Supporting Information

The synthesis and structure of an amazing and stable carbonized material Cu-PC@OFM and catalytic applications in water with mechanism explorations

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Table of contents

1. **General Experiments.**

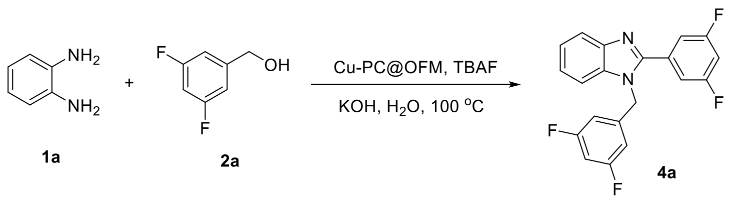
All the obtained products were characterized ^{1}H NMR spectra and ^{13}C NMR spectra (400 or 100 MHz). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; All the reagents were purchased from commercial sources and used without further purification.

2. Details of experimental procedures.

2.1. Synthesis of Cu-PC@OFM

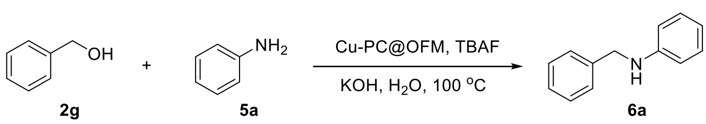
Cu-MOF-199 was synthesized to the procedure reported previously using trimesic acid as a modulator. Thereafter, the mixed solution was filtered, washed, and dried to obtain blue crystals. Afterward, the obtained solid was then placed in a muffle furnace and purged with nitrogen, raised to 400 °C at the rate of 1 °C/min, and reacted for 5 hours. Thereafter, the temperature was lowered to room temperature to obtain dark brown solid powder.

2.2. Typical procedure for the synthesis of 4a



In a 25ml Schlenk tube, benzene-1,2-diamine **1a** (1 mmol), KOH (1.5 mmol), Cu-PC@OFM (10mg), TBAF (0.15 mmol) and (3,5-difluorophenyl)methanol **2a** (2.6 mmol) were added followed by H_2O (4mL), and then the reaction mixture was heated at 100°C for 48h. After the reaction was completed, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether=1:20, v/v) to give 1-benzyl-2-aryl-1*H*-benzo[d]imidazole **4a**.

2.3. Typical procedure for the synthesis of 6a



In a 25ml Schlenk tube, phenylmethanol **2g** (1.2 mmol), KOH (1.0 mmol), Cu-PC@OFM (10mg), TBAF (0.15 mmol) and aniline **5a** (1.0 mmol) were added followed by H_2O (4mL), and then the reaction mixture was heated at 110°C for 48h. After the reaction was completed, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether=1:60, v/v) to give N-benzyl compound **6a**.

2.4. The original data of Leaching of the metal-catalysts experiments

The test data

Sample number	The sample quality m_0(g)	Constant volume V_0(mL)	Test element	The concentration of elements in the solution C_0(mg/L)	Dilution multiplef	Element concentration of digestion solution / original sample solution C_1 (mg/L)	Element content of sample C (mg/kg)	Element content of sample W(%)
1	0.9229	10	Cu	0.7238	1	0.7238	7.84	0.0008%

2.5. Hot filtration test for the reaction of phenylenediamine and benzyl alcohols

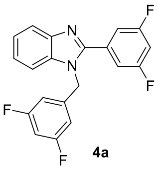
Entry	Catalyst	Time(h)	Yield
1	With catalyst	12	53
2	After filtration	24	53

CondItions: **1a** (1 mmol), **2a** (2.6 mmol), Cu-PC@OFM (10 mg), KOH (1.0 equiv.), TBAF (15 mol%), H_2O (4 mL), 100 ^oC.

3. Characterization Data

3.1 Characterization Data for 4a-4o

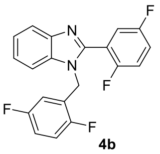
4a: 1-(3,5-difluorobenzyl)-2-(3,5-difluorophenyl)-1H-benzo[d]imidazole



4a

Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.88(d, *J*=8.0 Hz, 1H, Ar-H), 7.38-7.29(m, 2H, Ar-H), 7.22-7.19(m, 3H, Ar-H), 6.97-6.91(m, 1H, Ar-H), 6.79-6.73(m, 1H, Ar-H), 6.60(d, *J*=5.6 Hz, 2H, Ar-H), 5.43(s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm) 164.83 (d, JCF = 12.7 Hz), 164.25 (d, JCF = 12.8 Hz), 162.34 (d, JCF = 12.7 Hz), 161.76 (d, JCF = 12.8 Hz), 151.23, 142.90, 139.86, 135.84, 132.69, 124.08, 123.43, 120.53, 112.37, 112.10, 110.14, 109.06, 108.79, 105.59, 103.73, 47.63.

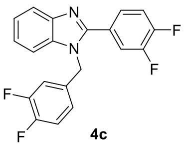
4b: 1-(2,5-difluorobenzyl)-2-(2,5-difluorophenyl)-1H-benzo[d]imidazole



4b

Yield: 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.87(d, *J*=7.2 Hz, 1H, Ar-H), 7.40-7.36(m, 1H, Ar-H), 7.37-7.30(m, 2H, Ar-H), 7.28-7.24(m, 1H, Ar-H), 7.21-7.16(m, 2H, Ar-H), 7.03-6.97(m, 1H, Ar-H), 6.94-6.88(m, 1H, Ar-H), 6.49-6.45(m, 1H, Ar-H), 5.36(s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm) 159.91 (dd, JCF = 6.1, 2.3 Hz), 157.23 (dd, JCF = 14.9, 2.5 Hz), 157.48 (dd, JCF = 7.3, 2.2 Hz), 154.81 (dd, JCF = 12.0, 2.6 Hz), 147.91, 143.23, 135.12, 123.82, 123.07, 120.47, 117.48, 117.32, 116.73, 116.57, 116.20, 116.05, 115.03, 114.80, 110.33, 42.14.

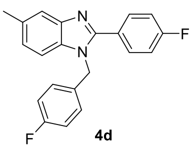
4c: 1-(3,4-difluorobenzyl)-2-(3,4-difluorophenyl)-1H-benzo[d]imidazole



4c

Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.89(d, *J*=4.8 Hz Hz, 1H, Ar-H), 7.55-7.50(m, 1H, Ar-H), 7.38-7.34(m, 2H, Ar-H), 7.33-7.29(m, 1H, Ar-H), 7.24-7.21(m, 2H, Ar-H), 7.18-7.11 (m, 1H, Ar-H), 6.93-6.88(m, 1H, Ar-H), 6.80(d, *J*=12.0 Hz, 1H, Ar-H), 5.39(s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm) 152.89 (d, JCF = 12.4 Hz), 152.12 (d, JCF=12.4 Hz), 150.36 (d, JCF = 12.5 Hz), 149.56 (d, JCF = 13.1 Hz), 148.69, 142.61, 135.63, 125.52, 123.91, 123.42, 121.87, 120.22, 118.72, 118.54, 118.30, 118.11, 117.93, 115.03, 110.21, 47.37.

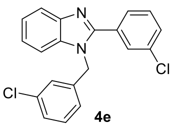
4d: 1-(4-fluorobenzyl)-2-(4-fluorophenyl)-5-methyl-1H-benzo[d]imidazole



4d

Yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.72 (d, *J*=8.0Hz, 1H, Ar-H), 7.63-7.58(m, 2H, Ar-H), 7.14-7.08(m, 3H, Ar-H), 7.06(s, 1H, Ar-H), 7.02-6.97 (m, 4H, Ar-H), 5.32(s, 2H, CH_2), 2.45(d, *J*=20.0Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm) 164.75 (d, JCF = 2.9 Hz),, 162.27 (d, JCF = 2.8 Hz) 160.87, 152.43, 143.29, 141.07, 136.06, 133.21, 132.43, 131.00, 127.47, 126.20, 124.35, 119.42, 116.02, 115.85, 115.64, 109.97, 47.50, 21.66.

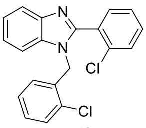
4e: 1-(3-chlorobenzyl)-2-(3-chlorophenyl)-1H-benzo[d]imidazole



4e

Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.88(d, *J*=8.0Hz, 1H, Ar-H), 7.72-7.71(m, 1H, Ar-H), 7.50-7.45(m, 2H, Ar-H), 7.39(d, *J*=8.0Hz, 1H, Ar-H), 7.36-7.32(m, 1H, Ar-H), 7.30-7.26(m, 3H, Ar-H), 7.24-7.21(m, 1H, Ar-H), 7.11(s, 1H, Ar-H), 6.94-6.92(d, *J*=8.0Hz, 1H, Ar-H), 5.40(s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm) 152.46, 143.06, 138.17, 135.91, 135.17, 134.94, 131.64, 130.45, 130.11, 130.02, 129.48, 128.25, 127.02, 126.19, 124.05, 123.61, 123.07, 120.29, 110.29, 47.86.

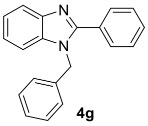
4f: 1-(2-chlorobenzyl)-2-(2-chlorophenyl)-1H-benzo[d]imidazole



4f

Yield: 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.89(d, *J*=8.0Hz, 1H, Ar-H), 7.51(d, *J*=8.0Hz, 1H, Ar-H), 7.46-7.41(m, 2H, Ar-H), 7.34-7.29(m, 3H, Ar-H), 7.28-7.25(m, 1H, Ar-H), 7.22(s, 1H, Ar-H), 7.20-7.15(m, 1H, Ar-H), 7.07-7.04(m, 1H, Ar-H), 6.64-6.62(d, *J*=8.0Hz, 1H, Ar-H), 5.36(s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm) 151.47, 143.03, 134.78, 134.33, 133.26, 132.35, 132.10, 131.37, 129.87, 129.65, 129.55, 128.94, 127.73, 127.07, 126.91, 123.34, 122.68, 120.34, 110.48, 45.67.

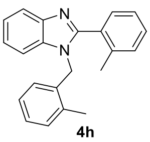
4g: 1-benzyl-2-phenyl-1H-benzo[d]imidazole



4g

Yield: 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.87(d, *J*=8.0Hz, 1H, Ar-H), 7.69-7.67(m, 2H, Ar-H), 7.46-7.43(m, 3H, Ar-H), 7.34-7.28(m, 4H, Ar-H), 7.22-7.18(m, 2H, Ar-H), 7.10-7.08(d, *J*=8.0Hz, 2H, Ar-H), 5.44(s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm) 154.08, 143.12, 136.33, 136.00, 130.03, 129.83, 129.20, 128.97, 128.67, 127.70, 125.91, 122.97, 122.60, 119.92, 110.45, 48.30.

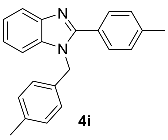
4h: 1-(2-methylbenzyl)-2-(o-tolyl)-1H-benzo[d]imidazole



4h

Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.87(d, *J*=8.0Hz, 1H, Ar-H), 7.32(d, *J*=8.0Hz, 1H, Ar-H), 7.28-7.24(m, 3H, Ar-H), 7.21-7.18(m, 1H, Ar-H), 7.16-7.13(m, 2H, Ar-H), 7.10-7.07(m, 2H, Ar-H), 6.99-6.95(m, 1H, Ar-H), 6.63-6.61(d, *J*=8.0Hz, 1H, Ar-H), 5.15(s, 2H, CH_2), 2.22(s, 3H, CH_3), 2.11(s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm) 153.65, 142.92, 138.10, 134.85, 134.59, 133.81, 130.34, 130.14, 129.62, 129.57, 127.29, 126.10, 125.81, 125.38, 122.59, 122.10, 119.78, 110.31, 45.52, 19.56, 18.78.

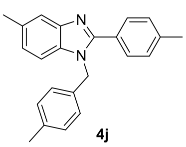
4i: 1-(4-methylbenzyl)-2-(p-tolyl)-1H-benzo[d]imidazole



4i

Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.85(d, *J*=8.0Hz, 1H, Ar-H), 7.58(d, *J*=8.0Hz, 2H, Ar-H), 7.29-7.25(m, 1H, Ar-H), 7.24(s, 1H, Ar-H), 7.22-7.17(m, 3H, Ar-H), 7.11-7.09(d, *J*=8.0Hz, 2H, Ar-H), 6.98-6.96(d, *J*=8.0Hz , 2H, Ar-H), 5.36(s, 2H, CH_2), 2.37(s, 3H, CH_3), 2.30(s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm) 154.15, 143.03, 139.85, 137.26, 135.96, 133.32, 129.53, 129.28, 129.02, 127.06, 125.76, 122.68, 122.39, 119.65, 110.37, 48.01, 21.25, 20.91.

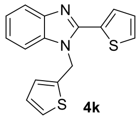
4j: 5-methyl-1-(4-methylbenzyl)-2-(p-tolyl)-1H-benzo[d]imidazole



4j

Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.56-7.54(m, 2H, Ar-H), 7.18-7.15(m, 2H, Ar-H), 7.08-7.03(m, 3H, Ar-H), 7.00-6.96(m, 1H, Ar-H), 6.93-6.90(m, 3H, Ar-H), 5.26(s, 2H, CH_2), 2.40(d, *J*=8.0Hz, 1H, CH_3), 2.32(s, 3H, CH_3), 2.26(d, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm) 153.87, 153.50, 143.28, 141.08, 139.48, 139.42, 136.94, 136.15, 133.97, 133.36, 132.45, 131.76, 129.36, 129.05, 128.75, 127.12, 125.50, 123.83, 119.31, 119.04, 109.99, 109.72, 47.64, 21.49, 21.04, 20.72.

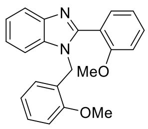
4k: 2-(thiophen-2-yl)-1-(thiophen-2-ylmethyl)-1H-benzo[d]imidazole



4k

Yield: 74%. ^{1}H NMR (400 MHz, DMSO) δ(ppm) 7.82(d, *J*=8.0Hz, 1H, Ar-H), 7.74-7.68(m, 3H, Ar-H), 7.40(d, *J*=8.0Hz, 1H, Ar-H), 7.31-7.24(m, 3H, Ar-H), 7.04 (d, *J*=4.0Hz, 1H, Ar-H), 6.97-6.95(m, 1H, Ar-H), 5.94(s, 2H, CH_2). ^{13}C NMR (101 MHz, DMSO) δ(ppm) 146.71, 142.36, 139.27, 135.78, 132.01, 129.60, 128.33, 127.81, 126.99, 126.01, 125.89, 122.86, 122.52, 118.90, 110.74, 43.00.

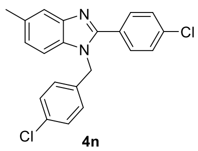
4m: 1-(2-methoxybenzyl)-2-(2-methoxyphenyl)-1H-benzo[d]imidazole



4m

Yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.87(d, *J*=4.0Hz, 1H, Ar-H), 7.66(d, *J*=8.0Hz, 2H, Ar-H), 7.33-7.28(m, 1H, Ar-H), 7.23-7.21(m, 2H, Ar-H), 7.05-6.97(m, 4H, Ar-H), 6.86(d, *J*=12.0Hz, 2H, Ar-H), 5.38(s, 1H, CH_2), 3.85(s, 3H, CH_3), 3.79(s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm) 160.91, 159.05, 153.99, 143.07, 136.00, 130.61, 128.39, 127.13, 122.63, 122.41, 122.37, 119.60, 114.34, 114.10, 110.33, 55.25, 55.17, 47.77.

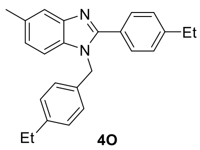
4n: 1-(4-chlorobenzyl)-2-(4-chlorophenyl)-5-methyl-1H-benzo[d]imidazole



4n

Yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.74-7.60(m, 1H, Ar-H), 7.56-7.54(m, 2H, Ar-H), 7.40-7.38(m, 2H, Ar-H), 7.28-7.26(m, 2H, Ar-H), 7.14-7.03(m, 1H, Ar-H), 7.00-6.96(m, 3H, Ar-H), 5.32(s, 1H, CH_2), 2.48-2.40(m, 3H, CH_3).^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm) 152.55, 152.18, 143.26, 141.07, 136.08, 134.67, 133.90, 133.57, 133.41, 132.57, 130.17, 129.18, 128.90, 128.38, 127.06, 124.77, 124.49, 119.49, 109.92, 47.46, 21.69.

