Supporting Information

Porous polymeric ligand promoted copper-catalyzed C-N coupling of (hetero)aryl chlorides under visible-light irradiation

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Table of Contents

1. General information

1.1 General reagent information

Tetrahydrofuran (THF) was distilled from sodium before use. Dimethyl sulfoxide (DMSO), dichloromethane (DCM) and *t*-butanol (*t*-BuOH) were distilled from CaH_2 before use. Dimethylformamide (DMF) and dimethylacetamide (DMAc) were distilled from NaH before use. CuI was washed by refluxing THF in Soxhlet extractor overnight before used and transferred to glove box for preservation. Other reagents and solvents were purchased from Sigma-Aldrich, Adamas or Aladdin Chemical, and used without further purification.

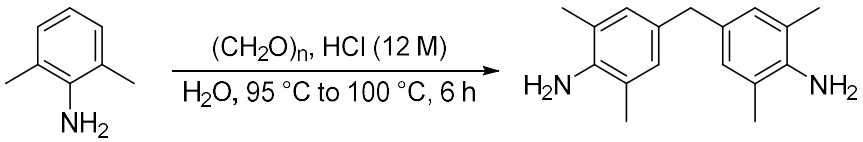
1.2 General analytical information

Liquid nuclear magnetic resonance (NMR) was recorded on an Advance III 400 MHz Bruker spectrometer at 298 K. ^{1}H NMR signals were measured relative to the signal for residual chloroform (7.26 ppm) in deuterochloroform ($CDCl_3$), and are reported in δ units, parts per million (ppm). ^{13}C NMR signals are reported in ppm units relative to $CDCl_3$ (77.1 ppm), and were obtained with 1H decoupling. Copies of ^{1}H NMR and ^{13}C NMR spectra of unknown compounds can be found at the end of the supporting information. ^{19}F NMR signals were reported in ppm units. Solid-state ^{13}C NMR spectra were recorded on a Bruker 400WB AVANCE Ⅲ spectrometer. The ^{13}C cross-polarization magic angle spinning nuclear magnetic resonance (CP/MAS NMR) spectra were recorded with a double-resonance MAS probe and with a sample spinning rate of 10.0 kHz. Fourier transform infrared spectrometry (FT-IR) measurements were recorded with a Thermofisher Nicolet 6700 instrument. Elemental analysis was measured with a vario EL Elemental Analyzer instrument (Analysemsysteme GmbH). Size exclusion chromatography (SEC) measurements were performed in DMF at 35°C with an elution rate of 0.35 mL/min on a TOSOH instrument equipped with a Bryce refractive index detector. Three columns were employed, including one 6 μm superMultipore HZ-H gel column and two 4 μm superMultipore HZ-M columns. The calibration was

performed with polystyrene standards. UV-Visible (UV-Vis) absorption spectra were collected with a Perkin-Elmer Lambda750 instrument. Inductively coupled plasma–atomic emission spectrometer (ICP-AES) was characterized by a ThermoFisher Scientific iCAP 7400 instrument. Gas chromatography (GC) measurements were carried out on SHIMADZU GC-2014 instrument using achiral capillary columns. The nitrogen adsorption and desorption isotherms were measured at 77 K using a JWGB-BK system. Surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) method. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDFT) method. Scanning electron microscopy (SEM) observations were performed on a Zeiss Ultra 55 microscope. High-resolution transmission electron microscope (HR-TEM) images were obtained with a JEOL F2100 instrument. The thermal properties of polymeric materials were evaluated using a thermogravimetric analysis (TGA) instrument (Mettler Toledo TGA 1) under N_2 with a heating rate of 20 °C/min. Melting points (m.p.) were taken on a SG X-4 capillary melting point apparatus. High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument. The polymeric ligands and catalysts were dried with a freeze drier (BIOCOOL, FD-1A-50). The copper-catalyzed C-N cross-coupling reactions were conducted with a photocatalytic parallel reaction apparatus (WATTCAS, WP-TEC-1020SL). Products were purified by flash column chromatography using silica gel (200-300 mesh).

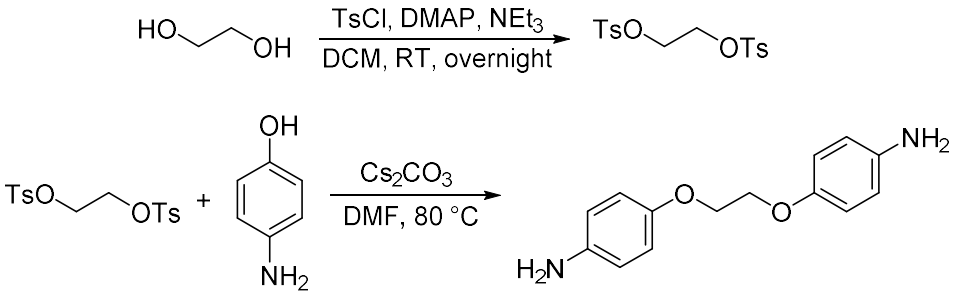
2. Synthesis and characterization of polymeric catalysts

2.1. Synthesis and characterization of diamine compounds



A 10 mL round bottom flask equipped with a stir bar was charged with 2, 6-dimethyl-aniline (1.27 g, 10.5 mmol) and 2 mL H_2O. The mixture was heated to 95 °C, then concentrated hydrochloric acid (0.88 mL, 12 M) was added, the

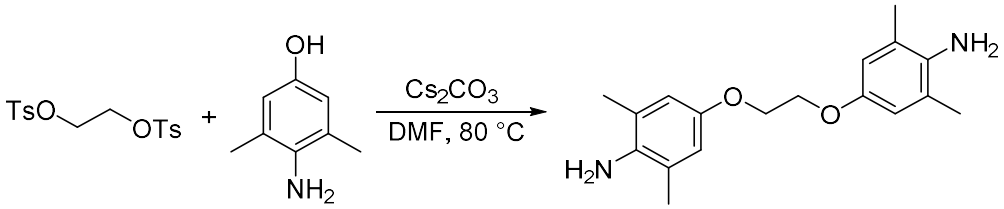
reaction mixture was stirred at 95 °C for 10 min, paraformaldehyde (0.15 g, 5.0 mmol) was added, and the reaction mixture was stirred at 100 °C for 6 h. After reaction, the reaction mixture was cooled to room temperature (RT) and diluted with H_2O, neutralized with a 20% aqueous solution of potassium hydroxide, and extracted with diethyl ether for three times. The combined organic layers were dried over anhydrous Na_2SO_4, concentrated under vacuum, and the product was recrystallized from methanol to afford a white solid[1] (1.11 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.79 (s, 4 H), 3.71 (s, 2 H), 3.48 (br, 4 H), 2.17 (s, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.6, 131.7, 128.7, 121.9, 40.4, 17.7 ppm.



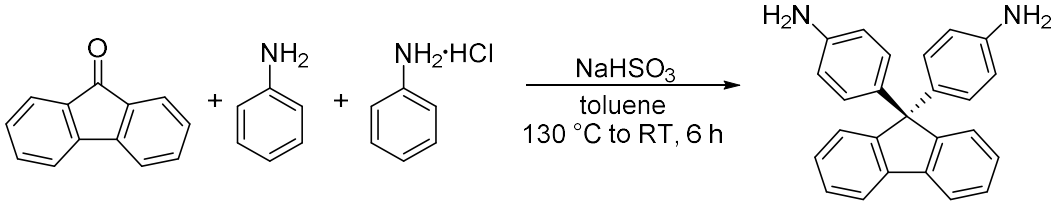
A 100 mL round bottom flask equipped with a stir bar was charged with ethylene glycol (0.62 g, 10 mmol), triethylamine (NEt_3, 3.34 mL, 24 mmol), *p*-tosylchloride (TsCl, 4.58 g, 24 mmol), 4-dimethylaminopyridine (DMAP, 0.12 g, 1 mmol) and 20 mL anhydrous DCM. The reaction mixture was stirred overnight at RT. After reaction, 20 mL H_2O was added and the solution was extracted with DCM for three times. The combined organic layers were dried over anhydrous Na_2SO_4, concentrated under vacuum. The obtained light yellow solid was rinsed with methanol to give target compound 1,2-bis(*p*-tolylsulfonyloxy) ethane as a white solid[2] (3.62 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, J = 8.4 Hz, 4 H), 7.36 (d, J = 8.4 Hz, 4 H), 4.20 (s, 4 H), 2.48 (s, 6 H). ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.4, 132.3, 130.0, 127.9, 66.7, 21.7 ppm.

A 50 mL round bottom flask equipped with a stir bar was charged with 1,2-bis(*p*-tolylsulfonyloxy) ethane (1.85 g, 5 mmol), 4-aminophenol (1.31 g, 12 mmol), Cs_2CO_3 (3.91 g, 12 mmol) and 10 mL DMF. The mixture was stirred at 80 °C for 12 h. After reaction, the mixture was cooled to RT and treated with 10 mL H_2O. The resulting mixture was extracted with DCM for three times. The combined organic

layers were dried over Na_2SO_4 and concentrated under vacuum. The obtained residue was purified by flash column chromatography over silica gel (eluting with 0-5% CH_3OH in DCM) to give target compound 1,2-bis[4-aminophenoxy]ethane (1.07 g, 88 %) as a light brown solid[3].^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.81 (d, *J* = 8.8 Hz, 4 H), 6.66 (d, *J* = 8.8 Hz, 4 H), 4.23 (s, 4 H), 3.50 (br, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.0, 142.7, 116.0, 115.3, 67.3 ppm.

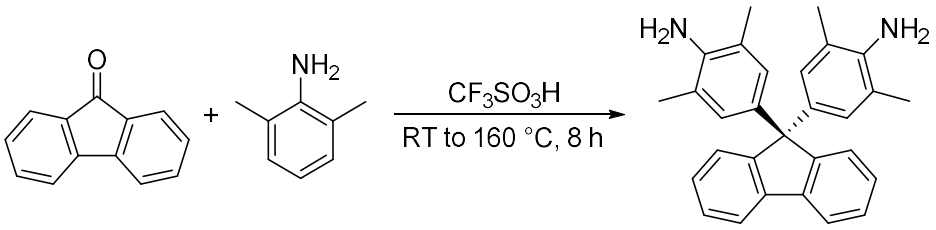


A 50 mL round bottom flask equipped with a stir bar was charged with 1,2-bis(*p*-tolylsulfonyloxy)ethane (1.85 g, 5 mmol), 4-amino-3,5-dimethylphenol (1.65 g, 12 mmol), Cs_2CO_3 (3.91 g, 12 mmol) and 10 mL DMF. The mixture was stirred at 80 °C for 12 h. After reaction, the mixture was cooled to RT and treated with 10 mL H_2O. The resulting mixture was extracted with DCM for three times. The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The obtained residue was purified by flash column chromatography over silica gel (eluting with 0-5% CH_3OH in DCM) to give target compound 1,2-bis[4-amino-3,5-dimethylphenoxy]ethane (1.28 g, 85 %) as a light brown solid.^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.63 (s, 4 H), 4.21 (s, 4 H), 3.34 (br, 4 H), 2.19 (s, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.1, 136.7, 123.1, 115.1, 67.4, 18.0 ppm. HRMS (ESI): m/z calculated for $C_{18}H_{25}N_2O_2^+$ [M+H$^+$]: 301.1911, found: 301.1912.



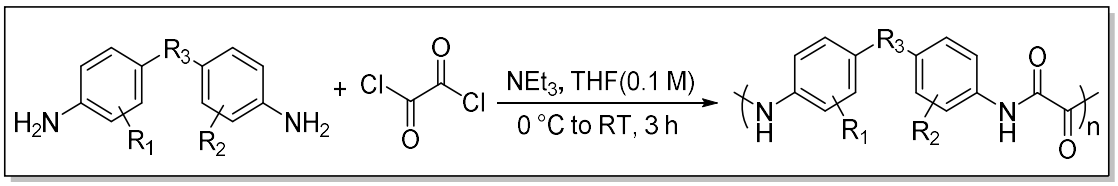
A 100 mL three-necked round-bottomed flask equipped with a stir bar, reflux condenser and oil-water separator was charged with 9-fluorenone (1.81 g, 10 mmol), aniline hydrochloride (1.94 g, 15 mmol), aniline (12 mL, 130 mmol), and toluene (5 mL). The mixture was refluxed at 130 °C for 6 h. After reaction, the

mixture was cooled to RT, treated with 10% NaOH aqueous solution, and stirred for 30 min. The crude product was washed by cold H_2O and CH_3OH, recrystallized from toluene and dried under dynamic vacuum at 60 °C for 12 h. Then the product was obtained as a white solid[4] (2.23 g, 64 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, *J* = 7.6 Hz, 2 H), 7.40 (d, *J* = 7.6 Hz, 2 H), 7.36 – 7.31 (m, 2 H), 7.28 – 7.23 (m, 2 H), 7.01 (d, *J* = 8.4 Hz, 4 H), 6.55 (d, *J* = 8.4 Hz, 4 H), 3.57 (br, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.8, 147.5, 139.8, 133.3, 128.6, 127.9, 127.4, 126.4, 120.7, 114.0, 64.0 ppm.

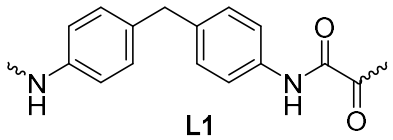


A 50 mL three-necked round-bottomed flask equipped with a stir bar and reflux condenser were charged with 9-fluorenone (3.60 g, 20 mmol) and 2,6-dimethylaniline (7.27 g, 60 mmol) under N_2. The mixture was stirred at RT for 10 min and then trifluoromethanesulfonic acid (0.88 mL, 10 mmol) was added to the mixture dropwise. The mixture was refluxed at 160 °C for 8 h. After reaction, the mixture was cooled to RT, neutralized with 10% NaOH aqueous solution, and stirred for 1 h. The crude product was washed by cold H_2O and ethanol, recrystallized from toluene and dried under dynamic vacuum at 60 °C for 12 h. Then the product was obtained as a yellow solid[5] (6.63 g, 82 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, *J* = 6.4 Hz, 2 H), 7.42 (d, *J* = 6.8 Hz, 2 H), 7.33 (td, *J* = 7.6, 1.2 Hz, 2 H), 7.26 (td, *J* = 7.6, 1.2 Hz, 2 H), 6.80 (s, 4 H), 3.49 (br, 4 H), 2.08 (s, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.6, 141.1, 139.9, 135.6, 128.0, 127.5, 126.8, 126.1, 121.3, 119.8, 64.3, 17.8 ppm.

2.2. Synthesis and characterization of polymeric ligands

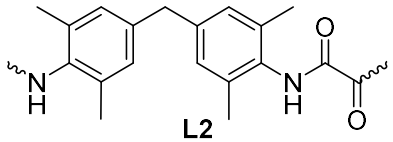


To a solution of the corresponding diamine compounds (1 eq.) in THF (0.1 M) was added NEt_3 (2.4 eq.). Oxalyl chloride (1.0 eq.) was then added to the solution dropwise under ice-water bath. The resulting mixture was stirred at RT for 3 h and concentrated under vacuum. Deionized H_2O was added to the obtained residue to dissolve NEt_3·HCl, then the slurry was filtered and the solid on filter paper was washed with water and cold diethyl ether. After freeze drying for 12 h, the corresponding oxamide-linked polymeric ligands **L1**-**L6** were all obtained in high yields (>98%). All the ligands were characterized by CP/MAS NMR, FT-IR and elemental analysis. In addition, contorted monomers have been proven to help increase the solubility of polymeric materials[4], therefore, the polymeric ligand **L5** was soluble in DMF (a low concentration ensured complete dissolution of ligand **L5**) and characterized by SEC measurement, however, the polymeric ligand **L1**-**L4** and **L6** were not soluble in a variety of solvents. Because we have verified that the polymeric ligand **L6** was the optimal ligand for copper-catalyzed C-N bond formation under visible-light irradiation and we were dying to know the molecular weight about **L6**, we used dilute solution of diamine compound in THF (0.01 M) as raw material through a reaction of 1 min with oxalyl chloride to obtain the polymeric ligand **L6'**, which was slightly soluble in DMF and characterized by SEC measurement.



