Transition metal-free formal hydro/deuteromethylthiolation of unactivated alkenes

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1 General Information

All reactions involving air or moisture sensitive reagents were carried out with flame-dried glassware under argon atmosphere using standard Schlenk techniques. Solvents were either freshly distilled or obtained in extra-dry grade from commercial sources, and store over molecular sieve (3 Å). Diethyl ether (Et_2O) was distilled over sodium/benzophenone and stored over activated molecular sieve (3 Å). Dichloromethane (CH_2Cl_2) was refluxed over CaH_2 and used as freshly distilled. Merck silica gel 60 F254 plates were used for thin layer chromatography (TLC) with UV light (254/366 nm) or $KMnO_4$ as stains. The NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz (^1H), 101 MHz (^{13}C) and 376 MHz (^{19}F) in $CDCl_3$ with tetramethylsilane as the internal standard. Chemical shifts (δ) were reported in parts per million (ppm). Splitting patterns were designated as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; dd, doublet of doublets; td, triplet of doublets; ddd, doublet of doublet of doublet; m, multiplet; Infrared (IR) data were recorded on Alpha-P Bruker FT-IR Spectrometer. Absorbance frequencies were reported in reciprocal centimeters (cm^{-1}).

2 Experimental Procedures

General Procedure A

Preparation of dimethyl(methylthio) sulfonium triflate[1] （DMTST）

At 0 °C, to a solution of methyl trifluoromethanesulfonate （0.12 mol, 13.6 mL, 1.2 equiv) in CH_2Cl_2 (100 mL), Me_2S_2 (0.1 mol, 8.85 mL, 1.0 equiv) was added dropwise in 30 min. The mixture was stirred for 1 h at that temperature, following by 18 h at room temperature. Upon completion, the mixture was cooled to -15 °C with a freezer to afford white solid. The precipitation was collected by filtration and washed with fresh distilled Et_2O under nitrogen atmosphere, yielding dimethyl(methylthio) sulfonium triflate (23.1 g, 90%) as a white solid.

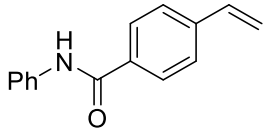
General Procedure B

General procedure for formal hydro/deuteromethylthiolation of alkene

A dry flask, charged with $MeSSMe_2OTf$ (1.2 equiv), was vacuumed and refilled with nitrogen (3 cycles). CH_2Cl_2 (3 mL) were added to the flask, following by the corresponding alkene. The reaction was stirred at room temperature, monitored by TLC. Upon the full conversion of the alkene, corresponding $NaBH_3CN$ or $NaBD_4$ (2.0 equiv) and THF (3 mL) was added. The reaction mixture was then stirred for 18 h at room temperature, before quenched with aqueous NH_4Cl. The mixture was extracted with CH_2Cl_2 (10 mL X 3), and the combined organic layer were washed with water and brine, dried over Na_2SO_4, filtrated and concentrated under reduced pressure. The crude product was then purified by column chromatography with silica gel.

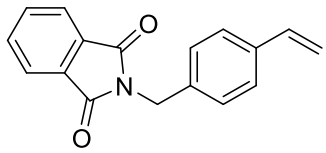
3 Characterization of prepared starting material and products

_N_-Phenyl-4-vinylbenzamide[2]



Under nitrogen atmosphere, a 50 mL flamed dried round bottom flask was charged with 4-vinylbenozic acid (533 mg, 3.6 mmol, 1.2 equiv), *N*-(3-dimethylamino-propyl)-*N'*-ethylcarbodiimide hydrochloride (690 mg, 3.6 mmol, 1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%) and benzenamine (279 mg, 3.0 mmol, 1.0 equiv) and DCM (30 mL, 0.1 M). After stirring at 23 °C for 24 hours, the reaction mixture was then concentrated in vacuo. The residue was purified by flash column chromatography on silica gel, eluting with petroleum ether : DCM (3 : 1 (v/v)) to afford the title compound as a white solid (349 mg, 52% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86–7.83 (m, 2H), 7.79 (s, 1H), 7.66–7.63 (m, 2H), 7.53–7.51 (m, 2H), 7.40–7.36 (m, 2H), 7.18–7.14 (m, 1H), 6.77 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.88 (d, *J* = 17.6 Hz, 1H), 5.39 (d, *J* = 10.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.3, 141.0, 137.8, 135.8, 133.9, 129.1, 127.3, 126.5, 124.6, 120.1, 116.3.

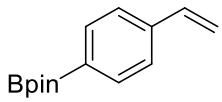
2-(4-Vinylbenzyl)isoindoline-1,3-dione[3]



Phthalimide (441 mg, 3.0 mmol), K_2CO_3 (498 mg, 3.6 mmol, 1.2 equiv) and DMF (0.2 M) were added to an 50 mL round flask. After that, 1-(chloromethyl)-4-vinylbenzene

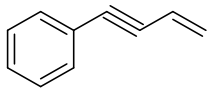
(458mg, 3.0 mmol) was injected. The mixture was stirred overnight at room temperature, before a dilution with Et_2O and water. After separation, the organic layer was washed successively with saturated $NaHCO_3$, and brine, and was then dried over Na_2SO_4, following by filtration and concentration. The residue was purified by flash column chromatography on silica gel, eluting with petroleum ether : EtOAc (20 : 1 (v/v)) to afford the title compound as a white solid (513 mg, 65% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87–7.82 (m, 2H), 7.72–7.69 (m, 2H), 7.41–7.34 (m, 4H), 6.67 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.71 (d, *J* = 17.6 Hz, 1H), 5.22 (d, *J* = 10.8 Hz, 1H), 4.83 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 137.2, 136.3, 135.8, 134.0, 132.1, 128.8, 126.5, 123.3, 114.1, 41.3.

4,4,5,5-Tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane[3]



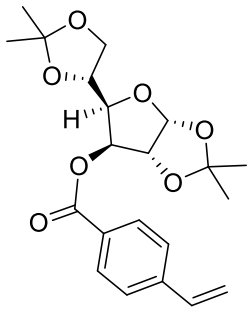
Pinacol (357 mg, 3.0 mmol) was added in one portion to a suspension of 4-vinylphenylboronic acid (445 mg, 3.0 mmol) and $MgSO_4$ (cat.) in THF (20 mL). The resulting mixture was stirred for 2 h at ambient temperature before filtration and concentration under vacuum. The crude product was then purified by column chromatography on silica gel, eluting with petroleum ether : EtOAc (10 : 1 (v/v)) to afford the title compound as a colourless oil (628 mg, 91%) . ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.58 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.67 (d, *J* = 18.4 Hz, 1H), 5.15 (d, *J* = 10.8 Hz, 1H), 1.20 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.2, 136.8, 135.0, 125.5, 114.9, 83.7, 24.8.

But-3-en-1-yn-1-ylbenzene[4]



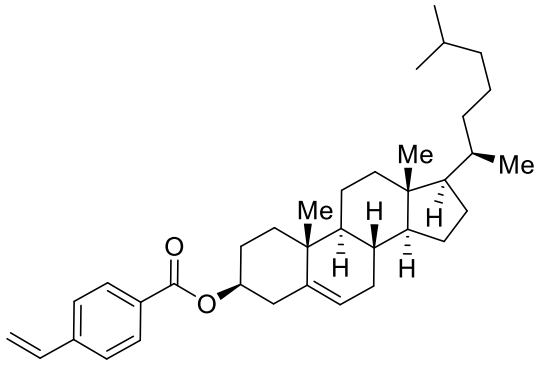
Ethynylbenzene (306 mg, 3.0 mmol, 1.0 equiv), vinyl bromide (476 mg, 4.5 mmol, 1.5 equiv), CuI (22.8 mg, 0.12 mmol, 0.04 equiv), $Pd(PPh_3)_4$ (52 mg, 0.045 mmol, 0.015 equiv) and triethylamine (3.0 mL, 1.0 M) were added to a 50 mL round flask. After 4 h of stirring under nitrogen atmosphere, the reaction mixture was quenched with H_2O (5.0 mL). The aqueous layer was extracted with EtOAc (3 × 10 mL). The organic layers were combined, dried ($MgSO_4$), filtrated and concentrated under vacuo. The residue was purified by chromatography on silica gel, eluting with petroleum ether : EtOAc (20 : 1 (v/v)) to afford the title compound as a colorless liquid (230 mg, 60% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47–7.45 (m, 2H), 7.33–7.31 (m, 3H), 6.03 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.75 (dd, *J* = 17.6, 2.0 Hz, 1H), 5.55 (dd, *J* = 11.2, 2.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 131.5, 128.3 (2), 126.9, 123.1, 117.2, 89.9, 88.1.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydro-furo[2,3-d][1,3]dioxol-6-yl 4-vinylbenzoate[5]



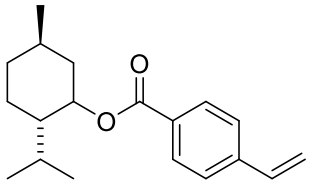
Under nitrogen atmosphere, a 50 mL flamed dried round bottom flask was charged with 4-vinylbenozic acid (445 mg, 3.0 mmol, 1.0 equiv), *N*,*N*'-dicyclohexylcarbodiimide (743 mg, 3.6 mmol, 1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%), diacetone-D-glucose (937 mg, 3.6 mmol, 1.2 equiv) and DCM (30 mL, 0.1 M). The reaction mixture was then stirred at 23 °C for 48 hours and concentrated under vacuo. The residue was purified by flash column chromatography on silica gel, eluting with petroleum ether : EtOAc (10 : 1 (v/v)) to afford the title compound as a colourless oil (550 mg, 47% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99–7.97 (m, 2H), 7.48–7.46 (m, 2H), 6.75 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.95 (d, *J* = 3.6 Hz, 1H), 5.88 (d, *J* = 17.6 Hz, 1H), 5.49 (d, *J* = 2.8 Hz, 1H), 5.41 (d, *J* = 10.8 Hz, 1H), 4.63 (d, *J* = 4 Hz, 1H), 4.37–4.34 (m, 2H), 4.14–4.07 (m, 2H), 1.56 (s, 3H), 1.41 (s, 3H), 1.32 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.0, 142.5, 135.8, 130.0, 128.5, 126.2, 117.0, 112.4, 109.4, 105.1, 83.4, 79.9, 76.6, 72.6, 67.2, 26.8, 26.7, 26.2, 25.2.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methyl-heptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-vinylbenzoate[6]



Under nitrogen atmosphere, a 50 mL flamed dried round bottom flask was charged with 4-vinylbenozic acid (445 mg, 3.0 mmol, 1.0 equiv), *N*,*N*′-dicyclohexylcarbodiimide (743 mg, 3.6 mmol, 1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%), cholesterol (1.55 g, 3.6 mmol, 1.2 equiv) and DCM (30 mL, 0.1 M). The reaction mixture was then stirred at 23 °C for 48 hours, and concentrated under vacuo after. The residue was purified by flash column chromatography on silica gel, eluting with petroleum ether : EtOAc (10 : 1 (v/v)) to afford the title compound as a white solid (635 mg, 41% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 6.75 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.86 (d, *J* = 17.6 Hz, 1H), 5.39 (dd, *J* = 15.6, 5.2 Hz, 2H), 4.90–4.81 (m, 1H), 2.46 (d, *J* = 8.4 Hz, 2H), 2.05–1.89 (m, 4H), 1.86–1.78 (m, 1H), 1.76–1.68 (m, 1H), 1.62–1.43 (m, 6H), 1.39–1.33 (m, 3H), 1.30–1.09 (m, 5H), 1.07 (s, 3H), 1.04–0.97 (m, 3H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.87 (dd, *J* = 6.8, 2.0 Hz, 6H), 0.69 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 141.7, 139.6, 136.1, 129.9, 129.8, 126.0, 122.8, 116.3, 74.5, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.0, 37.0, 36.6, 36.2, 35.8, 31.9, 31.8, 28.2, 28.0, 27.9, 24.3, 23.8, 22.8, 22.6, 21.0, 19.4, 18.7, 11.8.

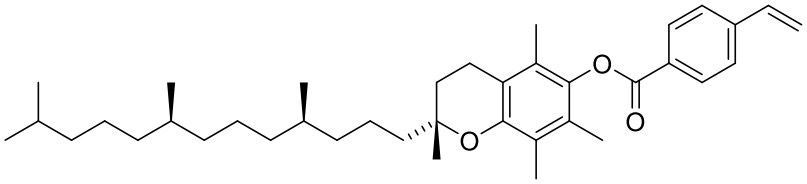
(2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-vinylbenzoate[7]



Under nitrogen atmosphere, a 50 mL flamed dried round bottom flask was charged with 4-vinylbenozic acid (445 mg, 3.0 mmol, 1.0 equiv), *N*,*N*′-dicyclohexylcarbodiimide (743 mg, 3.6 mmol, 1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%), (1*R*,2*S*,5*R*)-5-

methyl-2-(1-methylethyl)cyclohexanol (562 mg, 3.6 mmol, 1.2 equiv) and DCM (30 mL, 0.1 M). The reaction mixture was then stirred at 23 °C for 48 hours, and concentrated under vacuo after. The residue was purified by flash column chromatography on silica gel, eluting with petroleum ether : EtOAc (10 : 1 (v/v)) to afford the title compound as a colourless oil (601 mg, 70% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 6.75 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.86 (d, *J* = 17.6 Hz, 1H), 5.37 (d, *J* = 10.8 Hz, 1H), 4.96–4.89 (m, 1H), 2.15–2.10 (m, 1H), 2.00–1.92 (m, 1H), 1.76–1.70 (m, 2H), 1.60–1.50 (m, 2H), 1.18–1.05 (m, 2H), 0.98–0.87 (m, 7H), 0.79 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 141.7, 136.0, 129.9, 129.8, 126.0, 116.3, 74.7, 47.2, 40.9, 34.3, 31.4, 26.4, 23.6, 22.0, 20.8, 16.5.

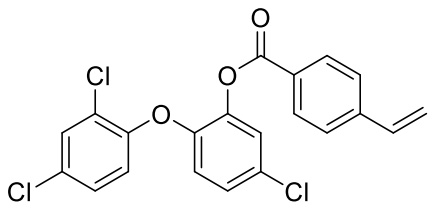
(*R*)-2,5,7,8-Tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)-chroman-6-yl 4-vinylbenzoate[8]



Under nitrogen atmosphere, a 50 mL flamed dried round bottom flask was charged with 4-vinylbenozic acid (445 mg, 3.0 mmol, 1.0 equiv), *N*,*N*'-dicyclohexylcarbodiimide (743 mg, 3.6 mmol, 1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%), (2*R*)-3,4-dihydro-2,5,7,8-tetramethyl-2-[(4*R*,8*R*)-4,8,12-trimethyltridecyl]-2*H*-1-benzo-pyran-6-ol (1.55 g, 3.6 mmol, 1.2 equiv) and DCM (30 mL, 0.1 M). The reaction mixture was then stirred at 23 °C for 48 hours, and concentrated under vacuo after. The residue was purified by

flash column chromatography on silica gel, eluting with petroleum ether : EtOAc (20 : 1 (v/v)) to afford the title compound as a colourless oil (1.08 g, 62% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 6.81 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.92 (d, *J* = 17.6 Hz, 1H), 5.43 (d, *J* = 10.8 Hz, 1H), 2.63 (t, *J* = 6.8 Hz, 2H), 2.13 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.87–1.77 (m, 2H), 1.61–1.47 (m, 4H), 1.46–1.35 (m, 4H), 1.31–1.20 (m, 10H), 1.17–1.04 (m, 6H), 0.91–0.85 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.9, 149.4, 142.4, 140.6, 136.0, 130.5, 128.7, 126.9, 126.3, 125.1, 123.1, 117.4, 116.8, 75.0, 40.4, 39.6, 39.4, 37.4, 37.3, 32.78, 31.2, 31.0, 28.0, 24.8, 24.4, 24.2, 23.7, 22.7, 22.6, 21.0, 20.6, 19.7, 19.7, 13.0, 12.2, 11.8.

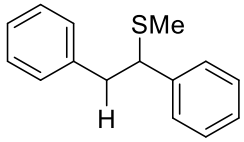
5-Chloro-2-(2,4-dichlorophenoxy)phenyl 4-vinylbenzoate



Under nitrogen atmosphere, a 50 mL flamed dried round bottom flask was charged with 4-vinylbenozic acid (445 mg, 3.0 mmol, 1.0 equiv), *N*,*N*′-dicyclohexylcarbodiimide (743 mg, 3.6 mmol, 1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%), 3-chloro-5-(3,5-dichlorophenoxy)-phenol (1.04 g, 3.6 mmol, 1.2 equiv) and DCM (30 mL, 0.1 M). The reaction mixture was then stirred at 23 °C for 48 hours, and concentrated under vacuo after. The residue was purified by flash column chromatography on silica gel, eluting with petroleum ether : EtOAc (20 : 1 (v/v)) to afford the title compound as a colourless oil (642 mg, 51% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02–8.00 (m, 2H),

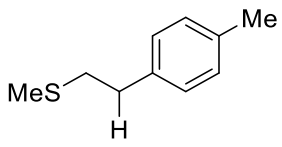
7.48–7.46 (m, 2H), 7.35 (dd, *J* = 12.4, 2.4 Hz, 2H), 7.22 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.15 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.92 (dd, *J* = 8.8, 2.0 Hz, 2H), 6.76 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.90 (d, *J* = 17.2 Hz, 1H), 5.42 (d, *J* = 11.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.7, 151.0, 146.7, 142.8, 141.8, 135.7, 130.5, 130.2, 129.3, 129.2, 128.0, 127.3, 126.9, 126.2, 125.8, 124.6, 120.3, 120.2, 117.1. IR (KBr) ν 3087, 2523, 2261, 2062, 1738, 1600, 1480, 1249, 1050, 866, 704, 574, 454. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{21}H_{13}Cl_3O_3$ 440.9828; Found 440.9823.

(1,2-Diphenylethyl)(methyl)sulfane[9] (1)



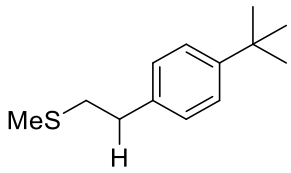
According to the general procedure for formal hydromethylthiolation of alkene, 54.1 mg (0.3 mmol, 1.0 equiv) of stilbene was applied. After purification by column chromatography on silica gel (DCM/petroleum ether 1:20), the title compound was obtained as a colourless oil (57.5 mg, 84% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31–7.19 (m, 8H), 7.11–7.08 (m, 2H), 3.94 (t, *J* = 7.6 Hz, 1H), 3.23–3.12 (m, 2H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.7, 139.0, 129.1, 128.3, 128.1, 128.0, 127.1, 126.3, 53.4, 42.8, 14.6.

Methyl(4-methylphenethyl)sulfane (2)



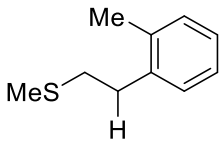
According to the general procedure for formal hydromethylthiolation of alkene, 35.4 mg (0.3 mmol, 1.0 equiv) of 4-methylstyrene was applied. After purification by column chromatography on silica gel (DCM/petroleum ether 1:10), the title compound was obtained as a colourless oil (41.4 mg, 83% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 (s, 4H), 2.90–2.86 (m, 2H), 2.78–2.73 (m, 2H), 2.35 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.4, 135.8, 129.1, 128.3, 35.9, 35.3, 21.0, 15.6. IR (KBr) ν 2919, 1623, 1508, 1424, 1267, 1016, 787, 525. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{14}S$ 189.0714; Found 189.0712.

(4-(*Tert*-butyl)phenethyl)(methyl)sulfane[9] (3)



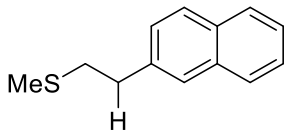
According to the general procedure for formal hydromethylthiolation of alkene, 48.1 mg (0.3 mmol, 1.0 equiv) of 4-*tert*-butylstyrene was applied. After purification by column chromatography on silica gel (DCM/petroleum ether 1:10), the title compound was obtained as a colourless oil (51.2 mg, 82% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.92–2.88 (m, 2H), 2.80–2.75 (m, 2H), 2.16 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.1, 137.5, 128.1, 125.3, 35.7, 35.3, 34.3, 31.3, 15.6.

Methyl(2-methylphenethyl)sulfane (4)



According to the general procedure for formal hydromethylthiolation of alkene, 35.4 mg (0.3 mmol, 1.0 equiv) of 2-methylstyrene was applied. After purification by column chromatography on silica gel (DCM/petroleum ether 1:20), the title compound was obtained as a colourless oil (42.8 mg, 86% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25–7.16 (m, 4H), 2.93–2.89 (m, 2H), 2.74–2.70 (m, 2H), 2.34 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.7, 135.8, 130.3, 129.0, 126.4, 126.0, 34.5, 33.3, 19.2, 15.7. IR (KBr) ν 2920, 1612, 1476, 1027, 735, 451. HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{10}H_{14}S$ 189.0714; Found 189.0713.

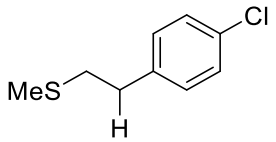
Methyl(2-(naphthalen-2-yl)ethyl)sulfane (5)



According to the general procedure for formal hydromethylthiolation of alkene, 46.3 mg (0.3 mmol, 1.0 equiv) of 2-vinylnaphthalene was applied. After purification by column chromatography on silica gel (DCM/petroleum ether 1:20), the title compound was obtained as a white solid (41.8 mg, 69% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84–7.80 (m, 3H), 7.68 (s, 1H), 7.50–7.43 (m, 2H), 7.38–7.36 (m, 1H), 3.11–3.07 (m, 2H), 2.89–2.85 (m, 2H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.0, 133.5, 132.1, 128.0, 127.6, 127.5, 127.0, 126.7, 126.0, 125.3, 36.0, 35.7, 15.7. IR (KBr) ν 2952, 2909, 1591, 1414, 1059, 880, 807,463. HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for

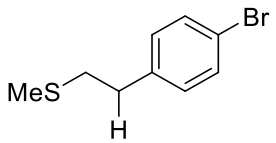
$C_{13}H_{14}S$ 225.0714; Found 225.0713.

(4-Chlorophenethyl)(methyl)sulfane[9] (6)



According to the general procedure for formal hydromethylthiolation of alkene, 41.6 mg (0.3 mmol, 1.0 equiv) of 4-chlorostyrene was applied. After purification by column chromatography on silica gel (DCM/petroleum ether 1:10), the title compound was obtained as a yellow oil (31.8 mg, 57% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28–7.25 (m, 2H), 7.16–7.13 (m, 2H), 2.89–2.85 (m, 2H), 2.75–2.71 (m, 2H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.9, 132.0, 129.8, 128.5, 35.6, 35.1, 15.7.

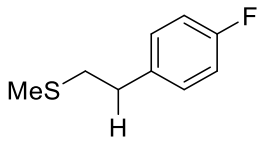
(4-Bromophenethyl)(methyl)sulfane (7)



According to the general procedure for formal hydromethylthiolation of alkene, 41.4 mg (0.3 mmol, 1.0 equiv) of 4-bromostyrene was applied. After purification by column chromatography on silica gel (DCM/petroleum ether 1:10), the title compound was obtained as a yellow oil (35.9 mg, 52% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43–7.40 (m, 2H), 7.10–7.08 (m, 2H), 2.87–2.83 (m, 2H), 2.75–2.70 (m, 2H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.4, 131.5, 130.2, 120.1, 35.5, 35.1, 15.7. IR (KBr) ν 2899, 1623, 1476, 1059, 1059, 995, 787,514. HRMS (ESI) m/z: $[M + Na]^+$

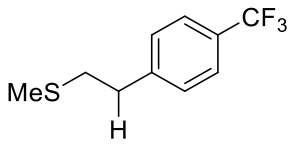
Calcd for $C_9H_{11}BrS$ 252.9663; Found 252.9662.

(4-Fluorophenethyl)(methyl)sulfane (8)



According to the general procedure for formal hydromethylthiolation of alkene, 36.6 mg (0.3 mmol, 1.0 equiv) of 4-fluorostyrene was applied. After purification by column chromatography on silica gel (DCM/petroleum ether 1:10), the title compound was obtained as a yellow oil (29.1 mg, 57% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18–7.15 (m, 2H), 7.01–6.96 (m, 2H), 2.89–2.85 (m, 2H), 2.75–2.71 (m, 2H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.5 (d, $J_{C\text{-}F}$ = 244.8 Hz), 136.1 (d, $J_{C\text{-}F}$ = 3.2 Hz), 129.9 (d, $J_{C\text{-}F}$ = 8.0 Hz), 115.2 (d, $J_{C\text{-}F}$ = 21.2 Hz), 35.8 (d, $J_{C\text{-}F}$ = 1.5 Hz), 34.9, 15.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -116.9. IR (KBr) ν 2930, 1623, 1498, 1215, 1006, 995, 818,536. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_9H_{11}FS$ 193.0463; Found 193.0452.

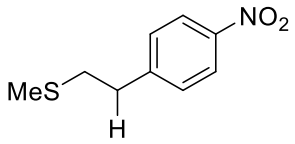
Methyl(4-(trifluoromethyl)phenethyl)sulfane (9)



According to the general procedure for formal hydromethylthiolation of alkene, 51.6 mg (0.3 mmol, 1.0 equiv) of 4-(trifluoromethyl)styrene was applied. After purification by column chromatography on silica gel (DCM/petroleum ether 1:10), the title

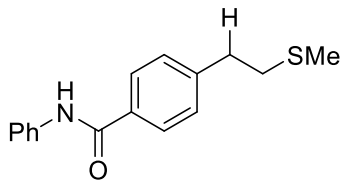
compound was obtained as a colourless oil (29.7 mg, 45% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57–7.55 (m, 2H), 7.34–7.31 (m, 2H), 2.98–2.94 (m, 2H), 2.79–2.75 (m, 2H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.5 (d, J_{C-F} = 1.8 Hz), 128.8, 128.7 (q, J_{C-F} = 32.4 Hz), 125.4 (q, J_{C-F} = 3.8 Hz), 124.2 (q, J_{C-F} = 273.0 Hz), 35.5, 35.4, 15.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.4. IR (KBr) ν 1627, 1324, 1713, 1172, 1127, 1062, 1017, 820. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{11}F_3S$ 221.0612; Found 221.0600.

Methyl(4-nitrophenethyl)sulfane (10)



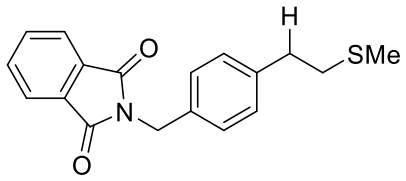
According to the general procedure for formal hydromethylthiolation of alkene, 44.7 mg (0.3 mmol, 1.0 equiv) of 4-nitrostyrene was applied. After purification by column chromatography on silica gel (DCM/petroleum ether 1:10), the title compound was obtained as a yellow oil (31.9 mg, 54% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16–8.14 (m, 2H), 7.38–7.36 (m, 2H), 3.02–2.98 (m, 2H), 2.80–2.76 (m, 2H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.1, 146.6, 129.4, 123.7, 35.4, 35.1, 15.7. IR (KBr) ν 2920, 1603, 1498, 1341, 1111, 995, 838, 504. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_9H_{11}NO_2S$ 220.0408; Found 220.0406.

4-(2-(Methylthio)ethyl)-*N*-phenylbenzamide (11)



According to the general procedure for formal hydromethylthiolation of alkene, 66.9 mg (0.3 mmol, 1.0 equiv) of *N*-phenyl-4-vinylbenzamide was applied. After purification by column chromatography on silica gel (EtOAc /petroleum ether 1:5), the title compound was obtained as a white solid (73.2 mg, 90% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84–7.82 (m, 2H), 7.80 (s, 1H), 7.65–7.62 (m, 2H), 7.39–7.32 (m, 4H), 7.17–7.13 (m, 1H), 2.97 (t, *J* = 7.2 Hz, 2H), 2.78 (t, *J* = 8.4 Hz, 2H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.5, 144.7, 137.9, 133.0, 129.1, 129.0, 127.2, 124.5, 120.1, 35.5, 35.4, 15.7. IR (KBr) ν 3339, 2899, 1665, 1591, 1525, 1434, 1317, 1251, 1083, 1012, 844, 753, 692, 631, 499. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}NOS$ 272.1109; Found 272.1106.

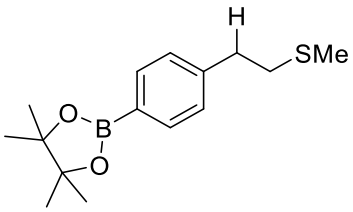
2-(4-(2-(Methylthio)ethyl)benzyl)isoindoline-1,3-dione (12)



According to the general procedure for formal hydromethylthiolation of alkene, 78.9 mg (0.3 mmol, 1.0 equiv) of 2-(4-vinylbenzyl)isoindoline-1,3-dione was applied. After purification by column chromatography on silica gel (EtOAc /petroleum ether 1:20), the title compound was obtained as a white solid (59.7 mg, 64% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83–7.81 (m, 2H), 7.69–7.67 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H),

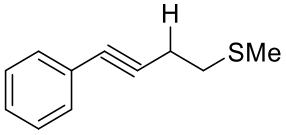
7.15 (d, *J* = 8.0 Hz, 2H), 4.81 (s, 2H), 2.86–2.82 (m, 2H), 2.72–2.67 (m, 2H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9, 140.1, 134.3, 133.9, 132.0, 128.7, 128.7, 123.2, 41.2, 35.6, 35.3, 15.6. IR (KBr) ν 2928, 1721, 1382, 1068, 942, 702, 515. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}NO_2S$ 312.1058; Found 312.1052.

4,4,5,5-Tetramethyl-2-(4-(2-(methylthio)ethyl)phenyl)-1,3,2-dioxaborolane (13)



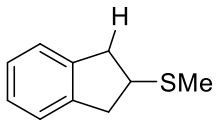
According to the general procedure for formal hydromethylthiolation of alkene, 69.0 mg (0.3 mmol, 1.0 equiv) of 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane was applied. After purification by column chromatography on silica gel ($EtOA_C$ /petroleum ether 1:20), the title compound was obtained as a yellow oil (59.2 mg, 71% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.93–2.89 (m, 2H), 2.77–2.73 (m, 2H), 2.12 (s, 3H), 1.34 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.8, 135.0, 127.9, 83.6, 36.0, 35.5, 24.8, 15.7. IR (KBr) ν 2972, 1623, 1361, 1132, 964, 850, 650. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{23}BO_2S$ 279.1590; Found 279.1584.

Methyl(4-phenylbut-3-yn-1-yl)sulfane (14)



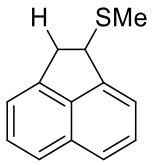
According to the general procedure for formal hydromethylthiolation of alkene, 38.4 mg (0.3 mmol, 1.0 equiv) of but-3-en-1-yn-1-ylbenzene was applied. After purification by column chromatography on silica gel (DCM/petroleum ether 1:20), the title compound was obtained as a colourless oil (21.1 mg, 40% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42–7.38 (m, 2H), 7.30–7.27 (m, 3H), 2.76–2.72 (m, 4H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 131.6, 128.2, 127.8, 123.5, 88.2, 81.5, 33.2, 20.5, 15.7. IR (KBr) ν 2920, 1650, 1490, 758, 678, 519. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{12}S$ 177.0738; Found 177.0734.

(2,3-Dihydro-1H-inden-2-yl)(methyl)sulfane[9] (15)



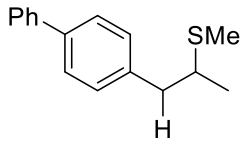
According to the general procedure for formal hydromethylthiolation of alkene, 34.8 mg (0.3 mmol, 1.0 equiv) of indene was applied. After purification by column chromatography on silica gel (DCM/petroleum ether 1:5), the title compound was obtained as a colourless oil (31.0 mg, 63% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23–7.16 (m, 4H), 3.61–3.57 (m, 1H), 3.37–3.31 (m, 2H), 3.00–2.95 (m, 2H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.8, 126.5, 124.3, 44.6, 40.0, 14.5.

(1,2-Dihydroacenaphthylen-1-yl)(methyl)sulfane (16)



According to the general procedure for formal hydromethylthiolation of alkene, 45.7 mg (0.3 mmol, 1.0 equiv) of acenaphthylene was applied. After purification by column chromatography on silica gel ($EtOA_C$ /petroleum ether 1:20), the title compound was obtained as a yellow oil (43.8 mg, 73% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70–7.64 (m, 2H), 7.56–7.47 (m, 3H), 7.30 (d, *J* = 6.8 Hz, 1H), 4.76 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.93 (dd, *J* = 16.4, 6.8 Hz, 1H), 3.47 (dd, *J* = 18.0, 3.6 Hz, 1H), 1.94 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.6, 142.6, 138.2, 131.1, 128.0, 128.0, 123.7, 122.6, 120.1, 119.3, 46.4, 39.9, 12.1. IR (KBr) ν 3045, 2899, 1591, 1404, 776, 682. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{12}S$ 223.0557; Found 223.0554.

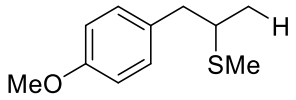
(1-([1,1'-Biphenyl]-4-yl)propan-2-yl)(methyl)sulfane (17)



According to the general procedure for formal hydromethylthiolation of alkene, 58.2 mg (0.3 mmol, 1.0 equiv) of 4-(1-propen-1-yl)-1,1'-biphenyl was applied. After purification by column chromatography on silica gel (DCM /petroleum ether 1:20), the title compound was obtained as a yellow oil (59.6 mg, 82% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ7.64–7.61 (m, 2H), 7.58–7.56 (m, 2H), 7.48–7.44 (m, 2H), 7.38–7.34 (m, 1H), 7.31–7.29 (m, 2H), 3.07–2.95 (m, 2H), 2.77–2.72 (m, 1H), 2.15 (s, 3H), 1.30 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.9, 139.2, 138.6, 129.6, 128.7, 127.0, 127.0, 126.9, 42.8, 42.7, 20.2, 13.7. IR (KBr) ν 3026, 2914, 1636, 1503, 1011, 758, 718, 506. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{18}S$ 243.1207; Found

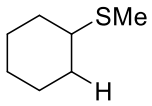
243.1203.

(1-(4-Methoxyphenyl)propan-2-yl)(methyl)sulfane (18)



According to the general procedure for formal hydromethylthiolation of alkene, 44.5 mg (0.3 mmol, 1.0 equiv) of 4-methoxyallylbenzene was applied. After purification by column chromatography on silica gel ($EtOA_C$ /petroleum ether 1:10), the title compound was obtained as a colourless oil (49.4 mg, 84% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.11 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 2.93–2.82 (m, 2H), 2.68–2.57 (m, 1H), 2.09 (s, 3H), 1.22 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.0, 131.6, 130.1, 113.6, 55.2, 43.0, 42.2, 20.1, 13.7. IR (KBr) ν 2925, 1610, 1509, 1433, 1244, 1168, 1029, 801, 523. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{16}OS$ 219.0820; Found 219.0819.

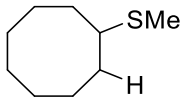
Cyclohexyl(methyl)sulfane[9] (19)



According to the general procedure for formal hydromethylthiolation of alkene, 24.6 mg (0.3 mmol, 1.0 equiv) of cyclohexene was applied. After purification by column chromatography on silica gel (DCM/petroleum ether 1:10), the title compound was obtained as a colourless oil (19.9 mg, 51% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.57–2.50 (m, 1H), 2.08 (s, 3H), 2.01–1.93 (m, 2H), 1.78–1.74(m, 2H), 1.35–1.23 (m,

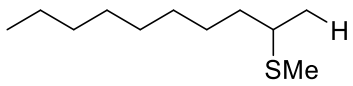
6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 44.9, 33.1, 26.1, 25.8, 13.3.

Cyclooctyl(methyl)sulfane[10] (20)



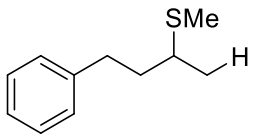
According to the general procedure for formal hydromethylthiolation of alkene, 33.1 mg (0.3 mmol, 1.0 equiv) of cyclooctene was applied. After purification by column chromatography on silica gel (EtOA$_C$ /petroleum ether 1:20), the title compound was obtained as a colourless oil (23.7 mg, 59% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.81–2.74 (m, 1H), 2.07 (s, 3H), 1.97–1.90 (m, 2H), 1.77–1.70 (m, 2H), 1.67–1.61 (m, 2H), 1.60–1.47 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 46.1, 32.0, 27.1, 25.8, 25.2, 14.3.

Decan-2-yl(methyl)sulfane[11] (21)



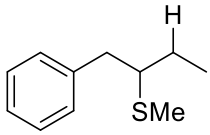
According to the general procedure for formal hydromethylthiolation of alkene, 42.1 mg (0.3 mmol, 1.0 equiv) of 1-decene was applied. After purification by column chromatography on silica gel (EtOA$_C$ /petroleum ether 1:20), the title compound was obtained as a colourless oil (44.0 mg, 78% yield). Data for the major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.68–2.59 (m, 1H), 2.05 (s, 3H), 1.39–1.36 (m, 3H), 1.26–1.24 (m, 14H), 0.87 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 41.2, 36.4, 31.9, 29.5 (2), 29.3, 27.1, 22.6, 20.7, 14.1, 13.1.

Methyl(4-phenylbutan-2-yl)sulfane (22)



According to the general procedure for formal hydromethylthiolation of alkene, 39.7 mg (0.3 mmol, 1.0 equiv) of 4-phenyl-1-butene was applied. After purification by column chromatography on silica gel (DCM/petroleum ether 1:10), the title compound was obtained as a colourless oil (47.0 mg, 87% yield). Data for the major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32–7.29 (m, 2H), 7.24–7.19 (m, 3H), 2.79–2.75 (m, 2H), 2.71–2.64 (m, 1H), 2.09 (s, 3H), 1.95–1.79 (m, 2H), 1.34 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.9, 128.4, 128.3, 125.8, 40.5, 37.9, 33.2, 20.8, 12.8. IR (KBr) ν 2020, 1644, 1445, 1278, 1017, 734, 682, 483. HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{11}H_{16}S$ 203.0870; Found 203.0871.

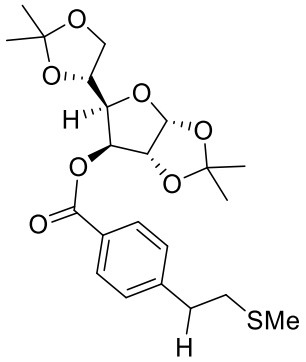
Methyl(1-phenylbutan-2-yl)sulfane (23)



According to the general procedure for formal hydromethylthiolation of alkene, 39.7 mg (0.3 mmol, 1.0 equiv) of 1-phenylbut-2-ene was applied. After purification by column chromatography on silica gel (DCM/petroleum ether 1:10), the title compound was obtained as a colourless oil (40.5 mg, 75% yield). Data for the major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33–7.28 (m, 2H), 7.25–7.18 (m, 3H), 2.93–2.88 (m, 1H), 2.84–2.65 (m, 2H), 2.02 (s, 3H), 1.68–1.46 (m, 2H), 1.02 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.8, 129.2, 128.2, 126.2, 50.1, 40.9, 26.0, 13.3,

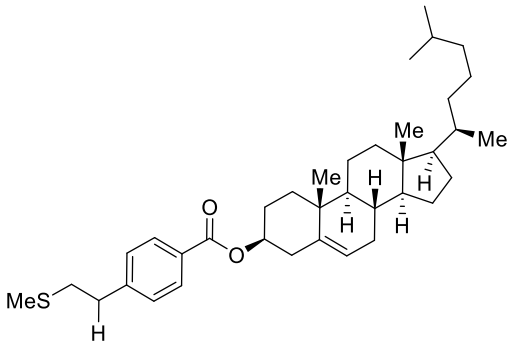
11.1. IR (KBr) ν 3034, 2973, 2921, 1624, 1502, 1450, 745, 683. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{11}H_{16}S$ 203.0870; Found 203.0860.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydro-furo[2,3-d][1,3]dioxol-6-yl 4-(2-(methylthio)ethyl)benzoate (24)



According to the general procedure for formal hydromethylthiolation of alkene, 117 mg (0.3 mmol, 1.0 equiv) of (3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydro-furo[2,3-d][1,3]dioxol-6-yl 4-vinylbenzoate was applied. After purification by column chromatography on silica gel (EtOA$_C$ /petroleum ether 1:10), the title compound was obtained as a colourless oil (46.0 mg, 35% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.94 (d, *J* = 3.6 Hz, 1H), 5.48 (d, *J* = 2.4 Hz, 1H), 4.62 (d, *J* = 3.6 Hz, 1H), 4.37–4.31 (m, 2H), 4.13– 4.06 (m, 2H), 2.98–2.94 (m, 2H), 2.78–2.75 (m, 2H), 2.12 (s, 3H), 1.55 (s, 3H), 1.41 (s, 3H), 1.31 (s, 3H), 1.26 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.1, 146.5, 129.9, 128.7, 127.6, 112.3, 109.3, 105.1, 83.3, 79.9, 76.5, 72.5, 67.2, 35.7, 35.3, 26.8, 26.7, 26.2, 25.2, 15.7. IR (KBr) ν 3002, 1745, 1624, 1382, 1276, 1214, 1172, 1084, 1015, 840, 727, 482. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{22}H_{30}O_7S$ 461.1610; Found 461.1606.

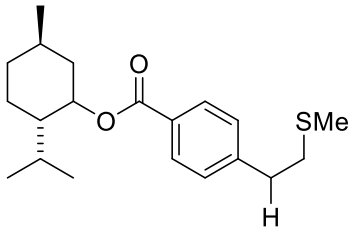
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(2-(methylthio)ethyl)benzoate (25)



According to the general procedure for formal hydromethylthiolation of alkene, 155 mg (0.3 mmol, 1.0 equiv) of (3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methyl-heptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenan-thren-3-yl 4-vinylbenzoate was applied. After purification by column chromatography on silica gel (EtOAc /petroleum ether 1:10), the title compound was obtained as a white solid (67.7 mg, 40% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.42–5.40 (m, 1H), 4.87–4.80 (m, 1H), 2.97–2.93 (m, 2H), 2.78–2.74 (m, 2H), 2.45 (d, *J* = 8.4 Hz, 2H), 2.12 (s, 3H), 2.04–1.88 (m, 4H), 1.86–1.81 (m, 1H), 1.74–1.70 (m, 1H), 1.61–1.43 (m, 6H), 1.36–1.30 (m, 3H), 1.28–1.23 (m, 2H), 1.21–1.09 (m, 6H), 1.06 (s, 3H), 1.03–0.95 (m, 3H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 1.6 Hz, 3H), 0.86 (d, *J* = 2 Hz, 3H), 0.68 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 145.6, 139.6, 129.8, 129.0, 128.5, 122.7, 74.4, 56.6, 56.1, 50.0, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.1, 35.8, 35.4, 31.9, 31.8, 28.2, 28.0, 27.9, 24.3, 23.8, 22.8, 22.6, 21.0, 19.4, 18.7, 15.7, 11.8. IR (KBr) ν 2937,

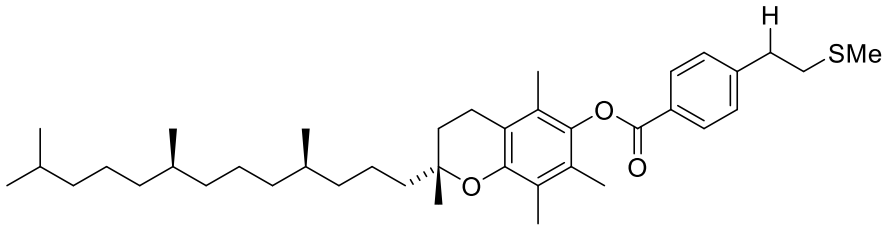
2342, 1721, 1627, 1469, 1279, 1100, 762, 483. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{37}H_{56}O_2S$ 587.3899; Found 587.3902.

(2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-(2-(methylthio)ethyl)benzoate (26)



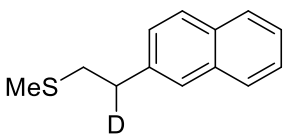
According to the general procedure for formal hydromethylthiolation of alkene, 85.9 mg (0.3 mmol, 1.0 equiv) of (2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-vinylbenzoate was applied. After purification by column chromatography on silica gel ($EtOA_C$ /petroleum ether 1:20), the title compound was obtained as a colourless oil (77.2 mg, 77% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.95–4.88 (m, 1H), 2.97–2.93 (m, 2H), 2.78–2.75 (m, 2H), 2.12 (s, 3H), 2.11–2.09 (m, 1H), 1.99–1.92 (m, 1H), 1.74–1.67 (m, 2H), 1.58–1.50 (m, 2H), 1.17–1.04 (m, 2H), 0.97–0.87 (m, 7H), 0.78 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 145.6, 129.7, 128.9, 128.5, 74.6, 47.2, 40.9, 35.7, 35.4, 34.2, 31.4, 26.4, 23.5, 22.0, 20.7, 16.4, 15.7. IR (KBr) ν 2930, 1707, 1435, 1267, 1173, 1111, 964, 755, 483. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{30}O_2S$ 335.2045; Found 335.2040.

(*R*)-2,5,7,8-Tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl 4-(2-(methylthio)ethyl)benzoate (27)



According to the general procedure for formal hydromethylthiolation of alkene, 168 mg (0.3 mmol, 1.0 equiv) of (*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)-chroman-6-yl 4-vinylbenzoate was applied. After purification by column chromatography on silica gel (EtOAc /petroleum ether 1:20), the title compound was obtained as a yellow oil (133 mg, 73% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 3.02–2.99 (m, 2H), 2.83–2.79 (m, 2H), 2.61 (t, *J* = 6.8 Hz, 2H), 2.16 (s, 3H), 2.12 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.85–1.76 (m, 2H), 1.59–1.49 (m, 5H), 1.45 (s, 1H), 1.43–1.33 (m, 4H), 1.29–1.25 (m, 8H), 1.16–1.10 (m, 3H), 1.08–1.04 (m, 2H), 0.87–0.84 (m, 13H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.1, 149.4, 146.4, 140.5, 130.4, 128.8, 127.7, 126.9, 125.1, 123.1, 117.4, 75.0, 39.3, 37.4, 37.2, 35.8, 35.4, 32.8, 31.2, 31.0, 30.3, 28.0, 24.8, 24.4, 24.2, 23.7, 22.7, 22.6, 21.0, 20.6, 19.7, 19.6, 15.7, 13.1, 12.2, 11.8. IR (KBr) ν 2920, 1731, 1610, 1460, 1245, 1170, 1104, 749. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{39}H_{60}O_3S$ 609.4341; Found 609.4337.

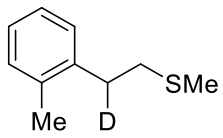
Methyl(2-(naphthalen-2-yl)ethyl-2-d)sulfane (28)



According to the general procedure for formal deuteromethylthiolation of alkene, 46.3

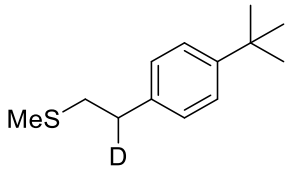
mg (0.3 mmol, 1.0 equiv) of 2-vinylnaphthalene was applied. After purification by column chromatography on silica gel ($EtOAc$ /petroleum ether 1:20), the title compound was obtained as a white solid (46.9 mg, 77% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85–7.80 (m, 3H), 7.68–7.67 (m, 1H), 7.51–7.43 (m, 2H), 7.38–7.36 (m, 1H), 3.09–3.05 (m, 1H), 2.87–2.85 (m, 2H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.9, 133.5, 132.1, 128.0, 127.6, 127.4, 127.0, 126.7, 126.0, 125.3, 35.6 (t, J =19.8 Hz), 35.6, 15.7. IR (KBr) ν 2914, 1583, 1423, 812, 479. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{13}DS$ 204.0957; Found 204.0951.