4o: 1-(4-ethylbenzyl)-2-(4-ethylphenyl)-5-methyl-1H-benzo[d]imidazole

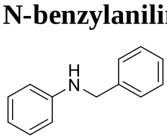


4O

Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.73(d, *J*=8.0Hz, 1H, Ar-H), 7.61-7.58(m, 2H, Ar-H), 7.25-7.22(m, 2H, Ar-H), 7.14-7.08(m, 3H, Ar-H), 7.01-6.97(m, 3H, Ar-H), 5.34(s, 2H, CH_2), 2.69-2.59(m, 4H, $2CH_2$), 2.39(s, 3H, CH_3), 1.25-1.17(m, 6H, $2CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm) 154.11, 153.74, 145.90, 143.49, 143.42, 141.22, 136.31, 134.11, 133.76, 132.64, 131.97, 129.03, 128.34, 128.04, 127.45, 125.74, 123.98, 119.48, 119.20, 110.16, 47.90, 28.31, 21.67, 15.17.

3.2 Characterization Data for 6a-6o

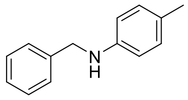
N-benzylaniline (6a)



6a

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.37-7.31 (m, 4H, Ar-H), 7.29-7.26 (m, 1H, Ar-H), 7.17 (t, J = 8.0 Hz，2H, Ar-H), 6.71 (t, J = 8.0 Hz, 1H, Ar-H), 6.63 (d, J = 7.6 Hz, 2H, Ar-H), 4.32 (s, 2H, CH_2), 4.01 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.10, 139.38, 129.23, 128.60, 127.47, 127.19, 117.51, 112.79, 48.26.

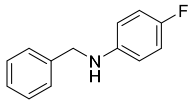
N-benzyl-4-methylaniline (6b)



6b

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.37-7.22 (m, 5H, Ar-H), 6.98 (d, J = 8.4 Hz, 2H, Ar-H), 6.57-6.54 (m, 2H, Ar-H), 4.30 (s, 2H, CH_2), 3.89 (s, 1H, NH), 2.23 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.88, 139.61, 129.71, 128.56, 127.45, 127.11, 126.70, 112.94, 48.58, 20.36.

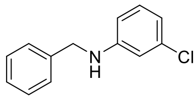
N-benzyl-4-fluoroaniline (6c)



6c

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.34-7.23 (m, 5H, Ar-H), 6.86 (t, J = 8.8 Hz, 2H, Ar-H), 6.57-6.53 (m, 2H, Ar-H), 4.27 (s, 2H, CH_2), 3.88 (s, 1H, NH); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 157.15, 154.81, 144.54, 139.31, 128.66, 127.48, 127.30, 115.77, 115.54, 113.76 (d, JCF = 7.4 Hz), 49.02.

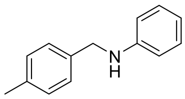
N-benzyl-3-chloroaniline (6d)



6d

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.35-7.23 (m, 5H, Ar-H), 7.05 (t, J = 8.0 Hz, 1H, Ar-H), 6.68-6.65 (m, 1H, Ar-H), 6.60 (t, J = 2.2 Hz, 1H, Ar-H), 6.78(dd, J = 1.6, 8.0 Hz, 1H, Ar-H), 4.29 (s, 2H, CH_2), 4.09 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 149.16, 138.69, 134.96, 130.17, 128.69, 127.42, 127.40, 117.35, 112.42, 111.08, 48.03.

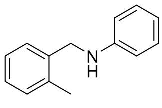
N-(4-methylbenzyl)aniline (6e)



6e

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.27-7.13 (m, 6H, Ar-H), 6.70(t, J = 7.2Hz, 1H, Ar-H), 6.62 (d, J = 7.6 Hz, 2H, Ar-H), 4.27 (s, 2H, CH_2), 3.96 (s, 1H, NH), 2.34 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.17, 136.83, 136.30, 129.27, 129.21, 127.48, 117.43, 112.77, 48.01, 21.07.

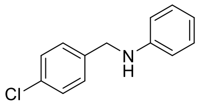
N-(2-methylbenzyl)aniline (6f)



6f

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.42-7.24 (m, 6H, Ar-H), 6.80 (t, J = 7.6 Hz, 1H, Ar-H), 6.71 (d, J = 7.6 Hz, 2H, Ar-H), 4.34 (s, 2H, CH_2), 3.90 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.24, 136.95, 136.31, 130.37, 129.24, 128.21, 127.38, 126.12, 117.40, 112.63, 46.32, 18.91.

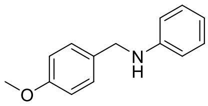
N-(4-chlorobenzyl)aniline (6g)



6g

^{1}H NMR (400 MHz, CDCl3) δ (ppm) 7.30 (s, 4H, Ar-H), 7.20 – 7.15 (m, 2H, Ar-H), 7.11 – 7.02 (m, 1H, Ar-H), 6.72 (t, J = 7.3 Hz, 1H, Ar-H), 6.60 (d, J = 8.5 Hz, 2H, Ar-H), 4.31 (s, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 147.80, 137.97, 132.85, 129.27, 128.81, 128.73, 117.78, 114.09, 113.76, 112.86, 47.58.

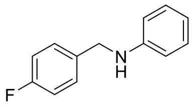
N-(4-methoxybenzyl)aniline (6h)



6h

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.30-7.15 (m, 4H, Ar-H), 6.89-6.86(m, 2H, Ar-H), 6.71(t, J = 7.6 Hz, 1H, Ar-H), 6.63 (d, J = 7.6Hz, 2H, Ar-H), 4.24 (s, 2H, CH_2), 3.94 (s, 1H, NH), 3.79 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 158.79, 148.15, 131.35, 129.21, 128.77, 117.45, 113.96, 112.78, 55.26, 47.73.

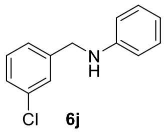
N-(4-fluorobenzyl)aniline (6i)



6i

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.34-7.15 (m, 4H, Ar-H), 7.01(t, J = 8.8 Hz, 3H, Ar-H), 6.72 (t, J = 7.2 Hz, 1H, Ar-H), 6.61 (d, J = 7.6 Hz, 2H, Ar-H), 4.28 (s, 2H, CH_2), 4.00 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.21, 160.77, 147.88, 135.06, 129.25, 128.95 (d, JCF =7.9 Hz), 117.68, 115.50, 115.29, 112.81, 47.54.

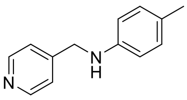
N-(3-chlorobenzyl)aniline (6j)



6j

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.41 (s, 1H, Ar-H), 7.40 – 7.29 (m, 3H, Ar-H), 7.21-7.25 (m, 2H, Ar-H), 6.81 (d, J=7.4Hz, 1H, Ar-H), 6.50 (d, J=8.6Hz, 2H, Ar-H), 4.20(s, 2H, CH_2), 4.12(s, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 147.81, 147.78, 134.56, 129.80, 129.34, 127.50, 127.42, 125.44, 117.92, 112.90, 47.82.

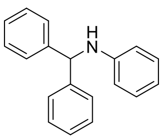
4-methyl-N-(pyridin-4-ylmethyl)aniline (6k)



6k

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.53 (d, J = 6.0 Hz, 2H, Py-H), 7.28 (d, J = 6.0 Hz, 2H, Py-H), 6.97 (d, J = 8.0 Hz, 2H, Ar-H), 6.50 (d, 2H, J = 8.4 Hz, Ar-H), 4.35 (s, 2H, CH_2), 4.11 (s, 1H, NH), 4.02 (s, 1H, NH), 2.23 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 149.87, 149.20, 145.10, 129.79, 127.25, 122.04, 112.94, 47.30, 20.32.

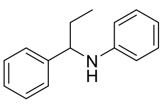
N-benzhydrylaniline (6l)



6l

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.39-7.29 (m, 8H, Ar-H), 7.27-7.23 (m, 3H, Ar-H), 6.70-6.66 (m, 1H, Ar-H), 5.09 (s, 1H, CH), 4.22 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 147.30, 142.88, 129.09, 128.72, 127.41, 127.32, 120.59, 117.60, 113.42, 63.00.

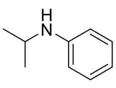
N-(1-phenylpropyl)aniline (6m)



6m

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.34-7.28 (m, 4H, Ar-H), 7.23-7.19 (m, 1H, Ar-H), 7.09-7.05 (m, 2H, Ar-H), 4.22 (t, J = 6.8 Hz，1H, CH), 4.05 (s, 1H, NH), 1.84-1.79 (m, 2H, CH_2), 0.95 (t, J = 7.6 Hz，3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 147.50, 143.90, 129.05, 128.46, 126.85, 126.45, 117.09, 113.22, 59.70, 31.63, 10.79.

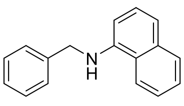
N-isopropylaniline (6n)



6n

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.18-7.14 (m, 2H, Ar-H), 6.69-6.57 (m, 3H, Ar-H), 3.65-3.59 (m, 1H, CH), 3.45-3.39 (m, 1H, NH), 1.20 (d, J = 6.4 Hz, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 147.42, 129.23, 116.92, 113.20, 44.16, 30.98, 22.97.

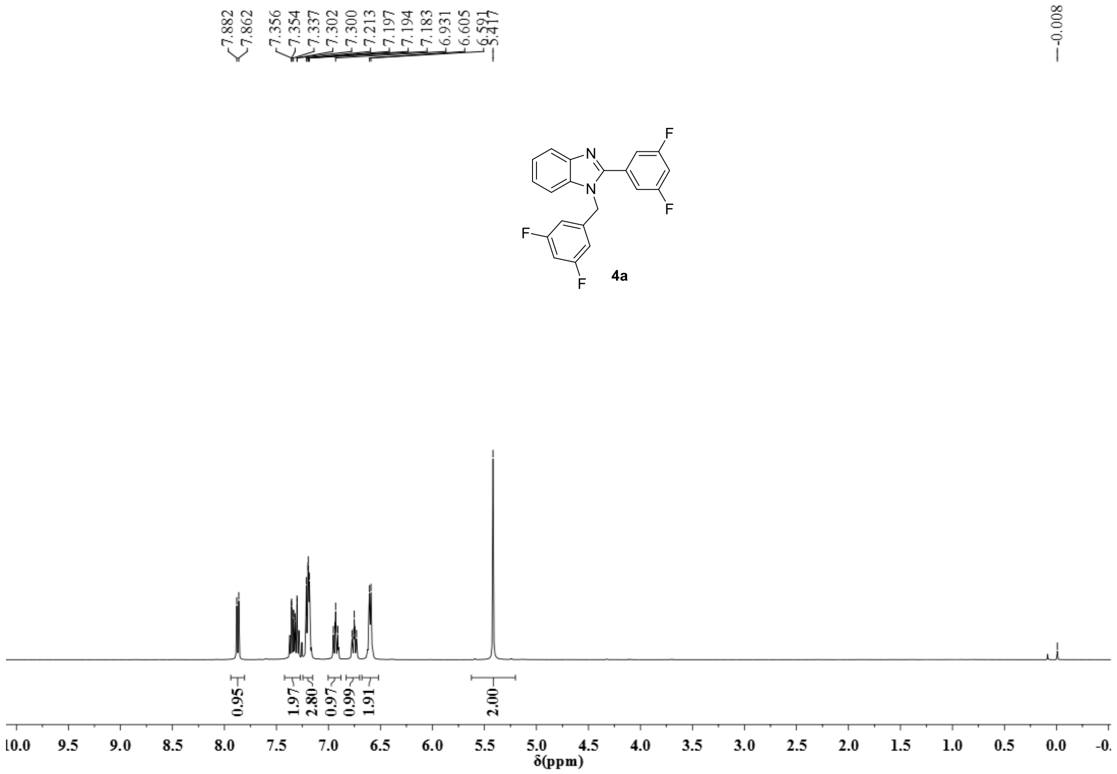
N-benzylnaphthalen-1-amine (6o)

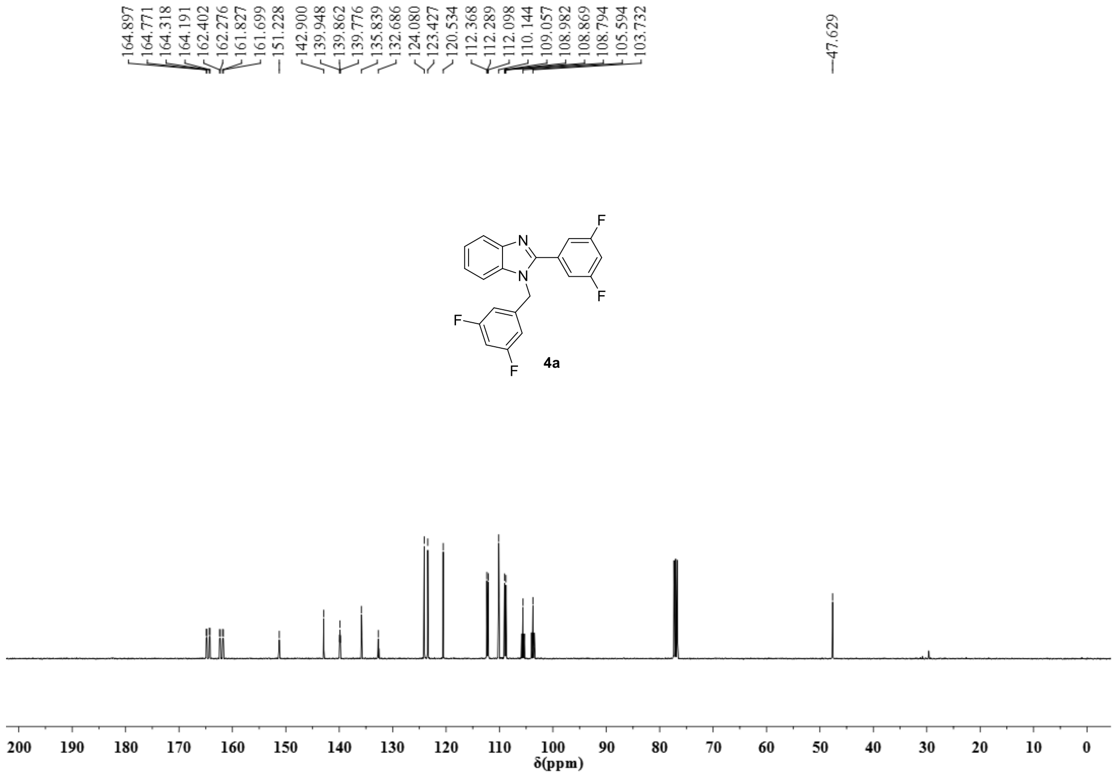


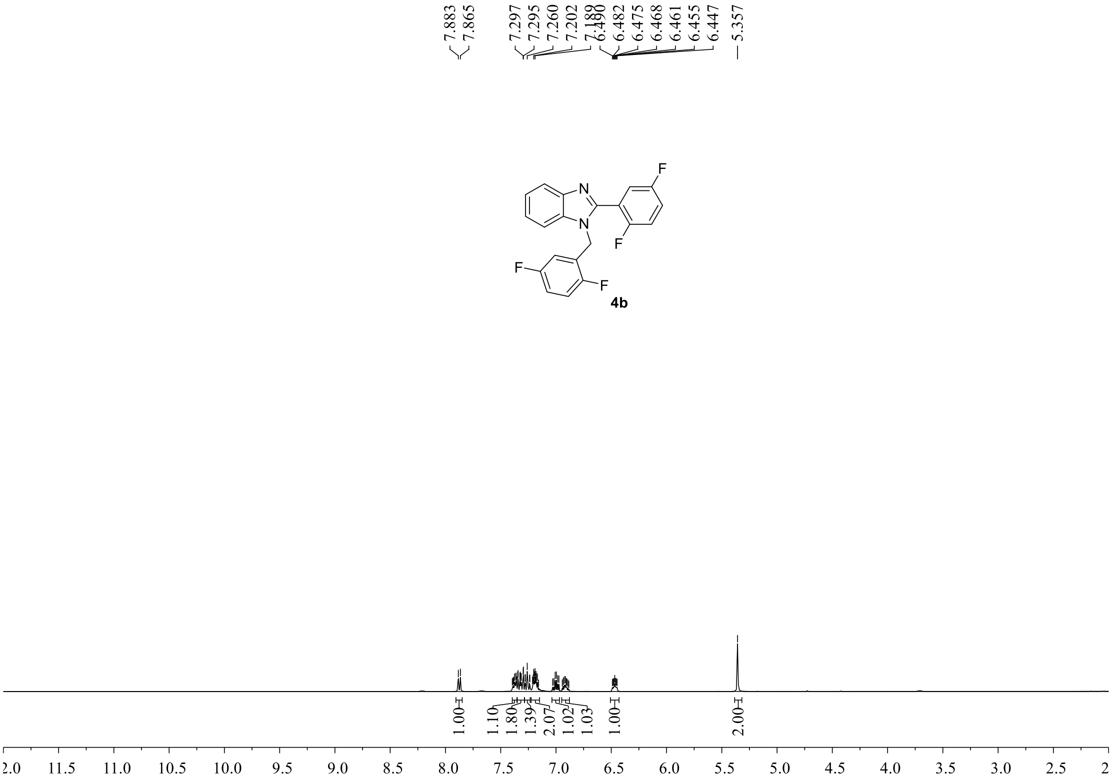
6o

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80 (d, J = 8.0 Hz, 2H, Ar-H), 7.35 (ddd, J = 52.9, 33.1, 12.3 Hz, 9H, Ar-H), 6.62 (d, J = 7.1 Hz, 1H, Ar-H), 4.69 (s, 1H, NH), 4.48 (s, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 143.14, 139.03, 134.22, 128.68, 127.70, 127.36, 126.57, 125.72, 124.72, 123.29, 119.85, 117.58, 104.68, 48.55.

