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Supporting InFoamation

Mechanochemical Deprotection of *t*-Butoxycarbonyl (Boc) Using Basic Alumina

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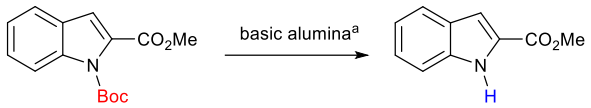
1. General Information

All reagents and all solvents were used directly as obtained commercially unless otherwise noted. The planetary ball mill (Lichen LC-PBM-0.4L) was purchased from Changsha Tianchuang Powder Technology Co., Ltd.. All types of alumina, including basic alumina (activated, basic, Brockmann I, 199443), were purchased from Sigma-Aldrich. Other reagents were purchased from Anhui Zesheng Science and Technology Co. and Shanghai Bide Pharmaceutical Technology Co.. Reactions were monitored by thin-layer chromatography (TLC) carried out on HSGF254 0.20 mm Huanghai silica gel plates using UV light as a visualizing agent and cerium(IV) ammonium nitrate (CAN) or basic aqueous $KMnO_4$ as a developing agent. Melting points (mp) are uncorrected and were recorded on a Büchi M-560 apparatus in open capillary tubes. High-resolution mass spectra (HRMS) were recorded on a Waters Xevo G2-XS QTof mass spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance DMX-400 instrument. Proton magnetic resonance spectra (^{1}H NMR) were recorded at 400 MHz and coupling constants (*J*) are reported to ± 0.5 Hz. The following abbreviations were utilized to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. Carbon magnetic resonance spectra (^{13}C NMR) were recorded at 101 MHz. Chemical shifts (H, C) are quoted in parts per million (ppm) and are referenced to the residual solvent peak ($CDCl_3$: δ_H = 7.26 and δ_C = 77.16; DMSO: δ_H = 2.50 and δ_C = 39.52).

2. Thermally Activated Boc Deprotection Reactions Using Basic Alumina

Table 1. Thermally activated Boc deprotection reactions using basic alumina



1a **2a**

Entry	Reaction conditions	Time [h]	Yield [%][b]
1	THF, 30°C	1	Trace
2	ethyl acetate, 30°C	1	Trace
3	acetonitrile, 30°C	1	Trace
4	toluene, 30°C	1	Trace
5	dichloroethane, 30°C	1	42(49)
6	**dichloroethane, 30°C**	**9**	**71(7)**
7	solvent-free, 30°C	1	11(83)
8	solvent-free, 30°C	9	60(19)
9	water, 50°C	1	Trace
10	ethanol, 50°C	1	Trace
9	dichloroethane, 50°C	1	53(10)
10	dichloroethane, 70°C	1	51
11	dichloroethane, 90°C	1	35

[a] Activated, basic alumina, Brockmann I (~150 mesh). [b] The yield of **2a** was determined from 1H NMR spectrum through adding 1,3,5-trimethoxybenzene as internal standard. The data in parentheses indicate the amounts of recovered **1a**.

3. A Comparison of the Mechanochemical De-Boc Reaction with Other Solvent-free De-Boc methods.

Table 2. A comparison of the mechanochemical de-Boc reaction with other solvent-free de-Boc methods.

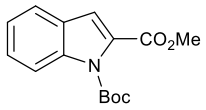
Entry	Ref. No. in paper	Reaction conditions	Time [h]	Yield [%]	cost of reagent [¥][a]	sustainability metrics
1	14a	$Yb(OTf)_3$, SiO_2, rt or 40 °C	1–60	96–100	11247	solvent-free
2	14b	$AlCl_3$, Al_2O_3, Microwave irradiation	1 min	76–95	2050	solvent-free
3	14c	SiO_2, Microwave irradiation	1 min	56–98	——	solvent-free no waste acid
4	14d	I_2, rt	0.5–4	80–98	240	solvent-free no waste acid
5	14e	NaCl, H_2SO_4, rt	1–20	>97	881.3	solvent-free easy to operate
6	17	*p*-TsOH, ball-milling	10 mins	>98	1463	solvent-free easy to operate
7	our method	basic Al_2O_3, ball-milling	9–24	72–99	5399	solvent-free no waste acid easy to operate

[a] The cost of reagent needed for 1 mol product, the price of catalyst from Sigma-Aldrich.

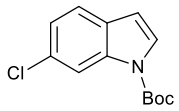
4. Spectroscopic Data of Substrates

Substrates **1b**, **1d**, **1e**, **1f**, **1r**, **3c**, **3e**, **5a**, **5b**, **5c, 7a**, and **7b** were purchased from Anhui Zesheng Science and Technology Co. Substrates **1a**, **1c**, **1g**, **1h**, **1k**, **1m**, **1o**, **1p**, **1q**, **1s**, **3a**, **3d**, **3f**, **3g**, **3h**, **5d**, **5e**, **5f**, **9a**, **9b**, and **9c** were prepared according to reported literature. Compounds **1i**, **1j**, **1l**, **1n**, **3b**, **3i**, **10c**, **11a**, **11b**, and **11c** were new compound.

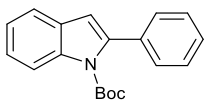
^{1}H and ^{13}C NMR spectroscopic data of known substrates **1a**, **1c**, **1g**, **1h**, **1k**, **1m**, **1o**, **1p**, **1q**, **1s**, **3a**, **3d**, **3f**, **3g**, **3h**, **5d**, **5e**, **5f**, **9a**, **9b**, and **9c** are as follows:



1-(*tert*-Butyl) 2-methyl 1*H*-indole-1,2-dicarboxylate (1a).[1] White solid. M. p. = 64.1–64.8 °C, reported: 65.0–65.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.11 (dt, J = 8.4, 0.9 Hz, 1H), 7.60 (dt, J = 7.8, 1.0 Hz, 1H), 7.42 (ddd, J = 8.5, 7.2, 1.3 Hz, 1H), 7.26 (td, J = 7.4, 1.0 Hz, 1H), 7.11 (d, J = 0.8 Hz, 1H), 3.93 (s, 3H), 1.63 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 162.4, 149.3, 137.9, 130.4, 127.5, 126.9, 123.3, 122.2, 114.9 (2C), 84.6, 52.3, 27.8.

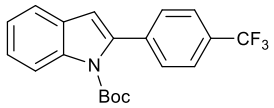


***tert*-Butyl 6-chloro-1*H*-indole-1-carboxylate (1c).**[2] Foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.21 (s, 1H), 7.58 (d, J = 3.7 Hz, 1H), 7.45 (dd, J = 8.4, 1.5 Hz, 1H), 7.21 (dd, J = 8.4, 1.9 Hz, 1H), 6.53 (d, J = 3.7 Hz, 1H), 1.69 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 149.4, 135.6, 130.2, 129.0, 126.5, 123.3, 121.6, 115.6, 107.1, 84.2, 28.2.

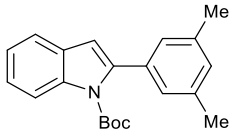


***tert*-Butyl 2-phenyl-1*H*-indole-1-carboxylate (1g).**[3] White solid. M. p. = 77.0–77.8 °C, reported: 76–78 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.32 (dd, J = 8.7, 3.9 Hz, 1H), 7.62 (dd, J = 7.8, 2.8 Hz, 1H), 7.51–7.39 (m, 6H), 7.35–7.30 (m, 1H), 6.72 (d, J = 2.7

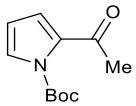
Hz, 1H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 150.3, 140.6, 137.6, 135.1, 129.3, 128.8, 127.9, 127.7, 124.4, 123.0, 120.5, 115.3, 110.0, 83.4, 27.6.



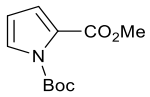
***tert*-Butyl 2-(4-(trifluoromethyl)phenyl)-1*H*-indole-1-carboxylate (1h).**[3] White solid. M. p. = 99.6–100.7 ℃, reported: 101–102 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.28 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 8.1 Hz, 2H), 7.61 (d, J = 7.7 Hz, 1H), 7.57 (d, J = 8.1 Hz, 2H), 7.43–7.39 (m, 1H), 7.33–7.29 (m, 1H), 6.64 (s, 1H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 150.0, 138.9, 138.7, 137.7, 129.1 (2C), 125.0, 124.9 (q, J = 3.9 Hz), 124.3 (q, J = 272.9 Hz), 123.3, 120.9, 115.5, 111.2, 84.0, 27.7, only peaks visible.



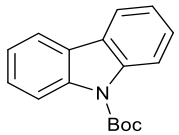
***tert*-Butyl 2-(3,5-dimethylphenyl)-1*H*-indole-1-carboxylate (1k).**[3] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19 (dd, J = 8.3, 0.9 Hz, 1H), 7.56–7.53 (m, 1H), 7.32 (ddd, J = 8.4, 7.2, 1.4 Hz, 1H), 7.26–7.22 (m, 1H), 7.04 (s, 2H), 7.00 (s, 1H), 6.54 (d, J = 0.7 Hz, 1H), 2.36 (s, 6H), 1.32 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 150.4, 141.0, 137.6, 137.3, 134.8, 129.4, 129.3, 126.7, 124.2, 123.0, 120.5, 115.2, 109.6, 83.3, 27.7, 21.4.



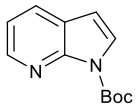
***tert*-Butyl 2-acetyl-1*H*-pyrrole-1-carboxylate (1m).**[4] Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.22–7.21 (m, 1H), 6.77–6.76 (m, 1H), 6.07–6.05 (m, 1H), 2.34 (s, 3H), 1.48 (s, 9H). ^{13}C NMR (101 MHz, CDCl3) δ (ppm) 188.2, 148.8, 134.0, 127.8, 121.1, 109.9, 84.6, 27.7, 27.4.



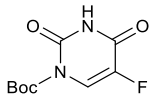
1-(*tert*-Butyl) 2-methyl 1*H*-pyrrole-1,2-dicarboxylate (1o).[5] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.23 (dd, J = 3.1, 1.8 Hz, 1H), 6.74 (dd, J = 3.5, 1.7 Hz, 1H), 6.06 (t, J = 3.3 Hz, 1H), 3.74 (s, 3H), 1.48 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 161.0, 148.2, 126.5, 125.0, 120.6, 110.0, 84.5, 51.6, 27.4.



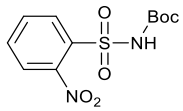
***tert*-Butyl 9*H*-carbazole-9-carboxylate (1p).**[6] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.42–8.39 (m, 2H), 8.01 (dd, J = 7.7, 1.3 Hz, 2H), 7.57–7.52 (m, 2H), 7.43–7.39 (m, 2H), 1.84 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 151.1, 138.5, 127.1, 125.8, 123.0, 119.6, 116.3, 83.9, 28.4.



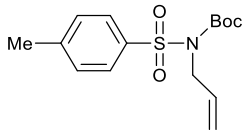
***tert*-Butyl 1*H*-pyrrolo[2,3-b]pyridine-1-carboxylate (1q).**[7] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.43 (dd, J = 4.8, 1.7 Hz, 1H), 7.78 (dd, J = 7.8, 1.7 Hz, 1H), 7.54 (d, J = 4.1 Hz, 1H), 7.09 (dd, J = 7.8, 4.8 Hz, 1H), 6.41 (d, J = 4.1 Hz, 1H), 1.58 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 148.2, 147.7, 144.9, 129.0, 126.4, 122.8, 118.4, 104.4, 83.9, 27.9.



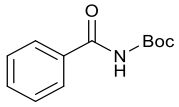
***tert*-Butyl 5-fluoro-2,4-dioxo-3,4-dihydropyrimidine-1(2*H*)-carboxylate (1s).**[8] White solid. M. p. = 262.4–264.6 ℃, reported: ＞250 ℃.^{1}H NMR (400 MHz, DMSO) δ (ppm) 11.93 (br s, 1H), 8.18 (d, J = 7.2 Hz, 1H), 1.52 (s, 9H). ^{13}C NMR (101 MHz, DMSO) δ (ppm) 157.1 (d, J = 27.1 Hz), 147.5, 146.2, 139.9 (d, J = 234.1 Hz), 124.6 (d, J = 37.1 Hz), 86.0, 27.3.



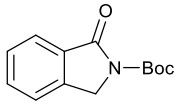
***tert*-Butyl ((2-nitrophenyl)sulfonyl)carbamate (3a).**[9] White solid. M. p. = 88.0–89.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.35–8.33 (m, 1H), 7.88–7.84 (m, 1H), 7.83–7.76 (m, 2H), 7.69 (br s, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 148.7, 148.2, 134.9, 133.4, 132.6, 132.1, 125.2, 85.0, 28.0.



***tert*-Butyl allyl(tosyl)carbamate (3d).**[10] Foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.78 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 5.92 (ddt, J = 17.1, 10.2, 5.7 Hz, 1H), 5.30 (dd, J = 17.1, 1.4 Hz, 1H), 5.22 (dd, J = 10.2, 1.3 Hz, 1H), 4.43 (dt, J = 5.8, 1.4 Hz, 2H), 2.42 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 150.8, 144.2, 137.3, 133.3, 129.3, 128.2, 118.1, 84.3, 48.9, 27.9, 21.7.

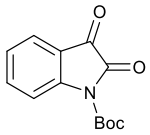


***tert*-Butyl benzoylcarbamate (3f).**[11] White solid. M. p. = 146.5–148.2 °C, reported: 149–151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.25 (br s, 1H), 7.82–7.80 (m, 2H), 7.56–7.51 (m, 1H), 7.45–7.41 (m, 2H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 165.4, 149.9, 133.3, 132.8, 128.8, 127.6, 82.8, 28.0.

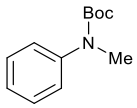


***tert*-Butyl 1-oxoisoindoline-2-carboxylate (3g).**[12] White solid. M. p. = 118.2–119.3 °C, reported: 121–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.87–7.85 (m, 1H), 7.59 (td, J = 7.5, 1.2 Hz, 1H), 7.46–7.42 (m, 2H), 4.72 (s, 2H), 1.57 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 166.7, 150.4, 140.7, 133.6, 131.5, 128.5, 125.0, 123.1, 83.1, 49.2,

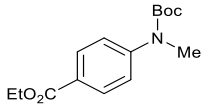
28.2.



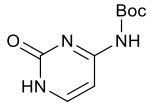
***tert*-Butyl 2,3-dioxoindoline-1-carboxylate (3h).**[13] Foam. ^{1}H NMR (400 MHz, DMSO-*d*6) δ (ppm) 7.94 (dt, J = 8.3, 0.8 Hz, 1H), 7.78–7.73 (m, 1H), 7.70–7.68 (m, 1H), 7.31 (td, J = 7.5, 0.9 Hz, 1H), 1.59 (s, 9H). ^{13}C NMR (101 MHz, DMSO-*d*6) δ (ppm) 179.8, 156.0, 148.2, 147.4, 137.7, 124.9, 124.4, 119.3, 116.1, 84.1, 27.7.



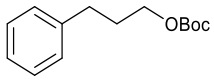
***tert*-Butyl methyl(phenyl)carbamate (5d).**[14] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.34–7.30 (m, 2H), 7.26–7.23 (m, 2H), 7.19–7.14 (m, 1H), 3.26 (s, 3H), 1.47 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 154.7, 143.7, 128.5, 125.5, 125.3, 80.1, 37.2, 28.2.



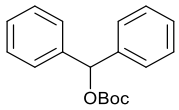
Ethyl 4-((*tert*-butoxycarbonyl)(methyl)amino)benzoate (5e).[15] Foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97 (d, J = 8.7 Hz, 2H), 7.30 (d, J = 8.7 Hz, 2H), 4.34 (q, J = 7.1 Hz, 2H), 3.27 (s, 3H), 1.45 (s, 9H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 166.2, 154.3, 147.9, 130.1, 126.9, 124.5, 81.1, 61.0, 37.0, 28.4, 14.4.



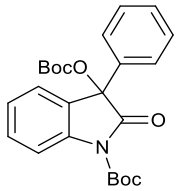
***tert*-Butyl (2-oxo-1,2-dihydropyrimidin-4-yl)carbamate (5f).**[16] White solid. M. p. = 275 °C (dec.), reported: 270 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d6) δ (ppm) 7.74 (d, J = 7.1 Hz, 1H), 6.88 (d, J = 7.0 Hz, 1H), 1.45 (s, 9H).



***tert*-Butyl (3-phenylpropyl) carbonate (9a).**[17] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31–7.28 (m, 2H), 7.22–7.18 (m, 3H), 4.10 (t, J = 6.6 Hz, 2H), 2.72 (dd, J = 8.8, 6.7 Hz, 2H), 2.03–1.96 (m, 2H), 1.52 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 153.5, 141.0, 128.3 (2C), 125.9, 81.6, 66.2, 31.9, 30.2, 27.7.

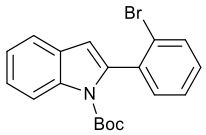


Benzhydryl *tert*-butyl carbonate (9b).[18] White solid. M. p. = 74.0–74.7 ℃, reported: 72–74 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.43–7.29 (m, 10H), 6.70 (s, 1H), 1.51 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 153.0, 140.2, 128.6, 128.0, 127.0, 82.5, 79.9, 27.9.

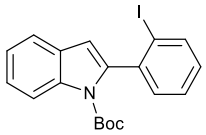


***tert*-Butyl 3-((*tert*-butoxycarbonyl)oxy)-2-oxo-3-phenylindoline-1-carboxylate (9c).**[19] White solid. M. p. = 134.9–135.8 ℃, reported: 135–137 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.99 (d, J = 8.2 Hz, 1H), 7.45 (td, J = 7.9, 1.5 Hz, 1H), 7.34–7.30 (m, 6H), 7.26–7.22 (m, 1H), 1.61 (s, 9H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 171.7, 151.1, 149.2, 140.7, 136.0, 130.5, 129.2, 128.6, 127.4, 126.8, 125.1, 124.1, 115.5, 84.6, 84.0, 81.7, 28.1, 27.6.

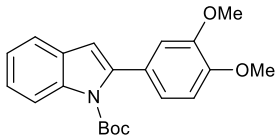
General procedure for the preparation of substrates**1i**, **1j**, **1l**, and **1n**: Add unprotected heterocyclic compounds (10.0 mmol), 4-dimethylaminopyridine (25.0 mg, 0.200 mmol), Et_3N (1.72 g, 17.0 mmol) and 10 mL of DCM into the reaction flask. Then Add Boc_2O (2.40 g dissolved in 20 mL DCM, 11.0 mmol) to the reaction system at 0–5 °C for 10 min. After completion of the reaction, it was quenched with saturated aqueous $NaHCO_3$ (50 mL). After extraction with CH_2Cl_2 (3 × 25 mL), the combined organic phases were washed with brine (20 mL), dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under vacuum, and the residue was purified by flash column chromatography using ethyl acetate/petroleum ether as the eluent.



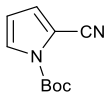
***tert*-Butyl 2-(2-bromophenyl)-1*H*-indole-1-carboxylate (1i).** Yellow solid (2.93 g, 79%). M. p. = 81.3–82.6 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.44–8.41 (m, 1H), 7.69–7.63 (m, 2H), 7.48–7.39 (m, 3H), 7.36–7.26 (m, 2H), 6.60–6.57 (m, 1H), 1.36 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 149.8, 138.2, 137.0, 136.7, 132.1, 131.3, 129.4, 129.0, 127.0, 124.8, 124.7, 123.0, 120.7, 115.7, 110.3, 83.2, 27.6. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{18}BrNNaO_2^+$: 394.0413; found: 394.0418.



***tert*-Butyl 2-(2-bromophenyl)-1*H*-indole-1-carboxylate (1j).** Yellow oil (3.06 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.57 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 7.9 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.53–7.47 (m, 3H), 7.41 (t, J = 7.4 Hz, 1H), 7.18–7.14 (m, 1H), 6.61 (s, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 149.5, 141.0, 140.6, 138.2, 136.4, 130.5, 129.3, 128.9, 127.5, 124.5, 122.9, 120.6, 115.7, 110.0, 100.7, 82.9, 27.5. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{18}INNaO_4^+$: 442.0274; found: 442.0284.

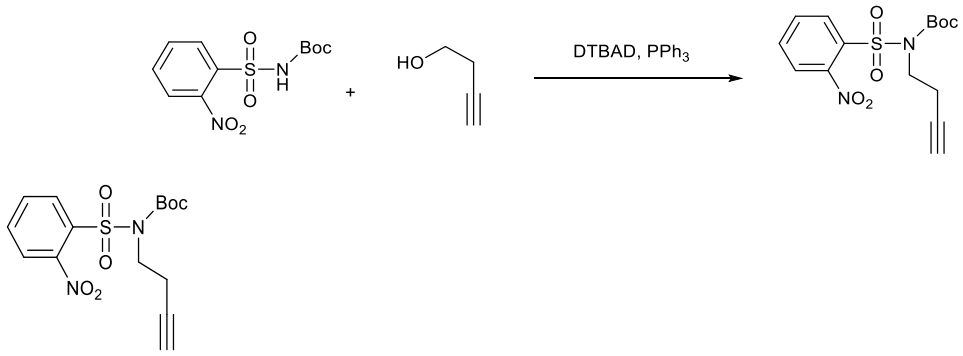


***tert*-Butyl 2-(3,4-dimethoxyphenyl)-1*H*-indole-1-carboxylate (1l).** White solid (3.11 g, 88%). M. p. = 92.9–93.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19 (dd, J = 8.3, 1.0 Hz, 1H), 7.55 (dt, J = 7.7, 1.0 Hz, 1H), 7.33 (ddd, J = 8.4, 7.2, 1.4 Hz, 1H), 7.26 (td, J = 7.4, 1.1 Hz, 1H), 7.01 (dd, J = 8.2, 2.0 Hz, 1H), 6.95 (d, J = 2.0 Hz, 1H), 6.92 (d, J = 8.3 Hz, 1H), 6.55 (s, 1H), 3.94 (s, 3H), 3.91 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 150.3, 148.7, 148.3, 140.5, 137.3, 129.3, 127.6, 124.2, 123.0, 121.1, 120.4, 115.2, 112.1, 110.5, 109.7, 83.4, 56.0 (2C), 27.8. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{21}H_{23}NaO_4^+$: 376.1519; found: 376.1528.



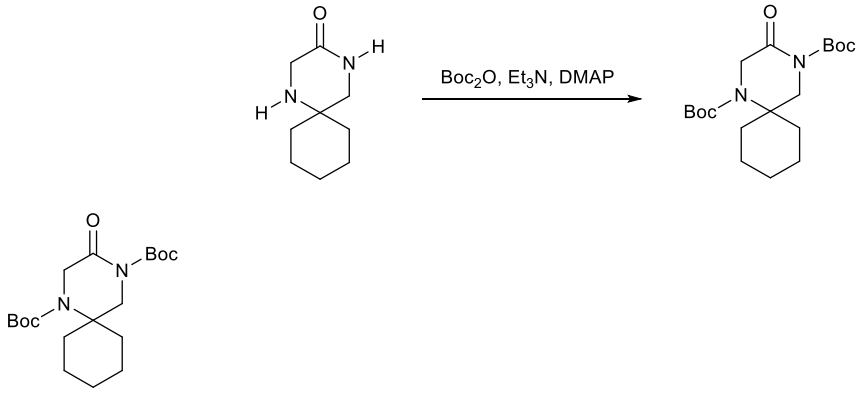
***tert*-Butyl 2-cyano-1*H*-pyrrole-1-carboxylate (1n).** Foam (1.75 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40–7.38 (m, 1H), 6.90–6.88 (m, 1H), 6.22–6.20 (m, 1H), 1.58 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 146.7, 125.6, 125.6, 112.8, 111.7, 103.5, 86.7, 27.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{10}H_{12}N_2NaO_2^+$: 215.0791; found: 215.0793.

Add *o*-NsBocNH (3.02 g, 10.0 mmol), but-3-yn-1-ol (840 mg, 12.0 mmol), PPh_3 (3.15 g, 12.0 mmol) and 20 mL of THF into the reaction flask. Then Add di-*tert*-butyl azodicarboxylate (DTBAD, 2.75 g 12.0 mmol) to the reaction system at 0–5 °C for 10 min. After completion of the reaction, it was quenched with saturated aqueous $NaHCO_3$ (50 mL). After extraction with CH_2Cl_2 (3 × 25 mL), the combined organic phases were washed with brine (20 mL), dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under vacuum, and the residue was purified by flash column chromatography using ethyl acetate/petroleum ether (1: 5) as the eluent.



***tert*-Butyl but-3-yn-1-yl((2-nitrophenyl)sulfonyl)carbamate (3b).** Foam (3.22 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.38–8.25 (m, 1H), 7.85–7.64 (m, 3H), 4.06–3.85 (m, 2H), 2.83–2.42 (m, 2H), 2.06 (t, J = 2.7 Hz, 1H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 150.2, 147.7, 134.4, 133.6, 133.5, 131.9, 124.5, 85.5, 80.2, 70.8, 46.2, 27.9, 20.1. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{15}H_{18}N_2NaO_6S^+$: 377.0778; found: 377.0787.

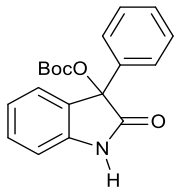
Add unprotected amide (1.68 g, 10.0 mmol), 4-dimethylaminopyridine (50.0 mg, 0.400 mmol), Et_3N (3.44 g, 34.0 mmol) and 20 mL of DCM into the reaction flask. Then Add Boc_2O (4.80 g dissolved in 20 mL DCM, 22.0 mmol) to the reaction system at 0–5 °C for 10 min. After completion of the reaction, it was quenched with saturated aqueous $NaHCO_3$ (50 mL). After extraction with CH_2Cl_2 (3 × 25 mL), the combined organic phases were washed with brine (20 mL), dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under vacuum, and the residue was purified by flash column chromatography using ethyl acetate/petroleum ether as the eluent.



Di-*tert*-Butyl 3-oxo-1,4-diazaspiro[5.5]undecane-1,4-dicarboxylate (3i). White solid (2.60 g, 75%). M. p. = 207.6–210.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.14

(s, 2H), 3.90 (s, 2H), 2.63–2.57 (m, 2H), 1.69–1.61 (m, 3H), 1.52 (s, 9H), 1.43 (s, 9H), 1.39–1.18 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 168.2, 151.2, 84.0, 80.8, 59.3, 49.3, 48.1, 29.9, 28.5, 28.1, 24.9, 23.3, only peaks visible. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{33}N_2O_5^+$: 369.2384; found: 369.2385.

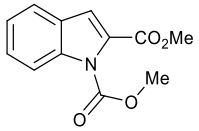
Sequentially add **9c** (1.00 mmol, 1.00 equiv), basic alumina (5.10 g, 50.0 mmol, 50.0 equiv), and 90 g of steel balls into a 50 mL steel vessel. Place the mixture in a planetary ball mill. The mechanochemical reaction was conducted at room temperature at the rotate speed of 500 rpm in 9 hours with the milling cycle, consisting of a 10-minute grinding time followed by a 60-minute pause. After that, the mixture in the vessel was transferred into a 250 mL Erlenmeyer flask, and 50 mL CH_2Cl_2 was added to dissolve the organic compounds. The mixture in the flask was filtered through a microfiltration membrane (diameter 50 mm, aperture 0.45 um). The solvent was removed under vacuum, and the residue was purified by flash column chromatography using ethyl acetate/petroleum ether (1: 5) as the eluent.



***tert*-Butyl (2-oxo-3-phenylindolin-3-yl) carbonate (10c).** Foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.64 (br s, 1H), 7.38 (ddt, J = 6.0, 3.1, 1.7 Hz, 2H), 7.32–7.25 (m, 5H), 7.07 (td, J = 7.6, 0.9 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 176.3, 151.2, 141.8, 136.2, 130.3, 129.0, 128.6, 126.4, 124.6, 123.2, 110.7, 83.8, 82.4, 27.7, only peaks visible. HRMS (ESI): m/z $[M+Na]^+$ calcd for C19H19NNaO4$^+$: 348.1206; found: 348.1216.

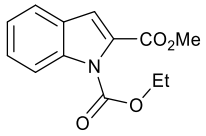
Sequentially add **2a** (1.00 g, 5.71 mmol), dimethyl carbonate (7.20 g, 80.0 mmol), DABCO (64.0 mg, 0.57 mmol) and 1 mL of DMF into the reaction flask. The reaction system was stirred at 94 °C for 2 h. After completion of the reaction, it was quenched with saturated aqueous $NaHCO_3$ (20 mL). After extraction with CH_2Cl_2 (3 × 15 mL),

the combined organic phases were washed with brine (20 mL), dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under vacuum, and the residue was purified by flash column chromatography using ethyl acetate/petroleum ether (1: 3) as the eluent.



Dimethyl 1*H*-indole-1,2-dicarboxylate (11a). Foam (1.12 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.69 (dt, J = 8.0, 1.1 Hz, 1H), 7.44–7.33 (m, 2H), 7.30 (d, J = 0.8 Hz, 1H), 7.16 (ddd, J = 7.9, 6.4, 1.5 Hz, 1H), 4.09 (s, 3H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 162.8, 139.8, 127.8, 126.0, 125.1, 122.7, 120.7, 110.4, 110.3, 51.8, 31.7, only peaks visible. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{12}H_{12}NO_4^+$: 234.0761; found: 234.0770.

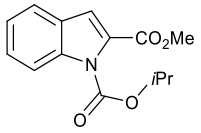
Sequentially add **2a** (1.00 g, 5.71 mmol), diethyl carbonate (1.02 g, 6.30 mmol), DAMP (139 mg, 1.14 mmol), 20 mL of THF, and Et_3N (638 mg, 6.30 mmol) into the reaction flask. The reaction system was stirred at 30 °C for 4 h. After completion of the reaction, it was quenched with saturated aqueous $NaHCO_3$ (20 mL). After extraction with CH_2Cl_2 (3 × 15 mL), the combined organic phases were washed with brine (20 mL), dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under vacuum, and the residue was purified by flash column chromatography using ethyl acetate/petroleum ether (1: 5) as the eluent.



1-Ethyl 2-methyl 1*H*-indole-1,2-dicarboxylate (11b). Colorless oil (1.37 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.08 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.45–7.41 (m, 1H), 7.28 (t, J = 7.4 Hz, 1H), 7.15 (s, 1H), 4.47 (q, J = 7.1 Hz, 2H), 3.92 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 162.3, 150.9,

137.7, 130.4, 127.7, 127.1, 123.6, 122.4, 115.7, 115.1, 64.1, 52.5, 14.2. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{13}H_{13}NNaO_4^+$: 270.0737; found: 270.0744.

Sequentially add **2a** (1.00 g, 5.71 mmol), 10 mL of THF, and NaH (343 g, 8.57 mmol), into the reaction flask at 0–5°C. Then add isopropyl chlorocarbonate (1.05 g, 8.57 mmol) into the reaction system dropwise. After completion of the reaction, it was quenched with saturated aqueous $NaHCO_3$ (20 mL). After extraction with CH_2Cl_2 (3 × 15 mL), the combined organic phases were washed with brine (20 mL), dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under vacuum, and the residue was purified by flash column chromatography using ethyl acetate/petroleum ether (1: 5) as the eluent.



1-Isopropyl 2-methyl 1*H*-indole-1,2-dicarboxylate (11c). Colorless oil (1.10 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (dd, J = 8.5, 0.9 Hz, 1H), 7.57 (dd, J = 7.9, 1.0 Hz, 1H), 7.40 (ddd, J = 8.5, 7.2, 1.3 Hz, 1H), 7.26–7.22 (m, 1H), 7.11 (d, J = 0.9 Hz, 1H), 5.22 (p, J = 6.4 Hz, 1H), 3.90 (s, 3H), 1.40 (d, J = 6.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 162.2, 150.2, 137.6, 130.3, 127.5, 126.8, 123.4, 122.2, 115.2, 114.92, 72.4, 52.3, 21.6. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{14}H_{15}NNaO_4^+$: 284.0893; found: 284.0903.

5. Experimental Procedure of Mechanochemical Boc Deprotection Reaction and Spectroscopic Data of Products

General procedure of mechanochemical Boc deprotection reaction： Sequentially add Boc compound (1.00 mmol, 1.00 equiv), basic alumina (5.10 g, 50.0 mmol, 50.0 equiv), and 90 g of steel balls into a 50 mL steel vessel. Place the mixture in a planetary ball mill. The mechanochemical reaction was conducted at room temperature (22–28°C) at the rotate speed of 500 rpm in 9, 16 or 24 hours with the milling cycle, consisting of a 10-minute grinding time followed by a 60-minute pause. After that, the mixture in the vessel was transferred into a 250 mL Erlenmeyer flask, and 50 mL CH_2Cl_2 was added to dissolve the organic compounds. The mixture in the flask was filtered through a microfiltration membrane (diameter 50 mm, aperture 0.45 um). Finally, the filtrate was concentrated to afford the product.

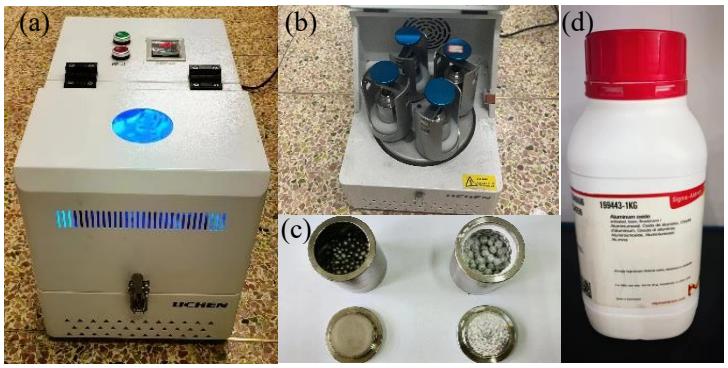
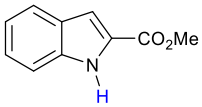
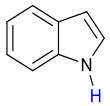


Fig.1. Experimental equipment. (a) Planetary ball mill (Lichen LC-PBM-0.4L). (b) Four 50 mL steel vessels. (c) Two vessels containing the reaction mixture and balls. The left was before the milling process, and the right was after the process. (d) Auxiliary agent: Alumina, activated, basic, Brockmann I, from Sigma-Aldrich

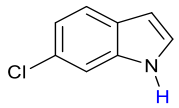


Methyl 1*H*-indole-2-carboxylate (2a).[20] White solid (157.6 mg, 90%). M. p. = 148.9–150.6 °C, reported: 152.5–153.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.29 (br s,

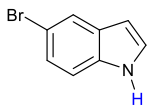
1H), 7.73–7.70 (m, 1H), 7.46–7.43 (m, 1H), 7.34 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.25 (dd, J = 2.2, 1.0 Hz, 1H), 7.17 (ddd, J = 8.1, 6.9, 1.0 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 162.8, 137.1, 127.6, 127.2, 125.5, 122.7, 120.9, 112.1, 108.9, 52.2.



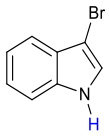
1*H*-indole (2b).[21] White solid (100.5 mg, 86%). M. p. = 51.4–51.8 ℃, reported: 52–53 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06 (br s, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.42–7.40 (m, 1H), 7.28–7.23 (m, 1H), 7.21–7.16 (m, 2H), 6.62–6.60 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 135.7, 127.8, 124.4, 122.0, 120.8, 119.9, 111.2, 102.4.



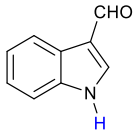
6-Chloro-1*H*-indole (2c).[22] White solid (131.8 mg, 87%). M. p. = 88.5–89.6 ℃, reported: 86–88 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09 (br s, 1H), 7.57 (dd, J = 8.4, 0.8 Hz, 1H), 7.37 (dd, J = 1.8, 0.9 Hz, 1H), 7.18 (dd, J = 3.3, 2.4 Hz, 1H), 7.13 (dd, J = 8.4, 1.8 Hz, 1H), 6.56–6.55 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 136.2, 127.9, 126.5, 125.0, 121.7, 120.7, 111.1, 102.9.



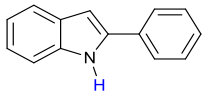
5-Bromo-1*H*-indole (2d).[22] White solid (186.2 mg, 95%). M. p. = 89.9–91.2 ℃, reported: 88.6–89.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.13 (br s, 1H), 7.81 (d, J = 1.9 Hz, 1H), 7.31 (dd, J = 8.6, 1.9 Hz, 1H), 7.25–7.23 (m, 1H), 7.19–7.18 (m, 1H), 6.53–6.51 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 134.5, 129.7, 125.6, 124.9, 123.2, 113.1, 112.6, 102.3.



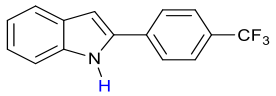
3-Bromo-1*H*-indole (2e).[23] White solid (170.5 mg, 87%). M. p. = 65.3–66.0 ℃ (dec.), reported: 65–66 ℃ (dec.). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19 (br s, 1H), 7.60 (dd, J = 7.3, 1.5 Hz, 1H), 7.39–7.37 (m, 1H), 7.28–7.26 (m, 1H), 7.25–7.20 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 135.4, 126.9, 123.5, 123.2, 120.8, 119.2, 111.5, 91.7.



1*H*-indole-3-carbaldehyde (2f).[24] White solid (136.4 mg, 94%). M. p. = 195.1–196.2 ℃, reported: 196–198 ℃. ^{1}H NMR (400 MHz, DMSO-*d*6) δ (ppm) 12.14 (br s, 1H), 9.94 (s, 1H), 8.29 (d, J = 2.9 Hz, 1H), 8.12–8.10 (m, 1H), 7.53–7.51 (m, 1H), 7.28–7.20 (m, 2H). ^{13}C NMR (101 MHz, DMSO-*d*6) δ (ppm) 185.0, 138.5, 137.1, 124.1, 123.5, 122.1, 120.9, 118.2, 112.4.

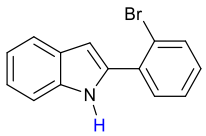


2-Phenyl-1*H*-indole (2g).[25] White solid (181.6 mg, 94%). M. p. = 189.7–190.5 ℃, reported: 190–191 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.32 (br s, 1H), 7.69–7.66 (m, 3H), 7.48–7.45 (m, 2H), 7.42 (dt, J = 8.0, 1.0 Hz, 1H), 7.37–7.33 (m, 1H), 7.24 (ddd, J = 8.2, 7.1, 1.3 Hz, 1H), 7.17 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 6.86 (dd, J = 2.2, 0.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 138.0, 136.9, 132.5, 129.4, 129.1, 127.8, 125.3, 122.5, 120.8, 120.4, 111.0, 100.1.

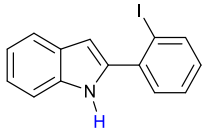


2-(4-(Trifluoromethyl)phenyl)-1*H*-indole (2h).[25] White solid (235.0 mg, 90%). M. p.

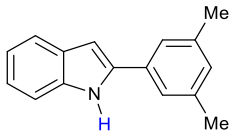
= 232.4–235.4 °C, reported: 234–236 °C. ^{1}H NMR (400 MHz, DMSO-*d*6) δ (ppm) 11.73 (br s, 1H), 8.07 (d, J = 8.2 Hz, 2H), 7.80 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 7.9 Hz, 1H), 7.44 (d, J = 8.1 Hz, 1H), 7.15 (ddd, J = 8.2, 6.9, 1.2 Hz,1H), 7.07 (d, J = 2.2 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-*d*6) δ (ppm) 137.5, 136.1 (q, J = 1.0 Hz), 135.8, 128.4, 127.4, 125.8 (q, J = 3.8 Hz), 125.3, 124.3 (q, J = 272.7 Hz), 122.4, 120.5, 119.7, 111.5, 100.7.



