Supporting Information

High Activity Mesoporous Pt@KIT-6 Nanocomposite for Selective Hydrogenation of Halogenated Nitroarenes in Continuous-flow Microreactor

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Table S1. The content of Pt investigated by ICP-OES/MS.

Entry	ICP-OES	ICP-OES	ICP-MS
	Pristine Pt@KIT-6 nanocomposite	Running 24 hours Pt@KIT-6 nanocomposite	Operation 24 hours Reaction solution
Pt	5.06±0.01%(w/w)	5.05±0.01%(w/w)	trace

Table S2. Comparison of the 4-nitrobromobenzene conversion and the 4-bromoaniline selectivity for Pt@KIT-6 nanocomposite in our study and some catalysts reported in the literature with the optimized conditions.

Catalyst	H_2 Pres. (MPa)	Temp. (°C)	Time (min)	Conv. (%)	Selec. (%)	Stability (h)	Reference
Pt@KIT-6 nanocomposite	1.0	20	5	> 99	> 99	72	This work
Pt/NOMC	1.0	25	30	> 99	95.5	5	[1]
Pt/C	0.1	80	10	> 99	87.9	-	[2]
Pt@PNIPAM-SH	1.0	40	120	> 99	98.8	30	[3]
Pt/Fe_3O_4	1.0	30	120	98.4	95.1	10	[4]
PtZn/SiO_2	0.1	40	72	> 99	> 99	-	[5]
Pt/H-NCNTs	0.5	40	20	> 99	> 99	1.3	[6]

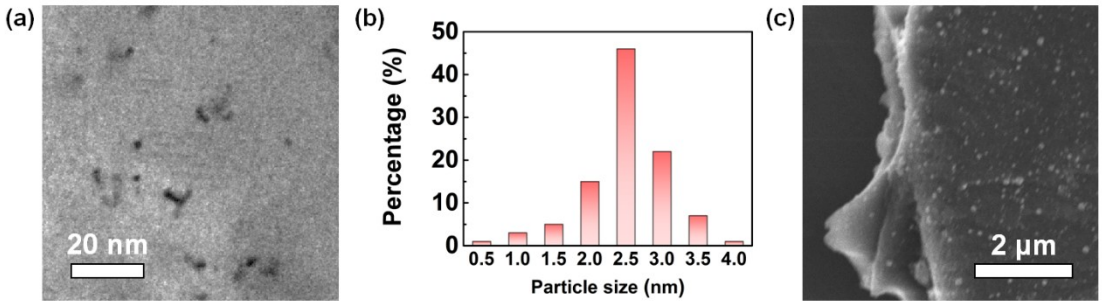


Figure S1. (a) HRTEM image of Pt@KIT-6 nanocomposite; (b) Particle size distribution of Pt nanoparticles in Pt@KIT-6 nanocomposite; (c) SEM image of commercial bulk Pt/C.

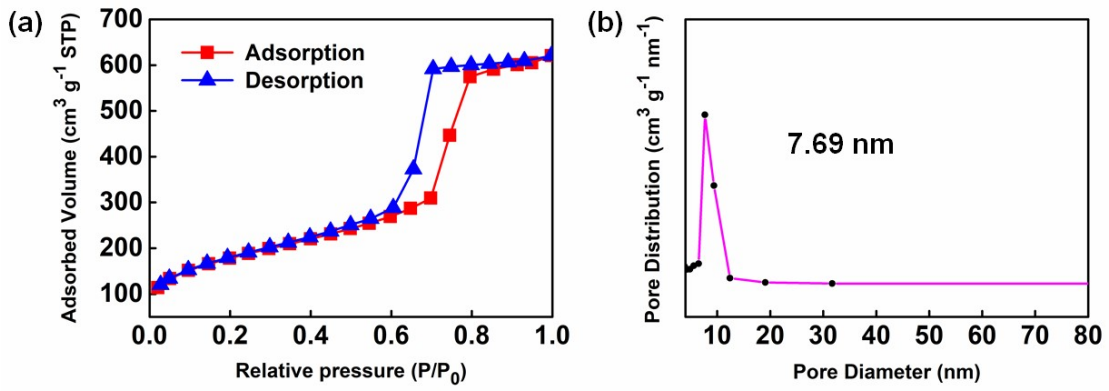


Figure S2. (a) N_2 adsorption-desorption isotherms and (b) pore size distribution of the KIT-6 treated similarly to the entire Pt@KIT-6 nanocomposite synthesis process without the addition of $PtCl_4$.

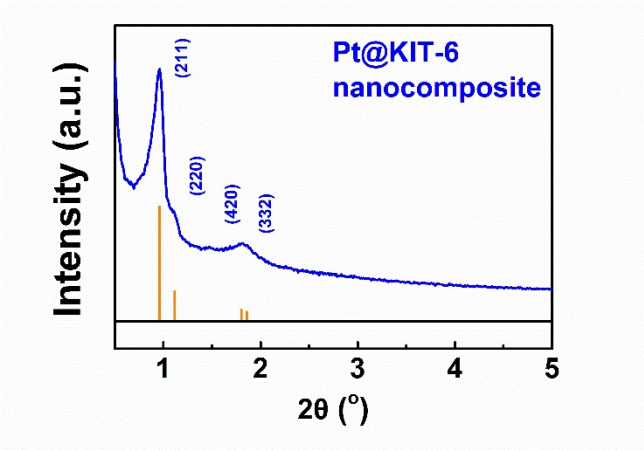


Figure S3. Small-angle XRD pattern of Pt@KIT-6 nanocomposite after 24 h of reaction.

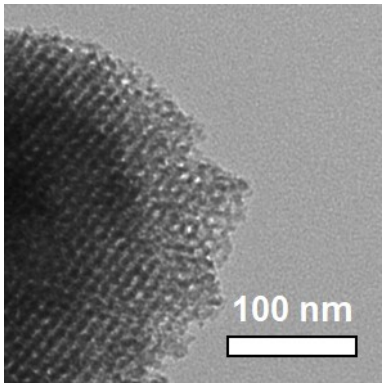


Figure S4. TEM image of Pt@KIT-6 nanocomposite after 24 h of reaction.

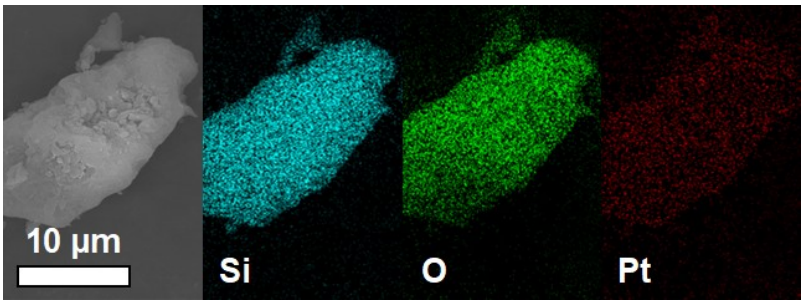


Figure S5. EDS elemental mappings of Pt@KIT-6 nanocomposite after 24 h of reaction.

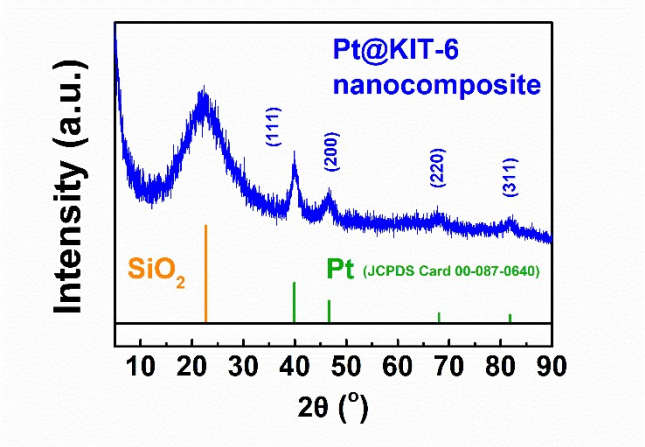


Figure S6. Wide-angle XRD pattern of Pt@KIT-6 nanocomposite after 24 h of reaction.

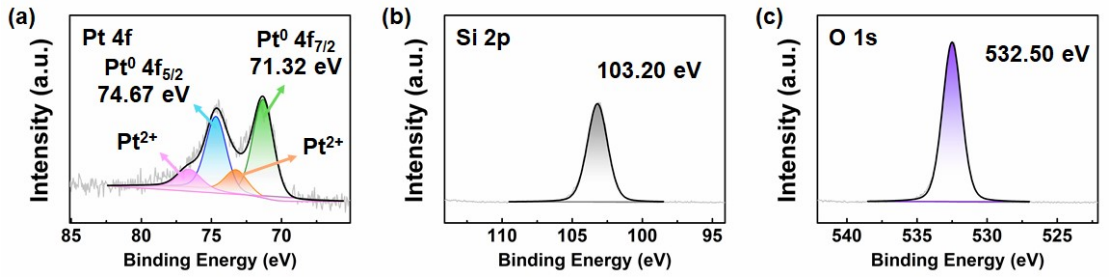


Figure S7. XPS spectrums of Pt@KIT-6 nanocomposite after 24 h of reaction: (a) Pt 4f, (b) Si 2p, (c) O 1s.

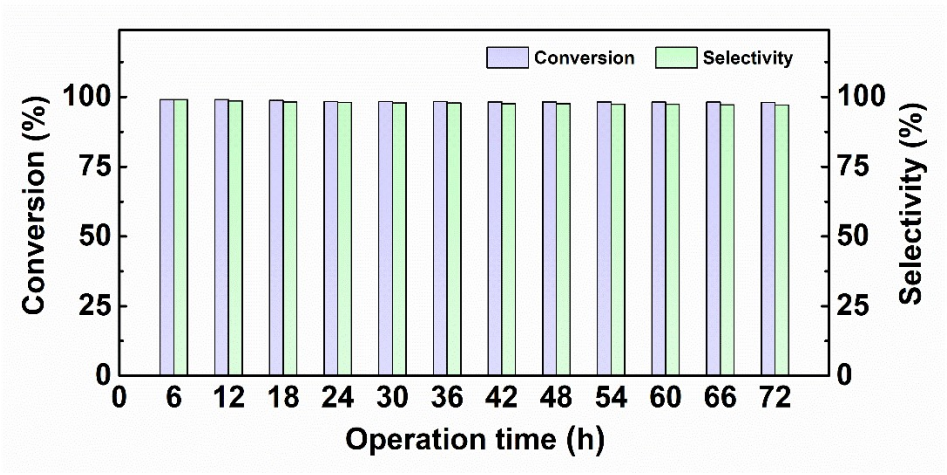


Figure S8. Catalytic stability test of Pt@KIT-6 nanocomposite. Reaction conditions: 4-chloronitrobenzene (0.1 mol/L, methanol as solvent), catalyst (Pt@KIT-6 nanocomposite, 50 mg), flow rate (0.10 mL/min), H_2 (1.0 MPa), back-pressure (0.9 MPa), 20 ˚C, 5.0 min.

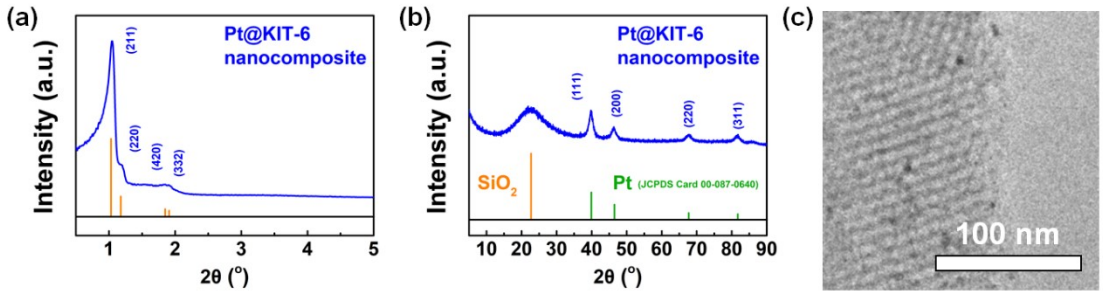


Figure S9. (a) Small-angle XRD pattern, (b) Wide-angle XRD pattern, (c) TEM image of Pt@KIT-6 nanocomposite after 72 h of reaction.

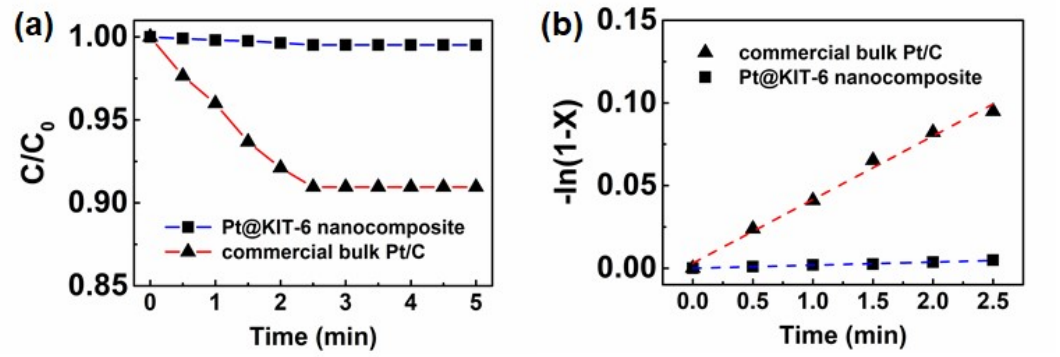
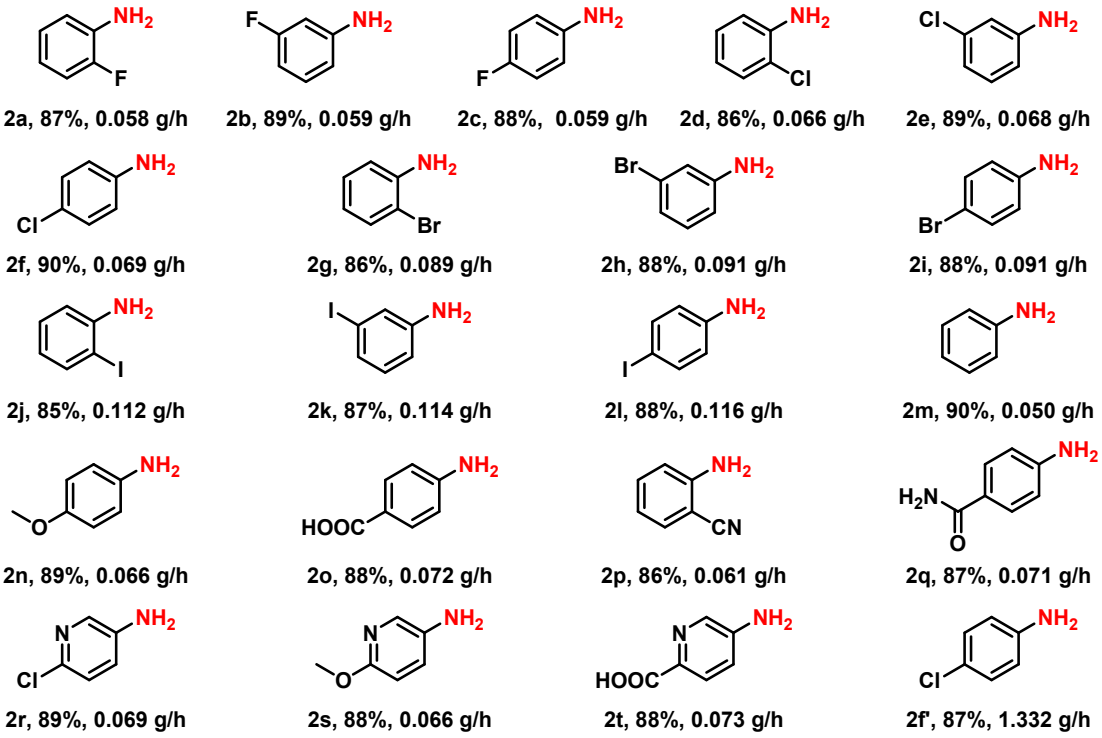


Figure S10. (a) 4-Bromoaniline adsorption test of Pt@KIT-6 nanocomposite and commercial bulk Pt/C; (b) Determination of the adsorption rate constant k.



Scheme S1. Isolated yields and production rates of the isolated arylamines.

Synthesis of KIT-6.