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



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F
F
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1.02
1.03
1.00
2.00
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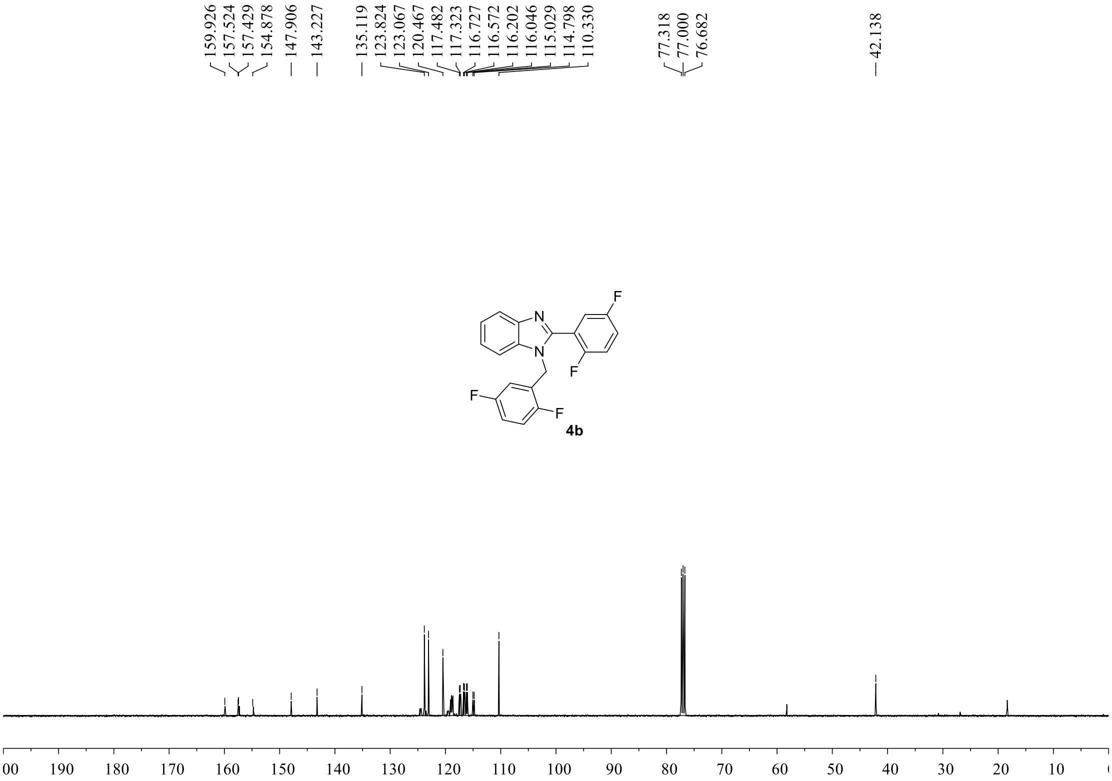
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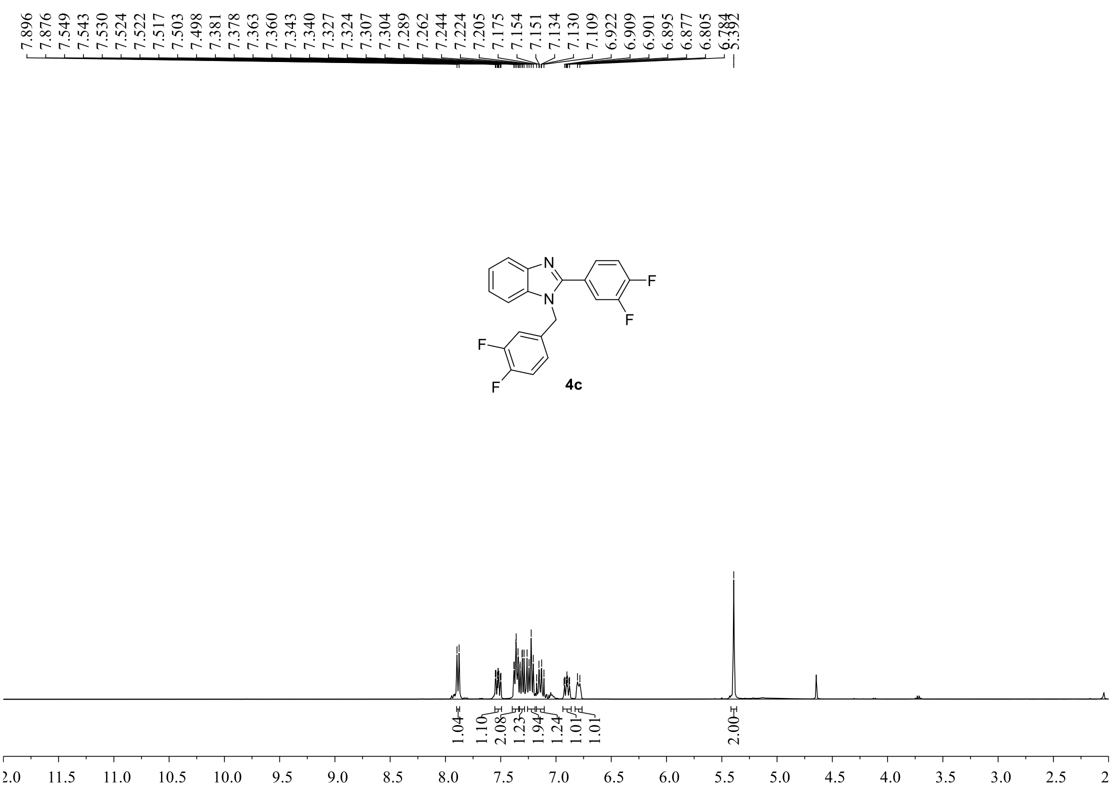
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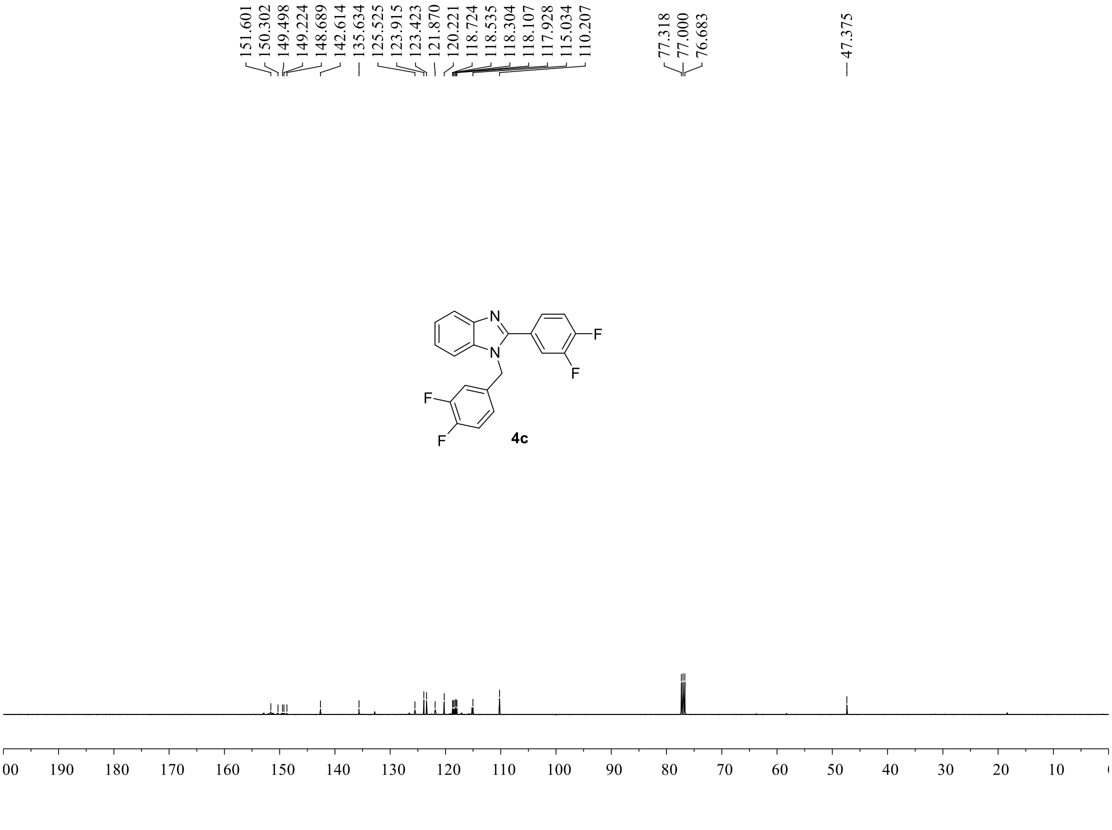
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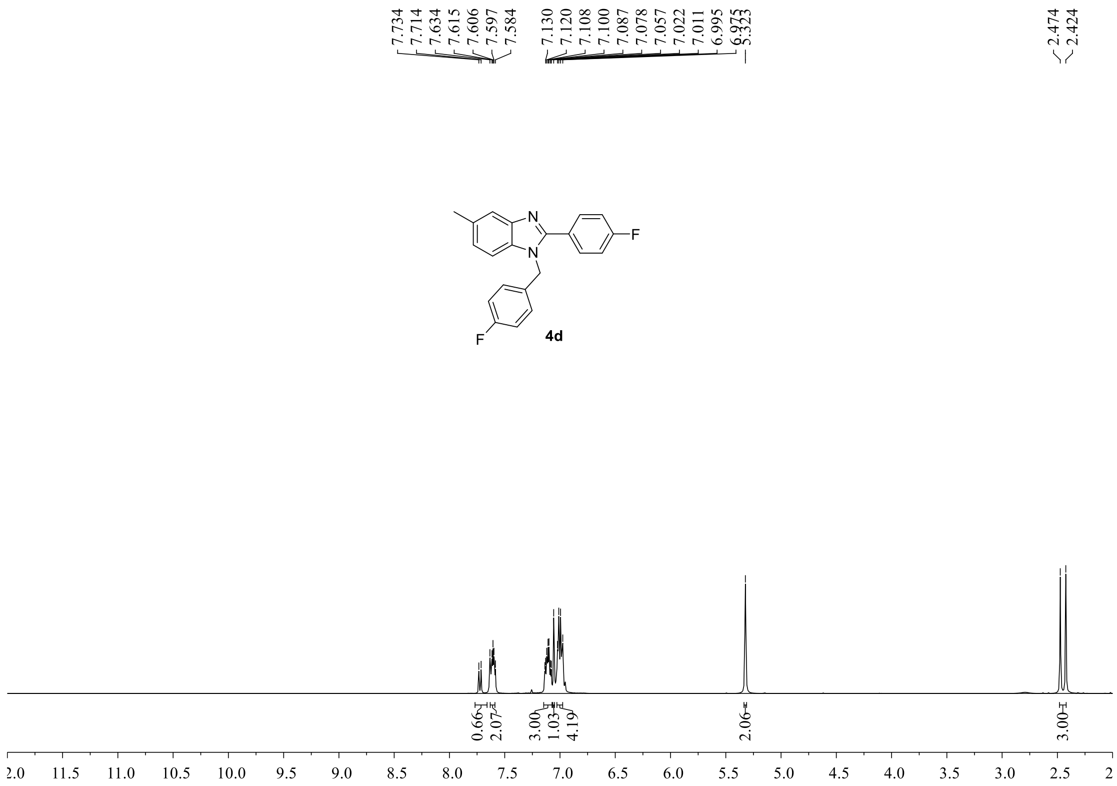
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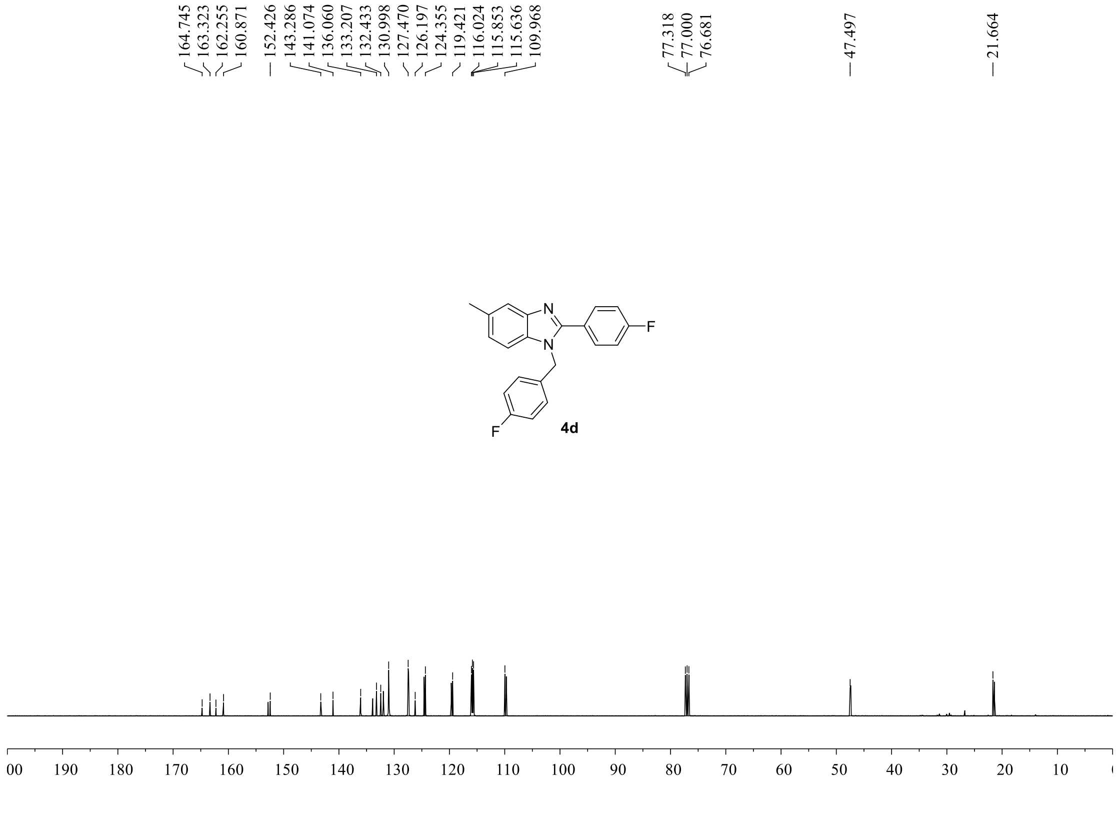
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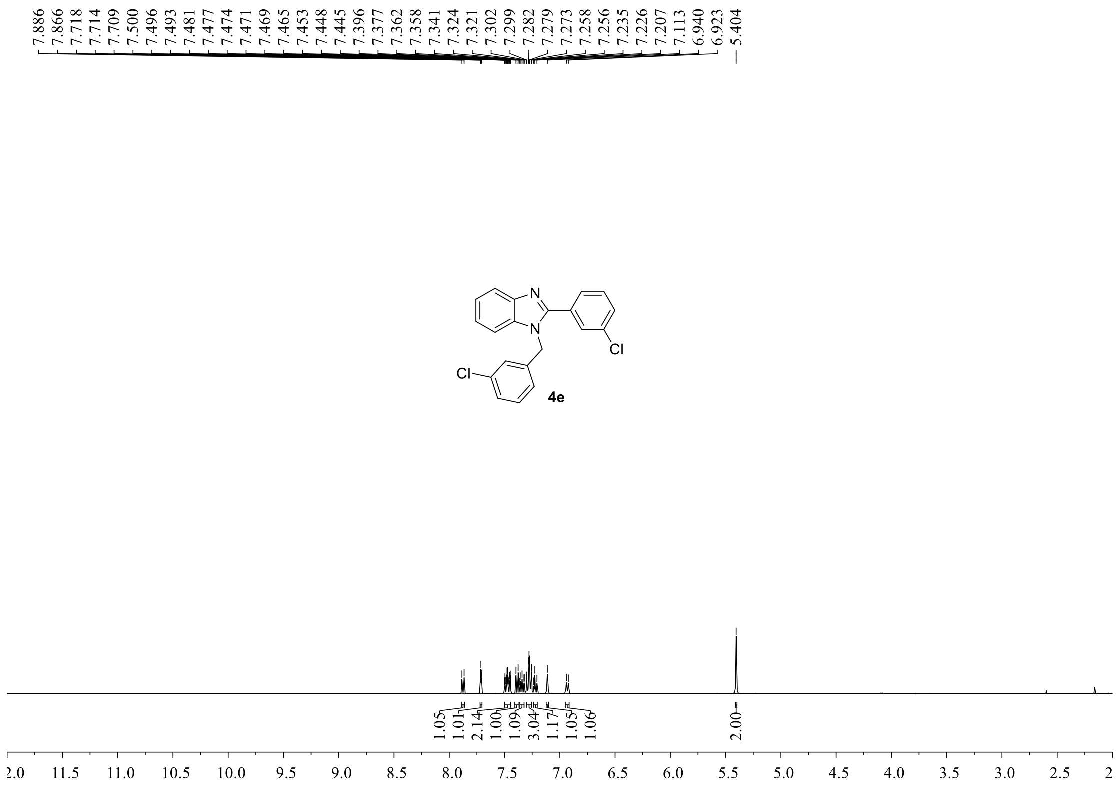
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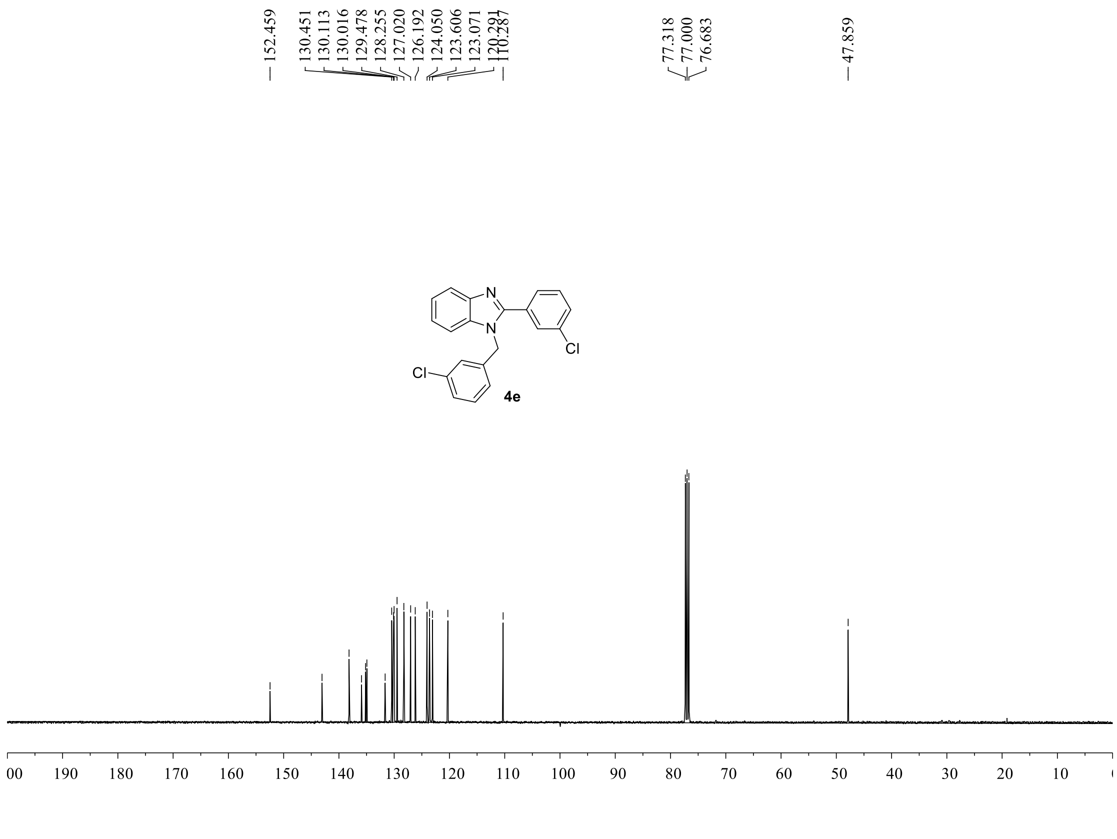
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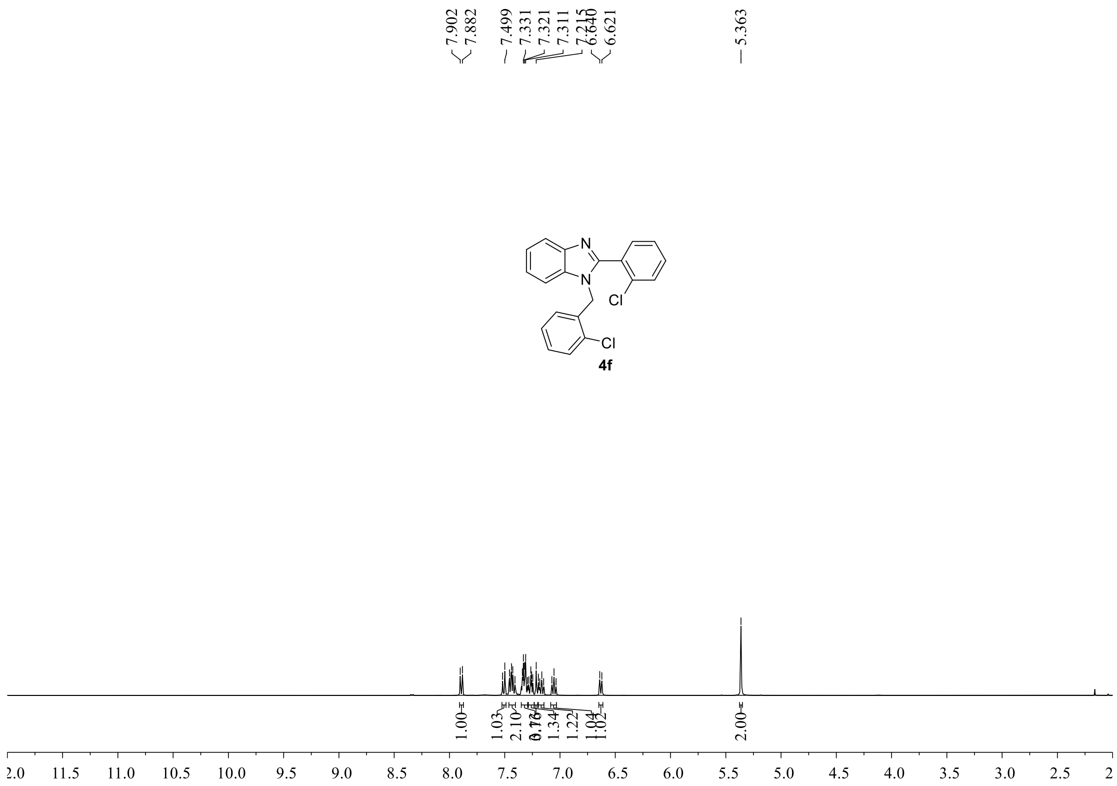
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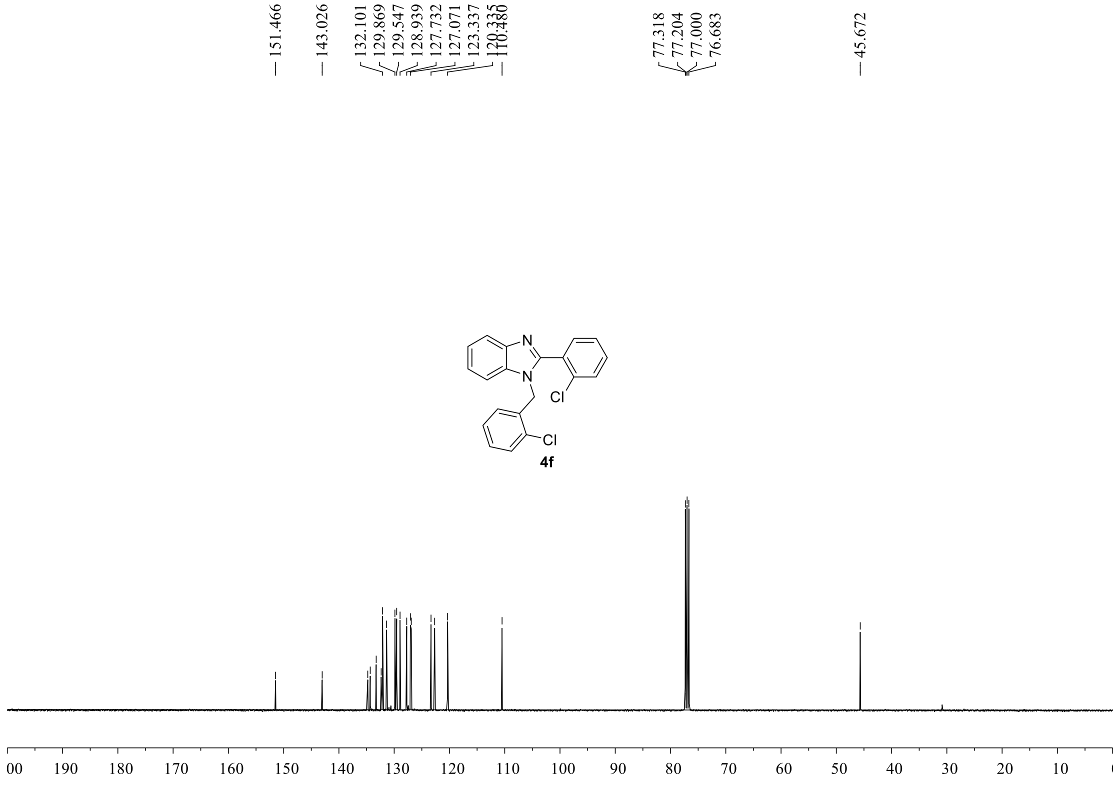
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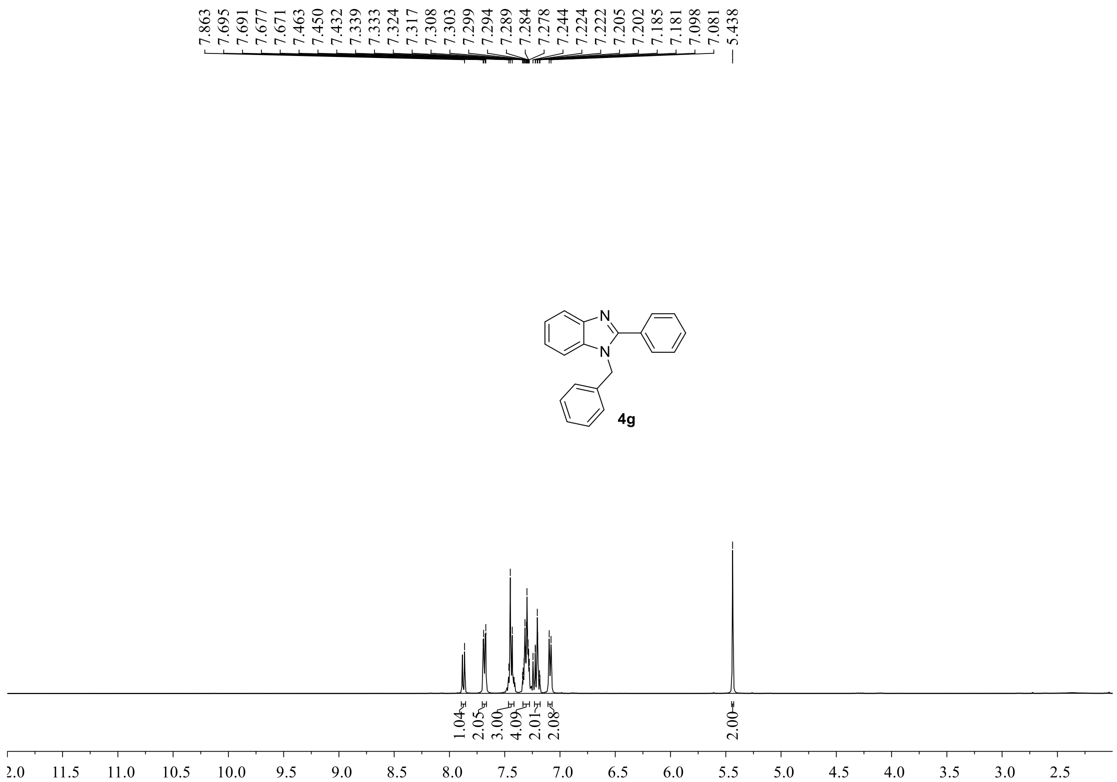
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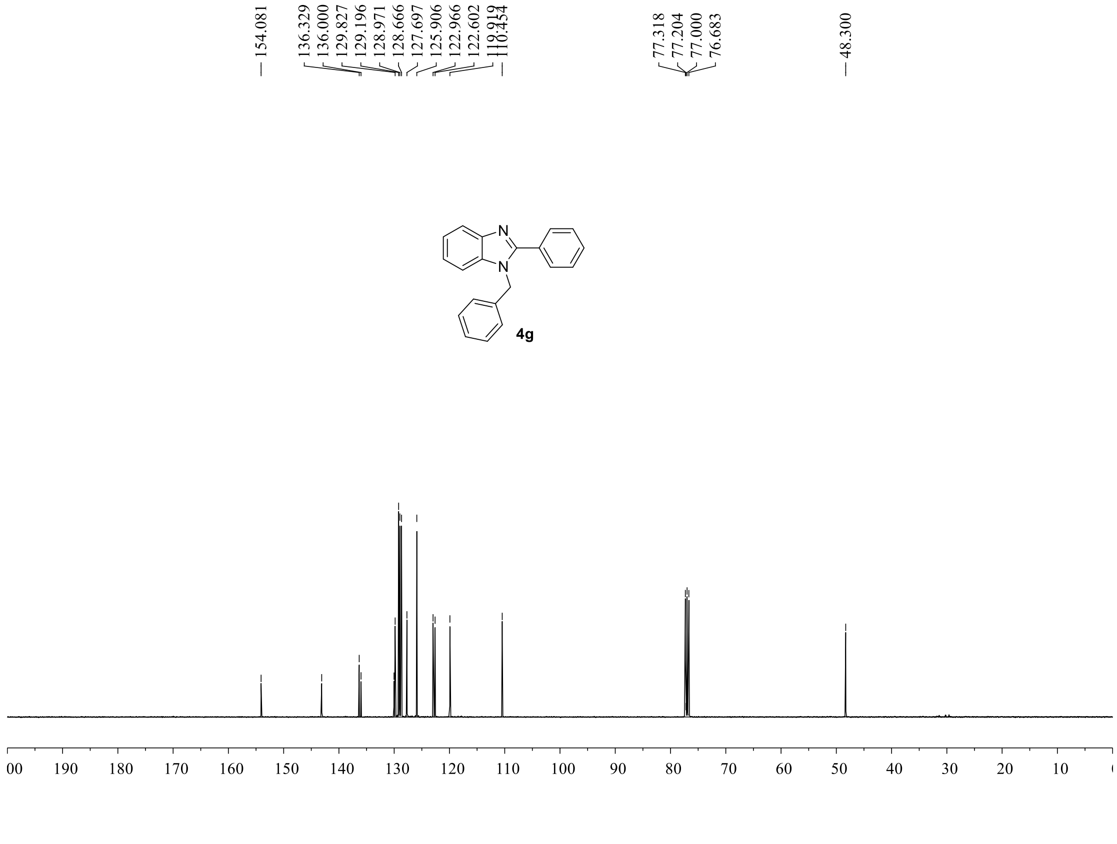
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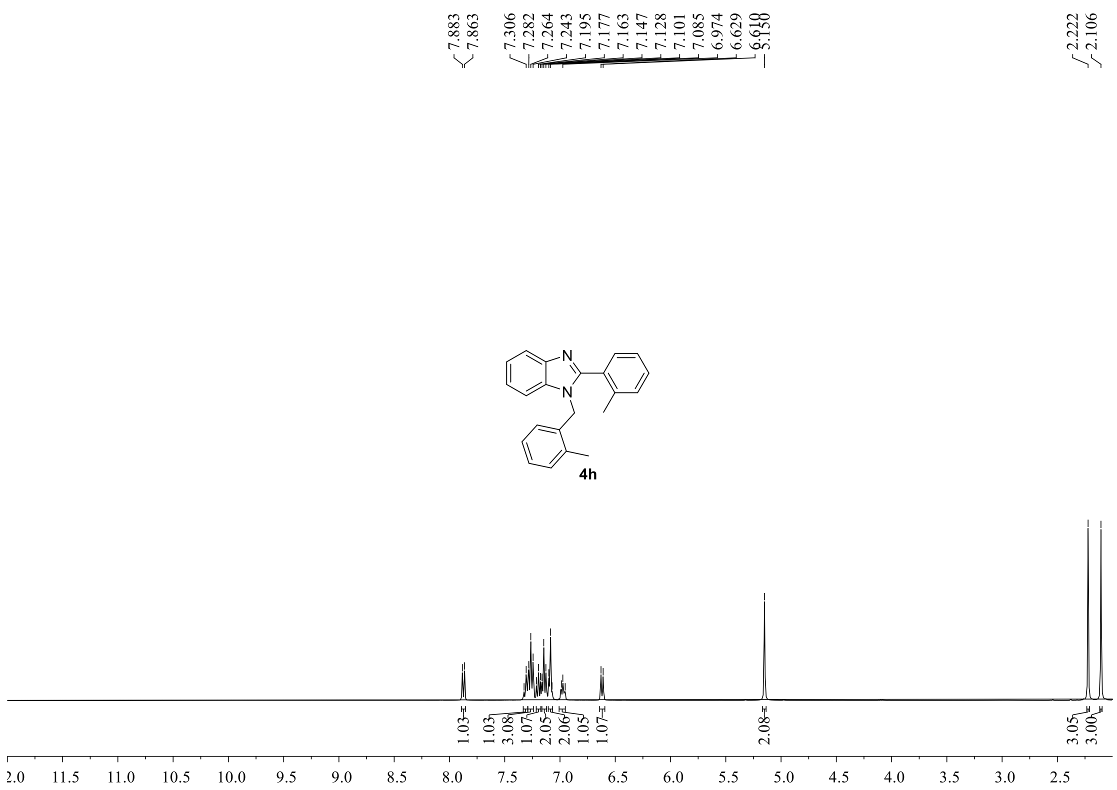
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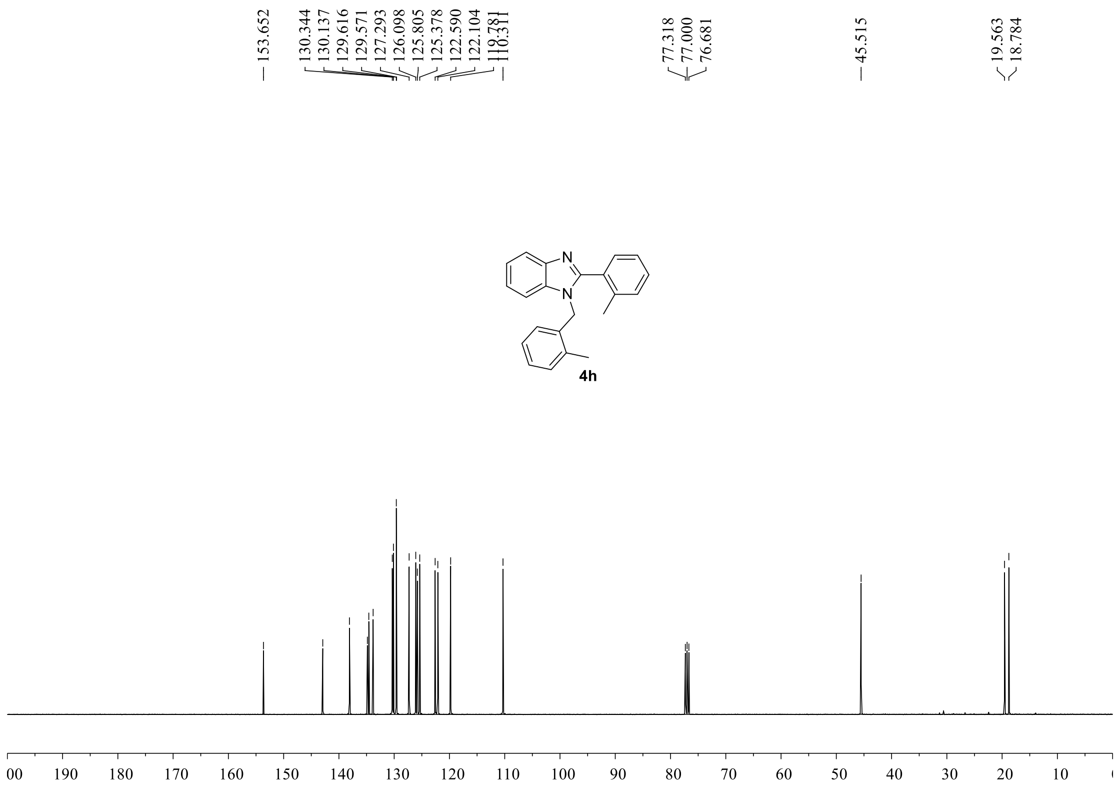
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77.000
76.681
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19.563
18.784
N
N
4h