Methyl(2-(o-tolyl)ethyl-2-d)sulfane (29)



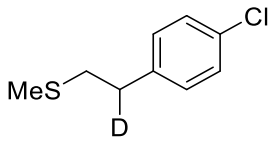
According to the general procedure for formal deuteromethylthiolation of alkene, 35.4 mg (0.3 mmol, 1.0 equiv) of 2-methylstyrene was applied. After purification by column chromatography on silica gel ($EtOAc$ /petroleum ether 1:20), the title compound was obtained as a colourless oil (25 mg, 50% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16–7.14(m, 4H), 2.90–2.86 (m, 1H), 2.71–2.69 (m, 2H), 2.33 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.7, 135.9, 130.3, 129.0, 126.5, 126.1, 34.4, 33.0 (t, J =19.9 Hz), 19.3, 15.7. IR (KBr) ν 2903, 1624, 1471, 1249, 749. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{13}DS$ 190.0777; Found 190.0779.

(2-(4-(*Tert*-butyl)phenyl)ethyl-2-d)(methyl)sulfane (30)



According to the general procedure for formal deuteromethylthiolation of alkene, 48.1 mg (0.3 mmol, 1.0 equiv) of 4-*tert*-butylstyrene was applied. After purification by column chromatography on silica gel ($EtOA_C$ /petroleum ether 1:20), the title compound was obtained as a yellow oil (44.5 mg, 71% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35–7.33 (m, 2H), 7.17–7.15 (m, 2H), 2.90–2.85 (m, 1H), 2.75 (d, *J* = 8.8 Hz, 2H), 2.15 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.1, 137.4, 128.1, 125.3, 35.7, 34.9 (t, *J* =19.8 Hz), 34.4, 31.3, 15.7. IR (KBr) ν 2958, 1639, 1513, 1360, 1263, 777, 541. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{19}DS$ 210.1427; Found 210.1419.

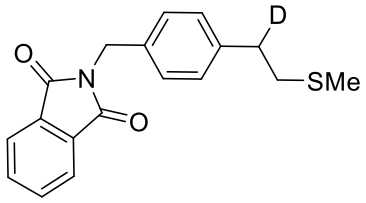
(2-(4-Chlorophenyl)ethyl-2-d)(methyl)sulfane (31)



According to the general procedure for formal deuteromethylthiolation of alkene, 41.6 mg (0.3 mmol, 1.0 equiv) of 4-chlorostyrene was applied. After purification by column chromatography on silica gel ($EtOA_C$ /petroleum ether 1:20), the title compound was obtained as a yellow oil (28.1 mg, 50% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28–7.26 (m, 2H), 7.16–7.13 (m, 2H), 2.85 (t, *J* = 8.8 Hz, 1H), 2.72 (d, *J* = 8.4 Hz, 2H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.9, 132.1, 129.8, 128.5, 35.6, 34.7 (t, *J* =19.9 Hz), 15.7. IR (KBr) ν 2910, 1623, 1498, 1100, 787, 504. HRMS

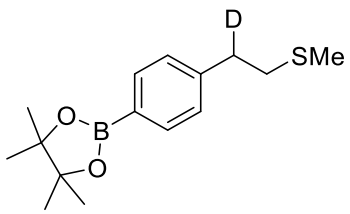
(ESI) m/z: $[M + H]^+$ Calcd for $C_9H_{10}DClS$ 18.0411; Found 18.0405.

2-(4-(2-(Methylthio)ethyl-1-d)benzyl)isoindoline-1,3-dione (32)



According to the general procedure for formal deuteromethylthiolation of alkene, 78.9 mg (0.3 mmol, 1.0 equiv) of 2-(4-vinylbenzyl)isoindoline-1,3-dione was applied. After purification by column chromatography on silica gel ($EtOA_C$ /petroleum ether 1:20), the title compound was obtained as a white solid (37.5 mg, 40% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85–7.80 (m, 2H), 7.72–7.67 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 4.81 (s, 2H), 2.83 (t, *J* = 8.8 Hz, 1H) 2.69 (d, *J* = 7.6 Hz, 2H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 140.1, 134.3, 133.9, 132.0, 128.8, 128.7, 123.3, 41.2, 35.5, 35.0 (t, *J* =19.5 Hz), 15.6. IR (KBr) ν 2916, 1707, 1388, 1096, 930, 707, 541. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{16}DNO_2S$ 313.1121; Found 313.1115.

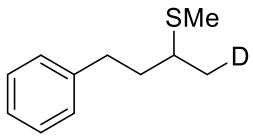
4,4,5,5-Tetramethyl-2-(4-(2-(methylthio)ethyl-1-d)phenyl)-1,3,2-dioxaborolane (33)



According to the general procedure for formal deuteromethylthiolation of alkene, 69.0

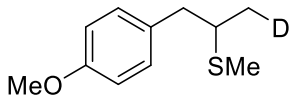
mg (0.3 mmol, 1.0 equiv) of 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane was applied. After purification by column chromatography on silica gel (EtOAc /petroleum ether 1:20), the title compound was obtained as a colourless oil (50.2 mg, 60% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.89 (t, *J* = 8.4 Hz, 1H), 2.74 (d, *J* = 8.0 Hz, 2H), 2.12 (s, 3H), 1.34 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.8, 135.0, 127.9, 83.7, 35.9 (t, *J* =15.5 Hz), 35.5, 24.8, 15.7. IR (KBr) ν 2972, 1612, 1364, 1152, 1085, 853, 651. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{22}DBO_2S$ 280.1653; Found 280.1651.

Methyl(4-phenylbutan-2-yl-1-d)sulfane (34)



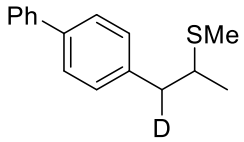
According to the general procedure for formal deuteromethylthiolation of alkene, 39.7 mg (0.3 mmol, 1.0 equiv) of 4-phenyl-1-butene was applied. After purification by column chromatography on silica gel (EtOAc /petroleum ether 1:20), the title compound was obtained as a colourless oil (20.1 mg, 37% yield). Data for the major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31–7.27 (m, 2H), 7.22–7.18 (m, 3H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.70–2.63 (m, 1H), 2.08 (s, 3H), 1.94–1.74 (m, 2H), 1.32–1.29 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.9, 128.4, 128.3, 125.8, 40.4, 37.9, 33.2, 20.5 (t, *J* =19.5 Hz), 12.8. IR (KBr) ν 2916, 1610, 1458, 1253, 1019, 745. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{15}DS$ 182.1114; Found 182.1115.

(1-(4-Methoxyphenyl)propan-2-yl-3-d)(methyl)sulfane (35)



According to the general procedure for formal deuteromethylthiolation of alkene, 44.5 mg (0.3 mmol, 1.0 equiv) of 4-methoxyallylbenzene was applied. After purification by column chromatography on silica gel (EtOAc /petroleum ether 1:20), the title compound was obtained as a yellow oil (20.1 mg, 34% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.11 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.79 (s, 3H), 2.93–2.83 (m, 2H), 2.64–2.59 (m, 1H), 2.09 (s, 3H), 1.23–1.19 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.0, 131.6, 130.1, 113.6, 55.2, 43.0, 42.2, 19.8 (t, *J* =19.6 Hz), 13.7. IR (KBr) ν 2903, 1624, 1513, 1221, 1040, 819. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{15}DOS$ 220.0882; Found 220.0882.

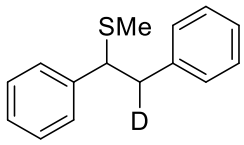
(1-([1,1'-Biphenyl]-4-yl)propan-2-yl-1-d)(methyl)sulfane (36)



According to the general procedure for formal deuteromethylthiolation of alkene, 58.2 mg (0.3 mmol, 1.0 equiv) of 4-(1-propen-1-yl)-1,1'-biphenyl was applied. After purification by column chromatography on silica gel (DCM /petroleum ether 1:30), the title compound was obtained as a yellow oil (59.8 mg, 82% yield, d.r. > 20:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62–7.60 (m, 2H), 7.57–7.54 (m, 2H), 7.47–7.43 (m, 2H), 7.38–7.32 (m, 1H), 7.30–7.27 (m, 2H), 3.02–2.94 (m, 2H), 2.14 (s, 3H), 1.28 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.9, 139.2, 138.6, 129.6, 128.7, 127.1,

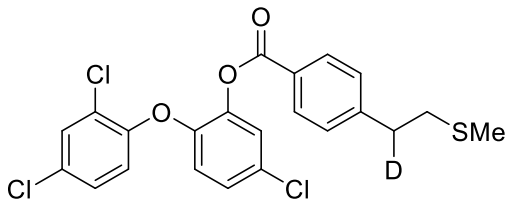
127.0, 127.0, 42.7, 42.4 (t, *J* =19.8 Hz), 20.2, 13.7. IR (KBr) ν 2930, 1610, 1486, 1082, 694, 513. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}DS$ 244.1270; Found 244.1263.

(1,2-Diphenylethyl-2-d)(methyl)sulfane (37)



According to the general procedure for formal deuteromethylthiolation of alkene, 54.1 mg (0.3 mmol, 1.0 equiv) of stilbene was applied. After purification by column chromatography on silica gel ($EtOA_C$ /petroleum ether 1:20), the title compound was obtained as a colourless oil (41.2 mg, 60% yield, d.r. > 20:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35–7.21 (m, 8H), 7.13–7.10 (m, 2H), 3.95 (d, *J* = 7.2 Hz, 1H), 3.20 (d, *J* = 7.2 Hz, 1H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.7, 138.9, 129.1, 128.3, 128.1, 127.9, 127.1, 126.3, 53.3, 42.4 (t, *J* =19.8 Hz), 14.6. IR (KBr) ν 3026, 2910, 1621, 1456, 1068, 710, 516. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{15}DS$ 230.1114; Found 230.1116.

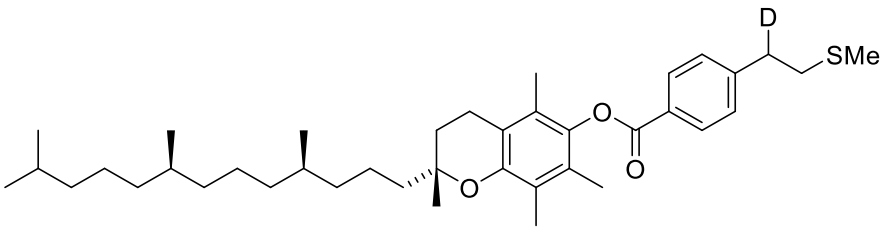
5-Chloro-2-(2,4-dichlorophenoxy)phenyl 4-(2-(methylthio)ethyl-1-d)benzoate (38)



According to the general procedure for formal deuteromethylthiolation of alkene, 125 mg (0.3 mmol, 1.0 equiv) of 5-chloro-2-(2,4-dichlorophenoxy)phenyl 4-vinylbenzoate was applied. After purification by column chromatography on silica gel ($EtOA_C$

/petroleum ether 1:20), the title compound was obtained as a colourless oil (86.9 mg, 62% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.33–7.29 (m, 4H), 7.21 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.14 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.92 (d, *J* = 4 Hz, 1H), 6.89 (d, *J* = 4 Hz, 1H), 2.96 (t, *J* = 7.6 Hz, 1H), 2.77 (d, *J* = 8.0 Hz, 2H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.9, 151.1, 147.0, 146.8, 141.8, 130.5, 130.3, 129.3, 129.2, 128.7, 128.0, 127.0, 126.5, 125.9, 124.6, 120.4, 120.3, 35.4 (t, *J* =19.7 Hz), 35.2, 15.7. IR (KBr) ν 3077, 2920, 1748, 1613, 1476, 1267, 1059, 800, 743, 563, 471. HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{22}H_{16}DCl_3O_3S$ 489.9924; Found 489.9918.

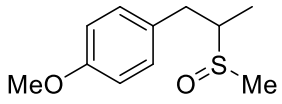
(*R*)-2,5,7,8-Tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl 4-(2-(methylthio)ethyl-1-d)benzoate (39)



According to the general procedure for formal deuteromethylthiolation of alkene, 168 mg (0.3 mmol, 1.0 equiv) of (*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)-chroman-6-yl 4-vinylbenzoate was applied. After purification by column chromatography on silica gel (EtOA$_C$ /petroleum ether 1:20), the title compound was obtained as a colourless oil (96.9 mg, 53% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 3.00 (t, *J* = 7.6 Hz, 1H), 2.81 (d, *J* = 7.6 Hz, 2H), 2.65–2.60 (m, 2H), 2.17 (s, 3H), 2.13 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H),

1.90–1.74 (m, 2H), 1.61–1.49 (m, 4H), 1.46–1.37 (m, 4H), 1.33–1.21 (m, 10H), 1.18–1.05 (m, 6H), 0.89–0.86 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.0, 149.4, 146.4, 140.5, 130.4, 128.7, 127.7, 126.9, 125.1, 123.0, 117.4, 75.0, 40.3, 39.5, 39.3, 37.4, 37.2, 35.6 (t, *J* = 15.1 Hz), 35.3, 32.8, 32.7, 32.6, 31.2, 31.0, 28.0, 24.8, 24.4, 24.2, 23.7, 22.7, 22.6, 21.0, 20.6, 19.7, 19.6, 15.7, 13.0, 12.2, 11.8. IR (KBr) ν 2899, 2261, 1937, 1728, 1603, 1446, 1257, 1079, 902, 723. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{39}H_{59}DO_3S$ 610.4404; Found 610.4396.

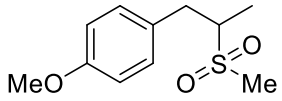
1-Methoxy-4-(2-(methylsulfinyl)propyl)benzene (40)



At –78 °C (liquid nitrogen and acetone), to a solution of (1-(4-methoxyphenyl)propan-2-yl)(methyl)sulfane (196 mg, 1.0 mmol, 1.0 equiv) in dichloromethane (10 mL) was added dropwise a solution of *m*-CPBA (173 mg, 1.0 mmol, 1.0 equiv) in dichloromethane (5 mL). After one hour stirring at that temperature, dichloromethane (5 mL) and saturated aqueous sodium bicarbonate solution (5 mL) were added, the layers were separated and the aqueous layer was extracted with dichloromethane (3 × 5 mL). The combined organic layers were dried over sodium sulfate, filtered and concentrated. The crude was purified by flash column chromatography on silica gel (methanol), the title compound was obtained as a colourless oil (180 mg, 85% yield, dr 1:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.02–6.99 (m, 2H), 6.75–6.70 (m, 2H), 3.66 (s, 3H), 3.11–2.98 (m, 1H), 2.67–2.59 (m, 1H), 2.53–2.47(m, 1H), 2.37 (d, *J* = 30.4 Hz, 3H), 1.05 (dd, *J* = 39.2, 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.2,

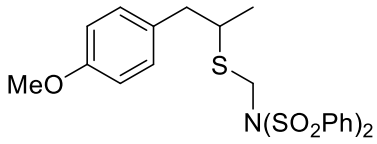
130.1, 129.9, 113.8, 57.3, 55.0, 35.2, 34.2, 10.4. IR (KBr) ν 2919, 2533, 2041, 1591, 1497, 1247, 1016, 535. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{16}O_2S$ 235.0769; Found 235.0766.

1-Methoxy-4-(2-(methylsulfonyl)propyl)benzene (41)



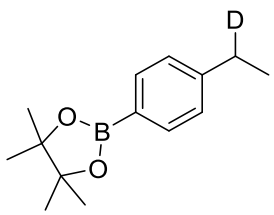
To a solution of (1-(4-methoxyphenyl)propan-2-yl)(methyl)sulfane (196 mg, 1.0 mmol, 1.0 equiv) in dichloromethane (10 mL) was added dropwise a solution of *m*-CPBA (346 mg, 2.0 mmol, 2.0 equiv) in dichloromethane (5 mL) at room temperature. After one hour, dichloromethane (5 mL) and saturated aqueous sodium bicarbonate solution (5 mL) were added, the layers were separated and the aqueous layer was extracted with dichloromethane (3 × 5 mL). The combined organic layers were dried over sodium sulfate, filtered and concentrated. The crude product was purified by flash column chromatography on silica gel ($EtOA_C$ /petroleum ether 1:3), the title compound was obtained as a colourless oil (203 mg, 89% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.11 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 3.79 (s, 3H), 3.38 (dd, *J* = 14.0, 4.4 Hz, 1H), 3.17–3.10 (m, 1H), 2.80 (s, 3H), 2.63 (dd, *J* = 13.6, 10.4 Hz, 1H), 1.30 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.6, 130.1, 128.5, 114.2, 60.8, 55.2, 38.0, 34.5, 12.8. IR (KBr) ν 2930, 2261, 2052, 1728, 1591, 1498, 1268, 1111, 1037, 954, 776, 494. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{16}O_3S$ 229.0898; Found 229.0895.

_N_-(((1-(4-Methoxyphenyl)propan-2-yl)thio)methyl)-_N_-(phenylsulfonyl)benzene-sulfonamide (42)



To a 10 mL reaction tube was sequentially added (1-(4-methoxyphenyl)propan-2-yl)(methyl)sulfane (58.8 mg, 0.3 mmol, 1.0 equiv), dry acetonitrile (2 mL), and *N*-fluorobis(benzenesulfonyl)imide (113 mg, 0.36 mmol, 1.2 equiv). The system was heated to 80 ˚C with an oil bath. After stirring for 1 h, dichloromethane (5 mL) was added, and the solution was transferred to a 25 mL flask. The solvent was removed under reduced pressure. After purification by column chromatography on silica gel ($EtOA_C$ /petroleum ether 1:20), the title compound was obtained as a colourless oil (60.4 mg, 41%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12–8.09 (m, 4H), 7.67–7.63 (m, 2H), 7.58–7.52 (m, 4H), 7.12–7.10 (m, 2H), 6.84–6.81 (m, 2H), 4.84 (d, *J* = 3.2 Hz, 2H), 3.79 (s, 3H), 3.22–3.16 (m, 1H), 2.85 (dd, *J* = 13.2, 6.0 Hz, 1H), 2.55 (dd, *J* = 13.6, 8.4 Hz, 1H), 1.09 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.1, 139.9, 133.9, 131.0, 130.4, 128.9, 128.5, 113.6, 55.2, 50.9, 43.0, 41.2, 20.4. IR (KBr) ν 2940, 1633, 1351, 1162, 577, 431. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{25}NO_5S_3$ 514.0793; Found 514.0791.

2-(4-(Ethyl-1-d)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (43)



A solution of 4,4,5,5-tetramethyl-2-(4-(2-(methylthio)ethyl-1-d)phenyl)-1,3,2-dioxaborolane (55.8 mg, 0.2 mmol) in 3 mL of EtOH was heated to 60 ˚C with an oil bath in the presence of approximately 500 mg of Raney nickel for overnight with stirring. The mixture was then filtrated, dissolved in water, extracted with ether, dried over Na_2SO_4, filtrated and concentrated. After purification by column chromatography on silica gel ($EtOA_C$ /petroleum ether 1:20), the title compound was obtained as a colourless oil (26.1 mg, 56%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.65 (q, *J* = 7.6 Hz, 1H), 1.34 (s, 12H), 1.23 (d, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.7, 134.9, 127.3, 83.6, 28.7 (t, *J* = 19.6 Hz), 24.8, 15.4. IR (KBr) ν 2972, 1603, 1351, 1152, 838, 650. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{20}DBO_2$ 234.1776; Found 234.1771.

4 References

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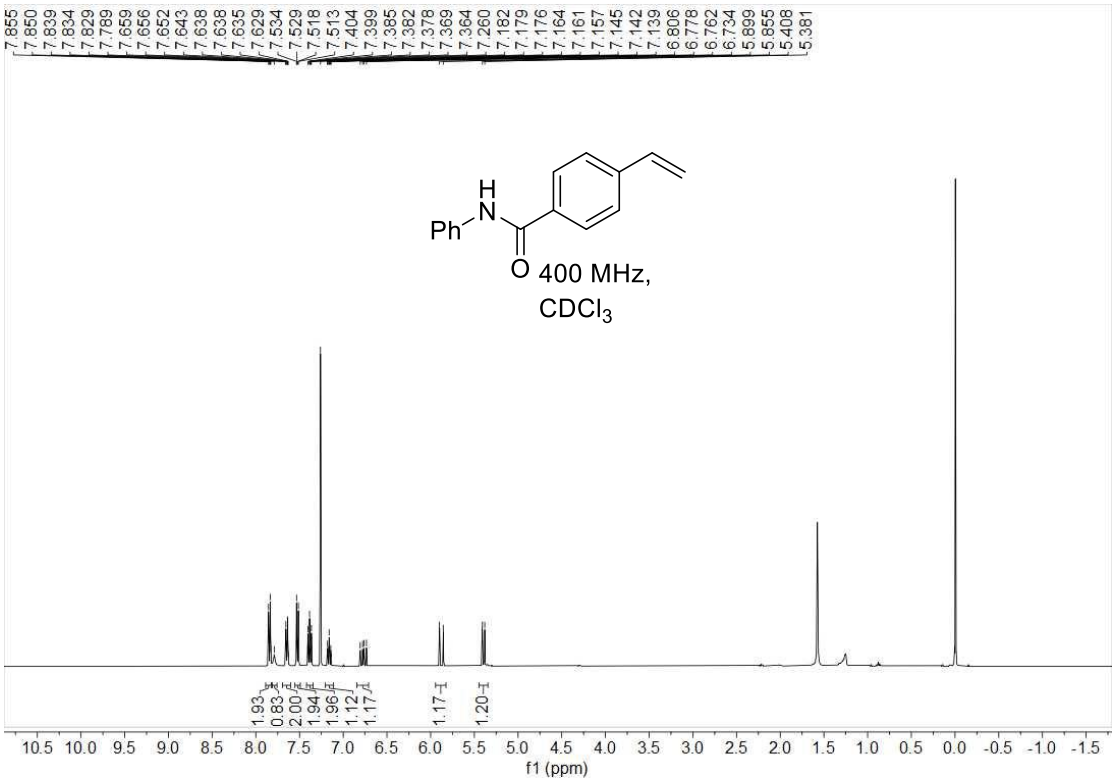
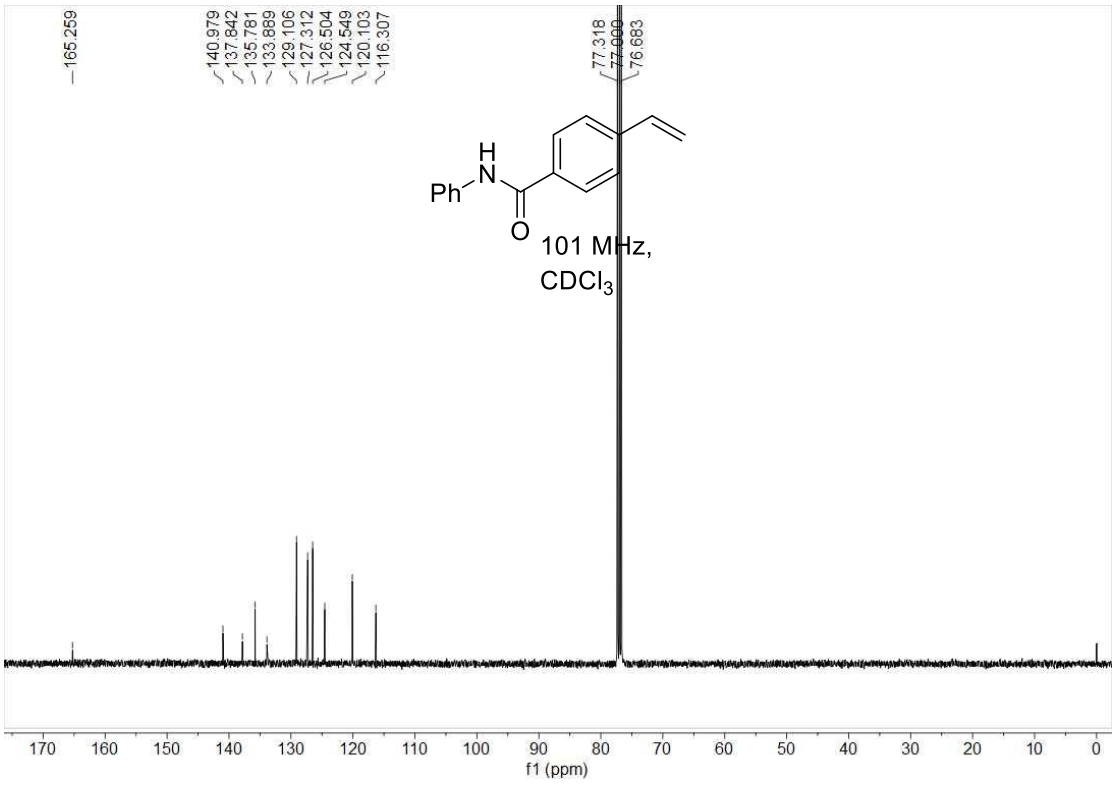
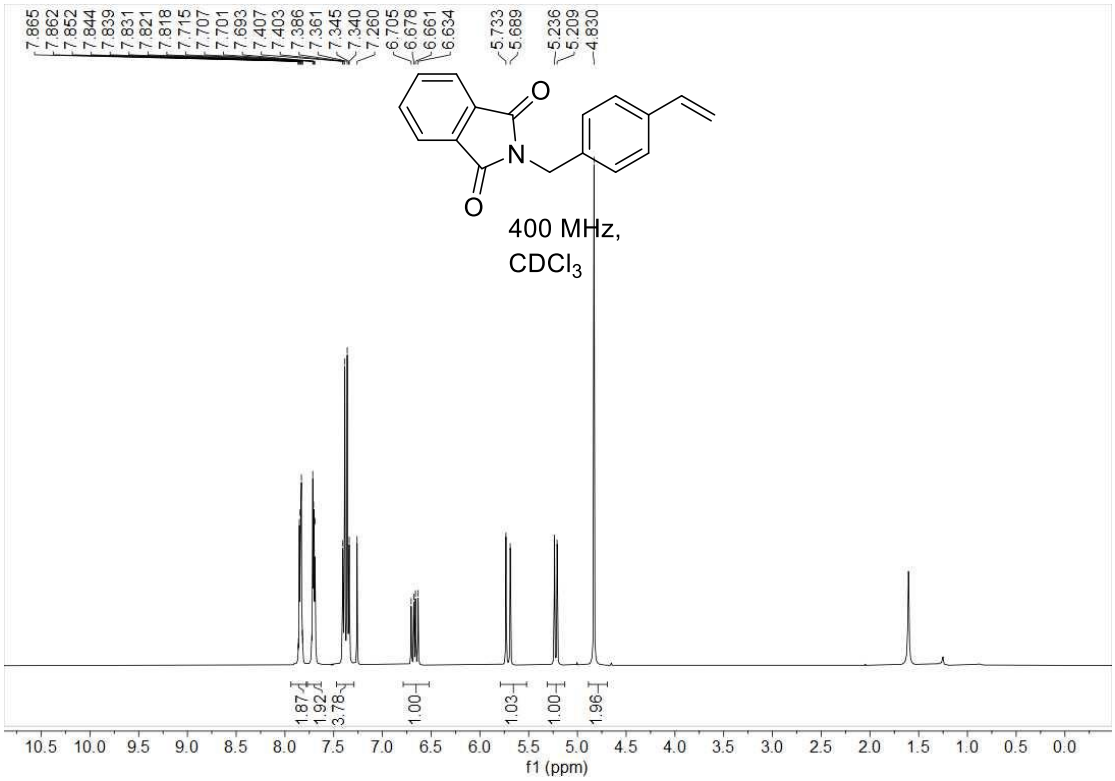
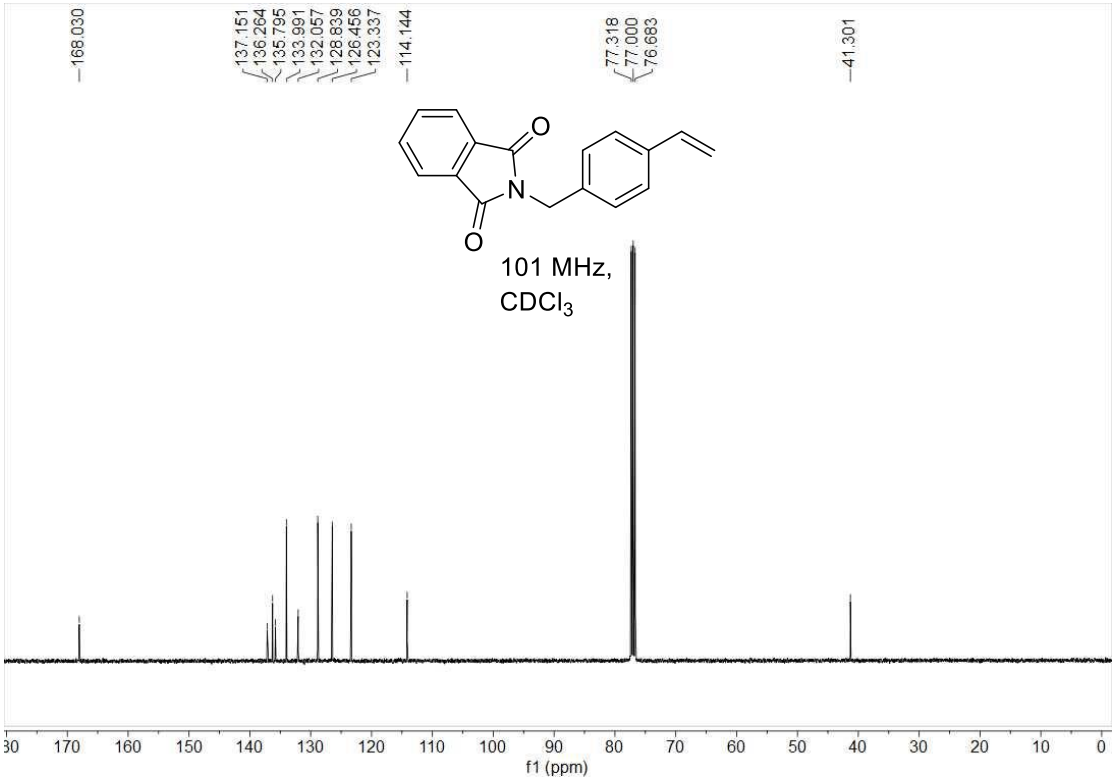
5 NMR spectra






7.865
7.862
7.852
7.844
7.839
7.831
7.821
7.818
7.715
7.707
7.701
7.693
7.407
7.403
7.386
7.361
7.345
7.340
7.260
6.705
6.678
6.661
6.634
5.733
5.689
5.236
5.209
4.830
O
N
O
400 MHz,
CDCl3
1.87
1.92
3.78
1.00
1.03
1.00
1.96
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.030
137.151
136.264
135.795
133.991
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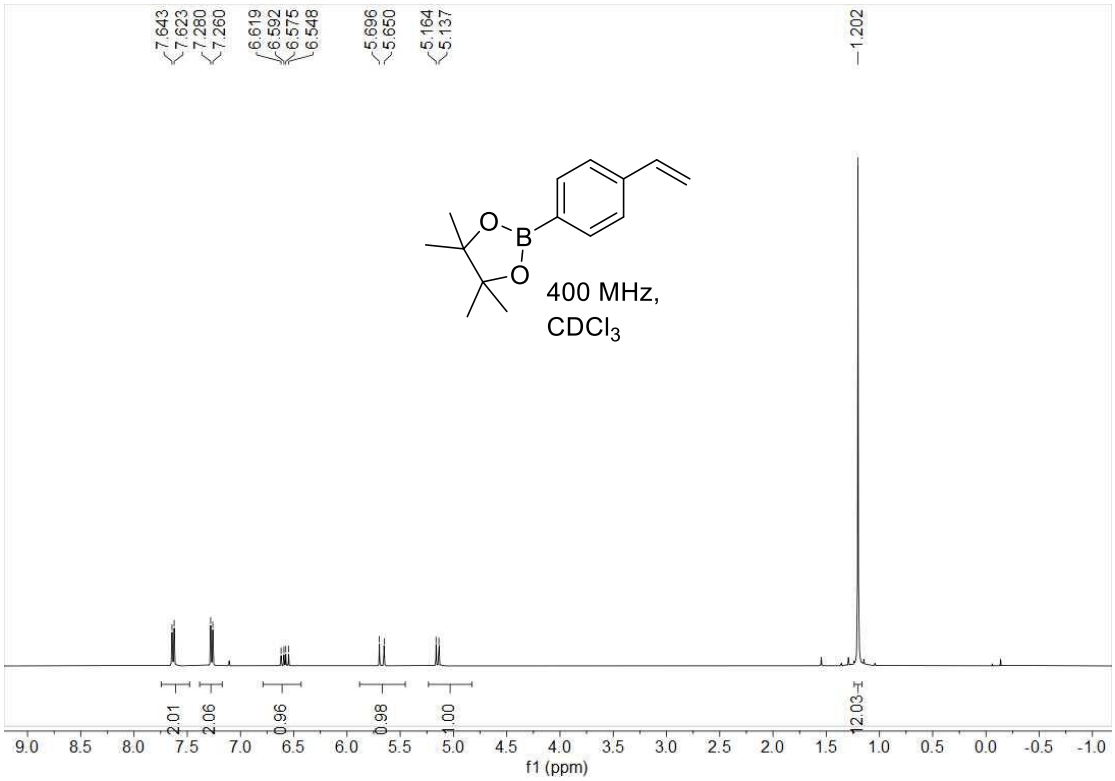
128.839
126.456
123.337
114.144
77.318
77.000
76.683
41.301
O
N
O
101 MHz,
CDCl3
30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.623
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7.260
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6.592
6.575
6.548
5.696
5.650
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5.137
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400 MHz,
CDCl3
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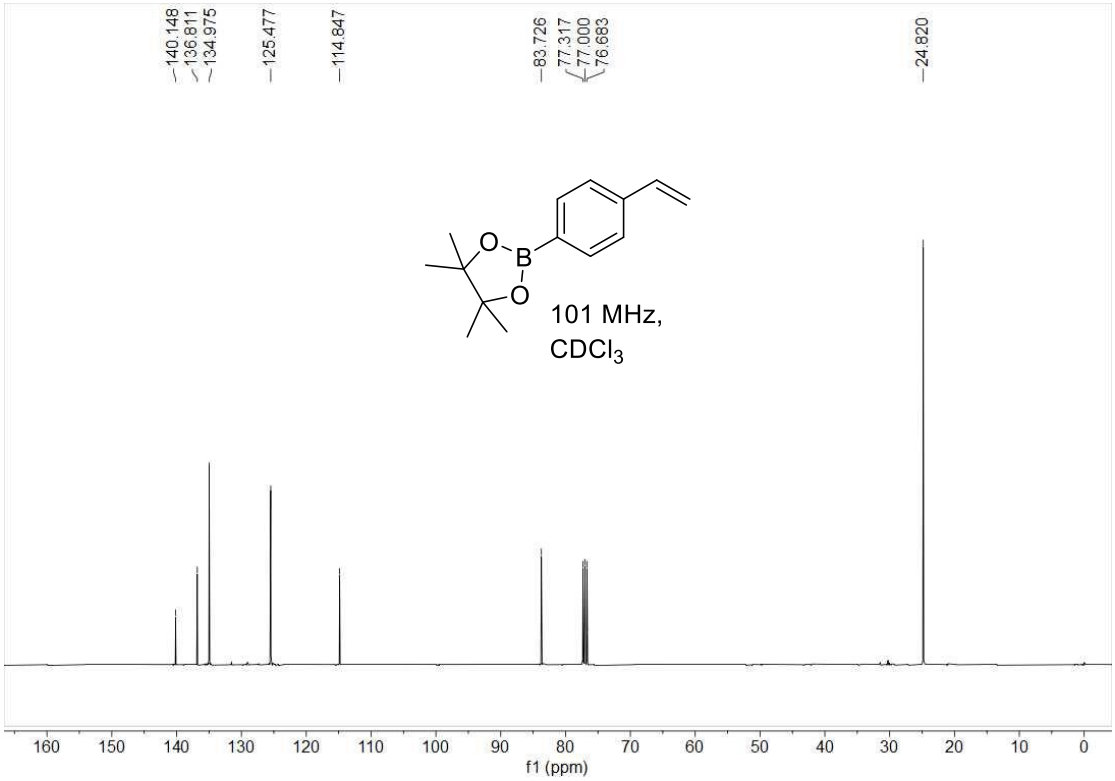
2.06
0.96
0.98
1.00
12.03
f1 (ppm)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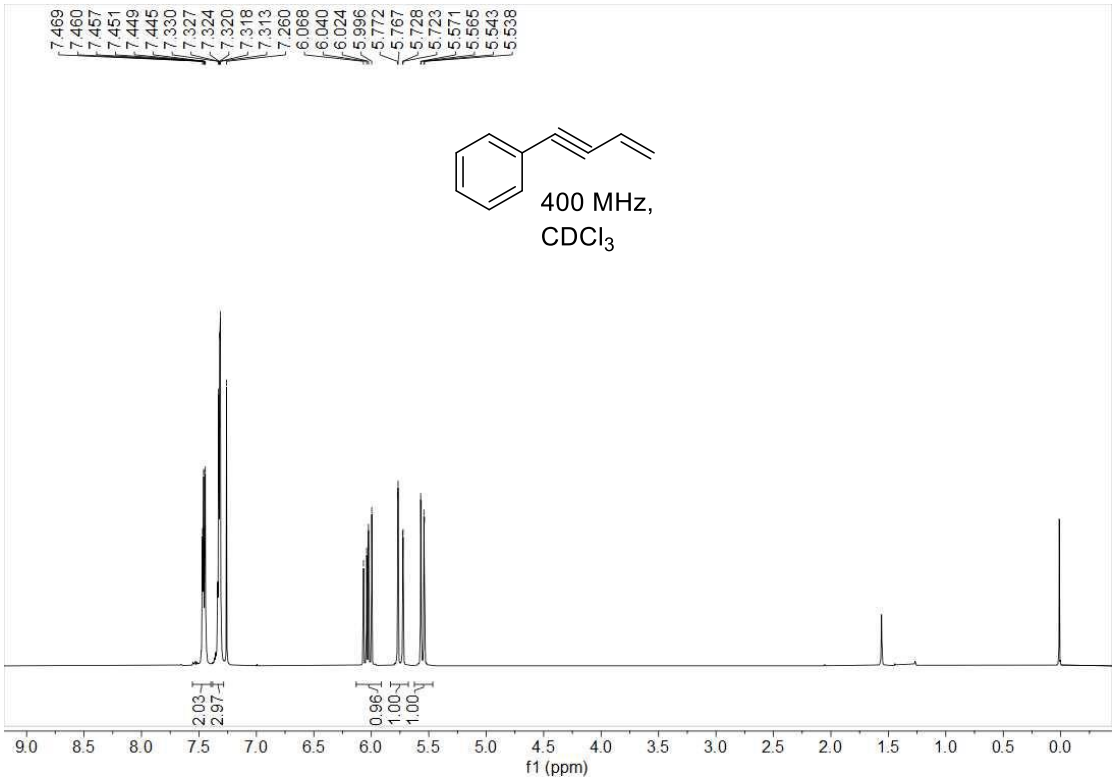
77.317
77.000
76.683
24.820
101 MHz,
CDCl3
f1 (ppm)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7.324
7.320
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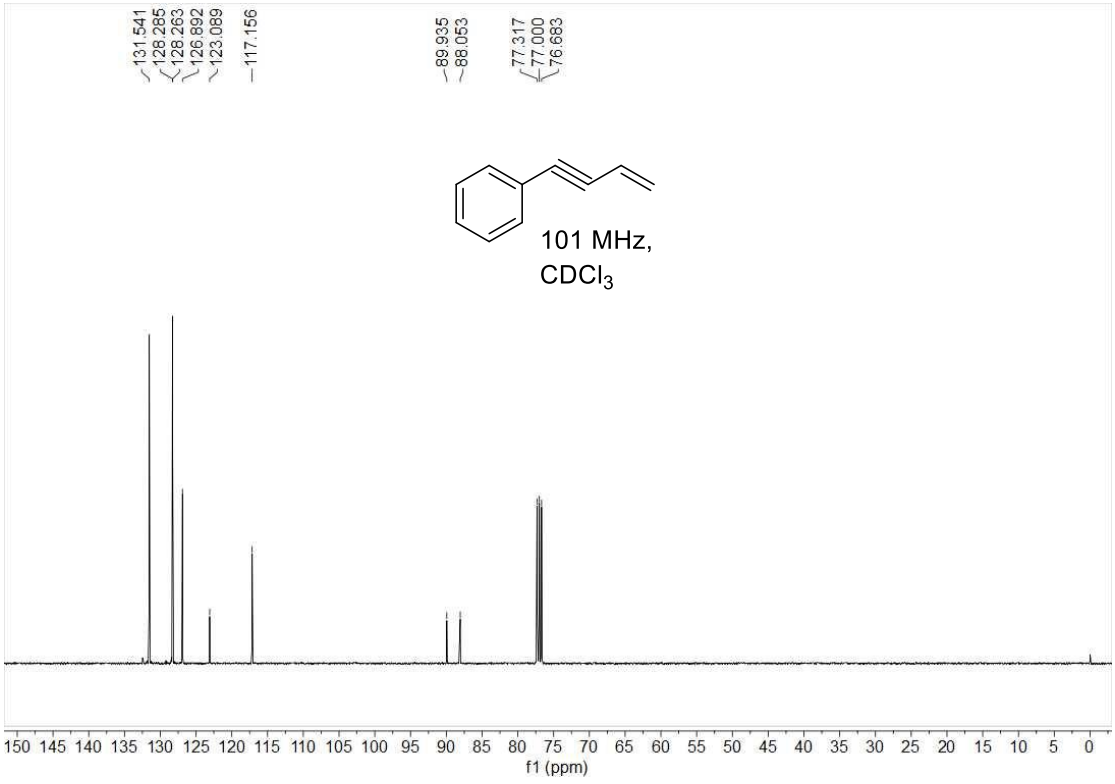
5.772
5.767
5.728
5.723
5.571
5.565
5.543
5.538
400 MHz,
CDCl3
2.03
2.97
0.96
1.00
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.263
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123.089
117.156
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CDCl3
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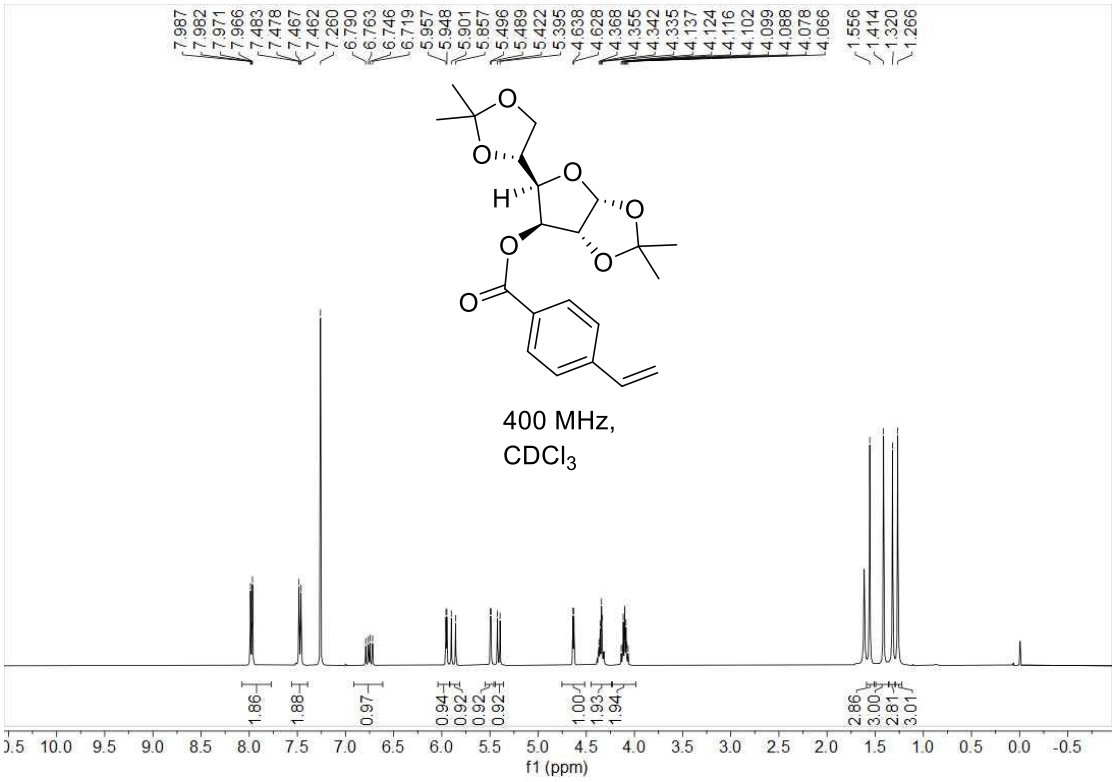
f1 (ppm)


