Electronic Supplementary Material (ESI) for ChemComm.

Nickel-Catalyzed Exo-Selective Hydroacylation/Suzuki Cross-Coupling Reaction

Supporting Information

Shao-Chi Lee, Dr. Lin Guo, and Magnus Rueping*

[†]Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany.
[‡]King Abdullah University of Science and Technology (KAUST), KAUST Catalysis Center (KCC)
Thuwal 23955-6900, Saudi Arabia

E-mail: magnus.rueping@rwth-aachen.de

Table of Contents

1. General Information

2. General Procedure for the Nickel-Catalyzed Intramolecular Hydroacylation/Suzuki Domino Cross-Coupling

3. References

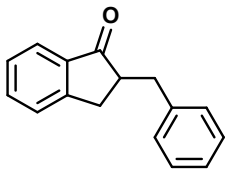
4. ^{1}H and ^{13}C-NMR Spectra

General information: Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were technical grade and distilled prior to use. Toluene used in reactions was analytical grade and distilled from benzophenone/Na. All *o*-allylaldehydes[1] and boronic acid neopentylglycol esters[2] were prepared according to literature. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator, visualised by irradiation with UV light. Column chromatography was performed using silica gel (Macherey Nagel, particle size 0.040-0.063 mm). Solvent mixtures are understood as volume/volume. ^{1}H-NMR and ^{13}C-NMR were recorded on a Varian AV400 or AV600 spectrometer in $CDCl_3$ and reported relative to the solvents residual 1H-signal ($CHCl_3$, δ(H) 7.26). Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (*J*) are in Hertz (Hz). IR spectra were recorded on a Perkin Elmer-100 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Mass spectra (MS-EI, 70eV) were conducted on a Finnigan SSQ 7000 mass spectrometer. HRMS were measured on Finnigan MAT 95 or LTQ Orbitrap XL spectrometer.

General procedure for the nickel-catalyzed intramolecular hydroacylation/suzuki domino cross-coupling

An oven-dried sealed tube was charged with *o*-allylbenzaldehyde (0.2 mmol, 1 equiv.), $Ni(cod)_2$ (0.05 equiv., 2.8 mg, 0.010 mmol), IPr·HCl (0.1 equiv., 8.54 mg, 0.020 mmol), cesium carbonate (2 equiv., 130 mg, 0.4 mmol), H_2O (5 equiv., 18 µL, 1.0 mmol), the appropriate boronic acid neopentylglycol ester (2.5 equiv., 0.500 mmol), and dry toluene (1 mL) under Ar. The reaction tube was warmed up to 130 °C and stirred for 16 h. After completion, the reaction mixture was cooled down to room temperature. The corresponding product **3** was obtained after purification by column chromatography on silica gel (SiO_2, EtOAc : Hexane = 1 : 30).

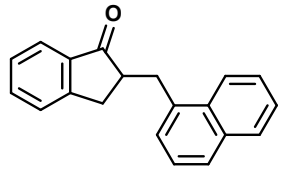
2-benzyl-2,3-dihydro-1*H*-inden-1-one (3a)



The title compound was prepared according to the general procedure, and isolated as colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.42 – 7.35 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.20 (m, 3H), 3.41 (dd, *J* = 14.0, 4.3 Hz, 1H), 3.17 (dd, *J* = 17.1, 7.8 Hz, 1H), 3.05 – 2.96 (m, 1H), 2.87 (dd, *J* = 17.2, 4.1 Hz, 1H), 2.67 (dd, *J* = 14.0, 10.5 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.98, 153.78, 139.79, 136.69, 134.96, 129.05, 128.67, 127.57,

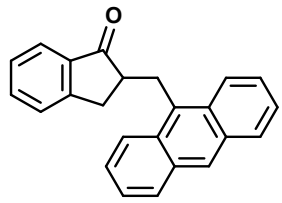
126.73, 126.49, 124.18, 49.08, 37.14, 32.33. The data are in agreement with the reported spectroscopic data.[3]

2-(naphthalen-1-ylmethyl)-2,3-dihydro-1*H*-inden-1-one (3b)



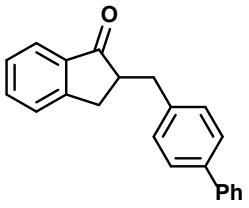
The title compound was prepared according to the general procedure, and isolated as pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.61 – 7.49 (m, 3H), 7.46 – 7.36 (m, 4H), 4.05 (dd, *J* = 14.3, 3.7 Hz, 1H), 3.27 – 3.15 (m, 1H), 3.10 (dd, *J* = 17.2, 7.8 Hz, 1H), 2.97 – 2.83 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.06, 153.76, 136.62, 135.99, 135.01, 134.12, 131.94, 129.05, 127.63, 127.47, 126.76, 126.63, 126.37, 125.88, 125.55, 124.24, 123.82, 48.36, 34.81, 32.897. **IR** (ATR): $\tilde{\nu}$ = 2923, 1705, 1602, 1459, 1271, 1202, 986, 785 cm^{-1}. **HRMS** (ESI): Calcd. for $C_{20}H_{16}ONa^+$ ($[M+Na]^+$): m/z 295.1093; found, 295.1093.

2-(anthracen-9-ylmethyl)-2,3-dihydro-1*H*-inden-1-one (3c)



The title compound was prepared according to the general procedure, and isolated as white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.38 (d, *J* = 8.8 Hz, 2H), 8.09 – 8.00 (m, 2H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.59 – 7.52 (m, 3H), 7.51 – 7.48 (m, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 4.37 (dd, *J* = 14.7, 4.2 Hz, 1H), 3.76 (dd, *J* = 14.7, 11.3 Hz, 1H), 3.37 – 3.27 (m, 1H), 2.98 (dd, *J* = 17.3, 4.2 Hz, 1H), 2.84 (dd, *J* = 17.3, 7.9 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.99, 153.73, 136.51, 135.03, 134.28, 132.32, 131.80, 130.13, 129.56, 127.65, 126.75, 126.70, 126.10, 125.10, 124.52, 124.28, 49.87, 32.51, 28.47. **IR** (ATR): $\tilde{\nu}$ = 2922, 1704, 1602, 1459, 1279, 1148, 889, 732 cm^{-1}. **HRMS** (ESI): Calcd. for $C_{24}H_{18}ONa^+$ ($[M+Na]^+$): m/z 345.1247; found, 345.1250.

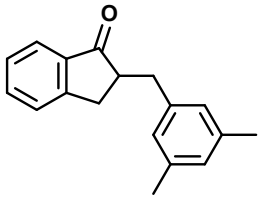
2-([1,1'-biphenyl]-4-ylmethyl)-2,3-dihydro-1*H*-inden-1-one (3d)



The title compound was prepared according to the general procedure, and isolated as colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.63 – 7.52 (m, 5H), 7.47 – 7.31 (m, 7H), 3.44 (dd, *J* = 14.1, 4.3 Hz, 1H), 3.23 (dd, *J* = 17.2, 7.8 Hz, 1H), 3.10 – 3.02 (m, 1H), 2.91 (dd, *J* = 17.2, 4.1 Hz, 1H), 2.73 (dd, *J* = 14.0, 10.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.93, 153.77, 140.99, 139.43, 138.87, 136.69, 134.99, 129.47, 128.88, 127.60, 127.37, 127.29,

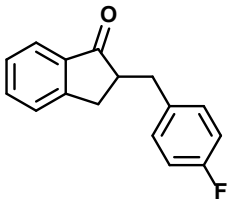
127.11, 126.75, 124.19, 49.04, 36.77, 32.39. The data are in agreement with the reported spectroscopic data.[3]

2-(3,5-dimethylbenzyl)-2,3-dihydro-1*H*-inden-1-one (3e)



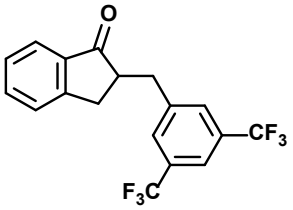
The title compound was prepared according to the general procedure, and isolated as colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.57 (td, *J* = 7.5, 1.3 Hz, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 6.87 (s, 3H), 3.35 (dd, *J* = 13.9, 4.3 Hz, 1H), 3.17 (dd, *J* = 17.2, 7.7 Hz, 1H), 3.00 – 2.96 (m, 1H), 2.86 (dd, *J* = 17.2, 4.1 Hz, 1H), 2.54 (dd, *J* = 13.9, 10.7 Hz, 1H), 2.30 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 208.15, 153.88, 139.79, 138.15, 136.72, 134.91, 128.12, 127.53, 126.84, 126.75, 124.17, 49.18, 37.10, 32.49, 21.45. **IR** (ATR): $\tilde{\nu}$ = 2920, 2854, 1711, 1605, 1464, 1281, 754, 705 cm^{-1}. **HRMS** (ESI): Calcd. for $C_{18}H_{18}ONa^+$ ($[M+Na]^+$): m/z 273.1249; found, 273.1250.

2-(4-fluorobenzyl)-2,3-dihydro-1*H*-inden-1-one (3f)



The title compound was prepared according to the general procedure, and isolated as colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.57 (td, *J* = 7.5, 1.3 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.22 – 7.18 (m, 2H), 7.01 – 6.94 (m, 2H), 3.33 (dd, *J* = 14.1, 4.4 Hz, 1H), 3.17 (dd, *J* = 17.1, 7.8 Hz, 1H), 2.99 – 2.94 (m, 1H), 2.83 (dd, *J* = 17.2, 4.1 Hz, 1H), 2.70 (dd, *J* = 14.1, 10.0 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.82, 161.67 (d, *J* = 244.3 Hz), 153.65, 136.62, 135.26 (d, *J* = 3.6 Hz), 135.04, 130.45 (d, *J* = 8.0 Hz), 127.63, 126.71, 124.16, 115.43 (d, *J* = 21.0 Hz), 49.02, 36.20, 32.13. **^{19}F NMR** (564 MHz, $CDCl_3$) δ -116.81 – -116.87 (m, 1F). The data are in agreement with the reported spectroscopic data.[3]

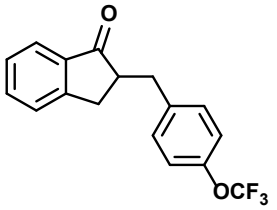
2-(3,5-bis(trifluoromethyl)benzyl)-2,3-dihydro-1*H*-inden-1-one (3g)



The title compound was prepared according to the general procedure, and isolated as colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.7 Hz, 1H), 7.75 (s, 1H), 7.71 (s, 2H), 7.61 (td, *J* = 7.5, 1.3 Hz, 1H), 7.46 – 7.37 (m, 2H), 3.51 (dd, *J* = 14.3, 4.5 Hz, 1H), 3.26 (dd, *J* = 17.0, 7.9 Hz, 1H), 3.08 – 2.97 (m, 1H), 2.88 – 2.75 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 206.66, 153.08, 142.34, 136.32, 135.36, 132.52 – 131.33 (m), 129.17, 127.94, 126.74, 124.35, 122.52, 120.80 – 120.69 (m), 48.41, 36.82, 32.30. **^{19}F NMR** (564 MHz, $CDCl_3$) δ -62.84. **IR** (ATR): =

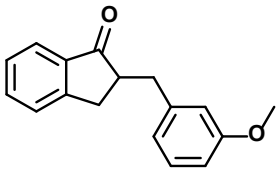
2920, 2853, 1701, 1613, 1463, 1380, 1279, 1169, 1115, 754 cm^{-1}. **HRMS** (ESI): Calcd. for $C_{18}H_{12}O_1F_6^+$ (M^+): m/z 358.0788; found, 358.0787.

2-(4-(trifluoromethoxy)benzyl)-2,3-dihydro-1*H*-inden-1-one (3h)



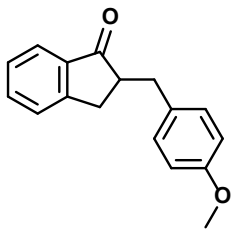
The title compound was prepared according to the general procedure, and isolated as colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7, 1H), 7.58 (td, *J* = 7.4, 1.2 Hz, 1H), 7.43 – 7.33 (m, 2H), 7.31 – 7.23 (m, 2H), 7.17 – 7.07 (m, 2H), 3.37 (dd, *J* = 14.0, 4.3 Hz, 1H), 3.20 (dd, *J* = 17.0, 7.8 Hz, 1H), 3.05 – 2.91 (m, 1H), 2.83 (dd, *J* = 17.0, 4.1 Hz, 1H), 2.71 (dd, *J* = 14.0, 10.1 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.58, 153.56, 147.93, 138.47, 136.57, 135.12, 130.32, 127.71, 126.73, 124.23, 121.23, 120.61 (d, *J* = 256.8 Hz), 48.88, 36.37, 32.25. **^{19}F NMR** (564 MHz, $CDCl_3$) δ -57.91. **IR** (ATR): = 2923, 2854, 1712, 1608, 1509, 1262, 1222, 1164, 749 cm^{-1}. **HRMS** (ESI): Calcd. for $C_{17}H_{14}O_2F_3^+$ ($[M+H]^+$): m/z 307.0951; found, 307.0940.

2-(3-methoxybenzyl)-2,3-dihydro-1*H*-inden-1-one (3i)



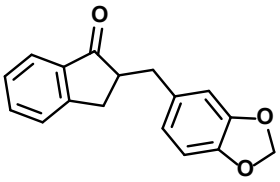
The title compound was prepared according to the general procedure, and isolated as colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.57 (td, *J* = 7.4, 1.2 Hz, 1H), 7.43 – 7.33 (m, 2H), 7.22 (t, *J* = 7.9 Hz, 1H), 6.89 – 6.70 (m, 3H), 3.38 (dd, *J* = 14.0, 4.3 Hz, 1H), 3.18 (dd, *J* = 17.2, 7.8 Hz, 1H), 3.01 – 2.98 (m, 1H), 2.87 (dd, *J* = 17.2, 4.1 Hz, 1H), 2.64 (dd, *J* = 14.0, 10.5 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.99, 159.82, 153.81, 141.42, 136.64, 134.98, 129.63, 127.56, 126.73, 124.15, 121.39, 114.73, 111.76, 55.28, 49.00, 37.18, 32.34. The data are in agreement with the reported spectroscopic data.[3]

2-(4-methoxybenzyl)-2,3-dihydro-1*H*-inden-1-one (3j)



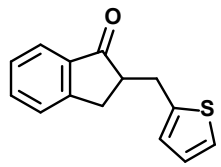
The title compound was prepared according to the general procedure, and isolated as colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.1 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.41 – 7.35 (m, 2H), 7.18 – 7.14 (m, 2H), 6.85 – 6.82 (m, 2H), 3.79 (s, 2H), 3.31 (dd, *J* = 14.1, 4.4 Hz, 1H), 3.16 (dd, *J* = 17.2, 7.8 Hz, 1H), 2.99 – 2.94 (m, 1H), 2.86 (dd, *J* = 17.2, 4.1 Hz, 1H), 2.65 (dd, *J* = 14.0, 10.2 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 208.16, 158.25, 153.85, 136.74, 134.93, 131.70, 130.02, 127.54, 126.73, 124.14, 114.03, 55.38, 49.26, 36.23, 32.22. The data are in agreement with the reported spectroscopic data[3].

2-(benzo[d][1,3]dioxol-5-ylmethyl)-2,3-dihydro-1*H*-inden-1-one (3k)



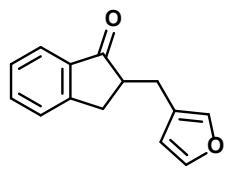
The title compound was prepared according to the general procedure, and isolated as colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.57 (td, *J* = 7.4, 1.2 Hz, 1H), 7.43 – 7.35 (m, 2H), 6.75 – 6.72 (m, 2H), 6.69 – 6.67 (m, 1H), 5.93 (s, 2H), 3.29 (dd, *J* = 14.1, 4.4 Hz, 1H), 3.17 (dd, *J* = 17.1, 7.8 Hz, 1H), 2.97 – 2.91 (m, 1H), 2.86 (dd, *J* = 17.2, 4.1 Hz, 1H), 2.62 (dd, *J* = 14.0, 10.2 Hz, 1H).**^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.94, 153.79, 147.84, 146.19, 136.69, 134.98, 133.46, 127.58, 126.74, 124.18, 121.99, 109.38, 108.37, 101.03, 49.24, 36.81, 32.16. **IR** (ATR): = 2920, 2854, 1707, 1607, 1489, 1442, 762 cm^{-1}. **HRMS** (ESI): Calcd. for $C_{17}H_{15}O_3^+$ ($[M+H]^+$): m/z 267.1014; found, 267.1016.

2-(thiophen-2-ylmethyl)-2,3-dihydro-1*H*-inden-1-one (3l)



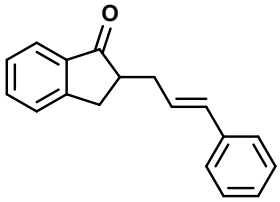
The title compound was prepared according to the general procedure, and isolated as colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.44 – 7.35 (m, 1H), 7.27 – 7.24 (m, 1H), 7.03 – 6.96 (m, 2H), 3.33 (dd, *J* = 14.5, 4.2 Hz, 1H), 3.25 (dd, *J* = 17.2, 7.8 Hz, 1H), 3.02 – 2.96 (m, 1H), 2.87 (dd, *J* = 17.1, 4.1 Hz, 1H), 2.82 (ddd, *J* = 14.5, 9.8, 1.5 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.99, 153.84, 139.86, 136.69, 134.99, 128.49, 127.58, 126.73, 125.88, 124.15, 121.59, 48.38, 32.49, 31.59. **IR** (ATR): $\tilde{\nu}$ = 2921, 1709, 1607, 1465, 1278, 755 cm^{-1}. **HRMS** (ESI): Calcd. for $C_{14}H_{12}ONaS^+$ ($[M+Na]^+$): m/z 251.0499; found, 251.0501.

2-(furan-3-ylmethyl)-2,3-dihydro-1*H*-inden-1-one (3m)



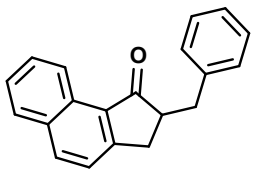
The title compound was prepared according to the general procedure, and isolated as colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.42 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 1.8 Hz, 1H), 6.28 (s, 1H), 3.27 (dd, *J* = 17.0, 7.7 Hz, 1H), 3.08 (dd, *J* = 14.7, 4.3 Hz, 1H), 2.95 – 2.88 (m, 1H), 2.86 (dd, *J* = 17.1, 4.2 Hz, 1H), 2.67 (dd, *J* = 14.7, 9.2 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 208.08, 153.87, 143.17, 139.85, 136.77, 134.99, 127.59, 126.73, 124.12, 122.30, 111.34, 47.79, 32.36, 26.23. The data are in agreement with the reported spectroscopic data.[3]

2-cinnamyl-2,3-dihydro-1*H*-inden-1-one (3n)



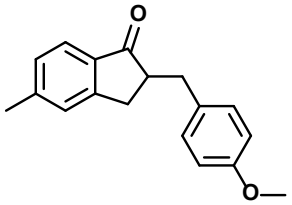
The title compound was prepared according to the general procedure, and isolated as colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.59 (td, *J* = 7.4, 1.3 Hz, 1H), 7.46 – 7.44 (m, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.34 – 7.27 (m, 4H), 7.23 – 7.19 (m, 1H), 6.49 (d, *J* = 15.7 Hz, 1H), 6.24 – 6.18 (m, 1H), 3.32 (dd, *J* = 17.2, 7.6 Hz, 1H), 2.93 (dd, *J* = 17.2, 3.7 Hz, 1H), 2.90 – 2.83 (m, 2H), 2.47 – 2.39 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 208.25, 153.89, 137.35, 136.77, 134.99, 132.33, 128.66, 127.57, 127.37, 126.79, 126.24, 124.10, 47.21, 34.95, 32.22. The data are in agreement with the reported spectroscopic data.[4]

2-benzyl-2,3-dihydro-1*H*-cyclopenta[a]naphthalen-1-one (3o)



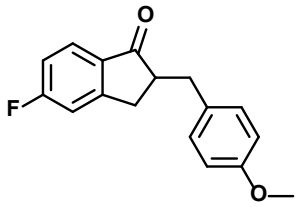
The title compound was prepared according to the general procedure, and isolated as pale yellow soild. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.83 – 7.76 (m, 2H), 7.69 – 7.58 (m, 2H), 7.36 – 7.29 (m, 4H), 7.26 – 7.21 (m, 1H), 3.53 – 3.48 (m, 2H), 3.21 – 3.11 (m, 2H), 2.72 (dd, *J* = 14.0, 10.6 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.82, 155.22, 139.87, 136.80, 134.12, 130.52, 129.39, 129.07 (d, *J* = 3.6 Hz), 128.77 (d, *J* = 5.7 Hz), 127.19, 126.56, 124.67, 119.86, 48.96, 37.45, 30.74. **IR** (ATR): = 2922, 2859, 1694, 1586, 1455, 1297, 1243, 1067, 815, 757, 697 cm^{-1}. **HRMS** (ESI): Calcd. for $C_{20}H_{16}ONa^+$ ($[M+Na]^+$): m/z 295.1095; found, 295.1093.

