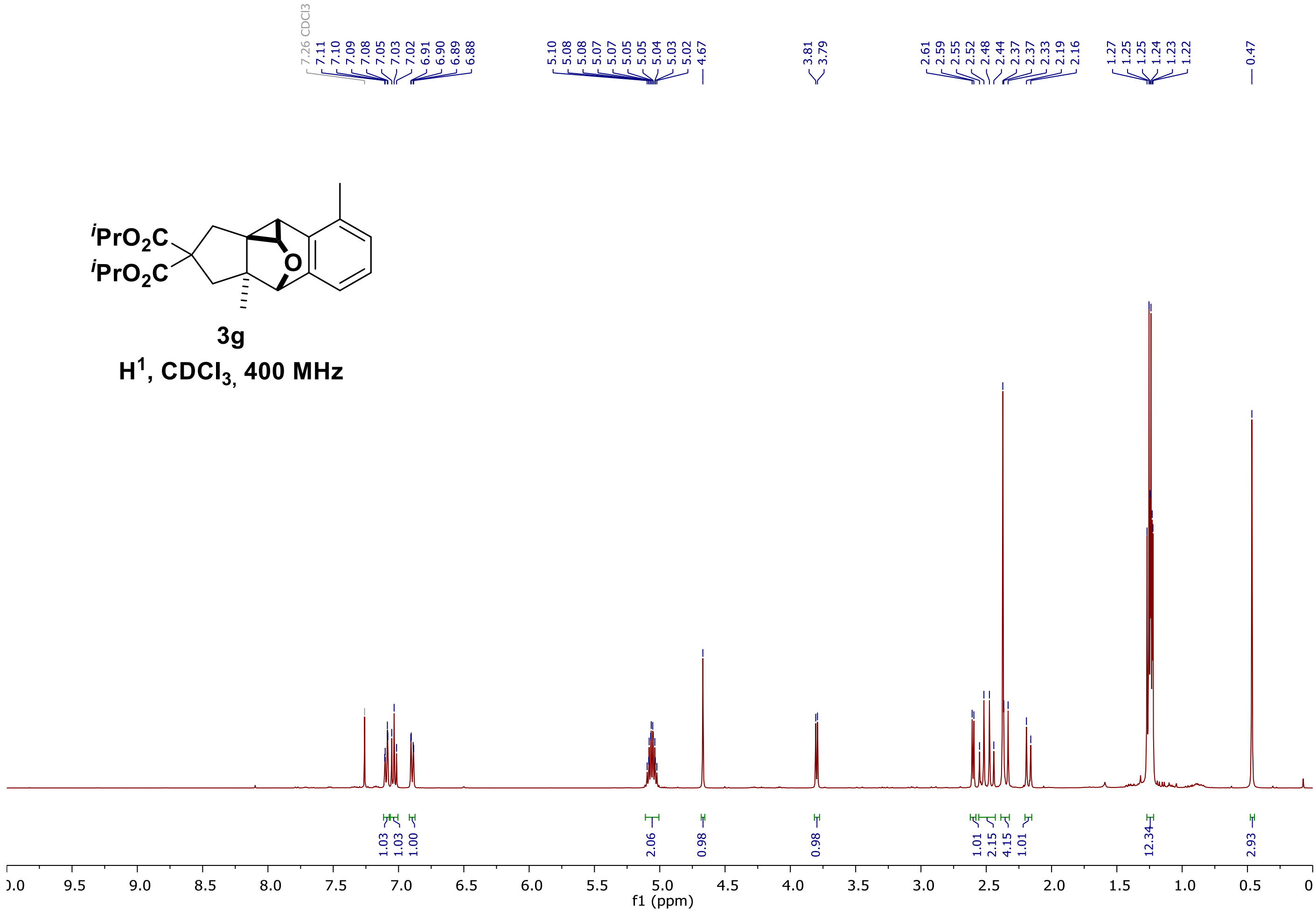


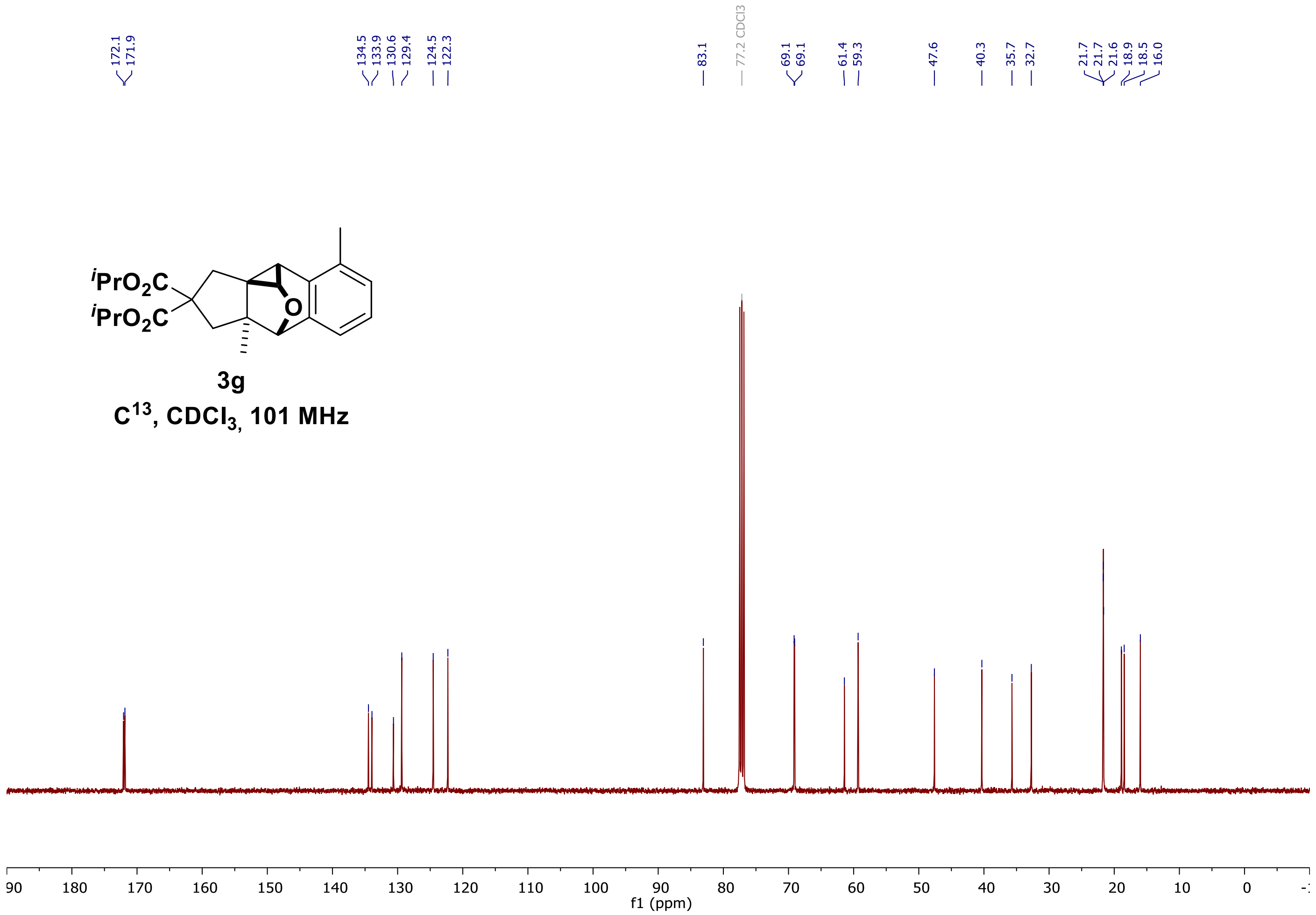


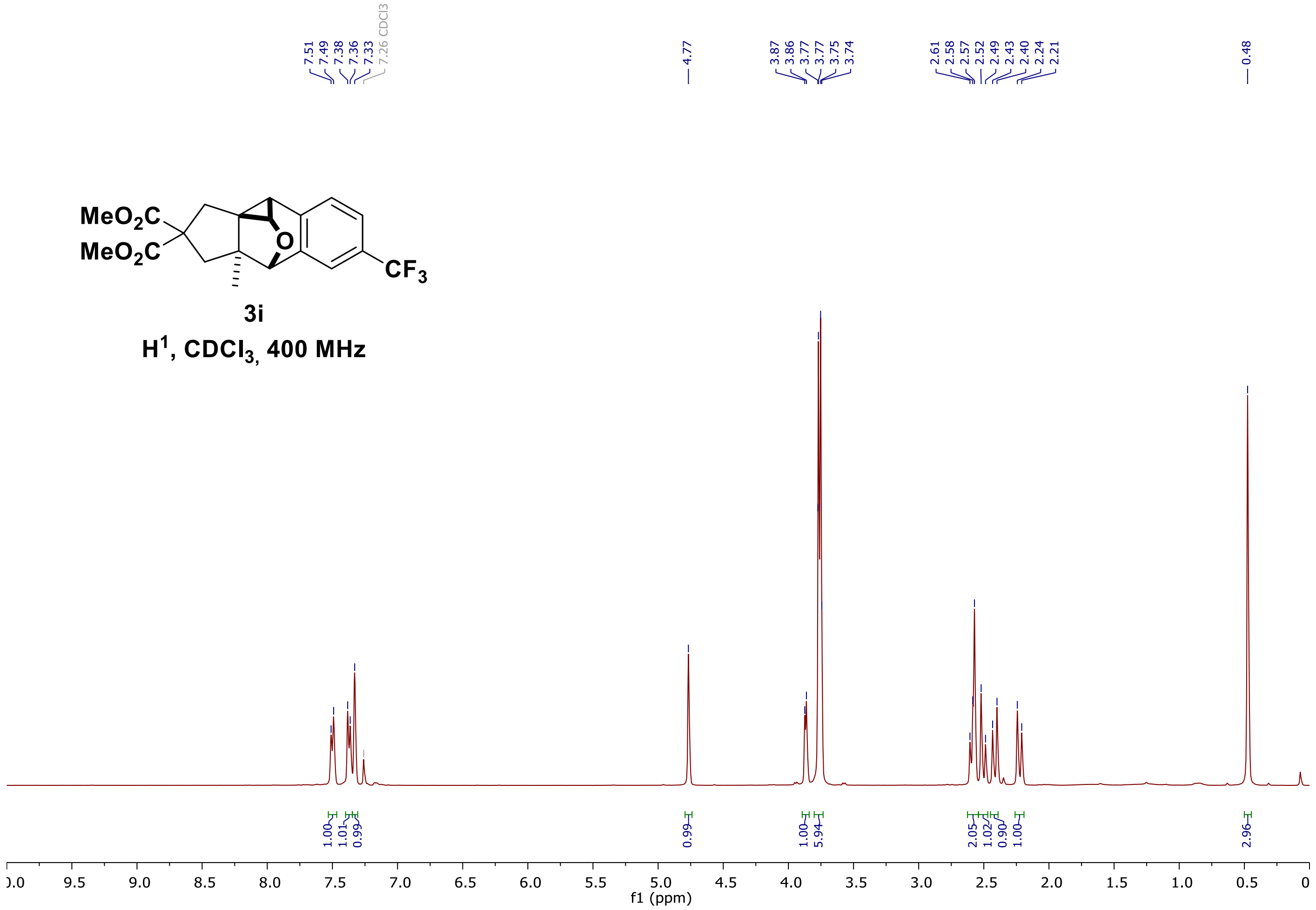
3f

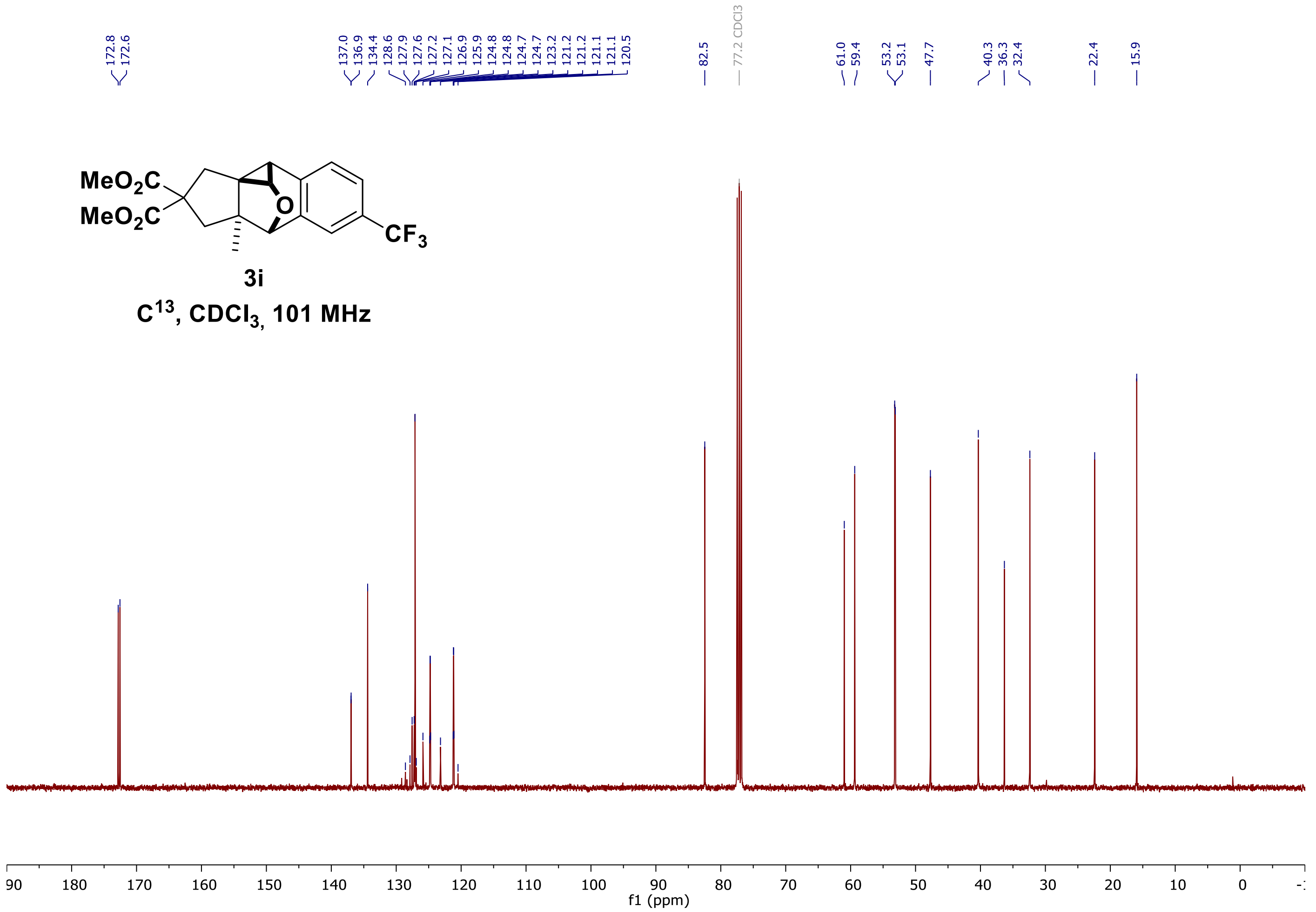
F^{19}, CDCl$_3$, 376 MHz

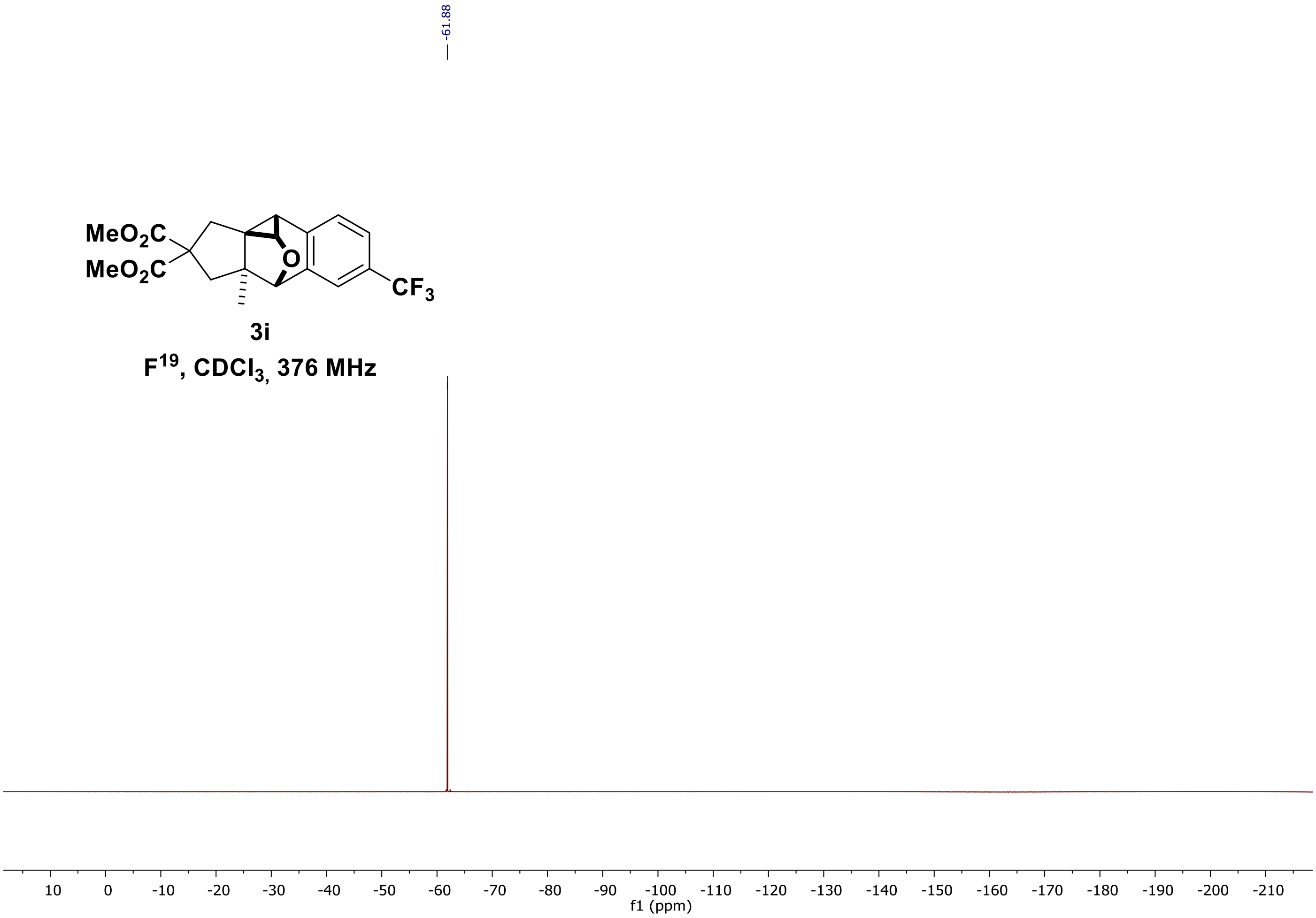



iPrO2C
iPrO2C
O
3g
H1, CDCl3, 400 MHz
7.26 CDCl3
7.11
7.10
7.09
7.08
7.05
7.03
7.02
6.91
6.90
6.89
6.88
5.10
5.08
5.08
5.07
5.07
5.05
5.05
5.04
5.03
5.02
4.67
3.81
3.79
2.61
2.59
2.55
2.52
2.48
2.44
2.37
2.37
2.33
2.19
2.16
1.27
1.25
1.25
1.24
1.23
1.22
0.47
1.03
1.03
1.00
2.06
0.98
0.98
1.01
2.15
4.15
1.01
12.34
2.93
f1 (ppm)


iPrO2C
iPrO2C
O
3g
C13, CDCl3, 101 MHz
172.1
171.9
134.5
133.9
130.6
129.4
124.5
122.3
83.1
77.2 CDCl3
69.1
69.1
61.4
59.3
47.6
40.3
35.7
32.7
21.7
21.7
21.6
18.9
18.5
16.0
f1 (ppm)


