Electronic Supplementary Information

Metal-organic framework-derived CoN_x nanoparticles on N-doped carbon for selective N-alkylation of aniline

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Chemicals

Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$), methanol, toluene and silica gel were purchased from Merck. 2-methylimidazole was purchased from Avra. Chloroform-D was purchased from Sigma Aldrich. Vulcan-XC-72R carbon was purchased from CABOT corporation. Alcohols and amines were obtained commercially from various chemical companies (Sigma Aldrich, Avra, and SRL). All catalytic experiments were carried out in a pressure sealed tube (Ace pressure tube, volume 15 mL, from Sigma).

Instruments

High resolution X-ray diffractions (HR-XRD) of the catalysts were carried out in Rigaku SmartLab 9kW Powder X-ray diffractometer (RIGAKU Corporation).

Scanning Electron Microscopy (FE-SEM) studies were carried out in Nova Nano SEM 450, FEI Company of USA (S.E.A.) PTE, LTD. Energy dispersive X-ray spectroscopy (EDX) images were collected by Team Pegasus Integrated EDS-EBSD with Octane plus and Hikari Pro EDX System. Elemental mapping was performed with the analyzer attached to SEM. TEM studies were carried out on Tecnai G2 20 TWIN transmission electron microscope connected with an energy-dispersive X-ray spectrometer (EDAX, r-TEM SUTW).

The X-ray photoelectron spectroscopy (XPS) measurements were performed in a K-Alpha X-ray photoelectron spectrometer from Thermo Fisher Scientific. The binding energies were calibrated using the C 1s peak located at 284.6 eV as the reference. Raman spectra were recorded in an STR-300 spectrometer (AIRIX Corp.) with a 532 nm excitation source.

^{1}H-NMR spectra were recorded on AVH D 500 AVANCE III HD 500 MHZ, One Bay NMR Spectrometer from Bruker Bio Spin International. The Chemical shifts were reported in ppm. Coupling constants are expressed in Hertz (Hz). The following abbreviations are used: s = singlet, bs = broad singlet d = doublet, t = triplet and m = multiple. The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra ($CDCl_3$: δ_H = 7.28-7.29 ppm, δ_C = 77.01-77.16 ppm).

The GC-MS analyses were recorded on Agilent 5977B instrument. Conversion and yields were determined by GC-FID, HP-5MS UI chromatograph with FID detector, (HP-5MS UI .025µ, 30 m x 0.25 mm) capillary column.

Experimental

Synthesis of ZIF-67@C[1]

200 mg Vulcan carbon was dispersed in 30 mL methanol and stirred for 30 minutes. $Co(NO_3)_2.6H_2O$ (1.00 mmol) was added to the previous dispersion of Vulcan and stirred for 10 minutes to form the dispersion A. 2-methylimidazole (4 mmol) was dissolved in 20 mL methanol and stirred for 10 minutes to get the solution B. Then, solution B was added to A at a time and stirred for 24 h. The precipitate of ZIF-67@C was obtained. The precipitate was collected by centrifugation (14000 rpm for 15 minutes) and washed five times with methanol. The obtained precipitate was dried at 60 °C in a hot air oven over night.

Synthesis of CoN_x@NC[1]

200 mg of ZIF-67@C was ground in a mortar pestle to get a fine powder. The powder was placed in a crucible boat and heated at 800 °C in the presence of N_2 for 3 h (in a tubular furnace with heating rate: 5 °C/min from 35 °C). The furnace was allowed to cool down to room temperature. The black powder was collected and denoted as CoN_x@NC.

Similarly, CoN_x@NC-1 and CoN_x@NC-2 were prepared from ZIF-67@C by changing the pyrolysis temperature to 700 °C and 900 °C, respectively.

Synthesis of Co@C[2]

200 mg Vulcan carbon was dispersed in 30 mL methanol and stirred for 30 minutes. $Co(NO_3)_2.6H_2O$ (1.00 mmol) was added to the previous dispersion of Vulcan and stirred for 10 minutes to form the dispersion A. $NaBH_4$ (2 mmol) was dissolved in 20 mL methanol and stirred for 1 minute to form the solution B. The solution B was added to A at a time and stirred for 24 h. The mixture yielded a black suspension of Co@C. The precipitate was collected by centrifugation (11000 rpm for 10 minutes) and washed five times with methanol. The obtained precipitate was dried at 60 °C in a hot air oven over night.

Figures

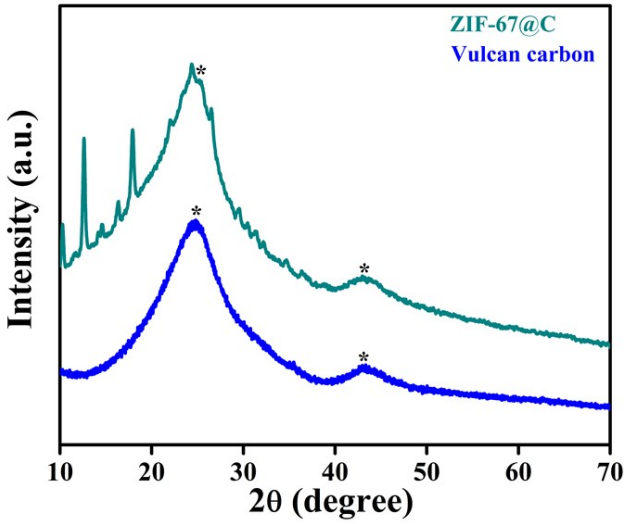


Figure S1. The PXRD patterns of ZIF-67@C and Vulcan carbon.

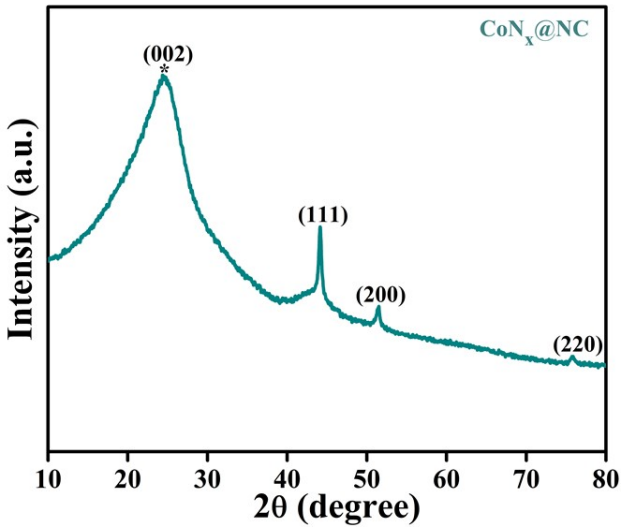


Figure S2. The PXRD pattern of CoN_x@NC. The PXRD of CoN_x@NC showed that cobalt crystallized in pure face-center cubic (*fcc*) phase (JCPDS: No.15-0806). The broad peak at $2\theta = 24.56^{o}$ is related to graphitic carbon.[3]

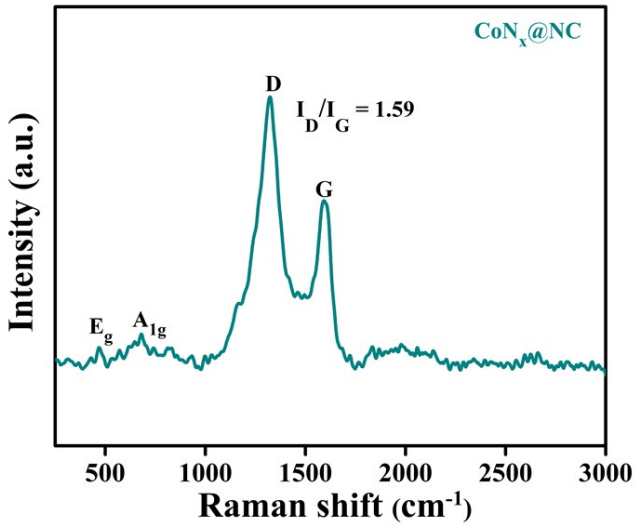


Figure S3. Raman spectra of CoN_x@NC showing the peaks at 1322 and 1596 cm^{-1} corresponding to D and G bands of graphitic carbon and peaks at 475 and 682 cm^{-1} correspond to vibration modes of E_g and A_{1g} of metallic Co. The I_D/I_G of CoN_x@NC catalyst is 1.59.[4]

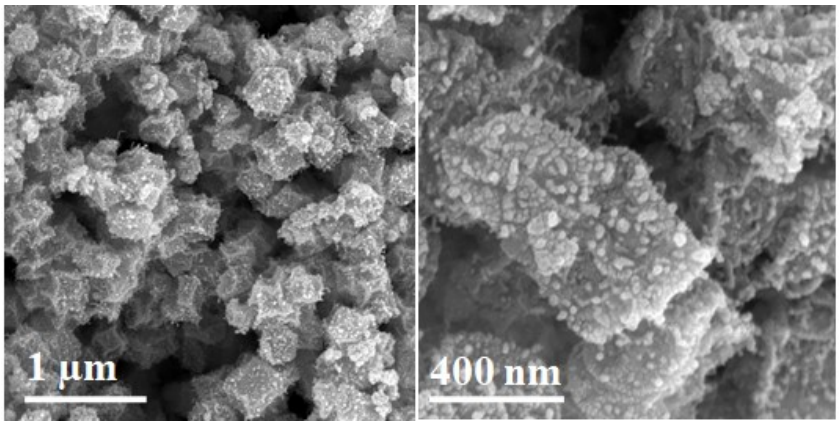


Figure S4. FE-SEM images of the CoN_x@NC showed rhombic dodecahedron morphology at different resolutions.

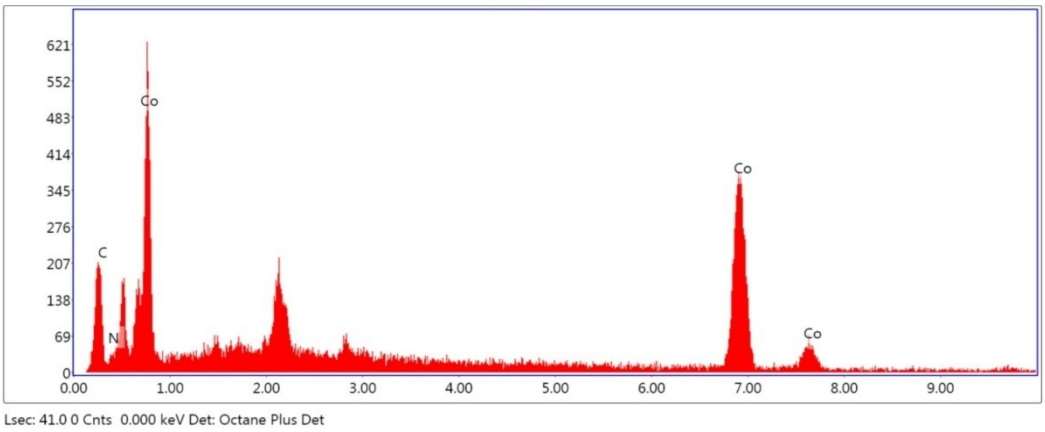


Figure S5. EDX spectrum of CoN_x@NC showing the presence of Co, C and N.

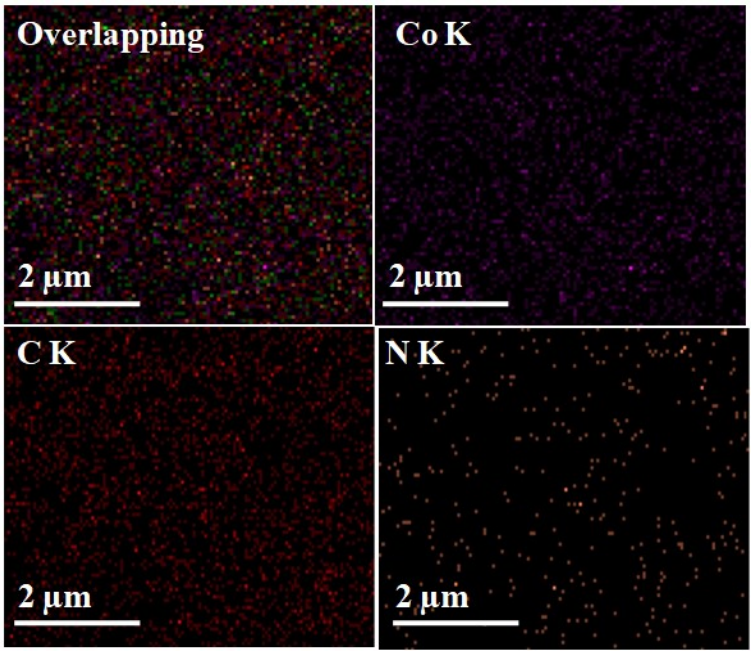


Figure S6. Elemental mapping of CoN_x@NC showing the homogeneously distributed of Co, C and N.

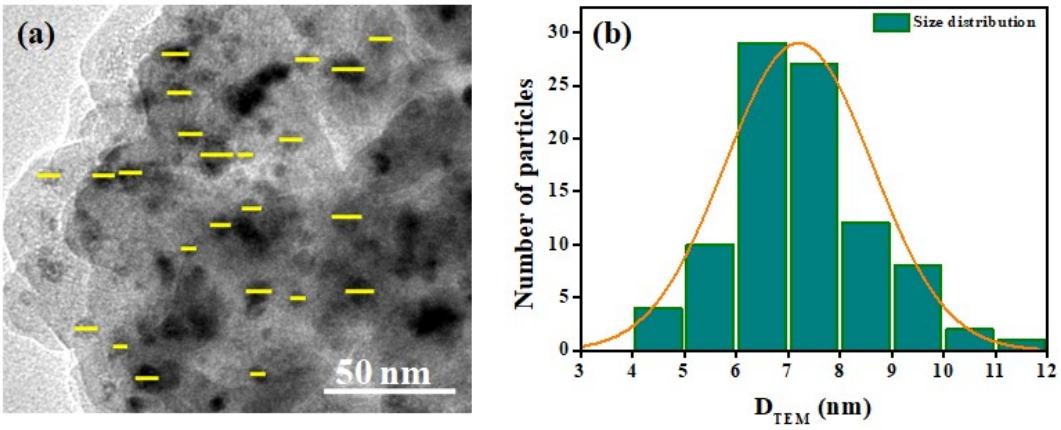


Figure S7. The average particles size of Co in CoN_x@NC is 6-7 nm.

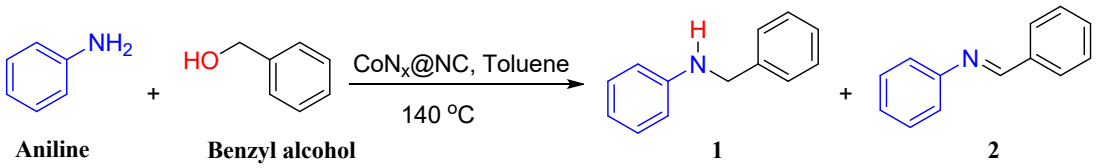
Catalytic Test

N-alkylation of amines with alcohols was carried out in a 15 mL pressure sealed tube. In a typical experiment, the sealed tube was filled with 1 mmol benzyl alcohol, 0.5 mmol aniline, 10 mg catalyst (CoN_x@NC) and toluene (2 mL) was used as a solvent. Then, the tube was capped and placed in the oil bath preheated at 140 °C and the reaction was continued for 18-24 h with stirring (500 rpm). After the reaction, the sealed tube was cooled down to room temperature and the mixture was centrifuged to separate the solid catalyst. The liquid part was collected and worked up.

The % of conversion and product yield was analyzed using an Agilent 7890 GC equipped with an HP-5MS UI (.025µ, 30 m x 0.25 mm, -60 to 350 ^{o}C) capillary column and ^{1}H NMR.

After each amination test, the catalyst was washed with ethanol and separated by centrifugation several times and dried for overnight for further testing of the recyclability of the catalyst.

Table S1: Optimization of the reaction condition



Aniline + **Benzyl alcohol** → **1** + **2**

Entry	Catalyst	Base	Solvent	Conv. (%)	Yield **1** (%)	Yield **2** (%)
Variation of catalyst						
1.	**CoN_x@NC**	***tert*-BuOK**	**Toluene**	**>99**	**99**	0
2.	CoN_x@NC-1	*tert*-BuOK	Toluene	96	87	9
3.	CoN_x@NC-2	*tert*-BuOK	Toluene	>99	90	9
4.	Co@C	*tert*-BuOK	Toluene	87	65	22
5.	Vulcan carbon	*tert*-BuOK	Toluene	35	28	7
6.	Co-ZIF@C	*tert*-BuOK	Toluene	56	46	9
7.	$Co(NO_3)_2.6H_2O$	*tert*-BuOK	Toluene	44	36	8
Variation of base						
8.	CoN_x@NC	-	Toluene	85	56	29
9.	CoN_x@NC	K_2CO_3	Toluene	54	40	14
10.	CoN_x@NC	Cs_2CO_3	Toluene	65	56	9
11.	CoN_x@NC	KOH	Toluene	86	73	13
12.	**CoN_x@NC**	***tert*-BuOK**	**Toluene**	**>99**	**99**	0
Variation of catalyst amount						
13.	CoN_x@NC (5 mg)	*tert*-BuOK	Toluene	85	76	8
14.	**CoN_x@NC (10 mg)**	***tert*-BuOK**	**Toluene**	**>99**	**99**	0
15.	CoN_x@NC (15 mg)	*tert*-BuOK	Toluene	>99	92	6
Variation of solvent						
16.	CoN_x@NC	*tert*-BuOK	CH_3CN	54	43	9
17.	CoN_x@NC	*tert*-BuOK	Dioxane	91	80	11
18.	CoN_x@NC	*tert*-BuOK	THF	97	86	11
19.	**CoN_x@NC**	***tert*-BuOK**	**Toluene**	**>99**	**99**	0

Reaction conditions: Benzyl alcohol (1 mmol), aniline (0.5 mmol), catalyst (10 mg), toluene (2 mL), *tert*-BuOK (0.5 mmol), temperature (140 °C) and time 18 h. Conversion and selectivity were detected by GC-MS and ^{1}H-NMR.

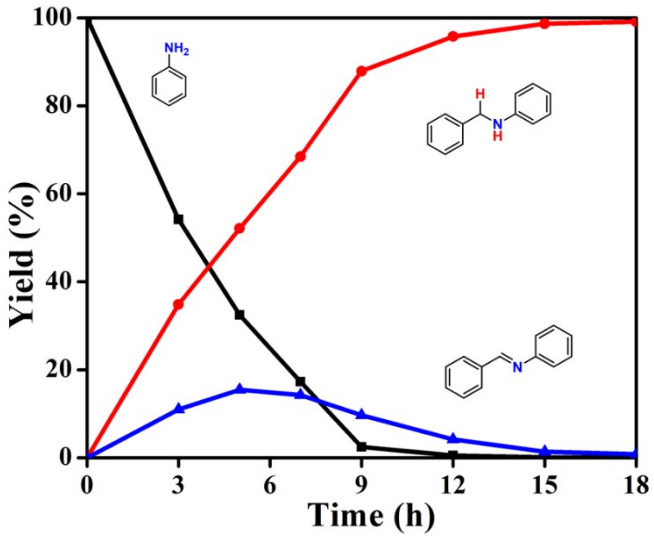


Figure S8. Progress of the N-alkylation reaction of aniline and benzyl alcohol with time. Reaction conditions: Benzyl alcohol (1 mmol), aniline (0.5 mmol), catalyst (10 mg), toluene (2 mL), *tert*-BuOK (0.5 mmol), temperature (140 °C) and time 18 h. Conversion and selectivity were detected by GC-MS.

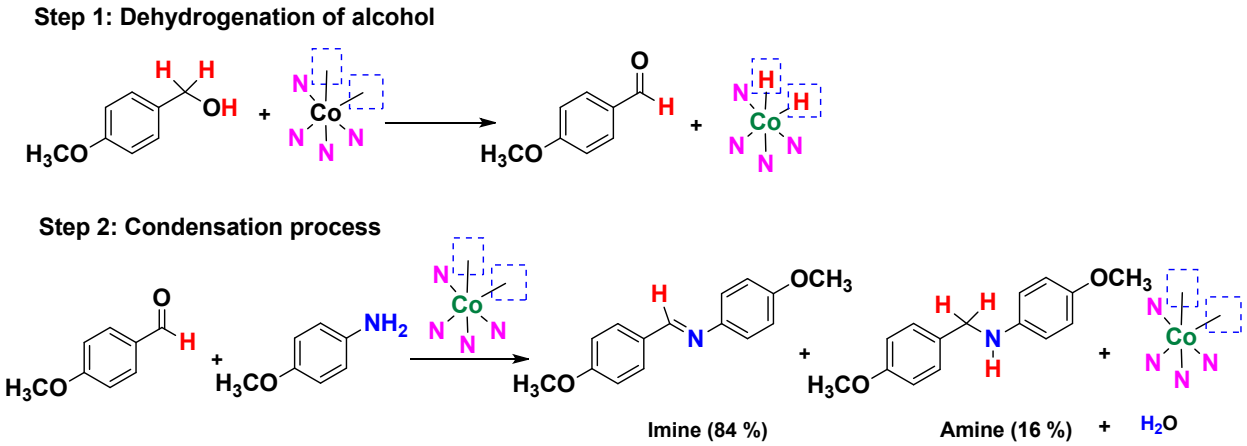
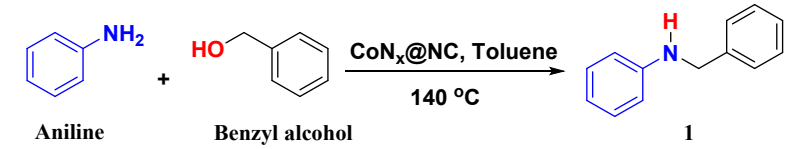


Figure S9. Sequence of the reaction involved as detected by ^{1}H NMR.



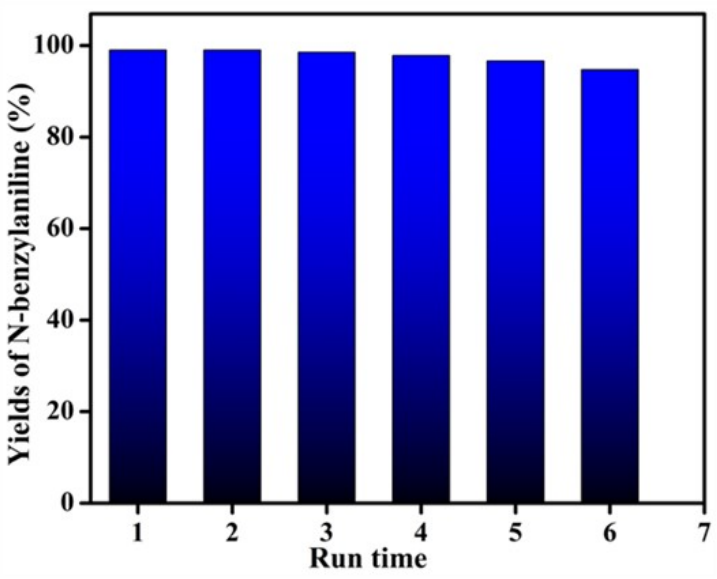
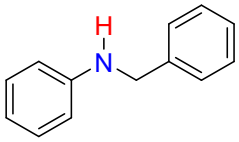
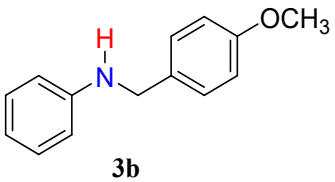
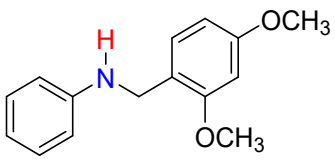
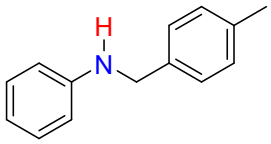
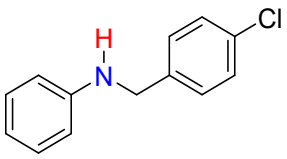
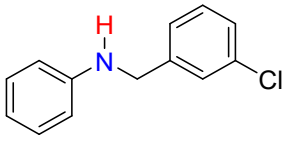
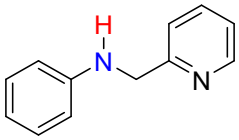
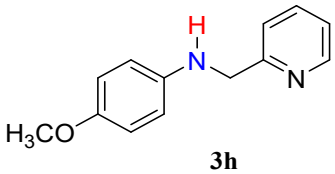
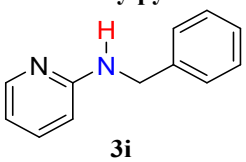
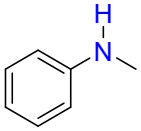
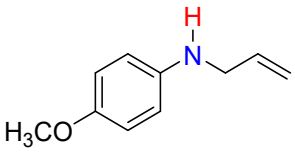
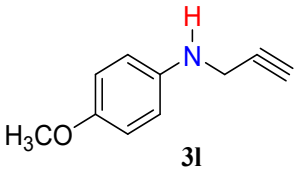


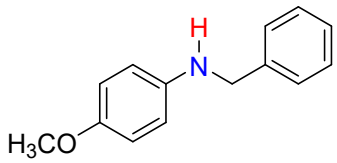
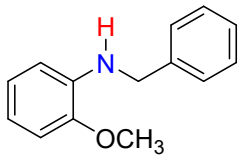
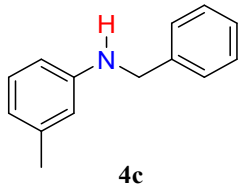
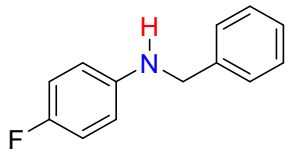
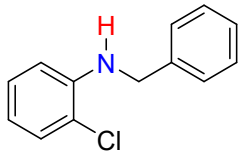
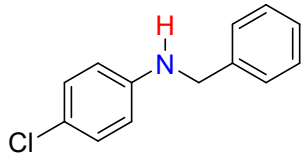
Figure S10: Recycling test of CoN_x@NC for the synthesis of N-benzylaniline. Reaction conditions: 1 mmol benzyl alcohol, 0.5 mmol aniline, 10 mg catalyst, 0.5 mmol *tert*-BuOK, 2 mL toluene, 140 °C, 24 h. Conversions and yields are based on aniline and determined by GC.

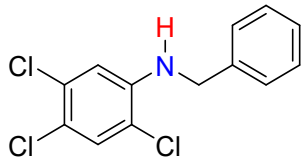
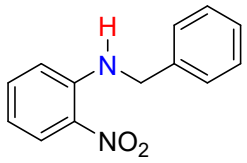
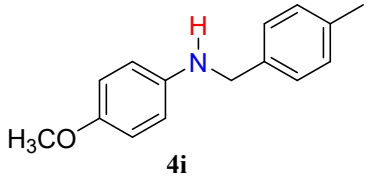
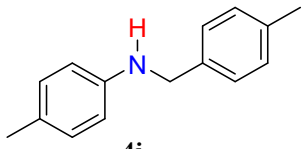
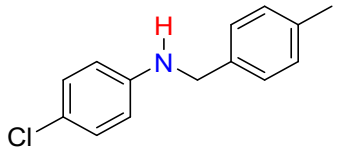
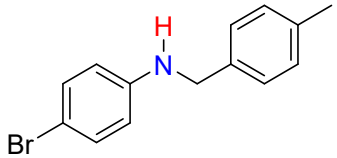
Table S2: Characterization of the products by ^{1}H NMR and ^{13}C NMR

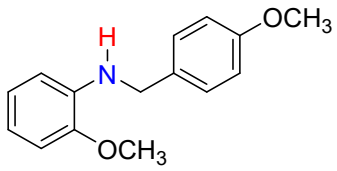
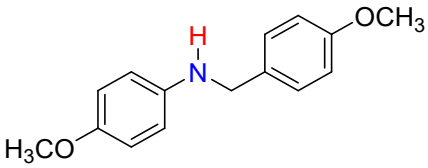
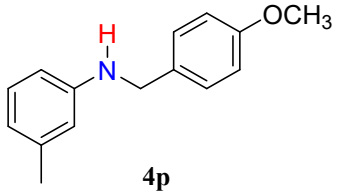
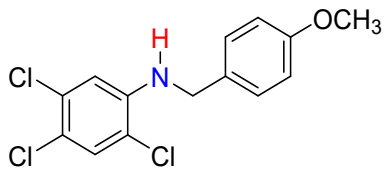
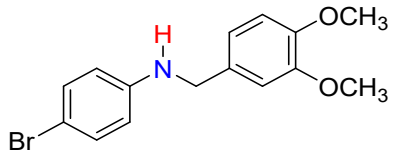
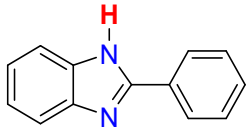
Note: For some compounds intensity of -NH peak is poor and hence not properly visible in ^{1}HNMR.