2-(4-methoxybenzyl)-5-methyl-2,3-dihydro-1*H*-inden-1-one (3p)



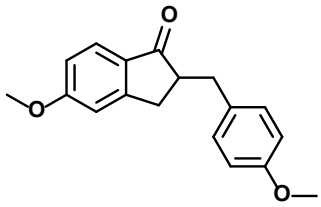
The title compound was prepared according to the general procedure, and isolated as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.8 Hz, 1H), 7.20 – 7.11 (m, 4H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 3.29 (dd, *J* = 14.0, 4.3 Hz, 1H), 3.10 (dd, *J* = 17.1, 7.8 Hz, 1H), 3.00 – 2.88 (m, 1H), 2.79 (dd, *J* = 17.2, 4.0 Hz, 1H), 2.62 (dd, *J* = 14.0, 10.2 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.68, 158.23, 154.38, 146.13, 134.46, 131.83, 130.02, 128.83, 127.06, 123.98, 114.02, 55.39, 49.38, 36.35, 32.04, 22.24. IR (ATR): = 2921, 2842, 1704, 158, 1459, 1283, 1152, 1045, 888, 752, 695 cm^{-1}. **HRMS** (ESI): Calcd. for $C_{18}H_{18}O_2Na^+$ ($[M+Na]^+$): m/z 289.1197; found, 289.1199.

5-fluoro-2-(4-methoxybenzyl)-2,3-dihydro-1*H*-inden-1-one (3q)



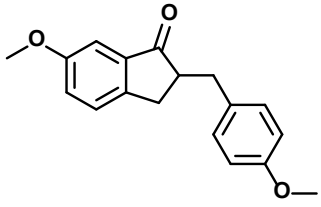
The title compound was prepared according to the general procedure, and isolated as colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 7.5, 2.6 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.30 – 7.27 (m, 1H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.85 – 6.82 (m, 2H), 3.79 (s, 3H), 3.29 (dd, *J* = 14.1, 4.4 Hz, 1H), 3.13 (dd, *J* = 17.0, 7.8 Hz 1H), 3.05 – 2.98 (m, 1H), 2.84 – 2.79 (m, 1H), 2.67 (dd, *J* = 14.1, 10.0 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.16, 163.27, 161.62, 158.34, 149.20, 138.47 (d, *J* = 6.8 Hz), 131.37, 130.02, 128.08 (d, *J* = 8.0 Hz), 122.62 (d, *J* = 23.8 Hz), 114.07, 109.89 (d, *J* = 21.6 Hz), 55.39, 50.14, 36.14, 31.62. **^{19}F NMR** (564 MHz, $CDCl_3$) δ -114.47. **IR** (ATR): = 2922, 2849, 1711, 1611, 1511, 1440, 1248, 1176, 1033, 818, 516 cm^{-1}. **HRMS** (ESI): Calcd. for $C_{17}H_{15}O_2FNa^+$ ($[M+Na]^+$): m/z 293.0944; found, 293.0948.

5-methoxy-2-(4-methoxybenzyl)-2,3-dihydro-1*H*-inden-1-one (3r)



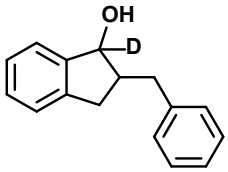
The title compound was prepared according to the general procedure, purified by silica column chromatography (SiO_2, EtOAc : Hexane = 1 :4) and isolated as white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.5 Hz, 1H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.89 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.85 – 6.79 (m, 3H), 3.86 (s, 3H), 3.79 (s, 3H), 3.29 (dd, *J* = 14.1, 4.4 Hz, 1H), 3.10 (dd, *J* = 17.2, 7.8 Hz, 1H), 3.00 – 2.91 (m, 1H), 2.80 (dd, *J* = 17.2, 4.0 Hz, 1H), 2.62 (dd, *J* = 14.1, 10.2 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 206.33, 165.53, 158.24, 156.83, 131.85, 130.04, 125.83, 115.51, 114.02, 109.82, 55.58 (d, J = 56.0 Hz), 49.38, 36.44, 32.24. The data are in agreement with the reported spectroscopic data.[5]

6-methoxy-2-(4-methoxybenzyl)-2,3-dihydro-1*H*-inden-1-one (3s)



The title compound was prepared according to the general procedure, purified by silica column chromatography (SiO_2, EtOAc : Hexane = 1 : 4) and isolated as white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.3 Hz, 1H), 7.20 (d, *J* = 2.5 Hz, 1H), 7.19 – 7.13 (m, 3H), 6.86 – 6.80 (m, 2H), 3.84 (s, 3H), 3.79 (s, 3H), 3.30 (dd, *J* = 14.1, 4.4 Hz, 1H), 3.08 (dd, *J* = 16.8, 7.6 Hz, 1H), 3.03 – 2.94 (m, 1H), 2.77 (dd, *J* = 16.8, 3.7 Hz, 1H), 2.64 (dd, *J* = 14.1, 10.1 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 208.17, 159.54, 158.26, 146.71, 137.85, 131.74, 130.01, 127.44, 124.38, 114.02, 105.19, 55.75, 55.39, 50.06, 36.33, 31.53. **IR** (ATR): = 2923, 2843, 2051, 1705, 1612, 1494, 1244, 1031, 821, 523 cm^{-1}. **HRMS** (ESI): Calcd. for $C_{18}H_{18}O_3Na^+$ ($[M+Na]^+$): m/z 305.1151; found, 305.1148.

2-benzyl-2,3-dihydro-1*H*-inden-1-d-1-ol (5)



Deuterated aldehyde **4** was prepared according to the literature.[6] The title compound (**5**) was prepared according to the general procedure, purified by silica column chromatography (SiO_2, EtOAc : Hexane = 1 : 3) and isolated as white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.3 Hz, 1H), 7.34 – 7.30 (m, 3H), 7.29 – 7.20 (m, 5H), 5.01 (d, *J* = 5.5 Hz, 0.11H), 3.11 (dd, *J* = 13.6, 7.4 Hz, 1H), 2.85 (d, *J* = 8.0 Hz, 2H), 2.78 (dd, *J* = 13.6, 8.3 Hz, 1H), 2.71 – 2.63 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.81, 143.67, 141.40, 129.05, 128.85, 128.58, 126.92, 126.08, 125.19, 124.90, 46.97, 36.03, 35.12. **IR** (ATR): = 3395, 2926, 1718, 1601, 1455, 1245, 1118, 1040, 955, 741, 696 cm^{-1}. **HRMS** (ESI): Calcd. for $C_{16}H_{15}{}^2H_1O_1^+$ (M^+): m/z 225.1263; found, 225.1258.

References

[1] a) Y. Qin, J. Lv, S. Luo and J.-P. Cheng, *Org. Lett*. 2014, **16**, 5032; b) Y. Hoshimoto, Y. Hayashi, H. Suzuki, M. Ohashi and S. Ogoshi, *Angew. Chem. Int. Ed*. 2012, **51**, 10812.

[2] T. L. Andersen, M. W. Frederiksen, K. Domino and T. Skrydstrup, *Angew. Chem. Int. Ed.* 2016, **55**, 10396.

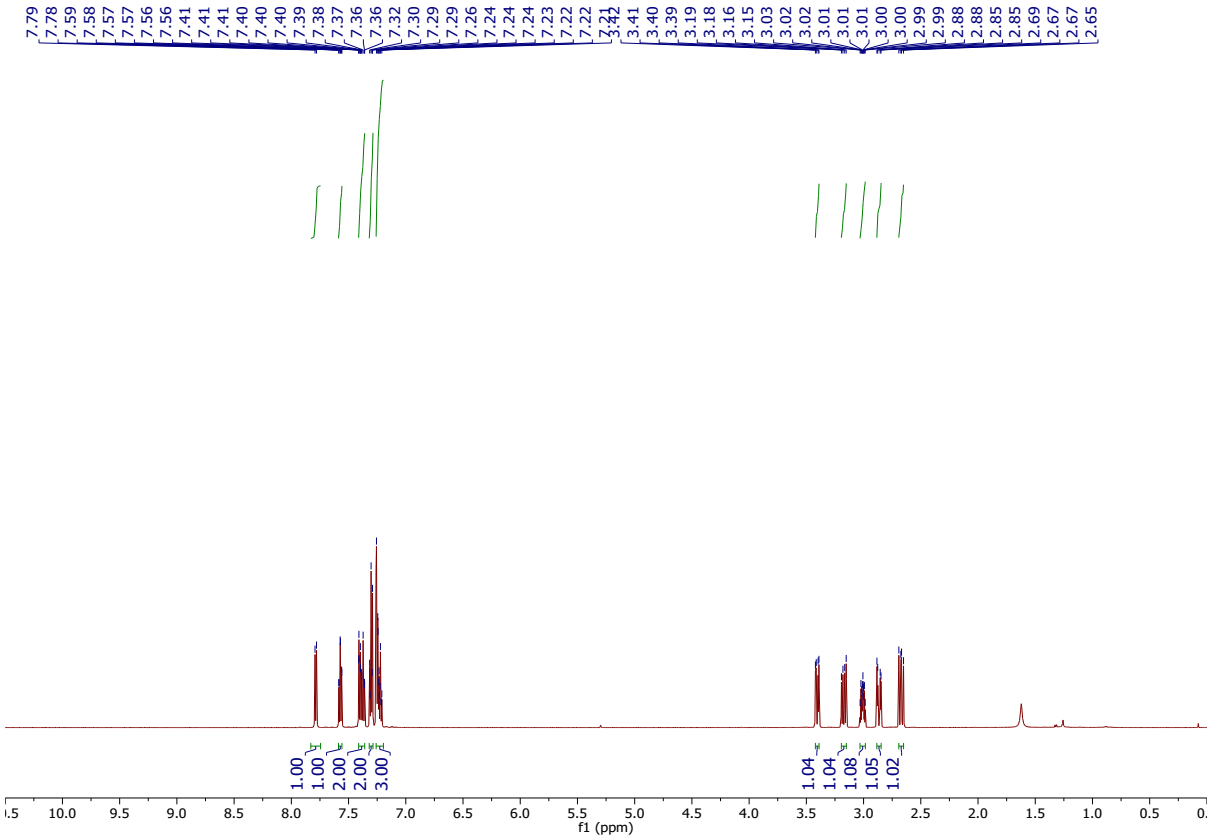
[3] J. A. Walker, K. L. Vickerman, J. N. Humke and L. M. Stanley, *J. Am. Chem. Soc*. 2017, **139**, 10228.

[4] X. Huo, G. Yang, D. Liu, Y. Liu, I. D. Gridnev and W. Zhang, *Angew. Chem. Int. Ed*. 2014, **53**, 6776.

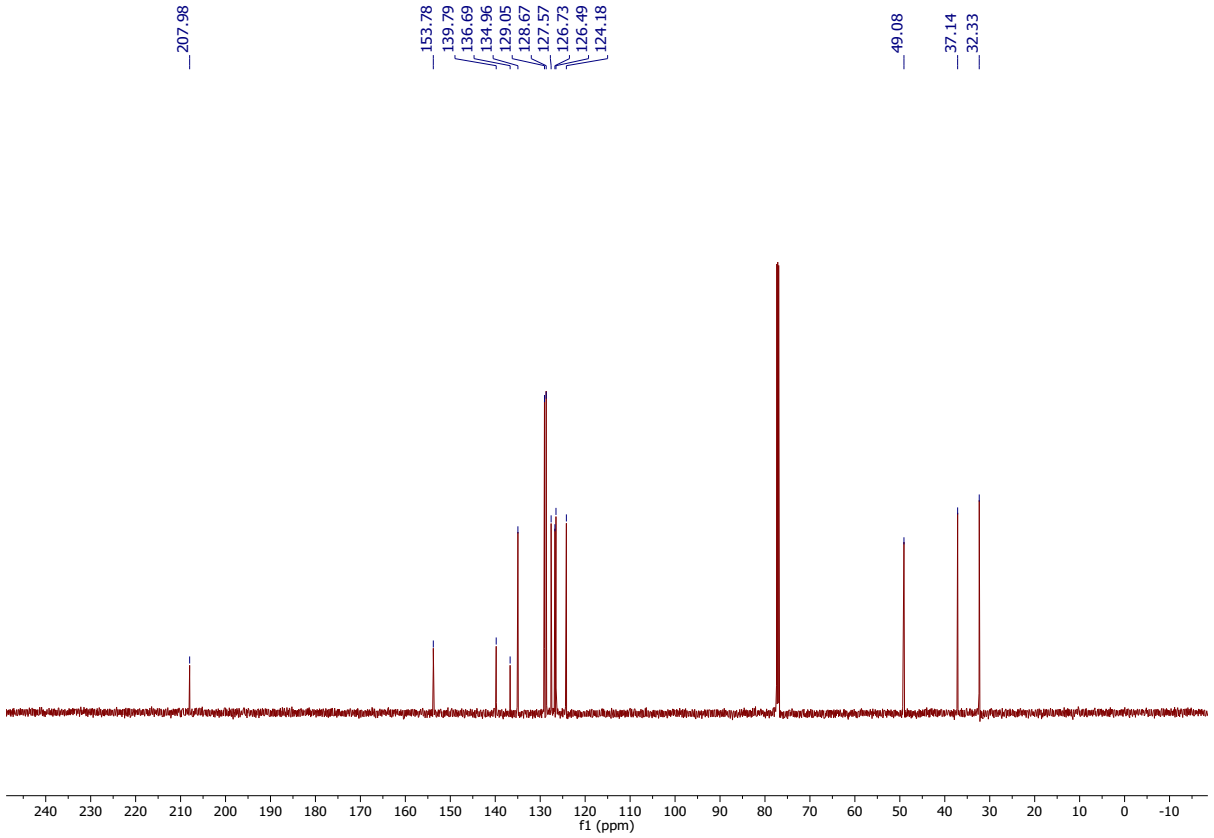
[5] V. Pathak, I. Ahmad, A. K. Kahlon, M. Hasanain, S. Sharma, K. K. Srivastava, J. Sarkar, K. Shankar, A. Sharmab and A. Gupta, *RSC Adv*. 2014, **4**, 35171.

[6] X. Li, S. Wu, S. Chen, Z. Lai, H.–B. Luo and C. Sheng, *Org. Lett*. 2018, **20**, 1712.

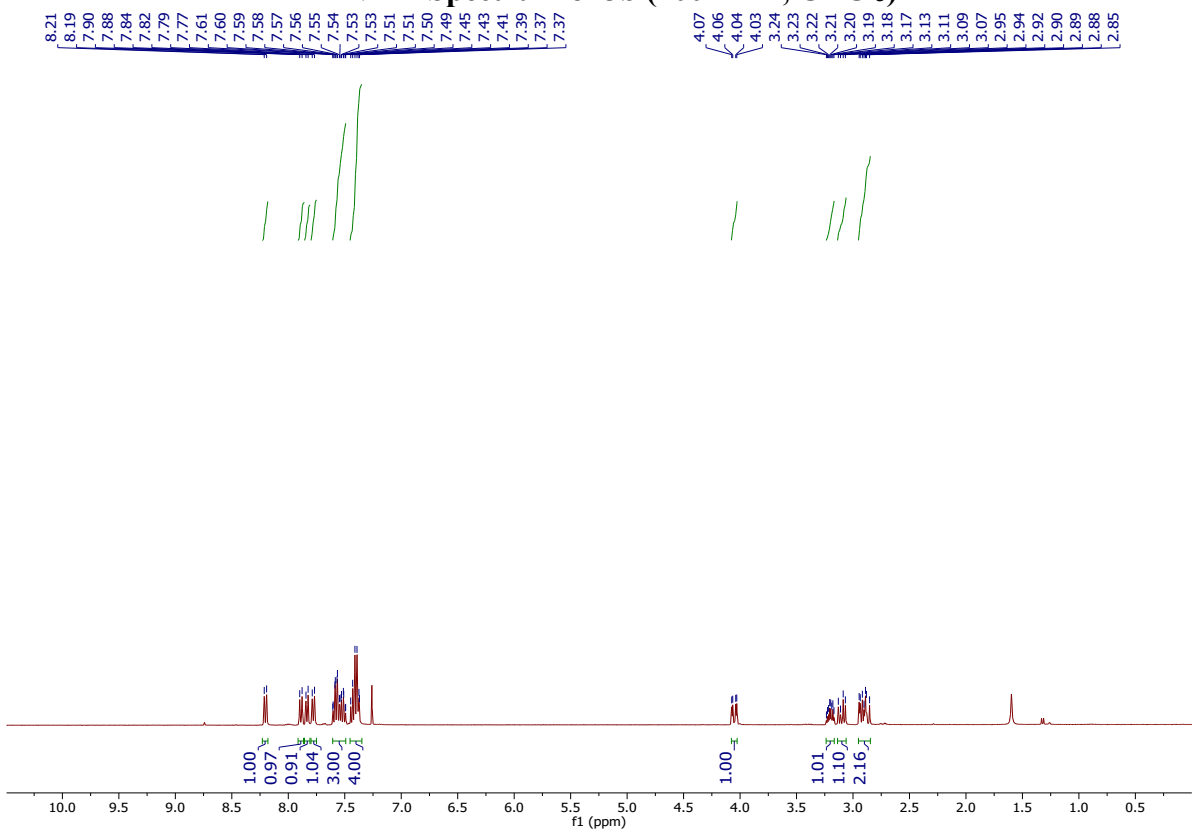
^{1}H NMR Spectrum of 3a (600 MHz, $CDCl_3$)



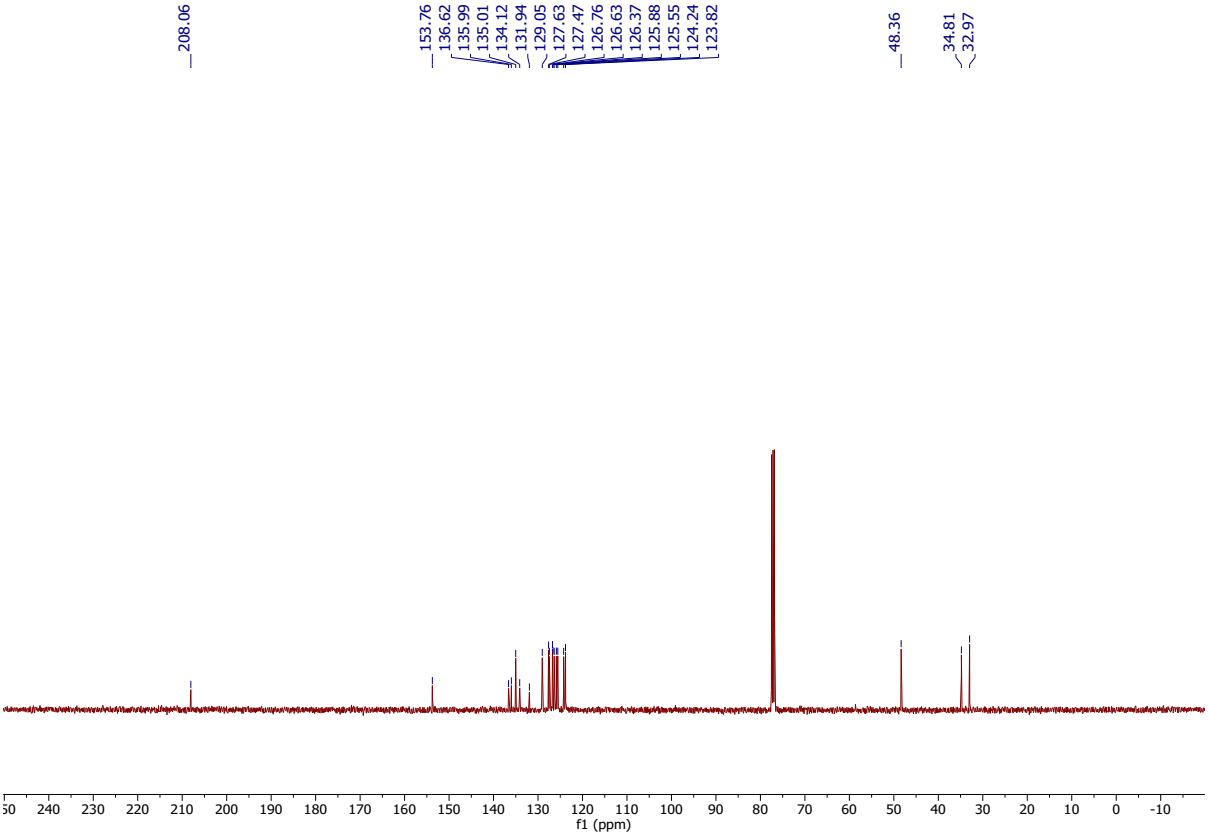
^{13}C NMR Spectrum of 3a (150 MHz, $CDCl_3$)



