Supporting Information

Visible-light-induced iron-catalyzed reduction of nitroarenes to anilines

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1. General information

All reactions were carried out under atmospheric pressure. Solvents were purified by standard techniques without special instructions. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance II-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C); $CDCl_3$, DMSO-d_6 and TMS were used as a solvent and an internal standard, respectively. The chemical shifts are reported in ppm downfield (δ) from TMS, the coupling constants J are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; brs, broad singlet. High resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometry. TLC was carried out on SiO_2 (silica gel 60 F_{254}, Merck), and the spots were located with UV light. Flash chromatography was carried out on SiO_2 (silica gel 60, 200-300 mesh). UV-vis spectra were obtained on a PerkinElmer Lambda 1500+ UV-vis spectrophotometer. Electron paramagnetic resonance (EPR) was carried out on Bruker A200-9.5/12. Transient absorption spectroscopy (TAS) measurements were performed on Edinburgh LP920 transient absorption spectrometer. equipped with a source pulsed laser beam generated from an Yb:KGW-based laser system. Cyclic voltammetry experiments were performed on a CH Instruments 600E potentiator using CHI600E software.

DMF is obtained by vacuum distillation from CaH_2 before use. Acetonitrile (CH_3CN) was purified by a Vigor solvent purification system. $FeCl_3$ were purchased from Macklin Biochemical. *N*-ethylmorpholine was purchased from Energy Chemistry. Other commercially available chemicals were purchased and used without additional purification unless noted otherwise. The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP-TEC-1020HSL) with 10W COB LED. The material of the irradiation is vessel quartz glass.

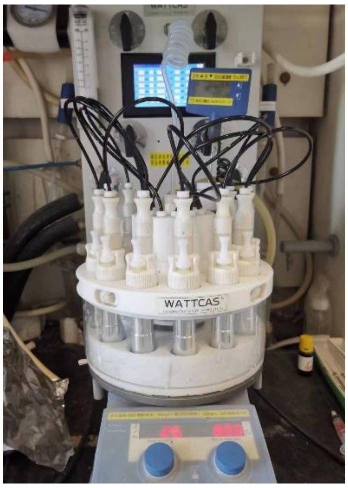
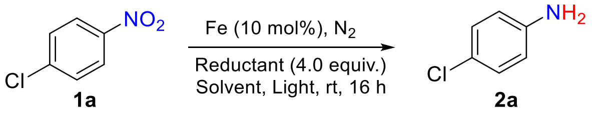


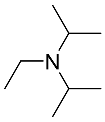
Figure S1. Parallel light reactor

2. Procedure for optimization studies

Table S1 Optimization of reaction conditions[a]



Entry	[Fe]	Reductants	Solvent	Light	Yield[%][b]
1	$FeCl_3$	DIPEA	DMF	400 nm	69
2	---	DIPEA	DMF	400 nm	ND
3	$FeCl_3$	---	DMF	400 nm	NR
4	$FeCl_3$	DIPEA	DMF	dark	NR
5	$FeCl_2$	DIPEA	DMF	400 nm	54
6	$FeBr_2$	DIPEA	DMF	400 nm	56
7	$FeCl_3·6H_2O$	DIPEA	DMF	400 nm	54
8	$Fe(acac)_3$	DIPEA	DMF	400 nm	36
9	$FeSO_4·7H_2O$	DIPEA	DMF	400 nm	33
10	$Fe(NO_3)_3·9H_2O$	DIPEA	DMF	400 nm	49
11	$FeCl_3$	DIPEA	DMF	400 nm	46
12[c]	$FeCl_3$	DIPEA	DMF	400 nm	65
13[d]	$FeCl_3$	TEA	DMF	400 nm	27
14	$FeCl_3$	DABCO	DMF	400 nm	Trace
15	$FeCl_3$	TMEDA	DMF	400 nm	46
16	$FeCl_3$	NMM	DMF	400 nm	75
17	$FeCl_3$	NEM	DMF	400 nm	90
18	$FeCl_3$	NMPPR	DMF	400 nm	80
19	$FeCl_3$	DIPA	DMF	400 nm	74
20	$FeCl_3$	$PhSiH_3$	DMF	400 nm	ND
21	$FeCl_3$	$B(OH)_3$	DMF	400 nm	ND
22	$FeCl_3$	$NH_3•BH_3$	DMF	400 nm	57
23	$FeCl_3$	iPrOH	DMF	400 nm	32
24[e]	$FeCl_3$	NEM	DMF	400 nm	83
25[f]	$FeCl_3$	NEM	DMF	400 nm	77
26	$FeCl_3$	NEM	DMSO	400 nm	50
27	$FeCl_3$	NEM	NMP	400 nm	60
28	$FeCl_3$	NEM	DCM	400 nm	70
29	$FeCl_3$	NEM	Toluene	400 nm	35
30	$FeCl_3$	NEM	1,4-dioxane	400 nm	49
31	$FeCl_3$	NEM	CH_3CN	400 nm	90
32[g]	$FeCl_3$	NEM	CH_3CN	400 nm	92
33[h]	$FeCl_3$	NEM	CH_3CN	400 nm	63
34[g]	$FeCl_3$	NEM	CH_3CN	380 nm	65
35[g]	$FeCl_3$	NEM	CH_3CN	400 nm	92
36[g]	$FeCl_3$	NEM	CH_3CN	425 nm	39
37[g]	$FeCl_3$	NEM	CH_3CN	450 nm	Trace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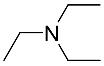
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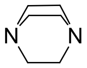
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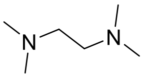
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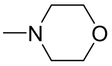
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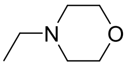
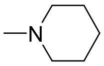

NEM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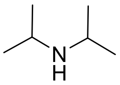
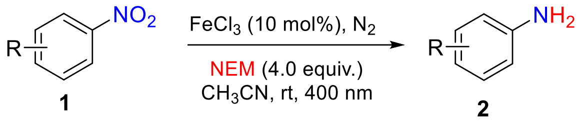

DIPA

[a]Conditions:**1a** (0.3 mmol), Iron catalysts (10 mol%), Reductants (4.0 equiv.), Solvent (2.0 mL), at rt under LEDs irradiation for 16 h. [b]Yields determined by ^{1}H NMR using CH_2Br_2 as internal standard. [c]$FeCl_3$ (5 mol%). [d]$FeCl_3$ (20 mol%). [e]3.0 equiv. of NEM. [f]5.0 equiv. of NEM. [g]CH_3CN 1.0 mL. [h] CH_3CN 4.0 mL.

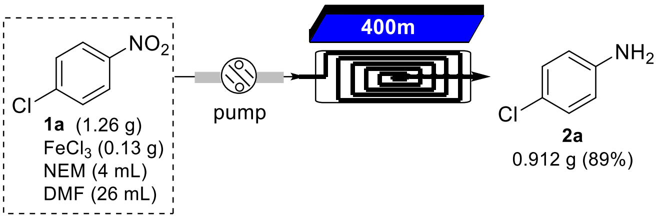
3. Experimental procedures

3.1 The reduction of nitroarenes (general procedures)



To an oven-dried 20 mL quartz tube equipped with a magnetic stir bar was added nitroarenes **1** (if solid, 0.30 mmol, 1.0 equiv.), $FeCl_3$ (4.8 mg, 0.03 mmol, 10 mol%). The tube was capped. After being evacuated and backfilled with nitrogen three times, NEM (152 μL, 1.2 mmol, 4.0 equiv.) and CH_3CN (1.0 mL) were added via gastight syringe under a nitrogen atmosphere. The mixture was stirred at room temperature under irradiation with 10 W 400-405 nm LEDs for 16 h. After completion of reaction, the mixture was diluted with ethyl acetate, and filtered through a short silica gel flash column (ethyl acetate), concentrated under reduced pressure. The residue was analyzed by ^{1}H NMR using Br_2CH_2 as internal standard. Isolated yield was obtained by silica gel flash column chromatography from the residue to give desired products.

3.2 The reduction of 4-chloronitrobenzene (flow reactor)



To a 100 mL three-neck flask were added **1a** (1.26 g, 8.0 mmol, 1.0 equiv.), $FeCl_3$ (0.13g, 0.8 mmol, 10 mol%). The flask was placed in the sealing casing and replaced five times with nitrogen gas by the Schlenk technique. Next, NEM (4.0 mL, 32 mmol, 4.0 equiv.) and DMF (26 mL) were added followed by via syringe under a nitrogen atmosphere. The mixture was stirred for 45 min residence time, and placed into reactor cells (6 m length, 1.0 mm internal diameter PFA tube). The flow rate of the mixture in the reactor cells was 0.1 mL/min under irradiation with 200 W 400 nm LEDs at room temperature. The mixture was quenched with water and extracted with ethyl acetate (3×50 mL), concentrated under reduced pressure. The crude product was purified by silica gel chromatography (petroleum ether: ethyl acetate = 5:1) to afford the desired product **2a** (0.912 g, 89%).

4. Mechanistic studies

4.1 UV-vis absorption spectroscopic measurements

UV-Visible analysis was performed on an Lambda 1050+ spectrophotometer. Experiments were recorded using a cuvette equipped with septa-lined screw cap. CH_3CN was chosen as the solvent.

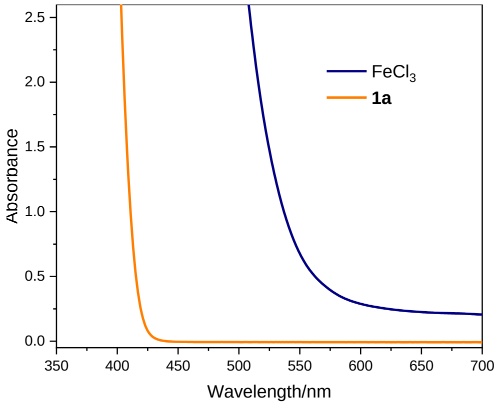


Figure S2. UV-Visible absorption spectra of $FeCl_3$ and **1a** in CH_3CN (under reaction concentration)

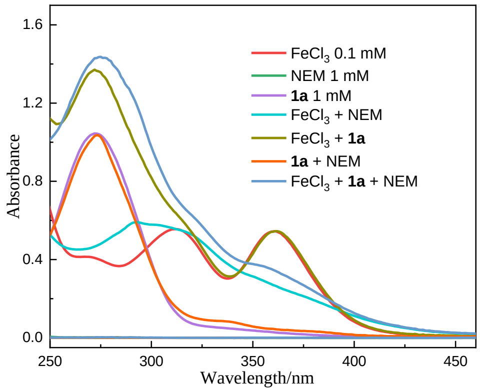


Figure S3. UV−vis spectroscopic absorption experiments on various combinations of $FeCl_3$ (0.1 mM), NEM (1.0 mM) and **1a** (1.0 mM) in CH_3CN.

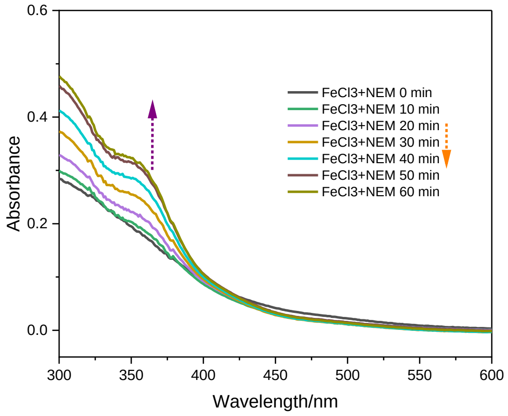


Figure S4. UV-vis absorption spectra of $FeCl_3$ (0.1 mM) and NEM (1.0 mM) in CH_3CN under irradiation for different time

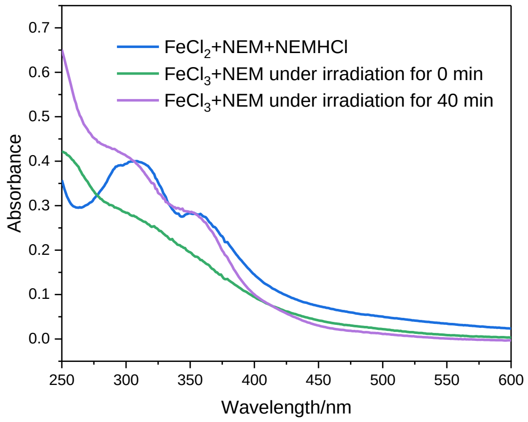


Figure S5. UV-vis absorption spectra of $FeCl_2$ (0.1 mM)+NEM (0.5 mM)+NEM·HCl (0.5 mM) and $FeCl_3$ (0.1 mM)+NEM (1.0 mM) under irradiation with 400−405 nm LEDs in CH_3CN

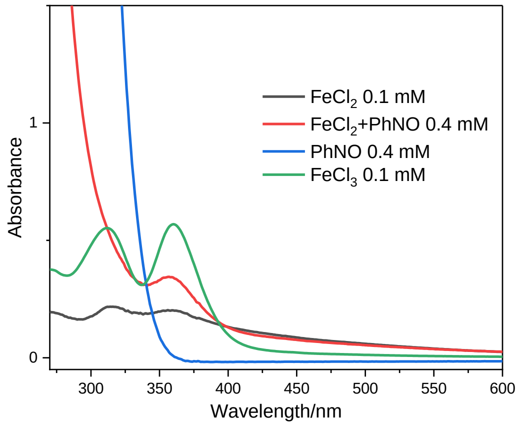


Figure S6. UV-Visible absorption spectra of $FeCl_2$ (0.1 mM), $FeCl_2$ (0.1 mM) + PhNO (0.4 mM), PhNO (0.4 M) and $FeCl_3$ (0.1 mM) in CH_3CN

4.2 Fluorescence emission spectroscopy

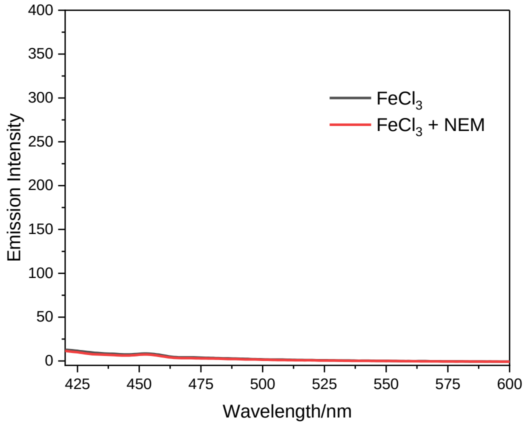


Figure S7. Fluorescence emission spectra of $FeCl_3$ (0.1 mM) and $FeCl_3$ (0.1 mM) + NEM (0.1 mM)

4.3 EPR measurements

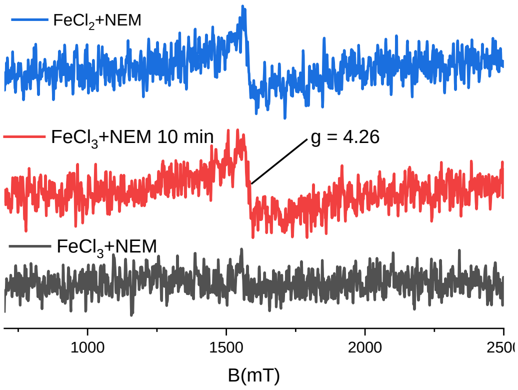


Figure S8. EPR spectra of $FeCl_3$+NEM (black line), $FeCl_3$+NEM after irradiation for 10 min (red line) and $FeCl_2$+NEM (blue line) pressed in CH_3CN collected at 300K with a frequency of 9.415 GHz.

4.4 Cyclic voltammetry experiments

Cyclic voltammetry experiments were performed on a CH Instruments 600E potentiostat using CHI600E software. Experiments were run at a scan rate of 0.1 V/s in a 25 mL three-neck round-bottom flask equipped with the appropriate electrodes. A glassy carbon working electrode, a platinum mesh counter electrode, and a saturated calomel electrode (SCE) reference electrode were employed for each measurement. The measurements were carried out as follows: a 0.1 (M) solution of tetabutylammonium hexafluorophosphate in acetonitrile was added to the measuring cell and the solution was degassed by nitrogen purge for 5 min.

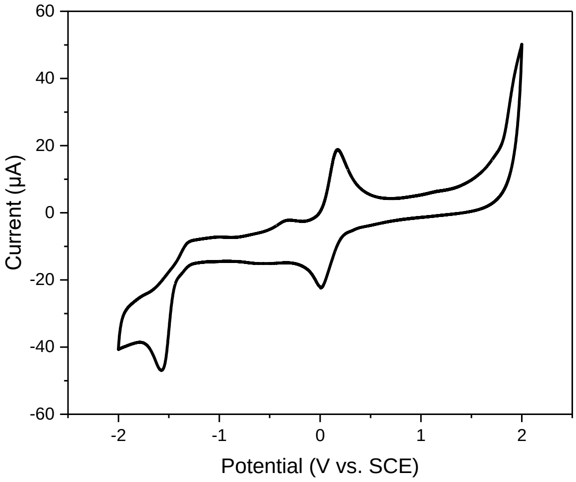


Figure S9. Cyclic voltammogram of $FeCl_3$ (1.0 mM) in CH_3CN with NBu_4PF_6 electrolyte.

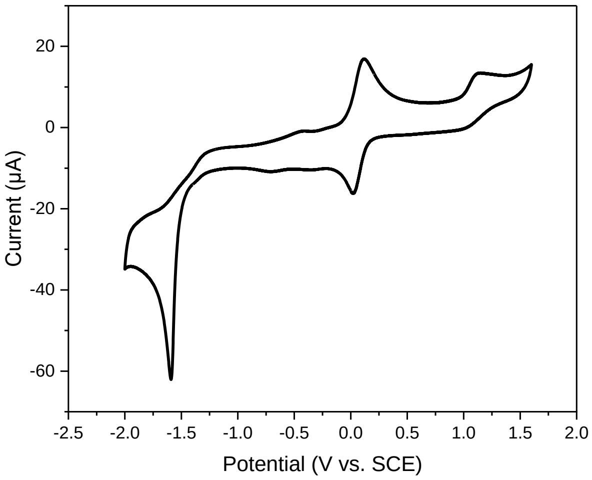


Figure S10. Cyclic voltammogram of $FeCl_3$ (1.0 mM) + NEM (1.0 M) in CH_3CN with NBu_4PF_6 electrolyte

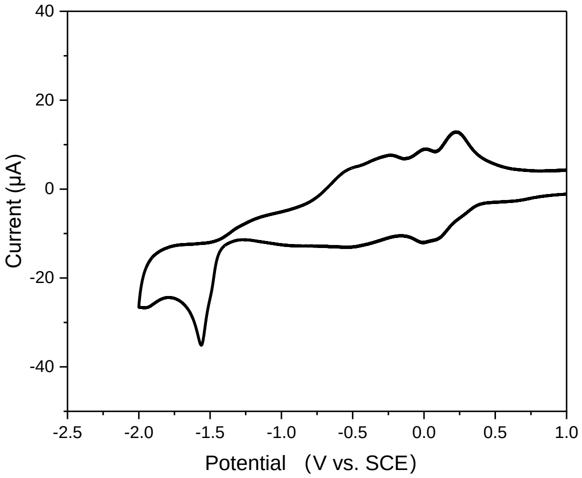


Figure S11. Cyclic voltammogram of $FeCl_2$ (1.0 mM) in CH_3CN with NBu_4PF_6 electrolyte.

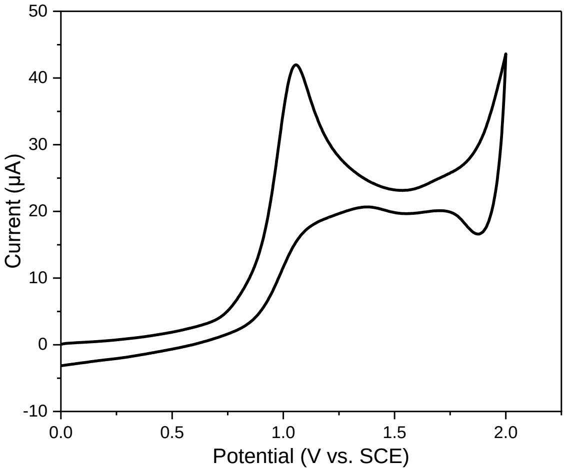


Figure S12. Cyclic voltammogram of NEM (1.0 mM) in CH_3CN with NBu_4PF_6 electrolyte

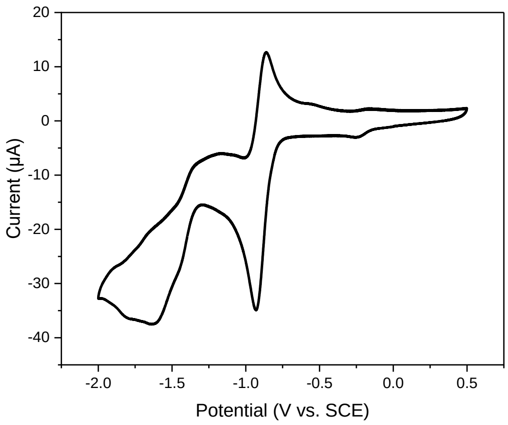


Figure S13. Cyclic voltammogram of Nitrosobenzene (1.0 mM) in CH_3CN with NBu_4PF_6 electrolyte

4.5 Transient absorption spectroscopy

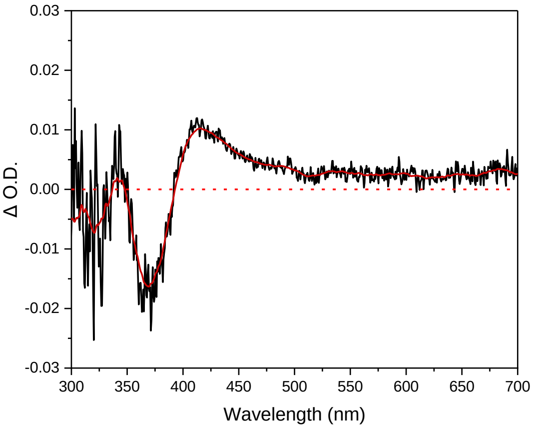


Figure S14. Transient absorption spectrum recorded after a laser pulse of 355 nm of $FeCl_3$ (0.3 mM) + NEM (0.6 mM) in CH_3CN

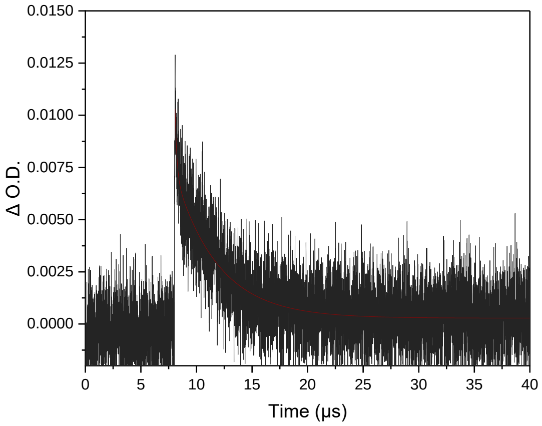


Figure S15. Decay traces of transient spectra arising from $FeCl_3$ (0.3 mM) + NEM (0.6 mM), recorded at λ_{abs} = 415 nm in CH_3CN

4.6 Probing mechanistic investigation

To an oven-dried 20 mL quartz tube equipped with a magnetic stir bar was added 4-chloronitrobenzene **1a** (0.30 mmol, 1.0 equiv.), $FeCl_3$ (4.8 mg, 0.03 mmol, 10 mol%), TEMPO (70.3 mg, 0.45 mmol, 1.5equiv.). The tube was capped. After being evacuated and backfilled with nitrogen three times, NEM (152 µL, 1.2 mmol, 4.0 equiv.) and CH_3CN (2.0 mL) were added via gastight syringe under a nitrogen atmosphere. The mixture was stirred at room temperature under irradiation with 10 W 400-405 nm LEDs for 16 h. After completion of reaction, add ethyl acetate 10 mL, and a portion of the mixture was subjected to high resolution mass spectrometer (HRMS). The yield of product was determined by gas chromatography (GC) analysis of the crude reaction mixture.

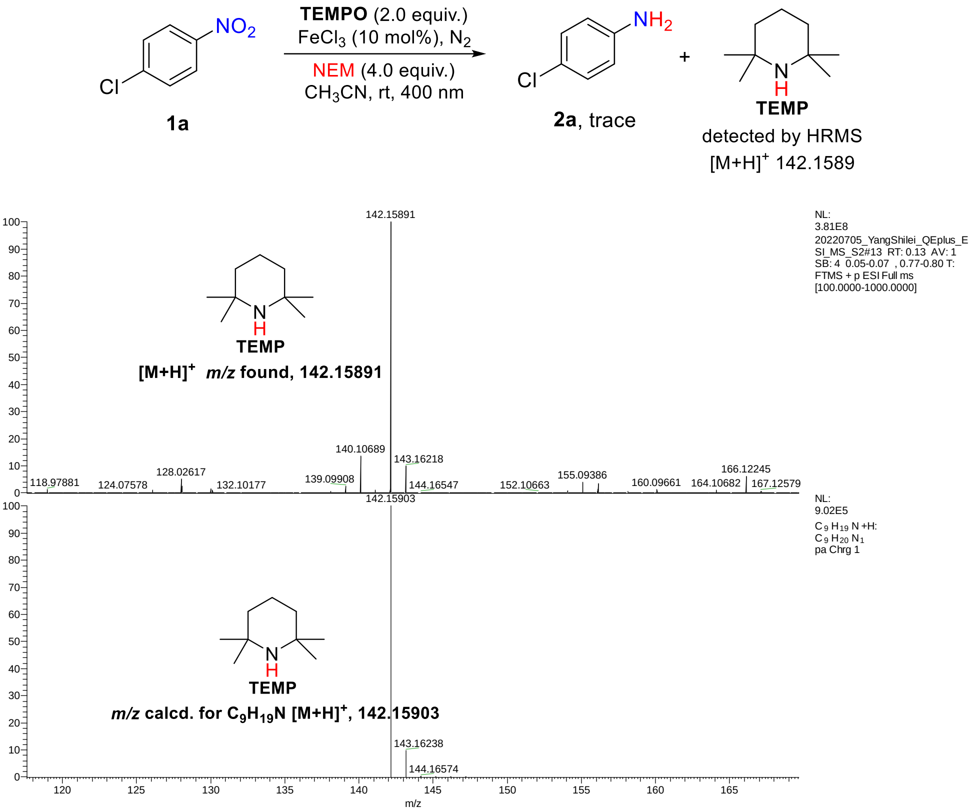


Figure S16. Probing experiments

4.7 Control experiments of reduction of nitroarenes

4-Chloroaniline (**2a**) was found to be the only reduction product while potential intermediate products such as nitrosobenzene (**3**), azoxybenzene (**4**) and azobenzene (**5**) were not observed were not observed. And morpholine was detected by HRMS (Figure S17).

