Supporting Information

HFIP-Assisted Reductive C–S, C−N, and C−X Coupling of Carbonyl Compounds: A Combined Computational and Experimental Mechanistic Study

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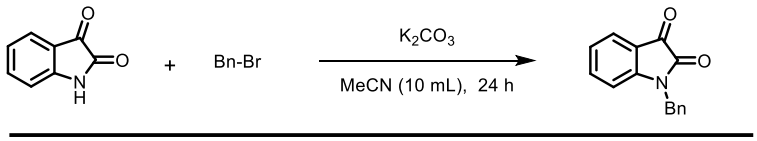
1. General Information:

All reagents and solvents were of pure analytical grade. Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (silica gel 60, F254, EMD Chemical). The vials (Wheaton® Standard Scintillation Vials, 1 dram, 15x45 mm with PTFE lined cap attached) were purchased from DAIHAN and dried in an oven overnight. High-resolution mass spectra (HRMS) were recorded on a mass spectrometer using electrospray ionization-time-of-flight (ESITOF) reflectron experiments. All reactions were run in flame- or oven-dried glassware. ^{1}H-NMR and ^{13}C-NMR were recorded on 400 MHz and 500 MHz spectrometers using $CDCl_3$ as a solvent; the chemical shifts are reported as parts per million (ppm) referenced to residual protium or carbon of the solvents; $CDCl_3$ δ H (7.26 ppm). Coupling constants were reported in Hertz (Hz). Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to protium; s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration). All reagents, such as aldehydes, ketone, isatin, thiols, trityl salt, and silanes, were purchased from Sigma-Aldrich, TCI, or Alfa Aesar.

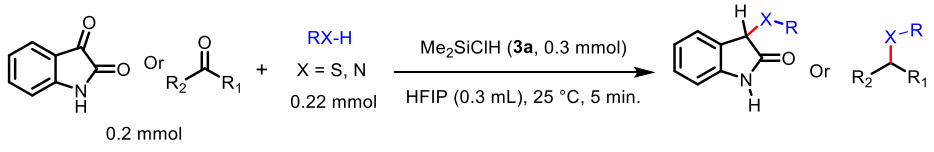
2. Synthesis of 1-Benzylindoline -2,3-dione: Isatin (1.2 mmol) was added to a mixture of benzyl bromide (1.0 mmol) and K_2CO_3 (1.0 mmol) in acetonitrile (10 mL) at 25 °C. After that, the reaction mixture was stirred for 24 h under reflux conditions. Then, the solvent was evaporated under a vacuum, and the crude product was purified by column chromatography (SiO_2, Hexane/EtOAc = 80:20) (Scheme S1).[1]



Scheme S1: 1-Benzylindoline -2,3-dione.

3. General Procedure

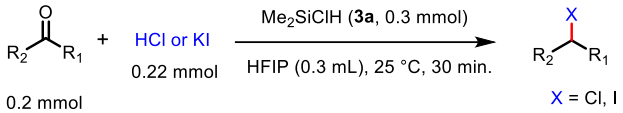
3.1 General Procedure for Reductive C−S and C−N Coupling of Carbonyl Groups with Thiols and Anilines **(A)**: A 5 mL Round-bottom flask was charged with carbonyl compounds (isatins or aldehydes, 0.2 mmol), nucleophiles (thiols or anilines, 0.22 mmol), Me_2SiHCl (**3a**, 33 µL, 0.3 mmol) in 0.3 mL HFIP. The reaction mixture was then stirred at 25 °C for 5.0 min. After completion, the crude reaction mixture was concentrated in rotavapor and purified by column chromatography over silica in the eluent system EtOAc/Hexane to give the desired product, which was confirmed by ^{1}H NMR, ^{13}C NMR and HRMS (Scheme S2A).



Scheme S2A: Reductive C−S and C−N Coupling of Carbonyl Groups with Thiols and Anilines.

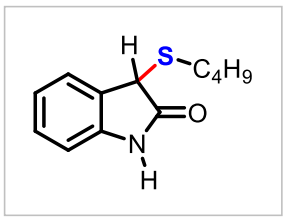
3.2 General Procedure for deoxygenated halogenation of Carbonyl Groups with HCl and KI **(B)**

A 5.0 mL Round-bottom flask was charged with carbonyl groups (0.2 mmol), HCl or KI (0.22 mmol), Me_2SiHCl (**3a**, 33 μL, 0.3 mmol) in 0.3 mL HFIP. The reaction mixture was then stirred at 25 °C for 30.0 min. After completion, the crude reaction mixture was concentrated and purified by column chromatography over silica in the eluent system hexane to give the desired products, which were confirmed by ^{1}H NMR, ^{13}C NMR, and HRMS (Scheme S2B).

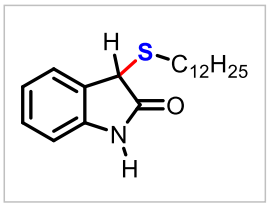


Scheme S2B: Reductive C−S Coupling of Carbonyl Groups with Thiols.

3. Characterization Data of Synthesized Products

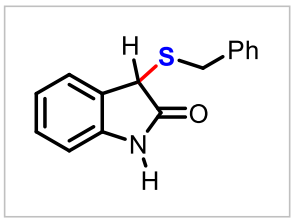


3-(Butylthio) indolin-2-one (4a)[2]; General procedure (**A**) was followed using isatin (**1a**, 29.5 mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 70/30) to afford the title compound as a pink solid (42 mg, 94%); mp = 52-54 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 4.31 (s, 1H), 2.73 – 2.61 (m, 1H), 2.54 – 2.41 (m, 1H), 1.58 – 1.45 (m, 2H), 1.43 – 1.31 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 178.4, 141.4, 129.1, 127.0, 125.4, 123.0, 110.2, 45.8, 31.2, 29.4, 22.0, 13.7.

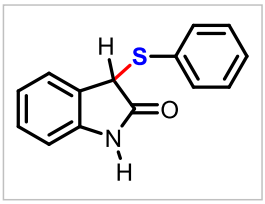


3-(Dodecylthio) Indolin-2-one(4b); General procedure (**A**) was followed using isatin (**1a**, 29.5 mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 70/30) to afford the title compound as a light yellow solid (62.5 mg, 94%); mp = 54-56 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 4.31 (s, 1H), 2.73 – 2.58 (m, 1H), 2.51 – 2.38 (m, 1H), 1.60 – 1.45 (m, 2H), 1.32 – 1.18 (m, 18H), δ 0.88 (t, *J* = 7.0 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 178.7, 141.5, 129.1, 127.0, 125.3, 123.0, 110.3, 45.9, 32.0, 29.75, 29.74, 29.68, 29.6, 29.5, 29.2, 29.1, 28.9, 22.8, 14.2; **HRMS** (ESI) m/z: $[M+Na]^+$calculated for $C_{20}H_{31}NONaS$: 356.2024; found: 356.2029.

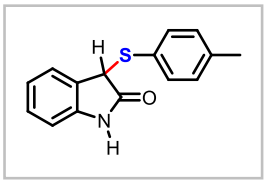
3-(Benzylthio) indolin-2-one (4c)[3]; General procedure (**A**) was followed using isatin (**1a**, 29.5 mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 70/30) to afford the title compound as a brown solid (46.5 mg, 91%); mp = 69-71 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.29 – 7.19 (m, 5H), 7.04 (t, *J* = 8.2 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 4.23 (s, 1H), 4.09 (d, *J* = 13.0 Hz, 1H), 3.73 (d, *J* = 13.0 Hz, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 178.5, 141.6, 137.2, 129.4, 129.2, 128.6, 127.4, 126.2, 125.4, 122.9, 110.3, 44.5, 34.3.



3-(Cyclohexylthio) indolin-2-one (4d)[2]; General procedure (**A**) was followed using isatin (**1a**, 29.5 mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 70/30) to afford the title compound as a light yellow solid (48 mg, 97%); mp = 103-105 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.34 (d, *J* = 7.3 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 4.37 (s, 1H), 3.16 – 2.91 (m, 1H), 2.06 (d, *J* = 12.7 Hz, 1H), 1.85 – 1.65 (m, 3H), 1.57 (d, *J* = 9.2 Hz, 1H), 1.50 – 1.38 (m, 1H), 1.33 – 1.21 (m, 4H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 178.9, 141.3, 128.9, 127.4, 125.3, 122.9, 110.3, 44.5, 42.7, 34.1, 33.5, 26.0, 25.9, 25.8.

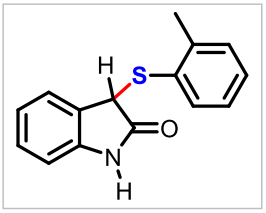


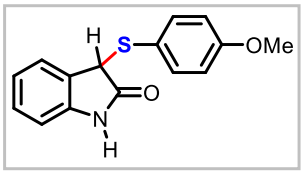
3-(Phenylsulfanyl) indolin-2-one (4e)[3]; General procedure (**A**) was followed using isatin (**1a**, 29.5 mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 70/30) to afford the title compound as a light pink solid (45.5 mg, 94%); mp = 131-133 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.42 – 7.34 (m, 3H), 7.25 – 7.14 (m, 4H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 7.0 Hz, 1H), 4.58 (s, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 177.0, 141.3, 134.1, 131.1, 129.2, 128.9, 128.7, 126.9, 125.7, 122.9, 110.1, 49.8.



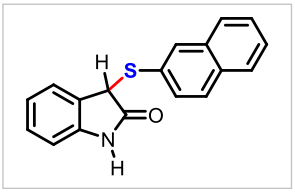
3-(*p*-Tolylthio) indolin-2-one (4f)[4]; General procedure (**A**) was followed using isatin (**1a**, 29.5 mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 70/30) to afford the title compound as a pink solid (46 mg, 90%); mp = 151-153 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 2H), 6.76 (d, *J* = 7.9 Hz, 1H), 4.52 (s, 1H), 2.25 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 177.5, 141.4, 139.0, 134.5, 129.6, 129.0, 127.03, 127.01, 125.4, 122.7, 110.3, 50.1, 21.3.

3-(o-Tolylthio) indolin-2-one (4g)[3]; General procedure (**A**) was followed using isatin (**1a**, 29.5 mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 75/25) to afford the title compound as a white solid (41 mg, 80%); mp = 59-61 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.26 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.24 (m, 4H), 7.17 (dt, *J* = 8.7, 4.3 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 4.76 (s, 1H), 2.54 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 177.4, 141.4, 140.9, 133.8, 131.4, 130.5, 129.2, 128.5, 126.8, 126.5, 125.5, 122.8, 110.3, 48.9, 21.1.

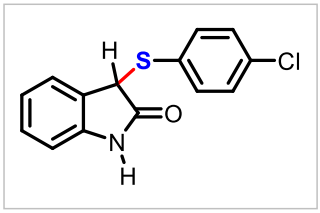




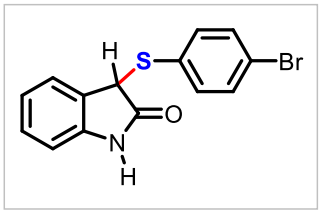
3-((4-Methoxyphenyl) thio) indolin-2-one (4h)[3]; General procedure (**A**) was followed using isatin (**1a**, 29.5 mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 70/30) to afford the title compound as a pink solid (41 mg, 75%); mp = 141-143 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.18 (s, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 8.7 Hz, 2H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 8.7 Hz, 2H), 4.42 (s, 1H), 3.66 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 177.4, 160.5, 141.5, 136.9, 128.9, 127.1, 125.5, 122.7, 120.7, 114.3, 110.2, 55.2, 50.5.



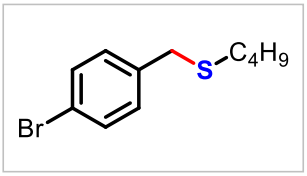
3-(Naphthalen-2-ylthio) indolin-2-one (4i)[3]; General procedure (**A**) was followed using isatin (**1a**, 29.5 mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 70/30) to afford the title compound as a pink solid (41 mg, 70%); mp = 132-134 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.90 (s, 1H), 7.74 (d, *J* = 9.2 Hz, 1H), 7.69 – 7.60 (m, 2H), 7.47 – 7.39 (m, 4H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 4.65 (s, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 176.6, 141.3, 133.6, 133.5, 133.0, 130.7, 129.2, 128.6, 128.4, 127.9, 127.7, 126.9, 126.8, 126.5, 125.7, 123.0, 110.1, 49.7.



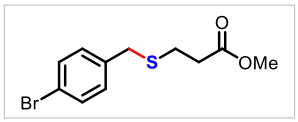
3-((4-Chlorophenyl) thio) indolin-2-one (4j)[3]; General procedure (**A**) was followed using isatin (**1a**, 29.5 mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 70/30) to afford the title compound as a white solid (36 mg, 65%); mp = 140-142 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 2H), 7.07 (t, *J* = 7.0 Hz, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 4.55 (s, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 176.8, 141.2, 135.6, 135.3, 129.4, 129.2, 129.1, 126.5, 125.6, 123.1, 110.3, 49.8.



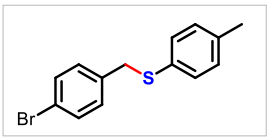
3-((4-Bromophenyl) thio) indolin-2-one (4k)[3]; General procedure (**A**) was followed using isatin (**1a**, 29.5 mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 70/30) to afford the title compound as a brown solid (42.5 mg, 67%); mp = 154-156 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.30 – 7.19 (m, 5H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 4.56 (s, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 176.3, 141.2, 135.8, 132.1, 130.1, 129.4, 126.5, 125.7, 123.5, 123.1, 110.1, 49.6.



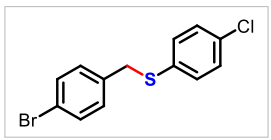
(4-Bromobenzyl) (butyl)sulfane (4l)[4]; General procedure (**A**) was followed using 4-bromobenzaldehyde (37mg, 0.2, mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 97/3) to afford the title compound as a colourless viscous (50 mg, 97%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 3.64 (s, 2H), 2.44 – 2.32 (m, 2H), 1.57 – 1.48 (m, 2H), 1.45 – 1.30 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 137.9, 131.6, 130.6, 120.8, 35.8, 31.4, 31.2, 22.1, 13.8.



Methyl 3-((4-bromobenzyl) thio) propanoate (4m); General procedure (**A**) was followed using 4-bromobenzaldehyde (37mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 95/5) to afford the title compound as a colourless viscous (53.5 mg, 93%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 3.68 (s, 3H), 3.67 (s, 2H), 2.67 (t, *J* = 7.3 Hz, 2H), 2.55 (t, *J* = 6.9 Hz, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 172.3, 137.3, 131.8, 130.6, 121.1, 51.9, 35.8, 34.4, 26.3; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{11}H_{13}Br^{79}NaO_2S$: 310.9711; found: 310.9714.

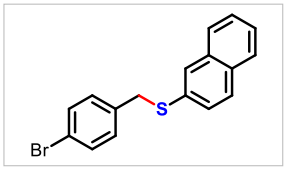


(4-Bromobenzyl) (*p*-tolyl) sulfane (4n)[5]; General procedure (**A**) was followed using 4-bromobenzaldehyde (37mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 97/3) to afford the title compound as a white sticky(55.5 mg, 95%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 3.84 (s, 2H), 2.17 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 137.0, 136.9, 131.8, 131.5, 131.1, 130.5, 129.7, 121.0, 39.3, 21.1.

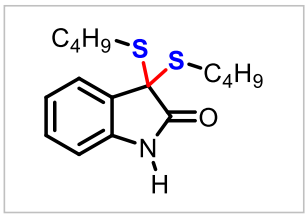


(4-Bromobenzyl) (4-chlorophenyl) sulfane (4o)[5]; General procedure (**A**) was followed using 4-bromobenzaldehyde (37mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 97/3) to afford the title compound as a white solid (58mg, 93%); mp = 82-84 °C; **^{1}H NMR**

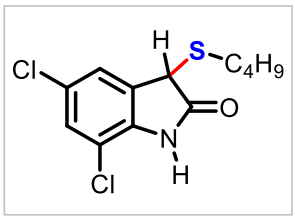
(500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.24 – 7.17 (m, 4H), 7.11 (d, *J* = 8.4 Hz, 2H), 4.00 (s, 2H); **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 136.5, 134.1, 133.0, 132.0, 131.8, 130.6, 129.2, 121.3, 39.0.



(4-Bromobenzyl) (naphthalen-2-yl) sulfane (4p)[5]; General procedure (**A**) was followed using 4-bromobenzaldehyde (37mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 95/5) to afford the title compound as a white solid (62 mg, 94%); mp = 87-89 °C; **^1H NMR** (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.3 Hz, 1H), 7.76 – 7.72 (m, 2H), 7.70 (s, 1H), 7.51 – 7.43 (m, 2H), 7.45 – 7.35 (m, 3H), 7.18 (d, *J* = 8.5 Hz, 2H), 4.15 (s, 2H); **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 136.7, 133.8, 133.3, 132.1, 131.7, 130.6, 128.6, 128.4, 128.0, 127.8, 127.3, 126.7, 126.1, 121.2, 38.6.

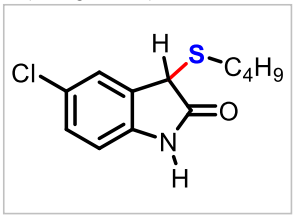


3,3-Bis (butylthio) indolin-2-one (5a)[2]; General procedure (**A**) was followed using isatin (**1a**, 29.5 mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 90/10) to afford the title compound as a white solid (28 mg, 45%); mp = 82-84 °C; **^1H NMR** (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.10 (t, *J* = 8.2 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 2.77 – 2.61 (m, 4H), 1.48 (p, *J* = 7.2 Hz, 4H), 1.40 – 1.28 (m, 4H), 0.84 (t, *J* = 7.3 Hz, 6H); **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 176.7, 139.3, 129.8, 129.6, 125.0, 123.3, 110.3, 57.0, 30.9, 30.0, 22.1, 13.7.

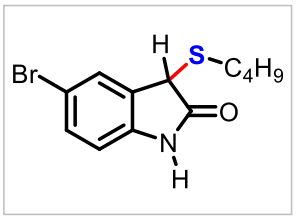


3-(Butylthio)-5,7-dichloroindolin-2-one (6a); General procedure (**A**) was followed using 5,7-dichloroindoline-2,3-dione (43mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 70/30) to afford the title compound as a white solid (56 mg, 96%); mp = 145-147 °C; **^1H NMR** (500 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.26 (s, 2H), 4.37 (s, 1H), 2.79 – 2.68 (m, 1H), 2.59 – 2.46 (m, 1H), 1.59 – 1.51 (m, 2H), 1.44 – 1.33 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 176.8, 137.9, 129.6, 128.8, 128.7, 124.2, 115.7, 46.2, 31.0, 29.8, 22.0, 13.7; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{12}H_{13}ONCl_2{}^{35}NaS$: 311.9993; found: 311.9995; νmax (cm^{-1}) 3382, 3142, 3064, 2960, 2928, 2861, 1709, 1619, 1588, 1463.

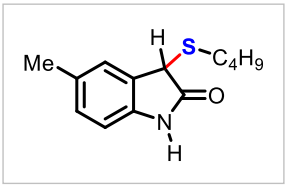
3-(Butylthio)-5-chloroindolin-2-one (6b)[2]; General procedure (**A**) was followed using 5-chloroindoline-2,3-dione (36.2mg, 0.2 mmol) to give a crude mixture of which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 70/30) to afford the title compound as a white solid (49 mg, 96%); mp = 82-84 °C; **^1H NMR** (500 MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.35 (s, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 4.29 (s, 1H), 2.71 – 2.61 (m, 1H), 2.51 – 2.41 (m, 1H),



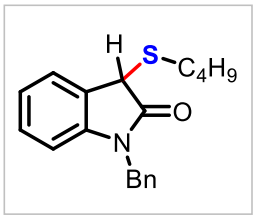
1.57 – 1.47 (m, 2H), 1.41 – 1.32 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 178.4, 139.9, 129.1, 128.8, 128.5, 125.7, 111.3, 45.9, 31.1, 29.5, 22.0, 13.7; ν_{max} (cm^{-1}) 3167, 2928, 2861, 1714, 1617, 1475, 1385, 1298, 1187, 1114.



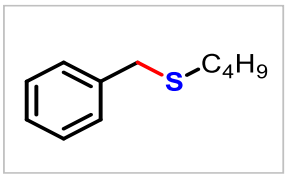
5-Bromo-3-(butylthio) indolin-2-one (6c); General procedure (**A**) was followed using 5-bromoindoline-2,3-dione (45.2mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 70/30) to afford the title compound as a white sticky (57 mg, 95%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.50 (s, 1H), 7.38 (d, *J* = 9.2 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 4.29 (s, 1H), 2.76 – 2.63 (m, 1H), 2.56 – 2.45 (m, 1H), 1.58 – 1.48 (m, 2H), 1.45 – 1.32 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H);**^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 178.4, 140.5, 132.0, 129.1, 128.4, 115.6, 111.8, 45.8, 31.0, 29.5, 22.0, 13.7. **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{12}H_{14}NNaOS\ Br^{79}$: 321.9877; found: 321.9879.



3-(Butylthio)-5-methylindolin-2-one (6d)[2]; General procedure (**A**) was followed using 5-methylindoline-2,3-dione (32.2mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 70/30) to afford the title compound as a pink sticky (44 mg, 94%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.18 (s, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 4.26 (s, 1H), 2.72 – 2.61 (m, 1H), 2.51 – 2.42 (m, 1H), 2.32 (s, 3H), 1.55 – 1.47 (m, 2H), 1.40 – 1.30 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 178.5, 139.0, 132.5, 129.4, 127.0, 126.0, 110.0, 45.9, 31.2, 29.4, 22.0, 21.2, 13.7.

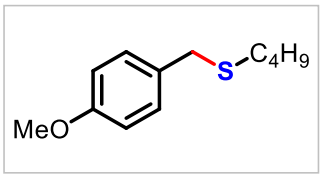


1-Benzyl-3-(butylthio) indolin-2-one (6e); General procedure (**A**) was followed using 1-benzylindoline-2,3-dione (74.4mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 70/30) to afford the title compound as a brown sticky (44 mg, 78%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.5 Hz, 1H), 7.33 – 7.22 (m, 5H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 4.97 (d, *J* = 15.5 Hz, 1H), 4.85 (d, *J* = 15.5 Hz, 1H), 4.37 (s, 1H), 2.82 – 2.70 (m, 1H), 2.60 – 2.48 (m, 1H), 1.60 – 1.47 (m, 2H), 1.43 – 1.30 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 175.7, 143.1, 135.7, 128.9, 128.8, 127.7, 127.4, 126.2, 125.1, 122.9, 109.2, 44.7, 44.0, 31.2, 29.5, 22.0, 13.6; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{19}H_{21}NNaOS$: 334.1242; found: 334.1245.

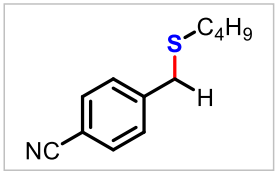


Benzyl(butyl)sulfane (6f)[4]; General procedure (**A**) was followed using benzaldehyde (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 97/3) to afford the title compound as a colorless viscous (30 mg, 82%); **^{1}H NMR** (500 MHz,

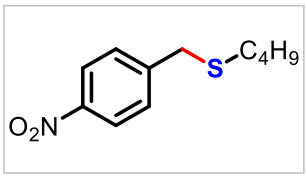
$CDCl_3$) δ 7.26 (d, *J* = 4.0 Hz, 4H), 7.21 – 7.15 (m, 1H), 3.65 (s, 2H), 2.43 – 2.27 (m, 2H), 1.48 (dd, *J* = 15.3, 7.6 Hz, 2H), 1.32 (h, *J* = 7.2 Hz, 2H), 0.83 (t, *J* = 7.3 Hz, 3H); **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 138.8, 129.0, 128.6, 127.0, 36.4, 31.4, 31.2, 22.1, 13.8.



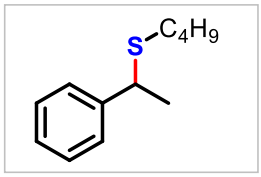
Butyl(4-methoxybenzyl) sulfane (6g)[4]; General procedure (**A**) was followed using 4-methoxybenzaldehyde (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 95/5) to afford the title compound as a colorless viscous (33 mg, 78%); **^1H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 3.67 (s, 2H), 2.48 – 2.31 (m, 2H), 1.62 – 1.49 (m, 2H), 1.45 – 1.31 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 158.6, 130.8, 130.0, 114.0, 55.4, 35.8, 31.5, 31.1, 22.1, 13.8.



4-((Butylthio)methyl) benzonitrile (6h)[4]; General procedure (**A**) was followed using 4-formylbenzonitrile (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 80/20) to afford the title compound as a colorless viscous (37 mg, 90%); **^1H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 3.71 (s, 2H), 2.45 – 2.32 (m, 2H), 1.58 – 1.45 (m, 2H), 1.43 – 1.28 (m, 2H) 0.87 (t, *J* = 7.3 Hz, 3H); **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 144.6, 132.4, 129.7, 118.9, 110.9, 36.2, 31.4, 31.3, 22.0, 13.7.

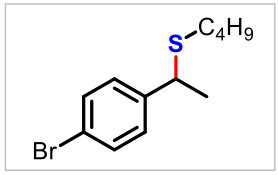


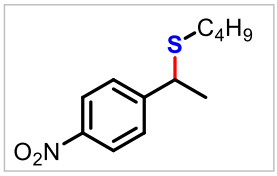
Butyl(4-nitrobenzyl) sulfane (6i)[4]; General procedure (**A**) was followed using 4-nitrobenzaldehyde (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 95/5) to afford the title compound as a colorless viscous (44 mg, 98%); **^1H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 6.7 Hz, 2H), 3.77 (s, 2H), 2.46 – 2.37 (m, 2H), 1.59 – 1.48 (m, 2H), 1.43 – 1.28 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H); **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 147.0, 146.7, 129.7, 123.8, 35.8, 31.3, 31.2, 22.0, 13.7.



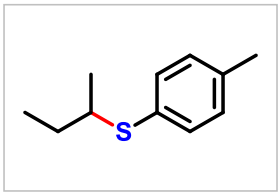
Butyl(1-phenylethyl) sulfane (6j)[6]; General procedure (**A**) was followed using acetophenone (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 95/5) to afford the title compound as a colorless viscous (30.5 mg, 78%); **^1H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 4H), 7.26 (t, *J* = 6.9 Hz, 1H), 3.98 (q, *J* = 7.0 Hz, 1H), 2.49 – 2.18 (m, 2H), 1.60 (d, *J* = 7.2 Hz, 3H), 1.55 – 1.45 (m, 2H), 1.41 – 1.32 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H); **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 144.4, 128.6, 127.4, 127.1, 44.2, 31.6, 31.1, 22.8, 22.2, 13.8.

(1-(4-Bromophenyl) ethyl) (butyl)sulfane (6k)[6]; General procedure (**A**) was followed using 1-(4-bromophenyl)ethan-1-one (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 95/5) to afford the title compound as a colorless viscous (44 mg, 81%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 3.90 (q, *J* = 7.0 Hz, 1H), 2.36 – 2.16 (m, 2H), 1.53 (d, *J* = 7.1 Hz, 3H), 1.50 – 1.42 (m, 2H), 1.37 – 1.26 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 143.5, 131.6, 129.1, 120.7, 43.6, 31.5, 31.1, 22.7, 22.1, 13.8.

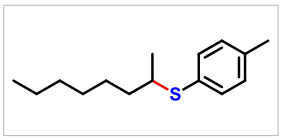




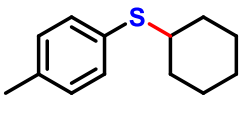
Butyl(1-(4-nitrophenyl) ethyl) sulfane (6l)[6]; General procedure (**A**) was followed using 1-(4-nitrophenyl)ethan-1-one (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 95/5) to afford the title compound as a colorless viscous (41.5 mg, 86%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 11.4 Hz, 2H), 7.51 (s, 2H), 4.01 (q, *J* = 7.1 Hz, 1H), 2.38 – 2.19 (m, 2H), 1.57 (d, *J* = 7.1 Hz, 3H), 1.51 – 1.39 (m, 2H), 1.38 – 1.22 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 152.3, 147.0, 128.2, 123.9, 43.7, 31.4, 31.1, 22.4, 22.0, 13.7.



Sec-butyl(*p*-tolyl) sulfane (6n)[7]; General procedure (**A**) was followed using butane-2-one (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane) to afford the title compound as a colorless viscous (34 mg, 94%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 3.08 (h, *J* = 6.8 Hz, 1H), 2.33 (s, 3H), 1.68 – 1.60 (m, 1H), 1.51 (dt, *J* = 13.9, 7.2 Hz, 1H), 1.25 (d, *J* = 6.7 Hz, 3H), 1.00 (t, *J* = 7.4 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 137.0, 132.9, 131.7, 129.7, 45.5, 29.6, 21.2, 20.7, 11.6.

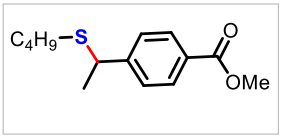


Octan-2-yl(*p*-tolyl) sulfane (6o)[7]; General procedure (**A**) was followed using octan-2-one (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane) to afford the title compound as a colorless viscous (43.5 mg, 92%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 3.08 (q, *J* = 6.6 Hz, 1H), 2.29 (s, 3H), 1.61 – 1.50 (m, 1H), 1.47 – 1.35 (m, 3H), 1.30 – 1.16 (m, 9H), 0.84 (t, *J* = 6.9 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 136.9, 132.9, 131.7, 129.6, 43.9, 36.8, 31.9, 29.3, 27.2, 22.8, 21.3, 21.2, 14.2.

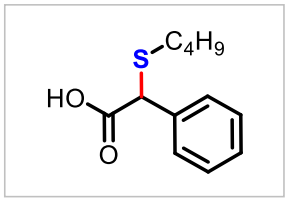


Cyclohexyl(*p*-tolyl) sulfane (6p)[8]; General procedure (A) was followed using cyclohexanone (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane) to afford the title compound as a colorless viscous (39 mg, 95%); **^{1}H NMR** (400 MHz, CDCl3) δ 7.33 (d,

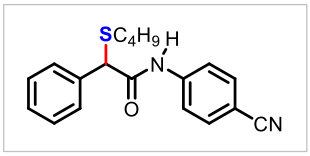
J = 8.2 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 2H), 3.12 – 2.81 (m, 1H), 2.34 (s, 3H), 1.98 (d, *J* = 12.7 Hz, 2H), 1.83 – 1.70 (m, 2H), 1.61 (dd, *J* = 11.4, 4.3 Hz, 1H), 1.43 – 1.16 (m, 5H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 137.0, 132.9, 131.3, 129.6, 47.2, 33.5, 26.2, 25.9, 21.2.



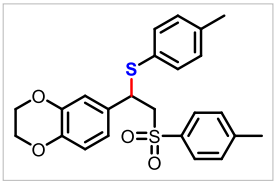
Methyl 4-(1-(butylthio) ethyl) benzoate (6q); General procedure (**A**) was followed using methyl 4-acetylbenzoate (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 90/10) to afford the title compound as a colorless viscous (48 mg, 95%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 3.97 (q, *J* = 7.0 Hz, 1H), 3.91 (s, 3H), 2.36 – 2.20 (m, 2H), 1.56 (d, *J* = 7.2 Hz, 3H), 1.49 – 1.40 (m, 2H), 1.35 – 1.25 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.1, 149.9, 130.0, 129.0, 127.4, 52.2, 44.0, 31.5, 31.1, 22.5, 22.1, 13.8; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{14}H_{20}SNaO_2$ 275.1076; found: 275.1063.



2-(Butylthio)-2-phenylacetic acid (6r); General procedure (**A**) was followed using 2-oxo-2-phenylacetic acid (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, DCM/MeOH = 95/5) to afford the title compound as a white sticky (35 mg, 78%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.48 – 7.44 (m, 2H), 7.36 – 7.29 (m, 3H), 4.56 (s, 1H), 2.66 – 2.32 (m, 2H), 1.60 – 1.50 (m, 2H), 1.37 (h, *J* = 7.3 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 177.1, 135.7, 128.8, 128.7, 128.5, 52.2, 32.0, 31.1, 22.0, 13.7; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{12}H_{16}SNaO_2$: 247.0763; found: 247.0764; νmax (cm^{-1}) 3030, 2958, 2928, 2868, 2676, 1709, 1493, 1455, 1411, 1286, 1222, 1179, 1075.

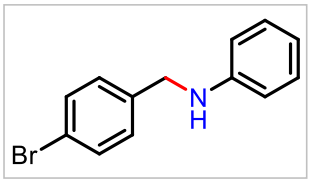


2-(Butylthio)-*N*-(4-cyanophenyl)-2-phenylacetamide (6s); General procedure (**A**) was followed using *N*-(4-cyanophenyl)-2-oxo-2-phenylacetamide (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 80/20) to afford the title compound as a white solid (61mg, 94%); mp = 82-84 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.91 (s, 1H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.34 (dt, *J* = 14.6, 7.1 Hz, 3H), 4.69 (s, 1H), 2.72 – 2.53 (m, 2H), 1.69 – 1.57 (m, 2H), 1.50 – 1.35 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 168.9, 141.6, 136.2, 133.4, 129.2, 128.6, 128.0, 119.6, 118.8, 107.6, 56.0, 32.7, 31.1, 22.0, 13.7; **HRMS** (ESI) m/z $[M+Na]^+$: calculated for $C_{19}H_{20}N_2NaOS$: 347.1194; found: 347.1194; ν_{max} (cm^{-1}) 3274, 2924, 2860, 2226, 1673, 1585, 1496, 1406, 1314, 1248.

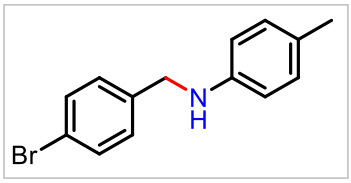


6-(1-(*p*-Tolylthio)-2-tosylethyl)-2,3-dihydrobenzo[b][1,4]dioxine (6t); General procedure (**A**) was followed using *N*-(4-cyanophenyl)-2-oxo-2-phenylacetamide (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 80/20) to afford the

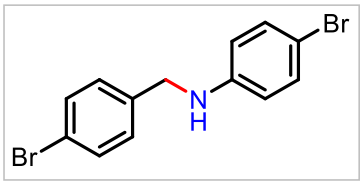
title compound as a white sticky (75 mg, 85%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.67 – 6.48 (m, 3H), 4.46 (dd, *J* = 10.7, 3.7 Hz, 1H), 4.22 – 4.14 (m, 4H), 3.72 (dd, *J* = 14.7, 10.8 Hz, 1H), 3.56 (dd, *J* = 14.6, 3.5 Hz, 1H), 2.38 (s, 3H), 2.33 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 144.2, 143.4, 138.7, 136.6, 133.7, 130.7, 130.1, 129.48, 129.45, 128.1, 121.3, 117.3, 116.8, 64.4, 64.4, 60.9, 47.3, 21.7, 21.3; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{24}H_{24}S_2O_4Na$: 463.1008; found: 463.0994.



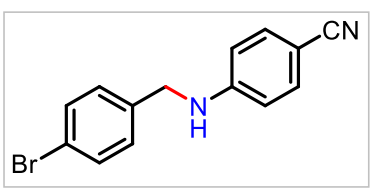
***N*-(4-Bromobenzyl) aniline (4aa)**[9]; General procedure (**A**) was followed using 4-bromobenzaldehyde (37mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 90/10) to afford the title compound as a light yellow sticky (47.5 mg, 91%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.15 (t, *J* = 8.0 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 2H), 4.25 (s, 2H), 4.02 (s, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.9, 138.7, 131.8, 129.4, 129.2, 121.0, 117.9, 113.0, 47.8.



***N*-(4-Bromobenzyl)-4-methylaniline (4ab)**[9]; General procedure (**A**) was followed using 4-bromobenzaldehyde (37mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 90/10) to afford the title compound as a light yellow solid (52.5 mg, 95%); mp = 59-61 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.53 (d, *J* = 8.4 Hz, 2H), 4.26 (s, 2H), 2.23 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.6, 138.8, 131.8, 129.9, 129.2, 127.2, 121.0, 113.2, 48.1, 20.5.

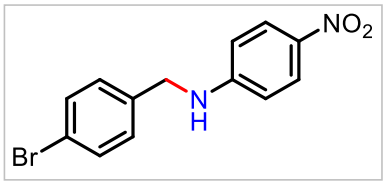


4-Bromo-*N*-(4-bromobenzyl) aniline (4ac)[9]; General procedure (**A**) was followed using 4-bromobenzaldehyde (37mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 90/10) to afford the title compound as a white solid (66 mg, 97%); mp = 101-103 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.19 (m, 4H), 6.47 (d, *J* = 8.9 Hz, 2H), 4.26 (s, 2H), 4.11 (s, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.8, 138.1, 132.1, 131.9, 129.1, 121.2, 114.6, 109.6, 47.7; **HRMS** (ESI) m/z: $[M+H]^+$ calculated for $C_{13}H_{12}NBr^{79}Br^{79}$: 339.9337; found: 339.9328.

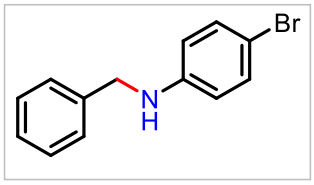


4-((4-Bromobenzyl)amino)benzonitrile (4ad)[9]; General procedure (**A**) was followed using 4-bromobenzaldehyde (37mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 80/20) to afford the title compound as a white solid (40 mg, 69%); mp = 109-111 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.9 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.56 (d, *J* = 8.9 Hz, 2H), 4.65 (s, 1H), 4.34 (d,

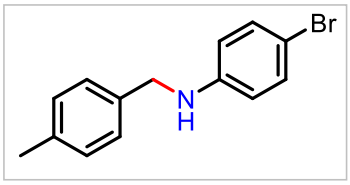
J = 5.8 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.9, 137.0, 133.9, 132.1, 129.0, 121.6, 120.4, 112.6, 99.6, 47.0; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{14}H_{11}N_2Br^{79}Na$: 309.0003; found: 308.9994.



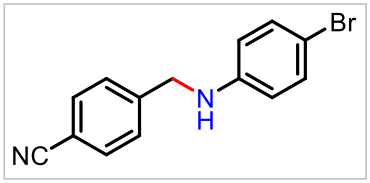
***N*-(4-Bromobenzyl)-4-nitroaniline (4ae)**[9]; General procedure (**A**) was followed using 4-bromobenzaldehyde (37mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 70/30) to afford the title compound as a green solid (35 mg, 57%); mp = 123-125 °C; **^{1}H NMR** (500 MHz, DMSO-*d*$_6$) δ 7.97 (d, *J* = 9.3 Hz, 2H), 7.83 (t, *J* = 6.3 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 9.3 Hz, 2H), 4.40 (d, *J* = 6.1 Hz, 2H); **^{13}C NMR** (126 MHz, DMSO-*d*$_6$) δ 154.3, 138.2, 136.3, 131.5, 129.5, 126.2, 120.2, 111.3, 45.3; **HRMS** (ESI) m/z: $[M+H]^+$ calculated for $C_{13}H_{12}N_2Br^{79}O_2$: 307.0082; found: 307.0071.



***N*-Benzyl-4-bromoaniline (4af)**[9]; General procedure (**A**) was followed using benzaldehyde (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 95/5) to afford the title compound as a white viscous (47.5 mg, 91%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 4.4 Hz, 4H), 7.29 – 7.27 (m, 1H), 7.26 – 7.21 (m, 2H), 6.50 (d, *J* = 8.9 Hz, 2H), 4.30 (s, 2H), 4.08 (s, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.2, 139.0, 132.1, 128.8, 127.54, 127.52, 114.6, 109.3, 48.4.

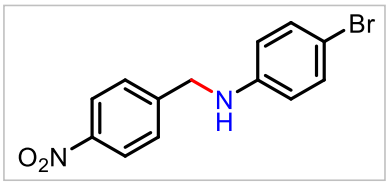


4-Bromo-*N*-(4-methyl benzyl) aniline (4ag)[9]; General procedure (**A**) was followed using 4-methylbenzaldehyde (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 95/5) to afford the title compound as a white solid (52.5 mg, 95%); mp = 74-76 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 4H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.53 (d, *J* = 8.9 Hz, 2H), 4.28 (s, 2H), 4.07 (s, 1H), 2.38 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.2, 137.2, 135.9, 132.0, 129.5, 127.5, 114.5, 109.1, 48.1, 21.2.

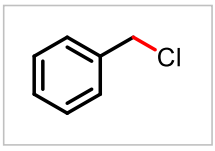


4-((4-Bromophenyl) amino) methyl) benzonitrile (4ah)[9]; General procedure (**A**) was followed using 4-formylbenzonitrile (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 80/20) to afford the title compound as a pale yellow solid (48 mg, 83%); mp = 102-104 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 9.0 Hz, 2H), 6.44 (d, *J* = 8.9 Hz, 2H), 4.40 (s, 2H), 4.28

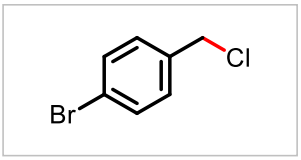
(s, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.5, 144.9, 132.6, 132.2, 127.8, 118.9, 114.6, 111.3, 109.9, 47.8; **HRMS** (ESI) m/z: $[M+H]^+$ calculated for $C_{14}H_{12}N_2Br^{79}$: 287.0184; found: 287.0174.



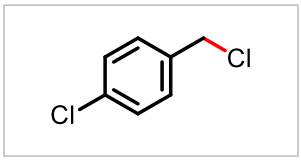
4-Bromo-*N*-(4-nitrobenzyl) aniline (4ai)[9]; General procedure (**A**) was followed using 4-nitrobenzaldehyde (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 80/20) to afford the title compound as a pale yellow solid (40 mg, 65%); mp = 79-81 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.7 Hz, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.9 Hz, 2H), 6.45 (d, *J* = 8.9 Hz, 2H), 4.45 (s, 2H), 4.28 (s, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.4, 146.9, 146.4, 132.3, 127.8, 124.1, 114.6, 110.1, 47.7.



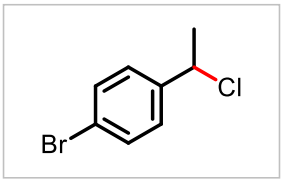
(Chloromethyl)benzene (5aa)[10]; General procedure (**B**) was followed using benzaldehyde (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane) to afford the title compound as a colorless viscous (10 mg, 40%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 – 7.17 (m, 5H), 4.51 (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.5, 128.7, 128.6, 128.4, 46.3.



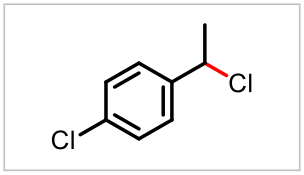
1-Bromo-4-(chloromethyl) benzene (5ab)[10]; General procedure (**B**) was followed using 4-bromobenzaldehyde (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane) to afford the title compound as a colorless viscous (31.5 mg, 77%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 4.56 (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.6, 132.0, 130.4, 122.6, 45.5.



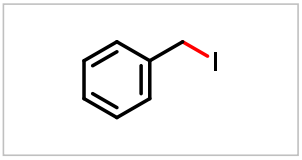
1-Chloro-4-(chloromethyl) benzene (5ac)[10]; General procedure (**B**) was followed using 4-chlorobenzaldehyde (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane) to afford the title compound as a colorless viscous (22 mg, 68%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 4H), 4.55 (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.1, 134.5, 130.1, 129.1, 45.5.



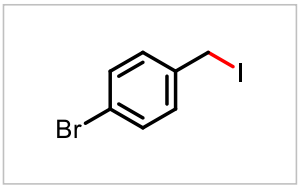
1-Bromo-4-(1-chloroethyl) benzene (5ad)[10]; General procedure (**B**) was followed using 4-bromoacetophenone (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane) to afford the title compound as a colorless viscous (35 mg, 81%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 5.04 (q, *J* = 6.8 Hz, 1H), 1.82 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.0, 131.9, 128.4, 122.2, 57.9, 26.6.



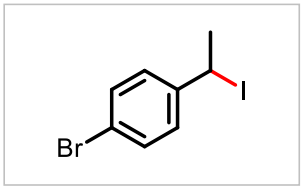
1-Chloro-4-(1-chloroethyl) benzene (5ae)[10]; General procedure (**B**) was followed using 4-chloroacetophenone (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane) to afford the title compound as a colorless viscous (24.5 mg, 70%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 1.7 Hz, 1H), 7.32 – 7.26 (m, 3H), 5.03 (q, *J* = 6.9 Hz, 1H), 1.83 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.9, 134.6, 130.1, 128.5, 126.9, 124.9, 57.8, 26.6.



(Iodomethyl)benzene (5af)[11]; General procedure (**B**) was followed using benzaldehyde (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane) to afford the title compound as a colourless viscous (22 mg, 50%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 4.47 (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.4, 129.0, 128.9, 128.0, 5.8.



1-Bromo-4-(iodomethyl) benzene (5ag)[11]; General procedure (**B**) was followed using 4-bromobenzaldehyde (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane) to afford the title compound as a white solid (52 mg, 88%); mp = 62-64 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.39 (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.5, 132.1, 130.5, 121.9, 4.3.

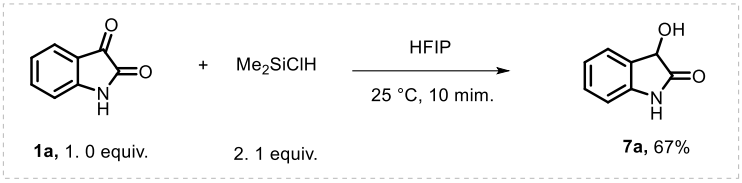


1-Bromo-4-(1-iodoethyl) benzene (5ah)[11]; General procedure (**B**) was followed using 4-bromoacetophenone (0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane) to afford the title compound as a dark pick viscous (54 mg, 87%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 5.33 (q, *J* = 7.0 Hz, 1H), 2.18 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.6, 132.0, 128.3, 121.7, 28.9, 24.4.

5. Control Experiment

a. Synthesis of 3-Hydroxyindolin-2-one (7a)[12]

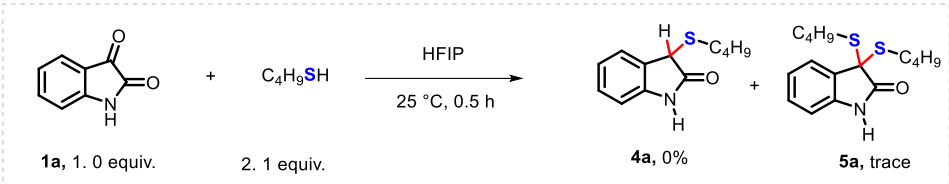
A reaction vial was charged with isatin (**1a**, 29.5 mg, 0.2 mmol) and Me_2SiClH (**3a**, 44 µL, 0.4 mmol) in 0.5 mL of HFIP. After that, the reaction mixture was stirred vigorously to complete the reaction at 25 °C. The reaction mixture was evaporated in rotavapor, and purification was done by column chromatography (SiO_2, Hexane/ethyl acetate = 60/40) to afford the 3-phenylindolin-2-one **7a** in 67% (20 mg); **^{1}H NMR** (500 MHz, CD_3OD) δ 7.36 (d, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 7.03 (t, *J* = 8.1 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 4.92 (s, 1H); **^{13} C{^{1}H} NMR** (126 MHz, CD_3OD) δ 180.6, 143.2, 130.5, 130.1, 126.0, 123.6, 111.1, 71.2.



Scheme S3a: Synthesis of 3-Hydroxyindolin-2-one.

b. Standard Reaction without Silane

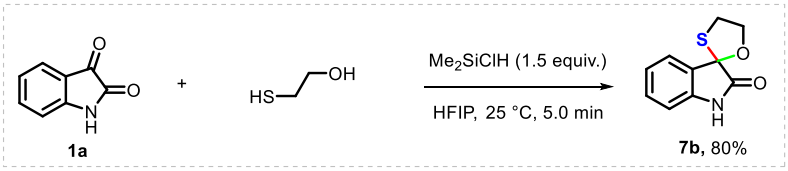
The 0.5 mL HFIP was added to a mixture of isatin (**1a**, 29.5 mg, 0.2 mmol) and butane-1-thiol (0.42 mmol) at 25 °C. After that, the reaction mixture was stirred vigorously for 0.5 h at 25 °C. The desired product was not formed, as confirmed by the crude ^{1}H NMR analysis.



Scheme S3b: Standard Reaction without Silane.

c. Synthesis of Spiro [indoline-3,2'-[1, 3] oxathiolan]-2-one (7b)

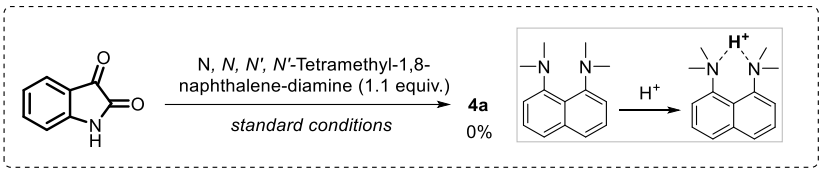
Isatin (**1a**, 29.5 mg, 0.2 mmol) was added at 25 °C in a solution of 2-mercaptoethanol-1-ol (0.22 mmol), Me_2SiHCl (**3a**, 33 µL, 0.3 mmol) in 0.5 mL HFIP. The reaction mixture was then stirred at 25 °C for 5.0 min. After the completion, the crude reaction mixture was concentrated in vacuo and purified by column chromatography over silica in the eluent system EtOAc/Hexane and afforded **7b** in 80% yield.



Scheme S3c: Synthesis of Spiro [indoline-3,2'-[1, 3] oxathiolan]-2-one.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.24 (m, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.79 (dt, *J* = 8.9, 6.3 Hz, 1H), 4.56 (dt, *J* = 8.7, 6.1 Hz, 1H), 3.72 – 3.62 (m, 1H), 3.47 (dt, *J* = 10.1, 6.1 Hz, 1H); **^{13} C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 178.1, 140.7, 130.9, 126.9, 125.8, 123.5, 110.6, 88.9, 72.7, 34.2; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{10}H_9SNO_2Na$: 230.0246; found: 230.0240.

d. Reaction with Proton Sponge:

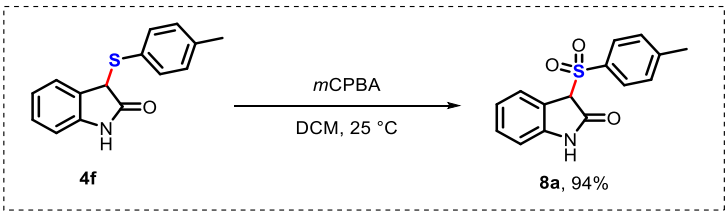


Scheme S3d: Reaction with Proton Sponge.

In control experiment **d,** we performed our standard reaction with substrate isatin (**1a**) (1.0 equiv., 0.2 mmol) and the butane-1-thiol (0.2 mmol) in the presence of *N*, *N*, *N′, N′*-tetramethyl-1,8-naphthalene-diamine (1.1 equiv.) as a proton scavenger. The reaction mixture was stirred at 25 °C for 0.5 h. It was observed that there was no product formed, as confirmed by the crude ^{1}H NMR analysis.

6. Further Derivatization

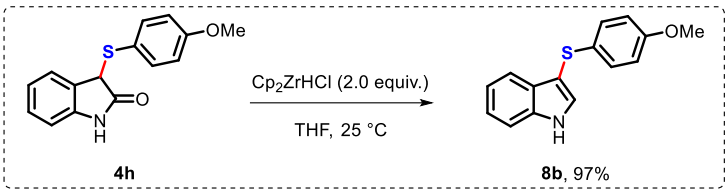
6.1 Synthesis of 3-Tosylindolin-2-one (8a)[13]: A reaction vial (5 mL) was charged with *m*CPBA (70 mg, 57-86 % *m*CPBA, 0.4 mmol, 4.0 equiv.), 3-(*p*-tolylthio) indolin-2-one (**4f**, 25.5 mg, 0.1 mmol, 1.0 equiv.) in CH_2Cl_2 (1.5 mL). After that, the reaction mixture was stirred vigorously for 2 hours at 25 °C. The reaction mixture was washed with aqueous saturated $NaHCO_3$, dried over ($MgSO_4$), and evaporated in vacuo. and purified by column chromatography (SiO_2, Hexane/ethyl acetate = 50/50) to afford the 3-tosylindolin-2-one as a brick red solid (27 mg, 94%).



Scheme S4a: Synthesis of 3-Tosylindolin-2-one.

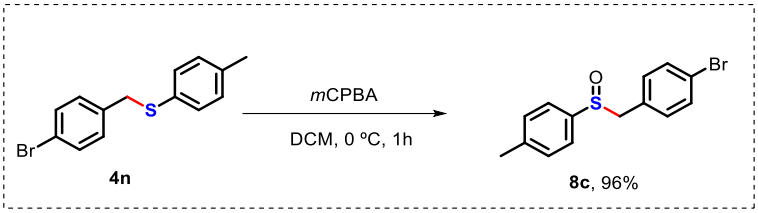
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.67 (s, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.46 – 7.24 (m, 4H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 5.68 (s, 1H), 2.38 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, DMSO-d_6) δ 168.5, 145.7, 143.7, 134.2, 130.8, 130.0, 129.3, 127.1, 122.5, 119.7, 110.3, 68.2, 21.5; vmax (cm^{-1}) 3422, 2925, 2855, 2254, 1721, 1645, 1468, 1319, 1150, 1026, 1001.

6.2 Synthesis of 3-((4-Methoxyphenyl) thio)-1*H*-indole (8b)[13]: Schwartz reagent, Cp_2ZrHCl (103 mg, 0.4 mmol) was added at 25 °C in a solution of 3-((4-methoxyphenyl) thio) indolin-2-one (54 mg, 0.2 mmol), in 2 mL of dry THF and reaction mixture was stirred at 25 °C for 2 h. The standard workup procedure provided a crude product which was further purified by column chromatography (SiO_2, Hexane/ethyl acetate = 80/25) to afford the 3-((4-methoxyphenyl) thio)-1*H*-indole as a pick solid (49.5 mg, 97%); mp = 109-111 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.31 – 7.25 (m, 3H), 6.86 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 157.9, 136.6, 130.2, 129.6, 129.1, 128.7, 123.1, 120.9, 119.7, 114.6, 111.7, 104.7, 55.5; **HRMS** (ESI) m/z: $[M+H]^+$ calculated for $C_{15}H_{14}SON$: 256.0796; found: 245.0790.



Scheme S4b: Synthesis of 3-((4-Methoxyphenyl) thio)-1*H*-indole.

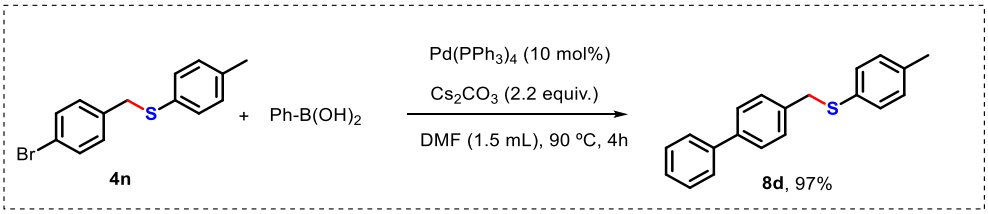
6.3 Synthesis of 1-Bromo-4-((*p*-tolylsulfinyl) methyl) benzene (8c): *m*CPBA (35 mg, 0.2 mmol, 1.0 equiv.) was added to the solution of (4-bromobenzyl) (*p*-tolyl) sulfane (0.2 mmol, 1.0 equiv.) in DCM (2.0 mL) at 0 °C The reaction mixture stirred vigorously for 1 hour. It was then washed with an aqueous solution of $NaHCO_3$ and dried over anhydrous Na_2SO_4.



Scheme S4c: Synthesis of 1-Bromo-4-((*p*-tolylsulfinyl) methyl) benzene.

The reaction mixture was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 80/20) to afford the desired product as a white solid (59 mg, 96%); mp = 129-131 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.5 Hz, 2H), 7.28 – 7.22 (m, 4H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.96 (s, 2H), 2.40 (s, 3H); **^{13} C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 141.9, 139.3, 132.1, 131.6, 129.8, 128.3, 124.5, 122.6, 62.6, 21.6; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{14}H_{13}SONaBr^{79}$ 330.9768; found: 330.9756; ν_{max} (cm^{-1}) 3432, 2963, 2916, 1988, 1591, 1485, 1402, 1306, 1140, 1035, 895.

6.4 Synthesis of [1,1'-Biphenyl]-4-yl(4-methylbenzyl) sulfane (8d): In a Schlenk tube (4-bromobenzyl) (*p*-tolyl) sulfane (0.2 mmol, 1.0 equiv.), Phenylboronic acid (0.4 mmol, 2.0 equiv.), $Pd(PPh_3)_4$ (10 mol%) and Cs_2CO_3 (0.4 mmol, 2.0 equiv.) were taken, and a vacuum was created using high vacuum pressure followed by N_2 pursing using an N_2 balloon. Solvent DMF (1 mL) was added, and the reaction mixture was stirred for 4 hours at 90 ºC in an oil bath. Then the reaction mixture was quenched with saturated NH_4Cl solution and extracted with ethyl acetate. The organic layer was collected, evaporated, and dried over Na_2SO_4.

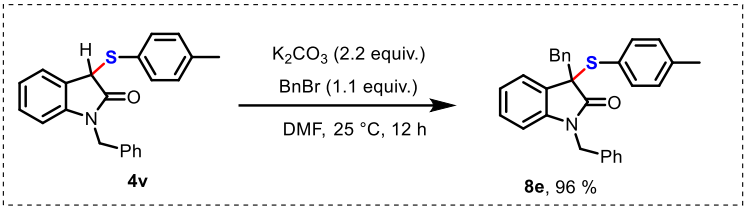


Scheme S4d: Synthesis of [1,1'-Biphenyl]-4-yl(4-methylbenzyl) sulfane.

The reaction mixture was purified by column chromatography using (SiO_2; Hexane) to afford the desired product as a white solid (57 mg, 97%); mp = 126-128 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61

(d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.35 (m, 3H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 4.13 (s, 2H), 2.35 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 140.9, 140.1, 137.0, 136.7, 132.6, 130.8, 129.8, 129.4, 128.9, 127.4, 127.3, 127.1, 39.6, 21.2; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{20}H_{18}SNa$ 313.1021; found: 313.1022.

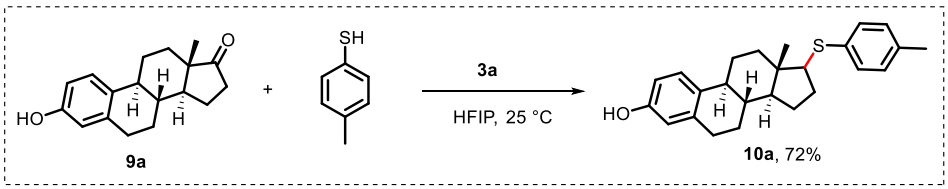
6.5 Synthesis of 1,3-Dibenzyl-3-(*p*-tolylthio) indolin-2-one (**8e**): In a 5 mL round bottom flask, K_2CO_3 (2.2 equiv.) and benzyl bromide (1.1 equiv.) were added to the solution of **4v** (0.2 mmol, 1.0 equiv.) in DMF (0.2 mL) at room temperature. After completion, H_2O (3 mL) was added, and the mixture was extracted with Et_2O (5 mL) three-time. The organic layer was collected, evaporated, and dried over Na_2SO_4, and purified by column chromatography (SiO_2, Hexane/ethyl acetate = 70/30) to afford the **8e** as a pale-yellow solid (83.5 mg, 96%); mp = 59-61 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 2H), 7.07 (t, *J* = 7.7 Hz, 5H), 7.01 – 6.91 (m, 5H), 6.49 (d, *J* = 7.6 Hz, 2H), 6.14 (d, *J* = 7.8 Hz, 1H), 4.72 (d, *J* = 16.0 Hz, 1H), 4.26 (d, *J* = 16.0 Hz, 1H), 3.58 (d, *J* = 13.0 Hz, 1H), 3.44 (d, *J* = 13.1 Hz, 1H), 2.28 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.5, 142.5, 139.7, 136.8, 135.1, 130.5, 129.3, 129.1, 128.7, 128.5, 128.0, 127.1, 126.9, 126.5, 126.1, 124.9, 122.4, 109.1, 60.3, 43.4, 41.5, 21.4; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated: for $C_{29}H_{25}SONNa$ 458.1555; found: 458.1557; ν_{max} (cm^{-1}) 3408, 3056, 3028, 2916, 2849, 1906, 1713, 1607, 1492, 1466, 1209.



Scheme S4e: Synthesis of 1,3-Dibenzyl-3-(*p*-tolylthio) indolin-2-one.

7. (a) Late-Stage Diversification for Synthesis of (*8R,9S,13S,14S*)-13-Methyl-17-(*p*-tolylthio)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-ol (10a)

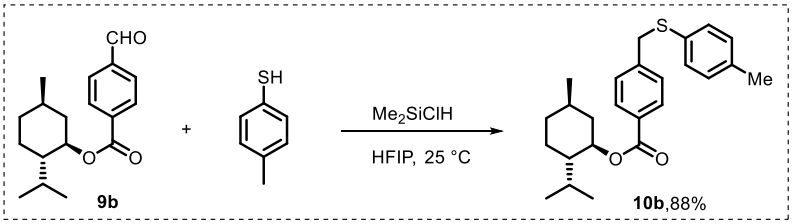
General procedure (**A**) was followed using estrone (**9a**) (54 mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 90/10) to afford the title white solid (55 mg, 72%); mp = 78-81 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 1H), 6.56 (s, 1H), 4.72 (s, 1H), 3.08 (t, *J* = 9.4 Hz, 1H), 2.88 – 2.74 (m, 2H), 2.32 (s, 3H), 2.28 – 2.20 (m, 2H), 2.21 – 2.12 (m, 1H), 1.91 – 1.84 (m, 2H), 1.82 – 1.70 (m, 2H), 1.49 – 1.29 (m, 5H), 1.25 – 1.17 (m, 1H), 0.85 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.4, 138.3, 136.4, 133.5, 132.8, 131.6, 129.6, 126.6, 115.4, 112.8, 59.6, 53.6, 44.9, 44.0, 39.3, 37.7, 31.1, 29.7, 27.7, 26.5, 24.3, 21.2, 13.5; **HRMS** (ESI) m/z: $[M-H]^-$ calculated for $C_{25}H_{29}OS$: 377.1939; found: 377.1948.



Scheme S5a: Synthesis of (*8R,9S,13S,14S*)-13-Methyl-17-(*p*-tolylthio)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-ol.