2-(2-Bromophenyl)-1*H*-indole (2i).[26] Yellow solid (234.0 mg, 86%). M. p. = 73.5–74.9 °C, reported: 75–77 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.60 (br s, 1H), 7.81–7.77 (m, 2H), 7.64 (dd, J = 7.8, 1.8 Hz, 1H), 7.49–7.47 (m, 1H), 7.44 (td, J = 7.6, 1.3 Hz, 1H), 7.35 (ddd, J = 8.2, 7.1, 1.3 Hz, 1H), 7.30–7.26 (m, 2H), 6.94 (dd, J = 7.6, 0.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 136.3, 136.2, 134.0, 133.4, 131.4, 129.2, 128.2, 127.7, 122.6, 121.4, 120.9, 120.2, 111.2, 103.7.

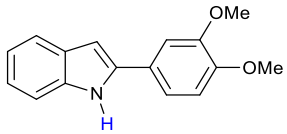


2-(2-Iodophenyl)-1*H*-indole (2j).[27] Yellow oil (261.7 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.24 (br s, 1H), 8.09 (dd, J = 8.0, 1.2 Hz, 1H), 7.82 (dd, J = 7.8, 1.1 Hz, 1H), 7.52 (dd, J = 7.7, 1.9 Hz, 1H), 7.49–7.44 (m, 2H), 7.38 (ddd, J = 8.1, 7.0, 1.3 Hz, 1H), 7.30 (ddd, J = 8.1, 7.0, 1.2 Hz, 1H), 7.13 (ddd, J = 7.9, 7.2, 1.9 Hz, 1H), 6.87 (dd, J = 2.3, 0.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 140.3, 138.7, 137.8, 136.0, 131.1, 129.6, 128.3, 128.2, 122.5, 120.9, 120.2, 111.2, 103.5, 97.2.

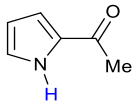


2-(3,5-Dimethylphenyl)-1*H*-indole (2k).[28] White solid (183.7 mg, 83%). M. p. =

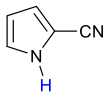
146.3–146.8 °C, reported: 146–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.32 (br s, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.41–7.39 (m, 1H), 7.31 (s, 2H), 7.20 (ddd, J = 8.1, 7.1, 1.3 Hz, 1H), 7.14 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 7.00–6.99 (m, 1H), 6.82 (m, 1H), 2.40 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 138.7, 138.3, 136.8, 132.4, 129.6, 129.4, 123.2, 122.3, 120.7, 120.3, 111.0, 99.9, 21.5.



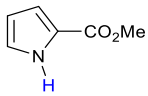
2-(3,4-Dimethoxyphenyl)-1*H*-indole (2l).[29] White solid (210.2 mg, 83%). M. p. = 186.9–190.4 °C, reported: 182–184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.39 (br s, 1H), 7.64 (dd, J = 7.7, 1.2 Hz, 1H), 7.37 (dd, J = 7.9, 1.0 Hz, 1H), 7.22–7.12 (m, 4H), 6.91 (d, J = 8.2 Hz, 1H), 6.75 (dd, J = 2.2, 0.9 Hz, 1H), 3.95 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 149.5, 149.0, 138.2, 136.8, 129.5, 125.7, 122.1, 120.5, 120.3, 117.7, 111.7, 110.9, 109.0, 99.1, 56.0 (2C).



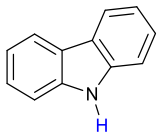
1-(1*H*-pyrrol-2-yl)ethan-1-one (2m).[30] White solid (106.9 mg, 98%). M. p. = 88.1–90.3 °C, reported: 88–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.65 (br s, 1H), 7.07 (dt, J = 3.8, 1.8 Hz, 1H), 6.94–6.92 (m, 1H), 6.26 (dt, J = 4.4, 2.5 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 188.5, 132.2, 125.5, 117.4, 110.5, 25.5.



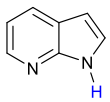
1*H*-pyrrole-2-carbonitrile (2n).[31] Colorless oil (90.2 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.87 (br s, 1H), 6.96 (td, J = 2.8, 1.4 Hz, 1H), 6.88 (ddd, J = 3.9, 2.4, 1.4 Hz, 1H), 6.26 (dt, J = 3.8, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 124.1, 120.3, 115.0, 109.9, 100.2.



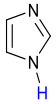
Methyl 1*H*-pyrrole-2-carboxylate (2o).[30] White solid (117.6 mg, 94%). M. p. = 72.6–73.5 ℃, reported: 74–77 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.89 (br s, 1H), 6.83–6.80 (m, 2H), 6.11 (dt, J = 3.8, 2.5 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 162.1, 123.5, 122.4, 115.5, 110.3, 51.4.



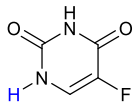
9*H*-carbazole (2p).[32] Ethyl acetate was used to dissolve the compound. White solid (150.4 mg, 90%). M. p. = 223.2–245.6 ℃, reported: 245–246 ℃. ^{1}H NMR (400 MHz, DMSO-*d*6) δ (ppm) 11.26 (br s, 1H), 8.11 (d, J = 7.8 Hz, 2H), 7.50 (dd, J = 8.1, 0.9 Hz, 2H), 7.39 (ddd, J = 8.2, 7.0, 1.2 Hz, 2H), 7.16 (ddd, J = 8.0, 7.1, 1.0 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-*d*6) δ (ppm) 139.7, 125.5, 122.4, 120.1, 118.5, 110.9.



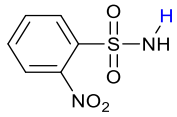
1*H*-pyrrolo[2,3-*b*]pyridine (2q).[21] White solid (93.3 mg, 79%). M. p. = 105.9–106.8 ℃, reported: 105–107 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.59 (br s, 1H), 8.42 (dd, J = 4.8, 1.6 Hz, 1H), 8.03 (dd, J = 7.9, 1.6 Hz, 1H), 7.47 (d, J = 3.5 Hz, 1H), 7.14 (dd, J = 7.8, 4.8 Hz, 1H), 6.56 (d, J = 3.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 149.0, 142.0, 129.1, 125.7, 120.8, 115.6, 100.4.



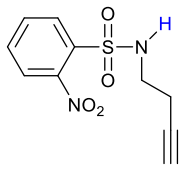
1*H*-imidazole (2r).[21] White solid (54.4 mg, 79%). M. p. = 89.3–90.0 ℃, reported: 88–90 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 13.42–13.36 (m, 1H), 7.75 (d, J = 1.1 Hz, 1H), 7.14 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 135.3, 121.9 (2C).



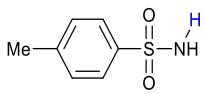
5-Fluoropyrimidine-2,4(1*H*,3*H*)-dione (2s).[33] After ball-milling, water is used to dissolve the compound. When the filtrate was concentrated, a white solid precipitates out from the solution, and another filtration afforded the product. White solid (105.3 mg, 81%). M. p. = 280.5–281.8 ℃ (dec.), reported: 280–281 ℃ (dec.). ^{1}H NMR (400 MHz, DMSO-*d*6) δ (ppm) 11.50 (s, 1H), 10.71 (s, 1H), 7.73 (d, J = 6.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-*d*6) δ (ppm) 158.1 (d, J = 25.9 Hz), 150.2, 140.0 (d, J = 227.1 Hz), 126.4 (d, J = 31.8 Hz).



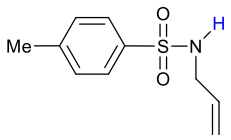
2-Nitrobenzenesulfonamide (4a).[34] Ethyl acetate was used to dissolve the compound. White solid (182.0 mg,90%). M. p. = 190.8–191.5 ℃, reported: 190–192 ℃. ^{1}H NMR (400 MHz, DMSO-*d*6) δ (ppm) 8.07 (dd, J = 7.8, 1.6 Hz, 1H), 7.95 (dd, J = 7.8, 1.6 Hz, 1H), 7.89–7.80 (m, 4H); ^{13}C NMR (101 MHz, DMSO-*d*6) δ (ppm) 147.2, 135.9, 133.5, 132.7, 129.0, 124.3.



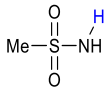
***N*-(But-3-yn-1-yl)-2-nitrobenzenesulfonamide(4b).**[35] White solid (241.5 mg, 95%). M. p. = 104.6–106.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.11–8.09 (m, 1H), 7.86–7.84 (m, 1H), 7.75–7.73 (m, 2H), 5.75 (t, J = 6.2 Hz, 1H), 3.25 (q, J = 6.5 Hz, 2H), 2.40 (td, J = 6.6, 2.6 Hz, 2H), 1.97 (t, J = 2.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 147.9, 133.9, 133.6, 133.1, 130.9, 125.5, 80.0, 71.1, 42.4, 19.8.



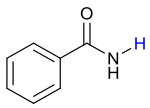
4-Methylbenzenesulfonamide (4c).[36] White solid (148.95 mg, 87%). M. p. = 135.9–138.8 °C, reported: 138–139 °C. ^{1}H NMR (400 MHz, DMSO-*d*6) δ (ppm) 7.71 (dd, J = 8.0, 1.8 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.27 (br s, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, DMSO-*d*6) δ (ppm) 141.8, 141.5, 129.3, 125.6, 20.9.



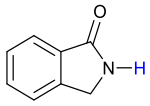
***N*-Allyl-4-methylbenzenesulfonamide(4d).**[24] White solid (209 mg, 99%). M. p. = 63.7–64.5 °C, reported: 64–65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.75 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 5.69 (ddt, J = 17.1, 10.2, 5.8 Hz, 1H), 5.14 (dd, J = 17.1, 1.5 Hz, 1H), 5.06–5.03 (m, 2H), 3.56–3.53 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 143.5, 136.9, 133.0, 129.8, 127.2, 117.6, 45.8, 21.6.



Methanesulfonamide(4e).[37] White solid (74.1 mg, 78%). M. p. = 87.3–88.4 °C, reported: 88.5–91.0 °C. ^{1}H NMR (400 MHz, DMSO-*d*6) δ (ppm) 6.78 (br s, 2H), 2.90 (s, 3H). ^{13}C NMR (101 MHz, DMSO-*d*6) δ (ppm) 43.3.

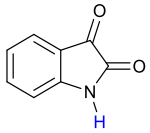


Benzamide (4f).[38] White solid (92.0 mg, 76%). M. p. = 128.6–130.4 °C, reported: 132–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.83–7.80 (m, 2H), 7.55–7.51 (m, 1H), 7.46–7.42 (m, 2H), 6.21 (br s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 169.9, 133.5, 132.1, 128.7, 127.5.

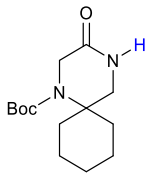


Isoindolin-1-one (4g).[39] White solid (103.8 mg, 78%). M. p. = 149.1–150.8 °C,

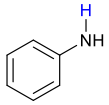
reported: 151–152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.89–7.87 (m, 1H), 7.63 (br s, 1H), 7.57 (td, J = 7.4, 1.2 Hz, 1H), 7.50–7.47 (m, 2H), 4.48 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 172.4, 143.8, 132.3, 131.8, 128.1, 123.8, 123.3, 45.9.



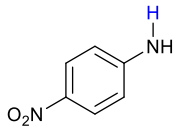
Indoline-2,3-dione (4h).[40] Orange solid (110.3 mg, 75%). M. p. = 201.7–203.4 °C, reported: 200–202 °C. ^{1}H NMR (400 MHz, DMSO-*d*6) δ (ppm) 11.03 (br s, 1H), 7.56 (td, J = 7.7, 1.4 Hz, 1H), 7.49–7.46 (m, 1H), 7.04 (td, J = 7.5, 0.9 Hz, 1H), 6.89 (dt, J = 7.9, 0.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-*d*6) δ (ppm) 184.4, 159.4, 150.8, 138.4, 124.7, 122.8, 117.8, 112.3.



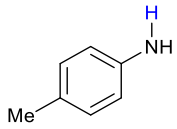
***tert*-Butyl 3-oxo-1,4-diazaspiro[5.5]undecane-1-carboxylate (4i).** White solid (198.6 mg, 74%). M. p. = 301.9–303.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.06 (br s, 1H), 4.05 (s, 2H), 3.37 (d, J = 4.0 Hz, 2H), 2.60 (td, J = 12.4, 4.3 Hz, 2H), 1.67–1.59 (m, 3H), 1.55–1.51 (m, 2H), 1.45 (s, 9H), 1.31–1.26 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 171.8, 153.8, 80.6, 58.4, 47.6, 46.3, 30.5, 28.6, 25.0, 23.2. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{25}N_2O_3^+$: 269.1860; found: 269.1864.



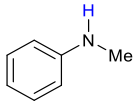
Aniline (6a).[21] Colourless oil (76.3 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.22–7.17 (m, 2H), 6.80 (tt, J = 7.4, 1.1 Hz, 1H), 6.73–6.69 (m, 2H), 3.59 (br s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 146.4, 129.2, 118.3, 115.0.



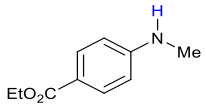
4-Nitroaniline (6b).[21] Yellow solid (110.5 mg, 80%). M. p. = 144.8–145.8 °C, reported: 147–148 °C. ^{1}H NMR (400 MHz, DMSO-*d*6) δ (ppm) 7.94 (d, J = 9.1 Hz, 2H), 6.71 (br s, 2H), 6.60 (d, J = 9.1 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-*d*6) δ (ppm) 155.7, 135.7, 126.4, 112.4.



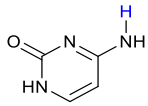
***p*-Toluidine (6c).**[21] Colourless oil (77mg,72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.02 (d, J = 8.2 Hz, 2H), 6.65 (d, J = 8.2 Hz, 2H), 3.55 (br s, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 143.9, 129.8, 127.8, 115.3, 20.5.



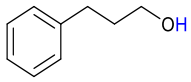
***N*-Methylaniline (6d).**[41] Colourless oil (92 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.25–7.19 (m, 2H), 6.76–6.72 (m, 1H), 6.66–6.64 (m, 2H), 3.67 (br s, 1H), 2.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 149.4, 129.2, 117.2, 112.4, 30.7.



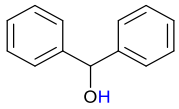
Ethyl 4-(methylamino)benzoate (6e).[42] White solid (144.6 mg, 84%). M. p. = 64.6–66.0 °C, reported: 57.1–57.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.87 (d, J = 8.8 Hz, 2H), 6.53 (d, J = 8.8 Hz, 2H), 4.30 (q, J = 7.1 Hz, 2H), 2.84 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 167.1, 153.0, 131.5, 118.3, 111.0, 60.2, 30.1, 14.5.



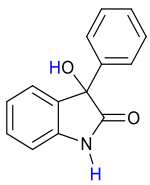
4-Aminopyrimidin-2(1*H*)-one (6f). Water is used to dissolve the compound. When the filtrate was concentrated, a white solid precipitates out from the solution, and another filtration afforded the product. White solid (93.3 mg, 84%). M. p. = 319.3–322.0 ℃, reported: 305 ℃. ^{1}H NMR (400 MHz, DMSO-*d*6) δ (ppm) 10.65 (br s, 1H), 7.34 (d, J = 7.0 Hz, 1H), 7.11 (br s, 2H), 5.59 (d, J = 7.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-*d*6) δ (ppm) 166.8, 157.1, 142.7, 92.7.



3-Phenylpropan-1-ol (10a).[43] Colourless oil (117 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.28–7.24 (m, 2H), 7.18–7.14 (m, 3H), 3.61 (t, J = 6.5 Hz, 2H), 2.66 (dd, J = 8.8, 6.8 Hz, 2H), 2.46 (br s, 1H), 1.89–1.82 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 141.9, 128.4 (2C), 125.8, 61.9, 34.1, 32.0.



Diphenylmethanol (10b).[44] White solid (154.7 mg, 84%). M. p. = 68.7–69.3 ℃, reported: 68 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.32–7.26(m, 8H), 7.23–7.19 (m, 2H), 5.76 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 143.9, 128.6, 127.6, 126.7, 76.3.



3-Hydroxy-3-phenylindolin-2-one (10d).[23] Ethyl acetate was used to dissolve the compound. White solid (168.9 mg, 75%). M. p. = 208.9–210 ℃, reported: 213–214 ℃. ^{1}H NMR (400 MHz, DMSO-*d*6) δ (ppm) 10.40 (br s, 1H), 7.33–7.23 (m, 6H), 7.09 (d, J = 7.4 Hz, 1H), 7.98–6.94 (m, 1H), 6.90 (d, J = 7.7 Hz, 1H), 6.62 (br s, 1H). ^{13}C NMR

(101 MHz, DMSO-*d*6) δ (ppm) 178.5, 141.9, 141.5, 133.8, 129.2, 128.1, 127.4, 125.4, 124.8, 122.0, 109.8, 77.3.

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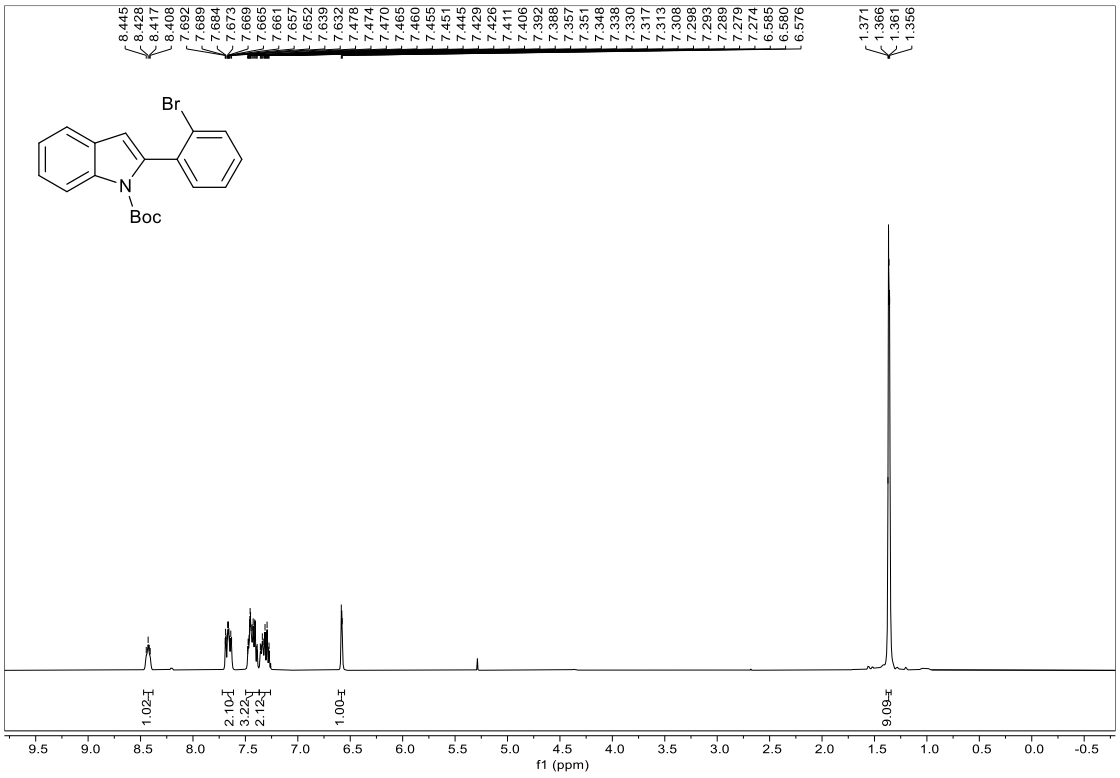
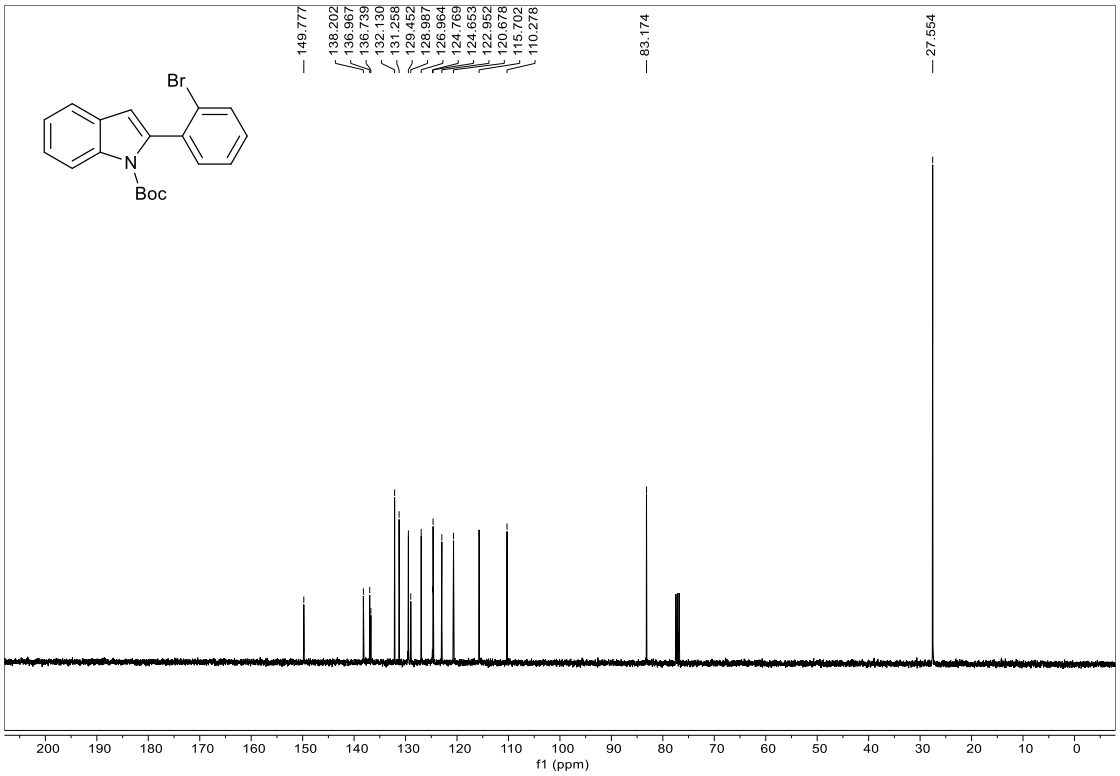
7. ^{1}H and ^{13}C NMR Spectra of Unknown Substrates

^{1}H NMR spectra of **1i** ($CDCl_3$, 400 MHz)



^{13}C NMR spectra of **1i** ($CDCl_3$, 101 MHz)



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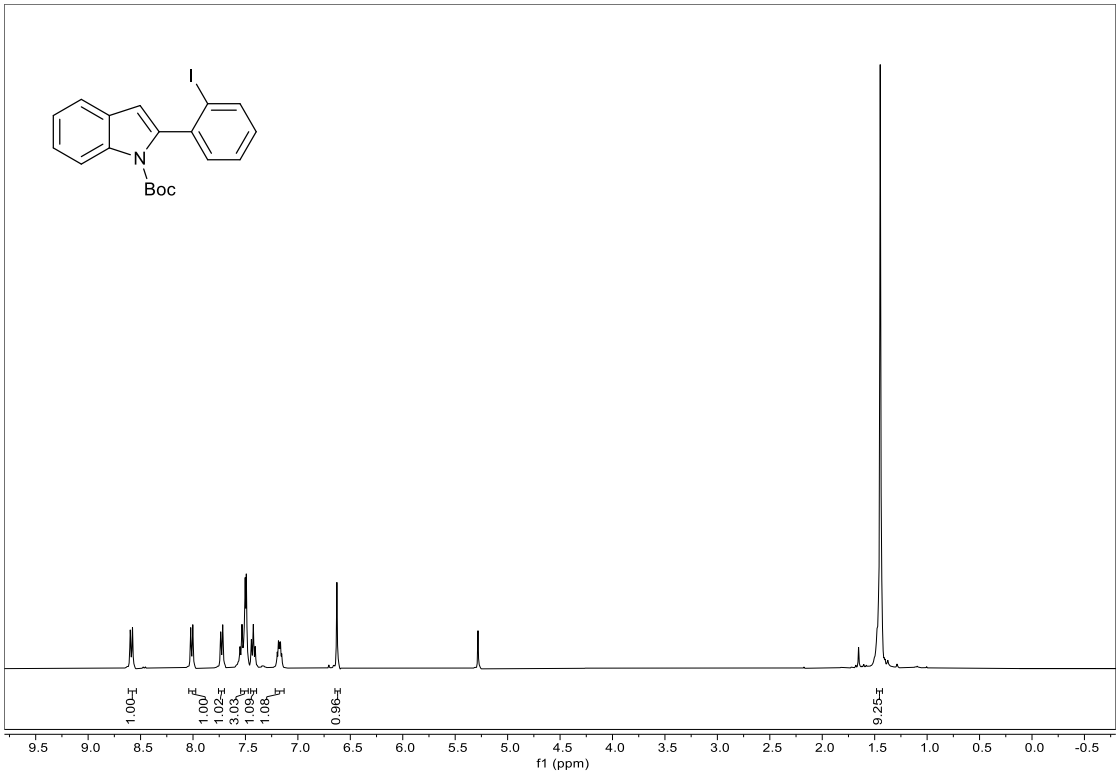

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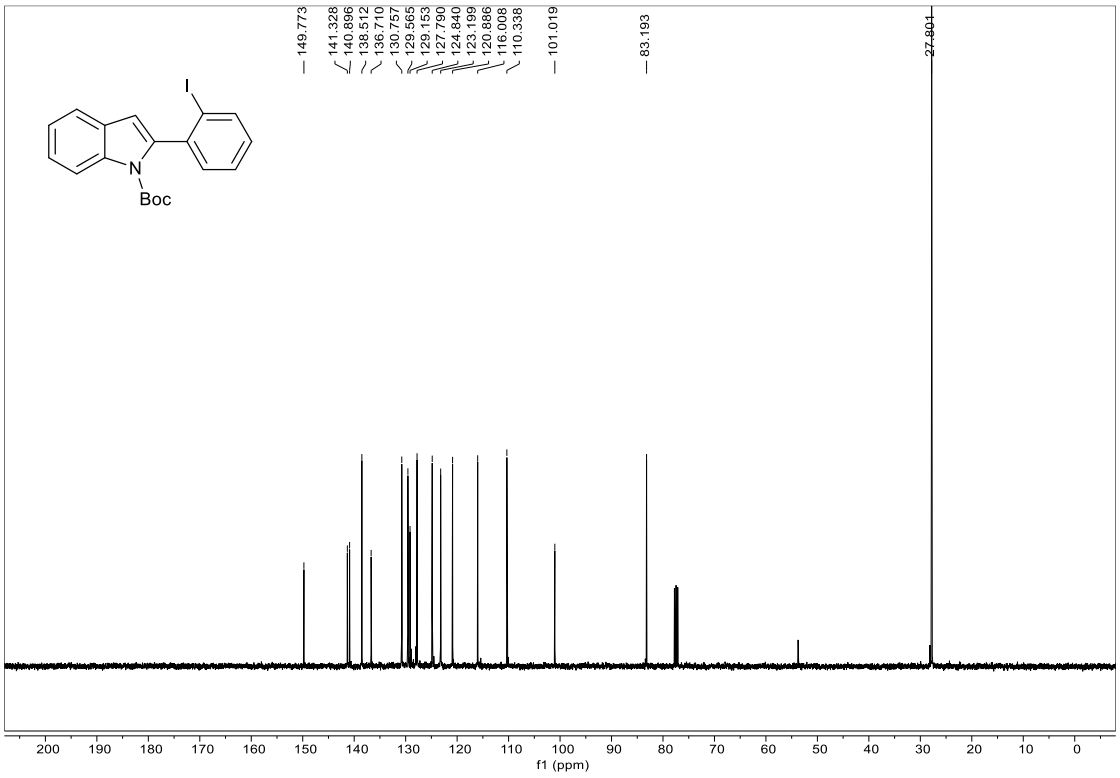
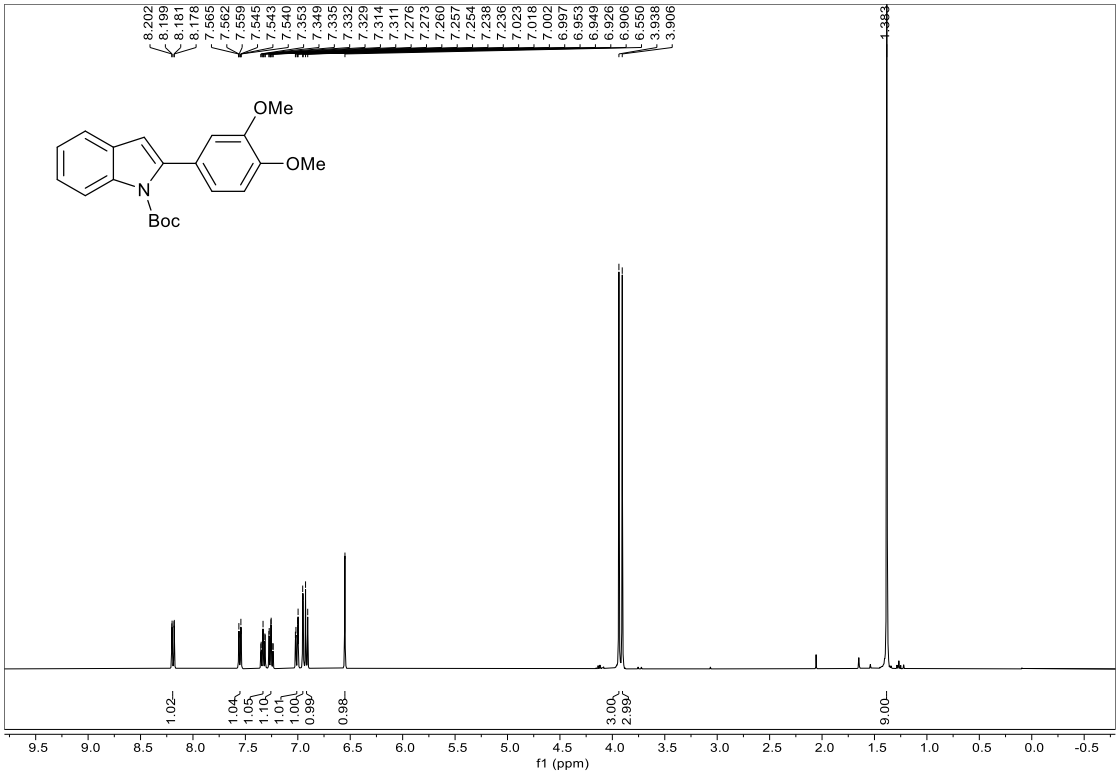


^{1}H NMR spectra of **1l** ($CDCl_3$, 400 MHz)



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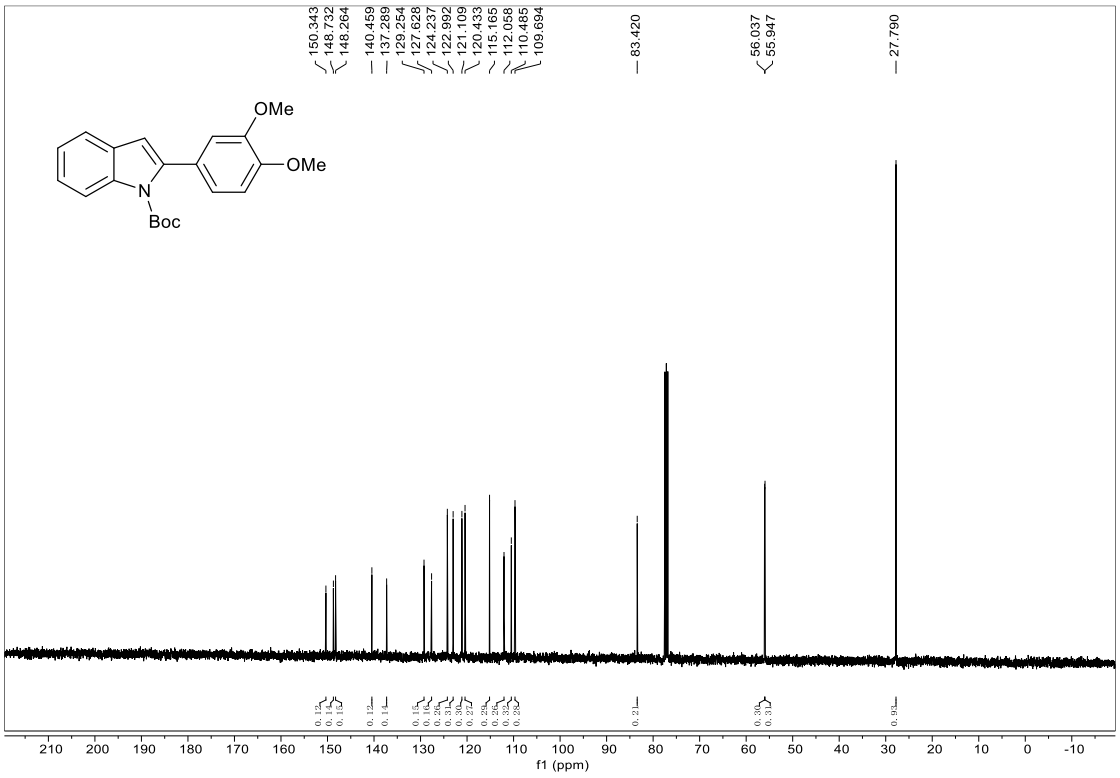

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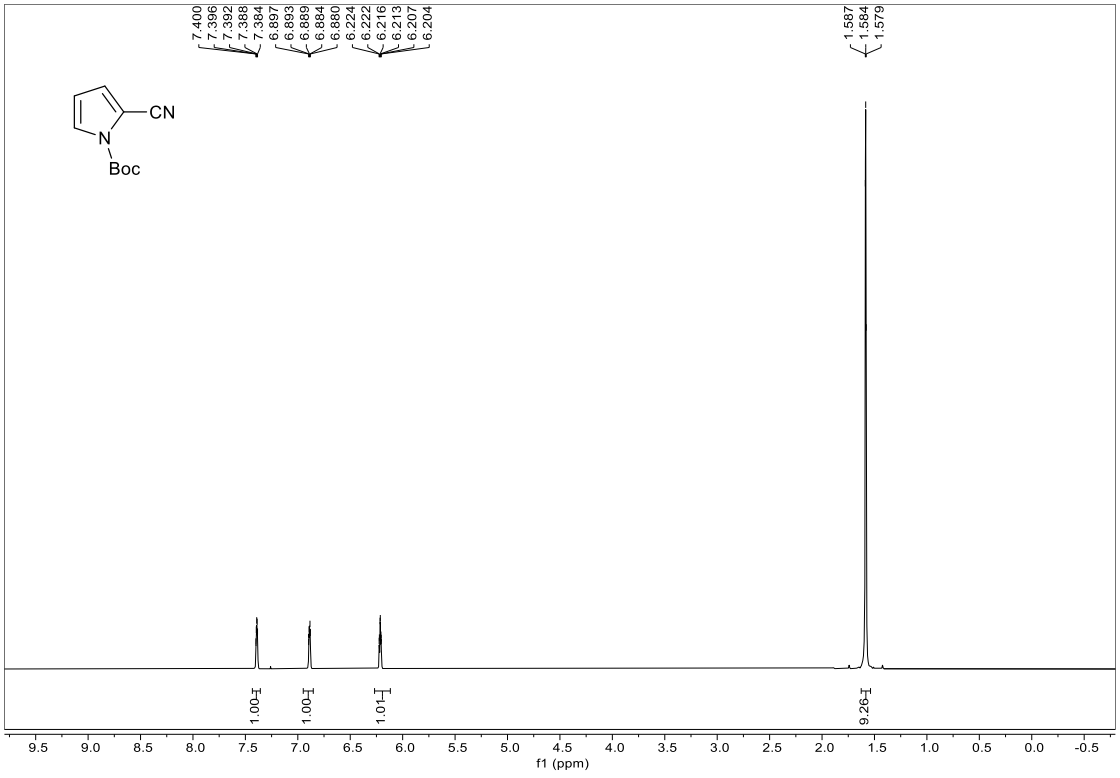