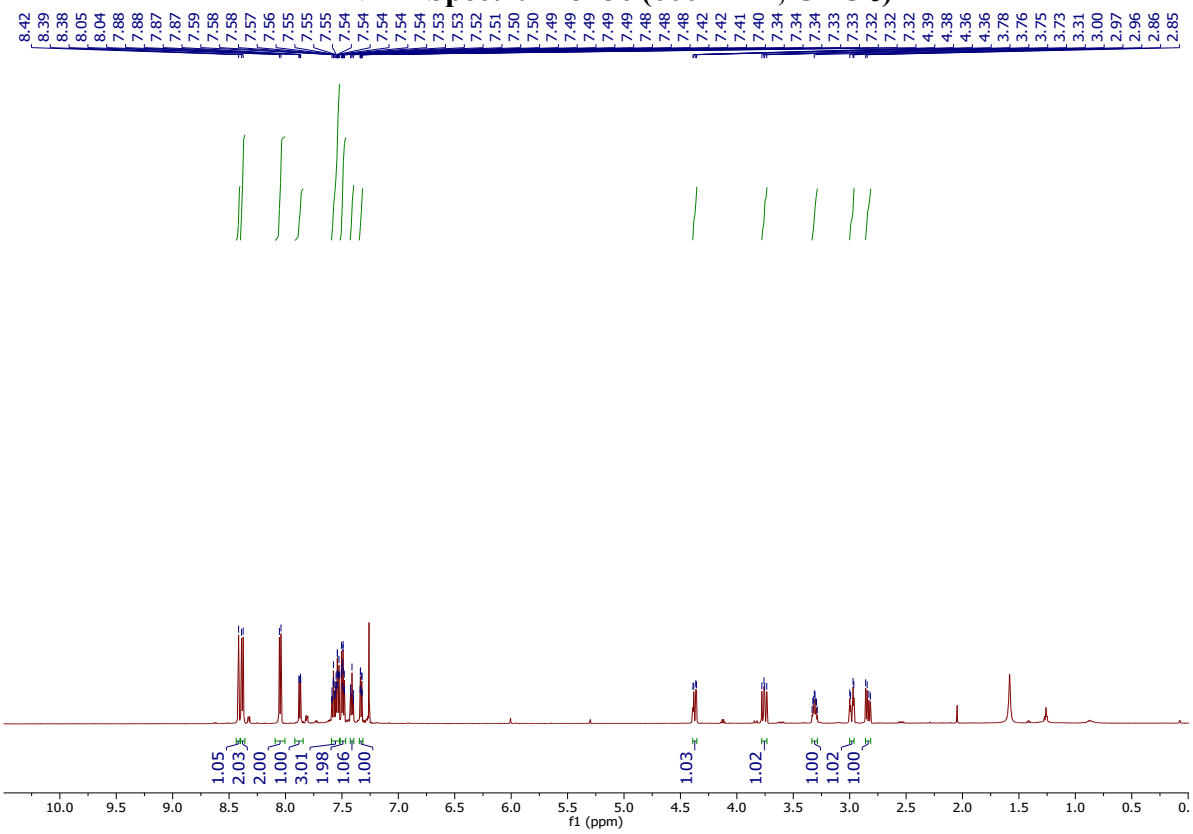
^{1}H NMR Spectrum of 3b (400 MHz, $CDCl_3$)



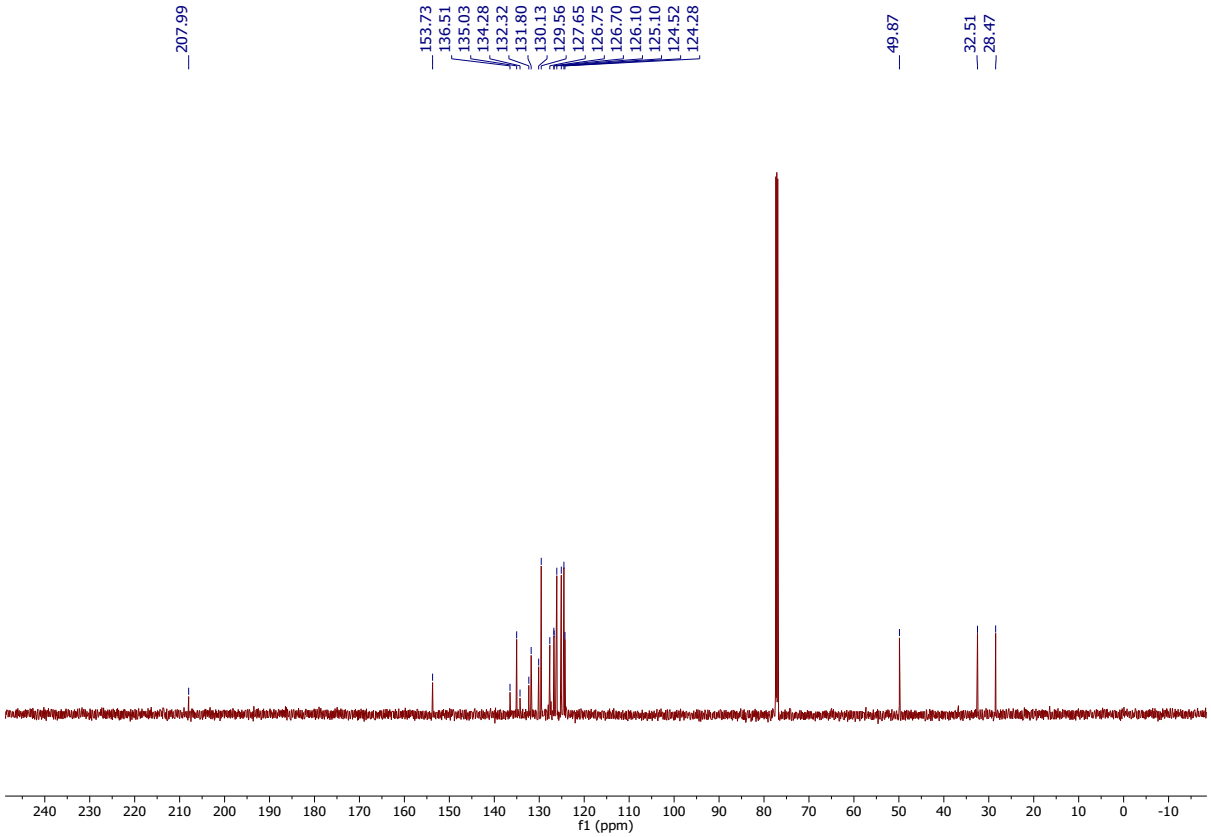
^{13}C NMR Spectrum of 3b (100 MHz, $CDCl_3$)



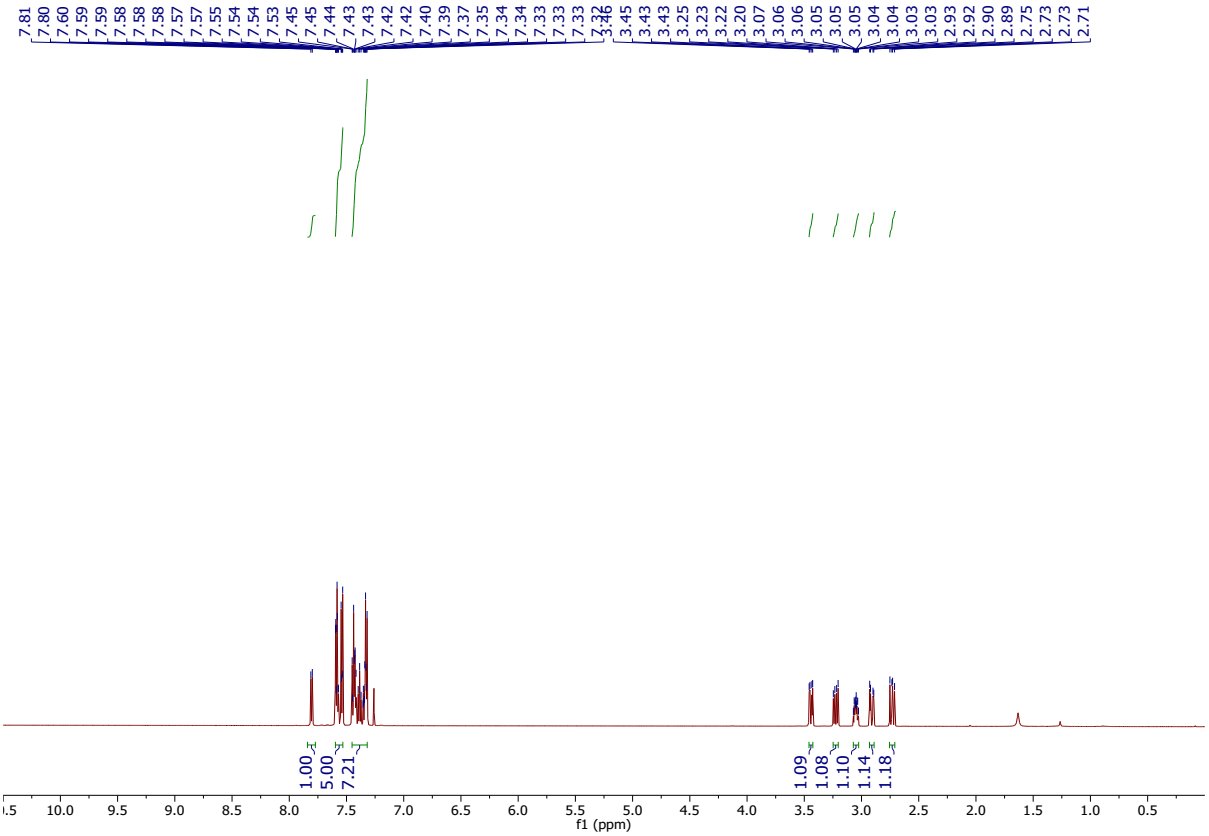
^{1}H NMR Spectrum of 3c (600 MHz, $CDCl_3$)



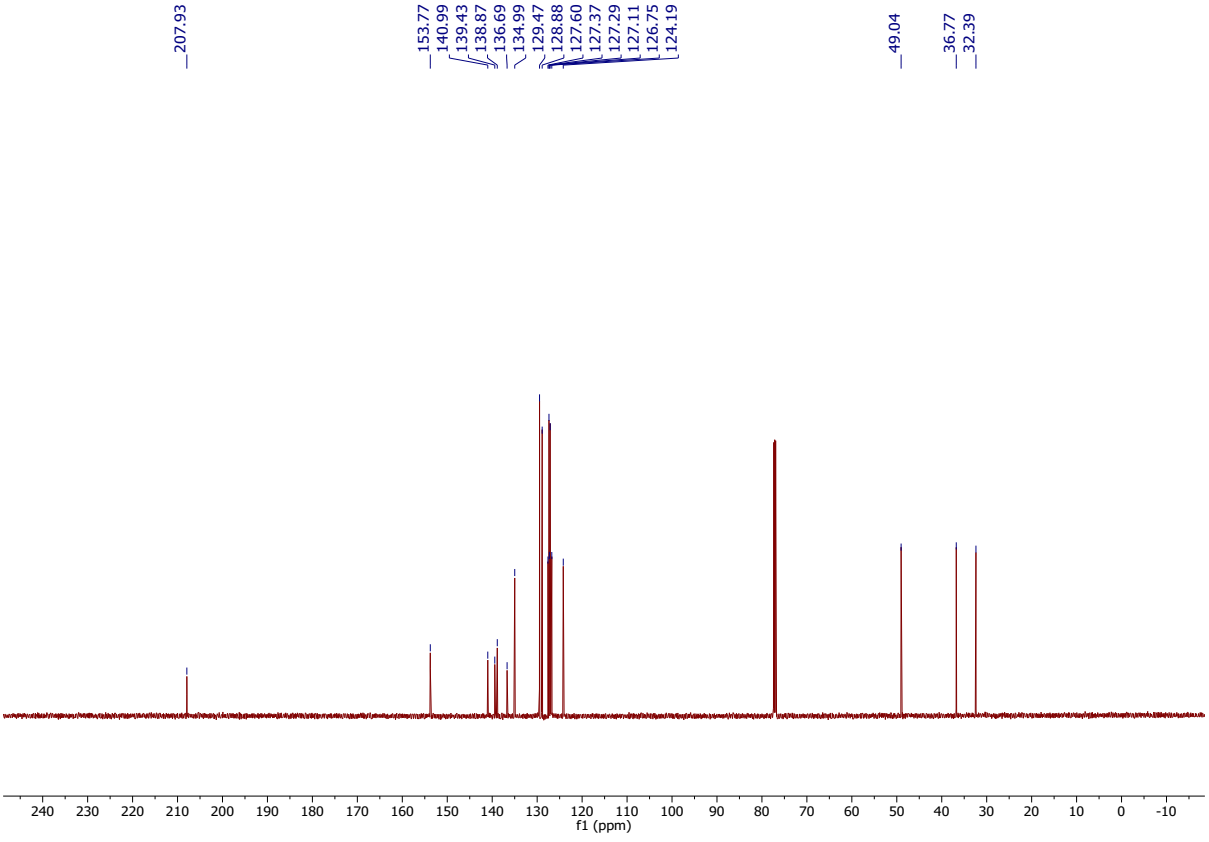
^{13}C NMR Spectrum of 3c (150 MHz, $CDCl_3$)



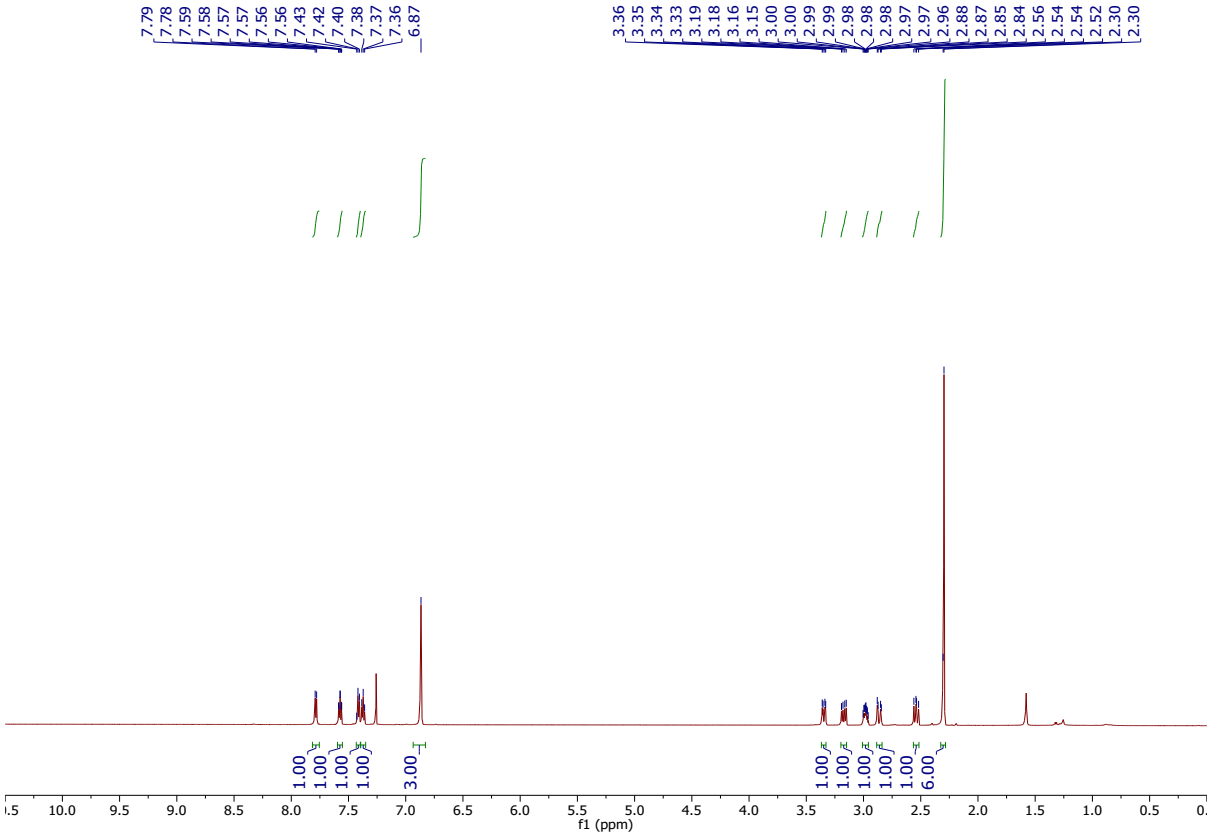
^{1}H NMR Spectrum of 3d (600 MHz, $CDCl_3$)



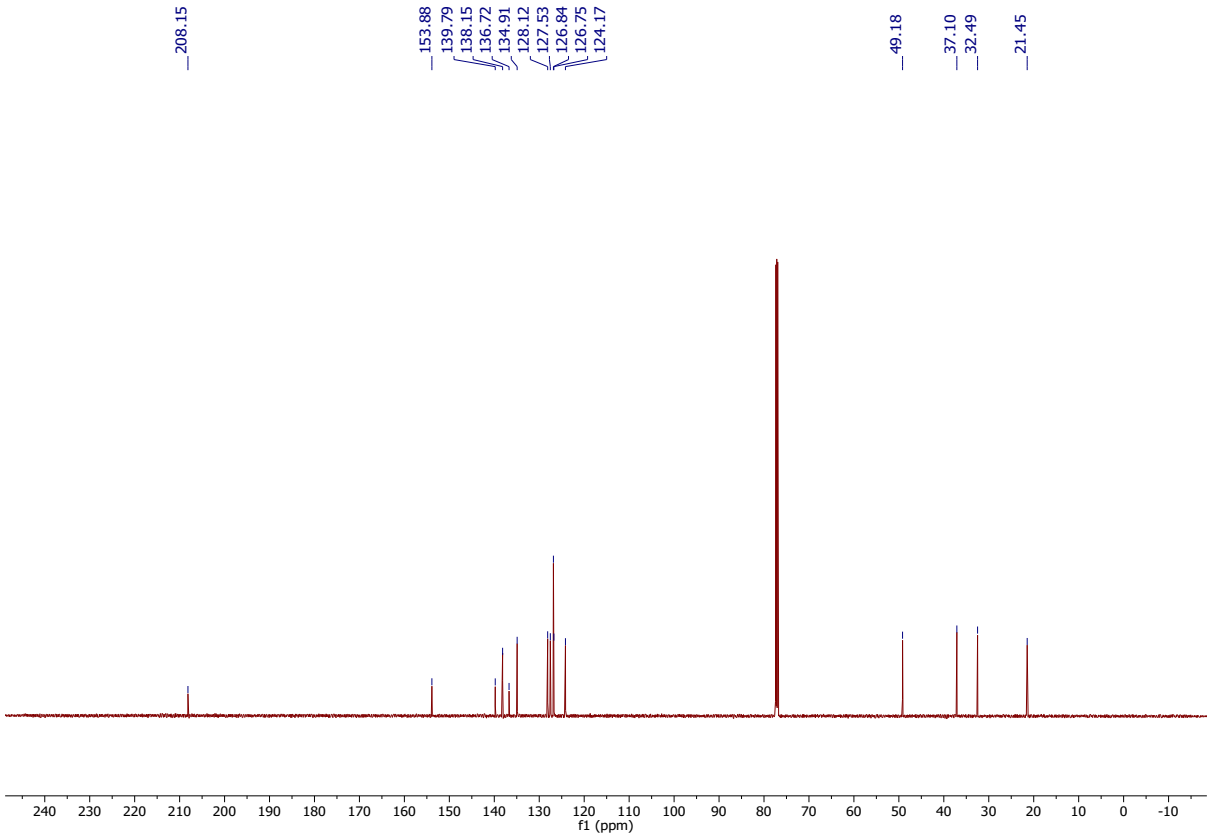
^{13}C NMR Spectrum of 3d (150 MHz, $CDCl_3$)



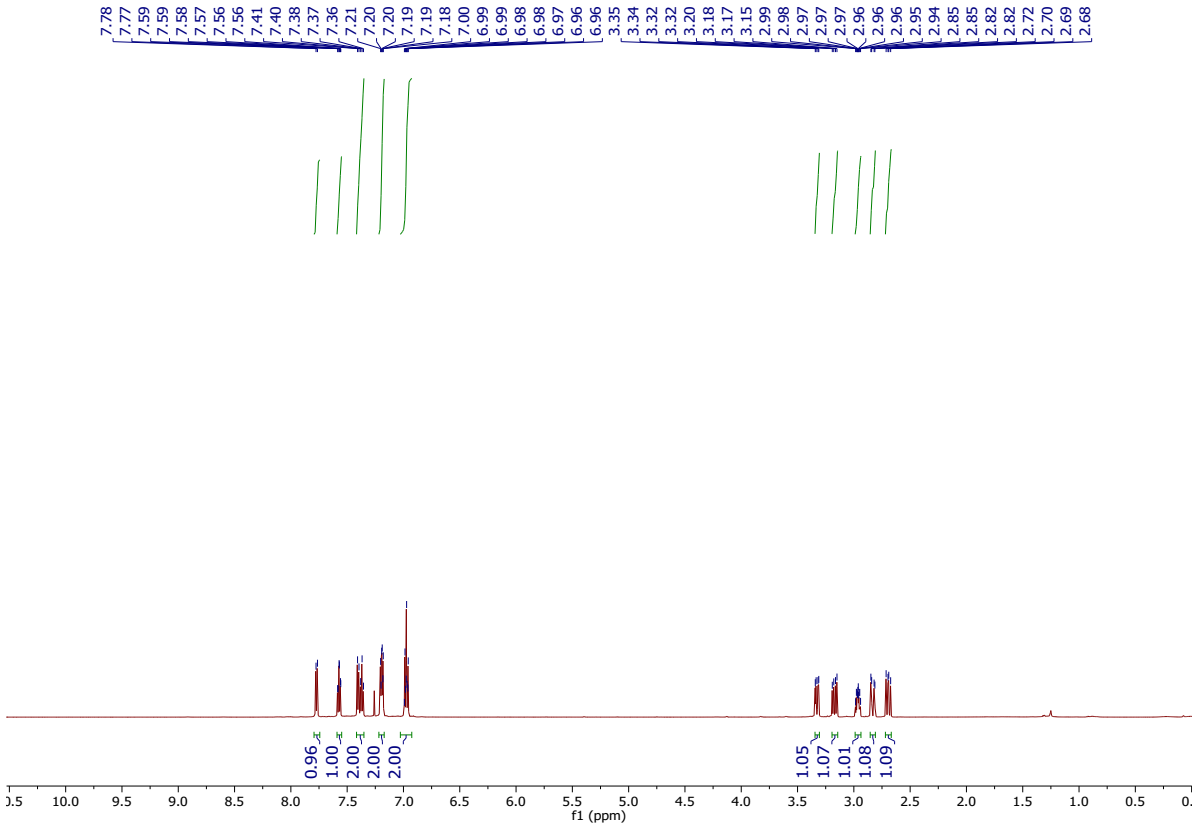
^{1}H NMR Spectrum of 3e (600 MHz, $CDCl_3$)