L1

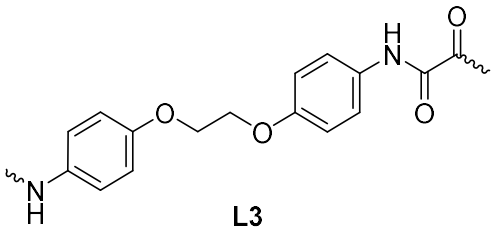
L1 (light yellow solid): ^{13}C CP/MAS NMR, δ: 157.6, 138.7, 135.2, 130.3, 121.7, 41.2 ppm. FT-IR (cm^{-1}): 3298, 3034, 2925, 1745, 1671, 1591, 1518, 1410, 1311, 1240, 812, 748. Elemental analysis: C (70.5%), N (10.6%), H (5.2%).[6]



L2

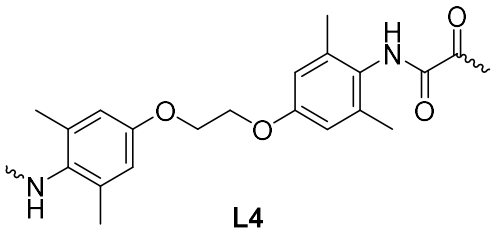
L2 (off-white solid): ^{13}C CP/MAS NMR, δ: 159.1, 140.9, 135.4, 131.4, 128.8, 41.7, 18.4 ppm. FT-IR (cm^{-1}): 3252, 2920, 2876, 2604, 1670, 1604, 1491, 1376, 850,

744, 705. Elemental analysis: C (72.2%), N (8.5%), H (7.1%).[6]



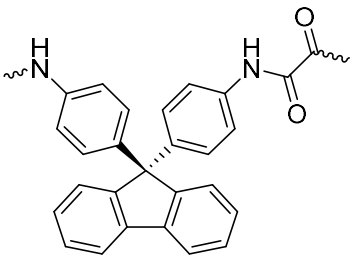
L3

L3 (brown solid): ^{13}C CP/MAS NMR, δ: 156.4, 129.5, 124.1, 117.5, 113.0, 64.4 ppm. FT-IR (cm^{-1}): 3293, 2927, 1664, 1596, 1511, 1414, 1299, 1229, 827, 721. Elemental analysis: C (62.9%), N (8.8%), H (5.1%).[6]



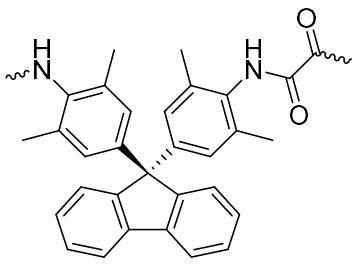
L4

L4 (light brown solid): ^{13}C CP/MAS NMR, δ: 156.5, 136.5, 125.8, 115.9, 108.5, 64.9, 18.9 ppm. FT-IR (cm^{-1}): 3349, 3244, 2941, 2739, 2676, 2605, 2495, 1677, 1643, 1599, 1492, 1321, 1233, 1146, 1069, 1035, 851, 702. Elemental analysis: C (65.7%), N (7.4%), H (7.0%).[6]



L5

L5 (brown solid): ^{13}C CP/MAS NMR, δ: 158.2, 151.6, 145.3, 140.3, 135.5, 127.6, 119.9, 115.2, 64.7 ppm. FT-IR (cm^{-1}): 3348, 3030, 1682, 1616, 1588, 1510, 1443, 1402, 1315, 1183, 819, 746. Elemental analysis: C (78.6%), N (6.1%), H (5.5%).[6] SEC measurement: number-average molecular weight (M_n, by SEC in DMF at 35 ºC) = 9211 g.mol^{-1}, *PDI* = 2.05.



L6 (PPL)

L6 (light purple solid): ^{13}C CP/MAS NMR, δ: 159.3, 152.0, 145.7, 140.8, 135.5, 132.2, 127.5, 120.4, 65.0, 18.1 ppm. FT-IR (cm^{-1}): 3363, 3249, 3035, 2920, 2858, 1675, 1598, 1489, 1445, 1403, 1299, 855, 741, 712. Elemental analysis: C (79.8%), N (5.6%), H (6.5%).[6] Because **L6** is not soluble in any solvent, a direct measurement of its molecular weight by SEC (GPC) or MALLS is not possible. To give more information about this compound, polymeric ligand **L6'** was synthesized (0.01 M diamine compound in THF, 1 min reaction time), affording **L6**' number-average molecular weight (M_n, by SEC in DMF at 35 ºC) = 2751 g.mol^{-1}, *PDI* = 1.40. The actual molecular weight of **L6** should be much higher than **L6'** due to the extended reaction time and poor solubility.

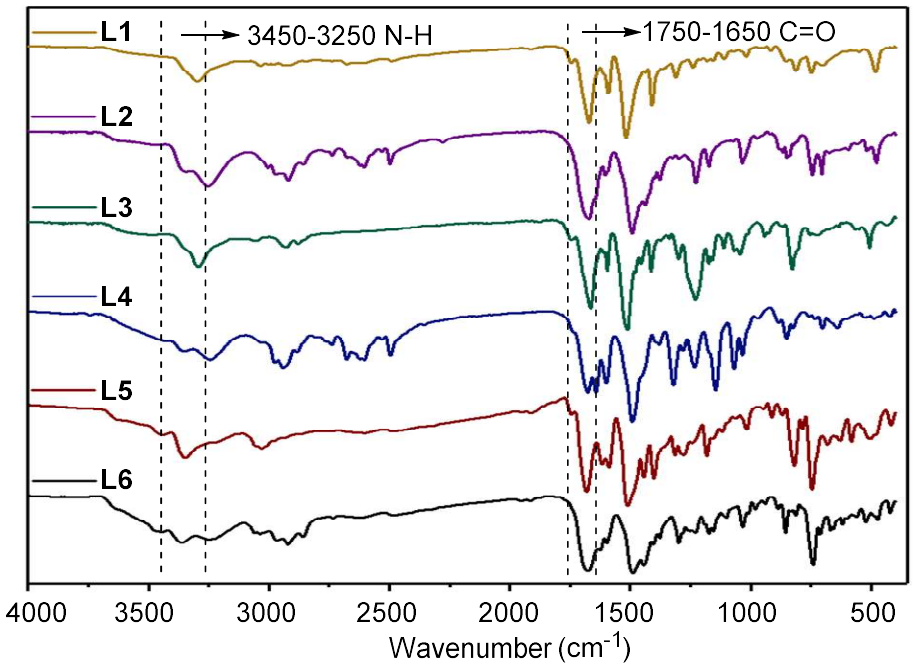


Figure S1. FT-IR spectra of oxamide-linked polymeric ligands

2.3. Synthesis and characterization of polymeric catalysts

An oven-dried 10 mL Schlenk flask equipped with a stir bar was charged with CuI (190.5 mg, 1 mmol) and 0.4 mL pyridine, and the mixture was stirred at RT under N_2 atmosphere for 2 min to dissolve CuI completely. Then, 2 mL DMSO and Ligand (the mole ratio of Cu and the repeat unit of polymer ligand is 1:1) were added successively under N_2 atmosphere. The mixture was stirred at RT for 24 h under N_2 atmosphere. After reaction, the mixture was treated with cold water and filtered, then the solid on filter paper was washed with water. The complex was further dried under freeze drying for 12 h to give polymeric catalysts Cu@Ligand.

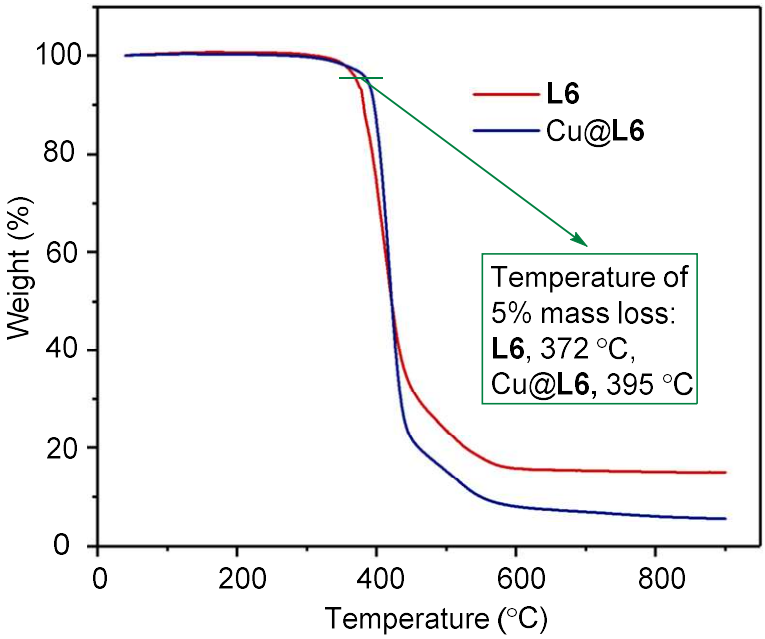


Figure S2. TGA spectra of **L6** and Cu@**L6**

In contrast, when **L6** and CuI were mixed at their solid states, and followed by the addition of DMSO and pyridine under N_2 atmosphere, less Cu was loaded onto the polymeric matrix. Importantly, as shown in Figure S3, many black dots, attributing to the formation of Cu nanoparticles promoted by the electron-beam induced reduction during HR-TEM measurement, have been observed in corresponding HR-TEM images.[7] The lattice fringes with a spacing distance of 0.21 nm in Figure S3b has confirmed the presence of Cu nanoparticles.[8]

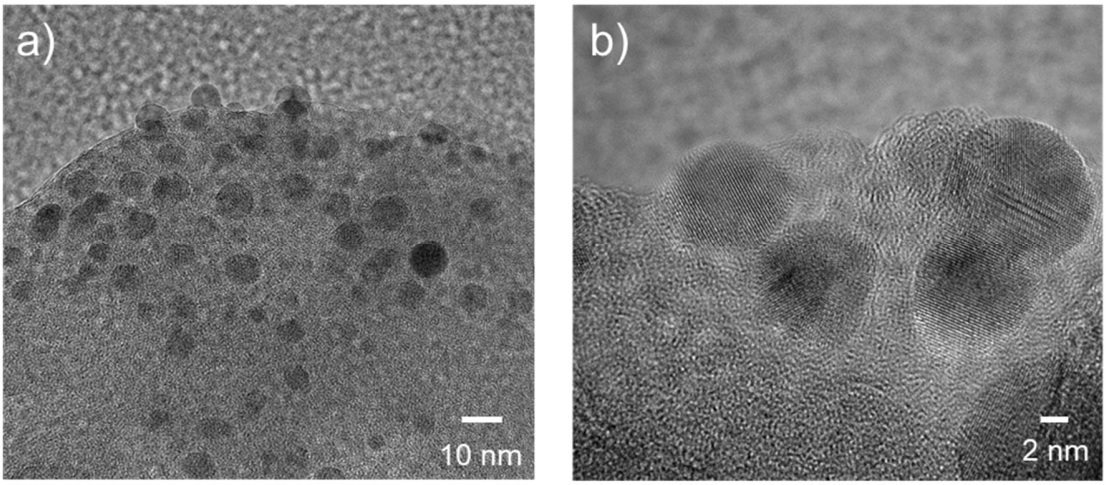


Figure S3. a) HR-TEM image of Cu-complex prepared by mixing CuI and **L6** at solid states; b) Magnified HR-TEM image of S3a.

3. Experiments of condition optimization and catalyst recycling

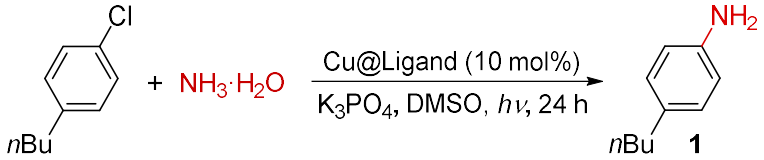
3.1. Experiments of condition optimization

Figure S4. Pictures of the photocatalytic parallel reaction apparatus

A reaction tube of photocatalytic parallel reaction apparatus (Figure S4, WATTCAS, WP-TEC-1020SL) equipped with a stir bar was charged with

Cu@Ligand (0.05 mmol) and base (0.6 mmol), and then the tube was evacuated and backfilled with nitrogen (three cycles). In addition, the reaction tube was placed above a 10 W LED lamp with an appropriate wavelength. Next, 4-*n*-butyl-chlorobenzene (0.5 mmol), aqueous ammonia (1 mmol) and solvent (0.5 mL) was added, and the resulting mixture was stirred under the corresponding condition of Table 1. After reaction, the mixture was cooled to RT. Biphenyl was added into the mixture as an internal standard. The resulting mixture was extracted with ethyl acetate for three times. The combined organic layers were dried over Na_2SO_4. A small aliquot of the organic layer was filtered through a short silica gel cartridge, and characterized with GC analysis to give GC yields of target product 4-*n*-butylaniline[9]. The condition details of every experiment could be seen in Table 1, and Table S1 was showed below as supplementary table.

Table S1. C-N bond formation between 4-*n*Bu-Ph-Cl and aqueous ammonia[a]



Entry	Ligand	Light irradiation	Temp. (°C)	Yield[b]
1	**L1**	white light	100	21
2	**L2**	white light	100	48
3	**L3**	white light	100	21
4	**L4**	white light	100	45
5	**L5**	white light	100	58
6	**L6**	white light	100	76

[a]General conditions: 4-*n*Bu-Ph-Cl (0.5 mmol), aqueous ammonia (1 mmol), Cu@Ligand (0.05 mmol), K_3PO_4 (0.6 mmol), DMSO (0.5 mL). [b]GC yield.

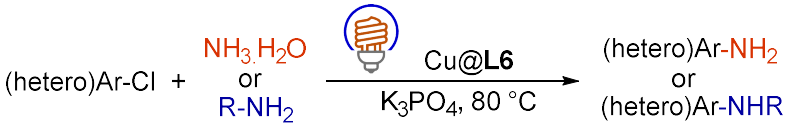
3.2. Experiments of catalyst recycling

A reaction tube of photocatalytic parallel reaction apparatus (Figure S4, WATTCAS, WP-TEC-1020SL) equipped with a stir bar was charged with Cu@**L6** (32.4 mg, 0.05 mmol), and K_3PO_4 (127.4 mg, 0.6 mmol), and then the tube was

evacuated and backfilled with nitrogen (three cycles). In addition, the reaction tube was placed above a 10 W LED lamp (405 nm). Next, *n*-Butyl-4-chlorobenzene (0.5 mmol), aqueous ammonia (1 mmol) and solvent (0.5 mL) was added, and the resulting mixture was stirred under 80 °C for 48 h under N_2 atmosphere. After reaction, the reaction mixture was cooled to RT. Biphenyl was added into the mixture as an internal standard. The resulting mixture was extracted with ethyl acetate for three times. The combined organic layers were dried over Na_2SO_4. A small aliquot of the organic layer was filtered through a short silica gel cartridge, and characterized with GC analysis to give GC yield of the first run as shown in Table 2. The heterogeneous catalyst was separated from the reaction mixture via simple filtration, then purified by washing with solvents and freeze-dried for 12 h. In the second run, the freeze-dried catalyst of the first run and K_3PO_4 (127.4 mg, 0.6 mmol) was added into the reaction tube, and then the tube was evacuated and backfilled with nitrogen (three cycles). Next, 4-*n*-butyl-chlorobenzene (0.5 mmol), aqueous ammonia (1 mmol) and solvent (0.5 mL) was added, and the resulting mixture was stirred under 80 °C for 48 h under N_2 atmosphere. After reaction, post-processing was conducted by using the same procedure as shown for the first run. In the following experiments of catalyst recycling from the third to the sixth runs, the catalyst was reused using the same procedure as indicated with the second run, and during each time less than 1 ppm of Cu was detected by ICP-AES in the reaction mixture after catalyst separation.

4. General procedure and characterization results for Scheme 1

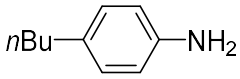
4.1. General procedure for Scheme 1



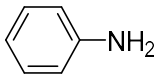
A reaction tube of photocatalytic parallel reaction apparatus (WATTCAS, WP-TEC-1020SL) equipped with a stir bar was charged with Cu@**L6** (32.4 mg, 0.05 mmol), (hetero)aryl chloride (if solid, 0.5 mmol), R-NH_2 (if solid, 0.6 mmol), K_3PO_4

(127.4 mg, 0.6 mmol), and then the tube was evacuated and backfilled with nitrogen (three cycles). In addition, the reaction tube was placed above a 10 W LED lamp (405 nm). Next, $NH_3.H_2O$ (w/w 25%, 75 μL, 1.0 mmol) or R-NH_2 (if liquid, 0.6 mmol), aryl chloride (if liquid, 0.5 mmol) and 0.5 mL DMSO were added, and the resulting mixture was stirred at 80 °C for 48 h under N_2 atmosphere. After reaction, the reaction mixture was cooled to RT. The resulting mixture was extracted with ethyl acetate for three times. The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The collected residue was purified by column chromatography using silica gel to give target compound. The product was characterized by ^1H and ^{13}C NMR measurements. Unknown compounds were further confirmed with HRMS.

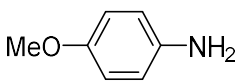
4.2. Characterization results for compounds in Scheme 1



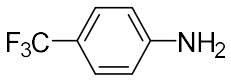
4-*n*-Butylaniline (1)[9] The target compound was isolated (73.8 mg, 99%) as a light yellow oil by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ: 6.98 (d, *J* = 8.0 Hz, 2 H), 6.63 (d, *J* = 8.0 Hz, 2 H), 3.54 (br, 2 H), 2.56 – 2.47 (m, 2 H), 1.64 – 1.50 (m, 2 H), 1.40 – 1.31 (m, 2 H), 0.93 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.9, 133.0, 129.1, 115.1, 34.7, 33.9, 22.3, 14.0 ppm.



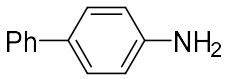
Aniline (2)[10] The target compound was isolated (44.7 mg, 96%) as a colourless oil by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.15-7.11 (m, 2 H), 6.73 (t, *J* = 7.6 Hz, 1 H), 6.64-6.61 (m, 2 H), 3.54 (br, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 146.6, 129.4, 118.6, 115.2 ppm.



