# Supporting Information

# Unsupported Nanoporous Platinum-Iron Bimetallic Catalyst for the Chemoselective Hydrogenation of Halonitrobenzenes to Haloanilines

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## 1. Characterization of Catalyst

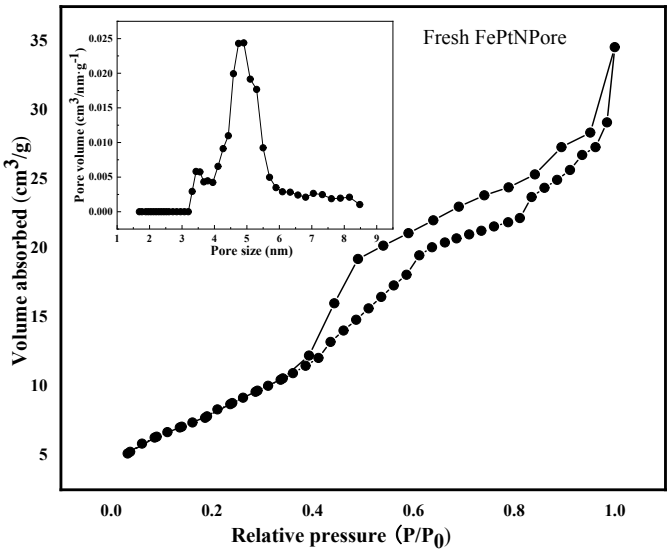



**Figure S1.** Nitrogen adsorption/desorption isotherm and corresponding pore size distribution curve (inset) of fresh PtFeNPore

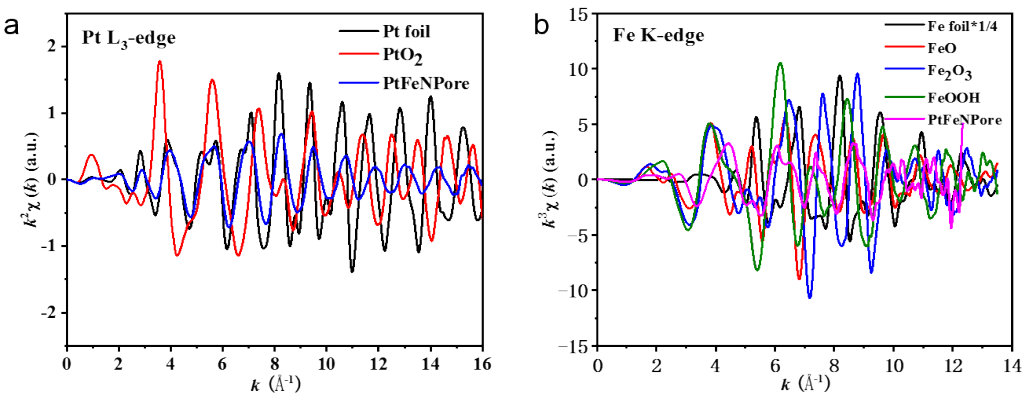



**Figure S2.** (a) Pt $L_3$-edge $k^2$-weighted EXAFS oscillation $k^2\chi(k)$ and (b) Fe K-edge $k^3$-weighted EXAFS oscillations $k^3\chi(k)$ of PtFeNPore. The data of Pt foil and $PtO_2$, Fe foil, FeO, $Fe_2O_3$ and FeOOH are shown for references, respectively.

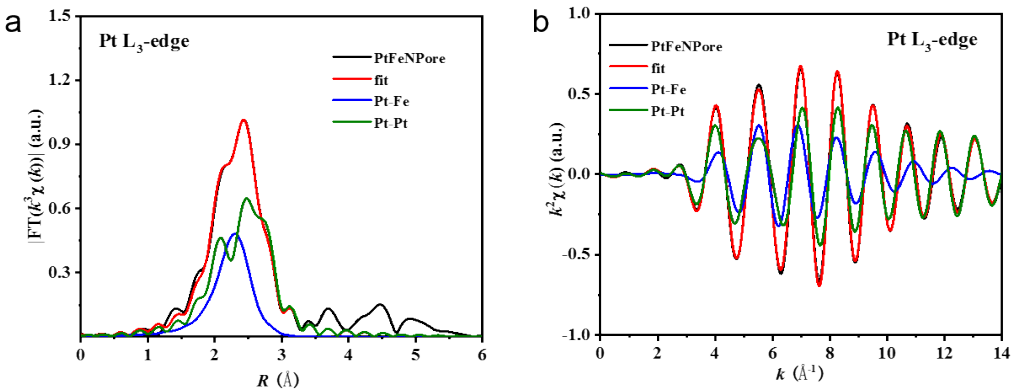



**Figure S3.** (a) The fitting curve of $k^2$-weighted EXAFS spectra and (b) $k^2\chi(k)$ oscillations of PtFeNPore at the Pt $L_3$-edge using the ARTEMIS module of IFEFFIT.

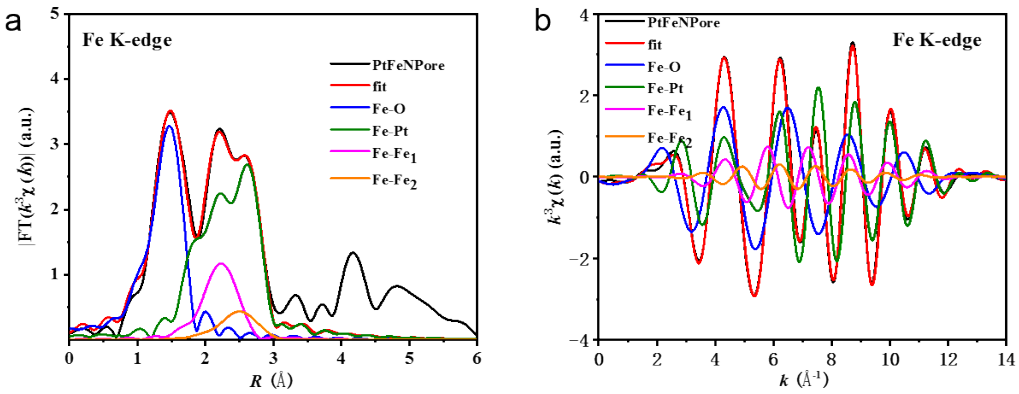



**Figure S4.** (a) The fitting curve of $k^3$-weighted EXAFS spectra and (b) $k^3\chi(k)$ oscillations of PtFeNPore at the Fe K-edge using the ARTEMIS module of IFEFFIT.

**Table S1.** Summary of EXAFS fitting results of PtFeNPore at Pt $L_3$-edge.

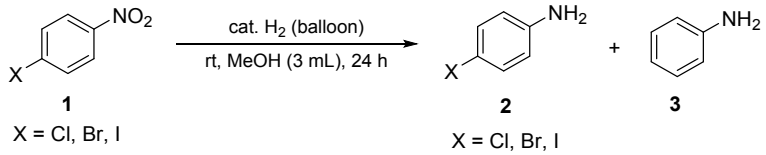
| Sample | Path | C.N, | R (Å) | $\sigma^2$ ($10^{-3}$Å$^2$) | ΔE (eV) | R factor |
|---|---|---|---|---|---|---|
| PtFeNPore | Pt-Fe | 2.2 | 2.66 | 8.8 | 6.3 | 0.0013 |
| | Pt-Pt | 5.9 | 2.72 | 7.2 | 5.0 | |

**Table S2.** Summary of EXAFS fitting results of PtFeNPore at Fe K-edge.

| Sample | Path | C.N, | R (Å) | $\sigma^2$ ($10^{-3}$Å$^2$) | ΔE (eV) | R factor |
|---|---|---|---|---|---|---|
| | Fe-O | 2.3 | 1.93 | 6.9 | -3.1 | |
| PtFeNPore | Fe-Pt | 4.9 | 2.66 | 10.5 | -7.3 | 0.0004 |
| | Fe-$Fe_1$ | 0.9 | 2.66 | 10.5 | -7.3 | |
| | Fe-$Fe_2$ | 0.8 | 2.99 | 13.7 | -7.3 | |

## 2. Comparative Experiments on the Activity and Selectivity of Several Catalysts

**Table S3.** Results of comparative experiments.[a]




| Entry | Cat. | X of substrate **1** | Yield (%)[b] | |
|---|---|---|---|---|
| | | | 2 | 3 |
| 1 | PtFeNPore | Cl | 90 | 0 |
| 2 | | Br | 88 | 0 |
| 3[c] | | I | 86 | 0 |
| 4 | Pt/C | Cl | 82 | 11 |
| 5 | | Br | 66 | 25 |
| 6 | | I | 0 | 94 |
| 7 | PdNPore[d] | Cl | 35 | 55 |
| 8 | | Br | 15 | 80 |
| 9 | | I | 70 | trace |
| 10 | FeNPore | Cl | NR[e] | |
| 11 | | Br | NR[e] | |
| 12 | | I | NR[e] | |

[a]Reaction conditions: halonitrobenzene (**1**, 0.5 mmol), $H_2$ (balloon), and catalyst (4 mol%) in MeOH (3 mL) for 24 h. [b] Isolated yield. [c]The reaction was conducted in MeOH at 35 °C under $H_2$ (balloon) atmosphere. [d]The hydrogenaion was catalyzed by PdNPore reported before. [e]No reaction.

## 3. Procedure for Experiment of Recycle Use of PtFeNPore Catalyst

4-Chloronitrobenzene (**1b**, 0.5 mmol, 78.7 mg), PtFeNPore (4.1 mg, Pt: 4 mol%, 0.025 mmol), and MeOH (3.0 mL) were successively placed in a autoclave (20 mL) with a magnetic stir bar in a $N_2$ atmosphere. The autoclave was purged thrice with $H_2$. Then the autoclave was filled with $H_2$ (balloon). The reaction mixture was stirred at room temperature for 24 h. Then, the remaining $H_2$ was vented. The mixture was evaporated to afford crude product, which was purified via alumina column chromatography (eluent: ethyl acetate/petroleum ether = 1/5) to afford product **2b**. The PtFeNPore catalyst was recovered by a magnet and purified by washing with

acetone (4.1 mg). Then the recovered catalyst was used in the next recycle under the same conditions.

## 4. $^1$H NMR Spectrum of Deuterium-Hydrogen Exchange Reaction

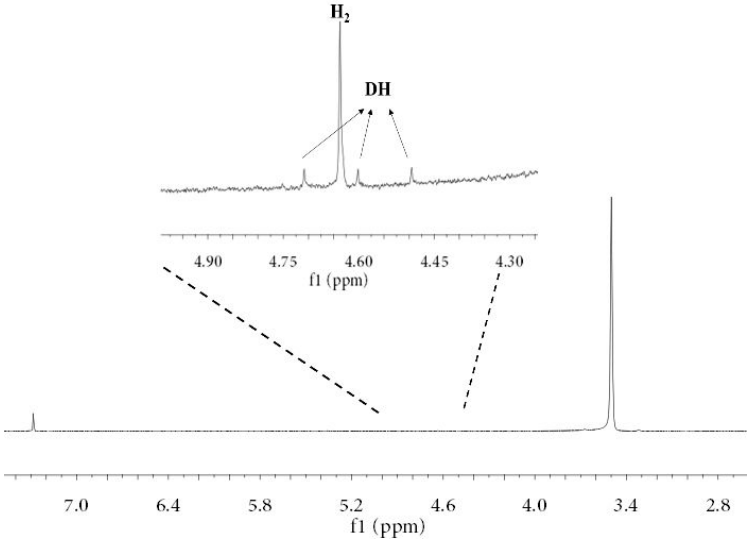
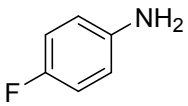



**Figure S5** $^1$H NMR Spectrum of Deuterium-hydrogen exchange reaction.

## 5. The Characterization of Products

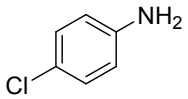
The spectroscopic data of all the products are presented. All the known compounds were in accordance with the data reported in the literatures.