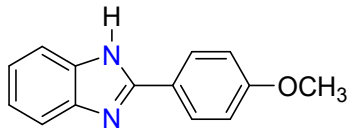
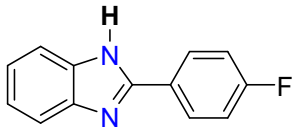
3a: N-benzylaniline  **3a**	**^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.43-7.31 (m, *J* = 7.1 Hz, 5H), 7.23 (m, *J* = 7.4 Hz, 2H), 6.77 (m, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 2H), 4.38 (s, 2H), 4.07 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 148.12, 139.40, 129.24, 128.6, 127.48, 127.20, 117.53, 112.81, 48.28. Yield of product: 99%, 90.2 mg and 0.49 mmol
3b: N-(4methoxybenzyl) aniline  **3b**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.33 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.5, 7.4 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.75 (m, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 2H), 4.29 (s, 2H), 3.98 (s, 1H), 3.84 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.89, 148.24, 131.44, 129.28, 128.84, 117.53, 114.05, 112.86, 55.33, 47.82. Yield of product: 97%, 103.6 mg and 0.48 mmol
3c: N-(2,4-dimethoxybenzyl) aniline  **3c**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.26–7.20 (m, 2H), 7.19 (d, *J* = 1.2 Hz, 2H), 6.71 (t, *J* = 6.8 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 2H), 6.50 (d, *J* = 2.3 Hz, 1H), 6.46 (m, *J* = 8.3, 2.4 Hz, 2H), 4.28 (s, 2H), 3.86 (s, 3H), 3.82 (s, 3H), 3.41 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.22, 158.45, 148.52, 129.71, 129.16, 119.80, 117.30, 113.12, 103.92, 98.65, 55.39, 43.18. Yield of product: 88%, 107.1 mg and 0.44 mmol
3d: N-(4-methylbenzyl) aniline  **3d**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.34 (t, *J* = 7.7 Hz, 2H), 7.25 (dd, *J* = 13.3, 5.9 Hz, 4H), 6.79 (m, *J* = 10.2 Hz, 1H), 6.71 (d, *J* = 7.3 Hz, 2H), 4.36 (s, 2H), 4.04 (s, 1H), 2.44 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 148.31, 136.92, 136.46, 129.35, 127.59, 117.56, 112.92, 48.14, 21.18. Yield of product: 88%, 86.8 mg and 0.44 mmol
3e: N-(4-chlorobenzyl) aniline  **3e**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.33 (d, 4H), 7.25–7.18 (m, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 2H), 4.34 (s, 2H), 4.09 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 147.94, 138.12, 132.98, 129.42, 128.84, 117.92, 113.00, 47.72. Yield of product: 86%, 94.0 mg and 0.43 mmol
3f: N-(3-chlorobenzyl)aniline  **3f**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.40 (s, 1H), 7.28 (t, 3H), 7.24–7.18 (m, 2H), 6.77 (m, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.7 Hz, 2H), 4.35 (s, 2H), 4.12 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 147.79, 141.75, 134.54, 129.89, 129.31, 127.40, 125.41, 117.87, 112.91, 47.80. Yield of product: 84%, 91.8 mg and 0.42 mmol.

3g: N-(pyridine-2-ylmethyl) aniline  **3g**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.60 (m, 1H), 7.66 (td, *J* = 1.8, 7.7 Hz, 1H), 7.36 (dt, *J* = 1.0, 7.8 Hz, 1H), 7.23–7.17 (m, 3H), 6.74 (m,1H), 6.69 (t, *J* = 7.7 Hz, 2H), 5.12–4.62 (m, 1H), 4.49 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.91, 149.58, 148.26, 137.06, 129.63, 122.50, 121.99, 117.99, 113.44, 49.67. Yield of product: 83%, 76.4 mg and 0.415 mmol.
3h: 4-methoxy-N-(pyridin-2-ylmethyl) aniline  **3h**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.60 (d, *J* = 5.6 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.22–7.16 (m, 1H), 6.80 (d, *J* = 8.9 Hz, 2H), 6.65 (d, *J* = 8.0 Hz, 2H), 4.44 (s, 2H), 3.86 (s, 1H), 3.76 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.89, 152.26, 149.21, 142.19, 136.64, 122.07, 121.68, 114.92, 114.33, 55.79, 50.28. Yield of product: 81%, 86.5 mg and 0.40 mmol
3i: N-benzylpyridin-2-amine  **3i**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.11 (d, *J* = 4.2 Hz, 1H), 7.49–7.31 (m, 5H), 7.32–7.26 (m, 1H), 6.67–6.56 (m, 1H), 6.39 (d, *J* = 8.4 Hz, 1H), 5.11 (s, 1H), 4.53 (d, *J* = 4.7 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.74, 148.17, 139.24, 137.68, 128.75, 127.41, 113.23, 106.89, 46.42. Yield of product: 82%, 75.5 mg and 0.41 mmol.
3j: N-methylaniline  **3j**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.27 (t, *J* = 7.9 Hz, 2H), 6.79 (t, *J* = 8.3 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 2H), 3.71 (s, 1H), 2.89 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.42, 129.26, 117.29, 112.48, 30.76. Yield of product: 72%, 39.1 mg and 0.36 mmol
3k: N-allylaniline  **3k**	**^{1}H NMR (500 MHz, $CDCl_3$):** δ 6.81 (d, *J* = 9.0 Hz, 2H), 6.63 (d, *J* = 8.9 Hz, 2H), 5.99 (ddd, *J* = 15.7, 10.4, 5.2 Hz, 1H), 5.31 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.19 (dd, *J* = 10.3, 1.5 Hz, 1H), 3.77 (s, 3H), 3.76 (d, *J* = 5.5 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 152.25 (s), 142.32 (s), 135.84 (s), 116.14 (s), 114.90 (s), 114.36 (s), 55.82 (s), 47.58 (s). Yield of product: 55%, 41.6 mg and 0.27 mmol.
3l: 4-methoxy-N-(prop-2-yn-1-yl) aniline  **3l**	**^{1}H NMR (500 MHz, $CDCl_3$):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 (d, *J* = 9.0 Hz, 2H), 6.70 (d, *J* = 9.0 Hz, 2H), 3.91 (s, 2H), 3.78 (s, 3H), 2.24 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 153.01, 140.97, 115.14, 114.86, 81.43, 71.26, 55.73, 34.60. Yield of product: 52%, 42.4 mg and 0.26 mmol.

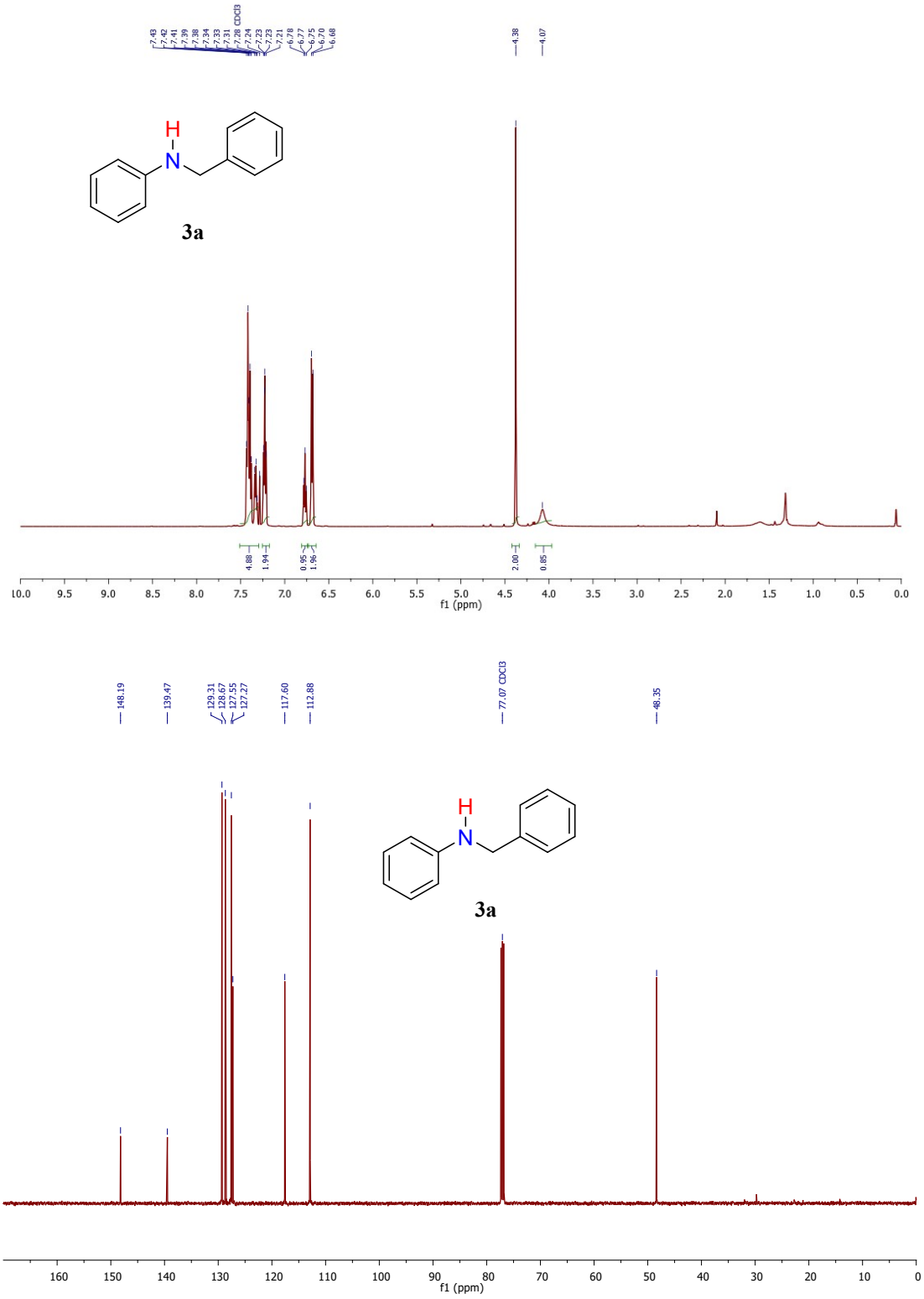
4a: N-benzyl-4-methoxyaniline  **4a**	**^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.48-7.39 (m, 4H), 7.35 (t, *J* = 6.7 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.7 Hz, 2H), 4.35 (s, 2H), 3.81 (s, 3H), 3.63 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.25, 142.55, 139.81, 128.68, 127.63, 127.24, 114.99, 114.19, 55.85, 49.28. Yield of product: 92%, 98.1 mg and 0.46 mmol.
4b: N-benzyl-2-methoxyaniline  **4b**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 (m, *J* = 7.3 Hz, 5H), 6.89 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.73 (t, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 4.69 (s, 1H), 4.40 (s, 2H), 3.90 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 146.90, 139.69, 138.23, 128.69, 127.63, 127.23, 121.39, 116.76, 110.21, 109.50, 55.52, 48.16. Yield of product: 86%, 91.7 mg and 0.40 mmol.
4c: N-benzyl-3-methylaniline  **4c**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.40-7.25 (m, 5H), 7.15-7.06 (m, 1H), 6.63 (t, *J* =0.8, 1H), 6.57-6.50 (m, 2H), 4.38 (s, 2H), 4.02 (s, 1H), 2.35 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 148.31, 139.65, 139.13, 129.25, 128.72, 127.63, 127.29, 118.62, 113.73, 110.05, 48.42, 21.75. Yield of product: 80%, 78.9 mg and 0.40 mmol.
4d: N-benzyl-4-fluoroaniline  **4d**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38-7.30 (m, 4H), 7.30-7.25 (m, 1H), 6.95-6.92 (d, *J* = 7.7 Hz, 2H), 6.62-6.57 (d, *J* = 13.1 Hz, 2H), 4.33 (s, 2H), 3.97 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 156.68, 154.81, 144.35, 139.10, 128.53, 127.35, 115.44, 113.53, 48.78. Yield of product: 84%, 84.5 mg and 0.40 mmol.
4e: N-benzyl-2-chloroaniline  **4e**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.45–7.39 (m, 3H), 7.39–7.29 (m, 5H), 6.73 – 6.71 (d, 1H), 4.77 (s, 1H), 4.39 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 143.38, 137.66, 131.78, 129.94, 129.02, 127.87, 127.42, 119.50, 117.83, 112.31, 47.95. Yield of product: 81%, 88.16 mg and 0.405 mmol
4f: N-benzyl-4-chloroaniline  **4f**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 (d, *J* = 4.6 Hz, 4H), 7.32 (dd, *J* = 8.7, 4.5 Hz, 1H), 7.14 (d, *J* = 8.9 Hz, 2H), 6.57 (d, *J* = 8.9 Hz, 2H), 4.32 (s, 2H), 4.07 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 146.70, 139.13, 129.12, 128.76, 127.45, 122.12, 113.98, 48.37. Yield of product: 82%, 88.2 mg and 0.405 mmol.

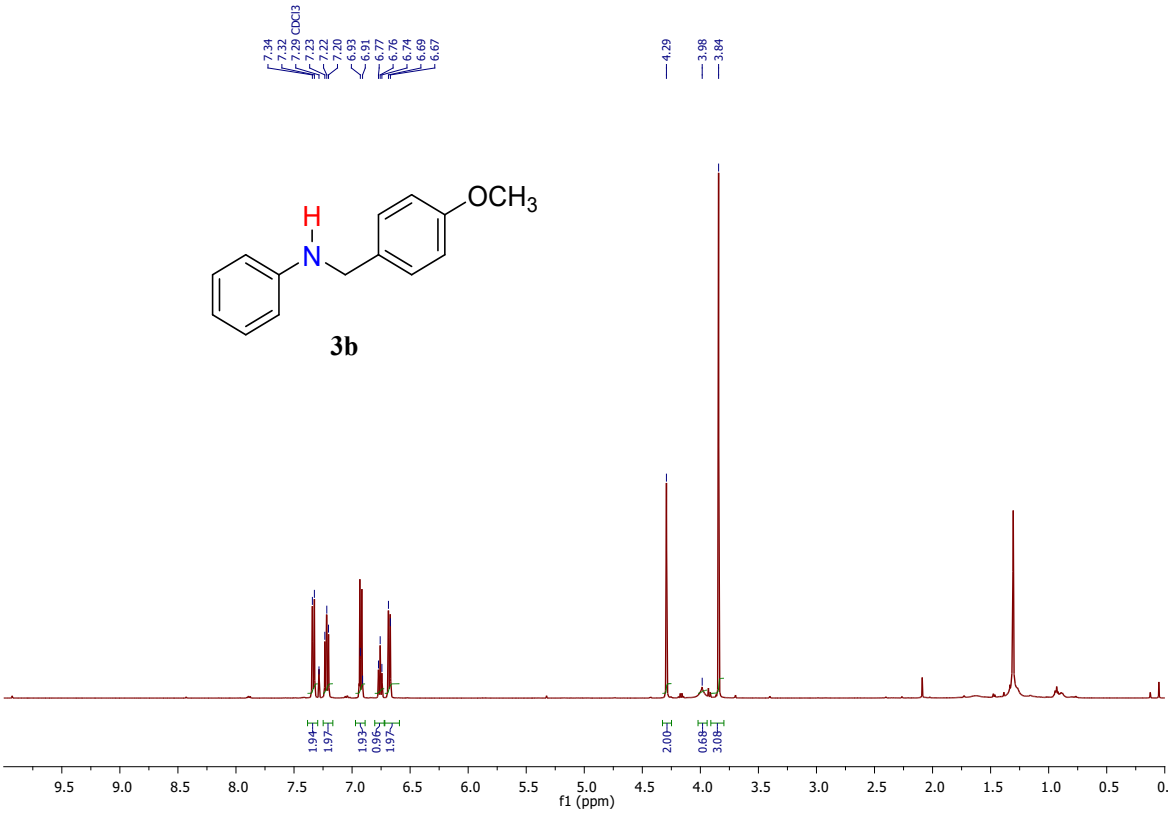
4g: N-benzyl-2,4,5-trichloroaniline  **4g**	^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.33 (m, 6H), 6.71 (s, 1H), 4.76 (s, 1H), 4.38 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.68, 131.80, 129.96, 129.04, 127.88, 127.43, 119.53, 117.86, 112.33, 47.97. Yield of product: 81%, 116.23 mg and 0.40 mmol.
4h: N-benzyl-2-nitroaniline  **4h**	**^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.46 (s, 1H), 8.22 (d, *J* = 8.6 Hz, 1H), 7.43 – 7.31 (m, 6H), 6.84 (d, 1H), 6.69 (, 1H), 4.57 (s, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 145.27, 137.37, 136.24, 132.29, 128.95, 127.72, 127.06, 126.89, 115.74, 114.21, 47.11. Yield of product: 72%, 82.2 mg and 0.36 mmol.
4i: 4-methoxy-N-(4-methylbenzyl) aniline  **4i**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.29 (d, *J* = 9.0 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.64 (d, *J* = 8.9 Hz, 2H), 4.27 (s, 2H), 3.78 (s, 3H), 2.38 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.26, 142.65, 136.93, 136.71, 129.39, 127.68, 115.02, 114.24, 55.94, 49.13, 21.23. Yield of product: 89%, 101.4 mg and 0.44 mmol.
4j: 4-methyl-N-(4-methylbenzyl) aniline  **4j**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.33 (d, *J* = 7.7 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.63 (d, *J* = 8.1 Hz, 2H), 4.32 (s, 2H), 3.91 (s, 1H), 2.41 (s, 3H), 2.31 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 146.07, 136.81, 136.66, 129.79, 129.33, 127.56, 126.71, 113.06, 48.46, 21.15, 20.45. Yield of product: 88%, 73.23 mg and 0.44 mmol.
4l: 4-chloro-N-(4-methylbenzyl) aniline  **4l**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.29-7.26 (m, 2H), 7.20 (d, *J* = 7.4 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 4.29 (s, 2H), 4.05 (s, 1H), 2.39 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 146.74, 137.05, 135.89, 129.39, 129.07, 127.44, 122.03, 113.92, 48.13, 21.13. Yield of product: 84%, 97.5 mg and 0.42 mmol.
4m: 4-bromo-N-(4-methylbenzyl) aniline  **4m**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.31-7.25 (m, 4H), 7.20 (d, *J* = 7.8 Hz, 2H), 6.53 (d, *J* = 8.8 Hz, 2H), 4.29 (s, 2H), 4.07 (s, 1H), 2.39 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 147.16, 137.08, 135.83, 131.94, 129.41, 127.44, 114.44, 109.05, 48.02, 21.13 Yield of product: 81%, 112.1 mg and 0.406 mmol.
4n: N-(4-methoxybenzyl)-2-methoxyaniline	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.33 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.7

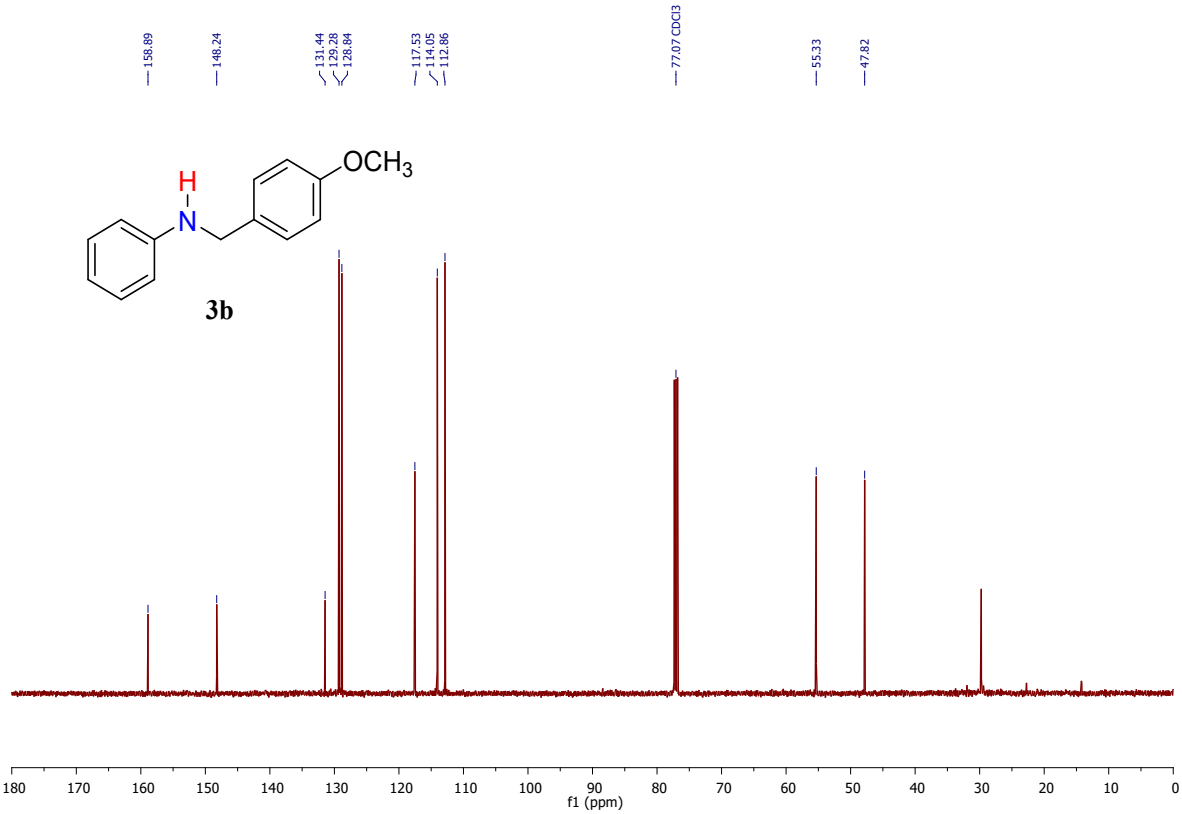
 **4n**	Hz, 2H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 9.2 Hz, 1H), 6.70 (t, *J* = 8.5 Hz, 1H), 6.64 (d, *J* = 9.2 Hz, 1H), 4.63 (s, 1H), 4.30 (s, 2H), 3.86 (s, 3H), 3.83 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.92, 146.91, 138.30, 131.68, 128.96, 121.40, 116.72, 114.14, 110.20, 109.49, 55.48, 47.66. Yield of product: 86%, 104.8 mg and 0.43 mmol.
4o: N-(4-methoxybenzyl)-4-methoxyaniline  **4o**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 6.8 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 8.9 Hz, 2H), 4.22 (s, 2H), 3.81 (s, 3H), 3.75 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.84, 152.19, 142.55, 131.70, 128.86, 114.93, 114.08, 55.84, 55.32, 48.76. Yield of product: 89%, 108.3 mg and 0.44 mmol.
4p: N-(4-methoxybenzyl)-3-methylaniline  **4p**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.31 (d, *J* = 8.7 Hz, 2H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 7.4 Hz, 1H), 6.51-6.46 (m, 2H), 4.26 (s, 2H), 3.97 (s, 1H), 3.83 (s, 3H), 2.30 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.96, 148.36, 139.17, 131.63, 129.27, 128.98, 118.64, 114.14, 113.78, 110.13, 55.44, 47.99, 21.77. Yield of product: 86%, 98.12 mg and 0.43 mmol.
4q: 2,4,5-trichloro-N-(4-methoxybenzyl) aniline  **4q**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.36 (s, 1H), 7.29 (d, *J* = 5.3 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.72 (s, 1H), 4.66 (s, 1H), 4.30 (s, 2H), 3.84 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.21, 143.32, 131.66, 129.82, 129.50, 128.70, 119.29, 117.71, 114.29, 112.21, 55.34, 47.39. Yield of product: 81%, 128.7 mg and 0.40 mmol.
4r: 4-bromo-N-(3,4-dimethoxybenzyl) aniline  **4r**	**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.31-7.22 (d, 2H), 6.91 (d, *J* = 8.3 Hz, 2H), 6.87 (s, 1H), 6.53 (d, *J* = 8.7 Hz, 2H), 4.24 (s, 2H), 4.05 (s, 1H), 3.89 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.25, 148.39, 147.16, 131.94, 131.39, 119.65, 116.71, 114.47, 111.32, 110.74, 77.06, 55.91, 48.18. Yield of product: 79%, 127.65 mg and 0.39 mmol.
5a: 1-phenyl-1H-benzimidazole 	**^{1}H NMR (500 MHz, DMSO-D_6)** δ 12.95 (brs, 1H), 8.21 (d, J = 7.1 Hz, 2H), 7.73 – 7.47 (m, 5H), 7.22 (d, 2H). **^{13}C NMR (125 MHz, DMSO-D_6)** δ 151.72, 144.27, 135.44, 130.67, 130.30, 129.41, 126.92, 122.72, 122.20, 119.29, 111.82. Yield of product: 86%, 83.5 mg and 0.43 mmol.
5b: 2-(4-methoxyphenyl)-1H-benzimidazole	**^{1}H NMR (600 MHz, DMSO-D_6)** δ 12.78 (brs, 1H), 8.17 (d, J = 8.1 Hz,

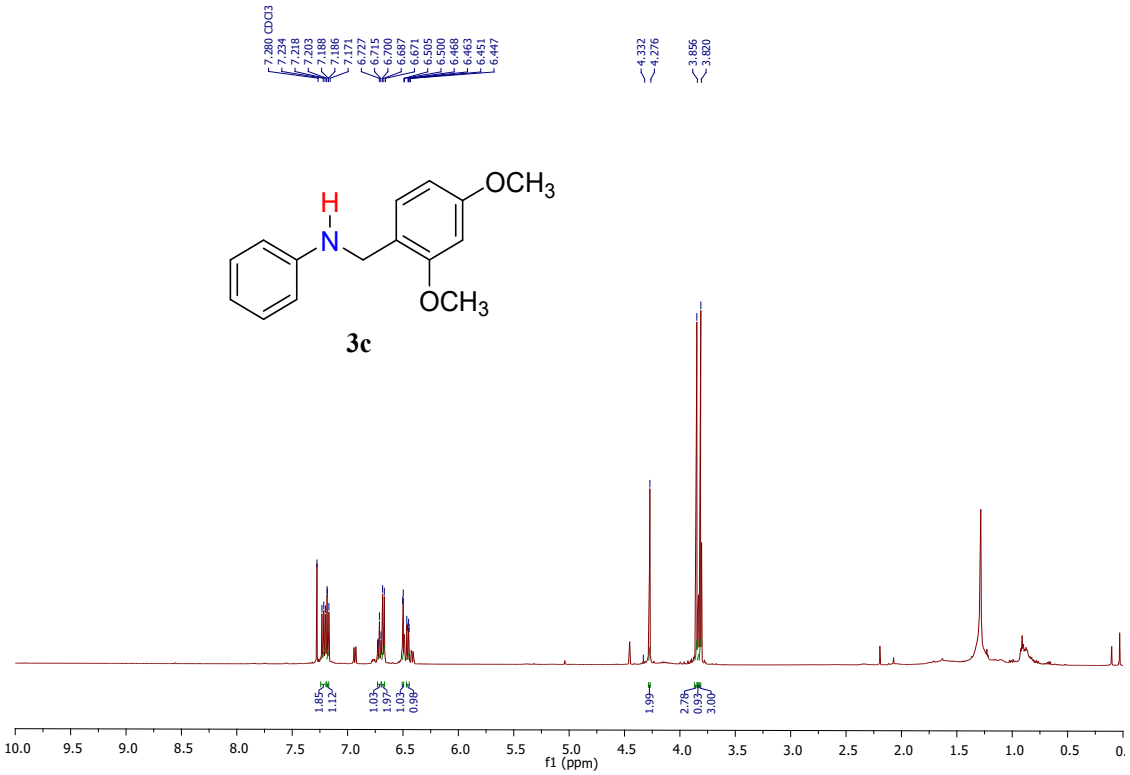
	2H), 7.60 (d, 2H), 7.21 (m, 2H), 7.15 (d, 2H), 3.88 (s, 3H). Yield of product: 84%, 94.2 mg and 0.42 mmol.
5c: 2-(4-flurophenyl)-1H-benzimidazole 	**^{1}H NMR (600 MHz, DMSO-D$_6$)** δ 12.75 (brs, 1H), 8.13 (d, J = 8.7 Hz, 2H), 7.56 – 7.53 (m, 2H), 7.25 (d, 2H), 7.20 (d, 2H). **^{13}C NMR (150 MHz, DMSO-D$_6$)** δ 163.11, 161.49, 160.06, 151.74, 133.48, 130.59, 130.53 128.48, 123.44, 115.84, 115.67. Yield of product: 78%, 82.7 mg and 0.39 mmol.