7.51
7.49
7.38
7.36
7.33
7.26 CDCl3
4.77
3.87
3.86
3.77
3.77
3.75
3.74
2.61
2.58
2.57
2.52
2.49
2.43
2.40
2.24
2.21
0.48
MeO2C
MeO2C
O
CF3
3i
H1, CDCl3, 400 MHz
1.00
1.01
0.99
0.99
1.00
5.94
2.05
1.02
0.90
1.00
2.96
f1 (ppm)


172.8
172.6
137.0
136.9
134.4
128.6
127.9
127.6
127.2
127.1
126.9
125.9
124.8
124.8
124.7
124.7
123.2
121.2
121.2
121.1
121.1
120.5
82.5
77.2 CDCl3
61.0
59.4
53.2
53.1
47.7
40.3
36.3
32.4
22.4
15.9
MeO2C
MeO2C
O
CF3
3i
C13, CDCl3, 101 MHz
f1 (ppm)

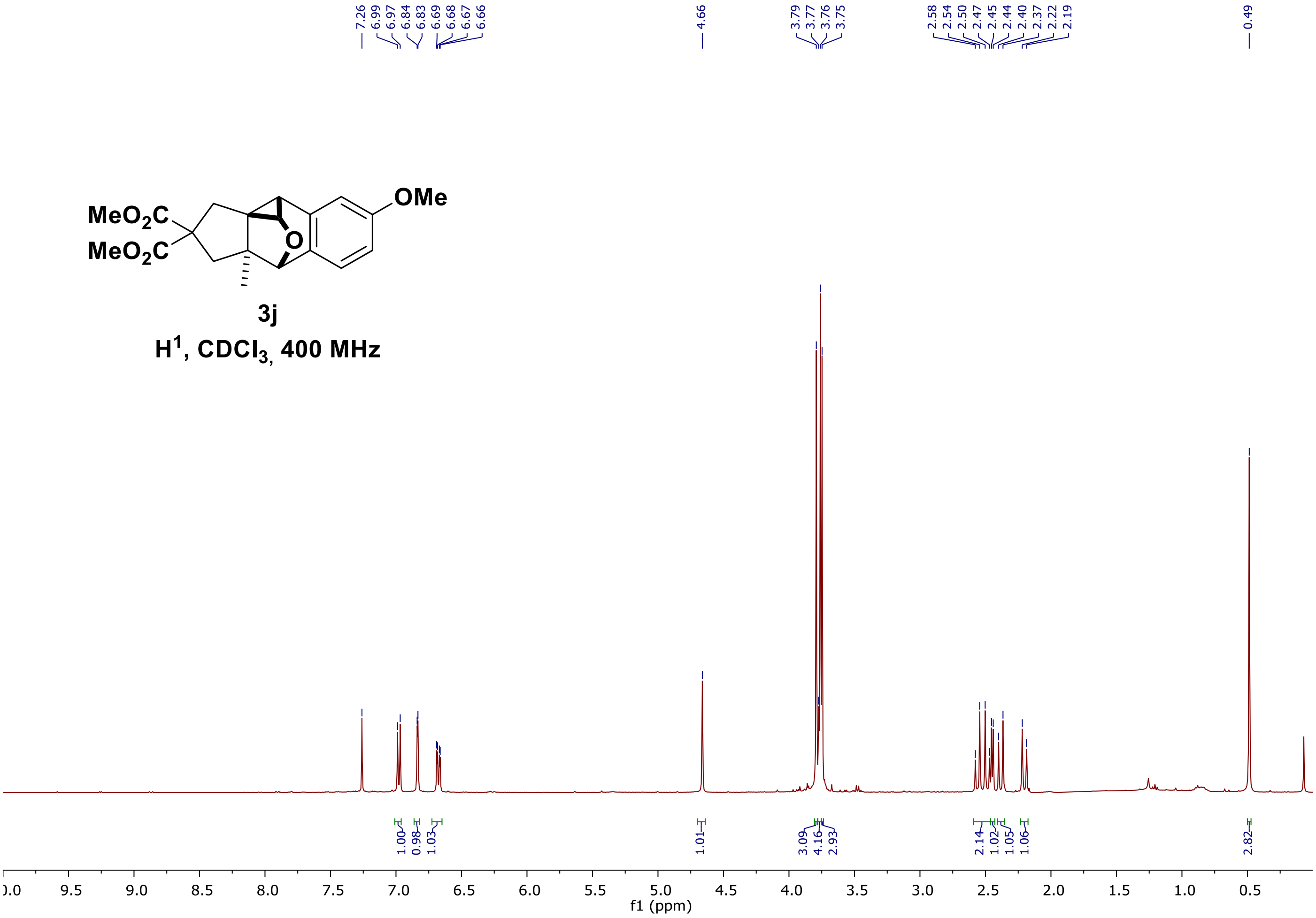


3i

F[19], $CDCl_3$, 376 MHz

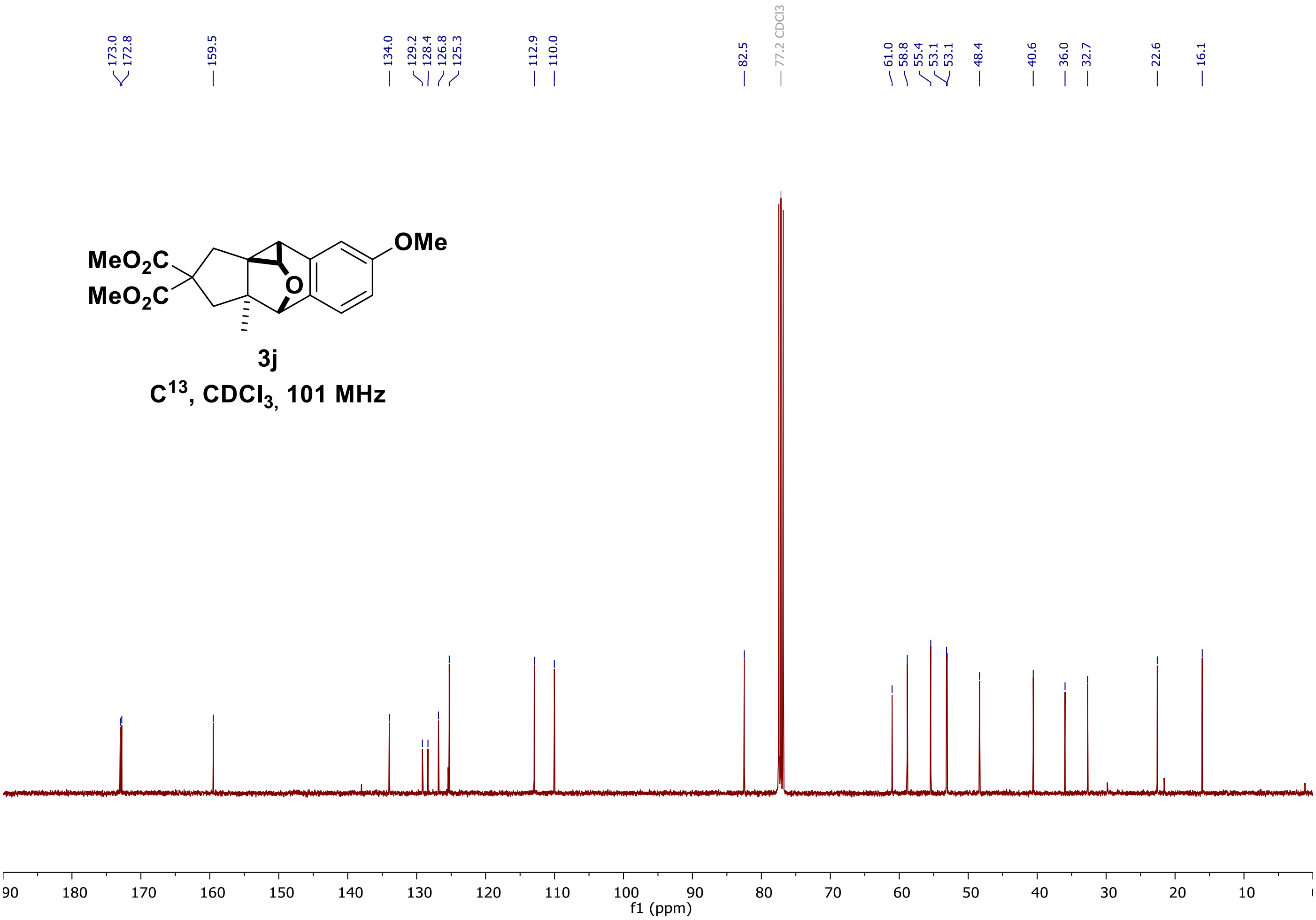
3j

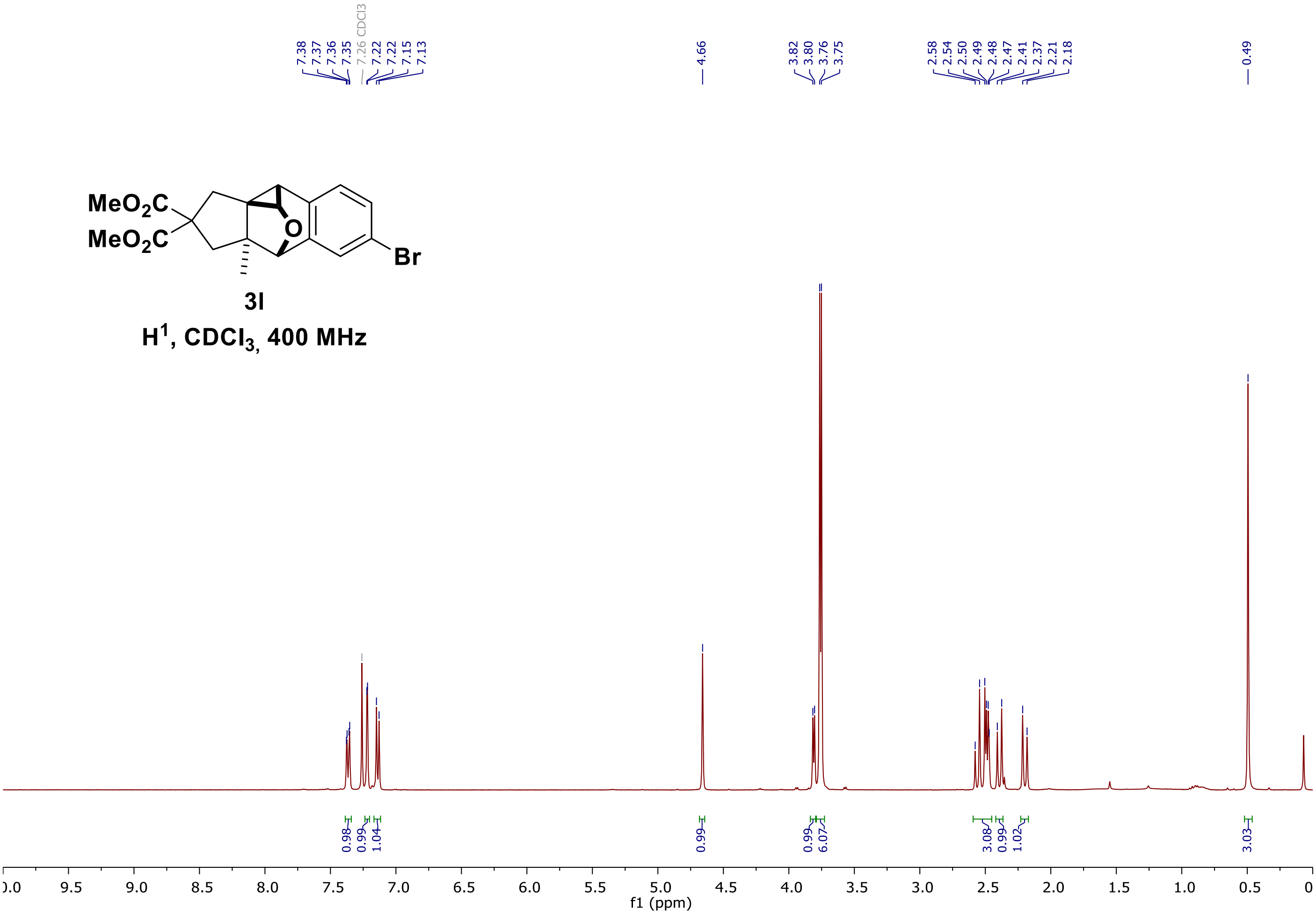
H[1], $CDCl_3$, 400 MHz

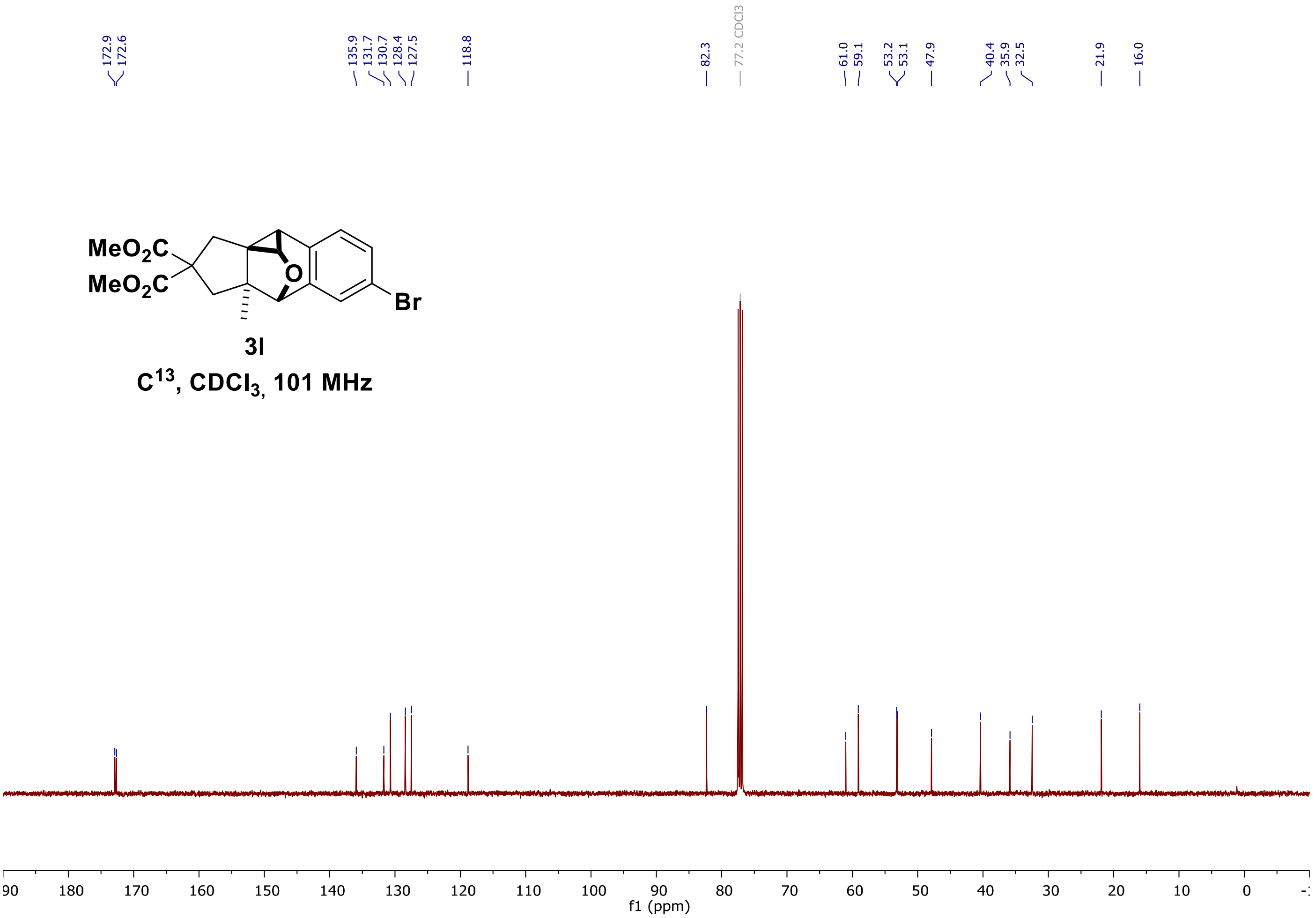


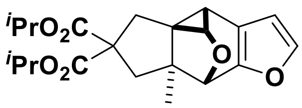
3j

C[13], $CDCl_3$, 101 MHz



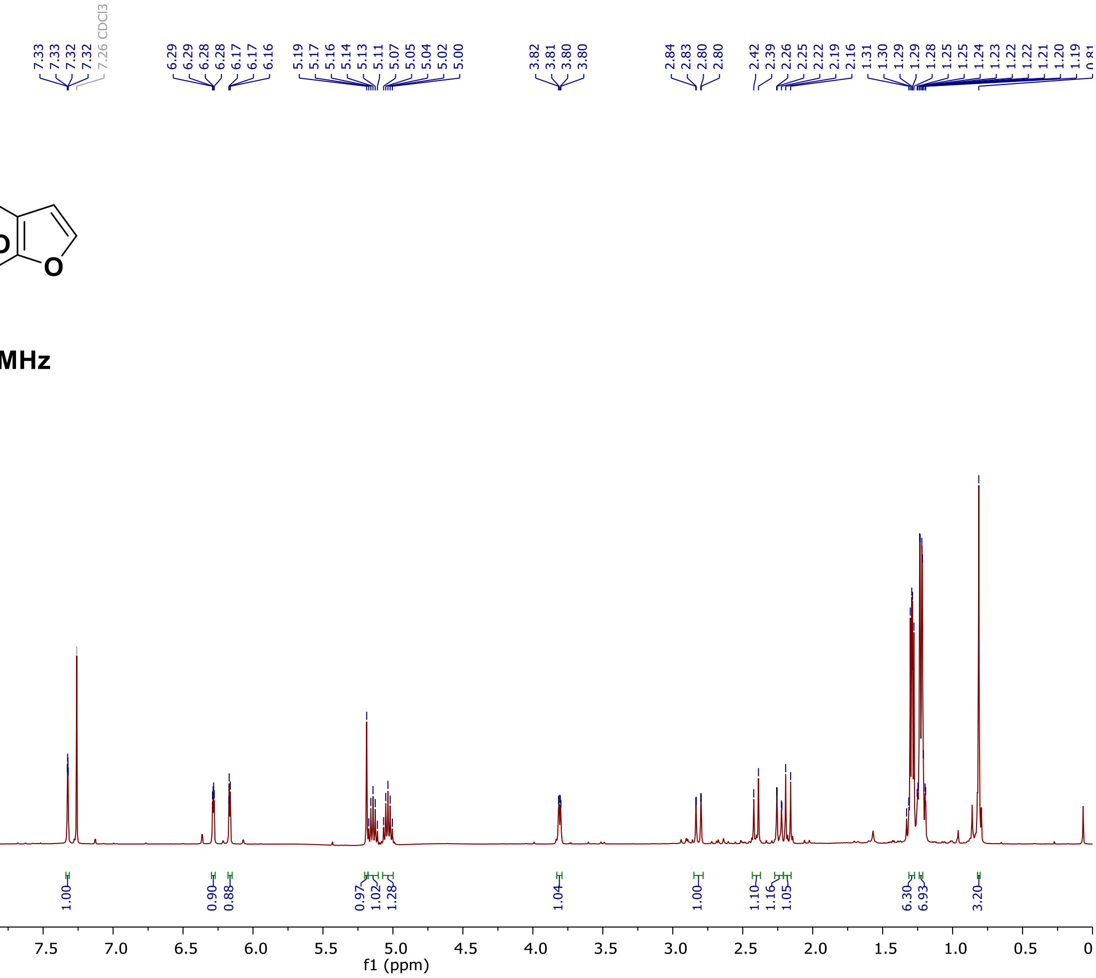

7.38
7.37
7.36
7.35
7.26 CDCl3
7.22
7.22
7.22
7.15
7.13
4.66
3.82
3.80
3.76
3.75
2.58
2.54
2.50
2.49
2.48
2.47
2.41
2.37
2.21
2.18
0.49
MeO2C
MeO2C
O
Br
3l
H1, CDCl3, 400 MHz
0.98
0.99
1.04
0.99
0.99
6.07
3.08
0.99
1.02
3.03
f1 (ppm)

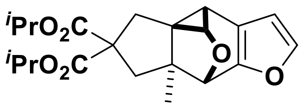

172.9
172.6
135.9
131.7
130.7
128.4
127.5
118.8
82.3
77.2 CDCl3
61.0
59.1
53.2
53.1
47.9
40.4
35.9
32.5
21.9
16.0
MeO2C
MeO2C
O
Br
3l
C13, CDCl3, 101 MHz
f1 (ppm)