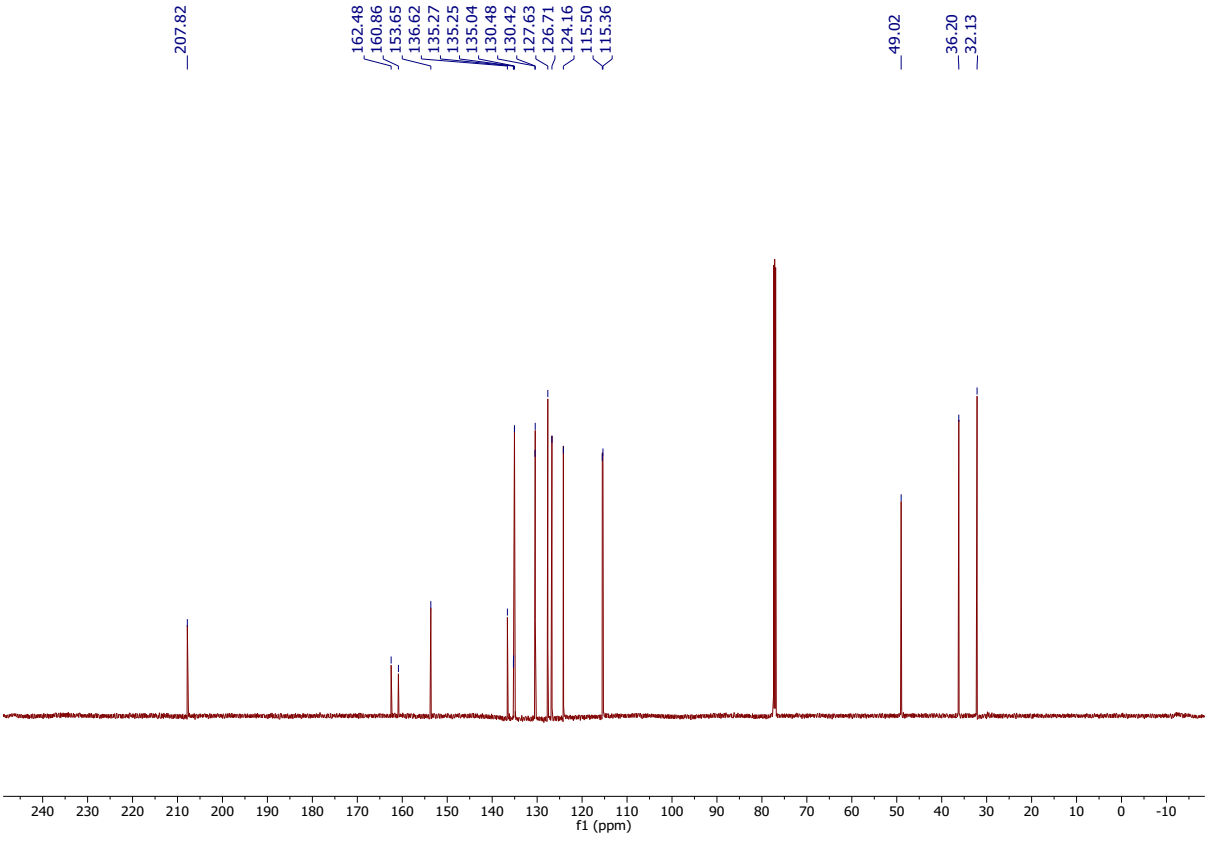
^{13}C NMR Spectrum of 3e (150 MHz, $CDCl_3$)



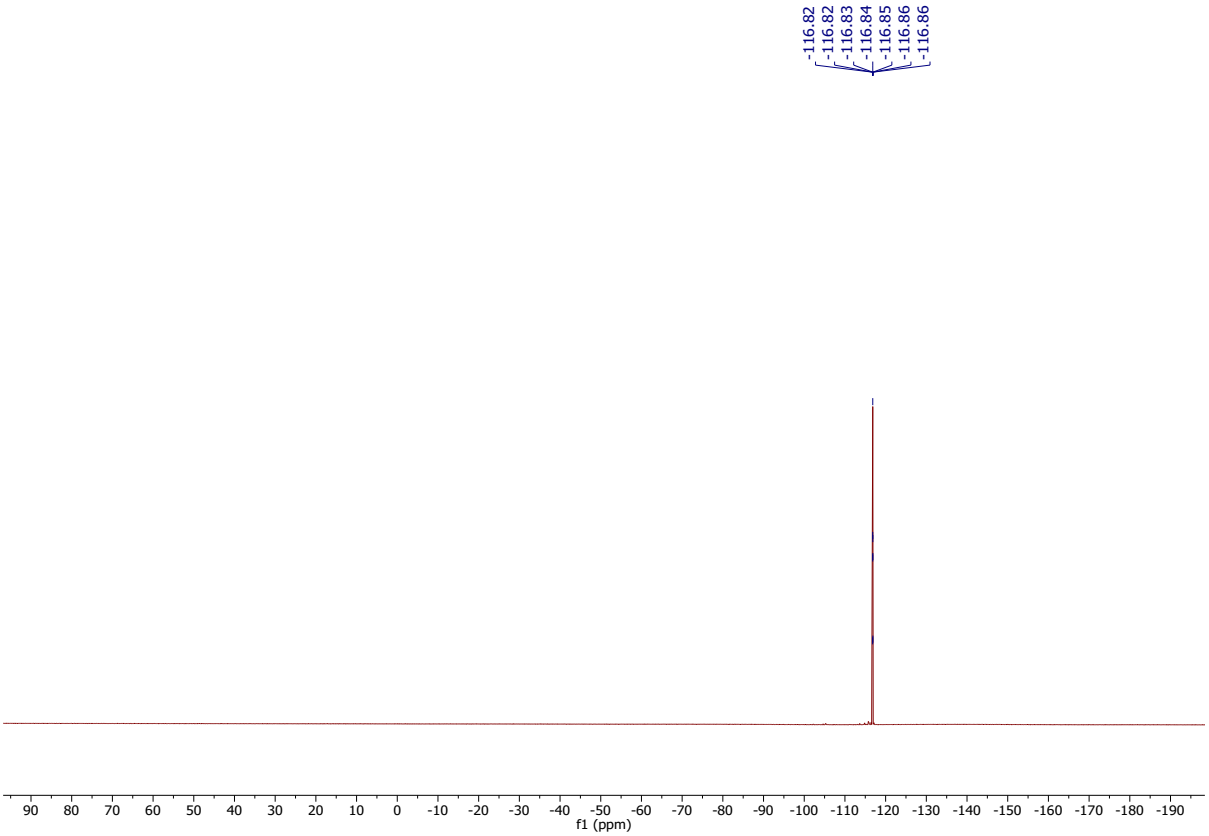
^{1}H NMR Spectrum of 3f (600 MHz, $CDCl_3$)



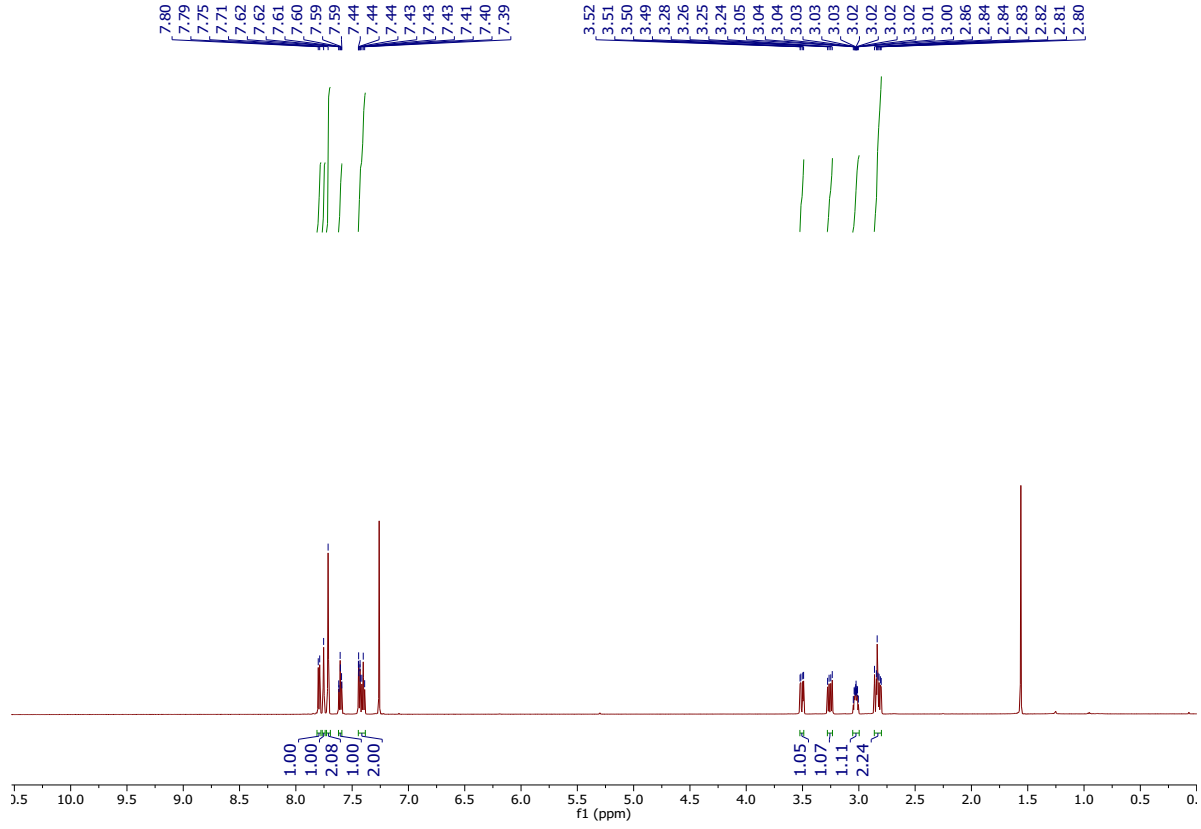
^{13}C NMR Spectrum of 3f (150 MHz, $CDCl_3$)



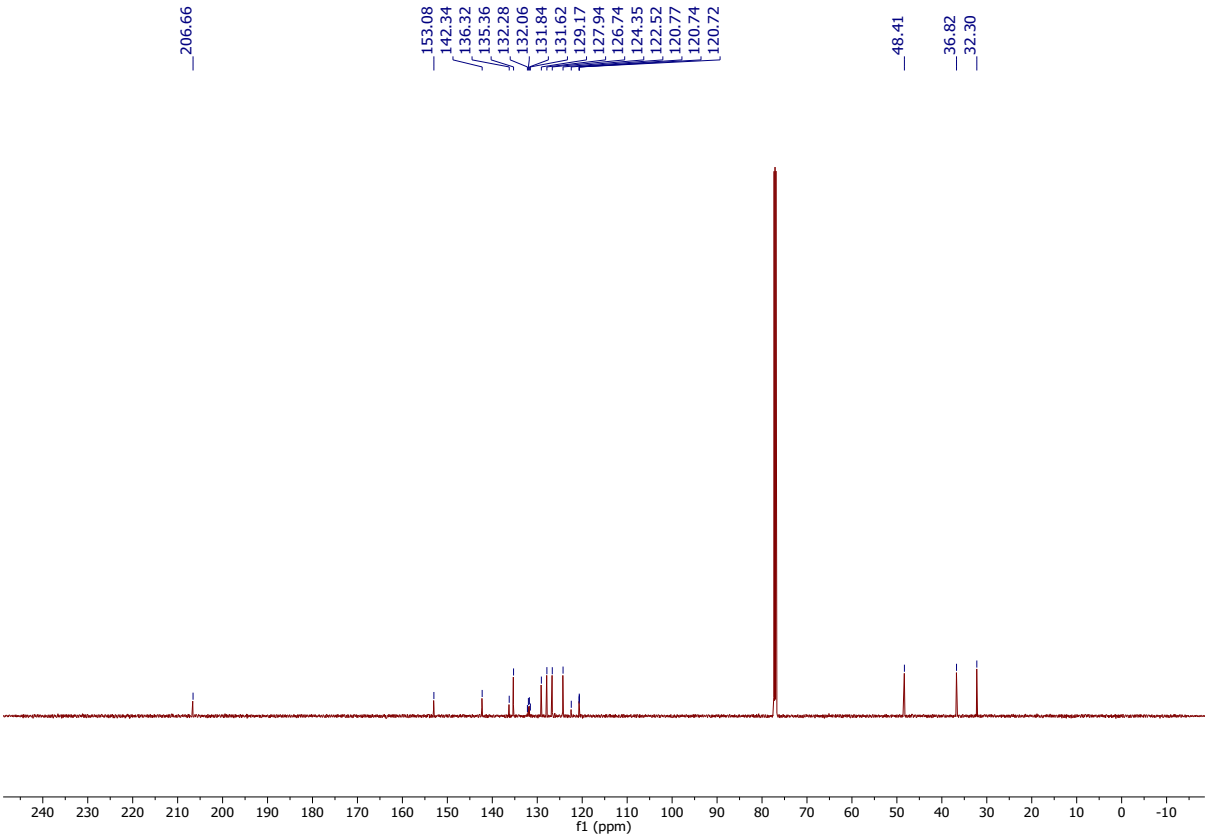
^{19}F NMR Spectrum of 3f (564 MHz, $CDCl_3$)



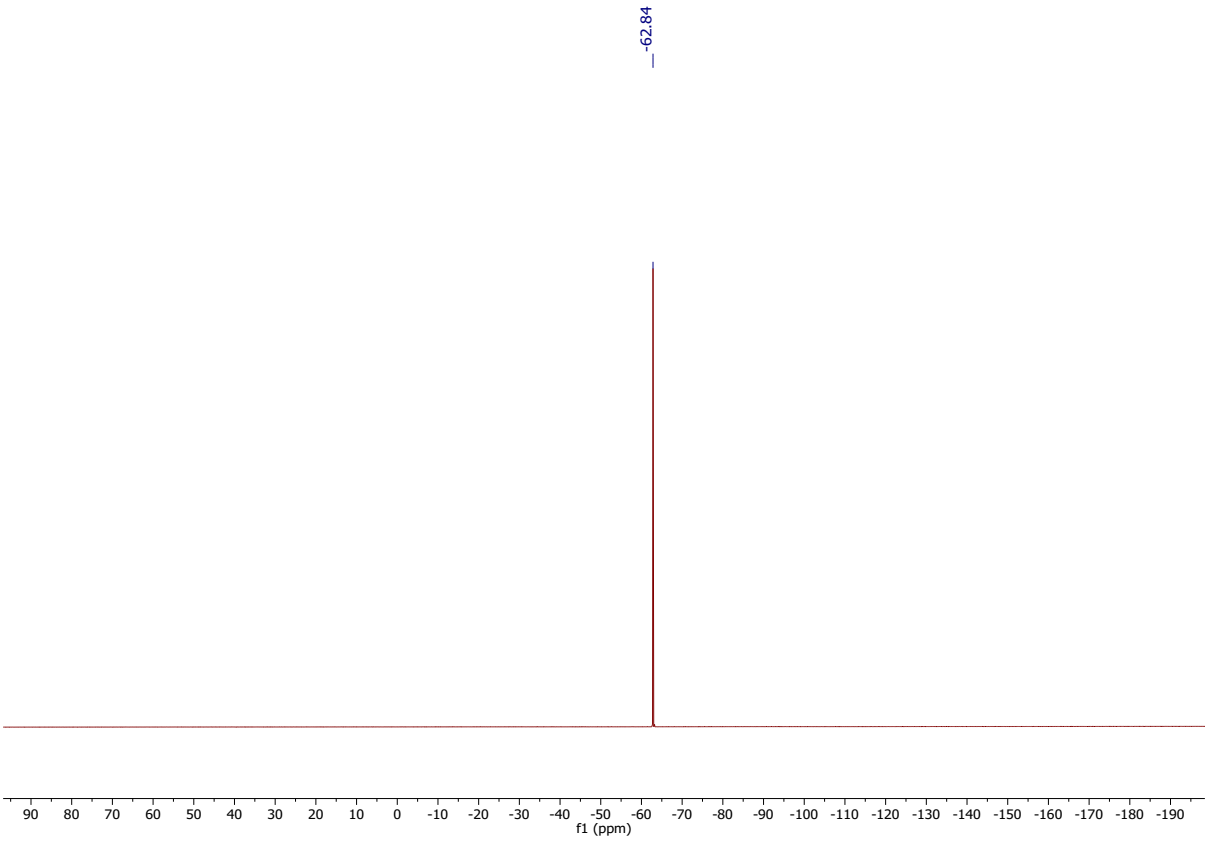
^{1}H NMR Spectrum of 3g (600 MHz, $CDCl_3$)



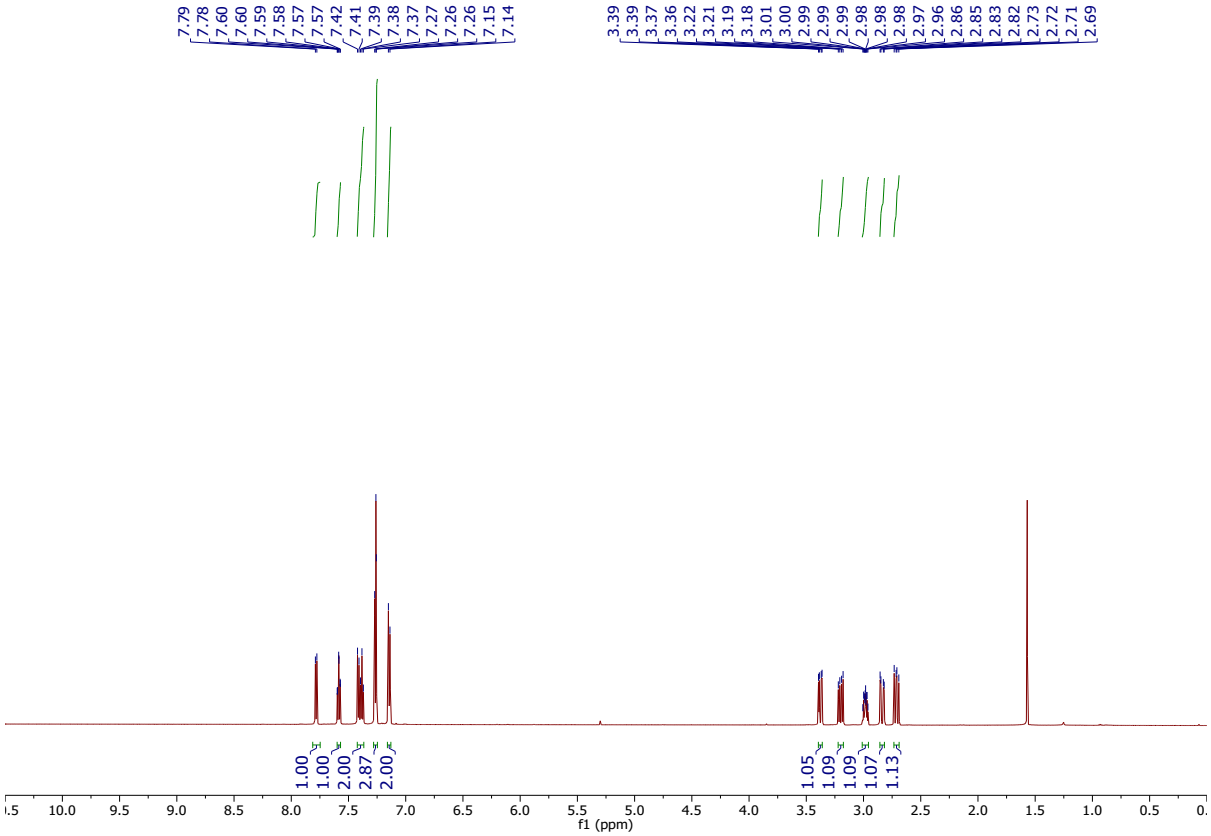
^{13}C NMR Spectrum of 3g (150 MHz, $CDCl_3$)