**4-Fluoroaniline (2a)**[1]



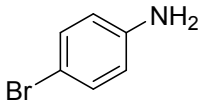

Red-brown oil (63.5 mg, 90%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.86 (t, $J$ = 8.6 Hz, 2H), 6.74–6.48 (m, 2H), 3.49 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 157.61, 155.27, 142.44, 116.11, 116.03, 115.79, 115.57, 77.39, 77.08, 76.76.

**4-Chloroaniline (2b)**[2]



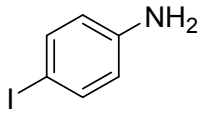

Light yellow solid (57.4 mg, 90%), mp 69–71 °C (lit.[3] mp 69–71 °C). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.10 (d, $J$ = 8.7 Hz, 2H), 6.60 (d, $J$ = 8.7 Hz, 2H), 3.62 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 145.01, 129.13, 123.11, 116.26, 77.43, 77.11, 76.79.

**4-Bromoaniline (2c)**[2]



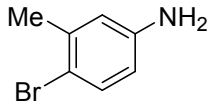

Light yellow solid (86.9 mg, 86%), mp 58–60 °C (lit.[4] mp 58–60 °C). $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.10 (d, $J$ = 8.7 Hz, 2H), 6.60 (d, $J$ = 8.7 Hz, 2H), 3.62 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 145.42, 132.02, 116.71, 110.22, 77.34, 77.03, 76.71.

**4-Iodoaniline (2d)**[5]



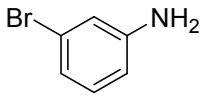

White solid (94.2 mg, 86%), mp 61–63 °C (lit.[6] mp 61 °C). $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.41 (d, $J$ = 8.4 Hz, 2H), 6.47 (d, $J$ = 8.4 Hz, 2H), 3.66 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 146.08, 137.92, 117.32, 79.39, 77.39, 77.08, 76.76.

**4-Bromo-3-methylaniline (2e)**[7]



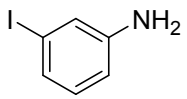

Gray solid (80.9 mg, 87%), mp 81°C (lit.[8] mp 80.7–81.2 °C) $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.25 (d, $J$ = 8.4 Hz, 1H), 6.57 (d, $J$ = 2.6 Hz, 1H), 6.39 (dd, $J$ = 8.4, 2.7 Hz, 1H), 3.59 (s, 2H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 145.66, 138.42, 132.75, 117.47, 114.29, 112.94, 77.35, 77.03, 76.71, 22.88.

**3-Bromoaniline (2f)**[9]



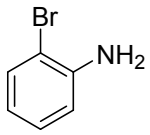

Light yellow oil (81.7 mg, 95%). $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.01 (t, $J$ = 8.0 Hz, 1H), 6.91–6.85 (m, 1H), 6.83 (t, $J$ = 2.2 Hz, 1H), 6.58 (dd, $J$ = 8.0, 2.4 Hz, 1H), 3.71 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.33, 131.00, 123.17, 121.29, 117.93, 114.06, 78.10, 77.78, 77.46.

**3-Iodoaniline (2g)**[10]



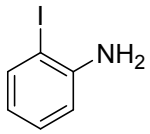
Light yellow oil (101.8 mg, 93%). $^{1}$H NMR (400 MHz, $CDCl_3$): $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.13–6.97 (m, 2H), 6.86 (t, $J$ = 7.9 Hz, 1H), 6.62 (d, $J$ = 7.9 Hz, 1H), 3.65 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 147.76, 130.79, 123.75, 114.32, 94.98, 77.41, 77.10, 76.78.

**2-Bromoaniline (2h)**[11]



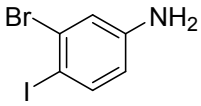
Light yellow solid (77.4 mg, 90%), mp 31 ºC (lit.[12] mp 31 °C). $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.44 (d, $J$ = 8.0 Hz, 1H), 7.13 (t, $J$ = 7.6 Hz, 1H), 6.77 (dd, $J$ = 8.0, 1.4 Hz, 1H), 6.65 (t, $J$ = 7.6 Hz, 1H), 4.09 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 144.19, 132.65, 128.44, 119.48, 115.88, 109.39, 77.56, 77.24, 76.92.

**2-Iodoaniline (2i)**[13]



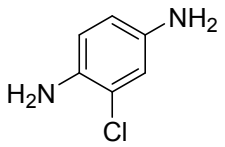
Light yellow solid (97.5 mg, 89%), mp 57–59 ºC (lit.[14] mp 57–59 ºC) $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.64 (dd, $J$ = 7.9, 1.1 Hz, 1H), 7.17–7.07 (m, 1H), 6.75 (dd, $J$ = 8.0, 1.2 Hz, 1H), 6.53–6.43 (m, 1H), 4.08 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 146.77, 139.01, 129.35, 119.99, 114.74, 84.18, 77.37, 77.05, 76.74.

**3-Bromo-4-Iodoaniline (2j)**[15]



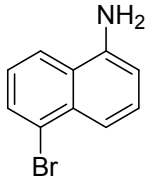
Pale yellow oil (134 mg, 90%). $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.52 (d, $J$ = 8.5 Hz, 1H), 6.98 (d, $J$ = 2.7 Hz, 1H), 6.35 (dd, $J$ = 8.5, 2.7 Hz, 1H), 3.74 (s, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 147.61, 140.26, 129.92, 119.00, 115.89, 85.59.

**2-Chloro-1,4-phenylenediamine (2k)**[16]



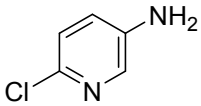

Dark brown solid (65.6 mg, 92%), mp 61–62 ºC (lit.[17] 61–62 ºC). $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.66 (d, $J$ = 2.5 Hz, 1H), 6.63 (s, 1H), 6.49 (d, $J$ = 2.5 Hz, 1H), 3.46 (s, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 139.16, 135.19, 120.37, 117.39, 116.43, 115.58, 77.45, 77.14, 76.82.

**5-amino-1-bromonaphthalene (2l)**[18]




Brown oil (92.2 mg, 83%). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.80 (dd, $J$ = 8.0, 4.7 Hz, 2H), 7.75 (dd, $J$ = 8.5, 2.4 Hz, 1H), 7.42 (dd, $J$ = 8.0, 8.0 Hz, 1H), 7.31–7.26 (m, 1H), 6.85 (dd, $J$ = 7.6, 2.3 Hz, 1H), 4.19 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 142.48, 132.96, 130.17, 127.81, 124.93, 124.79, 123.70, 120.79, 118.18, 110.73, 77.41, 77.10, 76.78.

**6-chloro-pyridin-3-ylamine (2m)**[19]




Light yellow solid (61.7 mg, 96%), mp 61–62 ºC (lit.[19] 60–62 ºC). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, $J$ = 3.0 Hz, 1H), 7.04 (d, $J$ = 8.5 Hz, 1H), 6.93 (dd, $J$ = 8.5, 3.0 Hz, 1H), 3.74 (s, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.90, 140.00, 136.28, 124.87, 124.14, 77.44, 77.12, 76.81.

## 6. References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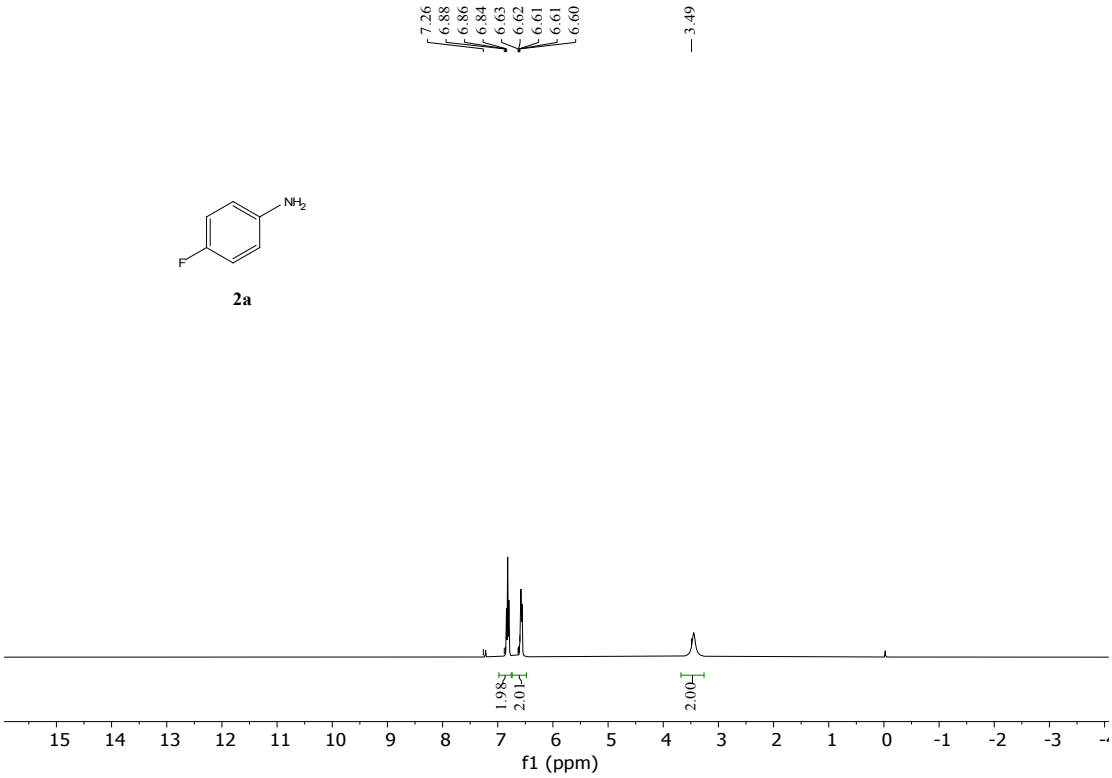
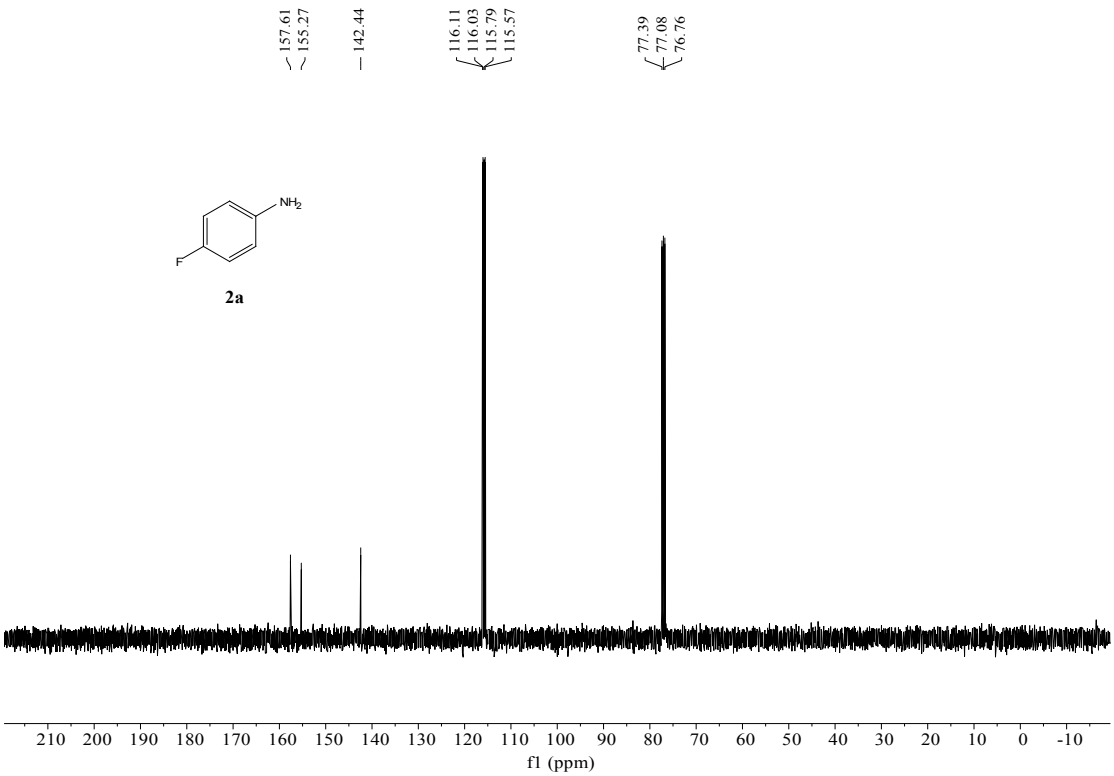
## 7. Copies of $^{1}H$ and $^{13}C$ NMR Spectra of Products