Mesoporous silica template KIT-6 was synthesized following the conventional method reported in the literature.[7] 18 g of Pluronic®P-123 and 30 mL of HCl (12 M) was added into 651 mL of water and the mixture was stirred at 35 ˚C to dissolve completely. Then, 18 g of *n*-butanol was added and stirred for 1 h at 35 ˚C. Next, 38.7 g of TEOS was added to the above solution and stirred for 24 h at 35 ˚C, the solution was then heated under closed conditions for 24 h at 100 ˚C. After cooling the mixture to room temperature, it was filtered and washed thoroughly using ethanol. The Pluronic®P-123 was then removed by calcination in a muffle furnace at 550 ˚C in the air for 5 h (heating rate = 1.5 ˚C min^{-1}).

Hydrogenation residence time in the MFBR.

When the catalyst loading and reactor geometry (diameter and length) are set, the residence time is controlled according to the solution flow rate. We compared the actual volume of liquid collected and the volume of solution consumed in the continuous flow system with steady state operation and found them to be consistent. The overall hydrogenation residence time is therefore the residence time of the solution in the MFBR. Add sufficient water to the MFBR and obtain a weight difference. The void volume of the MFBR is the volume of water corresponding to the weight difference, which is 0.5 mL. If we want to change the residence time in this continuous flow system, we only need to change the flow rate of the solution. The optimization experiments of the flow rate are also carried out to obtain the optimum residence time. Thus, when the optimum flow rate was 0.10 mL/min, the corresponding optimum residence time was 5.0 min.

Adsorption test

To test the adsorption behaviors of different catalysts, 8.6 mg 4-bromoaniline was added to 100 mL methanol and completely dissolved at 20 ˚C, followed by adding 100 mg catalyst. The solution was sampled at given time intervals and the concentration of the left 4-bromoaniline in solution was determined by HPLC (Agilent 1100 Series). According to the change of 4-bromoaniline concentration (C) with the time (t), the adsorption kinetic was studied based on the adsorption equation,

$$\frac{dC}{dt} = kC^n$$

where k and n referred to the adsorption rate constant and adsorption order, respectively.

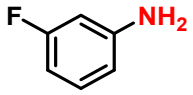
Characterization of the products

2-Fluoroaniline (2a) [8]

^{1}H NMR (600 MHz, DMSO) δ 6.96 (ddd, *J* = 11.9, 8.1, 1.2 Hz, 1H), 6.89 – 6.84 (m, 1H), 6.81 – 6.76 (m, 1H), 6.56 – 6.46 (m, 1H), 5.07 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 151.16 (d, *J* = 235.6 Hz), 136.82 (d, *J* = 12.1 Hz), 124.91 (d, *J* = 3.0 Hz), 116.75 (d, *J* = 4.5 Hz), 116.40 (d, *J* = 6.0 Hz), 115.23 (d, *J* = 18.1 Hz).

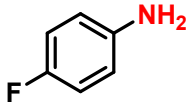
3-Fluoroaniline (2b) [8]



^{1}H NMR (600 MHz, DMSO) δ 7.00 (dd, *J* = 15.2, 8.1 Hz, 1H), 6.39 (ddd, *J* = 8.1, 2.0, 0.7 Hz, 1H), 6.34 (dt, *J* = 12.0, 2.3 Hz, 1H), 6.24 (tdd, *J* = 8.9, 2.5, 0.7 Hz, 1H), 5.37 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 163.83 (d, *J* = 240.1 Hz), 151.34 (d, *J* = 10.6 Hz), 130.62 (d, *J* = 10.6 Hz), 110.38 (d, *J* = 3.0 Hz), 102.09 (d, *J* = 21.1 Hz), 100.48 (d, *J* = 24.2 Hz).

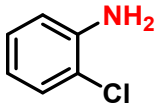
4-Fluoroaniline (2c) [8]



^{1}H NMR (600 MHz, DMSO) δ 6.89 – 6.78 (m, 2H), 6.63 – 6.51 (m, 2H), 4.92 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 154.73 (d, *J* = 231.0 Hz), 145.59 (d, *J* = 1.5 Hz), 115.53 (d, *J* = 22.7 Hz), 115.12 (d, *J* = 7.6 Hz).

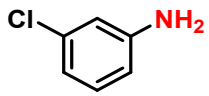
2-Chloroaniline (2d) [9]



^{1}H NMR (600 MHz, DMSO) δ 7.18 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.02 (ddd, *J* = 8.1, 7.3, 1.4 Hz, 1H), 6.82 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.61 – 6.47 (m, 1H), 5.30 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 145.10 (s), 129.42 (s), 128.09 (s), 117.59 (s), 117.30 (s), 115.94 (s).

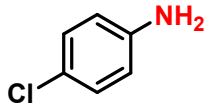
3-Chloroaniline (2e) [9]



^{1}H NMR (600 MHz, DMSO) δ 7.00 (t, *J* = 8.0 Hz, 1H), 6.62 (t, *J* = 2.1 Hz, 1H), 6.52 (ddd, *J* = 8.1, 2.1, 0.8 Hz, 1H), 6.49 (ddd, *J* = 7.8, 2.0, 0.8 Hz, 1H), 5.38 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 150.82 (s), 133.88 (s), 130.77 (s), 115.47 (s), 113.53 (s), 112.87 (s).

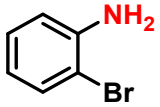
4-Chloroaniline (2f) [9]



^{1}H NMR (600 MHz, DMSO) δ 7.60 – 6.76 (m, 2H), 6.73 – 6.33 (m, 2H), 5.22 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 148.15 (s), 128.95 (s), 119.22 (s), 115.68 (s).

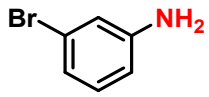
2-Bromoaniline (2g) [10]



^{1}H NMR (600 MHz, DMSO) δ 7.33 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.12 – 7.01 (m, 1H), 6.82 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.55 – 6.38 (m, 1H), 5.27 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 146.21 (s), 132.57 (s), 128.74 (s), 117.84 (s), 115.92 (s), 107.97 (s).

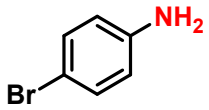
3-Bromoaniline (2h) [9]



^{1}H NMR (600 MHz, DMSO) δ 6.94 (t, *J* = 8.0 Hz, 1H), 6.76 (t, *J* = 2.0 Hz, 1H), 6.65 – 6.59 (m, 1H), 6.55 (dd, *J* = 8.1, 2.0 Hz, 1H), 5.37 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 151.05 (s), 131.12 (s), 122.57 (s), 118.30 (s), 116.40 (s), 113.20 (s).

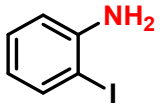
4-Bromoaniline (2i) [11]



^{1}H NMR (600 MHz, DMSO) δ 7.37 – 6.87 (m, 2H), 6.79 – 6.18 (m, 2H), 5.24 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 148.50 (s), 131.79 (s), 116.30 (s), 106.61 (s).

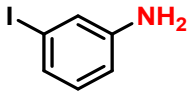
2-Iodoaniline (2j) [8]



^{1}H NMR (600 MHz, DMSO) δ 7.54 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.17 – 6.99 (m, 1H), 6.78 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.33 (td, *J* = 7.8, 1.4 Hz, 1H), 5.19 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 148.87 (s), 138.91 (s), 129.53 (s), 118.62 (s), 114.91 (s), 83.69 (s).

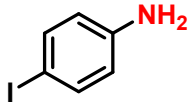
3-Iodoaniline (2k) [9]



^{1}H NMR (600 MHz, DMSO) δ 6.96 (d, *J* = 1.7 Hz, 1H), 6.86 – 6.72 (m, 2H), 6.56 (dt, *J* = 7.2, 1.9 Hz, 1H), 5.28 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 150.93 (s), 131.30 (s), 124.36 (s), 122.41 (s), 113.68 (s), 95.74 (s).

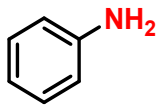
4-Iodoaniline (2l) [8]



^{1}H NMR (600 MHz, DMSO) δ 7.43 – 7.17 (m, 2H), 6.64 – 6.30 (m, 2H), 5.26 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 148.96 (s), 137.56 (s), 117.03 (s), 76.24 (s).

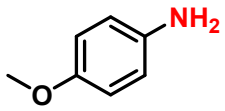
Aniline (2m) [11]



^{1}H NMR (600 MHz, DMSO) δ 7.03 (t, *J* = 7.8 Hz, 2H), 6.59 (d, *J* = 7.6 Hz, 2H), 6.51 (t, *J* = 7.3 Hz, 1H), 4.99 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 149.05 (s), 129.28 (s), 116.19 (s), 114.41 (s).

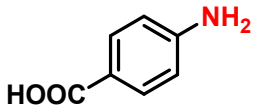
4-Anisidine (2n) [11]



^{1}H NMR (600 MHz, DMSO) δ 6.71 – 6.63 (m, 2H), 6.59 – 6.51 (m, 2H), 4.59 (s, 2H), 3.63 (s, 3H).

^{13}C NMR (151 MHz, DMSO) δ 151.20 (s), 142.73 (s), 115.49 (s), 114.97 (s), 55.75 (s).

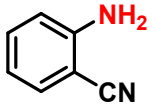
4-Aminobenzoic Acid (2o) [8]



^{1}H NMR (600 MHz, DMSO) δ 11.94 (s, 1H), 7.76 – 7.50 (m, 2H), 6.71 – 6.40 (m, 2H), 5.87 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 167.98 (s), 153.61 (s), 131.69 (s), 117.37 (s), 113.06 (s).

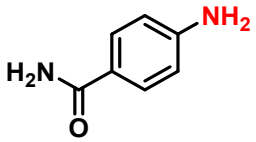
2-Aminobenzonitrile (2p) [12]



^{1}H NMR (600 MHz, DMSO) δ 7.36 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.32 – 7.26 (m, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.58 (t, *J* = 7.5 Hz, 1H), 6.01 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 152.06 (s), 134.39 (s), 132.86 (s), 118.59 (s), 116.37 (s), 115.67 (s), 93.91 (s).

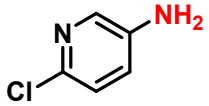
4-Aminobenzamide (2q) [13]



^{1}H NMR (600 MHz, DMSO) δ 7.60 (d, *J* = 8.6 Hz, 2H), 7.54 (s, 1H), 6.84 (s, 1H), 6.53 (d, *J* = 8.6 Hz, 2H), 5.60 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 168.59 (s), 152.15 (s), 129.59 (s), 121.39 (s), 112.95 (s).

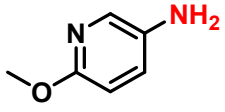
5-Amino-2-chloropyridine (2r) [14]



^{1}H NMR (600 MHz, DMSO) δ 7.72 (d, *J* = 2.9 Hz, 1H), 7.08 (d, *J* = 8.5 Hz, 1H), 7.00 (dd, *J* = 8.5, 3.0 Hz, 1H), 5.49 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 144.99 (s), 136.51 (s), 135.59 (s), 124.26 (s), 124.19 (s).

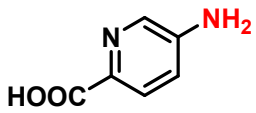
2-Methoxy-5-amino pyridine (2s) [15]



^{1}H NMR (600 MHz, DMSO) δ 7.54 (d, *J* = 2.5 Hz, 1H), 7.03 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.55 (dd, *J* = 8.6, 2.2 Hz, 1H), 4.74 (s, 2H), 3.72 (d, *J* = 2.6 Hz, 3H).

^{13}C NMR (151 MHz, DMSO) δ 156.21 (s), 139.86 (s), 131.58 (s), 126.82 (s), 110.42 (s), 53.10 (s).

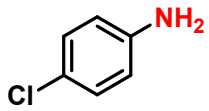
5-Amino-2-pyridinecarboxylic acid (2t) [16]



^{1}H NMR (600 MHz, DMSO) δ 7.98 (d, *J* = 2.5 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 6.95 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.17 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 166.61 (s), 148.54 (s), 135.70 (s), 135.06 (s), 126.60 (s), 118.98 (s).

4-Chloroaniline (2f') [9]

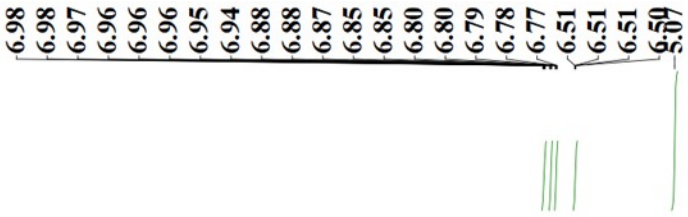


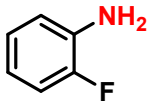
^{1}H NMR (600 MHz, DMSO) δ 7.12 – 6.92 (m, 2H), 6.70 – 6.46 (m, 2H), 5.22 (s, 2H).

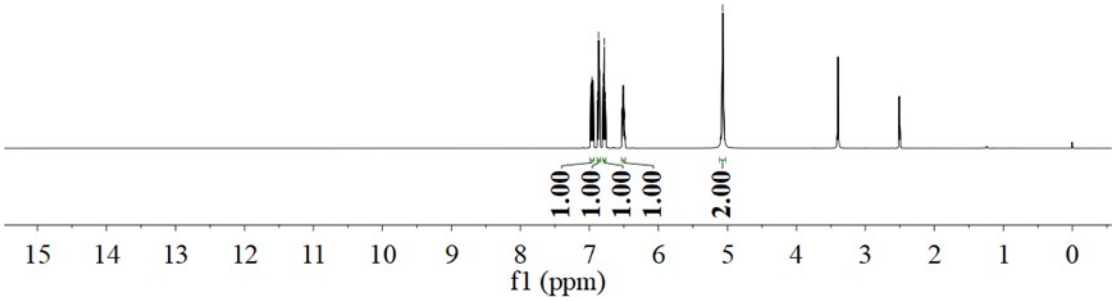
^{13}C NMR (151 MHz, DMSO) δ 148.12 (s), 128.94 (s), 119.29 (s), 115.70 (s).