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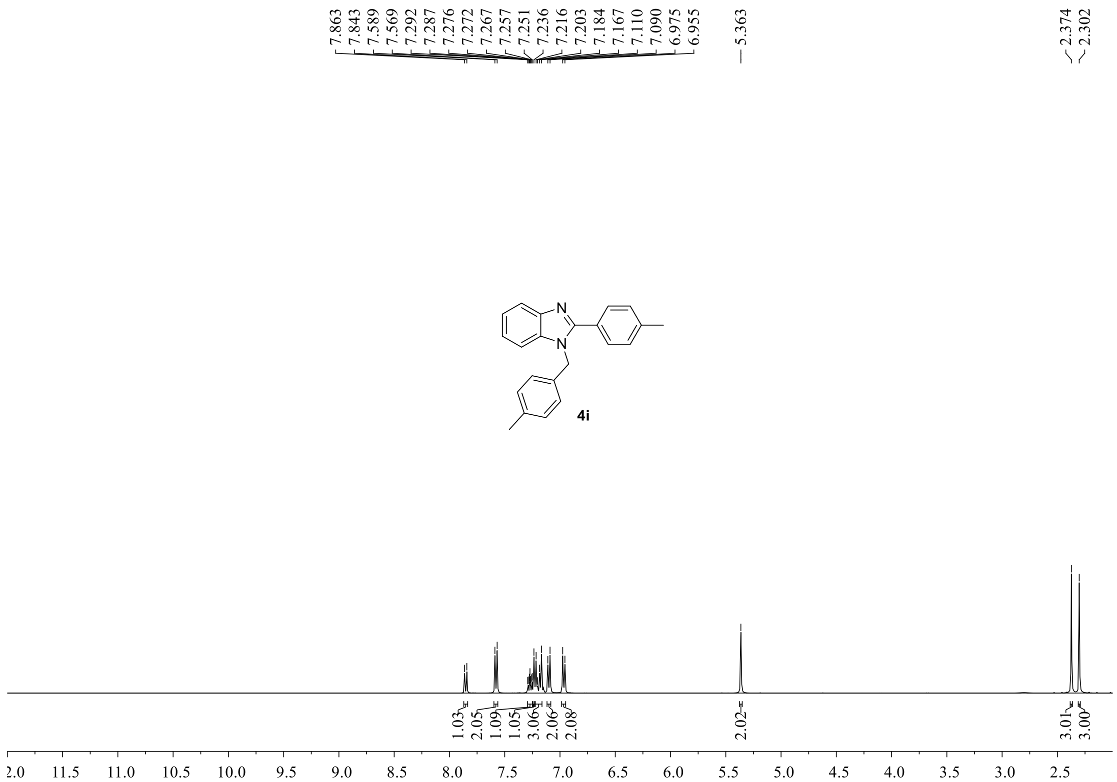
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6.955
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2.302
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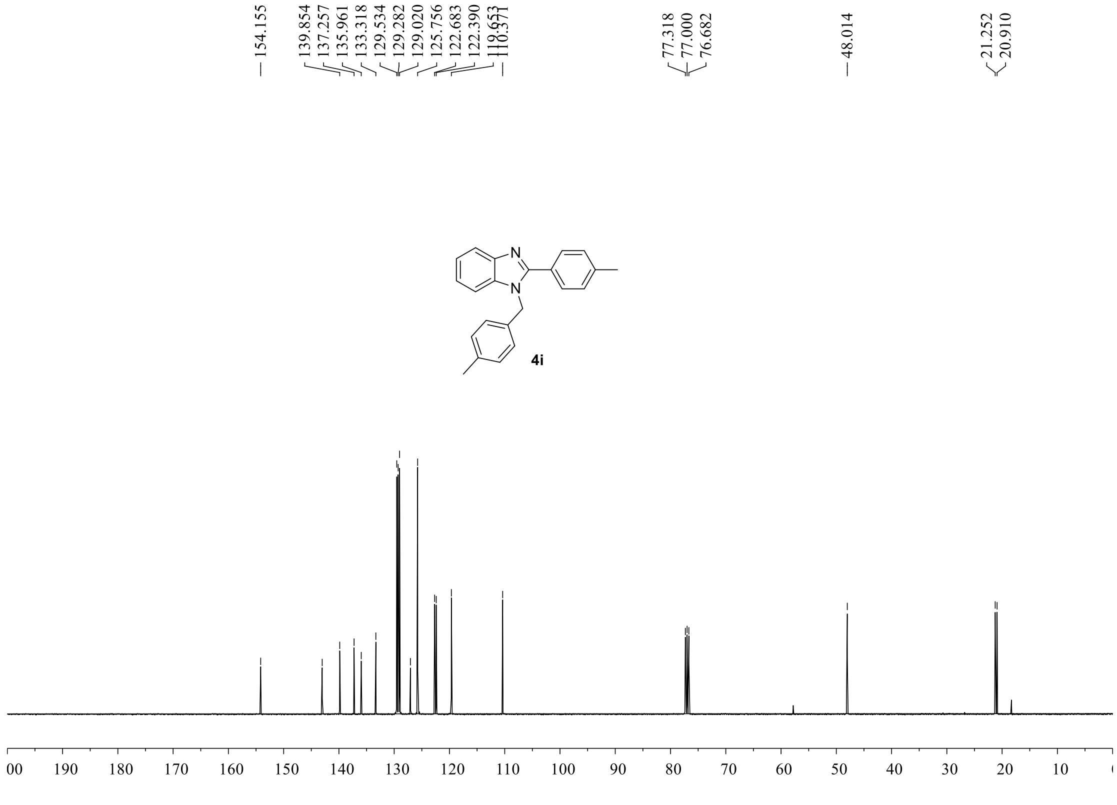
3.00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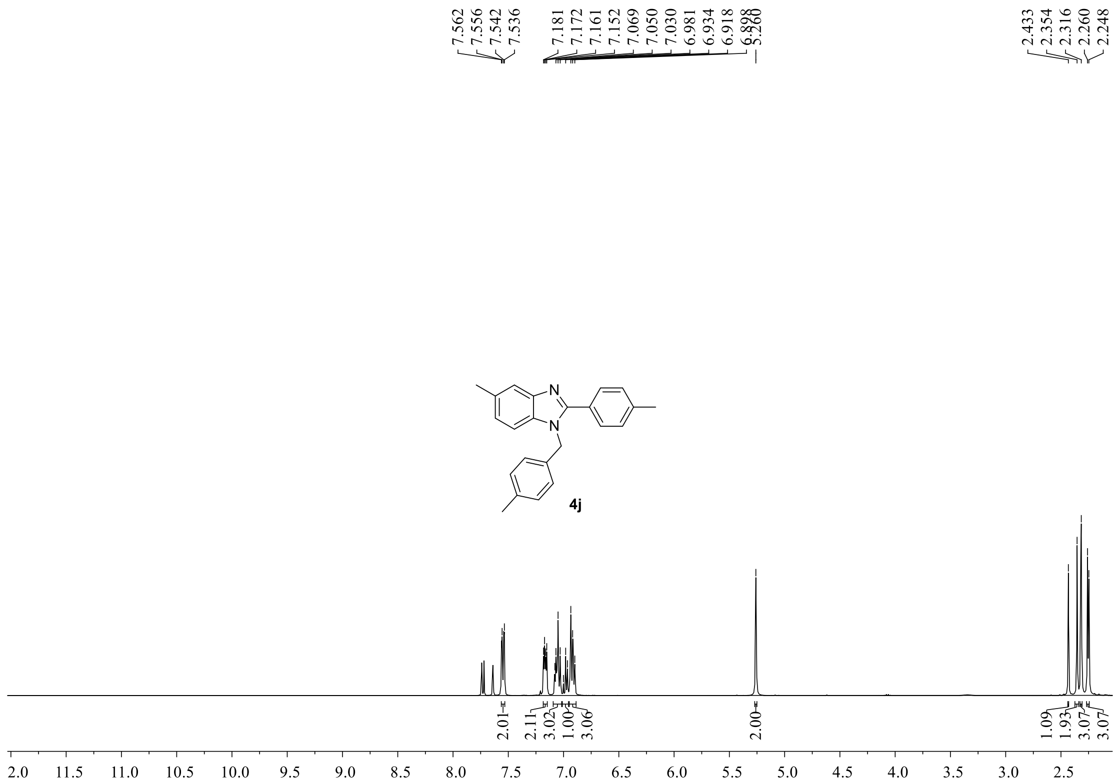
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2.354
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2.260
2.248
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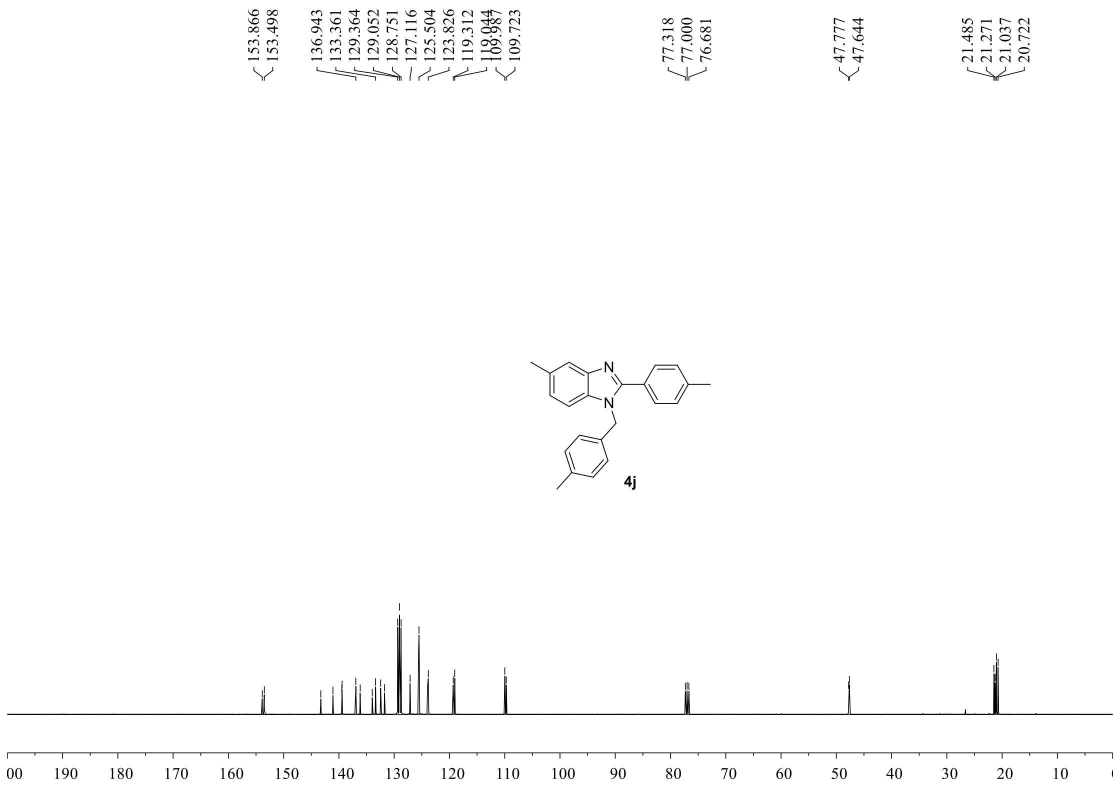
3.07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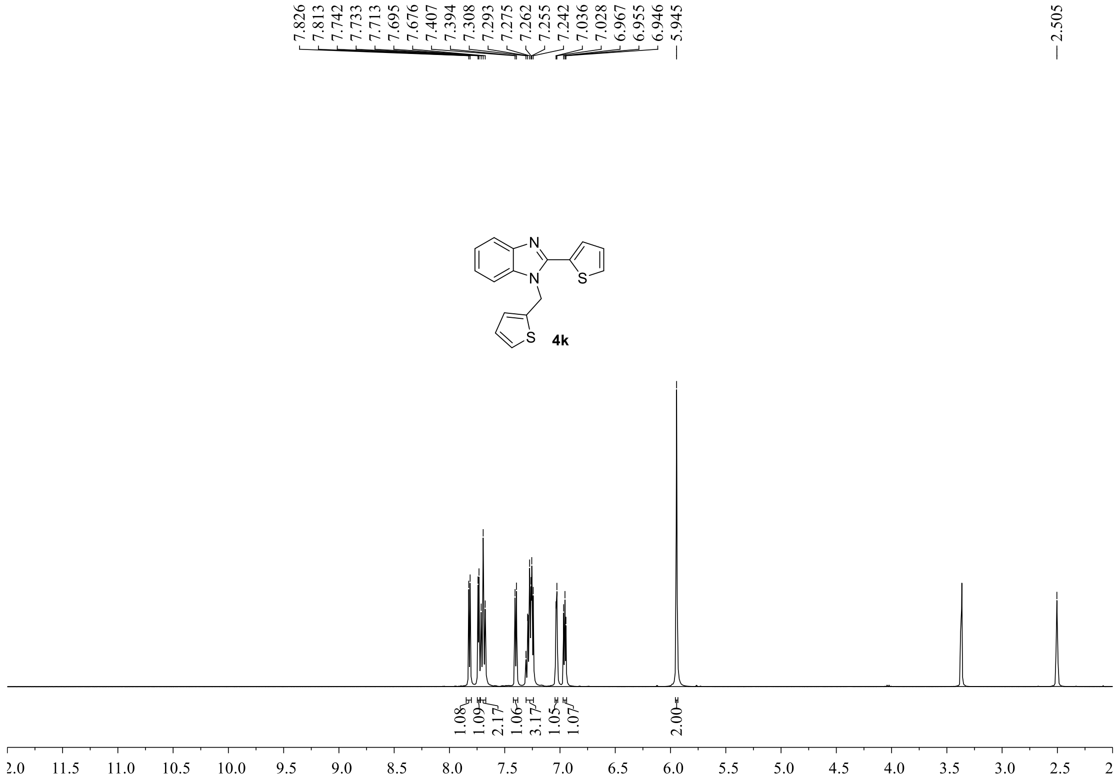
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7.036
7.028
6.967
6.955
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5.945
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N
N
S
S
4k
1.08
1.09
2.17
1.06
3.17
1.05
1.07
2.00
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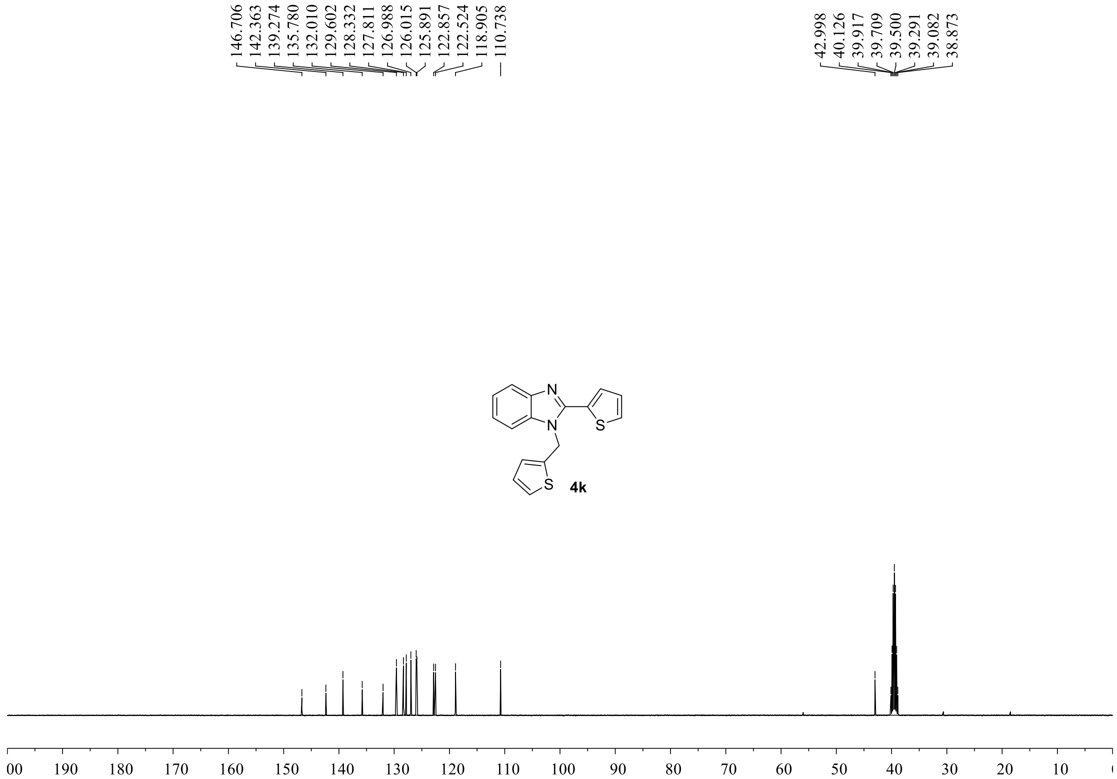
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42.998
40.126
39.917
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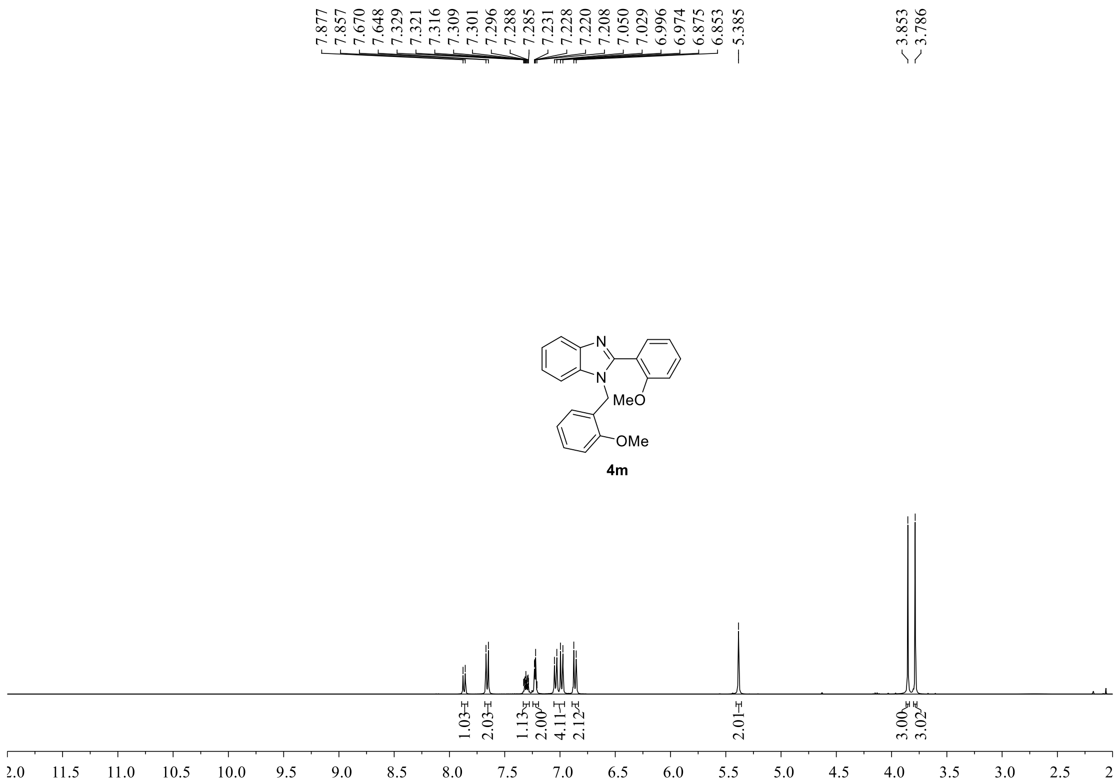
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7.309
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7.285
7.231
7.228
7.220
7.208
7.050
7.029
6.996
6.974
6.875
6.853
5.385
3.853
3.786
N
MeO
OMe
4m
1.03
2.03
1.13
2.00
4.11
2.12
2.01
3.00
3.02
2.0
11.5
11.0
10.5
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9.5