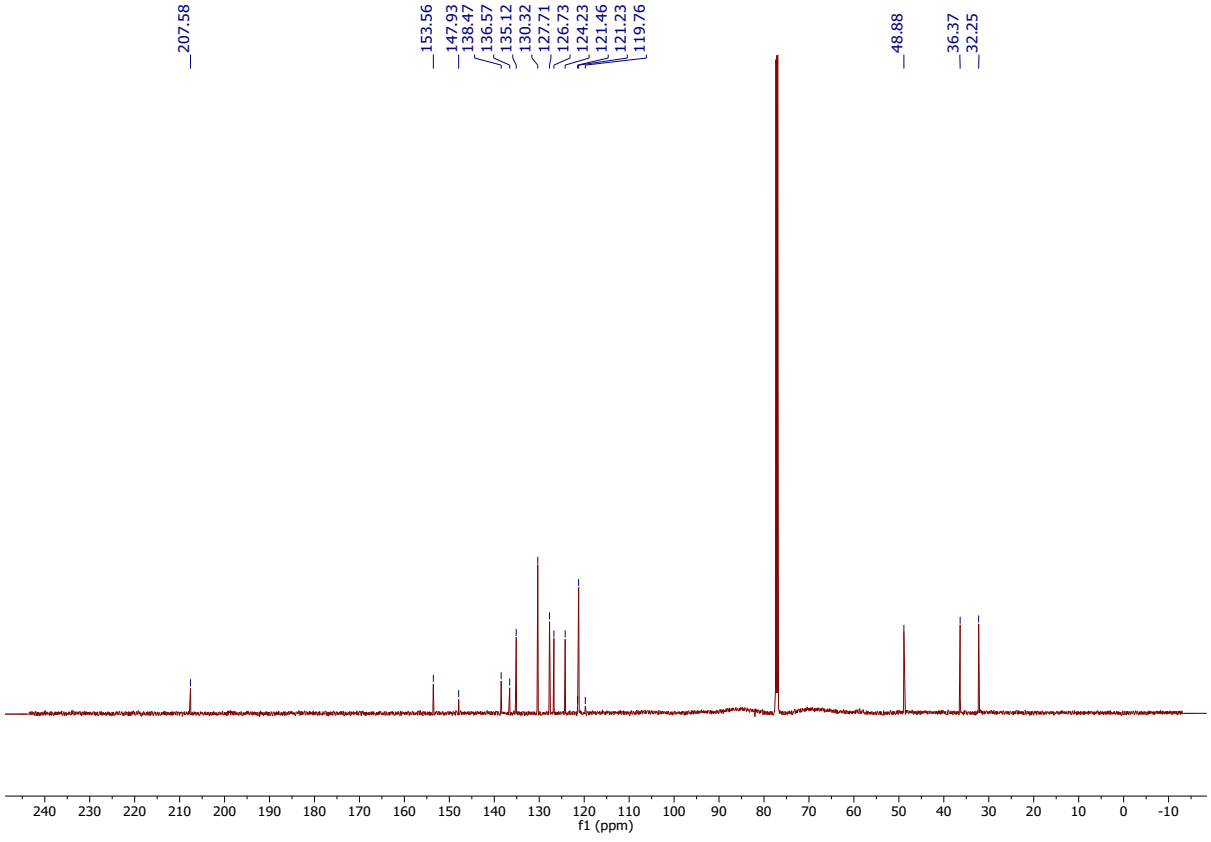
^{19}F NMR Spectrum of 3g (564 MHz, $CDCl_3$)



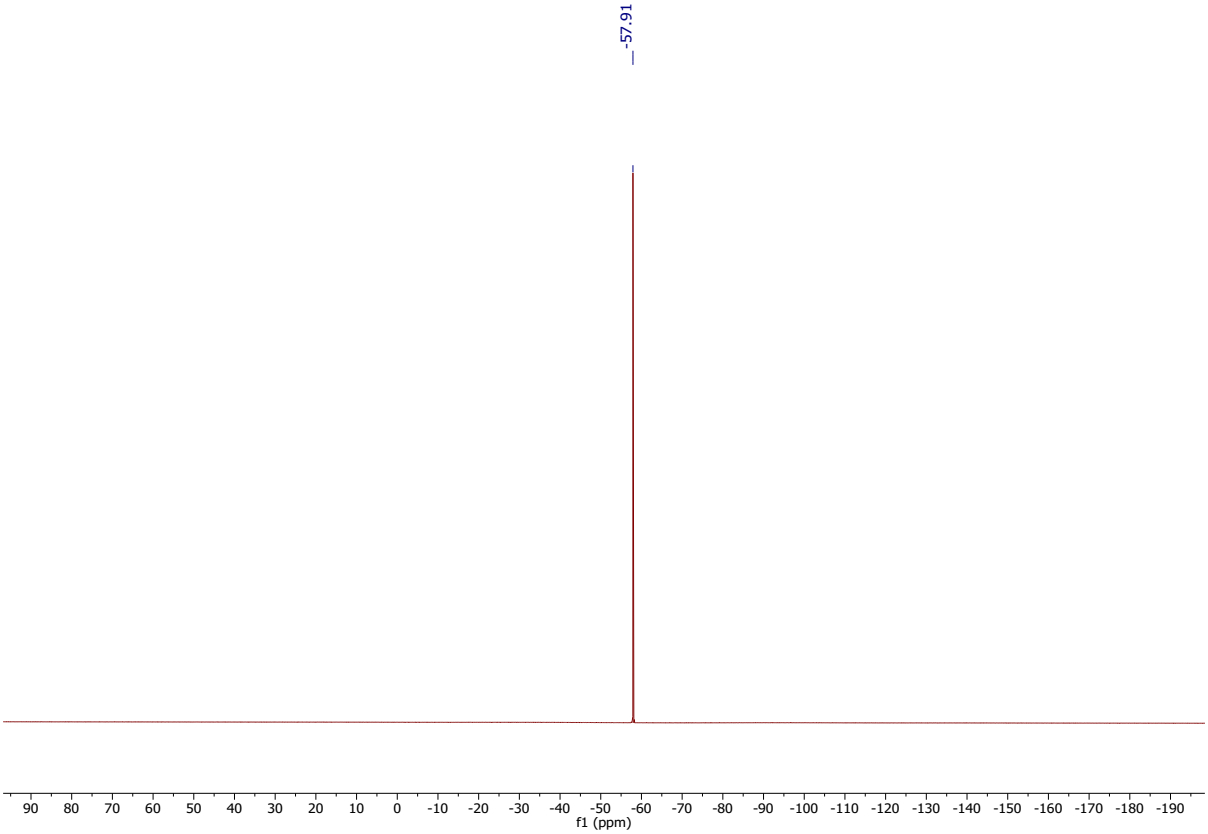
^{1}H NMR Spectrum of 3h (600 MHz, $CDCl_3$)



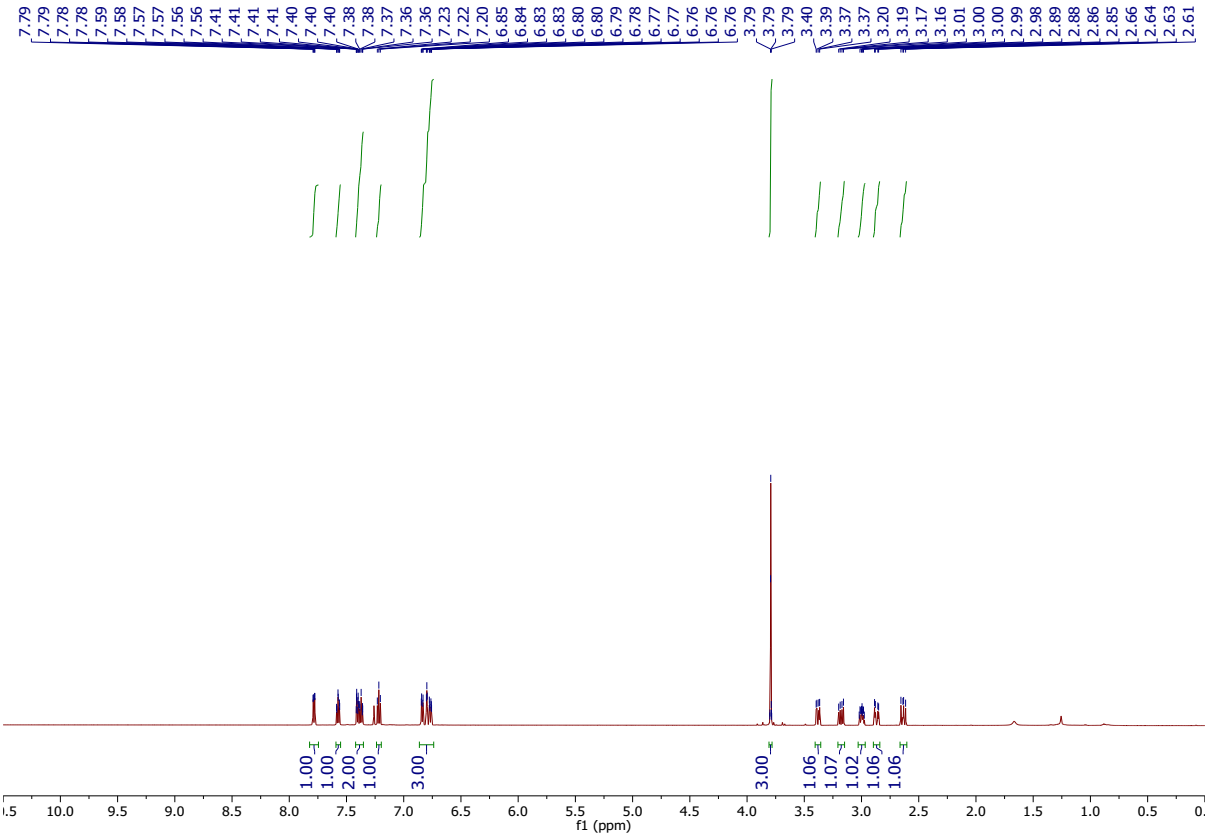
^{13}C NMR Spectrum of 3h (150 MHz, $CDCl_3$)



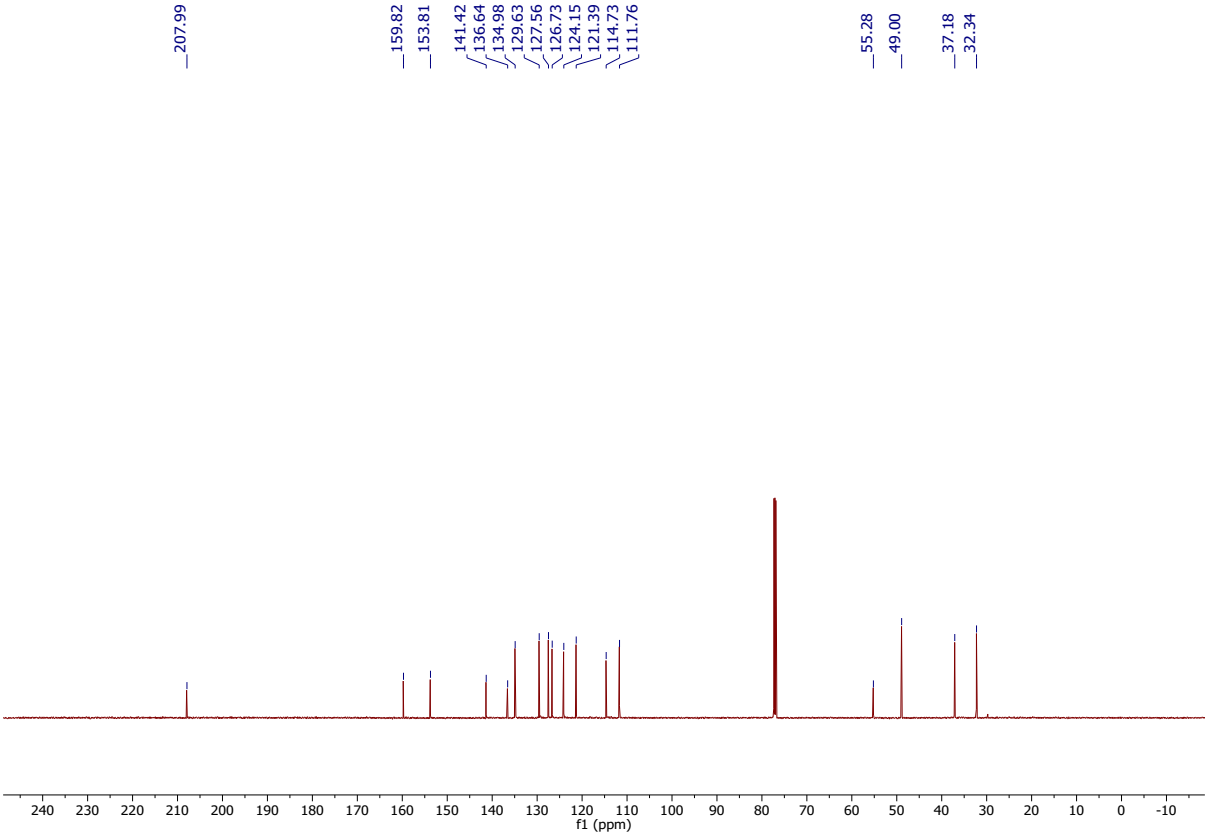
^{19}F NMR Spectrum of 3h (564 MHz, $CDCl_3$)



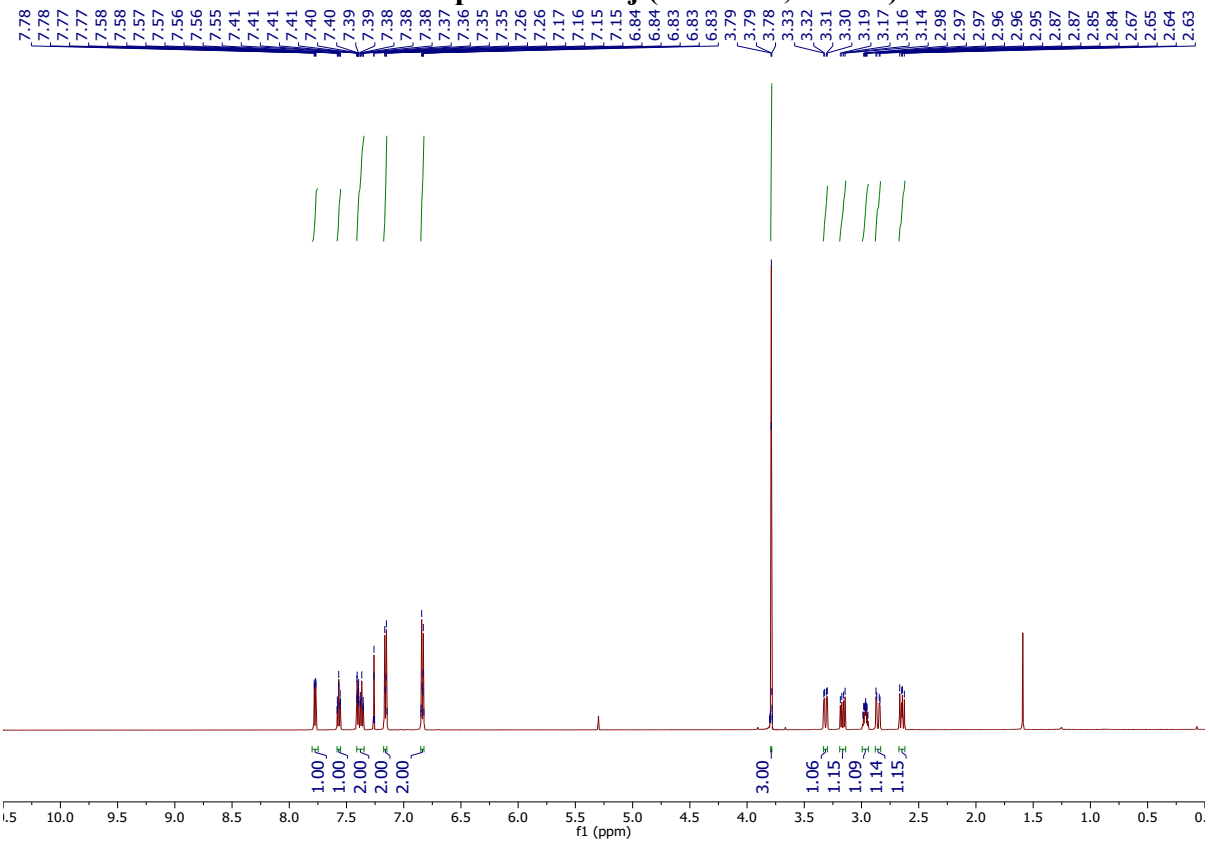
^{1}H NMR Spectrum of 3i (600 MHz, $CDCl_3$)



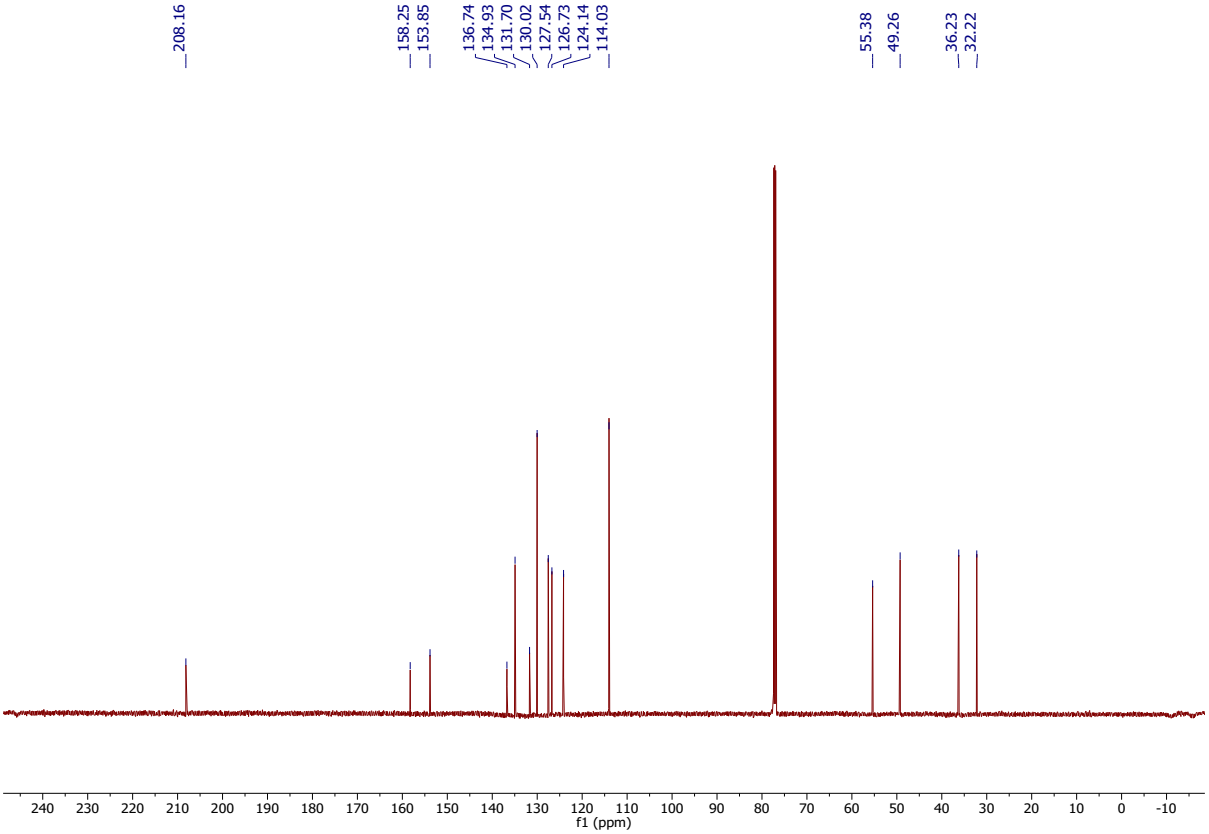
^{13}C NMR Spectrum of 3i (150 MHz, $CDCl_3$)



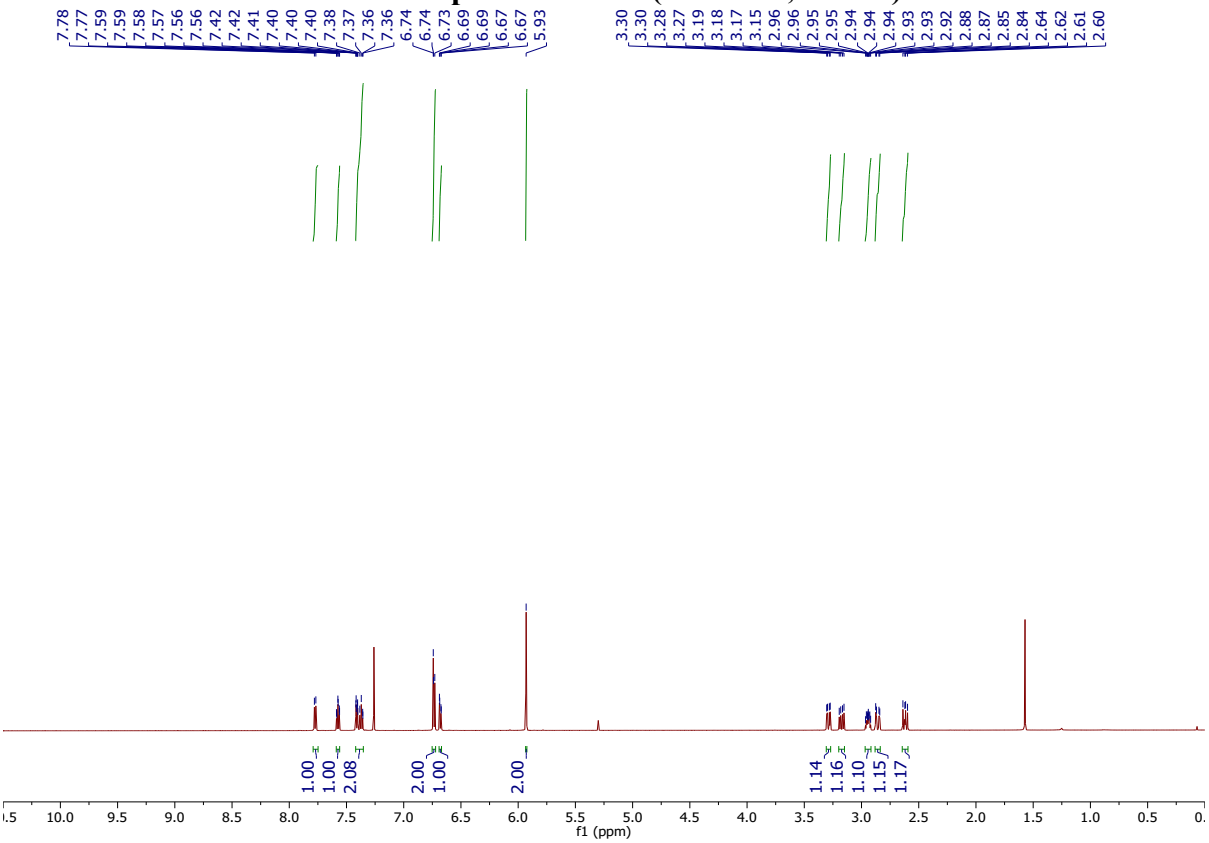
^{1}H NMR Spectrum of 3j (600 MHz, $CDCl_3$)