3n

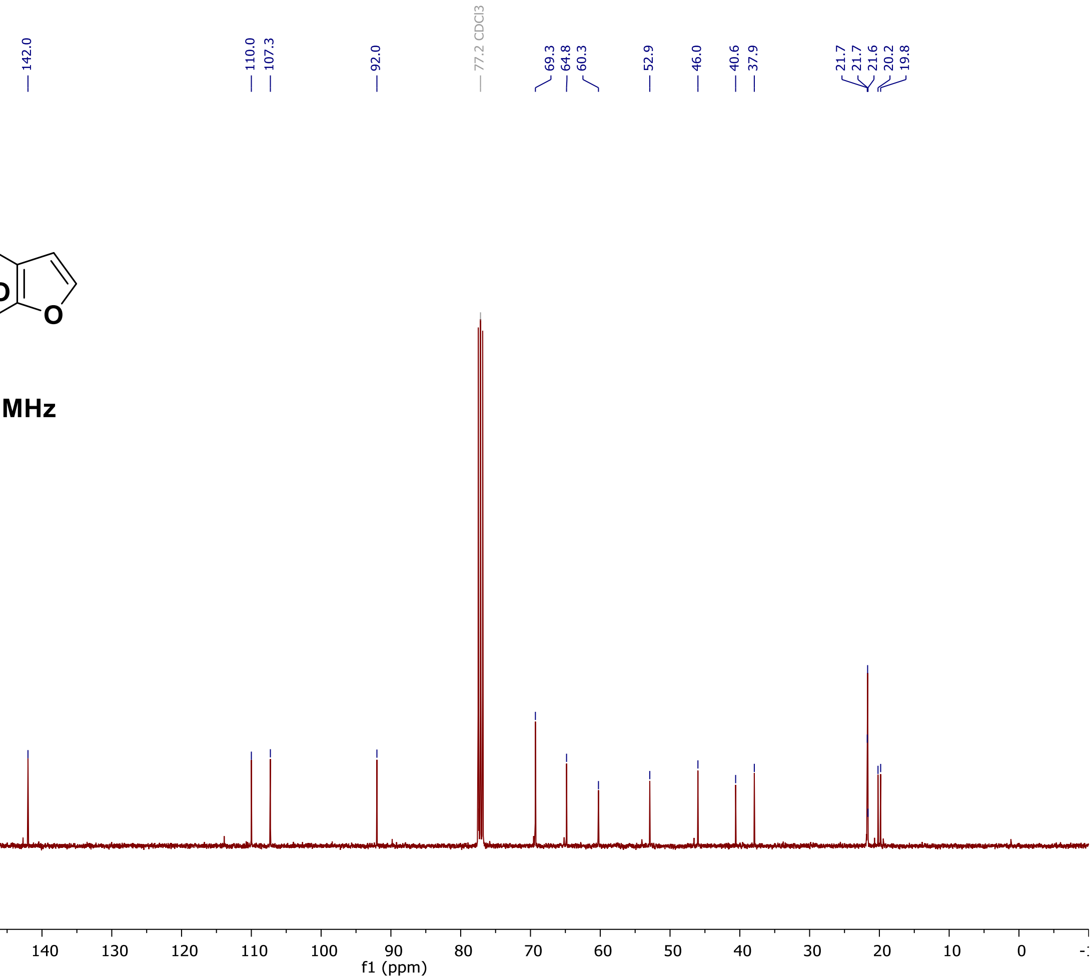
H^1, $CDCl_3$, 400 MHz

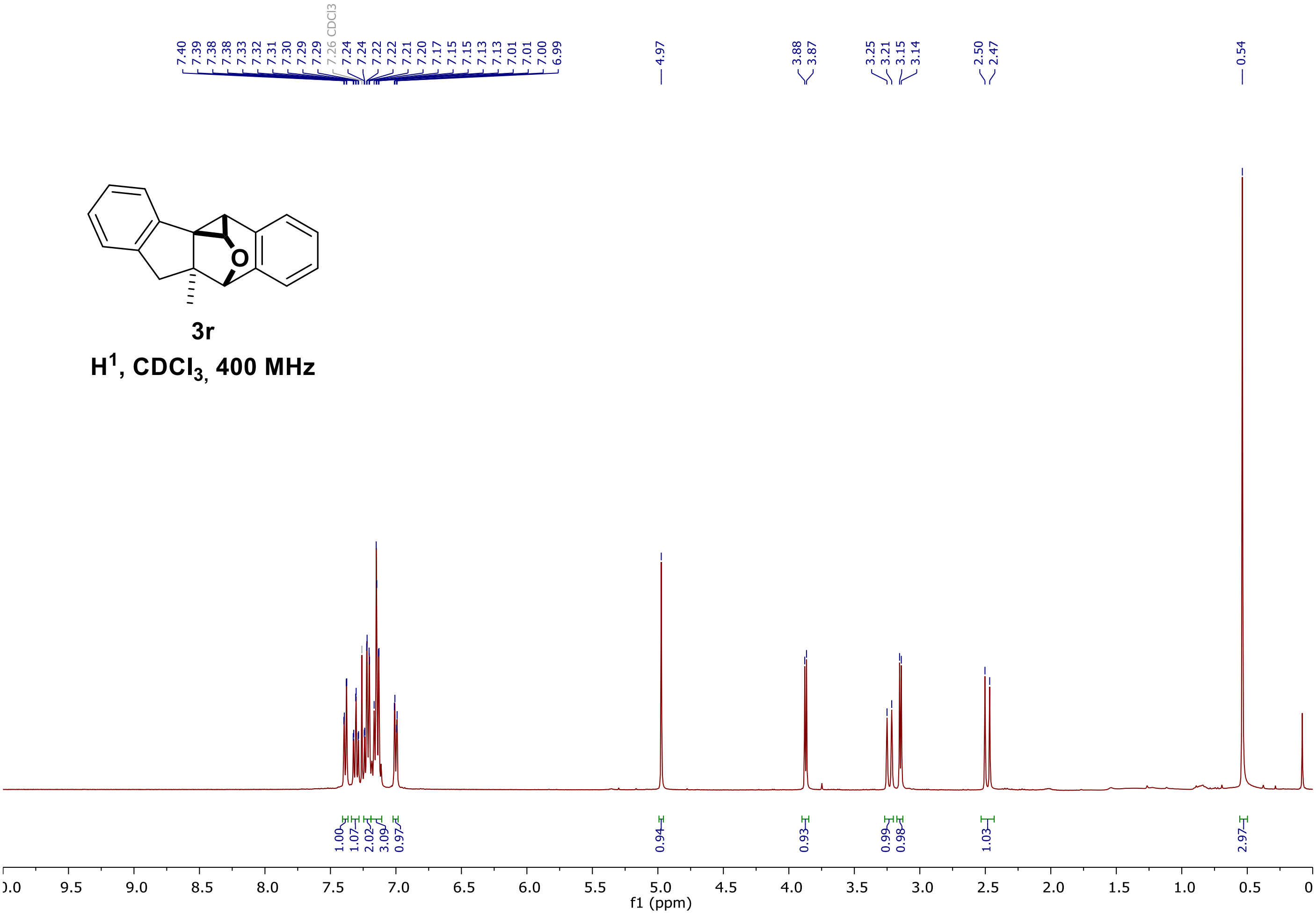


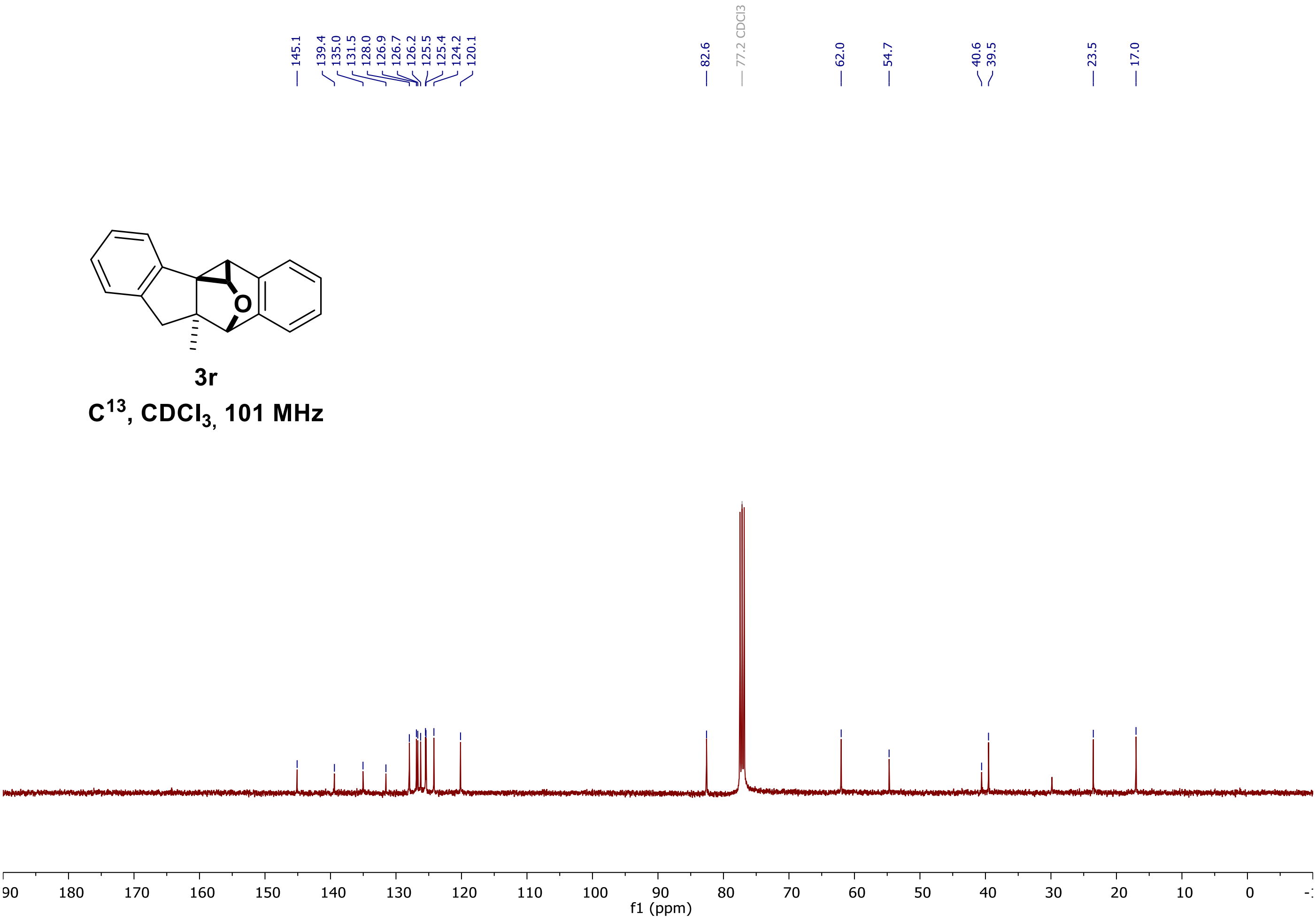


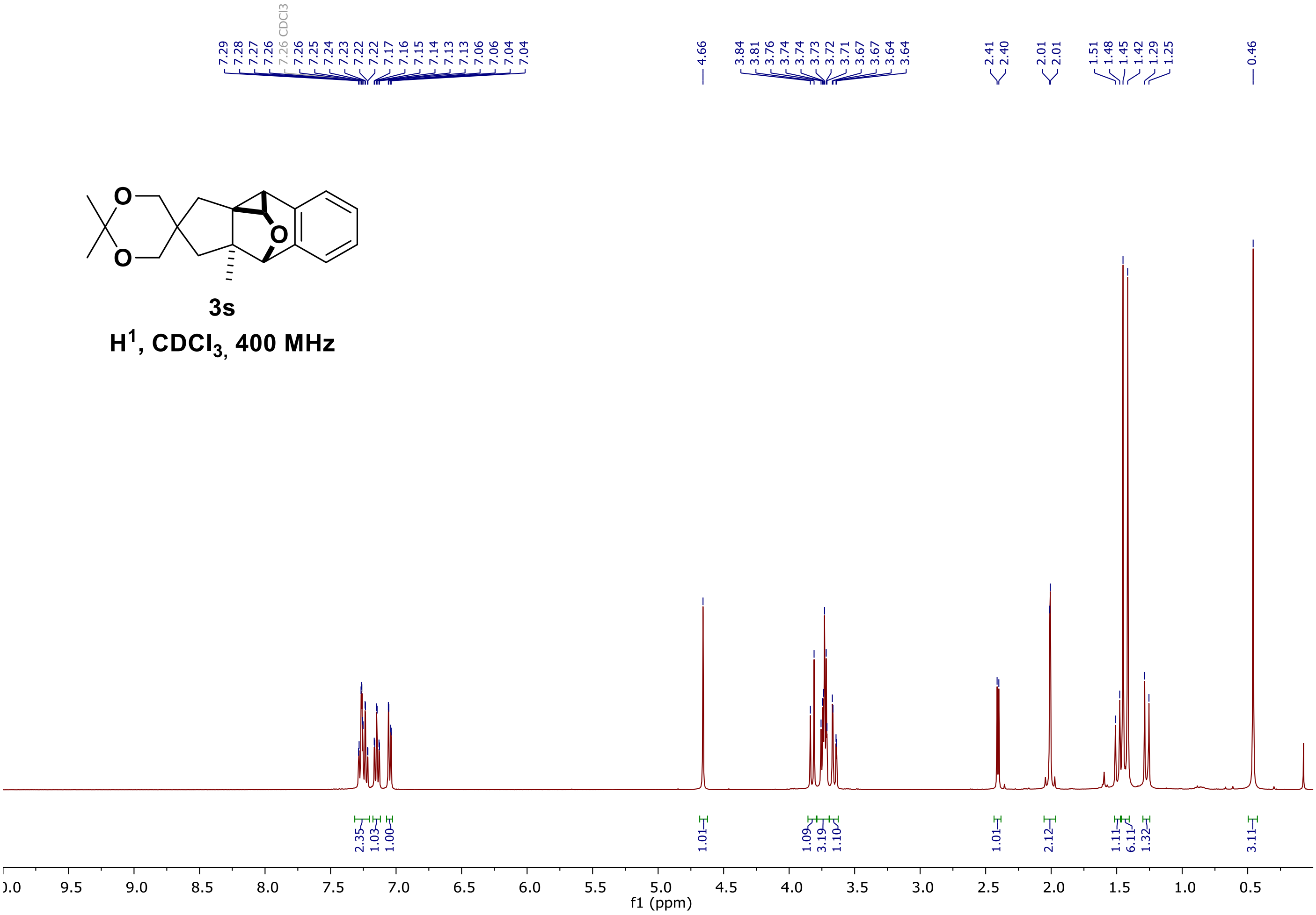
3n

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



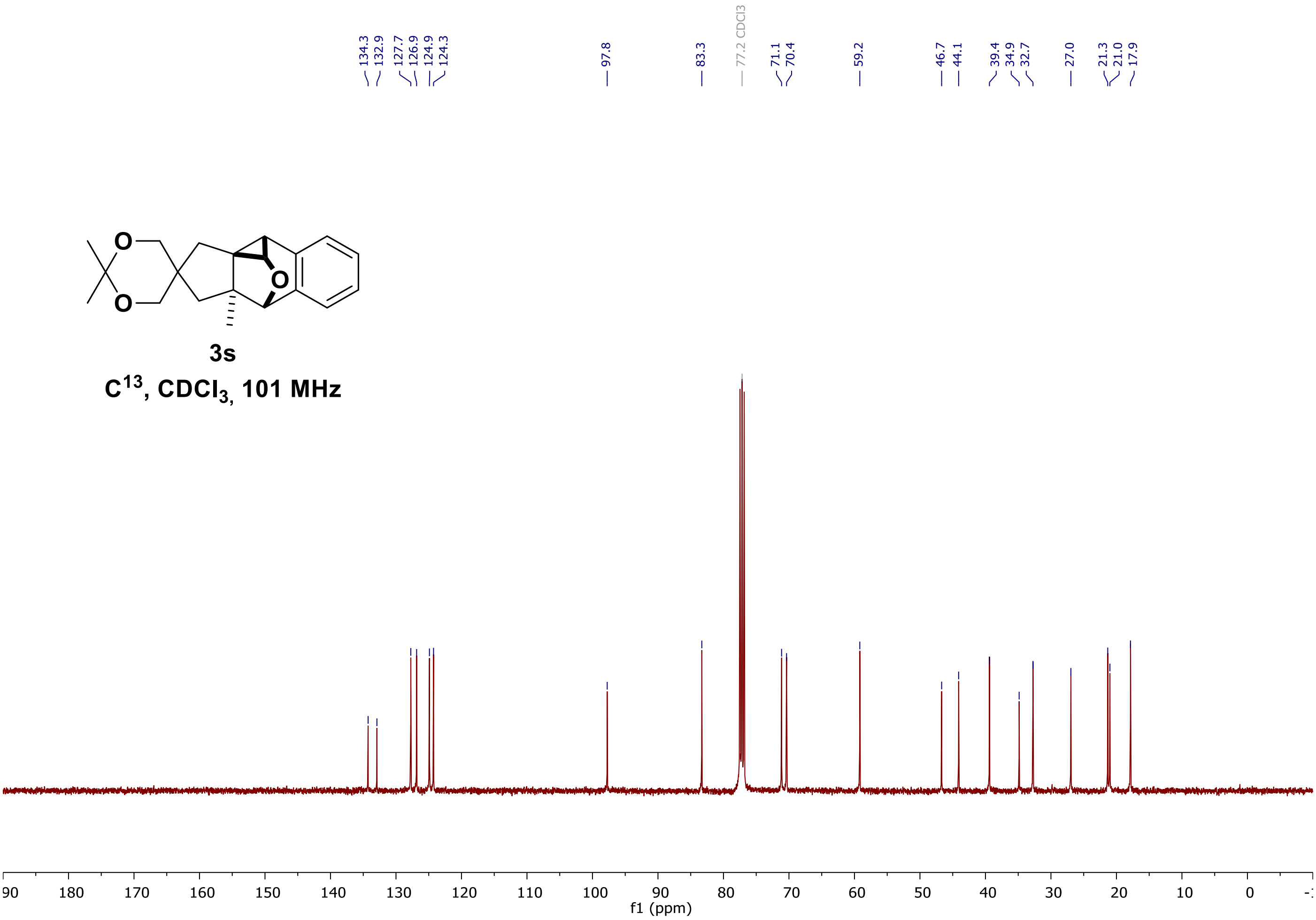

7.40 7.39 7.38 7.33 7.32 7.31 7.30 7.29 7.29 7.26 CDCl3 7.24 7.24 7.22 7.22 7.21 7.20 7.17 7.15 7.15 7.13 7.13 7.01 7.01 7.00 6.99
4.97
3.88 3.87
3.25 3.21 3.15 3.14
2.50 2.47
0.54
3r
H1, CDCl3, 400 MHz
1.00 1.07 2.02 3.09 0.97
0.94
0.93
0.99 0.98
1.03
2.97
f1 (ppm)


145.1 139.4 135.0 131.5 128.0 126.9 126.7 126.2 125.5 125.4 124.2 120.1
82.6
77.2 CDCl3
62.0
54.7
40.6 39.5
23.5
17.0
3r
C13, CDCl3, 101 MHz
f1 (ppm)