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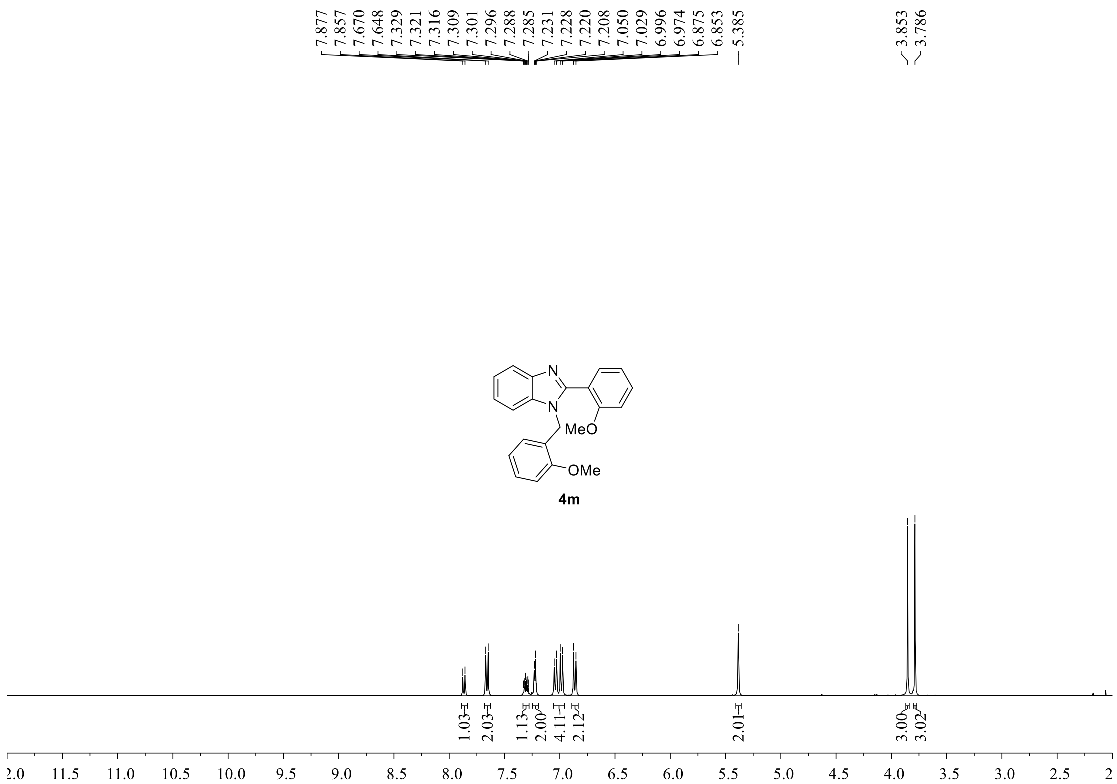
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7.220
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7.029
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N
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OMe
4m
1.03
2.03
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2.01
3.00
3.02
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
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3.0
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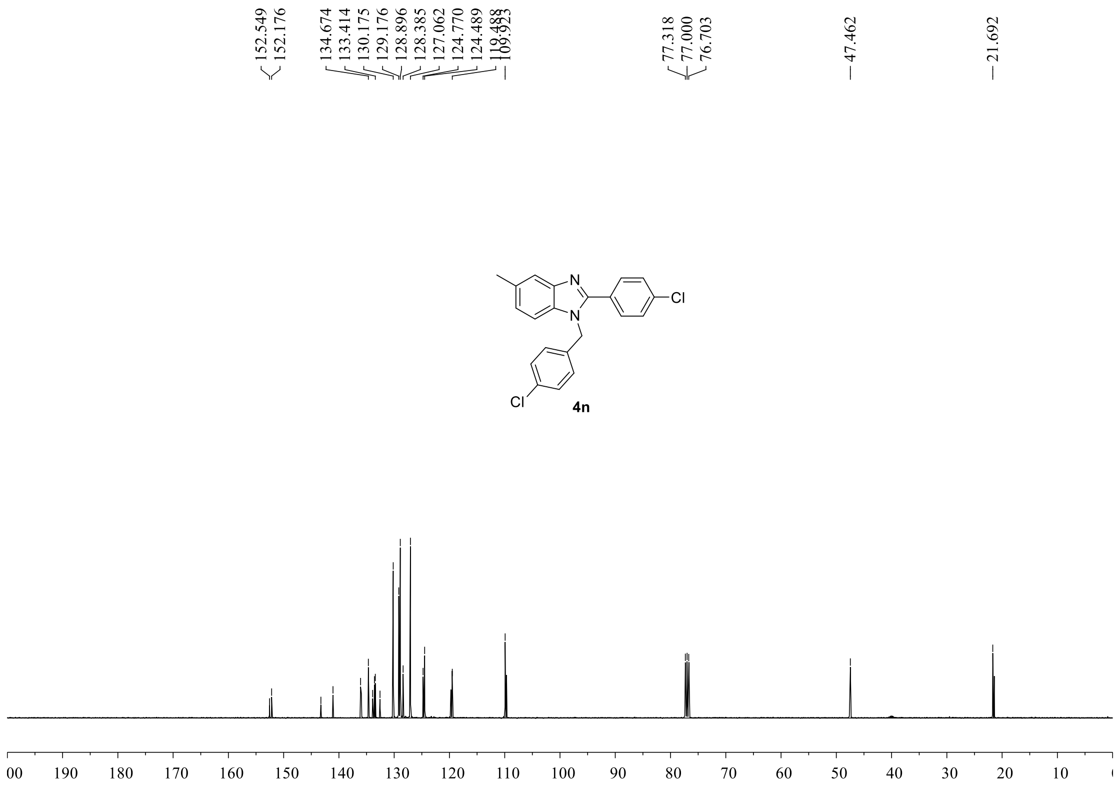
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Cl
Cl
4n
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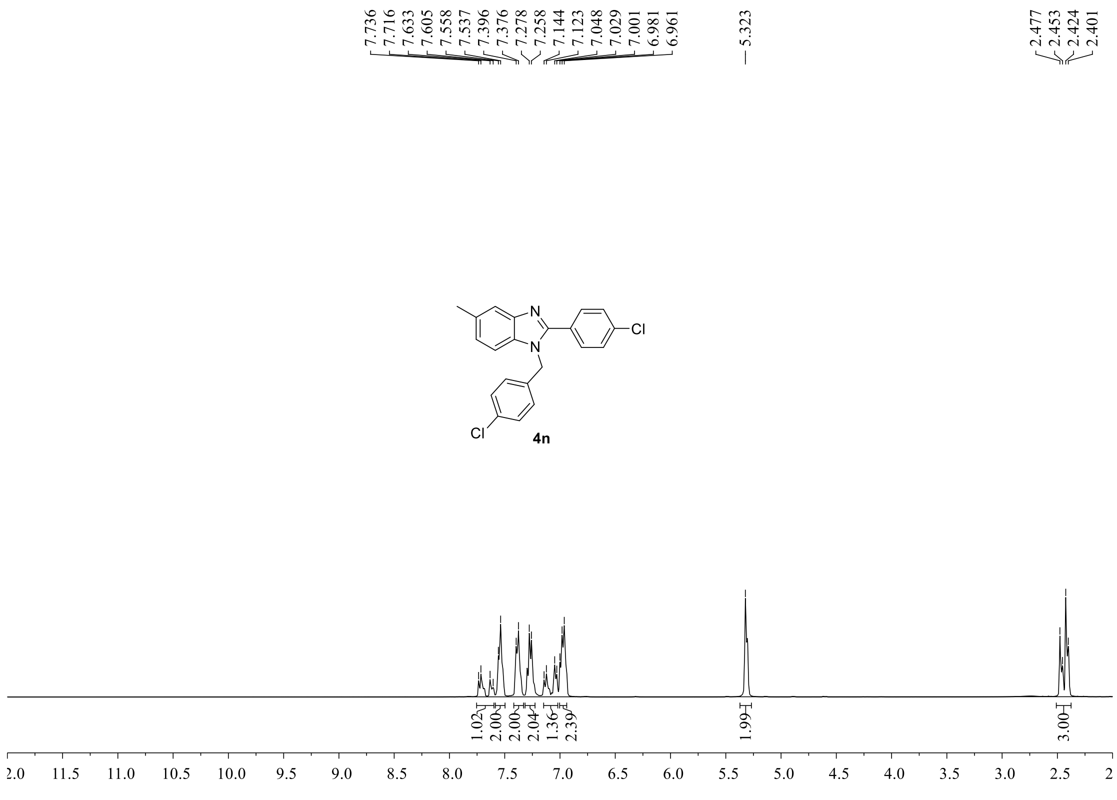
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7.029
7.001
6.981
6.961
5.323
2.477
2.453
2.424
2.401
N
N
Cl
Cl
4n
1.02
2.00
2.00
2.04
1.36
2.39
1.99
3.00
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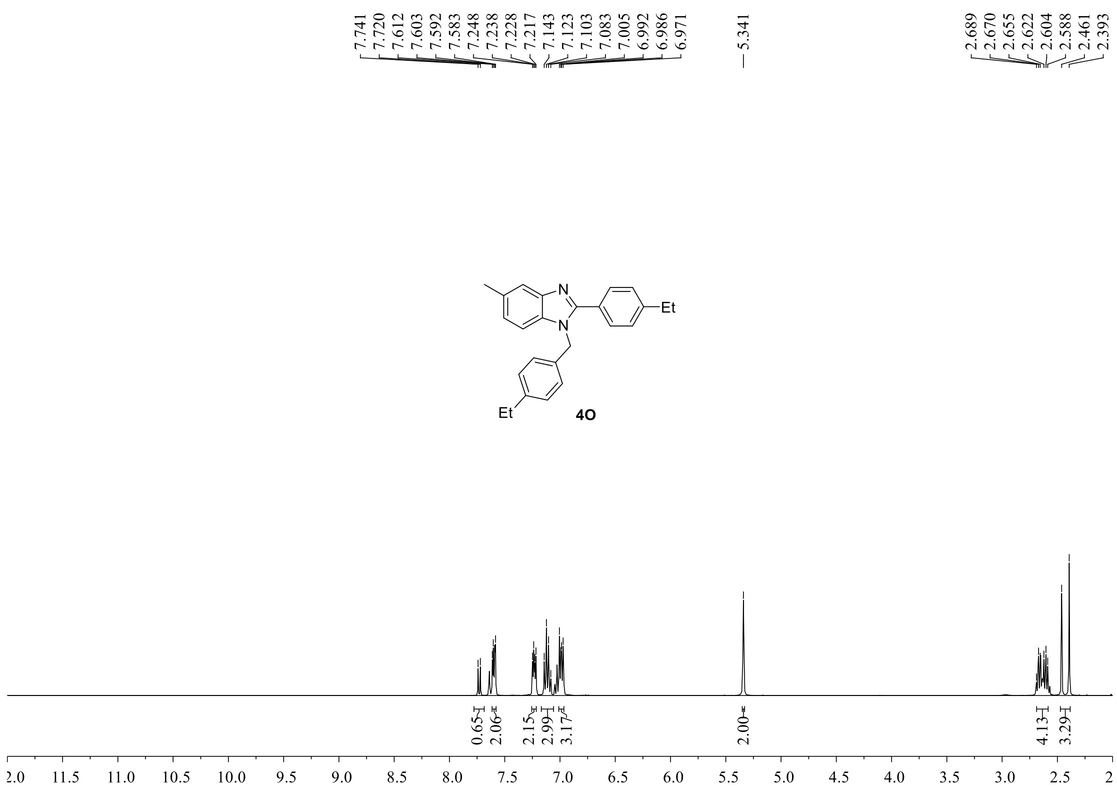
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7.083
7.005
6.992
6.986
6.971
5.341
2.689
2.670
2.655
2.622
2.604
2.588
2.461
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Et
4O
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3.17
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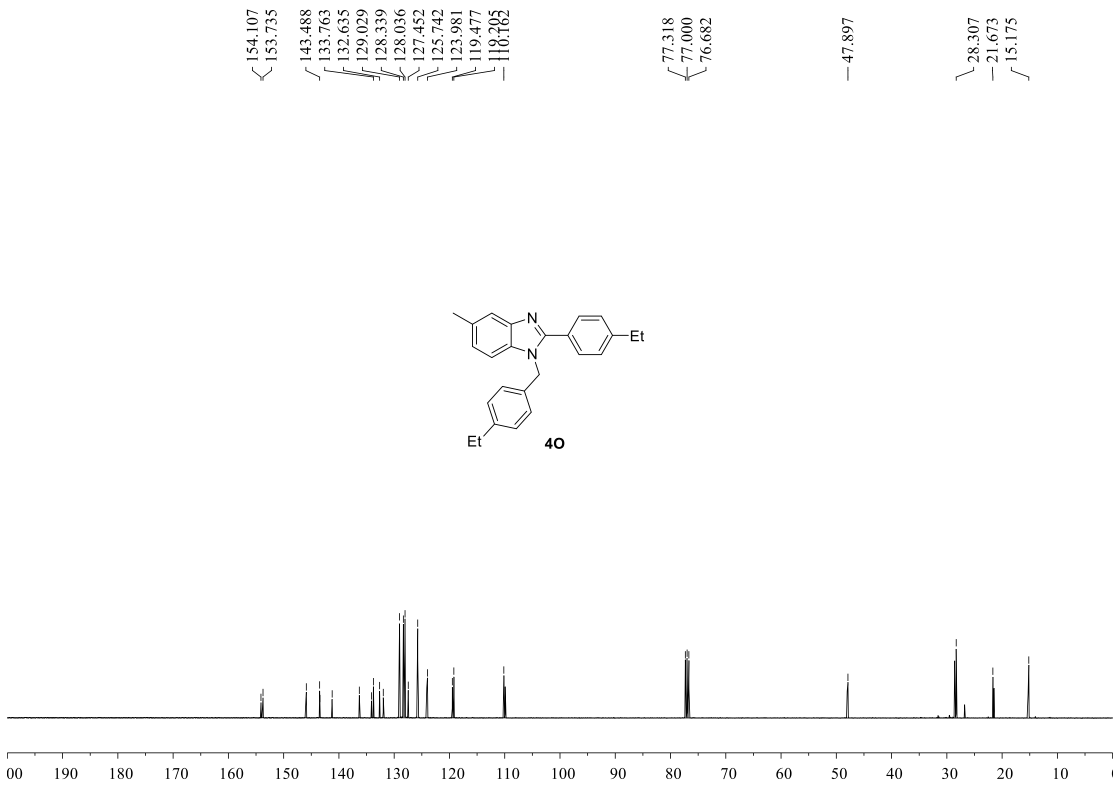
3.29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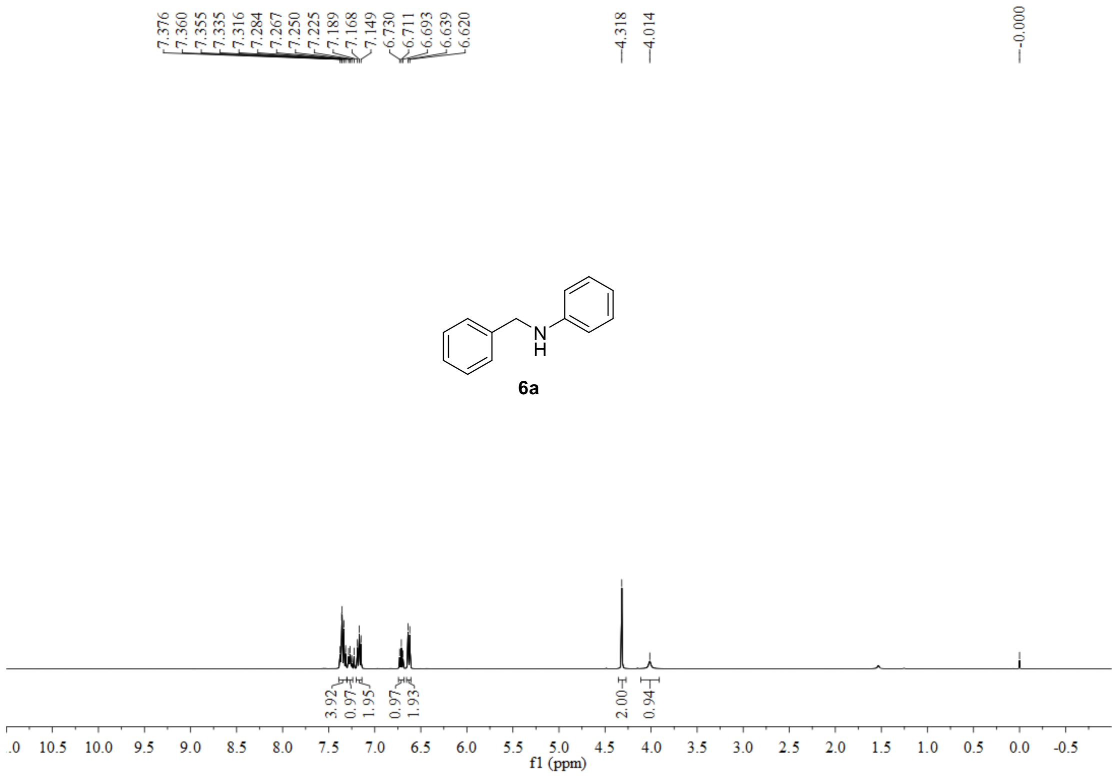
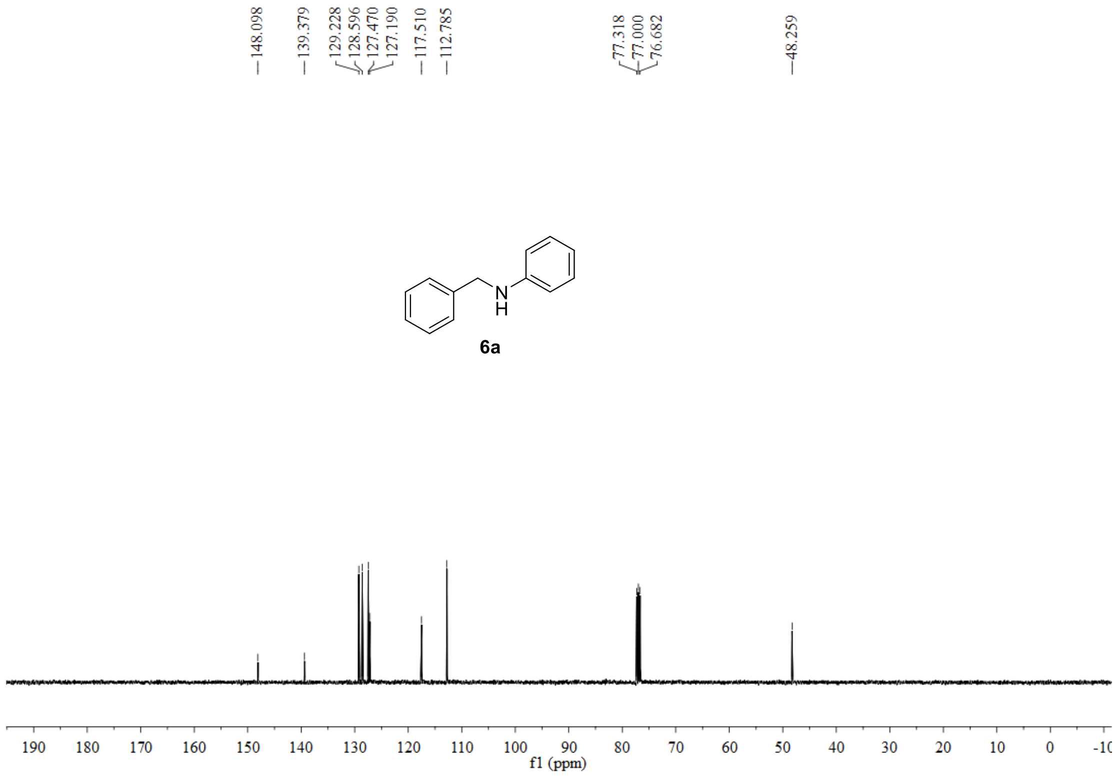
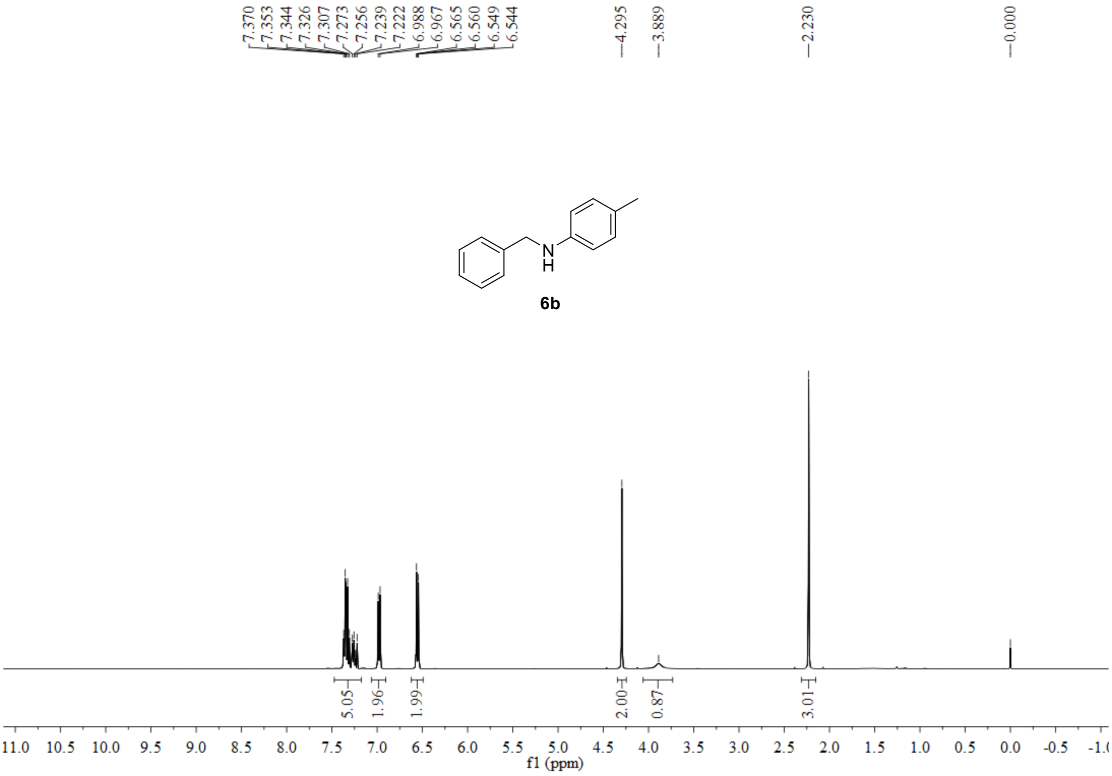
N
Et
Et
4O