^{1}H and ^{13}C NMR spectra of the products

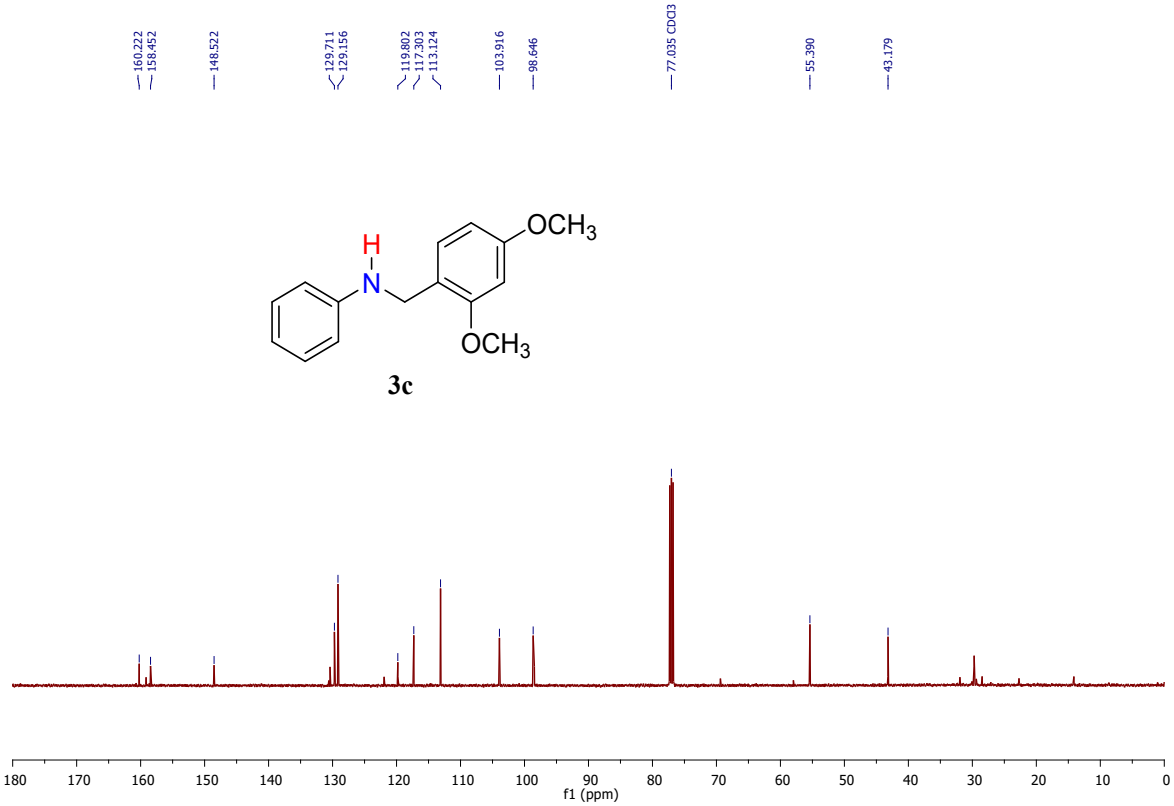



7.34
7.32
7.29 CDCl3
7.23
7.22
7.20
6.93
6.91
6.77
6.76
6.74
6.69
6.67
4.29
3.98
3.84
H
N
OCH3
3b
1.94
1.97
1.93
0.96
1.97
2.00
0.68
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

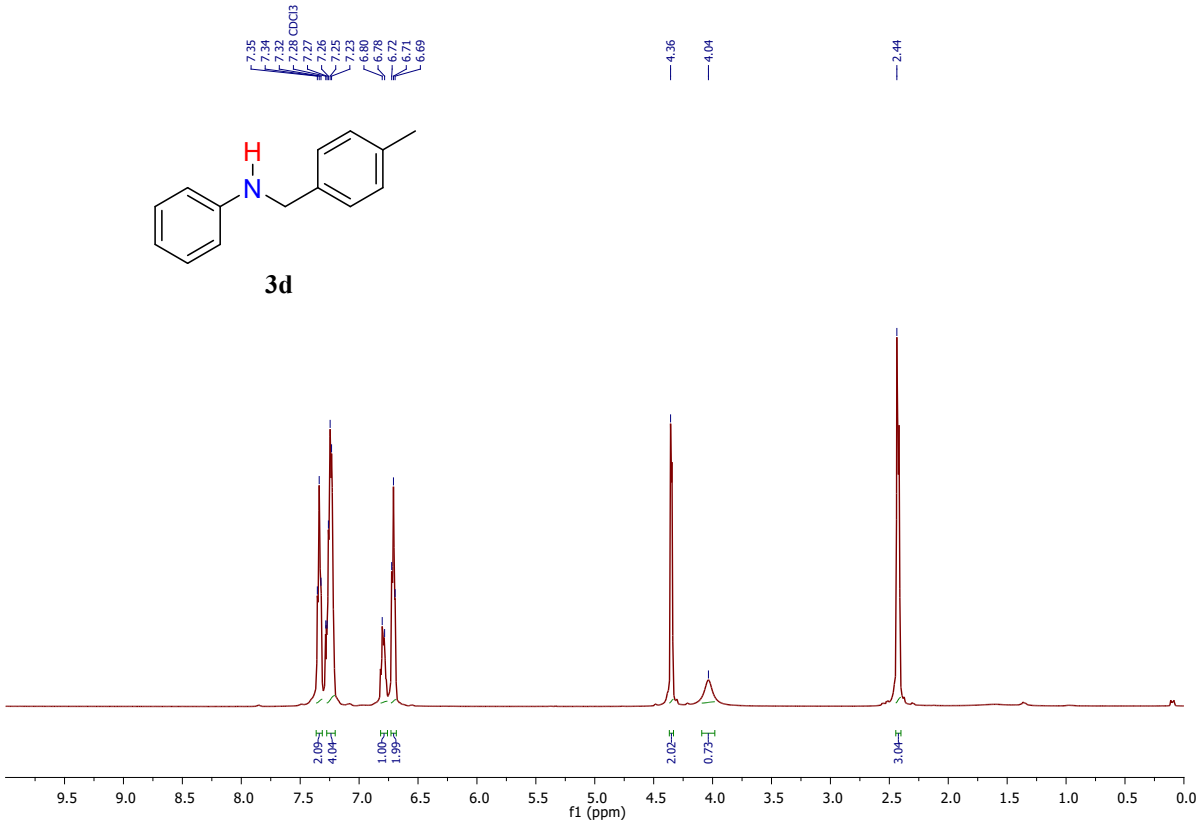

158.89
148.24
131.44
129.28
128.84
117.53
114.05
112.86
77.07 CDCl3
55.33
47.82
H
N
OCH3
3b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.280 CDCl3
7.234
7.218
7.203
7.188
7.186
7.171
6.727
6.715
6.700
6.687
6.671
6.505
6.500
6.468
6.463
6.451
6.447
4.332
4.276
3.856
3.820
OCH3
H
N
OCH3
1.85
1.12
1.03
1.97
1.03
0.98
1.99
2.78
0.93
3.00
f1 (ppm)

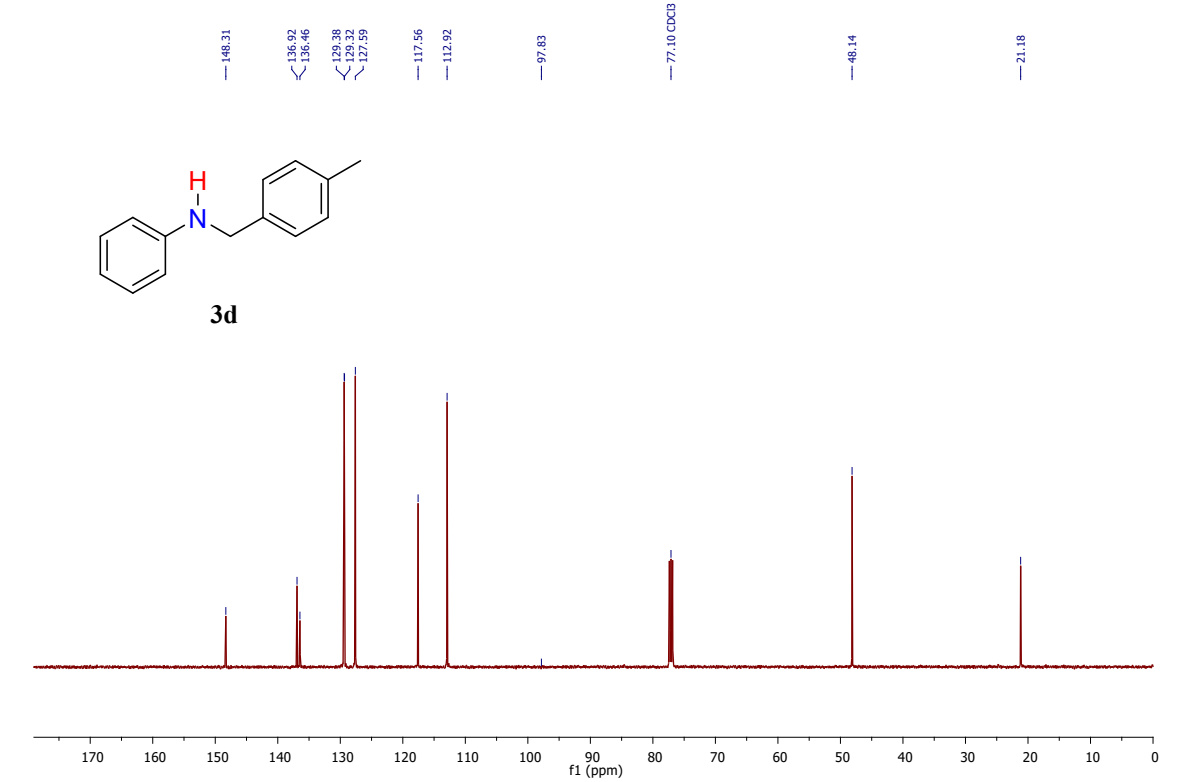
3c


160.222
158.452
148.522
129.711
129.156
119.802
117.303
113.124
103.916
98.646
77.035 CDCl3
55.390
43.179
OCH3
H
N
OCH3
f1 (ppm)

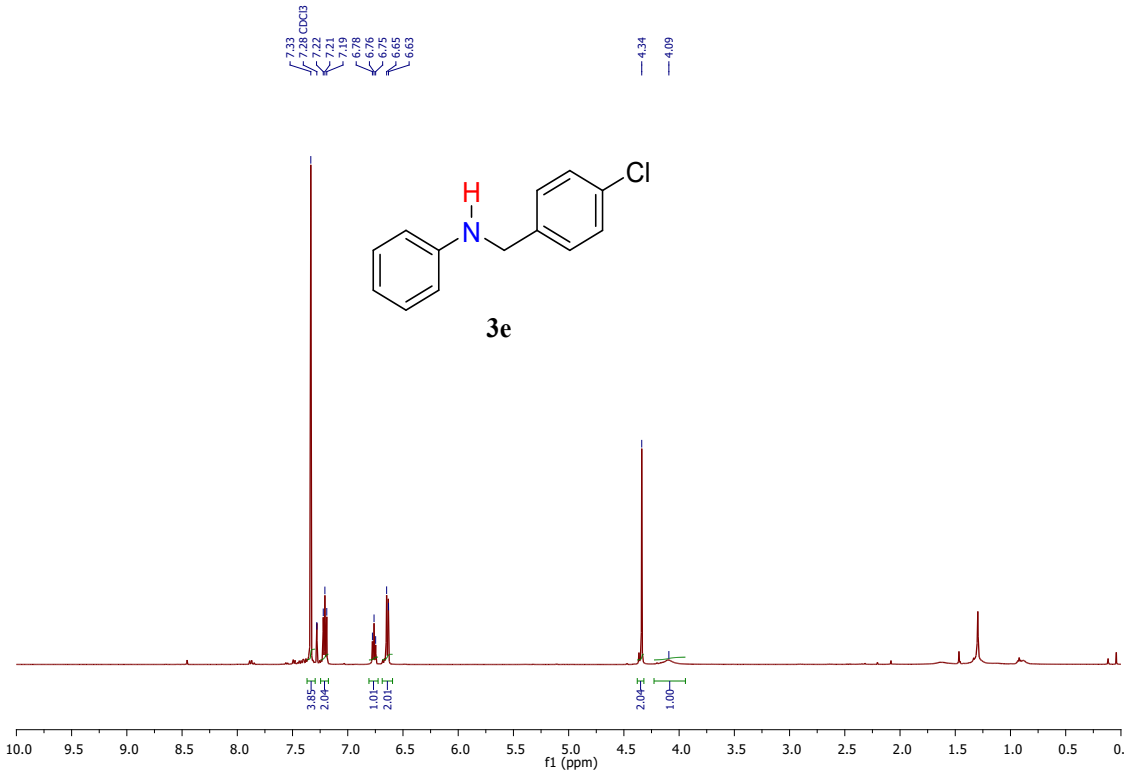
3c

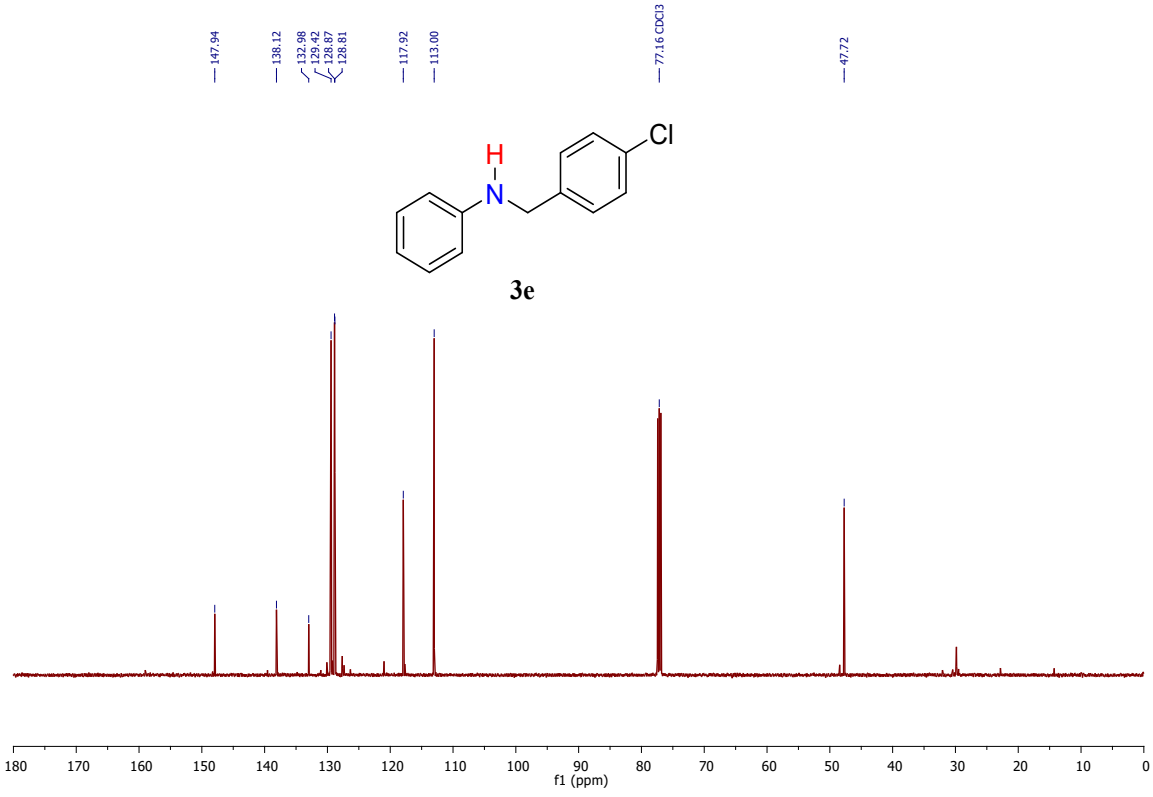

7.35
7.34
7.32
7.28 CDCl3
7.27
7.26
7.25
7.23
6.80
6.78
6.72
6.71
6.69
4.36
4.04
2.44
H
N
2.09
4.04
1.00
1.99
2.02
0.73
3.04
f1 (ppm)

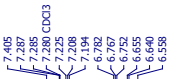
3d

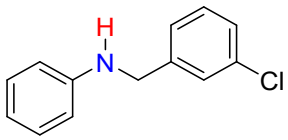

148.31
136.92
136.46
129.38
129.32
127.59
117.56
112.92
97.83
77.10 CDCl3
48.14
21.18
H
N
f1 (ppm)

3d

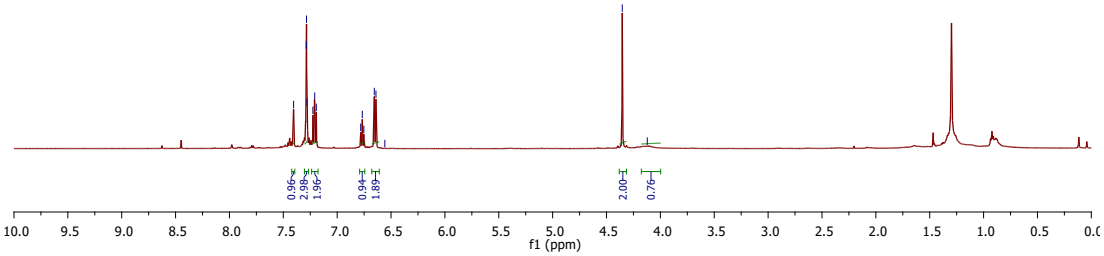

7.33
7.28 CDCl3
7.22
7.21
7.19
6.78
6.76
6.75
6.65
6.63
4.34
4.09
H
N
Cl
3e
3.85
2.04
1.01
2.01
2.04
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)


147.94
138.12
132.98
129.42
128.87
128.81
117.92
113.00
77.16 CDCl3
47.72
H
N
Cl
3e
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

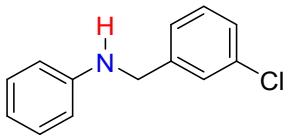

7.405
7.287
7.285
7.280 CDCl3
7.225
7.208
7.194
6.782
6.767
6.752
6.655
6.640
6.558
4.354
4.121


H
N
Cl

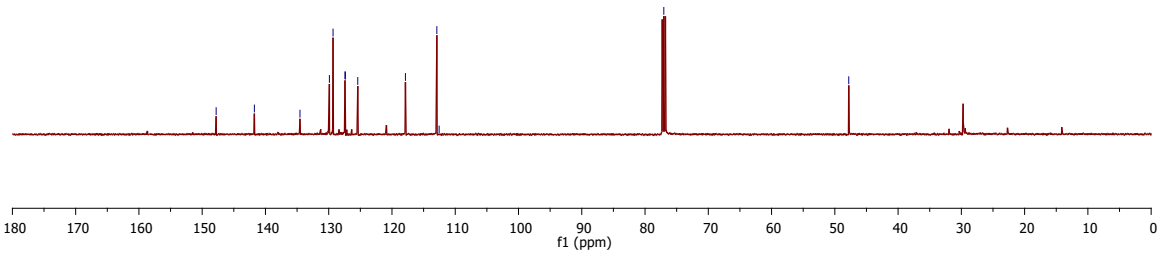
3f

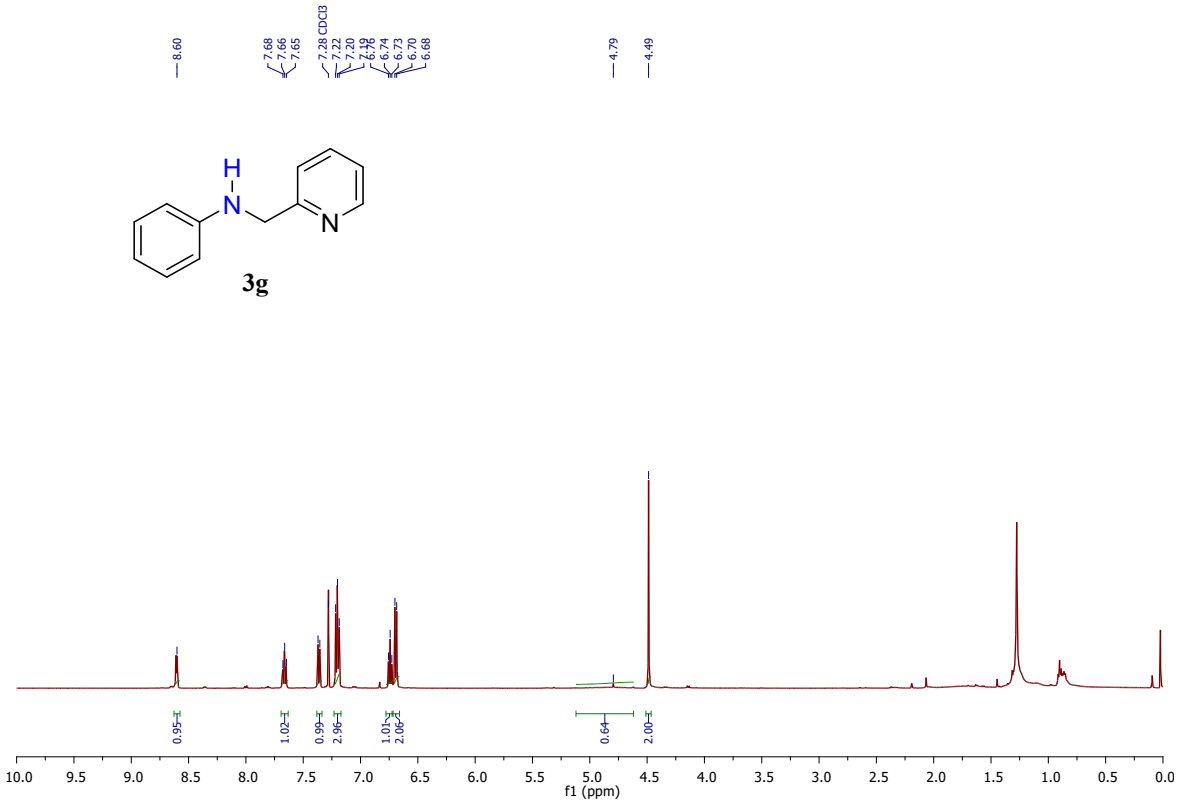

0.96
2.98
1.96
0.94
1.89
2.00
0.76
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

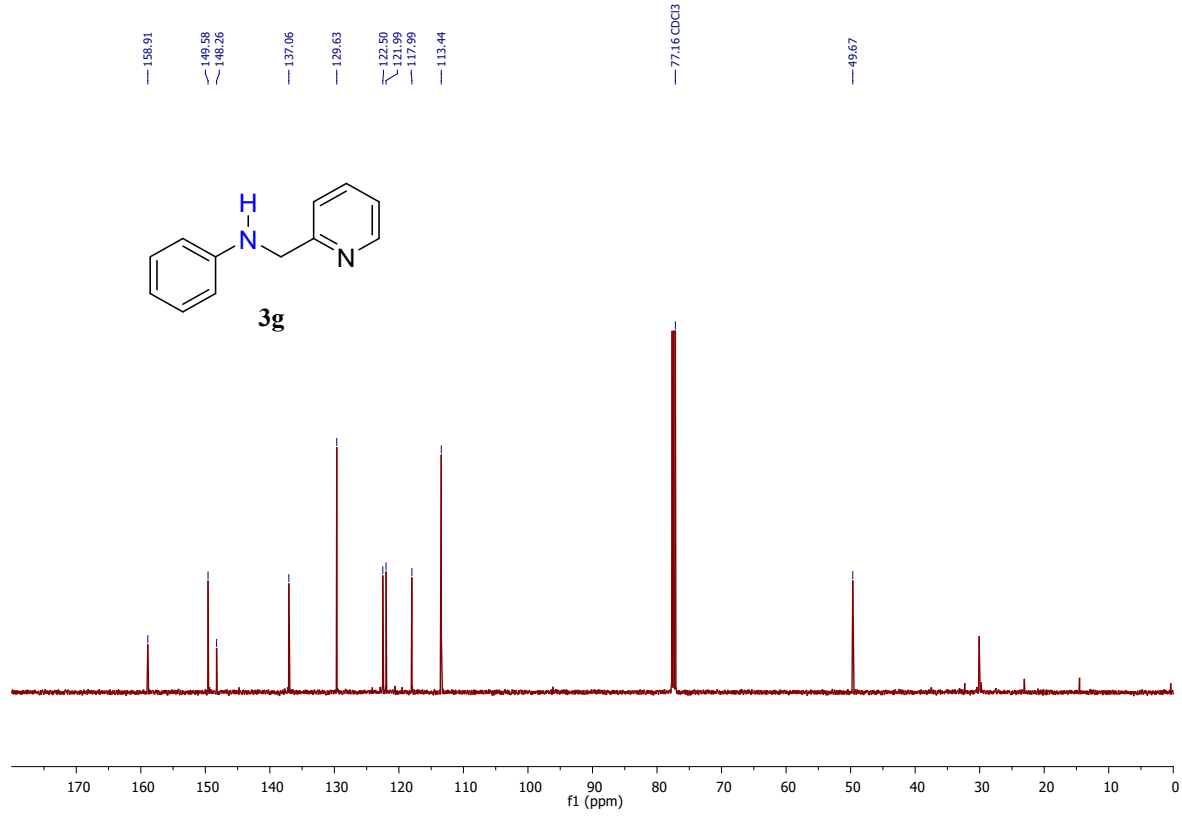

147.792
141.750
134.542
129.892
129.314
127.426
127.369
125.408
117.873
112.907
112.545
77.031 CDCl3
47.798

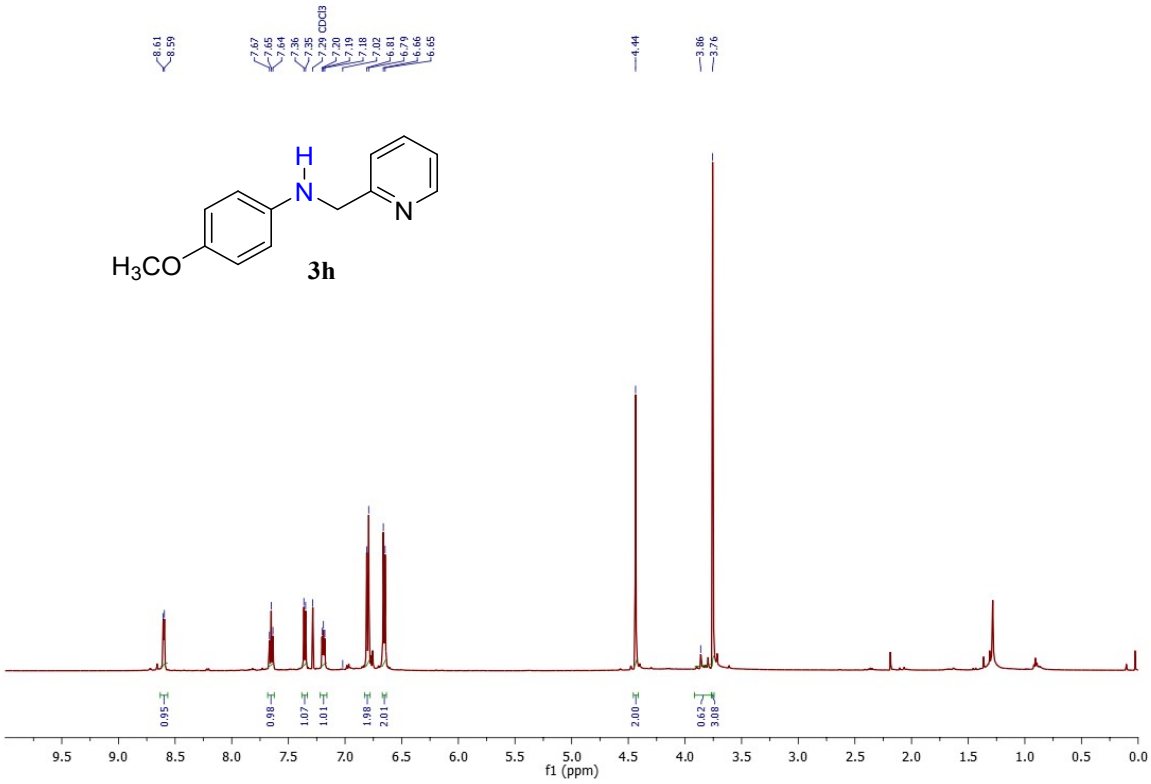

H
N
Cl

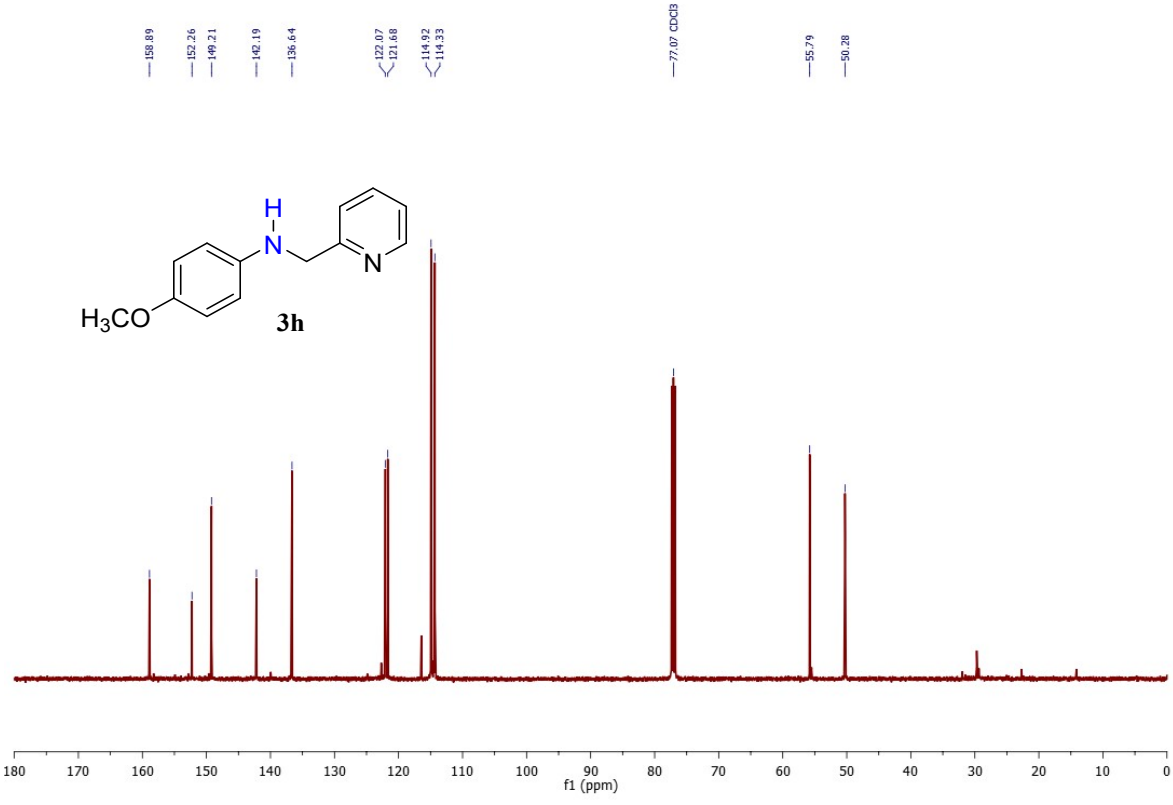
3f

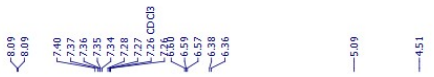

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

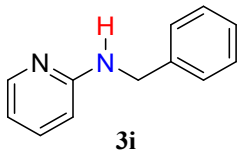

8.60
7.68
7.66
7.65
7.28 CDCl3
7.22
7.20
6.74
6.73
6.70
6.68
4.79
4.49
H
N
N
3g
0.95
1.02
0.99
2.96
1.01
2.06
0.64
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