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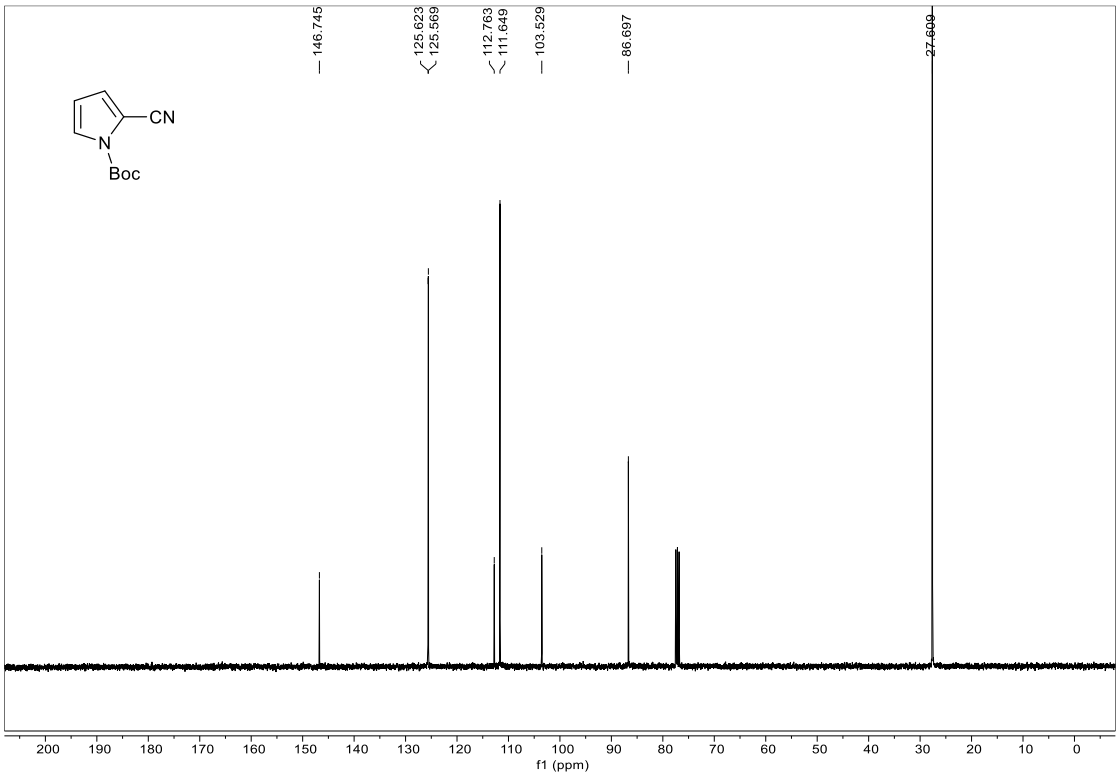
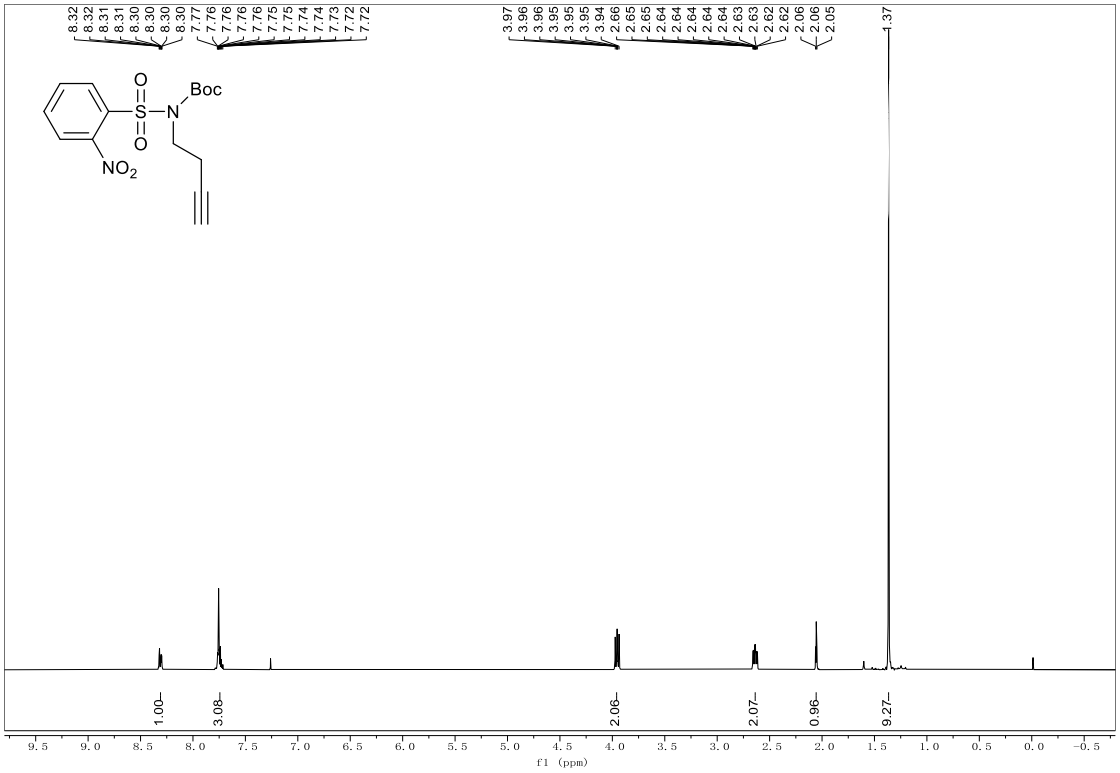
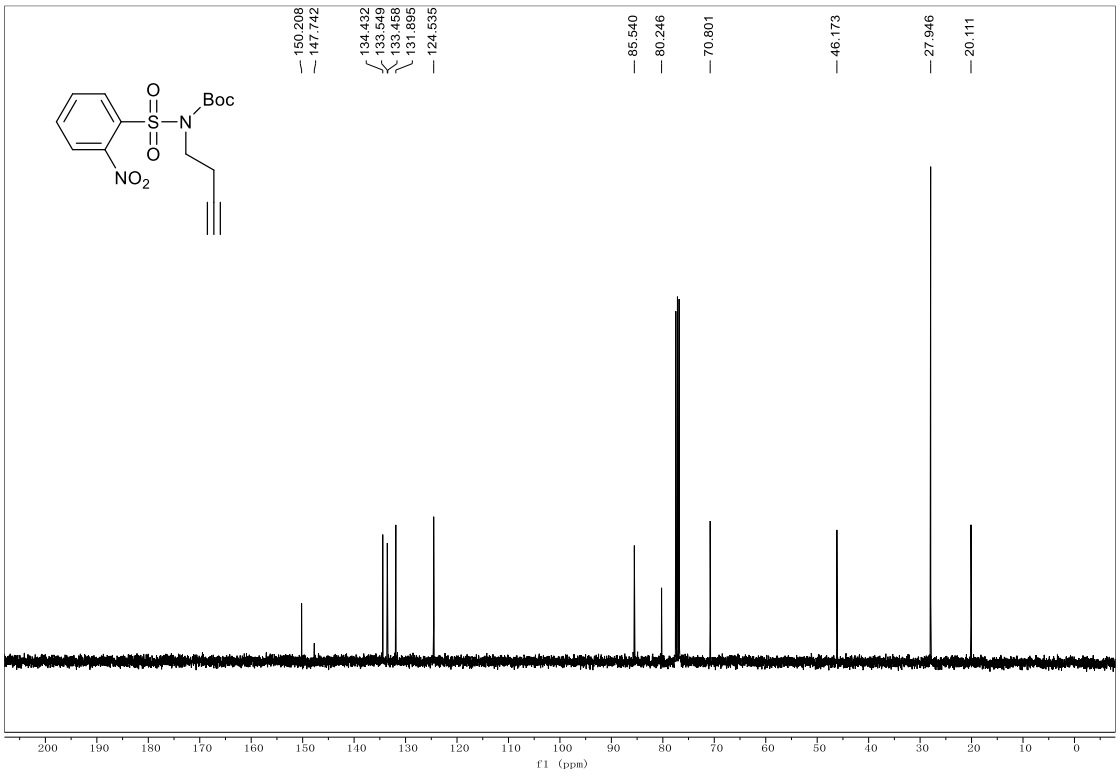


^{1}H NMR spectra of **3b** ($CDCl_3$, 400 MHz)



^{13}C NMR spectra of **3b** ($CDCl_3$, 101 MHz)



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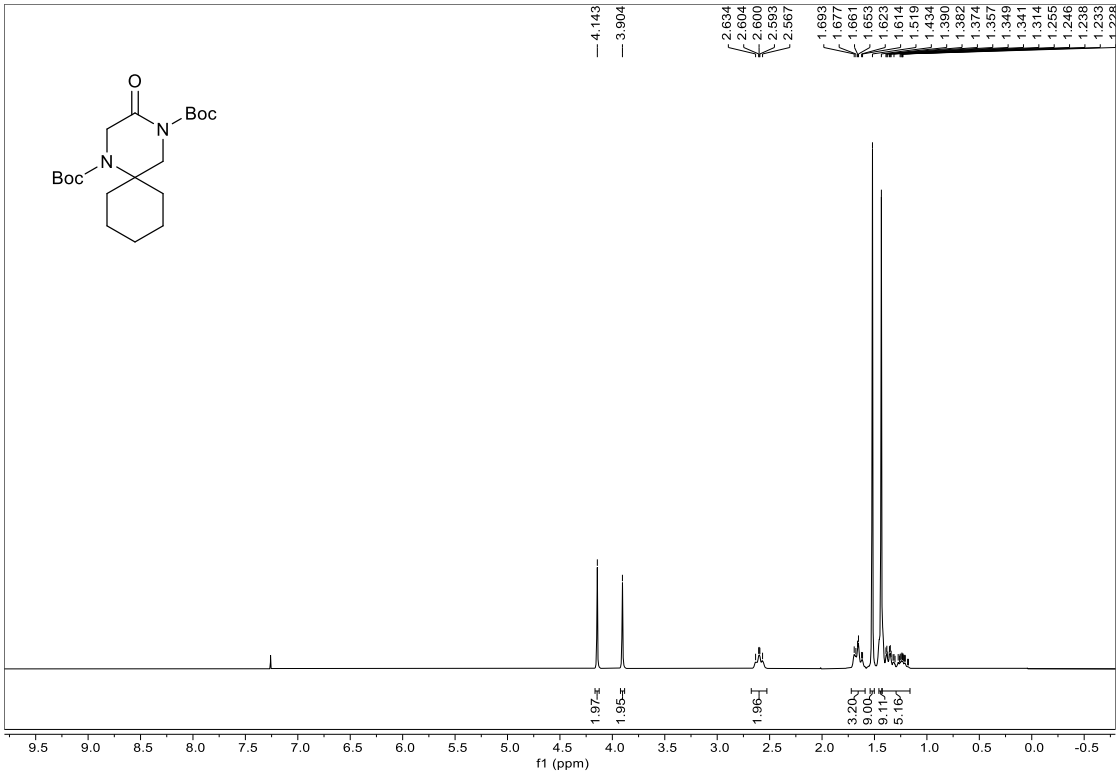

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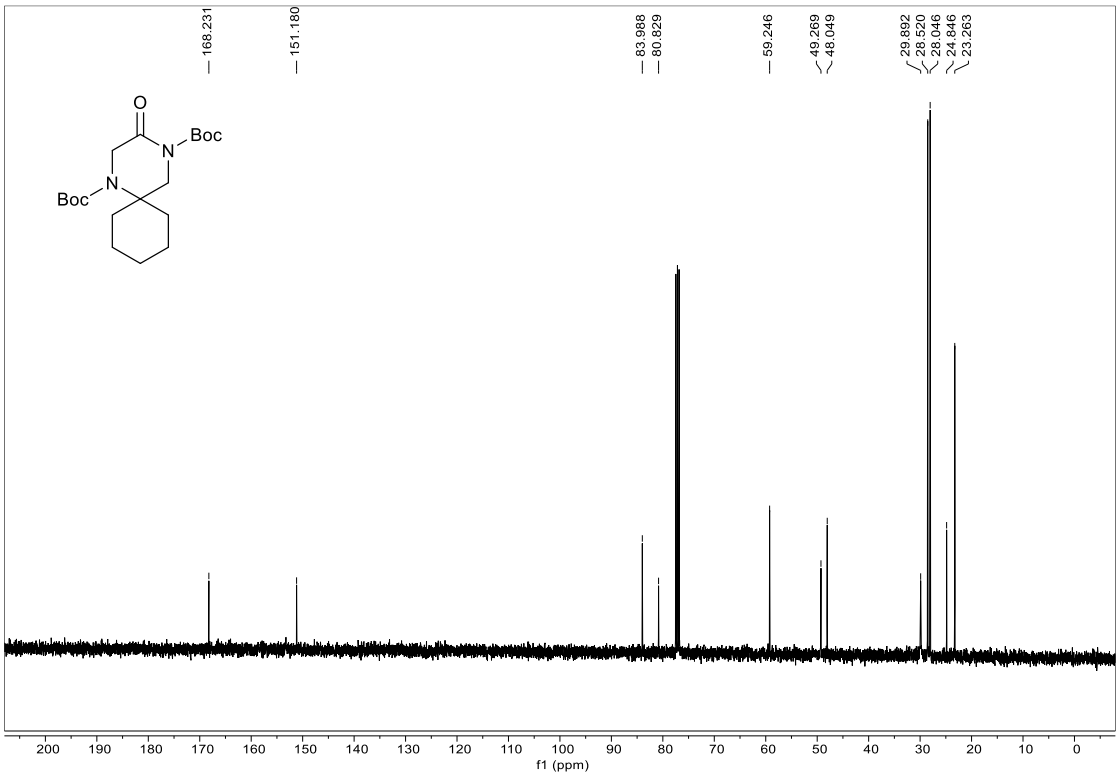
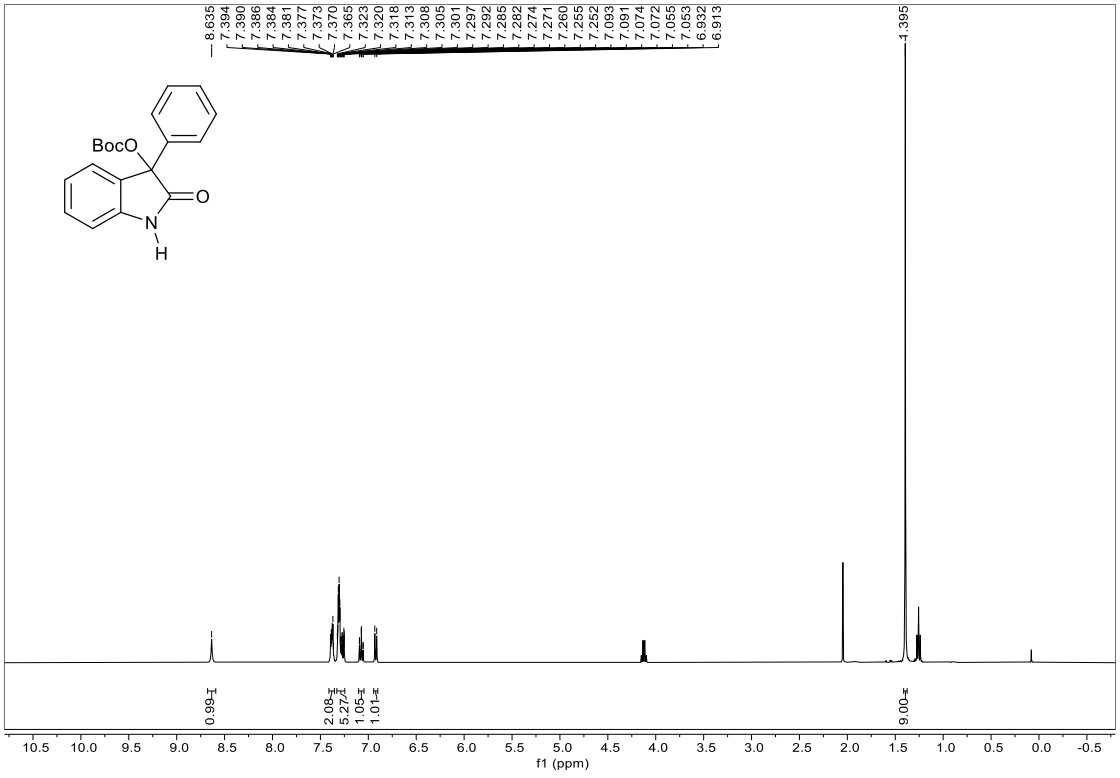


^{1}H NMR spectra of **10c** ($CDCl_3$, 400 MHz)



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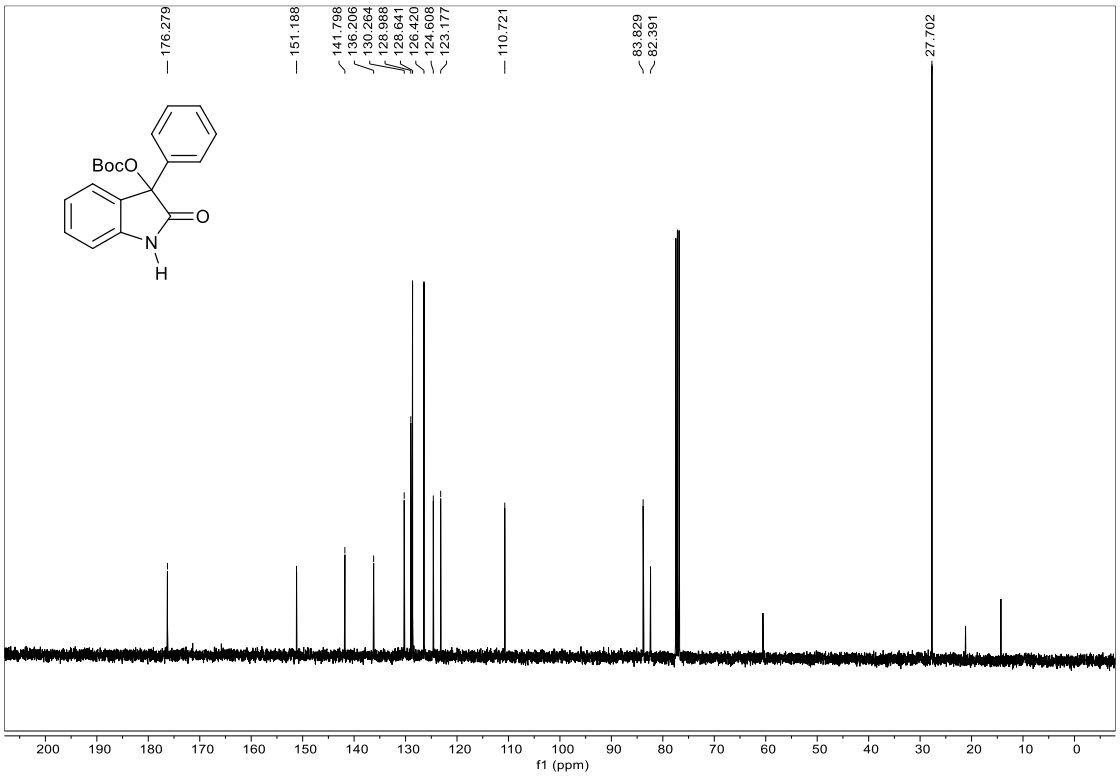
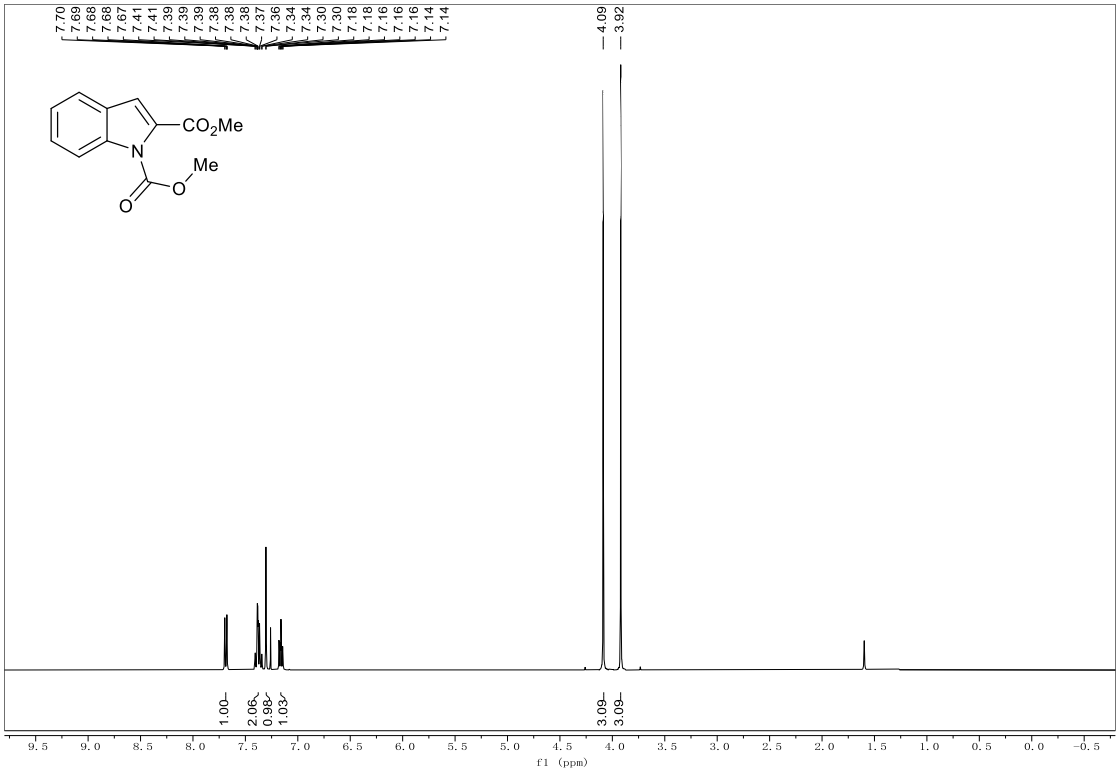
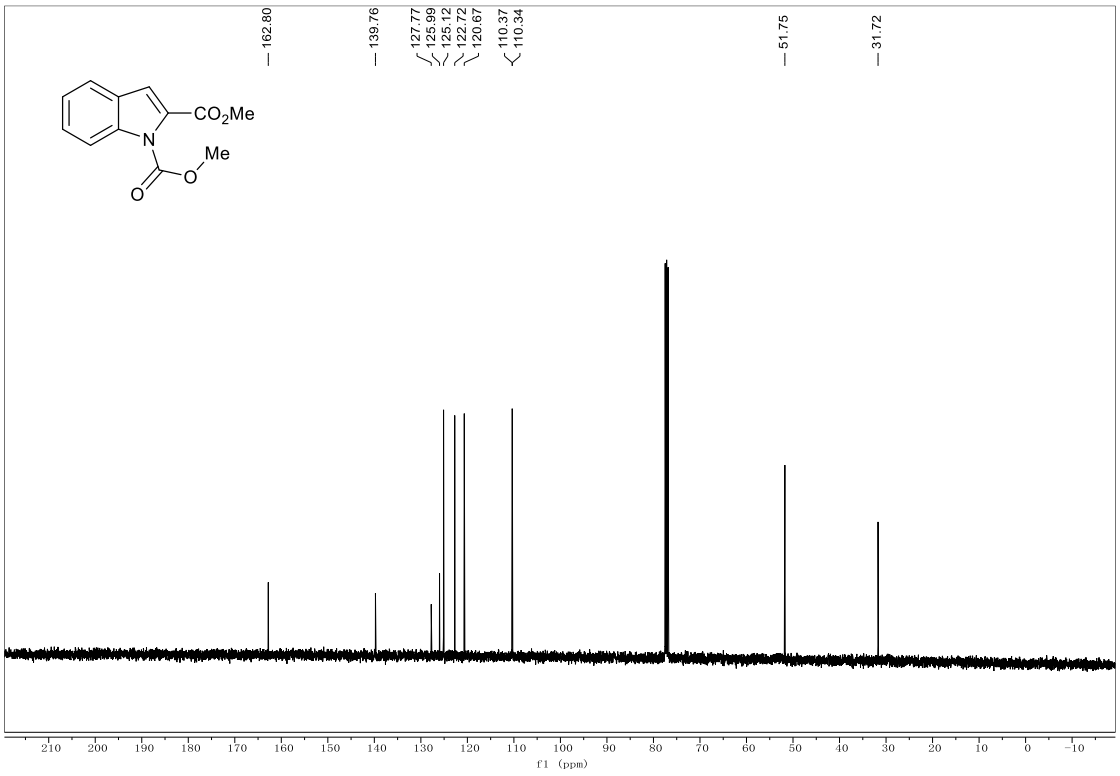


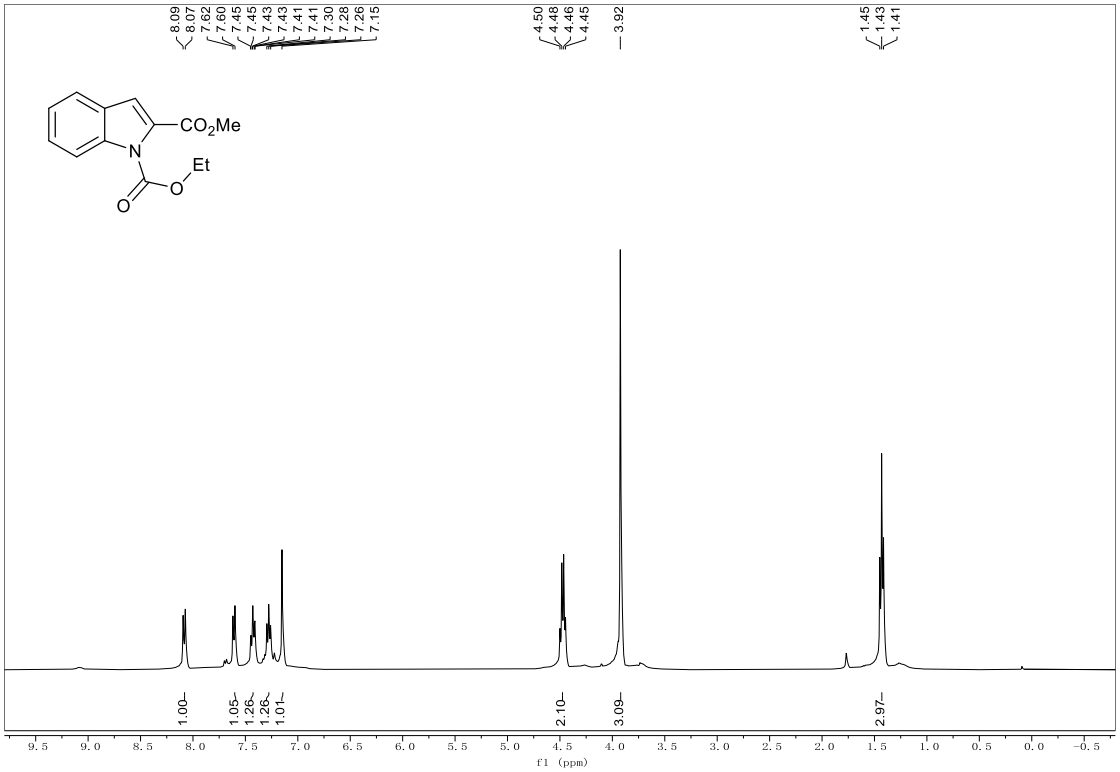
^{1}H NMR spectra of **11a** ($CDCl_3$, 400 MHz)



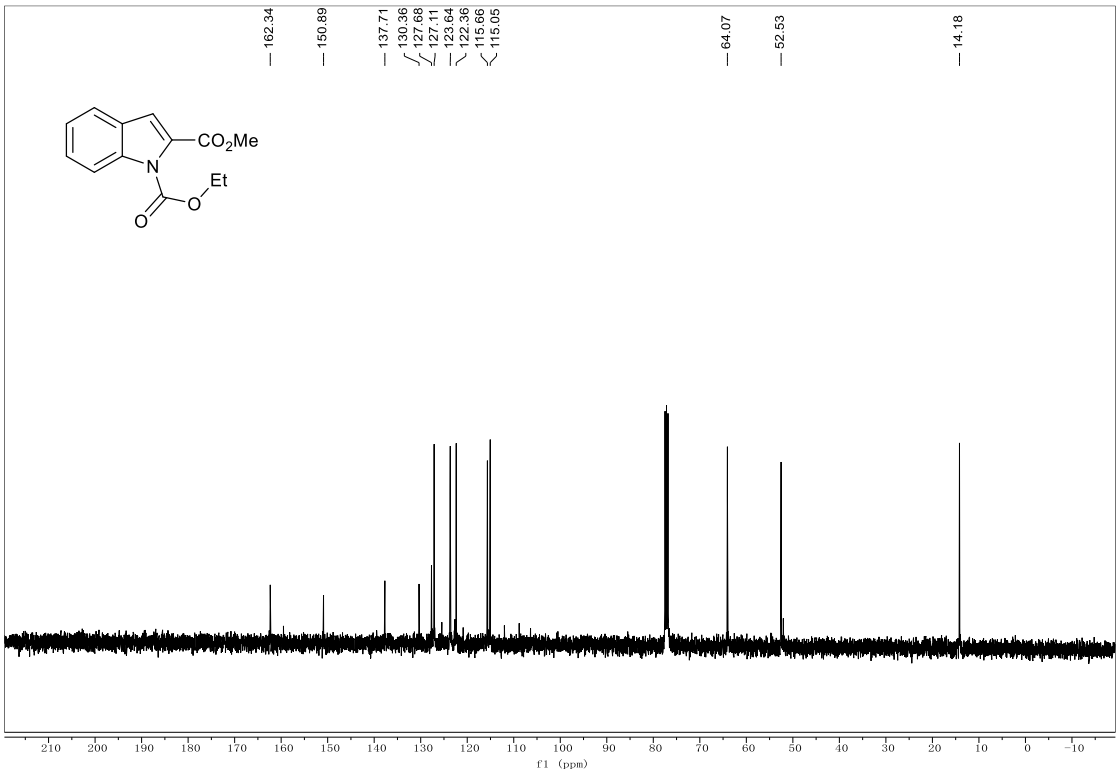
^{13}C NMR spectra of **11a** ($CDCl_3$, 101 MHz)



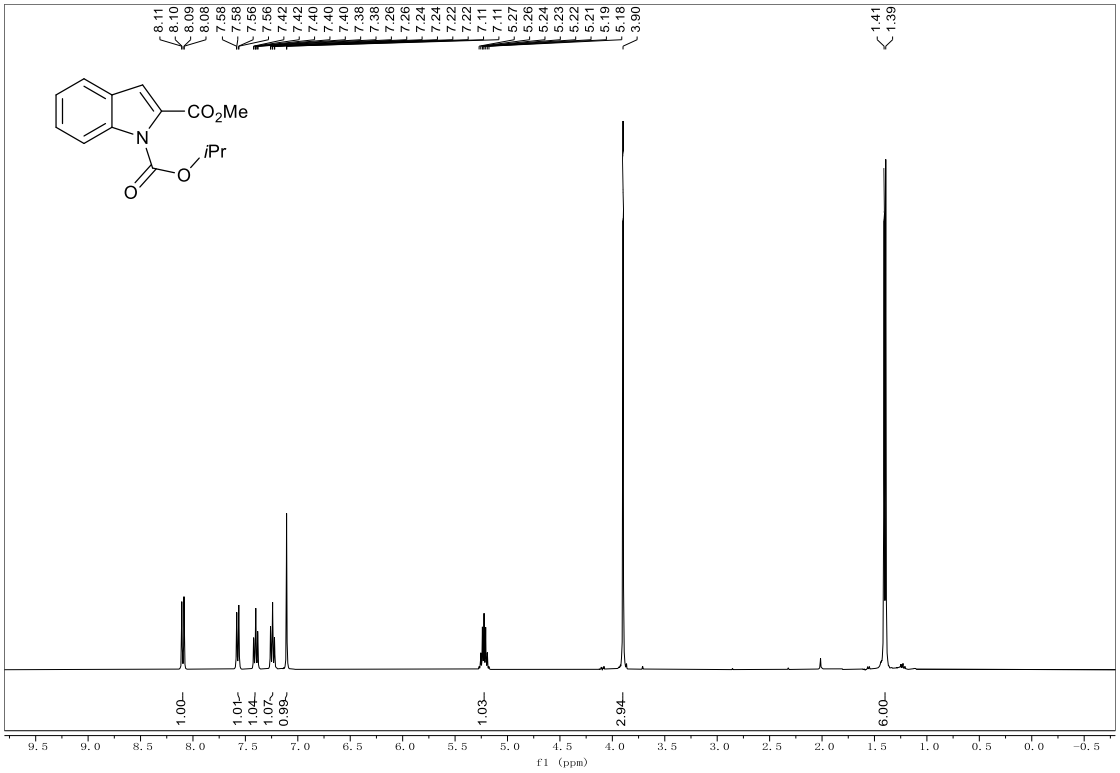
^{1}H NMR spectra of **11b** ($CDCl_3$, 400 MHz)



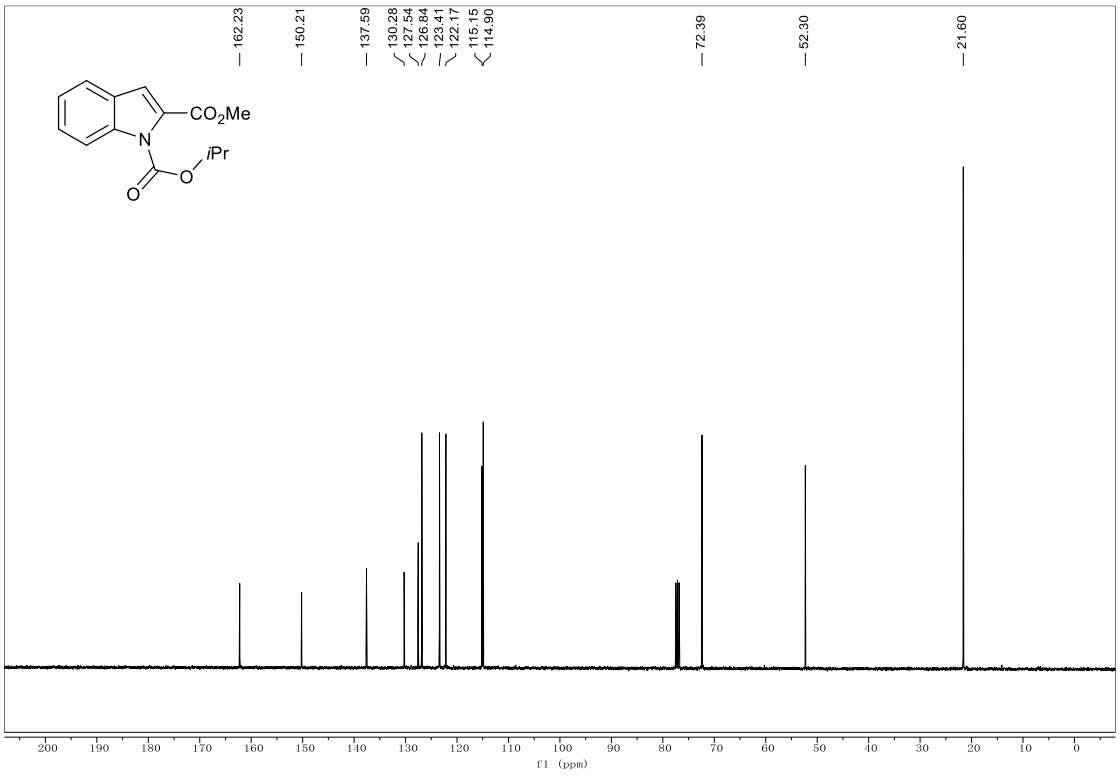
^{13}C NMR spectra of **11b**($CDCl_3$, 101 MHz)



^{1}H NMR spectra of **11c** ($CDCl_3$, 400 MHz)

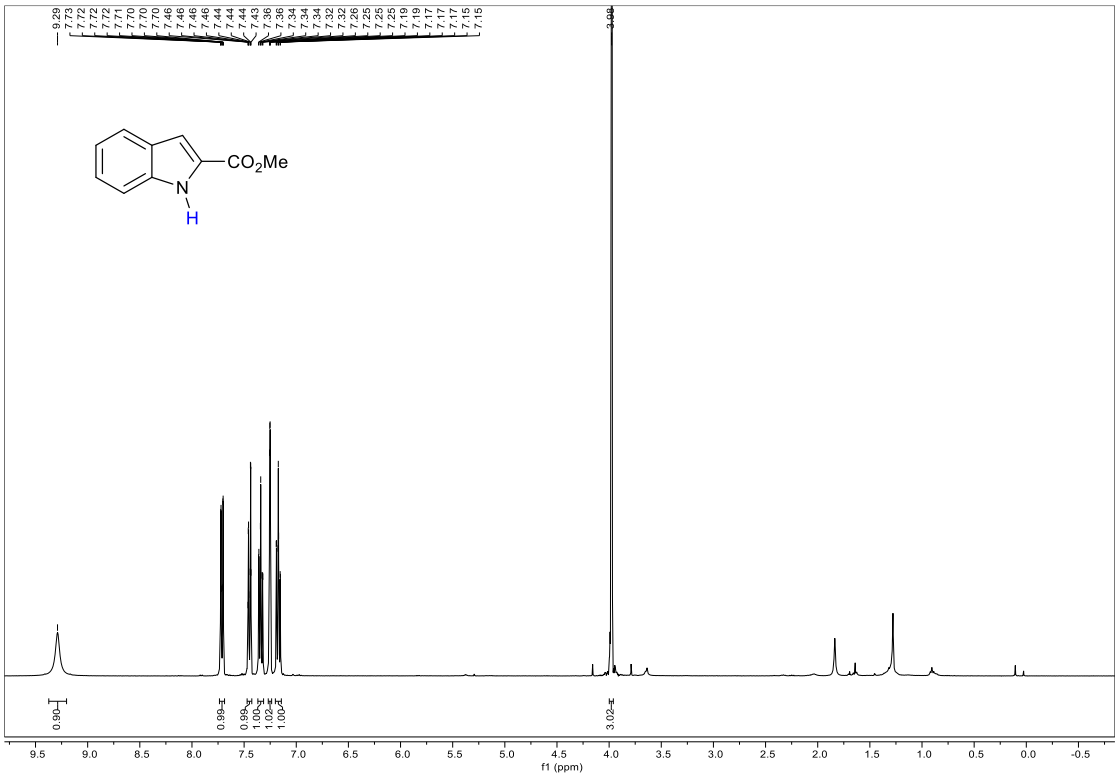


^{13}C NMR spectra of **11c**($CDCl_3$, 101 MHz)

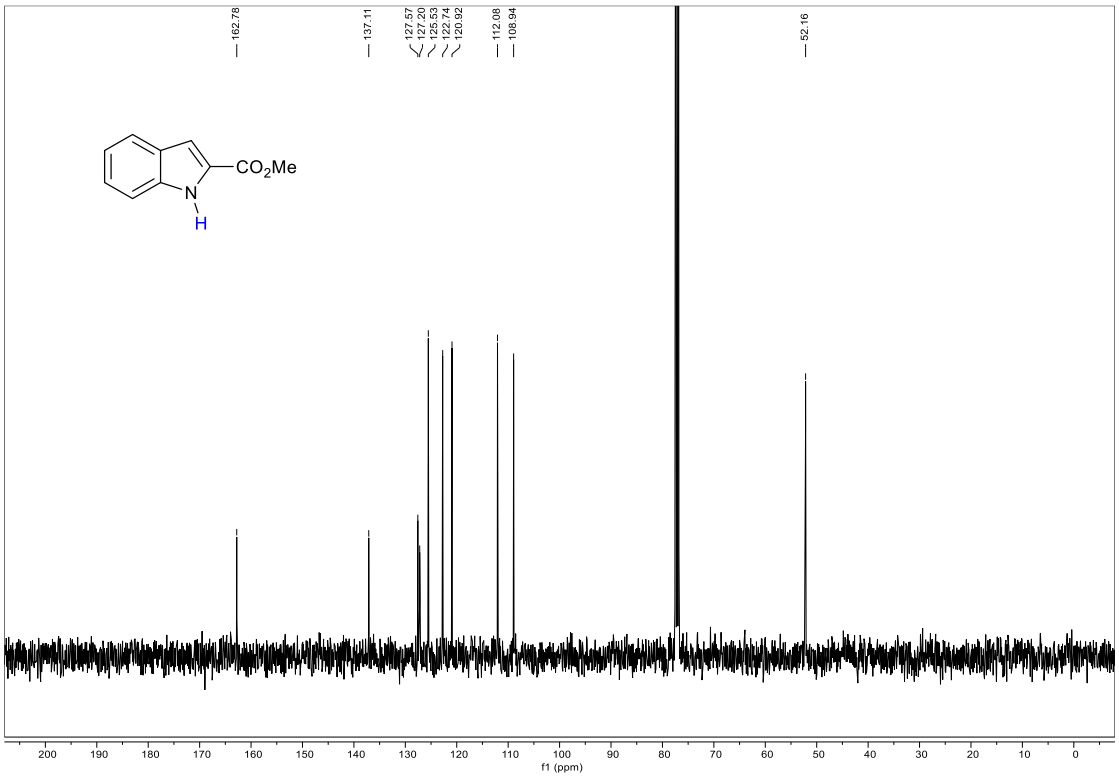


8. ^{1}H and ^{13}C NMR Spectra of Products

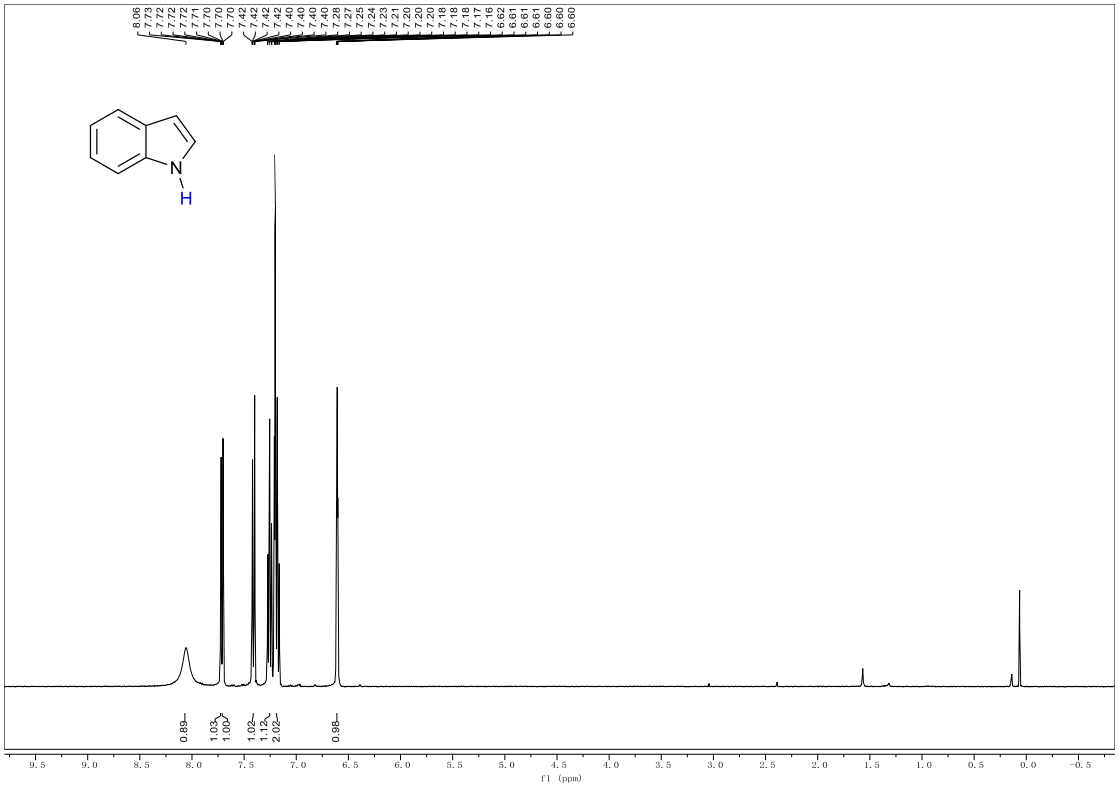
^{1}H NMR spectra of **2a** ($CDCl_3$, 400 MHz)



