Supporting Information

Ortho-[1-(p-MeOPhenyl) Vinyl] Benzoate (PMPVB) as a Recyclable auxiliary for C-O and C-S bond formation Reactions Under Brønsted acid Catalysis

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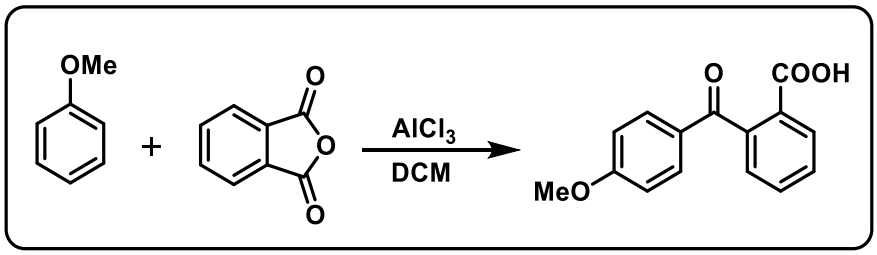
General Information

All solvents purchased were of commercial grade, and reagents were purchased from Sigma-Aldrich, Merck, Carbosynth, Spectrochem, Alfa Aesar, and Avra and used without further purification for reactions.

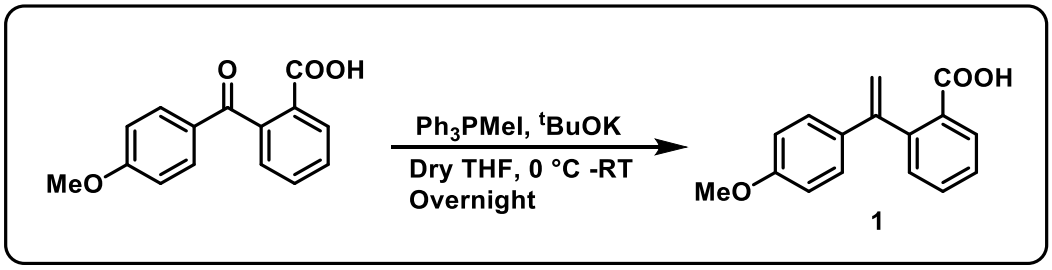
Analysis

Reactions were monitored by TLC on Kiesel gel 60 F254 (Merck). Detection was done by examination under UV light (254nm). Purification was performed in normal phase using silica gel [Merck, 60-120 mesh]. Extracts were concentrated in vacuo using both Büchi rotary evaporator (bath temperatures up to 40 °C) at a pressure of either 15 mmHg (diaphragm pump) and 0.7 mmHg (oil pump) at rt. ^{1}H- and ^{13}C NMR were recorded on a Bruker 600 MHz,500 MHz, and 400 MHz spectrometers using Chloroform-d as solvent. Chemical shift values are reported in ppm with the solvent as the internal standard (Chloroform-d: 7.26 for ^{1}H, δ 77.16 for ^{13}C). Data are reported as follows: chemical shifts (δ), multiplicity (s=singlet, d=doublet, dd = doublet of doublet, ddd = doublet of doublet of doublets, dt=doublet of triplet, t = triplet, td = triplet of doublet, q = quartet, m = multiplet) etc., coupling constants J(Hz), and integration. High-resolution mass measurements were performed using Agilent technologies mass spectrometer (QTOF-ESI mode). Suitable crystals for single-crystal X-ray diffraction (SCXRD) analysis were obtained by dissolving "**1a** and **3as"** in CH_2Cl_2 and Hexane, followed by slow evaporation of solvent mixture at room temperature. The X-ray diffraction data were collected at 296 K with Mo K α radiation (λ=0.71073 Å) using a Micro focused based Bruker D8 QUEST diffractometer equipped with a graphite monochromator. Apex IV software was used for data collection and indexing of the reflections and determining the unit cell parameters; the collected data were integrated using Saint Software. The structures were solved by Intrinsic phasing and refined by full-matrix least-squares calculations using SHELXTL 2018 software.

Synthesis of *ortho*-[1-(p-methoxyphenyl)vinyl]benzoic acid



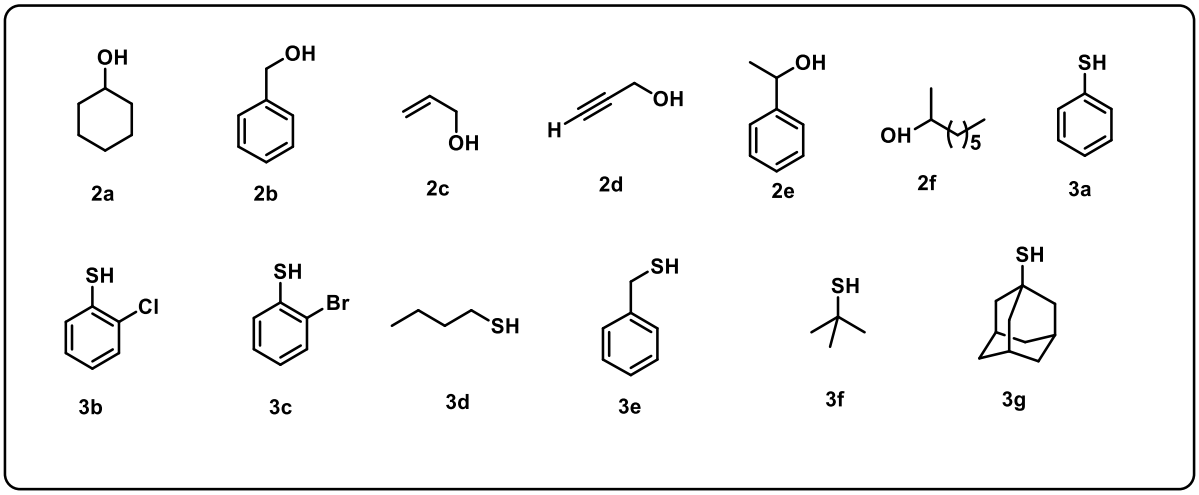
Scheme1. Preparation of 2-(4-methoxybenzoyl) benzoic acid



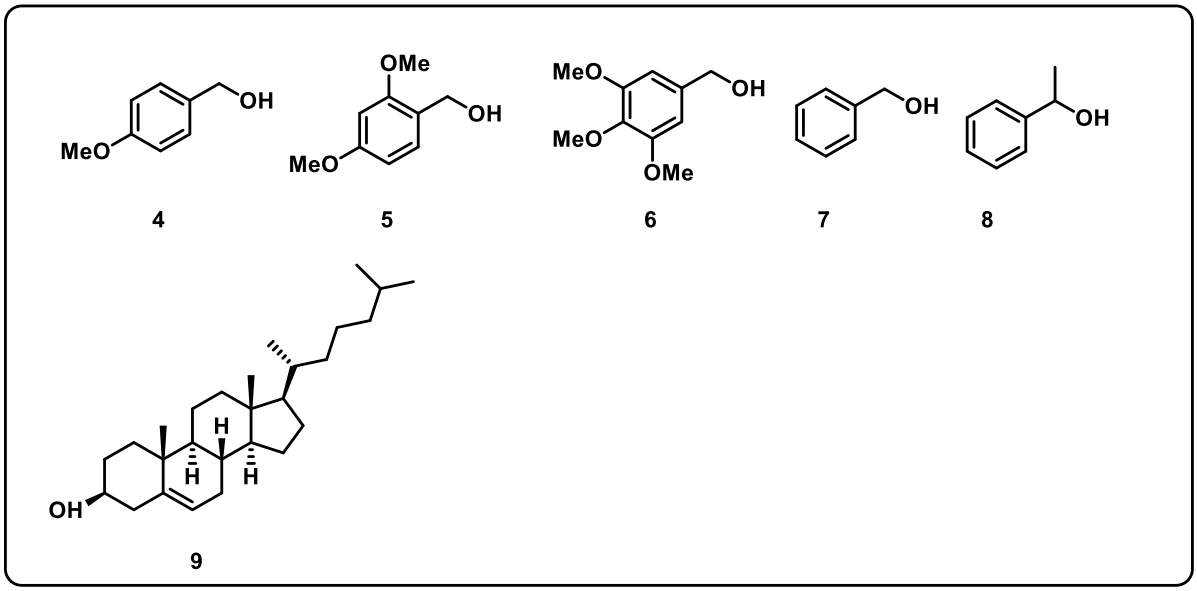
Scheme2. Preparation of *ortho*-[1-(p-methoxyphenyl) vinyl] benzoic acid

Compound 1 was formed by following the procedures described in the literature.[1]

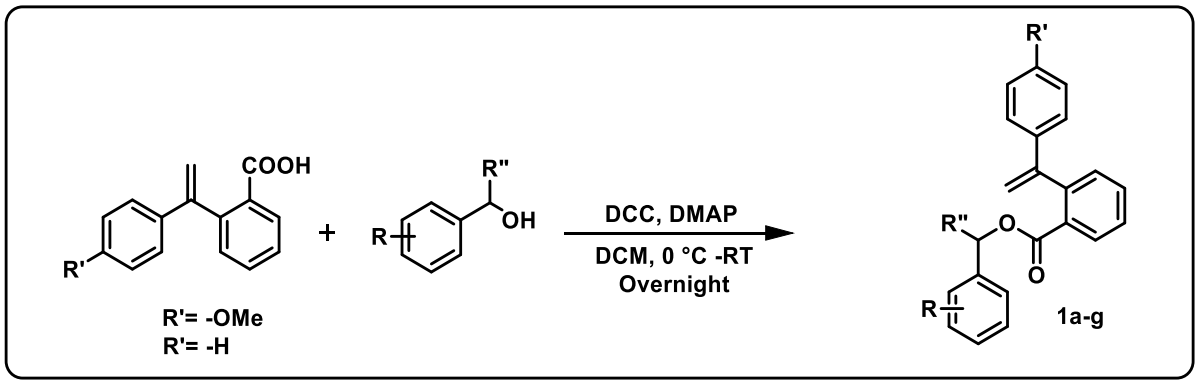
Different nucleophiles used in this study



Different primary and secondary alcohol used in this study



General scheme for the synthesis of PMPVB donors



Scheme3. Different PMPVB donors were used for this study

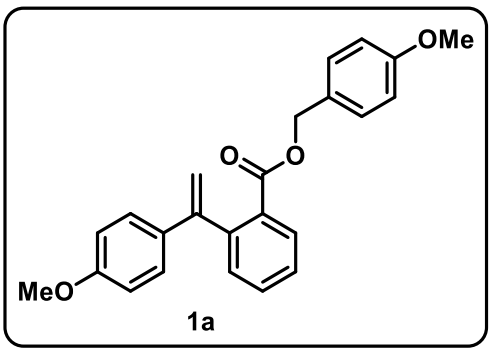
Different methoxy substituted benzyl alcohols, and ortho-[1-(p-methoxyphenyl) vinyl] benzoic acid was used in the synthesis.

General procedure 1

At 0°C, 4-dimethylaminopyridine (0.2equiv.) and N, N'-dicyclohexylcarbodiimide (2 equiv.) were added to the mixture of different substituted primary and secondary alcohol (1.0 equiv.) and benzoic acid (2.0 equiv.) in dry DCM. The mixture was allowed to cool to room temperature before being stirred overnight. After the reaction was finished, the solution was diluted with CH_2Cl_2 and washed with water and brine. The organic layer was filtered and concentrated in vacuo after drying over Na_2SO_4. The residue was purified using flash

column chromatography to obtain the PMPVB donors (**1a-1g**).

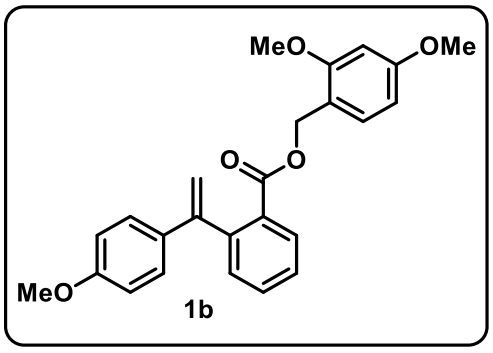
Synthesis of 4-methoxybenzyl-2-(1-(4-methoxyphenyl)vinyl)benzoate (1a)



1a

General procedure 1 was used to make compound **1a** from **4** (200.2 mg, 1.46 mmol). To obtain this, the crude product was purified using flash column chromatography,**1a** (499.17 mg, 92 %) as a white solid, Rf = 0.6 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.80 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.48 (td, *J* = 7.6, 1.4 Hz, 1H), 7.41 – 7.29 (m, 2H), 7.16 – 7.07 (m, 4H), 6.85 – 6.71 (m, 4H), 5.53 (s, 1H), 5.09 (s, 1H), 4.93 (s, 2H), 3.79 (s, 4H), 3.78 (s, 3H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 167.8, 159.5, 159.2, 148.8, 142.9, 133.5, 131.5, 131.4, 131.1, 130.0, 129.8, 128.0, 127.9, 127.5, 113.7, 113.5, 112.5, 66.5, 55.3, 55.2. **HRMS (ESI)** calcd for $C_{24}H_{22}KO_4$ $[M+K]^+$ 413.1150, found 413.1145.

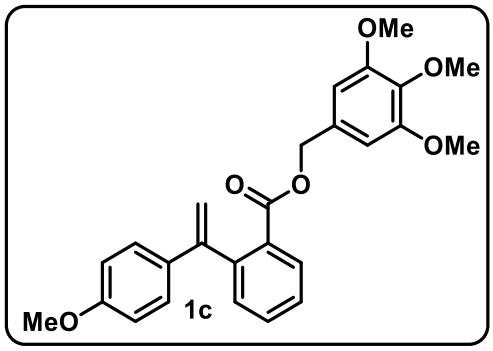
Synthesis of 2,4-dimethoxybenzyl-2-(1-(4-methoxyphenyl)vinyl)benzoate (1b)



1b

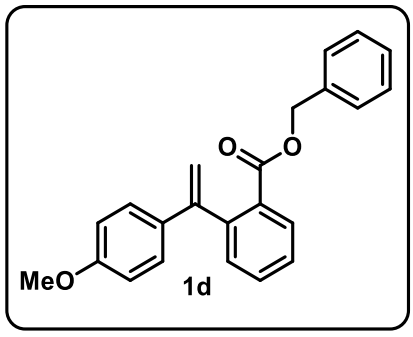
General procedure 1 was used to make compound **1b** from **5** (205.4 mg, 1.22 mmol). To obtain this, the crude product was purified using flash column chromatography, **1** (419.85 mg, 85 %) as a colourless oil, Rf = 0.3 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.80 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.41 – 7.28 (m, 2H), 7.15 – 7.10 (m, 2H), 7.06 (d, *J* = 8.1 Hz, 1H), 6.79 – 6.71 (m, 2H), 6.42 – 6.33 (m, 2H), 5.50 (d, *J* = 1.1 Hz, 1H), 5.09 (d, *J* = 1.1 Hz, 1H), 5.00 (s, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 3.71 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 167.9, 161.0, 159.0, 158.7, 148.8, 142.8, 133.6, 131.6, 131.2, 131.0, 131.0, 129.7, 128.0, 127.4, 116.6, 113.4, 112.5, 103.8, 98.2, 62.0, 55.3, 55.3, 55.2. **HRMS (ESI)** calcd for $C_{25}H_{24}NaO_5$ $[M+Na]^+$ 427.1516, found 427.1509.

Synthesis of 2,4,6-trimethoxybenzyl-2-(1-(4-methoxyphenyl)vinyl)benzoate (1c)



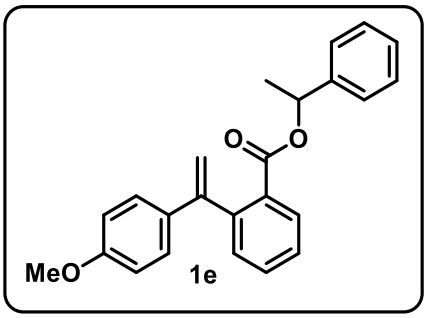
General procedure 1 was used to make compound **1c** from **6** (202 mg, 1.02 mmol). To obtain this, the crude product was purified using flash column chromatography, **1c** (358.65 mg, 81 %) as a colourless oil, Rf = 0.45 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (600 MHz, Chloroform-d)** δ 7.82 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.51 (td, *J* = 7.5, 1.4 Hz, 1H), 7.40 (td, *J* = 7.5, 1.3 Hz, 1H), 7.34 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.14 – 7.07 (m, 2H), 6.78 – 6.71 (m, 2H), 6.47 (s, 2H), 5.52 (d, *J* = 1.1 Hz, 1H), 5.11 (s, 1H), 4.91 (s, 2H), 3.83 (s, 3H), 3.79 (s, 6H), 3.77 (s, 3H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 167.8, 159.2, 153.2, 149.0, 142.8, 138.0, 133.5, 131.6, 131.2, 131.1, 129.8, 128.0, 127.6, 113.5, 112.4, 105.6, 67.0, 60.8, 56.1, 55.2. **HRMS (ESI)** calcd for $C_{26}H_{27}O_6$ $[M+H]^+$ 435.1802, found 435.1803.

Synthesis of benzyl-2-(1-(4-methoxyphenyl)vinyl)benzoate (1d)



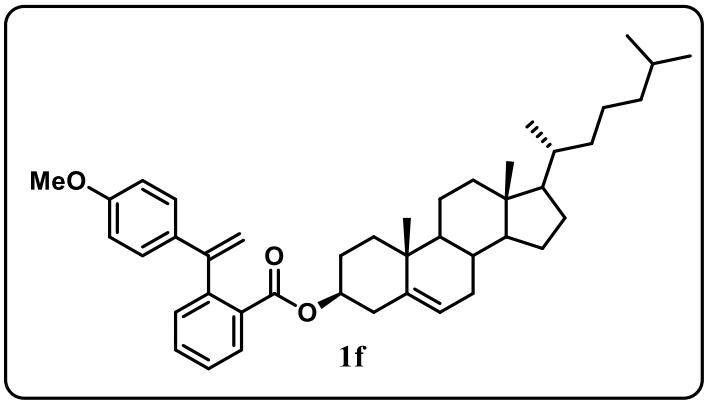
General procedure 1 was used to make compound **1d** from **7** (203.6 mg, 1.88 mmol). To obtain this, the crude product was purified using flash column chromatography, **3d** (531.72 mg, 82 %) as a white solid, Rf = 0.65 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.41 – 7.31 (m, 2H), 7.26 (q, *J* = 2.7 Hz, 3H), 7.21 – 7.08 (m, 4H), 6.78 – 6.72 (m, 2H), 5.53 (s, 1H), 5.11 (s, 1H), 4.99 (s, 2H), 3.76 (s, 3H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 167.6, 159.2, 148.8, 142.9, 135.7, 133.5, 131.5, 131.2, 129.8, 128.3, 128.1, 127.9, 127.5, 113.5, 112.5, 66.6, 55.3. **HRMS (ESI)** calcd for $C_{23}H_{21}O_3$ $[M+H]^+$ 345.1485, found 345.1479.

Synthesis of 1-phenylethyl-2-(1-(4-methoxyphenyl)vinyl)benzoate (1e)



General procedure 1 was used to make compound **1e** from **8** (207.6 mg, 1.70 mmol). To obtain this, the crude product was purified using flash column chromatography, **3f** (536.04 mg, 88%) as a colourless oil, Rf = 0.3 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.82 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.37 (td, *J* = 7.6, 1.4 Hz, 1H), 7.31 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.26 – 7.13 (m, 7H), 6.78 – 6.69 (m, 2H), 5.81 (q, *J* = 6.5 Hz, 1H), 5.56 (d, *J* = 1.0 Hz, 1H), 5.09 (d, *J* = 1.0 Hz, 1H), 3.76 (s, 3H), 1.33 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 167.1, 159.1, 148.4, 142.7, 141.3, 133.3, 131.5, 131.4, 131.1, 129.7, 128.2, 127.9, 127.6, 127.4, 126.1, 113.4, 112.3, 73.2, 55.2, 21.8. **HRMS (ESI)** calcd for $C_{24}H_{22}KO_3$ $[M+K]^+$ 397.1201, found 397.1200.

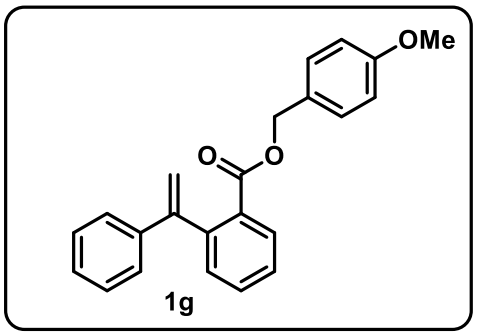
Synthesis of cholesteryl-2-(1-(4-methoxyphenyl)vinyl)benzoate (1f)



General procedure 1 was used to make compound **1f** from **9** (209.2 mg, 0.54 mmol). To obtain this, the crude product was purified using flash column chromatography, **3f** (337.04 mg, 84%) as a white solid, Rf = 0.25 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.80 (d, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.41 – 7.28 (m, 2H), 7.19 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 5.61 (d, 1H), 5.28 (d, *J* = 5.6 Hz, 1H), 5.11 (d, 1H), 4.52 (dq, *J* = 10.6, 5.6 Hz, 1H), 3.76 (s, 3H), 2.16 – 2.05 (m, 2H), 1.96 (ddt, *J* = 22.7, 13.7, 3.1 Hz, 2H), 1.87 – 1.68 (m, 3H), 1.62 – 1.29 (m, 11H), 1.19 – 1.00 (m, 10H), 0.99 – 0.78 (m, 12H), 0.66 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 167.1, 159.2, 148.8, 142.6, 139.7, 133.5, 131.8, 131.2,

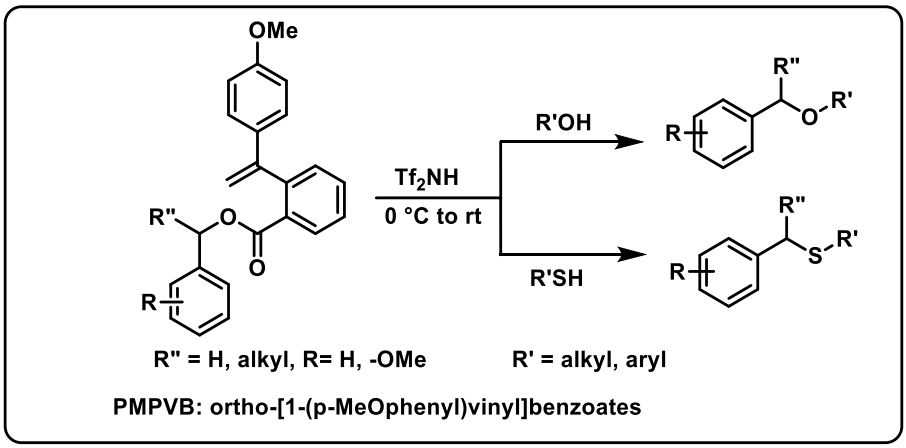
131.1, 129.5, 127.9, 127.4, 122.4, 113.5, 112.3, 74.7, 56.7, 56.1, 55.2, 50.0, 42.3, 39.7, 39.5, 37.5, 36.9, 36.5, 36.2, 35.8, 31.9, 31.8, 28.2, 28.0, 27.2, 24.3, 23.8, 22.8, 22.6, 21.0, 19.2, 18.7, 11.8. **HRMS (ESI)** calcd for $C_{43}H_{59}O_3$ $[M+H]^+$ 623.4459, found 623.4471.

Synthesis of 4-methoxybenzyl-2-(1-phenyl)vinyl)benzoate



General procedure 1 was used to make compound **1g** from **7** (205.3 mg, 1.83 mmol). To obtain this, the crude product was purified using flash column chromatography, **3d** (409.42 mg, 80%) as a colourless oil, Rf = 0.7 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.41 – 7.32 (m, 2H), 7.26 – 7.16 (m, 5H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 5.63 (s, 1H), 5.21 (s, 1H), 4.89 (s, 2H), 3.79 (s, 3H). **^{13}C NMR (126 MHz, Chloroform-d)** 167.6, 159.4, 149.4, 142.6, 140.7, 131.6, 131.2, 129.9, 129.9, 128.1, 127.8, 127.6, 127.5, 126.7, 114.2, 113.7, 66.4, 55.2, 30.9. **HRMS (ESI)** calcd for $C_{23}H_{21}O_3$ $[M+H]^+$ 345.1485, found 345.1472.

General scheme for *O* and *S* bond formation

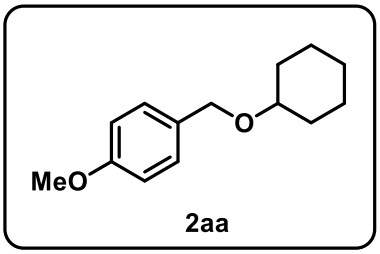


General procedure 2

A different primary and secondary derived PMPVB donor (1 equiv) and nucleophile (2 equiv) solution in dry DCM (0.05M) was mixed at room temperature and stirred for 12 h for the alcohol nucleophile and 2 h for the thiol nucleophile under Ar atmosphere and then RB was

allowed to cool to 0 °C and TF_2NH was added. After completion of reaction TLC were checked. The reaction was quench by the addition of Et_3N and work up with water, wash with brine, dried by Na_2SO_4 and concentrated in rotavapor. The resulting crude reaction mixture was purified through Flash column chromatography to afford the unsymmetrical ether and thioether product.

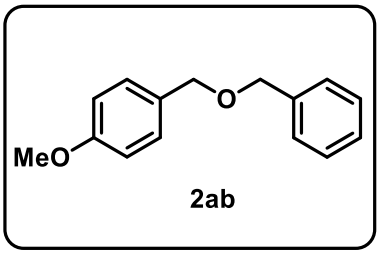
Synthesis of 1-((Cyclohexyloxy)methyl)-4-methoxybenzene (2aa)[2]



2aa

General procedure 2 was used to prepared compound **2aa** from **1a** (51.2mg, 0.14 mmol). Flash column chromatography was used to refine the crude product to get **2aa** (24.70 mg, 82%) as a Colourless oil, Rf = 0.8 (Hexane/EtOAc, , 9:1, v/v).**^{1}H NMR (500 MHz, Chloroform-d)** δ 7.26 (d, *J* = 9.2, 2.5 Hz, 2H), 6.87 (d, *J* = 7.0 Hz, 2H), 4.47 (s, *J* = 1.8 Hz, 2H), 3.79 (s, 3H), 3.33 (m, *J* = 9.1, 4.6, 2.8 Hz, 1H), 1.96-1.88 (d, *J* = 11.3 Hz, 2H), 1.80 – 1.71 (m, 2H), 1.56 – 1.49 (m, 1H), 1.29-1.37 (m, *J* = 10.8 Hz, 2H), 1.22-1.28 (m, *J* = 10.3 Hz, 3H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 159.0, 131.5, 129.0, 113.8, 76.7, 69.3, 55.3, 32.3, 25.9, 24.2.

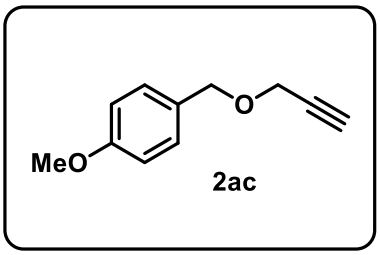
Synthesis of 1-((Benzyloxy)methyl)-4-methoxybenzene (2ab)[2]



2ab

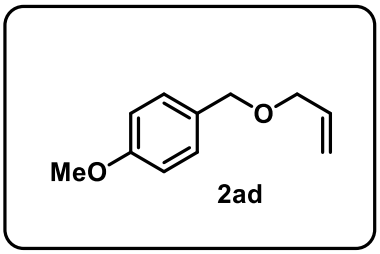
General procedure 2 was used to prepared compound **2ab** from **1a** (51.2mg, 0.14 mmol). Flash column chromatography was used to refine the crude product to get **2ab** (22.52 mg, 73%) as a Colourless oil, Rf = 0.7 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (600 MHz, Chloroform-d)** δ 7.38 – 7.32 (m, 4H), 7.32 – 7.25 (m, 3H), 6.89 (d, *J* = 8.6 Hz, 2H), 4.53 (s, 2H), 4.49 (s, 2H), 3.80 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-d)** δ 159.2, 138.4, 130.4, 129.4, 128.4, 127.8, 127.6, 113.8, 71.8, 71.8, 55.3.

Synthesis of 1-methoxy-4-((prop-2-yn-1-yloxy)methyl)benzene (2ac)[2]



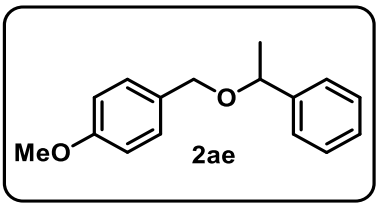
General procedure 2 was used to prepared compound **2ac** from **1a** (53.2mg, 0.14 mmol). Flash column chromatography was used to refine the crude product to get **2ac** (19.52 mg, 78 %) as a yellow oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.54 (s, 2H), 4.14 (d, *J* = 2.6 Hz, 2H), 3.80 (s, 3H), 2.45 (t, *J* = 2.4 Hz, 1H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 159.5, 129.8, 129.4, 113.9, 79.8, 74.5, 71.2, 56.7, 55.3.

Synthesis of 1-((allyloxy)methyl)-4-methoxybenzene (2ad)[3]



General procedure 2 was used to prepared compound **2ad** from **1a** (50.6mg, 0.14 mmol). Flash column chromatography was used to refine the crude product to get **2ad** (18.10 mg,75%) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.29 (d, *J* = 2.8 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.90-6.00 (m, *J* =16.0, 10.8, 5.6 Hz, 1H), 5.30 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.20 (dd, *J* = 11.2, 2.1 Hz, 1H), 4.46 (s, 2H), 4.00 (dt, *J* = 5.6, 1.4 Hz, 2H), 3.81 (s, 3H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 159.2, 134.9, 130.4, 129.4, 117.1, 113.8, 71.8, 70.9, 55.2.

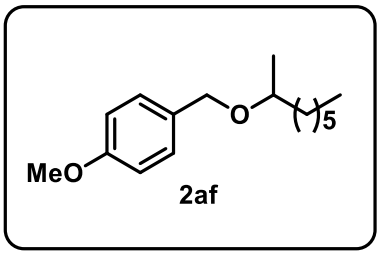
Synthesis of 1-((phenylethoxy)methyl)-4-methoxybenzene (2ae)[4]



General procedure 2 was used to prepared compound **2ae** from **1a** (54.3mg, 0.14 mmol). Flash column chromatography was used to refine the crude product to get **2ae** (29.17 mg, 83%) as a colourless oil, Rf = 0.65 (Hexane/EtOAc, 9:1 , v/v. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.40 – 7.27 (m, 5H), 7.23 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.48 (q, *J* = 6.5 Hz,

1H), 4.38 (d, *J* = 11.3 Hz, 1H), 4.22 (d, *J* = 11.4 Hz, 1H), 3.80 (s, 3H), 1.46 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 159.1, 143.8, 130.7, 129.3, 128.5, 127.5, 126.4, 113.8, 77.3, 77.0, 76.9, 76.7, 69.9, 55.3, 24.3.

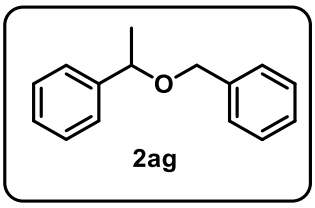
Synthesis of 1-((octan-2-yloxy)methyl)-4-methoxybenzene (2af)[5]



2af

General procedure 2 was used to prepared compound **2af** from **1a** (52mg, 0.14 mmol). Flash column chromatography was used to refine the crude product to get **2af** (27.82 mg, 80%) as a colourless oil, Rf = 0.7 (Hexane/EtOAc, , v/v. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.27 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 4.49 (d, *J* = 11.3 Hz, 1H), 4.39 (d, *J* = 11.4 Hz, 1H), 3.80 (s, 3H), 3.48 (q, *J* = 6.0 Hz, 1H), 1.64 – 1.26 (m, 10H), 1.17 (d, *J* = 6.1 Hz, 3H), 0.88 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 159.0, 131.3, 129.2, 113.7, 74.6, 69.9, 55.3, 36.7, 31.9, 29.4, 25.5, 22.6, 19.6, 14.1.

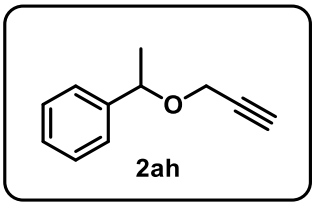
Synthesis of 1-(benzyloxy)ethyl)benzene (2ag)[6]



2ag

General procedure 2 was used to prepared compound **2ag** from **1e** (52.6mg, 0.15 mmol). Flash column chromatography was used to refine the crude product to get **2ag** (23.40 mg, 75%) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v. **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.39 – 7.25 (m, 10H), 4.50 (q, *J* = 6.5 Hz, 1H), 4.45 (d, *J* = 11.9 Hz, 1H), 4.30 (d, *J* = 11.8 Hz, 1H), 1.48 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 142.7, 137.7, 127.5, 127.3, 126.7, 126.5, 126.4, 125.3, 76.2, 69.3, 23.2.

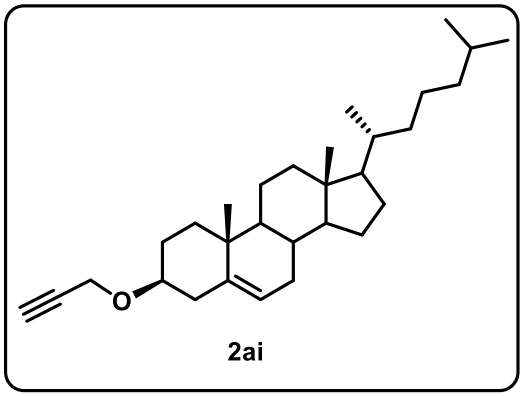
Synthesis of 1-(prop-2-yn-1-yloxy)ethyl)benzene (2ah)[7]



2ah

General procedure 2 was used to prepared compound **2ah** from **1e** (50.4 mg, 0.14 mmol). Flash column chromatography was used to refine the crude product to get **2ah** (17.60 mg, 78%) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1 , v/v. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.33 – 7.14 (m, 5H), 4.59 (q, *J* = 6.5 Hz, 1H), 4.01 (dd, *J* = 15.7, 2.4 Hz, 1H), 3.81 (dd, *J* = 15.7, 2.4 Hz, 1H), 2.33 (t, *J* = 2.3 Hz, 1H), 1.41 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 142.5, 128.6, 127.8, 126.5, 80.1, 76.7, 74.0, 55.5, 23.7.

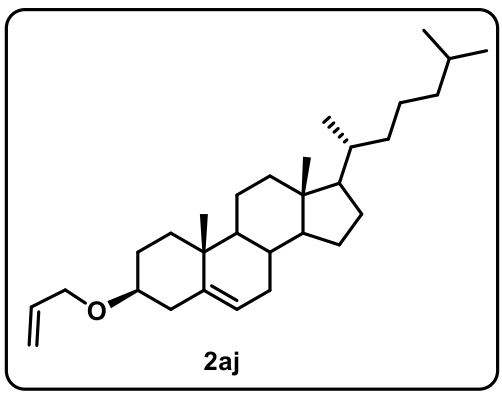
Synthesis of 3-(prop-2-yn-1-yloxy)-cholest-5-ene (2ai)[8]



2ai

General procedure 2 was used to prepared compound **2ai** from **1f** (53.2 mg, 0.10 mmol). Flash column chromatography was used to refine the crude product to get **2ai** (30 mg, 82%) as a colourless oil, *R*f = 0.65 (Hexane/EtOAc, 9:1 , v/v. **^{1}H NMR (500 MHz, Chloroform-d)** δ 5.36 (d, *J* = 5.0 Hz, 1H), 4.19 (d, *J* = 2.3 Hz, 2H), 3.38 (tt, *J* = 11.0, 4.6 Hz, 1H), 2.38 (dt, *J* = 11.8, 3.8 Hz, 2H), 2.27 – 2.18 (m, 1H), 2.05 – 1.77 (m, 5H), 1.59 – 1.41 (m, 7H), 1.39 – 1.26 (m, 4H), 1.24 – 1.05 (m, 8H), 1.00 (s, 5H), 0.92 (d, *J* = 6.6 Hz, 4H), 0.86 (dd, *J* = 6.6, 2.2 Hz, 6H), 0.68 (s, 3H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 140.6, 121.9, 80.5, 78.2, 73.7, 56.8, 56.2, 55.1, 50.2, 42.4, 39.8, 39.6, 38.8, 37.2, 36.9, 36.2, 35.8, 32.0, 31.9, 28.2, 28.1, 28.0, 24.3, 23.9, 22.8, 22.6, 21.1, 19.4, 18.7, 11.9.

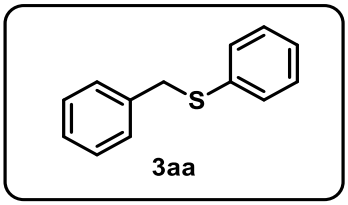
Synthesis of 3-(allyloxy)-cholest-5-ene (2aj)[9]



2aj

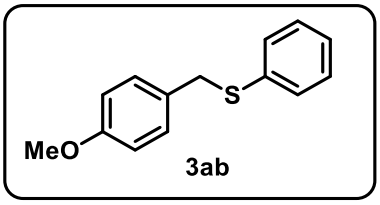
General procedure 2 was used to prepared compound **2aj** from **1f** (50.1mg, 0.10 mmol). Flash column chromatography was used to refine the crude product to get **2aj** (27 mg, 78%) as a colourless oil, Rf = 0.6 (Hexane/EtOAc, 9:1 , v/v. **^{1}H NMR (500 MHz, Chloroform-d)** δ 5.93 (ddt, *J* = 16.0, 10.7, 5.6 Hz, 1H), 5.34 (d, *J* = 3.5 Hz, 1H), 5.27 (d, *J* = 17.2 Hz, 1H), 5.15 (d, *J* = 10.4 Hz, 1H), 4.02 (d, *J* = 5.8 Hz, 2H), 3.20 (dq, *J* = 11.4, 5.6 Hz, 1H), 2.41 – 2.33 (m, 1H), 2.22 (t, *J* = 11.8 Hz, 1H), 2.07 – 1.78 (m, 5H), 1.55 – 1.42 (m, 6H), 1.40 – 1.31 (m, 4H), 1.20 – 1.06 (m, 8H), 1.00 (s, 5H), 0.92 (d, *J* = 6.6 Hz, 4H), 0.87 (dd, *J* = 6.6, 2.2 Hz, 6H), 0.68 (s, 3H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 141.0, 135.6, 121.6, 116.5, 78.6, 69.0, 56.8, 56.2, 50.3, 42.4, 39.9, 39.6, 39.2, 37.3, 36.9, 36.2, 35.8, 32.0, 31.9, 28.5, 28.3, 28.0, 24.3, 23.9, 22.8, 22.6, 21.1, 19.4, 18.8, 11.9.

Synthesis of 1-((phenylthio)methyl)-benzene (3aa)[10]



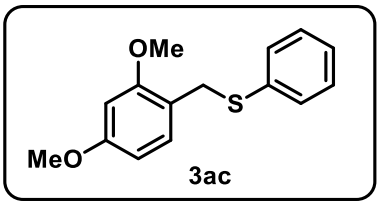
General procedure 2 was used to prepared compound **3aa** from **1d** (54.2 mg, 0.16 mmol). Flash column chromatography was used to refine the crude product to get **3aa** (23.33 mg, 74%) as a white solid, Rf = 0.7 (Hexane/EtOAc, 9:1 , v/v). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.32 – 7.14 (m, 10H), 4.10 (s, 2H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 137.5, 136.9, 136.4, 129.9, 128.8, 128.5, 127.2, 126.3, 39.1.

Synthesis of 1-((phenylthio)methyl)-4-methoxyl-benzene (3ab)[11]



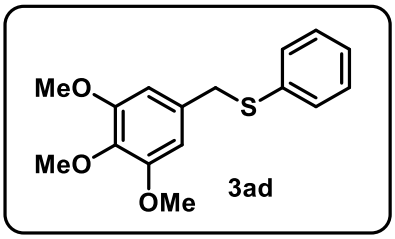
General procedure 2 was used to prepared compound **3ab** from **1a** (51.7 mg, 0.14 mmol). Flash column chromatography was used to refine the crude product to get **3ab** (26.08 mg, 87%) as a white solid, Rf = 0.8 (Hexane/EtOAc, 9:1 , v/v). **^{1}H NMR (600 MHz, Chloroform-d)** δ 7.36 – 7.12 (m, 7H), 6.81 (d, *J* = 8.7 Hz, 2H), 4.07 (s, 2H), 3.77 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-d)** δ 158.7, 137.0, 129.9, 129.7, 129.4, 128.8, 126.2, 113.9, 55.2, 38.4

Synthesis of 1-((phenylthio)methyl)-2,4- dimethoxyl-benzene (3ac)[9]



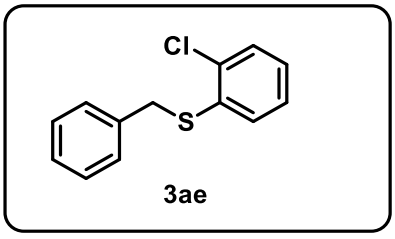
General procedure 2 was used to prepared compound **3ac** from **1b** (52.3mg, 0.13 mmol). Flash column chromatography was used to refine the crude product to get **3ac** (28.62 mg, 85%) as a colourless oil, Rf = 0.75 (Hexane/EtOAc, 9:1 , v/v. **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.35 – 7.29 (m, 2H), 7.28 – 7.21 (m, 2H), 7.20 – 7.13 (m, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 6.44 (d, *J* = 2.6 Hz, 1H), 6.39 (dd, *J* = 8.3, 2.5 Hz, 1H), 4.10 (s, 2H), 3.80 (s, 3H), 3.79 (s, 3H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 160.2, 158.2, 137.2, 130.7, 129.8, 128.6, 126.0, 118.1, 104.1, 98.6, 55.5, 55.3, 33.0.

Synthesis of 1-((phenylthio)methyl)-2,4,6-trimethoxyl-benzene (3ad)[9]



General procedure 2 was used to prepared compound **3ad** from **1c** (51.6 mg, 0.12 mmol). Flash column chromatography was used to refine the crude product to get **3ad** (30.34 mg, 88%) as a white solid, Rf = 0.7 (Hexane/EtOAc, 9:1 , v/v. **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.35 – 7.17 (m, 5H), 6.47 (s, 2H), 4.05 (s, 2H), 3.82 (s, 3H), 3.79 (s, 6H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 153.3, 137.4, 136.4, 133.3, 130.6, 129.0, 126.7, 106.0, 61.0, 56.2, 39.9.

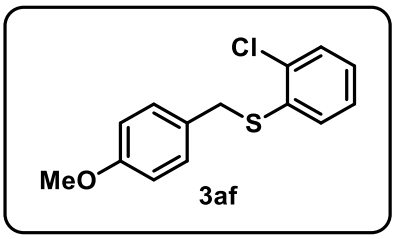
Synthesis of 1-((2-chlorophenylthio)methyl)-benzene (3ae)[8]



General procedure 2 was used to prepared compound **3ae** from **1d** (54.2 mg, 0.16 mmol). Flash column chromatography was used to refine the crude product to get **3ae** (26.22 mg, 71%) as a white solid, Rf = 0.75 (Hexane/EtOAc, 9:1 , v/v). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.41 – 7.19 (m, 7H), 7.13 (m, *J* = 21.3, 7.4, 1.6 Hz, 2H), 4.15 (s, 2H). **^{13}C NMR (126**

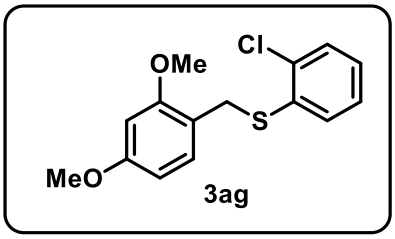
MHz, Chloroform-d) δ 136.3, 135.7, 133.8, 129.6, 129.3, 128.9, 128.6, 127.4, 127.1, 126.9, 37.5.

Synthesis of 1-((2-chlorophenylthio)methyl)-4-methoxyl-benzene (3af)[12]



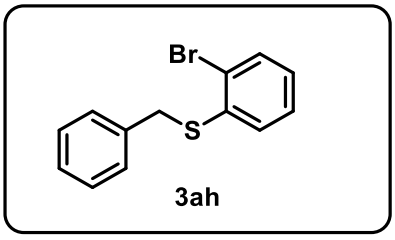
General procedure 2 was used to prepared compound **3af** from **1a** (50.7 mg, 0.14 mmol). Flash column chromatography was used to refine the crude product to get **3af** (27.24 mg, 76%) as a white solid, Rf = 0.7 (Hexane/EtOAc, 9:1 , v/v. **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.36 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.29 – 7.22 (m, 3H), 7.14-7.18 (m, *J* = 7.6, 1.6 Hz, 1H), 7.08-7.12 (m, *J* = 7.8, 1.8 Hz, 1H), 6.86 – 6.80 (m, 2H), 4.11 (s, 2H), 3.79 (s, 3H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 159.0, 136.0, 133.7, 130.1, 129.6, 129.4, 128.3, 127.0, 126.8, 114.0, 55.3, 37.0

.**Synthesis of 1-((2-chlorophenylthio)methyl)-2,4-dimethoxyl-benzene (3ag)**



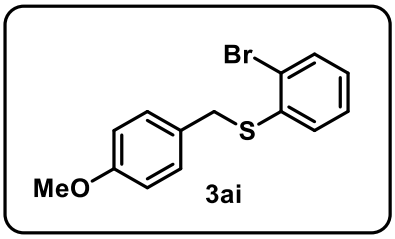
General procedure 2 was used to prepared compound **3ag** from **1b** (51.3mg, 0.13 mmol). Flash column chromatography was used to refine the crude product to get **3ag** (29.16 mg, 78%) as a colourless oil, Rf = 0.7 (Hexane/EtOAc, 9:1 , v/v. **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.35 (d, *J* = 7.9 Hz, 1H), 7.27 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.16 (td, *J* = 7.0, 1.8 Hz, 2H), 7.09 (td, *J* = 7.5, 1.6 Hz, 1H), 6.45 (d, *J* = 2.6 Hz, 1H), 6.41 (dd, *J* = 8.3, 2.5 Hz, 1H), 4.13 (s, 2H), 3.81 (s, 3H), 3.79 (s, 3H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 160.4, 158.4, 136.7, 133.4, 130.9, 129.5, 129.0, 127.0, 126.4, 116.8, 104.3, 98.6, 55.5, 55.4, 31.4. **HRMS (ESI)** calcd for $C_{15}H_{16}ClO_2S$ $[M+H]^+$ 295.0554 found 295.0541.

Synthesis of 1-((2-bromophenylthio)methyl)-benzene (3ah)[13]



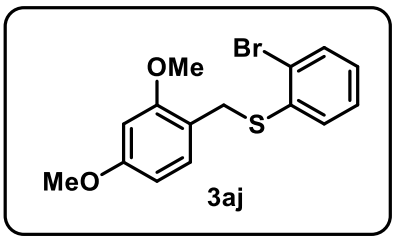
General procedure 2 was used to prepared compound **3ah** from **1d** (54.6 mg, 0.16 mmol). Flash column chromatography was used to refine the crude product to get **3ah** (32.31 mg, 73%) as a white solid, Rf = 0.7 (Hexane/EtOAc, 9:1 , v/v). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.58 – 6.98 (m, 9H), 4.15 (s, 2H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 137.9, 136.2, 132.9, 129.0, 128.9, 128.6, 127.7, 127.4, 126.9, 123.8, 38.0.