158.91
149.58
148.26
137.06
129.63
122.50
121.99
117.99
113.44
77.16 CDCl3
49.67
H
N
N
3g
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

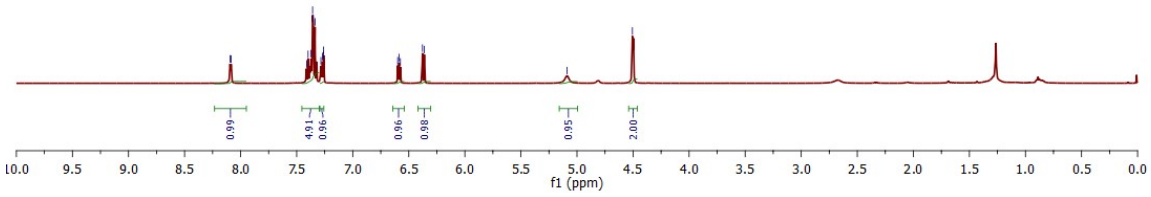

8.61
8.59
7.67
7.65
7.64
7.36
7.35
7.29 CDCl3
7.20
7.19
7.18
7.02
6.81
6.79
6.66
6.65
4.44
3.86
3.76
H
N
N
H3CO
3h
0.95
0.98
1.07
1.01
1.98
2.01
2.00
0.62
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


158.89
152.26
149.21
142.19
136.64
122.07
121.68
114.92
114.33
77.07 CDCl3
55.79
50.28
H
N
N
H3CO
3h
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

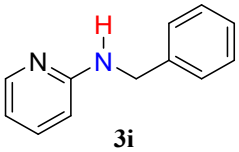

8.09
8.09
7.40
7.37
7.36
7.35
7.34
7.28
7.27
7.26 CDCl3
6.60
6.59
6.57
6.38
6.36
5.09
4.51


H
N
N

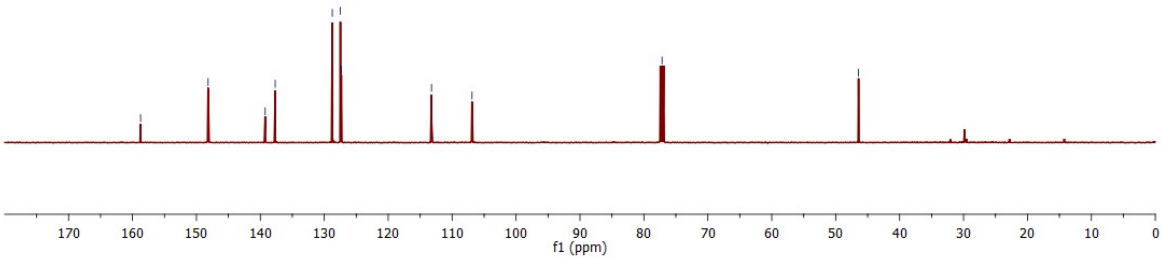
3i

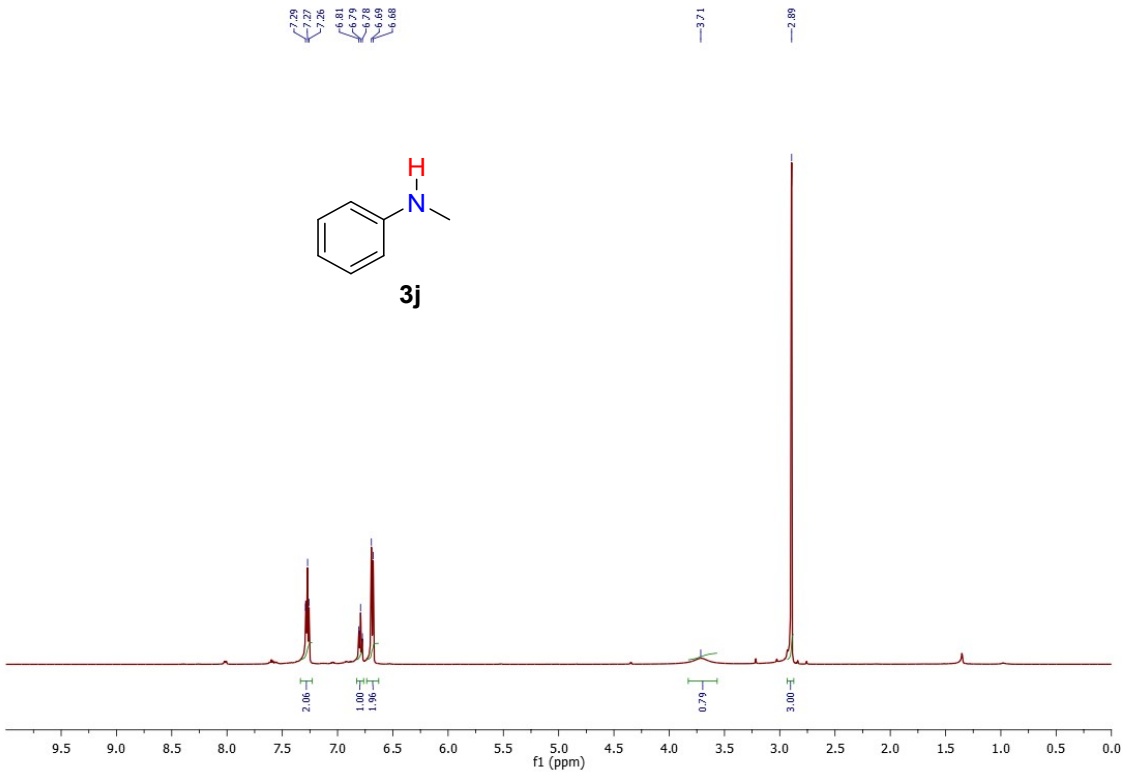

0.99
4.91
0.96
0.96
0.98
0.95
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

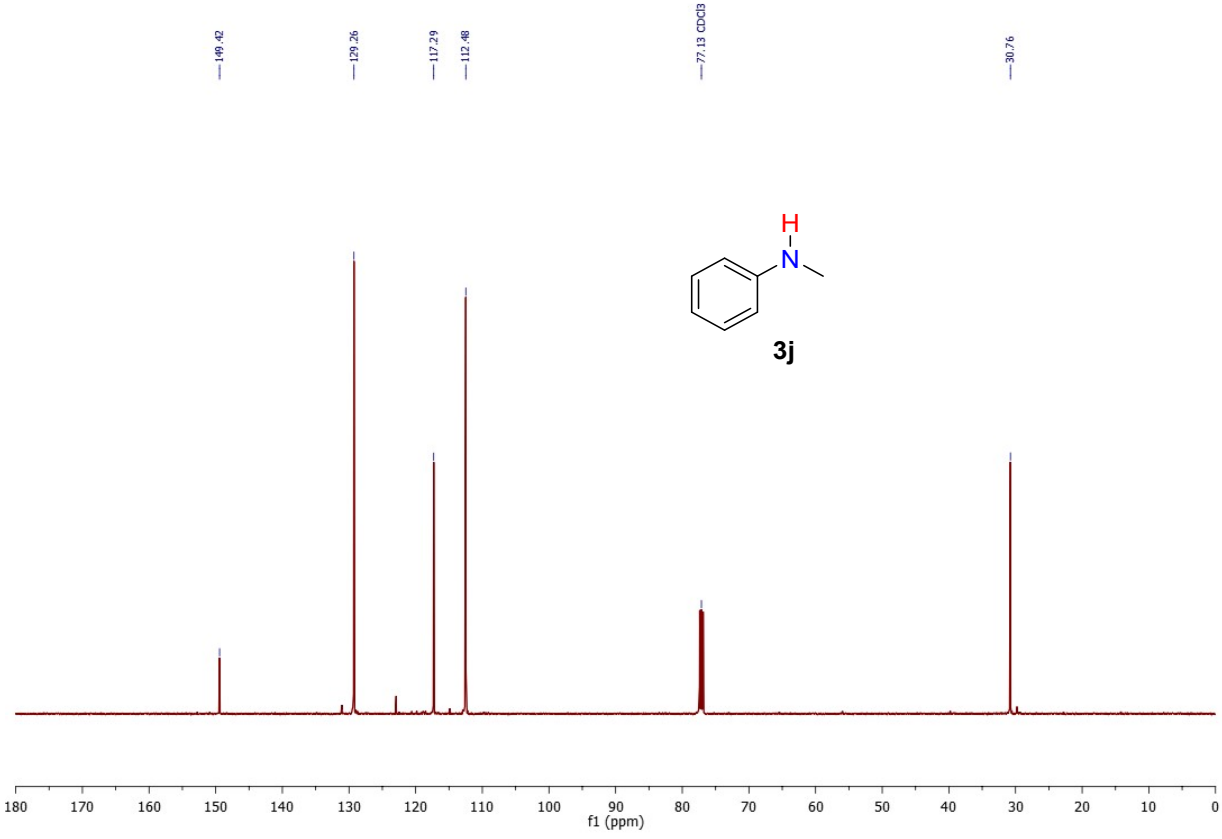

158.74
148.17
139.24
137.68
128.75
127.48
127.34
113.23
106.89
77.16 CDCl3
46.42

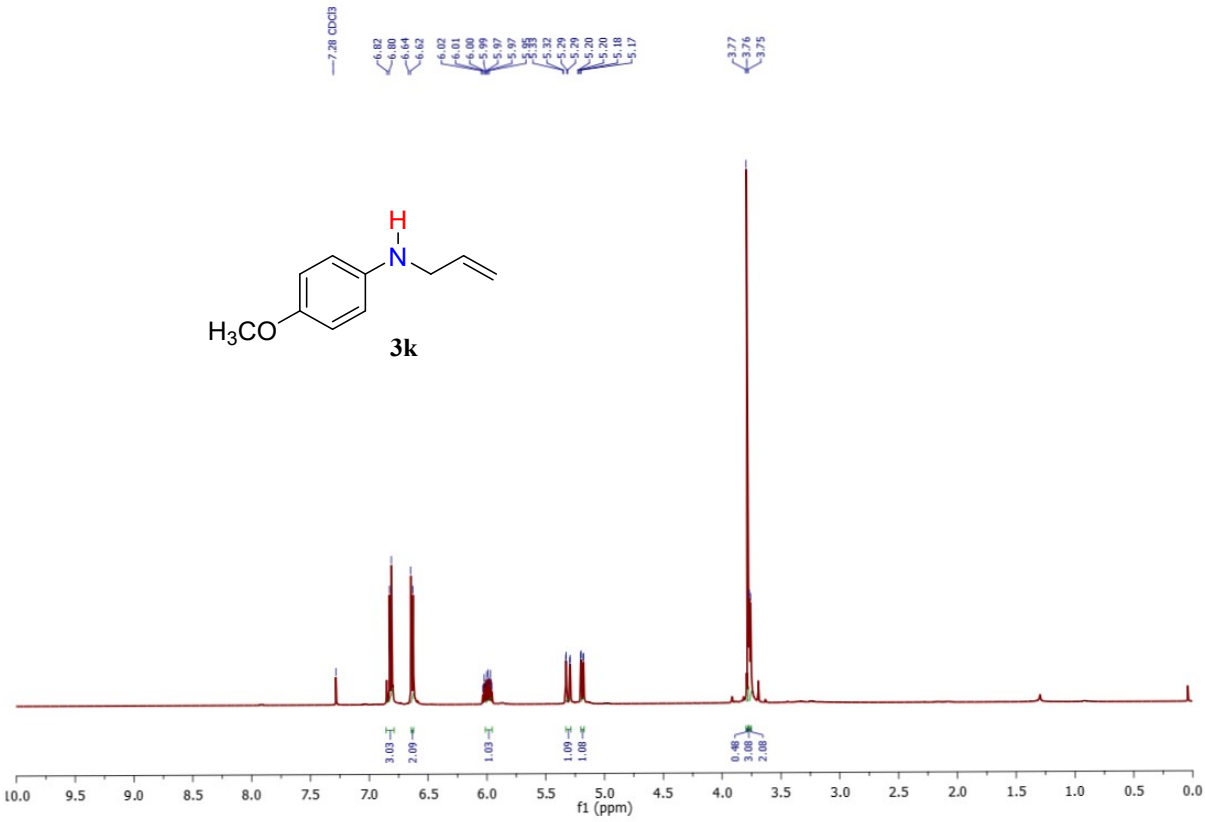

H
N
N

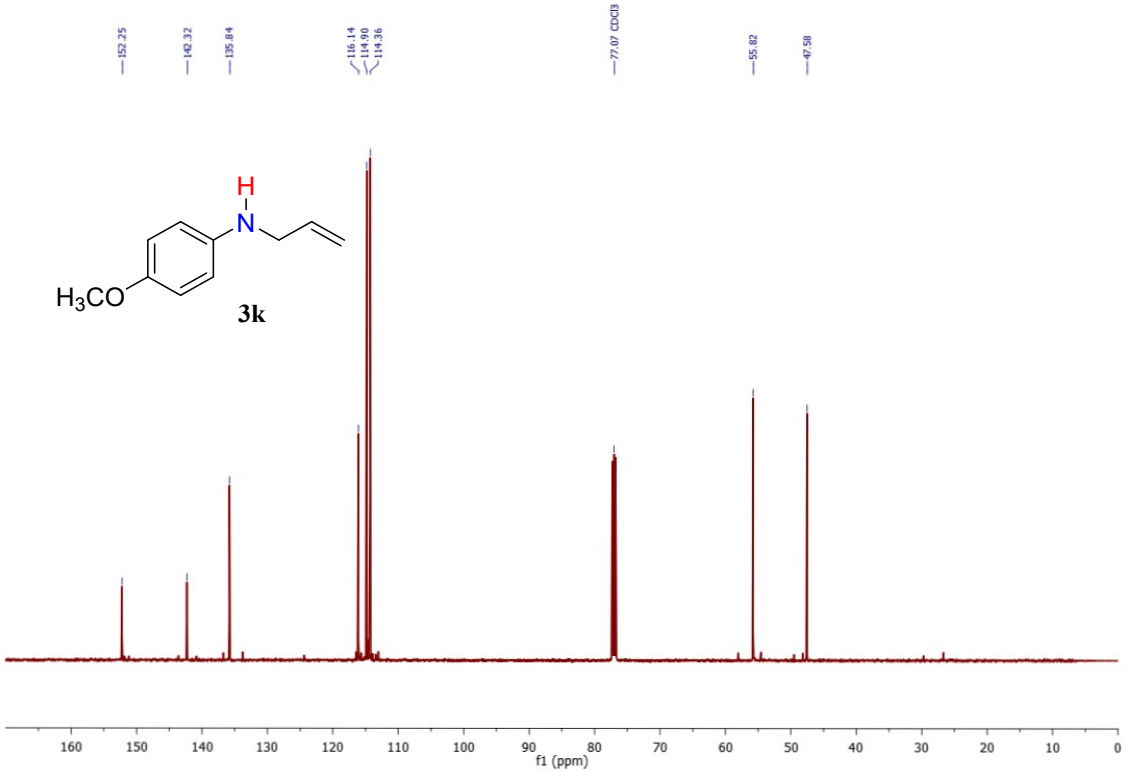
3i

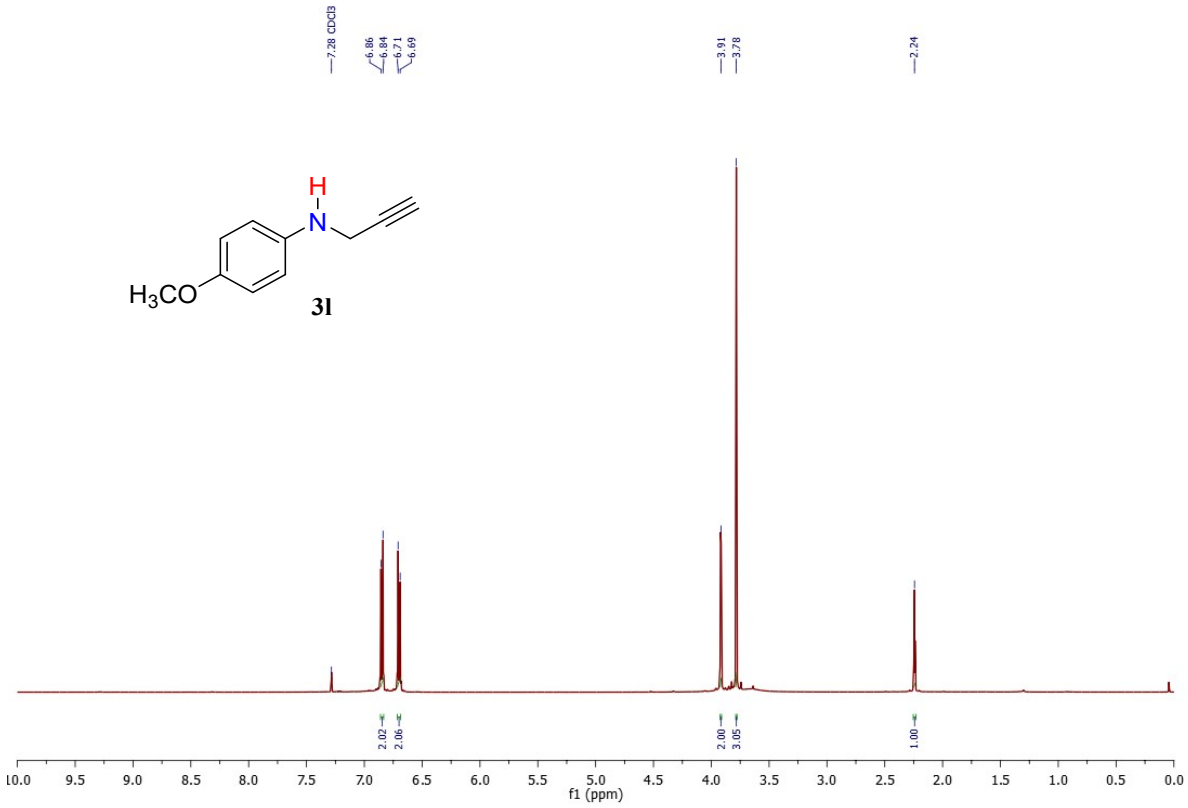

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

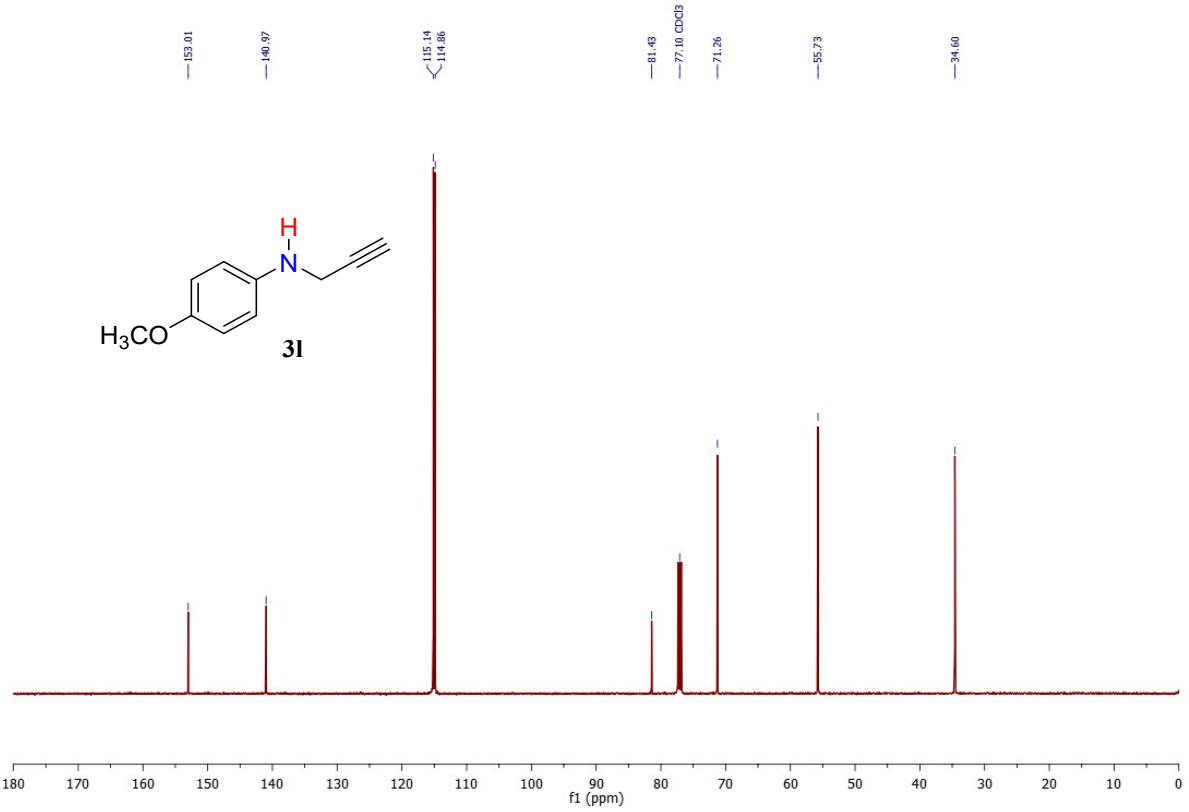

7.29
7.27
7.26
6.81
6.79
6.78
6.69
6.68
3.71
2.89
H
N
3j
2.06
1.00
1.96
0.79
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

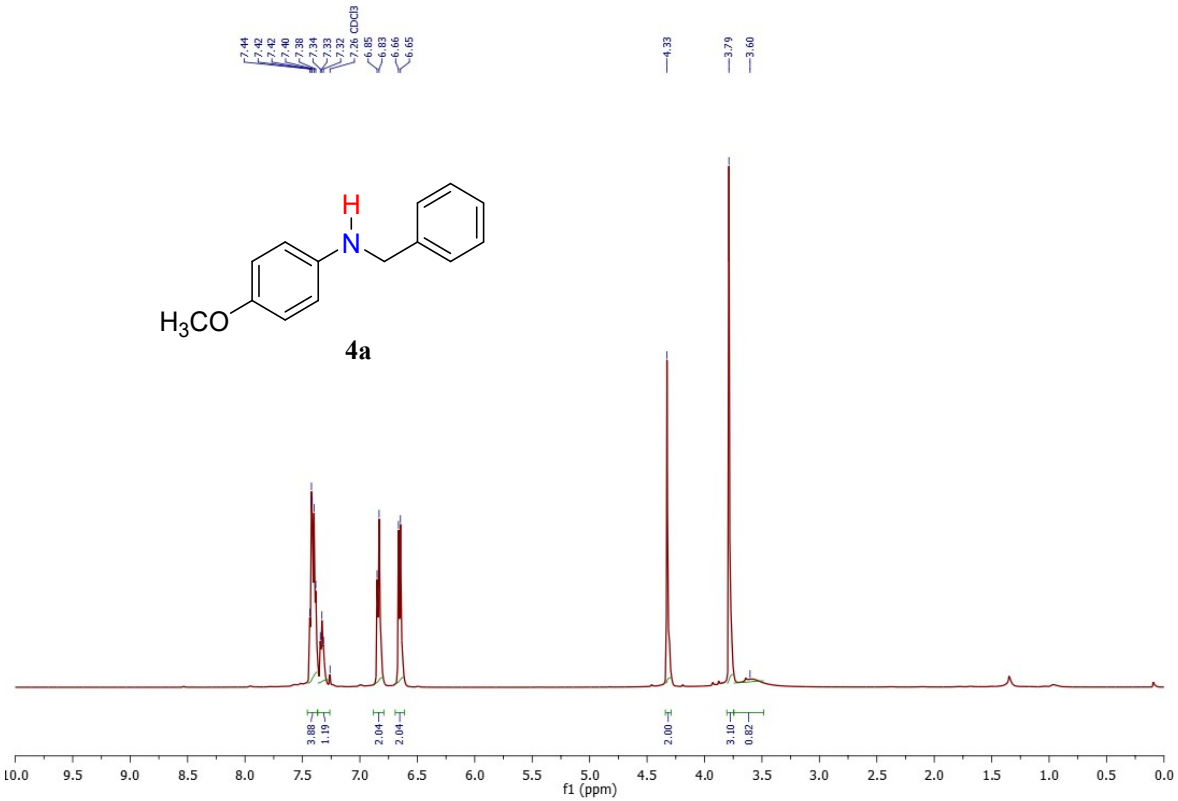

149.42
129.26
117.29
112.48
77.13 CDCl3
30.76
H
N
3j
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

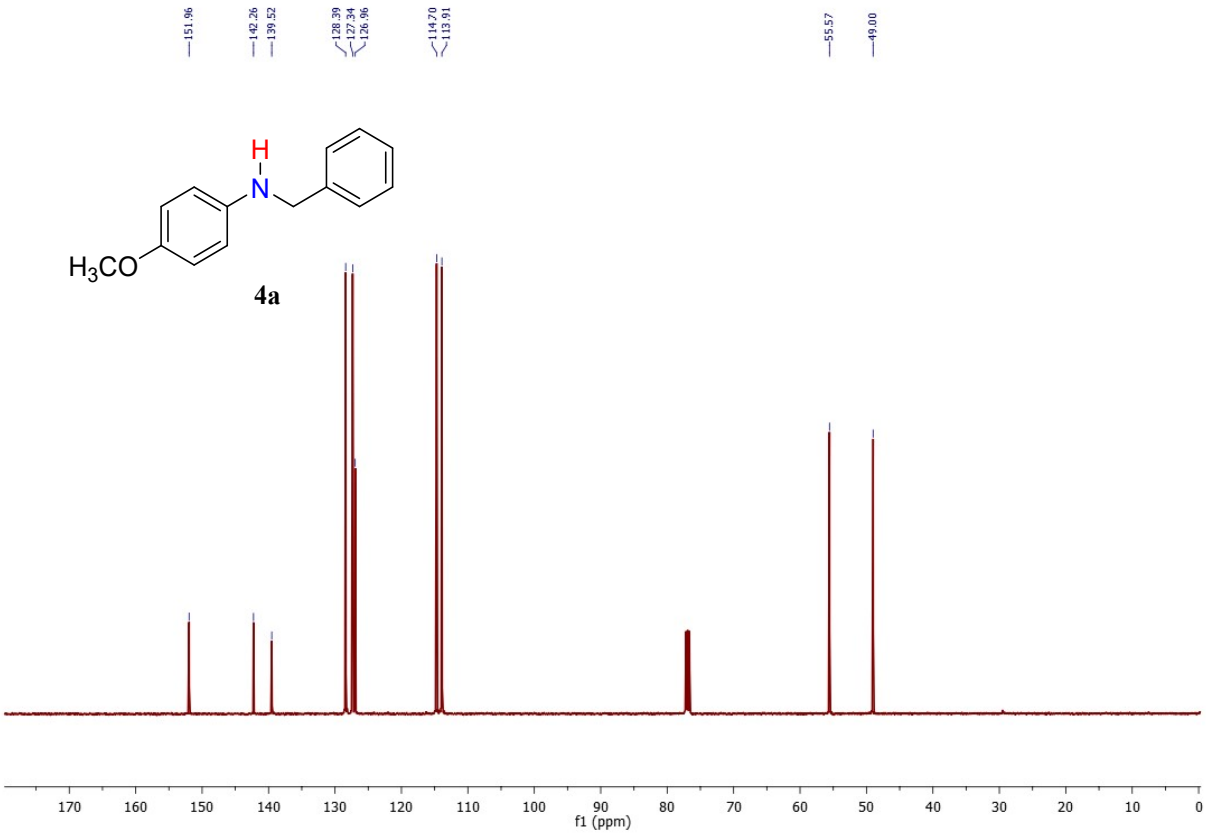

7.26 CDCl3
6.82
6.80
6.64
6.62
6.02
6.01
6.00
5.99
5.97
5.97
5.32
5.29
5.29
5.20
5.20
5.18
5.17
3.77
3.76
3.75
H
N
H3CO
3k
3.03
2.09
1.03
1.09
1.08
0.48
3.00
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