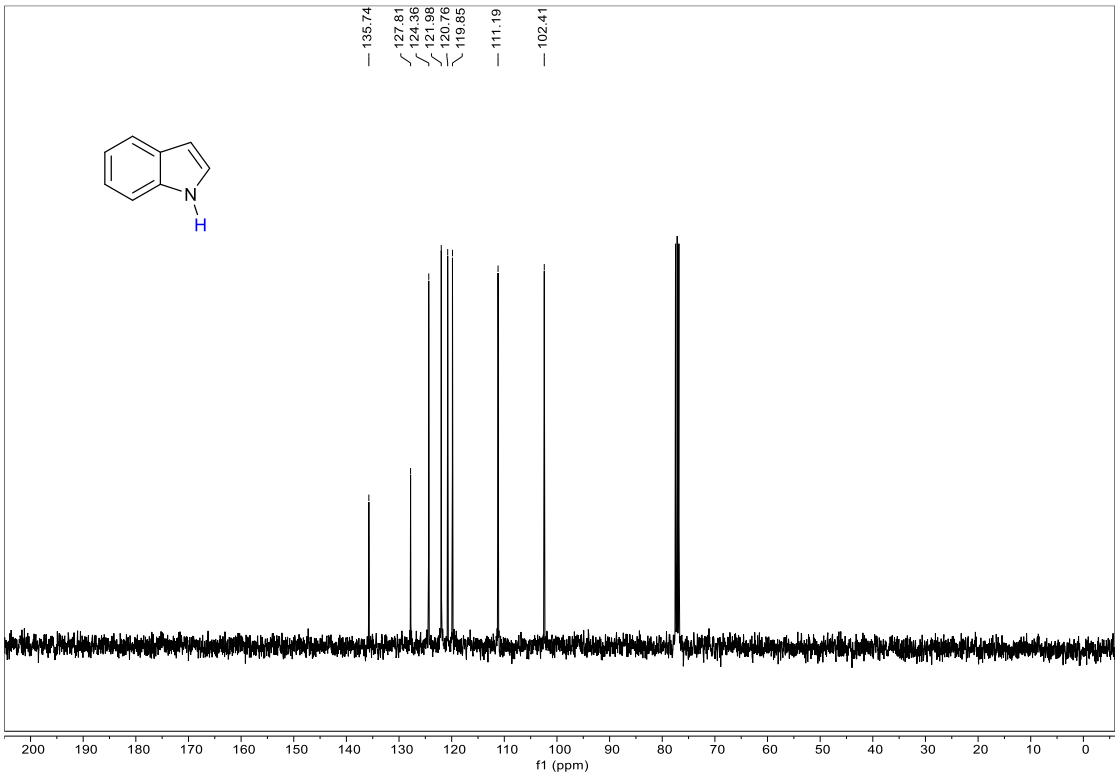
^{13}C NMR spectra of **2a** ($CDCl_3$, 101 MHz)



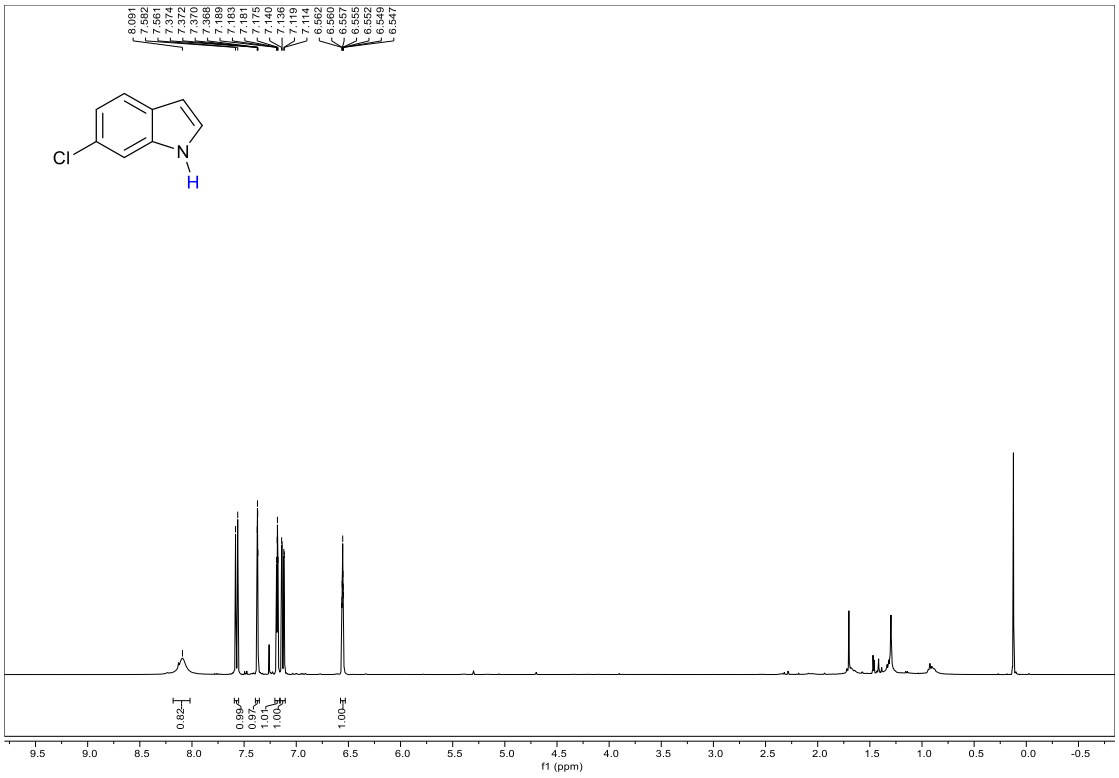
^{1}H NMR spectra of **2b** ($CDCl_3$, 400 MHz)



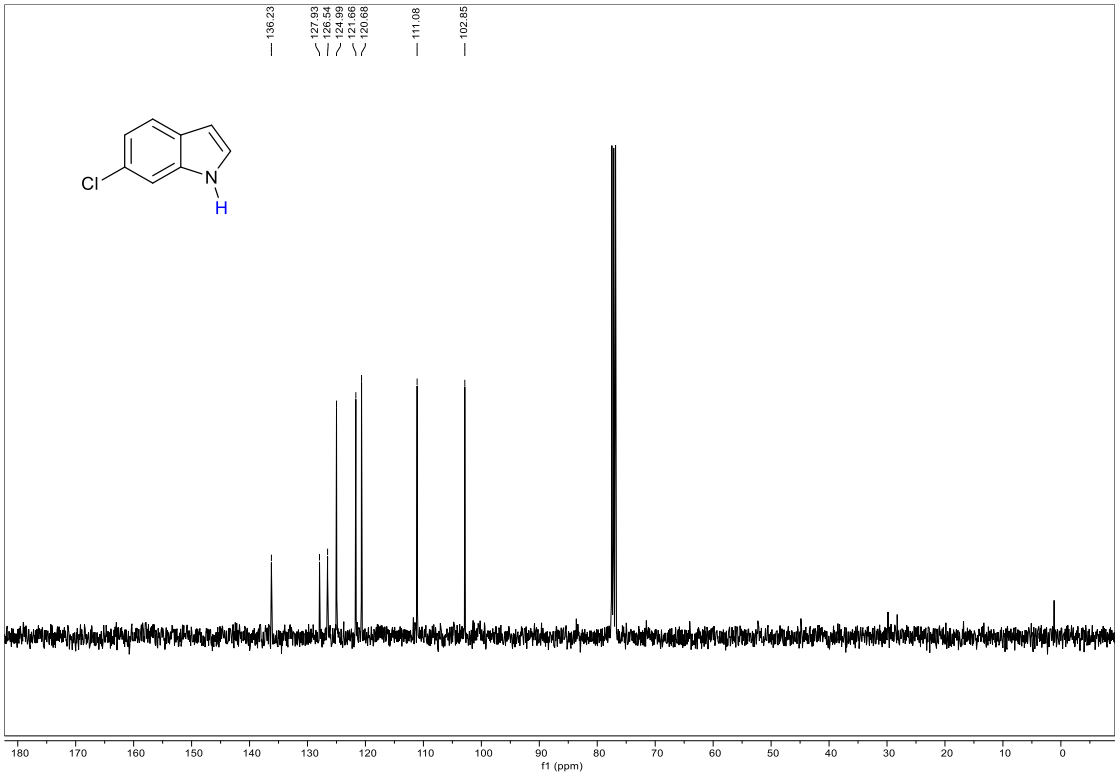
^{13}C NMR spectra of **2b** ($CDCl_3$, 101 MHz)



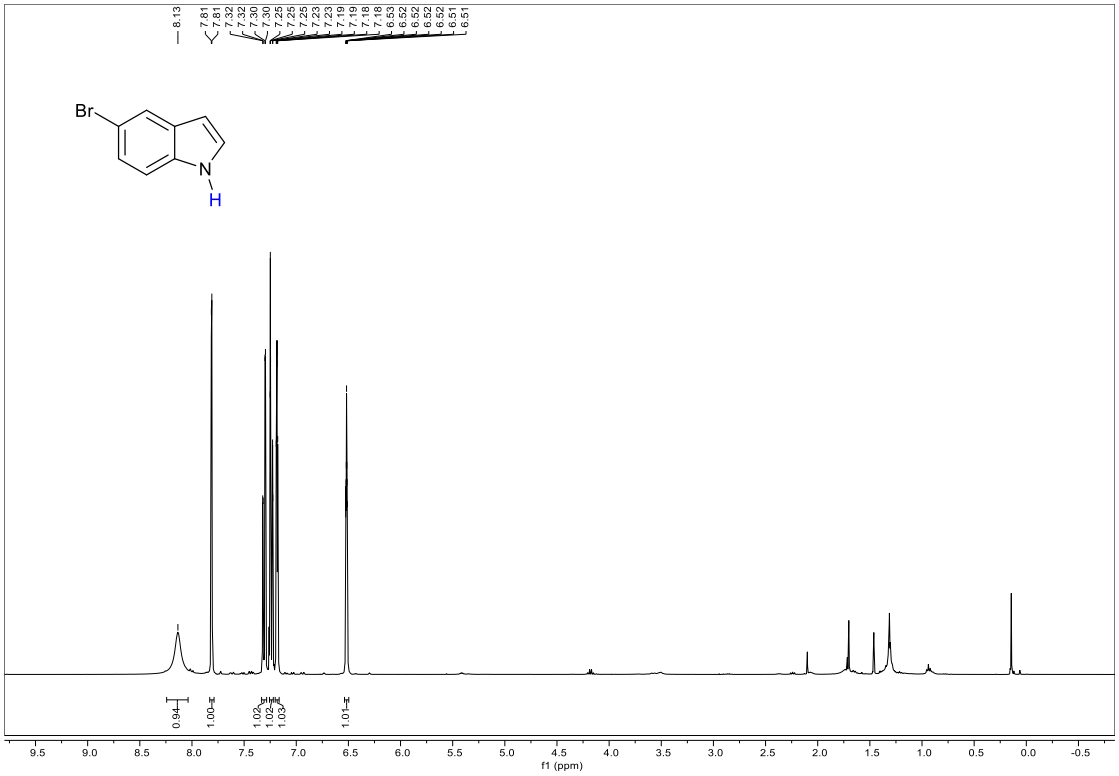
^{1}H NMR spectra of **2c** ($CDCl_3$, 400 MHz)



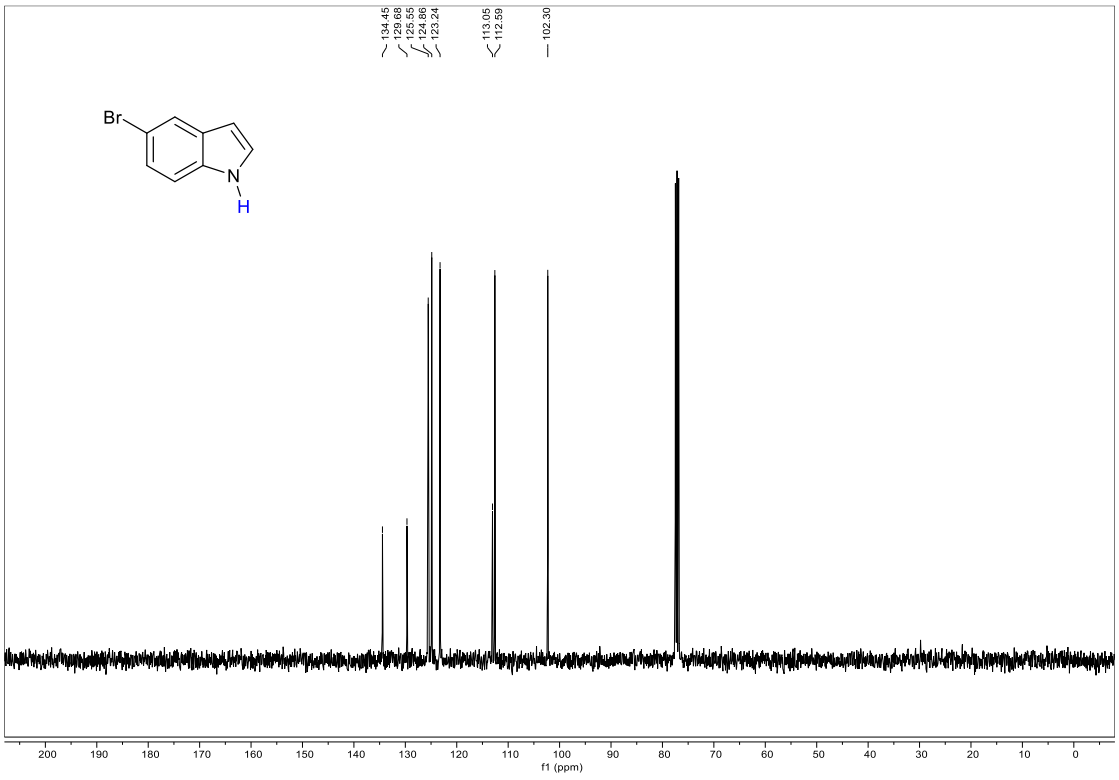
^{13}C NMR spectra of **2c** ($CDCl_3$, 101 MHz)



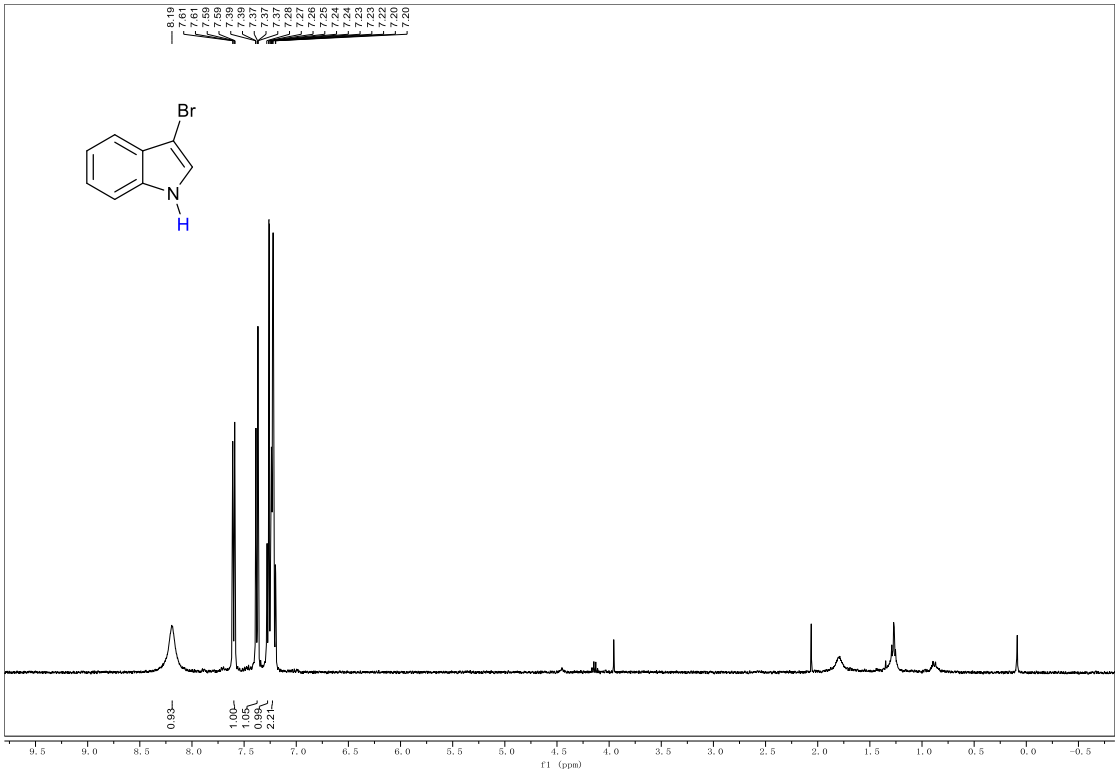
^{1}H NMR spectra of **2d** ($CDCl_3$, 400 MHz)



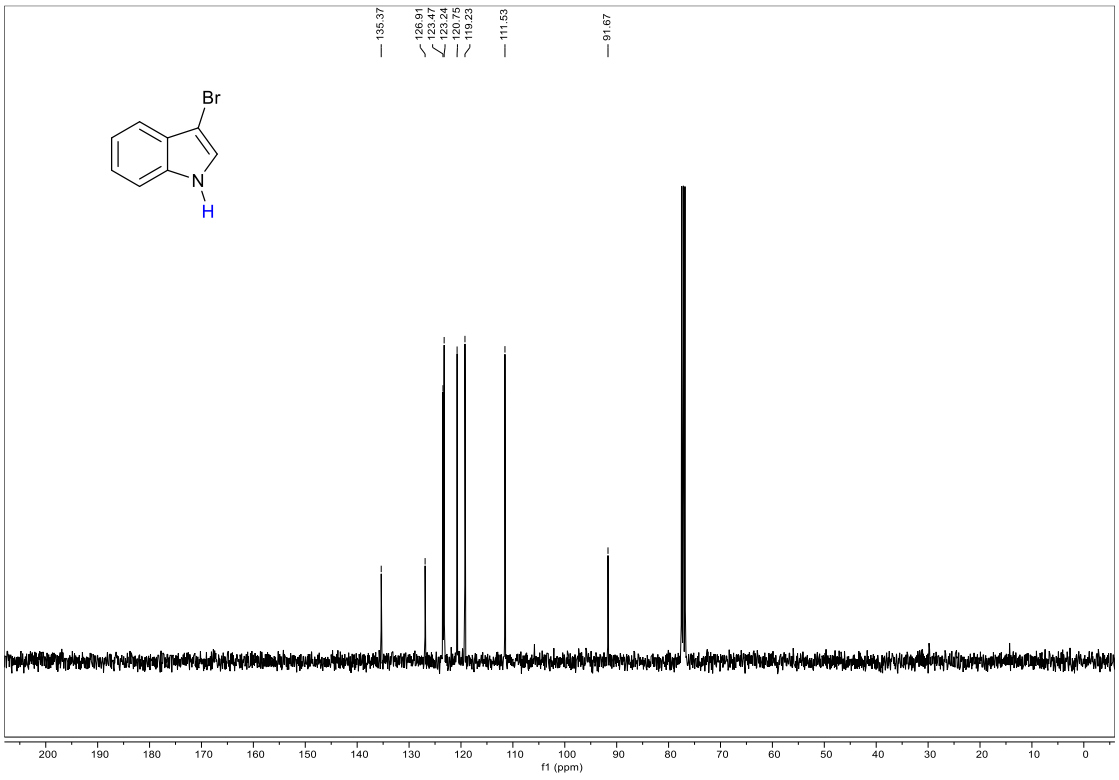
^{13}C NMR spectra of **2d** ($CDCl_3$, 101 MHz)



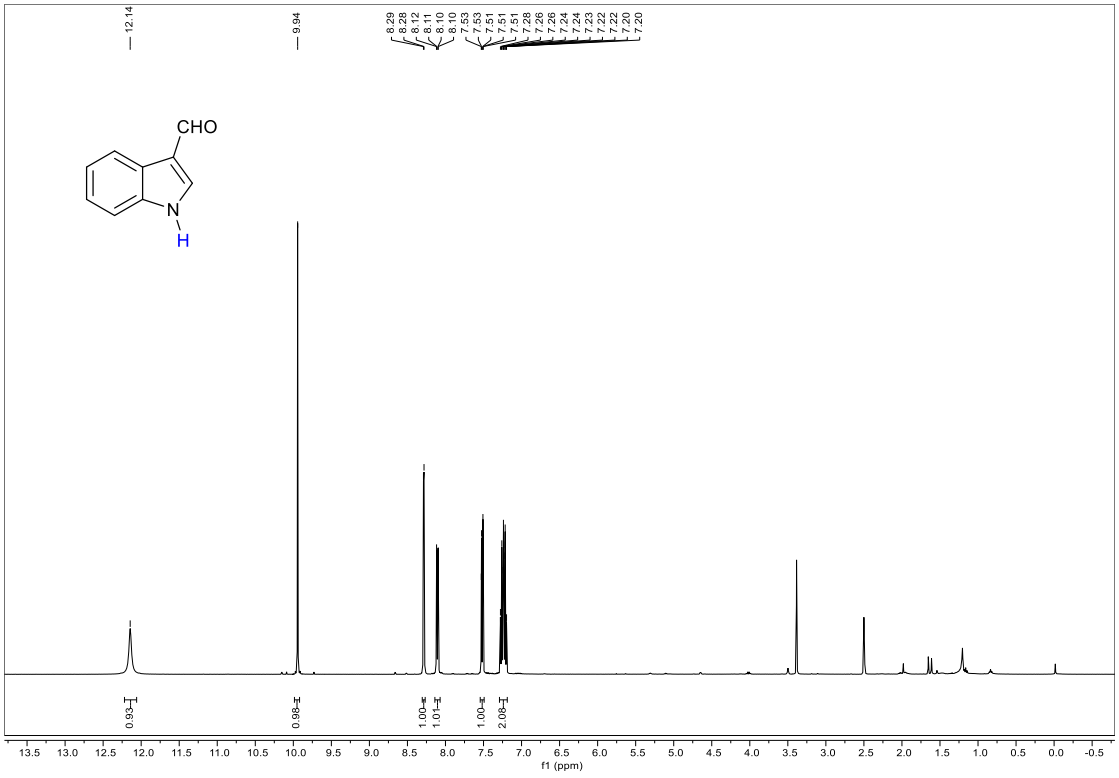
^{1}H NMR spectra of **2e** ($CDCl_3$, 400 MHz)



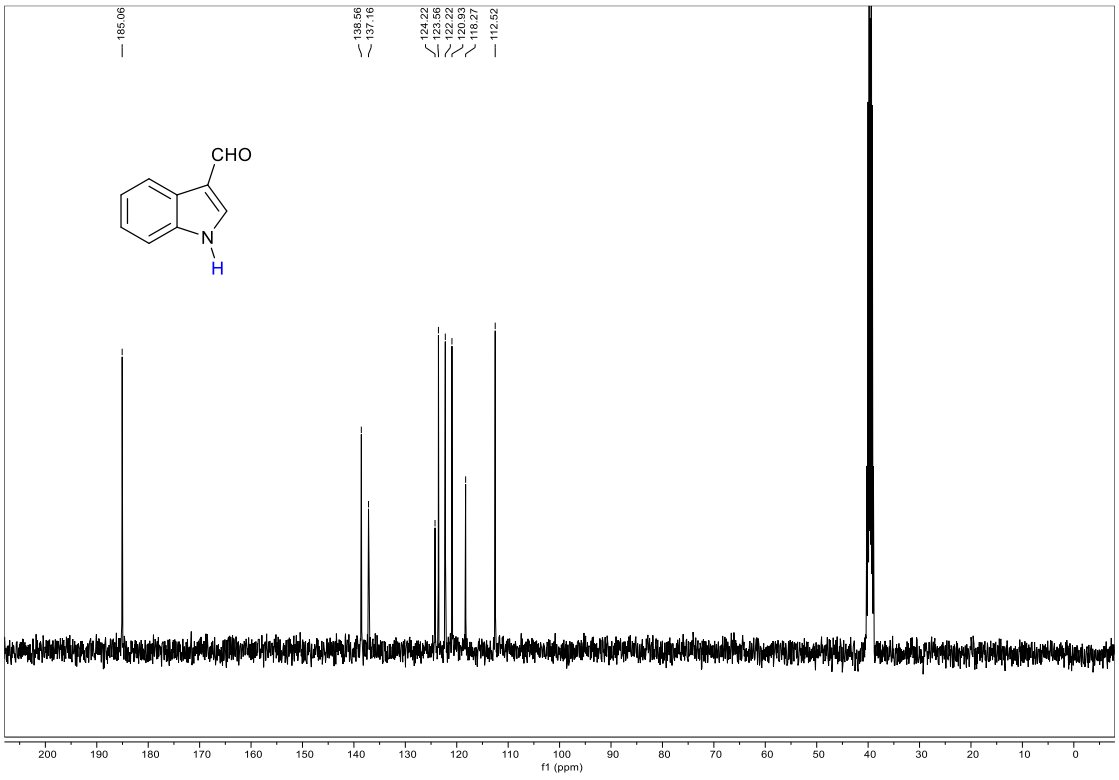
^{13}C NMR spectra of **2e** ($CDCl_3$, 101 MHz)



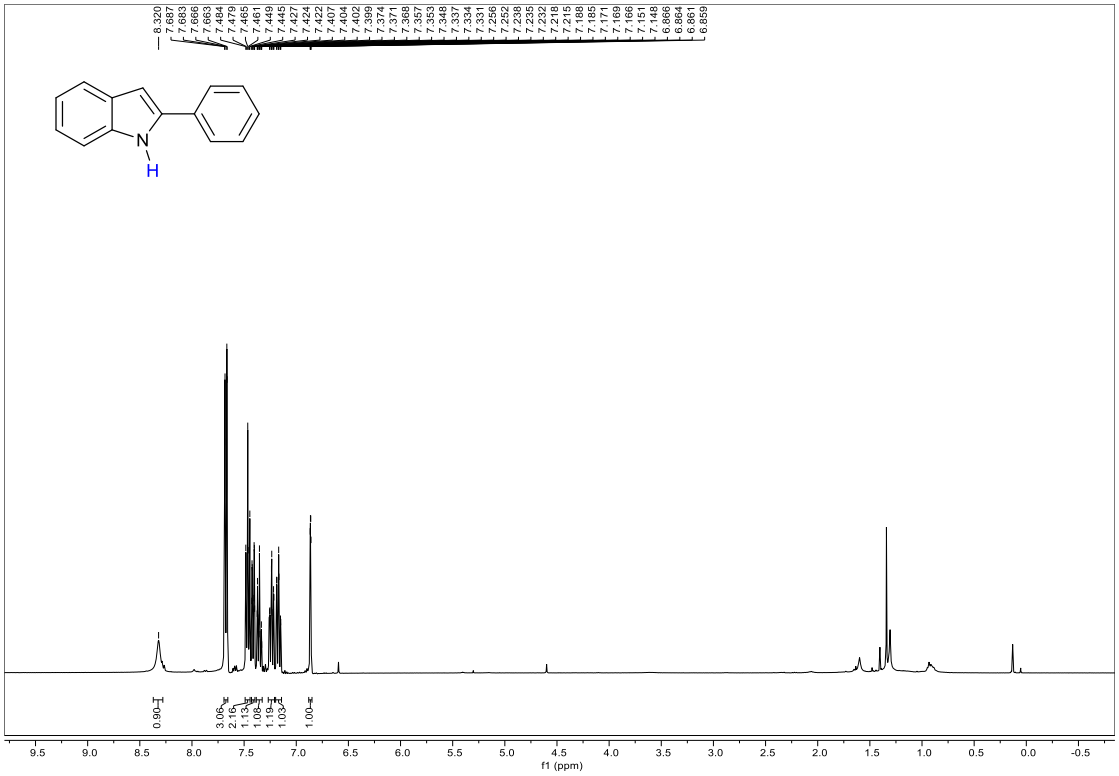
^{1}H NMR spectra of **2f** (DMSO-*d*6, 400 MHz)



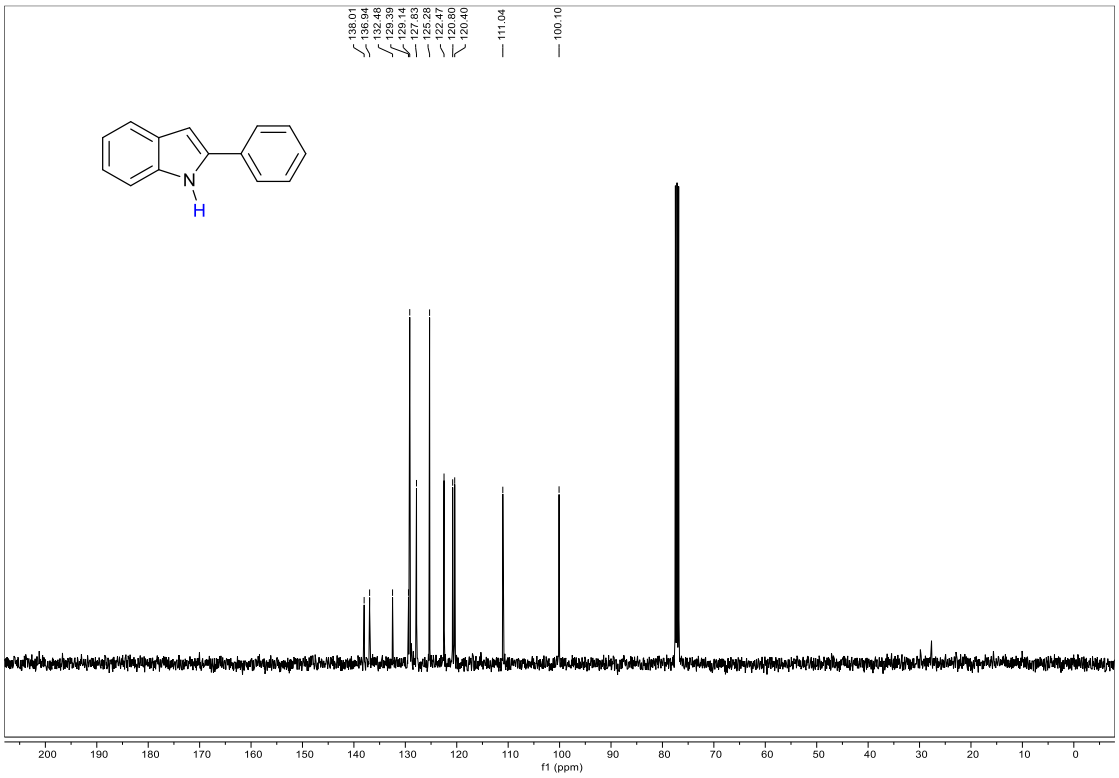
^{13}C NMR spectra of **2f** (DMSO-*d*6, 101 MHz)



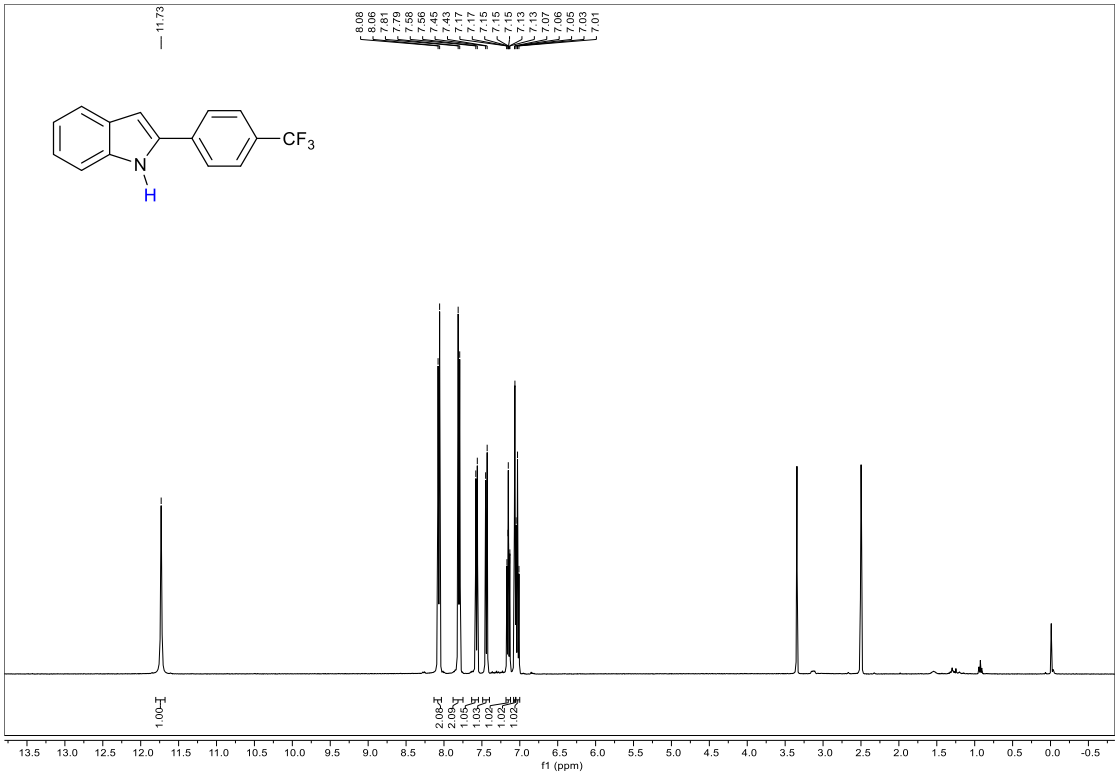
^{1}H NMR spectra of **2g** ($CDCl_3$, 400 MHz)



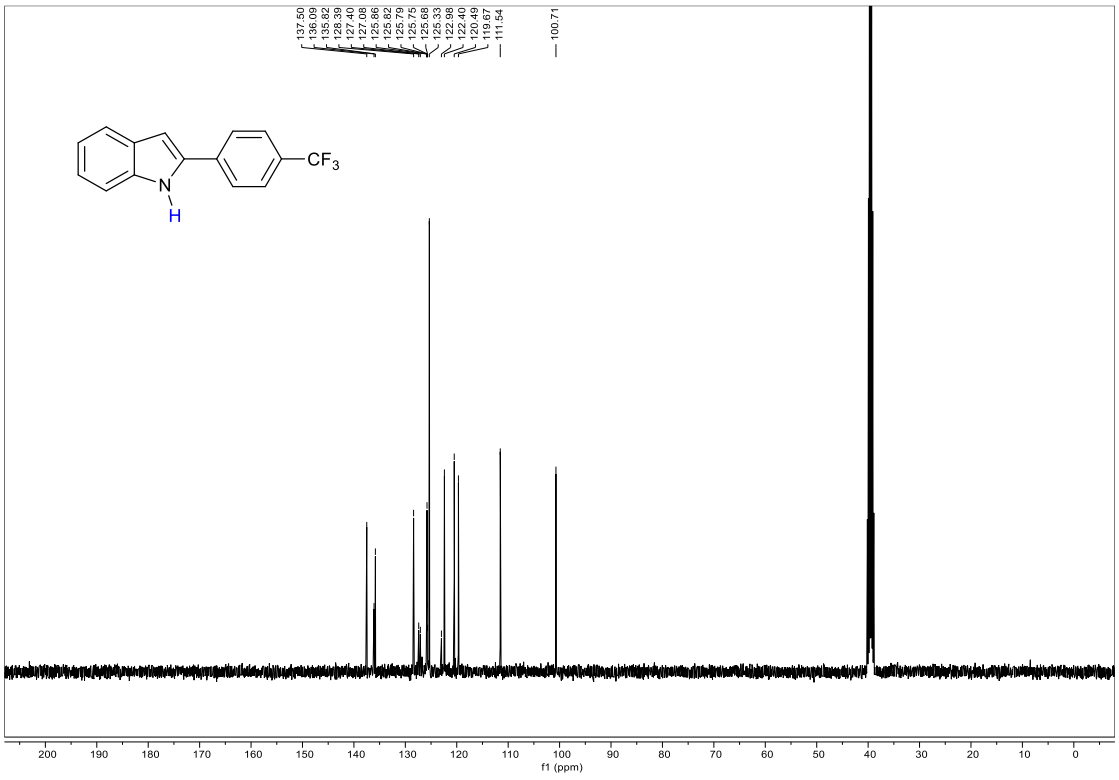
^{13}C NMR spectra of **2g** ($CDCl_3$, 101 MHz)



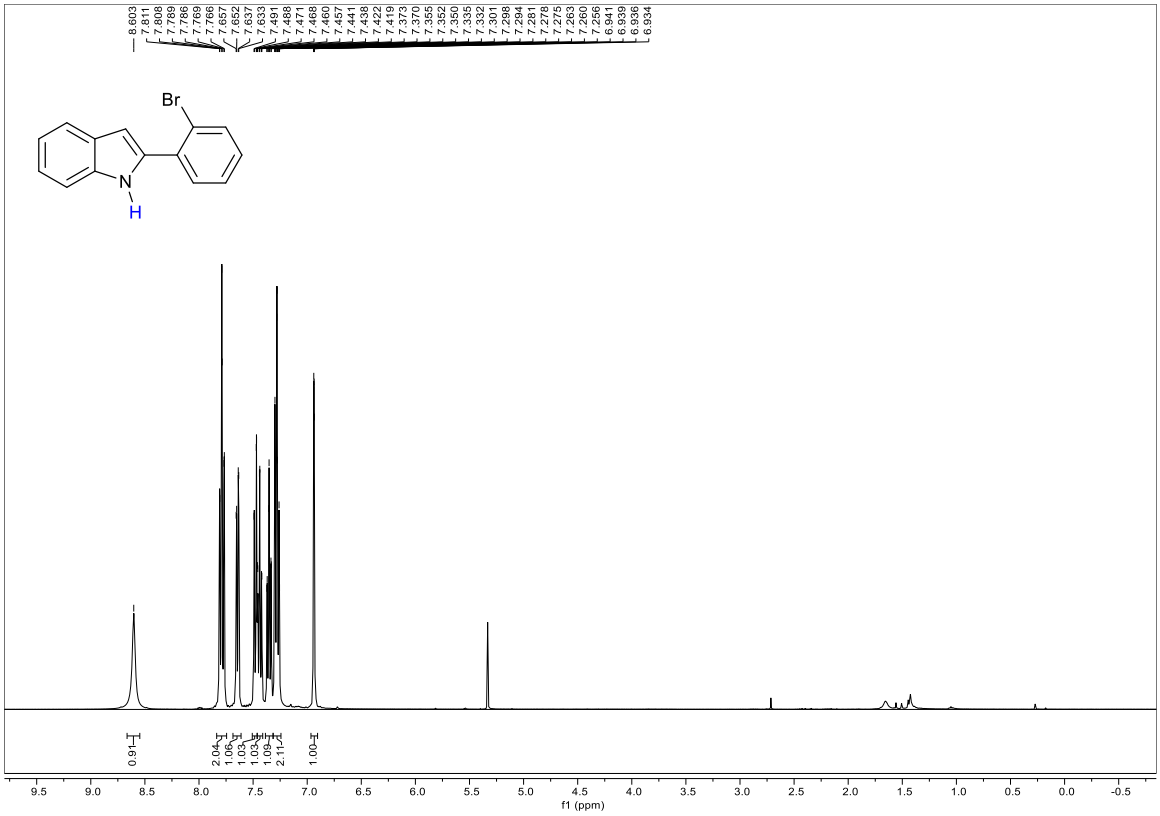
^{1}H NMR spectra of **2h** (DMSO-*d*6, 400 MHz)