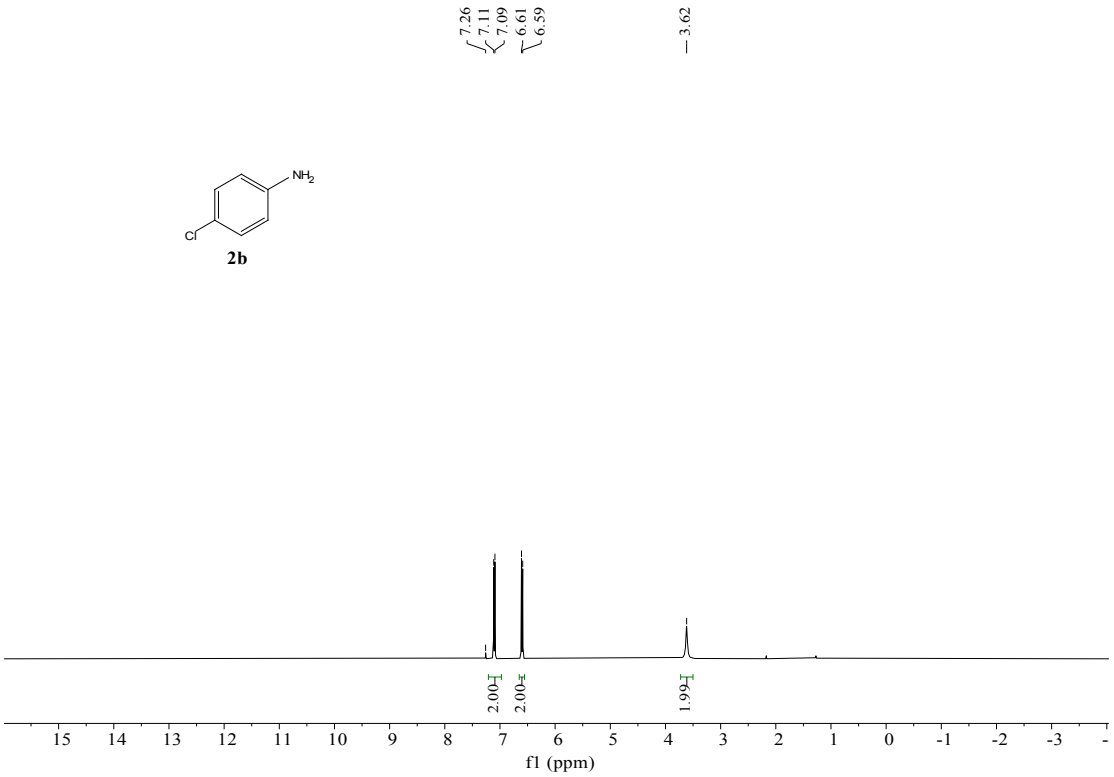
$^{1}H$ NMR, 400 MHz, $CDCl_3$



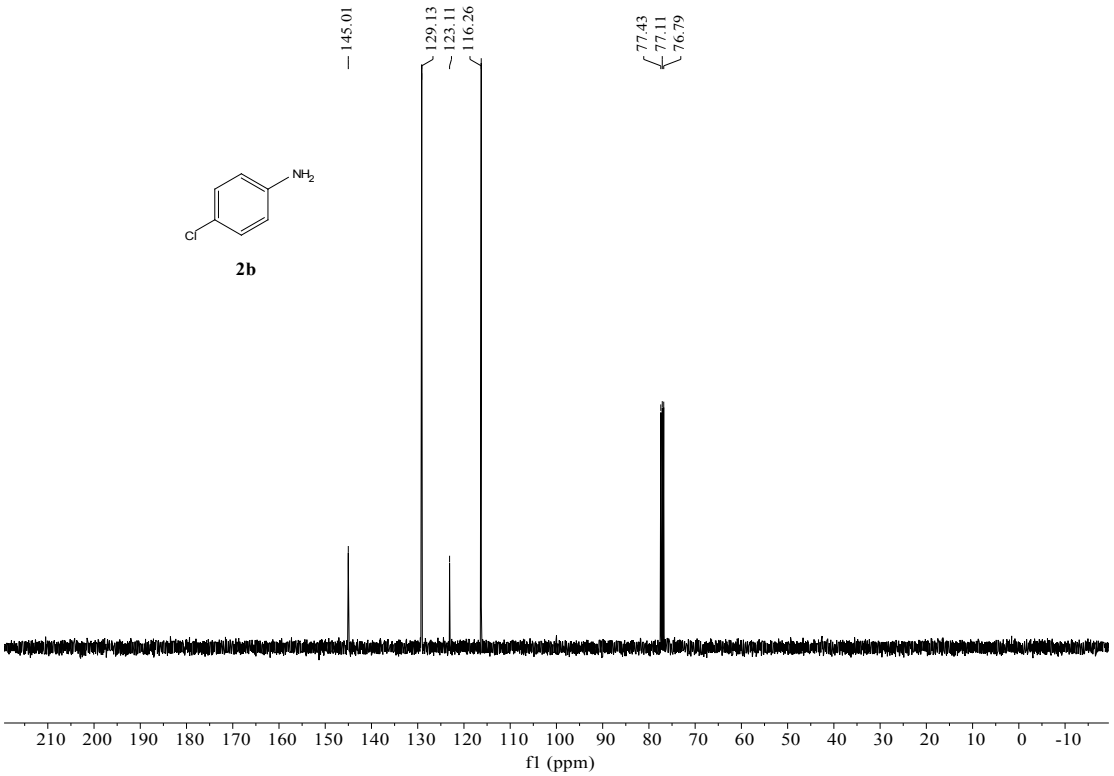

$^{13}C$ NMR, 100 MHz, $CDCl_3$



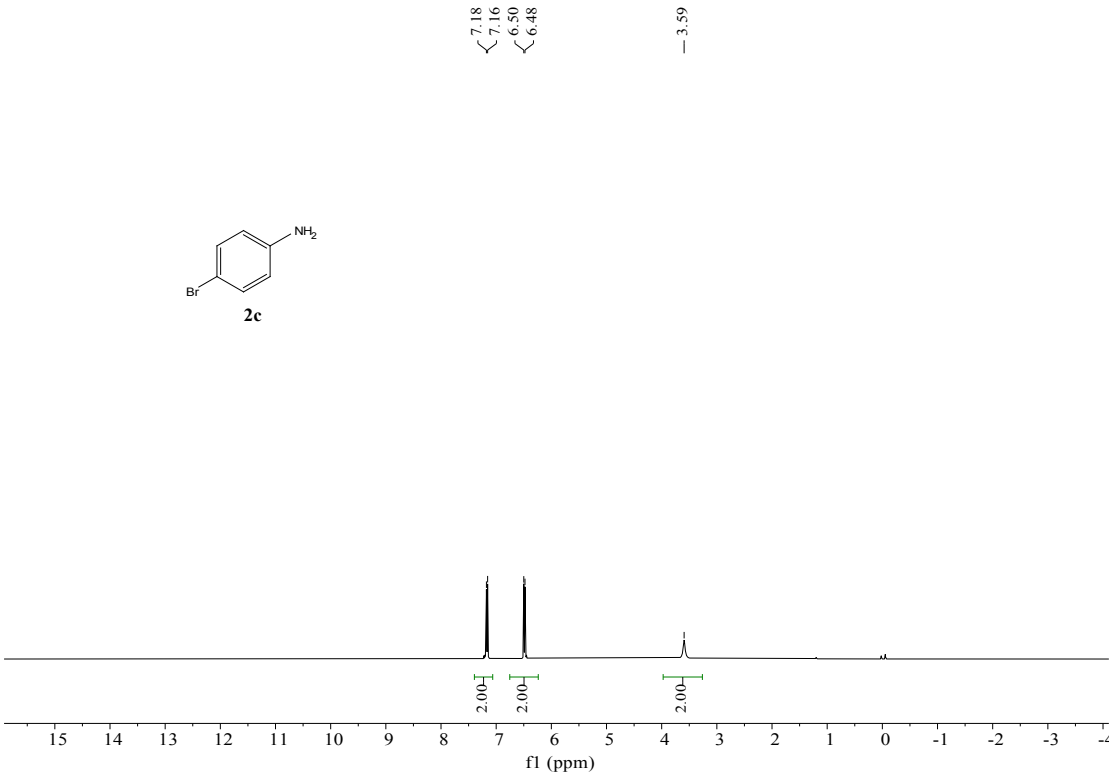
$^{1}H$ NMR, 400 MHz, $CDCl_3$



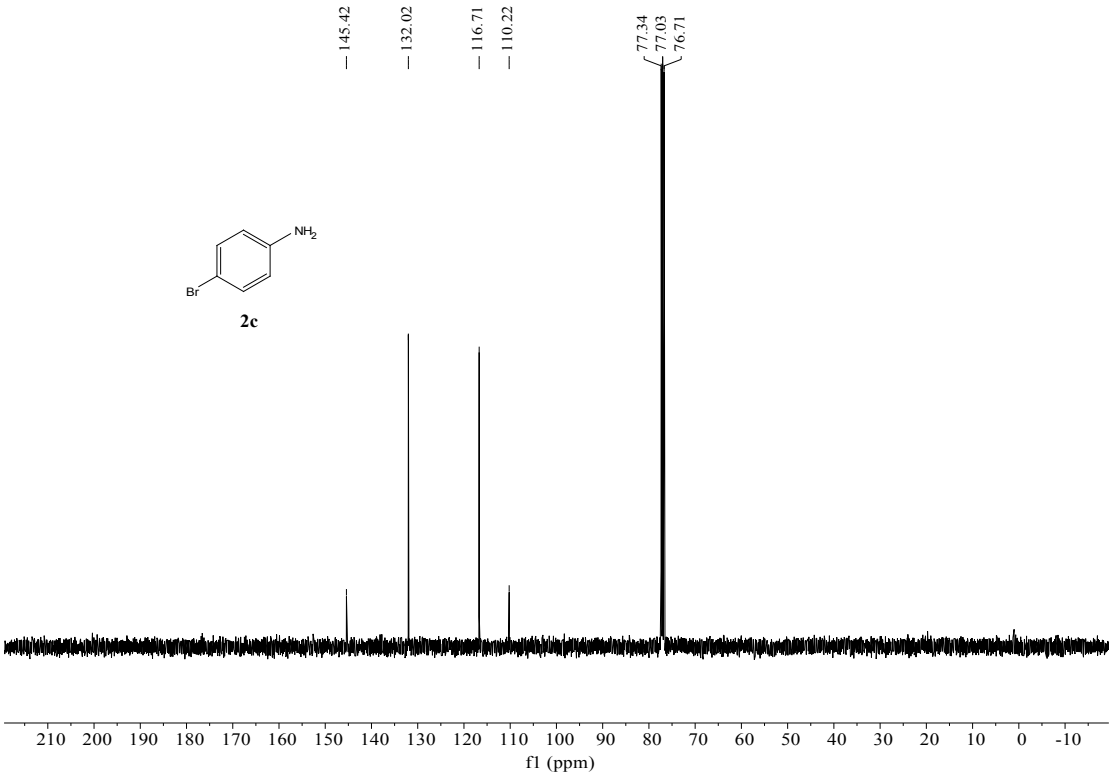

$^{13}C$ NMR, 100 MHz, $CDCl_3$