(b) Late-Stage Diversification for Synthesis of (1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-((*p*-tolylthio) methyl) benzoate (10b)

General procedure (**A**) was followed using (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-formylbenzoate (**9b**) (58 mg, 0.2 mmol) to give a crude mixture which was purified by column chromatography (SiO_2, Hexane/ethyl acetate = 95/5) and afforded white sticky (70 mg, 88%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 4.91 (td, *J* = 10.9, 4.4 Hz, 1H), 4.07 (s, 2H), 2.31 (s, 3H), 2.15 – 2.09 (m, 1H), 1.95 (pd, *J* = 6.9, 2.7 Hz, 1H), 1.76 – 1.68 (m, 2H), 1.58 – 1.49 (m, 4H), 1.17 – 1.03 (m, 2H), 0.92 (t, *J* = 6.5 Hz, 6H), 0.79 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.0, 143.3, 137.1, 131.8, 131.3, 129.9, 129.7, 128.9, 75.0, 47.4, 41.1, 39.8, 34.5, 31.6, 26.6, 23.8, 22.2, 21.2, 20.9, 16.7; **HRMS** (ESI) m/z: $[M-H]^-$ calculated for $C_{25}H_{31}O_2S$: 395.2045; found: 395.2052; ν_{max} (cm^{-1}) 3411, 2951, 2920, 2869, 1712, 1609, 1492, 1450, 1371, 1271.



Scheme S5b: Synthesis of (1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-((*p*-tolylthio) methyl) benzoate**.**

8. Computational Details

Structural optimization and total energy calculations were performed using density functional theory implemented in CP2K code.[14a] We have used module Quickstep where Kohn-Sham orbitals were modelled with atom-centered DZVP Gaussian basis set. The generalized gradient approximation (GGA) with the PBE form was employed to approximate the exchange-correlation interactions.[14b] We use DFT-D3 formalism for all the simulations to include the dispersion correction.[14c] The energy barriers associated with different steps of chemical reaction have been evaluated using the climbing image Nudged Elastic Band (NEB) calculations.[14d] We use eight images to map the reaction pathway for each step.

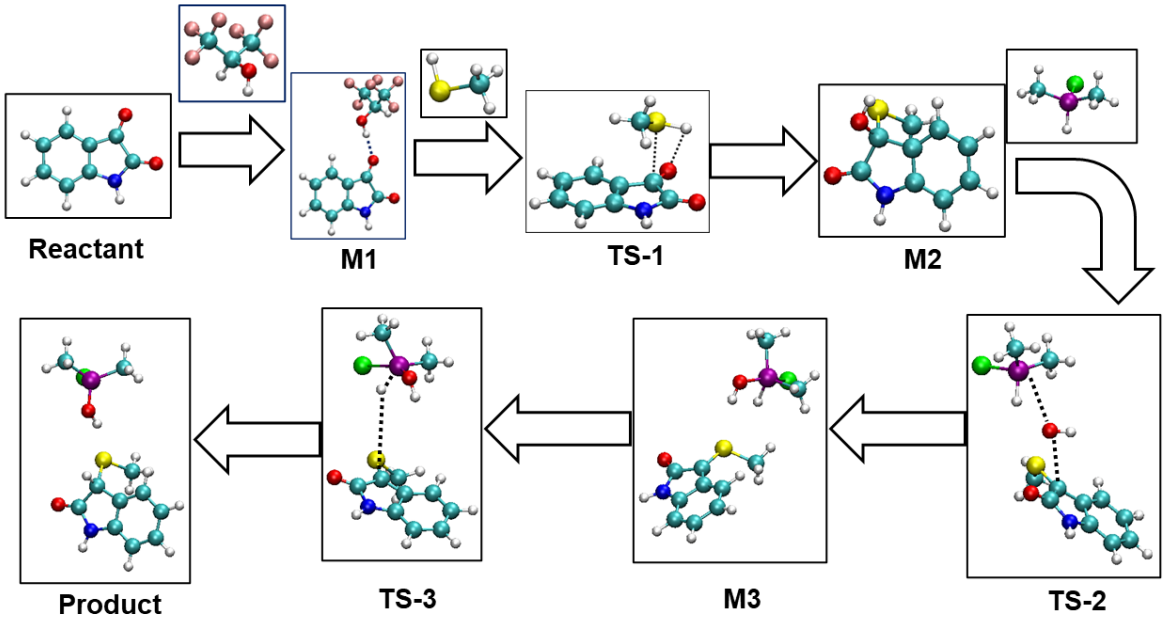


Fig. S1. Optimized molecular structures for the C-S coupling reaction using DFT-based simulations. The associated energy profile is presented in Figure S1, the main paper. The dotted lines indicate partial bond breaking and bond making at the transition state. Key: Hydrogen (white), carbon (cyan), oxygen (red), blue (nitrogen), sulfur (yellow), silicon (purple), chlorine (green), fluorine (pink).

8.1 The DFT-D3+PBE(GGA) optimized Cartesian coordinates (in Å) of reactants, intermediates, and product. Each structure is labeled by the name as used in Fig. S1. Total energy of each structure is given in Hartree unit.

Reactant (isatin)

E =	-90.4422413769		
C	8.0448183484	7.8195693409	7.4978765935
C	6.6327458821	7.7787120332	7.4975076406
C	5.8795604859	8.9464000171	7.4978735596
C	6.5737060615	10.1662174604	7.4987767292
C	7.9751334200	10.2208831442	7.4988385418
C	8.7215349507	9.0387827955	7.4982130074
H	4.7888823558	8.9223537304	7.4987885536
H	6.0029459938	11.0964219702	7.5000216045
H	8.4779108680	11.1881222621	7.5000875538
H	9.8126117349	9.0509630514	7.4993798021
C	7.2390613098	5.5438503625	7.5180422192
O	7.1645355941	4.3299903616	7.5443377241
N	6.1845638799	6.4490715611	7.5003130436
H	5.2061073801	6.1638488497	7.5089036141
C	8.5359940608	6.4367844231	7.5031775967

O	9.6730143257	5.9968252683	7.4978210604

HFIP

E =	-179.6918546906		
C	5.6598623128	5.3286325168	6.0038297096
H	6.0985082692	4.3186018404	6.0014154232
C	6.1489710984	6.0196345214	7.2933538690
C	6.1555735223	6.0203107101	4.7165193431
F	5.6888845002	7.2852433412	7.3845479813
F	5.6967597137	5.3235337009	8.3745585683
F	7.5079738117	6.0578769563	7.3641669629
F	5.7093748958	5.3104916591	3.6449548183
F	7.5161849710	6.0593343546	4.6656535416
F	5.6925591655	7.2821733159	4.5877450602
O	4.2458958472	5.3260881089	5.9935493476
H	3.9294017319	4.4073196548	6.0108691233

M1

E =	-270.1510292511		
C	7.1646390383	11.0006914925	9.9983165767
C	5.7482875523	10.9471046535	9.9997035512
C	4.9851984226	12.1086033285	10.0003095431
C	5.6689430777	13.3335668216	10.0001225874
C	7.0707304641	13.4028524233	9.9992025289
C	7.8303106393	12.2306157560	9.9980573427
H	3.8951398438	12.0756868748	10.0008342164
H	5.0889822489	14.2580826953	10.0007064937
H	7.5633141334	14.3750986276	9.9993312618
H	8.9209507014	12.2606960902	9.9969993954
C	6.3716241733	8.7204825552	9.9976810725
O	6.3091741643	7.5065246103	9.9982123118
N	5.3100148459	9.6164015966	9.9996186416
H	4.3343188369	9.3221256923	10.0033721893
C	7.6608868669	9.6283411237	9.9959665470
O	8.8012684432	9.1739538581	9.9930605960

C	12.4172403782	9.2002279689	10.0039259931
H	11.9830731850	8.1908631465	9.9045516386
C	13.2677179274	9.1711791186	11.2950272192
C	13.2677754370	9.4272295902	8.7327166479
F	13.9207137163	10.3349987203	11.5283899986
F	12.4553755336	8.9301263697	12.3597743356
F	14.2035409820	8.1807337953	11.2551670803
F	12.4544553178	9.4028967363	7.6408269113
F	14.2051787961	8.4527946018	8.5637421603
F	13.9196950331	10.6150321422	8.7452523151
O	11.4470212730	10.2109239076	10.1063824210
H	10.5453062444	9.8145547037	10.0527744621

TS-1

E = -108.67140691

C	7.030378	11.016184	9.408520
C	5.755044	11.121069	10.040763
C	5.058649	12.329091	10.046357
C	5.648613	13.421656	9.398675
C	6.901135	13.327783	8.757032
C	7.602551	12.125350	8.760920
H	4.095704	12.422733	10.543759
H	5.123878	14.375998	9.397540
H	7.319275	14.203817	8.266231
H	8.573575	12.026900	8.278080
C	6.406604	8.933157	10.354944
O	6.259005	7.723220	10.509727
N	5.424355	9.910583	10.627155
H	4.518830	9.669216	11.016090
C	7.521806	9.699656	9.663465
O	8.663313	9.194136	9.296421
S	8.735987	9.184646	12.027291
H	8.974331	8.767135	10.312927
C	8.128463	7.710559	12.874352
H	8.860849	6.897798	12.776085
H	7.948301	7.915666	13.936060

H	7.201556	7.370993	12.375390

M2

E = -108.7177992064

C	7.1229634153	10.9962022498	10.0775909273
C	5.7175031021	10.9701977756	10.0872885002
C	4.9657218471	12.1411673749	10.0701138593
C	5.6587790807	13.3602873774	10.0378164405
C	7.0568738890	13.4013285692	10.0313037299
C	7.7974082955	12.2096393121	10.0573648366
H	3.8750507536	12.1171858861	10.0709061352
H	5.0927184865	14.2928149192	10.0166702086
H	7.5721245102	14.3620340120	10.0086025876
H	8.8899560079	12.2357914182	10.0649754551
C	6.3183042587	8.7264436286	10.0208983156
O	6.2109915008	7.5193078824	9.9301966549
N	5.2735684984	9.6405825984	10.1029388390
H	4.3004569622	9.3464766096	10.0389247335
C	7.6344207248	9.5769389614	10.0701523629
O	8.3884016631	9.2058710800	8.9291406550
S	8.6531860327	9.1290027981	11.5534811296
C	7.8808446184	10.0715795535	12.8971547111
H	8.4187168379	9.7720427789	13.8072871339
H	7.9837599251	11.1546534707	12.7577240916
H	6.8231828607	9.8046021649	13.0220307718
H	9.2207579065	9.7160085840	8.9558375266

SiMe2Cl(H)

E = -50.5838041950

Si	7.0316948844	7.2889201494	7.1375492421
C	7.6684546254	8.2187519506	5.6553591134

H	7.3045848494	9.2560665075	5.6549225513
H	8.7680237917	8.2393498731	5.6445068436
H	7.3298355564	7.7358907899	4.7242329660
C	7.6746741416	5.5438075160	7.2014437690
H	8.7739283737	5.5220224501	7.2109903189
H	7.3116133211	5.0256668946	8.1003625508
H	7.3324640636	4.9782037365	6.3192865264
Cl	7.6372758220	8.2816964360	8.8508275906
O	5.3766430997	7.3269000573	7.2239882115
H	4.8864743551	6.9167831081	6.4931637845

TS-2

E = -143.1717117

C	9.972895	13.770221	12.646377
C	8.573792	13.698836	12.385629
C	7.777235	14.840528	12.364073
C	8.395409	16.084623	12.571606
C	9.779103	16.180014	12.762747
C	10.573621	15.025195	12.793350
H	6.705190	14.770741	12.190435
H	7.789385	16.987787	12.570381
H	10.244737	17.155905	12.883052
H	11.651883	15.118579	12.910167
C	9.340505	11.501258	12.259484
O	9.304156	10.284259	12.085529
N	8.226231	12.365273	12.179616
H	7.309538	12.022961	11.908909
C	10.455394	12.401121	12.642807
O	13.225859	12.030442	11.975543
S	11.892975	11.722595	13.098975
C	12.354336	12.715917	14.556220
H	13.417129	12.580045	14.780567
H	12.097012	13.774077	14.444028
H	11.745948	12.287363	15.368349
H	13.088619	12.898576	11.550061

Si	16.421009	10.887311	12.068936
H	15.121427	10.976601	12.718486
C	17.173330	12.554253	11.668497
H	17.128170	13.220629	12.539845
H	18.230131	12.415539	11.404078
H	16.684408	13.060338	10.823166
C	16.452339	9.727293	10.604364
H	17.490261	9.445786	10.385455
H	15.886561	8.811798	10.821841
H	16.029078	10.179114	9.695054
Cl	17.529234	10.039919	13.641018

M3

E = -143.16188850

C	10.0457009669	13.7062667690	12.6999703974
C	8.6140865576	13.6380388701	12.5634723673
C	7.8207663235	14.7808165808	12.5243132663
C	8.4624081843	16.0244571060	12.5655361640
C	9.8679827896	16.1215406038	12.6117692982
C	10.6598324343	14.9810711788	12.6824915031
H	6.7332399767	14.7127904815	12.4657419115
H	7.8601823278	16.9355822570	12.5489285131
H	10.3378034330	17.1044183223	12.5880645615
H	11.7469017962	15.0783855944	12.6782313546
C	9.3441760384	11.4525459652	12.5495642934
O	9.3116077299	10.2336059432	12.4578572628
N	8.2299654480	12.3085274804	12.4944532803
H	7.2932271532	11.9688329444	12.2927319396
C	10.5185625835	12.3638672023	12.7812133124
O	14.6876064666	11.6320677083	10.5878960715
S	11.9970455576	11.6151739352	13.1916744693
C	12.8161989912	12.8074577446	14.2840415757
H	13.8780578322	12.5354737703	14.2757269333
H	12.6971609180	13.8396526752	13.9513109084
H	12.3996001043	12.6856522615	15.2917762254
H	13.8334235319	11.7788066064	11.0263484901

Si	15.9367495900	11.2564883349	11.6975180775
H	14.8095096140	10.8868123119	12.7444342691
C	16.7720987493	12.8397671354	12.2781023038
H	16.4251004920	13.1761367714	13.2636021914
H	17.8532312387	12.6653513004	12.3653832234
H	16.6133202688	13.6489742668	11.5510424075
C	17.0221904256	10.2931070918	10.5144143154
H	18.0565634086	10.2370850827	10.8753019192
H	16.6483678115	9.2692200499	10.3811871262
H	16.9960050189	10.7956022714	9.5350679893
Cl	16.6745353447	9.8874820699	13.5701373462

TS-3

E = -143.14774841

C	10.075771	13.731643	12.964589
C	8.830749	13.540984	12.258614
C	8.085575	14.623604	11.796099
C	8.614800	15.909464	11.978131
C	9.878777	16.116129	12.574732
C	10.607525	15.041816	13.075569
H	7.122111	14.474813	11.312180
H	8.047693	16.769300	11.623605
H	10.282208	17.127235	12.633183
H	11.592292	15.202785	13.513029
C	9.622299	11.434776	12.750484
O	9.679317	10.211468	12.773897
N	8.583401	12.185361	12.153159
H	7.829979	11.738680	11.635449
C	10.551642	12.449059	13.340797
O	14.768188	12.113275	9.854073
S	11.775099	11.965881	14.438228
C	11.689800	13.312491	15.672690
H	12.129368	12.890348	16.584135
H	12.244467	14.209298	15.379951
H	10.633620	13.552516	15.850075
H	13.997575	12.667780	10.056841

Si	15.627151	11.510151	11.192983
H	14.508102	11.066036	12.121542
C	16.617044	12.877738	12.035499
H	16.173292	13.163451	12.999764
H	17.630396	12.496544	12.233380
H	16.690187	13.760680	11.385052
C	16.719398	10.214804	10.406443
H	17.604630	10.041759	11.033439
H	16.191402	9.257705	10.289362
H	17.028942	10.575122	9.414047
Cl	15.853359	9.910312	13.539736

Product

E = -143.28776548

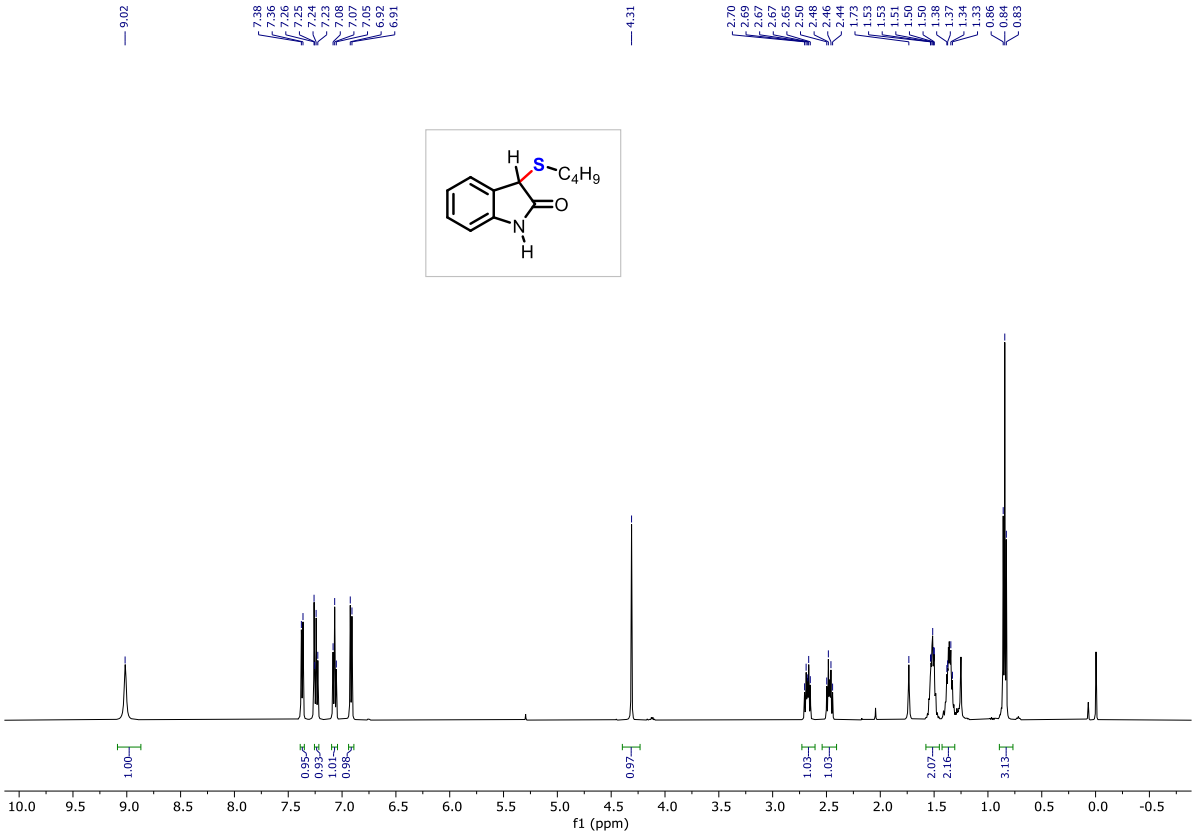
C	10.3060484133	13.6636976025	12.3246885964
C	8.9015671719	13.5845634611	12.4251933035
C	8.1020043504	14.7220015482	12.5131811480
C	8.7460265625	15.9688831068	12.5197544847
C	10.1403388885	16.0657603552	12.4398358584
C	10.9290387256	14.9072375287	12.3377048928
H	7.0175692331	14.6474001776	12.5758311633
H	8.1457388946	16.8740371695	12.5913401343
H	10.6150469481	17.0445656584	12.4575227222
H	12.0146900485	14.9758461950	12.2809592603
C	9.5961057431	11.3627724318	12.3580435489
O	9.5320482706	10.1484938406	12.3718787950
N	8.5132145940	12.2376497306	12.4254989512
H	7.5588812309	11.8977139748	12.5012593739
C	10.8573885803	12.2650032211	12.2429971157
O	14.6447225602	11.5499933174	11.2101525486
S	12.1933736448	11.7974227945	13.4147217666
C	11.8432230265	12.8322034597	14.8674356720
H	12.5696481724	12.5100565658	15.6254199080
H	11.9810071454	13.8985978577	14.6565365423
H	10.8306953254	12.6519845168	15.2486753332
H	14.0415531156	11.8181871311	11.9380184624

Si	16.2095010486	11.2184716231	11.6053795070
H	11.3083940724	12.0600115308	11.2585931926
C	17.1411163240	12.7673250379	12.0500088696
H	16.7027338614	13.2512861000	12.9329635005
H	18.1933196845	12.5464566963	12.2733714170
H	17.1048430501	13.4826744755	11.2162794594
C	16.9755388700	10.2864318271	10.1931024823
H	18.0267704498	10.0557396180	10.4141762372
H	16.4502717777	9.3398539059	10.0109387057
H	16.9426968188	10.8819371909	9.2697925377
Cl	16.2488632248	9.9921241905	13.2989561360

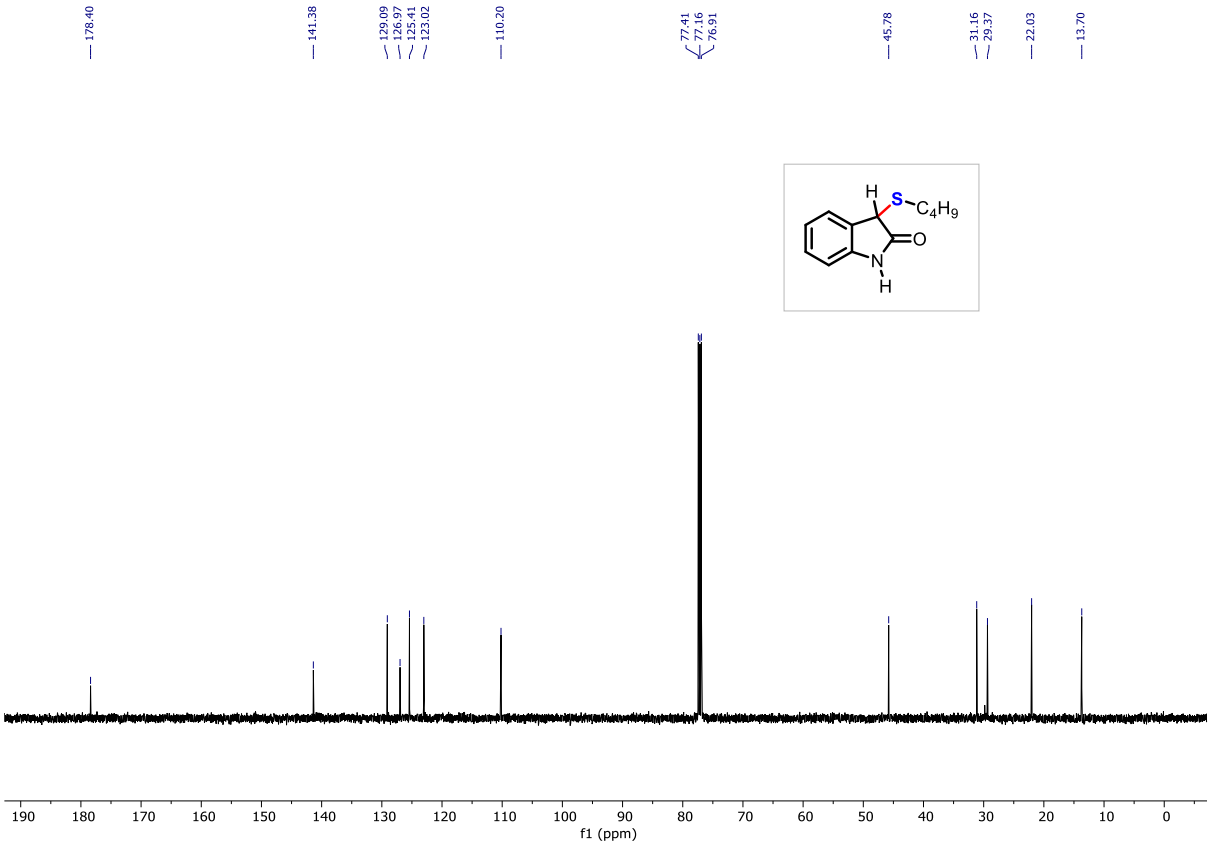
9. Copies of ^{1}H and ^{13}C $\{^{1}H\}$ NMR Spectra of Starting Materials and Products

3-(Butylthio) indolin-2-one (4a)

^{1}H NMR (500 MHz, $CDCl_3$)

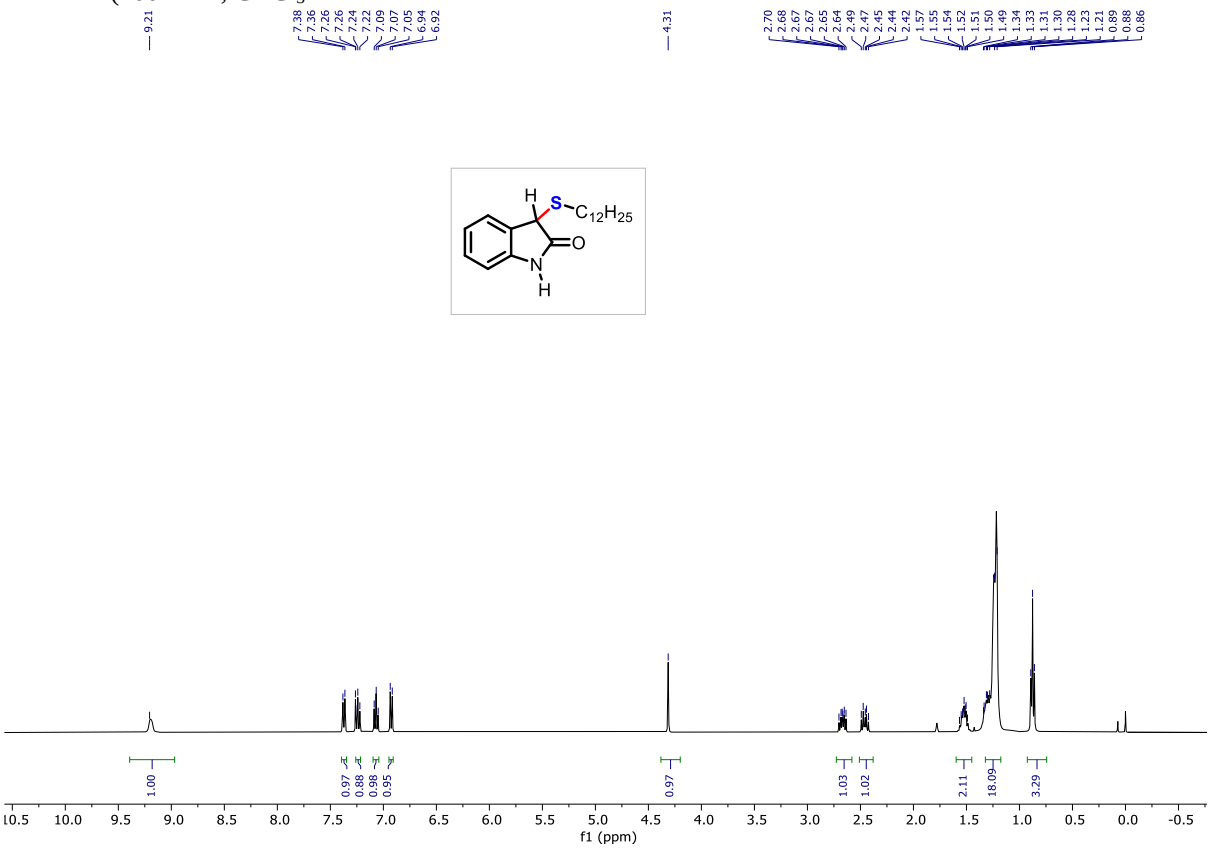


$^{13}C\{^{1}H\}$ NMR (126 MHz $CDCl_3$)

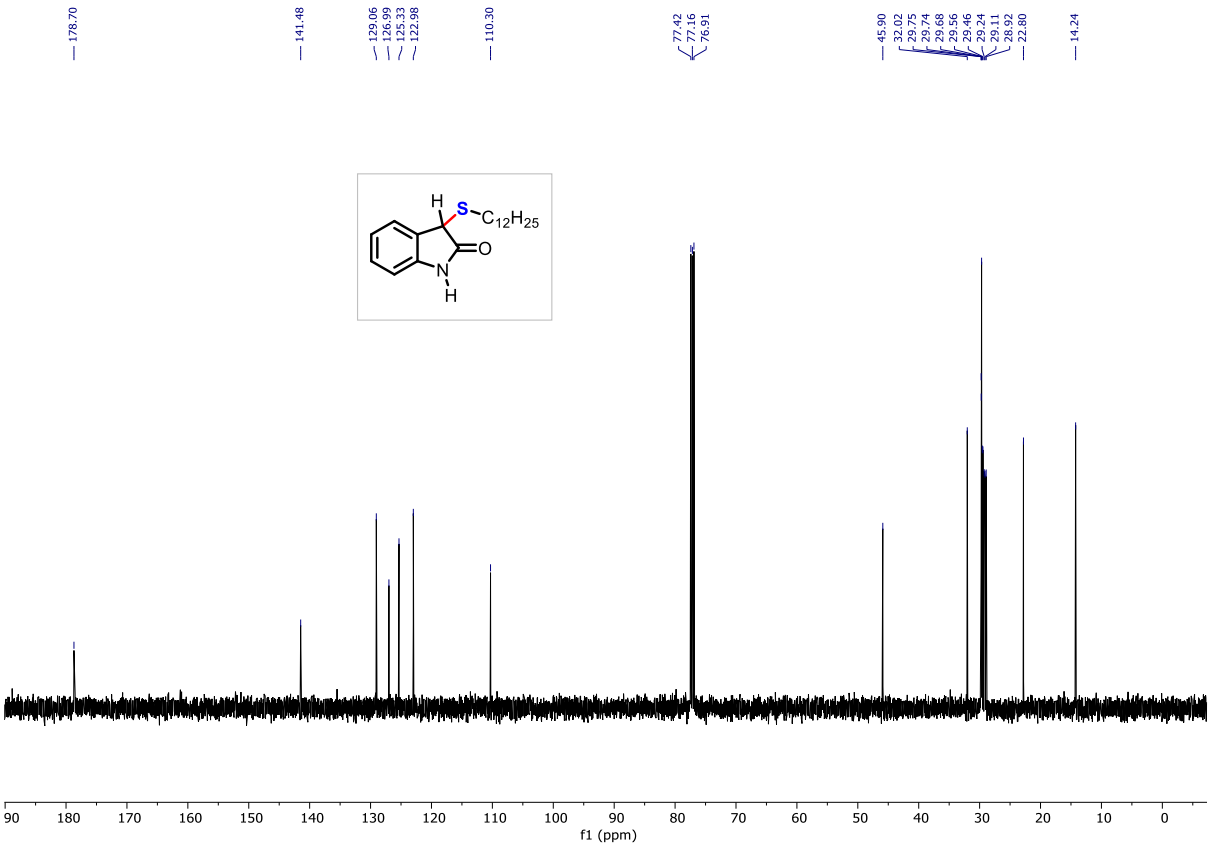


3-(Dodecylthio) Indolin-2-one (4b)

^{1}H NMR (400 MHz, $CDCl_3$

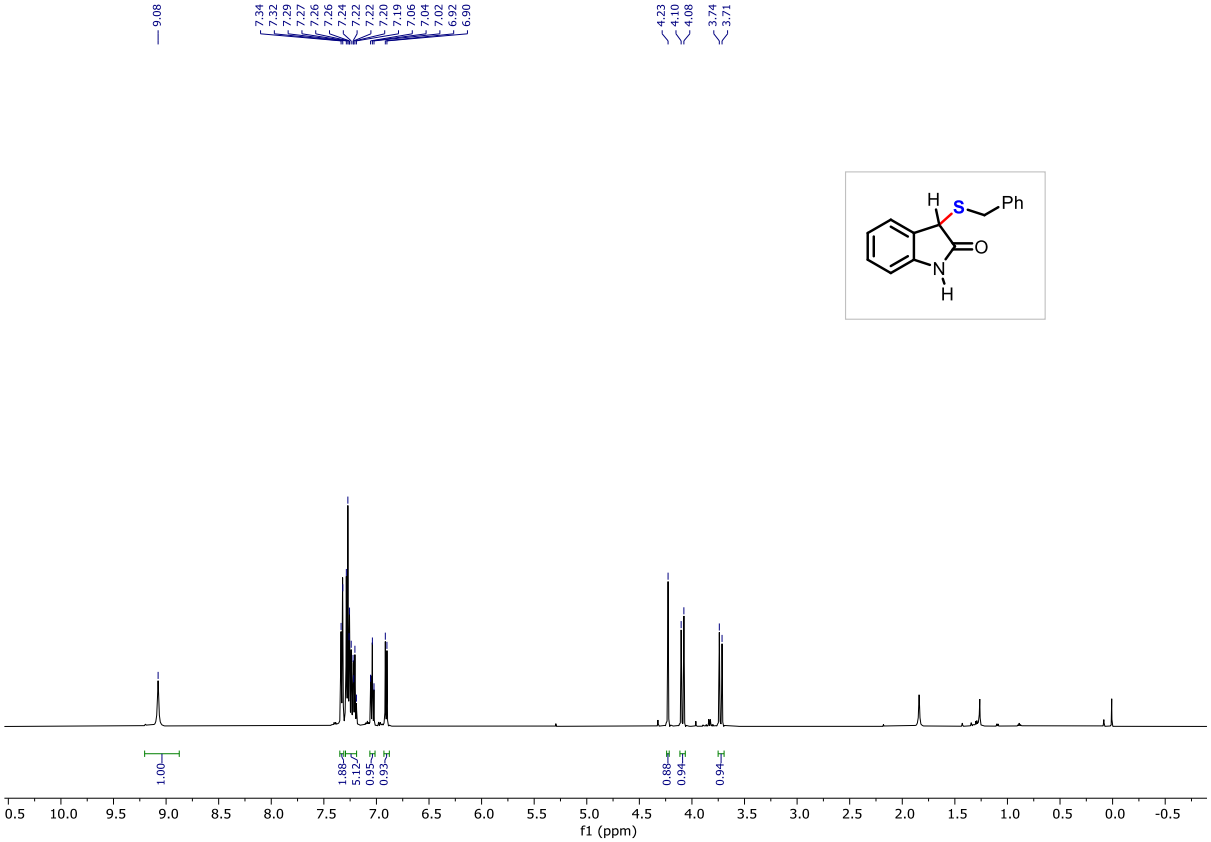


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

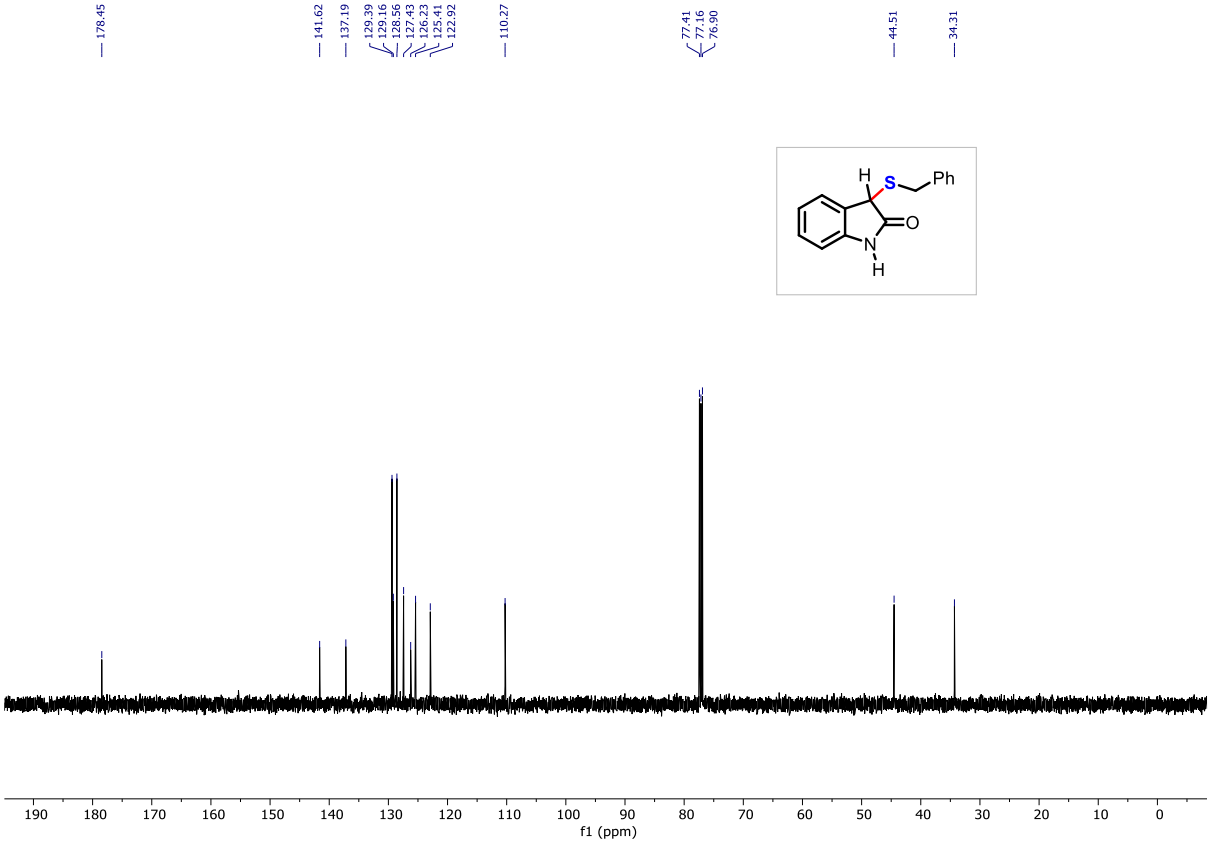


3-(Benzylthio) indolin-2-one (4c)

^{1}H NMR (500 MHz, $CDCl_3$)

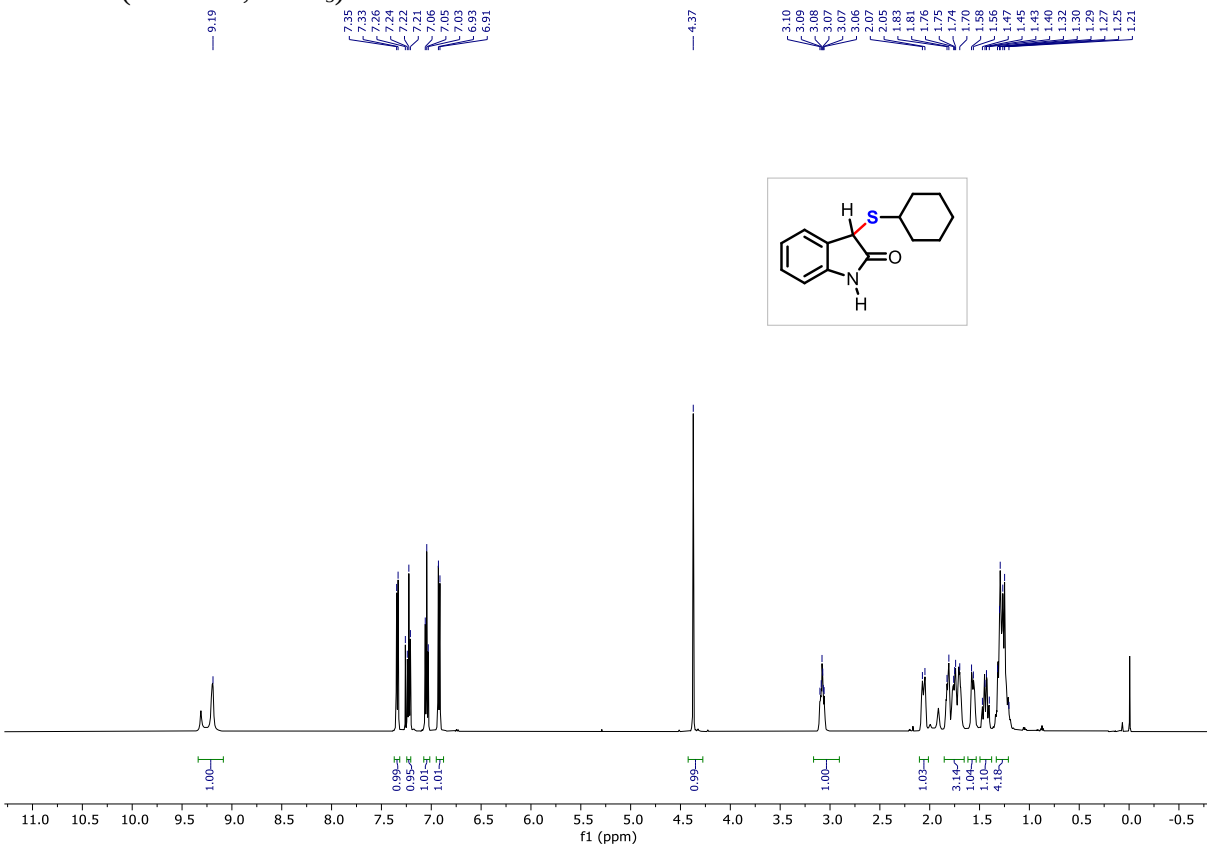


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

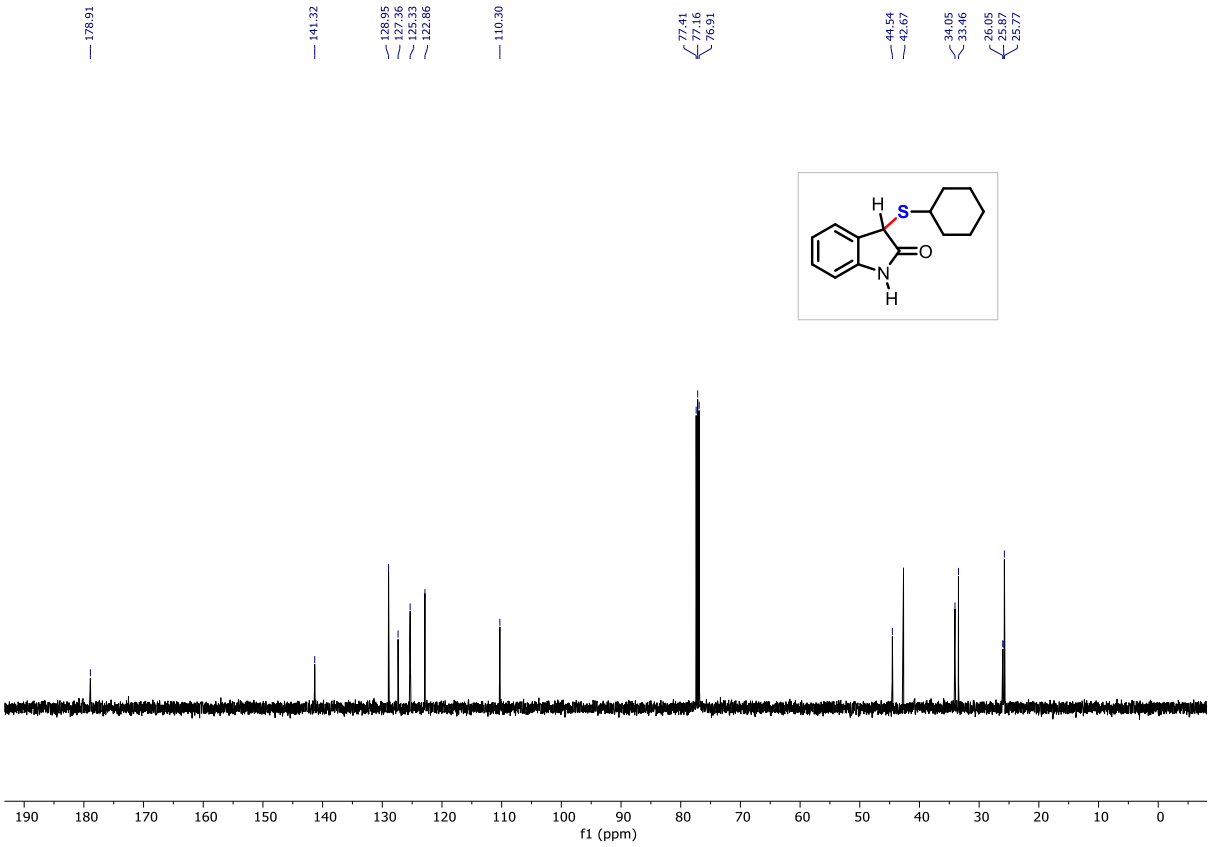


3-(Cyclohexylthio) indolin-2-one (4d)

^{1}H NMR (500 MHz, $CDCl_3$)

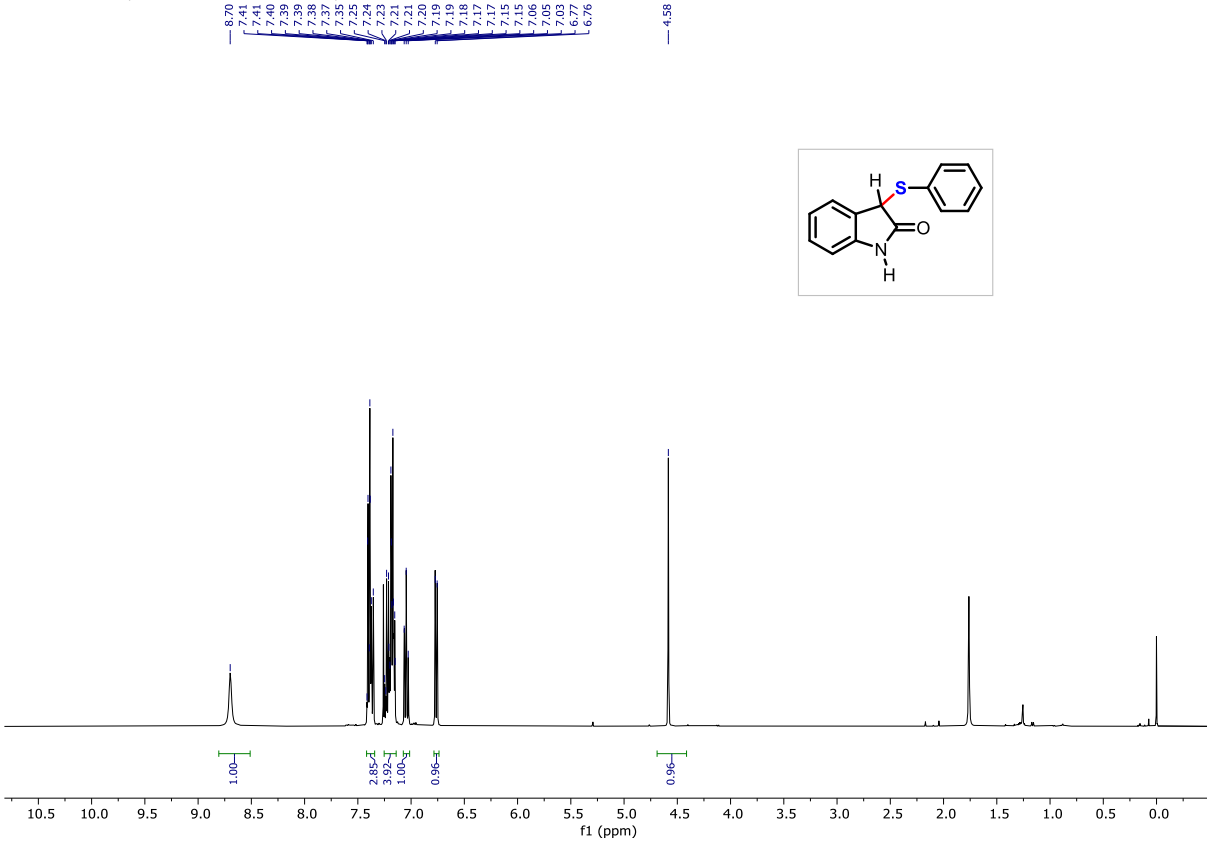


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

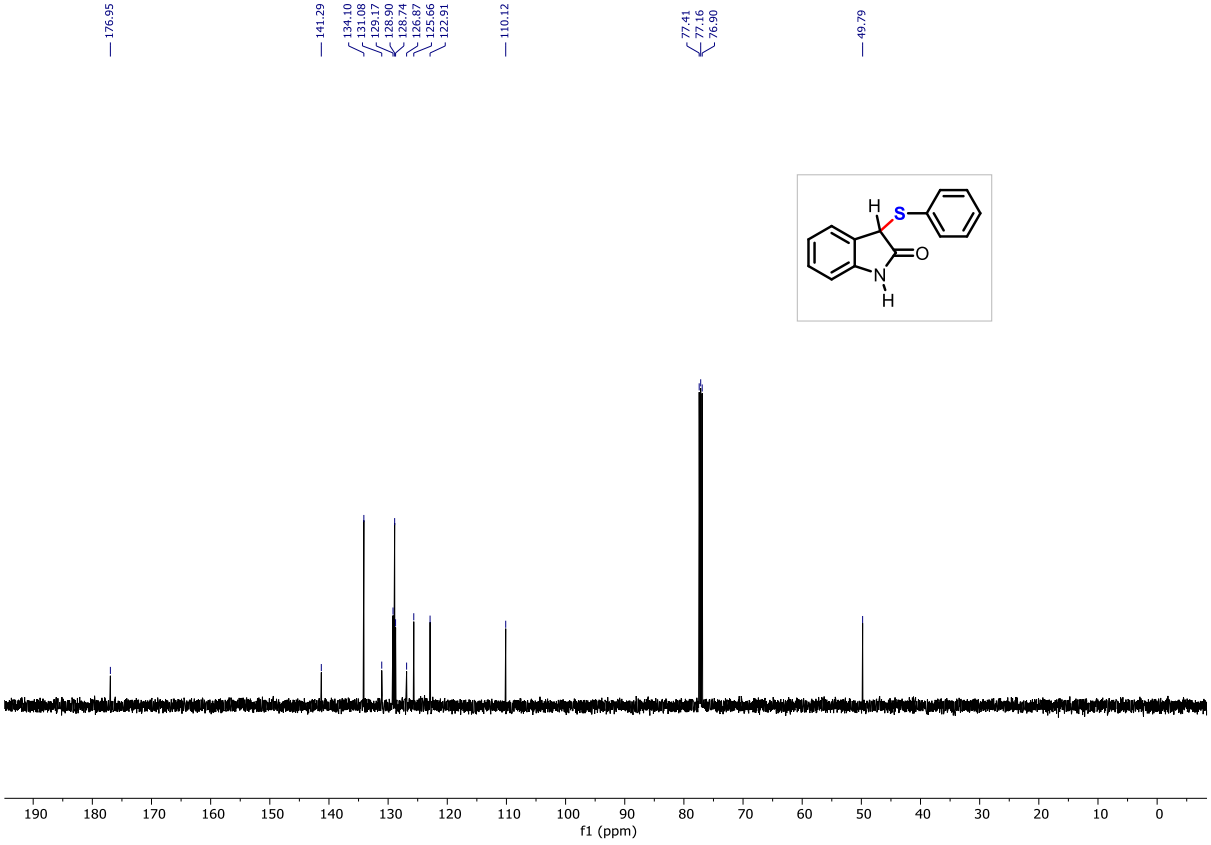


3-(Phenylsulfanyl) indolin-2-one (4e)

^{1}H NMR (500 MHz, $CDCl_3$)

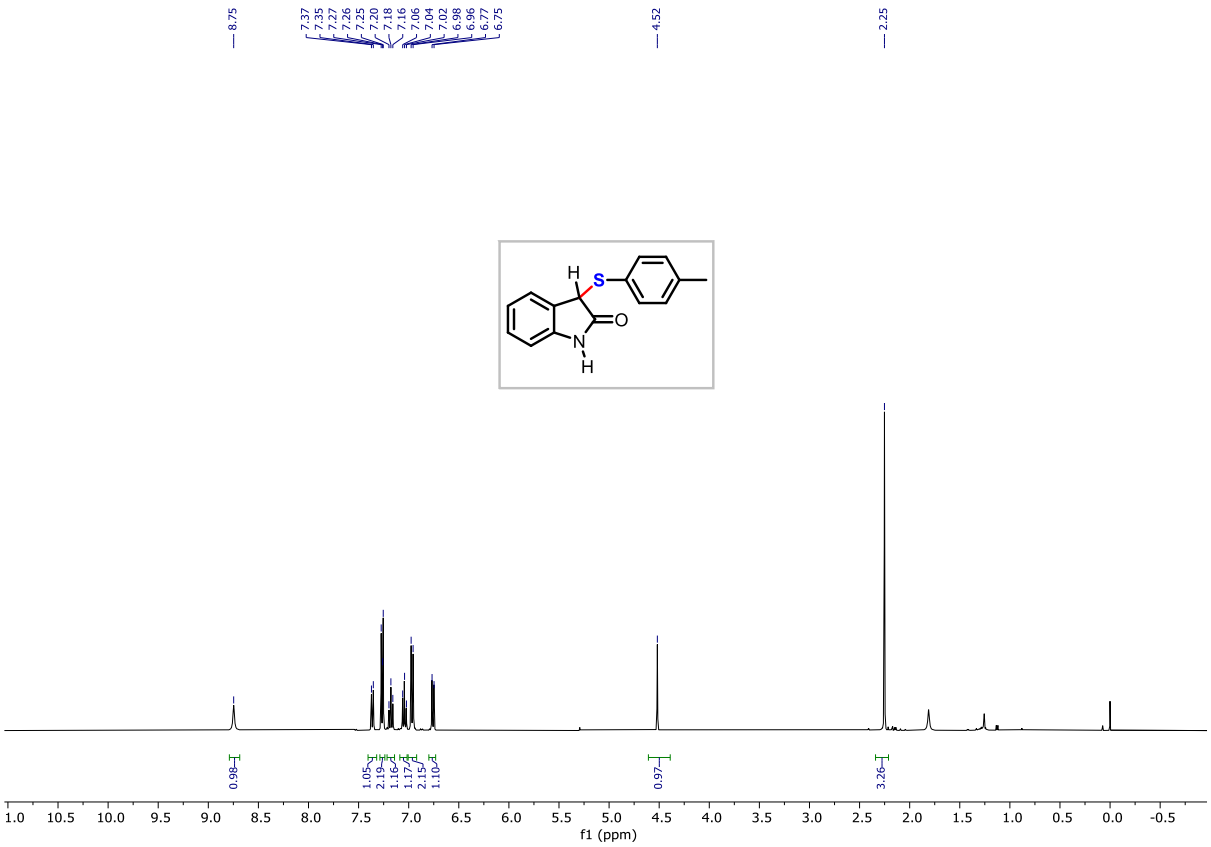


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

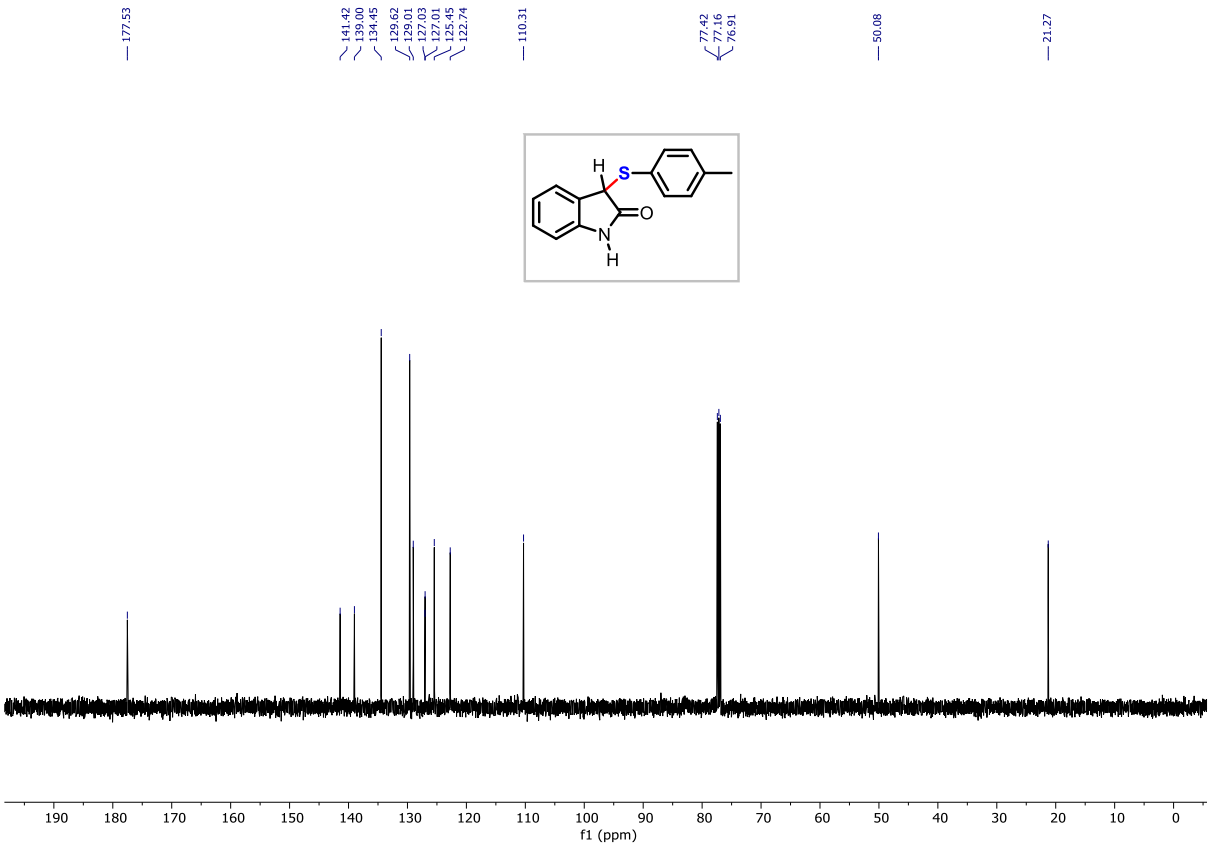


3-(*p*-Tolylthio) indolin-2-one (4f)

^{1}H NMR (500 MHz, $CDCl_3$)

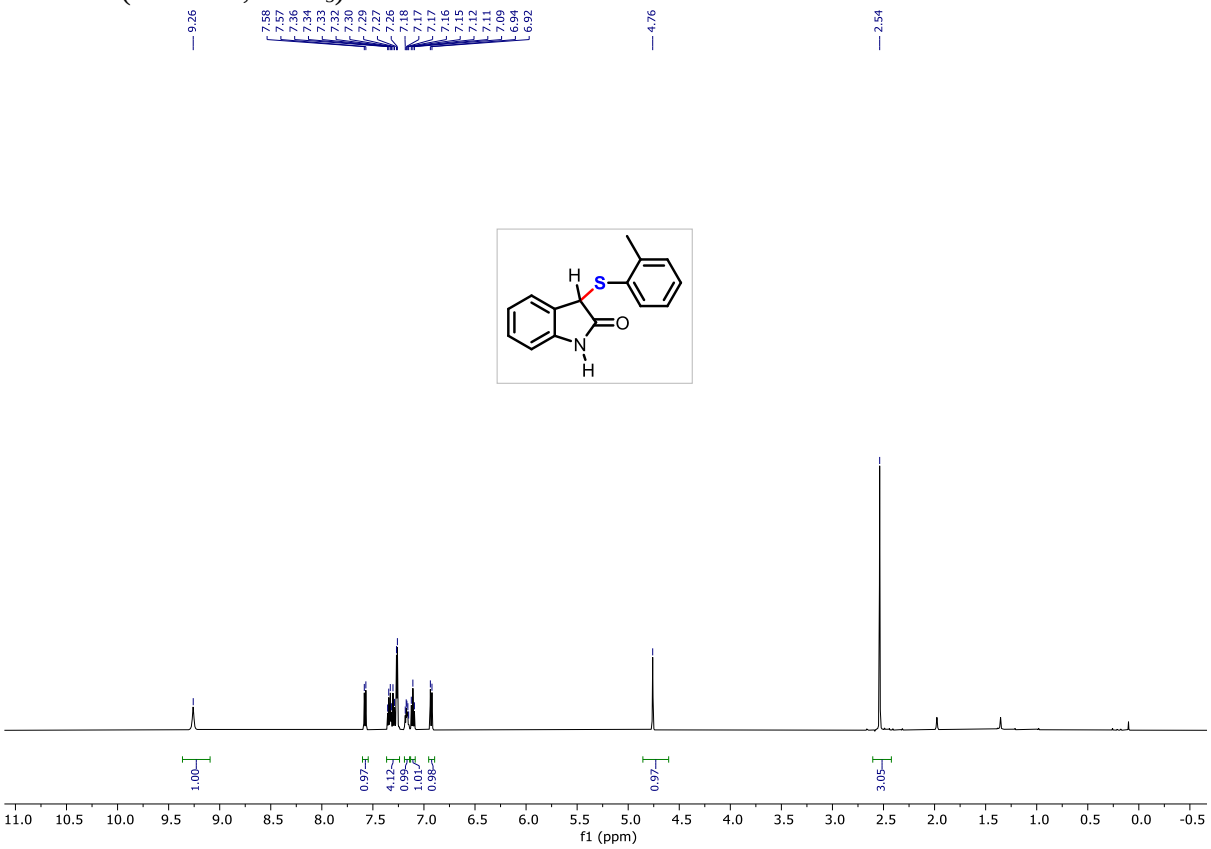


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

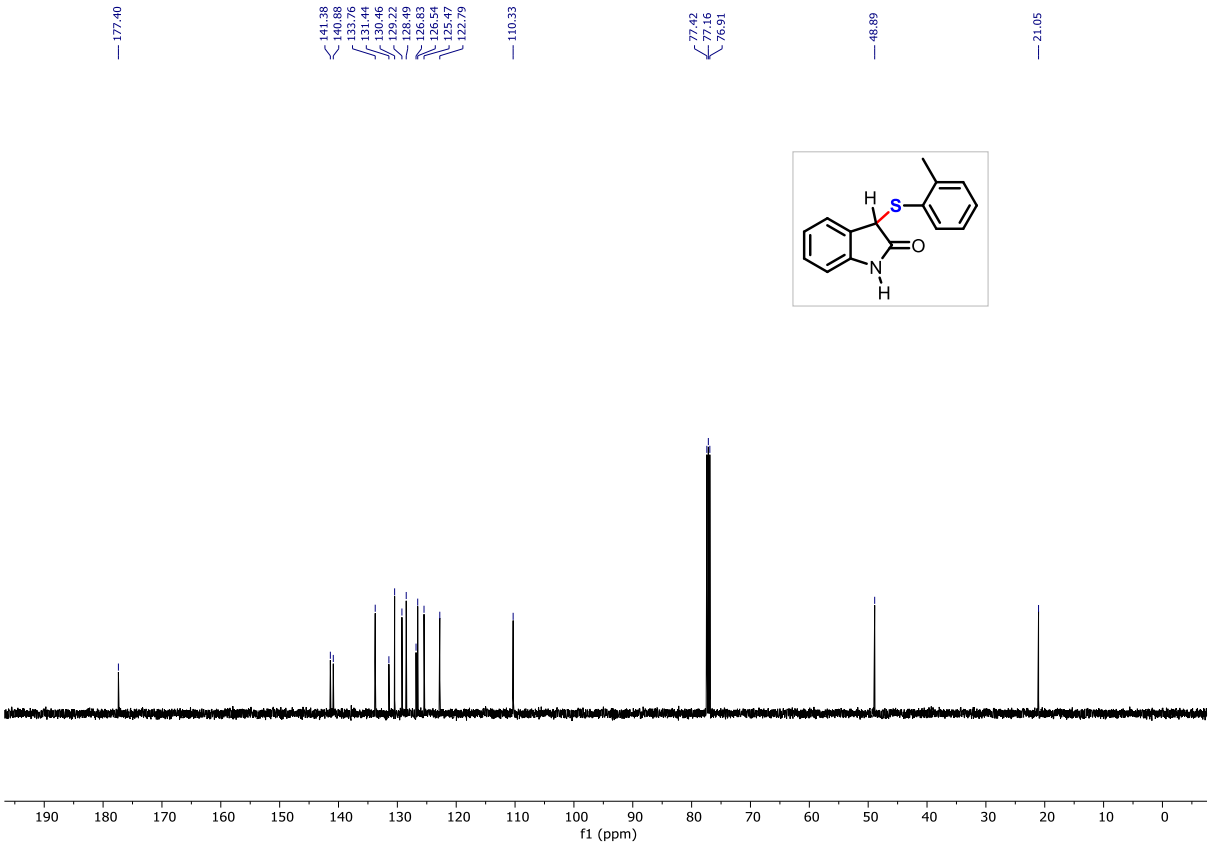


3-(o-Tolylthio) indolin-2-one (4g)

