Supporting Information

Direct Organocatalytic Esterification of Carboxylic Acids and Alcohols by Redox Neutral Sulfur (IV) Catalysis *via* Intramolecularly Interrupted Pummerer Intermediates.

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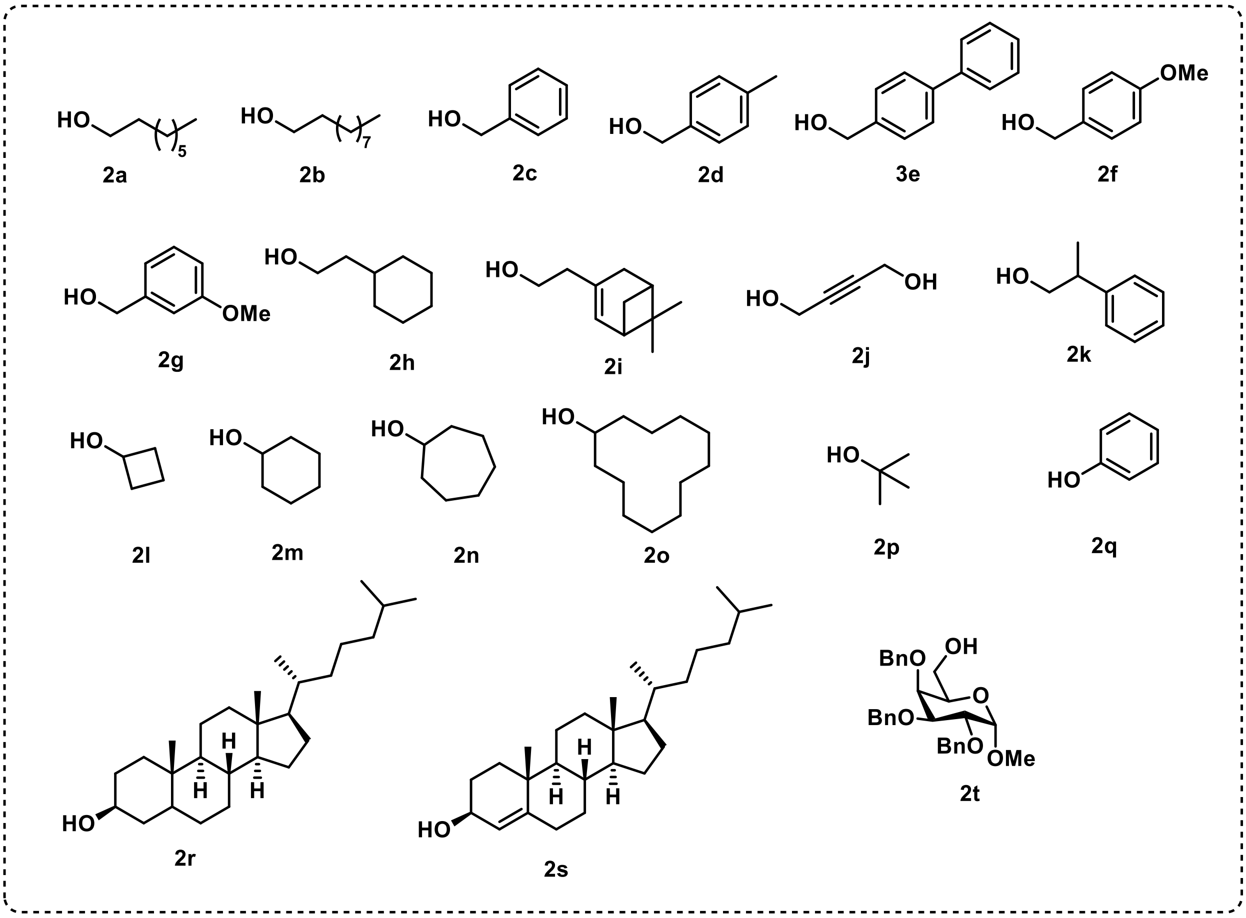
General Information

All solvents used were in commercial grade for the reaction without further purification. Reagents were purchased from Sigma-Aldrich, Merck, Spectro-chem, Alfa Aesar, Loba, BLD Pharm. and used without further purification.

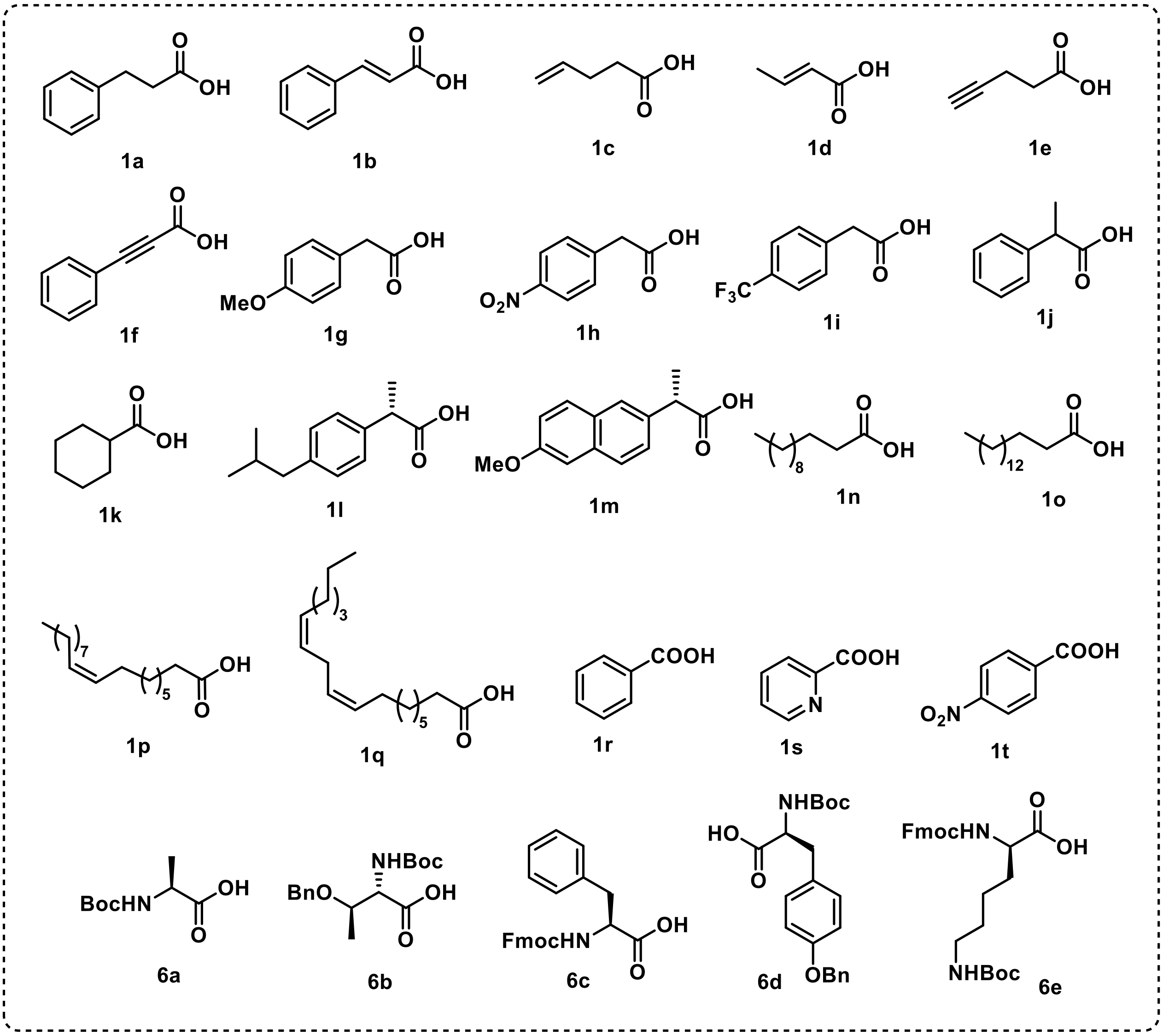
Analysis and characterization

Reactions were monitored by TLC on Kiesel-gel 60 F254 (Merck). Detection was done by examination under UV light (254 nm) and by charring with 10% sulfuric acid in water. Purification was performed in the normal phase using silica gel [Merck, 60-120 mesh]. Extracts were concentrated in vacuo using both Büchi rotary evaporators (bath temperatures up to 40°C) at a pressure of either 15 mmHg (diaphragm pump) and 0.7 mmHg (oil pump), at room temperature. ^{1}H and ^{13}C NMR were recorded on a Bruker 600MHz, 500MHz and 400MHz spectrometer using $CDCl_3$ as solvent. Chemical shift values are reported in ppm with the solvent as the internal standard ($CDCl_3$: δ 7.26 for 1H, δ 77.16 for 13C). Data are reported as follows: chemical shifts (δ), multiplicity (s = singlet, d = doublet, dd = double of doublet, ddd = 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 High-Resolution Mass spectrometer QTOF 6520. Structural assignments were made with additional information from gNOESY, gCOSY and gHSQC experiments. Suitable crystals for single-crystal X-ray diffraction (SCXRD) analysis were obtained by dissolving "X" in Ethyl Acetate/Hexane, followed by slow evaporation of the 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. Apex IV software was used for data collection, indexing the reflections, and determining the unit cell parameters; the collected data was integrated using Saint Software. The structures were solved by Intrinsic phasing and refined by full-matrix least-squares calculations using SHELXTL 2018 software.

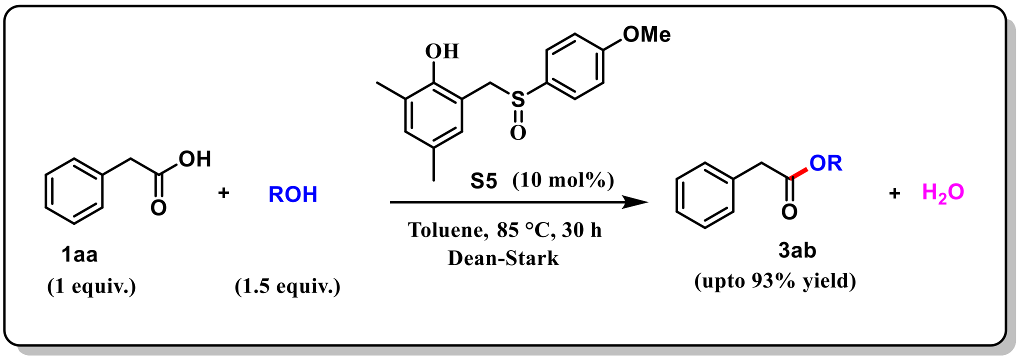
Different alcohols used in the study



Different acids used in the study



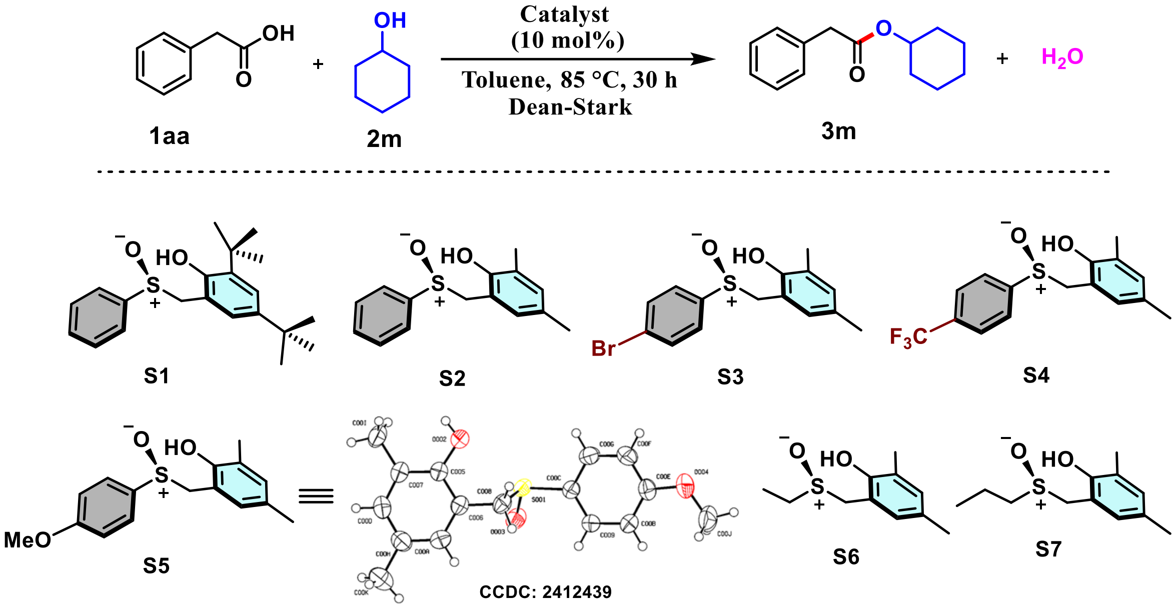
General procedure 1 (GP1) for Esterification reaction



Scheme 1: General procedure for Esterification reaction

A suspension of alcohol (1.5 equiv.), phenylacetic acid (1.0 equiv.) and catalyst **S5** (10 mol%) in Toluene (2 mL) was heated to reflux in a Dean-Stark apparatus and stirred for 30 hours. The reaction mixture was then cooled to room temperature, diluted with EtOAc and washed water twice then brine. The organic phase was dried over $MgSO_4$ and concentrated in vacuo. The crude residue was purified by flash column chromatography to afford the ester product.

Optimization study

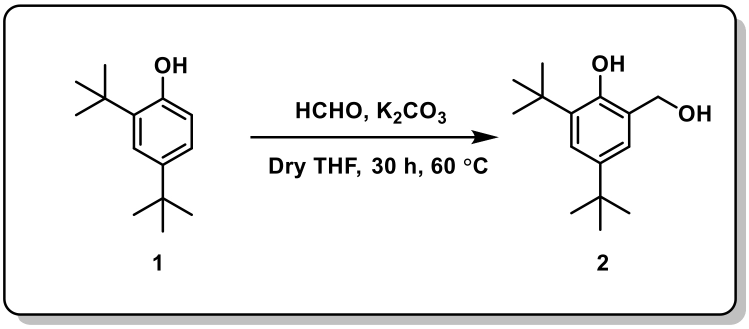


Optimization Table 1

Entry	Catalyst	Catalyst (mol%)	Yield (%)
1	S1	10	30
2	S2	10	45
3	S3	10	15
4	S4	10	10
5	S5	10	85
6	S6	10	20
7	S7	10	58
8	S5	15	55
9	S5	20	65

Reaction conditions: **1aa** (1.0 equiv. 0.7 mmol), **2m** (1.5 equiv. 1.09 mmol), catalyst (10 mol%) in toluene (2 ml) was refluxed in a Dean-Stark apparatus for 30 h.

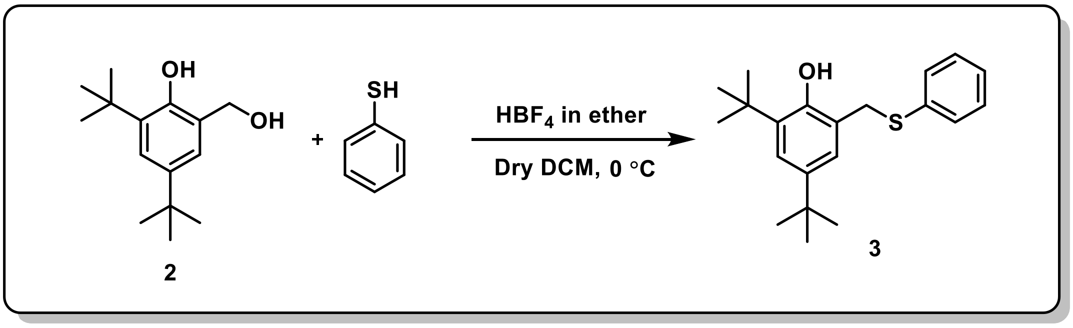
General procedure 2 (GP2) for synthesis of the precursor of the Catalyst



Scheme 2: synthesis of the precursor of the catalyst.

To a solution of 2,4-di-tertbutylphenol (**1**) (2.4 mmol) in dry THF then K_2CO_3 (4.8 mmol) was added and stirred at room temperature for 0.5 h in argon atmosphere. Paraformaldehyde (2.4 mmol) was added to the reaction mixture and stirred at 60 °c temperature for additional 30 h. then reaction mixture was poured over 10 ml of water and extracted with DCM 3 times. The organic extract was dried over Na_2SO_4, evaporated to over reduced pressure. The crude residue was then purified by column chromatography over silica gel (60-120 mesh) using hexane and ethyl acetate (8:2) as an eluent to afford the desired product (**2**) 86% yield. The identification and purification of the product was confirmed by spectroscopic analysis.

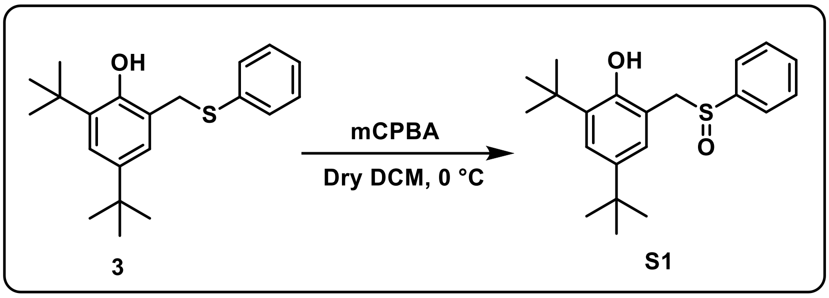
General procedure 3 (GP3) for synthesis of the precursor of the Catalyst



Scheme 3: synthesis of precursor of the catalyst.

To a solution of 2,4-di-tert-butyl-6-(hydroxymethyl) phenol (**2**) (1.6 mmol) in dry DCM then Thiophenol (1.8 mmol) was added and stirred at room temperature for 10 minutes in argon atmosphere at 0 °c. HBF_4 in ether (1.3 mmol) was added to the reaction mixture and stirred at 0 °c temperature for additional 3 h, then workup done by $NaHCO_3$ and extracted with DCM 3 times. The organic extract was dried over Na_2SO_4, evaporated to over reduced pressure. The crude residue was then purified by column chromatography over silica gel (60-120 mesh) using hexane and ethyl acetate (9:1) as an eluent to afford the desired product (**3)** 90 % yield. The identification and purification of the product was confirmed by spectroscopic analysis.

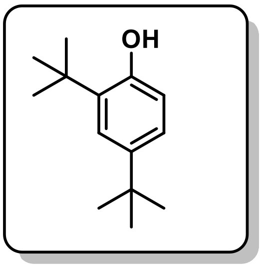
General procedure 4 (GP4) for synthesis of the sulfoxide Catalyst



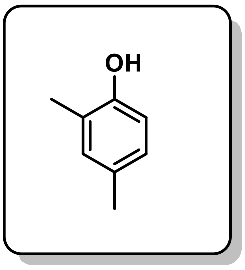
Scheme 4: synthesis of the sulfoxide catalyst **S1.**

To a solution of 2,4-di-tert-butyl-6-((phenylthio)methyl) phenol (**3**) (1.52 mmol) in CH_2Cl_2 at 0 °c was added mCPBA (1.5 mmol) after which the mixture was warmed at room temperature stirring to 2 h before quenching with $NaHCO_3$, workup done by DCM 3 times, washing with brine, drying and concentration. The crude residue was then purified by column chromatography over silica gel (60-120 mesh) using hexane and ethyl acetate (7:3) as an eluent to afford the desired product (**S1)** 80 % yield. The identification and purification of the product was confirmed by spectroscopic analysis.

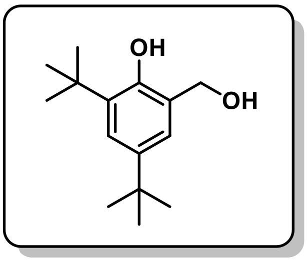
2,4-di-tert-butylphenol (1)



2,4-dimethylphenol (4)

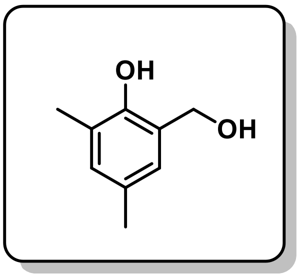


Synthesis of 2,4-di-tert-butyl-6-(hydroxymethyl)phenol (2)



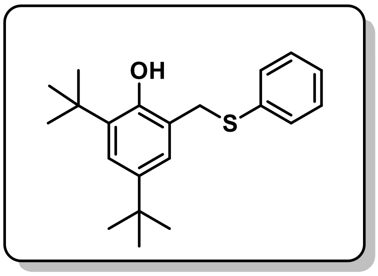
General procedure 2 was used to prepared compound **2** from **1** (500 mg, 2.4 mmol). Flash column chromatography was used to refine the crude product to get **2** (490 mg, 86%) as a white solid, Rf = 0.5 (Hexane/EtOAc, 8:2, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 7.53 (s, 1H), 7.28 (d, *J* = 2.6 Hz, 1H), 6.89 (d, *J* = 2.2 Hz, 1H), 4.83 (d, *J* = 6.0 Hz, 2H), 2.12 (t, *J* = 5.8 Hz, 1H), 1.43 (s, 9H), 1.28 (s, 9H). **^{13}C NMR (126 MHz, chloroform-d)** δ 152.07, 140.59, 135.49, 123.05, 122.94, 121.57, 64.85, 33.91, 33.18, 30.70, 28.64. **HRMS (ESI)** calcd for $C_{15}H_{24}O_2$ $[M+Na]^+$ 259.1669, found 259.1661.

Synthesis of 2-(hydroxymethyl)-4,6-dimethylphenol (5)



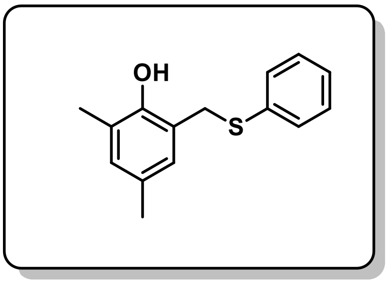
General procedure 2 was used to prepared compound **5** from **4** (300 mg, 2.4 mmol). Flash column chromatography was used to refine the crude product to get **5** (310 mg, 80%) as a yellow syrup, Rf = 0.6 (Hexane/EtOAc, 8:2, v/v). **^{1}H NMR (500 MHz, chloroform-d)** δ 7.21 (s, 1H), 6.87 (s, 1H), 6.63 (s, 1H), 4.72 (s, 2H), 2.68 (s, 1H), 2.20 (d, *J* = 4.2 Hz, 6H). **^{13}C NMR (126 MHz, chloroform-d)** δ 150.85, 130.31, 127.72, 124.87, 124.05, 122.91, 63.61, 19.30, 14.50. **HRMS (ESI)** calcd for $C_9H_{12}O_2$ $[M+Na]^+$ 175.0730, found 175.0735.

Synthesis of 2,4-di-tert-butyl-6-((phenylthio)methyl)phenol (3)



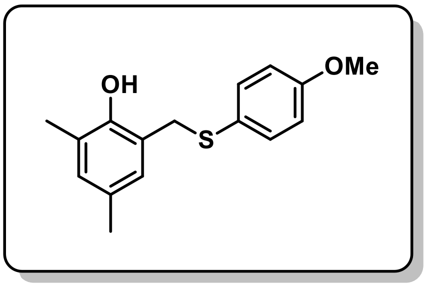
General procedure 3 was used to prepared compound **3** from **2** (400 mg, 1.6 mmol). Flash column chromatography was used to refine the crude product to get **3** (505 mg, 90%) as a yellow oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 7.24 (dd, *J* = 8.0, 1.9 Hz, 2H), 7.19 – 7.10 (m, 4H), 6.72 (d, *J* = 2.6 Hz, 1H), 6.07 (s, 1H), 4.06 (s, 2H), 1.35 (s, 9H), 1.13 (s, 9H). **^{13}C NMR (126 MHz, chloroform-d)** δ 150.44, 141.32, 136.02, 132.93, 130.57, 127.85, 126.37, 124.39, 122.69, 120.76, 36.76, 33.92, 33.12, 30.46, 28.80.
. **HRMS (ESI)** calcd for $C_{21}H_{28}OS$ $[M+Na]^+$ 351.1753, found 351.1740.

Synthesis of 2,4-dimethyl-6-((phenylthio)methyl)phenol (6)



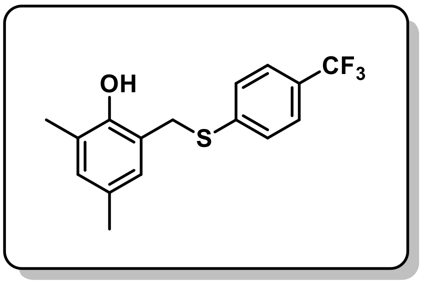
General procedure 3 was used to prepared compound **6** from **5** (270 mg, 1.6 mmol). Flash column chromatography was used to refine the crude product to get **6** (354 mg, 90%) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, chloroform-d)** δ 7.38 – 7.31 (m, 2H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 2.2 Hz, 1H), 6.72 (d, *J* = 2.2 Hz, 1H), 5.71 (s, 1H), 4.12 (s, 2H), 2.22 (s, 3H), 2.17 (s, 3H). **^{13}C NMR (126 MHz, chloroform-d)** δ 149.64, 133.98, 130.16, 129.44, 128.41, 127.90, 127.64, 125.89, 124.01, 120.64, 34.90, 19.32, 14.79. **HRMS (ESI)** calcd for $C_{15}H_{16}OS$ $[M+Na]^+$ 267.0814, found 267.0810.

Synthesis of 2-(((4-methoxyphenyl)thio)methyl)-4,6-dimethylphenol (7)



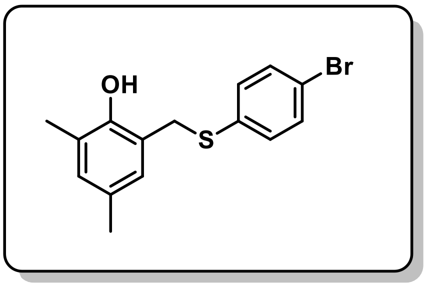
General procedure 3 was used to prepared compound **7** from **5** (100 mg, 0.65 mmol). Flash column chromatography was used to refine the crude product to get **7** (150 mg, 91%) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 7.32 – 7.25 (m, 3H), 6.85 (d, *J* = 2.2 Hz, 1H), 6.82 – 6.77 (m, 2H), 6.59 (d, *J* = 2.2 Hz, 1H), 5.89 (s, 1H), 4.01 (s, 2H), 3.78 (s, 3H), 2.23 (s, 3H), 2.15 (s, 3H). **^{13}C NMR (126 MHz, chloroform-d)** δ 158.54, 149.73, 133.27, 130.06, 128.27, 127.65, 124.14, 123.67, 121.05, 113.54, 54.31, 37.10, 19.31, 14.80. **HRMS (ESI)** calcd for $C_{16}H_{18}O_2S$ $[M+Na]^+$ 297.0920, found 297.0929.

Synthesis of 2,4-dimethyl-6-(((4-(trifluoromethyl)phenyl)thio)methyl)phenol (8)



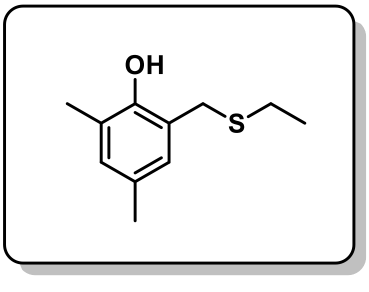
General procedure 3 was used to prepared compound **8** from **5** (100 mg, 0.65 mmol). Flash column chromatography was used to refine the crude product to get **8** (180 mg, 84 %) as a colourless oil, Rf = 0.5 (Hexane/EtOAc, 8:2, v/v). **^{1}H NMR (500 MHz, chloroform-d)** δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 2.4 Hz, 1H), 6.82 (d, *J* = 2.4 Hz, 1H), 5.32 (s, 1H), 4.19 (s, 2H), 2.22 (s, 3H), 2.19 (s, 3H). **^{13}C NMR (126 MHz, chloroform-d)** δ 149.31, 140.15, 130.33, 128.75, 127.71, 127.52, 124.66, 124.63, 124.59, 124.56, 123.47, 120.14, 32.90, 19.33, 14.73. **^{19}F NMR (471 MHz, chloroform-d)** δ -62.46. **HRMS (ESI)** calcd for $C_{16}H_{15}F_3OS$ $[M+Na]^+$ 335.0688, found 335.0680.

Synthesis of 2-(((4-bromophenyl)thio)methyl)-4,6-dimethylphenol (9)



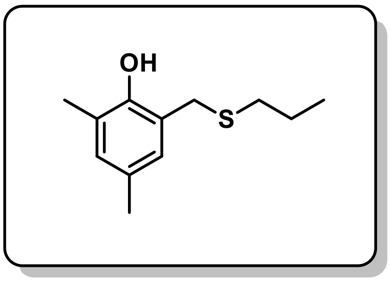
General procedure 3 was used to prepared compound **9** from **5** (150 mg, 0.98 mmol). Flash column chromatography was used to refine the crude product to get **9** (280 mg, 88 %) as a white solid, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, chloroform-d)** δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 2.4 Hz, 1H), 6.71 (d, *J* = 2.4 Hz, 1H), 5.53 (s, 1H), 4.09 (s, 2H), 2.21 (s, 3H), 2.17 (s, 3H).**^{13}C NMR (126 MHz, chloroform-d)** δ 149.43, 133.26, 130.91, 130.25, 128.53, 127.68, 123.75, 120.43, 119.85, 34.59, 19.34, 14.78. **HRMS (ESI)** calcd for $C_{15}H_{15}BrOS$ $[M+Na]^+$ 344.9919, found 344.9920.

Synthesis of 2-((ethylthio)methyl)-4,6-dimethylphenol (10)



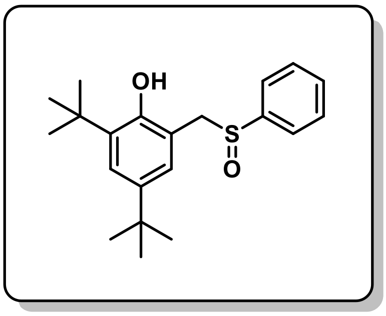
General procedure 3 was used to prepared compound **10** from **5** (200 mg, 1.31 mmol). Flash column chromatography was used to refine the crude product to get **10** (220 mg, 85 %) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, chloroform-d)** δ 6.88 (d, *J* = 2.1 Hz, 1H), 6.72 (d, *J* = 2.4 Hz, 1H), 6.55 (s, 1H), 3.76 (s, 2H), 2.42 (q, *J* = 7.4 Hz, 2H), 2.22 (d, *J* = 2.1 Hz, 6H), 1.23 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, chloroform-d)** δ 150.33, 130.03, 127.96, 127.46, 124.65, 120.44, 31.70, 23.73, 19.38, 14.77, 13.21. **HRMS (ESI)** calcd for $C_{11}H_{16}OS$ $[M+Na]^+$ 219.0814, found 219.813.

Synthesis of 2,4-dimethyl-6-((propylthio)methyl)phenol (11)



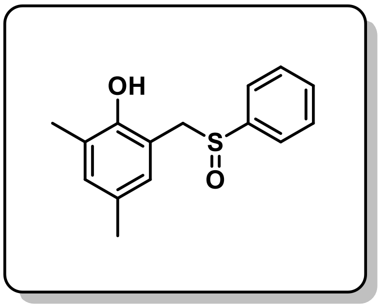
General procedure 3 was used to prepared compound **11** from **5** (300 mg, 1.97 mmol). Flash column chromatography was used to refine the crude product to get **11** (350 mg, 84 %) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 6.89 (d, *J* = 2.2 Hz, 1H), 6.71 (d, *J* = 2.2 Hz, 1H), 6.59 (s, 1H), 3.75 (s, 2H), 2.38 (t, *J* = 7.3 Hz, 2H), 2.22 (d, *J* = 1.7 Hz, 6H), 1.63 – 1.55 (m, 3H), 0.95 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (126 MHz, chloroform-d)** δ 150.36, 130.03, 127.96, 127.47, 124.66, 120.51, 32.11, 31.77, 21.33, 19.38, 14.78, 12.32. **HRMS (ESI)** calcd for $C_{12}H_{18}OS$ $[M+Na]^+$ 233.0971, found 233.0960.

Synthesis of 2,4-di-tert-butyl-6-((phenylsulfinyl)methyl)phenol (S1)



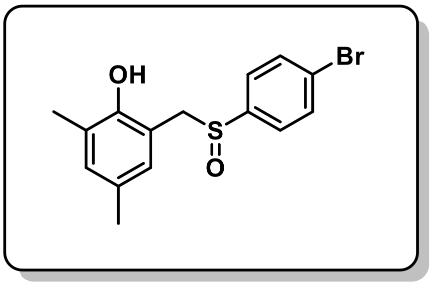
General procedure 4 was used to prepared catalyst **S1** from **3** (500 mg, 1.52 mmol). Flash column chromatography was used to refine the crude product to get **S1** (420 mg, 80 %) as a white solid, Rf = 0.5 (Hexane/EtOAc, 7:3, v/v). **^{1}H NMR (500 MHz, chloroform-d)** *δ* 8.94 (s, 1H), 7.49 – 7.40 (m, 5H), 7.19 (d, *J* = 2.4 Hz, 1H), 6.33 (d, *J* = 2.6 Hz, 1H), 4.47 (d, *J* = 13.7 Hz, 1H), 3.90 (d, *J* = 13.7 Hz, 1H), 1.43 (s, 9H), 1.11 (s, 9H). **^{13}C NMR (126 MHz, chloroform-d)** *δ* 152.53, 141.21, 139.56, 138.01, 130.40, 128.05, 125.27, 123.49, 123.11, 117.74, 58.75, 34.07, 33.01, 30.39, 28.78. **HRMS (ESI)** calcd for $C_{21}H_{28}O_2S$ $[M+H]^+$ 345.1883, found 325.1880.

Synthesis of 2,4-dimethyl-6-((phenylsulfinyl)methyl)phenol (S2)



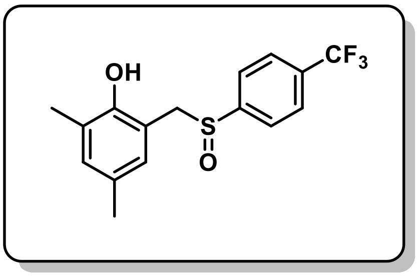
General procedure 4 was used to prepared catalyst **S2** from **6** (300 mg, 1.22 mmol). Flash column chromatography was used to refine the crude product to get **S2** (280 mg, 88%) as a white solid, Rf = 0.5 (Hexane/EtOAc, 7:3, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 8.71 (s, 1H), 7.58 – 7.44 (m, 5H), 6.86 (d, *J* = 2.6 Hz, 1H), 6.32 (d, *J* = 2.6 Hz, 1H), 4.22 (d, *J* = 13.8 Hz, 1H), 4.00 (d, *J* = 13.8 Hz, 1H), 2.25 (s, 3H), 2.09 (s, 3H). **^{13}C NMR (126 MHz, chloroform-d)** δ 151.87, 140.08, 131.29, 130.53, 128.54, 128.25, 128.16, 126.55, 123.12, 116.83, 58.93, 19.12, 15.33. **HRMS (ESI)** calcd for $C_{15}H_{16}O_2S$ [M+H]$^+$ 261.0944, found 261.0943.

Synthesis of 2-(((4-bromophenyl)sulfinyl)methyl)-4,6-dimethylphenol (S3)



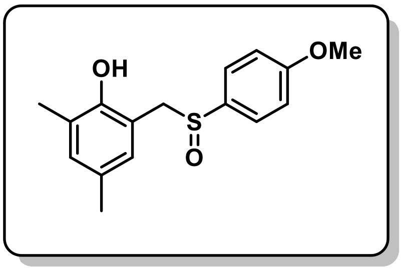
General procedure 4 was used to prepared compound **S3** from **9** (170 mg, 0.52 mmol). Flash column chromatography was used to refine the crude product to get **S3** (140 mg, 78%) as a white solid, Rf = 0.5 (Hexane/EtOAc, 7:3, v/v). **^{1}H NMR (500 MHz, chloroform-d)** δ 8.39 (s, 1H), 7.59 – 7.52 (m, 2H), 7.33 – 7.29 (m, 2H), 6.81 (d, *J* = 2.4 Hz, 1H), 6.21 (d, *J* = 2.4 Hz, 1H), 4.22 (d, *J* = 13.7 Hz, 1H), 3.87 (d, *J* = 13.7 Hz, 1H), 2.17 (s, 3H), 2.03 (s, 3H). **^{13}C NMR (126 MHz, chloroform-d)** δ 151.73, 139.08, 131.47, 131.36, 128.52, 128.46, 126.65, 125.10, 124.76, 116.32, 58.71, 19.16, 15.31. **HRMS (ESI)** calcd for $C_{15}H_{15}BrO_2S$ [M+H]$^+$ 339.0049, found 339.0049.

Synthesis of 2,4-dimethyl-6-(((4-(trifluoromethyl)phenyl)sulfinyl)methyl)phenol (S4)



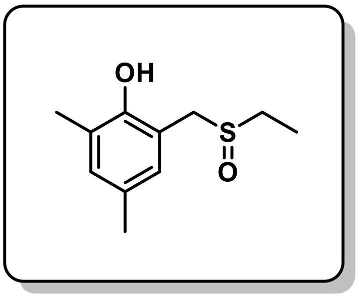
General procedure 4 was used to prepared compound **S4** from **8** (130 mg, 0.41 mmol). Flash column chromatography was used to refine the crude product to get **S4** (100 mg, 73%) as a white solid, Rf = 0.4 (Hexane/EtOAc, 7:3, v/v). **^{1}H NMR (500 MHz, chloroform-d)** δ 8.24 (s, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 2.4 Hz, 1H), 6.19 (d, *J* = 2.1 Hz, 1H), 4.40 (d, *J* = 13.7 Hz, 1H), 3.94 (d, *J* = 13.7 Hz, 1H), 2.24 (s, 3H), 2.05 (s, 3H). **^{13}C NMR (126 MHz, chloroform-d)** δ 168.75, 151.58, 144.25, 131.55, 129.21, 128.80, 128.57, 128.47, 125.05, 123.73, 115.99, 58.46, 19.00, 15.28. **^{19}F NMR (471 MHz, chloroform-d)** δ -62.96. **HRMS (ESI)** calcd for $C_{16}H_{15}F_3O_2S$ $[M+H]^+$ 329.0818, found 329.0818.

Synthesis of 2-(((4-methoxyphenyl)sulfinyl)methyl)-4,6-dimethylphenol (S5)



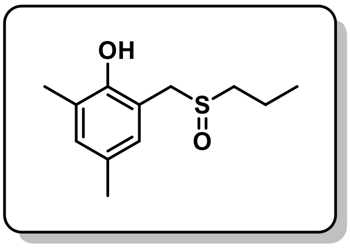
General procedure 4 was used to prepared Catalyst **S5** from **7** (100 mg, 0.36 mmol). Flash column chromatography was used to refine the crude product to get **S5** (90 mg, 85%) as a white solid, Rf = 0.5 (Hexane/EtOAc, 7:3, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 8.87 (s, 1H), 7.52 – 7.45 (m, 2H), 7.03 – 6.96 (m, 2H), 6.89 (d, *J* = 2.2 Hz, 1H), 6.37 (d, *J* = 2.6 Hz, 1H), 4.15 (d, *J* = 13.3 Hz, 1H), 4.01 (d, *J* = 13.3 Hz, 1H), 3.85 (s, 3H), 2.26 (s, 3H), 2.12 (s, 3H). **^{13}C NMR (126 MHz, chloroform-d)** δ 157.71, 148.28, 127.55, 127.30, 124.87, 124.51, 122.94, 121.42, 113.29, 110.00, 55.51, 50.83, 15.47, 11.63. **HRMS (ESI)** calcd for $C_{16}H_{18}O_3S$ $[M+H]^+$ 291.1049, found 291.1048.

Synthesis of 2-((ethylsulfinyl)methyl)-4,6-dimethylphenol (S6)



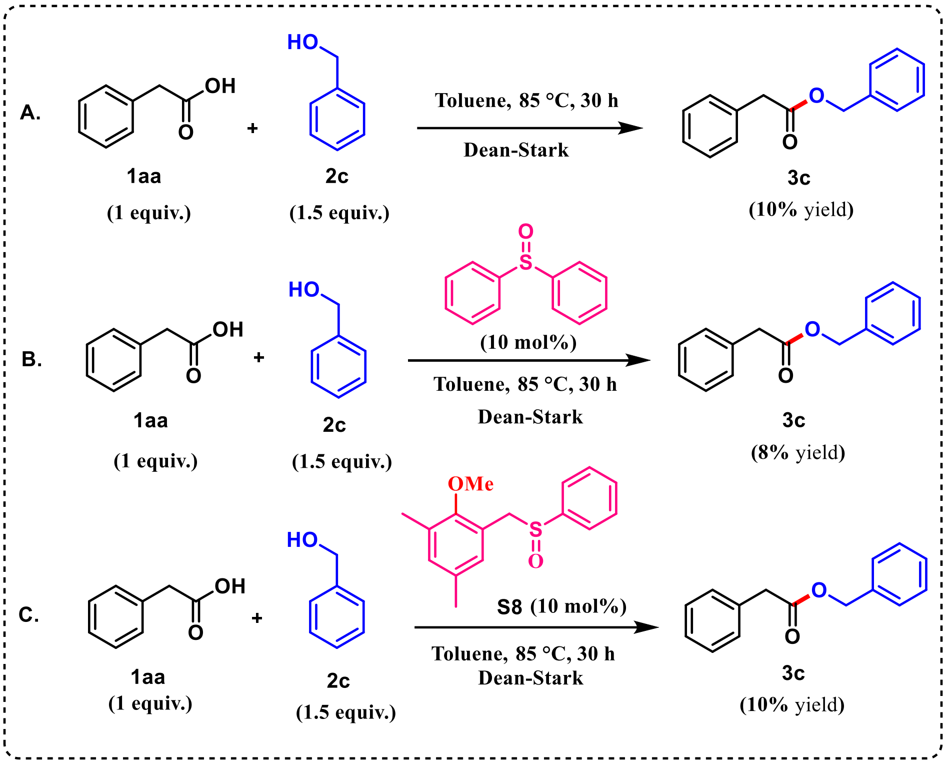
General procedure 4 was used to prepared compound **S6** from **10** (100 mg, 0.50 mmol). Flash column chromatography was used to refine the crude product to get **S6** (75 mg, 73%) as a colourless oil, Rf = 0.4 (Hexane/EtOAc, 7:3, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 9.03 (s, 1H), 6.94 (d, J = 2.2 Hz, 1H), 6.65 (d, J = 2.2 Hz, 1H), 4.34 (d, J = 14.2 Hz, 1H), 3.79 (d, J = 14.2 Hz, 1H), 2.80 – 2.57 (m, 2H), 2.24 (d, J = 3.4 Hz, 6H), 1.31 (t, J = 7.5 Hz, 3H). **^{13}C NMR (126 MHz, chloroform-d)** δ 150.45, 132.09, 129.67, 128.80, 126.72, 114.03, 76.26, 76.00, 75.75, 54.52, 44.33, 19.36, 15.15, 5.28. **HRMS (ESI)** calcd for $C_{11}H_{16}OS$ $[M+Na]^+$ 235.0763, found 235.0760.

Synthesis of 2,4-dimethyl-6-((propylsulfinyl)methyl)phenol (S7)



General procedure 4 was used to prepared compound **S7** from **11** (350 mg, 1.66 mmol). Flash column chromatography was used to refine the crude product to get **S7** (300 mg, 79%) as a white solid, Rf = 0.4 (Hexane/EtOAc, 7:3, v/v).**^{1}H NMR (400 MHz, chloroform-d)** δ 8.96 (s, 1H), 6.87 (d, J = 2.6 Hz, 1H), 6.58 (d, J = 2.6 Hz, 1H), 4.29 (d, J = 14.2 Hz, 1H), 3.70 (d, J = 14.2 Hz, 1H), 2.70 – 2.59 (m, 1H), 2.51 – 2.41 (m, 1H), 2.17 (d, J = 2.6 Hz, 6H), 1.76 – 1.64 (m, 2H) 1.00 (t, J = 7.5 Hz, 3H).**^{13}C NMR (126 MHz, chloroform-d)** δ 151.62, 131.47, 128.74, 128.18, 127.01, 116.41, 52.40, 50.86, 19.32, 15.42, 15.27, 12.36. **HRMS (ESI)** calcd for $C_{12}H_{18}O_2S$ $[M+H]^+$ 227.1100, found 270.1092.

Control experiments:



Scheme 5. Reactions condition **1aa** (1equv.) and **2c** (1.5equv.) in 2 ml dry toluene at 85 °C for 30h, **A.** Without catalyst 10% yield **B.** Diphenyl sulfoxide (10 mol%), 8% yield **C**. Catalyst **S8** (10mol%), 10% yield, all the rection yield was NMR calculated yield with internal standard **1,3,5-trimethoxy benzene**.

^{1}H NMR of all the controls experiments

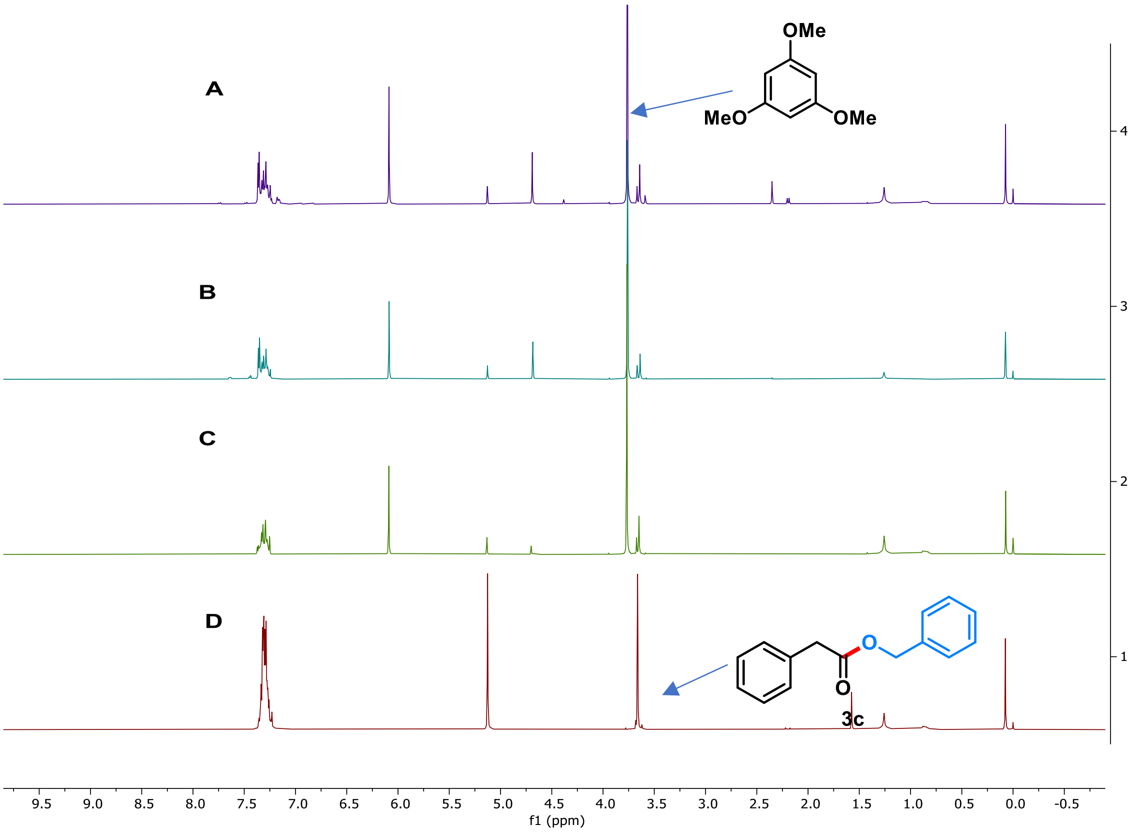
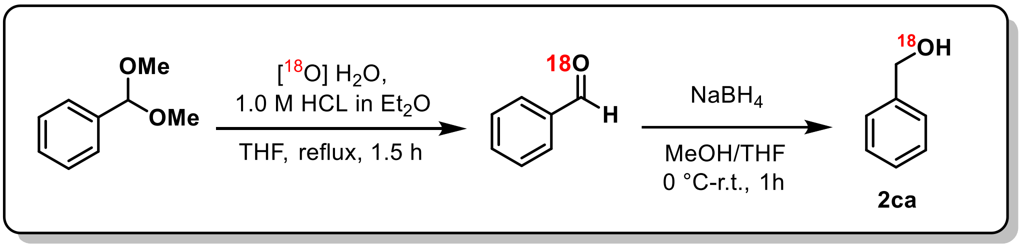


Figure 1. A, B, C are the **^{1}H NMR** of all the controls experiments and **D** was **^{1}H NMR** of reference ester product **3c.**

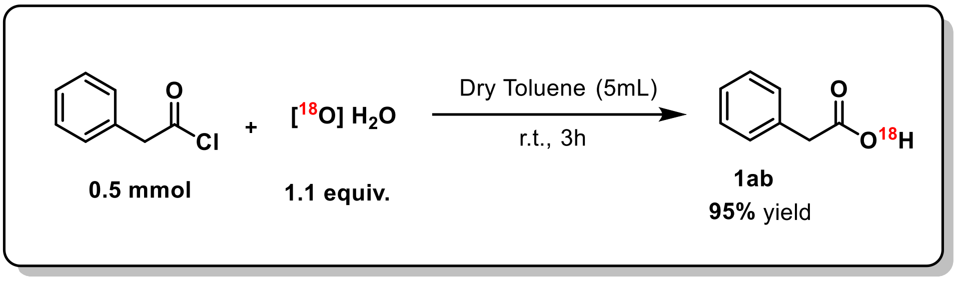
Procedures for the Mechanistic Experiments

^{18}O-enriched benzyl alcohol (2ca)



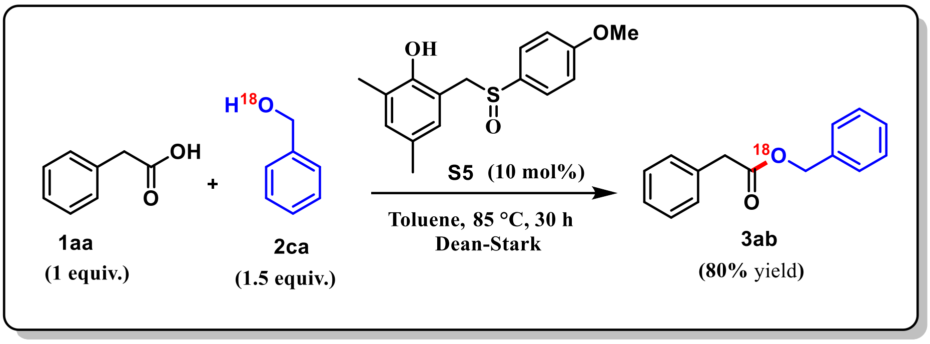
The dimethoxymethyl benzene (0.47 ml, 3.2 mmol) was dissolved in THF (1 mL) and [^{18}O] H_2O (60 µL, 3.9 mmol, 95% ^{18}O isotopic purity) was added, followed by HCl (16 µL of a 1.0 M solution in Et_2O). The reaction flask was fitted with an empty Dean-Stark trap and run under argon. The reaction was refluxed for 1.5 hours. Additional THF (10 mL), 1.0 M HCl in Et_2O (0.1 mL) and [^{18}O] H_2O (30 µL, 1.95 mmol, 95% ^{18}O isotopic purity) were added and the reaction mixture was refluxed for a further 1.5 hours. The reaction was concentrated in vacuo, and the crude residue was dissolved in THF (2 mL) under argon and cooled to 0 °C. $NaBH_4$ (228 mg, 5.9 mmol), was added, and dry CH_3OH (~1mL) was then added slowly over 15 min. The reaction was stirred for 1 h, then diluted with Et_2O (5 mL). The organic phase was washed with H_2O (10 mL), HCl (10 mL of a 1.0 M solution in H_2O), then brine (30 mL), then dried over $MgSO_4$, then concentrated in vacuo. The crude residue was purified by flash column chromatography (Hexane/EtOAc, 9:1, v/v) to afford the title compound as a colourless oil (220 mg, 61%).**^{1}H NMR (500 MHz, chloroform-d)** δ 7.35 (d, *J* = 1.6 Hz, 4H), 7.31 – 7.25 (m, 1H), 4.65 (s, 2H), 2.04 (s, 1H). ^{13}C **NMR (126 MHz, chloroform-d)** δ 139.84, 127.53, 126.60, 125.96, 64.27(0.51 C, $C^{16}O$), 64.25(0.49 C,$C^{18}O$). **HRMS (ESI)** calcd for $C_7H_7{}^{18}O$ $[M+K]^+$ 149.0249, found 149.0239. High-resolution ^{13}C NMR (126 MHz) indicated approximately 49% ^{18}O incorporation by integration of the two peaks at 64.27 and 64.25 ppm.

^{18}O-enriched phenylacetic acid (2ab)



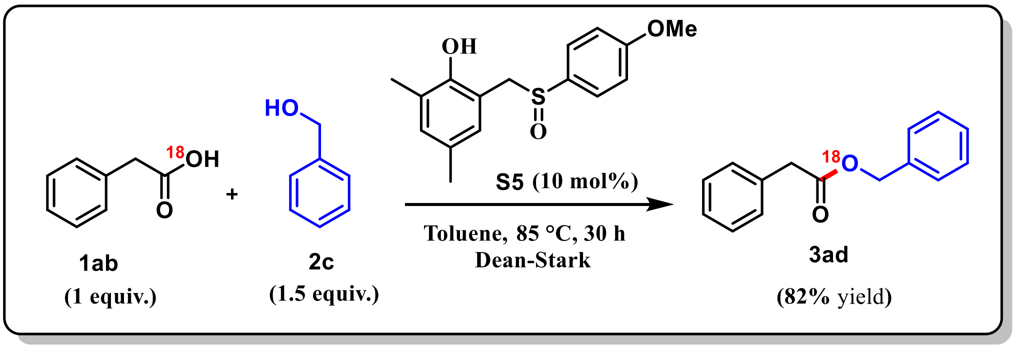
Briefly, in oven-dried screw cap reaction vial (cooled in a nitrogen atmosphere to room temperature) with a magnetic string bar 2-phenylacetyl chloride (77.3 mg, 0.5 mmol, 1.0 equiv.), dry Toluene (5 mL) and $H_2{}^{18}O$ (11 mg, 0.55 mmol, 1.1 equiv.), was charged. The mixture was stirred for 3 h at room temperature (constant temperature oil-bath pan and 98% ^{18}O isotope water was used here). The mixture was diluted with CH_2Cl_2 (10 mL) and washed successively with saturated aqueous $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel and eluted with MeOH/CH_2Cl_2 (1:50, v/v) to afford the corresponding ^{18}O- phenylacetic acid. **^{1}H NMR (500 MHz, chloroform-d)** δ 7.35 – 7.30 (m, 2H), 7.30 – 7.25 (m, 3H), 3.63 (s, 2H). **^{13}C NMR (126 MHz, chloroform-d)** δ 177.20 (0.48 C, $C^{16}O$), 177.18 (0.52 C, $C^{18}O$), 132.20, 128.34, 127.61, 126.32, 40.05. **HRMS (ESI)** calcd for $C_8H_8O^{18}O$ $[M+K]^+$ 177.0198, found 177.0207. High-resolution ^{13}C NMR (126 MHz) indicated approximately 52% ^{18}O incorporation by integration of the two peaks at 177.20 and 177.18 ppm.

Synthesis of 3ab ^{18}O enriched ester product



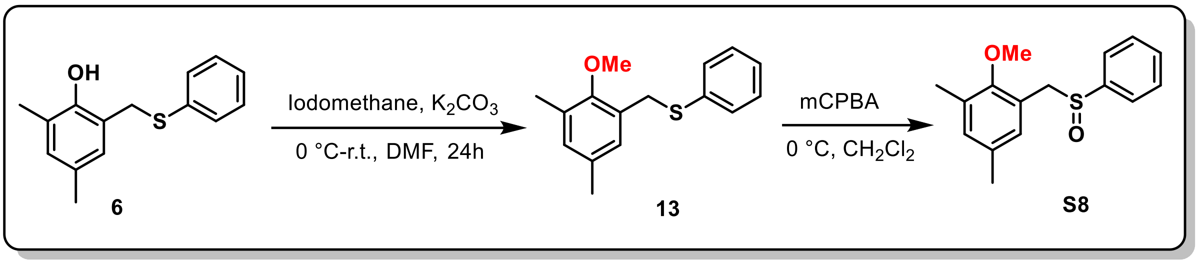
General procedure 1 was used to prepared compound **3ab** from **1aa** (55 mg, 0.40 mmol). Flash column chromatography was used to refine the crude product to get **3a** (67 mg, 80%) as a yellow oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, chloroform-d)** *δ* 7.37 – 7.24 (m, 10H), 5.13 (s, 2H), 3.67 (s, 2H). **^{13}C NMR (126 MHz, chloroform-d)** δ 170.38, 134.83, 132.87, 128.28, 127.55, 127.51, 127.19, 127.09, 126.10, 65.58 (0.49 C, C^{16}O), 65.55 (0.51 C, C^{18}O), 40.32. **HRMS (ESI)** calcd for $C_{15}H_{14}{}^{16}O$ $[M+K]^+$ 249.0886, found 249.0886 and also $C_{15}H_{14}{}^{18}O$ $[M+K]^+$ 251.0928, found 251.0938. High-resolution ^{13}C NMR (126 MHz) indicated approximately 51% ^{18}O incorporation by integration of the two peaks at 65.58 and 65.55 ppm.

Synthesis of 3ad ^{18}O enriched ester product



General procedure 1 was used to prepared compound **3ad** from **1ab** (40 mg, 0.77 mmol). Flash column chromatography was used to refine the crude product to get **3ad** (155 mg, 80%) as a yellow oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, chloroform-d)** *δ* 7.30 (pd, *J* = 8.8, 4.9 Hz, 10H), 5.13 (s, 2H), 3.66 (s, 2H). **^{13}C NMR (126 MHz, chloroform-d)** *δ* 170.37(0.72C, C^{16}O), 170.33(0.28C, C^{18}O), 134.82, 132.86, 128.27, 127.55, 127.50, 127.18, 127.09, 126.09, 65.58, 40.31. **HRMS (ESI)** calcd for $C_{15}H_{14}{}^{16}O$ $[M+K]^+$ 249.0886, found 249.0884 and also $C_{15}H_{14}{}^{18}O$ $[M+K]^+$ 251.0928, found 251.0937. High-resolution ^{13}C NMR (126 MHz) indicated approximately 22% ^{18}O incorporation by integration of the two peaks at 170.37 and 170.33 ppm.

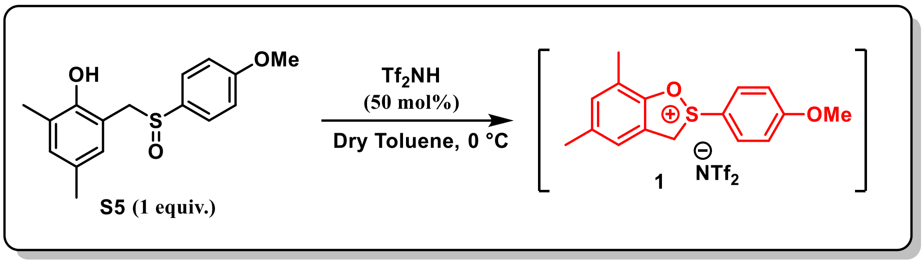
Synthesis of sulfoxide catalyst S8



Iodomethane was added to a solution of 2,4-dimethyl-6-((phenylthio) methyl) phenol (**6**) in dry DMF via a syringe followed by K_2CO_3 under Ar. The mixture was stirred at room temperature for additional 24 h, then poured into ice-water. The aqueous solution was extract with ethyl acetate 3 times then washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (60-120 mesh) using hexane and ethyl acetate (95:5) as an eluent to afford (2-methoxy-3,5-dimethylbenzyl) (phenyl)sulfane (**13**) product 82 % yield. **^{1}H NMR (400 MHz, chloroform-d)** *δ* 7.38 – 7.32 (m, 2H), 7.30 – 7.23 (m, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 6.93 – 6.87 (m, 2H), 4.14 (s, 2H), 3.77 (s, 3H), 2.26 (s, 3H), 2.21 (s, 3H). **^{13}C NMR (126 MHz, chloroform-d)** δ 153.53, 136.11, 132.28, 130.29, 129.72, 128.52, 127.98, 127.85, 127.80, 125.11, 60.01, 32.26, 19.63, 15.08. **HRMS (ESI)** calcd for $C_{16}H_{18}OS[M+Na]^+$ 281.0971, found 281.0980.

To a solution of (2-methoxy-3,5-dimethylbenzyl) (phenyl)sulfane (**13**) (1.52 mmol) in CH_2Cl_2 at 0 °c was added mCPBA (1.5 mmol) after which the mixture was warmed at room temperature stirring to 2 h before quenching with $NaHCO_3$, workup done by DCM 3 times, washing with brine, drying and concentration. The crude residue was then purified by flash column chromatography over silica gel (60-120 mesh) using hexane and ethyl acetate (8:2) as an eluent to afford the desired product **(S8)** 80 % yield. The identification and purification of the product was confirmed by spectroscopic analysis. Flash column chromatography was used to refine the crude product to get **S8** (155 mg, 80%) as a white solid, Rf = 0.4 (Hexane/EtOAc, 8:2, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 7.78 – 7.71 (m, 2H), 7.65 – 7.57 (m, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 2.6 Hz, 1H), 6.83 (d, *J* = 2.2 Hz, 1H), 4.39 (s, 2H), 3.59 (s, 3H), 2.19 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR (126 MHz, chloroform-d)** δ 155.57, 138.88, 133.59, 133.21, 133.12, 130.78, 130.08, 128.84, 128.66, 120.60, 60.93, 56.66, 20.62, 16.36. **HRMS (ESI)** calcd for $C_{17}H_{18}O_2S[M+Na]^+$ 297.0920, found 297.0930.

Intermediate trapping experiment



Scheme 6. reaction condition **S5** (1.0 equiv. 0.0 mmol), **Tf₂NH** (50 mol%) in toluene (2 mL) was in Dean-Stark apparatus for 1 hour.

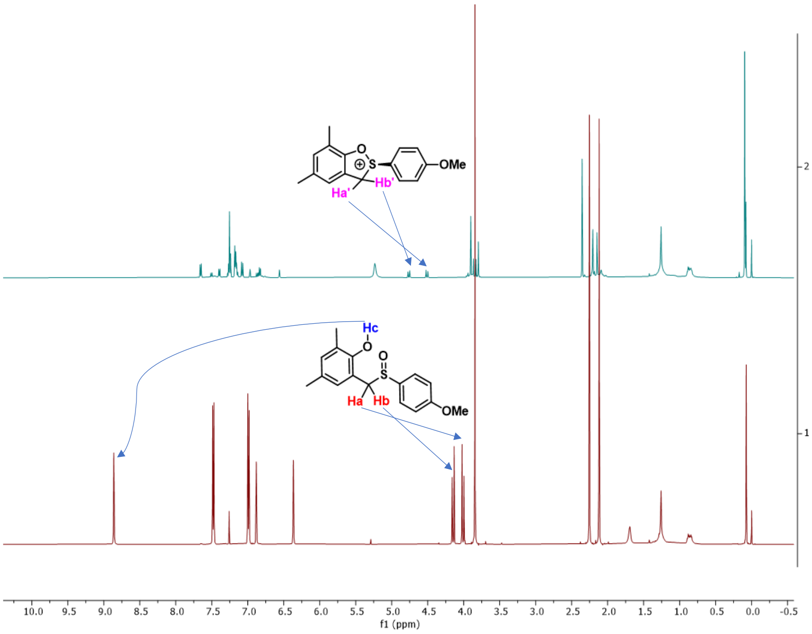
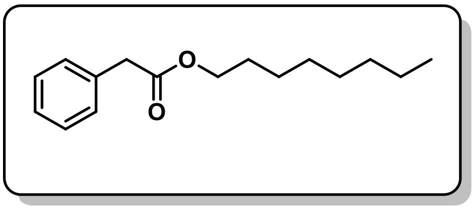


Figure 2. ^{1}H NMR of **S5** and intermediate **1**.

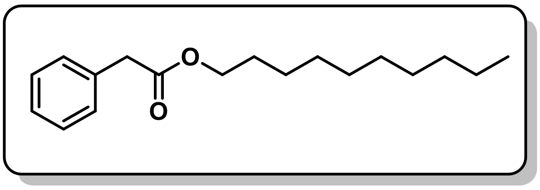
Spectral data of compounds

Synthesis of octyl 2-phenylacetate (3a)



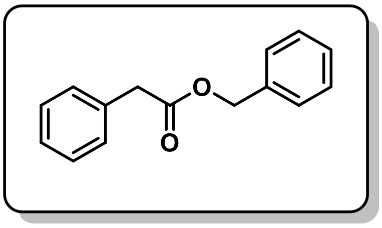
General procedure 1 was used to prepared compound **3a** from **1a** (105.2 mg, 0.77 mmol). Flash column chromatography was used to refine the crude product to get **3a** (155 mg, 80%) as a yellow oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 7.28 – 7.14 (m, 5H), 3.93 (d, *J* = 6.0 Hz, 2H), 3.54 (s, 2H), 1.46 (q, *J* = 5.8 Hz, 1H), 1.25 – 1.15 (m, 8H), 0.79 (m, *J* = 6.9 Hz, 6H). **^{13}C NMR (126 MHz, chloroform-d)** δ 170.74, 133.23, 128.23, 127.48, 125.98, 66.23, 40.58, 37.74, 29.36, 27.85, 22.76, 21.93, 12.99, 9.95. **HRMS (ESI)** calcd for $C_{16}H_{24}O_2$ $[M+Na]^+$ 271.1669, found 271.1660.

Synthesis of decyl 2-phenylacetate (3b)



General procedure 1 was used to prepared compound **3b** from **1a** (103.5 mg, 0.76 mmol). Flash column chromatography was used to refine the crude product to get **3b** (170 mg, 85%) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, chloroform-d)** δ 7.35 – 7.23 (m, 5H), 4.08 (t, *J* = 6.7 Hz, 2H), 3.61 (s, 2H), 1.59 (q, *J* = 6.8 Hz, 2H), 1.27 (m, 14H), 0.88 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz**, **chloroform-d**) δ 170.67, 133.19, 128.22, 127.49, 125.99, 64.01, 40.47, 30.87, 28.53, 28.49, 28.28, 28.17, 27.54, 24.81, 21.66, 13.10. HRMS (ESI) calcd for $C_{18}H_{28}O_2$ $[M+Na]^+$ 299.1982 found 299.1980.

