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Supplementary Information

Unravelling 2-Aminoquinazolin-4(*3H*)-one as an Organocatalyst for the Chemoselective Reduction of Nitroarenes

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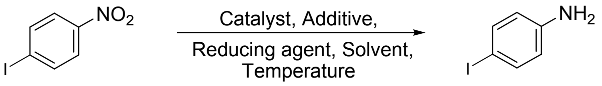
1. General Information

High purity solvents were used for all reactions. Silica gel (60-120, 230-400 mesh, S. D. Fine make) was used for column chromatography. All reactions were monitored by thin-layer chromatography (TLC) using pre-coated silica plates (Merck F_{254}, 0.25 mm thickness). Nitro compounds, NMR solvents were purchased from sigma Aldrich and spectrochem. The GC-MS analysis was carried out on a Shimadzu (QP 2010) series Gas Chromatogram-Mass Spectrometer (Tokyo, Japan), AOC-20i auto-sampler coupled, and a DB-5 MS capillary column, (30 m × ×0.25 mm i.d., 0.25 µm). The initial temperature of column was 70 °C held for 4 minute and was programmed to 230 °C at 4°C/min., then held for 15 minute at 230 °C; the sample injection volume was 2 µL in GC grade dichloromethane. Nitrogen was used as carrier gas at a flow rate of 1.1 mL min^{-1} on split mode (1: 50). ^{1}H NMR and ^{13}C NMR experiments were performed on Bruker Avance-300 and 600 spectrometers. Chemical shifts are reported in parts per million (ppm) downfield from an internal standard. Mass spectra were recorded on Water Q-TOF mass spectrometer.

2. General procedure for reduction of nitro compounds

Hydrazine hydrate (3 mmol) was added to the mixture of nitroarene (0.5 mmol), K_2CO_3 (0.5 mmol) and 2-aminoquinazolin-4(*3H*)-one (10 mol%) in solvent (H_2O/CH_3OH according to reactant) 3 mL at 100 °C for 2-12 h. However, in case of methanol as a solvent, it was also added to the vessel during the progress of reaction before it become dry. After completion of the reaction (as monitored by TLC and GC-MS), reaction vessel was kept at room temeperature and product was extracted with ethyl acetate (3 × 5 mL). Combined organic layer was washed with brine and distilled water (3 × 5 mL), dried on anhydrous sodium sulphate and solvent was evaporated under vaccum. Crude product was analyzed directly using GC-MS and product was isolated from crude by column chromatography.

3. Optimisation of reaction conditions:



S.No	Catalyst	Reducing agent	Additive	Solvent	Yield[b]
1	**L1**	$N_2H_4.H_2O$	-	CH_3OH	16
2	**L2**	$N_2H_4.H_2O$	-	CH_3OH	34
3	**L3**	$N_2H_4.H_2O$	-	CH_3OH	27
4	**L4**	$N_2H_4.H_2O$	-	CH_3OH	19
5	**L5**	$N_2H_4.H_2O$	-	CH_3OH	13
6	**L2**	$N_2H_4.H_2O$	-	CH_3OH	14[c]
7	**L2**	$N_2H_4.H_2O$	-	CH_3OH	36[d]
8	**L2**	**$N_2H_4.H_2O$**	**K_2CO_3**	**CH_3OH**	**78**
9	**L2**	$N_2H_4.H_2O$	Na_2CO_3	CH_3OH	21
10	**L2**	$N_2H_4.H_2O$	KCl	CH_3OH	22
11	**L2**	$N_2H_4.H_2O$	NaCl	CH_3OH	24
12	**L2**	$N_2H_4.H_2O$	K_2CO_3	CH_3OH	55[c]
13	**L2**	$N_2H_4.H_2O$	K_2CO_3	CH_3OH	81[d]
14	-	$N_2H_4.H_2O$	K_2CO_3	CH_3OH	51
15	**L2**	HCOOH	K_2CO_3	CH_3OH	N.R.
16	**L2**	$PhSiH_3$	K_2CO_3	CH_3OH	N.R.
17	**L2**	PMHS	K_2CO_3	CH_3OH	N.R.
18	**L2**	$N_2H_4.H_2O$	K_2CO_3	CH_3OH	80[e]
19	**L2**	$N_2H_4.H_2O$	K_2CO_3	CH_3OH	60[f]
20	**L2**	$N_2H_4.H_2O$	K_2CO_3	Ethanol	62
21	**L2**	$N_2H_4.H_2O$	K_2CO_3	H_2O	48
22	**L2**	$N_2H_4.H_2O$	K_2CO_3	DMSO	N.R.
23	**L2**	$N_2H_4.H_2O$	K_2CO_3	DMF	N.R.
24	**L2**	$N_2H_4.H_2O$	K_2CO_3	ACN	N.R.
25	**L2**	$N_2H_4.H_2O$	K_2CO_3	Toluene	N.R.
26	**L2**	$N_2H_4.H_2O$	K_2CO_3	CH_3OH	53[g]
27	**L2**	$N_2H_4.H_2O$	K_2CO_3	CH_3OH	22[h]

[a] Reaction conditions: 4-Iodonitrobenzene (0.1 mmol), catalyst (10 mol%), reducing agent (6 equiv.), additive (1 equiv.), solvent (2 mL) at 100 °C for 5h.

[b] Isolated yield.

[c] 8 equiv. hydrazine hydrate.

[d] 4 equiv. hydrazine hydrate.

[e] K_2CO_3 (2 equiv.)

[f] K_2CO_3 (0.5 equiv.)

[g] Reaction carried out at 80 °C.

[h] Reaction carried out at 60 °C.

4. Infrared study for H-B interactions:

The infrared spectra of hot aqueous solution of hydrazine hydrate and **L2** were compared with IR spectra of the reaction of $N_2H_4.H_2O$ with **L2** in water.

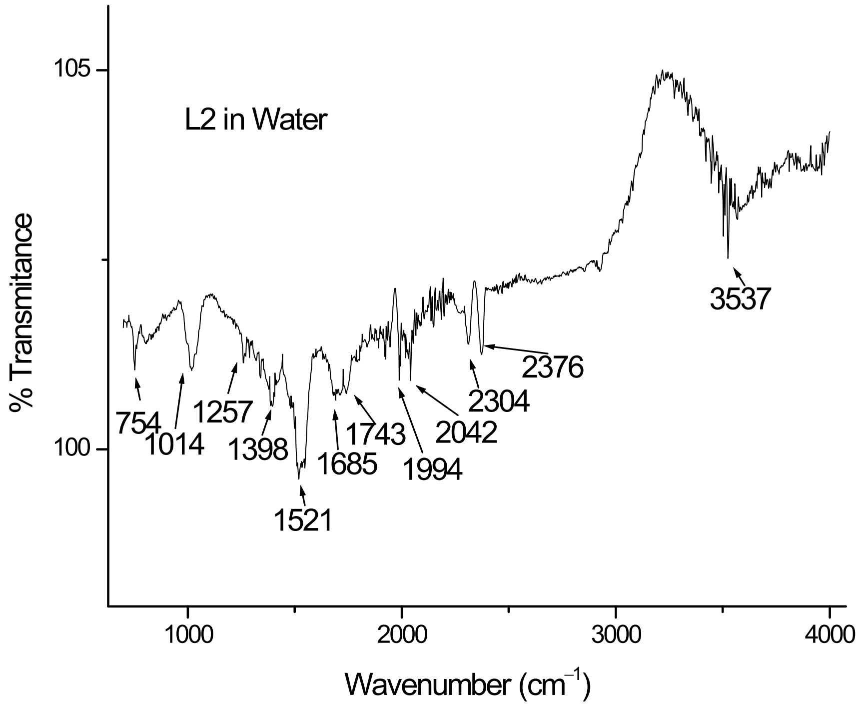


Fig. 1 The infrared spectra of the L2 in water.

During comparison in between the three infrared spectra(Fig. 1, Fig. 2 and Fig. 3), blue shift was observed for N-N stretching frequency from 1082 to 1089 cm^{-1} indicating decrease in N-N bond length of hydrazine while red shift is observed for N-H bending frequency from 1612 to 1606 cm^{-1} showed N-H bond elongation of N_2H_4.[1] Also new peaks at 2017, 2032, 2158 and 2181 cm^{-1} might be due to polarization of C=O, C=N and C-N bonds of **L2** because of hydrogen bond interactions.[2]

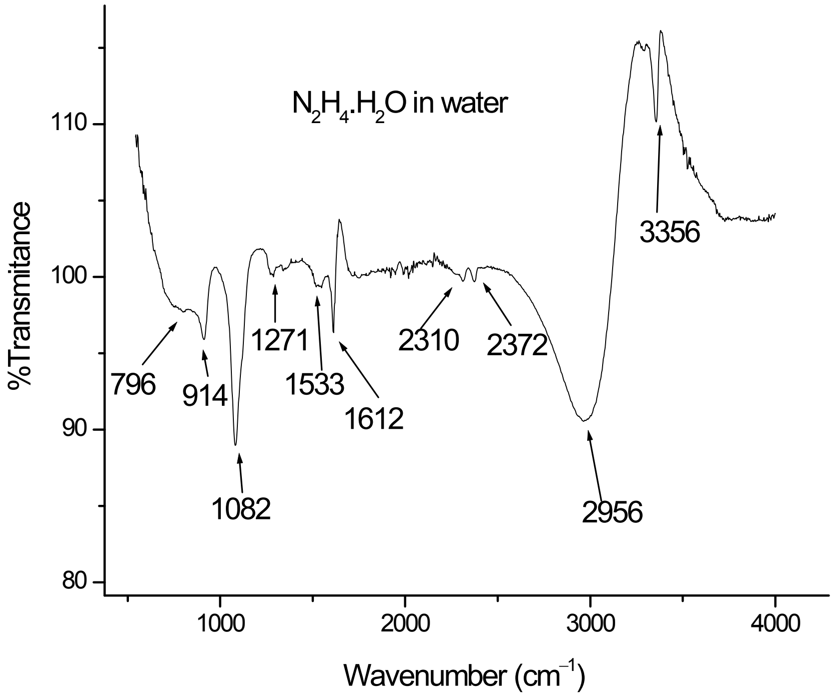


Fig. 2 The infrared spectra of hydrazine hydrate in water.

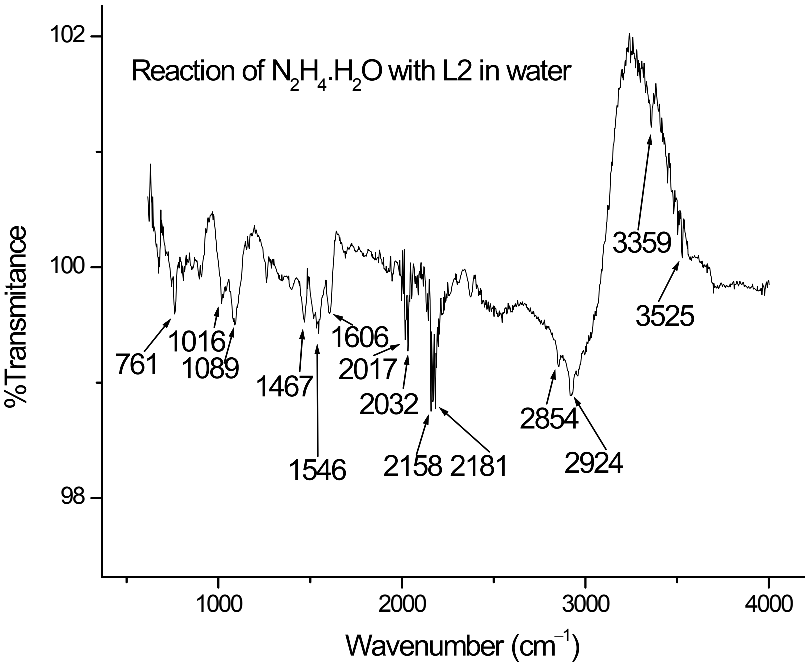


Fig. 3 The infrared spectra of the reaction between hydrazine hydrate and L2 in water.

5. UV-Vis-Fluorescence study for H-B interactions:

In UV-Vis spectroscopy, 2-aminoquinazolin-4(*3H*)-one (**L2**) showed absorption at 260 nm and 315 nm in methanol. However, on the addition of hydrazine hydrate and heating it to 100 °C, the intensity of the band at 260 nm decreases, without alteration in 315 nm.

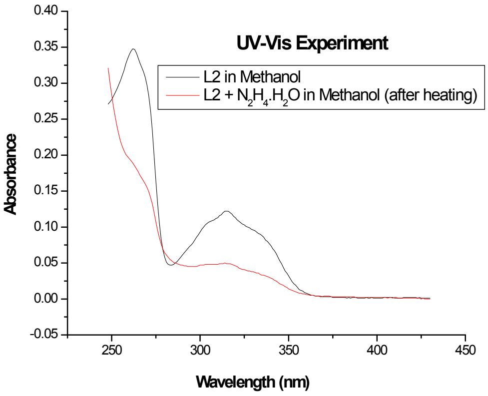


Fig. 4: UV-Vis spectra of L2 and its reaction with hydrazine hydrate

Moreover, in fluoresence experiment, excitation at 315 nm, it exhibited a blue emission at 400 nm. Further, the addition of hydrazine hydrate resulted in quenching of emission spectrum. Thus, absorption and emission results suggested that the hydrazine hydrate attack at the nucleophilic carbonyl centre and distorts the conjugation in molecules.

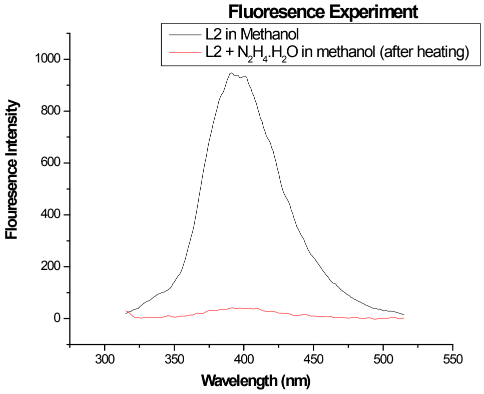


Fig. 5: Flouresence spectra of L2 and its reaction with hydrazine hydrate

6. Characterization of nitro reduction products

All compounds were identified by spectral comparison with literature data.

4-Iodoaniline (1b):[3a] Reaction was performed in CH_3OH for 5 hour and product was obtained by following general procedure described above (method **A**) and purified by column chromatography (*n*-hexane: ethyl acetate (9: 1)) as brown solid. Yield 85 mg, 78%; ^1H NMR (600 MHz, d_6-DMSO): δ 7.24 (d, J = 8.64 Hz, 2H), 6.39 (d, J = 8.58 Hz, 2H), 5.23 (s, 2H); ^{13}C NMR (150 MHz, d_6-DMSO): δ 148.9, 137.5, 117.0, 76.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for C_6H_6NI 219.9623; Found 219.9611.

3-Bromoaniline (2b):[3b] Reaction was performed in CH_3OH for 5 hour and product was obtained by following general procedure described above (method **A**) and purified by column chromatography (*n*-hexane: ethyl acetate (9: 1)) as brown solid. Yield 56 mg, 65%; ^1H NMR (600 MHz, d_6-DMSO): δ 6.91 (t, J = 7.95 Hz, 1H), 6.71 (t, J = 1.98 Hz, 1H), 6.59-6.58 (m, 1H), 6.51-6.50 (m, 1H), 5.3 (brs, 2H); ^{13}C NMR (150 MHz, d_6-DMSO): δ 151.0, 131.1, 122.5, 118.2, 116.3, 113.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for C_6H_6NBr; Found 171.9749.

4-Chloroaniline (3b):[3c] Reaction was performed in CH_3OH for 5 hour and product was obtained by following general procedure described above (method **A**) and purified by column chromatography (*n*-hexane: ethyl acetate (9: 1)) as white solid. Yield 39 mg, 62%; ^1H NMR (600 MHz, $CDCl_3$): δ 7.09 (d, J = 8.7 Hz, 2H), 6.60 (d, J = 8.7 Hz, 2H), 3.64 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 144.9, 129.1, 123.1, 116.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for C_6H_6NCl 128.0267; Found 128.0255.

2-Chloro-4-aminoaniline (4b):[3d] Reaction was performed in CH_3OH for 12 hour and product was obtained by following general procedure described above (method **A**) and purified by column chromatography (*n*-hexane: ethyl acetate (4: 1)) as brown solid. Yield 50 mg, 70%; ^1H NMR (600 MHz, $CDCl_3$): δ 6.78 (d, J = 8.46 Hz, 1H), 6.02 (d, J = 2.58 Hz, 1H), 5.83 (dd, J = 8.43 Hz, 2.55 Hz, 1H), 4.93 (brs, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 148.5, 145.0, 129.3, 105.5, 104.9, 101.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_6H_8ClN_2$143.0376; Found 143.0387.

Aniline (5b):[3e] Reaction was performed in CH_3OH for 8 hour and product was obtained by following general procedure described above (method **A**) and purified by column chromatography (*n*-hexane: ethyl acetate (9: 1)) as brown liquid. Yield 21 mg, 45%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.26-7.23 (m, 2H), 6.87-6.84 (m, 1H), 6.75 (d, J = 8.40 Hz, 2H), 3.6 (brs, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.5, 129.3, 118.6, 115.2. HRMS (ESI-TOF) m/z:$[M+H]^+$calcd for C_6H_7N is 94.0657; Found 94.0633.