^{1}H NMR (500 MHz, $CDCl_3$)

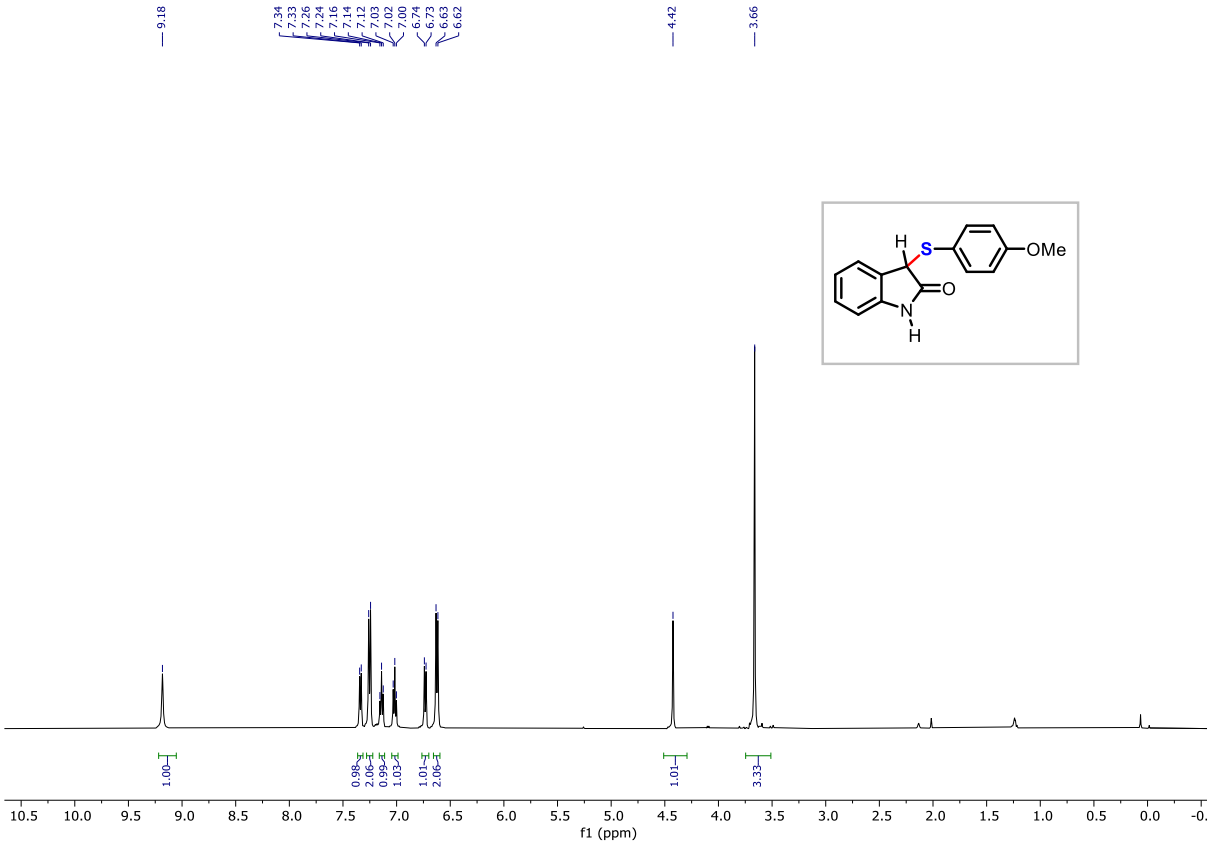


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

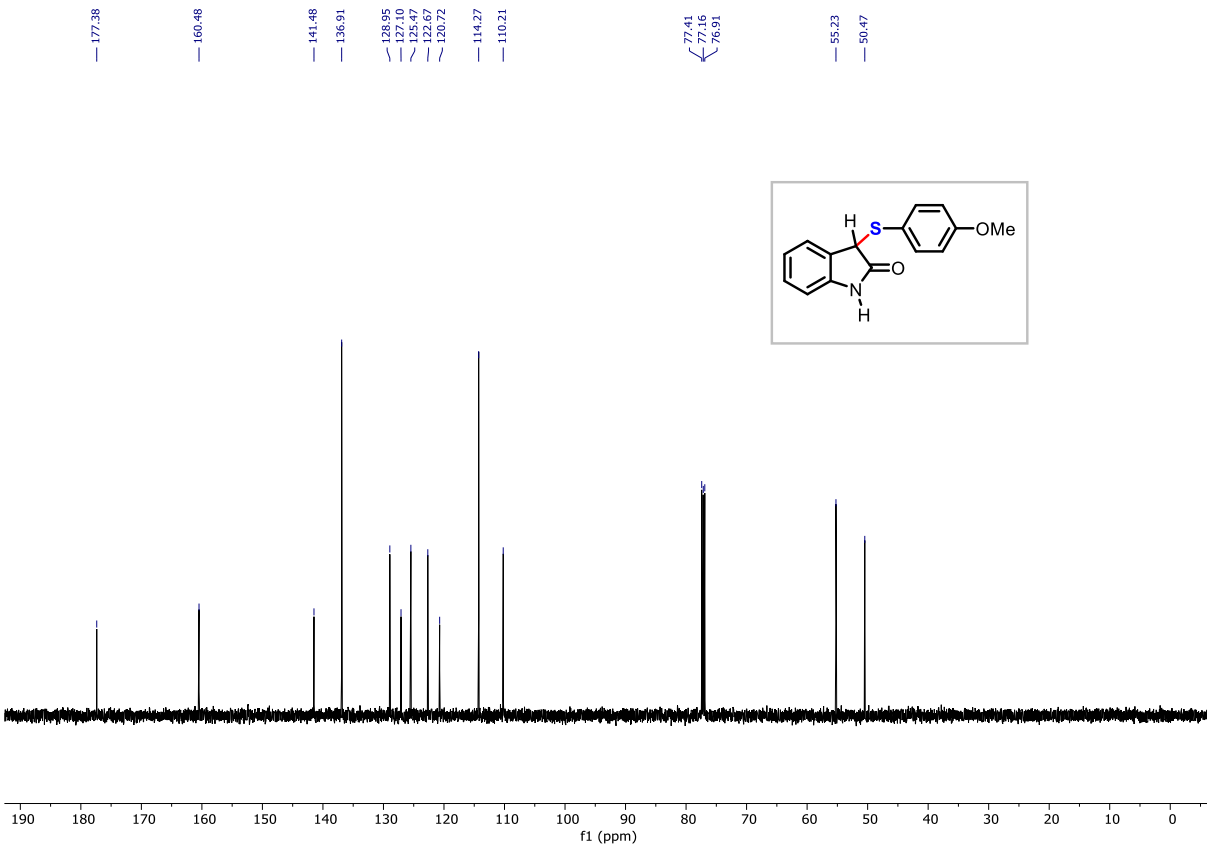


3-((4-Methoxyphenyl) thio) indolin-2-one (4h)

^{1}H NMR (500 MHz, $CDCl_3$)

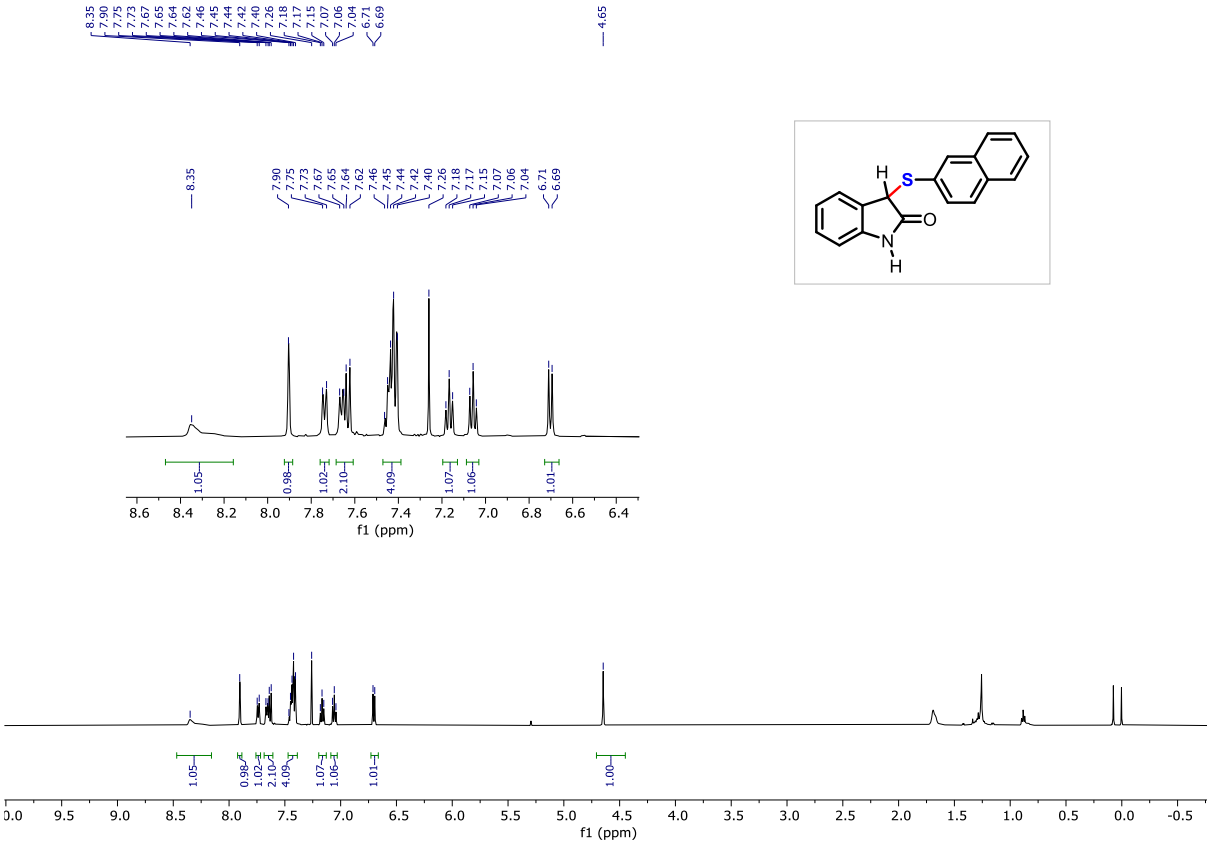


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

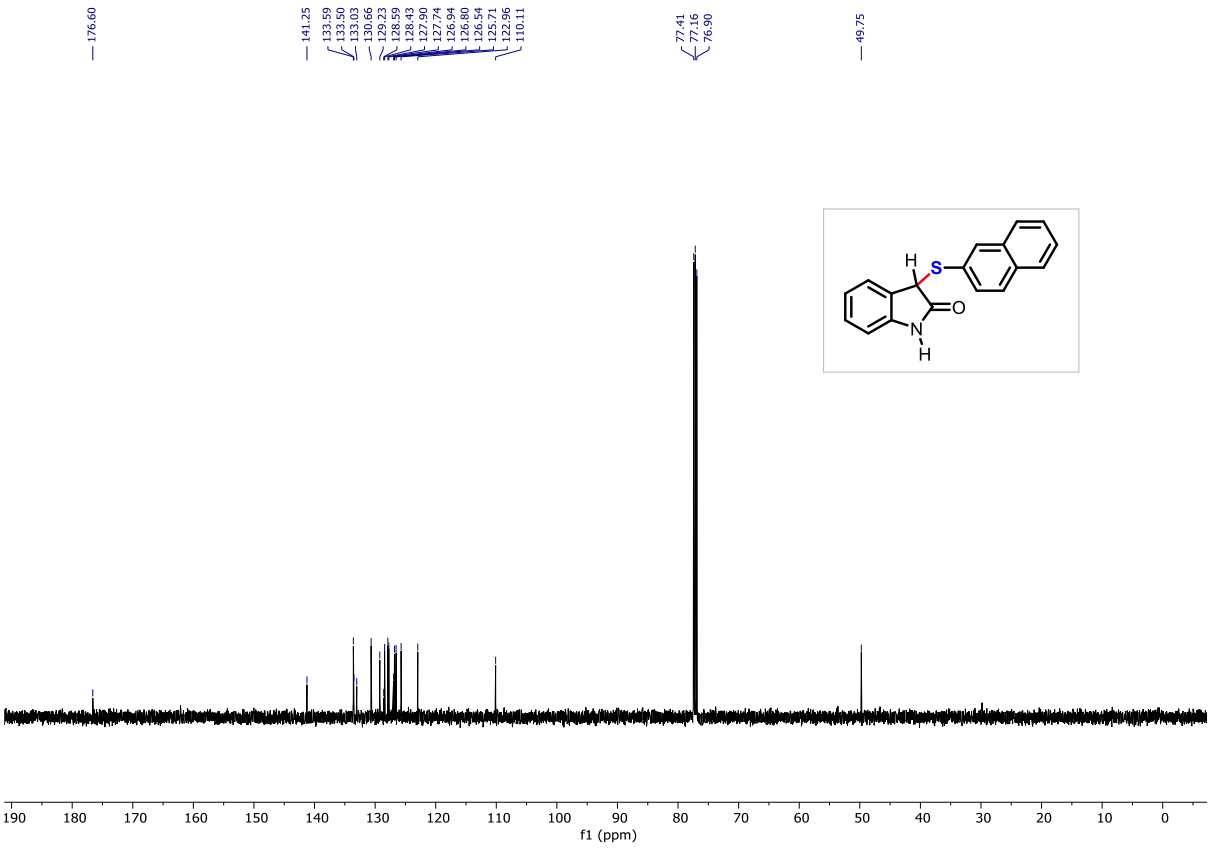


3-(Naphthalen-2-ylthio) indolin-2-one (4i)

^{1}H NMR (500 MHz, $CDCl_3$)

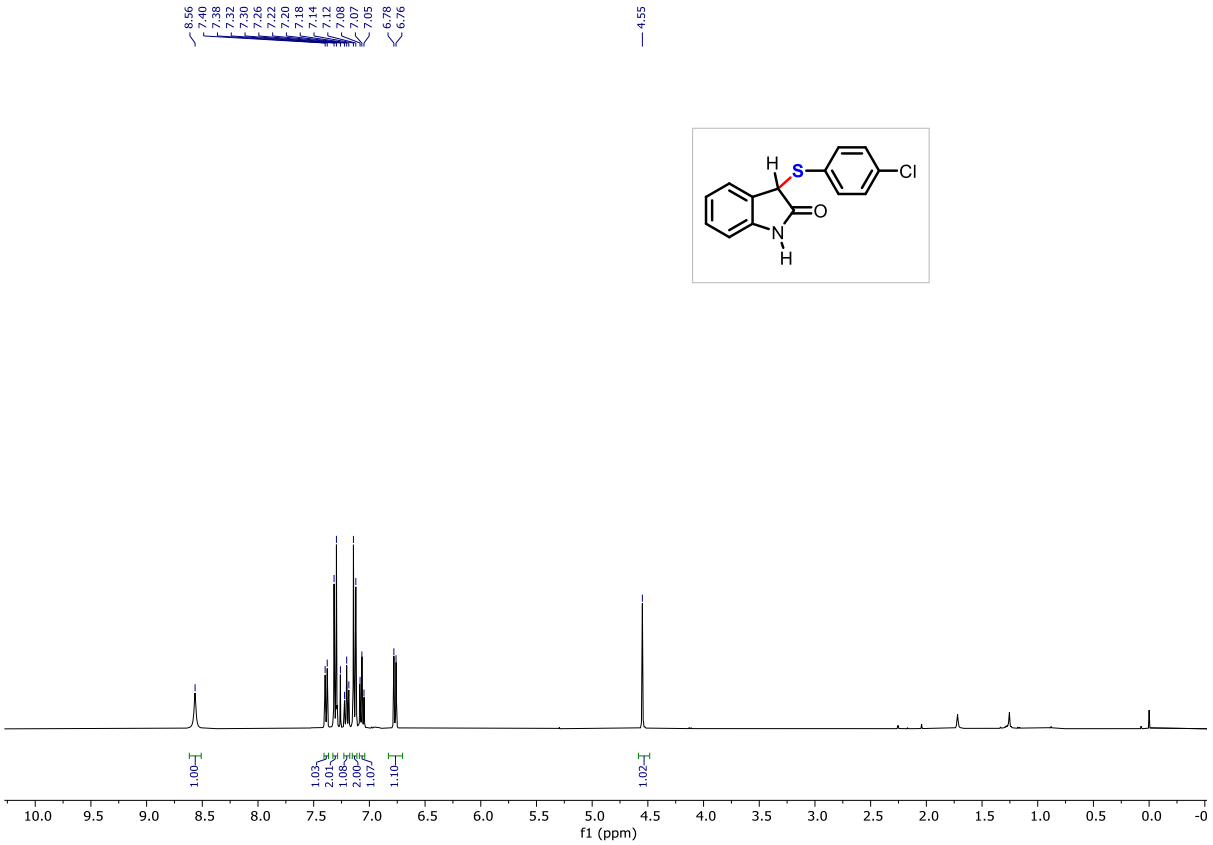


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

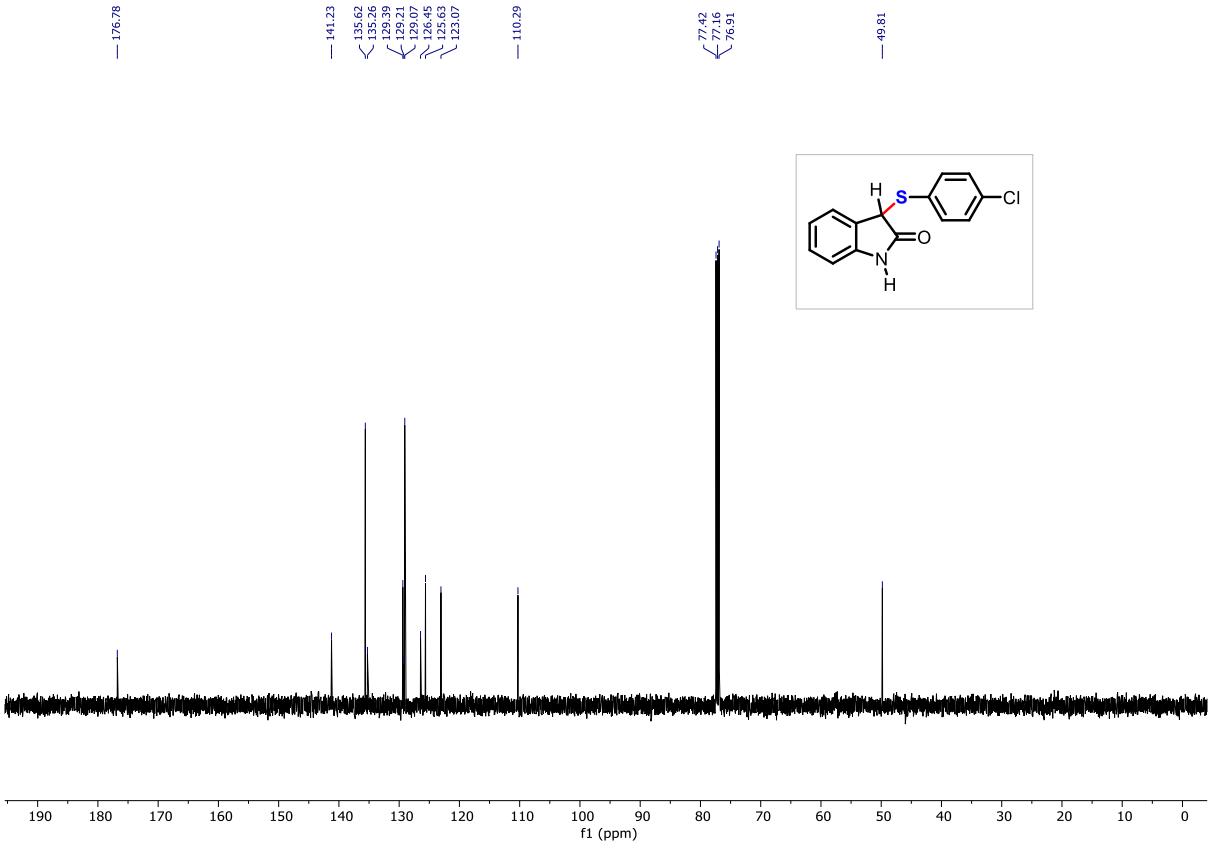


3-((4-Chlorophenyl) thio) indolin-2-one (4j)

^{1}H NMR (400 MHz, $CDCl_3$)

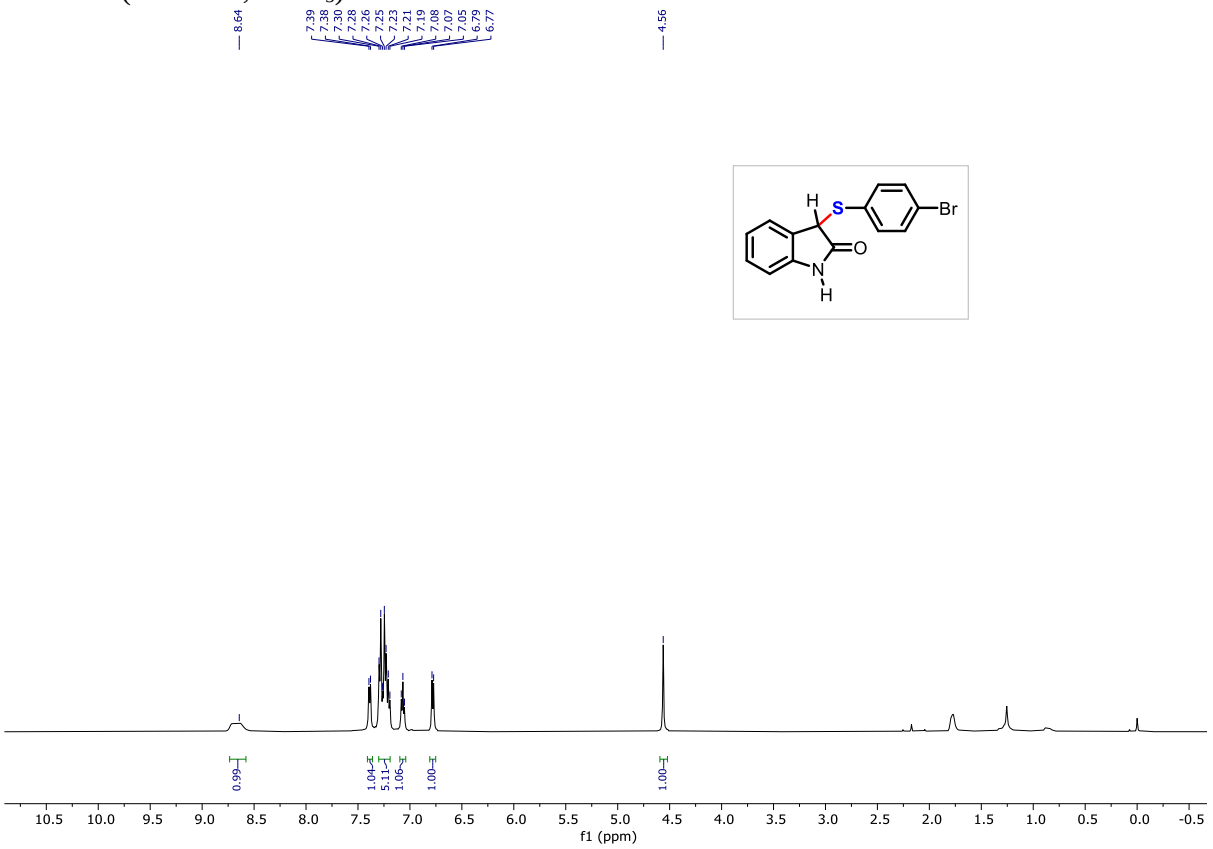


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

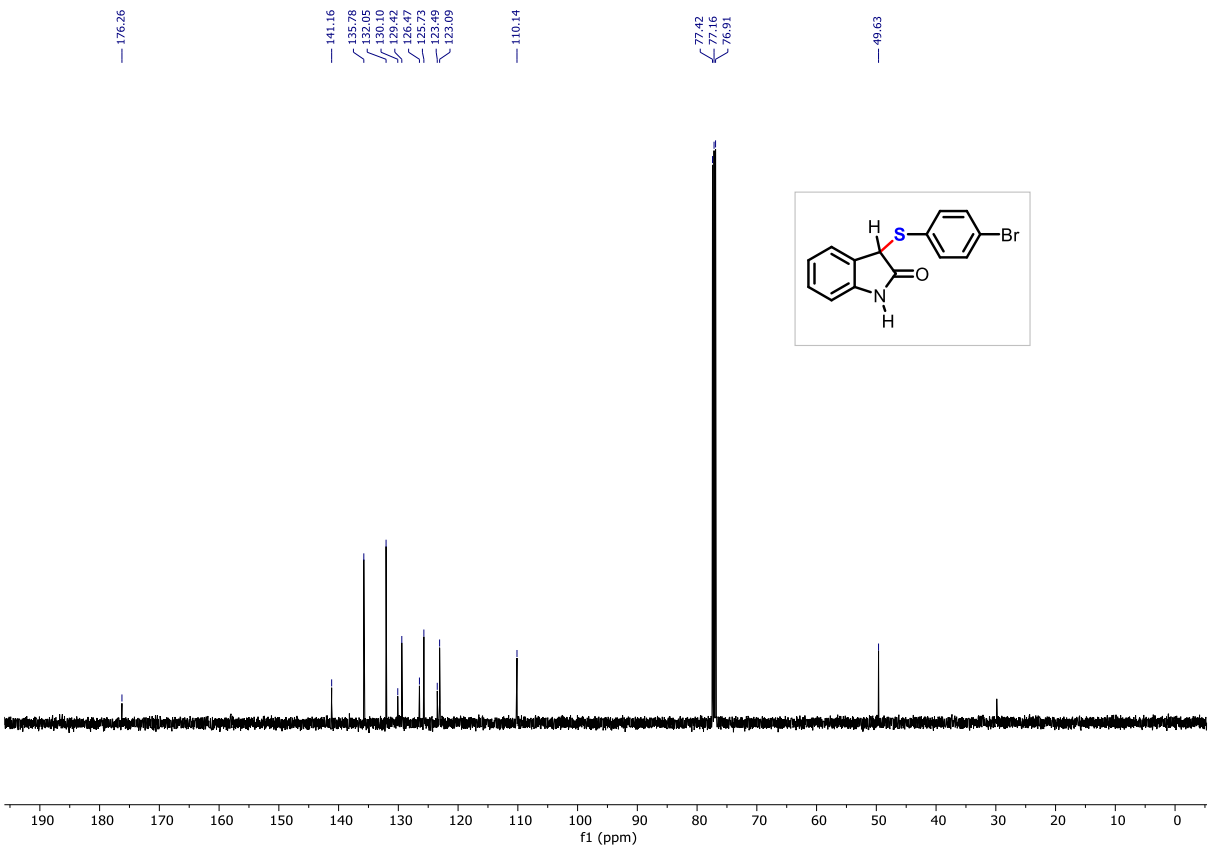


3-((4-Bromophenyl) thio) indolin-2-one (4k)

^{1}H NMR (500 MHz, $CDCl_3$)

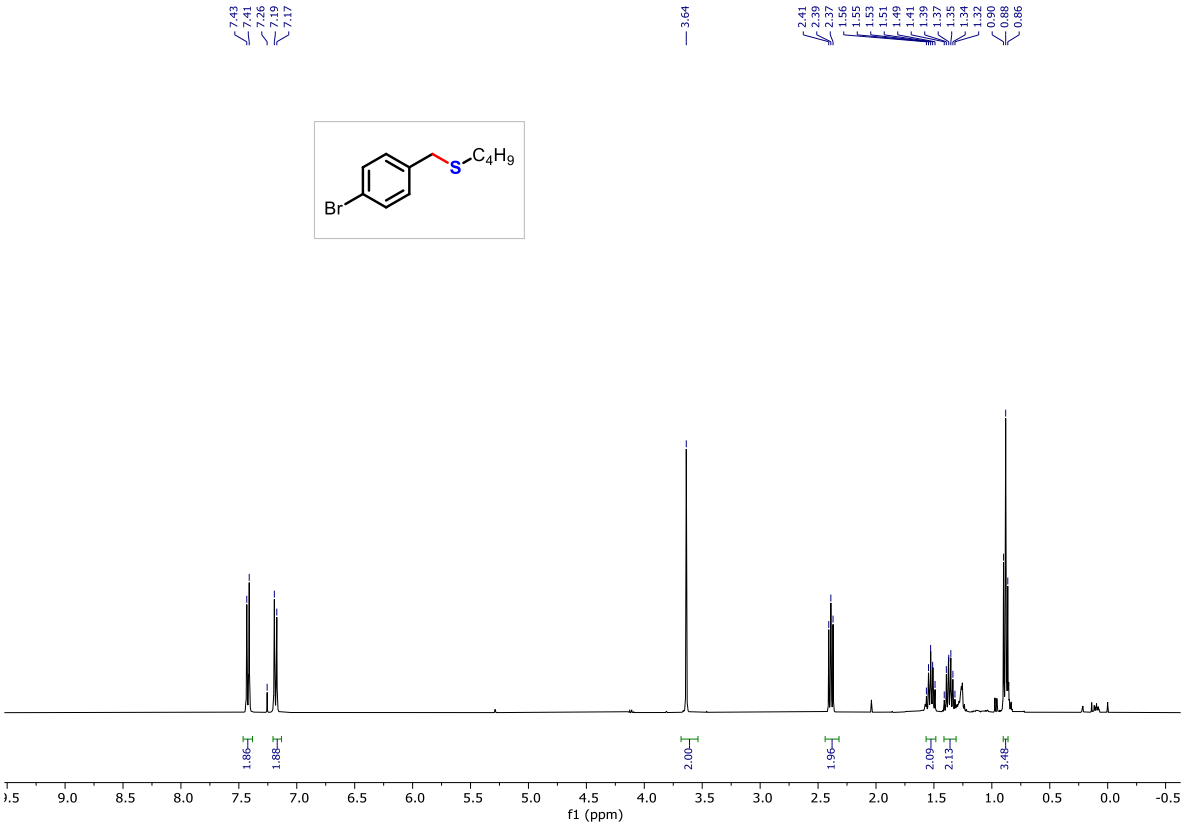


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

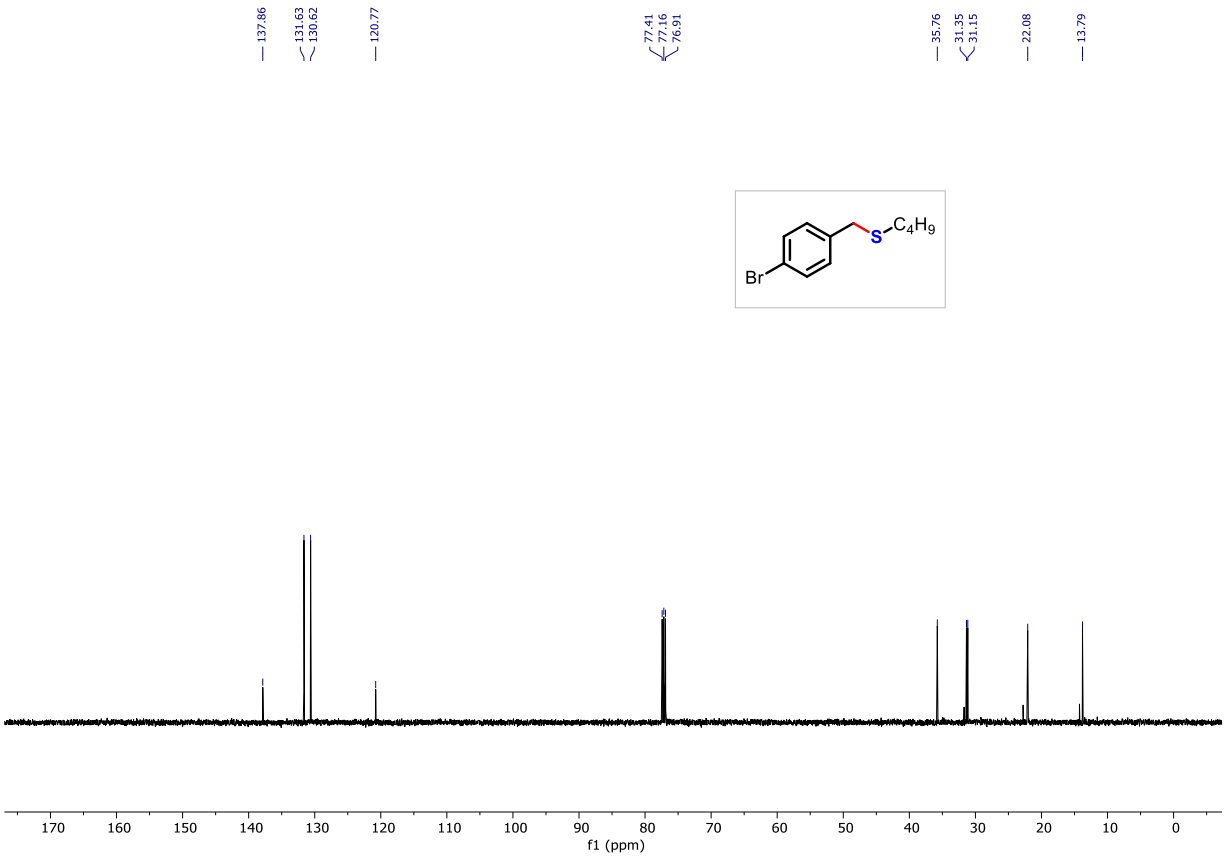


4-Bromobenzyl) (butyl)sulfane (4l)

^{1}H NMR (500 MHz, $CDCl_3$)

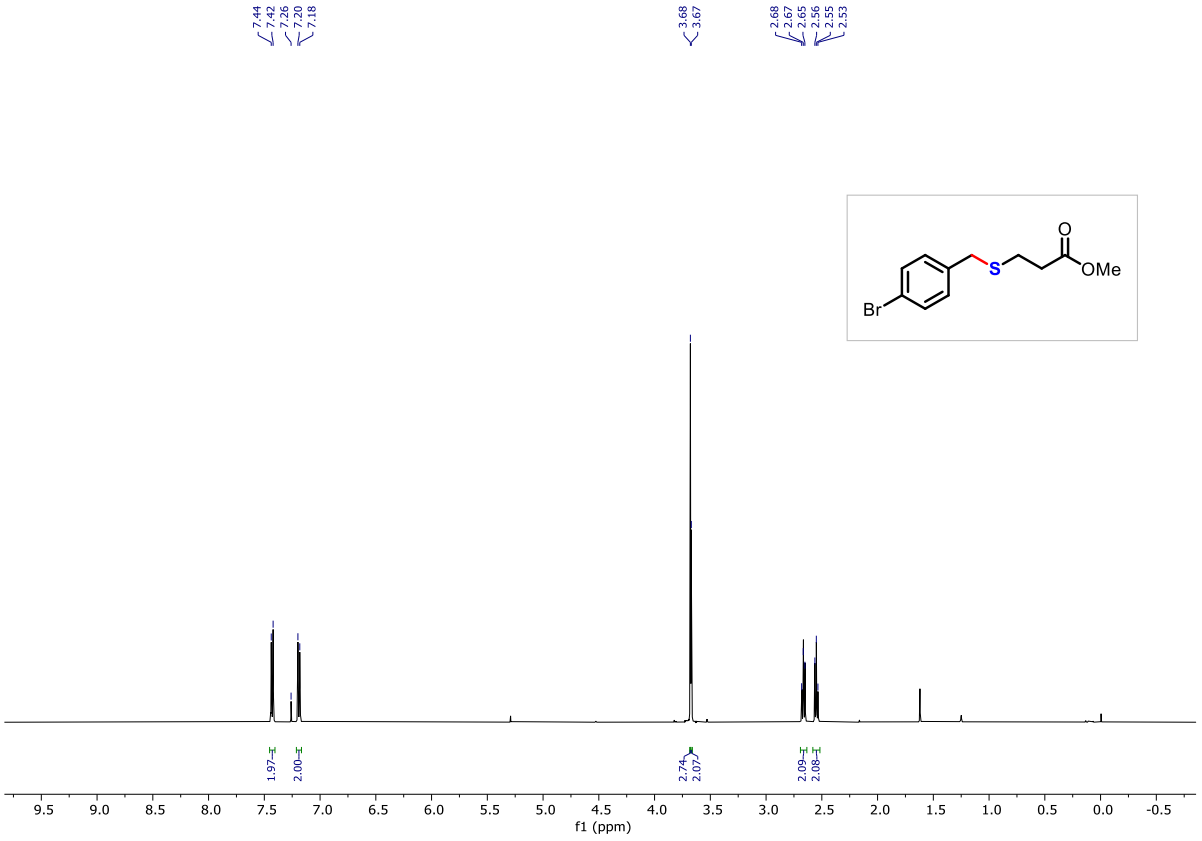


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

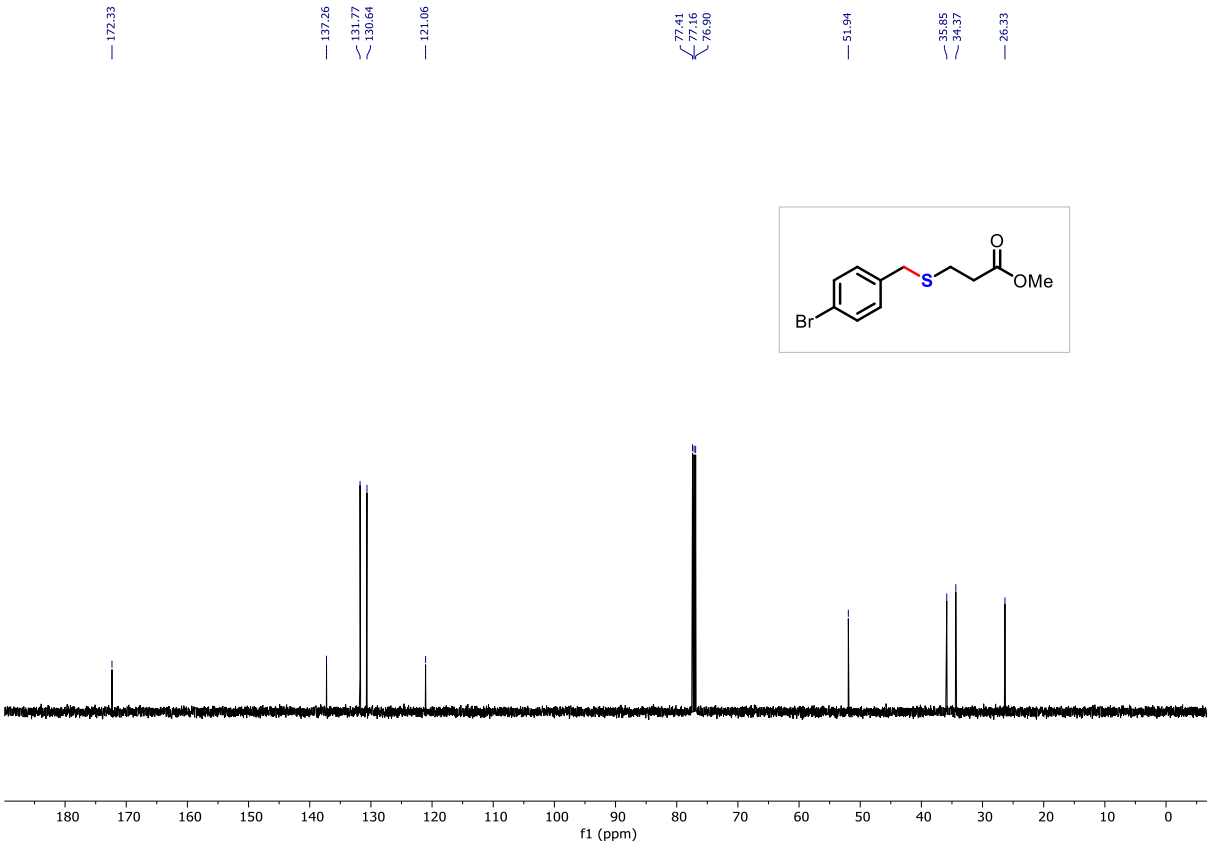


Methyl 3-((4-bromobenzyl) thio) propanoate (4m)

^{1}H NMR (500 MHz, $CDCl_3$)

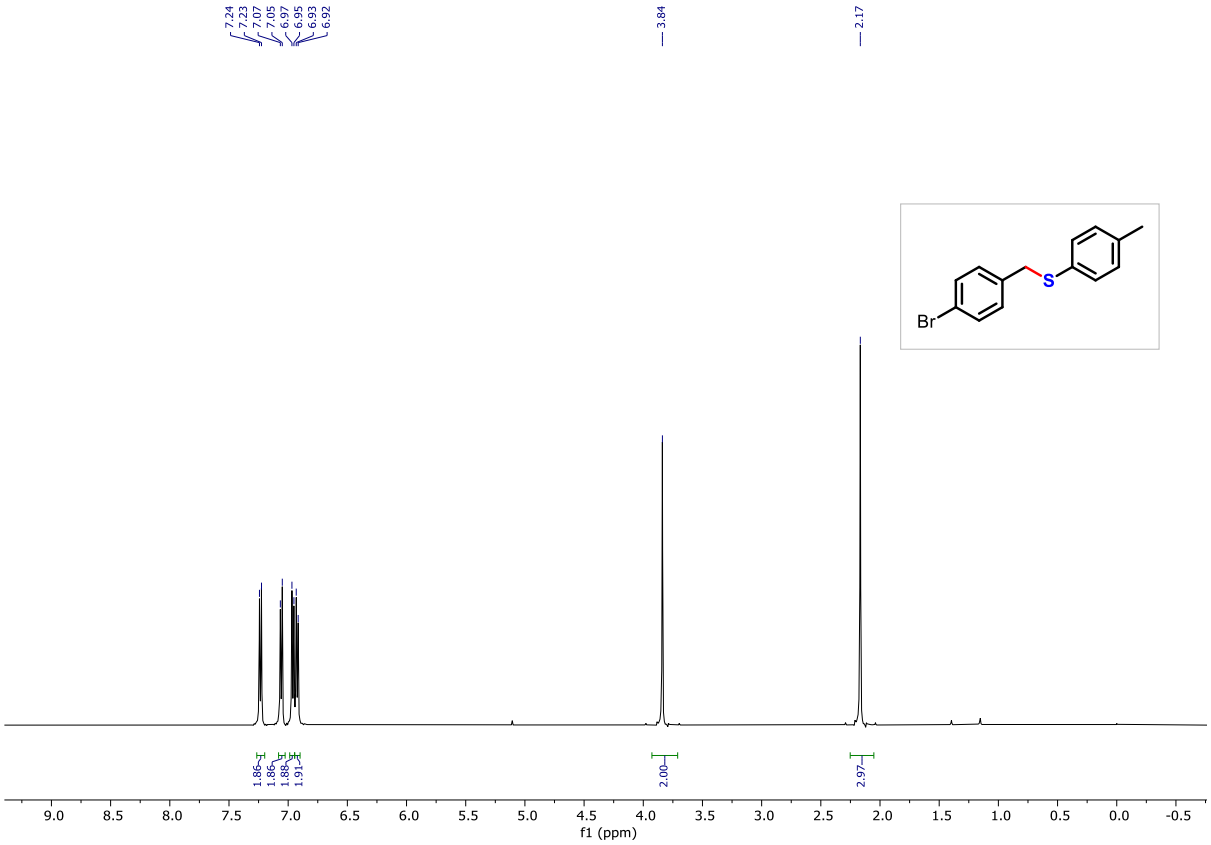


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

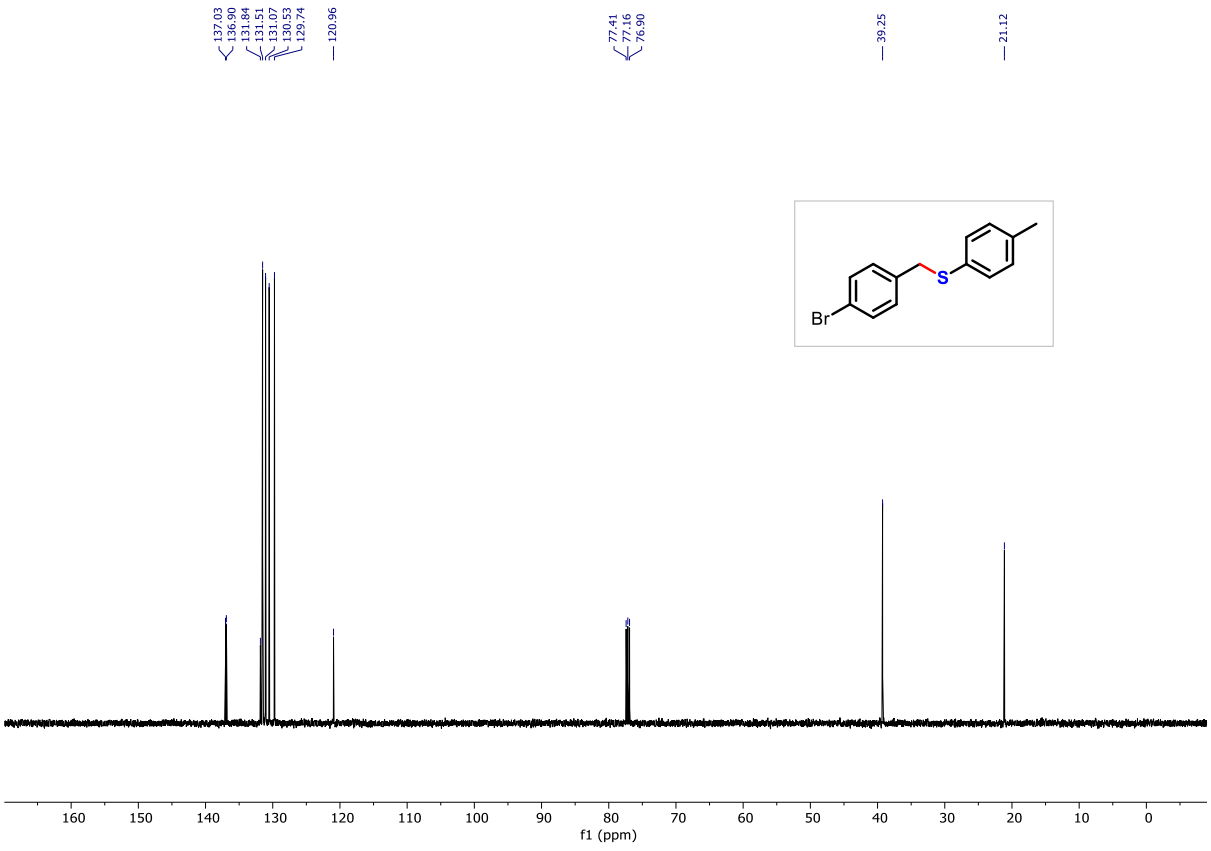


(4-Bromobenzyl) (*p*-tolyl) sulfane (4n)

^{1}H NMR (500 MHz, $CDCl_3$)

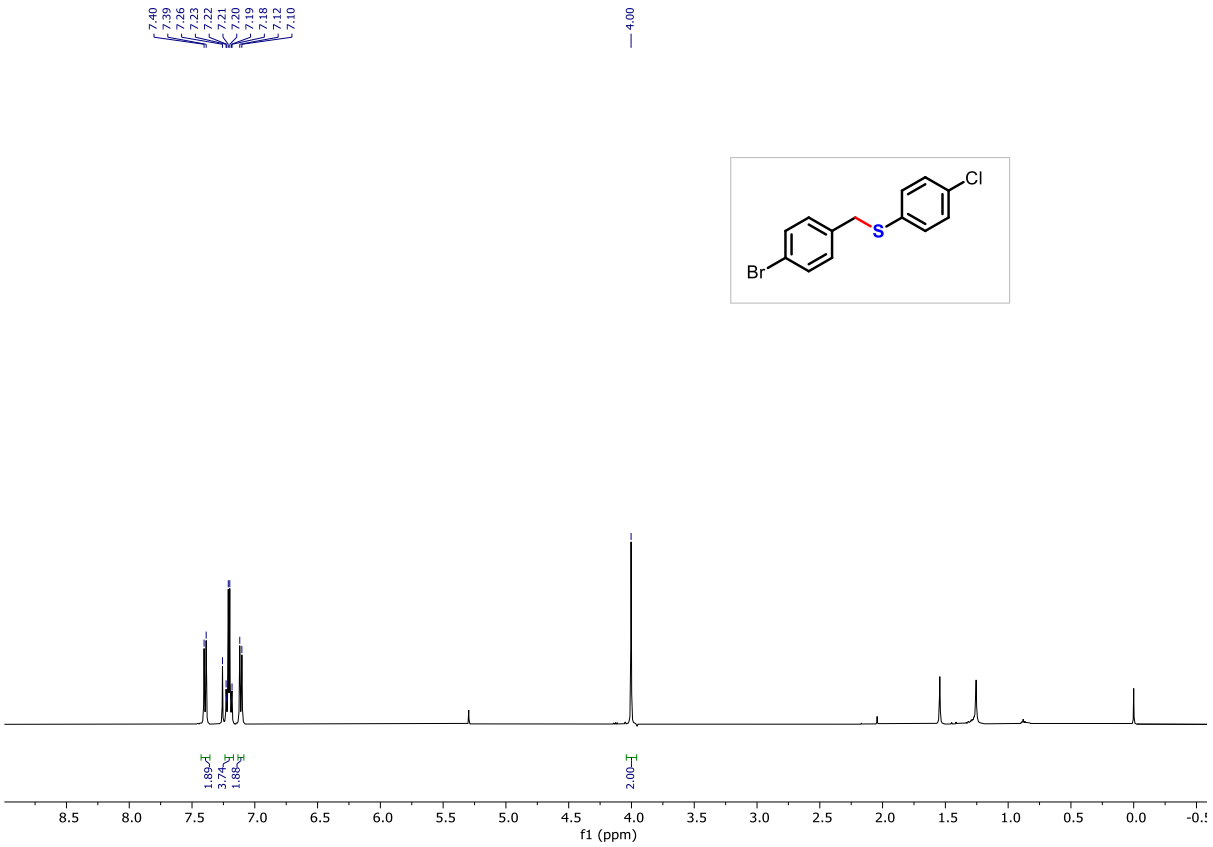


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

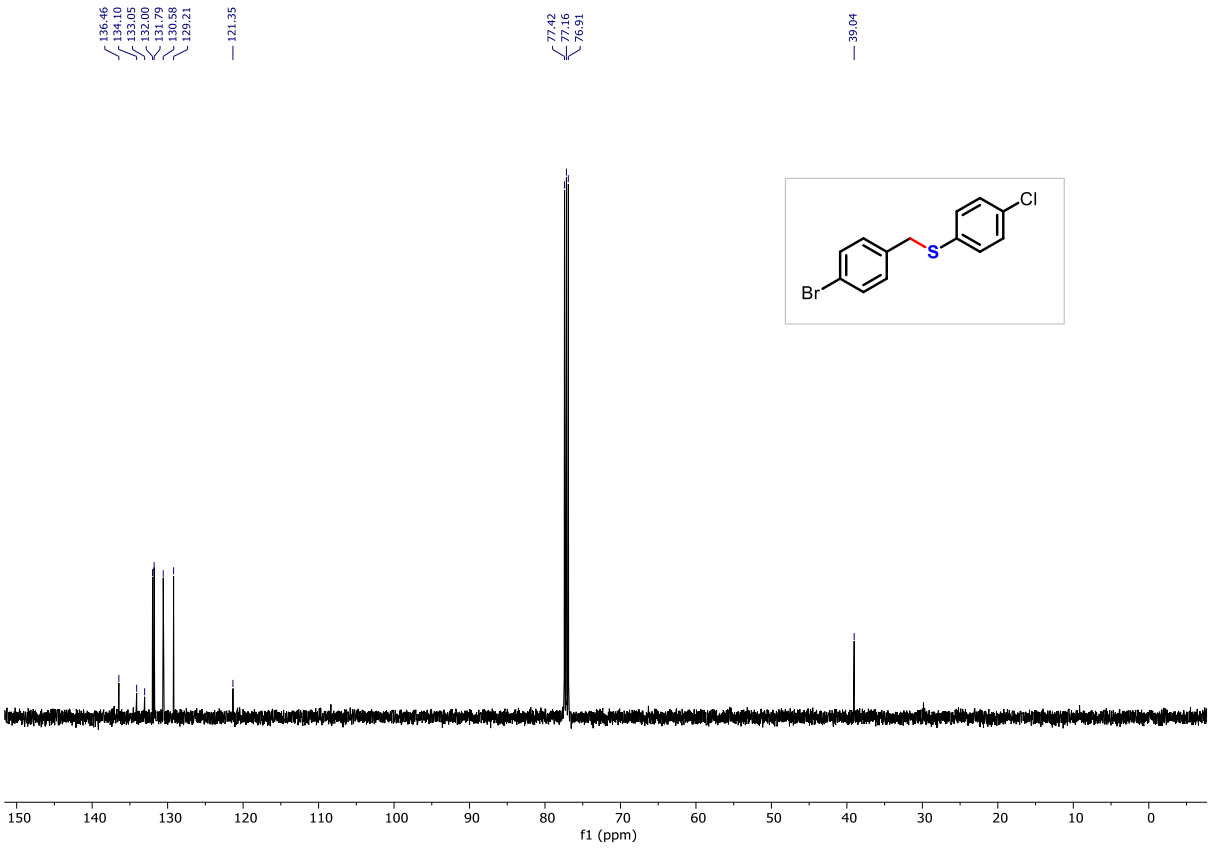


(4-Bromobenzyl) (4-chlorophenyl) sulfane (4o)

^{1}H NMR (500 MHz, $CDCl_3$)

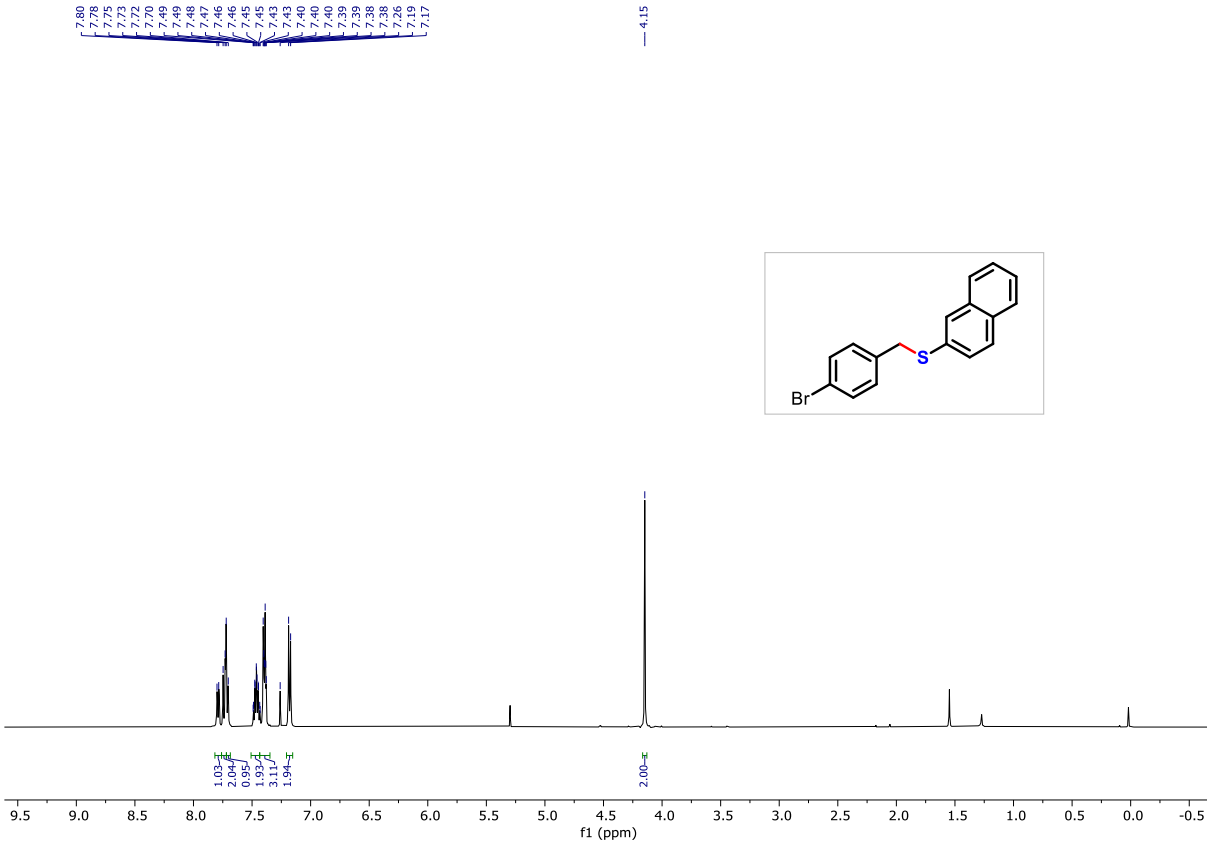


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

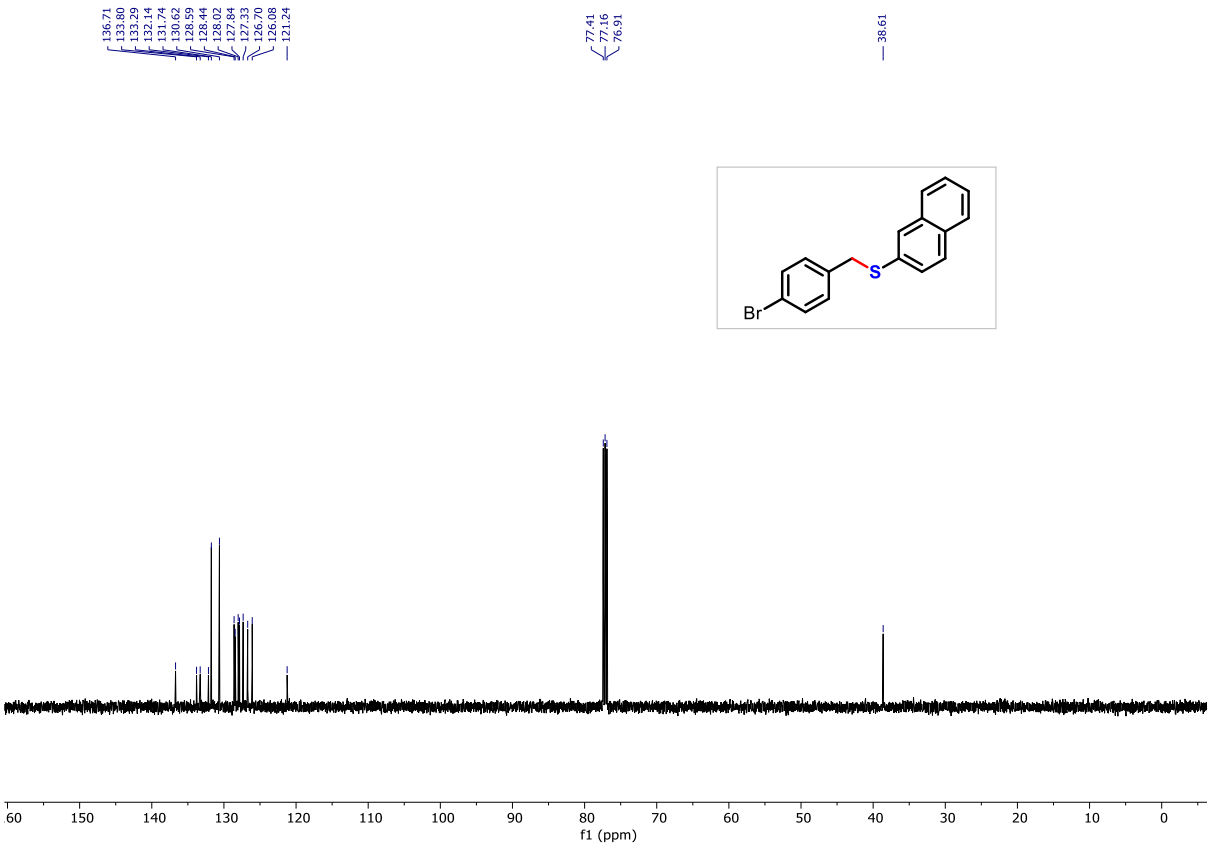


(4-Bromobenzyl) (naphthalen-2-yl) sulfane (4p)

^{1}H NMR (500 MHz, $CDCl_3$)

