Supporting Information for

Indium-Catalyzed Hydrosilylation of Nitroarenes to Aromatic Amines

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1. X-ray crystallographic analysis.

Single crystals of metal complexes **1**, **2,** and **3** were grown from a concentrated solution of THF/pentane at room temperature. A crystal of suitable dimensions of complexes **1**, **2,** and **3** was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil. All the crystals **1**, **2,** and **3** were measured at 293 K. All measurements were made on a Bruker Apex-IV Photon II detector (0.71073 Å) radiation. Crystal data and structure refinement parameters of complexes **1**, **2,** and **3** are summarized in Table S1. The structures were solved by direct methods (SIR2004[1] and refined on F^2 by full-matrix least-squares methods, using SHELXL-2016/6.[2] Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(Fo^2 - Fc^2)^2]$ ($w = 1 / [\sigma^2 (Fo^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(Fo^2,0) + 2Fc^2) / 3$ with $\sigma^2(Fo^2)$ from counting statistics. The function R_1 and wR_2 were $(\Sigma||Fo| - |Fc||) / \Sigma|Fo|$ and $[\Sigma w(Fo^2 - Fc^2)^2 / \Sigma(wFo^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecules of **1**, **2,** and **3**. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2374056 (**1**), 2374055 (**2**) and 2374057 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: + (44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

2. Table S1. Crystallographic data and refinement parameters of **1**, **2** and **3**.

Crystal Parameters	**1**	**2**	**3**
CCDC No.	2374056	2374055	2374057
Empirical Formula	$C_{18}H_{22}Cl_2InN_2OPS$	$C_{23}H_{24}Cl_3InN_2O$	$C_{22}H_{32}ClInN_6O_2$
Formula weight	531.12	565.61	562.80
T (K)	273(2) K	273(2) K	273(2) K
λ (Å)	0.71073 Å	0.71073 Å	0.71073 Å
Crystal System	Monoclinic	Triclinic	Monoclinic
Space group	*C*c	*P* -1	$P\ 2_1/c$
a (Å)	21.0292(11)	8.8110(3)	18.309(2)
b (Å)	7.9555(4)	14.1384(5)	9.8212(9)
c (Å)	14.0135(6)	19.8289(6)	15.5256(14)
α (°)	90	80.3650(10)	90
β (°)	112.329(2)	87.6050(10)	115.026(3)
γ (°)	90	82.2660(10)	90
V ($Å^3$)	2168.64(18)	2412.69(14)	2529.7
Z	4	4	4
D_{cal} g cm^{-3}	1.627	1.557	1.478
μ (mm^{-1})	1.516	1.329	1.069
F(000)	1064	1136	1152
Theta range for	2.979 to 27.169	2.084 to 27.110	2.410 to 27.163
2Data collection	Deg.	Deg.	Deg.
Limiting indices	$-26 \le h \le 26$	$-11 \le h \le 10$,	$-23 \le h \le 23$
	$-9 \le k \le 10$	$-18 \le k \le 17$,	$-12 \le k \le 12$
	$-17 \le l \le 17$	$-25 \le l \le 25$	$-19 \le l \le 19$
Reflections	19543/4746	48585/10647	76971/5619
Collected/unique	[R(int) = 0.0517]	[R(int) = 0.0439]	[R(int) = 0.0749]
Completeness to theta	99.6 %	99.9 %	100 %
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Refinement method	Full-matrix	Full-matrix	Full-matrix
	least-squares on F^2	least-squares on F^2	least-squares on F^2
Data/ restraints/ parameters	4746 / 2 / 236	10647 / 0 / 541	5619 / 0 / 289
Goodness-of-fit on F^2	1.016	1.020	1.019
Final R indices [I>2σ(I)]	R_1 = 0.0289, wR_2 = 0.0677	R_1 = 0.0374, wR_2 = 0.0837	R_1 = 0.0309, wR_2 = 0.0611
R indices (all data)	R_1 = 0.0320, wR_2 = 0.0688	R_1 = 0.0757, wR_2 = 0.0968	R_1 = 0.0536, wR_2 = 0.0676
Absolute structure parameter	0.819 and -0.723	0.644 and -0.526	0.444 and -0.377

3. NMR spectra of metal complexes

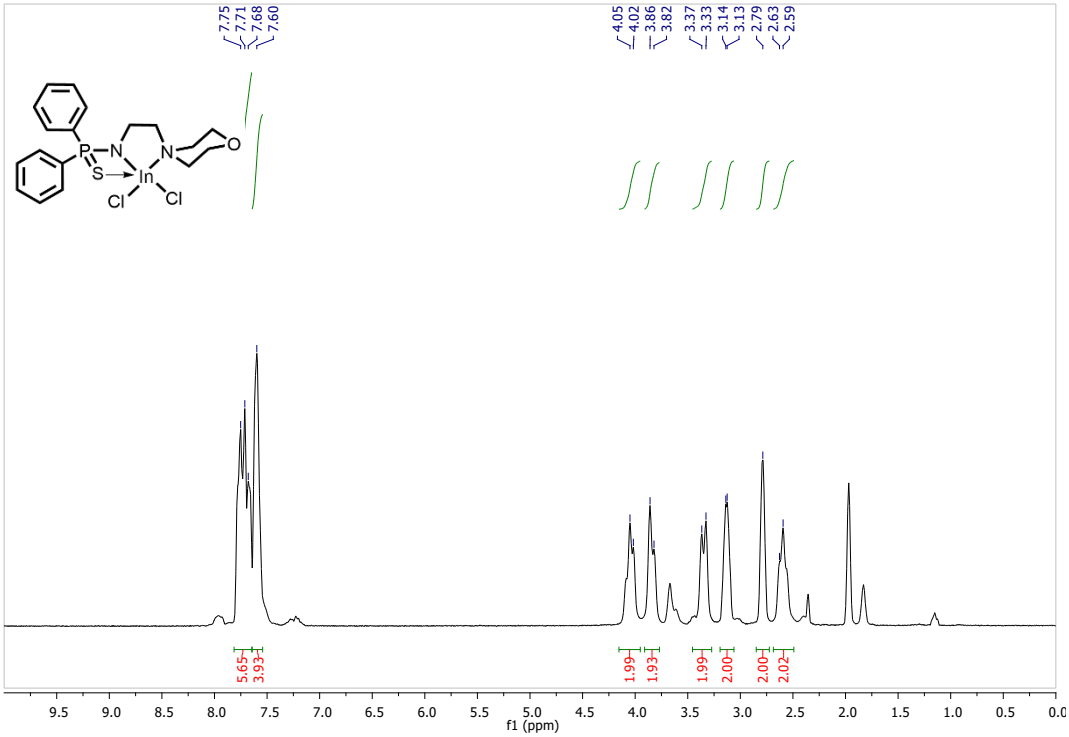


Figure S1. ^{1}H NMR Spectrum (300 MHz, 25 °C, CD_3CN) of indium metal complex **1**. THF-solvent peaks at 3.60 and 1.84 ppm. CD_3CN peak at 1.94 ppm.

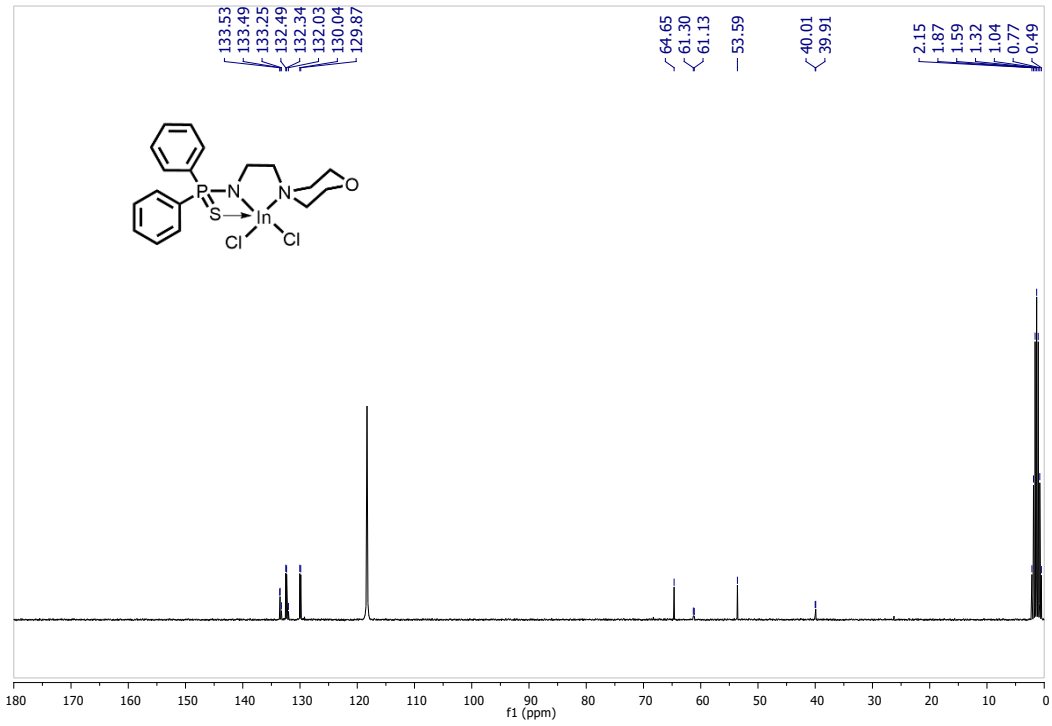


Figure S2. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, CD_3CN) of indium metal complex **1**. THF-solvent peaks at 64.6, 26.3 ppm. CD_3CN peak at 118.26 and 1.32 ppm.

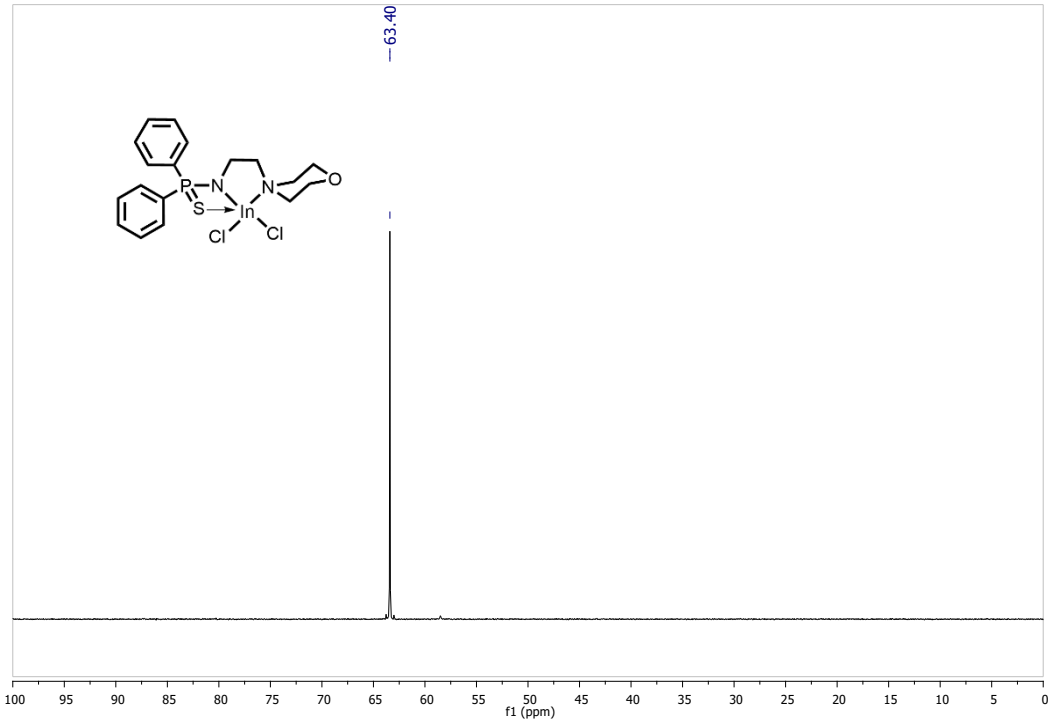


Figure S3. $^{31}P\{^{1}H\}$ NMR (121.5 MHz, 25 °C, CD_3CN) of indium metal complex **1**.

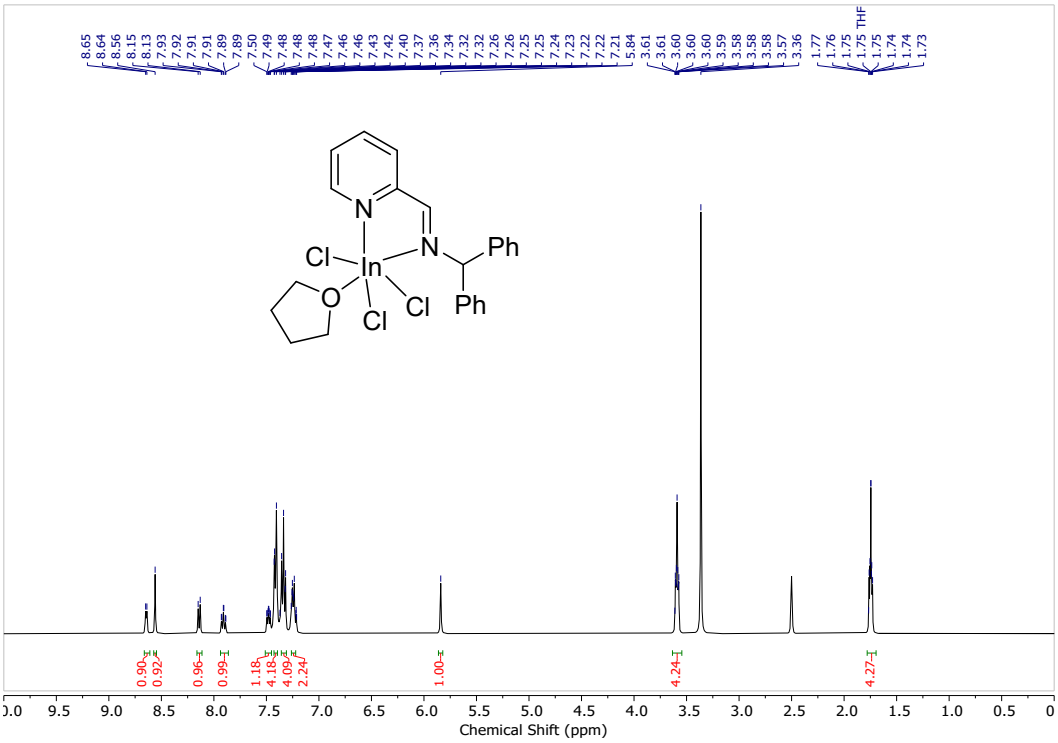


Figure S4. ^{1}H NMR spectrum (400 MHz, 25 °C, DMSO-d_6) of indium metal complex **2**. THF-solvent peak at 3.60 and 1.75 ppm. DMSO-d_6 at 2.50 ppm, H_2O peak at 3.33 ppm.

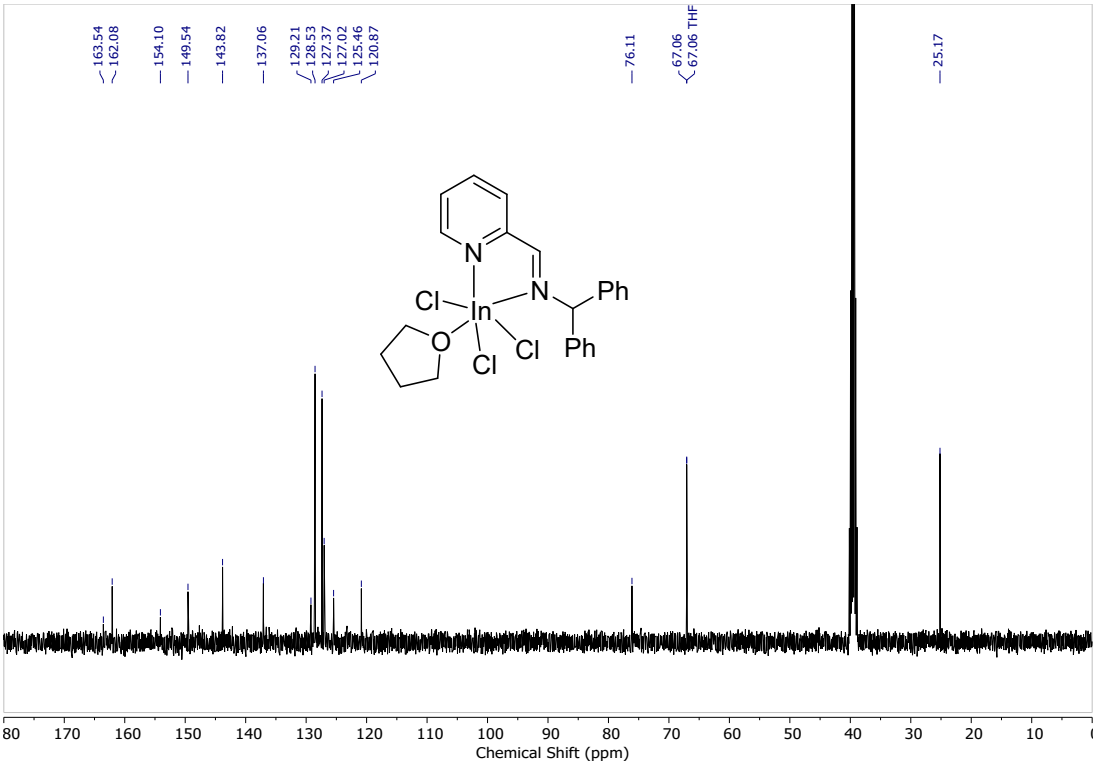


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, DMSO-d_6) of indium metal complex 2. THF-solvent peak at 67.1 and 25.2 ppm. DMSO-d_6 at 39.52 ppm.

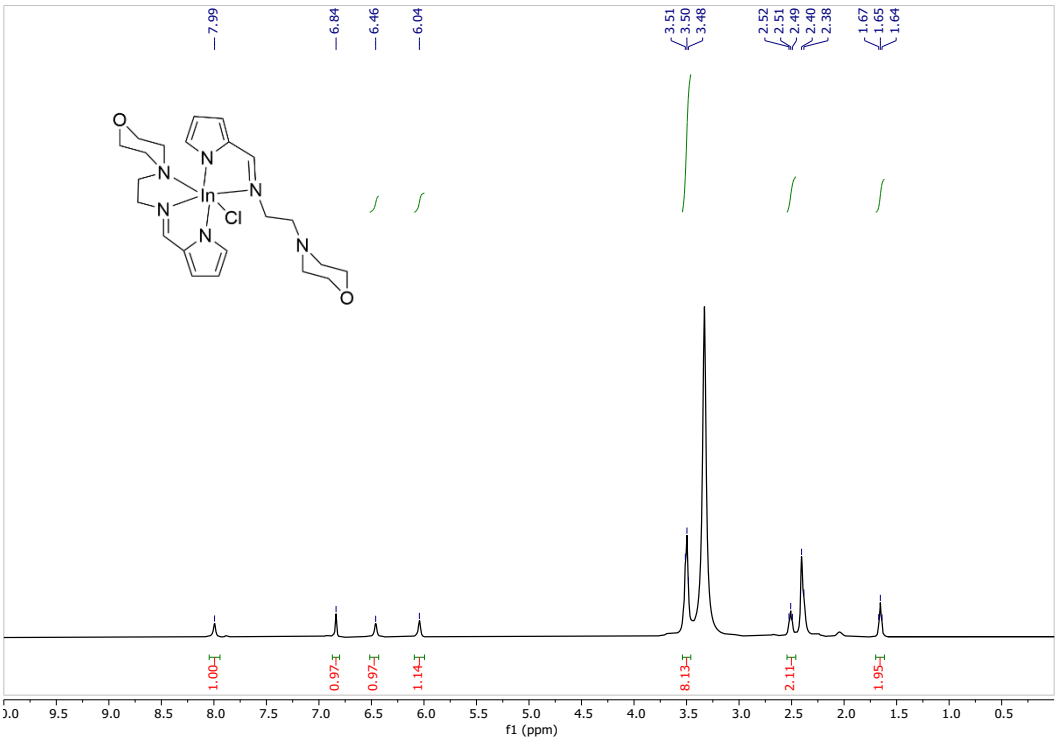


Figure S6. ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6) of indium metal complex **3**. DMSO-d_6 at 2.50 ppm, H_2O peak at 3.33 ppm.