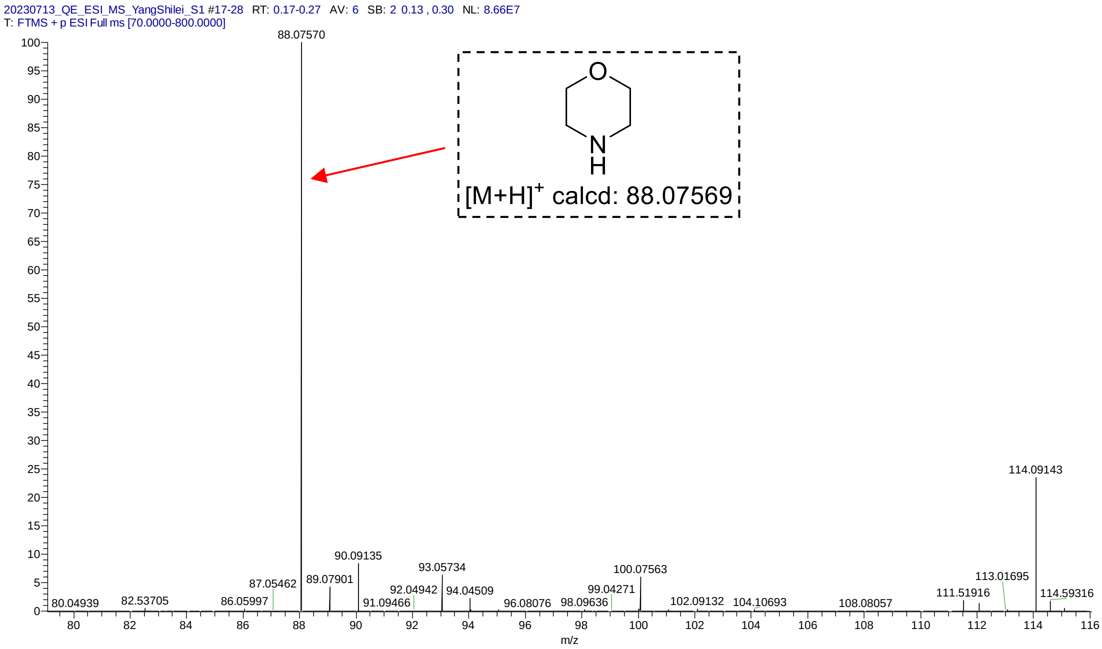


Figure S17. HRMS record from reaction mixture after light irradiation

To an oven-dried 20 mL quartz tube equipped with a magnetic stir bar was added the intermediate 4-chloronitrosobenzene (**3)** (0.30 mmol, 1.0 equiv.), $FeCl_3$ (4.8 mg, 0.03 mmol, 10 mol%). The tube was capped. After being evacuated and backfilled with nitrogen three times, NEM (152 μL, 1.2 mmol, 4.0 equiv.) and CH_3CN (1.0 mL) were added via gastight syringe under a nitrogen atmosphere. The mixture was stirred at room temperature under irradiation with 10 W 400-405 nm LEDs for 16 h. After completion of reaction, the mixture was stirred after adding ethyl acetate 10 mL for 5 min. The yield of products was determined by gas chromatography (GC) analysis of the crude reaction mixture using trimethylbenzene as internal standard. The relevant results are shown in Figure S18.

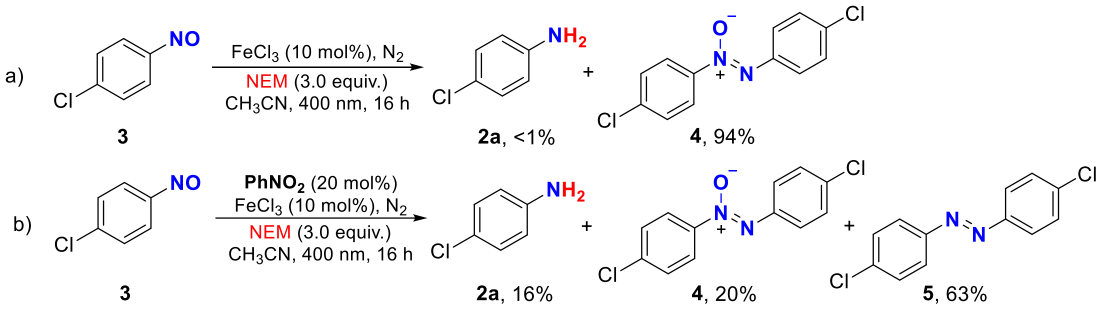


Figure S18. Control experiments

4.8 Light-dark reduction of nitroarenes and intermediates in two steps

To an oven-dried 20 mL quartz tube equipped with a magnetic stir bar was added $FeCl_3$. The tube was capped. After being evacuated and backfilled with nitrogen three times, NEM and CH_3CN (2.0 mL) were added via gastight syringe under a nitrogen atmosphere. The mixture was stirred at room temperature under irradiation with 10 W 400-405 nm LEDs for 10 h. Then, **1a** and **3** was added, respectively, and the resulting mixture was stirred under dark for 6 h. After completion of reaction, the mixture was stirred after adding ethyl acetate 10 mL for 5 min. The yield of product was determined by gas chromatography (GC) analysis of the crude reaction mixture using trimethylbenzene as internal standard.

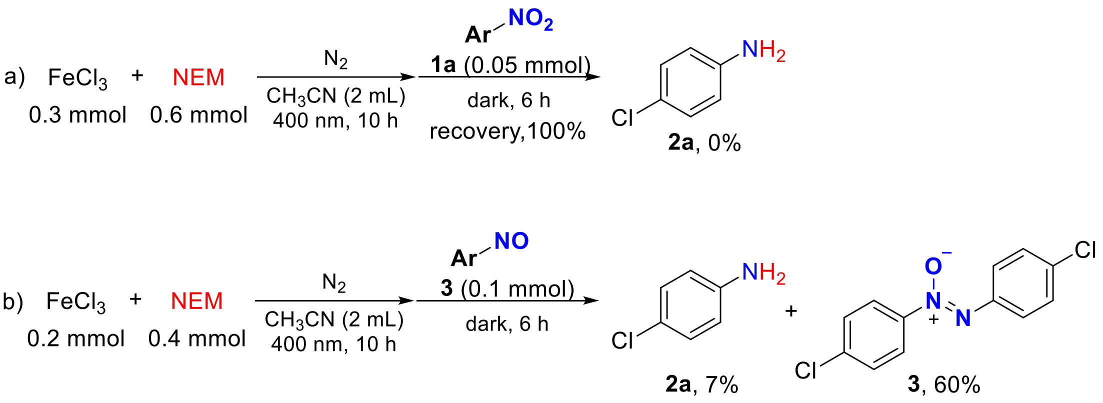


Figure S19. Light-dark reduction of nitroarenes and intermediates in two steps

4.9 Reduction of nitrobenzene and intermediates by ferrous chloride

To an oven-dried 20 mL quartz tube equipped with a magnetic stir bar was added **1a** (0.1 mmol, 15.7 mg, 1.0 equiv.) or **3** (0.1 mmol, 14.2 mg, 1.0 equiv.), $FeCl_3$ (64.8 mg, 4.0 equiv.) and NEM·HCl (60.4 mg, 4.0 equiv.). The tube was capped. After being evacuated and backfilled with nitrogen three times, CH_3CN (2.0 mL) was added via gastight syringe under a nitrogen atmosphere. The mixture was stirred at room temperature under dark for 6 h. After completion of reaction, the mixture was stirred after adding ethyl acetate 10 mL for 5 min. The yield of product was determined by gas chromatography (GC) analysis of the crude reaction mixture using trimethylbenzene as internal standard.

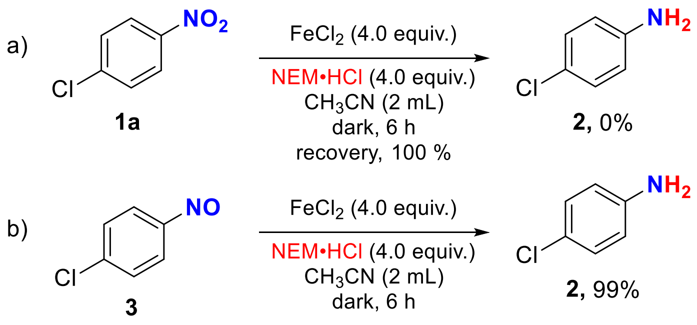
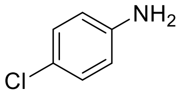


Figure S20. Reduction of **1a** and **3** by ferrous chloride

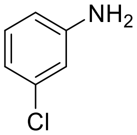
5. Characterization data for all products

Following anilines (obtained by reduction of nitroarenes follow by column chromatography) are known compounds and they are characterized by ^{1}H and ^{13}C NMR spectroscopies.



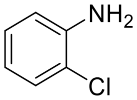
4-Chloroaniline (2a)[1]

Product **2a** was determined in 92% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 5:1) afforded **2a** as a pale yellow solid (34.4 mg, 90%), mp 68-70 °C, (lit.[1] mp 69-70 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.10 (d, J = 8.7 Hz, 2H), 6.60 (d, J = 8.7 Hz, 1H), 3.68 (brs, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 145.0, 129.1, 123.2, 116.2.



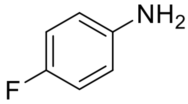
3-Chloroaniline (2b)[2]

Product **2b** was determined in 81% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 5:1) afforded **2b** as a pale yellow liquid (29.8 mg, 78%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.08-7.04 (m, 1H), 6.74-6.71 (m, 1H), 6.68-6.66 (m, 1H), 6.56-6.53 (m, 1H), 3.72 (brs, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 147.6, 134.8, 130.3, 118.5, 115.0, 113.2.



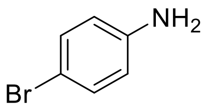
2-Chloroaniline (2c)[2]

Product **2c** was determined in 25% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: dichloromethane = 2:1) afforded **2c** as a brown liquid (9.2 mg, 24%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.18-7.16 (m, 1H), 7.01-6.96 (m, 1H), 6.68-6.59 (m, 2H), 3.89 (brs, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 143.0, 129.5, 127.7, 119.3, 119.1, 116.0.



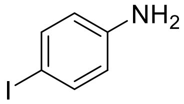
4-Fluoroaniline (2d)[3]

Product **2d** was determined in 58% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum: ethyl acetate = 5:1) afforded **2d** as a pale yellow liquid (18.7 mg, 56%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.89-6.84 (m, 2H), 6.63-6.59 (m, 2H), 3.55 (brs, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.4 (d, J = 235.3 Hz), 142.5 (d, J = 2.2 Hz), 116.1 (d, J = 7.6 Hz), 115.7 (d, J = 22.4 Hz); ^{19}F NMR (376 MHz, CDCl$_3$): δ -126.86.



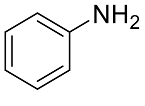
4-Bromoaniline (**2e**)[3]

Product **2e** was determined in 89% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 5:1) afforded **2e** as a light yellow solid (45.4 mg, 89%), mp 59-61 °C, (lit.[3] mp 60-61 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.23 (d, J = 8.7 Hz, 2H), 6.56 (d, J = 8.7 Hz, 2H), 3.66 (brs, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 145.5, 132.0, 116.7, 110.2.



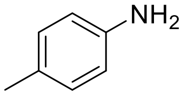
4-Iodoaniline (**2f**)[1]

Product **2f** was determined in 82% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 5:1) afforded **2f** as a white solid (53.9 mg, 82%), mp 61-64 °C, (lit.[1] mp 62-64 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.41 (d, J = 8.7 Hz, 2H), 6.47 (d, J = 8.7 Hz, 2H), 3.67 (brs, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 146.1, 137.9, 117.3, 79.4.



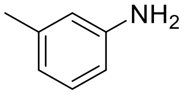
Aniline (**2g**)[4]

Product **2g** was determined in 96% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 5:1) afforded **2g** as a colorless liquid (26.5 mg, 95%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.15-7.11 (m, 2H), 6.75-6.72 (m, 1H), 6.64-6.62 (m, 2H), 3.55 (brs, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 146.6, 129.4, 118.6, 115.2.



4-Methylaniline (**2h**)[5]

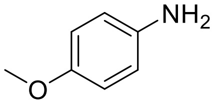
Product **2h** was determined in 86% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) afforded **2h** as a colorless solid (27.6 mg, 86%), mp 42-43 °C, (lit.[5] mp 42-43 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.97 (d, J = 8.4 Hz, 2H), 6.61 (d, J = 8.4 Hz, 2H), 3.80 (brs, 2H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 143.8, 129.8, 127.8, 115.3, 20.5.



3-Methylaniline (**2i**)[5]

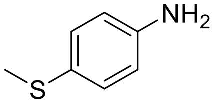
Product **2i** was determined in 80% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) afforded **2i** as a colorless liquid (25.1 mg, 78%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.12-7.08 (m, 1H), 6.65-6.63 (m, 1H), 6.56-6.53(m, 2H), 3.57 (brs, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ

146.5, 139.2, 129.2, 119.5, 116.0, 112.3.



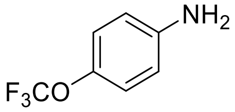
4-Methoxyaniline (2j)[1]

Product **2j** was determined in 83% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 5:1) afforded **2j** as a colorless solid (30.3 mg, 82%), mp 55-57 °C, (lit.[1] mp 56-57 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.75 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 8.8 Hz, 2H), 3.75 (s, 3H), 3.39 (brs, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.8, 139.9, 116.4, 114.8, 55.8.



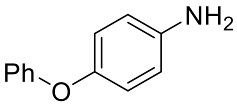
4-Methylthioaniline (2k)[4]

Product **2k** was determined in 81% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 5:1) afforded **2k** as a colorless liquid (33.8 mg, 81%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.18 (d, J = 8.5 Hz, 2H), 6.63 (d, J = 8.5 Hz, 2H), 3.66 (brs, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 145.1, 131.1, 125.8, 115.8, 18.8.



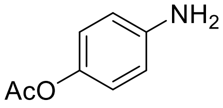
4-Trifluoromethoxyaniline (2l)[4]

Product **2l** was determined in 83% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 5:1) afforded **2l** as a yellow liquid (42.4 mg, 80%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.01 (d, J = 8.4 Hz, 2H), 6.64 (d, J = 8.8 Hz, 2H), 3.69 (brs, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 145.2, 141.3, 122.4, 120.6 (d, J = 255.8 Hz), 115.5; ^{19}F NMR (376 MHz, CDCl$_3$) δ -58.48.



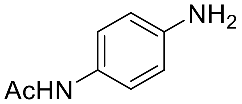
4-Phnoxyaniline (2m)[6]

Product **2m** was determined in 96% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 5:1) afforded **2m** as a white solid (52.8 mg, 95%), mp 82-84 °C, (lit.[6] mp 83-84 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.31-7.27 (m, 2H), 7.05-7.01 (m, 1H), 6.95 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.2 Hz, 2H), 6.68 (d, J = 8.1 Hz, 2H) 3.59 (brs, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 158.9, 148.6, 142.8, 129.6, 122.1, 121.2, 117.2, 116.3.



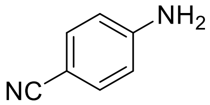
4-Acetoxyaniline (2n)[7]

Product **2n** was determined in 88% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) afforded **2n** as a yellow solid (39.9 mg, 88%), mp 71-73 °C, (lit.[7] mp 73 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.86 (d, J = 8.7 Hz, 2H), 6.66 (d, J = 8.7 Hz, 2H), 3.69 (brs, 2H), 2.26 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz,) δ 170.2, 144.2, 142.9, 122.2, 115.7, 21.1.



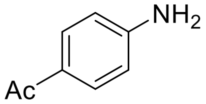
4-(Acetylamide)aniline (2o)[5]

Product **2o** was determined in 96% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (dichloromethane: methanol = 20:1) afforded **2o** as a pale brown solid (41.5 mg, 92%), mp 163-166 °C, (lit.[5] mp 165-167 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.47 (s, 1H), 7.19 (d, J = 8.7 Hz, 2H), 6.49 (d, J = 8.7 Hz, 2H), 4.83 (s, 2H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.7, 145.0, 129.1, 121.3, 114.3, 24.1.



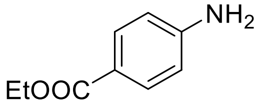
4-Cyanoaniline (2p)[1]

Product **2p** was determined in 94% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 5:1) afforded **2p** as a white solid (31.2 mg, 88%), mp 85-87 °C, (lit.[1] mp 86-87 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.39 (d, J = 8.6 Hz, 2H), 6.64 (d, J = 8.7 Hz, 2H), 4.20 (brs, 2H); ^{13}C NMR (100 MHz, CDCl$_3$); δ 150.5, 133.8, 120.2, 114.5, 100.0.



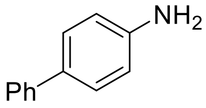
4-Aminoacetophnoe (2q)[3]

Product **2q** was determined in 92% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 5:1) afforded **2q** as a pale yellow powder (36.5 mg, 90%), mp 103-107 °C, (lit.[3] 103-107 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.79 (d, J = 8.7 Hz, 2H), 6.63 (d, J = 8.7 Hz, 2H), 4.21 (brs, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.6, 151.3, 130.8, 127.7, 113.7, 26.1.



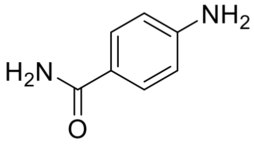
Ethyl 4-aminobenzoate (2r)[1]

Product **2r** was determined in 82% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 5:1) afforded **2r** as a white powder (39.6 mg, 80%), mp 86-89 °C, (lit.[1] mp 88-89 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.85 (d, J = 8.7 Hz, 3H), 6.63 (d, J = 8.7 Hz, 2H), 4.31 (q, J = 7.1 Hz, 2H), 4.09 (brs, 2H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.8, 150.9, 131.6, 120.0, 113.8, 60.3, 14.4.



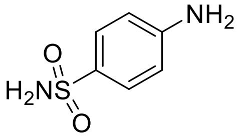
4-phenylaniline (2s)[5]

Product **2s** was determined in 95% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) afforded **2s** as a white solid (48.2 mg, 95%), mp 53-56 °C, (lit.[5] mp 54-55 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58-7.51 (m, 2H), 7.47-7.34 (m, 4H), 7.31-7.25 (m, 1H), 6.81-6.73 (m, 2H), 3.73 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 141.2, 131.6, 128.7, 128.0, 126.4, 126.3, 115.4.



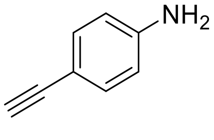
4-Aminobenzamide (2t)[1]

Product **2t** was determined in 96% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 2:1) afforded **2t** as a beige solid (37.6 mg, 92%), mp 174-176 °C, (lit.[1] mp 175-176 °C). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.58 (d, J = 8.5 Hz, 2H), 7.50 (s, 1H), 6.84 (s, 1H), 6.53 (d, J = 8.5 Hz, 2H), 5.61 (s, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz,) δ 168.7, 152.1, 129.6, 121.3, 113.0.



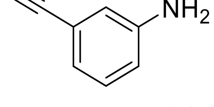
Sulfanilamide (2u)[8]

Product **2u** was determined in 92% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (dichloromethane: methanol = 20:1) afforded **2u** as a yellow solid (44.4 mg, 86%), mp 161-163 °C, (lit.[8] mp 161-162 °C). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.58 (d, J = 8.8 Hz, 2H), 6.68 (d, J = 8.8 Hz, 2H), 4.84 (brs, 4H); ^{13}C NMR (DMSO-d_6, 100 MHz,) δ 152.2, 129.9, 127.6, 113.1.



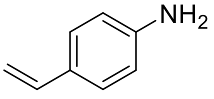
4-Ethynylaniline (2v)[9]

Product **2v** was determined in 99% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) afforded **2v** as a brown solid (34.4 mg, 98%), mp 84-88 °C, (lit.[9] mp 81-85 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29 (d, J = 8.6 Hz, 2H), 6.59 (d, J = 8.6 Hz, 2H), 3.81 (brs, 2H), 2.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 133.5, 114.6, 111.4, 84.4, 74.9.



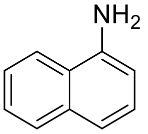
3-Ethynylaniline (2w)[10]

Product **2w** was determined in 70% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) afforded **2w** as a brown solid (24.6 mg, 70%), mp 65-88 °C, (lit.[10] mp 86-87 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.12-7.08 (m, 1H), 6.91-6.89 (m, 1H), 6.81-6.80 (m, 1H), 6.68-6.65 (m, 1H), 3.68 (brs, 2H), 3.02 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 129.3, 122.8, 122.5, 118.3, 115.8, 83.9, 76.5.



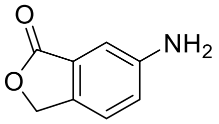
4-Vinylaniline (2x)[4]

Product **2x** was determined in 88% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) afforded **2x** as a colorless liquid (31.5 mg, 88%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24 (d, J = 8.4 Hz, 2H), 6.65-6.59 (m, 3H), 5.55 (dd, J = 17.6 Hz, 1.0 Hz, 1H), 5.05 (dd, J = 11.0 Hz, 1.0 Hz, 1H), 3.70 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 136.6, 128.4, 127.4, 115.0, 110.0.



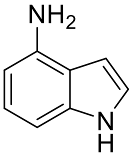
1-naphthylamine (2y)[5]

Product **2y** was determined in 91% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 5:1) afforded **2y** as a white solid (36.9 mg, 80%), mp 46-48 °C, (lit.[5] mp 47-48 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84-7.81 (m, 2H), 7.49-7.45 (m, 2H), 7.35-7.28 (m, 2H), 6.81-6.79 (m, 1H), 4.15 (brs, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz,) δ 142.1, 134.4, 128.6, 126.4, 125.9, 124.9, 123.7, 120.8, 119.0, 109.7.



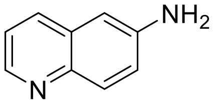
6-Nitrophthalide (2z)[11]

Product **2z** was determined in 89% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) afforded **2z** as a white solid (39.8 mg, 89%), mp 178-180 °C, (lit.[12] mp 178-180 °C). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.27 (d, J = 8.2 Hz, 1H), 6.98-6.95 (m, 1 H), 6.90 (d, = 2.1 Hz, 1H), 5.53 (brs, 2H), 5.20 (s, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz,) δ 174.2, 152.6, 137.2, 128.7, 125.9, 123.9, 110.1, 72.5.



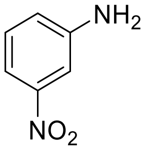
4-Aminoindole (2α)[5]

Product **2α** was determined in 83% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 5:1) afforded **2α** as a purple solid (30.9 mg, 78%), mp 105-107 °C, (lit.[5] mp 106-107 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.11 (brs, 1H), 7.12-7.10 (m, 1H), 7.05-7.01 (m, 2H), 6.87 (d, J = 8.1 Hz, 1H), 6.48-6.47 (m, 1H), 6.42 (d, J = 7.4 Hz, 1H), 3.93 (brs, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz,) δ 139.4, 136.9, 123.2, 122.4, 117.4, 104.2, 102.2, 98.9.



6-Aminoquinoline (2β)[13]

Product **2β** was determined in 86% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 5:1) afforded **2β** as a pale yellow solid (35.5 mg, 82%), mp 112-114 °C, (lit.[13] mp 113-116 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.64-8.63 (m, 1H), 7.91-7.86 (m, 2H), 7.26-7.23 (m, 1H), 7.15-7.12 (m, 1H), 6.87 (d, J = 2.6 Hz, 1H), 3.92 (brs, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz,) δ 146.8, 144.7,143.4, 133.8, 130.5, 129.8, 121.6, 121.4, 107.4.



3-Nitroaniline (2γ)[2]

Product **2γ** was determined in 67% yield by ^{1}H NMR; Purification by column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) afforded **2γ** as a yellow solid (26.9 mg, 65%), mp 110-113 °C, (lit.[2] mp 11-113 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58-7.55 (m, 1H), 7.49-7.47 (m, 1H), 7.29-7.25 (m, 1H), 6.96-6.93 (m, 1H), 4.02 (brs, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz,) δ 149.3, 147.5, 129.9, 120.7, 113.1, 109.0.