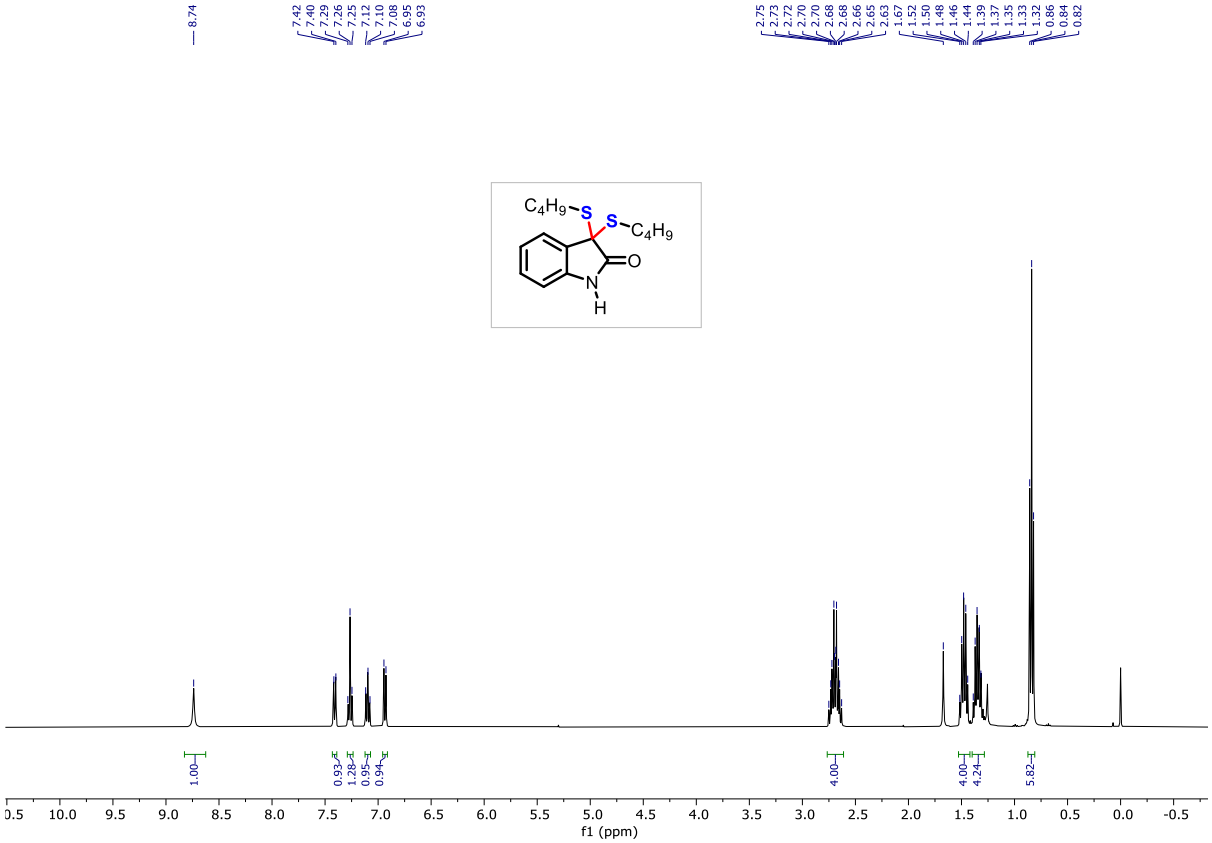


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

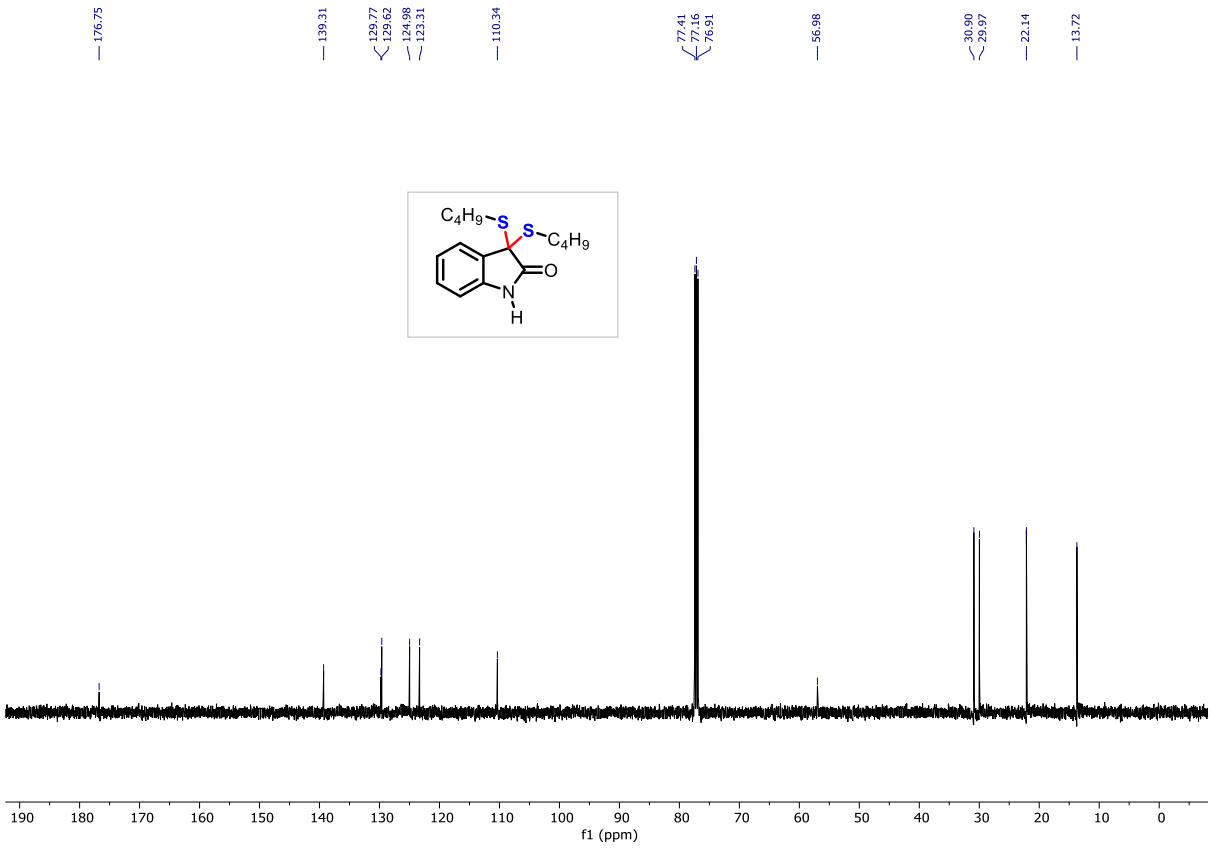


3,3-Bis (butylthio) indolin-2-one (5a)

^{1}H NMR (500 MHz, $CDCl_3$)

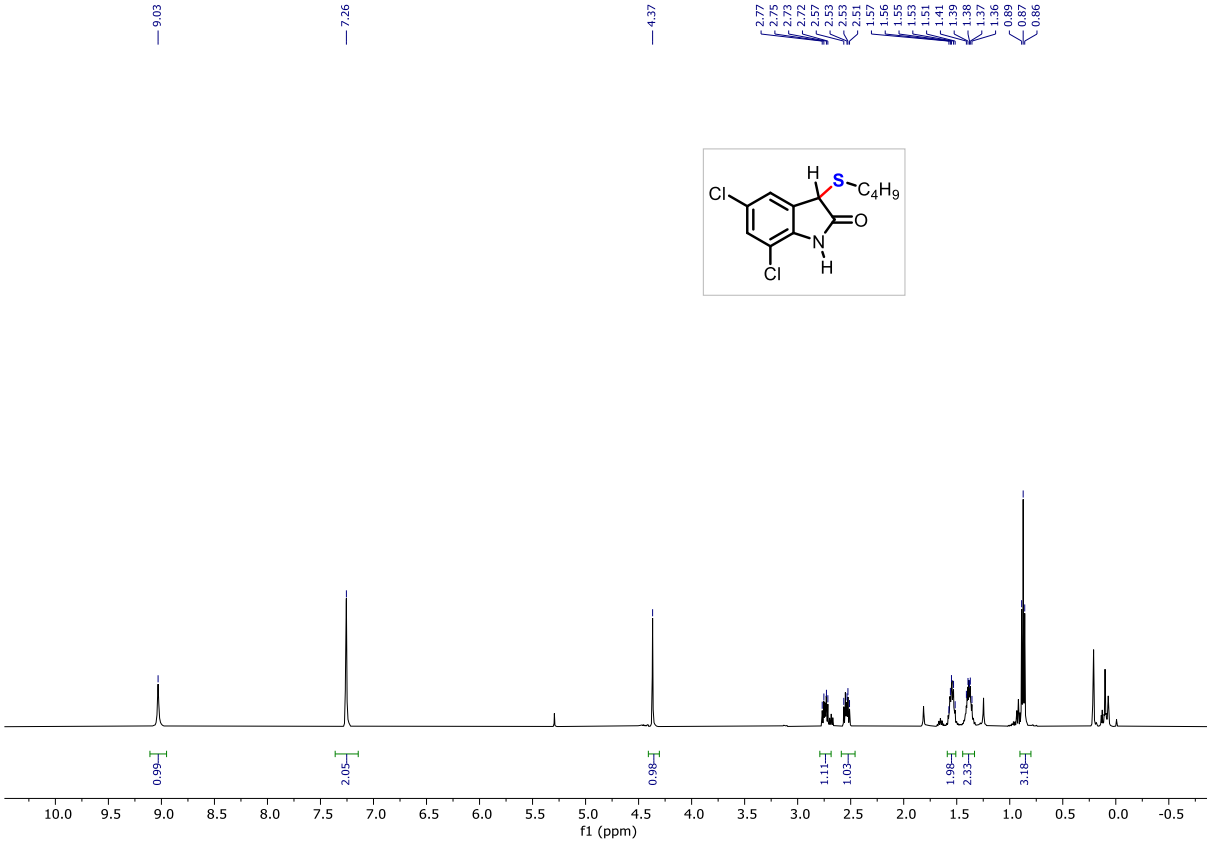


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

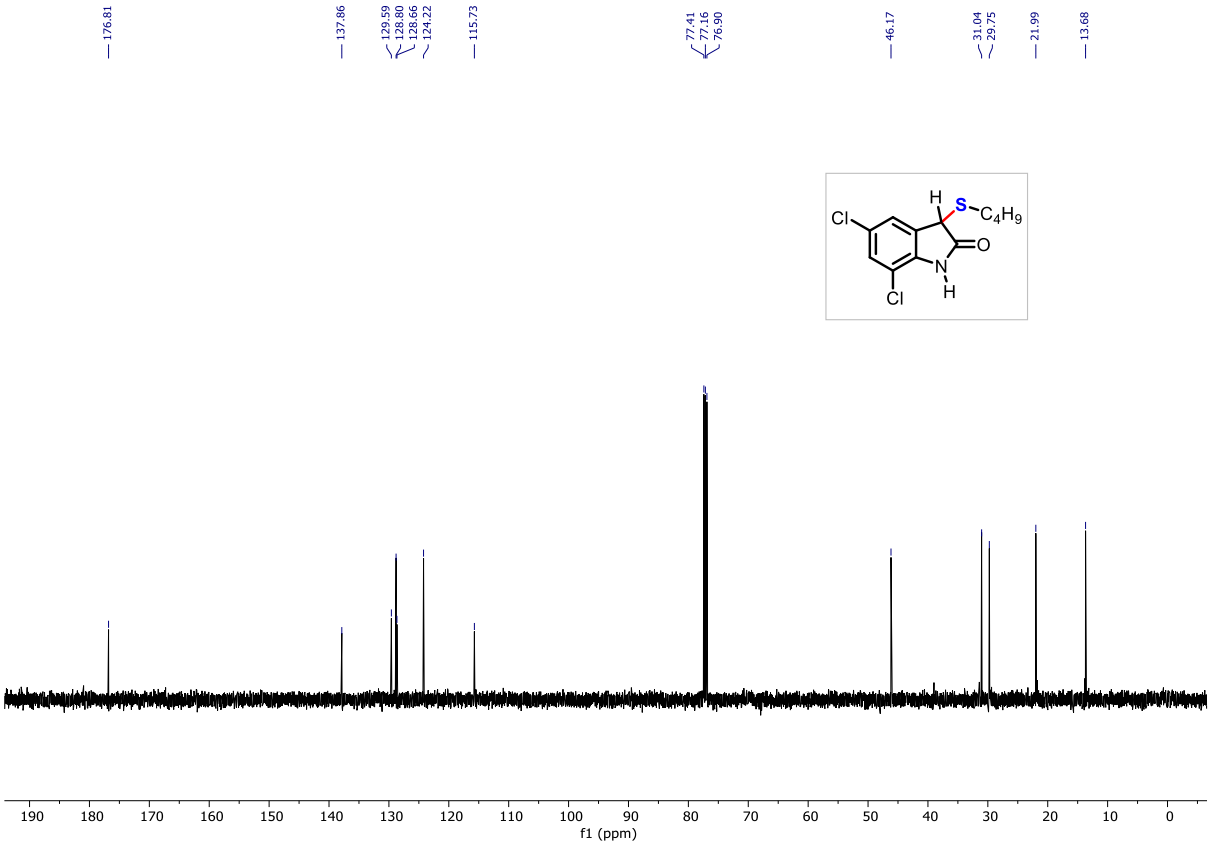


3-(Butylthio)-5,7-dichloroindolin-2-one (6a)

^{1}H NMR (500 MHz, $CDCl_3$)

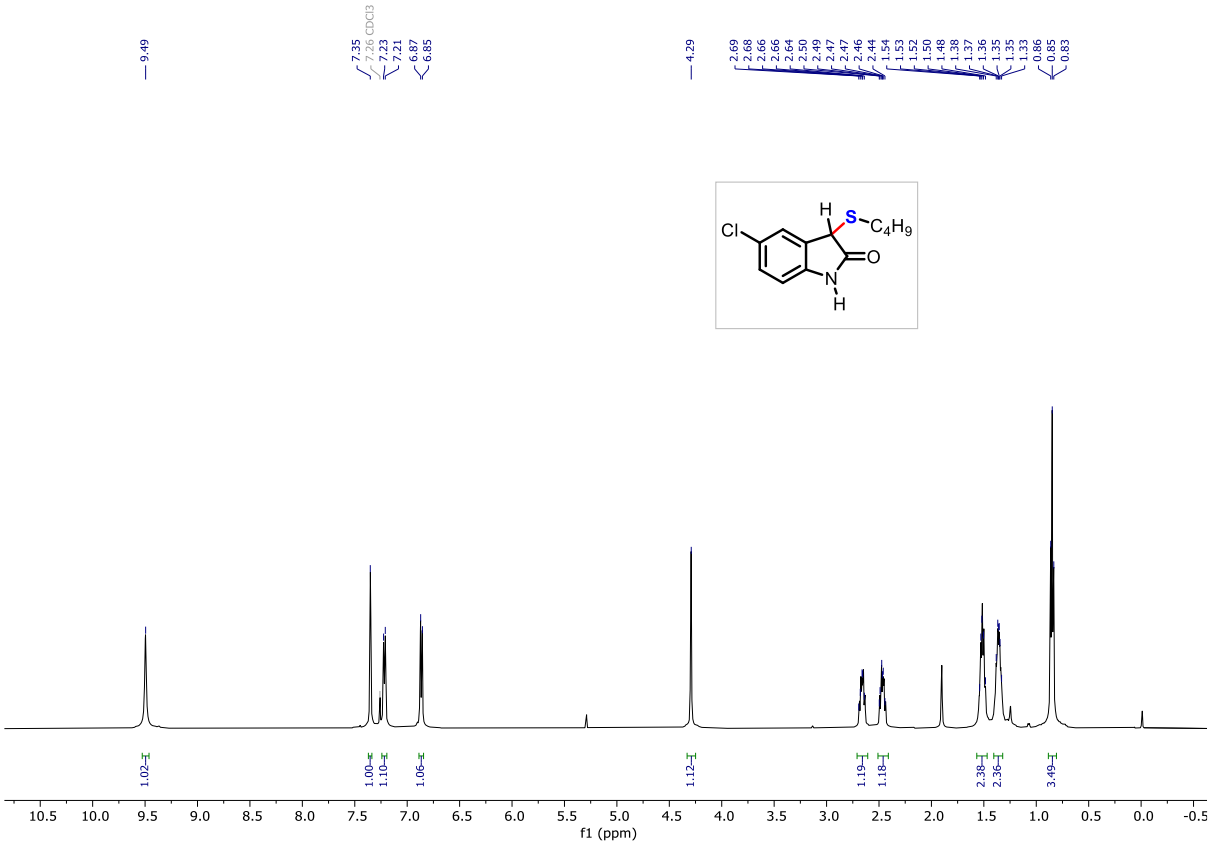


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

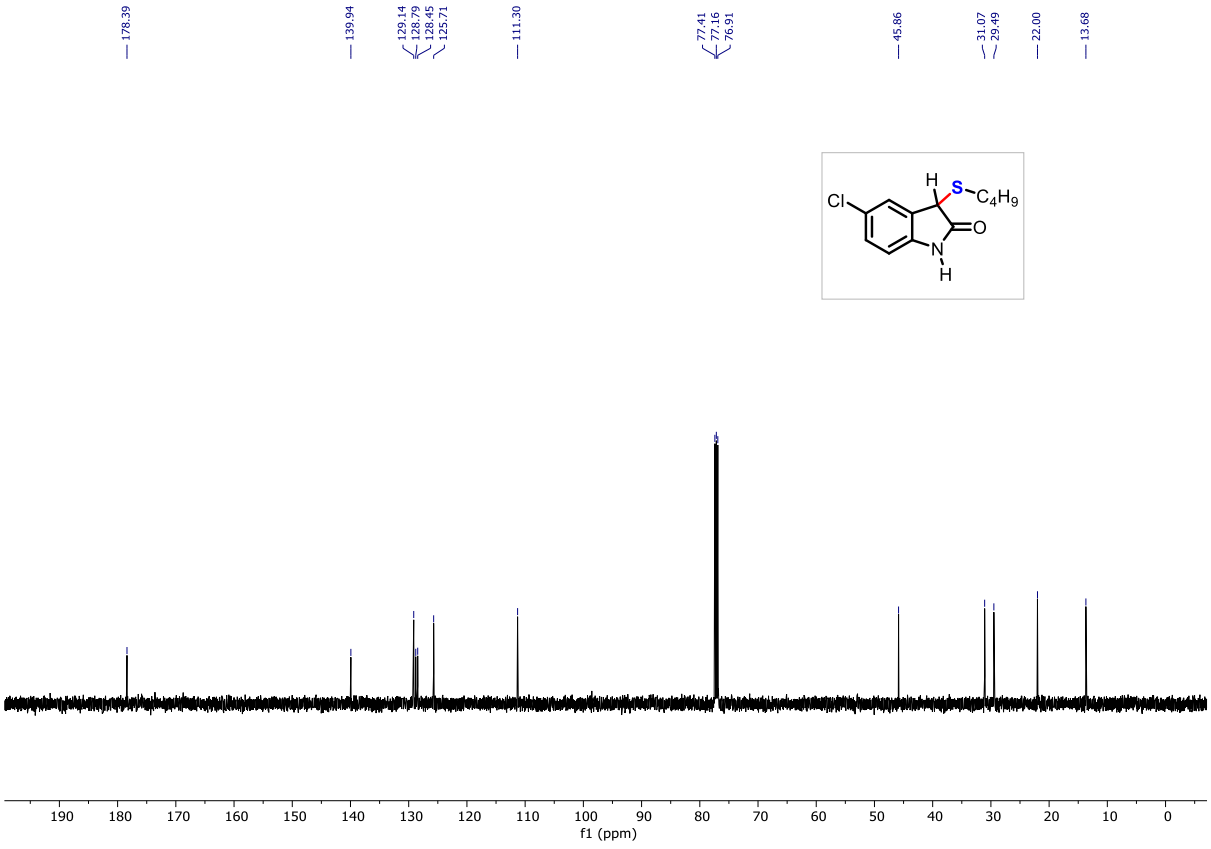


3-(Butylthio)-5-chloroindolin-2-one (6b)

^{1}H NMR (500 MHz, $CDCl_3$)

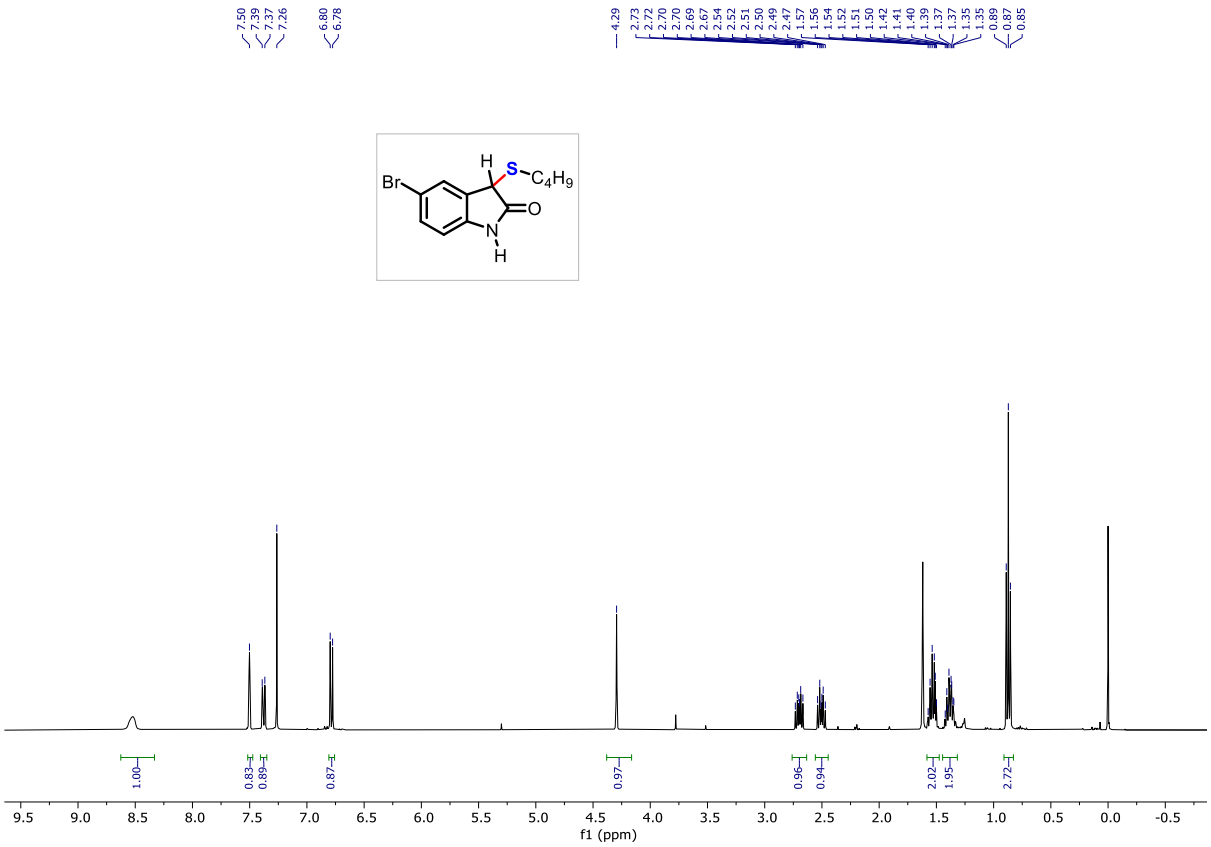


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

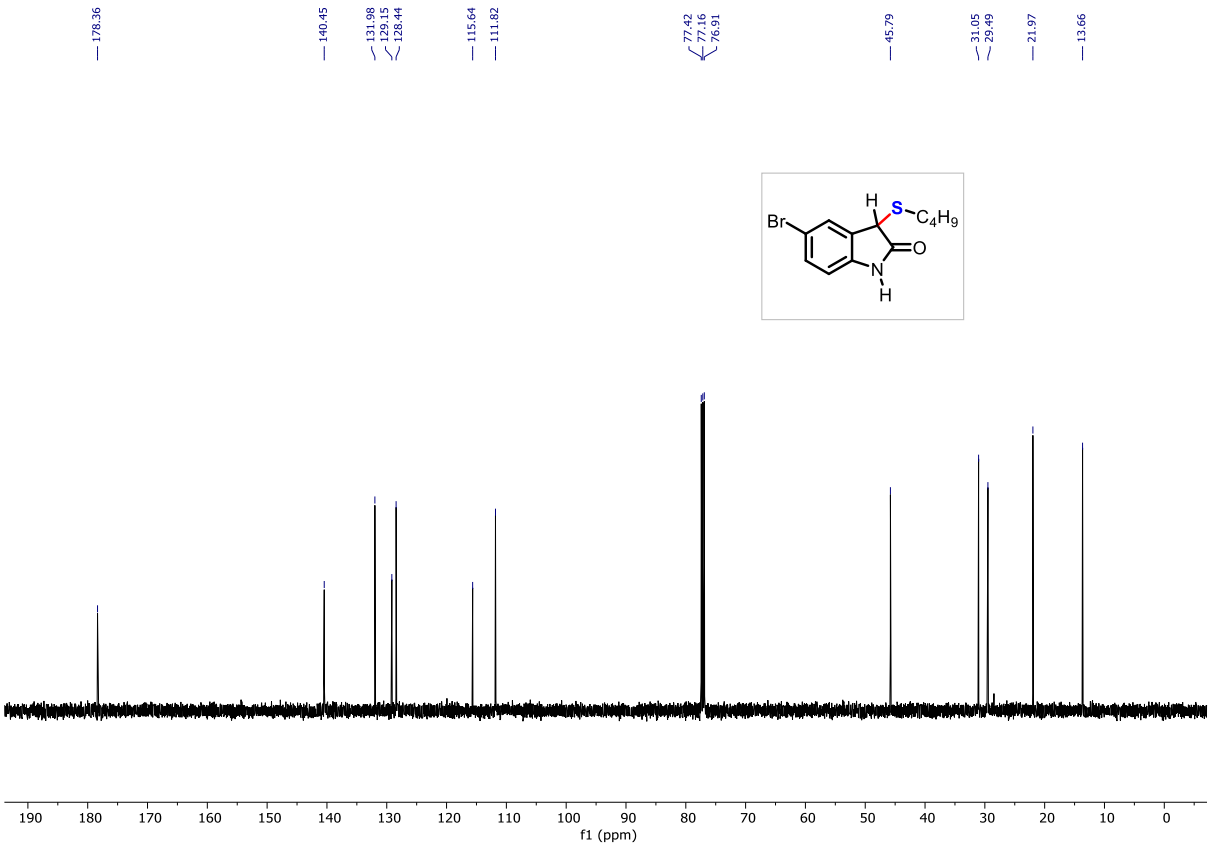


5-Bromo-3-(butylthio) indolin-2-one (6c)

^{1}H NMR (500 MHz, $CDCl_3$)

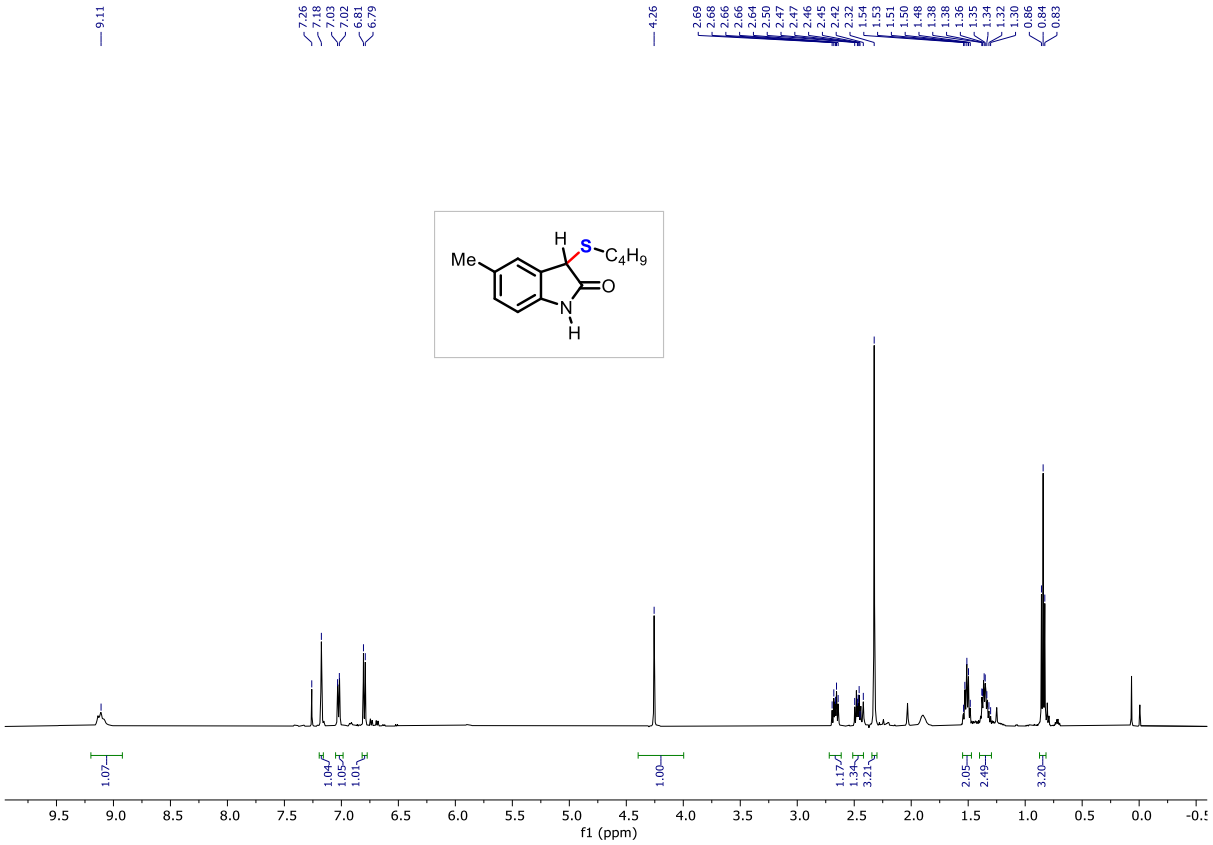


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

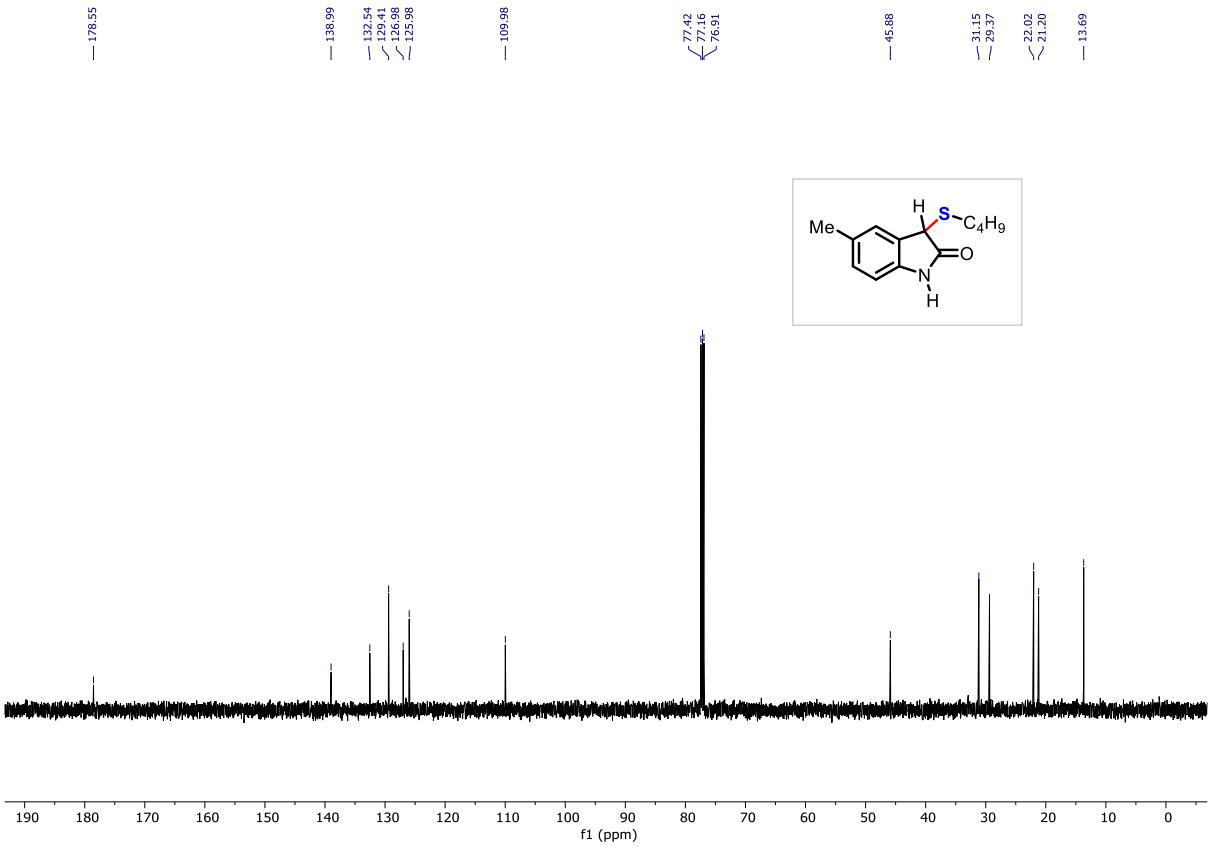


3-(Butylthio)-5-methylindolin-2-one (6d)

^{1}H NMR (500 MHz, $CDCl_3$)

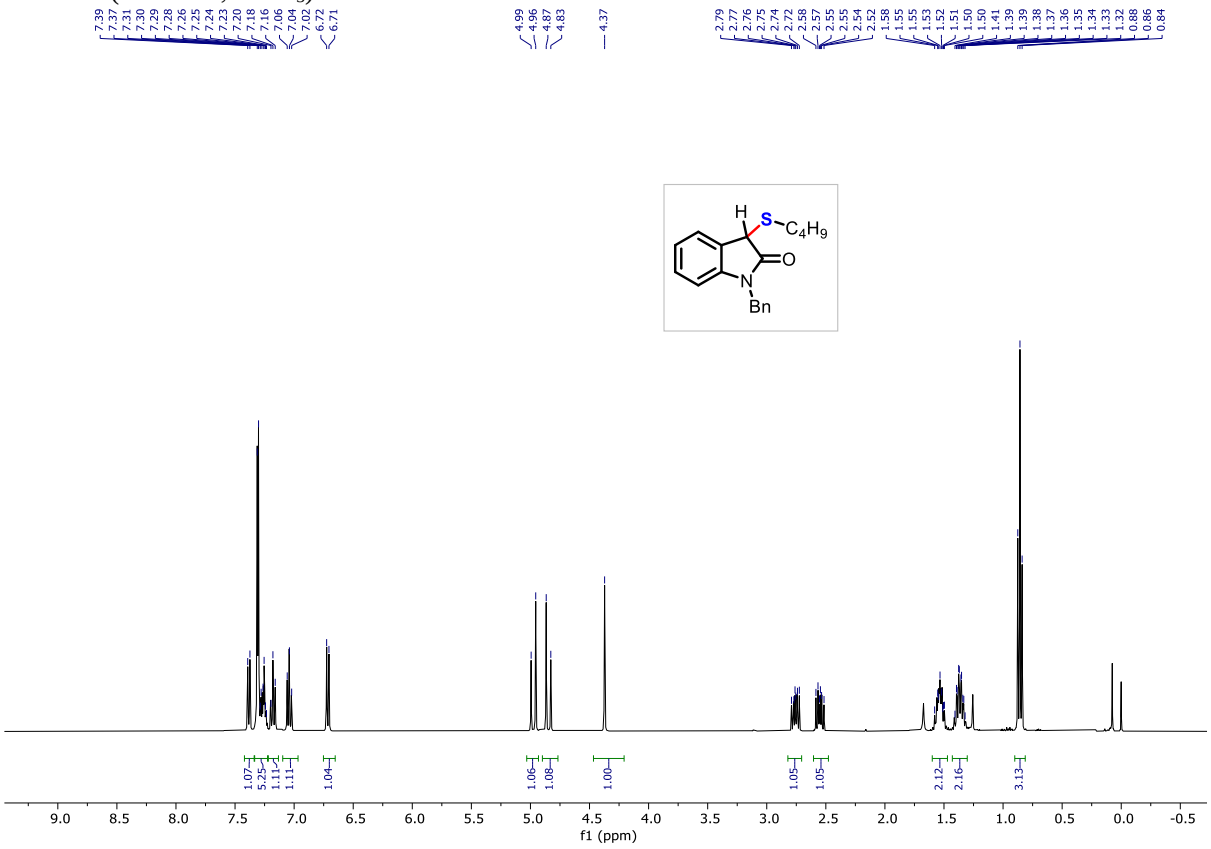


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

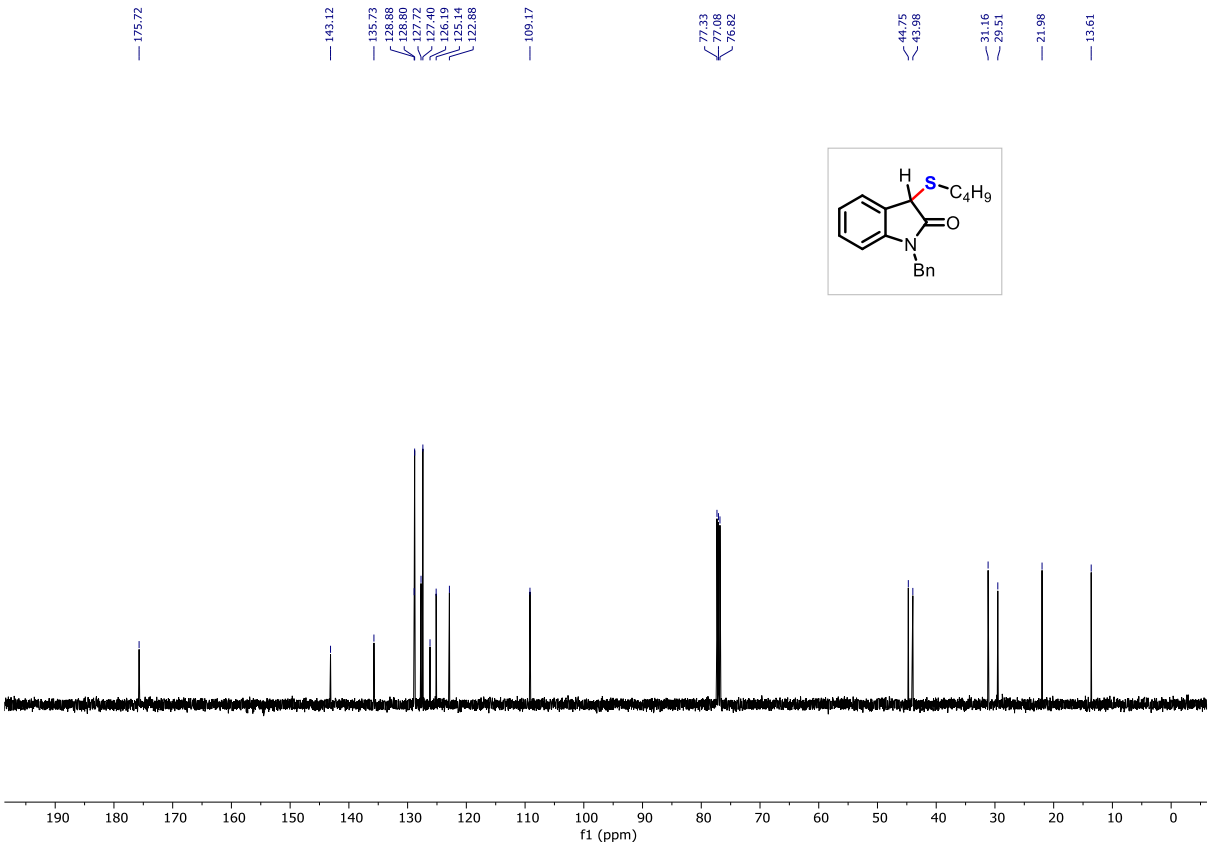


1-Benzyl-3-(butylthio) indolin-2-one (6e)

^{1}H NMR (400 MHz, $CDCl_3$)

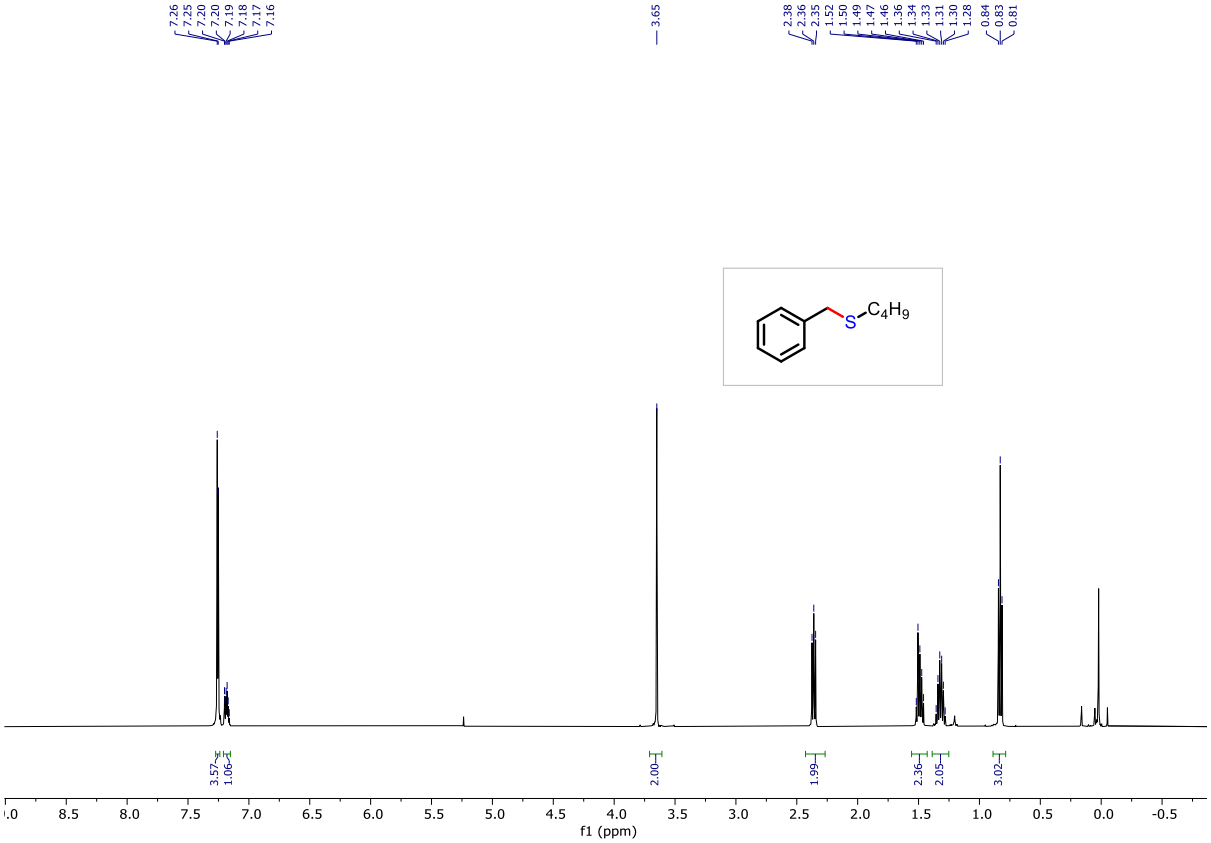


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

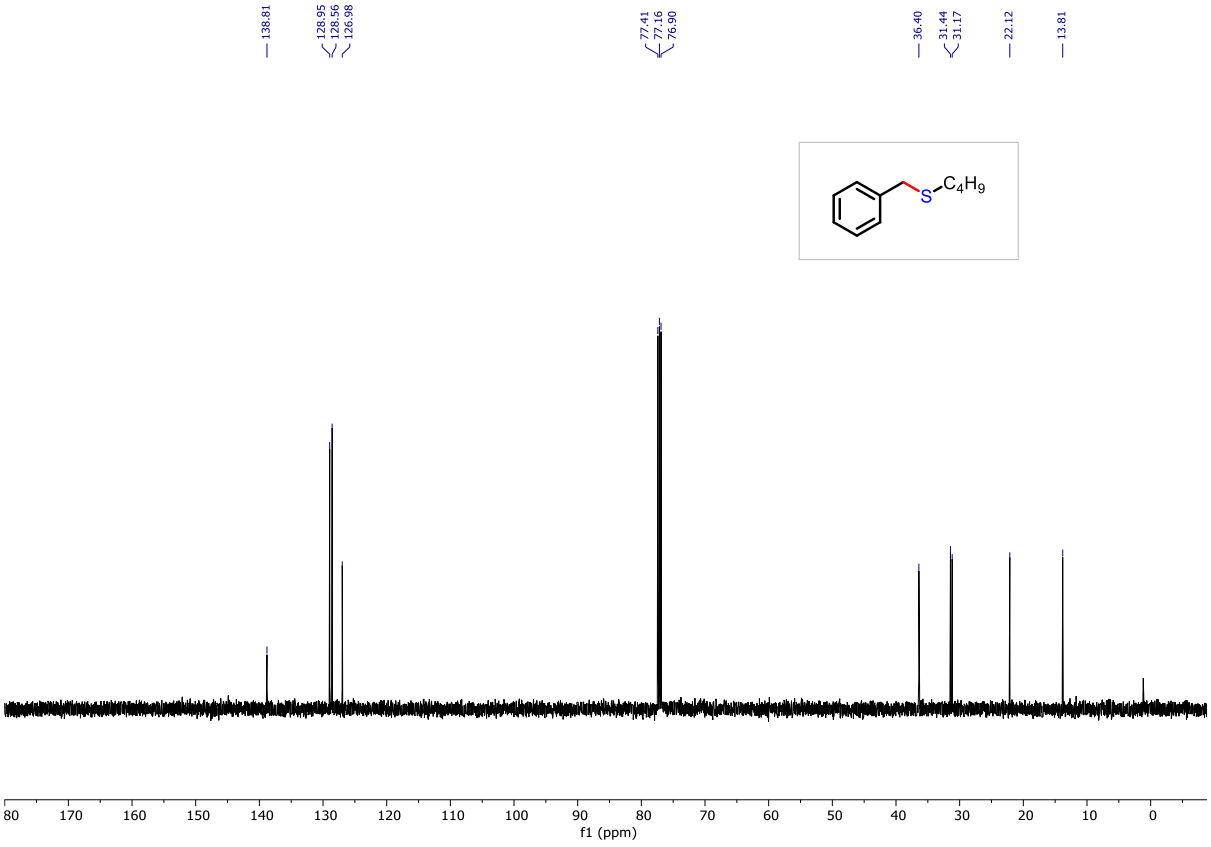


Benzyl(butyl)sulfane (6f)

^{1}H NMR (500 MHz, $CDCl_3$)

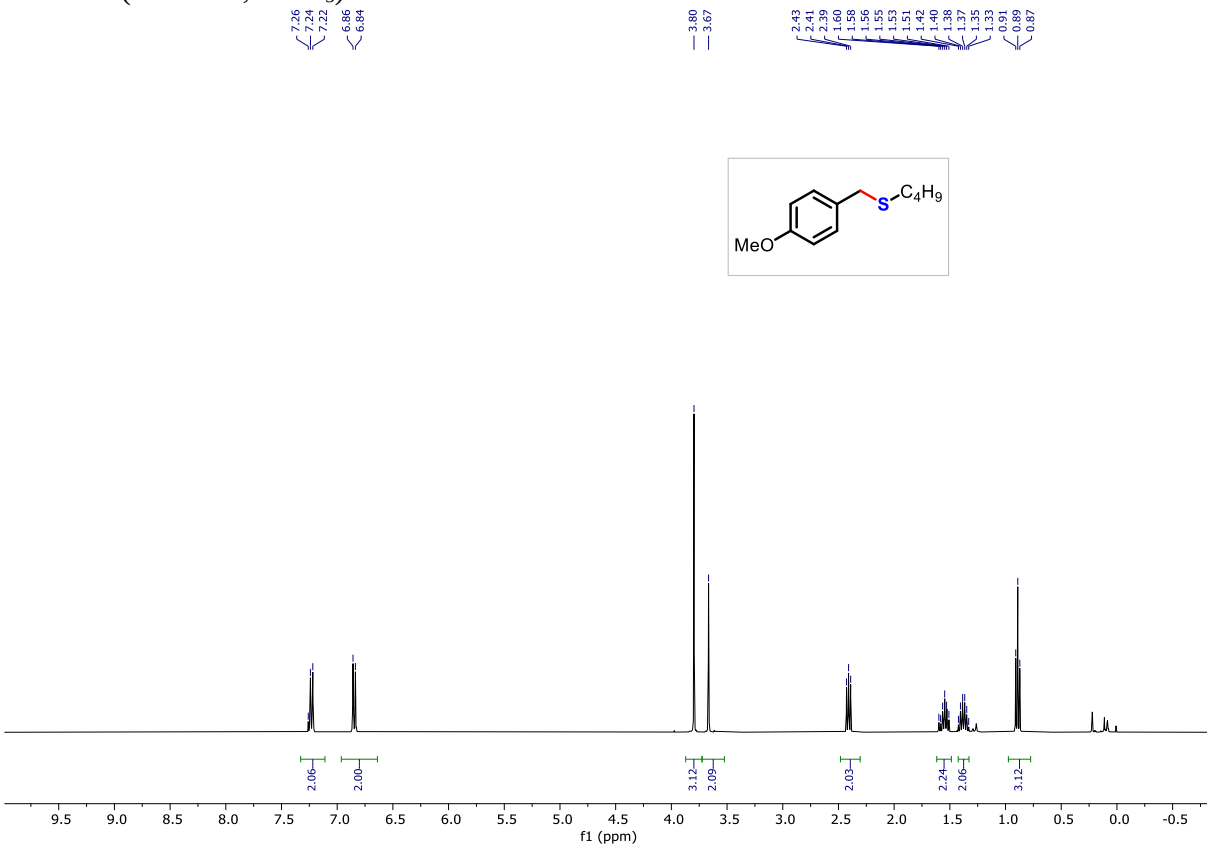


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

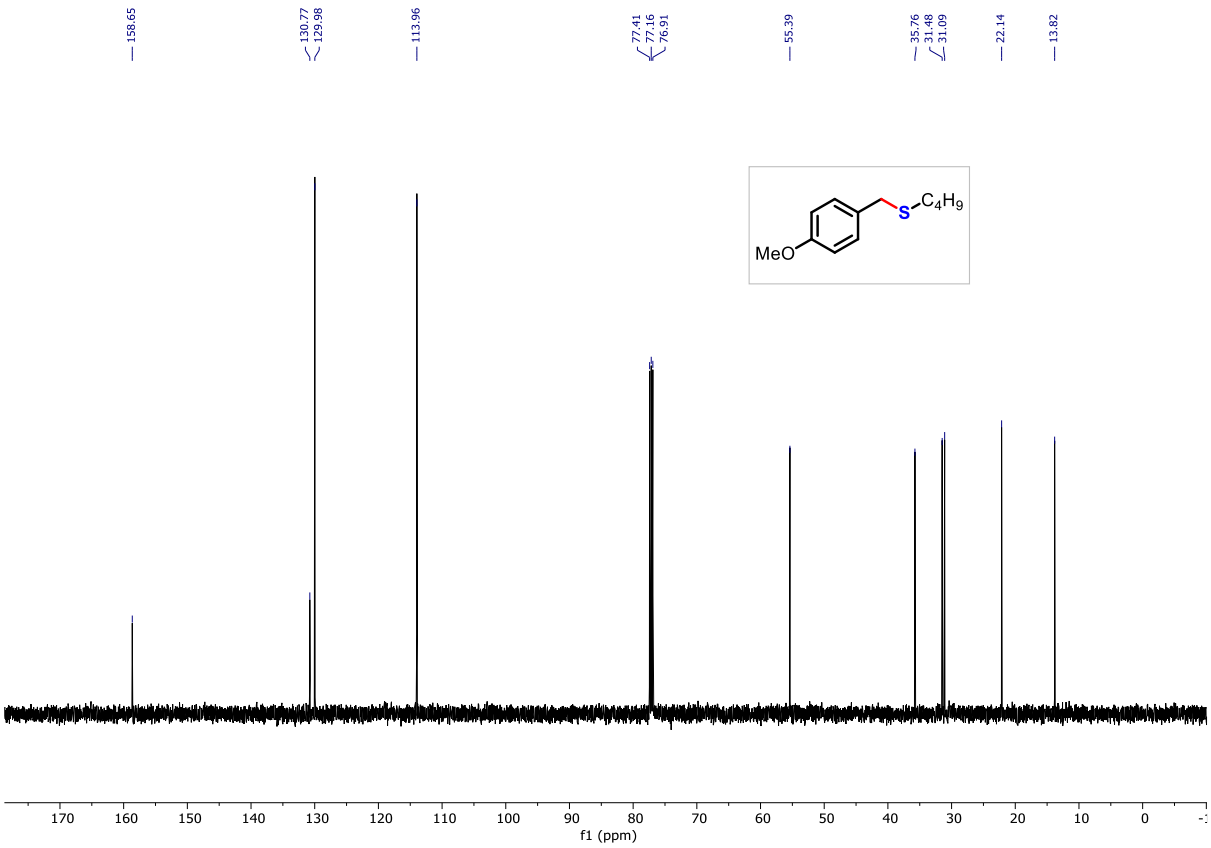


Butyl(4-methoxybenzyl) sulfane (6g)

^{1}H NMR (400 MHz, $CDCl_3$)

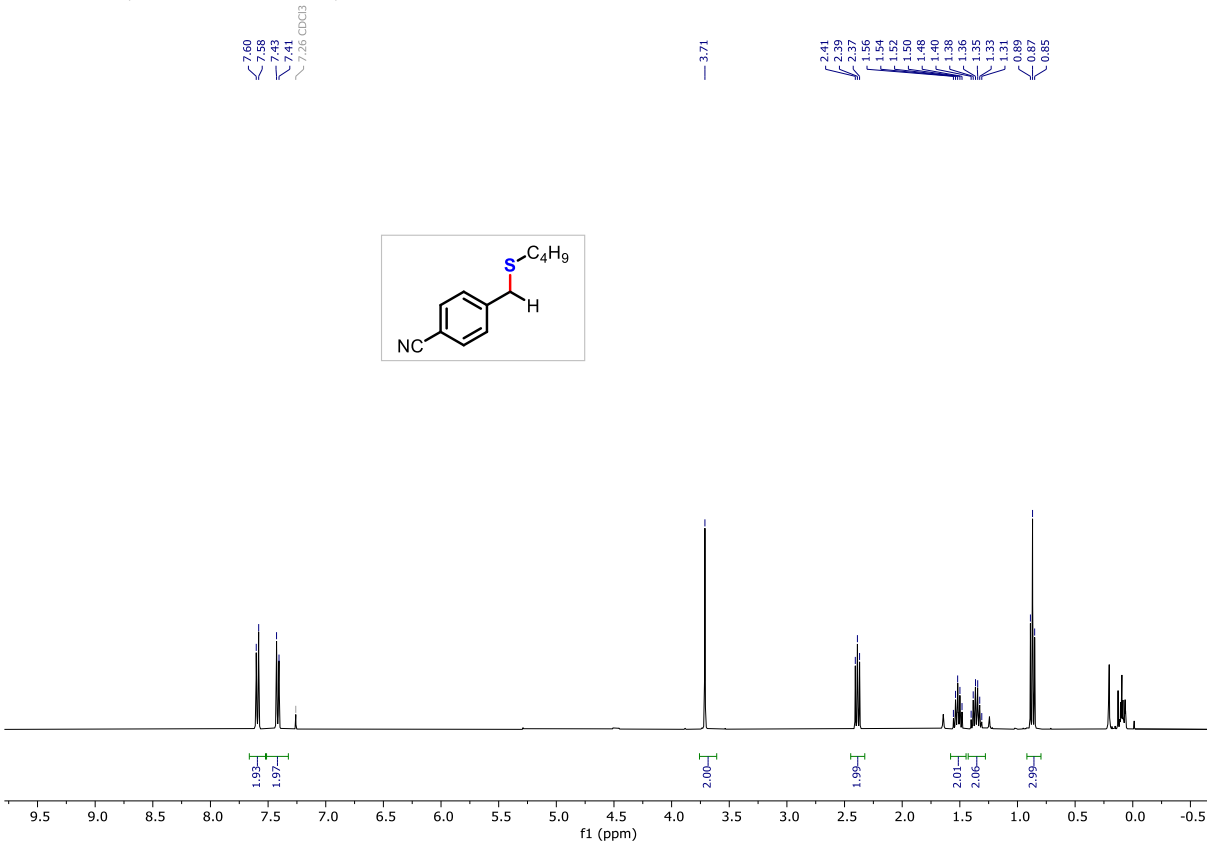


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

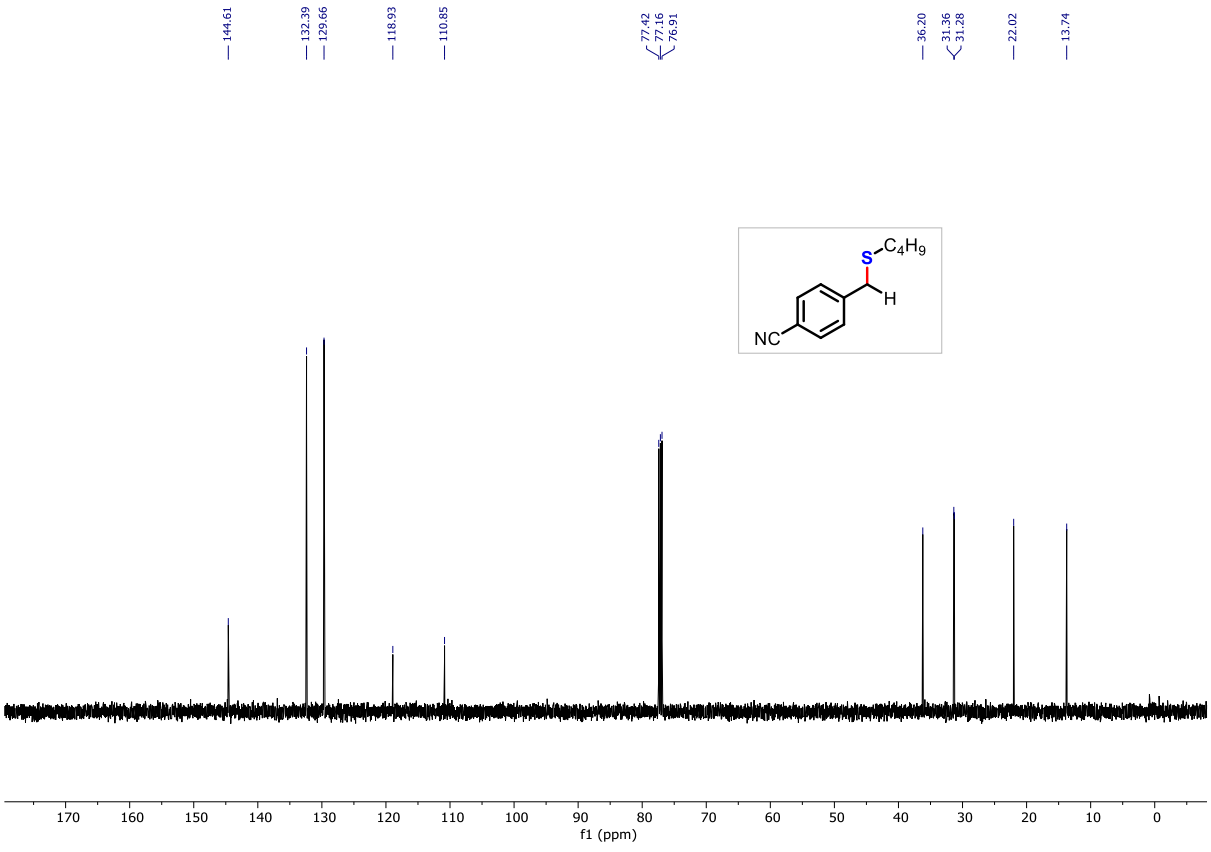


4-((Butylthio) methyl) benzonitrile (6h)