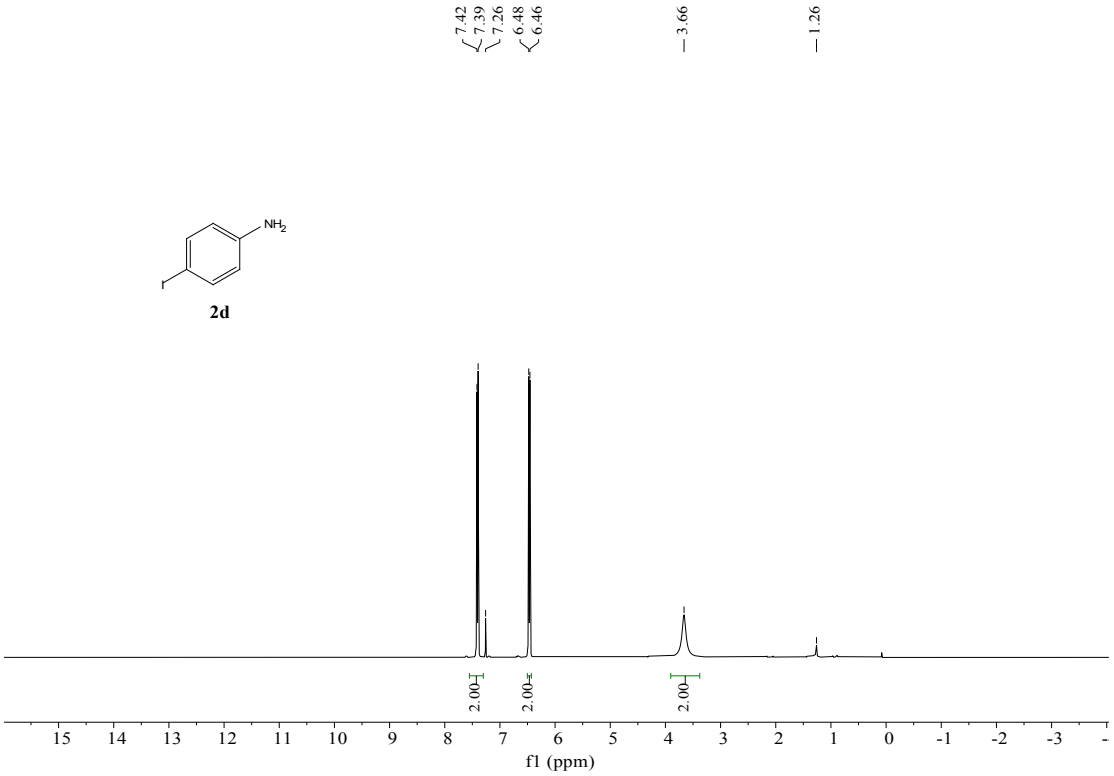
$^{1}$H NMR, 400 MHz, $CDCl_3$



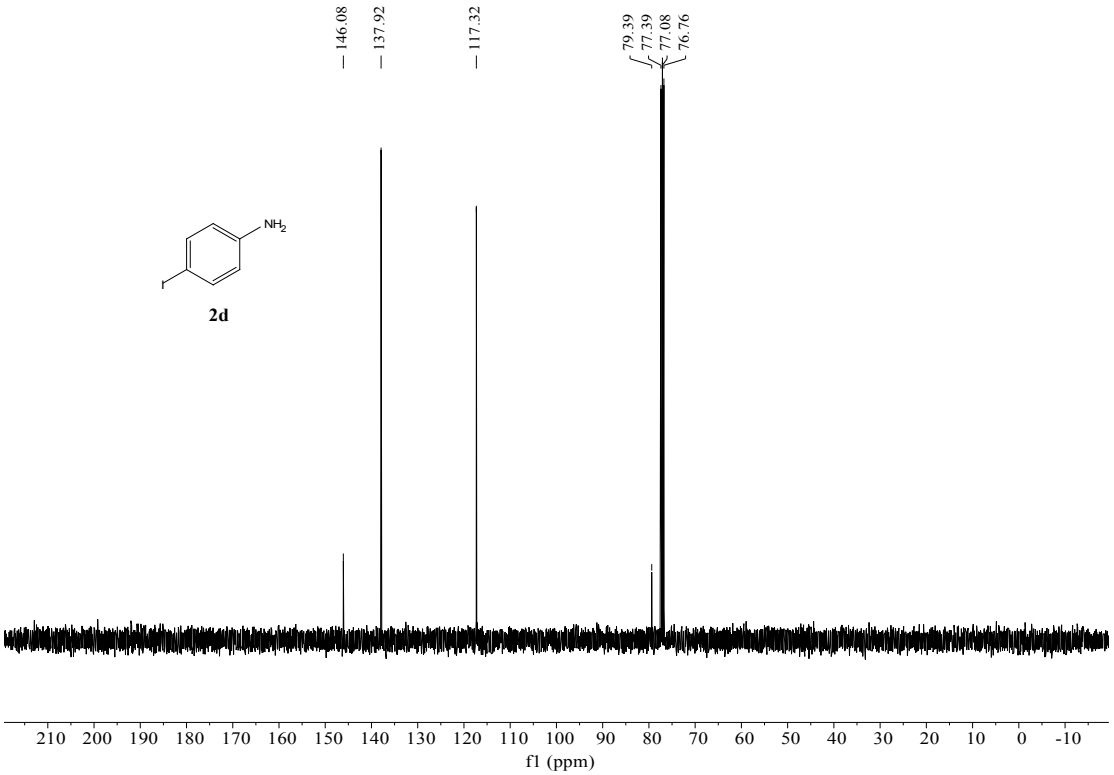

$^{13}$C NMR, 100 MHz, $CDCl_3$



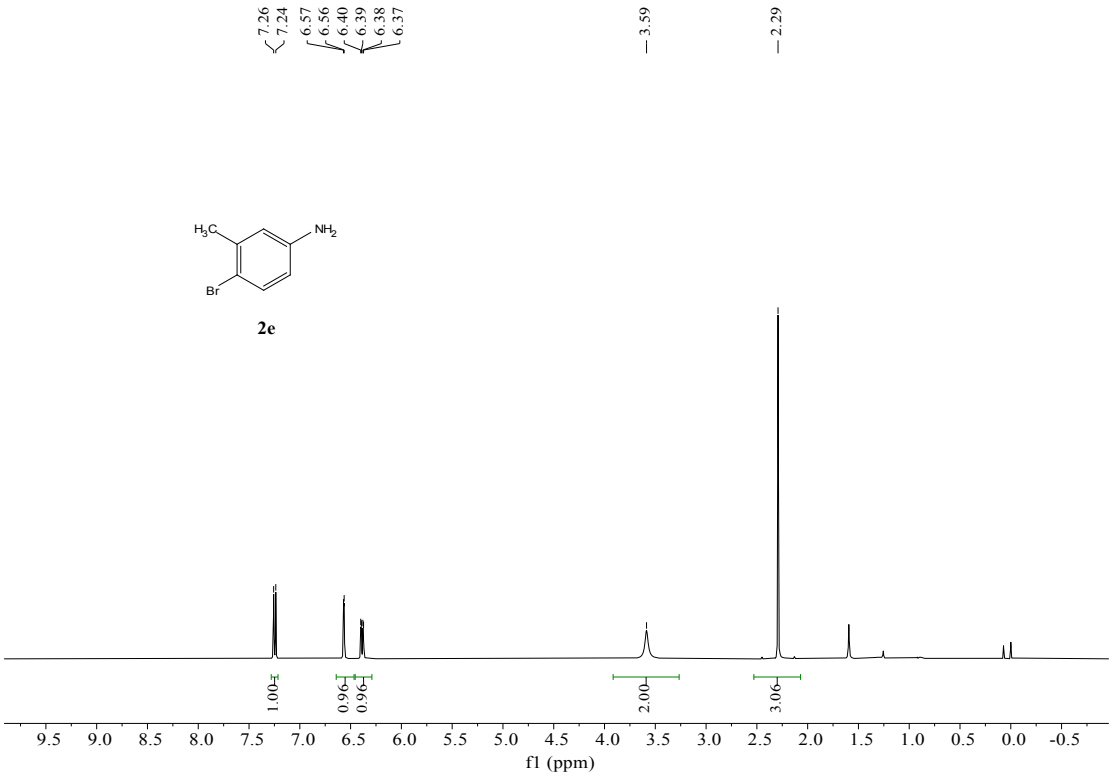
$^{1}H$ NMR, 400 MHz, $CDCl_3$



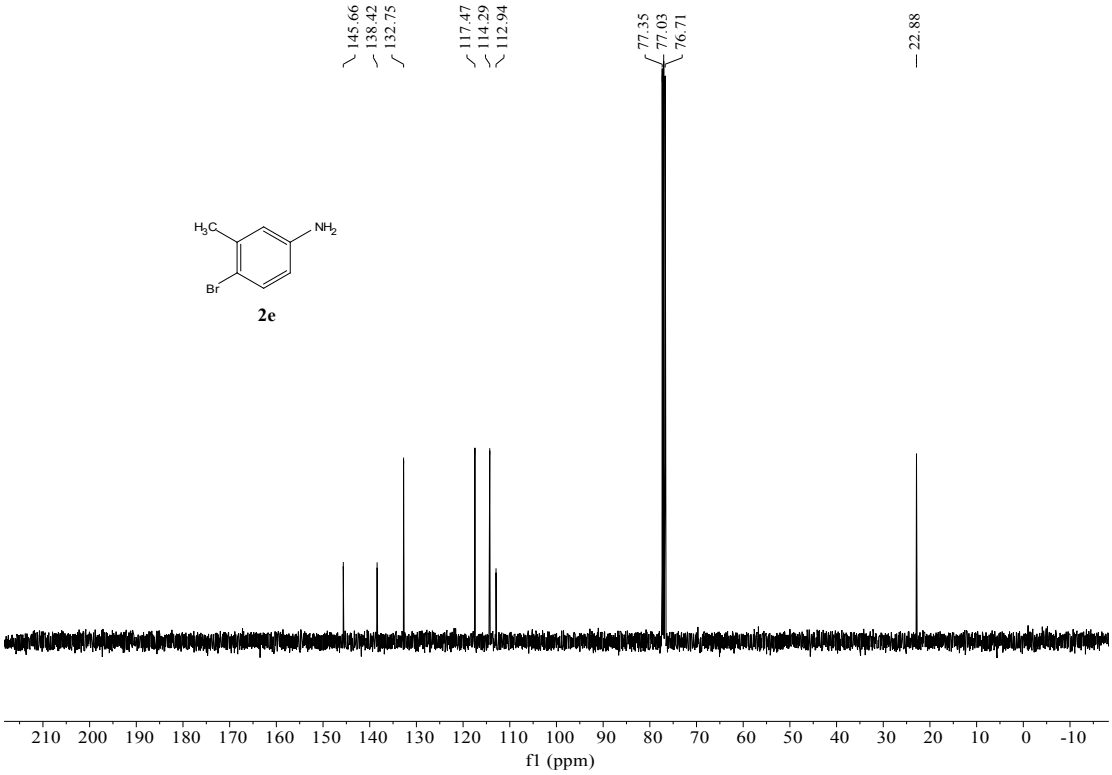

$^{13}C$ NMR, 100 MHz, $CDCl_3$



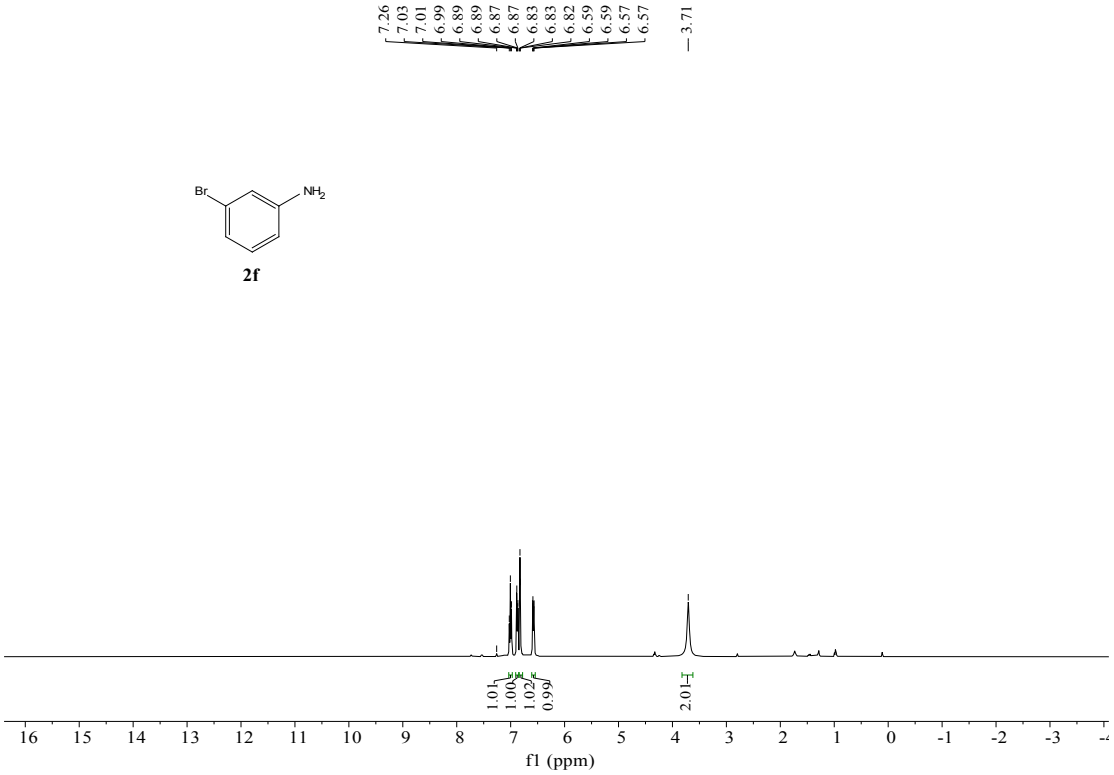