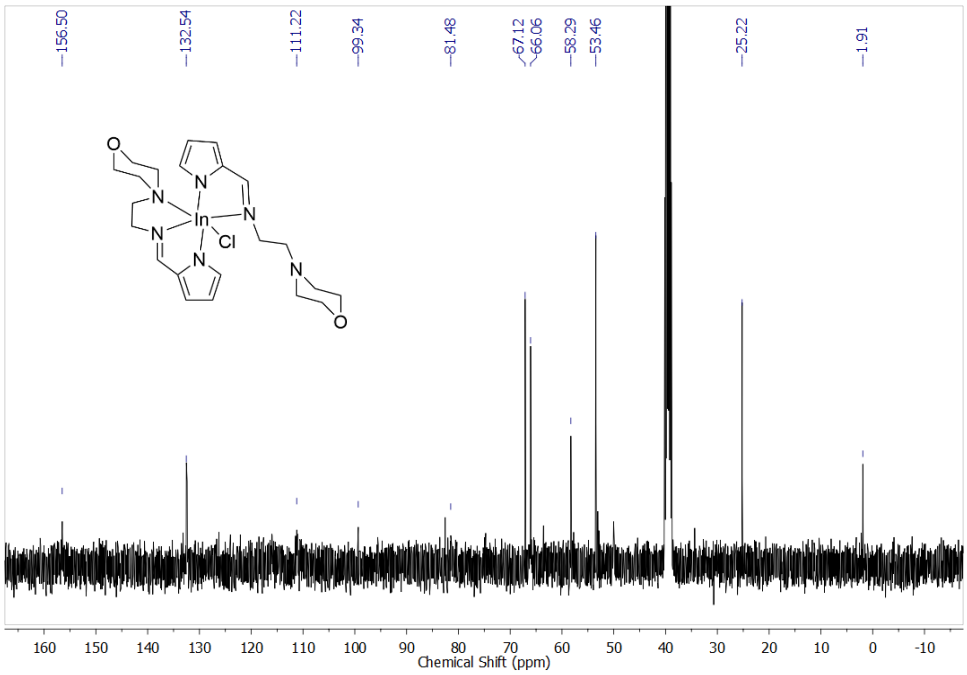
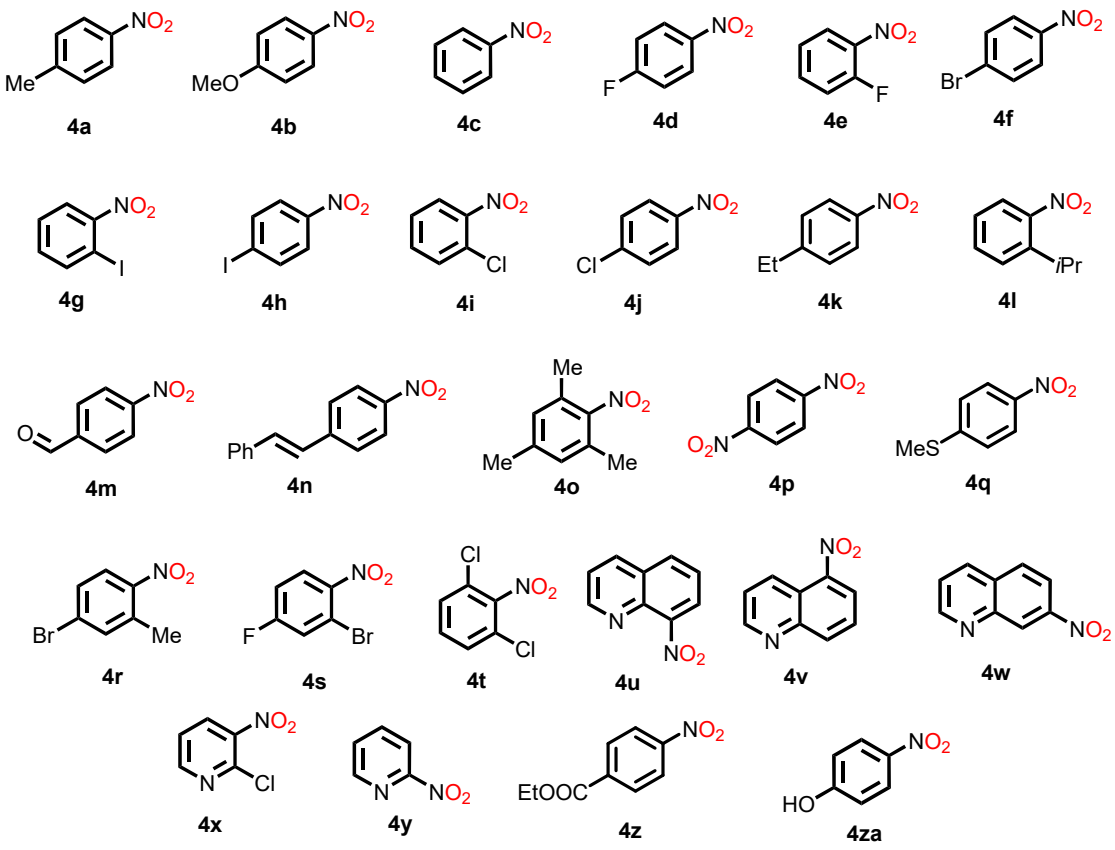


Figure S7. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, DMSO-d_6) of indium metal complex **3**. DMSO-d_6 at 39.5 ppm

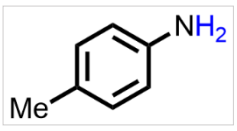
4. Nitro compounds used in this study



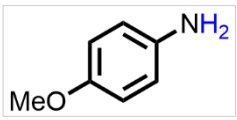
5. NMR data for anilines

General procedure for the reduction of nitroarenes

In a 25 mL Schlenk flask, indium metal complex **1** (5 mol%), nitroarene (0.5 mmol), NaI (10 mol%), and $PhSiH_3$ (1.0 mmol) were added inside glovebox. Then, toluene (0.5 mL) was added to it, and added to the reaction mixture to stir at 100 °C (preheated) for 12 h. The reaction mixture was allowed to come at room temperature and methanol/water was added to it. The reaction mixture was extracted in DCM and the organic layer was separated which was dried over anhydrous Na_2SO_4. The solvent was evaporated and the reaction mixture was purified by column chromatography using silica and a mixture of hexane and ethyl acetate as an eluent. The obtained products were characterized by using NMR spectroscopy.

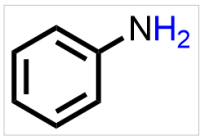


p-Toluidine, **5a**.[3] Yield: 88% (44 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 6.89 (m, 2H), 6.54 (m, 2H), 3.45 (b, 3H), 2.16 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 143.9, 129.8, 127.8, 115.3, 20.5 ppm.

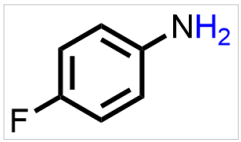


p-Anisidine, **5b**.[3] Yield: 88% (54 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 6.75 - 6.73 (d, 2H, J = 6 Hz), 6.65 - 6.63 (d, 2H, J = 6 Hz), 3.74 (s, 3H),

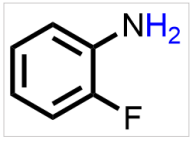
3.41 (b, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ_C 152.9, 140.1, 116.5, 114.9, 55.9 ppm.



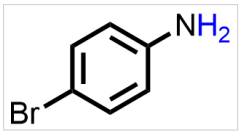
Aniline, **5c**.[3] Yield: 89% (41 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.13 - 7.10 (m, 2H), 6.74 - 6.71 (m, 1H), 6.61 - 6.59 (m, 2H), 3.54 (b, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ_C 146.4, 129.2, 118.4, 115.1 ppm.



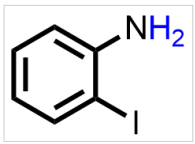
p-Fluoroaniline, **5d**.[3] Yield: 76% (42 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.89 - 6.83 (m, 2H), 6.64 - 6.59 (m, 2H), 3.34 (b, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ_C 157.7, 155.3, 142.5 (d, J = 2 Hz), 116.2 (d, J = 7 Hz), 115.9, 115.6 ppm.



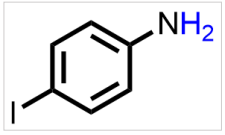
o-Fluoroaniline, **5e**.[3] Yield: 78% (43 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.00 - 6.90 (m, 2H), 6.79 - 6.68 (m, 2H), 3.70 (b, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ_C 153.2, 150.0, 134.5 (d, J = 12.75 Hz), 124.4 (d, J = 3.75 Hz), 118.4 (d, J = 6.0 Hz), 116.9, 115.1, 114.9 ppm.



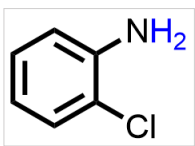
p-Bromoaniline, **5f**.[3] Yield: 83% (71 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.25 - 7.22 (m, 2H), 6.56 (d, 2H, J = 6 Hz), 3.41 (b, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ_C 145.51, 132.14, 116.85, 110.36 ppm.



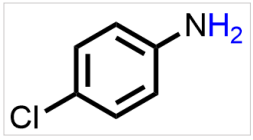
o-Iodoaniline, **5g**.[3] Yield: 78% (85 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.64 - 7.62 (m, 1H), 713 - 7.11 (m, 1H), 6.75 - 6.73 (m, 1H), 6.47 - 6.44 (m, 1H), 4.07 (b, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ_C 146.9, 139.1, 129.5, 120.1, 114.8, 84.3 ppm.



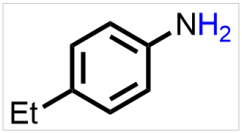
p-Iodoaniline, **5h**.[3] Yield: 86% (94 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.42 – 7.40 (m, 2H), 6.48 – 6.45 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ_C 146.1, 137.9, 117.4, 79.4 ppm.



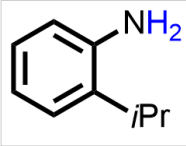
o-Chloroaniline, **5i**.[3] Yield: 82% (52 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.21 - 7.19 (m, 1H), 7.01 - 6.99 (m, 1H), 6.66 - 6.62 (m, 2H), 3.97 (b, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ_C 142.9, 129.4, 127.6, 119.2, 118.9, 115.9 ppm.



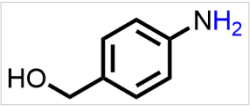
p-Chloroaniline, **5j**.[3] Yield: 85% (54 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.10 - 7.07 (d, 2H, J = 9 Hz), 6.60 - 6.57 (d, 2H, J = 9 Hz), 3.64 (b, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ_C 145.1, 129.2, 123.2, 116.3 ppm.



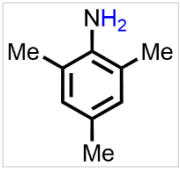
p-Ethylaniline, **5k**.[3] Yield: 75% (45 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.07 (d, J = 8 Hz, 2H), 6.69 (d, J = 8 Hz, 2H), 3.52 (b, 2H), 2.62 (q, J = 8 Hz, 2H), 1.25 (t, J = 8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ_C 144.1, 134.5, 128.6, 115.3, 28.0, 16.0 ppm.



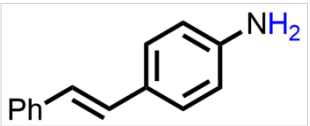
2-Isopropylaniline, **5l**.[3] Yield: 84% (57 mg). δ_H 7.14 - 7.12 (m, 1H), 7.01 (m, 1H), 6.78 (m, 1H), 6.67 - 6.65 (m, 1H), 3.62 (b, 2H), 2.90 - 2.87 (m, 1H), 1.25 (d, 6H, J = 6 Hz). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ_C 143.4, 132.7, 126.6, 125.5, 119.1, 115.9, 22.7, 22.4 ppm.



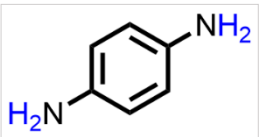
(4-Aminophenyl)methanol, **5m**.[3] Yield: 78% (48 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.13 - 7.12 (m, 2H), 6.67 – 6.65 (m, 2H), 4.52 (s, 2H), 3.53 (b, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ_C 146.1, 131.2, 128.8, 115.2, 65.3 ppm.



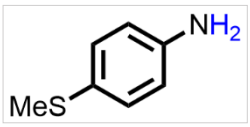
2,4,6-trimethylaniline, **5n**.[3] Yield: 82% (54 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 6.74 (m, 2H), 3.39 (s, 2H), 2.19 (s, 3H), 2.12 (s, 6H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ_C 140.1, 128.9, 127.1, 121.8, 20.4, 17.6 ppm.



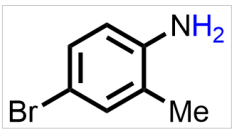
4-[(*E*)-2-Phenylethenyl]aniline, **5o**.[3] Yield: 80% (80 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.46 (m, 2H), 7.32 - 7.21 (m, 4H), 7.24 - 7.21 (m, 1H), 7.06 – 6.89 (m, 2H), 6.87 (d, 2H, J = 6 Hz), 3.71 (b, 2H). 1.26 (Hexane-solvent). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ_C 146.3, 138.1, 128.8, 128.7, 128.2, 127.9, 127.0, 126.2, 125.2, 115.3 ppm.



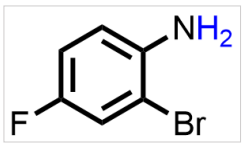
Benzene-1,4-diamine, **5p**.[3] Yield: 71% (38 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.57 (m, 4H), 3.33 (b, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ_C 138.7, 116.9 ppm.



4-(Methylthio)aniline, **5q**.[3] Yield: 78% (54 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.11 (m, 2H), 6.56 (m, 2H), 3.60 (b, 2H), 2.34 (s, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ_C 145.1, 131.1, 125.8, 115.8, 18.8 ppm.

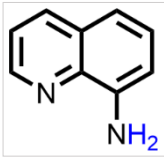


2-Methyl-4-bromoaniline, **5r**.[3] Yield: 85% (78 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.15 - 7.09 (m, 2H), 6.54 - 6.51 (m, 1H), 3.58 (b, 2H), 2.11 (s, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ_C 143.7, 132.9, 129.7, 124.5, 116.5, 110.2, 17.3 ppm.

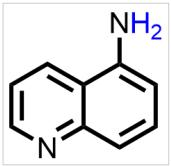


2-Methyl-4-bromoaniline, **5s**.[3] Yield: 78% (74 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.18 - 7.17 (m, 1H), 6.89 - 6.83 (m, 1H), 6.73 - 6.71 (m, 1H), 3.92 (b, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ_C 156.9, 153.7, 140.7, 119.3, 119.0, 116.0, 116.0 (d, J = 7.5 Hz), 115.4, 115.1, 108.6 (d, J = 9.75 Hz) ppm.

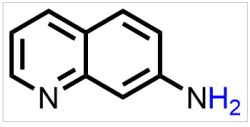
2,6-Dichloroaniline, **5t**.[3] Yield: 80% (64 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.18 - 7.15 (m, 2H), 6.63 - 6.58 (m, 1H), 4.44 (b, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ_C 140.2, 127.9, 119.8, 118.2 ppm.



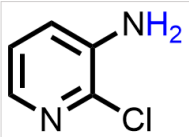
Quinoline-8-amine, **5u**.[3] Yield: 80% (58 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.76 - 8.75 (m, 1H), 8.06 - 8.04 (m, 1H), 7.36 - 7.31 (m, 2H), 7.15 - 7.13 (m, 1H), 6.93- 6.91 (m, 1H), 4.99 (b, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ_C 147.5, 144.1, 138.5, 136.1, 128.9, 127.5, 121.5, 116.1, 110.1 ppm.



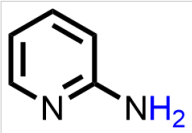
Quinoline-5-amine, **5v**.[3] Yield: 78% (56 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.78 (b, 1H), 8.08 (b, 1H), 7.42 (b, 3H), 7.23 - 7.22 (b, 1H), 6.71 (b, 1H), 4.04 (b, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ_C 150.3, 149.2, 142.5, 130.1, 129.7, 120.1, 119.7, 118.8, 110.1 ppm.



Quinoline-7-amine, **5w**.[3] Yield: 70% (50 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.73 (b, 1H), 7.95 (b, 1H), 7.58 - 7.57 (b, 1H), 7.23 (b, 1H), 7.11 (b, 1H), 6.97 (b, 1H), 4.23 (b, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ_C 150.6, 149.9, 147.9, 135.8, 128.9, 122.3, 118.8 117.7, 108.9 ppm.



2-Chloropyridin-3-amine, **5x**.[3] Yield: 75% (48 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.78 (b, 1H), 7.04 (b, 2H), 4.17 (b, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ_C 139.8, 138.6, 136.9, 123.4, 122.5 ppm.



Pyridin-2-amine, **5y**.[3] Yield: 78% (37 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 80.6 - 8.05 (m, 1H), 7.41 - 7.37 (m, 1H), 6.62 - 6.59 (m, 1H), 6.48 - 6.46 (d, 2H, J = 8 Hz). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ_C 158.6, 147.9, 137.7, 113.8, 108.6 ppm.

6. NMR spectra of compounds 5a-5x.

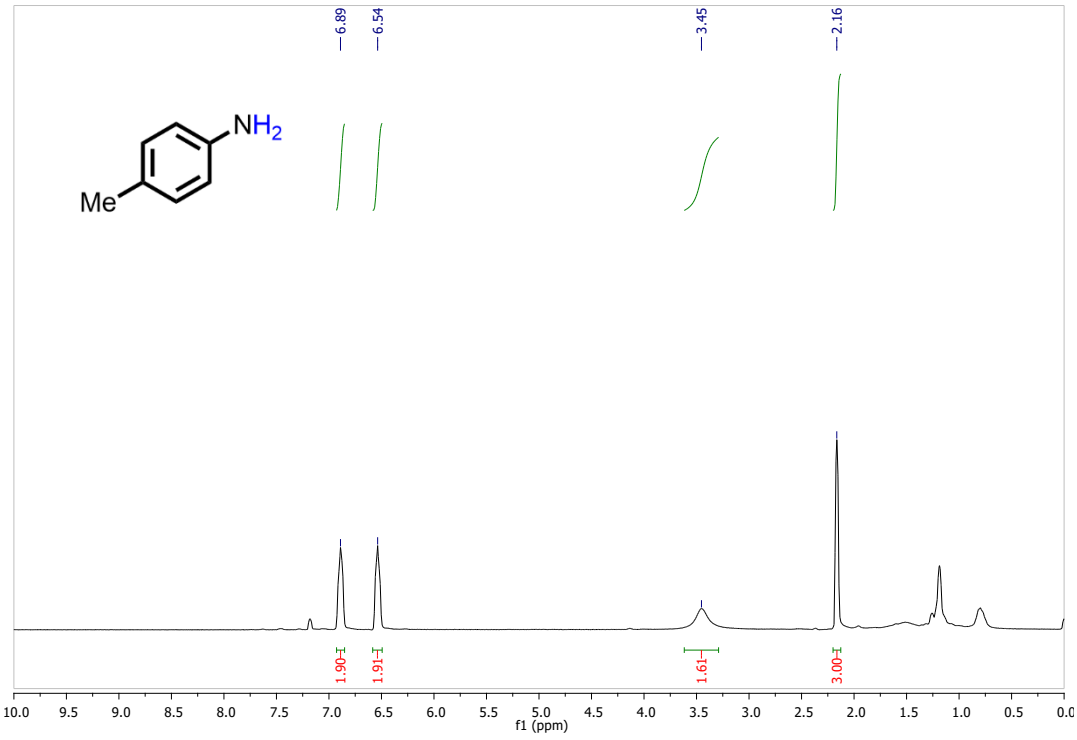


Figure S8. ^{1}H NMR Spectrum (300 MHz, 25 °C, $CDCl_3$) of **5a**.

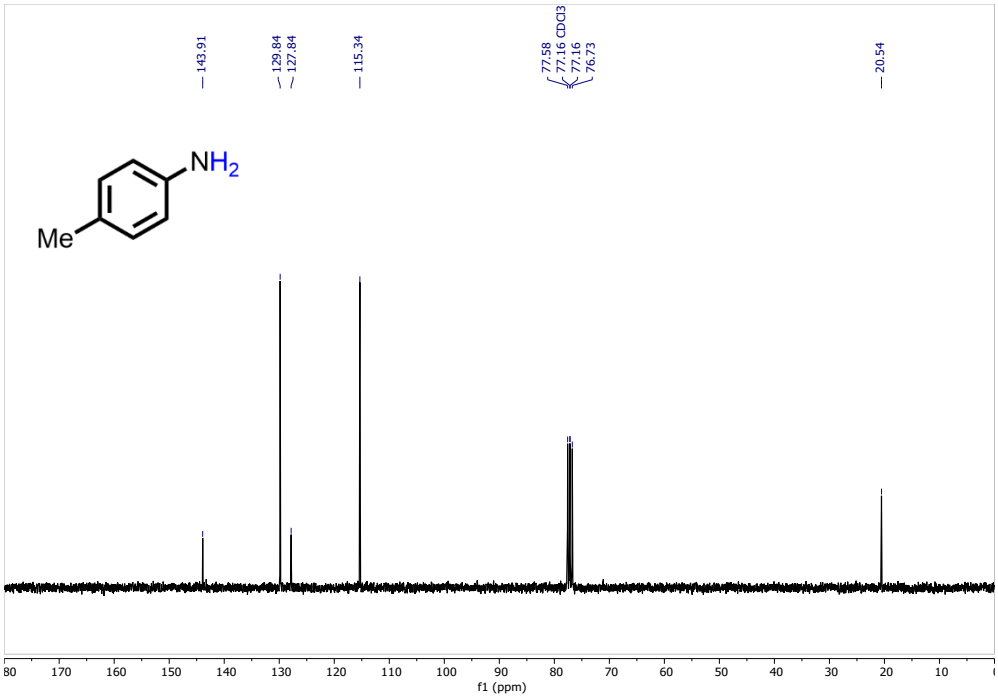


Figure S9. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, 25 °C, $CDCl_3$) of **5a**.

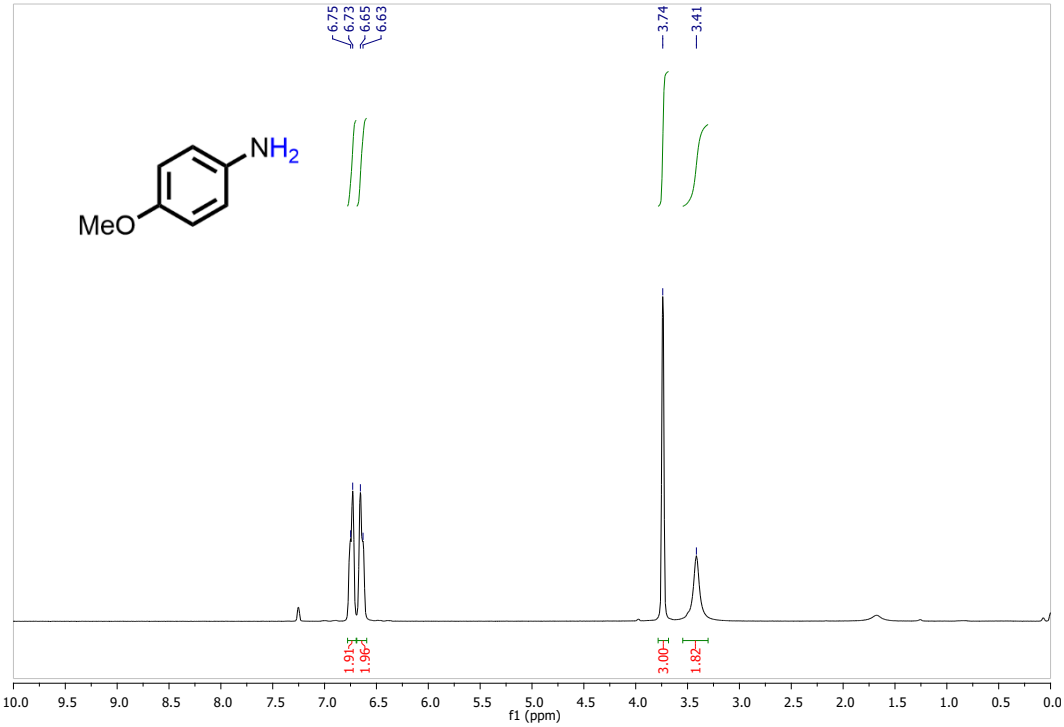


Figure S10. ^{1}H NMR Spectrum (300 MHz, 25 °C, $CDCl_3$) of **5b**.

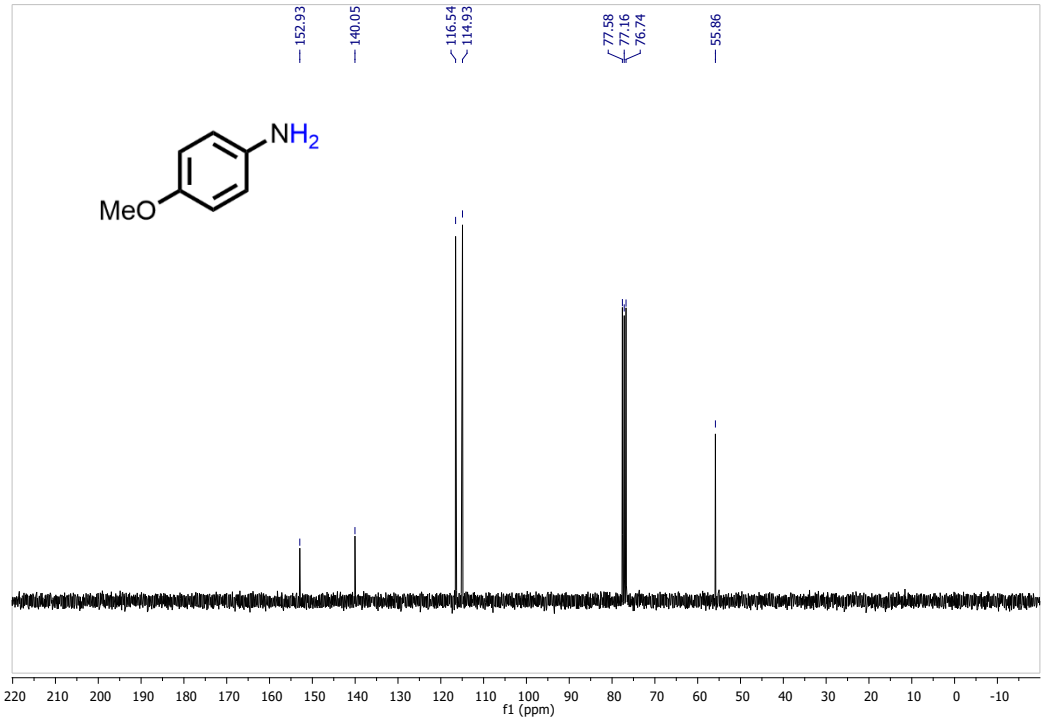


Figure S11. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, 25 °C, $CDCl_3$) of **5b**.