Synthesis of 1-((2-bromophenylthio)methyl)-4-methoxyl-benzene (3ai)[12]



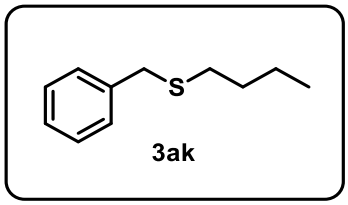
General procedure 2 was used to prepared compound **3ai** from **1a** (52.2mg, 0.14 mmol). Flash column chromatography was used to refine the crude product to get **3ai** (32.76 mg, 76%) as a white solid, Rf = 0.75 (Hexane/EtOAc, 9:1 , v/v. **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.53-7.58 (m, *J* = 7.6 Hz, 1H), 7.33 – 7.23 (m, 2H), 7.24 – 7.19 (m, 2H), 7.00-7.03 (m, *J* = 8.7, 6.2, 2.7 Hz, 1H), 6.86 – 6.79 (m, 2H), 4.10 (s, 2H), 3.78 (s, 3H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 158.9, 138.0, 132.9, 130.0, 128.7, 127.9, 127.7, 126.8, 123.5, 114.0, 55.2, 37.3.

Synthesis of 1-((2-bromophenylthio)methyl)-2,4-dimethoxyl-benzene (3aj)



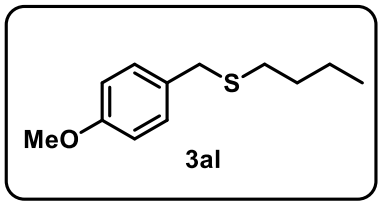
General procedure 2 was used to prepared compound **3aj** from **1b** (50.4 mg, 0.13 mmol). Flash column chromatography was used to refine the crude product to get **3aj** (33 mg, 78%) as a colourless oil, Rf = 0.75 (Hexane/EtOAc, 9:1 , v/v. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.53 (d, *J* = 7.9 Hz, 1H), 7.24 – 7.17 (m, 3H), 7.01 (td, *J* = 7.4, 2.1 Hz, 1H), 6.45 (d, *J* = 2.6 Hz, 1H), 6.42 (dd, *J* = 8.3, 2.5 Hz, 1H), 4.13 (s, 2H), 3.82 (s, 3H), 3.79 (s, 3H**). ^{13}C NMR (101 MHz, Chloroform-d)** δ 160.4, 158.4, 138.8, 132.7, 130.9, 128.6, 127.6, 126.4, 123.4, 116.6, 104.3, 98.6, 55.5, 55.4, 31.8. **HRMS (ESI)** calcd for $C_{15}H_{16}BrO_2S$ $[M+H]^+$ 339.0049 found 339.0041.

Synthesis of 1-((butylthio)methyl)-benzene (3ak)[14]



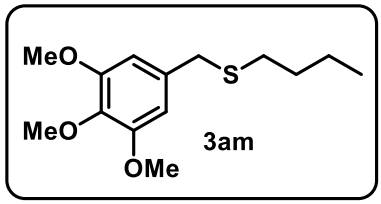
General procedure 2 was used to prepared compound **3ak** from **1d** (54 mg, 0.16 mmol). Flash column chromatography was used to refine the crude product to get **3ak** (22.05 mg, 78%) as a yellow oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.37 – 7.19 (m, 5H), 3.70 (s, 2H), 2.43-2.39 (m, 2H), 1.59 – 1.48 (m, 2H), 1.44 – 1.32 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 138.7, 128.8, 128.4, 126.8, 36.3, 31.3, 31.1, 22.0, 13.6.

Synthesis of 1-((butylthio)methyl)-4-methoxyl-benzene (3al)[14]



General procedure 2 was used to prepared compound **3al** from **1a** (53.2 mg, 0.14 mmol). Flash column chromatography was used to refine the crude product to get **3al** (25.10 mg, 84%) as a yellow oil, Rf = 0.8 (Hexane/EtOAc, 9:1 , v/v). **^{1}H NMR (600 MHz, Chloroform-d)** δ 7.22 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 3.66 (s, 2H), 2.43 – 2.34 (t, 2H), 1.54 (m, *J* = 7.5, 6.3 Hz, 2H), 1.37 (m, *J* = 7.3 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 2H). **^{13}C NMR (151 MHz, Chloroform-d)** δ 158.6, 130.7, 130.0, 114.0, 55.3, 35.7, 31.4, 31.0, 22.0, 13.7.

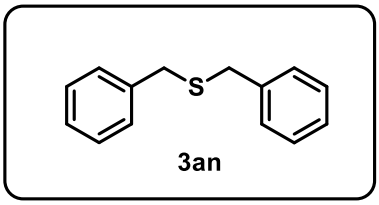
Synthesis of 1-((butylthio)methyl)-2,4,6-trimethoxyl-benzene (3am)



General procedure 2 was used to prepared compound **3am** from **1c** (52.5 mg, 0.12 mmol). Flash column chromatography was used to refine the crude product to get **3am** (29.40 mg, 90%) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1 , v/v. **^{1}H NMR (500 MHz, Chloroform-d)** δ 6.55 (s, 2H), 3.86 (s, 6H), 3.83 (s, 3H), 3.66 (s, 2H), 2.46 (t, *J* = 7.4 Hz, 2H), 1.56 (dd, *J* = 14.5, 7.3 Hz, 2H), 1.39 (h, *J* = 7.3 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (126 MHz,**

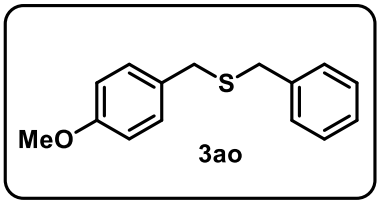
Chloroform-d) δ 153.2, 137.1, 134.2, 105.9, 60.9, 56.2, 36.9, 31.4, 22.0, 13.7. **HRMS (ESI)** calcd for $C_{14}H_{22}NaO_3S$ $[M+Na]^+$ 293.1182 found 293.1179.

Synthesis of 1-((benzylthio)methyl)-benzene (3an)[15]



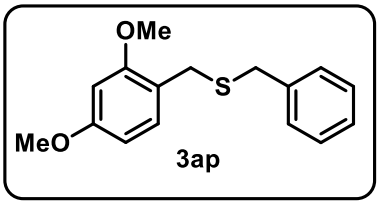
General procedure 2 was used to prepared compound **3an** from **1d** (50.2 mg, 0.15 mmol). Flash column chromatography was used to refine the crude product to get **3an** (22.81 mg, 73%) as a colourless oil, Rf = 0.85 (Hexane/EtOAc, 9:1 , v/v. **^{1}H NMR (600 MHz, Chloroform-d)** δ 7.35 – 7.22 (m, 10H), 3.60 (s, 4H). **^{13}C NMR (151 MHz, Chloroform-d)** δ 137.5, 136.9, 136.4, 129.9, 128.8, 128.5, 127.2, 126.3, 39.1.

Synthesis of 1-((benzylthio)methyl)-4-methoxyl-benzene (3ao)[16]



General procedure 2 was used to prepared compound **3ao** from **1a** (52.3mg, 0.14 mmol). Flash column chromatography was used to refine the crude product to get **3ao** (27.30 mg, 80%) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.33 – 7.16 (m, 7H), 6.85 (d, *J* = 6.1 Hz, 2H), 3.79 (s, 3H), 3.59 (s, 2H), 3.56 (s, 2H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 158.6, 138.3, 130.1, 129.0, 128.5, 126.9, 113.9, 55.3, 35.6, 35.0.

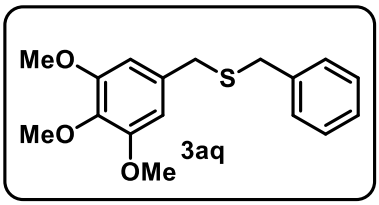
Synthesis of 1-((benzylthio)methyl)-2,4-dimethoxyl-benzene (3ap)



General procedure 2 was used to prepared compound **3ap** from **1b** (50.7 mg, 0.13 mmol). Flash column chromatography was used to refine the crude product to get **3ap** (28.20 mg, 82%) as a colourless oil, Rf = 0.7 (Hexane/EtOAc, 9:1 , v/v. **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.37 – 7.19 (m, 5H), 7.10 (d, *J* = 8.1 Hz, 1H), 6.47 – 6.40 (m, 2H), 3.80 (s, 6H), 3.67 (s, 2H), 3.61 (s, 2H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 160.1, 158.3, 138.7, 130.7, 129.0, 128.4,

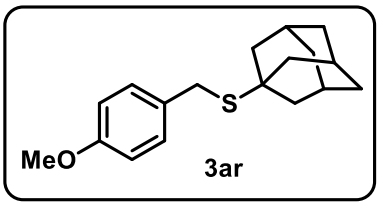
126.8, 119.1, 104.0, 98.8, 55.5, 55.4, 36.1, 29.7. **HRMS (ESI)** calcd for $C_{16}H_{19}O_2S$ $[M+H]^+$ 275.1100 found 275.1095.

Synthesis of 1-((benzylthio)methyl)-2,4,6-trimethoxyl-benzene (3aq)



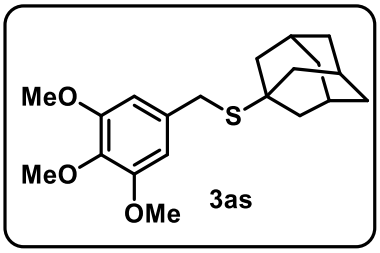
General procedure 2 was used to prepared compound **3aq** from **1c** (54.2 mg, 0.13 mmol). Flash column chromatography was used to refine the crude product to get **3aq** (32.27 mg, 85%) as a colourless oil, Rf = 0.65 (Hexane/EtOAc, 9:1, v/v. **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.41 – 7.17 (m, 5H), 6.49 (s, 2H), 3.83 (d, *J* = 8.4 Hz, 9H), 3.64 (s, 2H), 3.56 (s, 2H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 153.2, 138.1, 137.1, 133.7, 129.0, 128.5, 127.0, 106.0, 60.9, 56.1, 36.2, 36.0. **HRMS (ESI)** calcd for $C_{17}H_{20}NaO_3S$ $[M+Na]^+$ 327.1025 found 327.1028.

Synthesis of 1-((adamantanylthio)methyl)-4-methoxyl-benzene (3ar)



General procedure 2 was used to prepared compound **3ar** from **1a** (53.4 mg, 0.14 mmol). Flash column chromatography was used to refine the crude product to get **3ar** (29.21 mg, 71%) as a yellow oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.25 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H), 3.71 (s, 2H), 2.04 (dd, *J* = 6.8, 3.5 Hz, 3H), 1.90 (d, *J* = 2.9 Hz, 6H), 1.69 (qd, *J* = 10.5, 6.1 Hz, 6H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 158.5, 130.1, 130.0, 113.9, 55.3, 45.0, 43.6, 38.8, 36.4, 29.8**. HRMS (ESI)** calcd for $C_{18}H_{25}OS$ $[M+H]^+$ 289.1621 found 289.1620

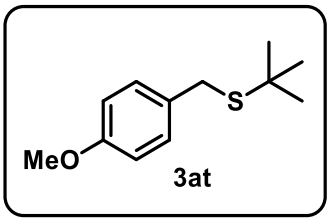
Synthesis of 1-((adamantanylthio)methyl)-2,4,6-trimethoxyl-benzene (3as)



General procedure 2 was used to prepared compound **3as** from **1c** (51.3mg, 0.12 mmol). Flash column chromatography was used to refine the crude product to get **3as** (31.70 mg, 77%) as a

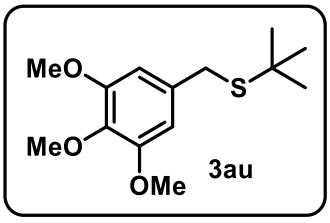
white solid, Rf = 0.75 (Hexane/EtOAc, 9:1, v/v. **^{1}H NMR (500 MHz, Chloroform-d)** δ 6.57 (s, 2H), 3.85 (s, 6H), 3.82 (s, 3H), 3.71 (s, 2H), 2.08 – 2.03 (m, 3H), 1.94 – 1.87 (m, 6H), 1.75 – 1.65 (m, 6H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 153.2, 136.9, 134.4, 106.0, 60.9, 56.2, 45.2, 43.6, 36.4, 31.2, 29.8. **HRMS (ESI)** calcd for $C_{20}H_{28}NaO_3S$ $[M+Na]^+$ 371.1651 found 371.1653.

Synthesis of 1-((tert-butylthio)methyl)-4-methoxyl-benzene (3at)[17]



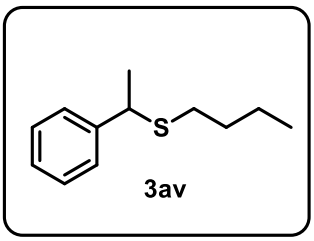
General procedure 2 was used to prepared compound **3at** from **1a** (52.6 mg, 0.14 mmol). Flash column chromatography was used to refine the crude product to get **3at** (21.27 mg, 72%) as a yellow oil, Rf = 0.8 (Hexane/EtOAc, 9:1 , v/v). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.25 (d, *J* = 8.7 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 1H), 3.78 (s, 2H), 3.72 (s, 1H), 1.35 (s, 6H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 158.5, 130.5, 130.0, 114.0, 55.3, 42.7, 32.8, 30.9.

Synthesis of 1-((tert-butylthio)methyl)-2,4,6-trimethoxyl-benzene (3au)



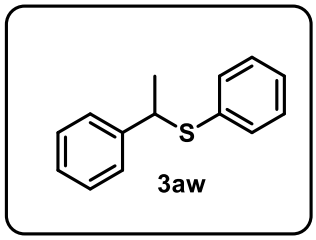
General procedure 2 was used to prepared compound **3au** from **1c** (54.3mg, 0.13 mmol). Flash column chromatography was used to refine the crude product to get **3au** (26.40 mg, 77%) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1 , v/v. **^{1}H NMR (500 MHz, Chloroform-d)** δ 6.57 (s, 2H), 3.86 (s, 6H), 3.82 (s, 3H), 3.72 (s, 2H), 1.37 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 153.2, 137.0, 134.0, 106.0, 60.9, 56.1, 42.9, 33.9, 30.9. **HRMS (ESI)** calcd for $C_{14}H_{22}NaO_3S$ $[M+Na]^+$ 293.1182 found 293.1180.

Synthesis of (1-(butylthio)ethyl)benzene (3av)[18]



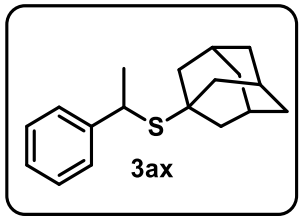
General procedure 2 was used to prepared compound **3av** from **1e** (51.5 mg, 0.15 mmol). Flash column chromatography was used to refine the crude product to get **3av** (22 mg, 80%) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1 , v/v. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.40 – 7.18 (m, 5H), 3.94 (q, *J* = 7.0 Hz, 1H), 2.39 – 2.22 (m, 2H), 1.56 (d, *J* = 7.3 Hz, 3H), 1.51 – 1.45 (m, 2H), 1.39 – 1.29 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 144.2, 128.4, 127.2, 126.9, 44.0, 31.4, 31.0, 22.6, 22.0, 13.7.

Synthesis of (1-(phenylthio)ethyl)benzene (3aw)[8]



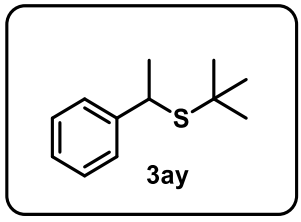
General procedure 2 was used to prepared compound **2ae** from **1e** (54.1 mg, 0.15 mmol). Flash column chromatography was used to refine the crude product to get **3aw** (27.17 mg, 84%) as a white solid, Rf = 0.75 (Hexane/EtOAc, 9:1 , v/v. **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.33 – 7.16 (m, 10H), 4.33 (q, *J* = 7.0 Hz, 1H), 1.63 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 143.3, 137.0, 135.2, 132.5, 128.7, 128.4, 127.3, 127.1, 48.0, 22.3.

Synthesis of (1-(adamantanylthio)ethyl)benzene (3ax)[19]



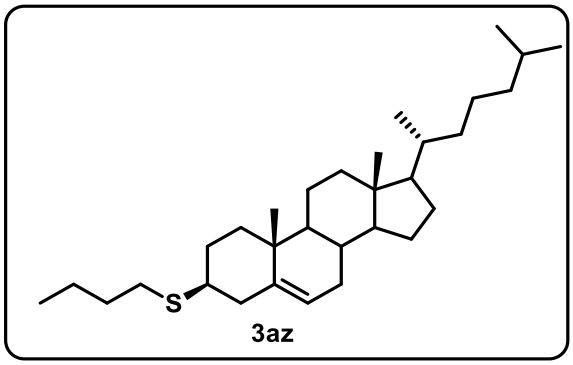
General procedure 2 was used to prepared compound **3ax** from **1e** (51.8 mg, 0.15 mmol). Flash column chromatography was used to refine the crude product to get **3ax** (32 mg, 81%) as a white solid, Rf = 0.8 (Hexane/EtOAc, 9:1 , v/v. **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.40 – 7.15 (m, 5H), 4.11 (q, *J* = 7.2 Hz, 1H), 2.02 – 1.94 (m, 3H), 1.86 – 1.73 (m, 6H), 1.63 (q, *J* = 12.2 Hz, 6H), 1.55 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, Chloroform-d)** δ 146.9, 128.4, 127.0, 126.5, 46.2, 43.9, 40.0, 36.3, 29.8, 25.8.

Synthesis of 1-(tert-butylthio)ethyl)benzene (3ay)[20]



General procedure 2 was used to prepared compound **3ay** from **1e** (53.2mg, 0.15 mmol). Flash column chromatography was used to refine the crude product to **3ay** (23.1 mg, 80%) as a colourless oil, Rf = 0.85 (Hexane/EtOAc, 9:1 , v/v. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.47 – 7.08 (m, 5H), 4.03 (q, *J* = 7.2 Hz, 1H), 1.56 (d, *J* = 7.2 Hz, 3H), 1.22 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 146.5, 128.4, 127.1, 126.6, 43.8, 42.4, 31.4, 25.4.

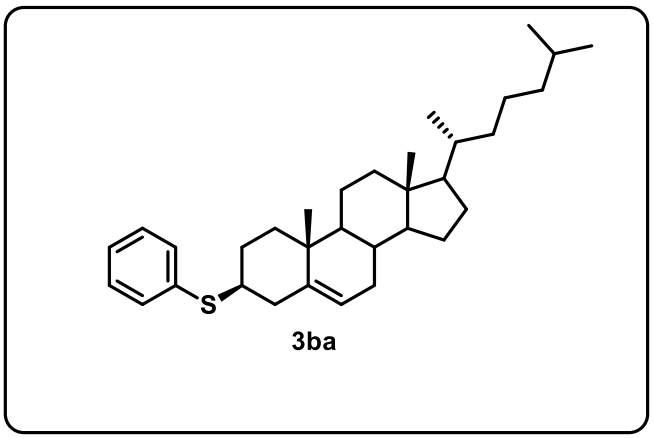
Synthesis of 3-(butylthio)-cholest-5-ene (3az)



3az

General procedure 2 was used to prepared compound **3az** from **1f** (51.5 mg, 0.1 mmol). Flash column chromatography was used to refine the crude product to get **3az** (32.4mg, 88%) as a colourless oil, Rf = 0.75 (Hexane/EtOAc, 9:1 , v/v. **^{1}H NMR (500 MHz, Chloroform-d)** δ 5.33 (d, *J* = 5.3 Hz, 1H), 2.55 (q, *J* = 6.2 Hz, 3H), 2.36 – 2.19 (m, 2H), 2.05 – 1.78 (m, 5H), 1.55 – 1.28 (m, 14H), 1.11 (dtd, *J* = 25.3, 10.5, 6.7 Hz, 8H), 1.00 (s, 6H), 0.91 (dt, *J* = 7.4, 4.1 Hz, 6H), 0.86 (dd, *J* = 6.6, 2.3 Hz, 6H), 0.68 (s, 3H).**^{13}C NMR (126 MHz, Chloroform-d)** δ 142.1, 120.8, 56.9, 56.2, 50.4, 44.5, 42.4, 40.2, 39.8, 39.7, 39.6, 37.0, 36.2, 35.8, 32.2, 32.0, 31.9, 29.9, 29.8, 28.3, 28.0, 24.3, 23.9, 22.8, 22.6, 22.1, 21, 19.4, 18.8, 13.7, 11.9. **HRMS (ESI)** calcd for $C_{31}H_{54}NaS$ $[M+Na]^+$ 481.3838 found 481.3817.

Synthesis of 1-(phenylthio)-cholest-5-ene (3ba)[21]

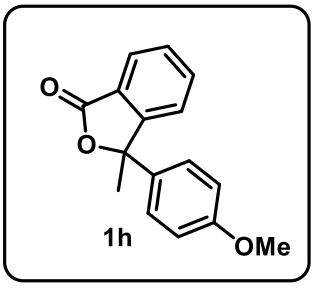


3ba

General procedure 2 was used to prepared compound **3ba** from **1f** (51.5 mg, 0.1 mmol). Flash column chromatography was used to refine the crude product to get **3ba** (32.4mg, 88%) as a white solid, Rf = 0.8 (Hexane/EtOAc, 9:1 , v/v). **^{1}H NMR (600 MHz, Chloroform-d)** δ 7.39

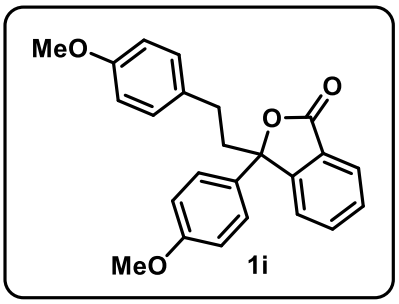
(d, *J* = 8.4 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 5.32 – 5.28 (m, 1H), 3.02 (dtd, *J* = 12.2, 8.2, 3.4 Hz, 1H), 2.31 (d, *J* = 8.1 Hz, 2H), 2.03 – 1.82 (m, 5H), 1.56 – 1.28 (m, 11H), 1.19 – 1.04 (m, 8H), 0.99 (s, 3H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.87 (d, *J* = 2.7 Hz, 3H), 0.86 (d, *J* = 2.6 Hz, 3H), 0.67 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-d)** δ 141.7, 134.9, 131.8, 128.8, 126.6, 121.2, 56.8, 56.2, 50.3, 47.4, 42.3, 39.8, 39.6, 39.5, 36.9, 36.2, 35.8, 31.9, 31.8, 29.5, 28.2, 28.0, 24.3, 23.8, 22.8, 22.6, 20.9, 19.4, 18.7, 11.9.

Synthesis of 3-(4-methoxyphenyl)-3-methylisobenzofuran-1-one (1h)[1]



Compound **1h** was islolated via flash column chromatography as a colourless oil. **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.83 (d, *J* = 7.7 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.29 – 7.23 (m, 2H), 6.82 – 6.76 (m, 2H), 3.71 (s, 3H), 1.95 (s, 3H).

Synthesis of 3-(4-methoxyphenethyl)-3-(4-methoxyphenyl)isobenzofuran-1-one (1i)



General procedure 2 was used to prepared compound **1i** from **1a** (52.8 mg, 0.14 mmol) without using any nucleophile. flash column chromatography was used to refine the crude product to get **1i** (24 mg, 45 %) as a colourless oil, Rf = 0.45 (Hexane/EtOAc, 9:1 , v/v). **^{1}H NMR (600 MHz, Chloroform-d)** δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.46 – 7.40 (m, 2H), 7.02 – 6.97 (m, 2H), 6.92 – 6.86 (m, 2H), 6.80 – 6.75 (m, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 2.73 (ddd, *J* = 14.1, 12.3, 4.3 Hz, 1H), 2.55 (td, *J* = 12.9, 4.3 Hz, 1H), 2.43 (ddd, *J* = 14.1, 12.1, 4.5 Hz, 1H), 2.34 (td, *J* = 12.9, 4.5 Hz, 1H). **^{13}C NMR (151 MHz, Chloroform-d)** δ 170.2, 159.4, 157.9, 153.0, 134.3, 133.0, 132.2, 129.2, 129.1, 126.4,

126.0, 125.5, 122.1, 114.1, 113.9, 89.8, 55.3, 55.3, 42.4, 29.2. **HRMS (ESI)** calcd for $C_{24}H_{23}O_4$ $[M+H]^+$ 375.1591 found 375.1589.

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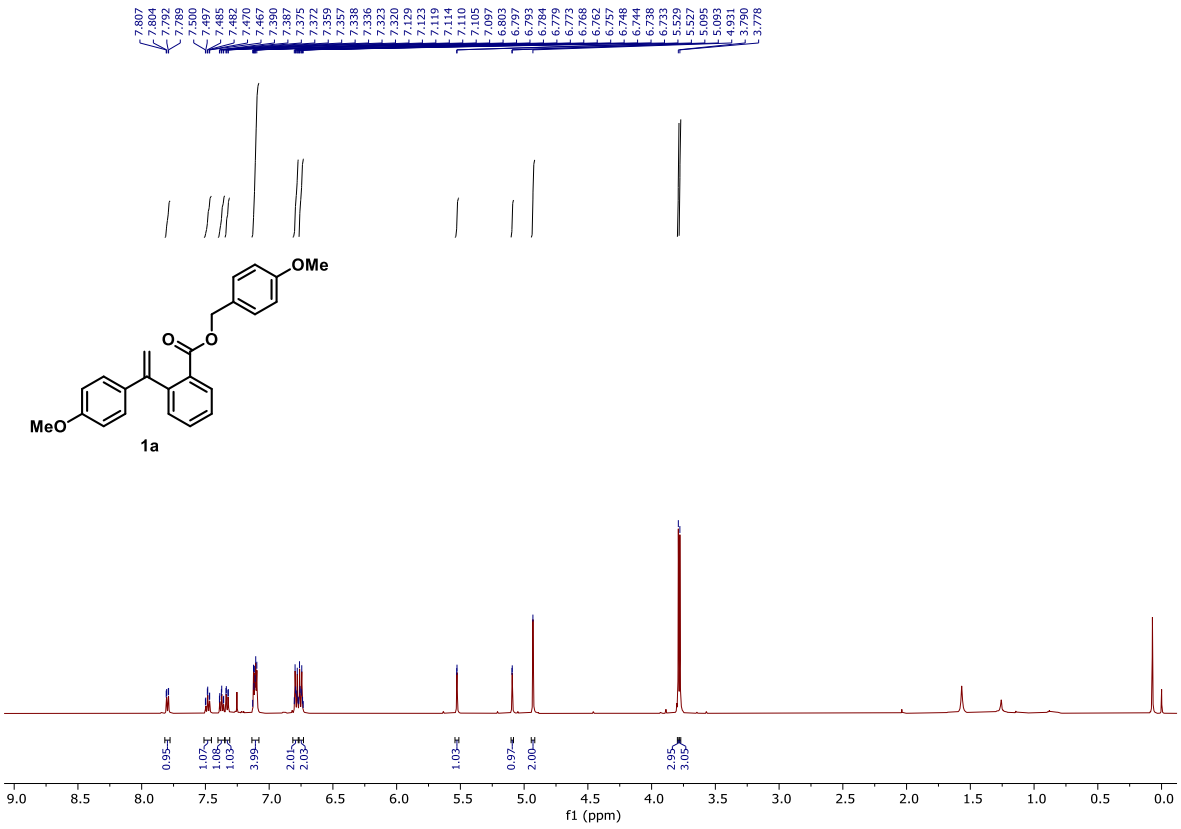
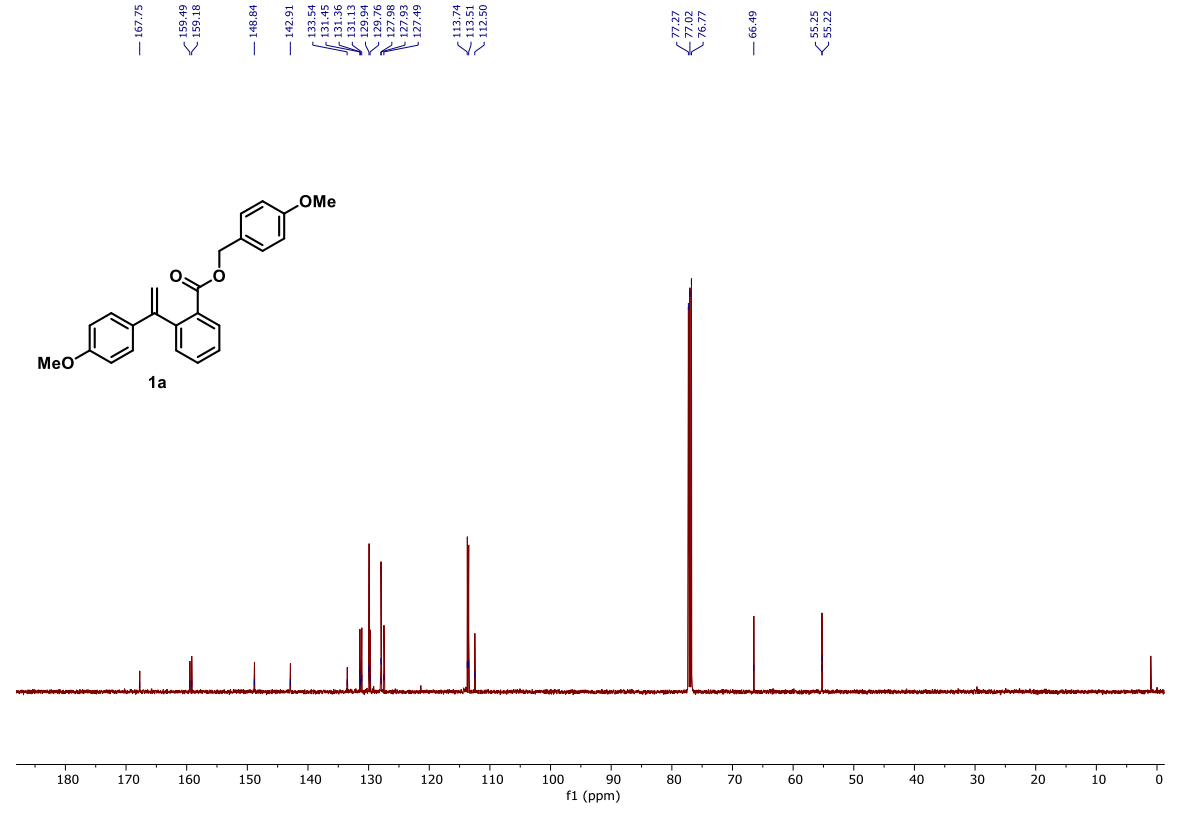
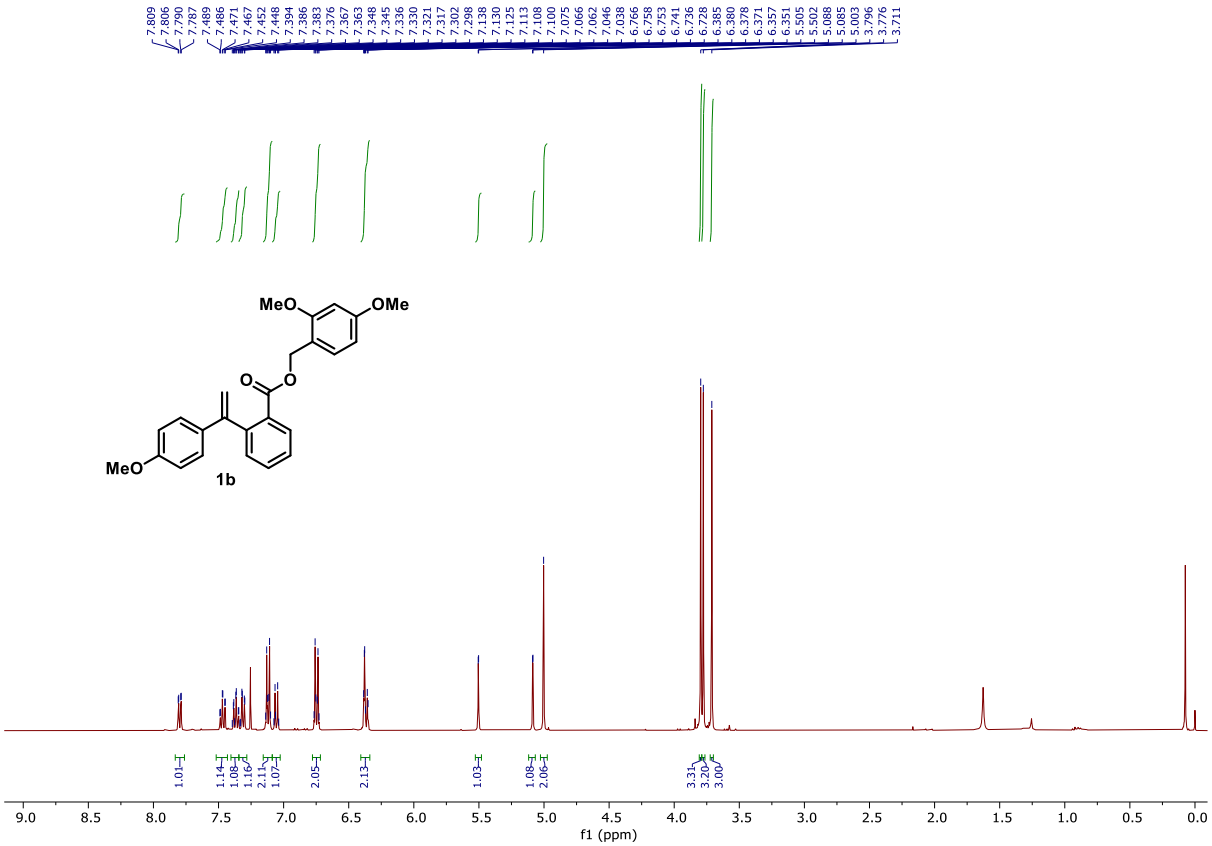
Spectra of Substrates



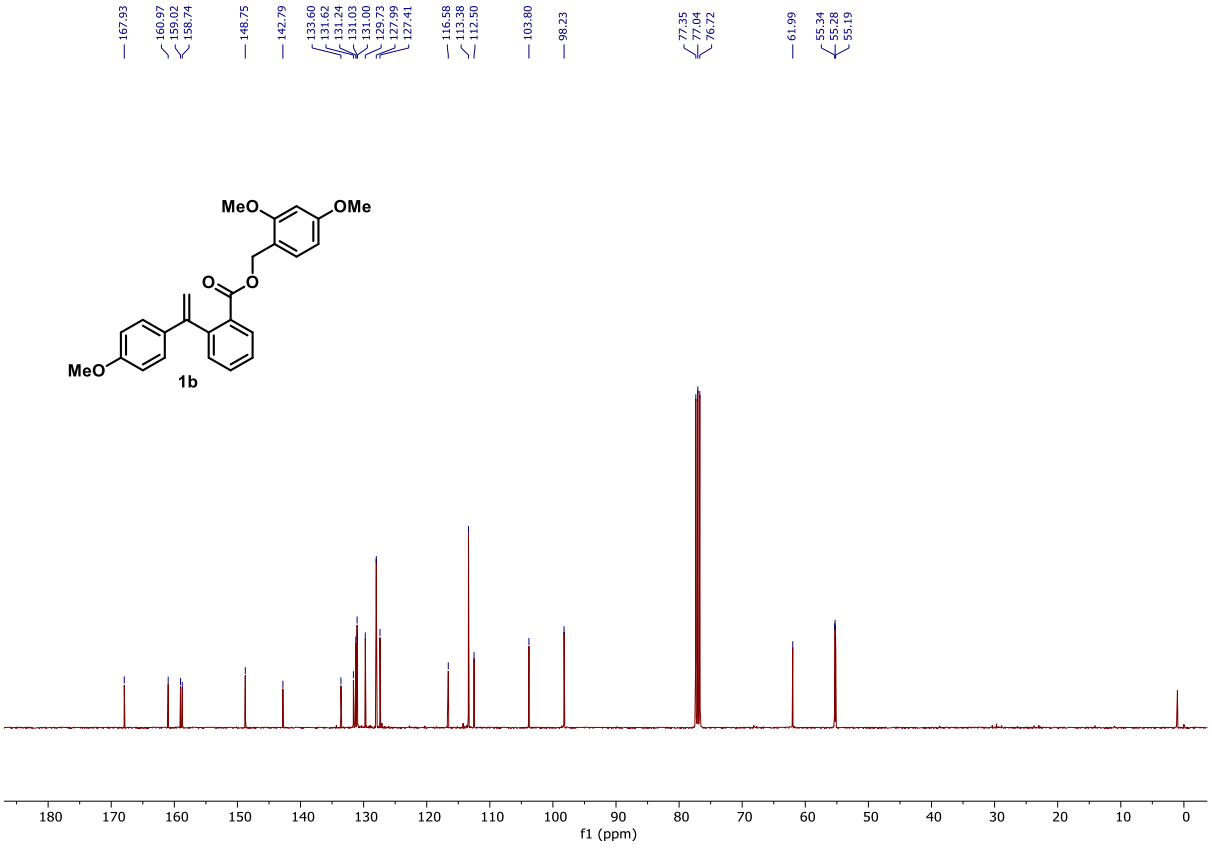
^{1}H NMR spectrum of compound 1a (500 MHz $CDCl_3$)



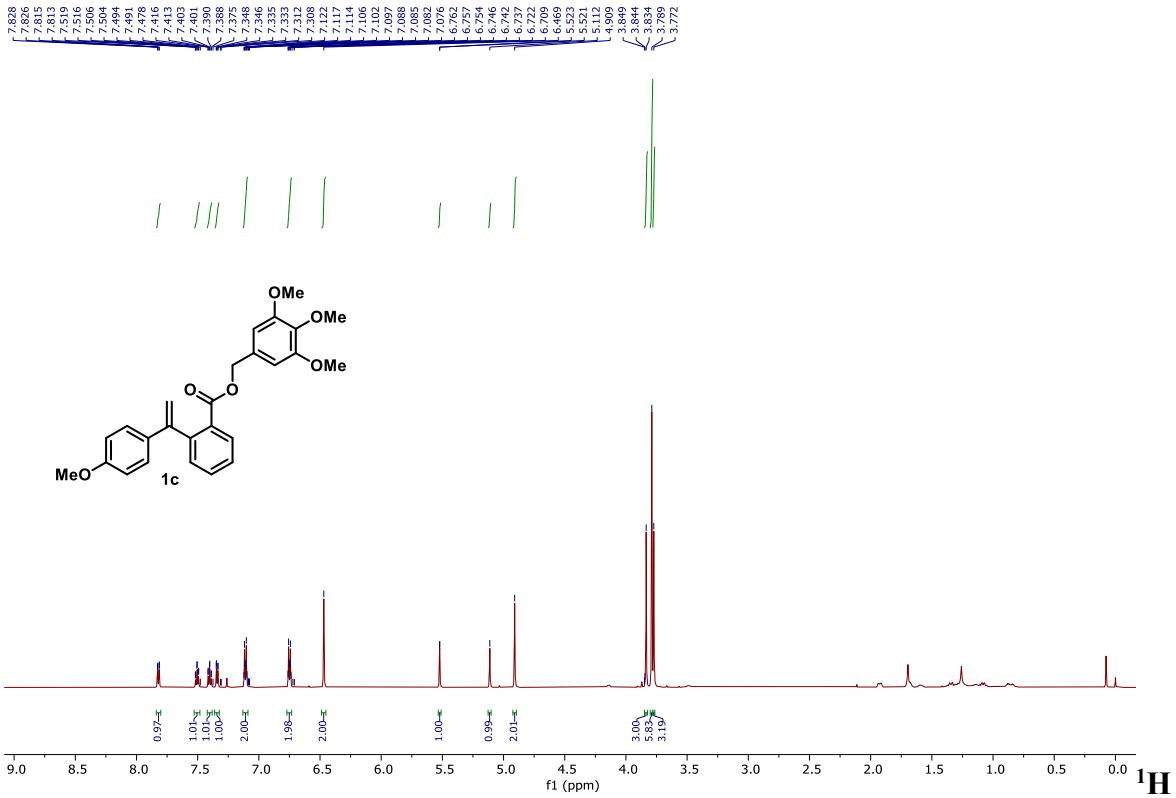
^{13}C NMR spectrum of compound 1a (126 MHz $CDCl_3$)



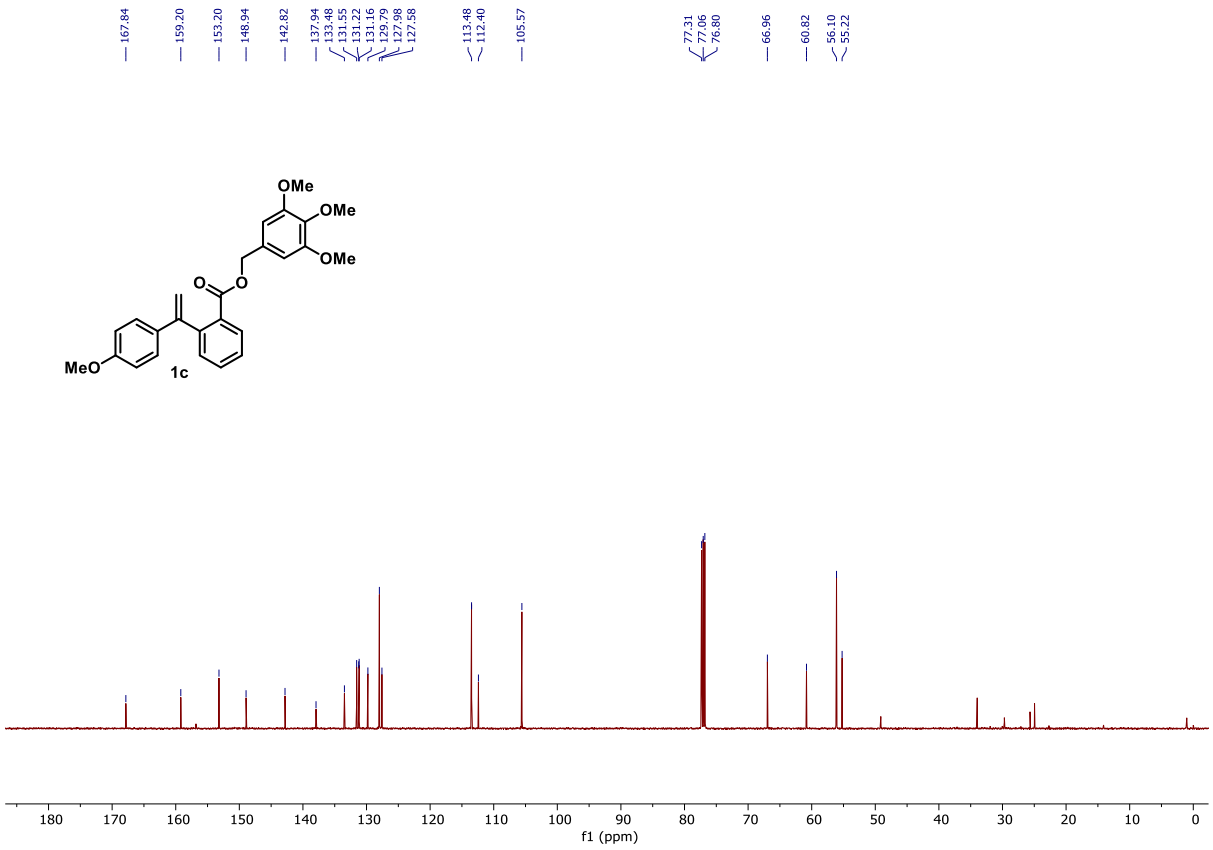
^{1}H NMR spectrum of compound 1b (400 MHz $CDCl_3$)



^{13}C NMR spectrum of compound 1a (101 MHz $CDCl_3$)



^{1}H NMR spectrum of compound 1c (600 MHz $CDCl_3$)



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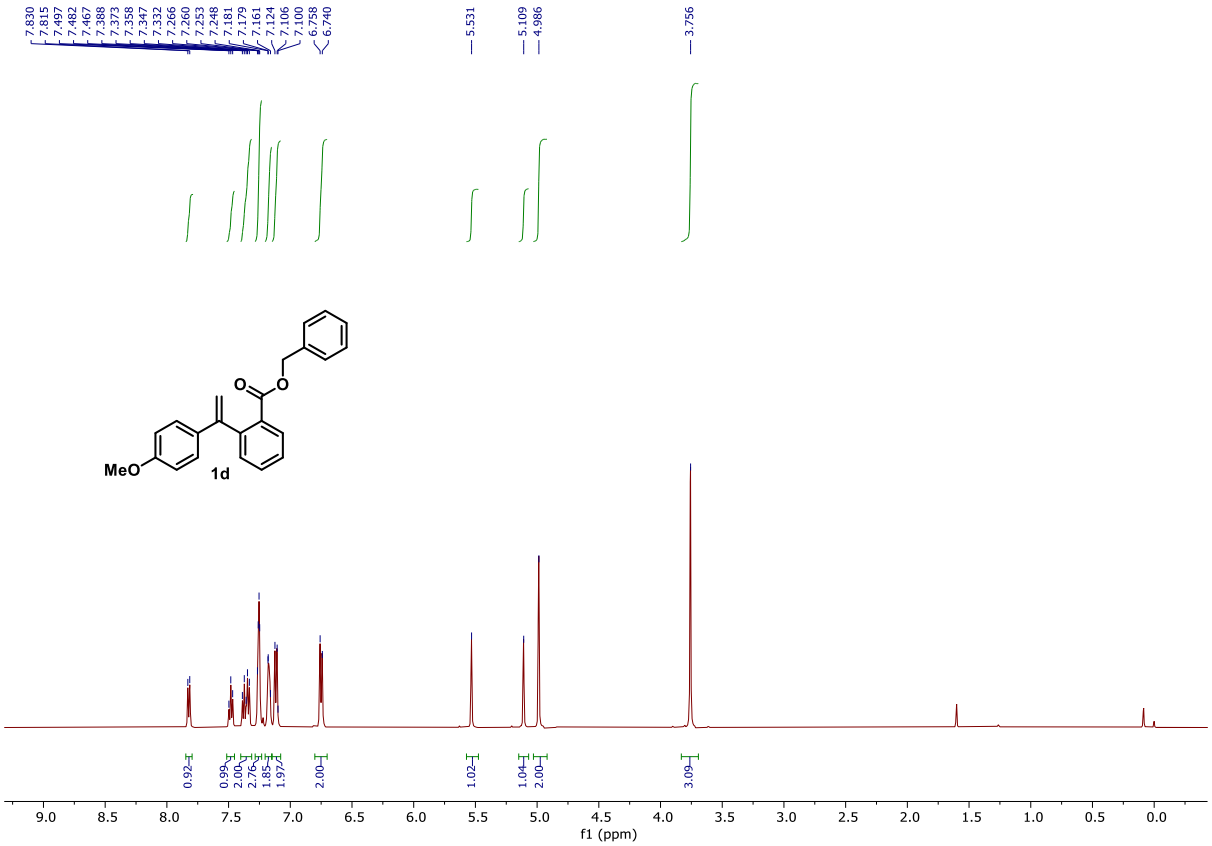