$^{1}$H NMR, 400 MHz, $CDCl_3$



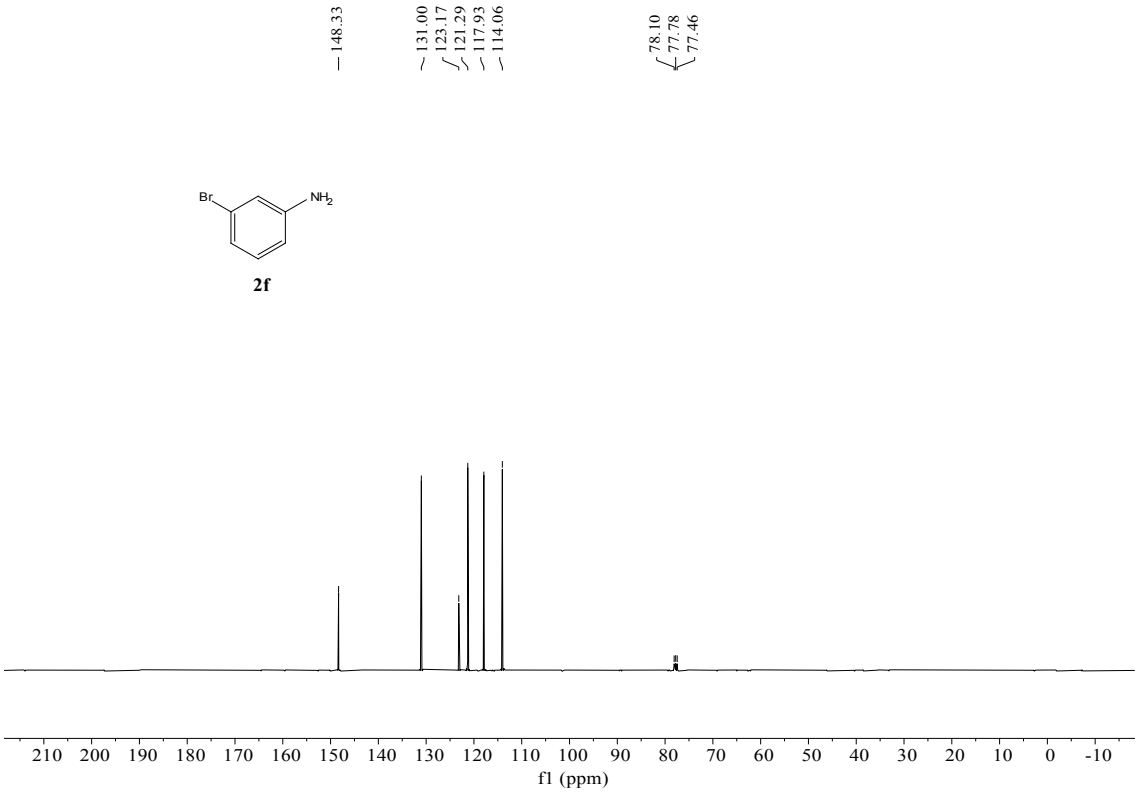

$^{13}$C NMR, 100 MHz, $CDCl_3$



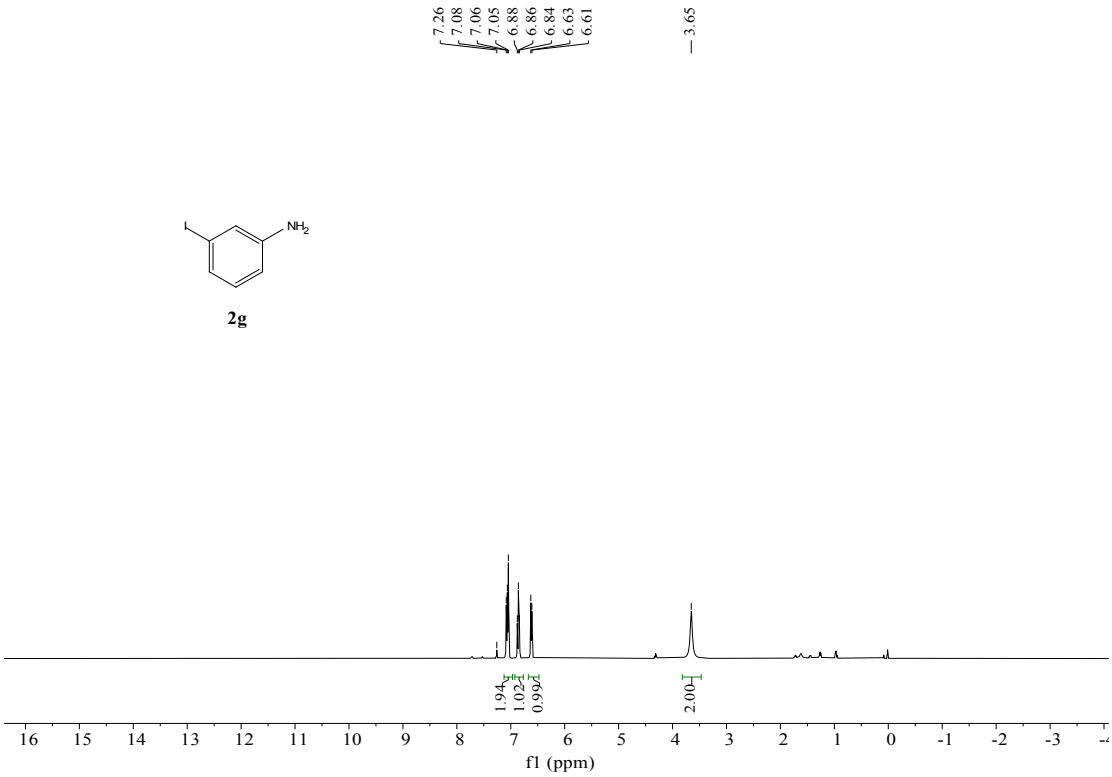
$^{1}$H NMR, 400 MHz, $CDCl_3$




$^{13}$C NMR, 100 MHz, $CDCl_3$

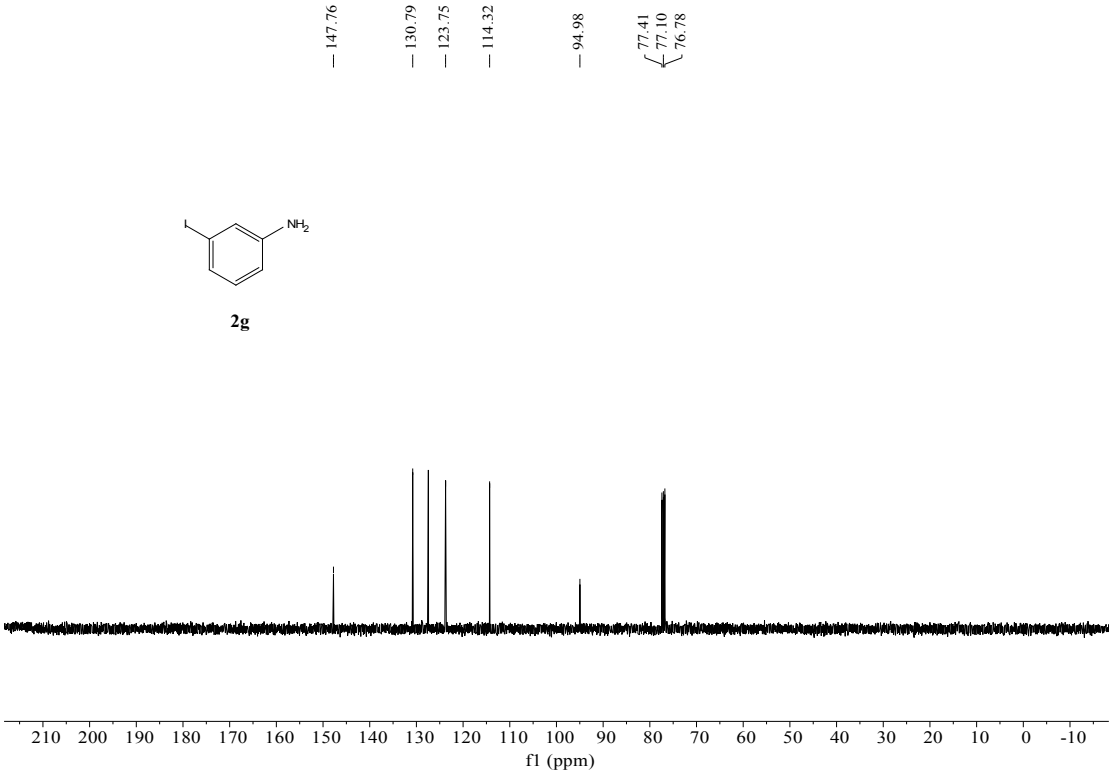


$^{1}$H NMR, 400 MHz, $CDCl_3$