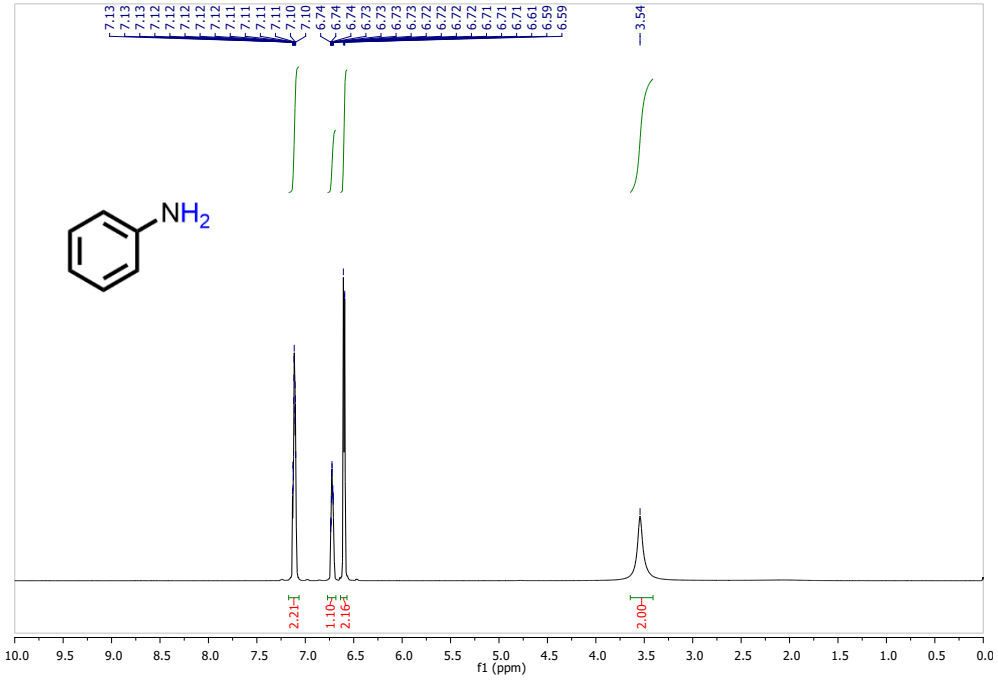


Figure S12. ^{1}H NMR Spectrum (400 MHz, 25 °C, $CDCl_3$) of **5c**.

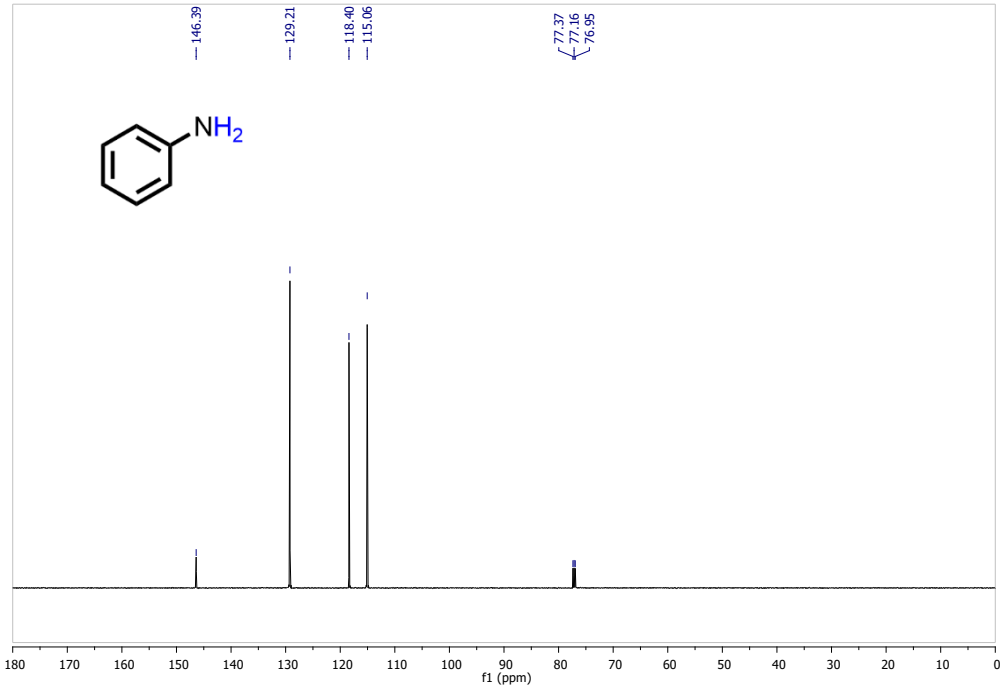


Figure S13. $^{13}C\{^{1}H\}$ NMR Spectrum (100 MHz, 25 °C, $CDCl_3$) of **5c**.

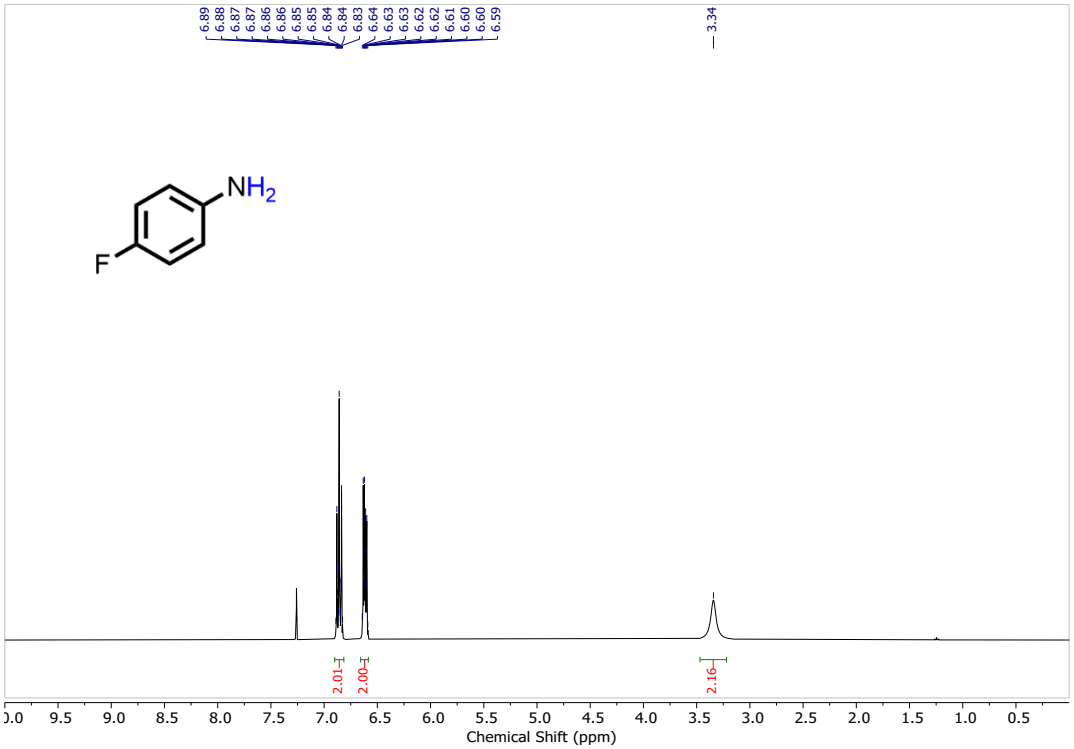


Figure S14. ^{1}H NMR Spectrum (400 MHz, 25 °C, $CDCl_3$) of **5d**.

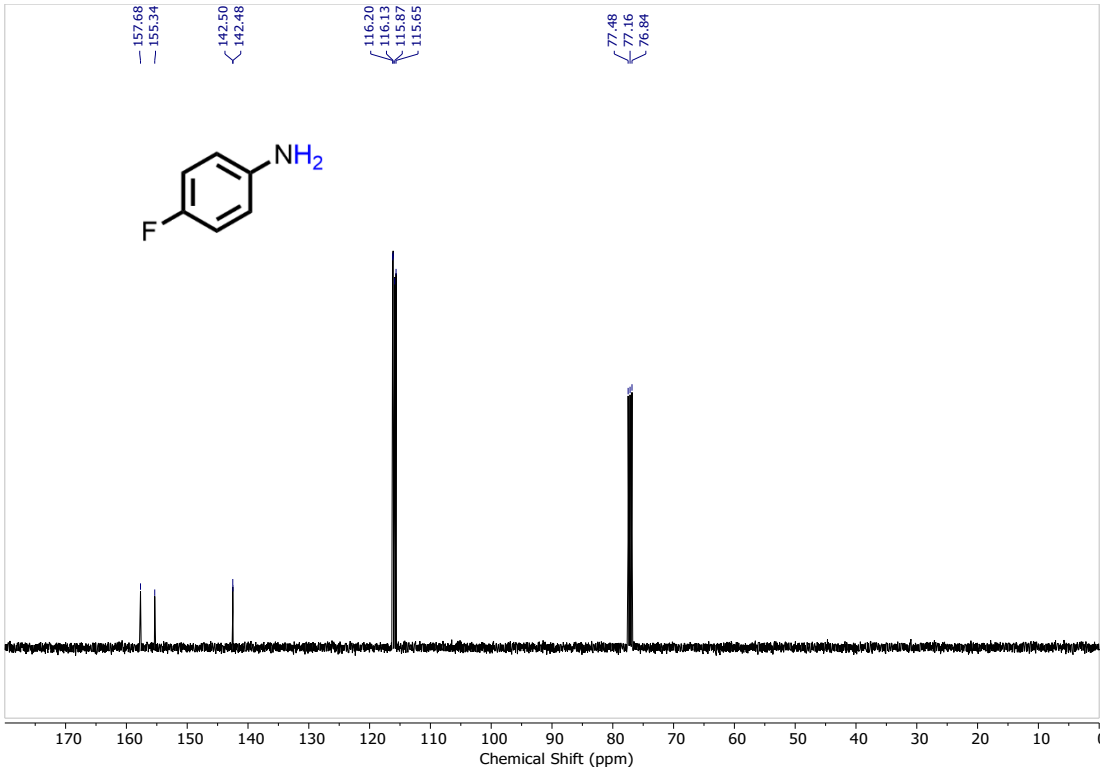


Figure S15. $^{13}C\{^{1}H\}$ NMR Spectrum (100 MHz, 25 °C, $CDCl_3$) of **5d**.

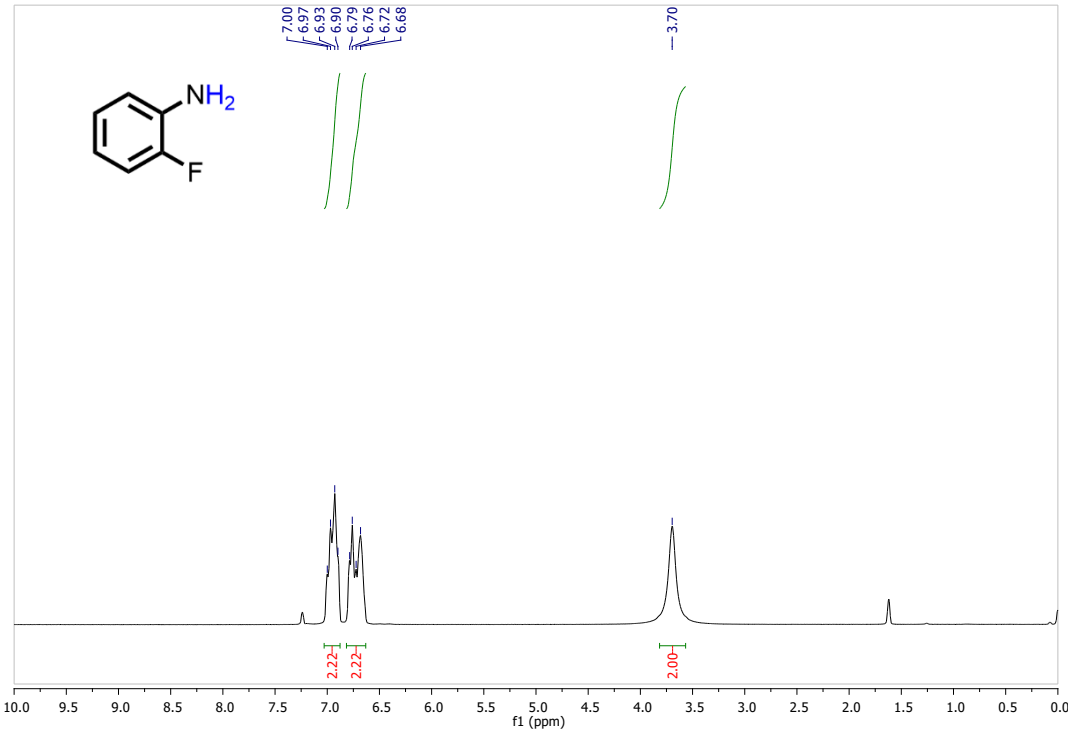


Figure S16. ^{1}H NMR Spectrum (300 MHz, 25 °C, $CDCl_3$) of **5e**.

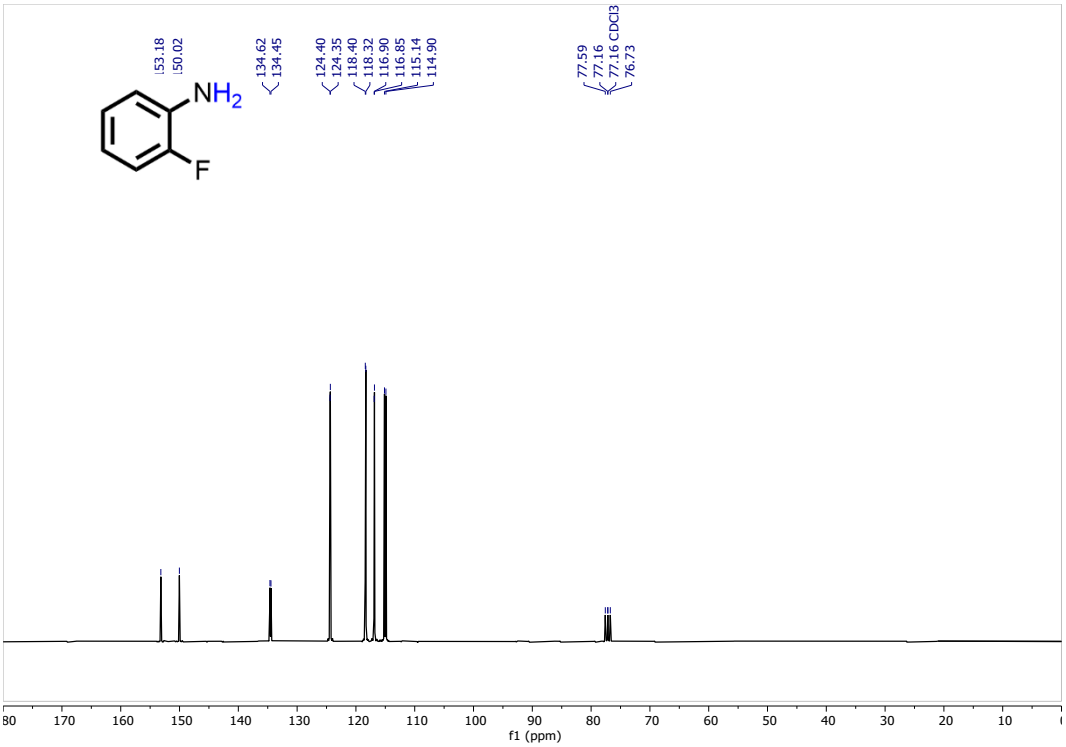


Figure S17. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, 25 °C, $CDCl_3$) of **5e**.

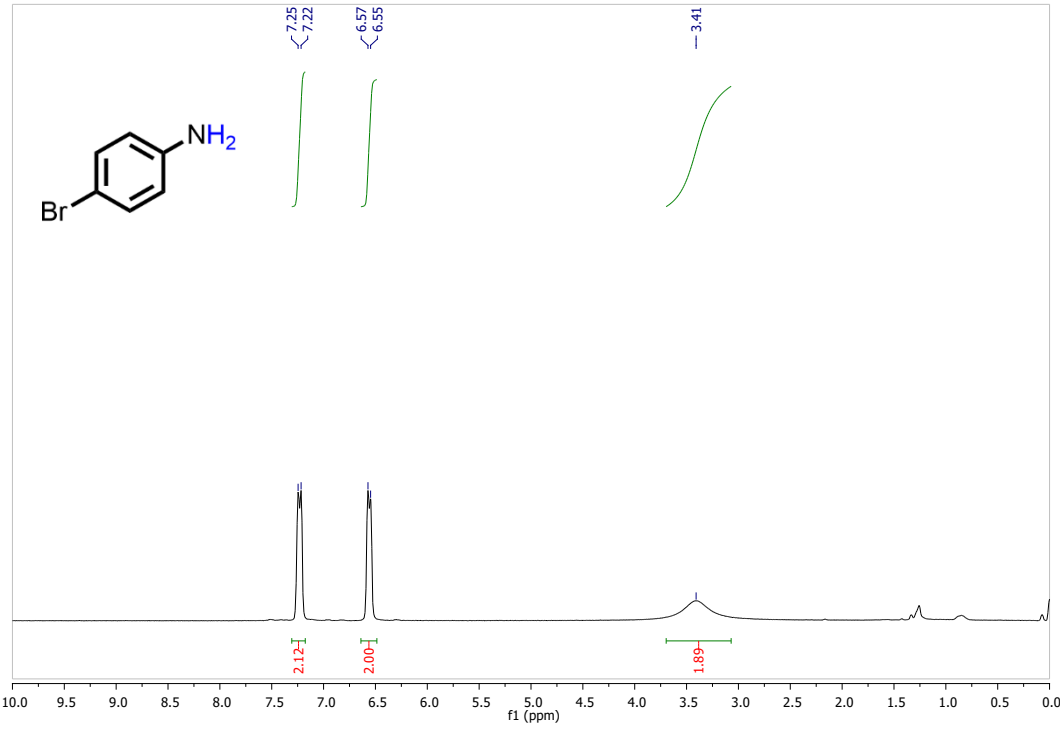


Figure S18. ^{1}H NMR Spectrum (300 MHz, 25 °C, $CDCl_3$) of **5f**.

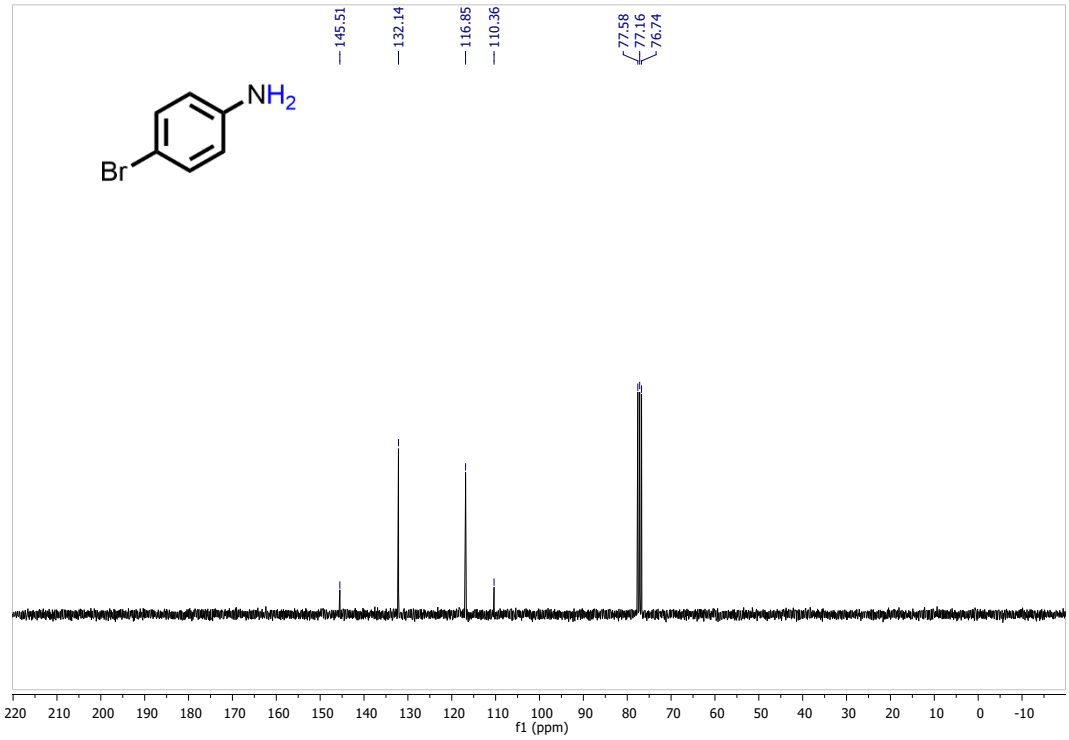


Figure S19. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, 25 °C, $CDCl_3$) of **5f**.