7.987
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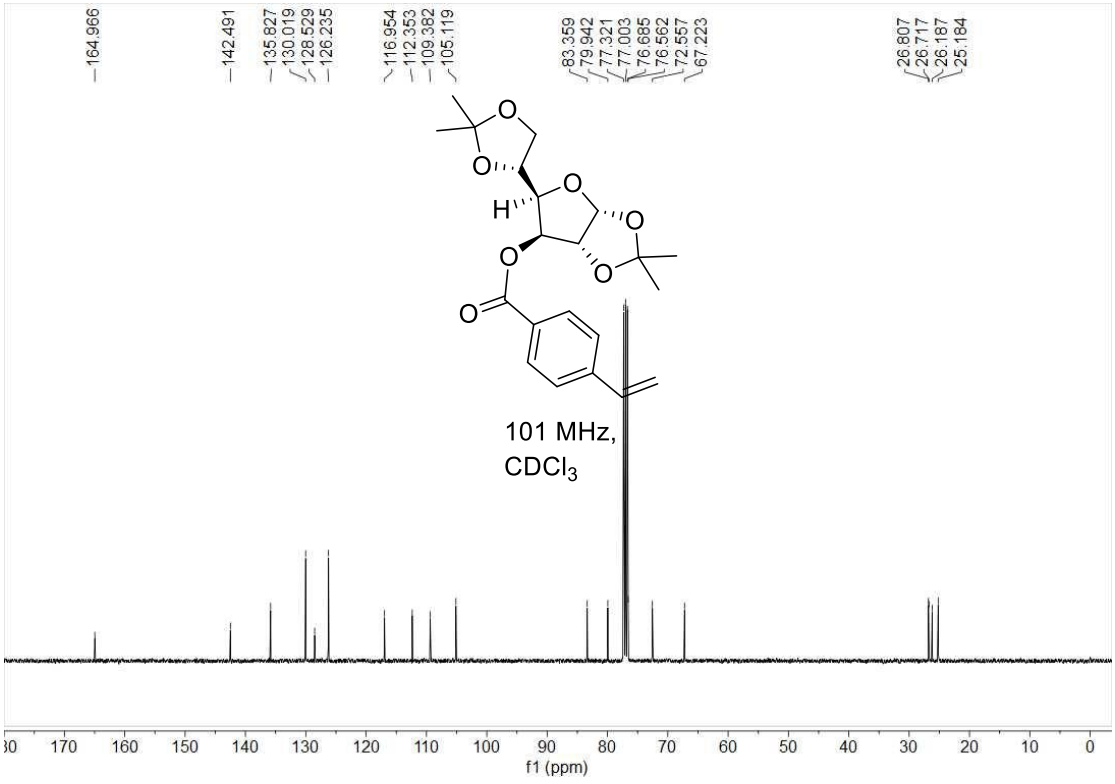
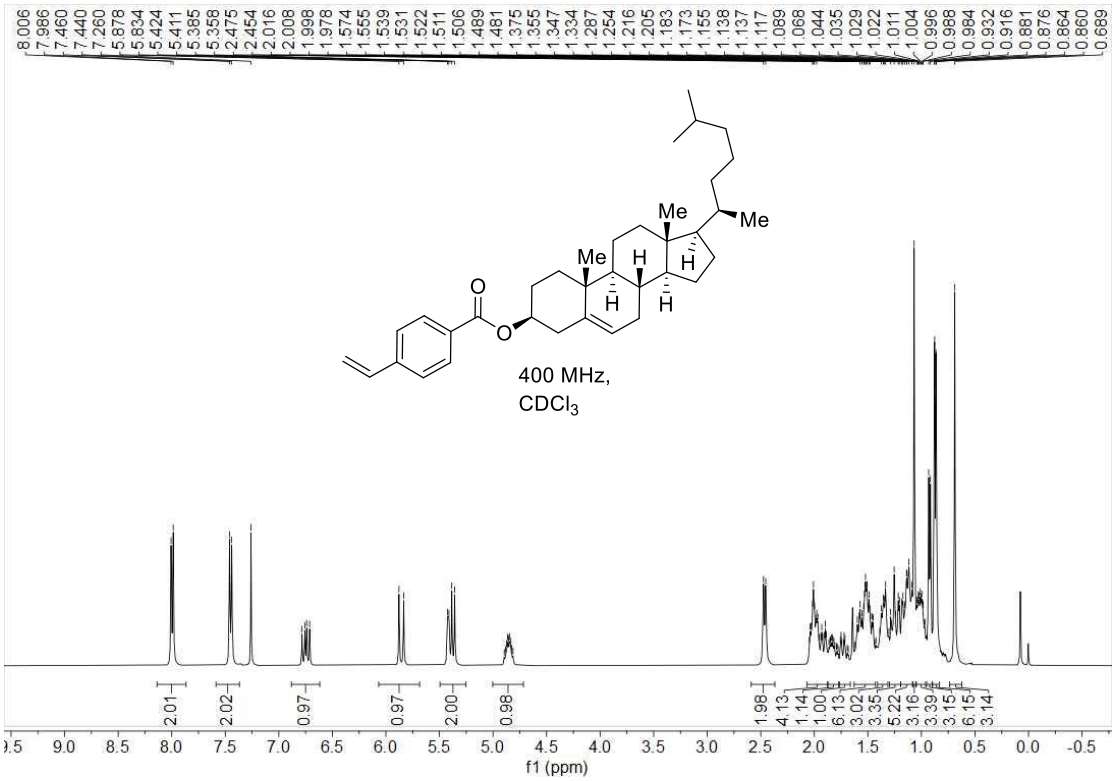
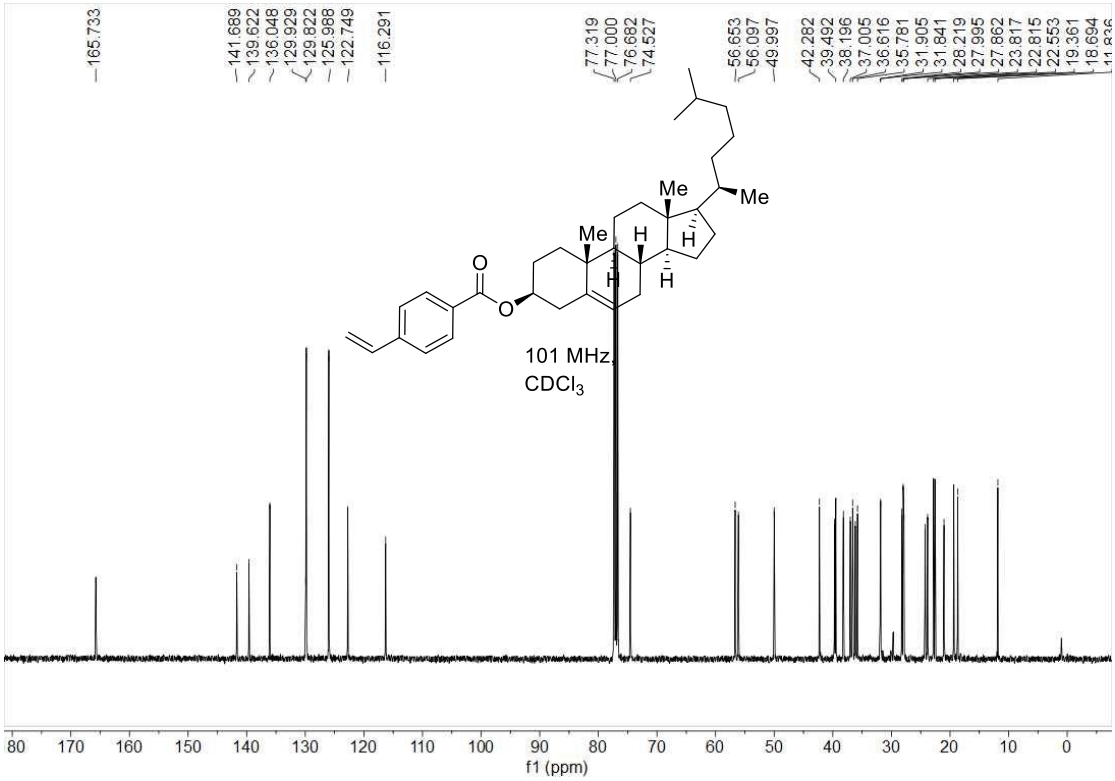
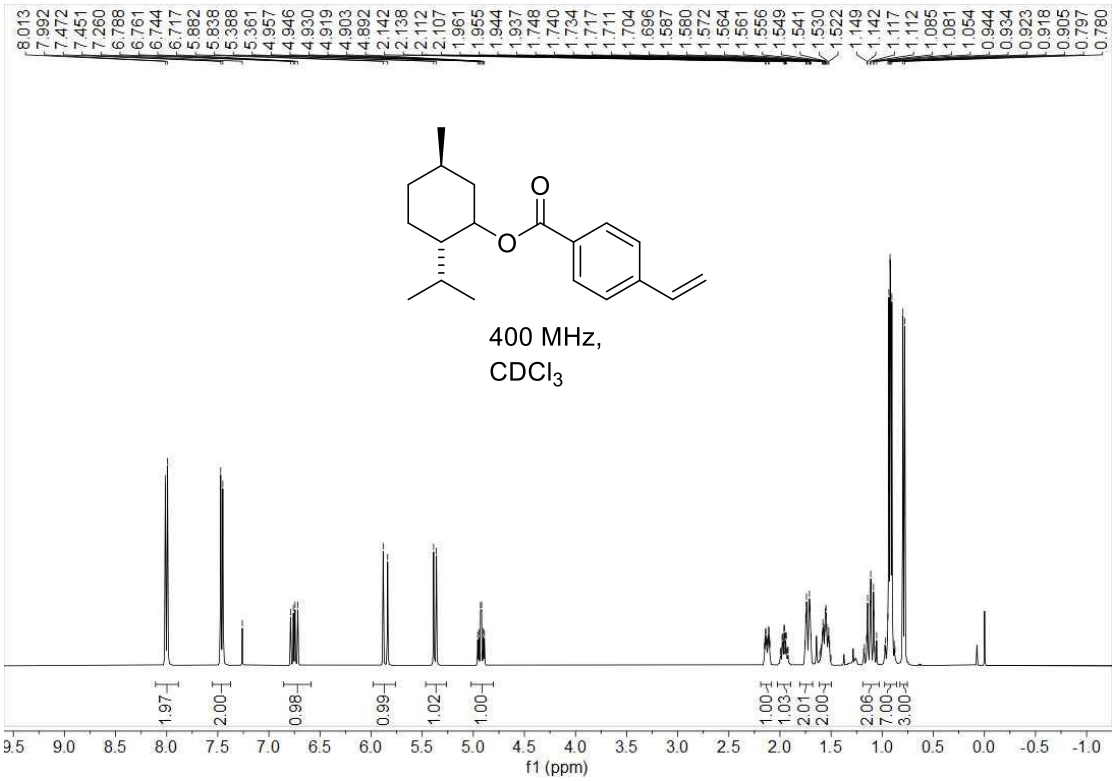
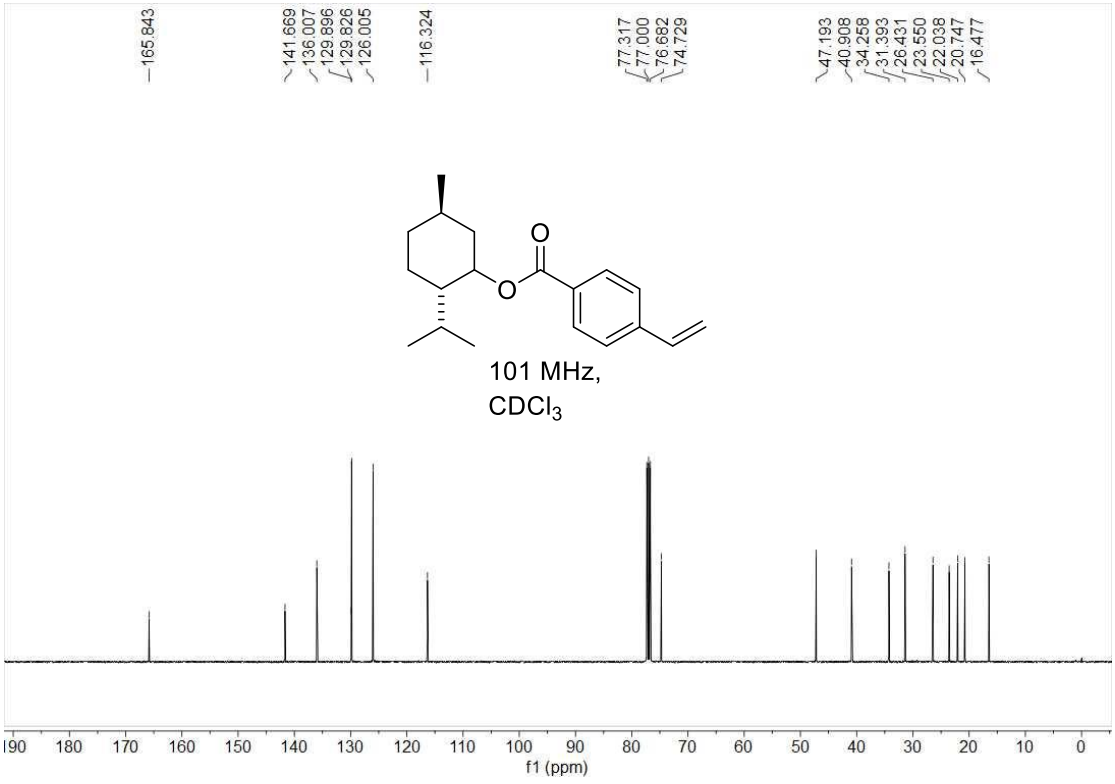
7.467
7.462
7.260
6.790
6.763
6.746
6.719
5.957
5.948
5.901
5.857
5.496
5.489
5.422
5.395
4.638
4.628
4.368
4.355
4.342
4.335
4.137
4.124
4.116
4.102
4.099
4.088
4.078
4.066
1.556
1.414
1.320
1.266
400 MHz,
CDCl3
1.86
1.88
0.97
0.94
0.92
0.92
0.92
1.00
1.93
1.94
2.86
3.00
2.81
3.01
f1 (ppm)

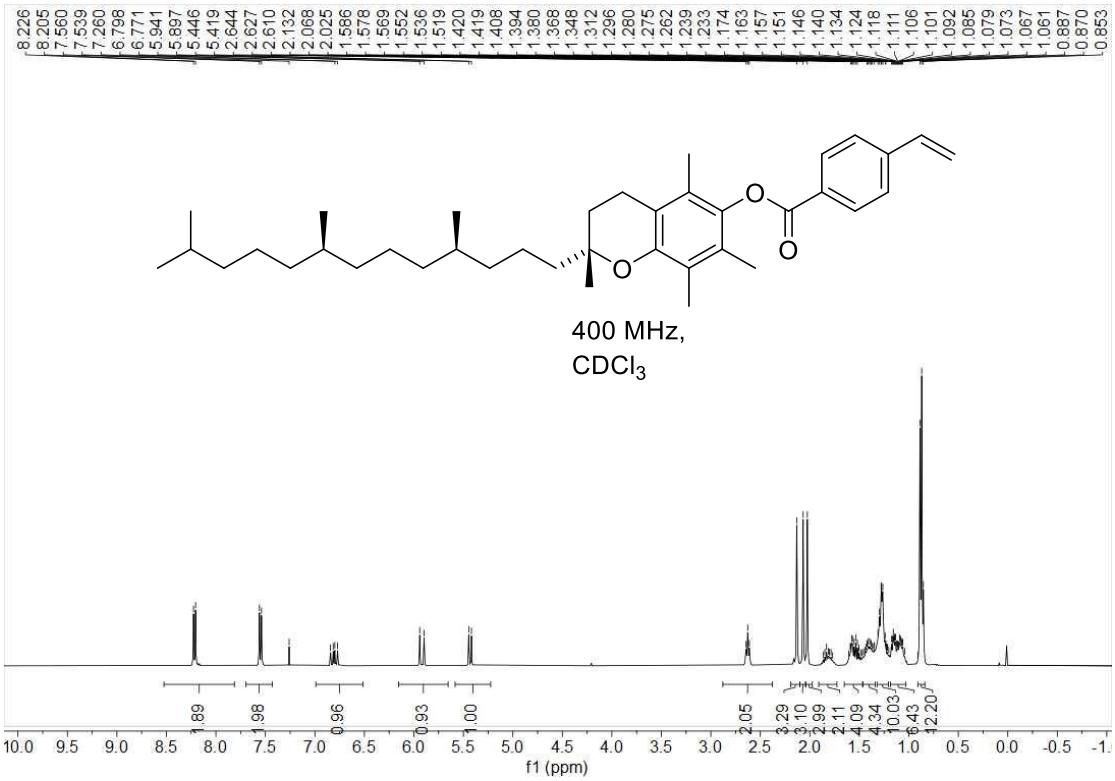

164.966
142.491
135.827
130.019
128.529
126.235
116.954
112.353
109.382
105.119
83.359
79.942
77.321
77.003
76.685
76.562
72.557
67.223
26.807
26.717
26.187
25.184
101 MHz,
CDCl3
f1 (ppm)

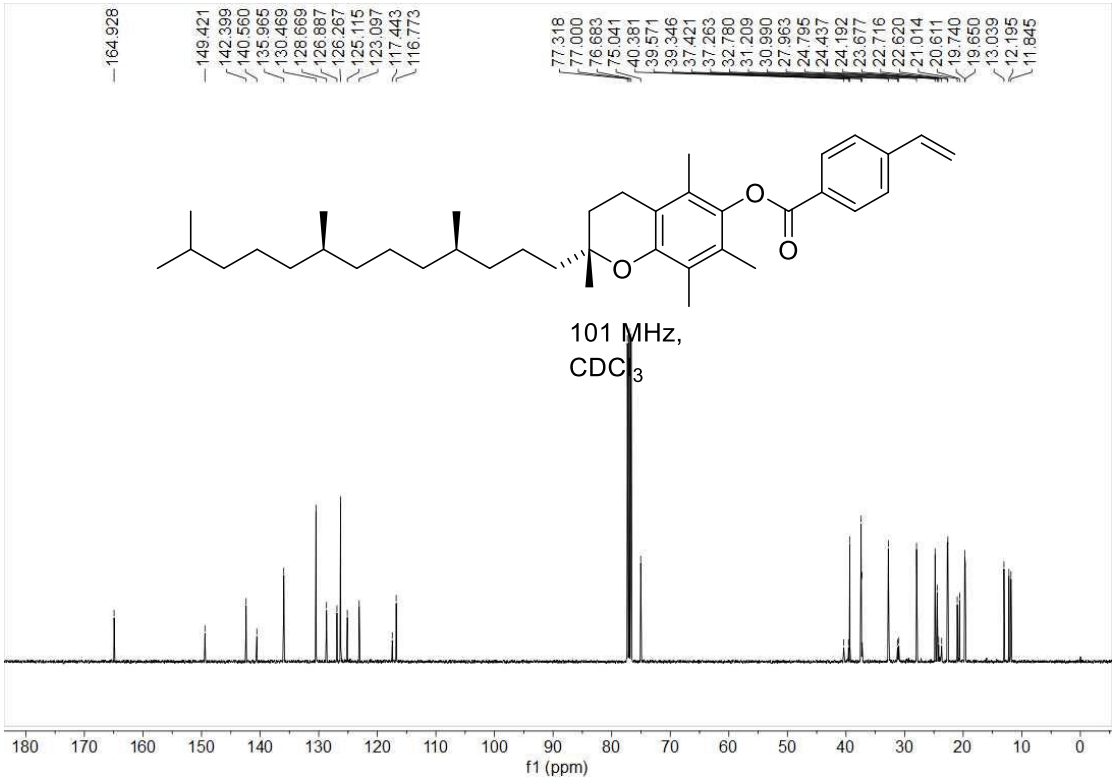

400 MHz,
CDCl3
f1 (ppm)

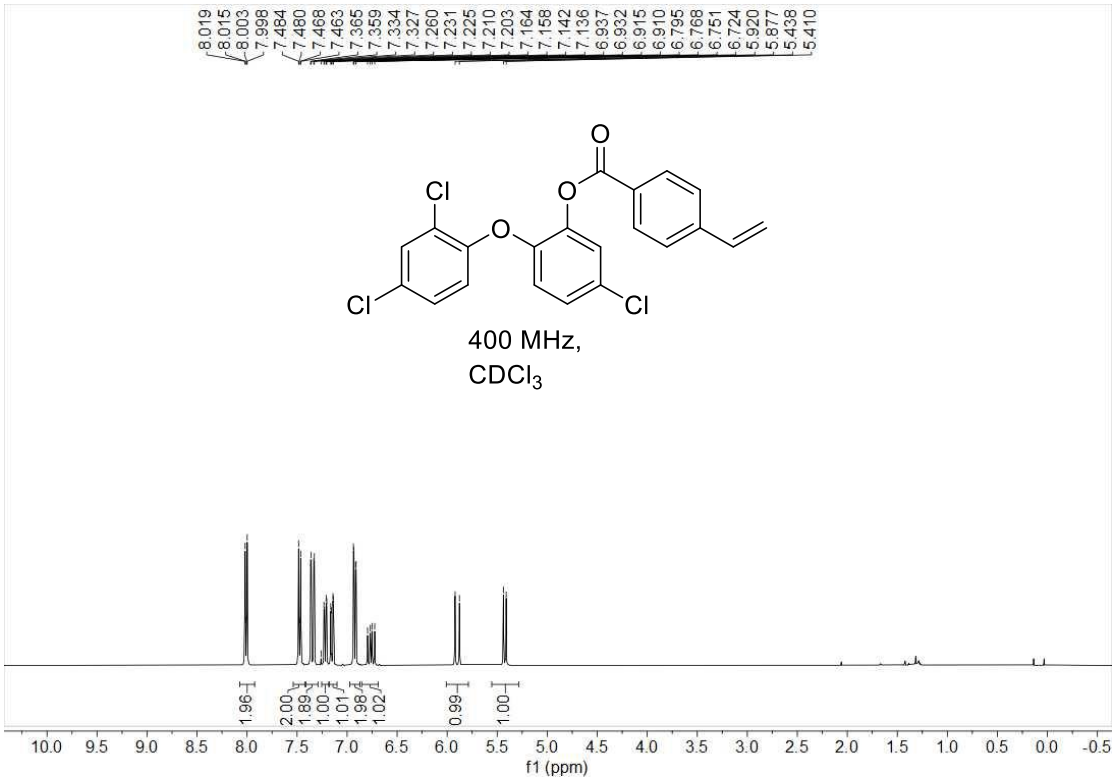

101 MHz,
CDCl3
f1 (ppm)

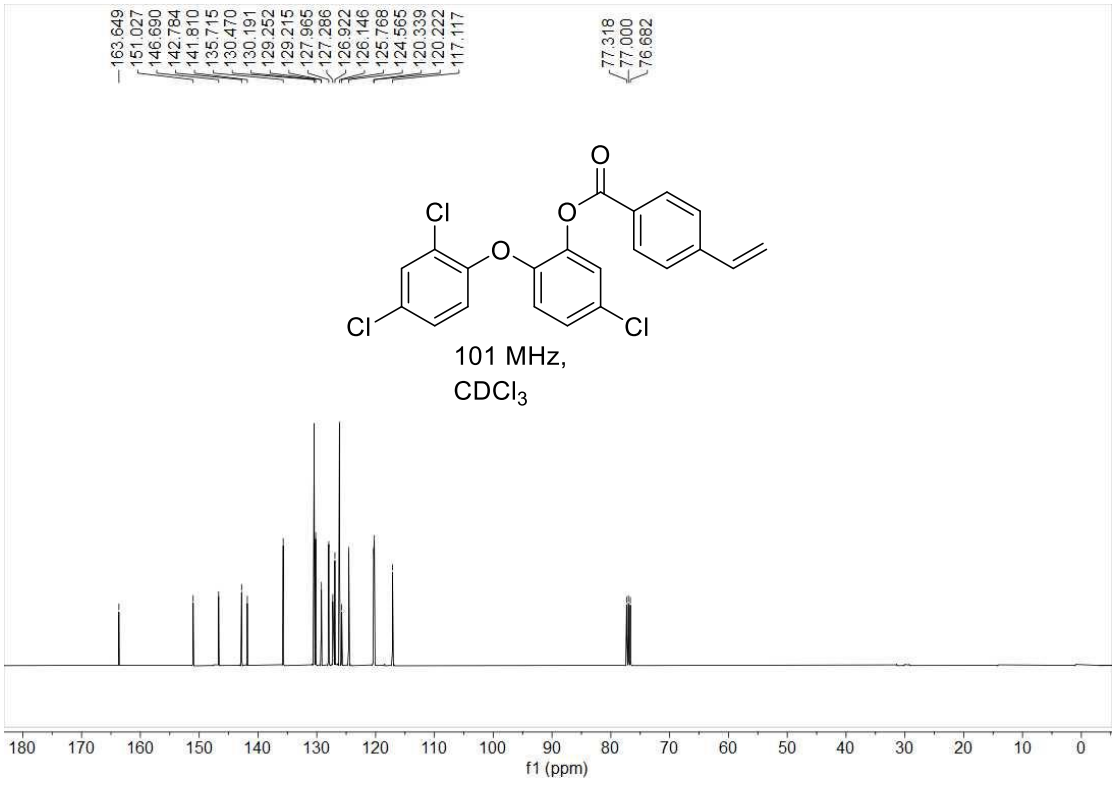

8.013
7.992
7.472
7.451
7.260
6.788
6.761
6.744
6.717
5.882
5.838
5.388
5.361
4.957
4.946
4.930
4.919
4.903
4.892
2.142
2.138
2.112
2.107
1.961
1.955
1.944
1.937
1.748
1.740
1.734
1.717
1.711
1.704
1.696
1.587
1.580
1.572
1.564
1.561
1.556
1.549
1.541
1.530
1.522
1.149
1.142
1.117
1.112
1.085
1.081
1.054
0.944
0.934
0.923
0.918
0.905
0.797
0.780
O
O
400 MHz,
CDCl3
1.97
2.00
0.98
0.99
1.02
1.00
1.00
1.03
2.01
2.00
2.06
7.00
3.00
f1 (ppm)

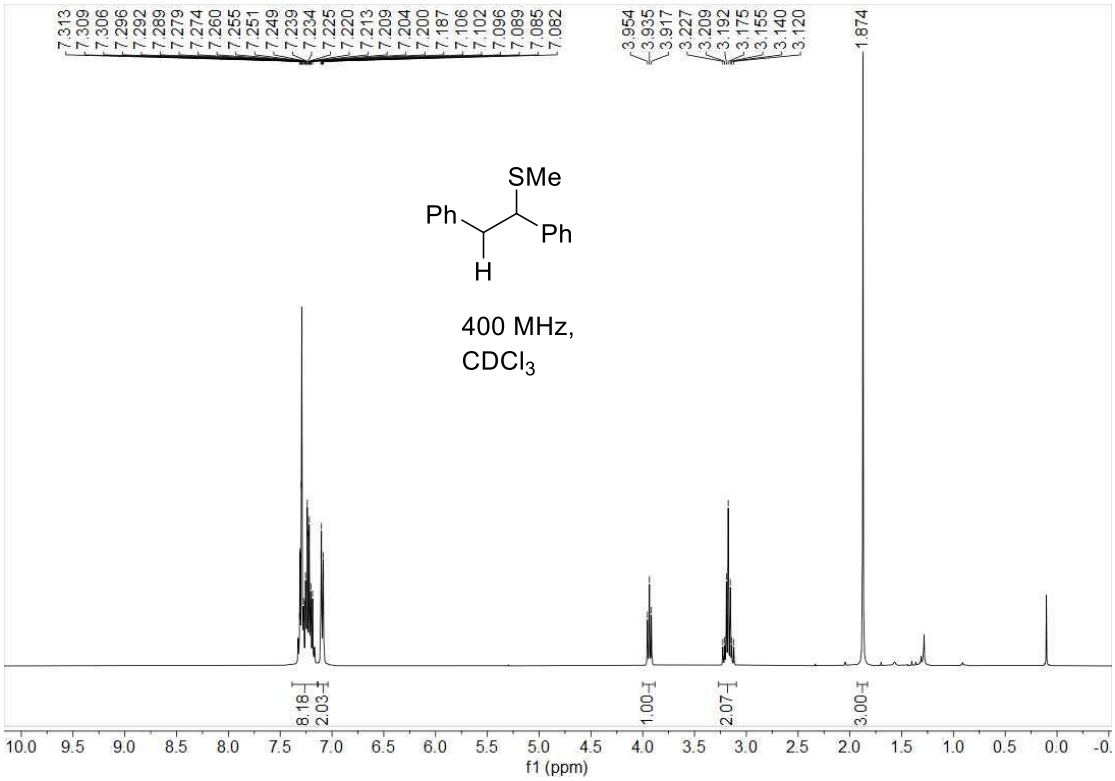

165.843
141.669
136.007
129.896
129.826
126.005
116.324
77.317
77.000
76.682
74.729
47.193
40.908
34.258
31.393
26.431
23.550
22.038
20.747
16.477
O
O
101 MHz,
CDCl3
f1 (ppm)

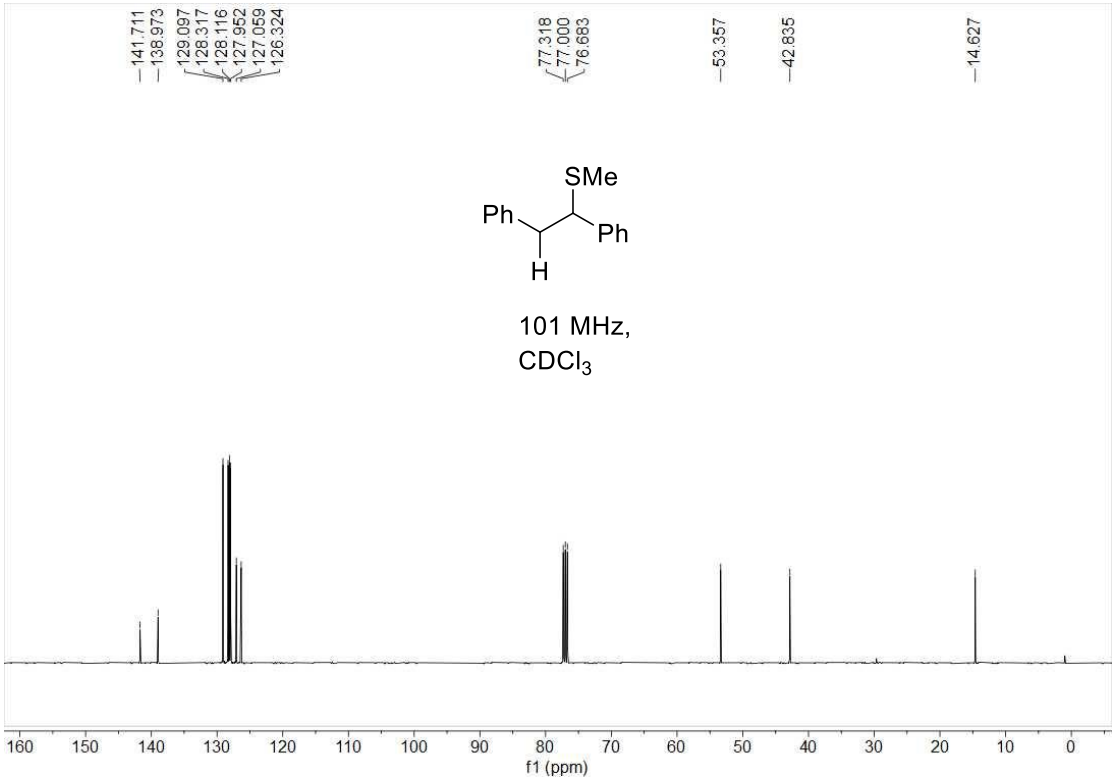

400 MHz,
CDCl3
f1 (ppm)

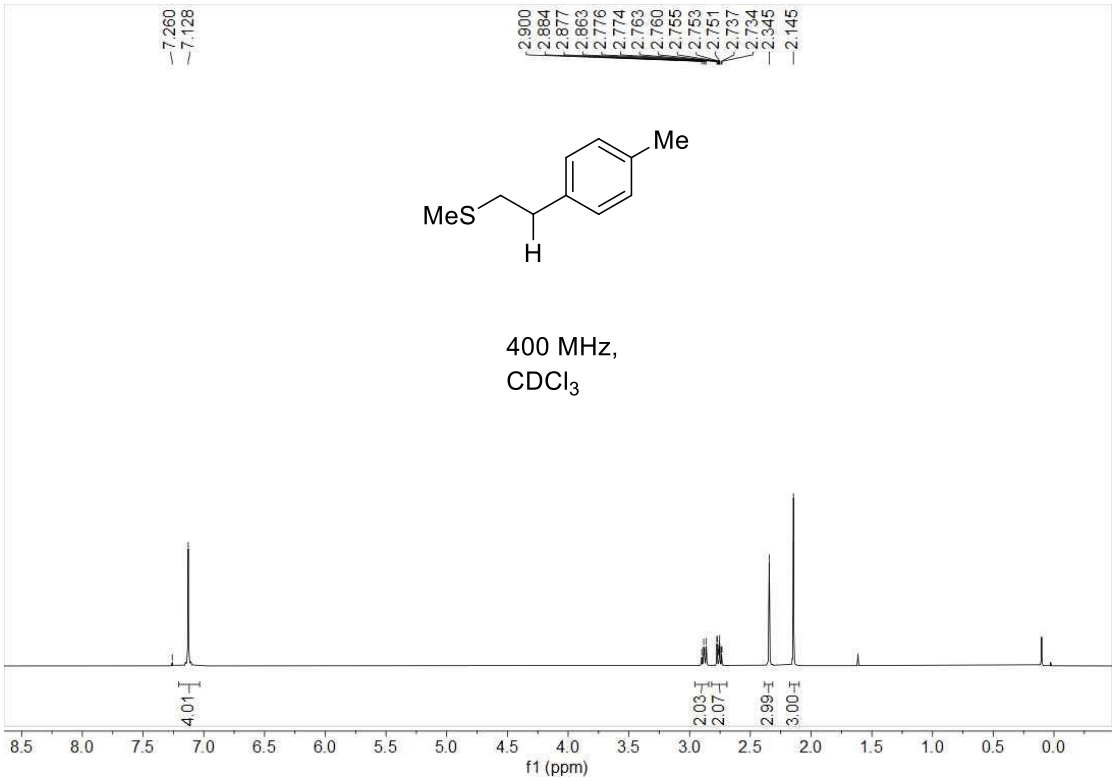

101 MHz,
CDCl3
f1 (ppm)

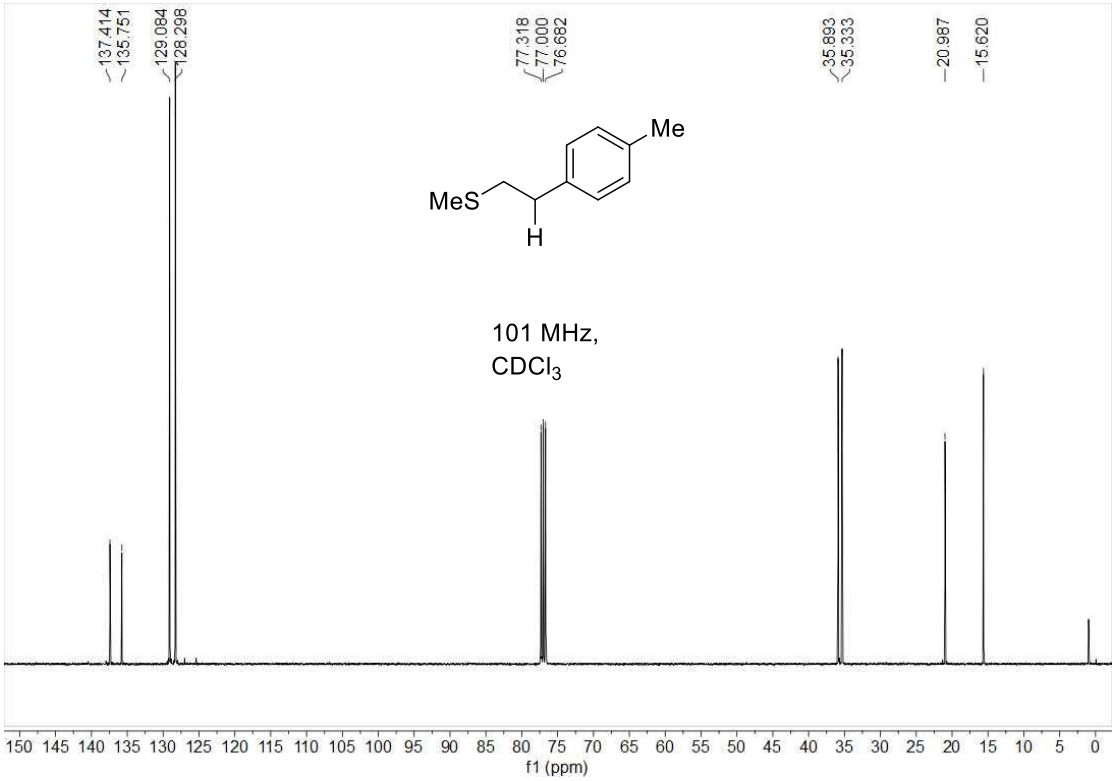

8.019
8.015
8.003
7.998
7.484
7.480
7.468
7.463
7.365
7.359
7.334
7.327
7.260
7.231
7.225
7.210
7.203
7.164
7.158
7.142
7.136
6.937
6.932
6.915
6.910
6.795
6.768
6.751
6.724
5.920
5.877
5.438
5.410
O
Cl
O
O
Cl
Cl
400 MHz,
CDCl3
1.96
2.00
1.89
1.00
1.01
1.98
1.02
0.99
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

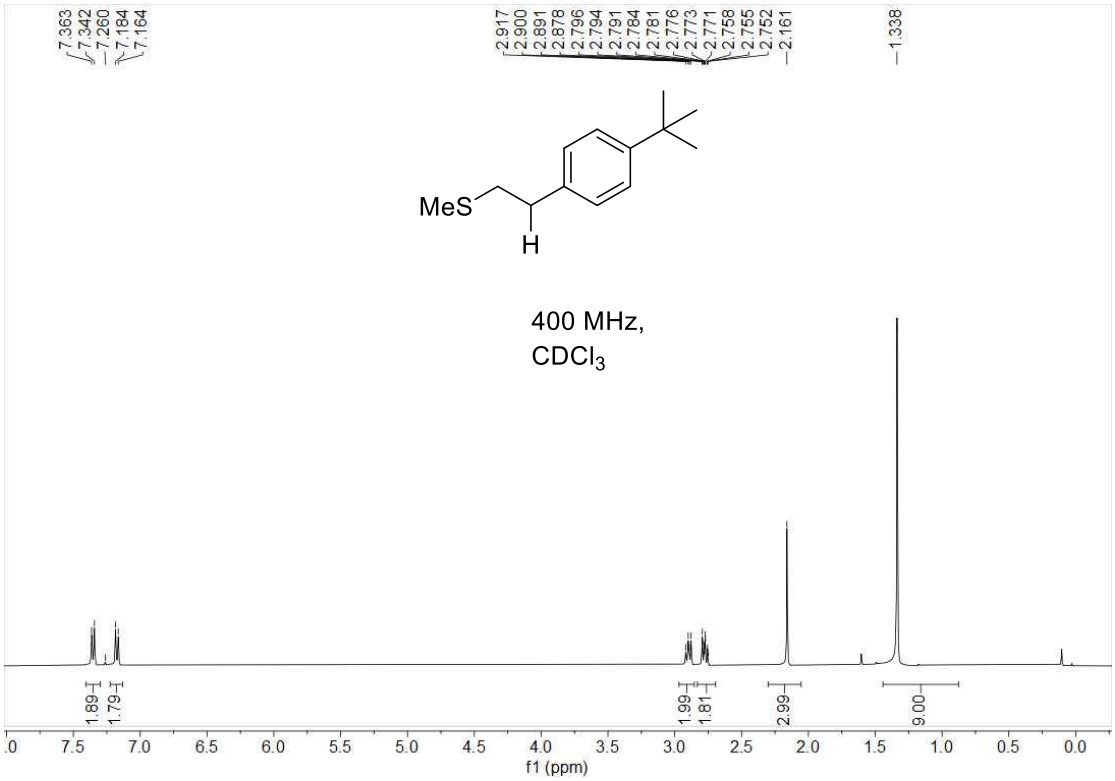

163.649
151.027
146.690
142.784
141.810
135.715
130.470
130.191
129.252
129.215
127.965
127.286
126.922
126.146
125.768
124.565
120.339
120.222
117.117
77.318
77.000
76.682
O
Cl
O
O
Cl
Cl
101 MHz,
CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

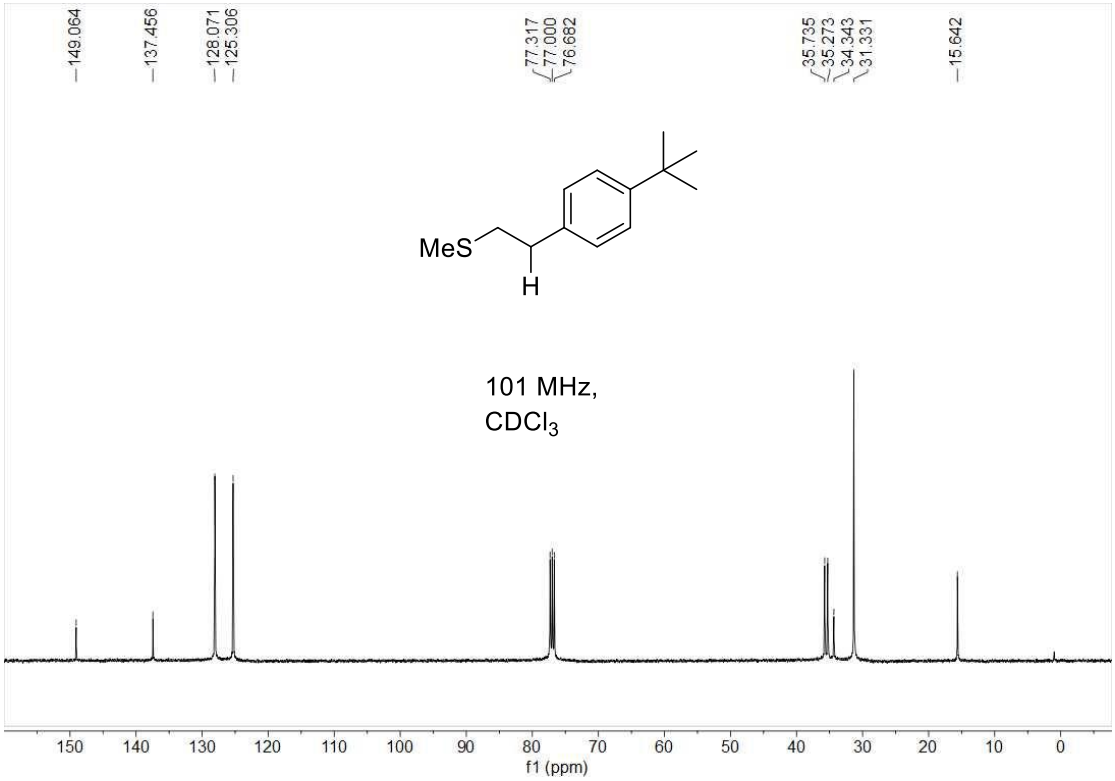

7.313
7.309
7.306
7.296
7.292
7.289
7.279
7.274
7.260
7.255
7.251
7.249
7.239
7.234
7.225
7.220
7.213
7.209
7.204
7.200
7.187
7.106
7.102
7.096
7.089
7.085
7.082
3.954
3.935
3.917
3.227
3.209
3.192
3.175
3.155
3.140
3.120
1.874
SMe
Ph
Ph
H
400 MHz,
CDCl3
8.18
2.03
1.00
2.07
3.00
f1 (ppm)

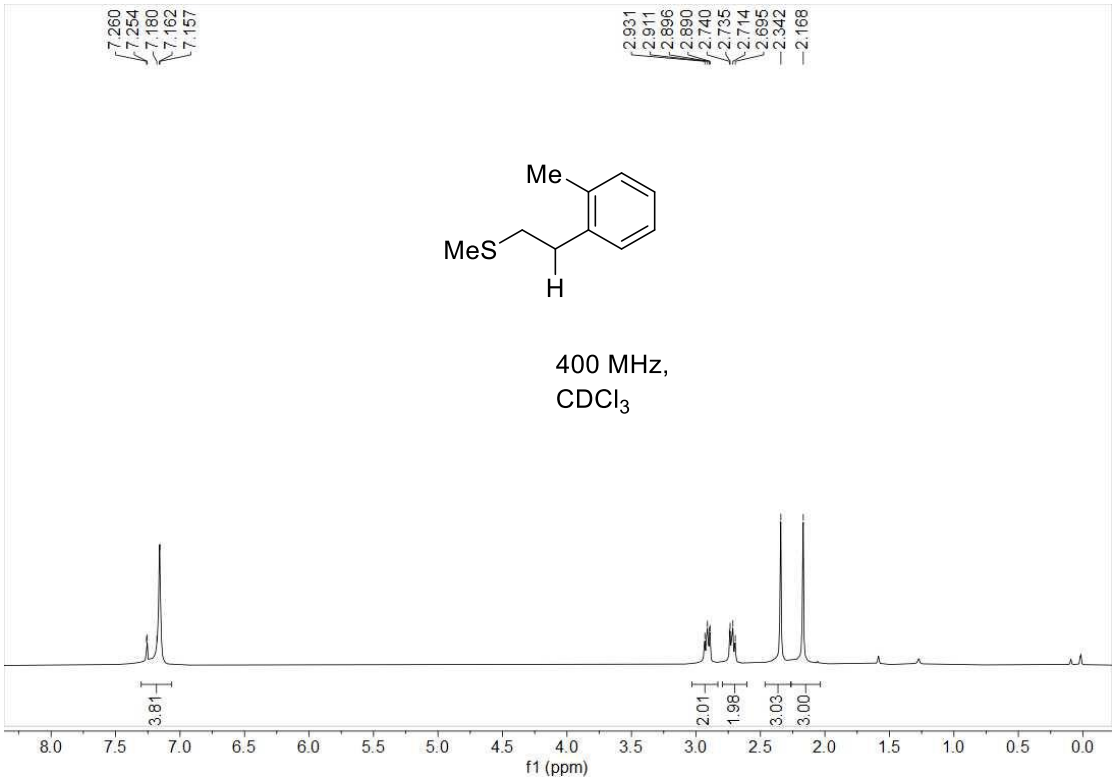

141.711
138.973
129.097
128.317
128.116
127.952
127.059
126.324
77.318
77.000
76.683
53.357
42.835
14.627
SMe
Ph
Ph
H
101 MHz,
CDCl3
f1 (ppm)

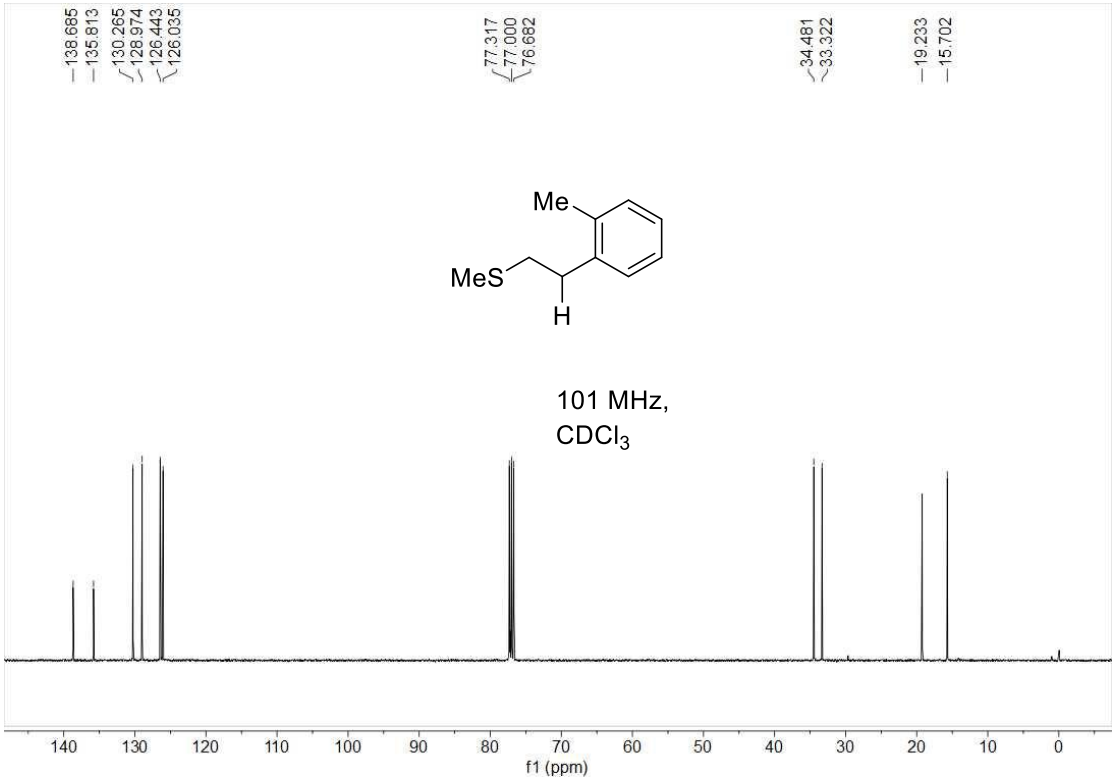

7.260
7.128
2.900
2.884
2.877
2.863
2.776
2.774
2.763
2.760
2.755
2.753
2.751
2.737
2.734
2.345
2.145
Me
MeS
H
400 MHz,
CDCl3
4.01
2.03
2.07
2.99
3.00
f1 (ppm)