Copies of ^{1}H and ^{13}C NMR Spectra

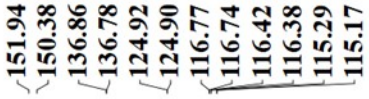
2a ^{1}H NMR

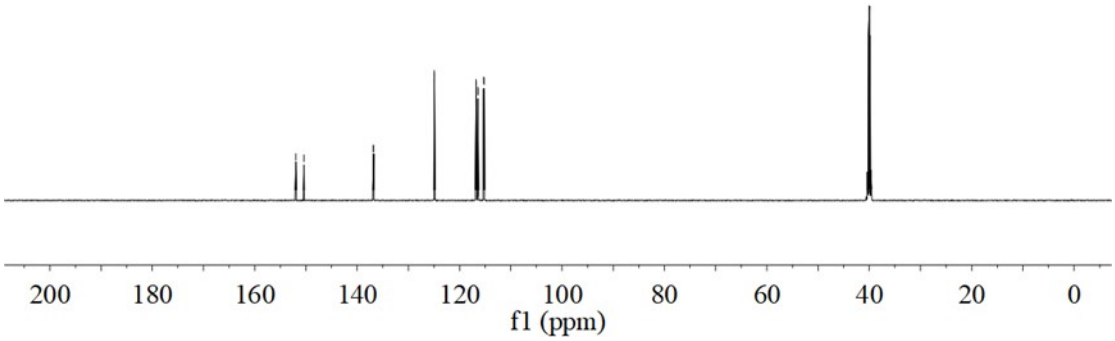




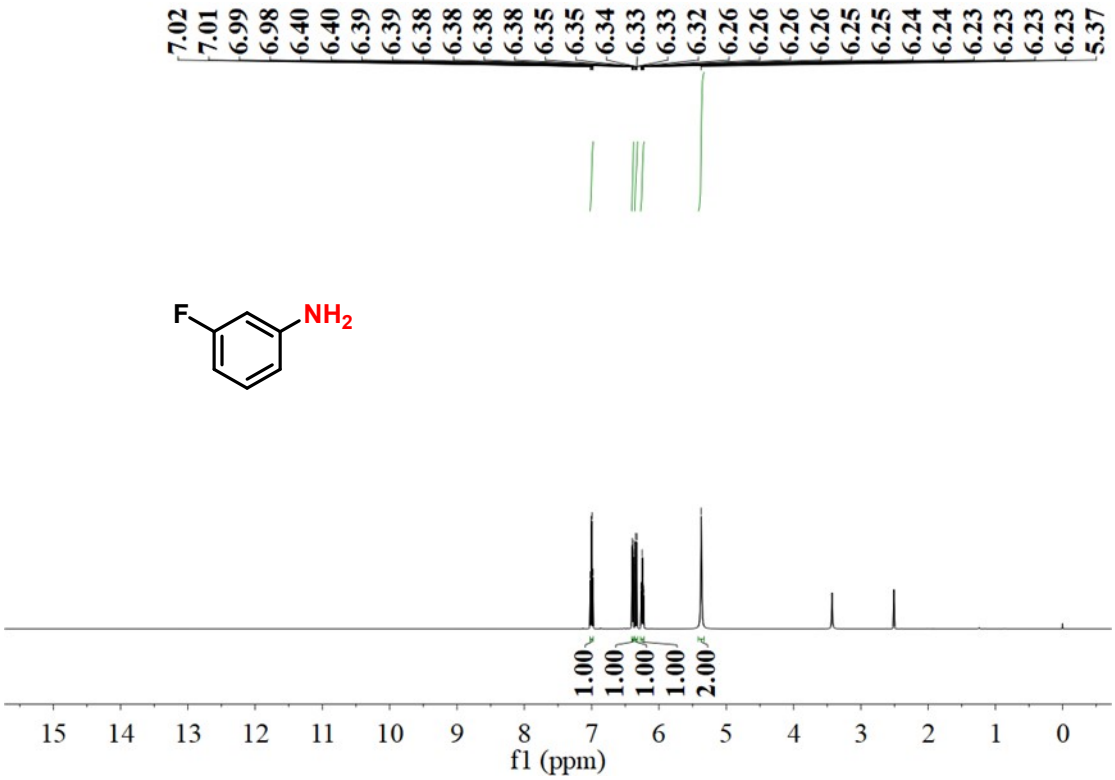


2a ^{13}C NMR

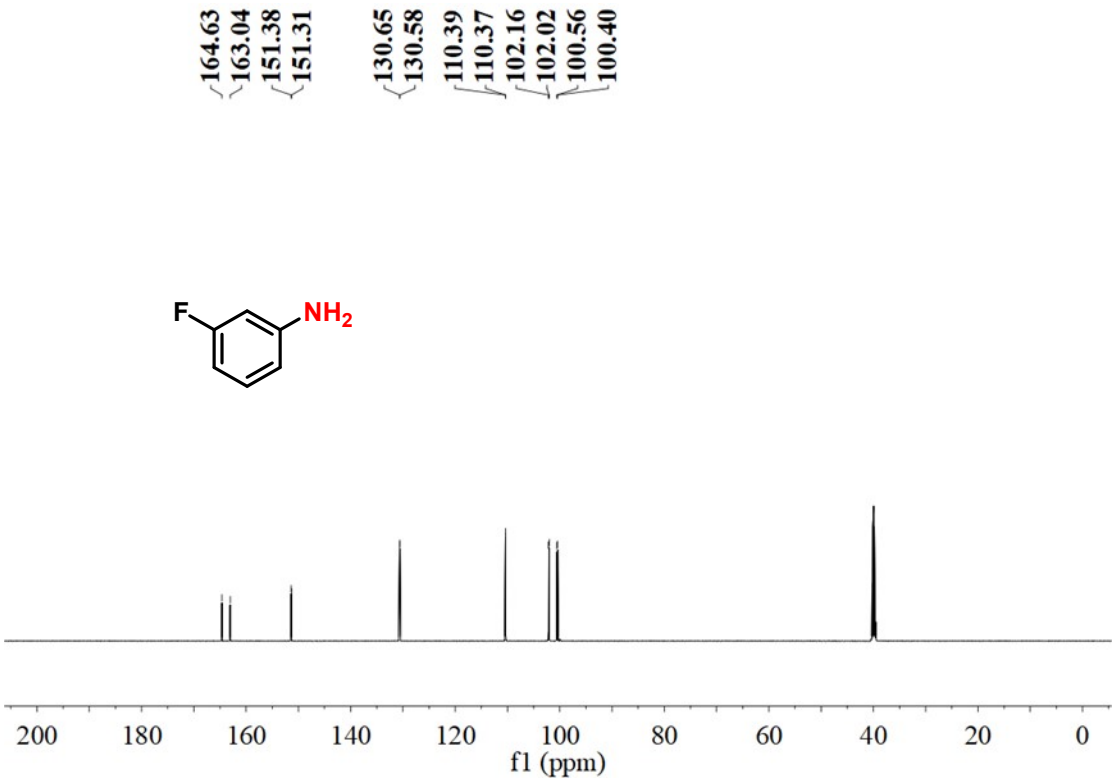




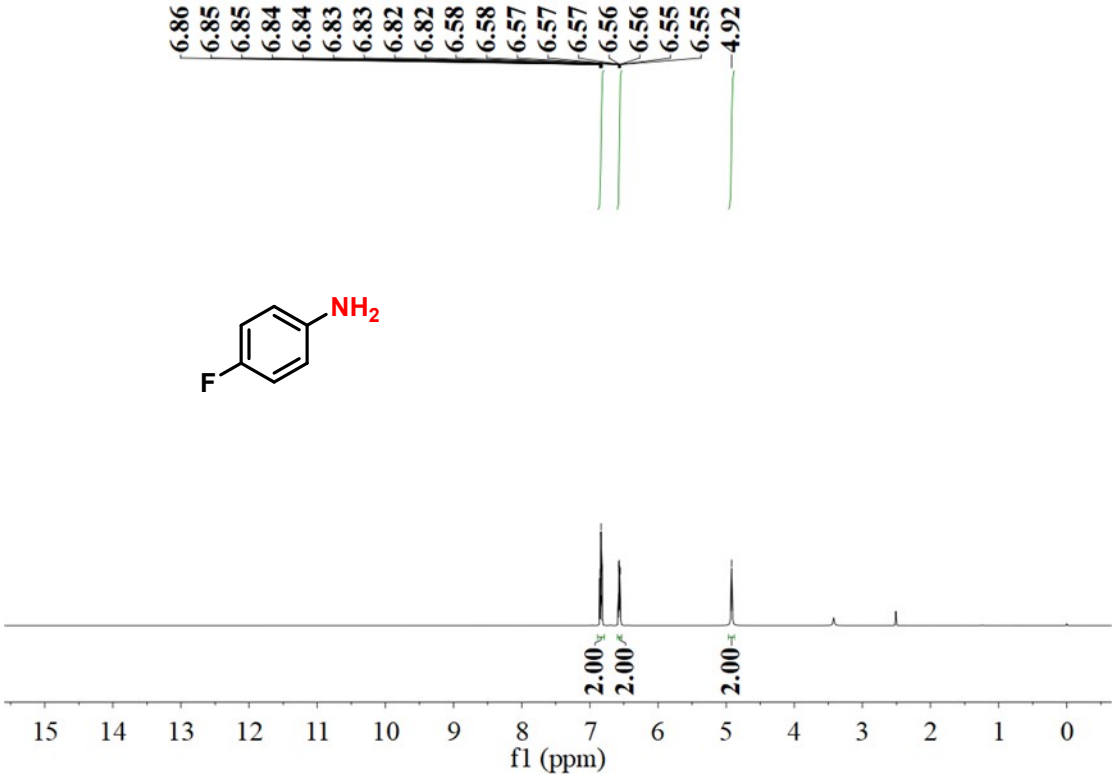
2b ^{1}H NMR



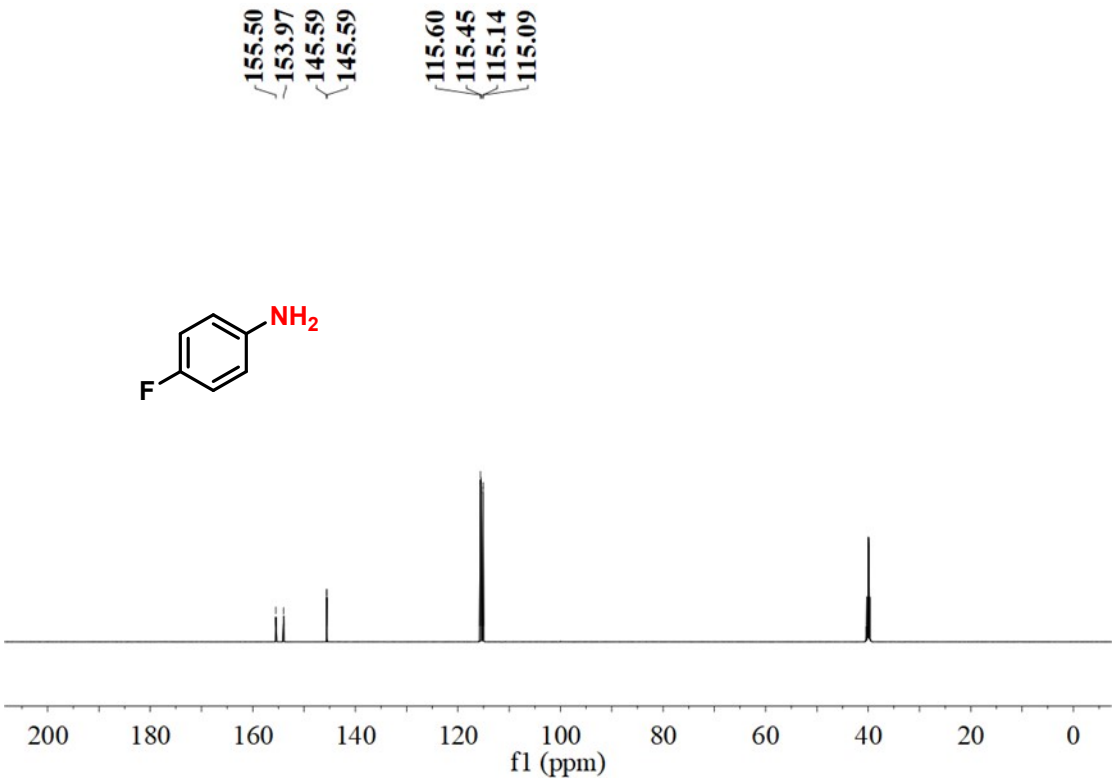
2b ^{13}C NMR



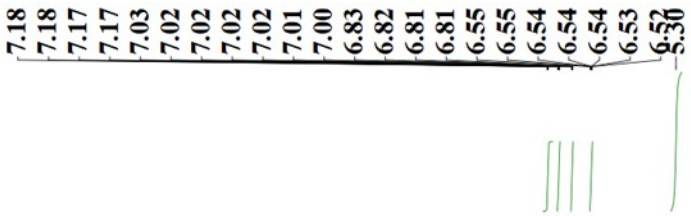
2c ^{1}H NMR

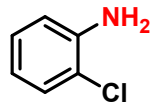


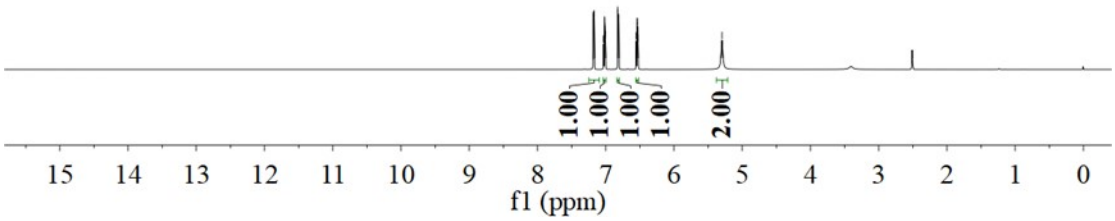
2c ^{13}C NMR



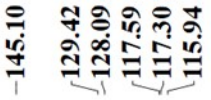
2d ^{1}H NMR

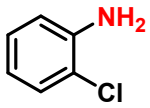


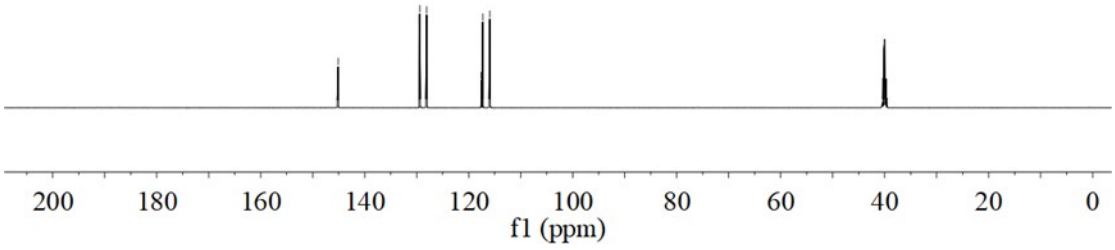




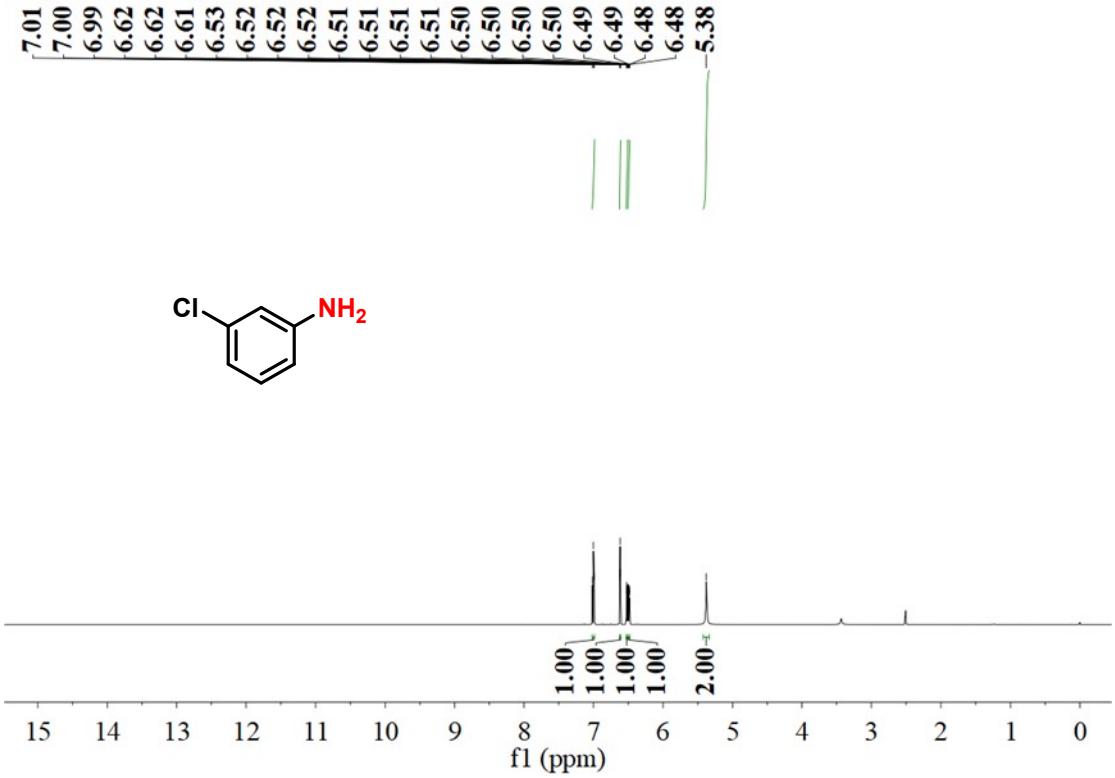
2d ^{13}C NMR



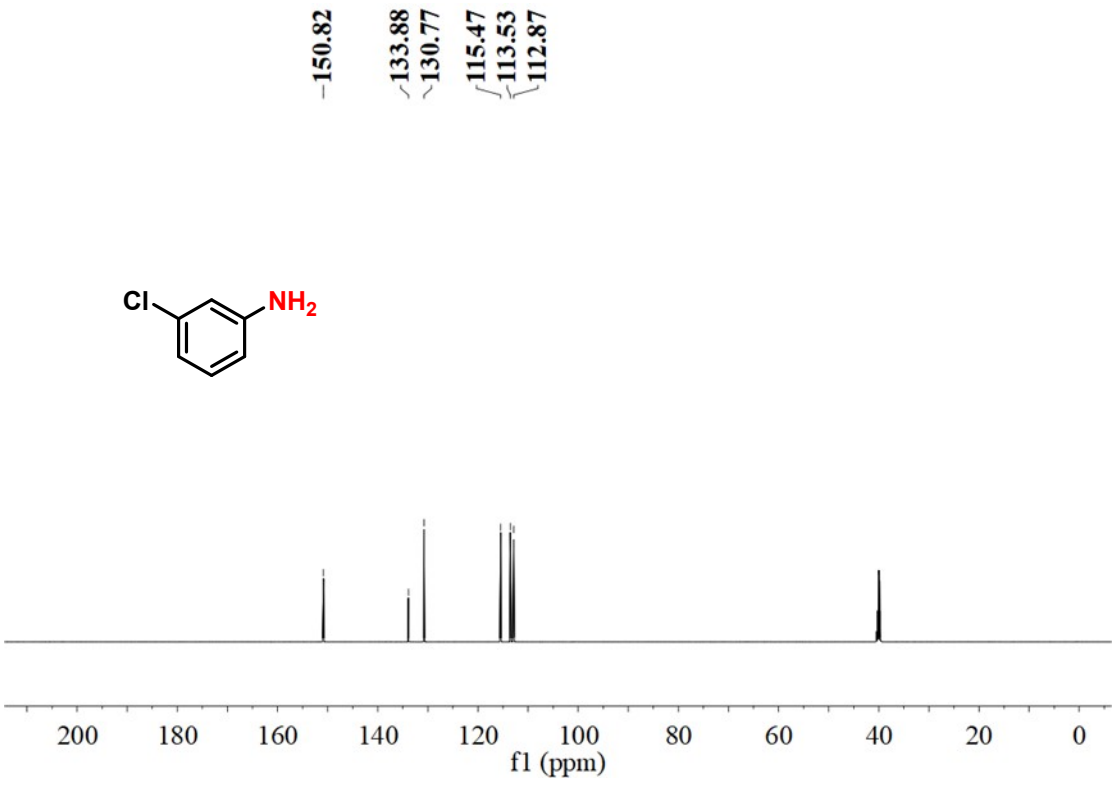




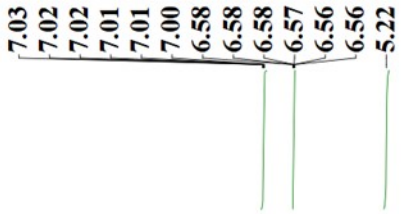
2e ^{1}H NMR

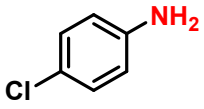