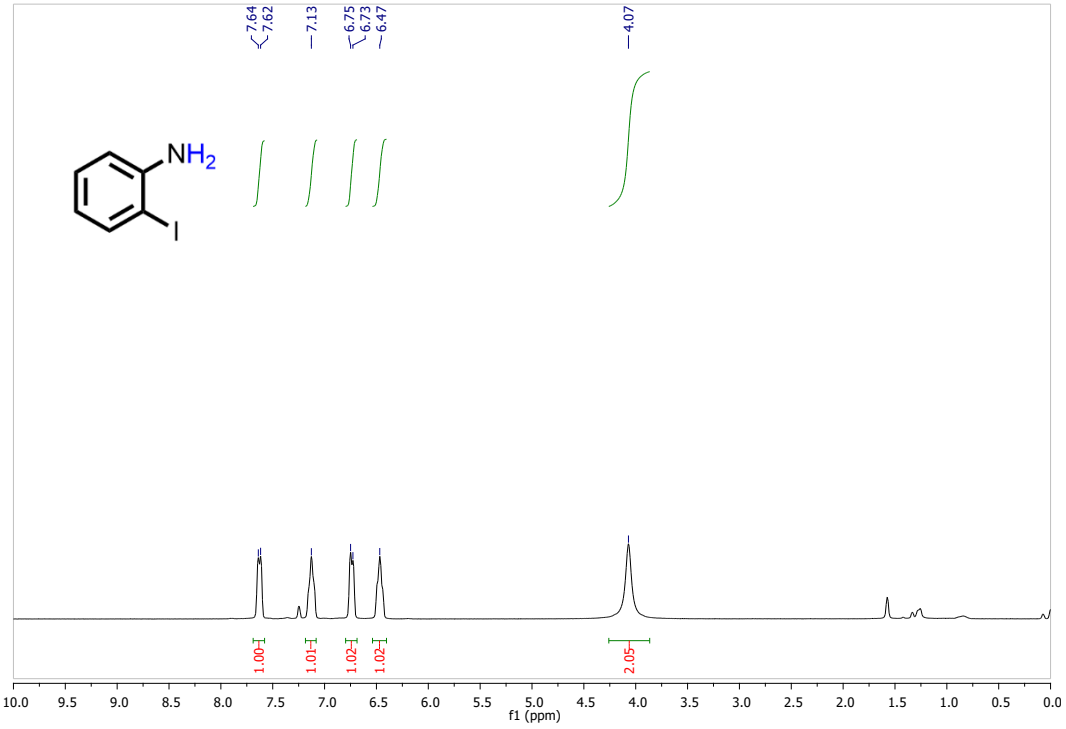


Figure S20. ^{1}H NMR Spectrum (300 MHz, 25 °C, $CDCl_3$) of **5g**.

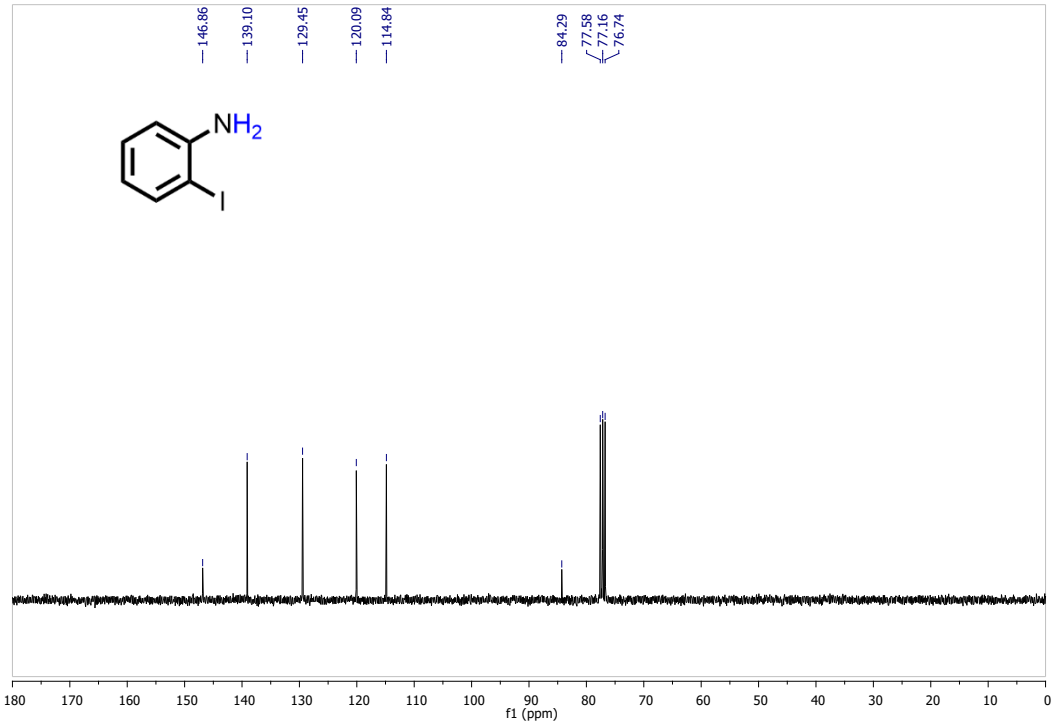


Figure S21. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, 25 °C, $CDCl_3$) of **5g**.

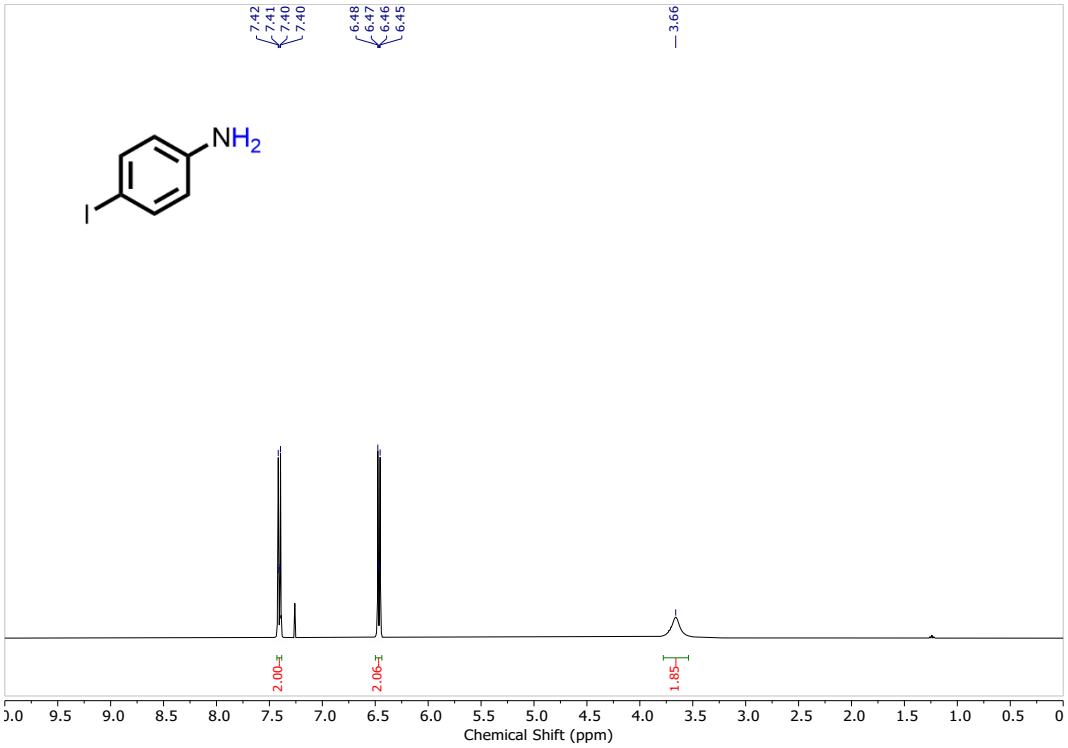


Figure S22. ^{1}H NMR Spectrum (400 MHz, 25 °C, $CDCl_3$) of **5h**.

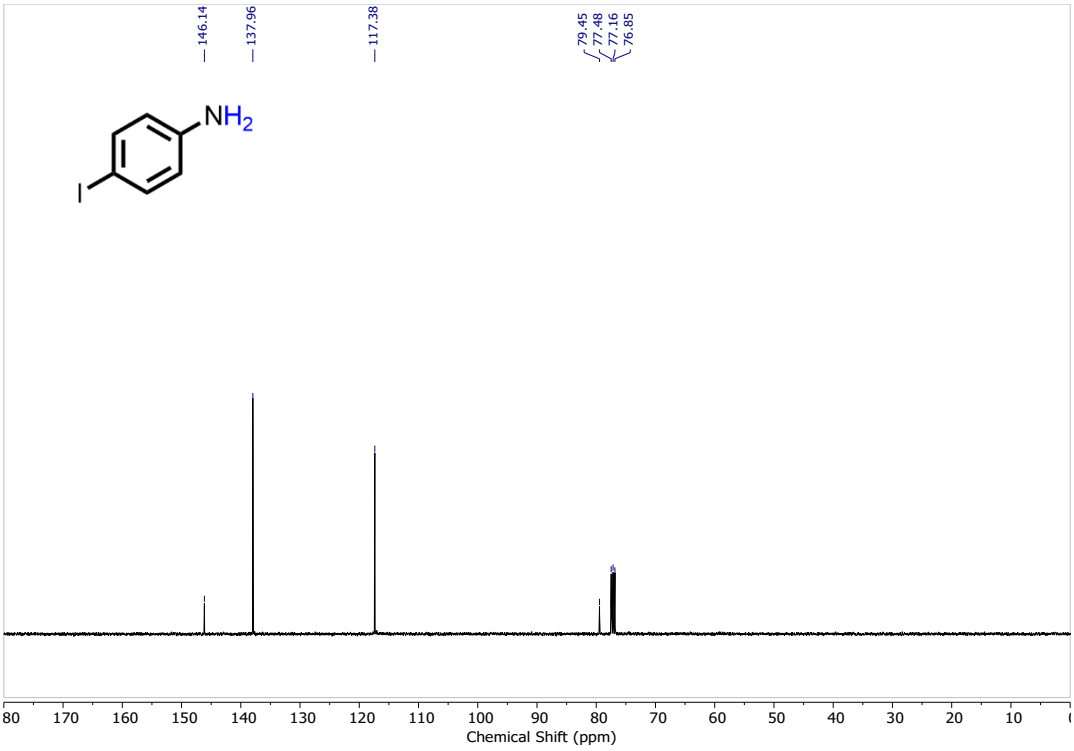


Figure S23. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, 25 °C, $CDCl_3$) of **5h**.

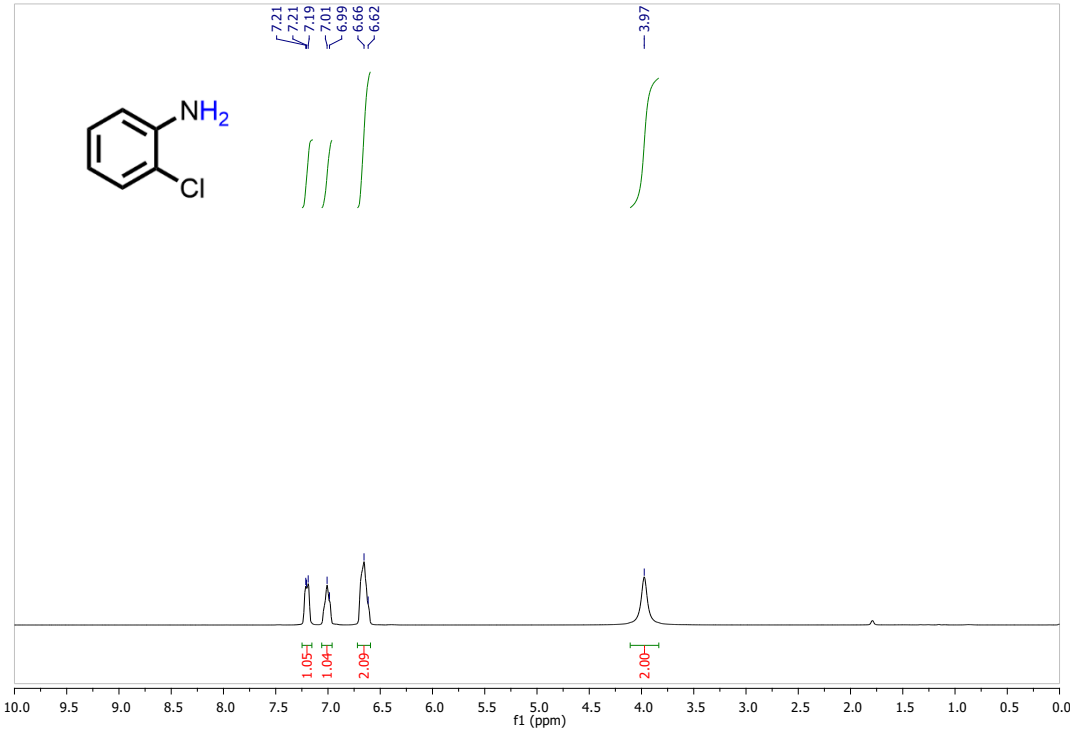


Figure S24. ^{1}H NMR Spectrum (300 MHz, 25 °C, $CDCl_3$) of **5i**.

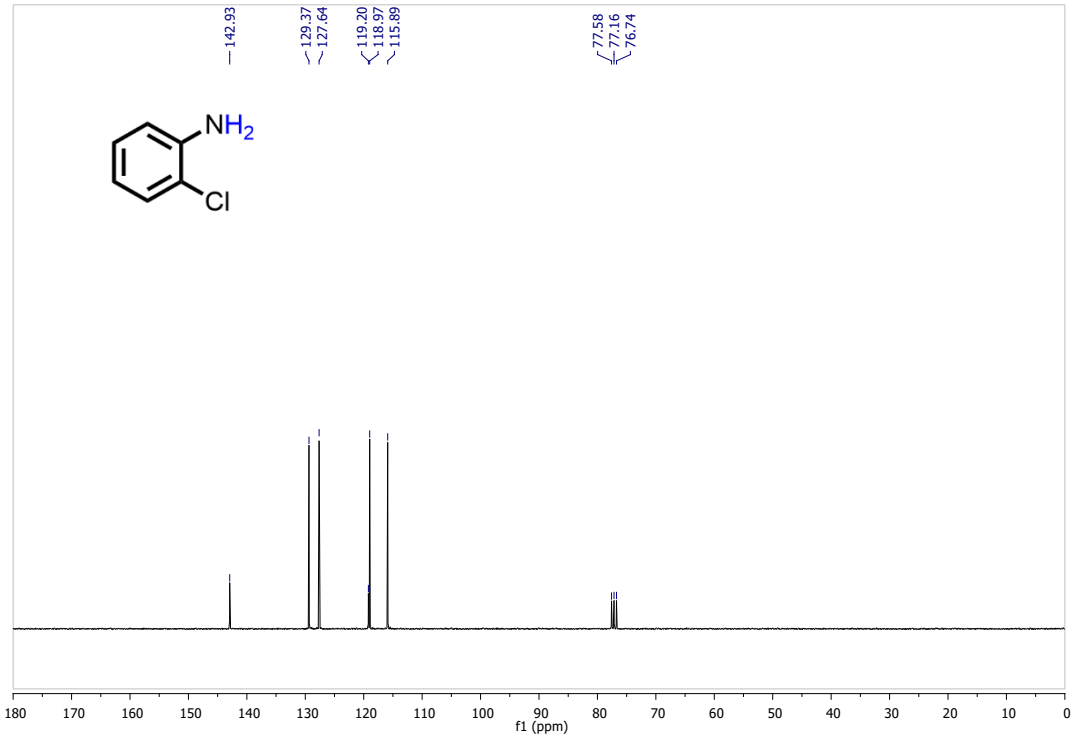


Figure S25. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, 25 °C, $CDCl_3$) of **5i**.

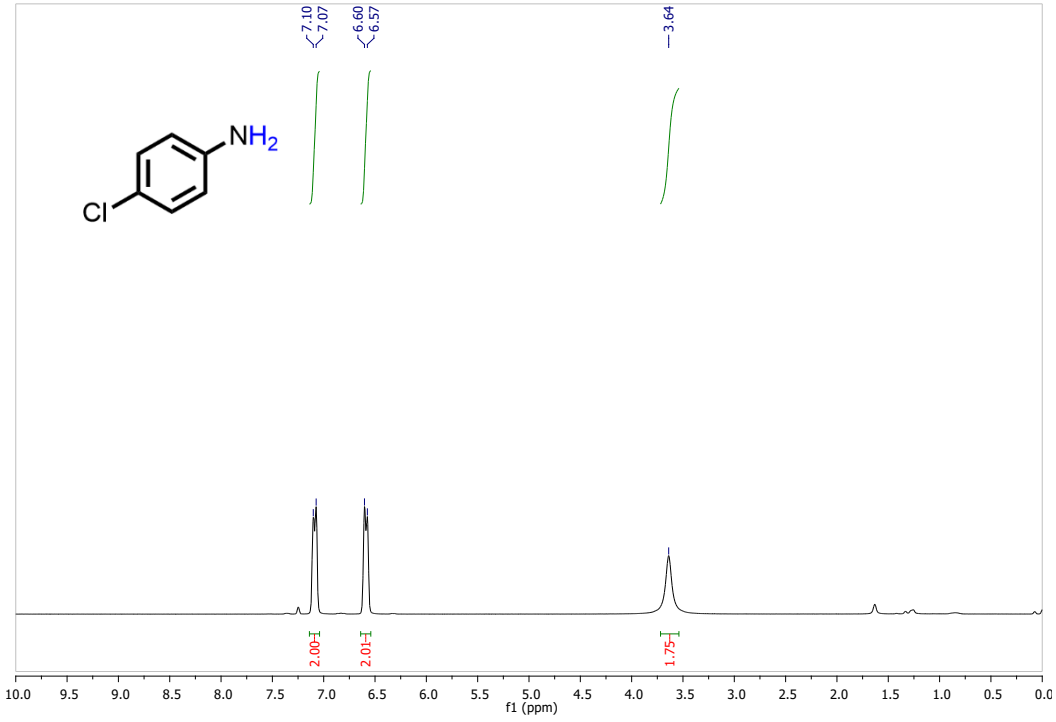


Figure S26. ^{1}H NMR Spectrum (300 MHz, 25 °C, $CDCl_3$) of **5j**.

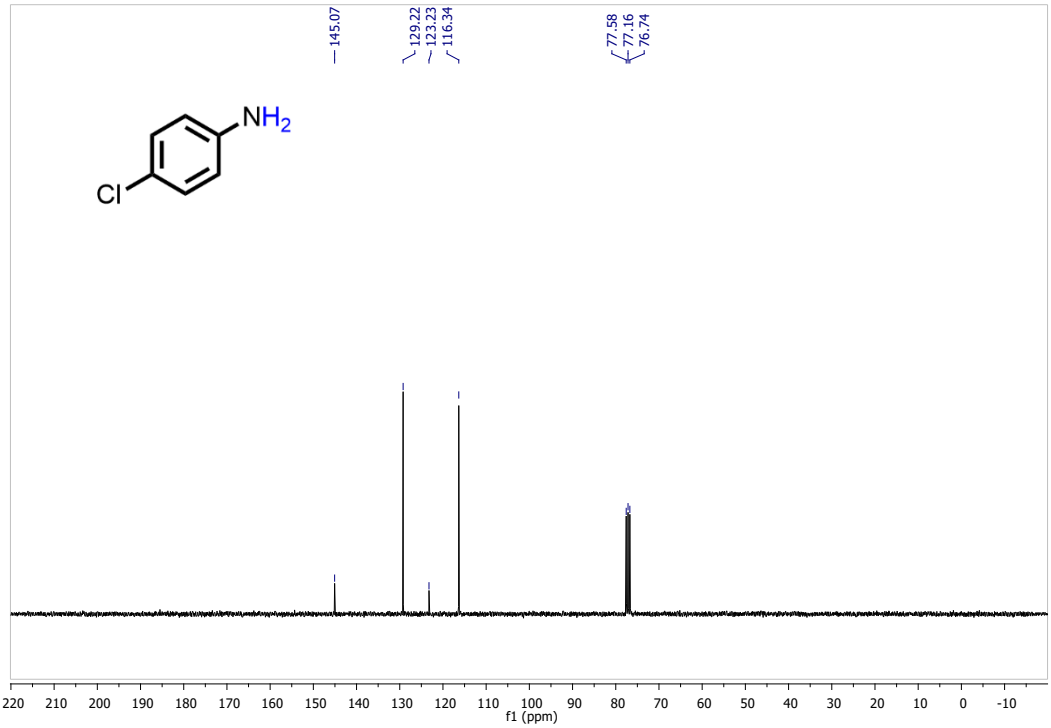


Figure S27. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, 25 °C, $CDCl_3$) of **5j**.

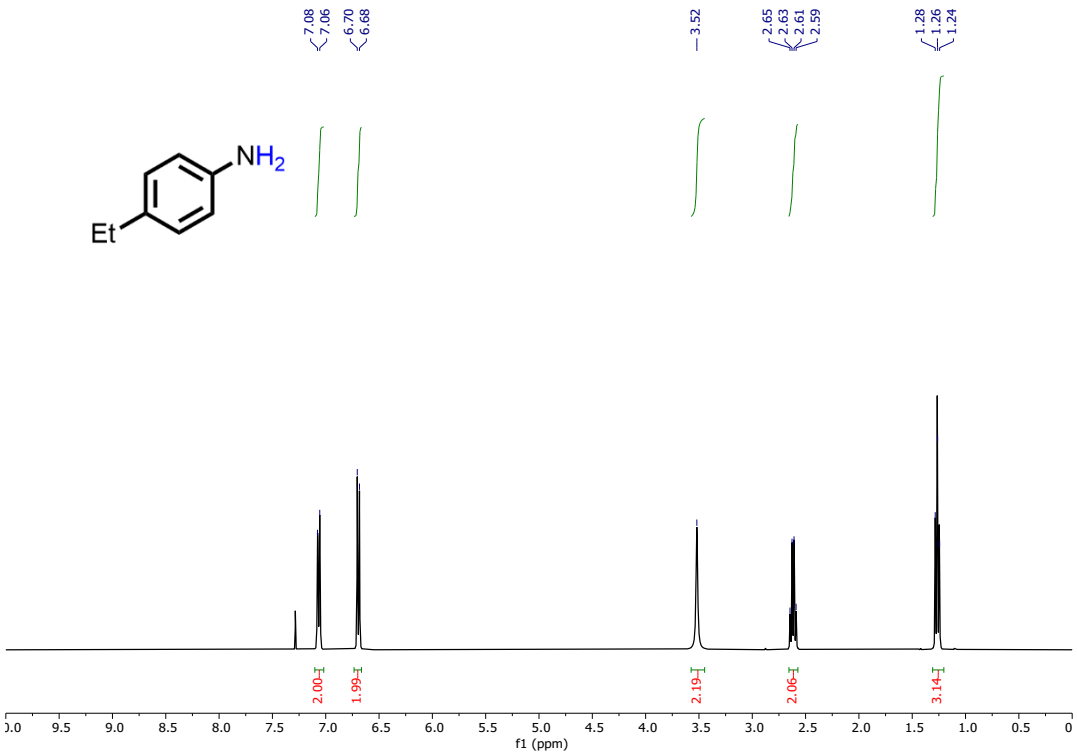


Figure S28. ^{1}H NMR Spectrum (400 MHz, 25 °C, $CDCl_3$) of **5k**.