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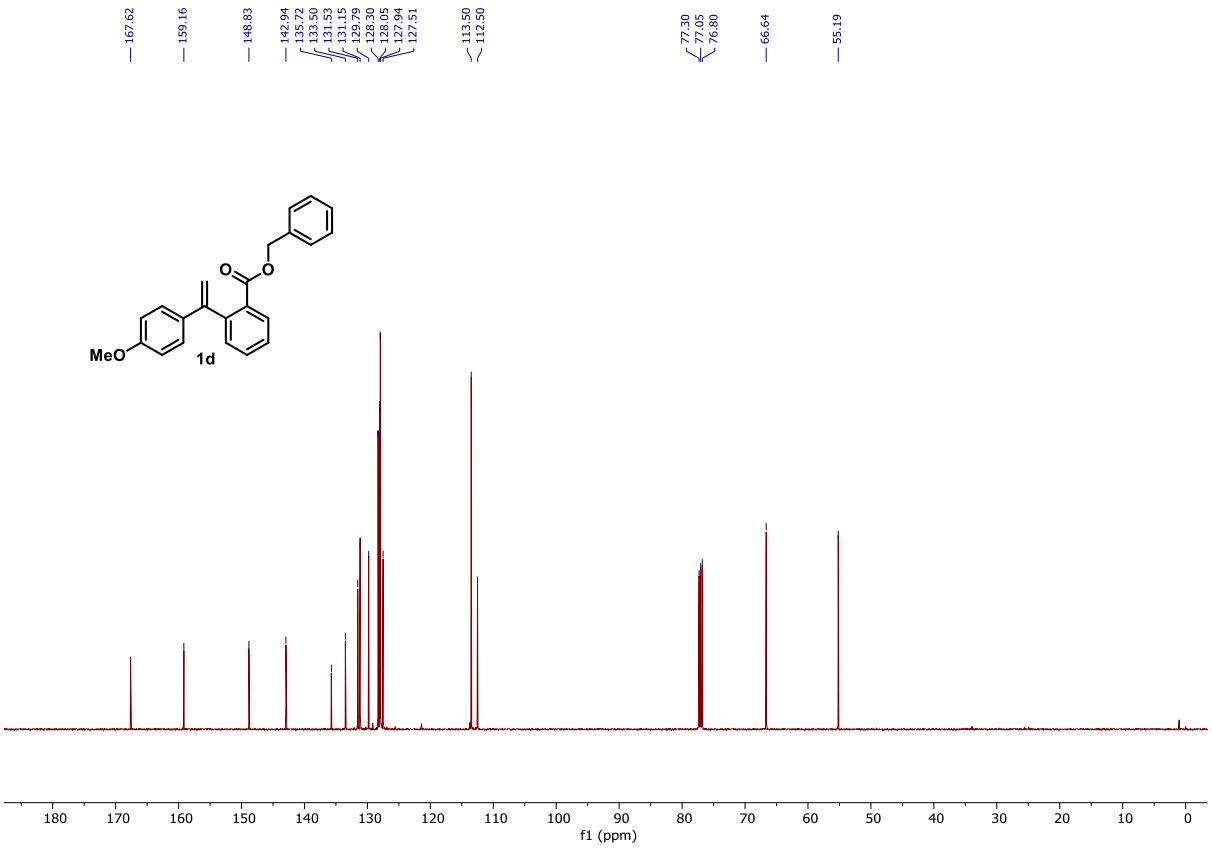

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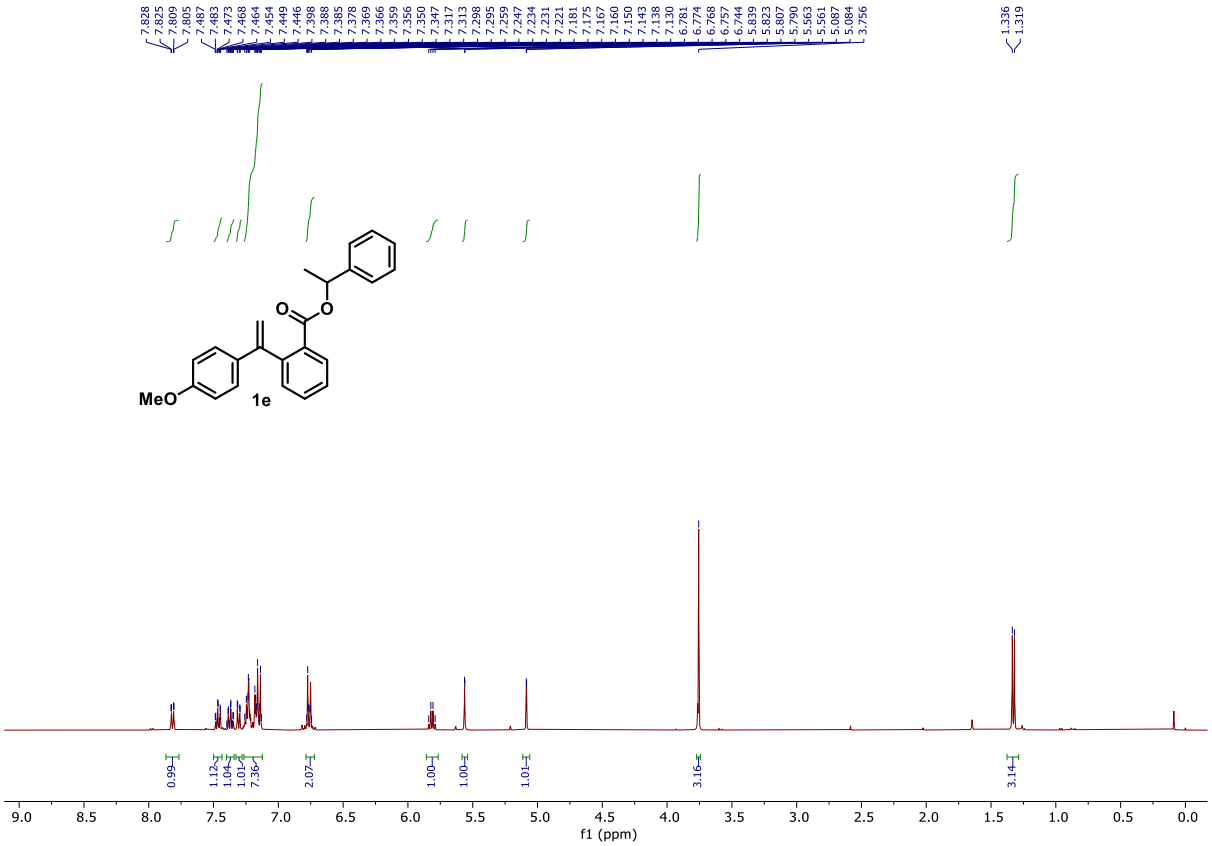

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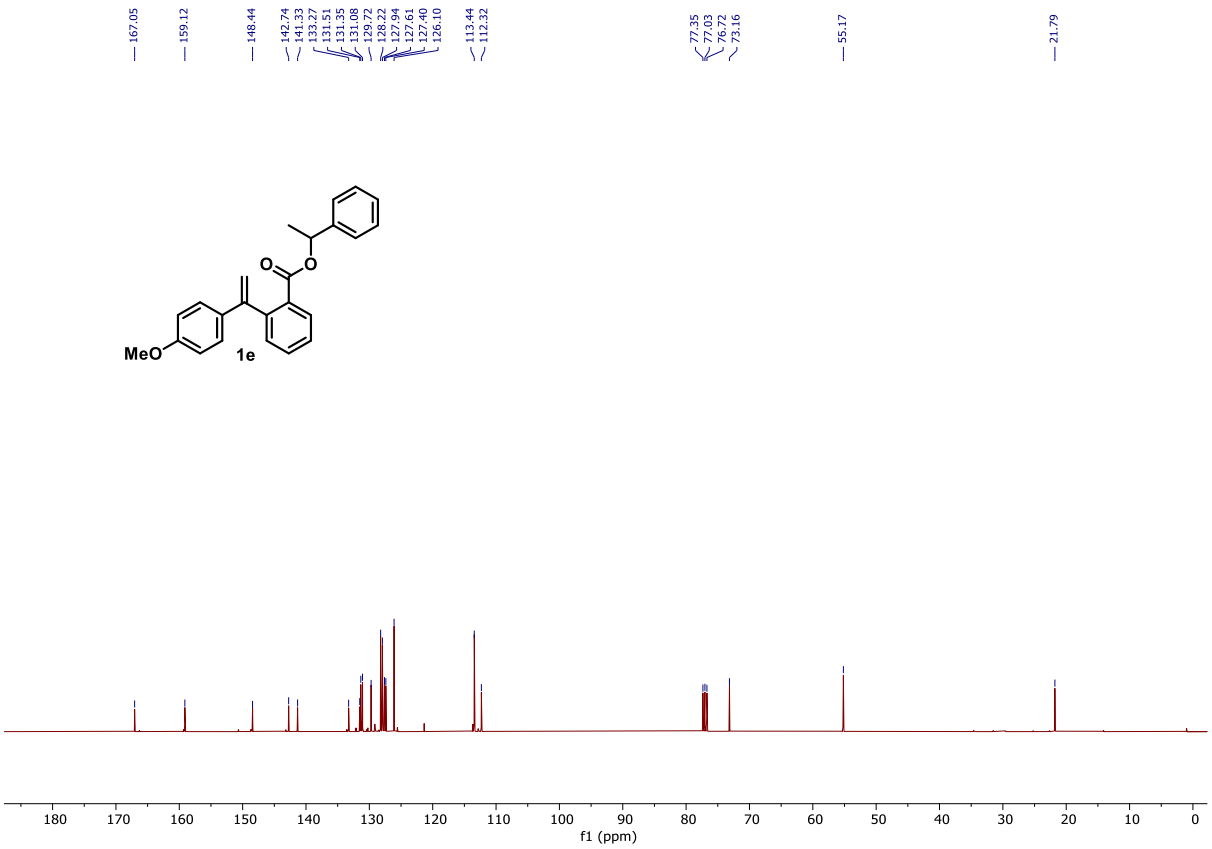

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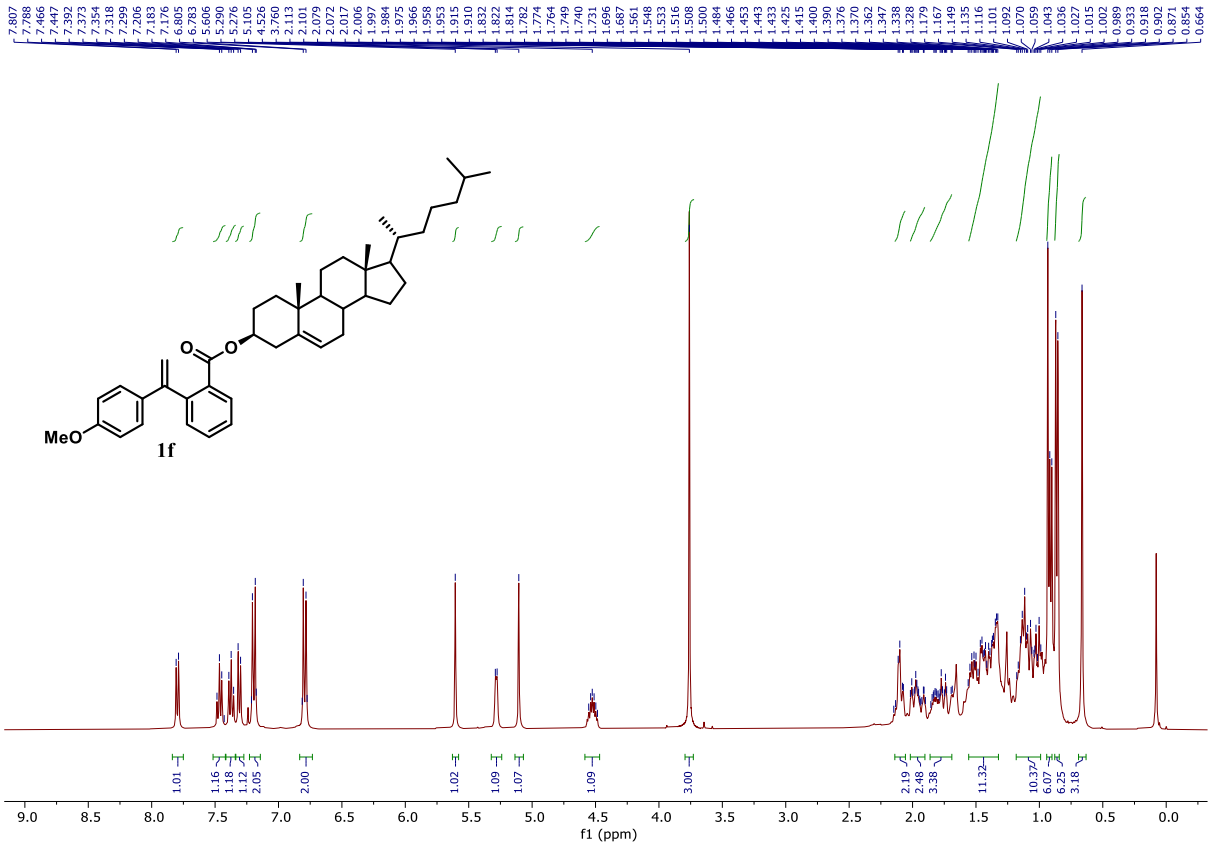
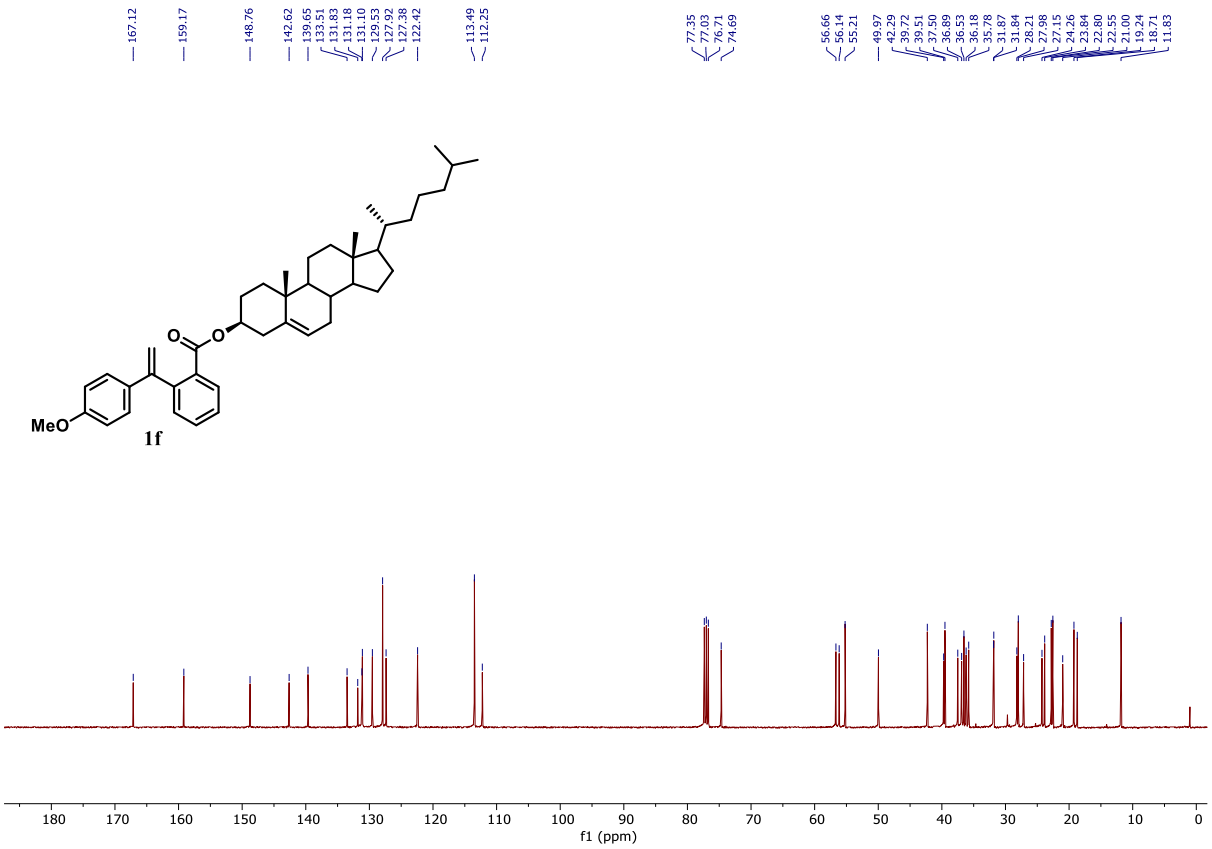


^{1}H NMR spectrum of compound 1f (400 MHz $CDCl_3$)



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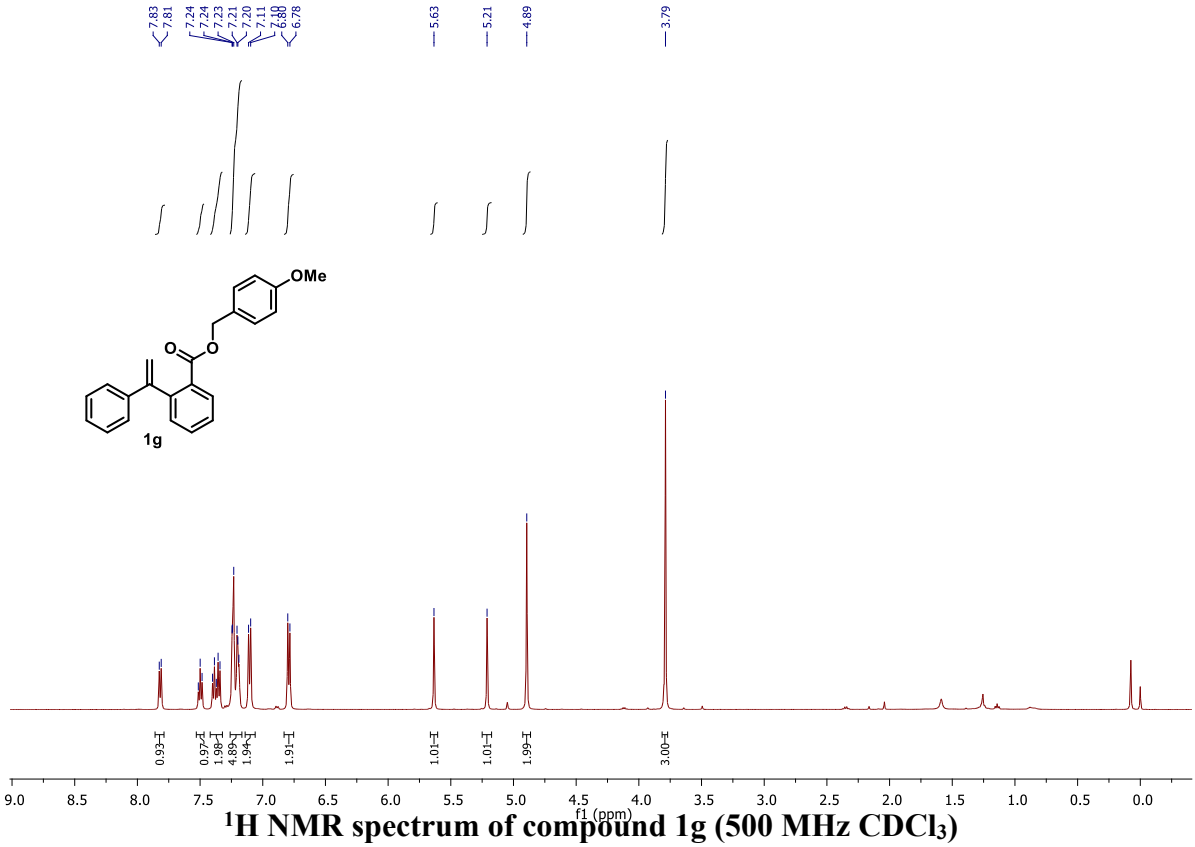

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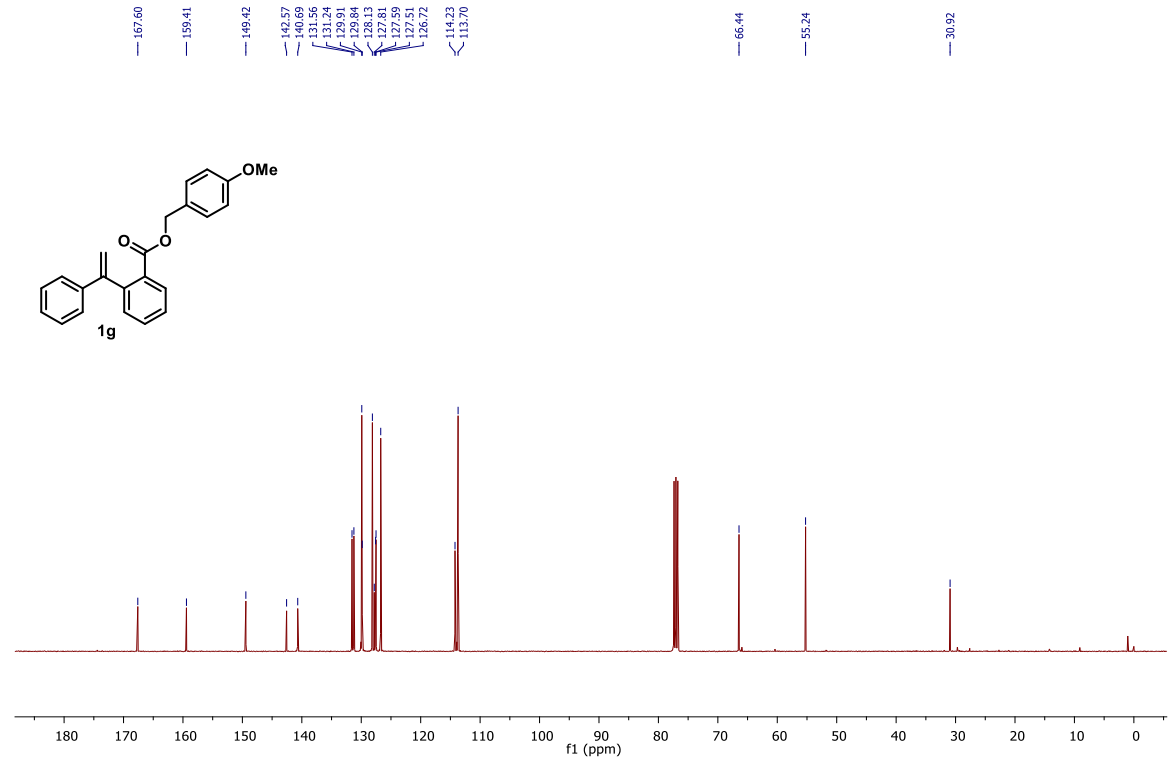
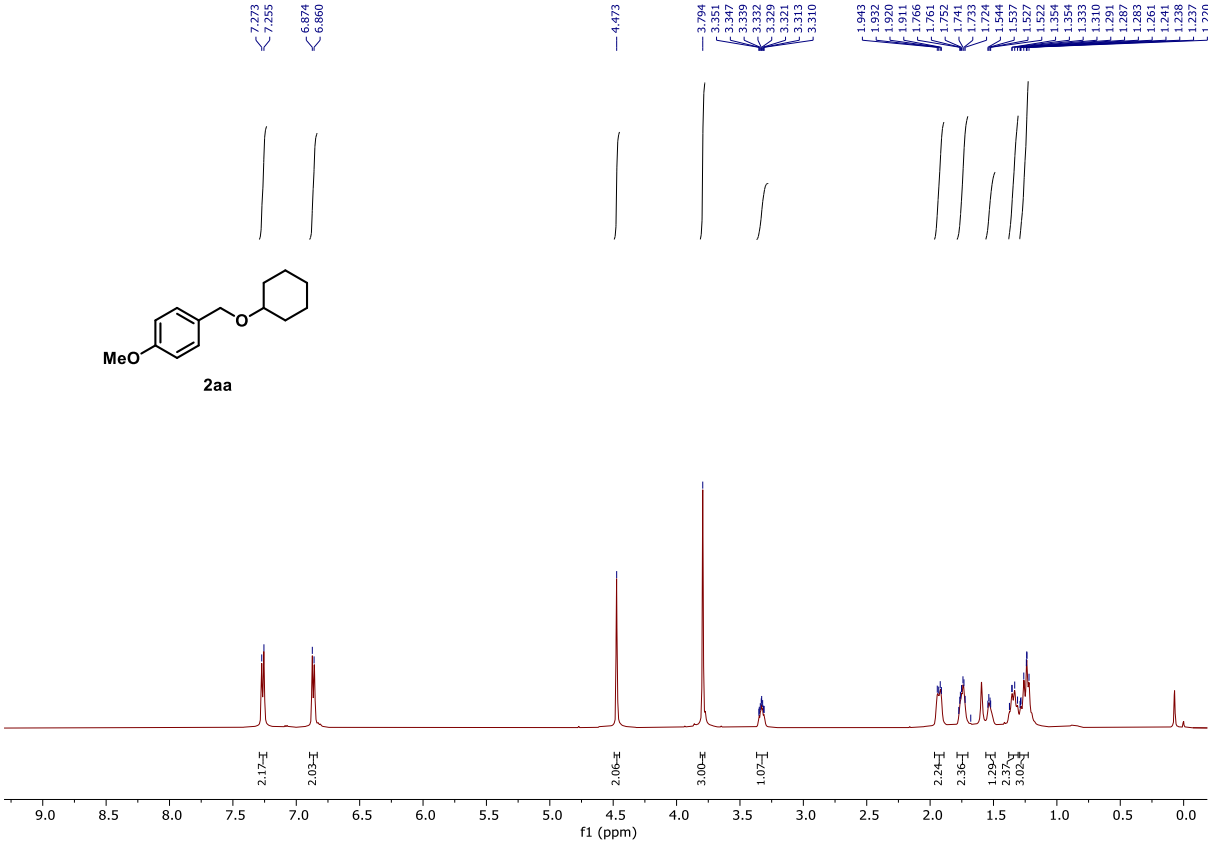


^{13}C NMR spectrum of compound 1g (126 MHz $CDCl_3$)



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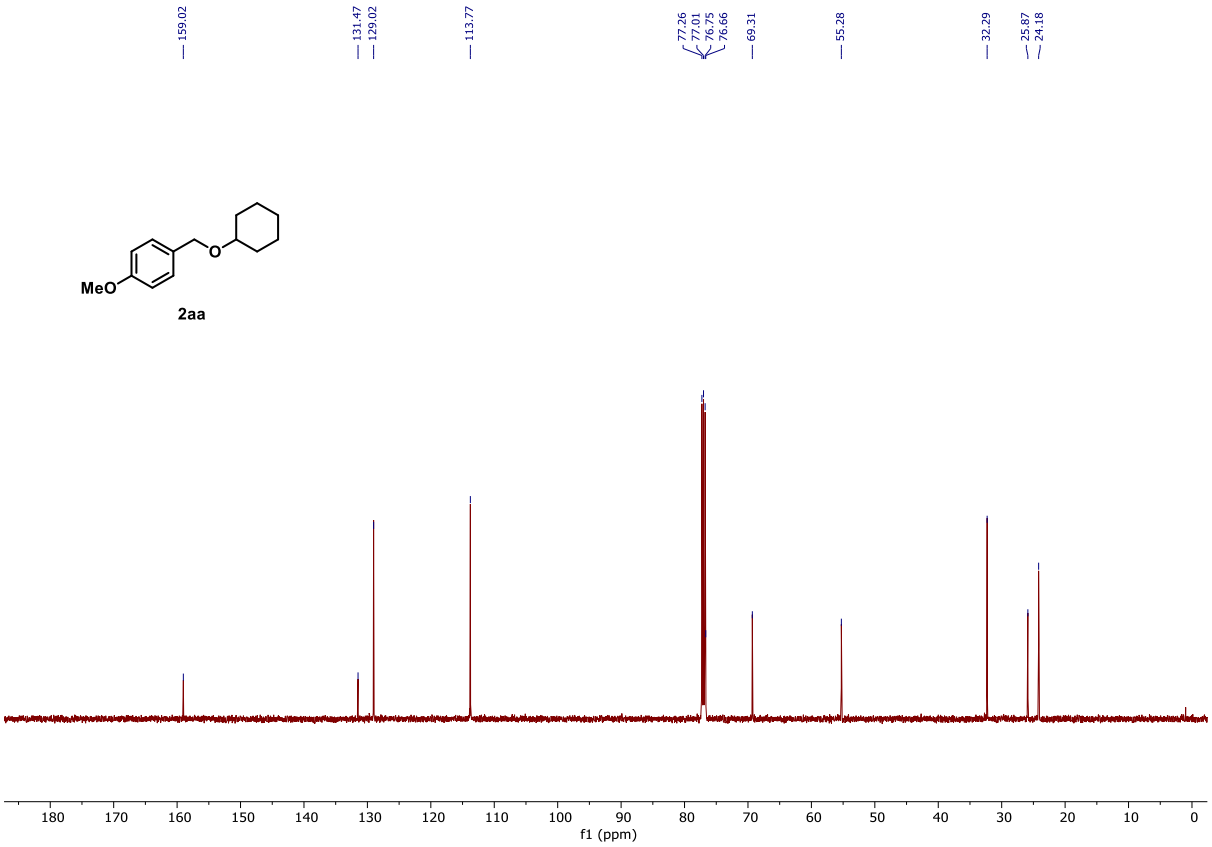
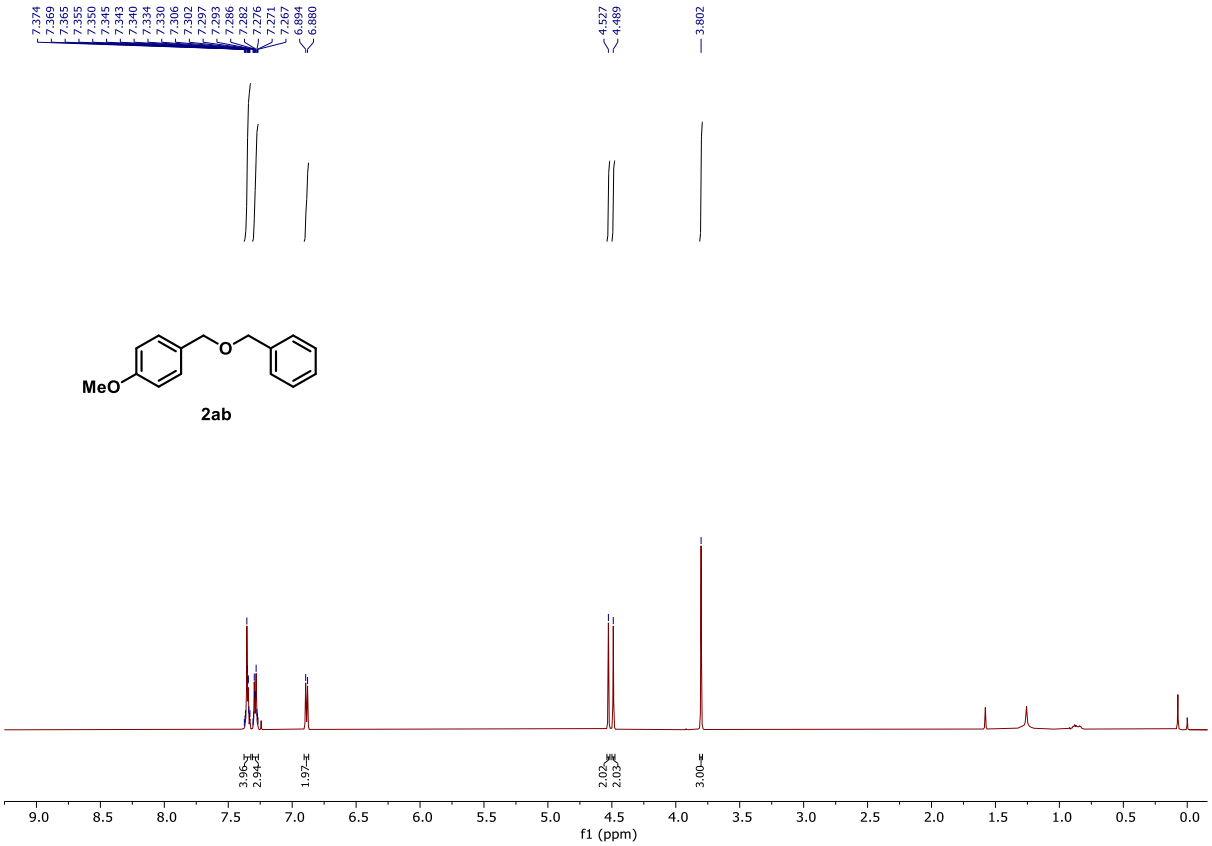


^{13}C NMR spectrum of compound 2aa (126 MHz $CDCl_3$)



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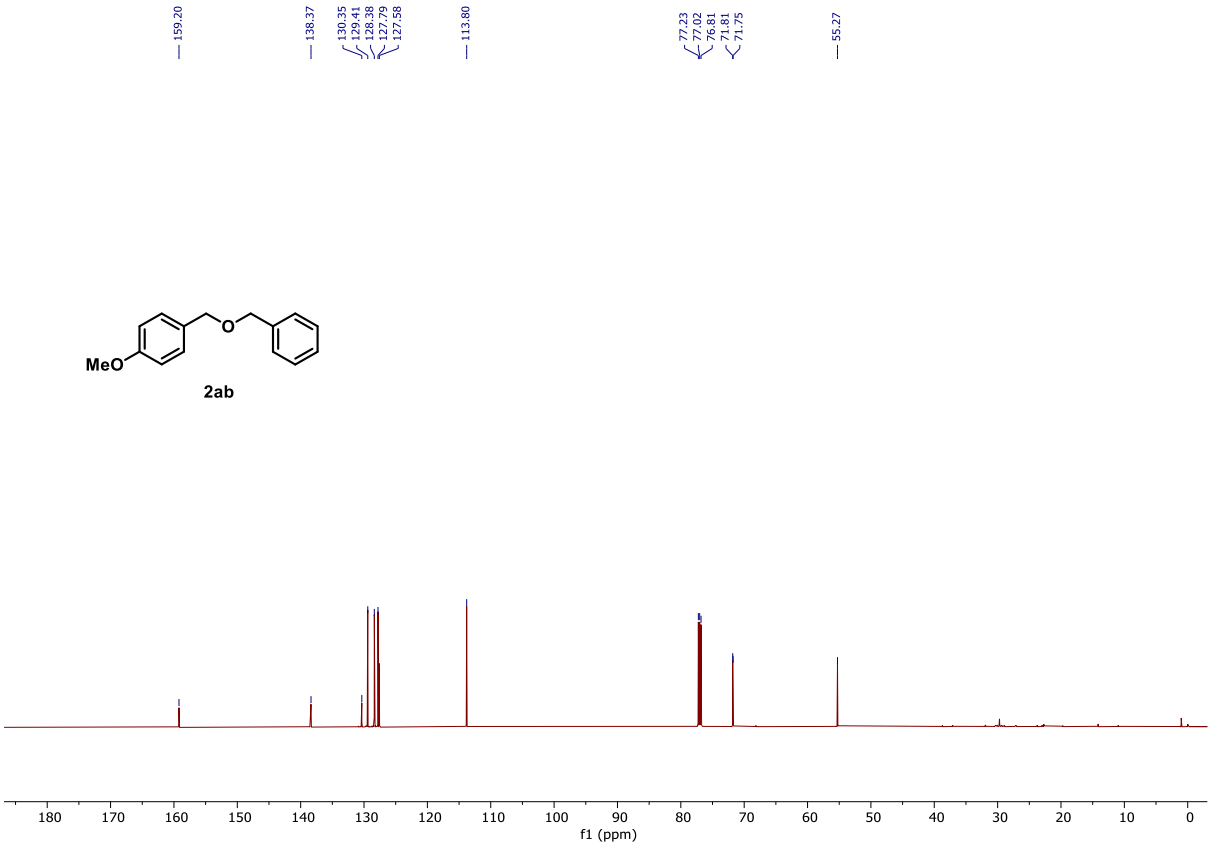

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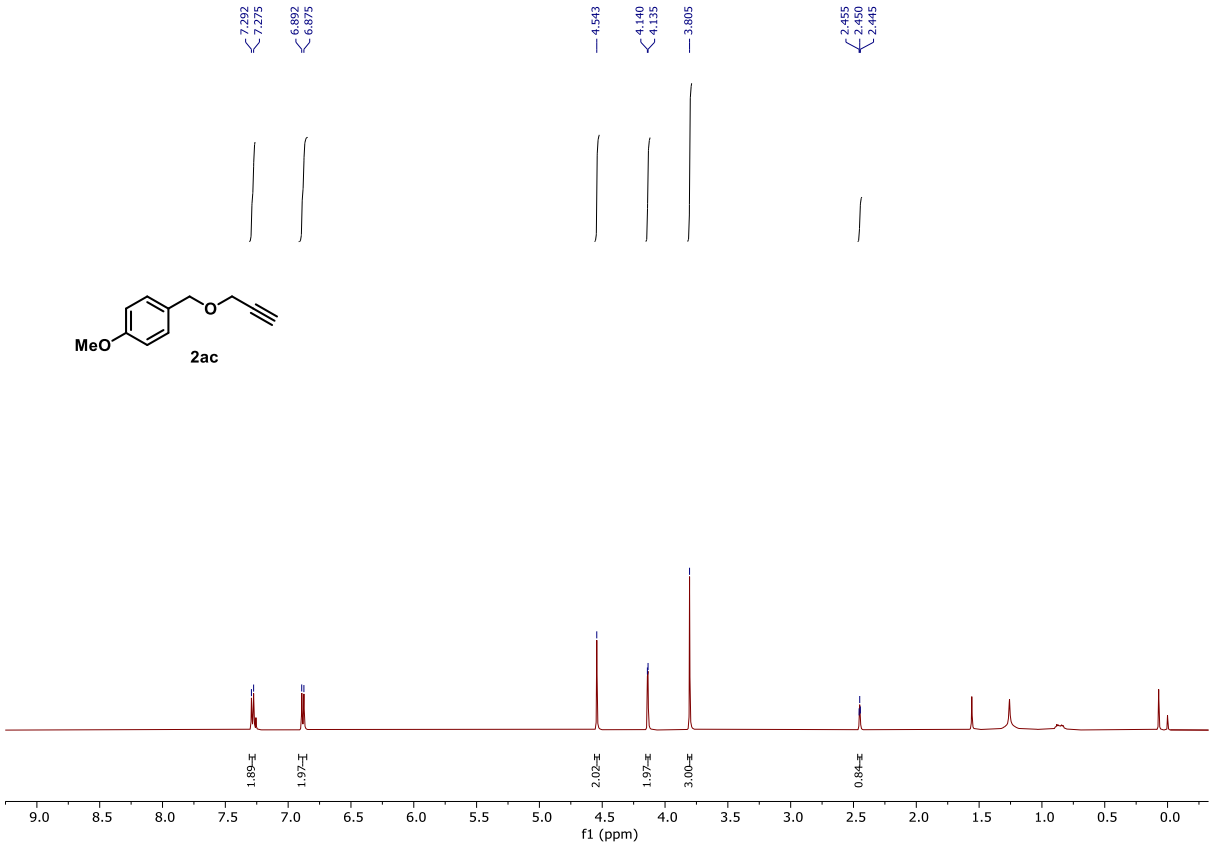

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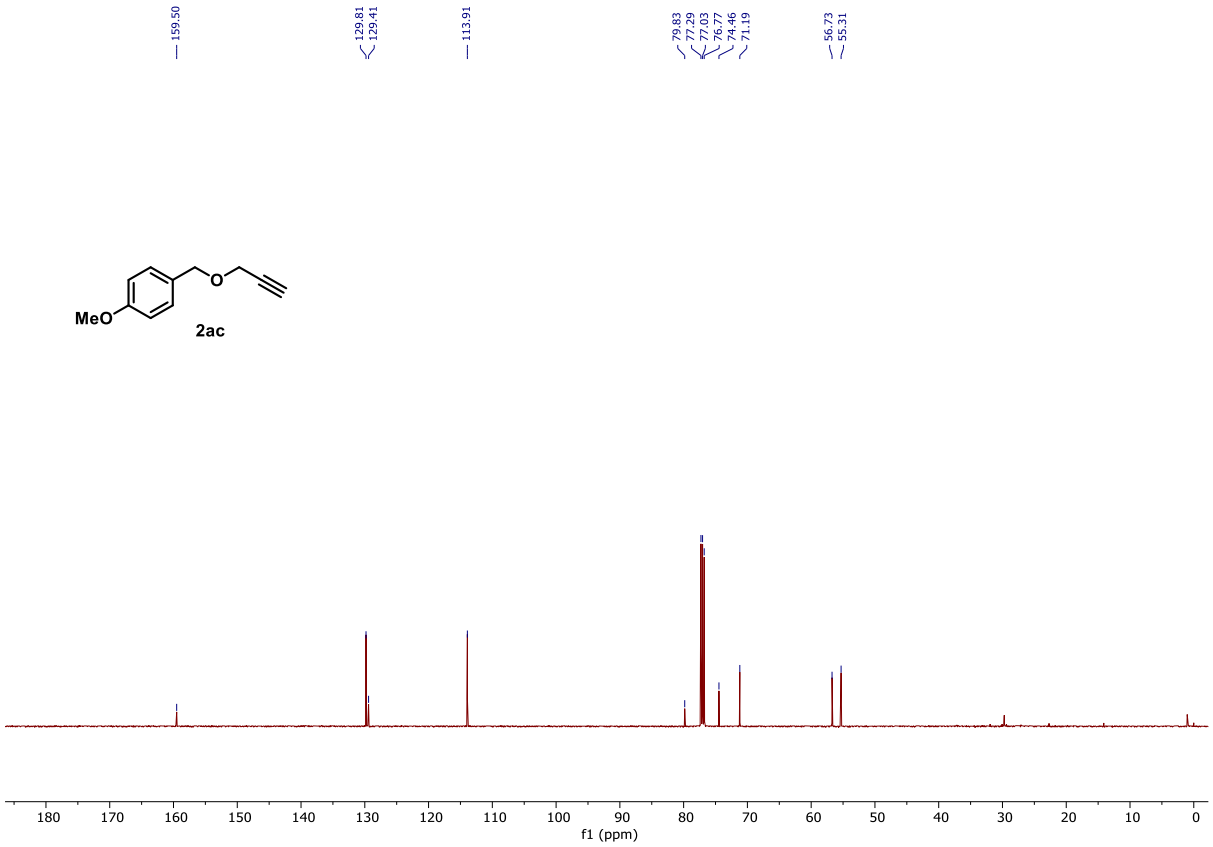

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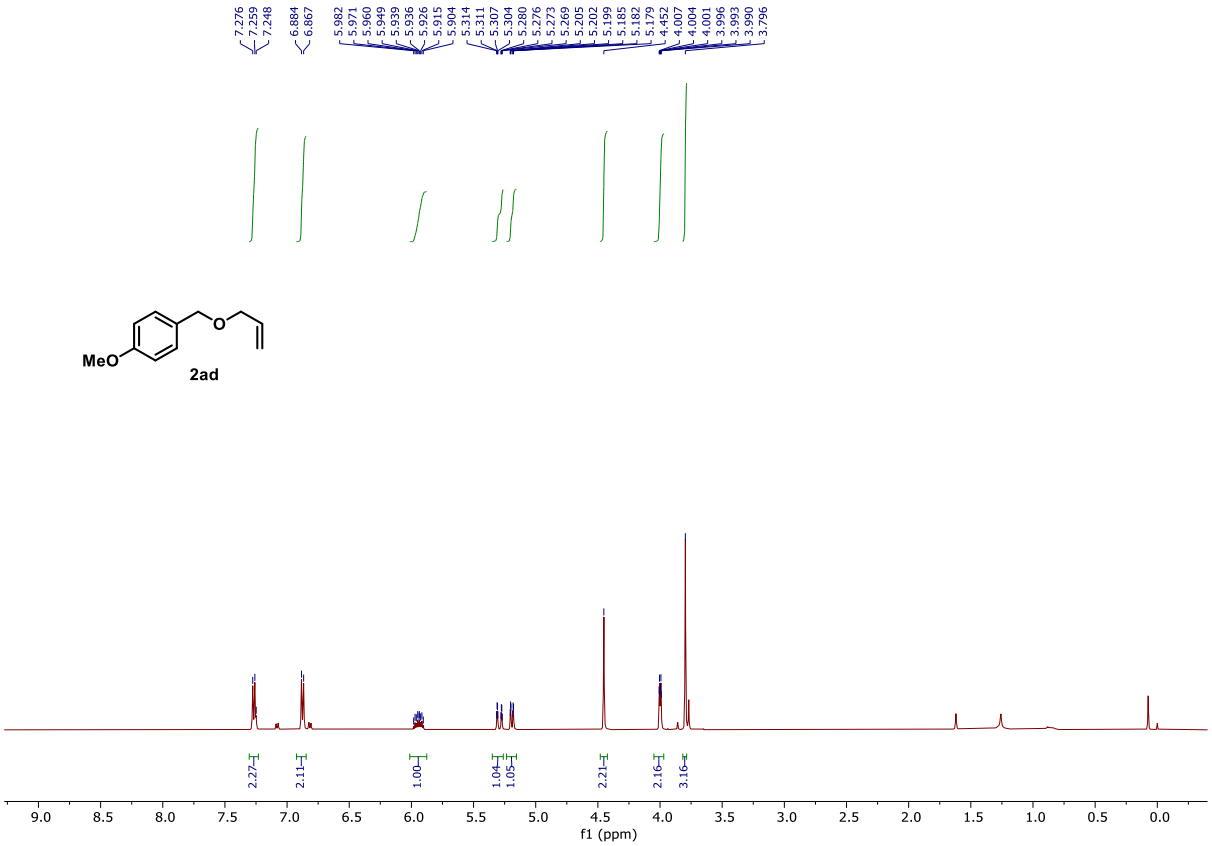