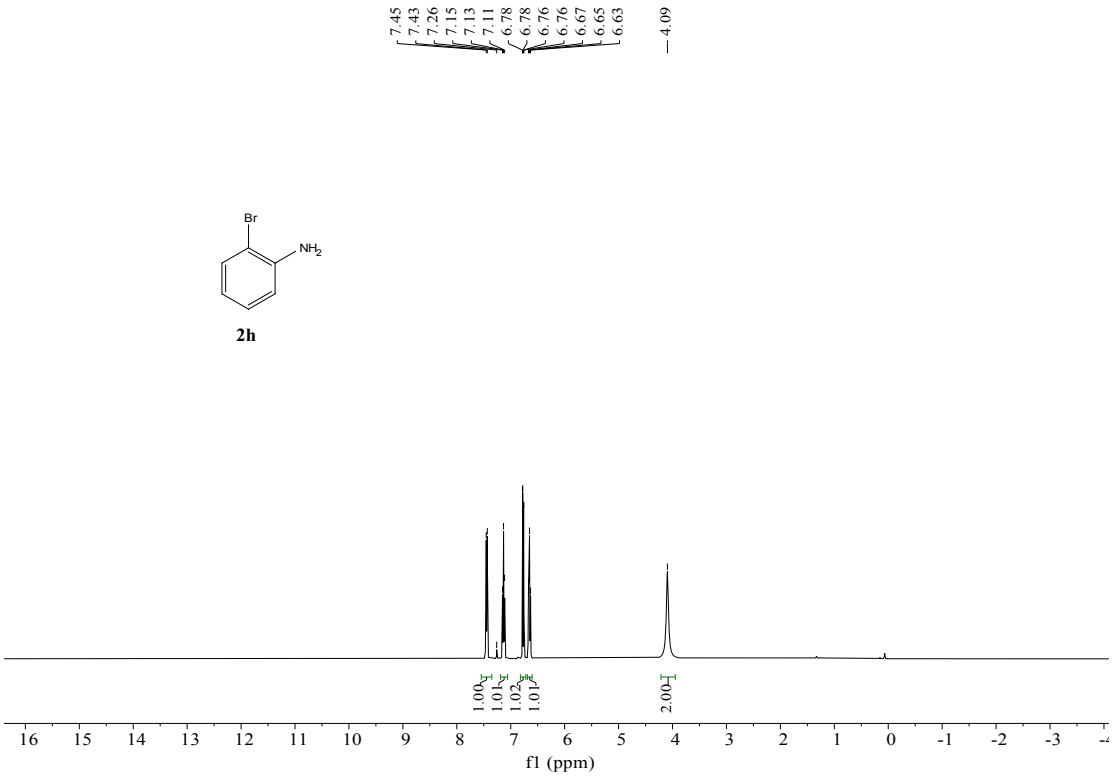

**2g**

$^{13}$C NMR, 100 MHz, $CDCl_3$

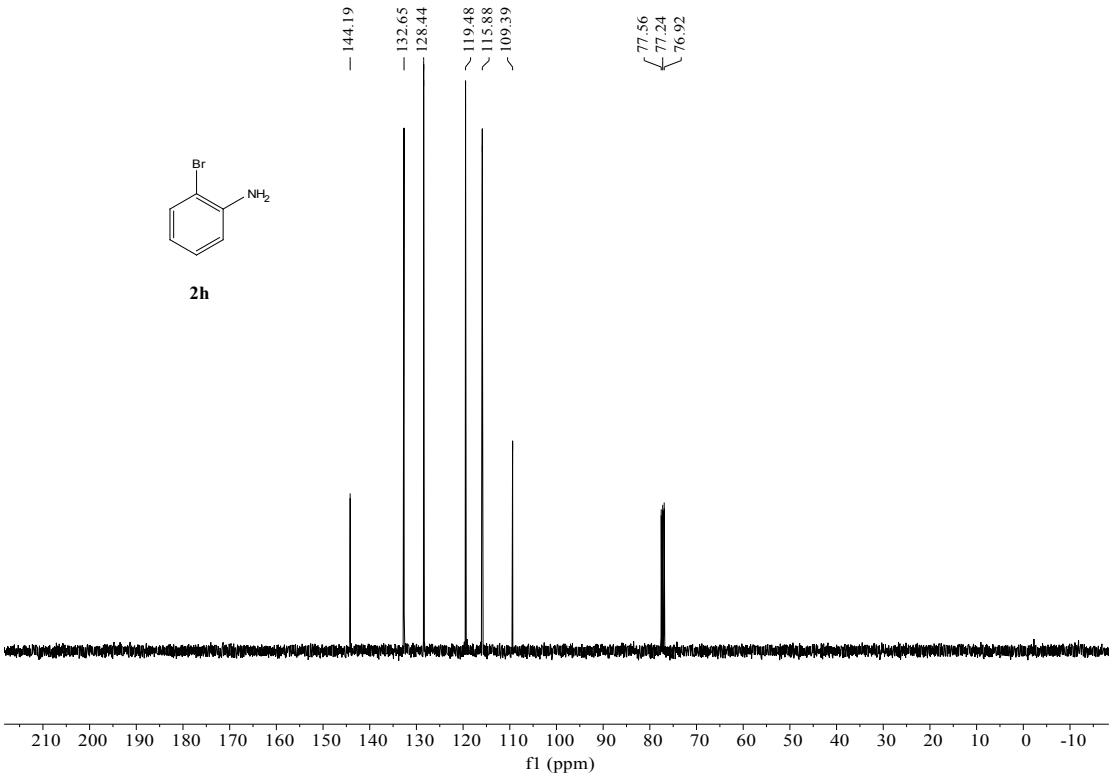



**2g**

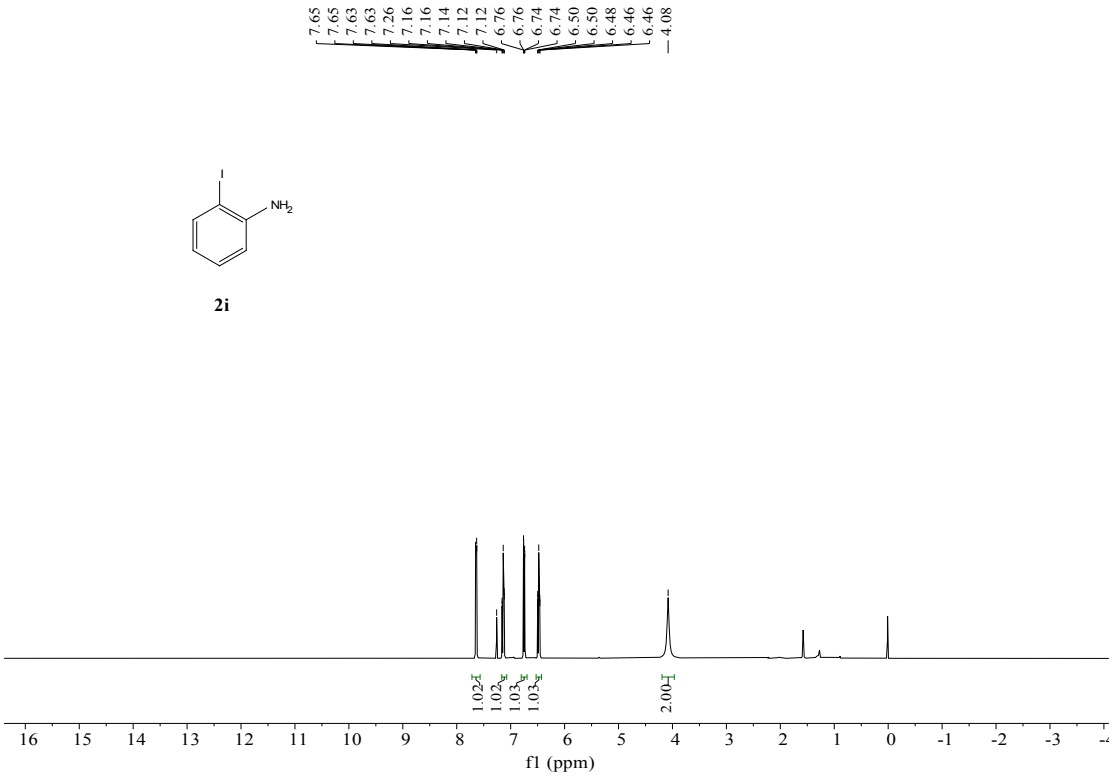
$^{1}$H NMR, 400 MHz, $CDCl_3$




$^{13}$C NMR, 100 MHz, $CDCl_3$

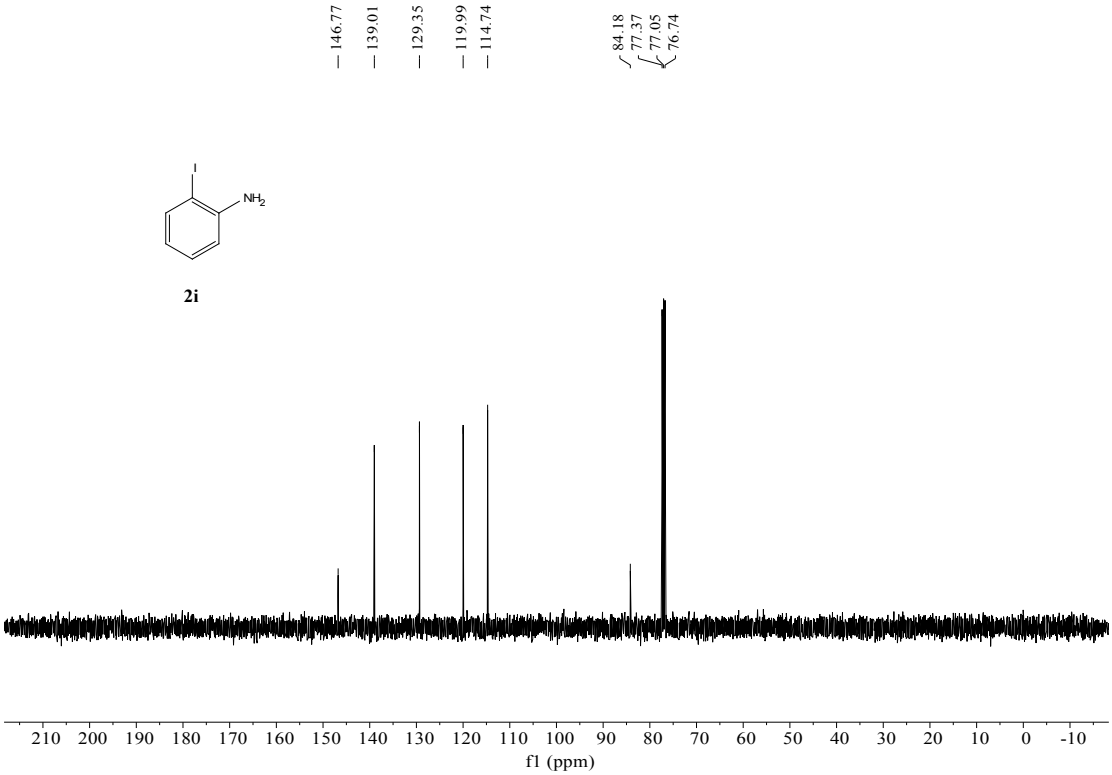


$^{1}$H NMR, 400 MHz, $CDCl_3$