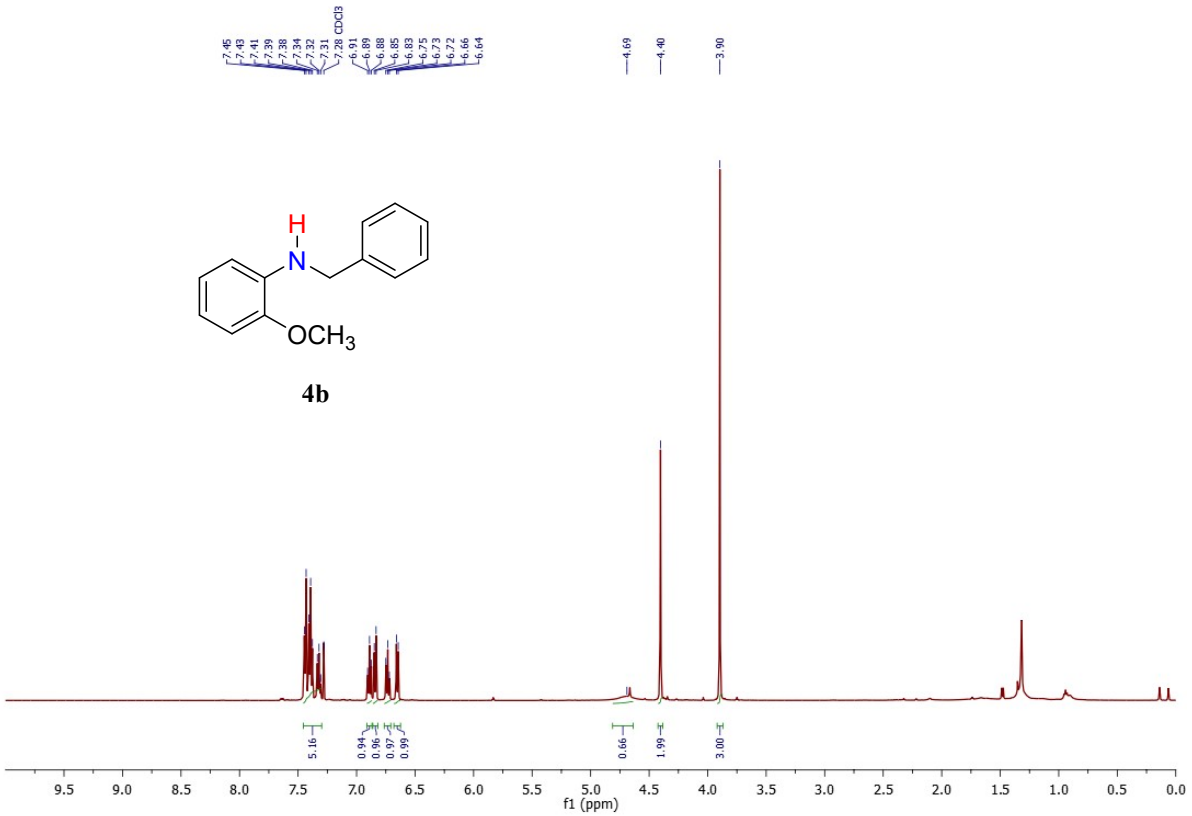

152.25
142.32
135.84
116.14
114.90
114.36
77.07 CDCl3
55.82
47.58
H
N
H3CO
3k
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.28 CDCl3
6.86
6.84
6.71
6.69
3.91
3.78
2.24
H
N
H3CO
3l
2.02
2.06
2.00
3.05
1.00
f1 (ppm)

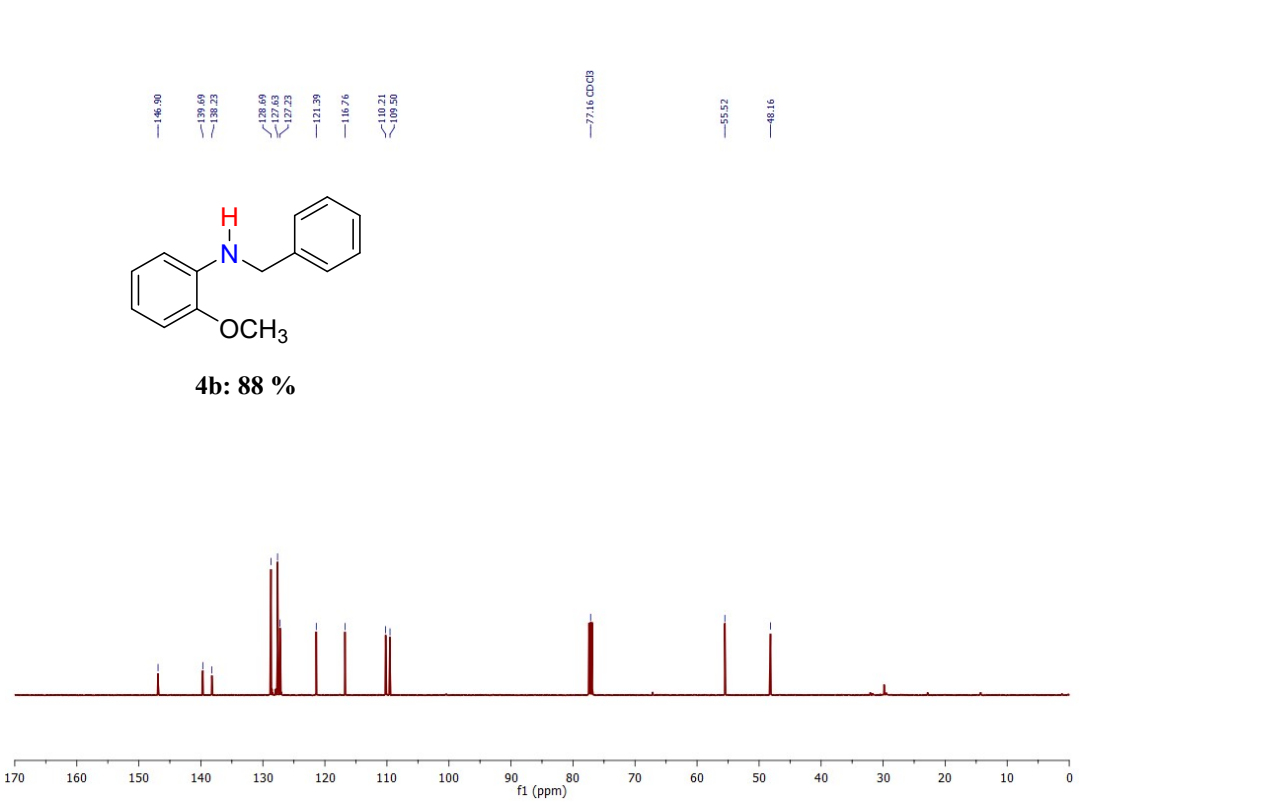

153.01
140.97
115.14
114.86
81.43
77.10 CDCl3
71.26
55.73
34.60
H
N
H3CO
3l
f1 (ppm)


7.44
7.42
7.42
7.40
7.38
7.34
7.33
7.32
7.26 CDCl3
6.85
6.83
6.66
6.65
4.33
3.79
3.60
H
N
H3CO
4a
3.88
1.19
2.04
2.04
2.00
3.10
0.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

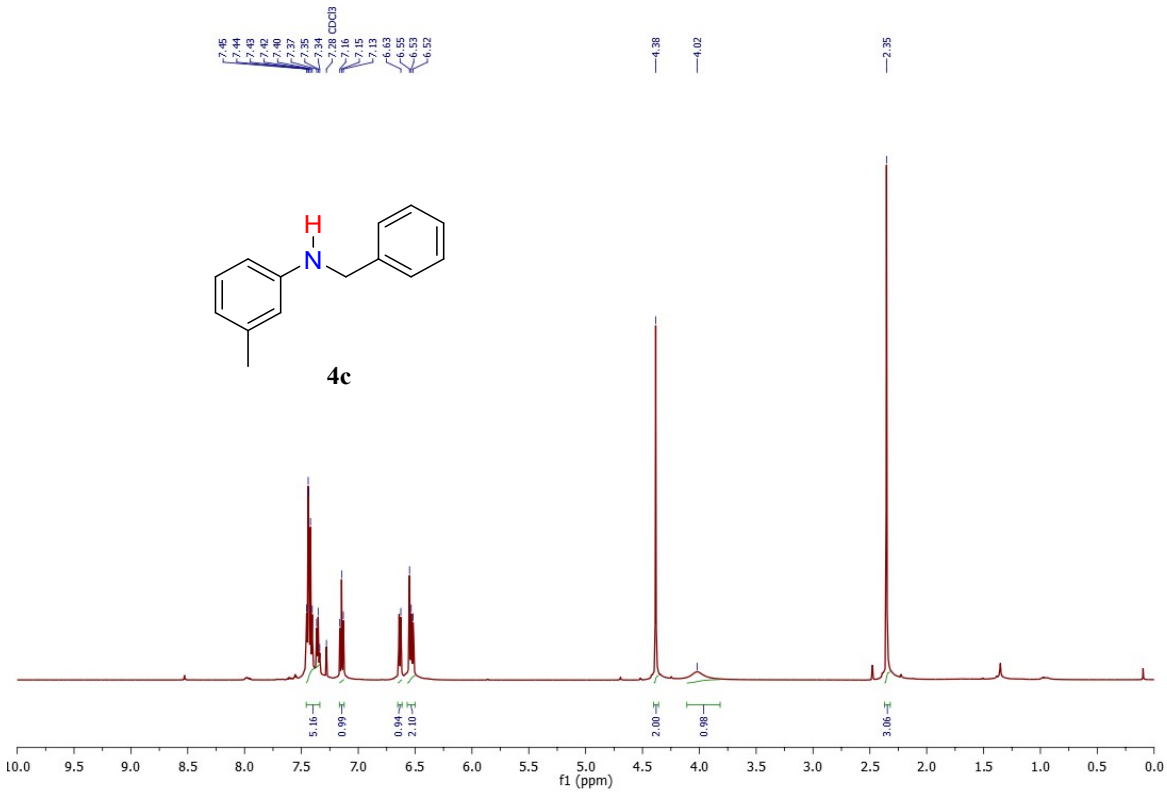

151.96
142.26
139.52
128.39
127.34
126.96
114.70
113.91
55.57
49.00
H
N
H3CO
4a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.45
7.43
7.41
7.39
7.38
7.34
7.32
7.31
7.28 CDCl3
6.91
6.89
6.88
6.85
6.83
6.75
6.73
6.72
6.66
6.64
4.69
4.40
3.90
H
N
OCH3
5.16
0.94
0.96
0.97
0.99
0.66
1.99
3.00
f1 (ppm)

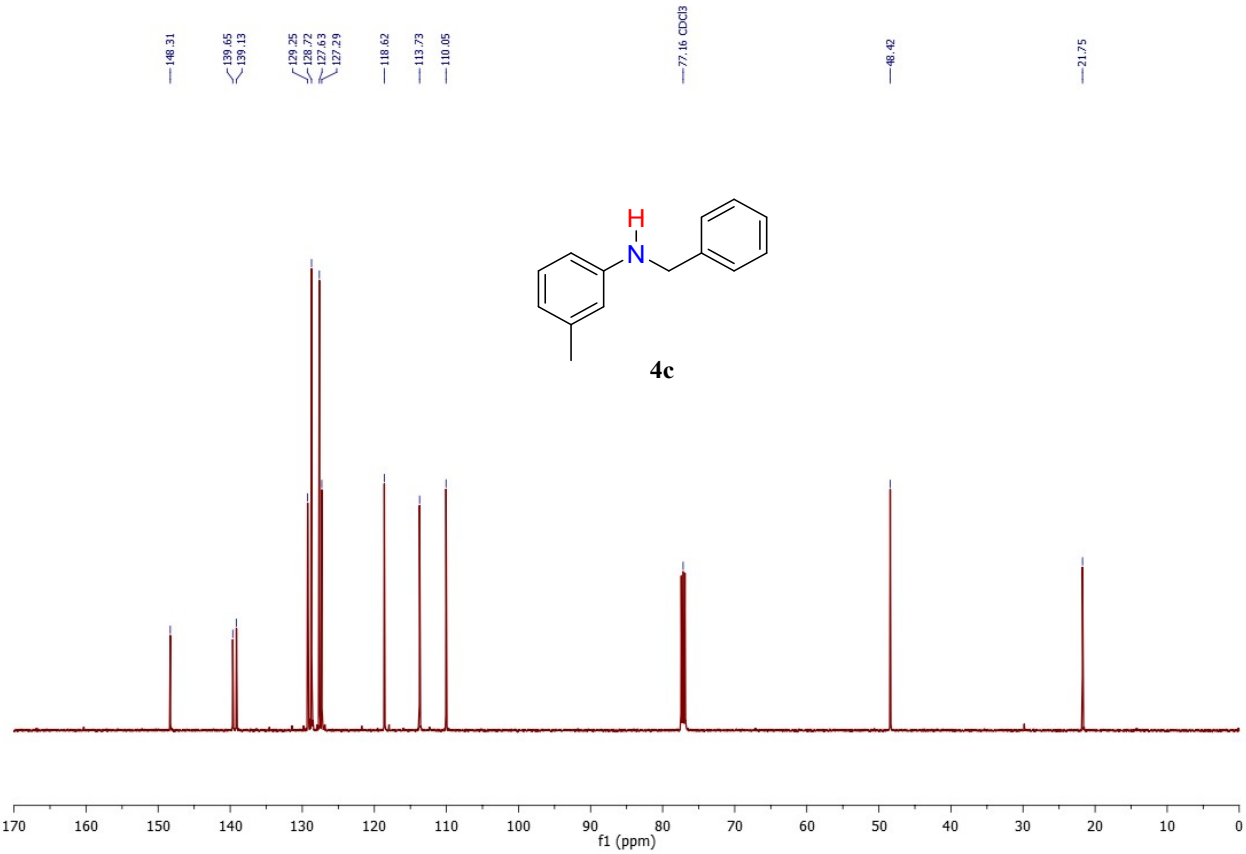
4b


146.90
139.69
138.23
128.69
127.63
127.23
121.39
116.76
110.21
109.50
77.16 CDCl3
55.52
48.16
H
N
OCH3
f1 (ppm)

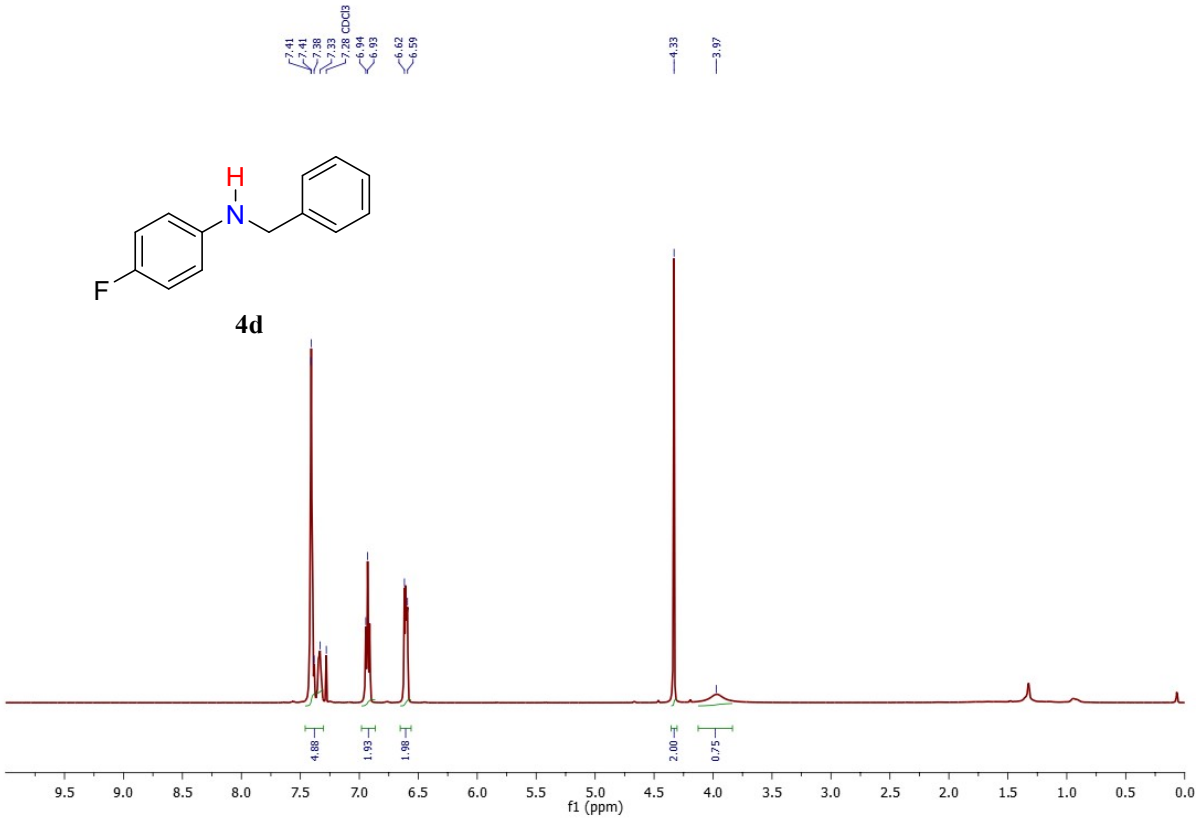
4b: 88 %


7.45
7.44
7.43
7.42
7.40
7.37
7.35
7.34
7.28 CDCl3
7.16
7.15
7.13
6.63
6.55
6.53
6.52
4.38
4.02
2.35
H
N
5.16
0.99
0.94
2.10
2.00
0.98
3.06
f1 (ppm)

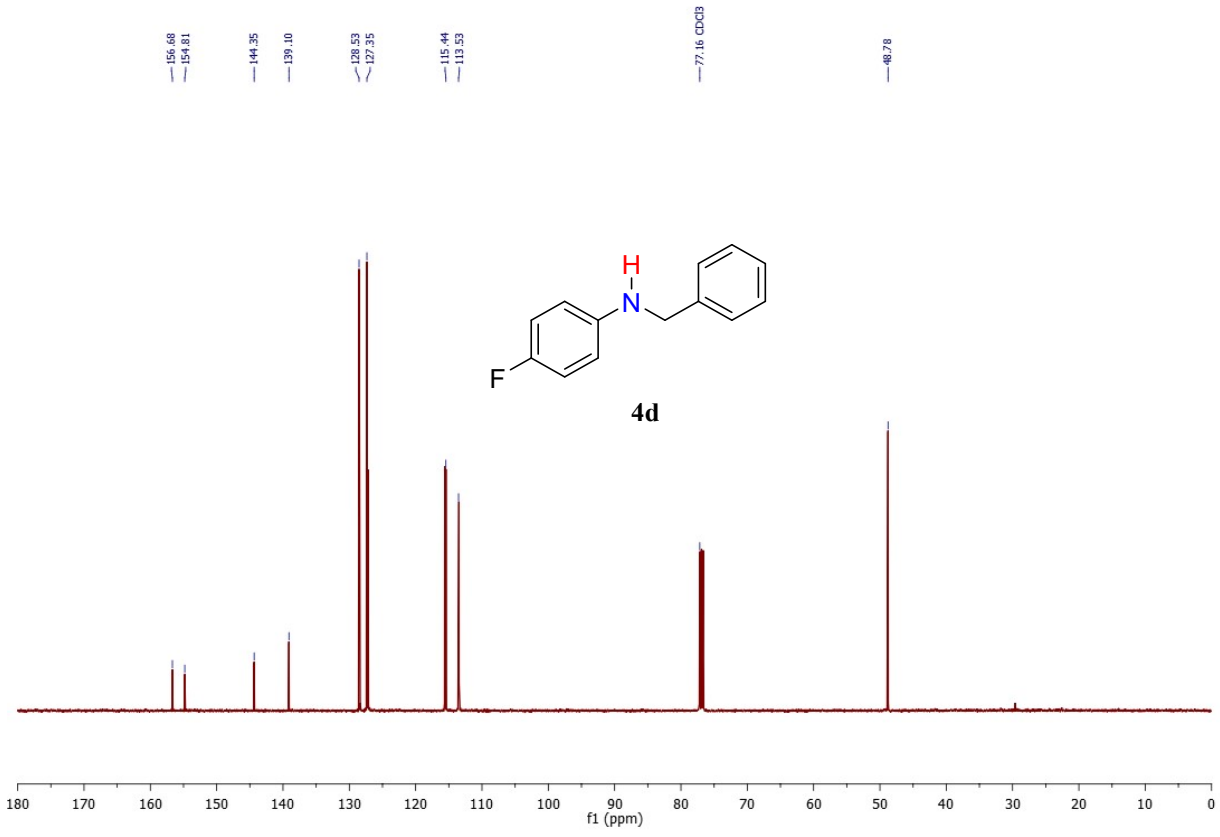
4c


148.31
139.65
139.13
129.25
128.72
127.63
127.29
118.62
113.73
110.05
77.16 CDCl3
48.42
21.75
H
N
f1 (ppm)

4c

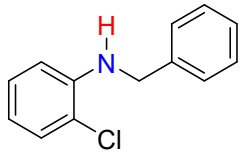

7.41
7.41
7.38
7.33
7.28 CDCl3
6.94
6.93
6.62
6.59
4.33
3.97
H
N
F
4.88
1.93
1.98
2.00
0.75
f1 (ppm)

4d

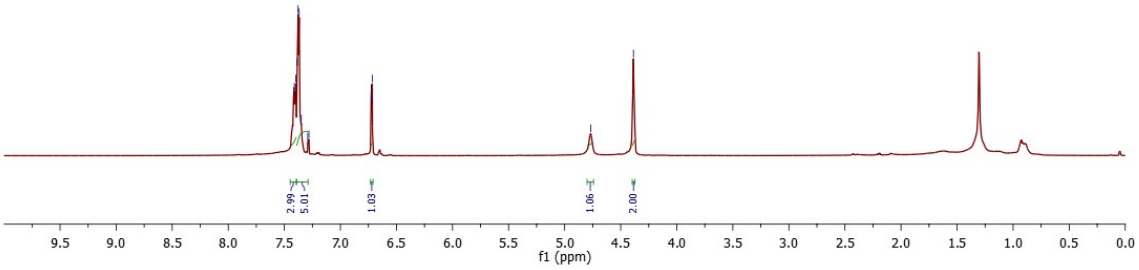

156.68
154.81
144.35
139.10
128.53
127.35
115.44
113.53
77.16 CDCl3
48.78
H
N
F
f1 (ppm)

4d

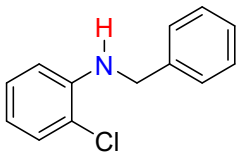

7.42
7.41
7.40
7.39
7.38
7.37
7.35
7.29
7.28 CDCl3
6.72
6.72
6.72
4.77
4.39


H
N
Cl

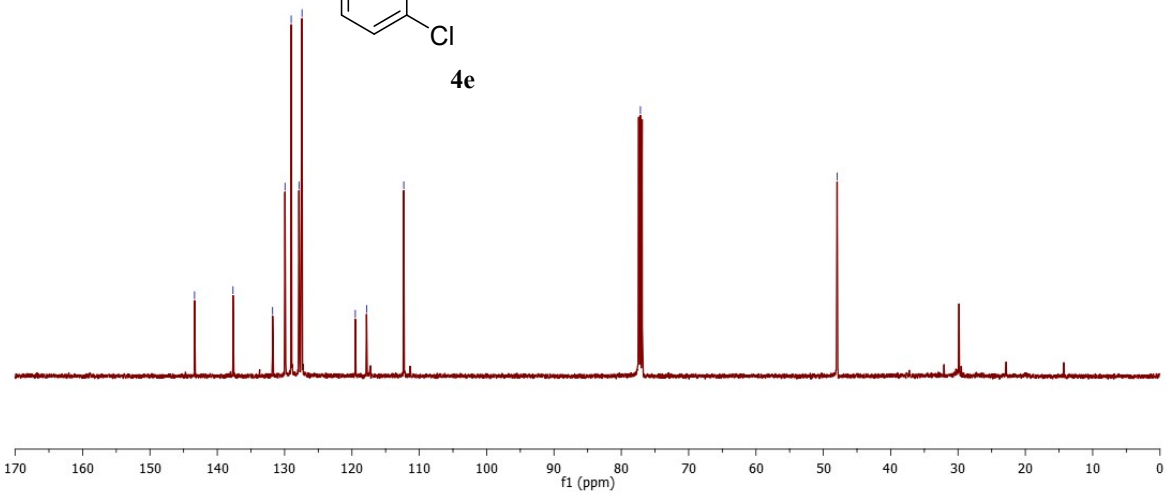
4e

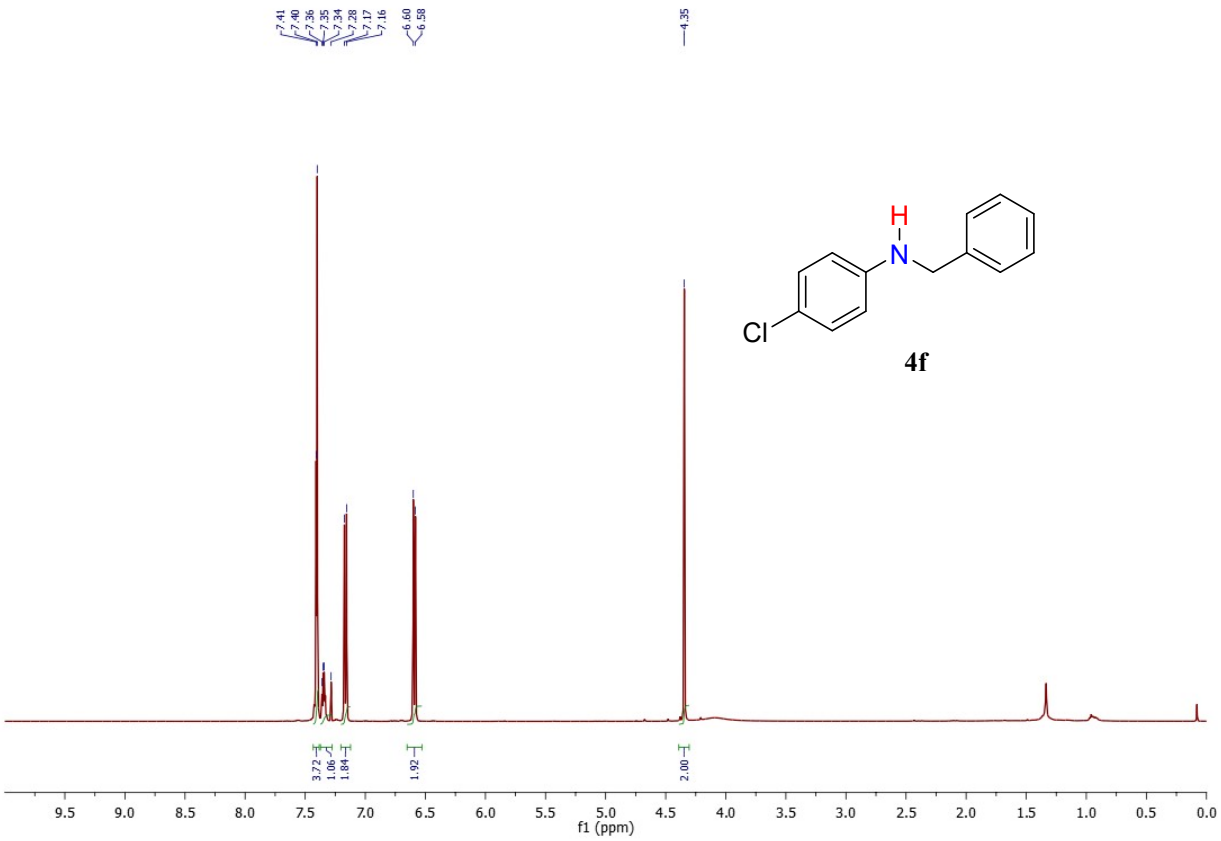

2.99
5.01
1.03
1.06
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


149.38
137.66
131.78
129.94
129.02
127.87
127.42
119.50
117.83
112.31
77.16 CDCl3
47.95