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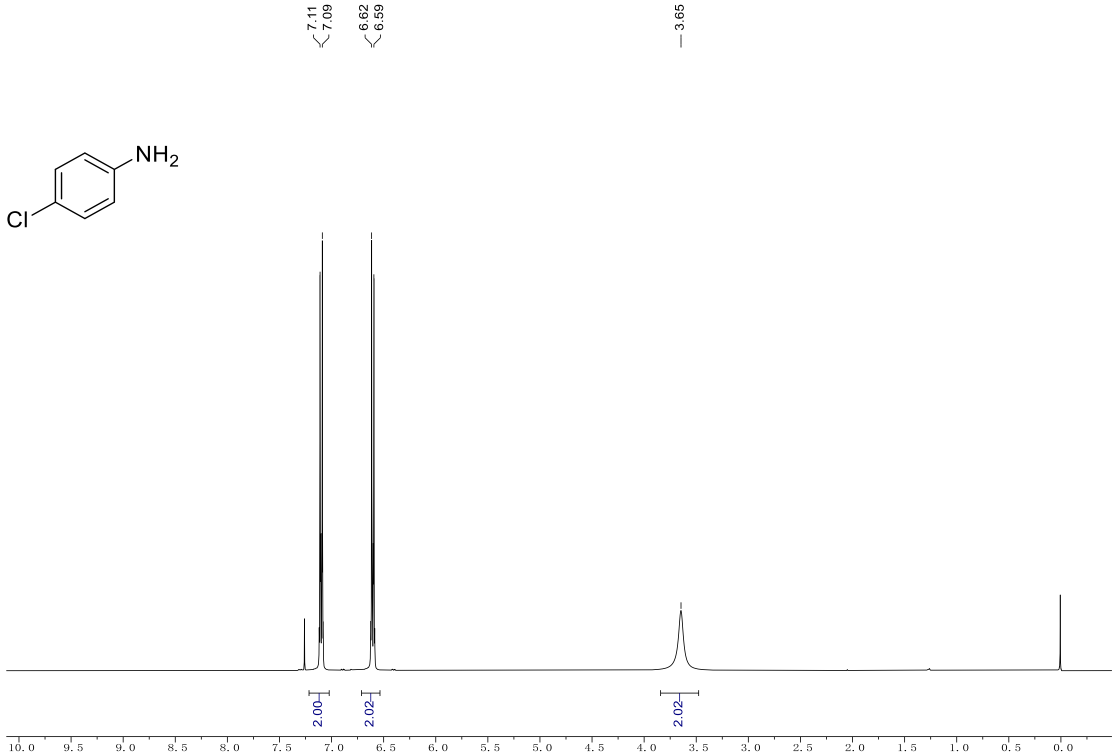
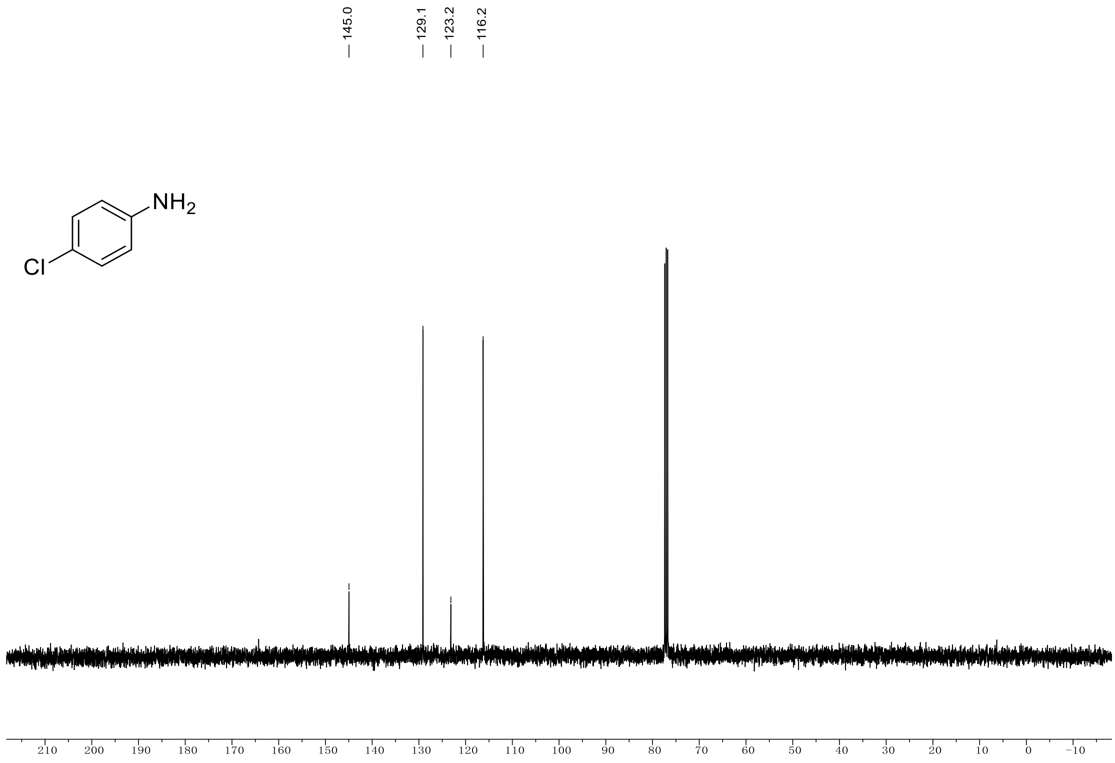
7. Copies of ^{1}H and ^{13}C NMR spectra of products

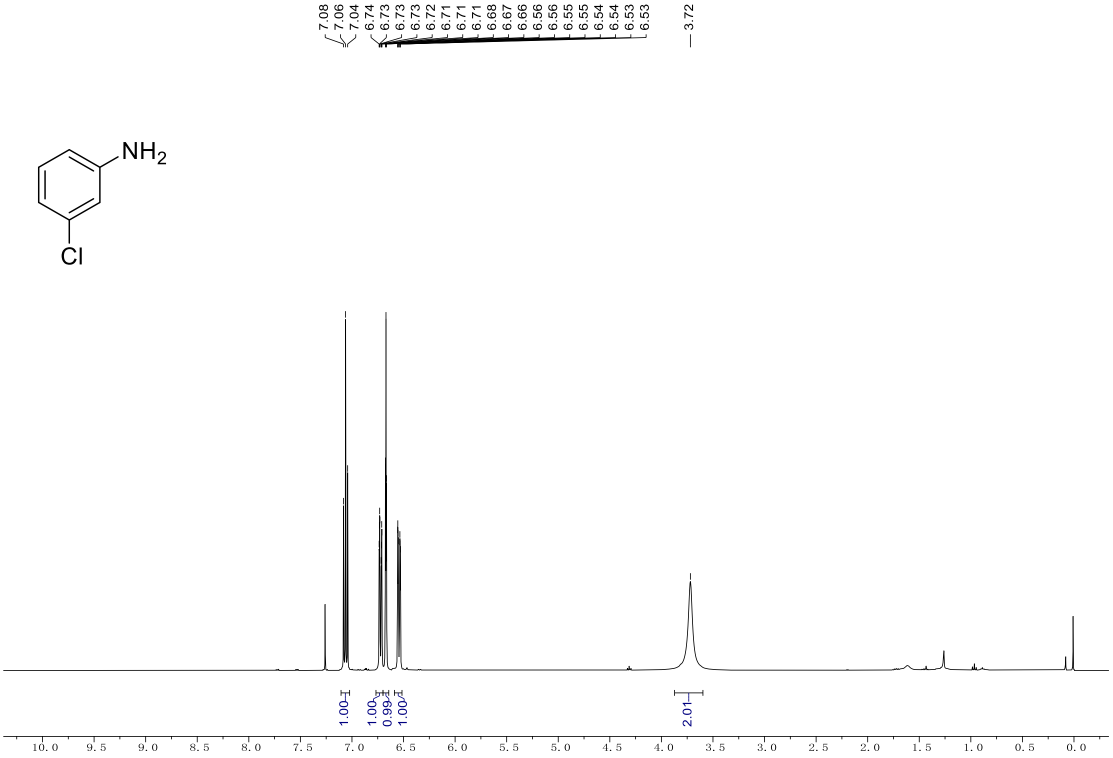
^{1}H NMR of **2a** ($CDCl_3$, 400 MHz)



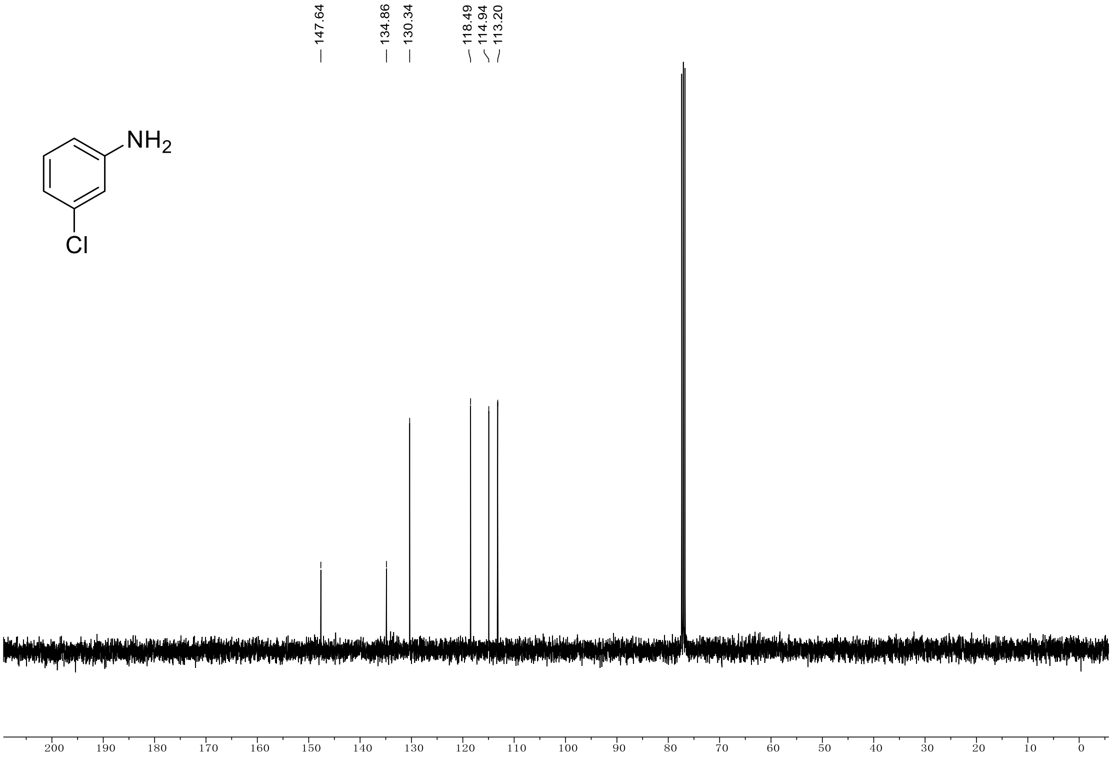
^{13}C NMR of **2a** ($CDCl_3$, 100 MHz)



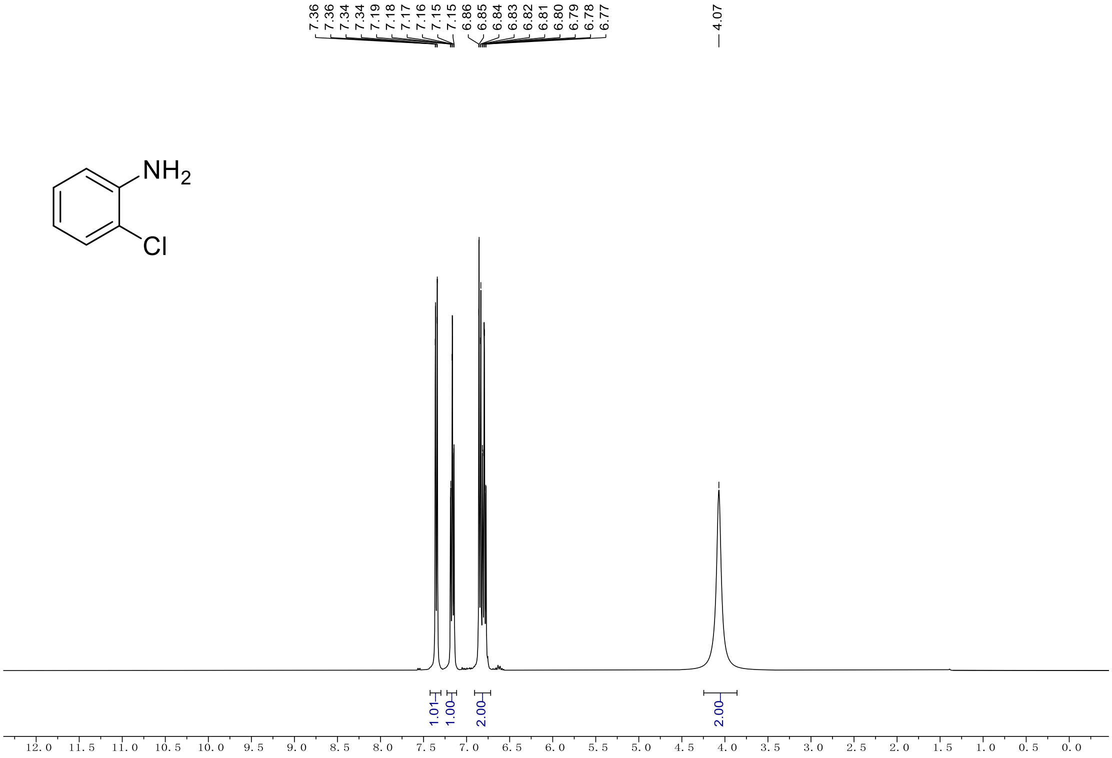
^{1}H NMR of **2b** ($CDCl_3$, 400 MHz)



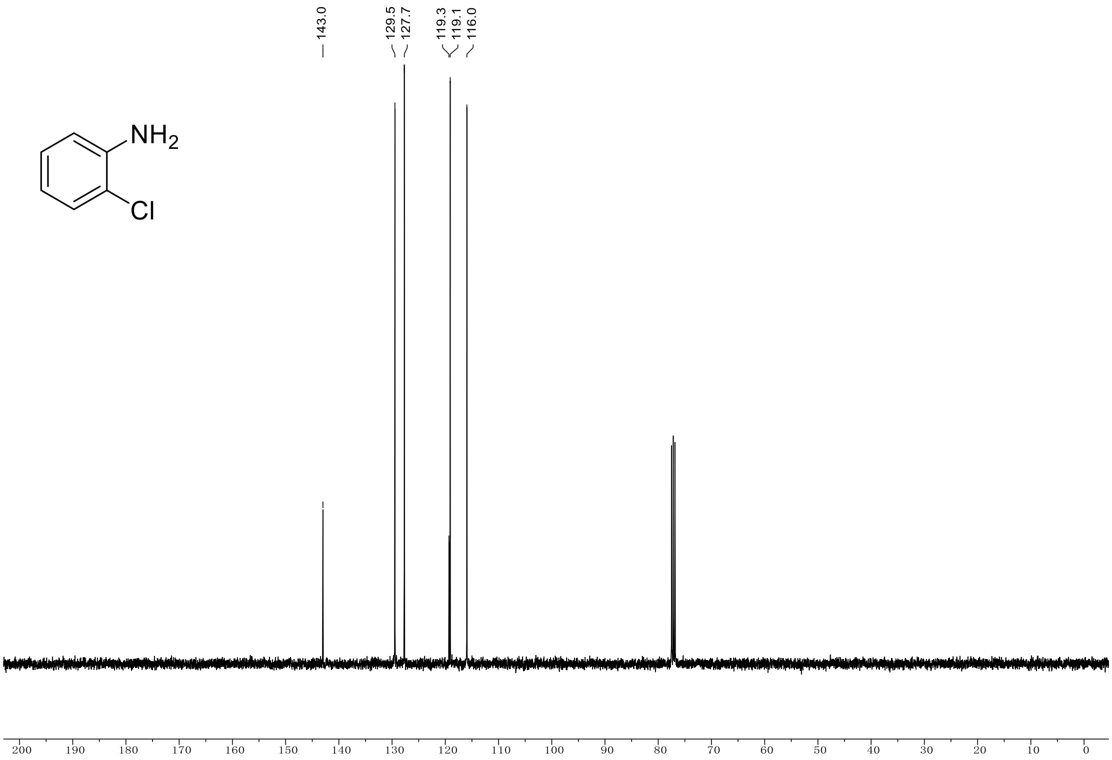
^{13}C NMR of **2b** ($CDCl_3$, 100 MHz)



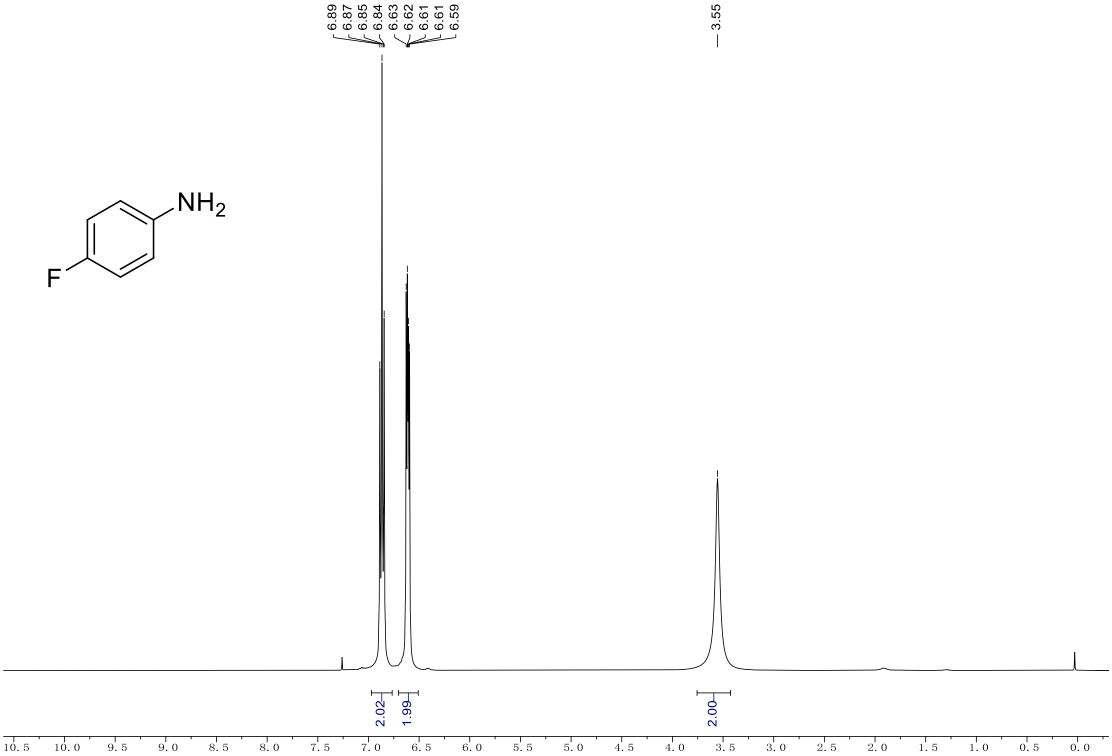
^{1}H NMR of **2c** (CDCl$_3$, 400 MHz)



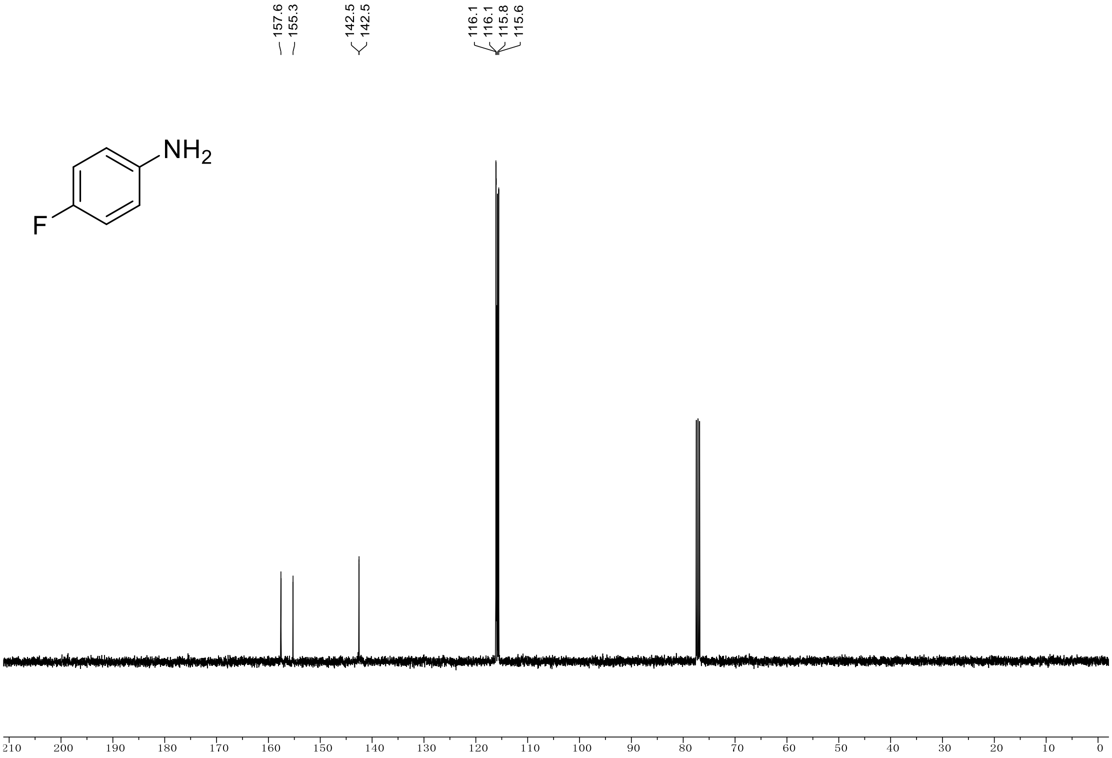
^{13}C NMR of **2c** (CDCl$_3$, 100 MHz)



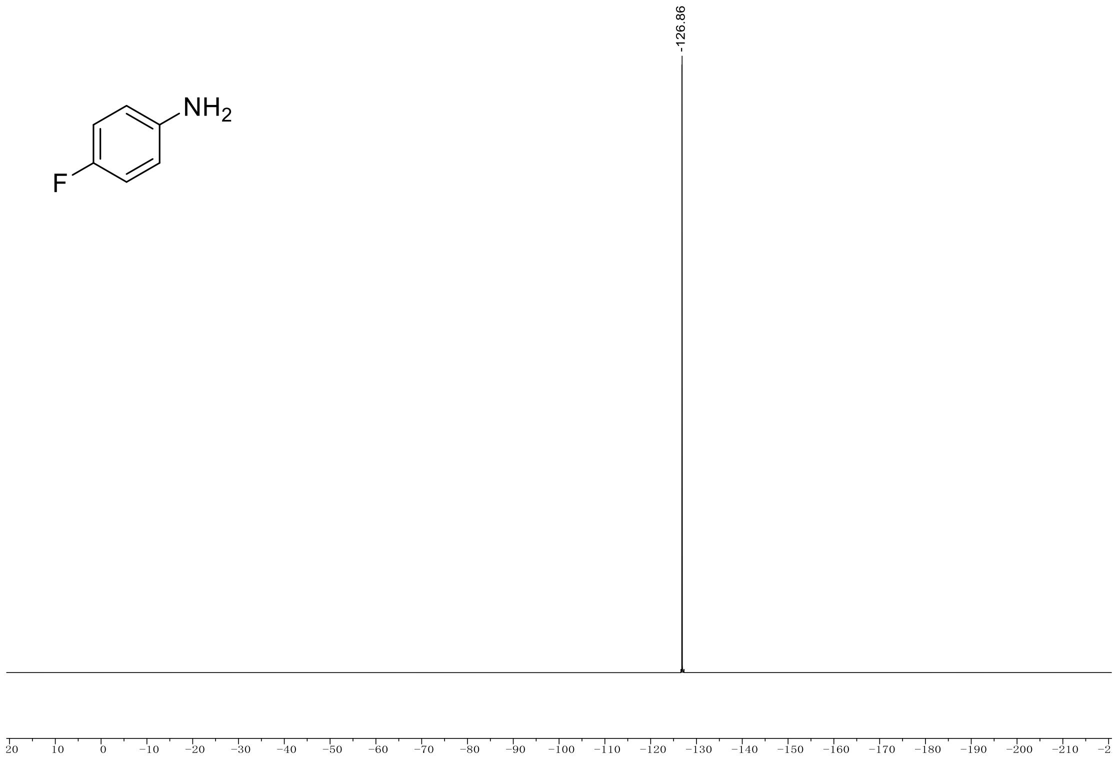
^{1}H NMR of **2d** ($CDCl_3$, 400 MHz)



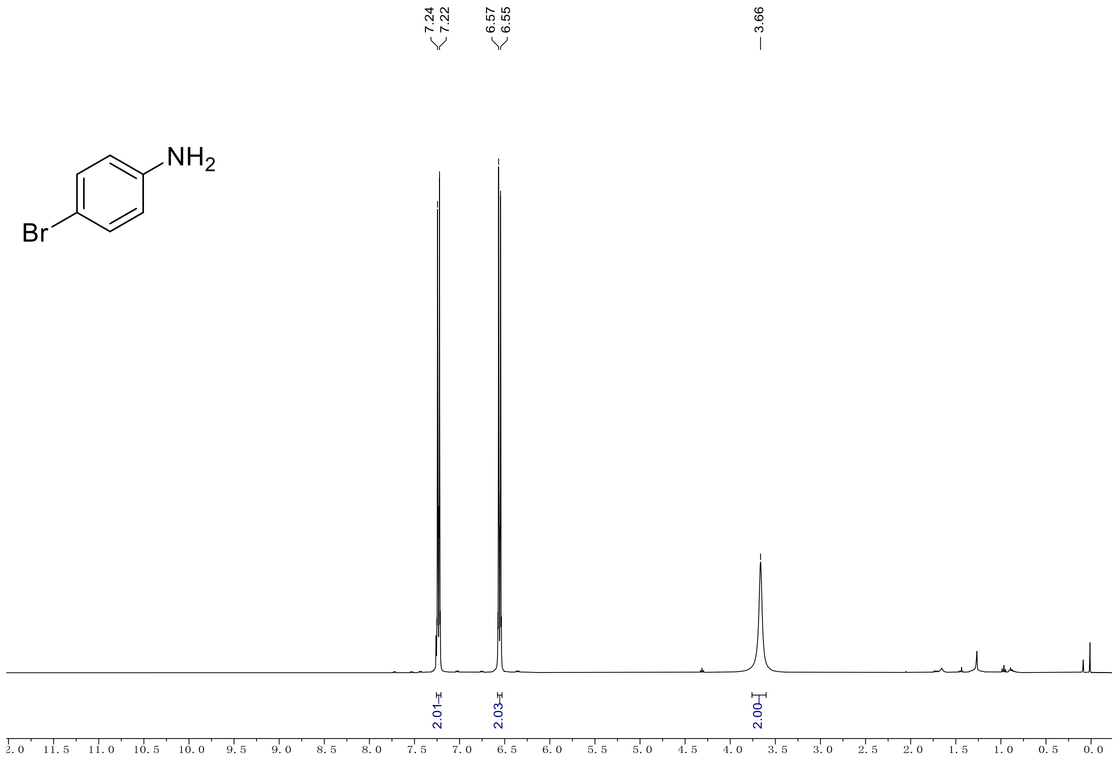
^{13}C NMR of **2d** ($CDCl_3$, 100 MHz)



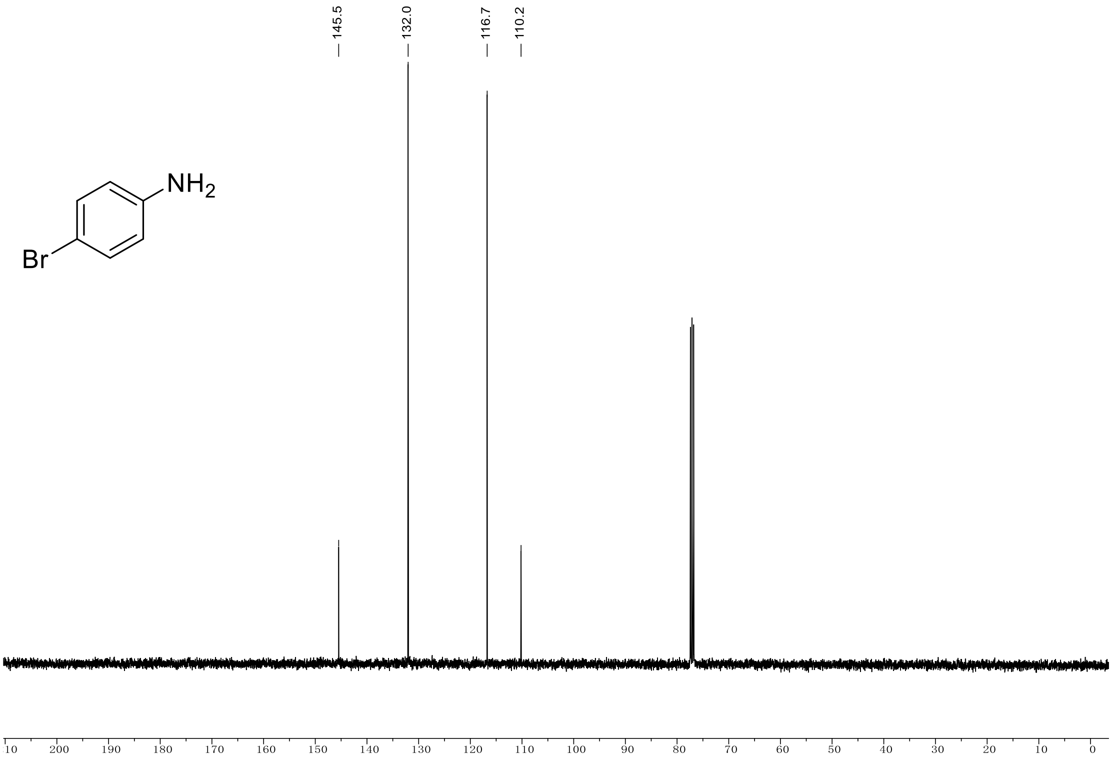
^{19}F NMR of **2d** (CDCl$_3$, 376 MHz)