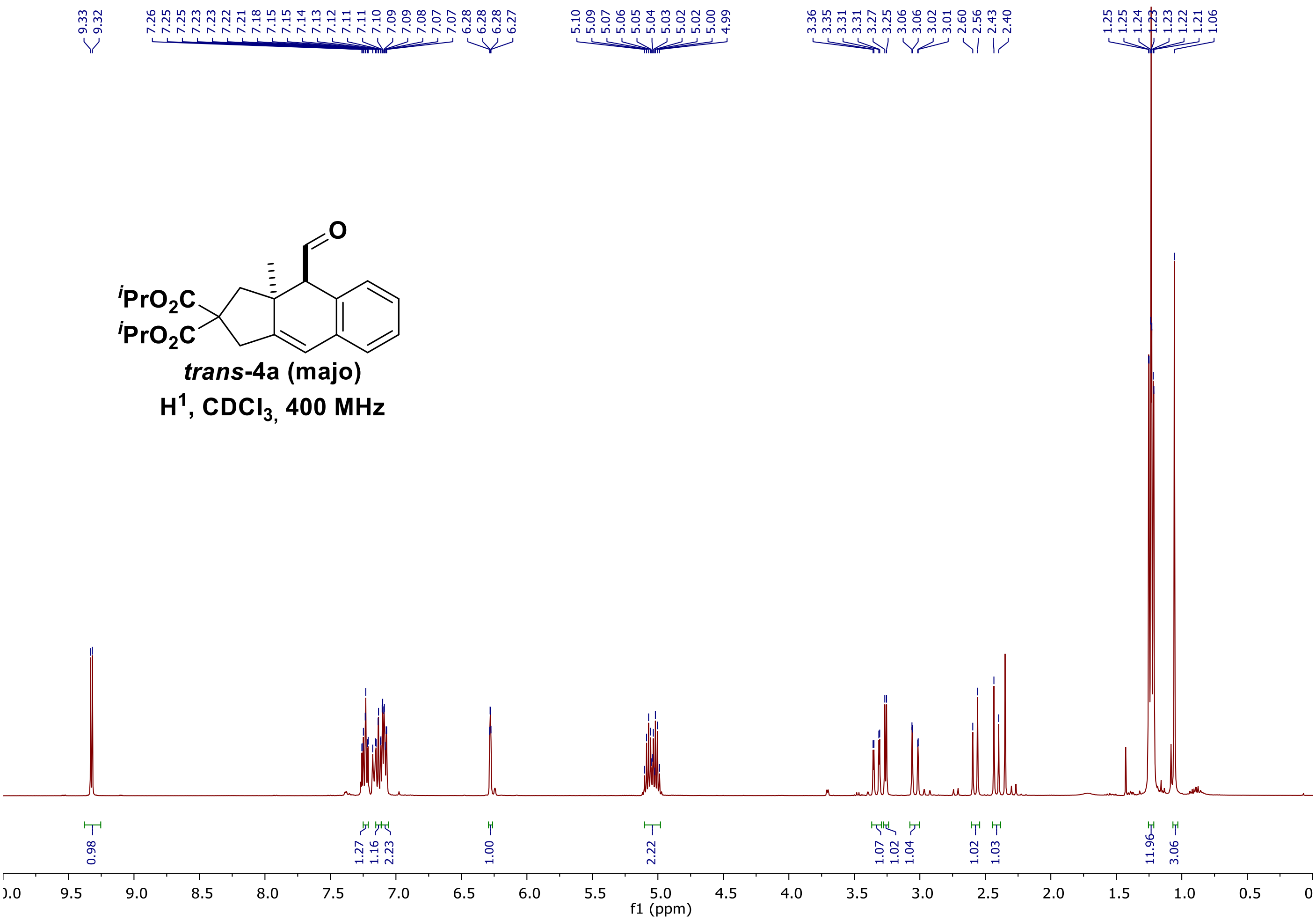
3s

H[1], CDCl$_3$, 400 MHz

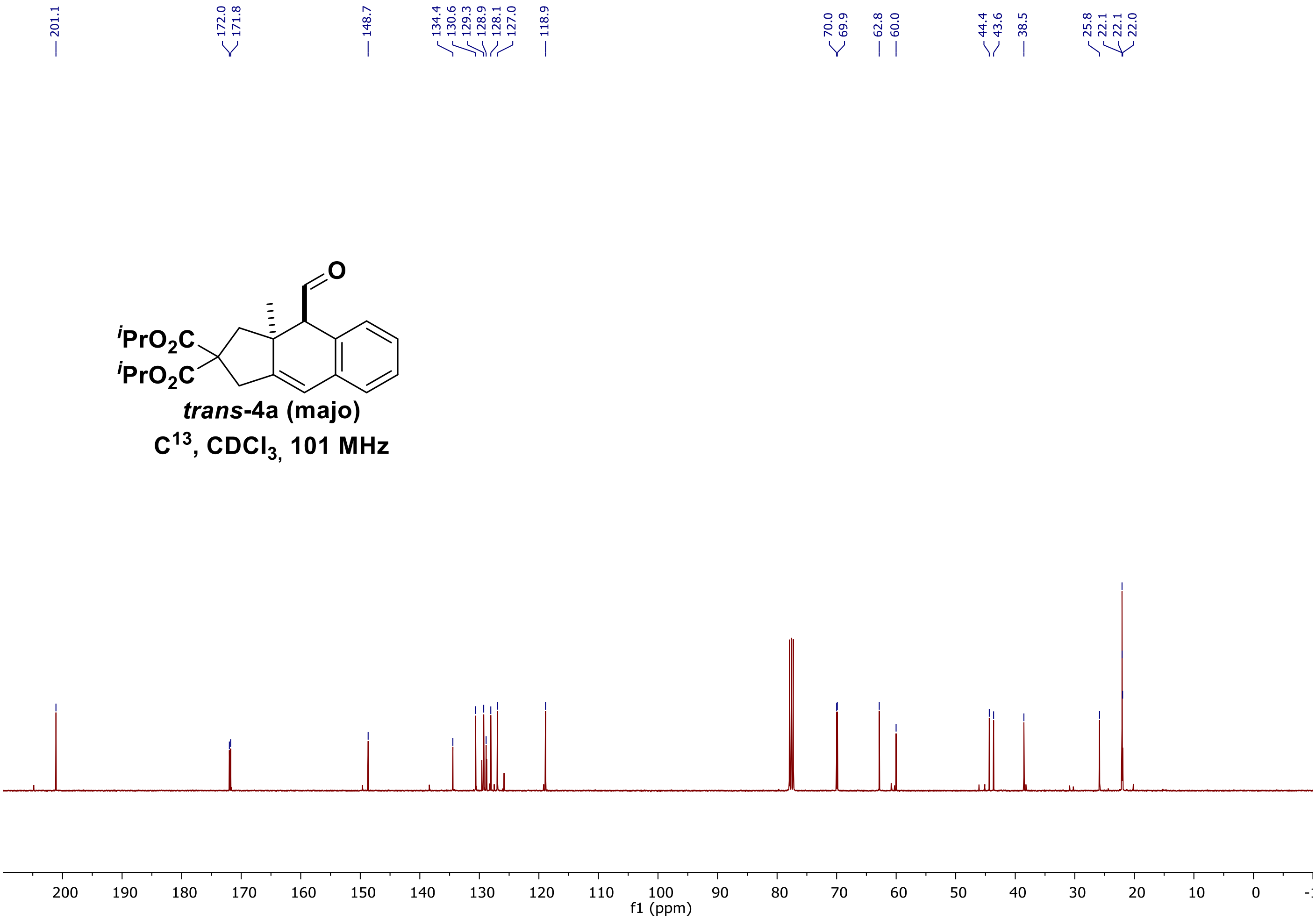


3s

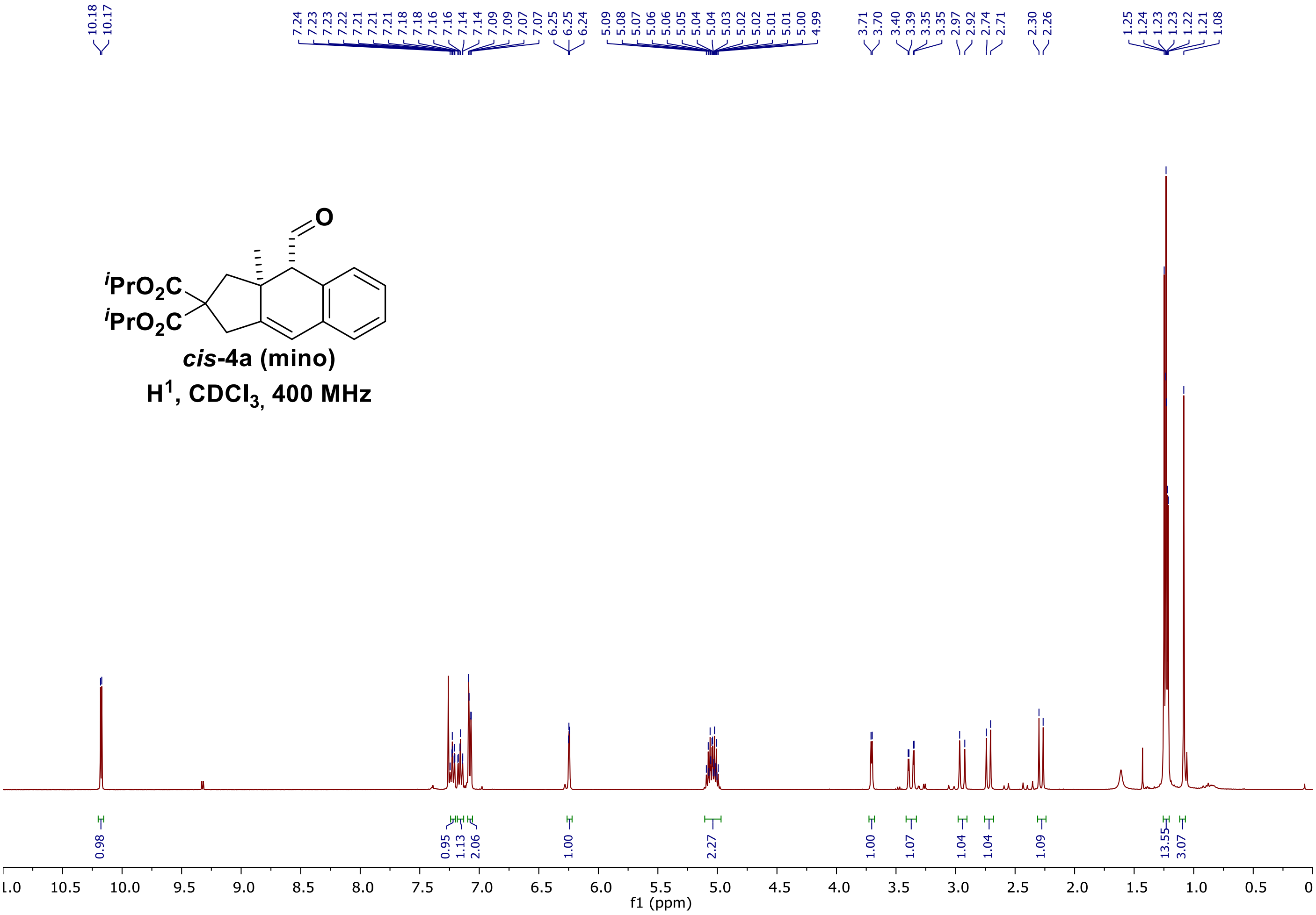
C[13], CDCl$_3$, 101 MHz

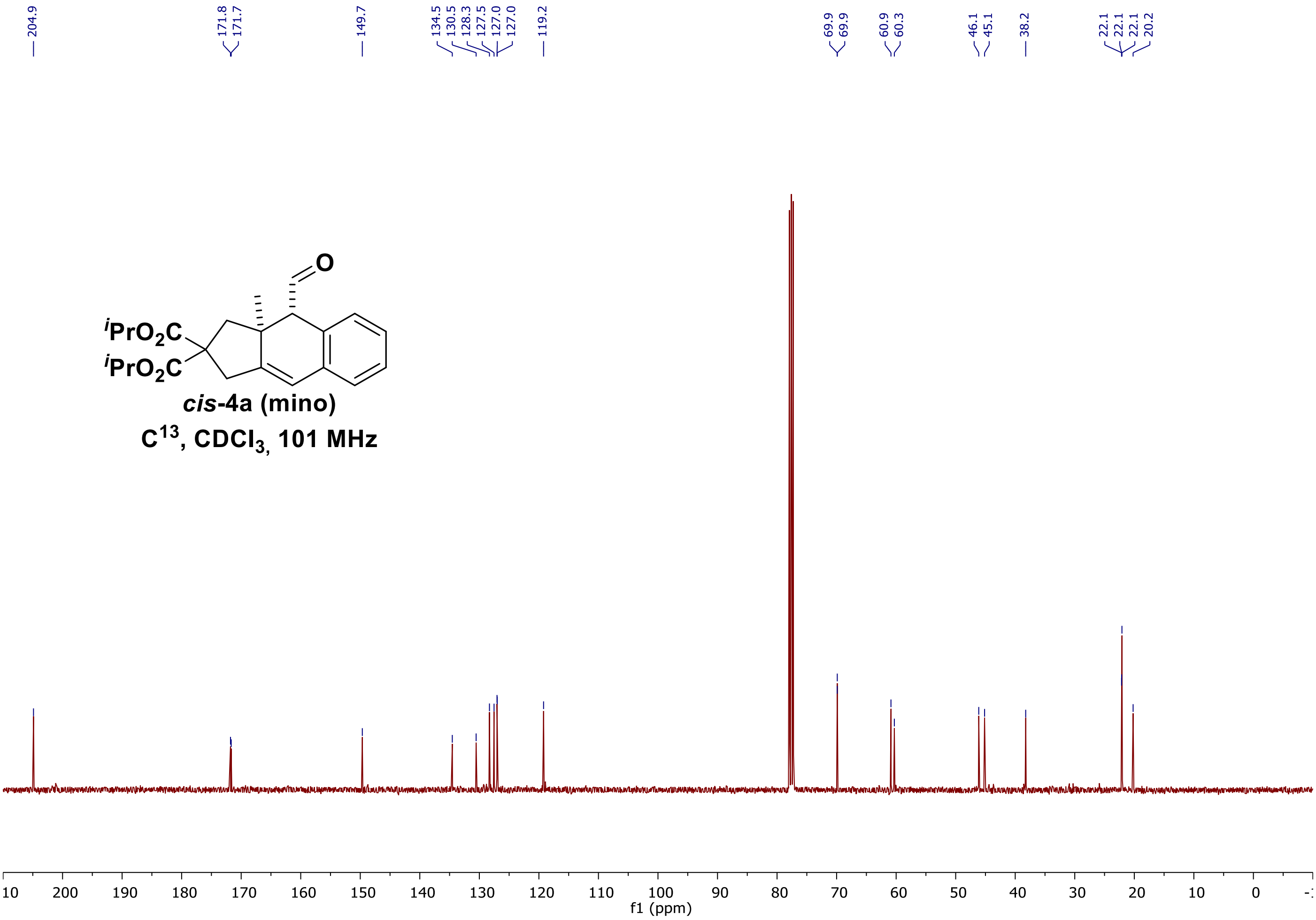


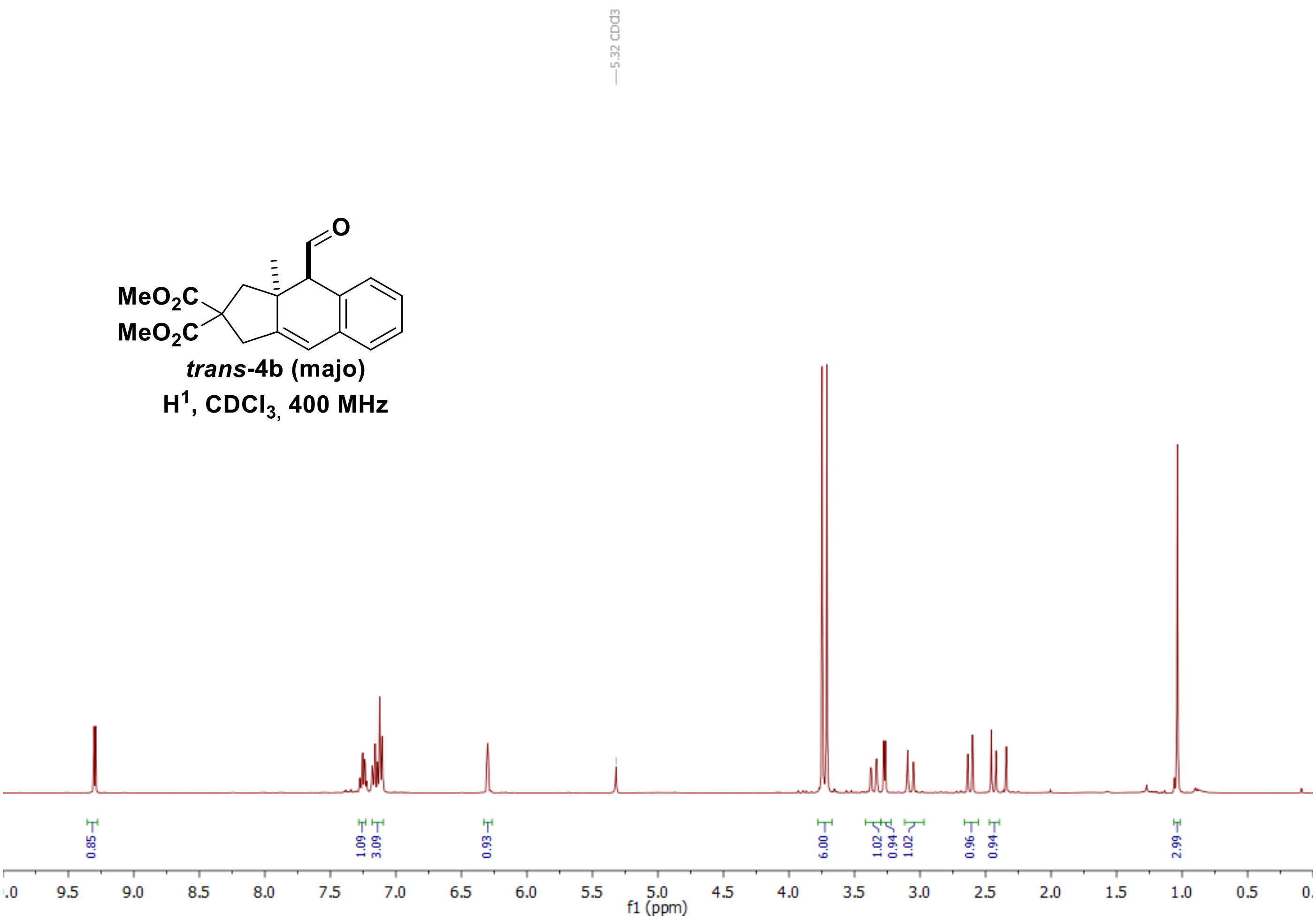
^{i}PrO$_2$C
^{i}PrO$_2$C
O
trans-4a (majo)
H^1, CDCl$_3$, 400 MHz
f1 (ppm)

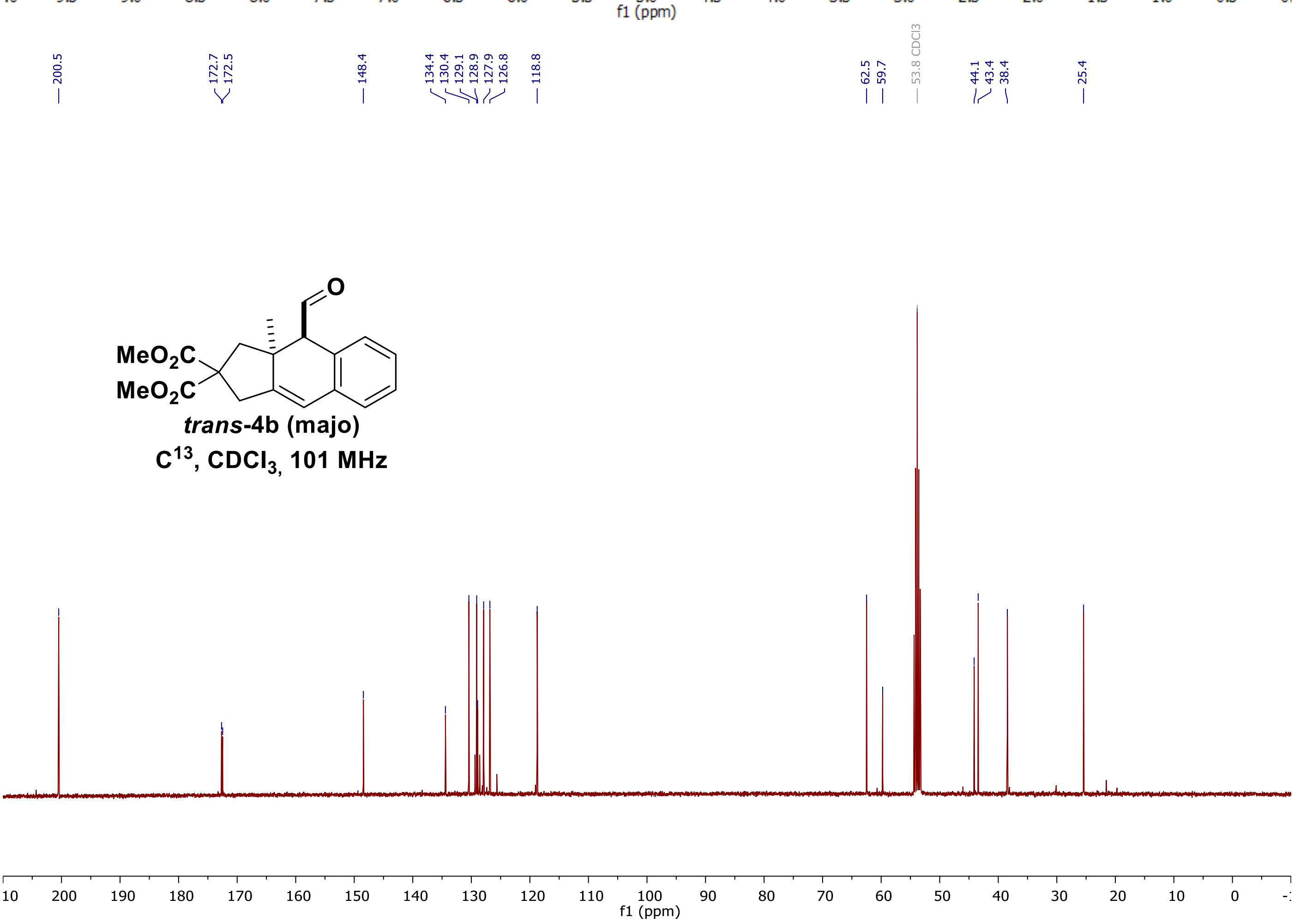


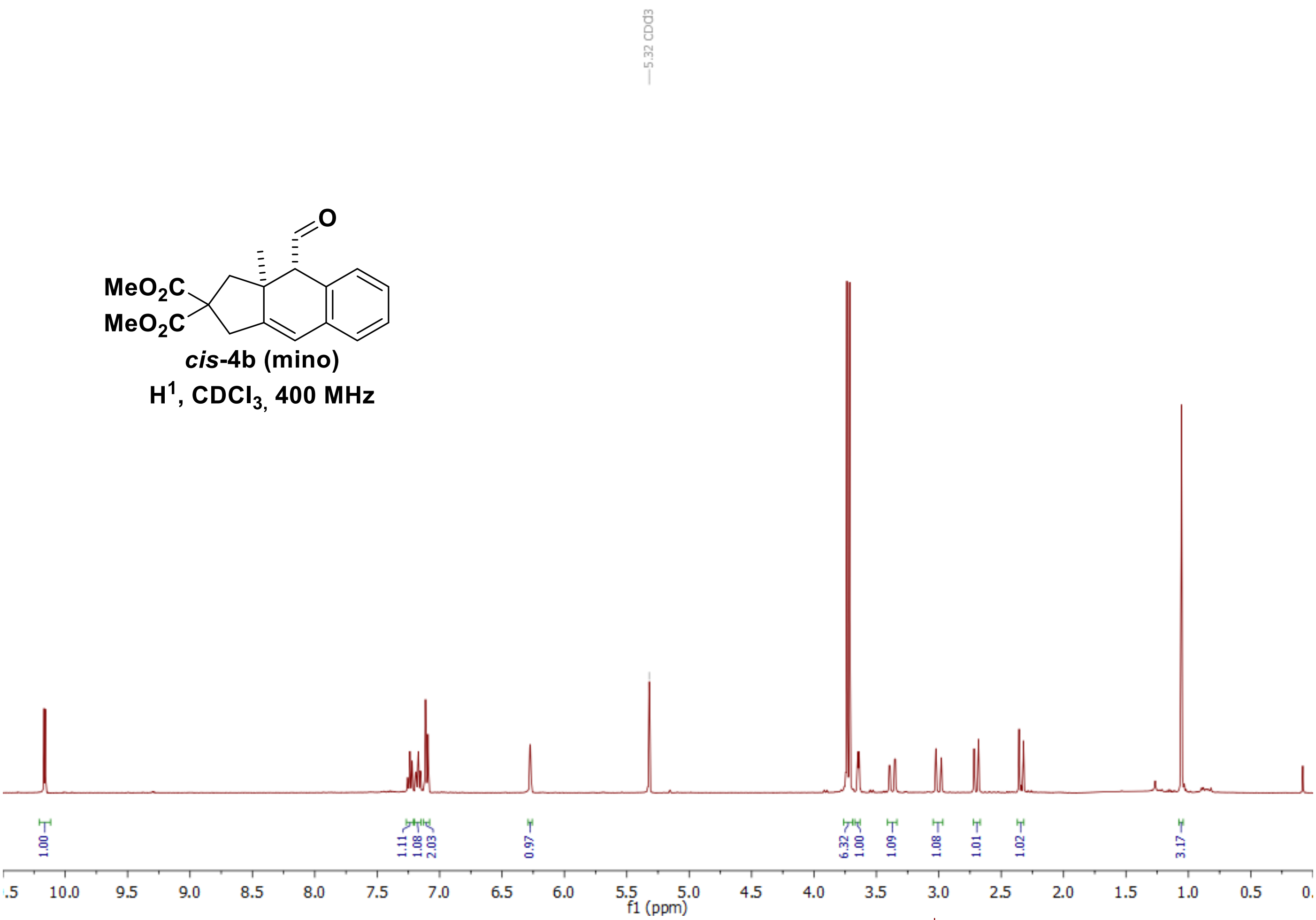
^{i}PrO$_2$C
^{i}PrO$_2$C
O
trans-4a (majo)
C^{13}, CDCl$_3$, 101 MHz
f1 (ppm)


10.18
10.17
7.24 7.23 7.23 7.22 7.21 7.21 7.21 7.18 7.18 7.16 7.16 7.14 7.14 7.09 7.09 7.07 7.07 6.25 6.25 6.24
5.09 5.08 5.07 5.06 5.06 5.05 5.04 5.04 5.03 5.02 5.02 5.01 5.01 5.00 4.99
3.71 3.70 3.40 3.39 3.35 3.35 2.97 2.92 2.74 2.71 2.30 2.26
1.25 1.24 1.23 1.23 1.22 1.21 1.08
$^{i}PrO_2C$
$^{i}PrO_2C$
O
cis-4a (mino)
H^1, $CDCl_3$, 400 MHz
0.98
0.95 1.13 2.06
1.00
2.27
1.00
1.07
1.04
1.04
1.09
13.55
3.07
f1 (ppm)