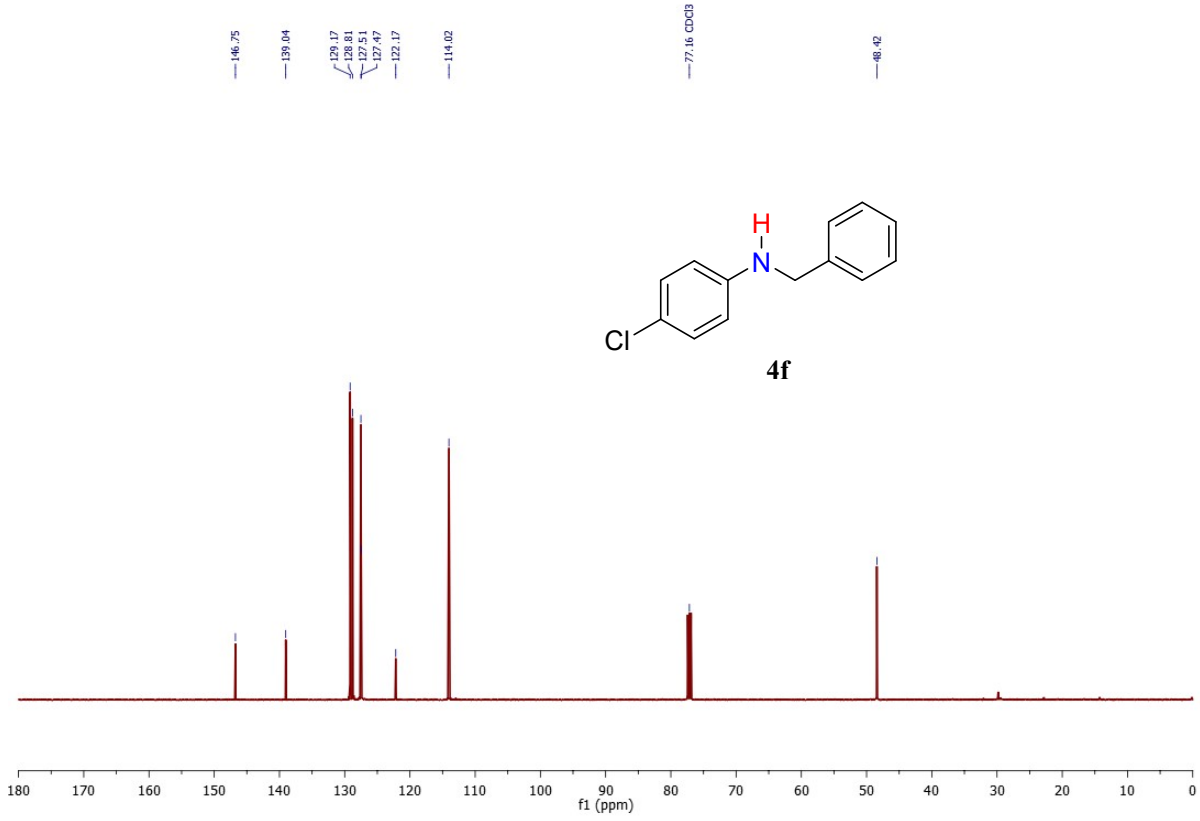

H
N
Cl

4e

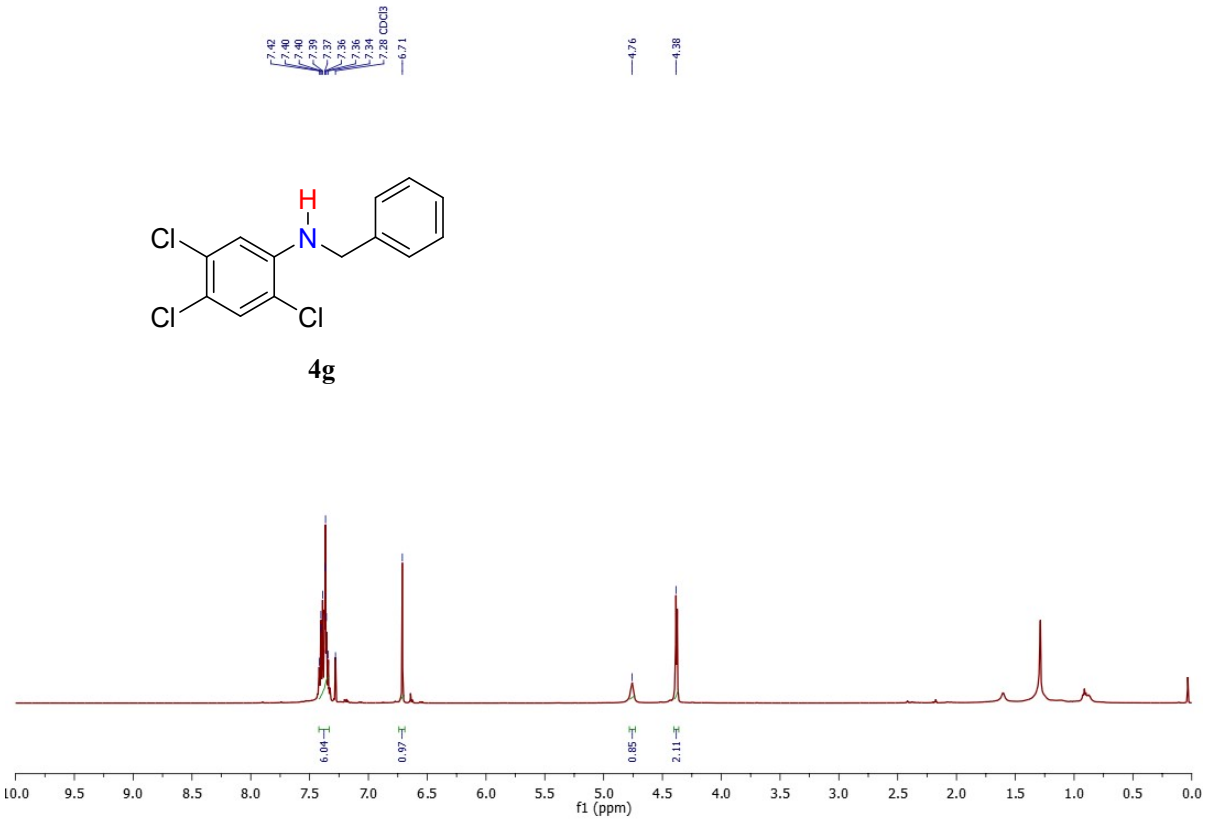

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.41
7.40
7.36
7.35
7.34
7.28
7.17
7.16
6.60
6.58
4.35
H
N
Cl
3.72
1.06
1.84
1.92
2.00
f1 (ppm)

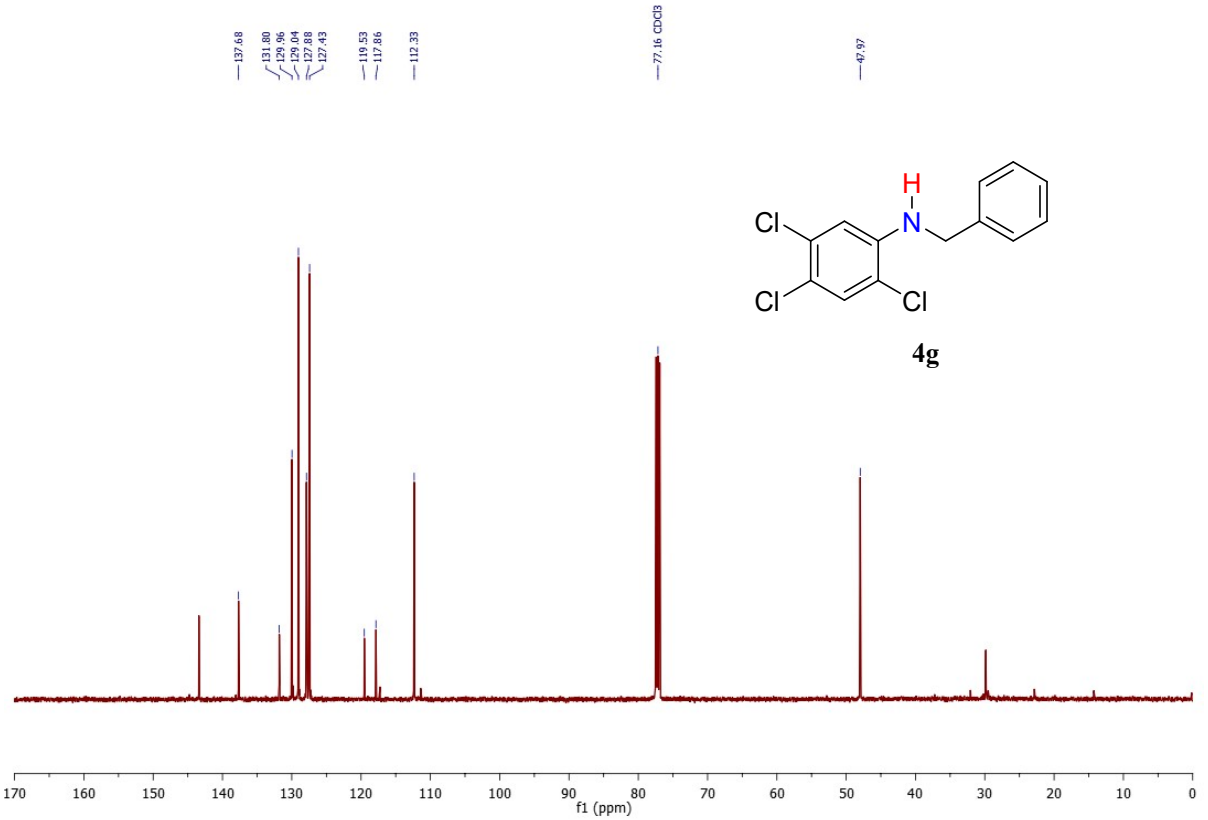
4f


146.75
139.04
129.17
128.81
127.51
127.47
122.17
114.02
77.16 CDCl3
48.42
H
N
Cl
f1 (ppm)

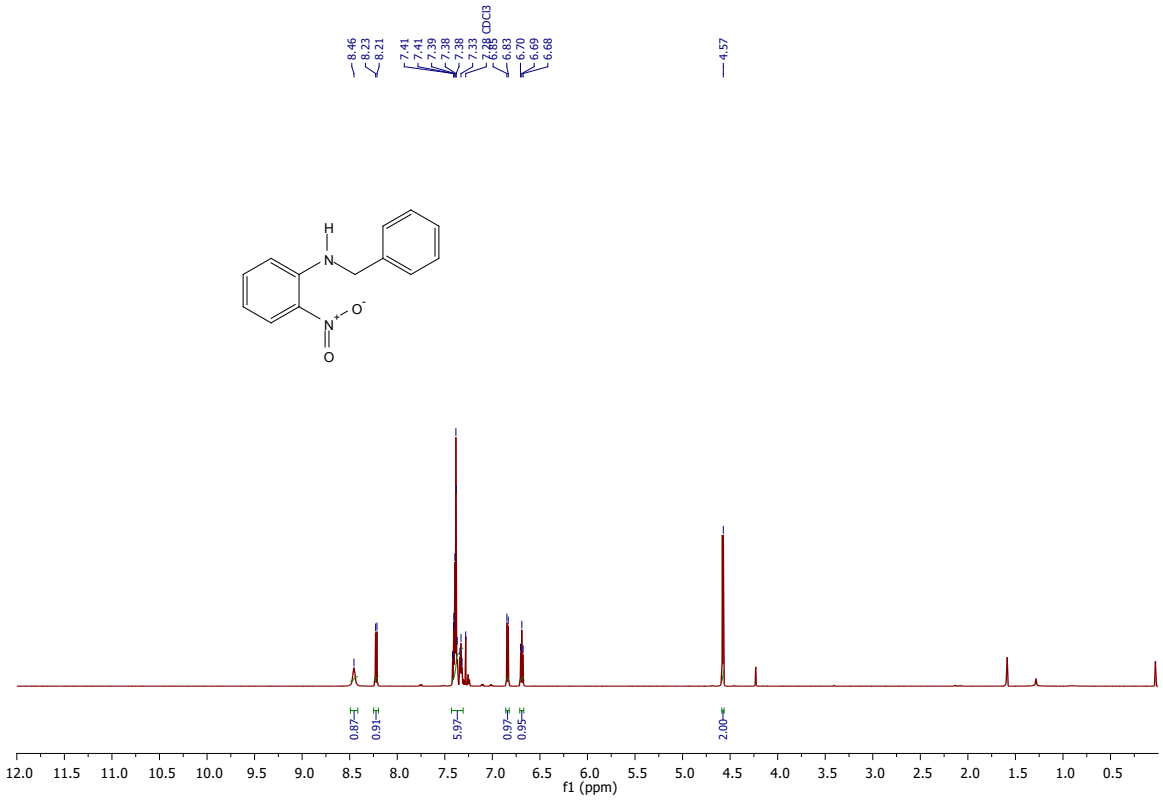
4f

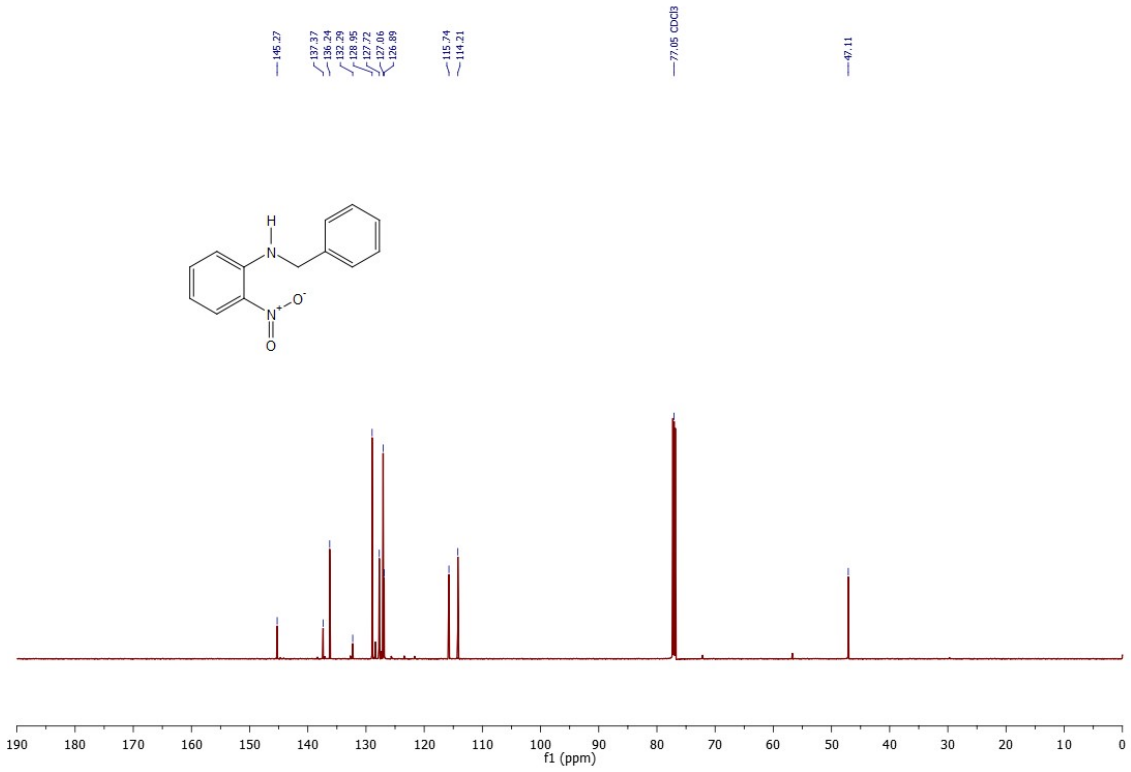

7.42
7.40
7.40
7.39
7.37
7.36
7.36
7.34
7.28 CDCl3
6.71
4.76
4.38
H
N
Cl
Cl
Cl
6.04
0.97
0.85
2.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

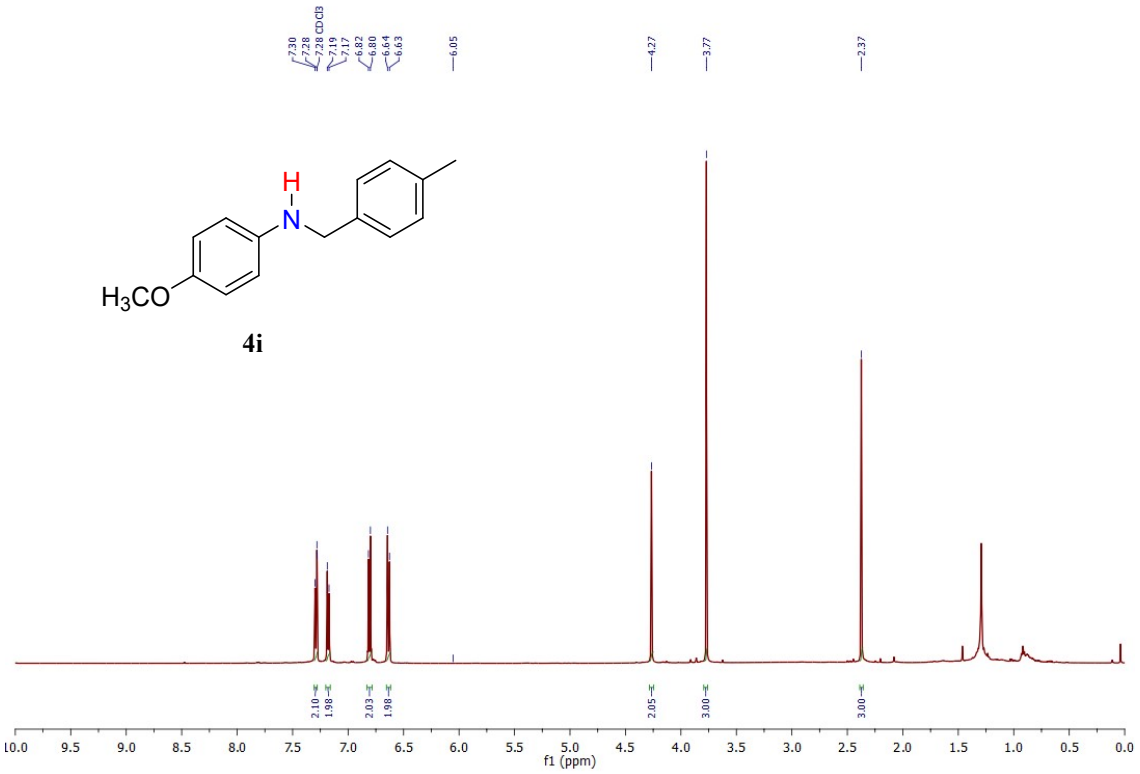
4g


137.68
131.80
129.96
129.04
127.88
127.43
119.53
117.86
112.33
77.16 CDCl3
47.97
H
N
Cl
Cl
Cl
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

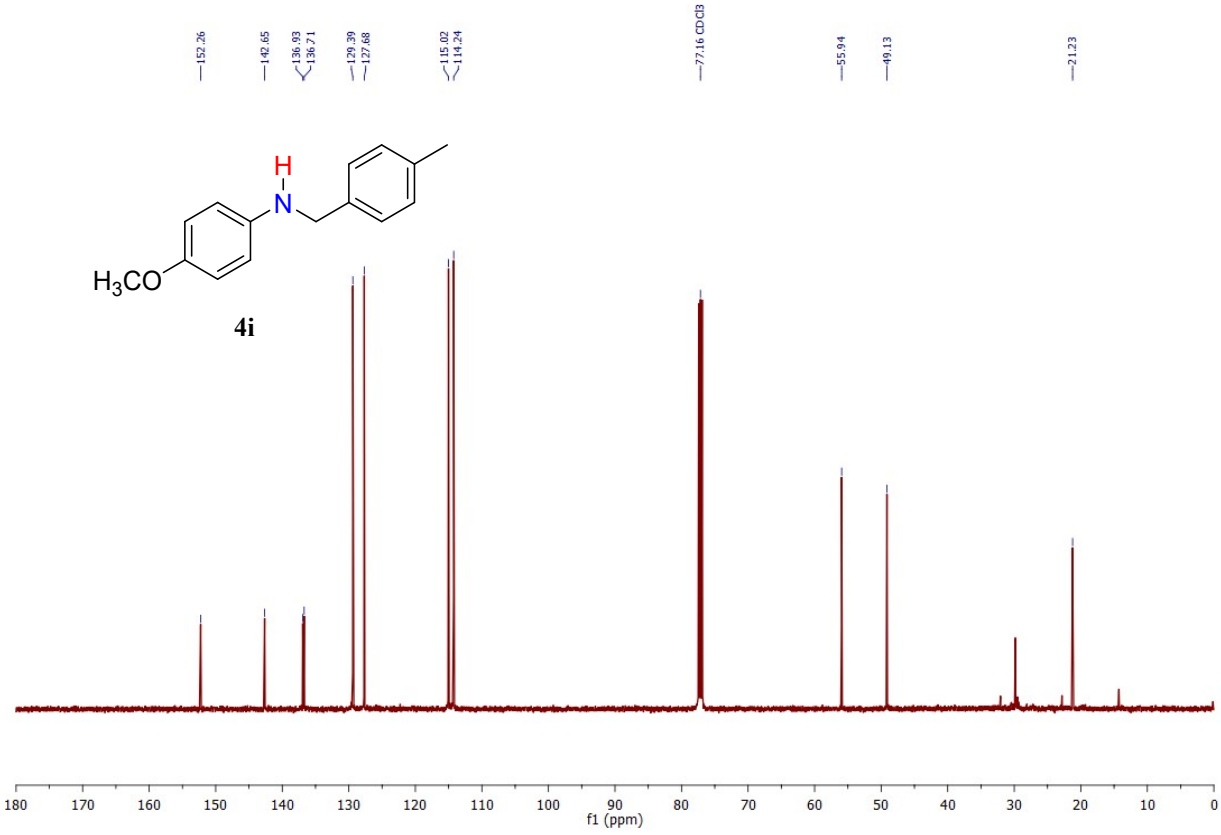
4g


8.46
8.23
8.21
7.41
7.41
7.39
7.38
7.38
7.33
7.28 CDCl3
6.83
6.70
6.69
6.68
4.57
H
N
O
N
O
0.87
0.91
5.97
0.97
0.95
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

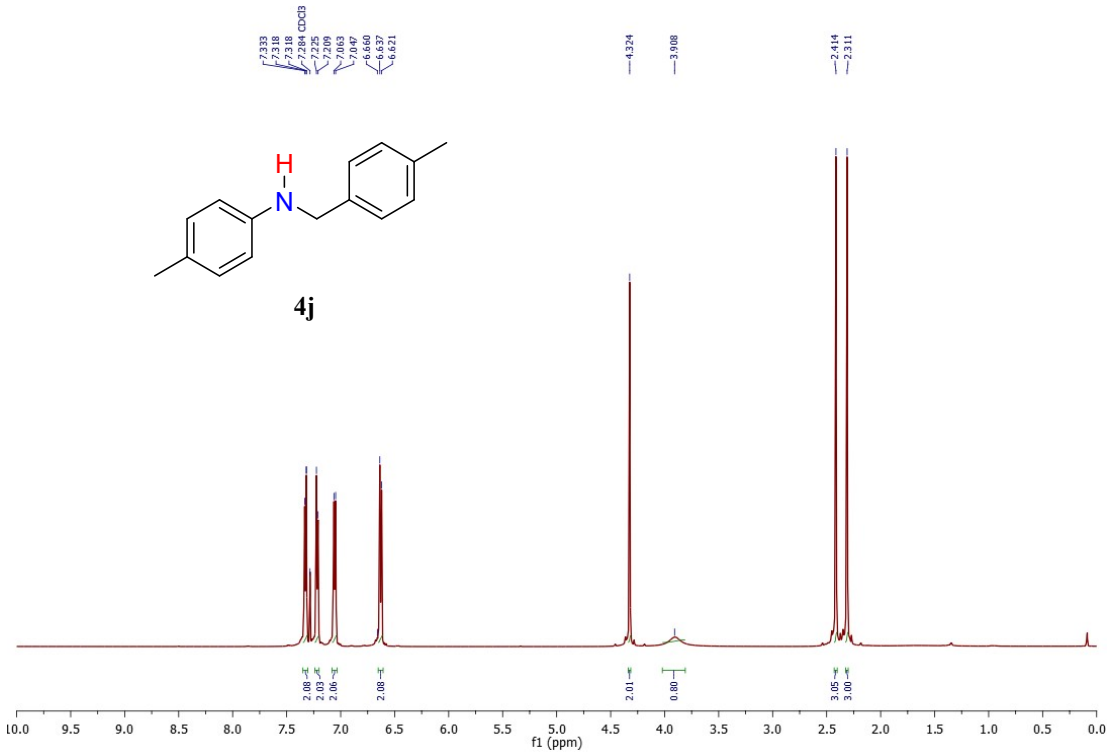

145.27
137.37
136.24
132.29
128.95
127.72
127.06
126.89
115.74
114.21
77.05 CDCl3
47.11
H
N
O
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.30
7.28
7.28 CDCl3
7.19
7.17
6.82
6.80
6.64
6.63
6.05
4.27
3.77
2.37
H
N
H3CO
2.10
1.98
2.03
1.98
2.05
3.80
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

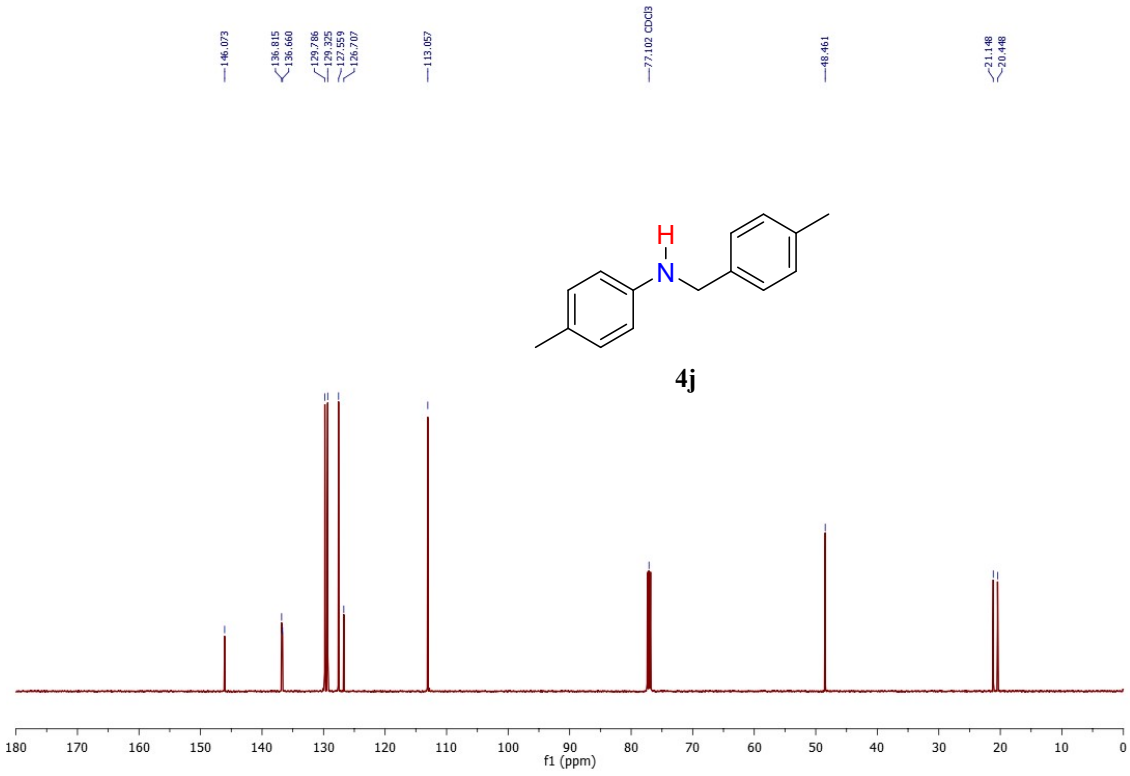
4i


152.26
142.65
136.93
136.71
129.39
127.68
115.02
114.24
77.16 CDCl3
55.94
49.13
21.23
H
N
H3CO
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

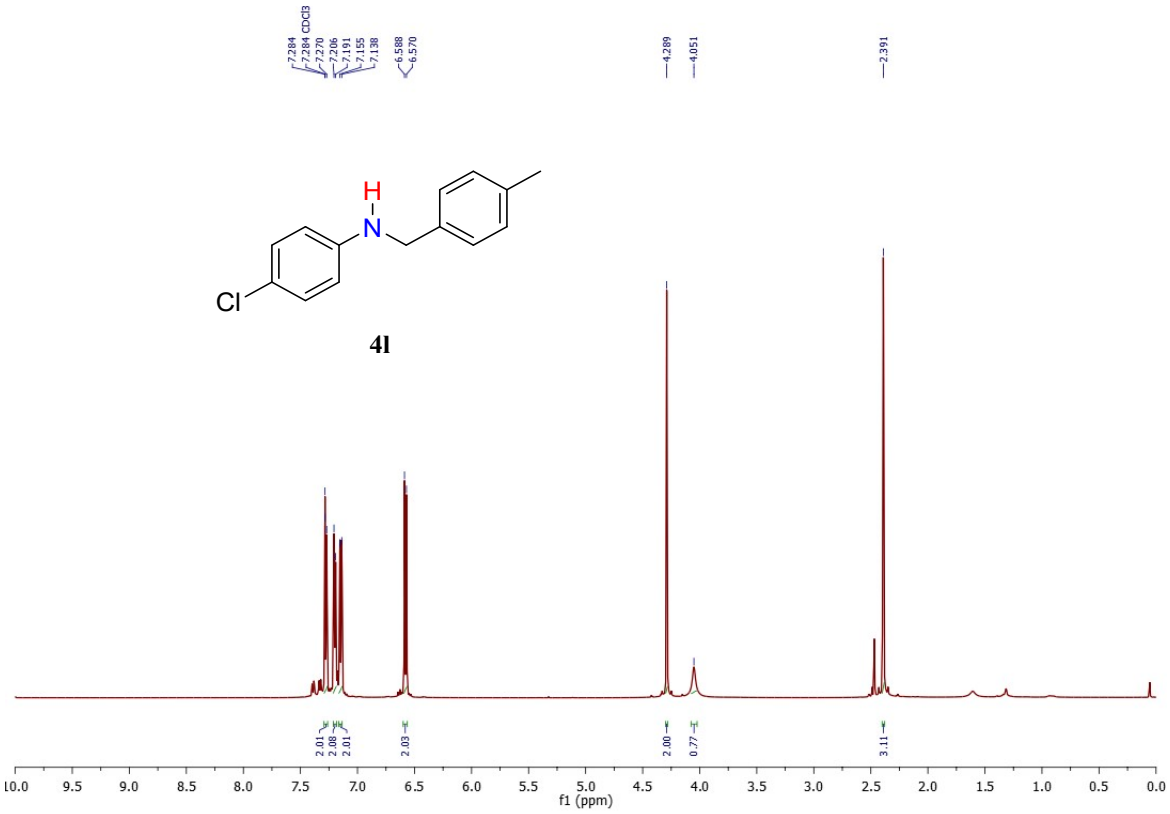
4i


7.333
7.318
7.318
7.284 CDCl3
7.275
7.209
7.063
7.047
6.660
6.637
6.621
4.324
3.908
2.414
2.311
H
N
2.08
2.03
2.06
2.08
2.01
0.80
3.05
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