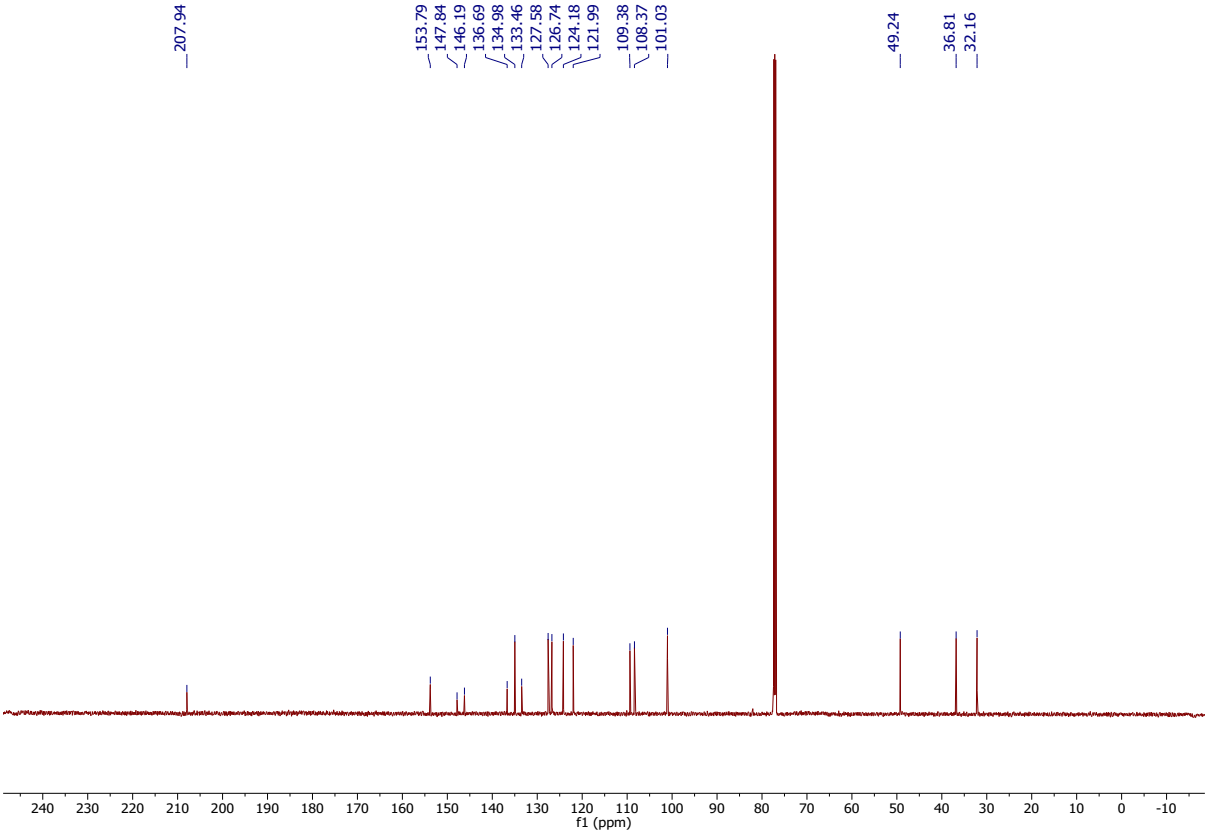
^{13}C NMR Spectrum of 3j (150 MHz, $CDCl_3$)



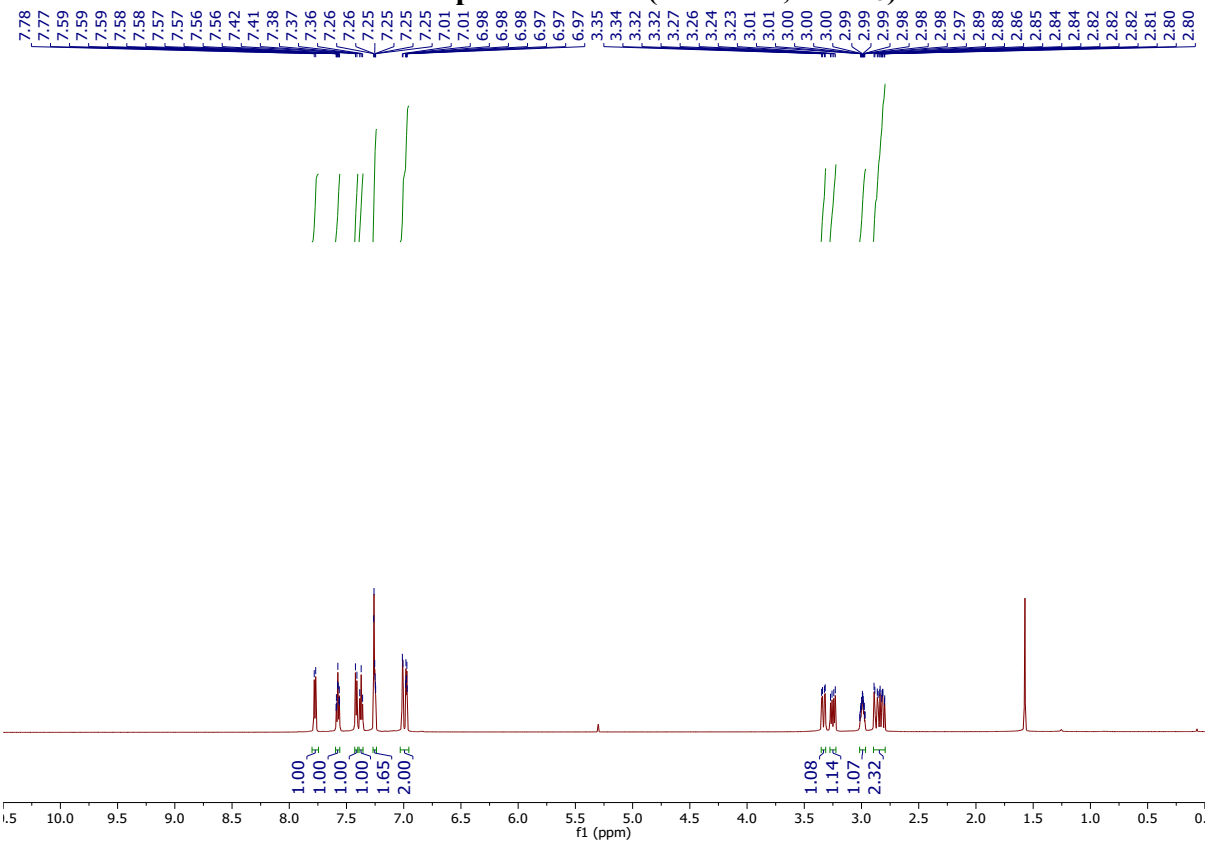
^{1}H NMR Spectrum of 3k (600 MHz, $CDCl_3$)



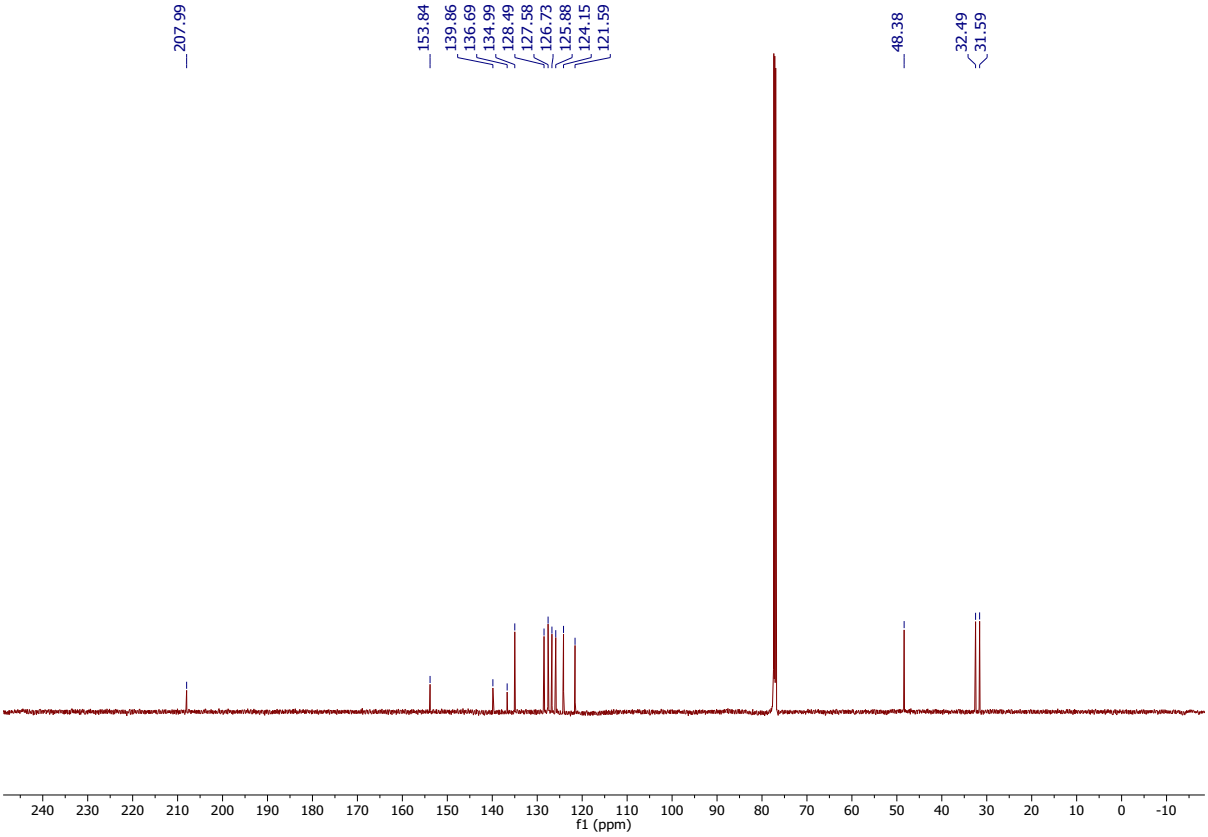
^{13}C NMR Spectrum of 3k (150 MHz, $CDCl_3$)



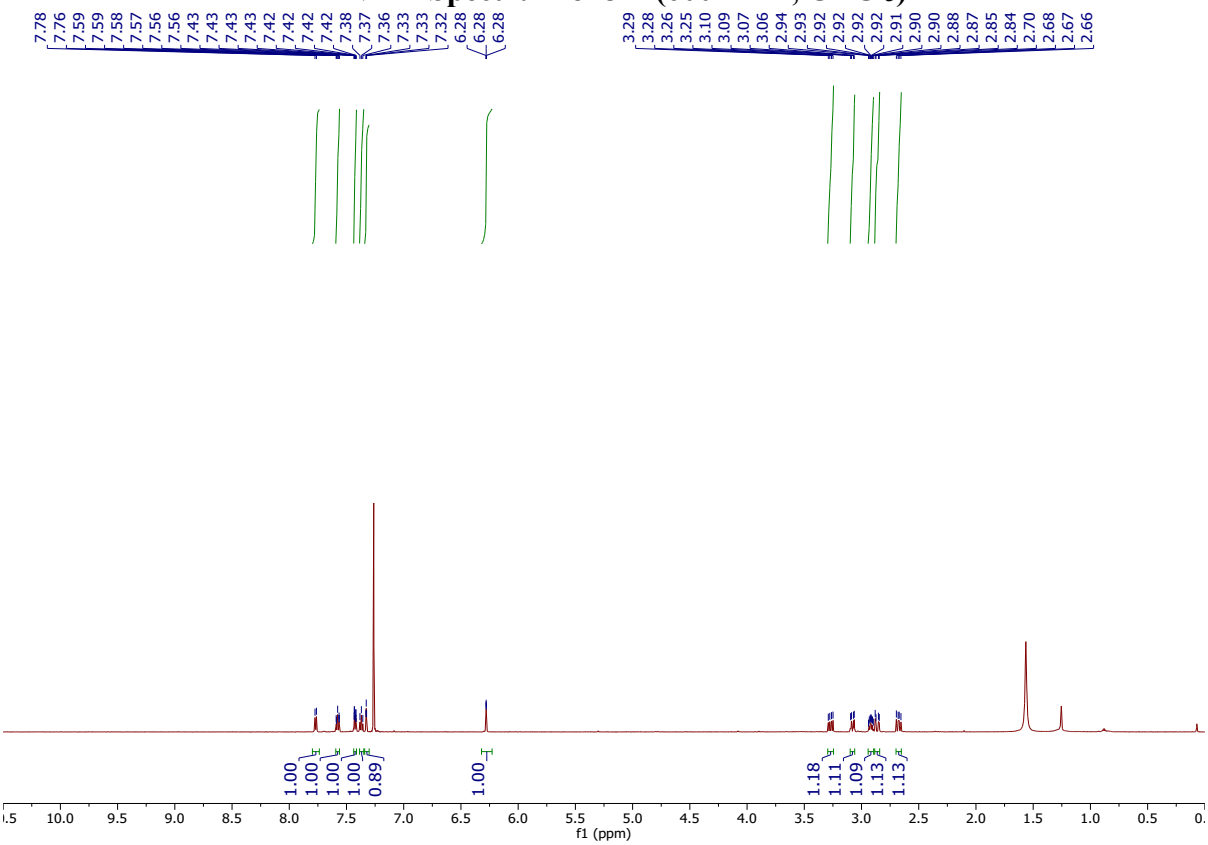
^{1}H NMR Spectrum of 3l (600 MHz, $CDCl_3$)



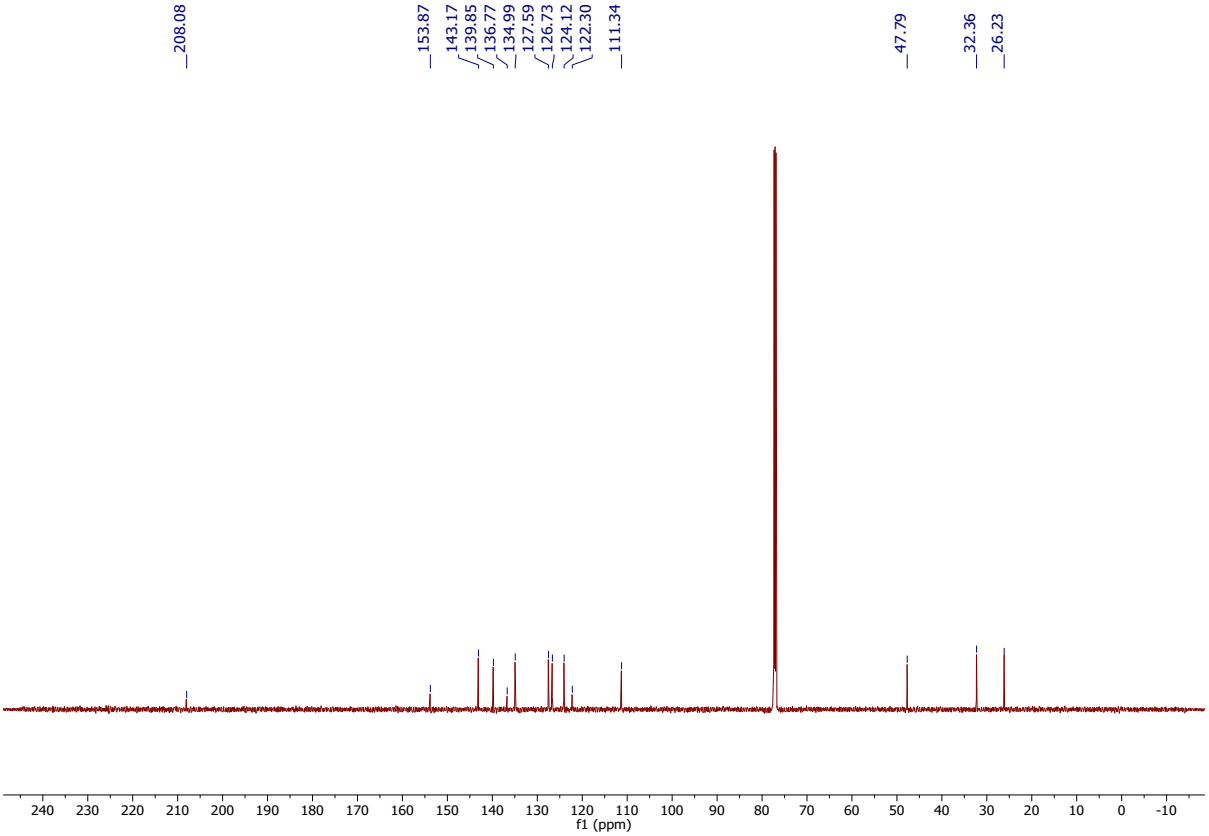
^{13}C NMR Spectrum of 3l (150 MHz, $CDCl_3$)



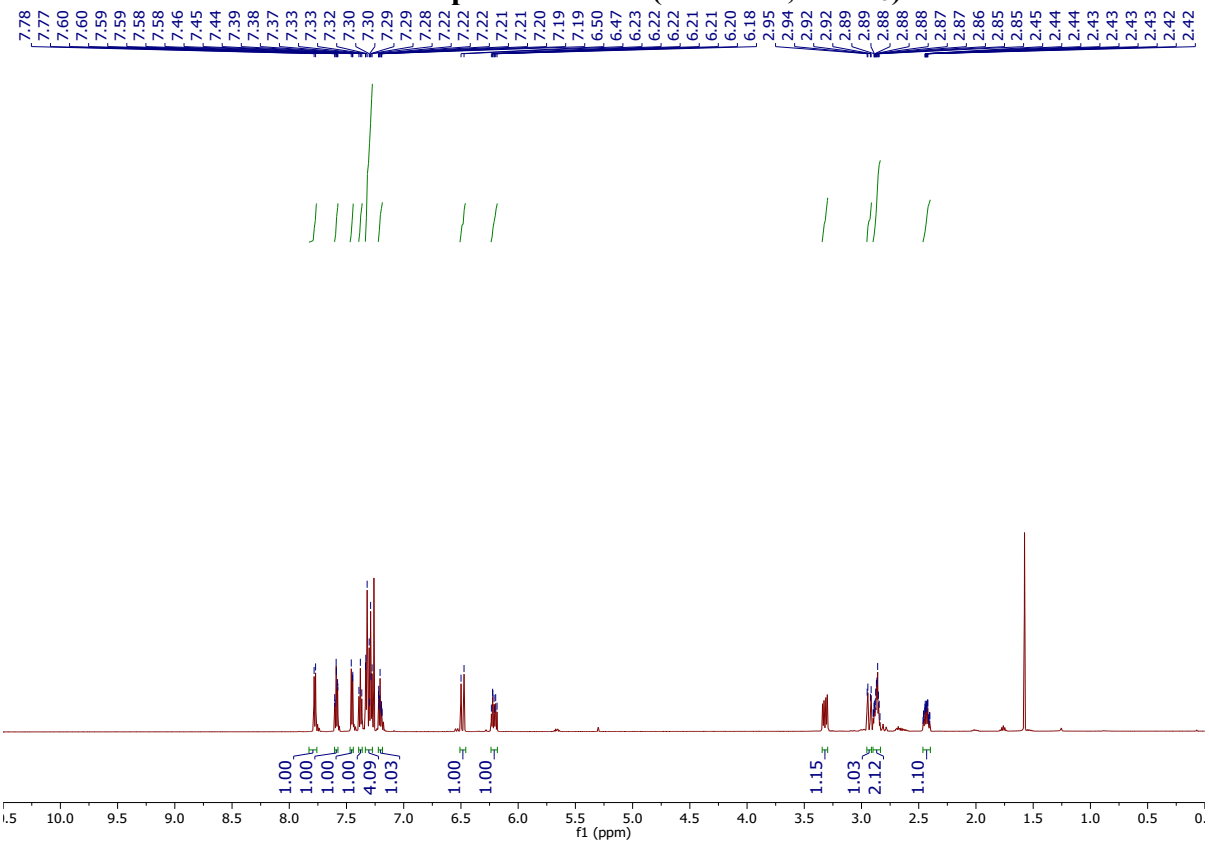
^{1}H NMR Spectrum of 3m (600 MHz, $CDCl_3$)