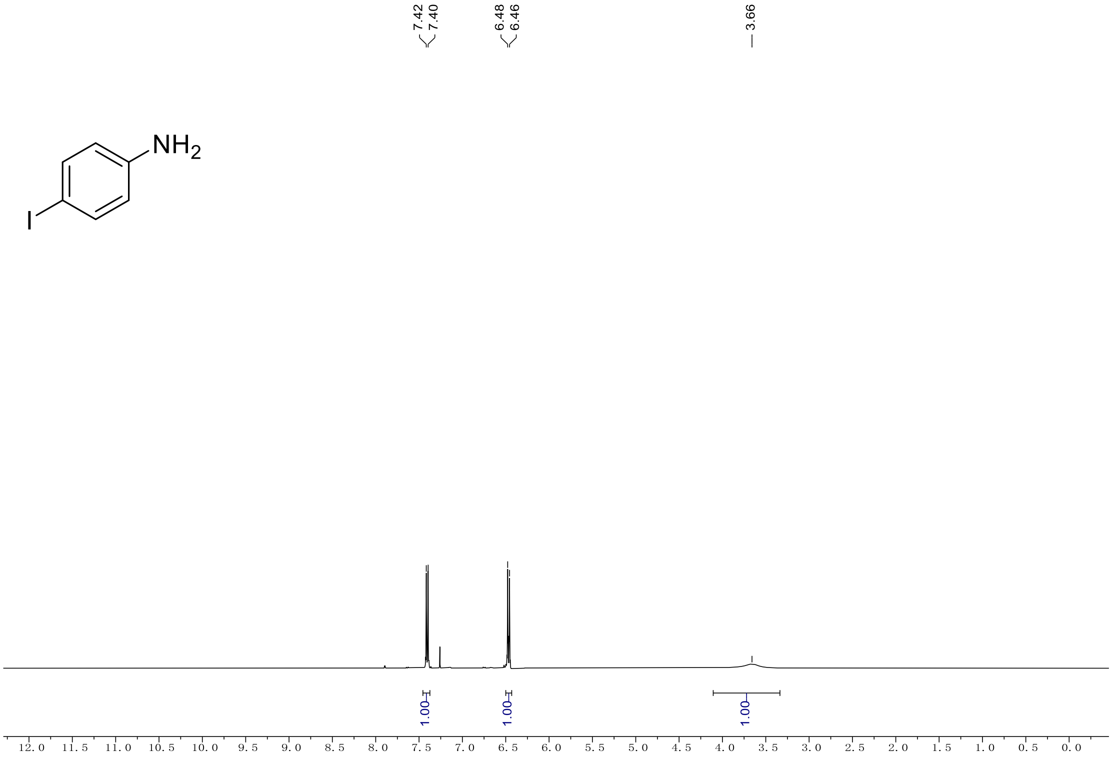
^{1}H NMR of **2e** (CDCl$_3$, 400 MHz)



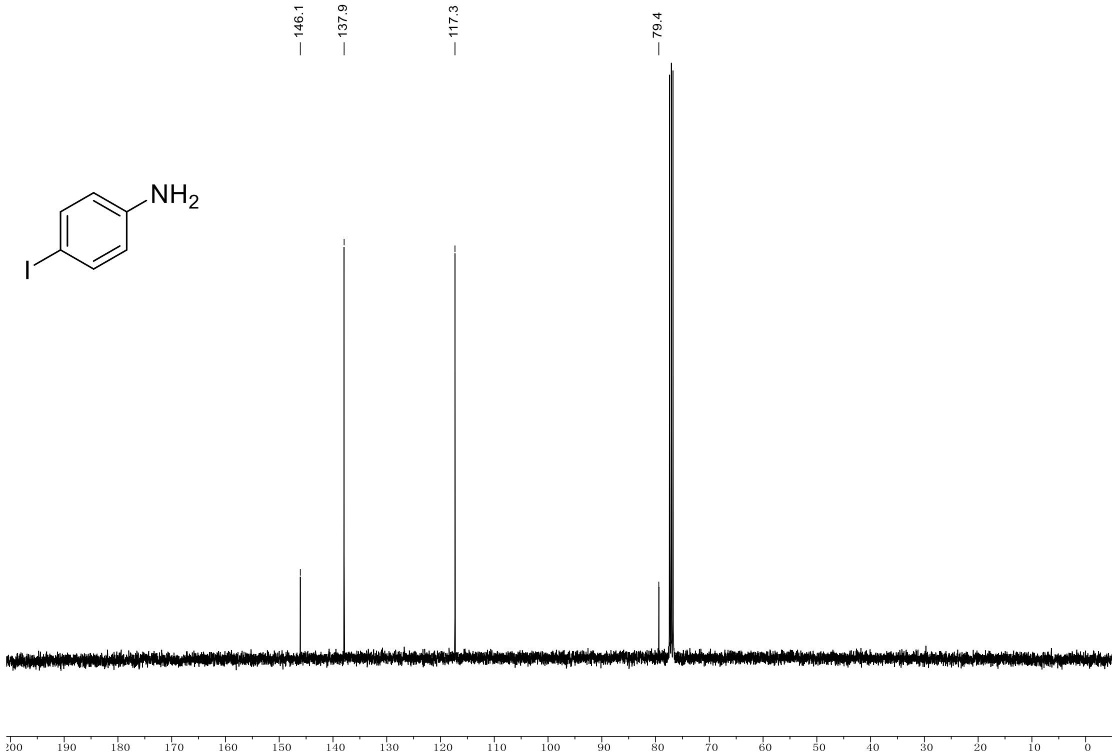
^{13}C NMR of **2e** (CDCl$_3$, 100 MHz)



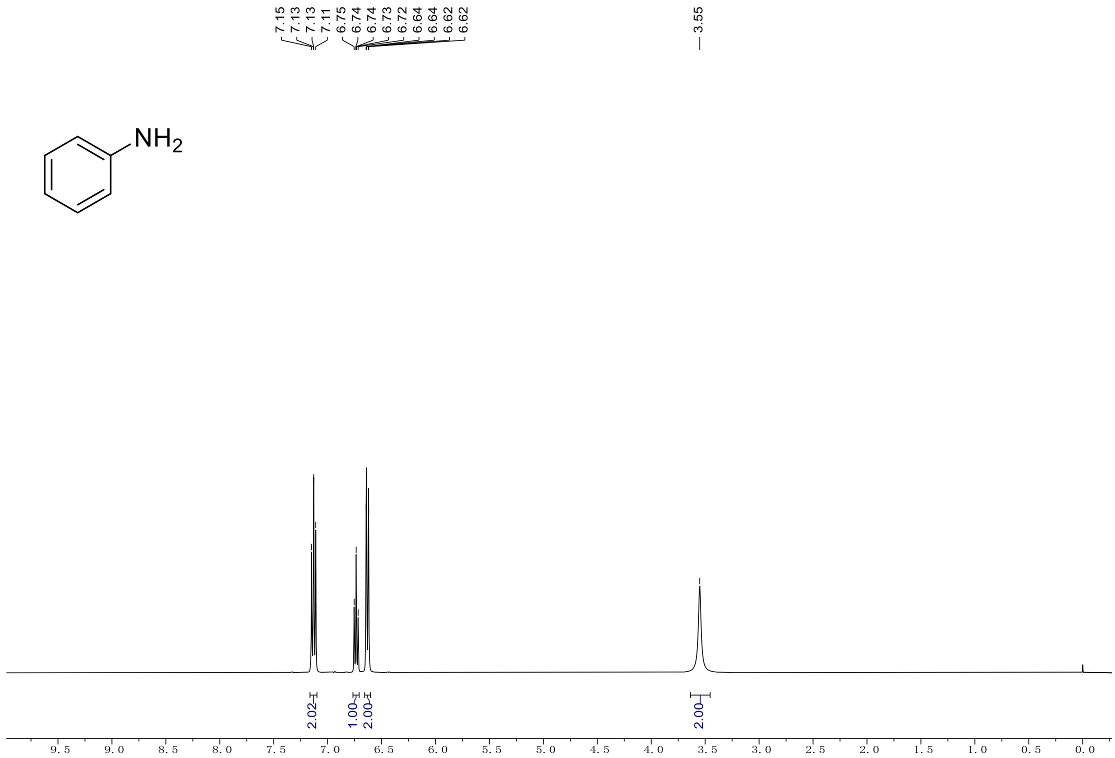
^{1}H NMR of **2f** (CDCl$_3$, 400 MHz)



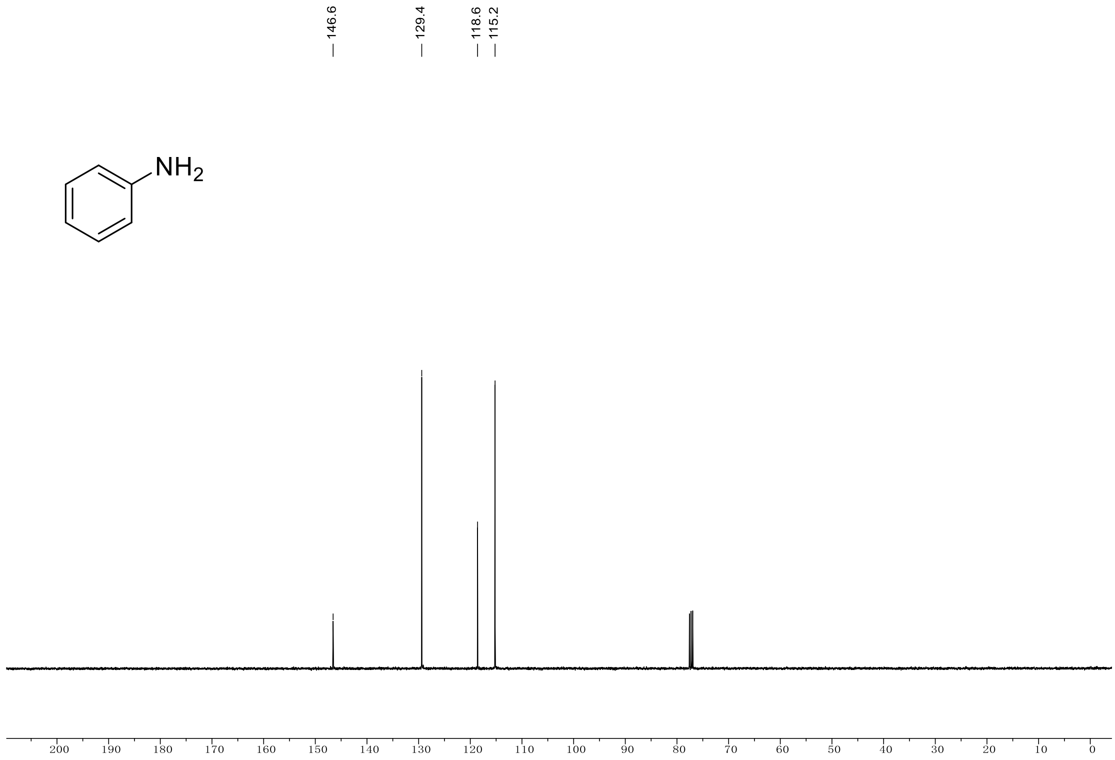
^{13}C NMR of **2f** (CDCl$_3$, 100 MHz)



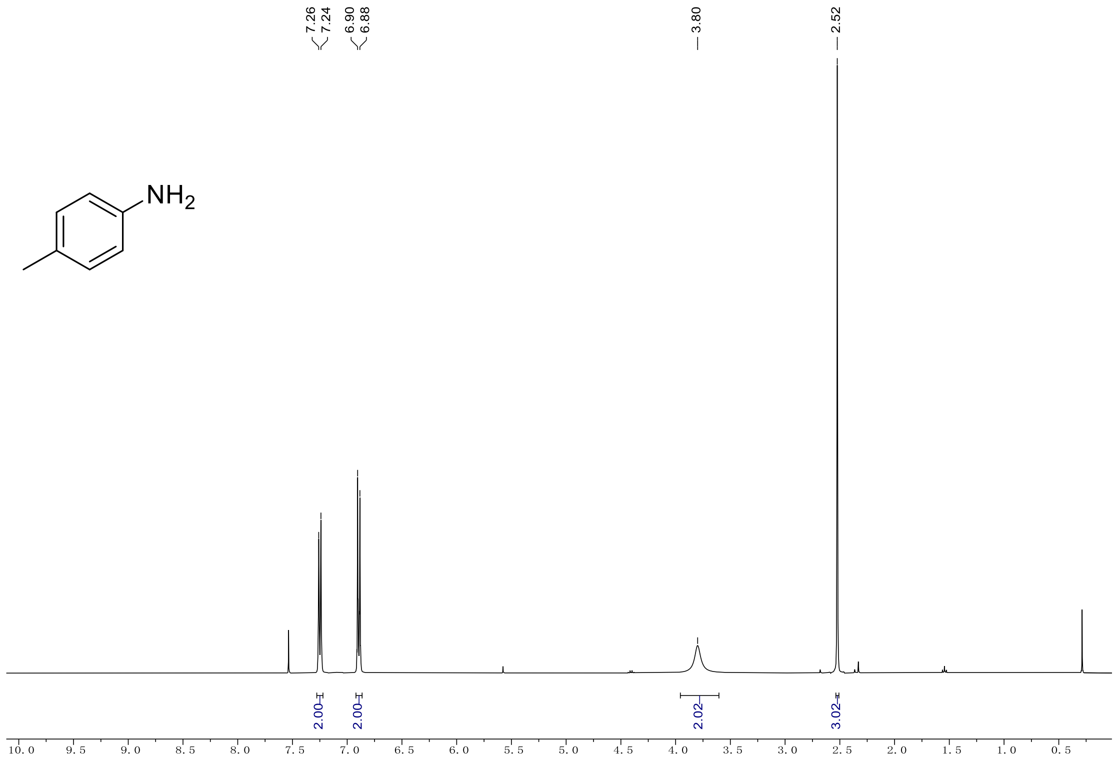
^{1}H NMR of **2g** (CDCl$_3$, 400 MHz)



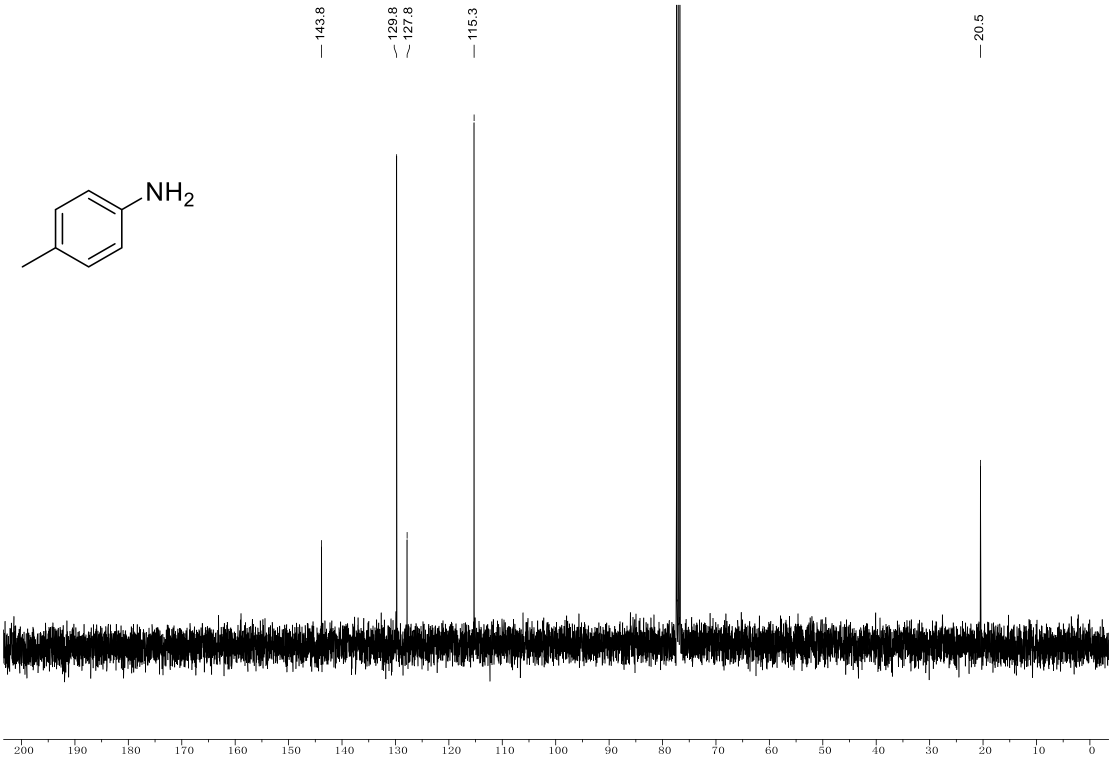
^{13}C NMR of **2g** (CDCl$_3$, 100 MHz)



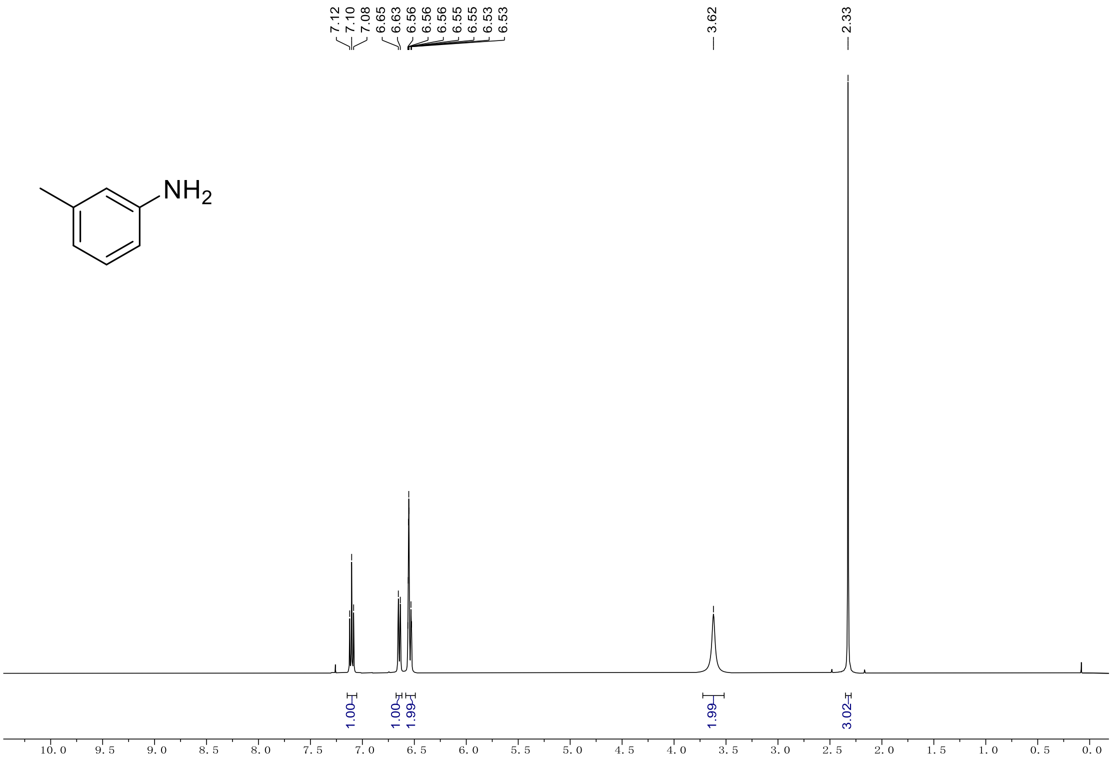
^{1}H NMR of **2h** (CDCl$_3$, 400 MHz)



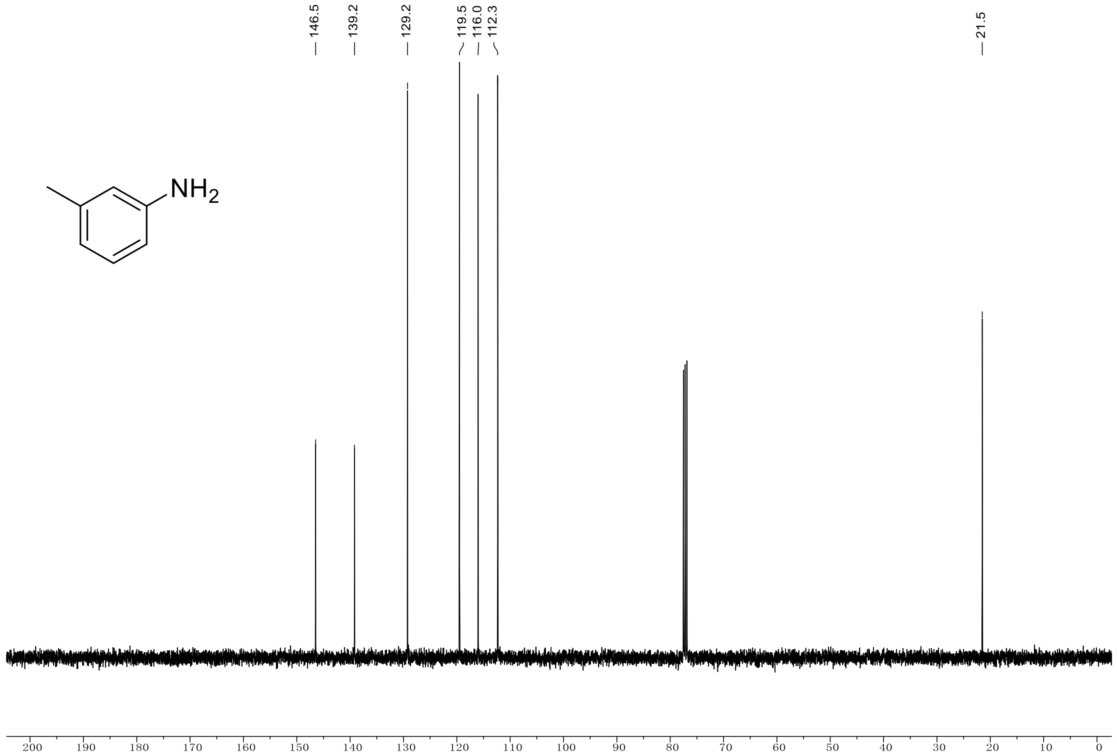
^{13}C NMR of **2h** ($CDCl_3$, 100 MHz)



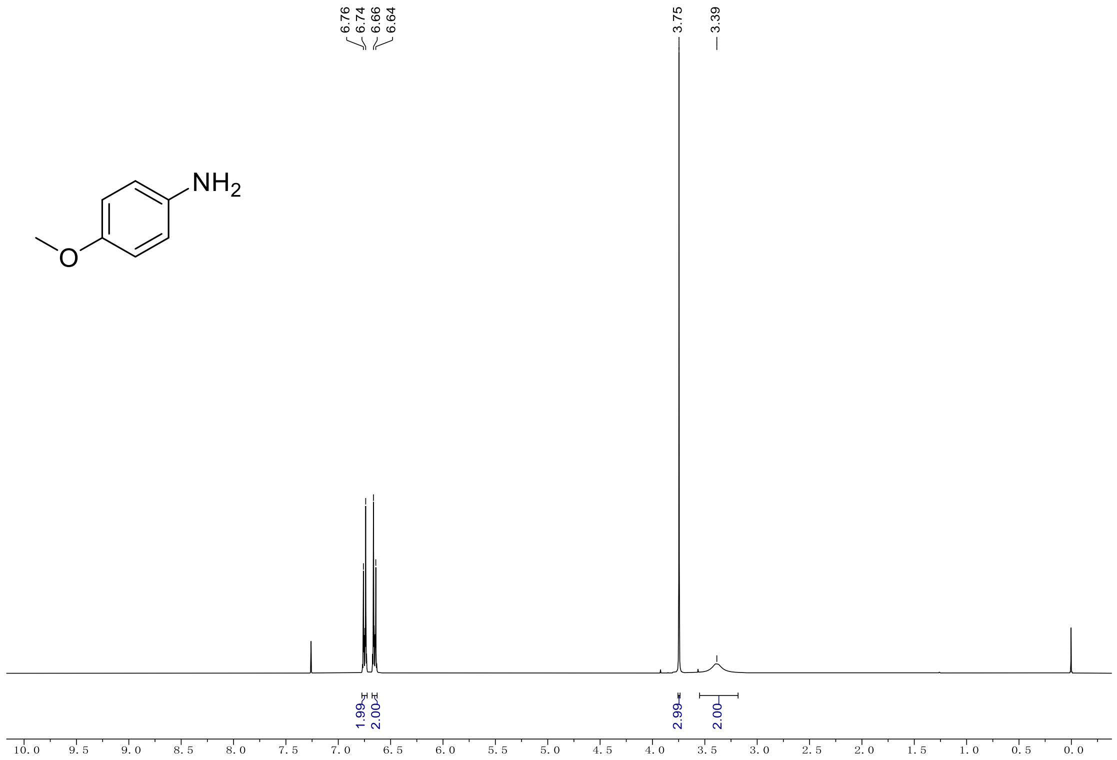
^{1}H NMR of **2i** ($CDCl_3$, 400 MHz)



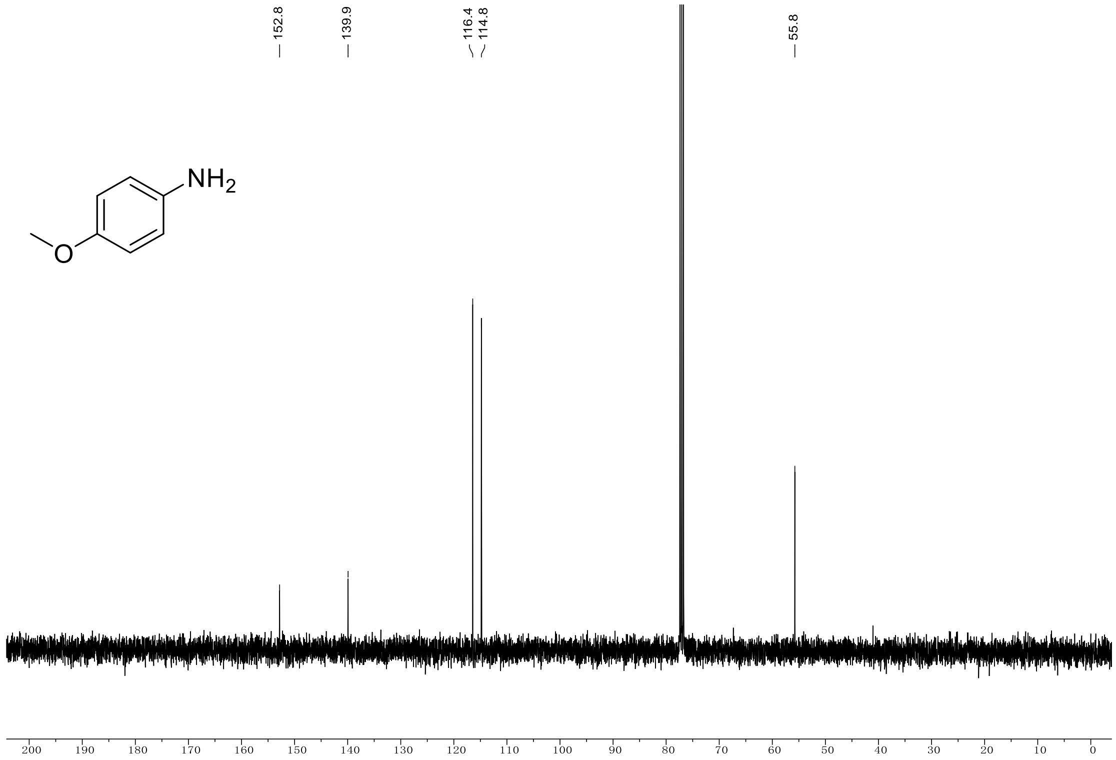
^{13}C NMR of **2i** ($CDCl_3$, 100 MHz)