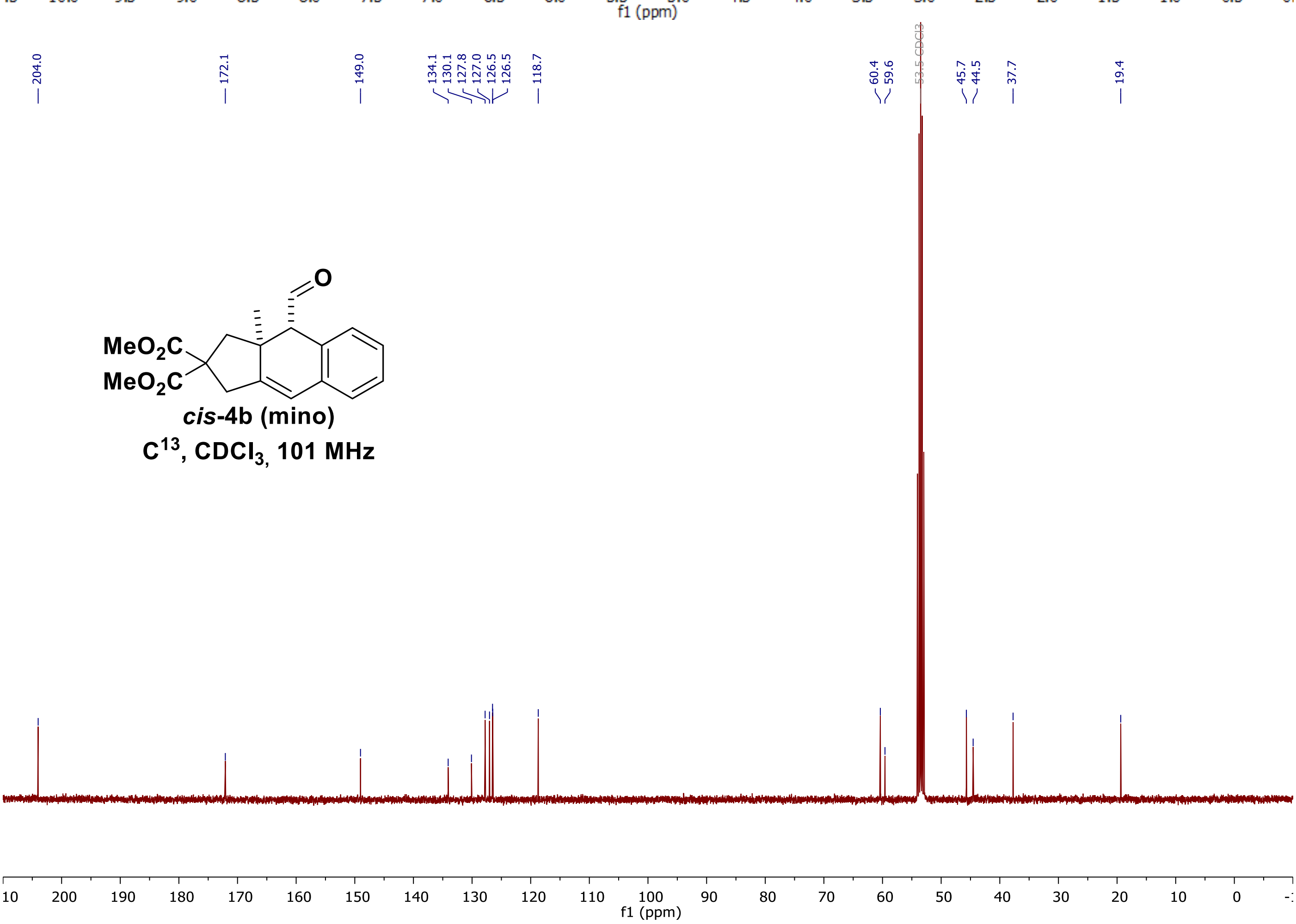

204.9
171.8 171.7
149.7
134.5 130.5 128.3 127.5 127.0 127.0
119.2
69.9 69.9
60.9 60.3
46.1 45.1
38.2
22.1 22.1 22.1 20.2
$^{i}PrO_2C$
$^{i}PrO_2C$
O
cis-4a (mino)
C^{13}, $CDCl_3$, 101 MHz
f1 (ppm)


MeO2C
MeO2C
O
trans-4b (majo)
H1, CDCl3, 400 MHz
5.32 CDCl3
0.85
1.09
3.09
0.93
6.00
1.02
0.94
1.02
0.96
0.94
2.99
f1 (ppm)

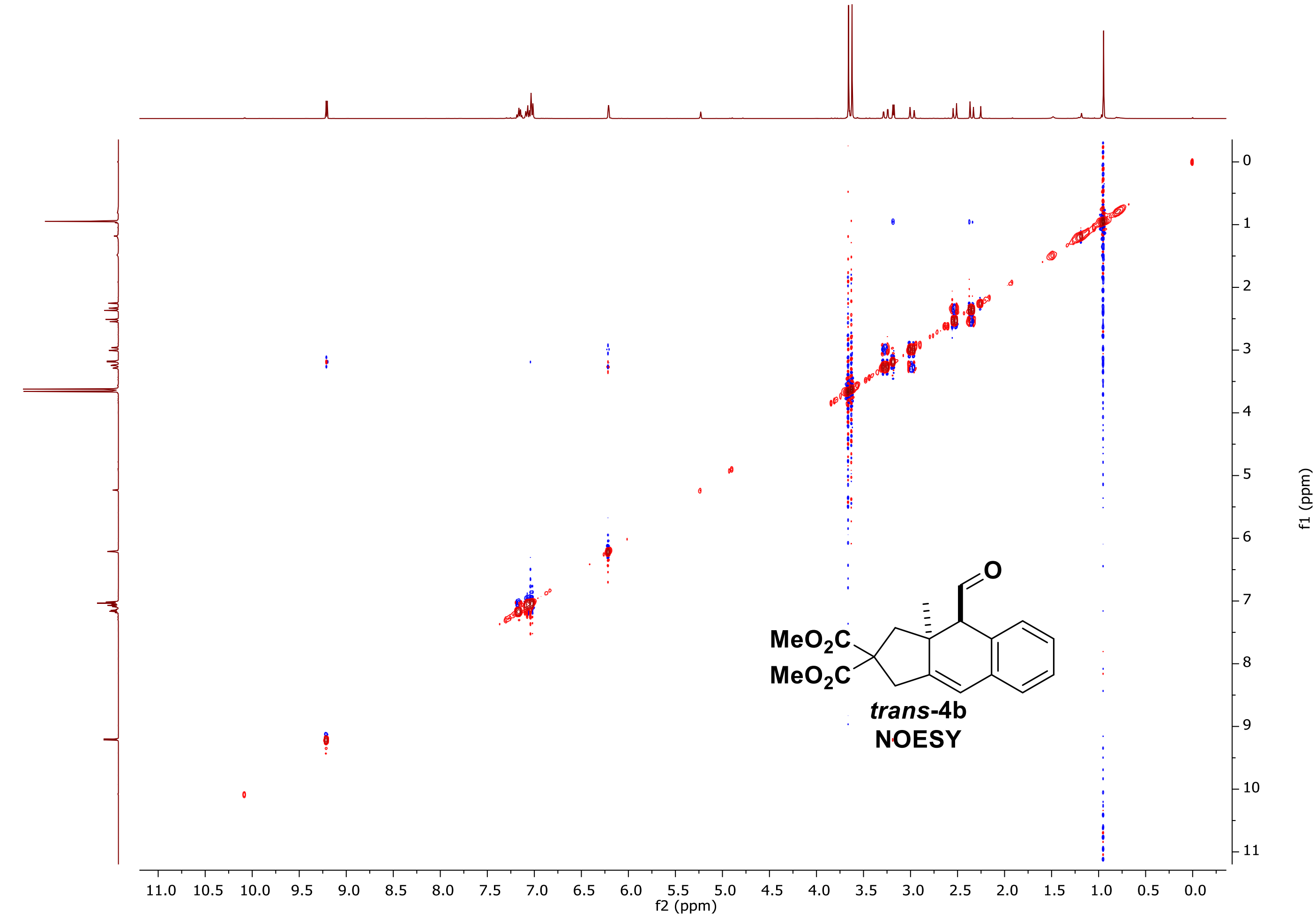

200.5
172.7
172.5
148.4
134.4
130.4
129.1
128.9
127.9
126.8
118.8
62.5
59.7
53.8 CDCl3
44.1
43.4
38.4
25.4
MeO2C
MeO2C
O
trans-4b (majo)
C13, CDCl3, 101 MHz
f1 (ppm)



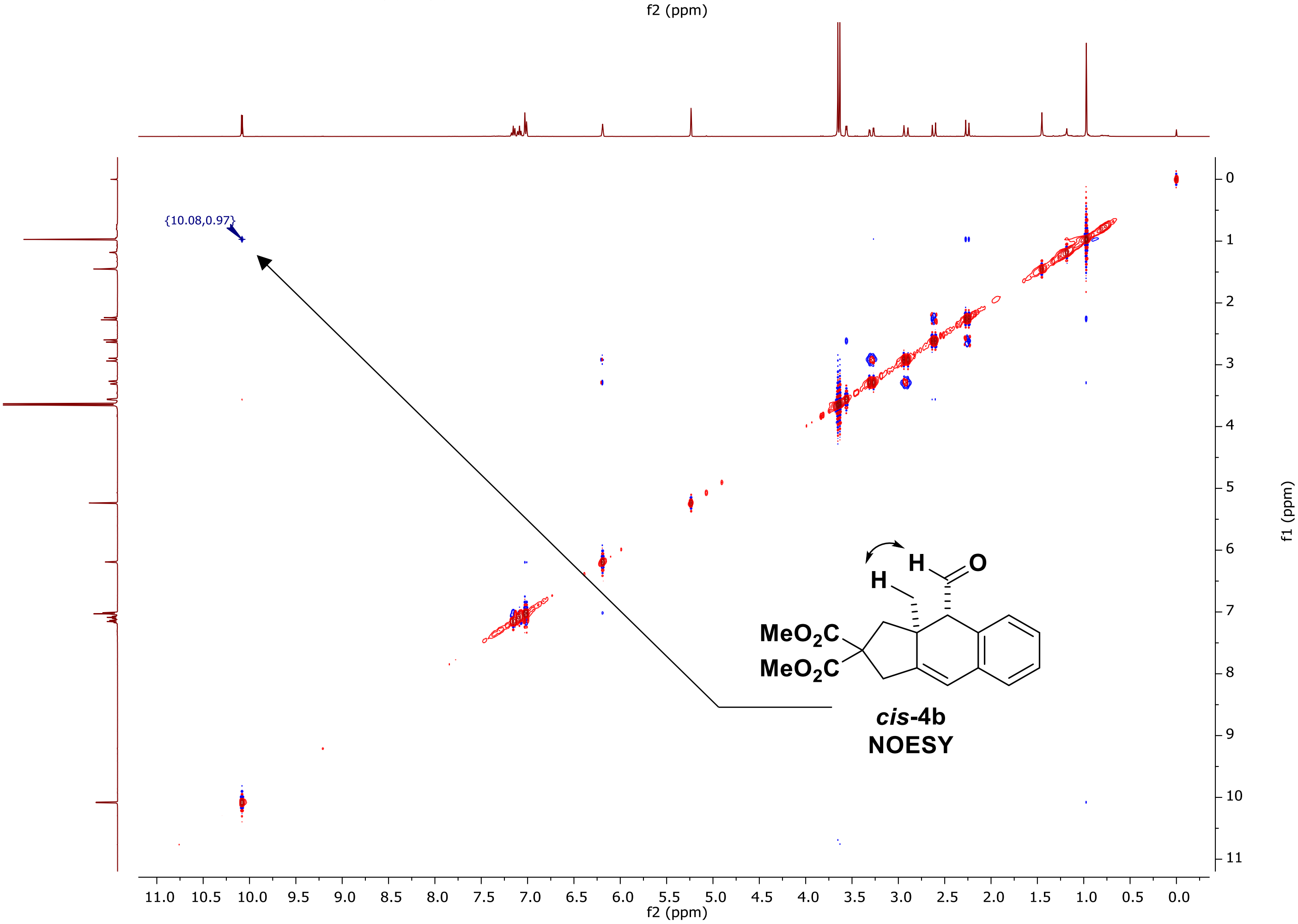
MeO2C
MeO2C
O
cis-4b (mino)
H1, CDCl3, 400 MHz
5.32 CDCl3
1.00
1.11
1.08
2.03
0.97
6.32
1.00
1.09
1.08
1.01
1.02
3.17
f1 (ppm)



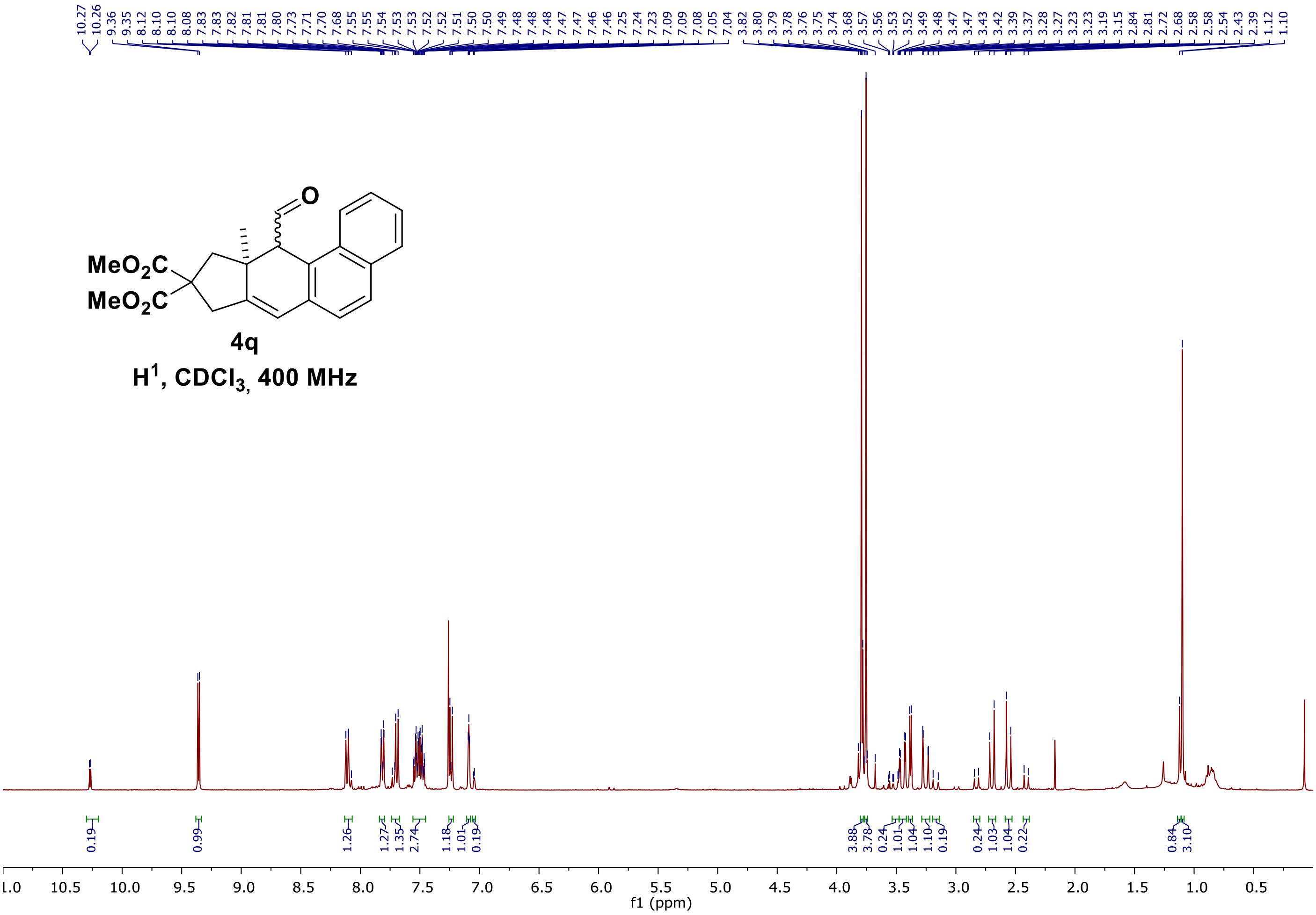
204.0
172.1
149.0
134.1
130.1
127.8
127.0
126.5
126.5
118.7
60.4
59.6
53.5 CDCl3
45.7
44.5
37.7
19.4
MeO2C
MeO2C
O
cis-4b (mino)
C13, CDCl3, 101 MHz
f1 (ppm)