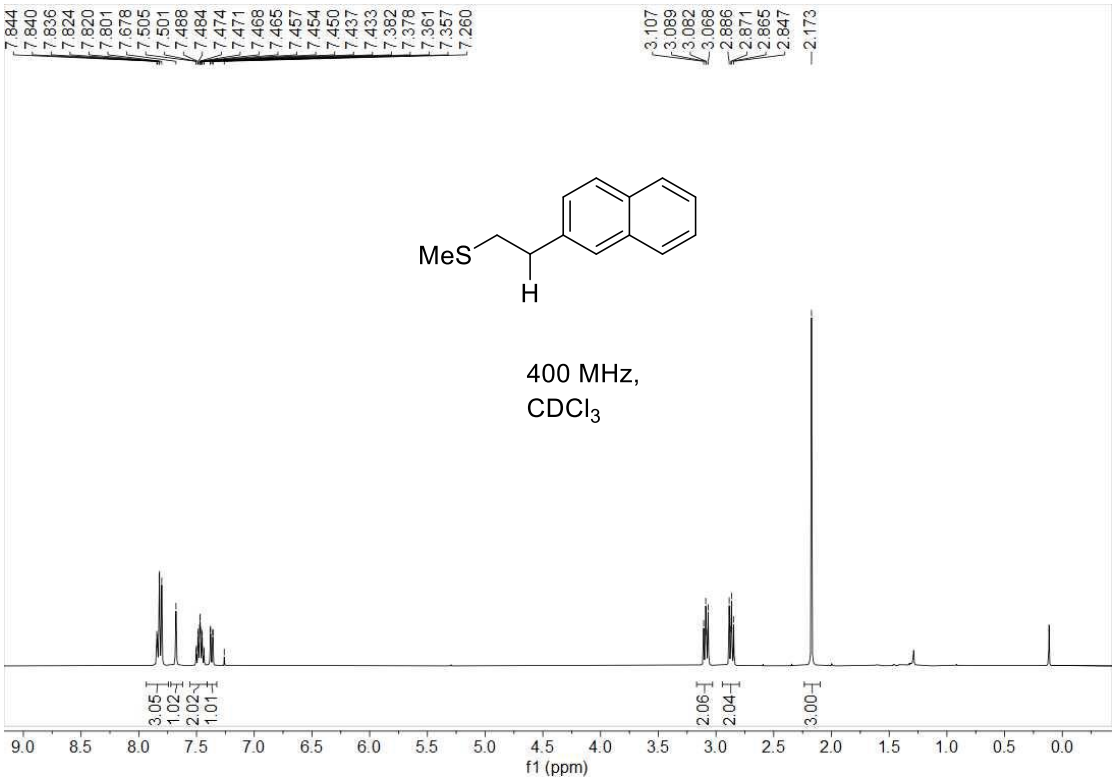

137.414
135.751
129.084
128.298
77.318
77.000
76.682
35.893
35.333
20.987
15.620
Me
MeS
H
101 MHz,
CDCl3
f1 (ppm)

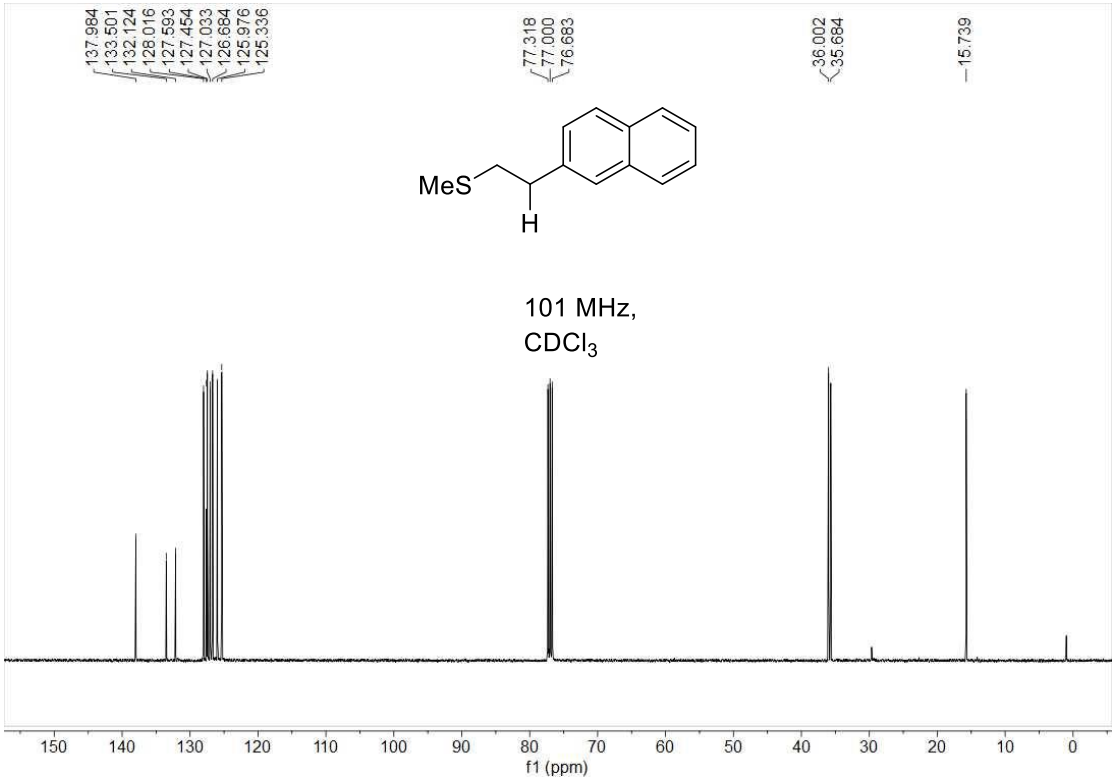

7.363
7.342
7.260
7.184
7.164
2.917
2.900
2.891
2.878
2.796
2.794
2.791
2.784
2.781
2.776
2.773
2.771
2.758
2.755
2.752
2.161
1.338
MeS
H
400 MHz,
CDCl3
1.89
1.79
1.99
1.81
2.99
9.00
f1 (ppm)

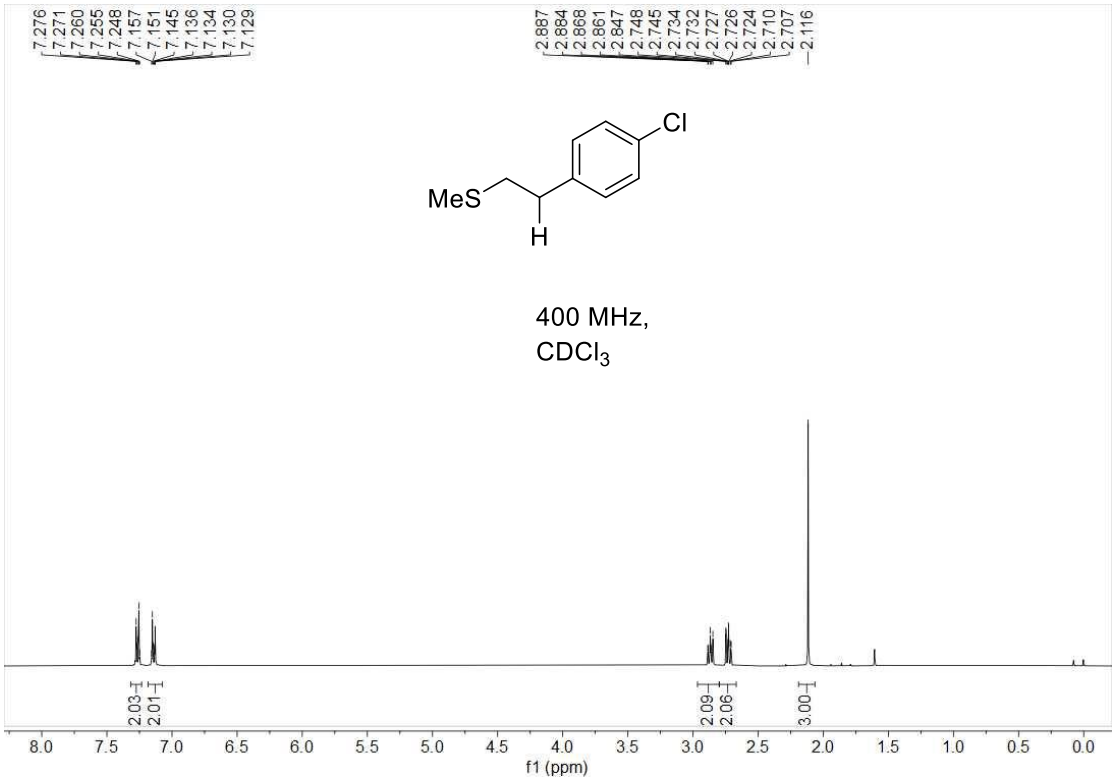

149.064
137.456
128.071
125.306
77.317
77.000
76.682
35.735
35.273
34.343
31.331
15.642
MeS
H
101 MHz,
CDCl3
f1 (ppm)

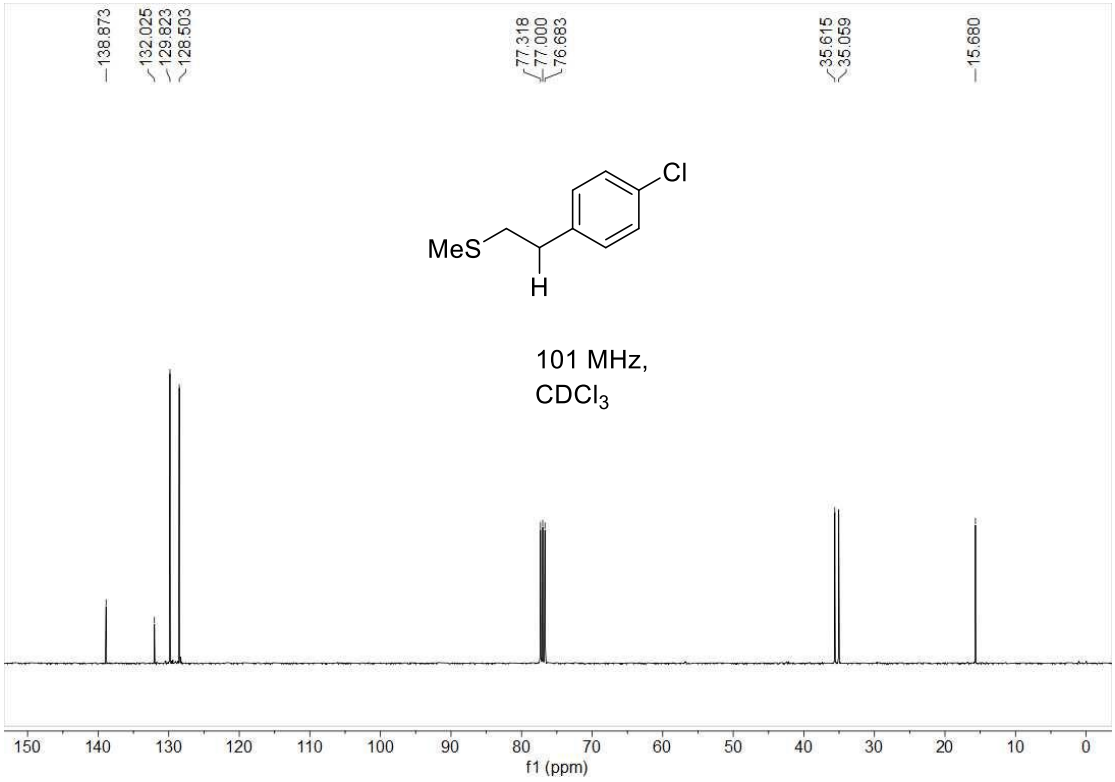

7.260
7.254
7.180
7.162
7.157
2.931
2.911
2.896
2.890
2.740
2.735
2.714
2.695
2.342
2.168
Me
MeS
H
400 MHz,
CDCl3
3.81
2.01
1.98
3.03
3.00
f1 (ppm)

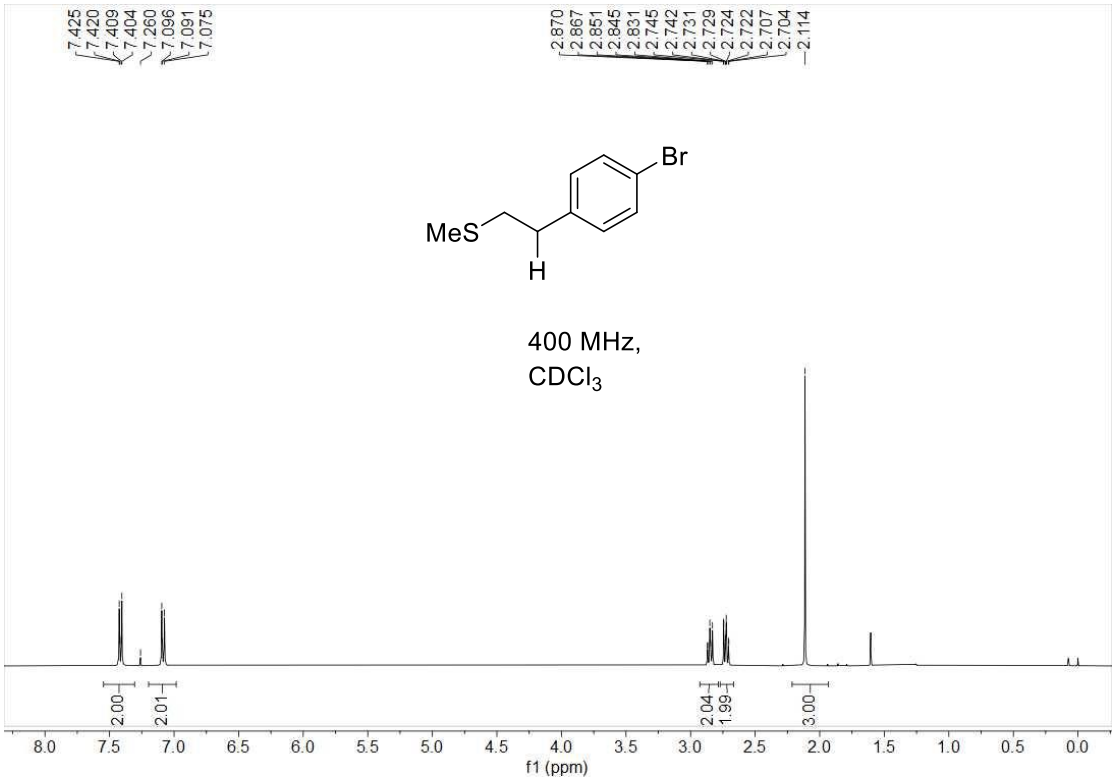

138.685
135.813
130.265
128.974
126.443
126.035
77.317
77.000
76.682
34.481
33.322
19.233
15.702
Me
MeS
H
101 MHz,
CDCl3
f1 (ppm)

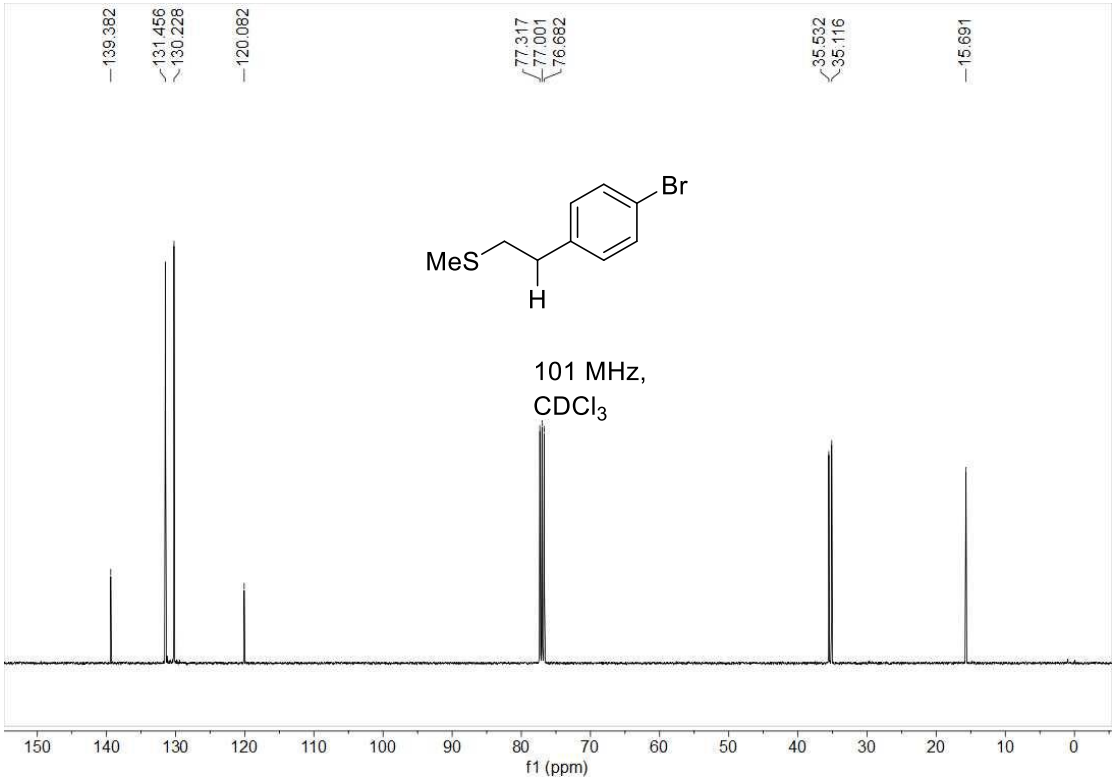

7.844
7.840
7.836
7.824
7.820
7.801
7.678
7.505
7.501
7.488
7.484
7.474
7.471
7.468
7.465
7.457
7.454
7.450
7.437
7.433
7.382
7.378
7.361
7.357
7.260
3.107
3.089
3.082
3.068
2.886
2.871
2.865
2.847
2.173
MeS
H
400 MHz,
CDCl3
3.05
1.02
2.02
1.01
2.06
2.04
3.00
f1 (ppm)

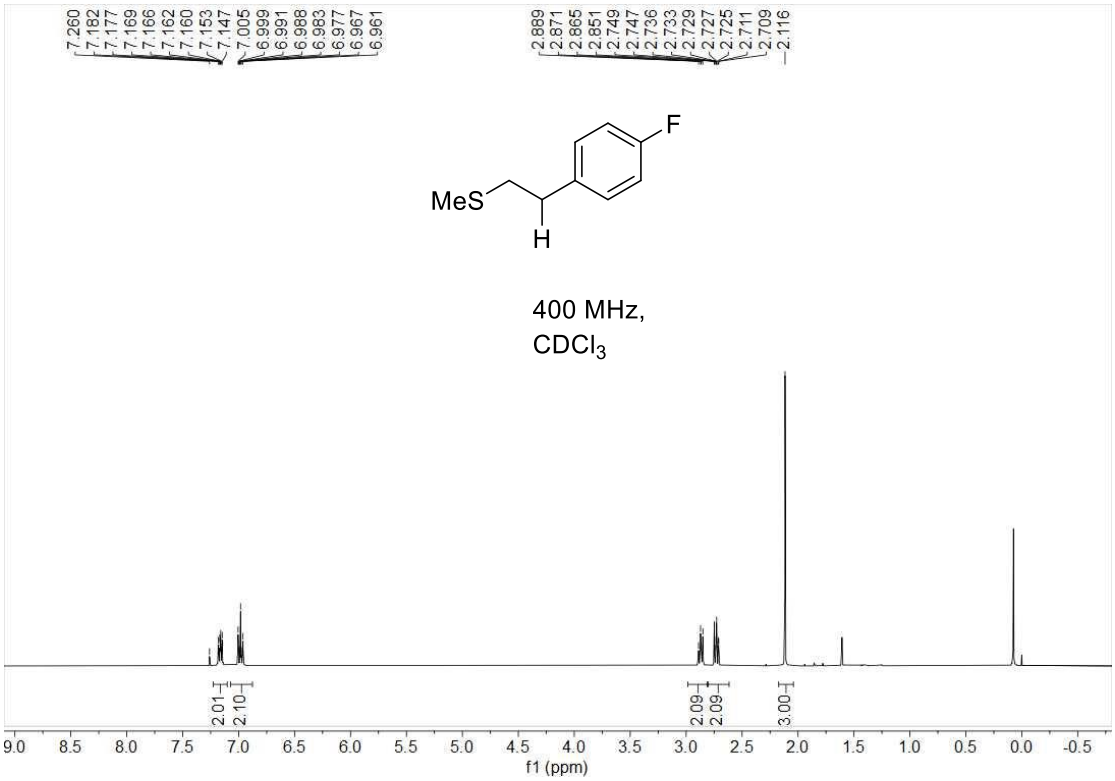

137.984
133.501
132.124
128.016
127.593
127.454
127.033
126.684
125.976
125.336
77.318
77.000
76.683
36.002
35.684
15.739
MeS
H
101 MHz,
CDCl3
f1 (ppm)

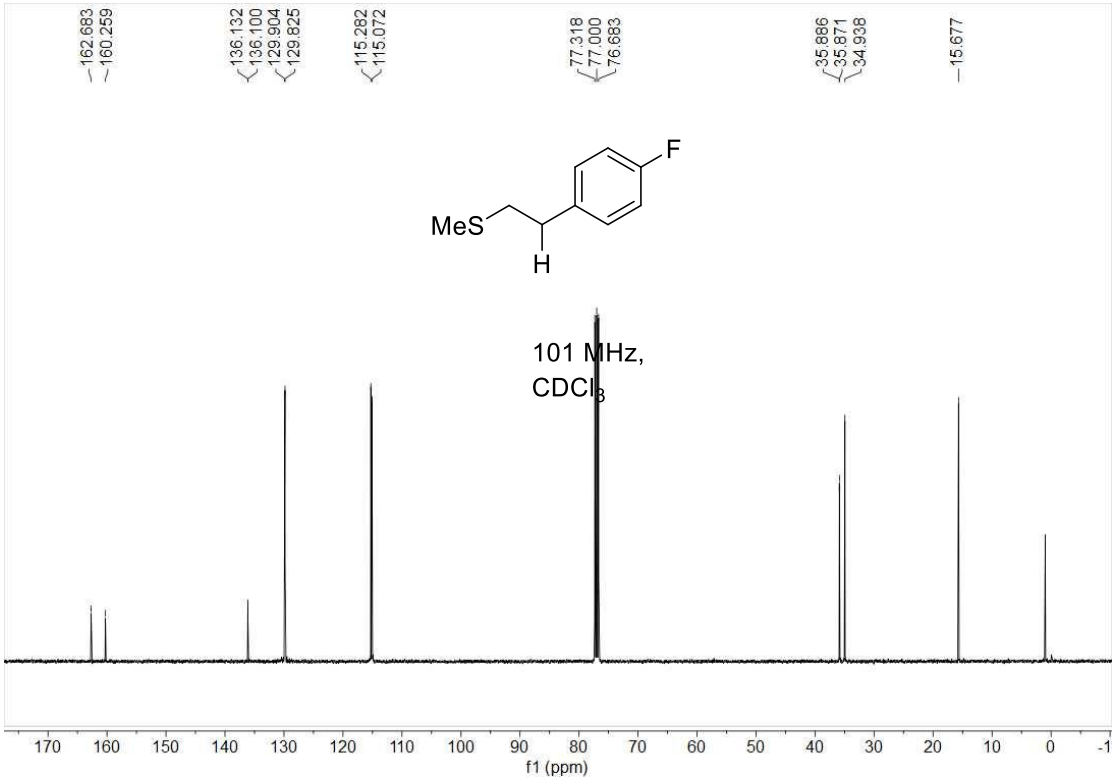

7.276
7.271
7.260
7.255
7.248
7.157
7.151
7.145
7.136
7.134
7.130
7.129
2.887
2.884
2.868
2.861
2.847
2.748
2.745
2.734
2.732
2.727
2.726
2.724
2.710
2.707
2.116
Cl
MeS
H
400 MHz,
CDCl3
2.03
2.01
2.09
2.06
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

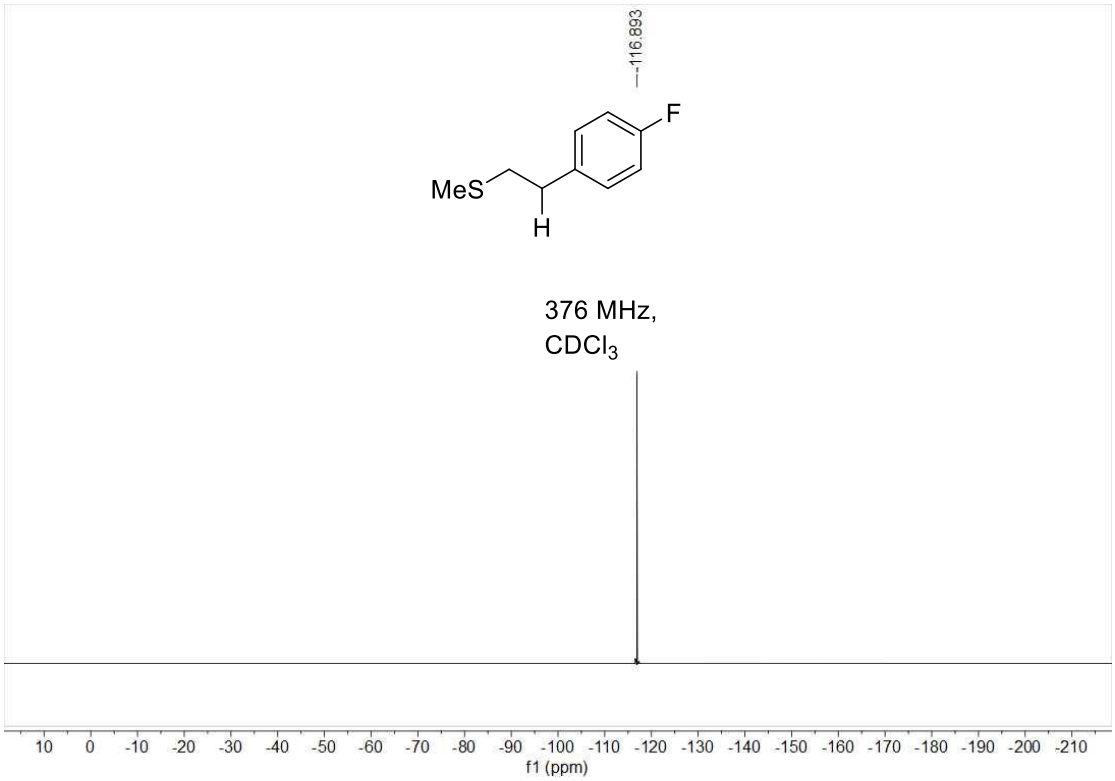

138.873
132.025
129.823
128.503
77.318
77.000
76.683
35.615
35.059
15.680
Cl
MeS
H
101 MHz,
CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

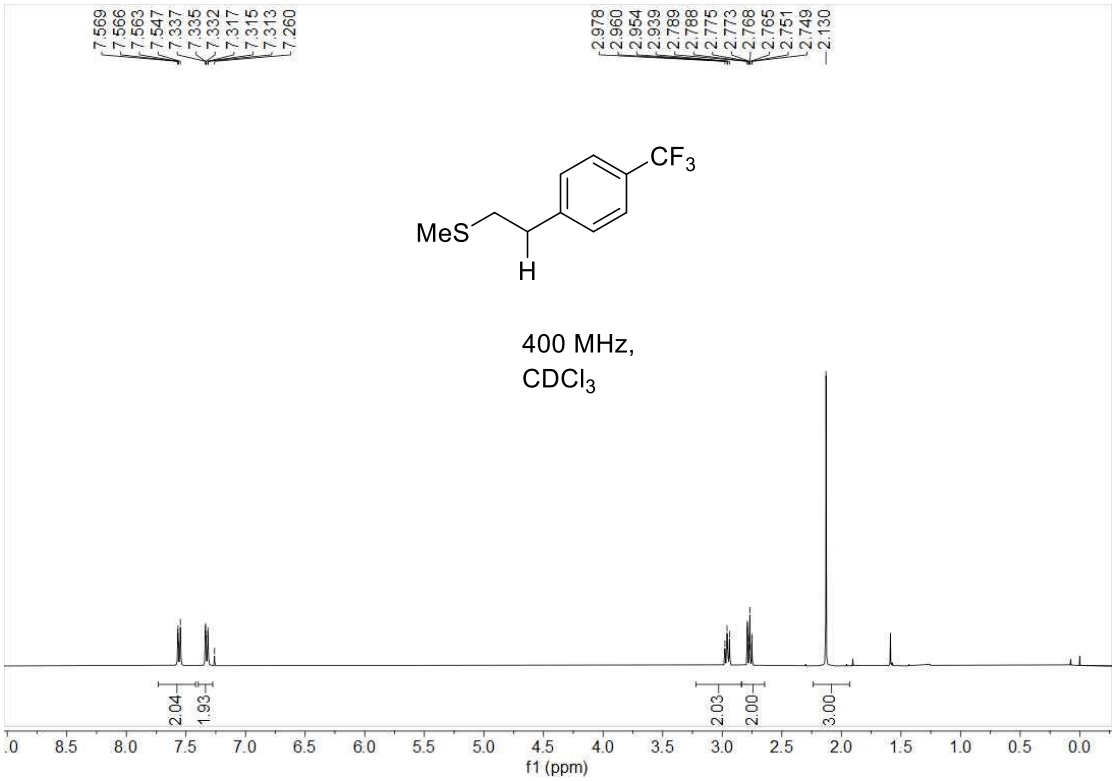

7.425
7.420
7.409
7.404
7.260
7.096
7.091
7.075
2.870
2.867
2.851
2.845
2.831
2.745
2.742
2.731
2.729
2.724
2.722
2.707
2.704
2.114
Br
MeS
H
400 MHz,
CDCl3
2.00
2.01
2.04
1.99
3.00
f1 (ppm)

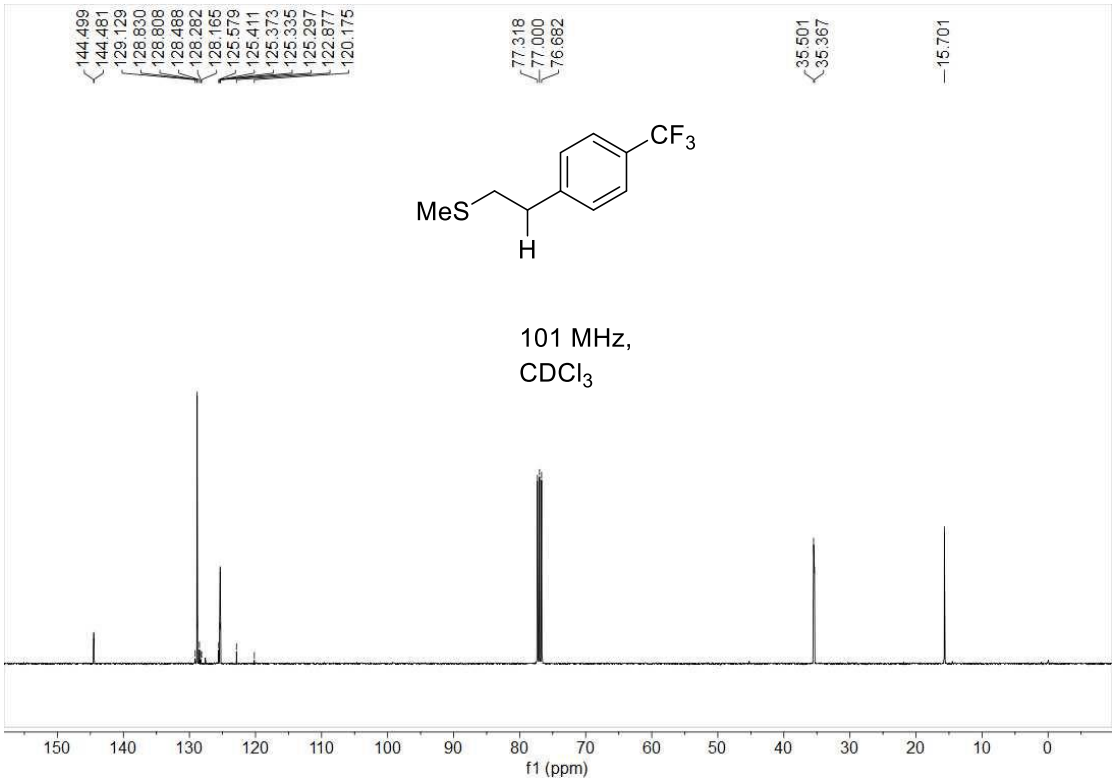

139.382
131.456
130.228
120.082
77.317
77.001
76.682
35.532
35.116
15.691
Br
MeS
H
101 MHz,
CDCl3
f1 (ppm)

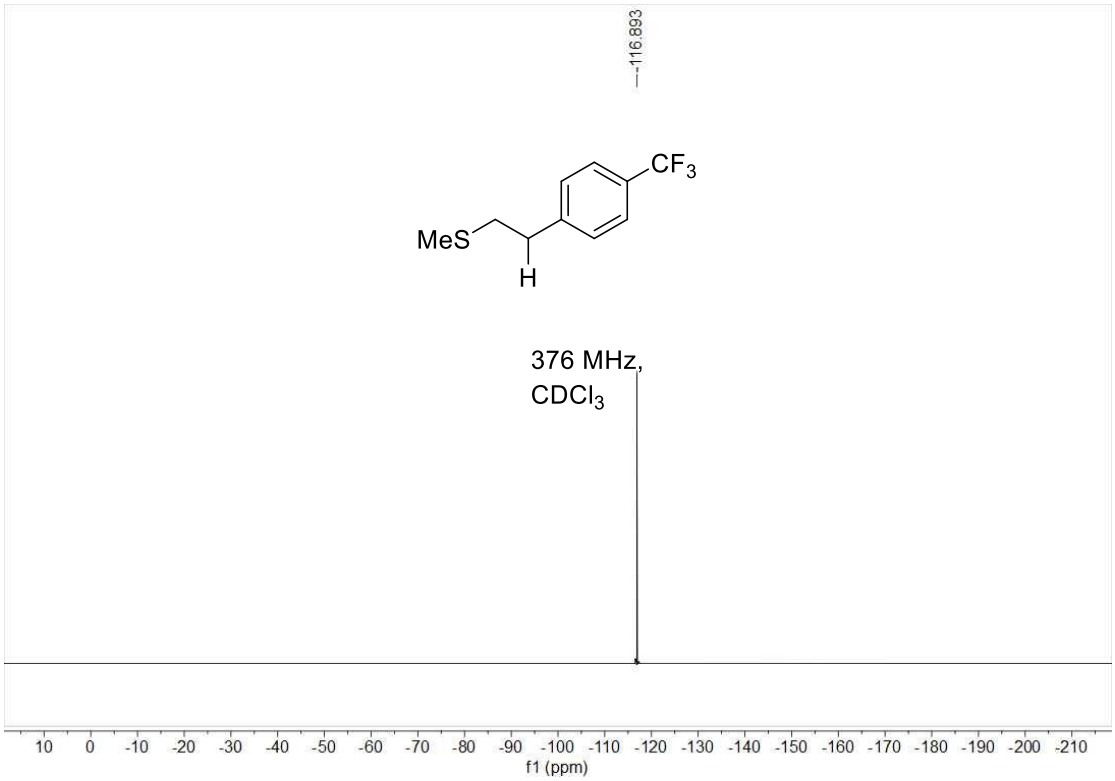

7.260
7.182
7.177
7.169
7.166
7.162
7.160
7.153
7.147
7.005
6.999
6.991
6.988
6.983
6.977
6.967
6.961
2.889
2.871
2.865
2.851
2.749
2.747
2.736
2.733
2.729
2.727
2.725
2.711
2.709
2.116
F
MeS
H
400 MHz,
CDCl3
2.01
2.10
2.09
2.09
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

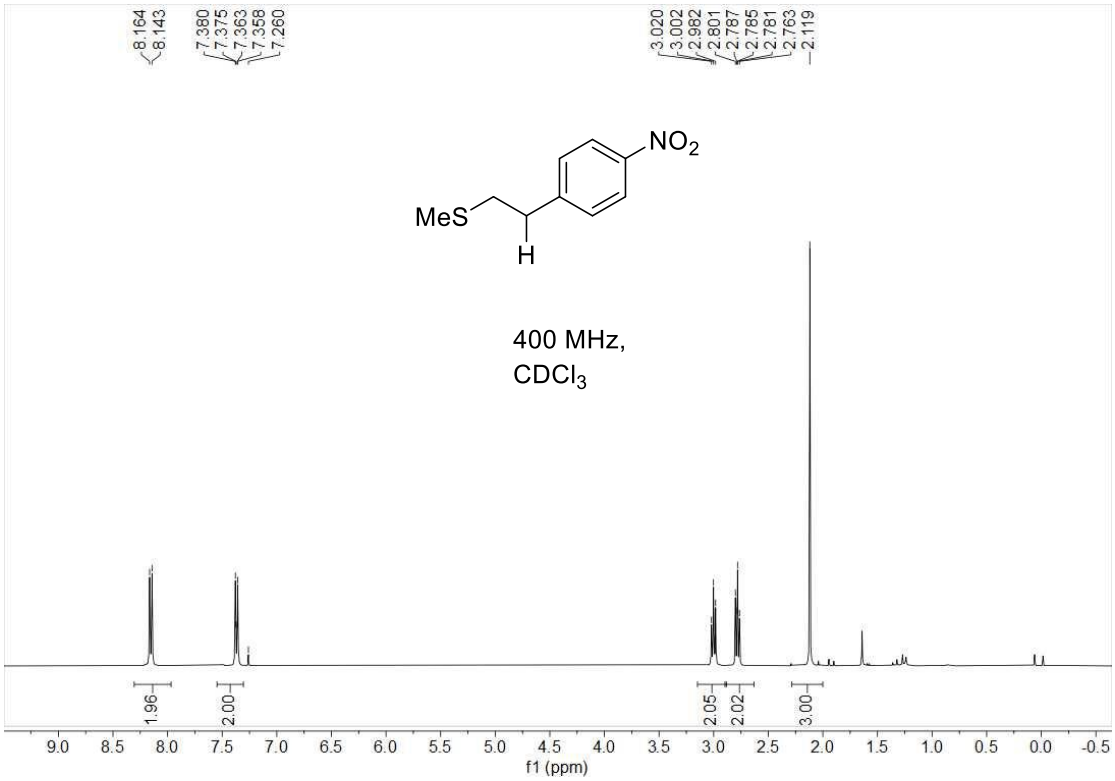

162.683
160.259
136.132
136.100
129.904
129.825
115.282
115.072
77.318
77.000
76.683
35.886
35.871
34.938
15.677
F
MeS
H
101 MHz,
CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


-116.893
F
MeS
H
376 MHz,
CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.569
7.566
7.563
7.547
7.337
7.335
7.332
7.317
7.315
7.313
7.260
2.978
2.960
2.954
2.939
2.789
2.788
2.775
2.773
2.768
2.765
2.751
2.749
2.130
CF3
MeS
H
400 MHz,
CDCl3
2.04
1.93
2.03
2.00
3.00
f1 (ppm)


144.499
144.481
129.129
128.830
128.808
128.488
128.282
128.165
125.579
125.411
125.373
125.335
125.297
122.877
120.175
77.318
77.000
76.682
35.501
35.367
15.701
CF3
MeS
H
101 MHz,
CDCl3
f1 (ppm)


-116.893
CF3
MeS
H
376 MHz,
CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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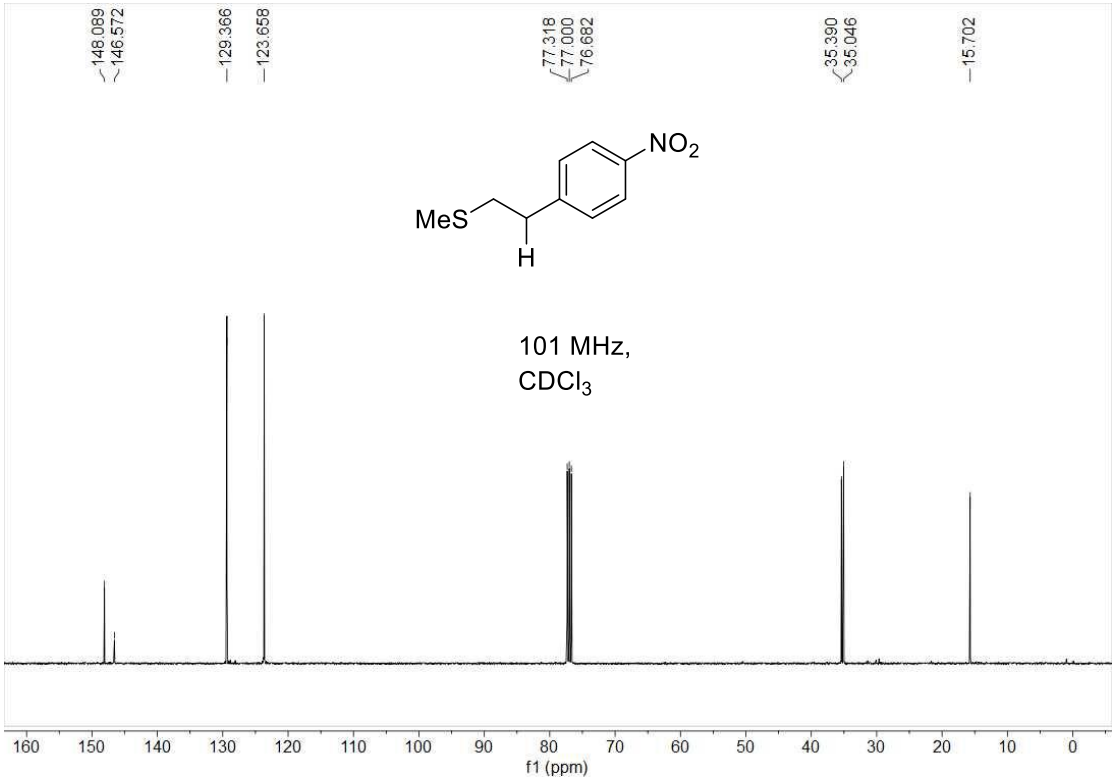
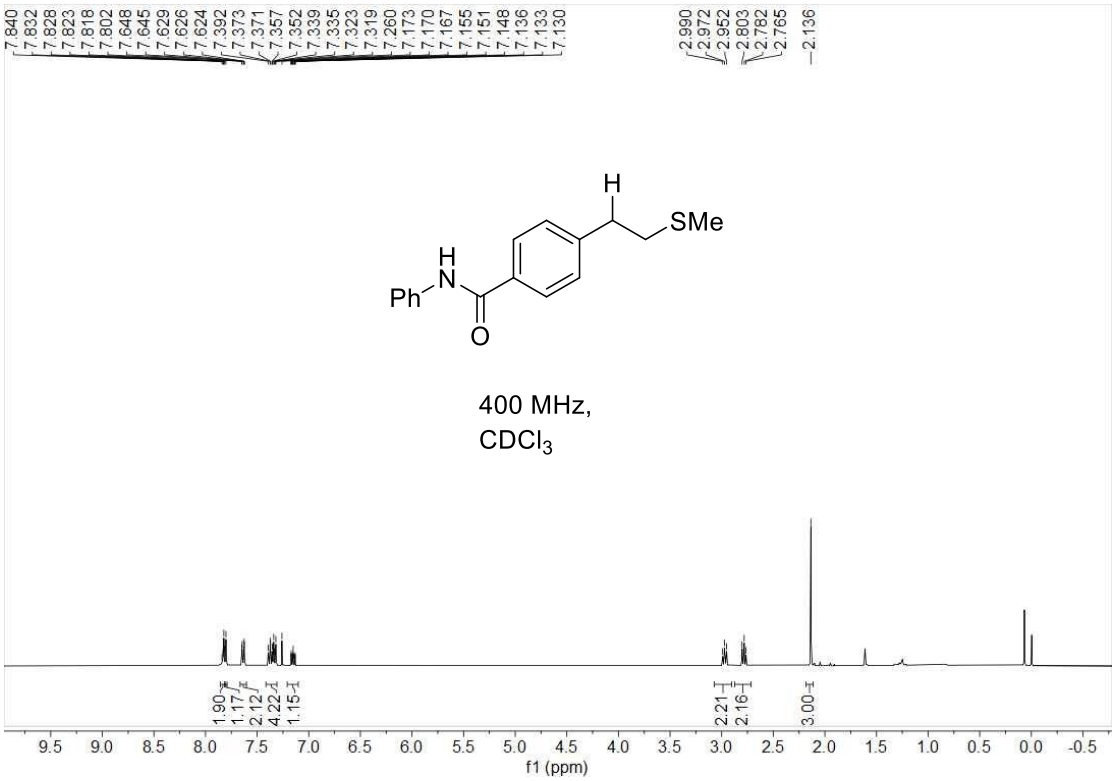
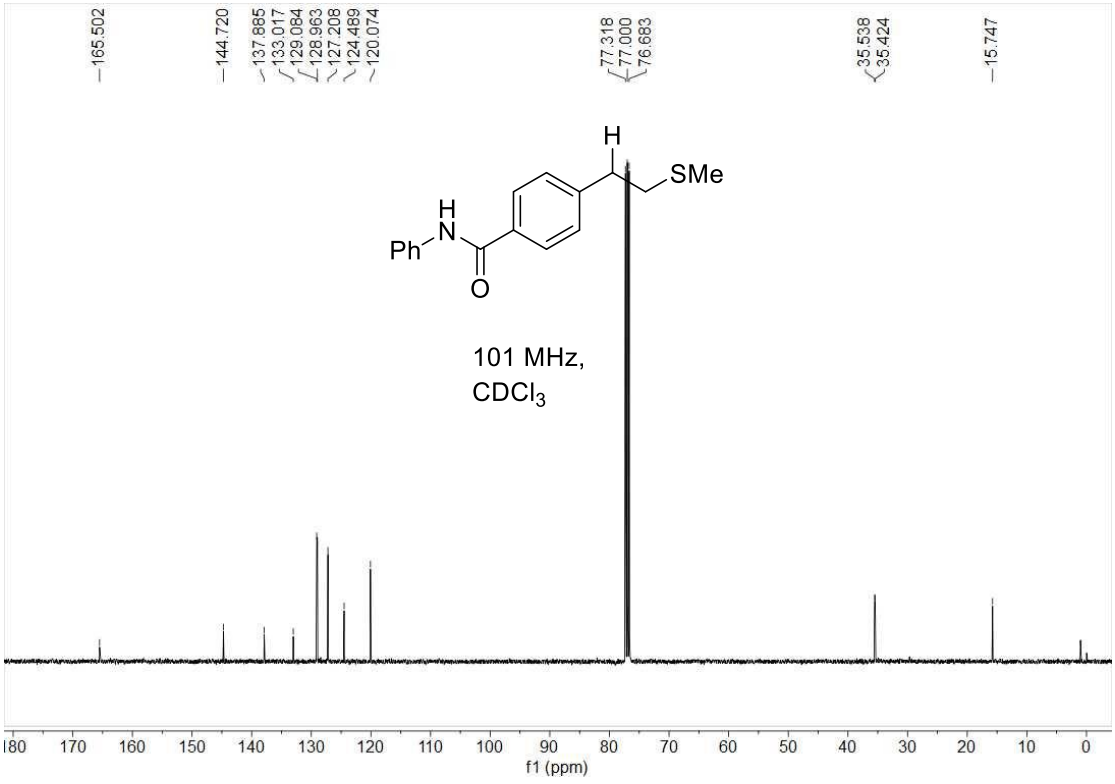
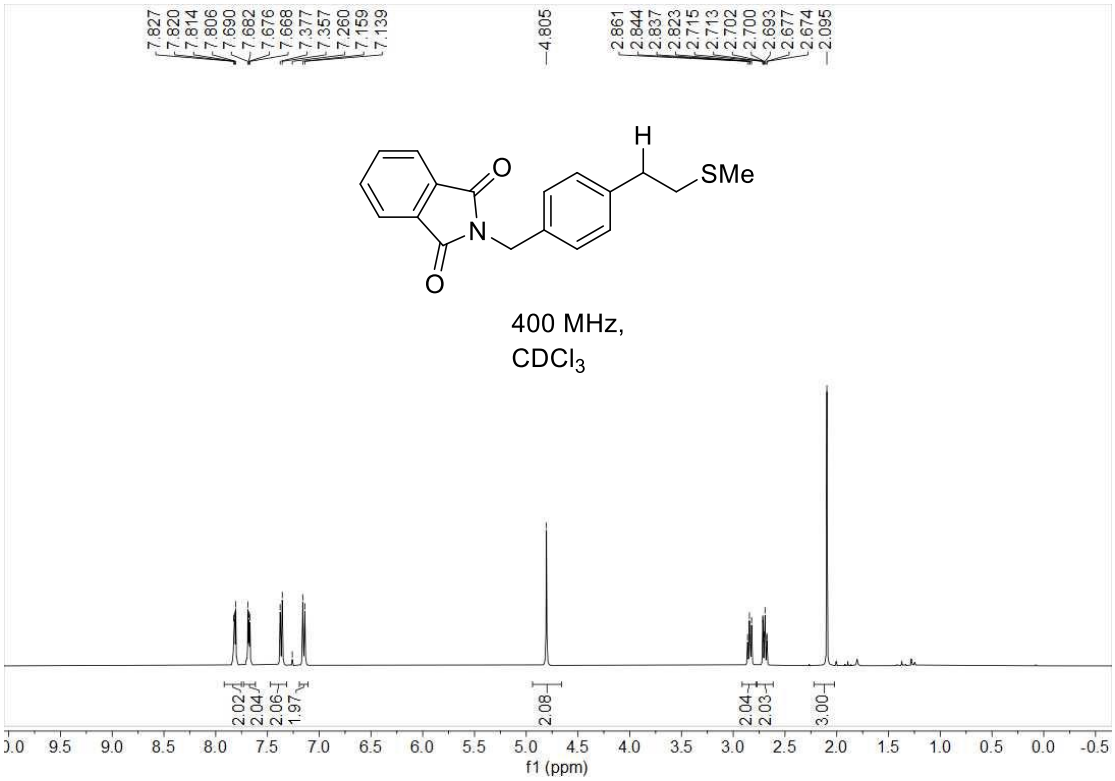
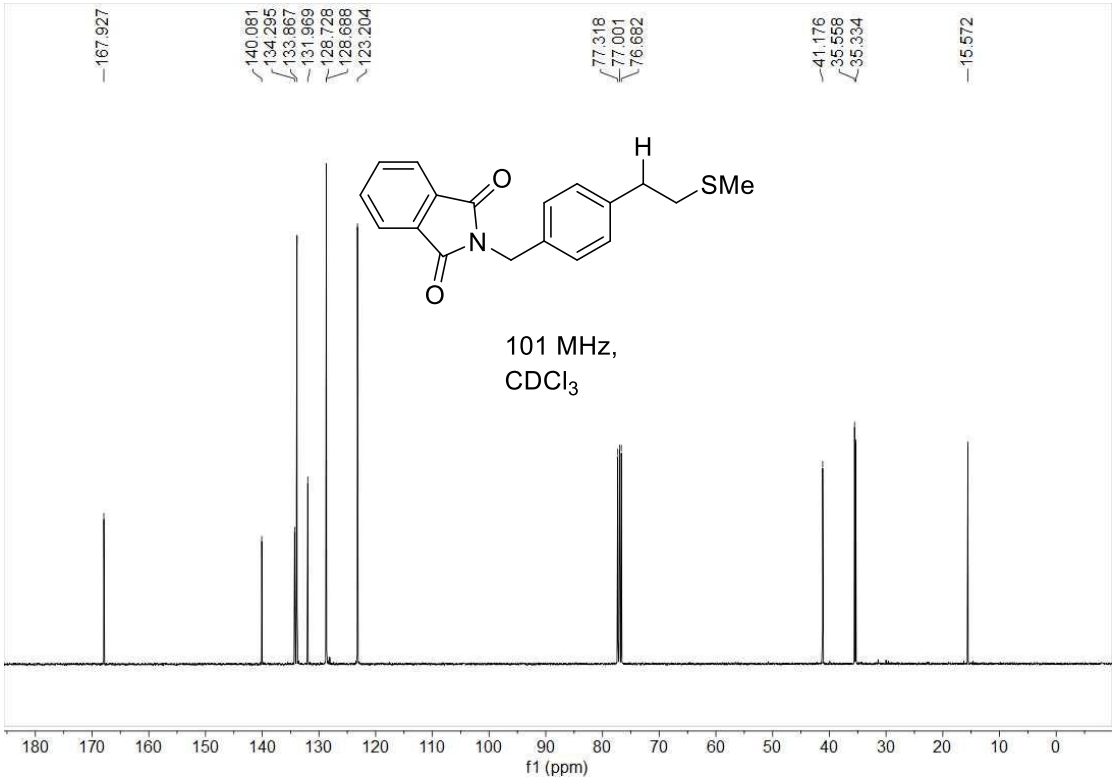
8.143
7.380
7.375
7.363
7.358
7.260
3.020
3.002
2.982
2.801
2.787
2.785
2.781
2.763
2.119
NO2
MeS
H
400 MHz,
CDCl3
1.96
2.00
2.05
2.02
3.00
f1 (ppm)