^{1}H NMR (500 MHz, $CDCl_3$**)**

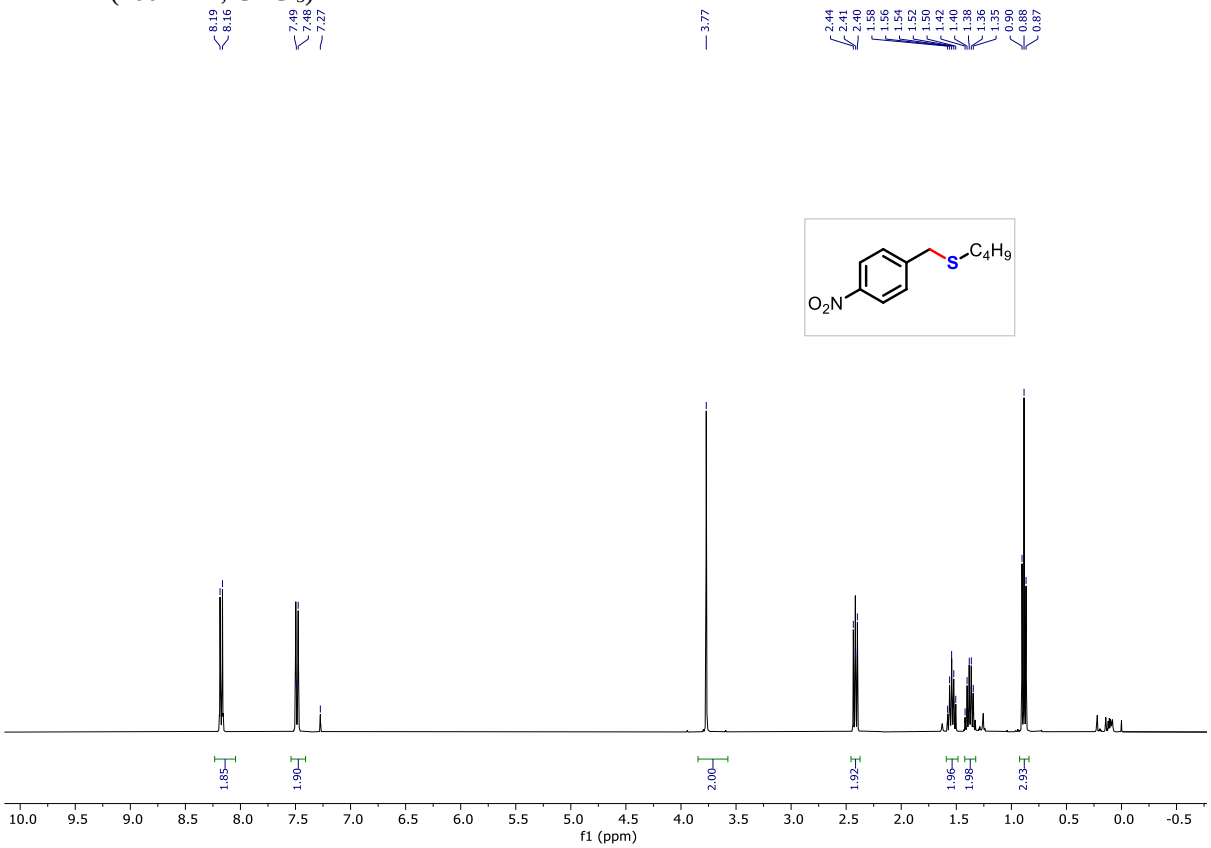


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

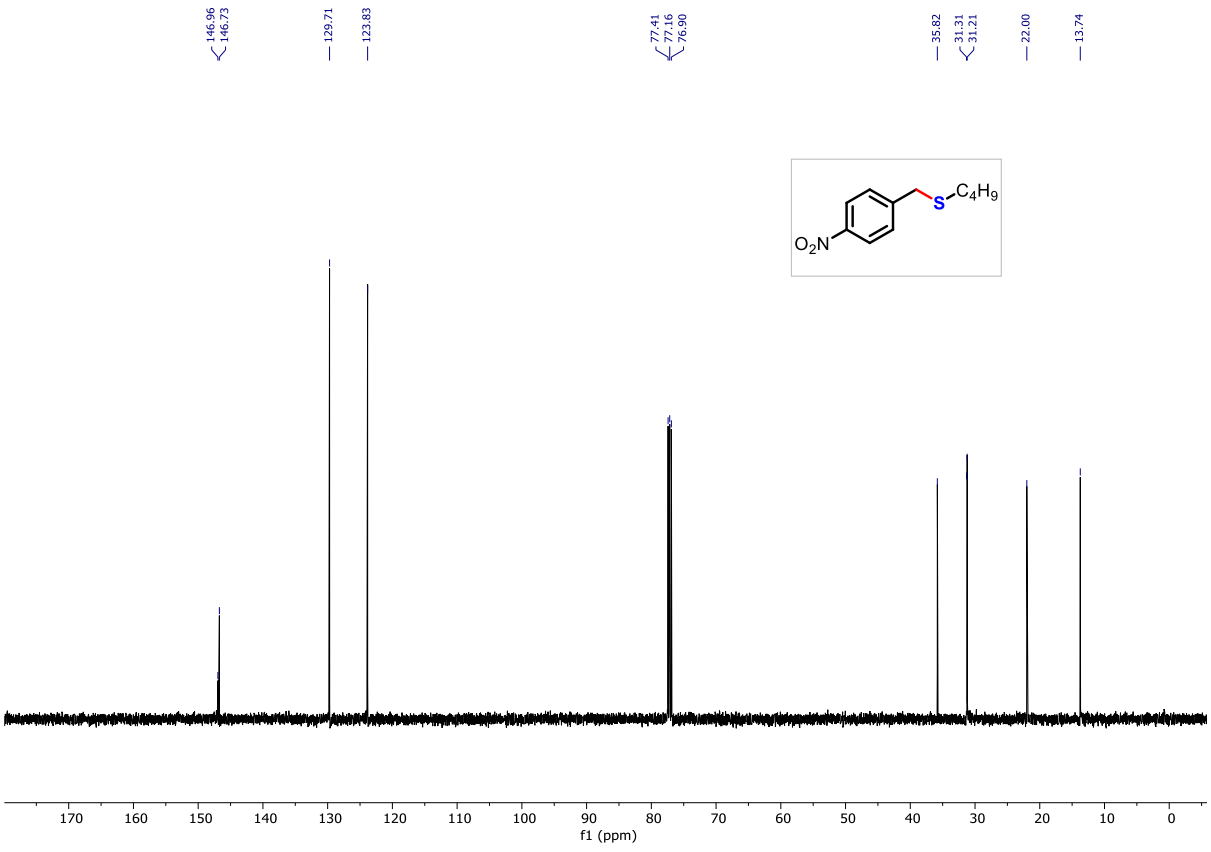


Butyl(4-nitrobenzyl) sulfane (6i)

^{1}H NMR (400 MHz, $CDCl_3$)

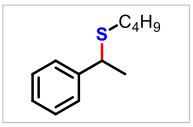


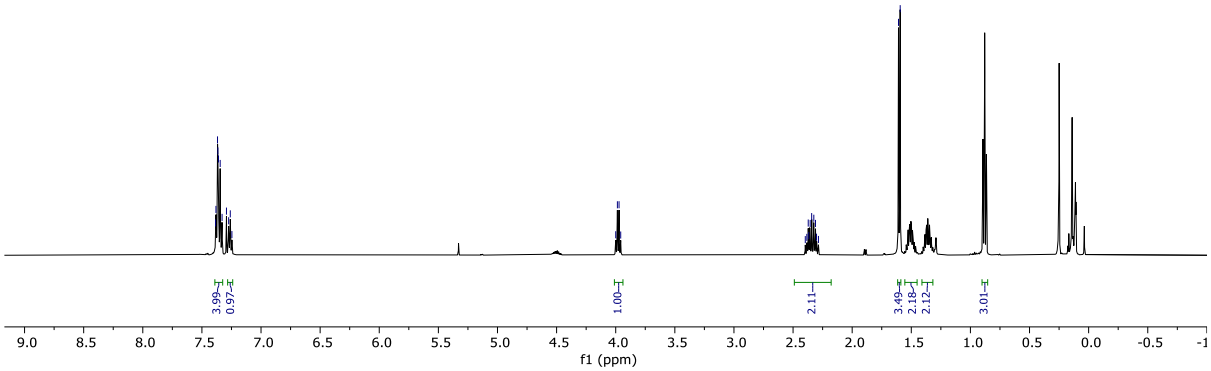
^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)



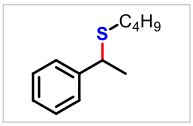
Butyl(1-phenylethyl) sulfane (6j)

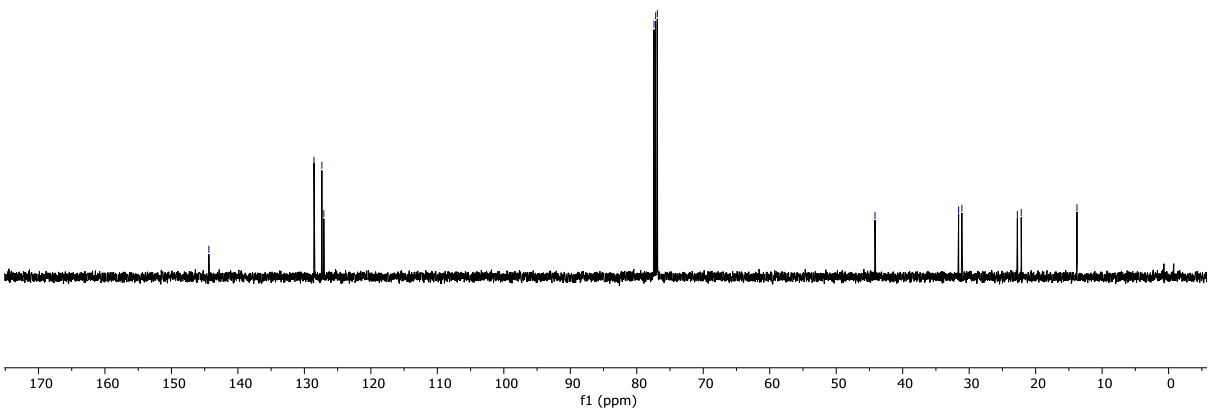
^{1}H NMR (500 MHz, $CDCl_3$**)**





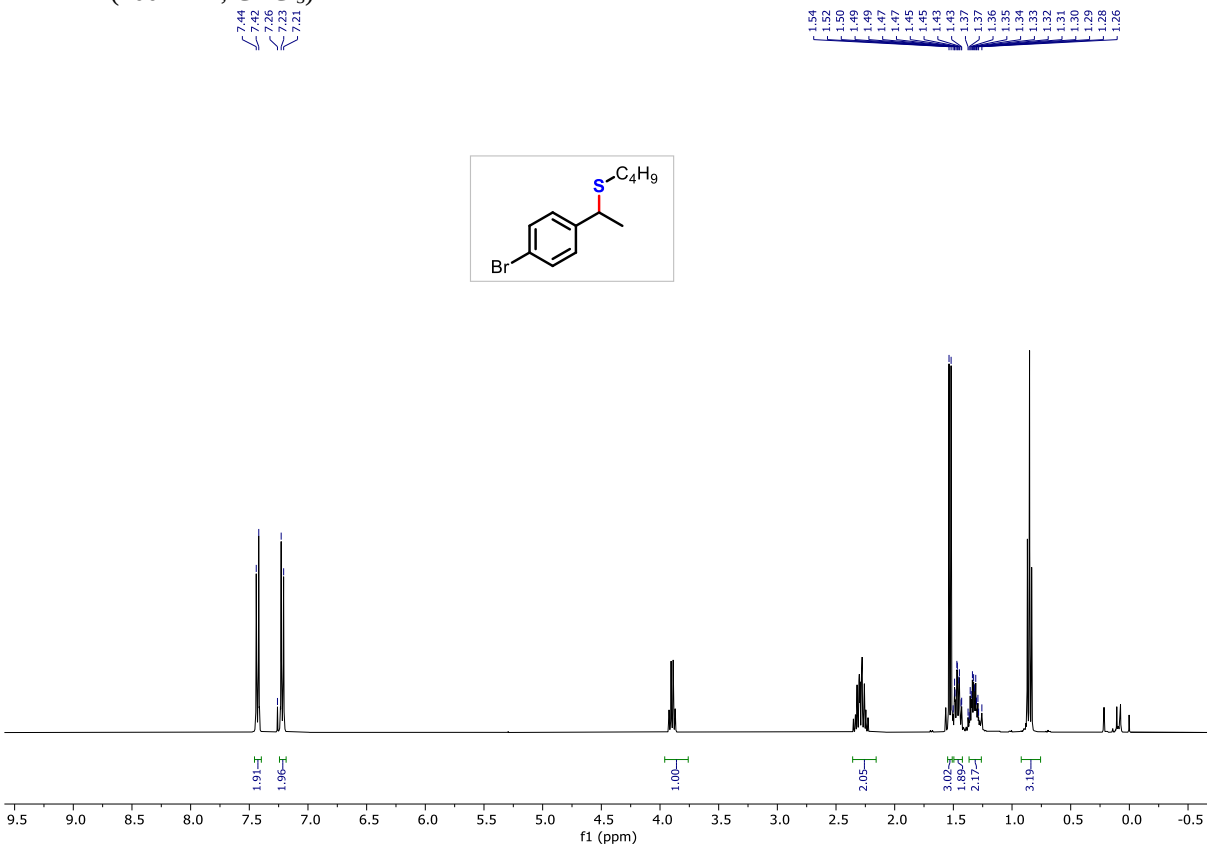
^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)



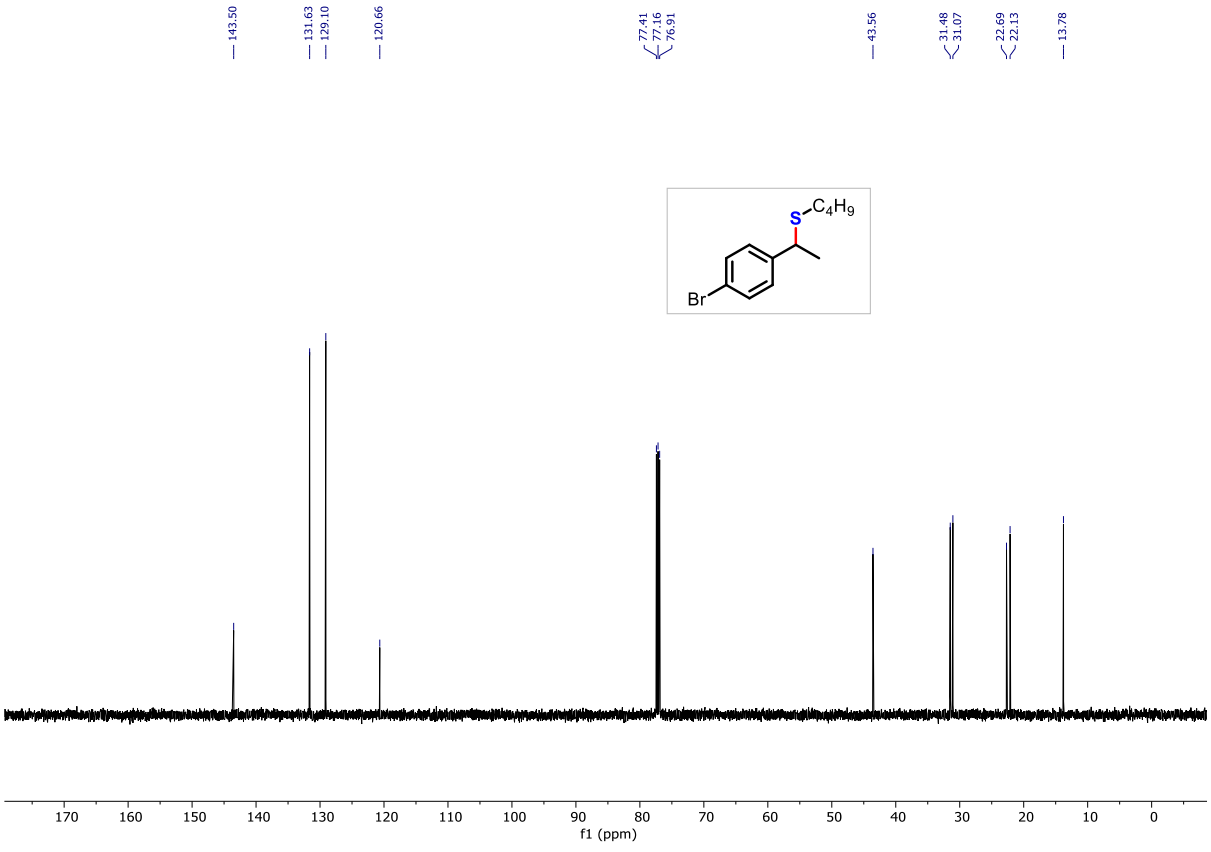


(1-(4-Bromophenyl) ethyl) (butyl)sulfane (6k)

^{1}H NMR (400 MHz, $CDCl_3$)

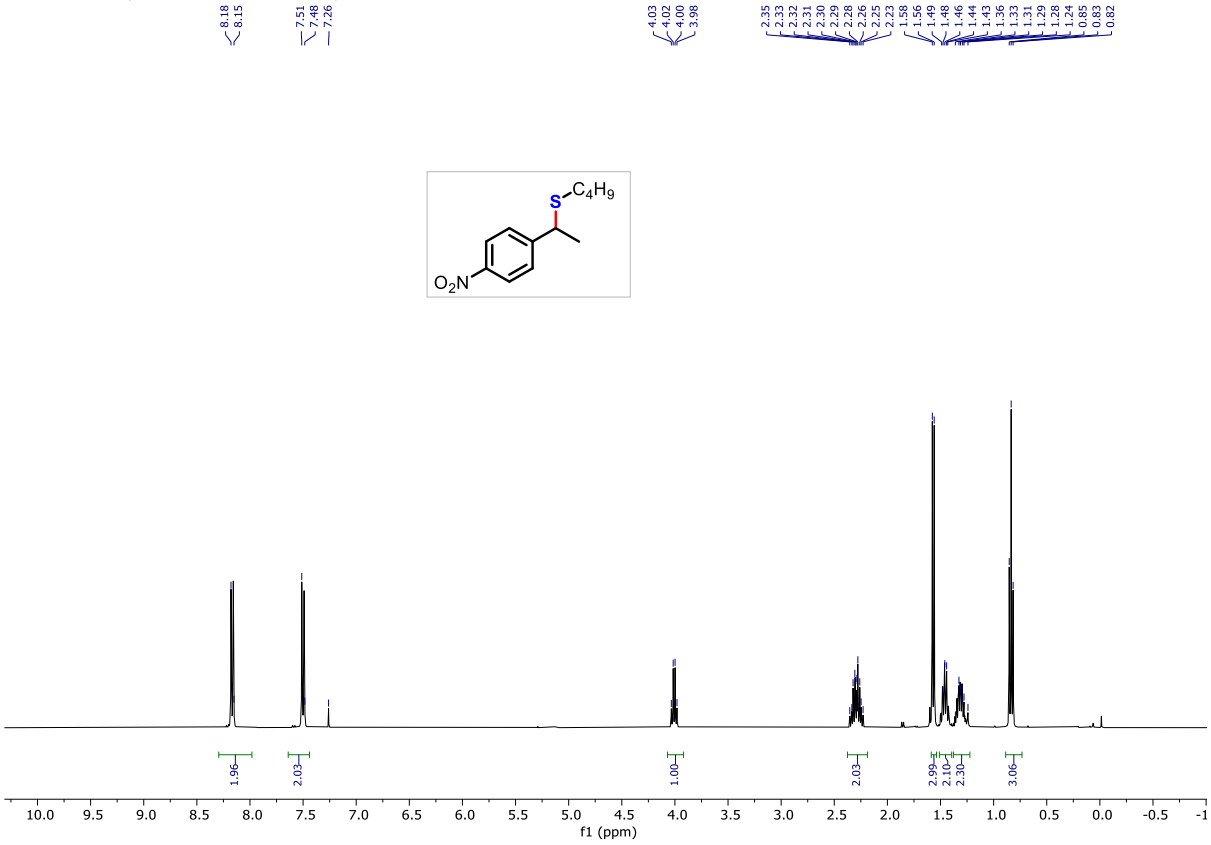


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

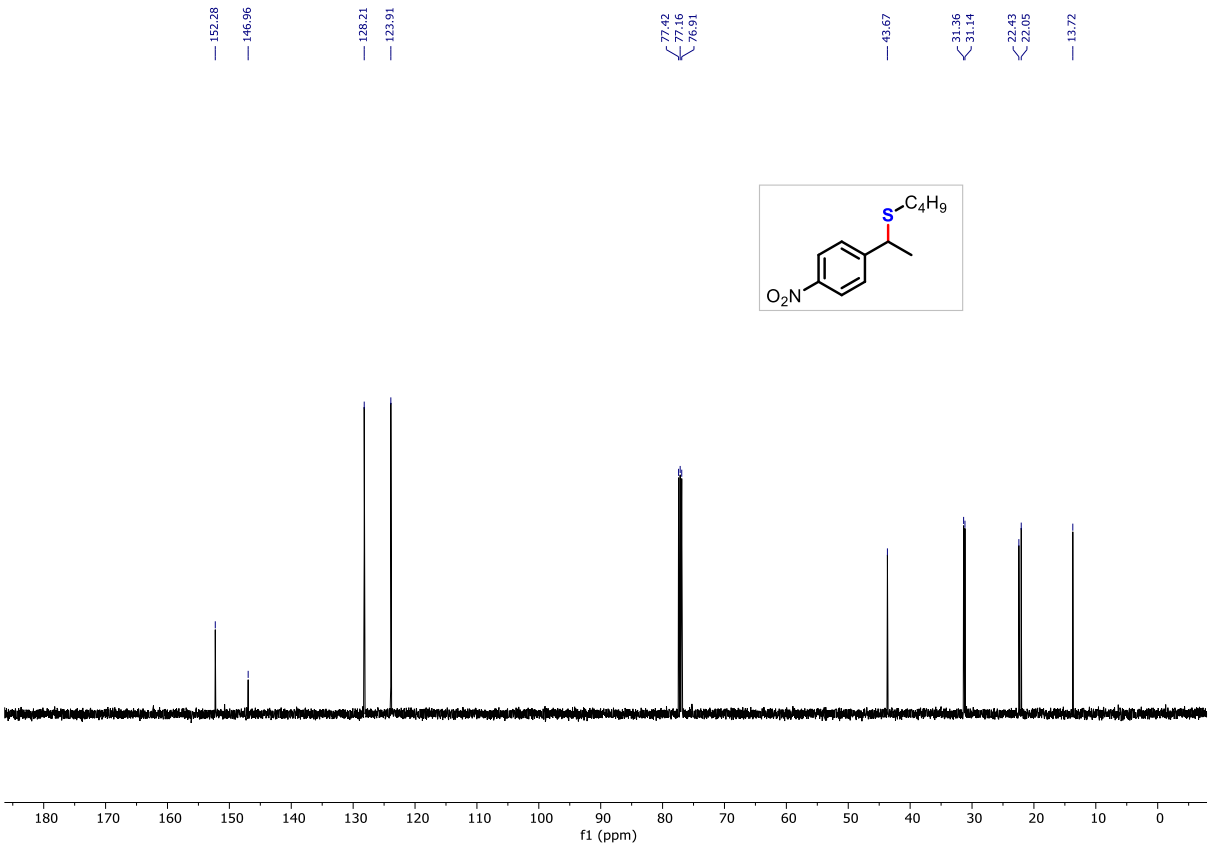


Butyl(1-(4-nitrophenyl) ethyl) sulfane (6l)

^{1}H NMR (400 MHz, $CDCl_3$)

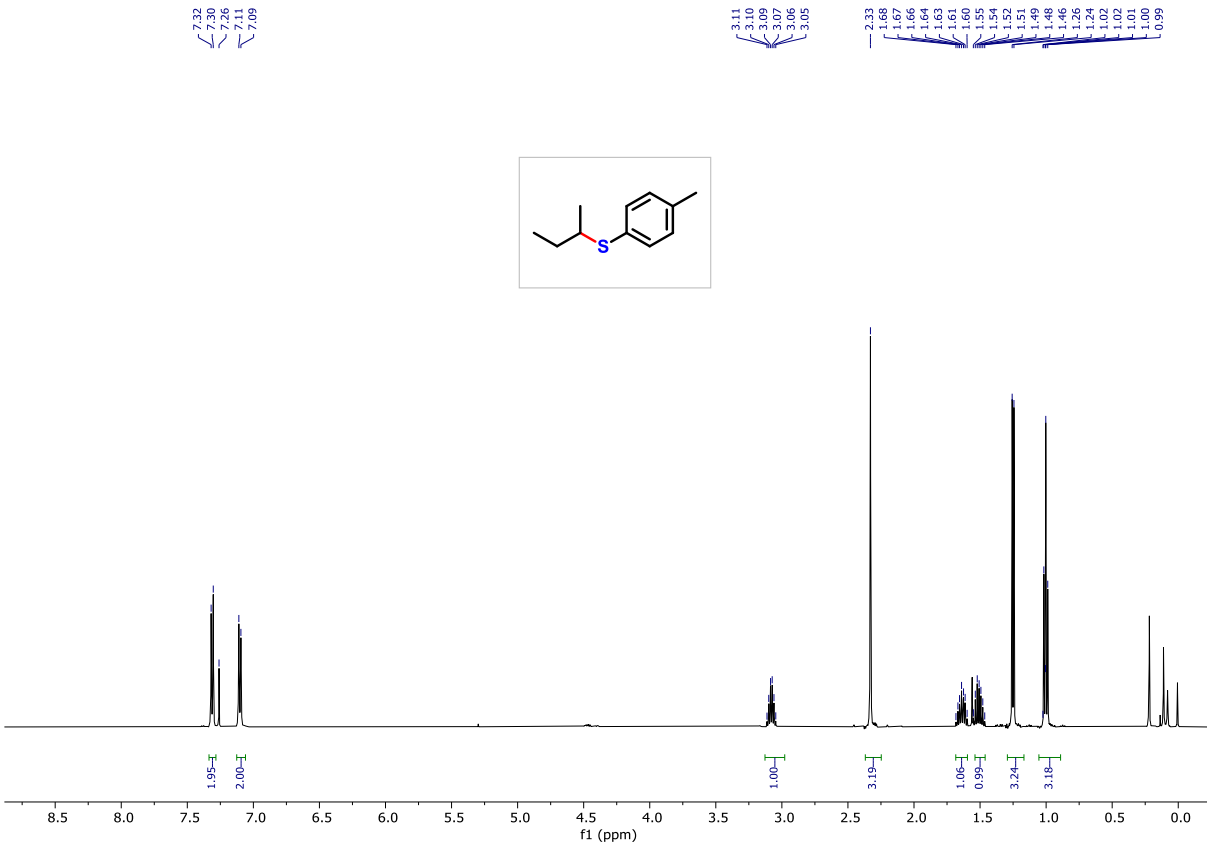


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

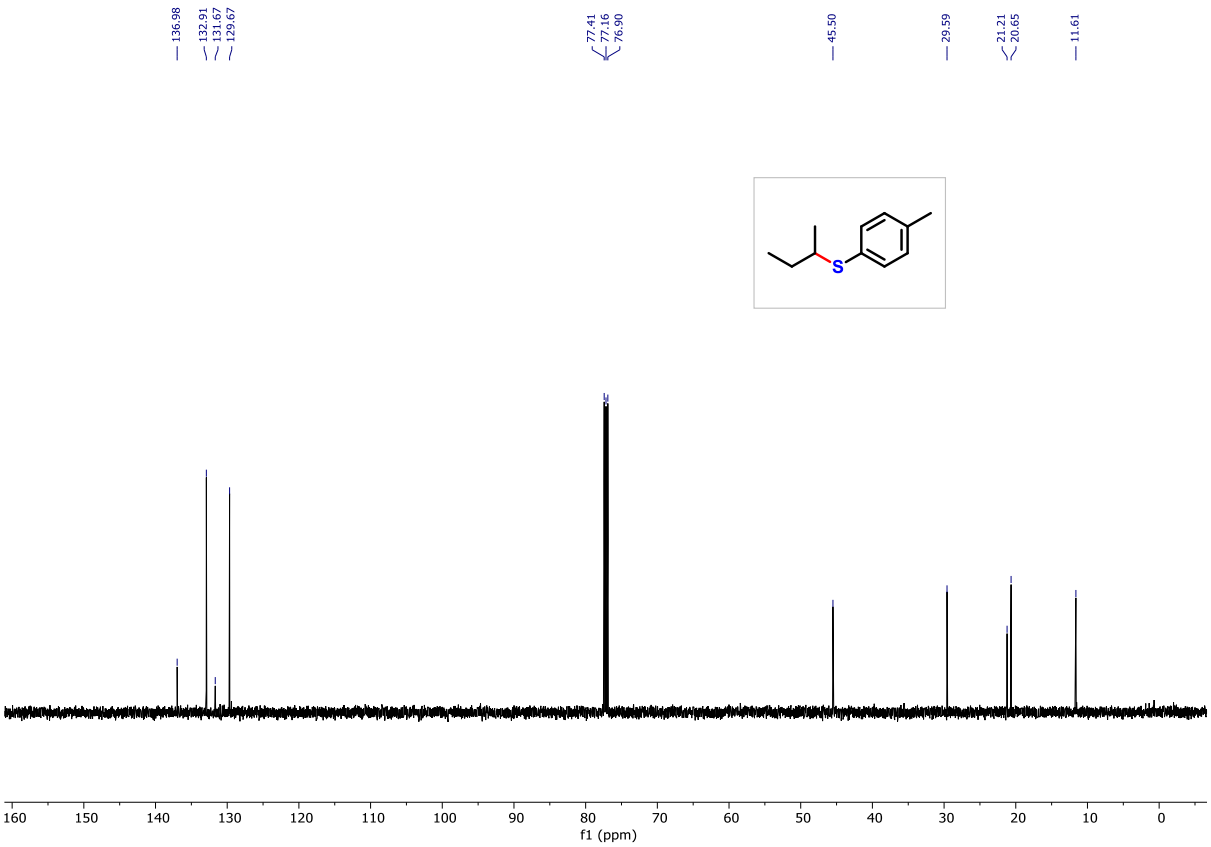


Sec-butyl(*p*-tolyl) sulfane (6n)

^{1}H NMR (500 MHz, $CDCl_3$)

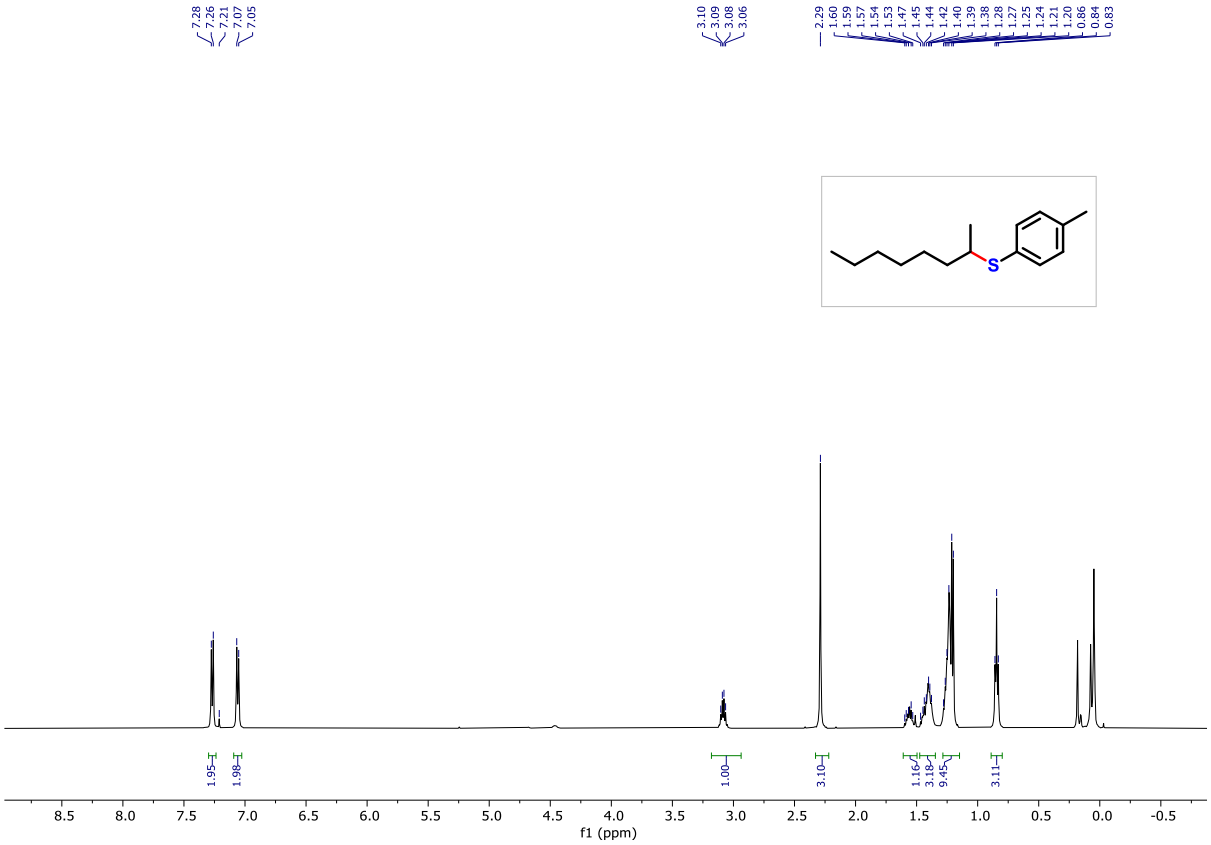


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

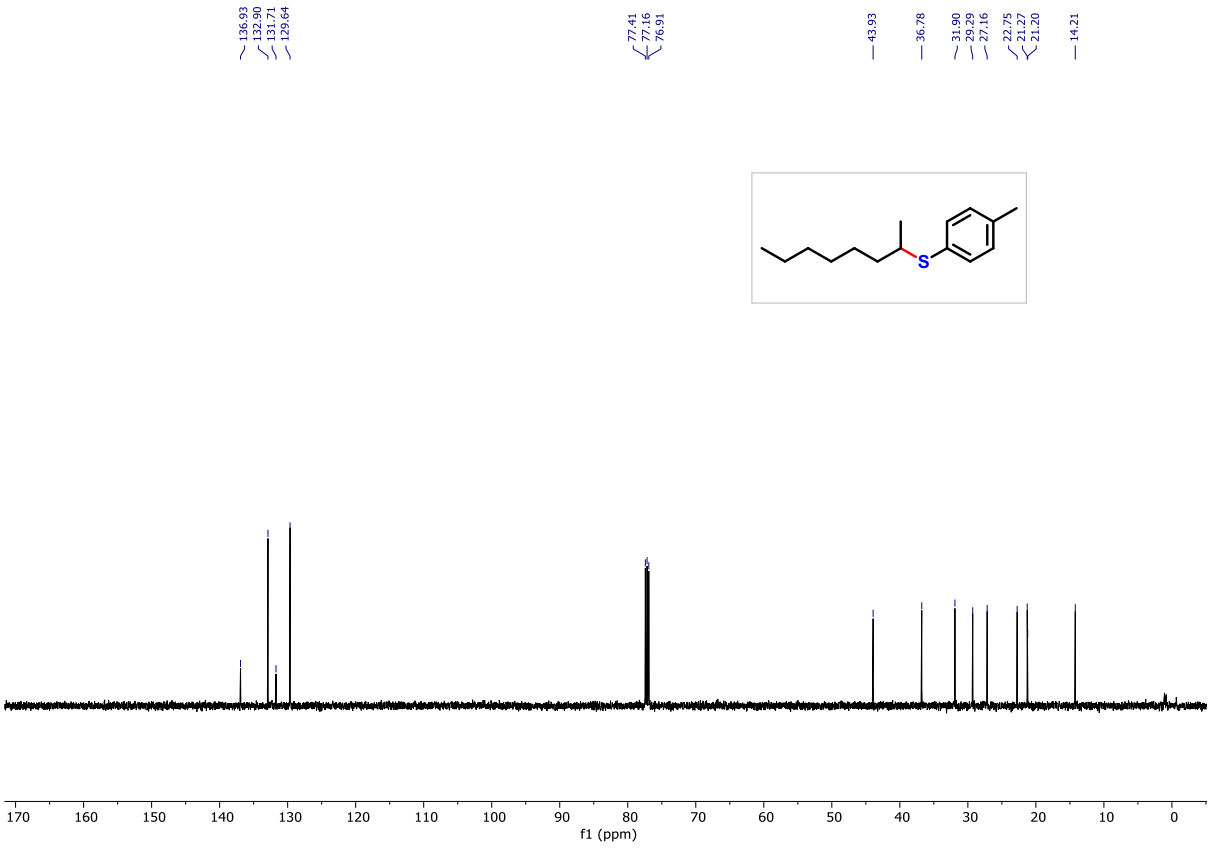


Octan-2-yl(*p*-tolyl) sulfane (6o)

^{1}H NMR (500 MHz, $CDCl_3$)

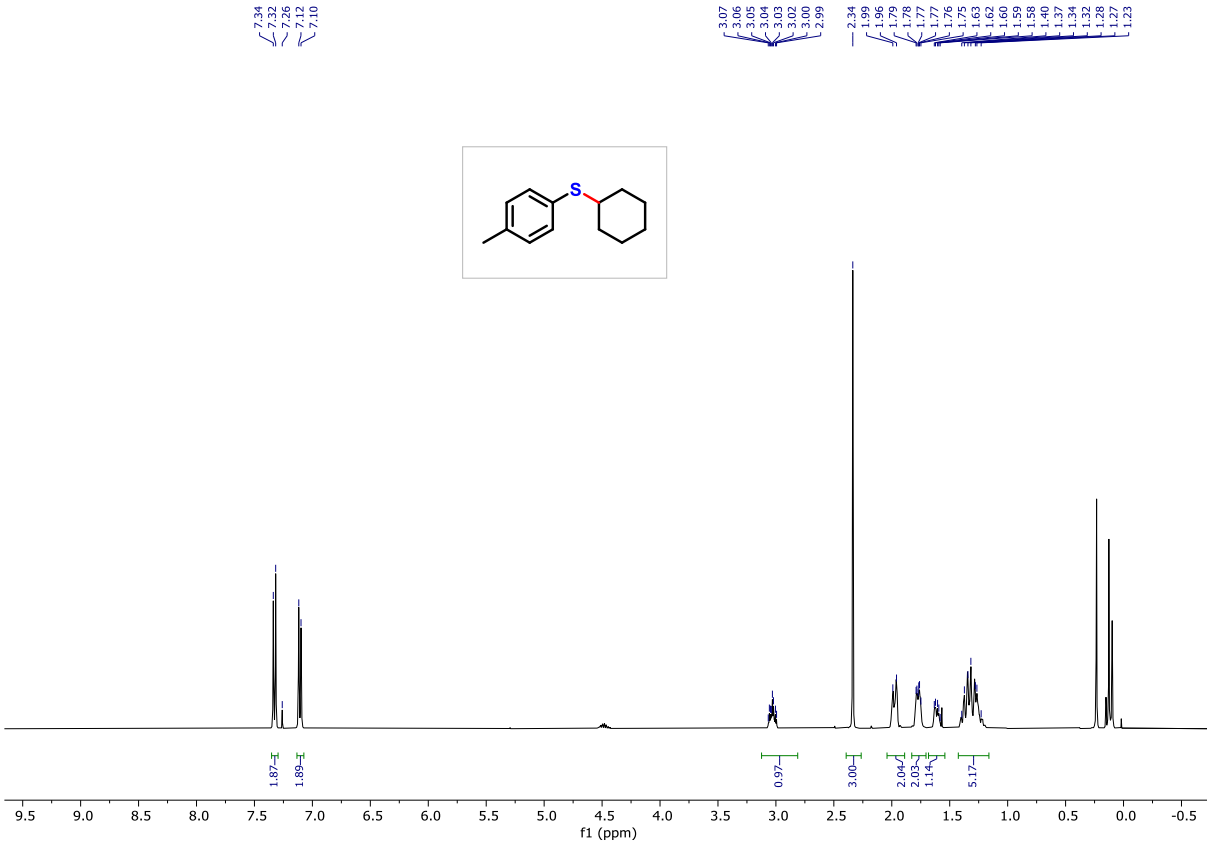


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

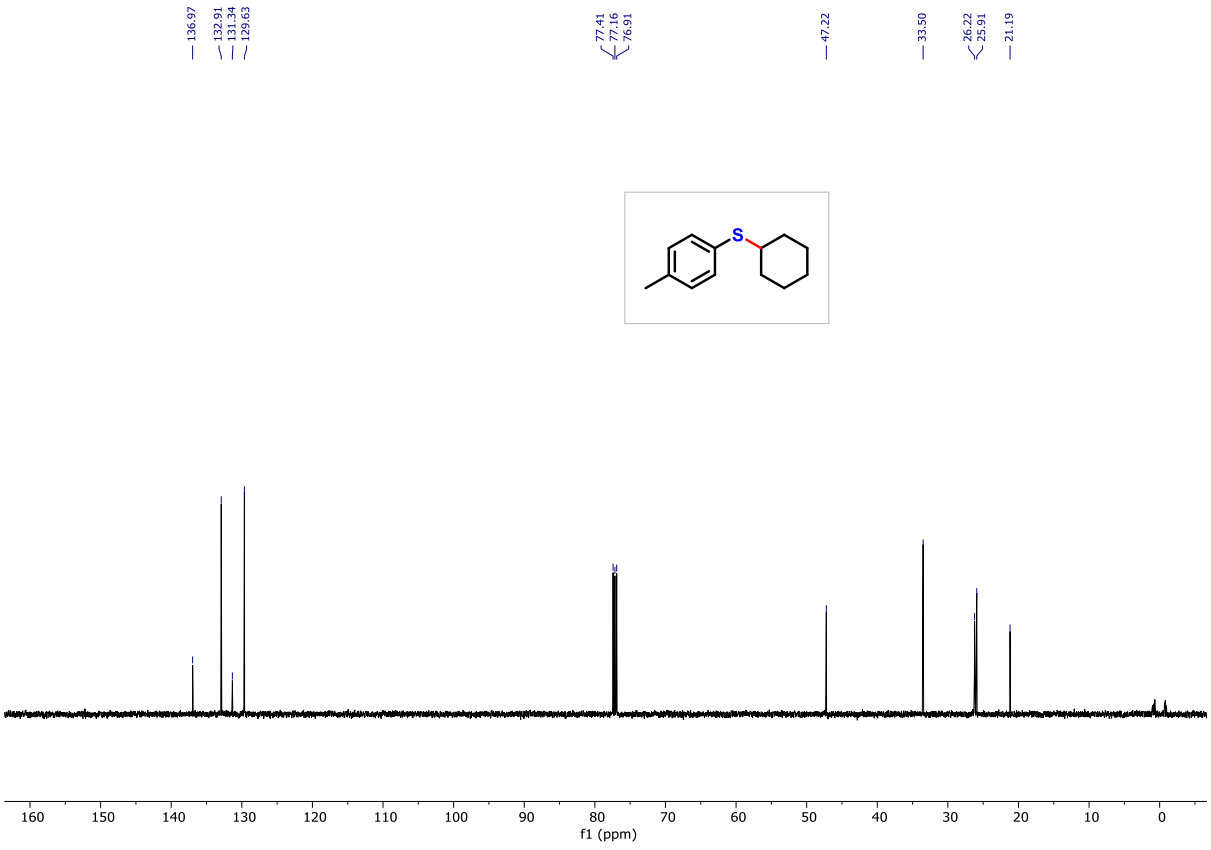


Cyclohexyl(*p*-tolyl) sulfane (6p)

^{1}H NMR (400 MHz, $CDCl_3$)

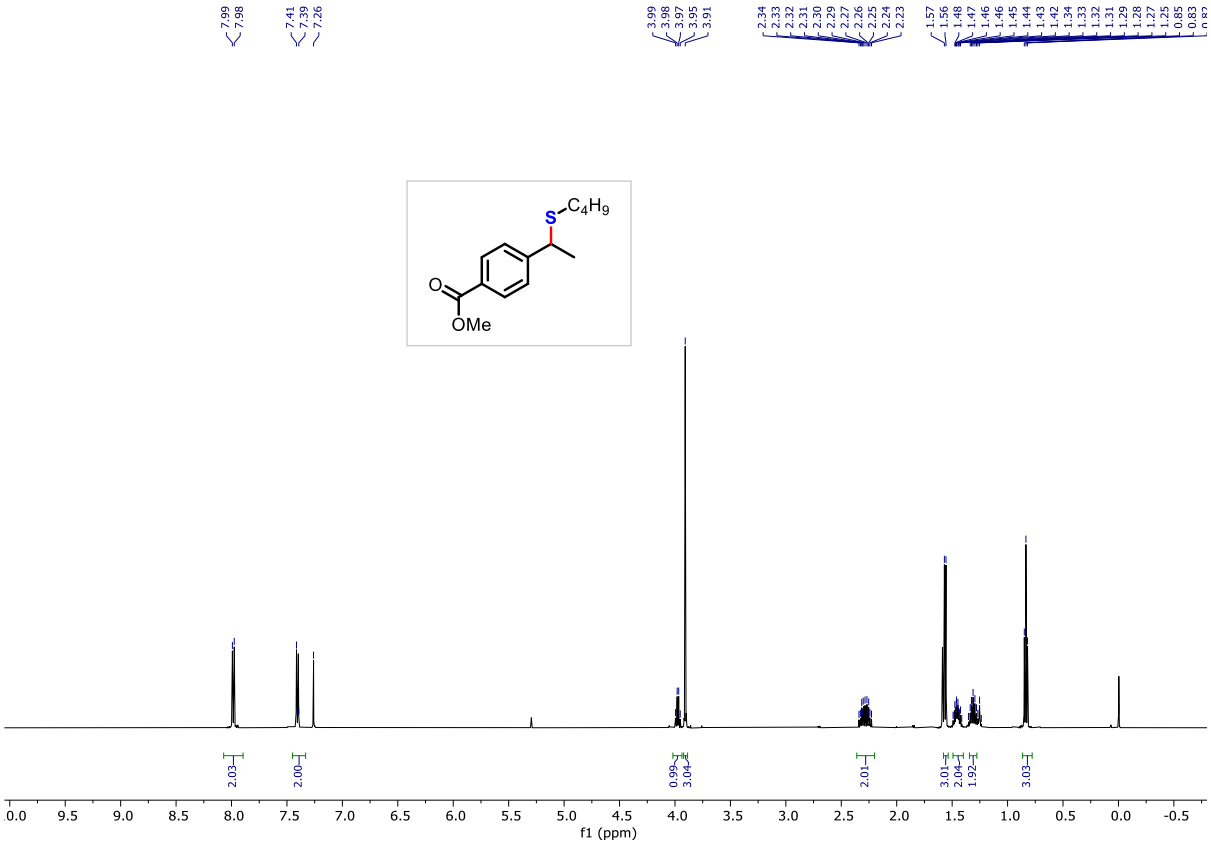


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

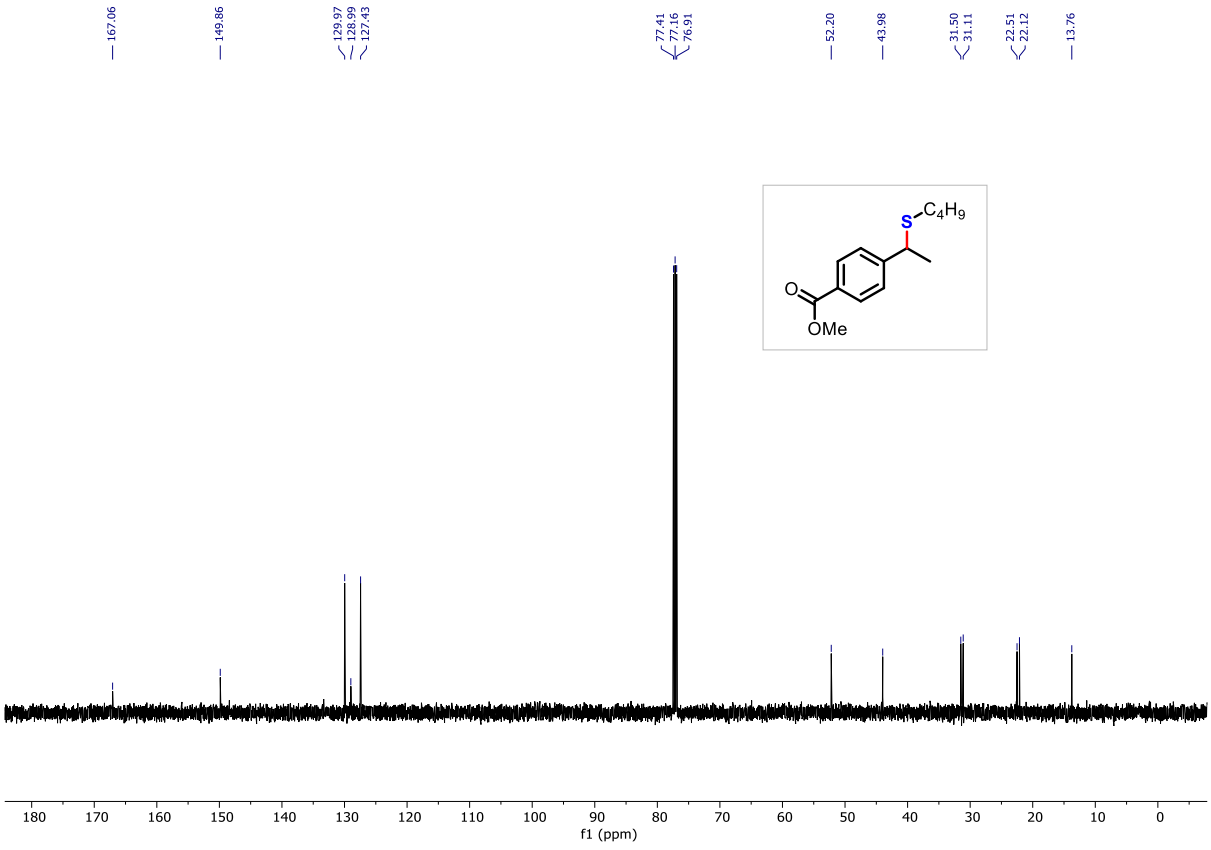


Methyl 4-(1-(butylthio) ethyl) benzoate (6q)

^{1}H NMR (500 MHz, $CDCl_3$)

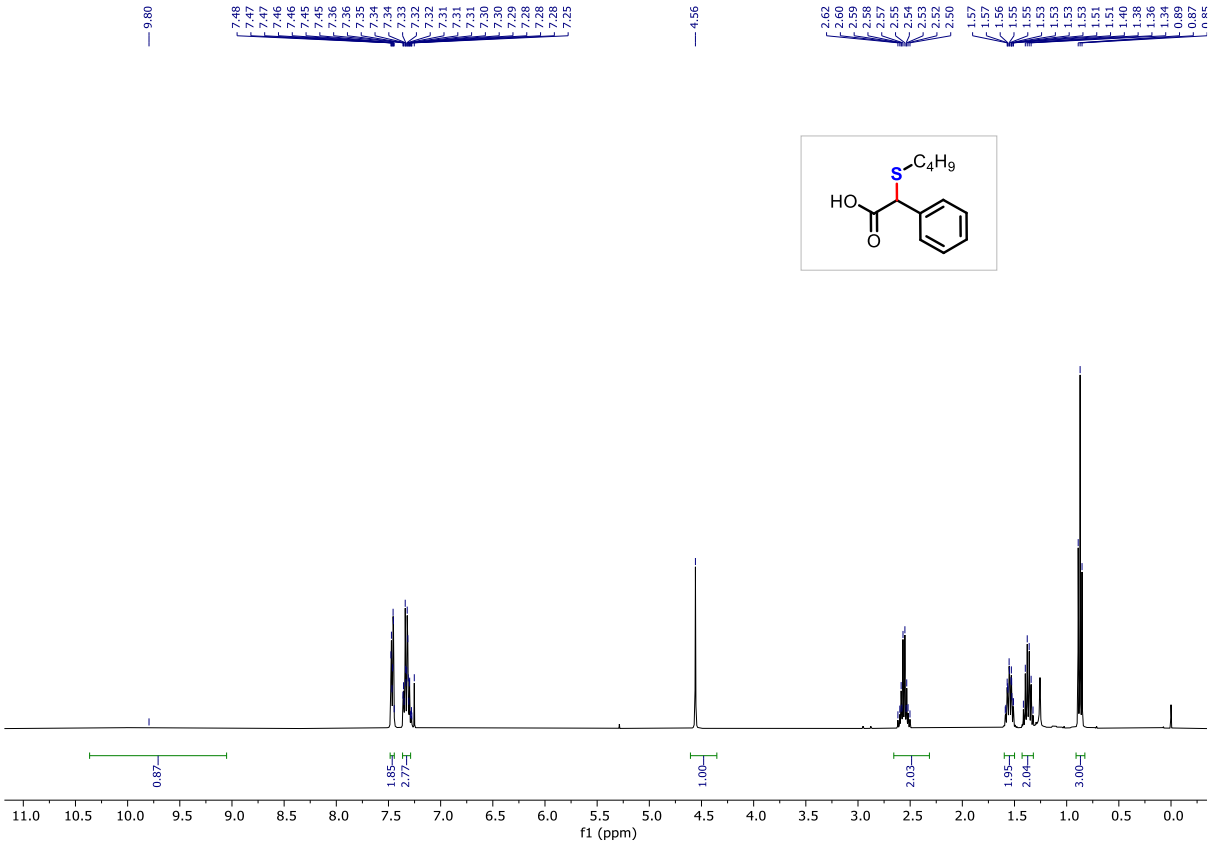


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

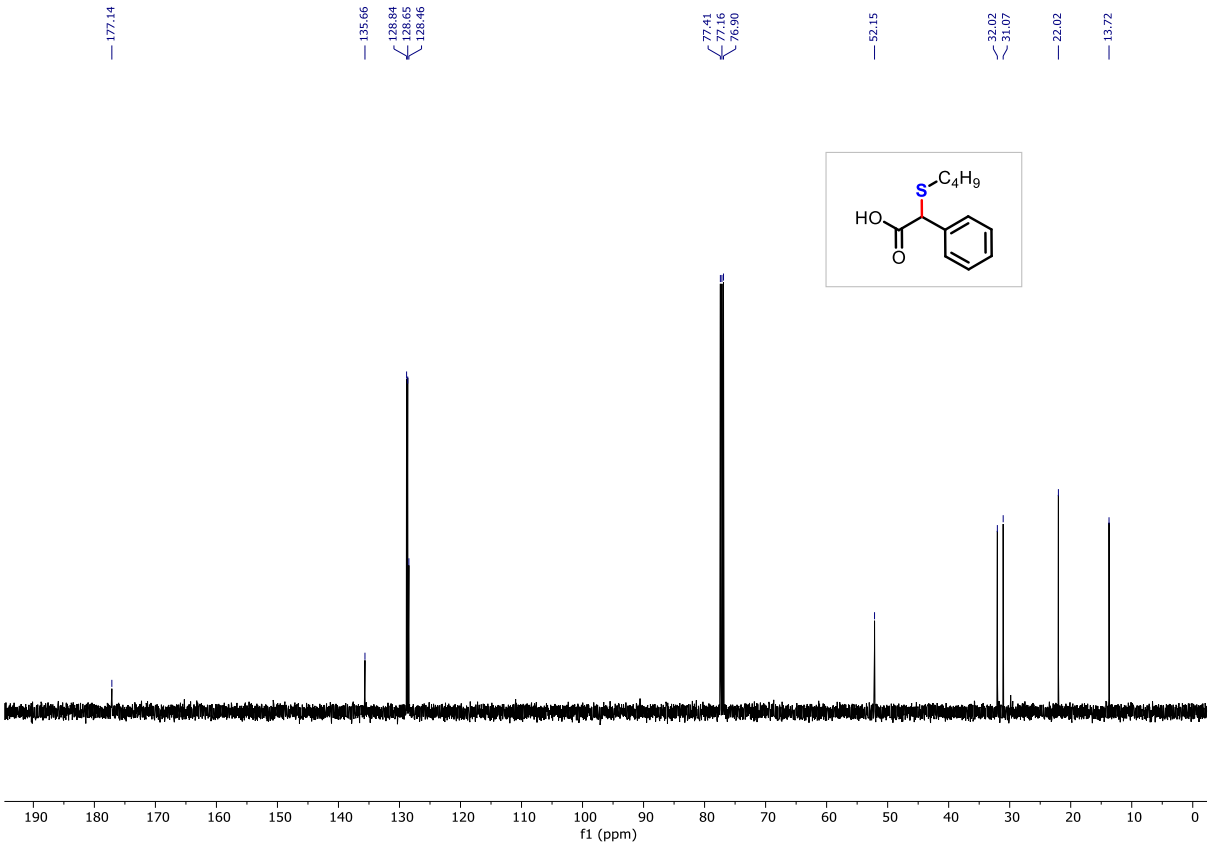


2-(Butylthio)-2-phenylacetic acid (6r)

^{1}H NMR (400 MHz, $CDCl_3$)

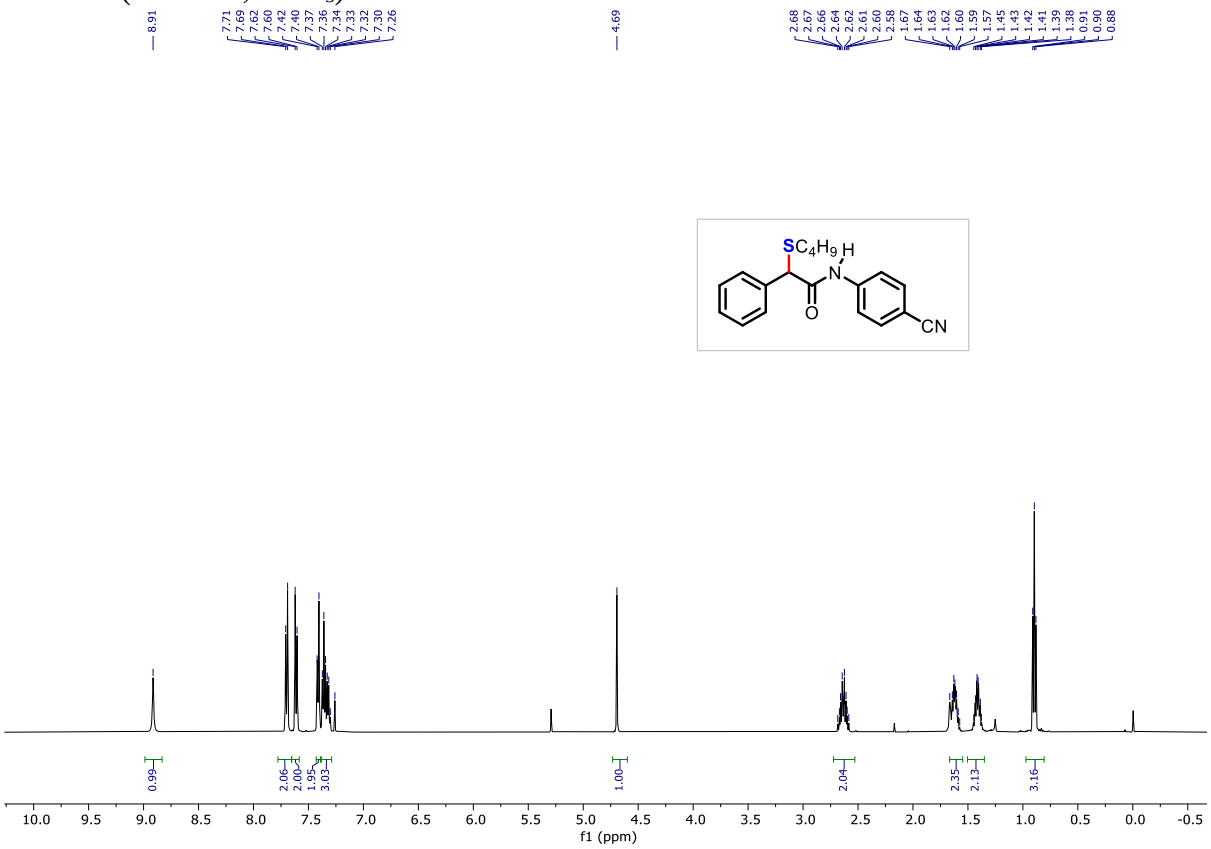


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

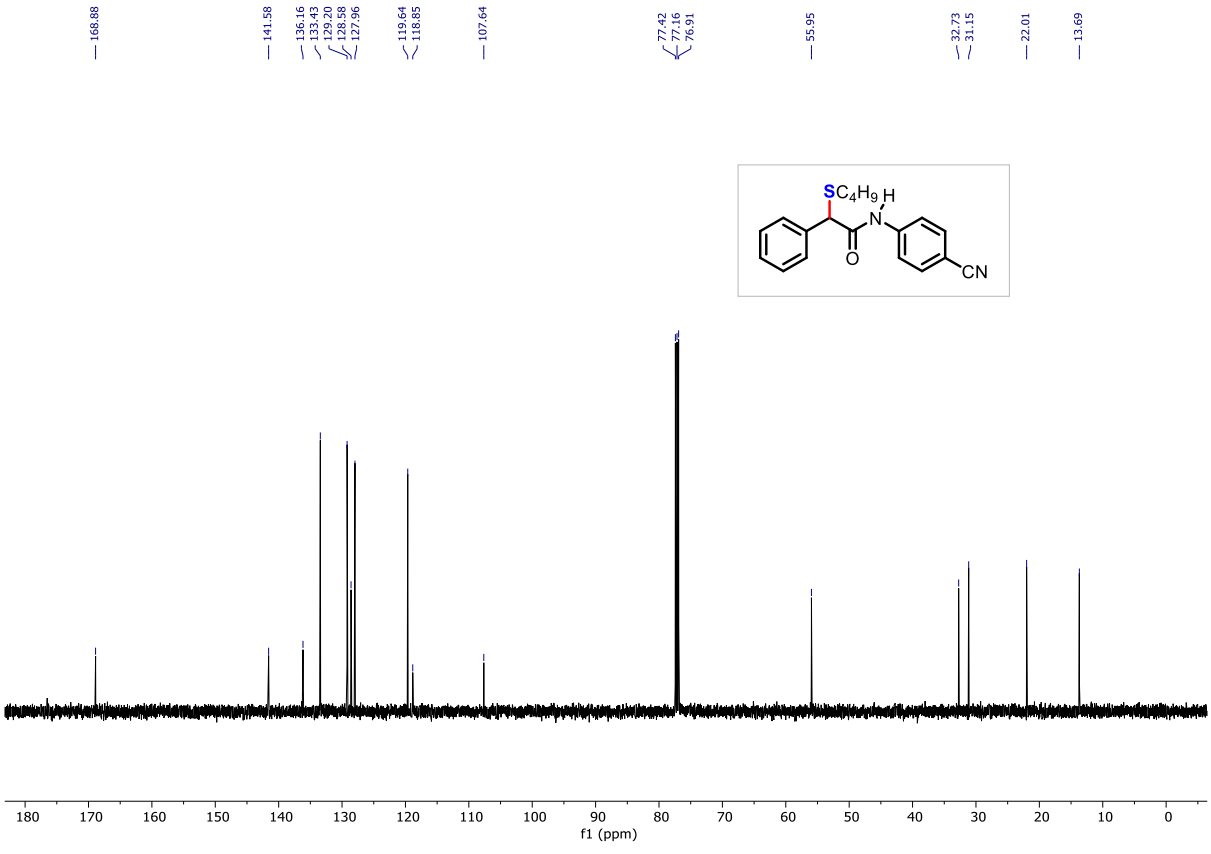


2-(Butylthio)-*N*-(4-cyanophenyl)-2-phenylacetamide (6s)

^{1}H NMR (500 MHz, $CDCl_3$)