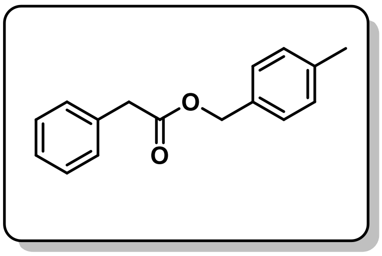
Synthesis of benzyl 2-phenylacetate (3c)



General procedure 1 was used to prepared compound **3c** from **1a** (100 mg, 0.73 mmol). Flash column chromatography was used to refine the crude product to get **3c** (150 mg, 90%) as a yellow oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 7.30 (m, *J* = 11.6, 6.9, 4.1 Hz, 10H), 5.13 (s, 2H), 3.66 (s, 2H). **^{13}C NMR (126 MHz, chloroform-d)** δ

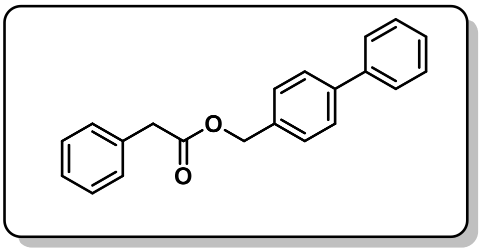
170.38, 134.82, 132.87, 128.27, 127.55, 127.51, 127.18, 127.09, 126.10, 65.58, 40.31**. HRMS (ESI)** calcd for $C_{15}H_{14}O_2$ $[M+Na]^+$ 249.0886, found 249.0882.

Synthesis of 4-methylbenzyl 2-phenylacetate (3d)



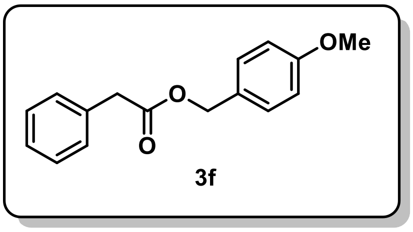
General procedure 1 was used to prepared compound **3d** from **1a** (100 mg, 0.73 mmol). Flash column chromatography was used to refine the crude product to get **3d** (140 mg, 80%) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, chloroform-d)** δ 7.34 – 7.25 (m, 5H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 5.09 (s, 2H), 3.65 (s, 2H), 2.35 (s, 3H). **^{13}C NMR (126 MHz, chloroform-d)** δ 170.45, 137.06, 132.93, 131.82, 128.28, 128.20, 127.54, 127.28, 126.08, 65.57, 40.34, 20.17. **HRMS (ESI)** calcd for $C_{16}H_{16}O_2$ $[M+Na]^+$ 263.1043, found 263.1031.

Synthesis of [1,1'-biphenyl]-4-ylmethyl 2-phenylacetate (3e)



General procedure 1 was used to prepared compound **3e** from **1a** (100 mg, 0.73 mmol). Flash column chromatography was used to refine the crude product to get **3e** (189 mg, 85%) as a white solid, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, chloroform-d)** δ 7.57 (m, *J* = 8.0, 4.6 Hz, 4H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.38 (m, *J* = 8.2 Hz, 3H), 7.36 – 7.25 (m, 5H), 5.17 (s, 2H), 3.69 (s, 2H). **^{13}C NMR (126 MHz, chloroform-d)** δ 170.43, 140.20, 139.63, 133.81, 132.86, 128.30, 127.78, 127.60, 127.57, 126.43, 126.28, 126.13, 126.10, 65.36, 40.36. **HRMS (ESI)** calcd for $C_{21}H_{18}O_2$ $[M+Na]^+$ 325.1199, found 325.1197.

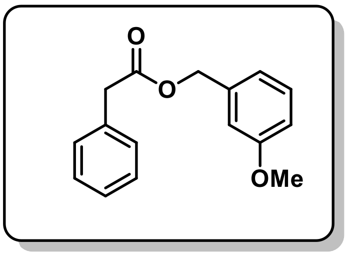
Synthesis of 4-methoxybenzyl 2-phenylacetate (3f)



3f

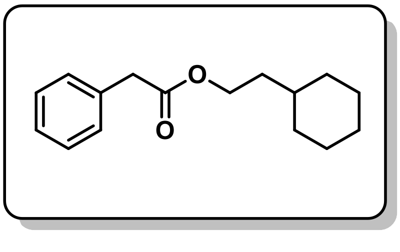
General procedure 1 was used to prepared compound **3f** from **1a** (100 mg, 0.73 mmol). Flash column chromatography was used to refine the crude product to get **3f** (150 mg, 80%) as a yellow syrup, Rf = 0.7 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 7H), 6.83 – 6.77 (m, 2H), 4.99 (s, 2H), 3.73 (s, 3H), 3.57 (s, 2H). **^{13}C NMR (126 MHz, chloroform-d)** δ 170.48, 158.62, 151.10, 129.00, 128.80, 128.26, 127.53, 126.06, 112.91, 65.45, 54.27, 40.35. **HRMS (ESI)** calcd for $C_{16}H_{16}O_3$ $[M+Na]^+$ 279.0992, found 279.0998.

Synthesis of 3-methoxybenzyl 2-phenylacetate (3g)



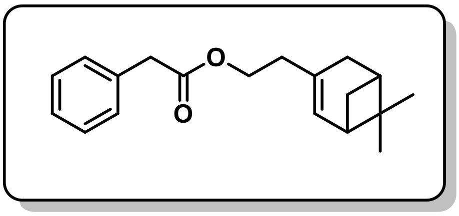
General procedure 1 was used to prepared compound **3g** from **1a** (70 mg, 0.51 mmol). Flash column chromatography was used to refine the crude product to get **3g** (100 mg, 76%) as a yellow syrup, Rf = 0.6 (Hexane/EtOAc, 9:1, v/v). ^{1}H NMR (500 MHz, **chloroform-d**) δ 7.35 – 7.22 (m, 6H), 6.91 – 6.80 (m, 3H), 5.11 (s, 2H), 3.77 (s, 3H), 3.68 (s, 2H). ^{13}C NMR (126 MHz, **chloroform-d**) δ 170.33, 158.71, 136.35, 132.87, 128.56, 128.29, 127.56, 126.11, 119.17, 112.85, 112.25, 65.41, 54.19, 40.35. **HRMS (ESI)** calcd for $C_{16}H_{16}O_3$ $[M+Na]^+$ 279.0992, found 279.0984.

Synthesis of 2-cyclohexylethyl 2-phenylacetate (3h)



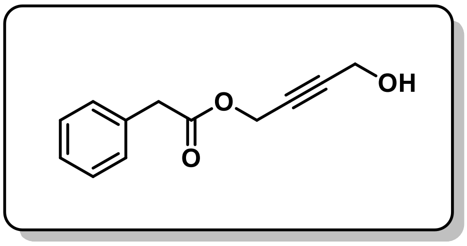
General procedure 1 was used to prepared compound **3h** from **1a** (103.5 mg, 0.76 mmol). Flash column chromatography was used to refine the crude product to get **3h** (155 mg, 82%) as a colourless oil, R_f = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, chloroform-d)** *δ* 7.35 – 7.23 (m, 5H), 4.12 (t, *J* = 6.8 Hz, 2H), 3.61 (s, 2H), 1.66 (d, *J* = 10.5 Hz, 5H), 1.50 (q, *J* = 6.8 Hz, 2H), 1.21 – 1.11 (m, 3H), 0.93 – 0.82 (m, 3H). **^{13}C NMR (126 MHz, chloroform-d)** *δ* 170.67, 133.20, 128.22, 127.50, 126.00, 62.16, 40.53, 34.86, 33.47, 32.09, 25.44, 25.17. **HRMS (ESI)** calcd for $C_{16}H_{22}O_2$ [M+H]$^+$ 247.1693, found 247.1682.

Synthesis of 2-(6,6-dimethylbicyclo[3.1.1]hept-2-en-3-yl)ethyl 2-phenylacetate (3i)



General procedure 1 was used to prepared compound **3i** from **1a** (105.3 mg, 0.76 mmol). Flash column chromatography was used to refine the crude product to get **3i** (135 mg, 62%) as a colourless oil, R_f = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, chloroform-d)** δ 7.35 – 7.23 (m, 5H), 5.26 – 5.19 (m, 1H), 4.10 (qt, *J* = 10.8, 6.8 Hz, 2H), 3.59 (s, 2H), 2.33 (dt, *J* = 8.7, 5.8 Hz, 1H), 2.26 (m, *J* = 5.5, 2.5 Hz, 2H), 2.23 – 2.15 (m, 2H), 2.08 – 2.04 (m, 1H), 2.01 (dd, *J* = 5.5, 1.6 Hz, 1H), 1.25 (s, 3H), 1.09 (d, *J* = 8.4 Hz, 1H), 0.78 (s, 3H).**^{13}C NMR (126 MHz, chloroform-d)** δ 170.55, 142.92, 133.10, 128.27, 127.49, 125.99, 117.84, 62.05, 44.62, 40.50, 39.69, 36.96, 34.87, 30.58, 30.31, 25.25, 20.06. **HRMS (ESI)** calcd for $C_{19}H_{24}O_2$ [M+Na]$^+$ 307.1669, found 307.1659.

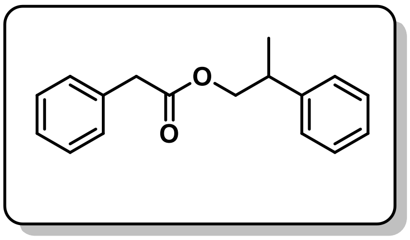
Synthesis of 4-hydroxybut-2-yn-1-yl 2-phenylacetate (3j)



General procedure 1 was used to prepared compound **3j** from **1a** (100 mg, 0.73 mmol). Flash column chromatography was used to refine the crude product to get **3j** (60 mg, 40%) as a colourless oil, Rf = 0.5 (Hexane/EtOAc, 6:4, v/v). ^{1}H NMR (500 MHz, **chloroform-d**) δ 7.35 – 7.24 (m, 5H), 4.72 (s, 2H), 4.26 (s, 2H), 3.66 (s, 2H), 2.19 (dd, *J* = 16.7, 5.4 Hz, 1H). ^{13}C

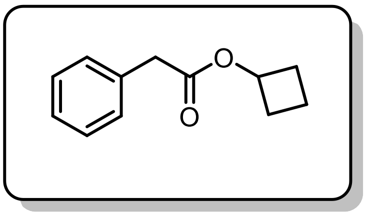
NMR (126 MHz, **chloroform-d**) δ 169.72, 132.37, 128.26, 127.62, 126.25, 79.78, 51.51, 51.45, 39.97, 39.91. **HRMS (ESI)** calcd for $C_{12}H_{12}O_2$ $[M+Na]^+$ 227.0679, found 227.0676.

Synthesis of 1-phenylpropan-2-yl 2-phenylacetate (3k)



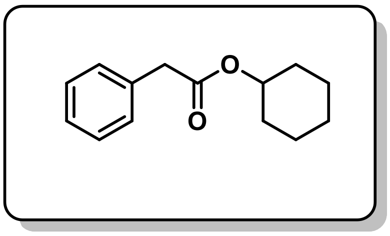
General procedure 1 was used to prepared compound **3k** from **1a** (102.5 mg, 0.75 mmol). Flash column chromatography was used to refine the crude product to get **3k** (173mg, 90%) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 7.27 (m, J = 7.7, 4.7 Hz, 5H), 7.21 (m, J = 10.1, 6.7 Hz, 3H), 7.15 (d, J = 7.3 Hz, 2H), 4.25 – 4.10 (m, 2H), 3.56 (s, 2H), 3.06 (m, J = 7.1 Hz, 1H), 1.24 (d, J = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, chloroform-d)** δ 170.42, 142.03, 132.98, 128.23, 127.48, 127.42, 126.27, 125.98, 125.61, 68.67, 40.41, 37.86, 16.87. **HRMS (ESI)** calcd for $C_{17}H_{18}O_2$ $[M+H]^+$ 277.1186, found 277.1186.

Synthesis of cyclobutyl 2-phenylacetate (3l)



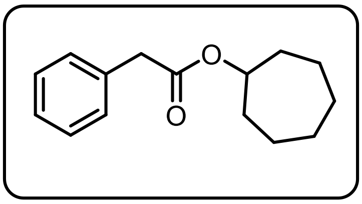
General procedure 1 was used to prepared compound **3k** from **1a** (100 mg, 0.73 mmol). Flash column chromatography was used to refine the crude product to get **3k** (84 mg, 60%) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 7.36 – 7.22 (m, 5H), 4.99 (p, J = 7.4 Hz, 1H), 3.59 (s, 2H), 2.33 (dtt, J = 10.4, 7.8, 2.7 Hz, 2H), 2.05 (qdd, J = 10.1, 7.9, 2.9 Hz, 2H), 0.92 – 0.80 (m, 2H). **^{13}C NMR (126 MHz, chloroform-d)** δ 169.98, 133.09, 128.21, 127.52, 126.00, 68.19, 40.34, 29.24, 28.69, 12.48. **HRMS (ESI)** calcd for $C_{12}H_{14}O_2$ $[M+Na]^+$ 213.0886, found 213.0880.

Synthesis of cyclohexyl 2-phenylacetate (3m)



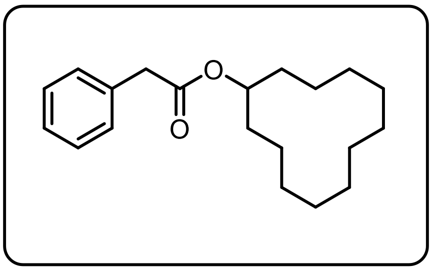
General procedure 1 was used to prepared compound **3m** from **1a** (100 mg, 0.73 mmol). Flash column chromatography was used to refine the crude product to get **3m** (128 mg, 85%) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 7.28 (m, J = 10.8, 7.3 Hz, 5H), 4.77 (m, J = 3.9 Hz, 1H), 3.59 (s, 2H), 1.87 – 1.76 (m, 2H), 1.67 (dd, J = 9.5, 3.4 Hz, 2H), 1.46 – 1.21 (m, 6H). **^{13}C NMR (126 MHz, chloroform-d)** δ 170.05, 133.42, 128.17, 127.46, 125.91, 72.00, 40.82, 30.48, 24.34, 22.59. **HRMS (ESI)** calcd for $C_{14}H_{18}O_2$ $[M+Na]^+$ 241.1199, found 241.1196.

Synthesis of cycloheptyl 2-phenylacetate (3n)



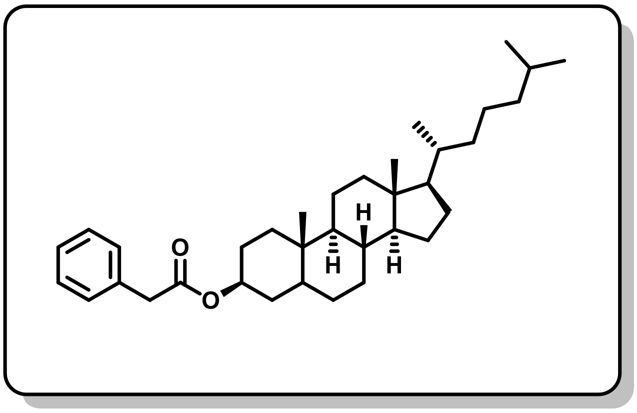
General procedure 1 was used to prepared compound **3n** from **1a** (100 mg, 0.73 mmol). Flash column chromatography was used to refine the crude product to get **3n** (119 mg, 70%) as a colourless oil, R_f = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, chloroform-d)** δ 7.28 – 7.14 (m, 5H), 4.86 (m, 1H), 3.51 (s, 2H), 1.84 – 1.73 (m, 2H), 1.57 (m, 4H), 1.48 – 1.45 (m, 4H), 1.35 (m, 2H). **^{13}C NMR (126 MHz, chloroform-d)** δ 169.94, 151.31, 128.17, 127.46, 125.89, 74.56, 40.85, 32.68, 32.50, 27.46, 27.17, 21.95, 21.66. **HRMS (ESI)** calcd for $C_{15}H_{20}O_2$ $[M+Na]^+$ 255.1356, found 255.1350.

Synthesis of cyclododecyl 2-phenylacetate (3o)



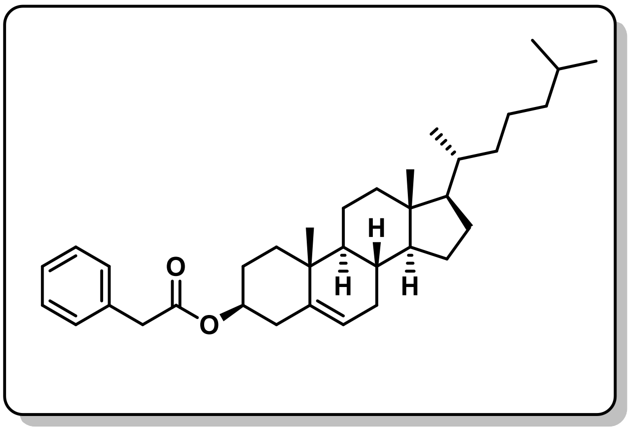
General procedure 1 was used to prepared compound **3o** from **1a** (100 mg, 0.73 mmol). Flash column chromatography was used to refine the crude product to get **3o** (133 mg, 60%) as a colourless oil, R$_f$ = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, chloroform-d)** δ 7.34 – 7.24 (m, 5H), 4.94 (m, 1H), 3.58 (s, 2H), 1.86 (m, 2H), 1.71 – 1.49 (m, 12H), 1.48 – 1.37 (m, 2H), 1.26 (s, 4H), 0.86 (dt, *J* = 18.4, 6.4 Hz, 2H). **^{13}C NMR (126 MHz, chloroform-d)** δ 169.95, 131.65, 128.18, 127.47, 125.91, 74.59, 54.36, 40.87, 32.69, 28.69, 27.18, 21.85, 13.09. **HRMS (ESI)** calcd for $C_{20}H_{30}O_2$ [M+Na]$^+$ 325.2138, found 325.2130.

Synthesis of (3S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-phenylacetate (3r)



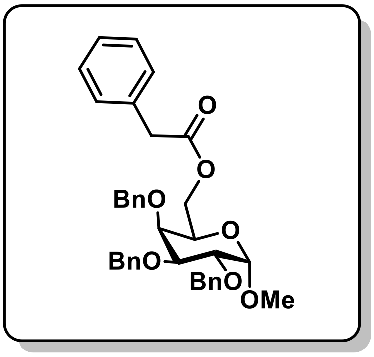
General procedure 1 was used to prepared compound **3r** from **1a** (100 mg, 0.73 mmol). Flash column chromatography was used to refine the crude product to get **3r** (145 mg, 40%) as a white solid, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, chloroform-d)** *δ* 7.40 – 7.21 (m, 5H), 4.70 (m, *J* = 11.1, 4.9 Hz, 1H), 3.58 (s, 2H), 1.95 (dt, *J* = 12.9, 3.6 Hz, 1H), 1.81 (m, 2H), 1.71 (dt, *J* = 13.3, 3.7 Hz, 1H), 1.67 – 1.61 (m, 1H), 1.61 – 1.52 (m, 4H), 1.38 – 1.29 (m, 6H), 1.29 – 1.22 (m, 6H), 1.10 (m, *J* = 14.2, 5.4 Hz, 5H), 1.00 (m, *J* = 11.3, 5.8 Hz, 4H), 0.89 (d, *J* = 6.5 Hz, 4H), 0.86 (dd, *J* = 6.6, 1.9 Hz, 6H), 0.81 (s, 3H), 0.64 (s, 3H). **^{13}C NMR (126 MHz, chloroform-d)** *δ* 170.15, 133.38, 128.14, 127.47, 125.90, 73.25, 55.39, 55.25, 53.18, 43.63, 41.57, 40.75, 38.96, 38.50, 35.71, 35.15, 34.78, 34.44, 32.92, 30.97, 28.69, 27.58, 27.22, 26.99, 26.41, 23.18, 22.82, 21.80, 21.54, 20.18, 17.65, 11.22, 11.05. **HRMS (ESI)** calcd for $C_{35}H_{54}O_2$ [M+Na]$^+$ 529.4016, found 529.4015.

Synthesis of (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-phenylacetate (3s)



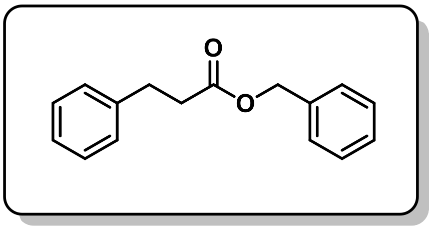
General procedure 1 was used to prepared compound **3s** from **1a** (100 mg, 0.73 mmol). Flash column chromatography was used to refine the crude product to get **3s** (166 mg, 45%) as a white solid, Rf = 0.5 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, chloroform-d)** *δ* 7.22 (m, 5H), 5.28 (d, *J* = 5.8 Hz, 1H), 4.60 – 4.51 (m, 1H), 3.52 (s, 2H), 2.24 (d, *J* = 7.1 Hz, 2H), 2.14 (s, 2H), 1.97 – 1.85 (m, 3H), 1.76 (td, *J* = 9.9, 5.0 Hz, 4H), 1.53 – 1.35 (m, 12H), 0.94 (s, 6H), 0.84 (d, *J* = 6.6 Hz, 3H), 0.79 (m, 9H), 0.60 (s, 3H). **^{13}C NMR (126 MHz, chloroform-d)** *δ* 170.00, 133.33, 128.17, 127.49, 125.95, 73.45, 55.76, 55.69, 55.17, 55.14, 49.02, 41.32, 40.72, 38.74, 38.52, 37.03, 36.03, 35.59, 35.18, 34.78, 30.86, 28.69, 27.21, 27.00, 26.72, 23.27, 22.82, 21.79, 21.55, 20.03, 18.31, 17.71, 10.85. **HRMS (ESI)** calcd for $C_{35}H_{52}O_2$ $[M+Na]^+$ 527.3860, found 527.3850.

Synthesis of ((2S,4S,5S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)methyl 2-phenylacetate (3t)



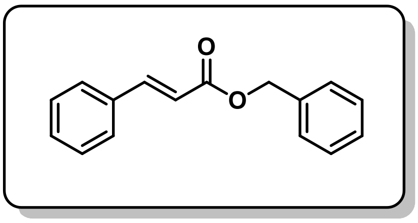
General procedure **1** was used to prepared compound **3t** from **1a** (25 mg, 0.18 mmol). Flash column chromatography was used to refine the crude product to get **3t** (75 mg, 75%) as a yellow oil, Rf = 0.8 (Hexane/EtOAc, 8:2, v/v). **^{1}H NMR (500 MHz, chloroform-d)** *δ* 7.41 – 7.33 (m, 6H), 7.33 – 7.22 (m, 14H), 4.92 – 4.79 (m, 3H), 4.73 – 4.62 (m, 3H), 4.47 (d, *J* = 11.6 Hz, 1H), 4.19 (dd, *J* = 11.2, 7.2 Hz, 1H), 4.02 (m, 2H), 3.88 (dd, *J* = 10.1, 3.0 Hz, 1H), 3.81 (t, *J* = 6.7 Hz, 1H), 3.74 (d, *J* = 3.4 Hz, 1H), 3.56 (s, 2H), 3.24 (s, 3H). **^{13}C NMR (126 MHz, chloroform-d)** *δ* 170.04, 137.68, 137.40, 137.25, 132.80, 128.25, 127.57, 127.41, 127.34, 127.30, 127.28, 127.08, 126.72, 126.58, 126.49, 126.14, 97.71, 77.93, 75.26, 73.87, 73.56, 72.60, 72.43, 67.09, 62.75, 54.16, 40.32. **HRMS (ESI)** calcd for $C_{36}H_{38}O_7$ $[M+Na]^+$ 605.2510, found 605.2510.

Synthesis of benzyl 3-phenylpropanoate (4a)



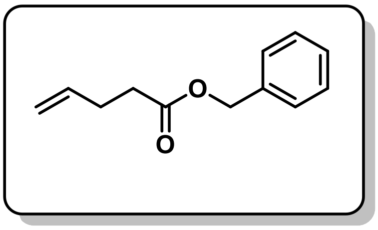
General procedure 1 was used to prepared compound **4a** from **2c** (70 mg, 0.46 mmol). Flash column chromatography was used to refine the crude product to get **4a** (100 mg, 90%) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 7.31 (m, *J* = 7.3 Hz, 5H), 7.25 (d, *J* = 7.3 Hz, 2H), 7.19 (m, *J* = 7.7 Hz, 3H), 5.10 (s, 2H), 2.96 (t, *J* = 7.7 Hz, 2H), 2.68 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR (126 MHz, chloroform-d)** δ 171.68, 139.36, 134.88, 127.50, 127.47, 127.37, 127.26, 127.17, 125.23, 65.24, 34.85, 29.90. **HRMS (ESI)** calcd for $C_{16}H_{16}O_2$ $[M+Na]^+$ 241.1223, found 241.1215.

Synthesis of benzyl cinnamate (4b)



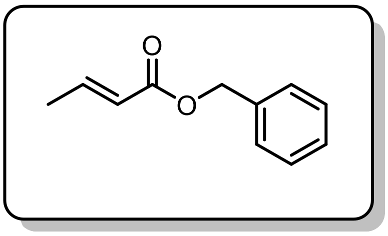
General procedure 1 was used to prepared compound **4b** from **2c** (100 mg, 0.67 mmol). Flash column chromatography was used to refine the crude product to get **4b** (140 mg, 88%) as a yellow syrup, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 7.72 (d, *J* = 15.9 Hz, 1H), 7.48 (dd, *J* = 6.7, 3.2 Hz, 2H), 7.44 – 7.26 (m, 8H), 6.47 (d, *J* = 15.9 Hz, 1H), 5.24 (s, 2H). **^{13}C NMR (126 MHz, chloroform-d)** δ 165.69, 144.11, 135.03, 133.30, 129.28, 127.83, 127.54, 127.22, 127.19, 127.05, 116.83, 65.28. **HRMS (ESI)** calcd for $C_{16}H_{14}O_2$ $[M+Na]^+$ 261.0886, found 261.0880.

Synthesis of benzyl pent-4-enoate (4c)



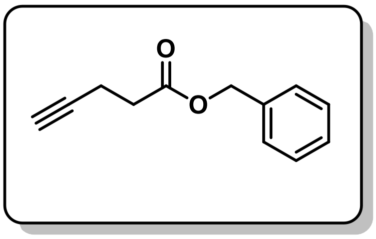
General procedure 1 was used to prepared compound **4c** from **2c** (100 mg, 0.73 mmol). Flash column chromatography was used to refine the crude product to get **4c** (126 mg, 90%) as a colourless oil, Rf = 0.5 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, chloroform-d)** *δ* 7.35 (d, *J* = 4.7 Hz, 5H), 5.82 (m, *J* = 16.8, 10.3, 6.2 Hz, 1H), 5.12 (s, 2H), 5.05 (d, *J* = 17.2 Hz, 1H), 5.00 (d, *J* = 9.9 Hz, 1H), 2.52 – 2.33 (m, 4H). **^{13}C NMR (126 MHz, chloroform-d)** *δ* 172.88, 136.60, 136.01, 128.55, 128.43, 128.22, 115.57, 66.24, 33.57, 28.85. **HRMS (ESI)** calcd for $C_{12}H_{14}O_2$ $[M+Na]^+$ 191.1067, found 191.1060.

Synthesis of benzyl (E)-but-2-enoate (4d)



General procedure 1 was used to prepared compound **4d** from **2c** (100 mg, 1.16 mmol). Flash column chromatography was used to refine the crude product to get **4d** (160 mg, 78%) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, chloroform-d)** *δ* 7.40 – 7.29 (m, 5H), 7.07 – 6.98 (m, 1H), 5.90 (dt, *J* = 15.6, 1.9 Hz, 1H), 5.17 (s, 2H), 1.88 (dd, *J* = 6.8, 1.8 Hz, 3H). **^{13}C NMR (126 MHz, chloroform-d)** *δ* 165.32, 144.16, 135.16, 127.51, 127.49, 127.13, 121.46, 64.94, 16.99. **HRMS (ESI)** calcd for $C_{11}H_{12}O_2$ $[M+Na]^+$ 199.0730, found 199.0718.

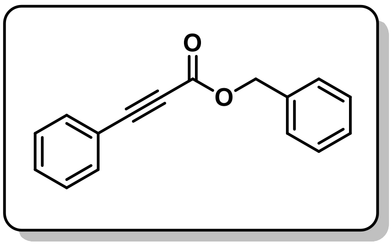
Synthesis of benzyl pent-4-ynoate (4e)



General procedure 1 was used to prepared compound **4e** from **2c** (100 mg, 0.73 mmol). Flash column chromatography was used to refine the crude product to get **4e** (124 mg, 90%) as a colourless oil, Rf = 0.5 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, chloroform-d)** *δ* 7.36

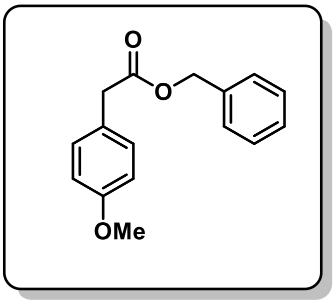
(m, *J* = 3.9 Hz, 5H), 5.15 (s, 2H), 2.64 – 2.57 (m, 2H), 2.56 – 2.49 (m, 2H), 1.97 (t, *J* = 2.6 Hz, 1H). **^{13}C NMR (126 MHz, chloroform-d)** *δ* 171.60, 135.76, 128.58, 128.31, 128.25, 82.41, 69.12, 66.53, 33.37, 14.37. **HRMS (ESI)** calcd for $C_{12}H_{12}O_2$ $[M+Na]^+$ 211.0730, found 211.0721.

Synthesis of benzyl 3-phenylpropiolate (4f)



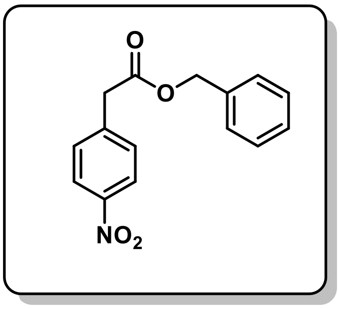
General procedure 1 was used to prepared compound **4f** from **2c** (100 mg, 0.68 mmol). Flash column chromatography was used to refine the crude product to get **4f** (113 mg, 70%) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, chloroform-d)** *δ* 7.57 (d, *J* = 7.6 Hz, 2H), 7.46 – 7.32 (m, 8H), 5.26 (s, 2H). **^{13}C NMR (126 MHz, chloroform-d)** *δ* 152.87, 133.88, 131.98, 129.66, 127.64, 127.59, 127.56, 127.53, 118.49, 85.70, 79.46, 66.67. **HRMS (ESI)** calcd for $C_{16}H_{12}O_2$ $[M+H]^+$ 237.0910, found 237.0901.

Synthesis of benzyl 2-(4-methoxyphenyl) acetate (4g)



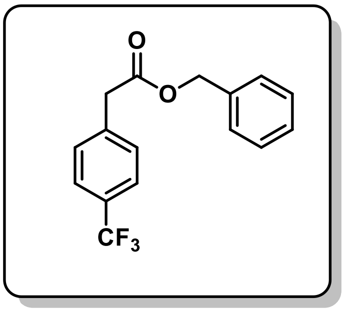
General procedure 1 was used to prepared compound **4g** from **2c** (100 mg, 0.60 mmol). Flash column chromatography was used to refine the crude product to get **4g** (115 mg, 75%) as a colourless oil, Rf = 0.6 (Hexane/EtOAc, 8:2, v/v). **^{1}H NMR (400 MHz, chloroform-d)** *δ* 7.39 – 7.28 (m, 5H), 7.24 – 7.17 (m, 2H), 6.90 – 6.82 (m, 2H), 5.12 (s, 2H), 3.79 (s, 3H), 3.61 (s, 2H). **^{13}C NMR (126 MHz, chloroform-d)** *δ* 170.72, 157.71, 134.89, 129.30, 127.51, 127.17, 127.10, 124.96, 112.99, 65.53, 54.24, 39.41. **HRMS (ESI)** calcd for $C_{16}H_{16}O_3$ $[M+Na]^+$ 257.1172, found 257.1158.

Synthesis of benzyl 2-(4-nitrophenyl) acetate(4h)



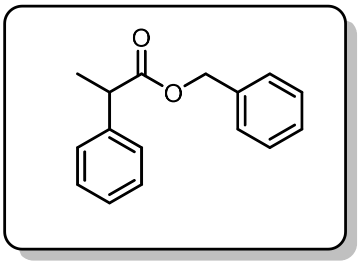
General procedure 1 was used to prepared compound **4h** from **2c** (100 mg, 0.55 mmol). Flash column chromatography was used to refine the crude product to get **4h** (143 mg, 93%) as a colourless oil, Rf = 0.5 (Hexane/EtOAc, 8:2, v/v). **^{1}H NMR (400 MHz, chloroform-d)** *δ* 8.23 – 8.13 (m, 2H), 7.49 – 7.41 (m, 2H), 7.39 – 7.28 (m, 5H), 5.15 (s, 2H), 3.78 (s, 2H). **^{13}C NMR (126 MHz, chloroform-d)** *δ* 165.25, 142.50, 136.43, 130.63, 125.59, 123.91, 123.78, 123.59, 119.02, 62.42, 36.23. **HRMS (ESI)** calcd for $C_{15}H_{13}NO_4$ $[M+Na]^+$ 294.0737, found 294.0730.

Synthesis of (trifluoromethyl)phenyl) acetate (4i)



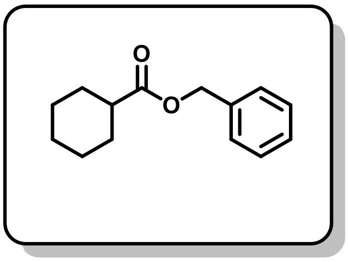
General procedure 1 was used to prepared compound **4i** from **2c** (102.5 mg, 0.50 mmol). Flash column chromatography was used to refine the crude product to get **4i** (133 mg, 90%) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 8:2, v/v). **^{1}H NMR (400 MHz, chloroform-d)** *δ* 7.58 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.33 (m, *J* = 7.1, 2.4 Hz, 5H), 5.14 (s, 2H), 3.72 (s, 2H). **^{13}C NMR (126 MHz, chloroform-d)** *δ* 169.55, 136.81, 134.54, 128.69, 128.65, 127.58, 127.37, 127.22, 124.50, 124.47, 65.91, 40.02. **^{19}F NMR** (471 MHz, **chloroform-d**) *δ* -62.54. **HRMS (ESI)** calcd for $C_{16}H_{13}F_3O_2$ $[M+Na]^+$ 317.0760, found 317.0739.

Synthesis of benzyl 2-phenylpropanoate (4j)



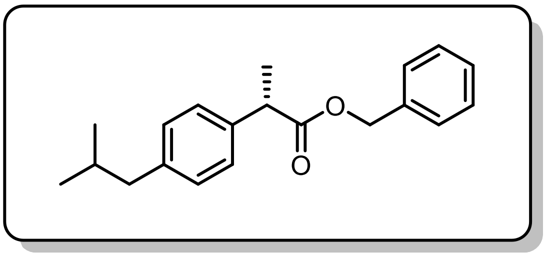
General procedure 1 was used to prepared compound **4j** from **2c** (100 mg, 0.66 mmol). Flash column chromatography was used to refine the crude product to get **4j** (135 mg, 85%) as a colourless oil, Rf = 0.5 (Hexane/EtOAc, 8:2, v/v). **^{1}H NMR (400 MHz, chloroform-d)** *δ* 7.29 (m, *J* = 2.8 Hz, 7H), 7.27 – 7.19 (m, 3H), 5.10 (q, *J* = 12.5 Hz, 2H), 3.77 (q, *J* = 7.1 Hz, 1H), 1.52 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR (126 MHz, chloroform-d)** *δ* 173.27, 139.39, 135.00, 127.57, 127.43, 127.02, 126.81, 126.51, 126.11, 65.37, 44.52, 17.44. **HRMS (ESI)** calcd for $C_{16}H_{16}O_2$ $[M+Na]^+$ 241.1213, found 241.1211.

Synthesis of benzyl cyclohexanecarboxylate (4k)



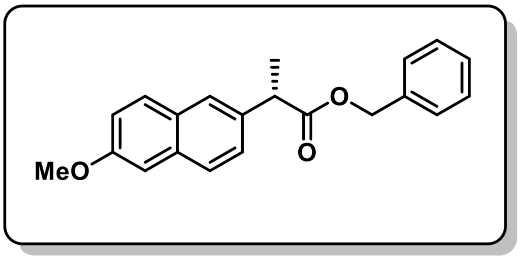
General procedure 1 was used to prepared compound **4k** from **2c** (100 mg, 0.78 mmol). Flash column chromatography was used to refine the crude product to get **4k** (150 mg, 88%) as a colourless oil, Rf = 0.5 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, chloroform-d)** *δ* 7.39 – 7.28 (m, 5H), 5.10 (s, 2H), 2.35 (tt, *J* = 11.6, 3.7 Hz, 1H), 1.93 (dd, *J* = 13.5, 3.8 Hz, 2H), 1.79 – 1.71 (m, 2H), 1.67 – 1.60 (m, 1H), 1.46 (m, *J* = 11.6, 3.7 Hz, 2H), 1.33 – 1.18 (m, 3H). **^{13}C NMR (126 MHz, chloroform-d)** *δ* 175.92, 136.36, 128.54, 128.07, 127.97, 65.90, 43.23, 29.04, 25.76, 25.46. **HRMS (ESI)** calcd for $C_{14}H_{18}O_2$ $[M+Na]^+$ 241.1199, found 241.1189.

Synthesis of benzyl (S)-2-(4-isobutylphenyl)propanoate (4l)



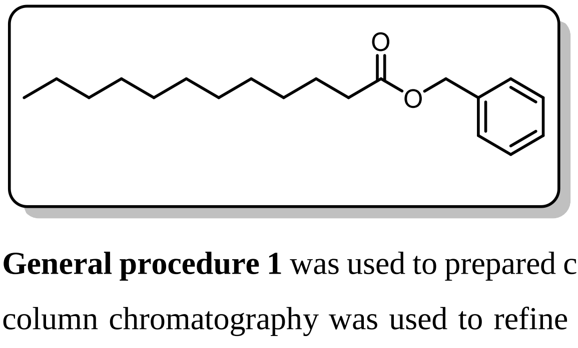
General procedure 1 was used to prepared compound **4l** from **2c** (100 mg, 0.48 mmol). Flash column chromatography was used to refine the crude product to get **4l** (120 mg, 84%) as a colourless oil, Rf = 0.6 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, chloroform-d)** δ 7.29 (d, *J* = 7.1 Hz, 3H), 7.26 – 7.17 (m, 4H), 7.08 (d, *J* = 8.2 Hz, 2H), 5.14 – 5.06 (m, 2H), 3.75 (q, *J* = 7.1 Hz, 1H), 2.45 (d, *J* = 7.4 Hz, 2H), 1.85 (m, 1H), 1.50 (d, *J* = 7.4 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR (126 MHz, chloroform-d)** δ 173.49, 139.53, 136.60, 135.09, 128.29, 127.40, 126.96, 126.73, 126.21, 65.25, 44.13, 44.02, 29.17, 21.35, 17.38. **HRMS (ESI)** calcd for $C_{20}H_{24}O_2$ [M+Na]$^+$ 319.1669, found 319.1669.

Synthesis of benzyl (S)-2-(6-methoxynaphthalen-2-yl) propanoate (4m)



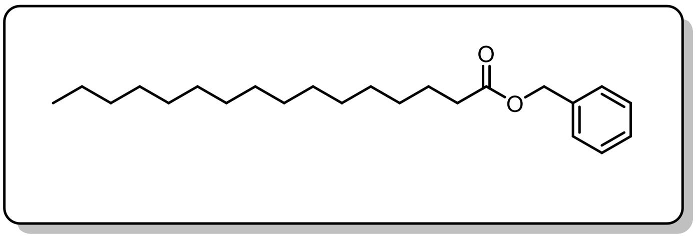
General procedure 1 was used to prepared compound **4m** from **2c** (100 mg, 0.43 mmol). Flash column chromatography was used to refine the crude product to get **4m** (110 mg, 80%) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, chloroform-d)** *δ* 7.64 – 7.54 (m, 3H), 7.31 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.22 – 7.13 (m, 5H), 7.08 – 7.00 (m, 2H), 5.09 – 4.97 (m, 2H), 3.83 (d, *J* = 7.4 Hz, 1H), 3.81 (s, 3H), 1.50 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, chloroform-d)** *δ* 173.41, 156.62, 134.99, 134.54, 132.69, 128.26, 127.91, 127.42, 127.03, 126.89, 126.10, 125.26, 124.91, 117.91, 104.58, 65.43, 54.25, 44.44, 17.50. **HRMS (ESI)** calcd for $C_{21}H_{20}O_3$ [M+H]$^+$ 321.1481, found 321.1481.

Synthesis of benzyl dodecanoate (4n)



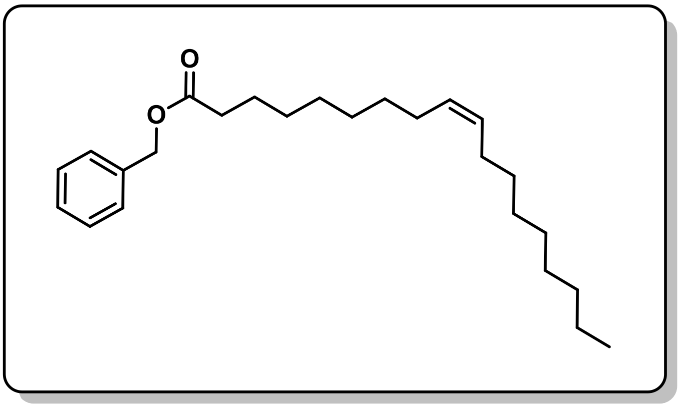
General procedure 1 was used to prepared compound **4n** from **2c** (105 mg, 0.52 mmol). Flash column chromatography was used to refine the crude product to get **4n** (128 mg, 85%) as a colourless oil, Rf = 0.8 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, chloroform-d)** *δ* 7.42 – 7.29 (m, 5H), 5.11 (s, 2H), 2.35 (t, *J* = 7.6 Hz, 2H), 1.64 (m, *J* = 7.4 Hz, 2H), 1.25 (m, 16H), 0.88 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, chloroform-d)** *δ* 173.73, 136.17, 128.55, 128.17, 66.06, 34.37, 31.93, 29.61, 29.46, 29.34, 29.26, 29.15, 24.98, 22.70, 14.13. **HRMS (ESI)** calcd for $C_{19}H_{30}O_2$ $[M+Na]^+$ 313.2138, found 313.2127.

Synthesis of benzyl palmitate (4o)



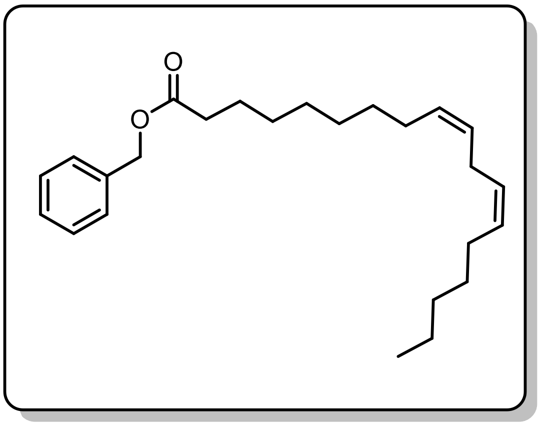
General procedure 1 was used to prepared compound **4o** from **2c** (100 mg, 0.35 mmol). Flash column chromatography was used to refine the crude product to get **4o** (120 mg, 91%) as a colourless oil, Rf = 0.5 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 7.32 – 7.22 (m, 5H), 5.04 (s, 2H), 2.28 (t, *J* = 7.5 Hz, 2H), 1.57 (p, *J* = 7.5 Hz, 2H), 1.19 (d, *J* = 12.5 Hz, 24H), 0.81 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, chloroform-d)** δ 172.67, 135.17, 127.51, 127.13, 65.03, 33.33, 30.92, 28.69, 28.66, 28.63, 28.58, 28.44, 28.35, 28.24, 28.12, 23.96, 21.68, 13.09. **HRMS (ESI)** calcd for $C_{23}H_{38}O_2$ $[M+Na]^+$ 369.2764, found 369.2751.

Synthesis of benzyl oleate (4p)



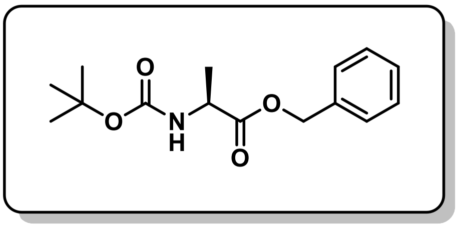
General procedure 1 was used to prepared compound **4p** from **2c** (100 mg, 0.35 mmol). Flash column chromatography was used to refine the crude product to get **4p** (115 mg, 88%) as a yellow syrup, Rf = 0.5 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (500 MHz, chloroform-d)** δ 7.32 – 7.22 (m, 5H), 5.32 – 5.22 (m, 2H), 5.04 (s, 2H), 2.28 (t, *J* = 7.6 Hz, 2H), 1.93 (q, *J* = 6.7 Hz, 4H), 1.57 (p, *J* = 7.4 Hz, 2H), 1.25 – 1.17 (m, 20H), 0.81 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, chloroform-d)** δ 172.65, 135.14, 128.98, 128.73, 127.52, 127.14, 65.03, 33.31, 30.89, 28.75, 28.66, 28.50, 28.31, 28.13, 28.08, 26.20, 26.15, 23.94, 21.66, 13.09. **HRMS (ESI)** calcd for $C_{25}H_{40}O_2$ $[M+Na]^+$ 395.2921, found 395.2907.

Synthesis of benzyl (9Z,12Z)-octadeca-9,12-dienoate (4q)



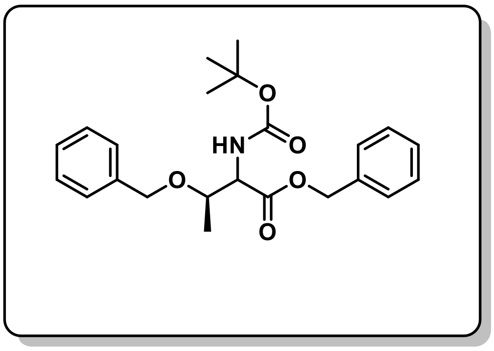
General procedure 1 was used to prepared compound **4q** from **2c** (100 mg, 0.35 mmol). Flash column chromatography was used to refine the crude product to get **4q** (120 mg, 91%) as a yellow syrup, Rf = 0.5 (Hexane/EtOAc, 9:1, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 7.40 – 7.28 (m, 5H), 5.36 (p, *J* = 6.2 Hz, 4H), 5.11 (s, 2H), 2.77 (t, *J* = 6.2 Hz, 2H), 2.35 (t, *J* = 7.5 Hz, 2H), 2.11 – 1.98 (m, 4H), 1.64 (p, *J* = 7.3 Hz, 2H), 1.34 – 1.25 (m, 14H), 0.89 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, chloroform-d)** δ 172.64, 135.13, 129.21, 129.03, 127.52, 127.14, 127.03, 126.90, 65.04, 33.31, 30.51, 28.56, 28.33, 28.13, 28.08, 26.19, 24.62, 23.93, 21.55, 13.05. **HRMS (ESI)** calcd for $C_{25}H_{38}O_2$ $[M+Na]^+$ 393.2764, found 393.2760.

Synthesis of benzyl (tert-butoxycarbonyl)-L-alaninate (5a)



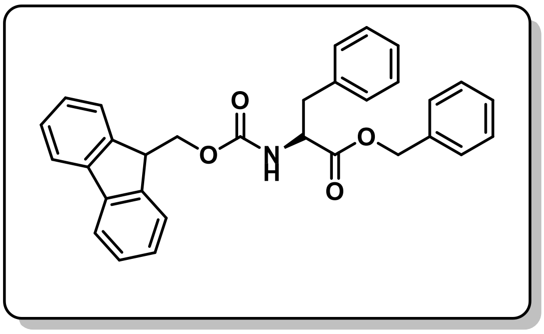
General procedure 1 was used to prepared compound **5a** from **2c** (100 mg, 0.52 mmol). Flash column chromatography was used to refine the crude product to get **5a** (65 mg, 51%) as a yellow syrup, Rf = 0.8 (Hexane/EtOAc, 8:2, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 7.41 – 7.29 (m, 5H), 5.17 (q, *J* = 12.5 Hz, 2H), 5.06 (d, *J* = 7.7 Hz, 1H), 4.35 (m, *J* = 7.5 Hz, 1H), 1.43 (s, 9H), 1.39 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR (151 MHz, chloroform-d)** δ 173.26, 155.13, 135.46, 128.62, 128.40, 128.16, 79.87, 67.01, 49.31, 28.34, 18.66. **HRMS (ESI)** calcd for $C_{15}H_{21}NO_4$ $[M+Na]^+$ 302.1363, found 302.1364.

Synthesis of benzyl (3R)-3-(benzyloxy)-2-((tert-butoxycarbonyl) amino)butanoate (5b)



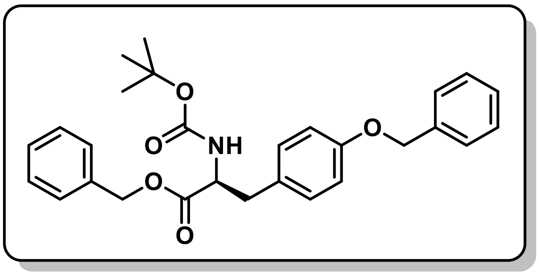
General procedure 1 was used to prepared compound **5b** from **2c** (100 mg, 0.32 mmol). Flash column chromatography was used to refine the crude product to get **5b** (90 mg, 70%) as a white solid, Rf = 0.5 (Hexane/EtOAc, 8:2, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 7.33 – 7.24 (m, 8H), 7.17 (dd, *J* = 7.5, 1.9 Hz, 2H), 5.31 (d, *J* = 9.5 Hz, 1H), 5.12 (s, 2H), 4.48 (d, *J* = 11.6 Hz, 1H), 4.34 (dd, *J* = 9.9, 2.2 Hz, 1H), 4.26 (d, *J* = 11.6 Hz, 1H), 4.15 (m, *J* = 6.0, 3.0 Hz, 1H), 1.44 (s, 9H), 1.25 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (151 MHz, chloroform-d)** δ 171.06, 156.22, 137.89, 135.39, 128.54, 128.39, 128.36, 128.34, 127.70, 127.62, 79.88, 74.59, 70.86, 67.10, 58.40, 28.32, 16.31. **HRMS (ESI)** calcd for $C_{23}H_{29}NO_5$ [M+Na]$^+$ 422.1938, found 422.1937.

Synthesis of benzyl (((9H-fluoren-9-yl)methoxy)carbonyl)-D-phenylalaninate (5c)



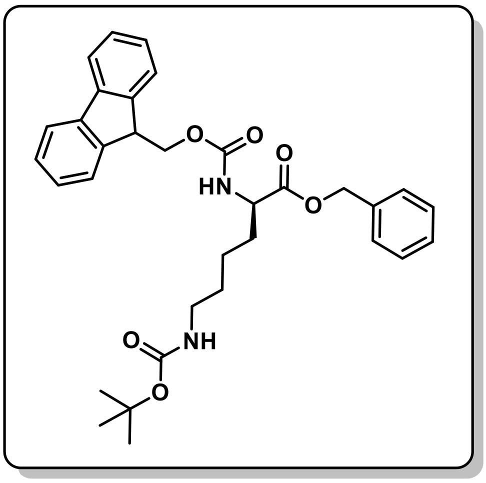
General procedure 1 was used to prepared compound **5c** from **2c** (100 mg, 0.25 mmol). Flash column chromatography was used to refine the crude product to get **5c** (80 mg, 55%) as a white solid, Rf = 0.7 (Hexane/EtOAc, 9:2, v/v). **^{1}H NMR (500 MHz, chloroform-d)** δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.59 – 7.51 (m, 2H), 7.41 – 7.28 (m, 8H), 7.25 – 7.17 (m, 4H), 7.00 (dd, *J* = 6.3, 2.9 Hz, 2H), 5.29 (d, *J* = 8.4 Hz, 1H), 5.14 (q, *J* = 12.2 Hz, 2H), 4.72 (q, *J* = 6.1 Hz, 1H), 4.43 (d, *J* = 7.1 Hz, 1H), 4.37 – 4.29 (m, 1H), 4.19 (t, *J* = 7.1 Hz, 1H), 3.11 (m, *J* = 13.9, 5.8 Hz, 2H). **^{13}C NMR (126 MHz, chloroform-d)** δ 171.33, 155.52, 143.85, 143.73, 141.30, 135.56, 135.03, 129.36, 128.62, 128.59, 127.70, 127.09, 127.05, 125.11, 125.05, 119.98, 67.29, 66.96, 54.78, 47.15, 38.18. **HRMS (ESI)** calcd for $C_{31}H_{27}NO_4$ [M+H]$^+$ 478.2013, found 478.2007.

Synthesis of tert-butyl (R)-(1-(benzyloxy)-2-(4-(benzyloxy)phenyl) ethyl) carbamate (5d)



General procedure 1 was used to prepared compound **5d** from **2c** (100 mg, 0.26 mmol). Flash column chromatography was used to refine the crude product to get **5d** (80 mg, 66%) as a white solid, Rf = 0.7 (Hexane/EtOAc, 8:2, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 7.46 – 7.27 (m, 10H), 6.94 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.20 – 5.06 (m, 2H), 5.01 (s, 2H), 4.97 (d, *J* = 8.2 Hz, 1H), 4.58 (q, *J* = 6.0 Hz, 1H), 3.02 (d, *J* = 6.5 Hz, 2H), 1.41 (s, 9H). **^{13}C NMR (126 MHz, chloroform-d)** δ 170.77, 156.86, 154.08, 136.00, 134.21, 129.35, 127.56, 127.54, 127.42, 127.07, 126.94, 126.43, 113.85, 78.86, 68.97, 66.03, 53.54, 36.38, 27.28. **HRMS (ESI)** calcd for $C_{28}H_{31}NO_5$ $[M+Na]^+$ 484.2094, found 484.2103.

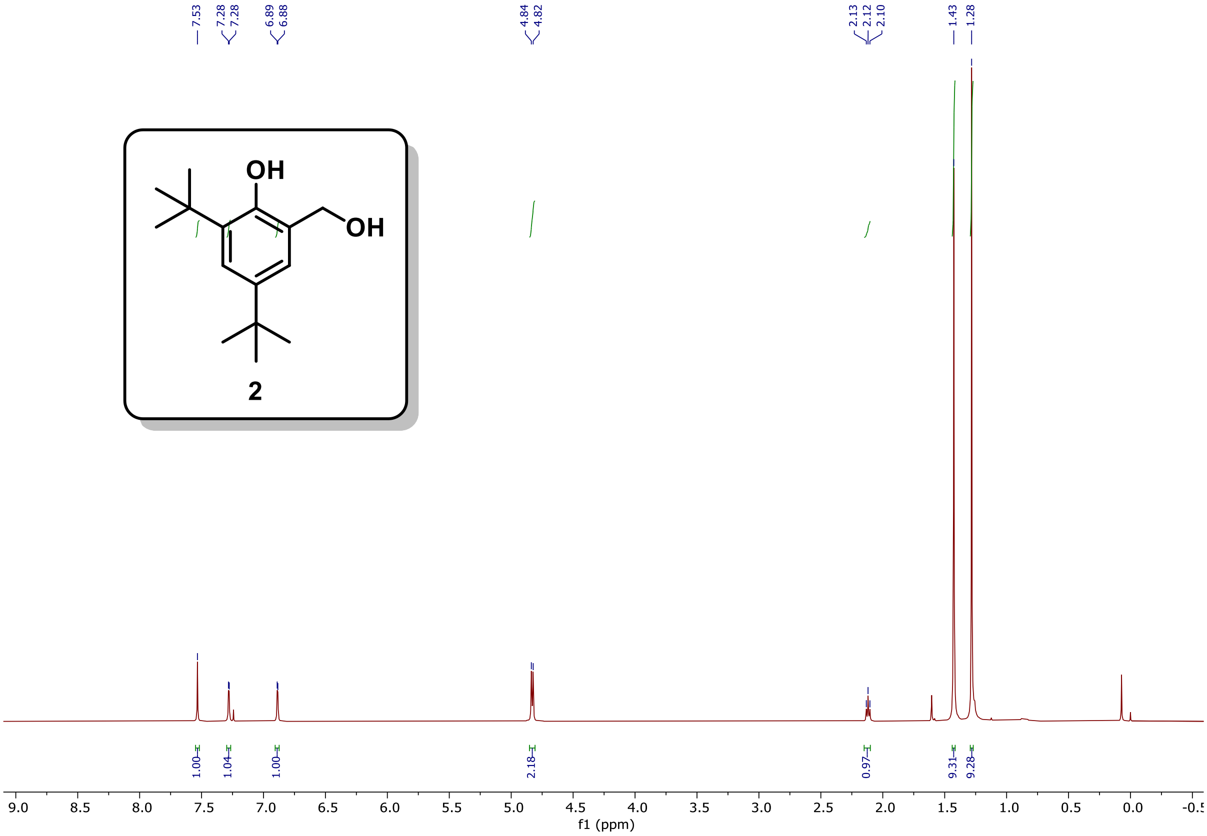
Synthesis of benzyl N2-(((9H-fluoren-9-yl)methoxy)carbonyl)-N6-(tert-butoxycarbonyl)lysinate (5e)



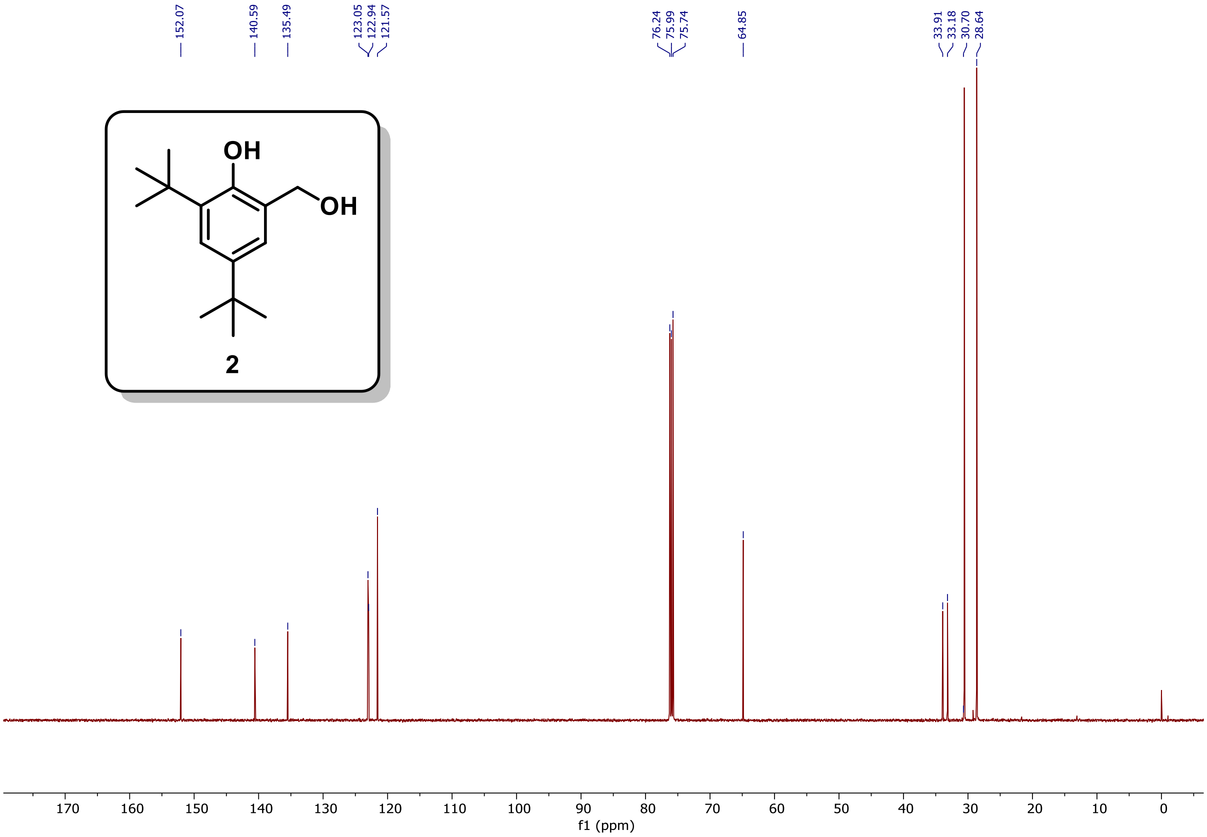
General procedure 1 was used to prepared compound **5e** from **2c** (100 mg, 0.21 mmol). Flash column chromatography was used to refine the crude product to get **5e** (71 mg, 60%) as a colourless oil, Rf = 0.5 (Hexane/EtOAc, 8:2, v/v). **^{1}H NMR (400 MHz, chloroform-d)** δ 7.76 (d, *J* = 7.3 Hz, 2H), 7.60 (d, *J* = 7.7 Hz, 2H), 7.47 – 7.27 (m, 9H), 5.40 (d, *J* = 8.2 Hz, 1H), 5.18 (q, *J* = 12.0 Hz, 2H), 4.56 – 4.33 (m, 4H), 4.21 (t, *J* = 7.3 Hz, 1H), 3.07 (d, *J* = 6.9 Hz, 2H), 1.92 – 1.80 (m, 1H), 1.65 (d, *J* = 32.3 Hz, 4H), 1.43 (s, 10H). **^{13}C NMR (126 MHz,**

chloroform-d) δ 172.30, 156.07, 155.99, 143.93, 143.76, 141.33, 135.29, 128.65, 128.54, 128.37, 127.71, 127.08, 125.11, 119.98, 79.19, 67.21, 67.05, 53.81, 47.19, 40.08, 29.70, 29.59, 28.43, 22.30. **HRMS (ESI)** calcd for $C_{33}H_{38}N_2O_6$ $[M+Na]^+$ 581.2622, found 581.2605.