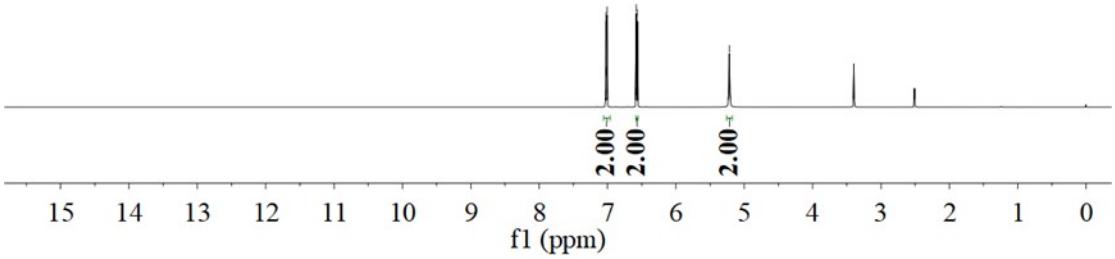
2e ^{13}C NMR



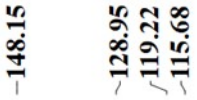
2f ^{1}H NMR

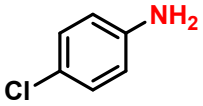


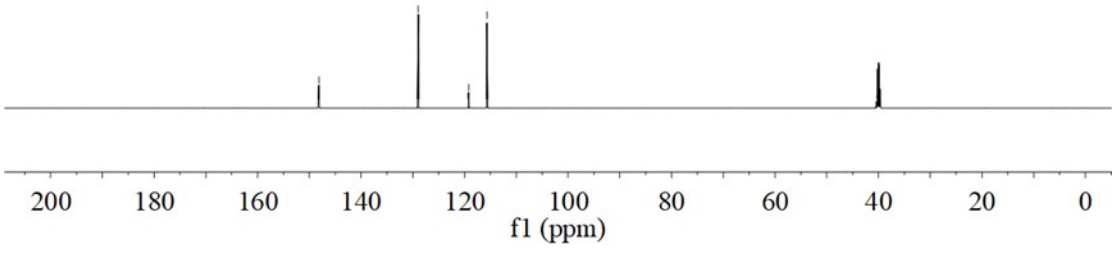




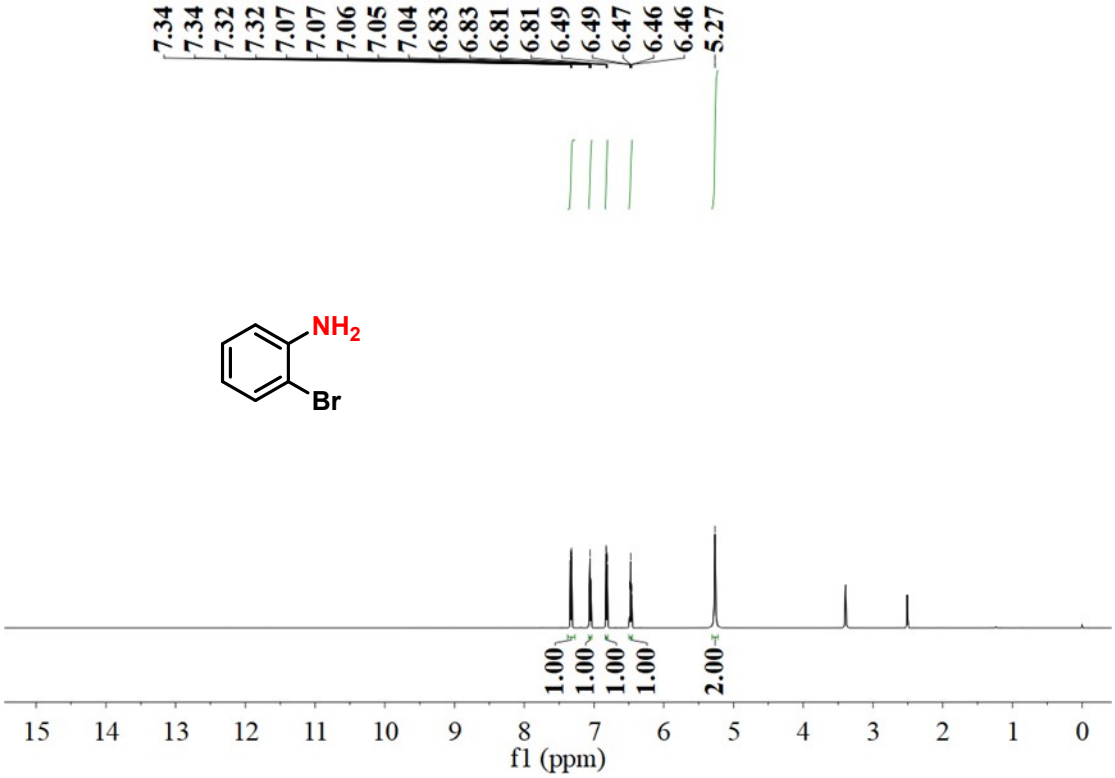
2f ^{13}C NMR



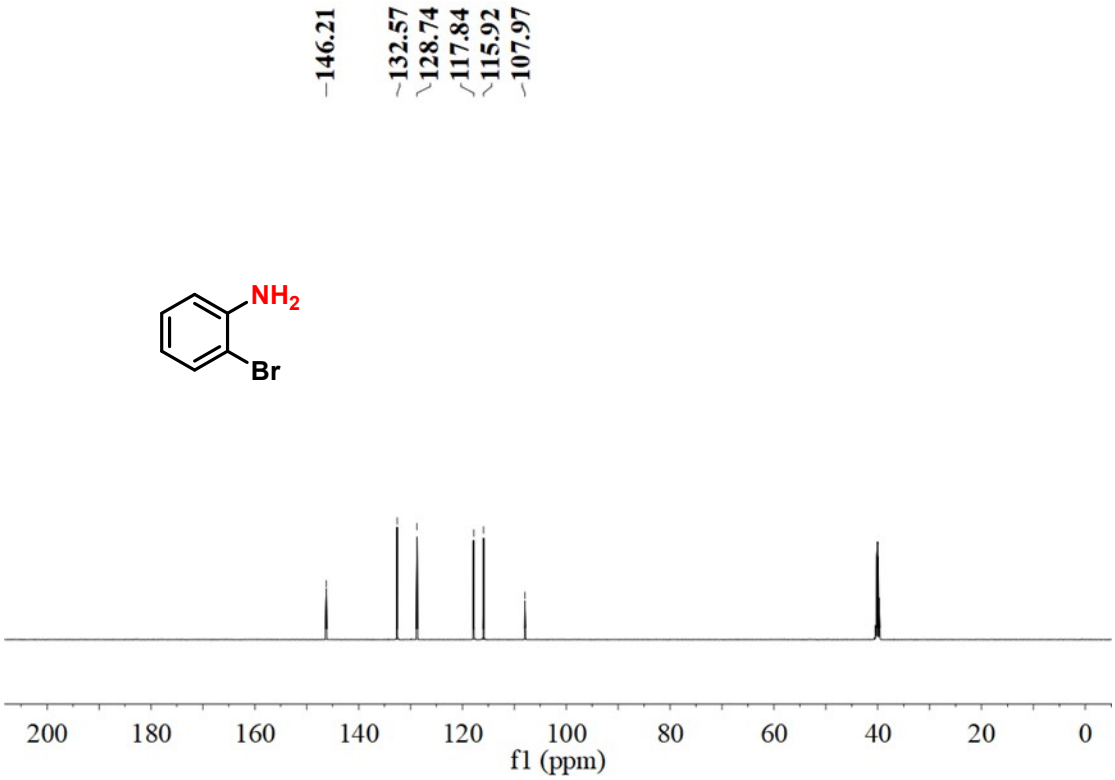




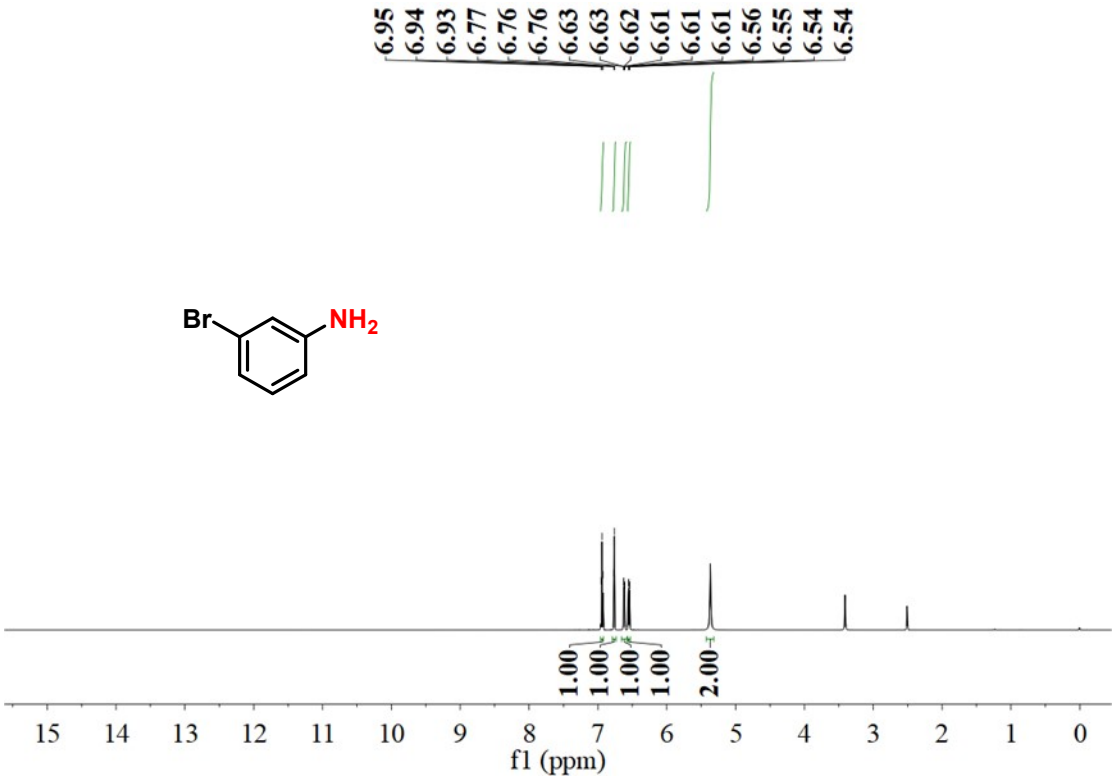
2g ^{1}H NMR



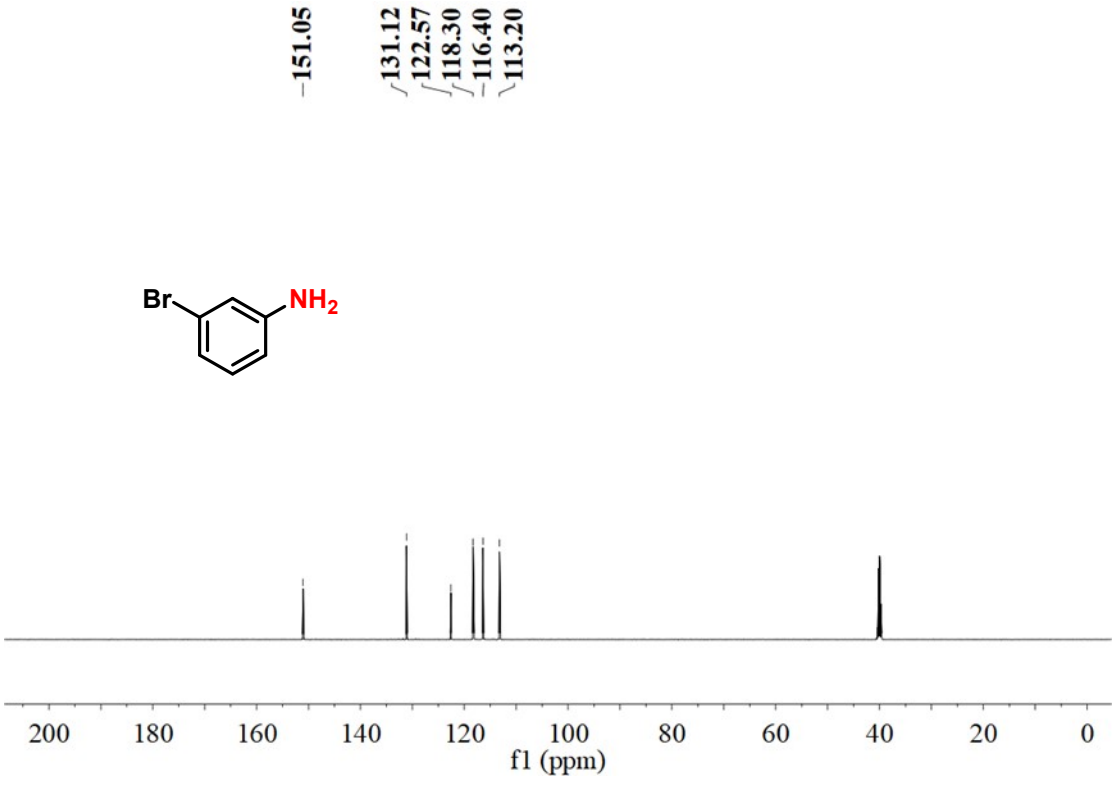
2g ^{13}C NMR



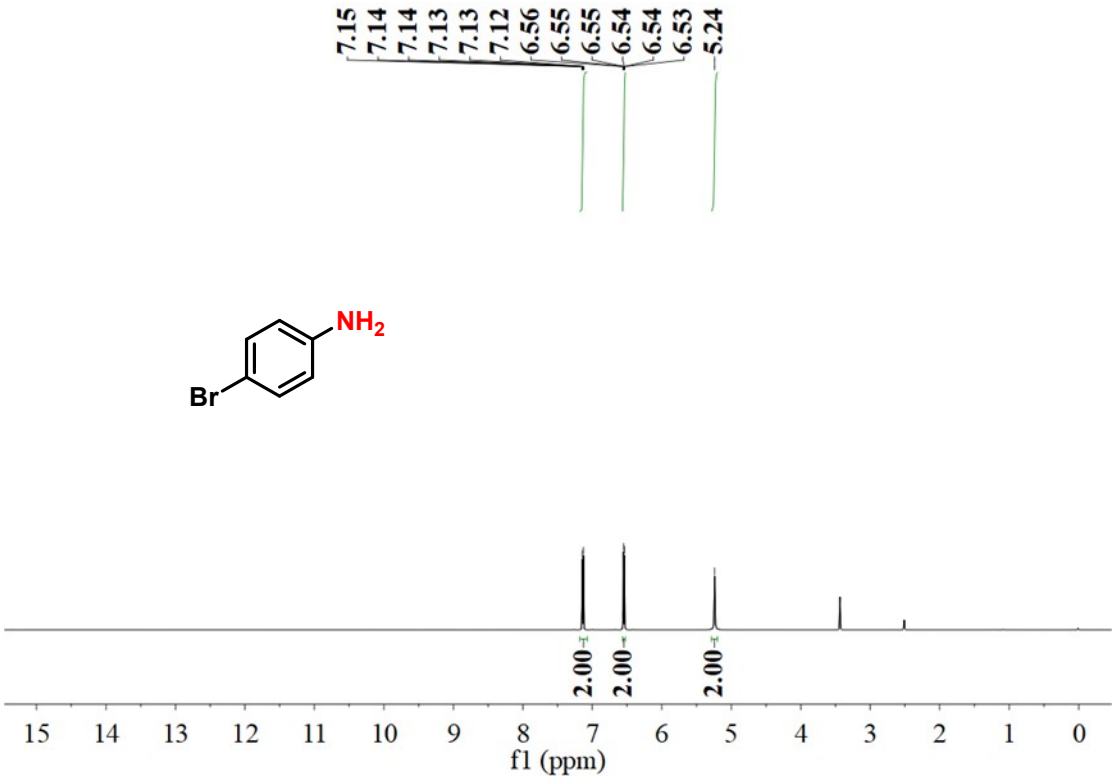
2h ^{1}H NMR



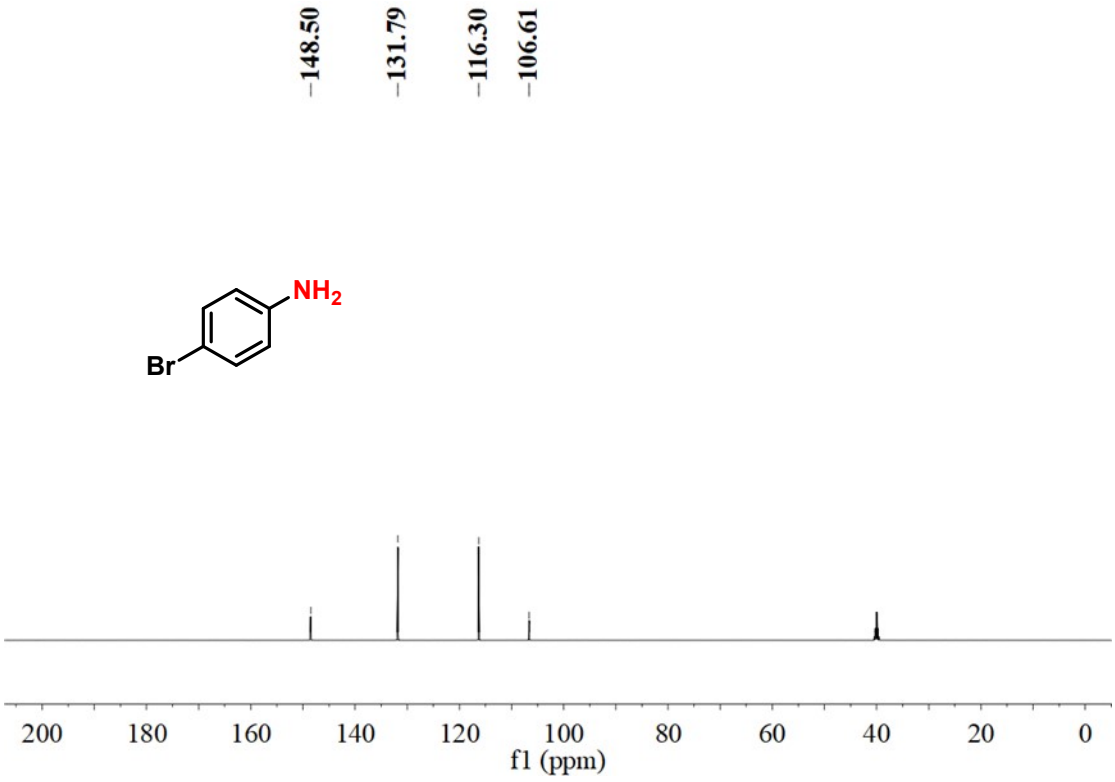
2h ^{13}C NMR



2i ^{1}H NMR



2i ^{13}C NMR



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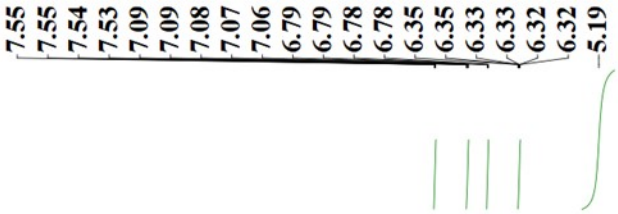
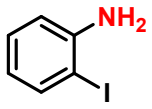
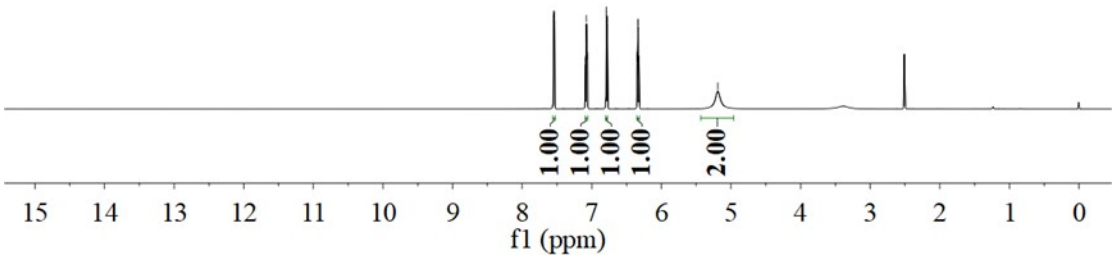
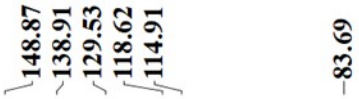
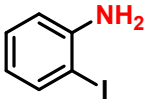