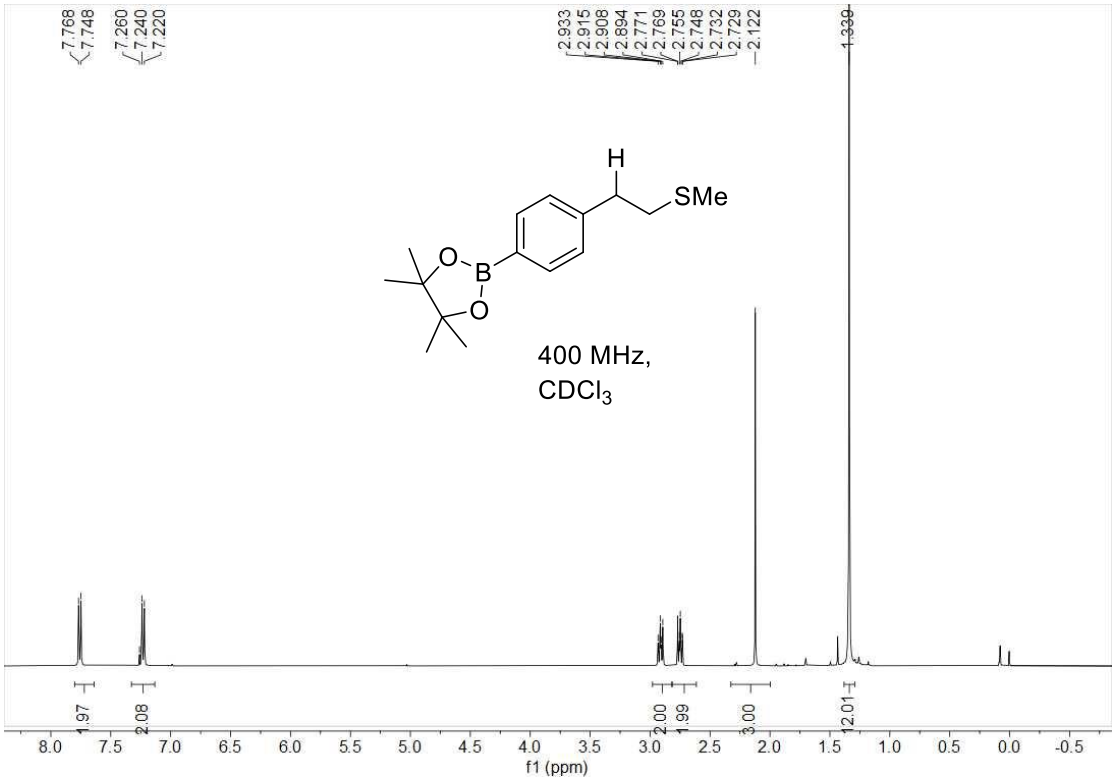

148.089
146.572
129.366
123.658
77.318
77.000
76.682
35.390
35.046
15.702
NO2
MeS
H
101 MHz,
CDCl3
f1 (ppm)

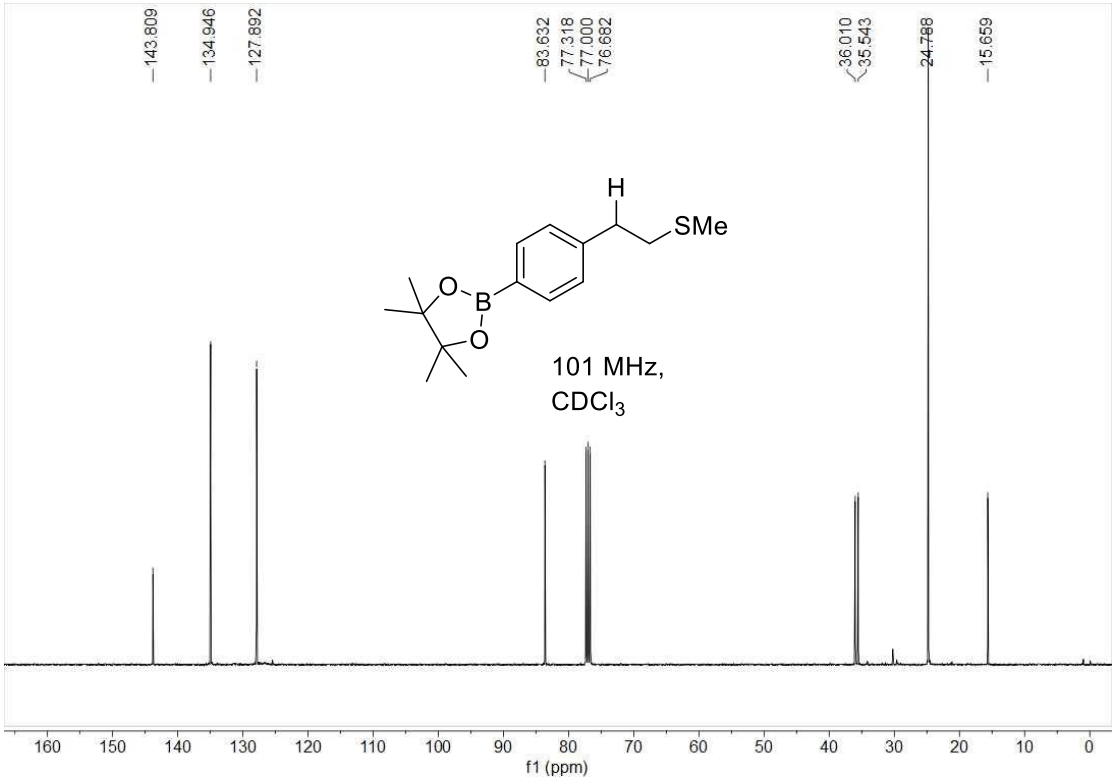

7.840
7.832
7.828
7.823
7.818
7.802
7.648
7.645
7.629
7.626
7.624
7.392
7.373
7.371
7.357
7.352
7.339
7.335
7.323
7.319
7.260
7.173
7.170
7.167
7.155
7.151
7.148
7.136
7.133
7.130
2.990
2.972
2.952
2.803
2.782
2.765
2.136
H
SMe
H
N
Ph
O
400 MHz,
CDCl3
1.90
1.17
2.12
4.22
1.15
2.21
2.16
3.00
9.5 9.0 8.5 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)

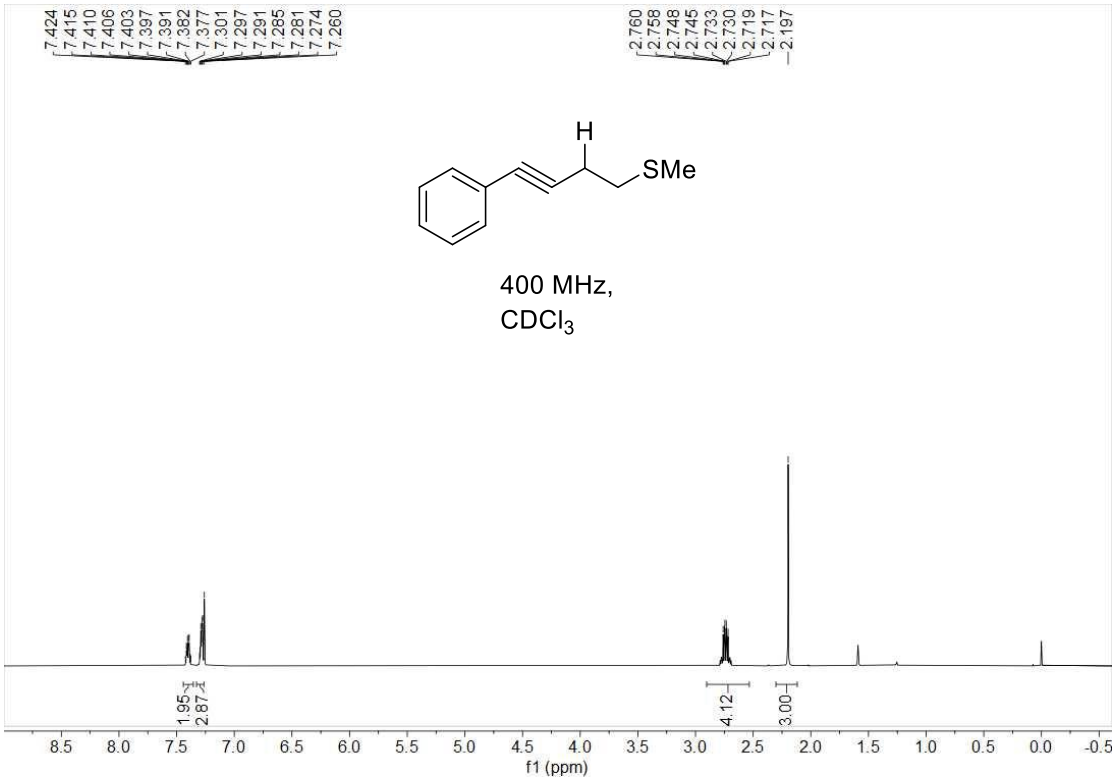

165.502
144.720
137.885
133.017
129.084
128.963
127.208
124.489
120.074
77.318
77.000
76.683
35.538
35.424
15.747
H
SMe
H
N
Ph
O
101 MHz,
CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

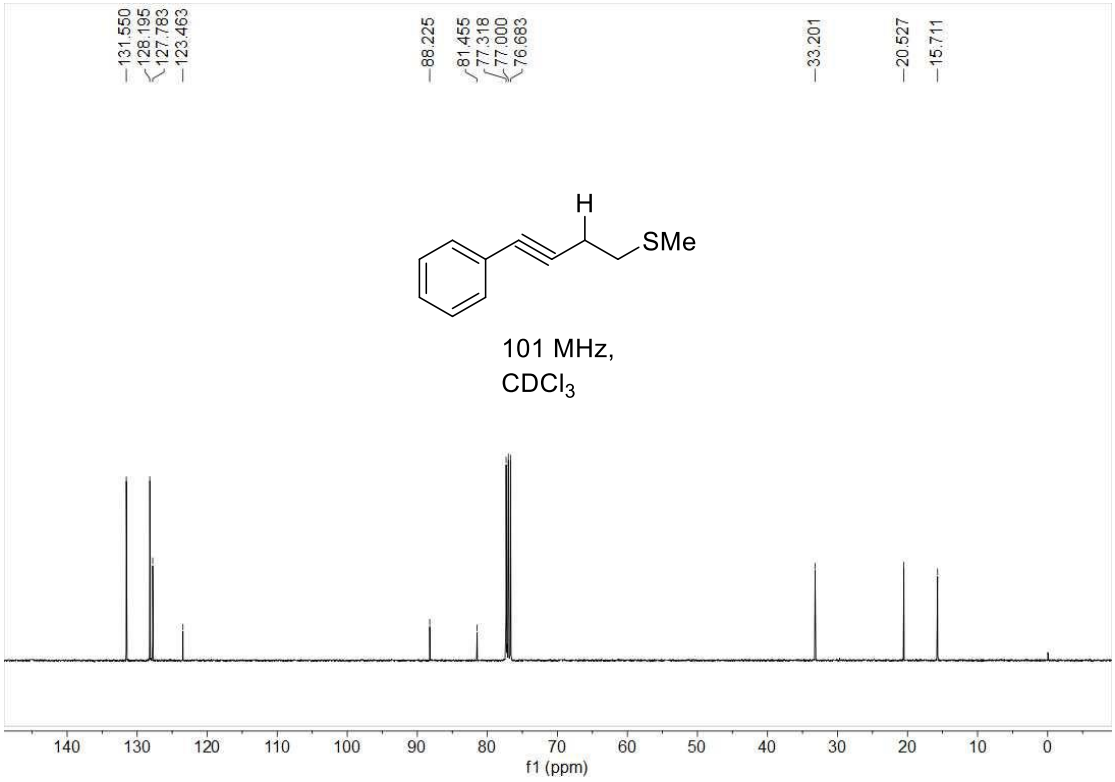

7.827
7.820
7.814
7.806
7.690
7.682
7.676
7.668
7.377
7.357
7.260
7.159
7.139
4.805
2.861
2.844
2.837
2.823
2.715
2.713
2.702
2.700
2.693
2.677
2.674
2.095
H
SMe
O
N
O
400 MHz,
CDCl3
2.02
2.04
2.06
1.97
2.08
2.04
2.03
3.00
f1 (ppm)

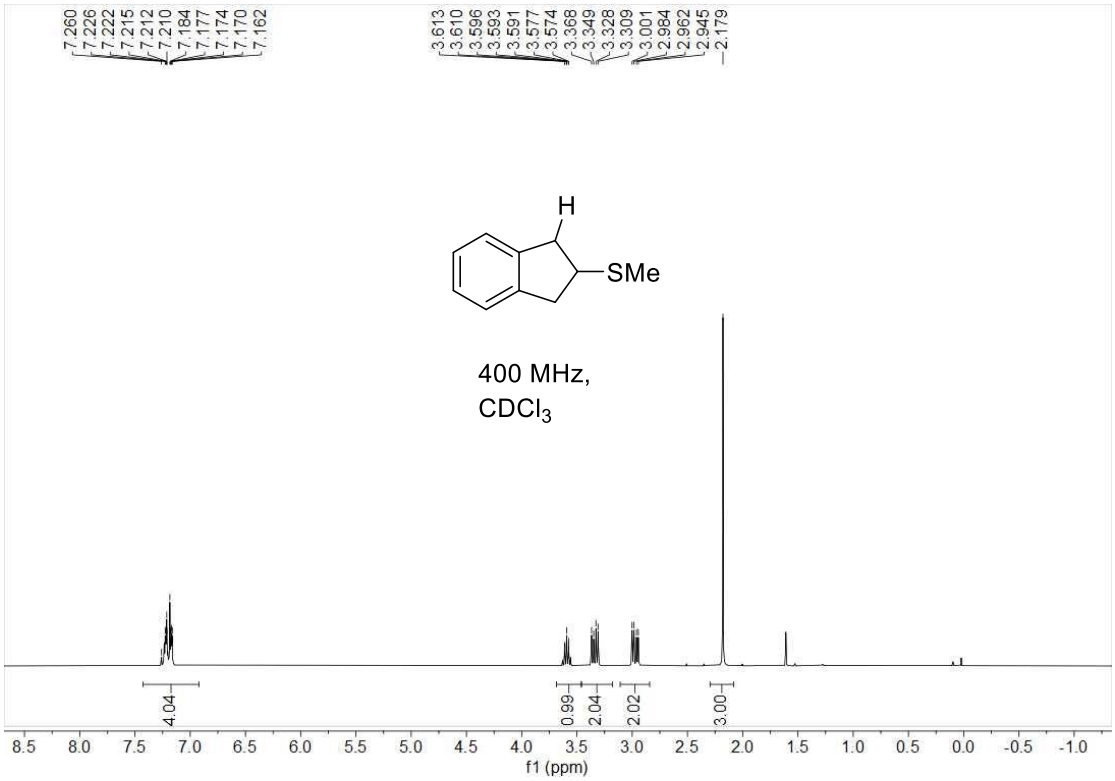

167.927
140.081
134.295
133.867
131.969
128.728
128.688
123.204
77.318
77.001
76.682
41.176
35.558
35.334
15.572
H
SMe
O
N
O
101 MHz,
CDCl3
f1 (ppm)

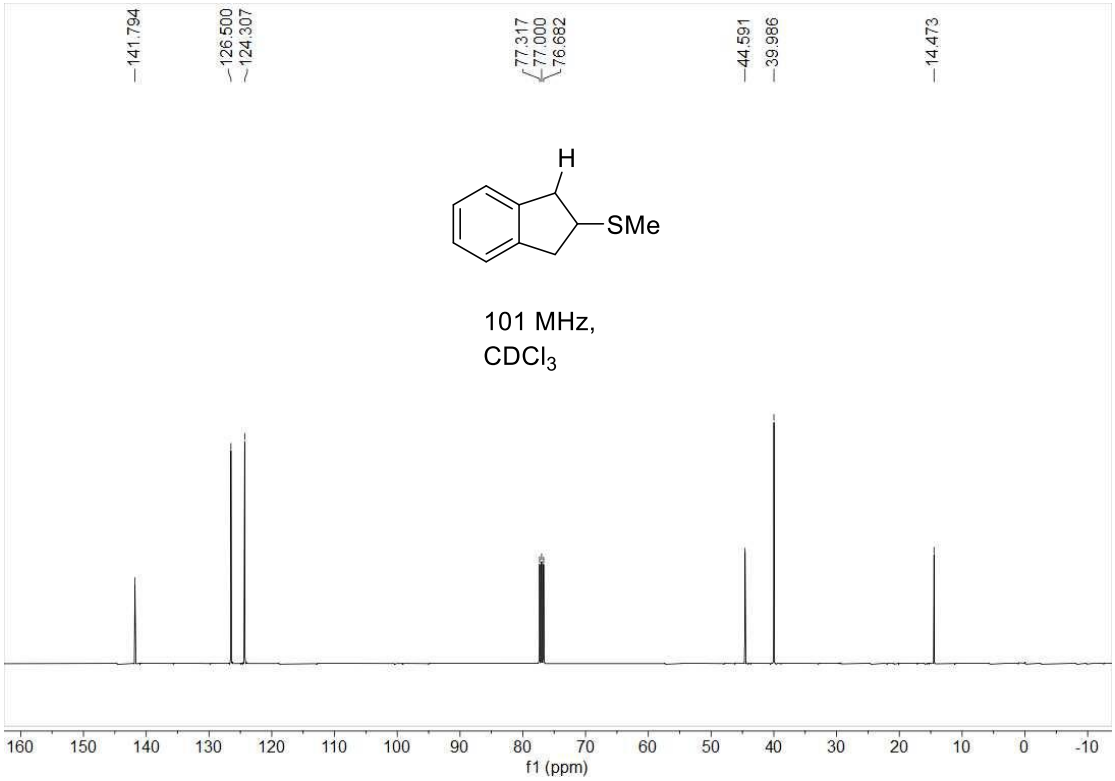

7.768
7.748
7.260
7.240
7.220
2.933
2.915
2.908
2.894
2.771
2.769
2.755
2.748
2.732
2.729
2.122
1.339
H
SMe
O
B
O
400 MHz,
CDCl3
1.97
2.08
2.00
1.99
3.00
12.01
f1 (ppm)

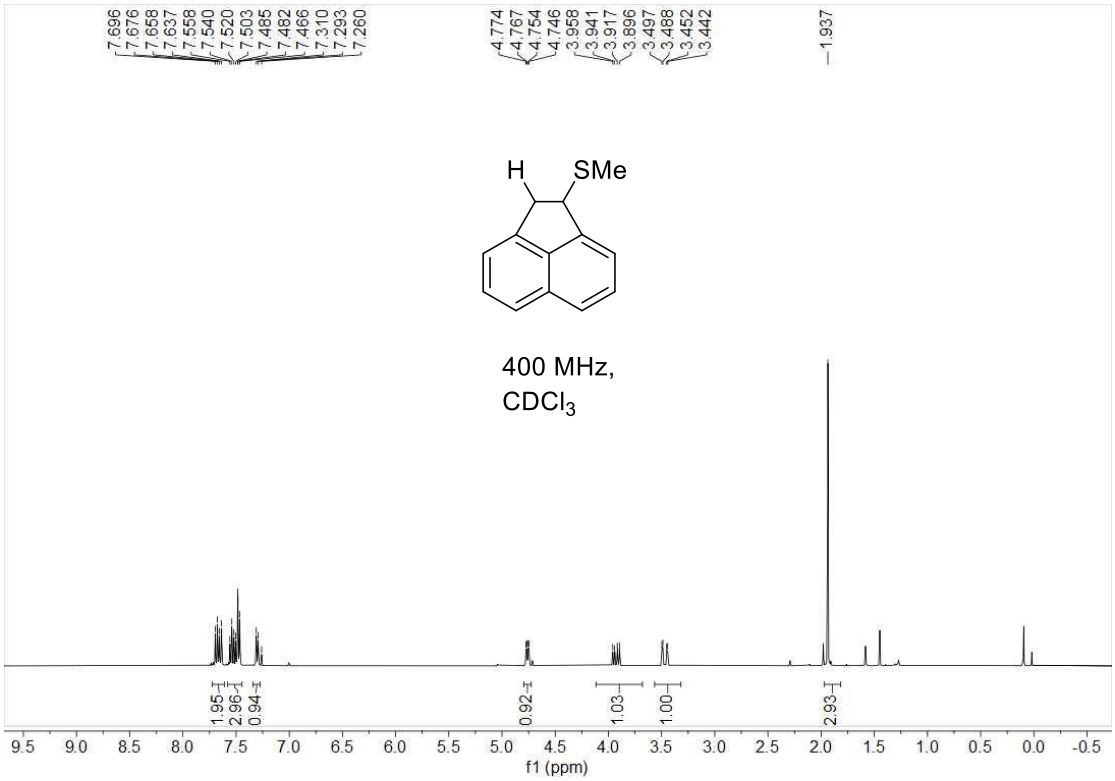

143.809
134.946
127.892
83.632
77.318
77.000
76.682
36.010
35.543
24.788
15.659
H
SMe
O
B
O
101 MHz,
CDCl3
f1 (ppm)

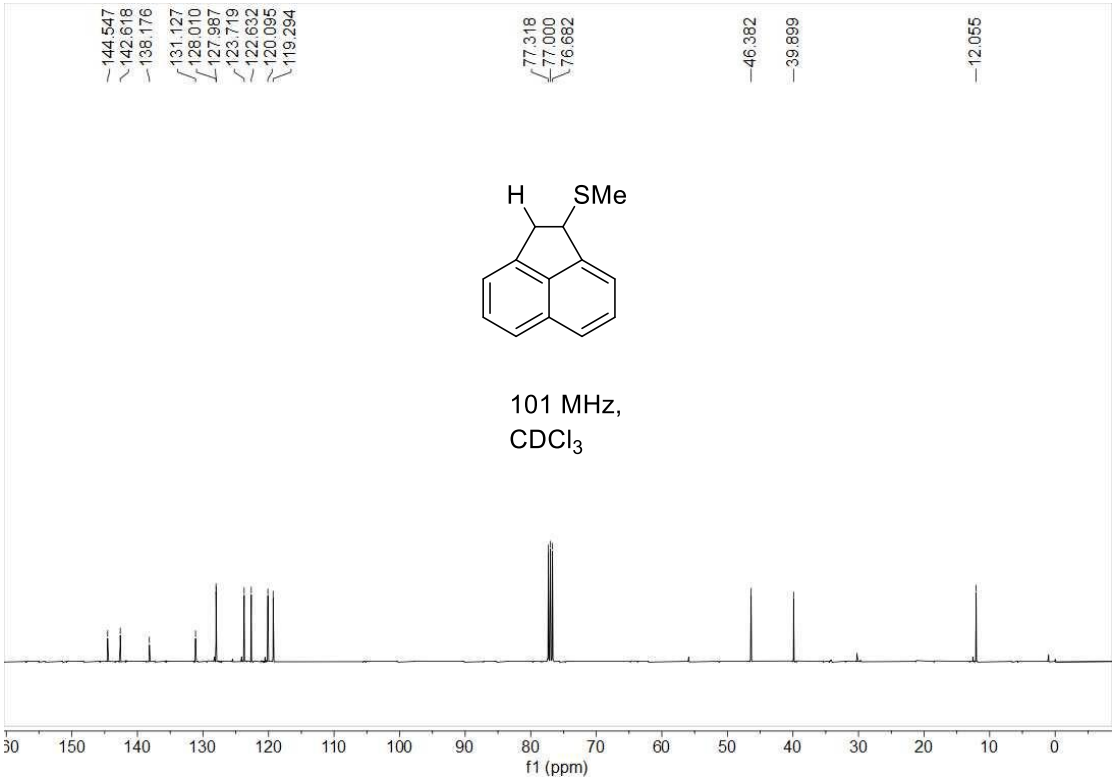

7.424
7.415
7.410
7.406
7.403
7.397
7.391
7.382
7.377
7.301
7.297
7.291
7.285
7.281
7.274
7.260
2.760
2.758
2.748
2.745
2.733
2.730
2.719
2.717
2.197
H
SMe
400 MHz,
CDCl3
1.95
2.87
4.12
3.00
f1 (ppm)

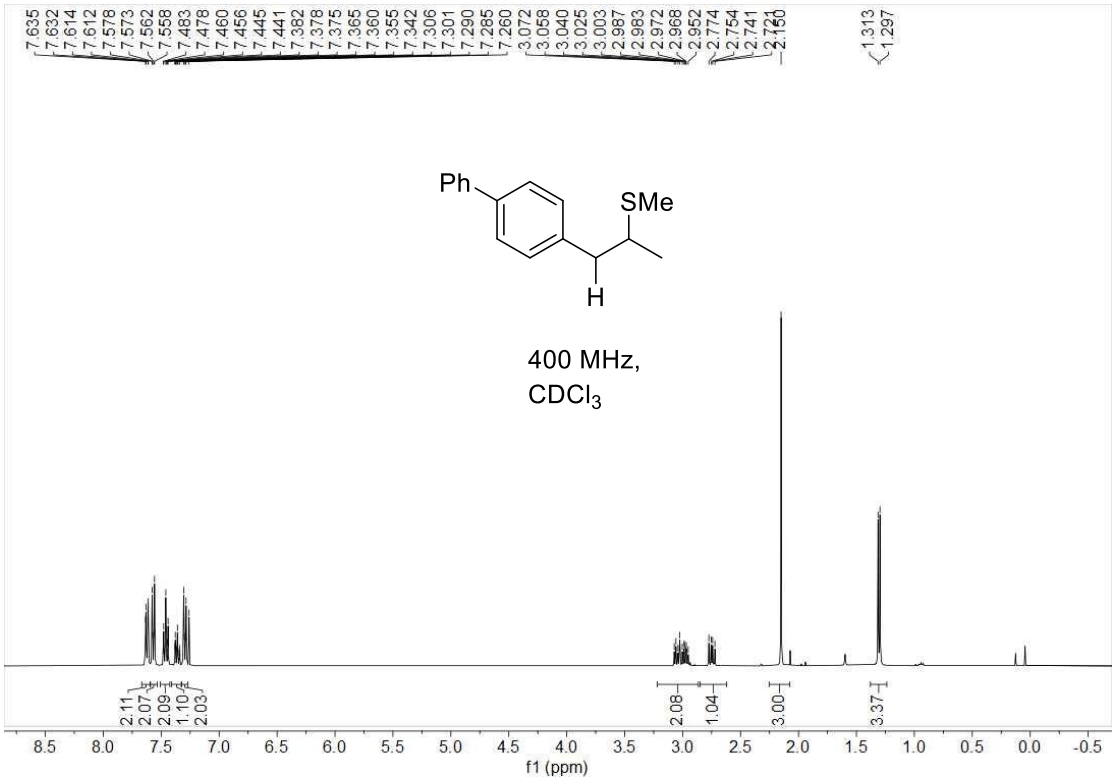

131.550
128.195
127.783
123.463
88.225
81.455
77.318
77.000
76.683
33.201
20.527
15.711
H
SMe
101 MHz,
CDCl3
f1 (ppm)

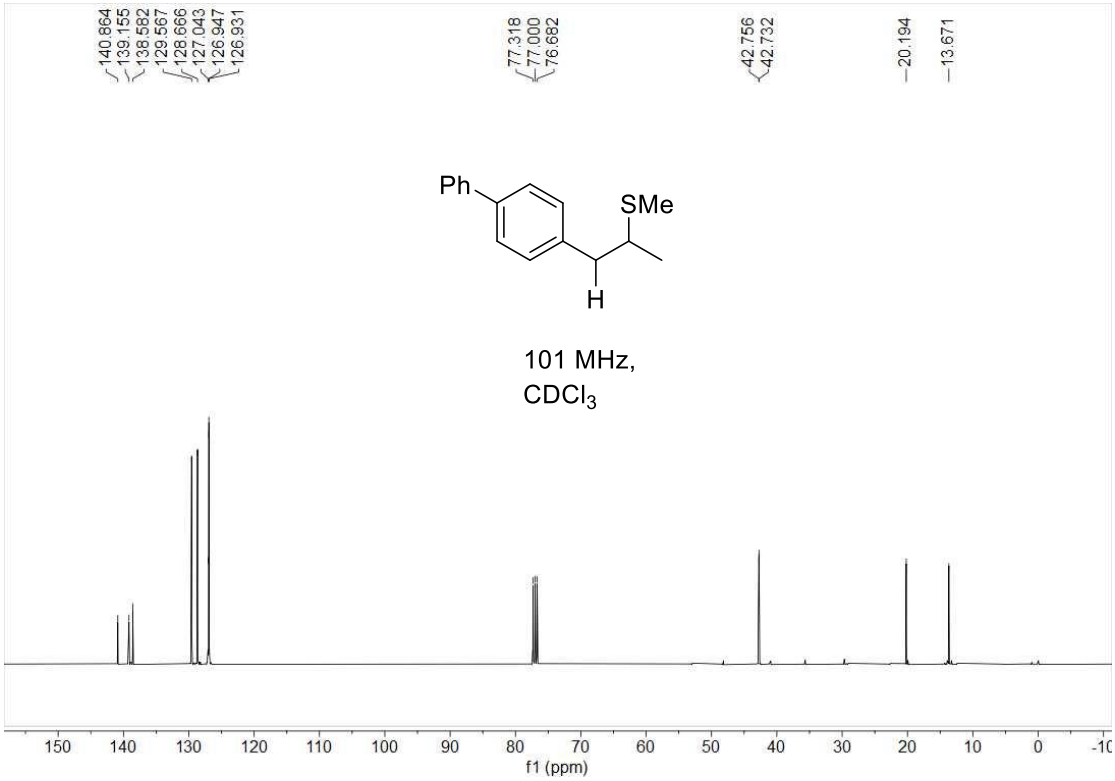

7.260
7.226
7.222
7.215
7.212
7.210
7.184
7.177
7.174
7.170
7.162
3.613
3.610
3.596
3.593
3.591
3.577
3.574
3.368
3.349
3.328
3.309
3.001
2.984
2.962
2.945
2.179
H
SMe
400 MHz,
CDCl3
4.04
0.99
2.04
2.02
3.00
f1 (ppm)

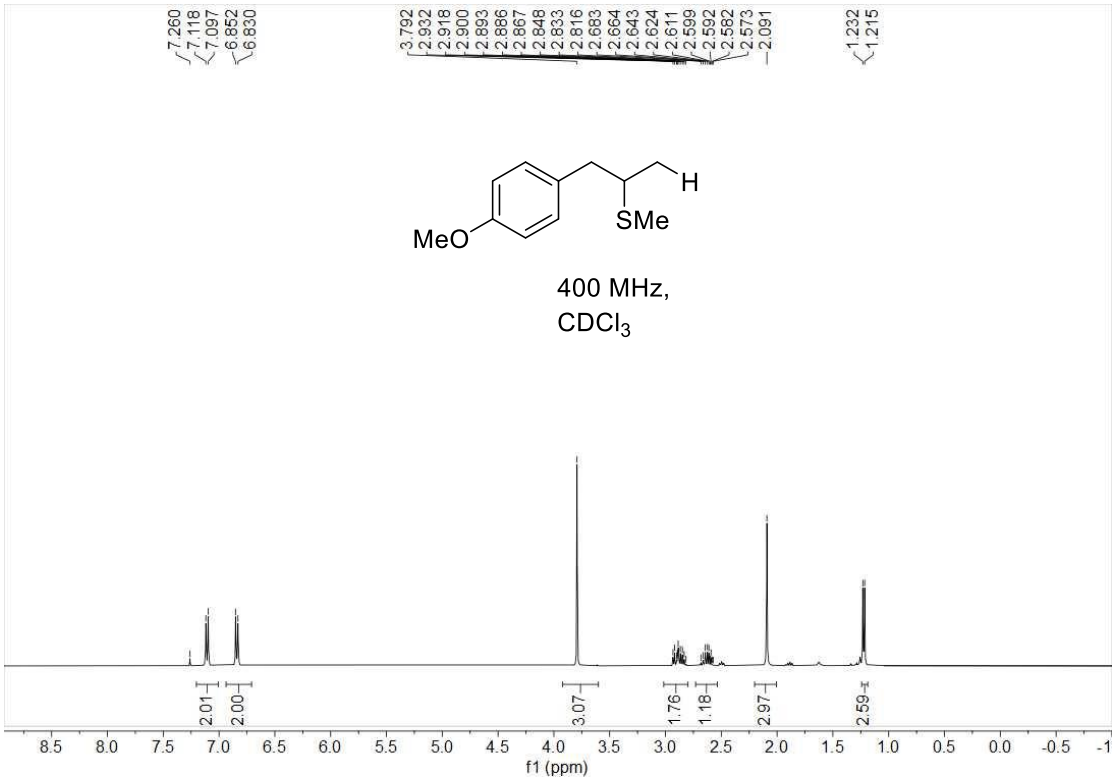

141.794
126.500
124.307
77.317
77.000
76.682
44.591
39.986
14.473
H
SMe
101 MHz,
CDCl3
f1 (ppm)


7.696
7.676
7.658
7.637
7.558
7.540
7.520
7.503
7.485
7.482
7.466
7.310
7.293
7.260
4.774
4.767
4.754
4.746
3.958
3.941
3.917
3.896
3.497
3.488
3.452
3.442
1.937
H
SMe
400 MHz,
CDCl3
1.95
2.96
0.94
0.92
1.03
1.00
2.93
f1 (ppm)

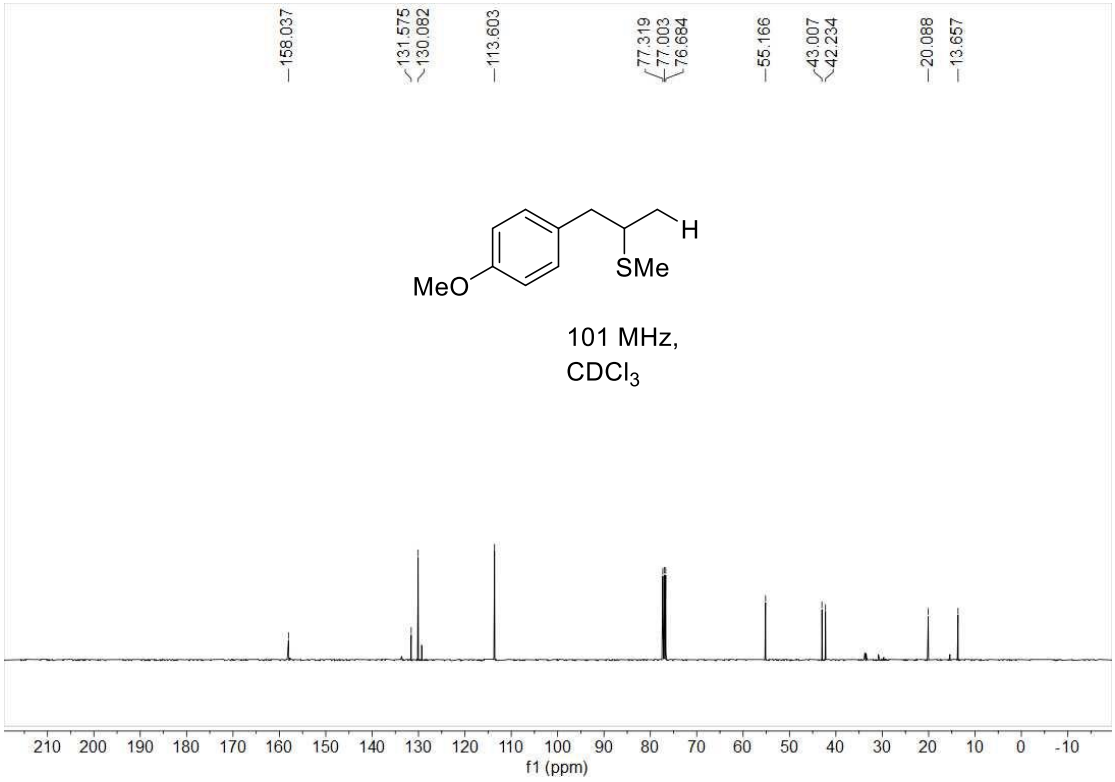

144.547
142.618
138.176
131.127
128.010
127.987
123.719
122.632
120.095
119.294
77.318
77.000
76.682
46.382
39.899
12.055
H
SMe
101 MHz,
CDCl3
f1 (ppm)


7.635
7.632
7.614
7.612
7.578
7.573
7.562
7.558
7.483
7.478
7.460
7.456
7.445
7.441
7.382
7.378
7.375
7.365
7.360
7.355
7.342
7.306
7.301
7.290
7.285
7.260
3.072
3.058
3.040
3.025
3.003
2.987
2.983
2.972
2.968
2.952
2.774
2.754
2.741
2.721
2.150
1.313
1.297
Ph
SMe
H
400 MHz,
CDCl3
2.11
2.07
2.09
1.10
2.03
2.08
1.04
3.00
3.37
f1 (ppm)

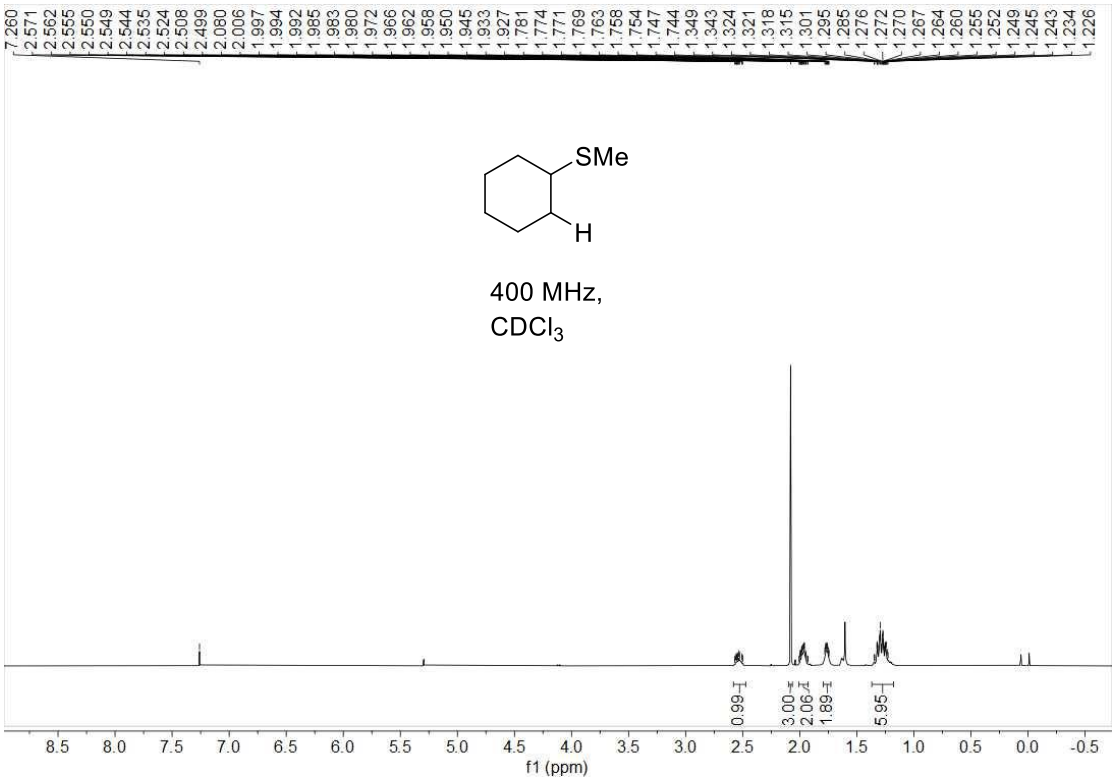

140.864
139.155
138.582
129.567
128.666
127.043
126.947
126.931
77.318
77.000
76.682
42.756
42.732
20.194
13.671
Ph
SMe
H
101 MHz,
CDCl3
f1 (ppm)