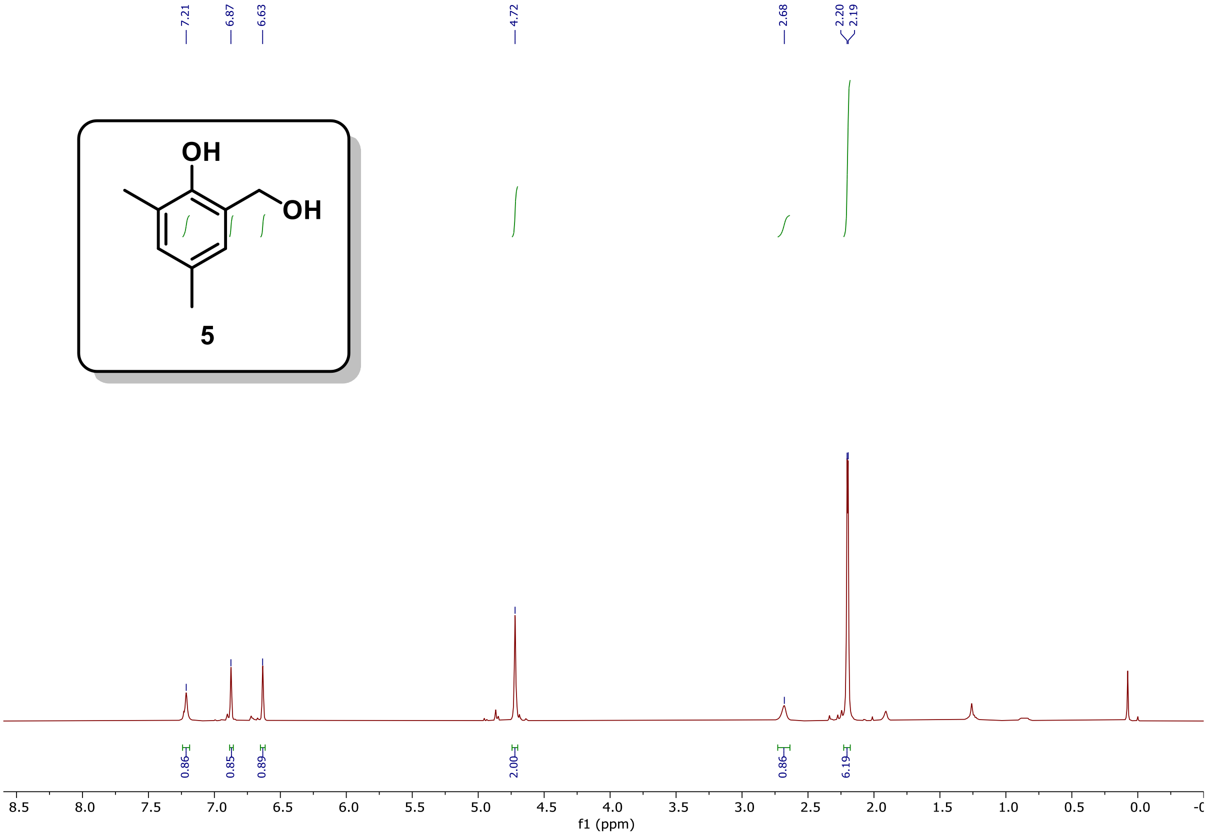
Spectra of catalysts



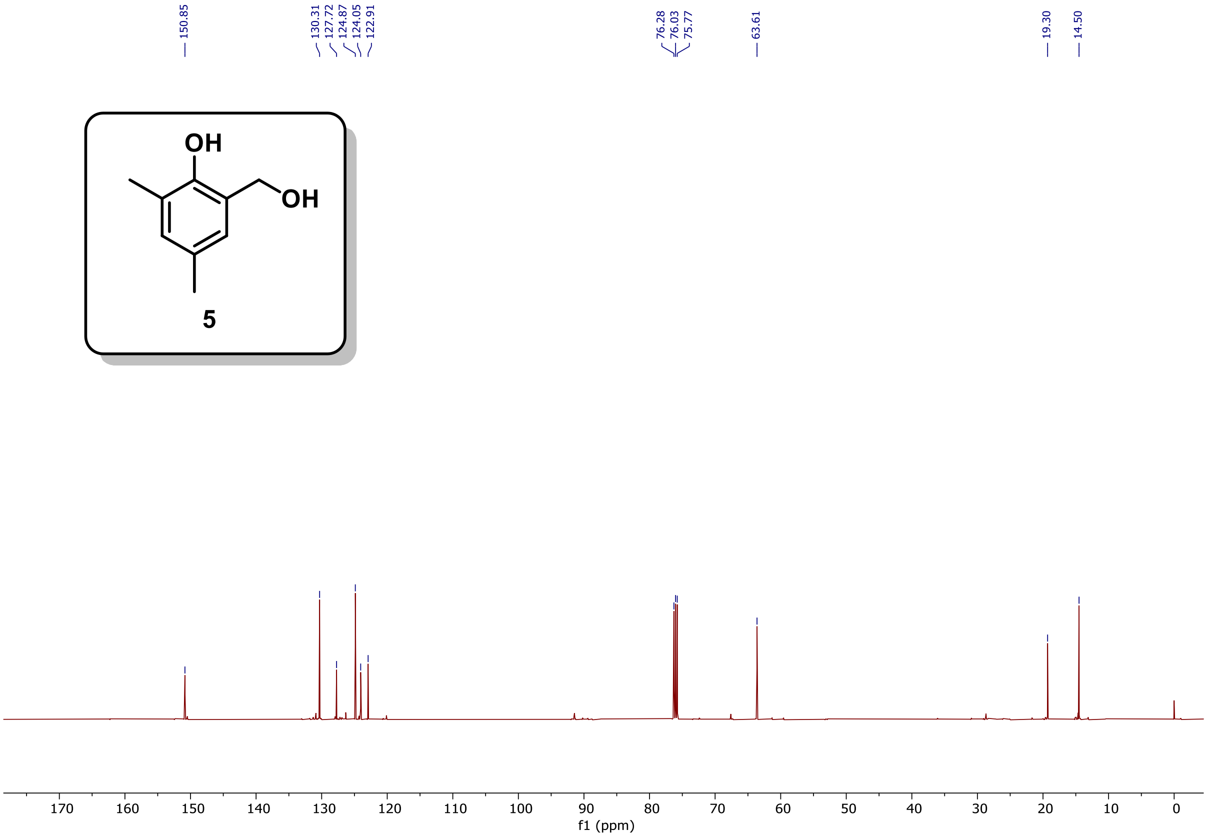
^{1}H NMR spectrum of compound 2 (500 MHz CDCl$_3$)



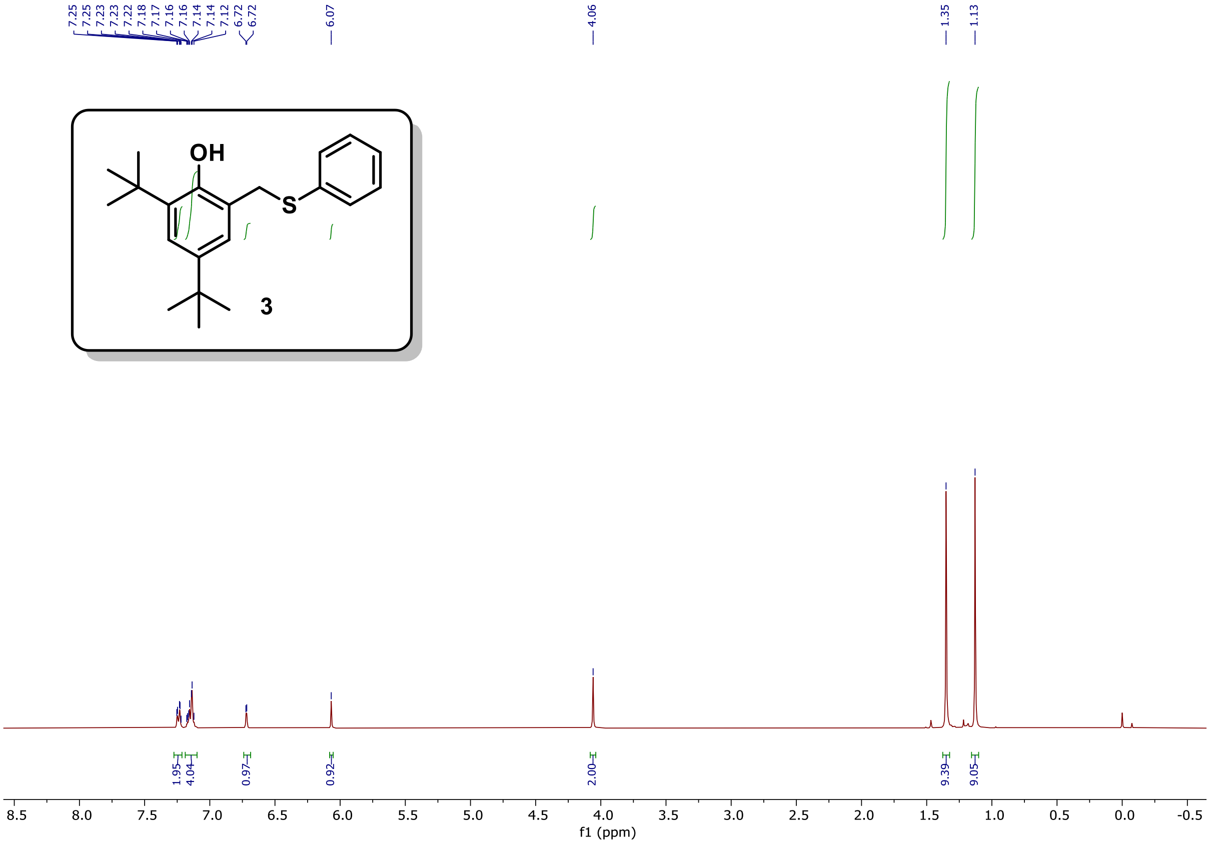
^{13}C{^{1}H} NMR spectrum of compound 2 (126 MHz CDCl$_3$)



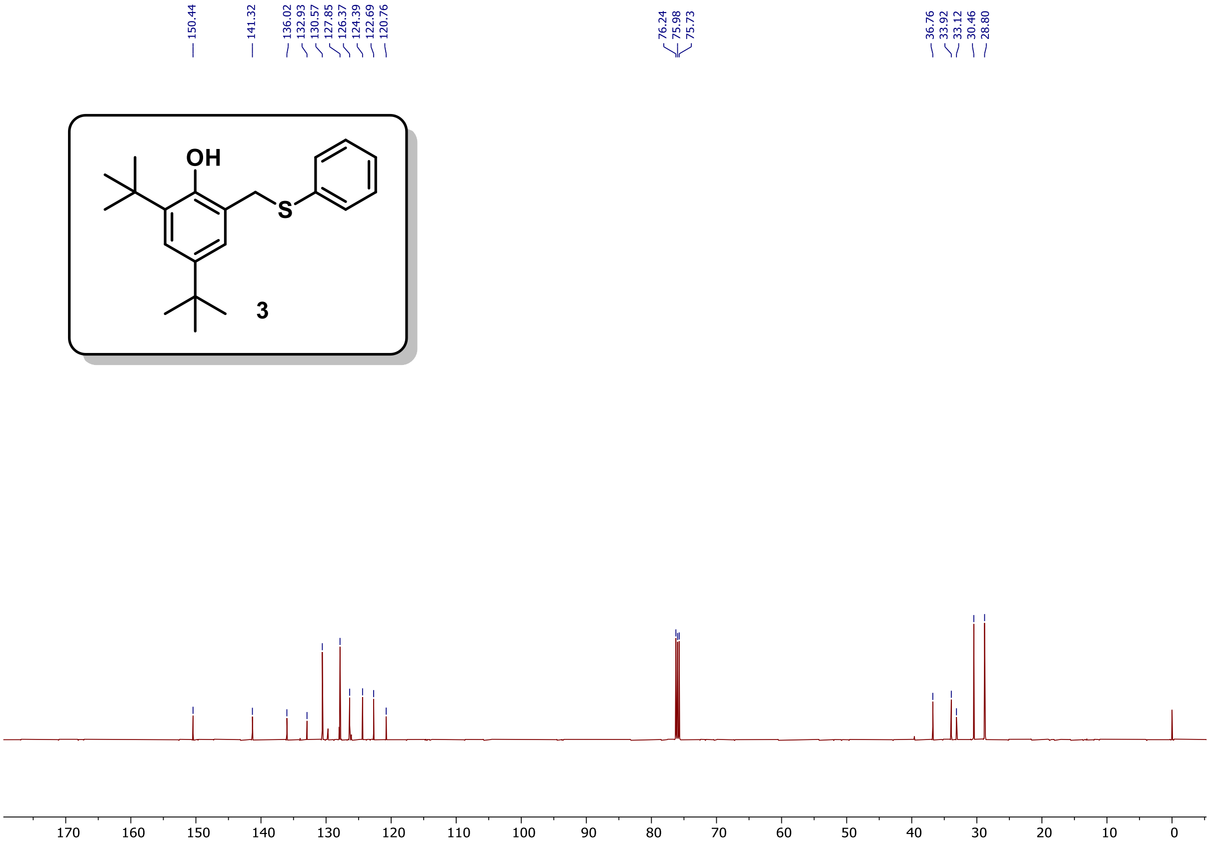
^{1}H NMR spectrum of compound 5 (500 MHz CDCl$_3$)



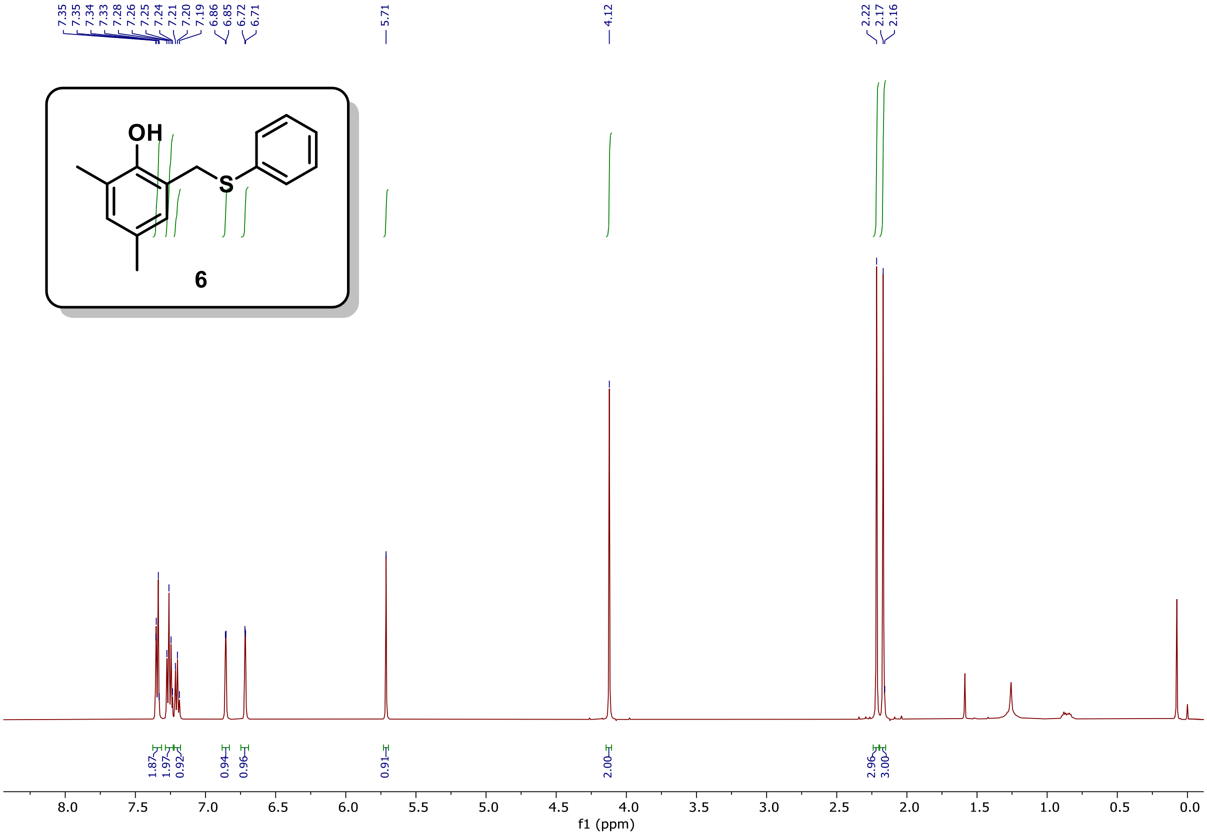
^{13}C{^{1}H} NMR spectrum of compound 5 (126 MHz CDCl$_3$)



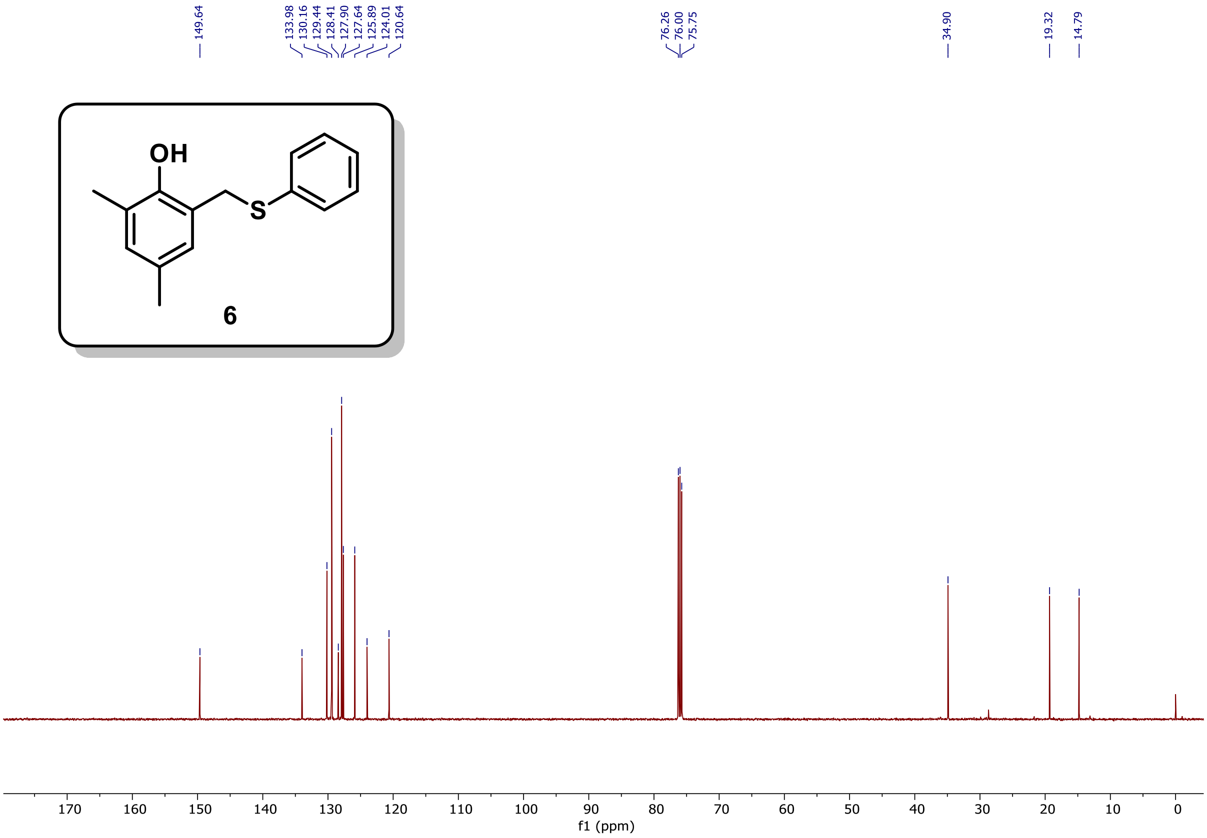
^{1}H NMR spectrum of compound 3 (500 MHz CDCl$_3$)



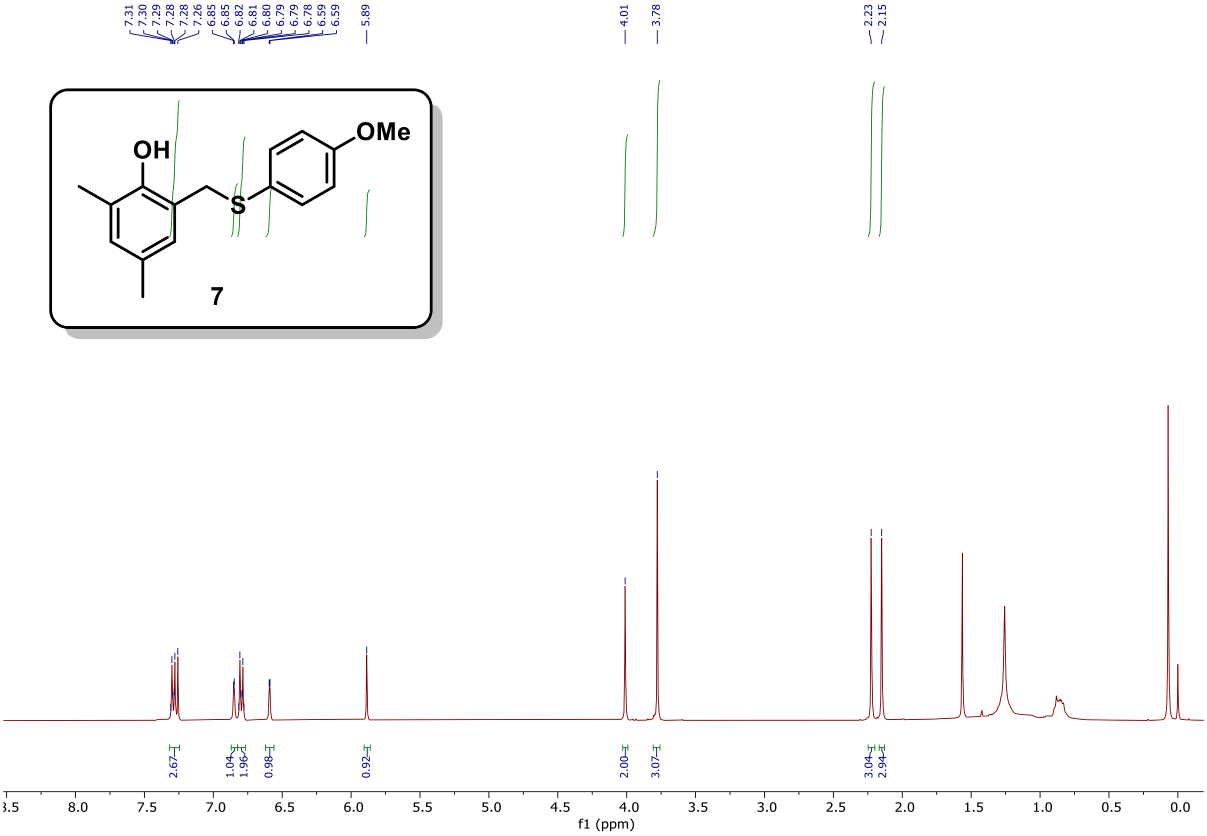
^{13}C{^{1}H} NMR spectrum of compound 3 (126 MHz CDCl$_3$)



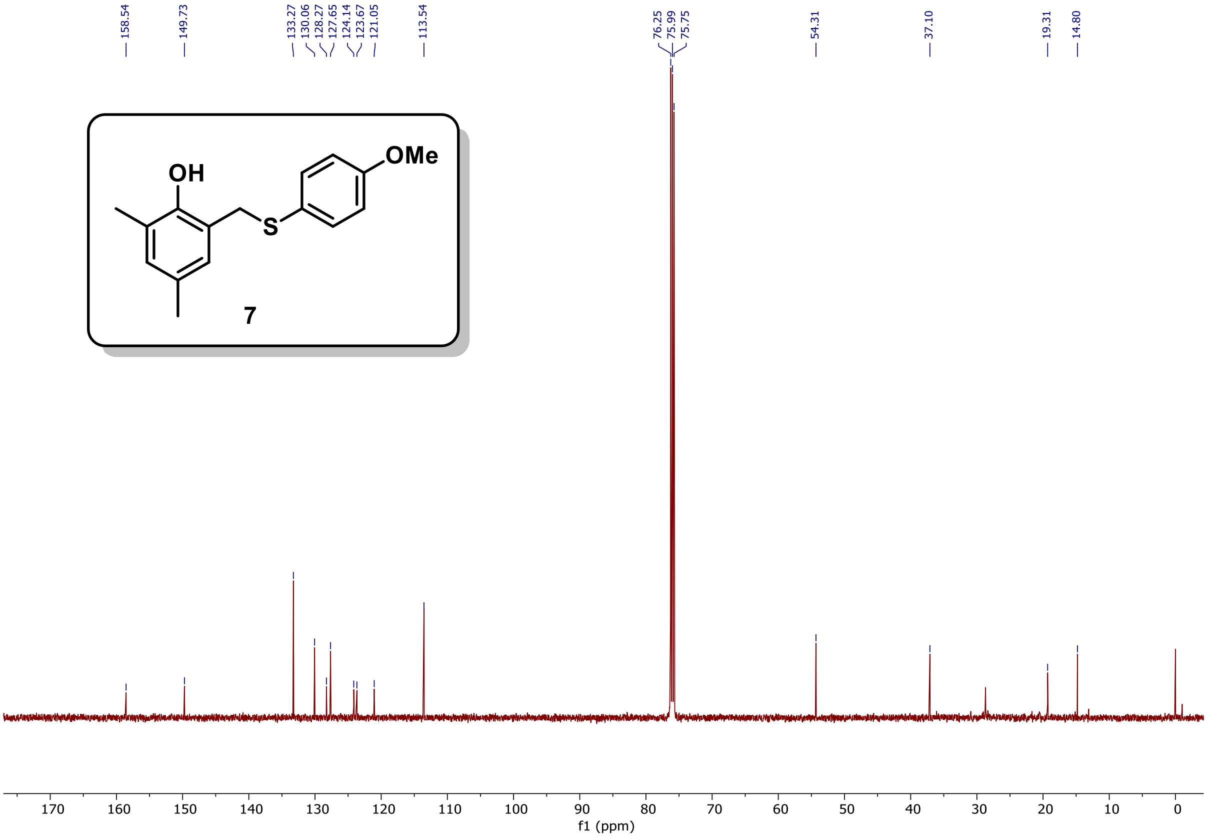
^{1}H NMR spectrum of compound 6 (500 MHz CDCl$_3$)



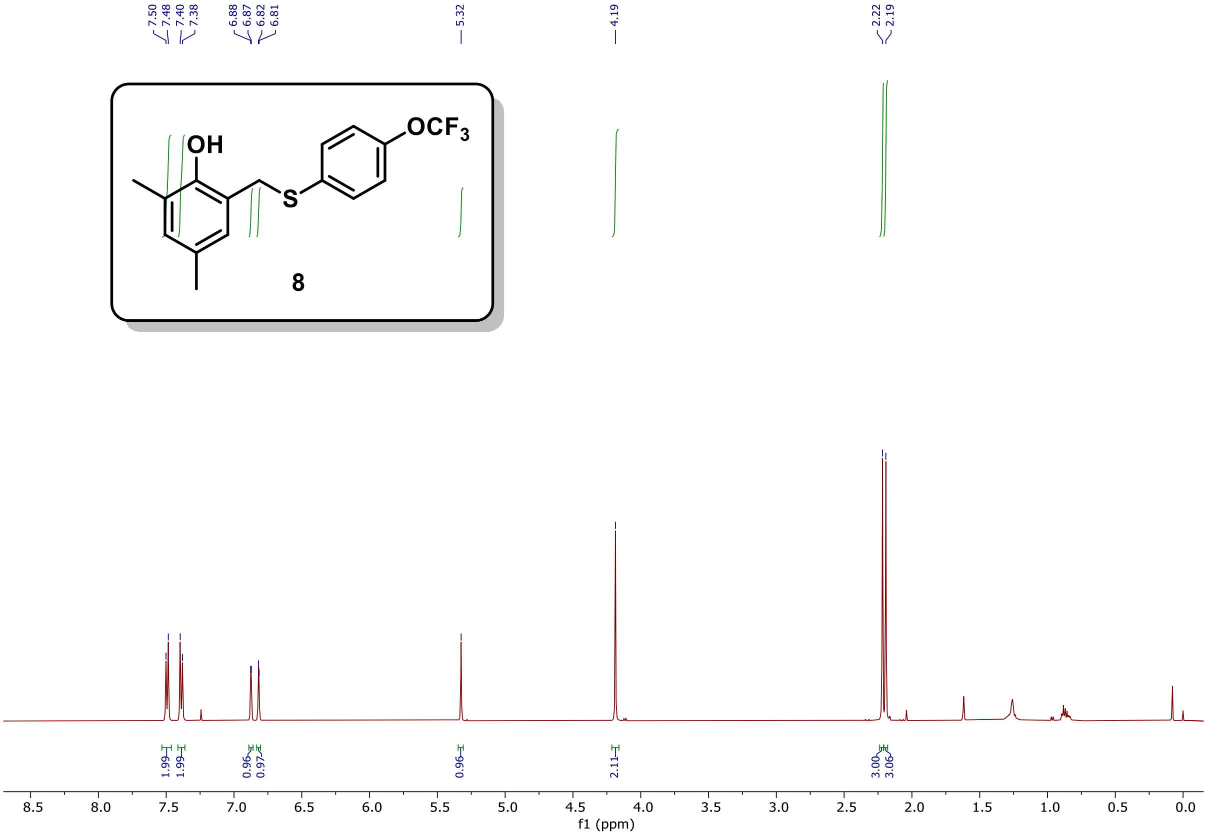
^{13}C{^{1}H} NMR spectrum of compound 6 (126 MHz CDCl$_3$)



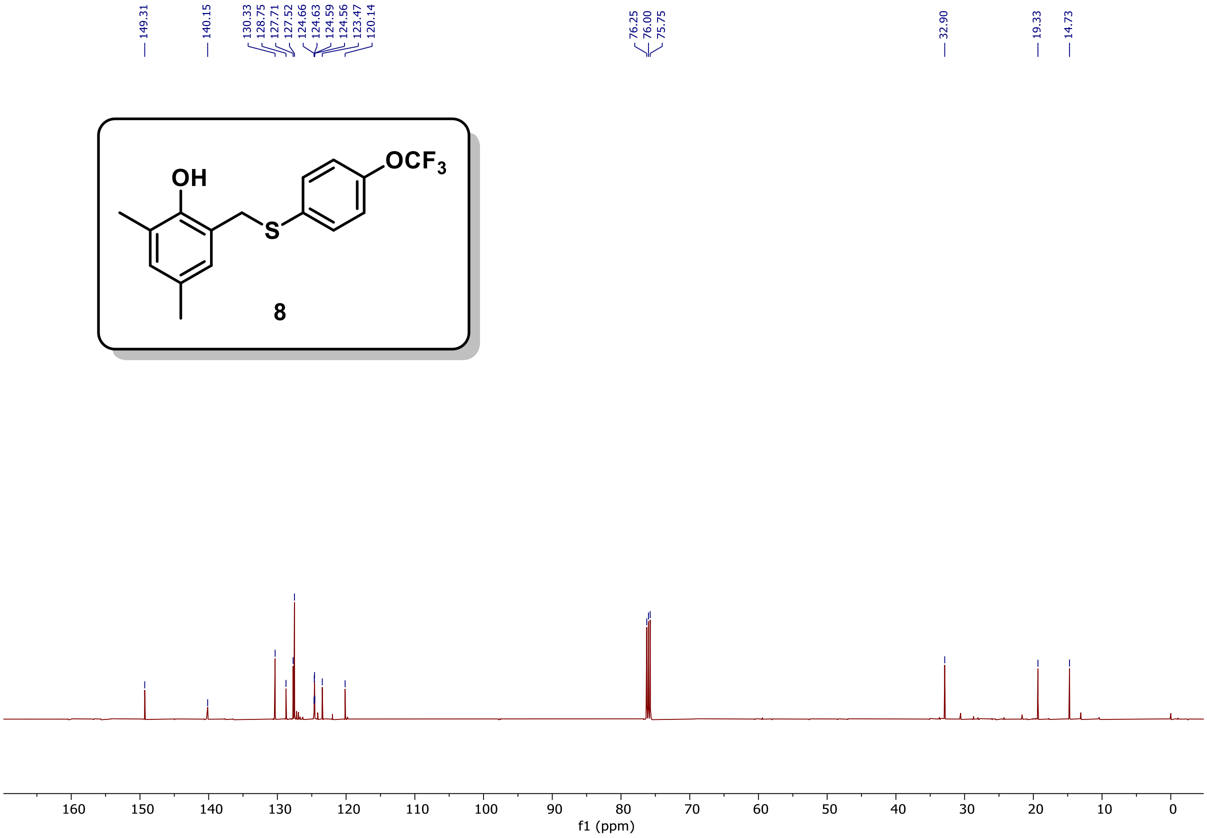
^{13}C{^{1}H} NMR spectrum of compound 7 (500 MHz CDCl$_3$)



^{13}C{^{1}H} NMR spectrum of compound 7 (126 MHz CDCl$_3$)

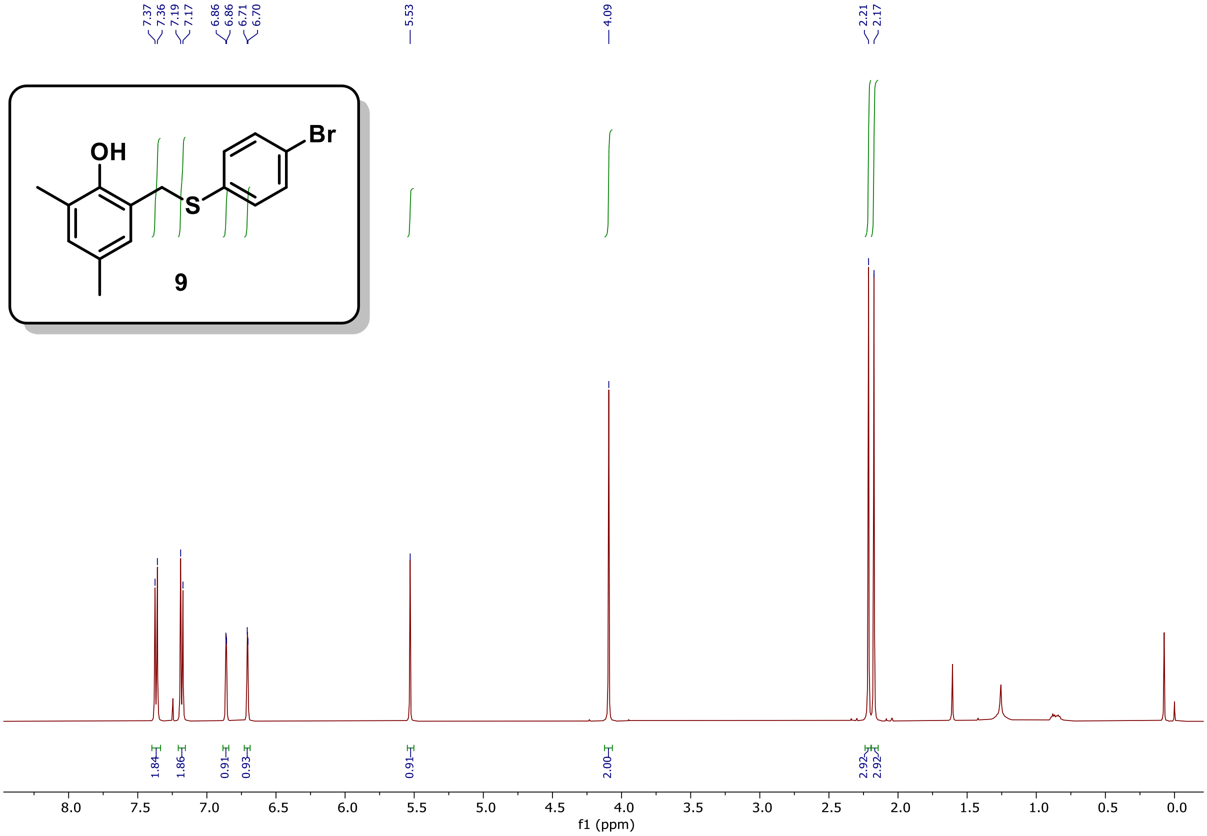


^{1}H NMR spectrum of compound 8 (500 MHz CDCl$_3$)

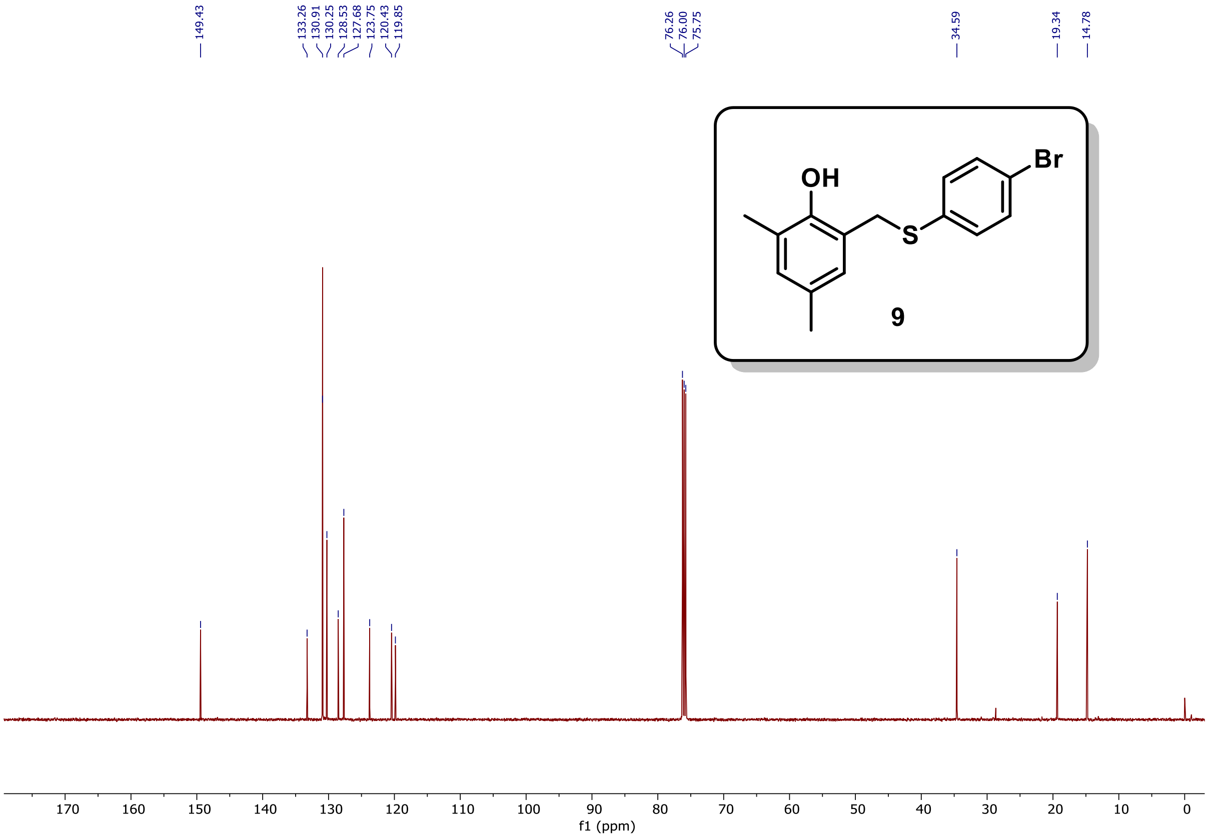


^{13}C{^{1}H} NMR spectrum of compound 8 (126 MHz CDCl$_3$)

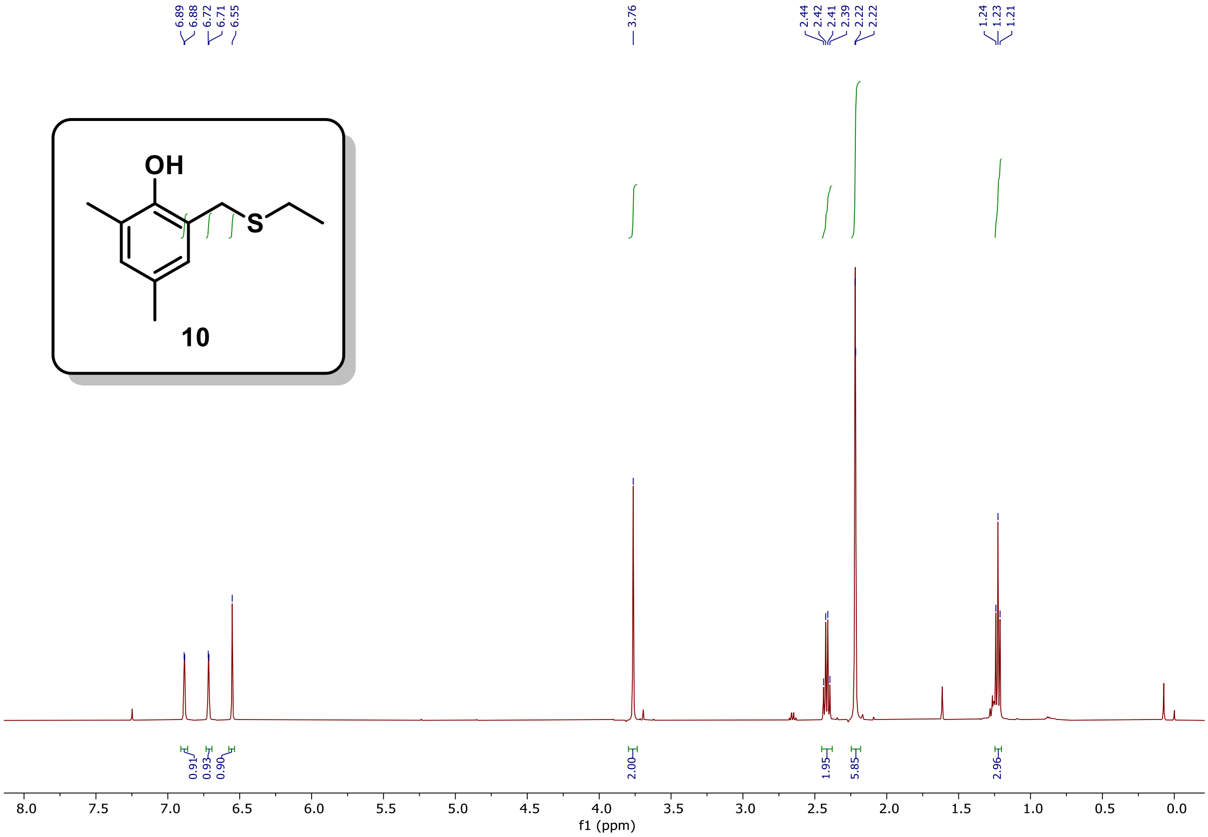
^{19}F NMR spectrum of compound 8 (471 MHz, CDCl$_3$)



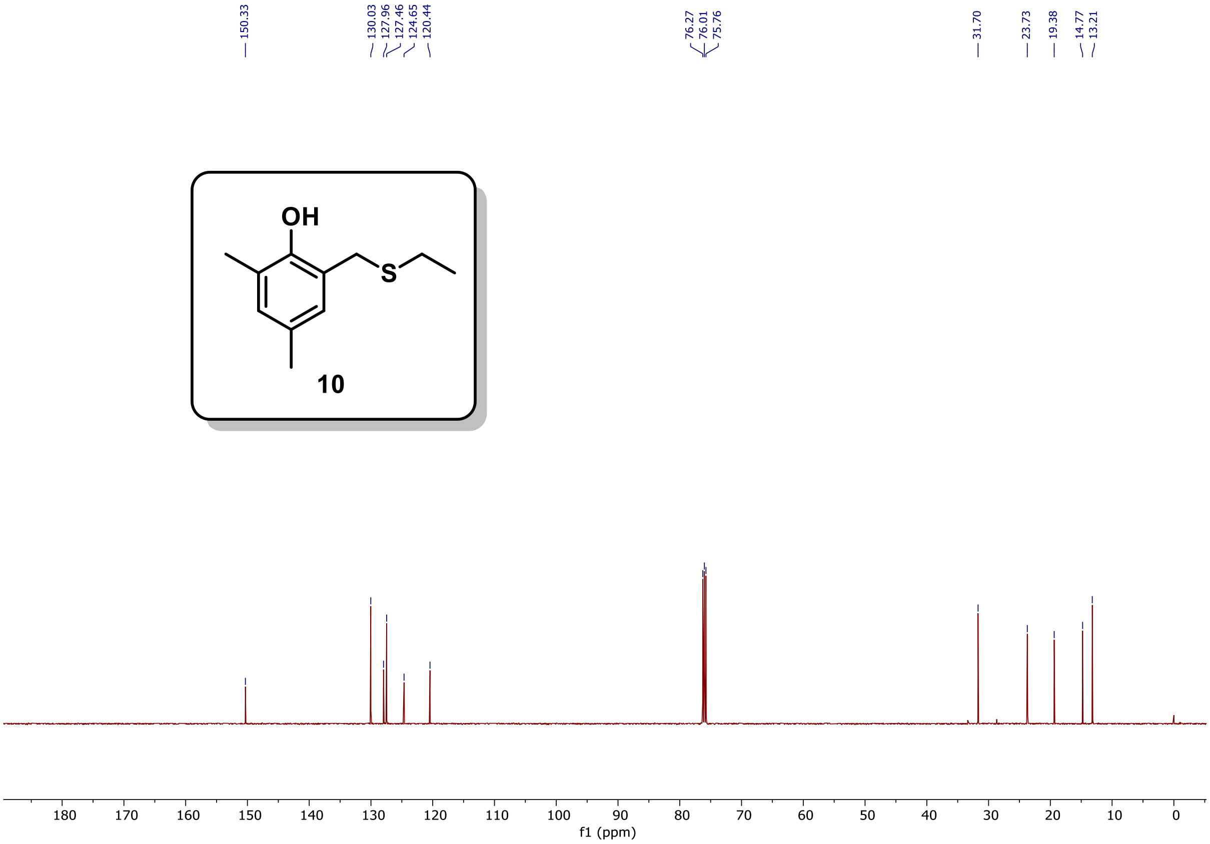
^{1}H NMR spectrum of compound 9 (500 MHz CDCl$_3$)



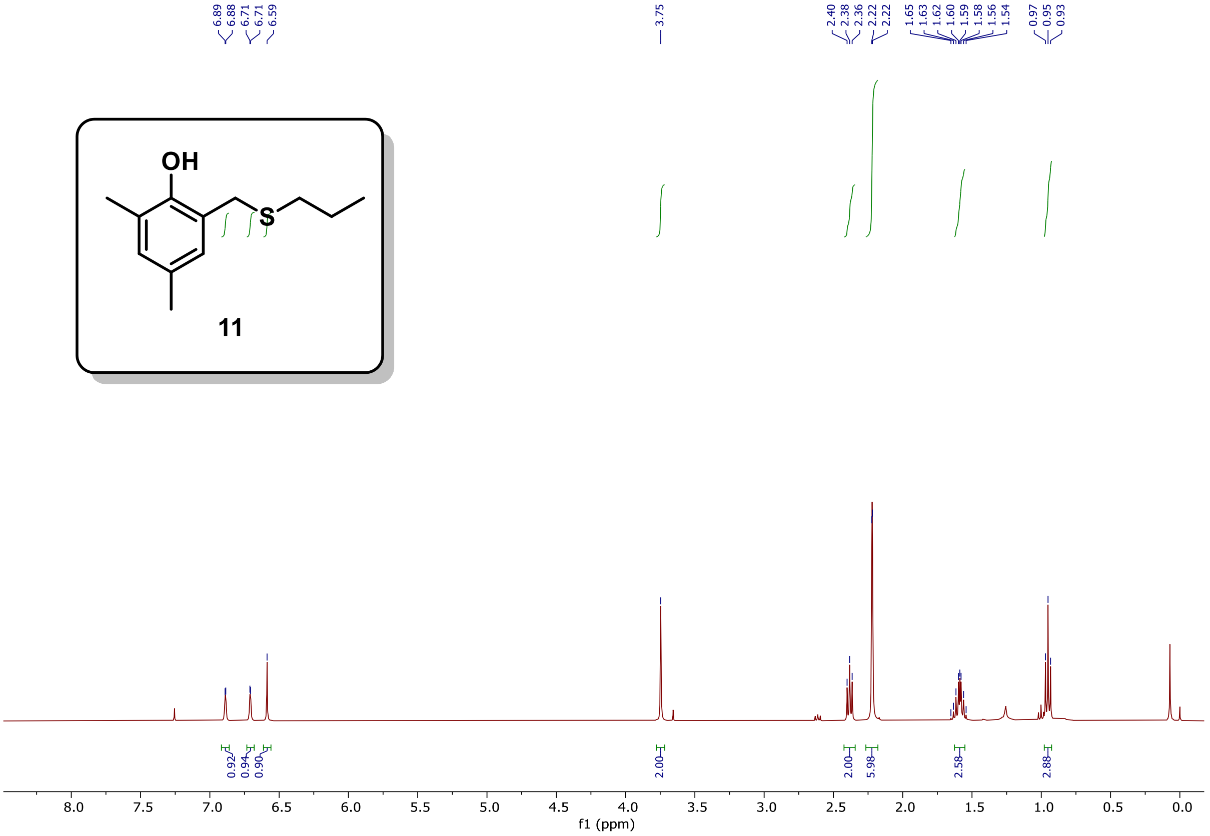
$^{13}C\{^1H\}$ **NMR spectrum of compound 9 (126 MHz CDCl₃)**



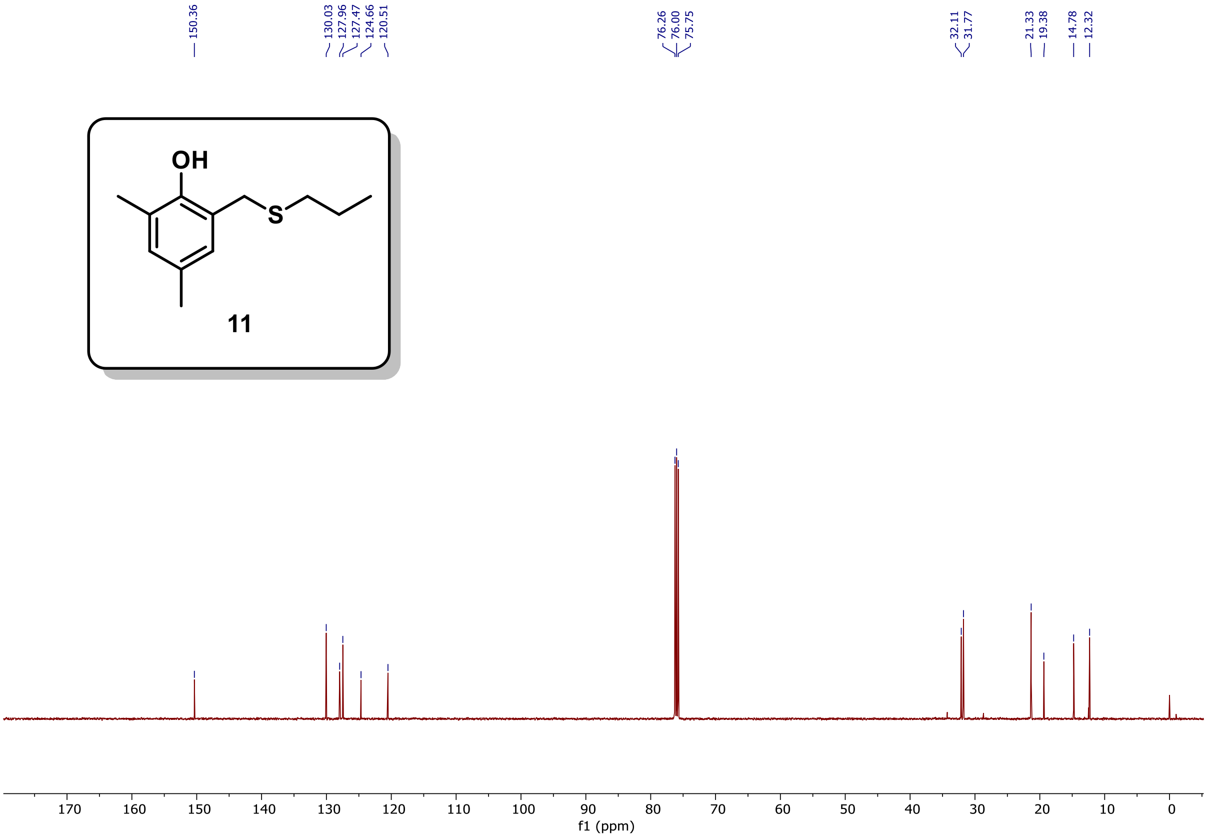
^1H **NMR spectrum of compound 10 (500 MHz CDCl₃)**



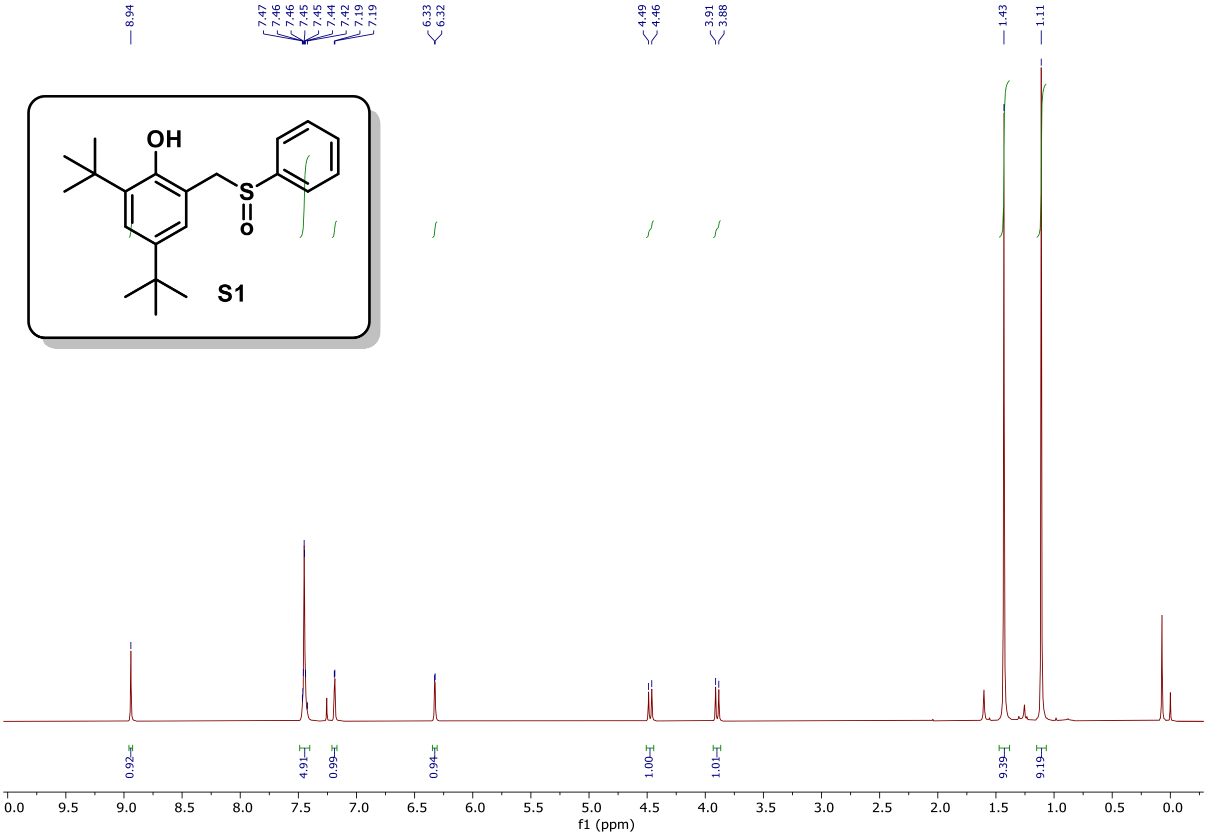
$^{13}C\{^{1}H\}$ **NMR spectrum of compound 10 (126 MHz CDCl$_3$)**



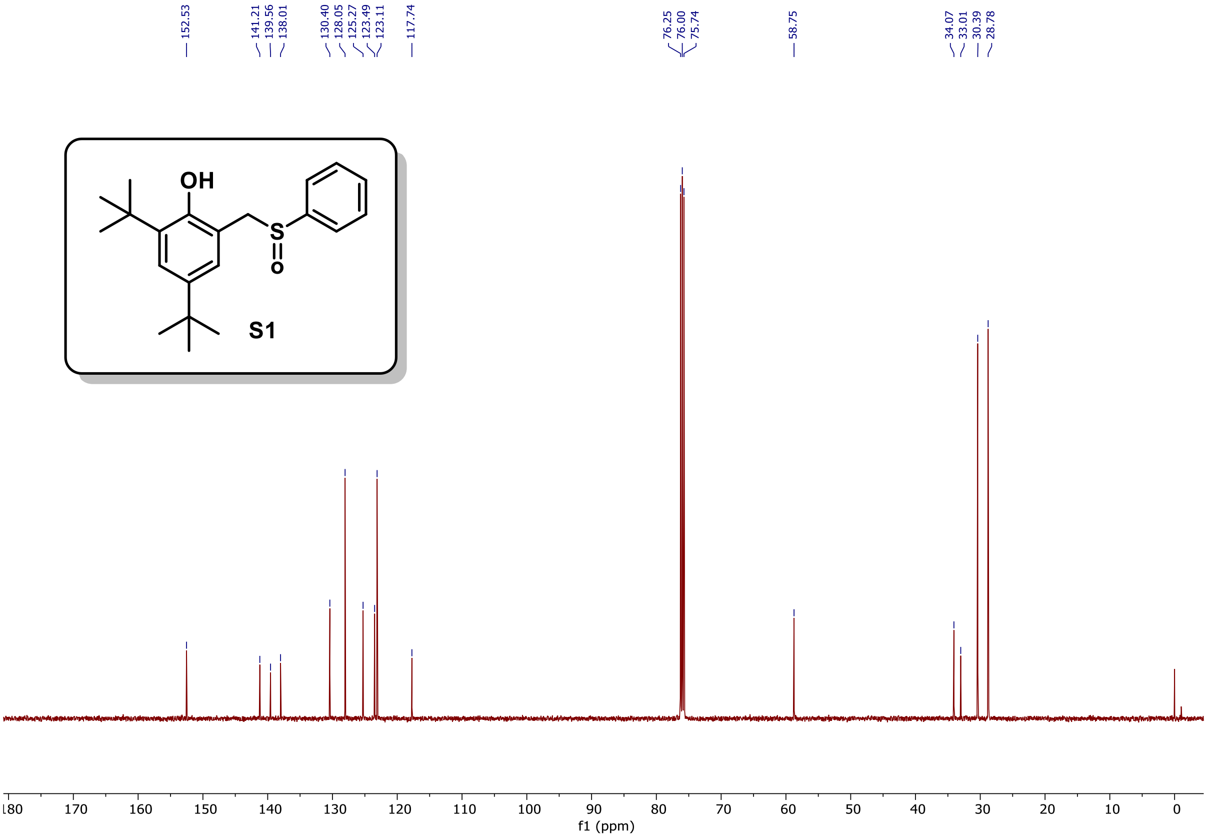
^{1}H **NMR spectrum of compound 11 (500 MHz CDCl$_3$)**



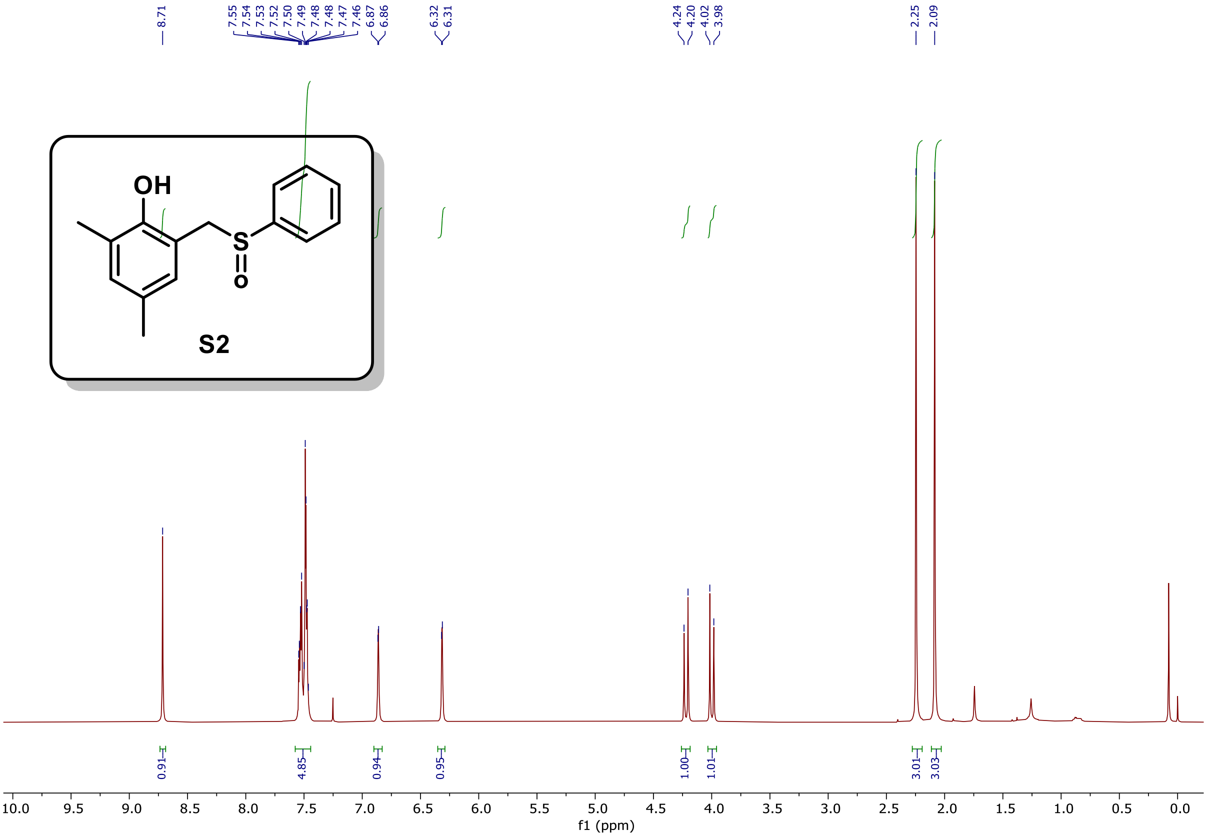
^{13}C{^{1}H} NMR spectrum of compound 11 (126 MHz CDCl$_3$)



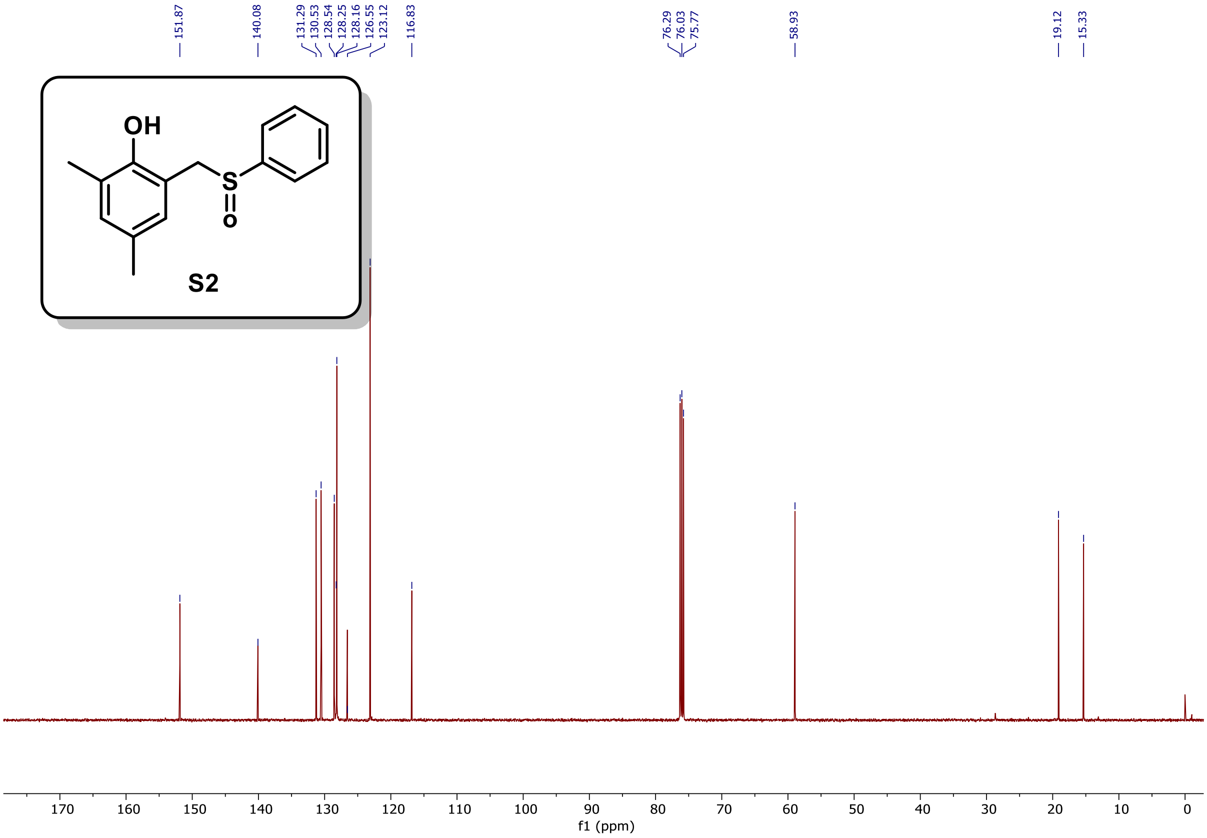
^{1}H NMR spectrum of compound S1 (500 MHz CDCl$_3$)



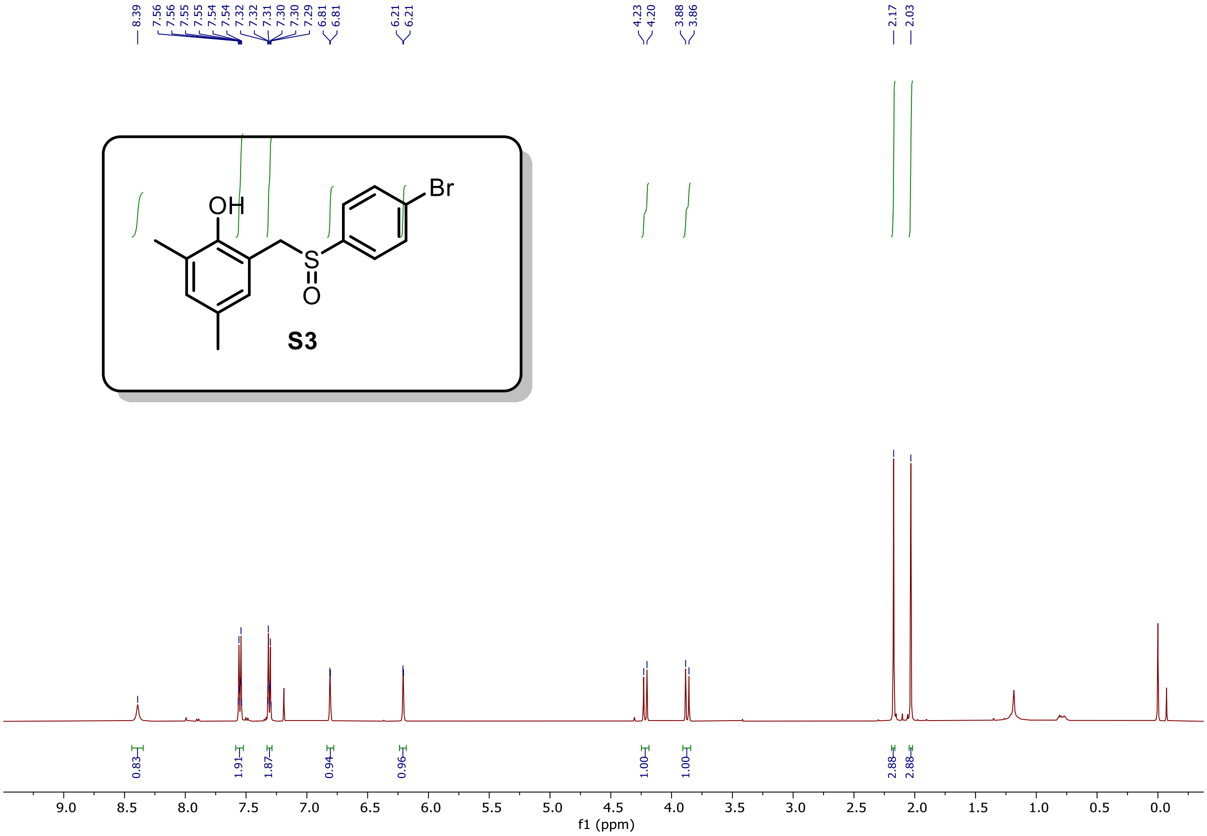
$^{13}C\{^{1}H\}$ NMR spectrum of compound S1 (126 MHz $CDCl_3$)



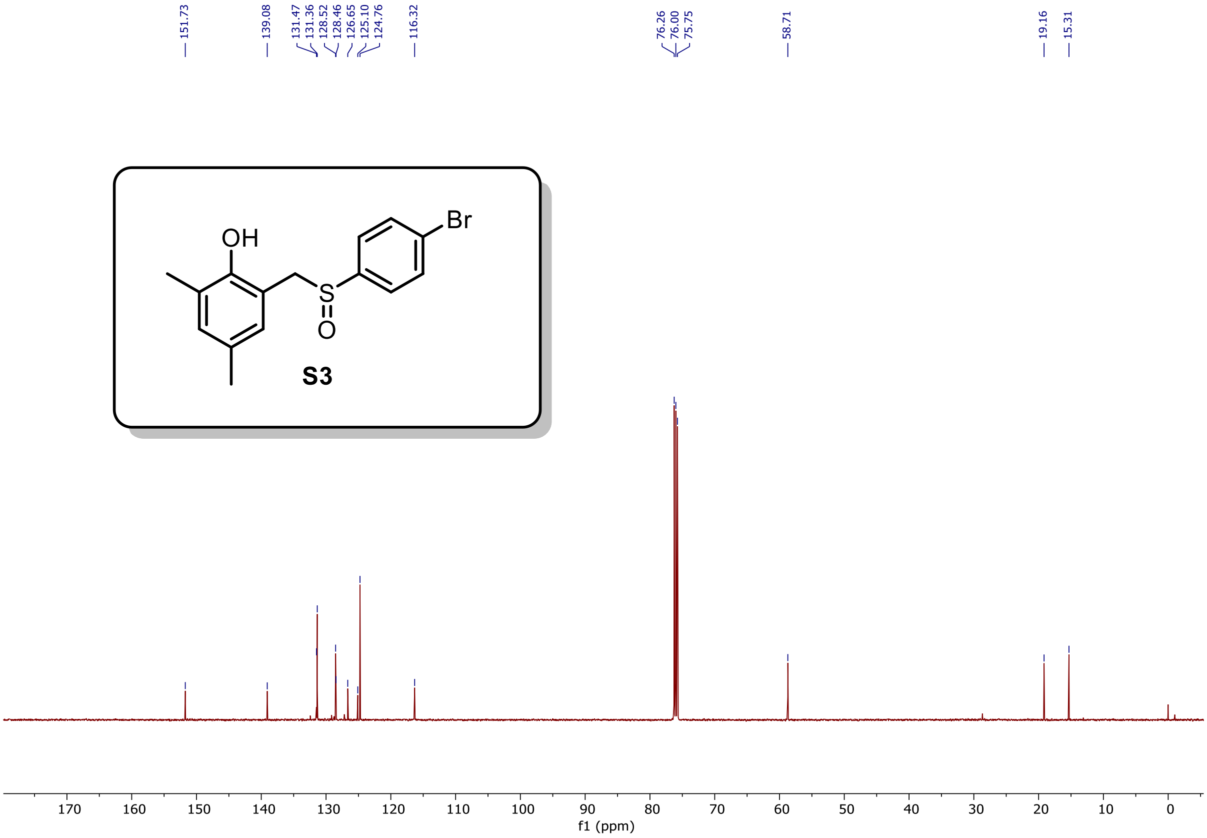
^{1}H NMR spectrum of compound S2 (500 MHz $CDCl_3$)