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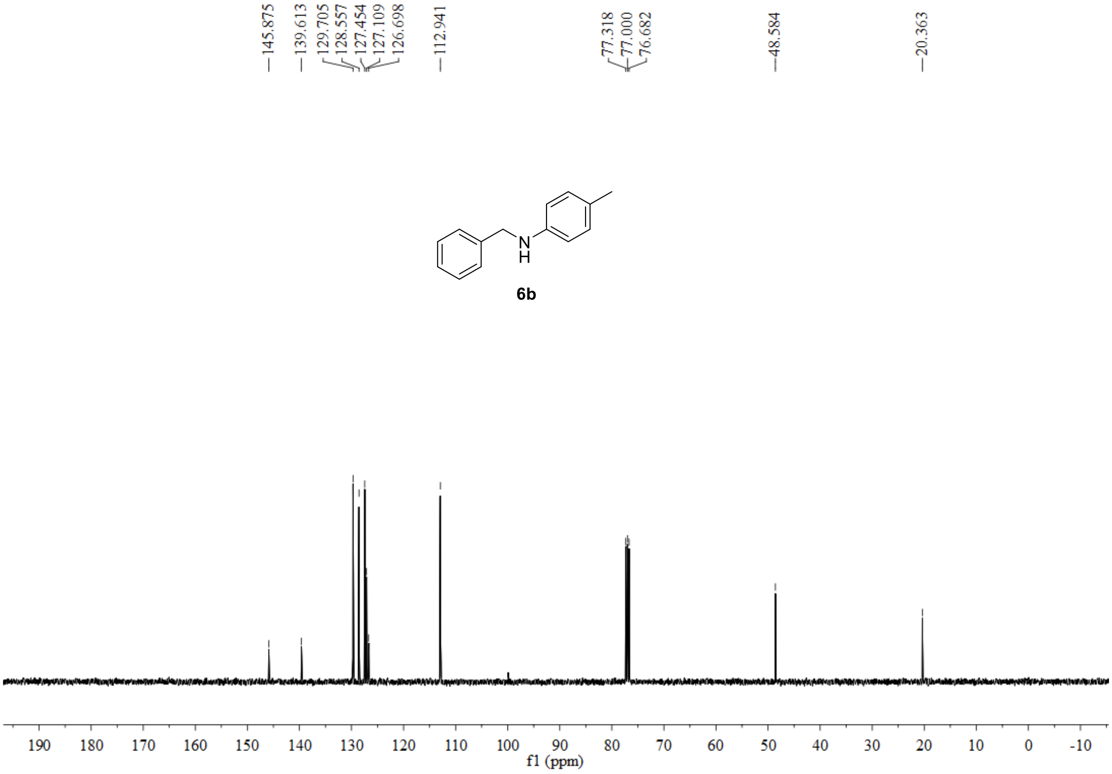
6.560
6.549
6.544
4.295
3.889
2.230
0.000
N
H
5.05
1.96
1.99
2.00
0.87
3.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