4-Aminobenzamide (6b):[3e] Reaction was performed in CH_3OH for 7 hour and product was obtained by following general procedure described above (method **A**) and purified by column chromatography (*n*-hexane: ethyl acetate (1: 4)) as white solid. Yield 45 mg, 66%; ^{1}H NMR (600 MHz, d_6-DMSO): δ 7.56 (d, J = 8.28 Hz, 2H), 7.50 (s, 1H), 6.82 (s, 1H), 6.50 (d, J = 8.28 Hz, 2H), 5.57 (s, 2H); ^{13}C NMR (150 MHz, d_6-DMSO): δ 168.5, 152.12, 129.5, 121.4, 112.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_7H_8N_2O$ 137.0715; Found 137.0702.

4-Aminobenzenesulphonamide (7b):[3d] Reaction was performed in CH_3OH for 5 hour and product was obtained by following general procedure described above (method **A**) and purified by column chromatography (*n*-hexane: ethyl acetate (3: 7)) as yellow solid. Yield 67 mg, 78%; ^{1}H NMR (600 MHz, d_6-DMSO): δ 7.43 (d, J = 8.64 Hz, 2H), 6.87 (s, 2H), 6.56 (d, J = 8.64 Hz, 2H), 5.78 (s, 2H); ^{13}C NMR (150 MHz, d_6-DMSO): δ 152.3, 130.5, 127.8, 112.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_6H_8N_2O_2S$ 173.0385; Found 173.0367.

4-Aminobenzoic acid (8b):[3c] Reaction was performed in CH_3OH for 7 hour and product was obtained by following general procedure described above (method **A**) and purified by column chromatography (*n*-hexane: ethyl acetate (1: 1)) as white solid. Yield 50 mg, 73%; ^{1}H NMR (600 MHz, d_6-DMSO): δ 11.8 (brs, 1H), 7.59 (d, J = 8.5 Hz, 2H), 6.52 (d, J = 8.6 Hz, 2H), 5.82 (s, 2H); ^{13}C NMR (150 MHz, d_6-DMSO): δ 167.9, 153.5, 131.6, 117.4, 113.0. HRMS (ESI-TOF) m/z:[M+H]$^+$calcd for $C_7H_7NO_2$ is 138.0555; Found 138.0576.

4-Aminobenzonitrile (10b):[3f] Reaction was performed in CH_3OH for 2 hour and product was obtained by following general procedure (method **A** in the absence of additive K_2CO_3) described above and purified by column chromatography (*n*-hexane: ethyl acetate (4: 1)) as pink solid. Yield 45 mg, 77%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 (d, J = 8.35 Hz, 2H), 6.64 (d, J = 8.50 Hz, 2H), 4.1 (brs, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 150.3, 133.8, 120.0, 114.4, 100.3. HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $C_7H_6N_2$119.0609;Found 119.0612.

3-Aminobenzamide (11b) (CAS NUMBER 3544-24-9**)**: Reaction was performed in CH_3OH for 7 hour and product was obtained by following general procedure described above (method **A**) and purified by column chromatography (*n*-hexane: ethyl acetate (1: 4)) as white solid. Yield 48 mg, 71%; ^{1}H NMR (600 MHz, d_6-DMSO): δ 7.67 (s, 1H), 7.08 (s, 1H), 7.04-7.01 (m, 2H), 6.95 (d, J = 7.74 Hz, 1H), 6.66-6.64 (m, 1H), 5.15 (s, 2H); ^{13}C NMR (150 MHz, d_6-DMSO): δ 169.1, 149.0, 135.6, 128.9, 116.9, 115.1, 113.5. HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $C_7H_8N_2O$ 137.0715; Found 137.0702.

3-Aminobenzonitrile (12b):[3g] Reaction was performed in CH_3OH for 2 hour and product was obtained by following general procedure described above (method **A** in the absence of additive K_2CO_3) and purified by column chromatography (*n*-hexane: ethyl acetate (9: 1)) as brown solid. Yield 47 mg, 81%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 (t, J = 7.86 Hz, 1H), 7.03 (t, J = 7.56 Hz, 1H), 6.91 (s, 1H), 6.89-6.87 (m, 1H), 3.90 (brs, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.9, 130.0, 121.9, 119.1, 117.4, 112.9. HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $C_7H_6N_2$119.0609; Found 119.0595.

3-Nitroaniline (13b):[3d] Reaction was performed in H_2O for 3 hour and product was obtained by following general procedure described above (method **A**) and purified by column chromatography (*n*-hexane: ethyl acetate (4: 1)) as yellow solid. Yield 58 mg, 84%; ^{1}H NMR

(600 MHz, $CDCl_3$): δ 7.57 (d, J = 8.1, 1H,), 7.48-7.48 (m, 1H), 7.28-7.25 (m, 1H), 6.95-6.93 (m, 1H), 3.99 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.3, 147.4, 129.9, 120.6, 113.1, 109.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_6H_7N_2O_2$139.0508; Found 139.0500.

4-Nitroaniline (14b):[3d] Reaction was performed in H_2O for 3 hour and product was obtained by following general procedure described above (method **A**) and purified by column chromatography (*n*-hexane: ethyl acetate (4: 1)) as yellow solid. Yield 56 mg, 81%; ^1H NMR (600 MHz, $CDCl_3$): δ 8.09 (d, J = 9.00 Hz, 1H), 6.64 (d, J = 9.06 Hz, 1H), 4.40 (brs, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.4, 139.1, 126.3, 113.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_6H_7N_2O_2$139.0508; Found 139.0441.

3-Amino-5-nitrobenzamide (15b): Reaction was performed in H_2O for 3 hour and product was obtained by following general procedure described above and purified by column chromatography (*n*-hexane: ethyl acetate (4: 1) as orange solid. Yield 43 mg, 48%; M.P. 222 °C; ^1H NMR (600 MHz, d_6-DMSO): δ 8.13 (s, 1H), 7.80 (s,1H), 7.50-7.44 (m, 3H), 6.0 (s, 2H); ^{13}C NMR (600 MHz, d_6-DMSO): δ 167.0, 150.5, 149.1, 136.8, 119.3, 109.7, 109.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_7H_7N_3O_3$182.0566 Found 182.0552.

3,3‘-Azobisaniline (18b): Reaction was performed in CH_3OH for 12 hour and product was obtained by following general procedure described above (method **A**) and purified by column chromatography (*n*-hexane: ethyl acetate (4: 1)) as brown solid. Yield 42 mg, 40%; M.P. 135 °C; ^1H NMR (600 MHz, d_6-DMSO): δ 7.21 (t, J = 7.77 Hz, 2H), 7.04-7.02 (m, 4H), 6.74-6.73 (m, 2H), 5.42 (brs, 4H); ^{13}C NMR(150 MHz, d_6-DMSO): δ 153.5, 150.09, 130.0, 117.3, 112.7, 105.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{12}H_{12}N_4$ 213.1140 Found 213.1130.

4-Methoxyaniline (16b):[3f] Reaction was performed in CH_3OH for 12 hour and product was obtained by following general procedure described above (method **A**) and purified by column chromatography (*n*-hexane: ethyl acetate (19: 1)) as brown solid. Yield 32 mg, 52%; ^1H NMR (600 MHz, d_6-DMSO): 6.62 (d, J = 8.76 Hz, 2H), 6.50 (d, J = 8.76 Hz, 2H), 4.58 (brs, 2H), 3.60 (s, 3H); (150 MHz, $CDCl_3$): 151.4, 142.7, 115.4, 114.9, 55.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for C_7H_9NO 124.0762; Found 124.0751.

3-Aminobiphenyl (17b):[3d] Reaction was performed in CH_3OH for 10 hour and product was obtained by following general procedure described above (method **A**) and purified by column chromatography (*n*-hexane: ethyl acetate (19: 1)) as brown solid. Yield 55 mg, 65%; ^1H NMR (600 MHz, $CDCl_3$): δ 7.57 (d, J = 7.50 Hz, 2H), 7.43-7.41 (m, 2H), 7.35-7.32 (m, 1H), 7.26-7.22 (m, 1H), 7.00 (d, J = 7.50 Hz, 1H), 6.91 (s, 1H), 6.68 (d, J = 7.32 Hz, 1H), 3.61 (brs, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.7, 142.4, 141.4, 129.6, 128.6, 127.2, 127.1, 117.7, 114.1, 113.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{12}H_{12}N$ 170.0970;Found 170.0984.

1-Aminonaphthalene (19b):[3d] Reaction was performed in CH_3OH for 8 hour and product was obtained by following general procedure described above (method **A**) and purified by column chromatography (*n*-hexane: ethyl acetate (19: 1)) as brown solid. Yield 53 mg, 75%;^1H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, J = 7.2 Hz, 2H), 7.48-7.47 (m, 2H), 7.35-7.31 (m, 2H), 6.79 (d, J = 7.02 Hz, 1H), 3.98 (brs, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 142.1, 134.4, 128.5, 126.3, 125.8, 124.9, 123.7, 120.8, 119.0, 109.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{10}H_{10}N$ 144.0813; Found 144.0834.

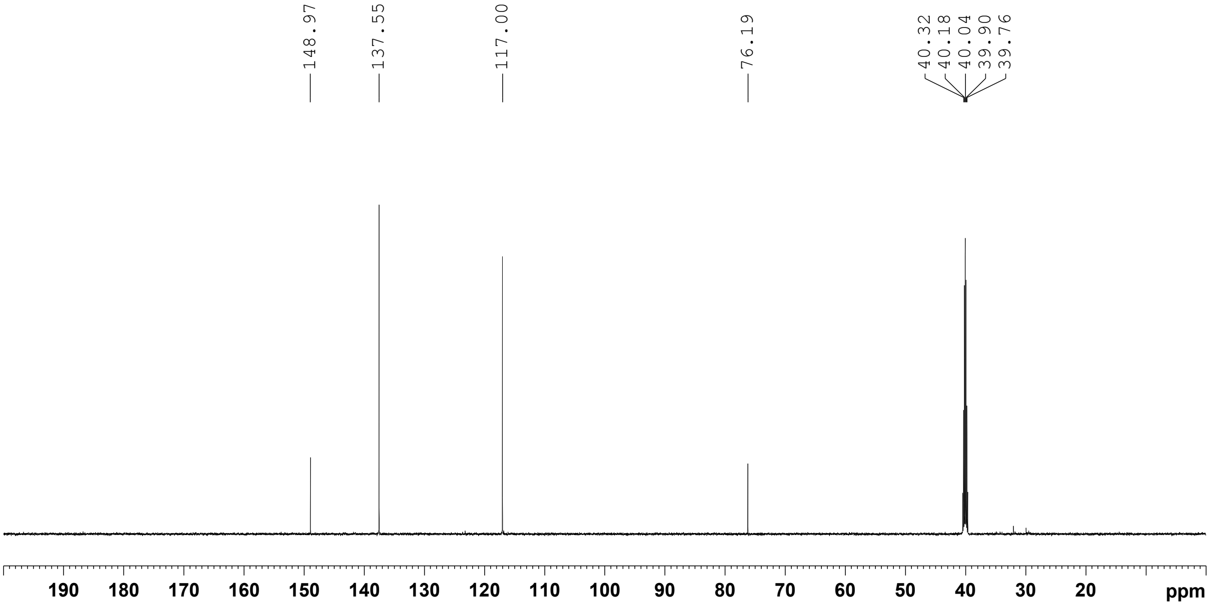
2-Aminofluorene (20b):[3a] Reaction was performed in CH_3OH for 12 hour and product was obtained by following general procedure described above (method **A**) and purified by column chromatography (*n*-hexane: ethyl acetate (6: 4)) as brown solid. Yield 54 mg, 61%; ^1H NMR (600 MHz, $CDCl_3$): δ 7.63 (d, J = 7.56 Hz, 1H), 7.56 (d, J = 8.04 Hz, 1H) 7.46 (d, J = 7.44 Hz, 1H), 7.31 (t, J =7.41 Hz, 1H), 7.20-7.17 (m, 1H), 6.8 (s, 1H), 6.71-6.70 (m, 1H), 3.81 (s, 2H), 3.75 (brs, 2H) ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.7, 145.1, 142.2, 142.1, 133.0, 126.6, 125.0, 124.7, 120.6, 118.5, 113.9, 111.8, 36.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_9H_9N_2$ 182.0970; Found 182.0959.

5-Aminoisoquinoline (21b):[3d] Reaction was performed in CH_3OH for 5 hour and product was obtained by following general procedure described above (method **A**) and purified by column chromatography (*n*-hexane: ethyl acetate (6: 4)) as brown solid. Yield 58 mg, 81%; ^1H NMR (300 MHz, $CDCl_3$): δ 9.20 (s, 1H), 8.50 (d, *J* = 5.88 Hz, 2H), 7.59 (d, *J* = 5.94 Hz, 1H), 7.42 (d, *J* = 4.02 Hz, 2H), 6.97 (t, *J* = 4.02 Hz, 1H), 4.25 (brs, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.3, 142.4, 141.6, 129.8, 128.1, 126.3, 118.3, 114.4, 113.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_9H_9N_2$145.0766; Found 145.0798.

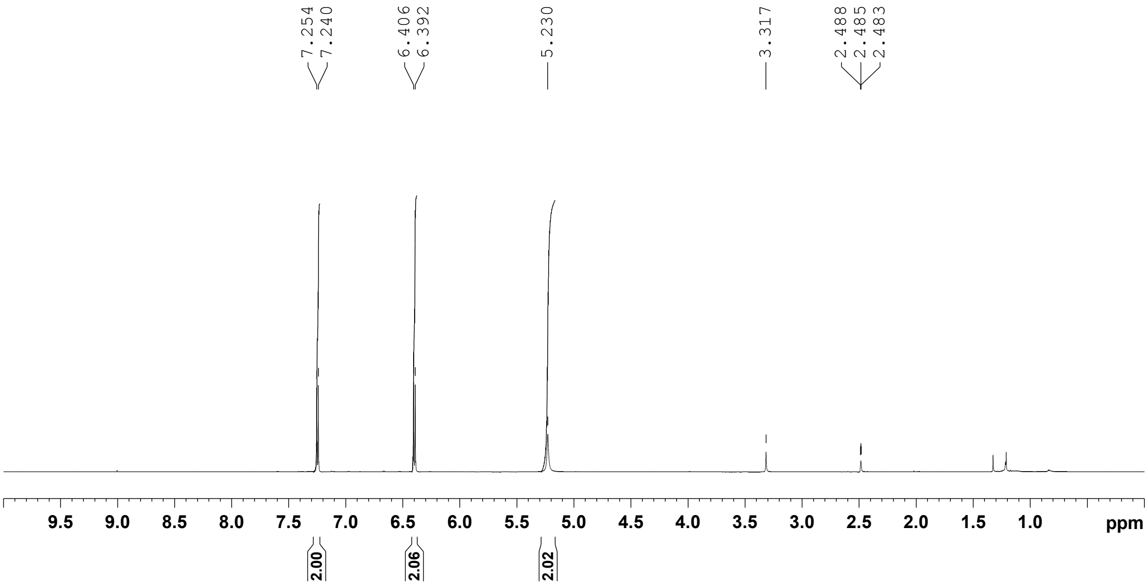
5-Aminoindole (22b) (CAS NUMBER 5192-03-0**):** Reaction was performed in CH_3OH for 12 hour and product was obtained by following general procedure described above (method A) and purified by column chromatography (*n*-hexane: ethyl acetate (6: 4)) as brown solid. Yield 43 mg, 66%; ^1H NMR (600 MHz, d_6-DMSO): δ 10.53 (s, 1H), 7.10 (s, 1H), 7.06 (d, *J* = 8.46 Hz, 1H), 6.67 (s, 1H), 6.48-6.47(m, 1H), 6.11 (s, 1H), 4.55 (brs, 2H); ^{13}C NMR (150 MHz, d_6-DMSO): 141.4, 130.2, 129.0, 125.1, 112.3, 111.8, 103.7, 100.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_9H_9N_2$133.0766; Found133.0755.