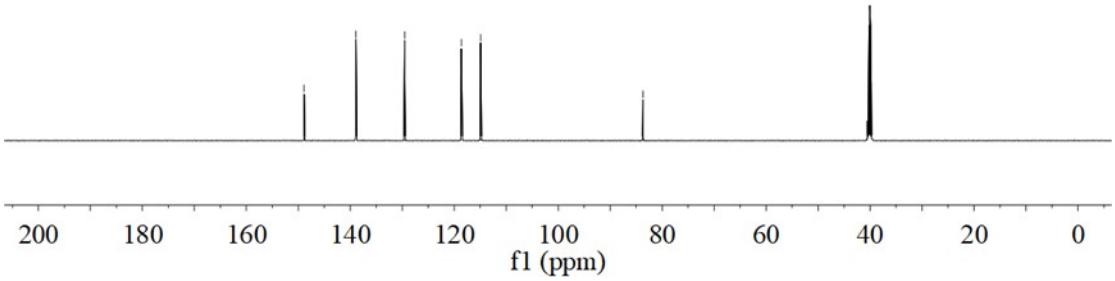




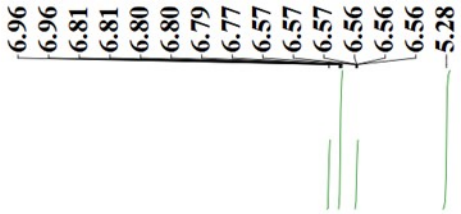
2j ^{13}C NMR

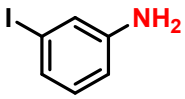


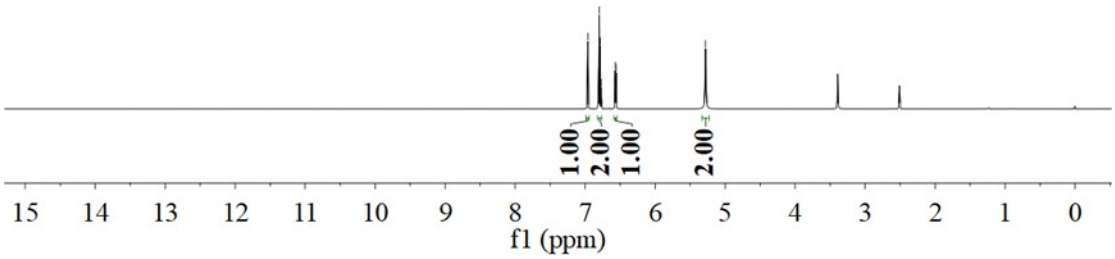




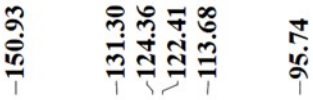
2k ^{1}H NMR

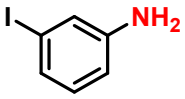


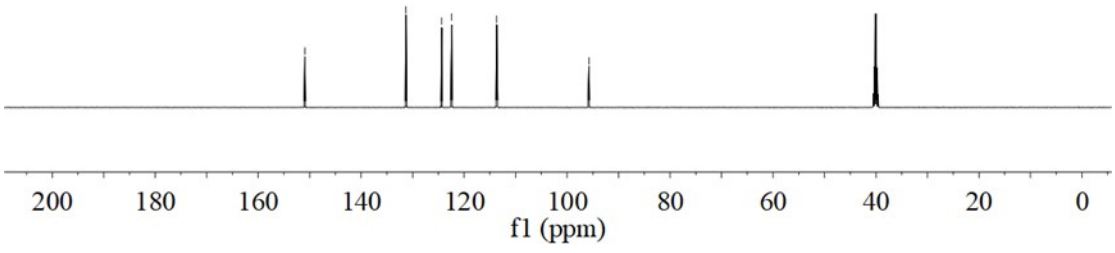




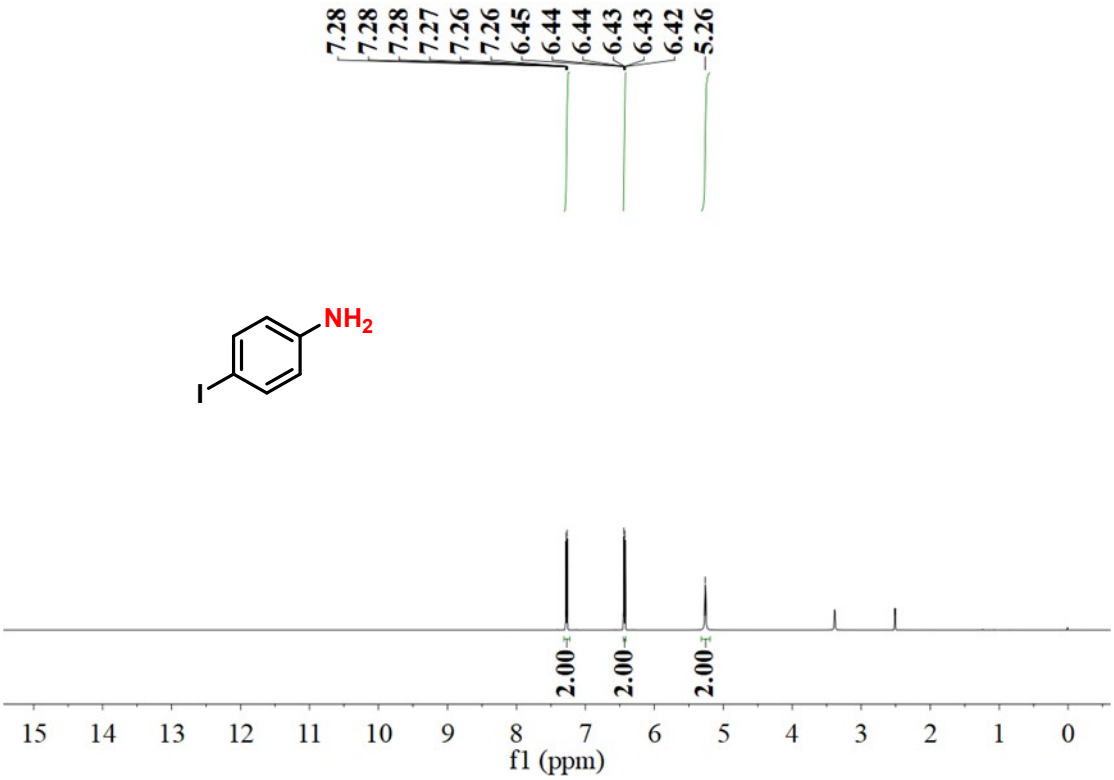
2k ^{13}C NMR