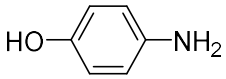
4-Anisidine (3)[10] The target compound was isolated (60.3 mg, 98%) as a light brown solid by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.82 – 6.73 (m, 2 H), 6.73 – 6.61 (m, 2 H), 3.77 (s, 3 H), 3.52 (br, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.8, 140.1, 116.4, 114.8, 55.8 ppm.



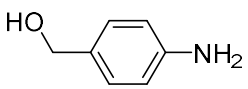
4-(Trifluoromethyl)aniline (4)[10] The target compound was isolated (69.3 mg, 86%) as a light yellow solid by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 – 7.37 (m, 2 H), 6.86 – 6.65 (m, 2 H), 3.97 (br, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.4, 126.7 (q, *J* = 4.0 Hz), 126.2 (q, *J* = 269.0 Hz), 120.3 (q, *J* = 32.0 Hz), 114.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.18 ppm.



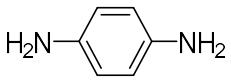
4-Biphenylamine (5)[11] The target compound was isolated (81.2 mg, 96%) as a white solid by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 – 7.53 (m, 2 H), 7.49 – 7.38 (m, 4 H), 7.33 – 7.27 (m, 1 H), 6.83 – 6.75 (m, 2 H), 3.75 (br, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.9, 141.3, 131.6, 128.7, 128.0, 126.4, 126.3, 115.4 ppm.



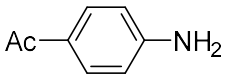
4-Hydroxyaniline (6)[12] The target compound was isolated (44.7 mg, 82%) as a white solid by column chromatography (eluting with 0-5% CH_3OH in DCM). ^{1}H NMR (400 MHz, DMSO) δ: 8.35 (br, 1 H), 6.49 (d, *J* = 8.8 Hz, 2 H), 6.42 (d, *J* = 8.8 Hz, 2 H), 4.37 (br, 2 H) ppm. ^{13}C NMR (100 MHz, DMSO) δ: 148.7, 141.1, 116.0, 115.7 ppm.



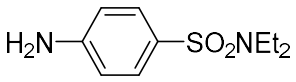
(4-Aminophenyl)methanol (7)[13] The target compound was isolated (57.8 mg, 94%) as a light brown solid by column chromatography (eluting with 0-5% CH_3OH in DCM). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.16 (d, *J* = 8.4 Hz, 2 H), 6.66 (d, *J* = 8.4 Hz, 2 H), 4.54 (d, *J* = 3.6 Hz, 2 H), 3.71 (br, 2 H), 2.00 (br, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.0, 131.1, 128.7, 115.1, 65.2 ppm.



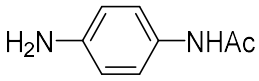
1,4-Benzenediamine (8)[14] The target compound was isolated (43.8 mg, 81%) as a brown solid by column chromatography (eluting with 0-5% CH_3OH in DCM). ^1H NMR (400 MHz, $CDCl_3$) δ: 6.59 (s, 4 H), 3.35 (br, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.2, 116.7 ppm.



1-(4-Aminophenyl)ethanone (9)[10] The target compound was isolated (59.4 mg, 88%) as a light brown solid by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.78 – 7.80 (m, 2 H), 6.62 – 6.64 (m, 2 H), 4.35 (br, 2 H), 2.49 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.8, 151.6, 130.9, 127.5, 113.7, 26.2 ppm.

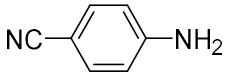


4-Amino-*N*,*N*-diethyl-benzenesulfonamide (10)[15] The target compound was isolated (99.3 mg, 87%) as a light brown solid by column chromatography (eluting with 0-30% ethyl acetate in petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 8.8 Hz, 2 H), 6.66 (d, *J* = 8.8 Hz, 2 H), 4.15 (br, 2 H), 3.18 (q, *J* = 6.8 Hz, 4 H), 1.11 (t, *J* = 6.8 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.2, 129.0, 128.5, 114.0, 42.0, 14.6 ppm.

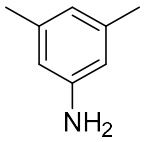


***N*-(4-Aminophenyl)acetamide (11)[14]** The target compound was isolated (66.8

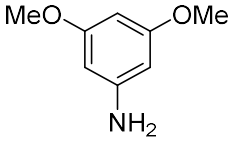
mg, 89%) as a light brown solid by column chromatography (eluting with 0-5% MeOH in DCM). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.18 (br, 1 H), 7.42 (d, *J* = 8.4 Hz, 2 H), 6.68 (d, *J* = 8.4 Hz, 2 H), 3.66 (br, 2 H), 2.27 (s, 3 H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ: 170.1, 142.4, 130.5, 122.6, 118.2, 22.6 ppm.



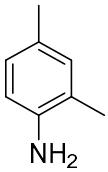
4-Cyanoaniline (12)[14] The target compound was isolated (53.1 mg, 90%) as an off-white solid by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (d, *J* = 8.8 Hz, 2 H), 6.67 (d, *J* = 8.8 Hz, 2 H), 4.19 (br, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.4, 133.8, 120.1, 114.5, 99.8 ppm.



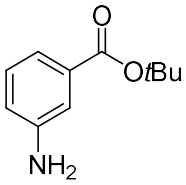
3,5-Dimethylbenzenamine (13)[10] The target compound was isolated (57.5 mg, 95%) as a colorless oil by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.92 (s, 1 H), 6.29 (s, 2 H), 3.48 (br, 2 H), 2.21 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.9, 140.1, 121.2, 113.7, 21.5 ppm.



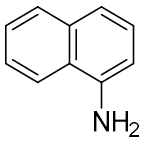
3,5-Dimethoxyaniline (14)[13] The target compound was isolated (71.2 mg, 93%) as a light brown solid by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.93 (t, *J* = 2.8 Hz, 1 H), 5.86 (d, *J* = 2.8 Hz, 2 H), 3.74 (s, 6 H), 3.65 (br, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.6, 148.2, 93.7, 90.9, 55.1 ppm.



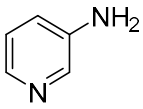
2,4-Dimethylbenzenamine (15)[16] The target compound was isolated (53.9 mg, 89%) as a colourless oil by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.85-6.81 (m, 2 H), 6.59 (d, *J* = 8.0 Hz, 1 H), 3.42 (br, 2 H), 2.23 (s, 3 H), 2.14 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.2, 131.4, 127.9, 127.5, 122.6, 115.3, 20.6, 17.5 ppm.



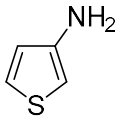
***t*-Butyl 3-aminobenzoate (16)[17]** The target compound was isolated (85.0 mg, 88%) as a white solid by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (d, *J* = 7.8 Hz, 1 H), 7.32 (s, 1 H), 7.21 (t, *J* = 7.8 Hz, 1 H), 6.85 (d, *J* = 7.8 Hz, 1 H), 3.80 (br, 2 H), 1.60 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.9, 146.4, 133.2, 129.1, 119.7, 118.9, 115.7, 80.8, 28.3 ppm.



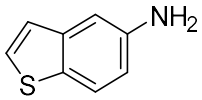
1-Naphthalenamine (17)[14] The target compound was isolated (64.4 mg, 90%) as a colorless solid by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 – 7.77 (m, 2 H), 7.53 – 7.44 (m, 2 H), 7.38 – 7.30 (m, 2 H), 6.81 (dd, *J* = 6.8, 1.6 Hz, 1 H), 4.14 (br, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.0, 134.4, 128.6, 126.3, 125.8, 124.9, 123.7, 120.8, 119.0, 109.7 ppm.



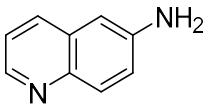
3-Pyridinylamine (18)[10] The target compound was isolated (44.2 mg, 94%) as a brown solid by column chromatography (eluting with 0-20% CH_3OH in dichloromethane). ^1H NMR (400 MHz, $CDCl_3$) δ: 8.12 (d, *J* = 2.8 Hz, 1 H), 8.04 (dd, *J* = 4.8, 1.2 Hz, 1 H), 7.09 (dd, *J* = 8.0, 4.8 Hz, 1 H), 7.02 – 6.95 (m, 1 H), 3.54 (br, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.6, 140.1, 137.6, 123.7, 121.5 ppm.



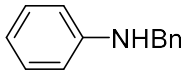
3-Thiophenamine (19)[10] The target compound was isolated (45.6 mg, 92%) as light yellow oil by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.13 (d, *J* = 5.2 Hz, 1 H), 6.65 (d, *J* = 5.2 Hz, 1 H), 6.17 (d, *J* = 3.2 Hz, 1 H), 3.60 (br, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.0, 125.1, 121.0, 100.1 ppm.



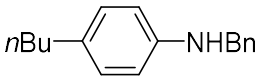
5-Aminobenzothiophene (20)[18] The target compound was isolated (67.9 mg, 91%) as a brown solid by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, *J* = 8.4 Hz, 1 H), 7.40 (d, *J* = 5.6 Hz, 1 H), 7.17 (d, *J* = 5.6 Hz, 1 H), 7.13 (d, *J* = 2.0 Hz, 1 H), 6.81 (dd, *J* = 8.4, 2.8 Hz, 1 H), 3.69 (br, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.5, 140.9, 130.5, 127.1, 123.1, 123.0, 114.9, 108.3 ppm.



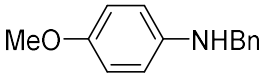
6-Aminoquinoline (21)[18] The target compound was isolated (69.2 mg, 96%) as a brown solid by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ: 8.64 (d, *J* = 3.2 Hz, 1 H), 7.89 (d, *J* = 8.8 Hz, 1 H), 7.83 (d, *J* = 8.0 Hz, 1 H), 7.22 (dd, *J* = 8.0, 4.0 Hz, 1 H), 7.12 (dd, *J* = 8.8, 2.0 Hz, 1 H), 6.82 (s, 1 H), 4.15 (br, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.9, 144.8, 143.6, 133.8, 130.5, 129.7, 121.6, 121.3, 107.5 ppm.



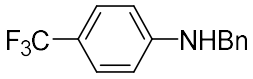
Benzylaniline (22)[19] The target compound was isolated (87.0 mg, 95%) as a colorless solid by column chromatography (eluting with 0-5% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: δ 7.47 – 7.35 (m, 4 H), 7.34 – 7.29 (m, 1 H), 7.25 – 7.16 (m, 2 H), 6.75 (t, *J* = 7.6 Hz, 1 H), 6.67 (d, *J* = 7.6 Hz, 2 H), 4.36 (s, 2 H), 4.06 (br, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.1, 139.4, 129.3, 128.6, 127.5, 127.2, 117.6, 112.8, 48.3 ppm.



***N*-Benzyl-4-*n*-aniline (23)[20]** The target compound was isolated (118.5 mg, 99%) as a colorless oil by column chromatography (eluting with 0-5% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 – 7.29 (m, 5 H), 6.99 (d, *J* = 8.0 Hz, 2 H), 6.58 (d, *J* = 8.0 Hz, 2 H), 4.29 (s, 2 H), 3.89 (br, 1 H), 2.49 (t, *J* = 7.2 Hz, 2 H), 1.55 – 1.50 (m, 2 H), 1.37 – 1.32 (m, 2 H), 0.91 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.2, 139.7, 132.1, 129.2, 128.6, 127.6, 127.2, 112.9, 48.7, 34.7, 34.0, 22.3, 14.0 ppm.

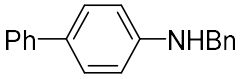


***N*-(4-Methoxyphenyl)benzylamine (24)[21]** The target compound was isolated (103.4 mg, 97%) as an off-white solid by column chromatography (eluting with 0-5% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 – 7.34 (m, 4 H), 7.33 – 7.29 (m, 1 H), 6.81 (d, *J* = 8.8 Hz, 2 H), 6.64 (d, *J* = 8.8 Hz, 2 H), 4.32 (s, 2 H, CH_2; br, 1 H, NH), 3.77 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.2, 142.5, 139.7, 128.6, 127.6, 127.2, 114.9, 114.1, 55.8, 49.3 ppm.

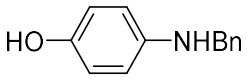


***N*-Benzyl-4-(trifluoromethyl)aniline (25)[21]** The target compound was isolated (113.1 mg, 90%) as a light yellow oil by column chromatography (eluting with 0-5% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 – 7.36 (m, 6

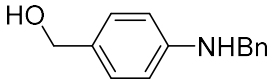
H), 7.35 – 7.26 (m, 1 H), 6.66 (d, *J* = 8.4 Hz, 2 H), 4.40 (s, 2 H, CH_2; br, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.5, 138.5, 128.8, 127.5, 127.4, 126.6 (q, *J* = 4.0 Hz), 124.9 (q, *J* = 272.0 Hz), 119.0 (q, *J* = 32.0 Hz), 112.0, 47.8 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -60.97 ppm.



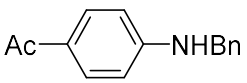
***N*-Benzyl-4-biphenylamine (26)[21]** The target compound was isolated (127.1 mg, 98%) as a white solid by column chromatography (eluting with 0-5% ethyl acetate in petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 8.4 Hz, 2 H), 7.50 – 7.29 (m, 9 H), 7.28 – 7.24 (m, 1 H), 6.74 (d, *J* = 8.4 Hz, 2 H), 4.41 (s, 2 H), 4.18 (br, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.5, 141.2, 139.2, 130.6, 128.6, 128.5, 128.0, 127.5, 127.3, 126.3, 126.1, 113.1, 48.3 ppm.



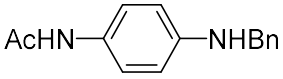
4-Benzylamino-phenol (27)[22] The target compound was isolated (89.7 mg, 90%) as a yellow oil by column chromatography (eluting with 0-5% CH_3OH in DCM). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.33 – 7.20 (m, 5 H), 6.62 (d, *J* = 8.0 Hz, 2 H), 6.48 (d, *J* = 8.0 Hz, 2 H), 4.24 (s, 2 H), 3.88 (br, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.2, 141.9, 139.4, 128.6, 127.7, 127.2, 116.3, 114.8, 49.5 ppm.



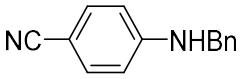
[4-(Benzylamino)phenyl]methanol (28)[21] The target compound was isolated (101.3 mg, 95%) as a light brown solid by column chromatography (eluting with 0-5% CH_3OH in DCM). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.43 – 7.29 (m, 5 H), 7.12 (d, *J* = 8.4 Hz, 2 H), 6.55 (d, *J* = 8.4 Hz, 2 H), 4.49 (s, 2 H), 4.30 (s, 2 H), 3.01 (br, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.8, 139.2, 130.1, 128.9, 128.7, 127.5, 127.3, 113.0, 65.4, 48.4 ppm.



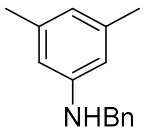
1-[4-(Benzylamino)phenyl]ethanone (29)[21] The target compound was isolated (99.1 mg, 88%) as a light yellow solid by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, *J* = 8.8 Hz, 2 H), 7.46 – 7.29 (m, 5 H), 6.62 (d, *J* = 8.8 Hz, 2 H), 4.63 (br, 1 H), 4.43 (d, *J* = 5.2 Hz, 2 H), 2.52 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.4, 151.9, 138.2, 130.8, 128.8, 127.6, 127.4, 127.0, 111.6, 47.6, 26.0 ppm.



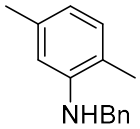
***N*-[4-[(Phenylmethyl)amino]phenyl]acetamide (30)[21]** The target compound was isolated (110.5 mg, 92%) as a grey solid by column chromatography (eluting with 0-5% CH_3OH in DCM). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 – 7.27 (m, 5 H), 7.24 – 7.20 (m, 2 H), 7.04 – 6.88 (m, 1 H), 6.63 – 6.55 (m, 2 H), 4.31 (s, 2 H), 4.01 (br, 1 H), 2.15 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.2, 145.5, 139.4, 128.7, 128.4, 127.6, 127.4, 122.5, 113.2, 48.6, 24.5 ppm.



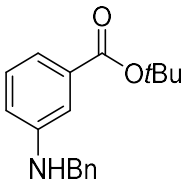
4-(*N*-Benzylamino)benzonitrile (31)[23] The target compound was isolated (96.8 mg, 93%) as a white solid by column chromatography (eluting with 0-5% CH_3OH in DCM). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 – 7.31 (m, 7 H), 6.62 (d, *J* = 6.4 Hz, 2 H), 4.83 (br, 1 H), 4.41 (d, *J* = 5.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.2, 137.9, 133.7, 128.9, 127.7, 127.3, 120.5, 112.4, 98.8, 47.4 ppm.



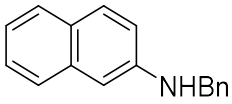
***N*-Benzyl-3,5-dimethylaniline (32)[19]** The target compound was isolated (104.5 mg, 99%) as a light yellow oil by column chromatography (eluting with 0-5% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 – 7.35 (m, 4 H), 7.35 – 7.28 (m, 1 H), 6.43 (s, 1 H), 6.33 (s, 2 H), 4.34 (s, 2 H), 3.93 (br, 1 H), 2.27 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.3, 139.7, 139.0, 128.6, 127.6, 127.2, 119.6, 110.8, 48.4, 21.5 ppm.