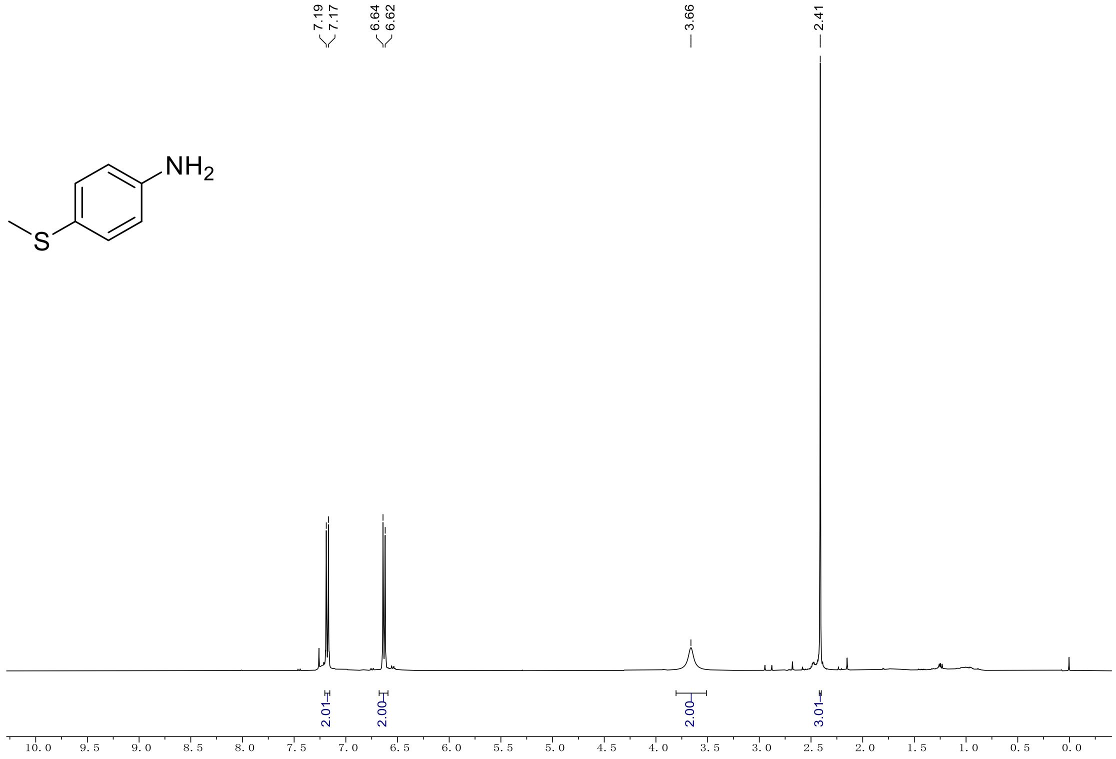
^{1}H NMR of **2j** ($CDCl_3$, 400 MHz)



^{13}C NMR of **2j** (CDCl$_3$, 100 MHz)



^{1}H NMR of **2k** (CDCl$_3$, 400 MHz)



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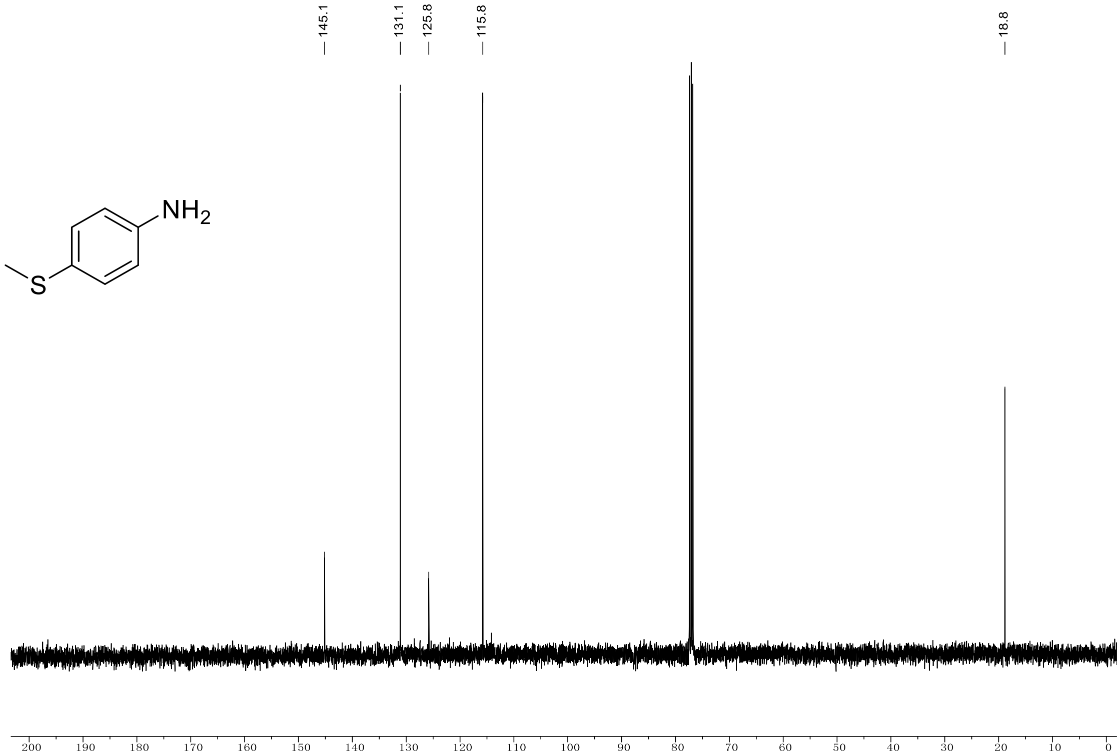
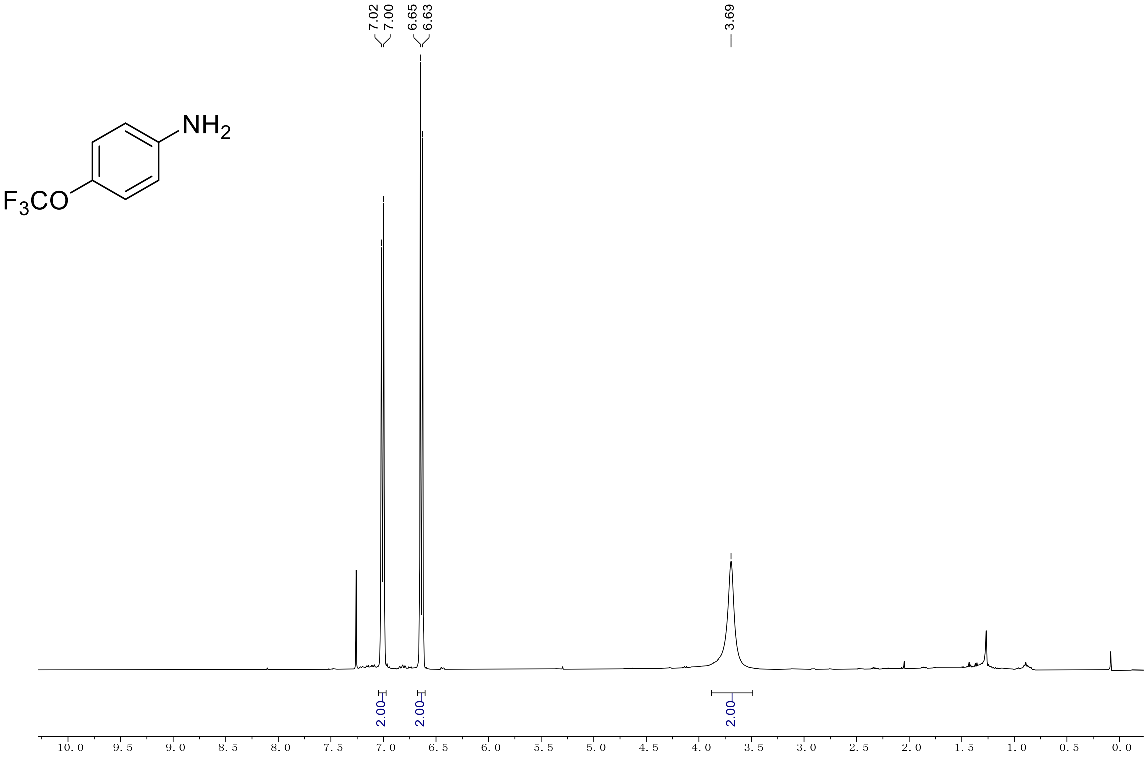
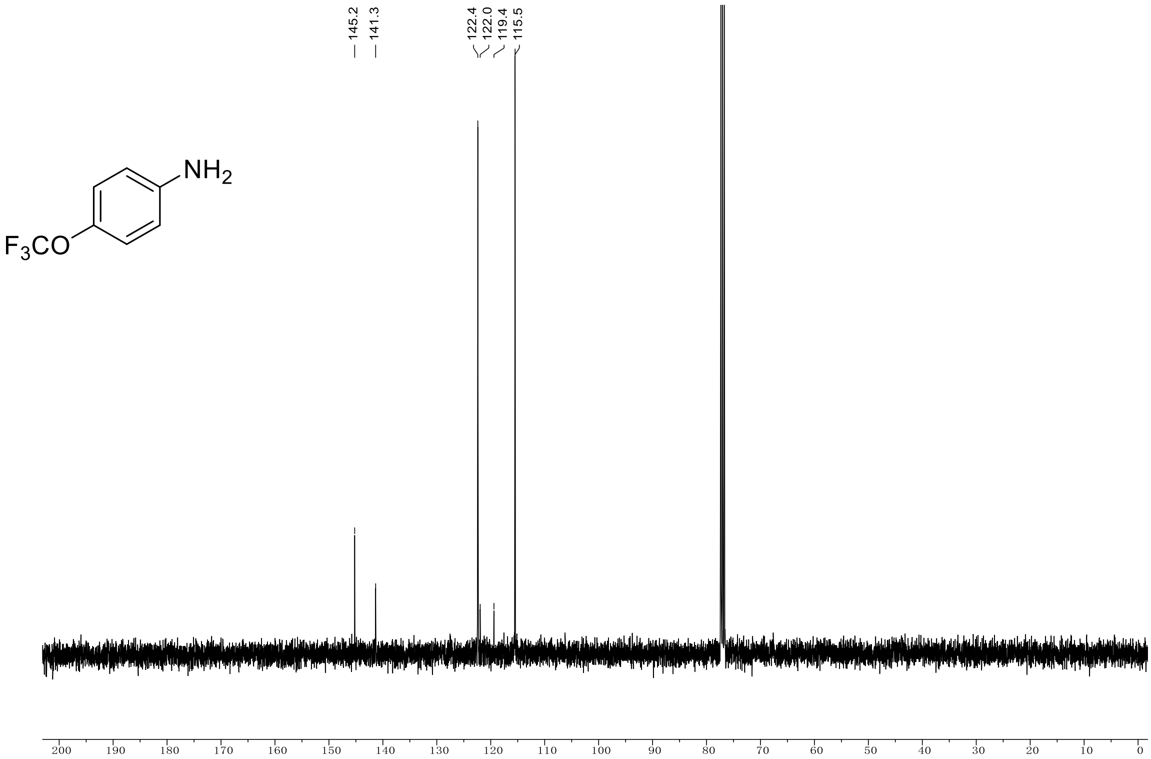


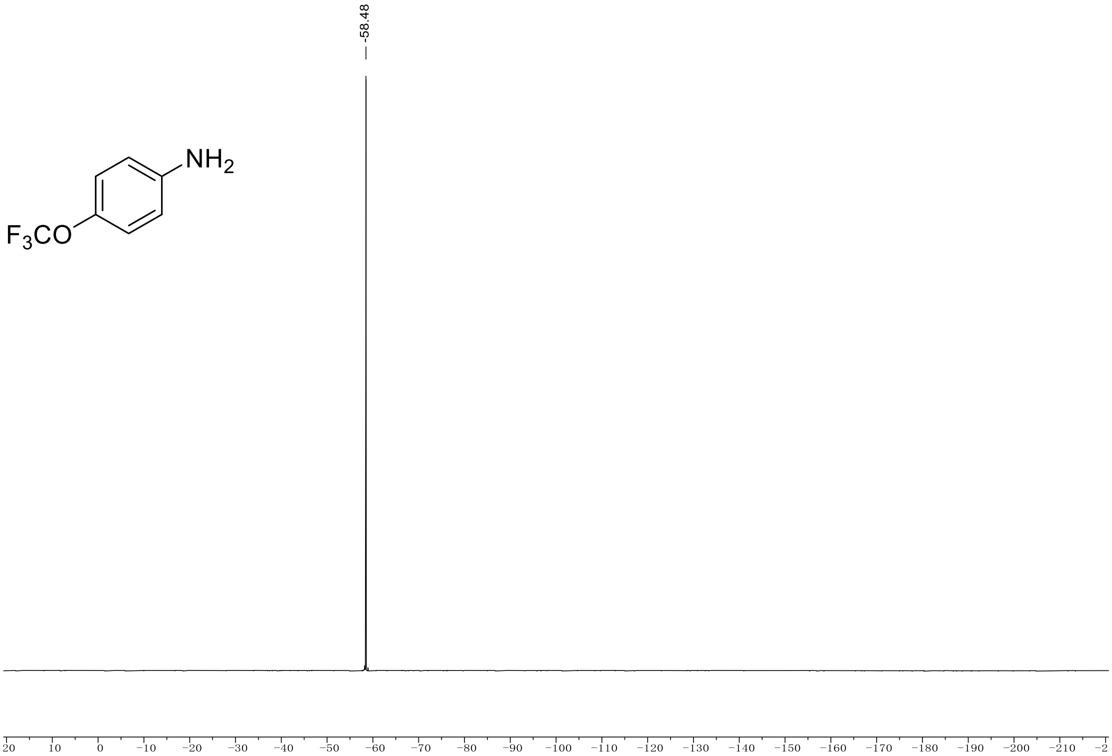
^{1}H NMR of **2l** ($CDCl_3$, 400 MHz)



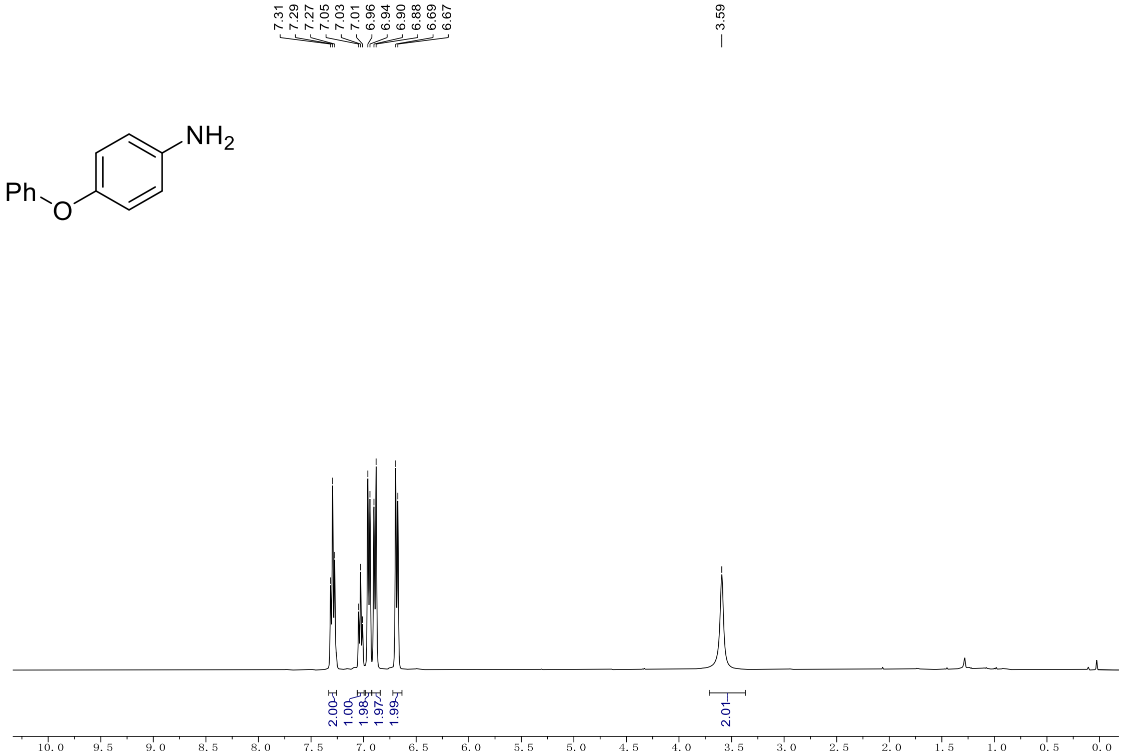
^{13}C NMR of **2l** ($CDCl_3$, 100 MHz)



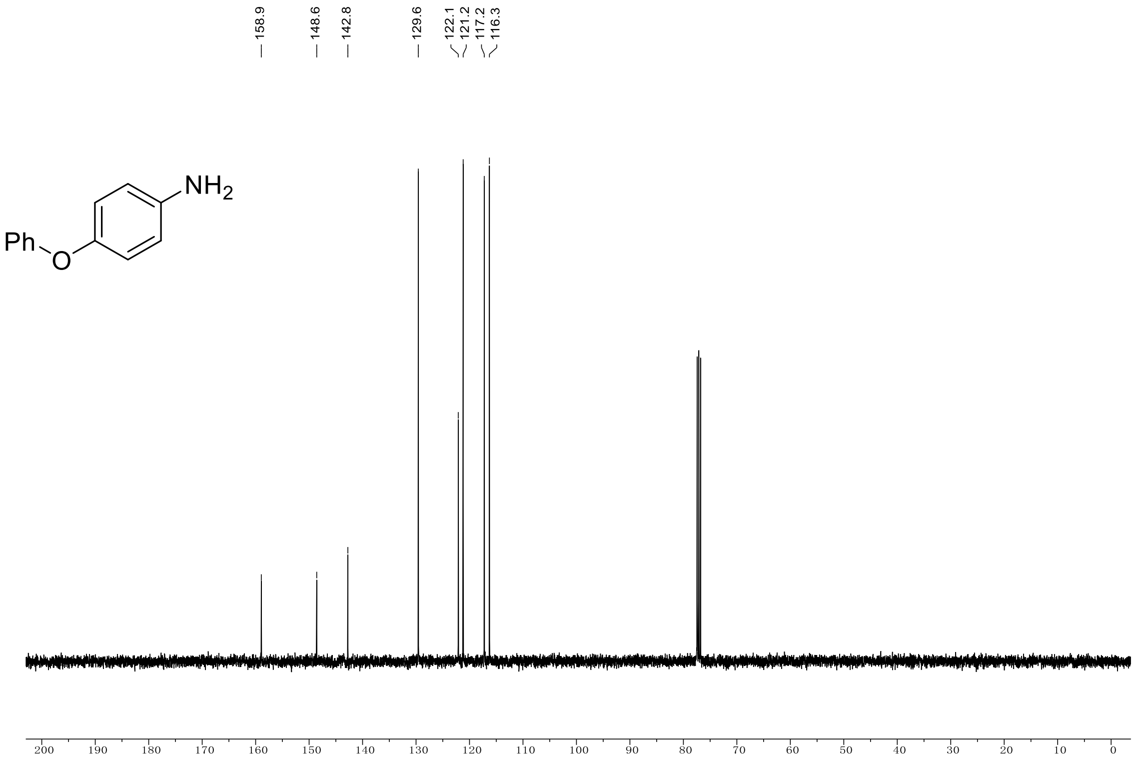
^{19}F NMR of **2l** ($CDCl_3$, 376 MHz)



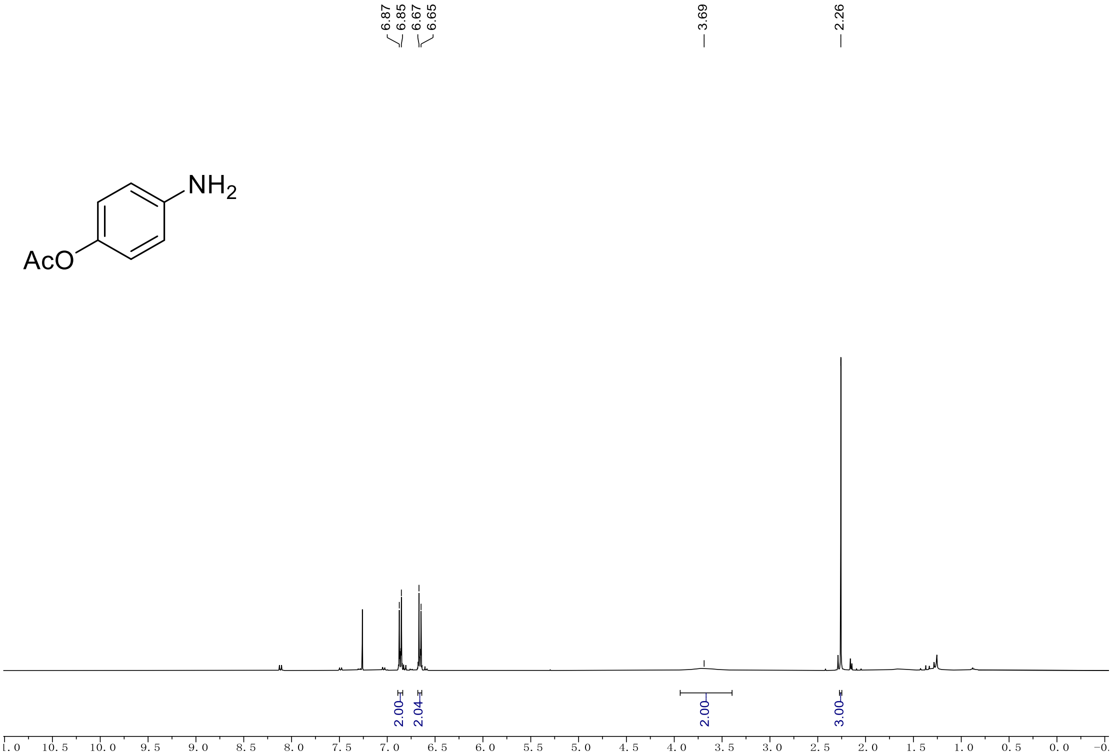
^{1}H NMR of **2m** ($CDCl_3$, 400 MHz)



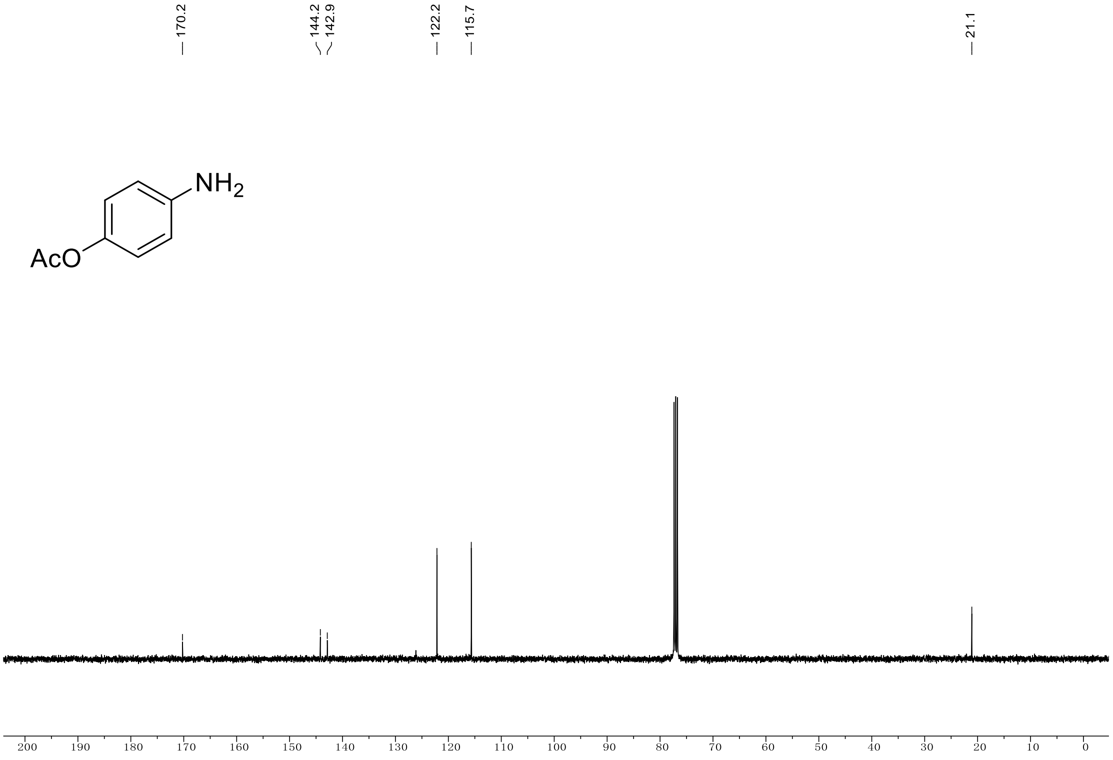
^{13}C NMR of **2m** ($CDCl_3$, 100 MHz)