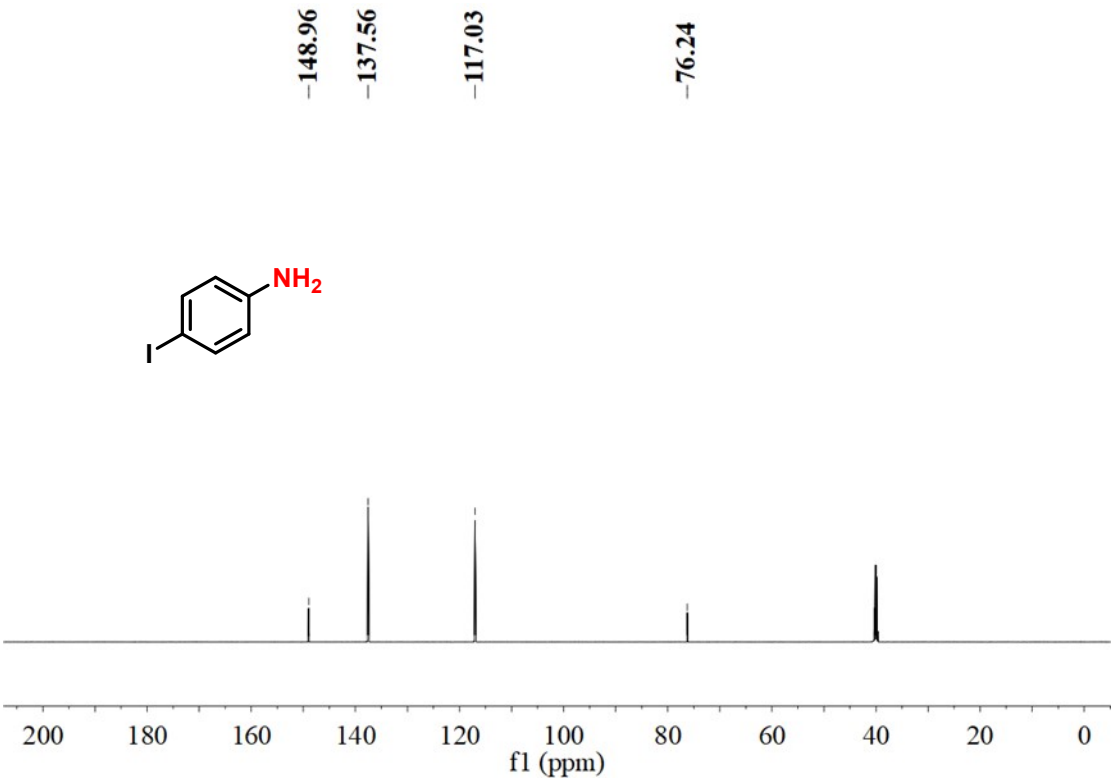




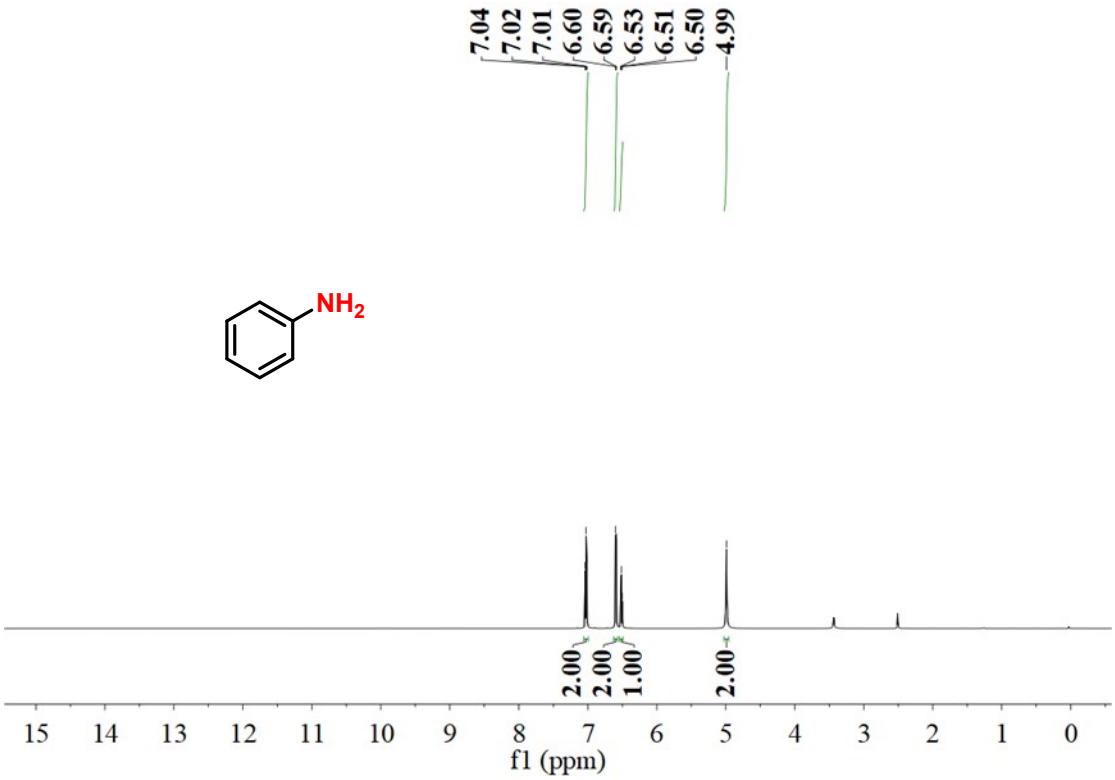
2l ^{1}H NMR



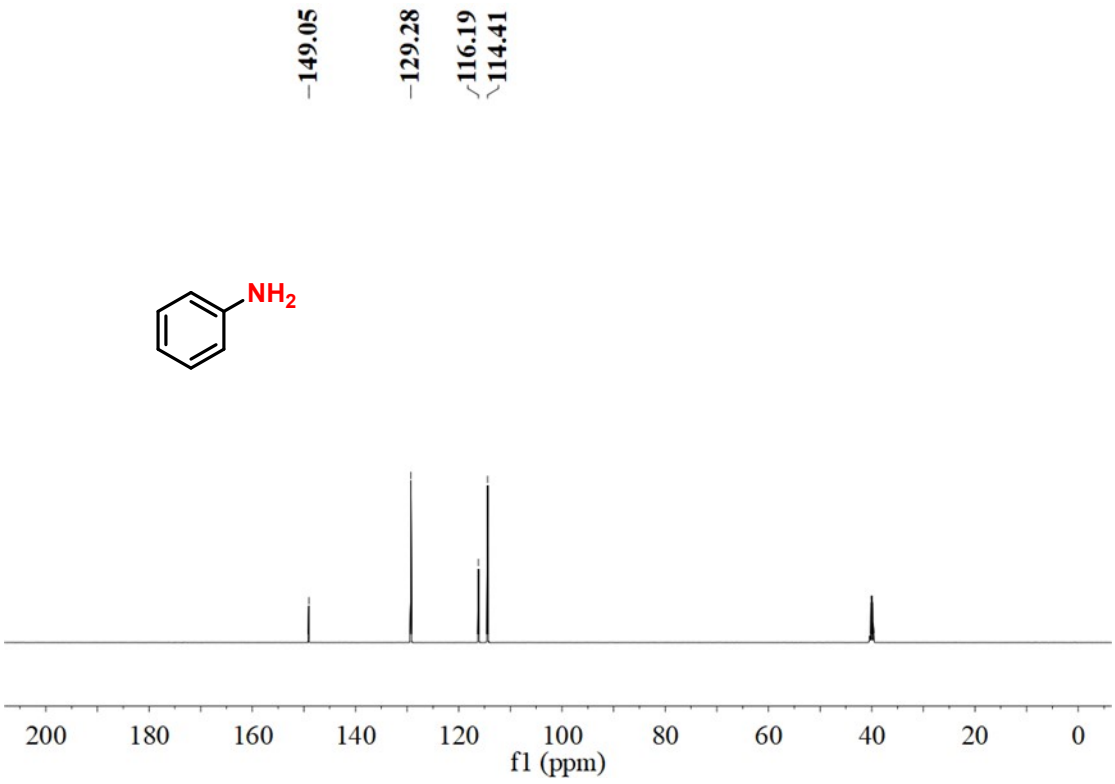
2l ^{13}C NMR



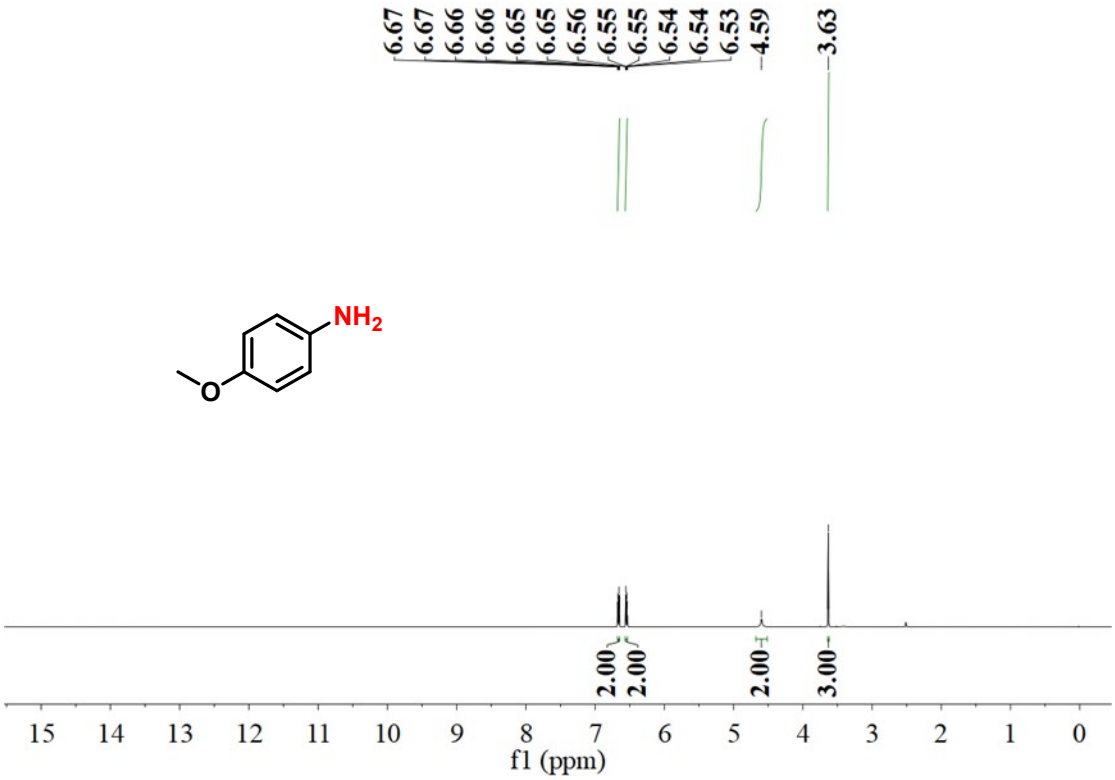
2m ^{1}H NMR



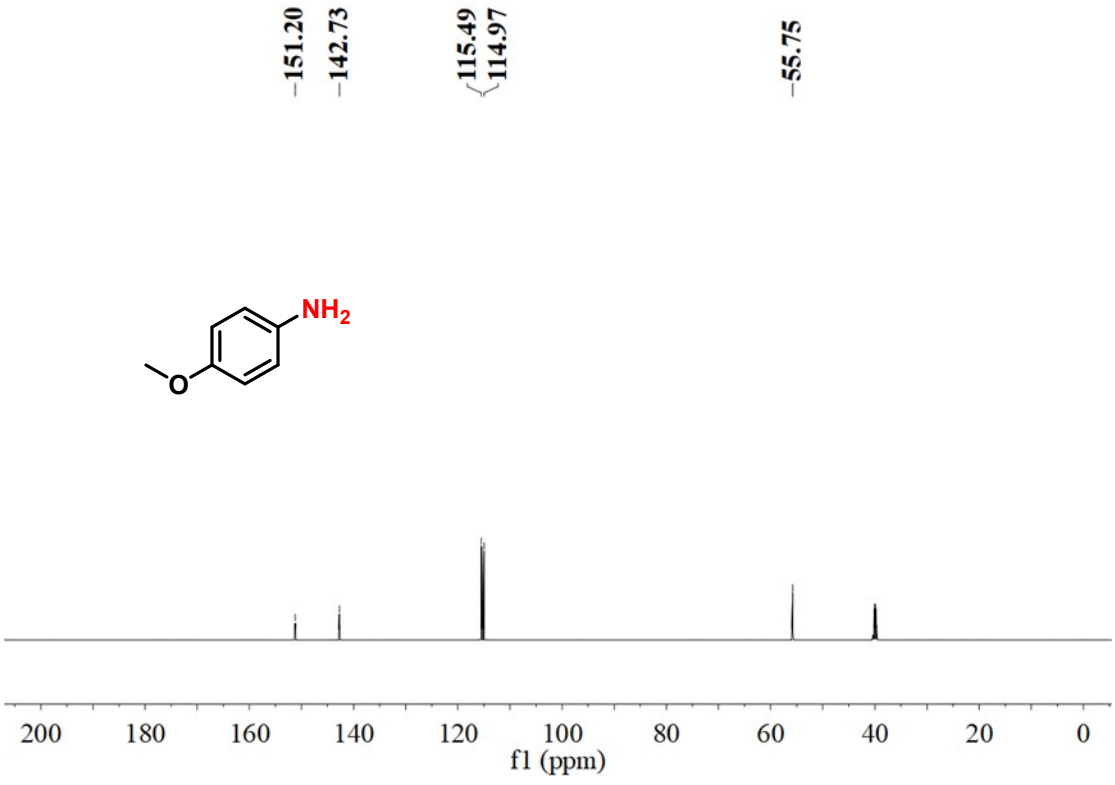
2m ^{13}C NMR



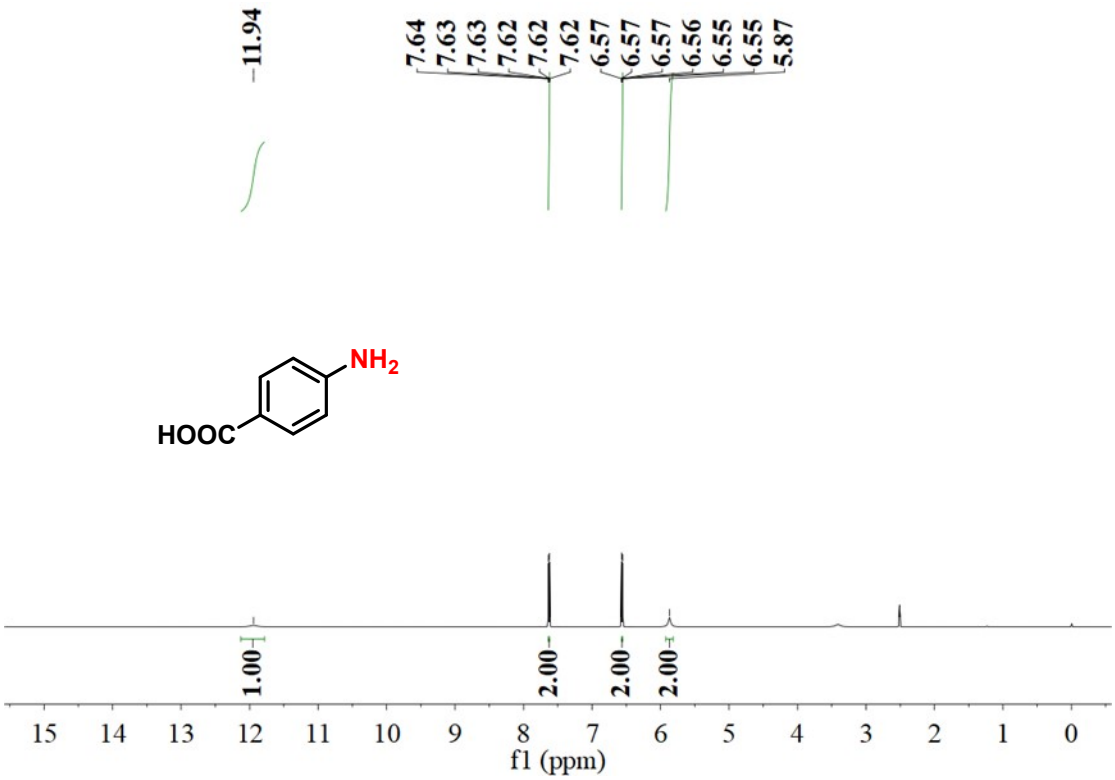
2n ^{1}H NMR



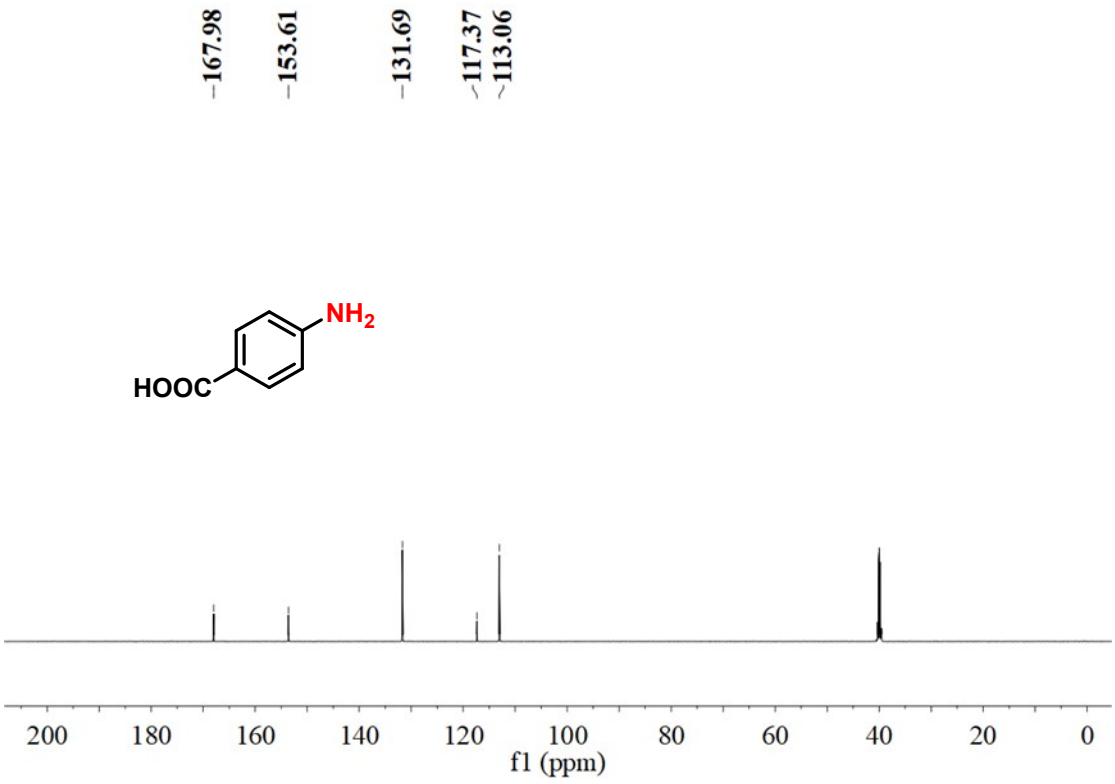
2n ^{13}C NMR