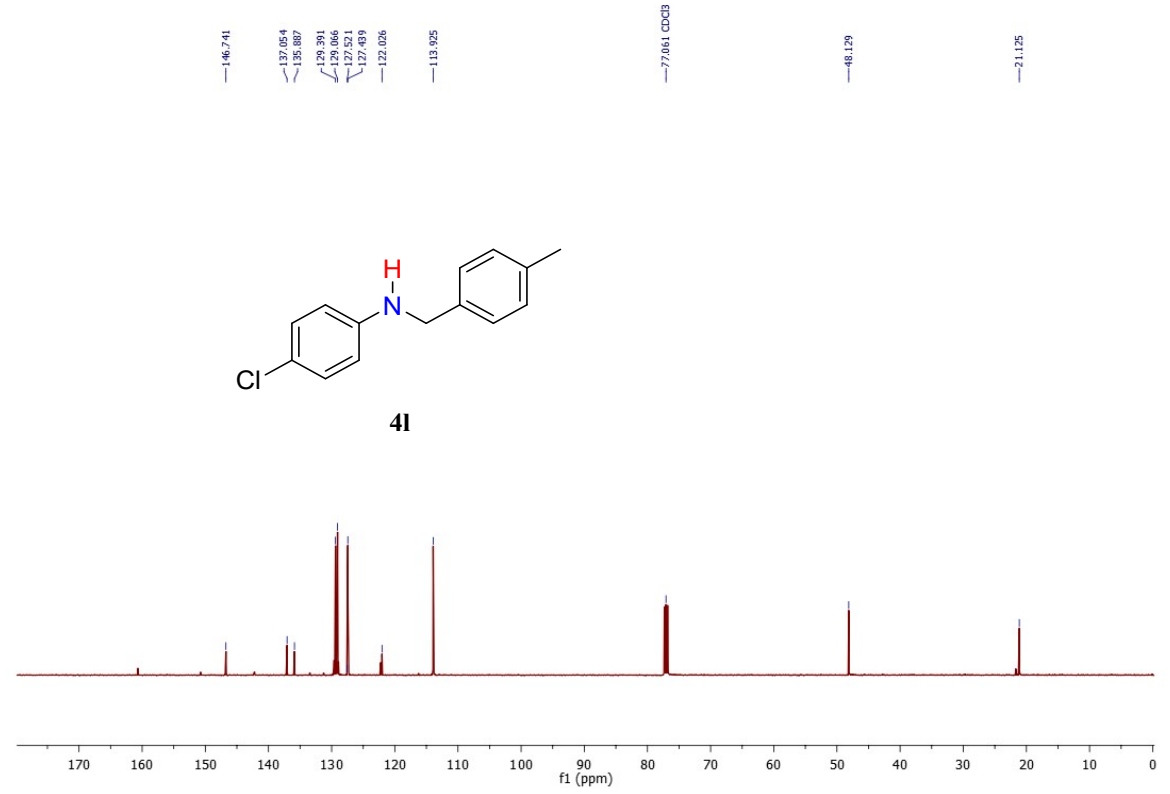
4j


146.073
136.815
136.660
129.786
129.335
127.555
126.707
113.057
77.102 CDCl3
48.461
21.148
20.448
H
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

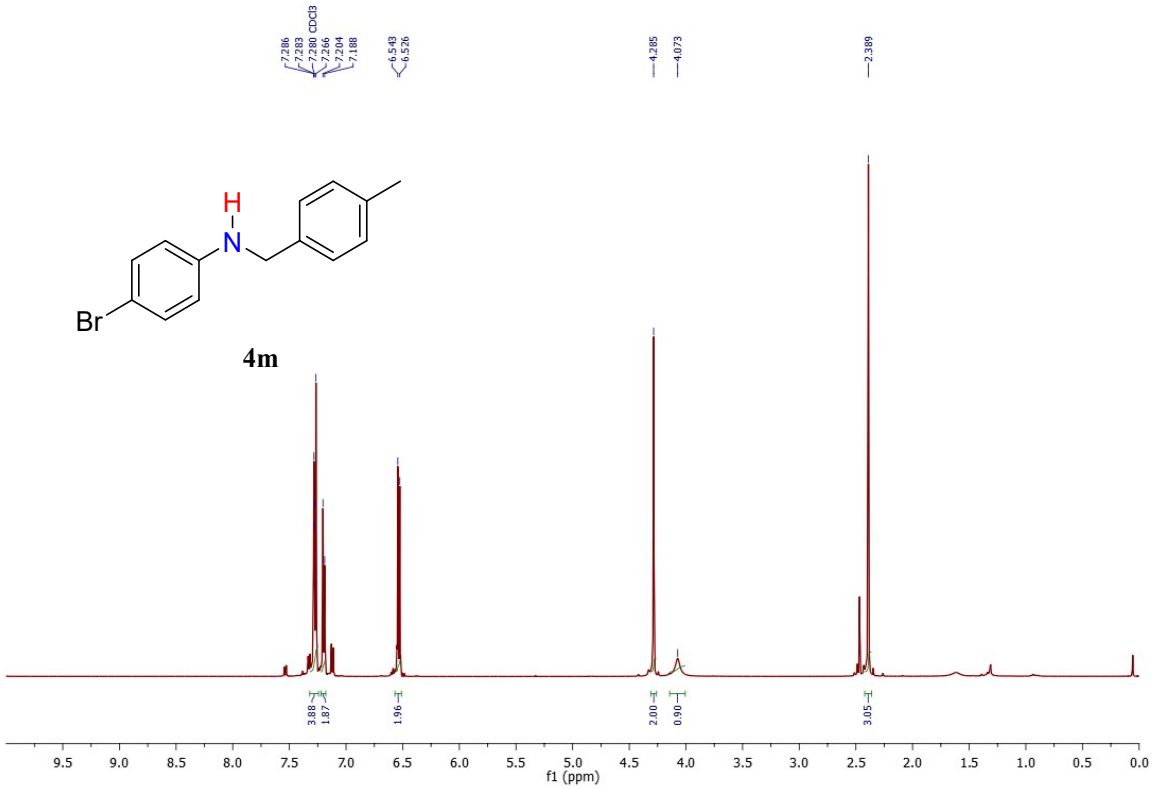
4j

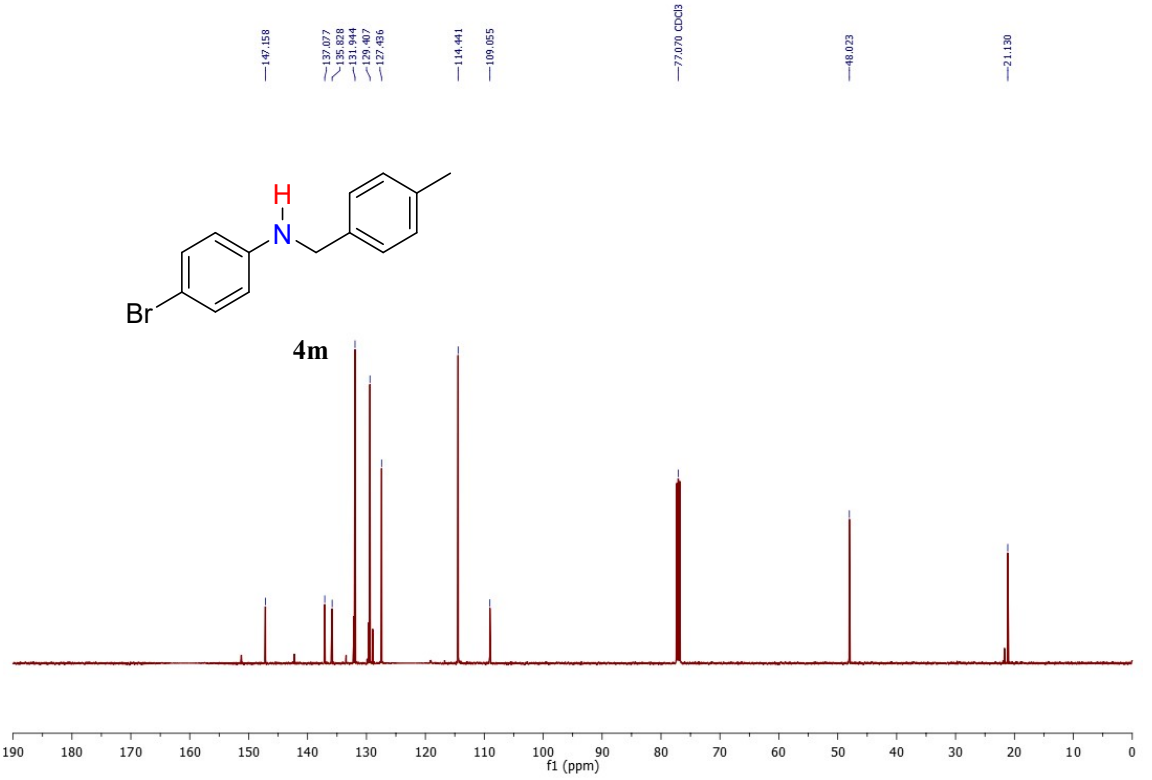

7.284
7.284 CDCl3
7.270
7.206
7.191
7.155
7.138
6.588
6.570
4.289
4.051
2.391
H
N
Cl
2.01
2.08
2.01
2.03
2.00
0.77
3.11
f1 (ppm)

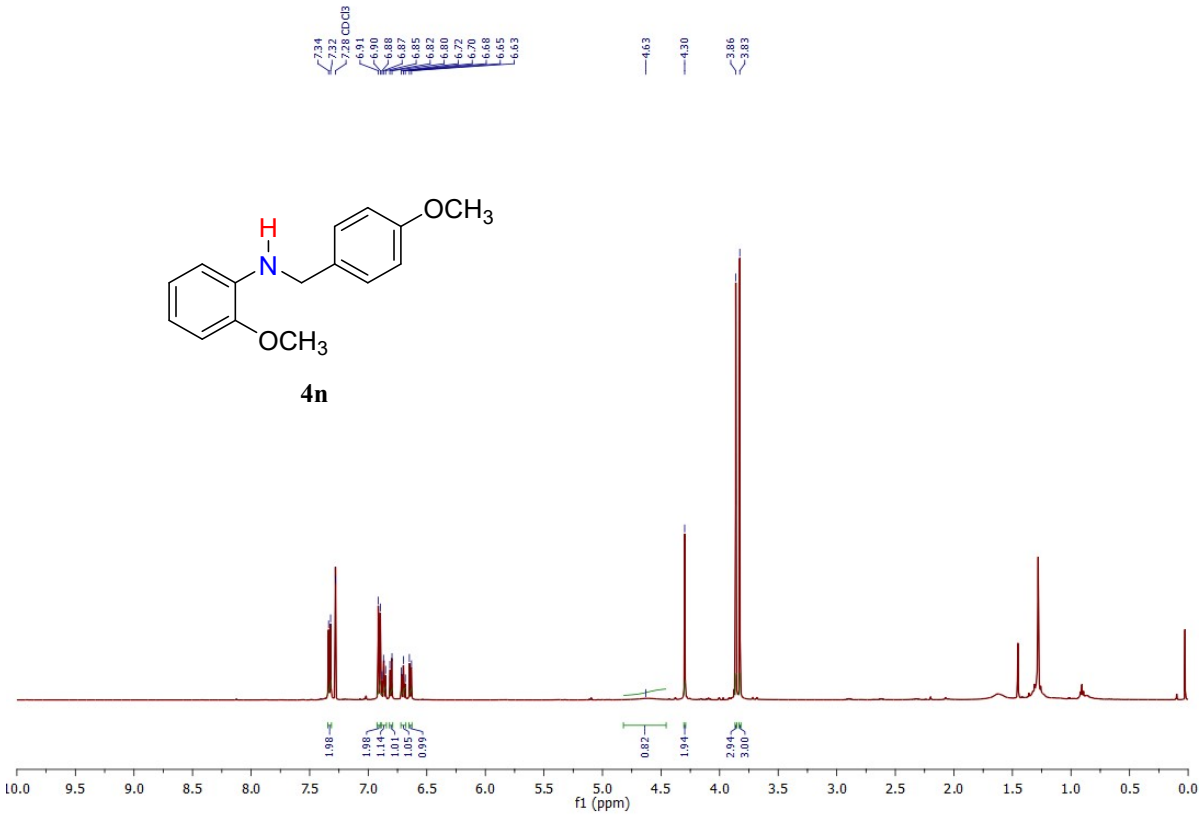
4l


146.741
137.054
135.887
129.391
129.066
127.521
127.439
122.026
113.925
77.061 CDCl3
48.129
21.125
H
N
Cl
f1 (ppm)

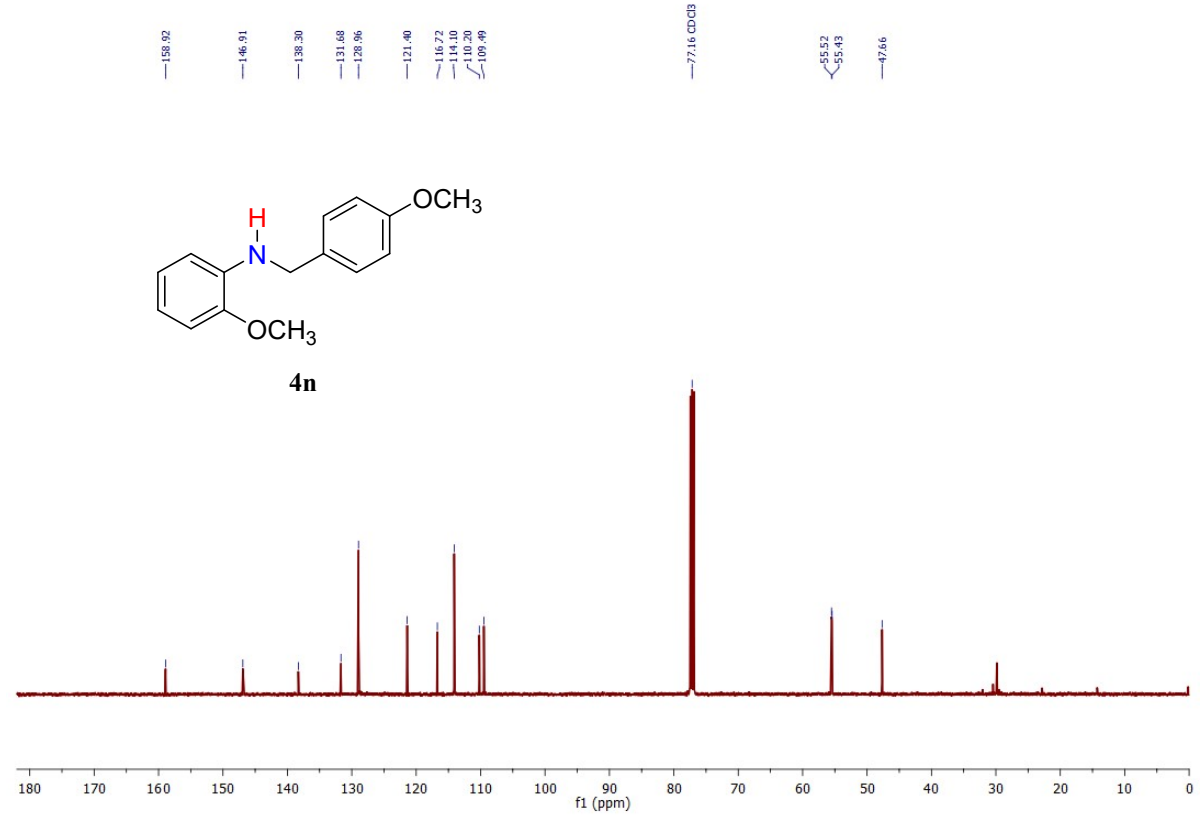
4l


7.286
7.283
7.280 CDCl3
7.266
7.204
7.188
6.543
6.526
4.285
4.073
2.389
H
N
Br
4m
3.88
1.87
1.96
2.00
0.90
3.05
f1 (ppm)

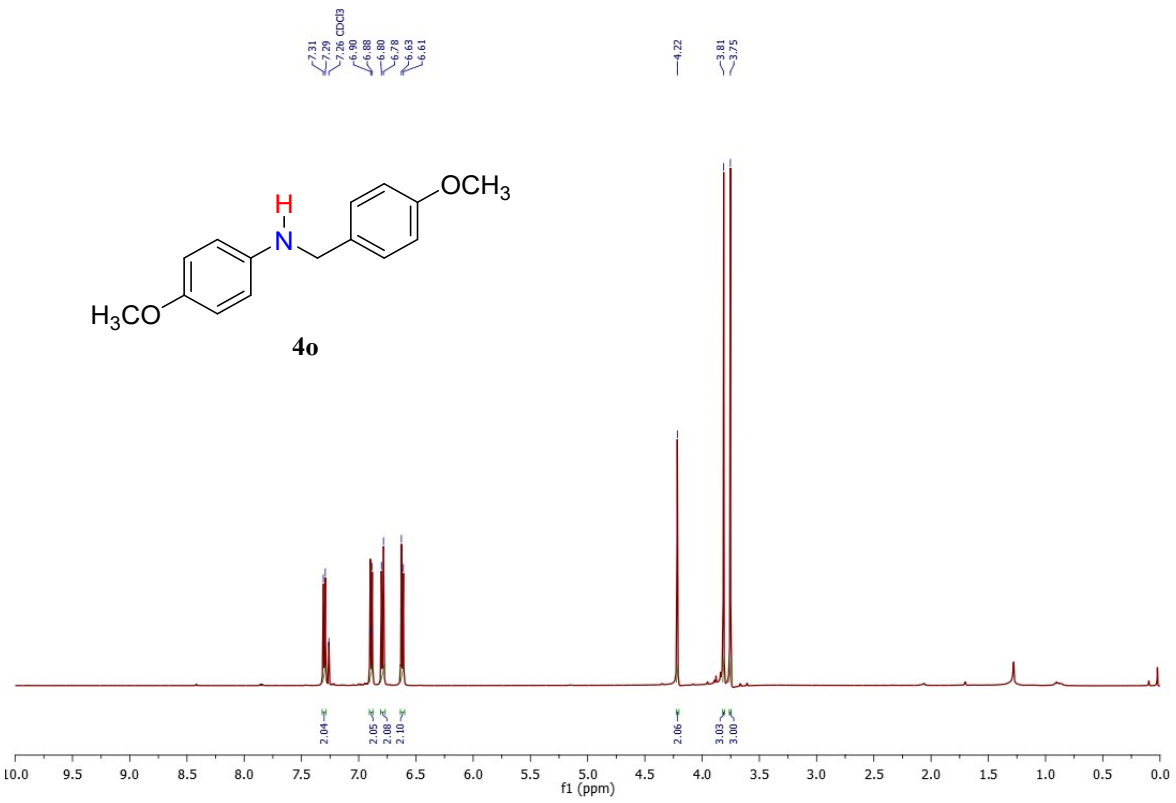

147.158
137.077
135.828
131.944
129.407
127.436
114.441
109.055
77.070 CDCl3
48.023
21.130
H
N
Br
4m
f1 (ppm)


7.34
7.32
7.28 CDCl3
6.91
6.90
6.88
6.87
6.85
6.82
6.80
6.72
6.70
6.68
6.65
6.63
4.63
4.30
3.86
3.83
H
N
OCH3
OCH3
1.98
1.98
1.14
1.01
1.05
0.99
0.82
1.94
2.94
3.00
f1 (ppm)

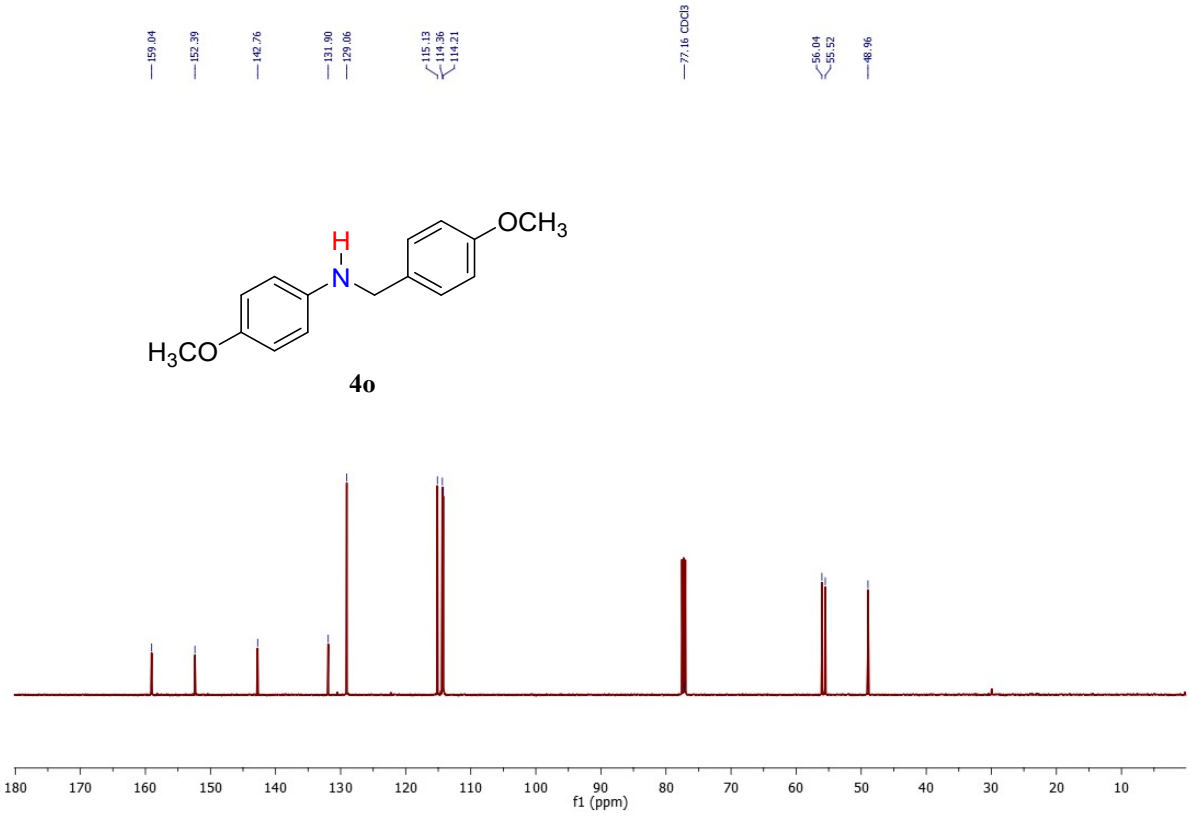
4n


158.92
146.91
138.30
131.68
128.96
121.40
116.72
114.10
110.20
109.49
77.16 CDCl3
55.52
55.43
47.66
H
N
OCH3
OCH3
f1 (ppm)

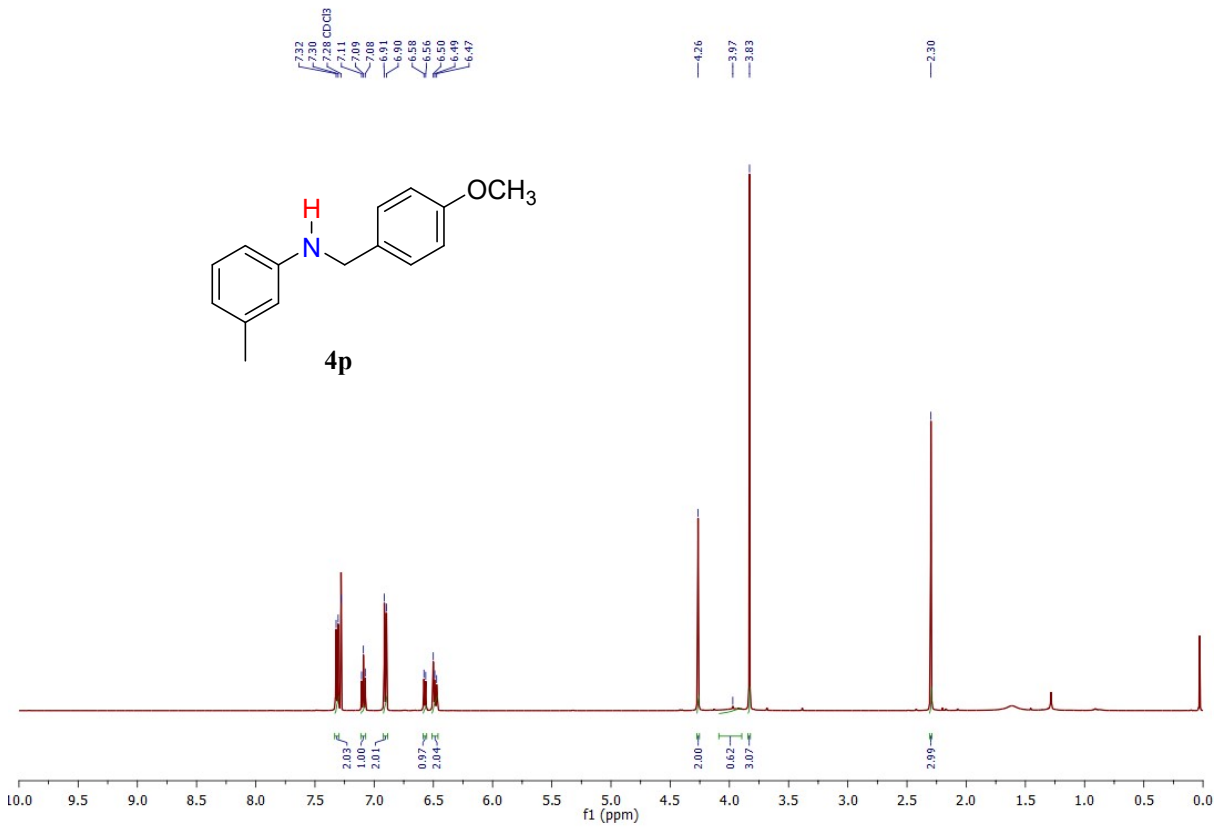
4n


7.31
7.29
7.26 CDCl3
6.90
6.88
6.80
6.78
6.63
6.61
4.22
3.81
3.75
OCH3
H
N
H3CO
2.04
2.05
2.08
2.10
2.06
3.03
3.00
f1 (ppm)

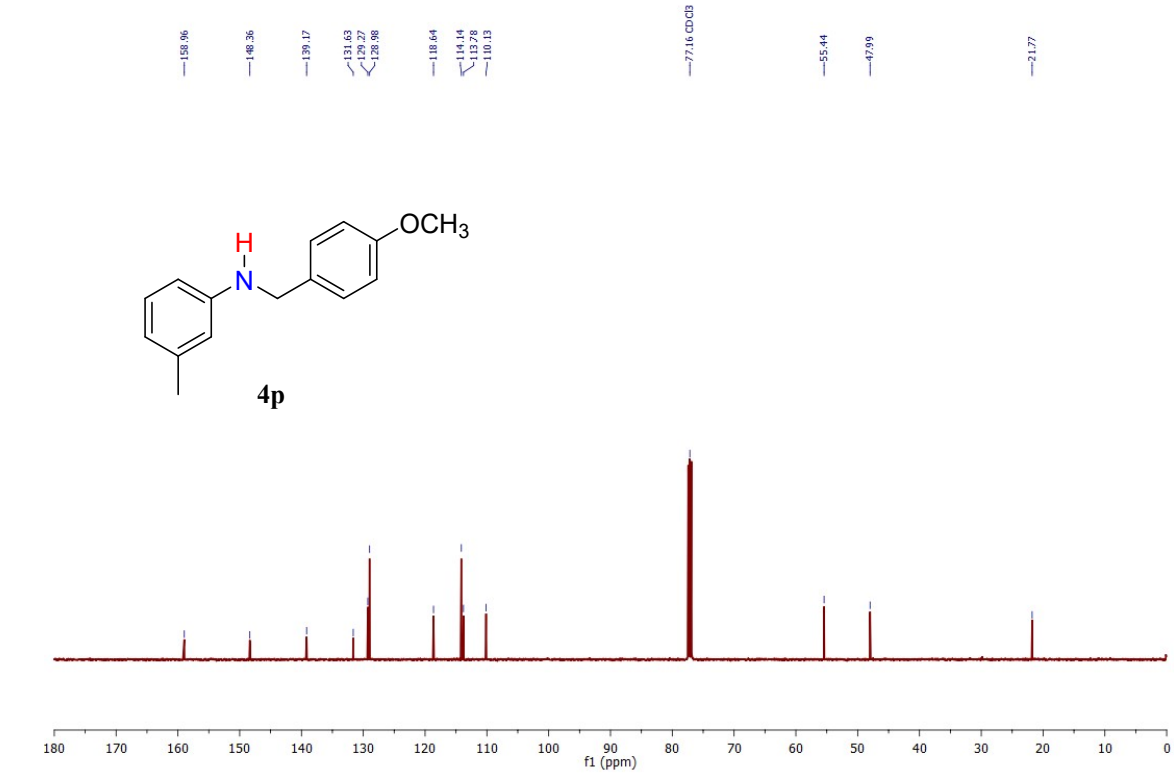
4o


159.04
152.39
142.76
131.90
129.06
115.13
114.36
114.21
77.16 CDCl3
56.04
55.52
48.96
OCH3
H
N
H3CO
f1 (ppm)