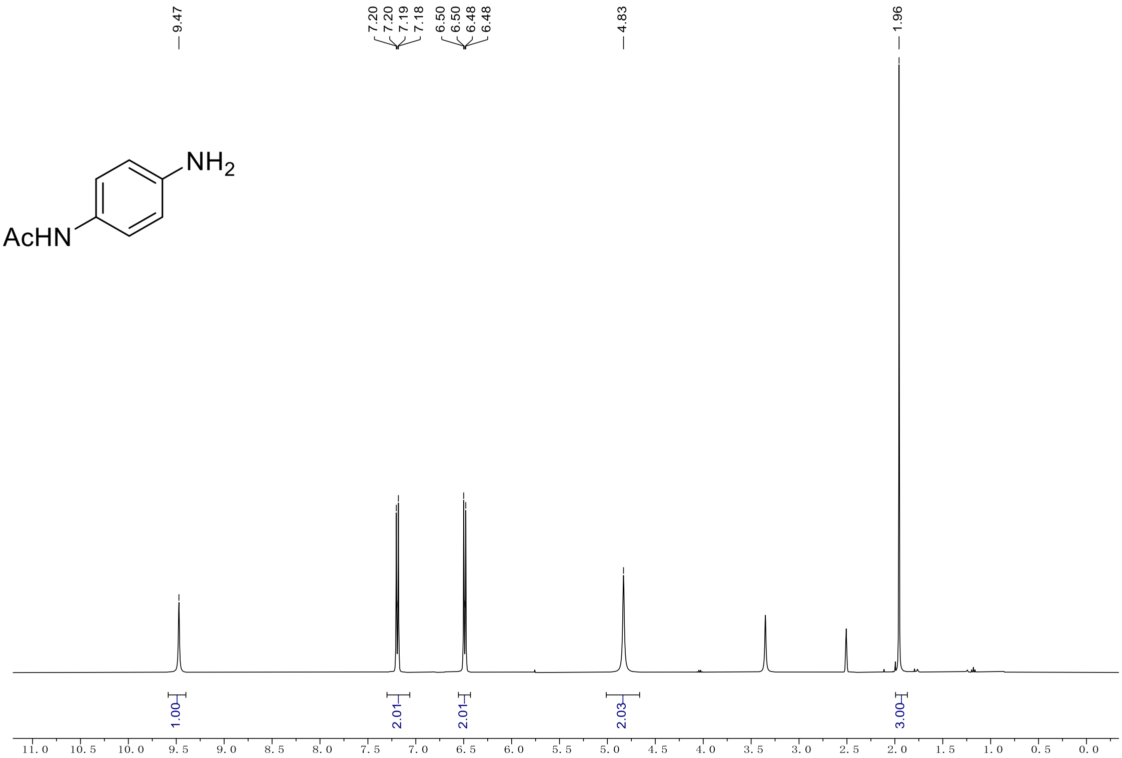
^{1}H NMR of **2n** ($CDCl_3$, 400 MHz)



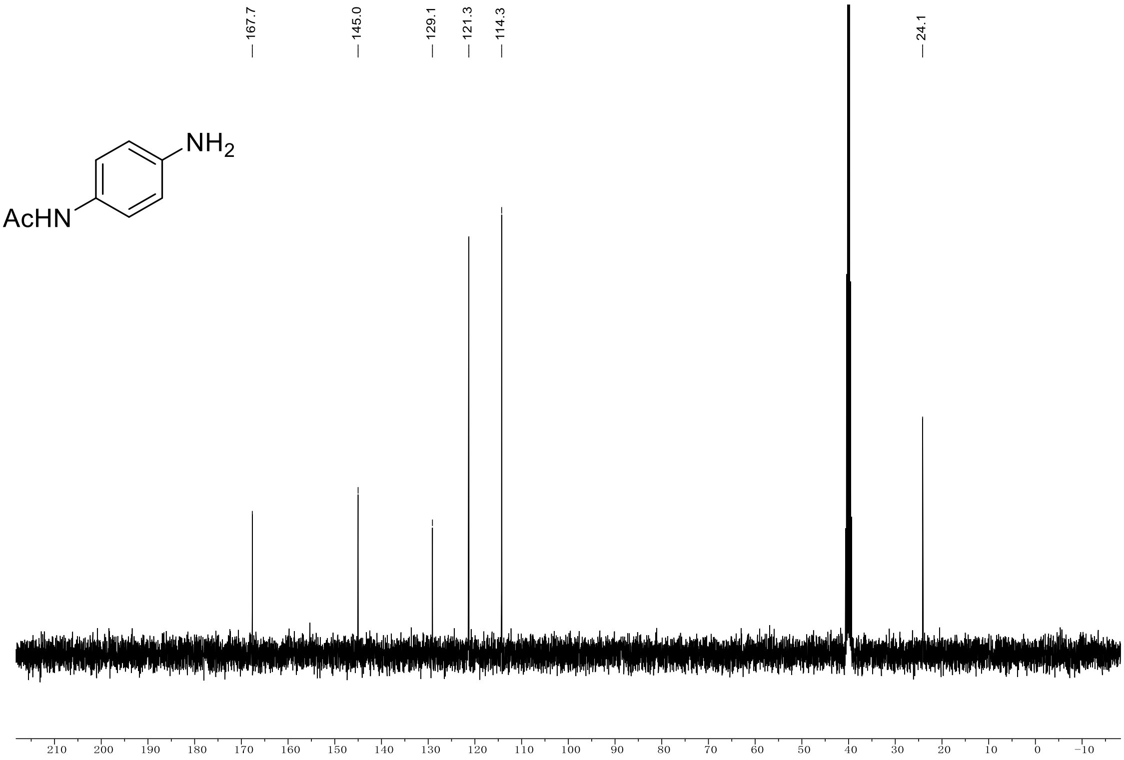
^{13}C NMR of **2n** ($CDCl_3$, 100 MHz)



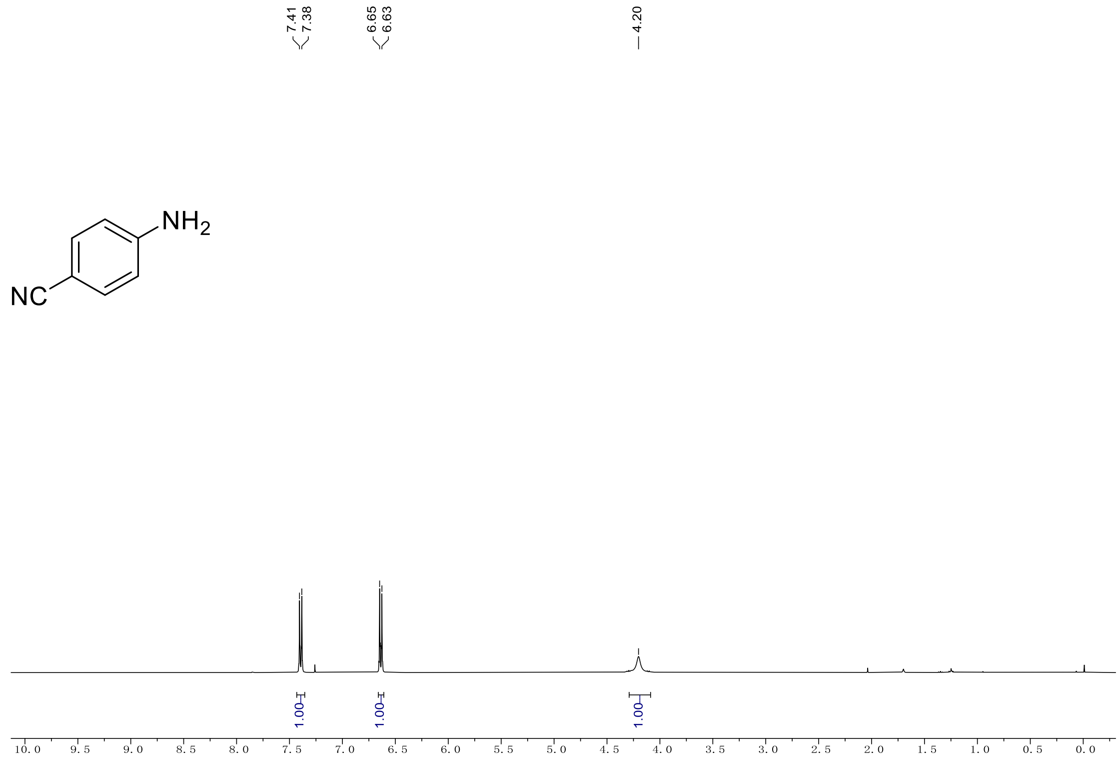
^{1}H NMR of **2o** (DMSO-*d*$_6$, 400 MHz)



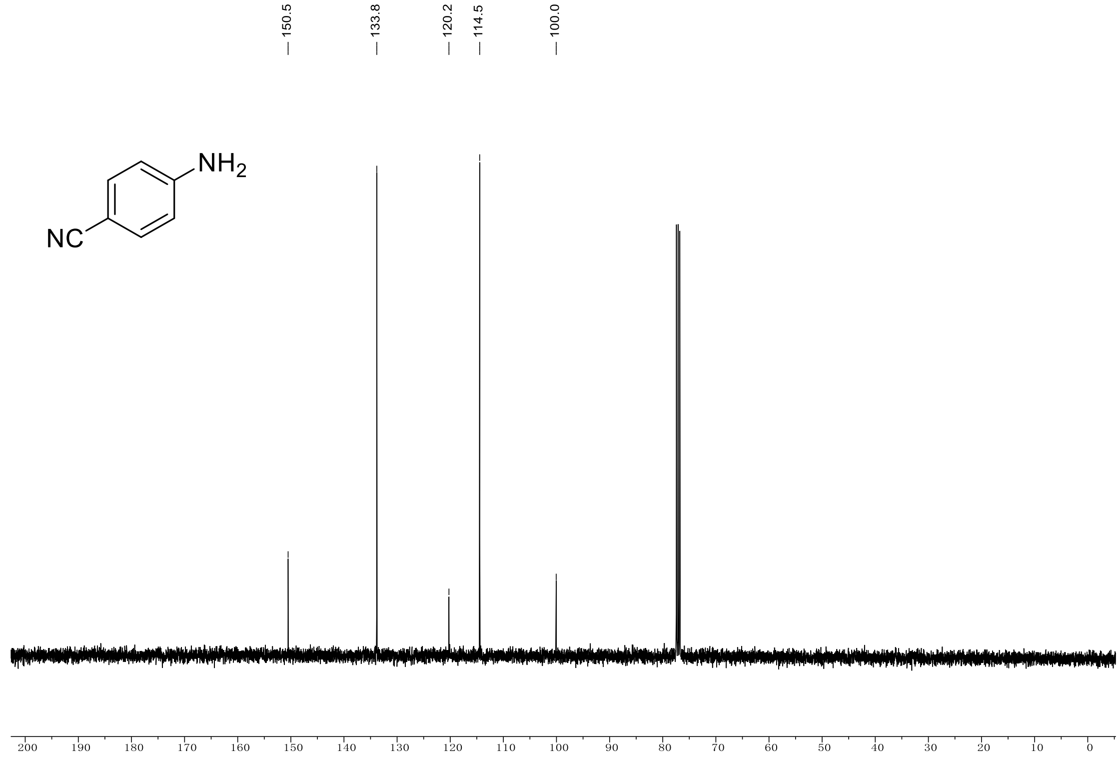
^{13}C NMR of **2o** (DMSO-*d*$_6$, 100 MHz)



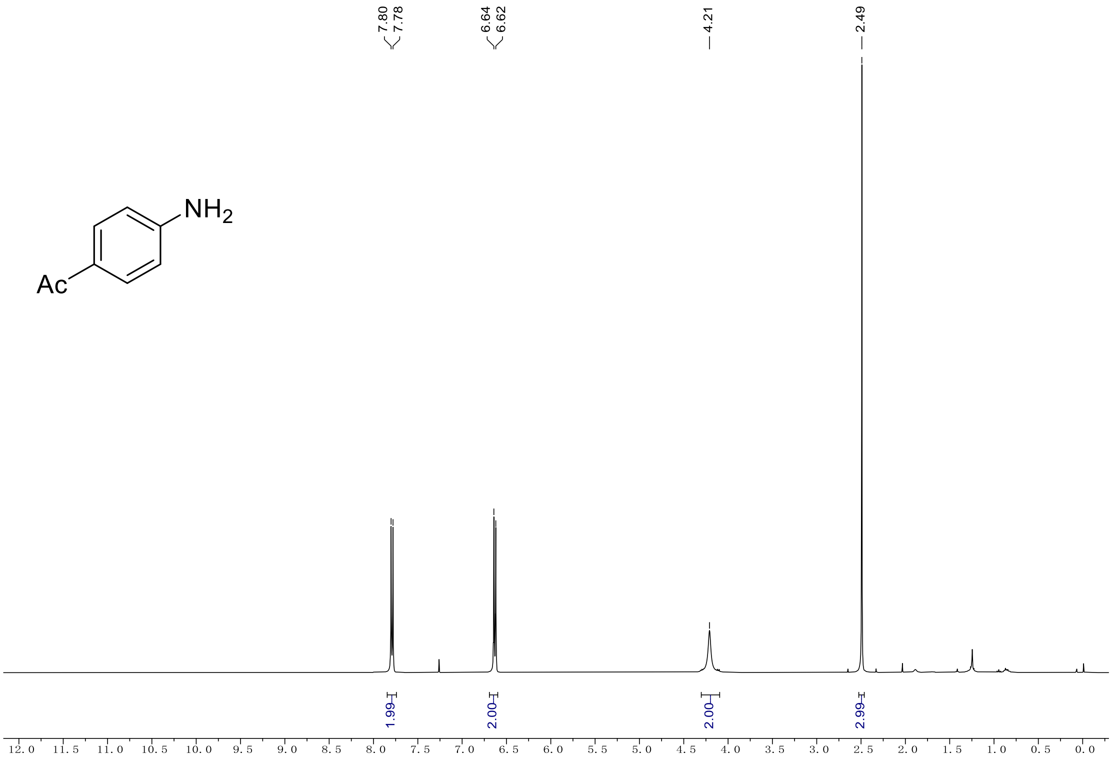
^{1}H NMR of **2p** ($CDCl_3$, 400 MHz)



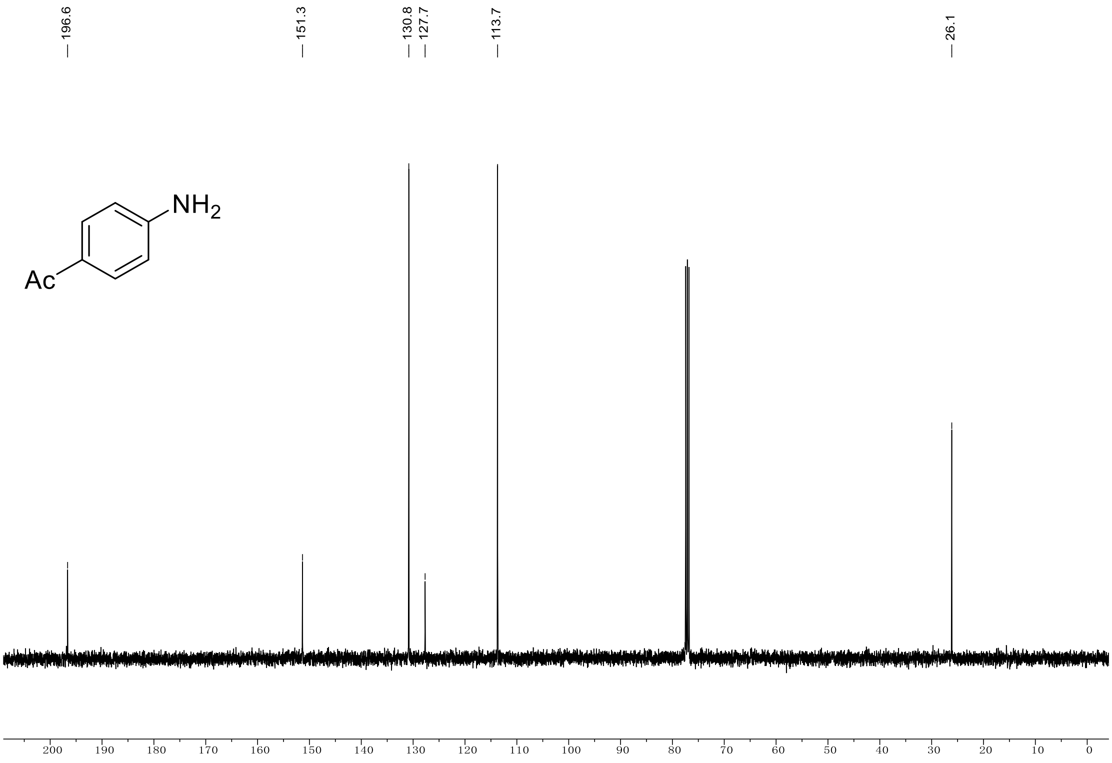
^{13}C NMR of **2p** ($CDCl_3$, 100 MHz)



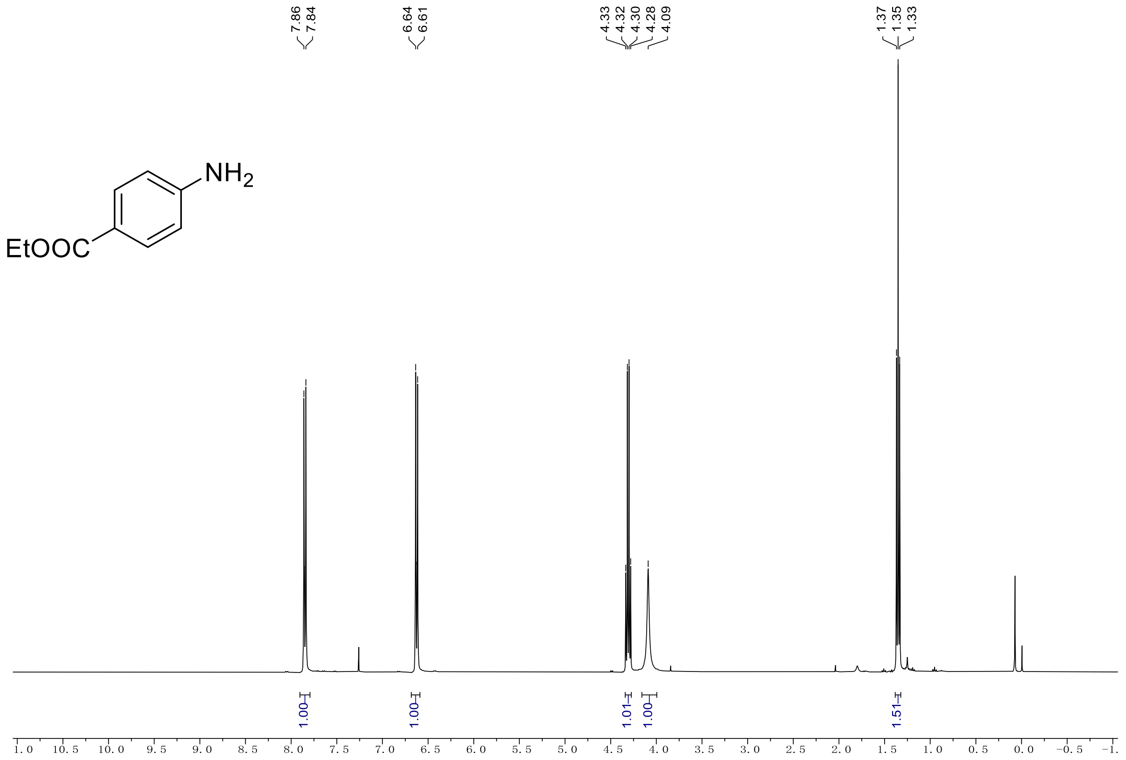
^{1}H NMR of **2q** ($CDCl_3$, 400 MHz)



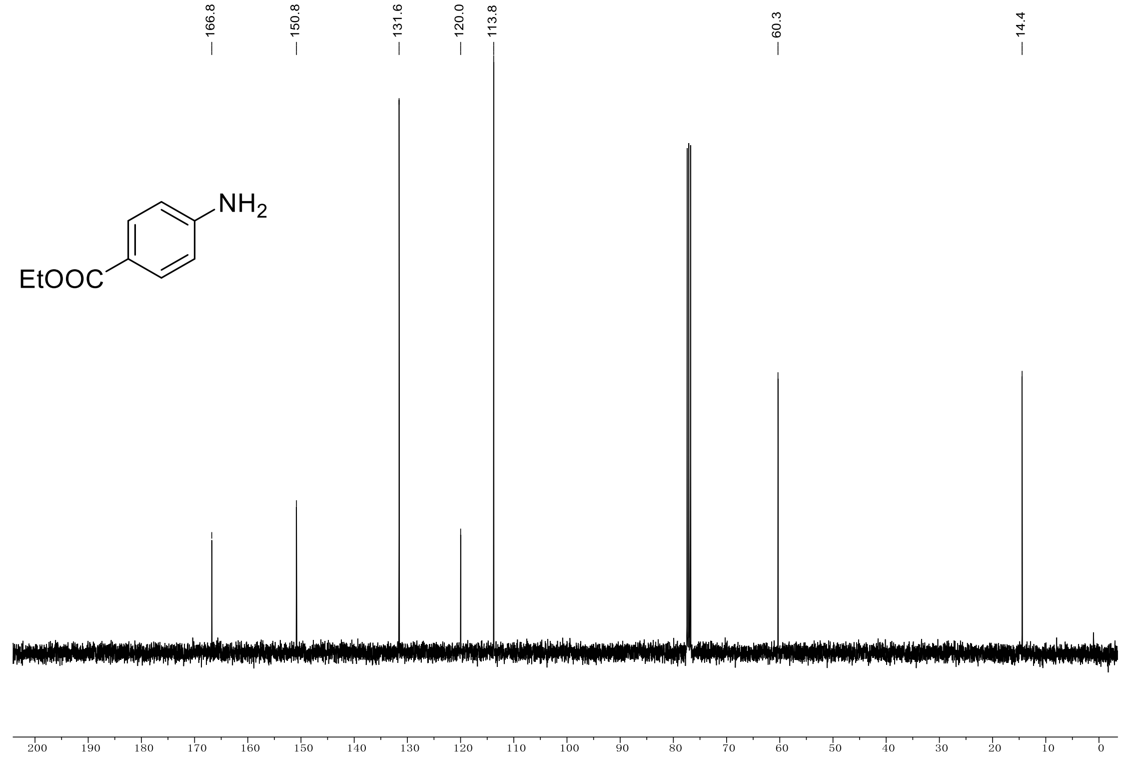
^{13}C NMR of **2q** ($CDCl_3$, 100 MHz)



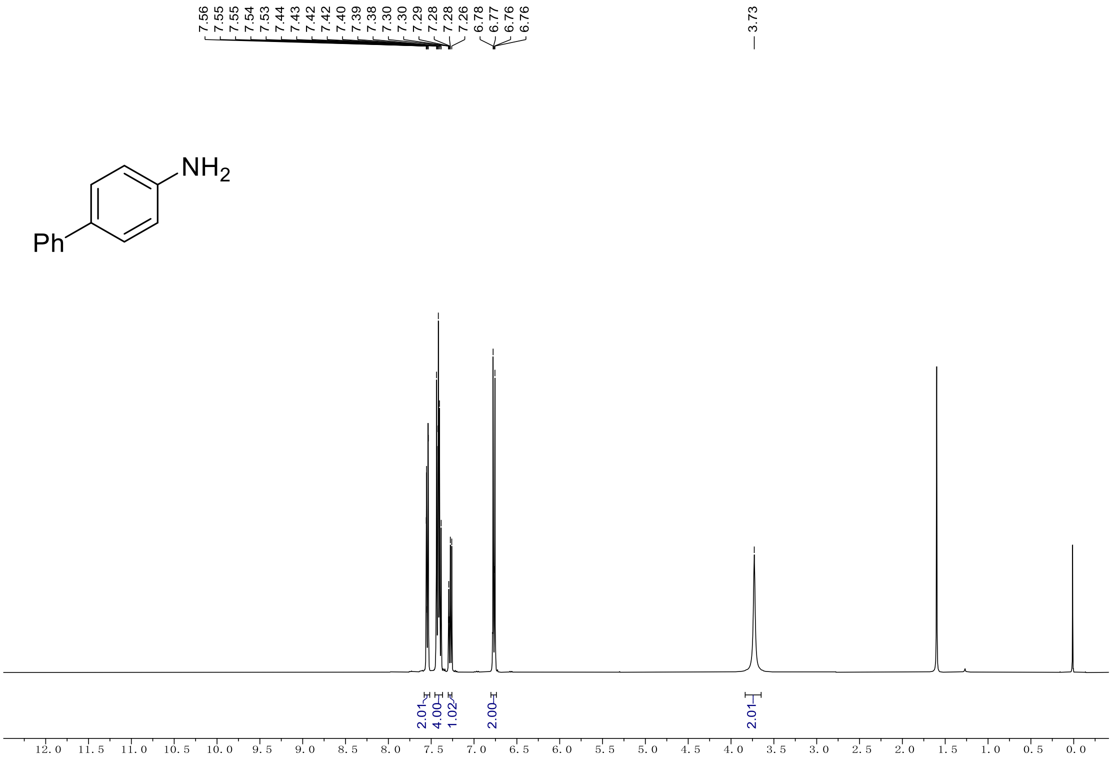
^{1}H NMR of **2r** ($CDCl_3$, 400 MHz)



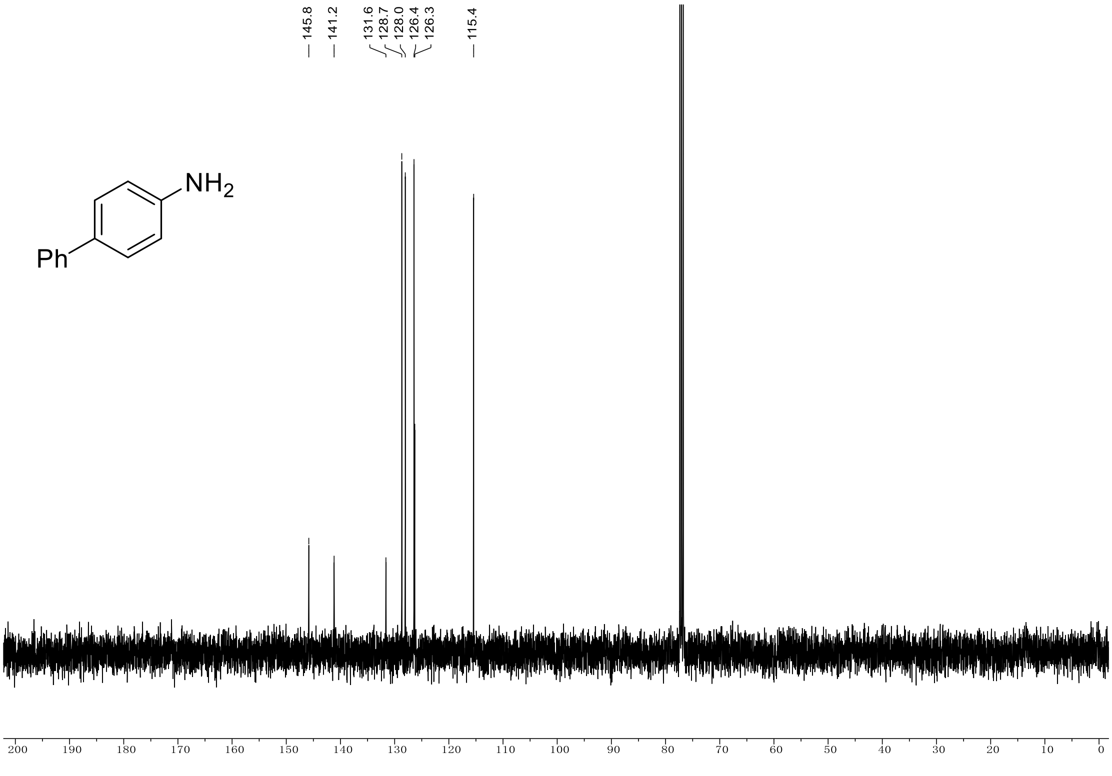
^{13}C NMR spectra of **2r** ($CDCl_3$, 100 MHz)