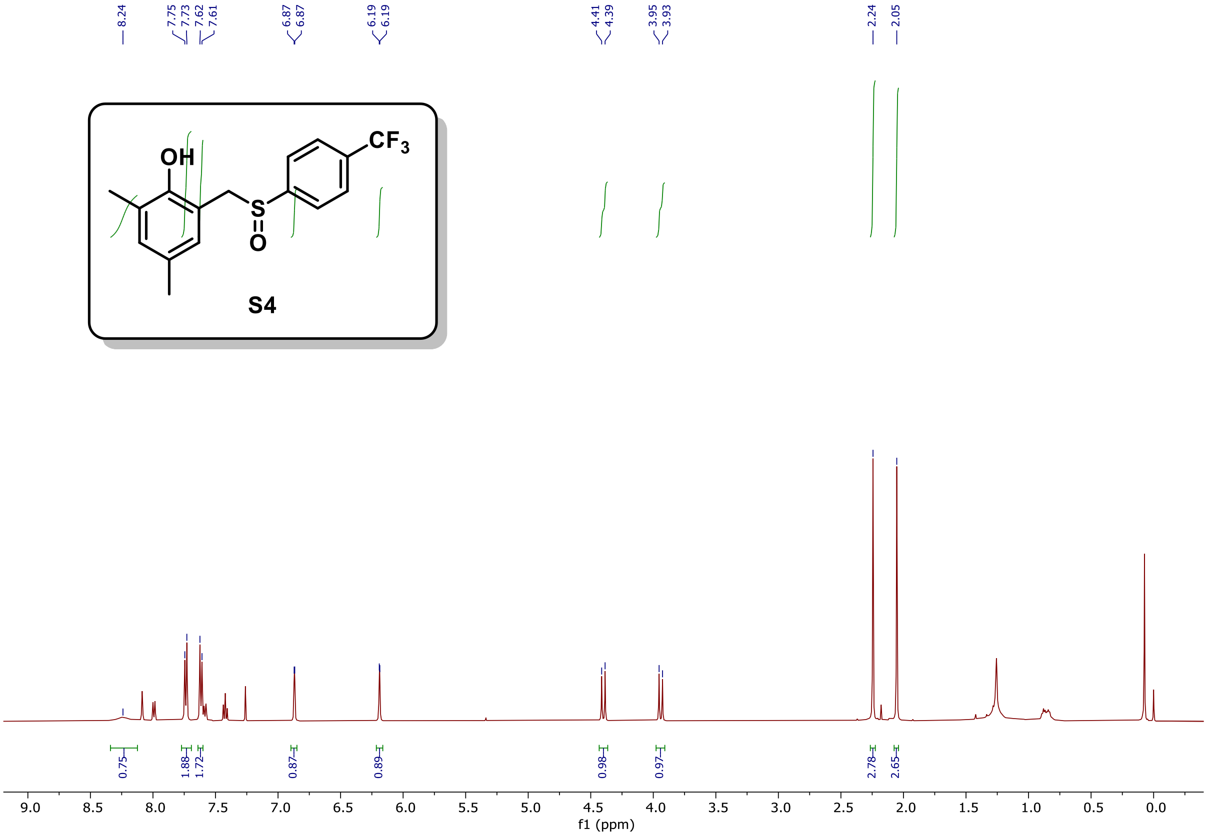
^{13}C{^{1}H} NMR spectrum of compound S2 (126 MHz CDCl$_3$)



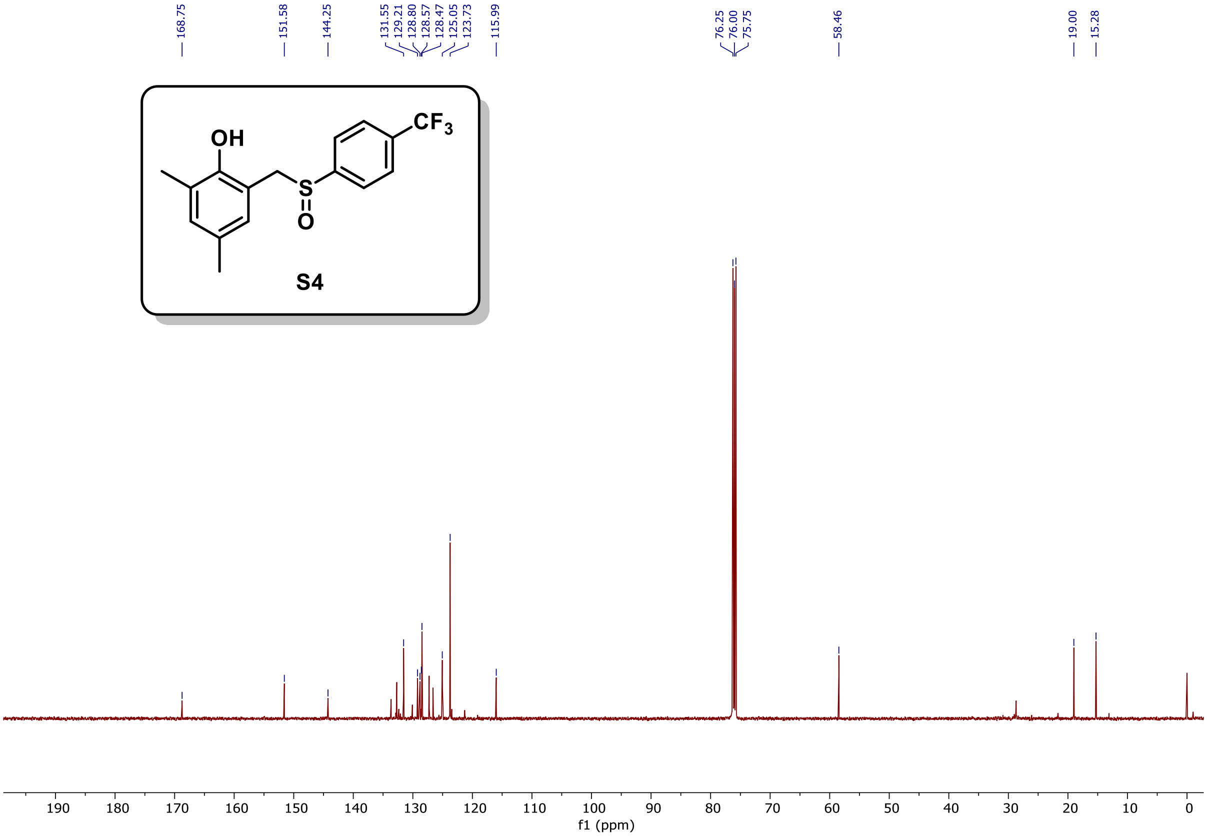
^{1}H NMR spectrum of compound S3 (500 MHz CDCl$_3$)



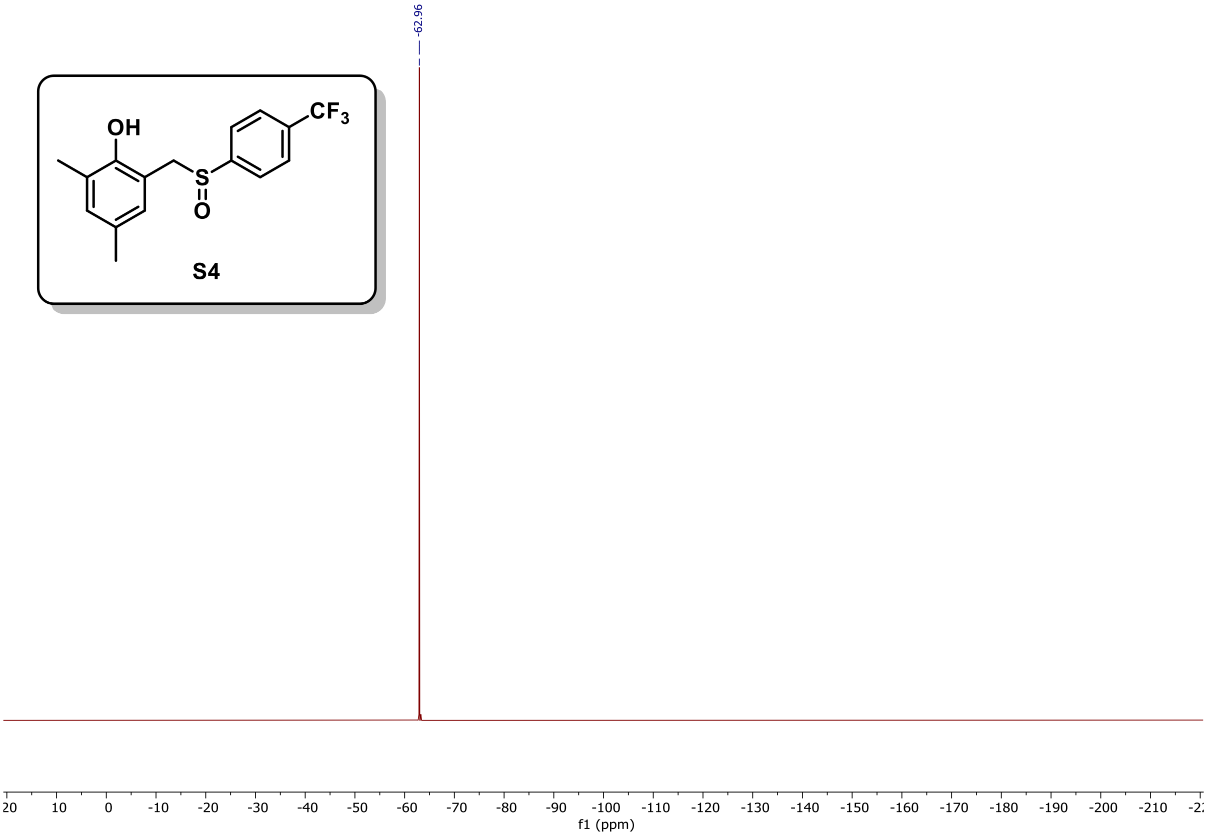
^{13}C{^{1}H} NMR spectrum of compound S3 (126 MHz CDCl$_3$)



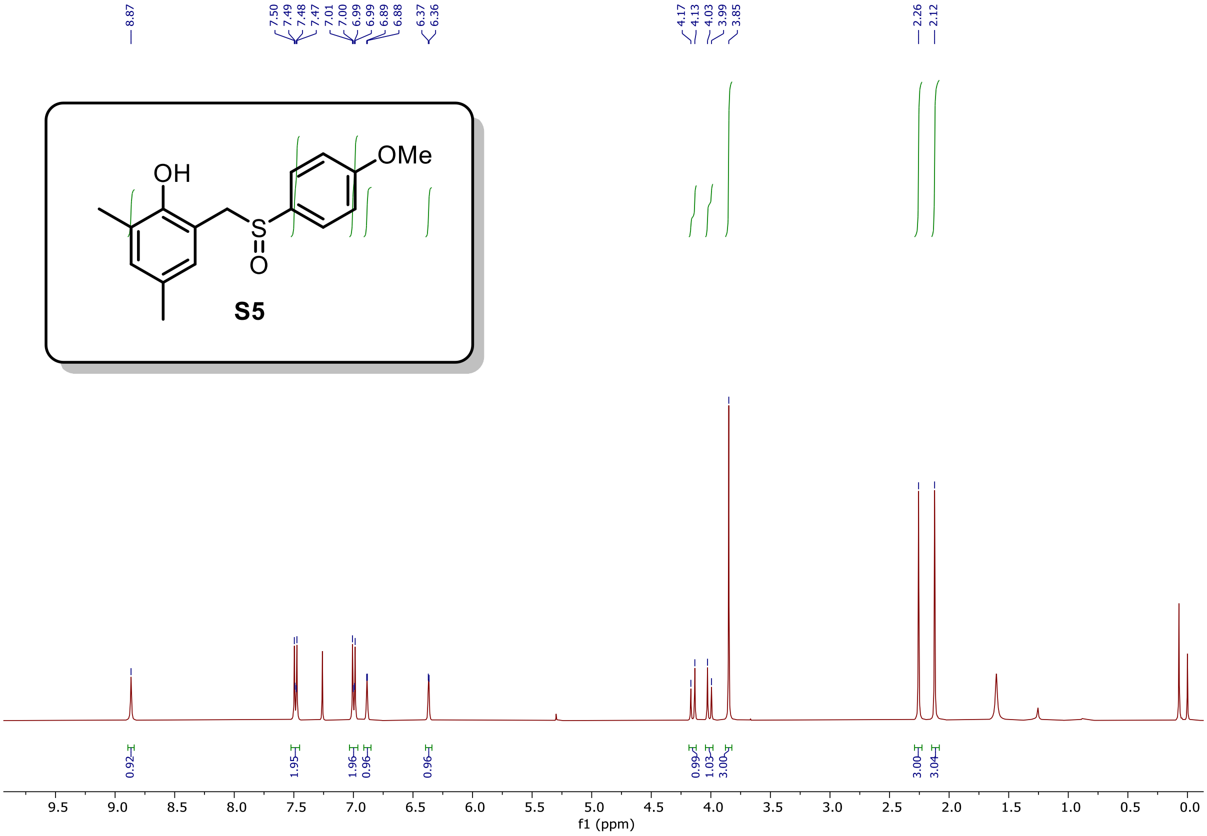
^{1}H NMR spectrum of compound S4 (500 MHz CDCl$_3$)



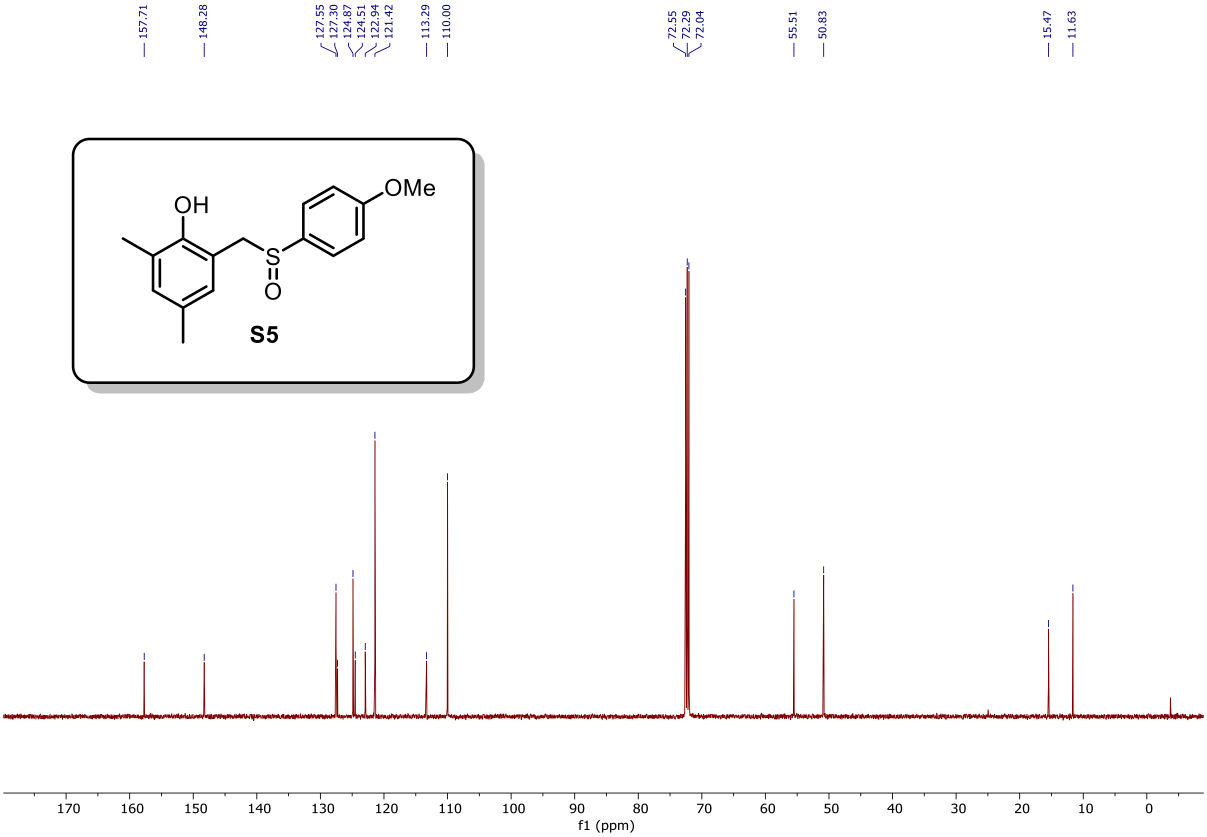
^{13}C{^{1}H} NMR spectrum of compound S4 (126 MHz CDCl$_3$)



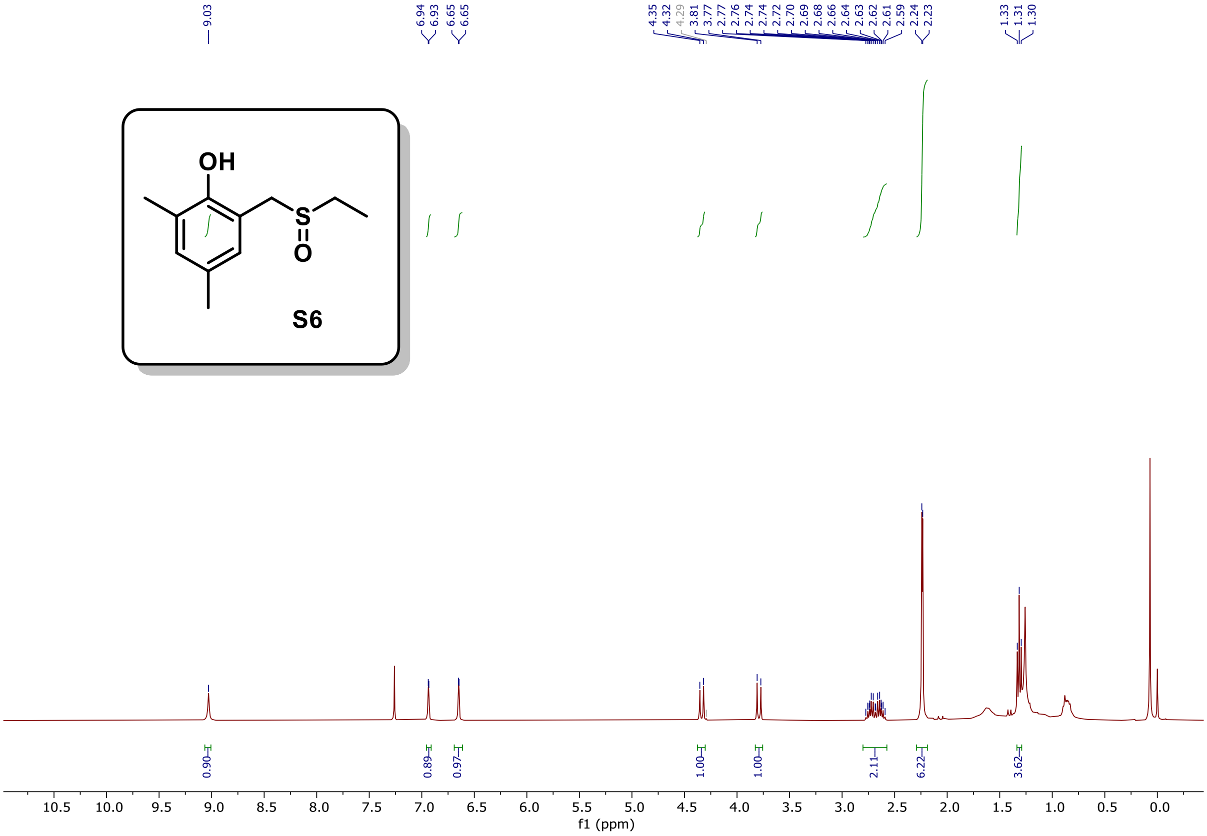
^{19}F NMR spectrum of compound S4 (471 MHz, CDCl$_3$)



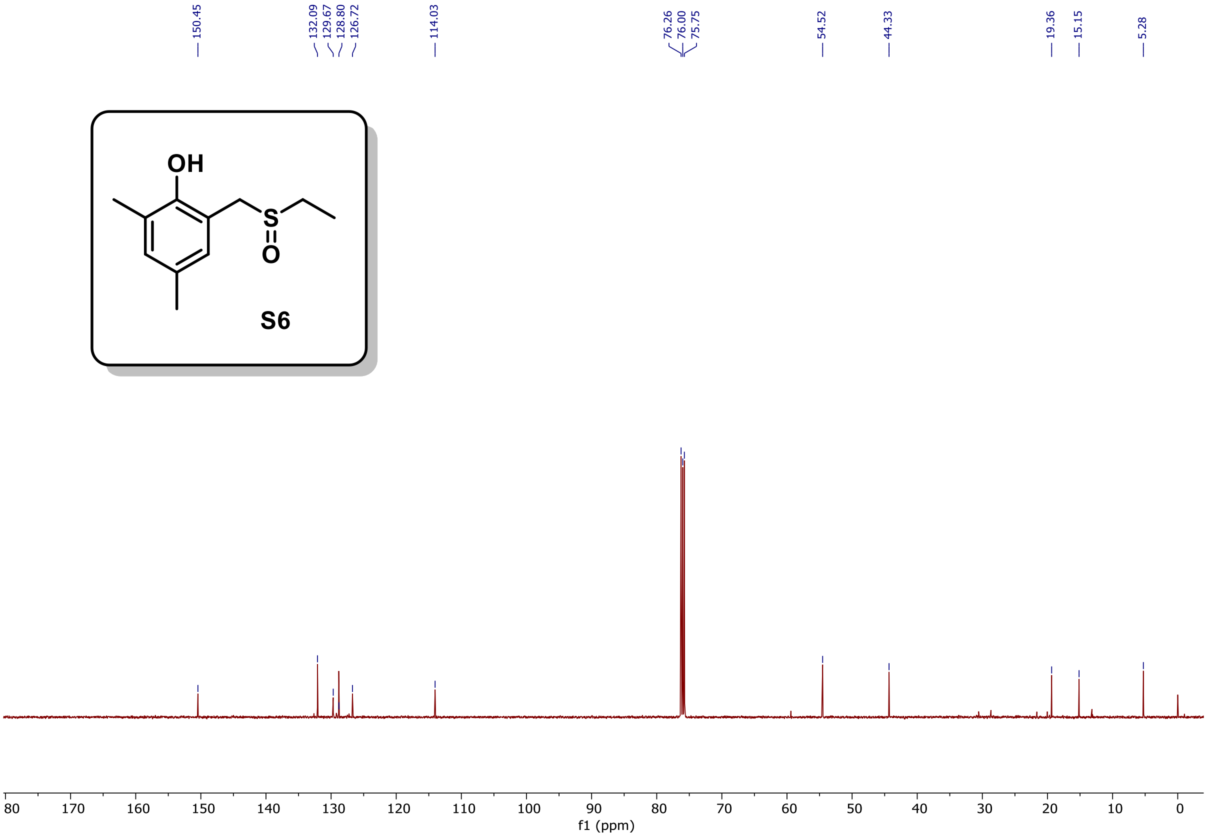
^{1}H NMR spectrum of compound S5 (500 MHz CDCl$_3$)



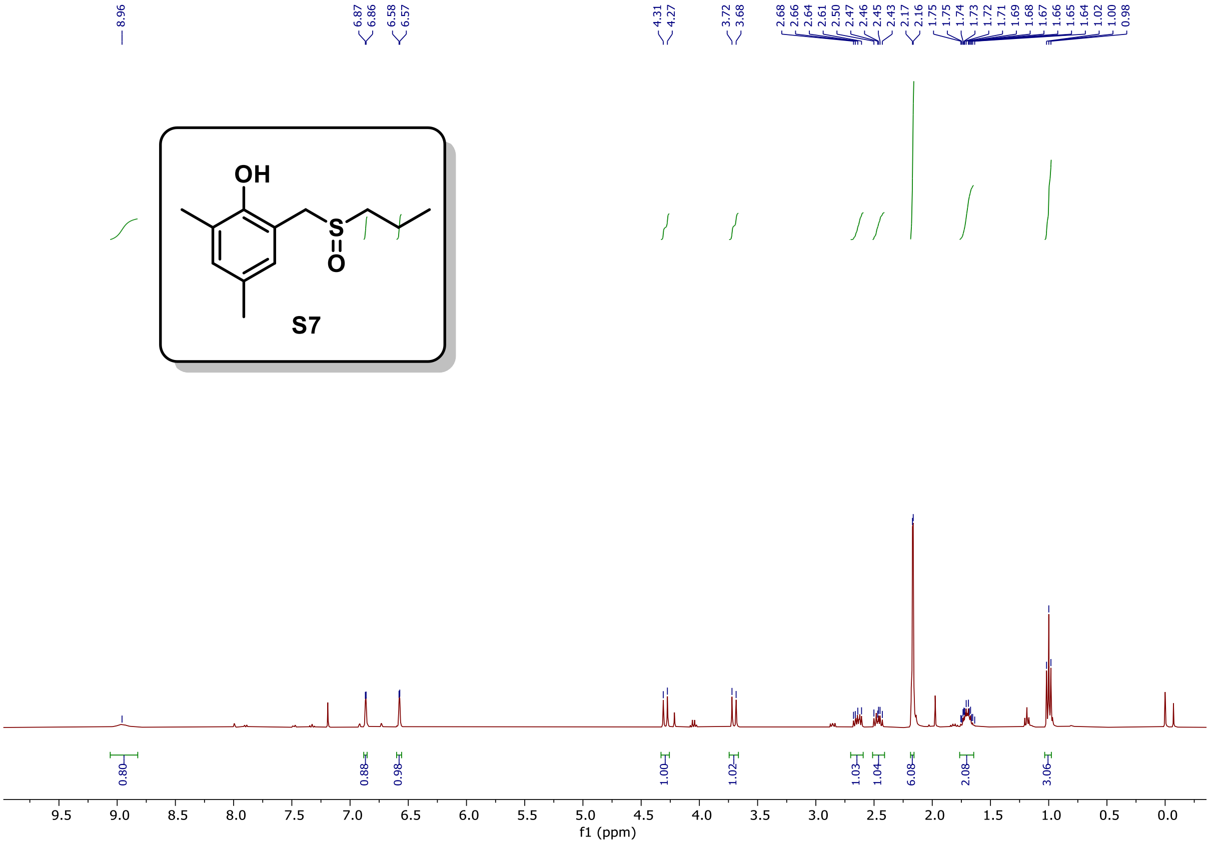
^{13}C{^{1}H} NMR spectrum of compound S5 (126 MHz CDCl$_3$



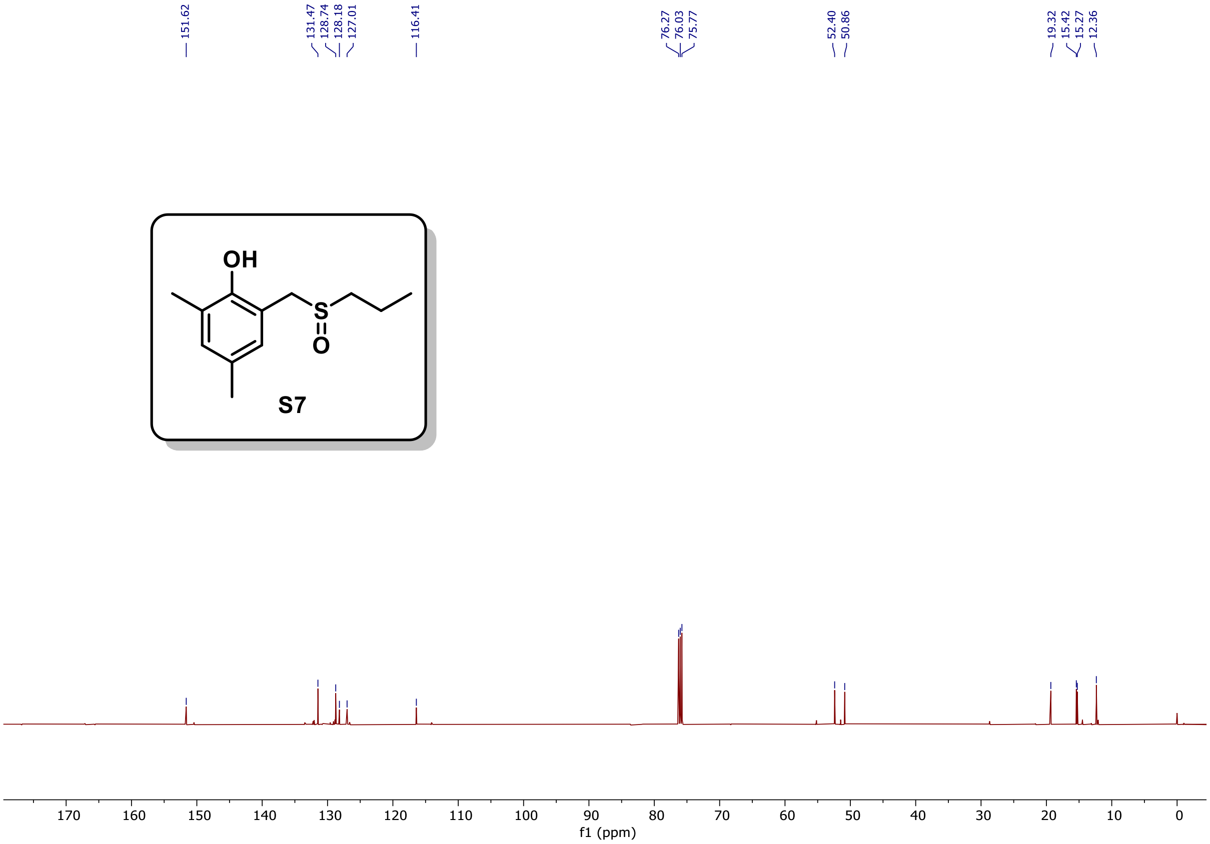
^{1}H NMR spectrum of compound S6 (500 MHz CDCl$_3$)



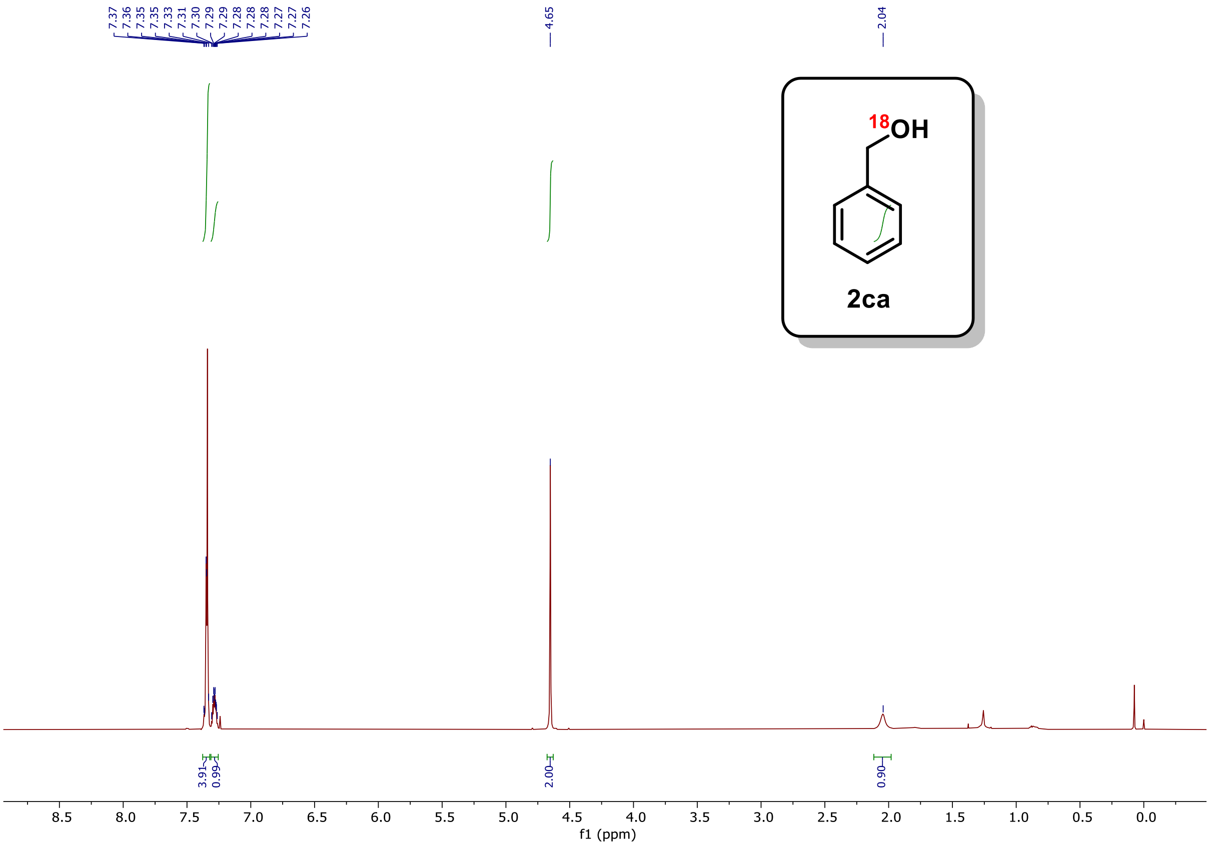
^{13}C{^{1}H} NMR spectrum of compound S6 (126 MHz CDCl$_3$)



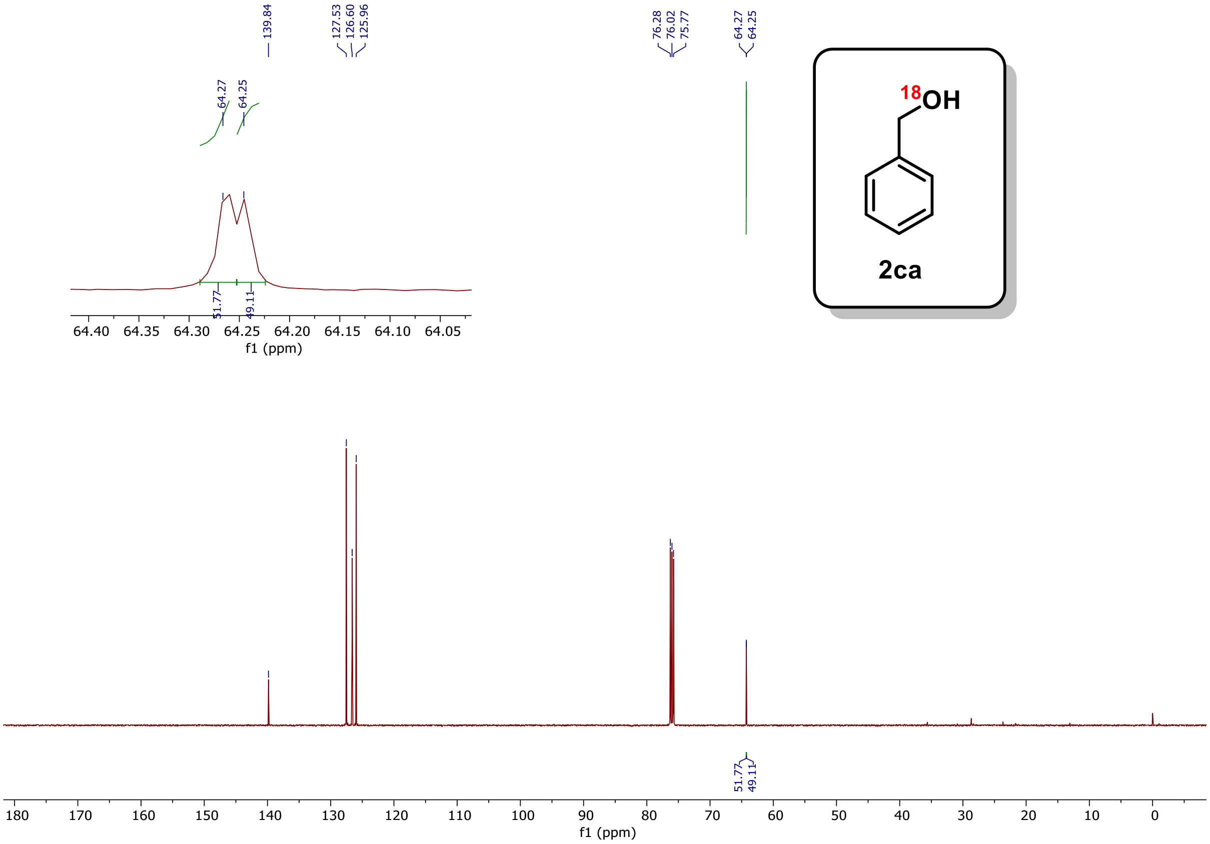
^{1}H NMR spectrum of compound S7 (500 MHz CDCl$_3$)



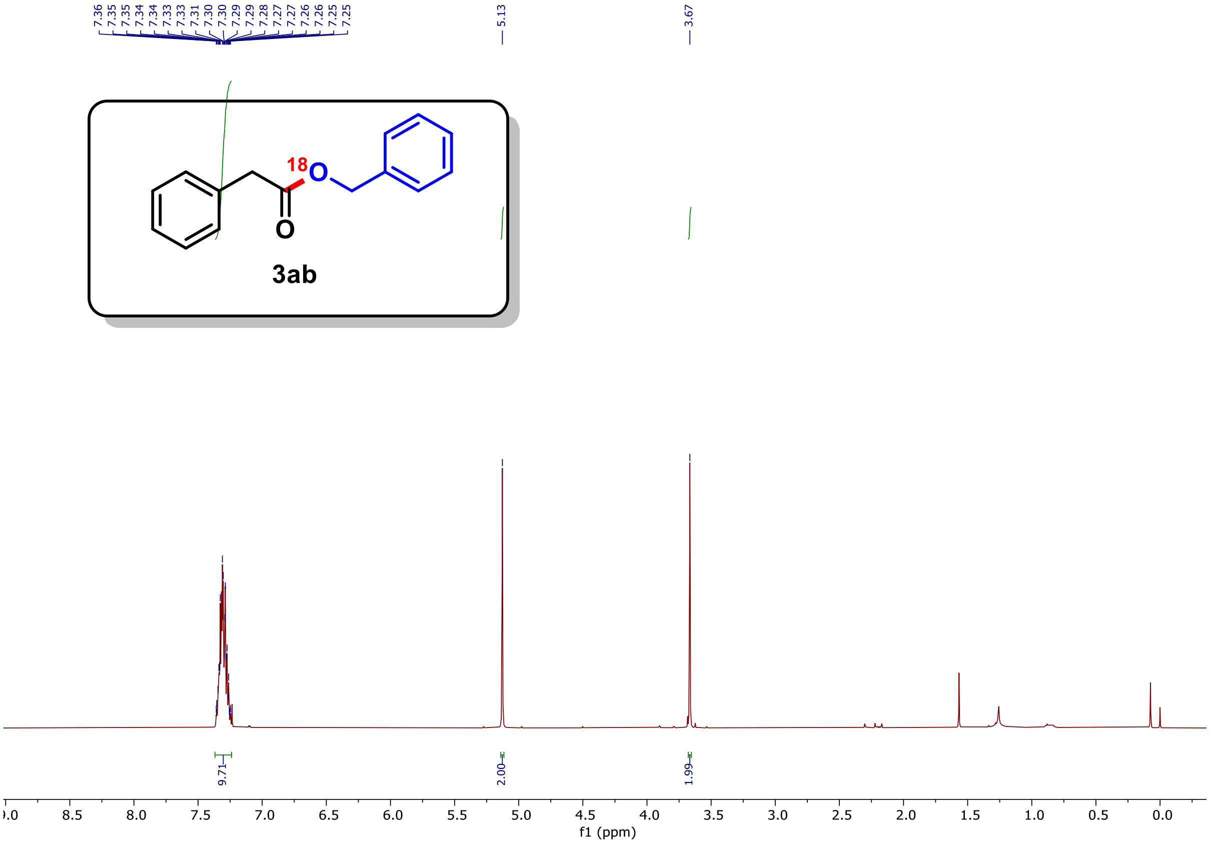
^{13}C{^{1}H} NMR spectrum of compound S7 (126 MHz CDCl$_3$)



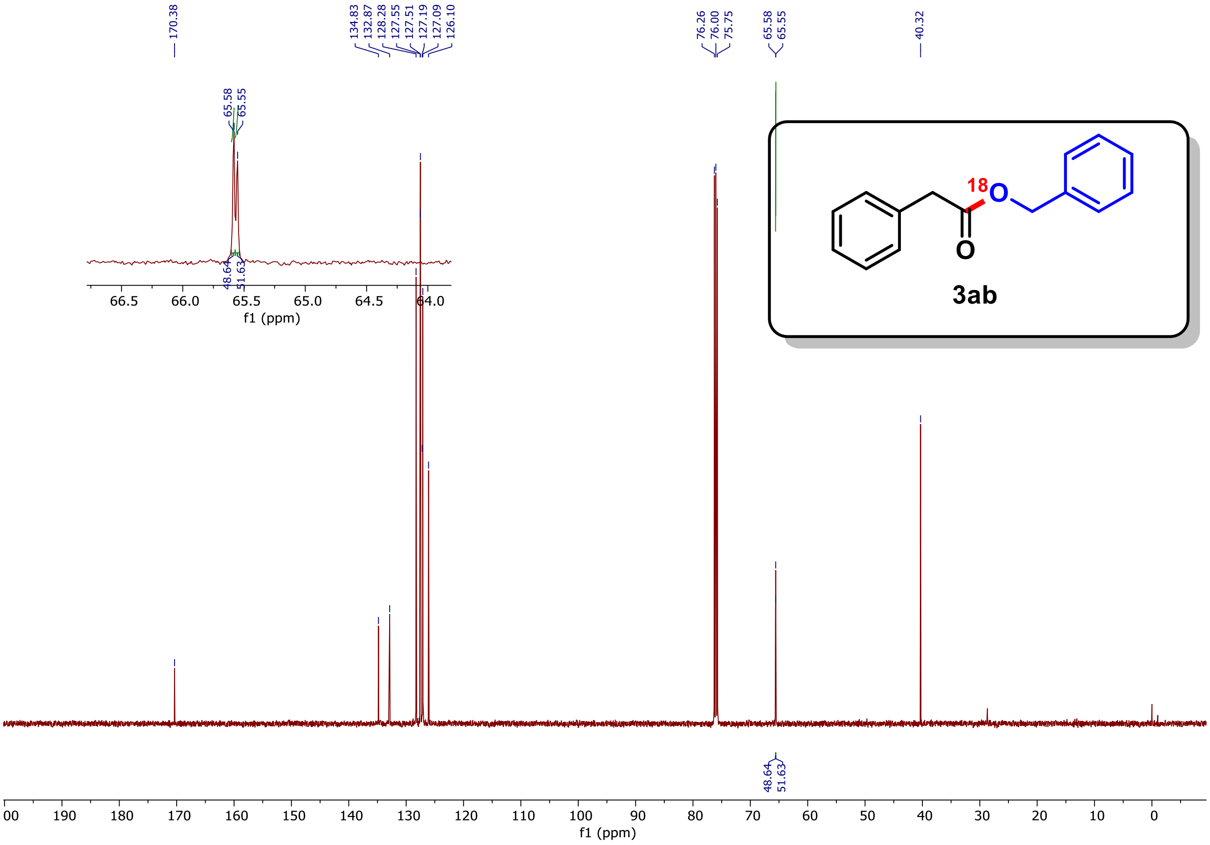
^{1}H NMR spectrum of compound ^{18}O-benzyl alcohol (2ca) (500 MHz $CDCl_3$)



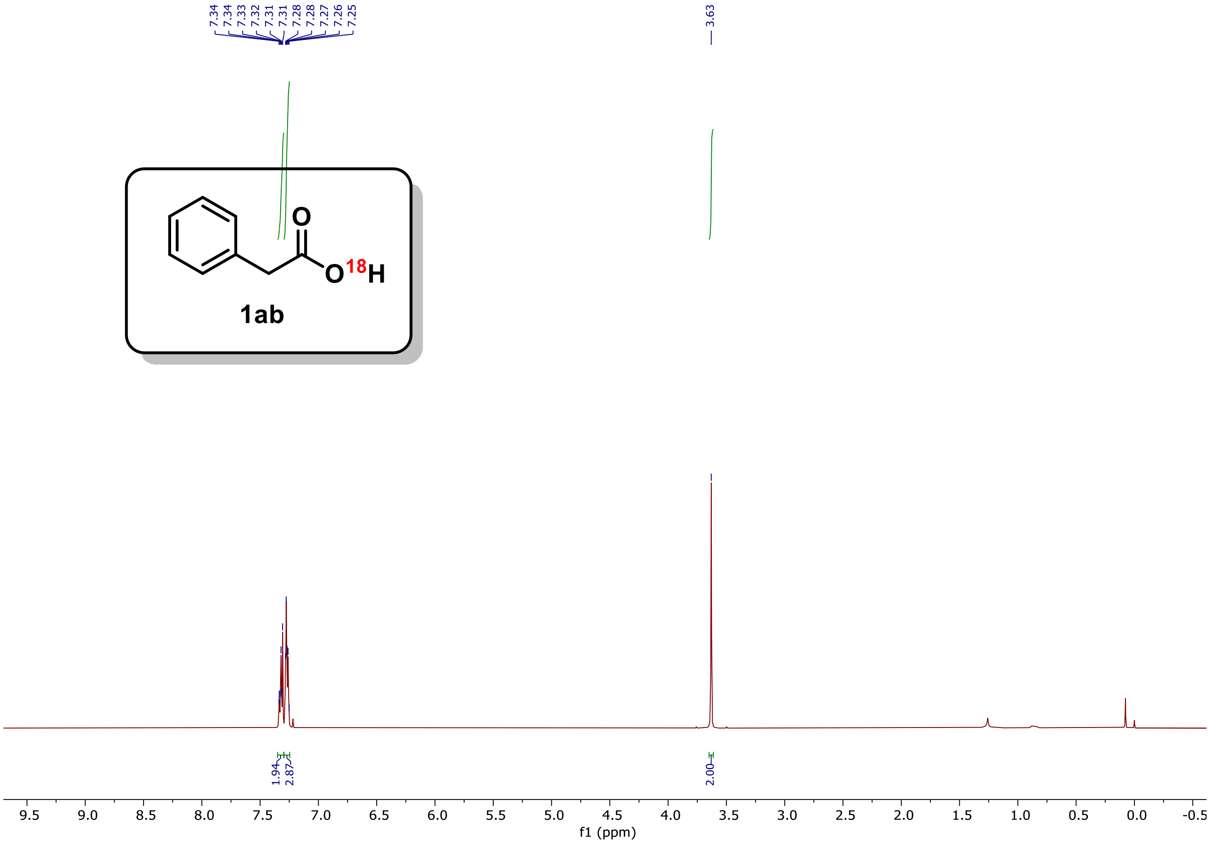
^{13}C{^{1}H} NMR spectrum of compound ^{18}O-benzyl alcohol (2ca) (126 MHz $CDCl_3$)



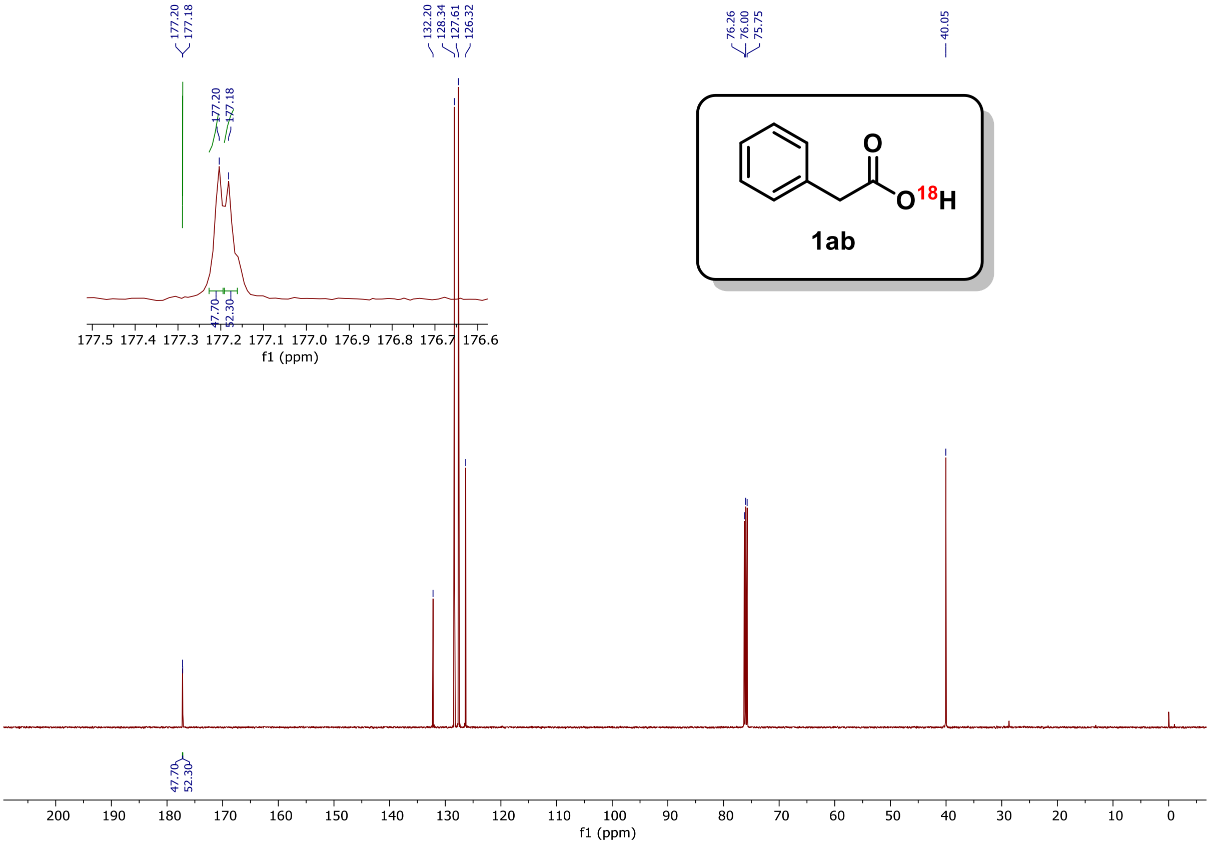
^{1}H NMR spectrum of compound 3ab (500 MHz $CDCl_3$) (Ester from ^{18}O-benzyl alcohol)



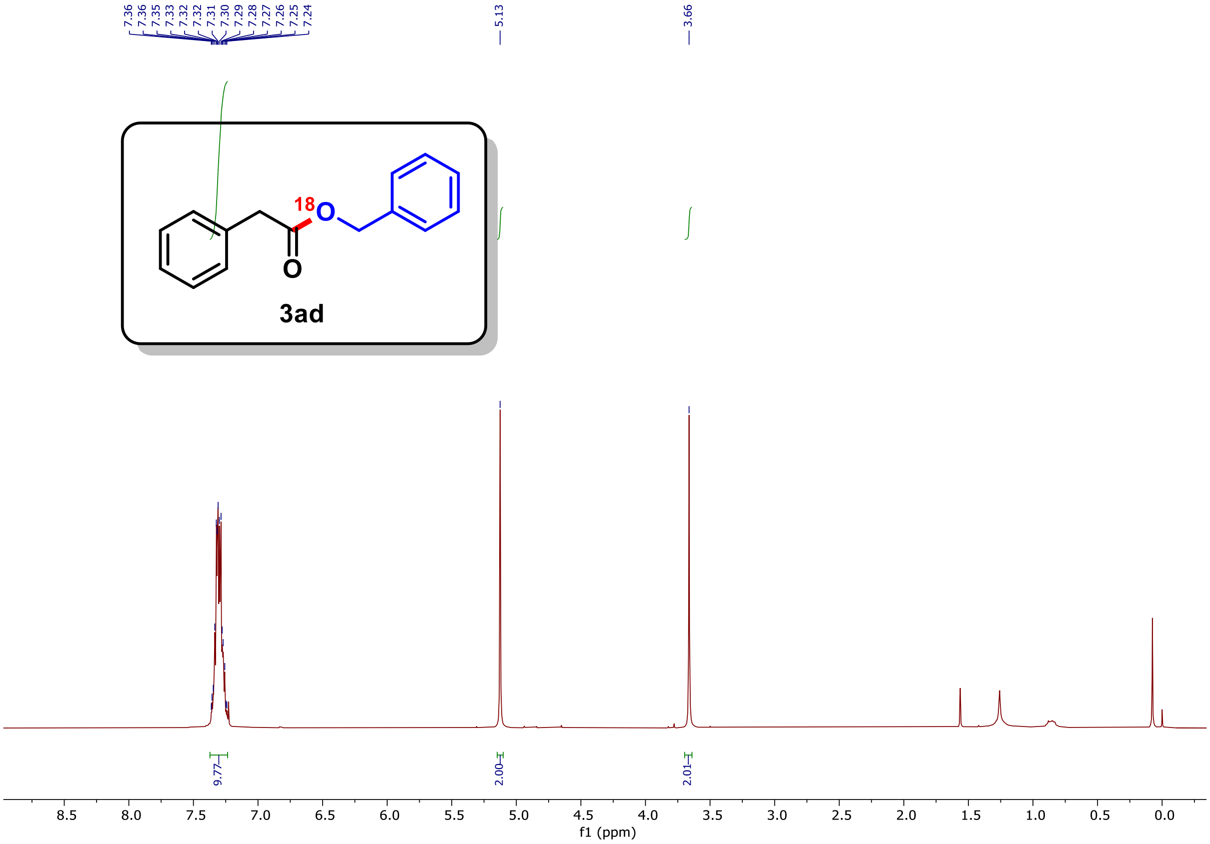
^{13}C{^{1}H} NMR spectrum of compound 3ab (126 MHz $CDCl_3$) (Ester from ^{18}O-benzyl alcohol)



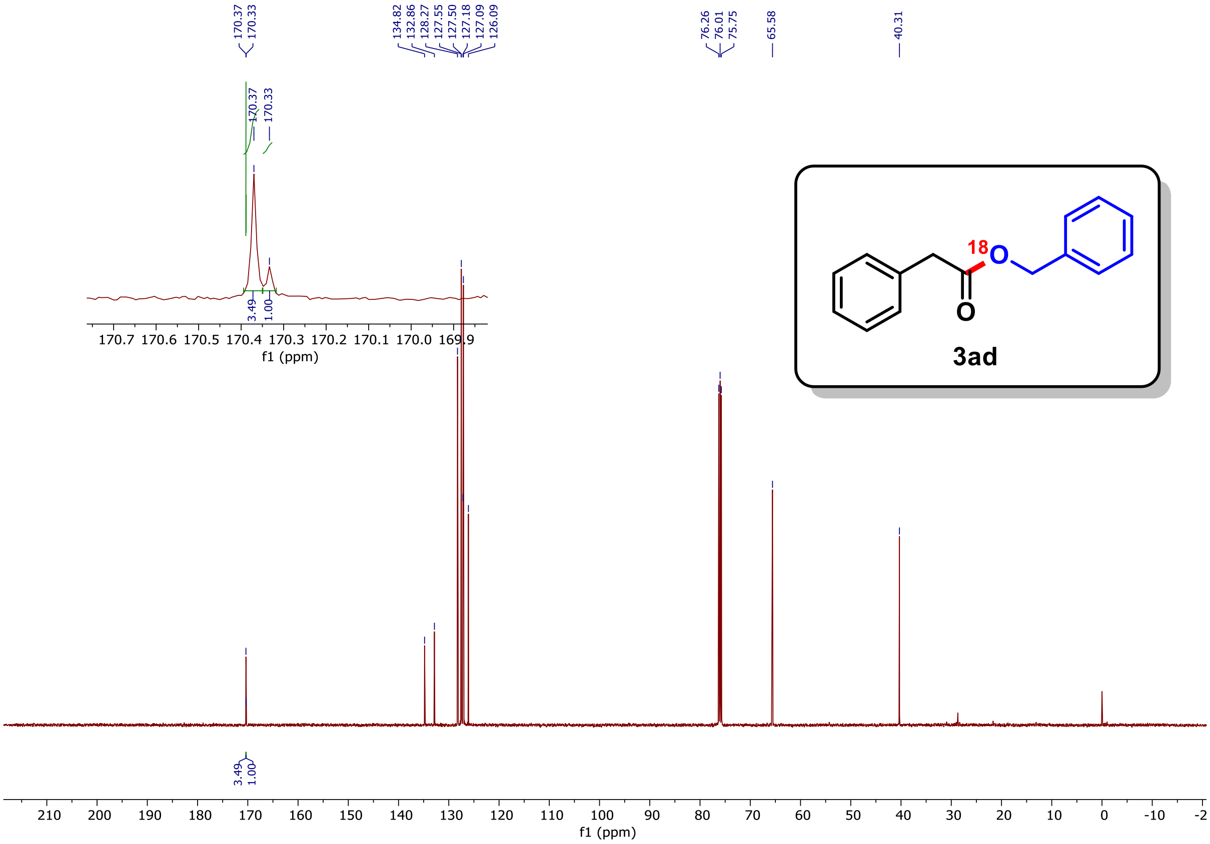
^{1}H NMR spectrum of compound ^{18}O-phenylacetic acid (1ab) (500 MHz CDCl$_3$)



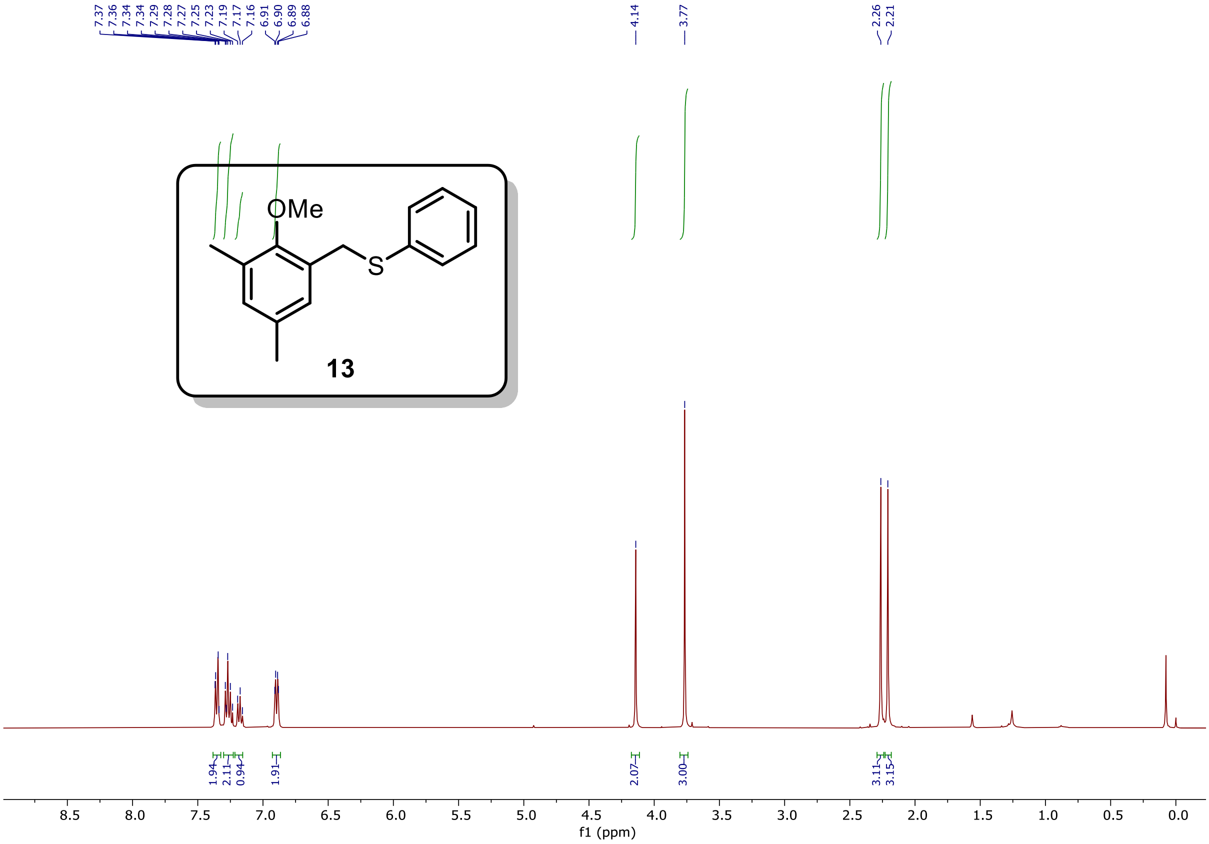
^{13}C{^{1}H} NMR spectrum of compound ^{18}O-phenylacetic acid (1ab) (126 MHz CDCl$_3$)



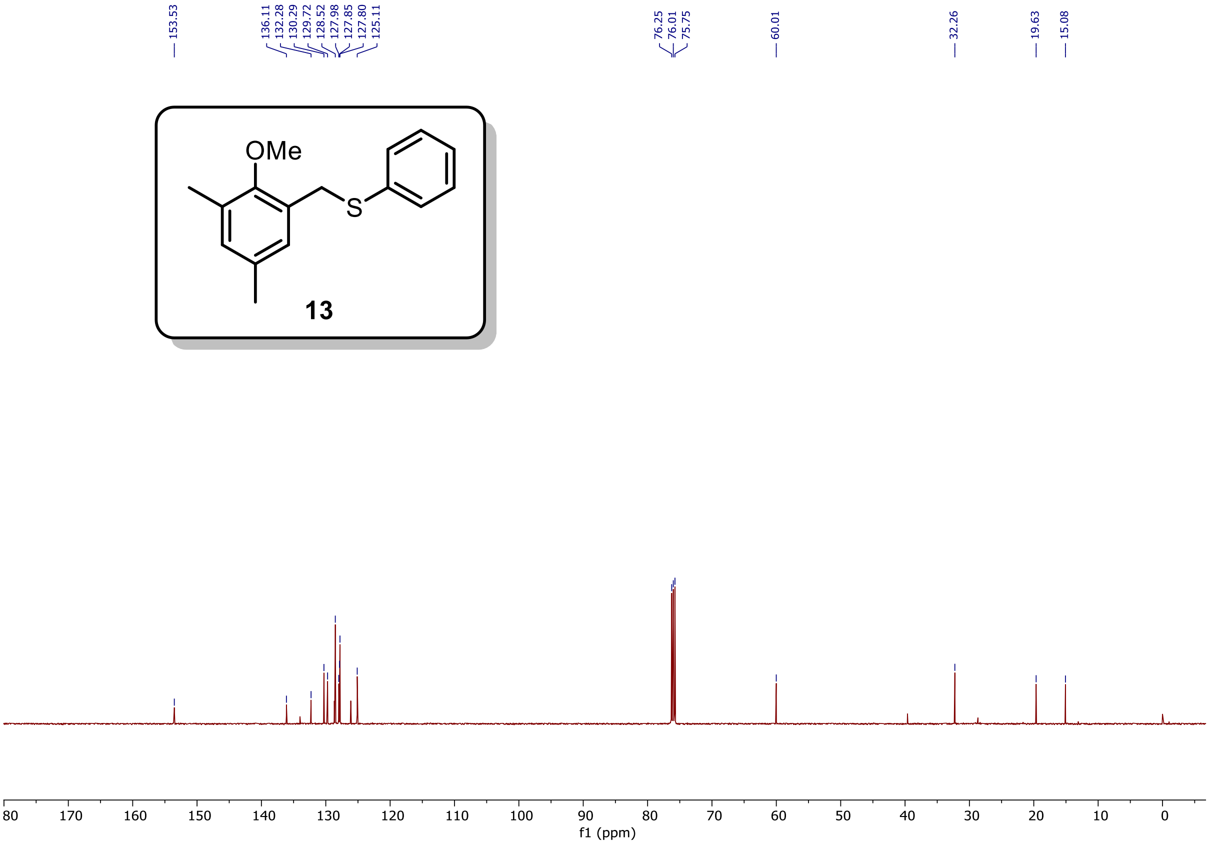
^{1}H NMR spectrum of compound 3ad (500 MHz CDCl$_3$) (Ester from ^{18}O-phenylacetic acid)



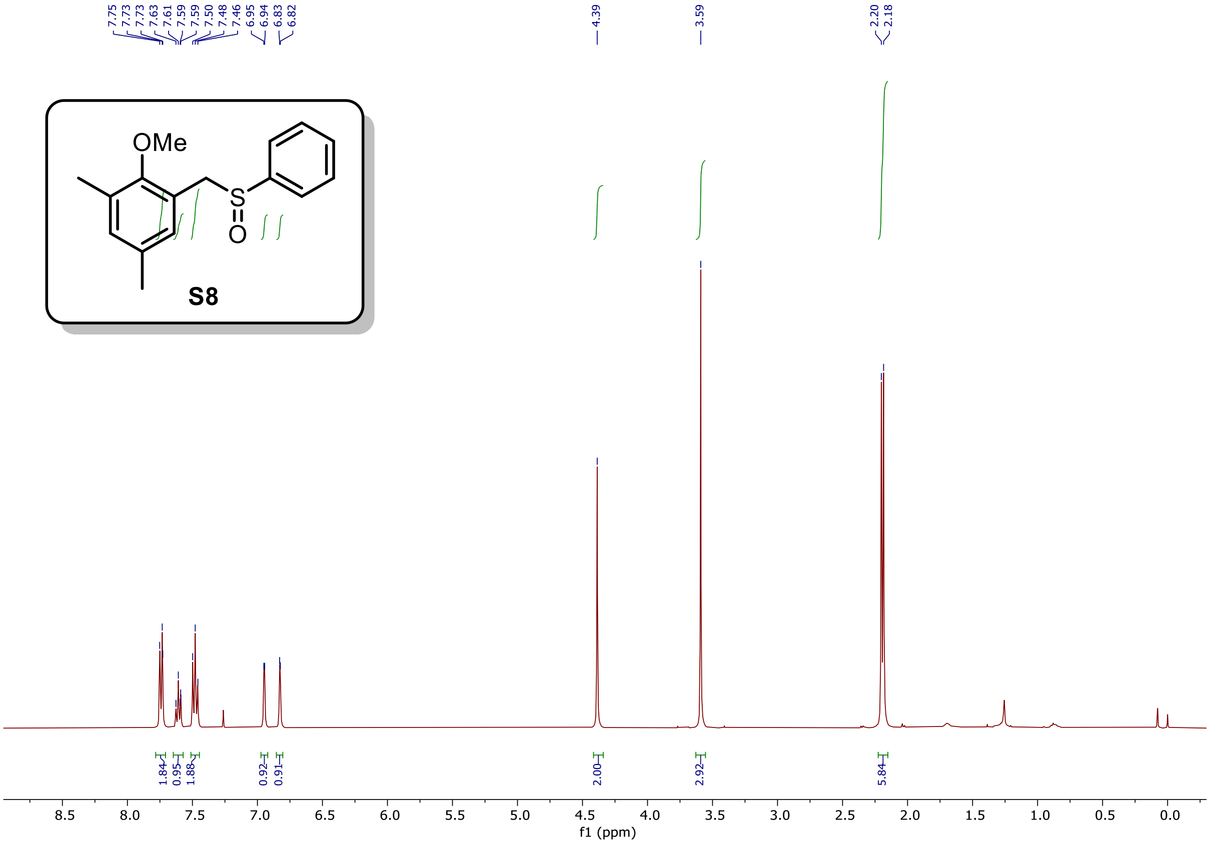
^{13}C{^{1}H} NMR spectrum of compound 3ad (126 MHz CDCl$_3$) (Ester from ^{18}O-phenylacetic acid)