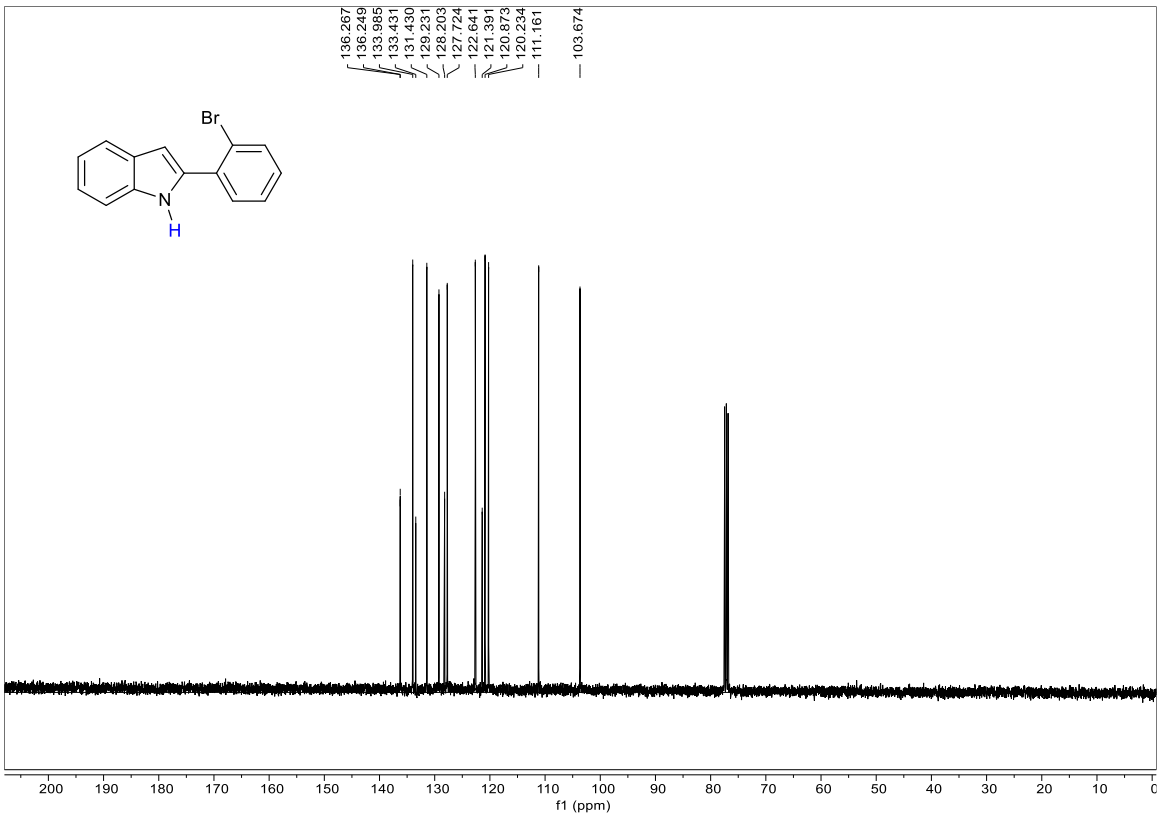
^{13}C NMR spectra of **2h** (DMSO-*d*6, 101 MHz)



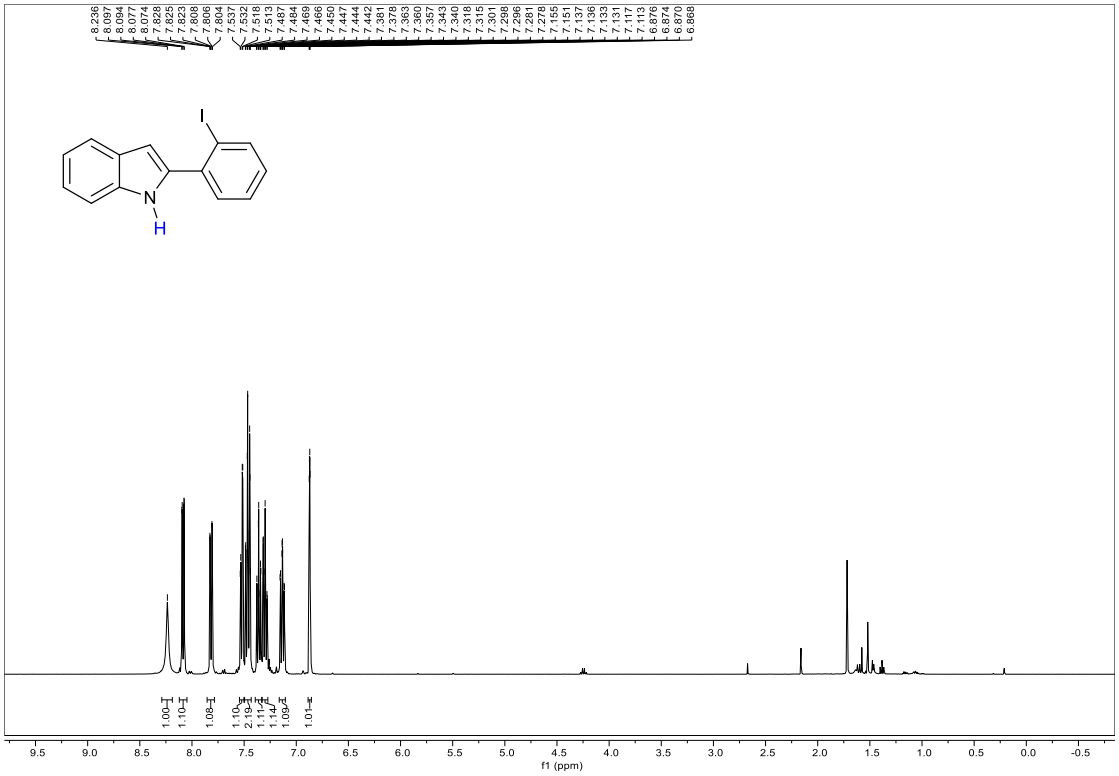
^{1}H NMR spectra of **2i** ($CDCl_3$, 400 MHz)



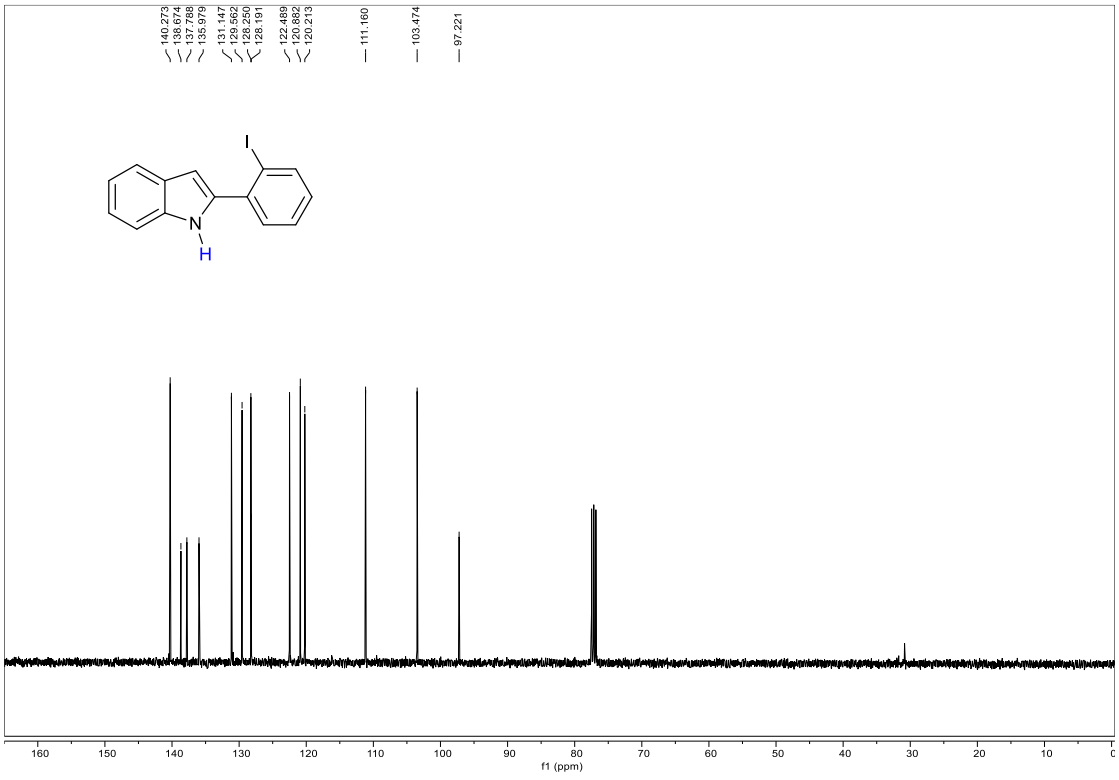
^{13}C NMR spectra of **2i** ($CDCl_3$, 101 MHz)



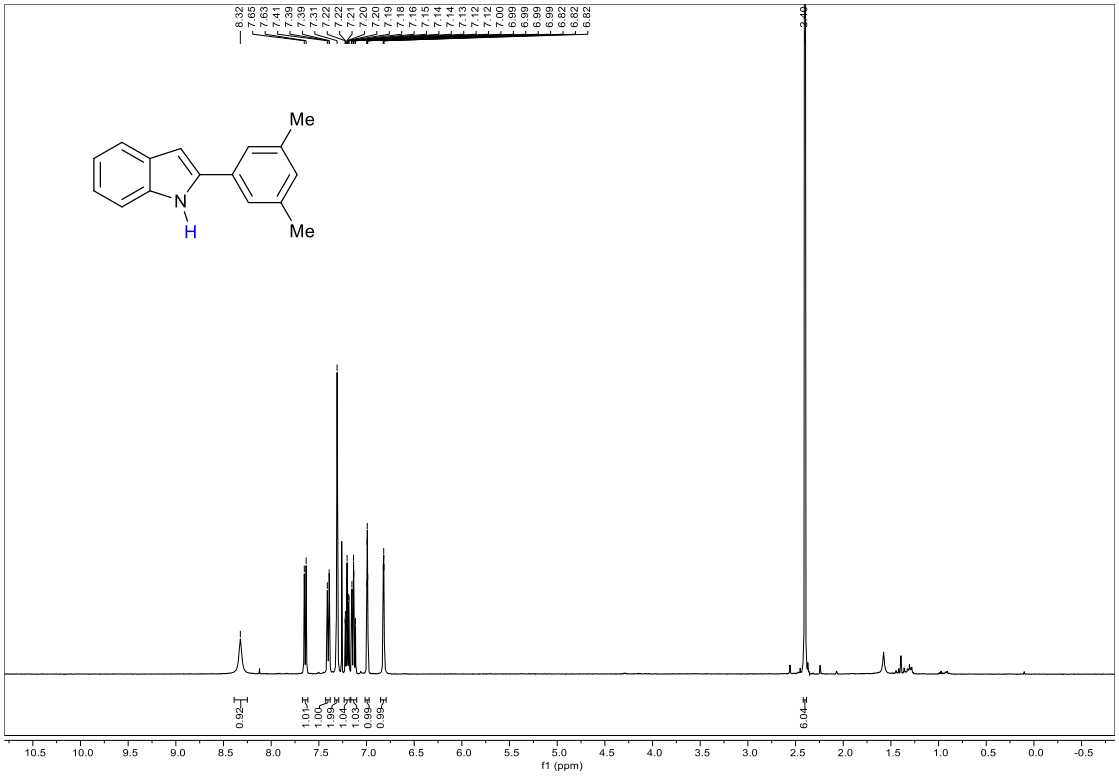
^{1}H NMR spectra of **2j** ($CDCl_3$, 400 MHz)



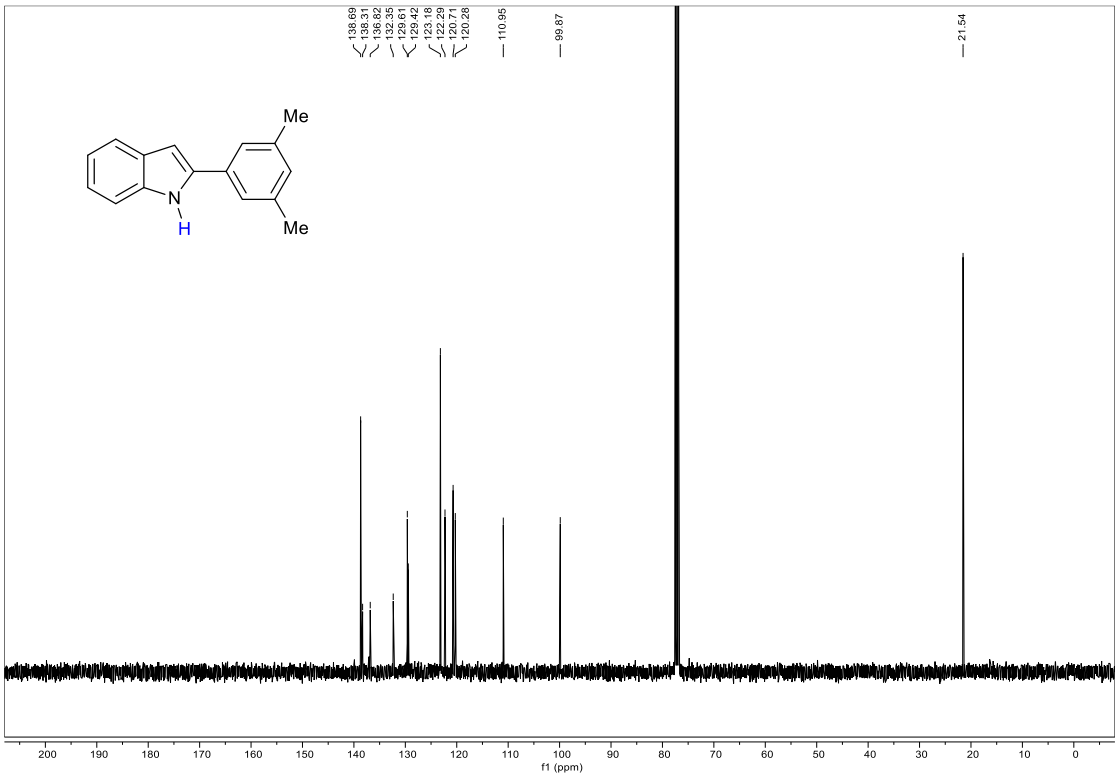
^{13}C NMR spectra of **2j** ($CDCl_3$, 101 MHz)



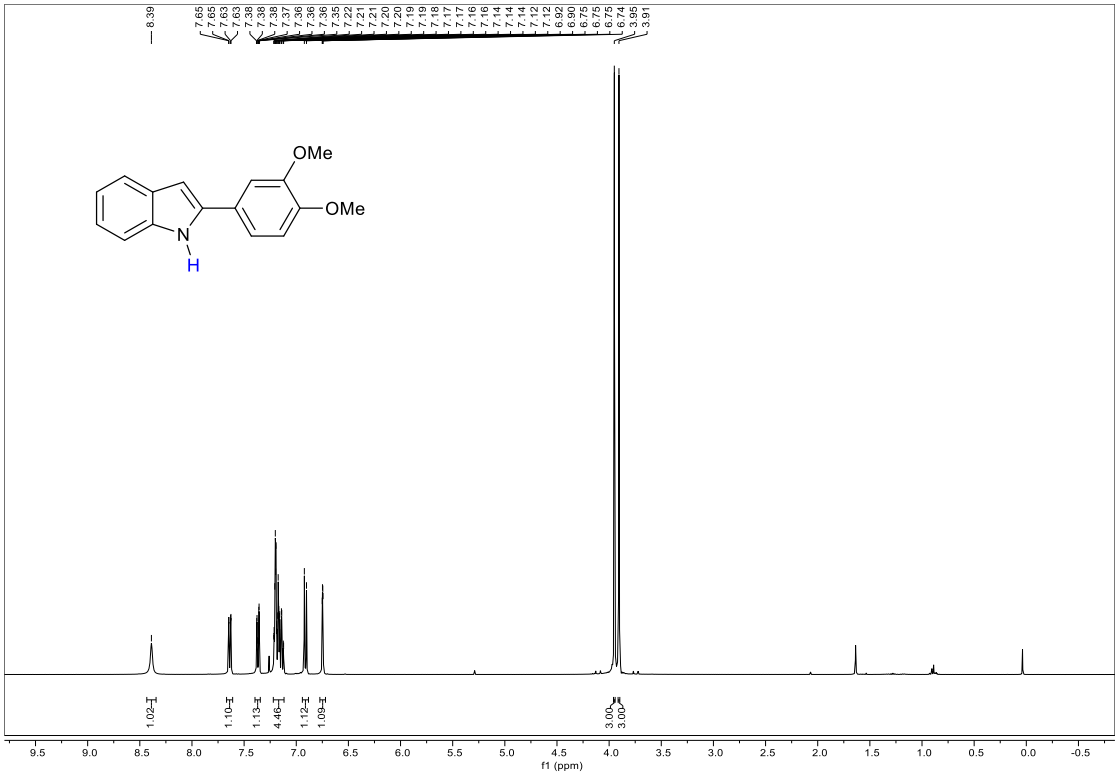
^{1}H NMR spectra of **2k** ($CDCl_3$, 400 MHz)



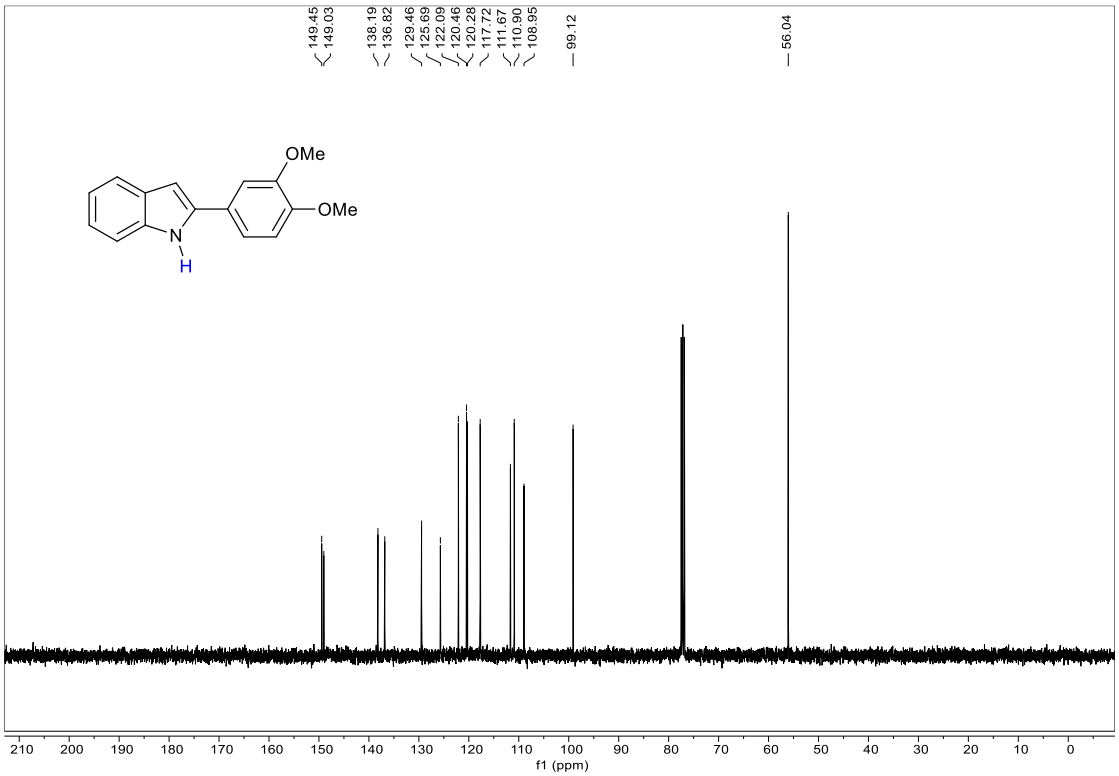
^{13}C NMR spectra of **2k** ($CDCl_3$, 101 MHz)



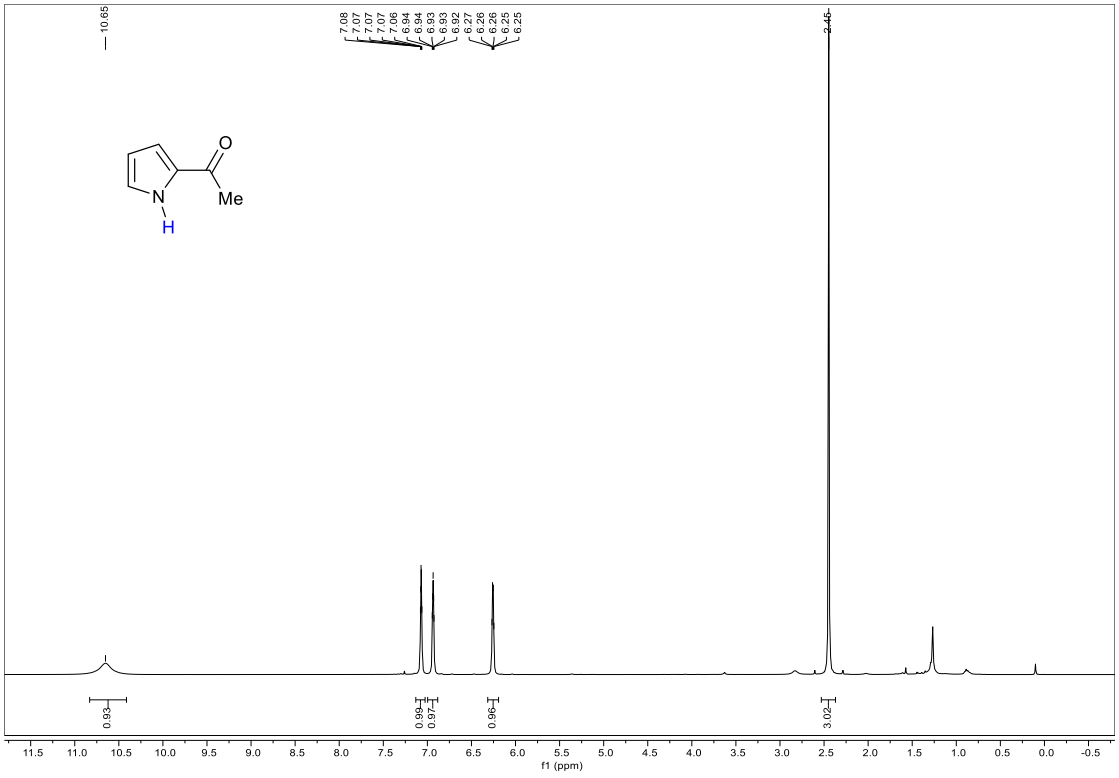
^{1}H NMR spectra of **2l** ($CDCl_3$, 400 MHz)



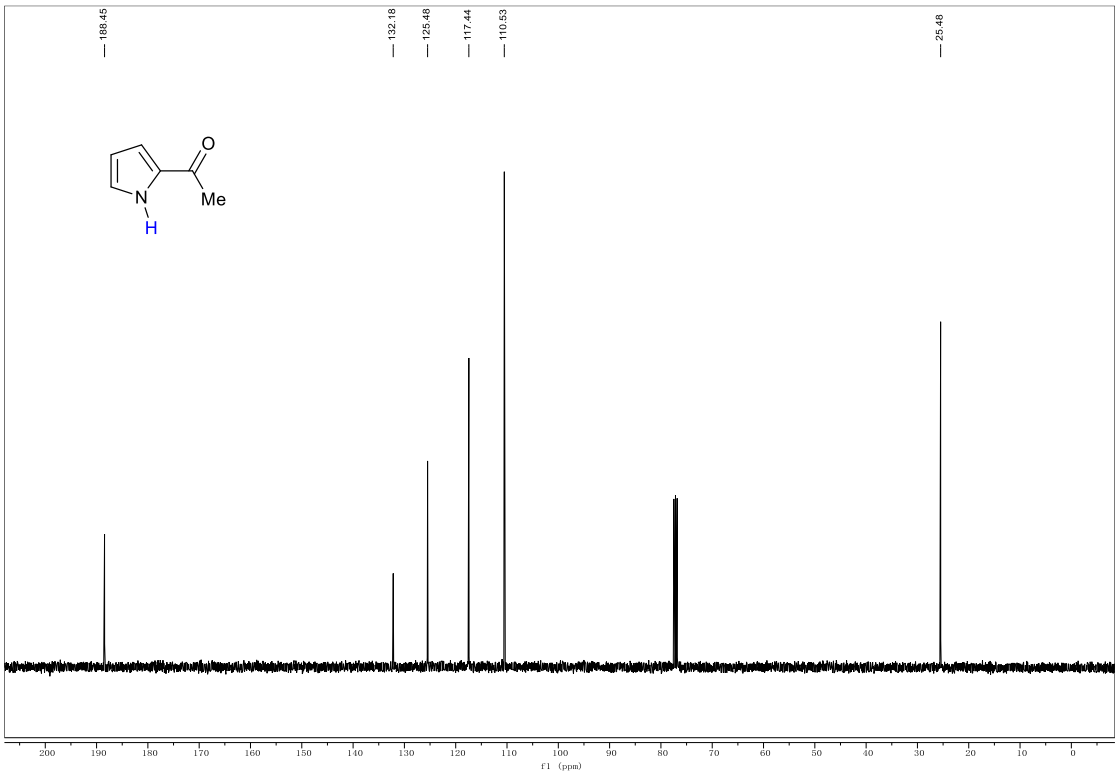
^{13}C NMR spectra of **2l** ($CDCl_3$, 101 MHz)



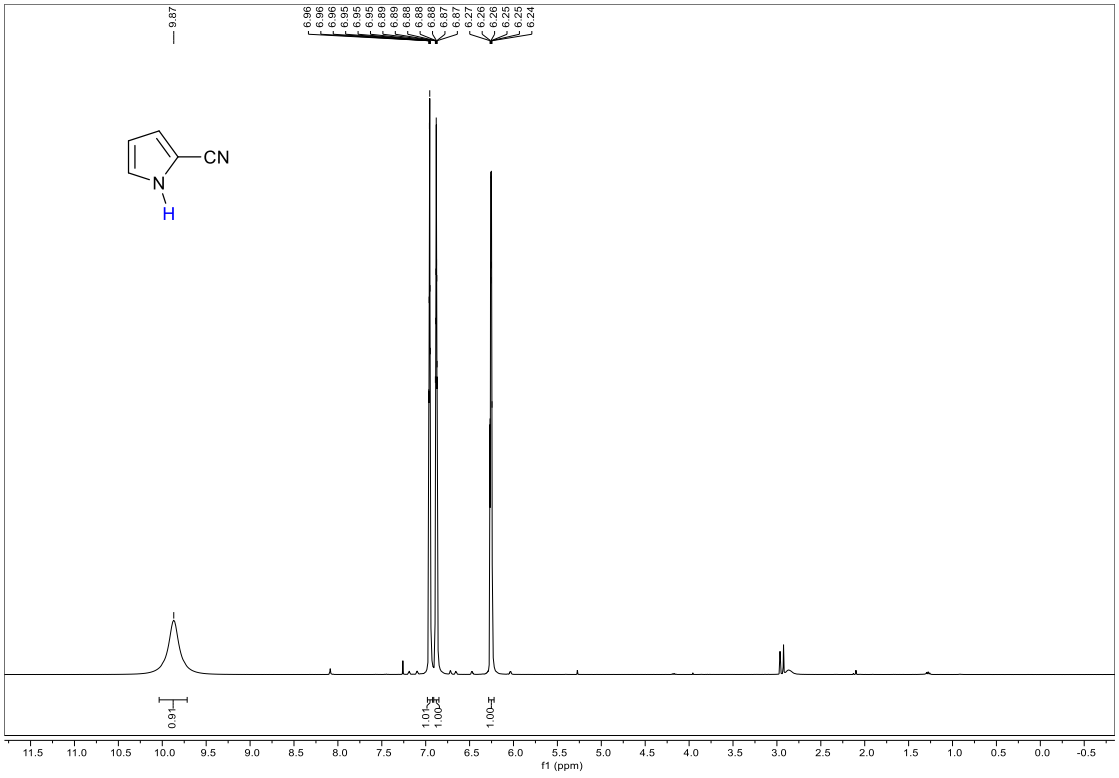
^{1}H NMR spectra of **2m** ($CDCl_3$, 400 MHz)



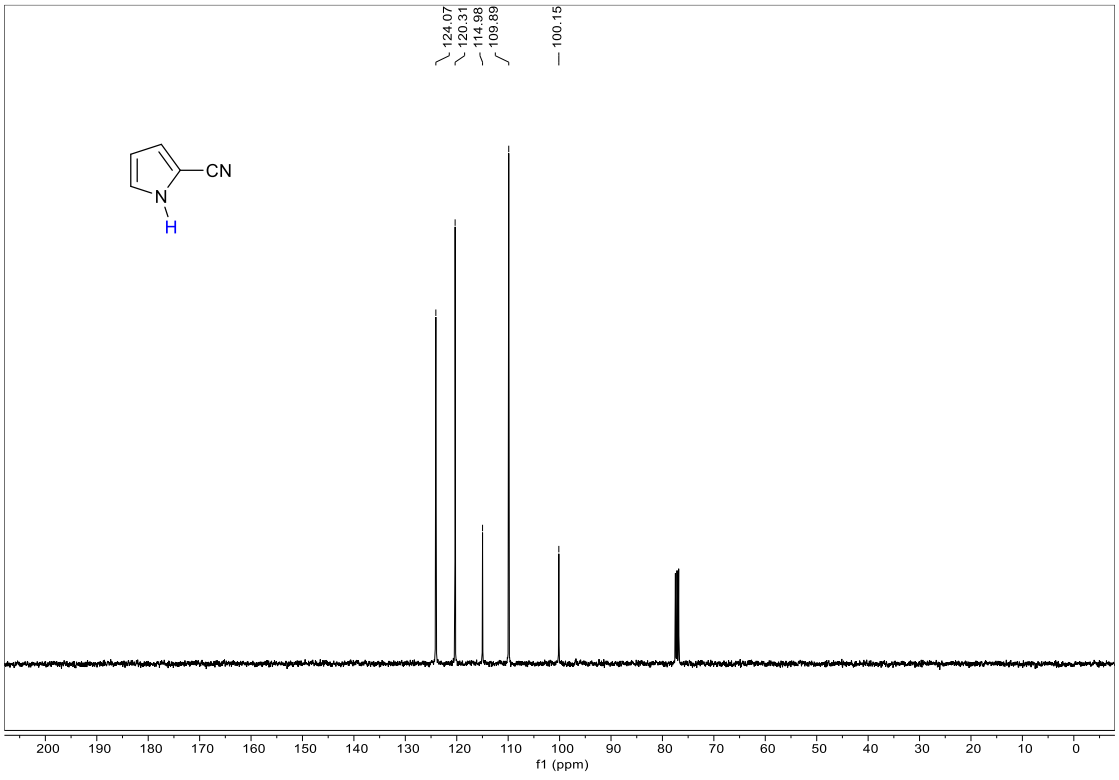
^{13}C NMR spectra of **2m** ($CDCl_3$, 101 MHz)



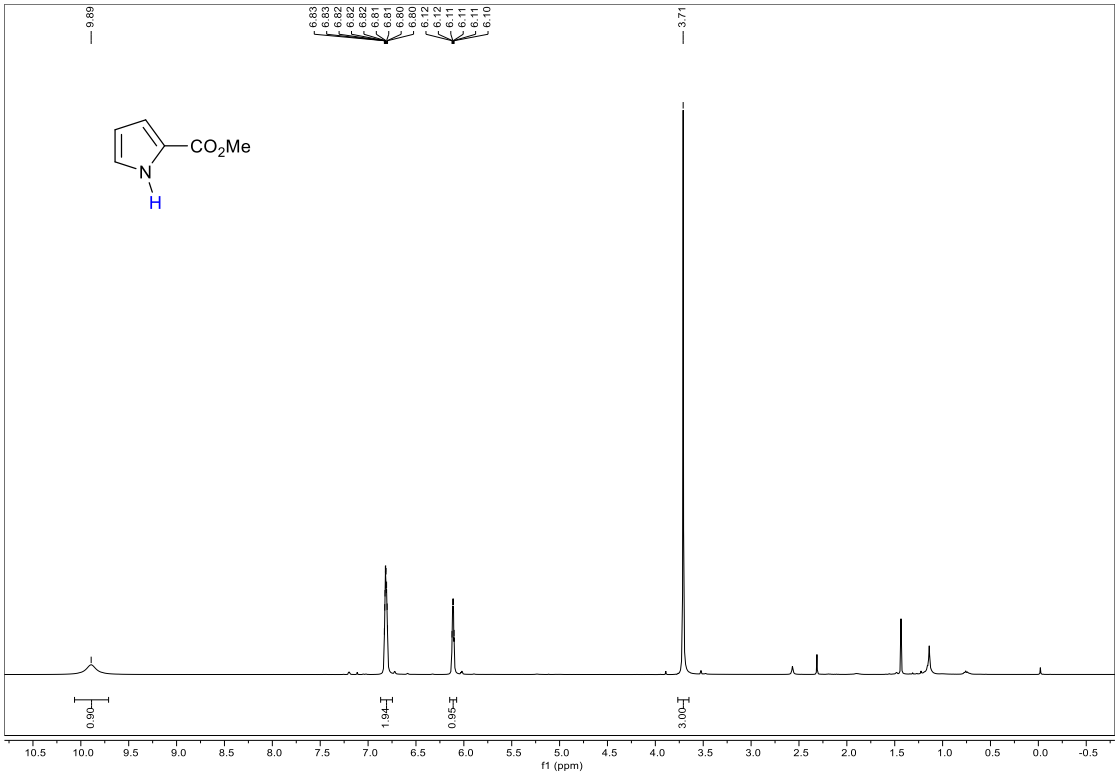
^{1}H NMR spectra of **2n** ($CDCl_3$, 400 MHz)



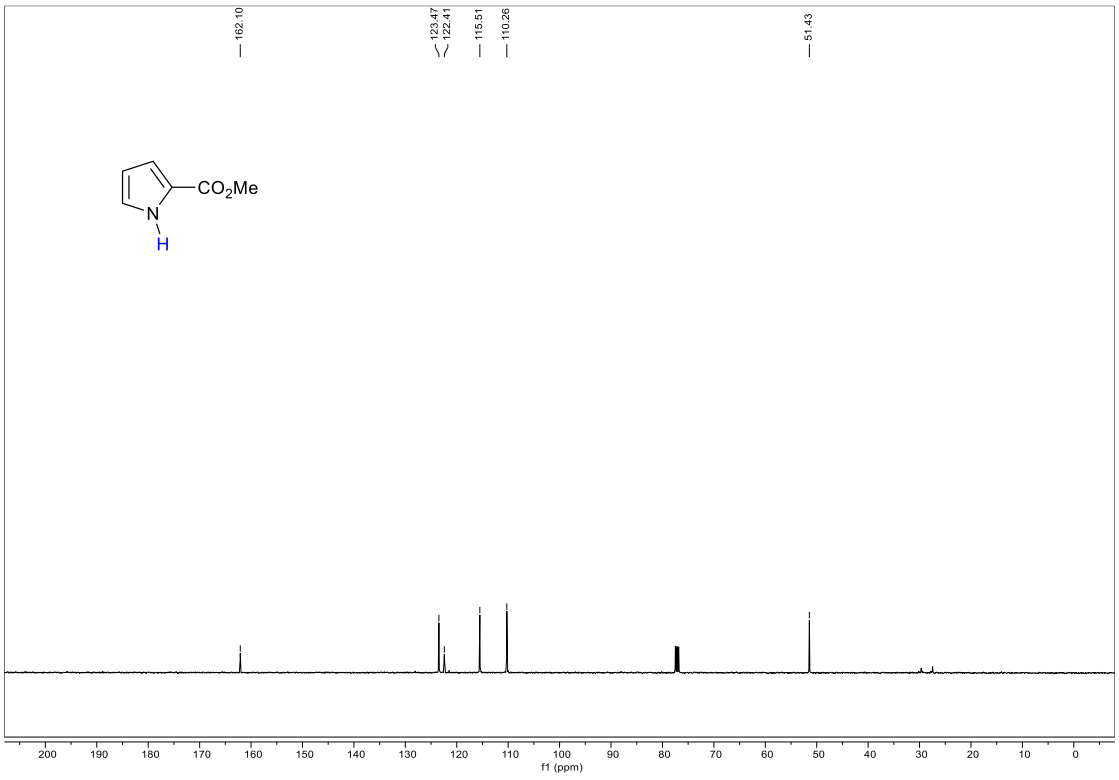
^{13}C NMR spectra of **2n** ($CDCl_3$, 101 MHz)



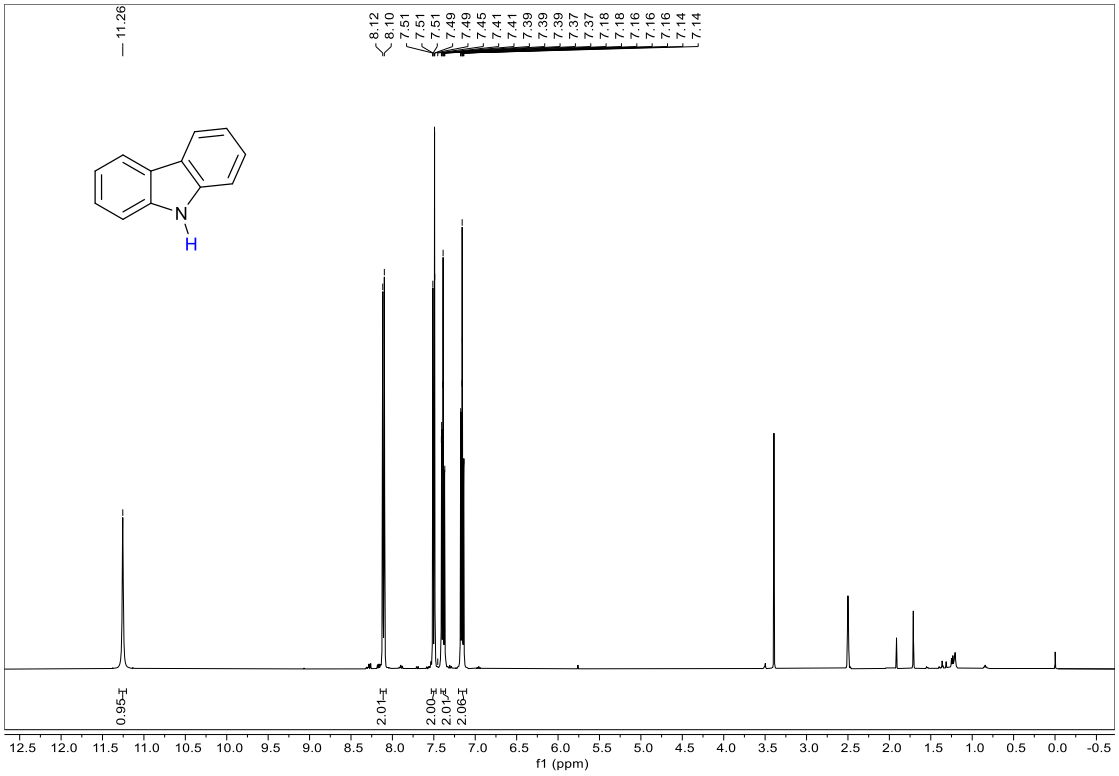
^{1}H NMR spectra of **2o** ($CDCl_3$, 400 MHz)