7. ^{1}H and ^{13}C NMR spectra of isolated compounds S7-S20

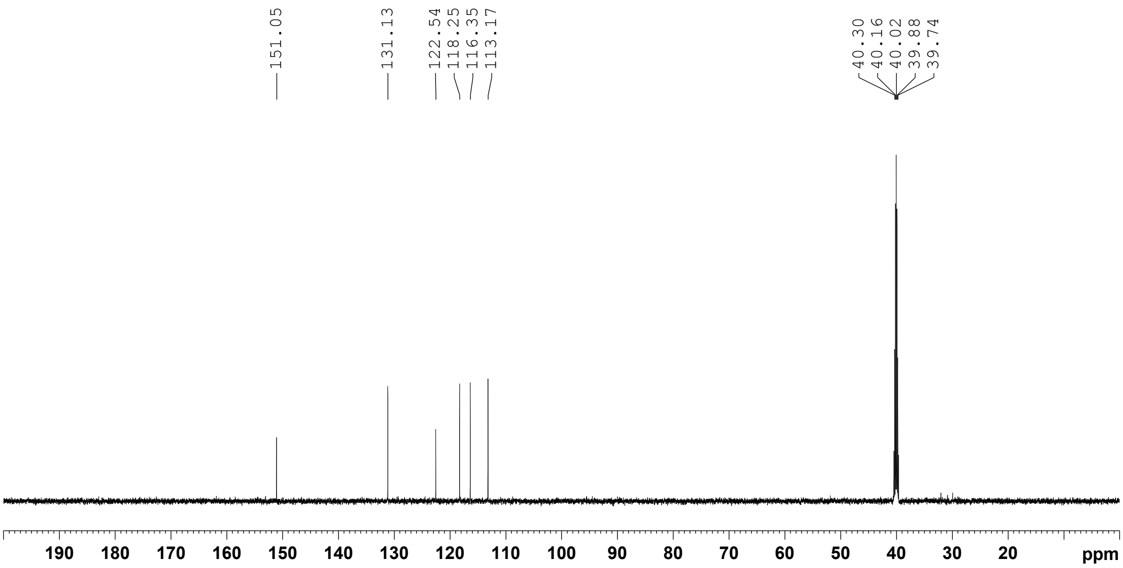
4-Iodoaniline (2a) ^{13}C NMR, *d₆*-DMSO



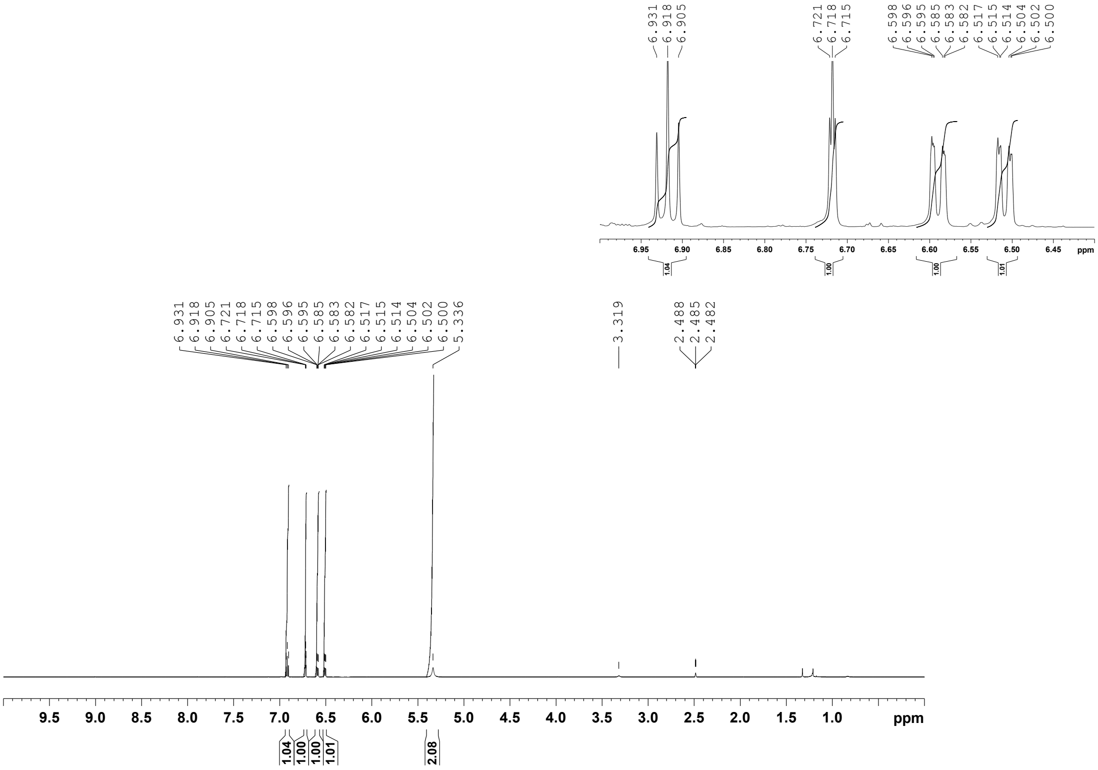
4-Iodoaniline (2a) ^{1}H NMR, *d₆*-DMSO

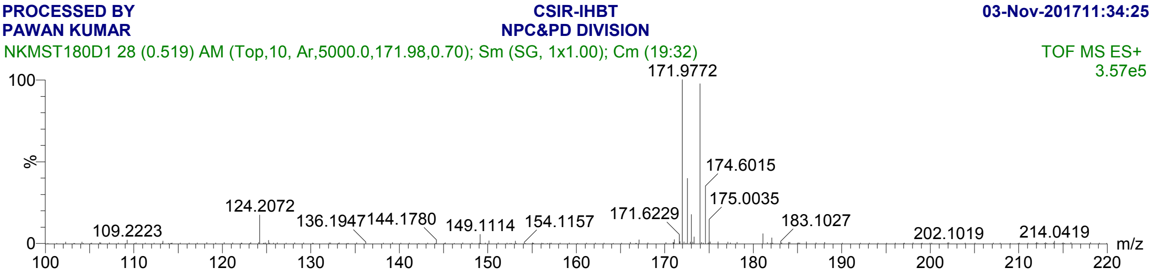


3-Bromoaniline (2b) ^{13}C NMR, *d$_6$*-DMSO

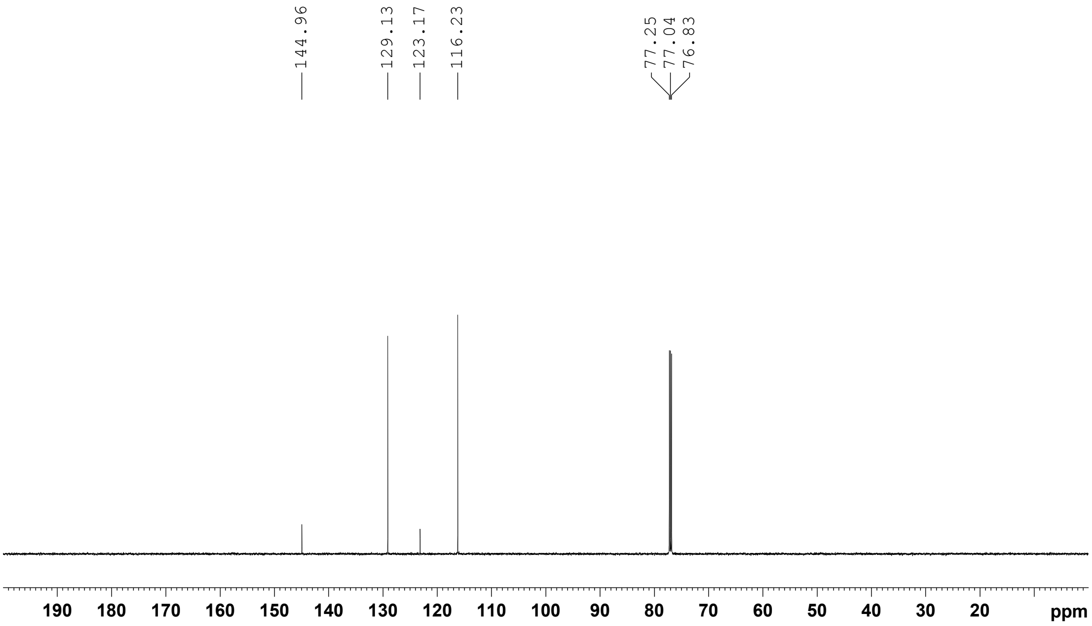


3-Bromoaniline (2b) ^{1}H NMR, *d$_6$*-DMSO

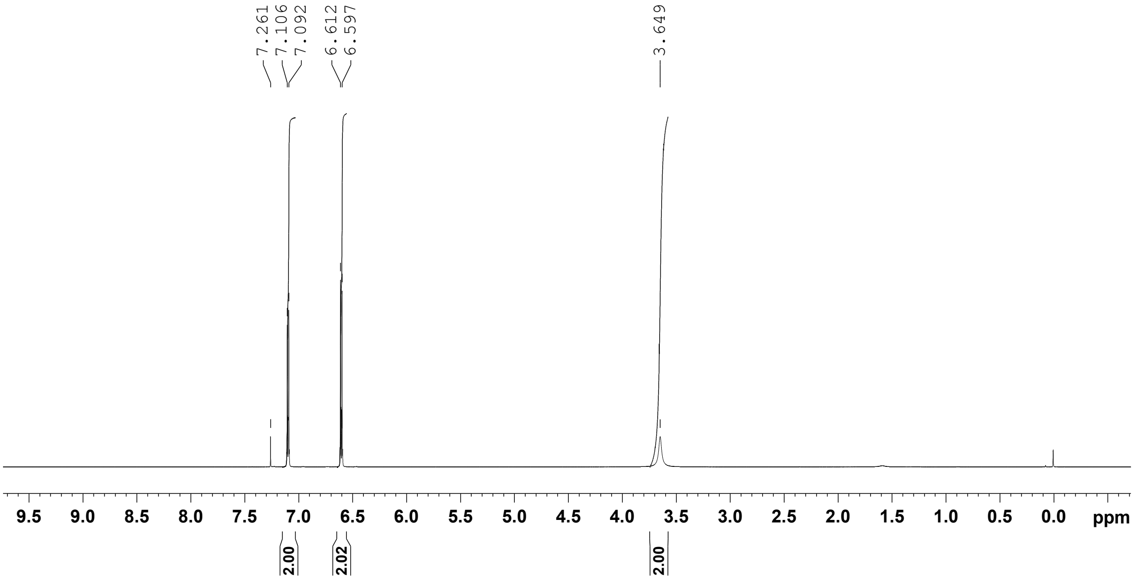


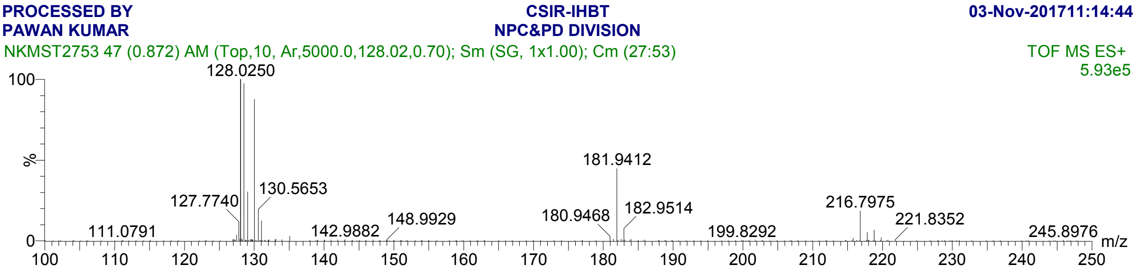


4-Chloroaniline (2c) ^{13}C NMR, CDCl$_3$

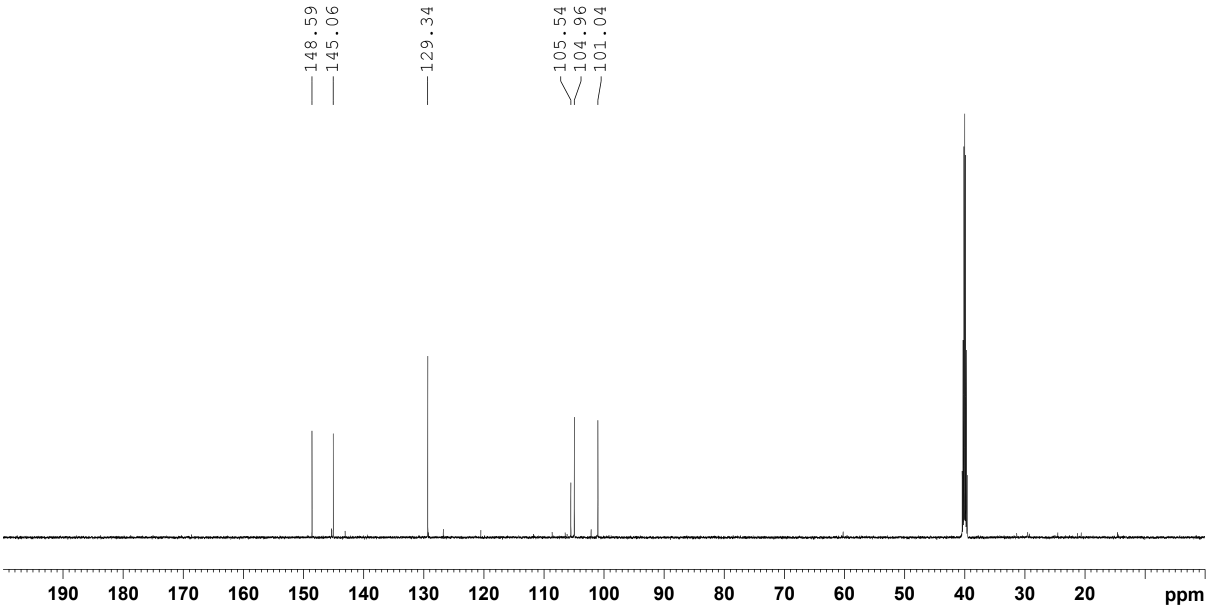


4-Chloroaniline (2c), ^{1}H NMR, CDCl$_3$

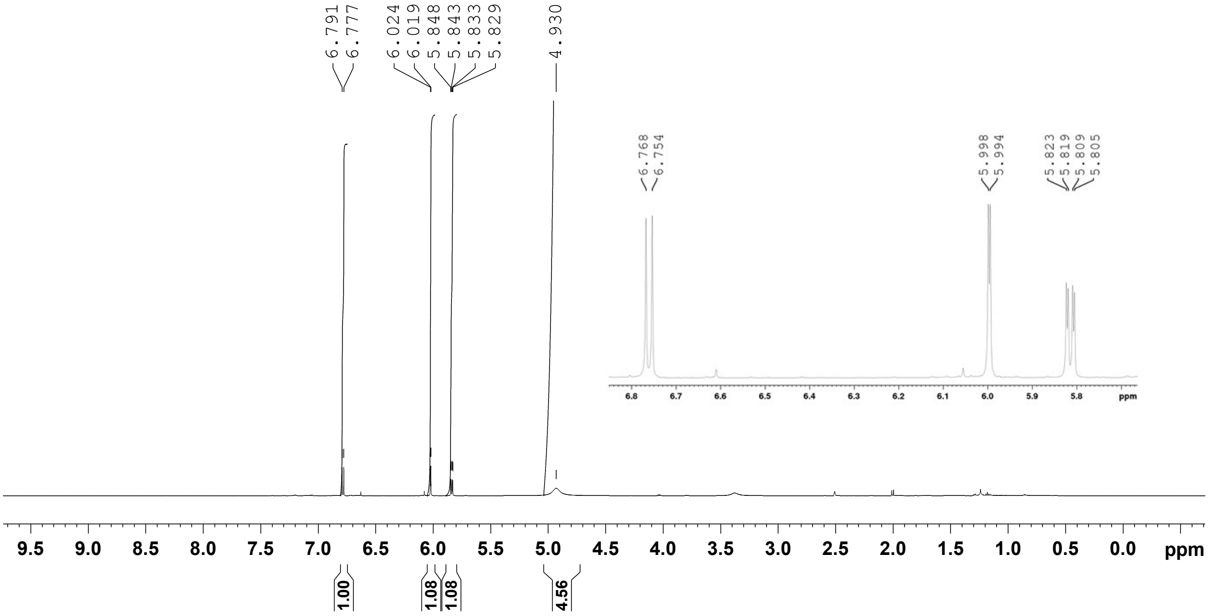




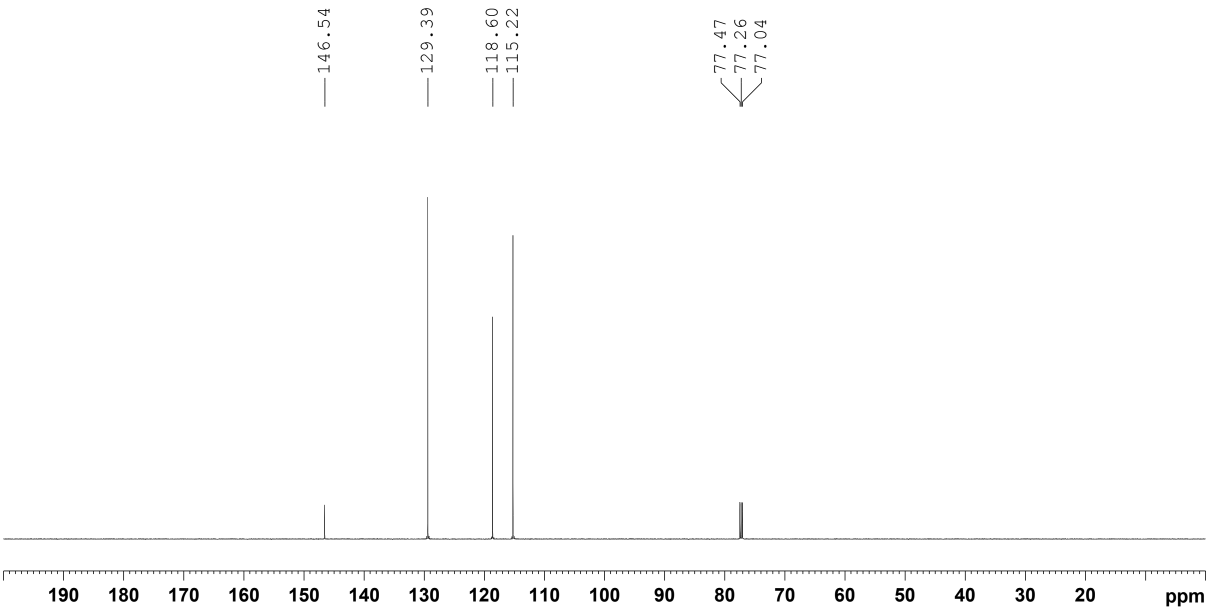
2-Chloro-4-aminoaniline (2d), ^{13}C NMR, $CDCl_3$