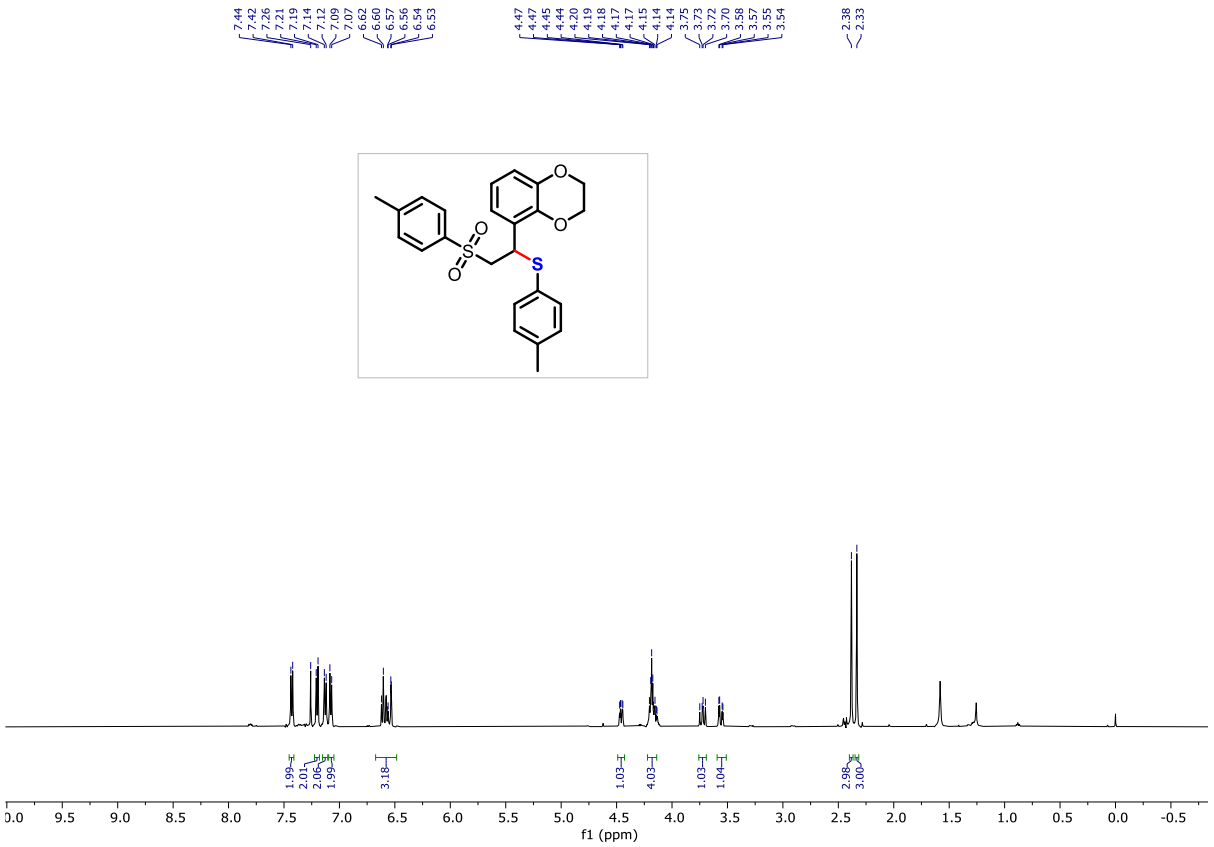


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

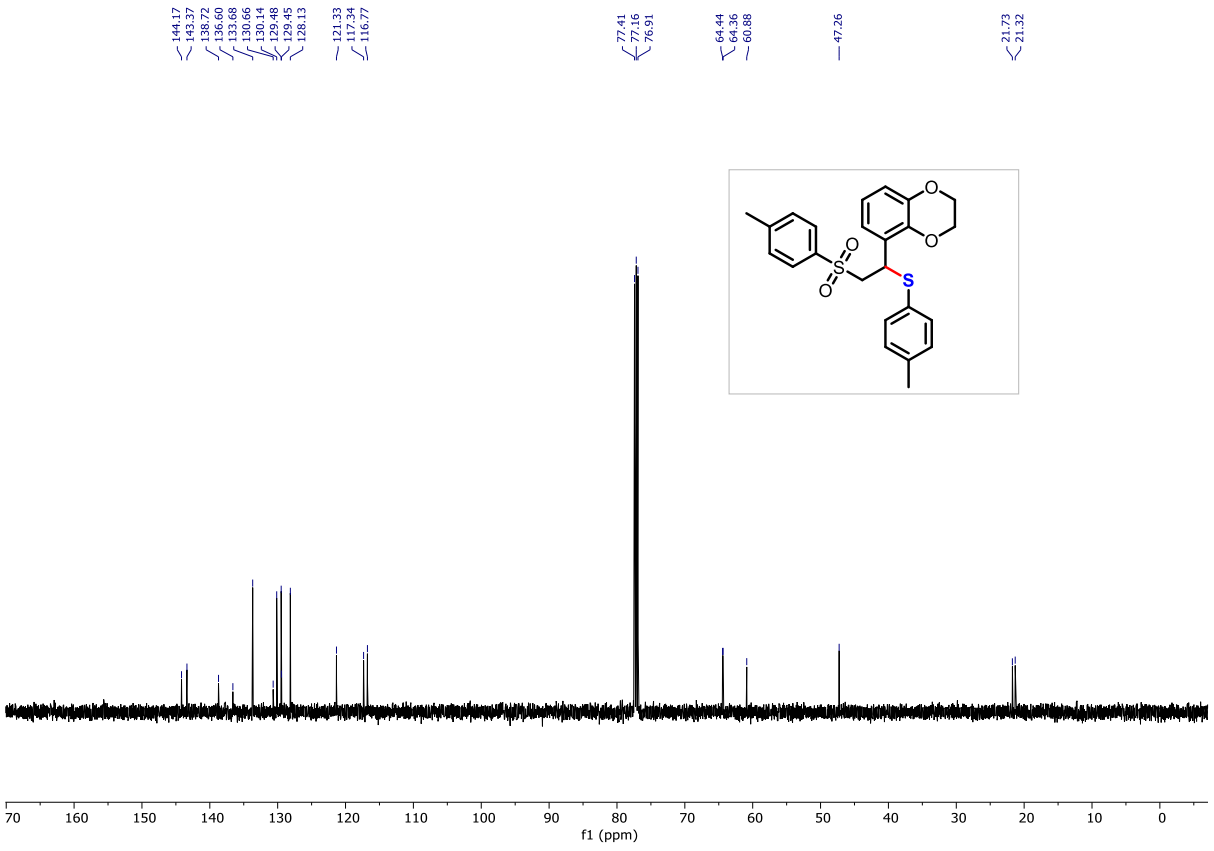


5-(1-(*p*-Tolylthio)-2-tosylethyl)-2,3-dihydrobenzo[b][1,4] dioxine (6t)

^{1}H NMR (500 MHz $CDCl_3$)

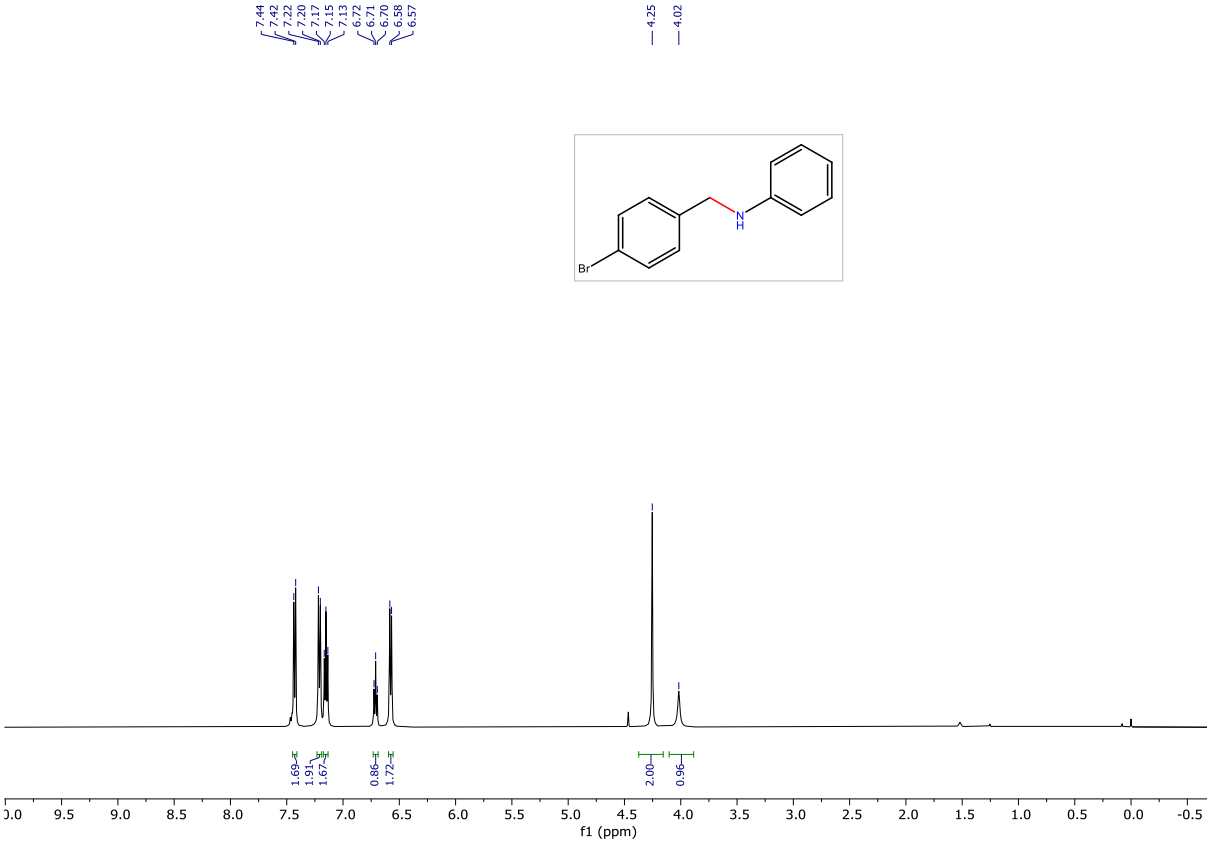


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

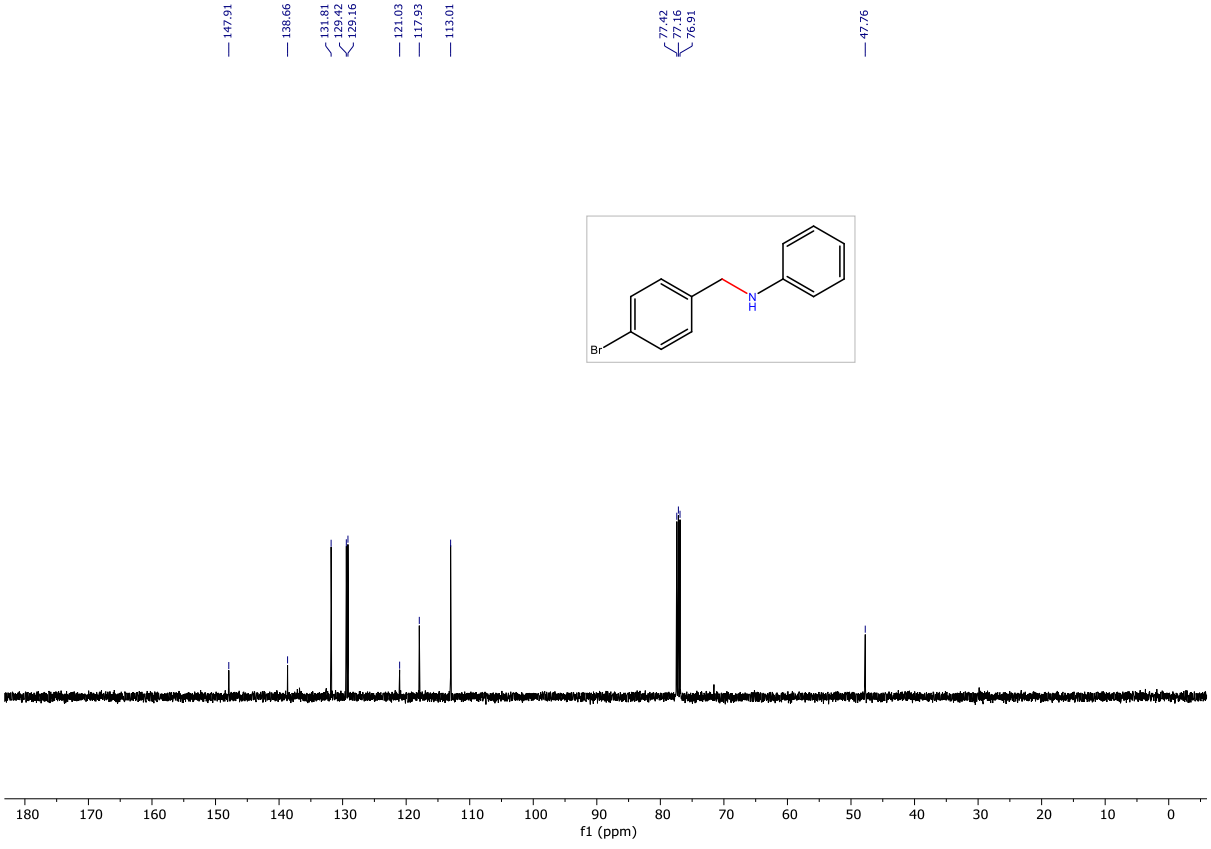


N-(4-Bromobenzyl) aniline (4aa)

^{1}H NMR (500 MHz, $CDCl_3$)

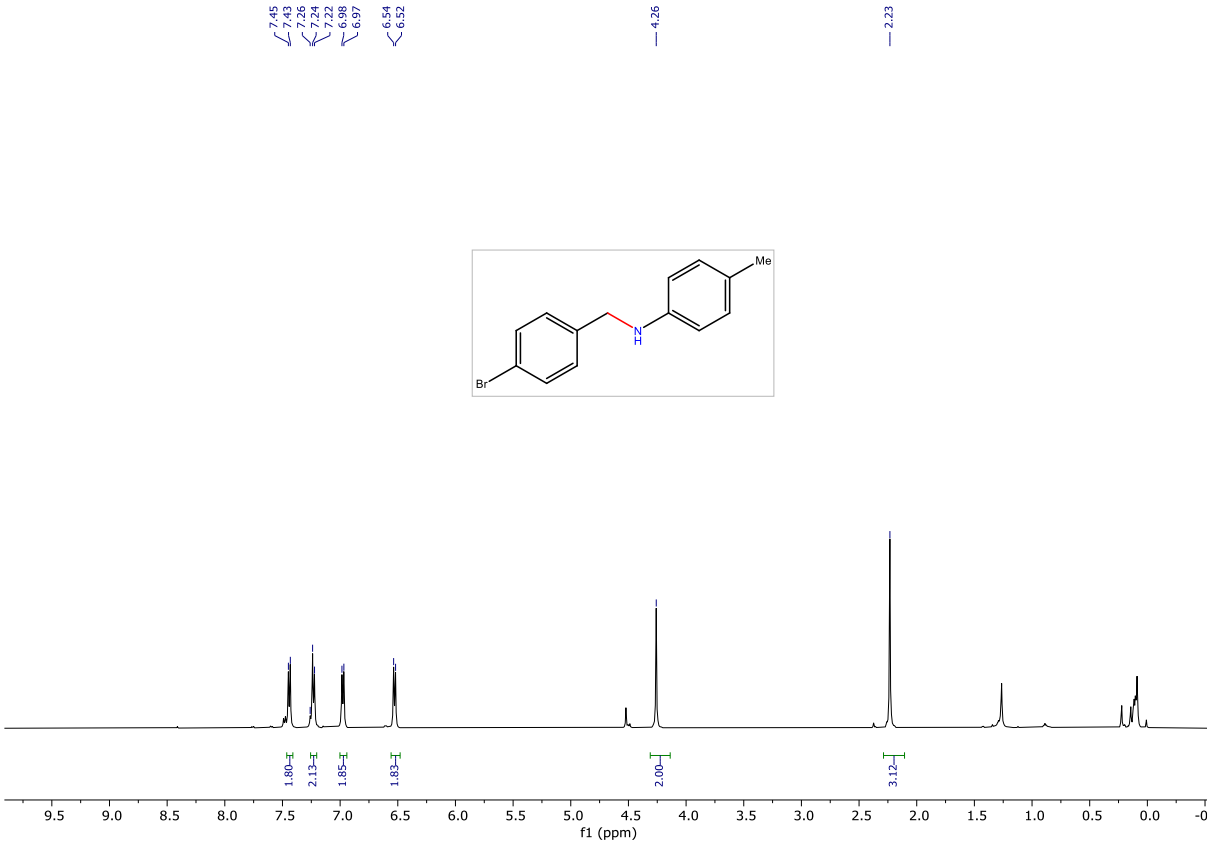


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

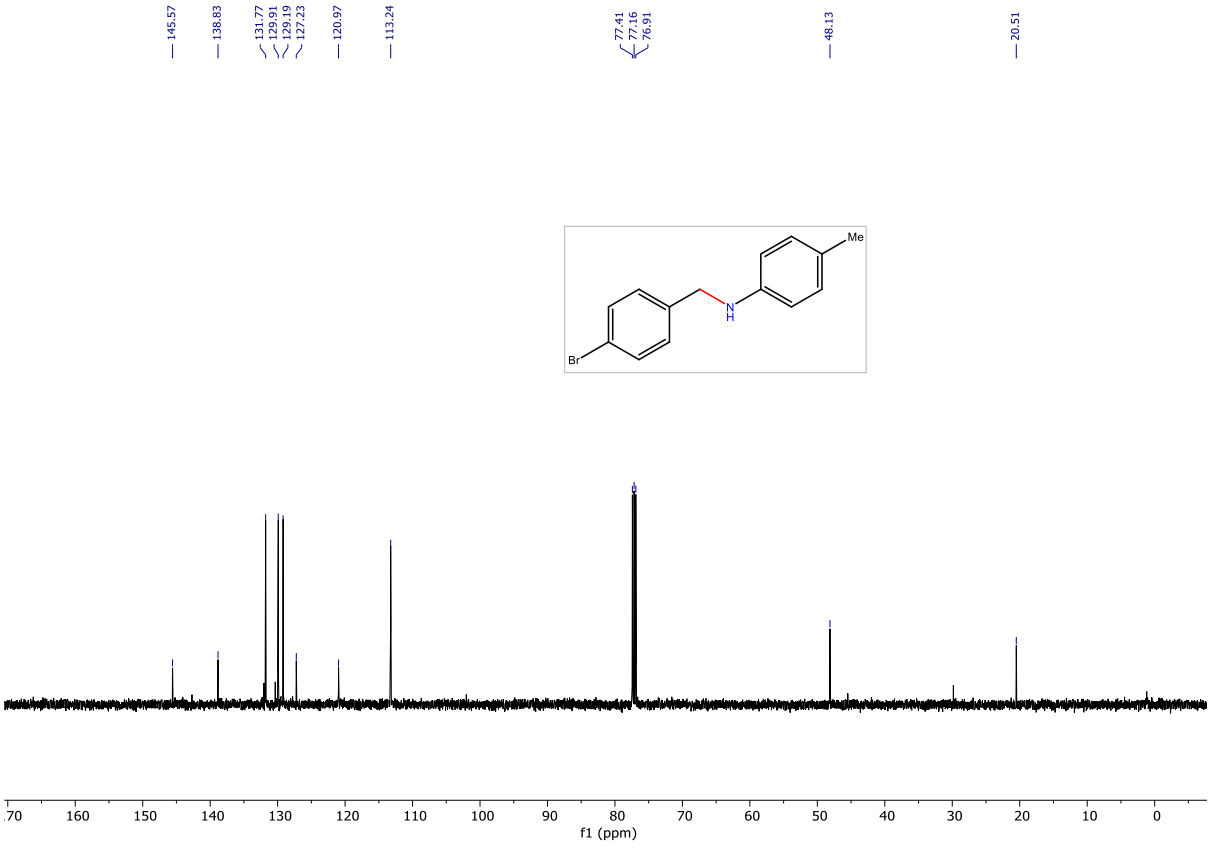


N-(4-Bromobenzyl)-4-methylaniline (4ab)

^{1}H NMR (500 MHz, $CDCl_3$)

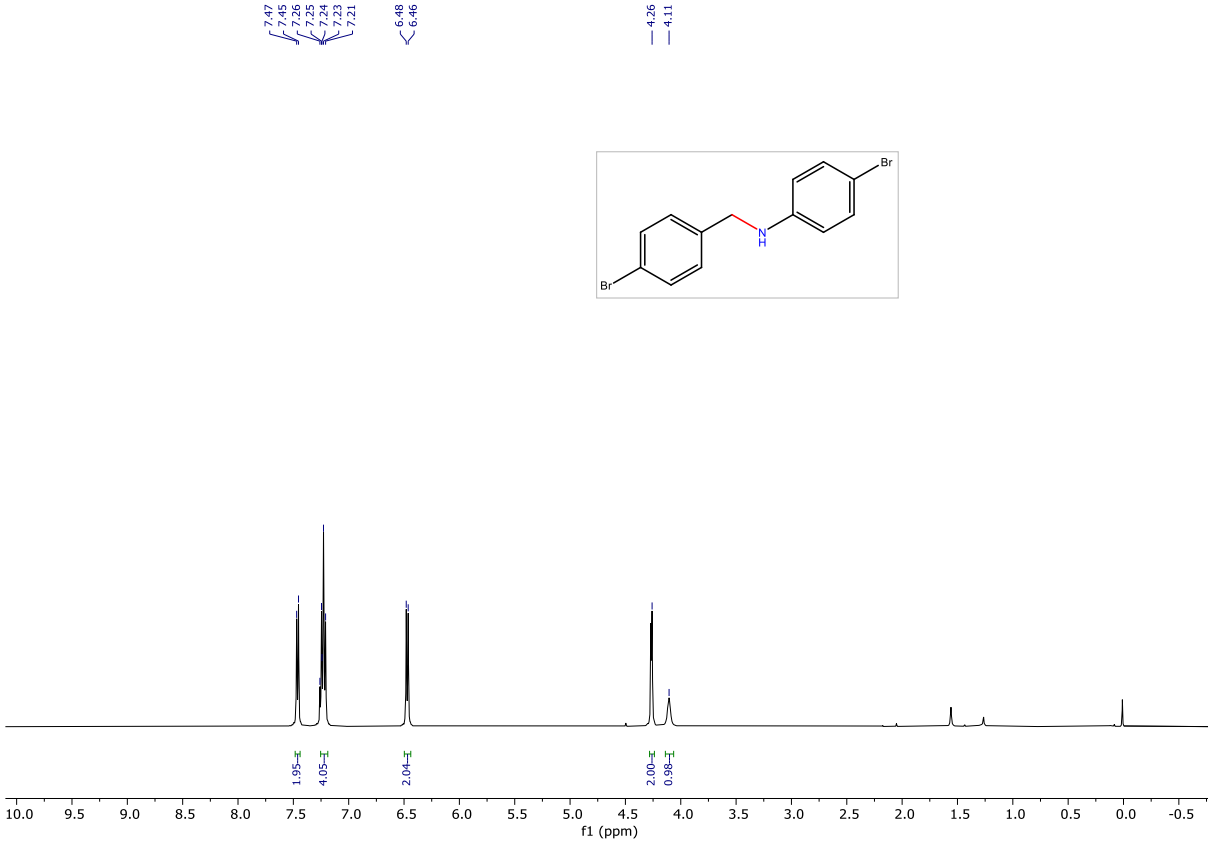


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

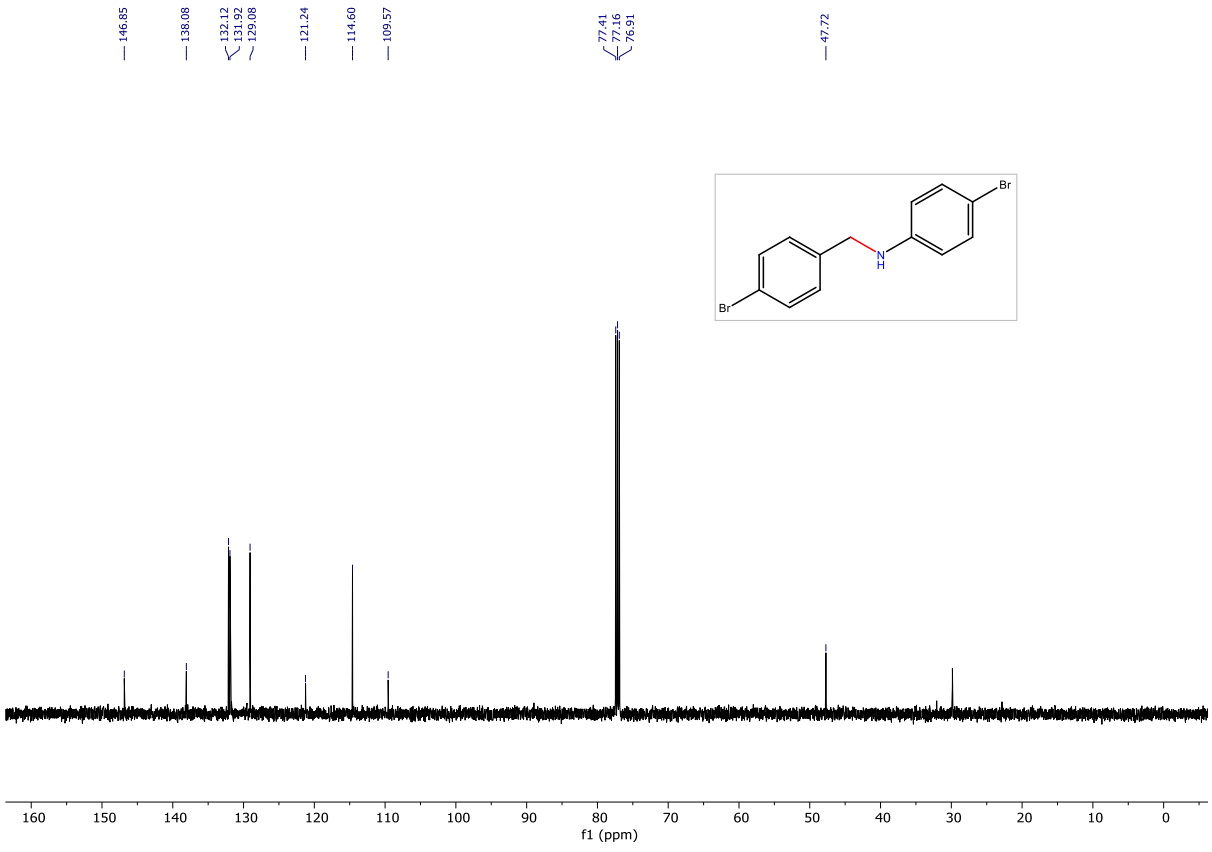


4-Bromo-*N*-(4-bromobenzyl) aniline (4ac)

^{1}H NMR (500 MHz, $CDCl_3$)

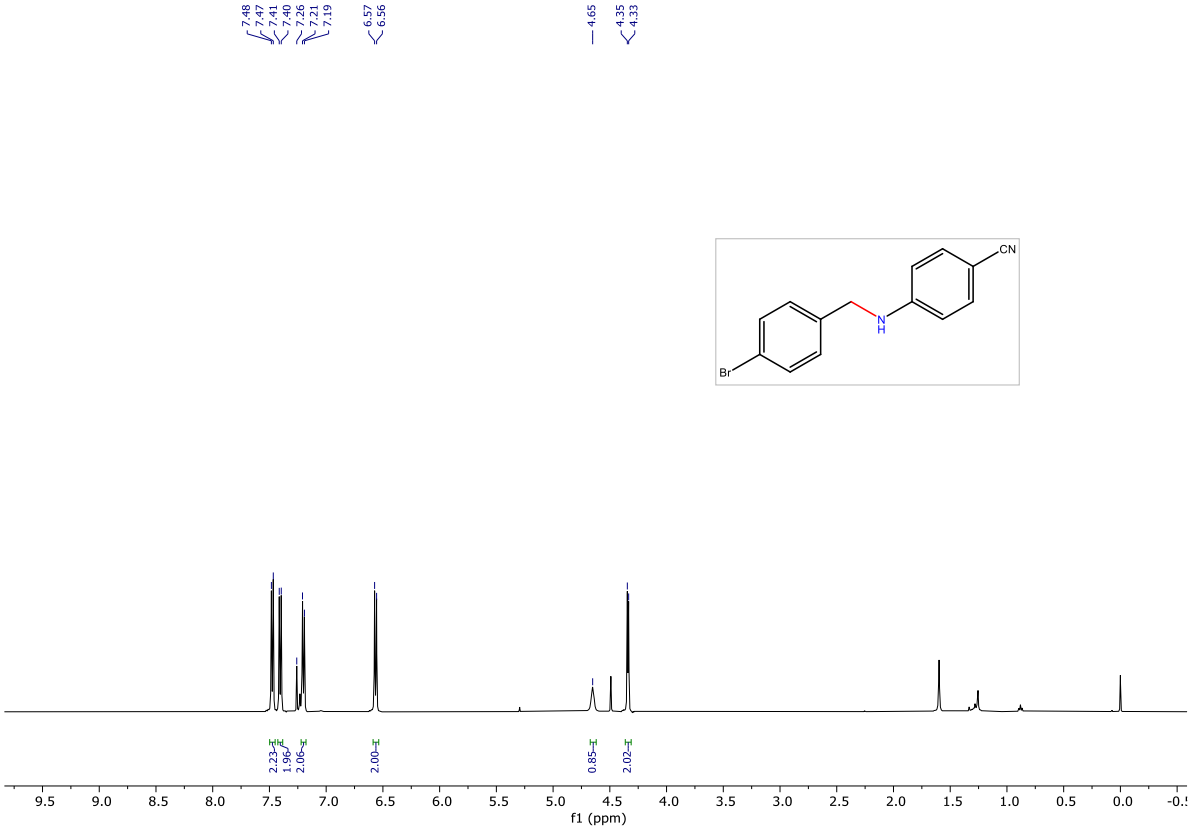


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

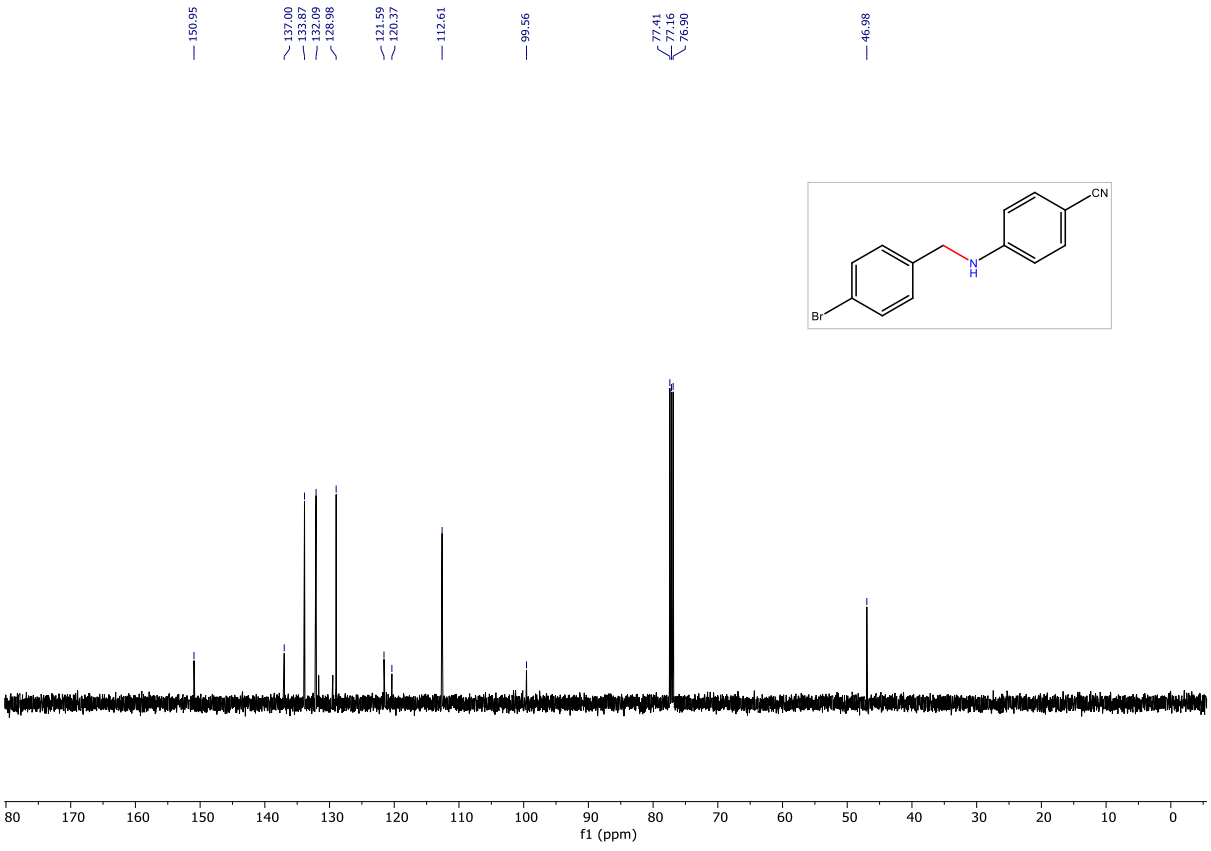


4-((4-Bromobenzyl) amino) benzonitrile (4ad)

^{1}H NMR (500 MHz, $CDCl_3$)

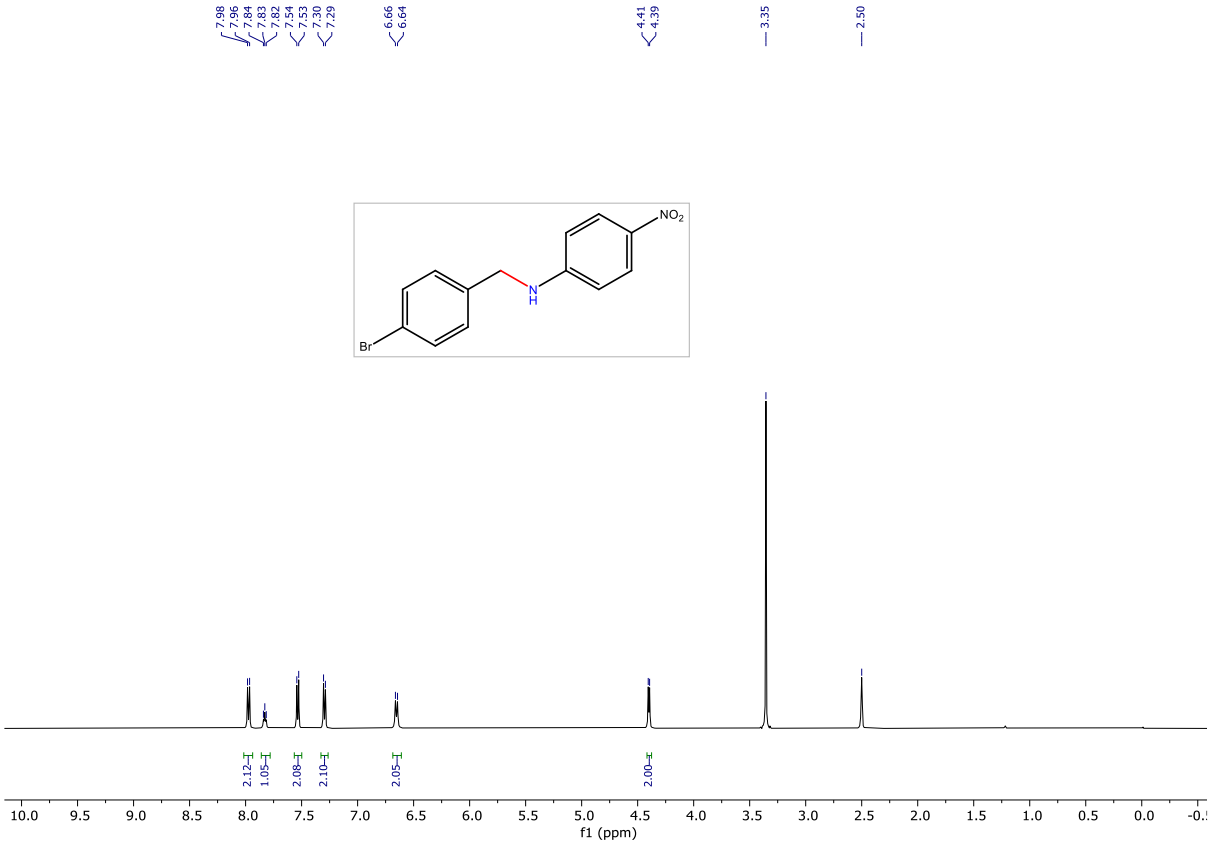


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

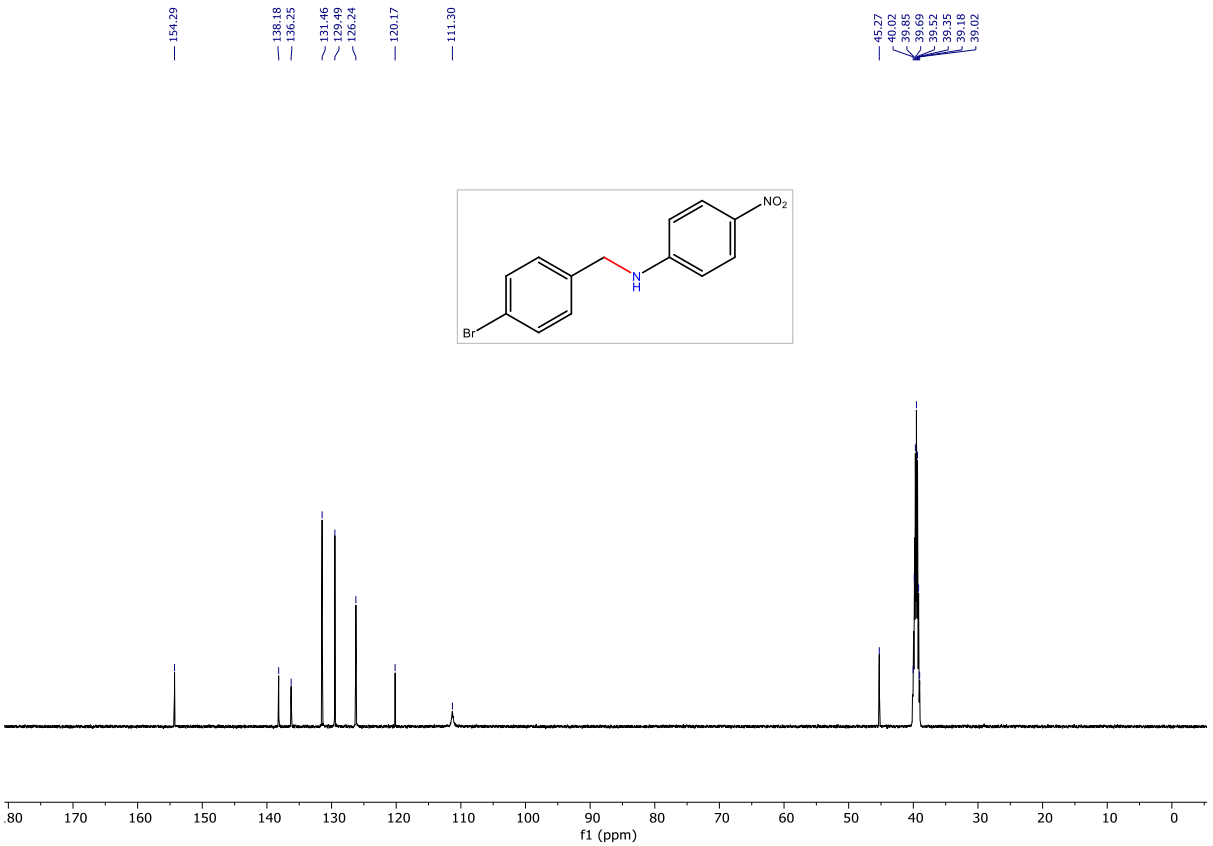


N-(4-Bromobenzyl)-4-nitroaniline (4ae)

^{1}H NMR (500 MHz, DMSO-d_6)

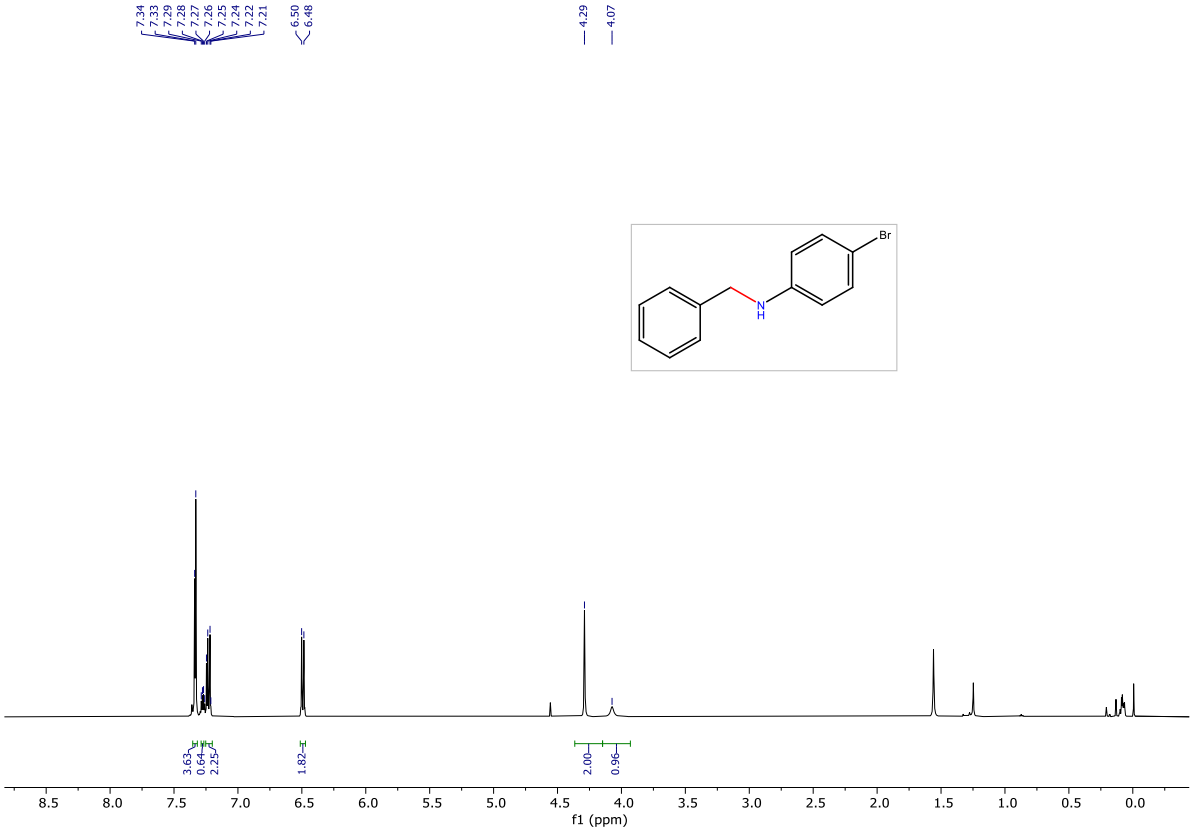


^{13}C{^{1}H} NMR (126 MHz DMSO-d_6)

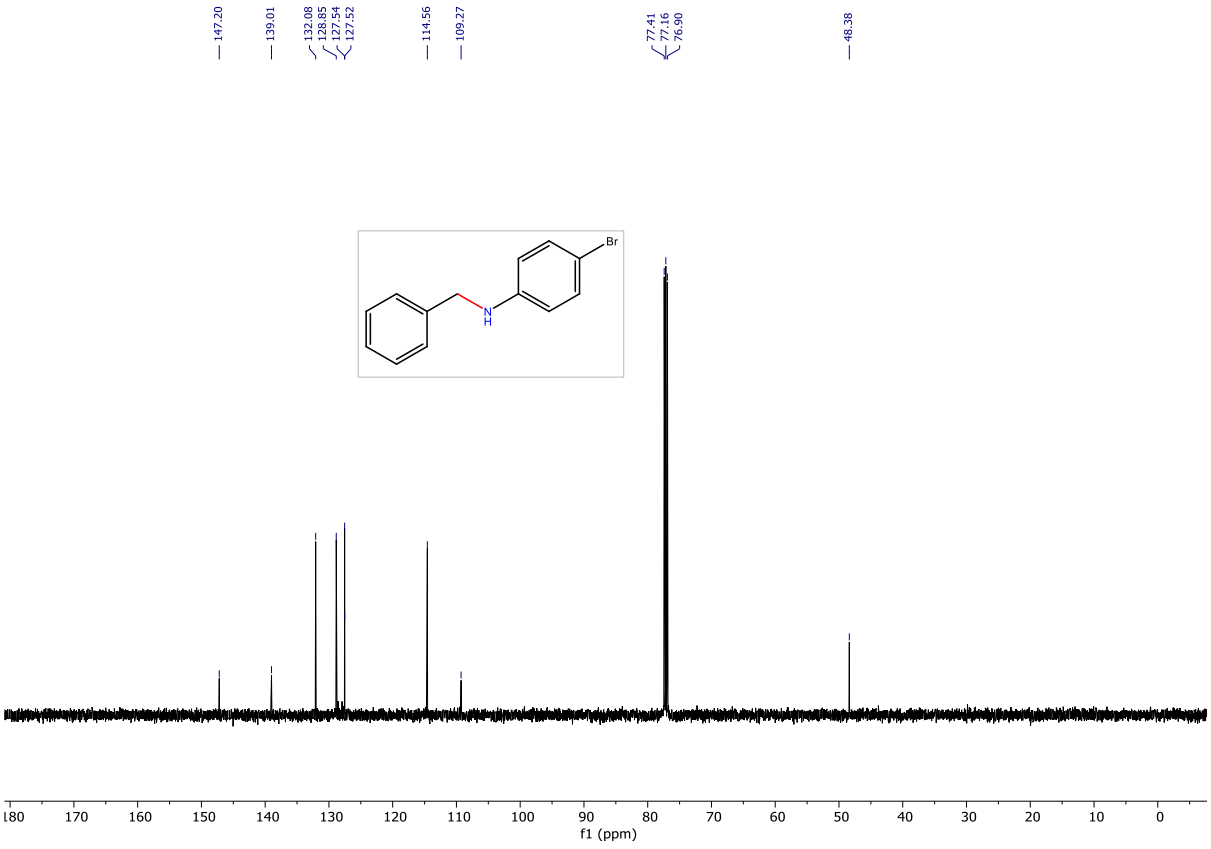


N-Benzyl-4-bromoaniline (4af)

^{1}H NMR (500 MHz $CDCl_3$)

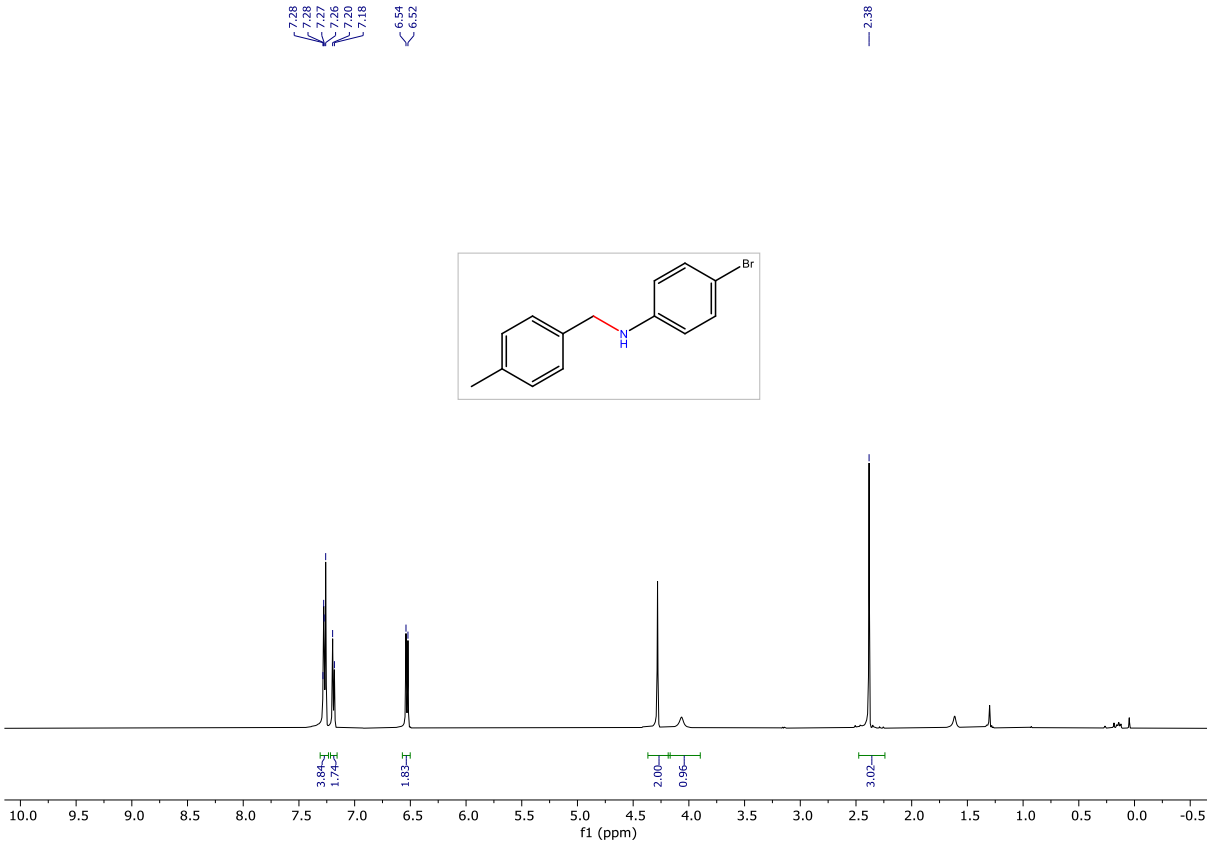


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

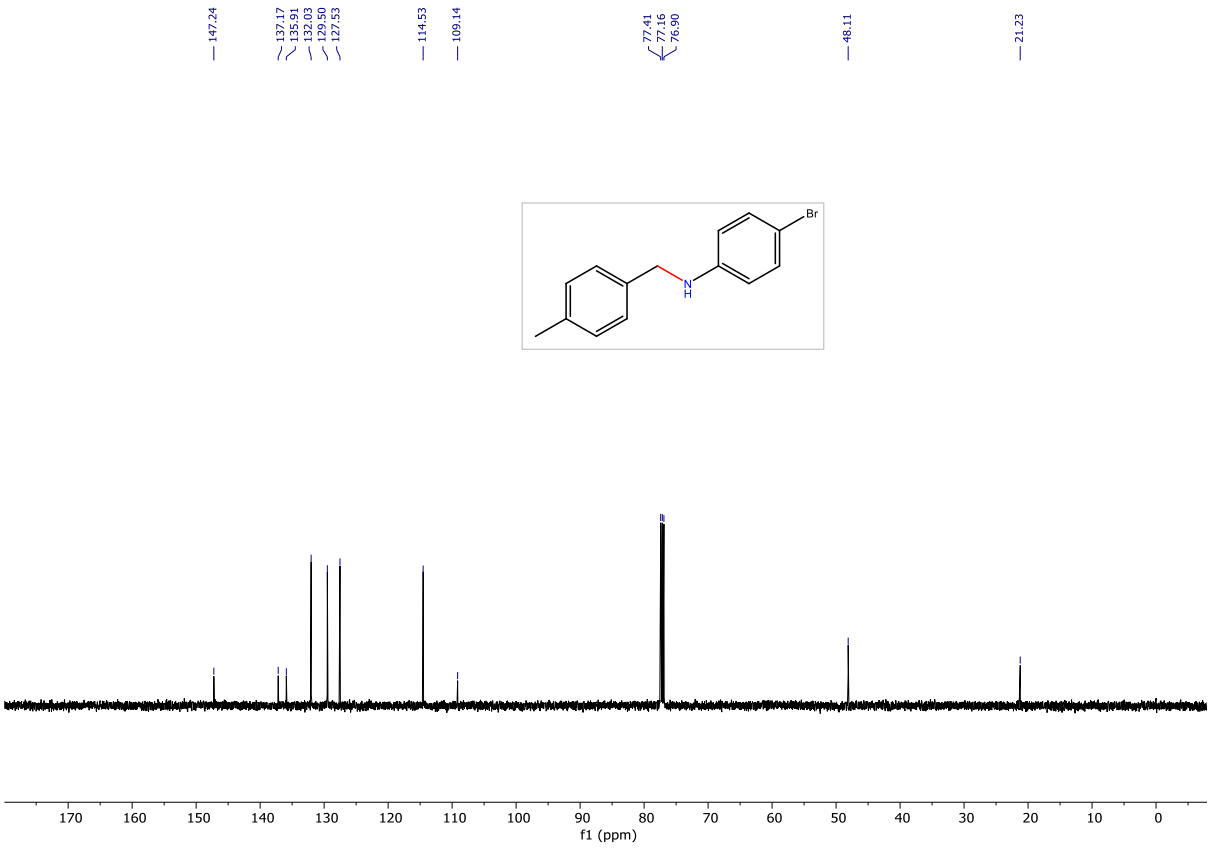


4-Bromo-*N*-(4-methylbenzyl) aniline (4ag)

^{1}H NMR (500 MHz $CDCl_3$)

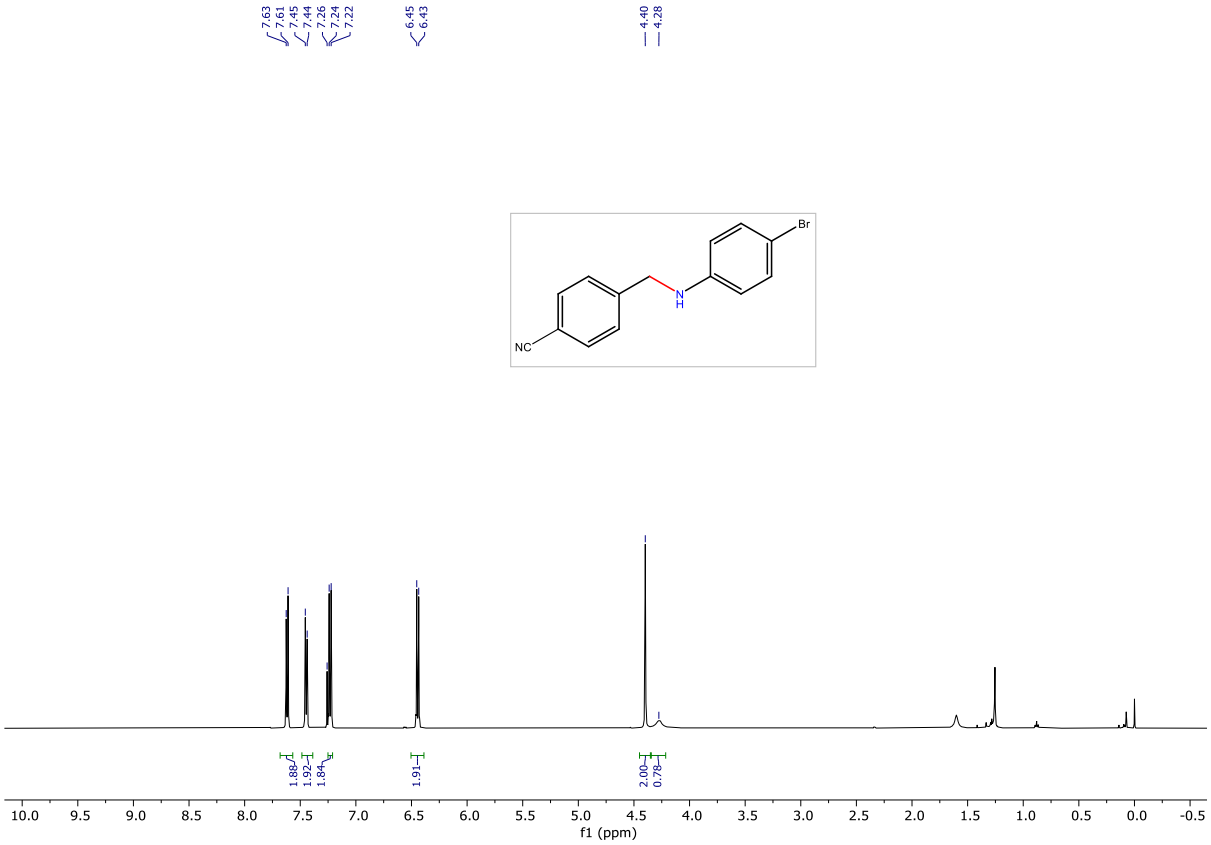


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

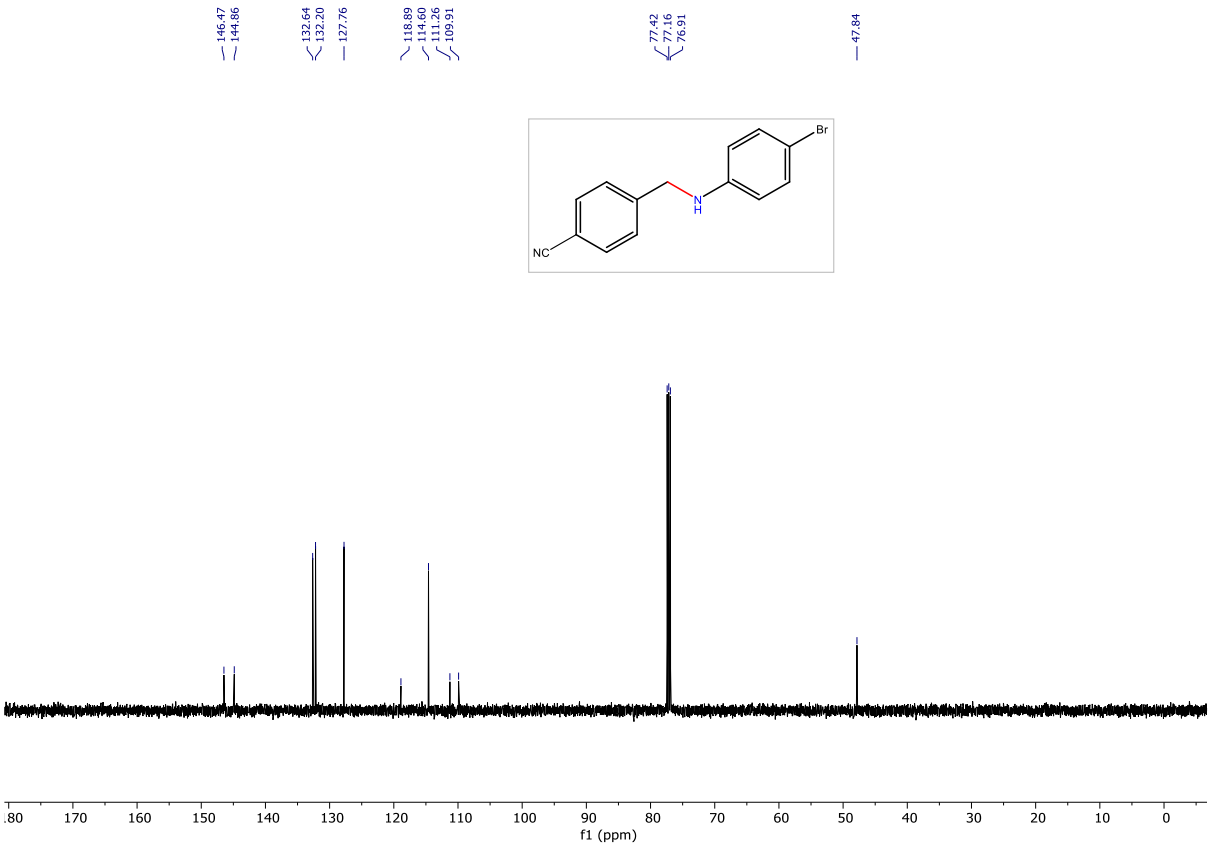


4-(((4-Bromophenyl) amino) methyl) benzonitrile (4ah)

^{1}H NMR (500 MHz $CDCl_3$)

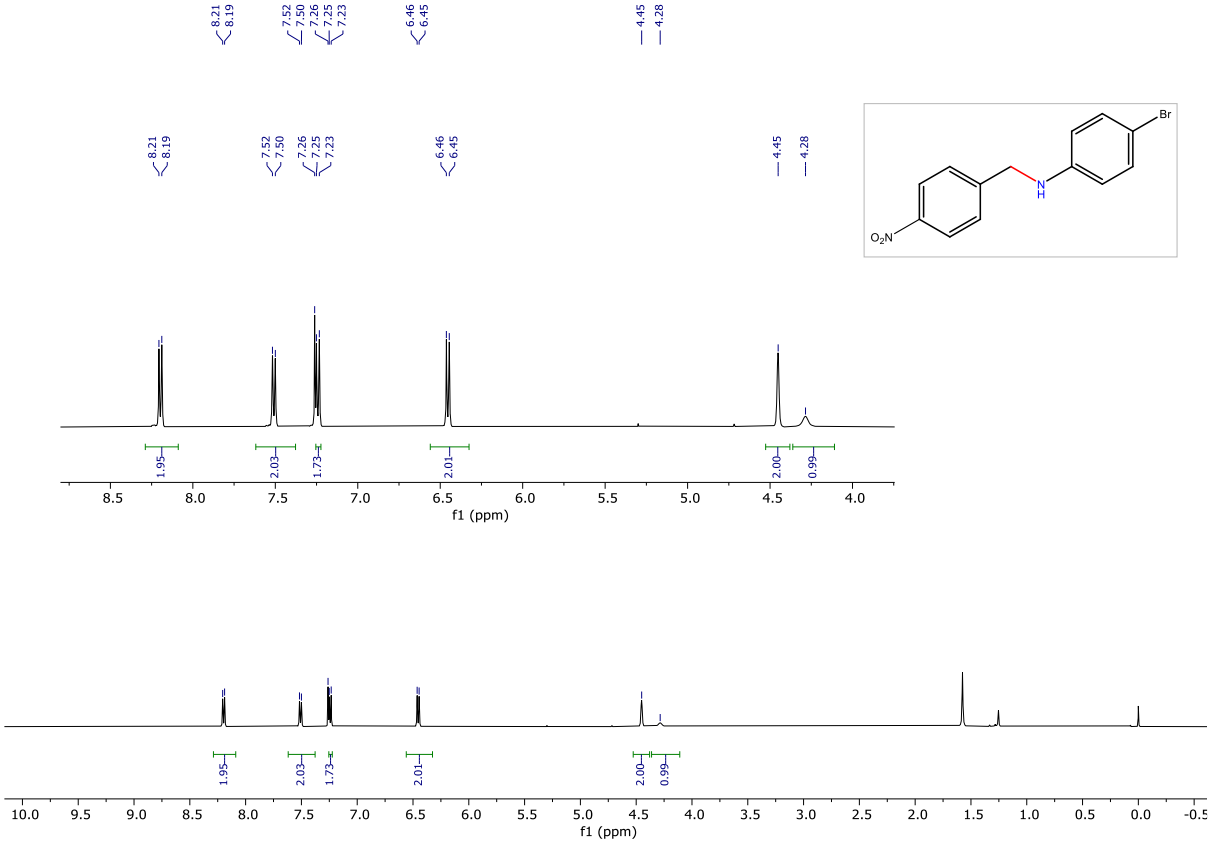


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

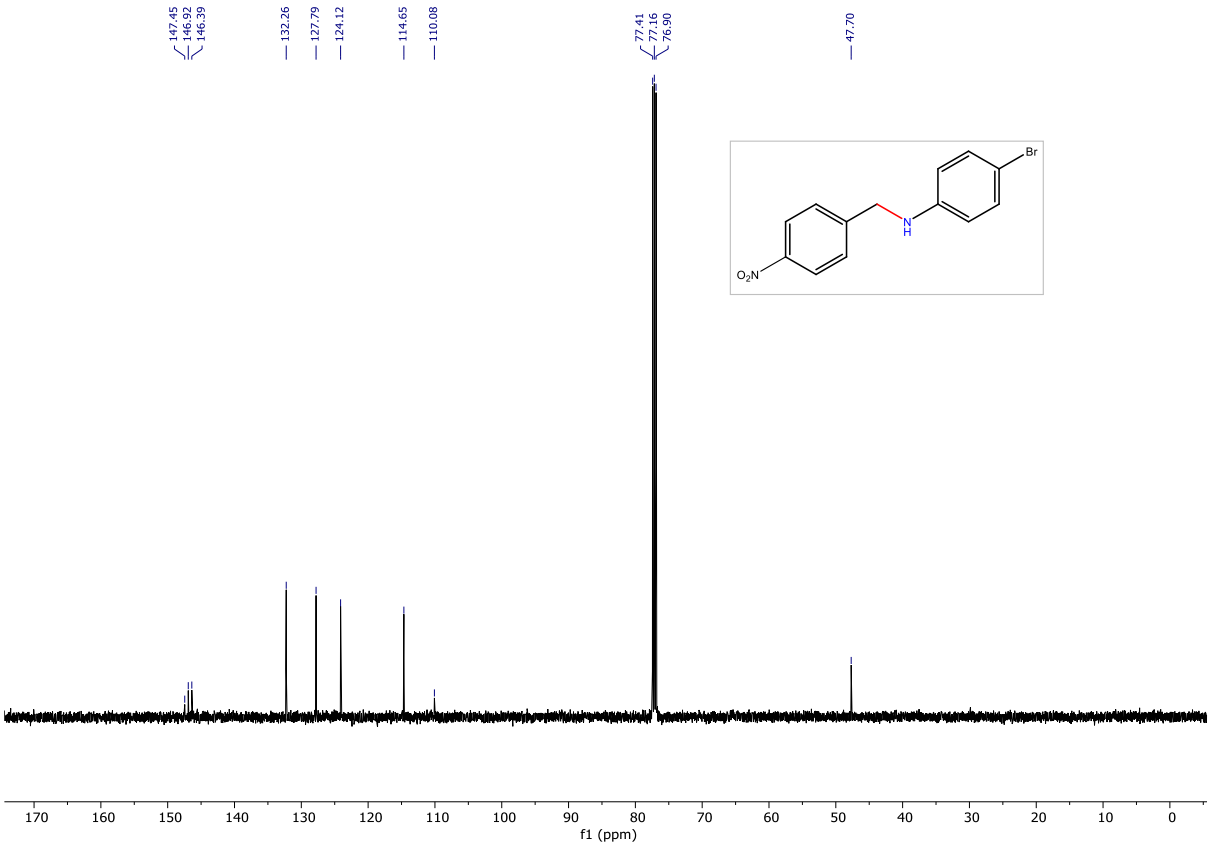


4-Bromo-*N*-(4-nitrobenzyl) aniline (4ai)