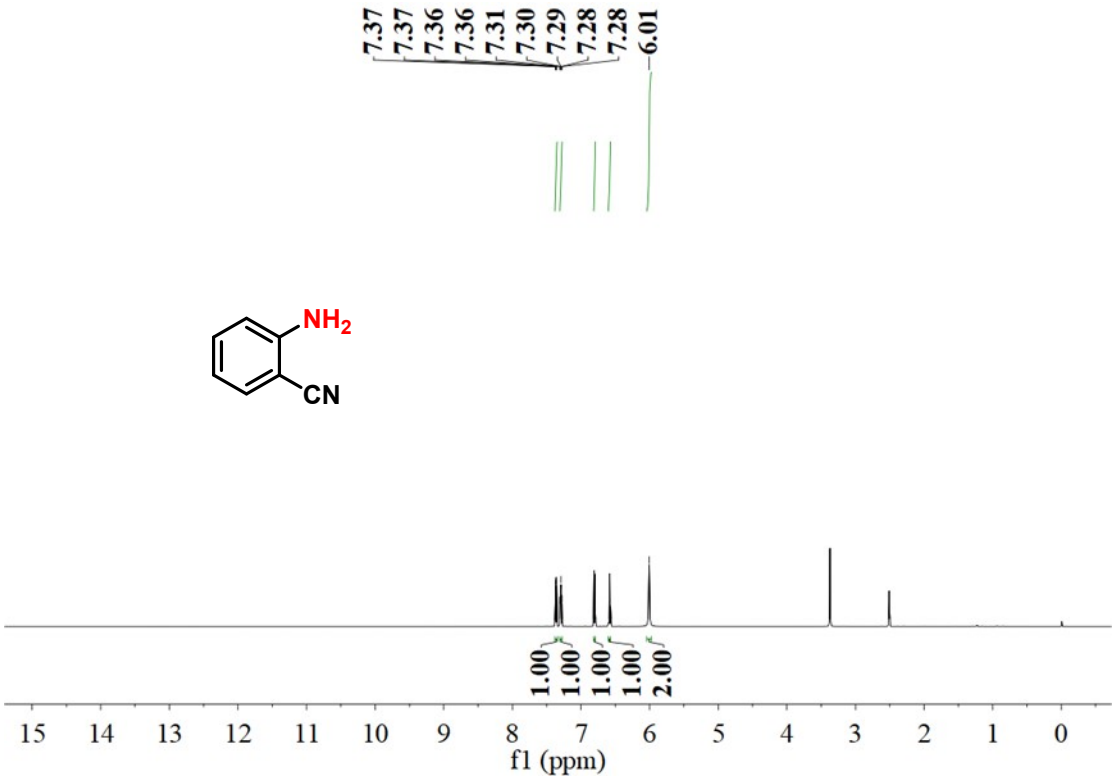
2o ^{1}H NMR



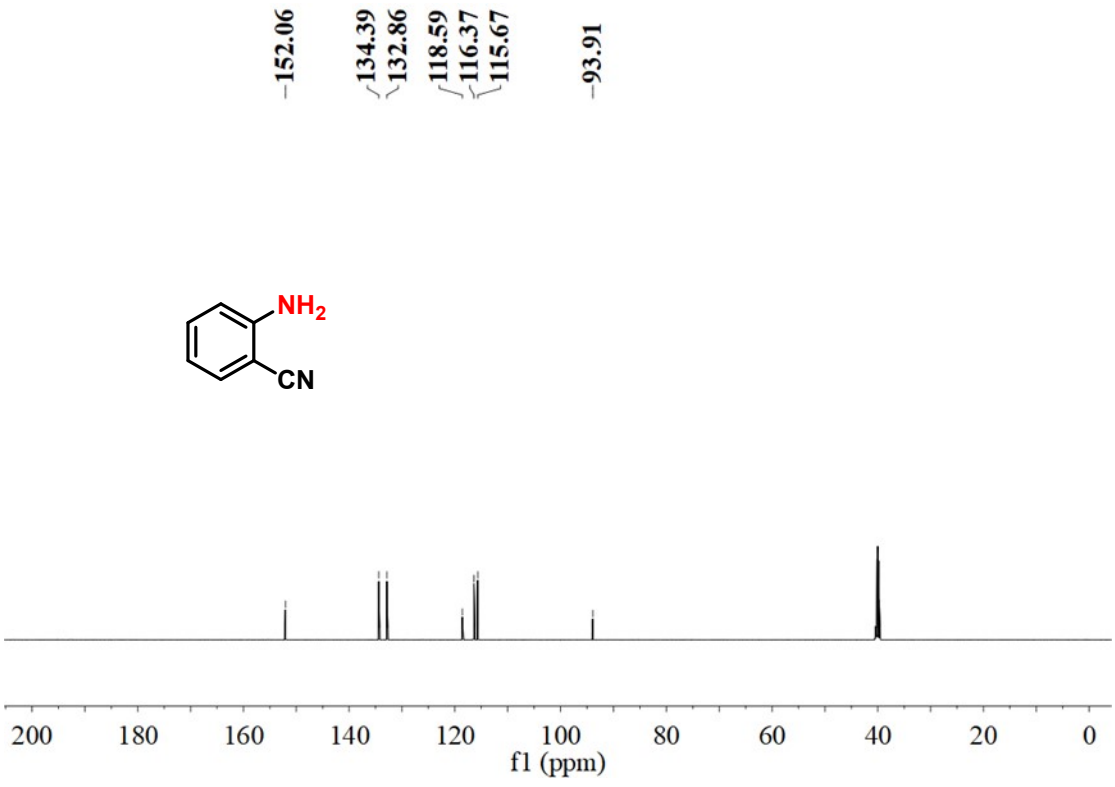
2o ^{13}C NMR



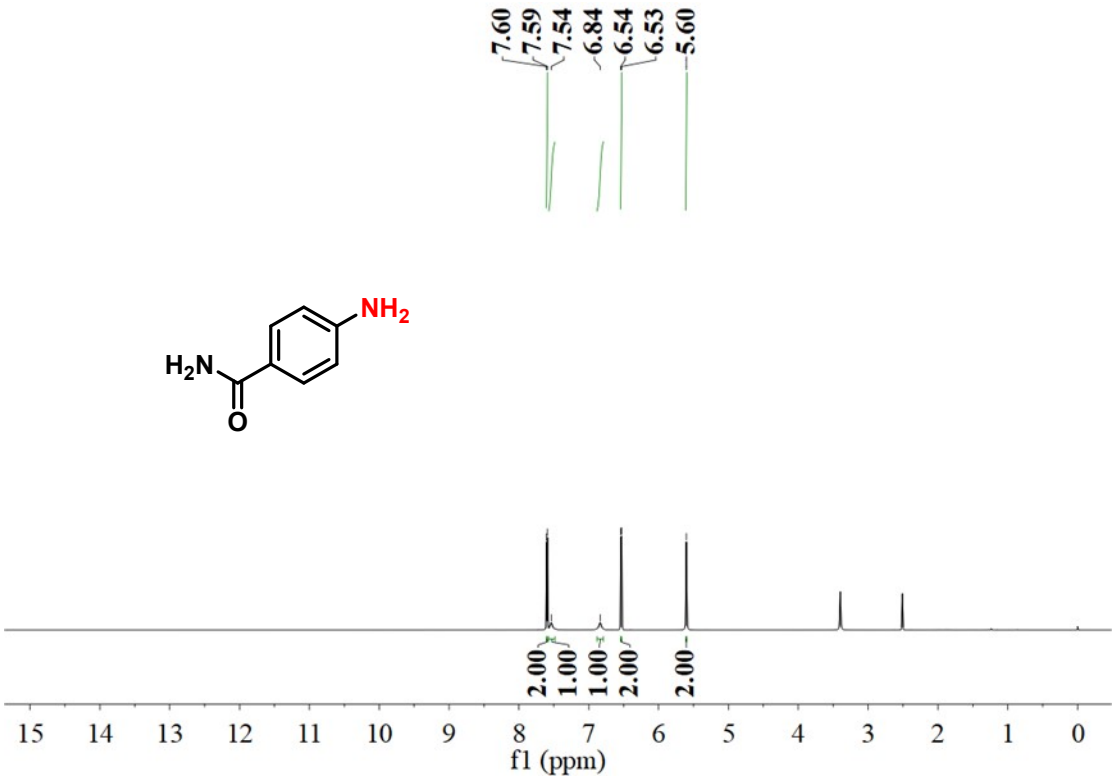
2p ^{1}H NMR



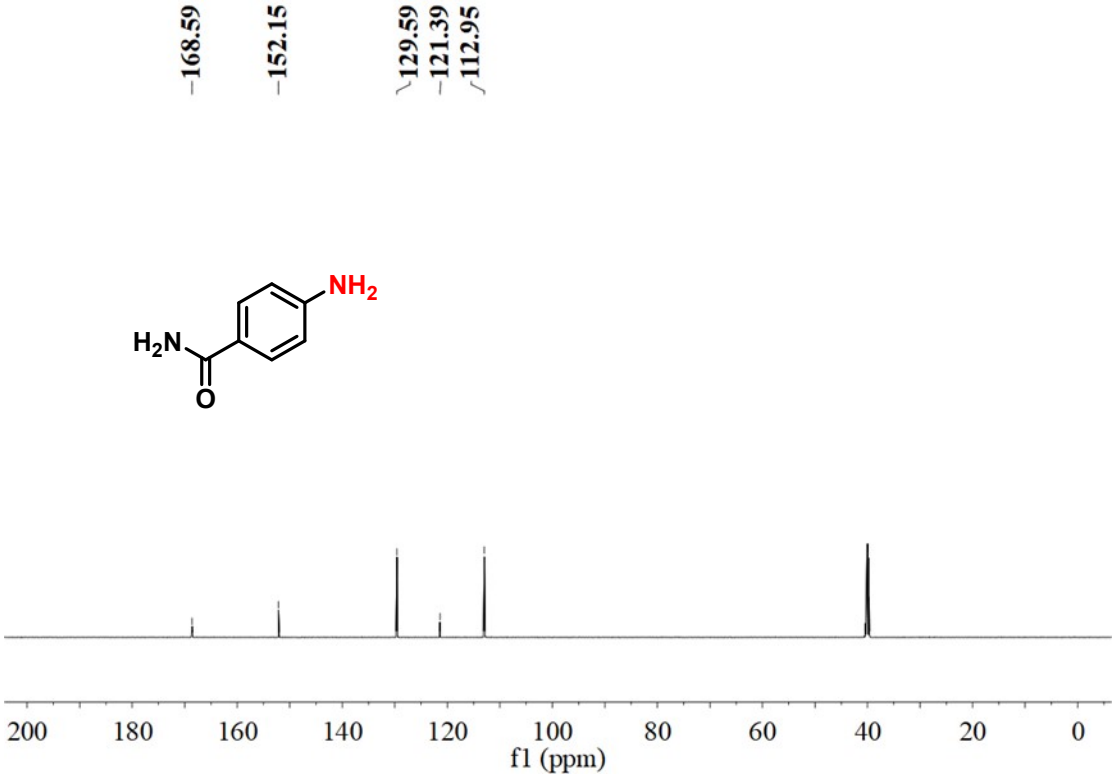
2p ^{13}C NMR



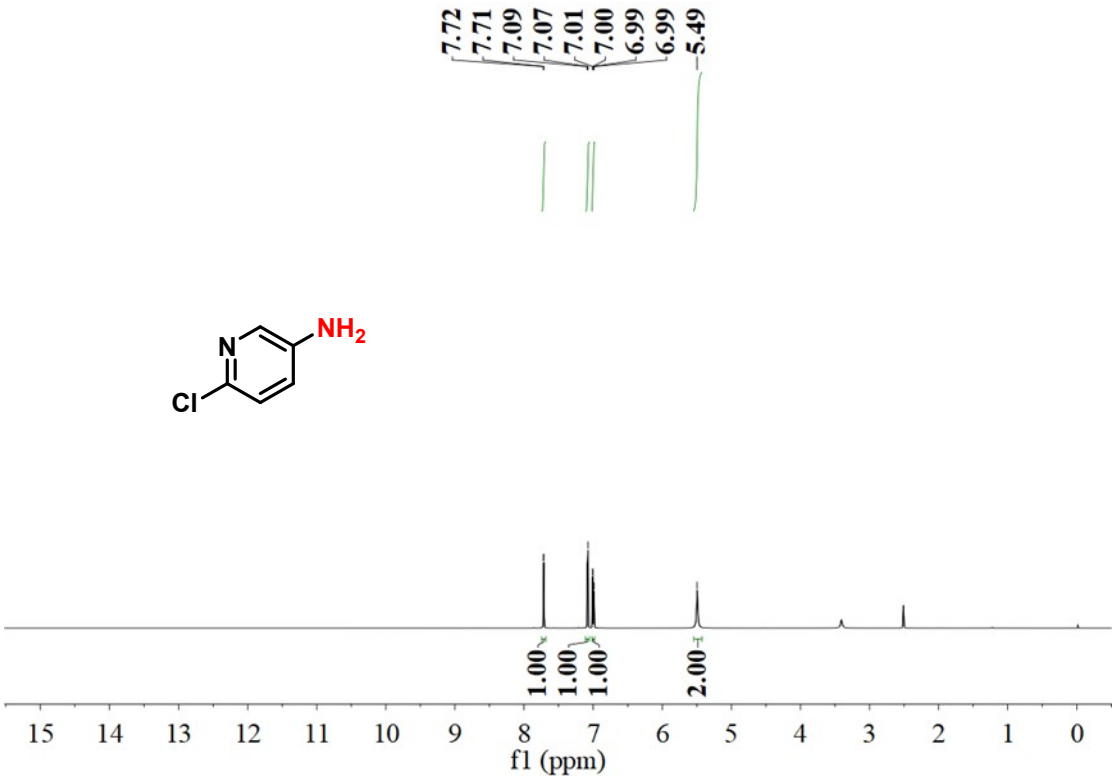
2q ^{1}H NMR



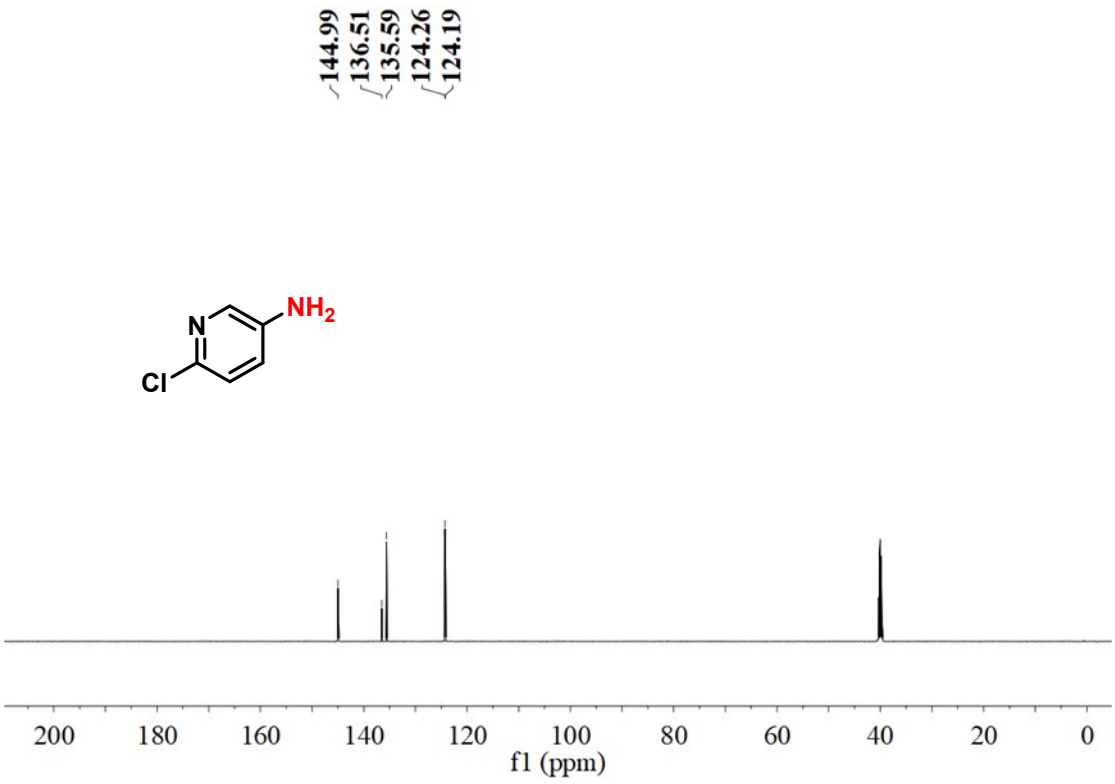
2q ^{13}C NMR



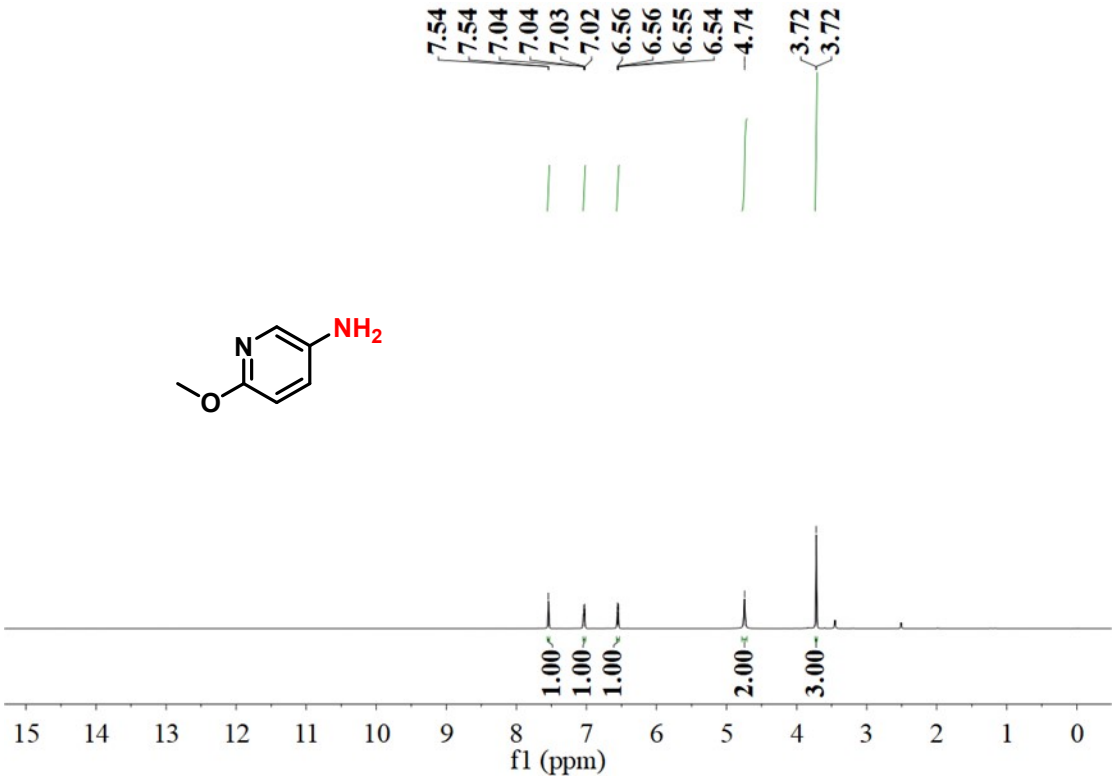
2r ^{1}H NMR