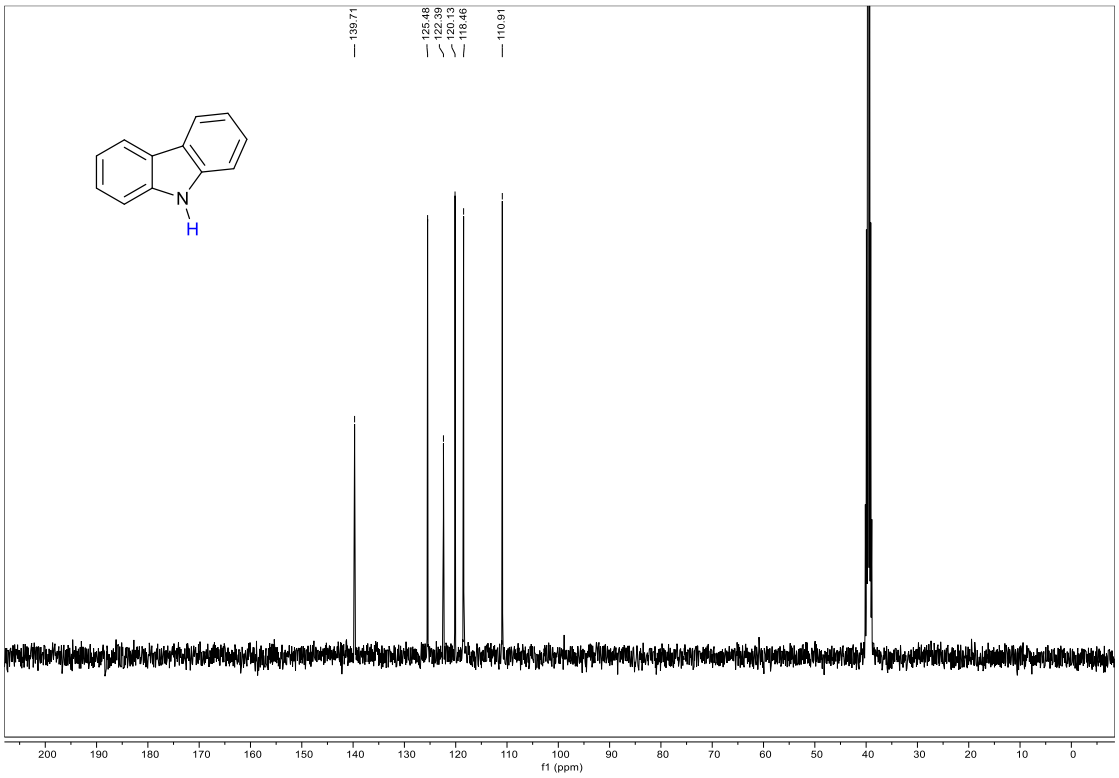
^{13}C NMR spectra of **2o** ($CDCl_3$, 101 MHz)



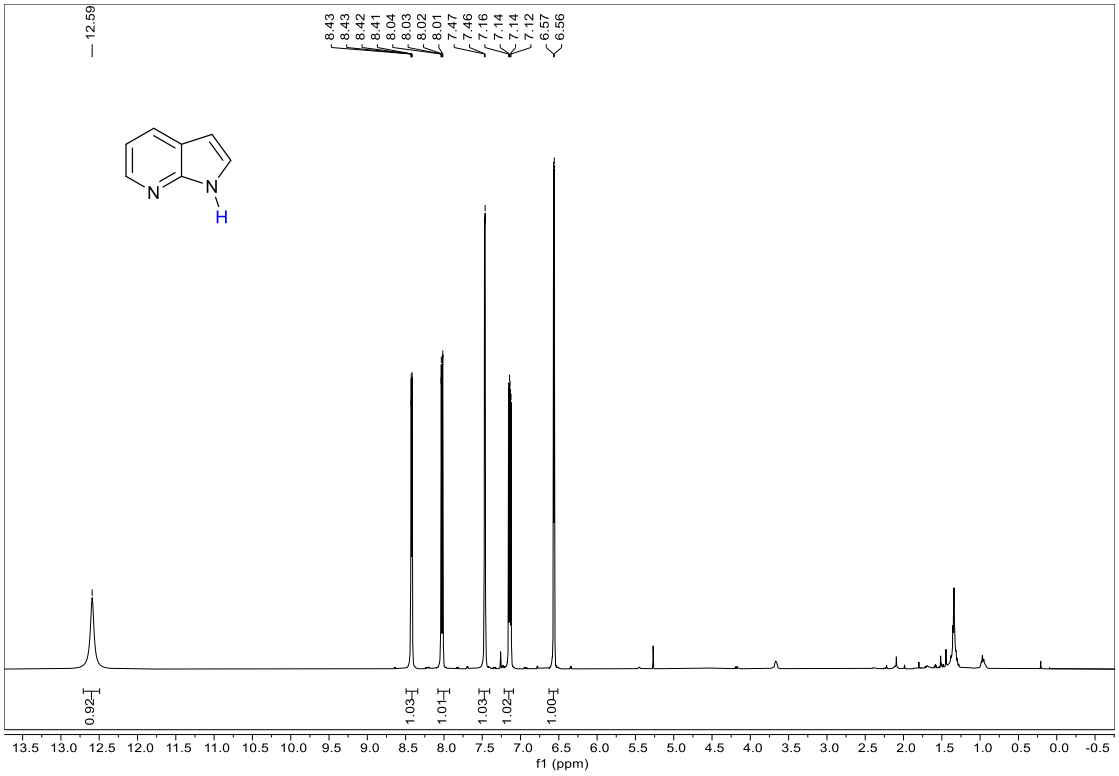
^{1}H NMR spectra of **2p** (DMSO-*d*6, 400 MHz)



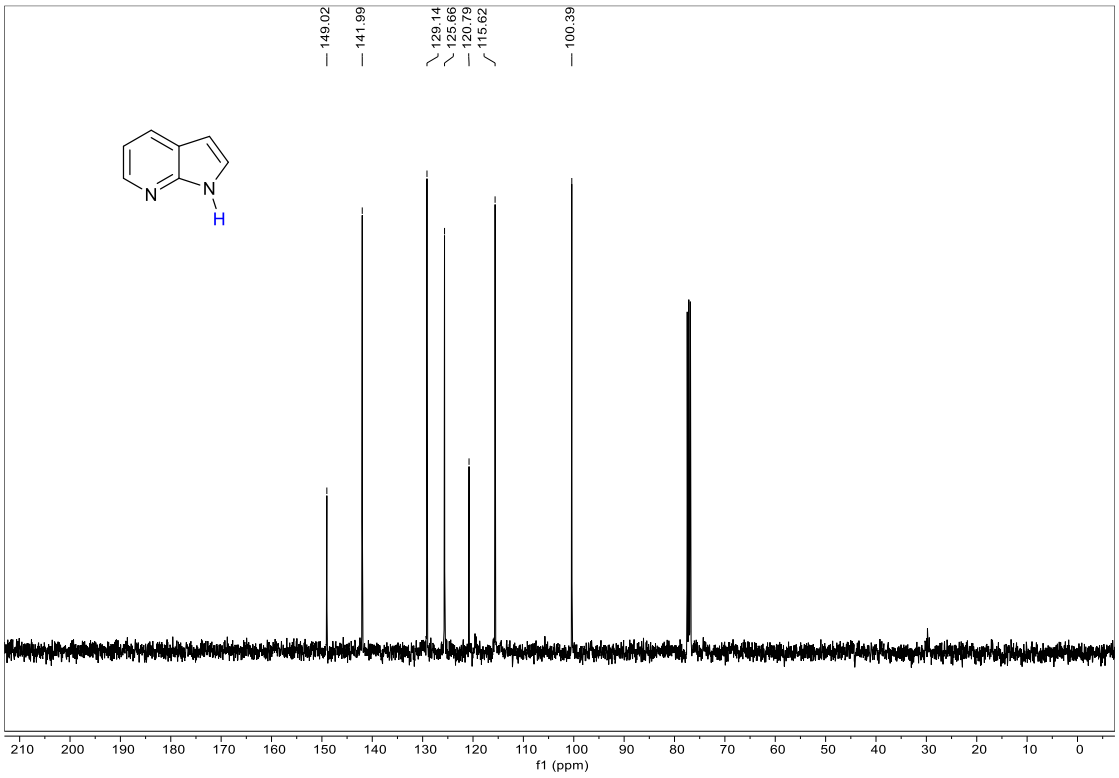
^{13}C NMR spectra of **2p** (DMSO-*d*6, 101 MHz)



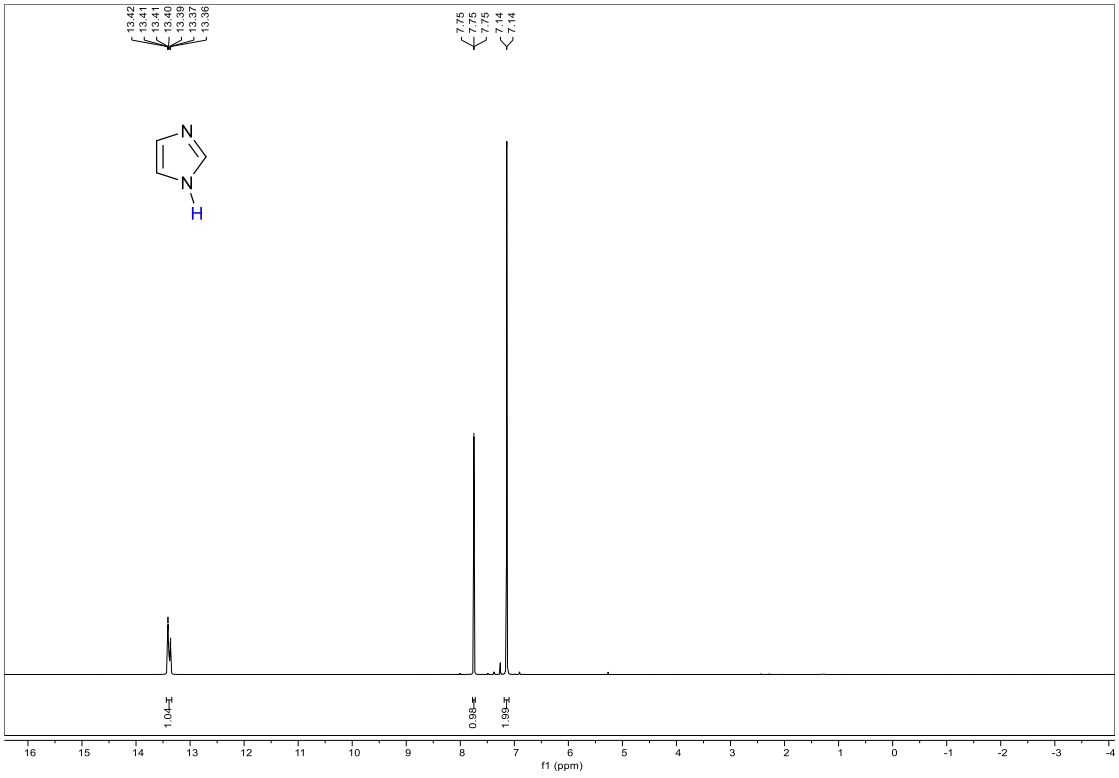
^{1}H NMR spectra of **2q** ($CDCl_3$, 400 MHz)



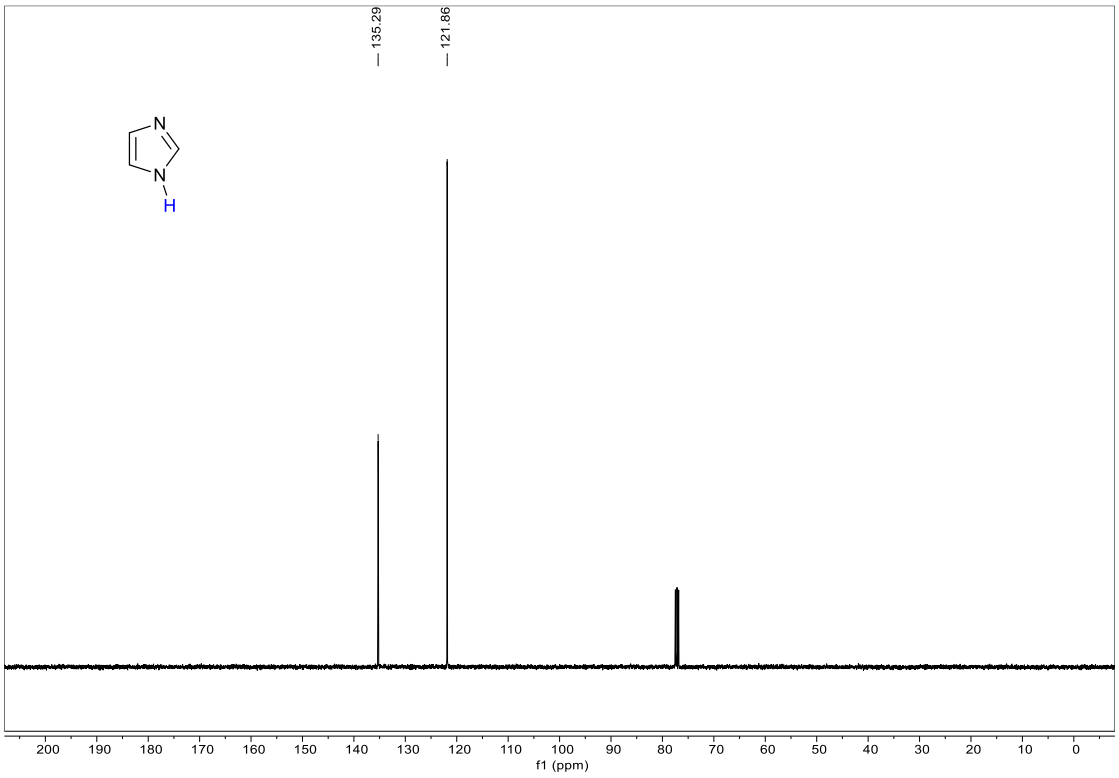
^{13}C NMR spectra of **2q** ($CDCl_3$, 101 MHz)



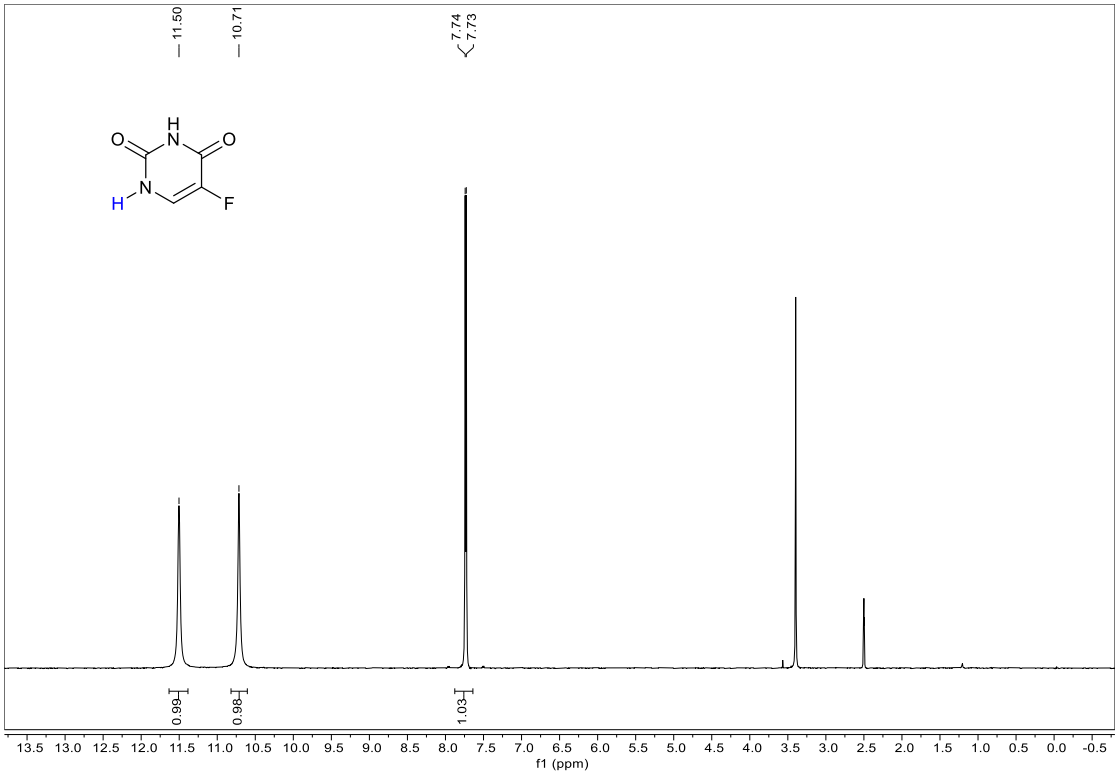
^{1}H NMR spectra of **2r** ($CDCl_3$, 400 MHz)



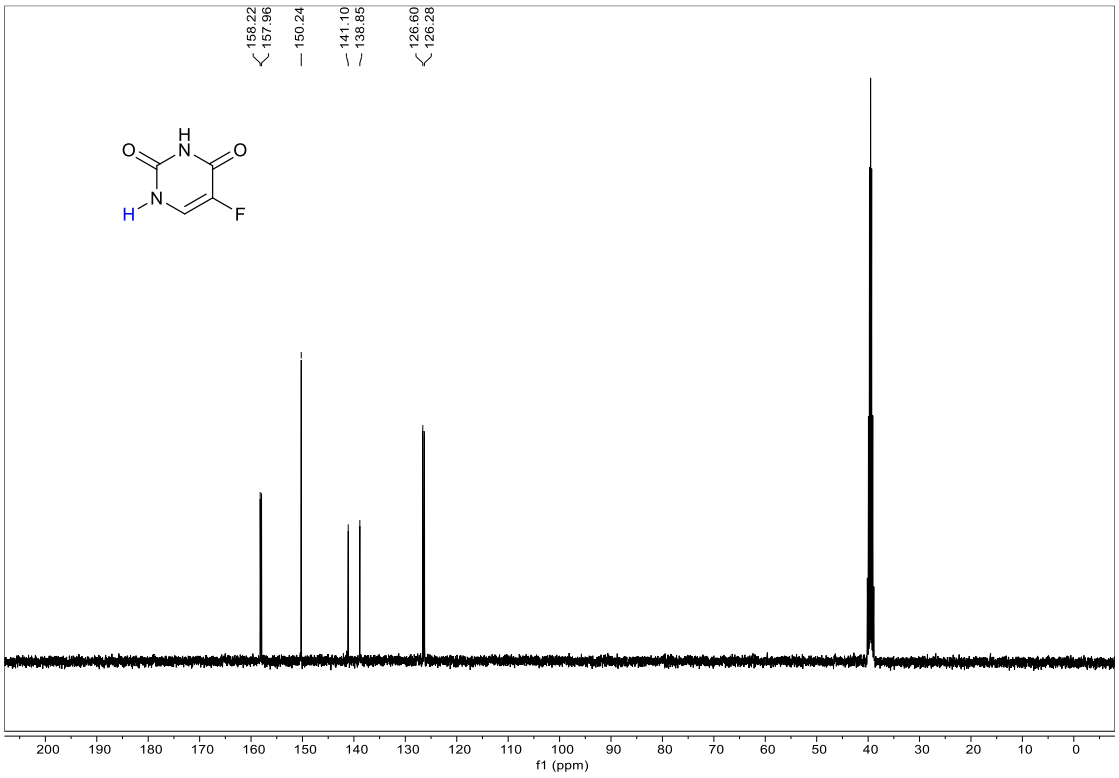
^{13}C NMR spectra of **2r** ($CDCl_3$, 101 MHz)



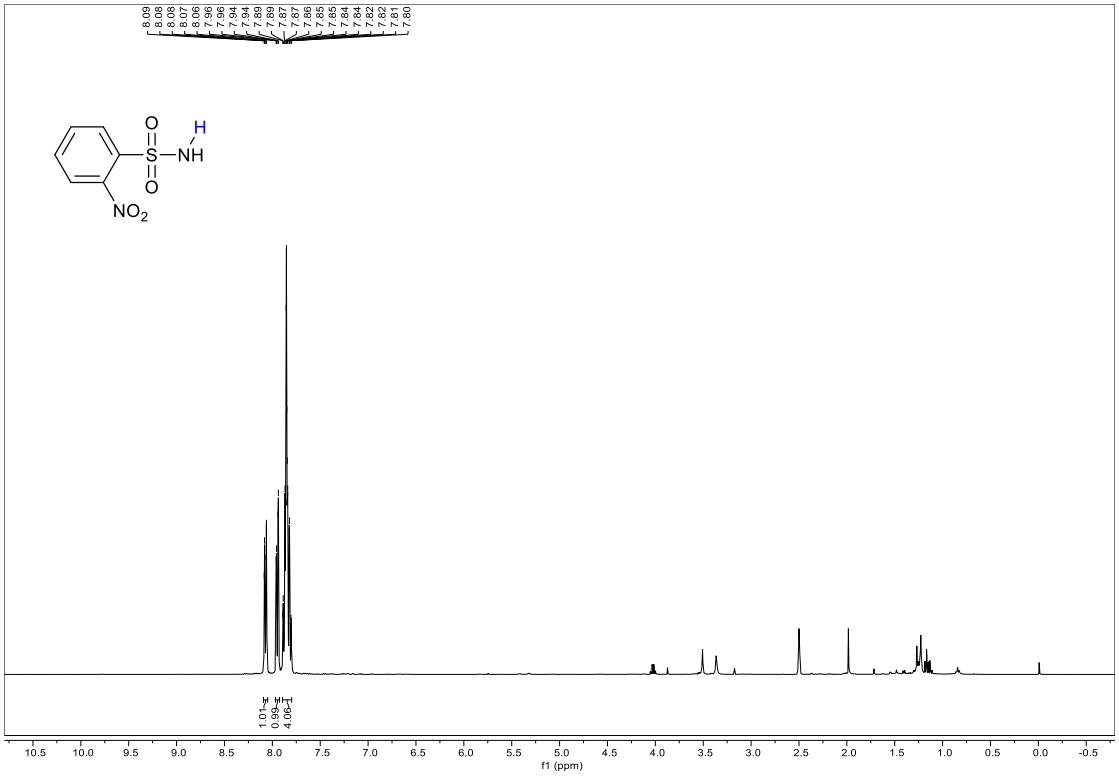
^{1}H NMR spectra of **2s** (DMSO-*d*6, 400 MHz)



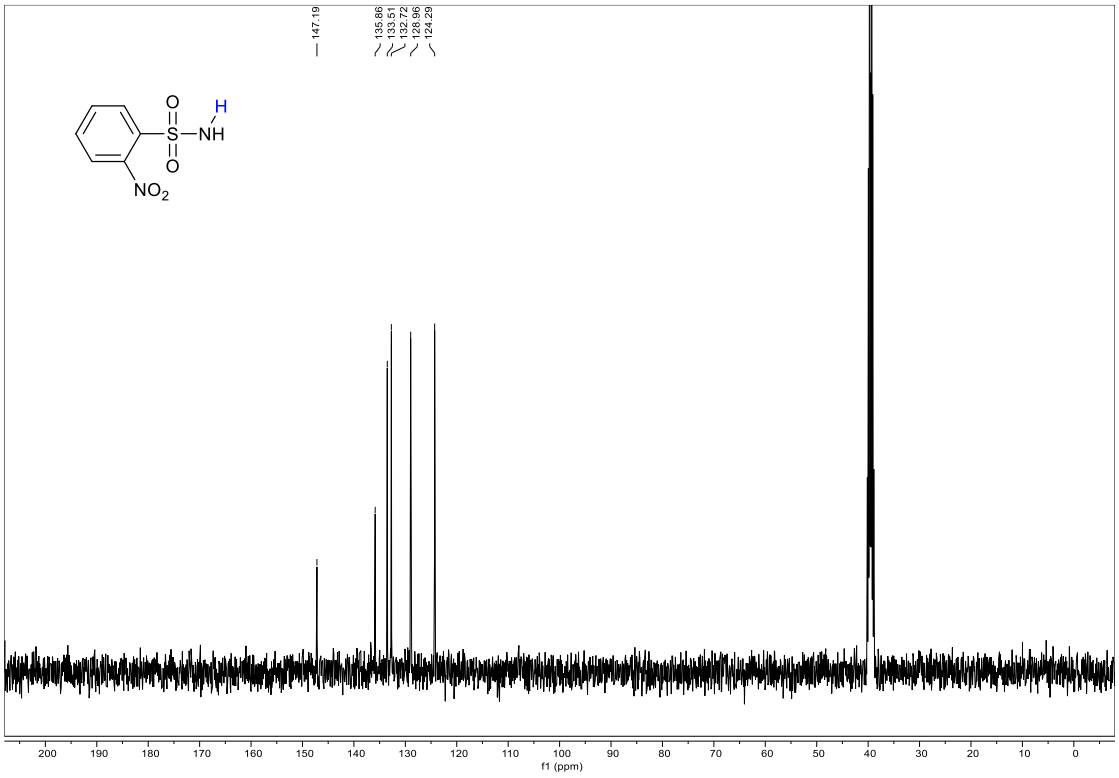
^{13}C NMR spectra of **2s** (DMSO-*d*6, 101 MHz)



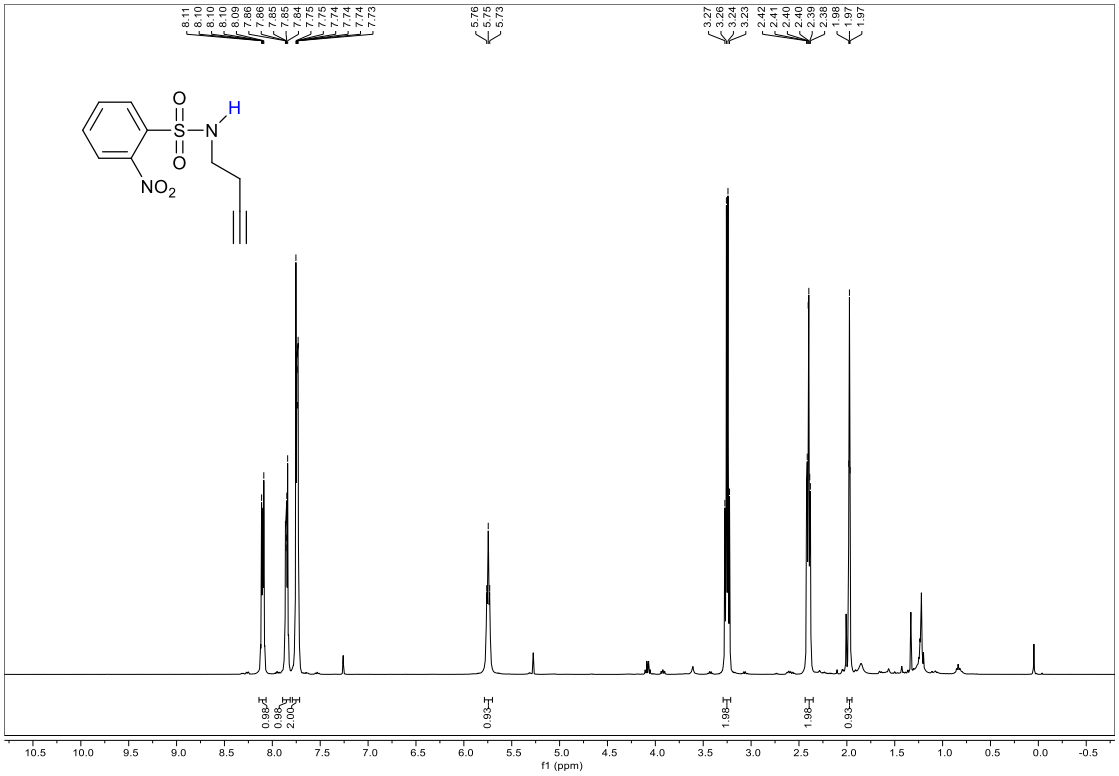
^{1}H NMR spectra of **4a** (DMSO-*d*6, 400 MHz)



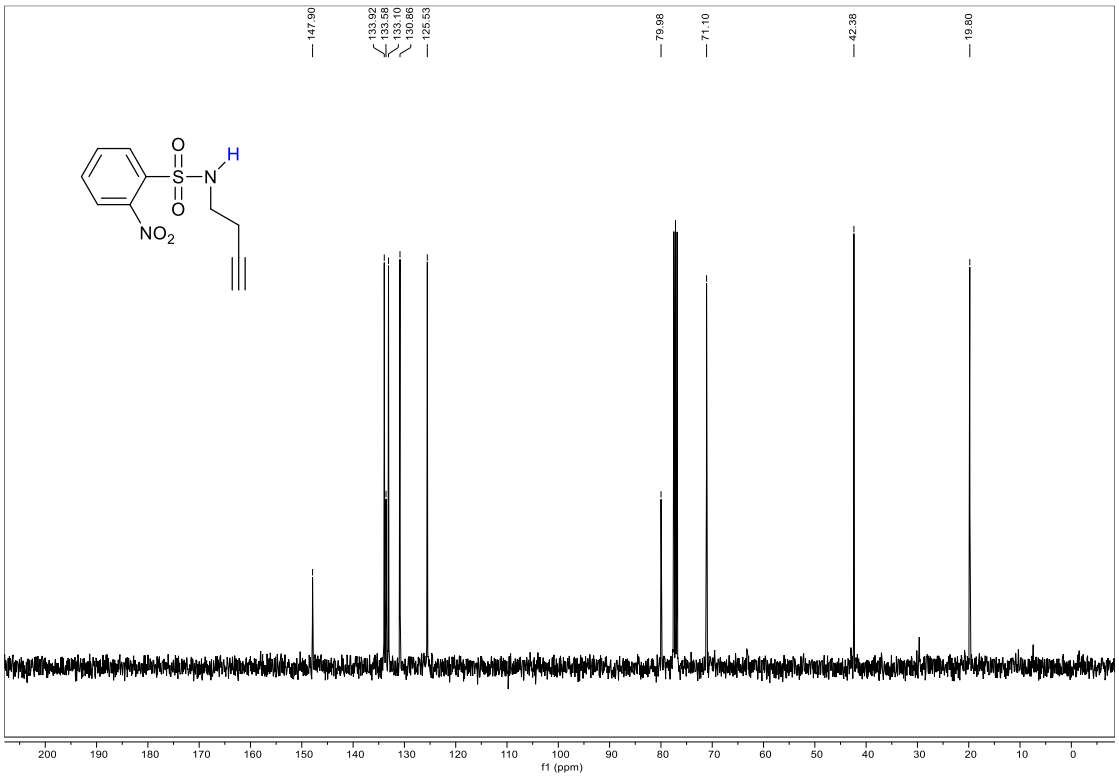
^{13}C NMR spectra of **4a** (DMSO-*d*6, 101 MHz)



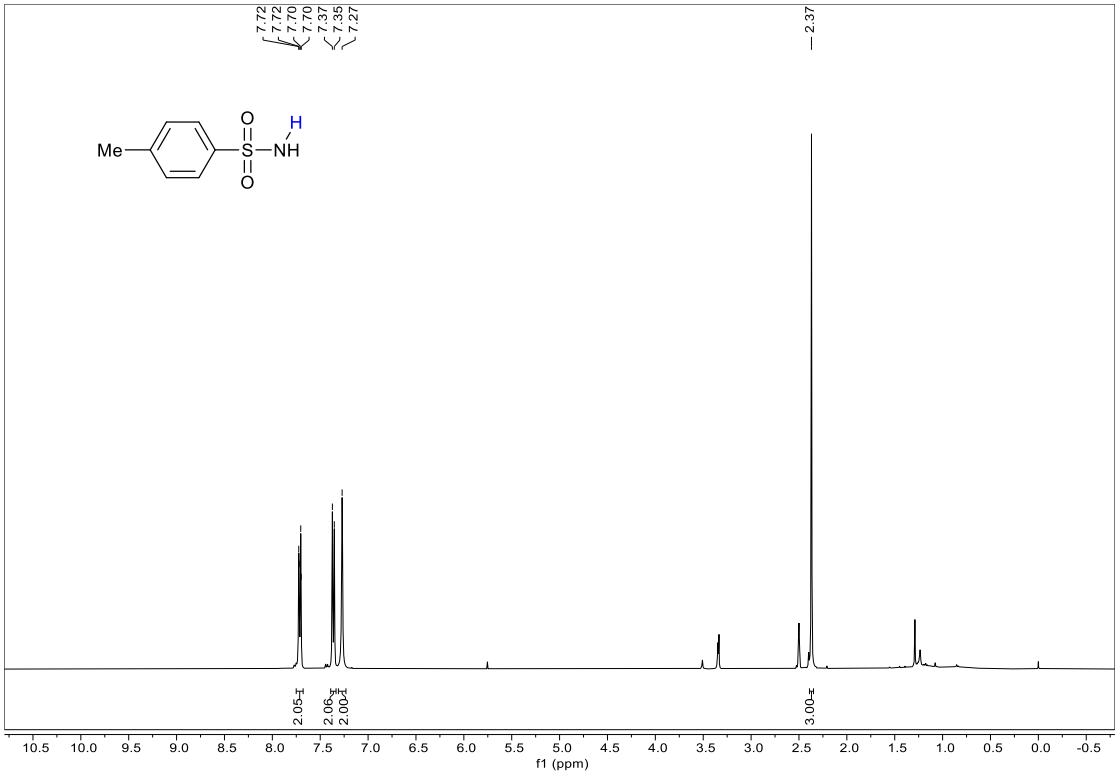
^{1}H NMR spectra of **4b** ($CDCl_3$, 400 MHz)



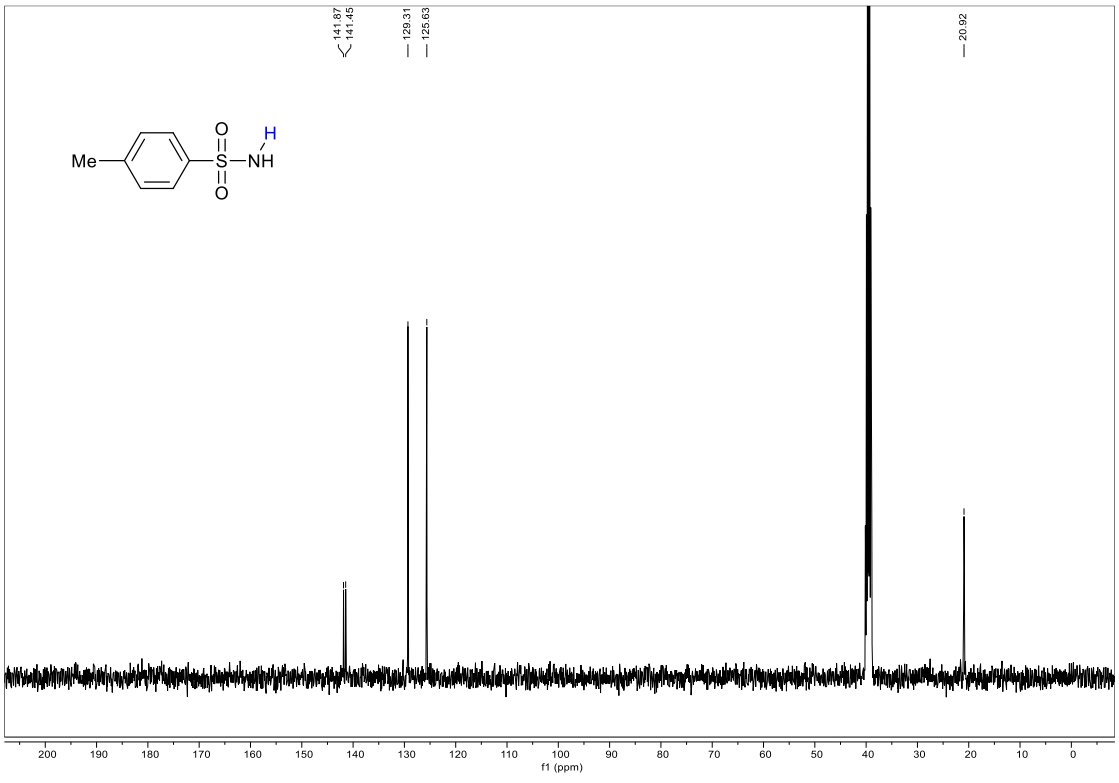
^{13}C NMR spectra of **4b** ($CDCl_3$, 101 MHz)



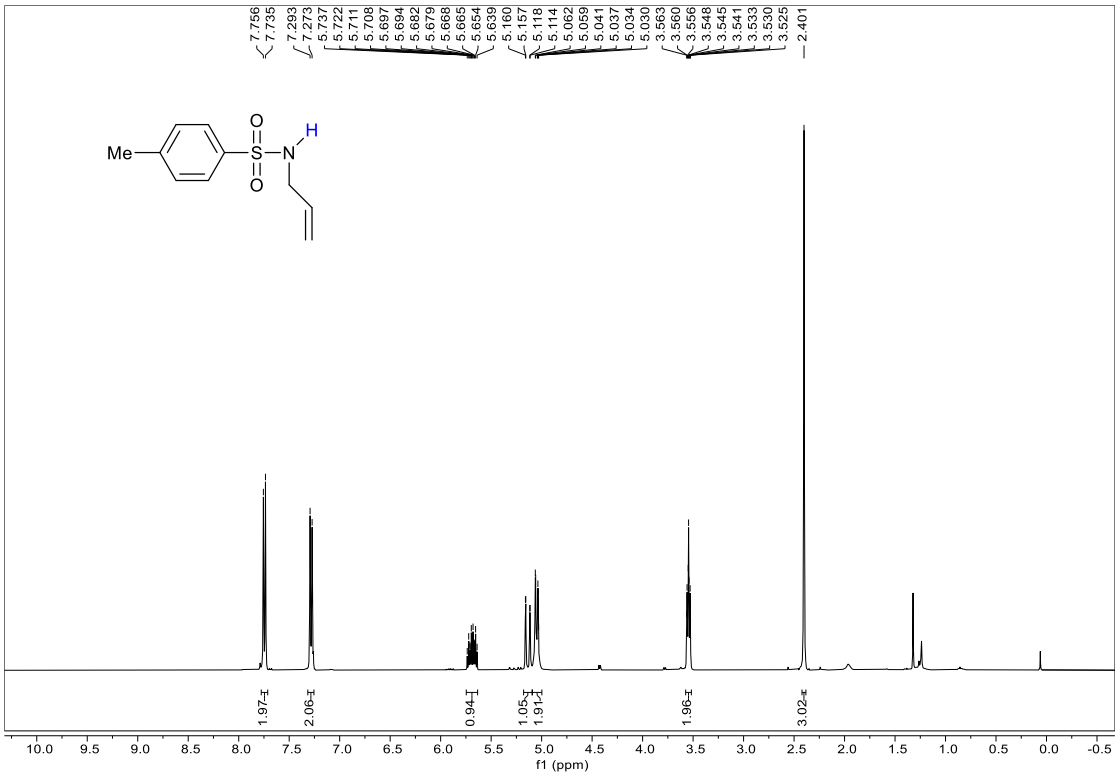
^{1}H NMR spectra of **4c** (DMSO-*d*6, 400 MHz)