6b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127.109
126.698
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20.363
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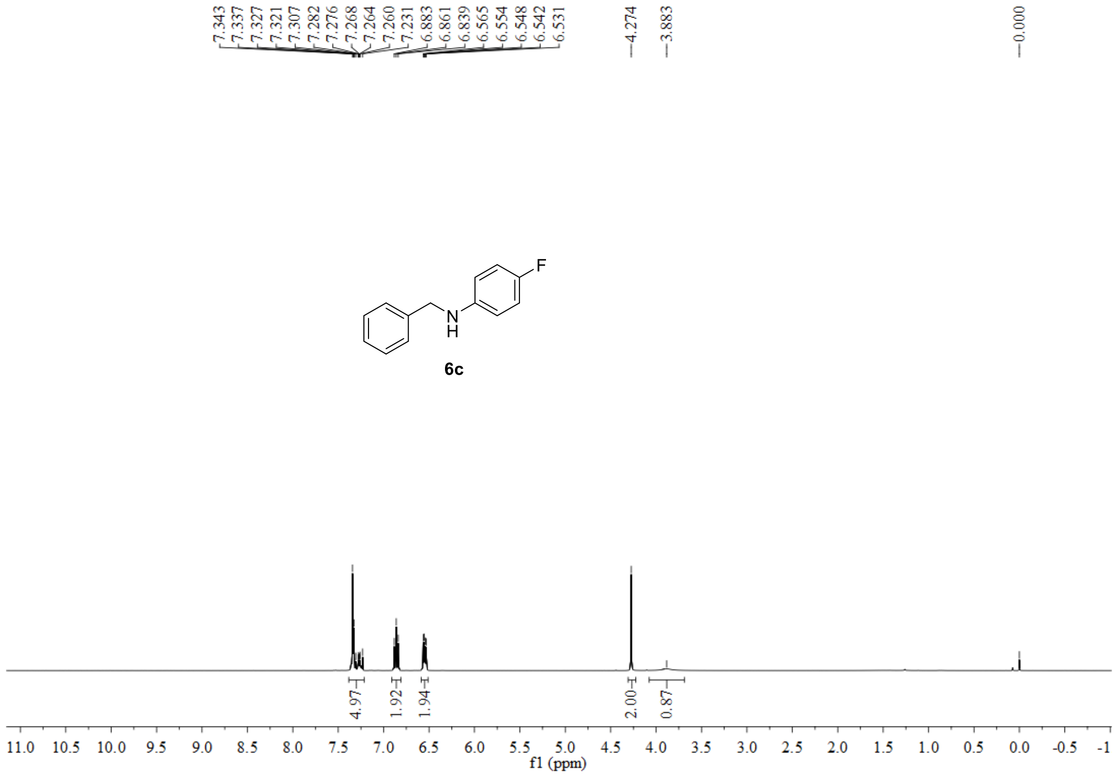
H
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