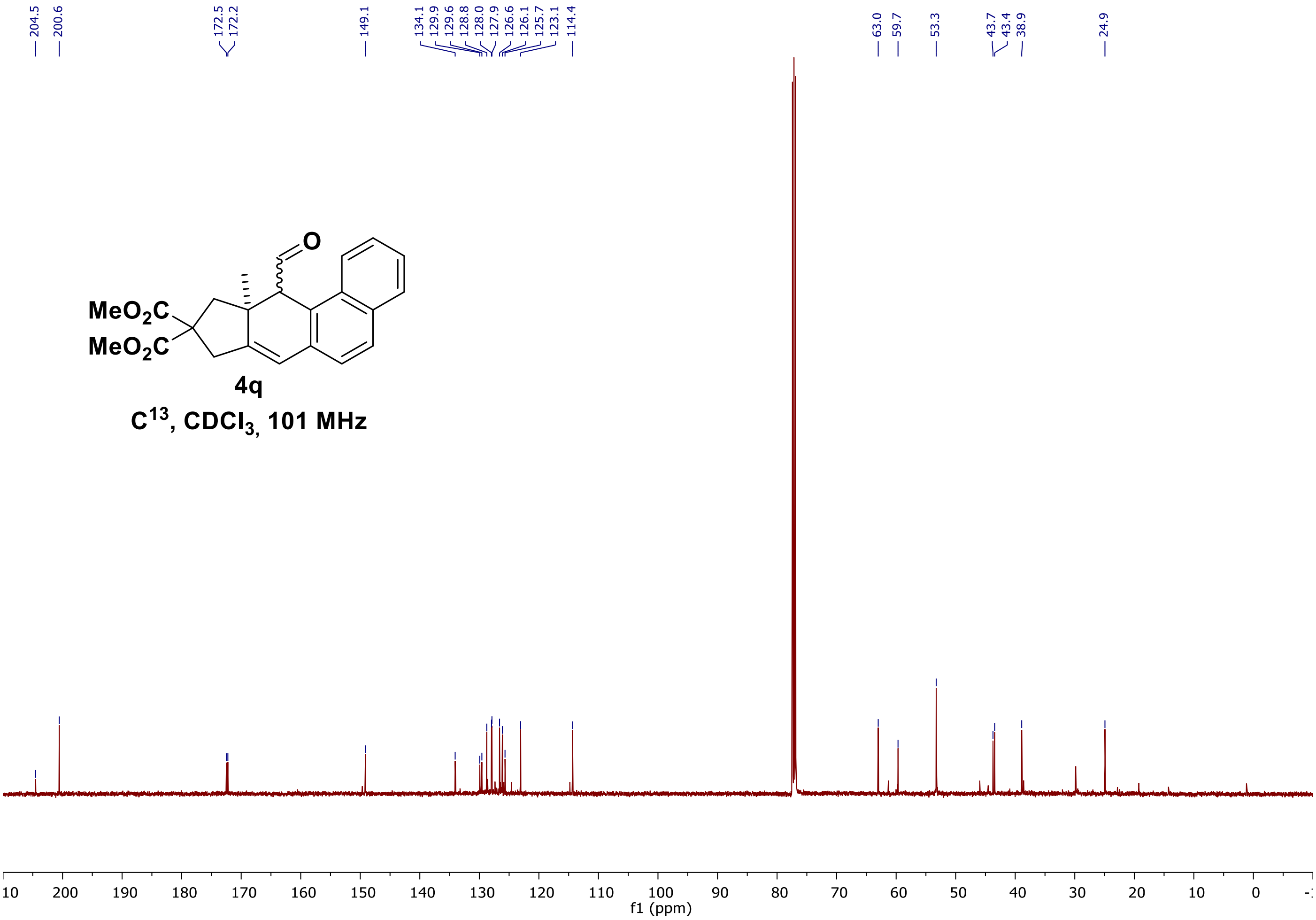


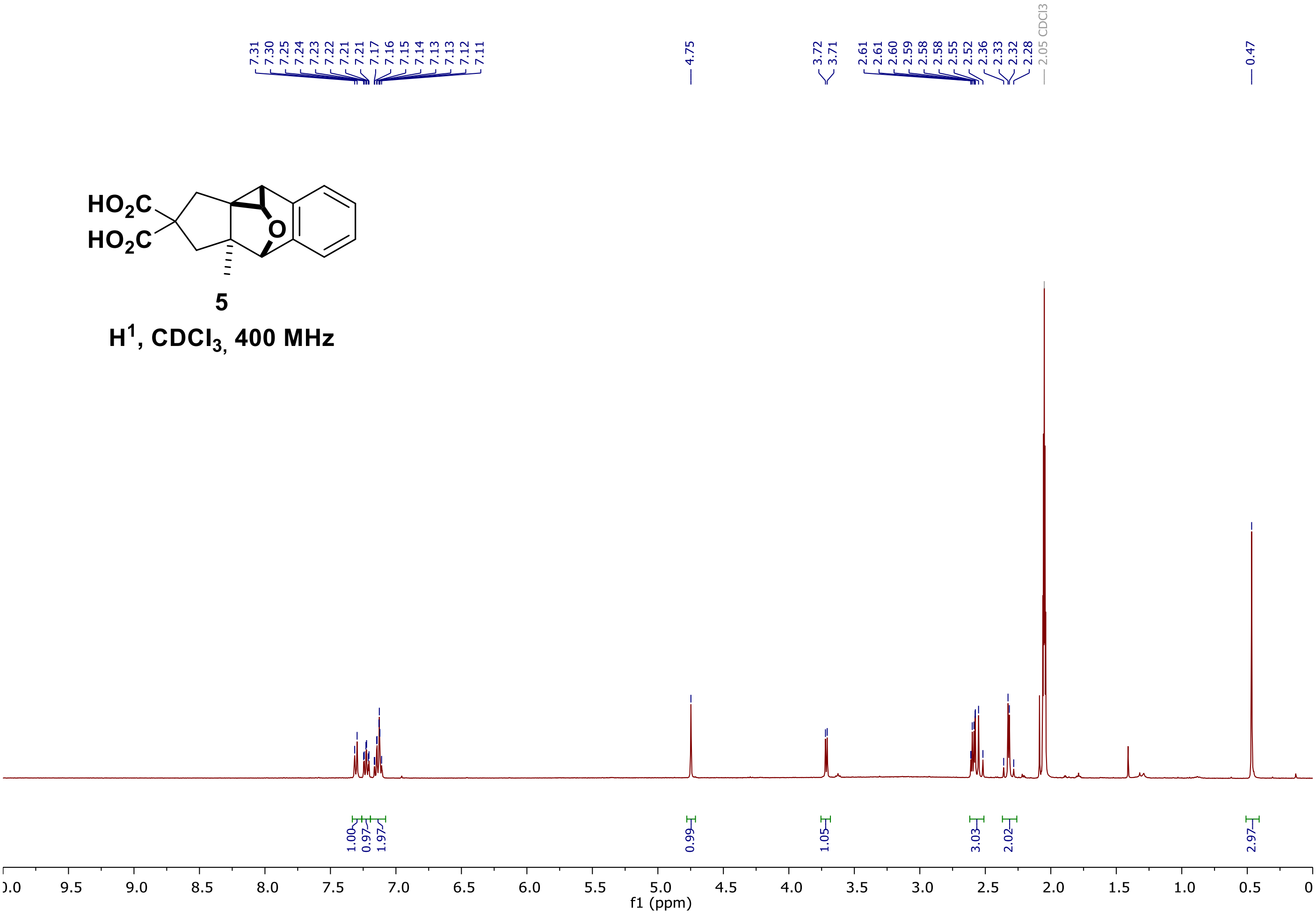
MeO2C
MeO2C
O
trans-4b
NOESY
f1 (ppm)
f2 (ppm)



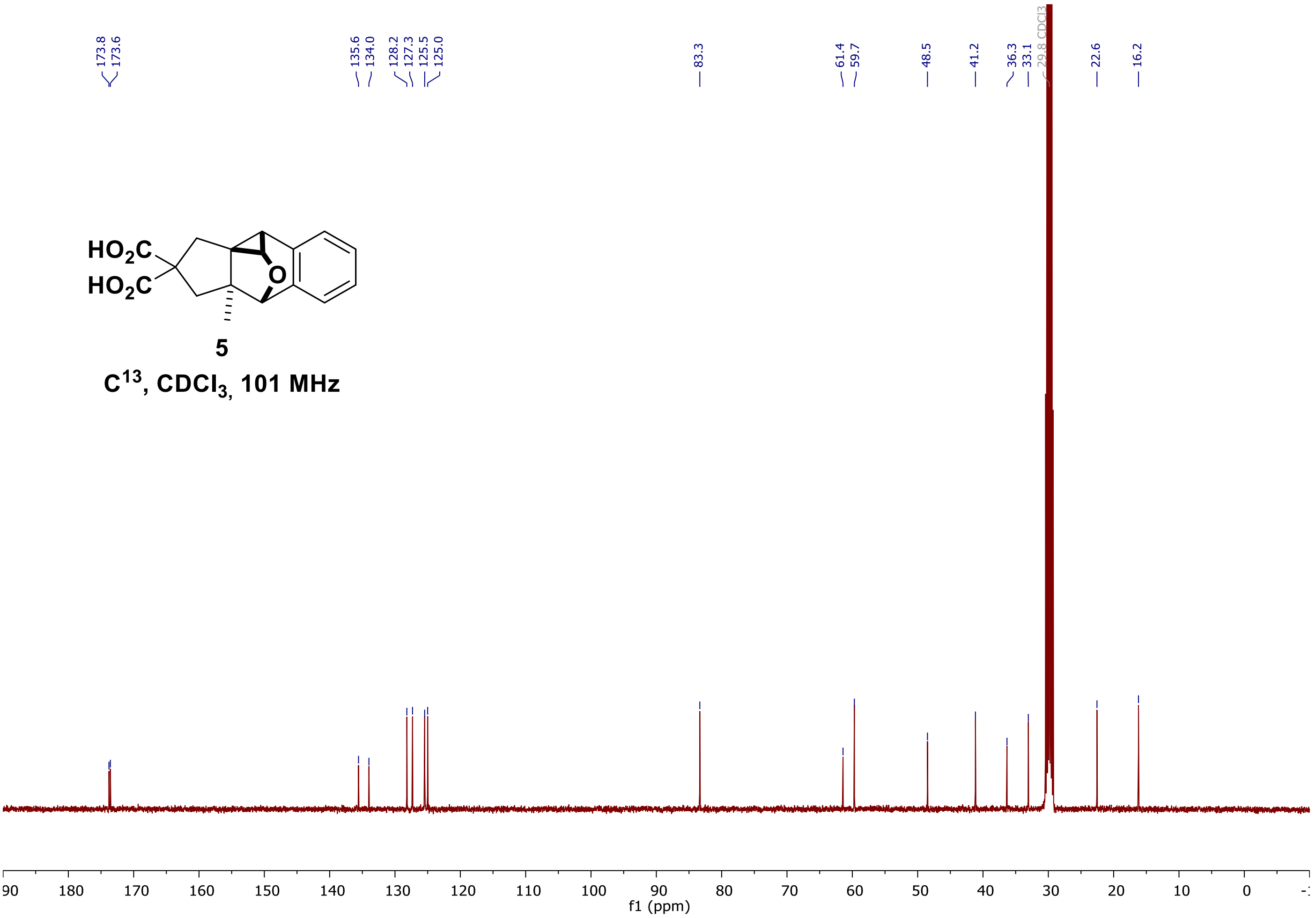
{10.08,0.97}
H
H
O
MeO2C
MeO2C
cis-4b
NOESY
f1 (ppm)
f2 (ppm)


10.27
10.26
9.36
9.35
8.12
8.10
8.10
8.08
7.83
7.83
7.82
7.81
7.81
7.80
7.73
7.71
7.70
7.68
7.55
7.55
7.54
7.53
7.53
7.52
7.52
7.51
7.50
7.50
7.49
7.48
7.48
7.48
7.47
7.47
7.46
7.25
7.24
7.23
7.09
7.09
7.08
7.05
7.04
3.82
3.80
3.79
3.78
3.76
3.75
3.74
3.68
3.57
3.56
3.53
3.52
3.49
3.48
3.47
3.47
3.43
3.42
3.39
3.37
3.28
3.27
3.23
3.23
3.19
3.15
2.84
2.81
2.72
2.68
2.58
2.58
2.54
2.43
2.39
1.12
1.10
O
MeO2C
MeO2C
4q
H1, CDCl3, 400 MHz
0.19
0.99
1.26
1.27
1.35
2.74
1.18
1.01
0.19
3.88
3.78
0.24
1.01
1.04
1.10
0.19
0.24
1.03
1.04
0.22
0.84
3.10
f1 (ppm)

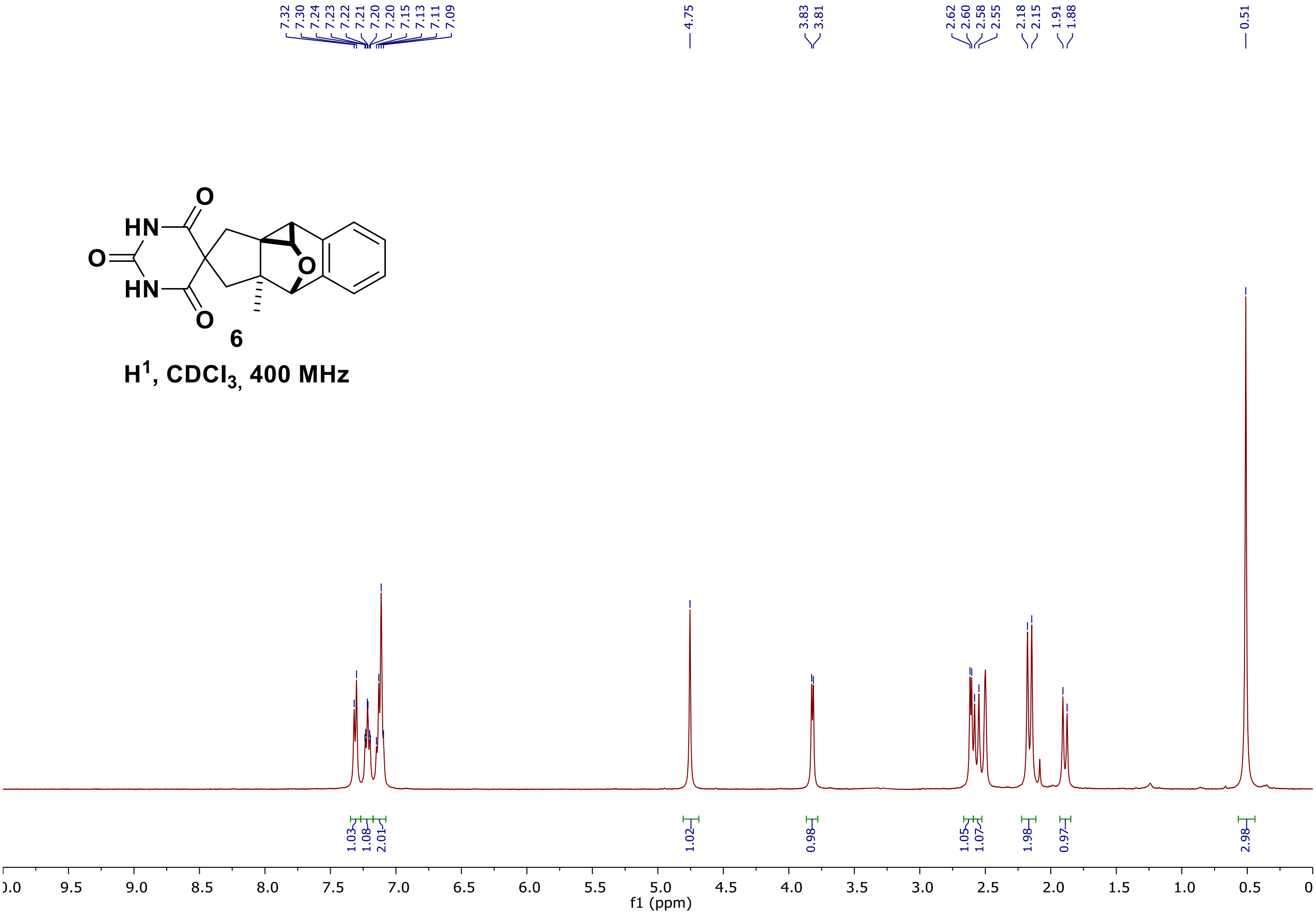

204.5
200.6
172.5
172.2
149.1
134.1
129.9
129.6
128.8
128.0
127.9
126.6
126.1
125.7
123.1
114.4
63.0
59.7
53.3
43.7
43.4
38.9
24.9
O
MeO2C
MeO2C
4q
C13, CDCl3, 101 MHz
f1 (ppm)