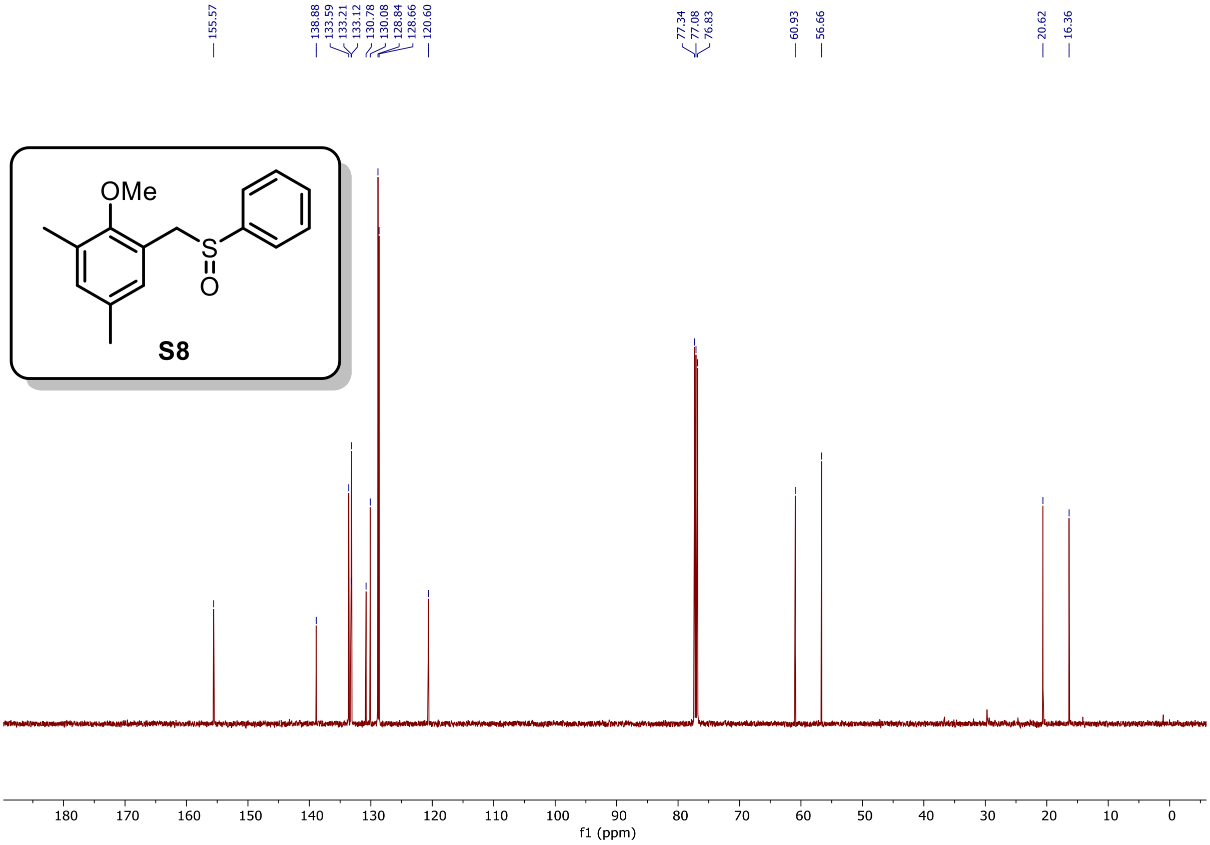
^{1}H NMR spectrum of compound 13 (500 MHz CDCl$_3$)



^{13}C{^{1}H} NMR spectrum of compound 13 (126 MHz CDCl$_3$)

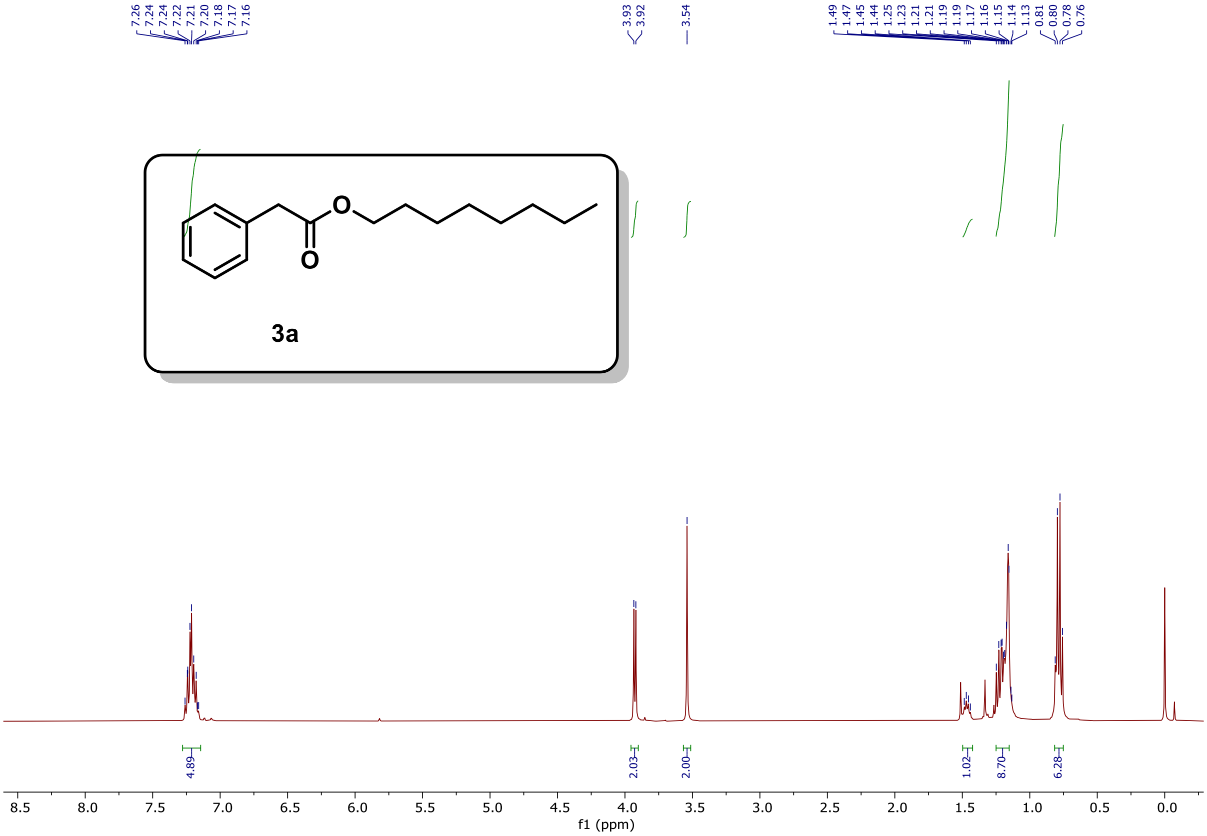


^{1}H NMR spectrum of compound S8 (500 MHz CDCl$_3$)

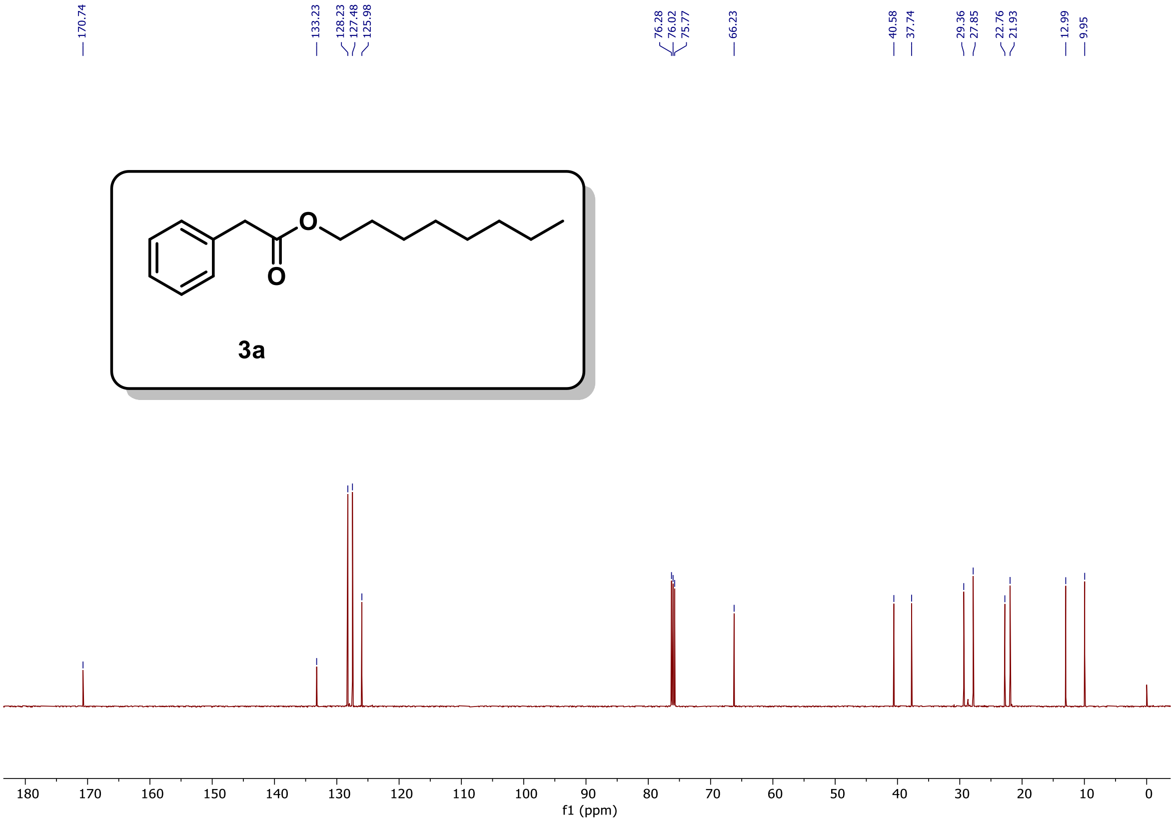


^{13}C{^{1}H} NMR spectrum of compound S8 (126 MHz CDCl$_3$)

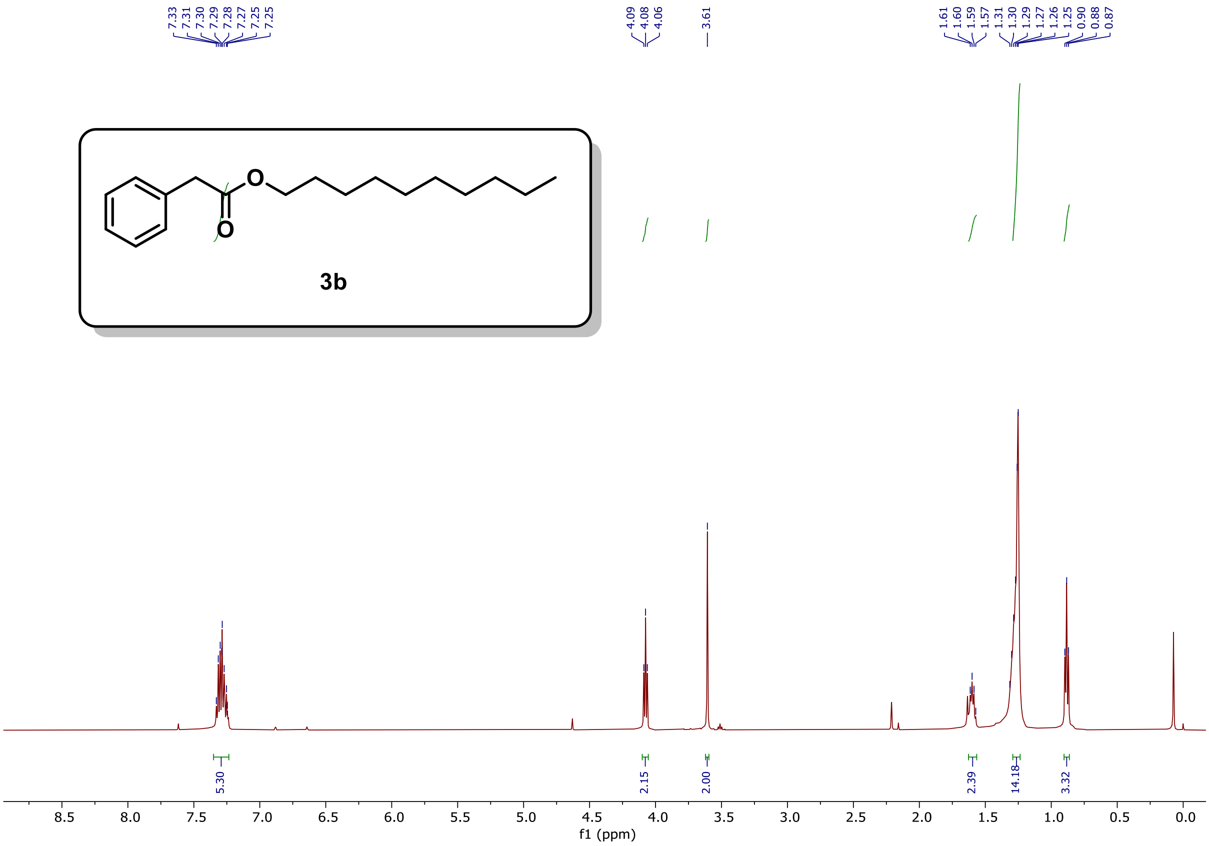
Spectra of substrates



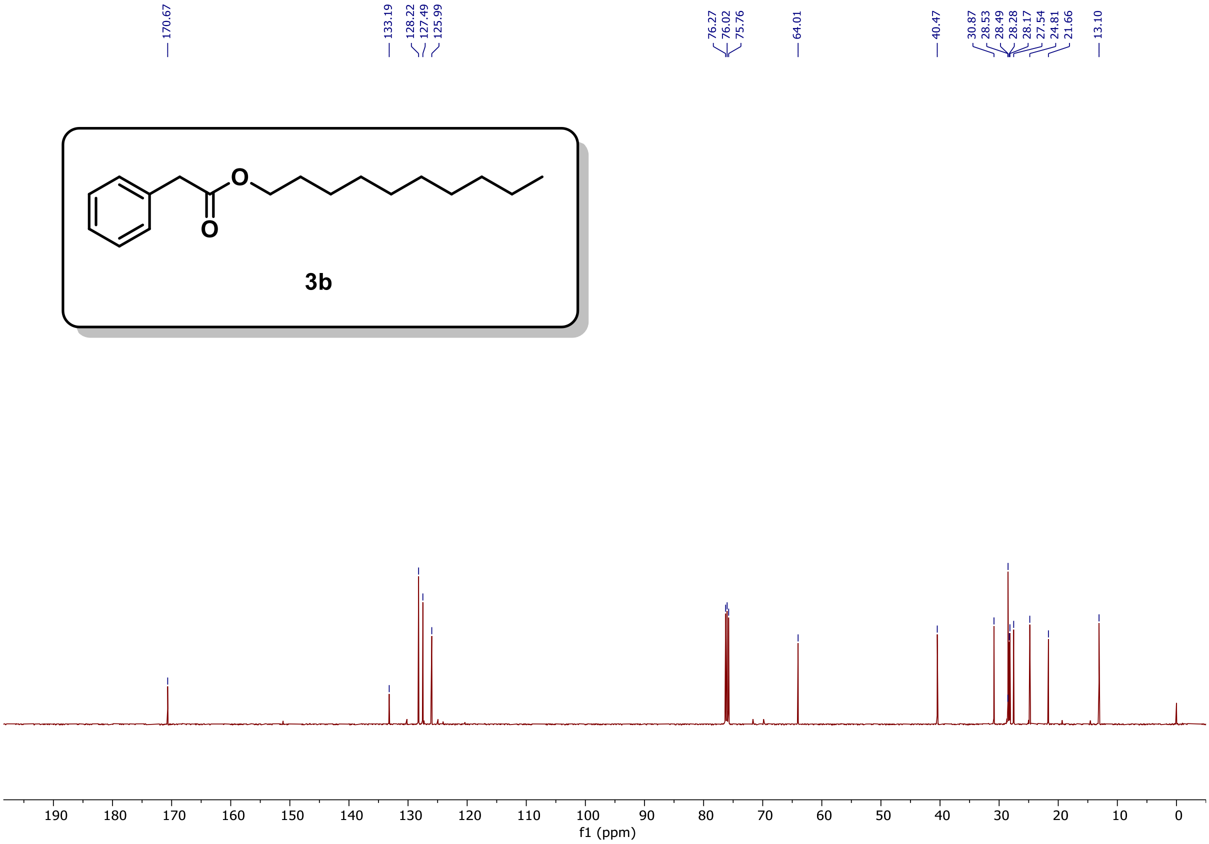
^{1}H NMR spectrum of compound 3a (500 MHz $CDCl_3$)



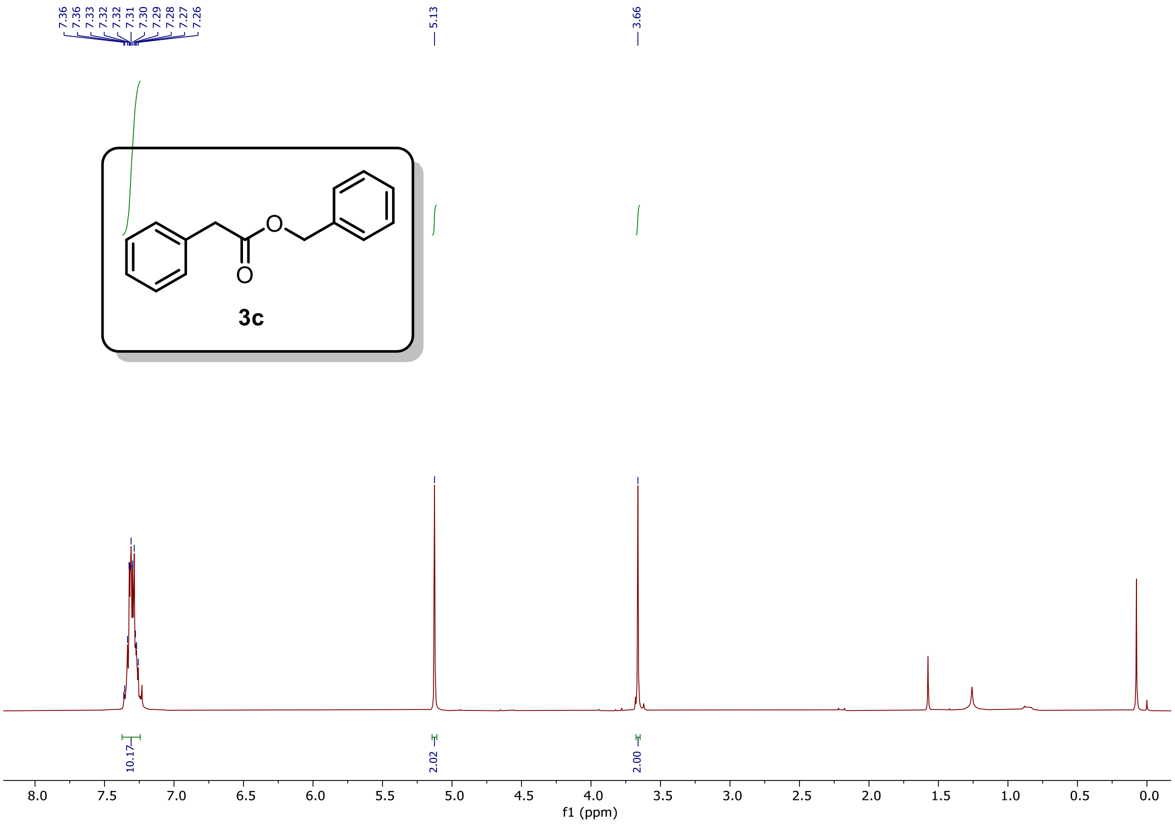
^{13}C{^{1}H} NMR spectrum of compound 3a (126 MHz $CDCl_3$)



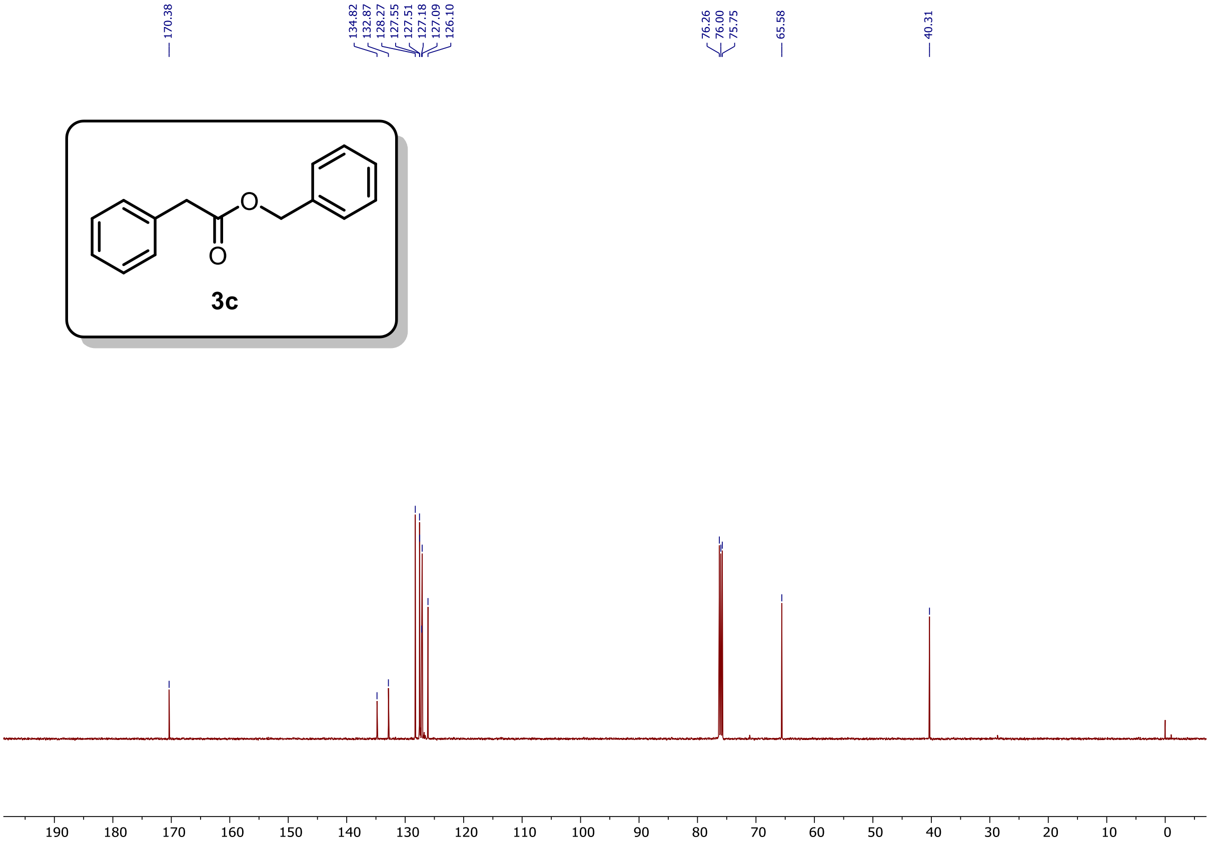
^{1}H NMR spectrum of compound 3b (500 MHz CDCl$_3$)



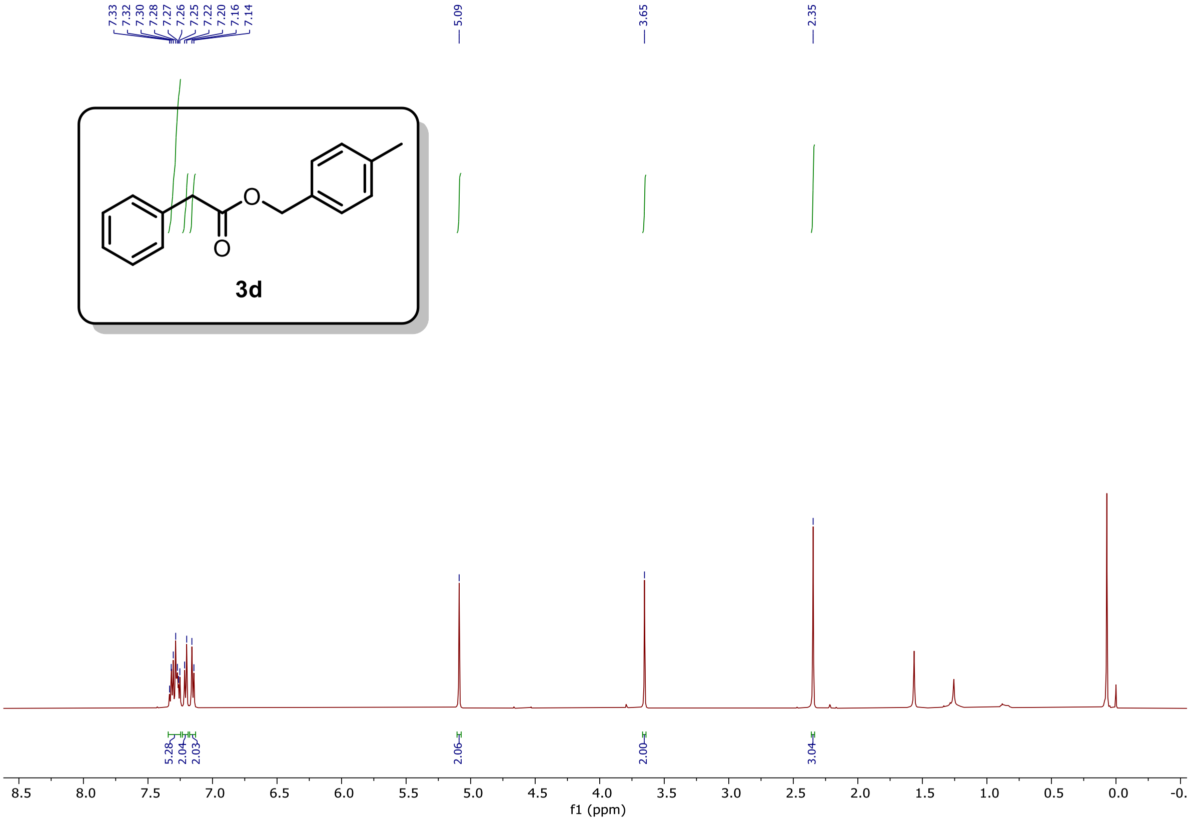
^{13}C{^{1}H} NMR spectrum of compound 3b (126 MHz CDCl$_3$)



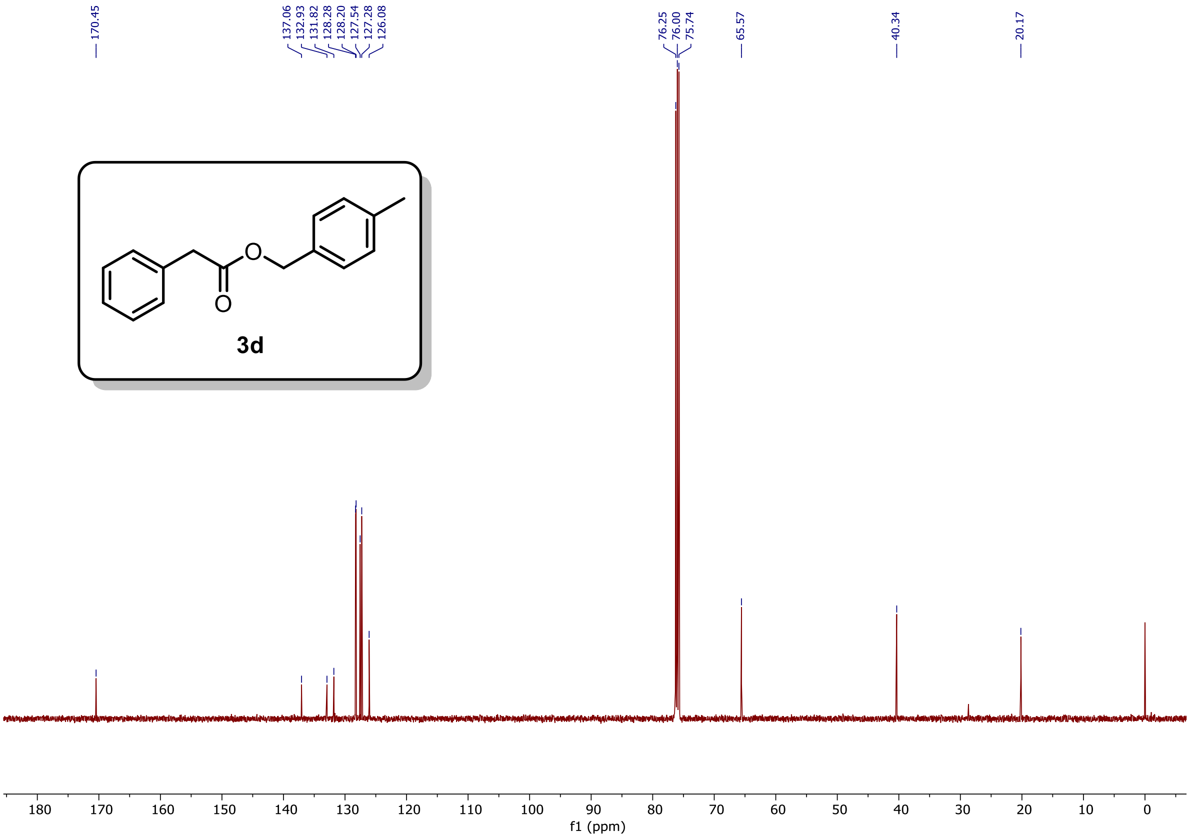
^{1}H NMR spectrum of compound 3c (500 MHz CDCl$_3$)



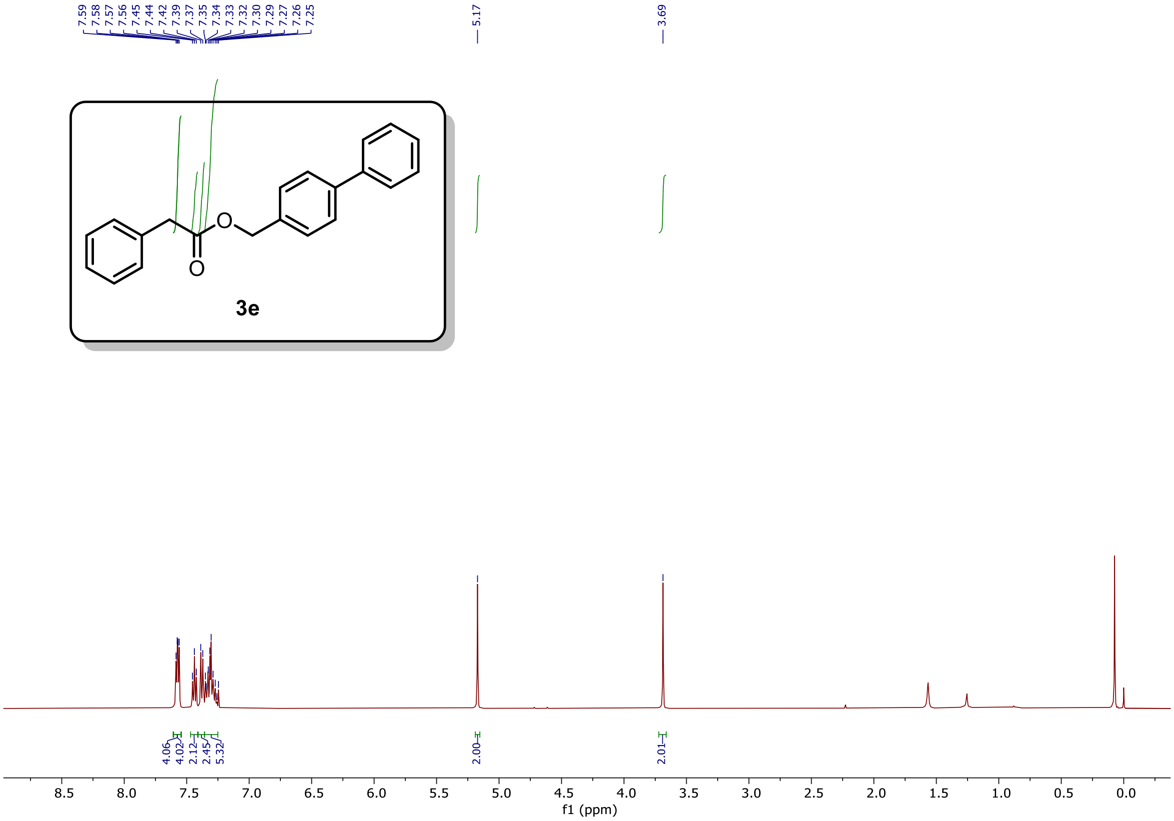
^{13}C{^{1}H} NMR spectrum of compound 3c (126 MHz CDCl$_3$)



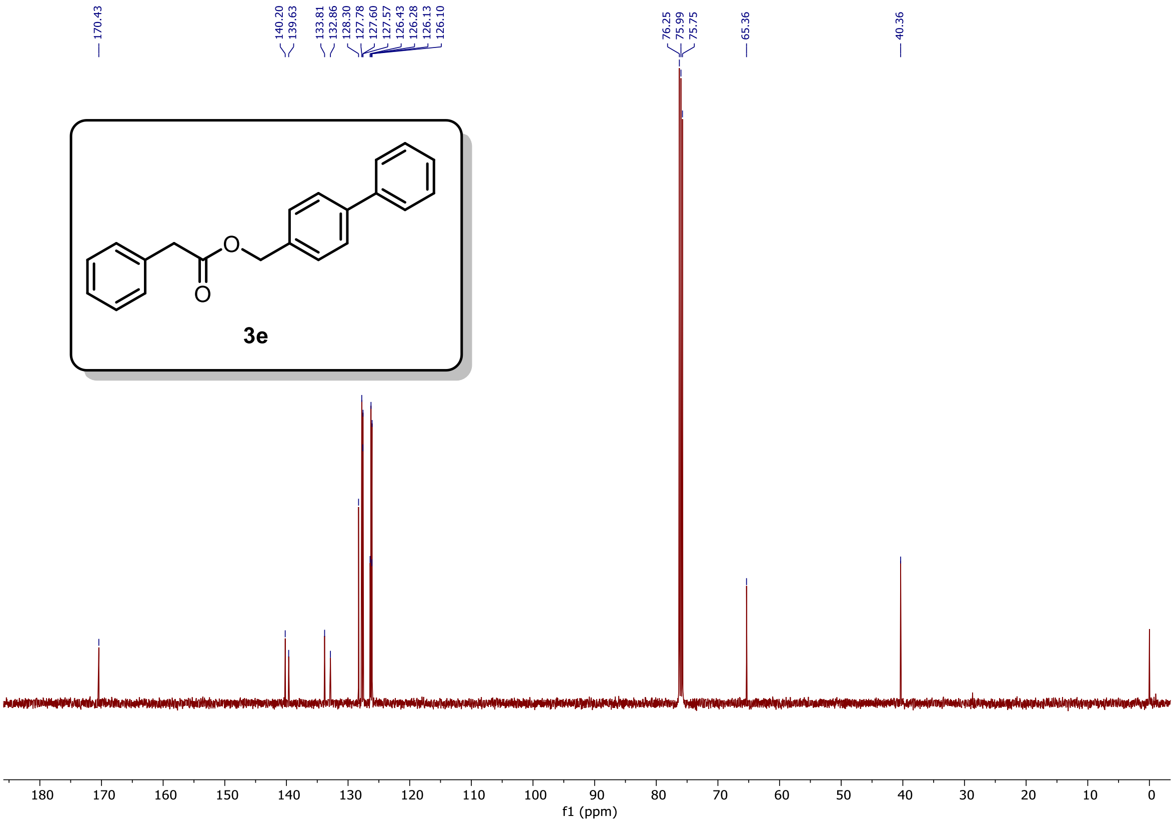
^{1}H NMR spectrum of compound 3d (500 MHz CDCl$_3$)



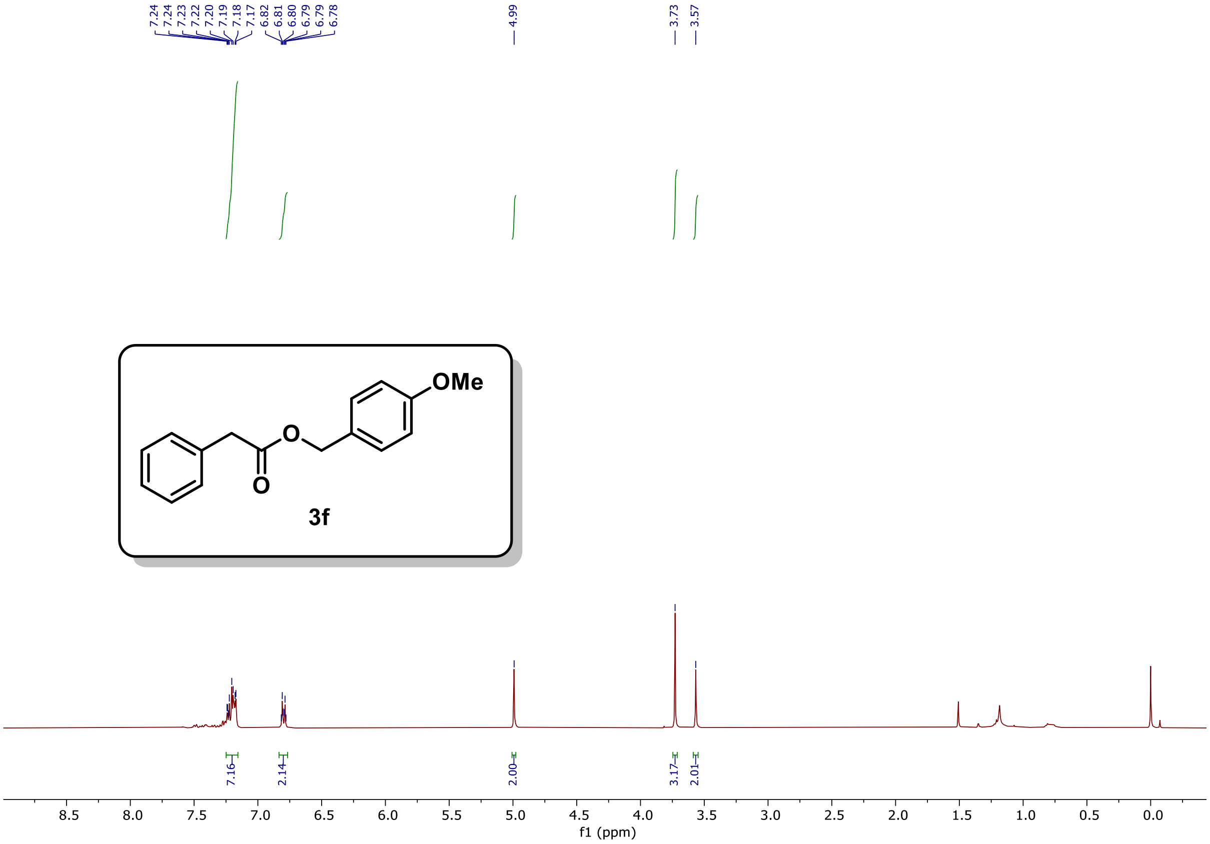
^{13}C{^{1}H} NMR spectrum of compound 3d (126 MHz CDCl$_3$)



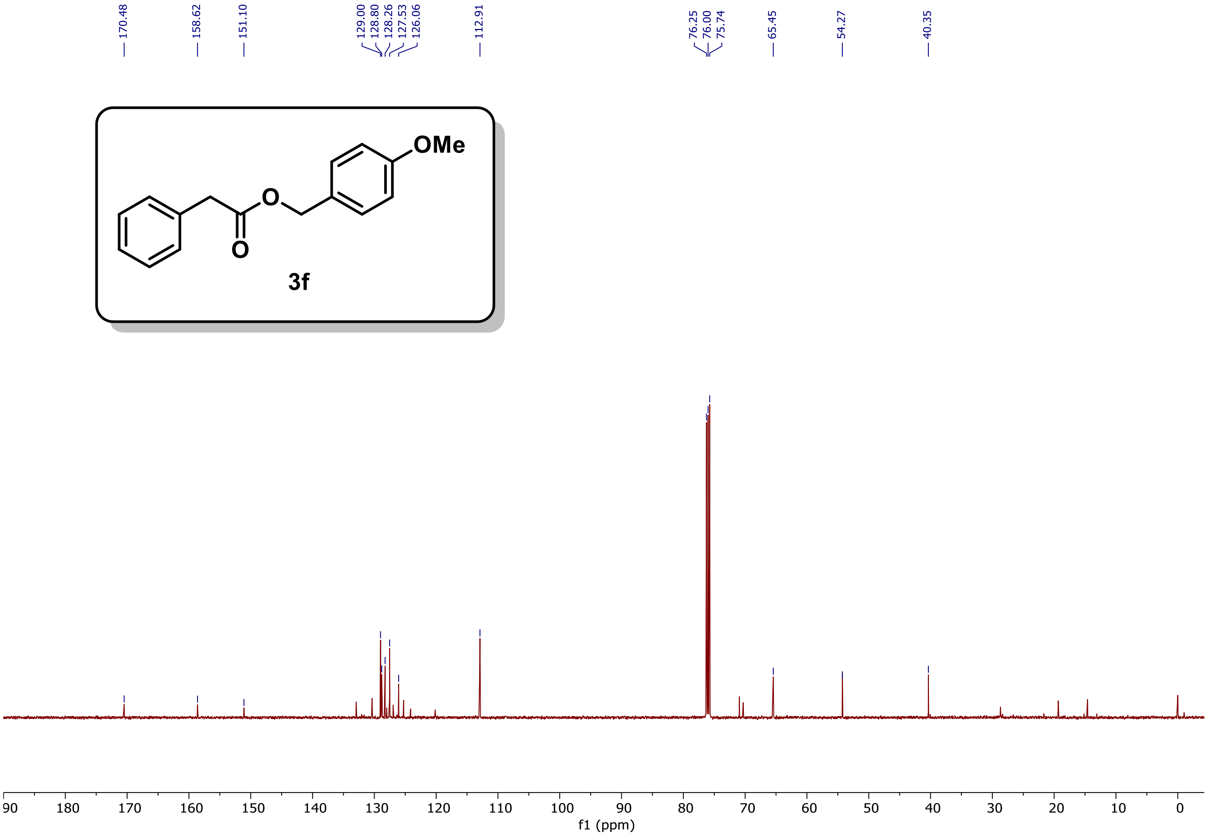
^{1}H NMR spectrum of compound 3e (500 MHz $CDCl_3$)



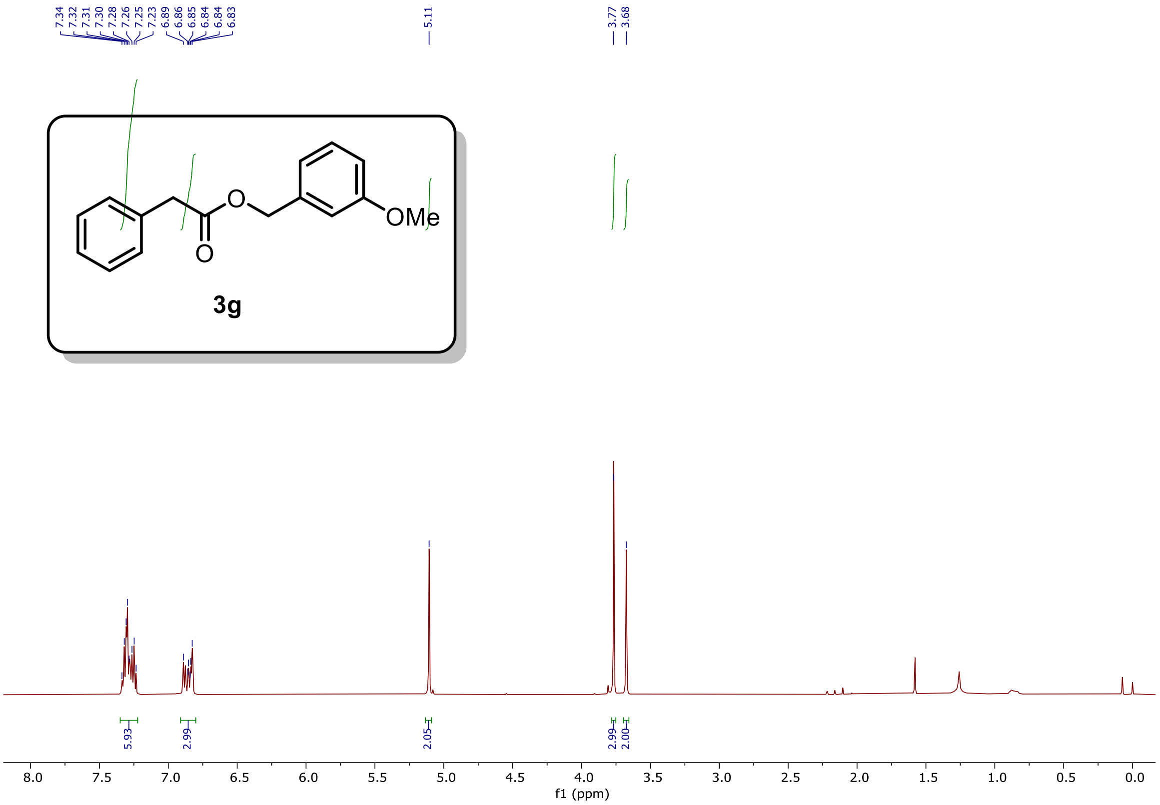
^{13}C{^{1}H} NMR spectrum of compound 3e (126 MHz $CDCl_3$)



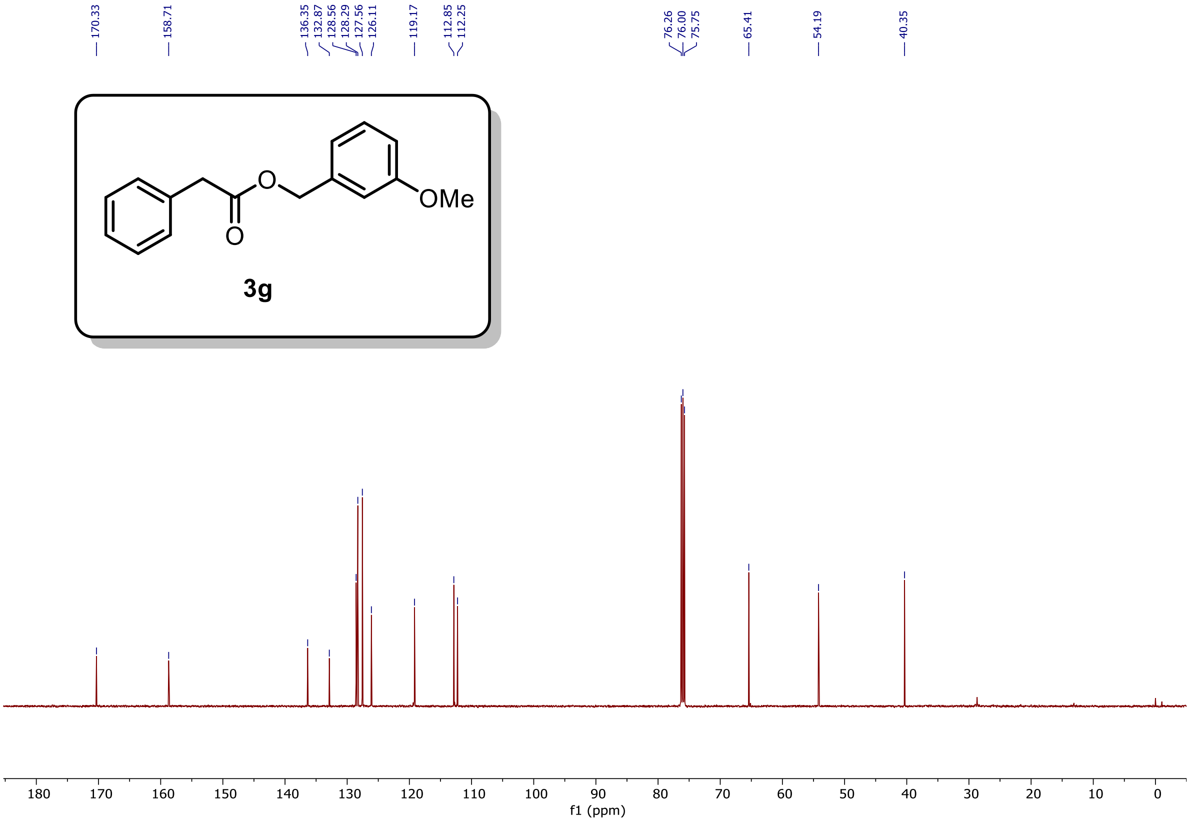
^{1}H NMR spectrum of compound 3f (500 MHz CDCl$_3$)



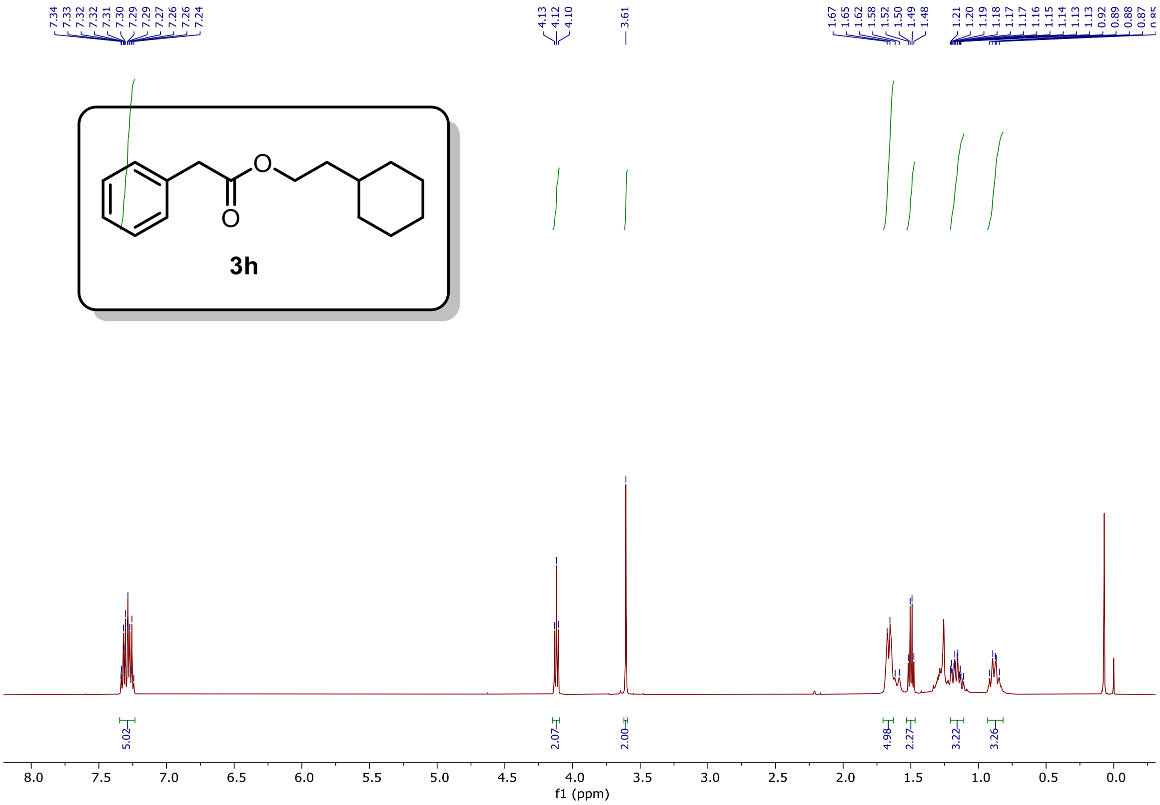
^{13}C{^{1}H} NMR spectrum of compound 3f (126 MHz CDCl$_3$)



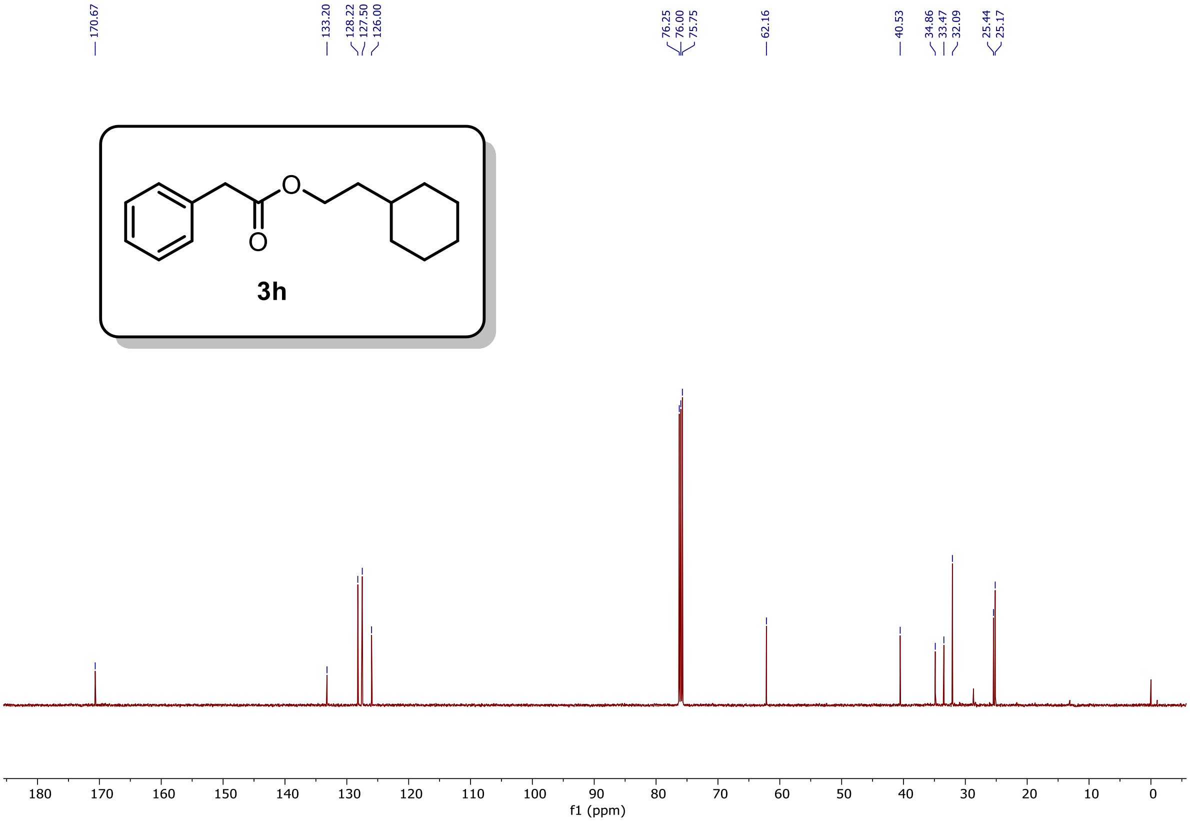
^{1}H NMR spectrum of compound 3g (500 MHz CDCl$_3$)



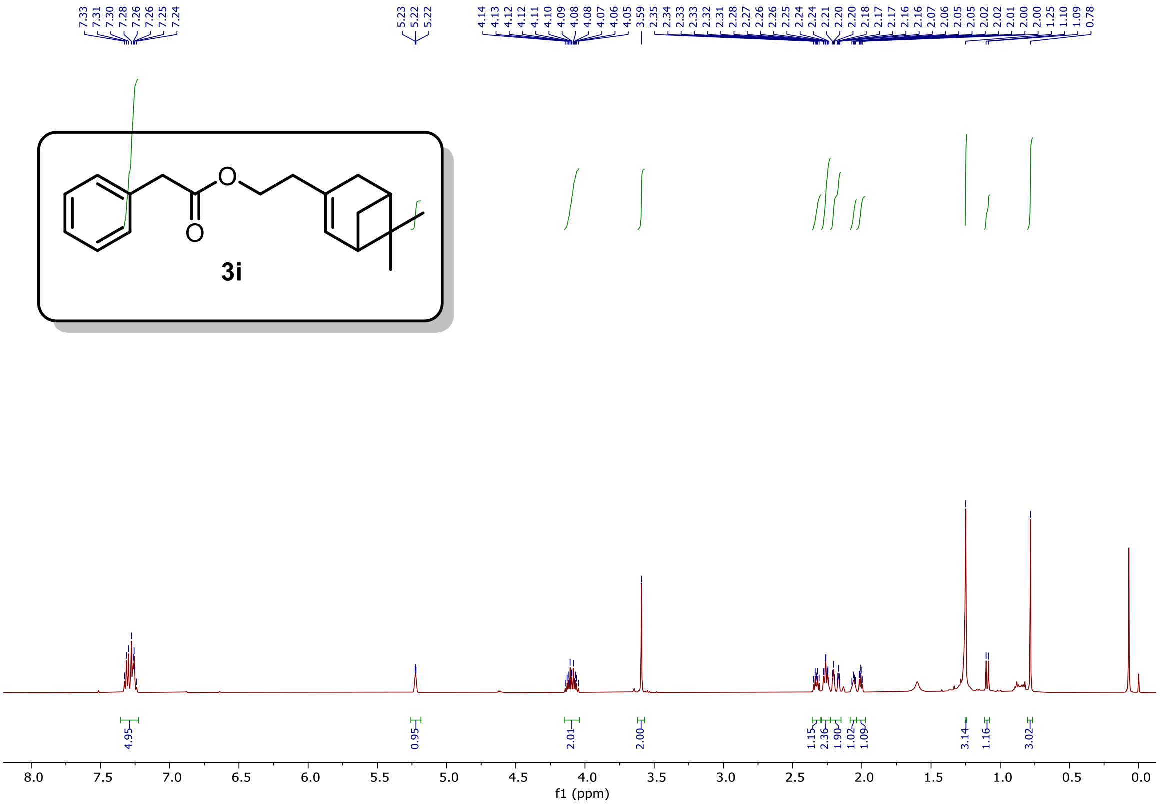
^{13}C{^{1}H} NMR spectrum of compound 3g (126 MHz CDCl$_3$)



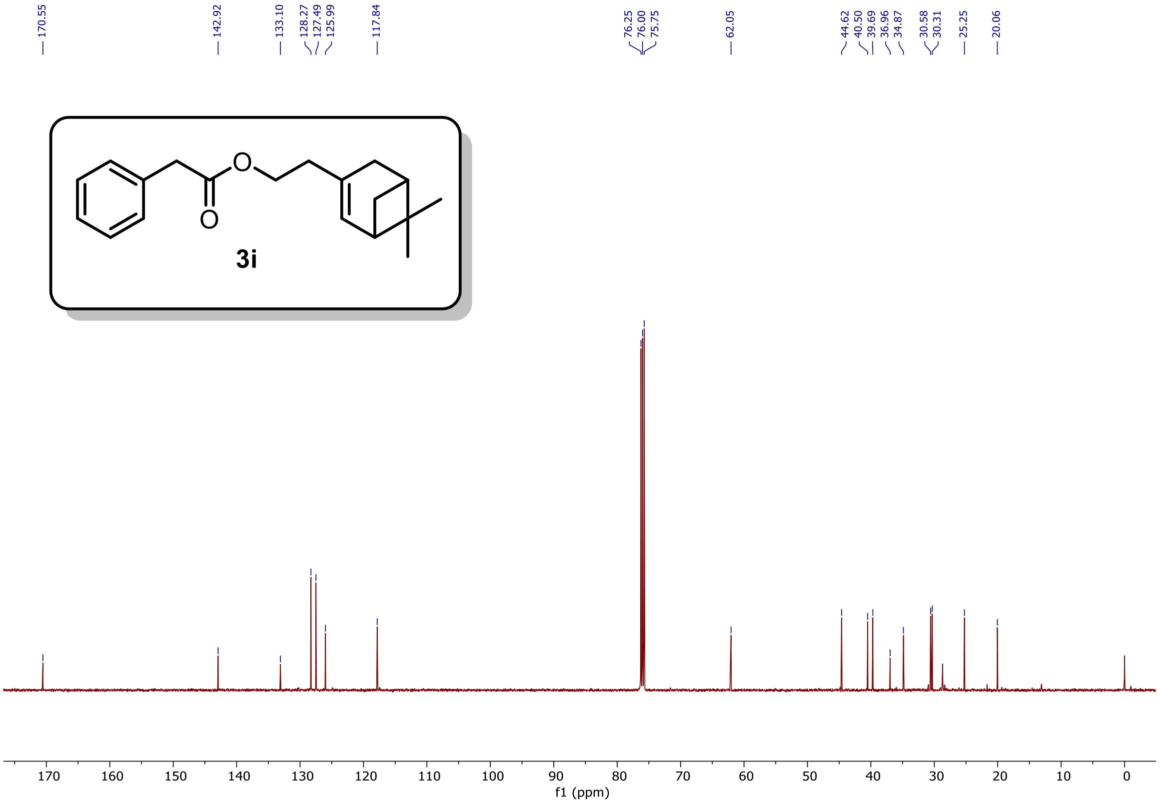
^{1}H NMR spectrum of compound 3h (500 MHz CDCl$_3$)



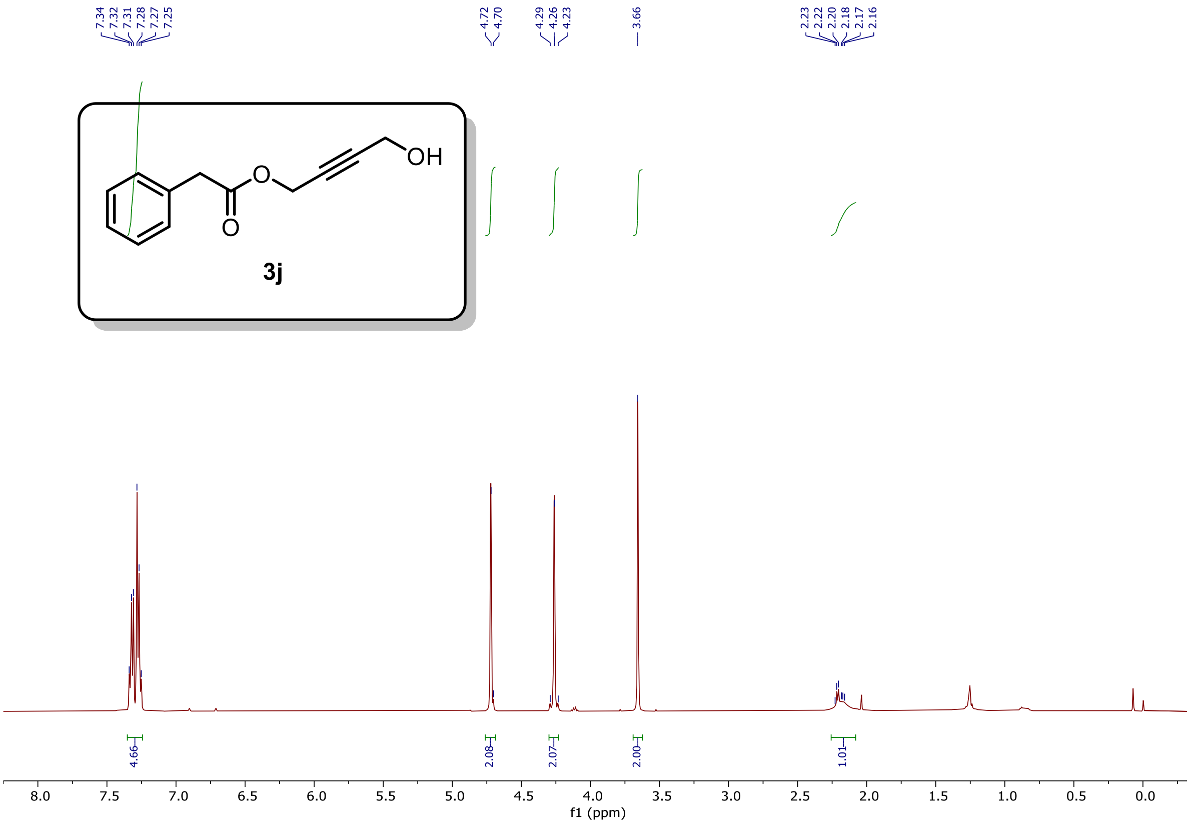
^{13}C{^{1}H} NMR spectrum of compound 3h (126 MHz CDCl$_3$)



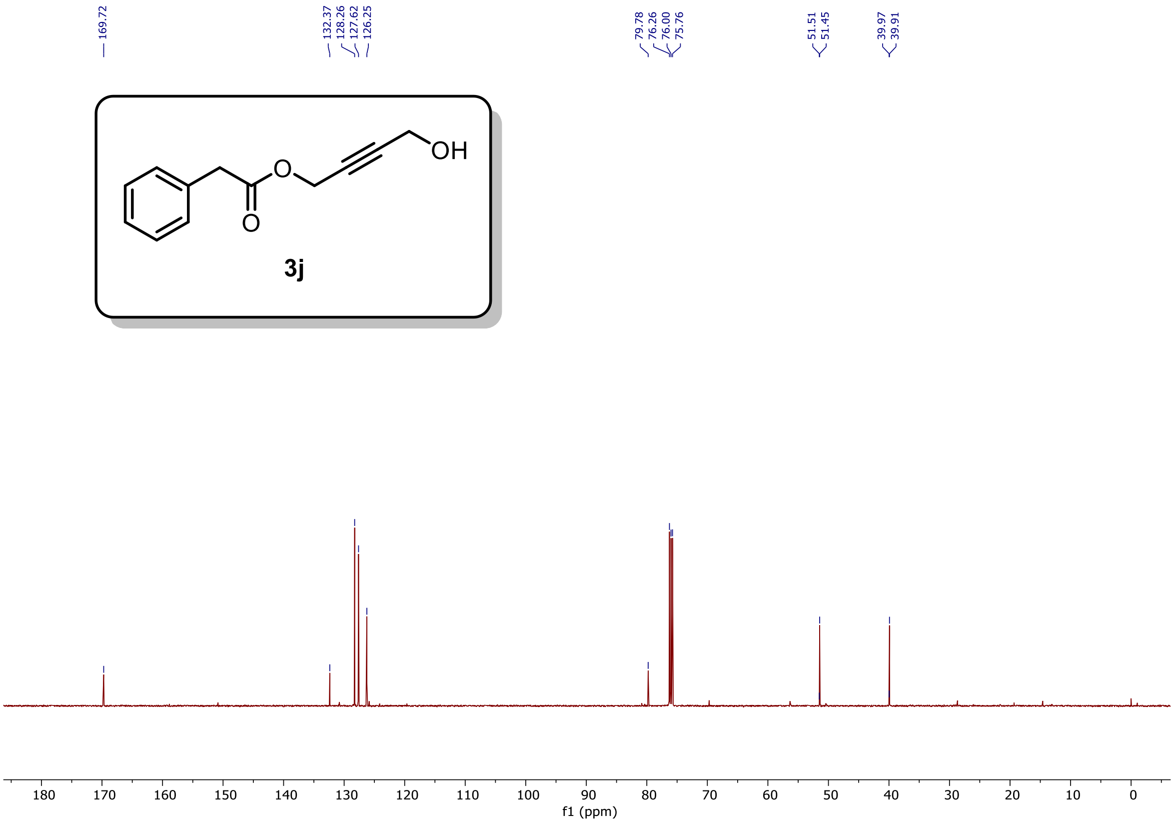
^{1}H NMR spectrum of compound 3i (500 MHz CDCl$_3$)