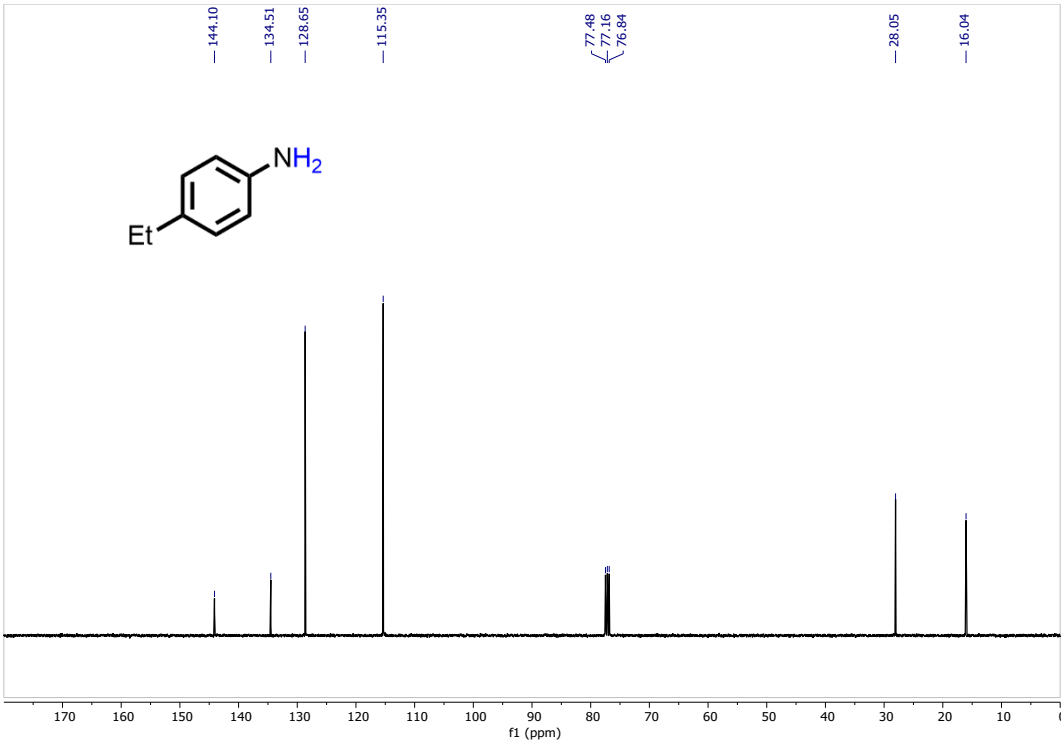


Figure S29. $^{13}C\{^{1}H\}$ NMR Spectrum (100 MHz, 25 °C, $CDCl_3$) of **5k**.

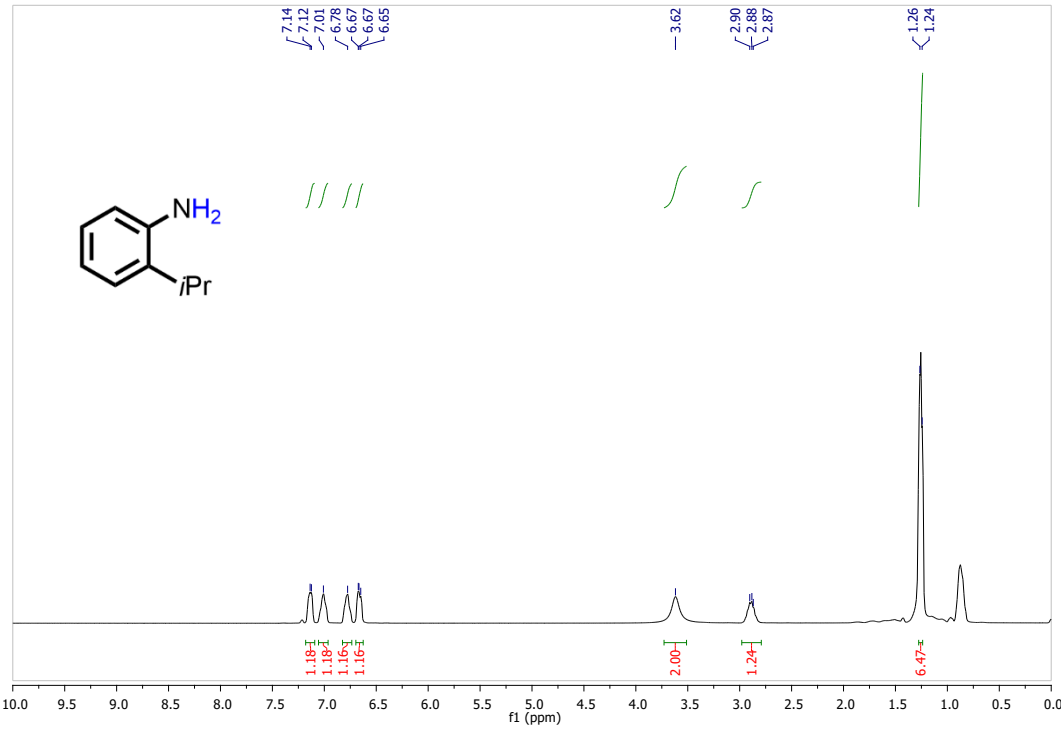


Figure S30. ^{1}H NMR Spectrum (300 MHz, 25 °C, $CDCl_3$) of **5l**.

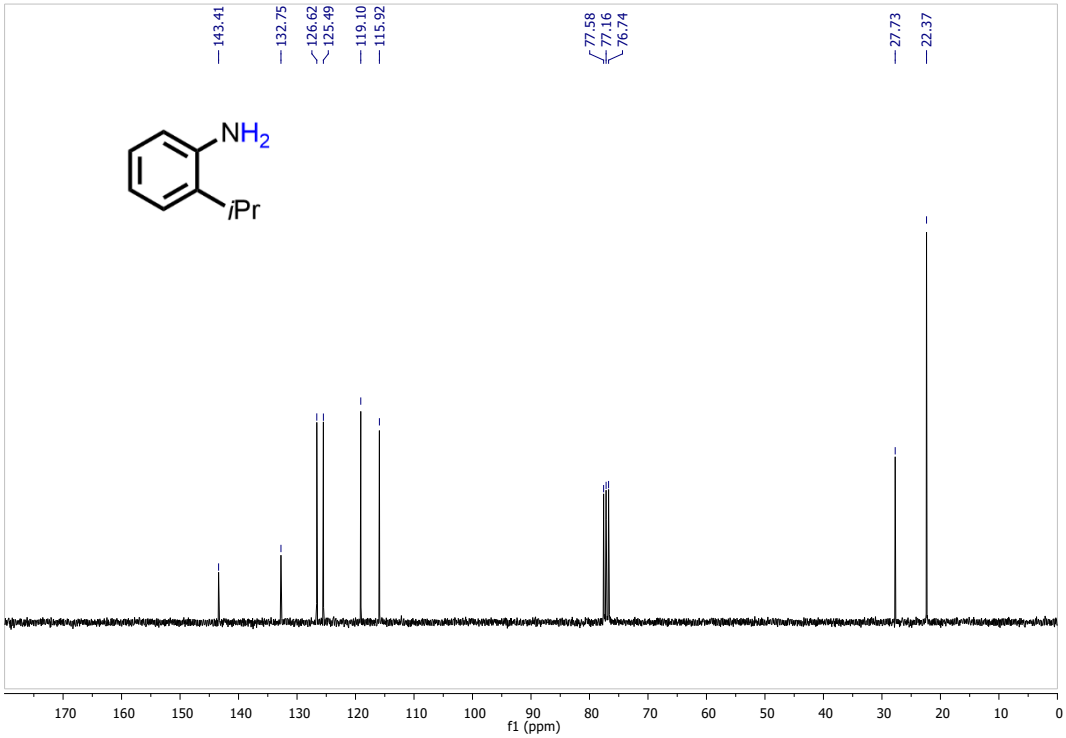


Figure S31. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, 25 °C, $CDCl_3$) of **5l**.

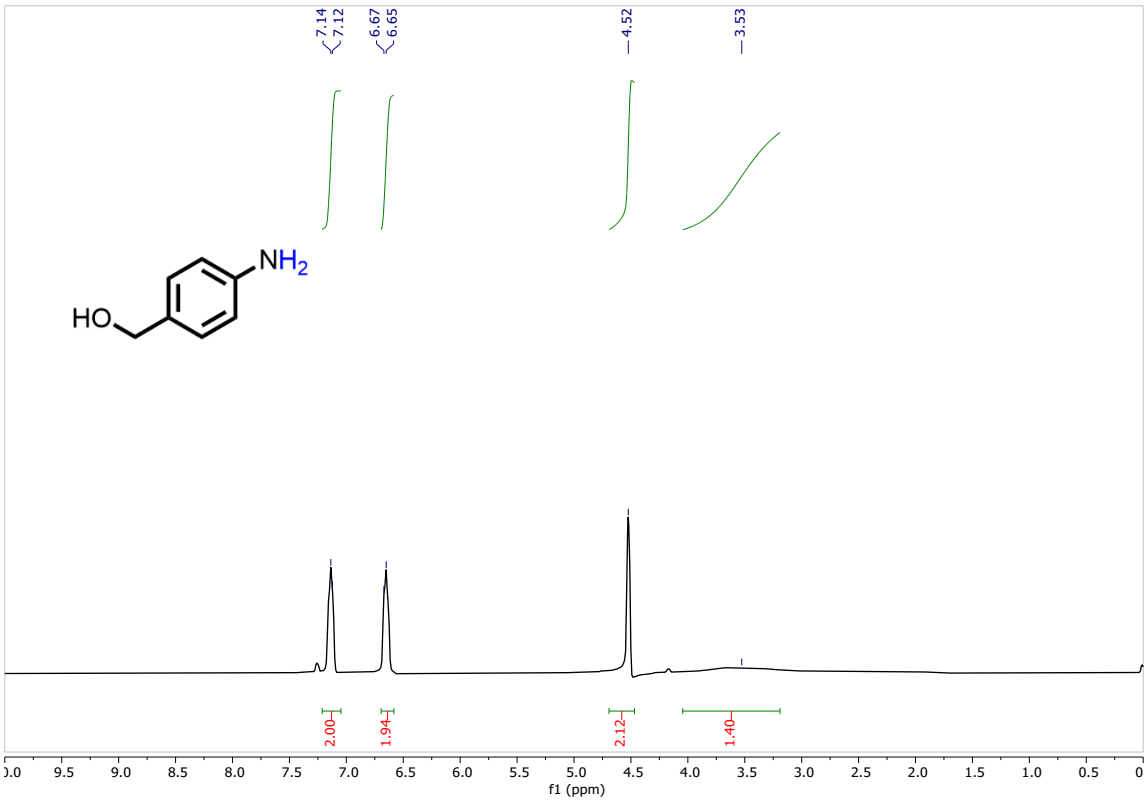


Figure S32. ^{1}H NMR Spectrum (300 MHz, 25 °C, $CDCl_3$) of **5m**.

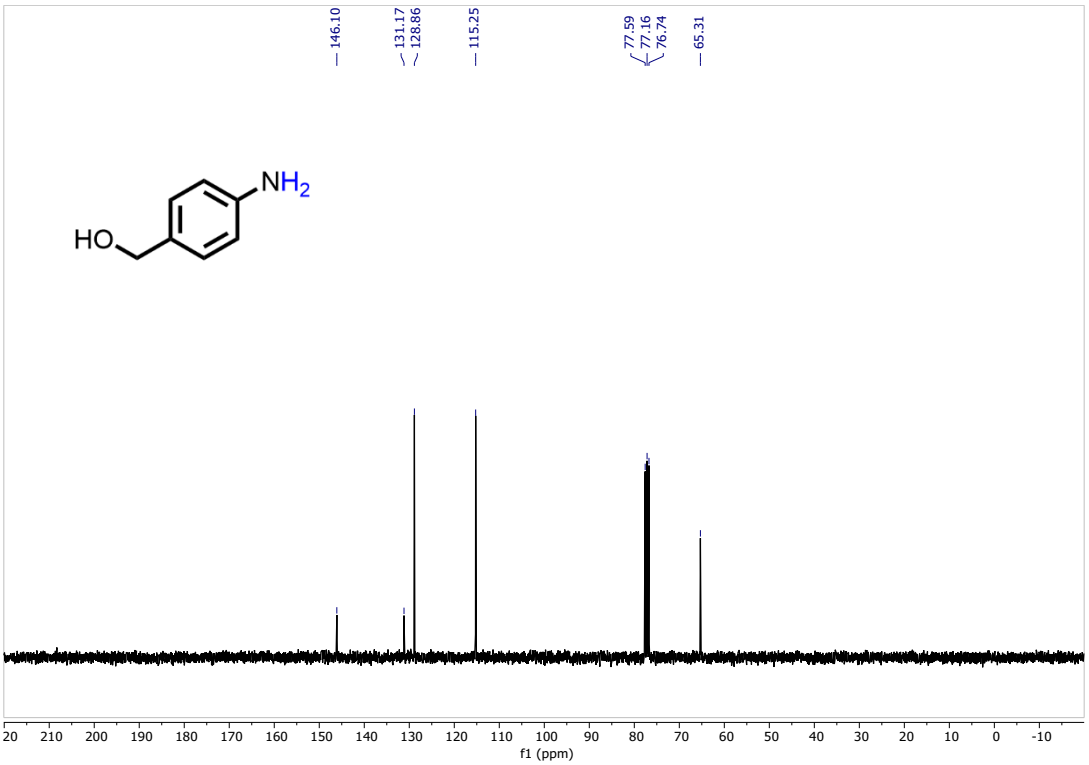


Figure S33. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, 25 °C, $CDCl_3$) of **5m**.

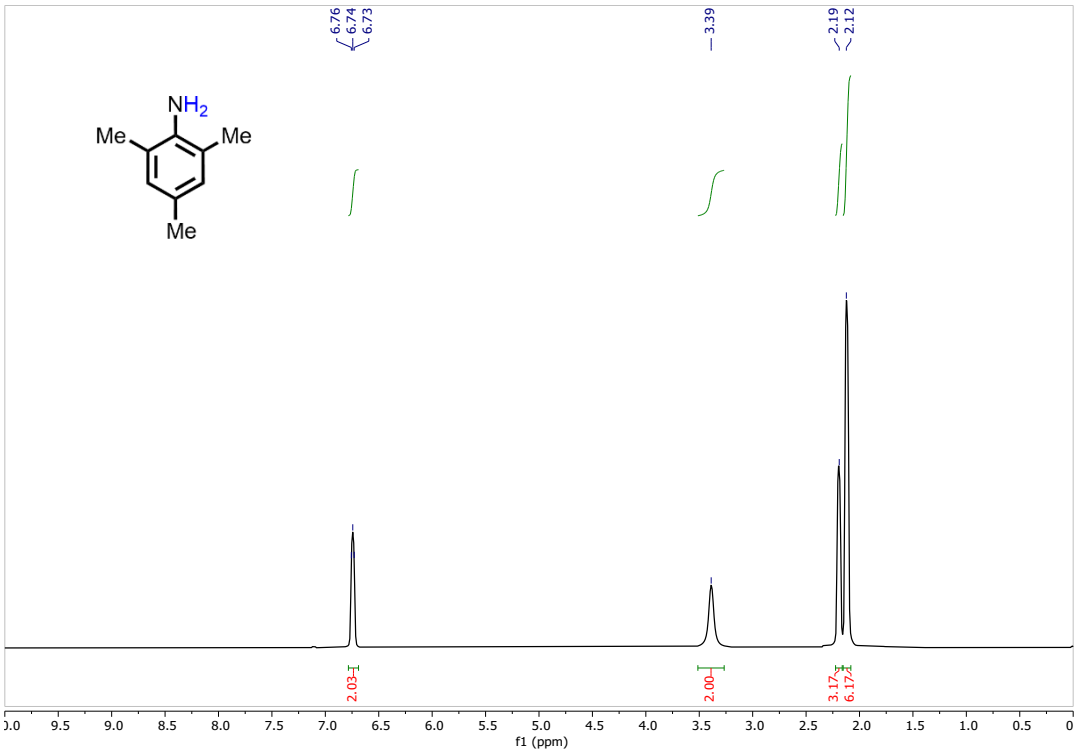


Figure S34. ^{1}H NMR Spectrum (300 MHz, 25 °C, $CDCl_3$) of **5n**.

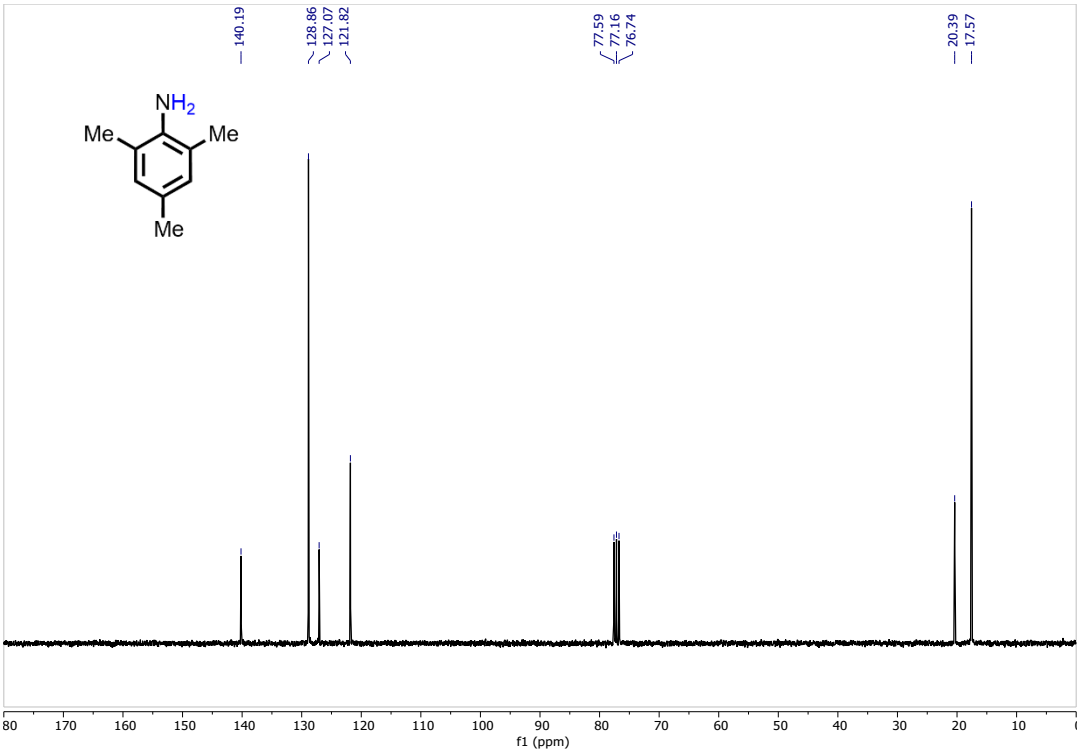


Figure S35. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, 25 °C, $CDCl_3$) of **5n**.

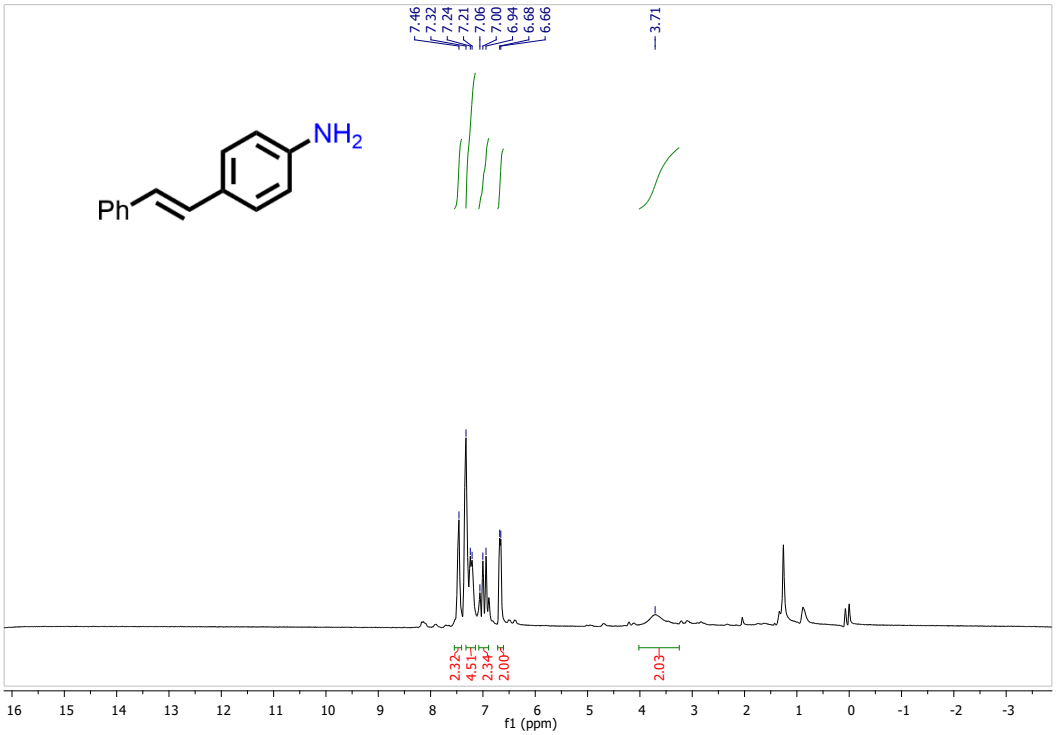


Figure S36. ^{1}H NMR Spectrum (300 MHz, 25 °C, $CDCl_3$) of **5o**. Hexane peak at 1.26 ppm.

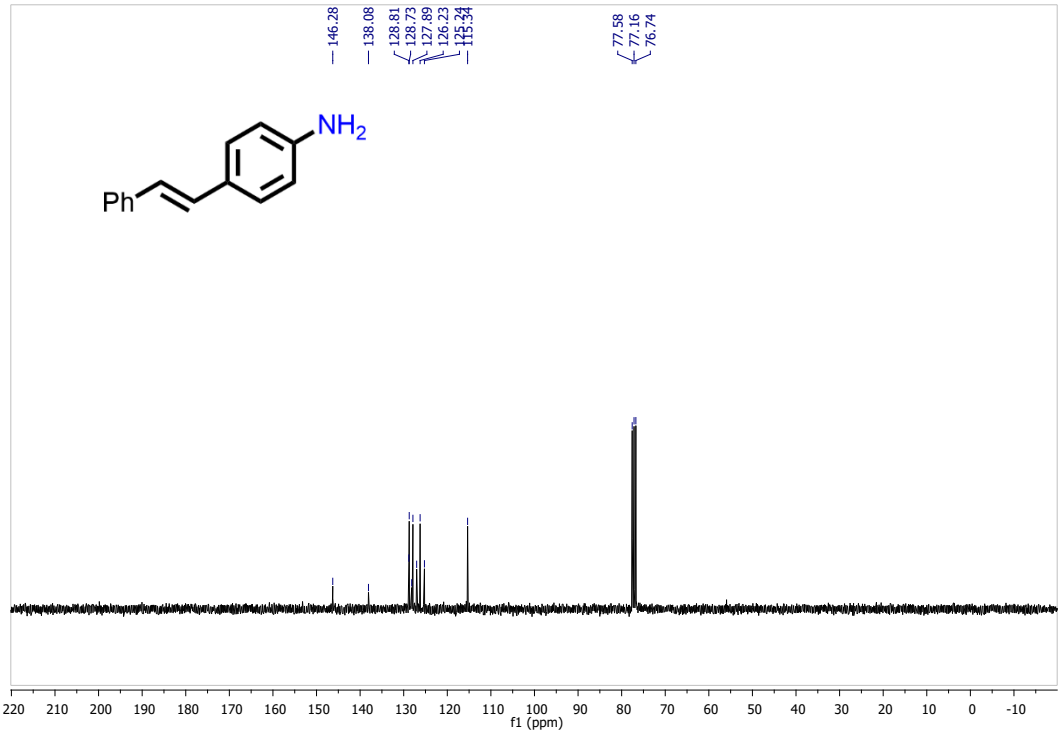


Figure S37. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, 25 °C, $CDCl_3$) of **5o**.