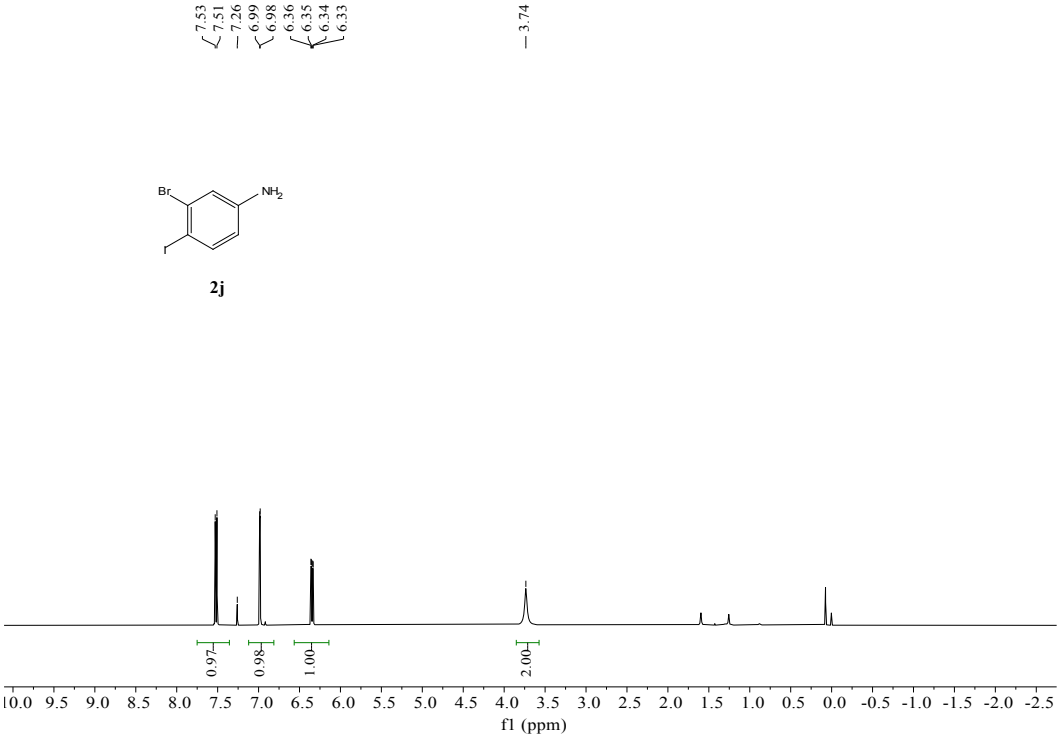

**2i**

$^{13}$C NMR, 100 MHz, $CDCl_3$

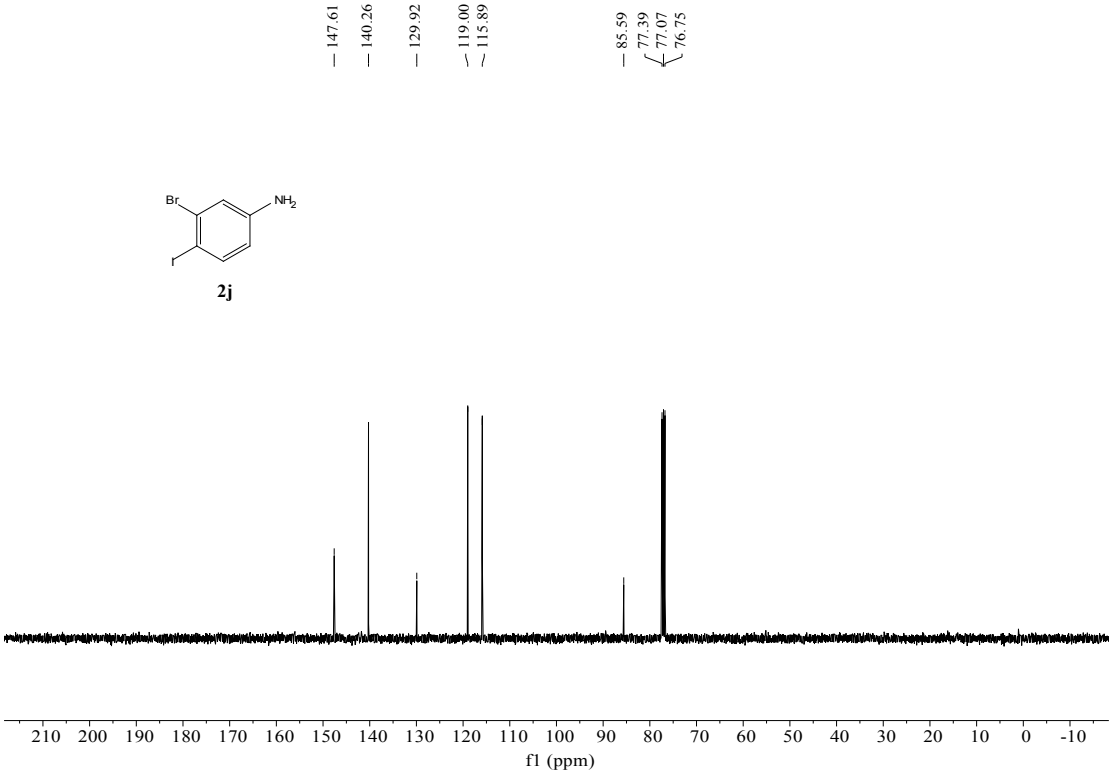



**2i**

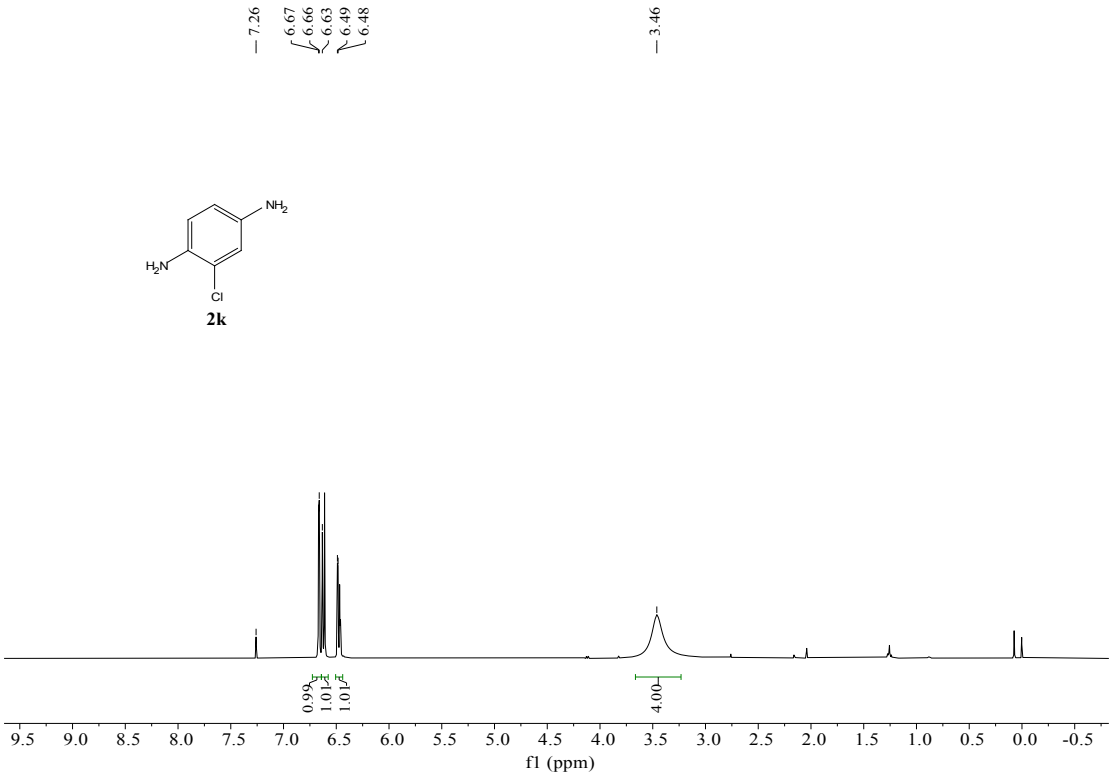
## $^{1}$H NMR, 400 MHz, $CDCl_3$



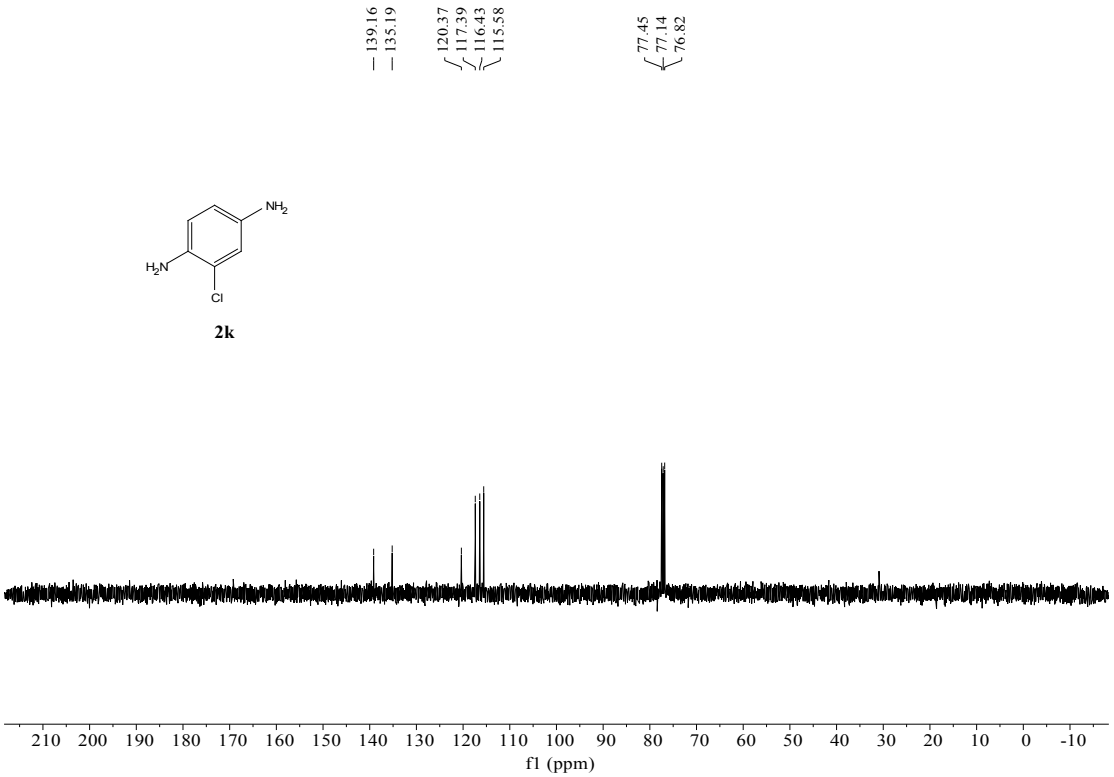

## $^{13}$C NMR, 100 MHz, $CDCl_3$



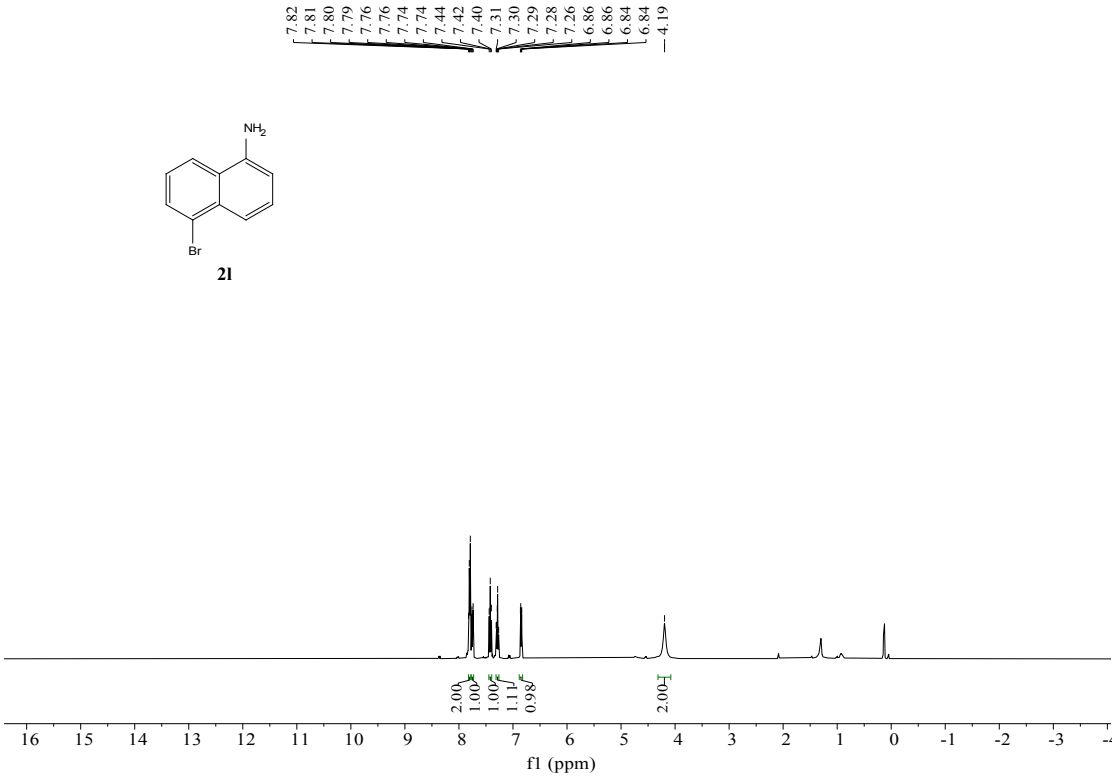