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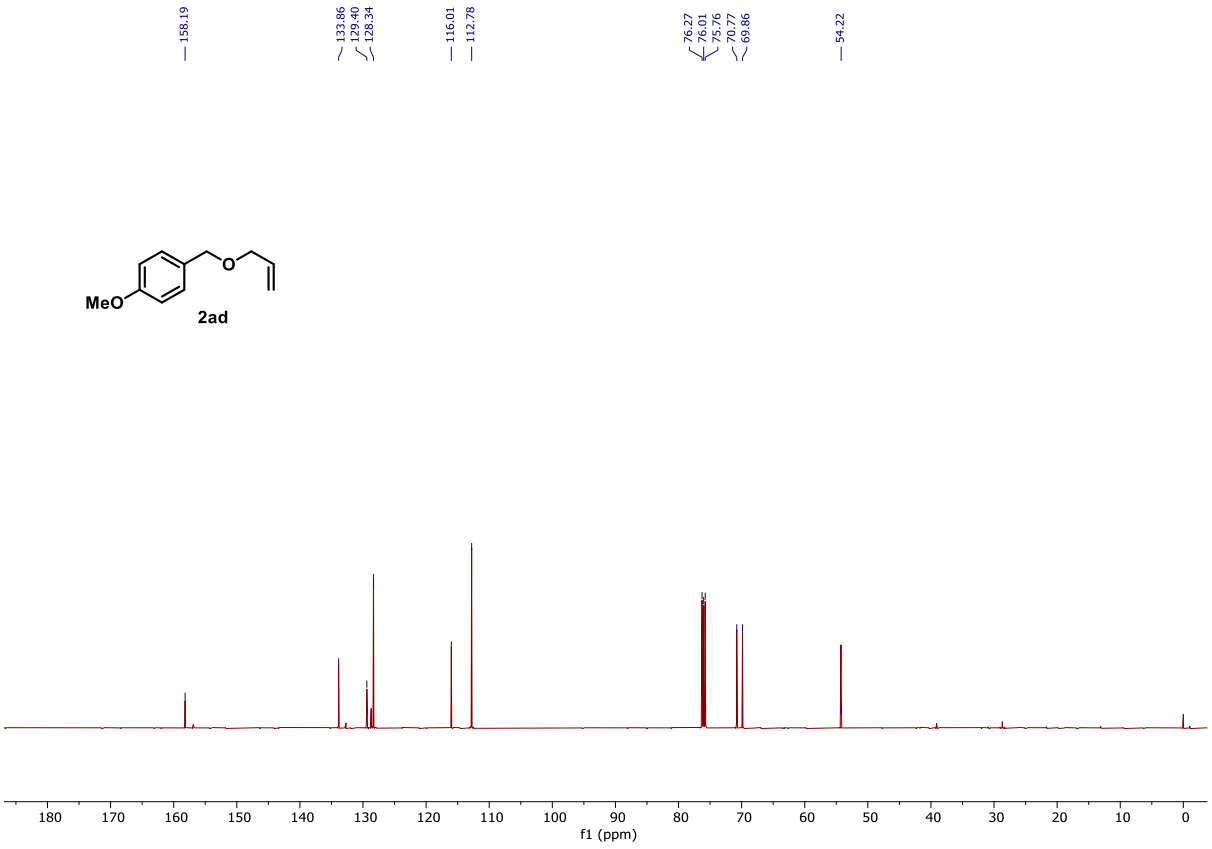

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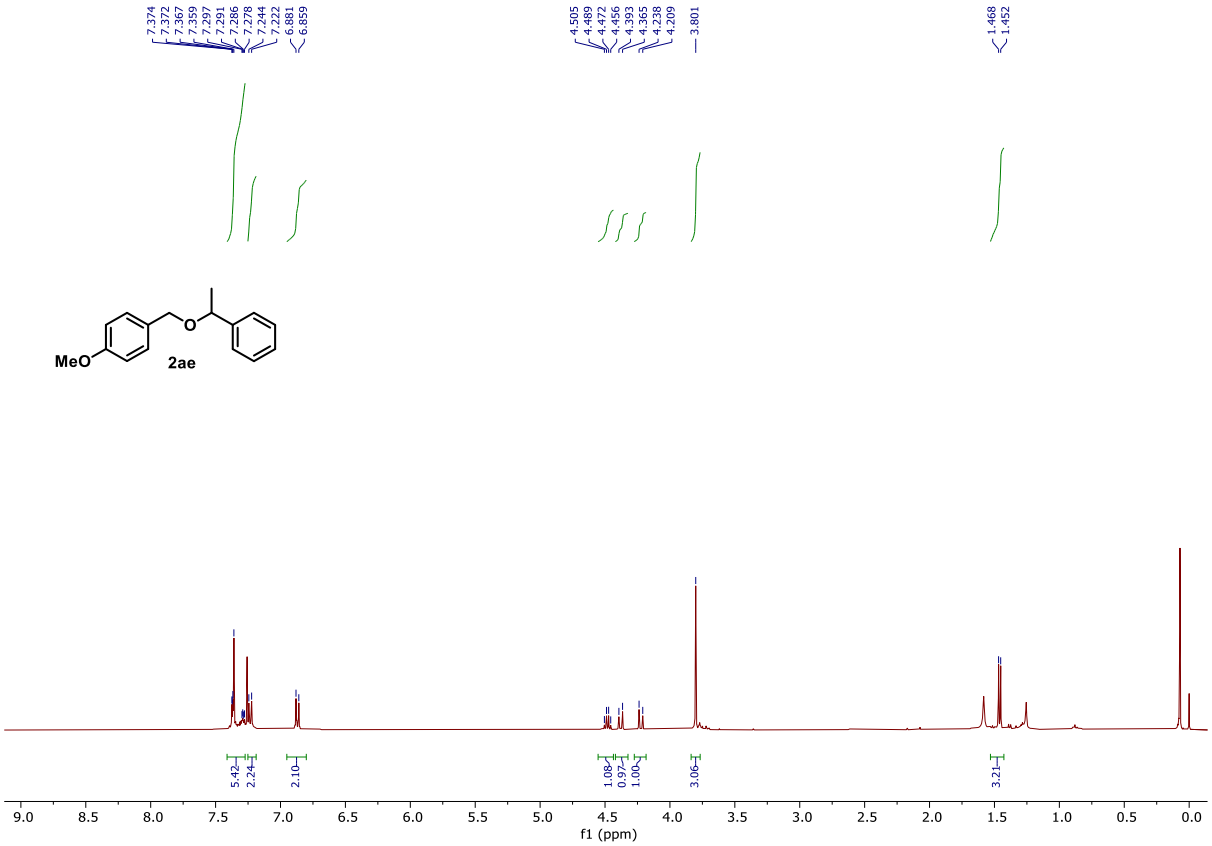

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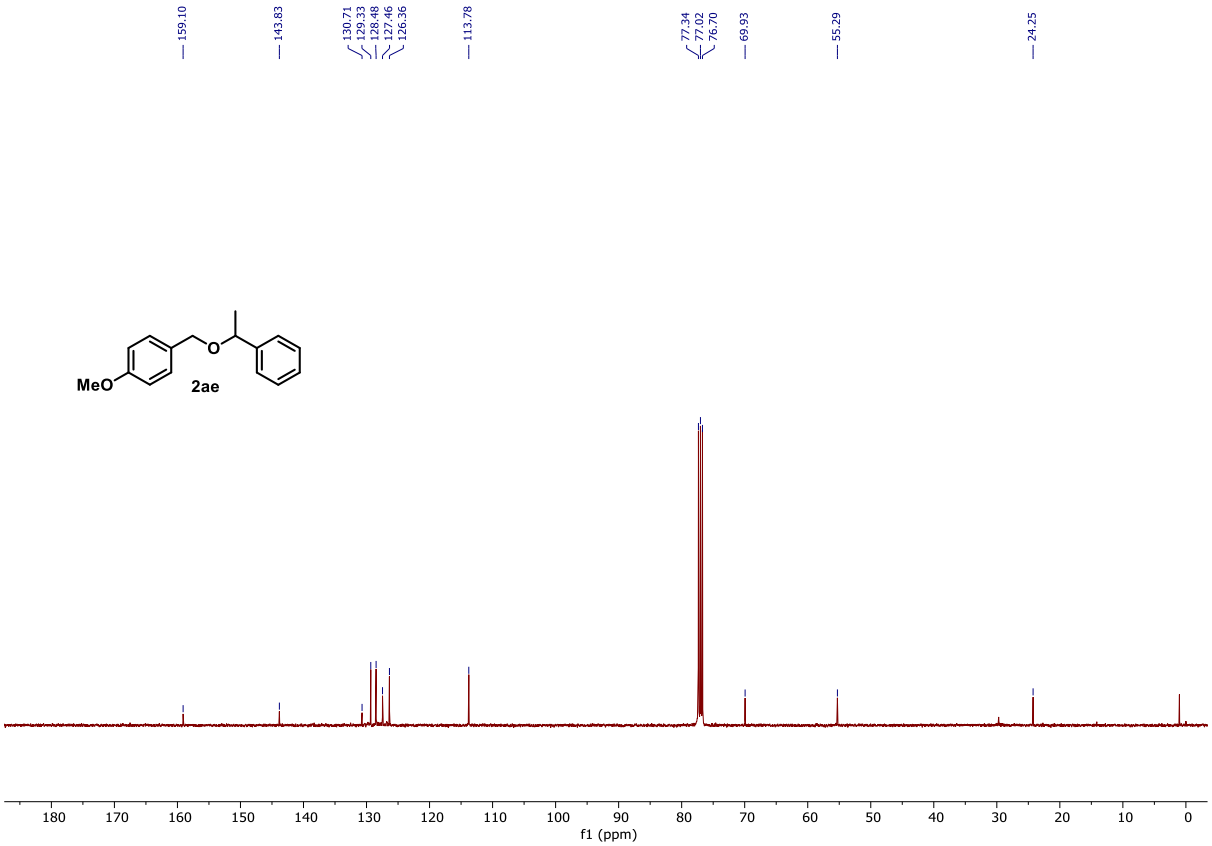
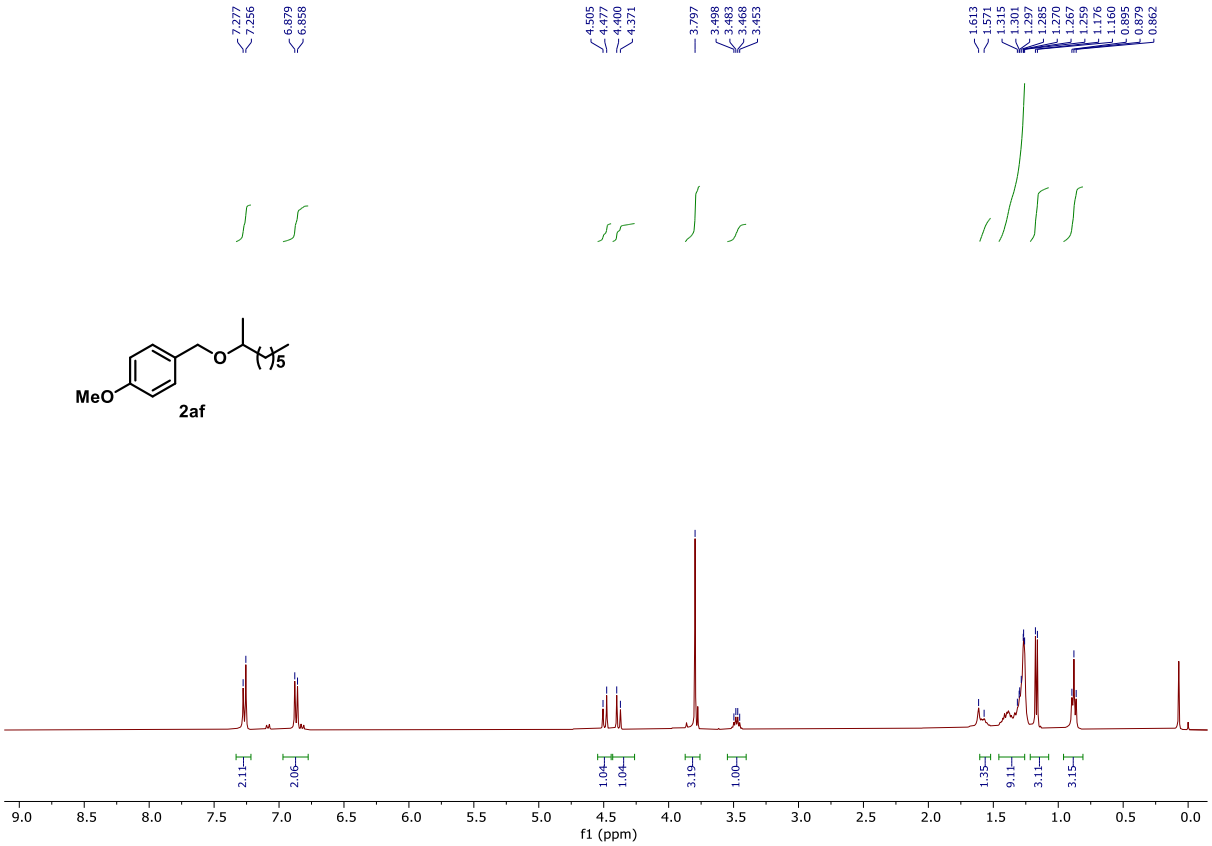


^{13}C NMR spectrum of compound 2ae (101 MHz $CDCl_3$)



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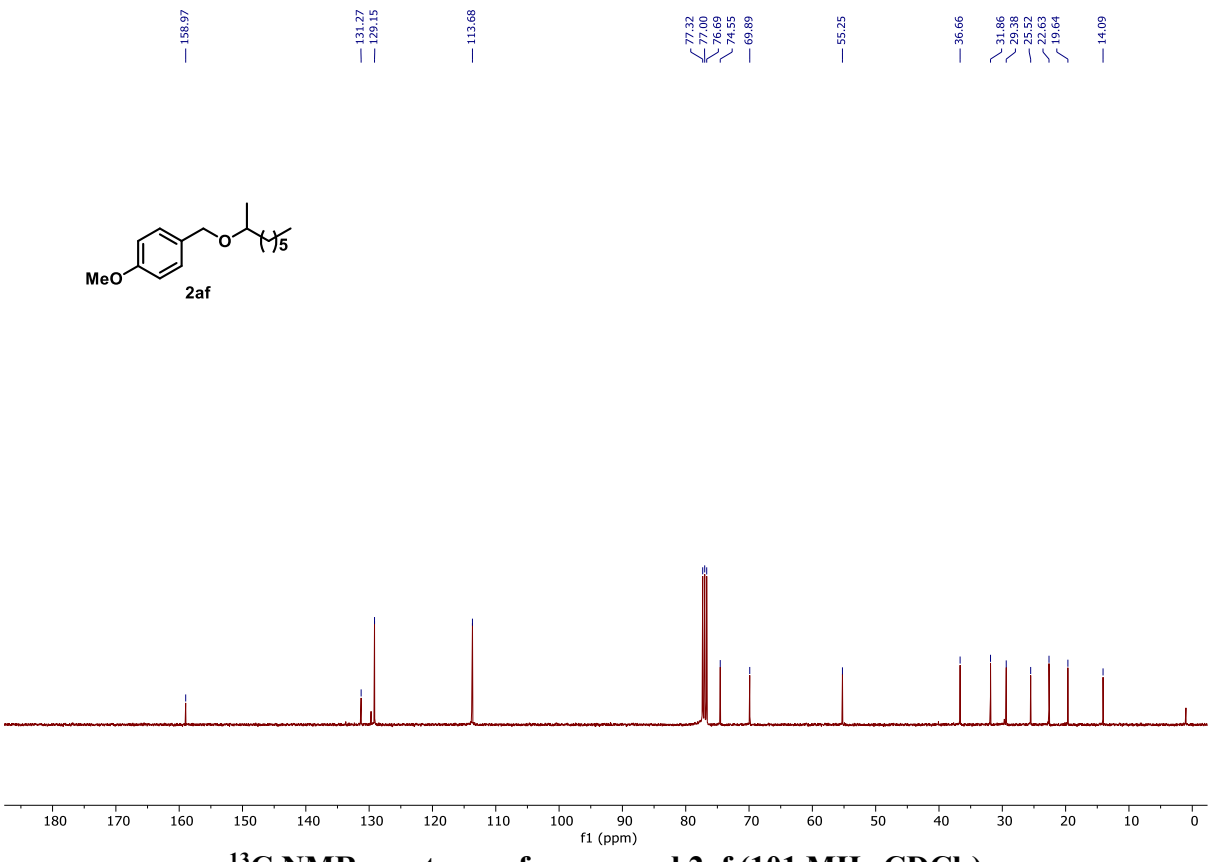

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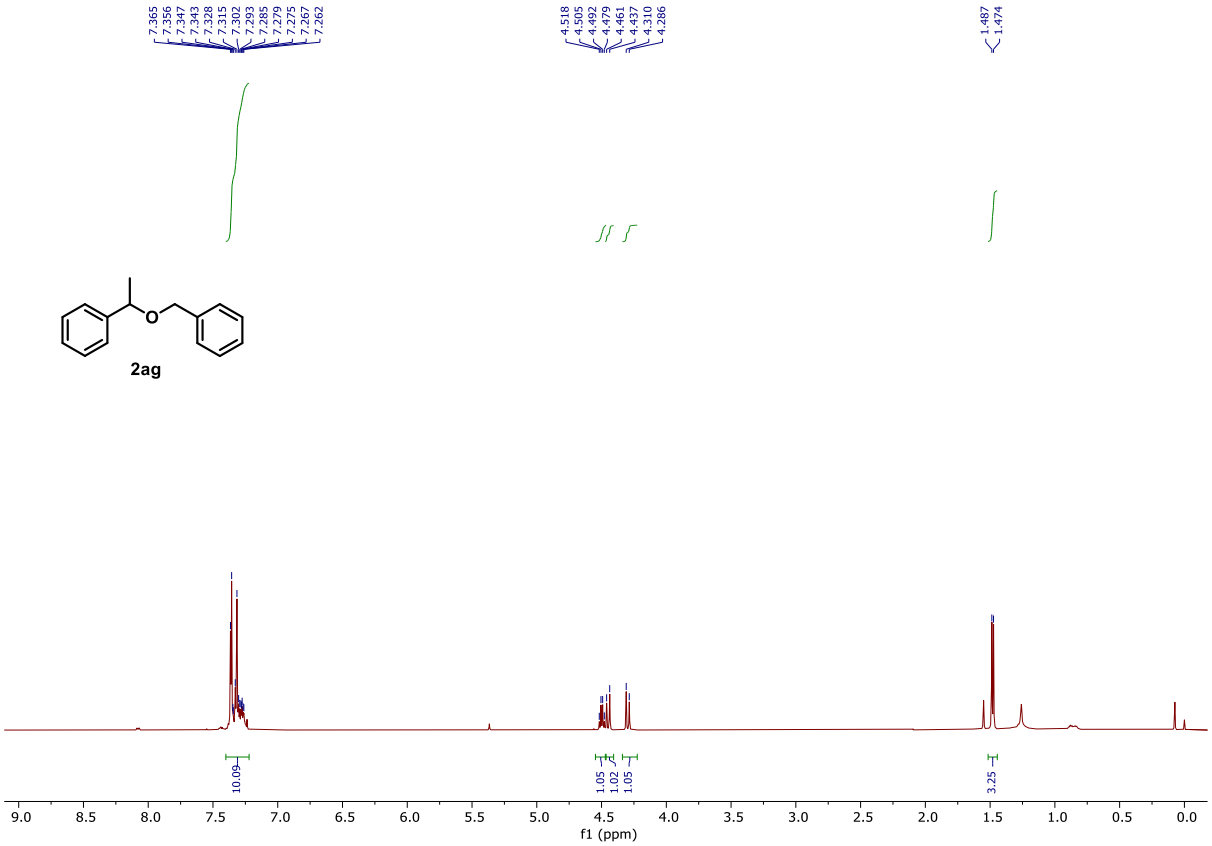

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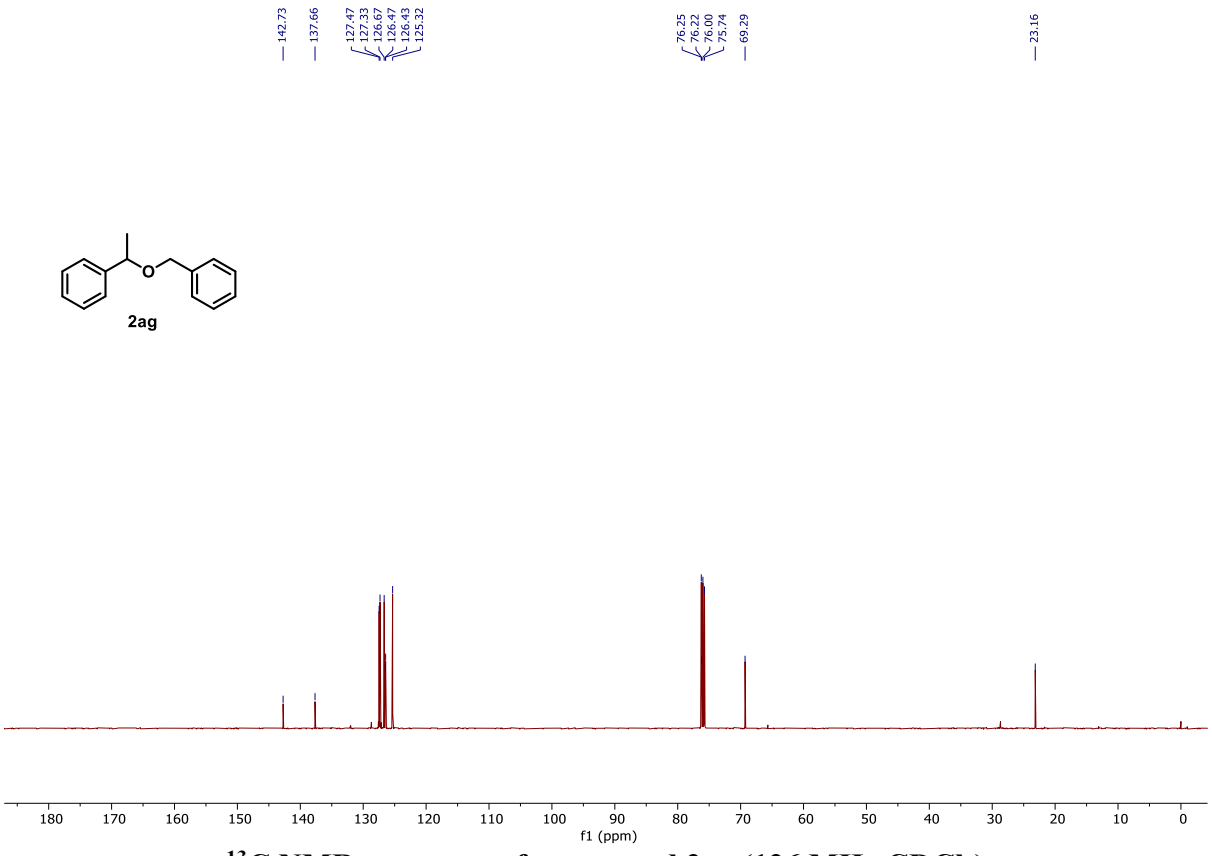

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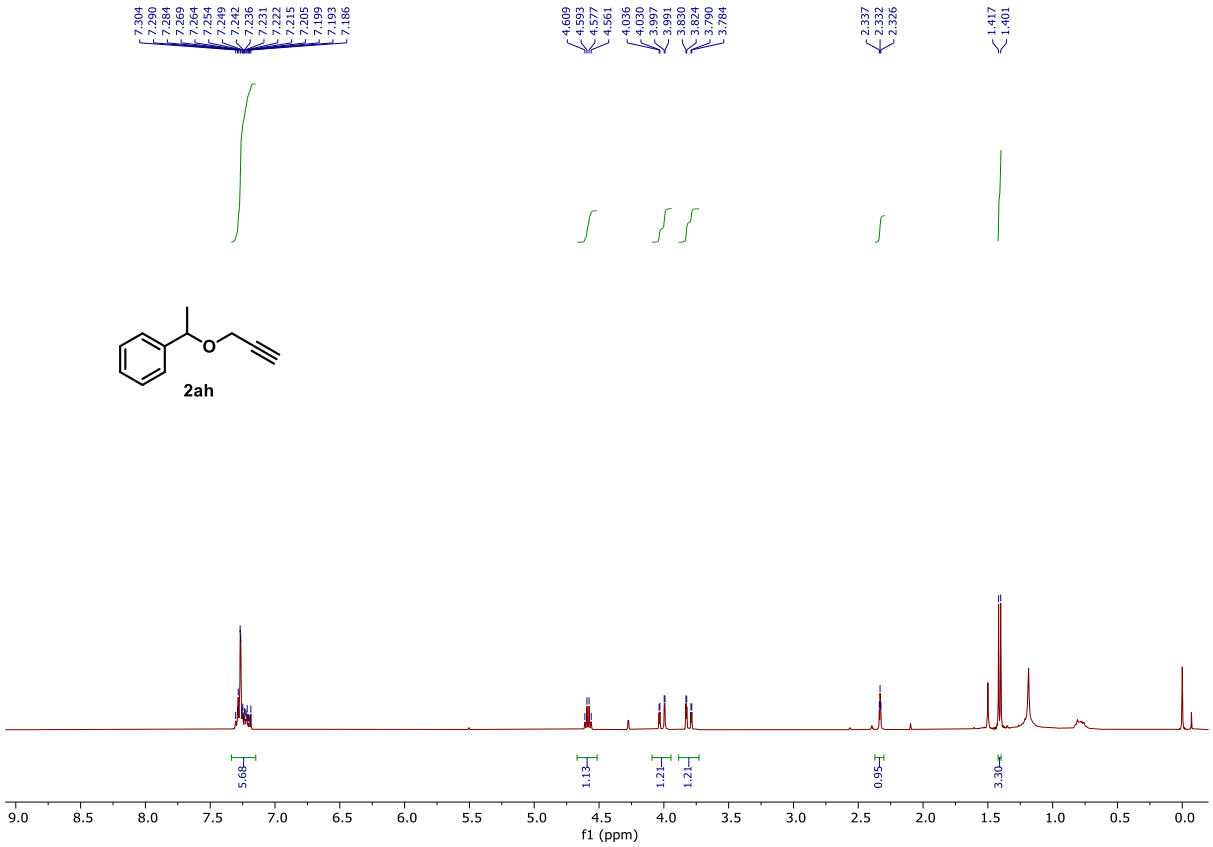

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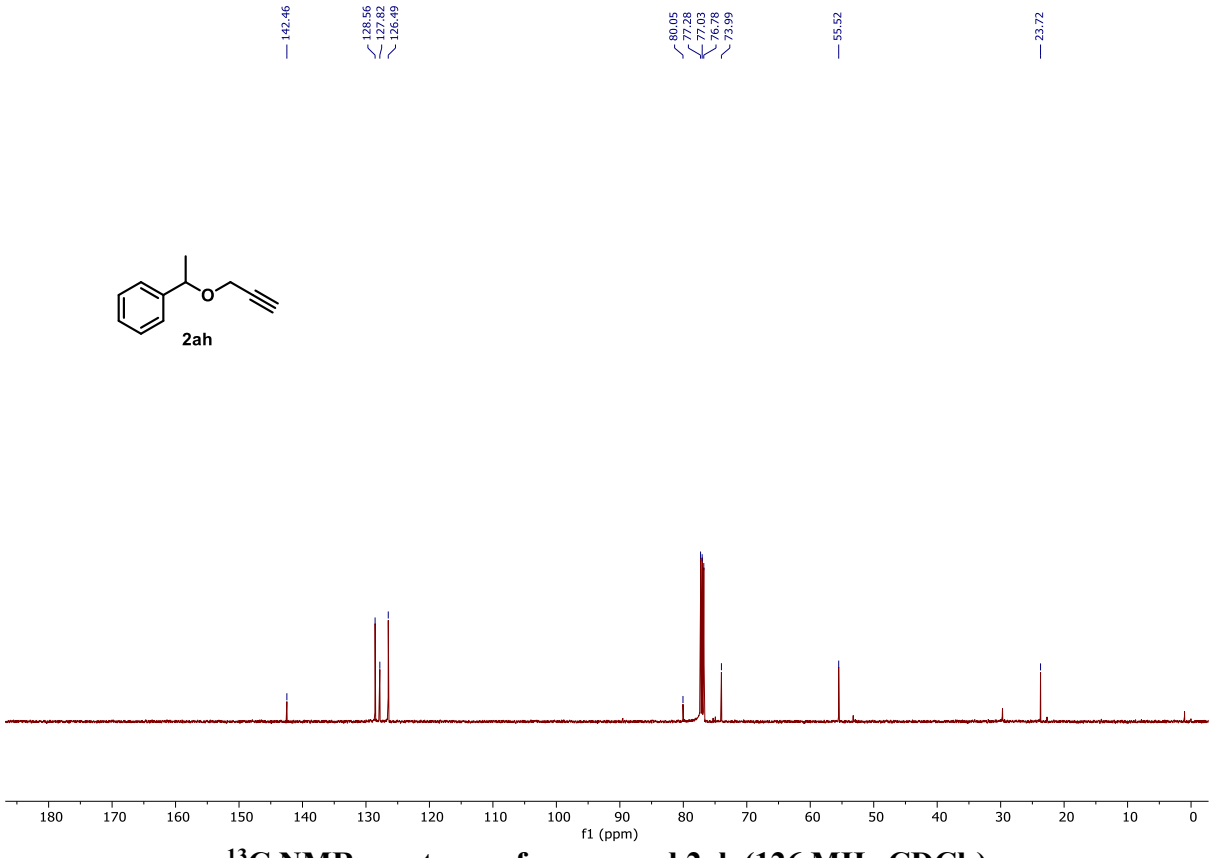

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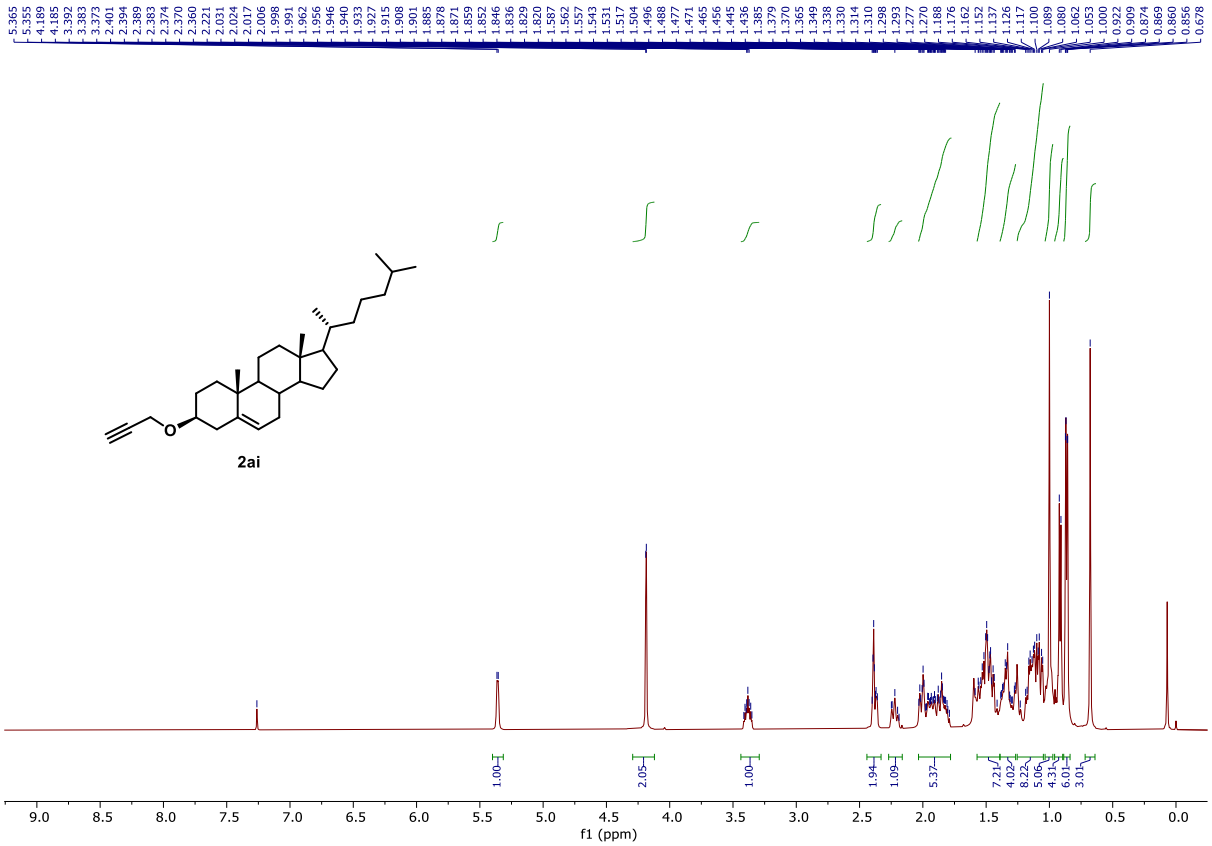

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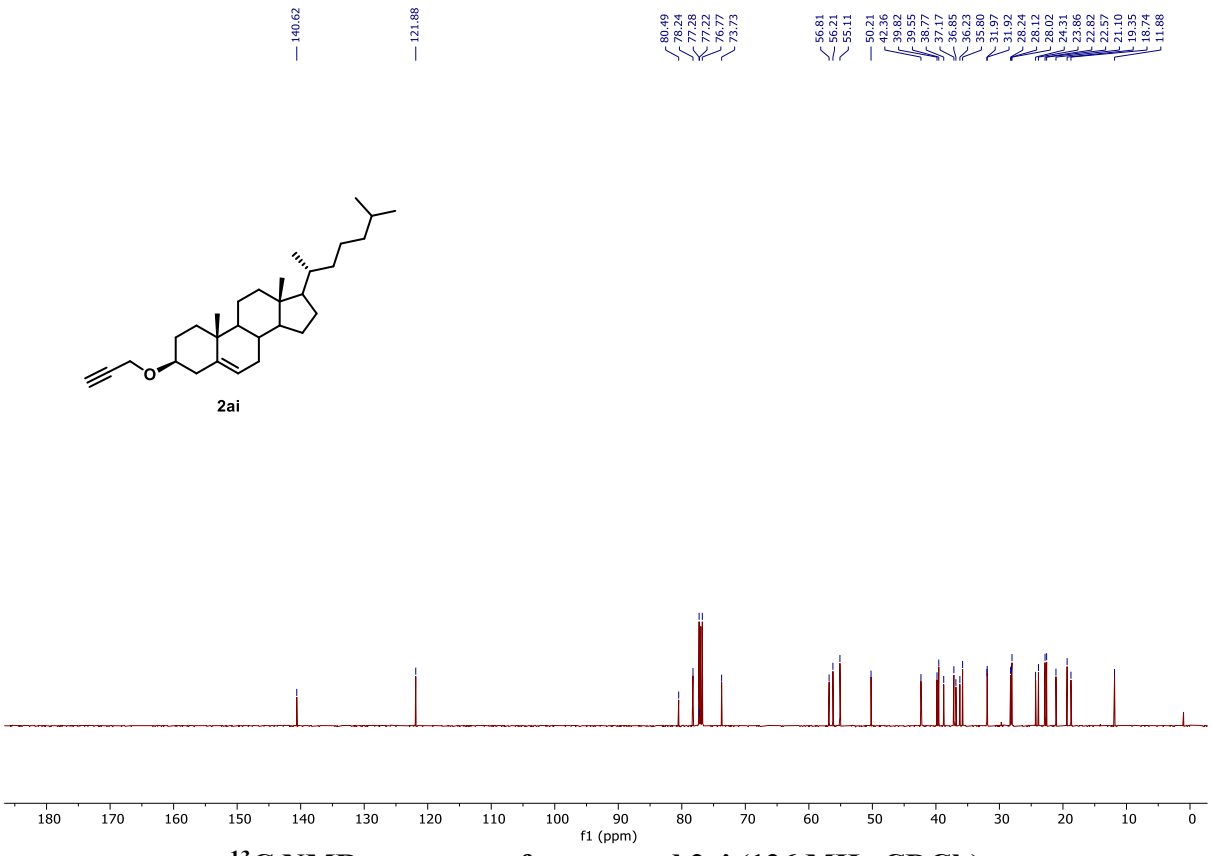

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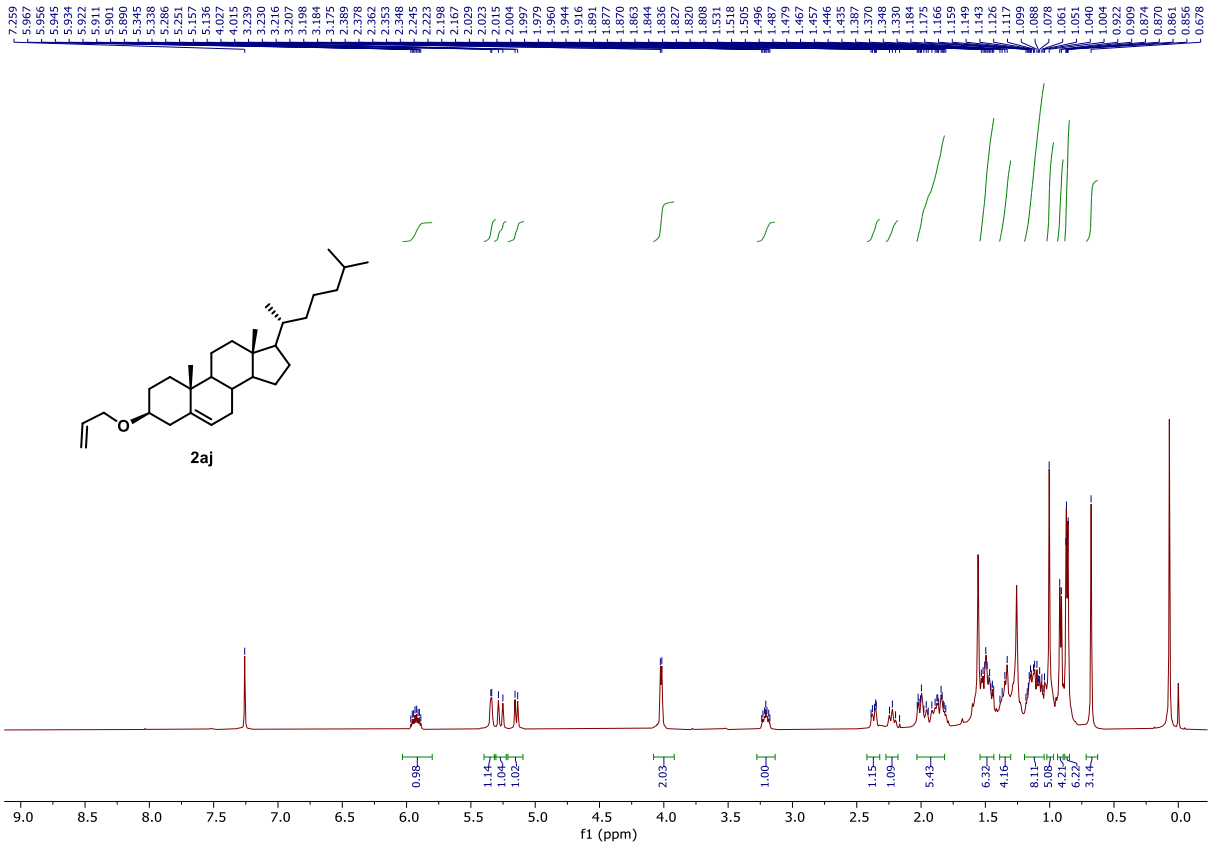

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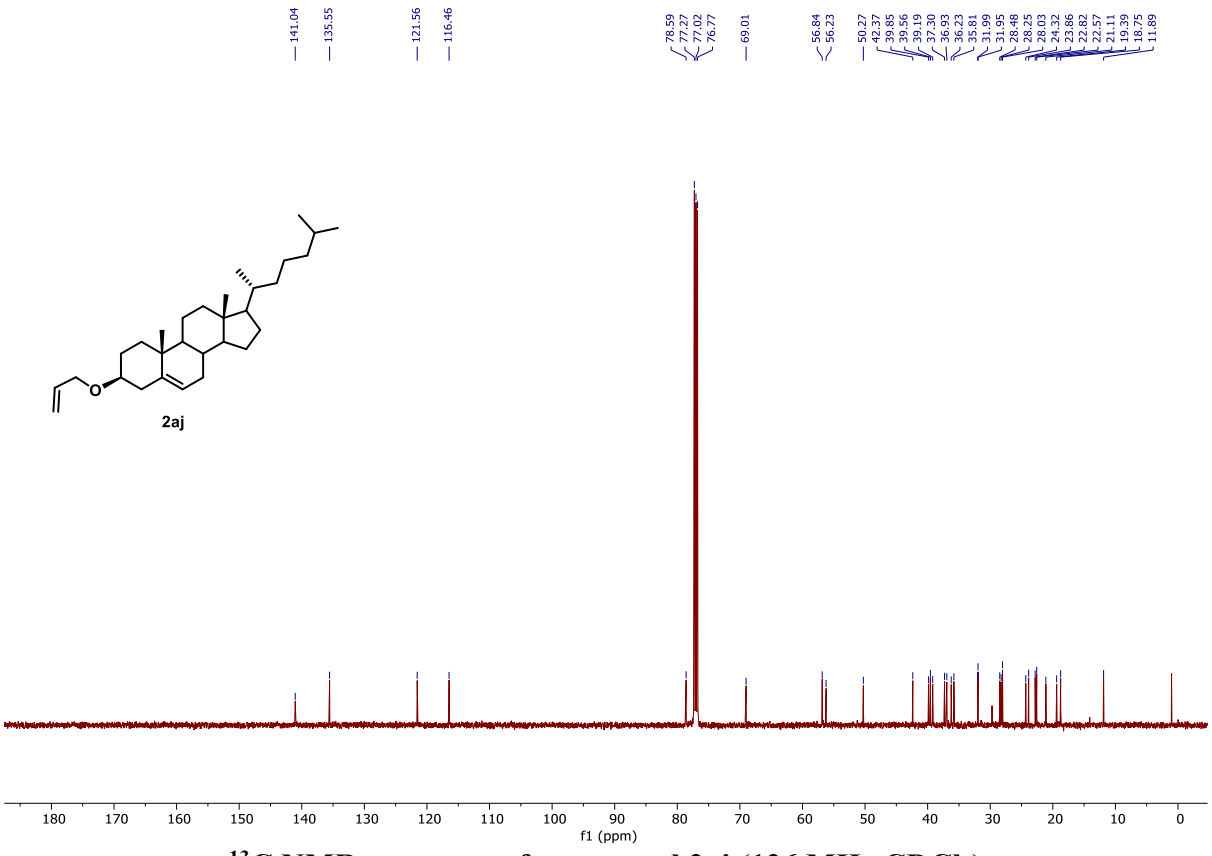

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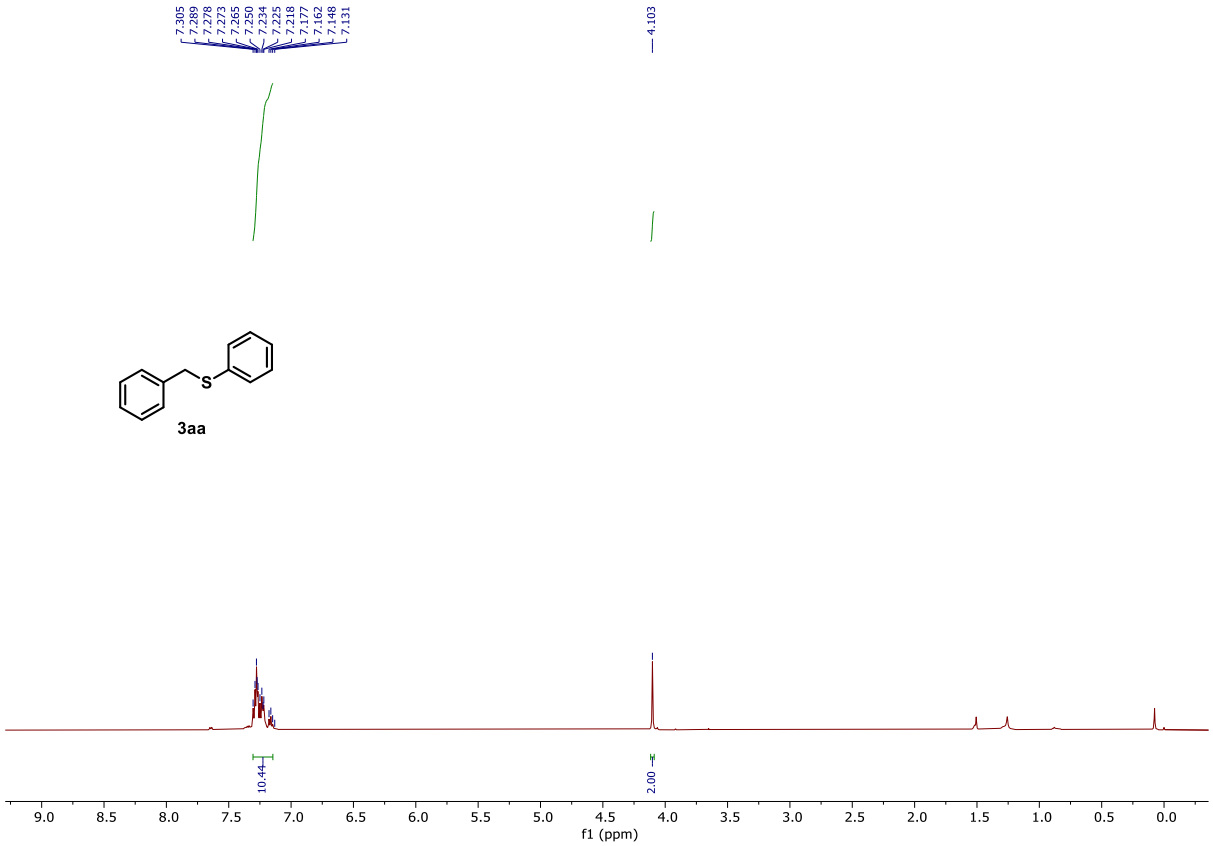

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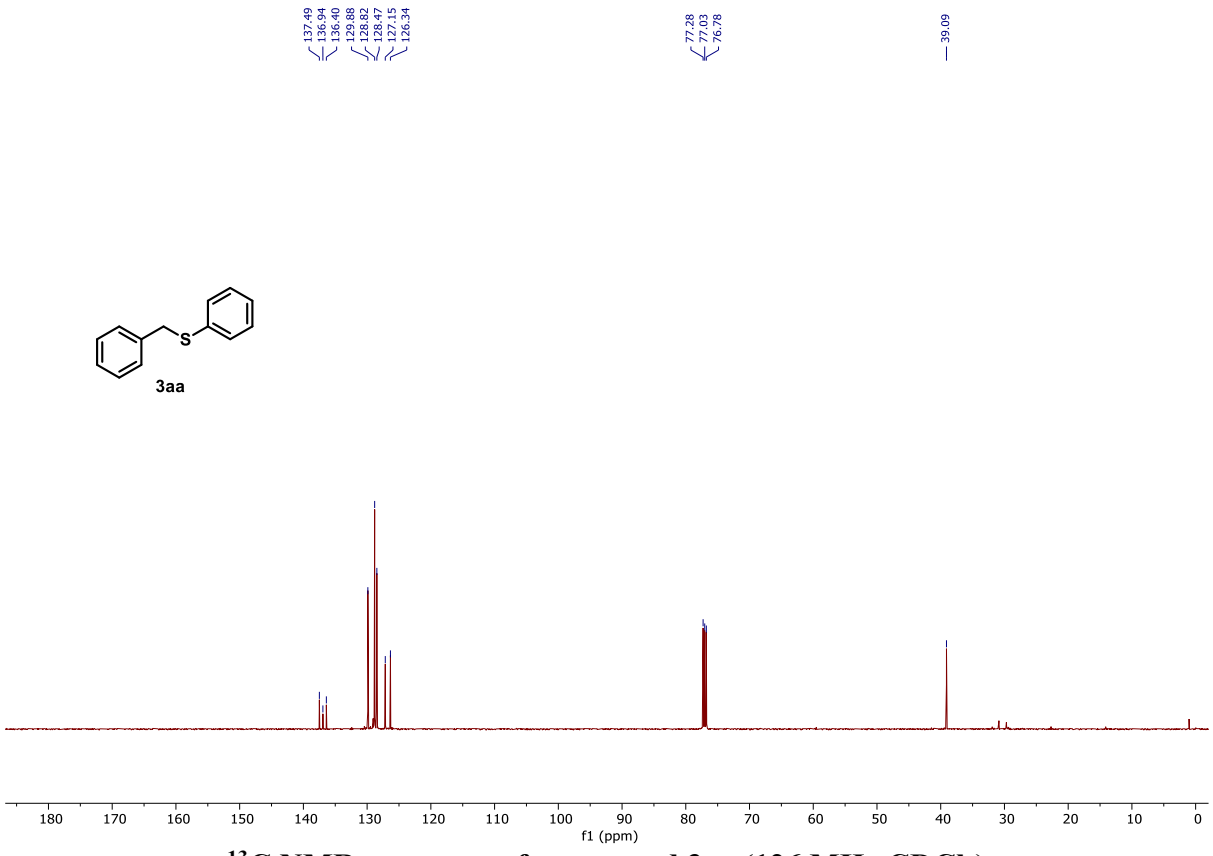