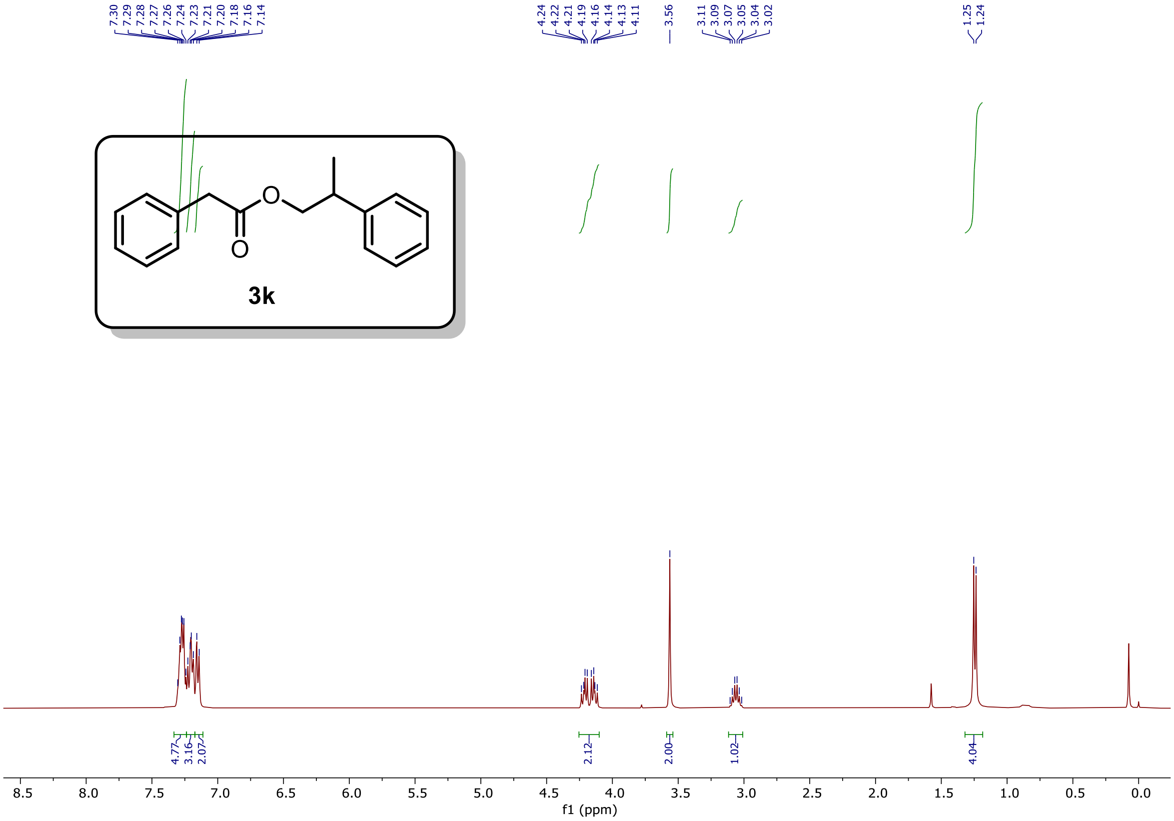
^{13}C{^{1}H} NMR spectrum of compound 3i (126 MHz CDCl$_3$)



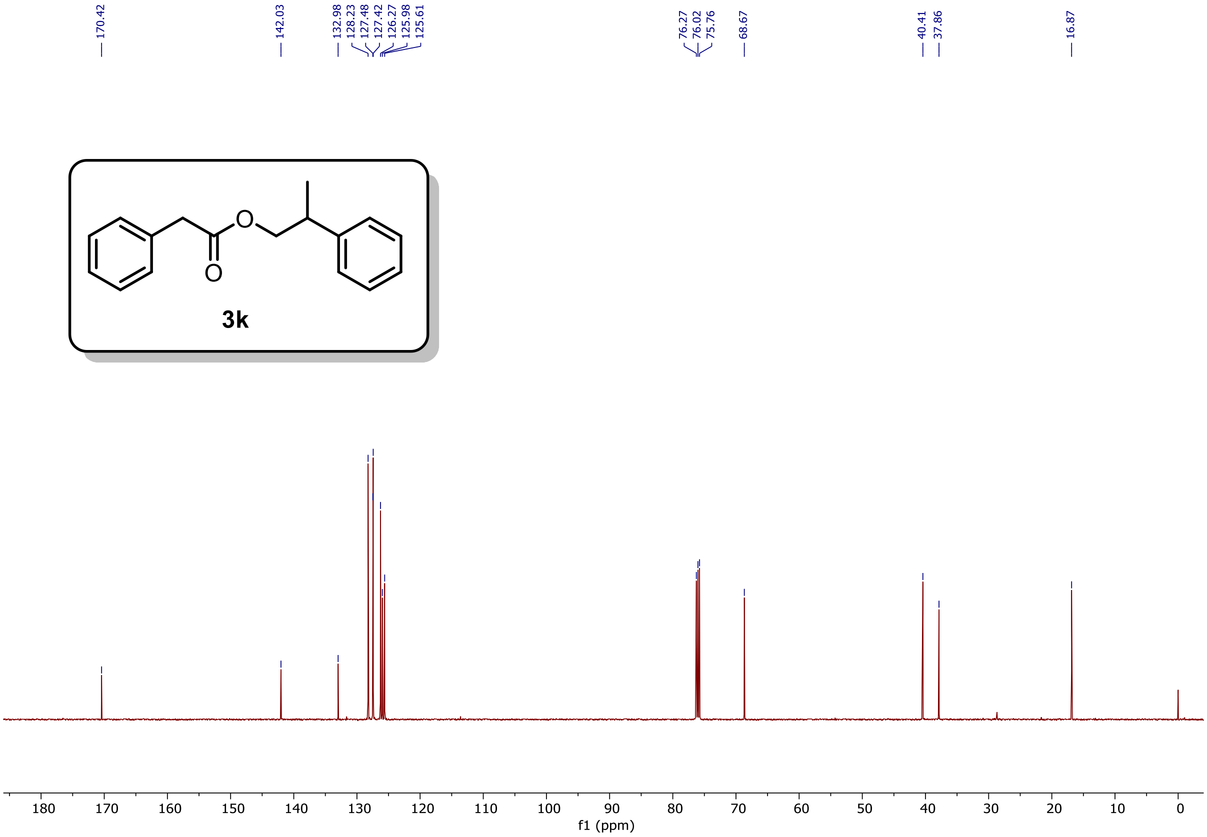
^{1}H NMR spectrum of compound 3j (500 MHz CDCl$_3$)



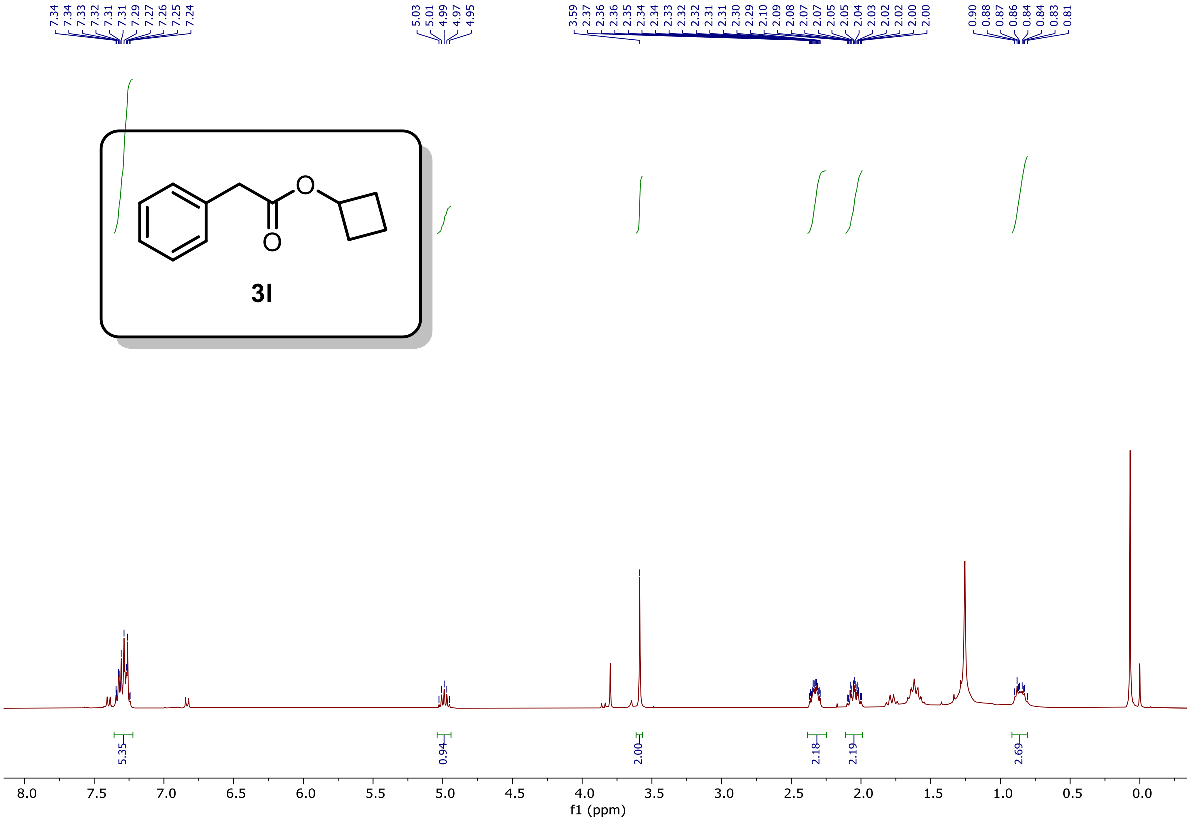
^{13}C{^{1}H} NMR spectrum of compound 3j (126 MHz CDCl$_3$)



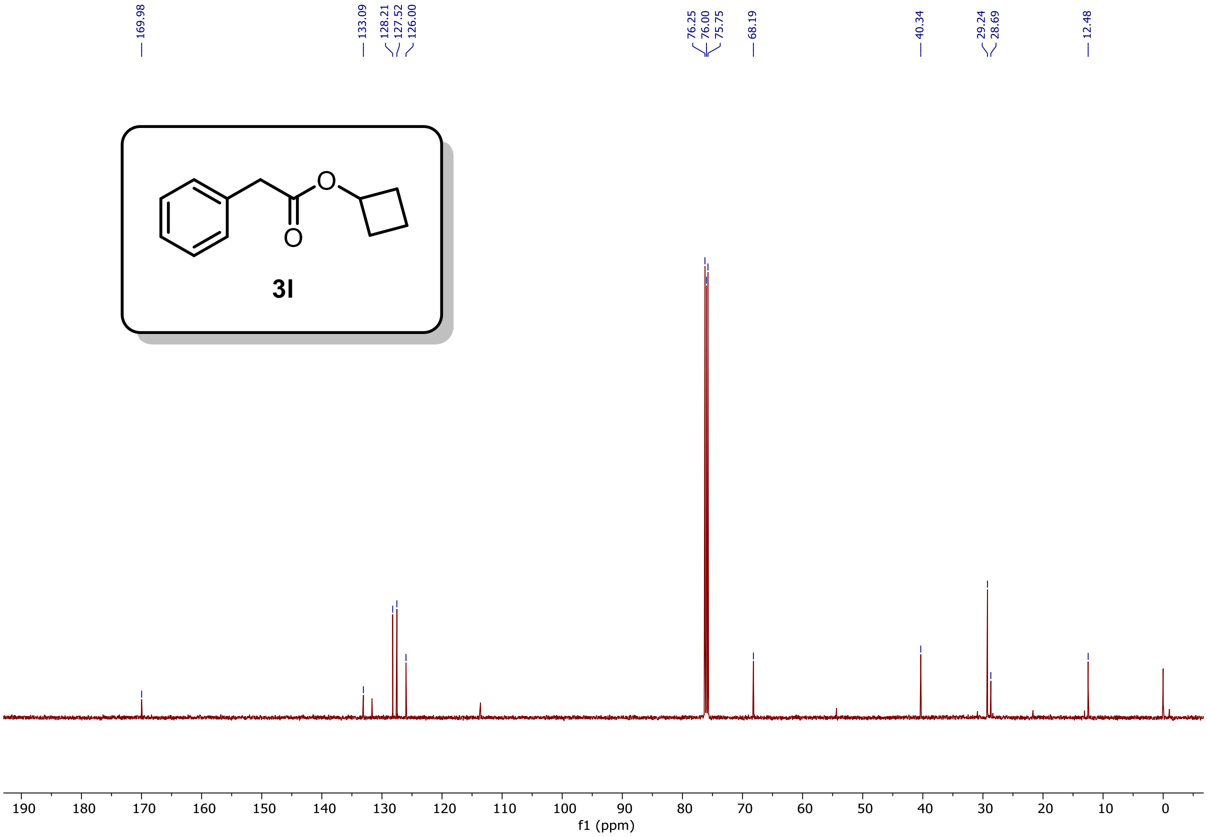
^{1}H NMR spectrum of compound 3k (500 MHz CDCl$_3$)



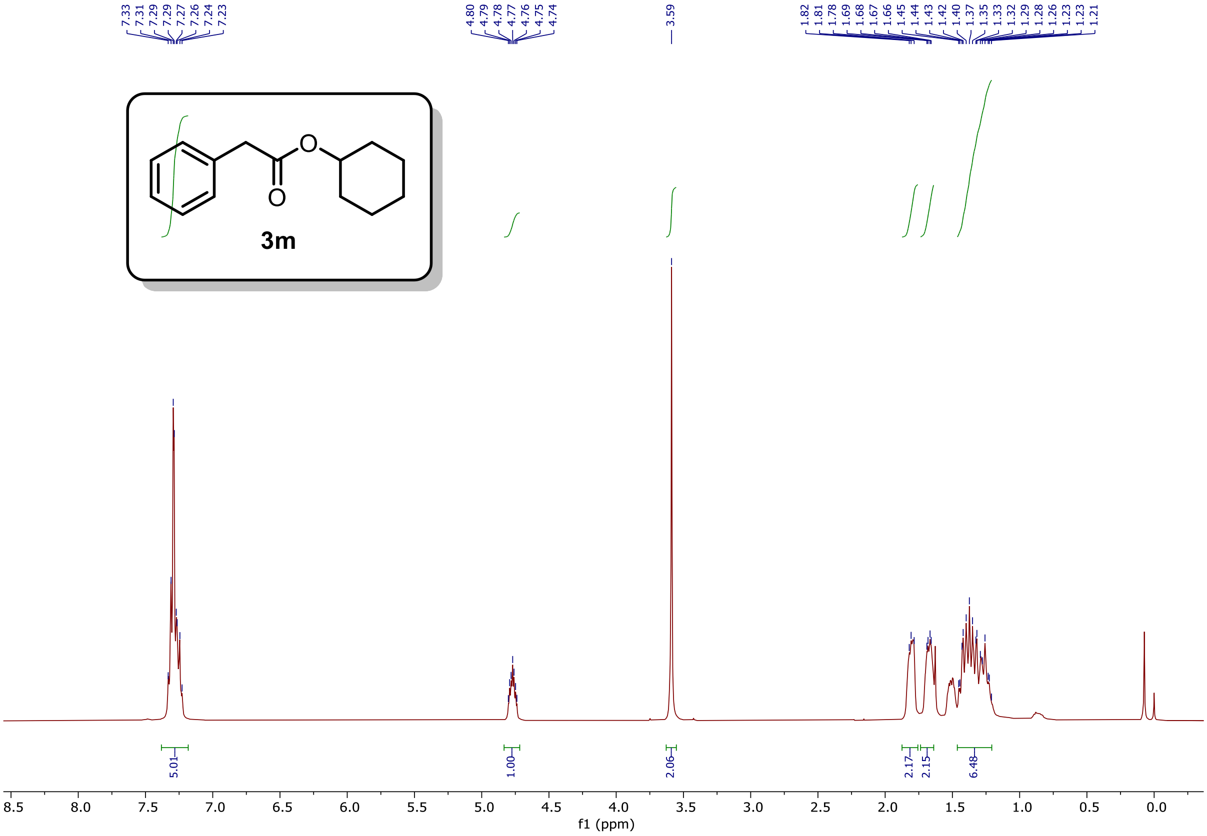
^{13}C{^{1}H} NMR spectrum of compound 3k (126 MHz CDCl$_3$)



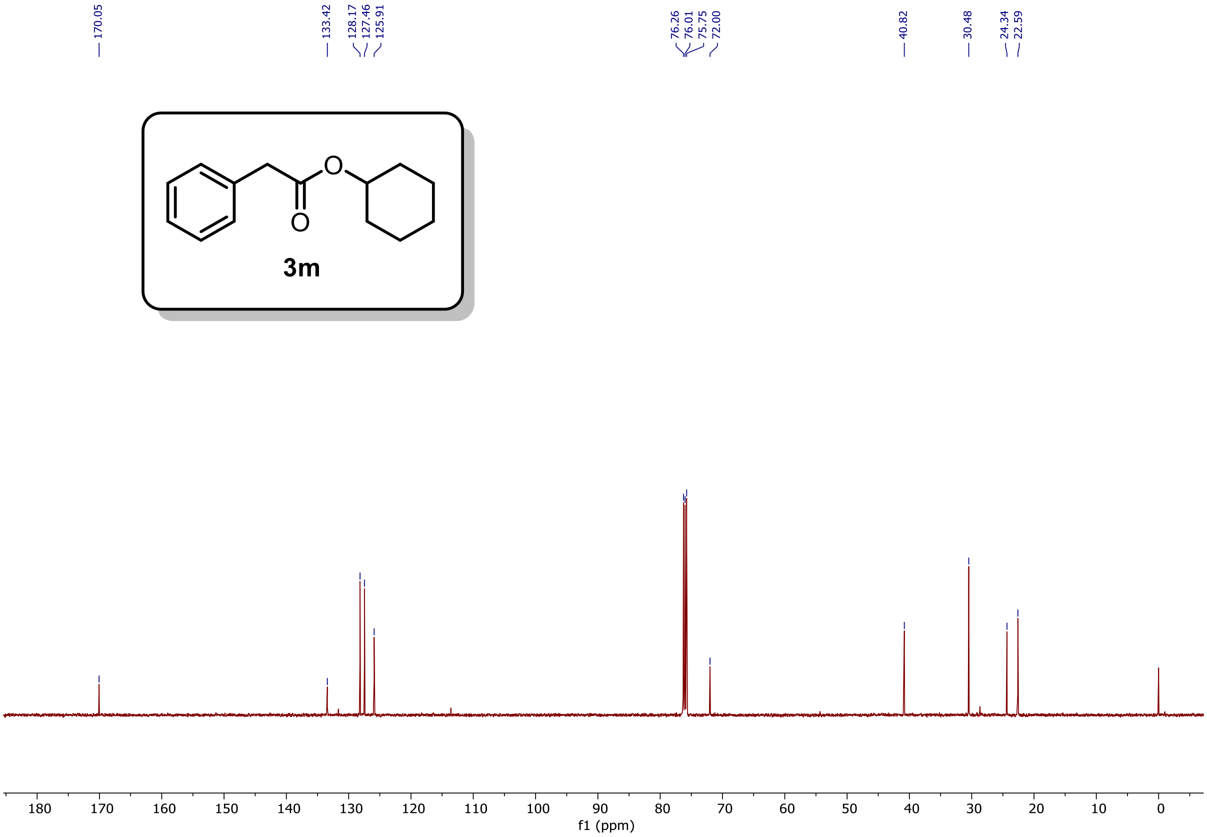
^{1}H NMR spectrum of compound 3l (500 MHz CDCl$_3$)



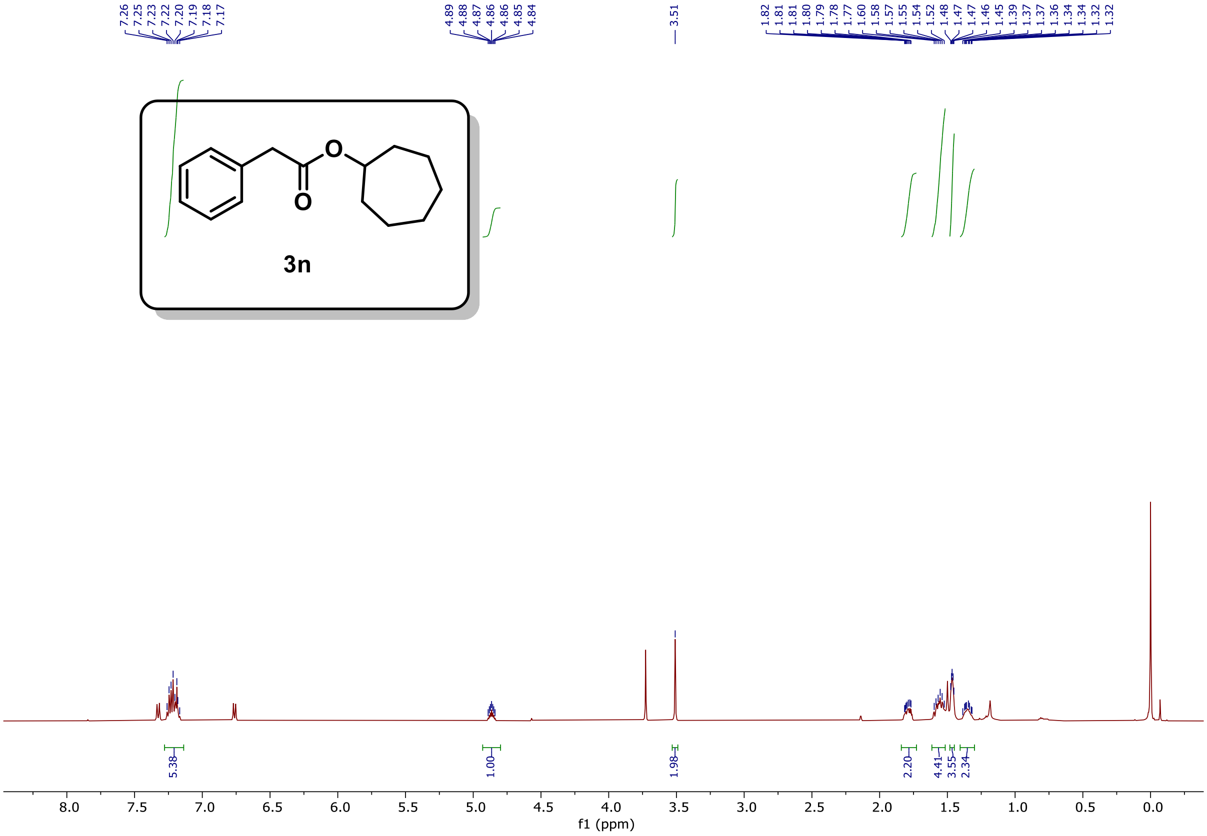
^{13}C{^{1}H} NMR spectrum of compound 3l (126 MHz CDCl$_3$)



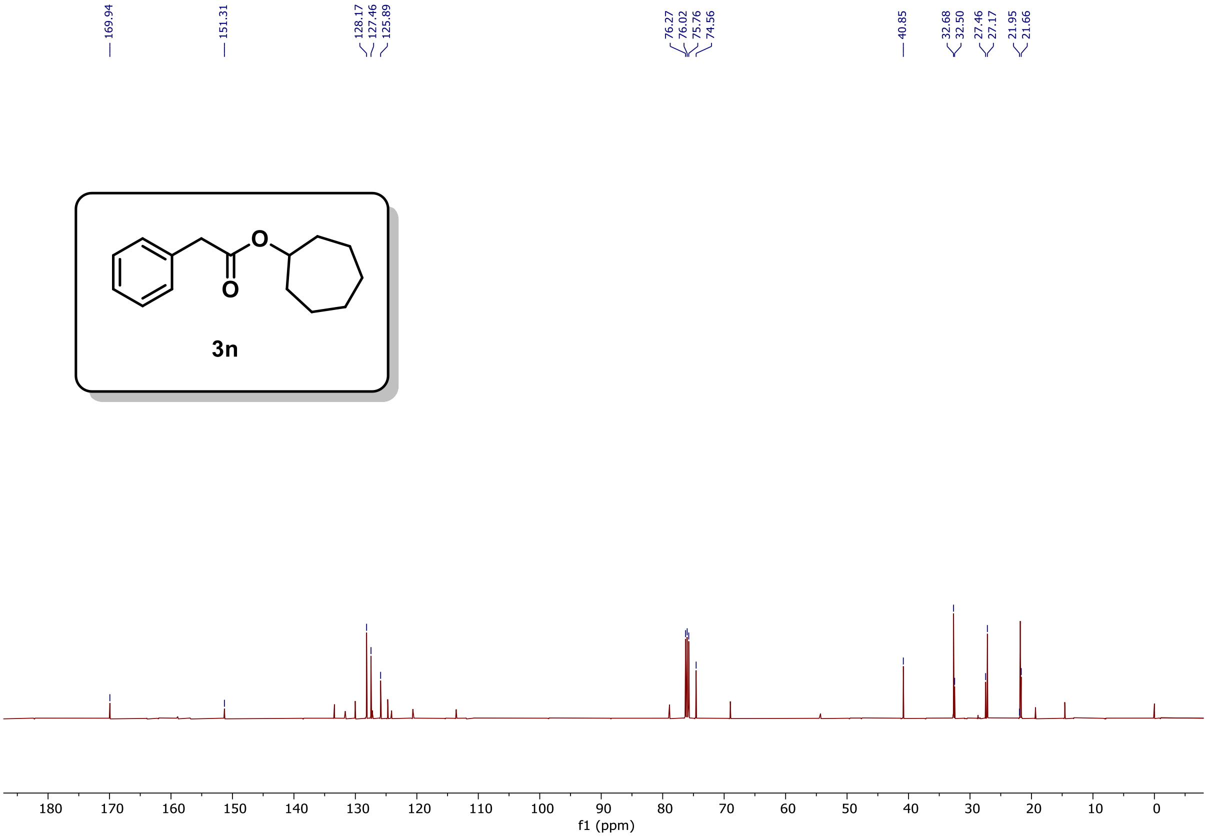
^{1}H NMR spectrum of compound 3m (500 MHz $CDCl_3$)



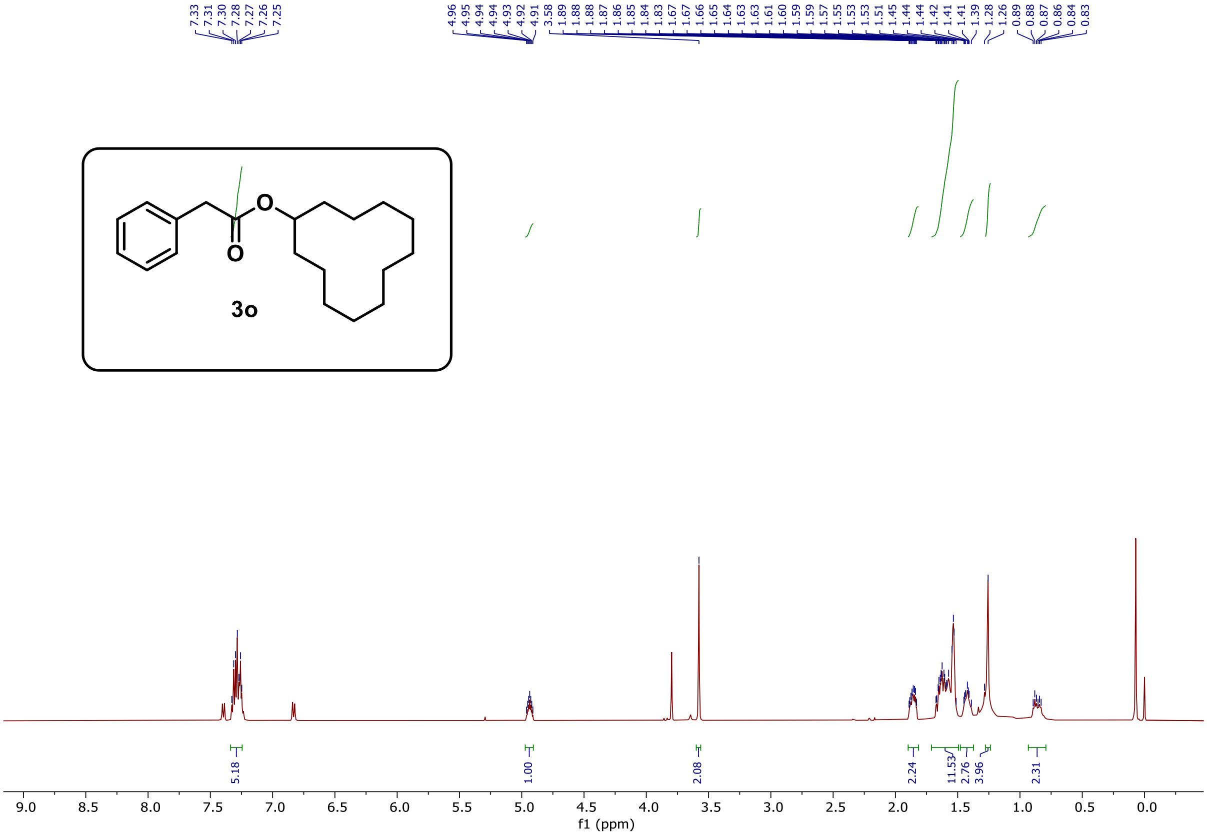
^{13}C{^{1}H} NMR spectrum of compound 3m (126 MHz $CDCl_3$)



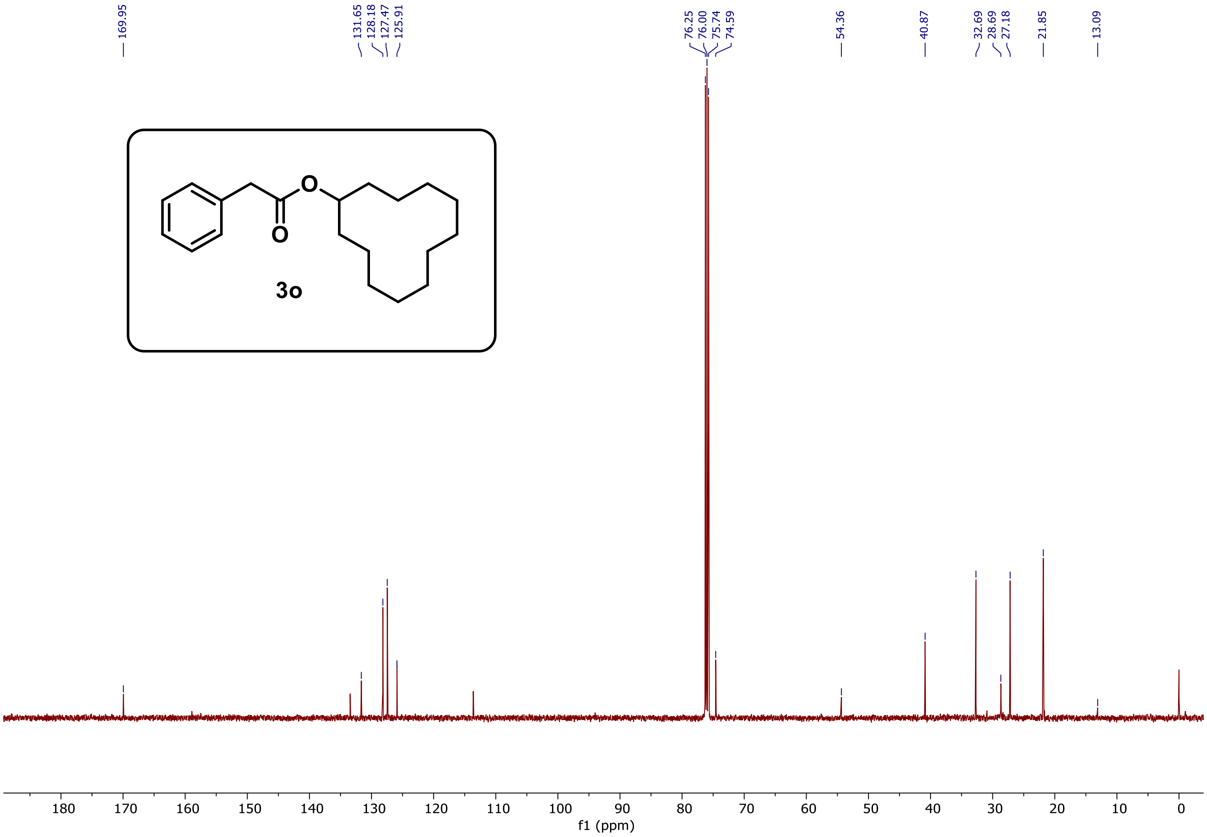
^{1}H NMR spectrum of compound 3n (500 MHz CDCl$_3$)



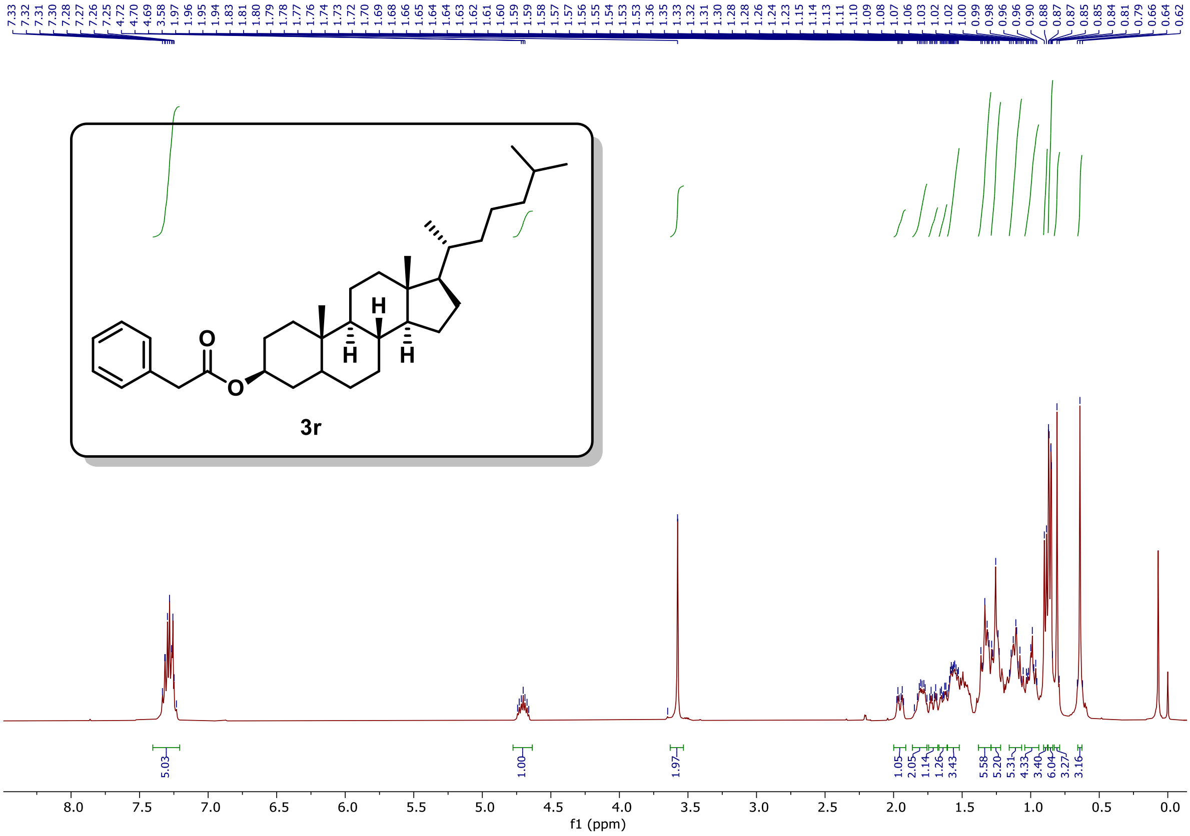
^{13}C{^{1}H} NMR spectrum of compound 3n (126 MHz CDCl$_3$)



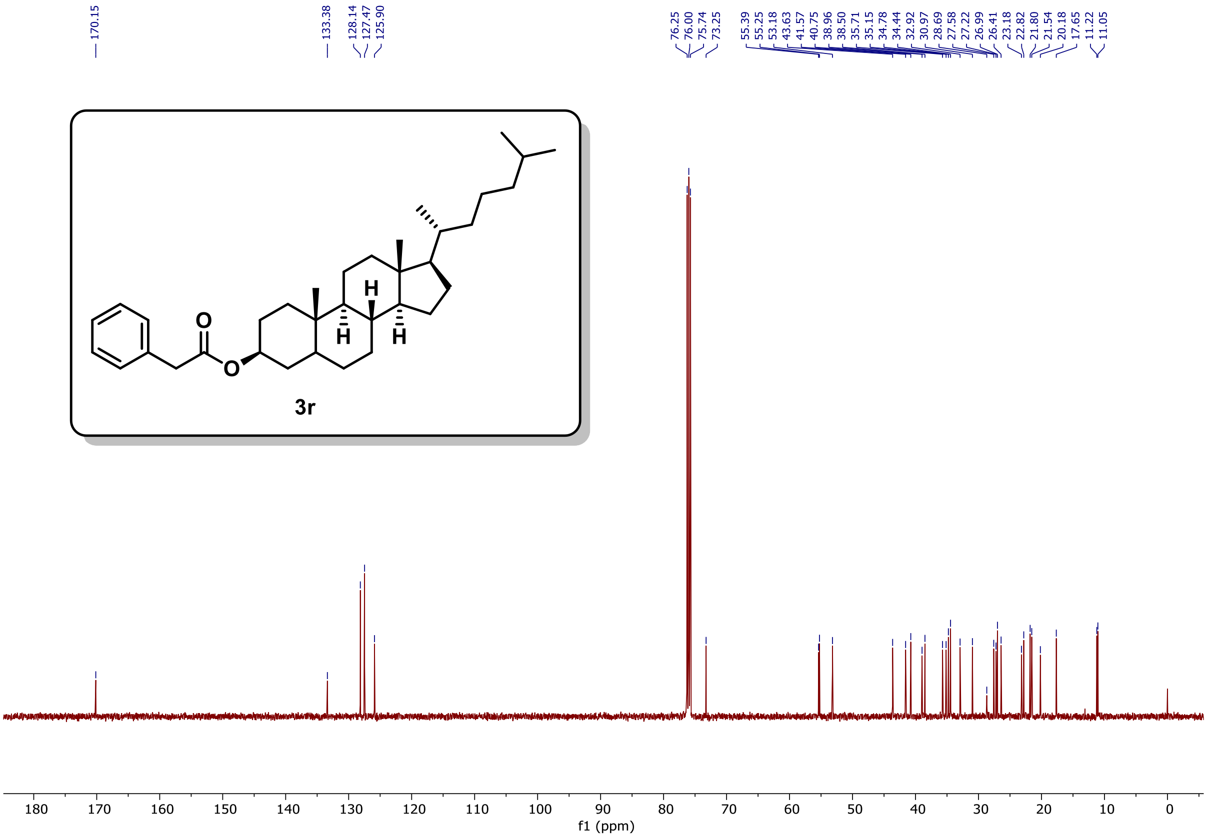
^{1}H NMR spectrum of compound 3o (500 MHz $CDCl_3$)



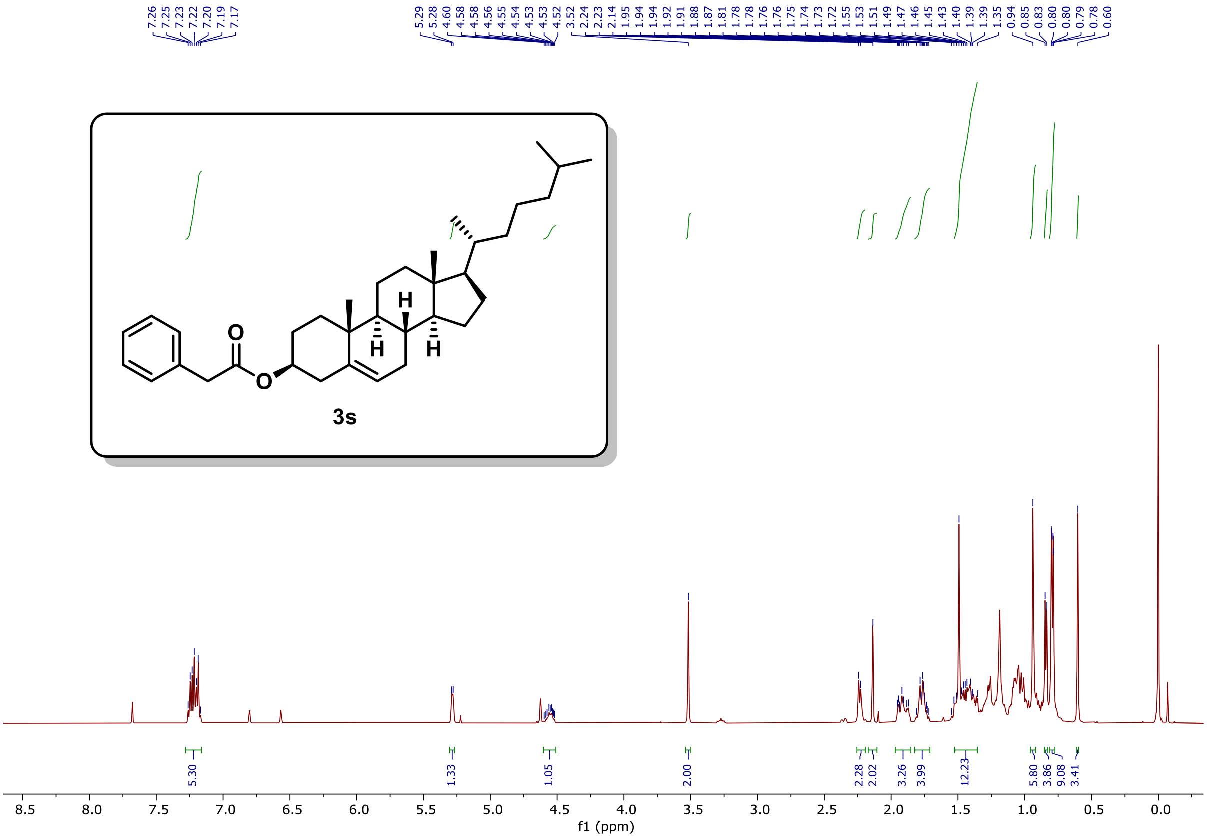
$^{13}C\{^1H\}$ NMR spectrum of compound 3o (126 MHz $CDCl_3$)



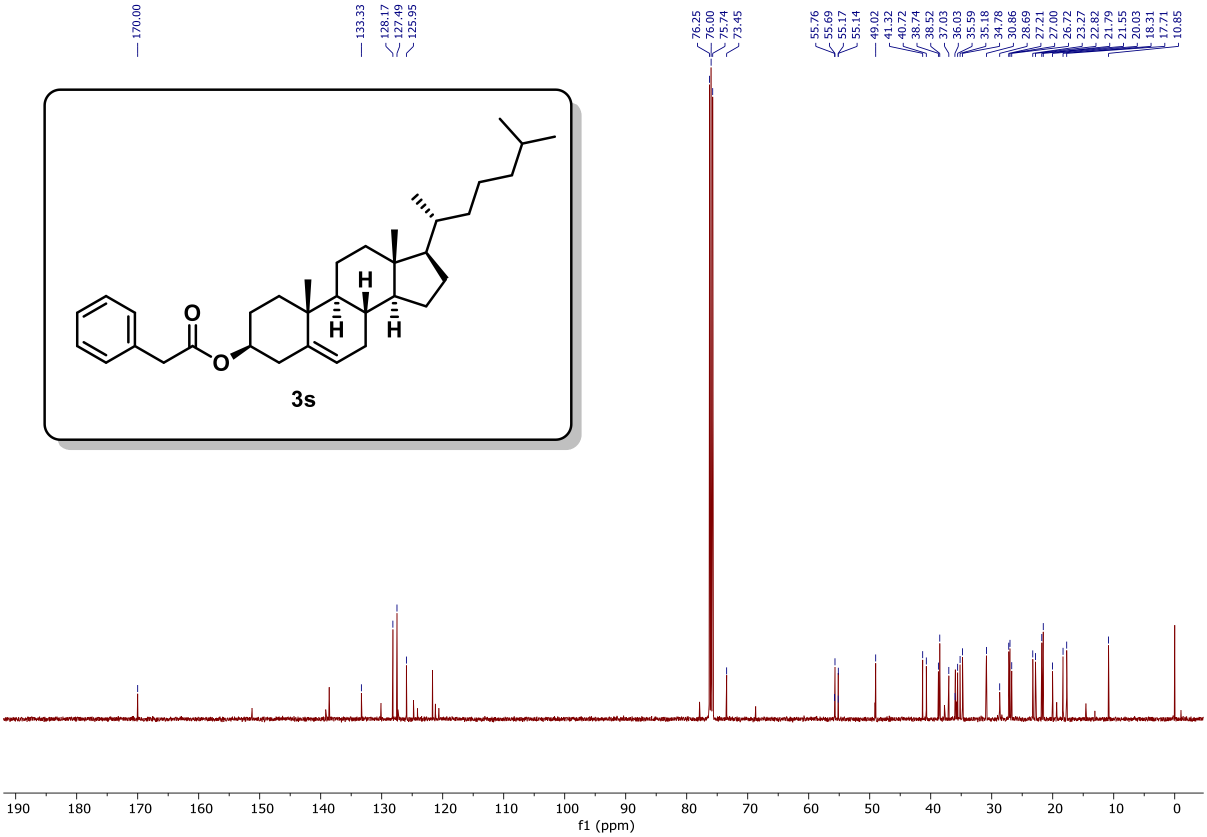
^{1}H NMR spectrum of compound 3r (500 MHz CDCl$_3$)



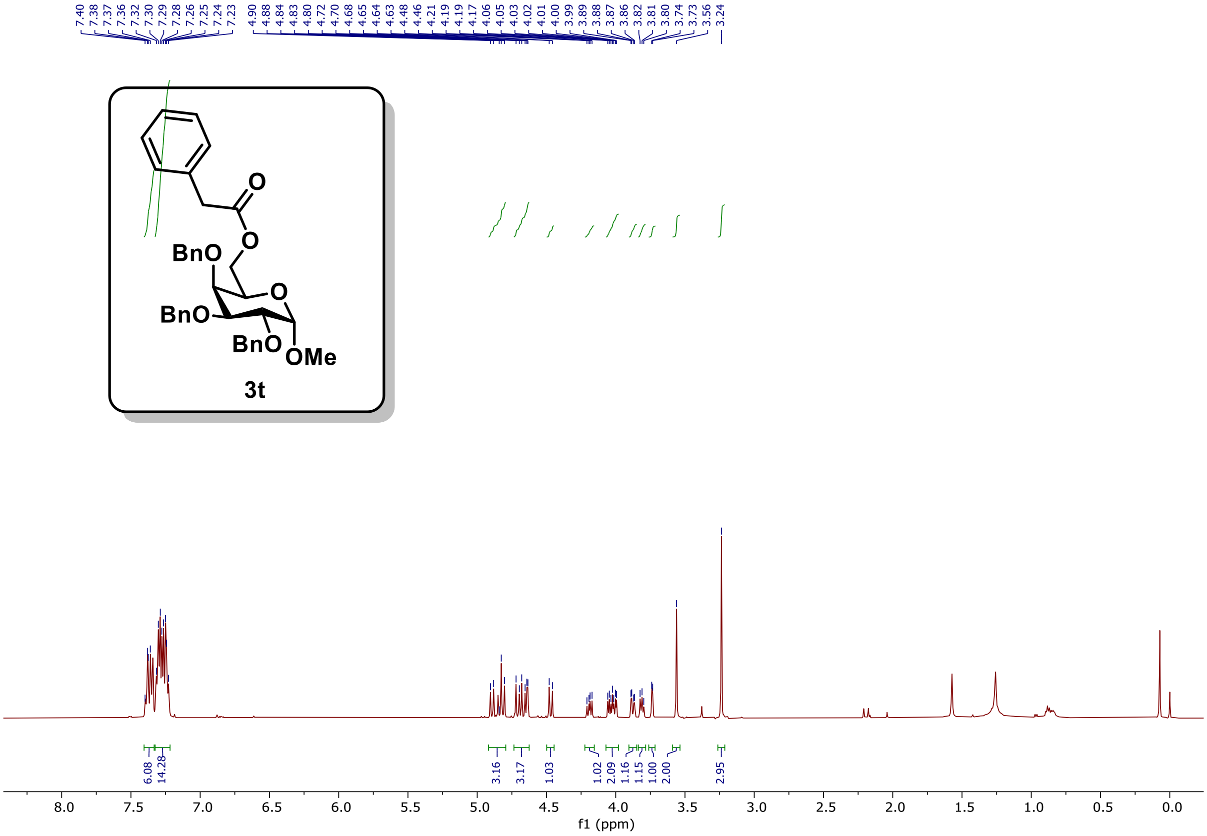
^{13}C{^{1}H} NMR spectrum of compound 3r (126 MHz CDCl$_3$)



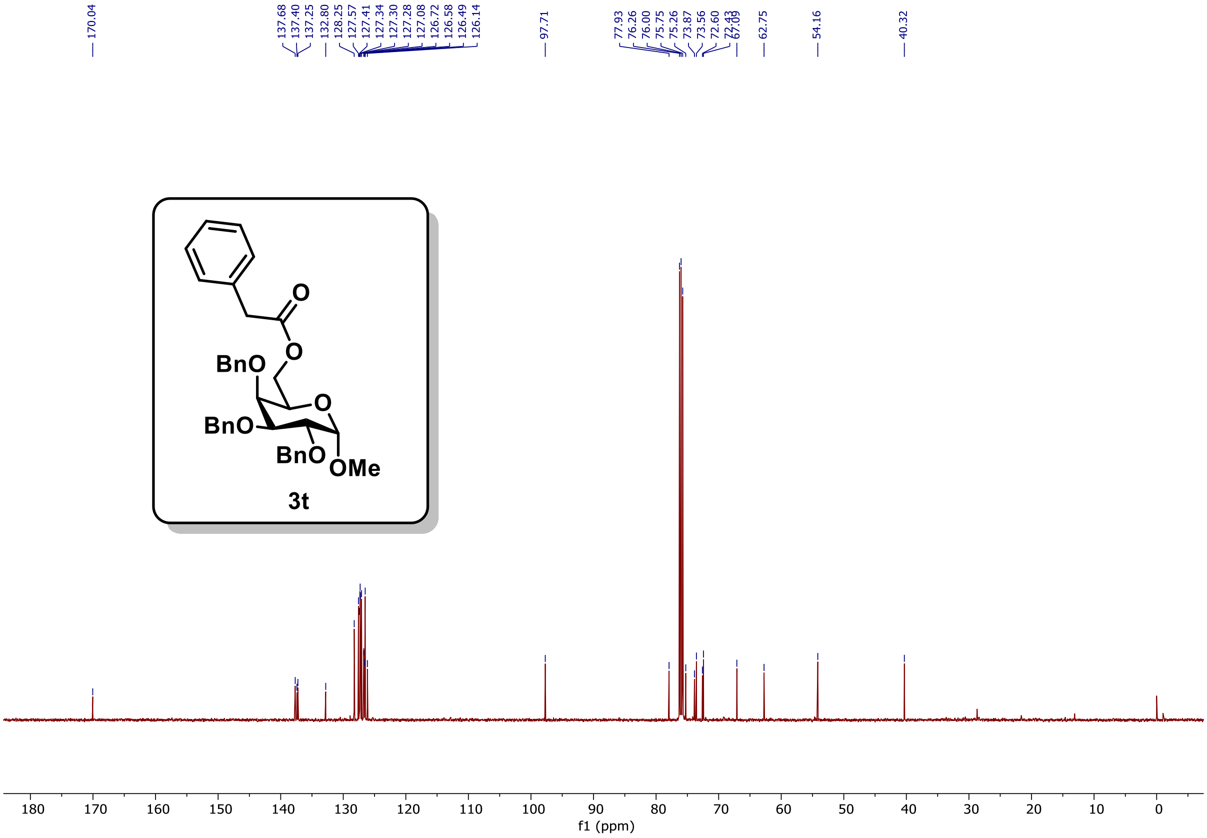
^{1}H NMR spectrum of compound 3s (500 MHz CDCl$_3$)



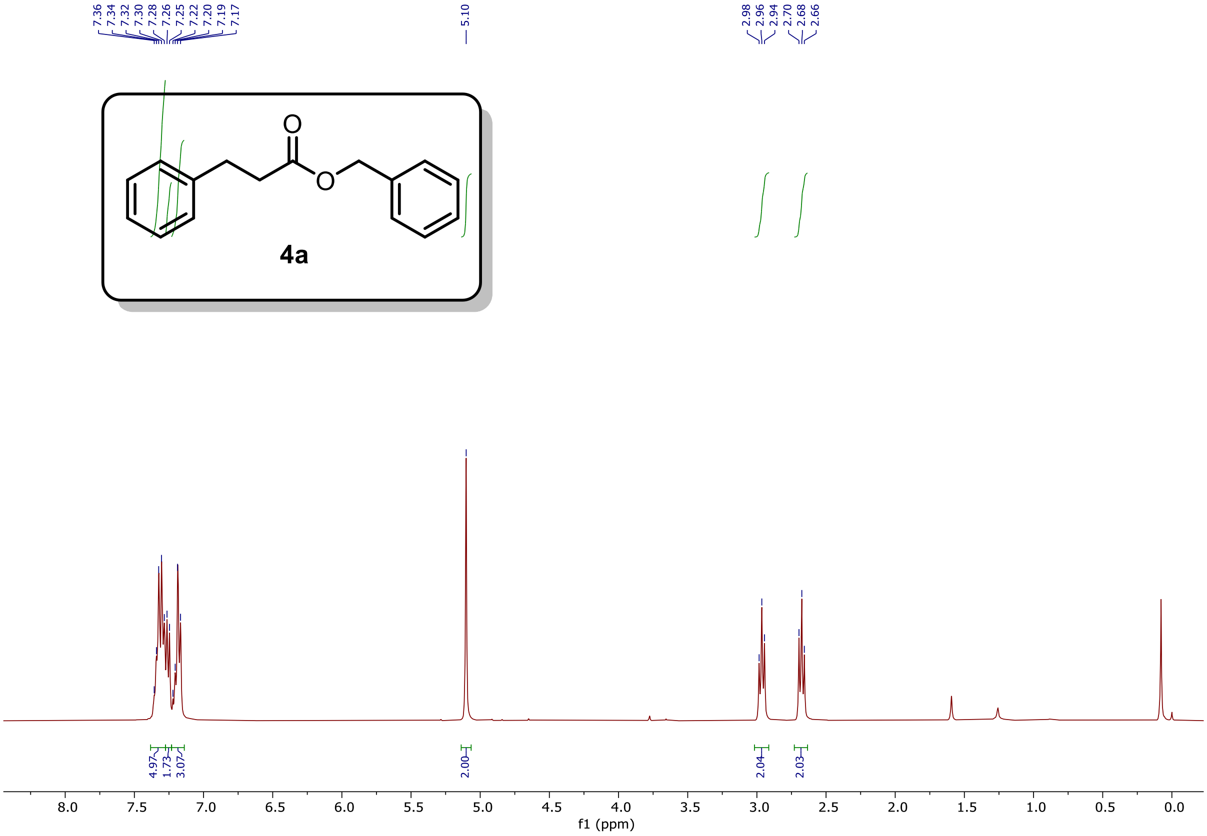
^{13}C{^{1}H} NMR spectrum of compound 3s (126 MHz CDCl$_3$



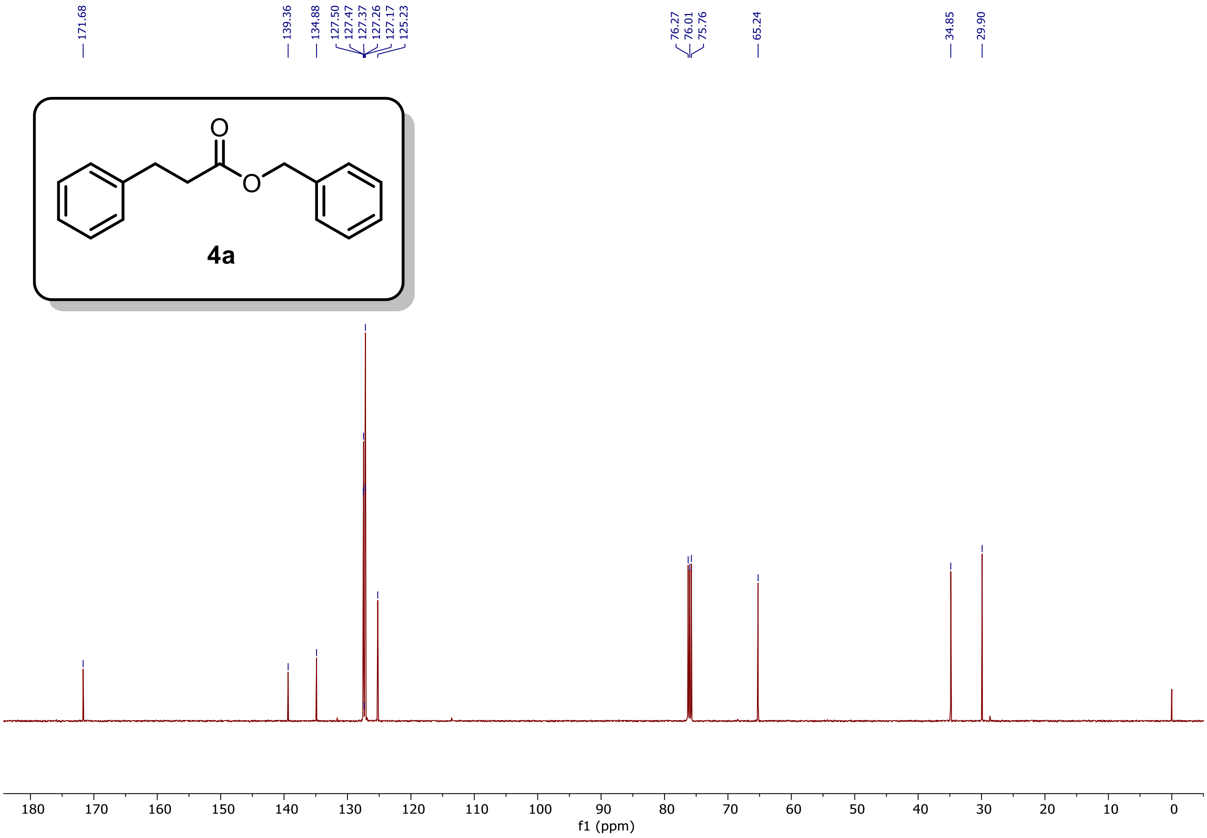
^{1}H NMR spectrum of compound 3t (500 MHz CDCl$_3$)



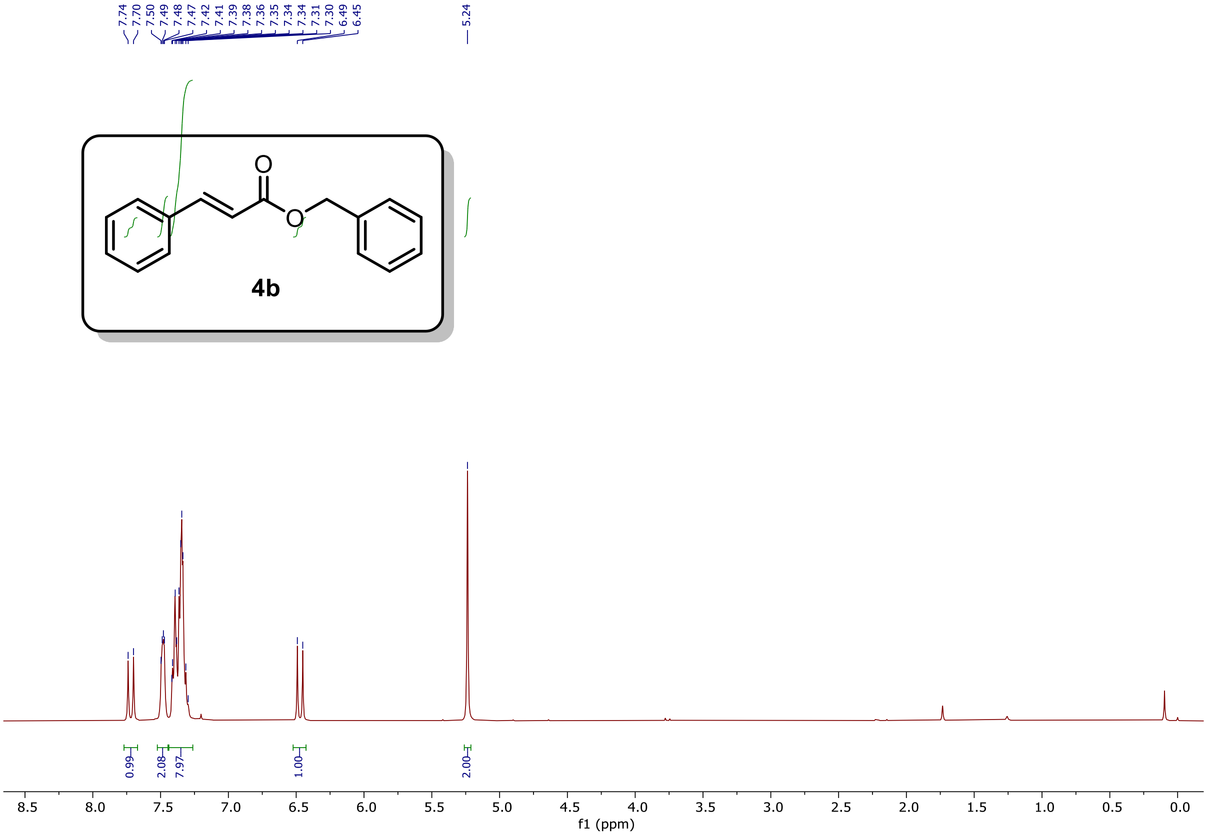
^{13}C{^{1}H} NMR spectrum of compound 3t (126 MHz CDCl$_3$)



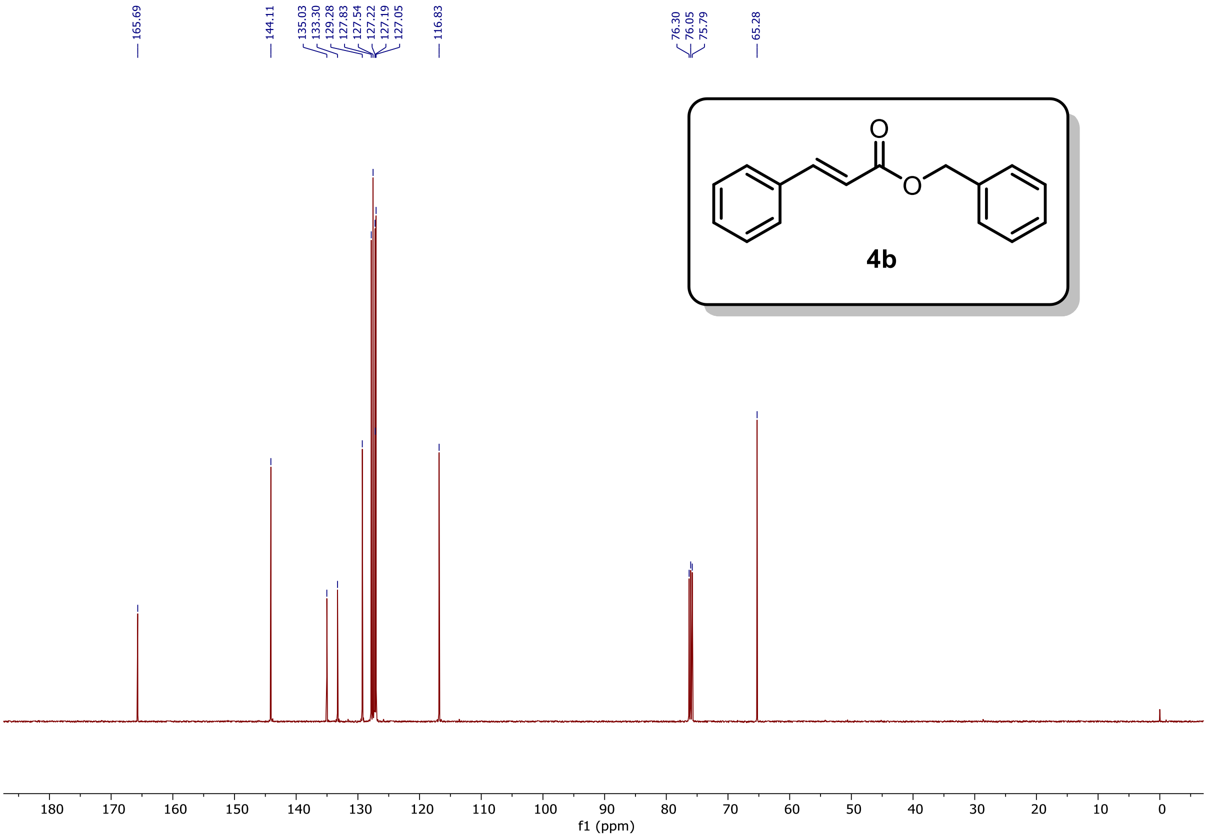
^{1}H NMR spectrum of compound 4a (500 MHz CDCl$_3$)