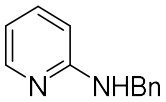
***N*-Benzyl-2,5-dimethylaniline (33)[24]** The target compound was isolated (95.2 mg, 90%) as a light yellow oil by column chromatography (eluting with 0-5% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 – 7.26 (m, 5 H), 6.99 (d, *J* = 7.6 Hz, 1 H), 6.53 (d, *J* = 7.6 Hz, 1 H), 6.50 (s, 1 H), 4.35 (s, 2 H), 3.77 (br, 1 H), 2.30 (s, 3 H), 2.15 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.9, 139.5, 136.8, 129.9, 128.7, 127.6, 127.2, 118.9, 117.8, 110.8, 48.4, 21.6, 17.1 ppm.



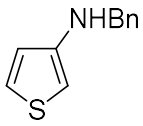
***t*-Butyl 3-(benzylamino)benzoate (34)[25]** The target compound was isolated (127.5 mg, 90%) as a white solid by column chromatography (eluting with 0-5% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 – 7.26 (m, 7 H), 7.18 (t, *J* = 7.6 Hz, 1 H), 6.77 (dd, *J* = 7.6 Hz, 2.4 Hz, 1 H), 4.36 (s, 2 H), 4.15 (s, br, 1 H), 1.58 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.1, 147.9, 139.0, 132.8, 128.9, 128.6, 127.4, 127.2, 118.4, 116.5, 113.4, 80.5, 48.0, 27.9 ppm.



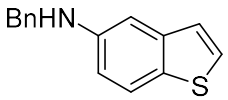
***N*-Benzyl-2-naphthalenamine (35)[21]** The target compound was isolated (108.5 mg, 93%) as a white solid by column chromatography (eluting with 0-5% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 – 7.60 (m, 3 H), 7.50 – 7.29 (m, 6 H), 7.24 (t, *J* = 7.6 Hz, 1 H), 6.95 (dd, *J* = 8.8, 2.4 Hz, 1 H), 6.88 (d, *J* = 2.2 Hz, 1 H), 4.47 (s, 2 H), 4.23 (br, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.8, 139.2, 135.2, 129.0, 128.9, 128.7, 127.6, 127.4, 127.3, 126.3, 126.0, 122.0, 117.9, 104.6, 48.4 ppm.



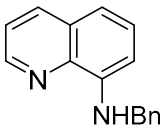
***N*-Benzyl-2-aminopyridine (36)[26]** The target compound was isolated (87.5 mg, 95%) as a white solid by column chromatography (eluting with 0-5% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14 (d, *J* = 5.2 Hz, 1 H), 7.46 – 7.29 (m, 6 H), 6.62 (dd, *J* = 7.2, 5.2 Hz, 1 H), 6.40 (d, *J* = 8.4 Hz, 1 H), 4.88 (br, 1 H), 4.54 (d, *J* = 5.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.6, 148.2, 139.3, 137.5, 128.6, 127.4, 127.3, 113.2, 106.8, 46.3 ppm.



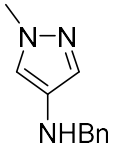
***N*-Benzylthiophen-3-amine (37)[21]** The target compound was isolated (84.2 mg, 89%) as a brown solid by column chromatography (eluting with 0-5% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42–7.25 (m, 5 H), 7.16–7.11 (m, 1 H), 6.62 (d, *J* = 5.2 Hz, 1 H), 5.94 (s, 1 H), 4.23 (s, 2 H), 3.94 (br, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.5, 139.3, 128.6, 127.7, 127.3, 125.2, 119.9, 96.1, 50.7 ppm.



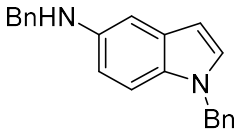
***N*-(Phenylmethyl)benzo[*b*]thiophen-5-amine (38)[21]** The target compound was isolated (112.5 mg, 94%) as a light brown solid by column chromatography (eluting with 0-5% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, *J* = 8.4 Hz, 1 H), 7.48 – 7.36 (m, 5 H), 7.36 – 7.30 (m, 1 H), 7.19 (d, *J* = 5.4 Hz, 1 H), 7.04 (d, *J* = 2.4 Hz, 1 H), 6.80 (dd, *J* = 8.4, 2.4 Hz, 1 H), 4.43 (s, 2 H), 4.11 (br, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.7, 141.0, 139.4, 129.5, 128.7, 127.5, 127.3, 126.9, 123.4, 122.9, 113.9, 105.0, 48.8 ppm.



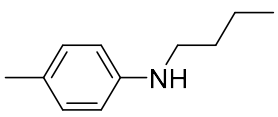
***N*-Benzyl-8-quinolinamine (39)[27]** The target compound was isolated (113.5 mg, 97%) as a light yellow solid by column chromatography (eluting with 0-5% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.76 – 8.73 (m, 1 H), 8.07 (d, *J* = 8.0 Hz, 1 H), 7.48 (d, *J* = 7.6 Hz, 2 H), 7.42 – 7.33 (m, 4 H), 7.33 – 7.29 (m, 1 H), 7.09 (d, *J* = 8.0 Hz, 1 H), 6.68 (d, *J* = 7.6 Hz, 1 H), 6.66 (br, 1 H), 4.59 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.0, 144.7, 139.4, 138.3, 136.1, 128.8, 128.7, 127.9, 127.5, 127.2, 121.5, 114.3, 105.2, 47.8 ppm.



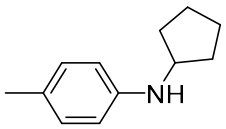
1-Methyl-*N*-(phenylmethyl)-1*H*-pyrazol-4-amine (40)[28] The target compound was isolated (82.4 mg, 88%) as a brown oil by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 – 7.28 (m, 5 H), 7.14 (s, 1 H), 6.86 (s, 1 H), 4.16 (s, 2 H), 3.78 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.6, 134.2, 128.7, 128.5, 127.7, 127.2, 116.7, 52.2, 39.1 ppm.



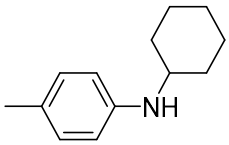
***N*,1-bis(phenylmethyl)-1*H*-Indol-5-amine (41)[21]** The target compound was isolated (132.8 mg, 85%) as a brown solid by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, *J* = 7.6 Hz, 2 H), 7.37 (dd, *J* = 7.6, 6.4 Hz, 2 H), 7.34 – 7.28 (m, 4 H), 7.17 – 7.04 (m, 4 H), 6.91 (s, 1 H), 6.65 (dd, *J* = 8.8, 2.0 Hz, 1 H), 6.40 (d, *J* = 3.2 Hz, 1 H), 5.28 (s, 2 H), 4.39 (s, 2 H), 3.86 (br, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.3, 140.1, 137.9, 131.3, 129.6, 128.7, 128.6, 128.4, 127.7, 127.5, 127.1, 126.7, 111.8, 110.4, 102.5, 100.6, 50.2, 49.7 ppm.



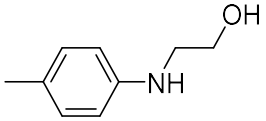
4-Methyl-*N*-*n*-butylaniline (42)[21] The target compound was isolated (80.8 mg, 99%) as light yellow oil by column chromatography (eluting with 0-5% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.01 (d, *J* = 8.0 Hz, 2 H), 6.57 (d, *J* = 8.4 Hz, 2 H), 3.45 (br, 1 H), 3.15 – 3.08 (m, 2 H), 2.27 (s, 3 H), 1.68 – 1.57 (m, 2 H), 1.54 – 1.40 (m, 2 H), 0.98 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.3, 129.7, 126.3, 112.9, 44.1, 31.8, 20.5, 20.3, 13.9 ppm.



(4-Aminophenyl)methanol (43)[21] The target compound was isolated (85.0 mg, 97%) as a light yellow oil by column chromatography (eluting with 0-5% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.01 (d, *J* = 8.4 Hz, 2 H), 6.57 (d, *J* = 8.4 Hz, 2 H), 3.85 – 3.73 (m, 1 H), 3.42 (br, 1 H), 2.27 (s, 3 H), 2.11 – 1.98 (m, 2 H), 1.81 – 1.70 (m, 2 H), 1.70 – 1.57 (m, 2 H), 1.55 – 1.43 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.8, 129.7, 126.1, 113.4, 55.0, 33.6, 24.1, 20.4 ppm.

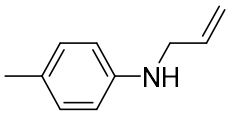


***N*-cyclohexyl-4-methylaniline (44)[21]** The target compound was isolated (90.8 mg, 96%) as a light yellow solid by column chromatography (eluting with 0-5% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.01 (d, *J* = 8.2 Hz, 2 H), 6.56 (d, *J* = 8.4 Hz, 2 H), 3.26 (br, 1 H), 2.27 (s, 3 H), 2.15 – 2.02 (m, 2 H), 1.84 – 1.74 (m, 2 H), 1.72 – 1.62 (m, 1 H), 1.48 – 1.04 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.1, 129.8, 126.1, 113.5, 52.1, 33.6, 26.0, 25.1, 20.4 ppm.

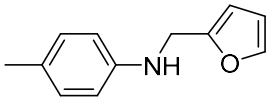


2-(4-Methylphenylamino)ethanol (45)[21] The target compound was isolated (71.1 mg, 94%) as a yellow solid by column chromatography (eluting with 0-20%

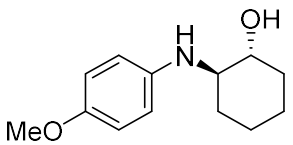
ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.03 (d, *J* = 8.0 Hz, 2 H), 6.61 (d, *J* = 8.4 Hz, 2 H), 3.82 (t, *J* = 5.2 Hz, 2 H), 3.29 (t, *J* = 5.2 Hz, 2 H), 2.83 (br, 2 H), 2.28 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.8, 129.8, 127.3, 113.5, 61.3, 46.5, 20.4 ppm.



***N*-Allyl-4-methylbezenamine (46)[29]** The target compound was isolated (69.9 mg, 95%) as a brown oil by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.96 (dd, *J* = 6.4, 2.0 Hz, 2 H), 6.54 (dd, *J* = 6.4, 2.0 Hz, 2 H), 5.96 – 5.90 (m, 1 H), 5.24 (dd, *J* = 17.2, 1.6 Hz, 1 H), 5.12 (dd, *J* = 17.2, 1.6 Hz, 1 H), 3.72 (d, *J* = 2.4 Hz, 2 H), 3.63 (br, 1 H), 2.23 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.7, 135.8, 129.4, 126.9, 116.1, 113.3, 47.0, 20.3 ppm.

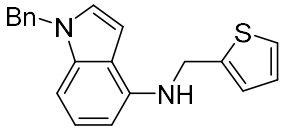


N-(4-Methylphenyl)-2-furanmethanamine (47)[21] The target compound was isolated (89.9 mg, 96%) as yellow oil by column chromatography (eluting with 0-5% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (dd, *J* = 2.0, 0.8 Hz, 1 H), 7.04 (d, *J* = 8.0 Hz, 2 H), 6.64 (d, *J* = 8.4 Hz, 2 H), 6.36 (dd, *J* = 3.2, 2.0 Hz, 1 H), 6.26 (dd, *J* = 3.2, 0.8 Hz, 1 H), 4.33 (s, 2 H), 3.93 (br, 1 H), 2.29 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.0, 145.4, 141.9, 129.7, 127.3, 113.4, 110.3, 106.9, 41.8, 20.4 ppm.

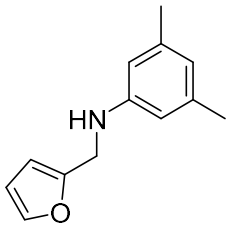


rel-(1R,2R)-2-[(4-Methoxyphenyl)amino]cyclohexanol (48)[30] The target compound was isolated (89.6 mg, 81%) as a brown solid by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^{1}H NMR

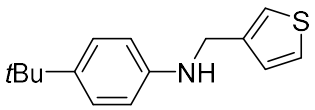
(400 MHz, $CDCl_3$) δ: 6.80 (d, *J* = 8.8 Hz, 2 H), 6.71 (d, *J* = 8.8 Hz, 2 H), 3.77 (s, 3 H), 3.42 – 3.26 (m, 1 H), 3.06 – 2.97 (m, 1 H), 2.82 (br, 2 H), 2.22 – 2.07 (m, 2 H), 1.86 – 1.63 (m, 2 H), 1.48 – 1.21 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.9, 141.6, 116.4, 114.9, 74.4, 61.7, 55.8, 33.1, 31.6, 25.1, 24.3 ppm.



1-Benzyl-*N*-(thiophen-2-ylmethyl)-1*H*-indol-4-amine (49) The target compound was isolated (146.9 mg, 92%) as a yellow solid by column chromatography (eluting with 0-10% ethyl acetate in petroleum ether) , m.p. = 118-119 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.34 – 7.25 (m, 4 H), 7.18 – 6.99 (m, 6 H), 6.80 (d, *J* = 8.4 Hz, 1 H), 6.48 (dd, *J* = 3.2, 0.8 Hz, 1 H), 6.42 (dd, *J* = 7.6, 0.8 Hz, 1 H), 5.32 (s, 2 H), 4.71 (s, 2 H), 4.37 (br, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.1, 140.9, 137.7, 137.0, 128.7, 127.5, 126.9, 126.8, 126.2, 125.2, 124.6, 123.2, 117.4, 100.8, 99.8, 97.7, 50.2, 43.6 ppm. HRMS (ESI): m/z calculated for $C_{20}H_{19}N_2S^+$ [M+H$^+$]: 319.1263, found: 319.1265.

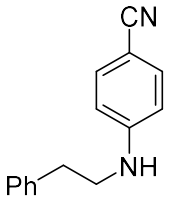


***N*-(3, 5-Dimethylphenyl)-2-furanmethanamine (50)[31]** The target compound was isolated (97.6 mg, 97%) as a yellow oil by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ: = 7.36 – 7.35 (m, 1 H), 6.41 (s, 1 H), 6.32 – 6.30 (m, 3 H), 6.23 – 6.21 (m, 1 H), 4.29 (s, 2 H), 3.93 (br, 1 H), 2.25 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.9, 147.7, 141.8, 138.9, 120.0, 111.2, 110.3, 106.8, 41.7, 21.5 ppm.



***N*-[4-(1,1-Dimethylethyl)phenyl]-3-thiophenemethanamine (51)** The target

compound was isolated (121.5 mg, 99%) as a light brown solid by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether) , m.p. = 33-34 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (dd, *J* = 5.2, 3.2 Hz, 1 H), 7.29 – 7.21 (m, 3 H), 7.12 (dd, *J* = 5.2, 1.2 Hz, 1 H), 6.66 (d, *J* = 8.4 Hz, 2 H), 4.36 (d, *J* = 1.2 Hz, 2 H), 3.91 (br, 1 H), 1.33 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.7, 140.7, 140.5, 129.9, 127.2, 126.1, 121.7, 112.7, 44.1, 33.9, 31.6 ppm. HRMS (ESI): m/z calculated for $C_{15}H_{20}NS^+$ [M+H$^+$]: 246.1311, found: 246.1309.

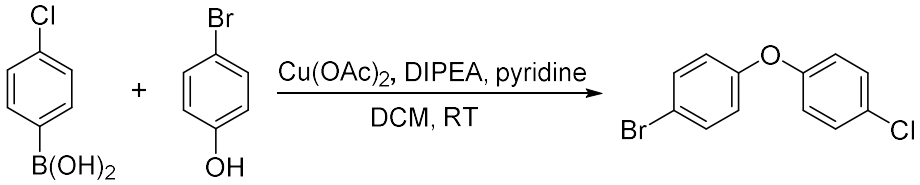


4-[(2-Phenylethyl)amino]benzonitrile (50)[32] The target compound was isolated (106.7 mg, 96%) as a colorless oil by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (d, *J* = 8.8 Hz, 2 H), 7.19-7.33 (m, 5 H), 6.54 (d, *J* = 8.8 Hz, 2 H), 4.33 (br, 1 H), 3.44 (t, *J* = 6.8 Hz, 2 H), 2.93 (t, *J* = 6.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.0, 138.4, 133.6, 128.7, 128.6, 126.6, 120.4, 112.2, 98.5, 44.1, 35.0 ppm.