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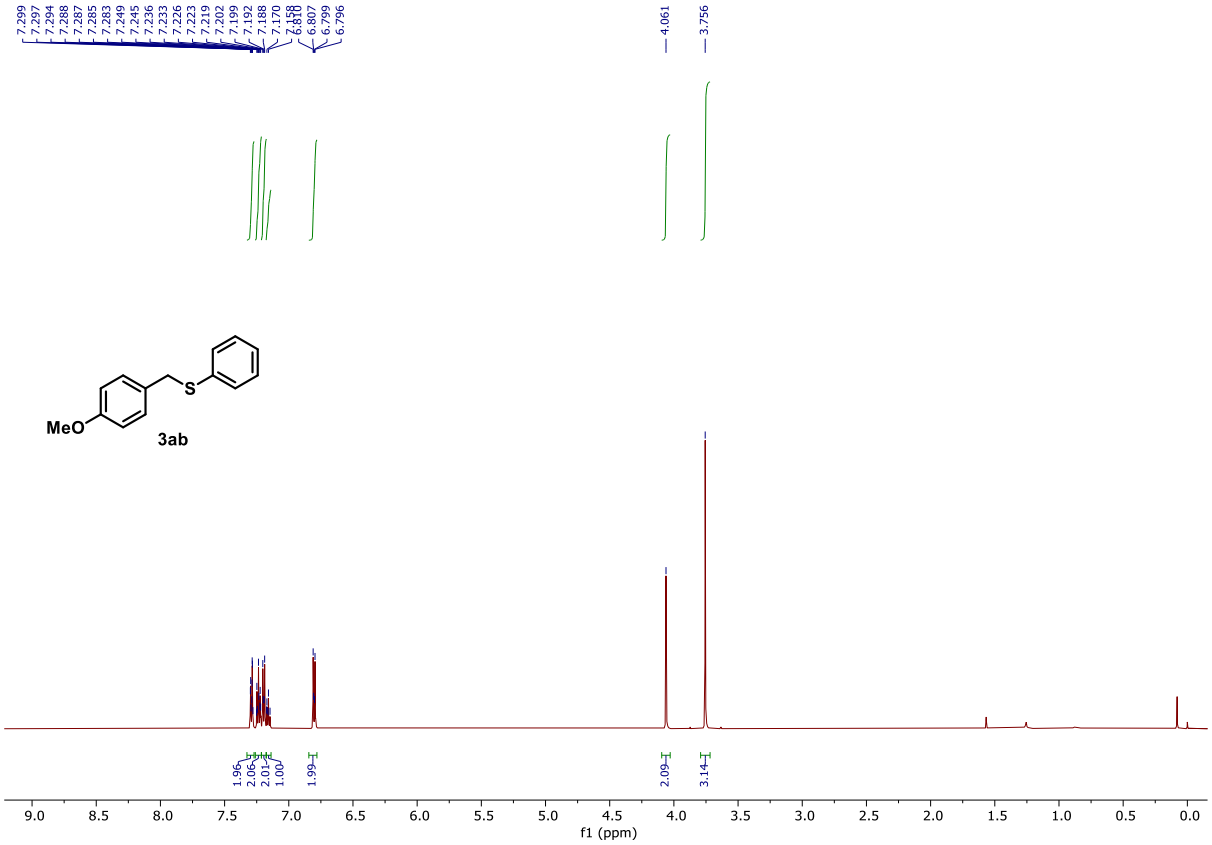

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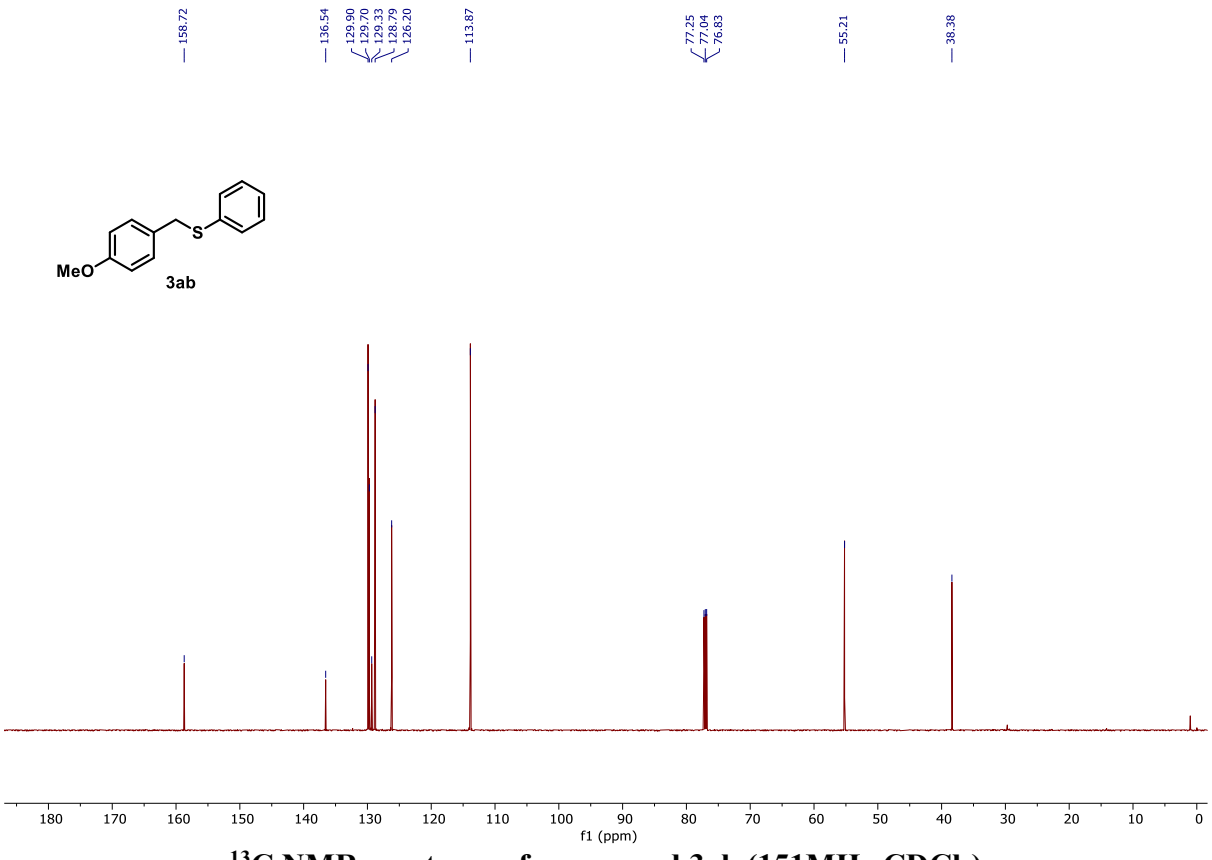

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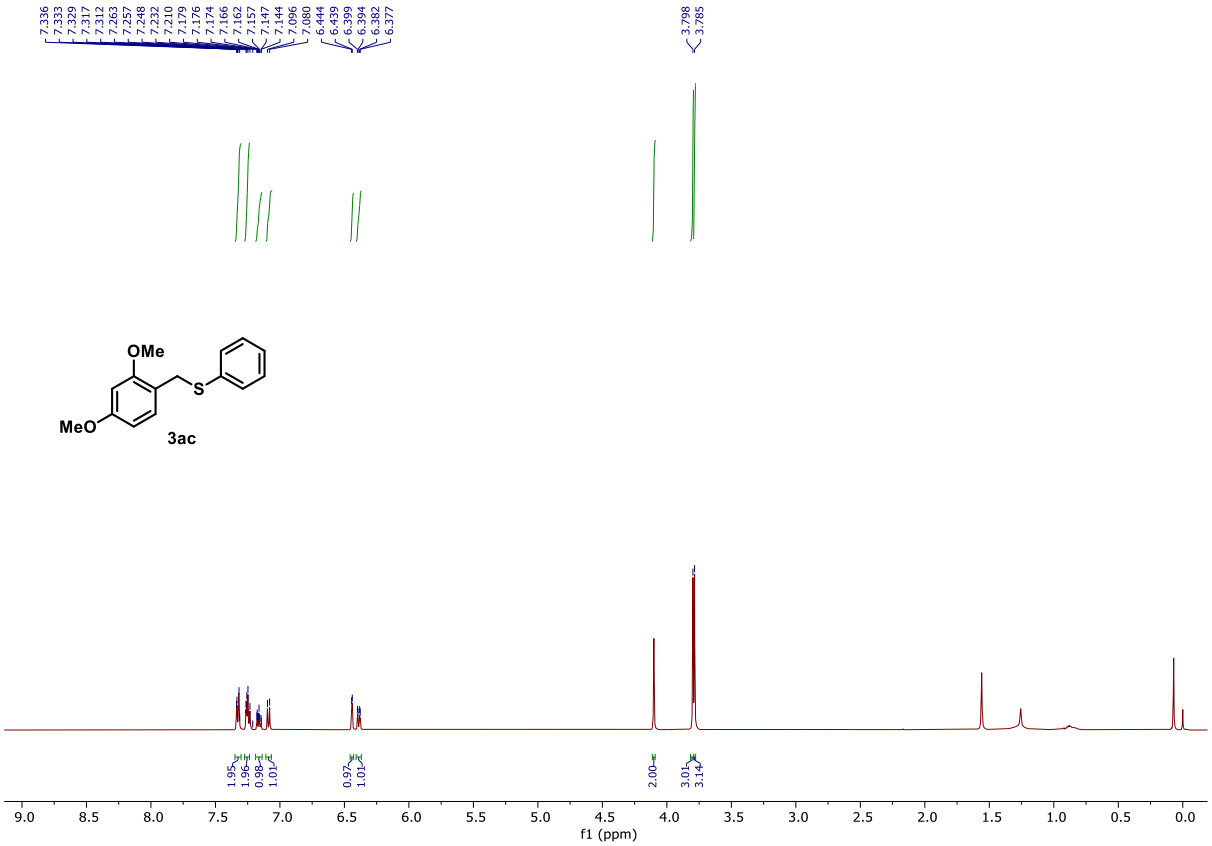

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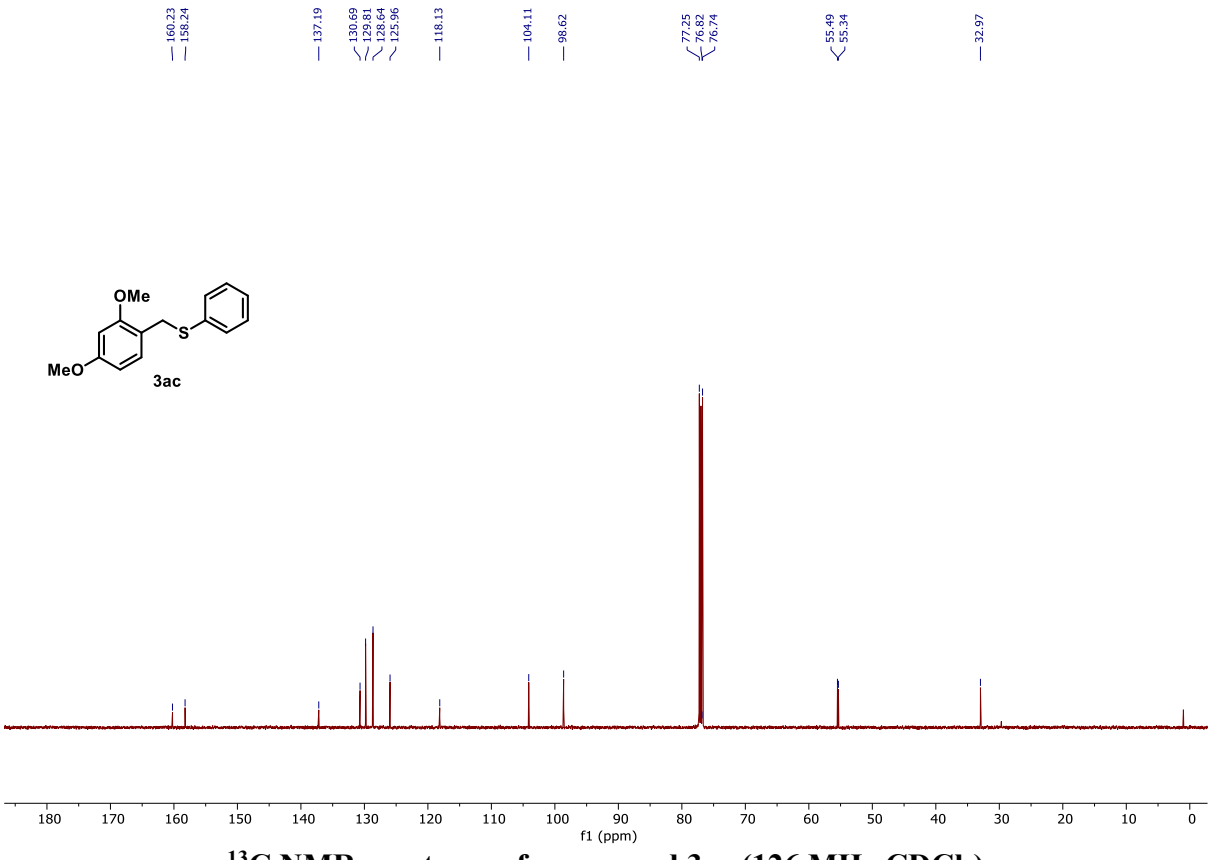

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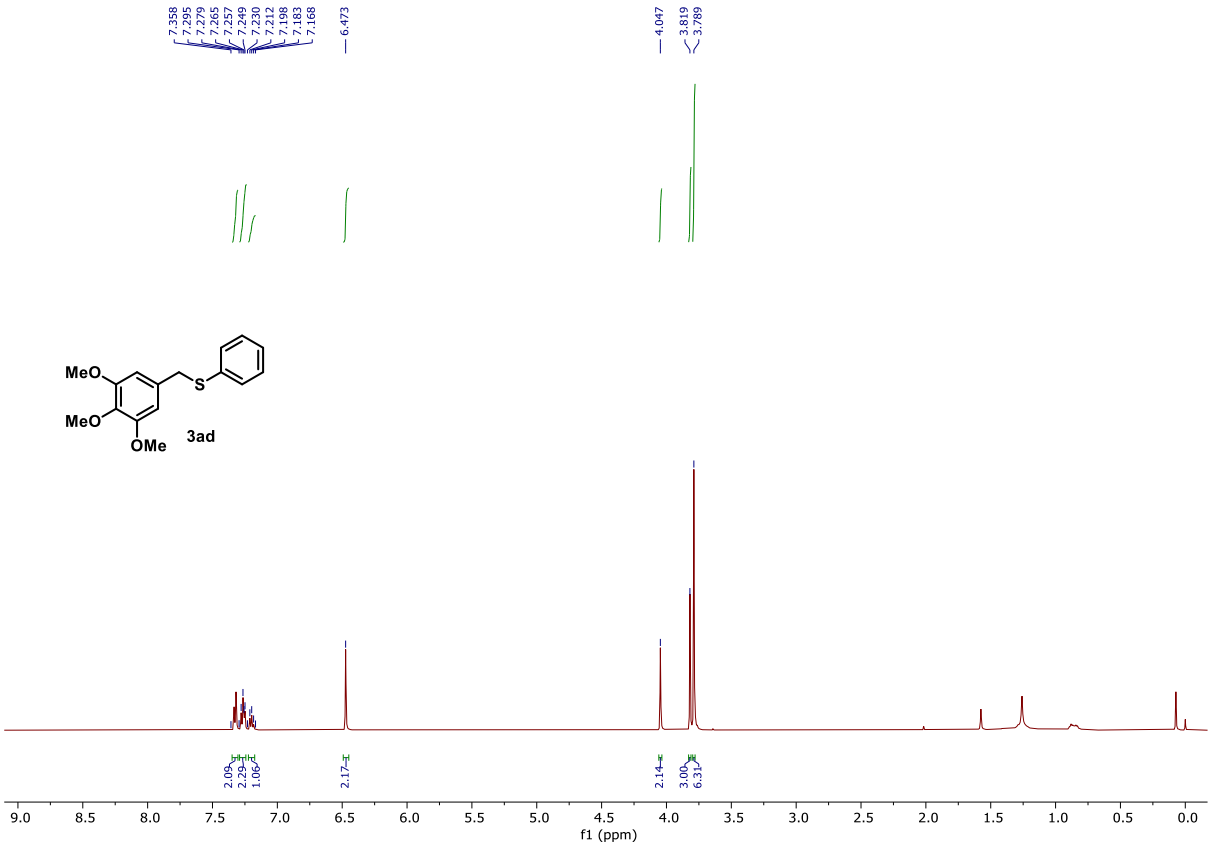

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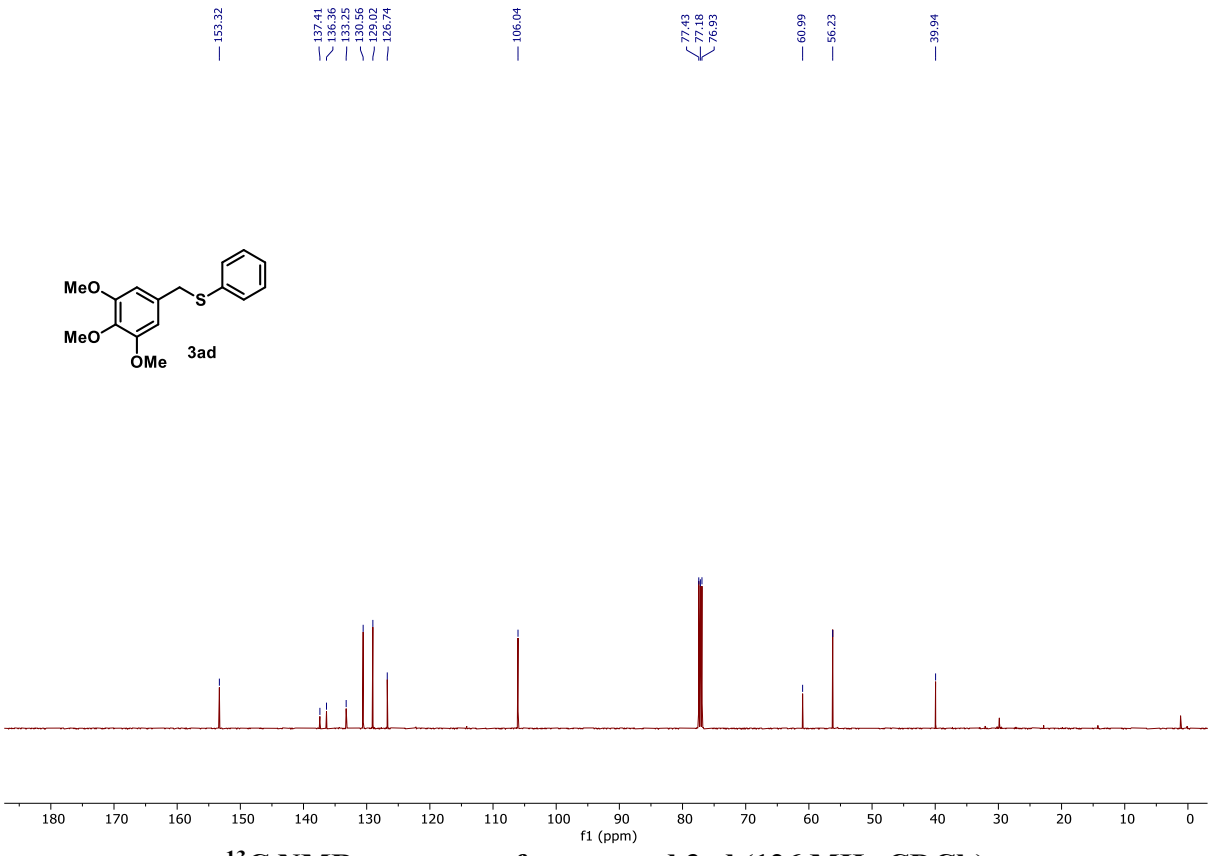

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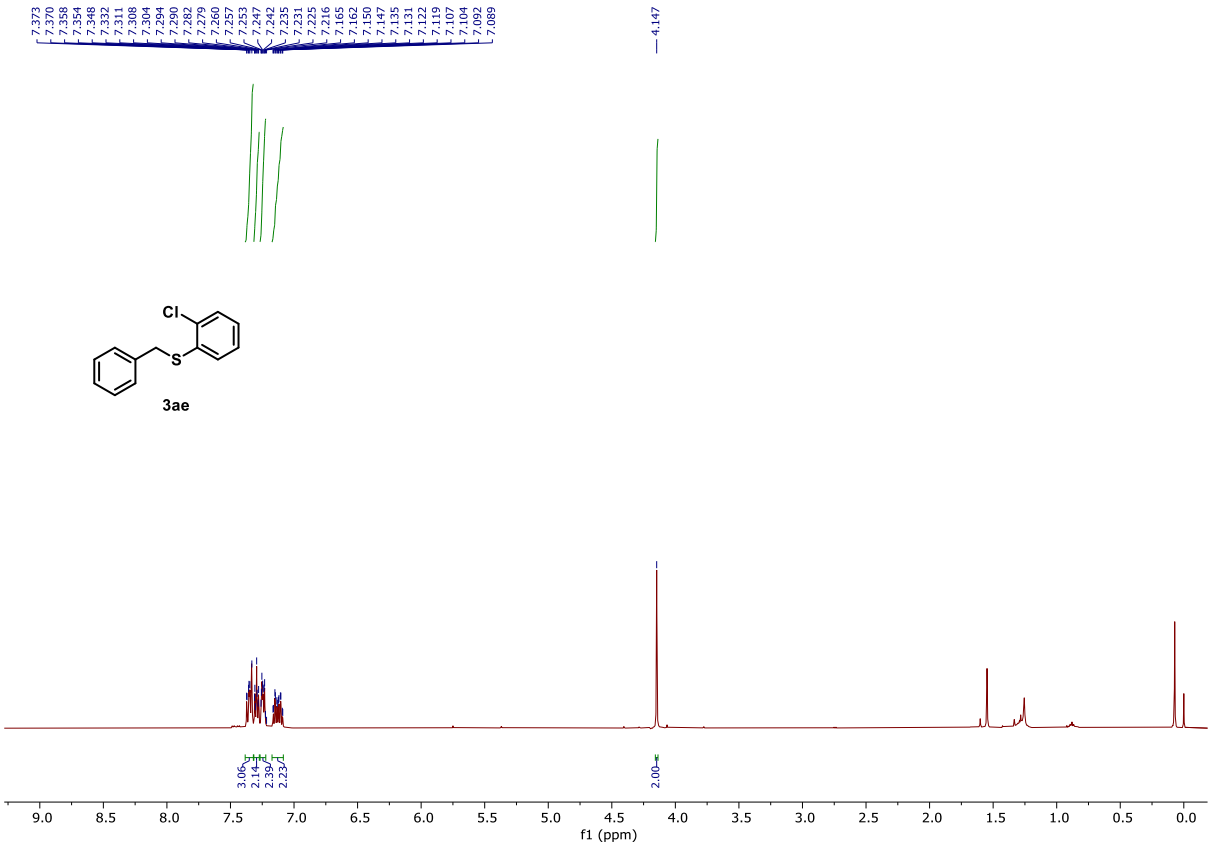

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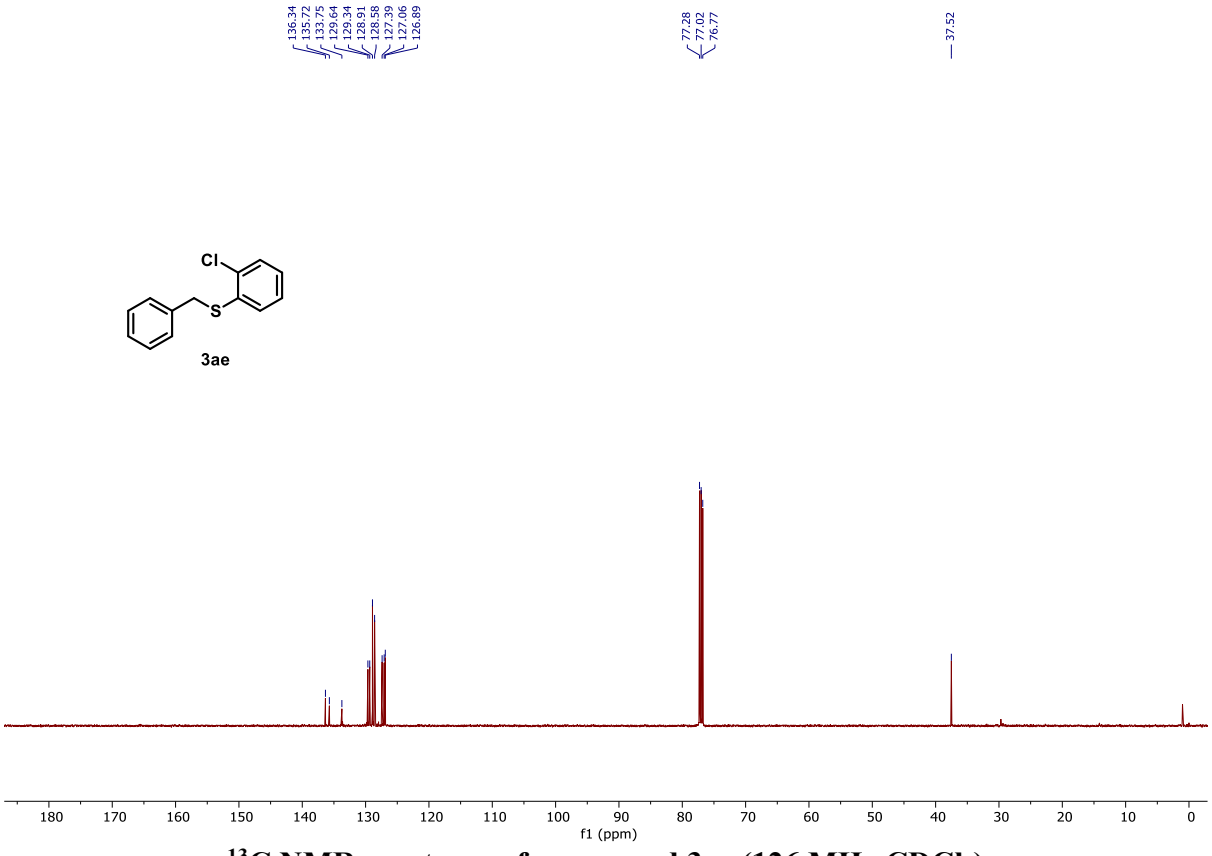

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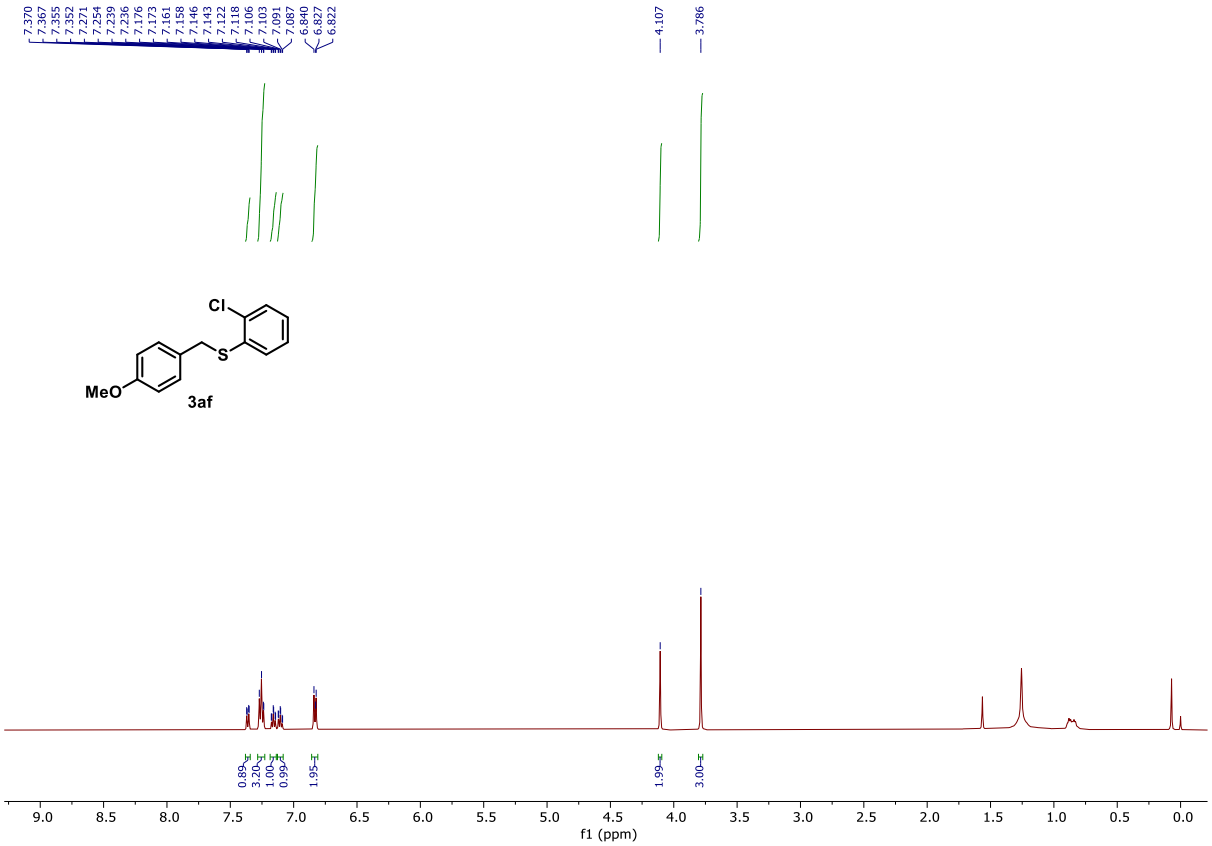

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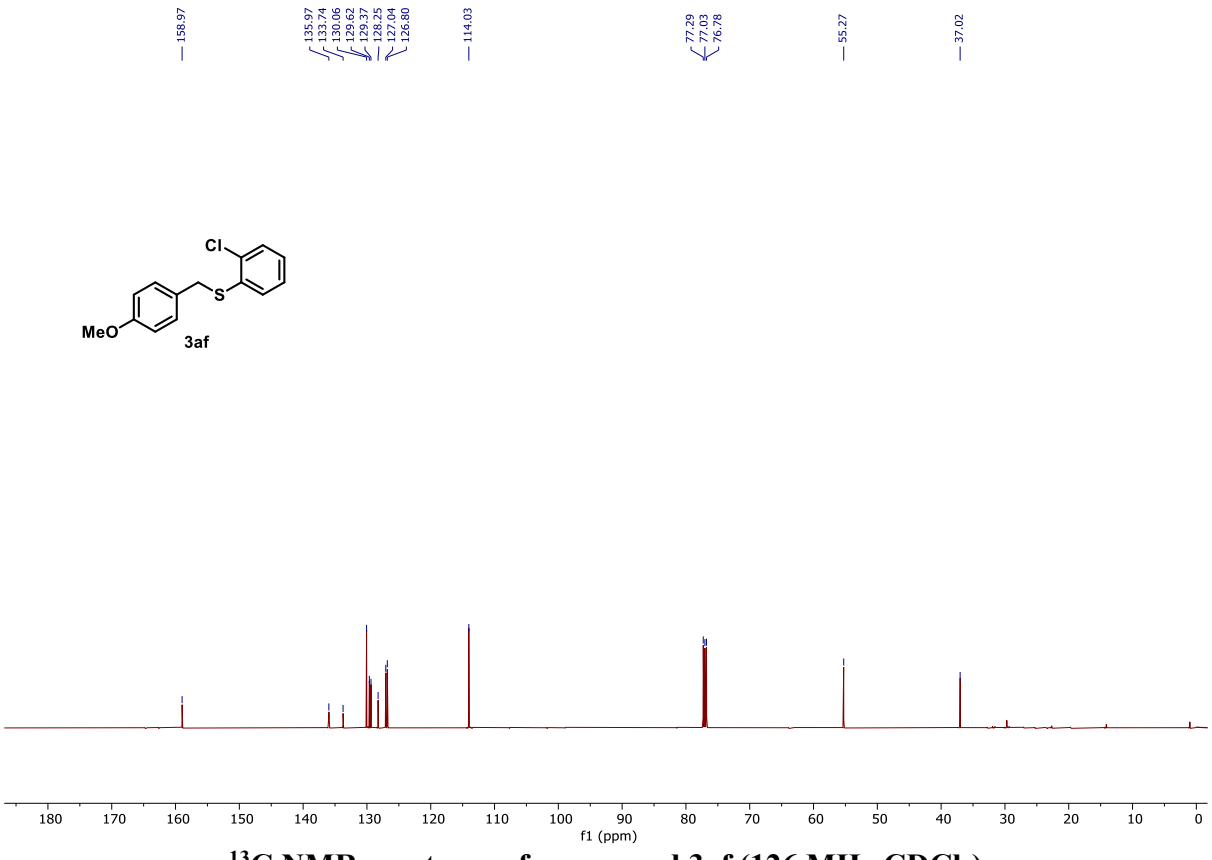
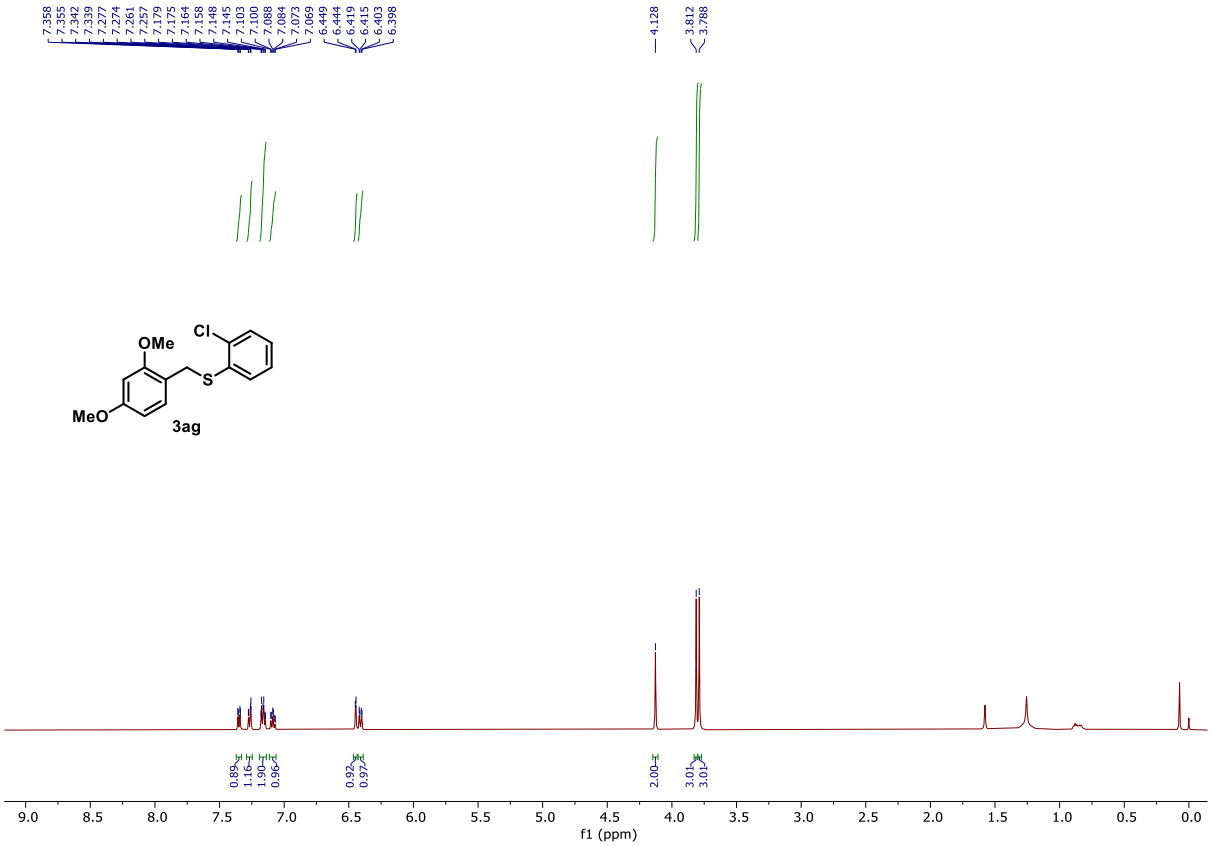
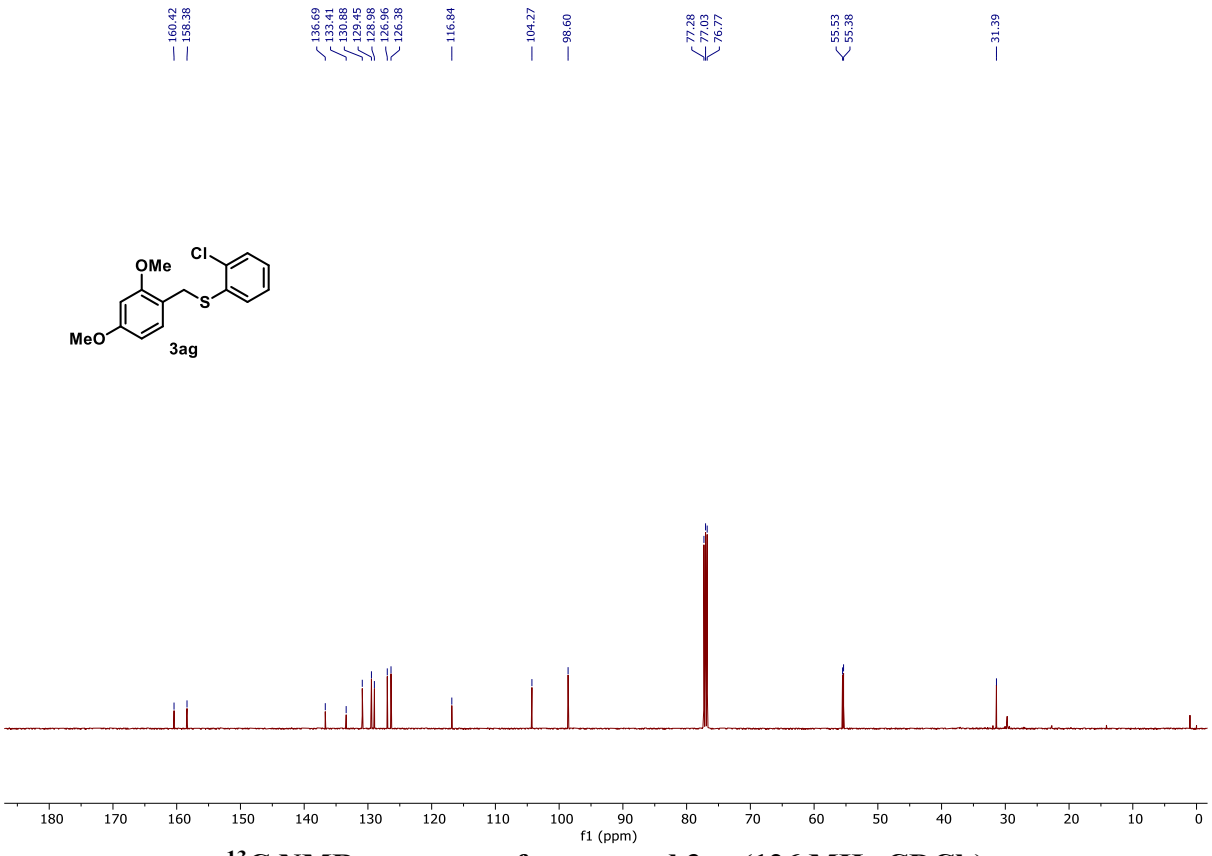


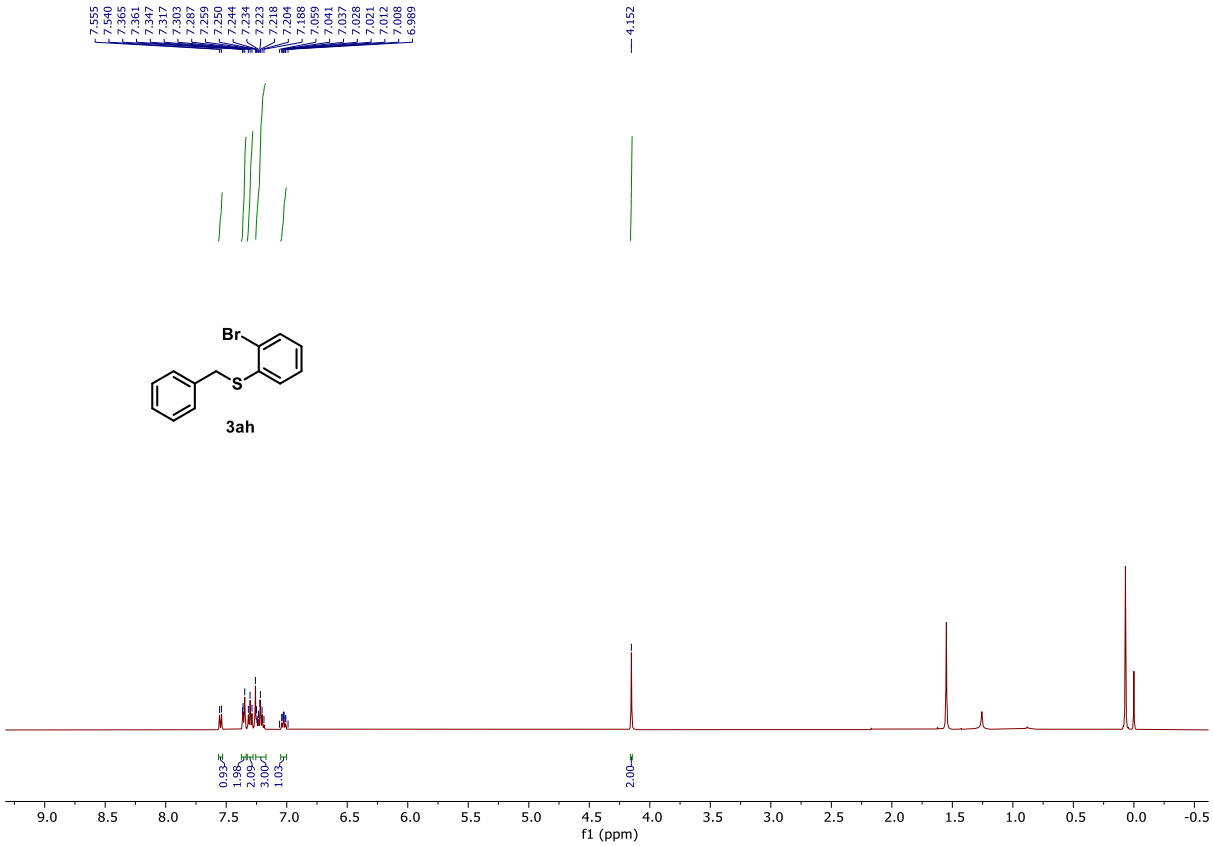
^{13}C NMR spectrum of compound 3af (126 MHz $CDCl_3$)



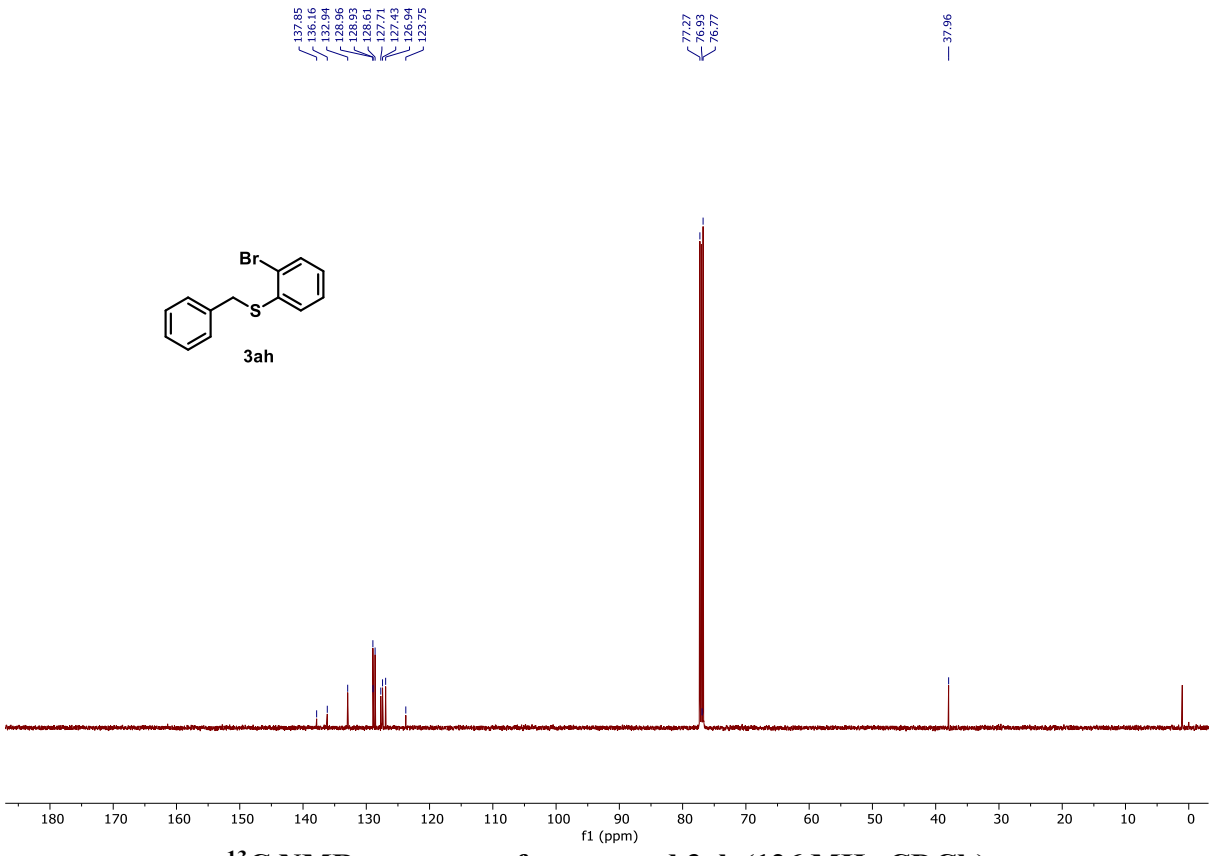
^{1}H NMR spectrum of compound 3ag (500 MHz $CDCl_3$)