$^{1}$H NMR, 400 MHz, $CDCl_3$



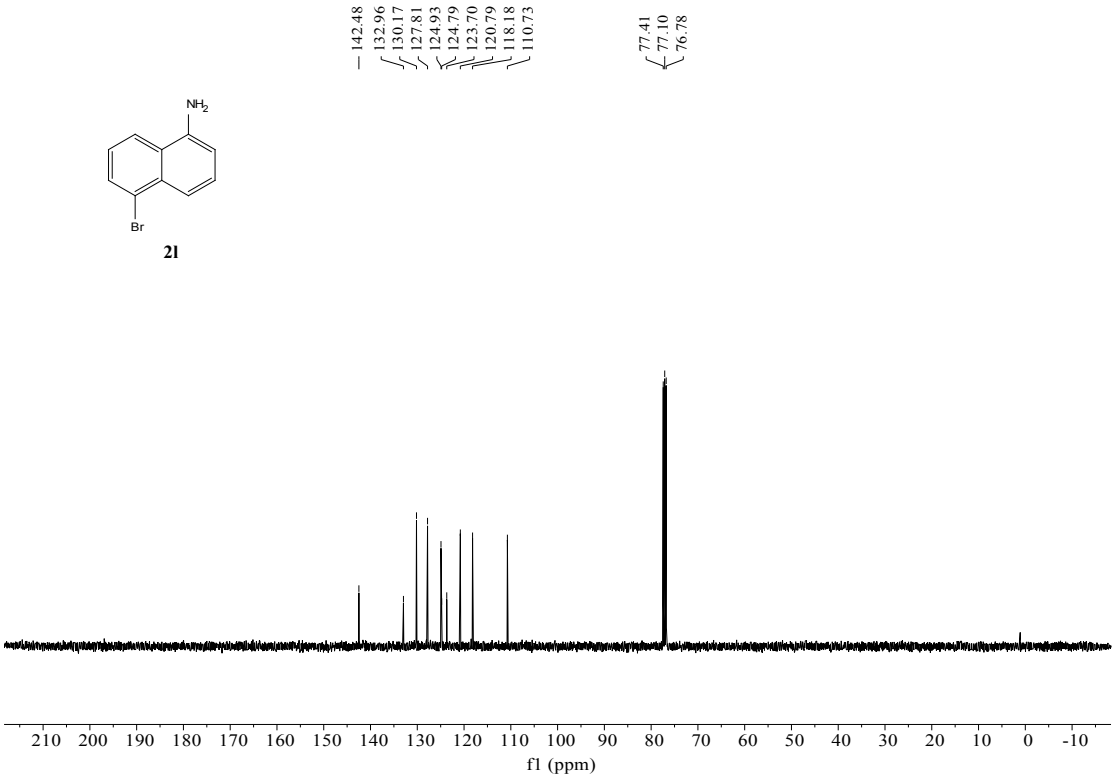

$^{13}$C NMR, 100 MHz, $CDCl_3$



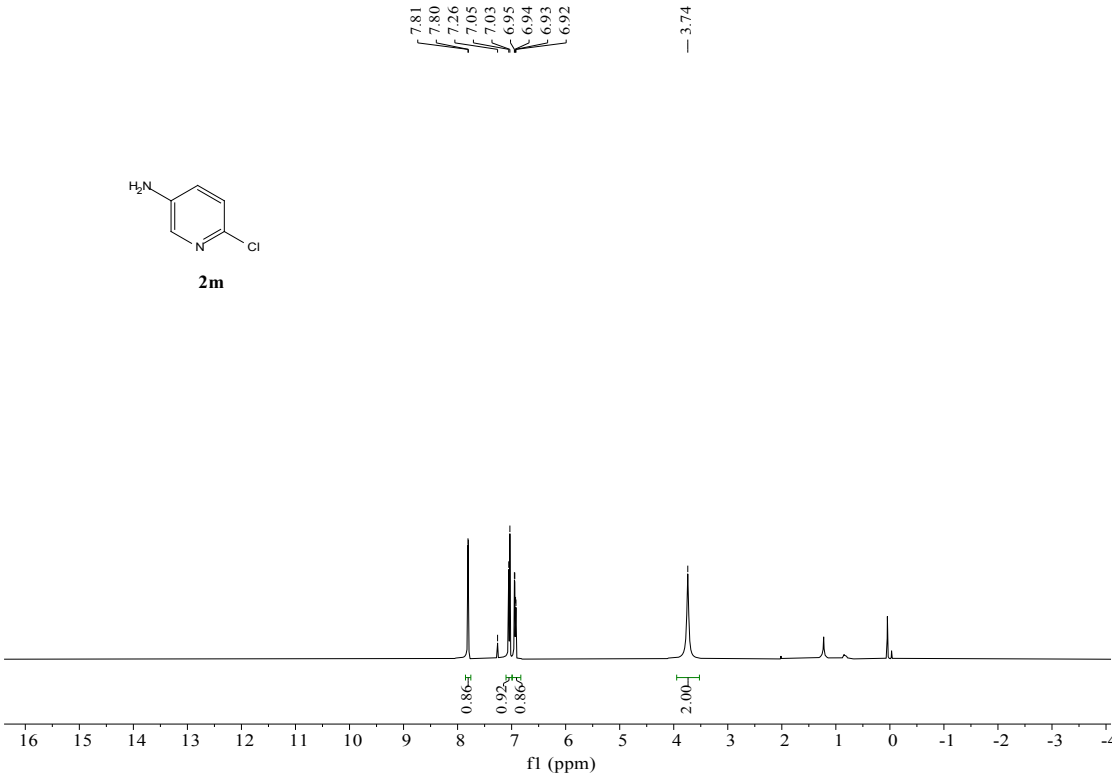
$^{1}$H NMR, 400 MHz, $CDCl_3$

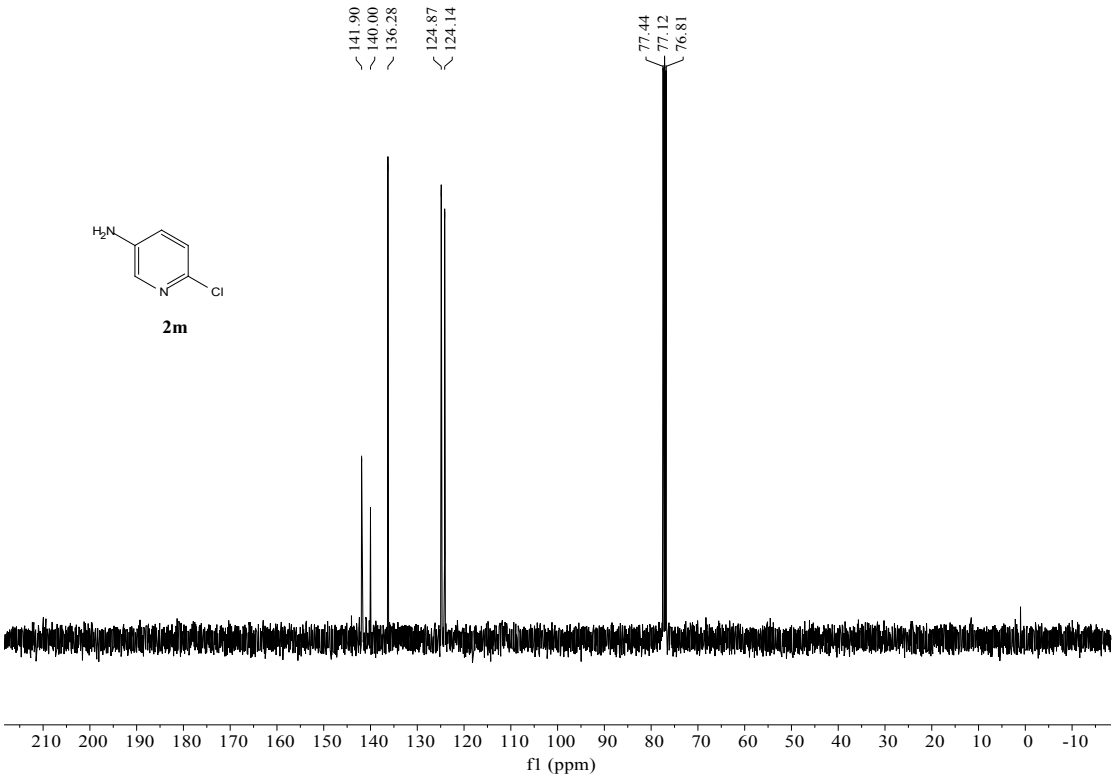



$^{13}$C NMR, 100 MHz, $CDCl_3$



$^{1}$H NMR, 400 MHz, $CDCl_3$




$^{13}$C NMR, 100 MHz, $CDCl_3$