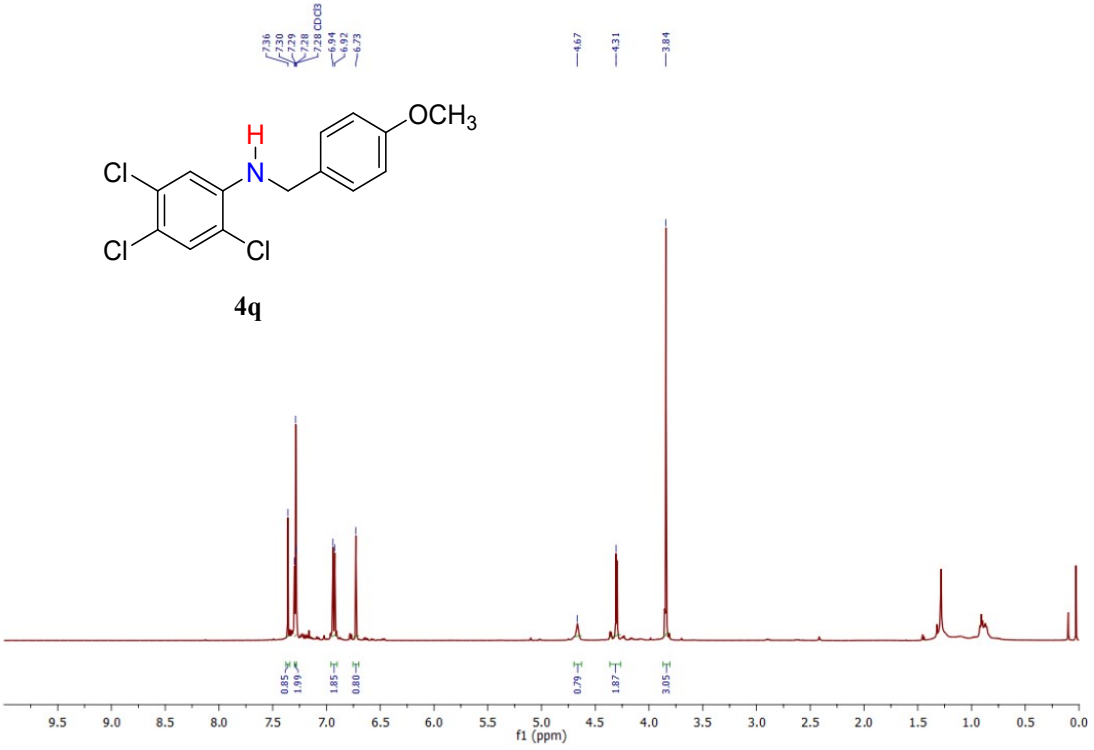
4o


7.32
7.30
7.28 CDCl3
7.11
7.09
7.08
6.91
6.90
6.58
6.56
6.50
6.49
6.47
4.26
3.97
3.83
2.30
OCH3
H
N
2.03
1.00
2.01
0.97
2.04
2.00
0.62
3.07
2.99
f1 (ppm)

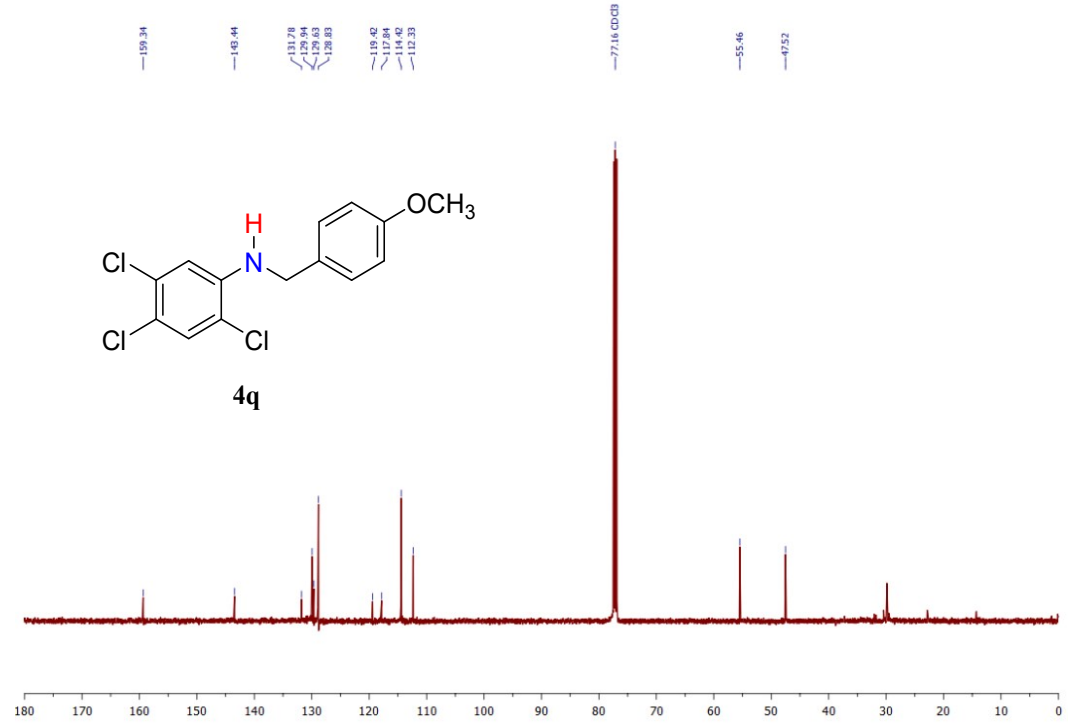
4p


158.96
148.36
139.17
131.63
129.27
128.98
118.64
114.14
113.78
110.13
77.16 CDCl3
55.44
47.99
21.77
OCH3
H
N
f1 (ppm)

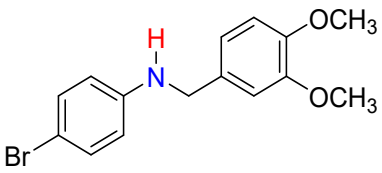
4p


7.36
7.30
7.29
7.28
7.28 CDCl3
6.94
6.92
6.73
4.67
4.31
3.84
OCH3
H
N
Cl
Cl
Cl
0.85
1.99
1.85
0.80
0.79
1.87
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

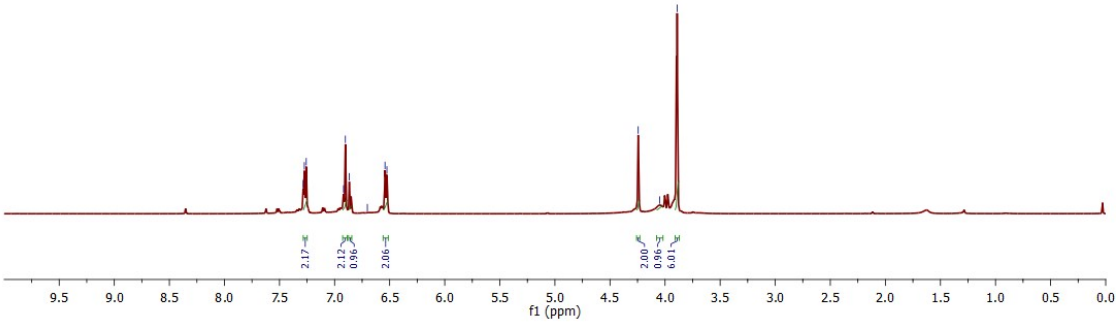
4q

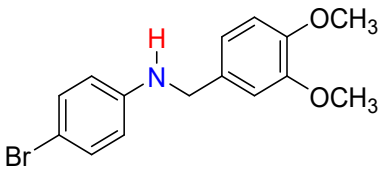

159.34
143.44
131.78
129.94
129.63
128.83
119.42
117.84
114.42
112.53
77.16 CDCl3
55.46
47.52
OCH3
H
N
Cl
Cl
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

4q

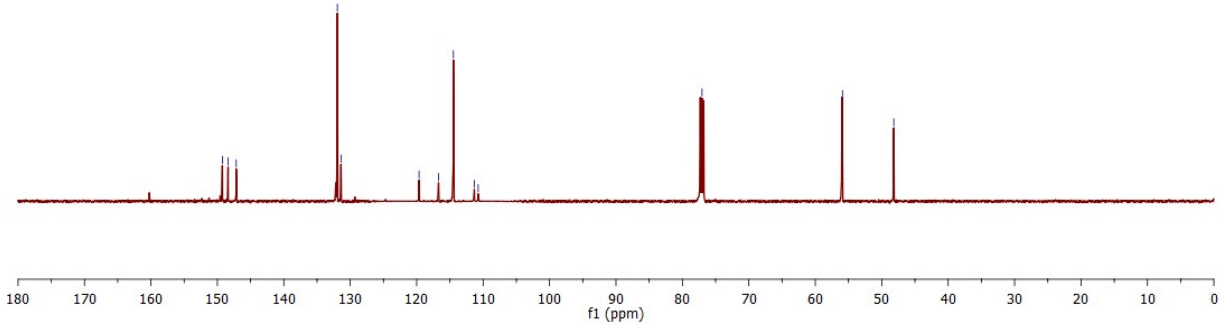


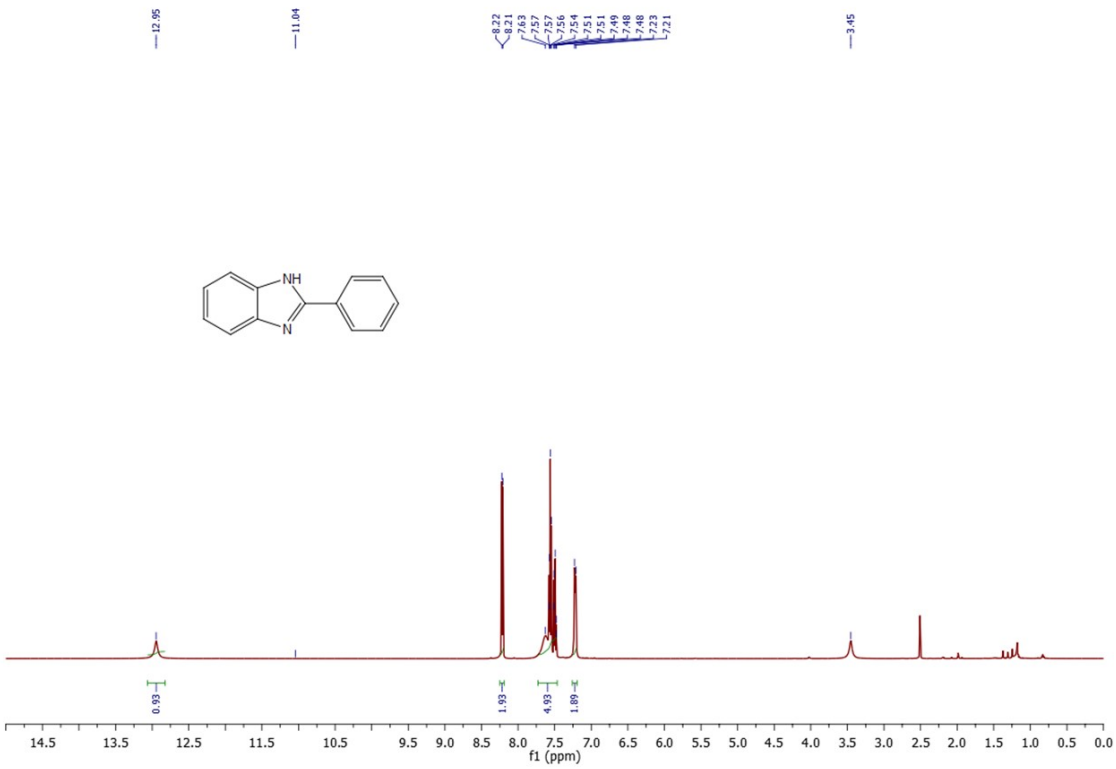
4r

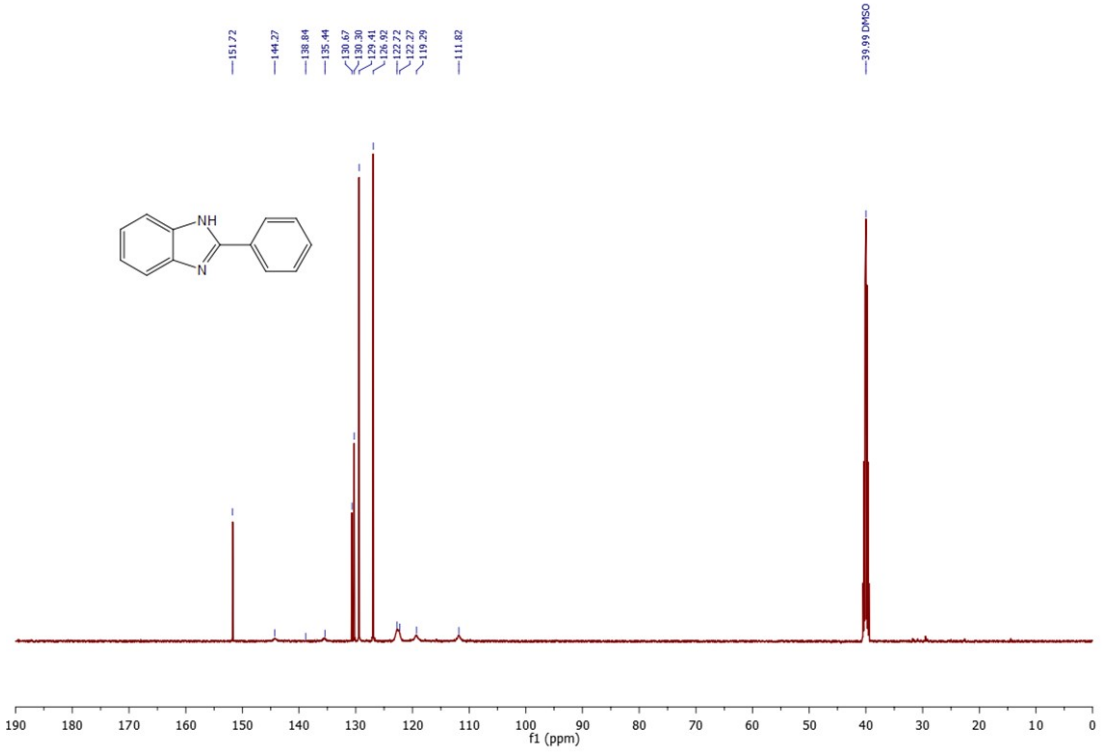


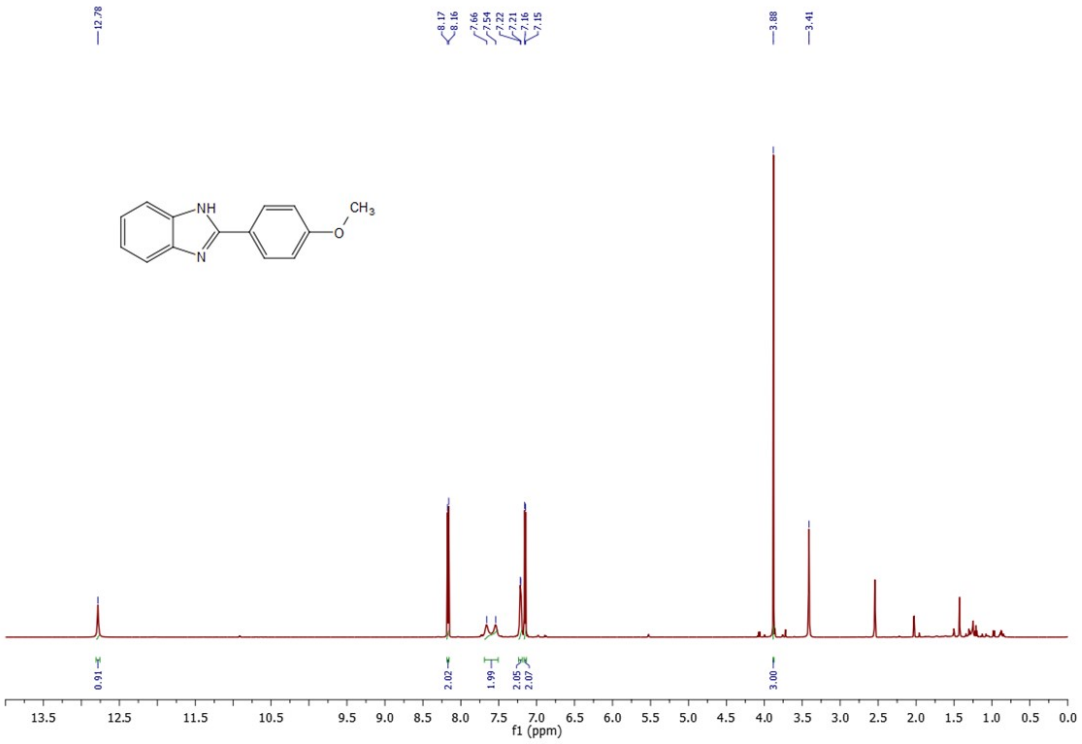


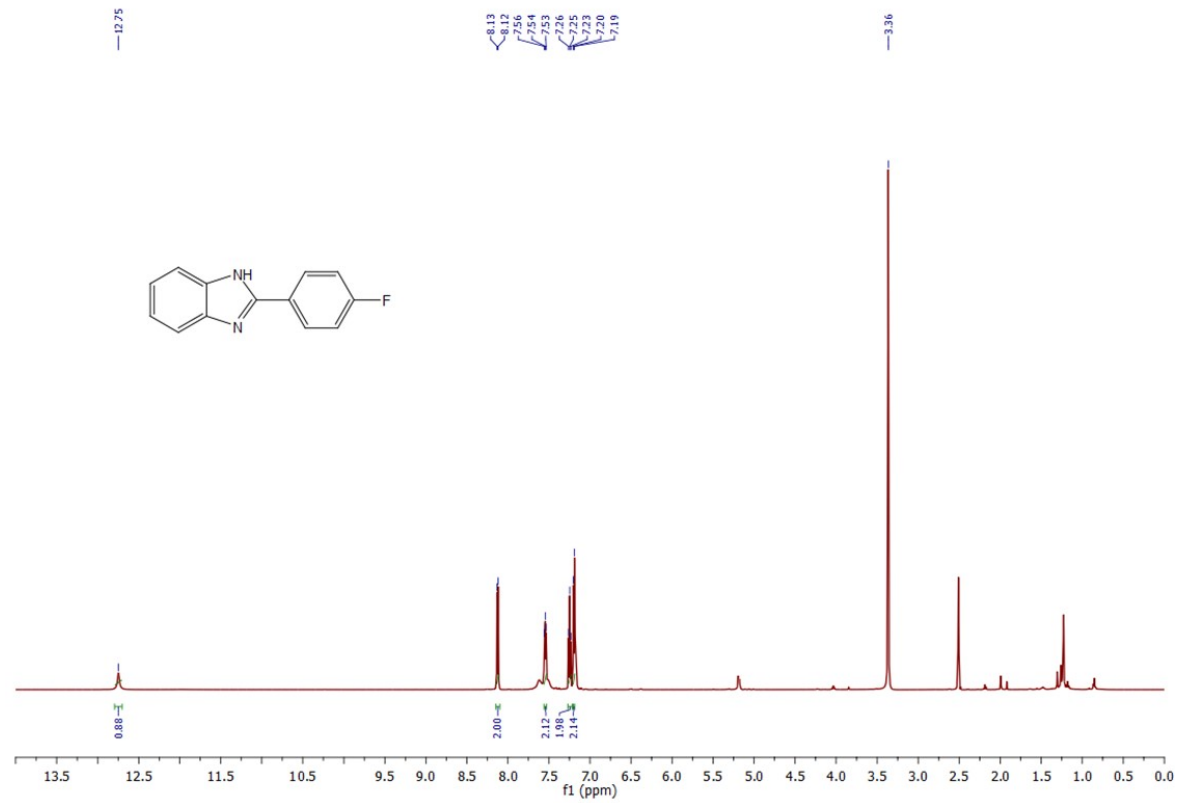
4r




12.95
11.04
8.22
8.21
7.63
7.57
7.57
7.56
7.54
7.51
7.51
7.49
7.48
7.48
7.23
7.21
3.45
NH
N
0.93
1.93
4.93
1.89
14.5 13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


151.72
144.27
138.84
135.44
130.67
130.30
129.41
126.92
122.72
122.27
119.29
111.82
39.99 DMSO
NH
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


12.78
8.17
8.16
7.66
7.54
7.22
7.21
7.16
7.15
3.88
3.41
NH
N
O
CH3
0.91
2.02
1.99
2.05
2.07
3.00
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


12.75
8.13
8.12
7.56
7.54
7.53
7.26
7.25
7.23
7.20
7.19
3.36
NH
N
F
0.88
2.00
2.12
1.98
2.14
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

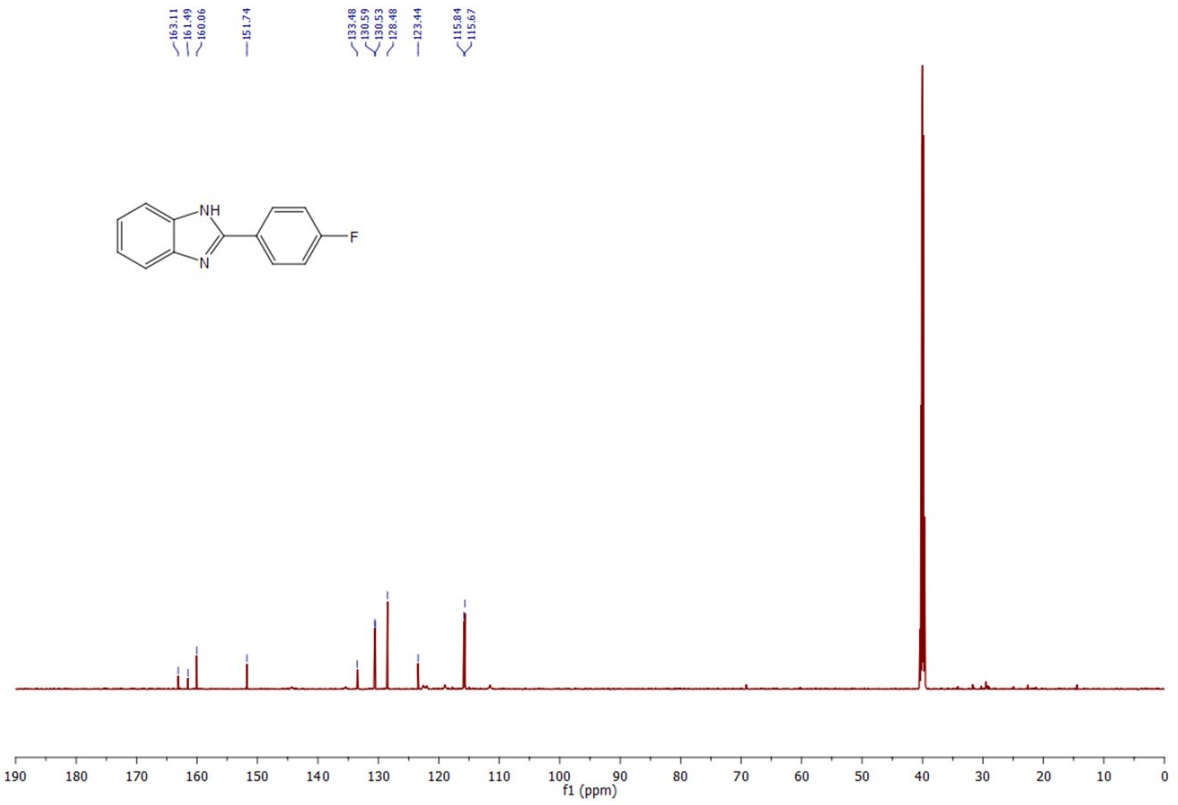

163.11
161.49
160.06
151.74
133.48
130.59
130.53
128.48
123.44
115.84
115.67
NH
N
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Figure S9: Step 1. ^{1}H NMR data

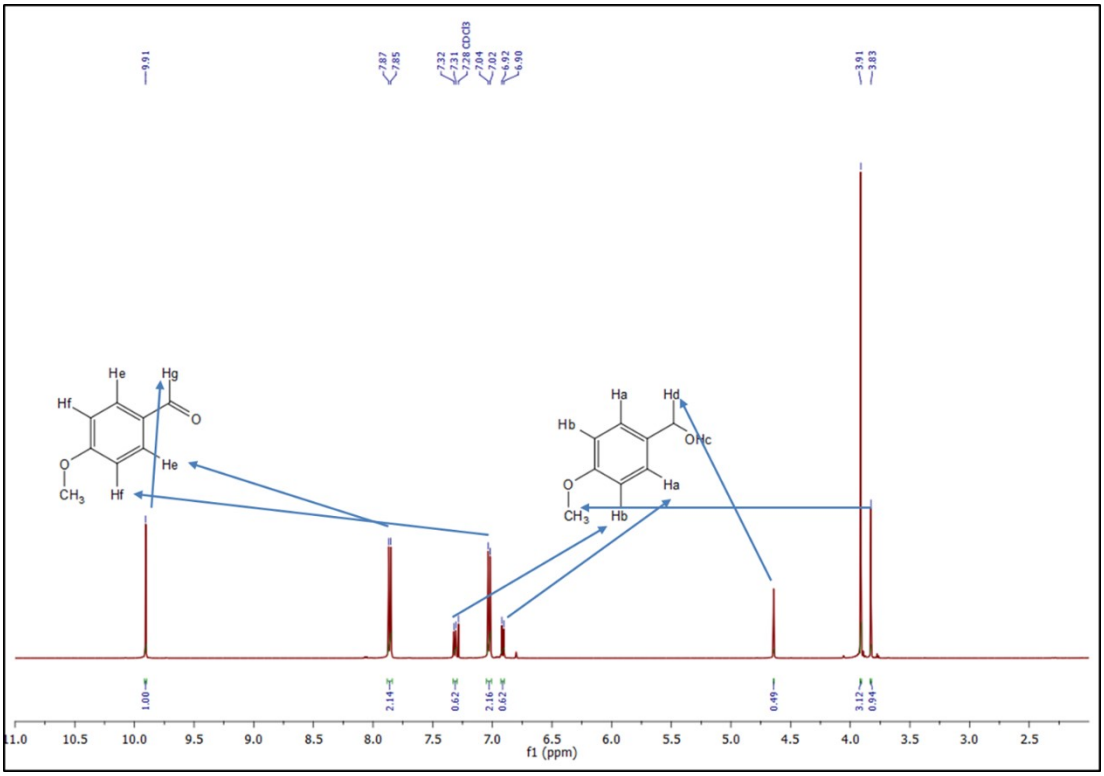
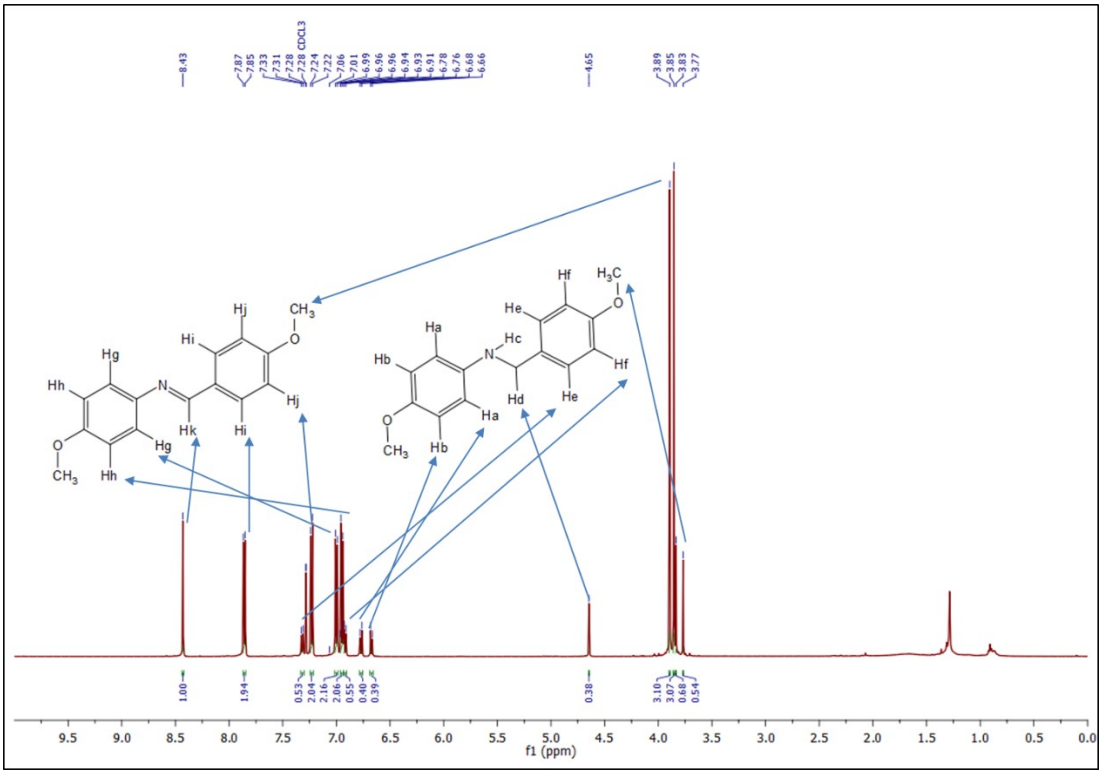


Figure S9: Step 2. ^{1}H NMR data



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