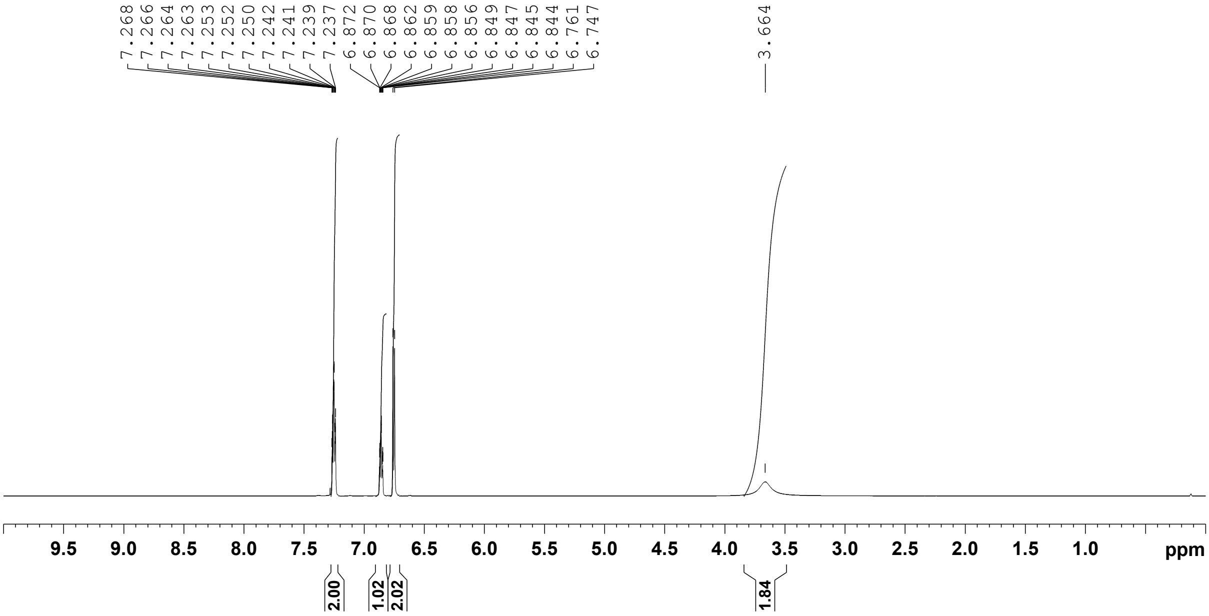
2-Chloro-4-aminoaniline (2d), ^1H NMR, $CDCl_3$



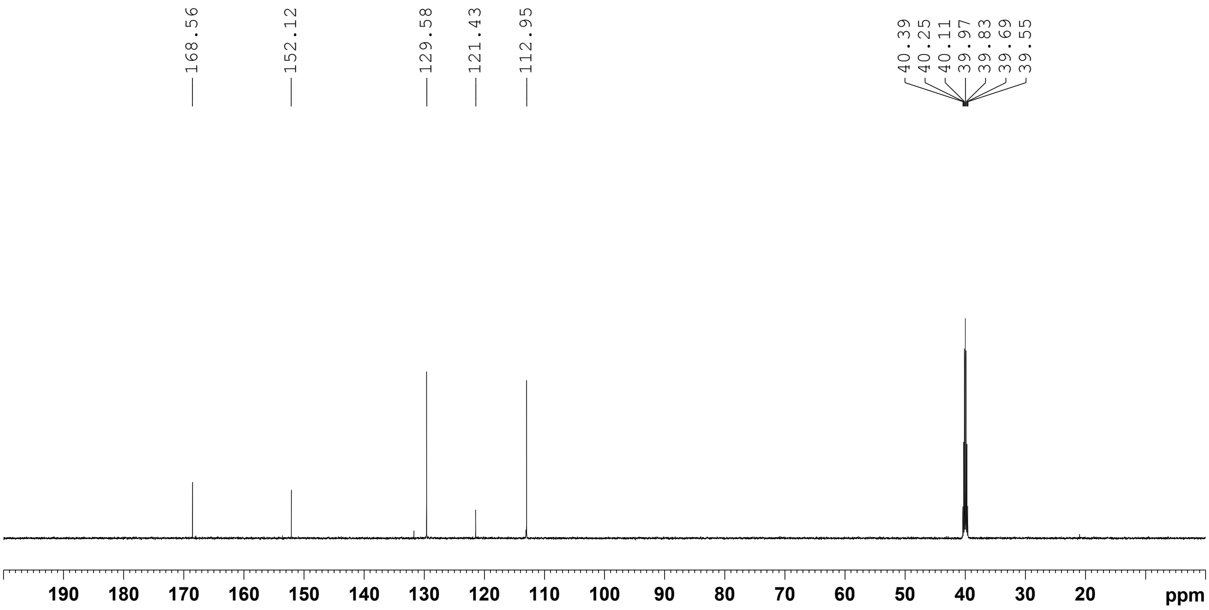
Aniline (2e), ^{13}C NMR, $CDCl_3$



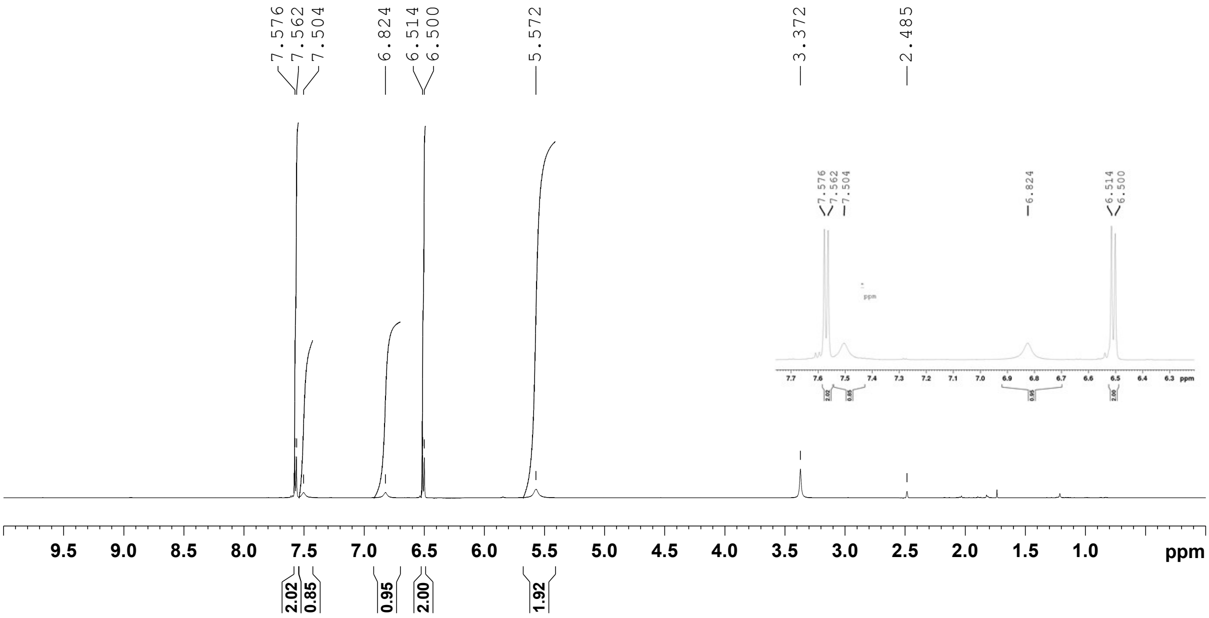
Aniline (2e) ^{1}H NMR, $CDCl_3$



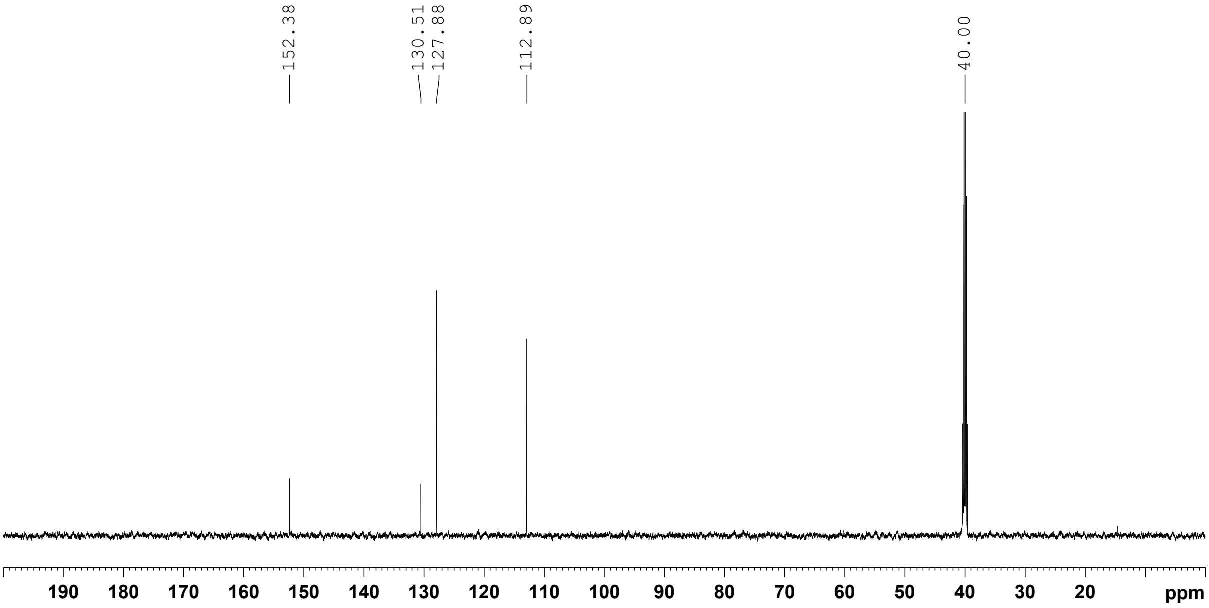
4-Aminobenzamide (2f), ^{13}C NMR, d_6-DMSO



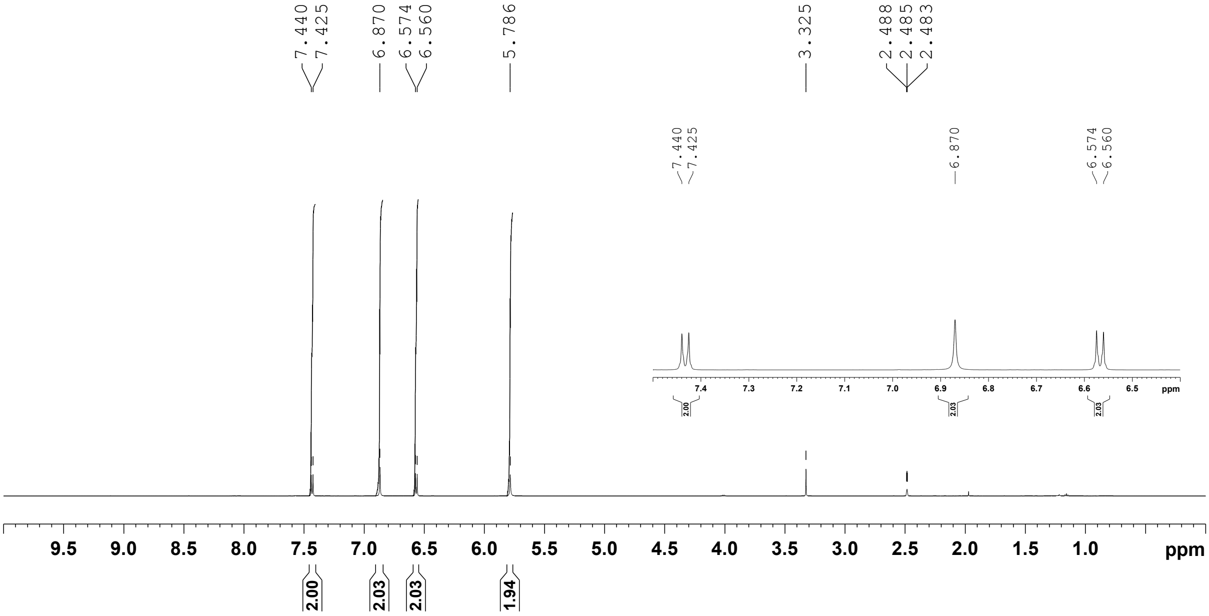
4-Aminobenzamide (2f), ^{1}H NMR, d_6-DMSO:



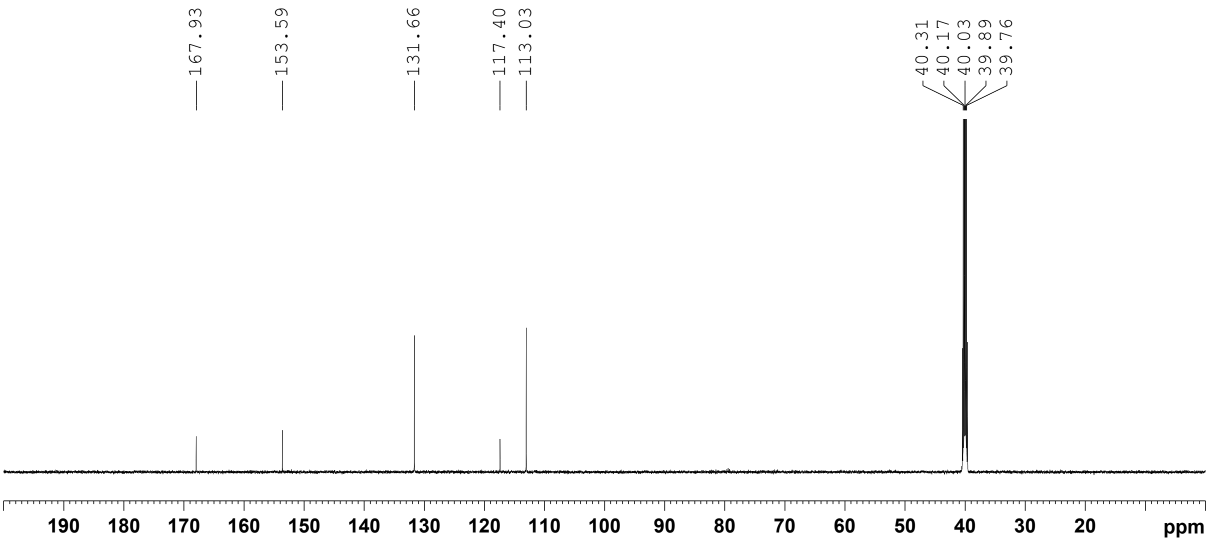
4-Aminobenzenesulphonamide (2g), ^{13}C NMR, d_6-DMSO



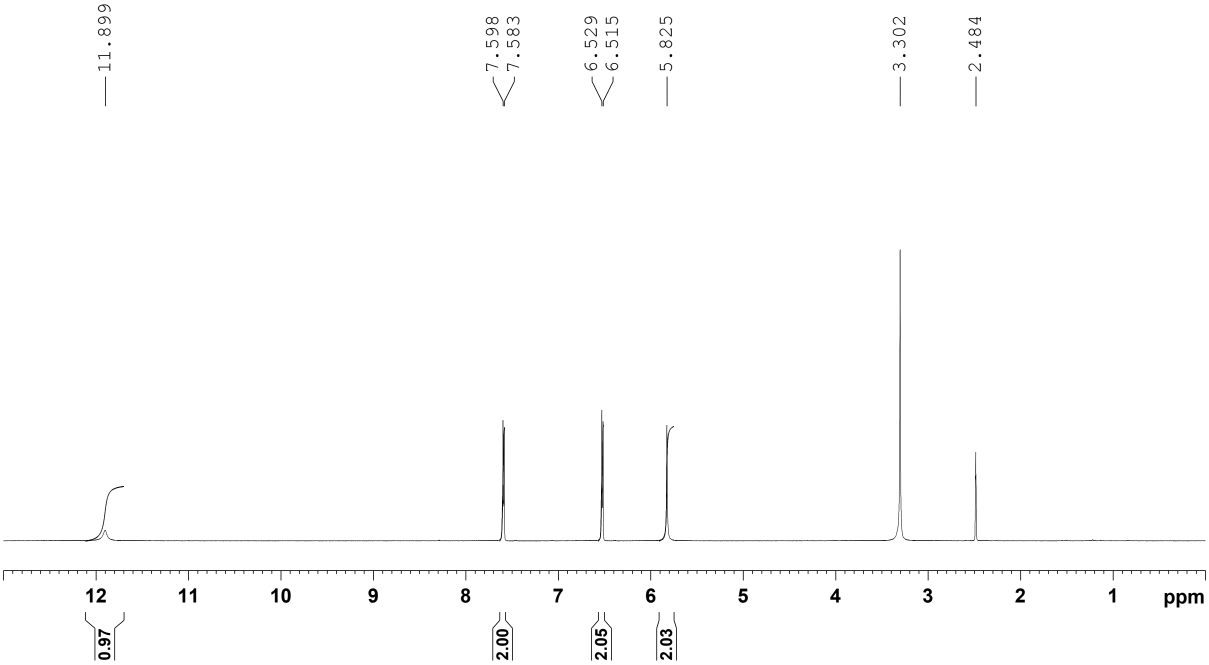
4-Aminobenzenesulphonamide (2g), ^1H NMR, d_6-DMSO