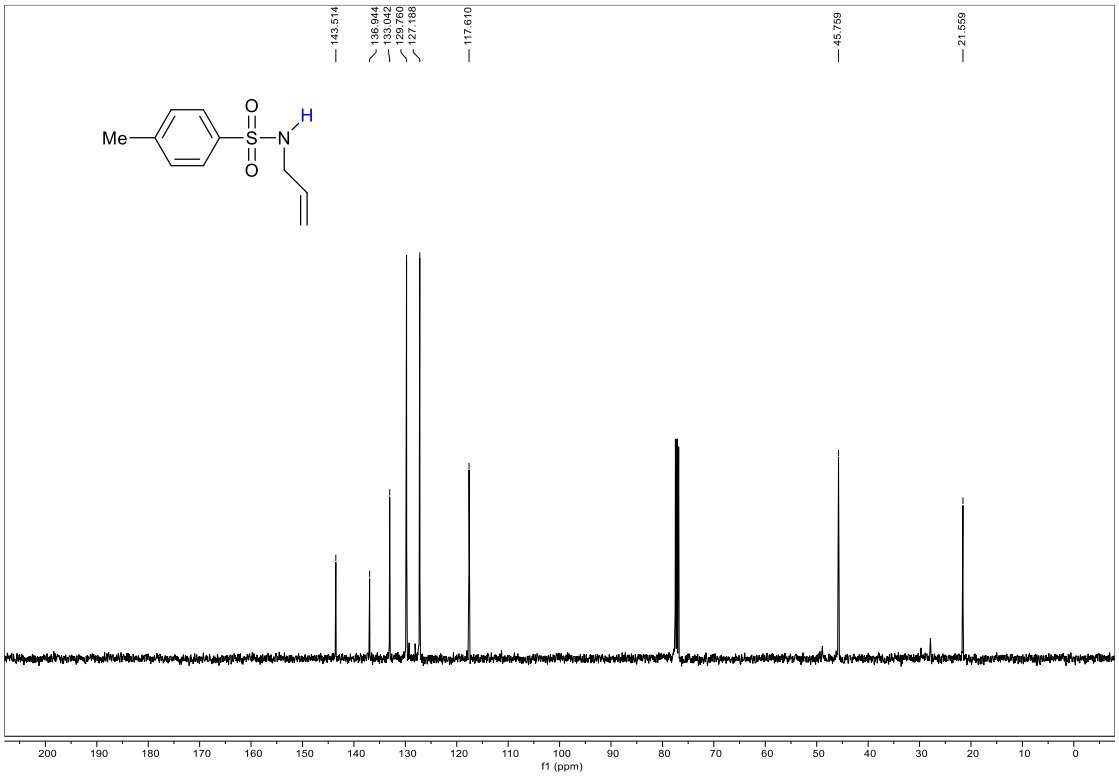
^{13}C NMR spectra of **4c** (DMSO-*d*6, 101 MHz)



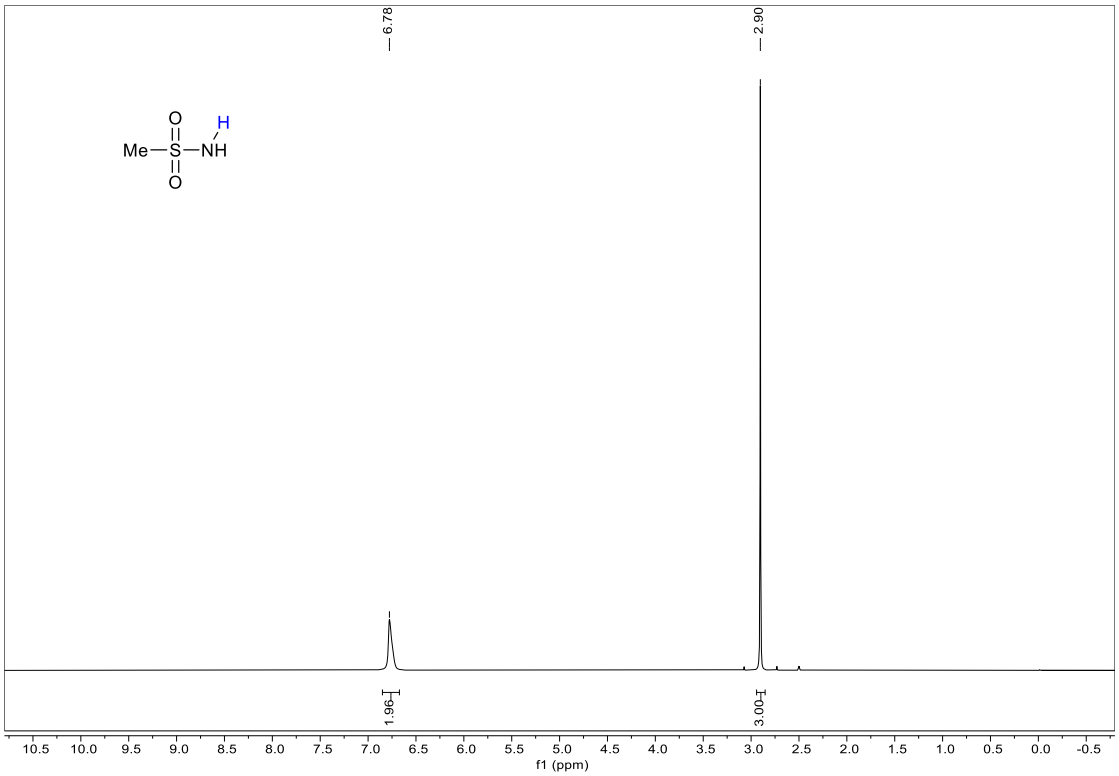
^{1}H NMR spectra of **4d** ($CDCl_3$, 400 MHz)



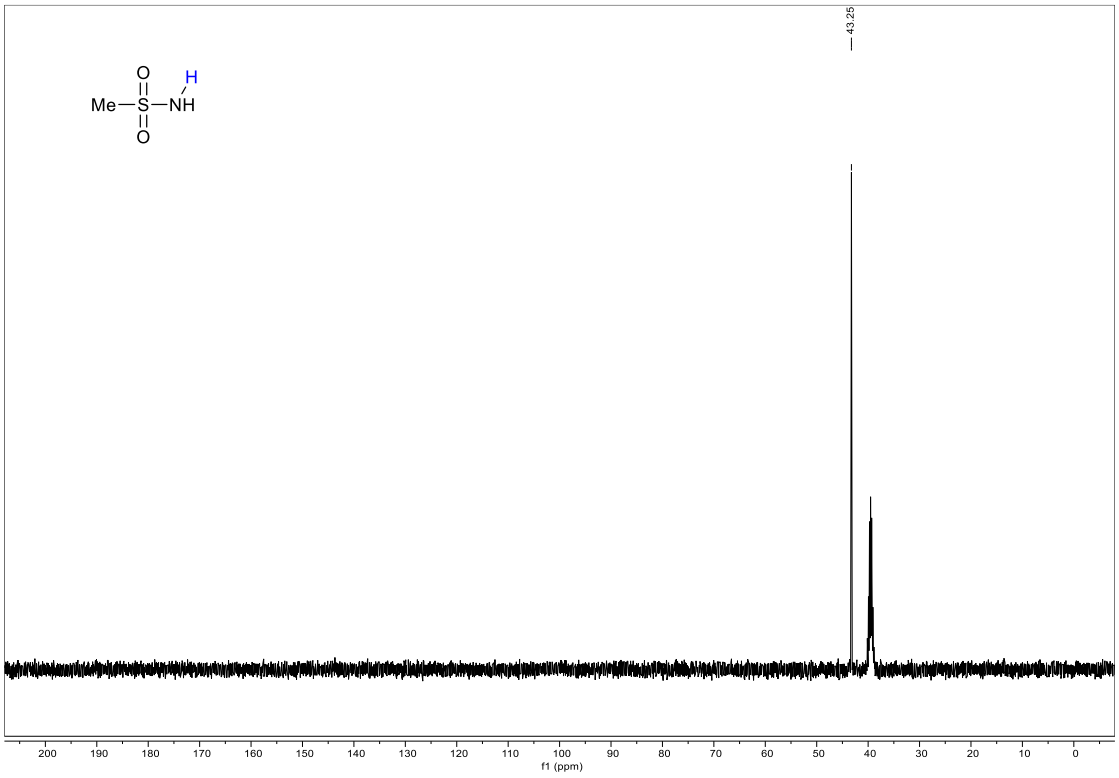
^{13}C NMR spectra of **4d** ($CDCl_3$, 101 MHz)



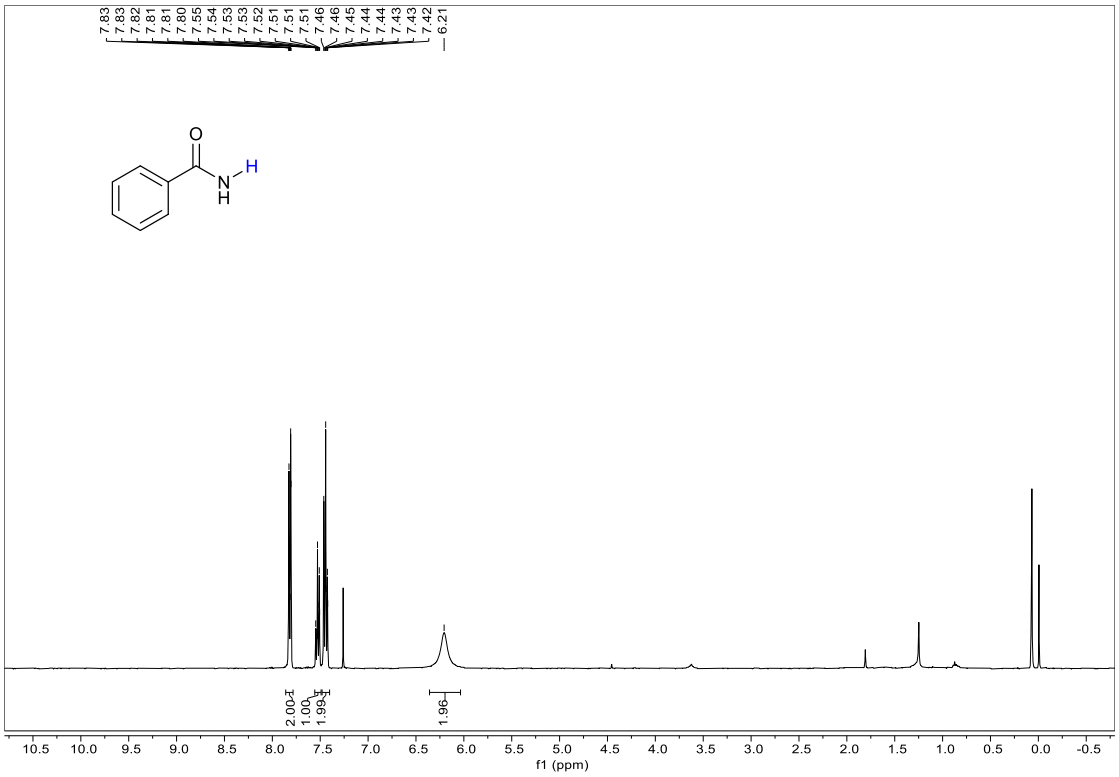
^{1}H NMR spectra of **4e** (DMSO-*d*6, 400 MHz)



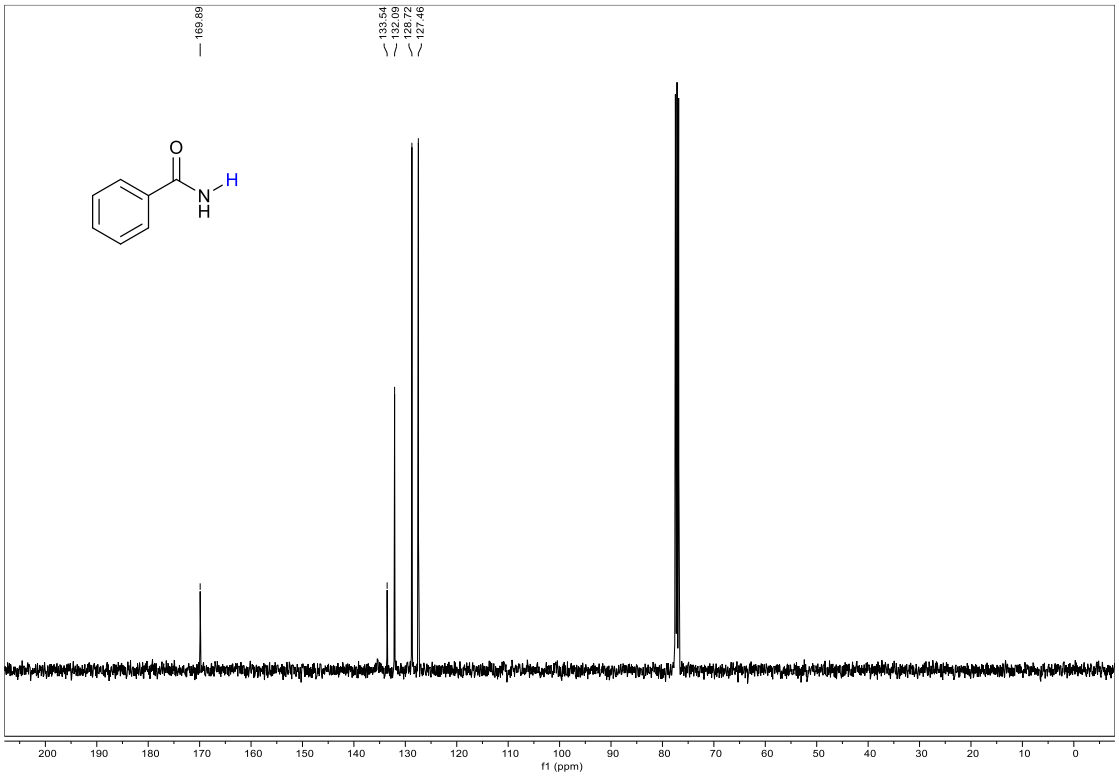
^{13}C NMR spectra of **4e** (DMSO-*d*6, 101 MHz)



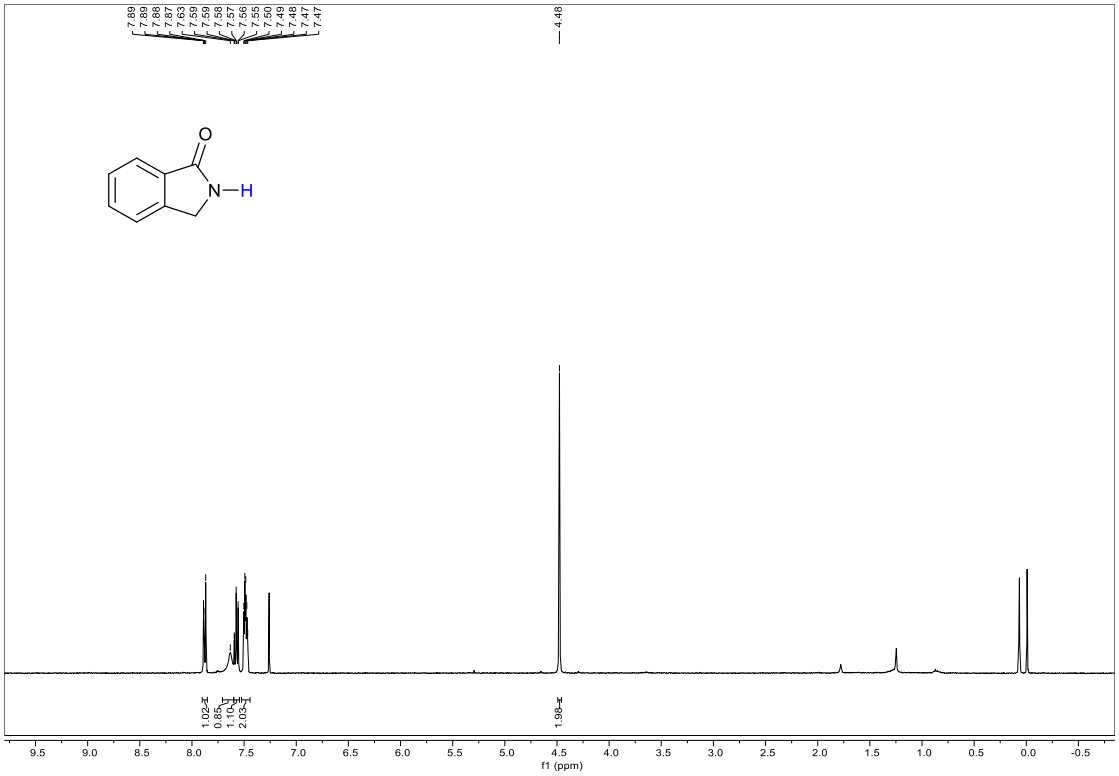
^{1}H NMR spectra of **4f** ($CDCl_3$, 400 MHz)



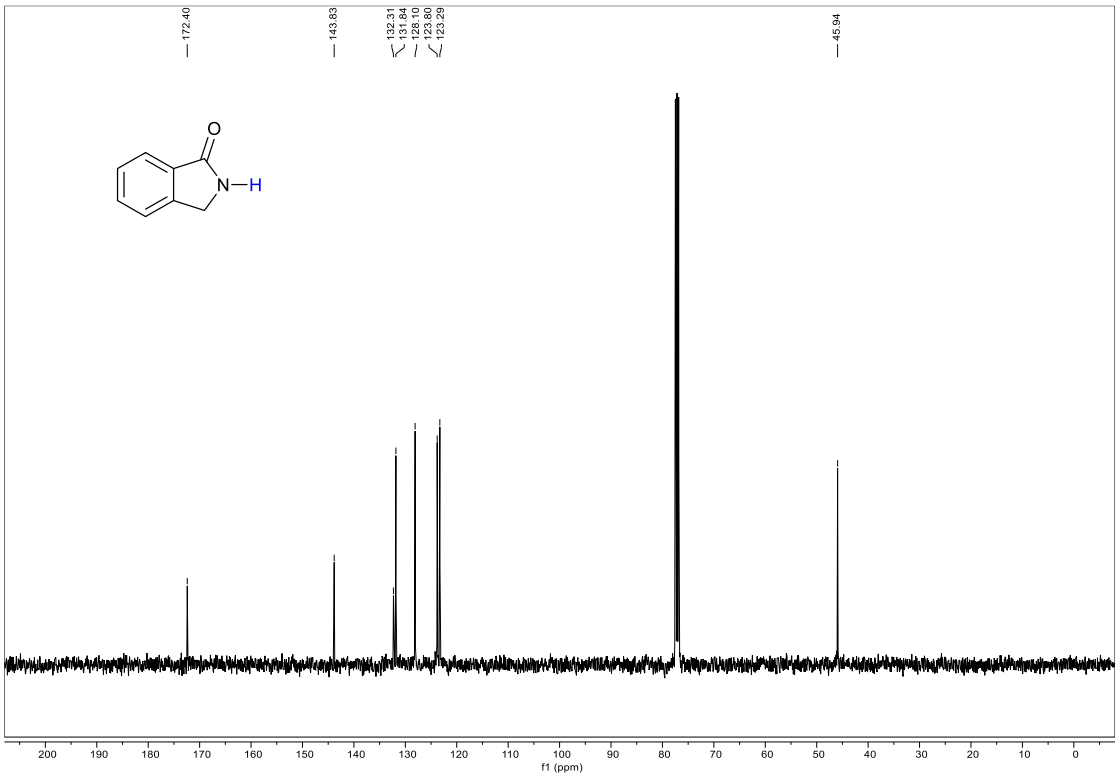
^{13}C NMR spectra of **4f** ($CDCl_3$, 101 MHz)



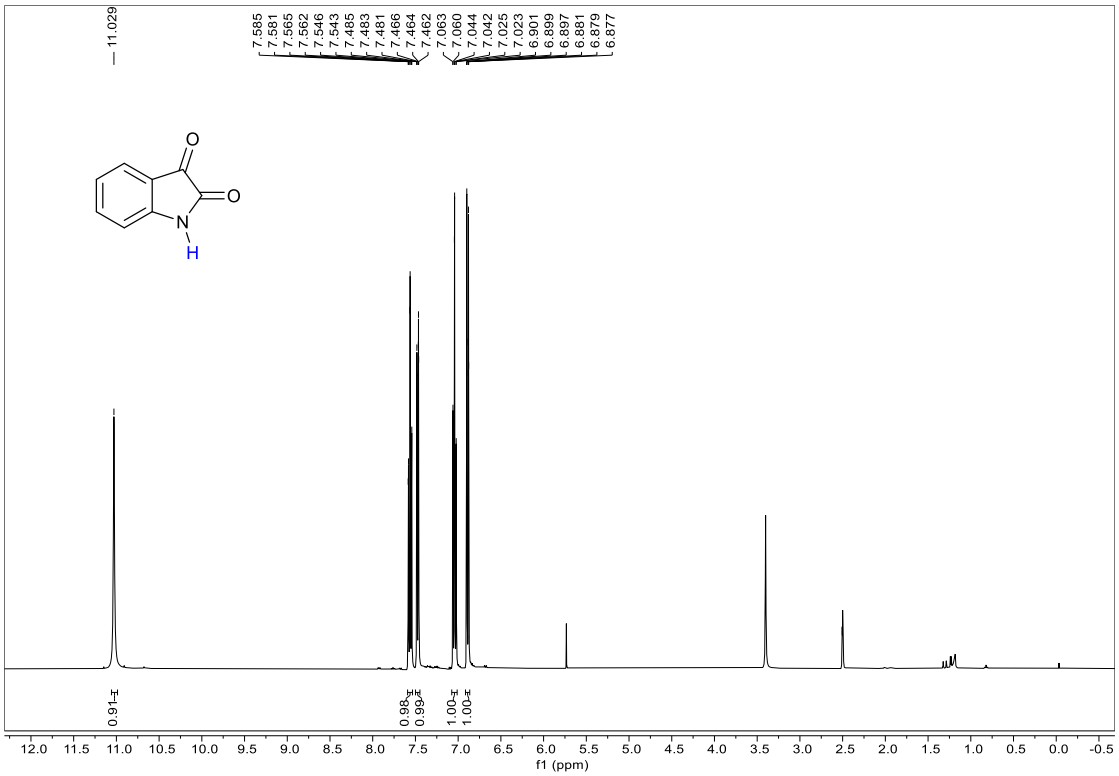
^{1}H NMR spectra of **4g** ($CDCl_3$, 400 MHz)



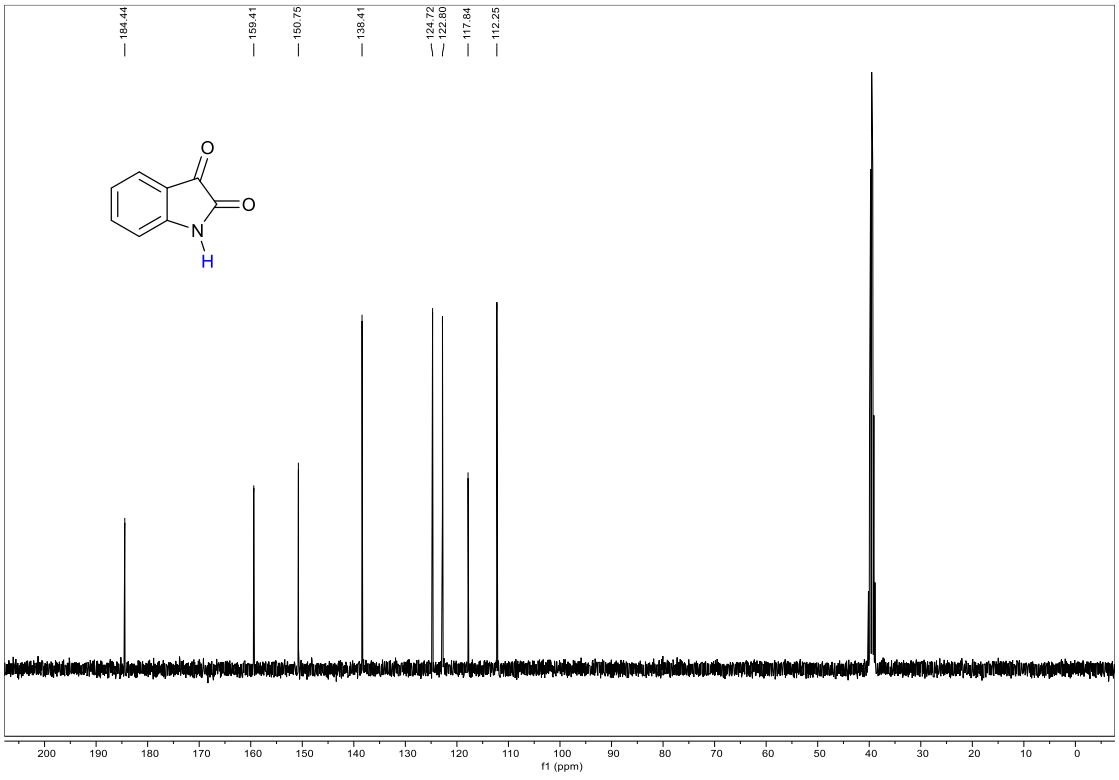
^{13}C NMR spectra of **4g** ($CDCl_3$, 101 MHz)



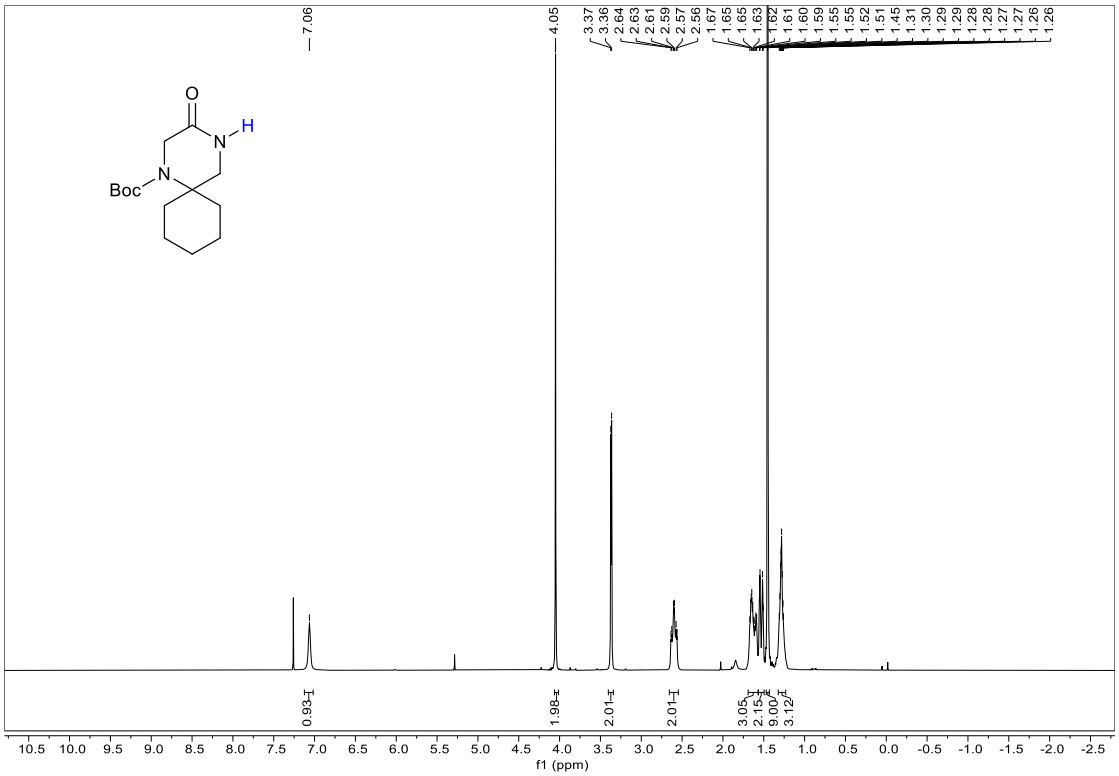
^{1}H NMR spectra of **4h** (DMSO-*d*6, 400 MHz)



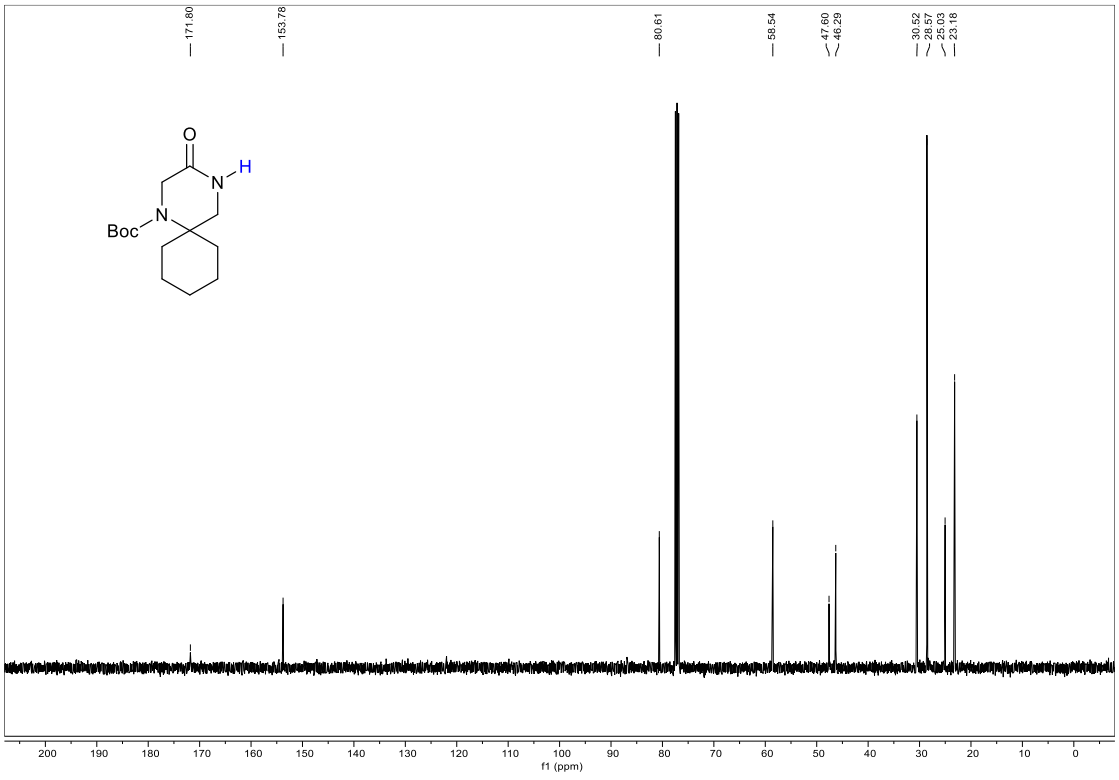
^{13}C NMR spectra of **4h** (DMSO-*d*6, 101 MHz)



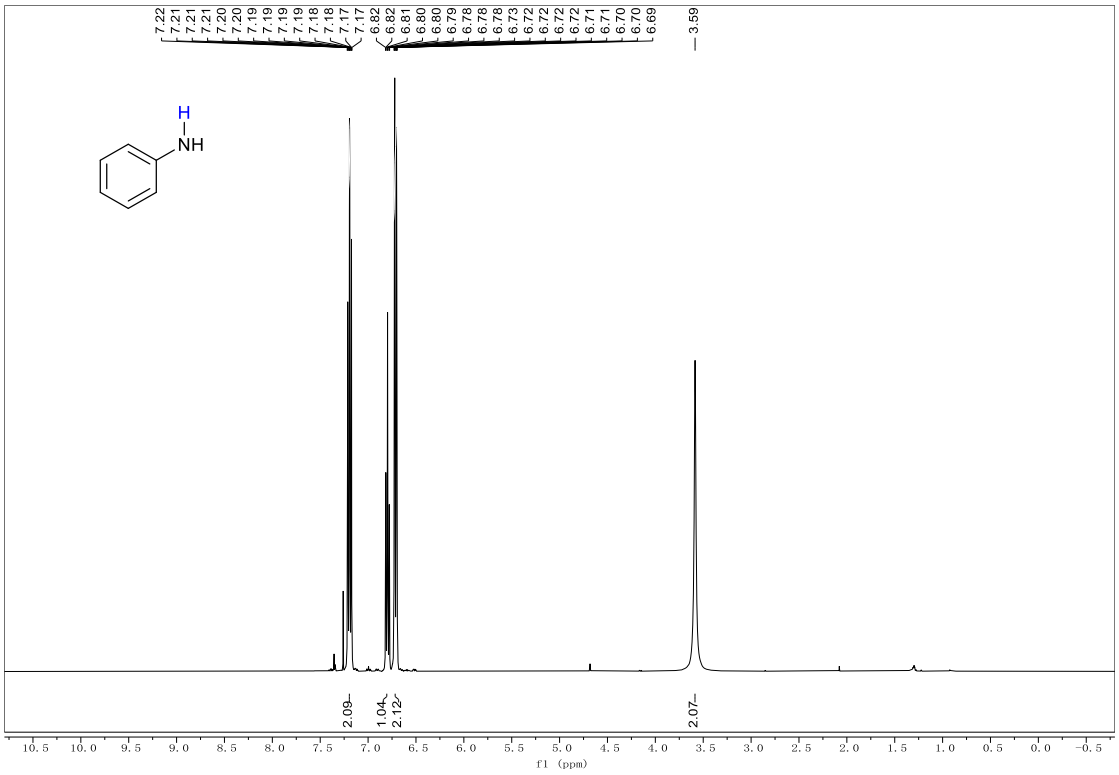
^{1}H NMR spectra of **4i** ($CDCl_3$, 400 MHz)



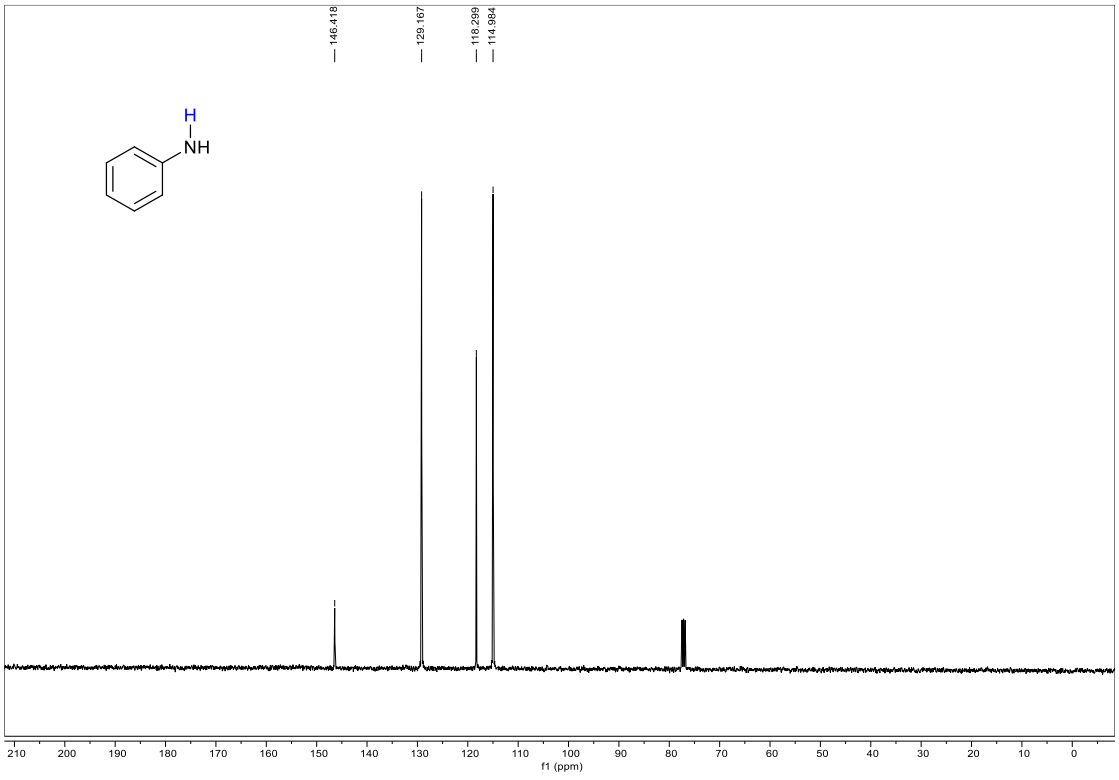
^{13}C NMR spectra of **4i** ($CDCl_3$, 101 MHz)



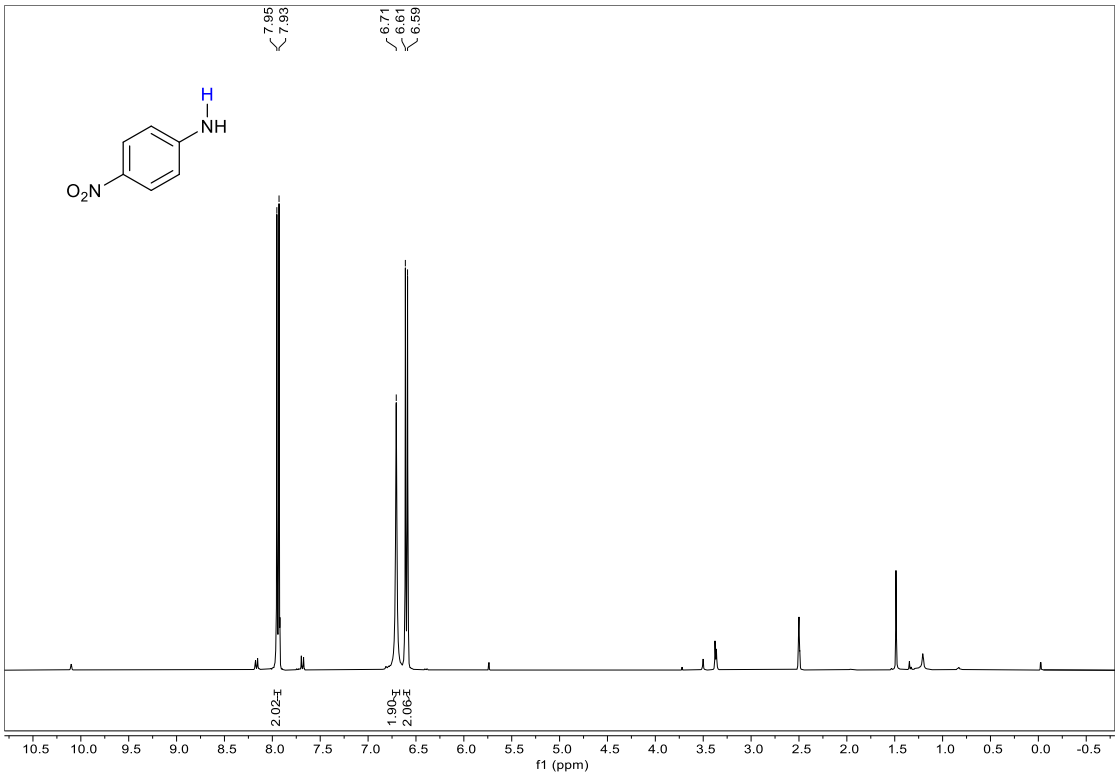
^{1}H NMR spectra of **6a** ($CDCl_3$, 400 MHz)