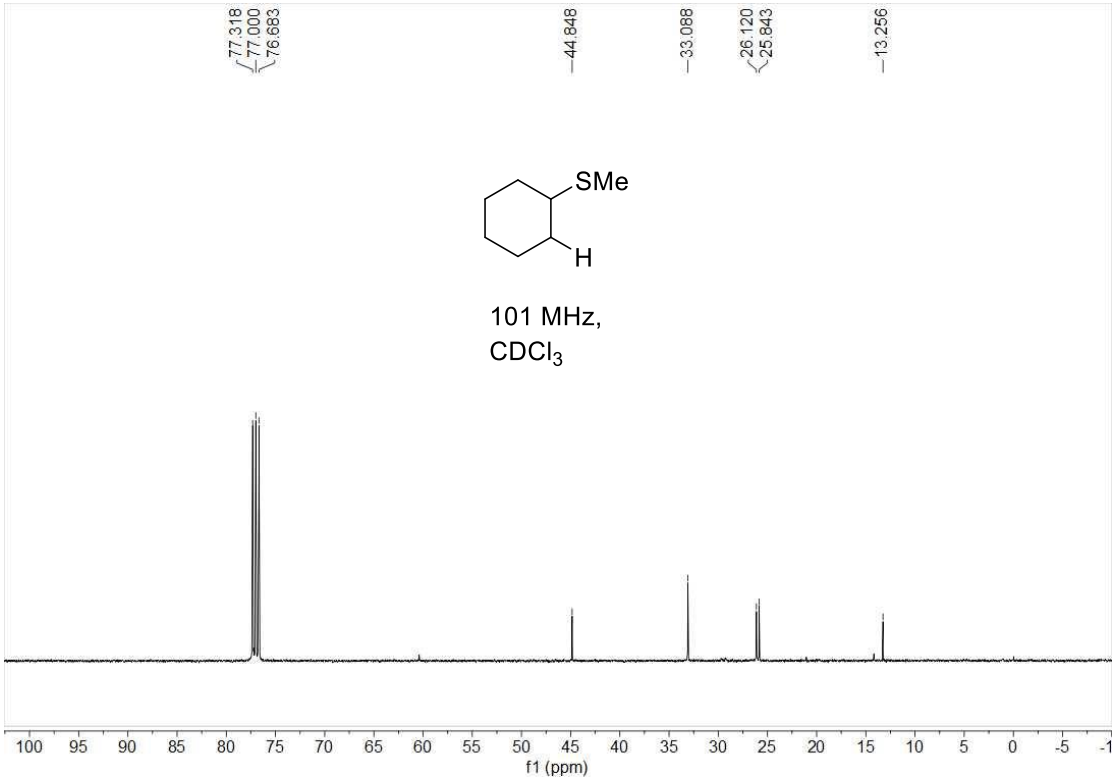


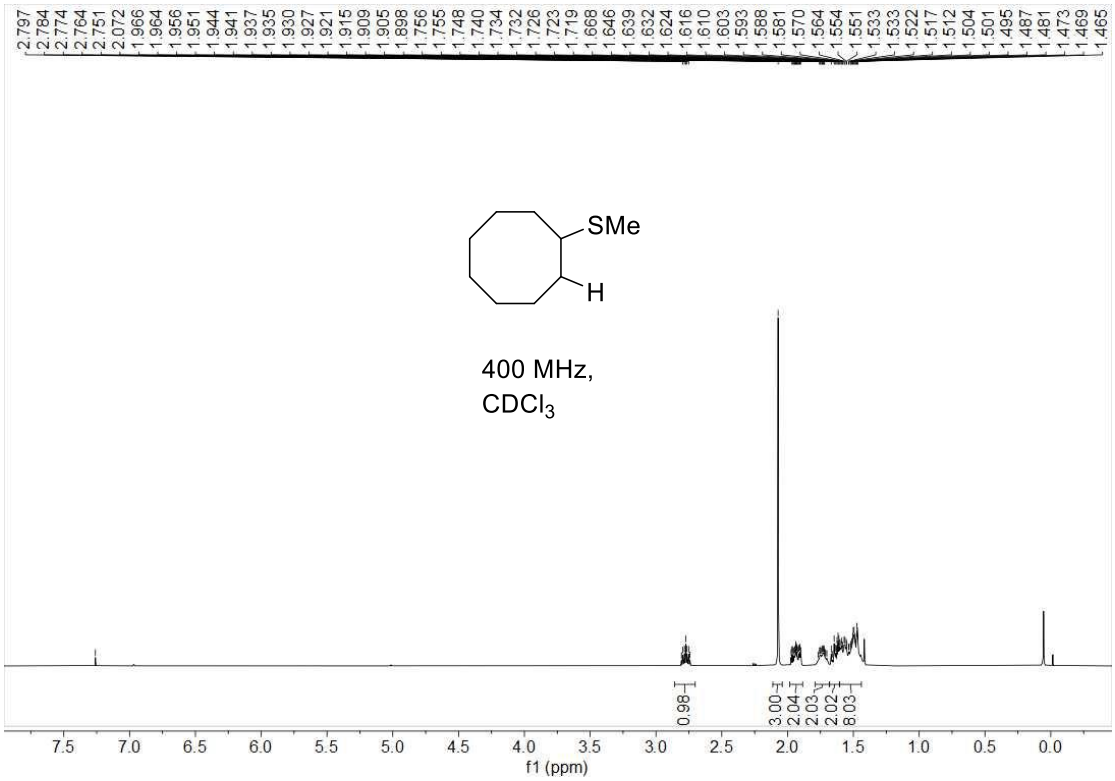
400 MHz,
$CDCl_3$

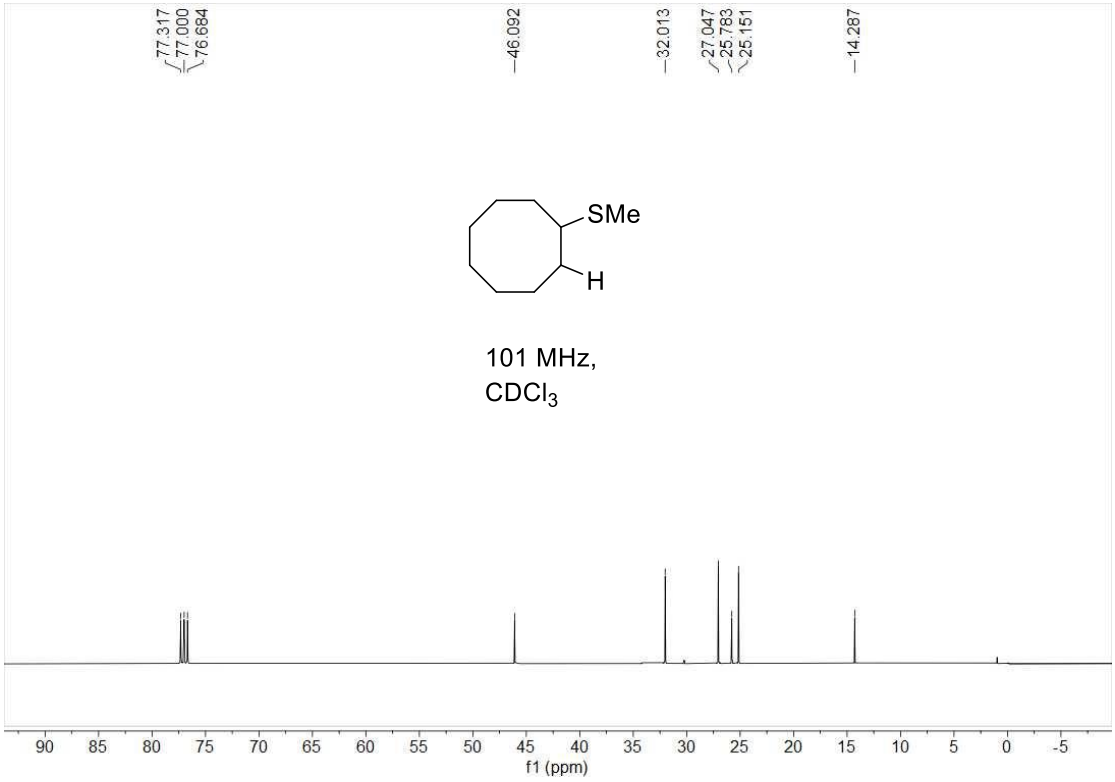


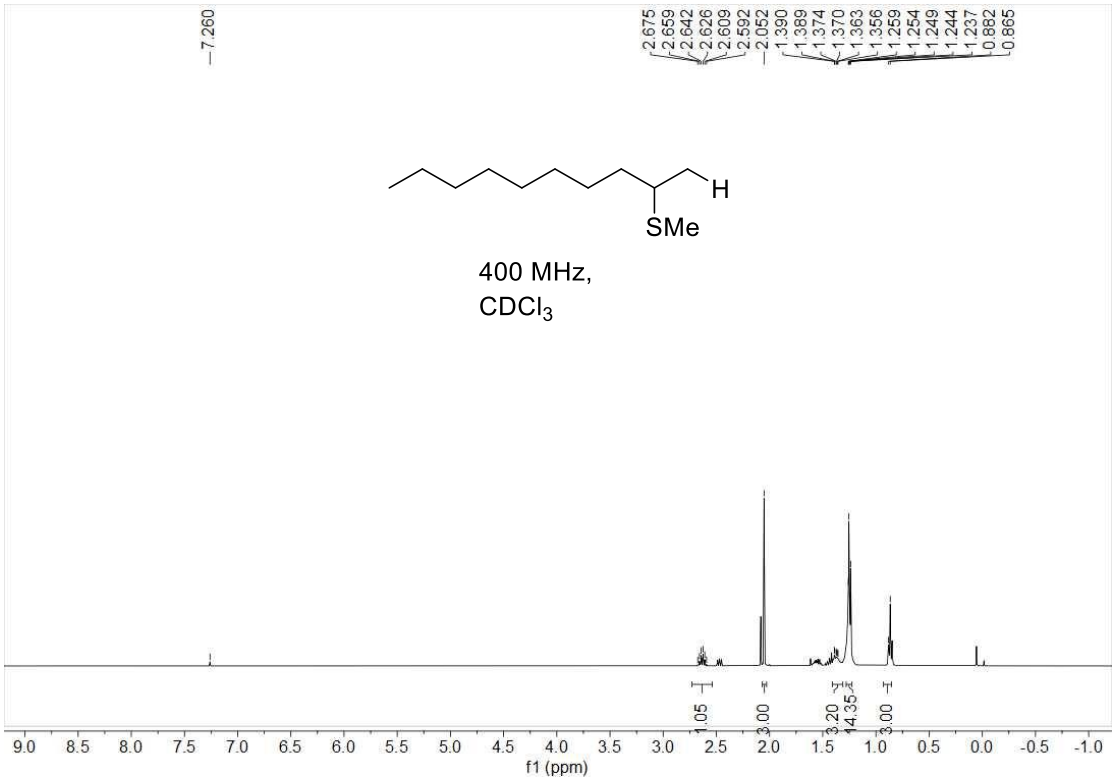
101 MHz,
$CDCl_3$


SMe
H
400 MHz,
CDCl3
f1 (ppm)

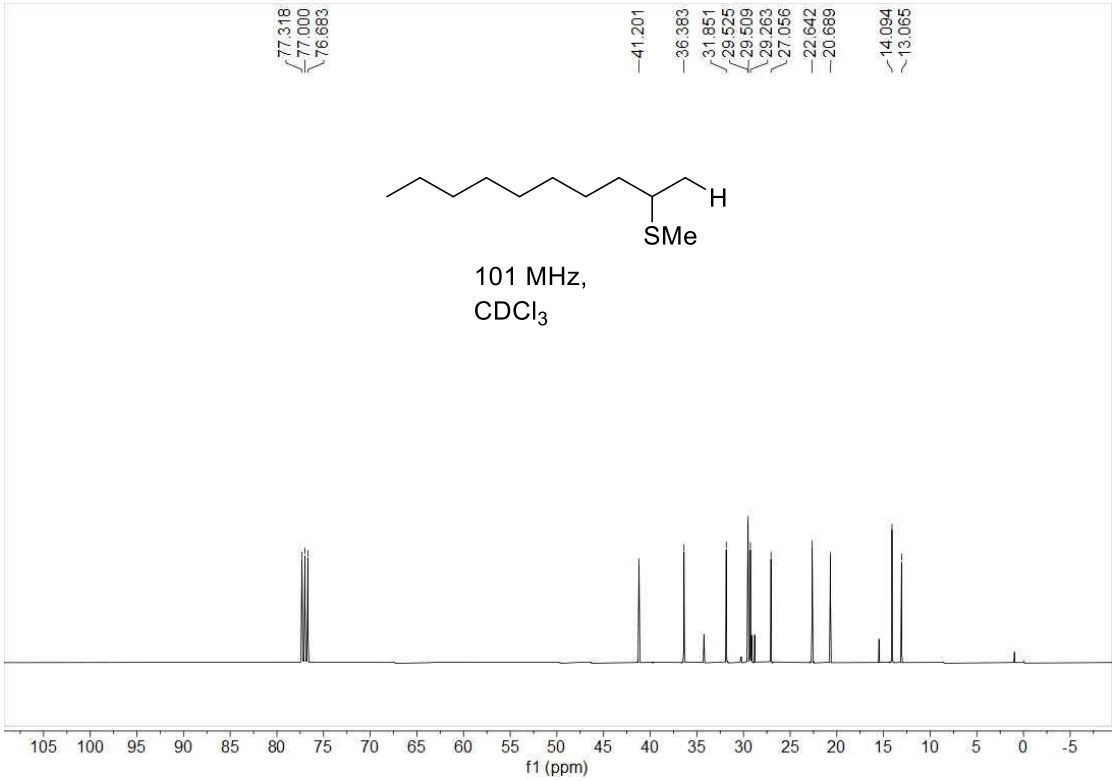

SMe
H
101 MHz,
CDCl3
f1 (ppm)


SMe
H
400 MHz,
CDCl3
f1 (ppm)

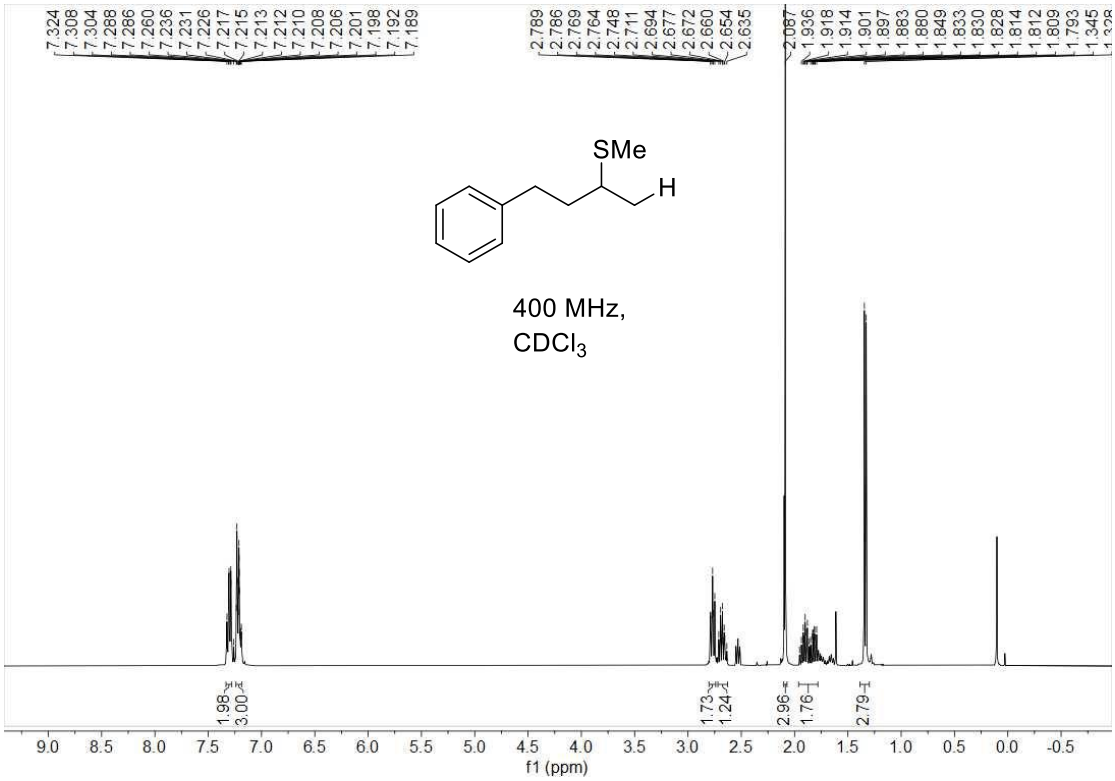

SMe
H
101 MHz,
CDCl3
f1 (ppm)

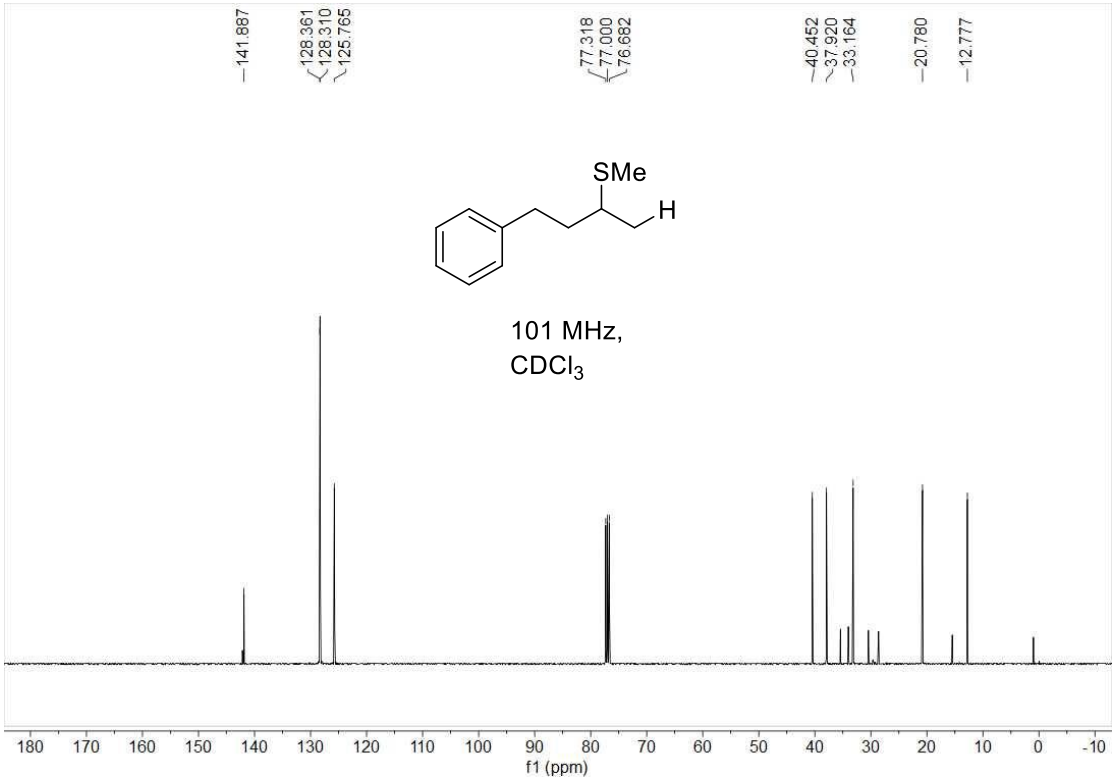


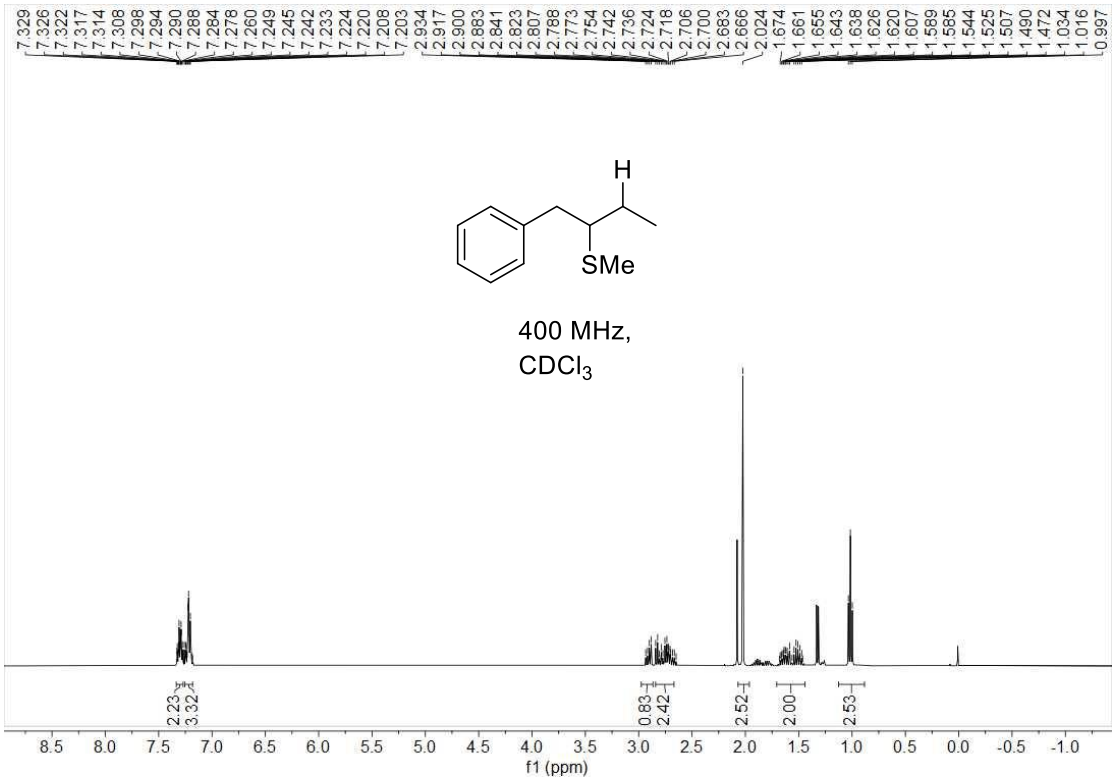
400 MHz,
$CDCl_3$



101 MHz,
$CDCl_3$


SMe
H
400 MHz,
CDCl3
f1 (ppm)


SMe
H
101 MHz,
CDCl3
f1 (ppm)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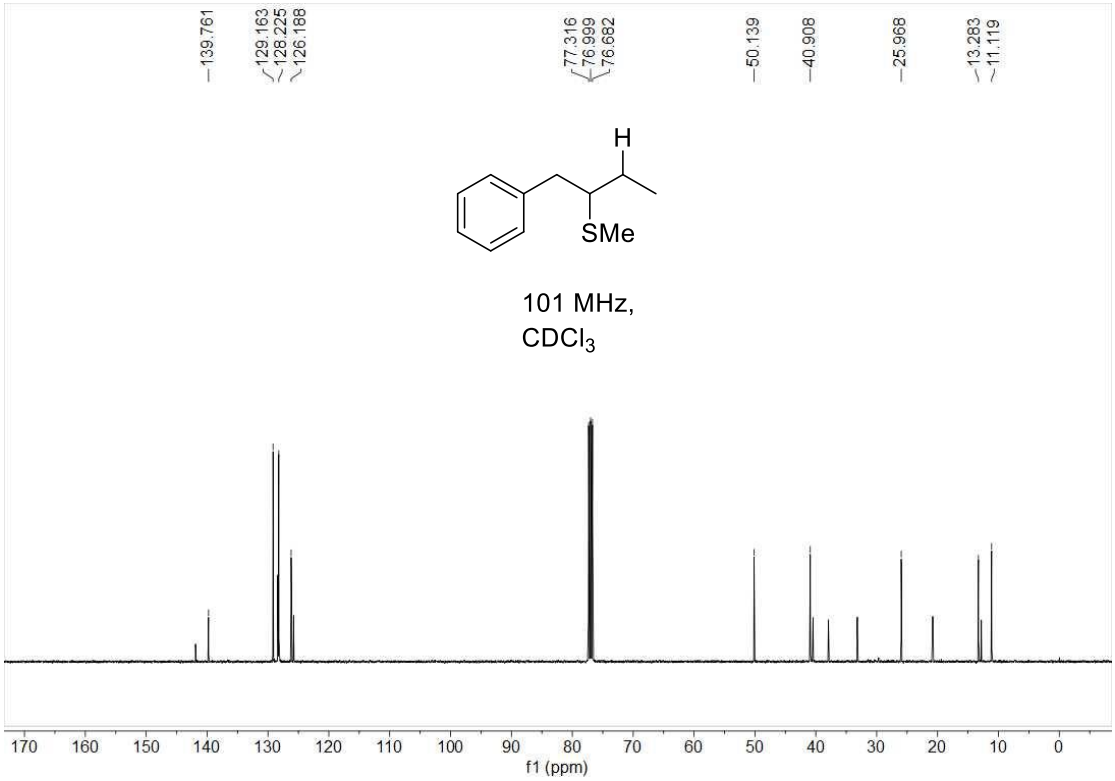
7.288
7.284
7.278
7.260
7.249
7.245
7.242
7.233
7.224
7.220
7.208
7.203
2.934
2.917
2.900
2.883
2.841
2.823
2.807
2.788
2.773
2.754
2.742
2.736
2.724
2.718
2.706
2.700
2.683
2.666
2.024
1.674
1.661
1.655
1.643
1.638
1.626
1.620
1.607
1.589
1.585
1.544
1.525
1.507
1.490
1.472
1.034
1.016
0.997
H
SMe
400 MHz,
CDCl3
2.23
3.32
0.83
2.42
2.52
2.00
2.53
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 -1.0
f1 (ppm)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77.316
76.999
76.682
50.139
40.908
25.968
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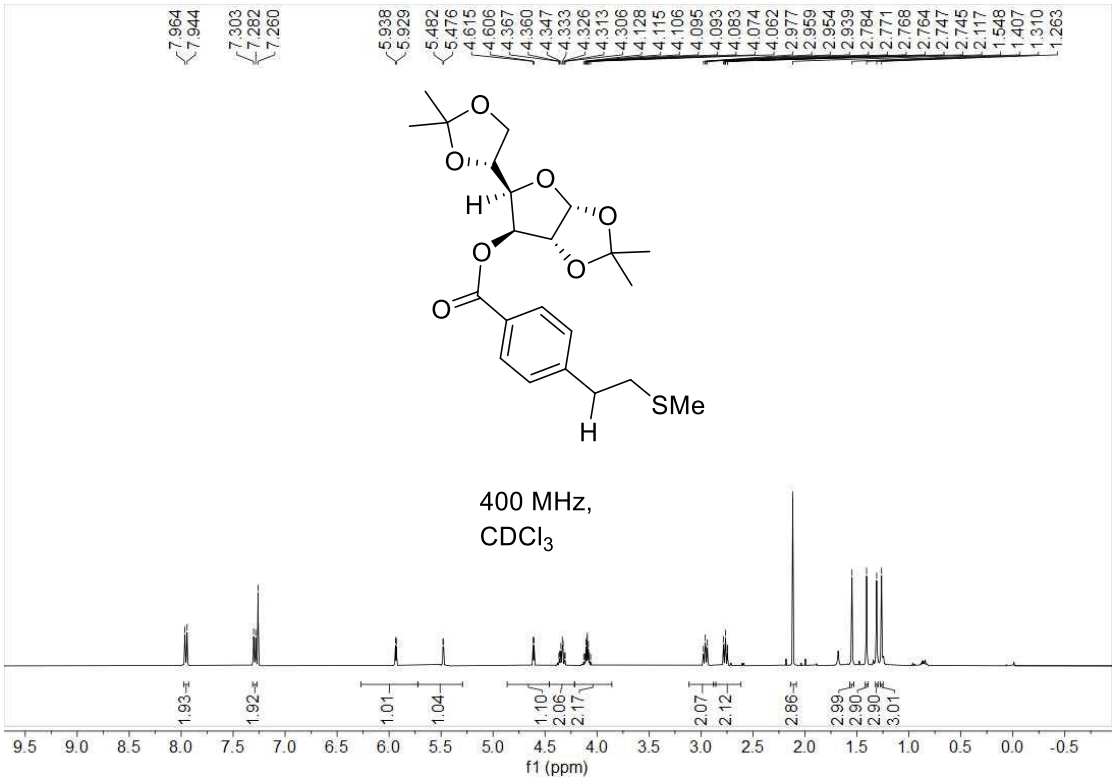
11.119
H
SMe
101 MHz,
CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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5.476
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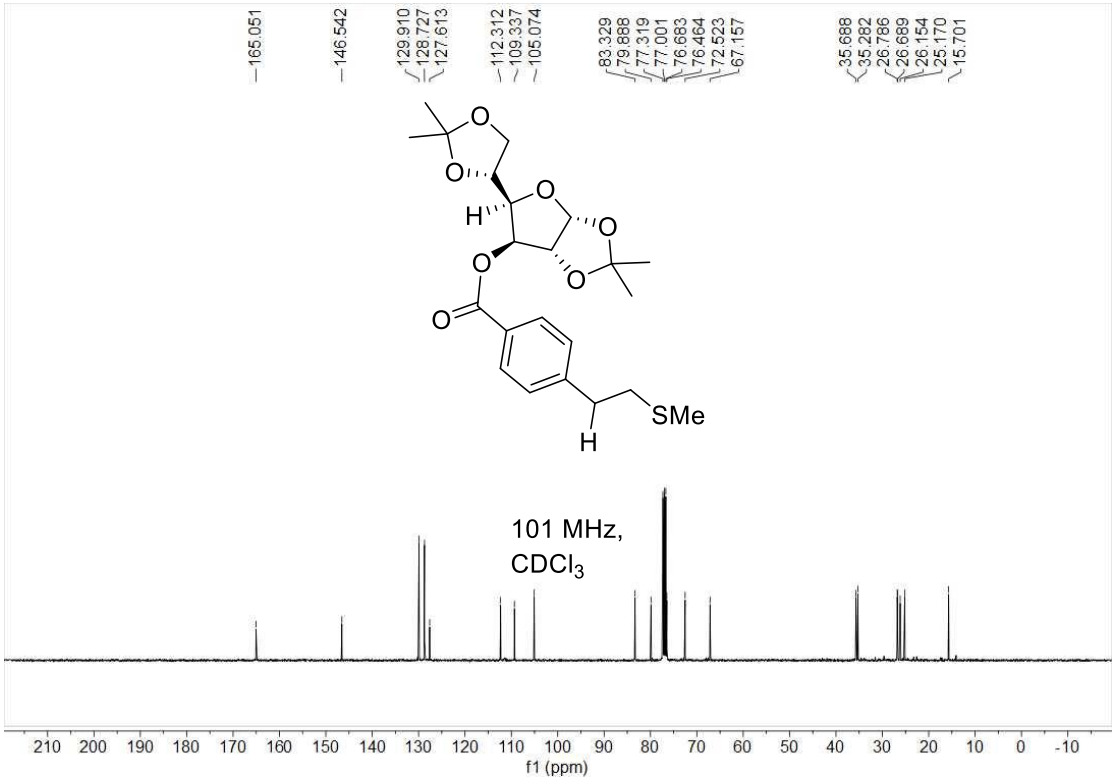
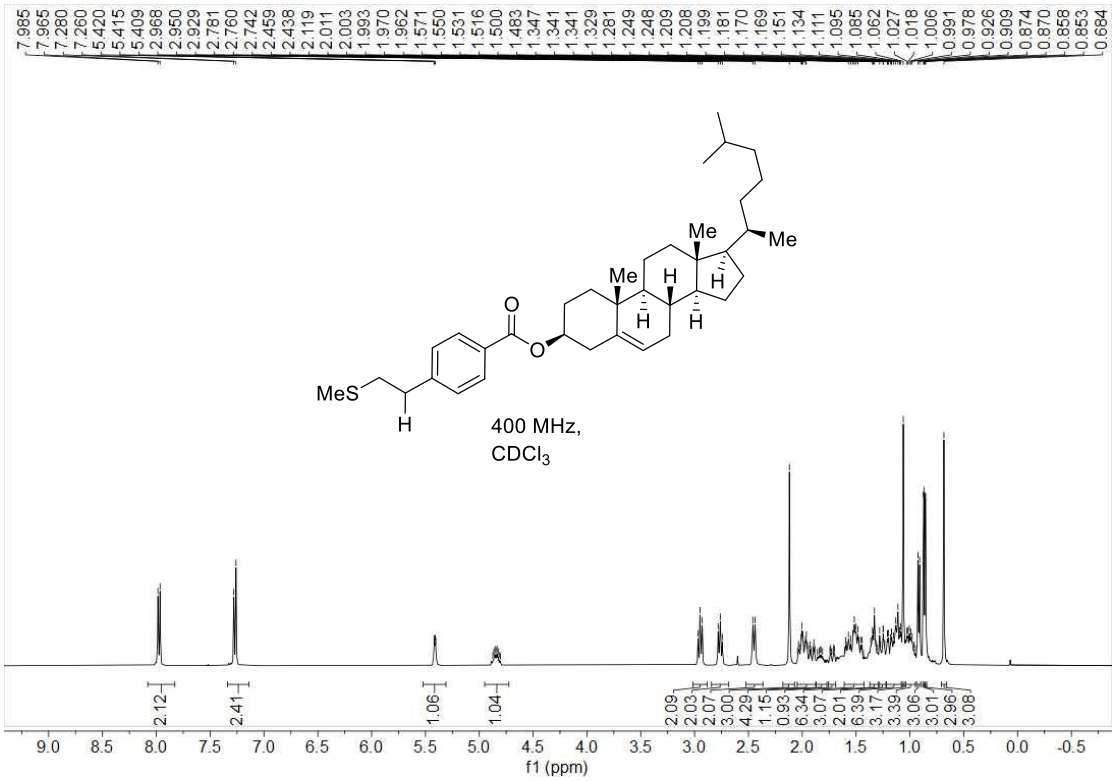
4.360
4.347
4.333
4.326
4.313
4.306
4.128
4.115
4.106
4.095
4.093
4.083
4.074
4.062
2.977
2.959
2.954
2.939
2.784
2.771
2.768
2.764
2.747
2.745
2.117
1.548
1.407
1.310
1.263
O
O
O
H
O
O
O
O
O
SMe
H
400 MHz,
CDCl3
1.93
1.92
1.01
1.04
1.10
2.06
2.17
2.07
2.12
2.86
2.99
2.90
2.90
3.01
9.5 9.0 8.5 8.0 7.5 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)


165.051
146.542
129.910
128.727
127.613
112.312
109.337
105.074
83.329
79.888
77.319
77.001
76.683
76.464
72.523
67.157
35.688
35.282
26.786
26.689
26.154
25.170
15.701
O
O
O
H
O
O
O
O
O
SMe
H
101 MHz,
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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2.968
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2.929
2.781
2.760
2.742
2.459
2.438
2.119
2.011
2.003
1.993
1.970
1.962
1.571
1.550
1.531
1.516
1.500
1.483
1.347
1.341
1.341
1.329
1.281
1.249
1.248
1.209
1.208
1.199
1.181
1.170
1.169
1.151
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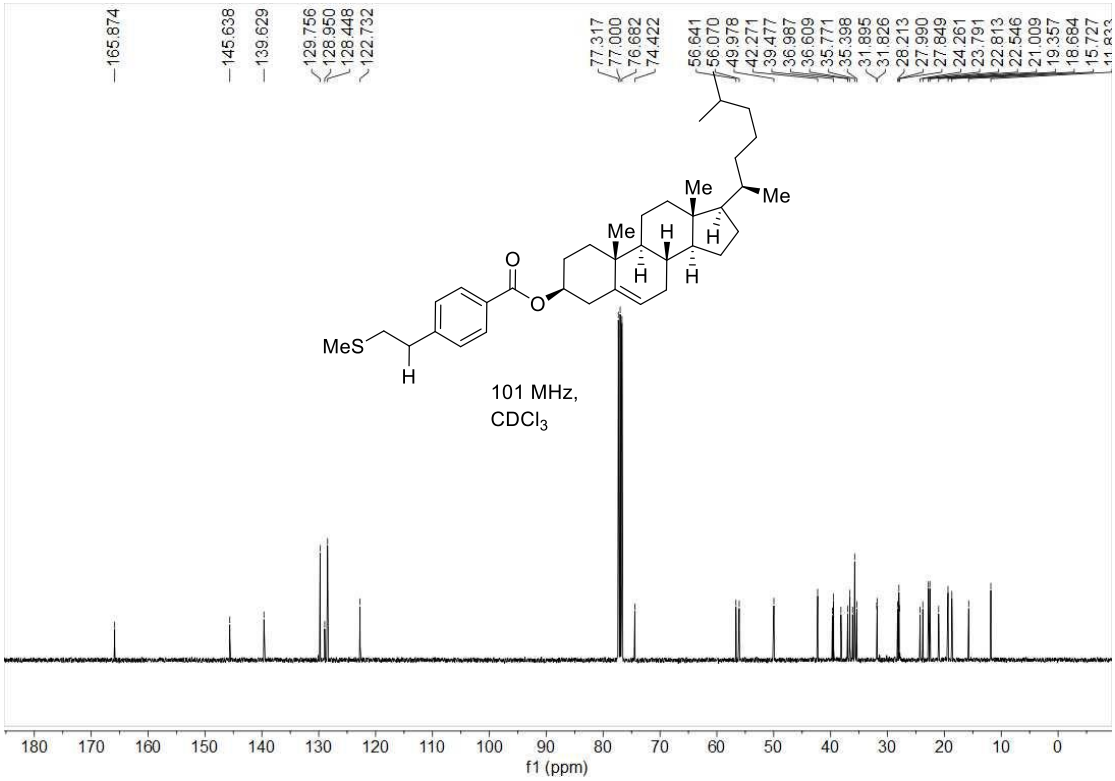
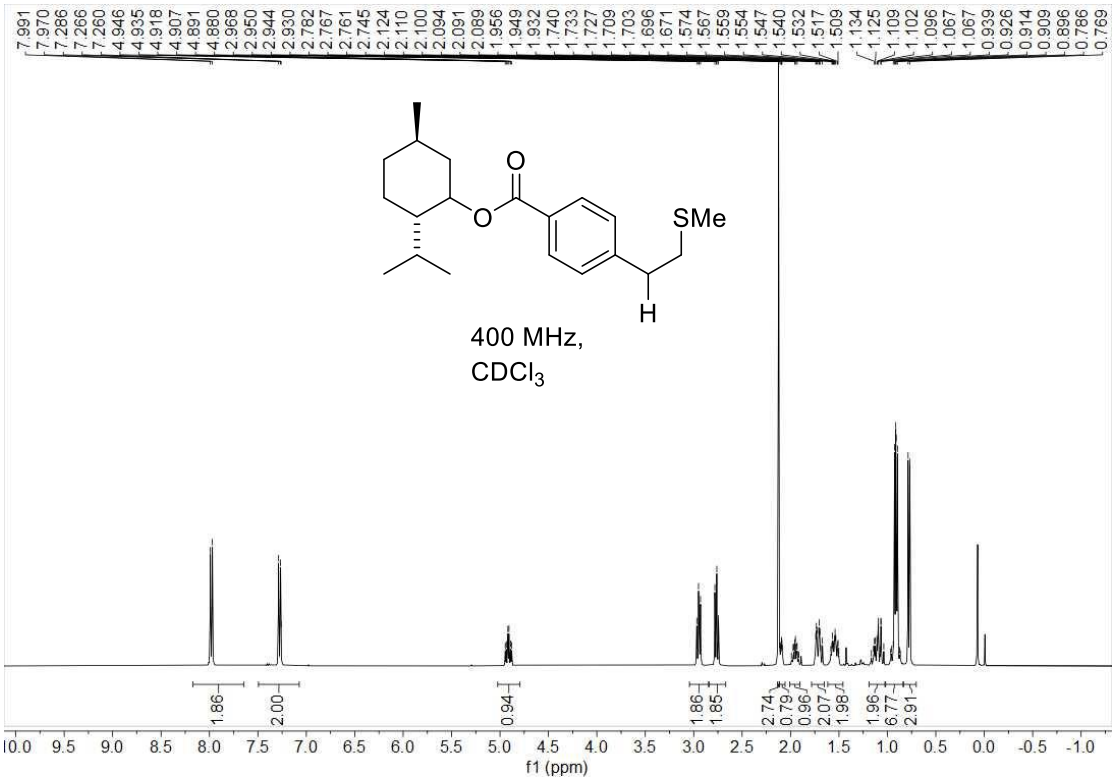
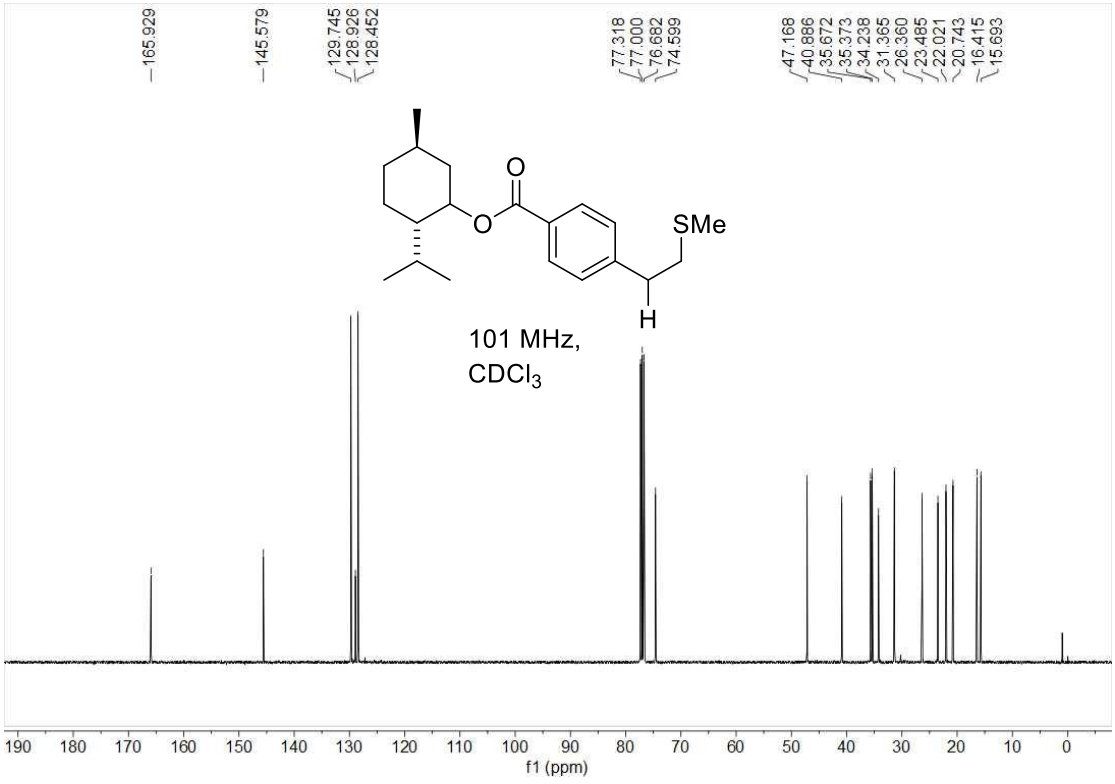
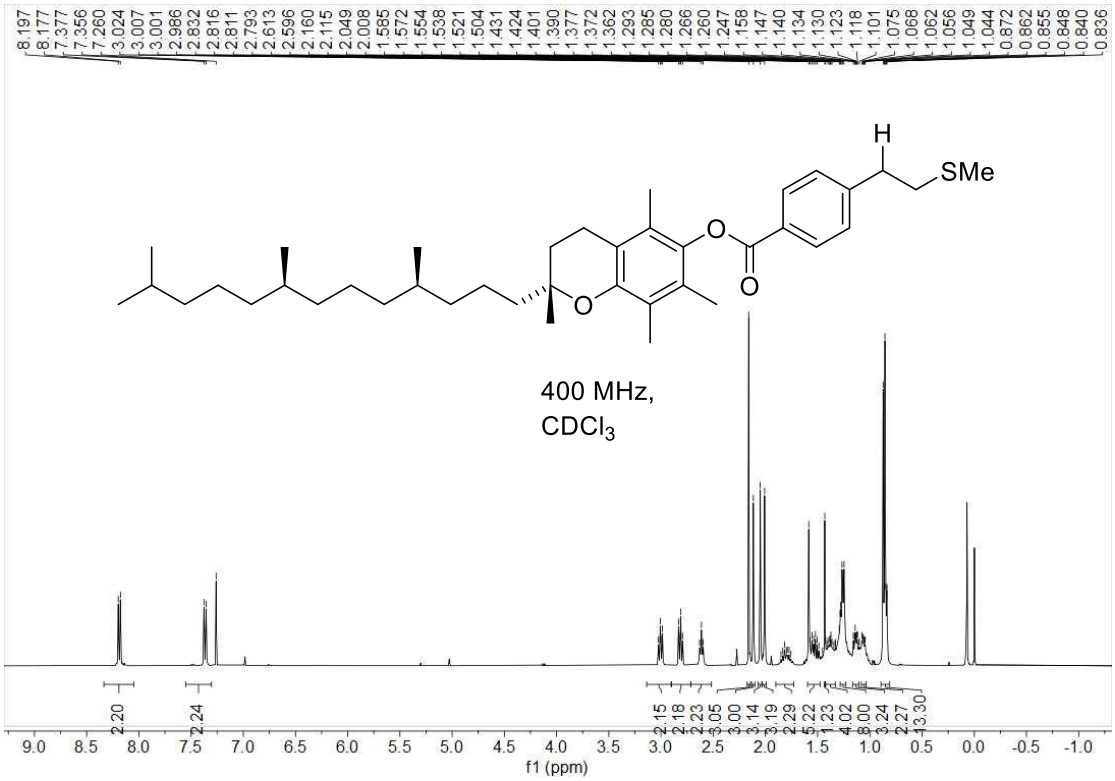
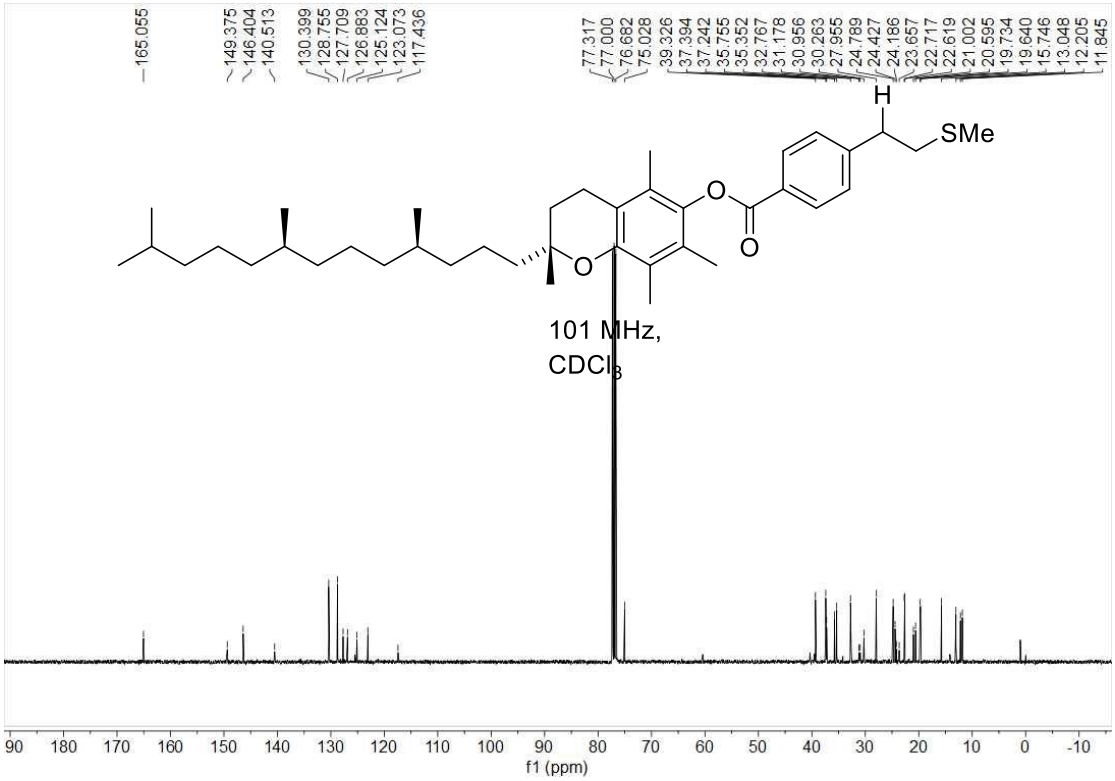
0.909
0.874
0.870
0.858
0.853
0.684
Me
Me
Me
H
H
H
H
O
O
MeS
H
400 MHz,
CDCl3
2.12
2.41
1.06
1.04
2.09
2.03
2.07
3.00
4.29
1.15
0.93
6.34
3.07
2.01
6.39
3.17
3.39
3.06
3.01
2.96
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