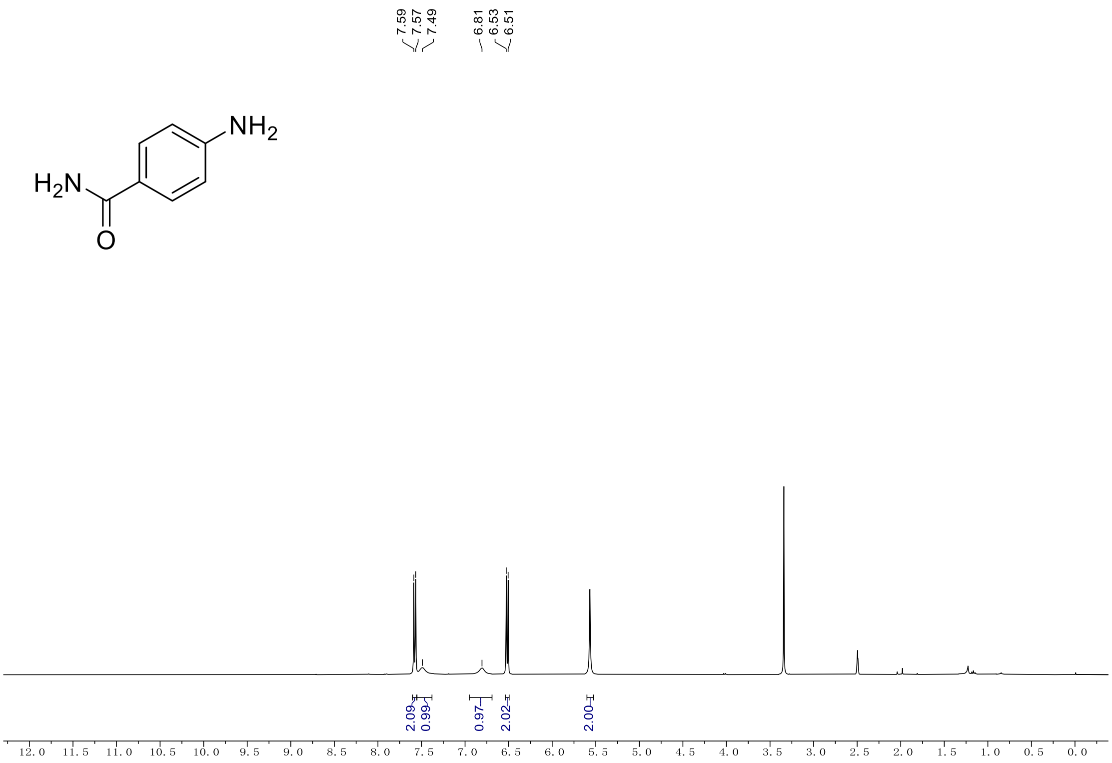
^{1}H NMR of **2s** ($CDCl_3$, 400 MHz)



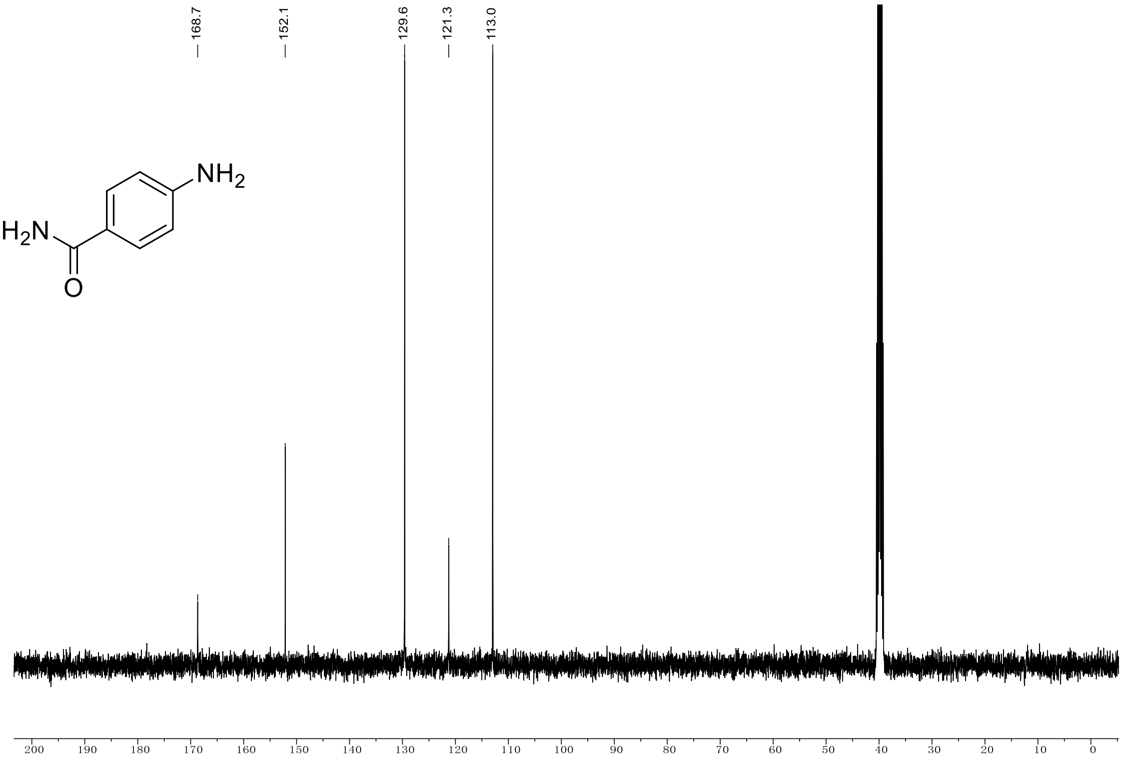
^{13}C NMR of **2s** ($CDCl_3$, 100 MHz)



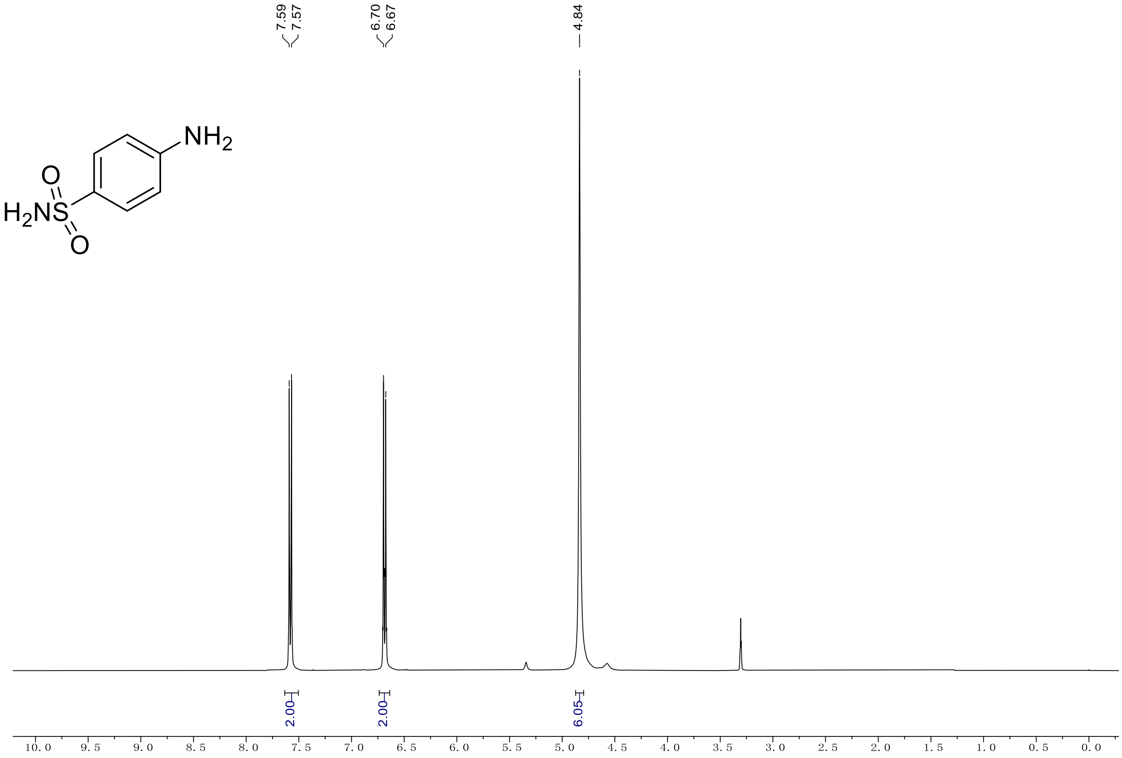
^{1}H NMR of **2t** (DMSO-d_6, 400 MHz)



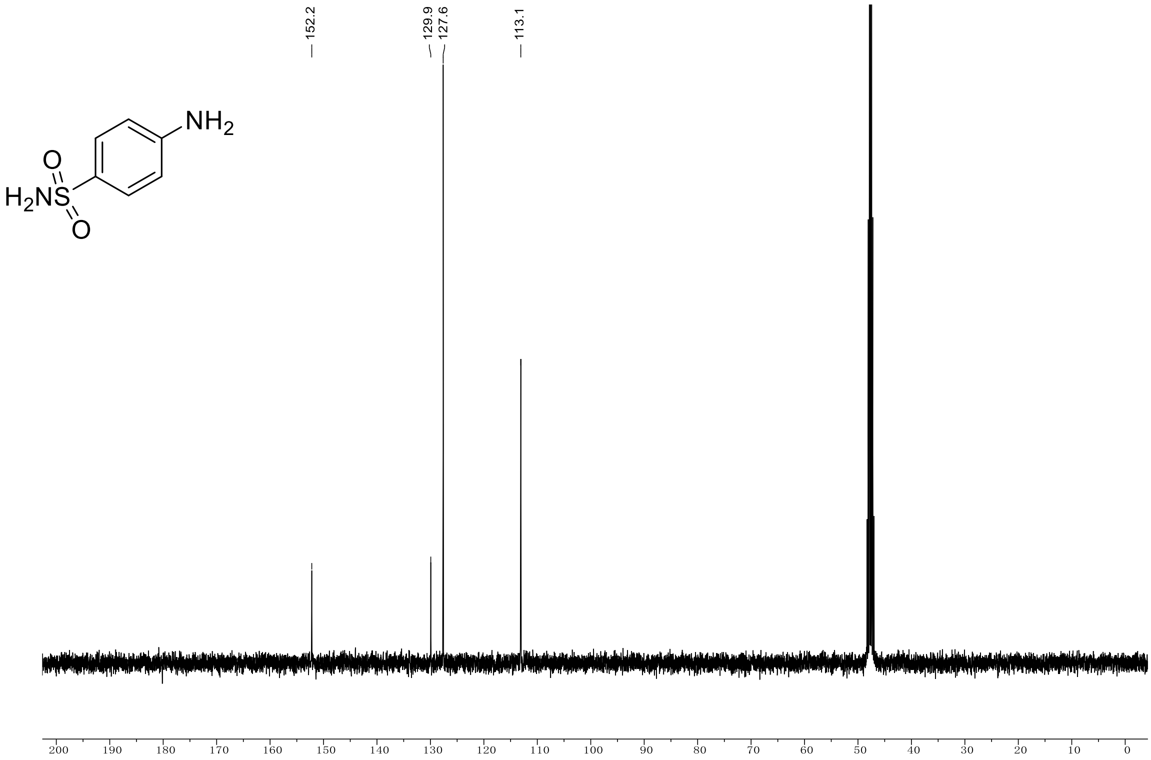
^{13}C NMR of **2t** (DMSO-d_6, 100 MHz)



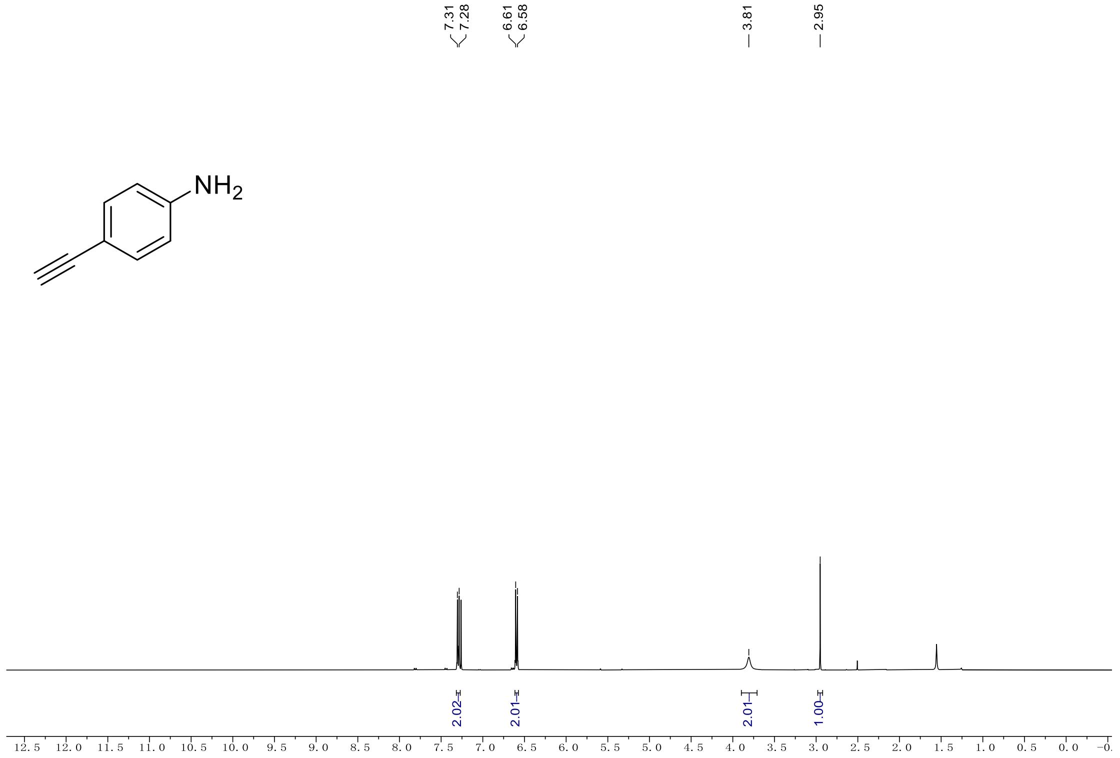
^{1}H NMR of **2u** (DMSO-d_6, 400 MHz)



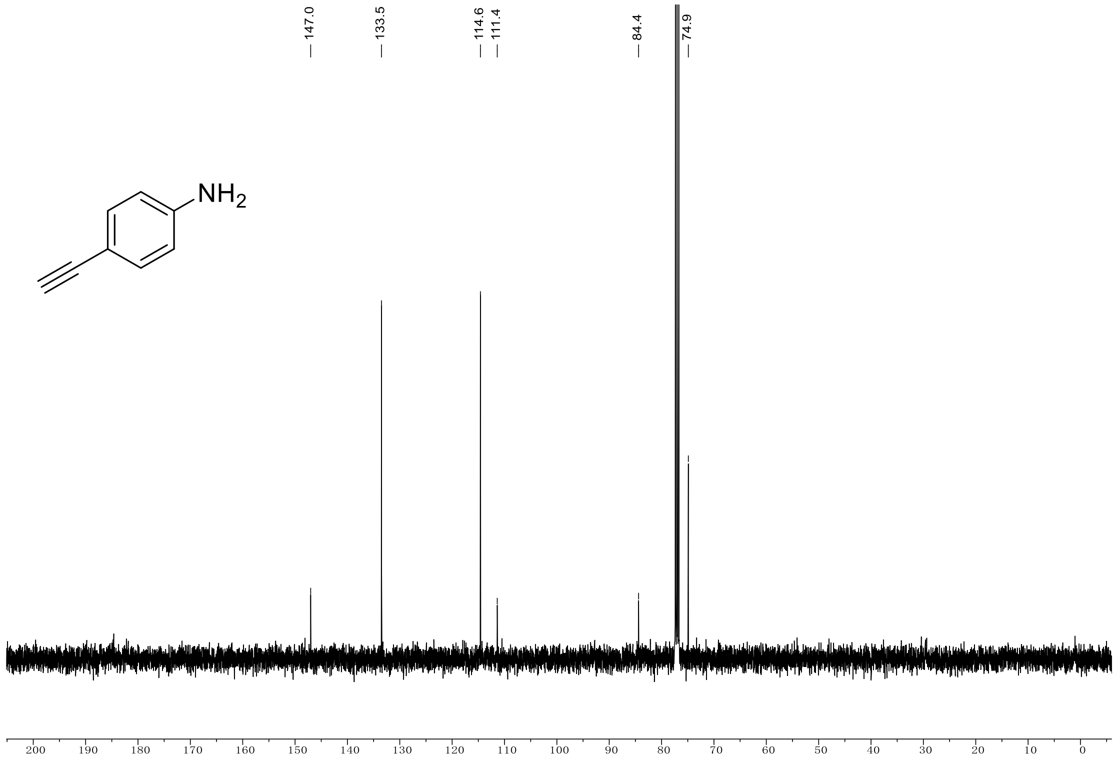
^{13}C NMR of **2u** (DMSO-d_6, 100 MHz)



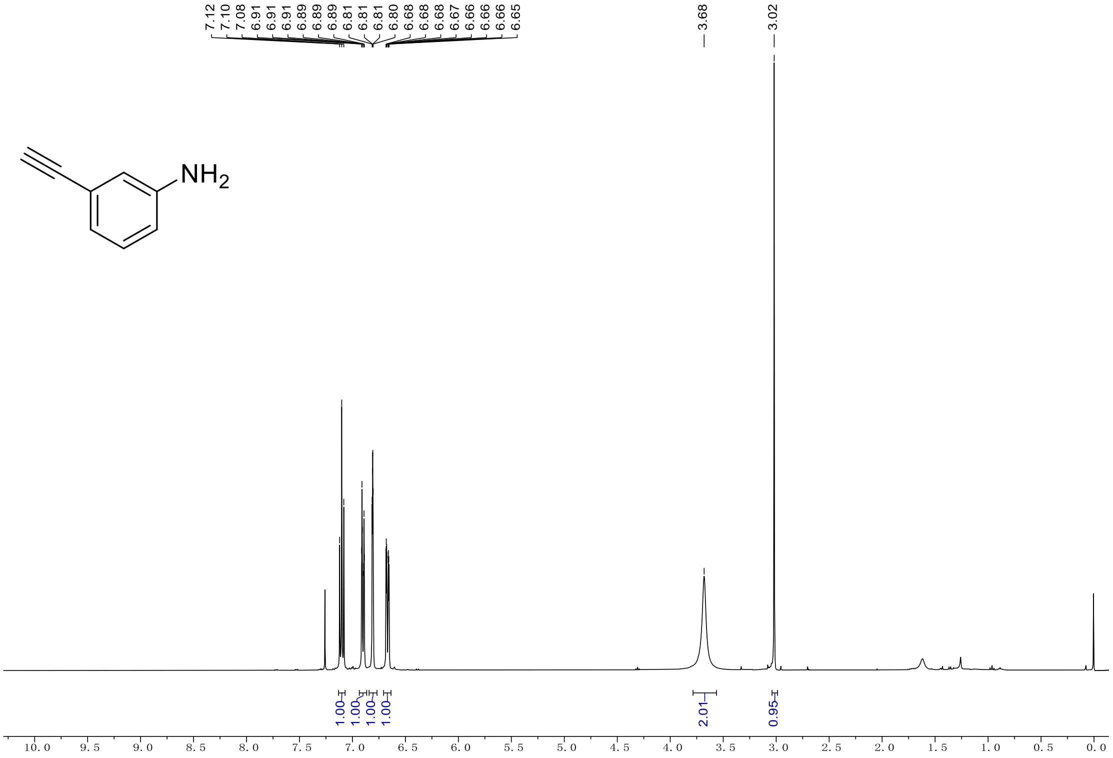
^{1}H NMR of **2v** ($CDCl_3$, 400 MHz)



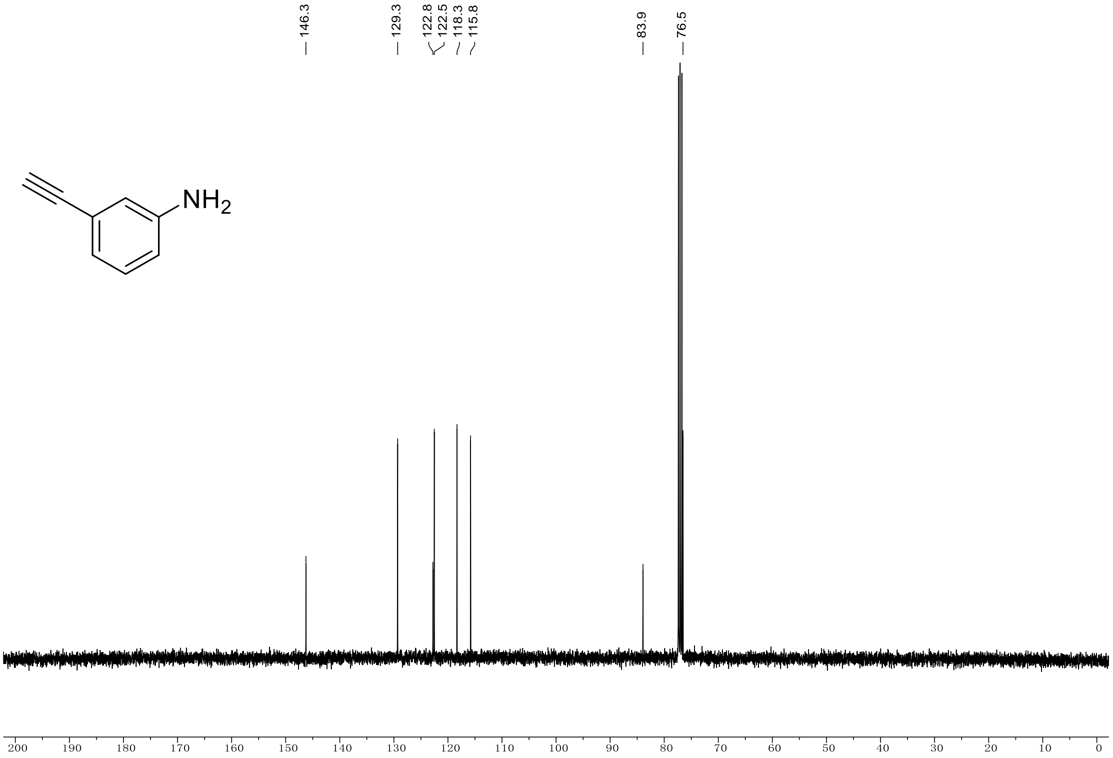
^{13}C NMR of **2v** ($CDCl_3$, 100 MHz)



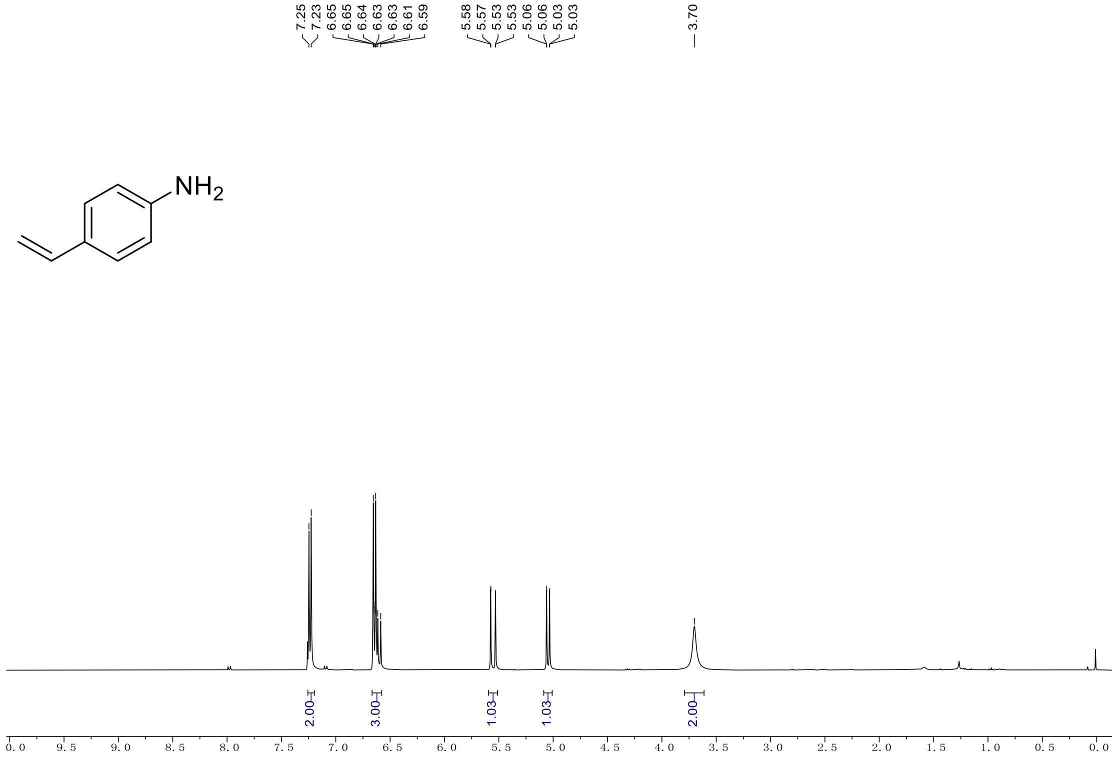
^{1}H NMR of **2w** (CDCl$_3$, 400 MHz)