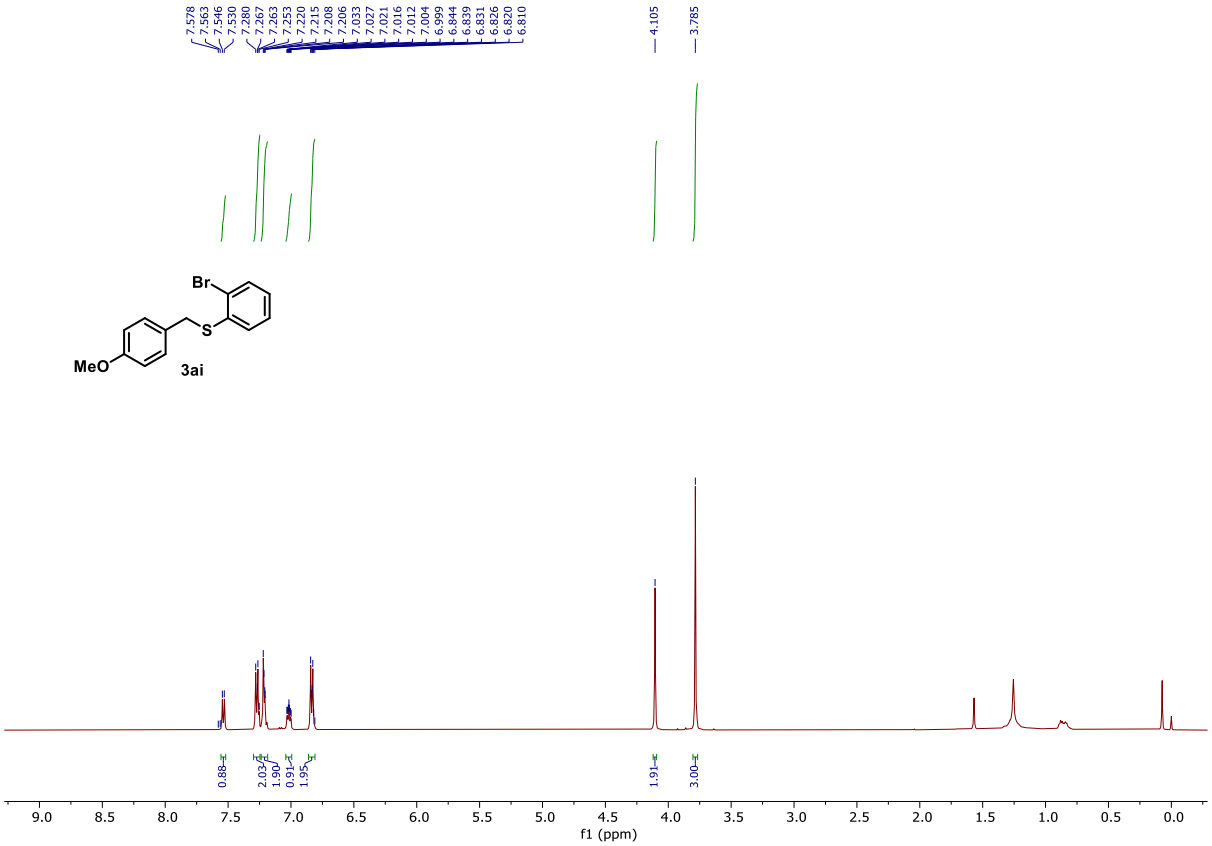
^{13}C NMR spectrum of compound 3ag (126 MHz $CDCl_3$)



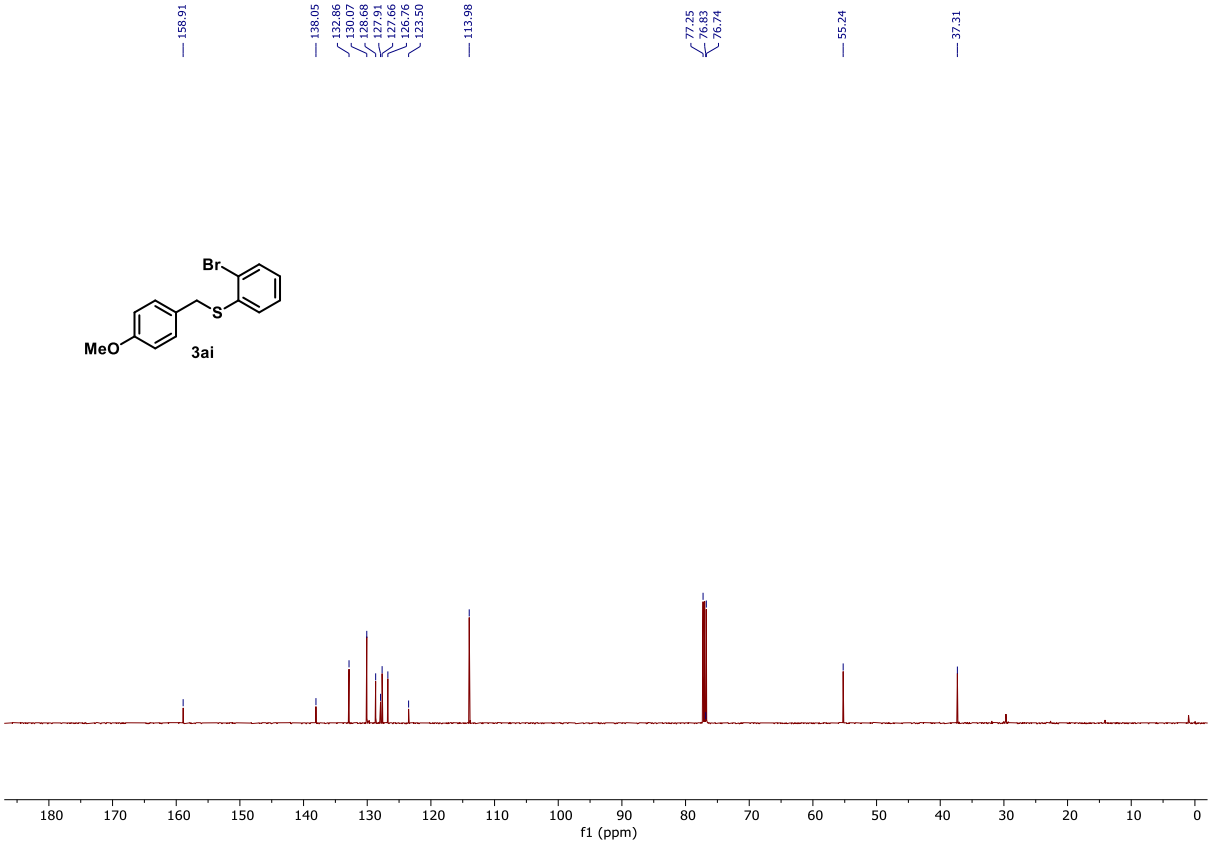
^{1}H NMR spectrum of compound 3ah (500 MHz $CDCl_3$)



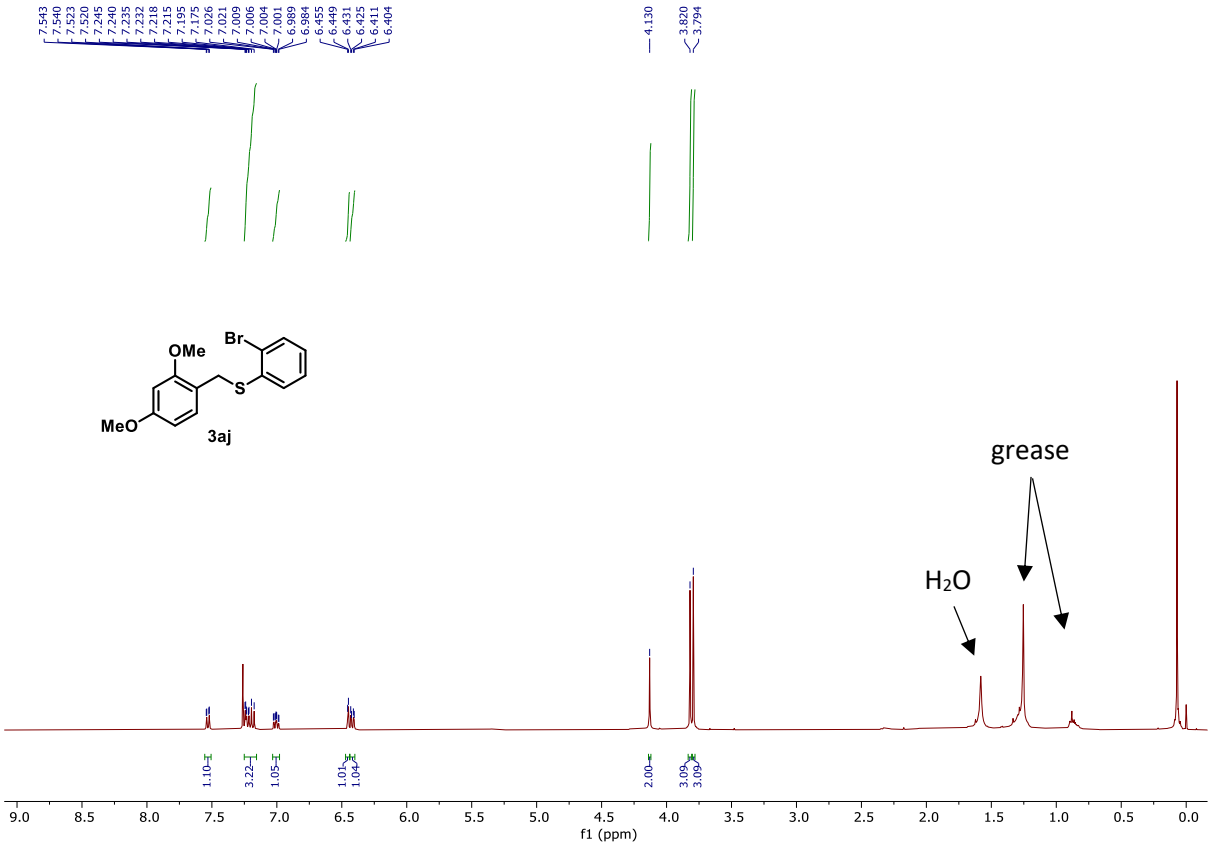
^{13}C NMR spectrum of compound 3ah (126 MHz $CDCl_3$)



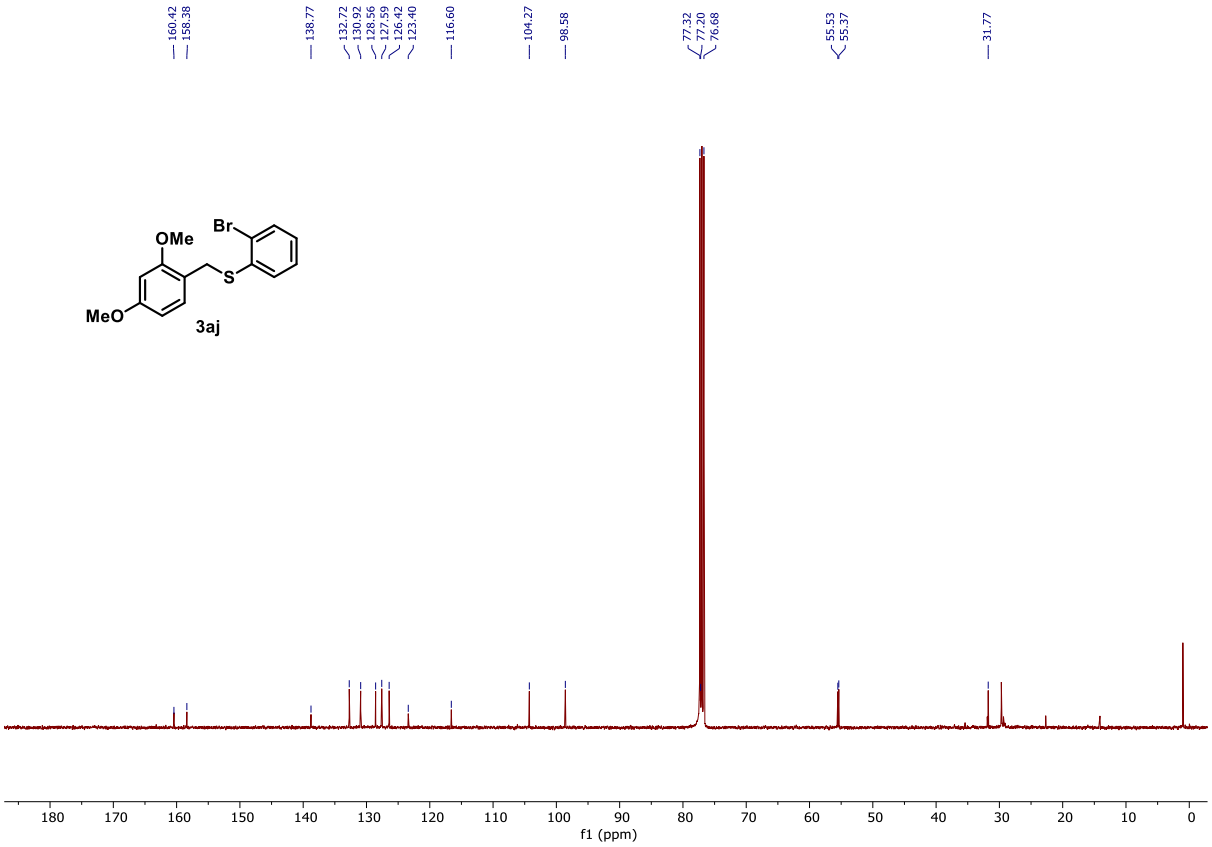
^{1}H NMR spectrum of compound 3ai (500 MHz $CDCl_3$)



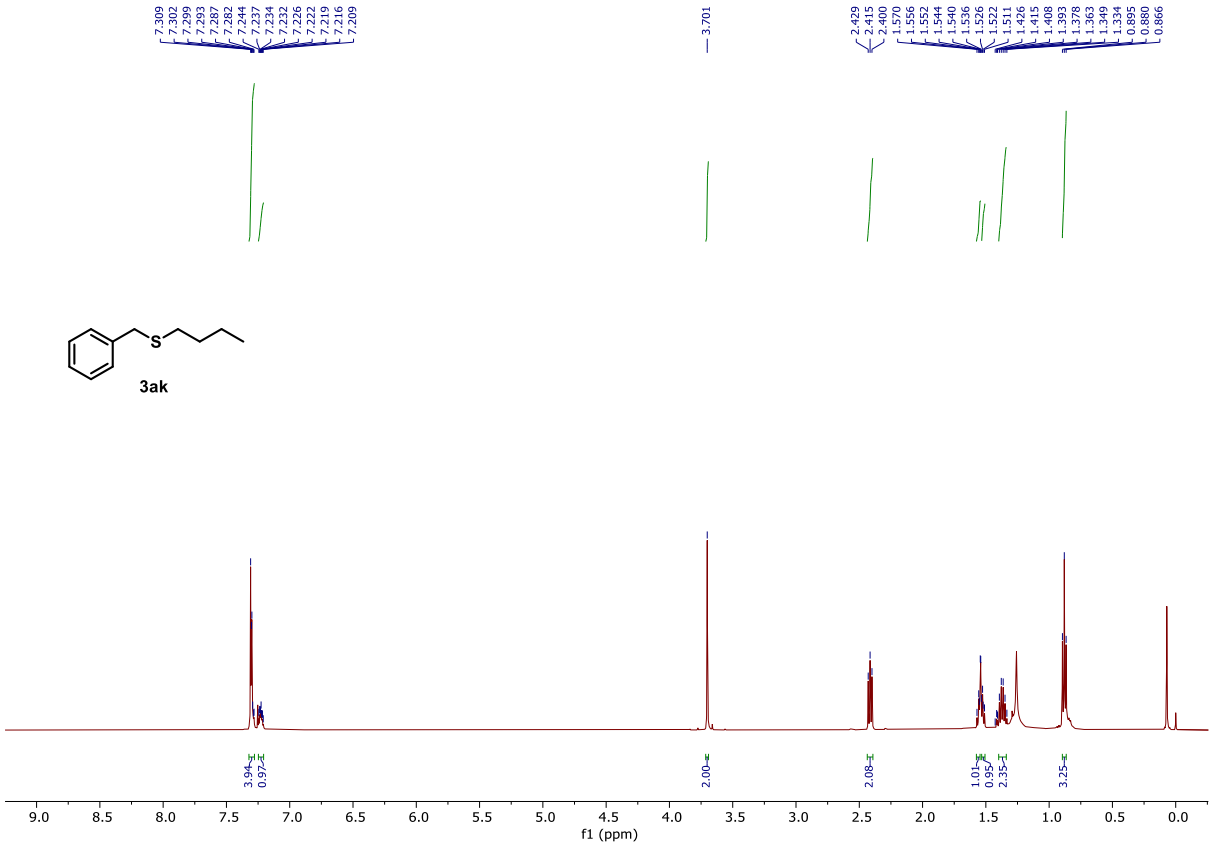
^{13}C NMR spectrum of compound 3ai (126 MHz $CDCl_3$)



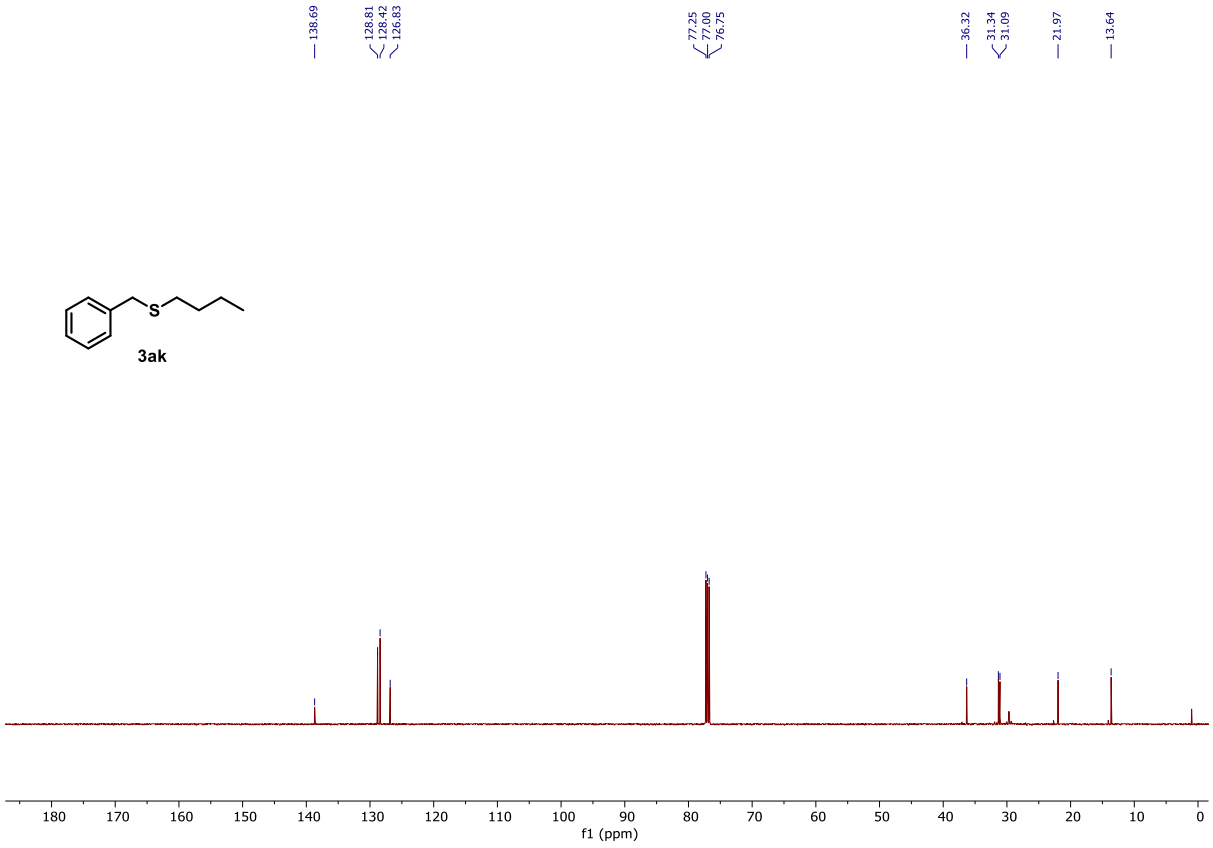
^{1}H NMR spectrum of compound 3aj (400 MHz $CDCl_3$)



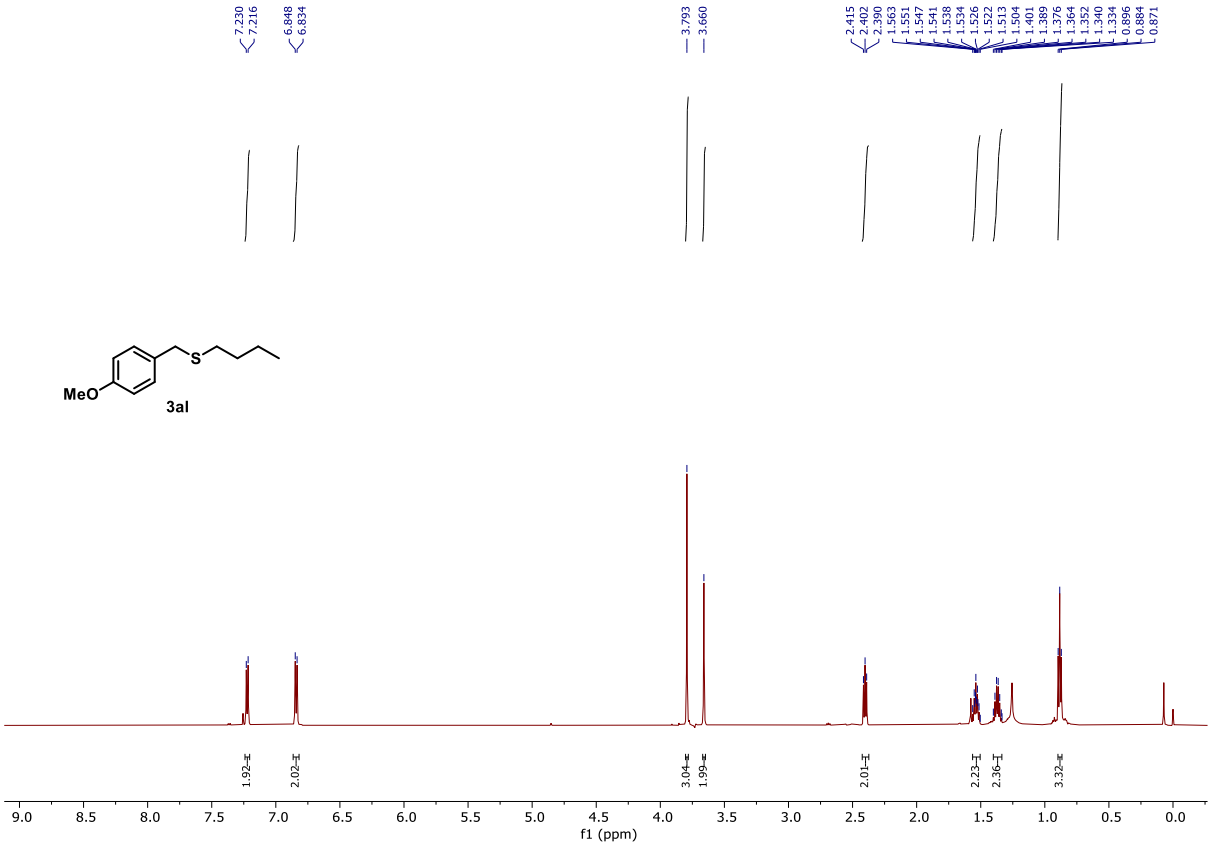
^{13}C NMR spectrum of compound 3aj (101 MHz $CDCl_3$)



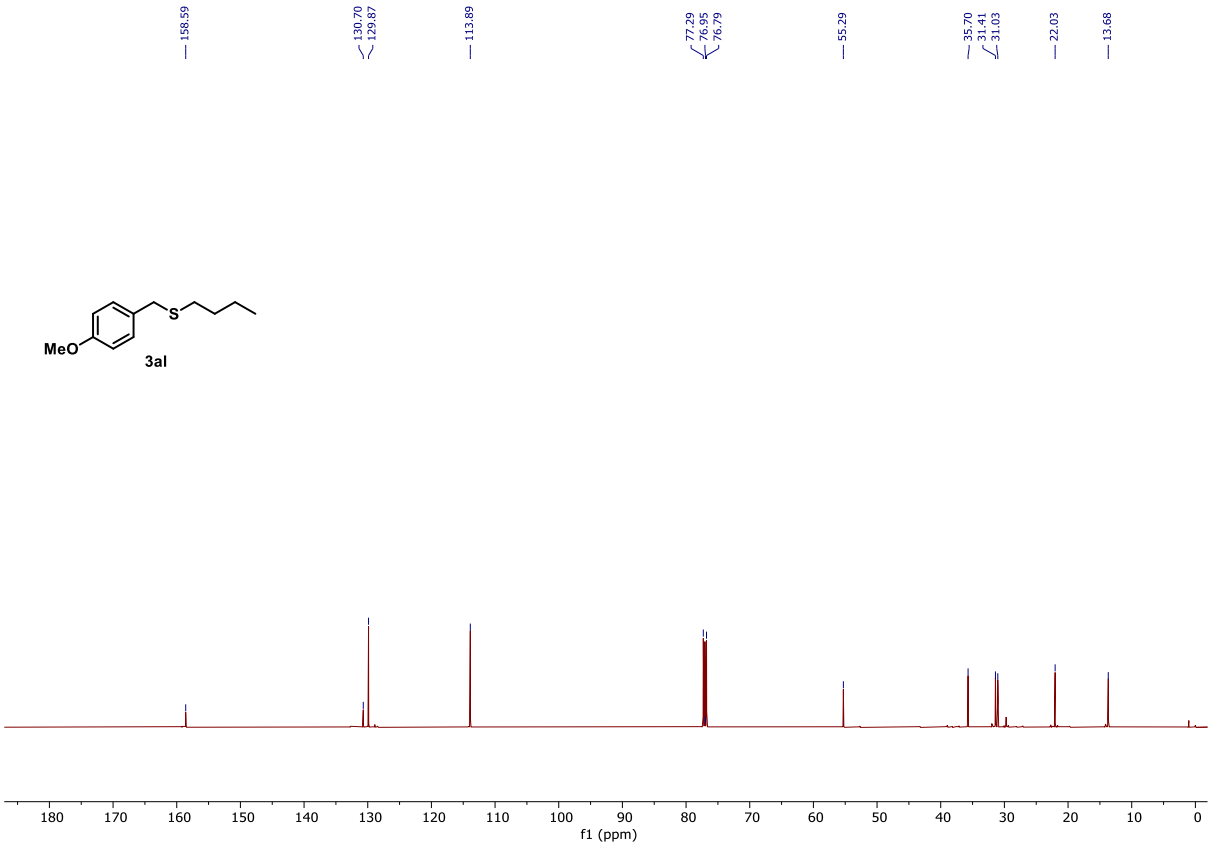
^{1}H NMR spectrum of compound 3ak



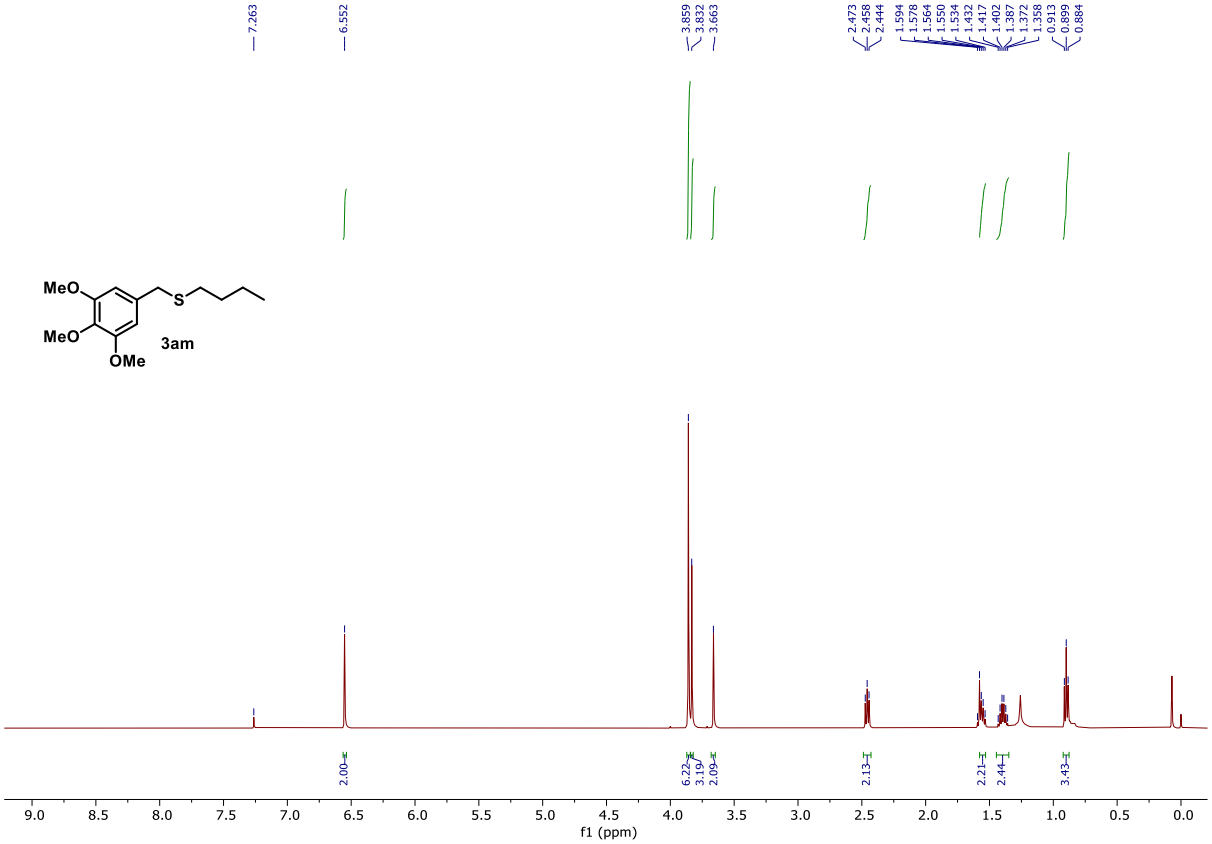
^{13}C NMR spectrum of compound 3ak



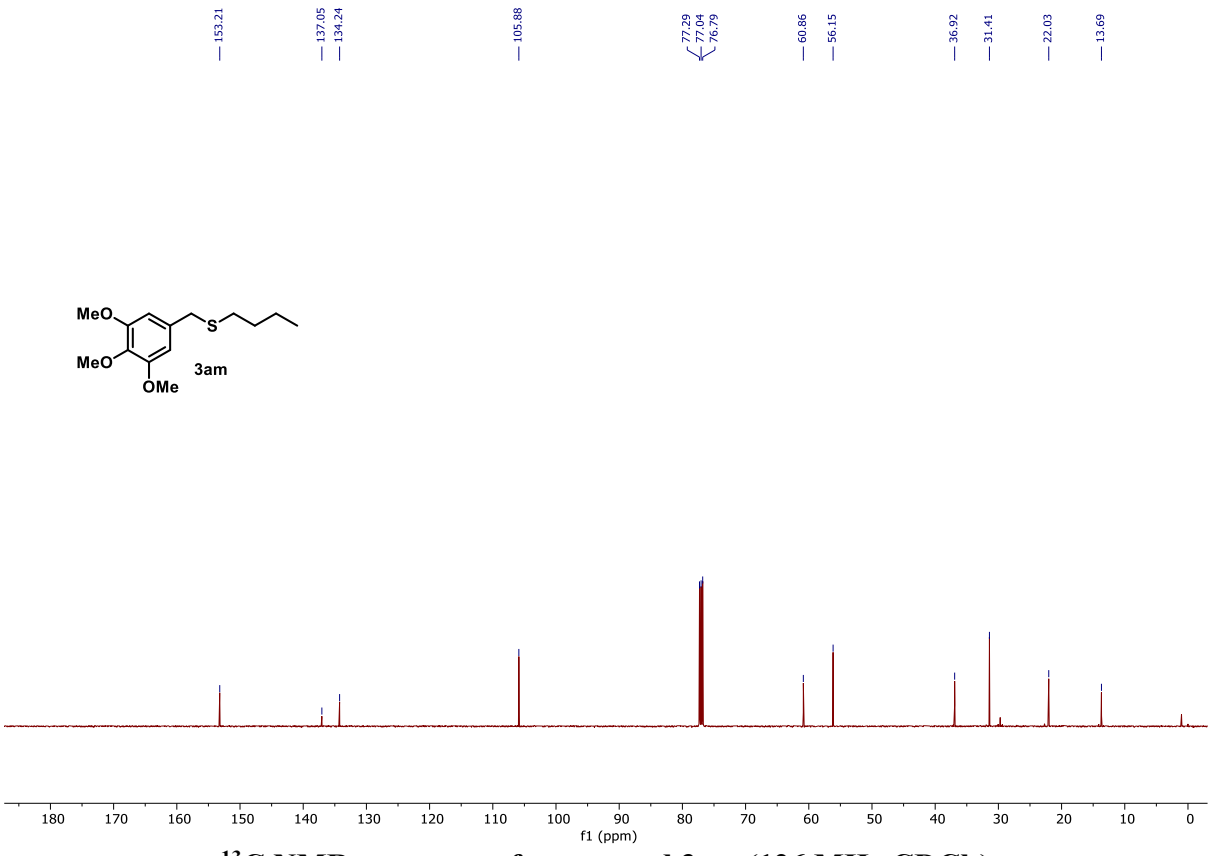
^{1}H NMR spectrum of compound 3al (600 MHz $CDCl_3$)



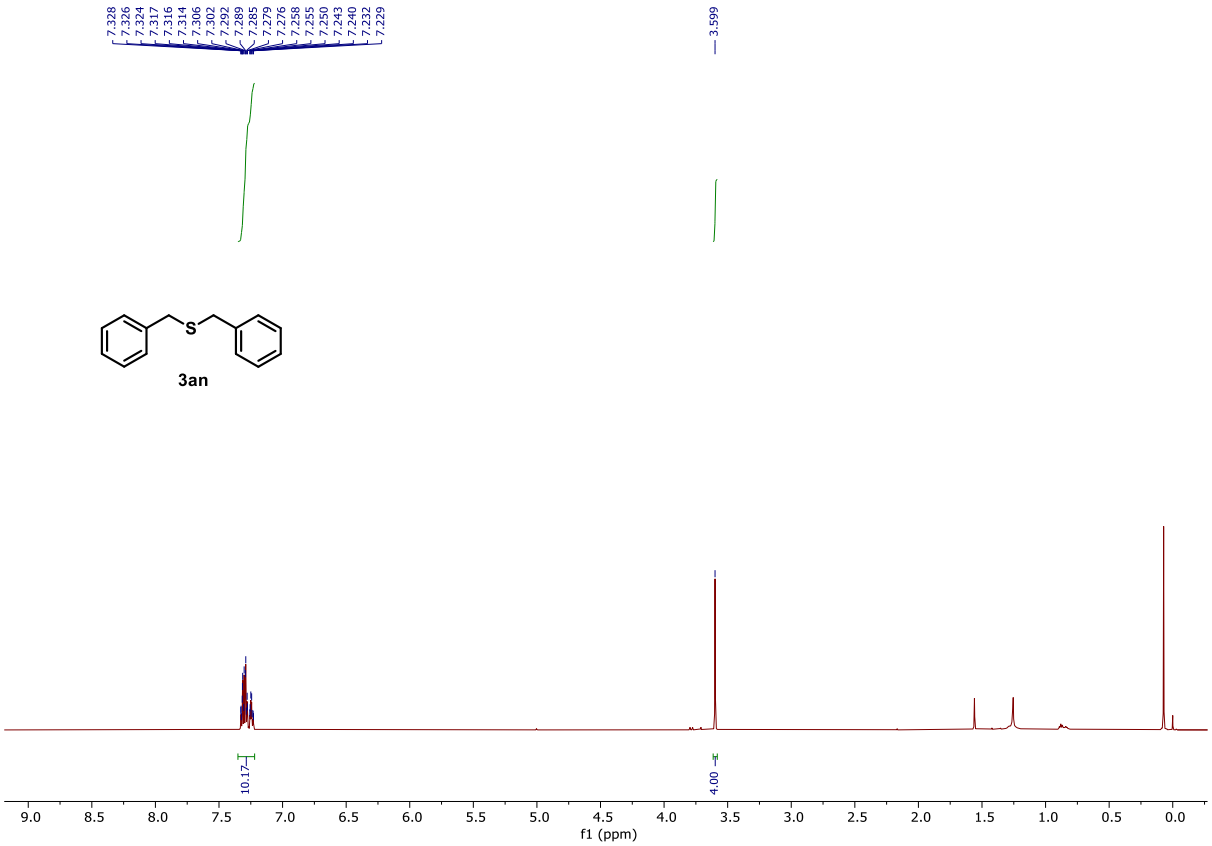
^{13}C NMR spectrum of compound 3al (151 MHz $CDCl_3$)



^{1}H NMR spectrum of compound 3am (500 MHz $CDCl_3$)

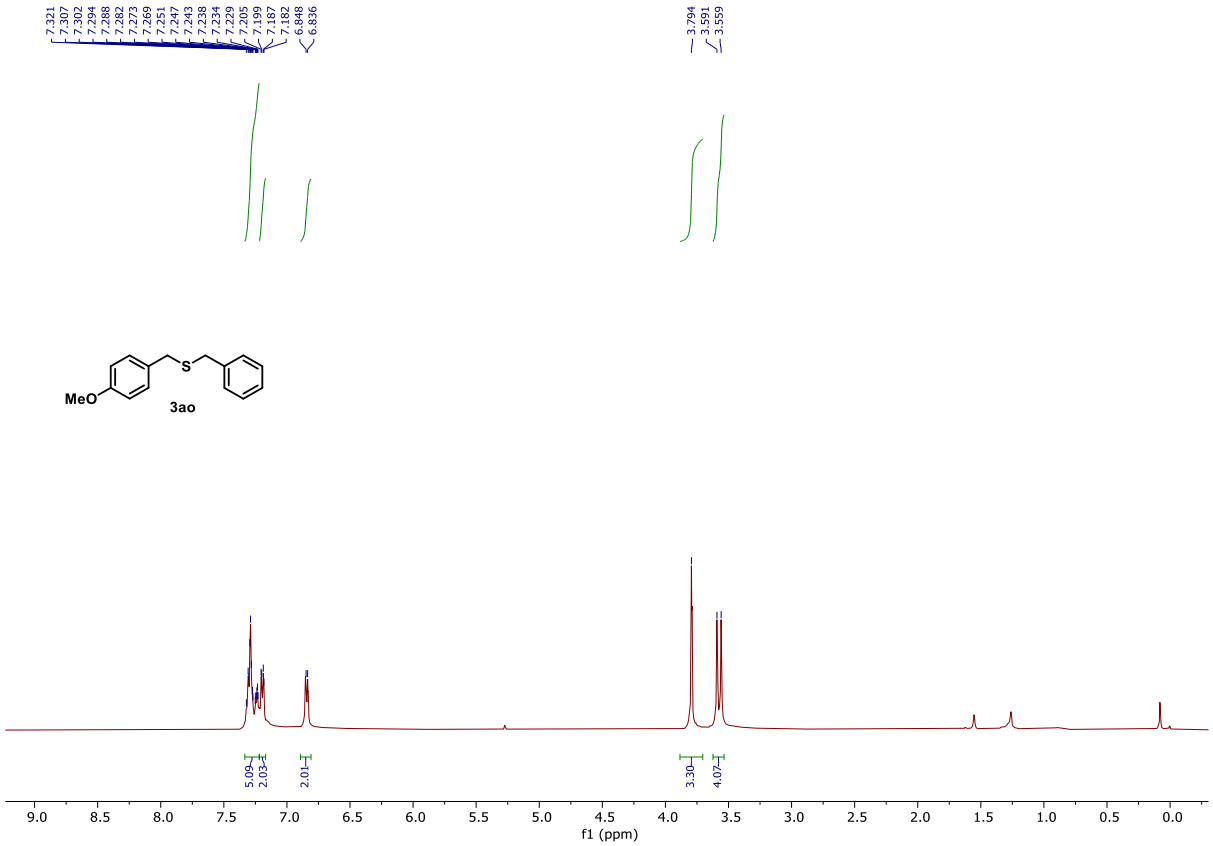


^{13}C NMR spectrum of compound 3am (126 MHz $CDCl_3$)

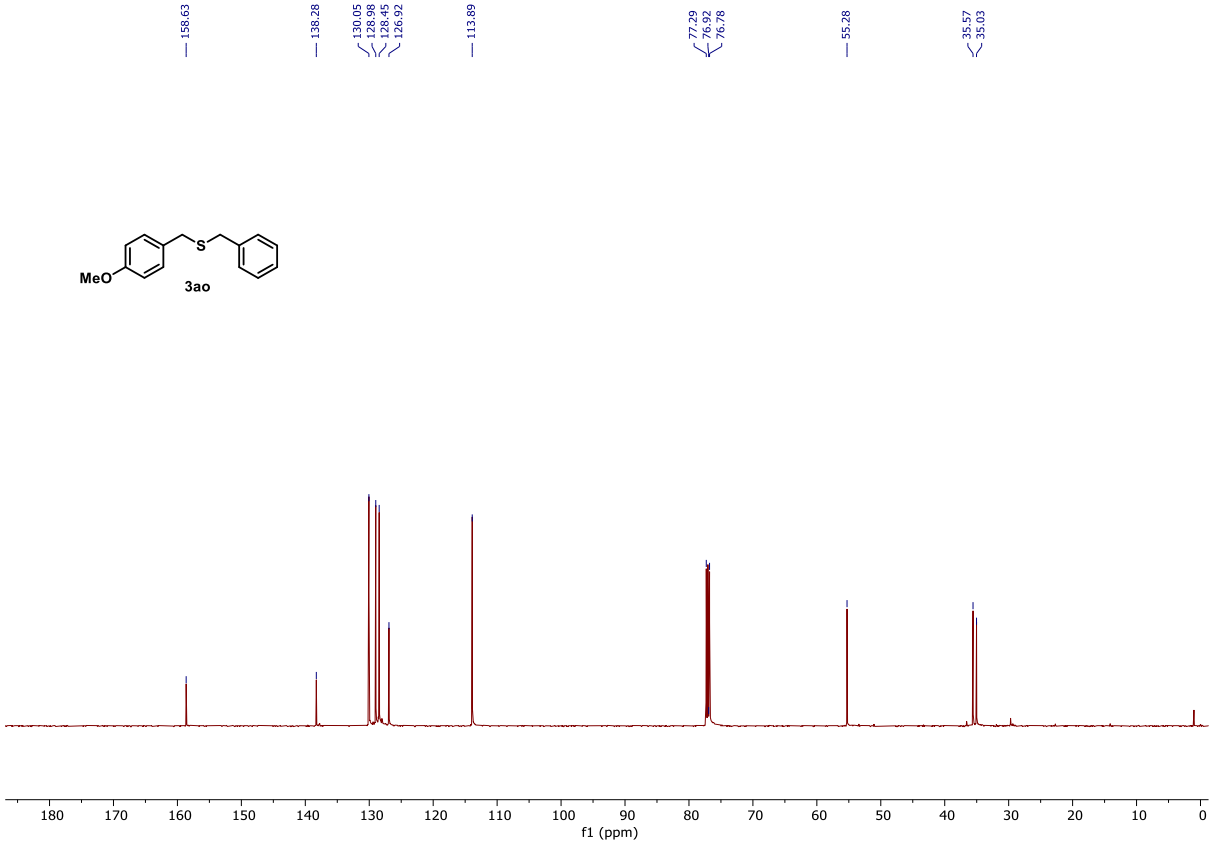


^{1}H NMR spectrum of compound 3an (600 MHz $CDCl_3$)

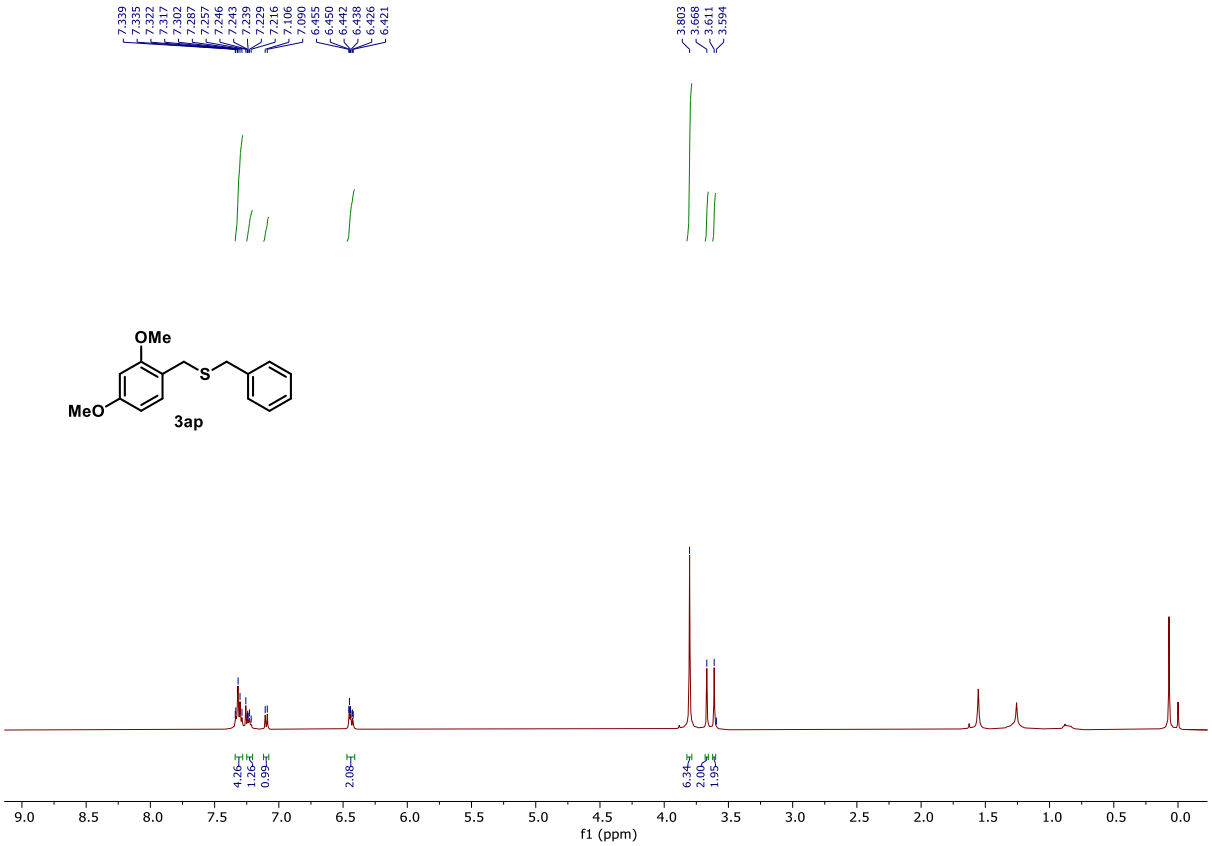
^{13}C NMR spectrum of compound 3an (151 MHz $CDCl_3$)