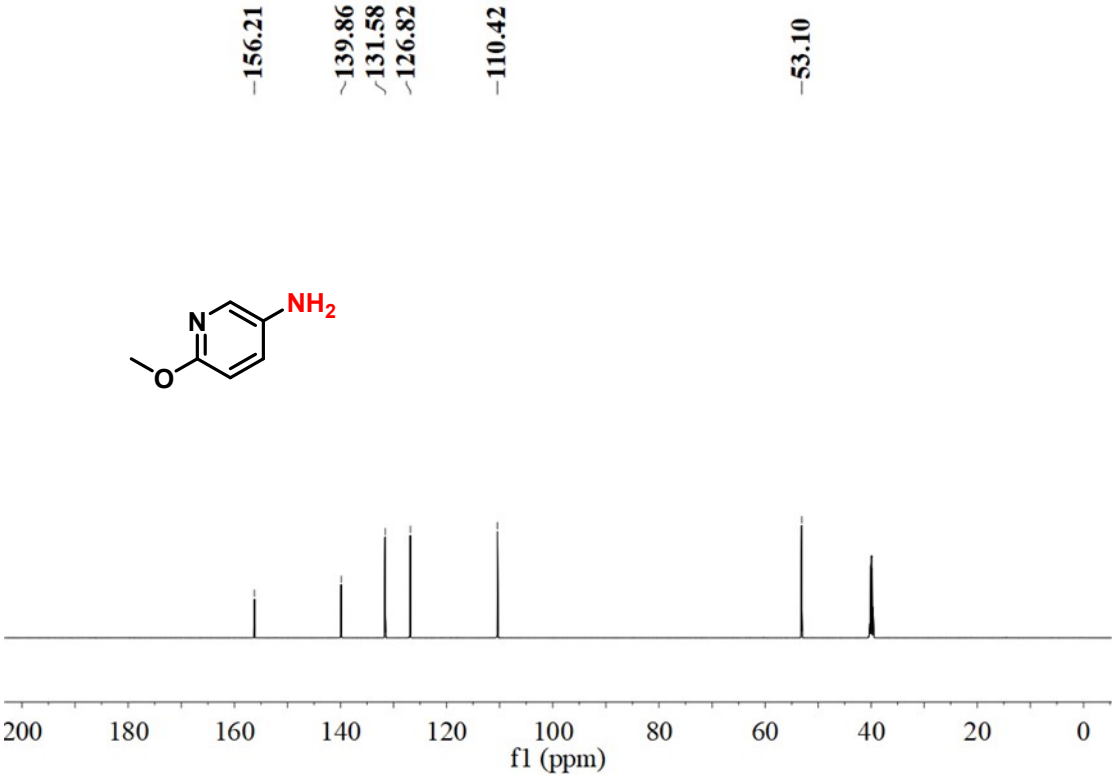
2r ^{13}C NMR



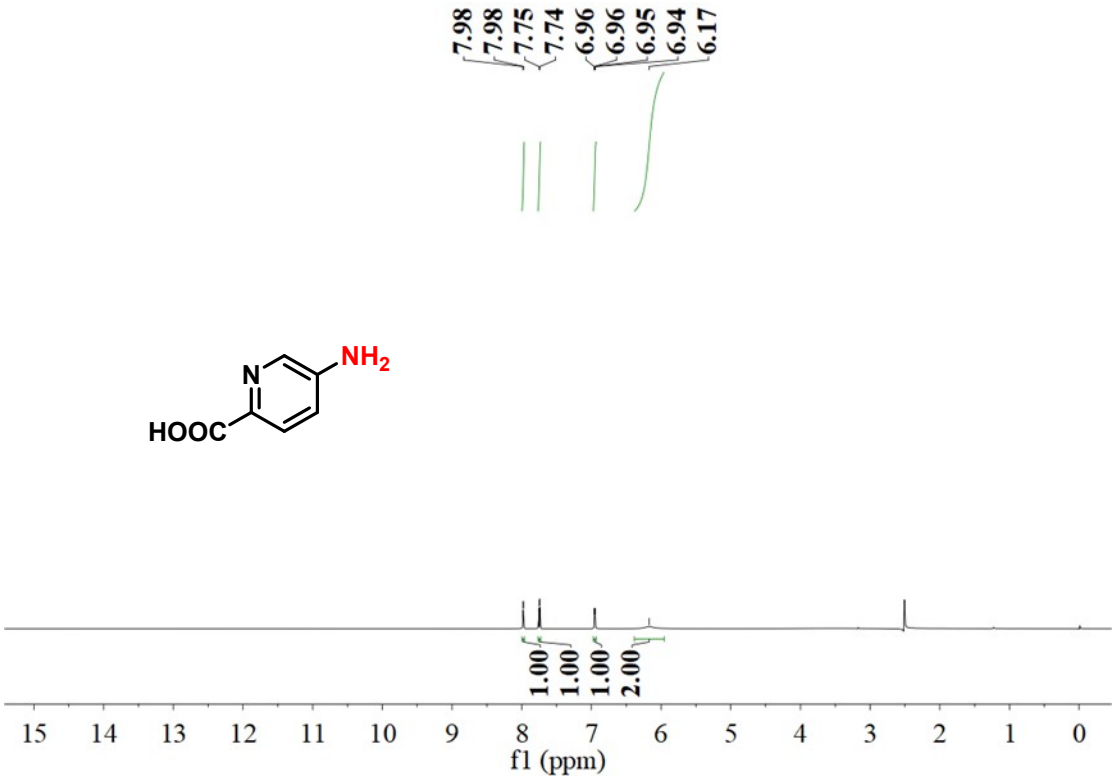
2s ^{1}H NMR



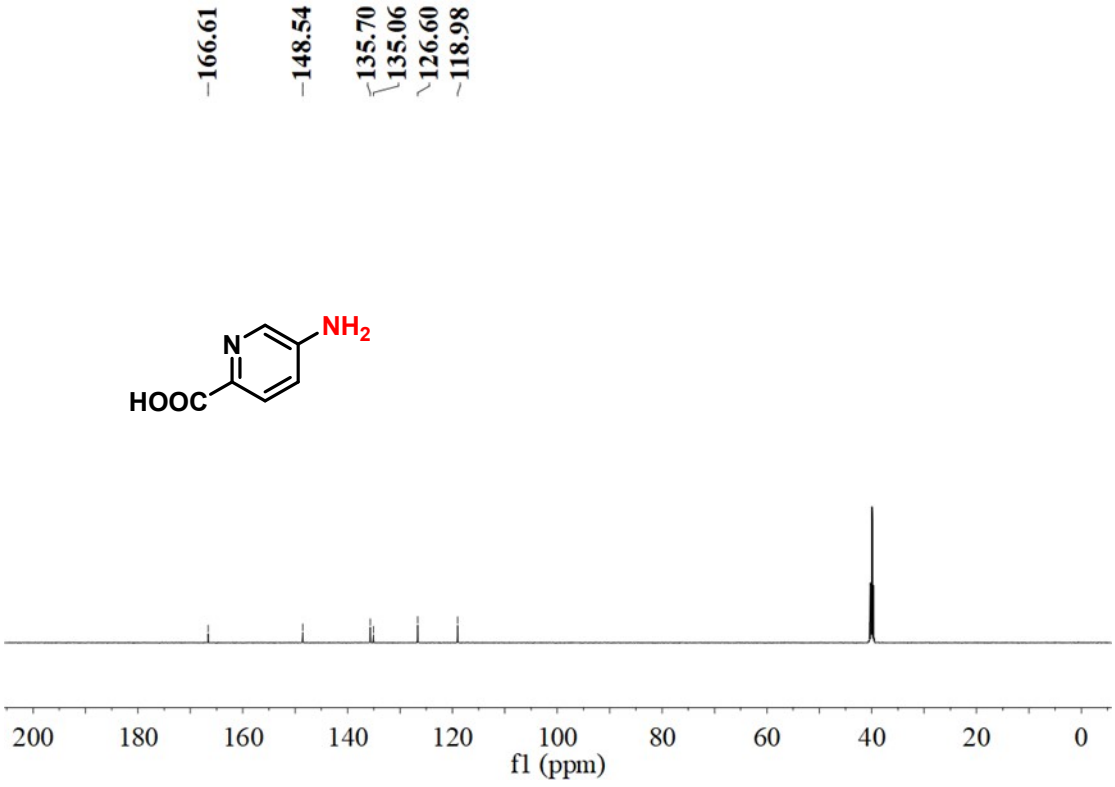
2s ^{13}C NMR



2t ^{1}H NMR



2t ^{13}C NMR



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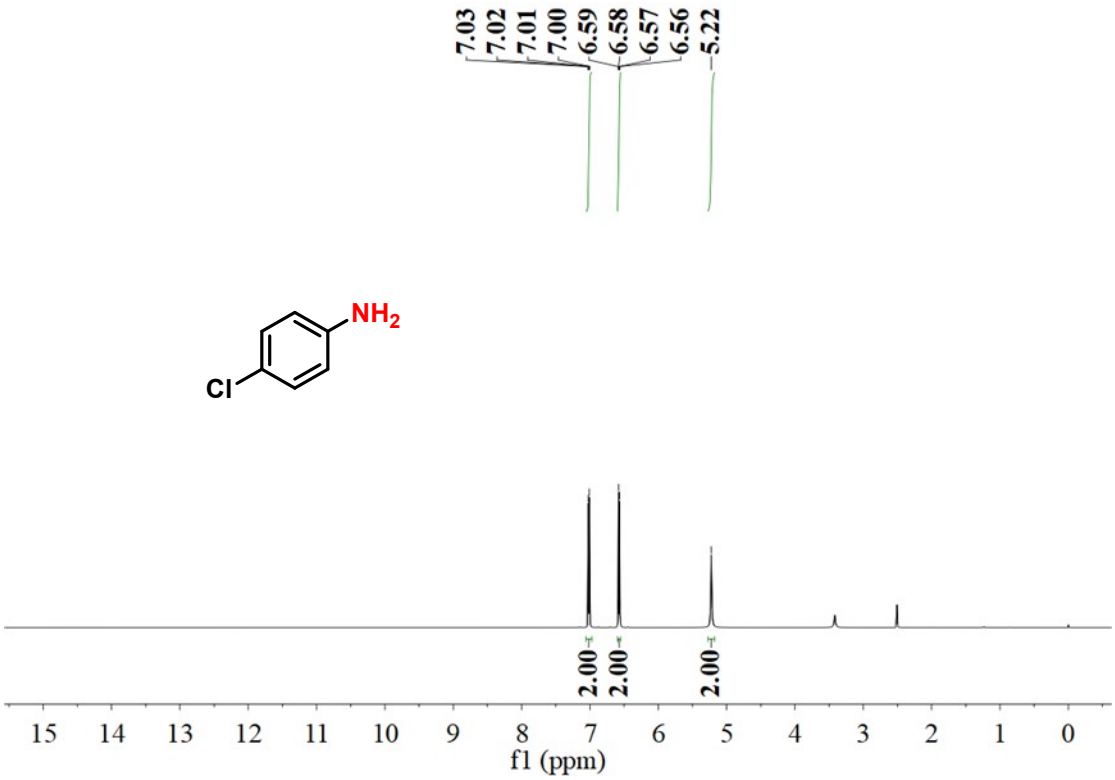
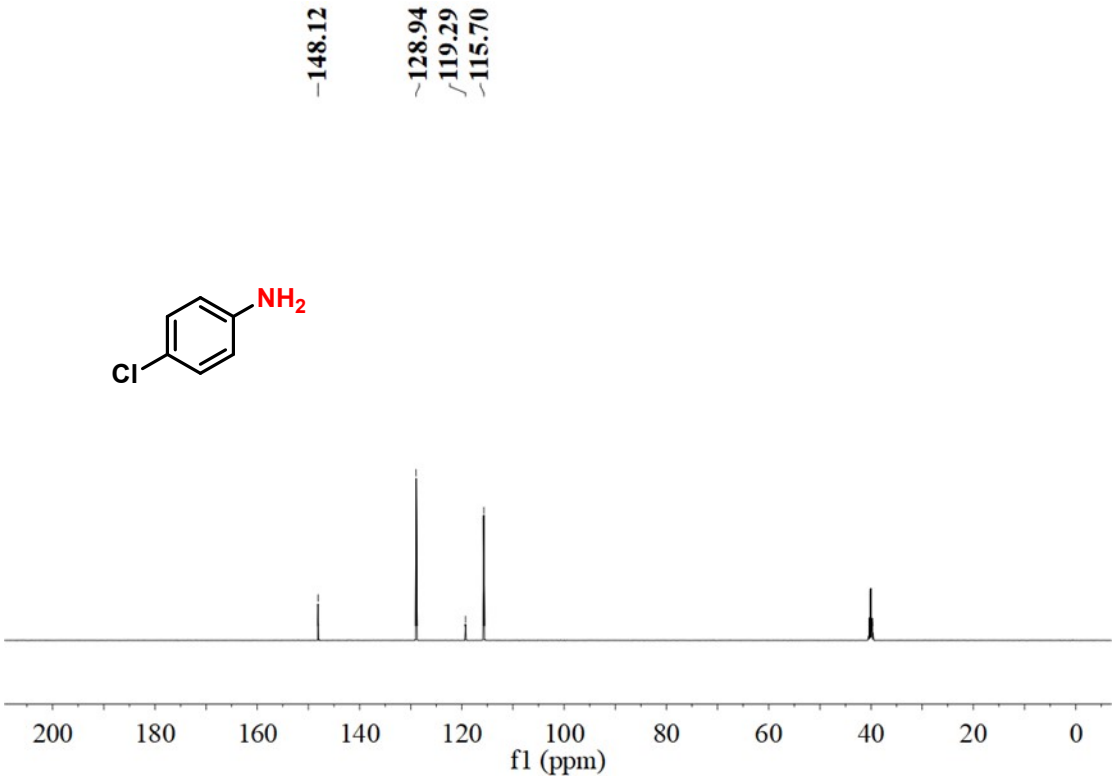


2f' ^{13}C NMR



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