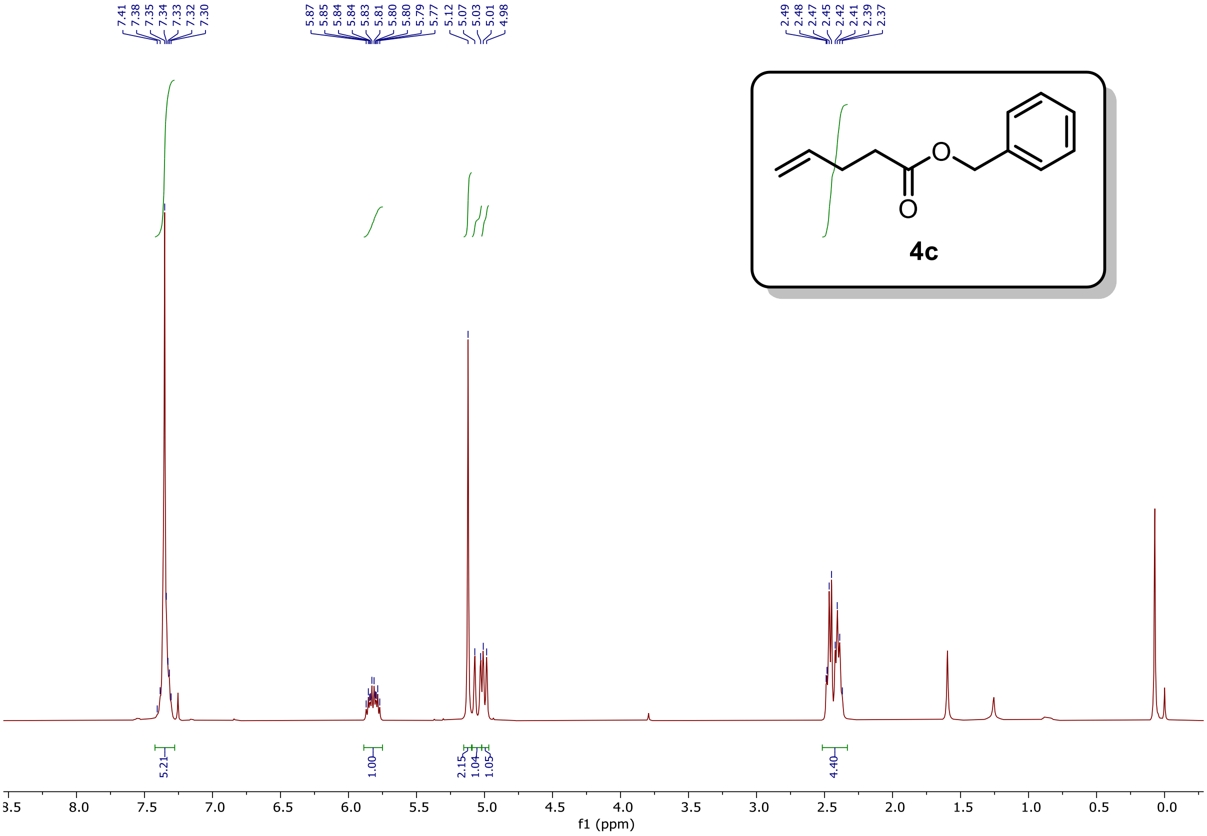
^{13}C{^{1}H} NMR spectrum of compound 4a (126 MHz CDCl$_3$)



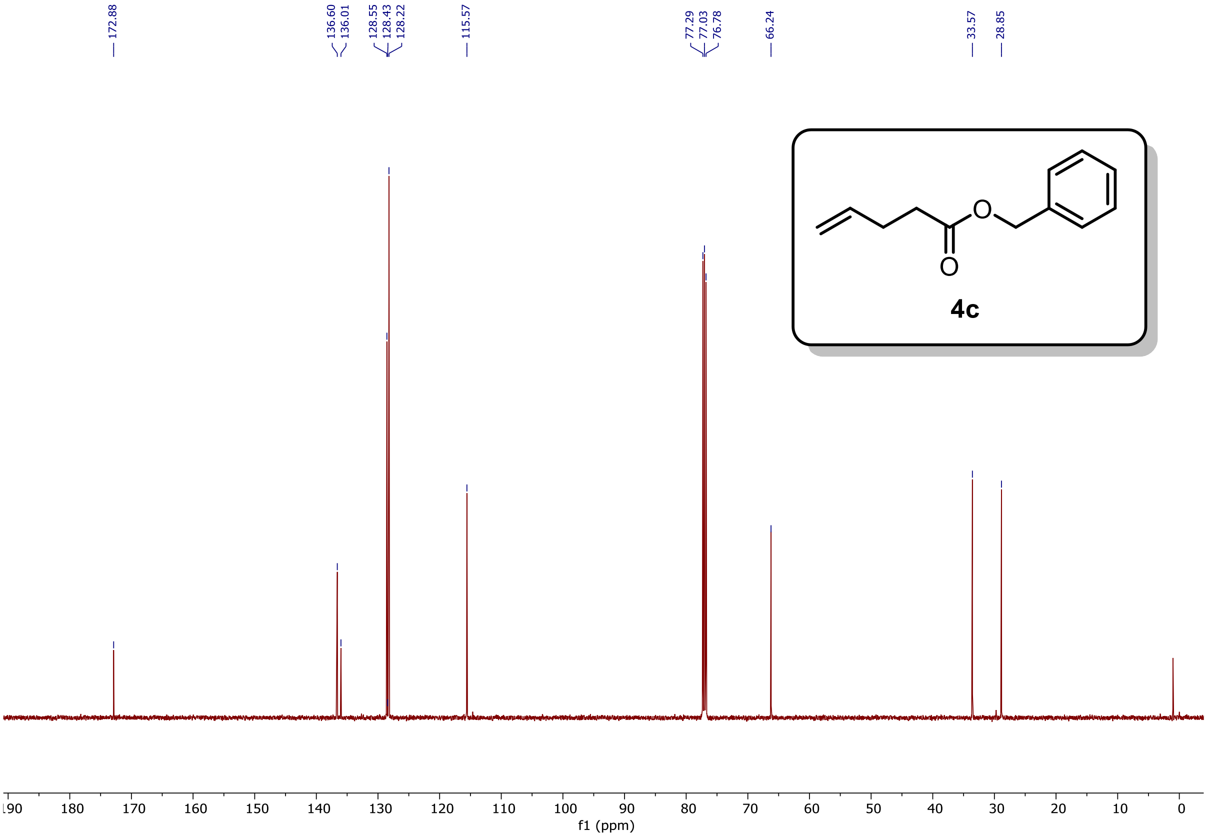
^{1}H NMR spectrum of compound 4b (500 MHz CDCl$_3$)



^{13}C{^{1}H} NMR spectrum of compound 4b (126 MHz CDCl$_3$)

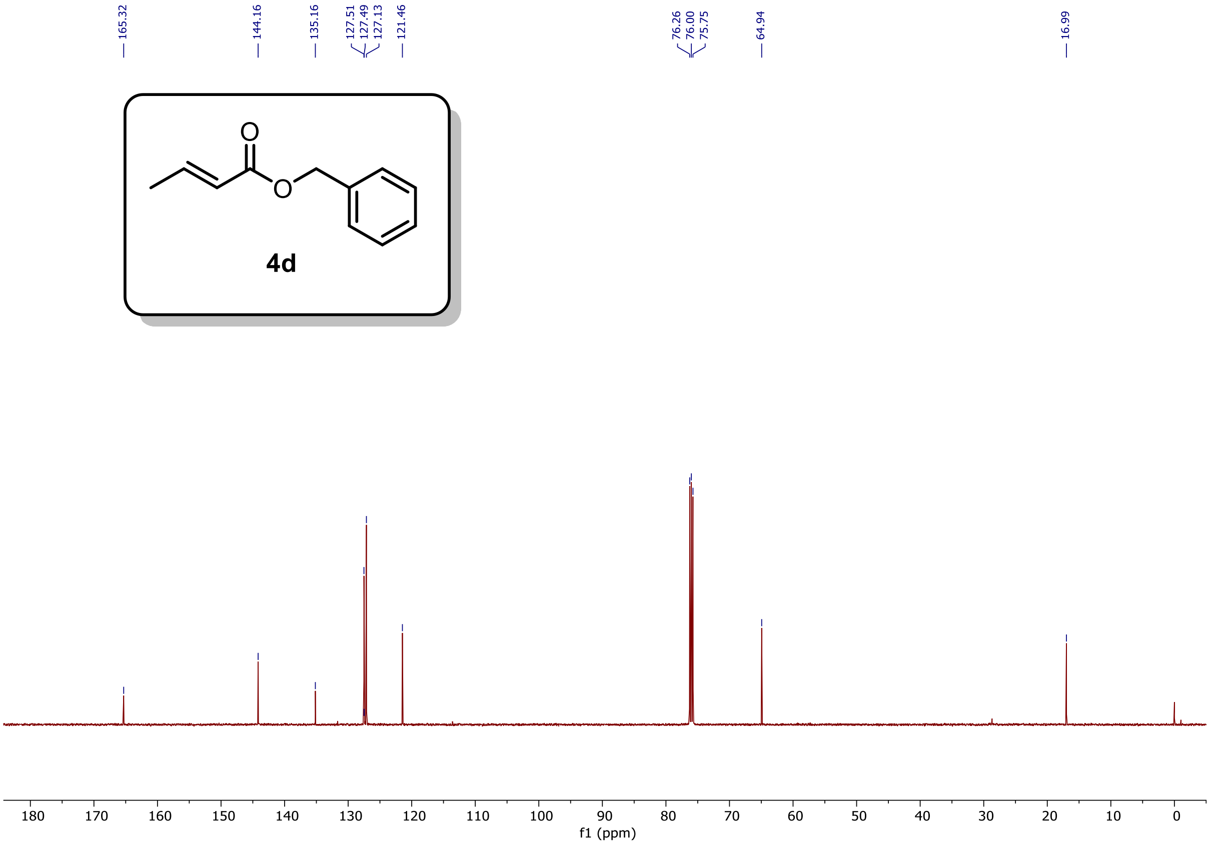


^{1}H NMR spectrum of compound 4c (500 MHz CDCl$_3$)

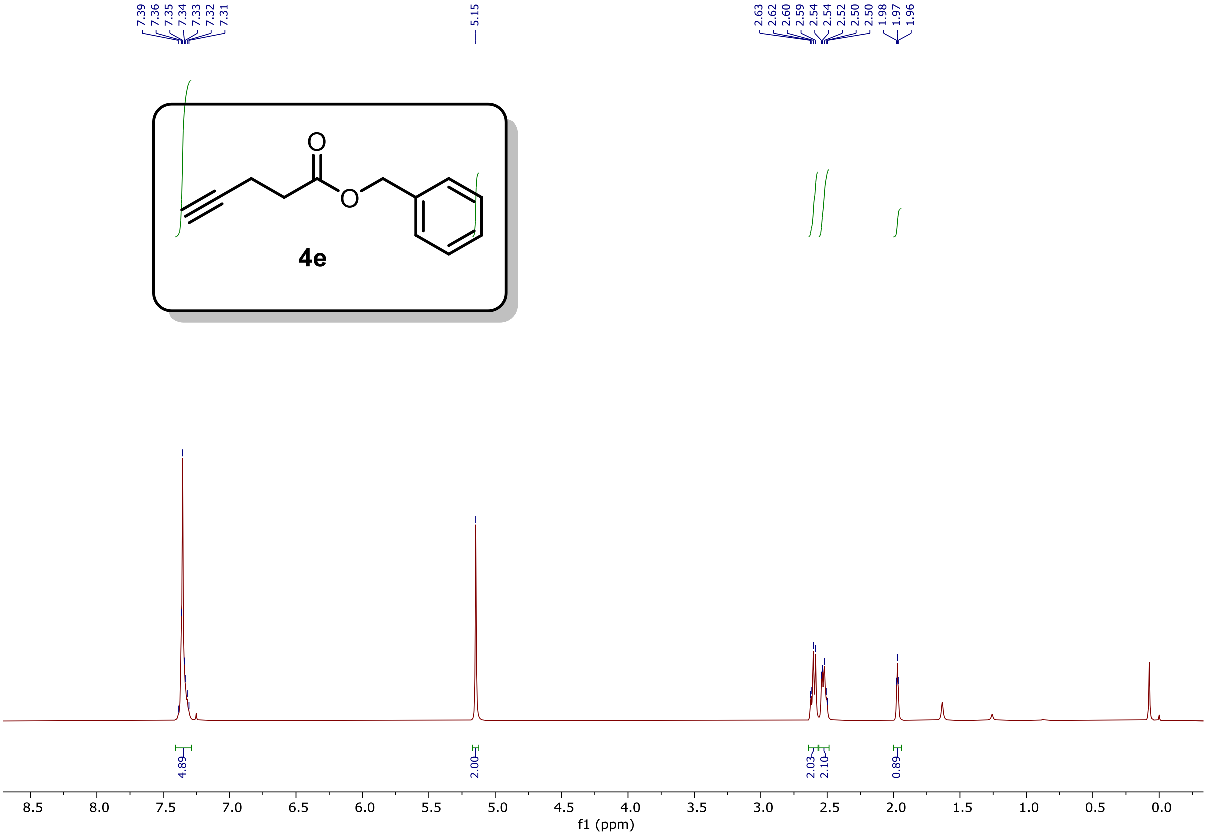


^{13}C{^{1}H} NMR spectrum of compound 4c (126 MHz CDCl$_3$)

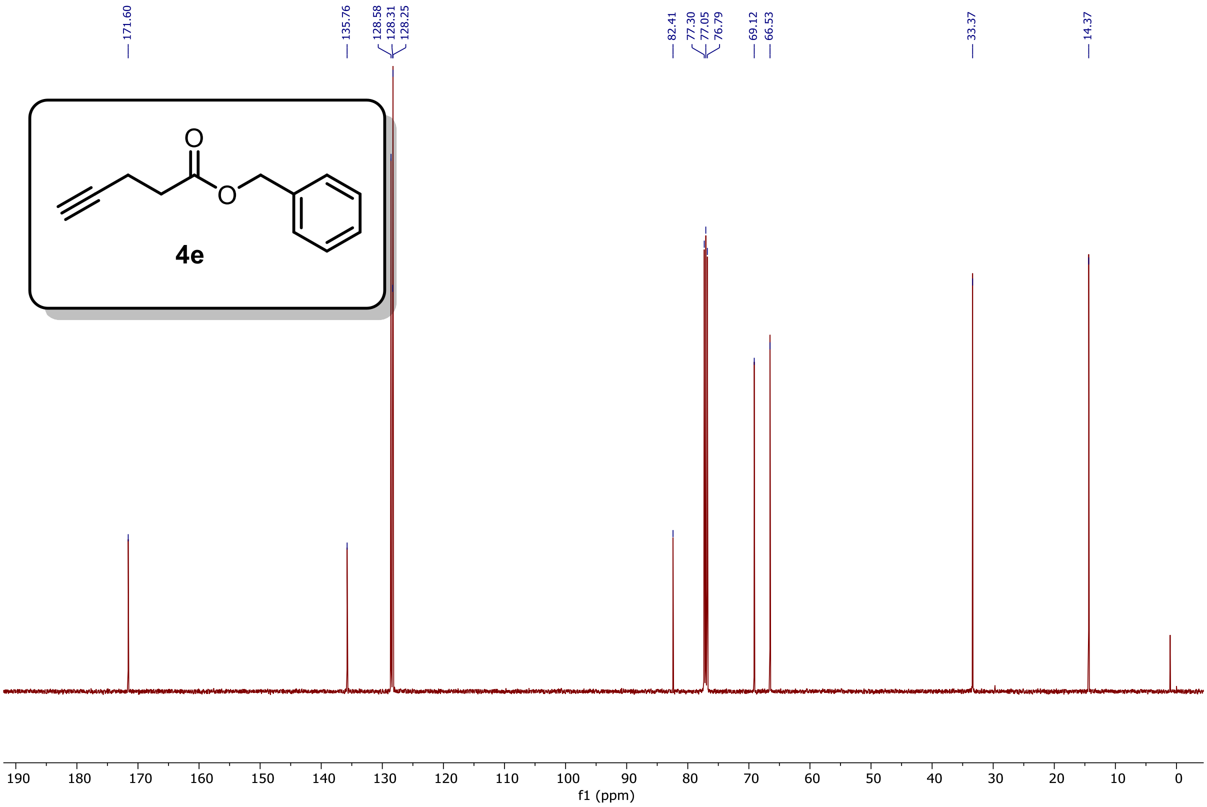
^{1}H NMR spectrum of compound 4d (500 MHz CDCl$_3$)



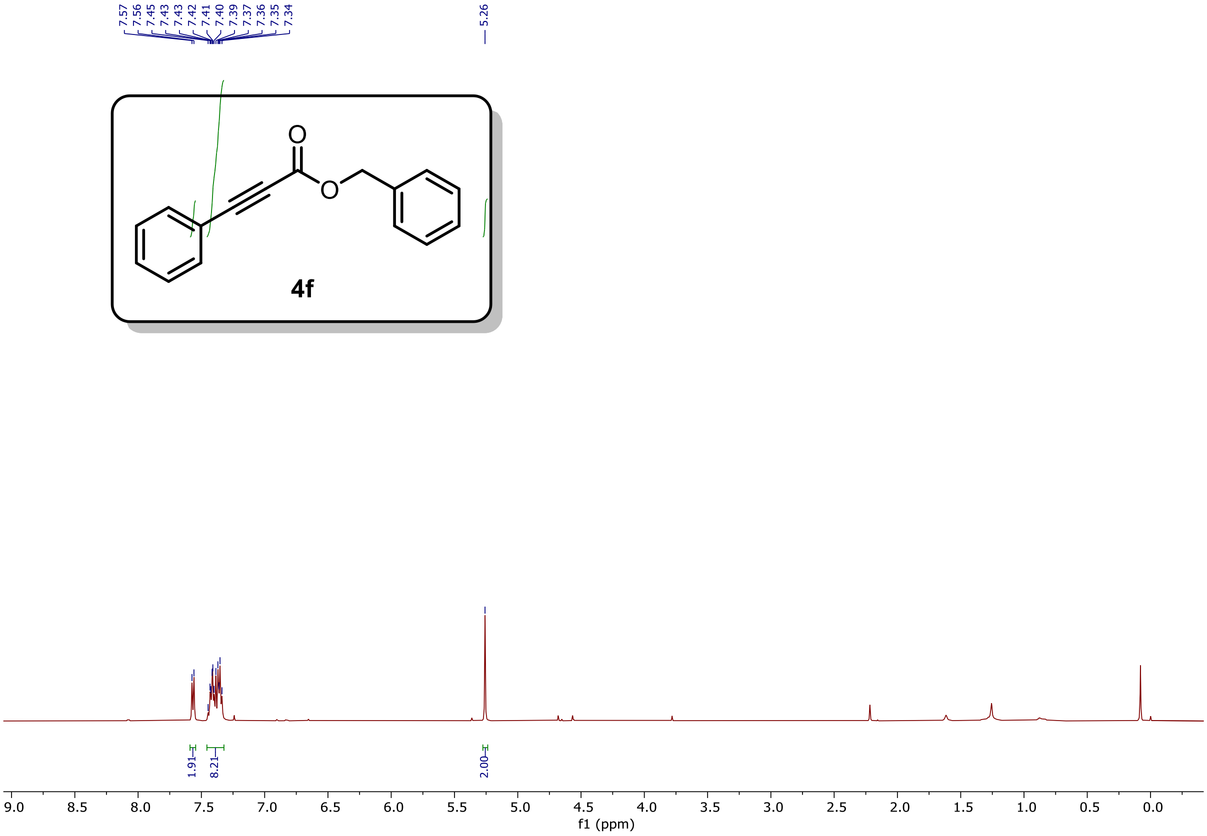
^{13}C{^{1}H} NMR spectrum of compound 4d (126 MHz CDCl$_3$)



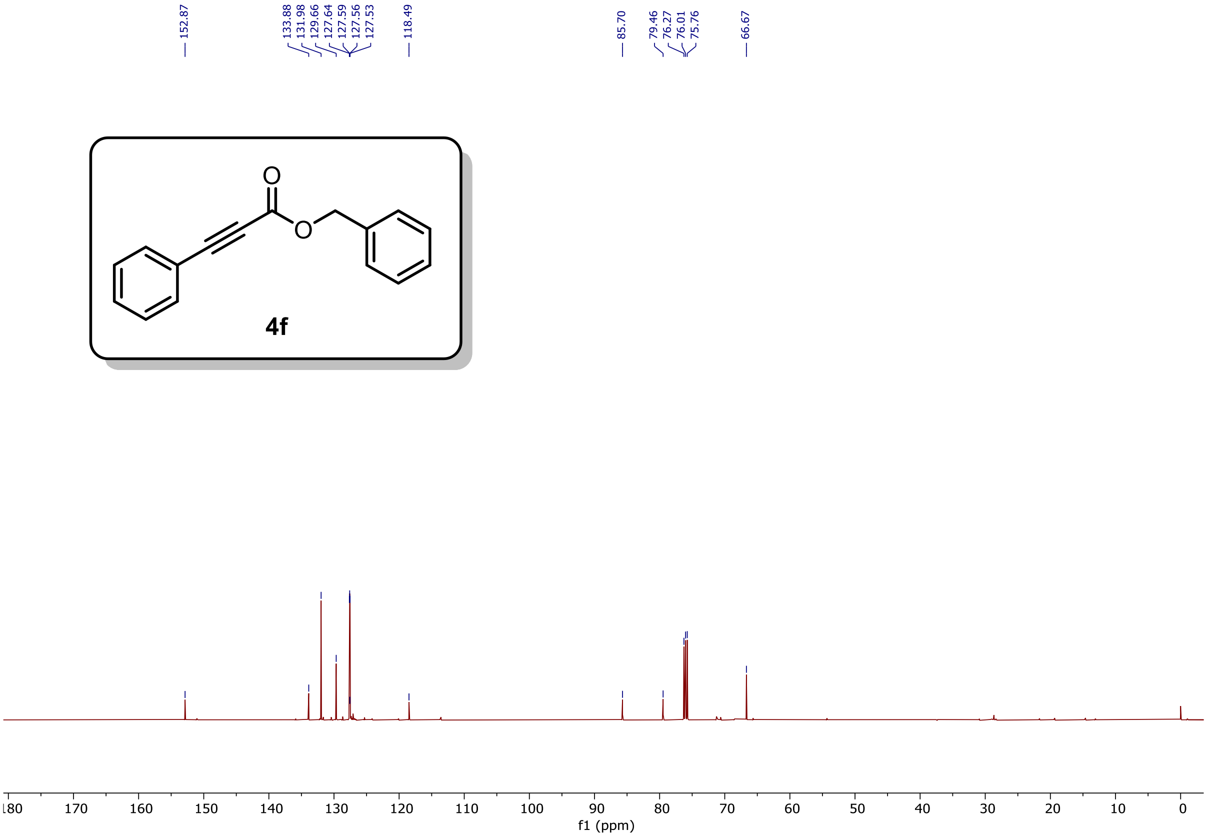
^{1}H NMR spectrum of compound 4e (500 MHz CDCl$_3$)



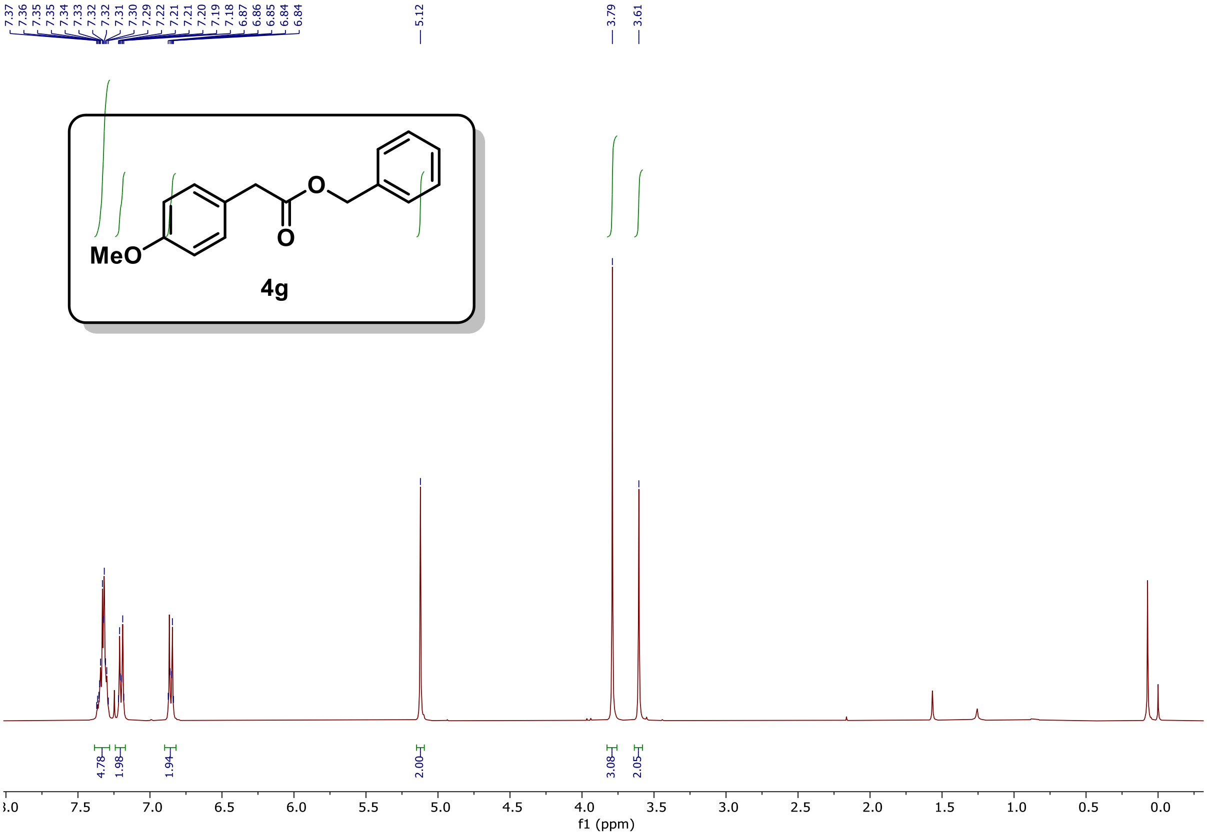
^{13}C{^{1}H} NMR spectrum of compound 4e (126 MHz CDCl$_3$)



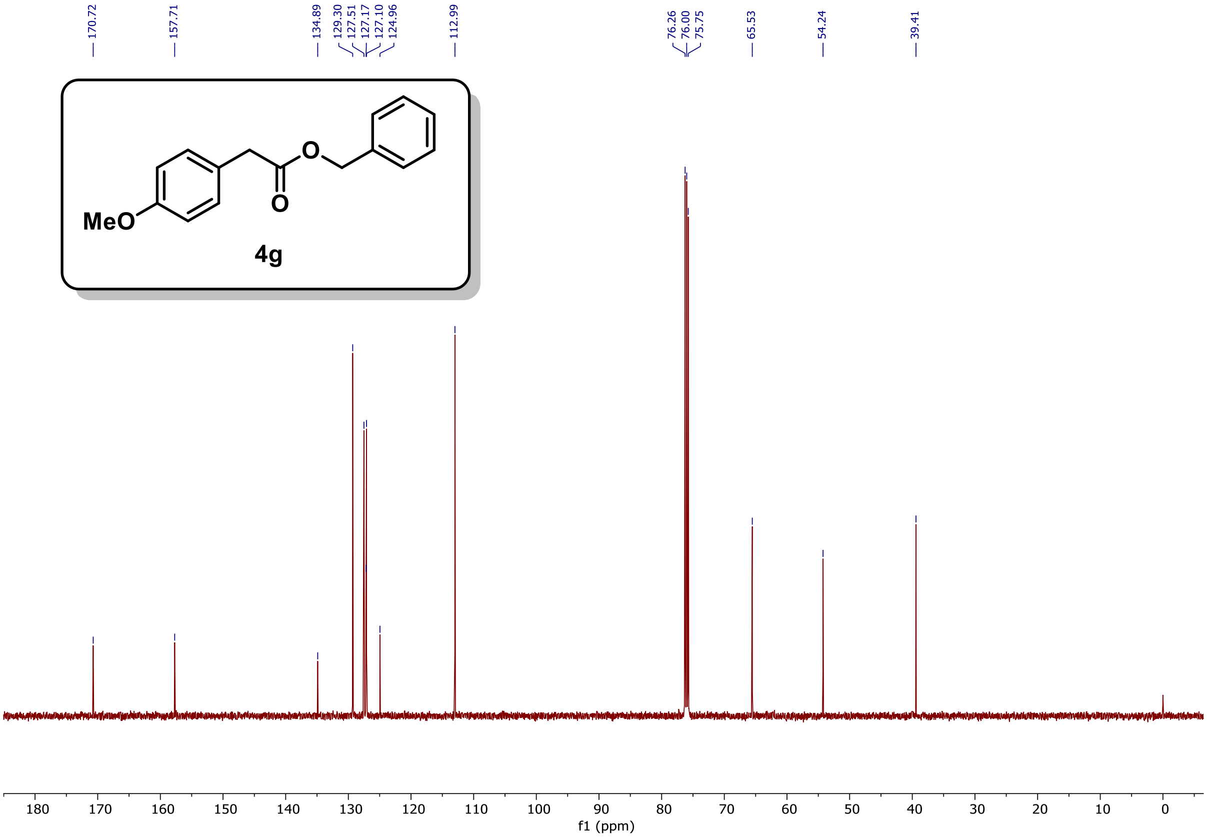
^{1}H NMR spectrum of compound 4f (500 MHz CDCl$_3$)



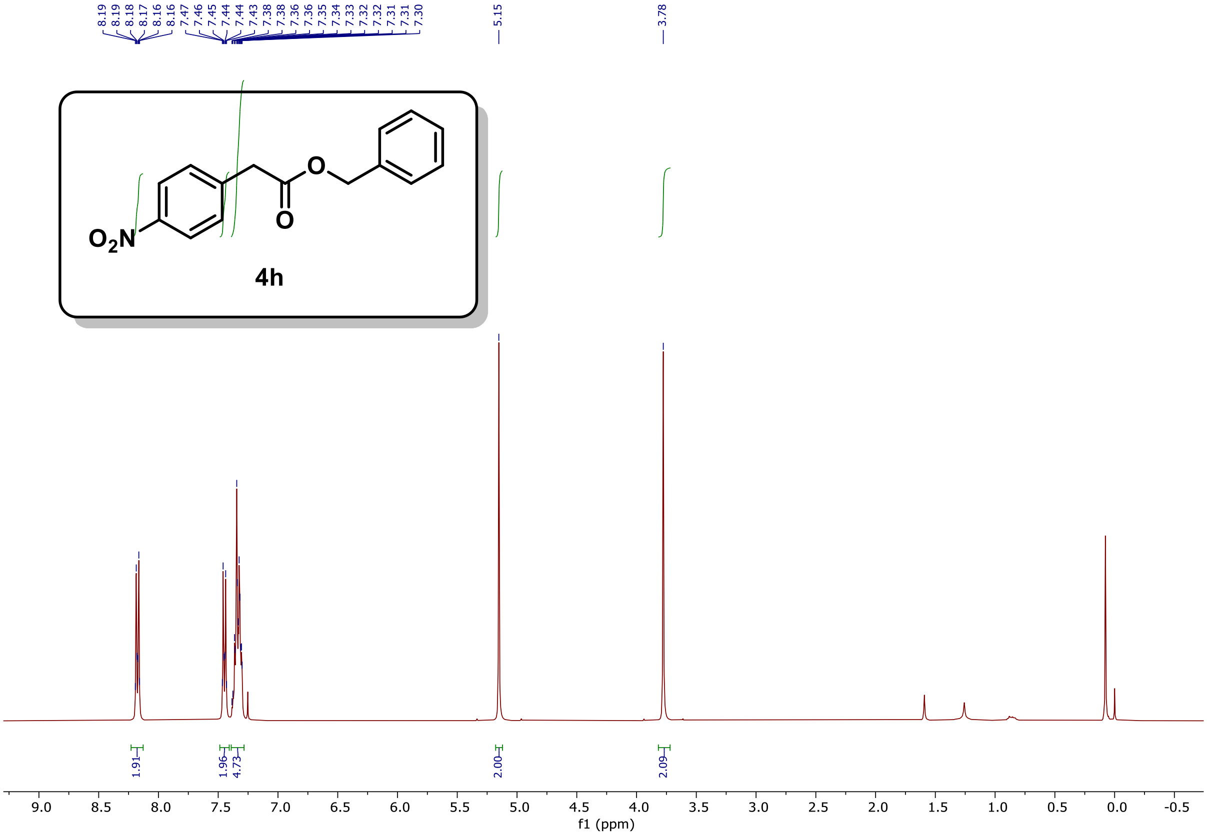
^{13}C{^{1}H} NMR spectrum of compound 4f (126 MHz CDCl$_3$)



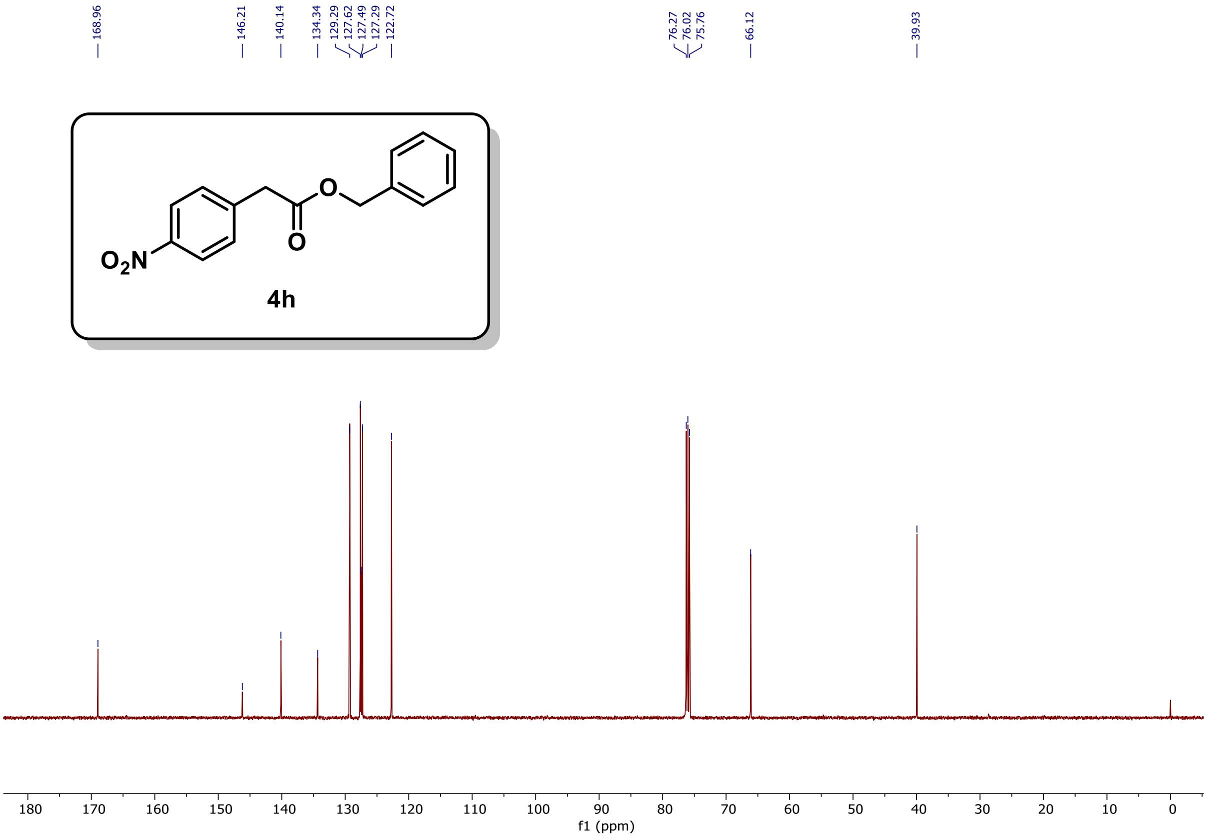
^{1}H NMR spectrum of compound 4g (500 MHz CDCl$_3$)



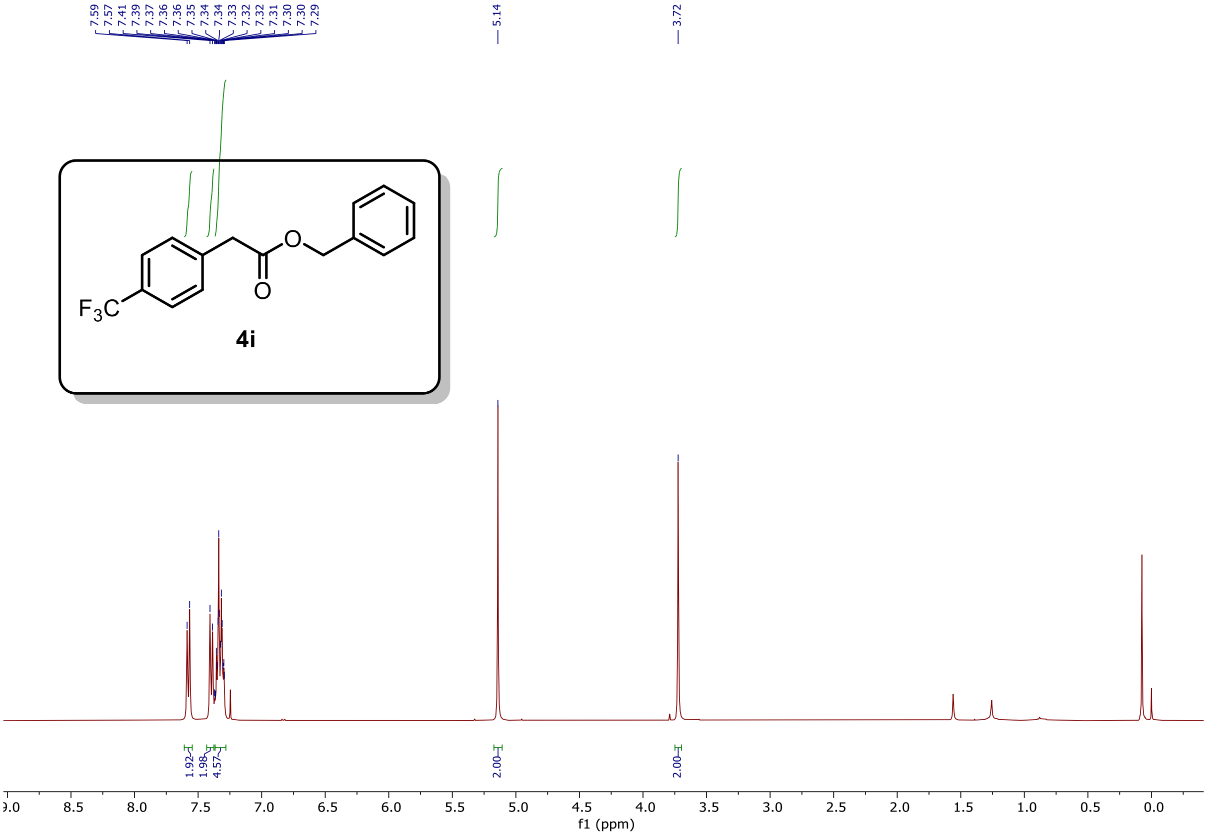
^{13}C{^{1}H} NMR spectrum of compound 4g (126 MHz CDCl$_3$)



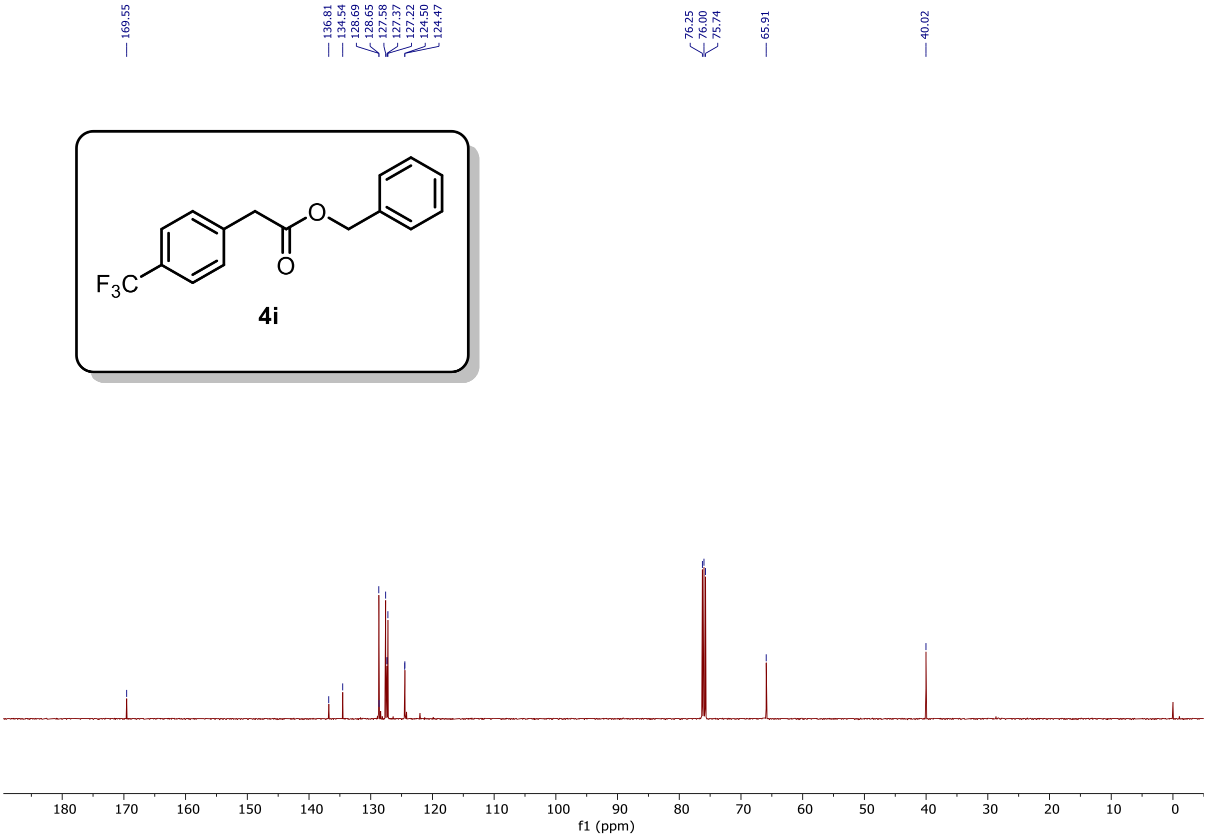
^{1}H NMR spectrum of compound 4h (500 MHz $CDCl_3$)



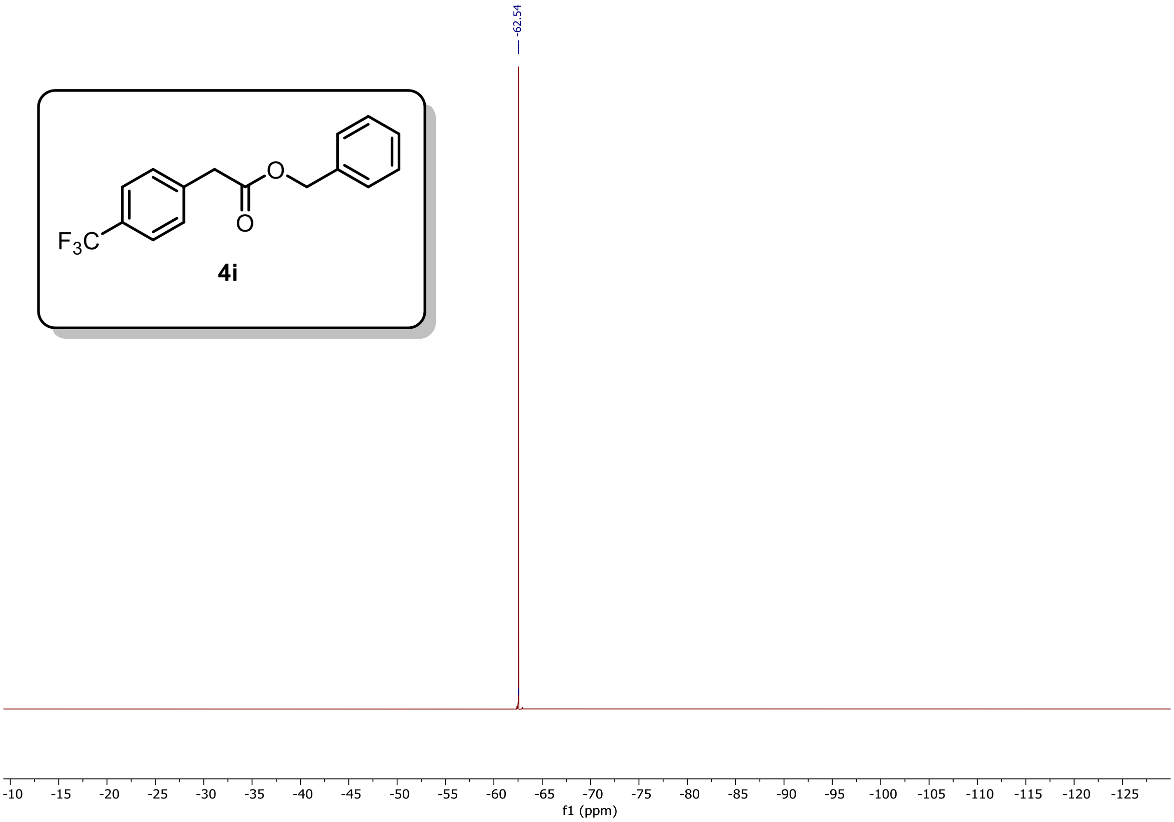
^{13}C{^{1}H} NMR spectrum of compound 4h (126 MHz $CDCl_3$)



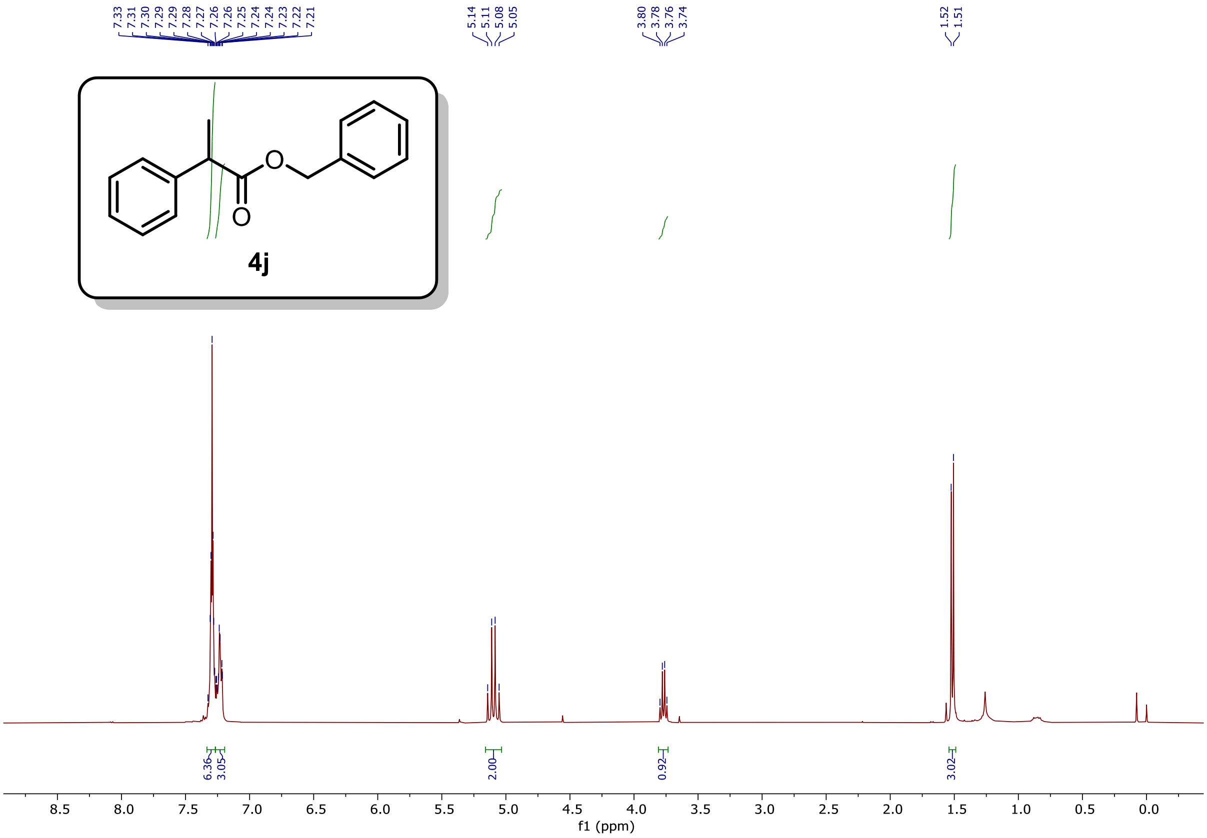
^{1}H NMR spectrum of compound 4i (500 MHz CDCl$_3$)



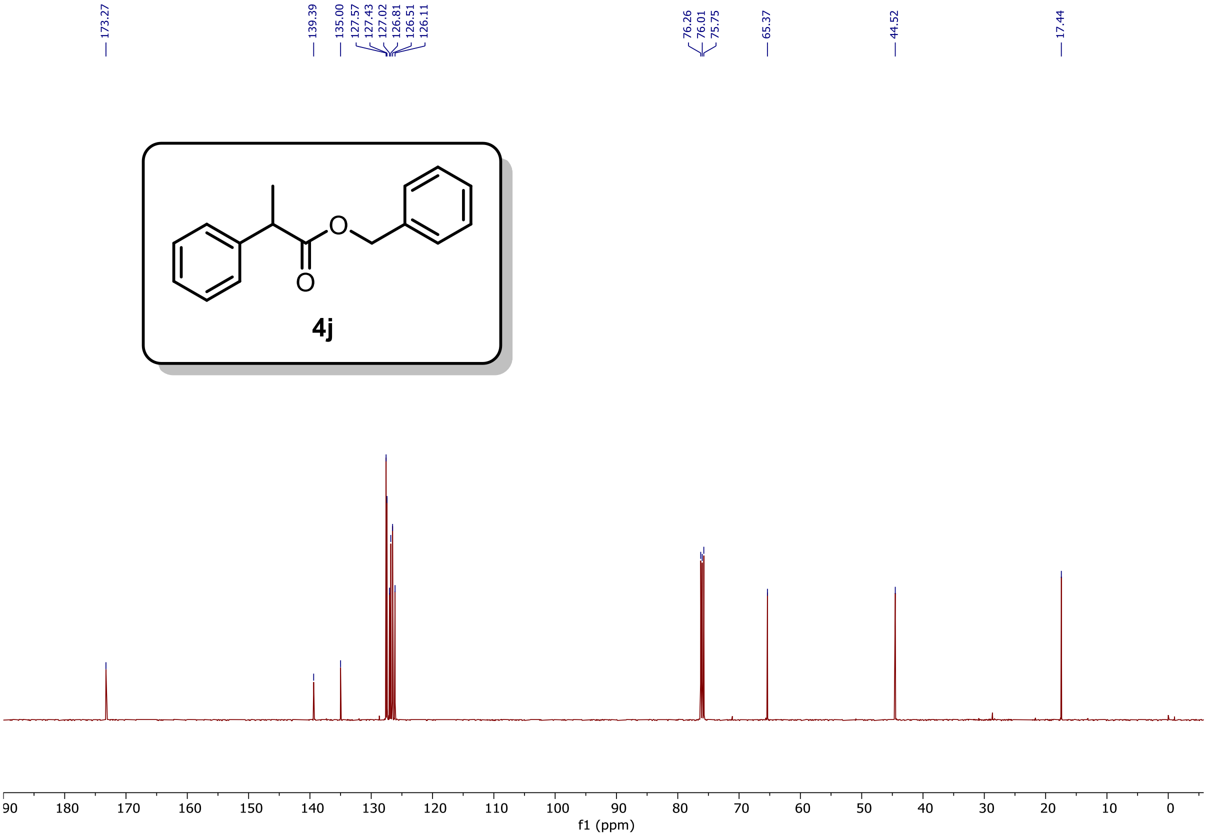
^{13}C{^{1}H} NMR spectrum of compound 4i (126 MHz CDCl$_3$)



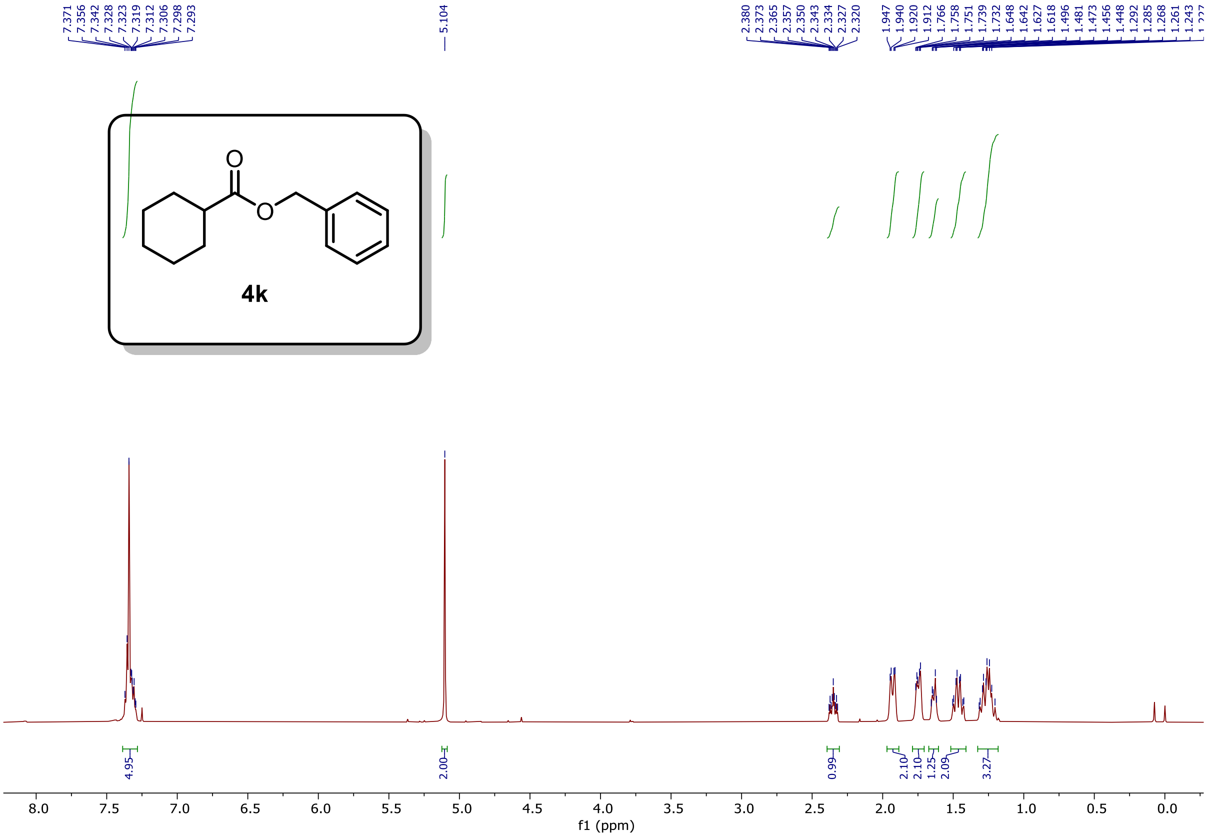
^{19}F NMR spectrum of compound 4i (471 MHz, CDCl$_3$)



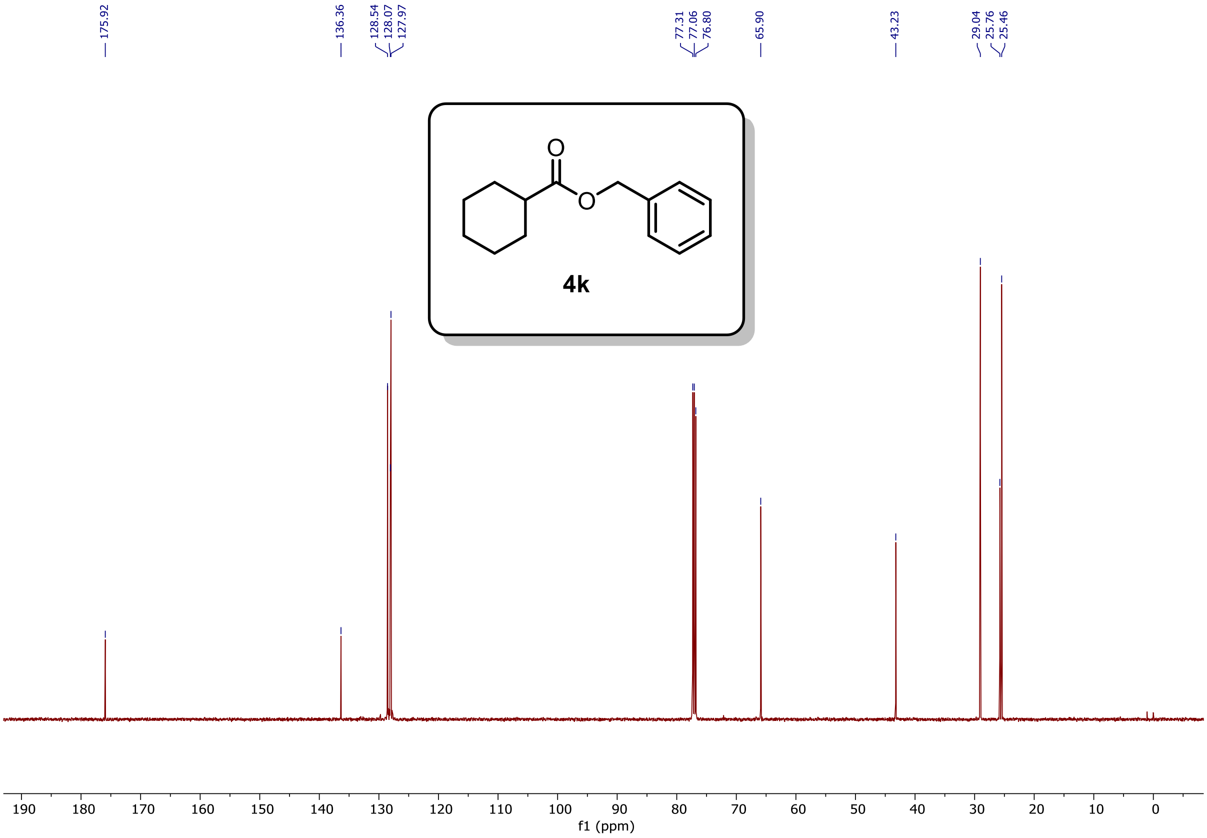
^{1}H NMR spectrum of compound 4j (500 MHz CDCl$_3$)



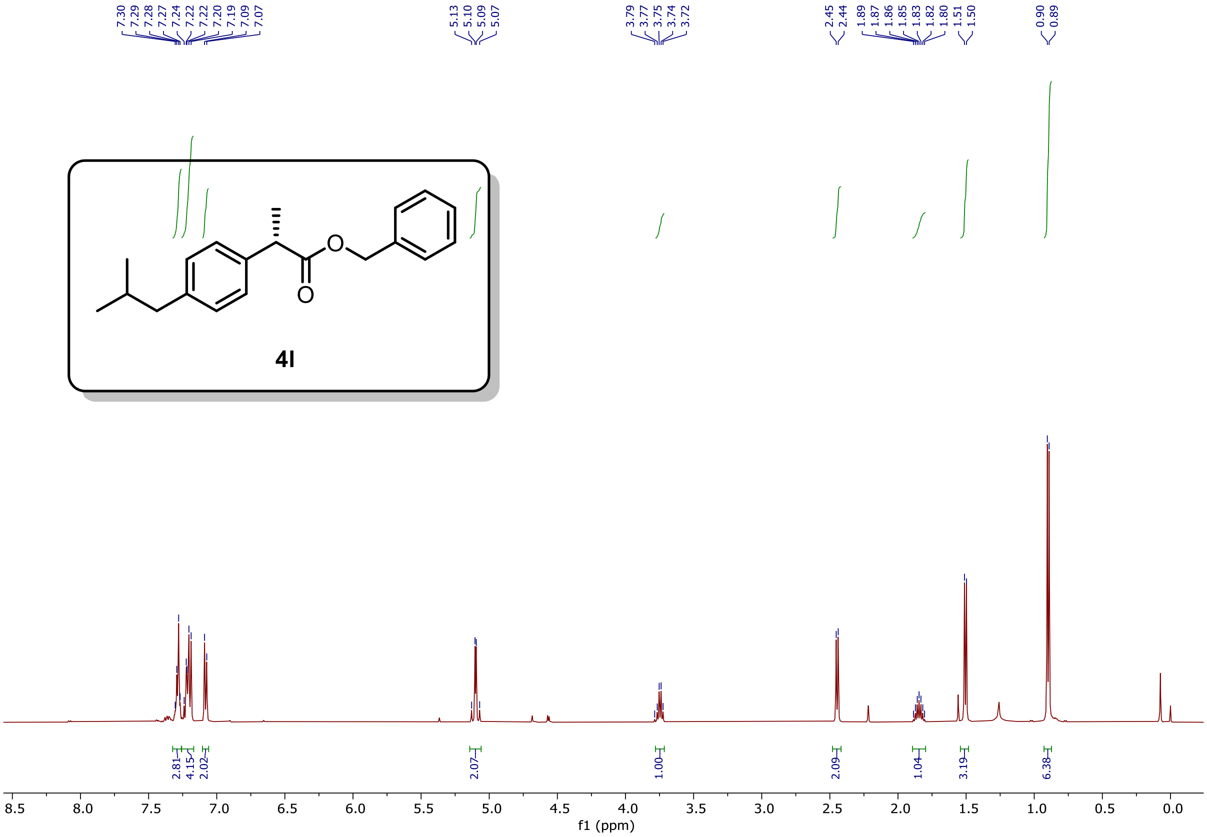
$^{13}C\{^1H\}$ NMR spectrum of compound 4j (126 MHz $CDCl_3$)



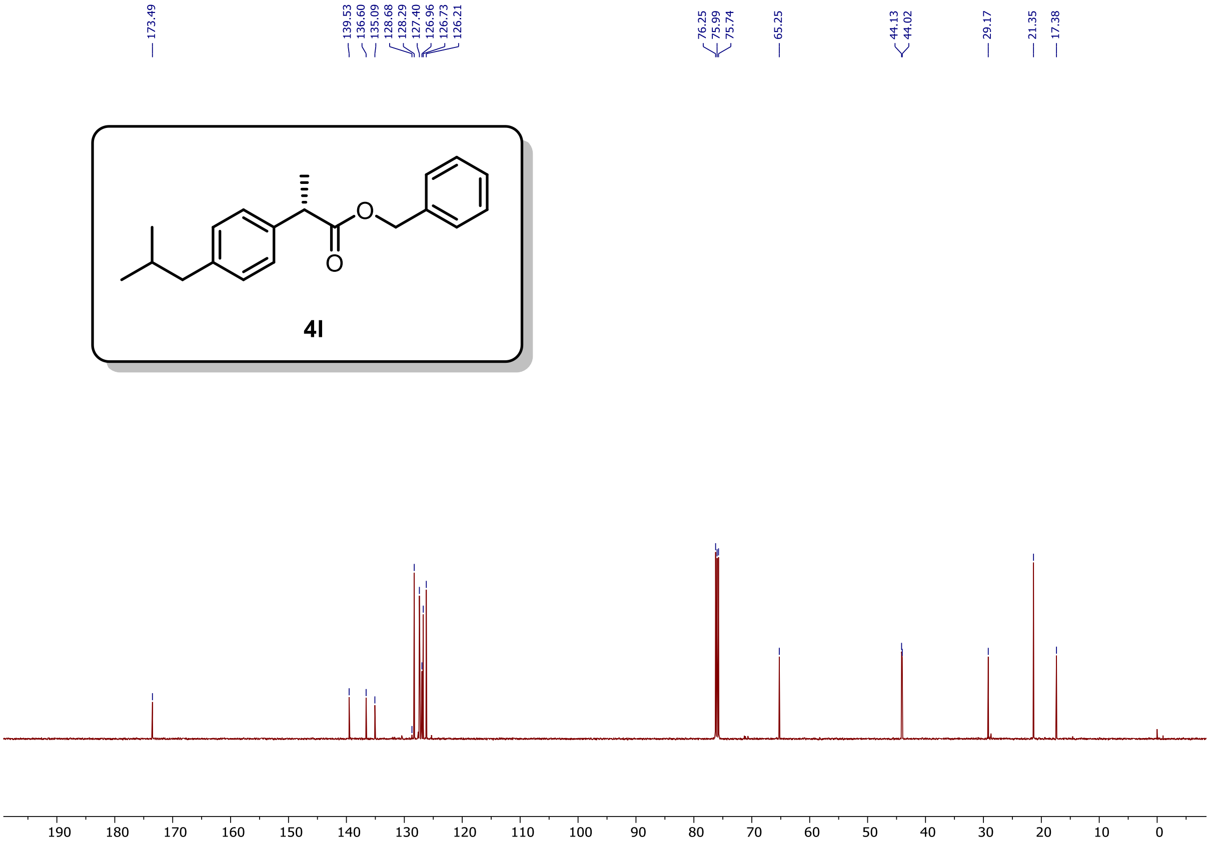
^1H NMR spectrum of compound 4k (500 MHz $CDCl_3$)