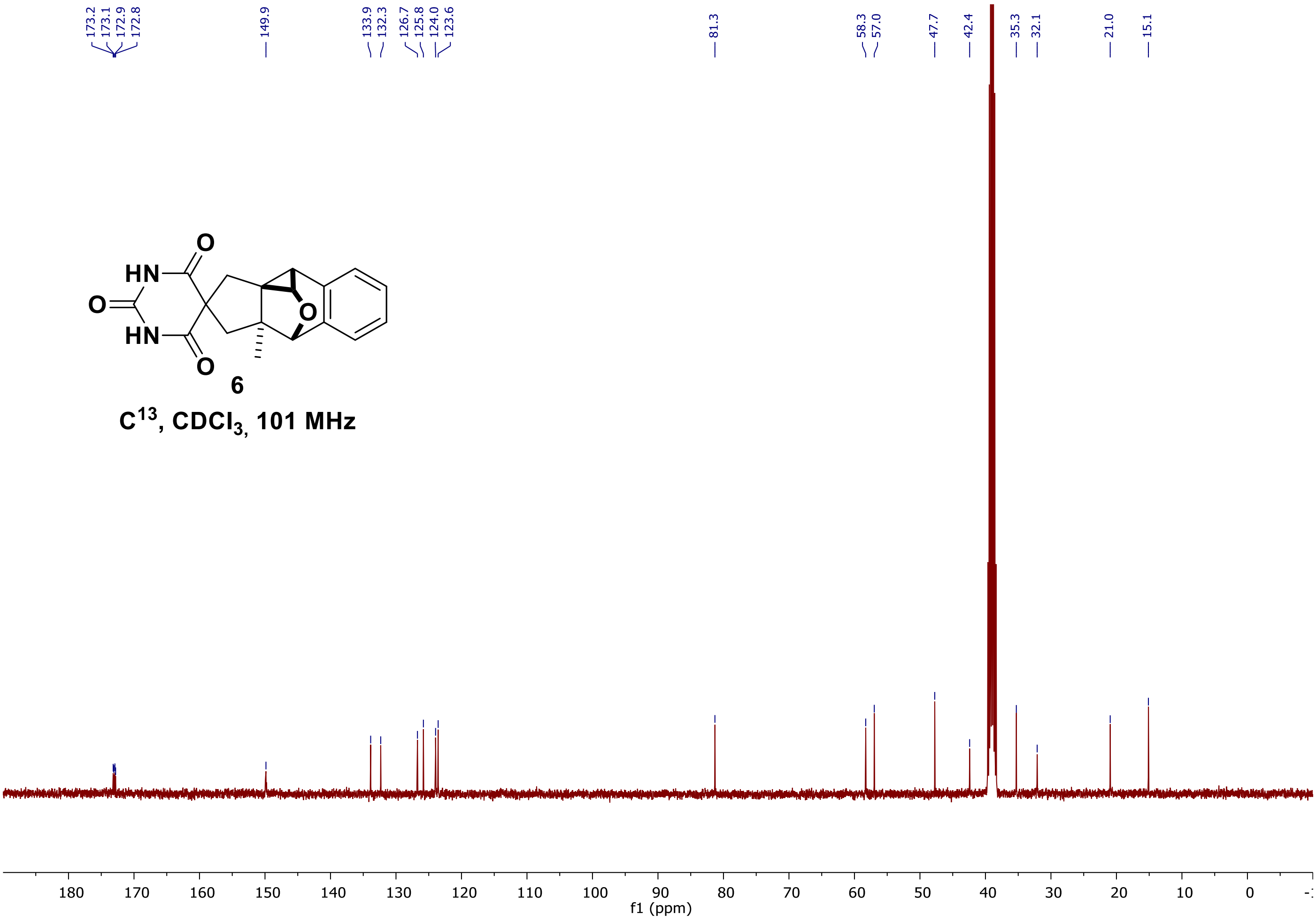


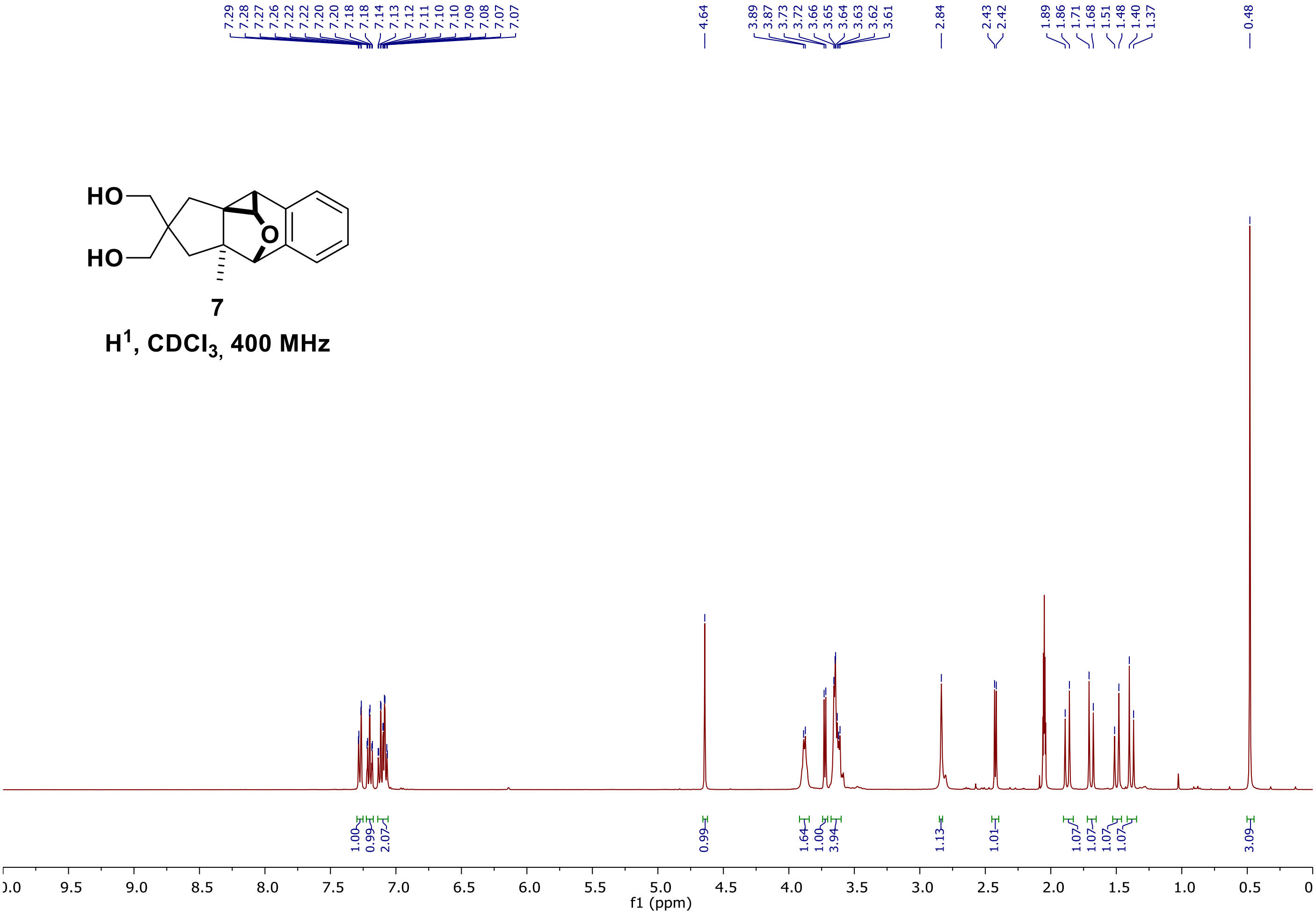
7.31 7.30 7.25 7.24 7.23 7.22 7.21 7.21 7.17 7.16 7.15 7.14 7.13 7.13 7.12 7.11
4.75
3.72 3.71
2.61 2.61 2.60 2.59 2.58 2.58 2.55 2.52 2.36 2.33 2.32 2.28
2.05 CDCl3
0.47
HO2C
HO2C
O
5
H1, CDCl3, 400 MHz
1.00 0.97 1.97
0.99
1.05
3.03 2.02
2.97
f1 (ppm)

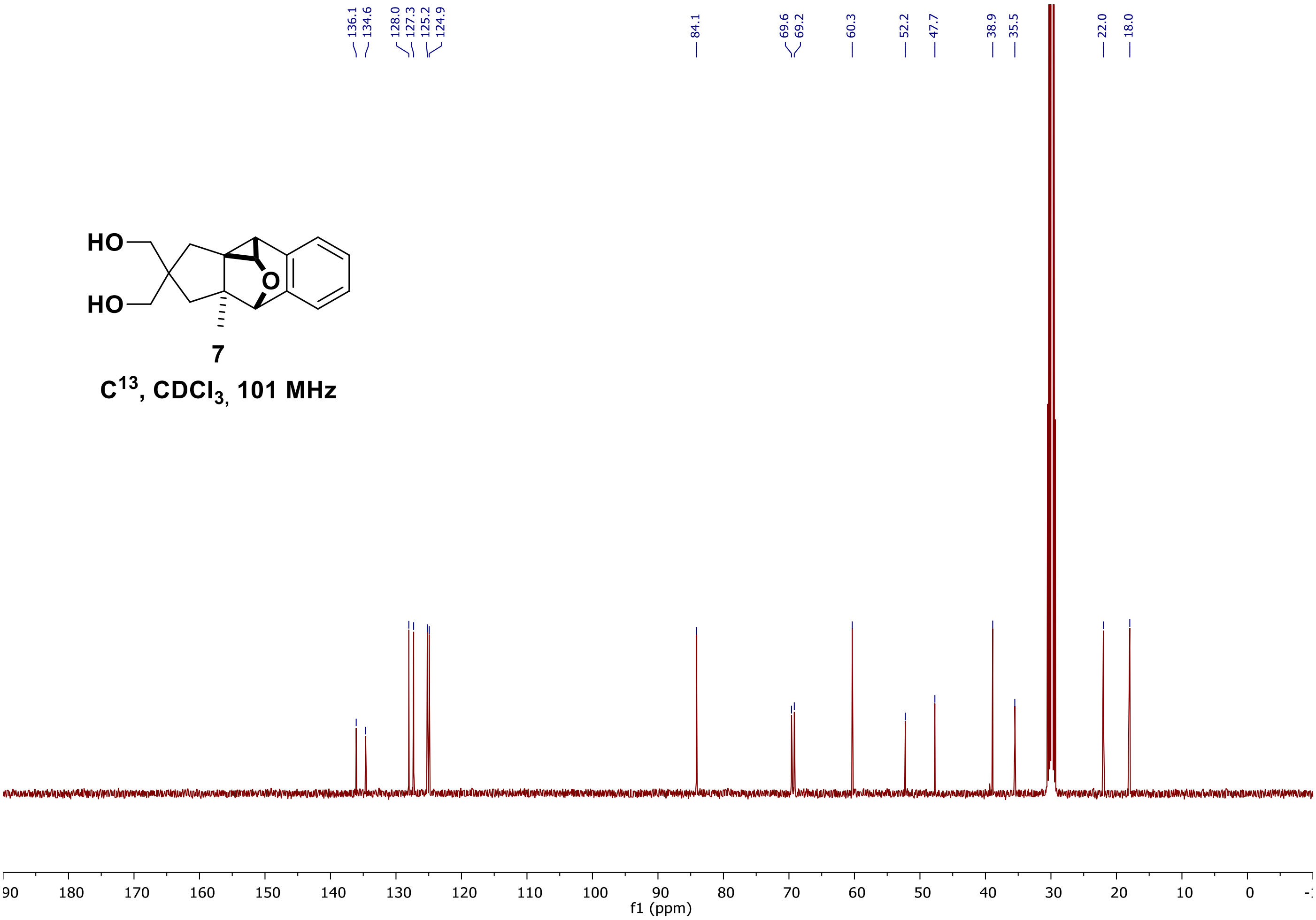


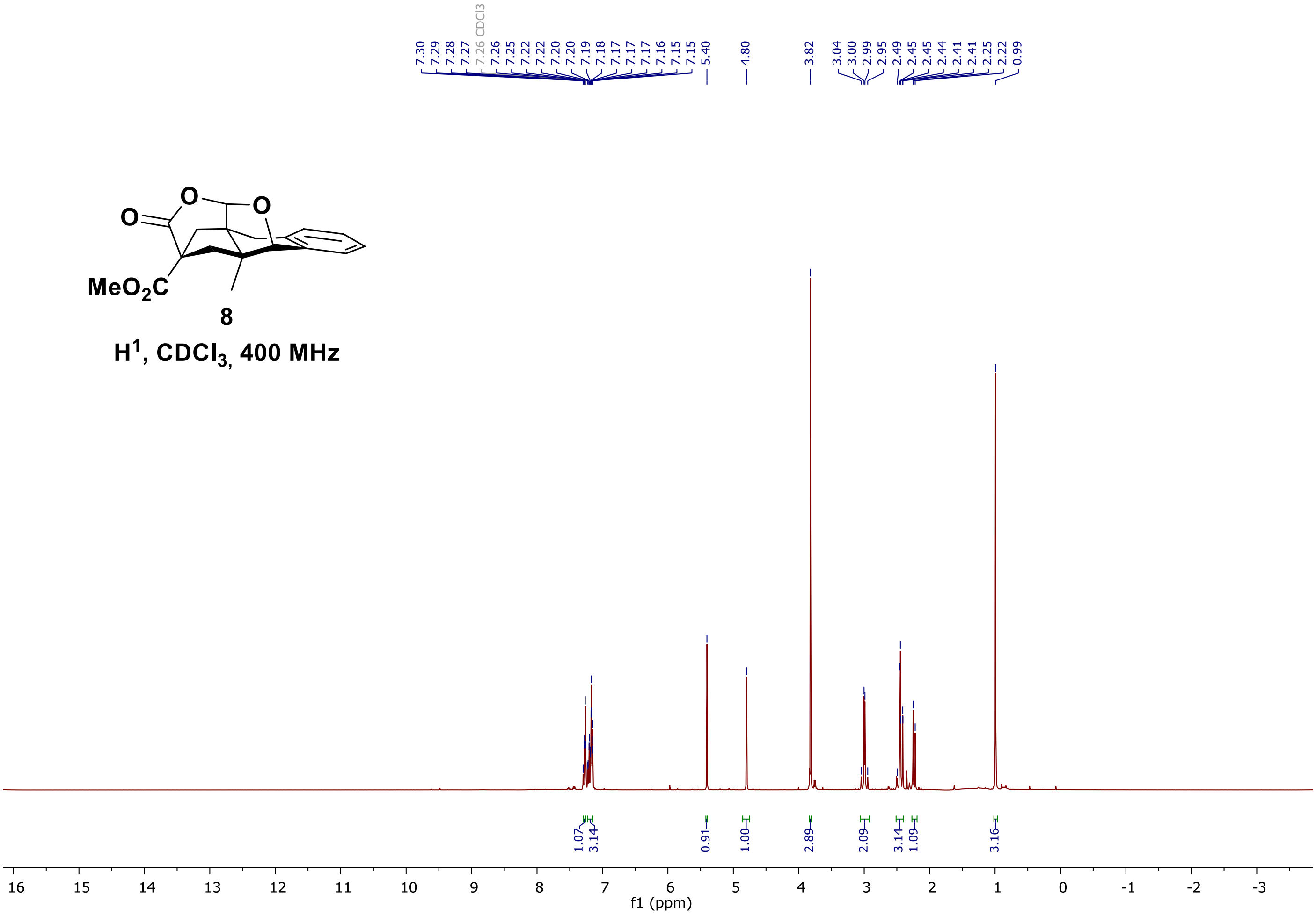
173.8 173.6
135.6 134.0 128.2 127.3 125.5 125.0
83.3
61.4 59.7
48.5
41.2
36.3 33.1
29.8 CDCl3
22.6
16.2
HO2C
HO2C
O
5
C13, CDCl3, 101 MHz
f1 (ppm)

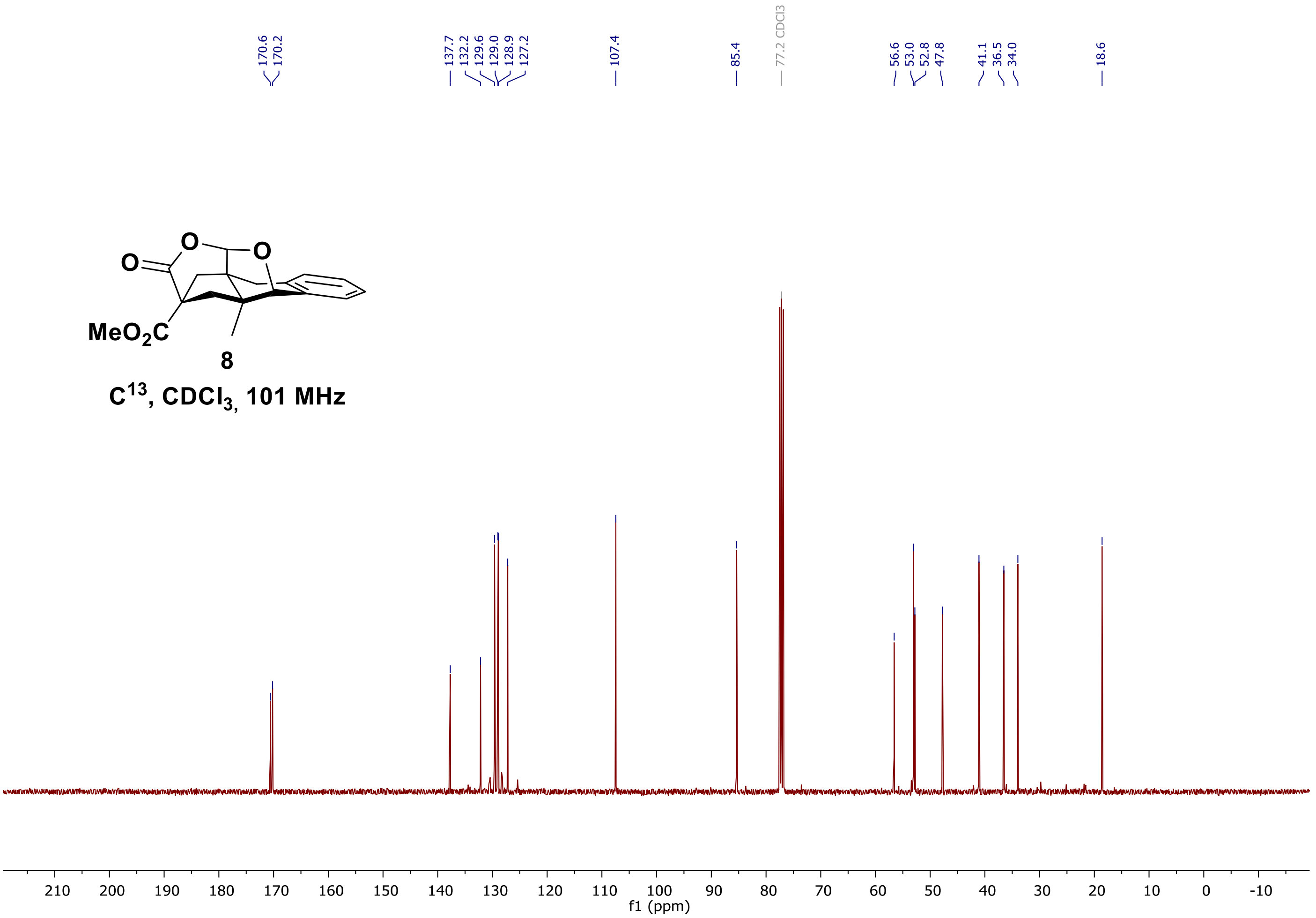

7.32 7.30 7.24 7.23 7.22 7.21 7.20 7.20 7.15 7.13 7.11 7.09
4.75
3.83 3.81
2.62 2.60 2.58 2.55 2.18 2.15 1.91 1.88
0.51
6
H1, CDCl3, 400 MHz
1.03 1.08 2.01 1.02 0.98 1.05 1.07 1.98 0.97 2.98
f1 (ppm)


173.2 173.1 172.9 172.8
149.9
133.9 132.3 126.7 125.8 124.0 123.6
81.3
58.3 57.0
47.7
42.4
35.3 32.1
21.0
15.1
6
C13, CDCl3, 101 MHz
f1 (ppm)


7.29
7.28
7.27
7.26
7.22
7.22
7.20
7.20
7.18
7.18
7.14
7.13
7.12
7.11
7.10
7.10
7.09
7.08
7.07
7.07
4.64
3.89
3.87
3.73
3.72
3.66
3.65
3.64
3.63
3.62
3.61
2.84
2.43
2.42
1.89
1.86
1.71
1.68
1.51
1.48
1.40
1.37
0.48
HO
HO
O
7
H1, CDCl3, 400 MHz
1.00
0.99
2.07
0.99
1.64
1.00
3.94
1.13
1.01
1.07
1.07
1.07
1.07
3.09
f1 (ppm)


136.1
134.6
128.0
127.3
125.2
124.9
84.1
69.6
69.2
60.3
52.2
47.7
38.9
35.5
22.0
18.0
HO
HO
O
7
C13, CDCl3, 101 MHz
f1 (ppm)


7.30 7.29 7.28 7.27 7.26 CDCl3 7.26 7.25 7.22 7.22 7.20 7.20 7.19 7.18 7.17 7.17 7.17 7.16 7.15 7.15 5.40 4.80 3.82 3.04 3.00 2.99 2.95 2.49 2.45 2.45 2.44 2.41 2.41 2.25 2.22 0.99
O
O
O
MeO2C
8
H1, CDCl3, 400 MHz
1.07 3.14 0.91 1.00 2.89 2.09 3.14 1.09 3.16
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


170.6 170.2 137.7 132.2 129.6 129.0 128.9 127.2 107.4 85.4 77.2 CDCl3 56.6 53.0 52.8 47.8 41.1 36.5 34.0 18.6
O
O
O
MeO2C
8
C13, CDCl3, 101 MHz
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)