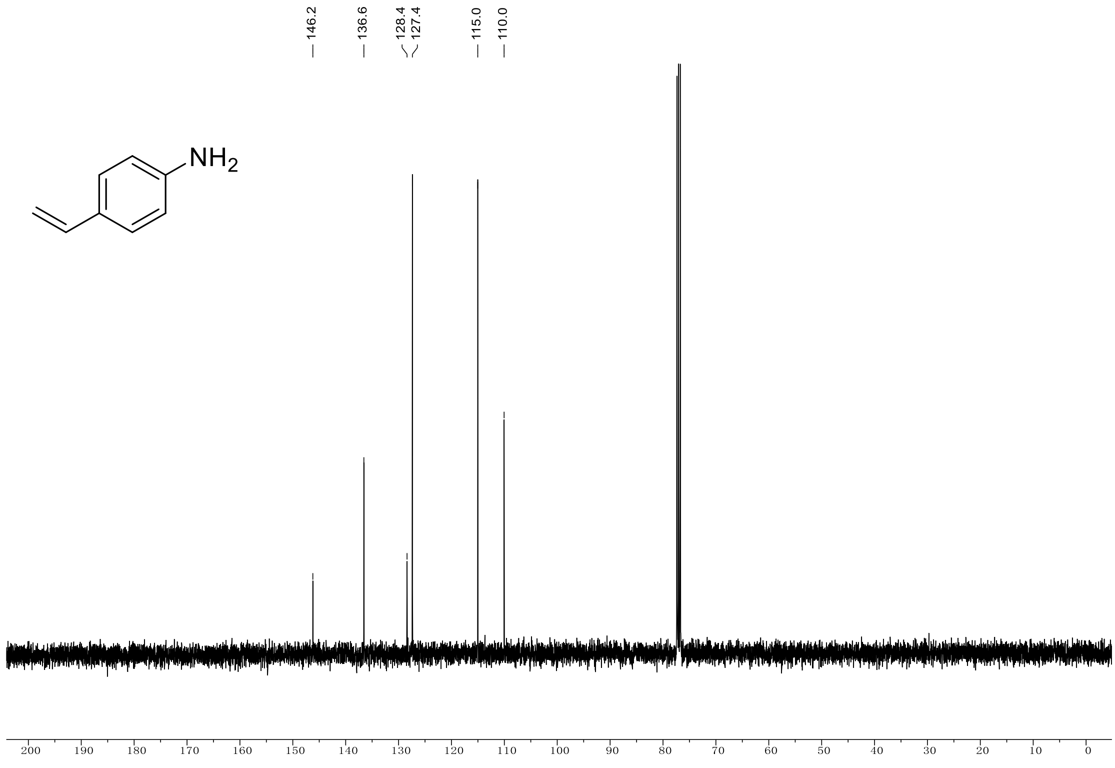
^{13}C NMR of **2w** (CDCl$_3$, 100 MHz)



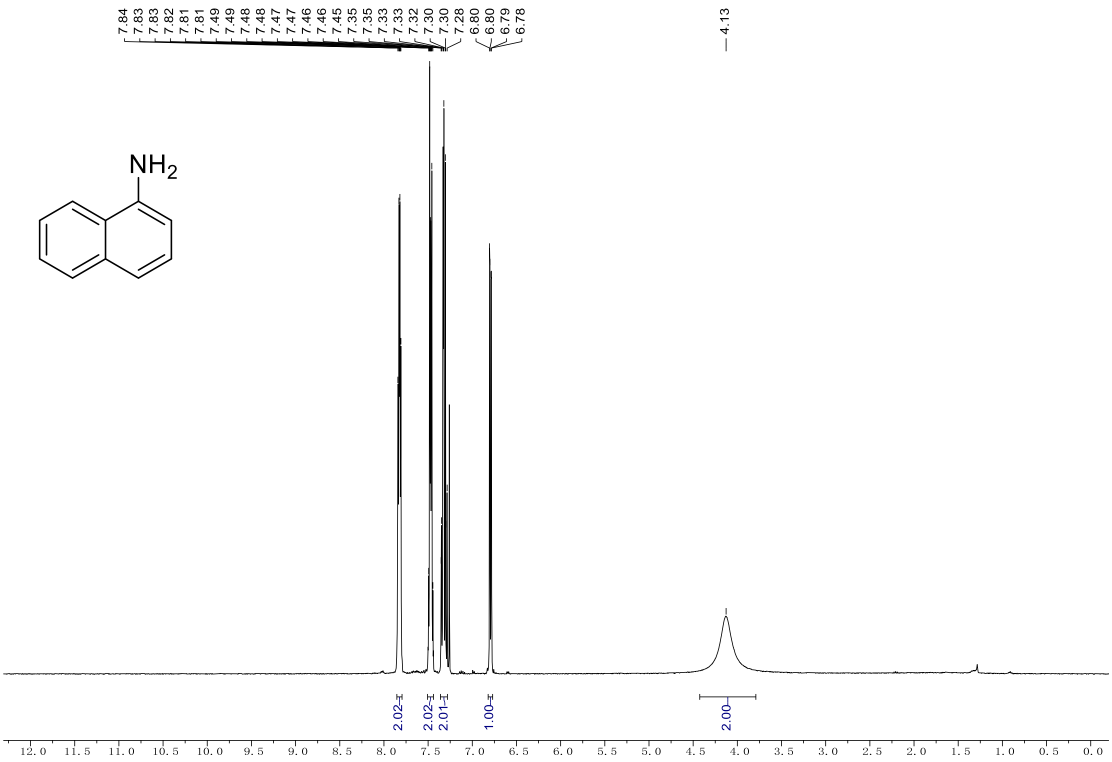
^{1}H NMR of **2x** (CDCl$_3$, 400 MHz)



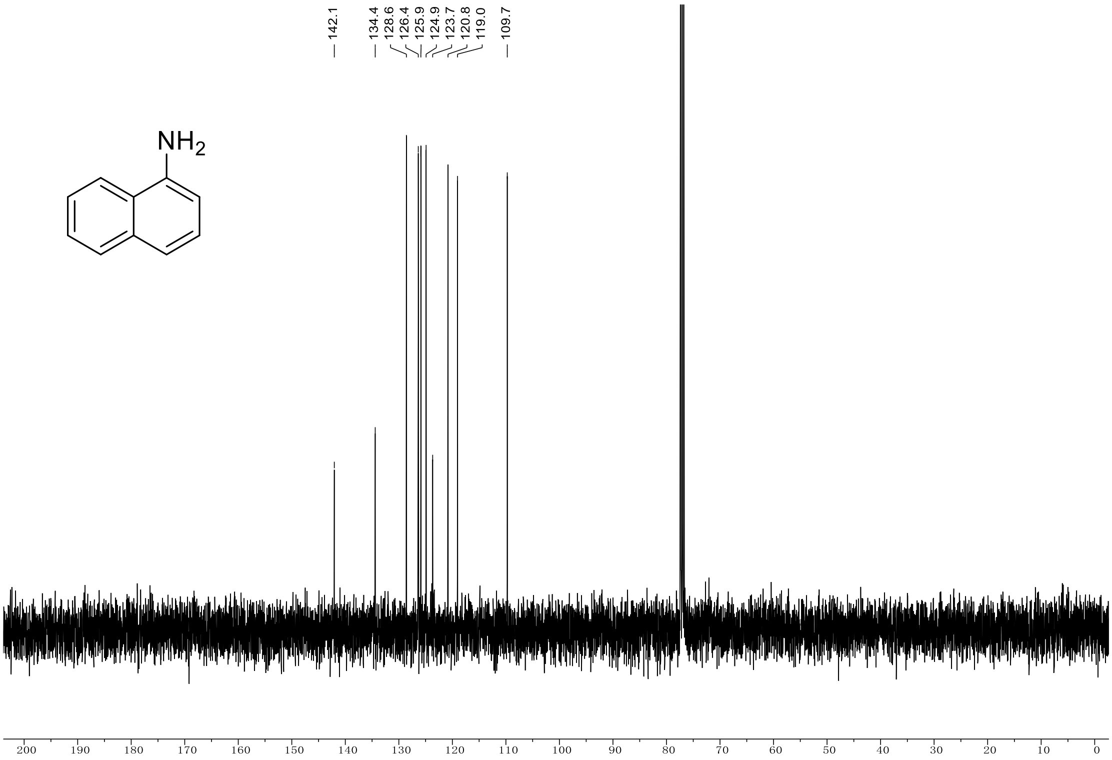
^{13}C NMR of **2x** (CDCl$_3$, 100 MHz)



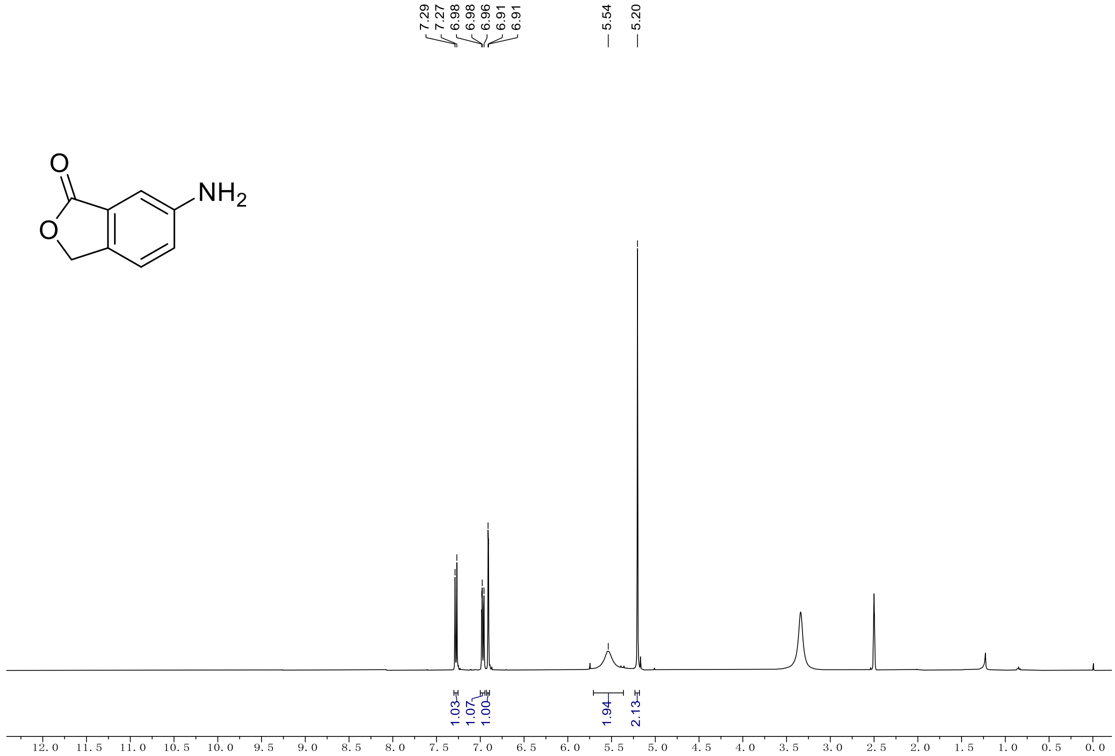
^{1}H NMR of **2y** (CDCl$_3$, 400 MHz)



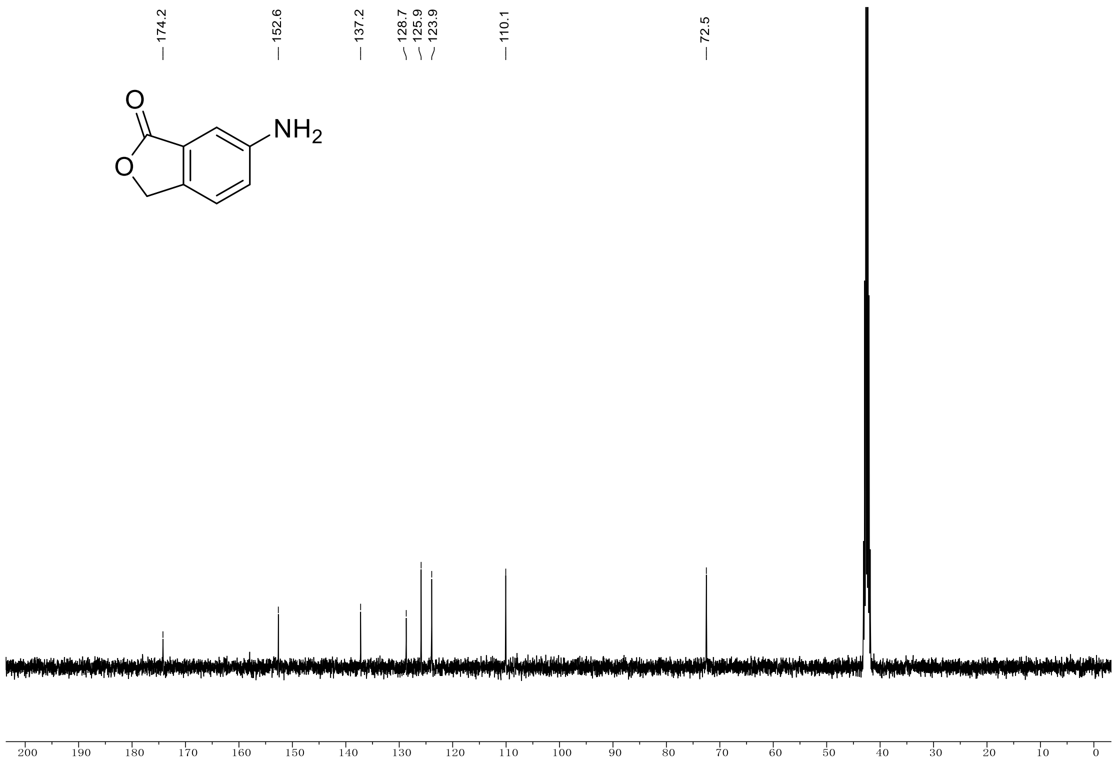
^{13}C NMR of **2y** (CDCl$_3$, 100 MHz)



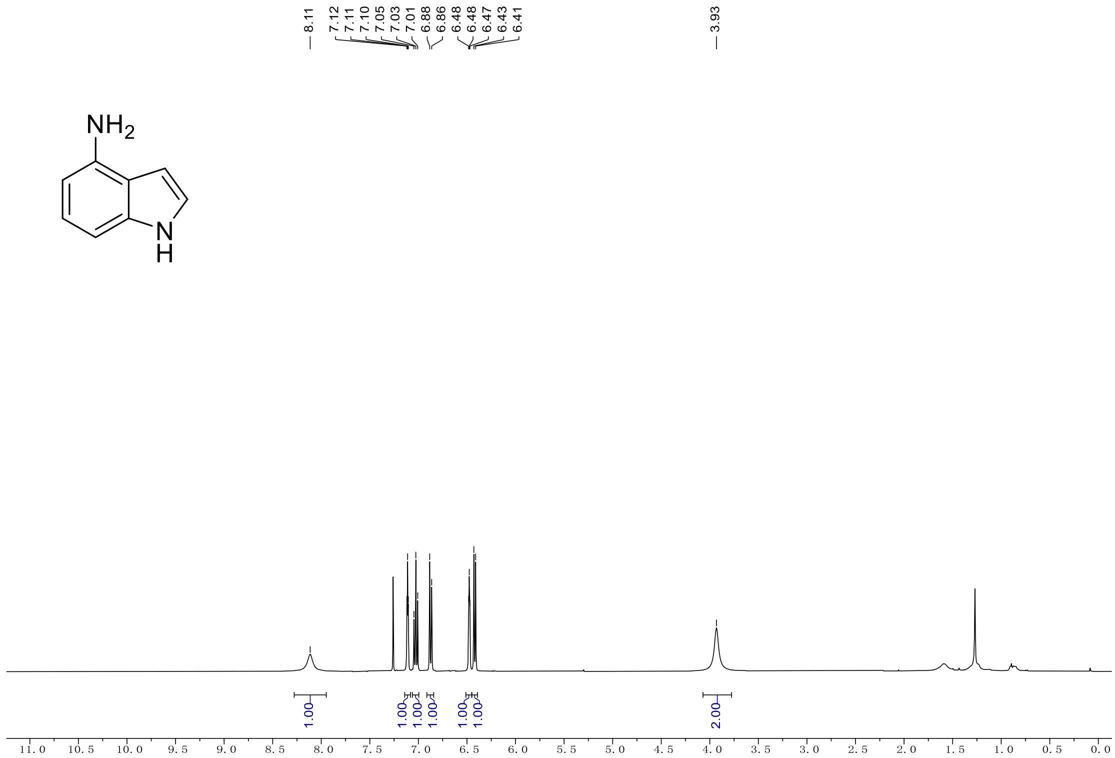
^{1}H NMR of **2z** (DMSO-*d*$_6$, 400 MHz)



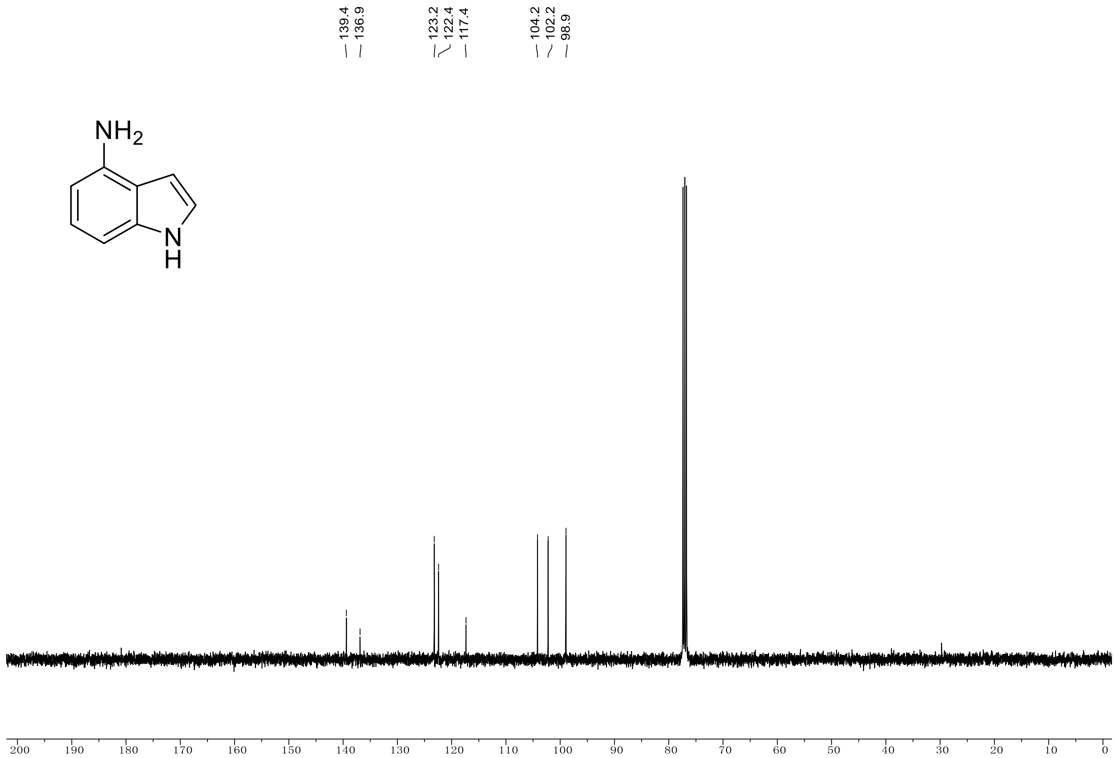
^{13}C NMR of **2z** (DMSO-*d*$_6$, 100 MHz)



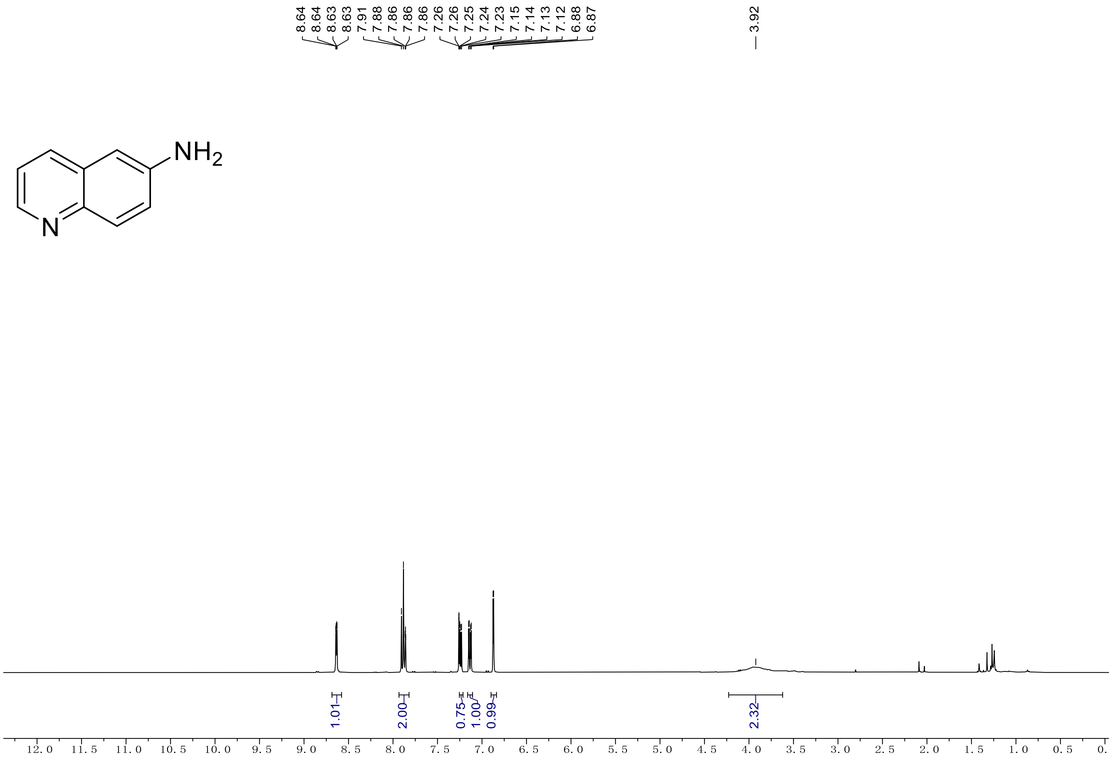
^{1}H NMR of **2a** ($CDCl_3$, 400 MHz)



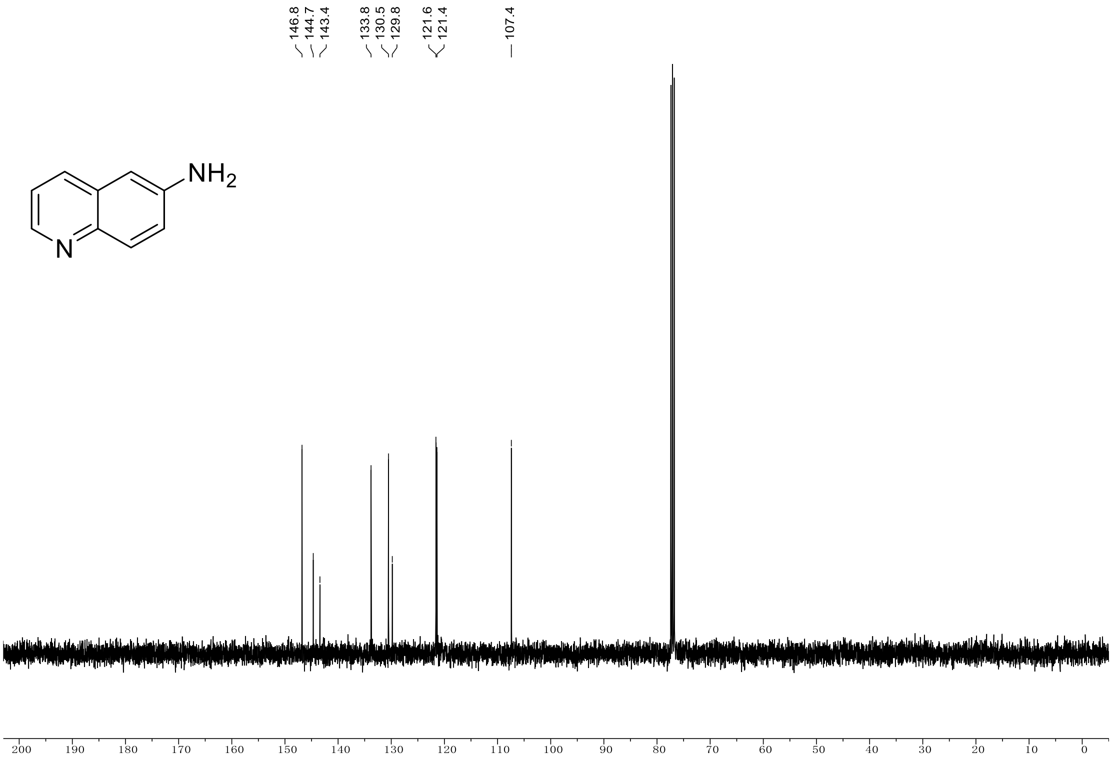
^{13}C NMR of **2a** ($CDCl_3$, 100 MHz)



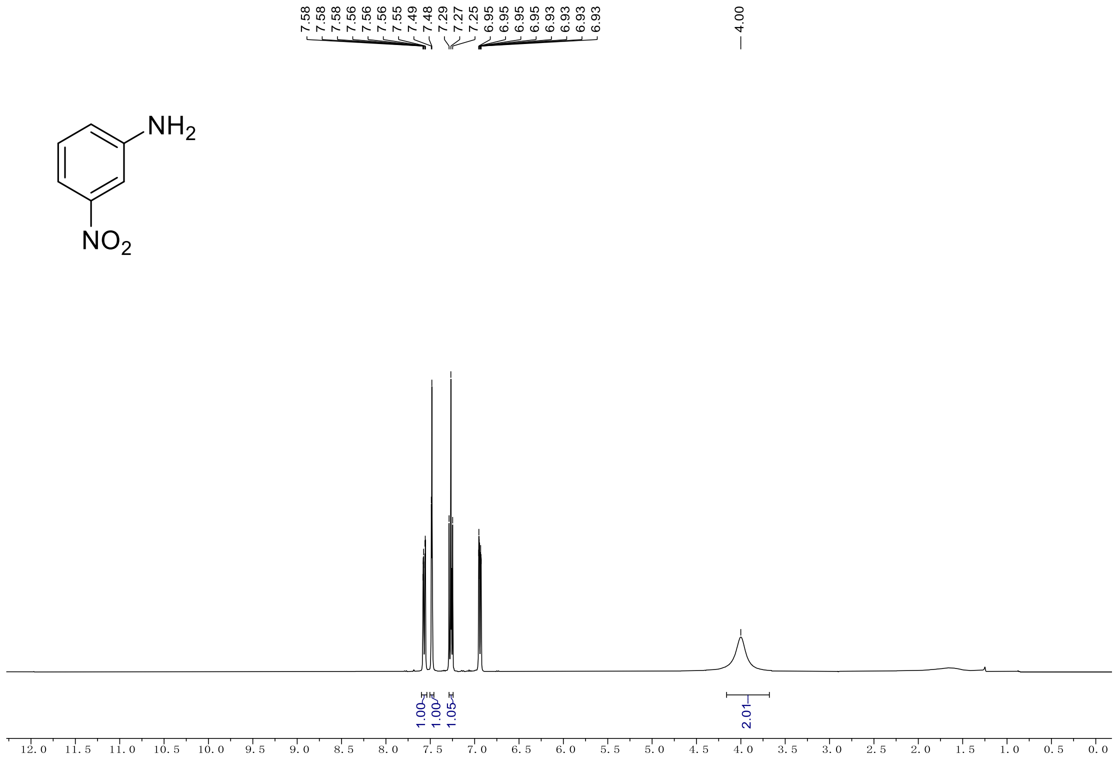
^{1}H NMR of **2β** ($CDCl_3$, 400 MHz)



^{13}C NMR of **2β** ($CDCl_3$, 100 MHz)



^{1}H NMR of **2γ** (CDCl$_3$, 400 MHz)



^{13}C NMR spectra of **2γ** (CDCl$_3$, 100 MHz)