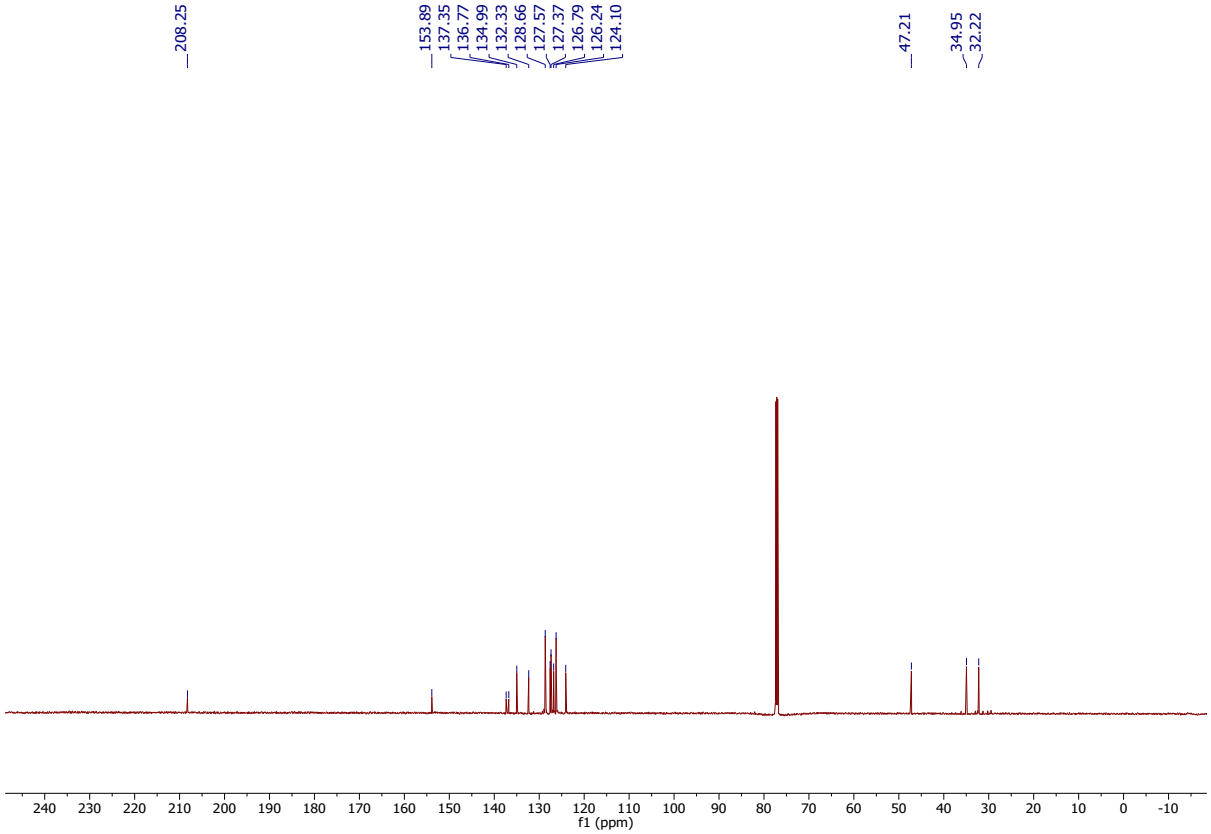
^{13}C NMR Spectrum of 3m (150 MHz, $CDCl_3$)



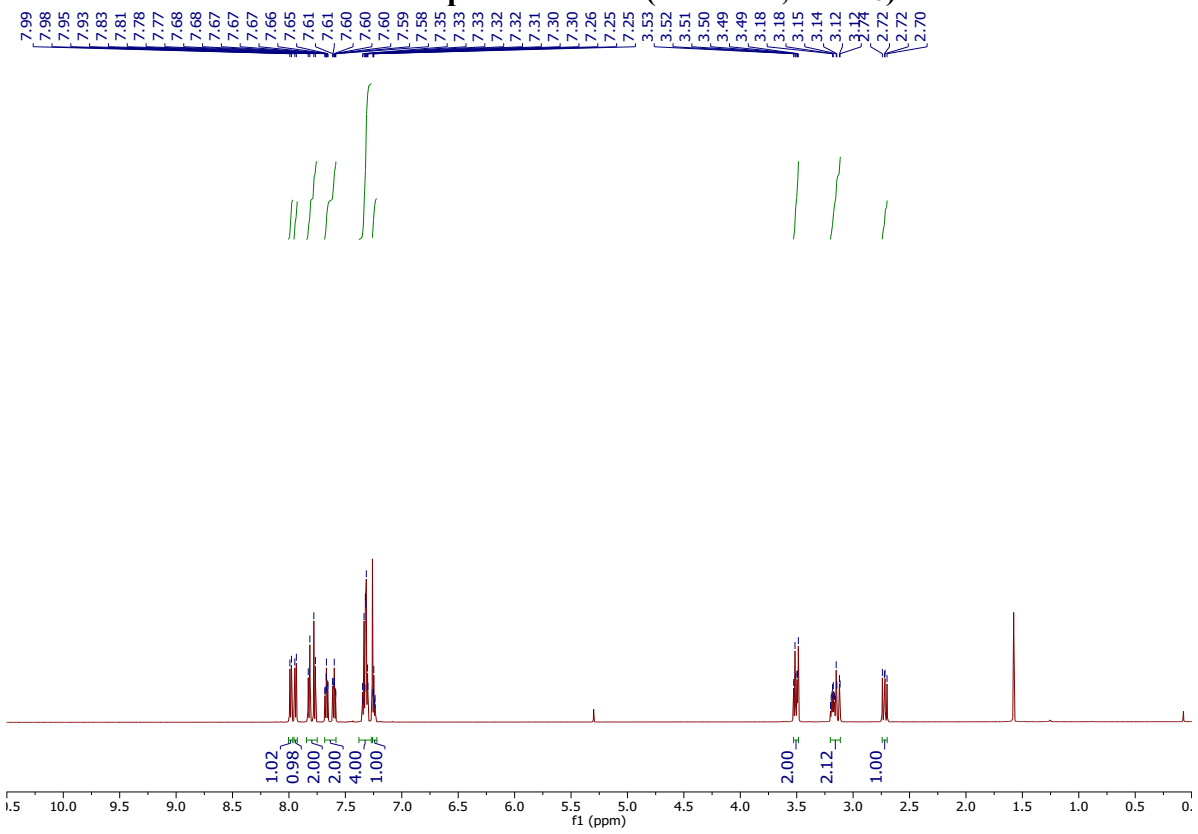
^{1}H NMR Spectrum of 3n (600 MHz, $CDCl_3$)



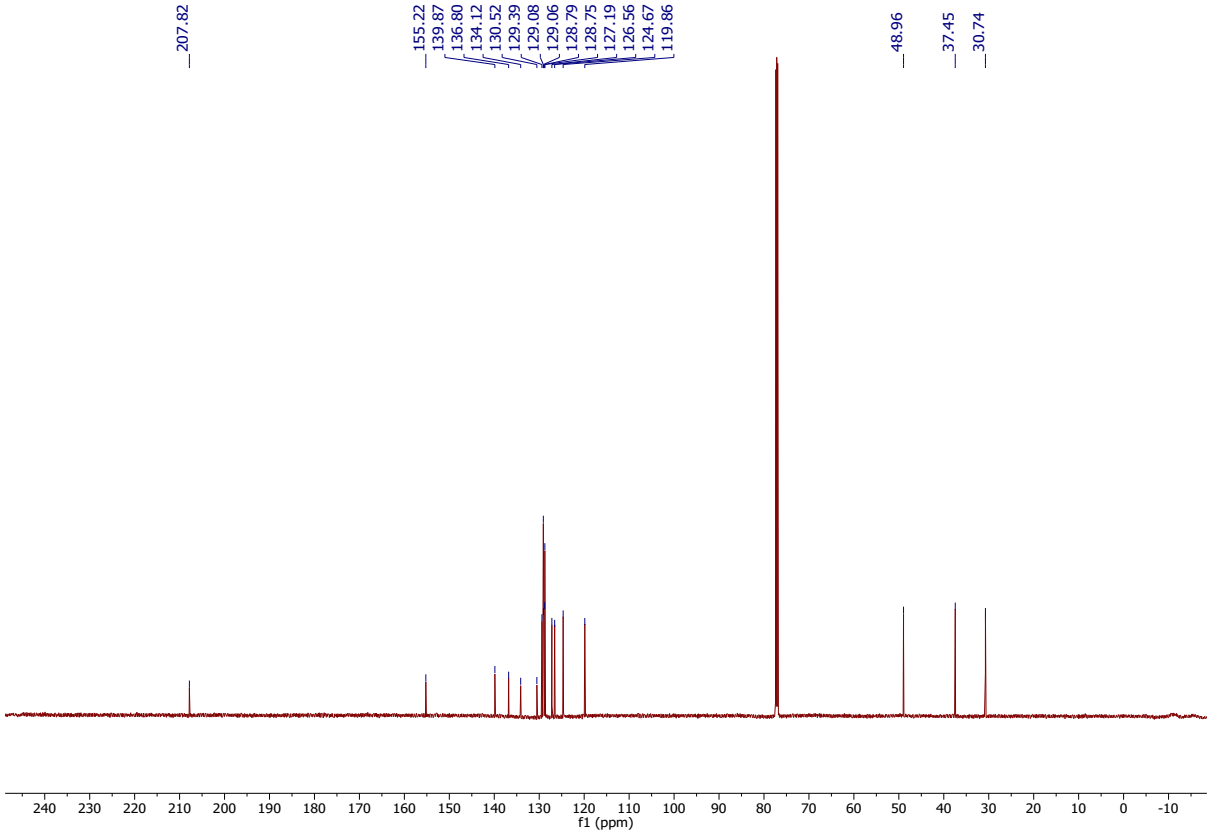
^{13}C NMR Spectrum of 3n (150 MHz, $CDCl_3$)



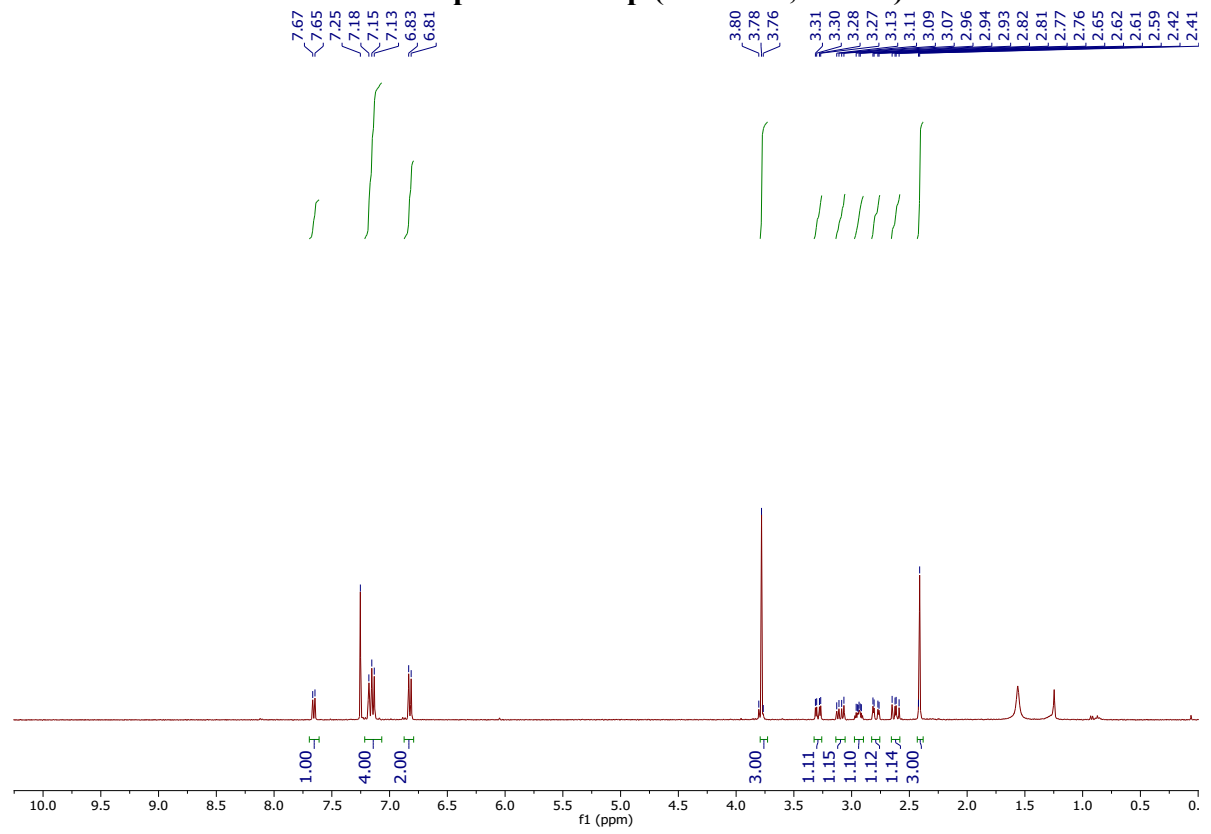
^{1}H NMR Spectrum of 3o (600 MHz, $CDCl_3$)



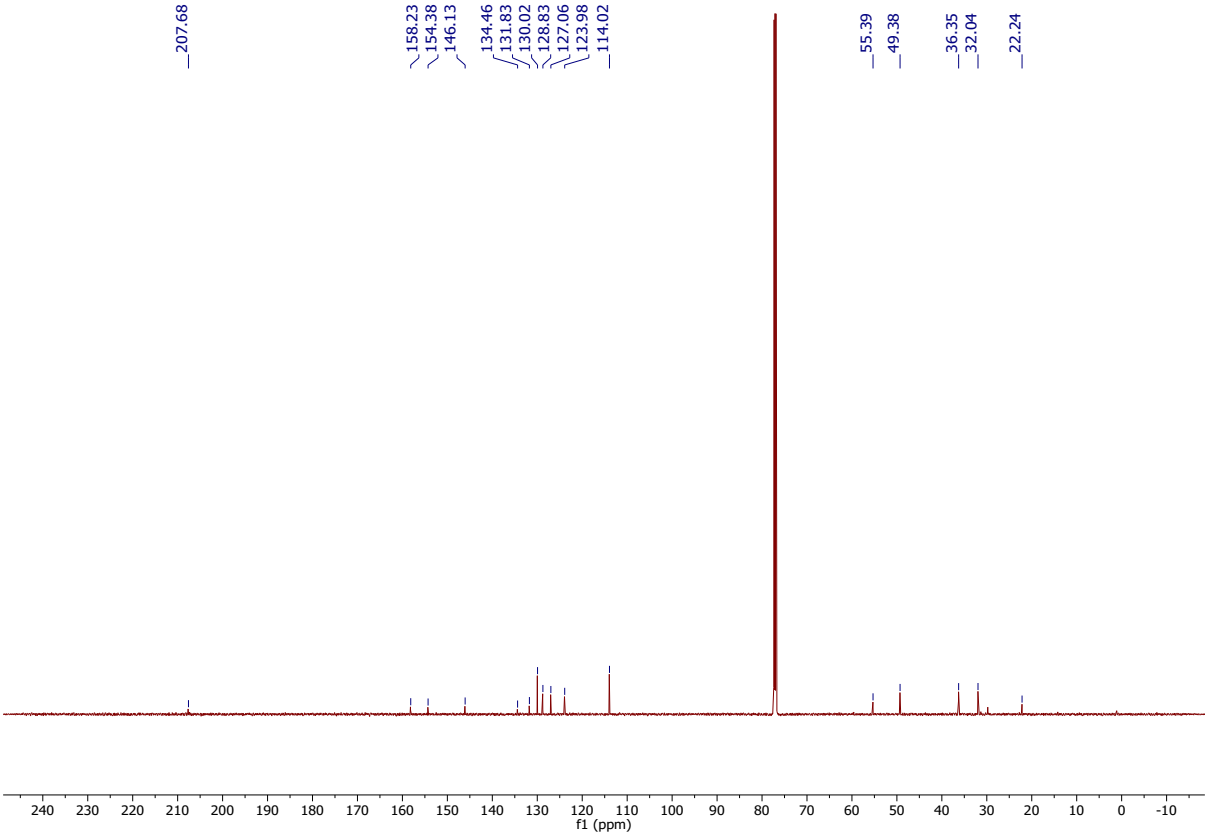
^{13}C NMR Spectrum of 3o (150 MHz, $CDCl_3$)



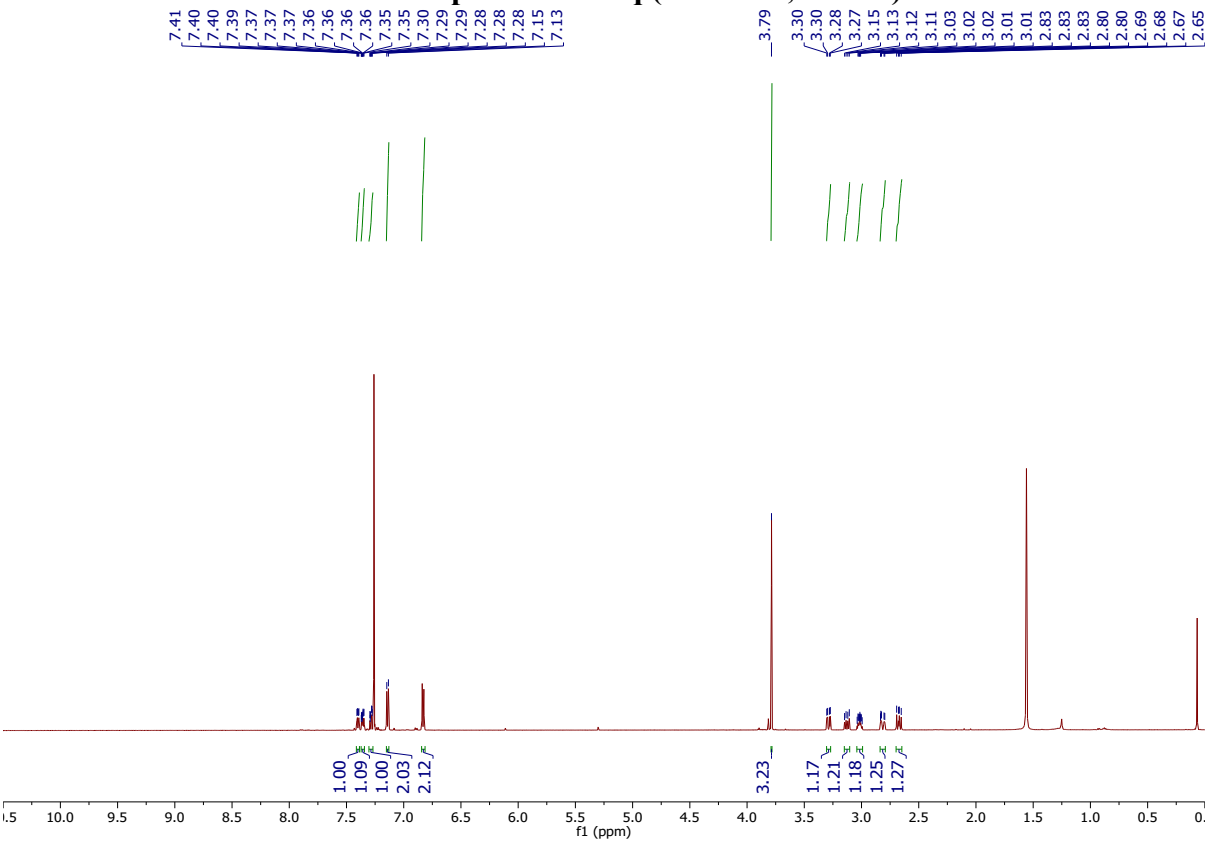
^{1}H NMR Spectrum of 3p (400 MHz, $CDCl_3$)



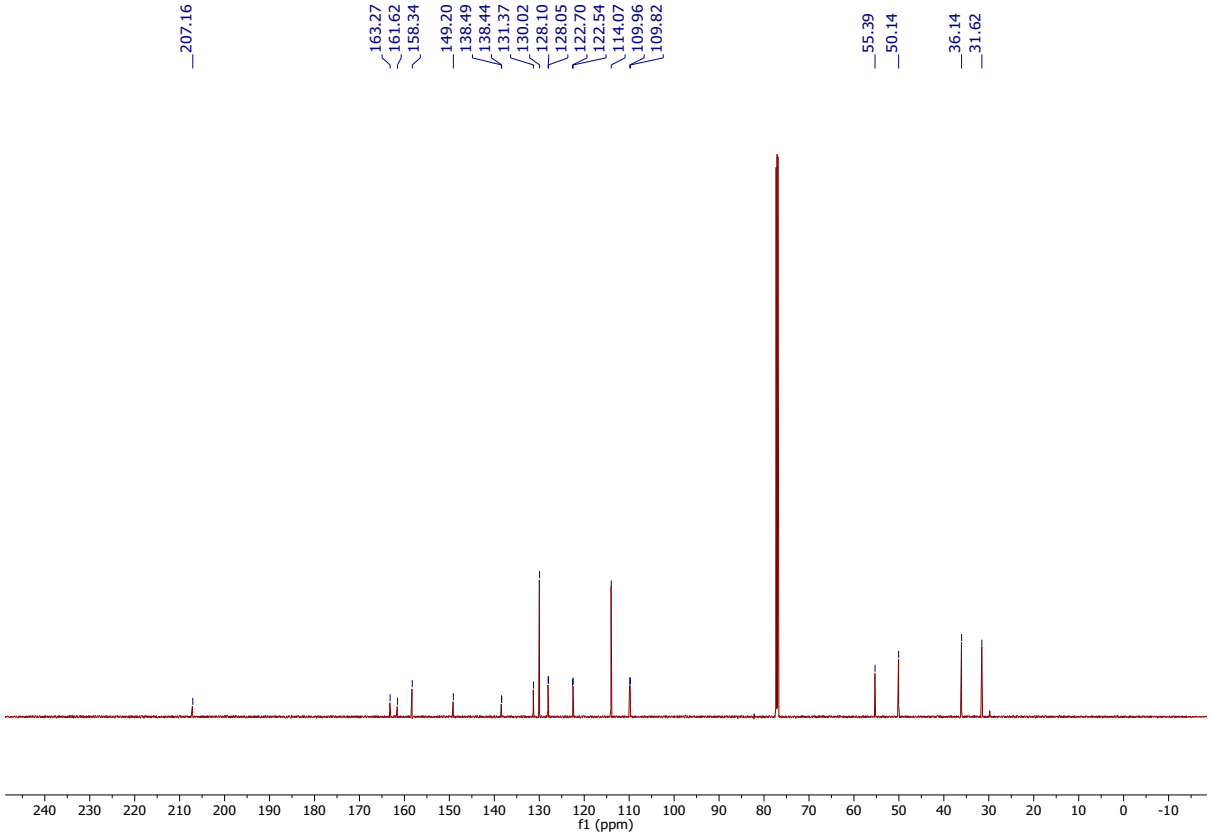
^{13}C NMR Spectrum of 3p (150 MHz, $CDCl_3$)