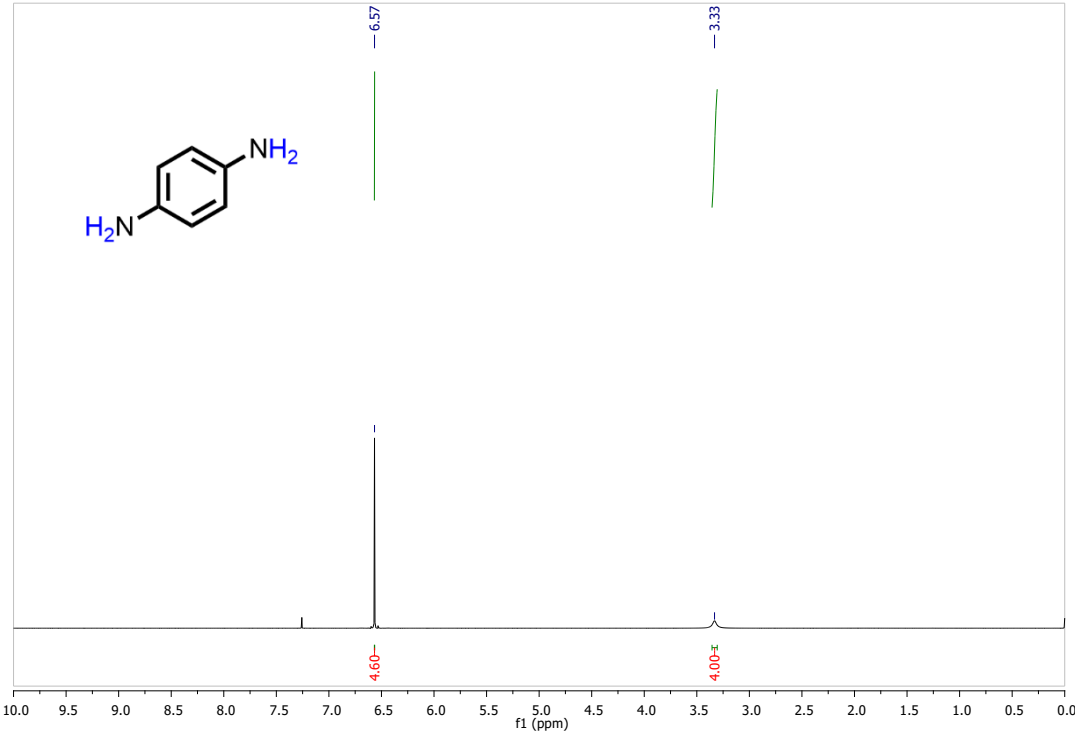


Figure S38. ^{1}H NMR Spectrum (400 MHz, 25 °C, $CDCl_3$) of **5p**.

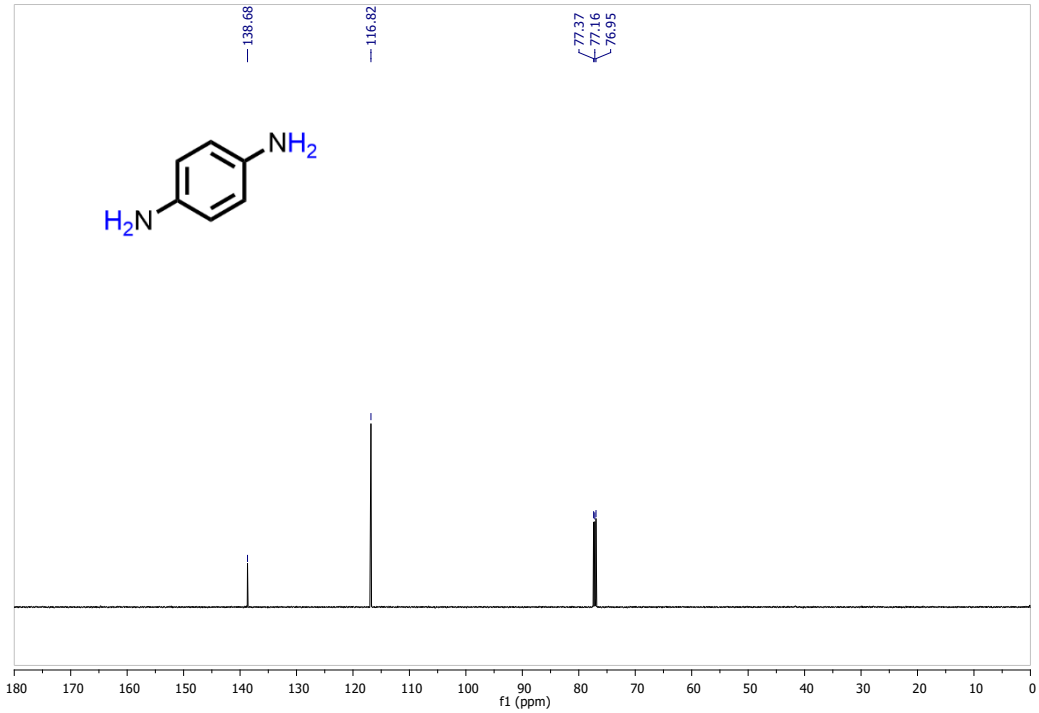


Figure S39. $^{13}C\{^{1}H\}$ NMR Spectrum (100 MHz, 25 °C, $CDCl_3$) of **5p**.

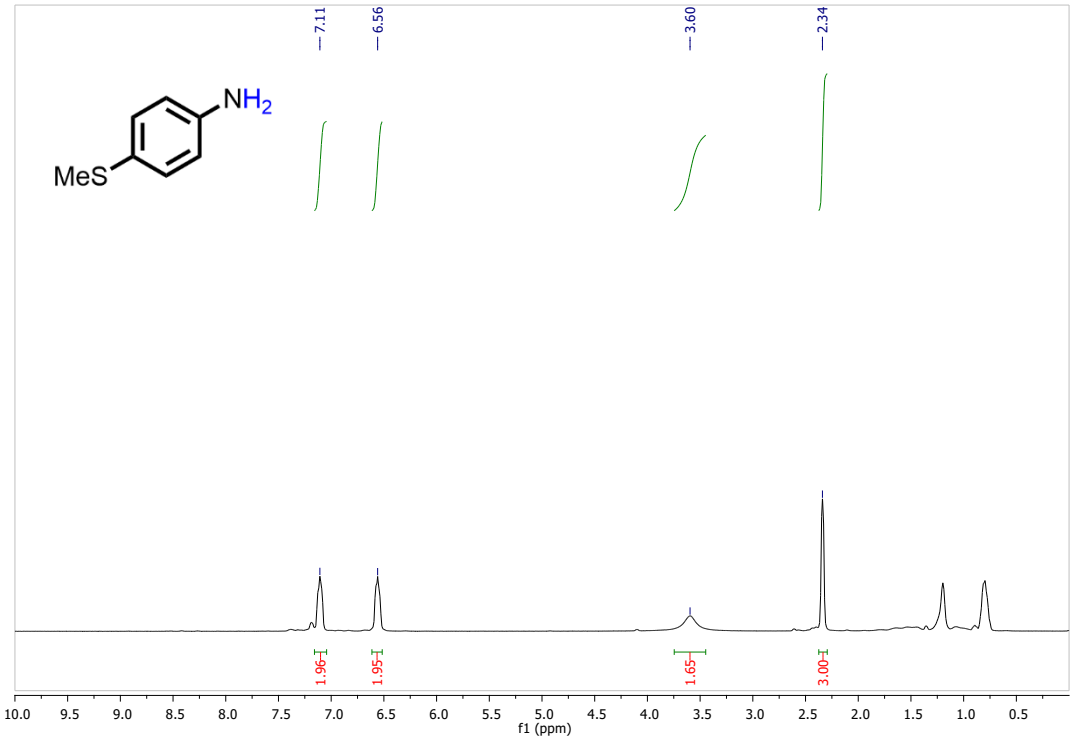


Figure S40. ^{1}H NMR Spectrum (300 MHz, 25 °C, $CDCl_3$) of **5q**.

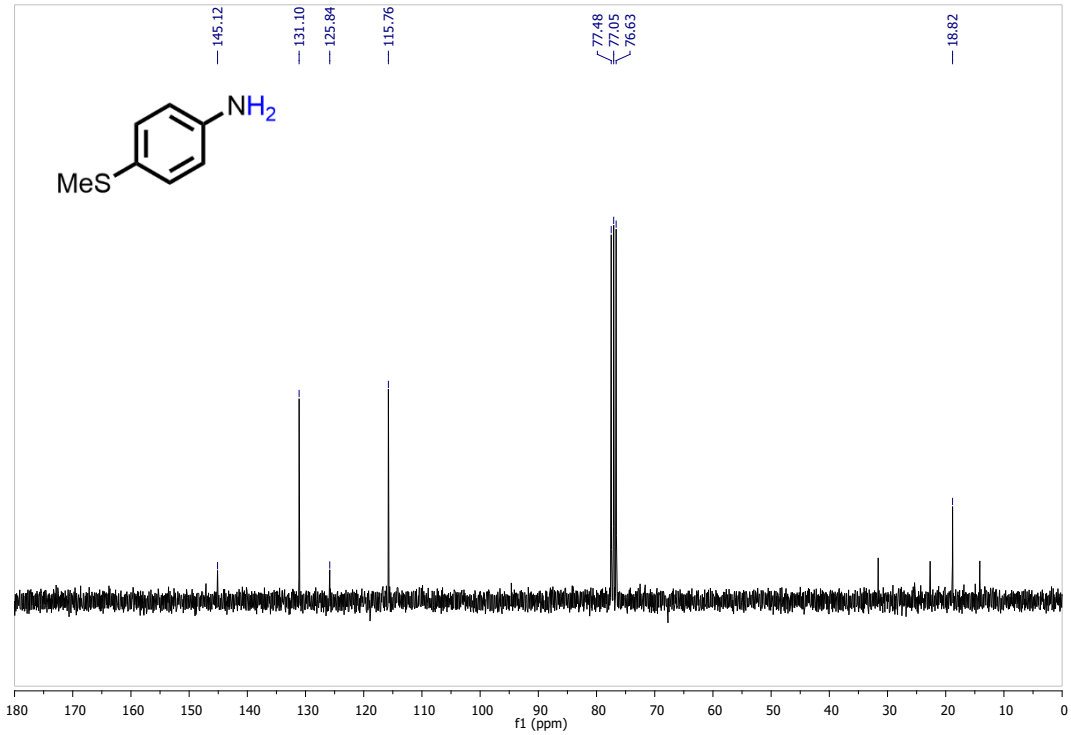


Figure S41. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, 25 °C, $CDCl_3$) of **5q**.

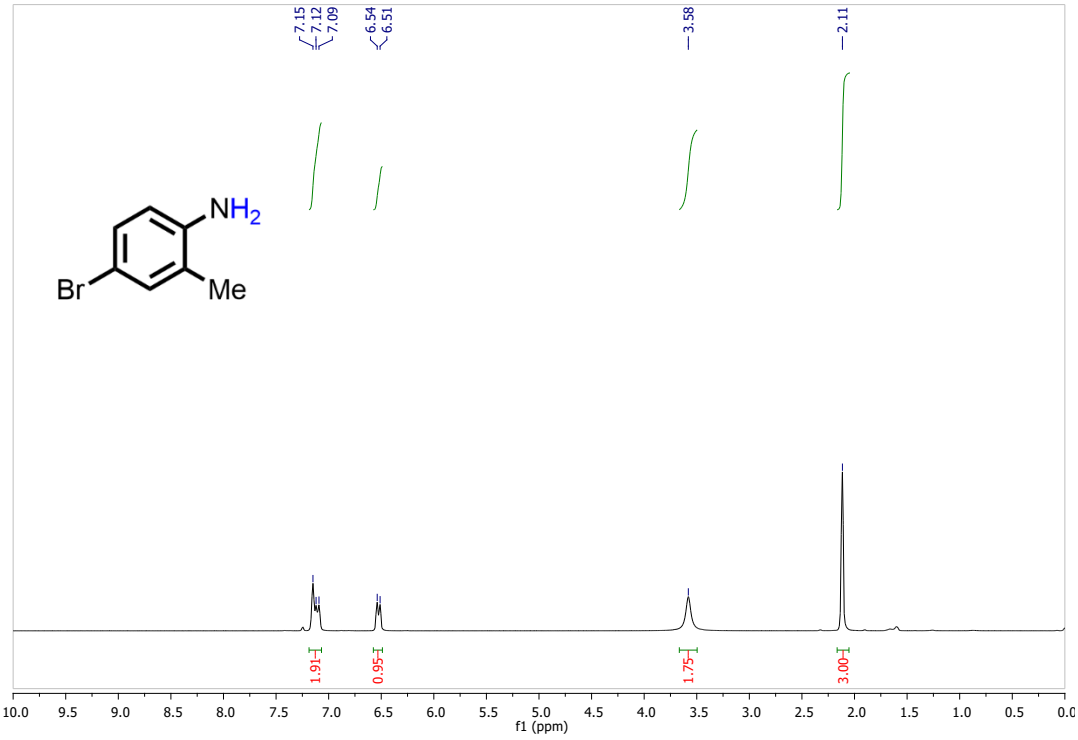


Figure S42. ^{1}H NMR Spectrum (300 MHz, 25 °C, $CDCl_3$) of **5r**.

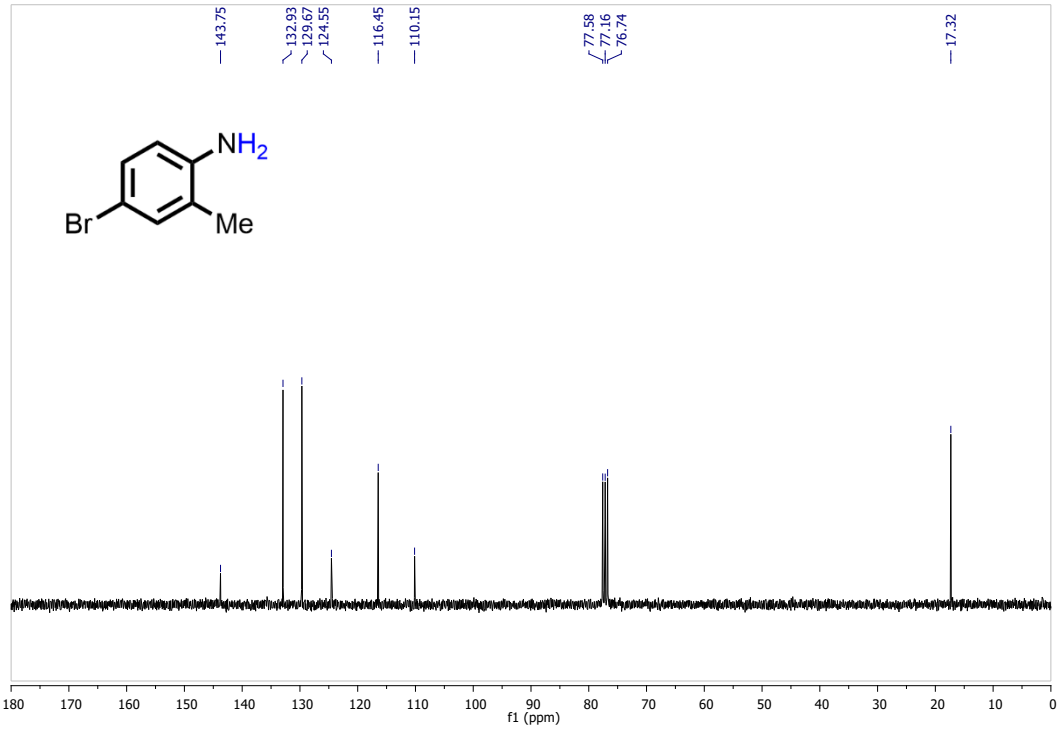


Figure S43. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, 25 °C, $CDCl_3$) of **5r**.

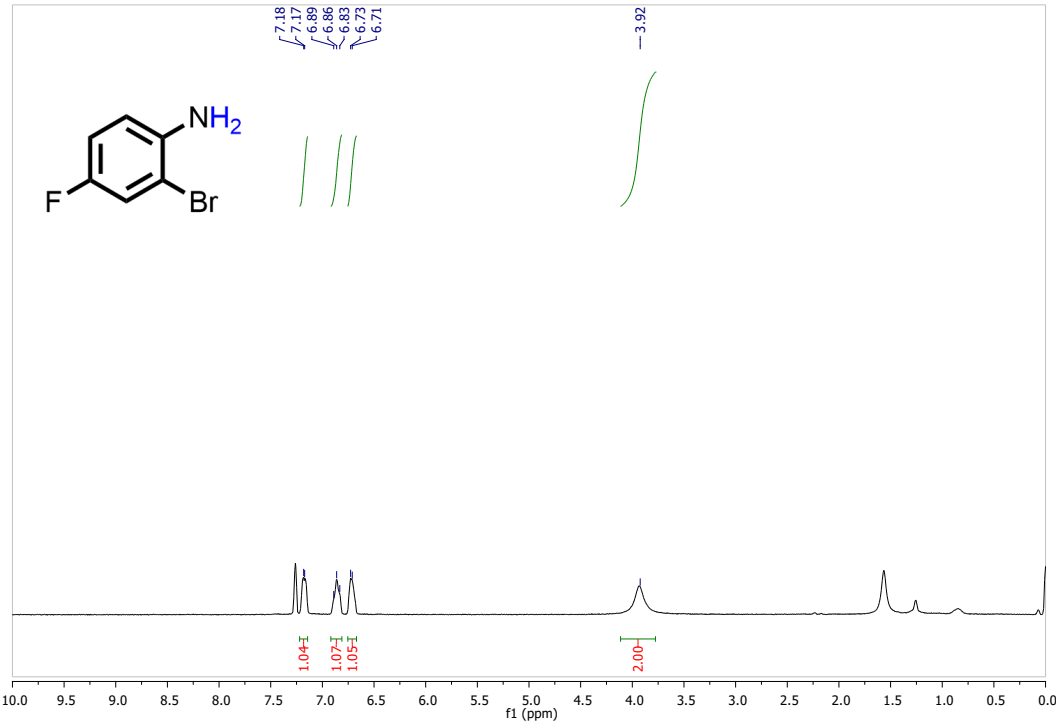


Figure S44. ^{1}H NMR Spectrum (300 MHz, 25 °C, $CDCl_3$) of **5s**.

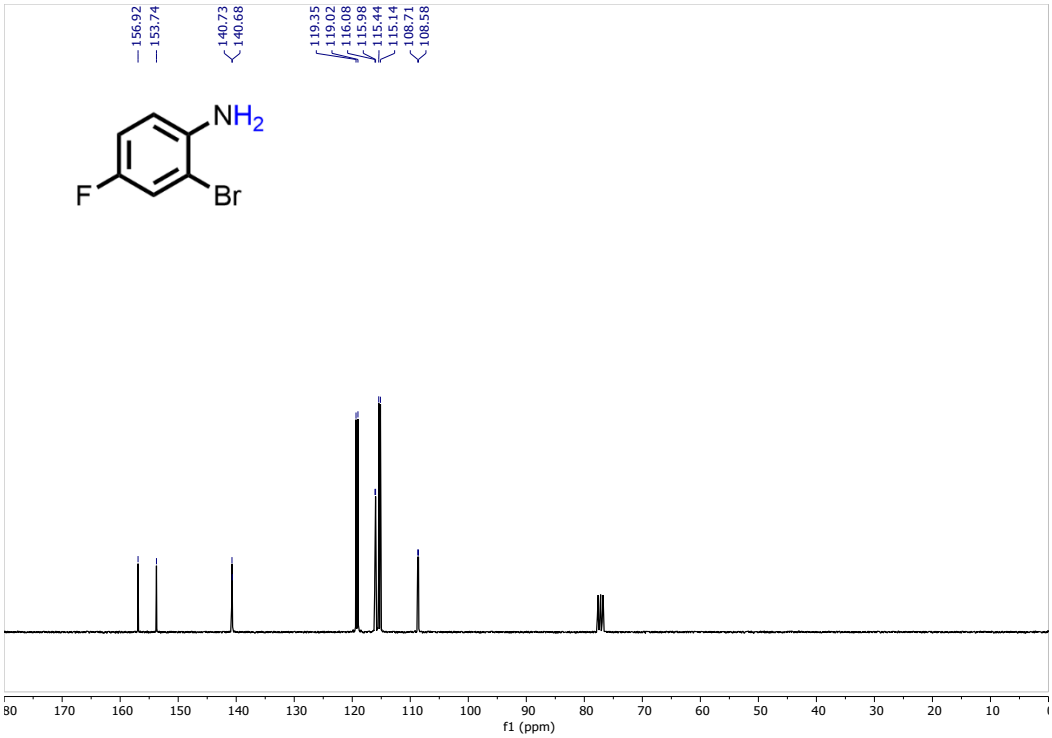


Figure S45. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, 25 °C, $CDCl_3$) of **5s**.

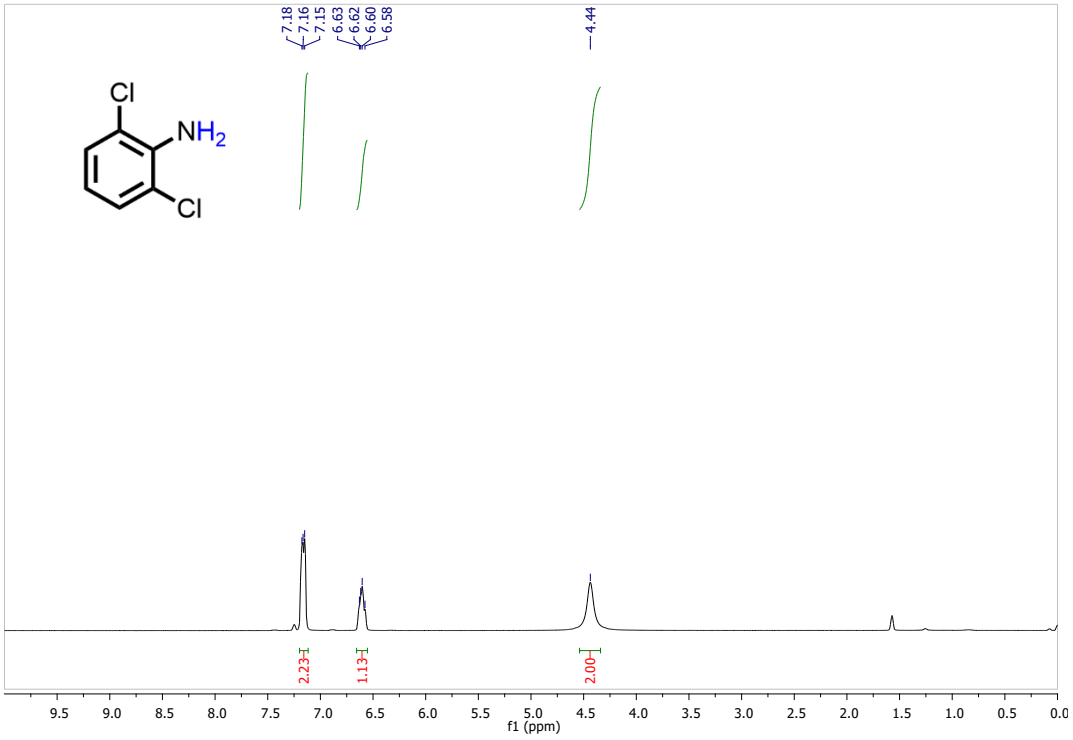


Figure S46. ^{1}H NMR Spectrum (300 MHz, 25 °C, $CDCl_3$) of **5t**.