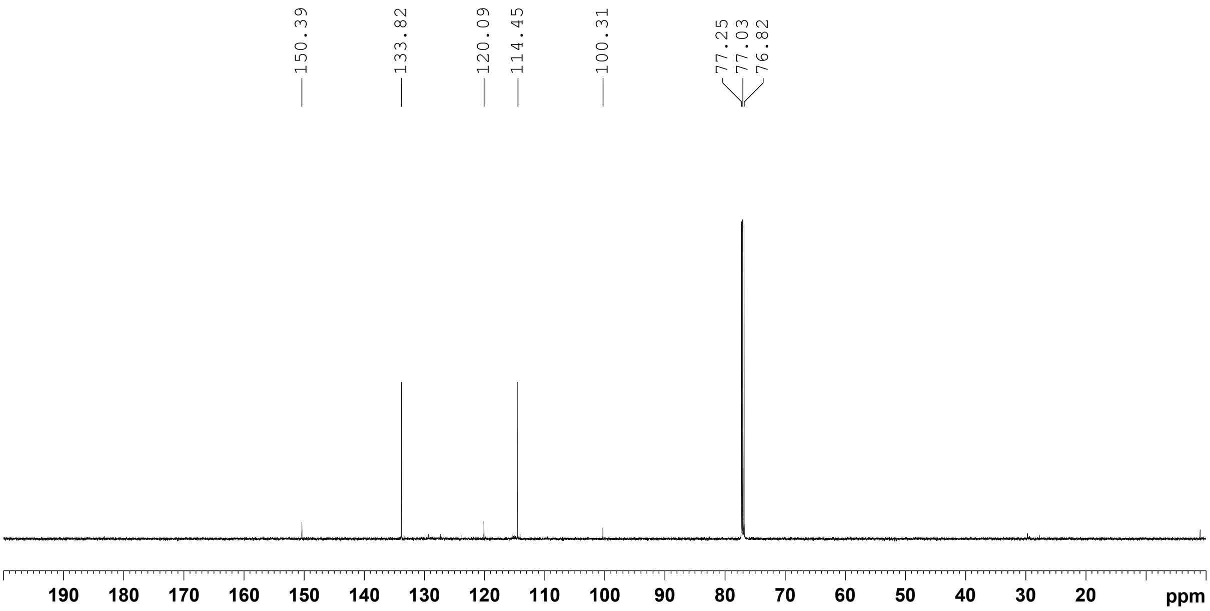
4-Aminobenzoic acid (2h), ^{13}C NMR, d_6-DMSO



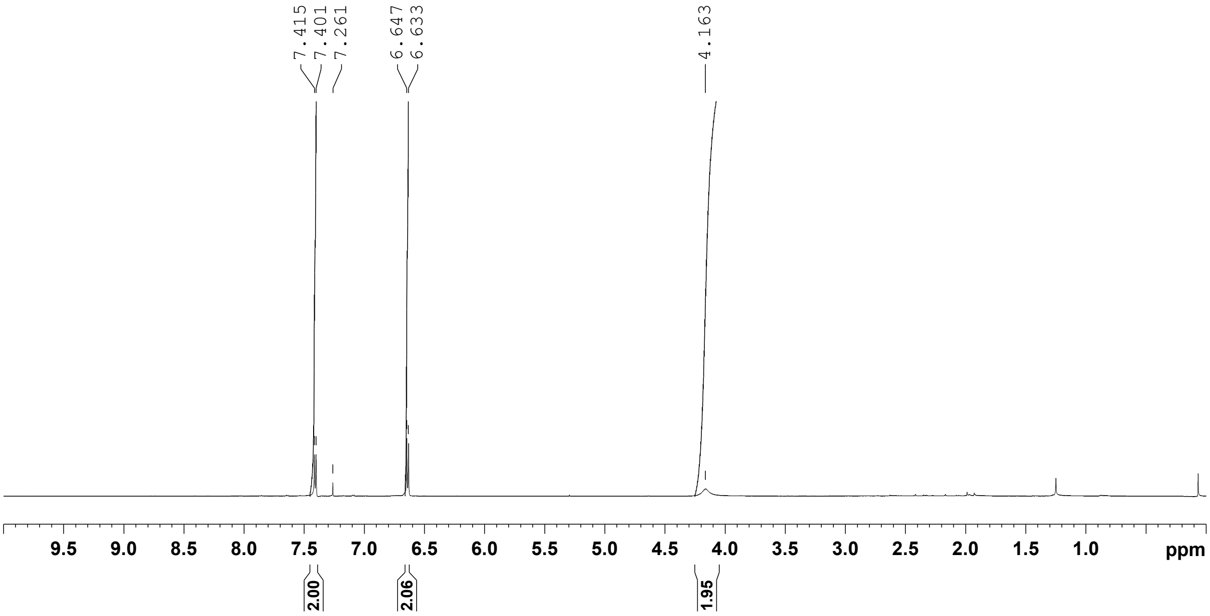
4-Aminobenzoic acid (2h), ^{1}H NMR, d_6-DMSO



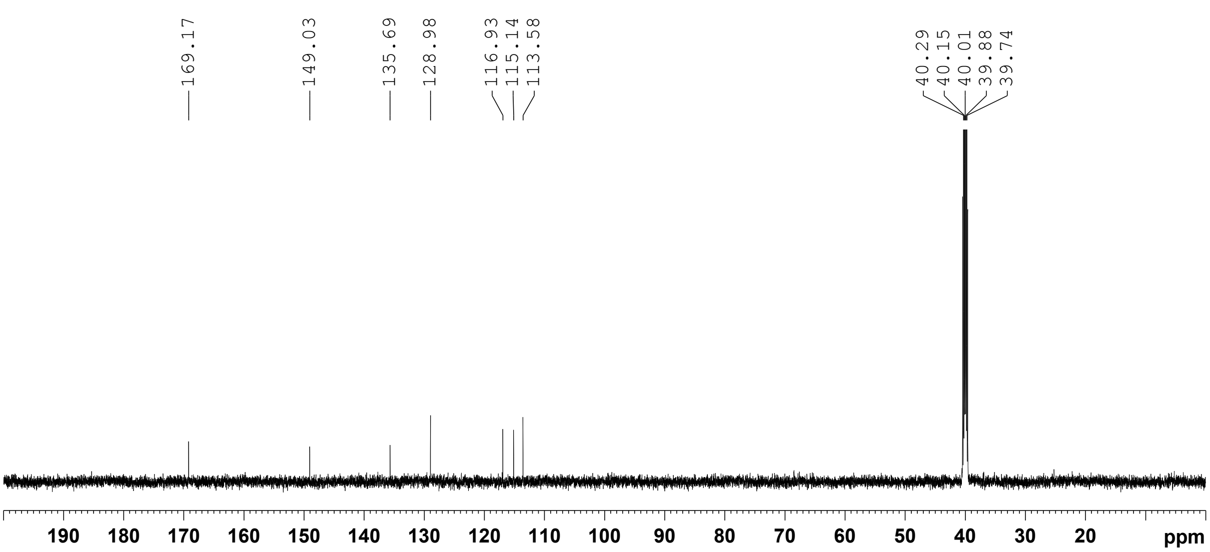
4-Aminobenzonitrile (2j) ^{13}C NMR, $CDCl_3$



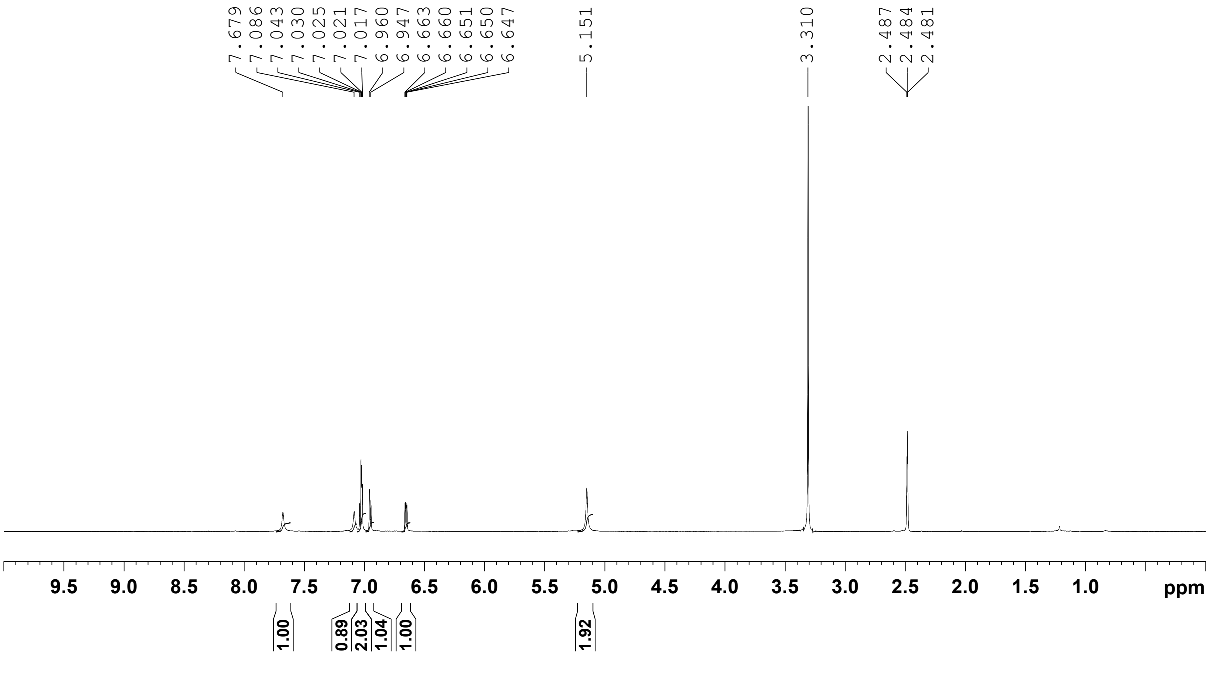
4-Aminobenzonitrile (2j), ^1H NMR, $CDCl_3$



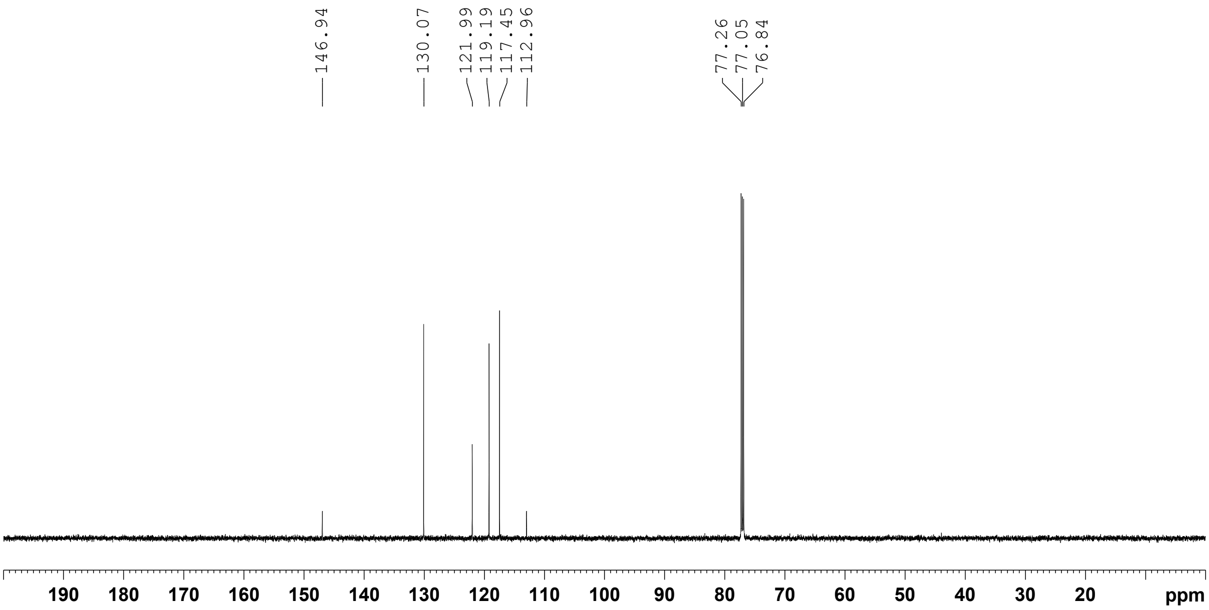
3-Aminobenzamide (2k), ^{13}C NMR, d_6-DMSO



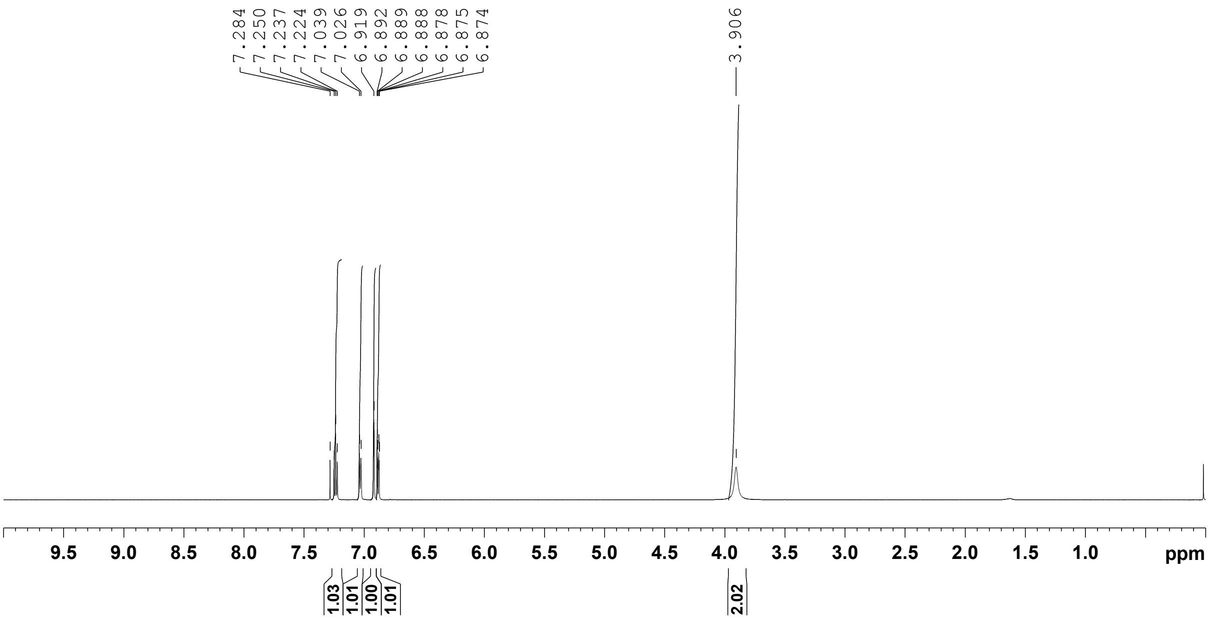
3-Aminobenzamide (2k), ^1H NMR, d_6-DMSO



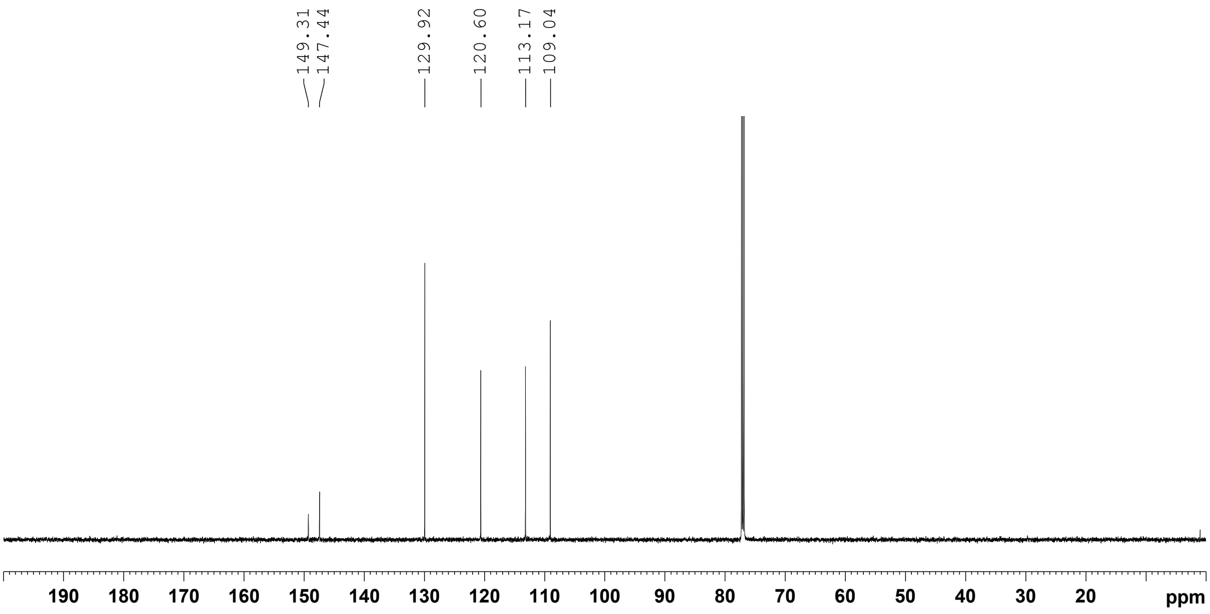
3-Aminobenzonitrile (2l), ^{13}C NMR, CDCl$_3$