5. General procedure and characterization results for Scheme 2

5.1. Synthesis and characterization of dihalide substrates

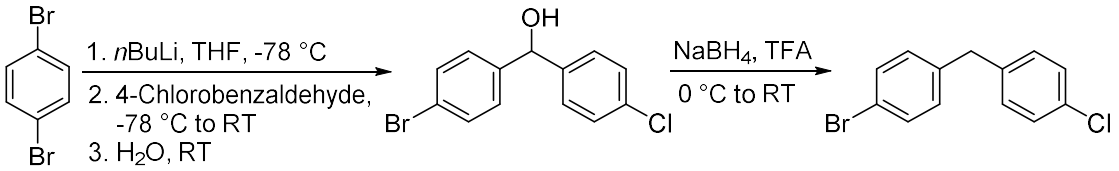
4-Bromo-4'-chlorodiphenyl ether



A 100 mL round bottom flask equipped with a stir bar was charged with 4-chlorophenylboronic acid (2.34 g, 15 mmol), 4-bromophenol (1.73 g, 10 mmol), copper (II) acetate (1.82 g, 10 mmol), diisopropylethylamine (DIPEA, 8.3 mL, 50 mmol), pyridine (4.0 mL, 50 mmol) and 20 mL DCM. The mixture was stirred at RT

under air atmosphere overnight. After reaction, the mixture was concentrated under vacuum, and treated with ethyl acetate. The obtained mixture was washed with 1 M HCl and brine, dried over Na_2SO_4 and concentrated under vacuum. The obtained residue was purified by flash column chromatography over silica gel (eluting with petroleum ether) to give target compound 4-bromo-4'-chlorodiphenyl ether (1.87 g, 66%) as a colorless oil[33]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50-7.42 (d, *J* = 8.0 Hz, 2 H), 7.35-7.29 (d, *J* = 8.0 Hz, 2 H), 6.99-6.93 (d, *J* = 8.0 Hz, 2 H), 6.93-6.86 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.1, 155.4, 132.8, 129.9, 120.5, 120.2, 120.1, 116.1 ppm.

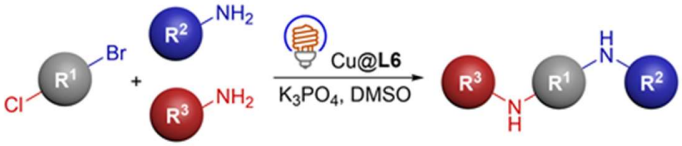
1-Bromo-4-[(4-chlorophenyl)methyl]benzene



A 100 mL Schlenk flask equipped with a stir bar was charged with 1,4-dibromobenzene (2.83 g, 12 mmol) and 10 mL THF. The mixture was stirred at -78 °C under N_2 atmosphere and *n*BuLi (1.6 M, 7.5 mL, 12 mmol) was added dropwise. The resulting slurry was kept stirring at -78 °C for 30 min and then 4-chlorobenzaldehyde (1.40 g, 10 mmol) was added as solid in one portion. The mixture was warmed to RT and stirred overnight. After reaction, 5 mL H_2O was added to quench the remaining *n*BuLi and the mixture was concentrated under vacuum, and treated with ethyl acetate. The obtained mixture was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The obtained residue was purified by flash column chromatography over silica gel (eluting with 0-20% ethyl acetate in petroleum ether) to give target compound (4-bromophenyl)(4-chlorophenyl)methanol (2.44 g, 82%) as a white solid**[34]**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (d, *J* = 8.4 Hz, 2 H), 7.38 (d, *J* = 8.4 Hz, 2 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 2 H), 5.74 (d, *J* = 3.2 Hz, 1 H), 2.44 (br, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.5, 141.9, 133.7, 131.8, 128.9, 128.3, 127.9, 121.8, 75.1 ppm.

A 50 mL Schlenk flask equipped with a stir bar was charged with (4-bromophenyl)(4-chlorophenyl)methanol (1.49 g, 5 mmol), 10 mL trifluoroacetic acid (TFA) and 10 mL DCM. The solution was stirred at 0 °C for 30 min. Sodium borohydride (0.57 g, 15 mmol) was added portion-wise and the mixture was stirred at RT for 2 h. After reaction, concentrated NaOH solution was added and the mixture was concentrated under vacuum, and treated with ethyl acetate. The obtained mixture was washed with brine, dried over Na_2SO_4 and concentrated under vacuum to give target compound 1-bromo-4-(4-chlorobenzyl)benzene (1.37 g, 97%) as a white solid[35]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 8.4 Hz, 2 H), 7.25 (d, *J* = 8.4 Hz, 2 H), 7.08 (d, *J* = 8.4 Hz, 2 H), 7.03 (d, *J* = 8.4 Hz, 2 H), 3.89 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.7, 139.0, 132.3, 131.8, 130.7, 130.3, 128.8, 120.3, 40.7 ppm.

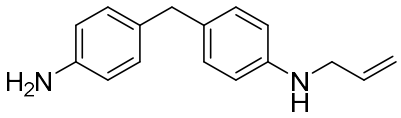
5.2. General procedure for Scheme 2



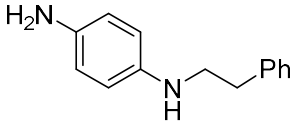
A reaction tube of photocatalytic parallel reaction apparatus equipped with a stir bar was charged with Cu@**L6** (32.4 mg, 0.05 mmol), dihalide compounds (if solid, 0.50 mmol), R^2-NH_2 (if solid, 0.51 mmol), K_3PO_4 (254.8 mg, 1.20 mmol), and the tube was evacuated and backfilled with nitrogen (three cycles). In addition, the reaction tube was placed above a 10 W purple LED lamp (405 nm). Next, R^2-NH_2 (if liquid, 0.51 mmol), dihalide compounds (if liquid, 0.50 mmol) and 0.5 mL DMSO were added, and the resulting mixture was stirred at 40 °C under N_2 atmosphere. After 24 h, the second amine R^3-NH_2 (1.00 mmol) was added under N_2 atmosphere, and the mixture was stirred at 80 °C for 48 h. After reaction, the tube was cooled to room temperature. The resulting mixture was extracted with ethyl acetate for three times. The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The collected residue was purified by column chromatography using silica gel to give target compound. The product was characterized by ^{1}H and ^{13}C NMR measurements. Unknown compounds were

further confirmed with HRMS.

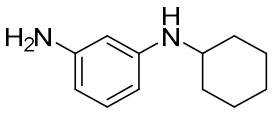
5.3. Characterization results for compounds in Scheme 2



***N*-allyl-4-(4-aminobenzyl)aniline (53)** The target compound was isolated (109.5 mg, 92%) as a light yellow oil by column chromatography (eluting with 0-5% CH_3OH in DCM). ^1H NMR (400 MHz, $CDCl_3$) δ: δ 7.01 (t, *J* = 7.6 Hz, 4 H), 6.64 (d, *J* = 8.4 Hz, 2 H), 6.59 (d, *J* = 8.4 Hz, 2 H), 6.05 – 5.92 (m, 1 H), 5.31 (dd, *J* = 17.2, 1.6 Hz, 1 H), 5.18 (dd, *J* = 10.4, 1.6 Hz, 1 H), 3.80 (s, 2 H), 3.78 (d, *J* = 5.4 Hz, 2 H), 3.53 (br, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.2, 144.3, 135.7, 132.2, 131.0, 129.7, 129.6, 116.2, 115.3, 113.1, 46.9, 40.2 ppm. HRMS (ESI): m/z calculated for $C_{16}H_{19}N_2^+$ [M+H$^+$]: 239.1543, found: 239.1545.

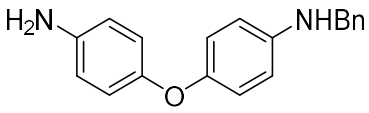


***N*^{1}-Phenethyl-1,4-benzenediamine (54)** The target compound was isolated (95.5 mg, 90%) as a brown solid by column chromatography (eluting with 0-5% CH_3OH in DCM), m.p. = 81-82 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.38 – 7.30 (m, 2 H), 7.27 – 7.23 (m, 3 H), 6.67 – 6.61 (m, 2 H), 6.58 – 6.52 (m, 2 H), 3.37 (br, 3 H; t, *J* = 7.2 Hz, 2 H), 2.92 (t, *J* = 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.1, 139.5, 137.9, 128.8, 128.6, 126.3, 116.9, 114.9, 46.3, 35.7 ppm. HRMS (ESI): m/z calculated for $C_{14}H_{17}N_2^+$ [M+H$^+$]: 213.1386, found: 213.1384.

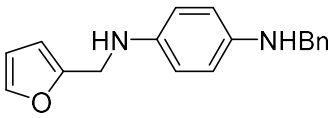


***N*^{1}-Cyclohexyl-1,3-benzenediamine (55)[36]** The target compound was isolated (84.7 mg, 89%) as a brown solid by column chromatography (eluting with 0-5% CH_3OH in DCM). ^1H NMR (400 MHz, $CDCl_3$) δ: 6.96 (t, *J* = 8.0 Hz, 1 H), 6.07 – 6.04 (m, 2 H), 5.97 (t, *J* = 2.0 Hz, 1 H), 3.54 (br, 3 H), 3.24 – 3.19 (m, 1 H), 2.18 –

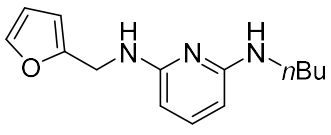
2.03 (m, 2 H), 1.81 – 1.73 (m, 2 H), 1.59 – 1.09 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.9, 147.6, 130.0, 104.6, 104.5, 99.9, 51.8, 33.6, 26.1, 25.0 ppm.



4-(4-Aminophenoxy)-*N*-benzylaniline (56) The target compound was isolated (137.9 mg, 95%) as a white solid by column chromatography (eluting with 0-5% CH_3OH in DCM), m.p. = 102-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 – 7.34 (m, 4 H), 7.34 – 7.29 (m, 1 H), 6.90 – 6.79 (m, 4 H), 6.69 – 6.58 (m, 4 H), 4.32 (s, 2 H), 3.59 (br, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.8, 144.0, 141.6, 139.5, 128.6, 127.6, 127.3, 119.7, 119.4, 116.3, 116.2, 113.8, 49.0 ppm. HRMS (ESI): m/z calculated for $C_{19}H_{19}N_2O^+$ [M+H$^+$]: 291.1492, found: 291.1494.



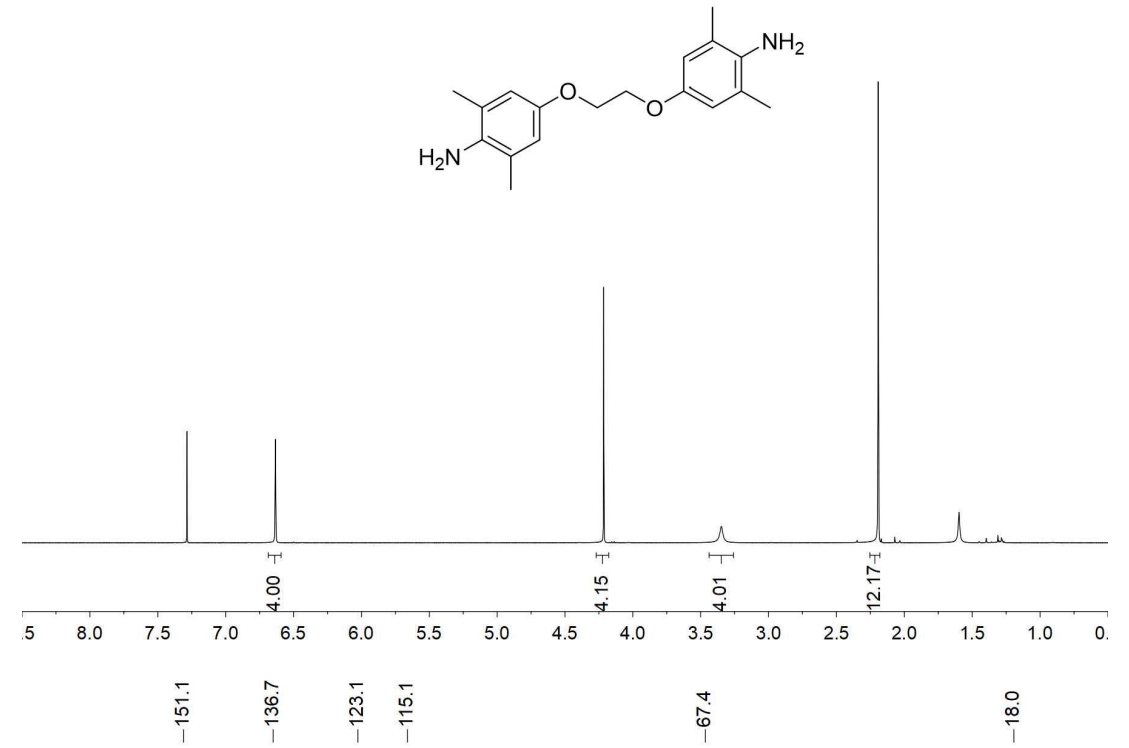
***N*^{1}-Benzyl-*N*^{4}-(furan-2-ylmethyl)-1,4-benzenediamine (57)** The target compound was isolated (122.5 mg, 88%) as a light brown solid by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether), m.p. = 61-63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 – 7.33 (m, 5 H), 7.32 – 7.29 (m, 1 H), 6.69 – 6.57 (m, 4 H), 6.33 (dd, *J* = 3.2, 2.0 Hz, 1 H), 6.23 (dd, *J* = 3.2, 0.8 Hz, 1 H), 4.28 (d, *J* = 7.6 Hz, 4 H), 3.65 (br, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.3, 141.8, 141.2, 140.0, 139.9, 128.6, 127.6, 127.1, 115.3, 114.5, 110.3, 106.8, 49.5, 42.8 ppm. HRMS (ESI): m/z calculated for $C_{18}H_{19}N_2O^+$ [M+H$^+$]: 279.1492, found: 279.1488.

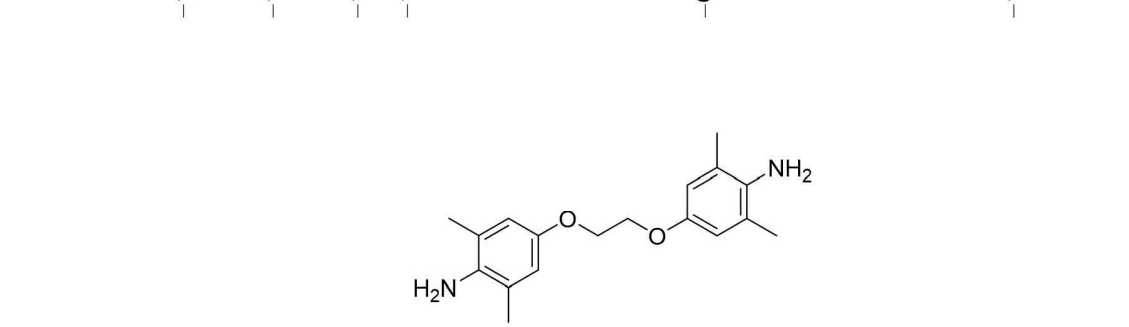


***N*^{2}-*n*-Butyl-*N*^{6}-(furan-2-ylmethyl)pyridine-2,6-diamine (58)** The target compound was isolated (105.5 mg, 86%) as a brown solid by column chromatography (eluting with 0-20% ethyl acetate in petroleum ether) , m.p. = 38-39 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (s, 1 H), 7.25 (t, *J* = 8.0 Hz, 1 H), 6.33

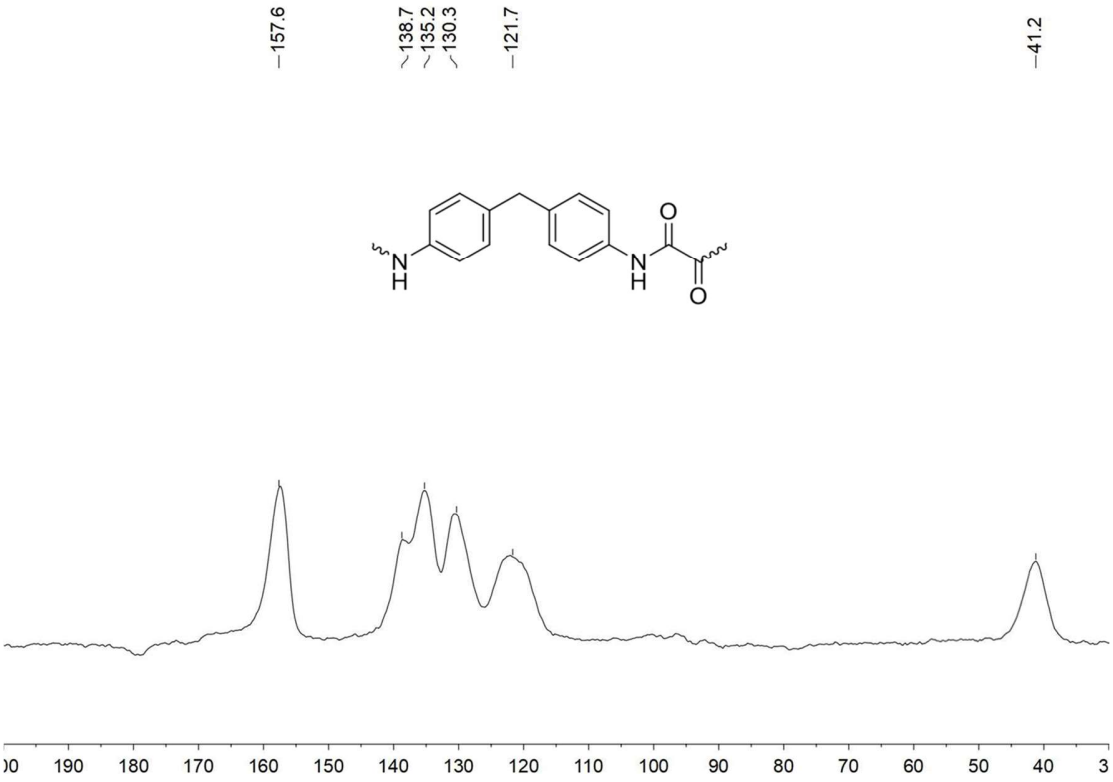
(dd, *J* = 3.2, 2.0 Hz, 1 H), 6.24 (d, *J* = 3.2 Hz, 1 H), 5.77 (dd, *J* = 10.8, 8.0 Hz, 2 H), 4.58 (br, 1 H), 4.46 (d, *J* = 5.6 Hz, 2 H), 4.30 (br, 1 H), 3.21 (q, *J* = 6.7 Hz, 2 H), 1.65 – 1.55 (m, 2 H), 1.50 – 1.39 (m, 2 H), 0.97 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 157.6, 153.2, 141.7, 139.0, 110.3, 106.6, 95.0, 94.8, 42.0, 39.5, 31.8, 20.3, 13.9 ppm. HRMS (ESI): m/z calculated for $C_{14}H_{20}N_3O^+$ [M+H$^+$]: 246.1601, found: 246.1600.