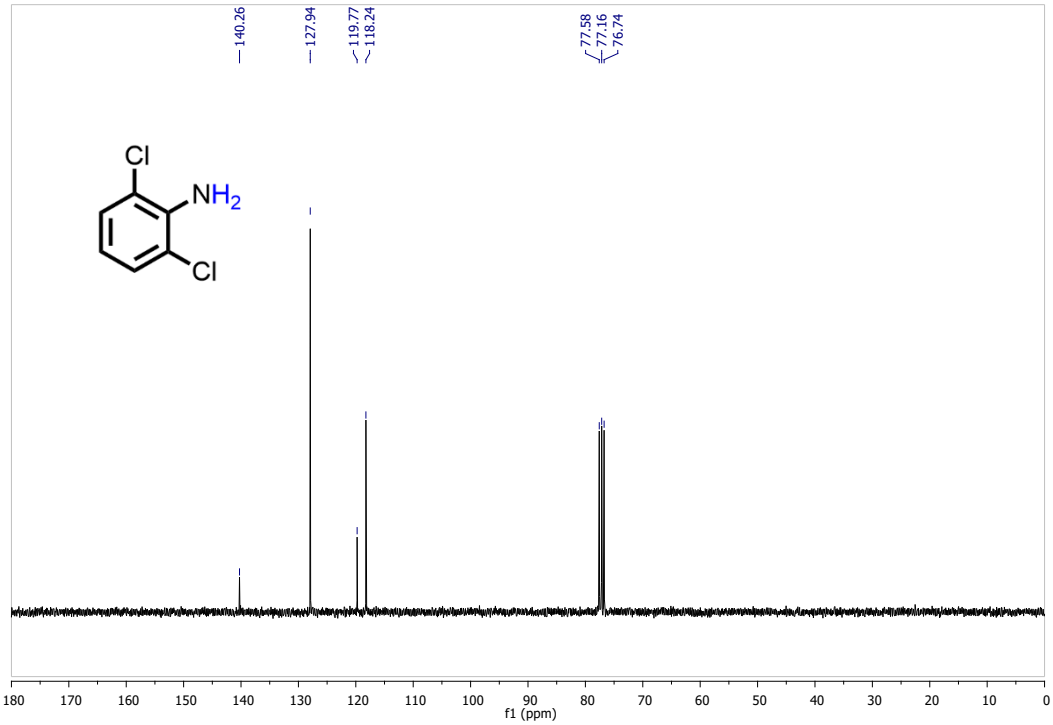


Figure S47. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, 25 °C, $CDCl_3$) of **5t**.

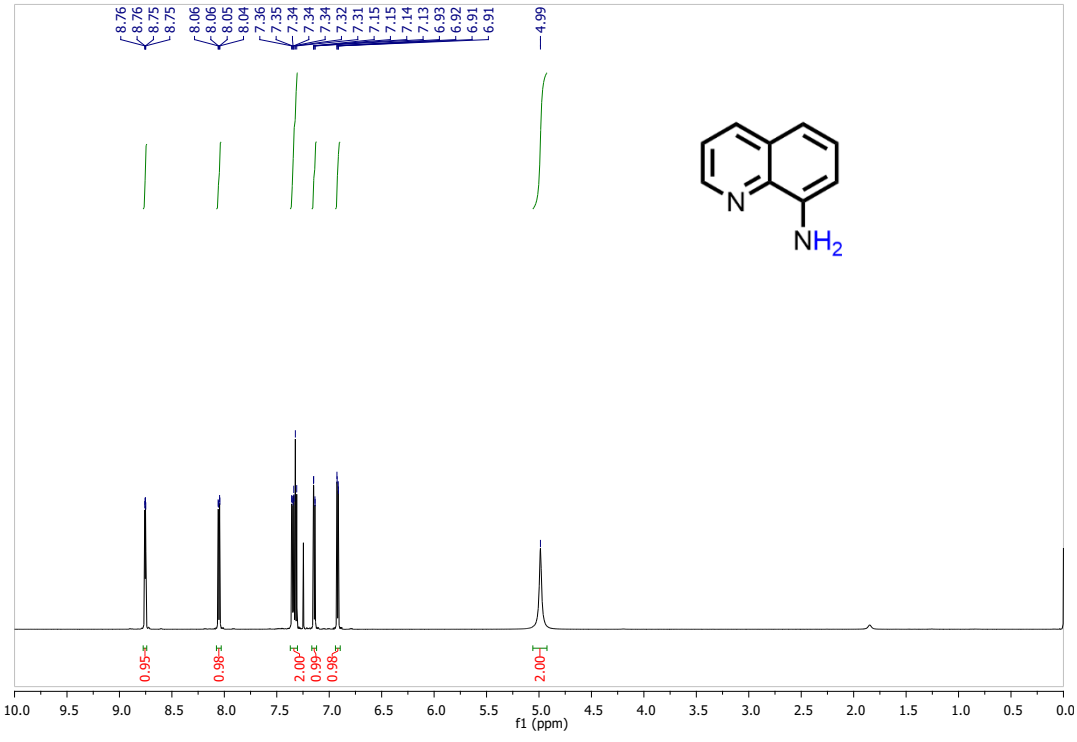


Figure S48. ^{1}H NMR Spectrum (400 MHz, 25 °C, $CDCl_3$) of **5u**.

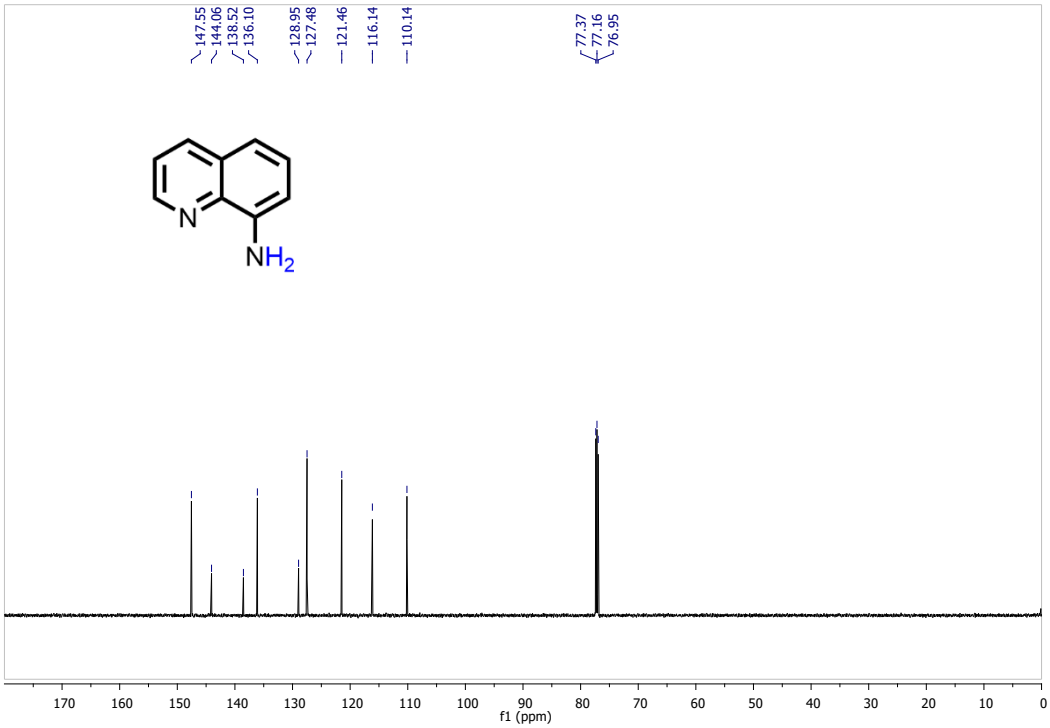


Figure S49. $^{13}C\{^{1}H\}$ NMR Spectrum (100 MHz, 25 °C, $CDCl_3$) of **5u**.

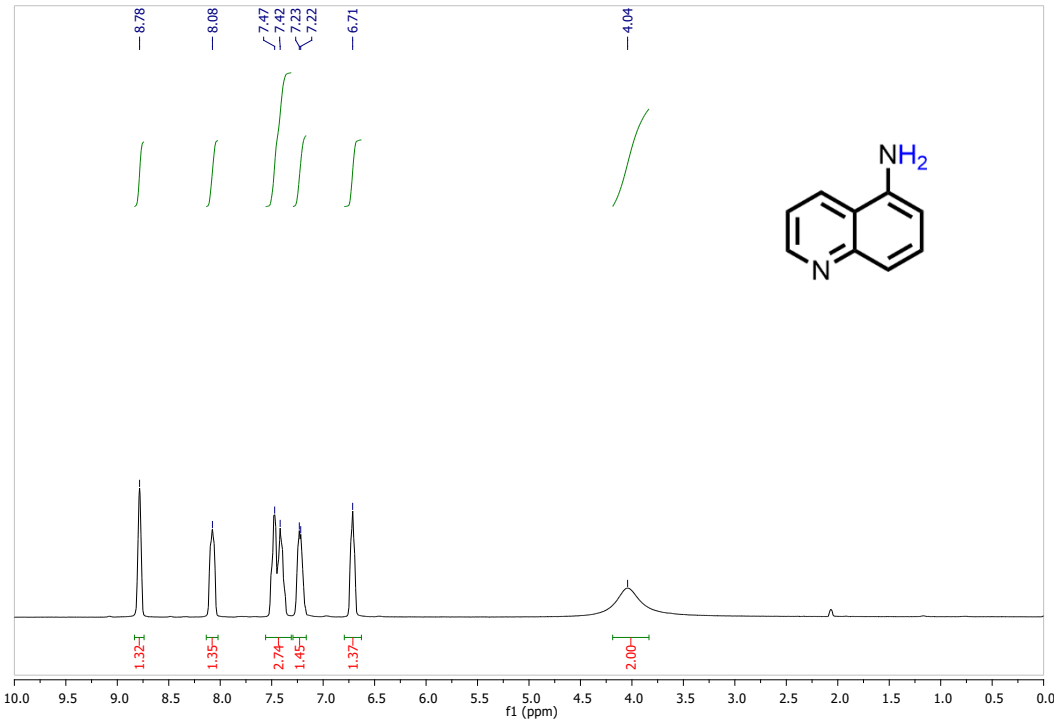


Figure S50. ^{1}H NMR Spectrum (300 MHz, 25 °C, $CDCl_3$) of **5v**.

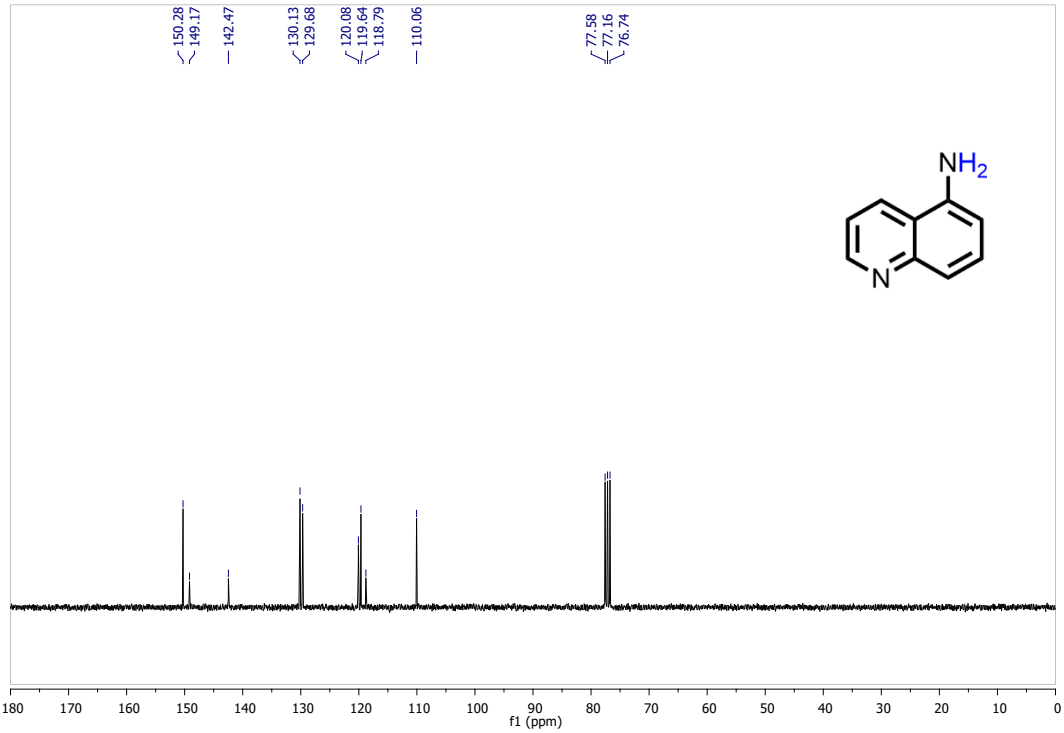


Figure S51. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, 25 °C, $CDCl_3$) of **5v**.

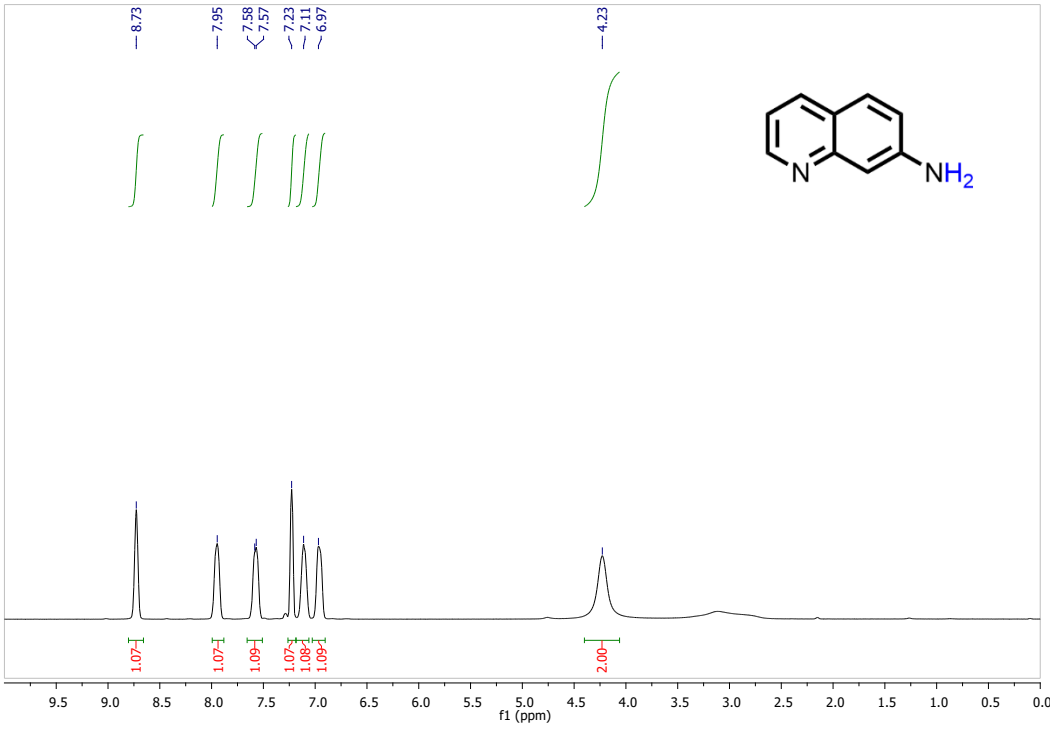


Figure S52. ^{1}H NMR Spectrum (300 MHz, 25 °C, $CDCl_3$) of **5w**.

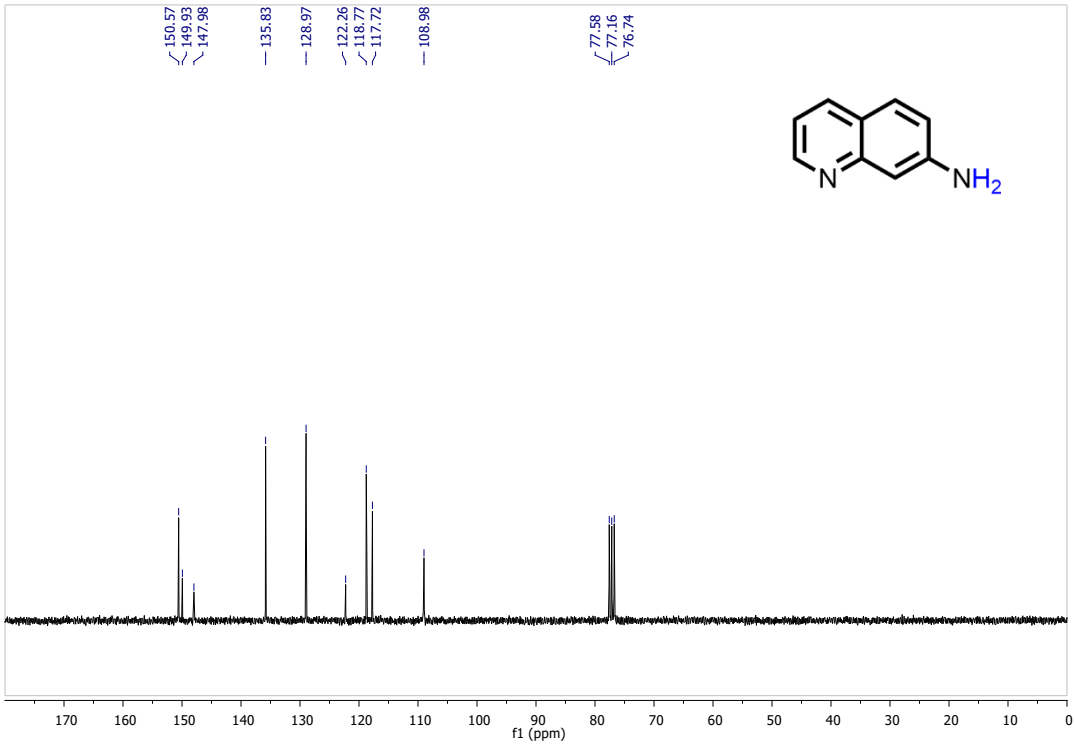


Figure S53. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, 25 °C, $CDCl_3$) of **5w**.

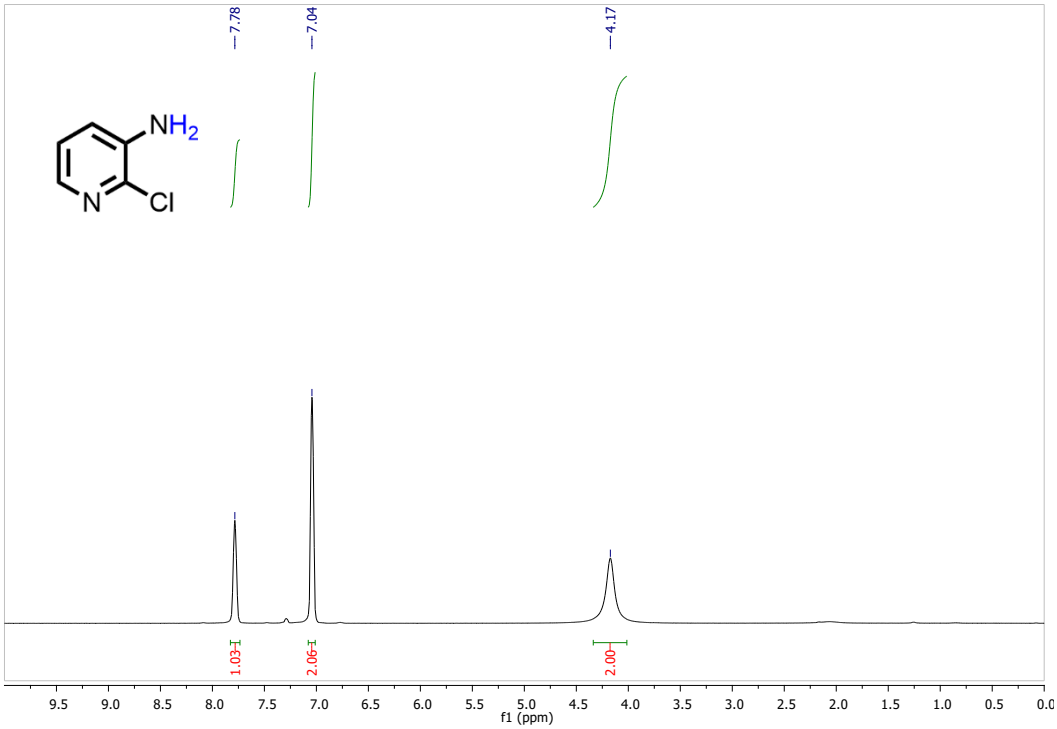


Figure S54. ^{1}H NMR Spectrum (300 MHz, 25 °C, $CDCl_3$) of **5x**.