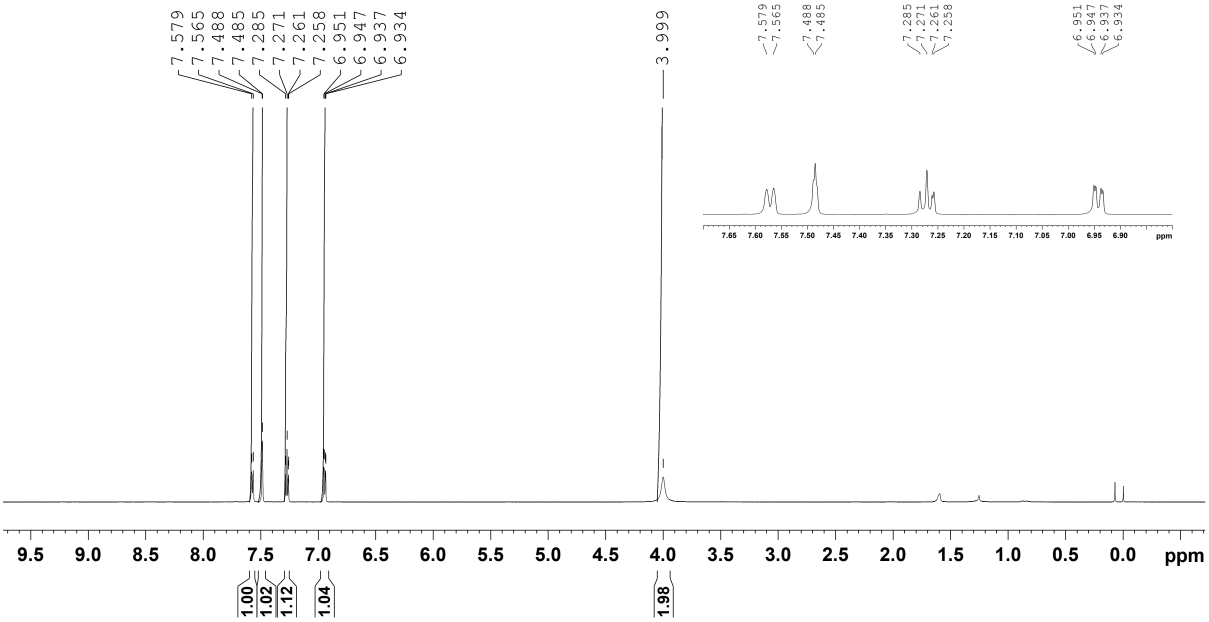
3-Aminobenzonitrile (2l), ^{1}H NMR, CDCl$_3$



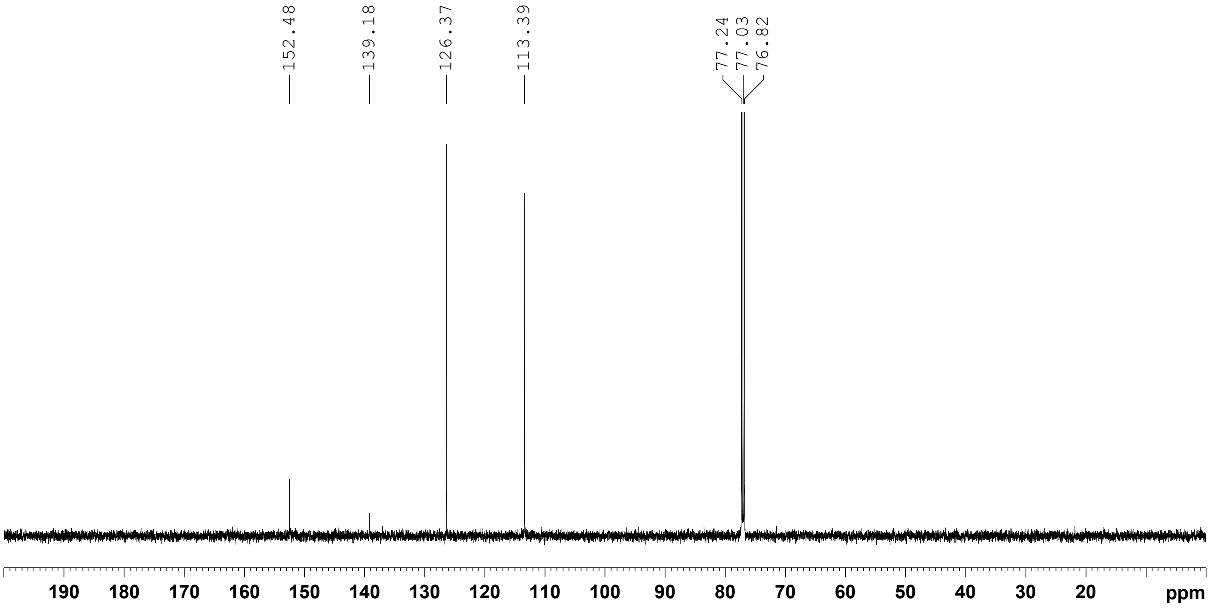
3-Nitroaniline (2m), ^{13}C NMR, CDCl$_3$



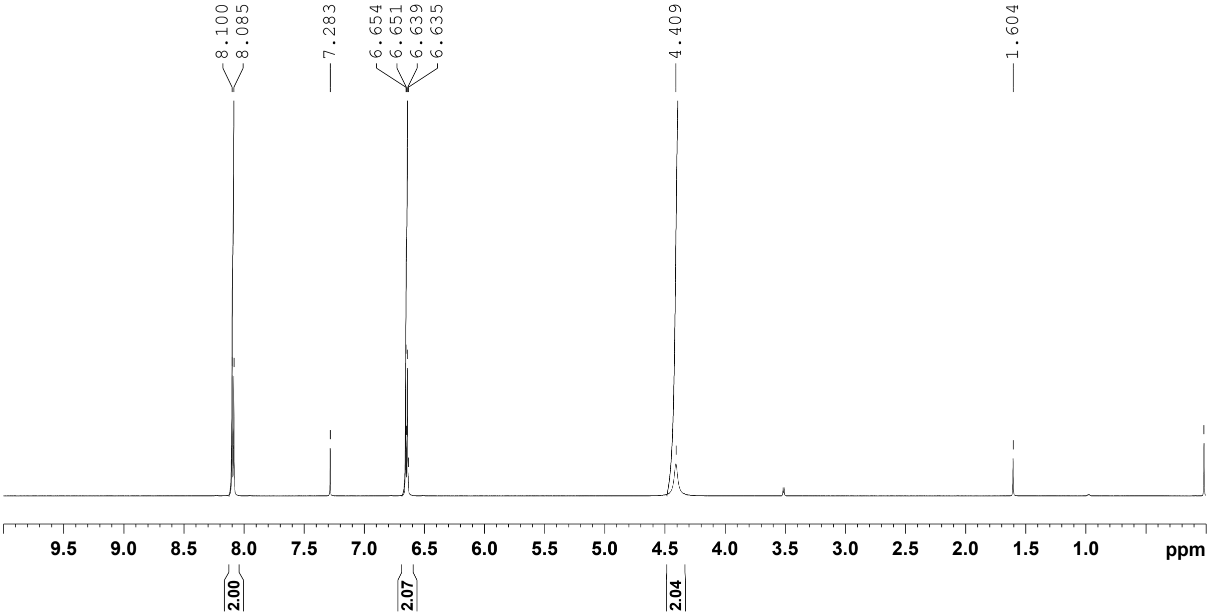
3-Nitroaniline (2m), ^{1}H NMR, CDCl$_3$



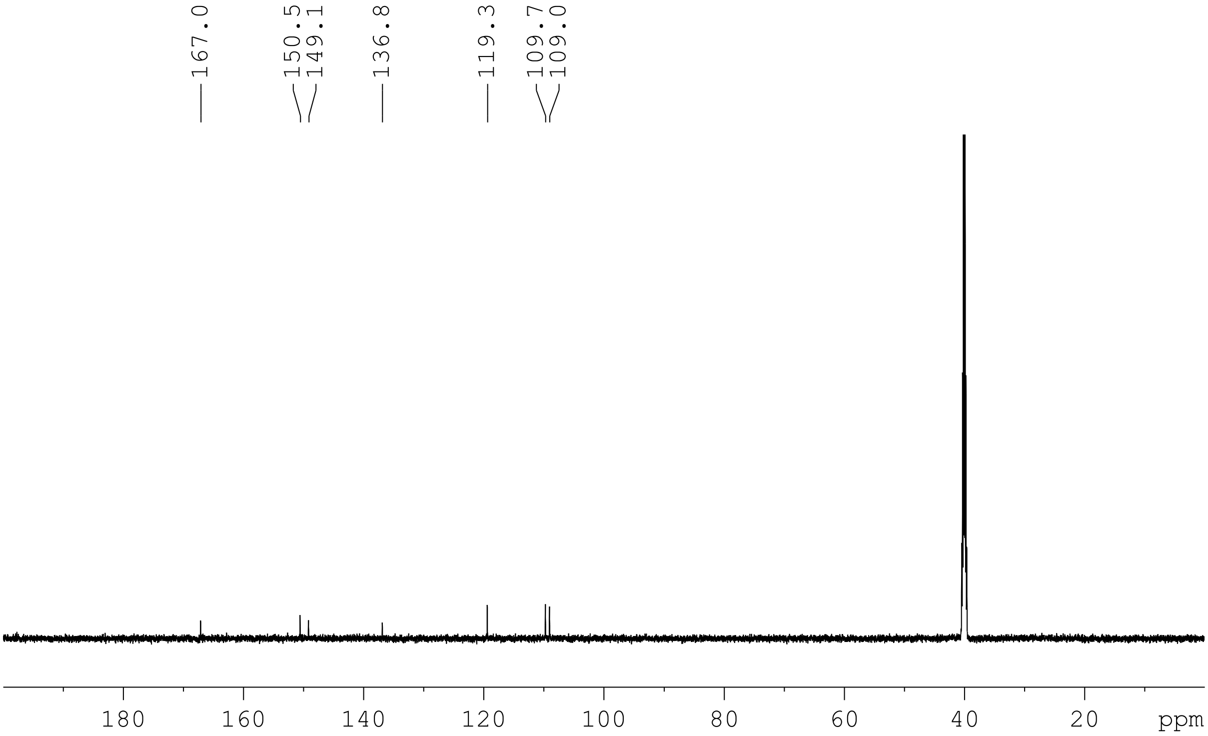
4-Nitroaniline (2n), ^{13}C NMR, $CDCl_3$



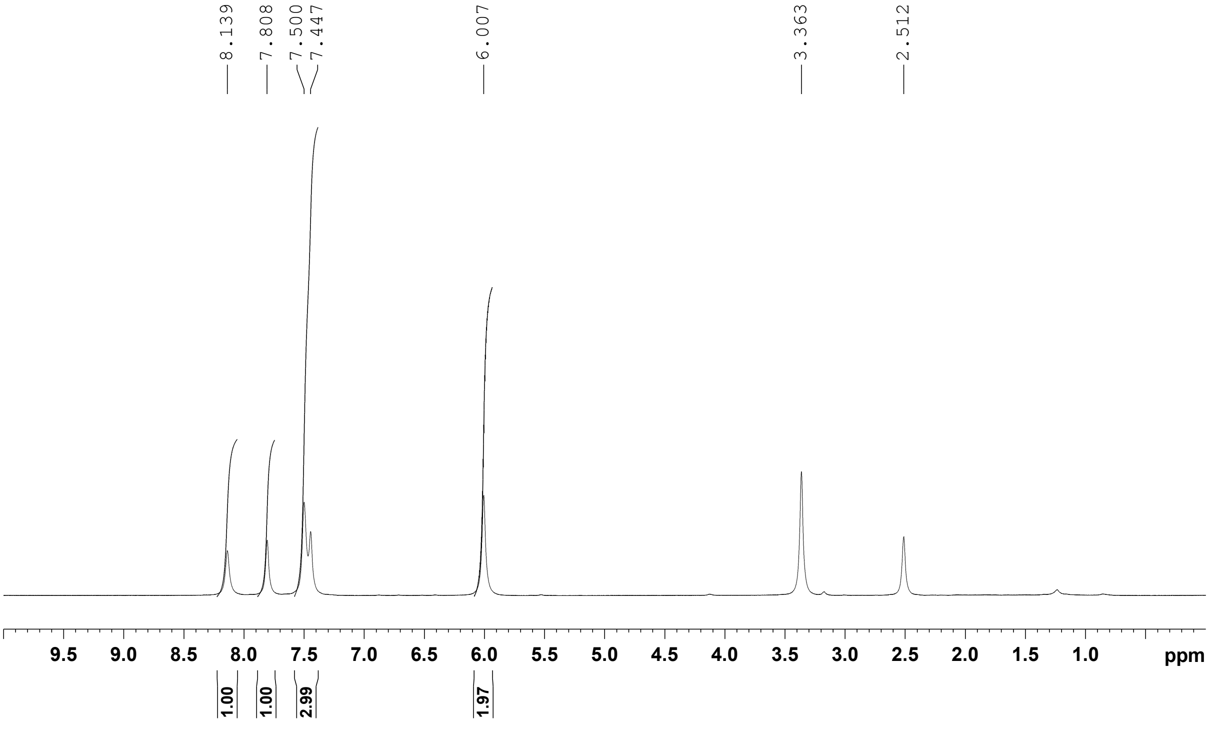
4-Nitroaniline (2n), ^1H NMR, $CDCl_3$



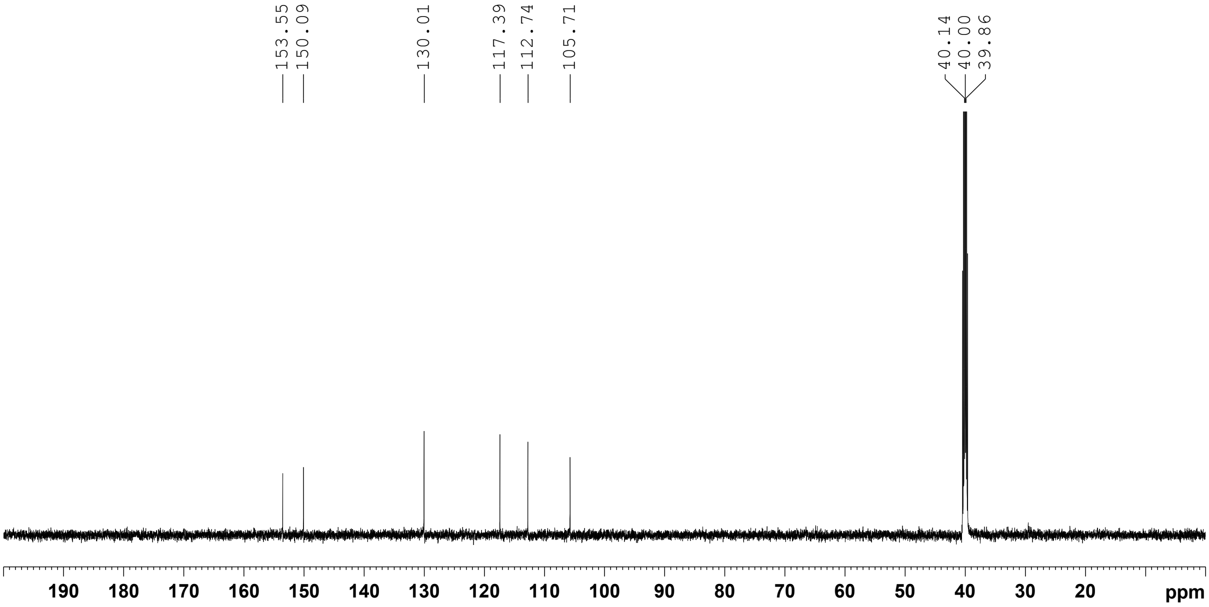
3-Amino-5-nitrobenzamide (2o), ^{13}C NMR, d_6-DMSO