6. NMR Spectra

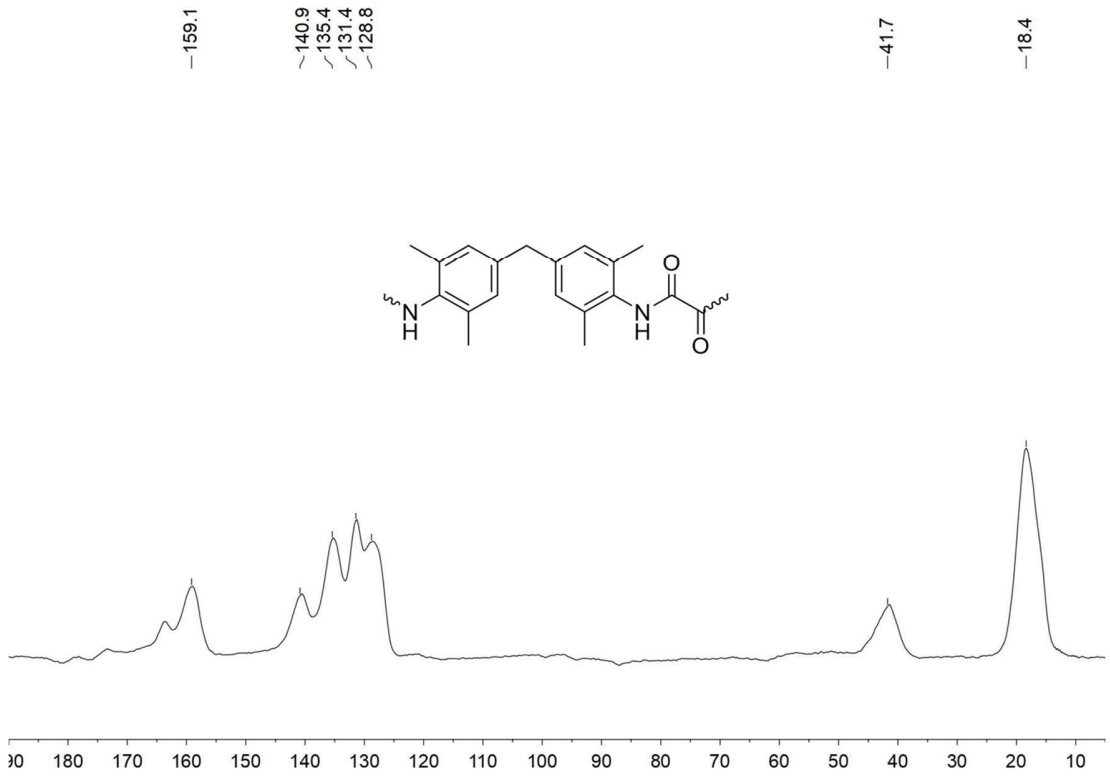




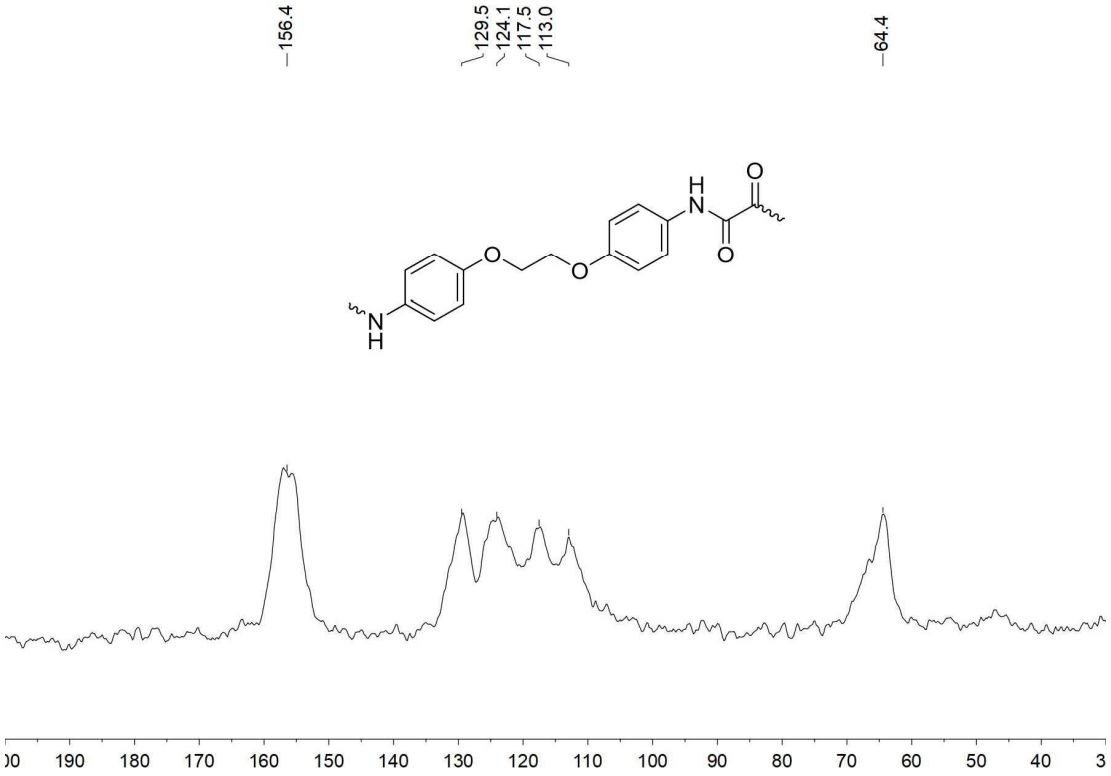
^{13}C CP/MAS NMR of polymeric ligand **L1**



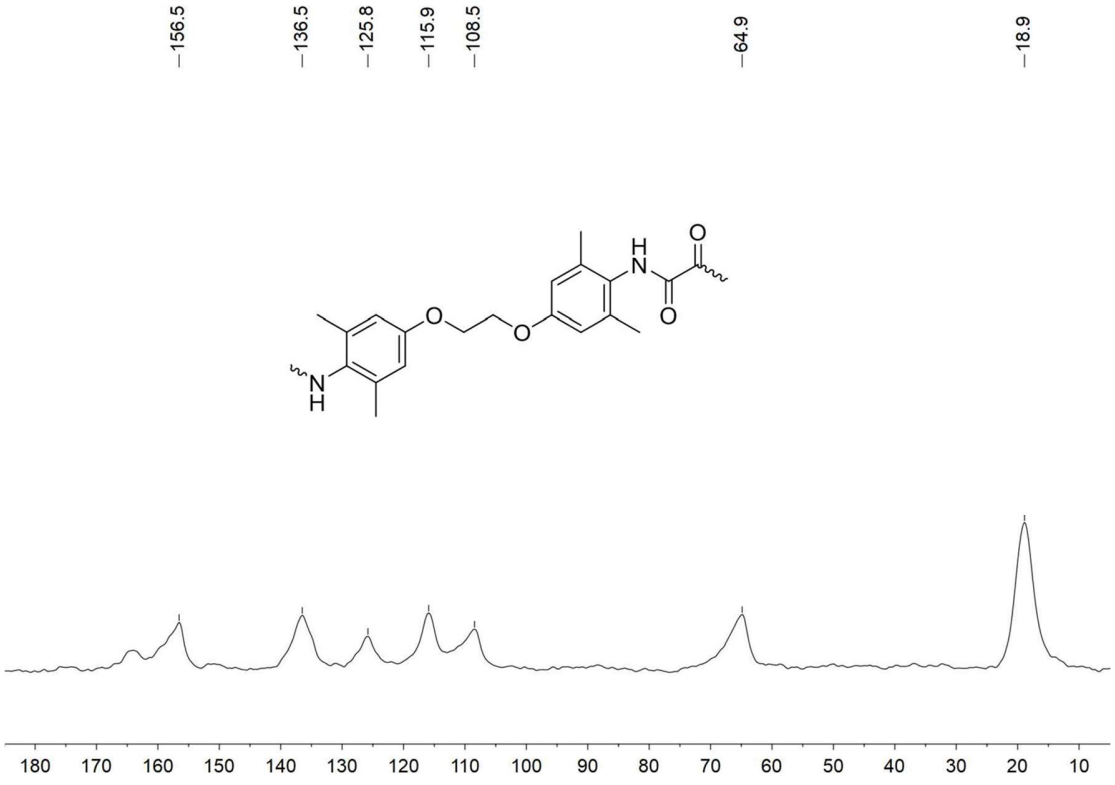
^{13}C CP/MAS NMR of polymeric ligand **L2**



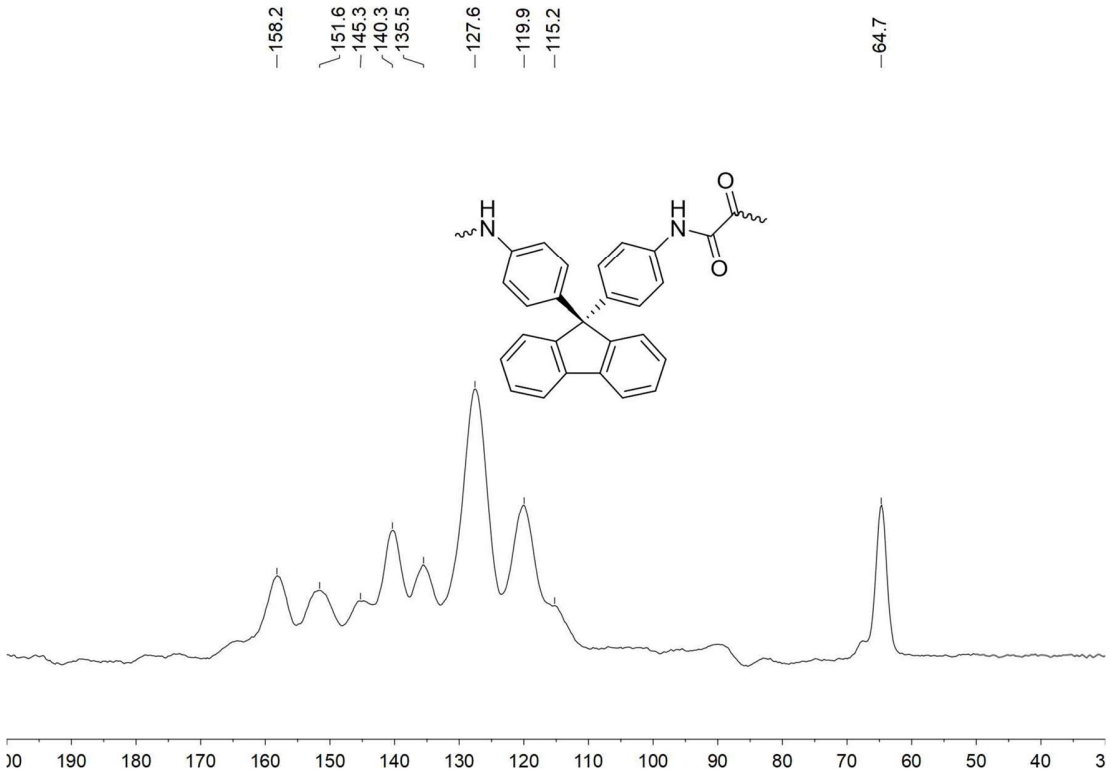
^{13}C CP/MAS NMR of polymeric ligand **L3**



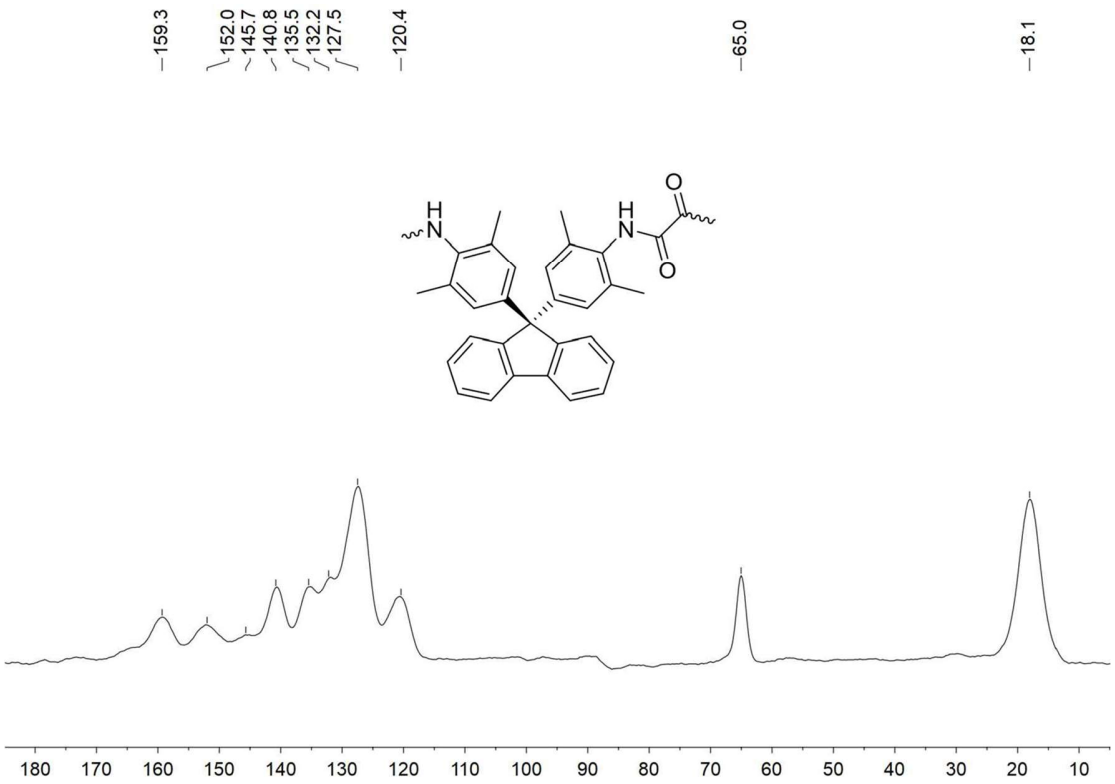
^{13}C CP/MAS NMR of polymeric ligand **L4**