^{1}H NMR (500 MHz $CDCl_3$)

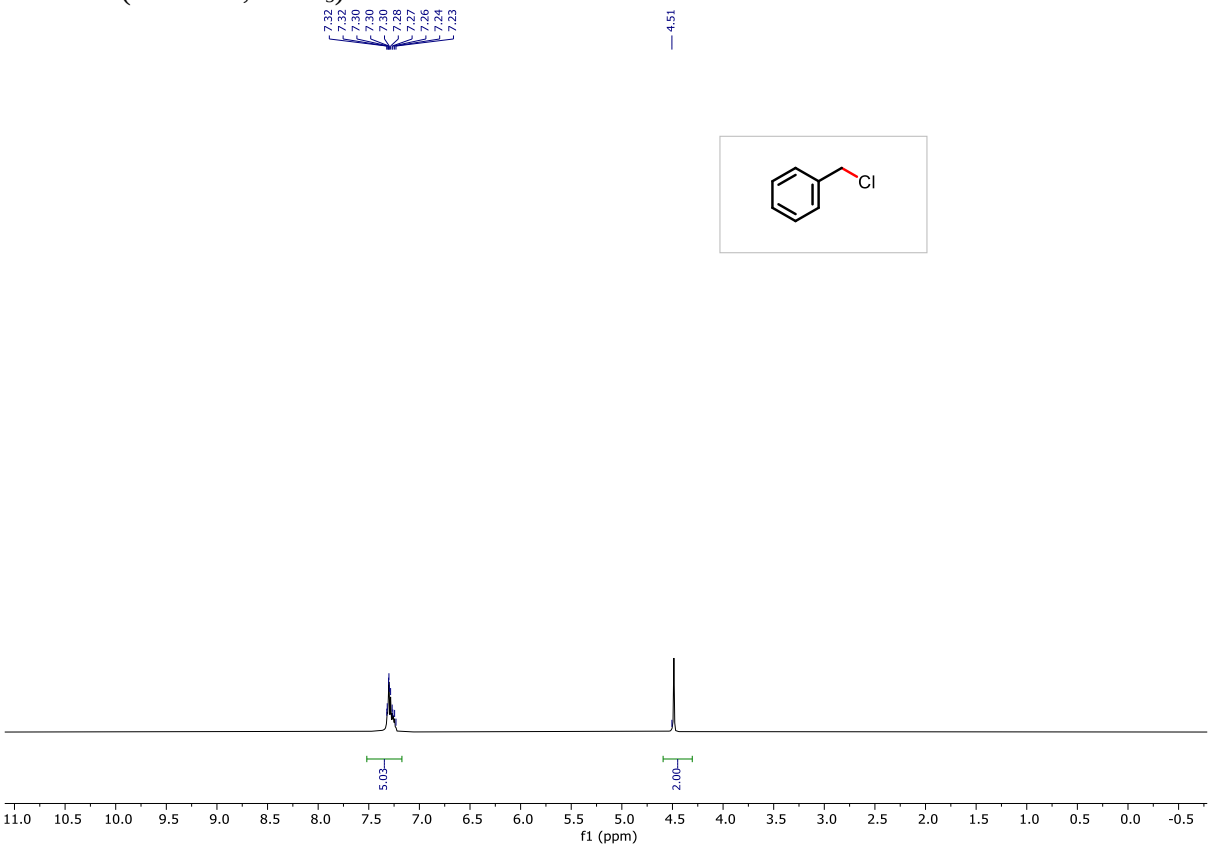


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

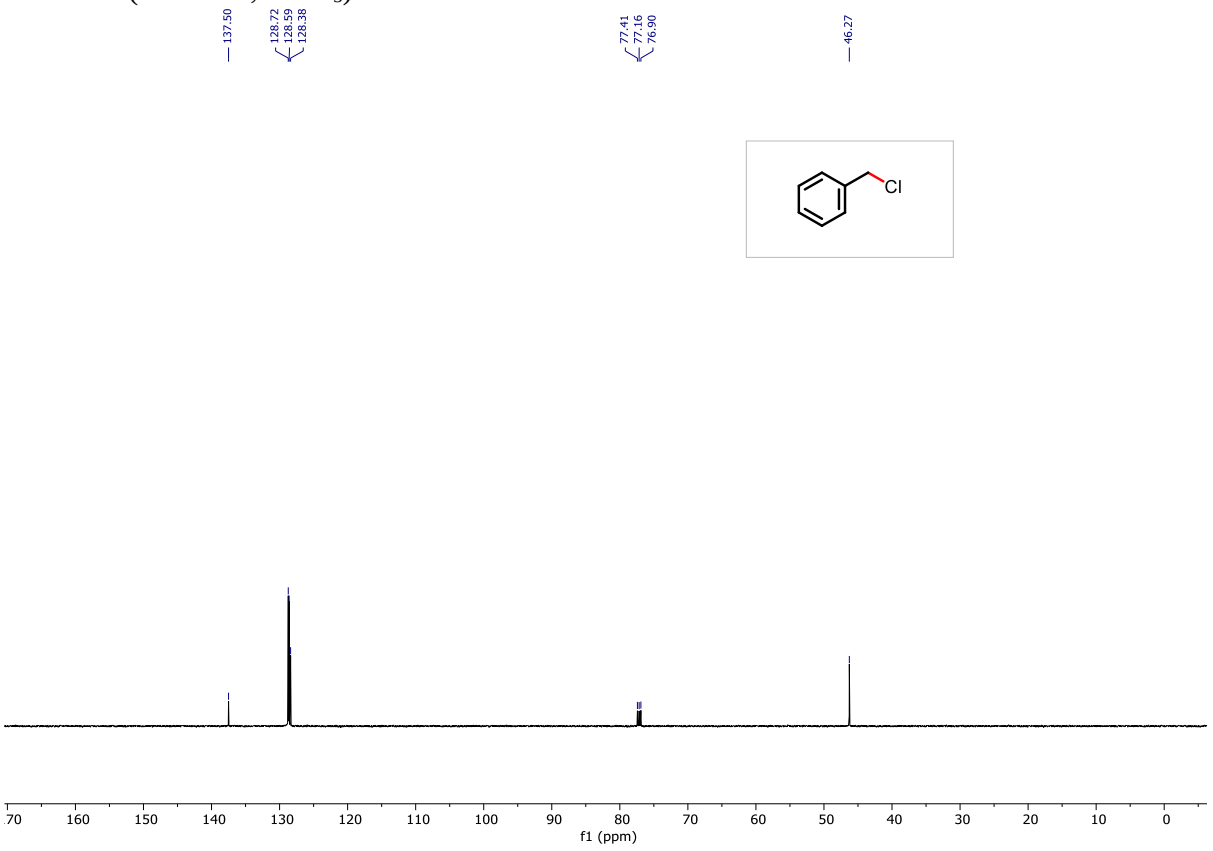


(Chloromethyl)benzene (5aa)

^{1}H NMR (500 MHz, $CDCl_3$)

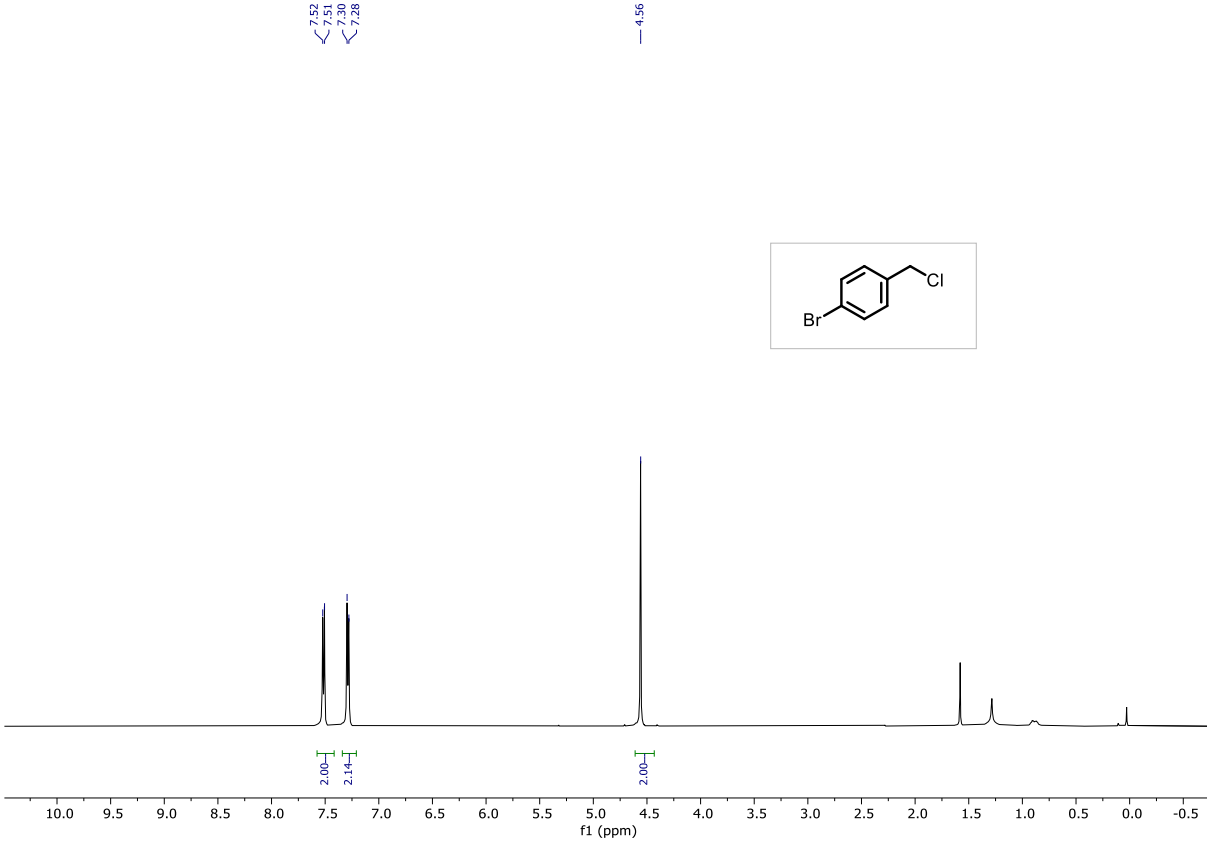


^{13}C NMR (126 MHz, $CDCl_3$)

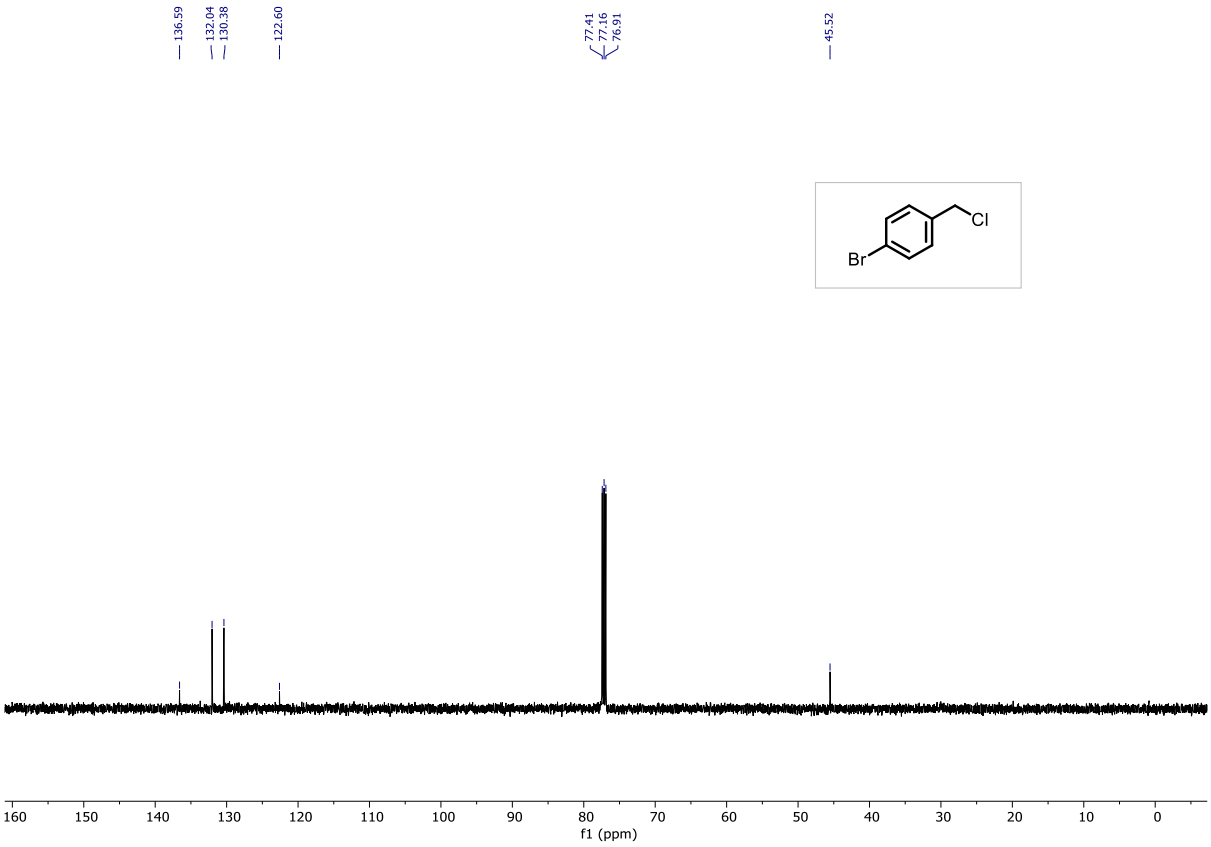


1-Bromo-4-(chloromethyl) benzene (5ab)

^{1}H NMR (500 MHz, $CDCl_3$)

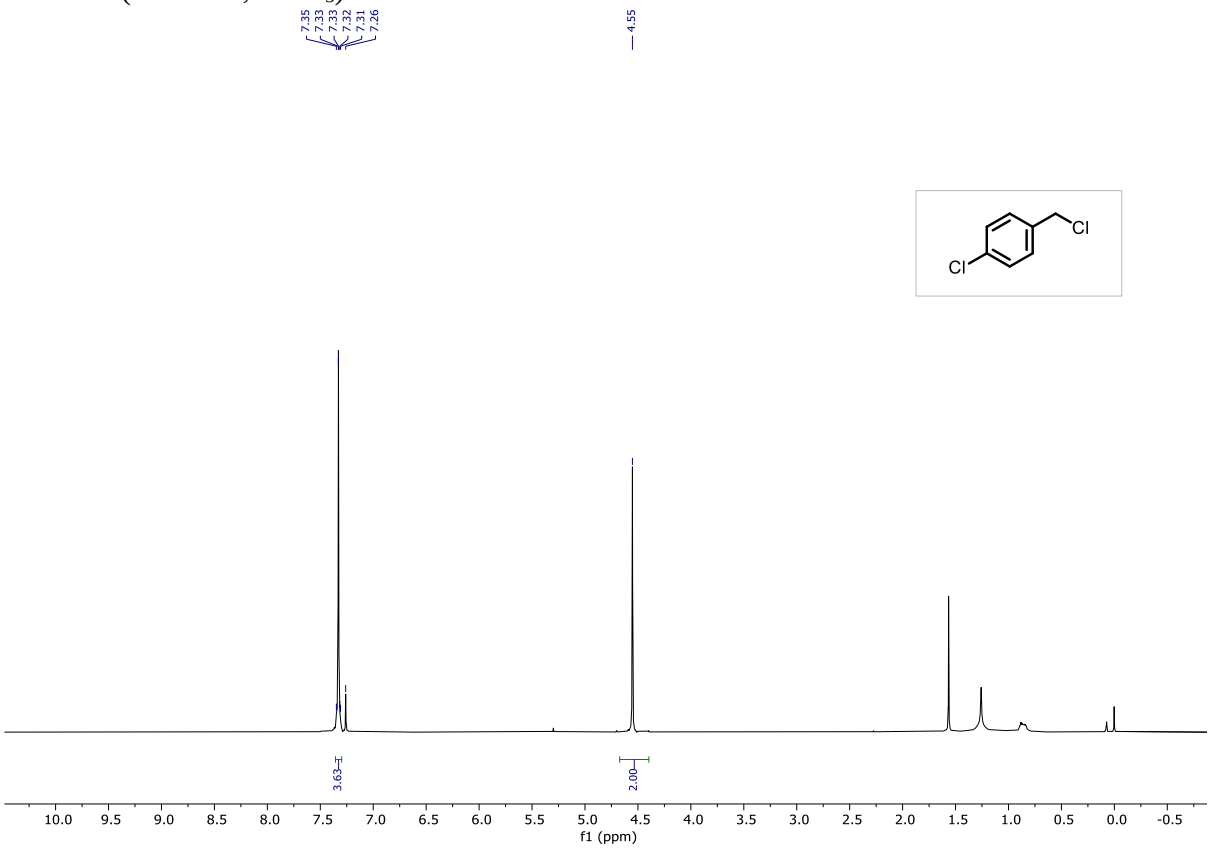


^{13}C NMR (126 MHz, $CDCl_3$)

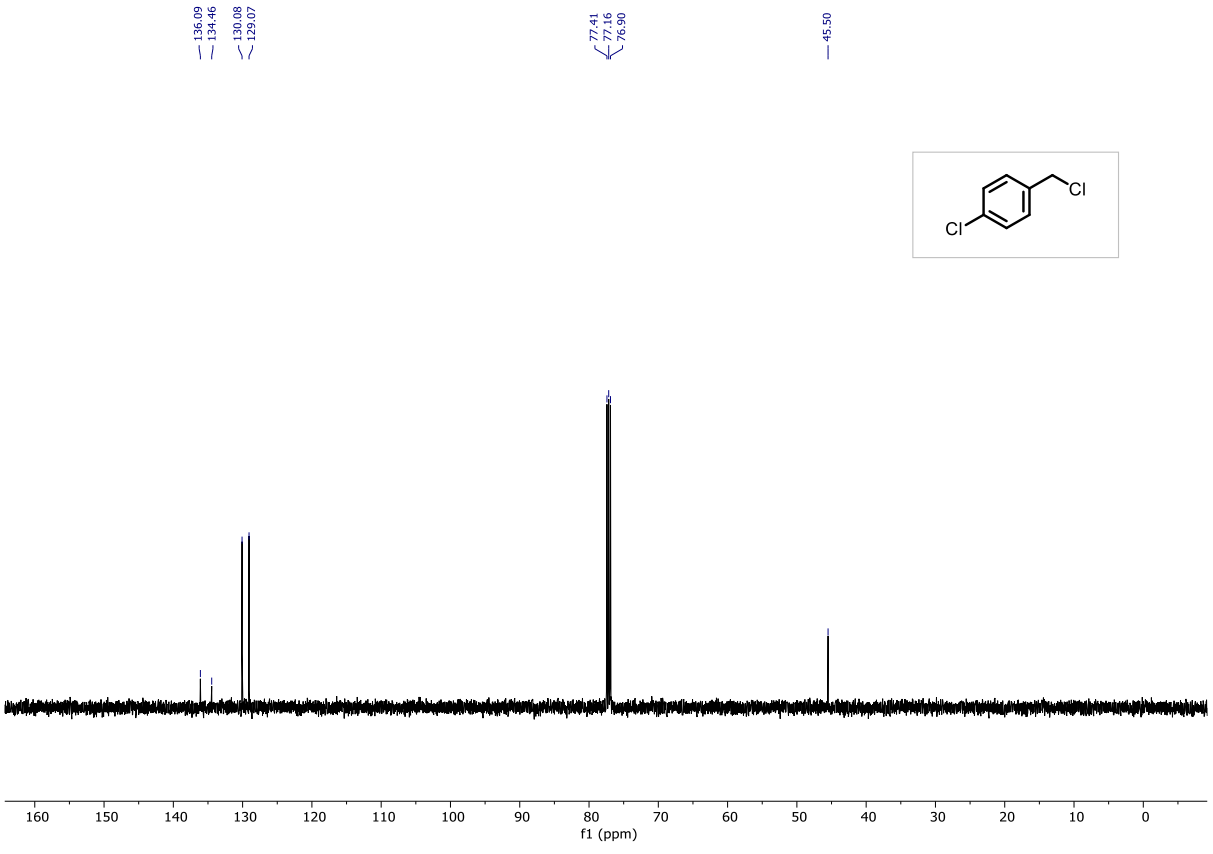


1-Chloro-4-(chloromethyl) benzene (5ac)

^{1}H NMR (500 MHz, $CDCl_3$)

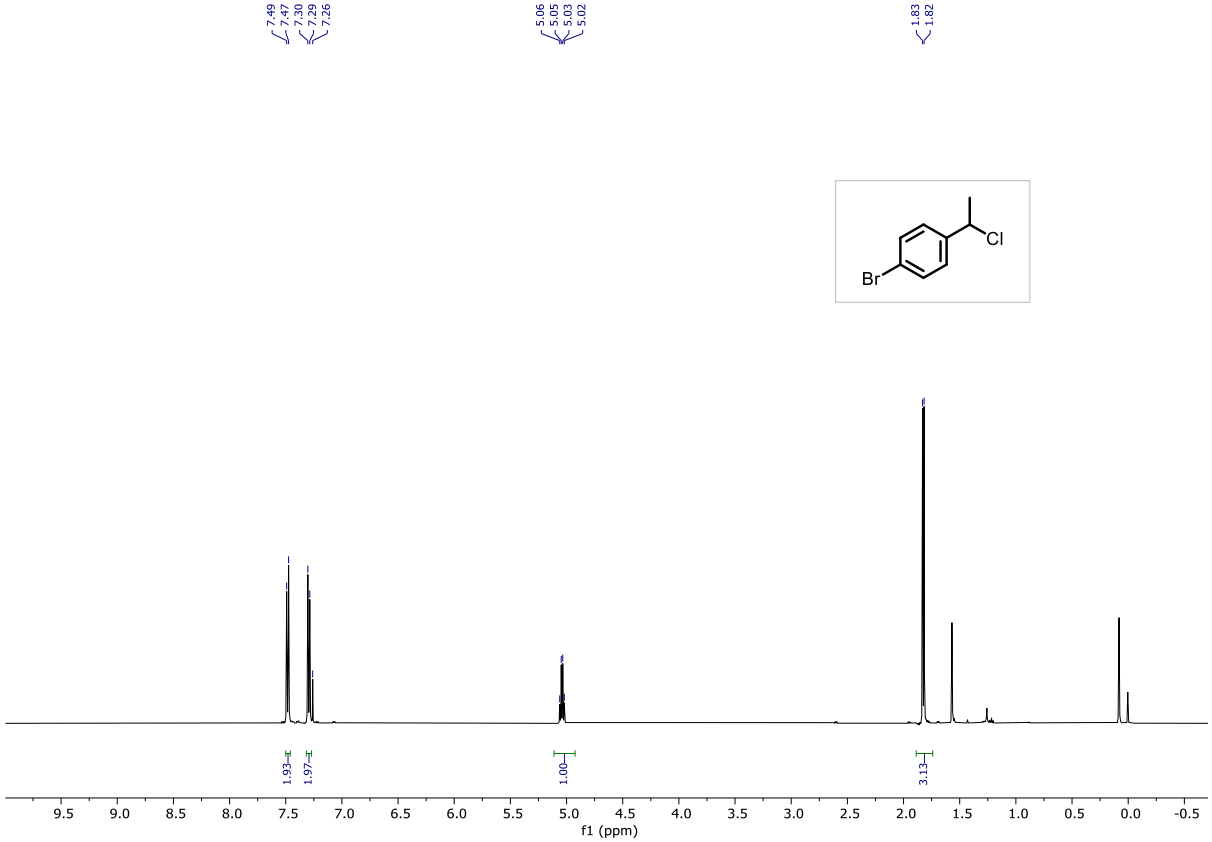


^{13}C NMR (126 MHz, $CDCl_3$)

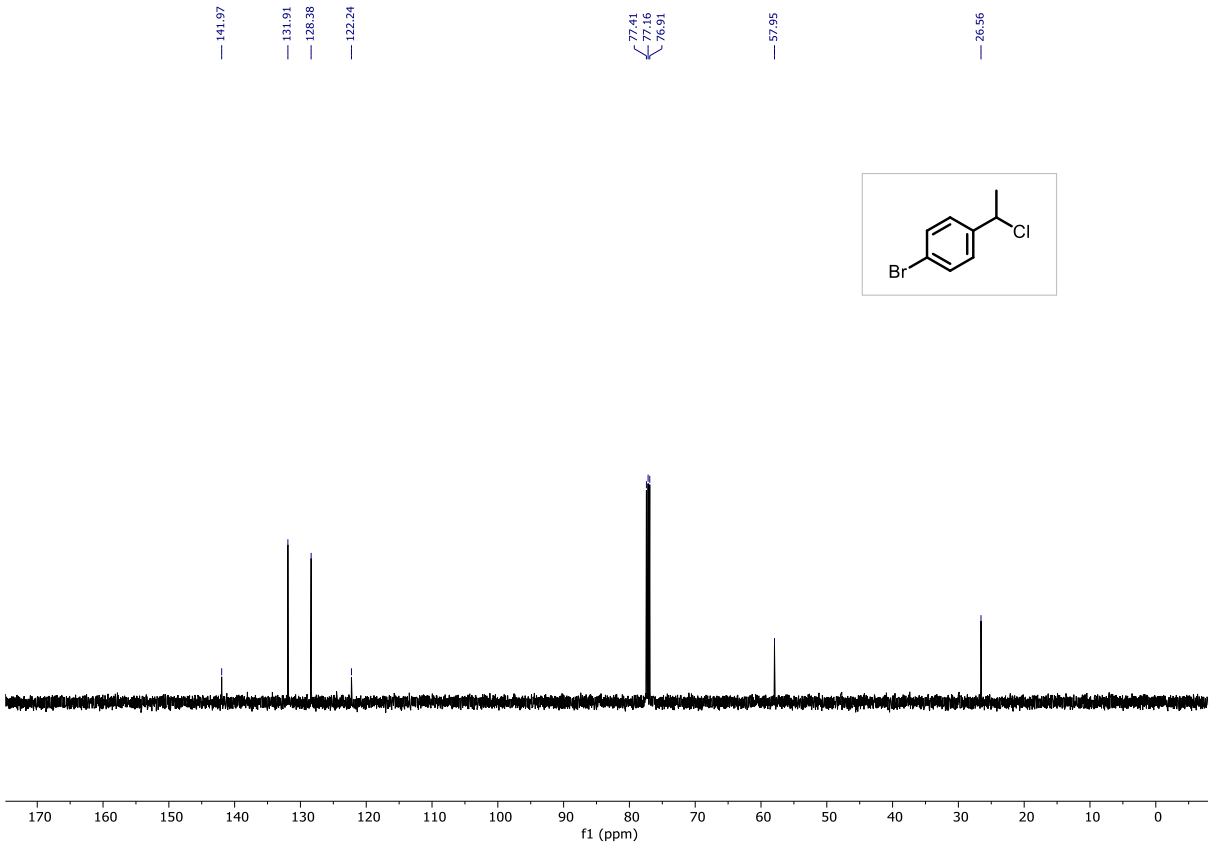


1-Bromo-4-(1-chloroethyl) benzene (5ad)

^{1}H NMR (500 MHz, $CDCl_3$)

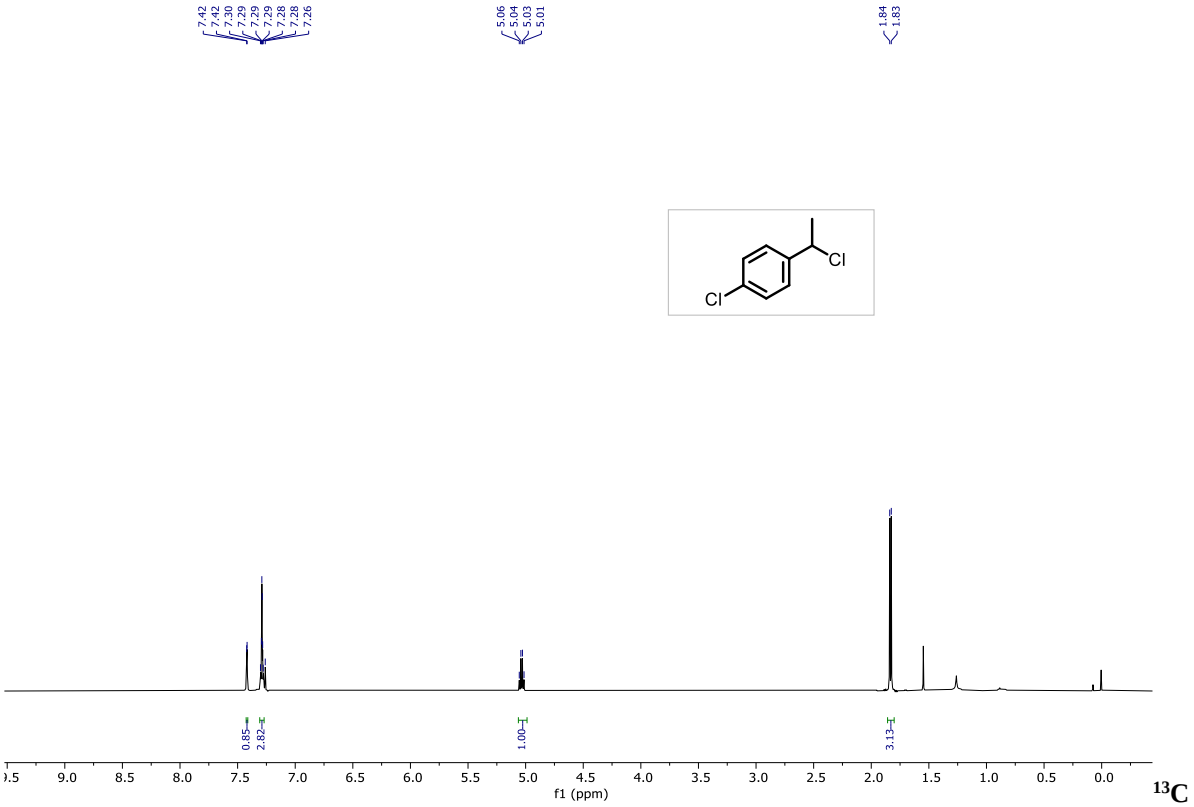


^{13}C NMR (126 MHz, $CDCl_3$)

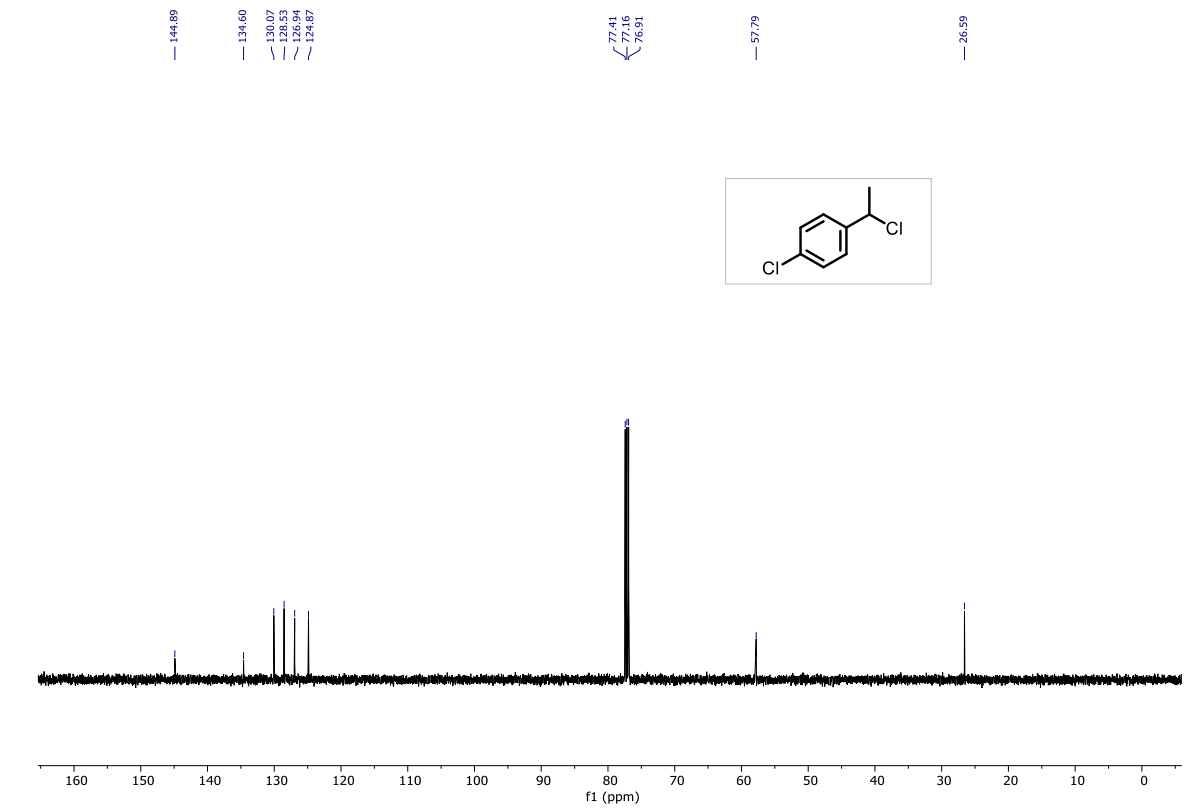


1-Chloro-4-(iodomethyl) benzene (5ae)

^{1}H NMR (500 MHz, $CDCl_3$)

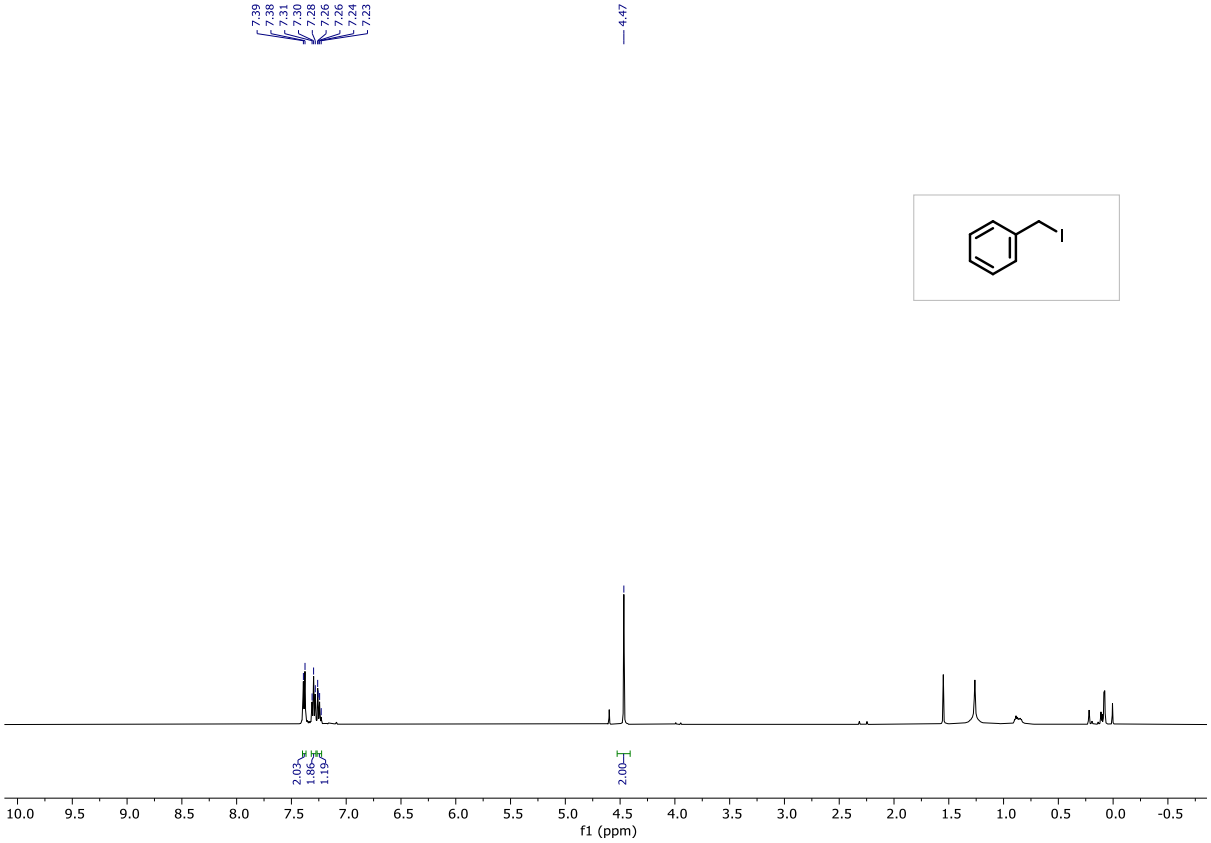


^{13}C NMR (126 MHz, $CDCl_3$)

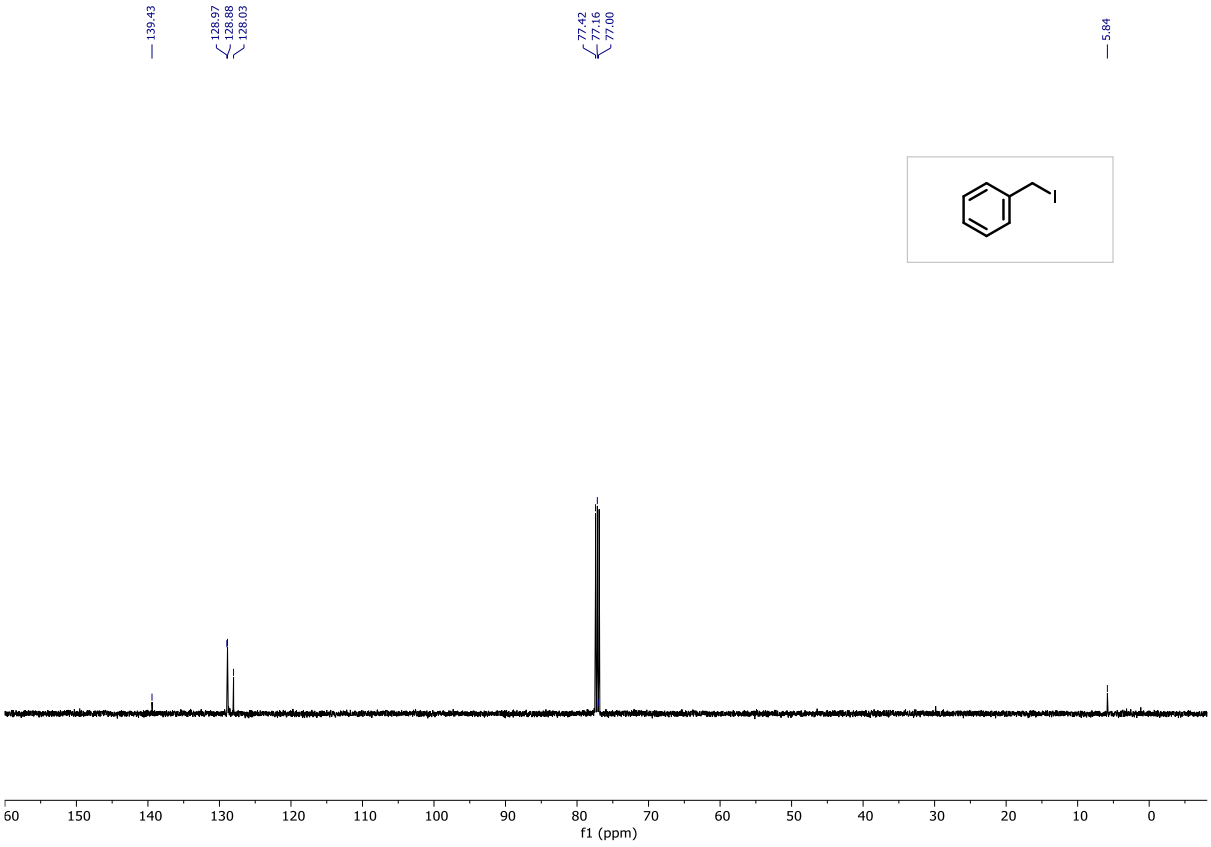


(Iodomethyl)benzene (5af)

^{1}H NMR (500 MHz, $CDCl_3$)

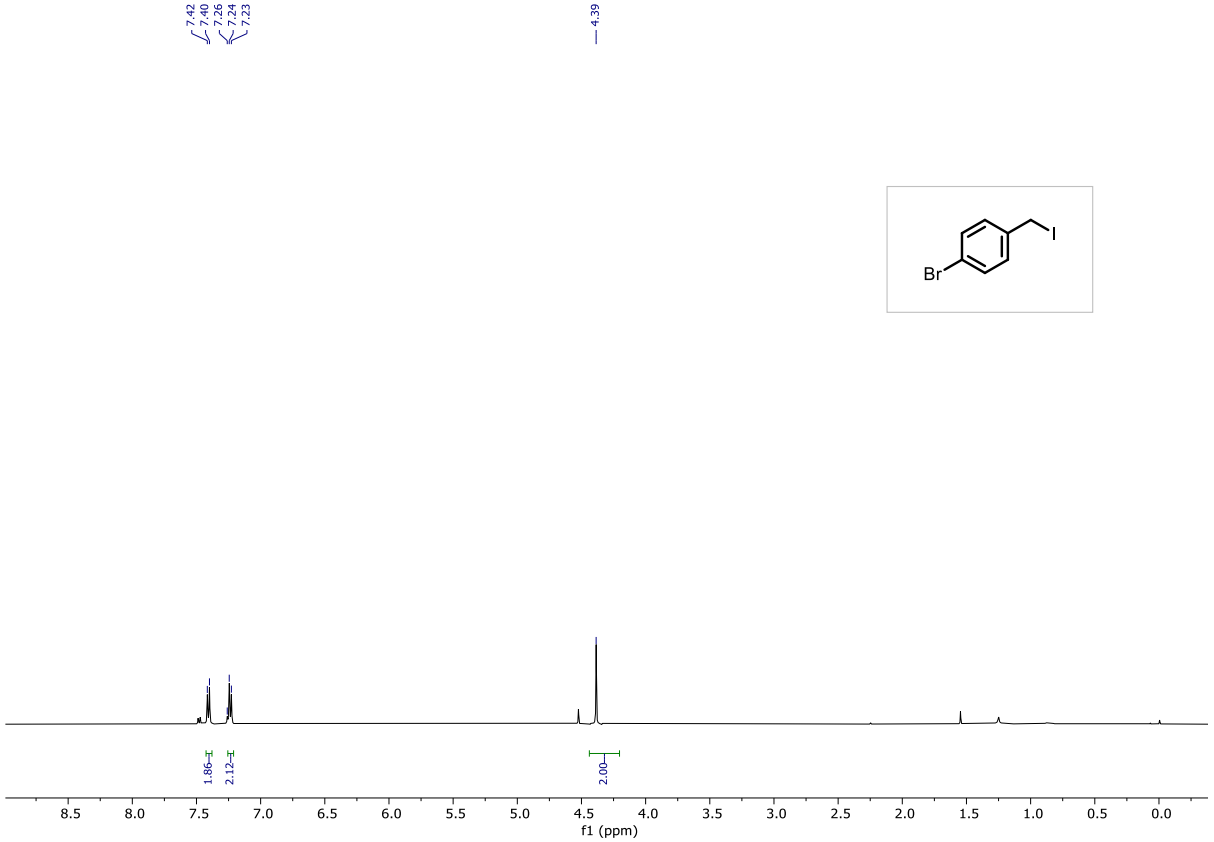


^{13}C NMR (126 MHz, $CDCl_3$)

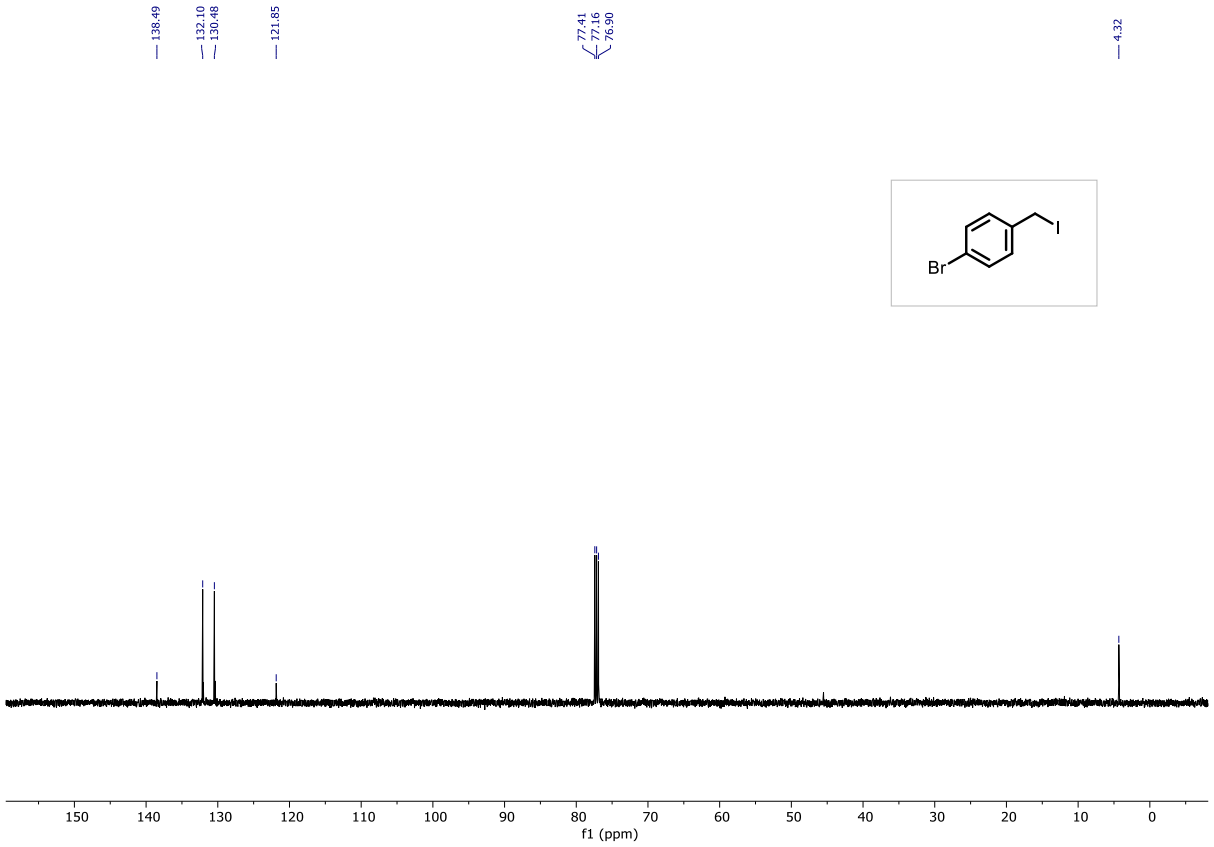


1-Bromo-4-(iodomethyl) benzene (5ag)

^{1}H NMR (500 MHz, $CDCl_3$)

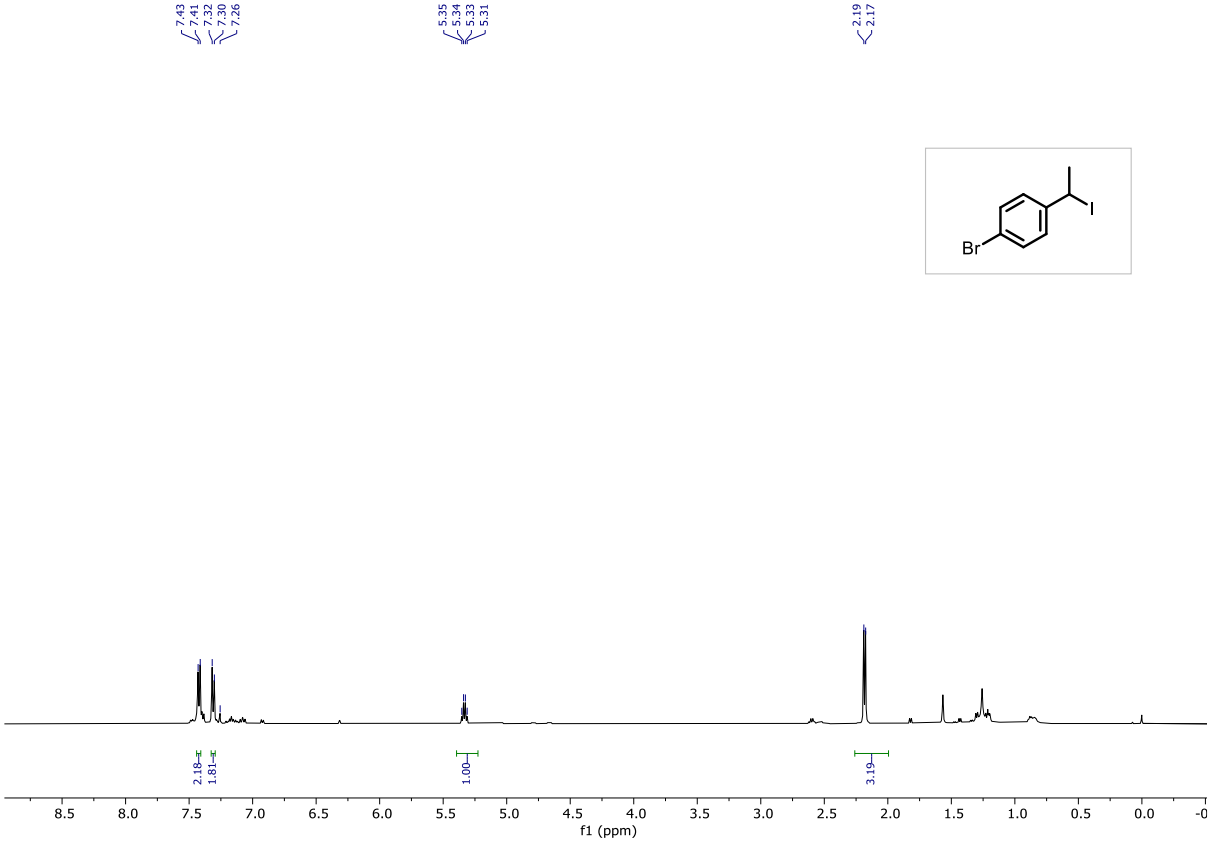


^{13}C NMR (126 MHz, $CDCl_3$)

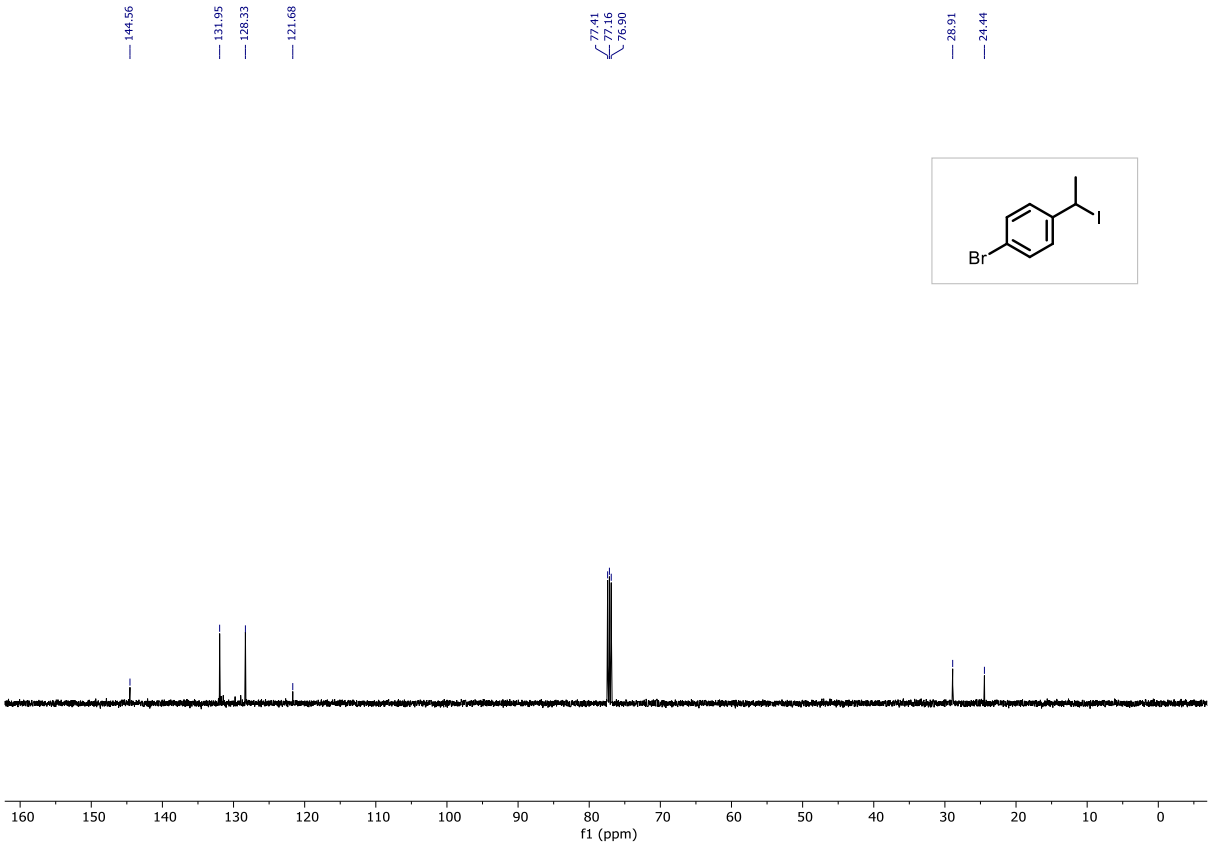


1-Bromo-4-(1-iodoethyl) benzene (5ah)

^{1}H NMR (500 MHz, $CDCl_3$)

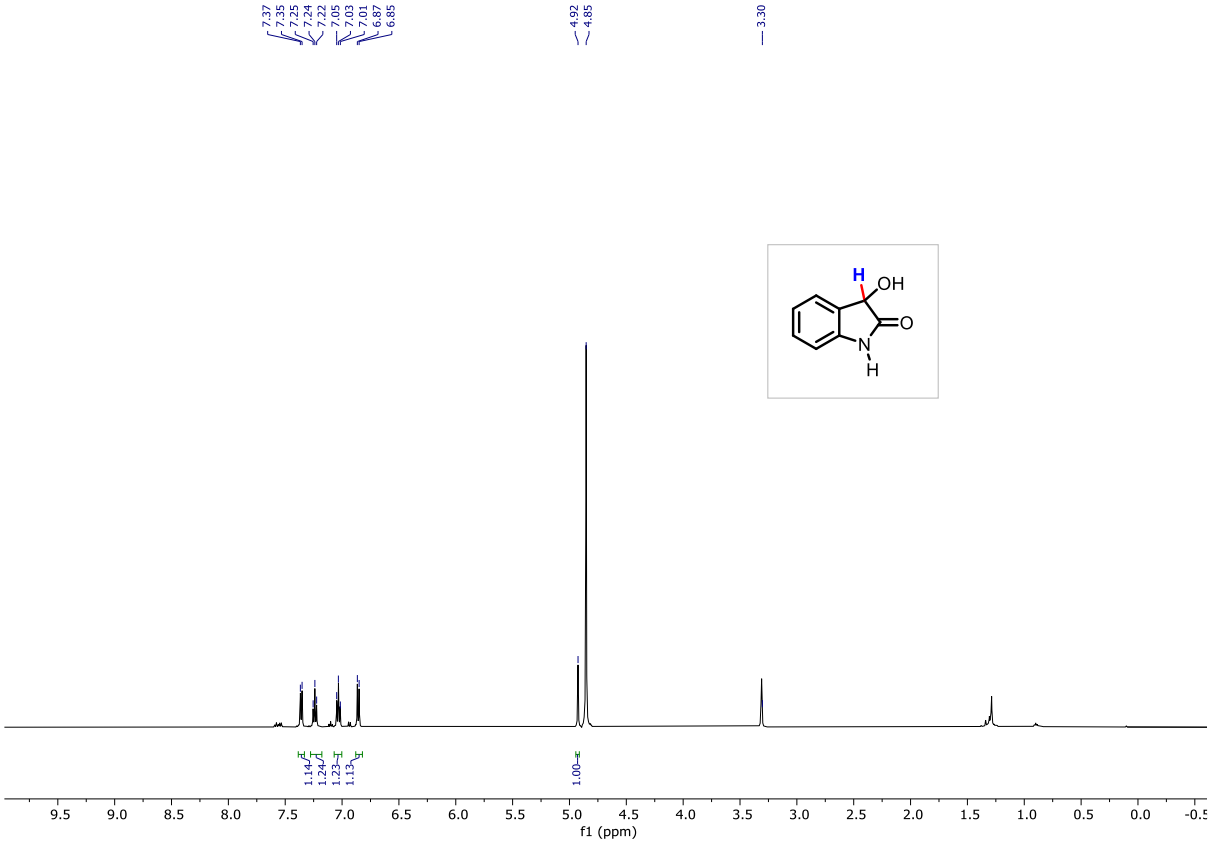


^{13}C NMR (126 MHz, $CDCl_3$)

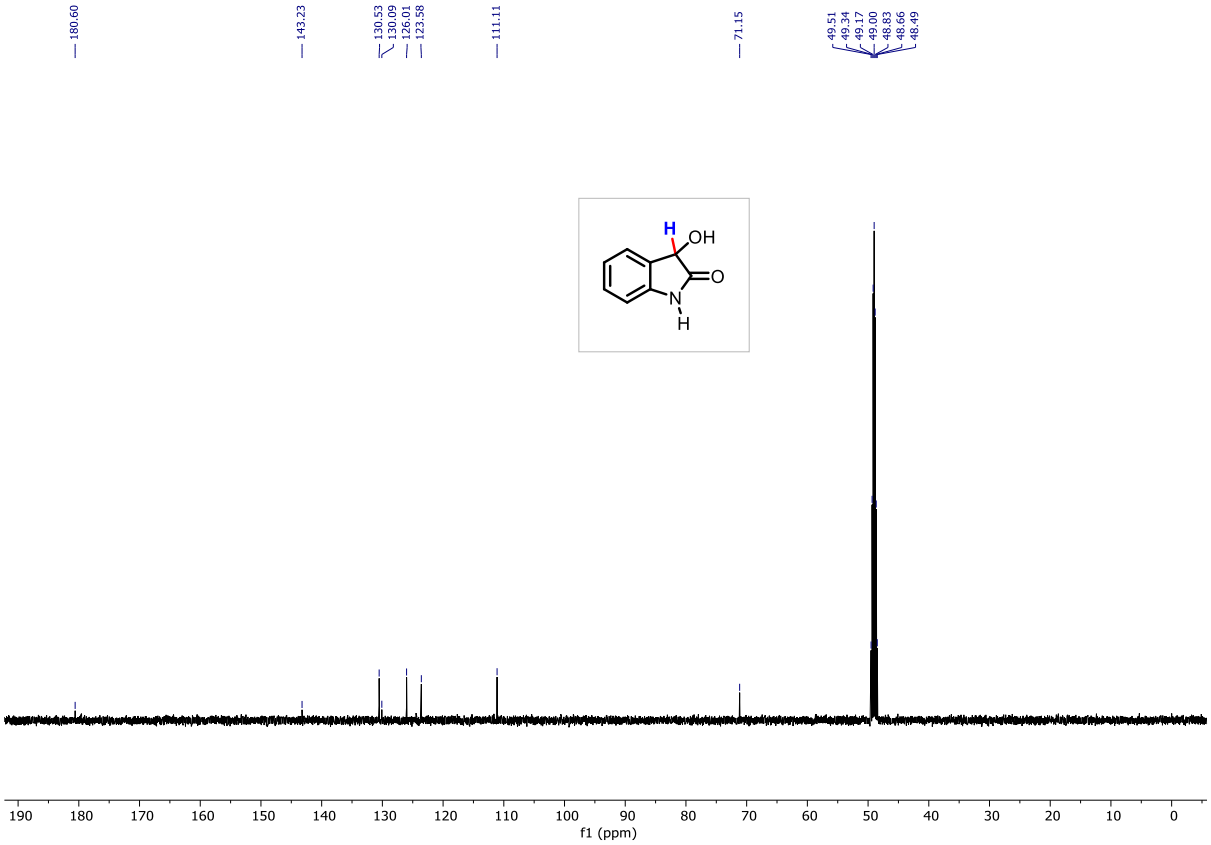


3-Hydroxyindolin-2-one (7a)