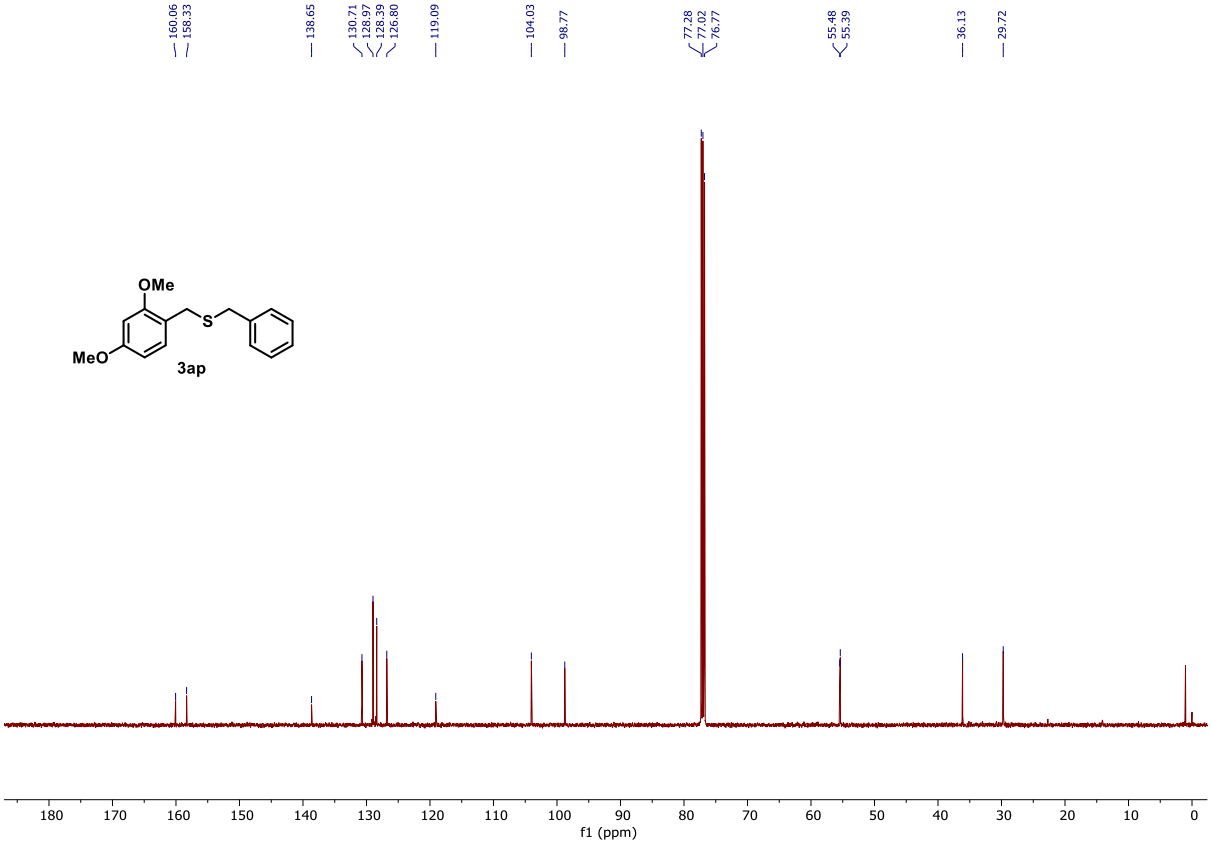
^{1}H NMR spectrum of compound 3ao (500 MHz $CDCl_3$)



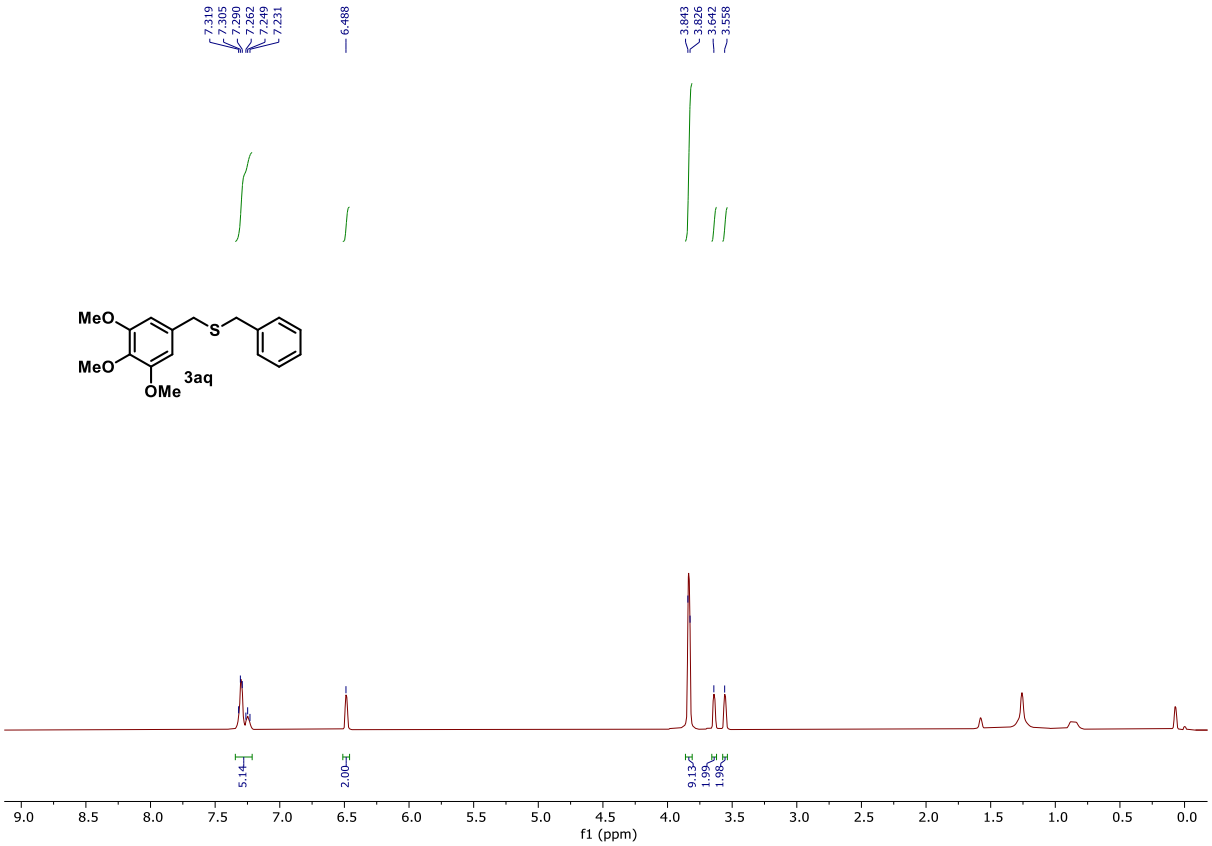
^{13}C NMR spectrum of compound 3ao (126 MHz $CDCl_3$)



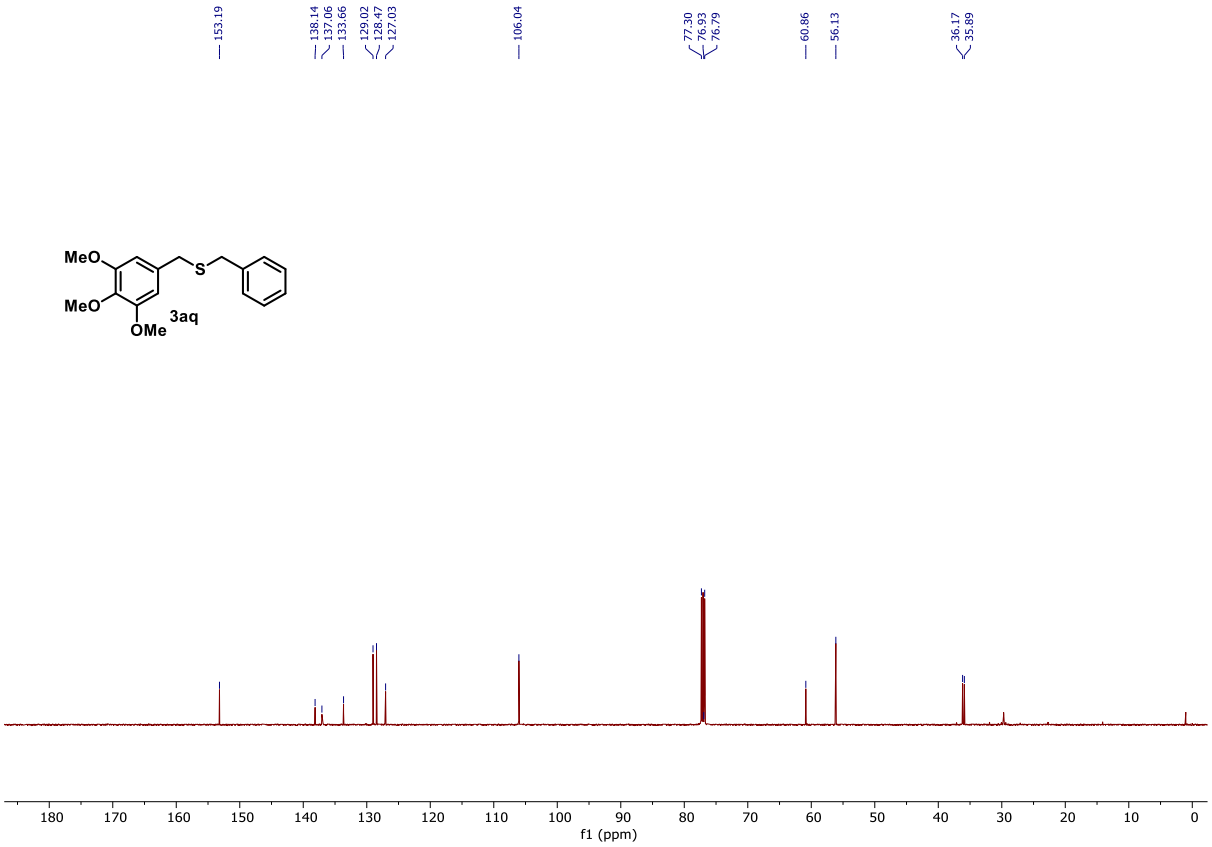
^{1}H NMR spectrum of compound 3ap (500 MHz $CDCl_3$)



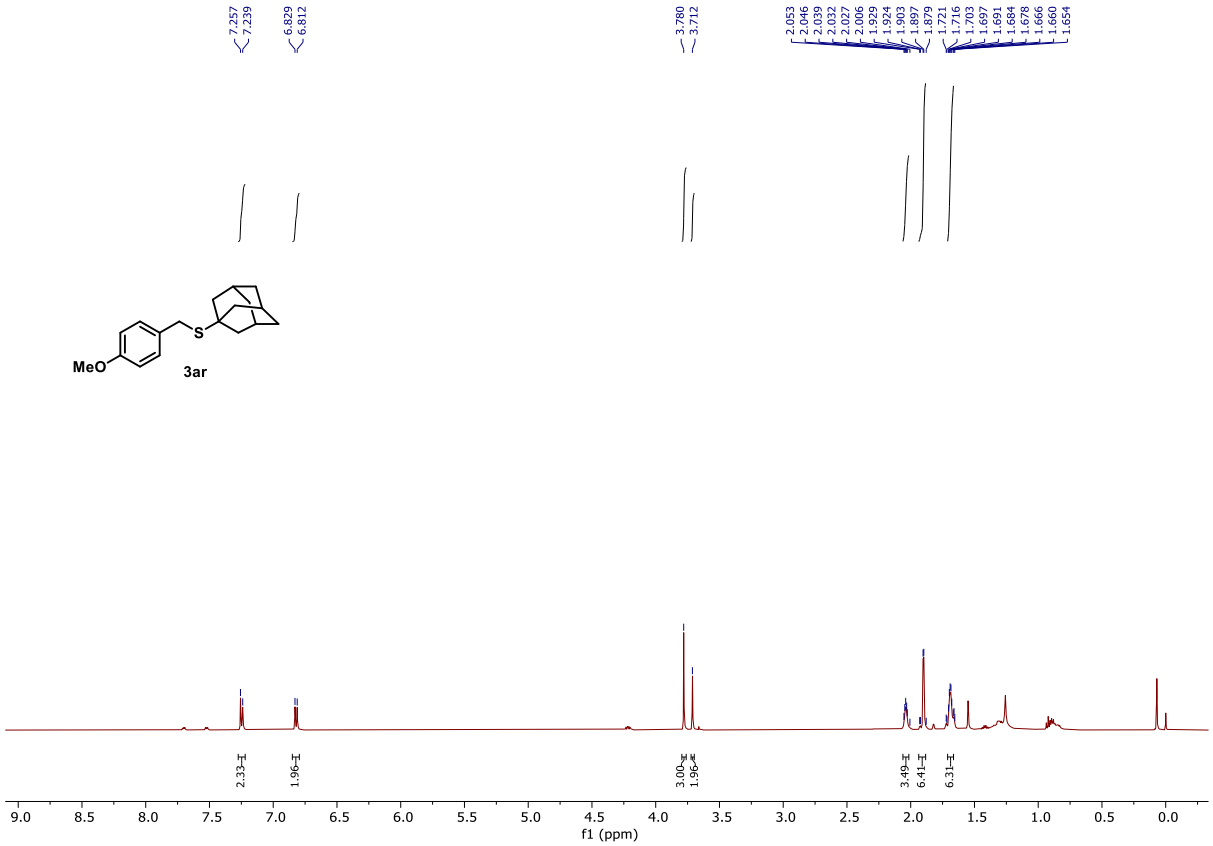
^{13}C NMR spectrum of compound 3ap (126 MHz $CDCl_3$)



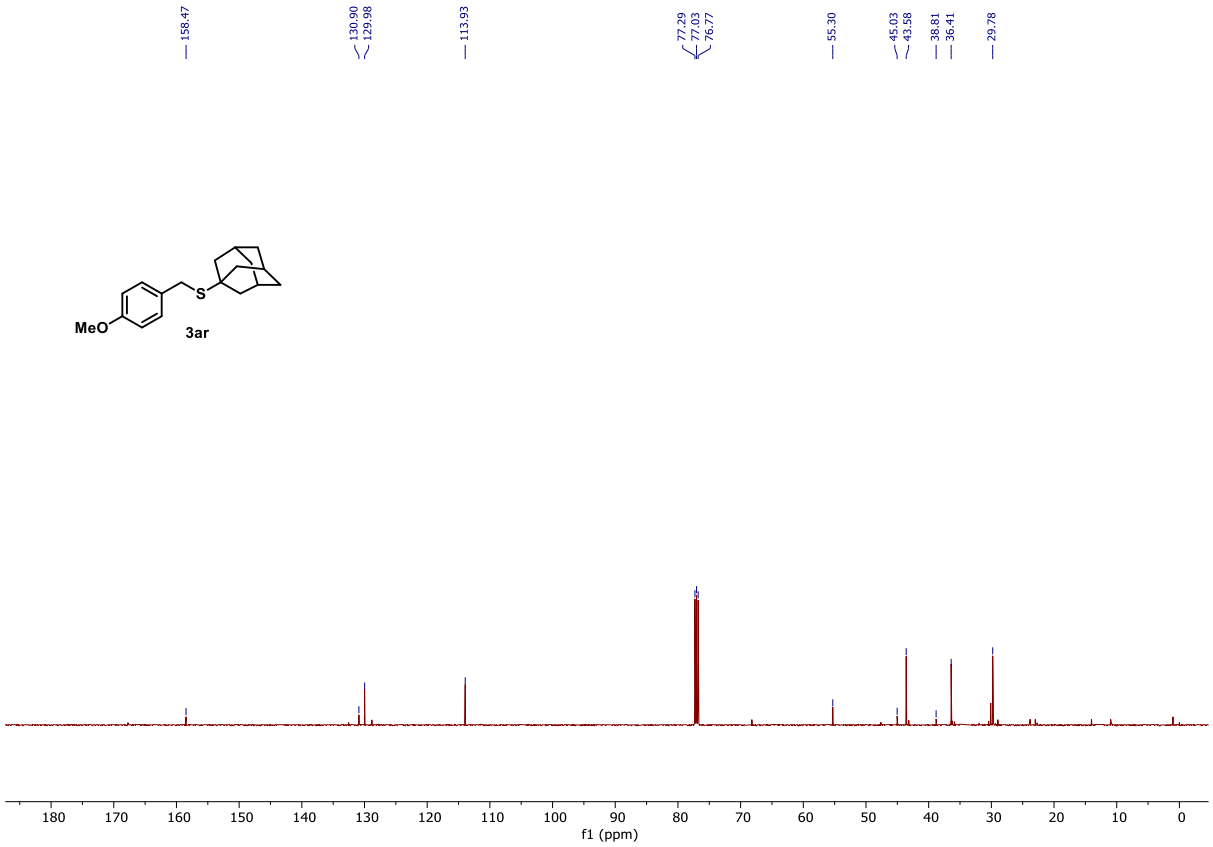
^{1}H NMR spectrum of compound 3aq (500 MHz $CDCl_3$)



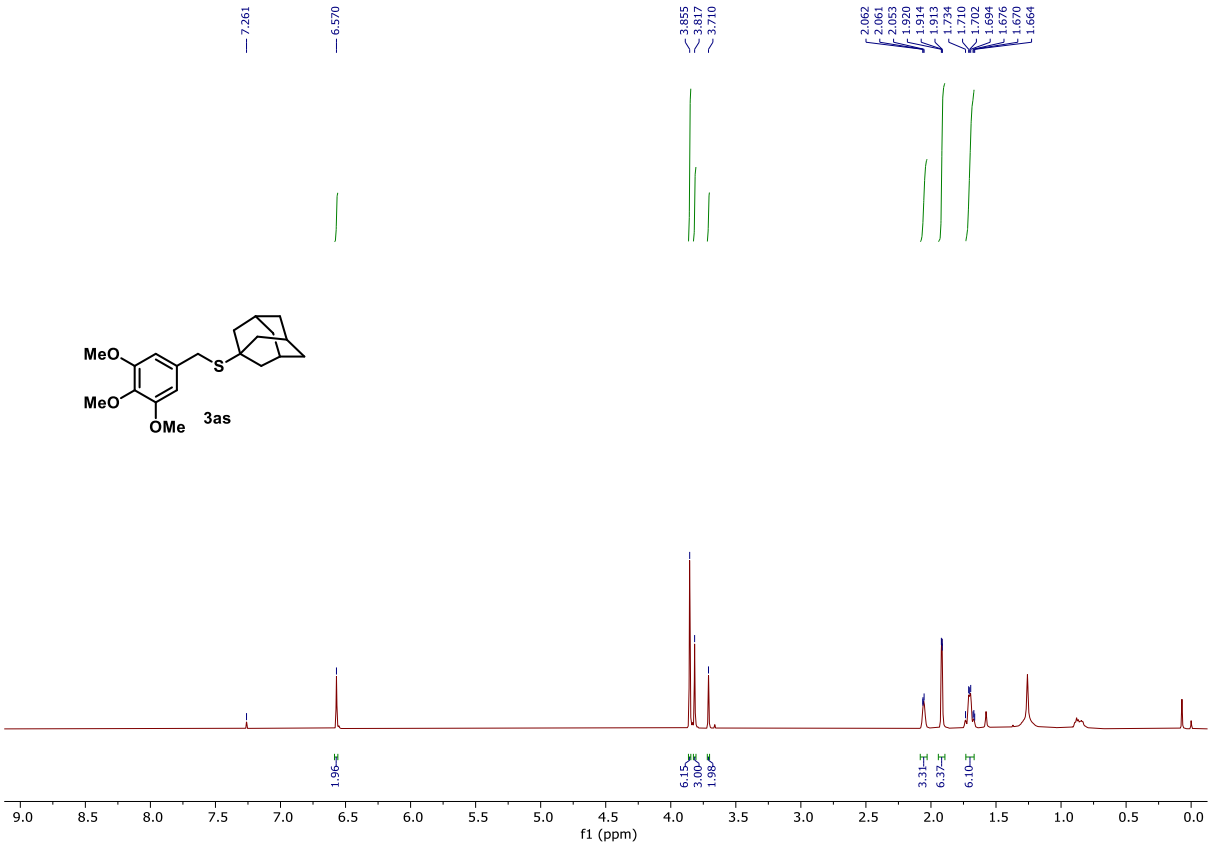
^{13}C NMR spectrum of compound 3aq (126 MHz $CDCl_3$)



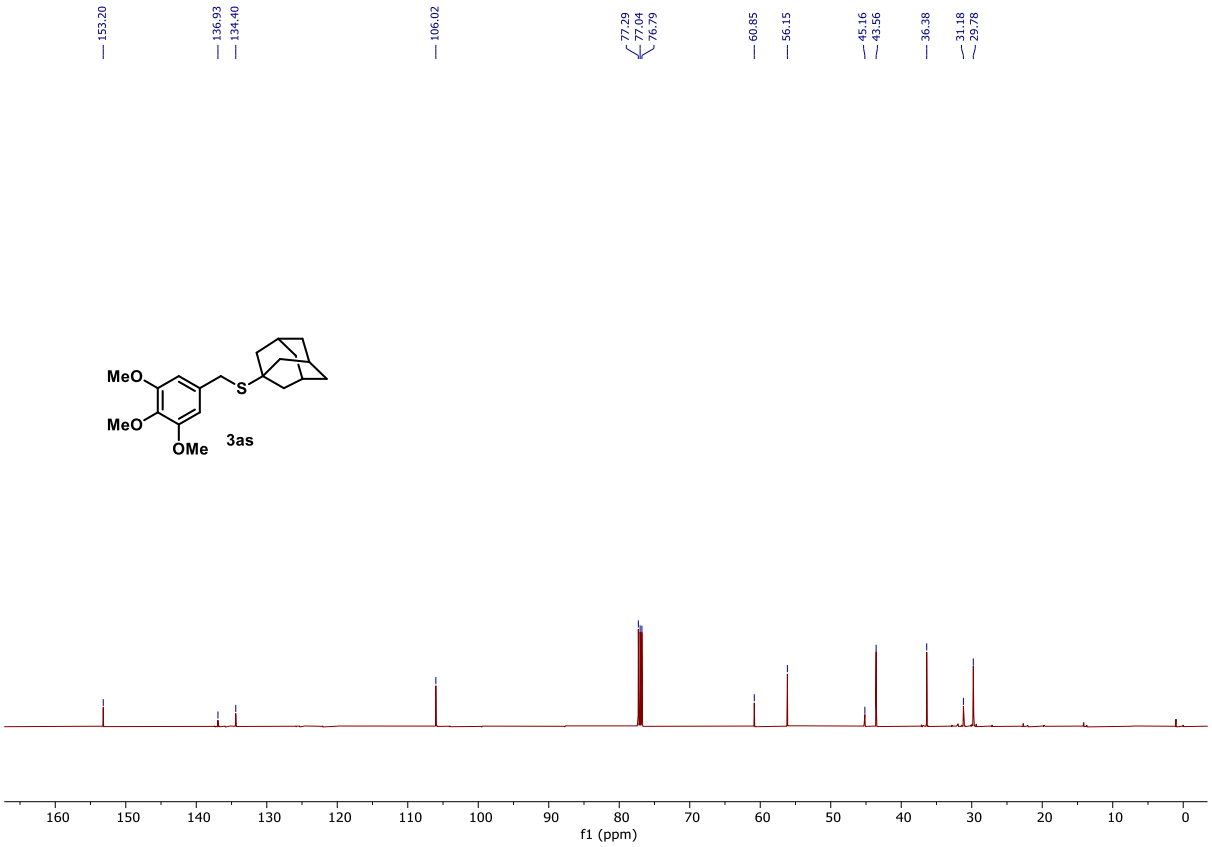
^{1}H NMR spectrum of compound 3ar (500 MHz $CDCl_3$)



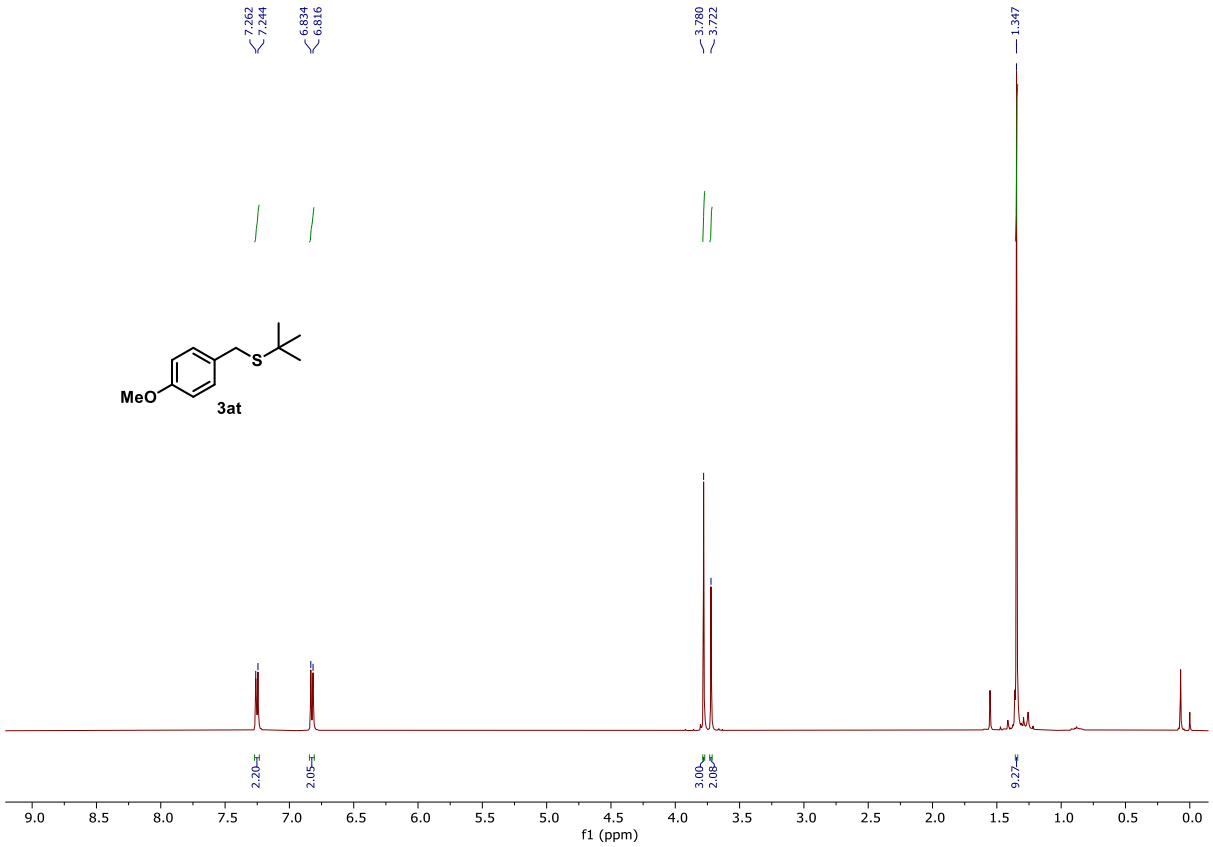
^{13}C NMR spectrum of compound 3ar (126 MHz $CDCl_3$)



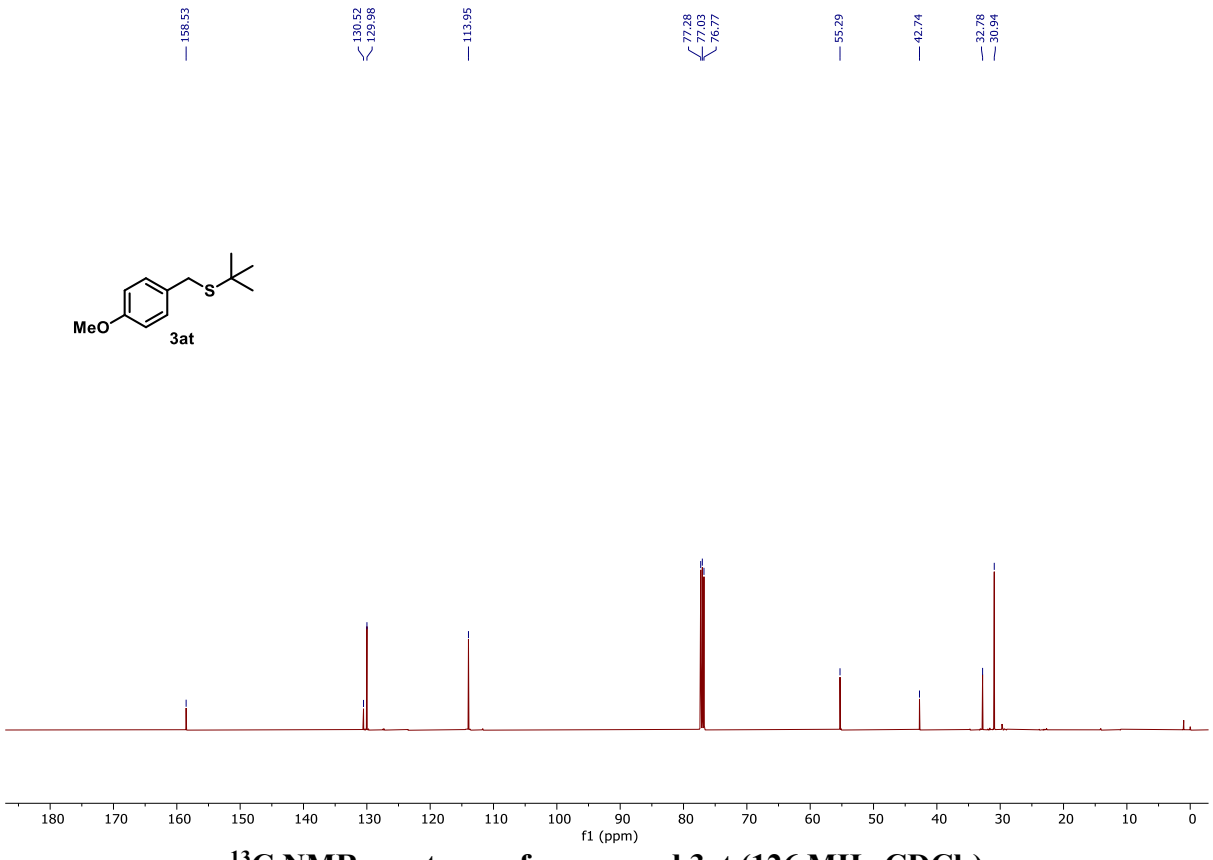
^{1}H NMR spectrum of compound 3as (500 MHz $CDCl_3$)



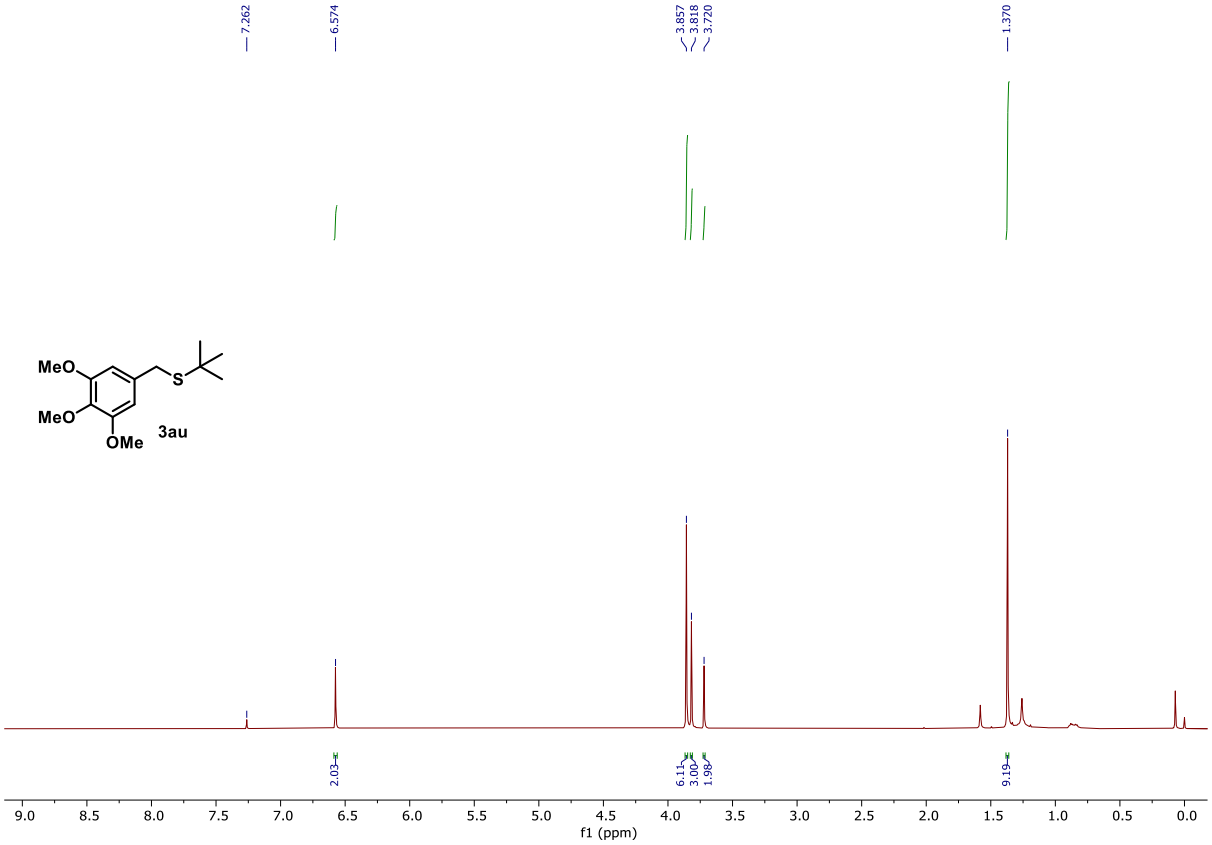
^{13}C NMR spectrum of compound 3as (126 MHz $CDCl_3$)



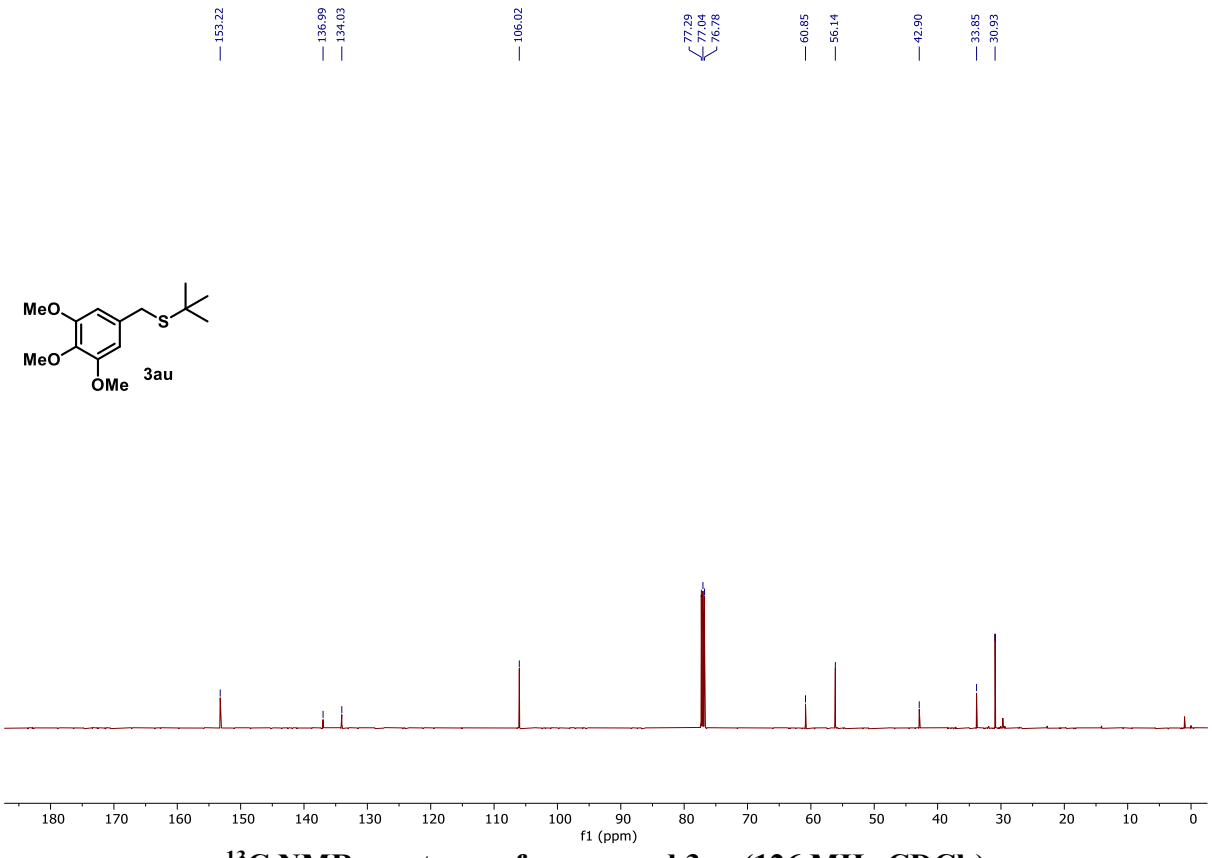
^{1}H NMR spectrum of compound 3at (500 MHz $CDCl_3$)



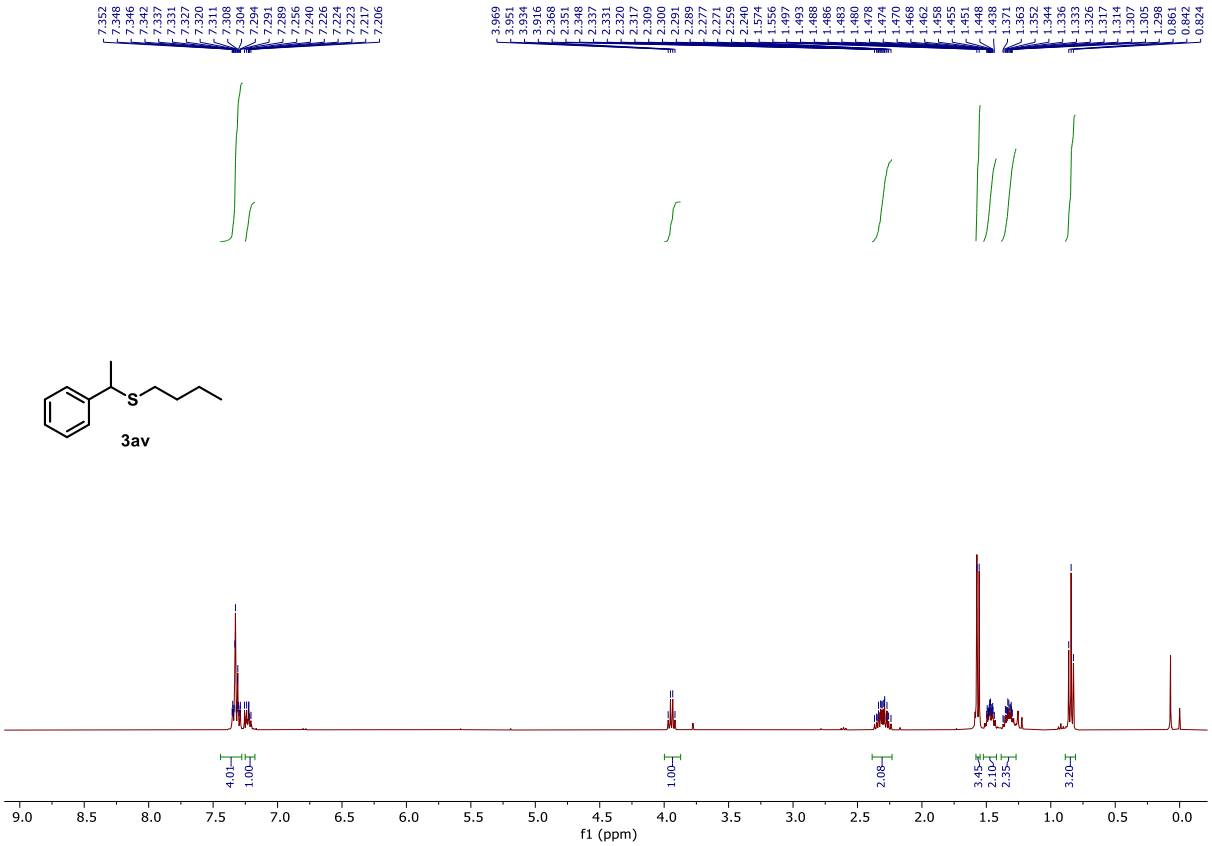
^{13}C NMR spectrum of compound 3at (126 MHz $CDCl_3$)



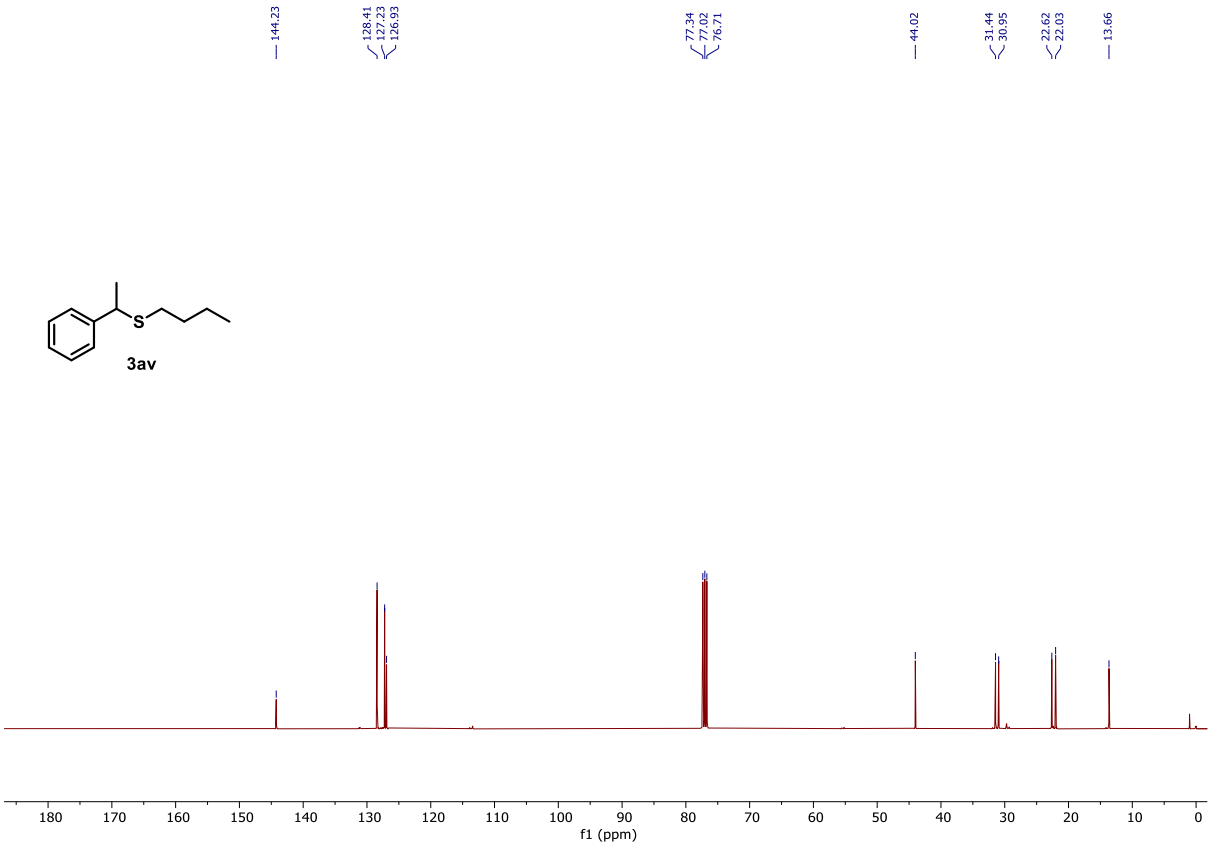
^{1}H NMR spectrum of compound 3au (500 MHz $CDCl_3$)



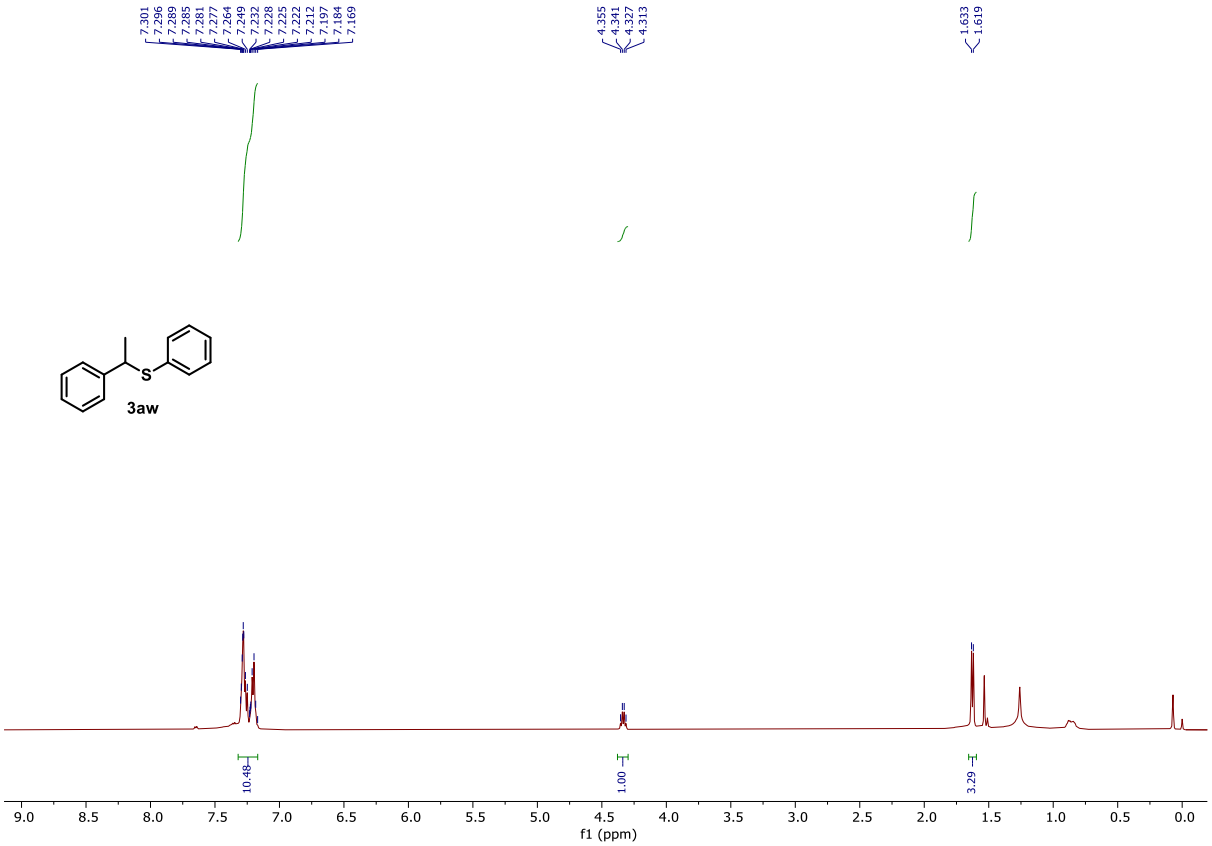
^{13}C NMR spectrum of compound 3au (126 MHz $CDCl_3$)