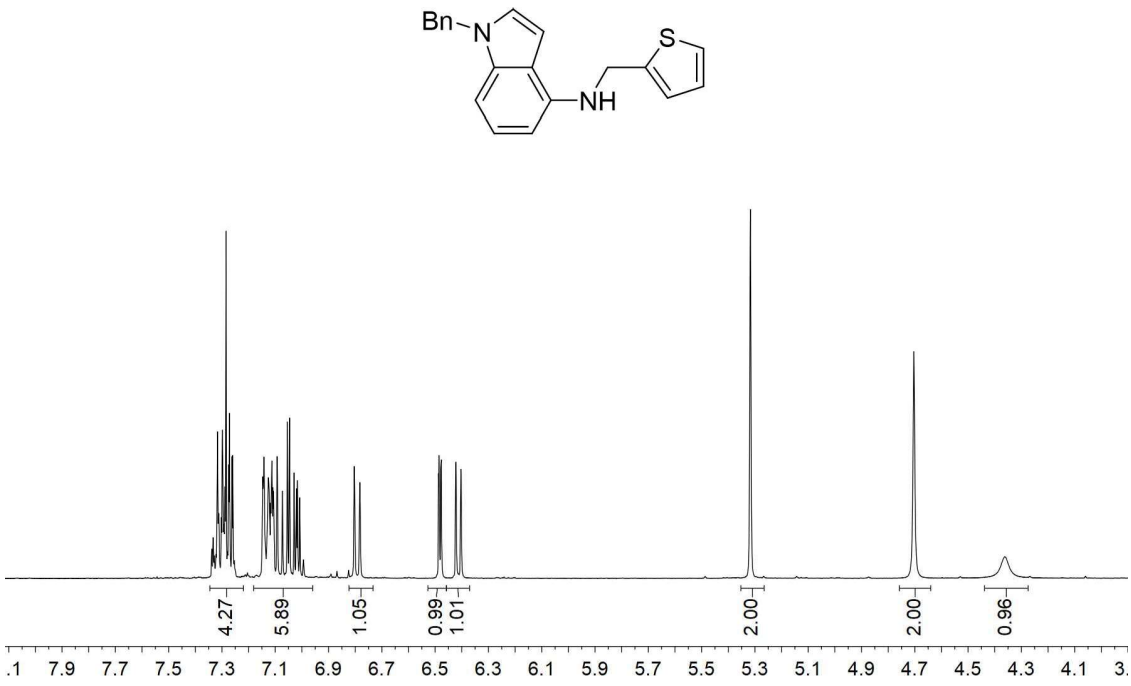


^{13}C CP/MAS NMR of polymeric ligand **L5**



^{13}C CP/MAS NMR of polymeric ligand **L6**

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S
NH
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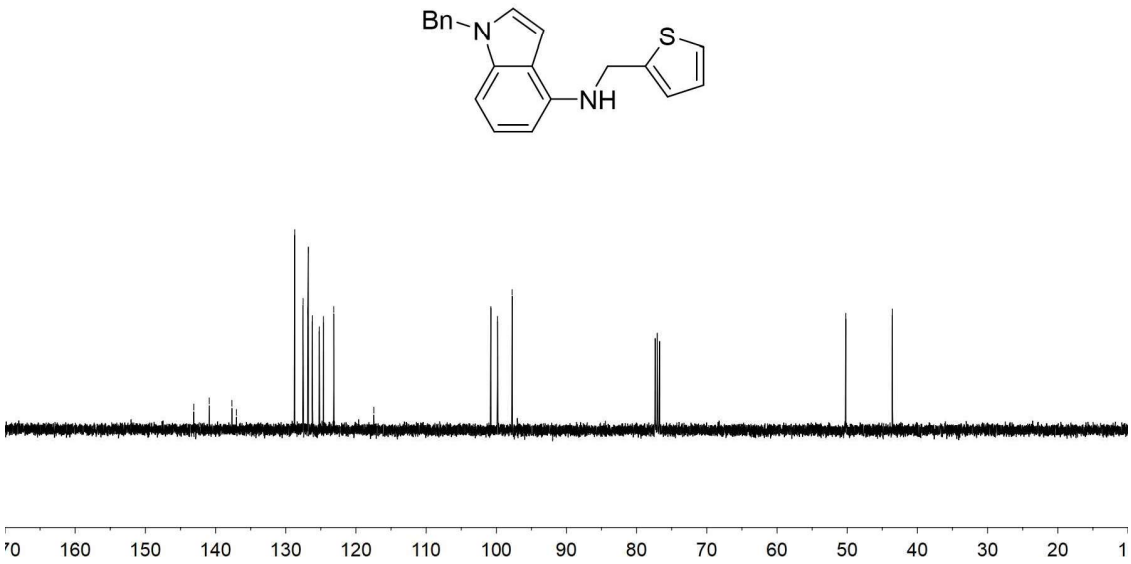
0.99
1.01
2.00
2.00
0.96
7.9
7.7
7.5
7.3
7.1
6.9
6.7
6.5
6.3
6.1
5.9
5.7
5.5
5.3
5.1
4.9
4.7
4.5
4.3
4.1