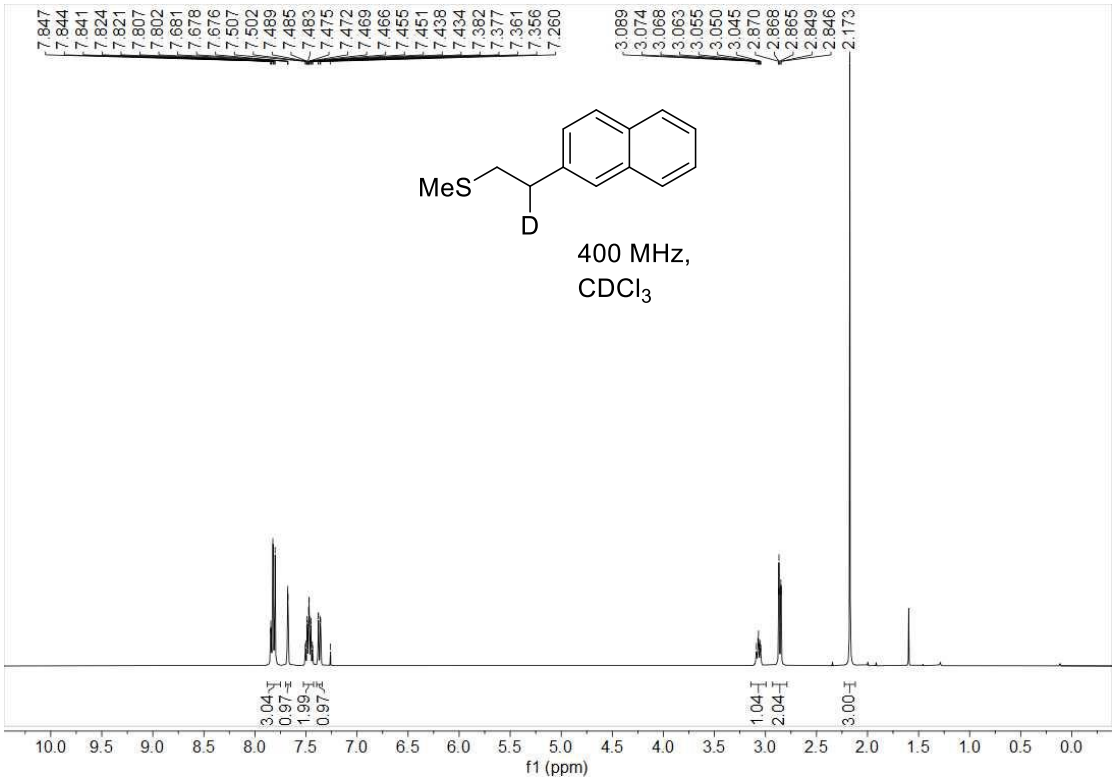

165.874
145.638
139.629
129.756
128.950
128.448
122.732
77.317
77.000
76.682
74.422
56.641
56.070
49.978
42.271
39.477
36.987
36.609
35.771
35.398
31.895
31.826
28.213
27.990
27.849
24.261
23.791
22.813
22.546
21.009
19.357
18.684
15.727
Me
Me
Me
H
H
H
H
O
O
MeS
H
101 MHz,
CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

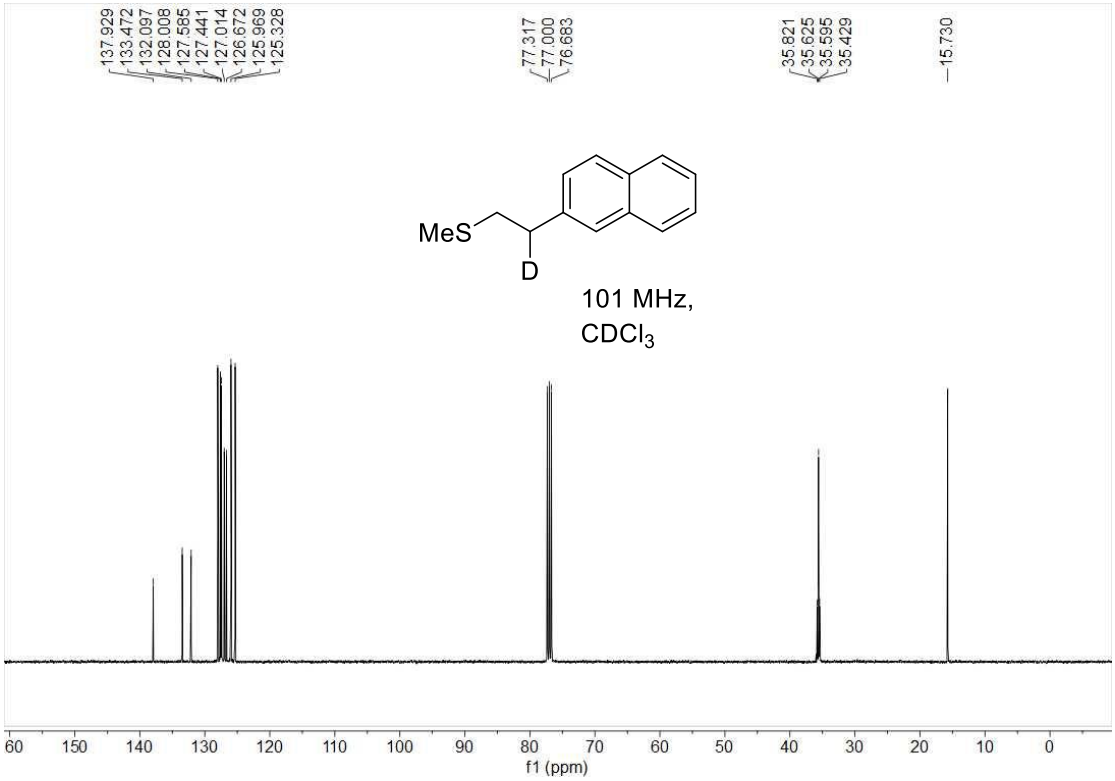

7.991
7.970
7.286
7.266
7.260
4.946
4.935
4.918
4.907
4.891
4.880
2.968
2.950
2.944
2.930
2.782
2.767
2.761
2.745
2.124
2.110
2.100
2.094
2.091
2.089
1.956
1.949
1.932
1.740
1.733
1.727
1.709
1.703
1.696
1.671
1.574
1.567
1.559
1.554
1.547
1.540
1.532
1.517
1.509
1.134
1.125
1.109
1.102
1.096
1.067
1.067
0.939
0.926
0.914
0.909
0.896
0.786
0.769
O
O
SMe
H
400 MHz,
CDCl3
1.86
2.00
0.94
1.86
1.85
2.74
0.79
0.96
2.07
1.98
1.96
6.77
2.91
f1 (ppm)

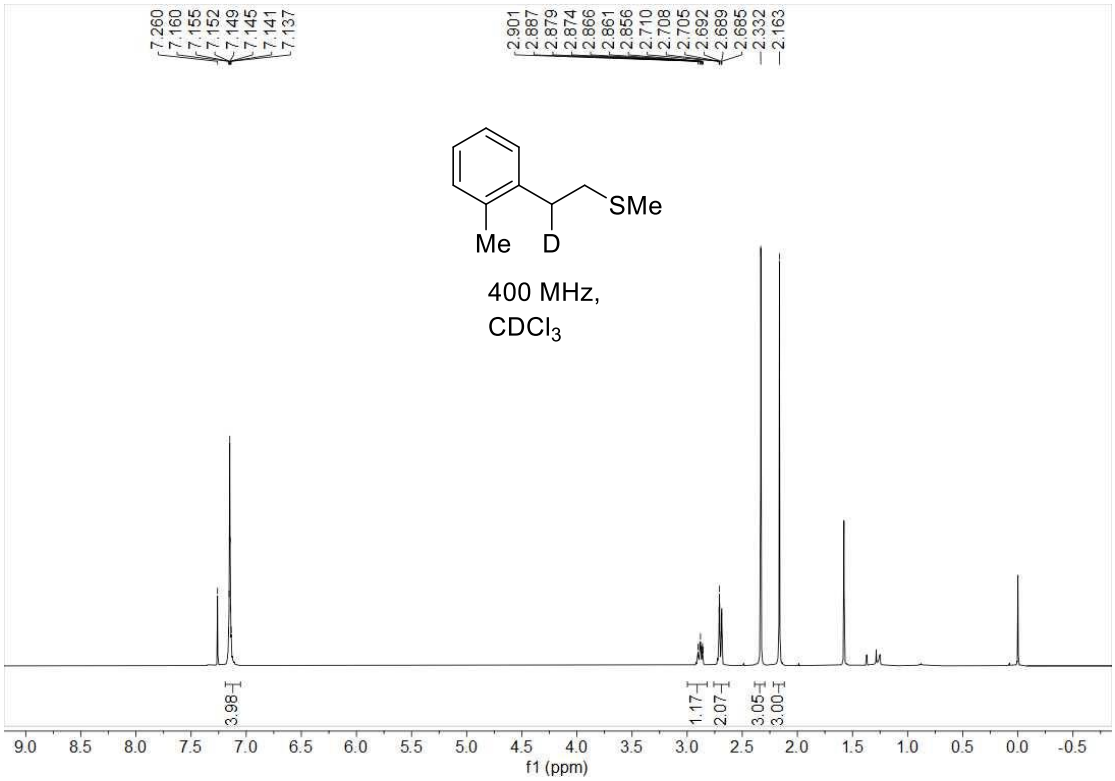

165.929
145.579
129.745
128.926
128.452
77.318
77.000
76.682
74.599
47.168
40.886
35.672
35.373
34.238
31.365
26.360
23.485
22.021
20.743
16.415
15.693
O
O
SMe
H
101 MHz,
CDCl3
f1 (ppm)

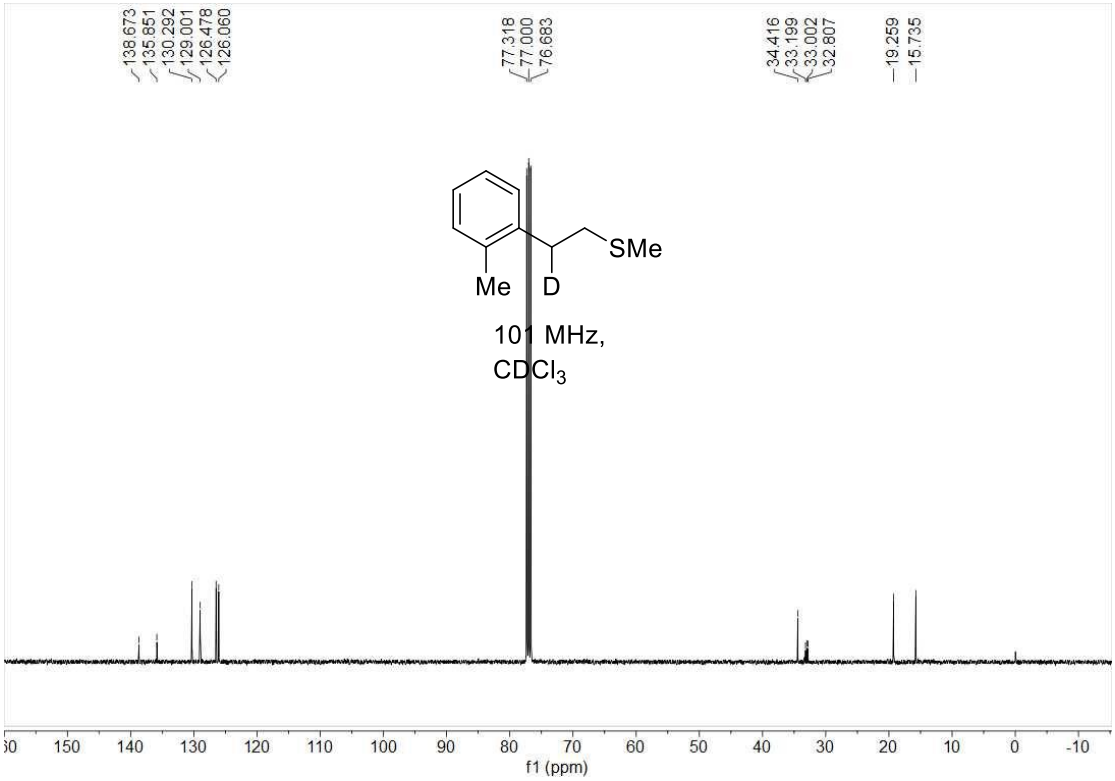

H
SMe
O
O
O
400 MHz,
CDCl3
f1 (ppm)

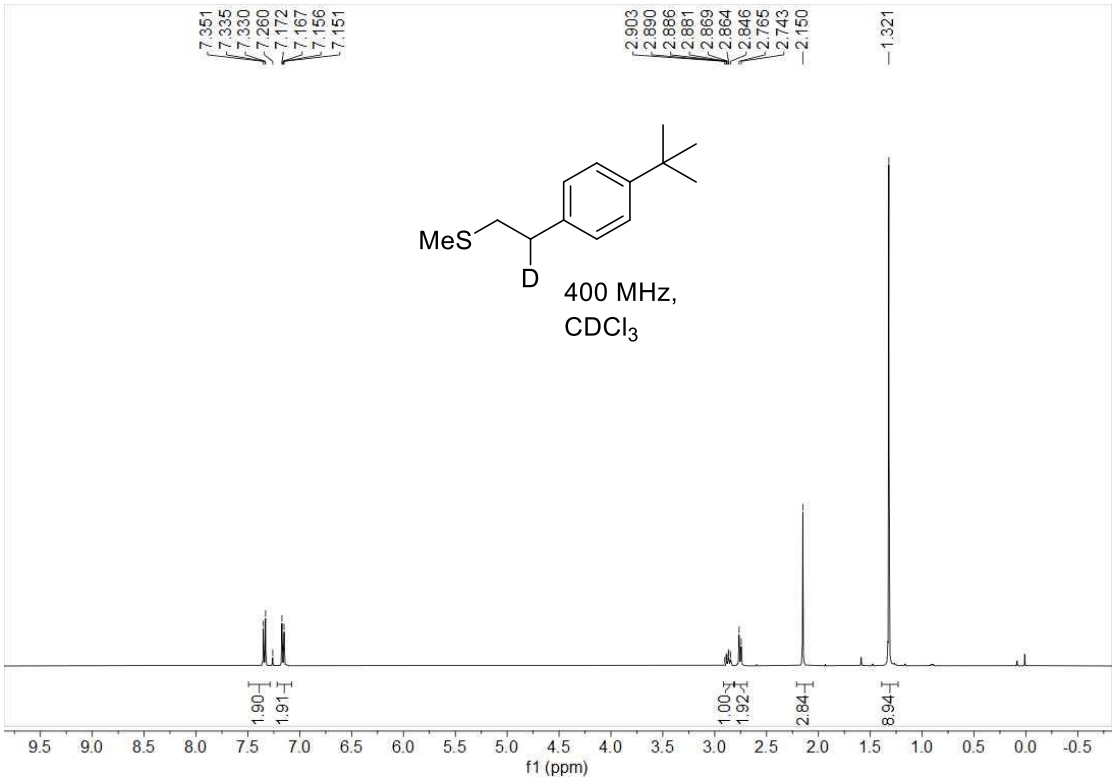

H
SMe
O
O
O
101 MHz,
CDCl3
f1 (ppm)

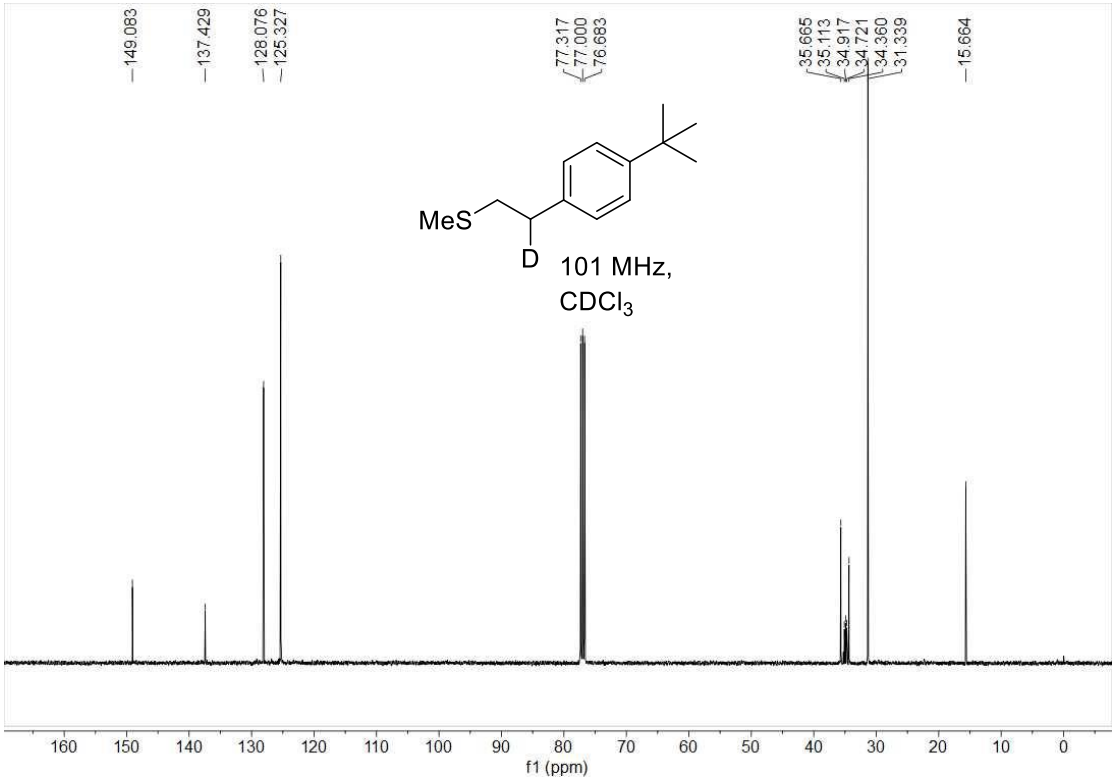

7.847
7.844
7.841
7.824
7.821
7.807
7.802
7.681
7.678
7.676
7.507
7.502
7.489
7.485
7.483
7.475
7.472
7.469
7.466
7.455
7.451
7.438
7.434
7.382
7.377
7.361
7.356
7.260
3.089
3.074
3.068
3.063
3.055
3.050
3.045
2.870
2.868
2.865
2.849
2.846
2.173
MeS
D
400 MHz,
CDCl3
3.04
0.97
1.99
0.97
1.04
2.04
3.00
f1 (ppm)

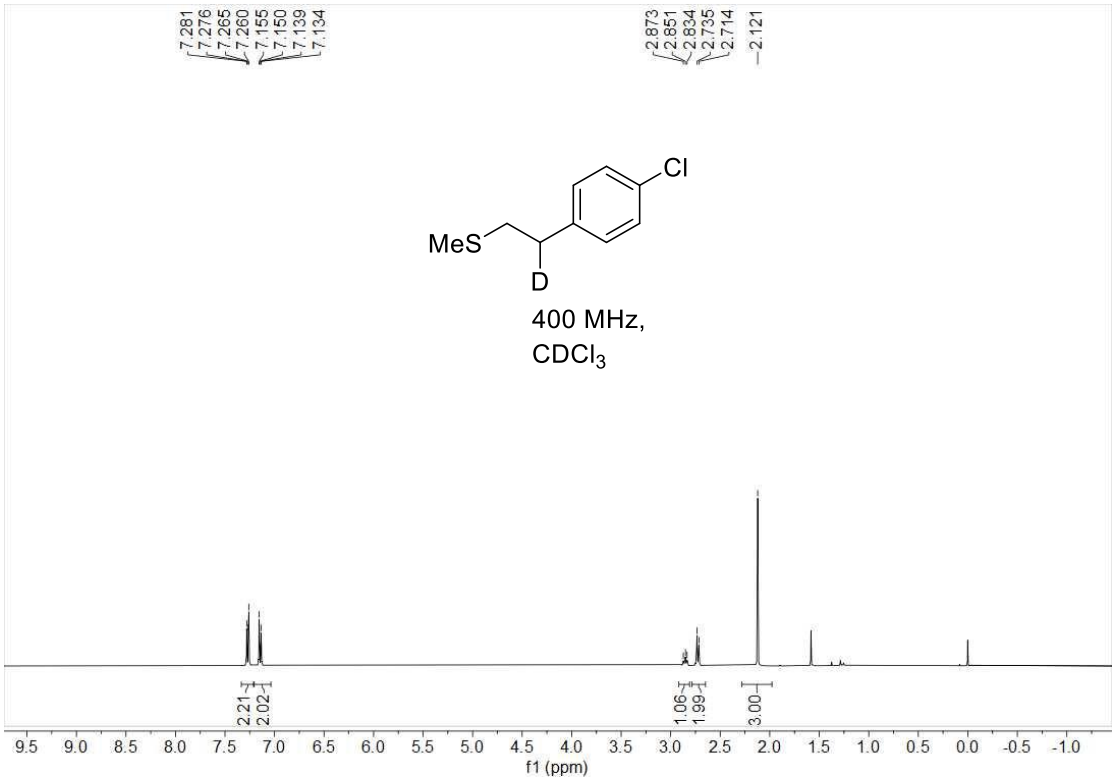

137.929
133.472
132.097
128.008
127.585
127.441
127.014
126.672
125.969
125.328
77.317
77.000
76.683
35.821
35.625
35.595
35.429
15.730
MeS
D
101 MHz,
CDCl3
f1 (ppm)

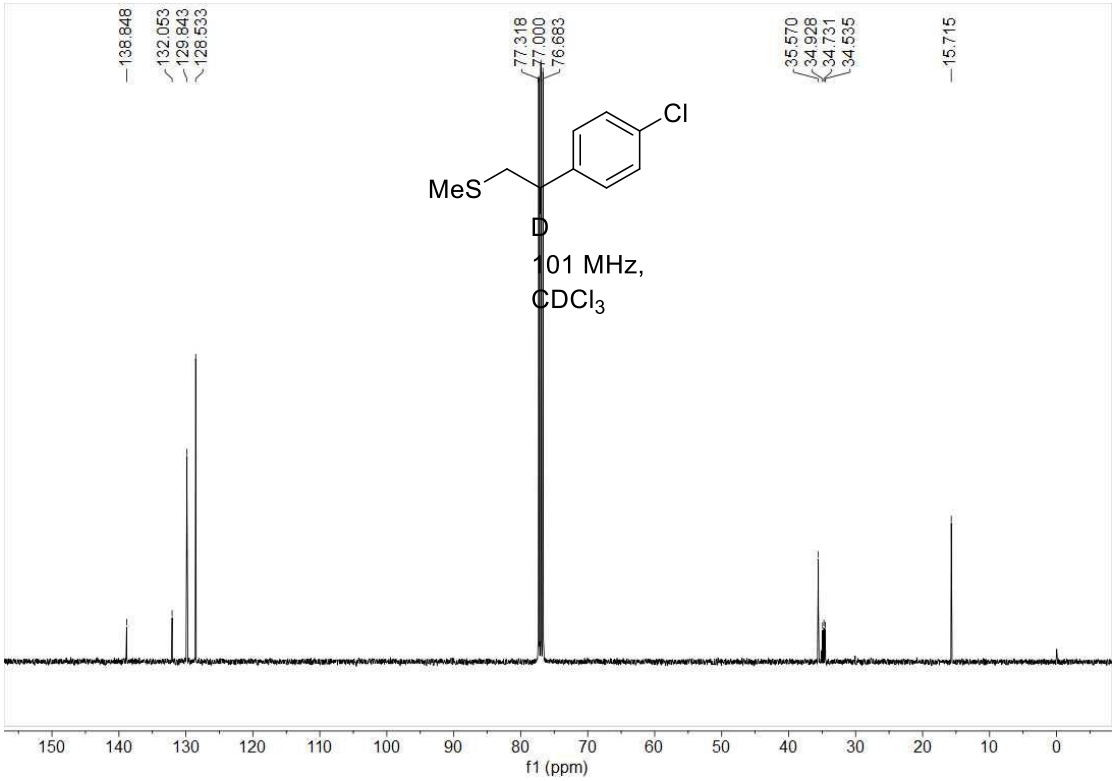

7.260
7.160
7.155
7.152
7.149
7.145
7.141
7.137
2.901
2.887
2.879
2.874
2.866
2.861
2.856
2.710
2.708
2.705
2.692
2.689
2.685
2.332
2.163
SMe
Me
D
400 MHz,
CDCl3
3.98
1.17
2.07
3.05
3.00
f1 (ppm)

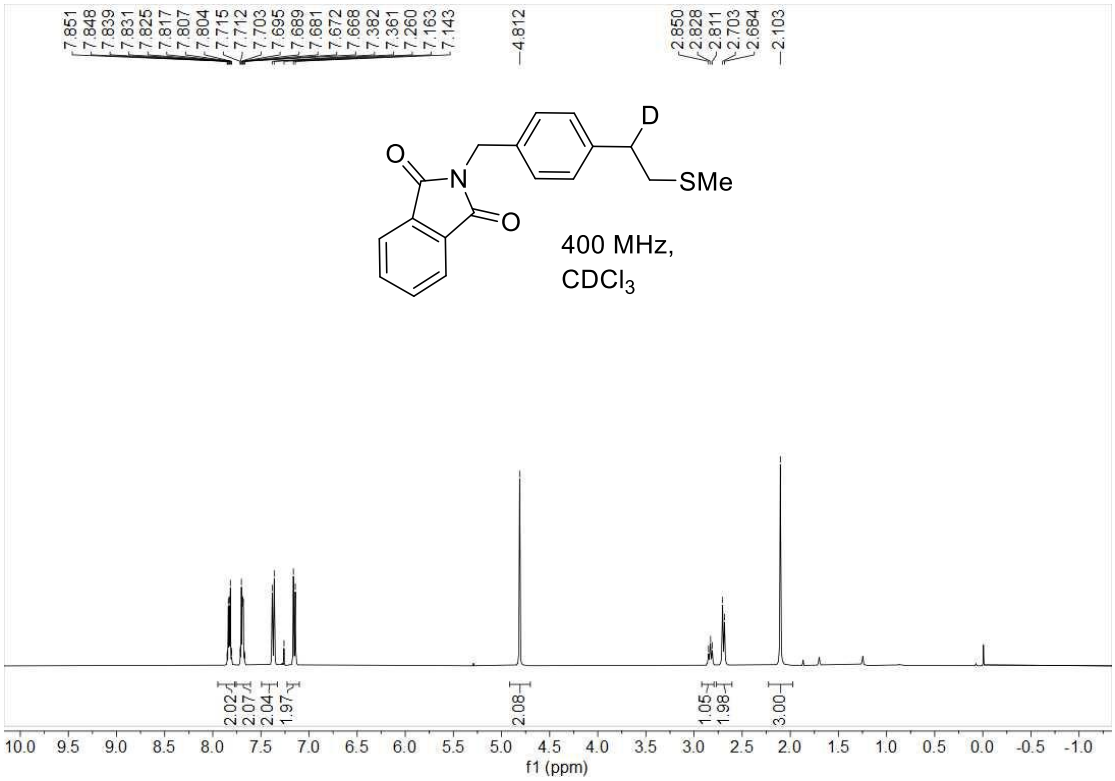

138.673
135.851
130.292
129.001
126.478
126.060
77.316
77.000
76.683
34.416
33.199
33.002
32.807
19.259
15.735
SMe
Me
D
101 MHz,
CDCl3
f1 (ppm)

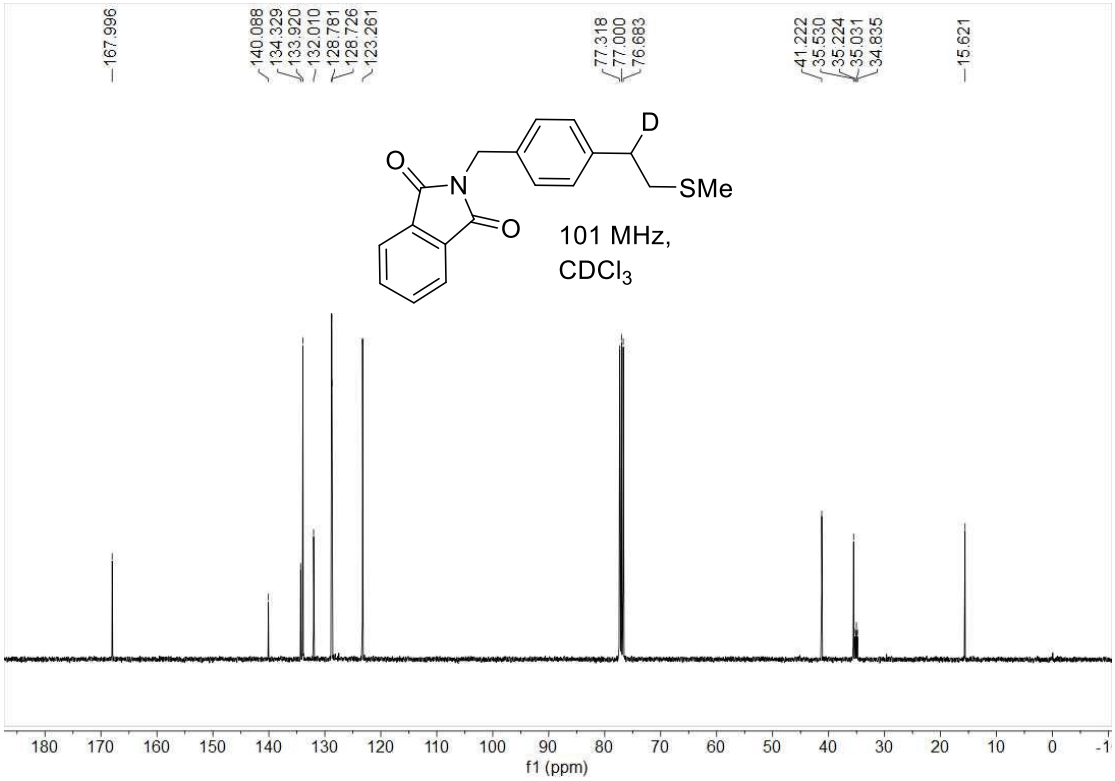

7.351
7.335
7.330
7.260
7.172
7.167
7.156
7.151
2.903
2.890
2.886
2.881
2.869
2.864
2.846
2.765
2.743
2.150
1.321
MeS
D
400 MHz,
CDCl3
1.90
1.91
1.00
1.92
2.84
8.94
f1 (ppm)

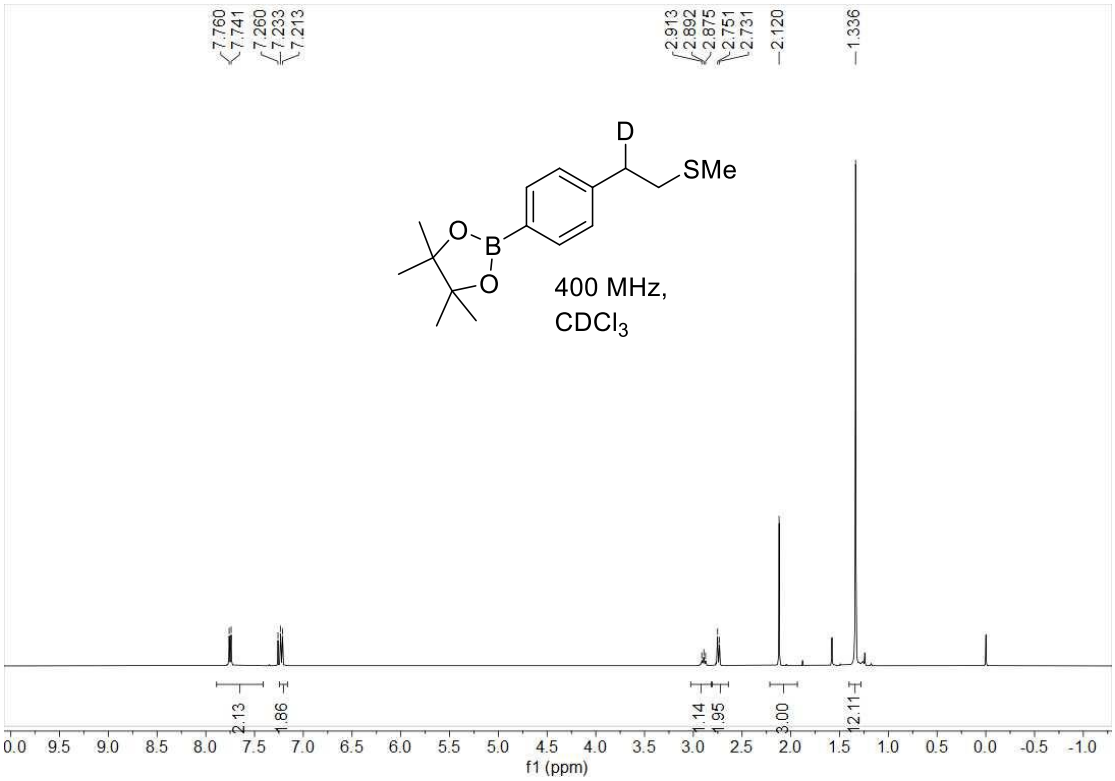

149.083
137.429
128.076
125.327
77.317
77.000
76.683
35.665
35.113
34.917
34.721
34.360
31.339
15.664
MeS
D
101 MHz,
CDCl3
f1 (ppm)

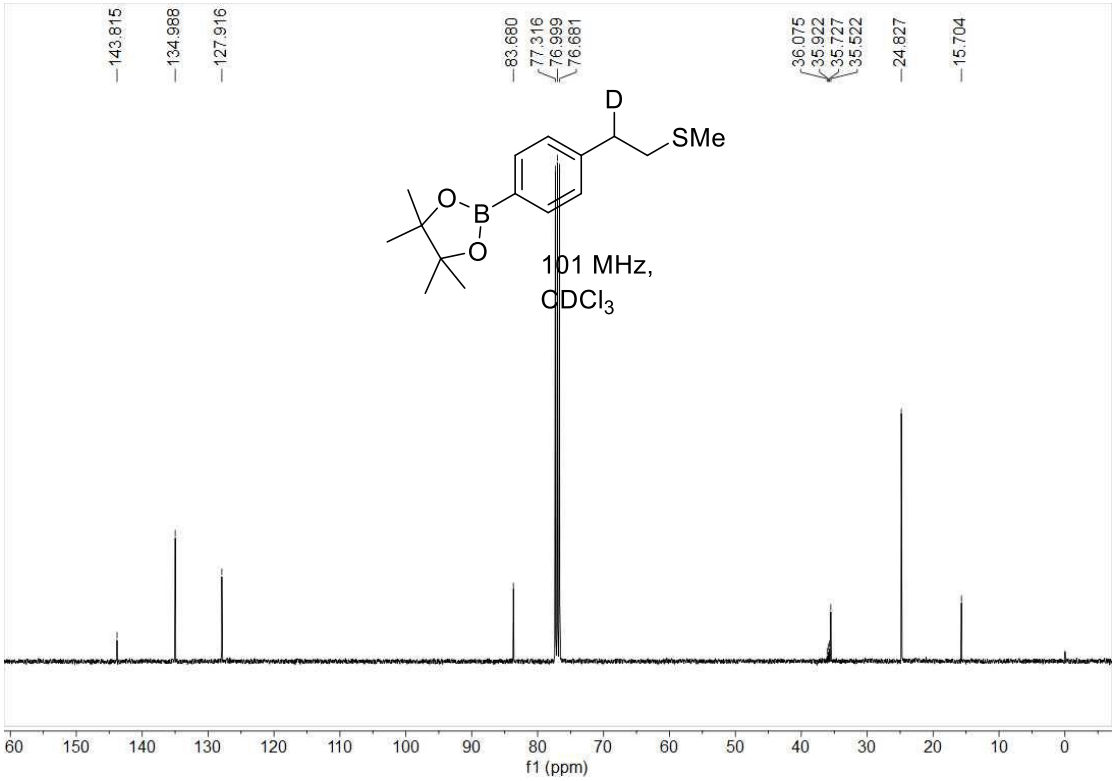

7.281
7.276
7.265
7.260
7.155
7.150
7.139
7.134
2.873
2.851
2.834
2.735
2.714
2.121
Cl
MeS
D
400 MHz,
CDCl3
2.21
2.02
1.06
1.99
3.00
f1 (ppm)

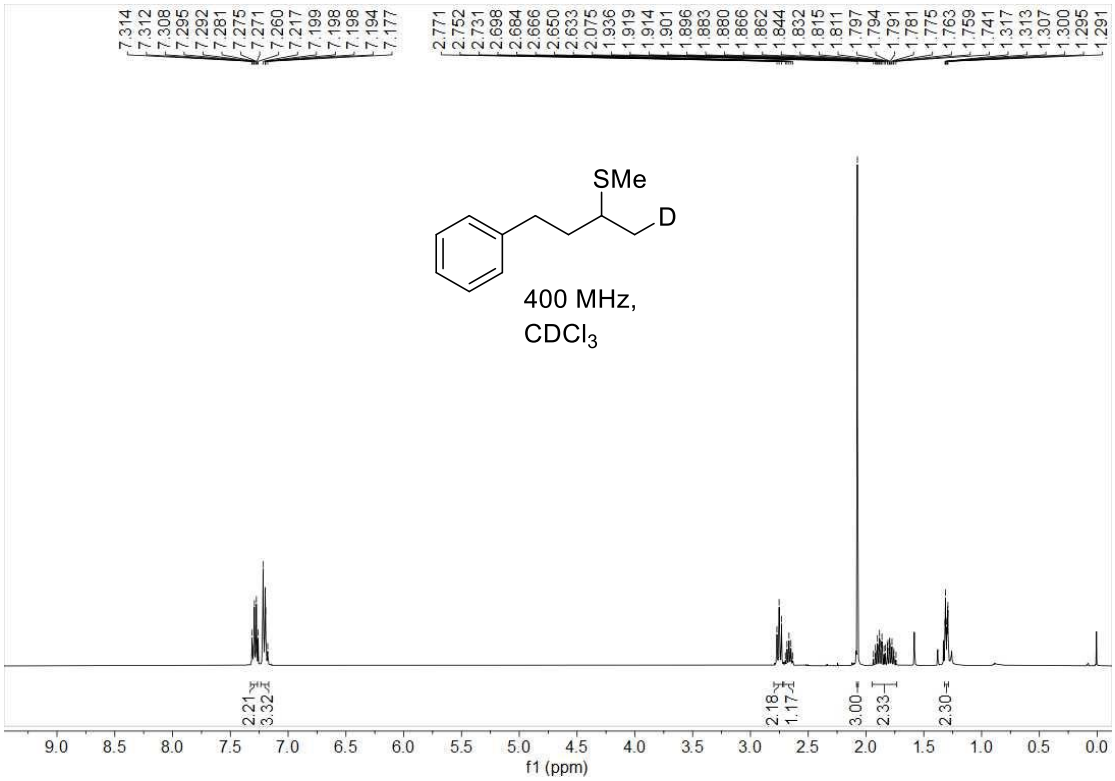

138.848
132.053
129.843
128.533
77.318
77.000
76.683
35.570
34.928
34.731
34.535
15.715
Cl
MeS
D
101 MHz,
CDCl3
f1 (ppm)

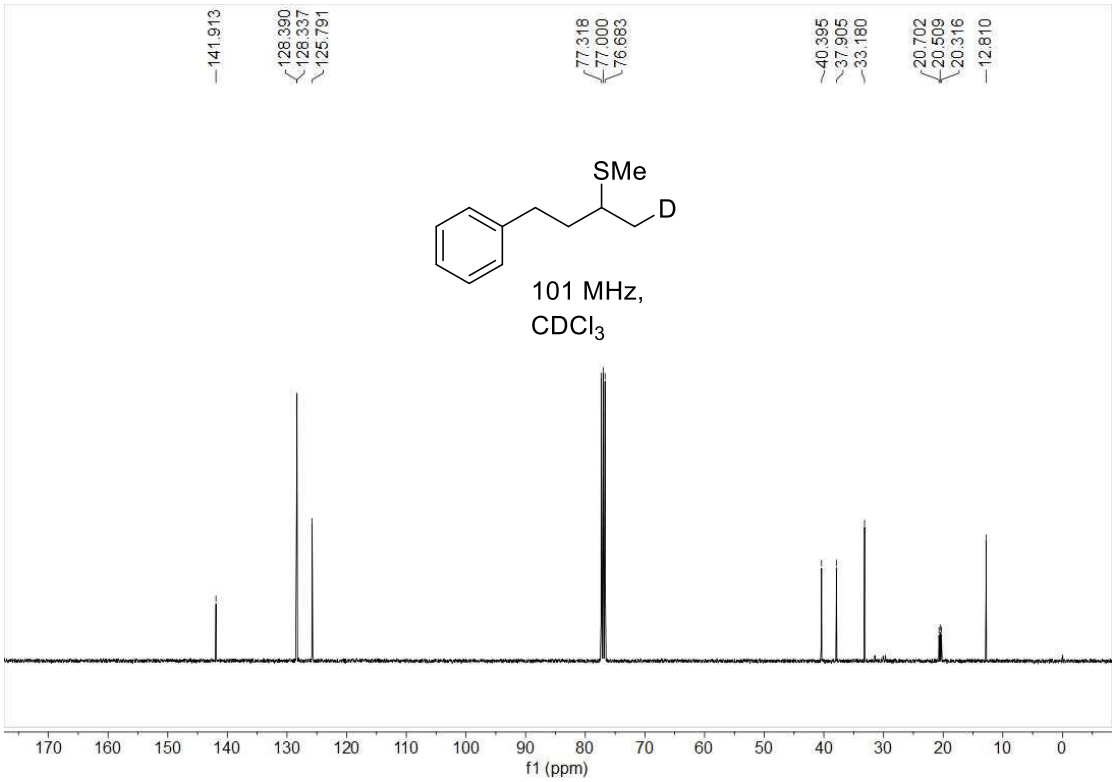

7.851
7.848
7.839
7.831
7.825
7.817
7.807
7.804
7.715
7.712
7.703
7.695
7.689
7.681
7.672
7.668
7.382
7.361
7.260
7.163
7.143
4.812
2.850
2.828
2.811
2.703
2.684
2.103
D
O
N
O
SMe
400 MHz,
CDCl3
2.02
2.07
2.04
1.97
2.08
1.05
1.98
3.00
f1 (ppm)

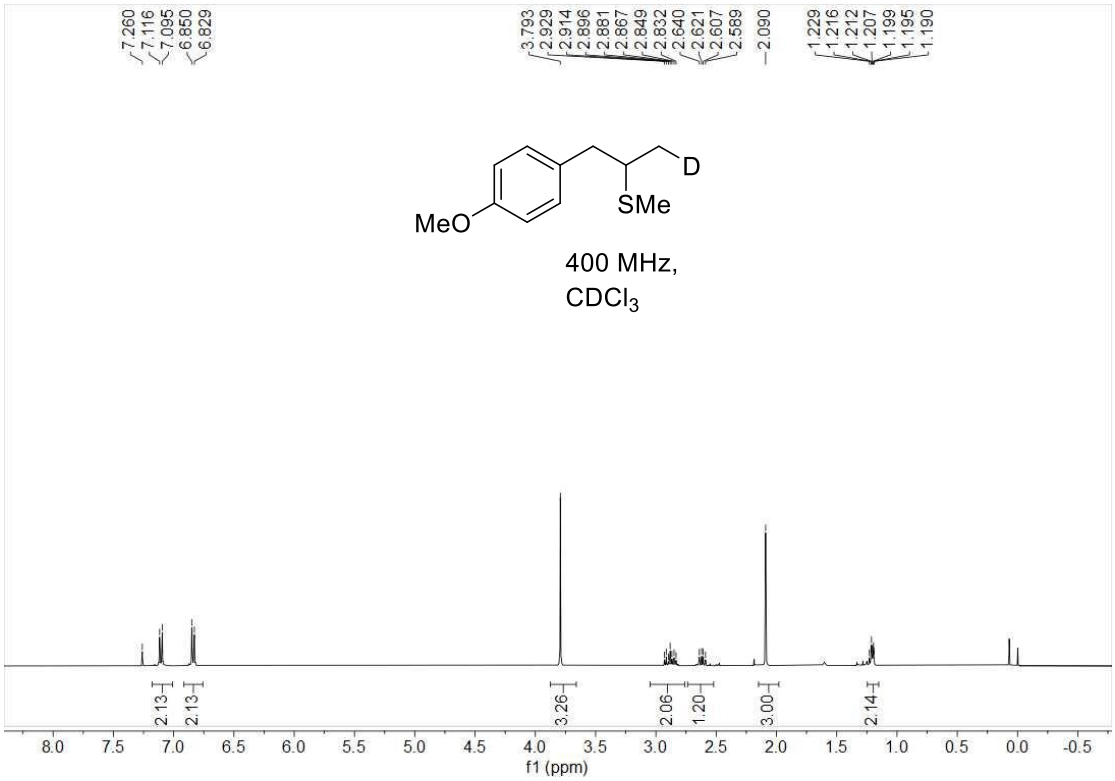

167.996
140.088
134.329
133.920
132.010
128.781
128.726
123.261
77.318
77.000
76.683
41.222
35.530
35.224
35.031
34.835
15.621
D
O
N
O
SMe
101 MHz,
CDCl3
f1 (ppm)

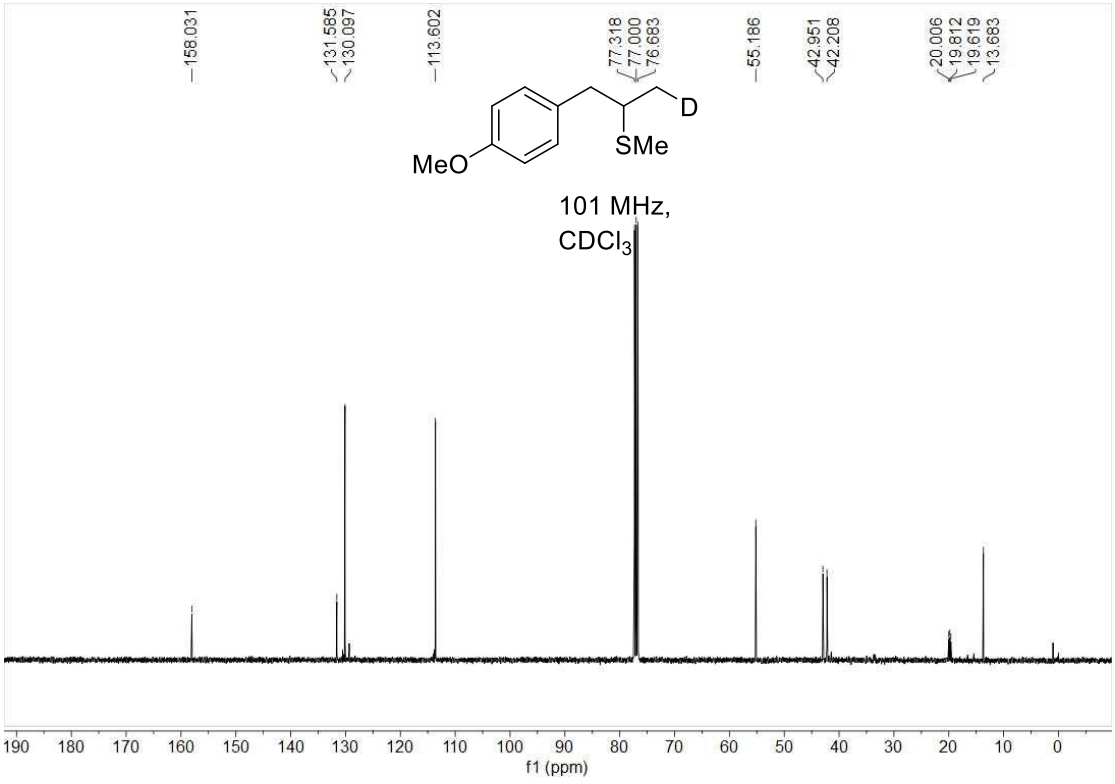

7.760
7.741
7.260
7.233
7.213
2.913
2.892
2.875
2.751
2.731
2.120
1.336
D
SMe
O
B
O
400 MHz,
CDCl3
2.13
1.86
1.14
1.95
3.00
12.11
f1 (ppm)