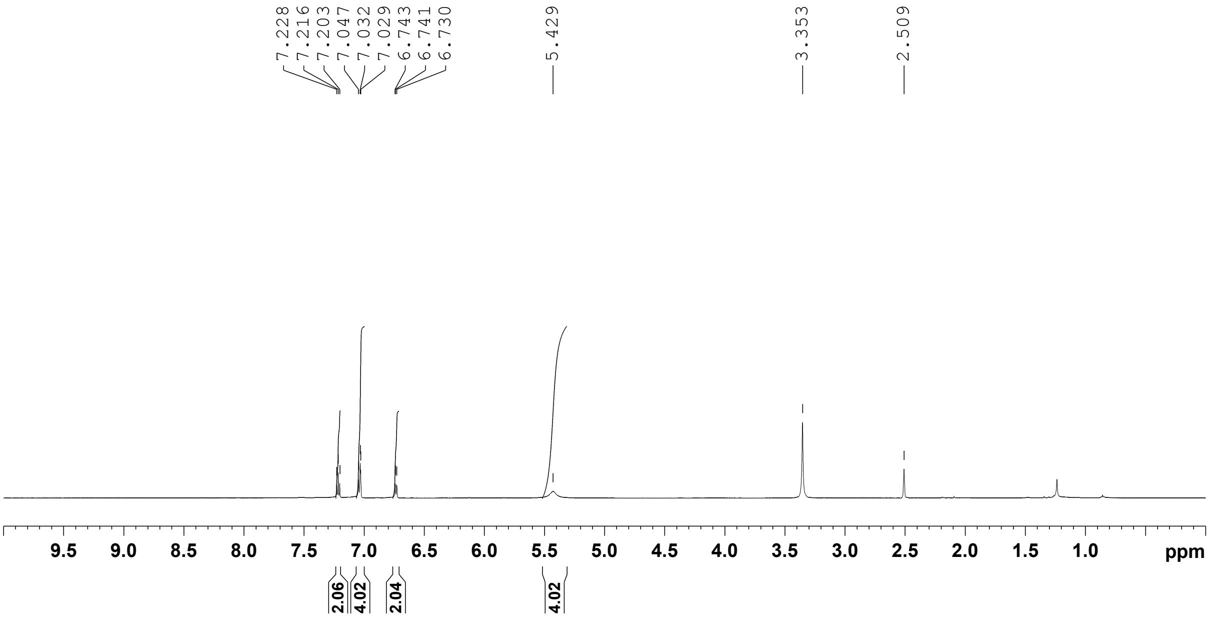
3-Amino-5-nitrobenzamide (2o), ^1H NMR, d_6-DMSO



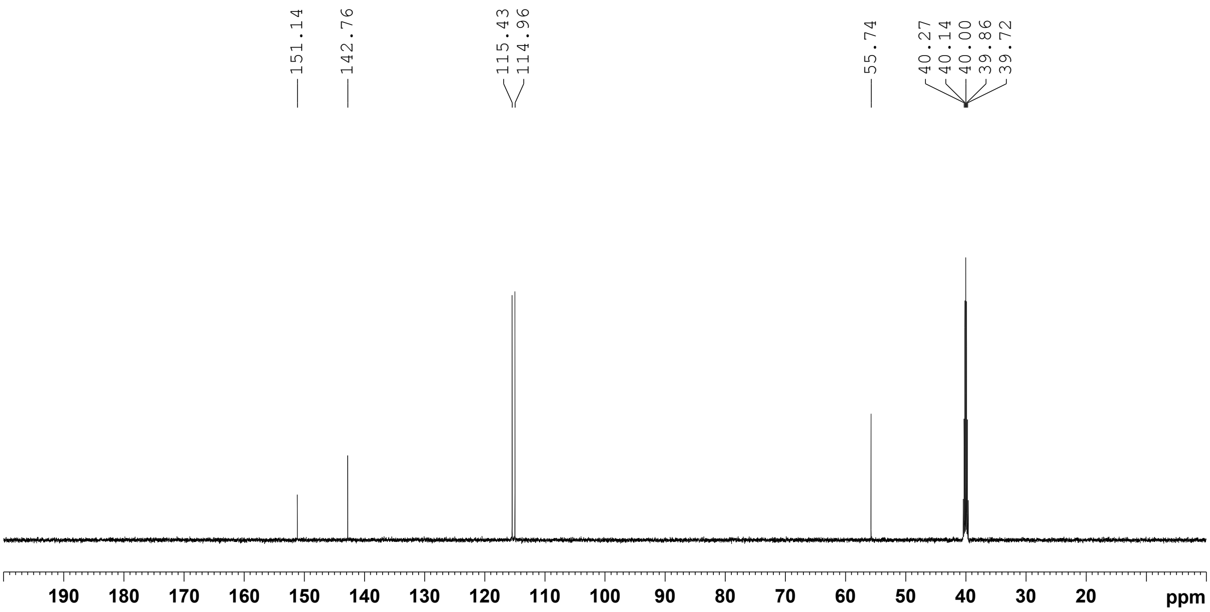
3,3‘-Azobisaniline (2p), ^{13}C NMR, d_6-DMSO



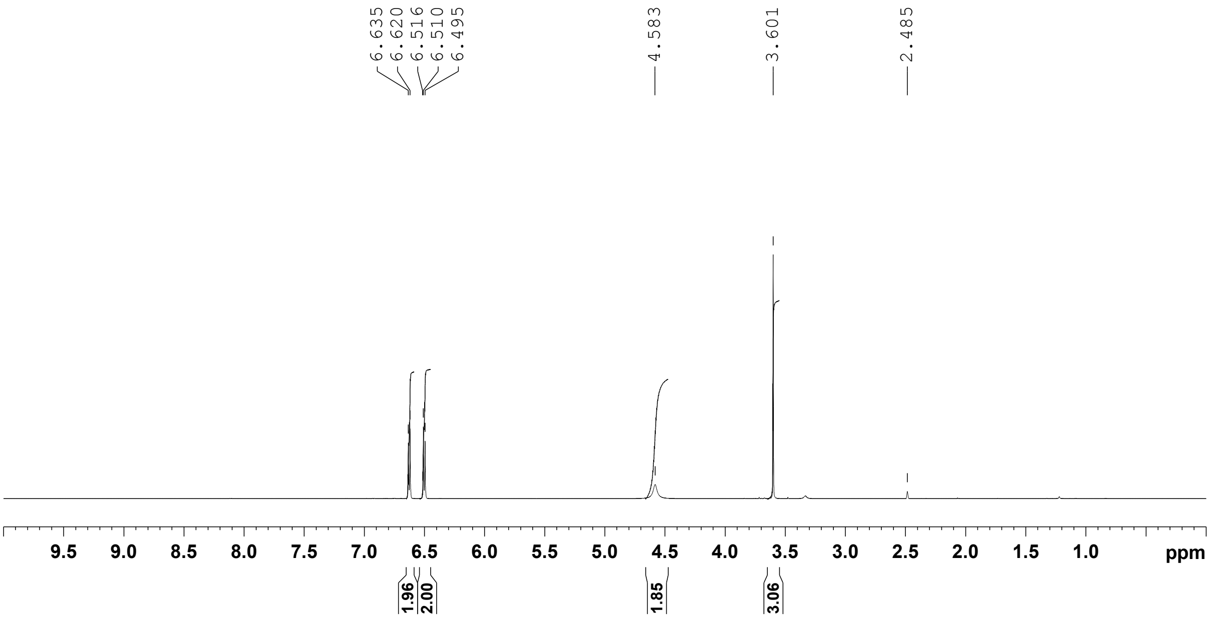
3,3‘-Azobisaniline (2p), ^{1}H NMR, d_6-DMSO



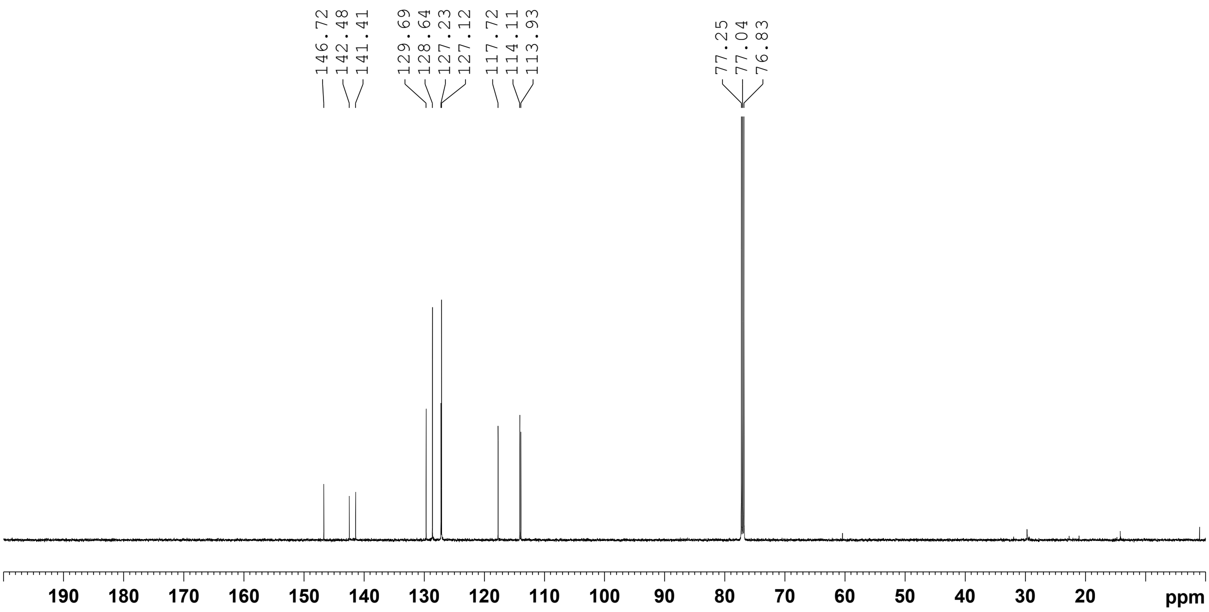
4-Methoxyaniline (2r), ^{13}C NMR, d_6-DMSO



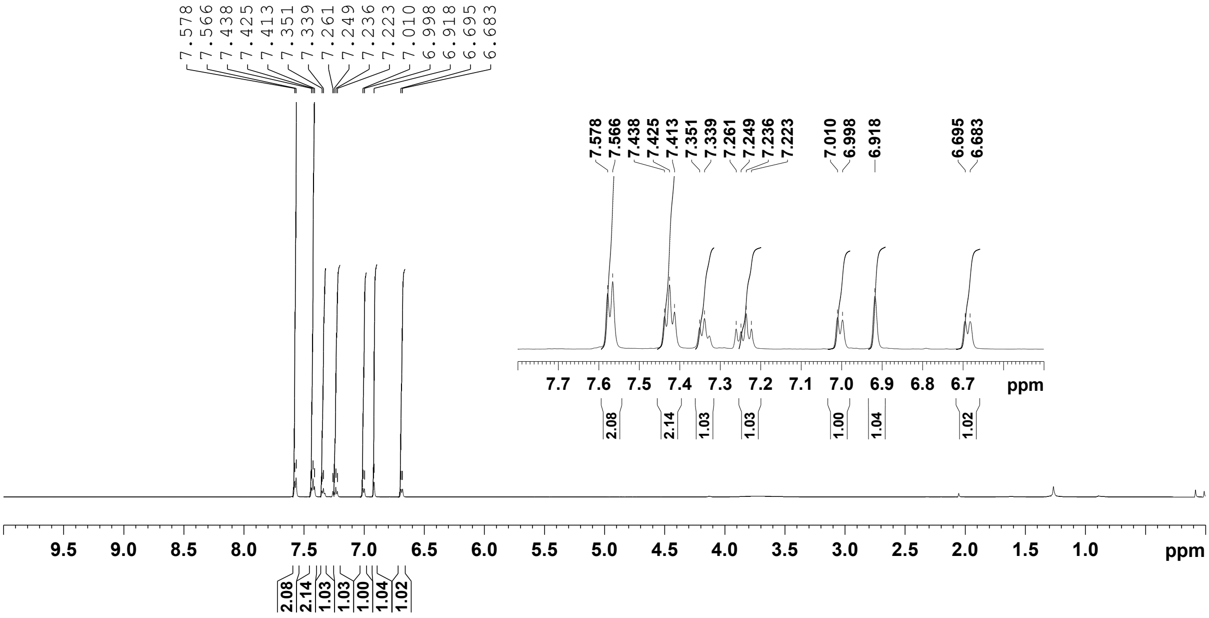
4-Methoxyaniline (2r), ^{1}H NMR, $CDCl_3$



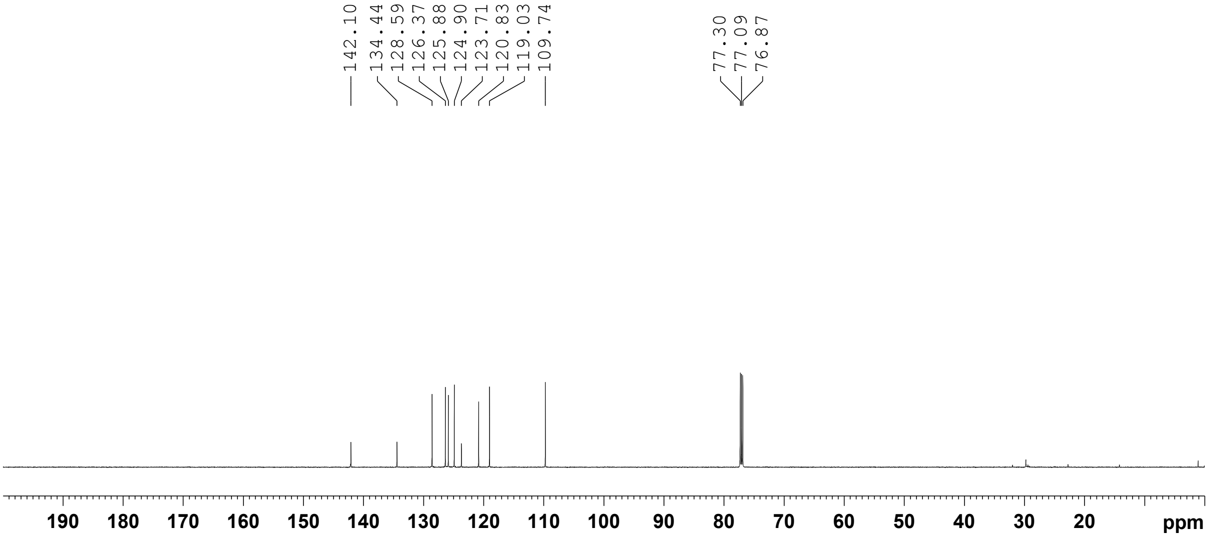
3-Aminobiphenyl (2q), ^{13}C NMR, CDCl$_3$



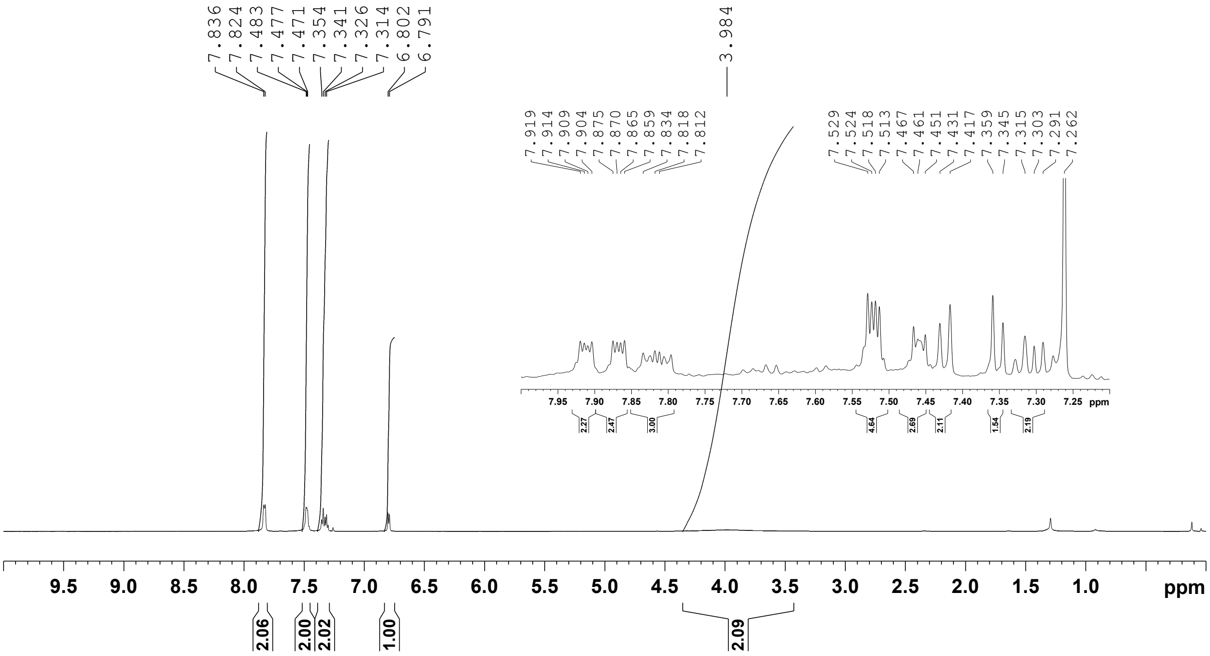
3-Aminobiphenyl (2q), ^{1}H NMR, CDCl$_3$