143.1
140.9
137.7
137.0
128.7
127.5
126.9
126.8
126.2
125.2
124.6
123.2
117.4
100.8
99.8
97.7
50.2
43.6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NH
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90
80
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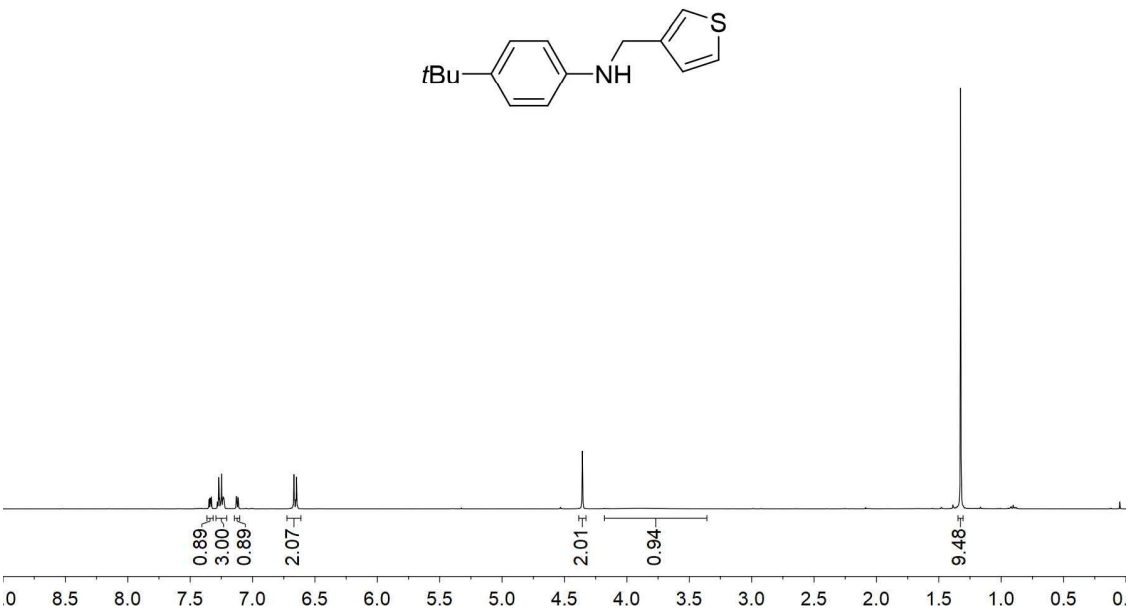
60
50
40
30
20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7.0
6.5
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5.0
4.5
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3.0
2.5
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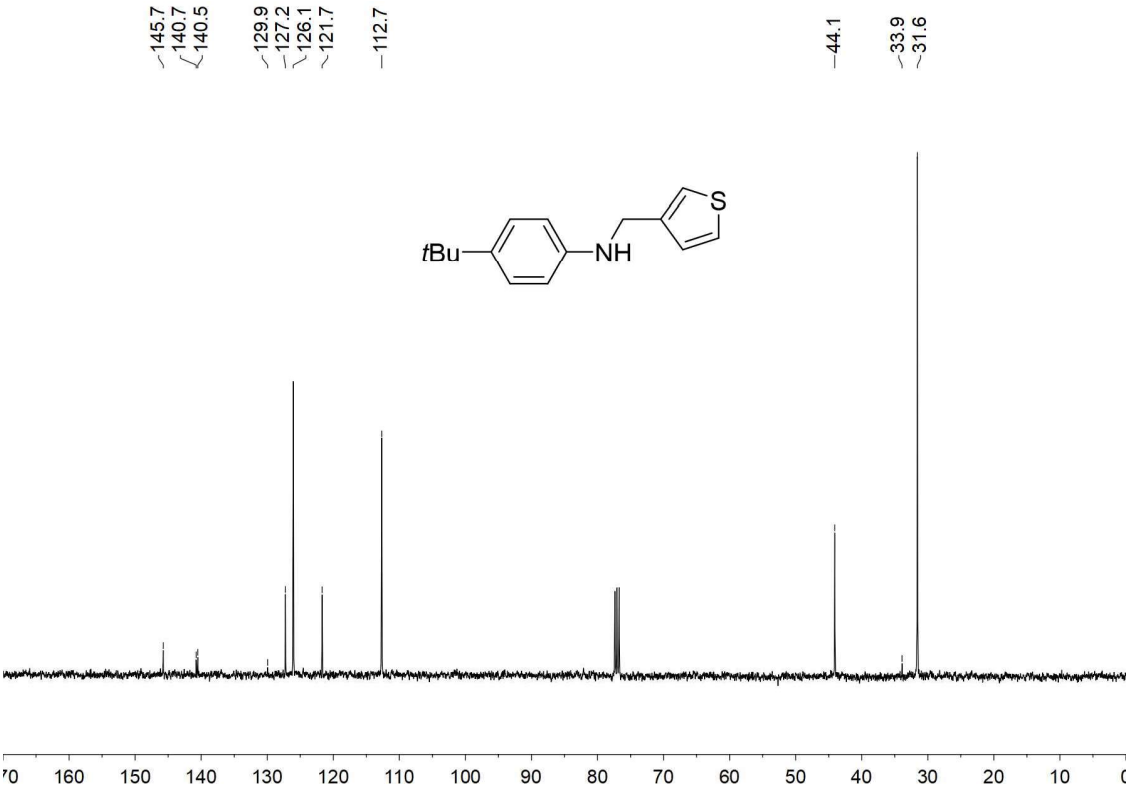
1.0
0.5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140.7
140.5
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126.1
121.7
112.7
44.1
33.9
31.6
tBu
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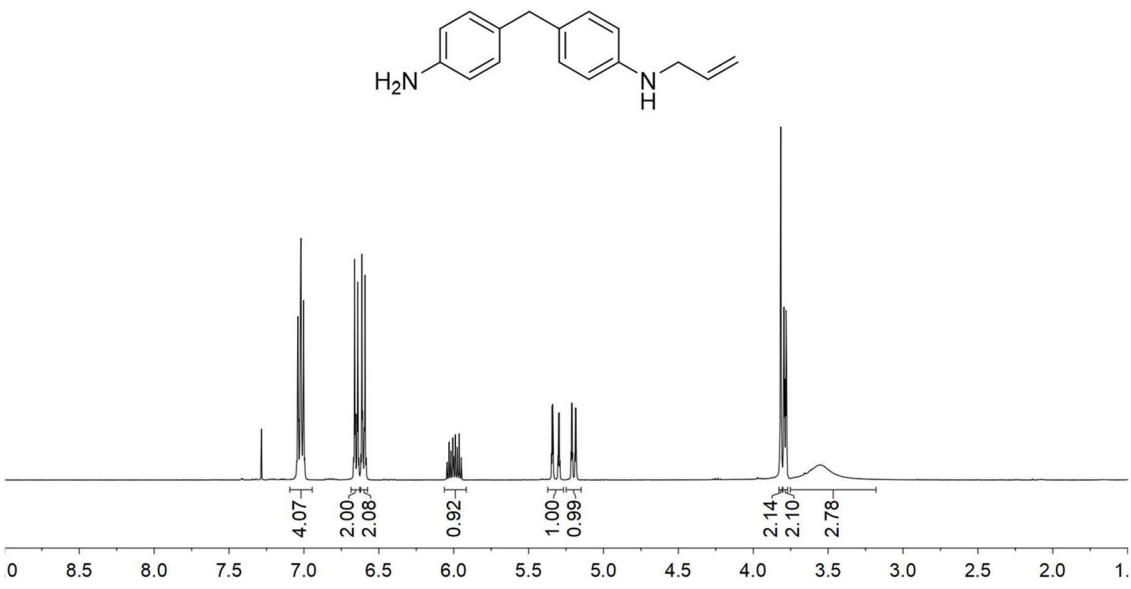
S
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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N
H
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0.99
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2.10
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8.0
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5.0
4.5
4.0
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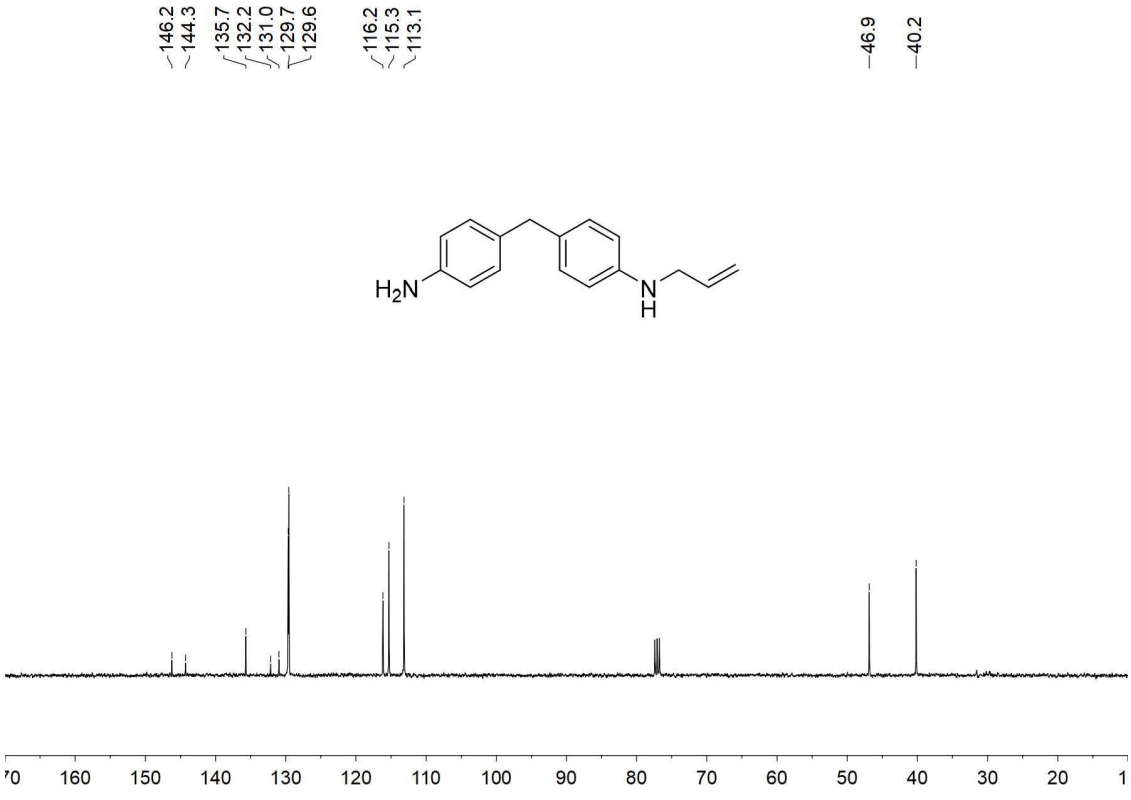
3.0
2.5
2.0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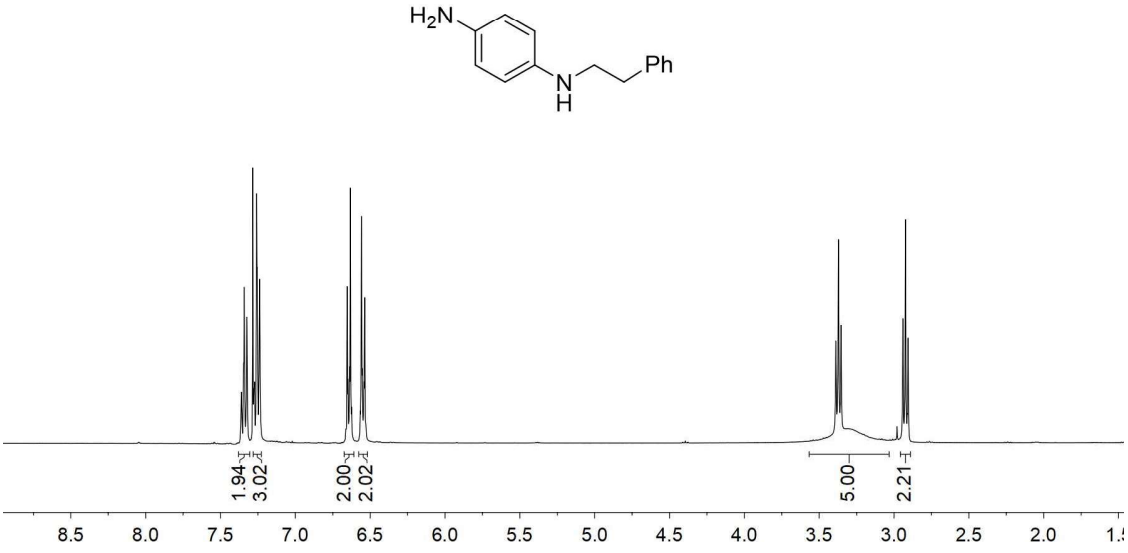
144.3
135.7
132.2
131.0
129.7
129.6
116.2
115.3
113.1
46.9
40.2
H2N
N
H
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20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H
Ph
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5.00
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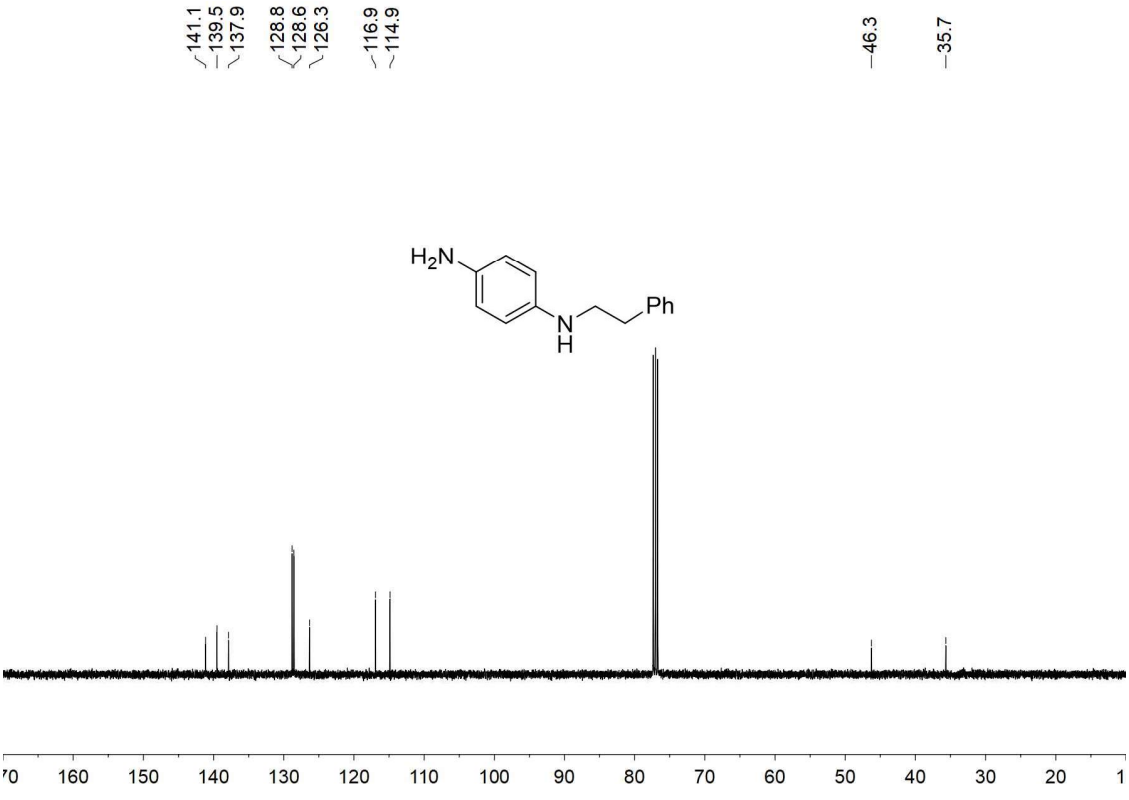
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139.5
137.9
128.8
128.6
126.3
116.9
114.9
46.3
35.7
H2N
N
H
Ph
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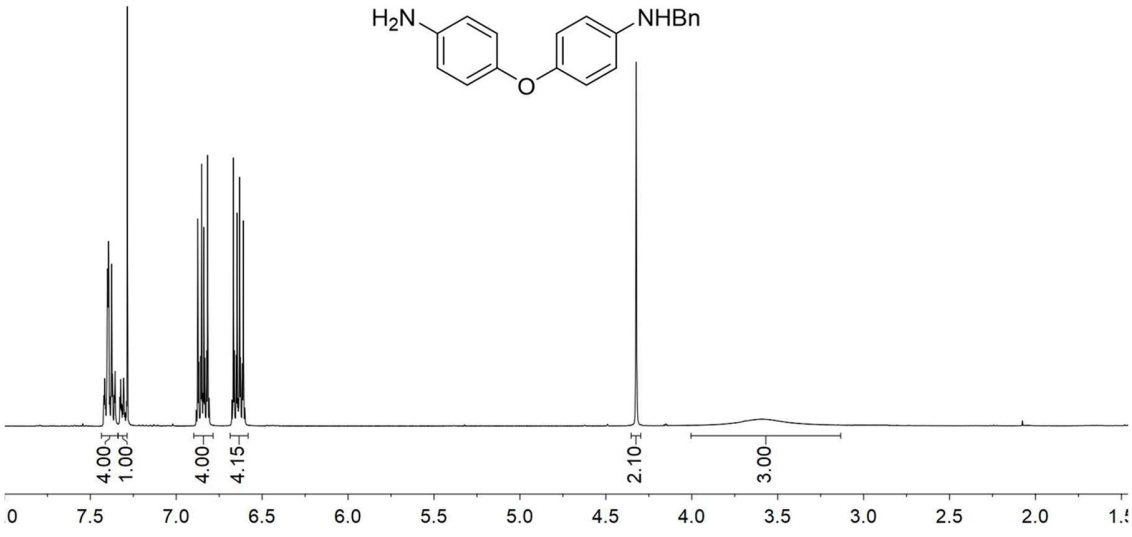
150
140
130
120
110
100
90
80
70
60
50
40
30
20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4.00
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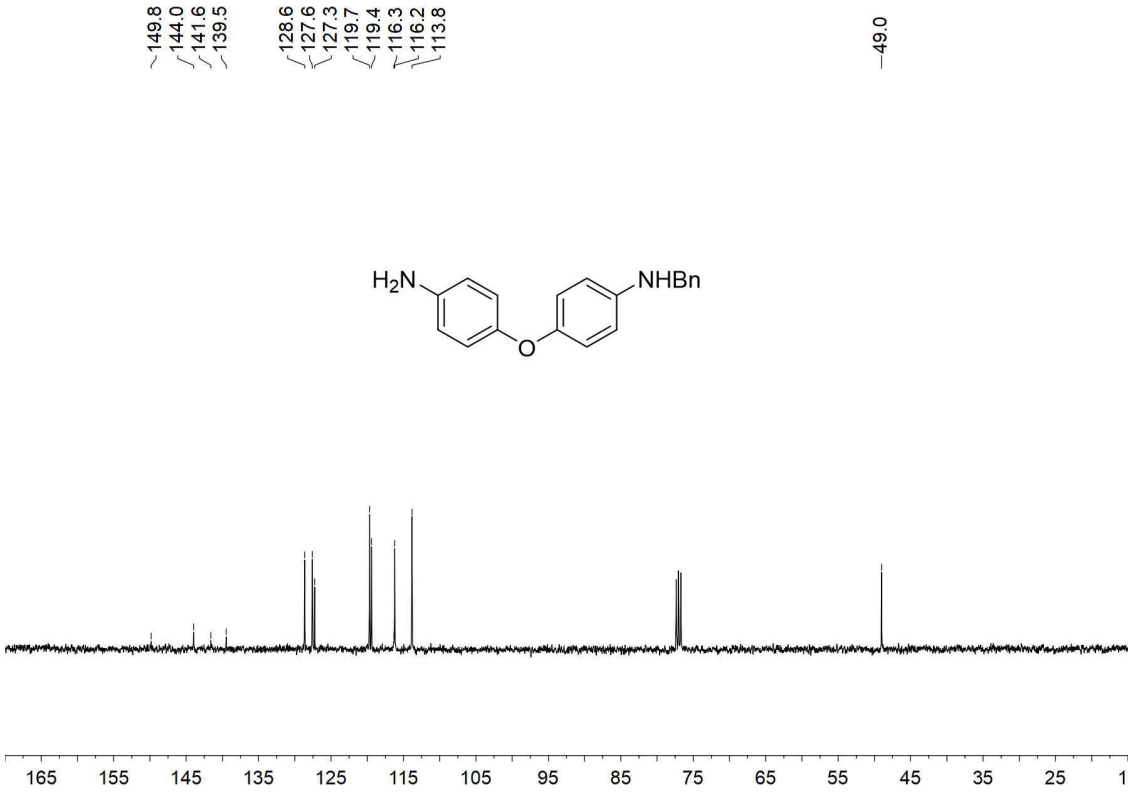
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119.7
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116.2
113.8
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O
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135
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95
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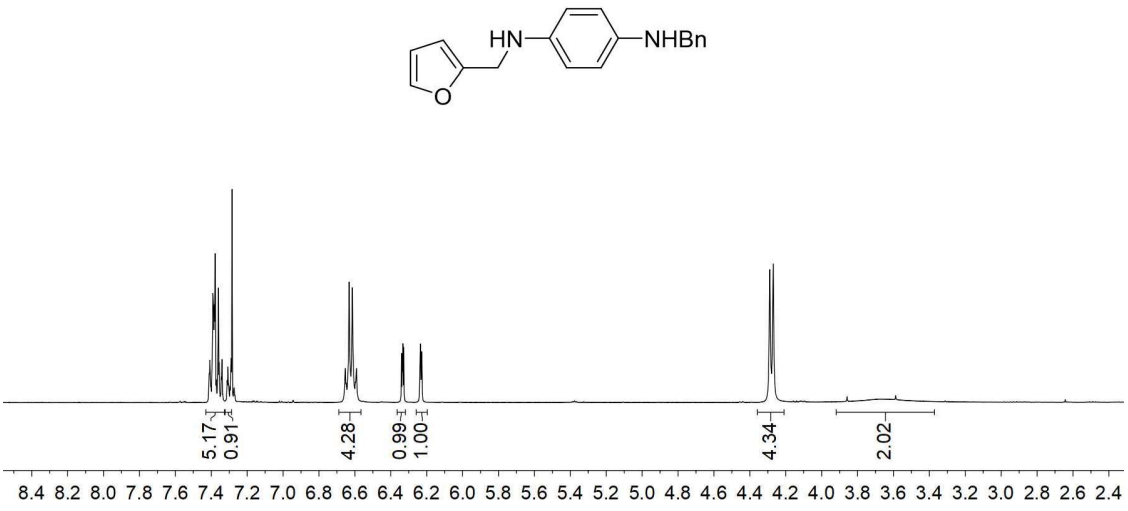
75
65
55
45
35
25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NHBn
O
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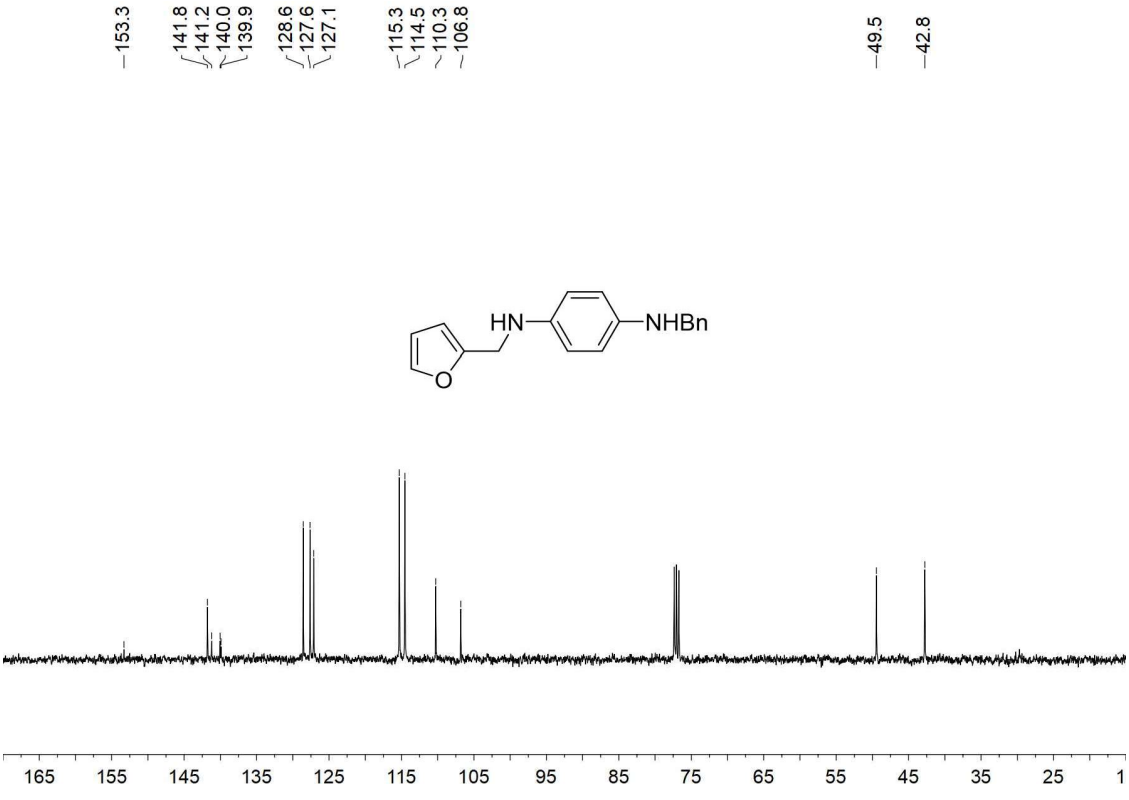
4.28
0.99
1.00
4.34
2.02
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4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106.8
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NHBn
O
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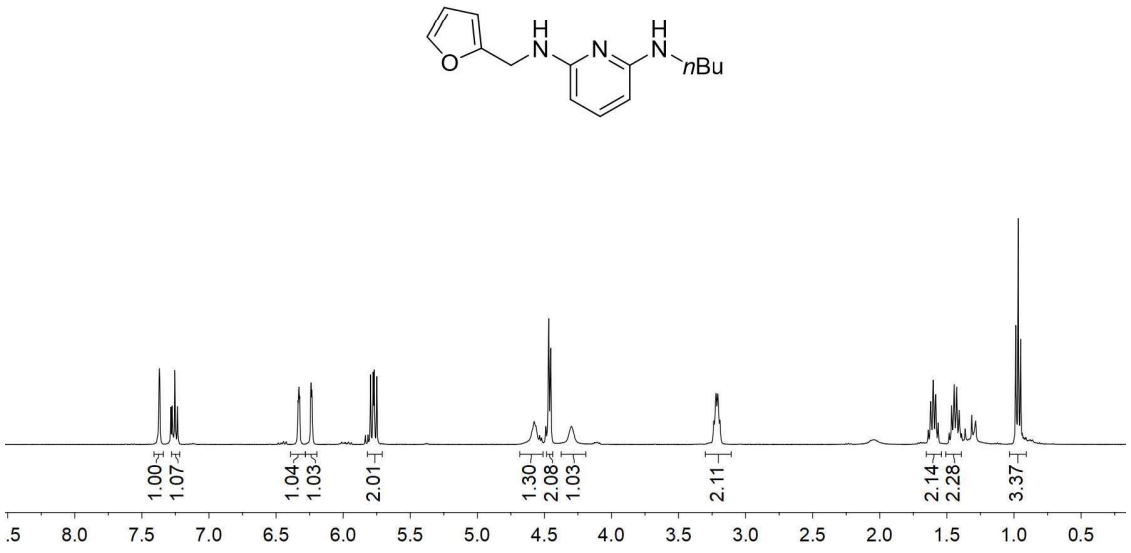
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O
N
H
N
nBu
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1.03
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2.11
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3.37
8.0
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7.0
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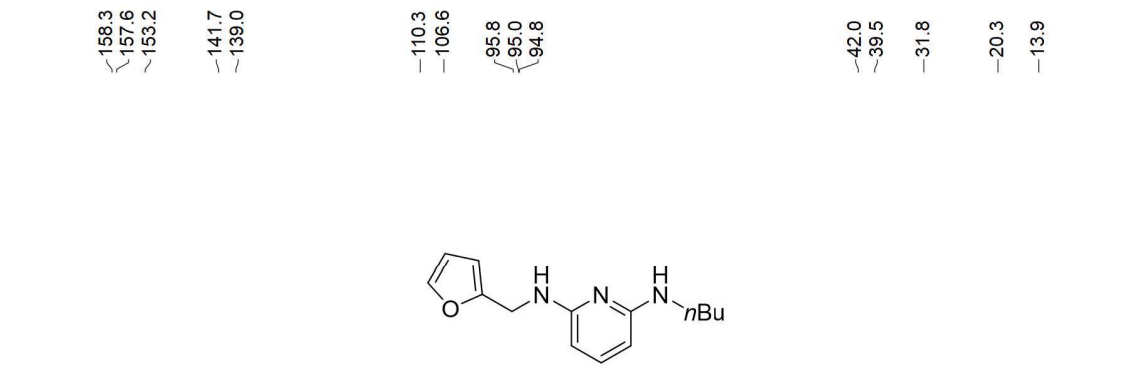
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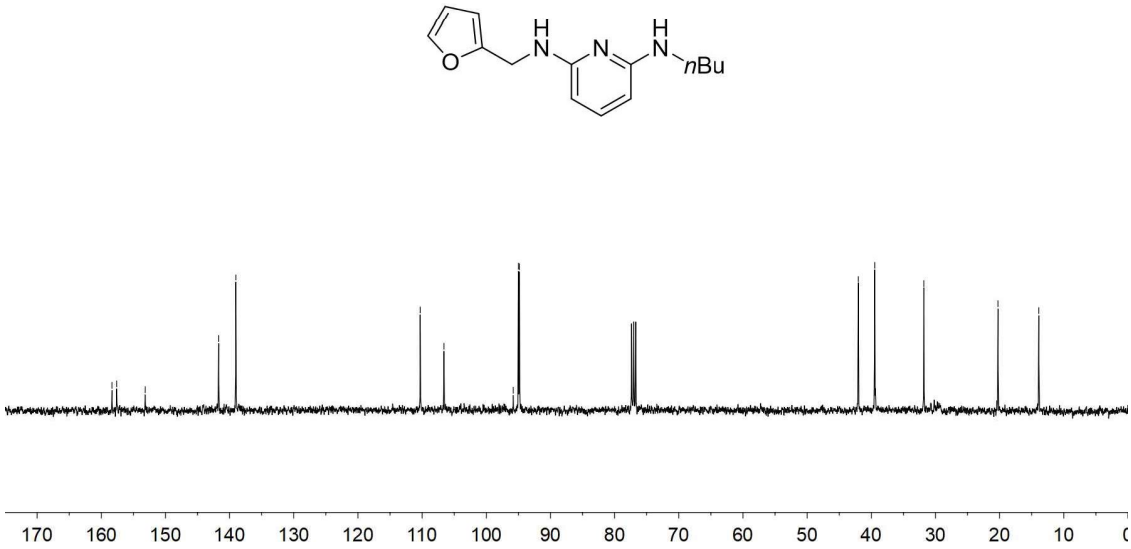
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O
N
H
N
nBu
170
160
150
140
130
120
110
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20
10

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37. Author contributions

E.W., X.L. and M.C. conceived the idea of this work. E.W., K.C., Y.C. and J.Z. performed the experiments and analyzed the data with feedback and guidance from M.C. and X.L. E.W., M.C. and X.L. wrote the manuscript.