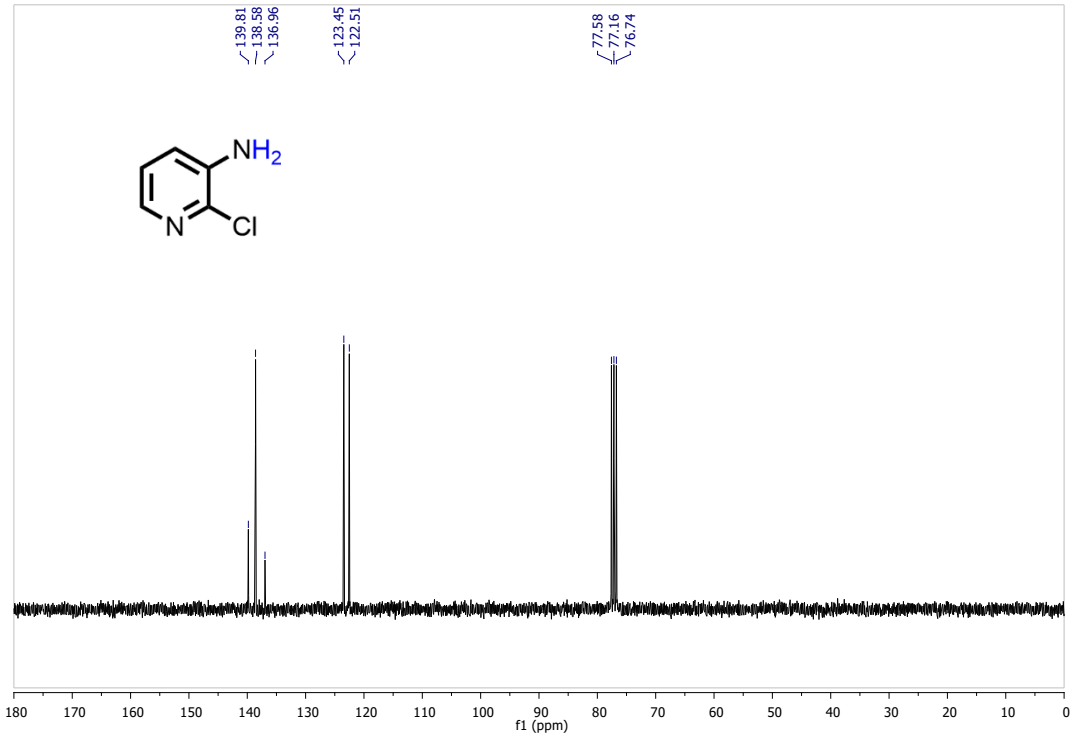


Figure S55. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, 25 °C, $CDCl_3$) of **5x**.

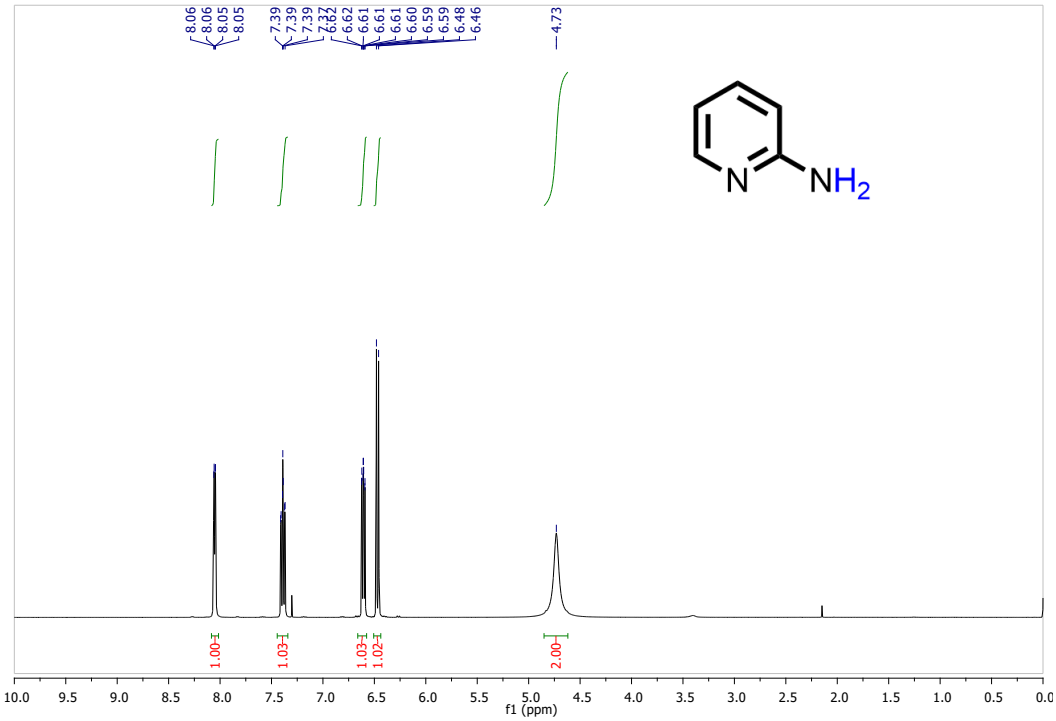


Figure S56. ^{1}H NMR Spectrum (400 MHz, 25 °C, $CDCl_3$) of **5y**.

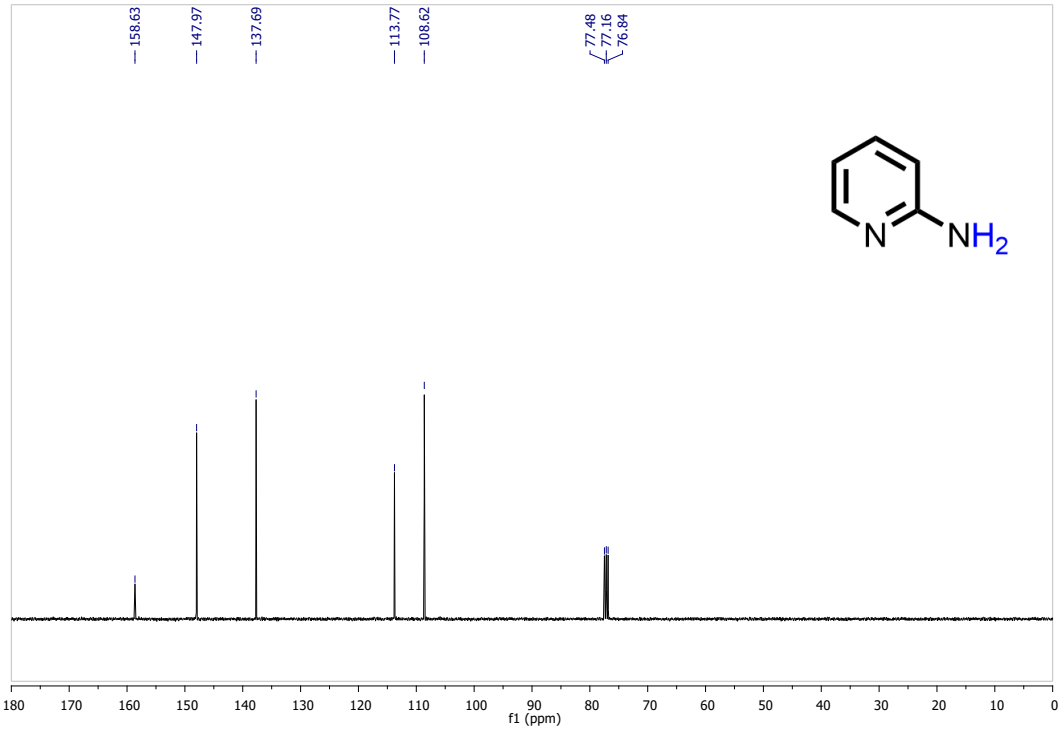
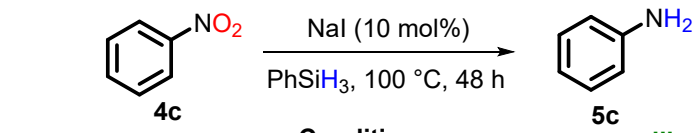


Figure S57. $^{13}C\{^{1}H\}$ NMR Spectrum (100 MHz, 25 °C, $CDCl_3$) of **5y**.

7. Gram scale reactions.

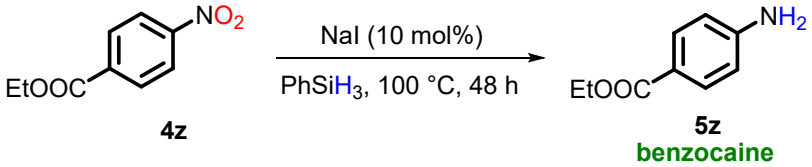
The gram scale reaction was performed under similar conditions where aniline and benzocaine were obtained in good yields.



4c **5c** **aniline**

Conditions

1. **4c** (5 mmol), catalyst **1** (1 mol%), **5c**: yield 65% (302 mg)
2. **4c** (5 mmol), catalyst **1** (3 mol%), **5c**: yield 82% (381 mg)

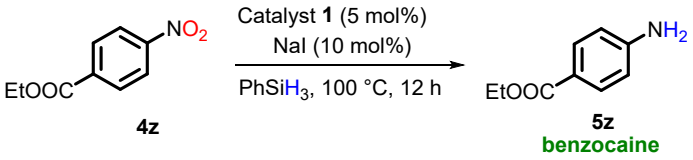


4z **5z** **benzocaine**

Conditions

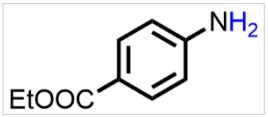
1. **4z** (5 mmol), catalyst **1** (1 mol%), **5z**: yield 62% (512 mg)
2. **4z** (5 mmol), catalyst **1** (3 mol%), **5z**: yield 74% (610 mg)

8. Synthesis of drug molecules 5z-5za and their NMR spectra.



4z **5z**
benzocaine

In a 25 mL Schlenk flask, indium metal complex **1** (5 mol%), ethyl-4-nitrobenzoate (0.5 mmol), NaI (10 mol%) and $PhSiH_3$ (2.0 mmol) were added inside glovebox. Then, toluene (0.5 mL) was added into it and allowed the reaction mixture to stir at 100 °C (preheated) for 12 h. The reaction mixture was allowed to come at room temperature and methanol/water was added into it. The reaction mixture was extracted in DCM and organic layer was separated which was dried over anhydrous Na_2SO_4. The solvent was evaporated and the reaction mixture was purified by column chromatography using silica and mixture of hexane and ethyl acetate as an eluent.



Ethyl-4-aminobenzoate, **5z**.[3] Yield: 78% (64 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.88 (m, 2H), 6.67 - 6.66 (m, 2H), 4.34 (t, 2H, J = 6 Hz), 4.09 (b, 2H), 1.38 (d, 3H, J = 6 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 166.8, 150.9, 131.7, 120.2, 113.9, 60.4, 14.5 ppm.

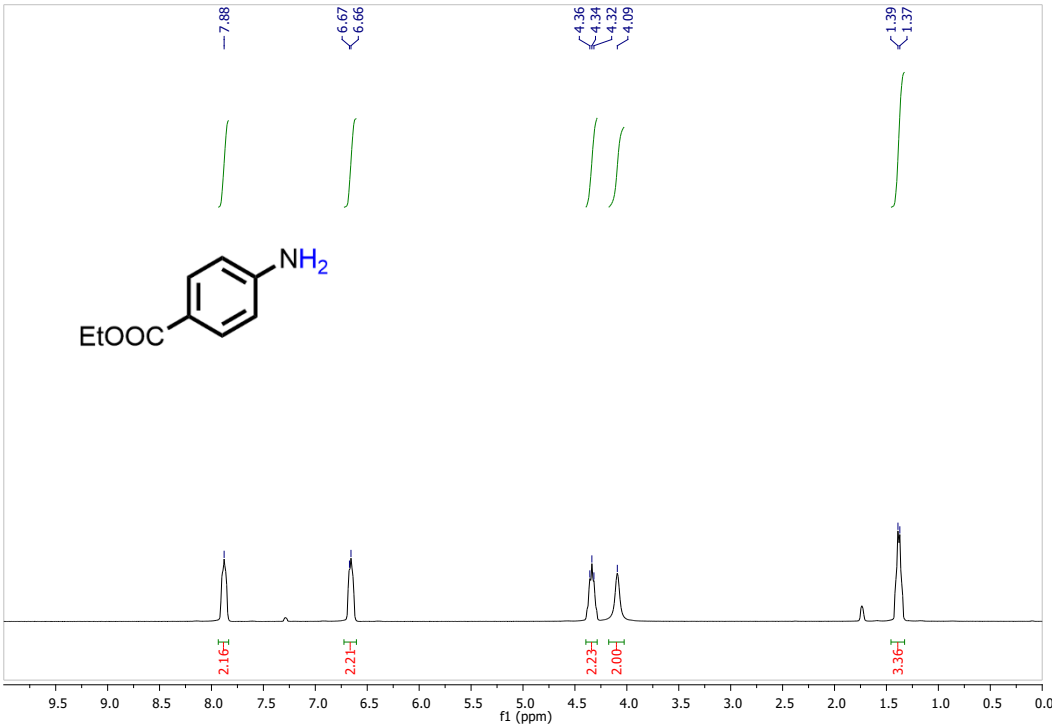


Figure S58. ^{1}H NMR Spectrum (300 MHz, 25 °C, $CDCl_3$) of **5z**.

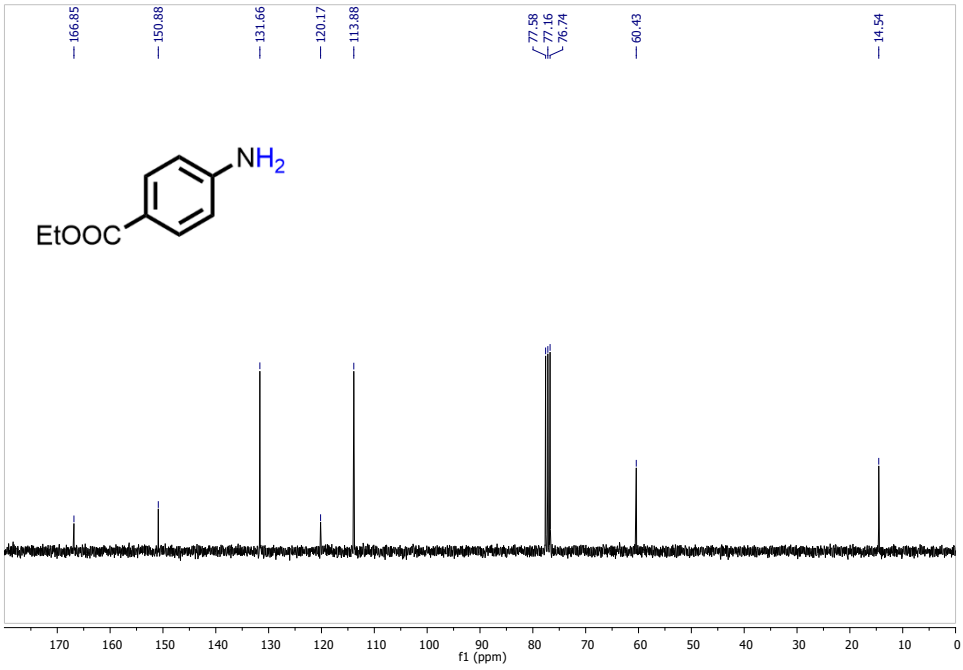
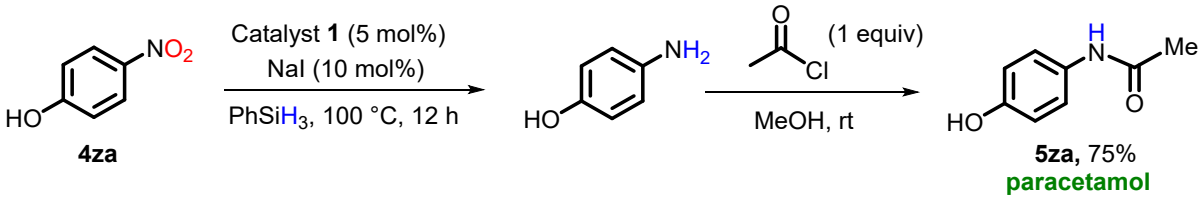
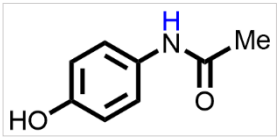


Figure S59. $^{13}C\{^{1}H\}$ NMR Spectrum (300 MHz, 25 °C, $CDCl_3$) of **5z**.



In a 25 mL Schlenk flask, indium metal complex **1** (5 mol%), 4-nitrophenol (0.5 mmol), NaI (10 mol%) and $PhSiH_3$ (2.0 mmol) were added inside glovebox. Then, toluene (0.5 mL) was added into it and allowed the reaction mixture to stir at 100 °C (preheated) for 12 h. The reaction mixture was allowed to come at room temperature and methanol/water was added into it. The reaction mixture was extracted in DCM and organic layer was separated which was dried over anhydrous Na_2SO_4. The solvent was evaporated and the reaction mixture was purified by column chromatography using silica and mixture of hexane and ethyl acetate as an eluent. To a solution of 4-aminophenol (54 mg, 0.5 mmol) in MeOH (5 mL) was added and allowed the reaction mixture to stir at room temperature. Then, acetylchloride (36 µL, 0.5 mmol) in MeOH (5 mL) was added dropwise into the reaction mixture. The reaction mixture was stirred for 3 h and the product was extracted with ethylacetate and dried over anhydrous $MgSO_4$. The crude product was isolated by column chromatography using silica and mixture of hexane and ethyl acetate as an eluent.



N-(4-hydroxyphenyl)acetamide, **5zz**.[3] Yield: 75% (57 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 9.67 (b, 1H), 9.20 (b, 1H), 7.35 (d, 2H, J = 8 Hz), 6.69 (d, 2H, J = 8 Hz), 1.99 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ_C 168.1, 153.6, 131.5, 121.3, 115.5, 24.2 ppm.

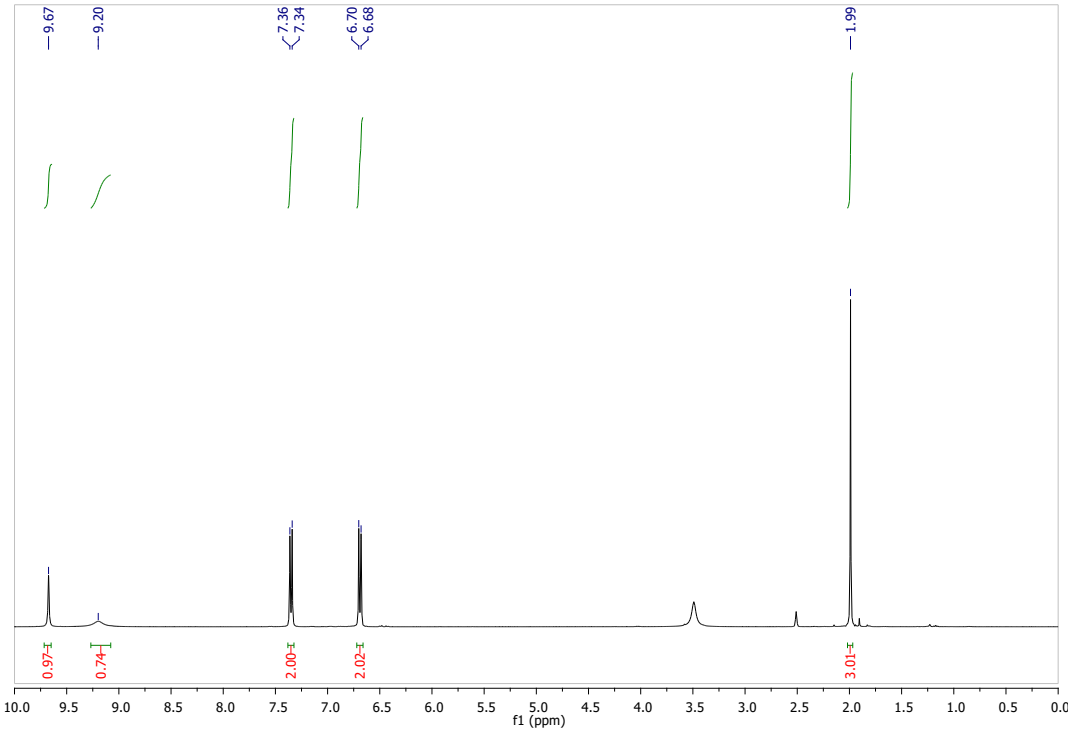


Figure S60. ^{1}H NMR Spectrum (400 MHz, 25 °C, DMSO-d_6) of **5za**.

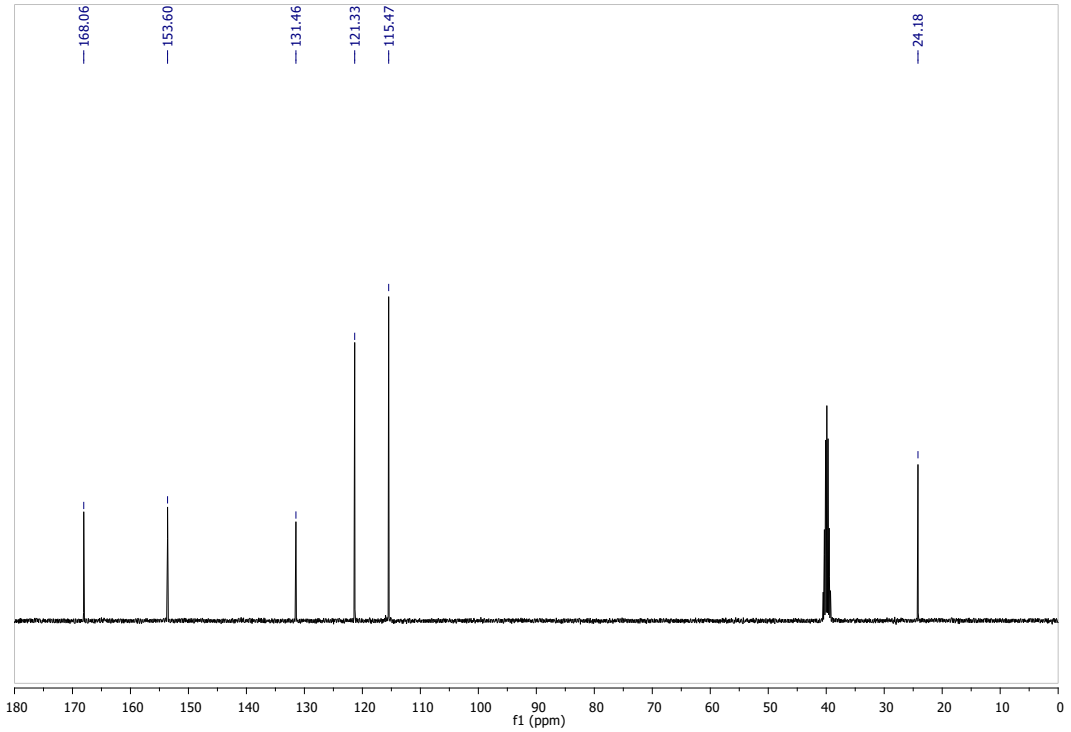


Figure S61. $^{13}C\{^{1}H\}$ NMR Spectrum (300 MHz, 25 °C, DMSO-d_6) of **5za**.

8. References

1. (a) A. Altomare, M. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.,* 1993, ***26***, 343; (b) M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori and R. Spagna, *J. Appl. Crystallogr.,* 2005, ***38***, 381.
2. G. M. Sheldrick, *Acta Crystallogr., Sect. A*: *Found. Crystallogr.*, 2008, ***64***, 112.
3. (a) R. R. Behera, S. Panda, R. Ghosh, A. A. Kumar and B. Bagh, *Org. Lett.*, 2022, **24**, 9179−9183. (b) G. V. Kumar and S. K. Mandal, *Dalton Trans.*, 2016, **45**, 7421-7426. (c) R. Lopes, M. M. Pereira and B. Royo, *ChemCatChem*, 2017, **15**, 3073-3077. (d) L. Zhao, C. Hu, X. Cong, G. Deng, L. L. Liu, M. Luo, and X. Zeng, *J. Am. Chem. Soc.*, 2021, **143**, 1618-1629.