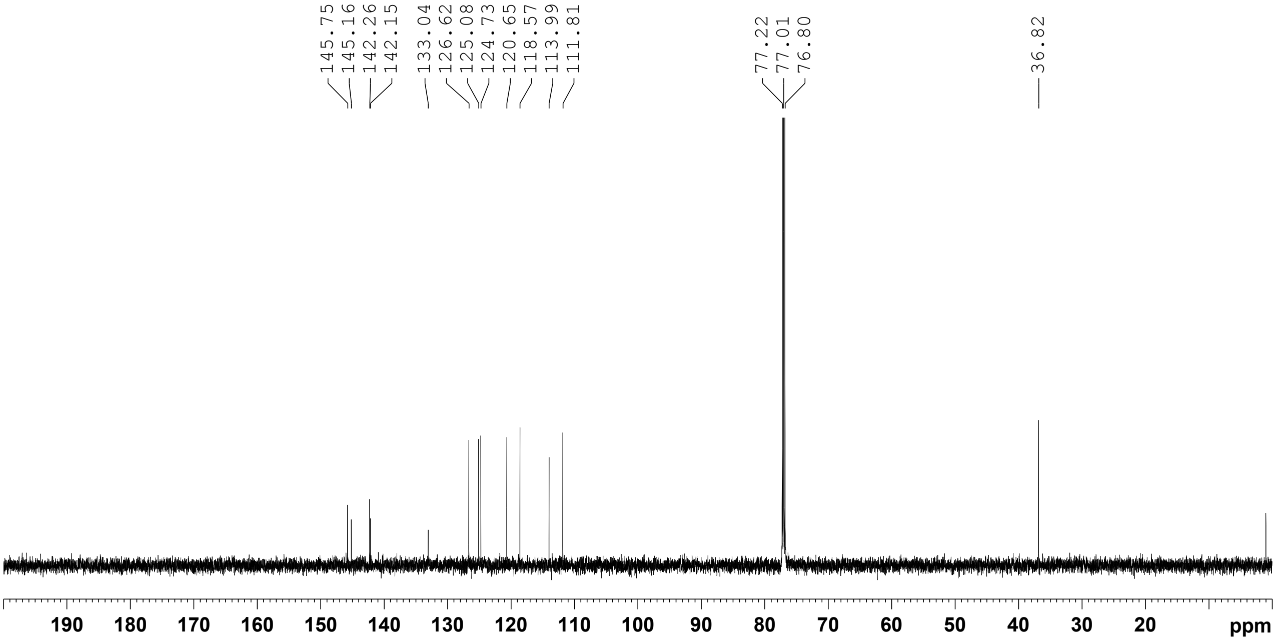
1-Aminonaphthalene (2s), ^{13}C NMR, CDCl$_3$



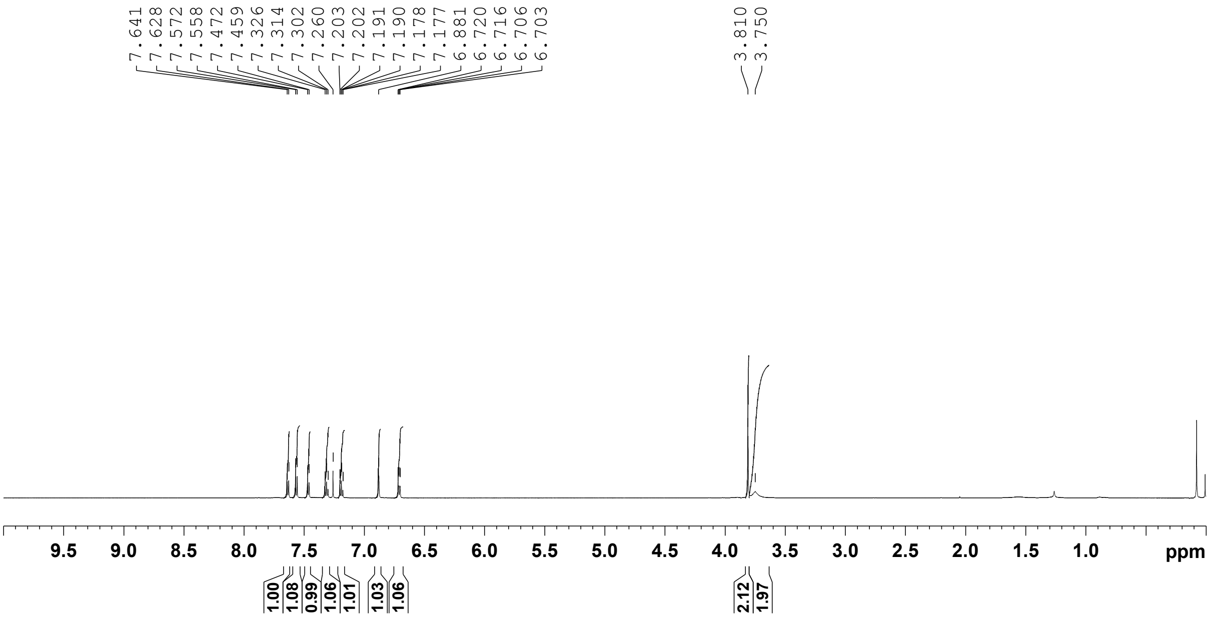
1-Aminonaphthalene (2s), ^{1}H NMR, CDCl$_3$



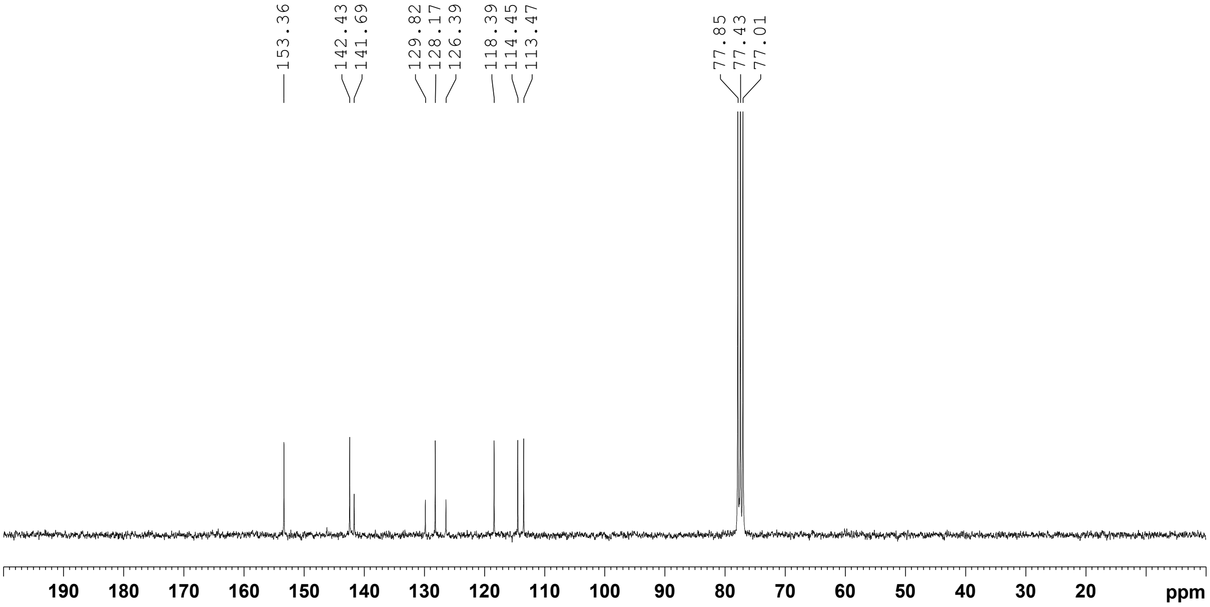
2-Aminoflourene (2t), ^{13}C NMR, $CDCl_3$



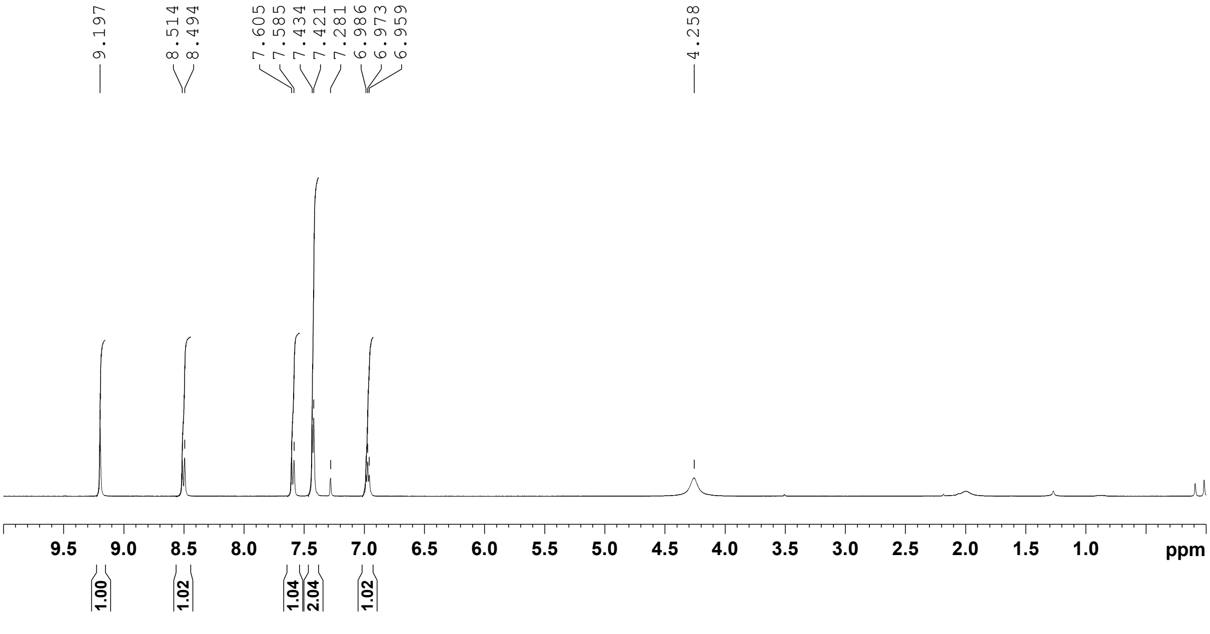
2-Aminoflourene (2t), ^{1}H NMR, $CDCl_3$



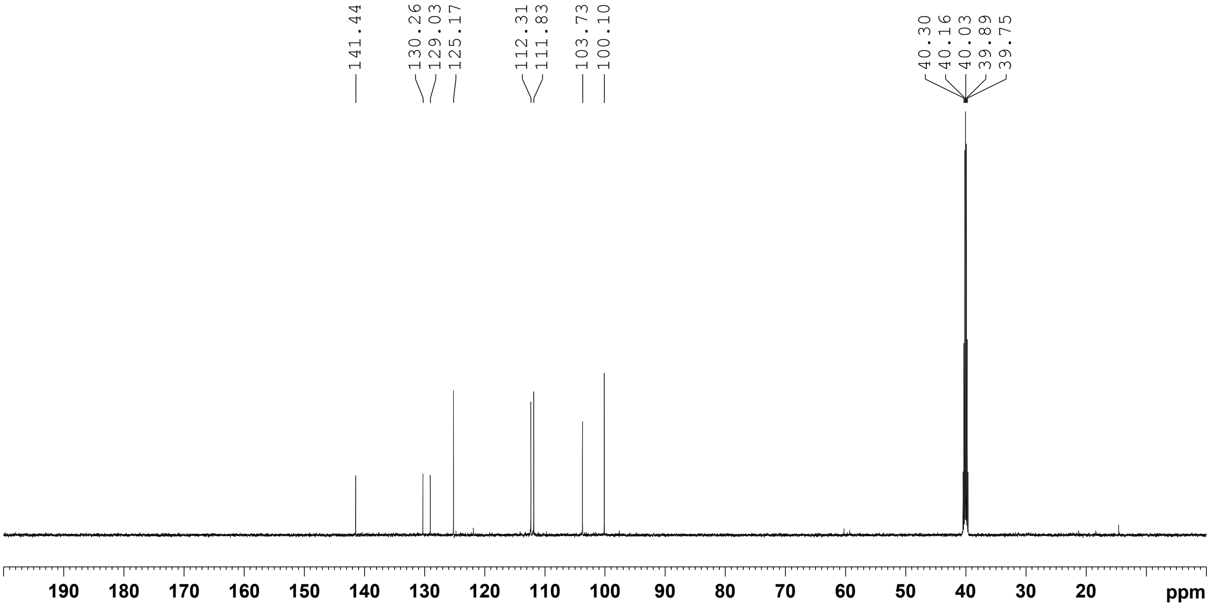
5-Aminoisoquinoline (2u), ^{13}C NMR, CDCl$_3$



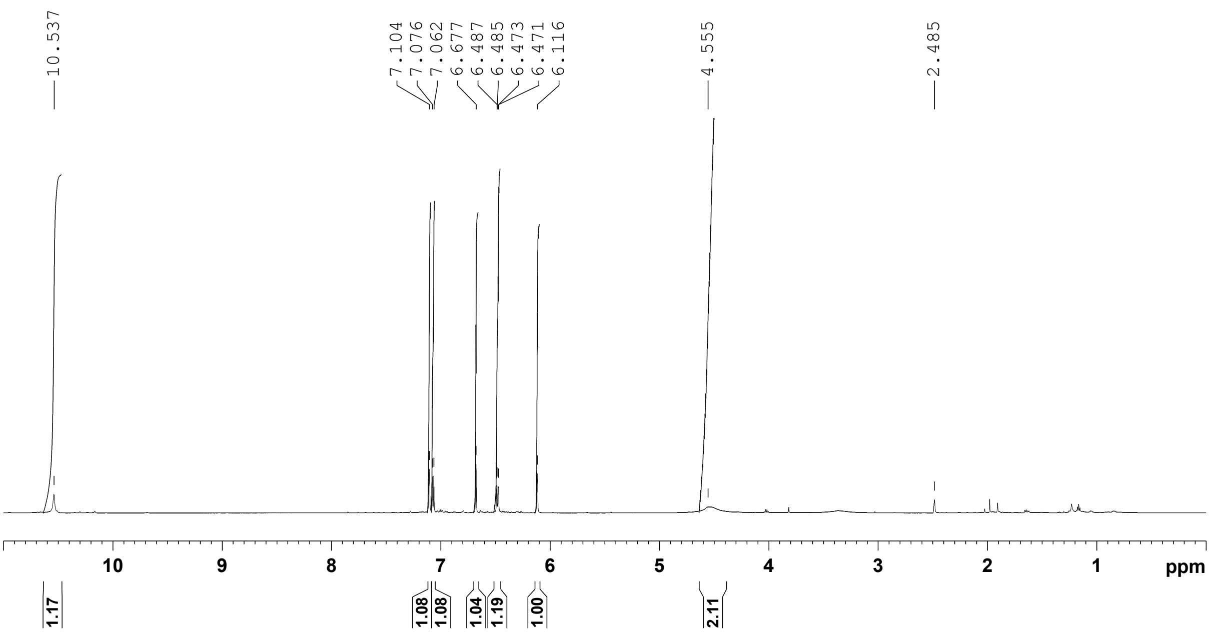
5-Aminoisoquinoline (2u), ^{1}H NMR, CDCl$_3$



5-Aminoindole (2v), ^{13}C NMR, d_6-DMSO



5-Aminoindole (2v), ^{1}H NMR, d_6-DMSO



8. Reference:

1) (a) I. Gulaczyk, M. Kreglewski and A Valentin, *J. Mol. Spec.,* 2003, **220**, 132; (b) F. Zimmermann, T. Lippert, C. Beyer, J. Stebani, O. Nuyken and A. Wokaun, *Appl. Spectrosc*., 1993, **47**, 986; (c) R. Lascola, R. Withnall and L. Andrews, *Inorg. Chem.,* 1988*,* **27**, 642; (d) G. G. Sheina, S. G. Stepanian, E. D. Radchenko and Y. P. Blagoi, *J. Mol. Struct.*, 1987, **158**, 275.

2) (a) H. Knoezinger and H. Krietenbrink, *J. Chem. Soc. Faraday Trans., 1*, 1975, **71**, 2421; (b) J. Joseph and E. D. Jemmis, *J. Am. Chem. Soc.*, 2007, **129**, 4620; (c) B. V. Lotsch and W. Schnick, *Z. Naturforsch. B Chem. Sci*., 2005, **60**, 377; (d) B. G. Alberding, M. H. Chisholm, J. C. Gallucci, Y. Ghosh and T. L. Gustafson, *Proc. Natl. Acad. Sci*., 2011, **108**, 8152.

3) (a) M. Kumar, U. Sharma, S. Sharma, V. Kumar, B. Singh and N. Kumar, *RSC Adv.*, 2013, **3**, 4894; (b) U. Sharma, P. Kumar, N. Kumar, V. Kumar and B. Singh, *Adv. Synth. Catal.* 2010, **352**, 1834; (c) M. Orlandi, F. Tosi, M. Bonsignore and M. Benaglia, *Org. Lett*., 2015, **17**, 3941; (d) S. Sharma, M. Kumar, V. Kumar and N. Kumar, *J. Org. Chem*., 2014, **79**, 9433; (e) U. Sharma, N. Kumar, P. K. Verma, V. Kumar and B. Singh, *Green Chem*., 2012, **14,** 2289; (f) M. Baron, E. Métay, M. Lemaire and F. Popowycz, *Green Chem*., 2013, **15**, 1006; (g) G. Vijaykumar and S. K. Mandal, *Dalton Trans*., 2016,**45**, 7421.