^{1}H NMR (500 MHz, CD_3OD)

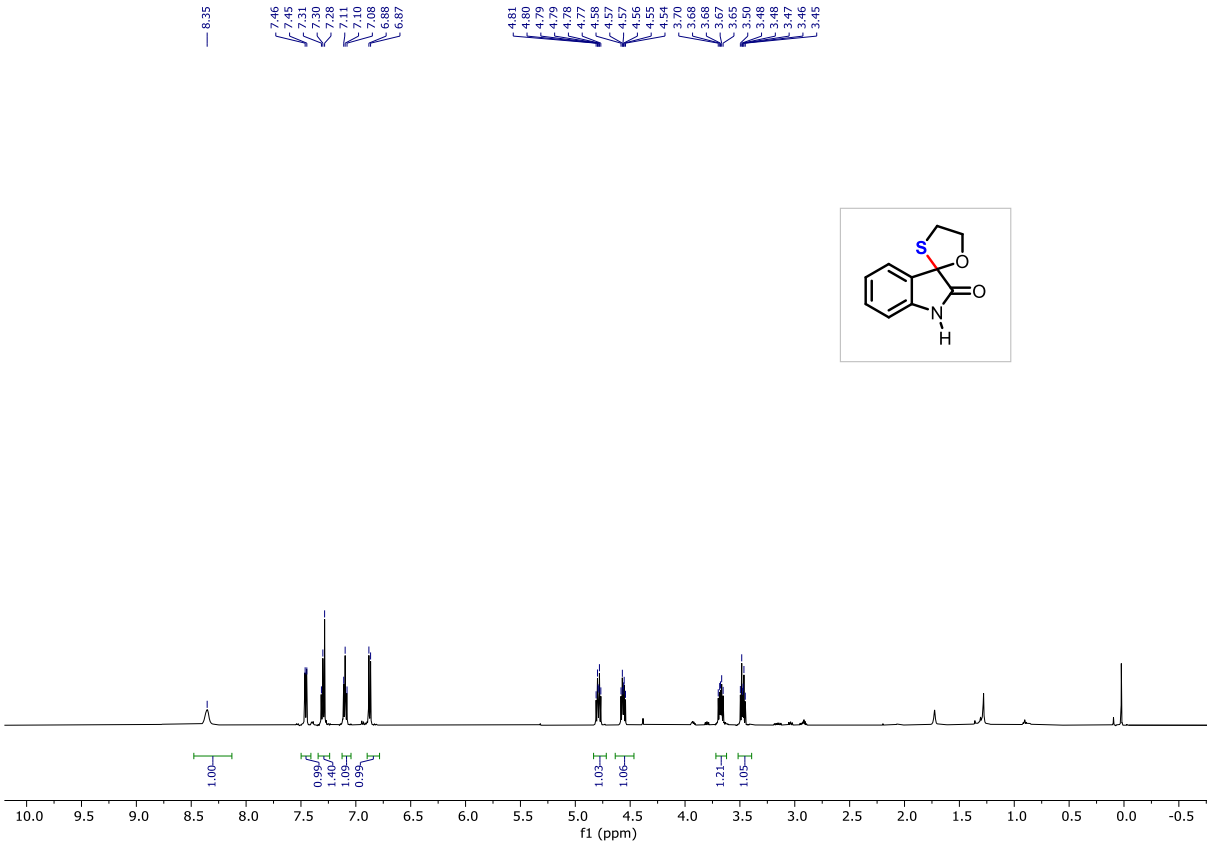


^{13}C{^{1}H} NMR (126 MHz CD_3OD)

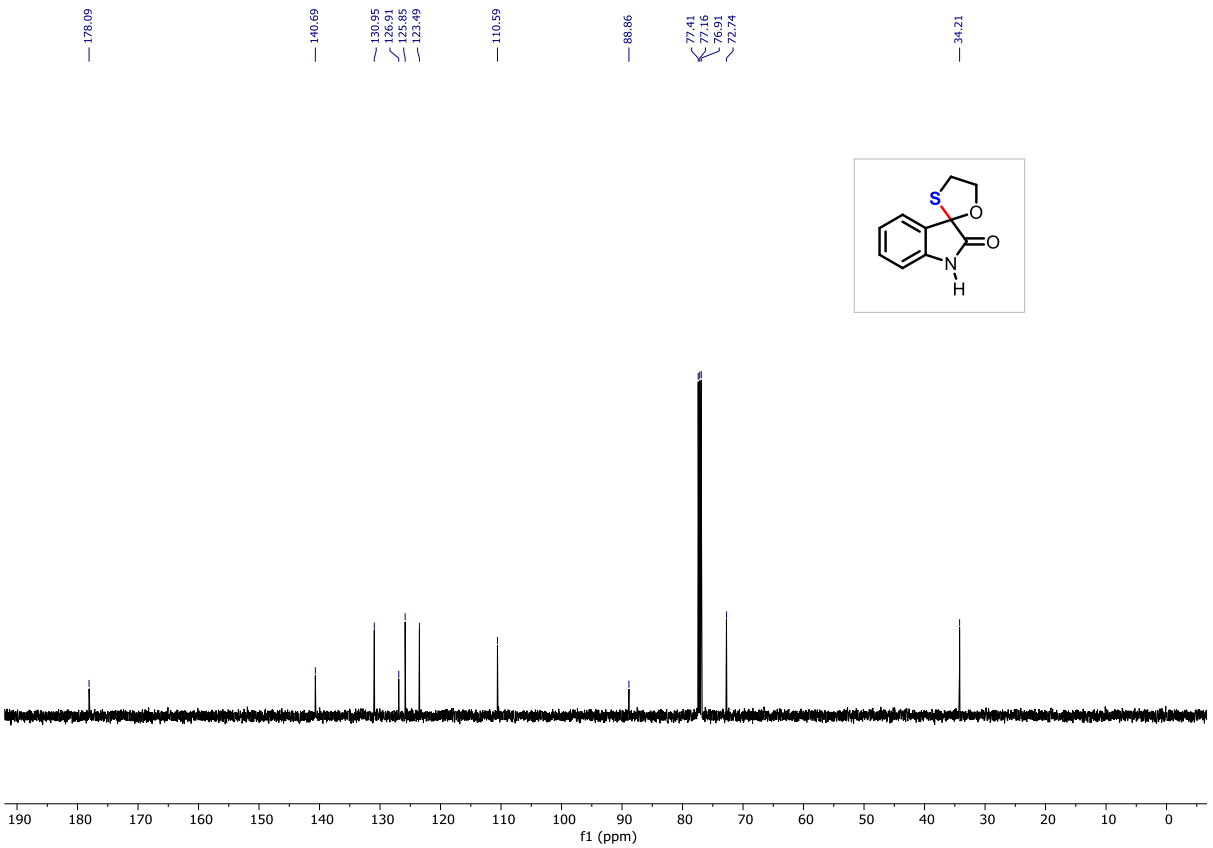


Spiro [indoline-3,2'-[1, 3] oxathiolan]-2-one (7b)

^{1}H NMR (500 MHz, $CDCl_3$)

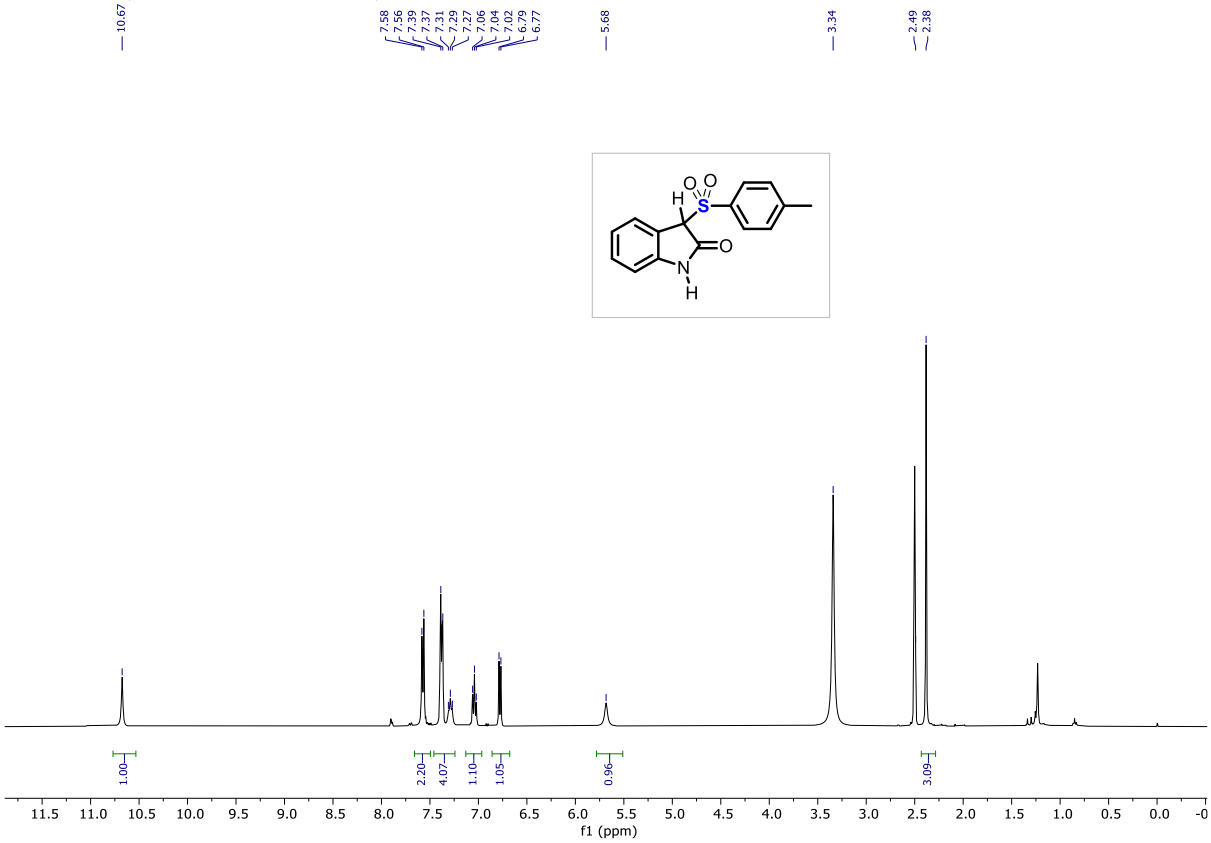


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

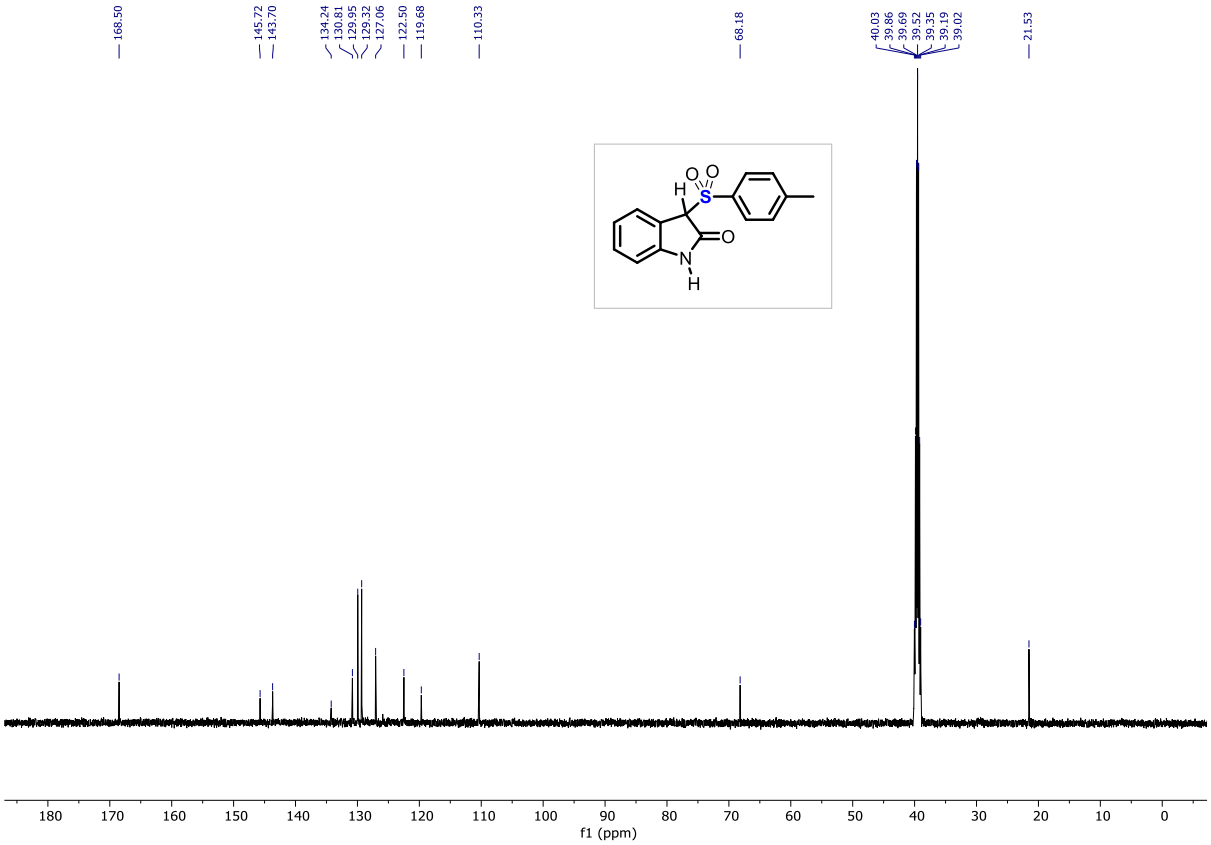


3-Tosylindolin-2-one (8a)

^{1}H NMR (400 MHz, DMSO-d_6)

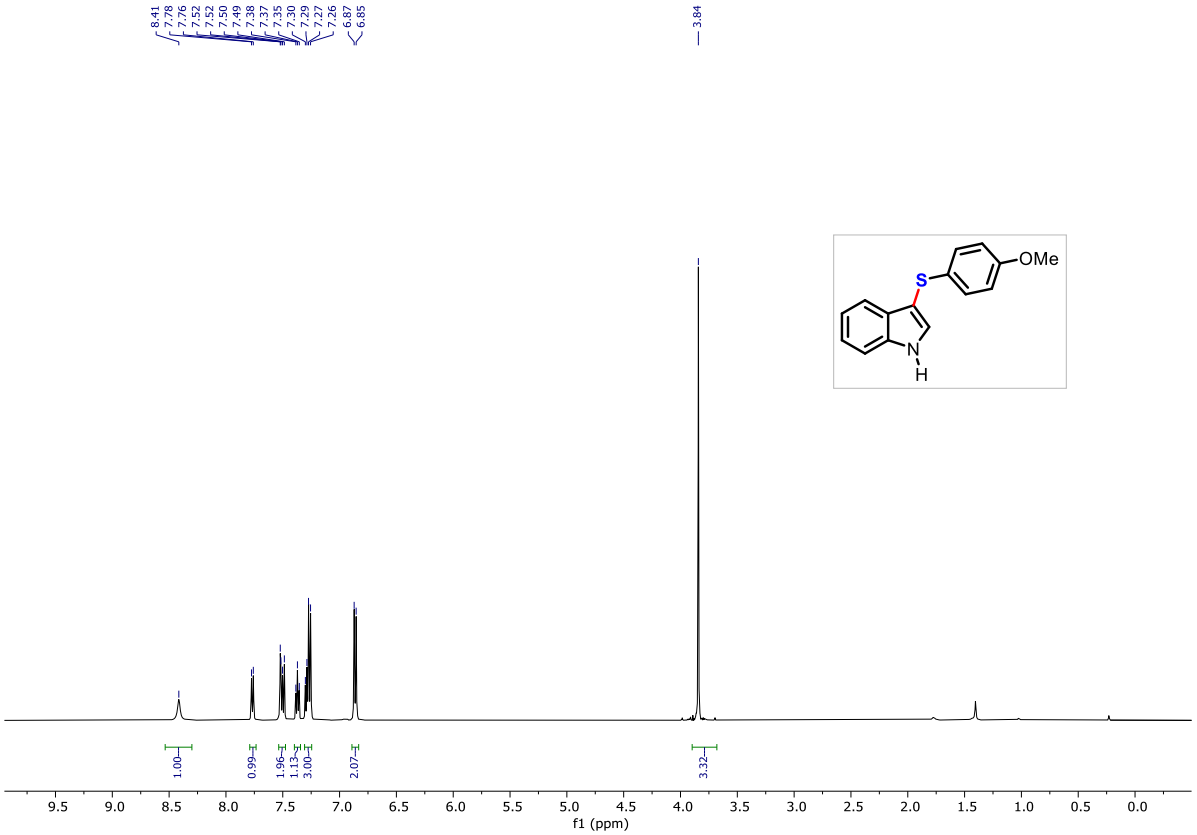


^{13}C NMR (126 MHz, DMSO-d_6)

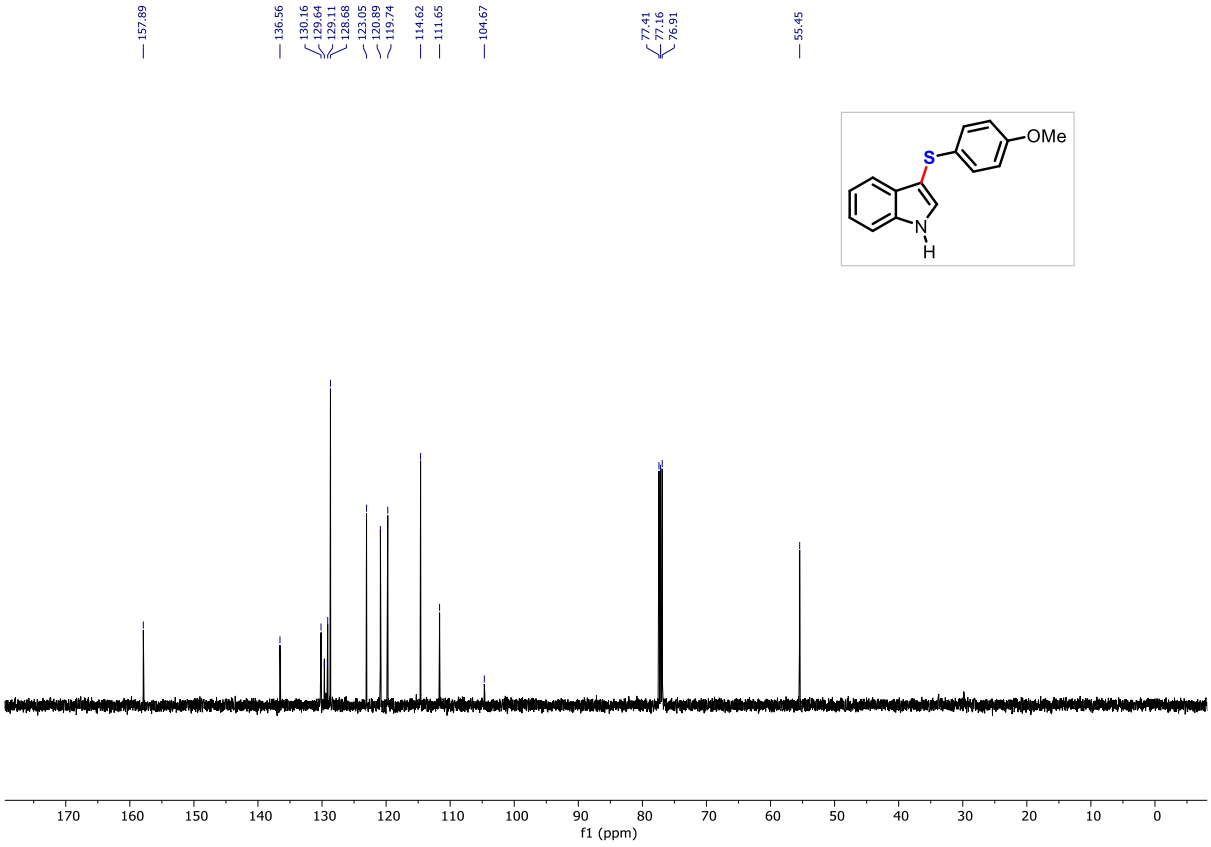


3-((4-Methoxyphenyl) thio)-1*H*-indole (8b)

^{1}H NMR (500 MHz, $CDCl_3$)

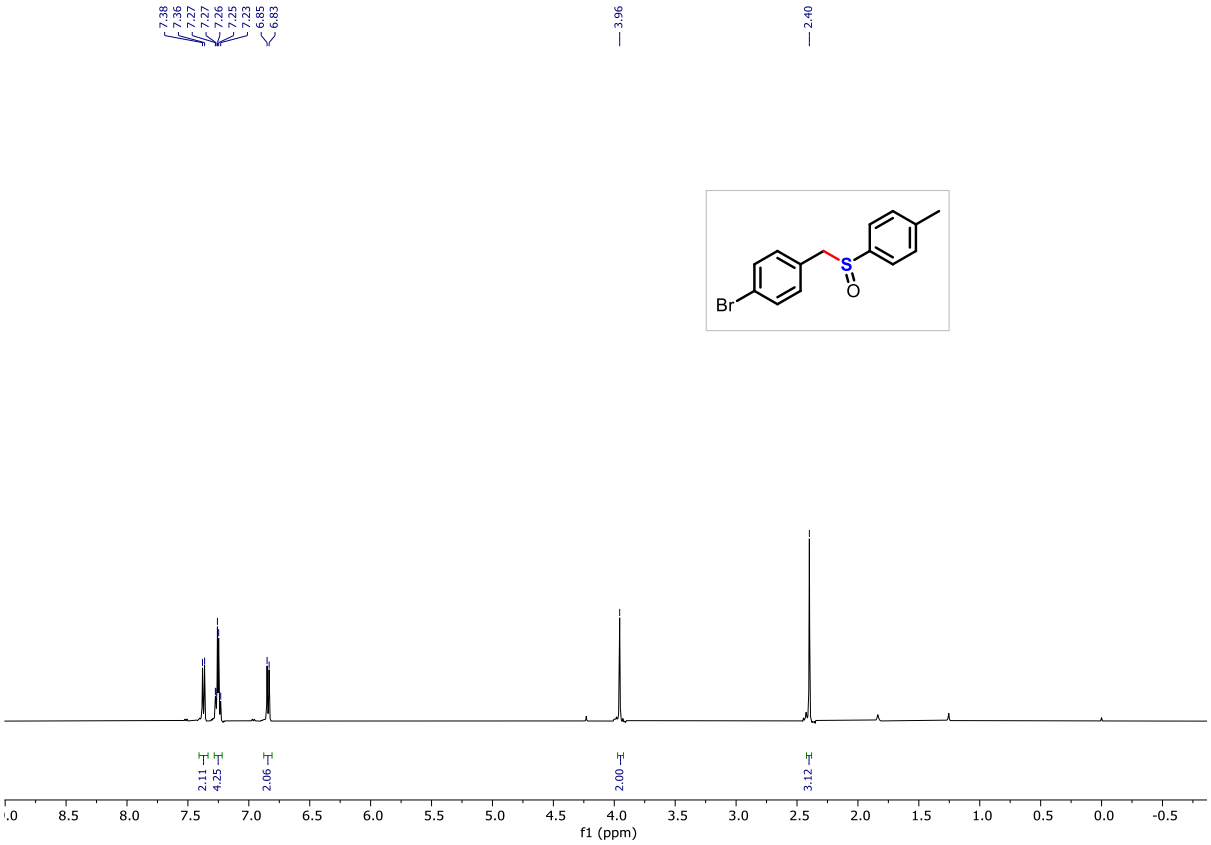


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

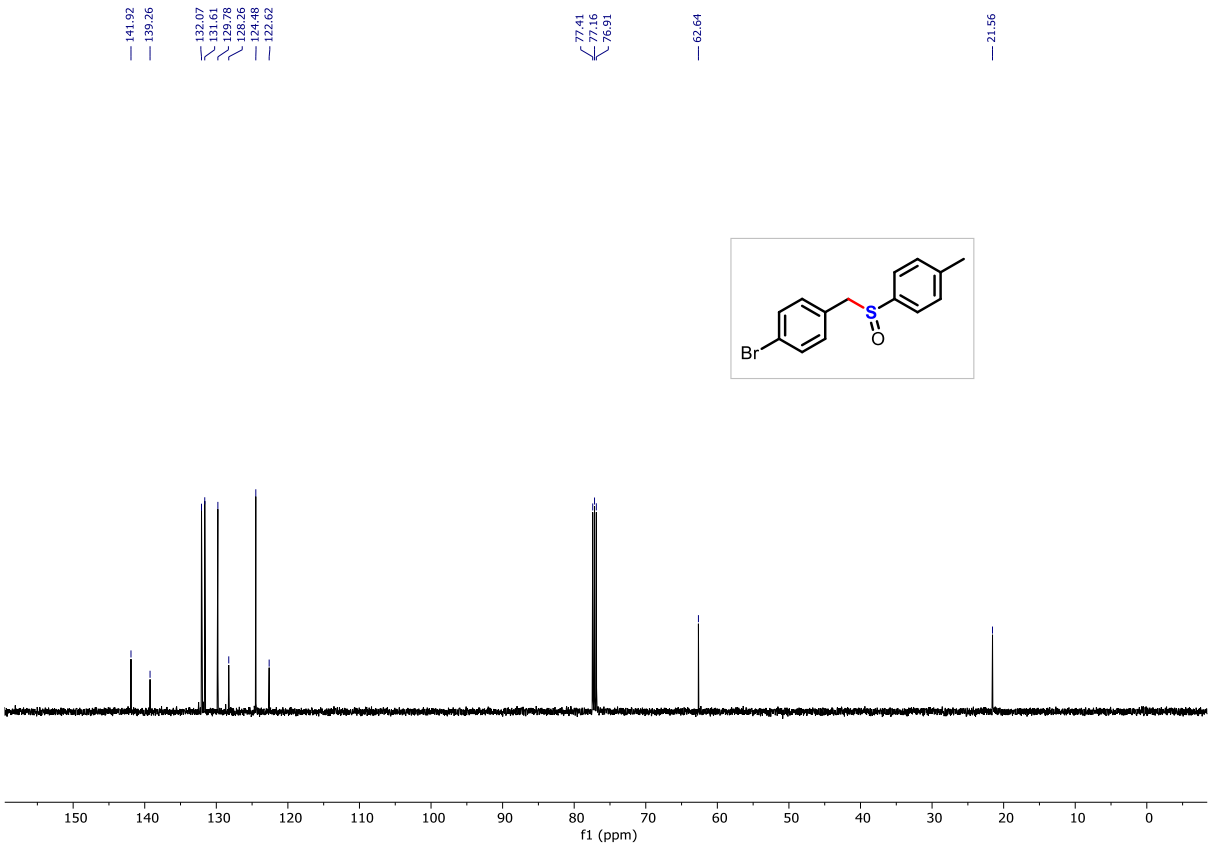


1-Bromo-4-((*p*-tolylsulfinyl) methyl) benzene (8c)

^{1}H NMR (500 MHz $CDCl_3$)

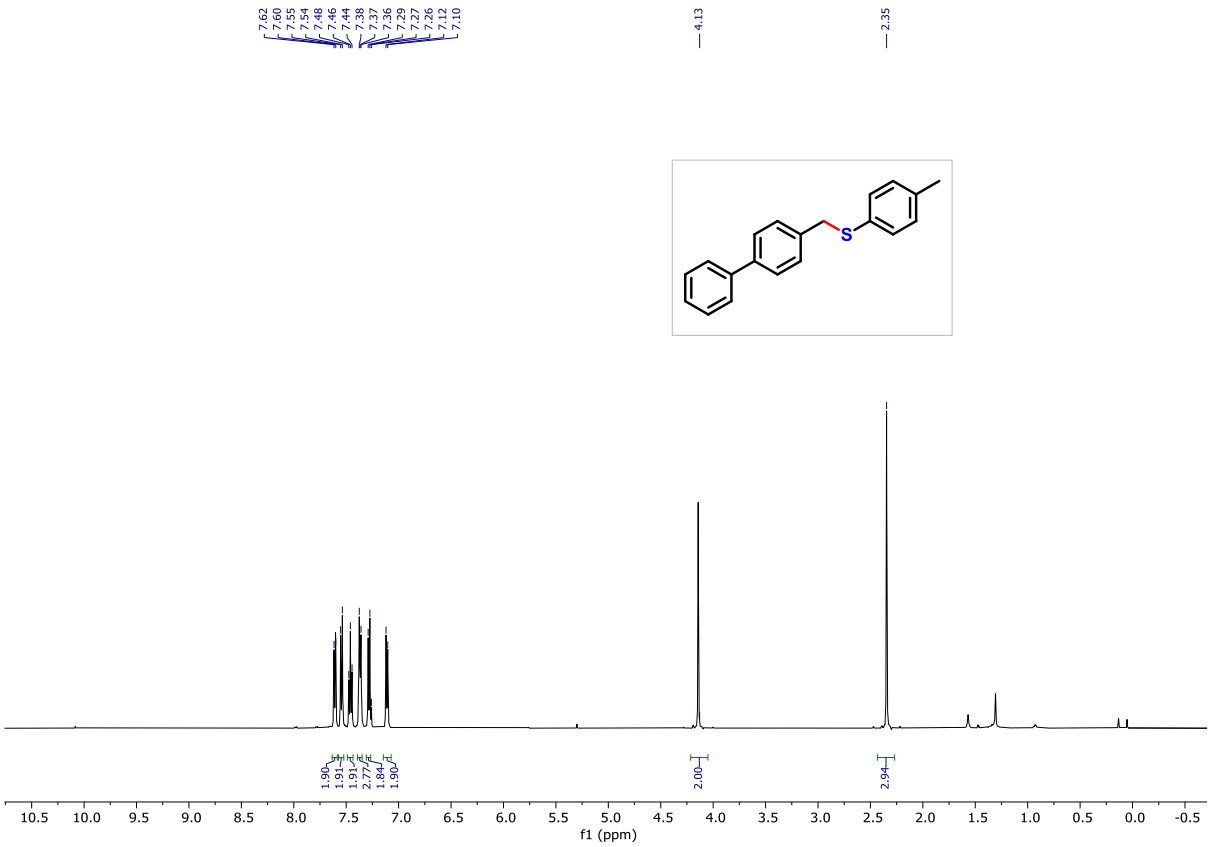


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

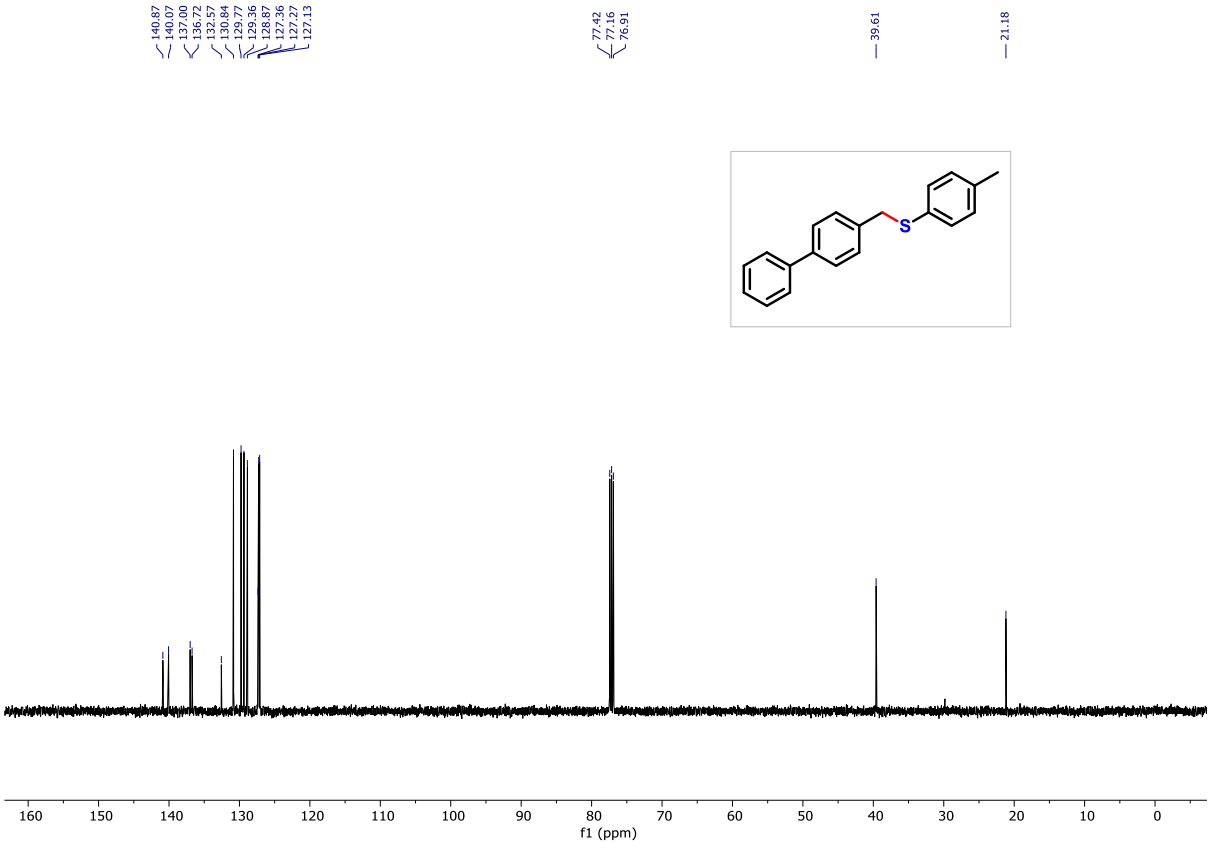


([1,1'-Biphenyl]-4-yl methyl) (*p*-tolyl) sulfane (8d)

^{1}H NMR (500 MHz $CDCl_3$)

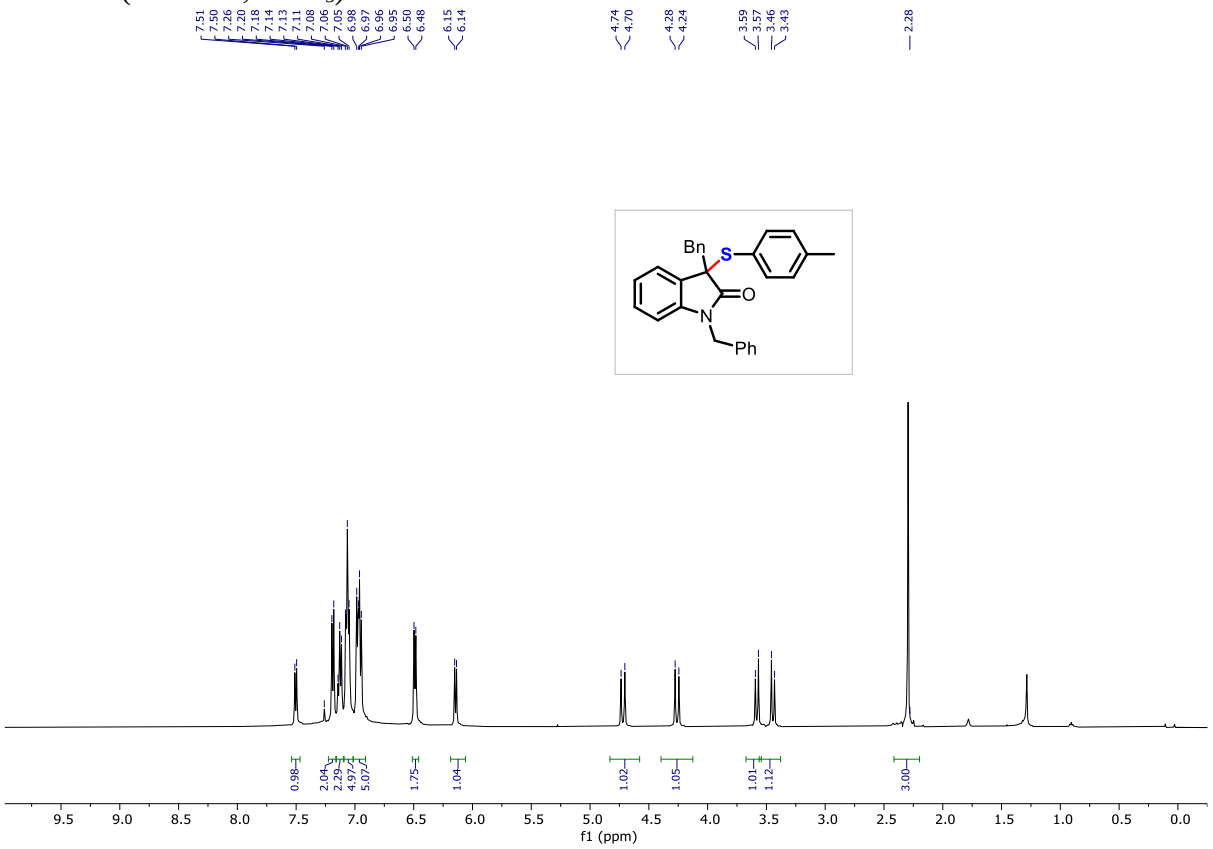


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

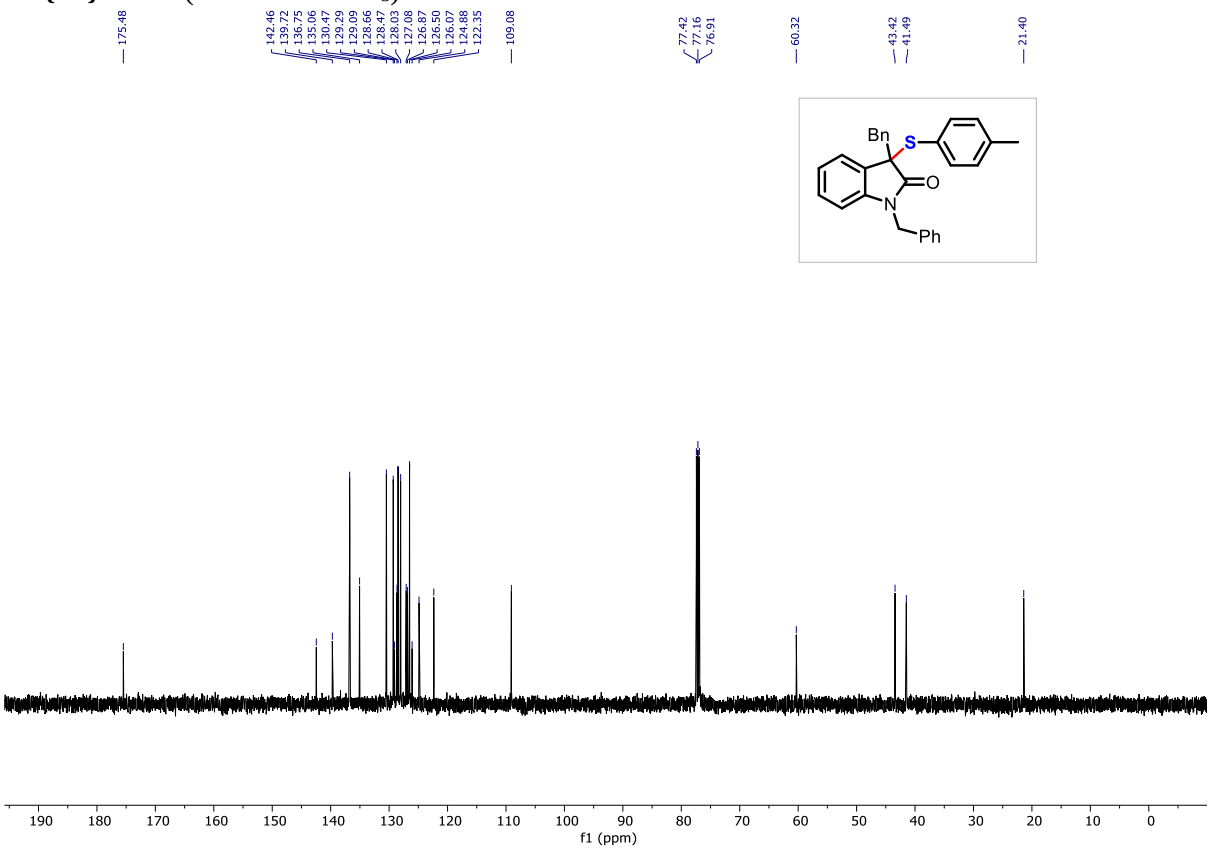


1,3-Dibenzyl-3-(*p*-tolylthio) indolin-2-one (8e)

^{1}H NMR (500 MHz, $CDCl_3$)

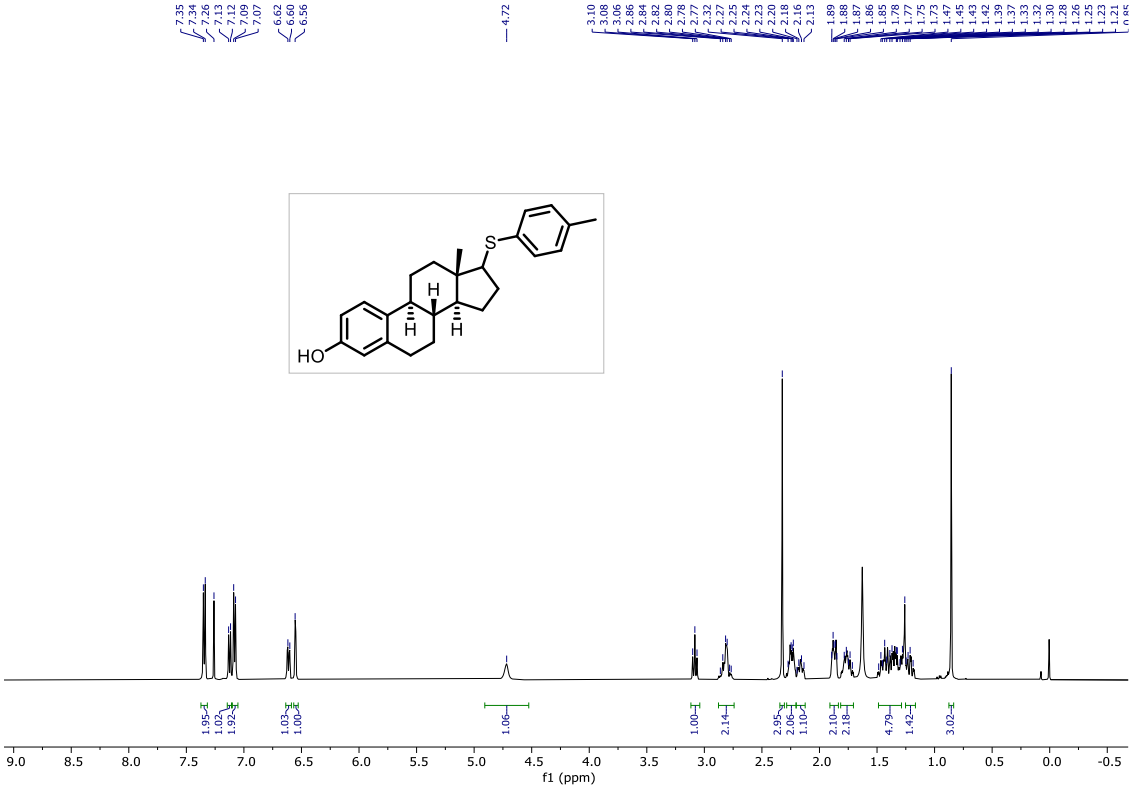


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

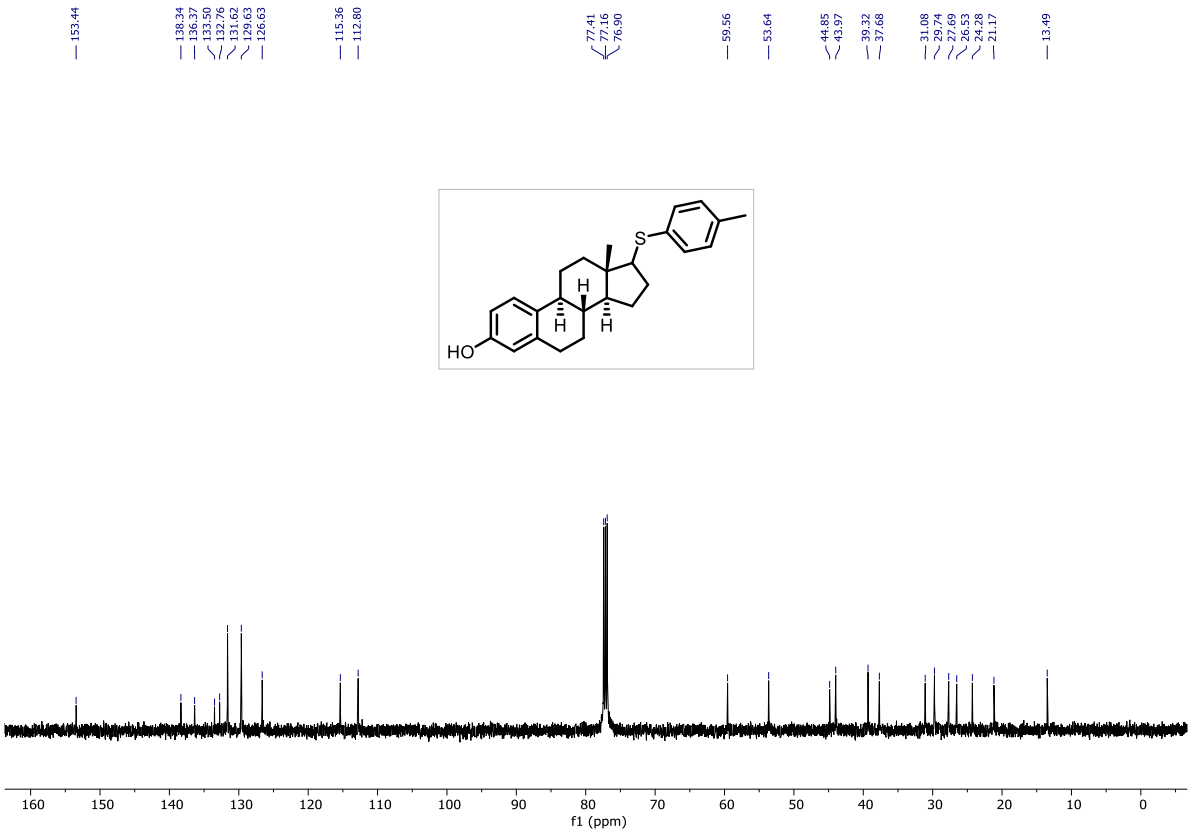


(*8R*,*9S*,*13S*,*14S*)-13-Methyl-17-(*p*-tolylthio)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-ol (10a)

^{1}H NMR (500 MHz $CDCl_3$)

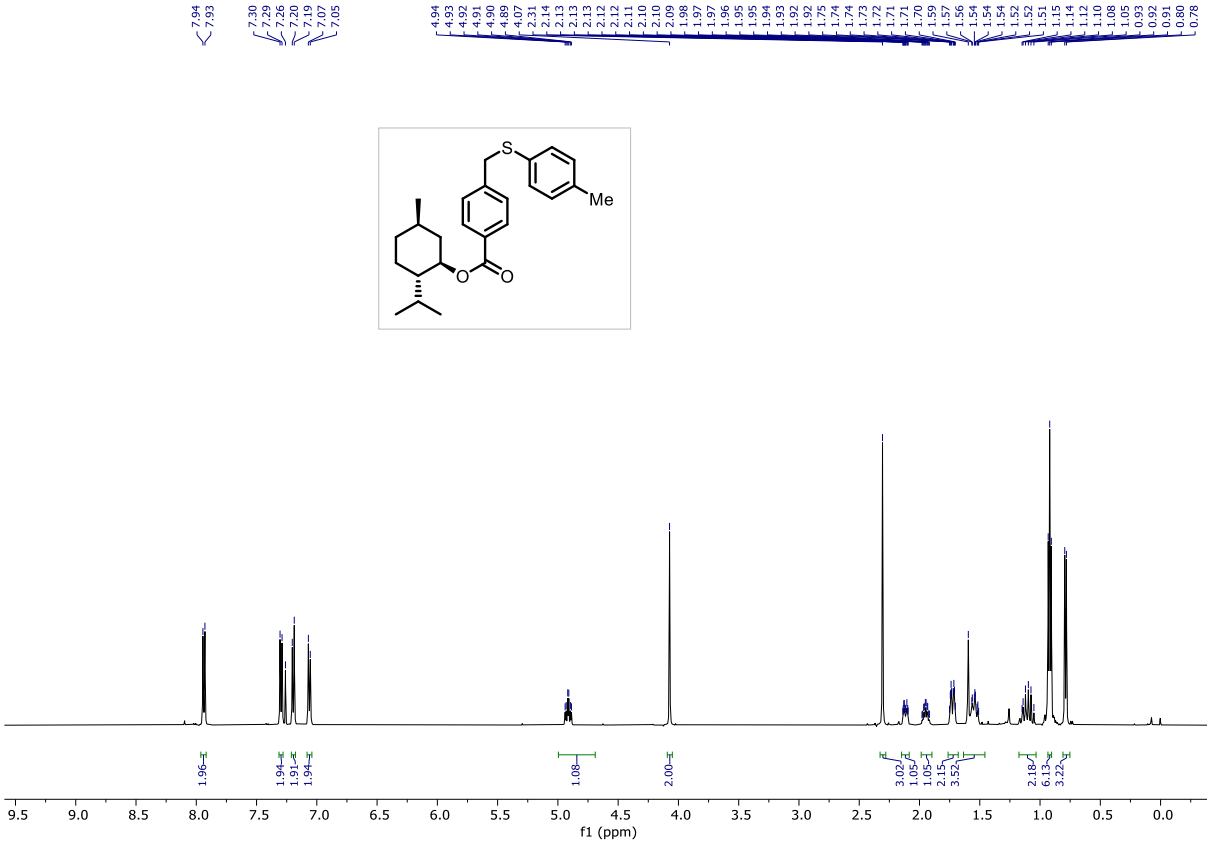


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

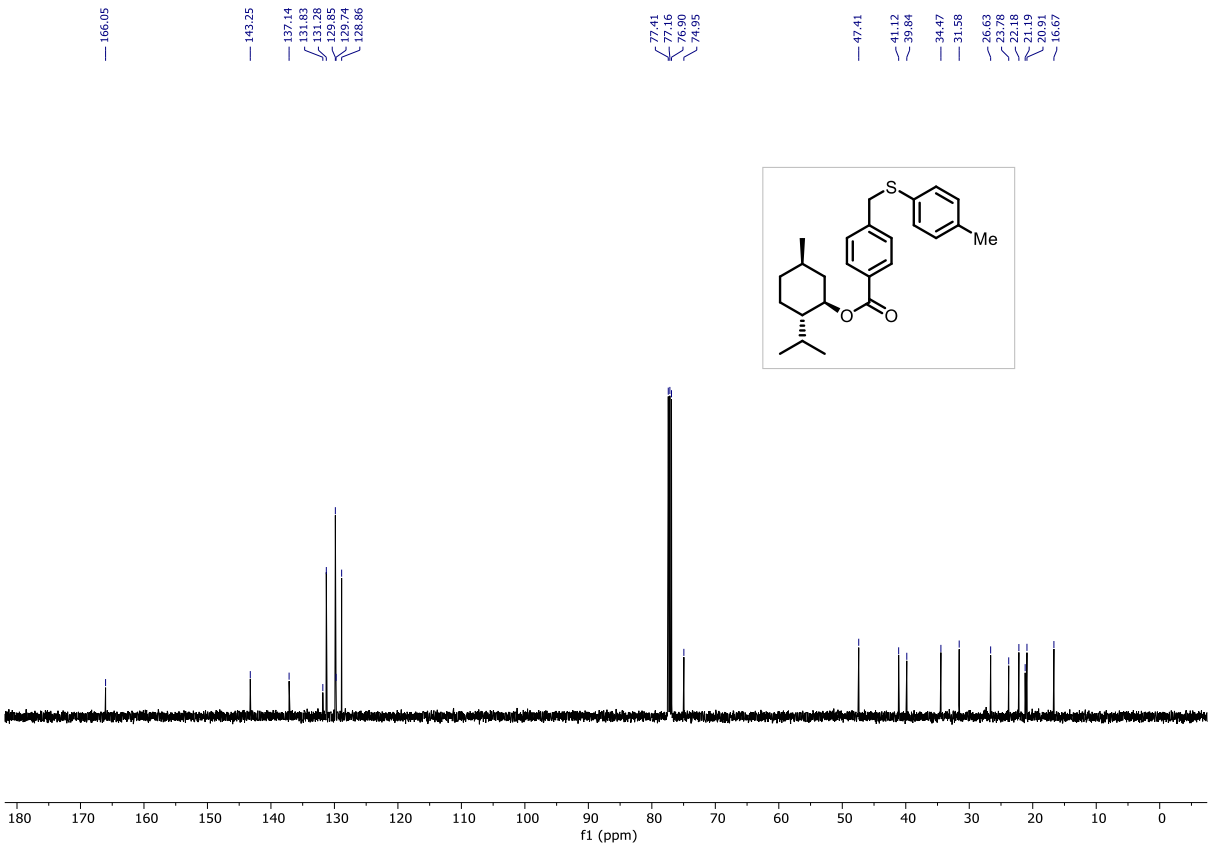


(1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl 4-((*p*-tolylthio) methyl) benzoate (10b)

^{1}H NMR (500 MHz $CDCl_3$)

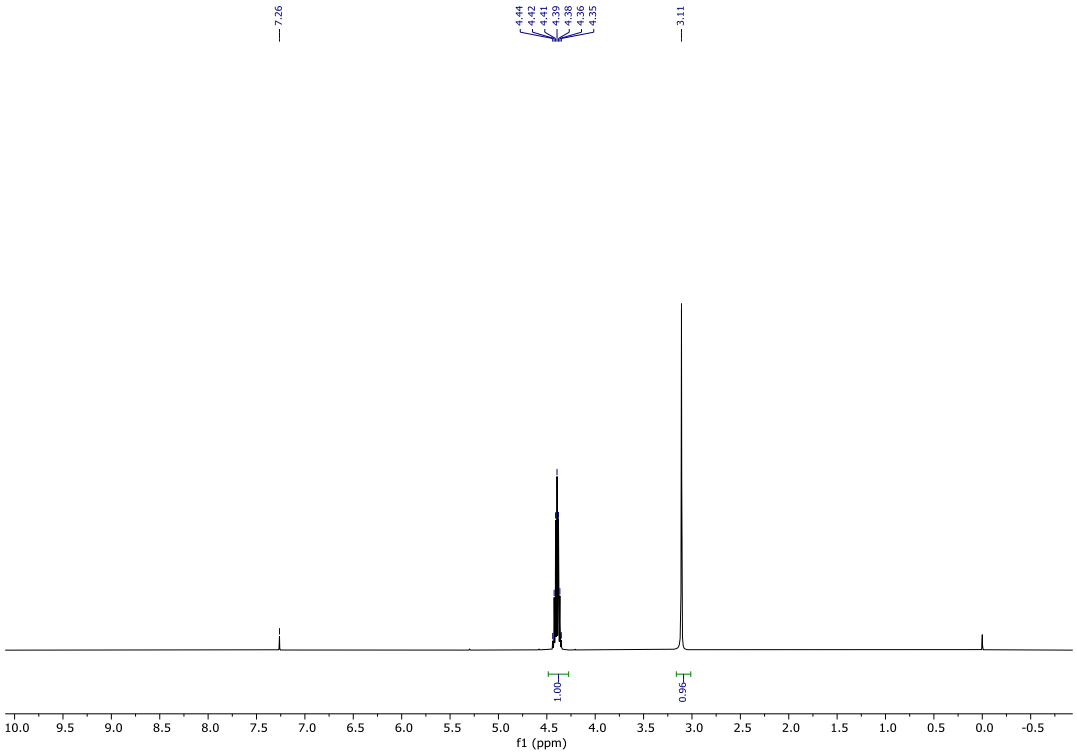


^{13}C{^{1}H} NMR (126 MHz $CDCl_3$)

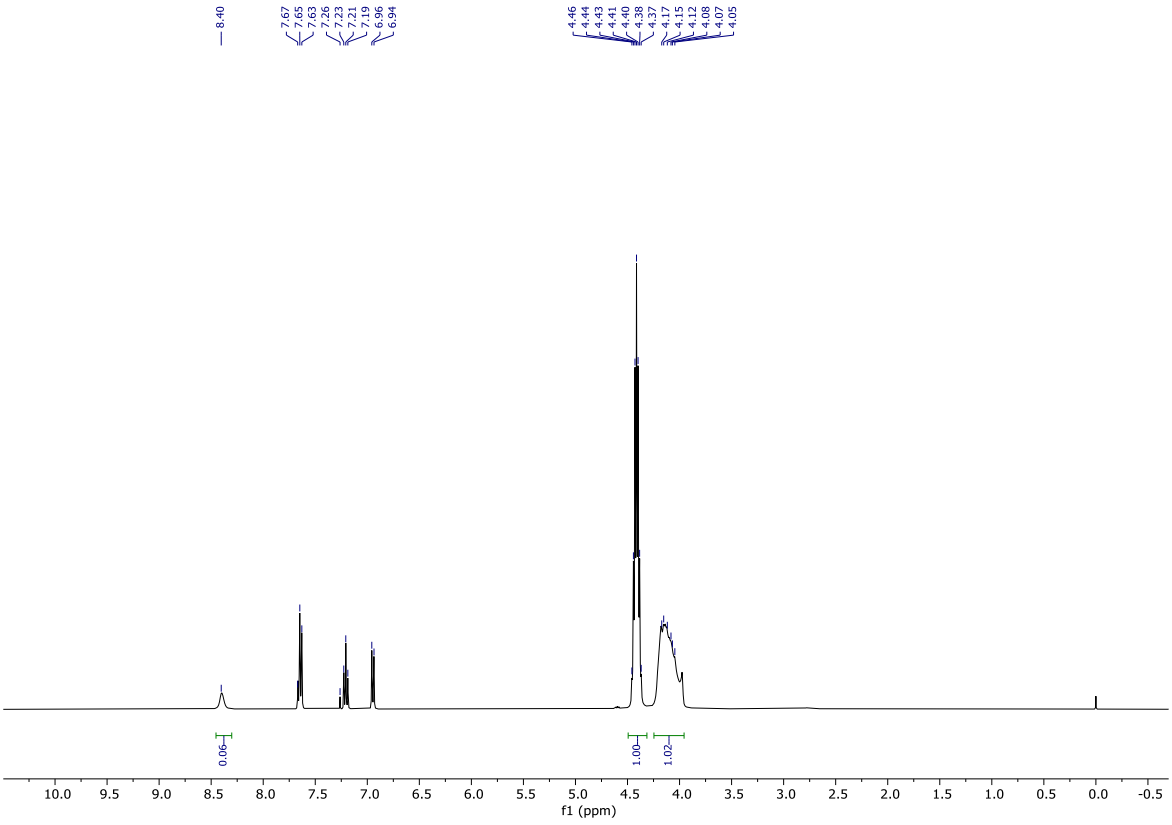


10. Copies of ^{1}H NMR Spectra of NMR Study

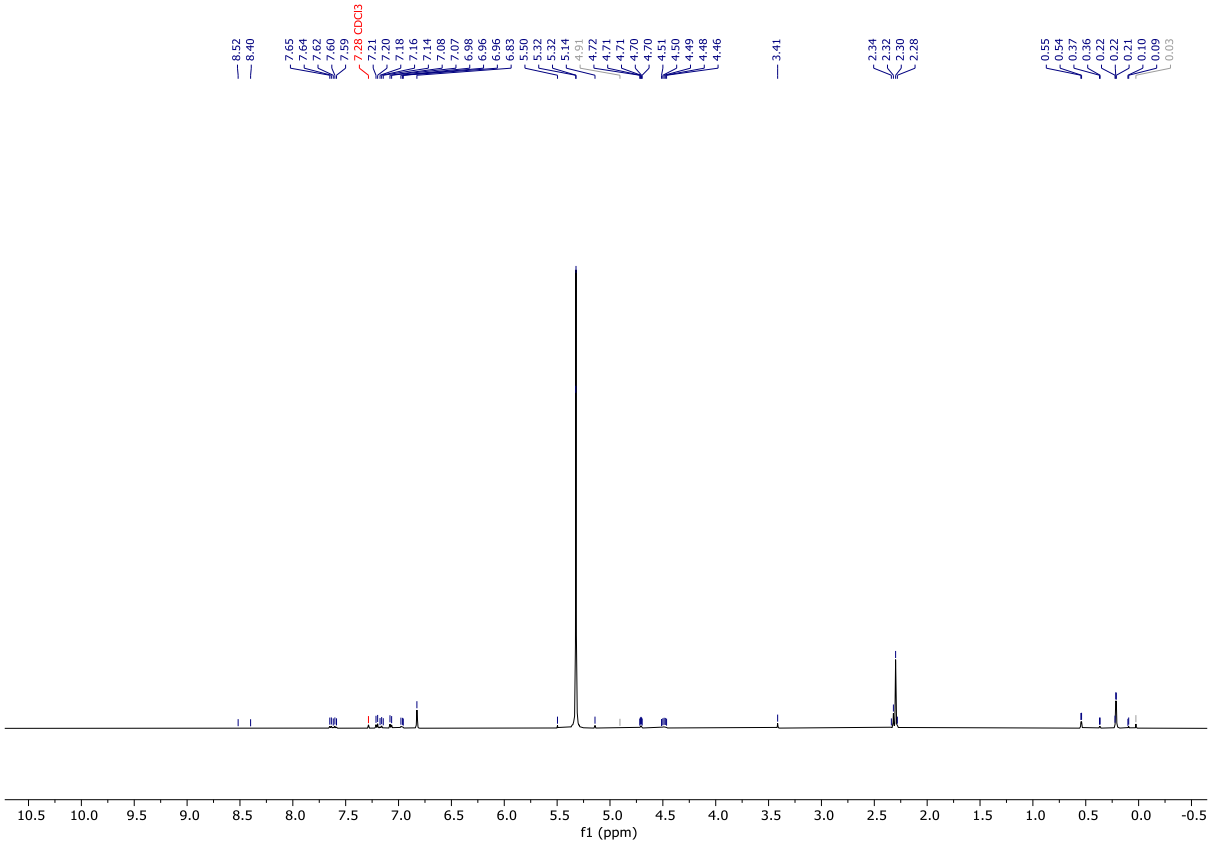
^{1}H NMR of HFIP



^{1}H NMR spectra of hydrogen bonded hydroxy group of HFIP with carbonyl group of isatin.



^{1}H NMR of reaction mixture (Isatin and *p*-methyl thiophenol) in catalytic HFIP and mesitylene as internal standard



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