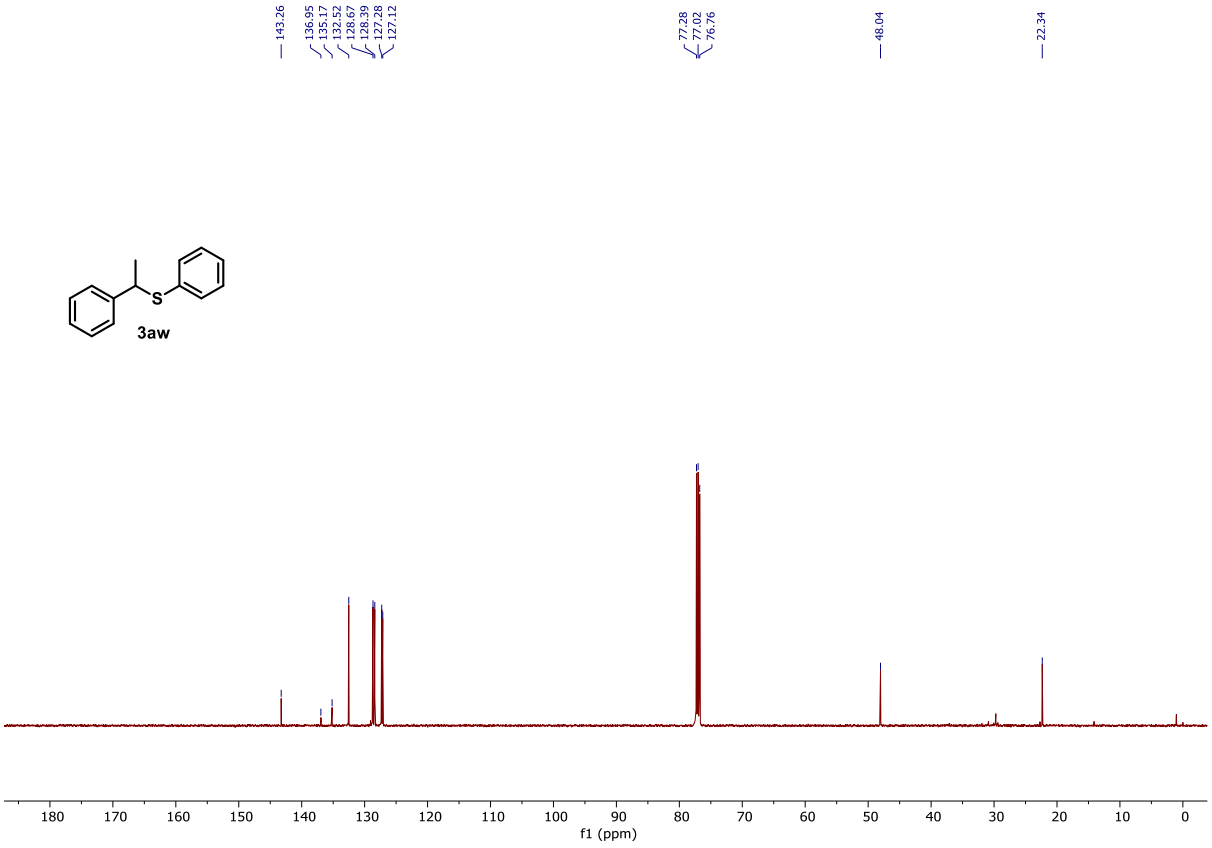
^{1}H NMR spectrum of compound 3av (400 MHz $CDCl_3$)



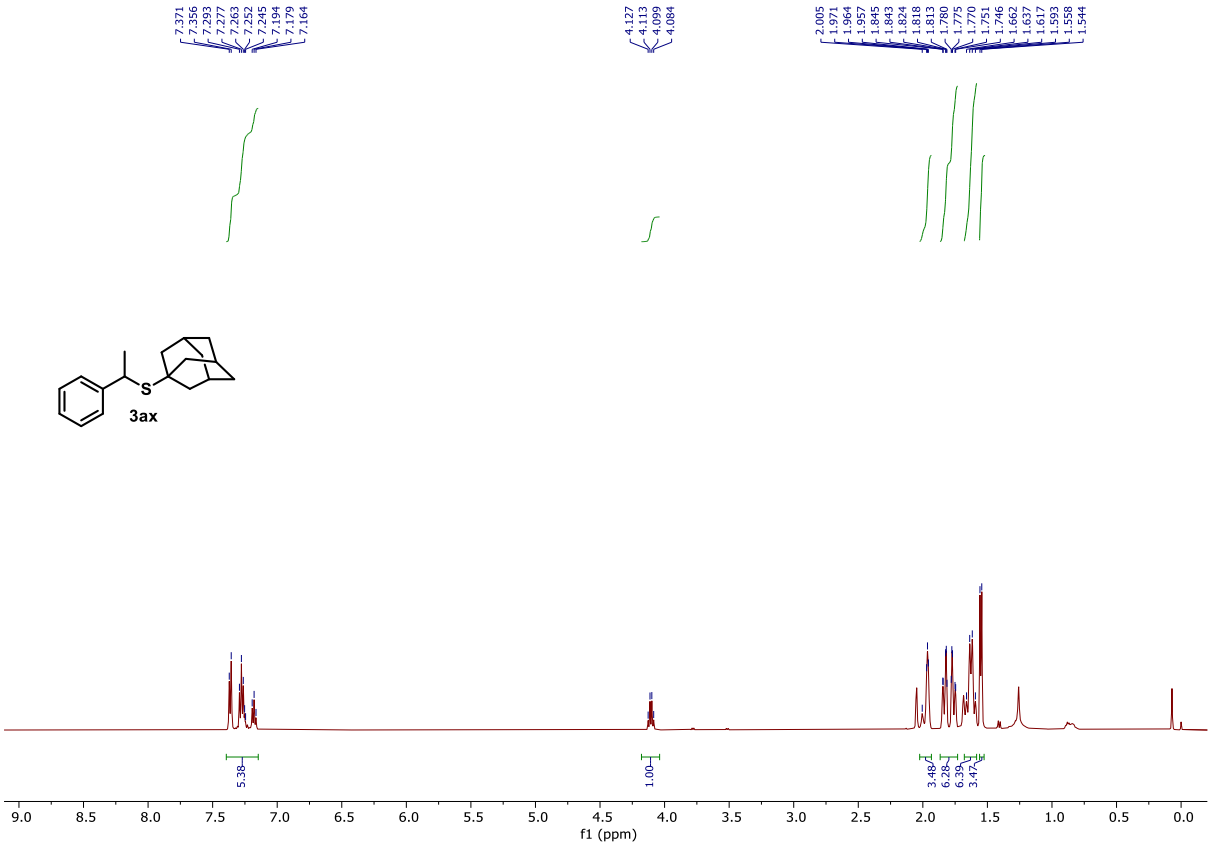
^{13}C NMR spectrum of compound 3av (101 MHz $CDCl_3$)



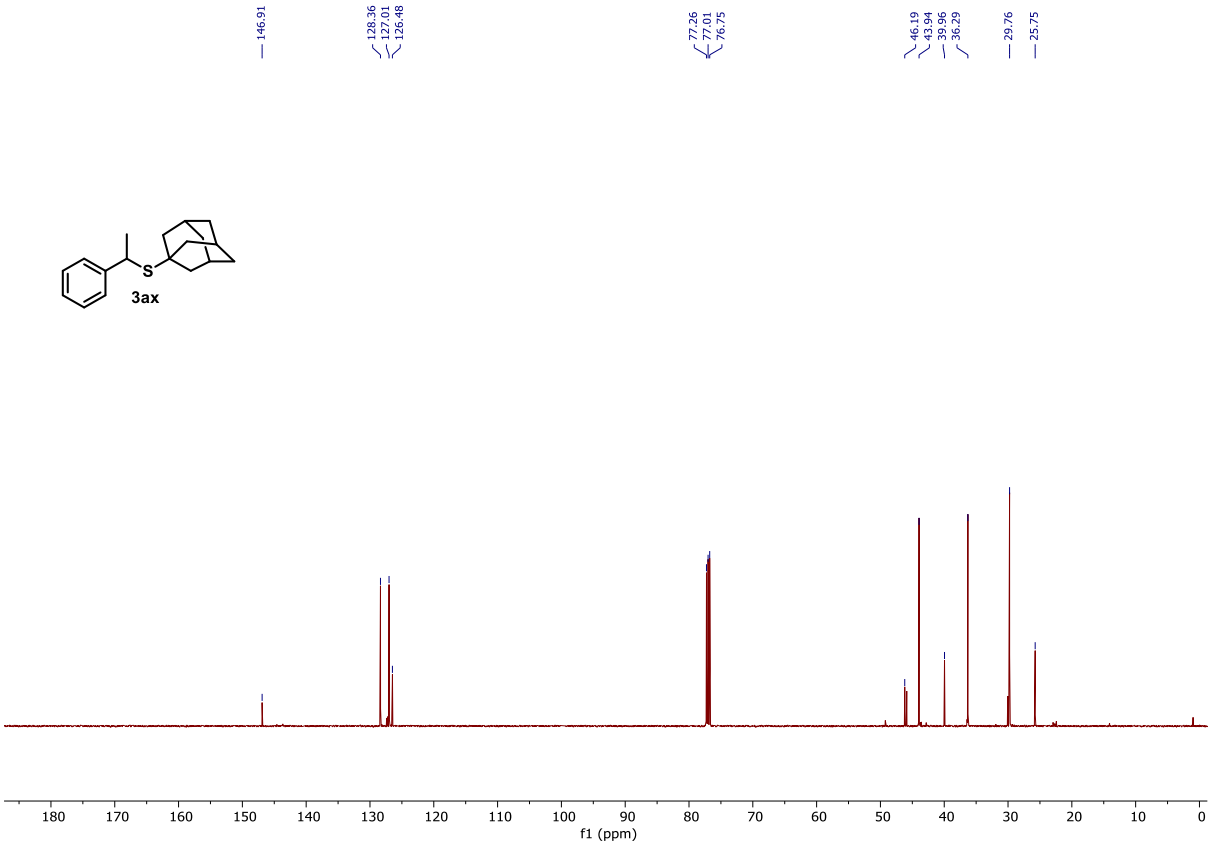
^{1}H NMR spectrum of compound 3aw (500 MHz $CDCl_3$)



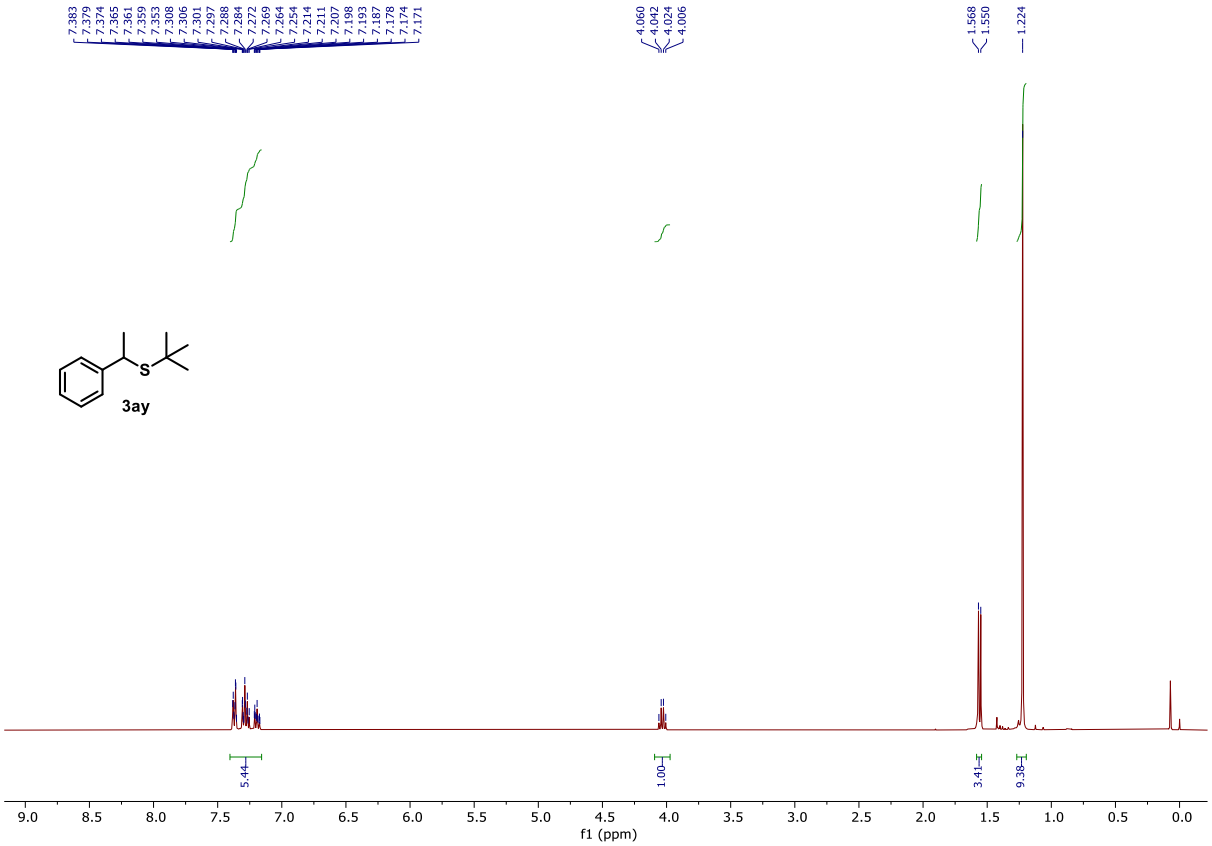
^{13}C NMR spectrum of compound 3aw (126 MHz $CDCl_3$)



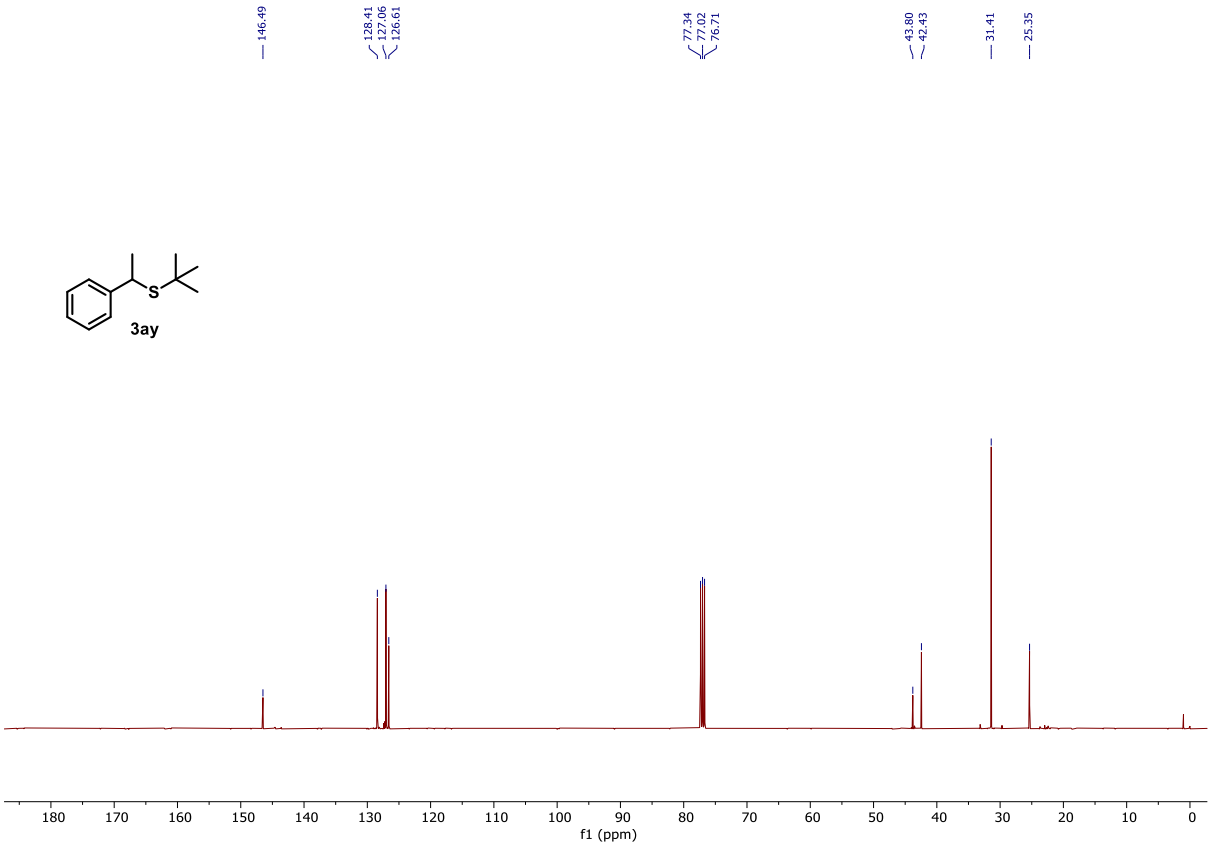
^{1}H NMR spectrum of compound 3ax (500 MHz $CDCl_3$)



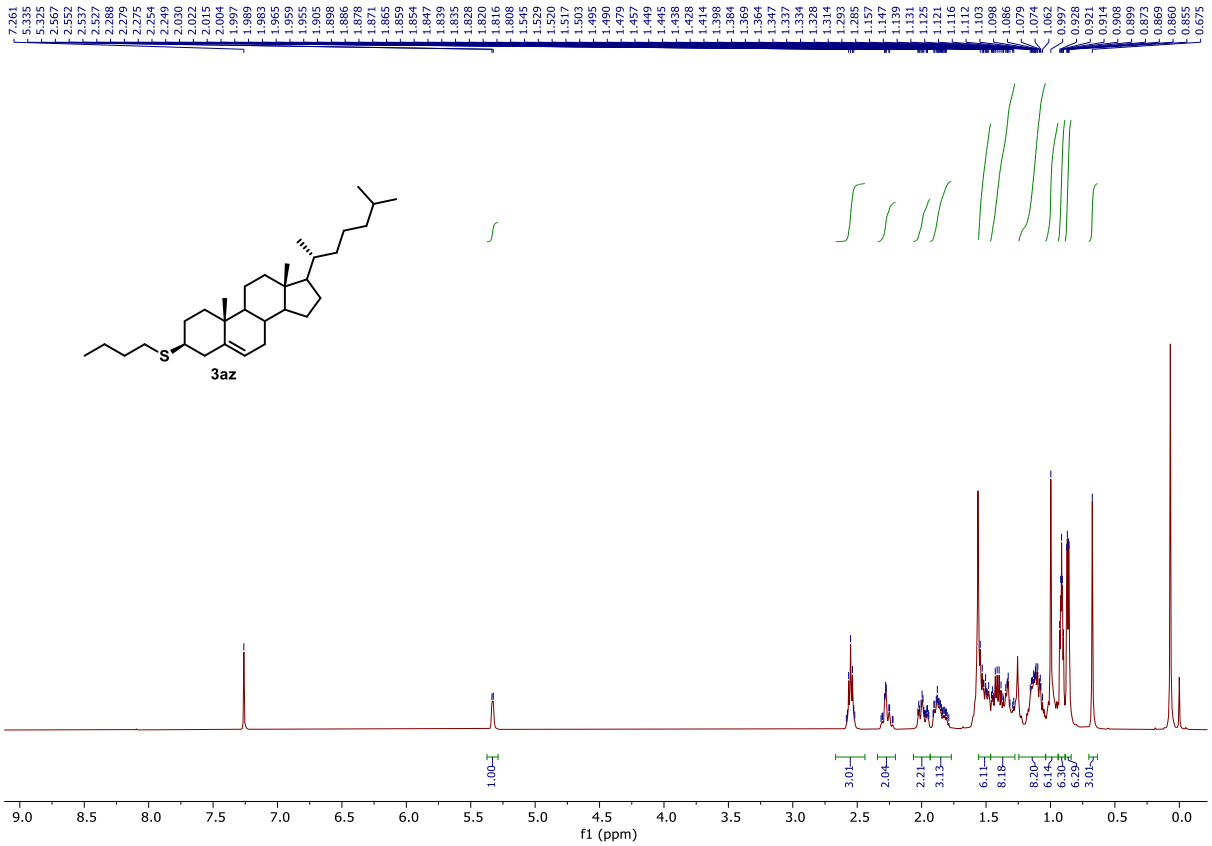
^{13}C NMR spectrum of compound 3ax (126 MHz $CDCl_3$)



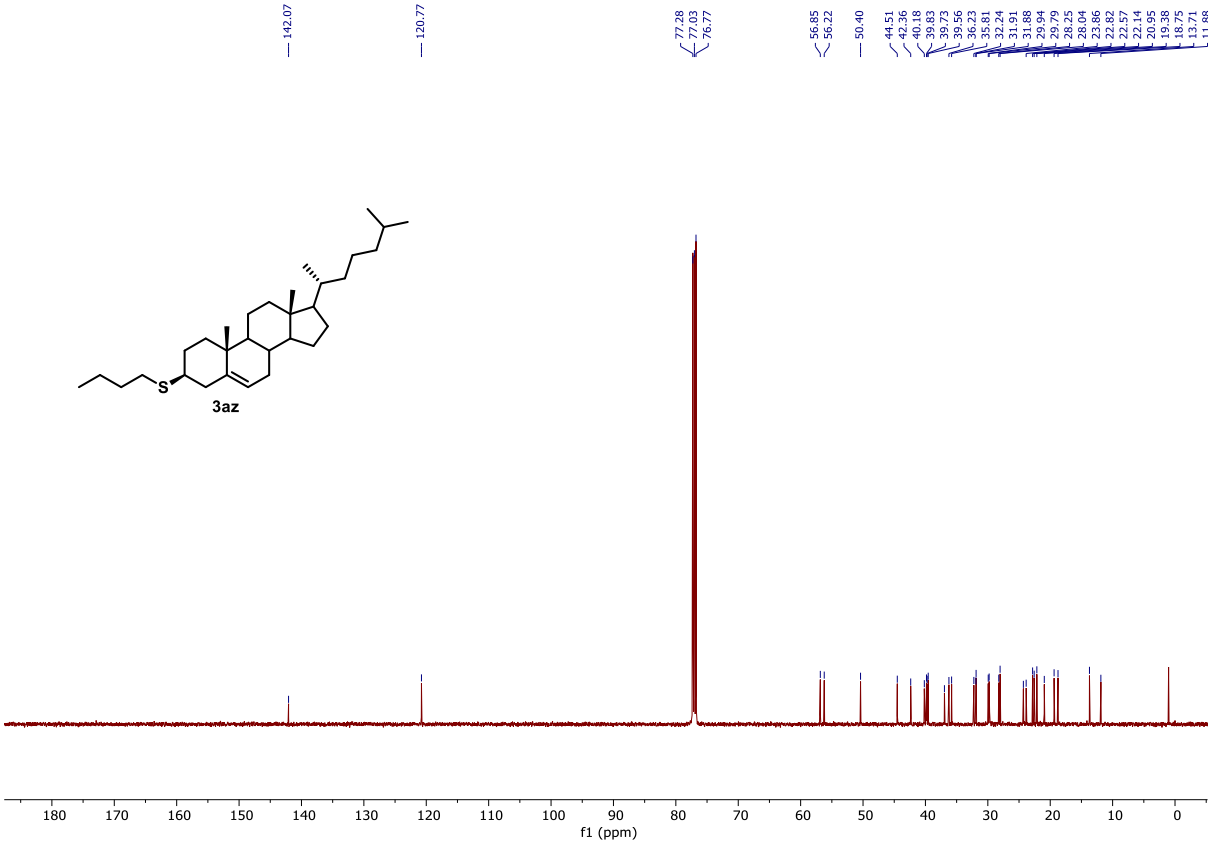
^{1}H NMR spectrum of compound 3ay (400 MHz $CDCl_3$)



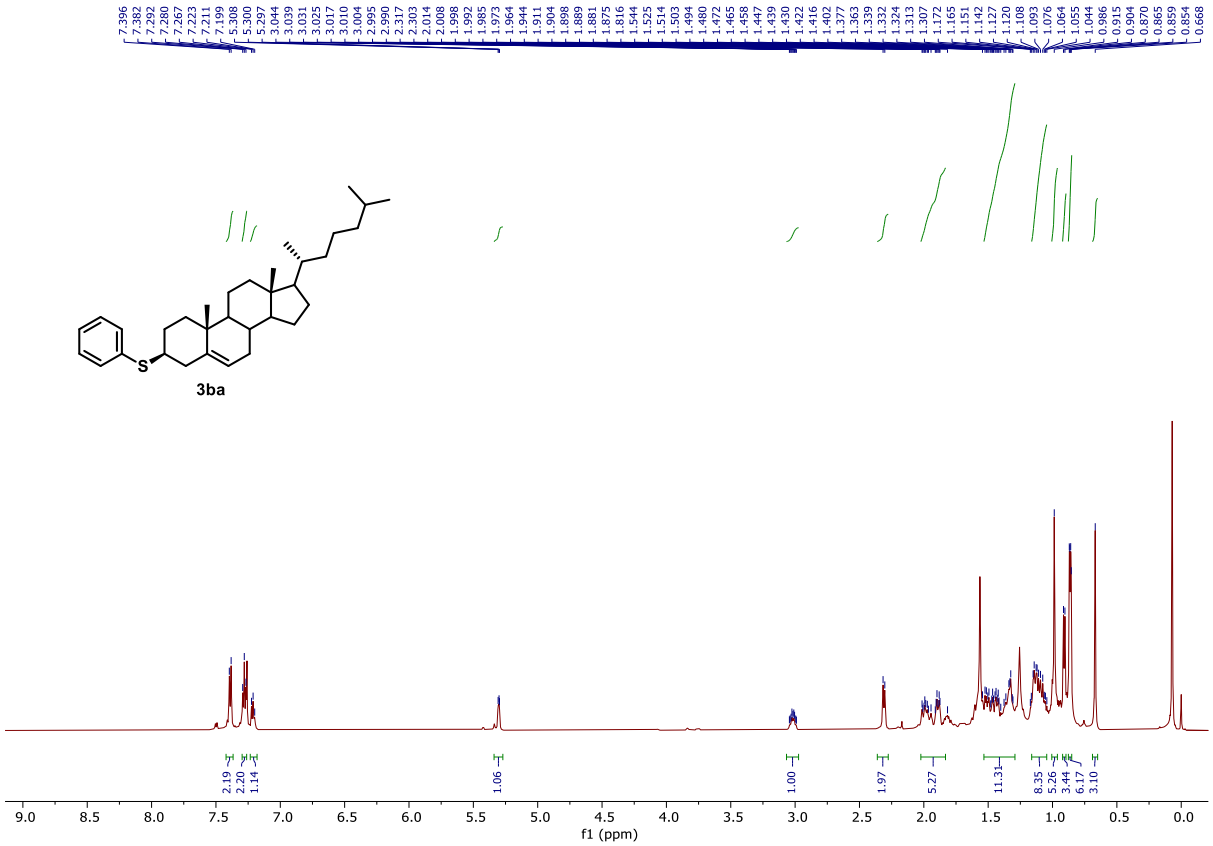
^{13}C NMR spectrum of compound 3ay (101 MHz $CDCl_3$)



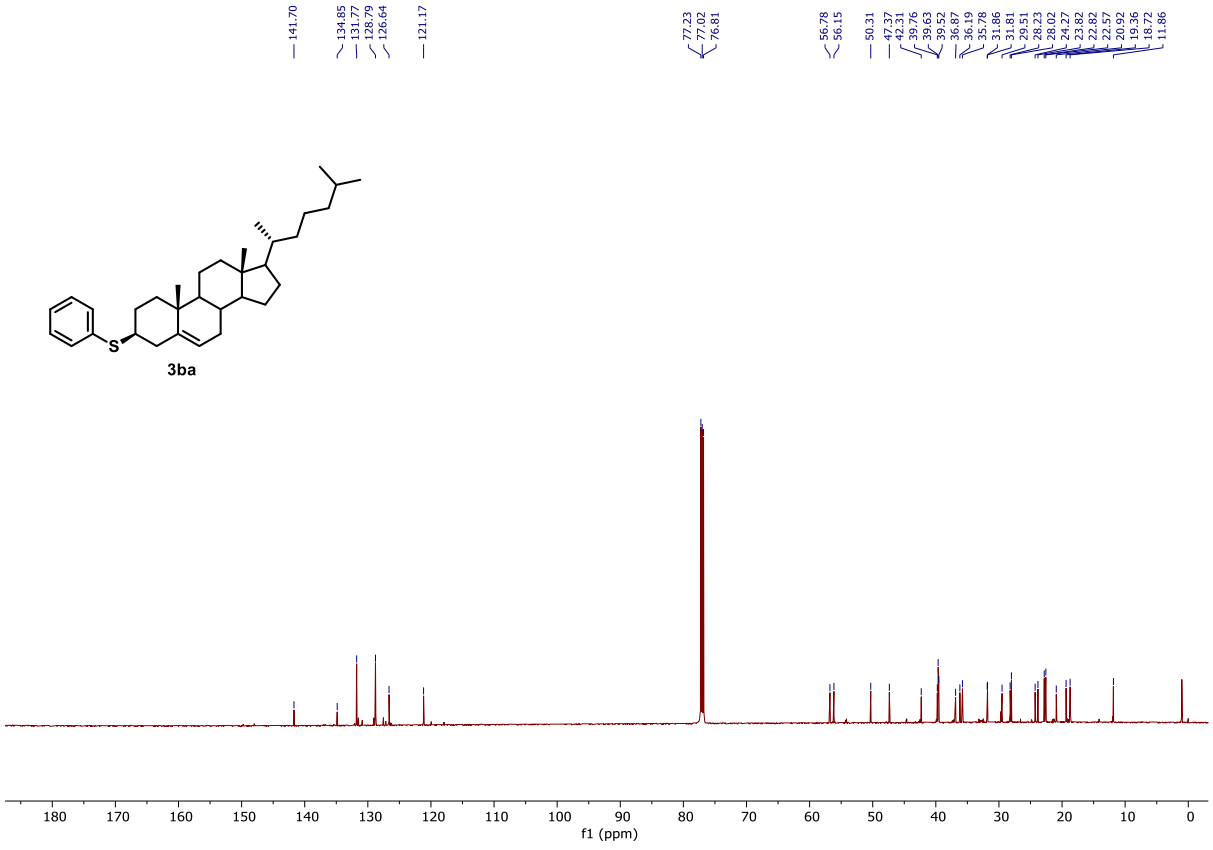
^{1}H NMR spectrum of compound 3az (500 MHz $CDCl_3$)



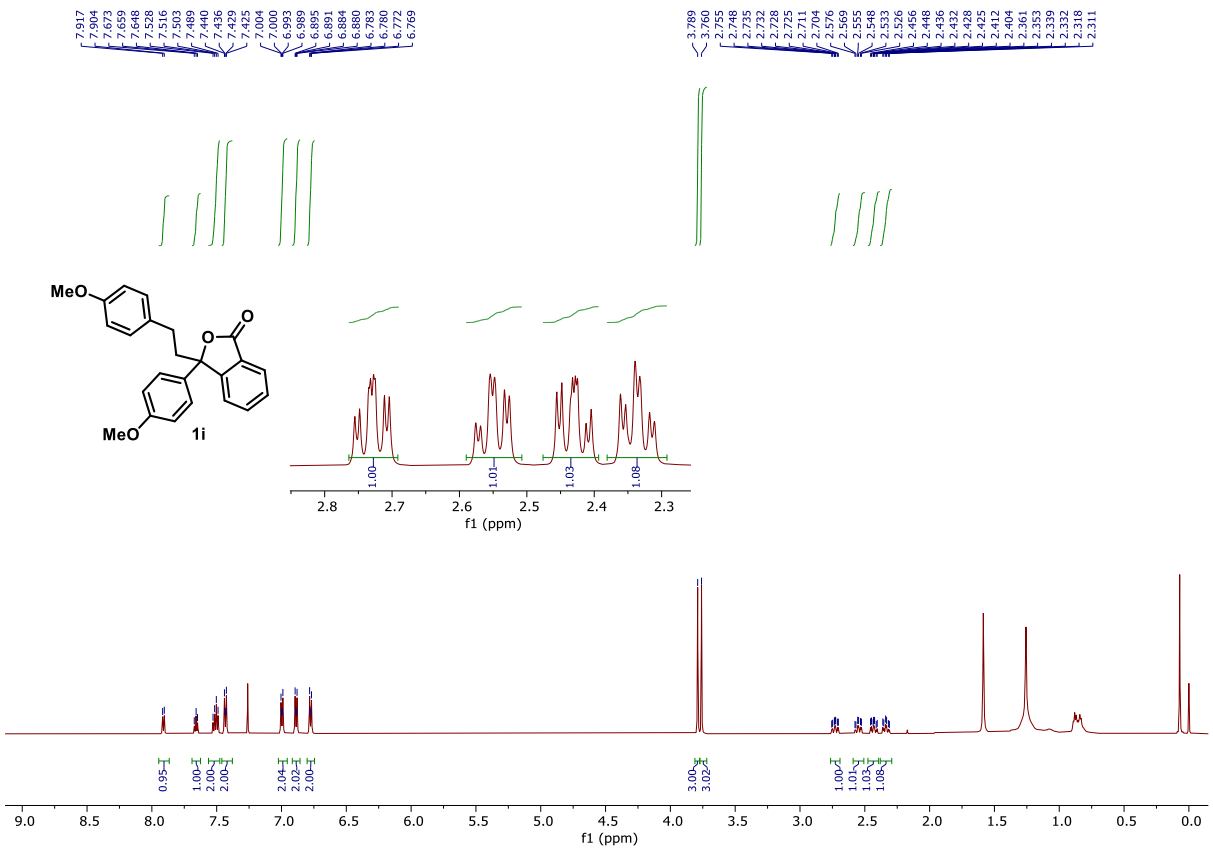
^{13}C NMR spectrum of compound 3az (126 MHz $CDCl_3$)



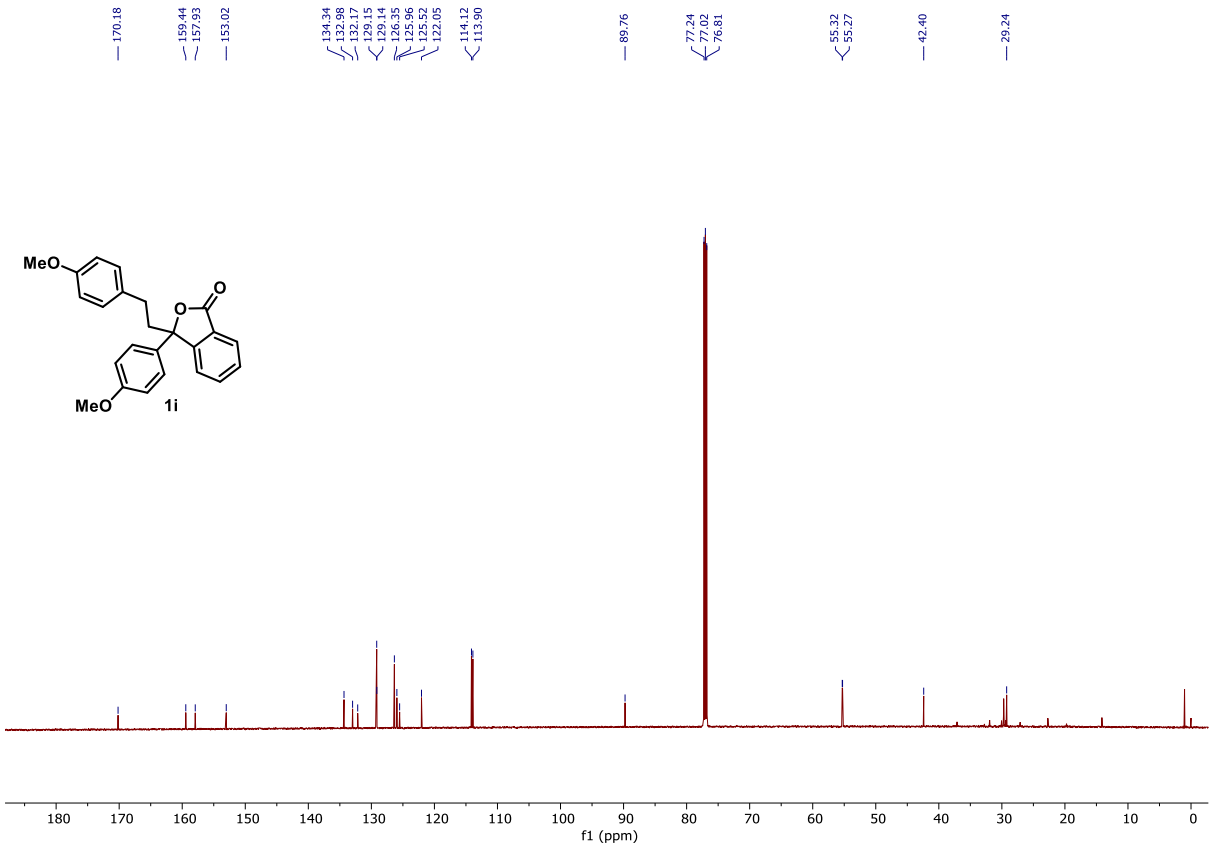
^{1}H NMR spectrum of compound 3ba (600 MHz $CDCl_3$)



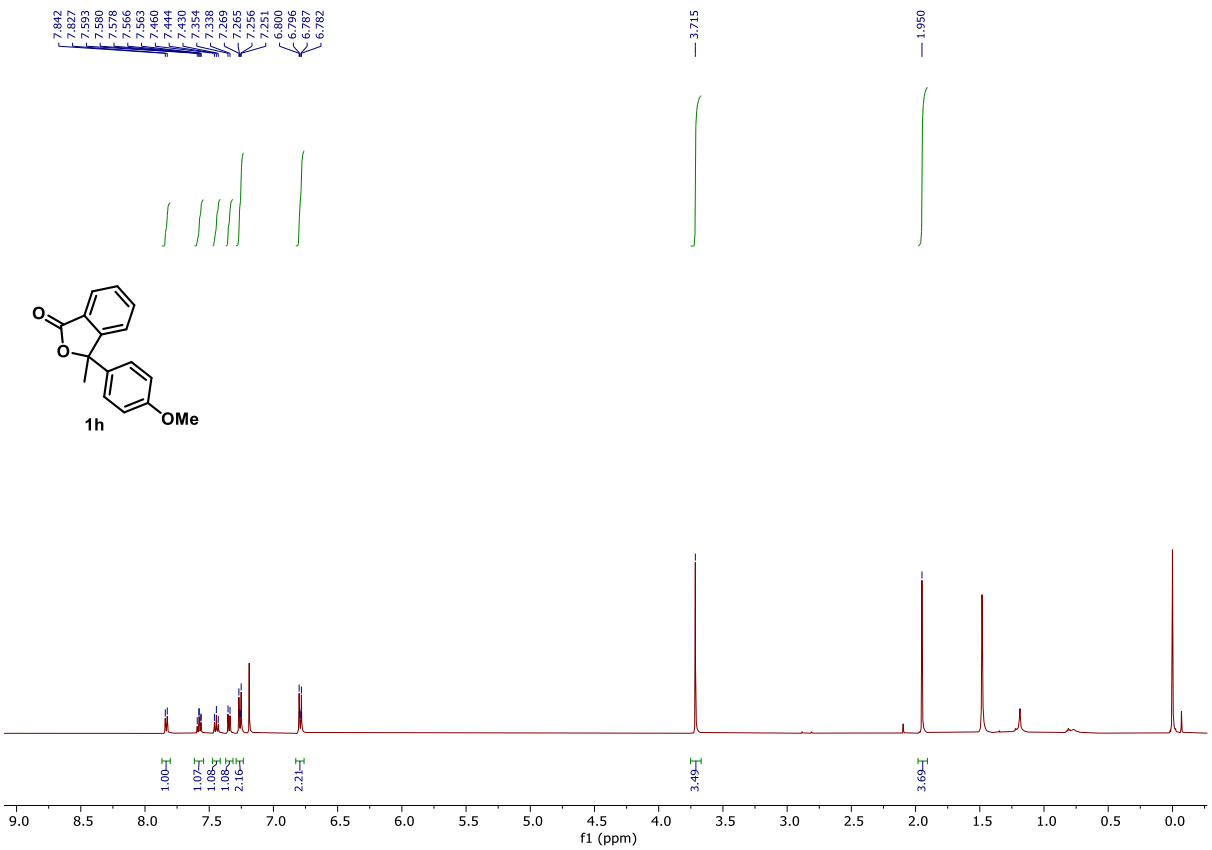
^{13}C NMR spectrum of compound 3ba (151 MHz $CDCl_3$)



^{1}H NMR spectrum of compound 1i (600 MHz $CDCl_3$)

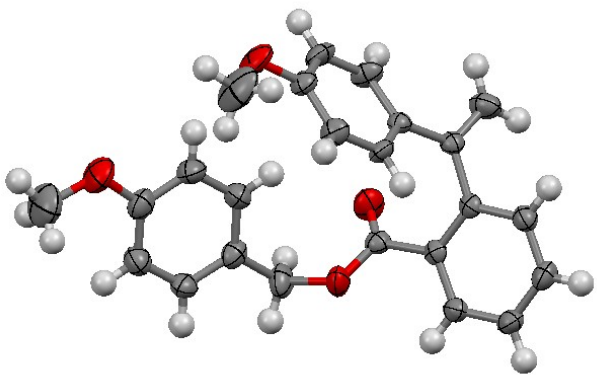


^{13}C NMR spectrum of compound 1i (151 MHz $CDCl_3$)



^{1}H NMR spectrum of compound 1h (500 MHz $CDCl_3$)

Crystal data of 1a:



The slow diffusion obtained a single crystal of compound **1a** from the solution in dichloromethane layered with n-hexane at room temperature.

Empirical formula	C_{24} H_{22} O_4
Formula Weight	374.42
Temperature/K	273
Crystal system	monoclinic
Space group	P 2_1
a/Å	7.2137 (5)
b/Å	6.6371(5)
c/Å	20.4802(15)
α/°	90
β/°	95.575(2)
γ/°	90
Volume/$Å^3$	975.91(12)
Z	2
ρ_{calc}**g/**cm^{-3}	1.274
μ/mm^{-1}	0.086
F/000	396.0
Radiation	Mo Kα (λ = 0.71073)
h,k,l/max	8,7,24
Data completeness	1.82/1.00
θ/max	24.997
R/reflections	0.0681(3141)
wR2/reflections	0.1882(3416)
S	1.133
N (par)	255

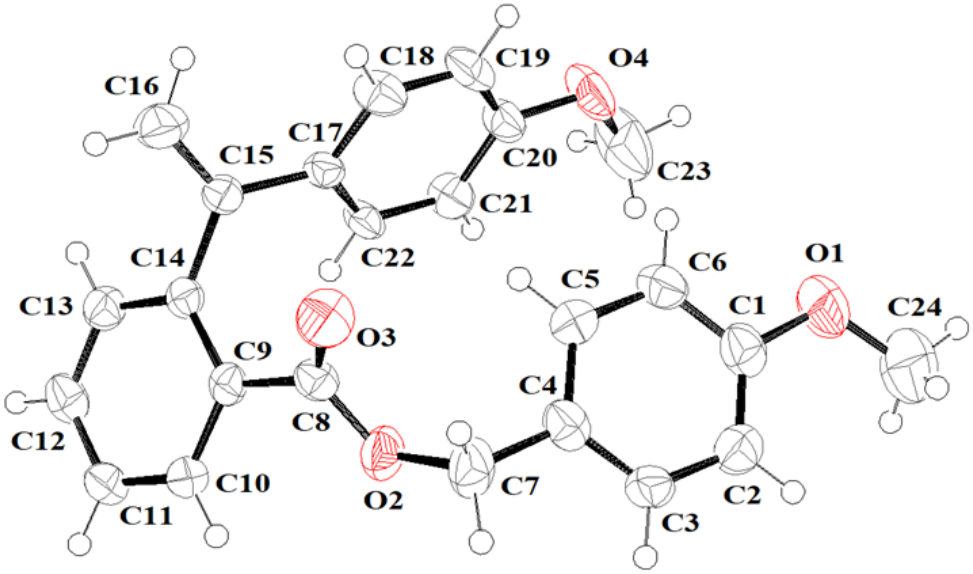
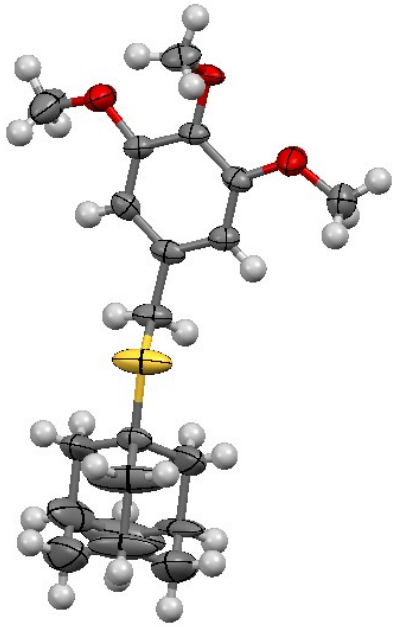


Figure: Ortep view of **1a**. The thermal ellipsoid contour probability level is 50%

Crystal data of 3as:



The slow diffusion obtained a single crystal of compound **3as** from the solution in dichloromethane layered with n-hexane at room temperature.

Empirical formula	C_{20} H_{28} O_3 S
Formula Weight	348.48
Temperature/K	273
Crystal system	monoclinic
Space group	P 2_1
a/Å	12.5684 (18)
b/Å	10.8101 (19)
c/Å	13.734 (3)
α/°	90
β/°	93.963 (15)
γ/°	90
Volume/$Å^3$	1861.5 (6)
Z	4
ρ_{calc}**g**/cm^{-3}	1.243
μ/mm^{-1}	0.188
F/000	752.0
Radiation	Mo Kα (λ = 0.71073)
h,k,l/max	14, 12, 16
Data completeness	0.992
θ/max	24.998
R/reflections	0.0851 (1116)
wR2/reflections	0.2251 (3250)
S	0.938
N (par)	220

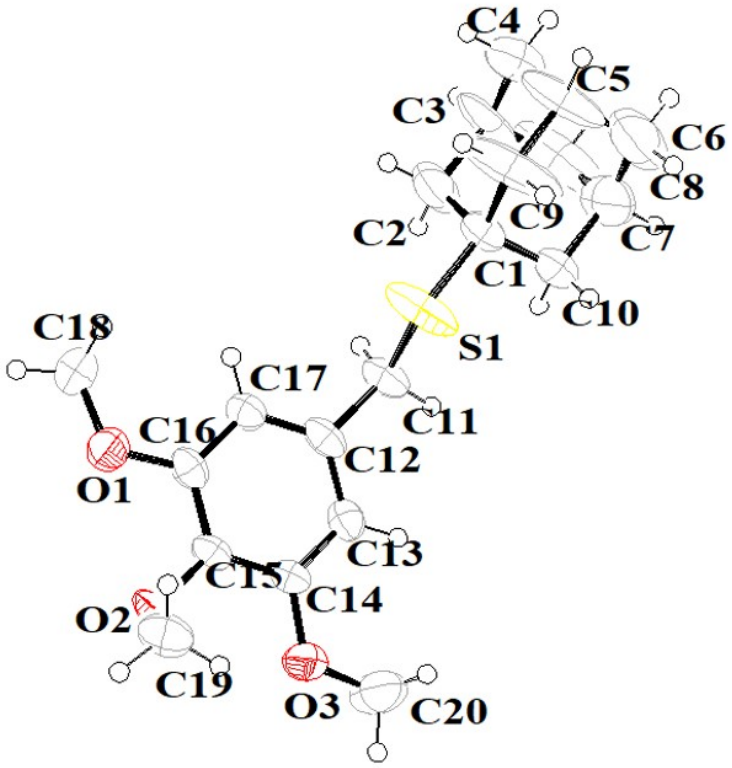


Figure: Ortep view of **3as**. The thermal ellipsoid contour probability level is 50%

Author's Response:

The crystal was grown numerous times in various possible ways, but it did not serve for data gathering; yet, the reported data is superior to other data collected.