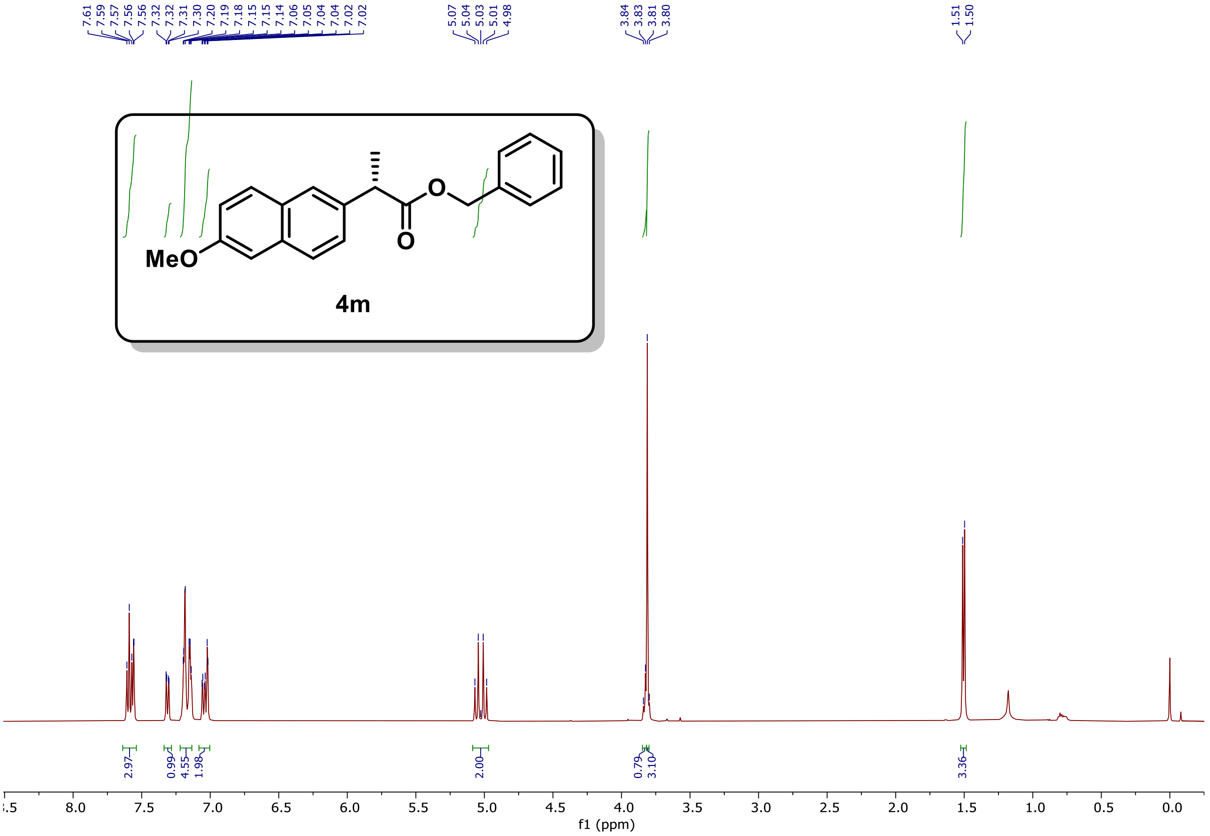
^{13}C{^{1}H} NMR spectrum of compound 4k (126 MHz CDCl$_3$)



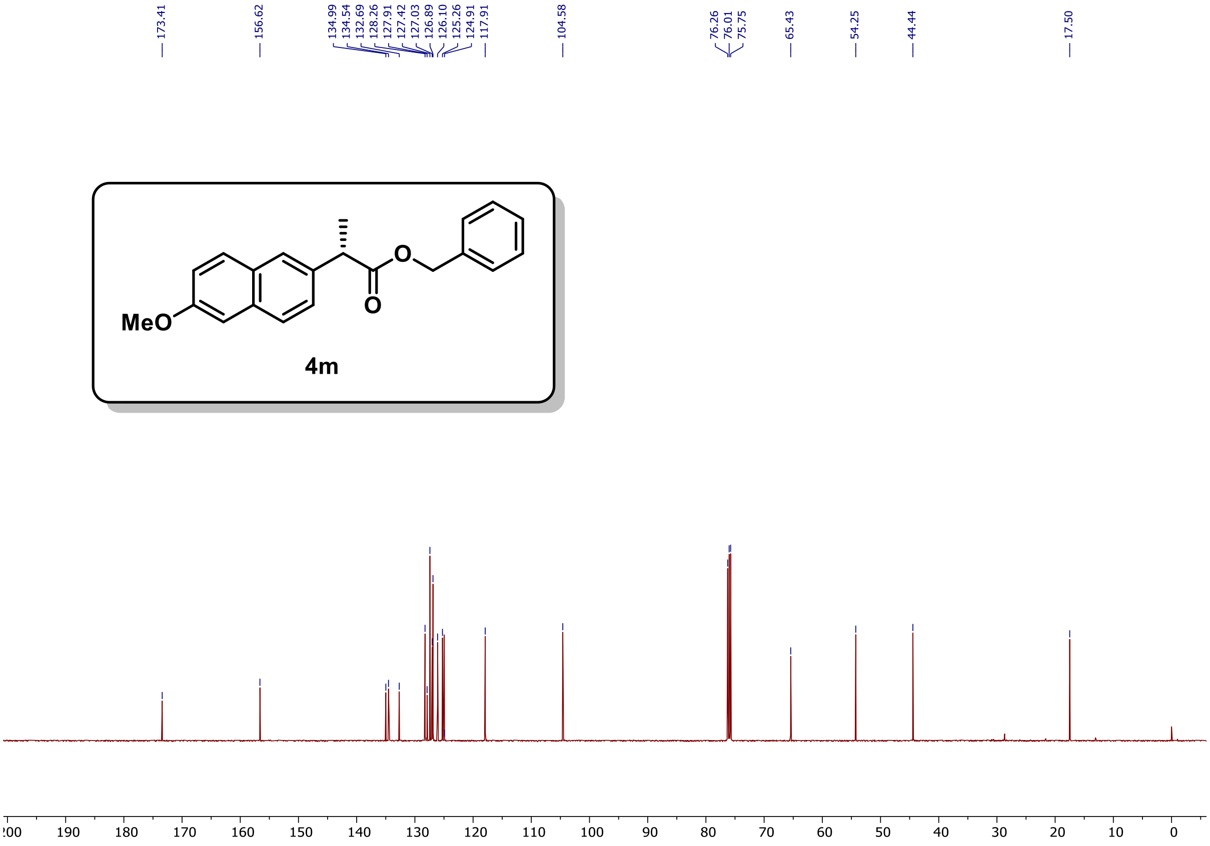
^{1}H NMR spectrum of compound 4l (500 MHz CDCl$_3$)



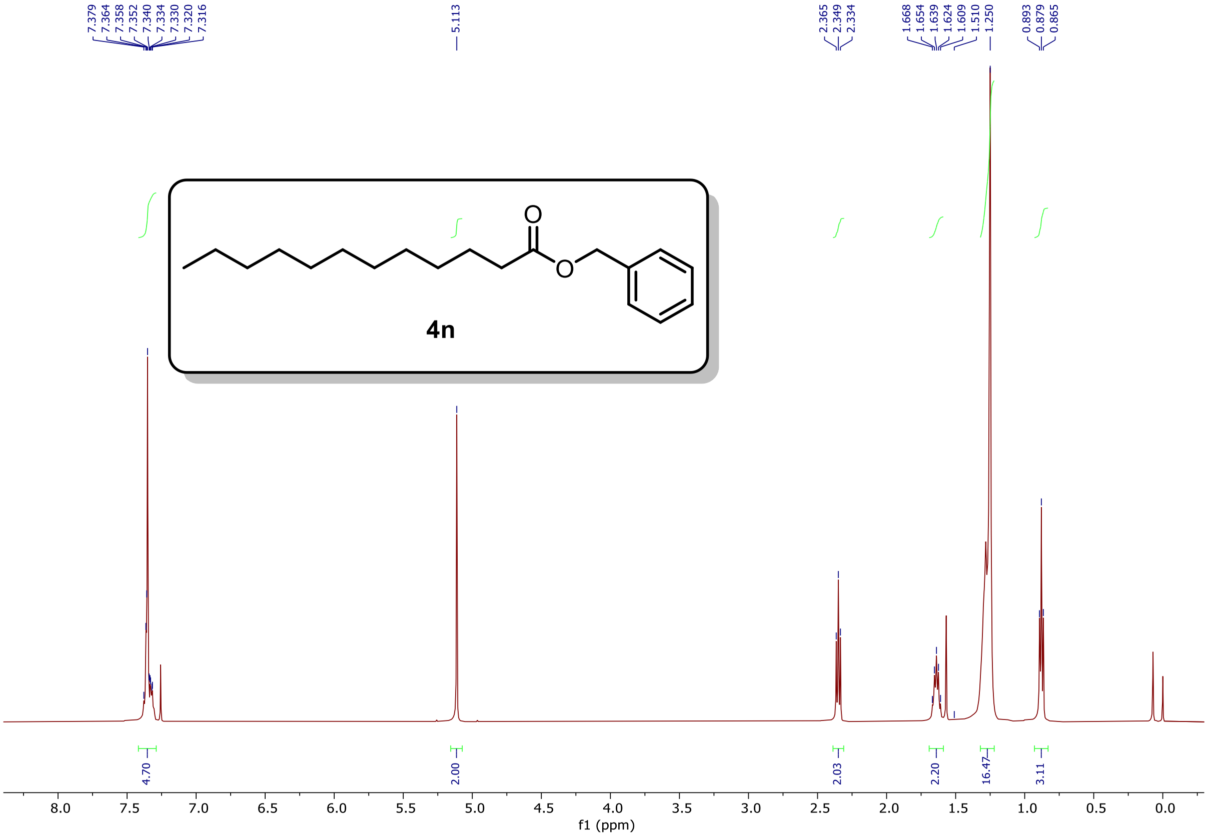
^{13}C{^{1}H} NMR spectrum of compound 4l (126 MHz CDCl$_3$)



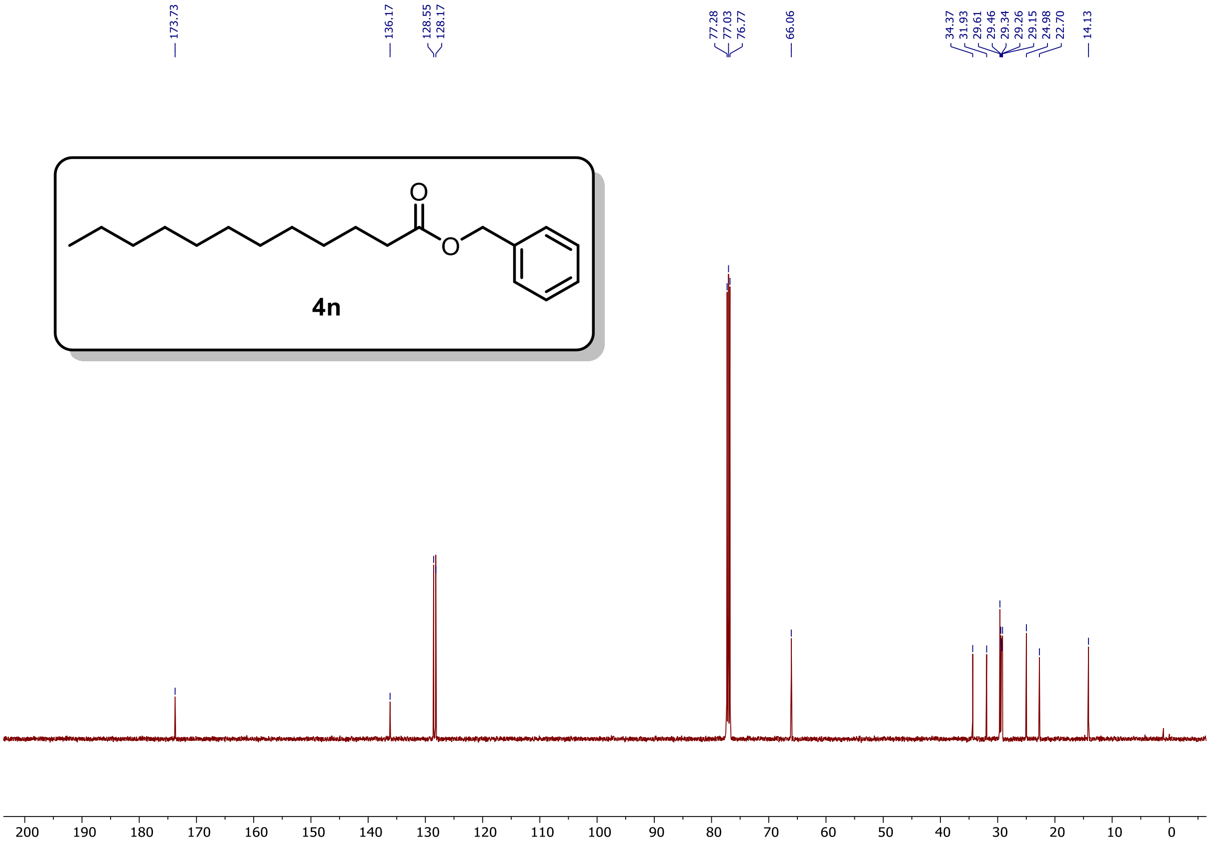
^{1}H NMR spectrum of compound 4m (500 MHz CDCl$_3$)



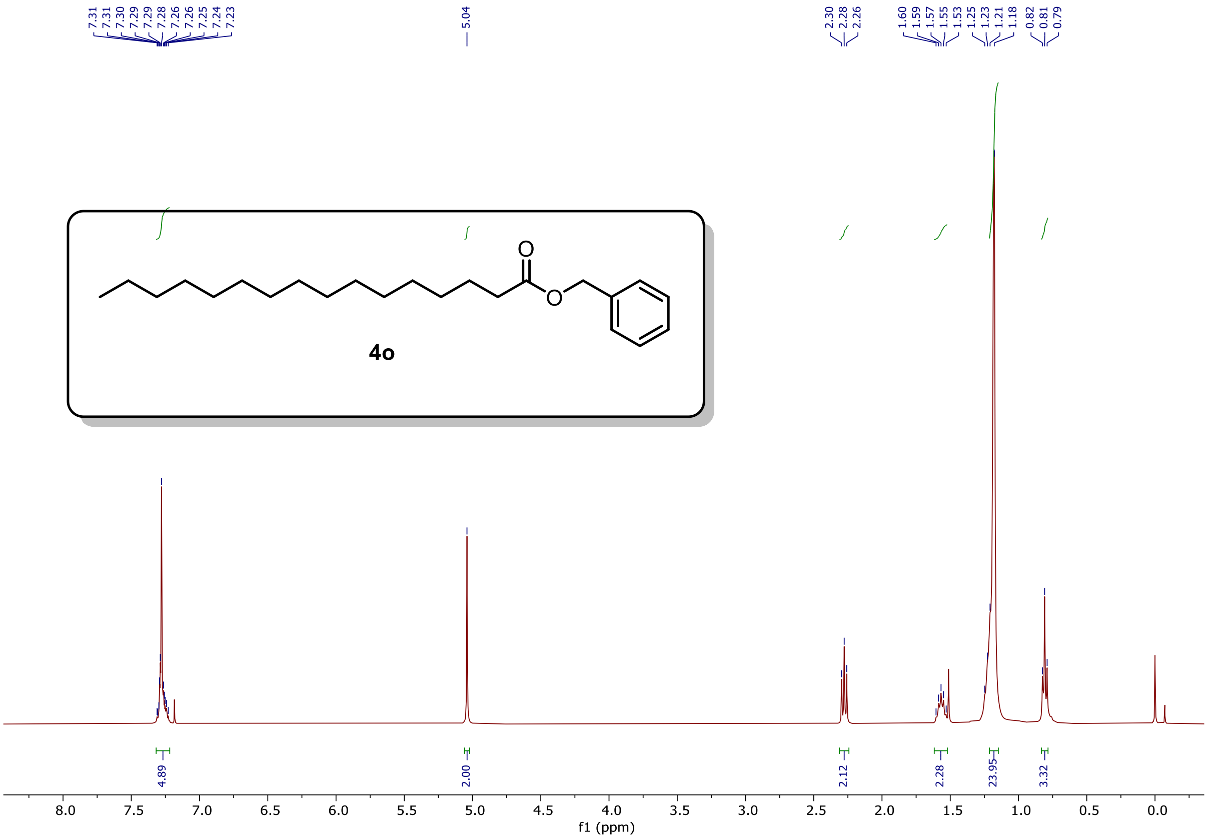
$^{13}C\{^1H\}$ NMR spectrum of compound 4m (126 MHz $CDCl_3$)



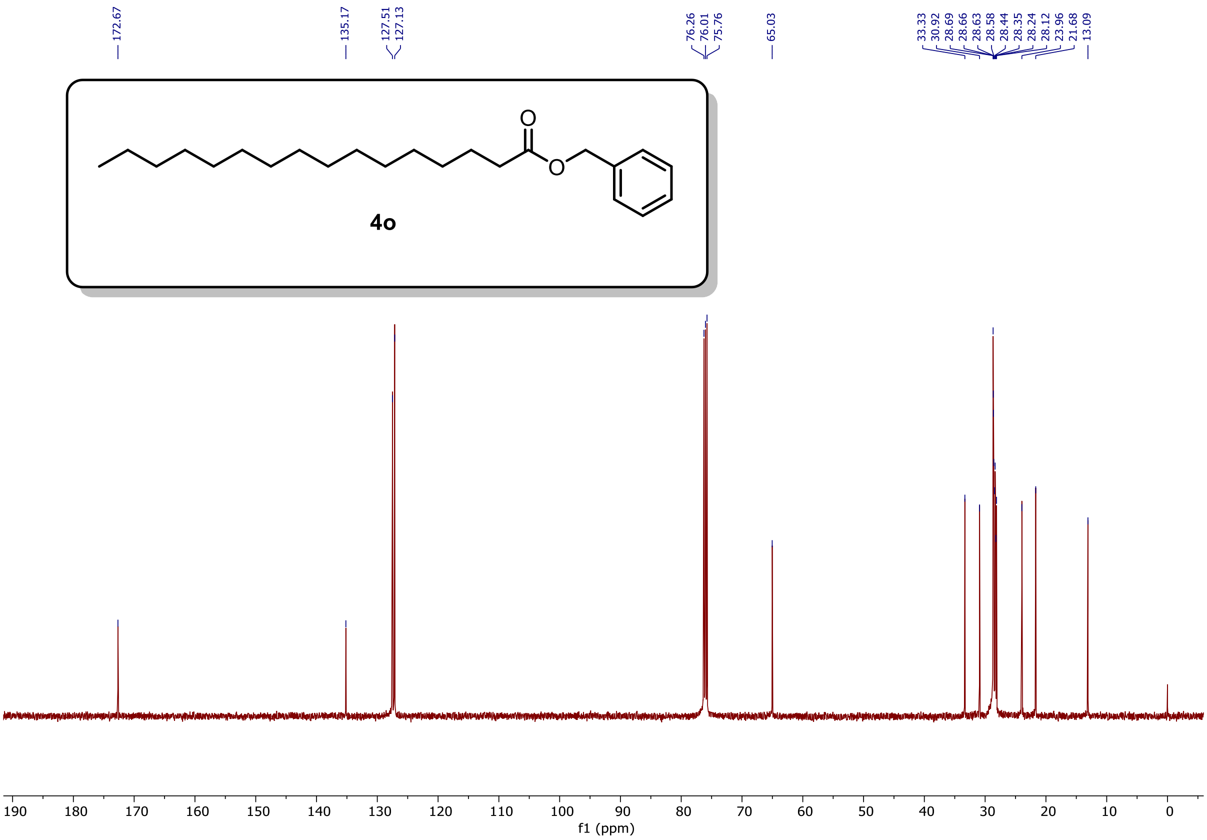
^1H NMR spectrum of compound 4n (500 MHz $CDCl_3$)



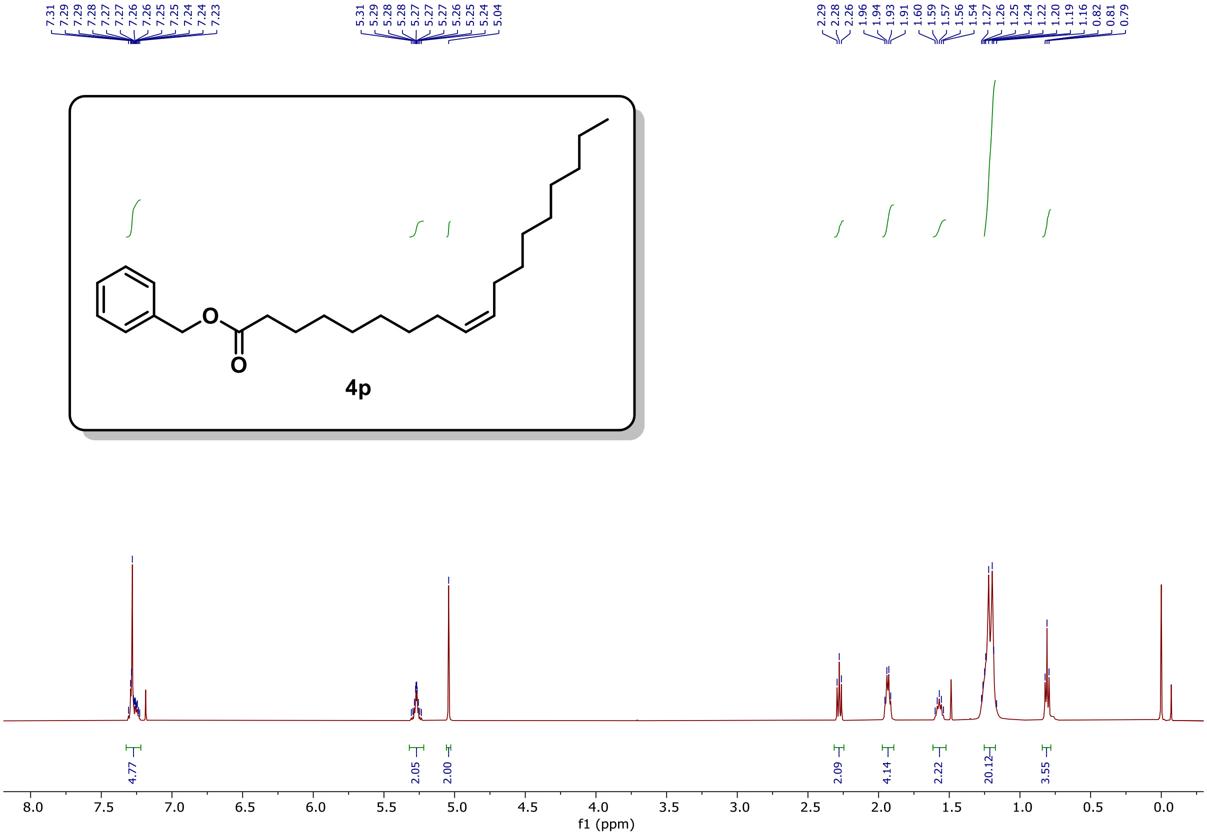
$^{13}C\{^1H\}$ NMR spectrum of compound 4n (126 MHz $CDCl_3$)



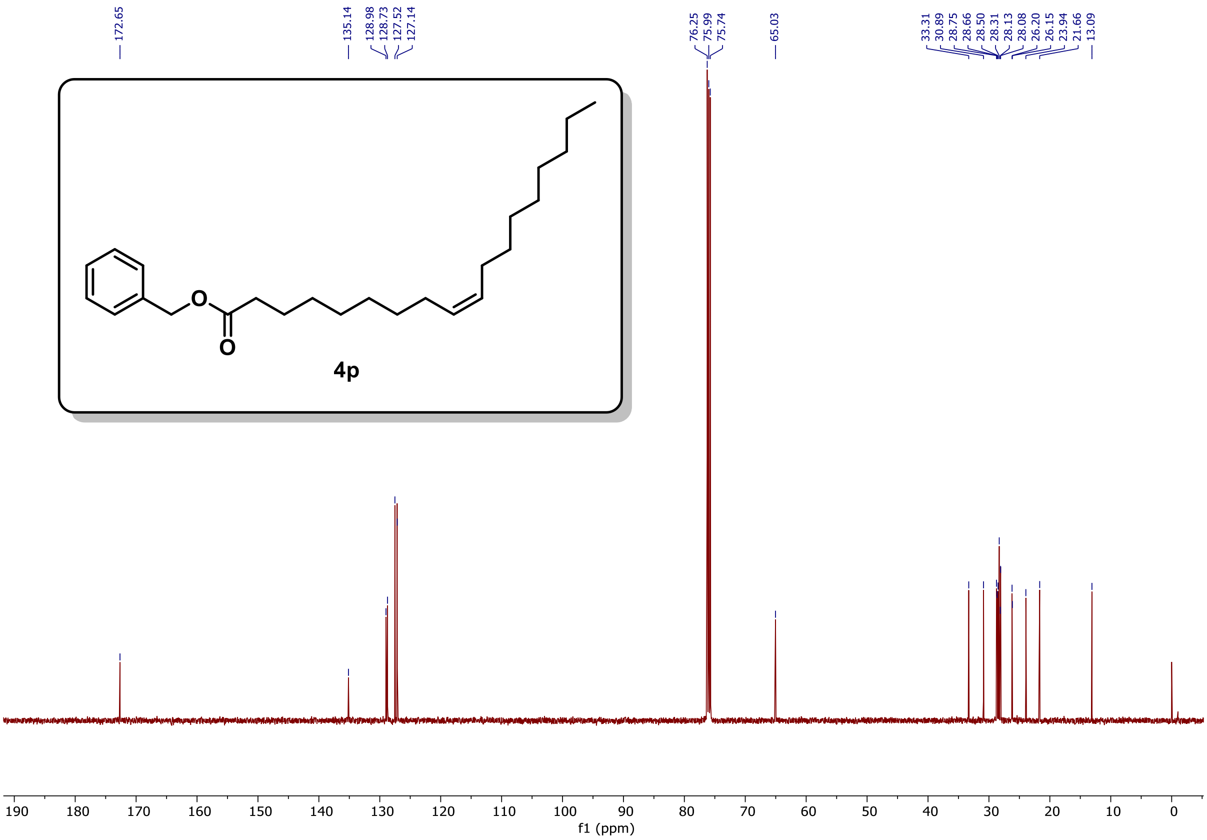
^{1}H NMR spectrum of compound 4o (500 MHz $CDCl_3$)



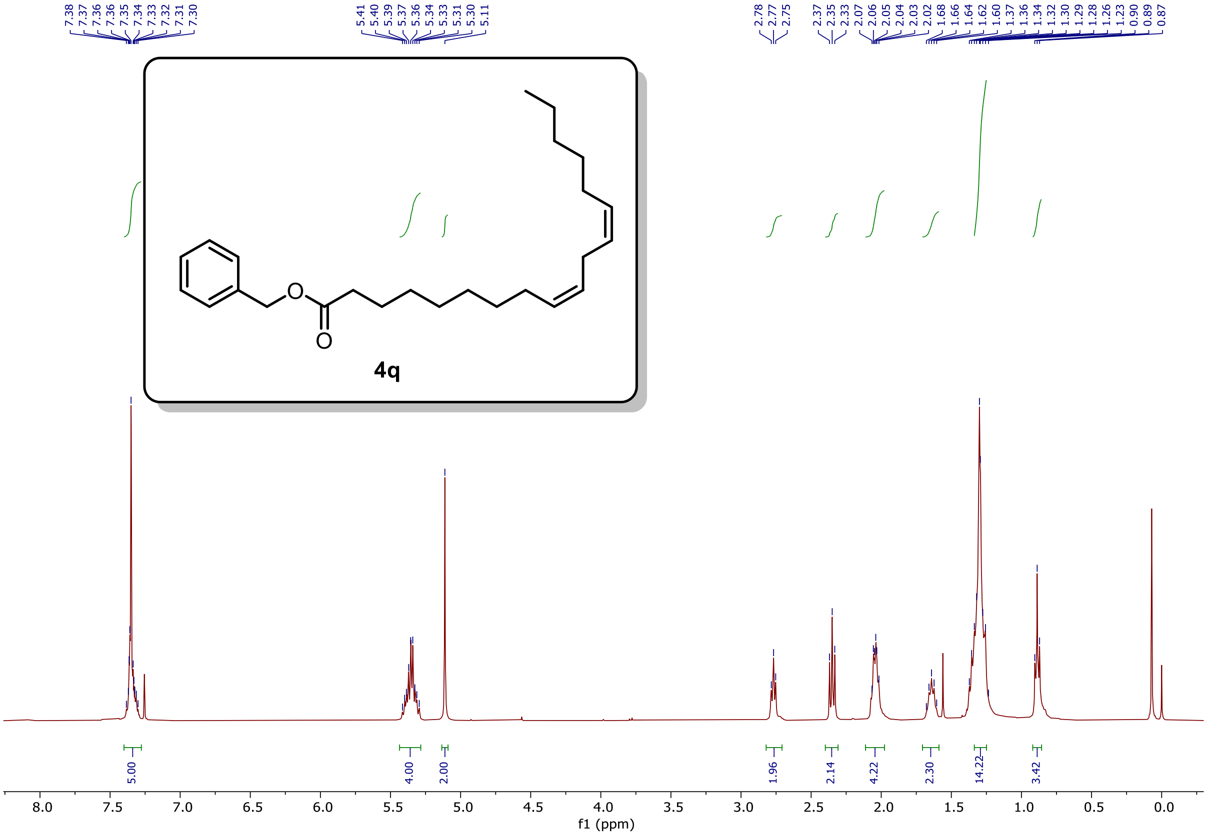
^{13}C{^{1}H} NMR spectrum of compound 4o (126 MHz $CDCl_3$)



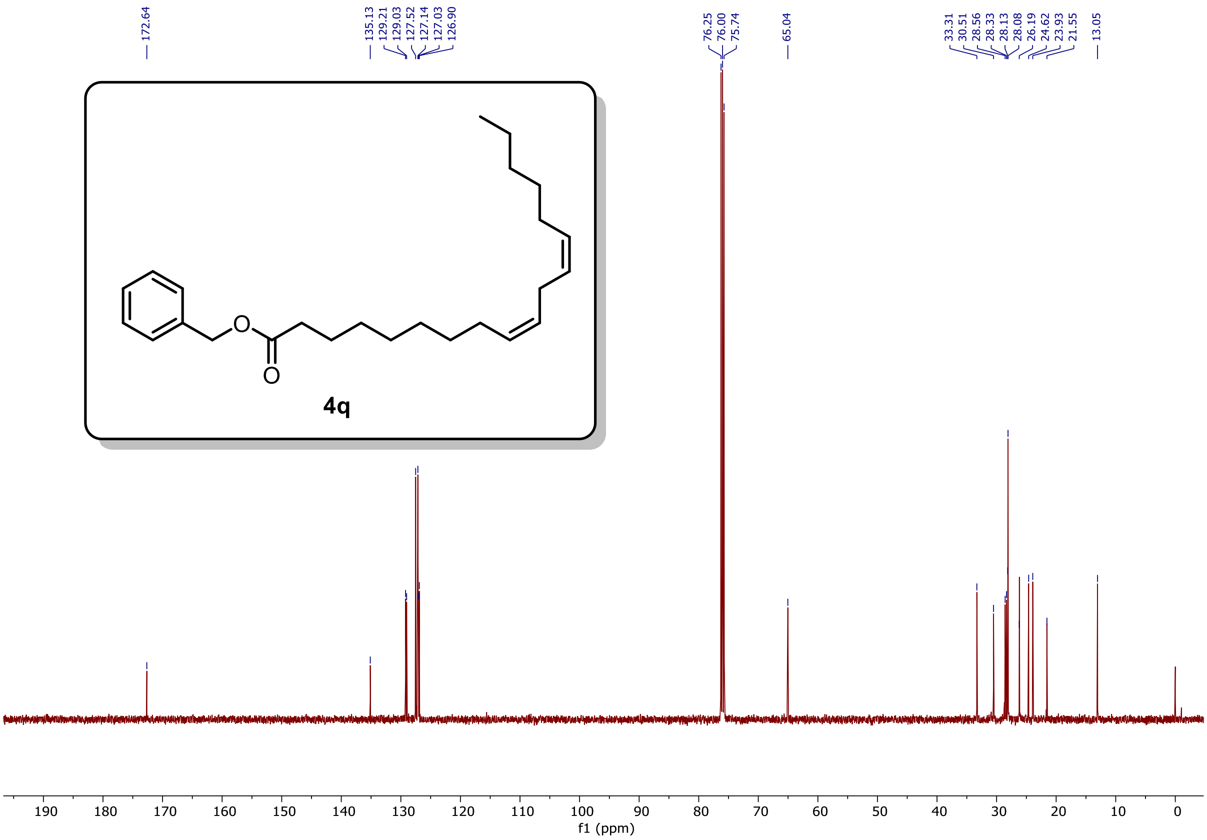
^{1}H NMR spectrum of compound 4p (500 MHz CDCl$_3$)



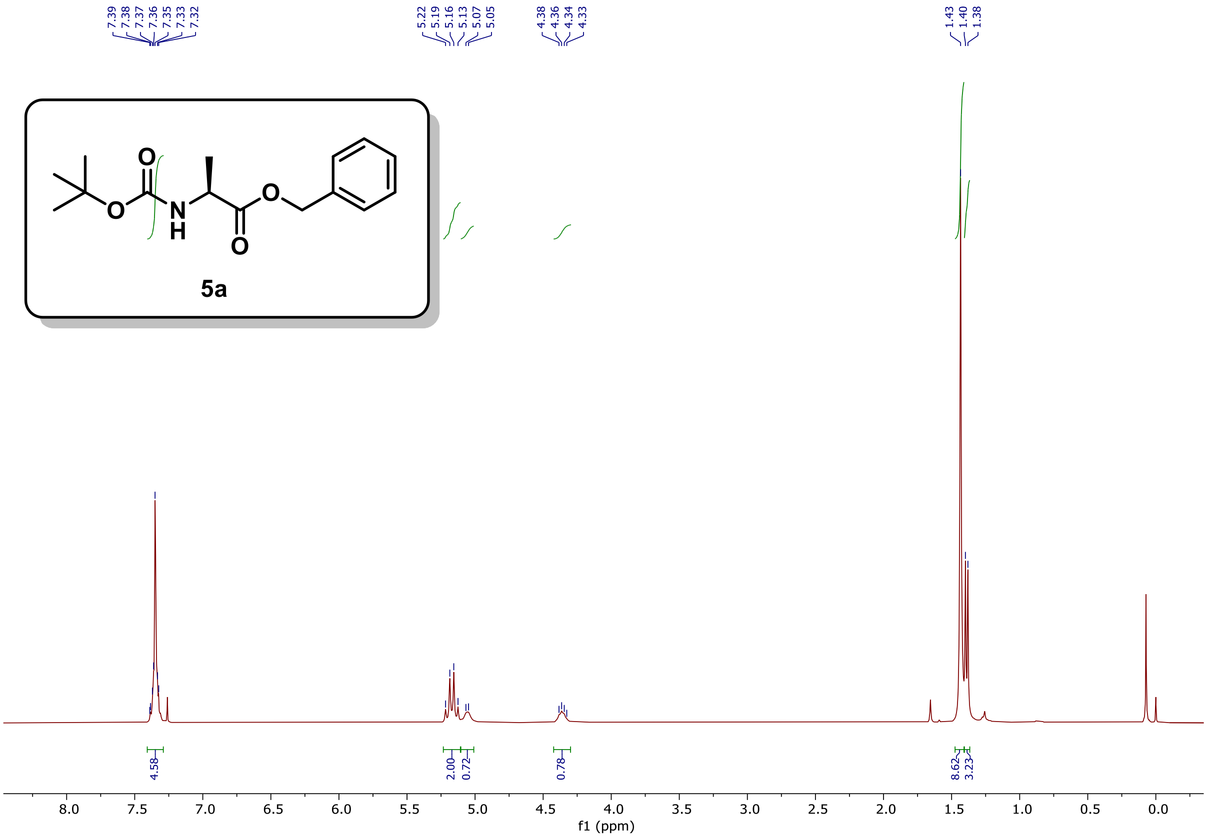
^{13}C{^{1}H} NMR spectrum of compound 4p (126 MHz CDCl$_3$)



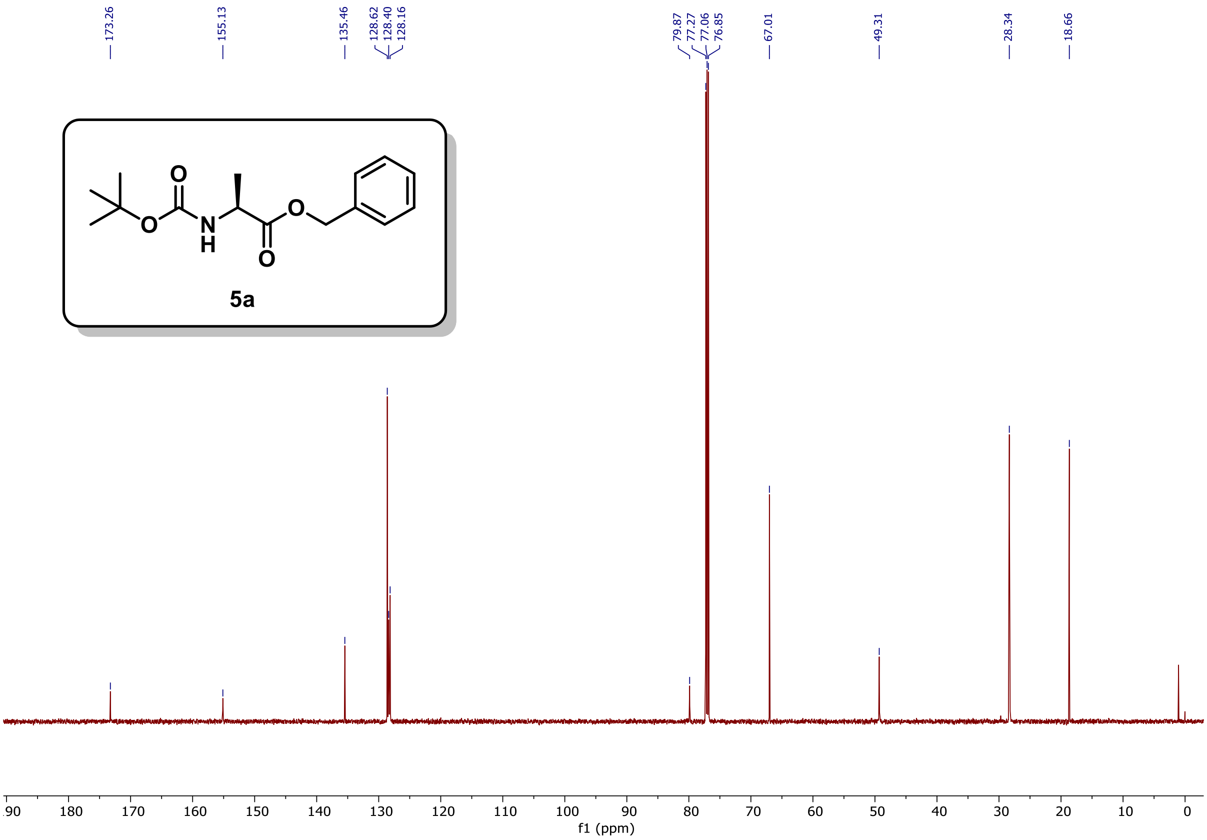
^{1}H NMR spectrum of compound 4q (500 MHz CDCl$_3$)



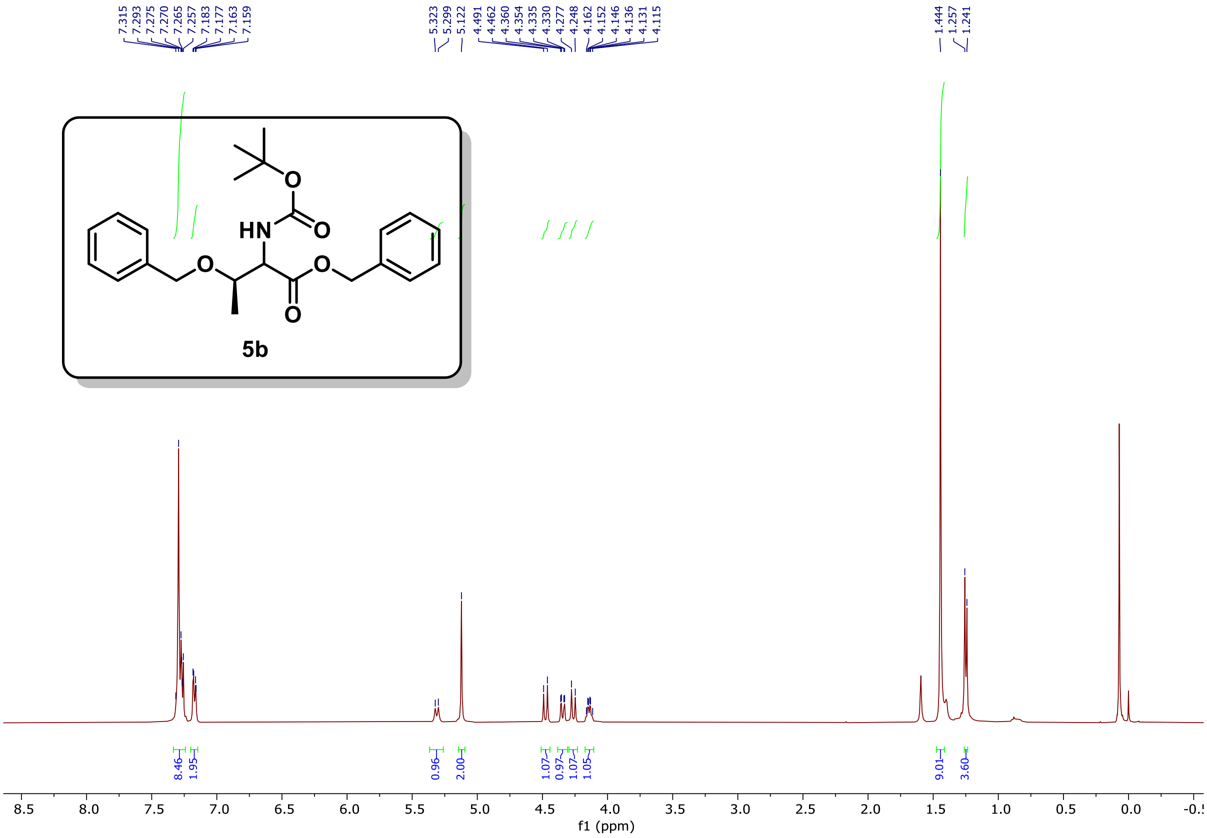
^{13}C{^{1}H} NMR spectrum of compound 4q (126 MHz CDCl$_3$)



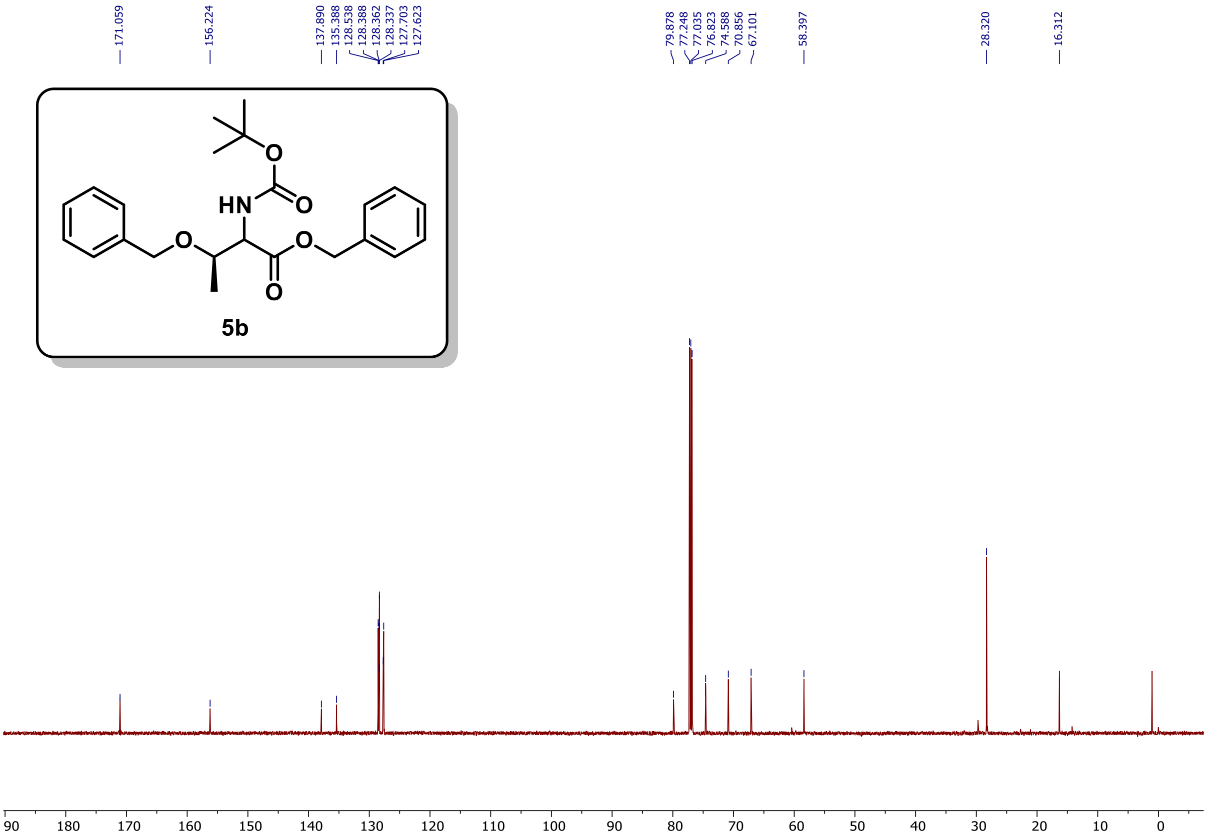
^{1}H NMR spectrum of compound 5a (500 MHz CDCl$_3$)



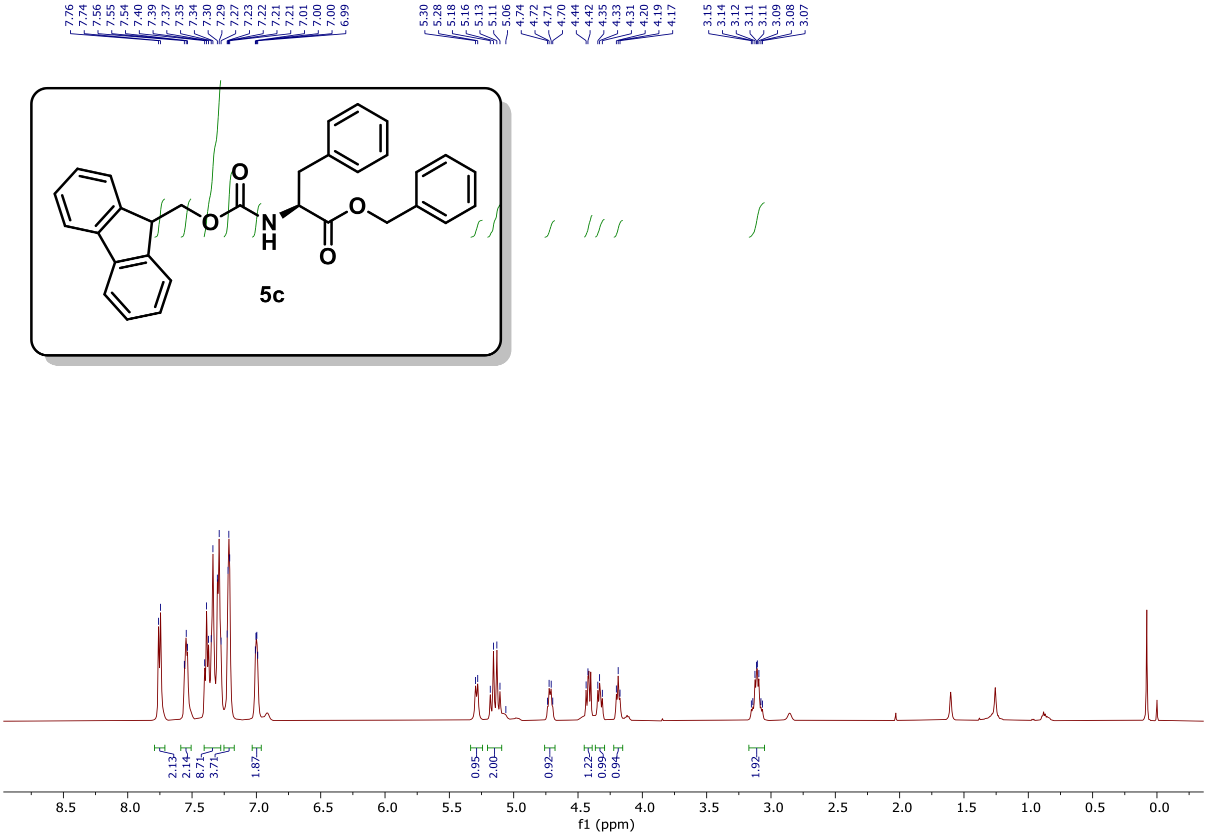
^{13}C{^{1}H} NMR spectrum of compound 5a (126 MHz CDCl$_3$)



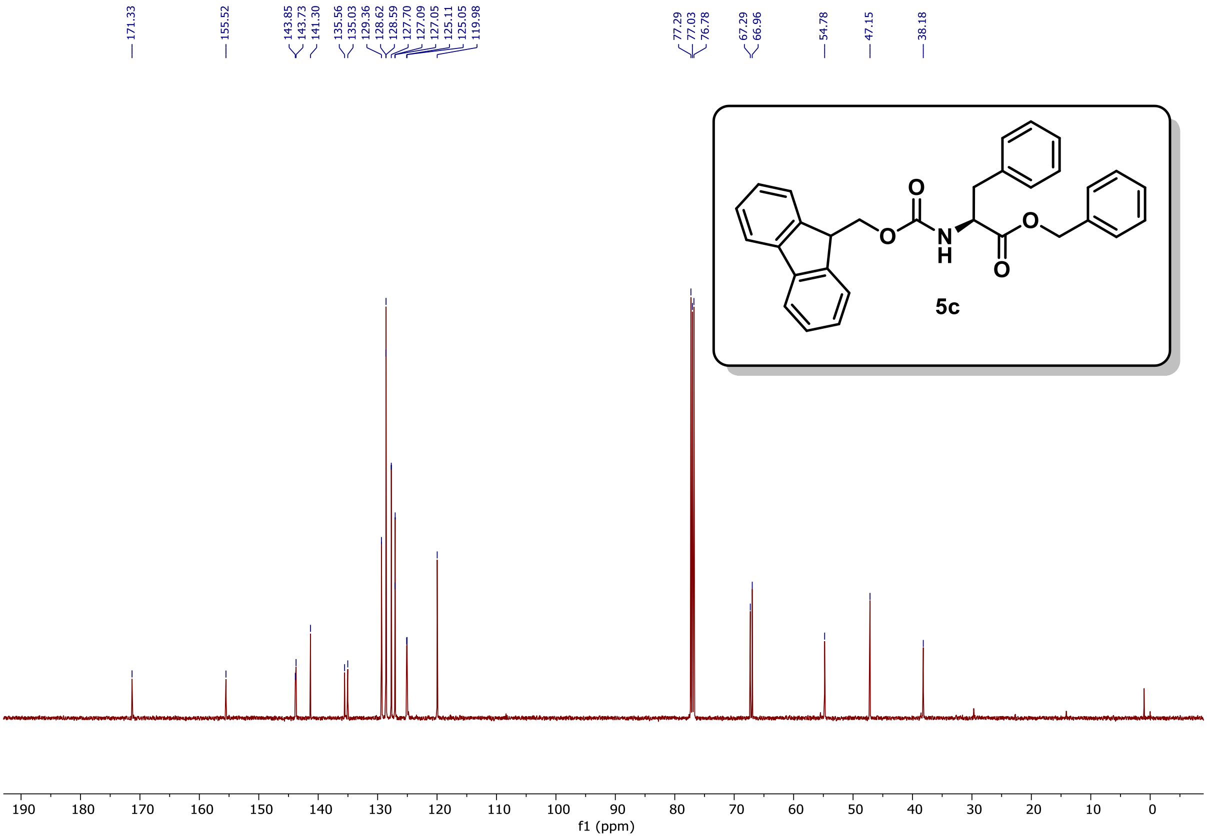
^{1}H NMR spectrum of compound 5b (500 MHz CDCl$_3$)



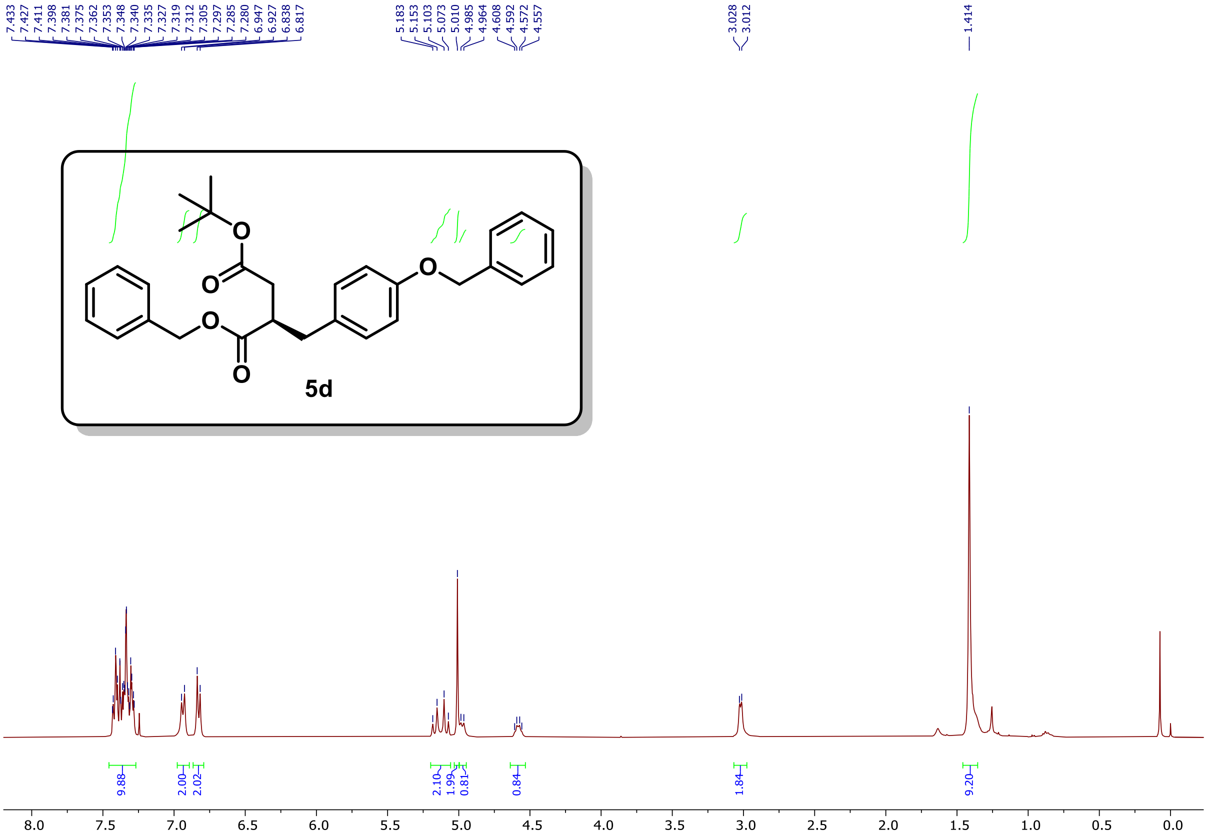
^{13}C{^{1}H} NMR spectrum of compound 5b (126 MHz CDCl$_3$)



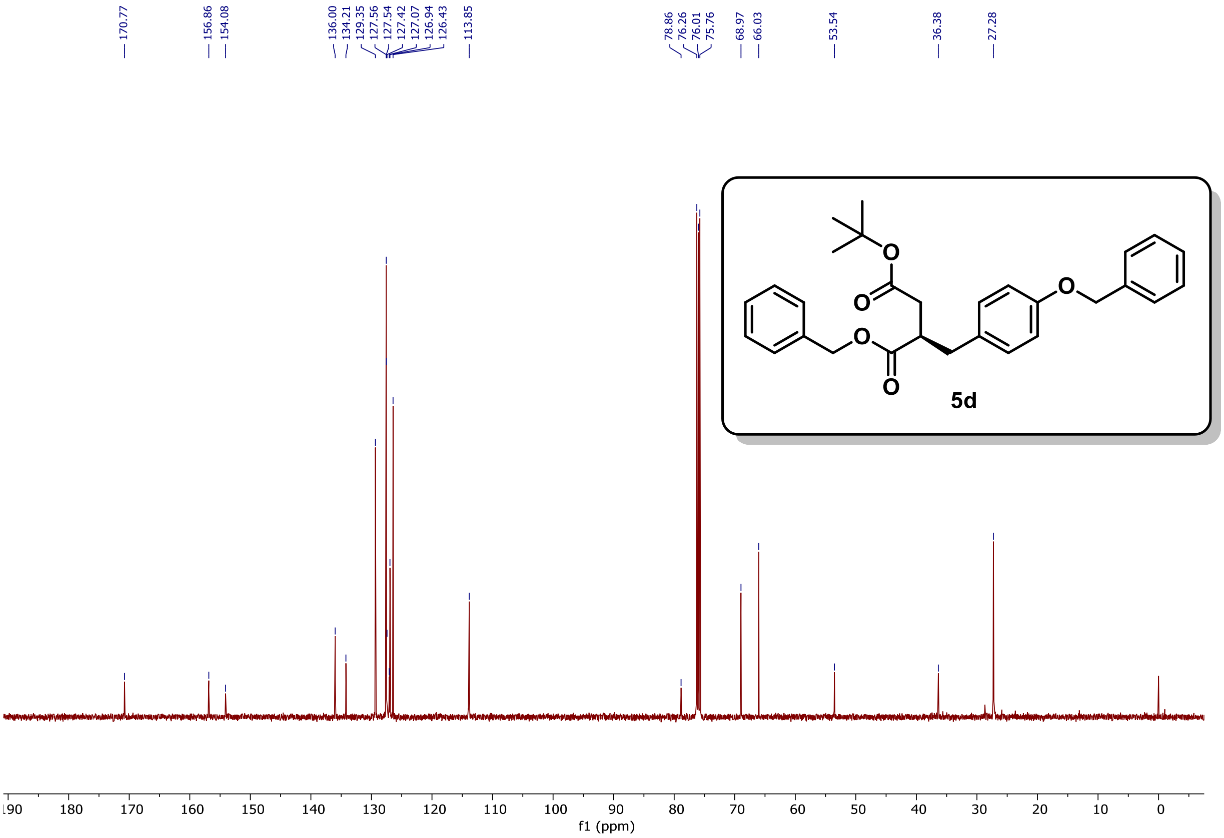
^{1}H NMR spectrum of compound 5c (500 MHz CDCl$_3$)



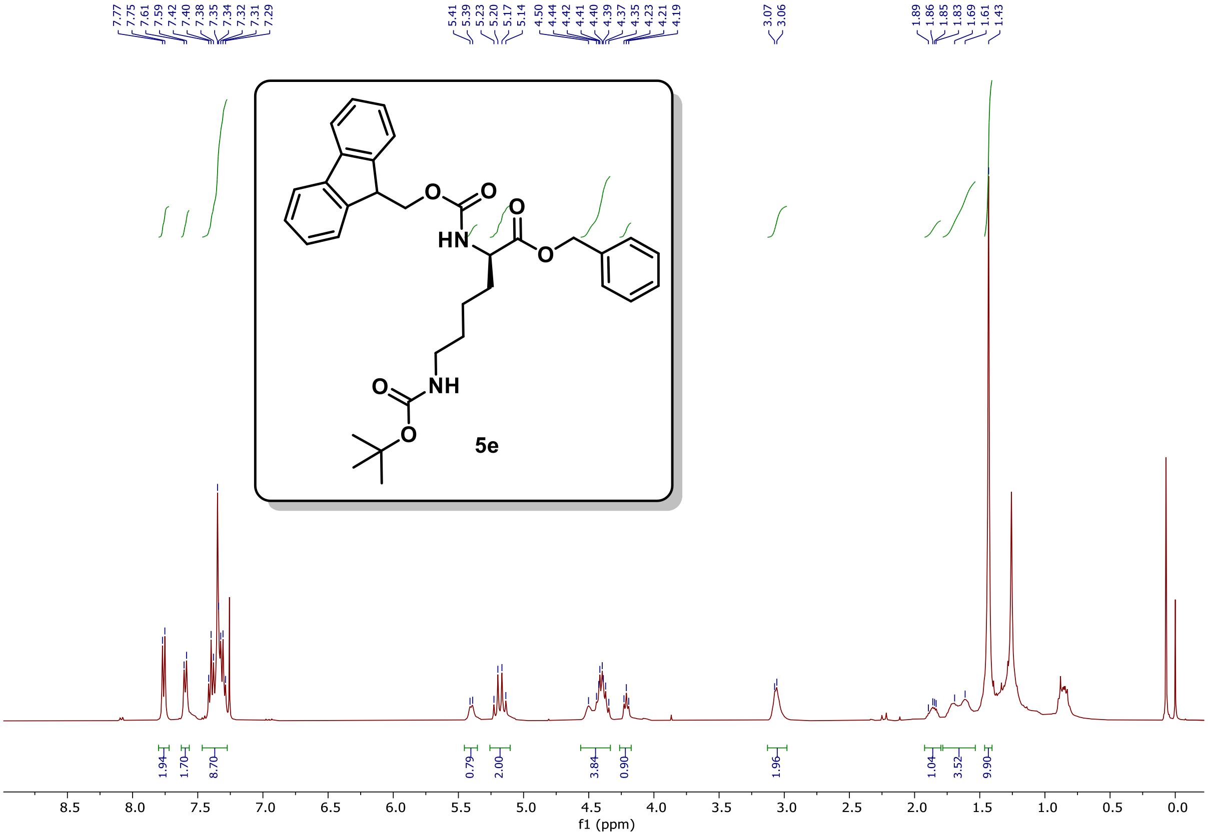
^{13}C{^{1}H} NMR spectrum of compound 5c (126 MHz CDCl$_3$)



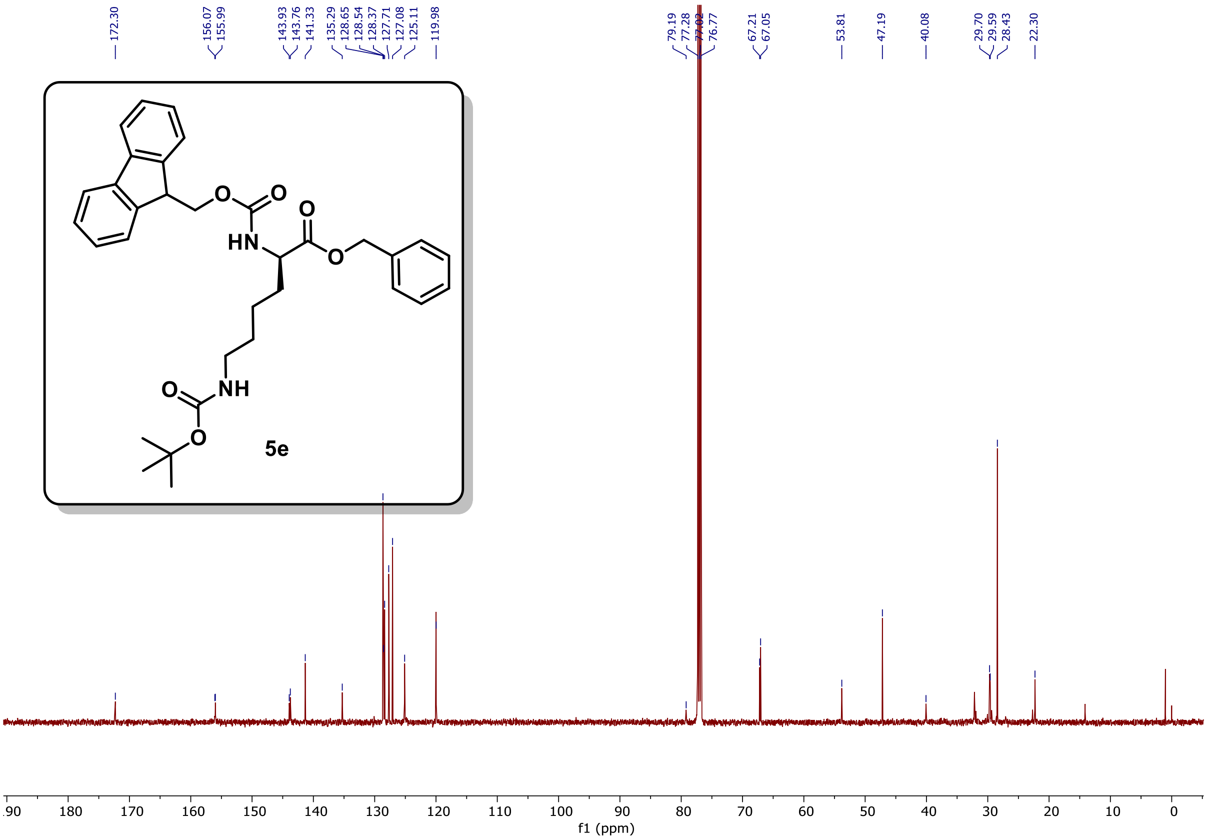
^{1}H NMR spectrum of compound 5d (500 MHz CDCl$_3$)



^{13}C{^{1}H} NMR spectrum of compound 5d (126 MHz CDCl$_3$)



^{1}H NMR spectrum of compound 5e (500 MHz CDCl$_3$)



^{13}C{^{1}H} NMR spectrum of compound 5e (126 MHz CDCl$_3$)

Table 2. Crystal parameters of compound **S5**

Compound **S5**	**CCDC 2412439**
Formula	$C_{16}H_{18}O_3S$
Formula weight	290.36
T/K	299(2)
Crystal system	Monoclinic
Space group	P 21/c
a/Å	23.9875(19)
b/Å	6.6512(5)
c/Å	9.5172(7)
α/º	90
β/º	99.885(2)
γ/º	90
V/Å^3	1495.9(2)
Z	4
Abs. Coeff./mm^{-1}	0.221
Abs. Correction	none
GOF on F^2	0.844
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0364
	$wR2$ = 0.1147
R indices [all data]	$R1$ = 0.0420
	$wR2$ = 0.1275

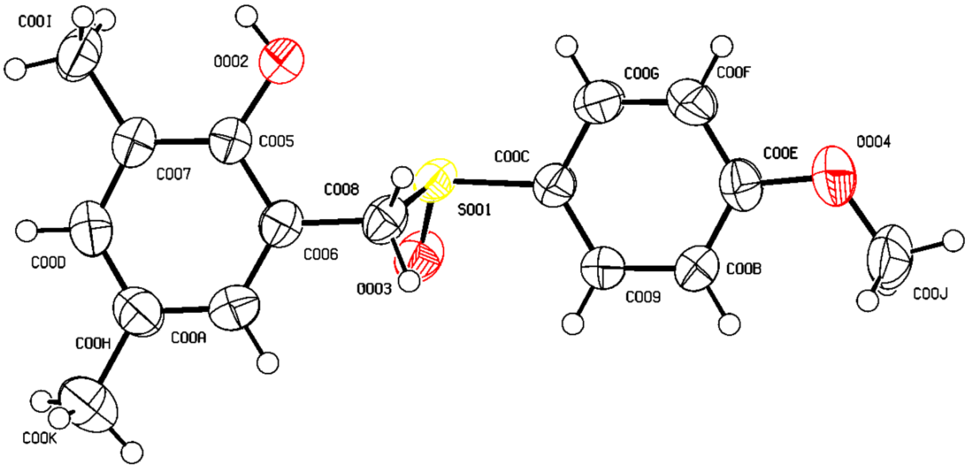


Figure 5. ORTEP diagram of compound **S5** with thermal ellipsoid of 50% probability.