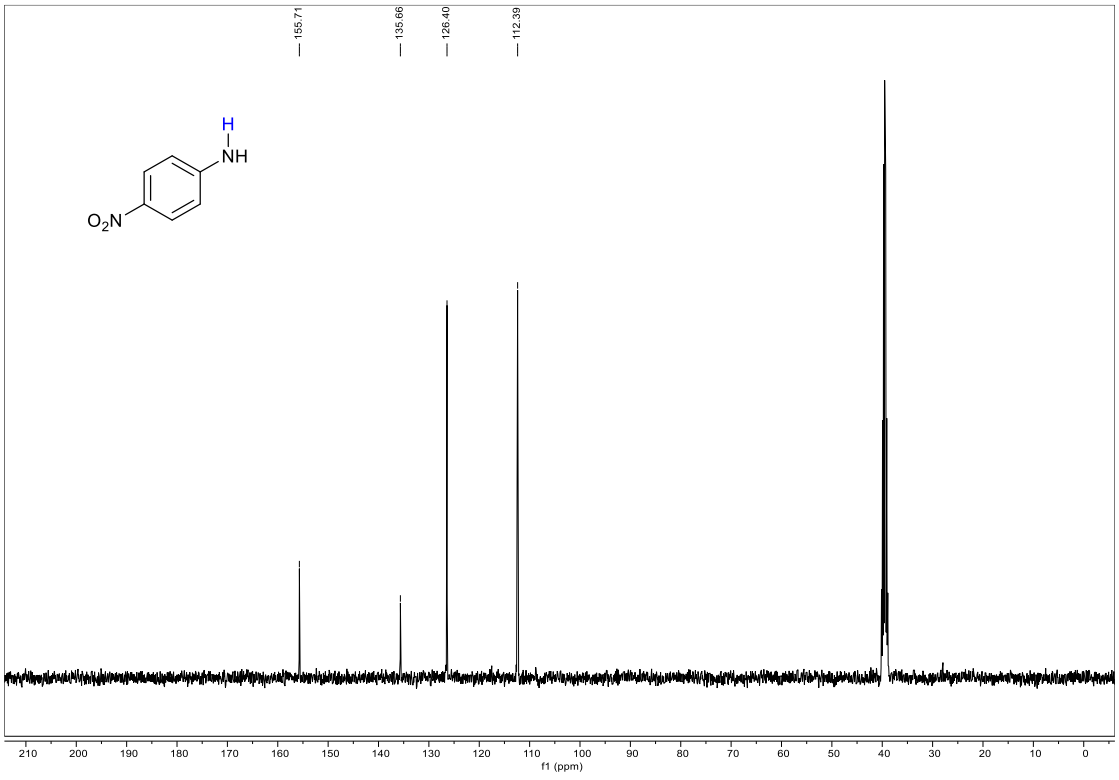
^{13}C NMR spectra of **6a** ($CDCl_3$, 101 MHz)



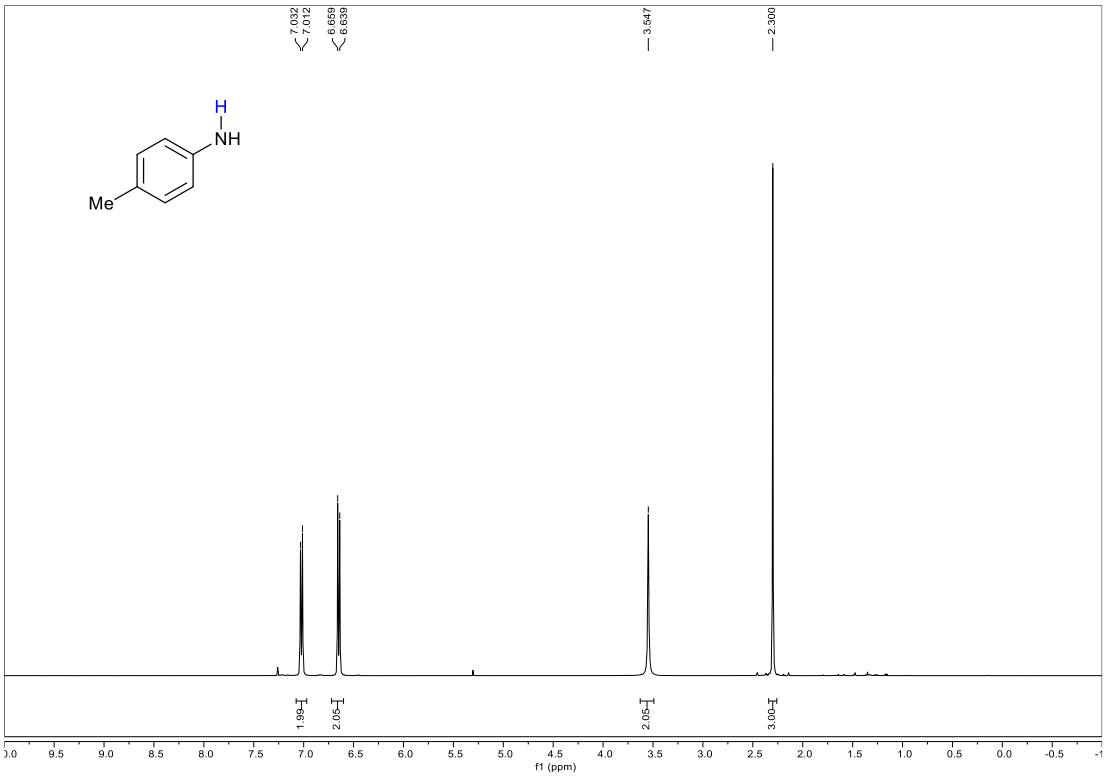
^{1}H NMR spectra of **6b** (DMSO-*d*6, 400 MHz)



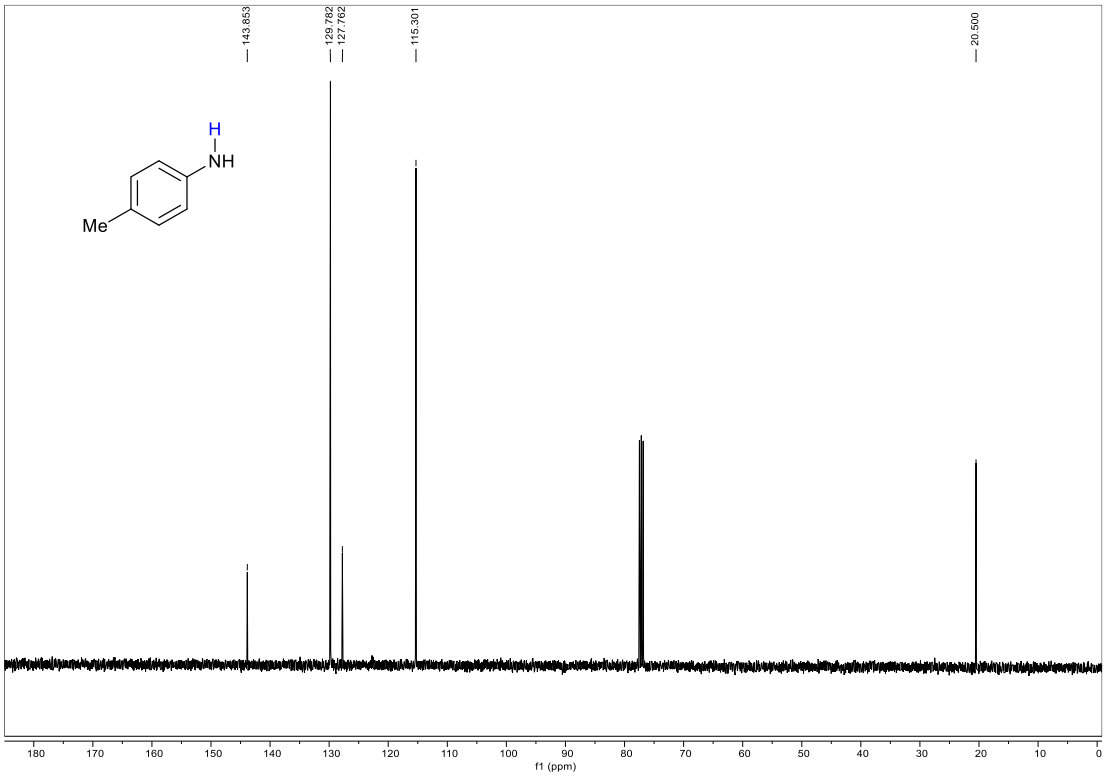
^{13}C NMR spectra of **6b** (DMSO-*d*6, 101 MHz)



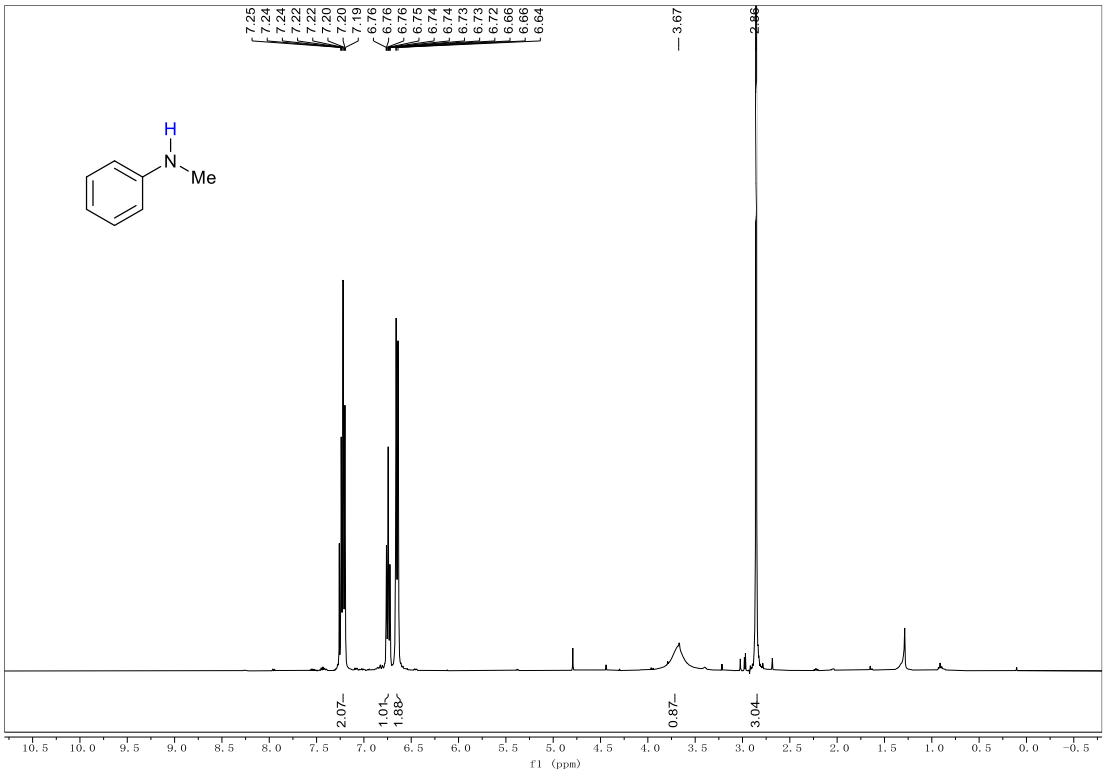
^{1}H NMR spectra of **6c** ($CDCl_3$, 400 MHz)



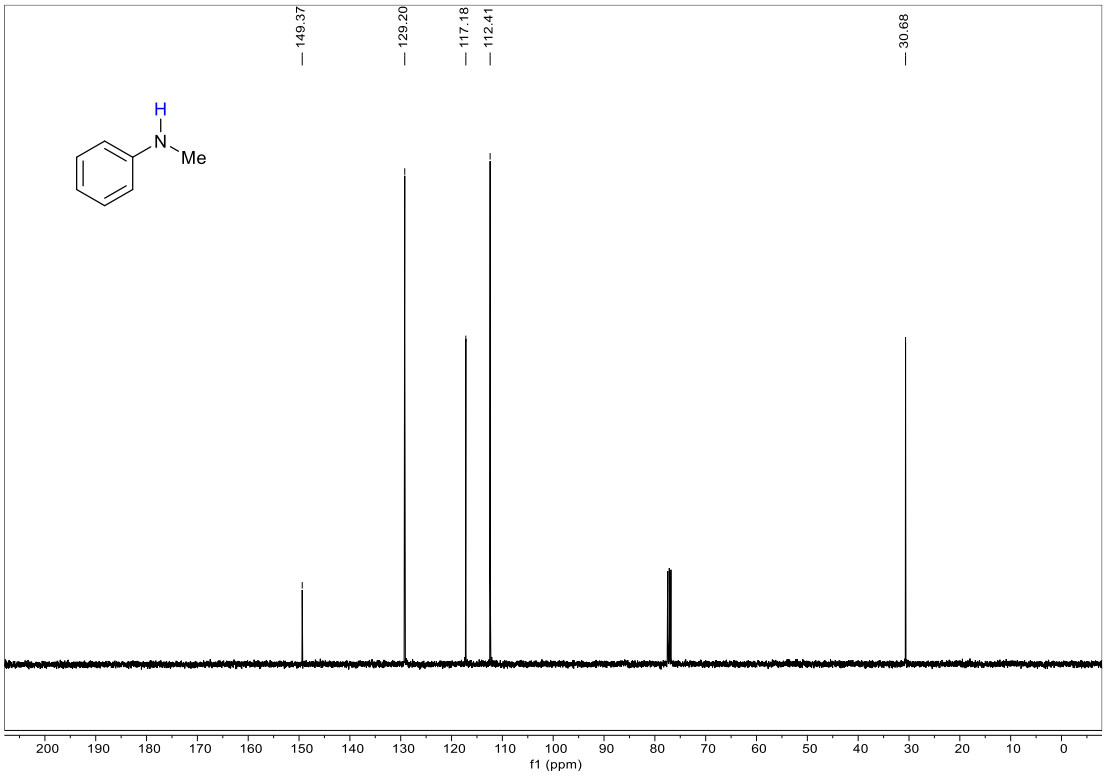
^{13}C NMR spectra of **6c** ($CDCl_3$, 101 MHz)



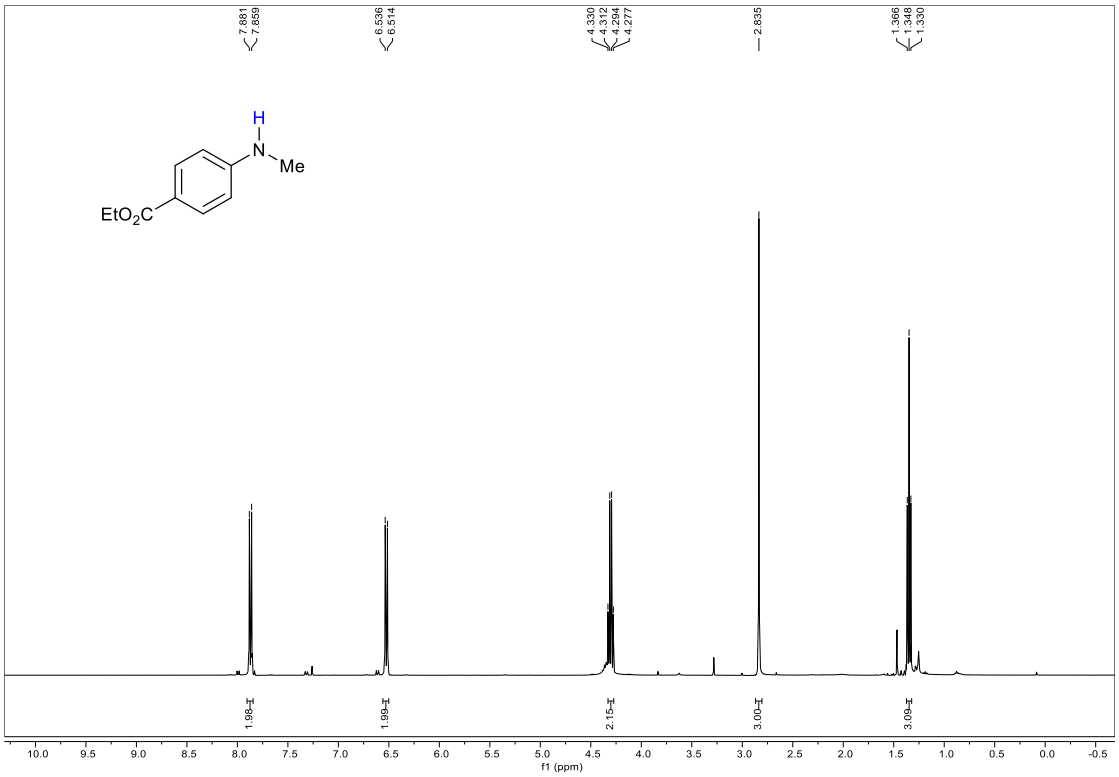
^{1}H NMR spectra of **6d** ($CDCl_3$, 400 MHz)



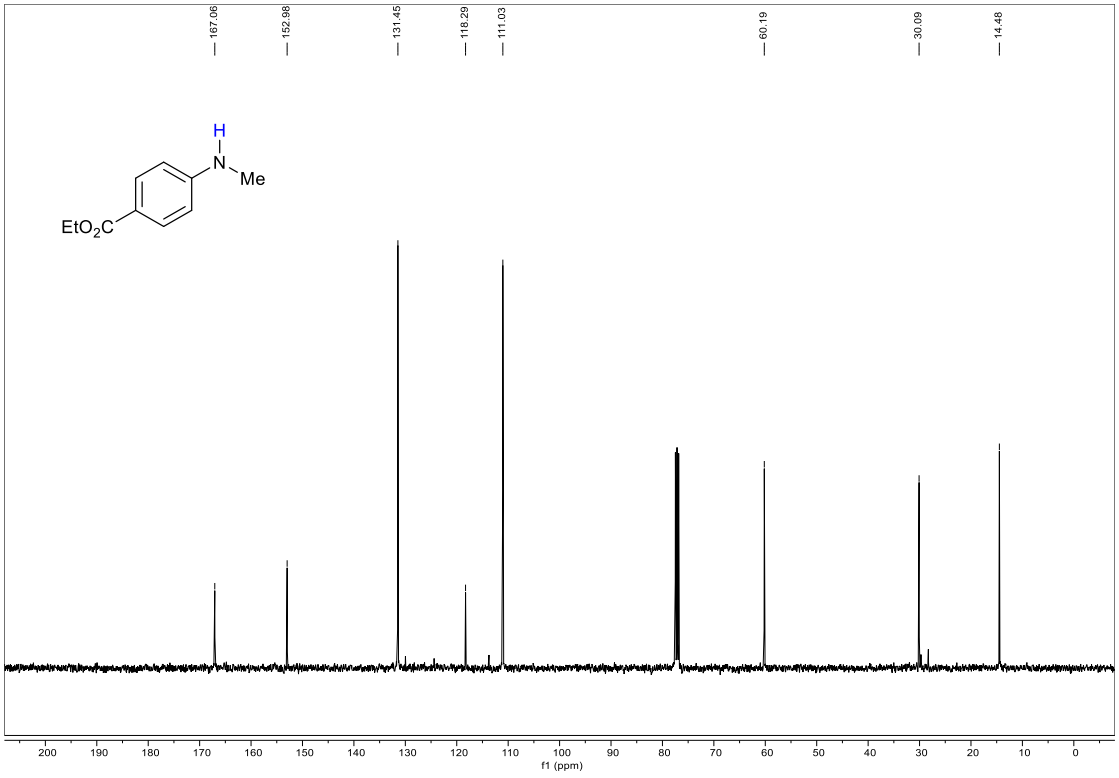
^{13}C NMR spectra of **6d** ($CDCl_3$, 101 MHz)



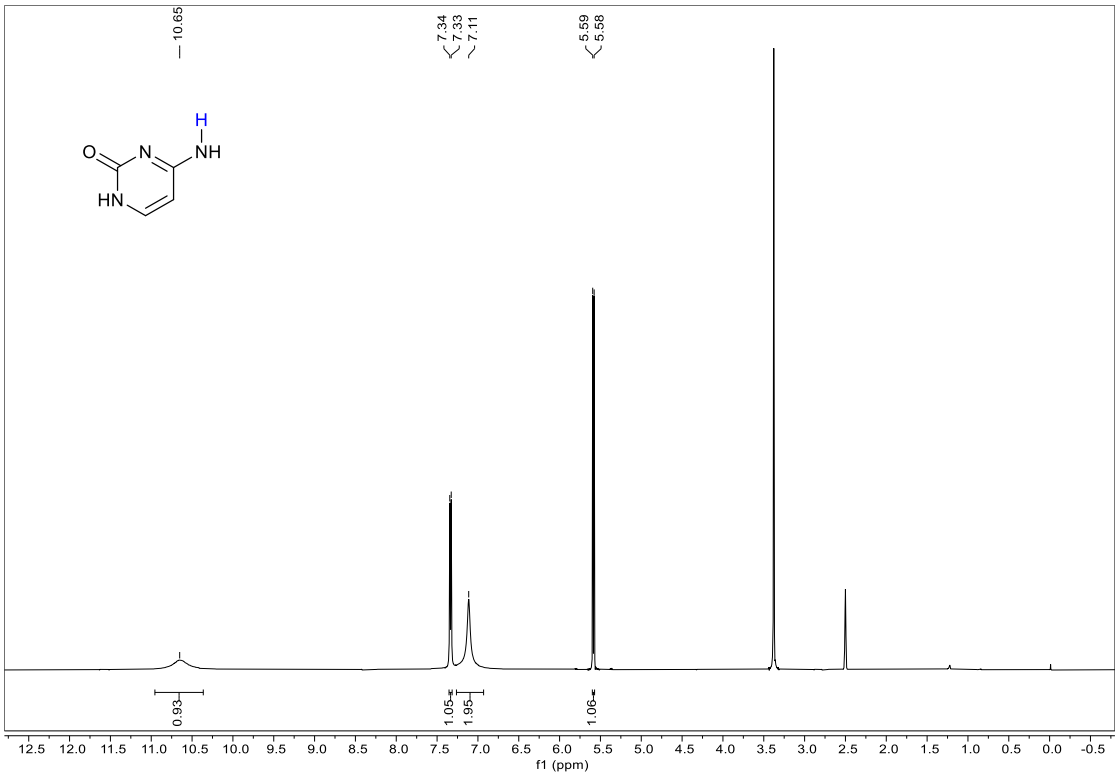
^{1}H NMR spectra of **6e** ($CDCl_3$, 400 MHz)



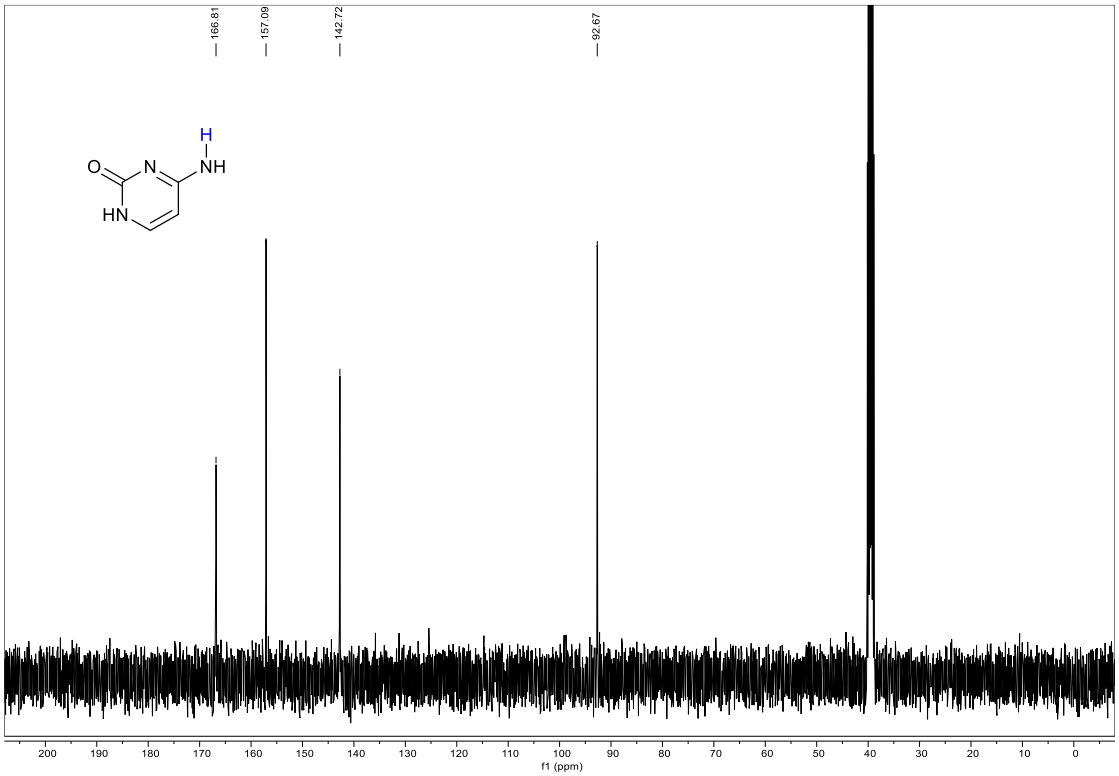
^{13}C NMR spectra of **6e** ($CDCl_3$, 101 MHz)



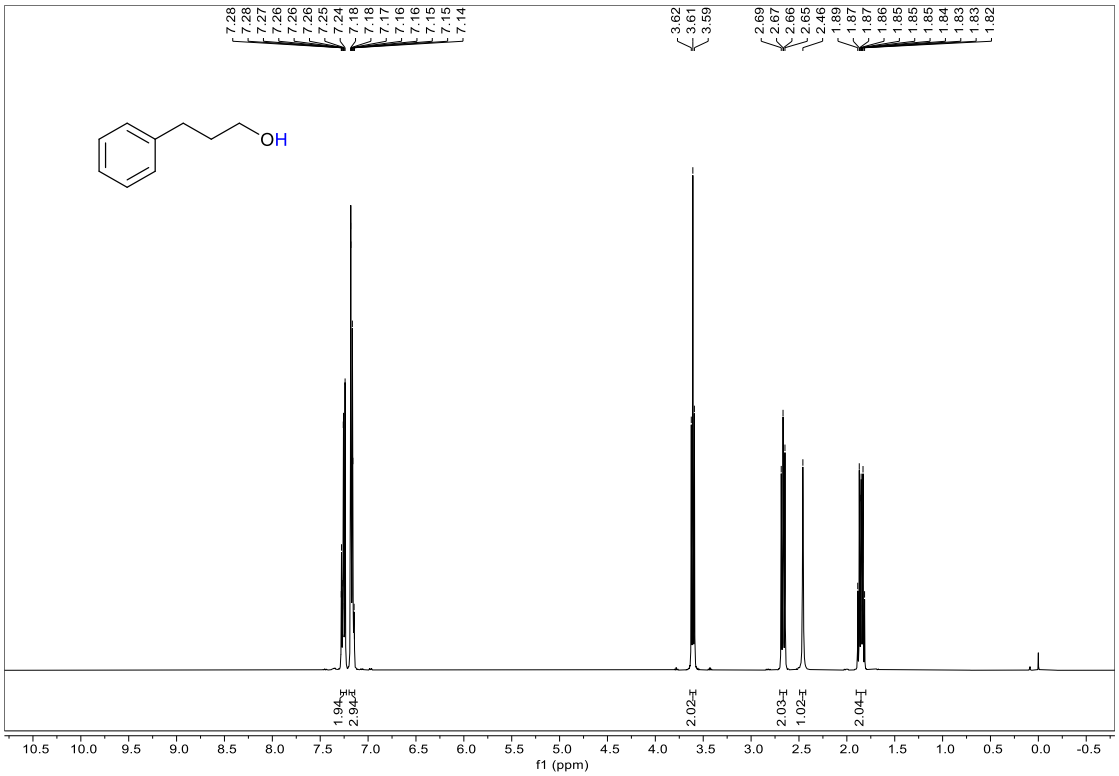
[1]HNMR spectra of **6f** (DMSO-*d*6, 400 MHz)



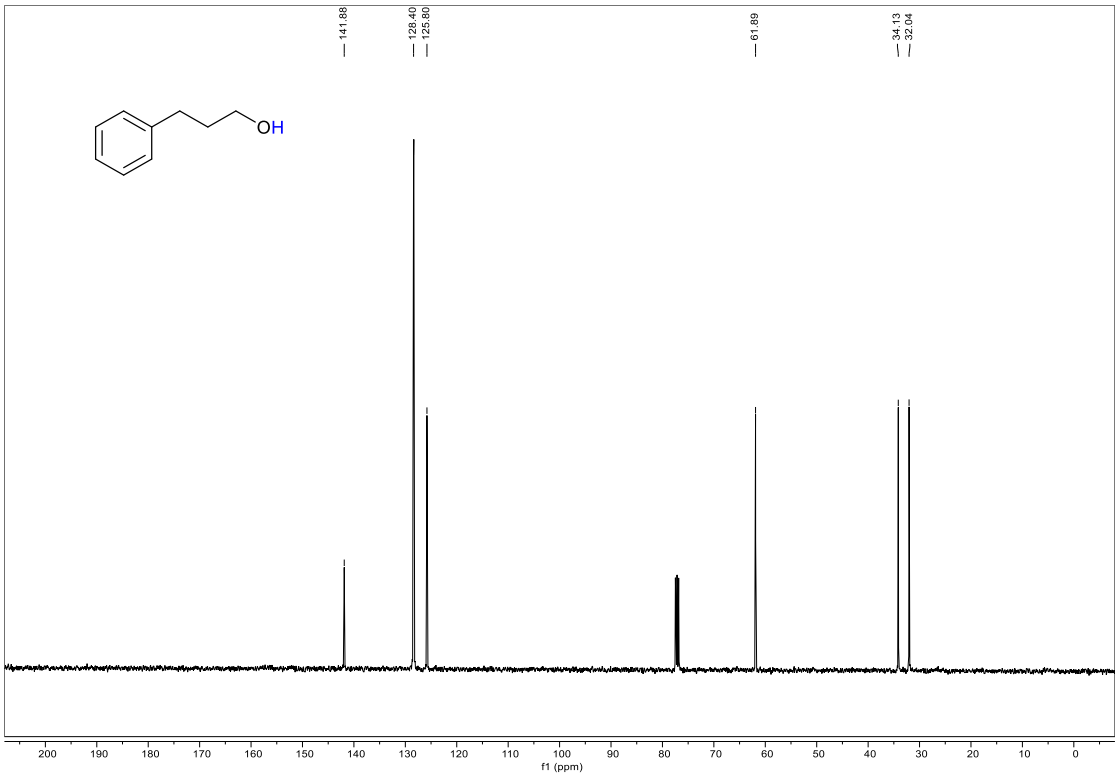
[13]C NMR spectra of **6f** (DMSO-*d*6, 101 MHz)



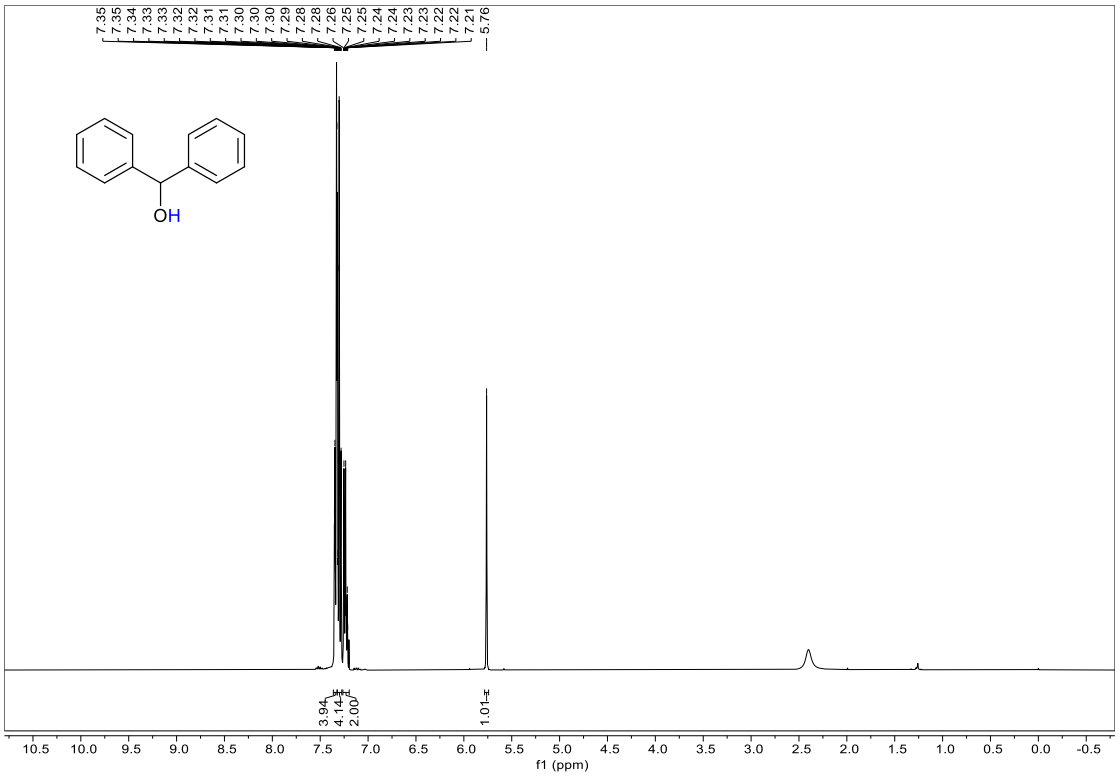
^{1}H NMR spectra of **10a** ($CDCl_3$, 400 MHz)



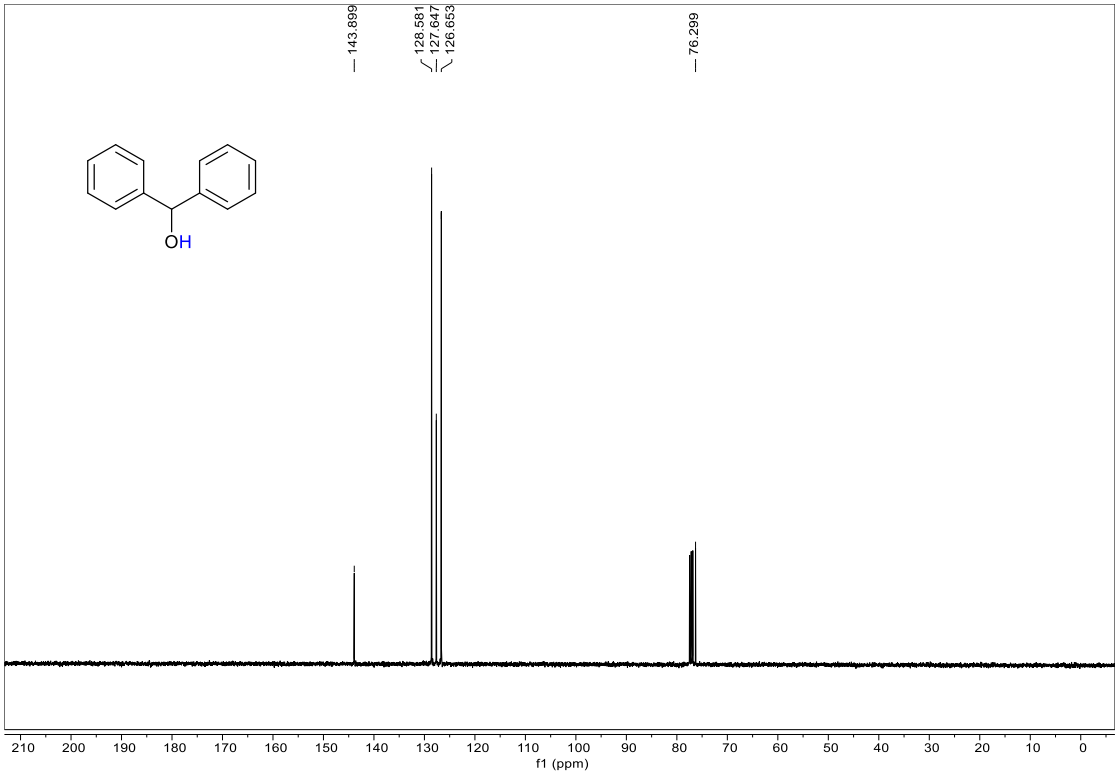
^{13}C NMR spectra of **10a** ($CDCl_3$, 101 MHz)



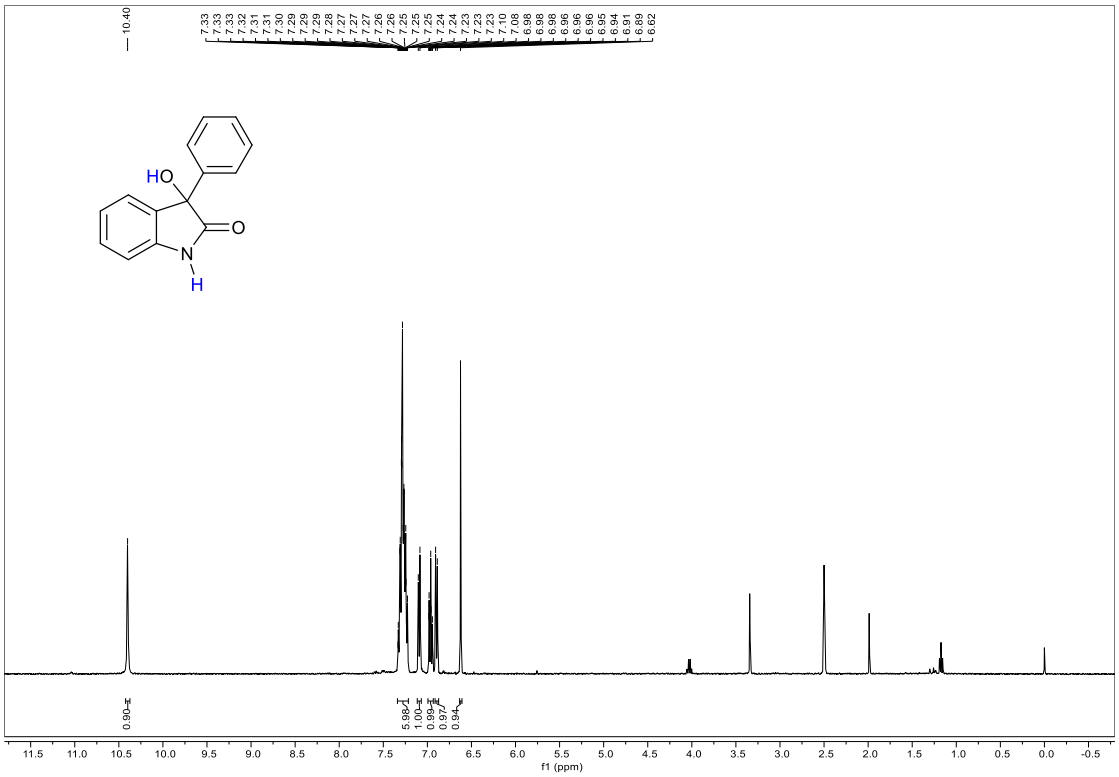
^{1}H NMR spectra of **10b** ($CDCl_3$, 400 MHz)



^{13}C NMR spectra of **10b** ($CDCl_3$, 101 MHz)



[1]HNMR spectra of **10d** (DMSO-*d*6, 400 MHz)



[13]C NMR spectra of **10d** (DMSO-*d*6, 101 MHz)