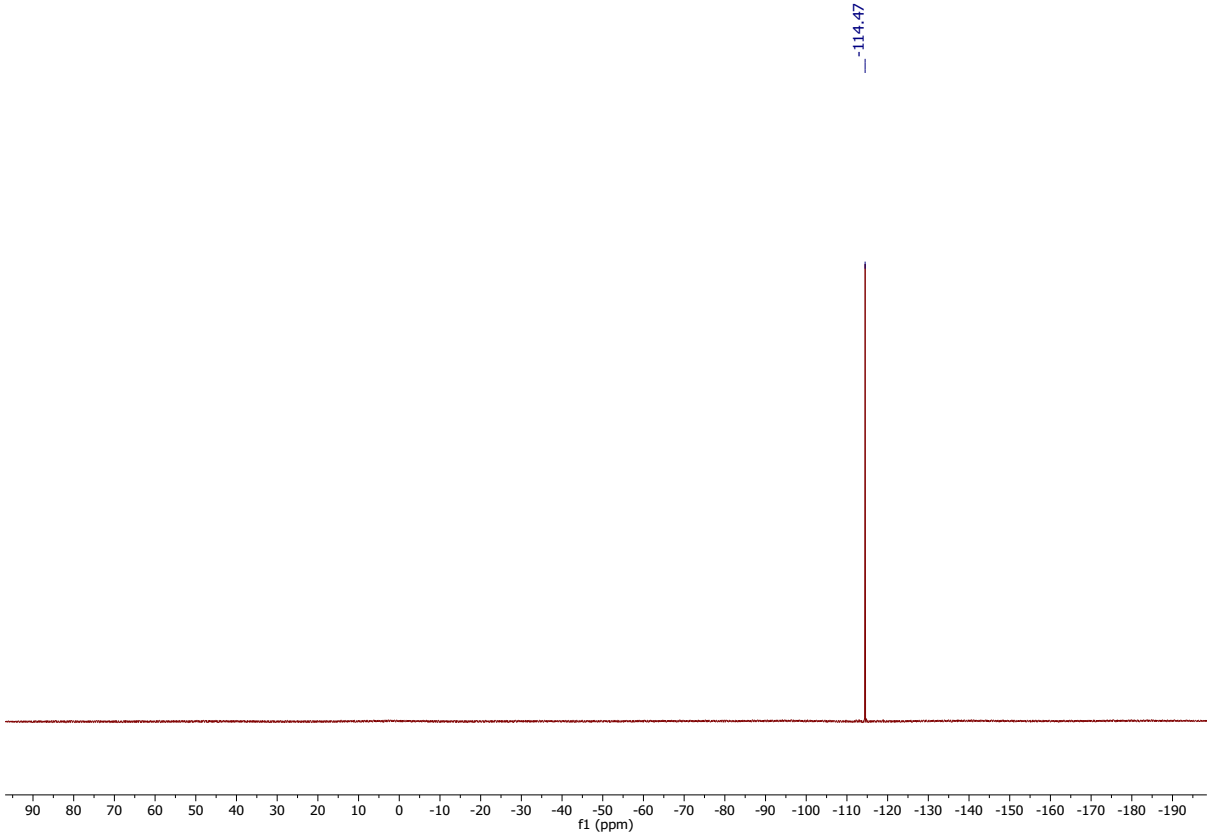
^{1}H NMR Spectrum of 3q (600 MHz, $CDCl_3$)



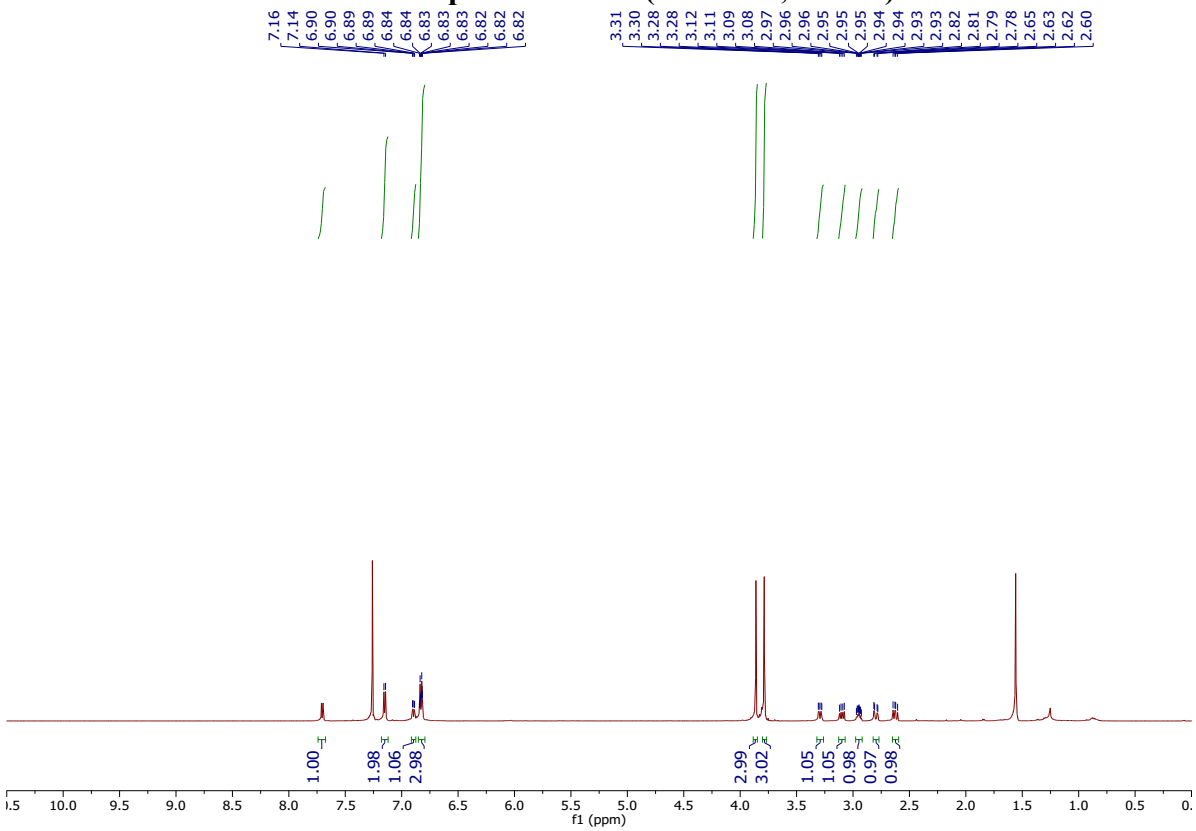
^{13}C NMR Spectrum of 3q (150 MHz, $CDCl_3$)



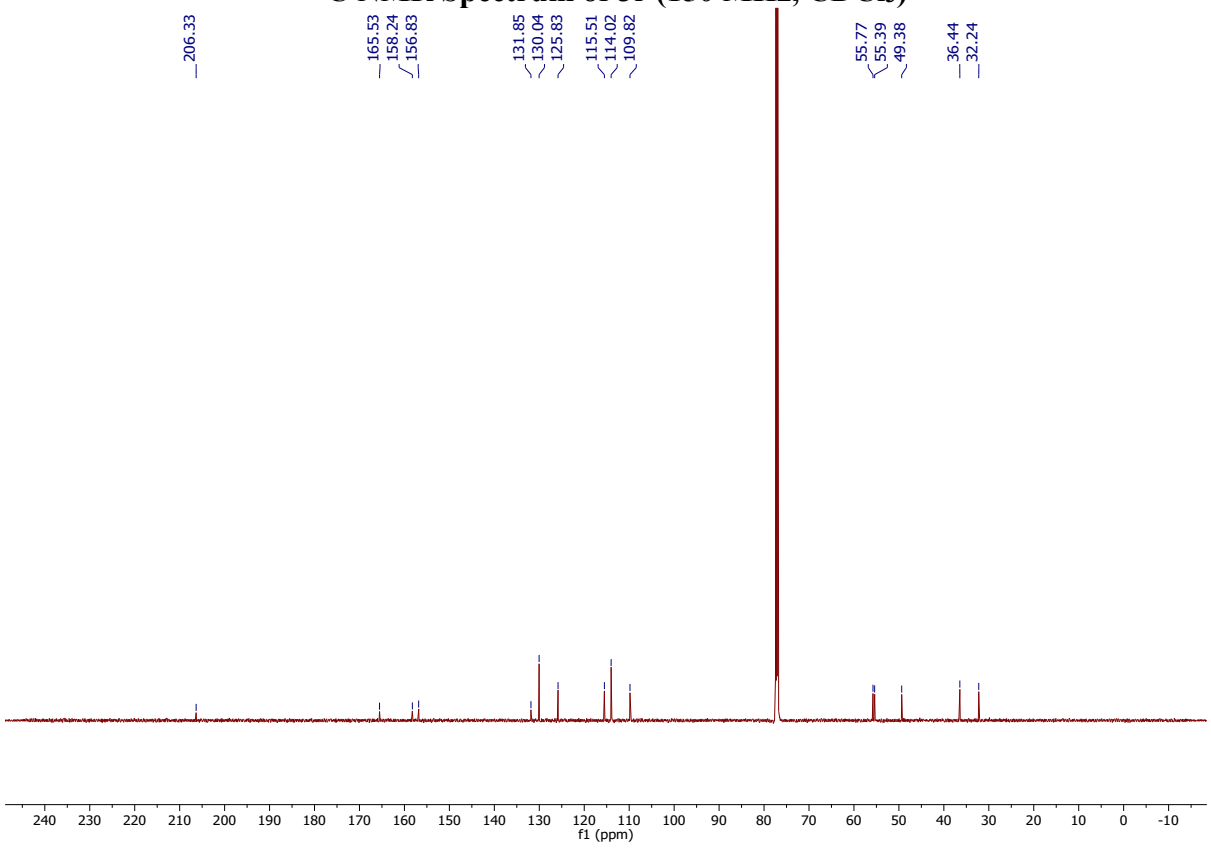
^{19}F NMR Spectrum of 3q (564 MHz, $CDCl_3$)



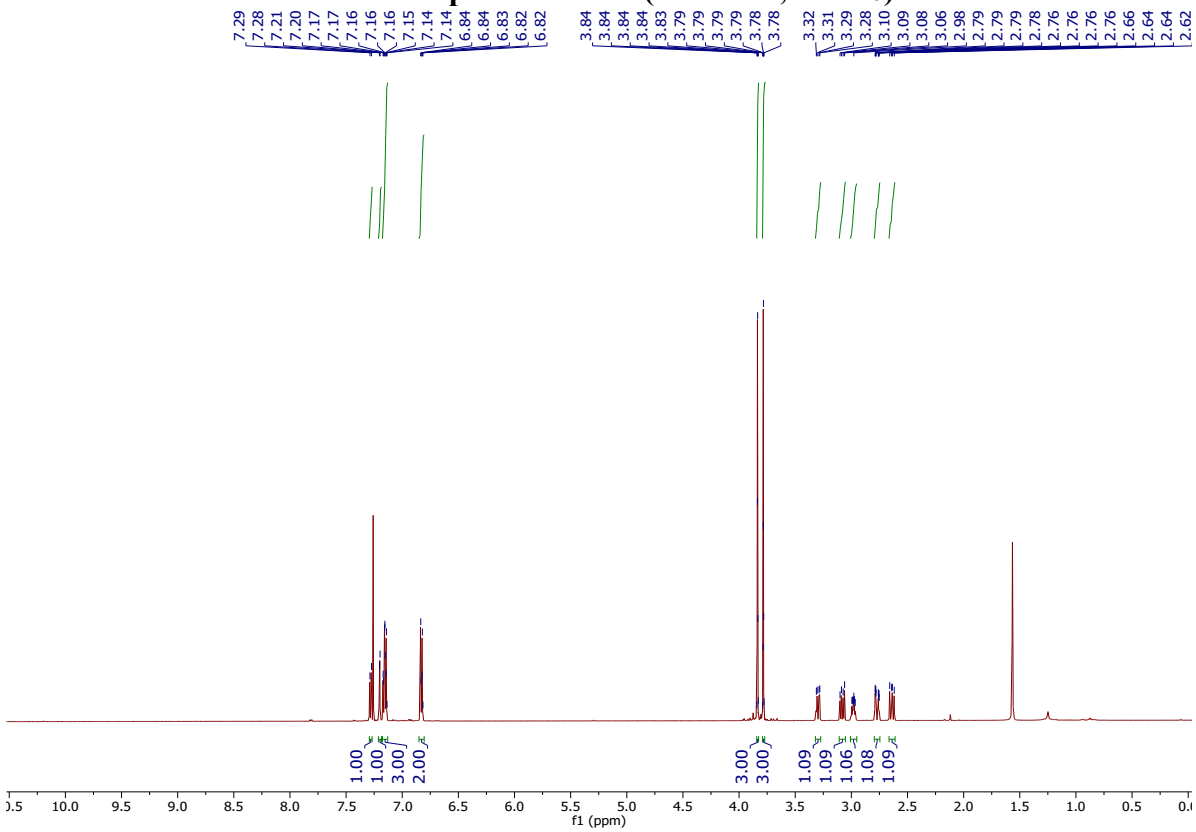
^{1}H NMR Spectrum of 3r (600 MHz, $CDCl_3$)



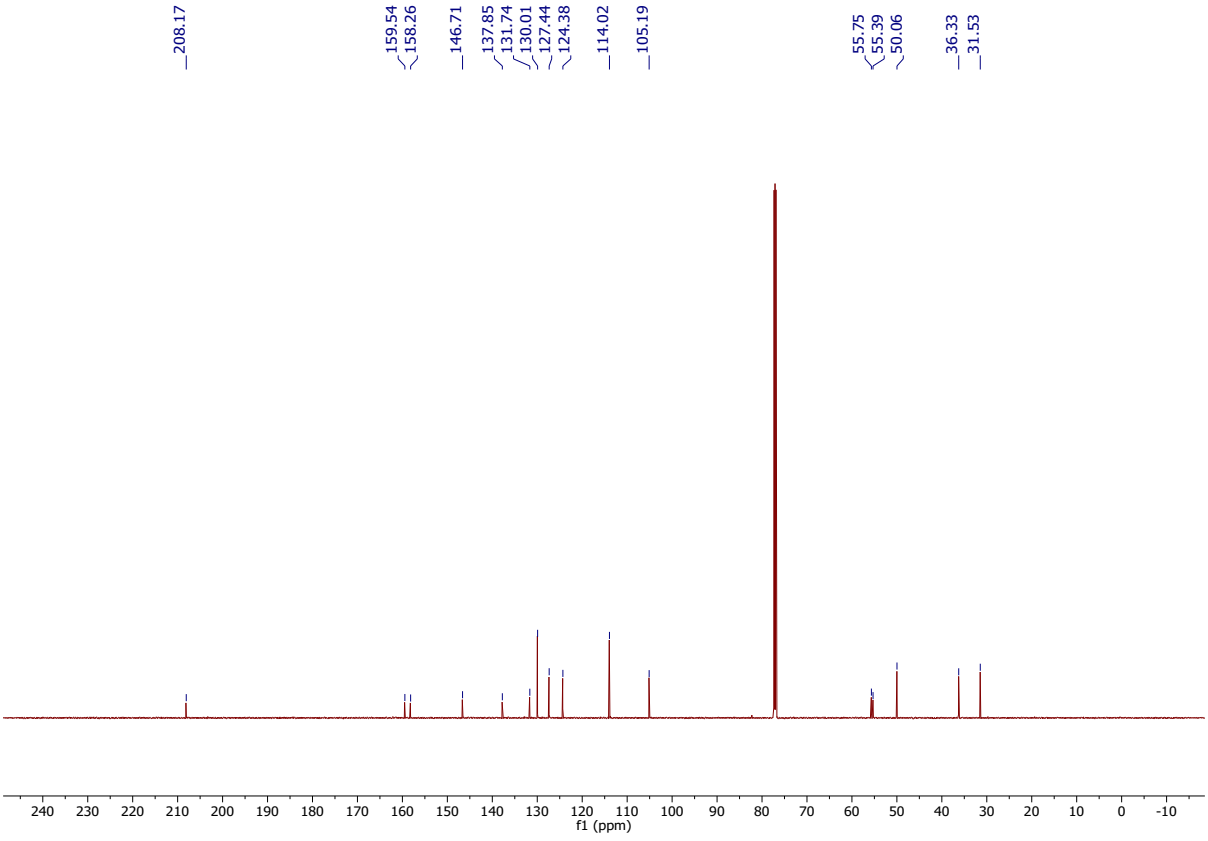
^{13}C NMR Spectrum of 3r (150 MHz, $CDCl_3$)



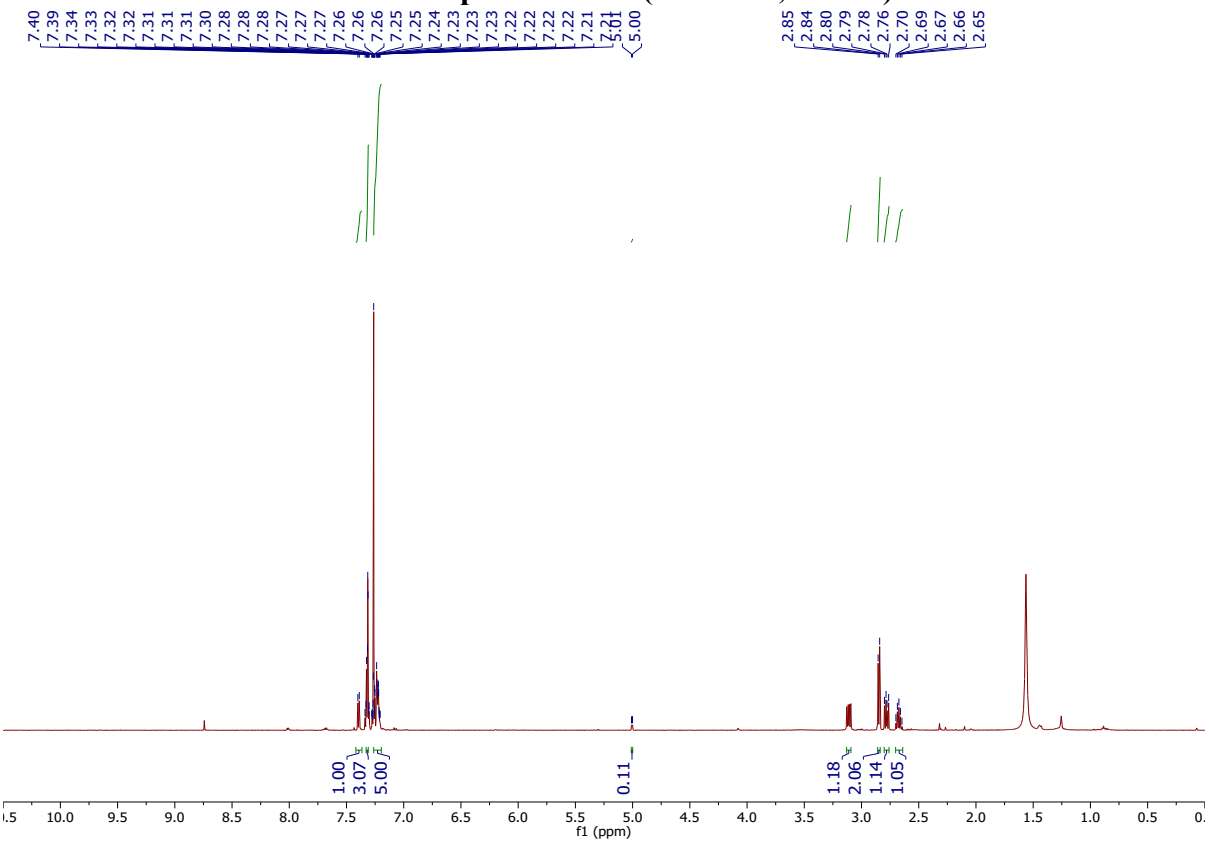
^{1}H NMR Spectrum of 3s (600 MHz, $CDCl_3$)



^{13}C NMR Spectrum of 3s (150 MHz, $CDCl_3$)



^{1}H NMR Spectrum of 5 (600 MHz, $CDCl_3$)



^{13}C NMR Spectrum of 5 (150 MHz, $CDCl_3$)