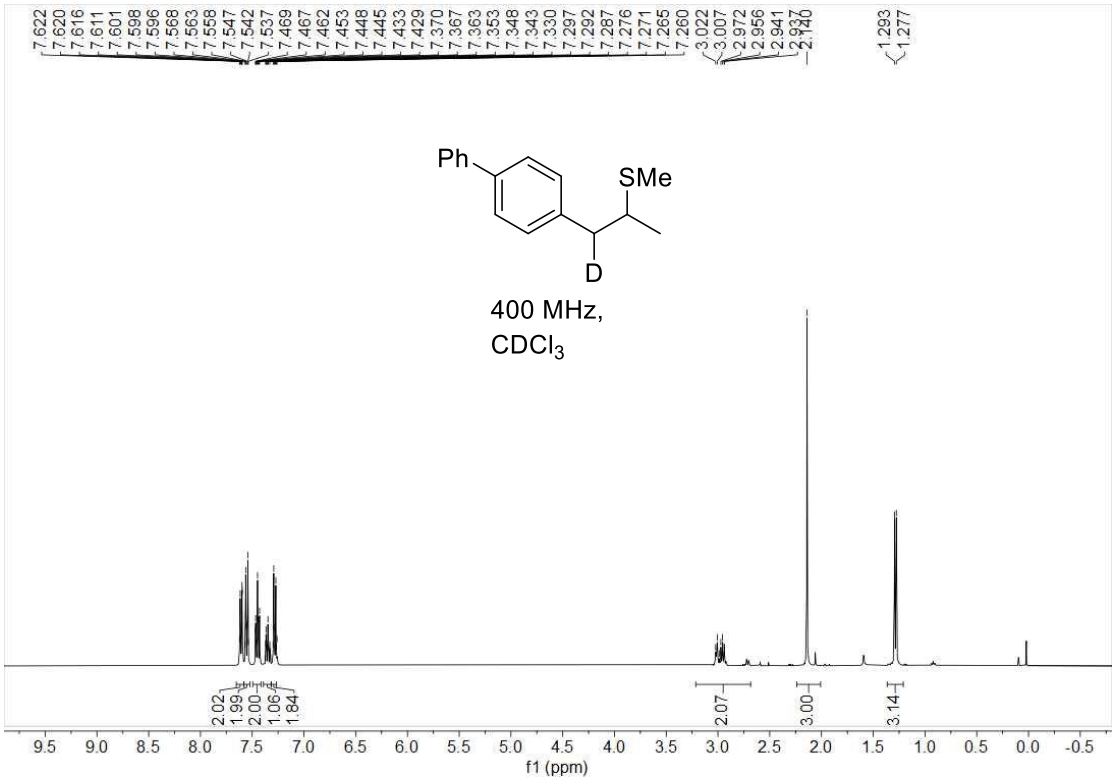

143.815
134.988
127.916
83.680
77.316
76.999
76.681
36.075
35.922
35.727
35.522
24.827
15.704
D
SMe
O
B
O
101 MHz,
CDCl3
f1 (ppm)

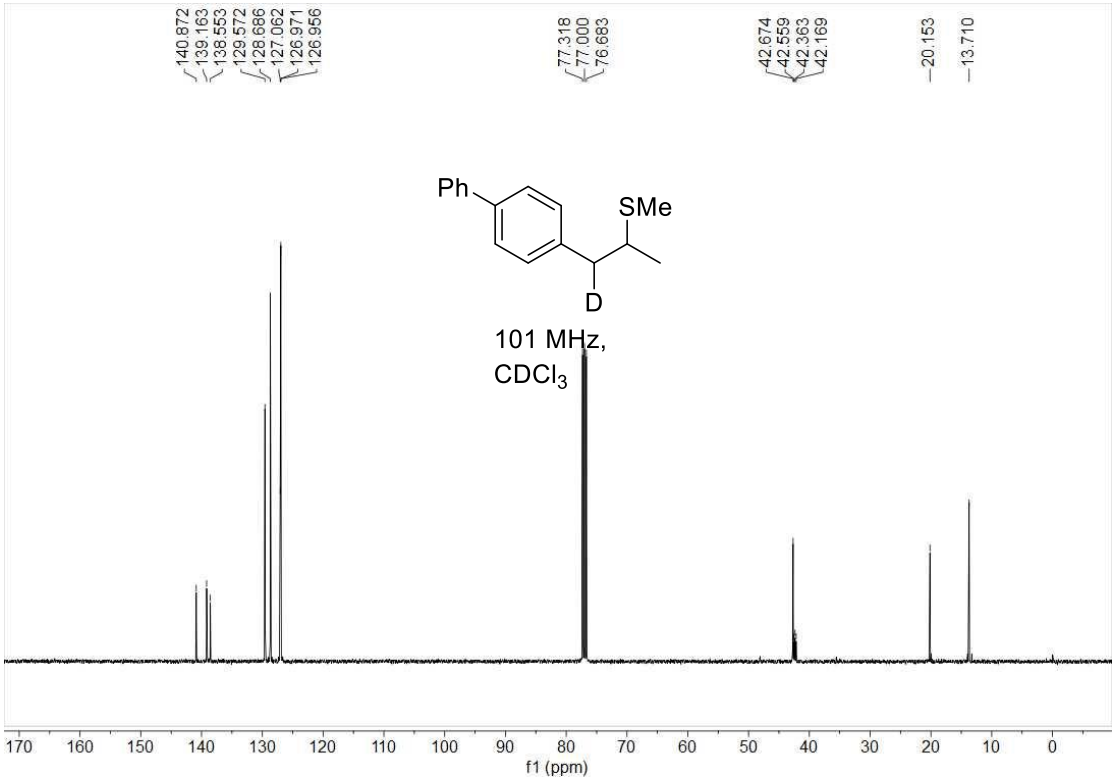

SMe
D
400 MHz,
CDCl3
f1 (ppm)

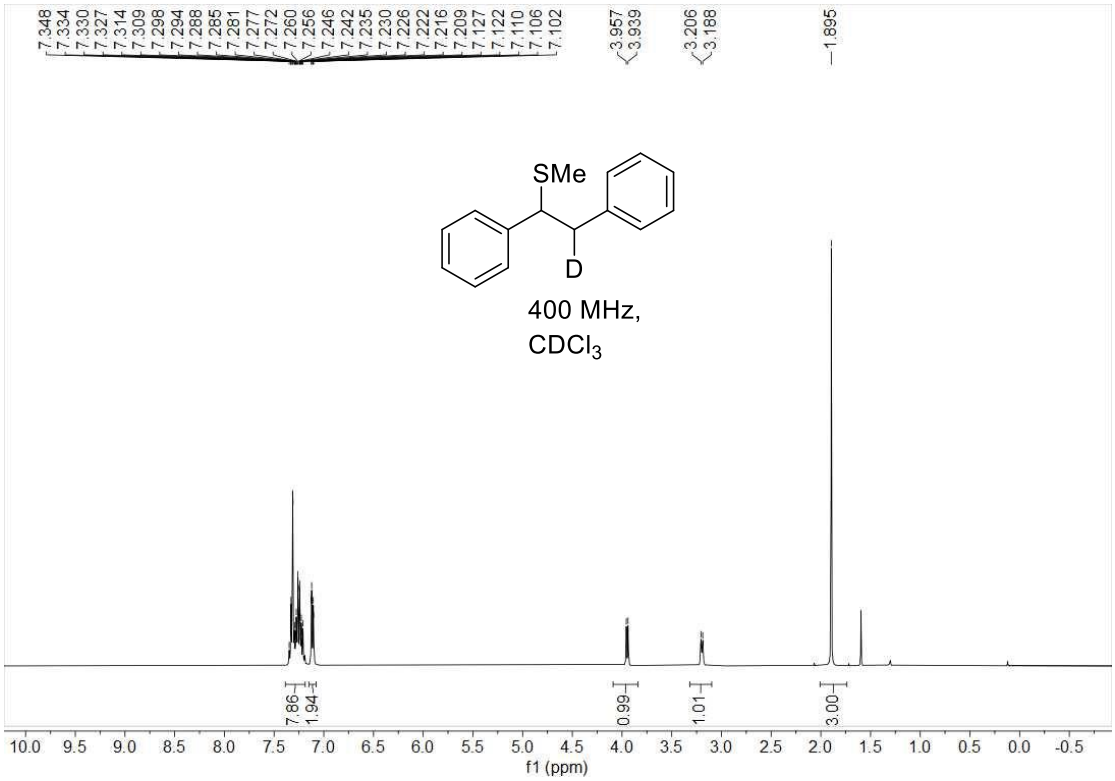

SMe
D
101 MHz,
CDCl3
f1 (ppm)

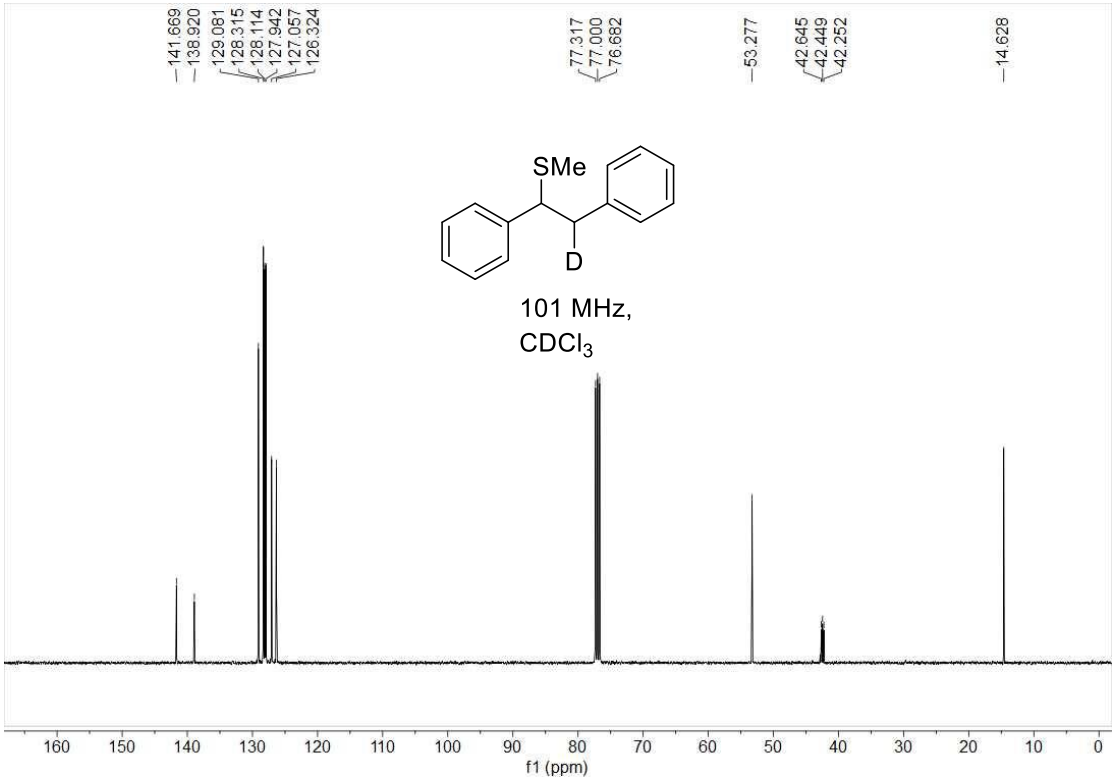

7.260
7.116
7.095
6.850
6.829
3.793
2.929
2.914
2.896
2.881
2.867
2.849
2.832
2.640
2.621
2.607
2.589
2.090
1.229
1.216
1.212
1.207
1.199
1.195
1.190
D
SMe
MeO
400 MHz,
CDCl3
2.13
2.13
3.26
2.06
1.20
3.00
2.14
f1 (ppm)

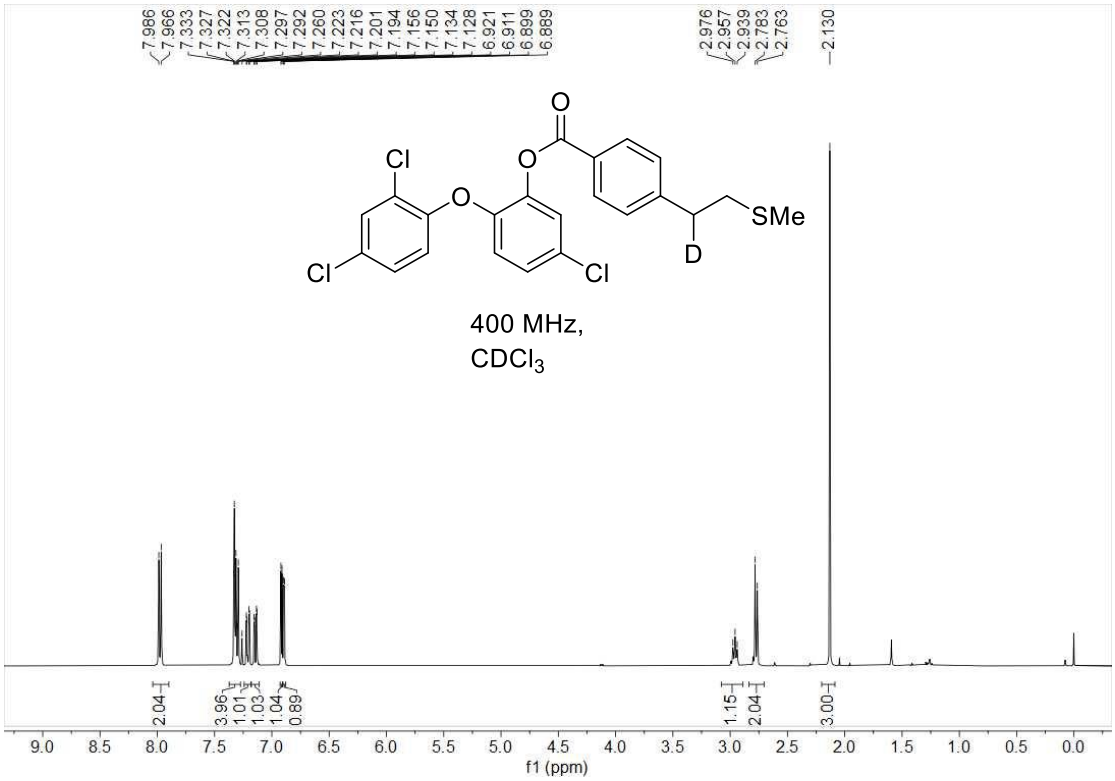

158.031
131.585
130.097
113.602
77.318
77.000
76.683
55.186
42.951
42.208
20.006
19.812
19.619
13.683
D
SMe
MeO
101 MHz,
CDCl3
f1 (ppm)

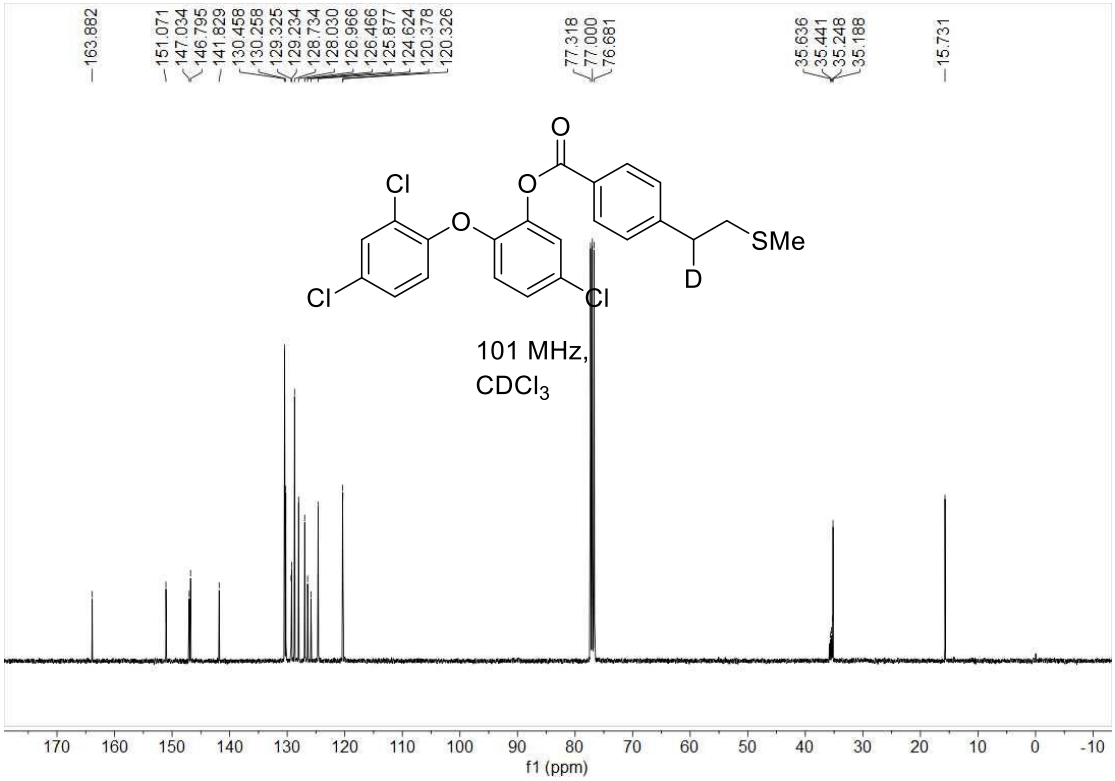

7.622
7.620
7.616
7.611
7.601
7.598
7.596
7.568
7.563
7.558
7.547
7.542
7.537
7.469
7.467
7.462
7.453
7.448
7.445
7.433
7.429
7.370
7.367
7.363
7.353
7.348
7.343
7.330
7.297
7.292
7.287
7.276
7.271
7.265
7.260
3.022
3.007
2.972
2.956
2.941
2.937
2.140
1.293
1.277
Ph
SMe
D
400 MHz,
CDCl3
2.02
1.99
2.00
1.06
1.84
2.07
3.00
3.14
f1 (ppm)

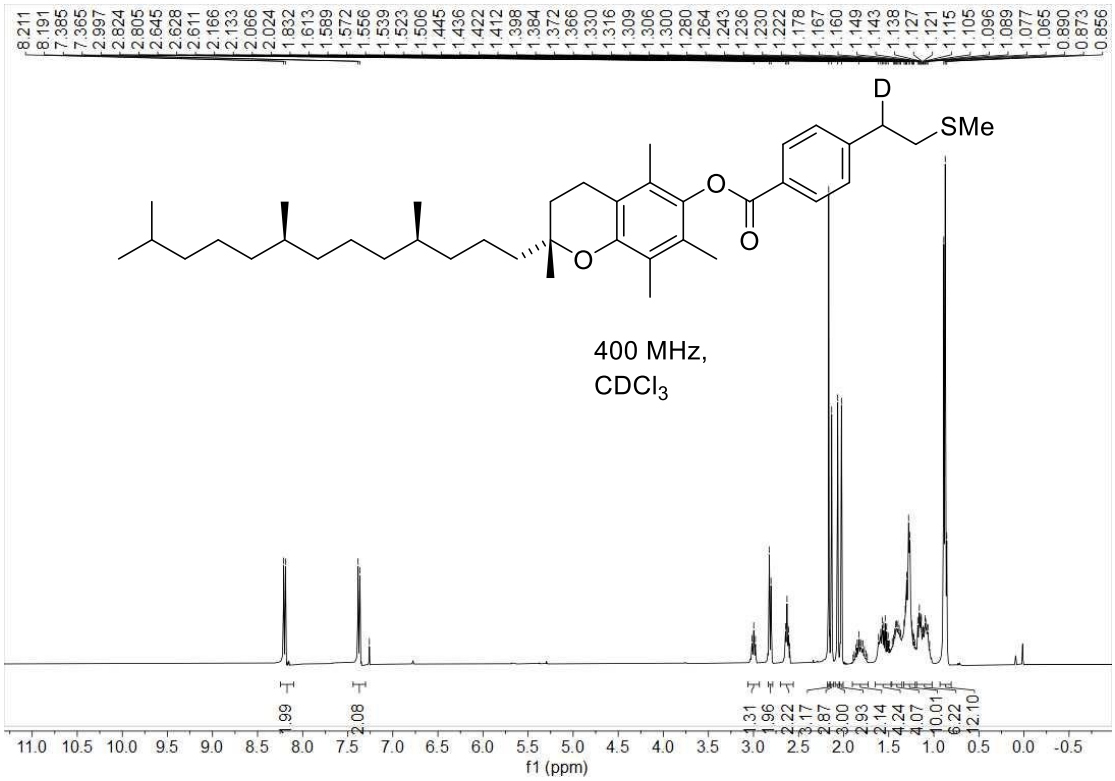

140.872
139.163
138.553
129.572
128.686
127.062
126.971
126.956
77.318
77.000
76.683
42.674
42.559
42.363
42.169
20.153
13.710
Ph
SMe
D
101 MHz,
CDCl3
f1 (ppm)

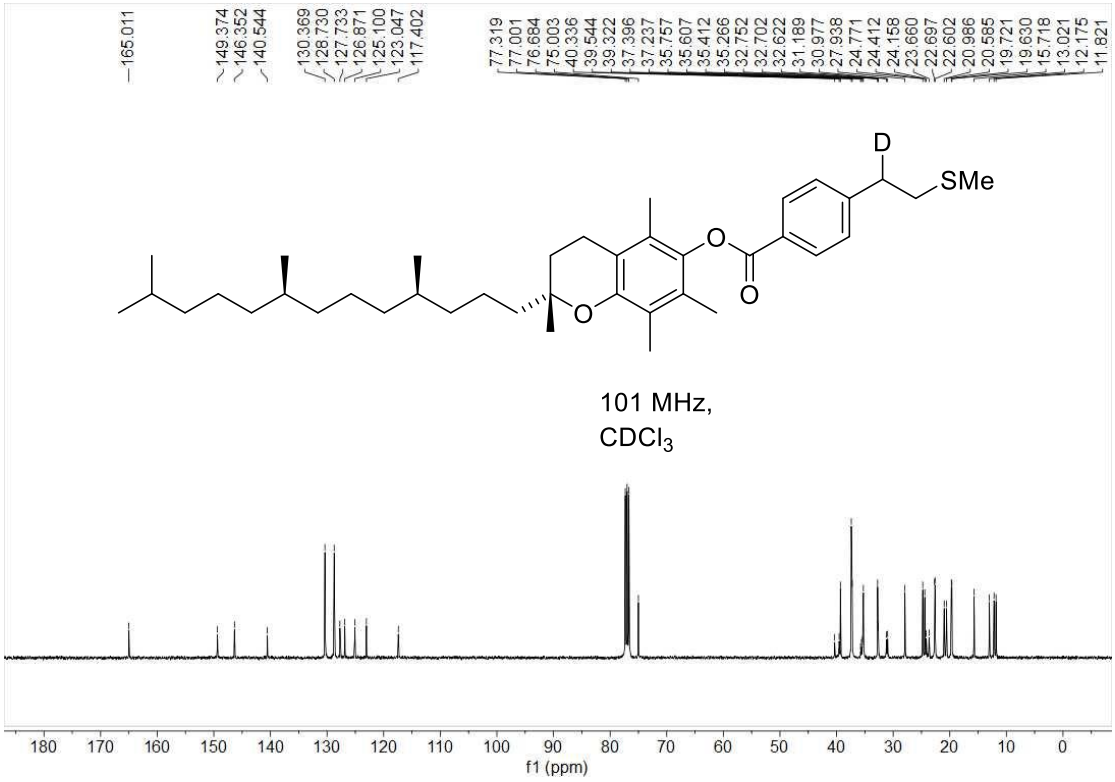

7.348
7.334
7.330
7.327
7.314
7.309
7.298
7.294
7.288
7.285
7.281
7.277
7.272
7.260
7.256
7.246
7.242
7.235
7.230
7.226
7.222
7.216
7.209
7.127
7.122
7.110
7.106
7.102
3.957
3.939
3.206
3.188
1.895
SMe
D
400 MHz,
CDCl3
7.86
1.94
0.99
1.01
3.00
f1 (ppm)

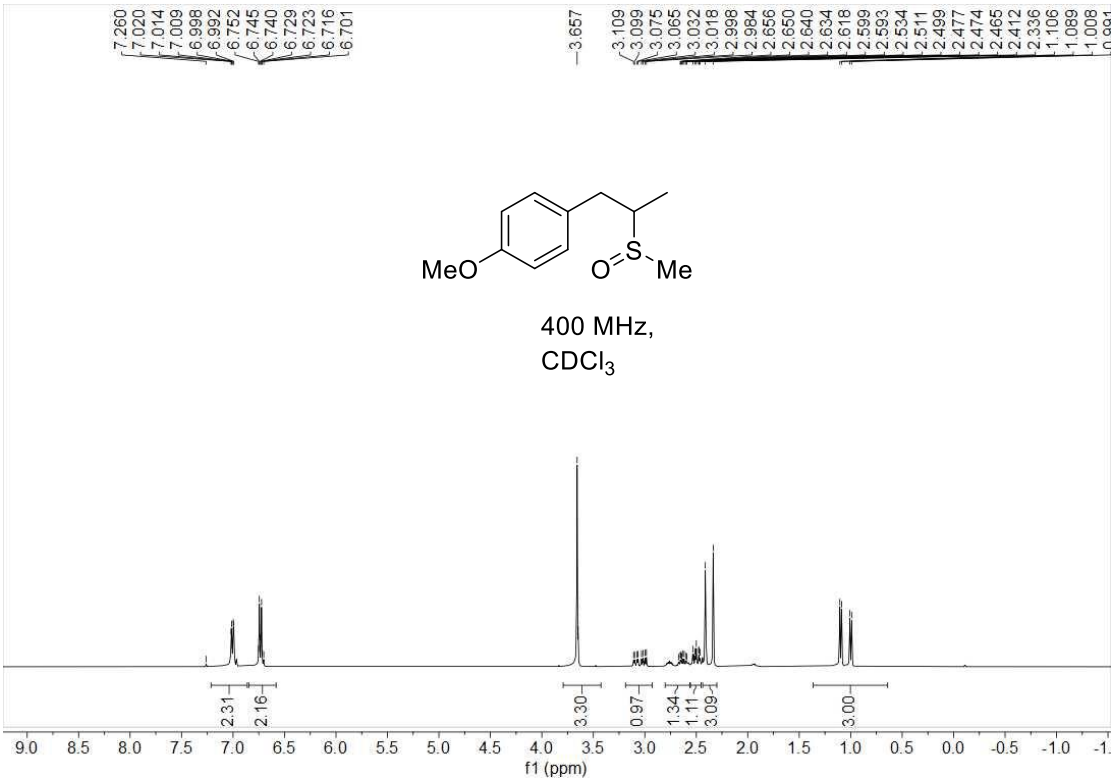

141.669
138.920
129.081
128.315
128.114
127.942
127.057
126.324
77.317
77.000
76.682
53.277
42.645
42.449
42.252
14.628
SMe
D
101 MHz,
CDCl3
f1 (ppm)

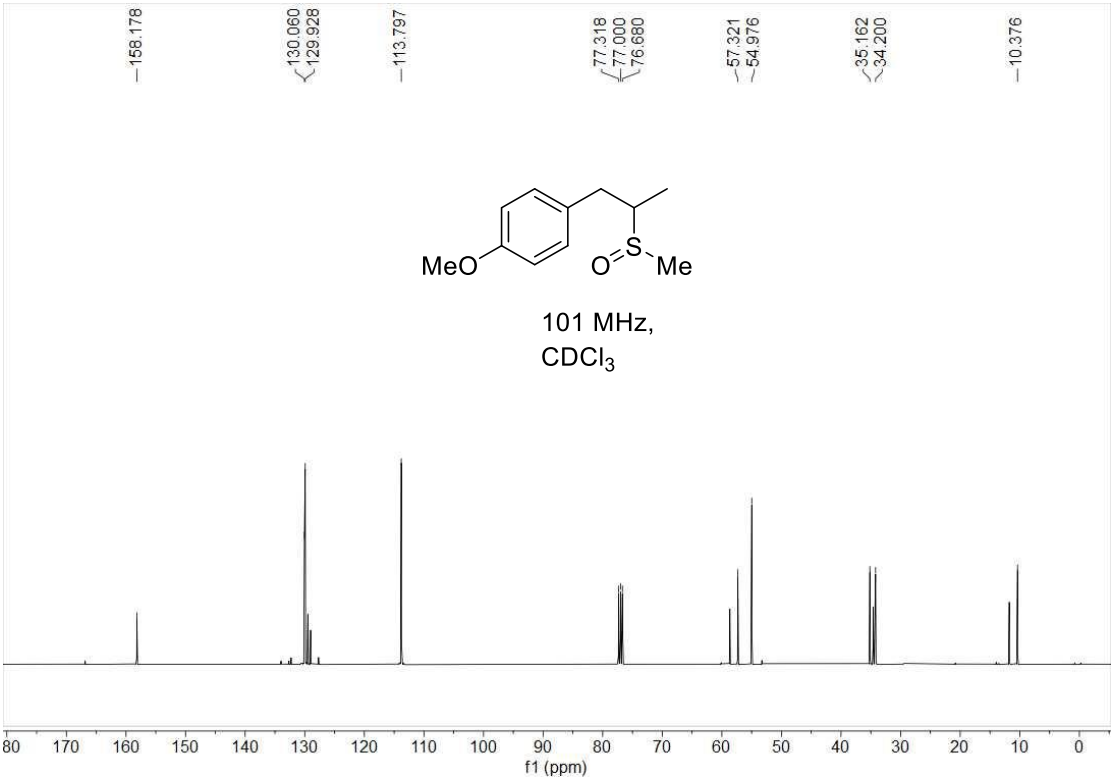

7.986
7.966
7.333
7.327
7.322
7.313
7.308
7.297
7.292
7.260
7.223
7.216
7.201
7.194
7.156
7.150
7.134
7.128
6.921
6.911
6.899
6.889
2.976
2.957
2.939
2.783
2.763
2.130
O
Cl
O
O
SMe
D
Cl
Cl
400 MHz,
CDCl3
2.04
3.96
1.01
1.03
1.04
0.89
1.15
2.04
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

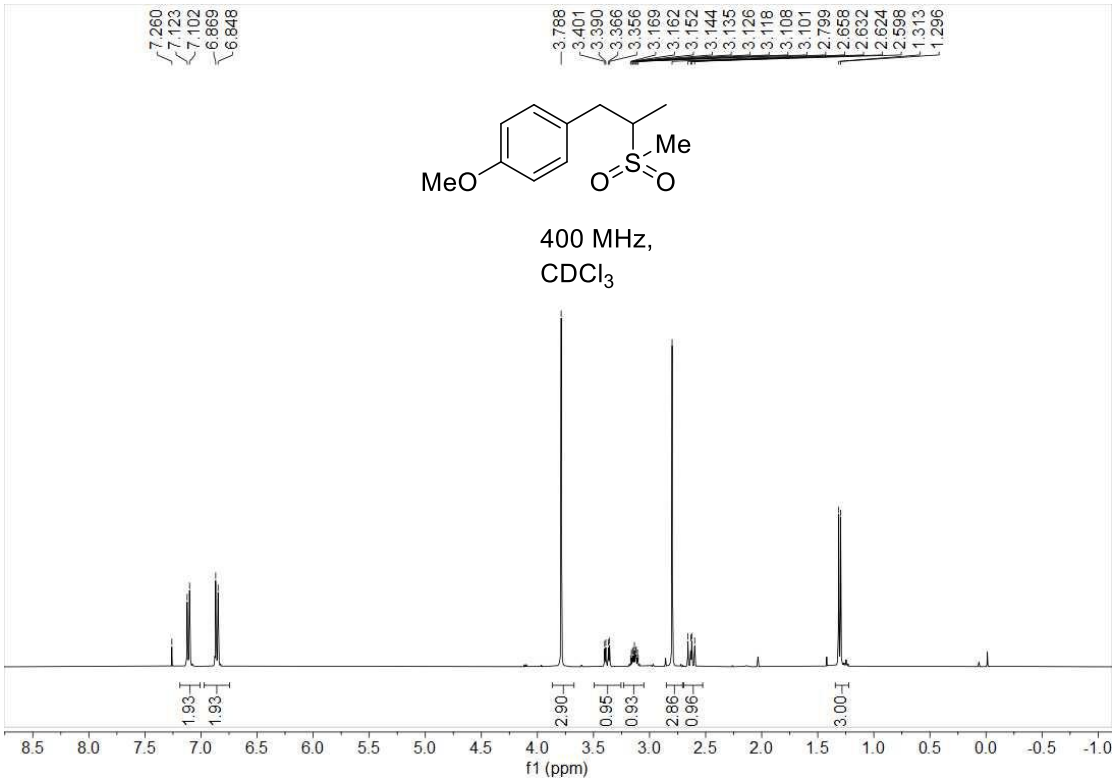

163.882
151.071
147.034
146.795
141.829
130.458
130.258
129.325
129.234
128.734
128.030
126.966
126.466
125.877
124.624
120.378
120.326
77.318
77.000
76.681
35.636
35.441
35.248
35.188
15.731
O
Cl
O
O
SMe
D
Cl
Cl
101 MHz,
CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


D
SMe
O
O
O
400 MHz,
CDCl3
f1 (ppm)

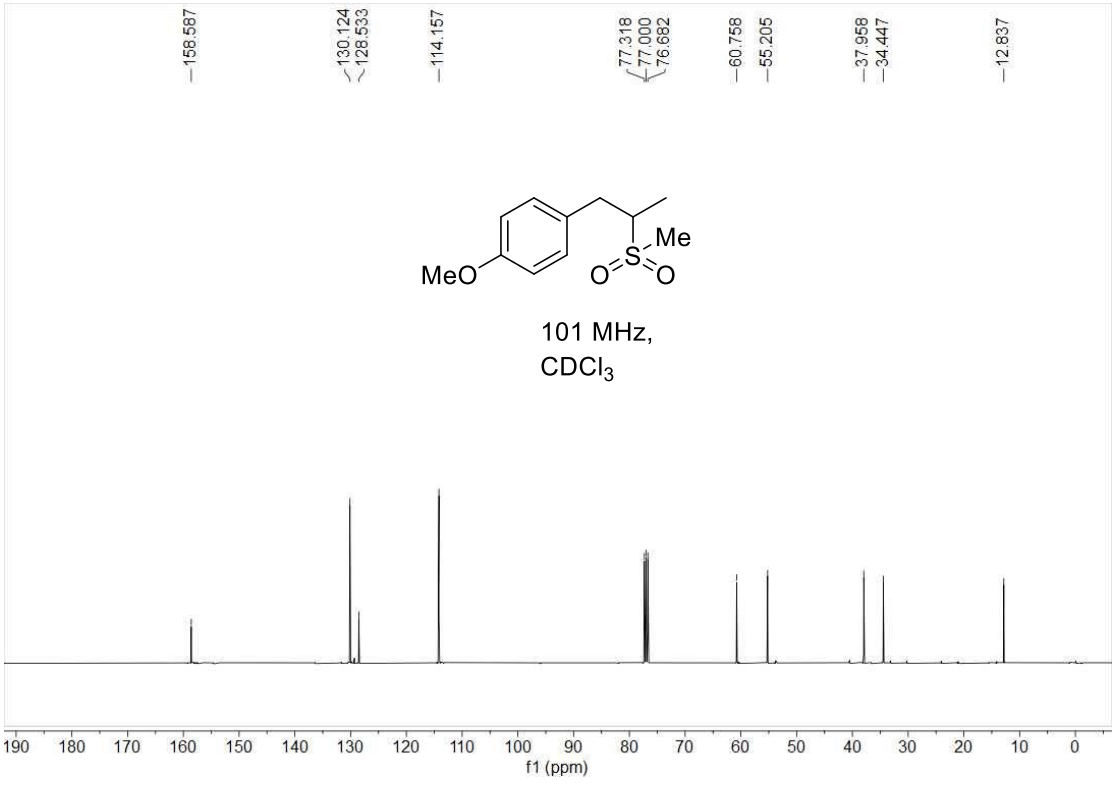

D
SMe
O
O
O
101 MHz,
CDCl3
f1 (ppm)


7.260
7.020
7.014
7.009
6.998
6.992
6.752
6.745
6.740
6.729
6.723
6.716
6.701
3.657
3.109
3.099
3.075
3.065
3.032
3.018
2.998
2.984
2.656
2.650
2.640
2.634
2.618
2.599
2.593
2.534
2.511
2.499
2.477
2.474
2.465
2.412
2.336
1.106
1.089
1.008
MeO
O
S
Me
400 MHz,
CDCl3
2.31
2.16
3.30
0.97
1.34
1.11
3.09
3.00
f1 (ppm)

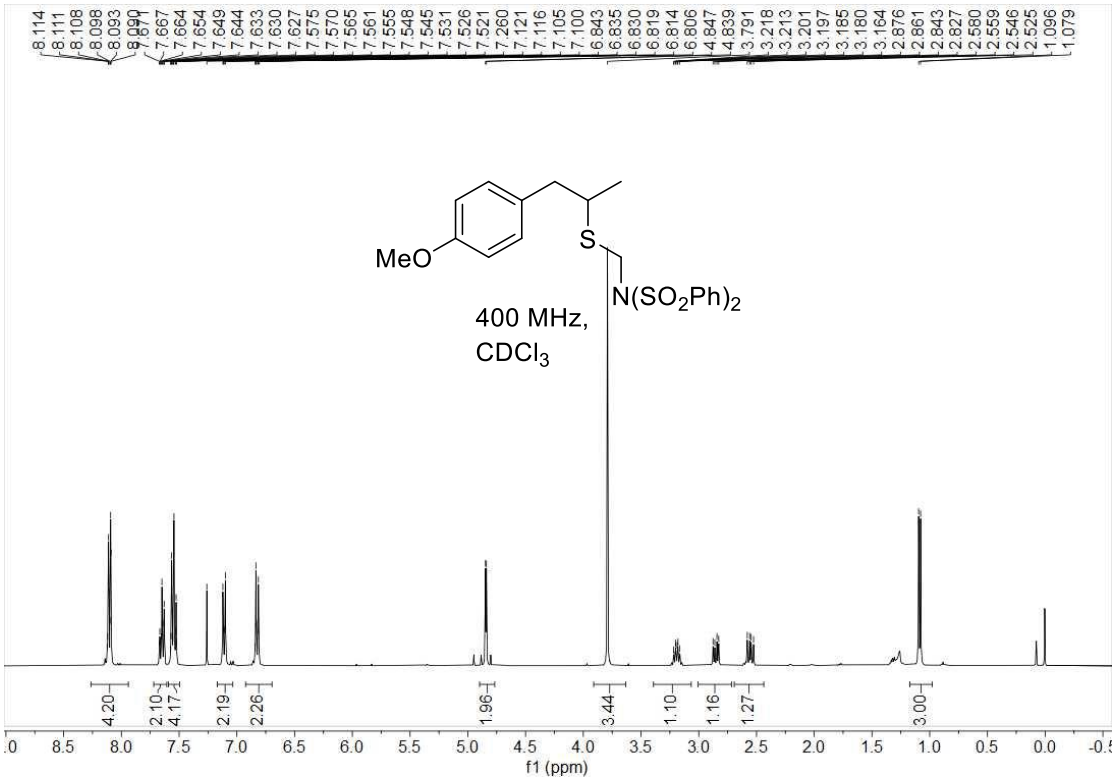

158.178
130.060
129.928
113.797
77.318
77.000
76.680
57.321
54.976
35.162
34.200
10.376
MeO
O
S
Me
101 MHz,
CDCl3
f1 (ppm)

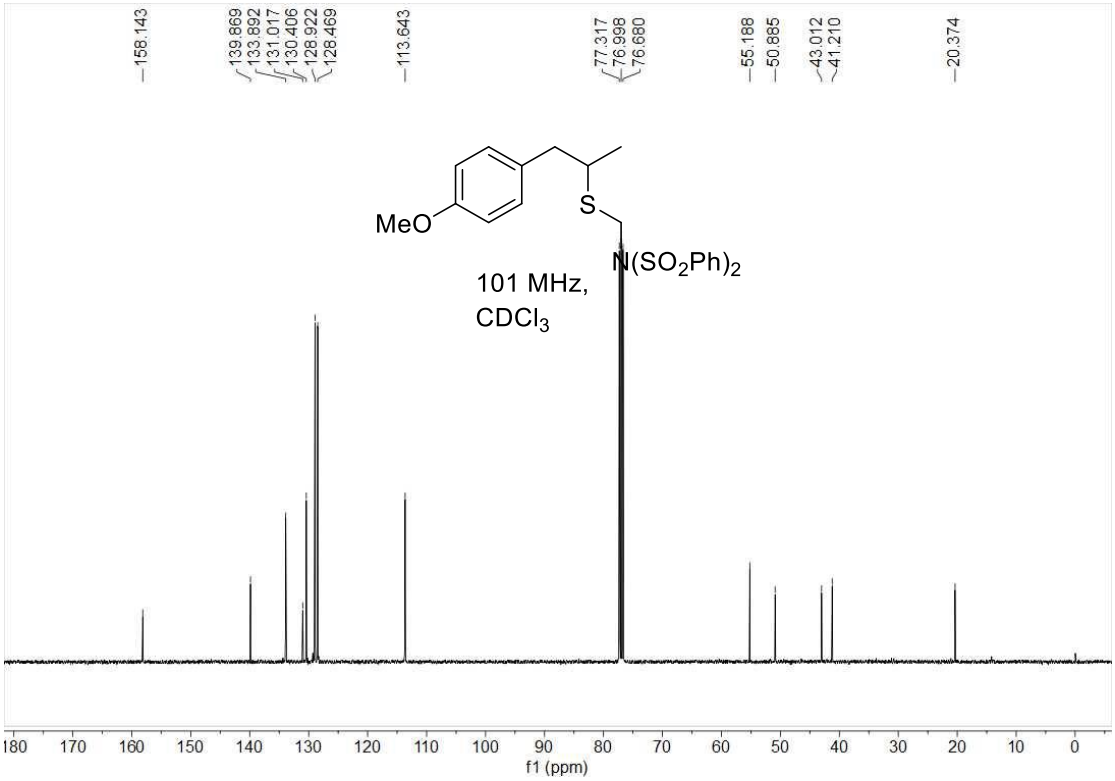


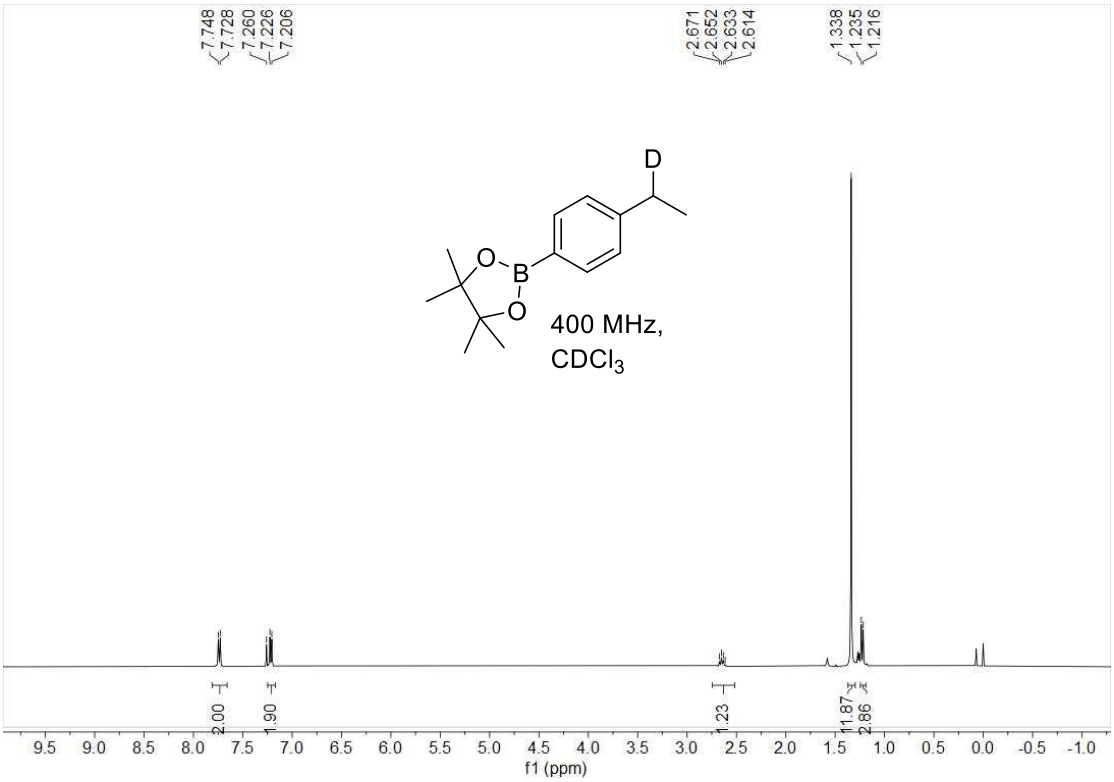
400 MHz,
$CDCl_3$

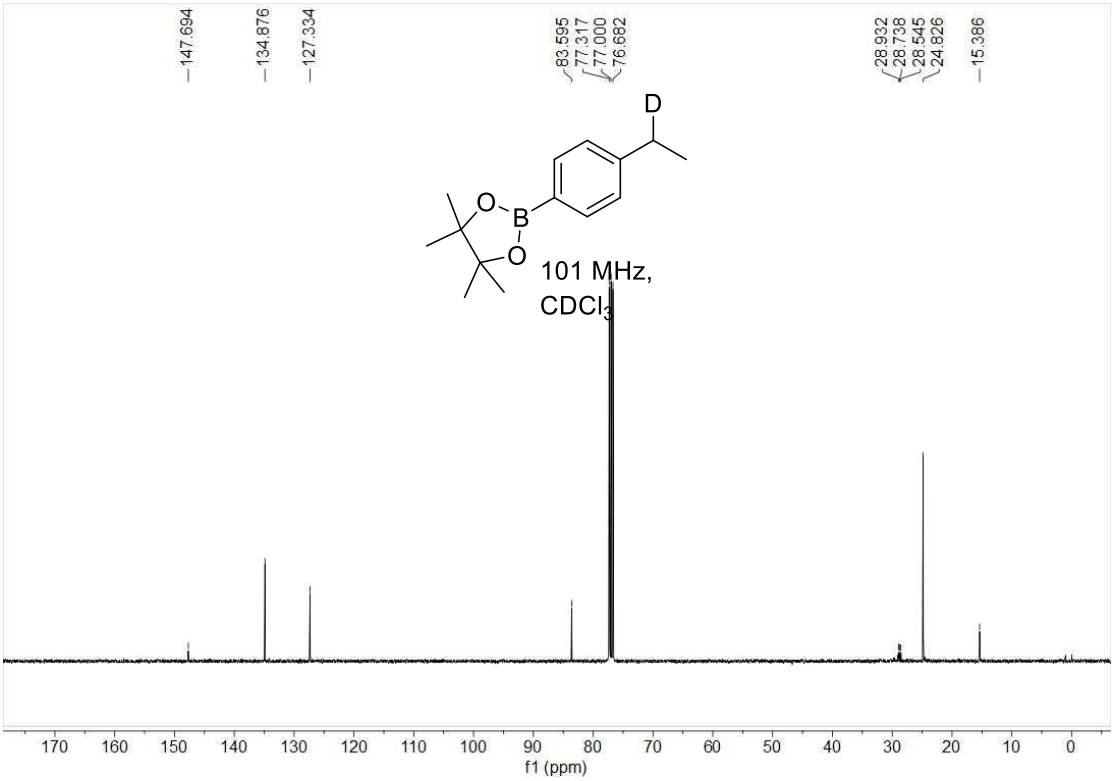


101 MHz,
$CDCl_3$


MeO
S
N(SO2Ph)2
400 MHz,
CDCl3
f1 (ppm)


MeO
S
N(SO2Ph)2
101 MHz,
CDCl3
f1 (ppm)


7.748
7.728
7.260
7.226
7.206
2.671
2.652
2.633
2.614
1.338
1.235
1.216
D
O
B
O
400 MHz,
CDCl3
2.00
1.90
1.23
11.87
2.86
f1 (ppm)


147.694
134.876
127.334
83.595
77.317
77.000
76.682
28.932
28.738
28.545
24.826
15.386
D
O
B
O
101 MHz,
CDCl3
f1 (ppm)