6b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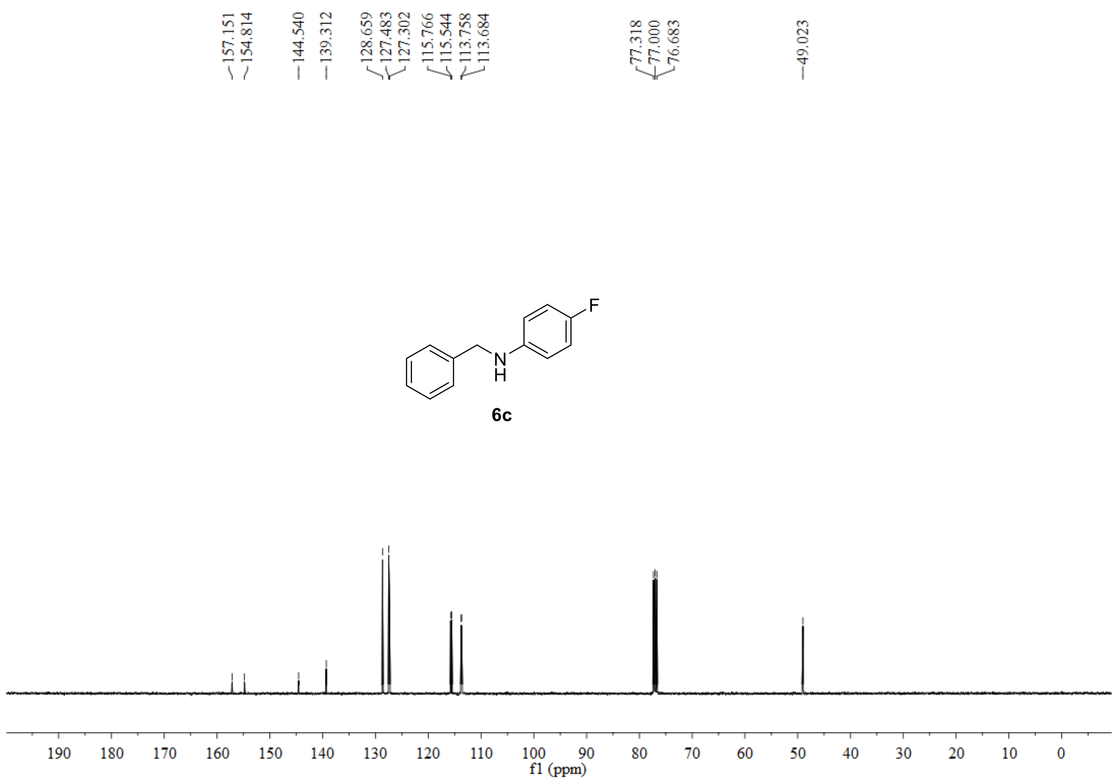
6.839
6.565
6.554
6.548
6.542
6.531
4.274
3.883
0.000
6c
4.97
1.92
1.94
2.00
0.87
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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77.000
76.683
49.023
6c
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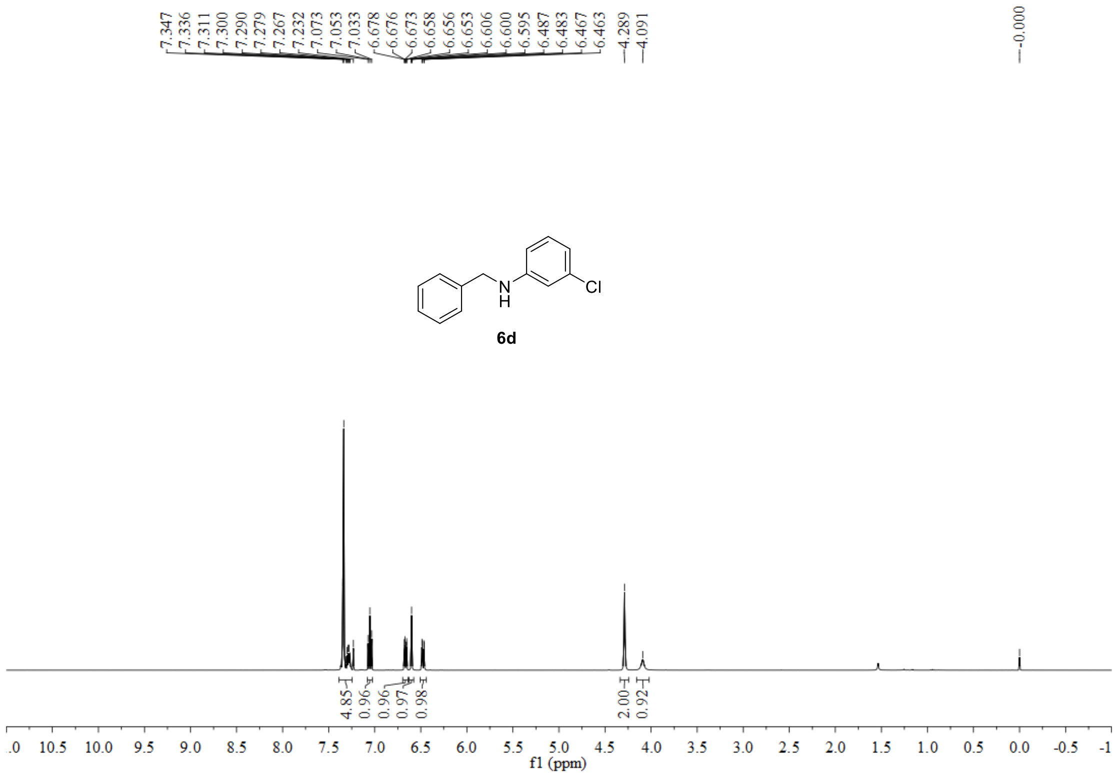
f1 (ppm)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7.267
7.232
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7.053
7.033
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6.487
6.483
6.467
6.463
4.289
4.091
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Cl
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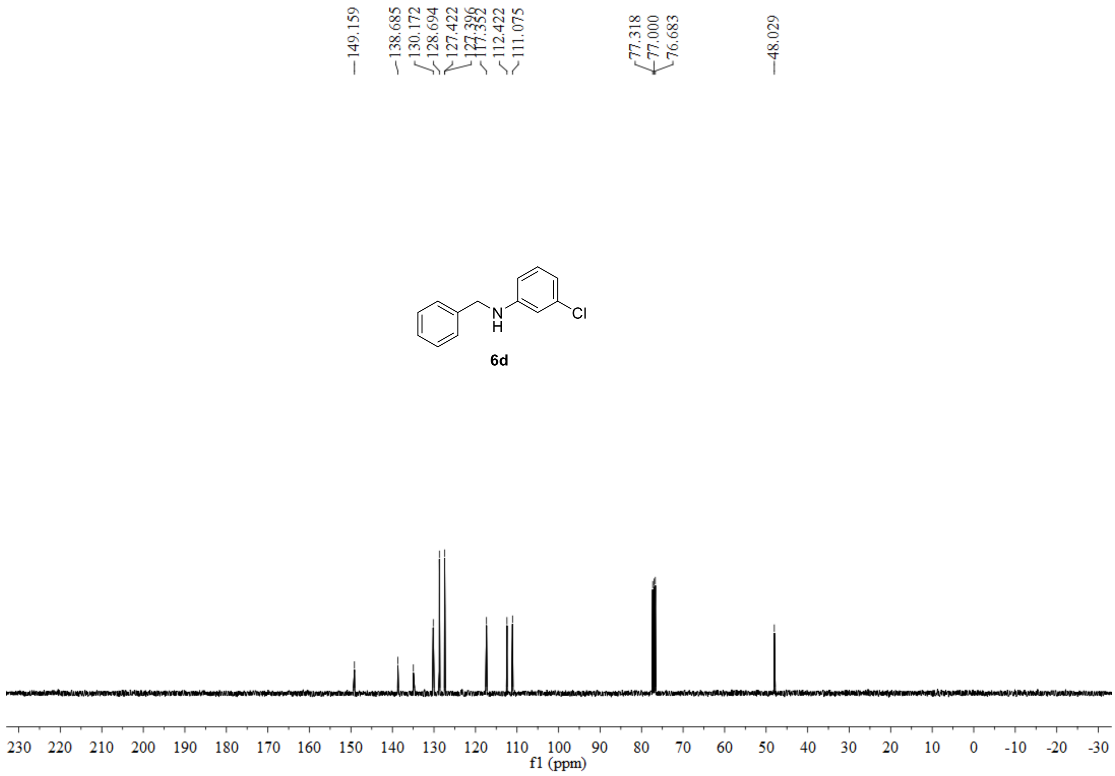
0.92
f1 (ppm)

6d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112.422
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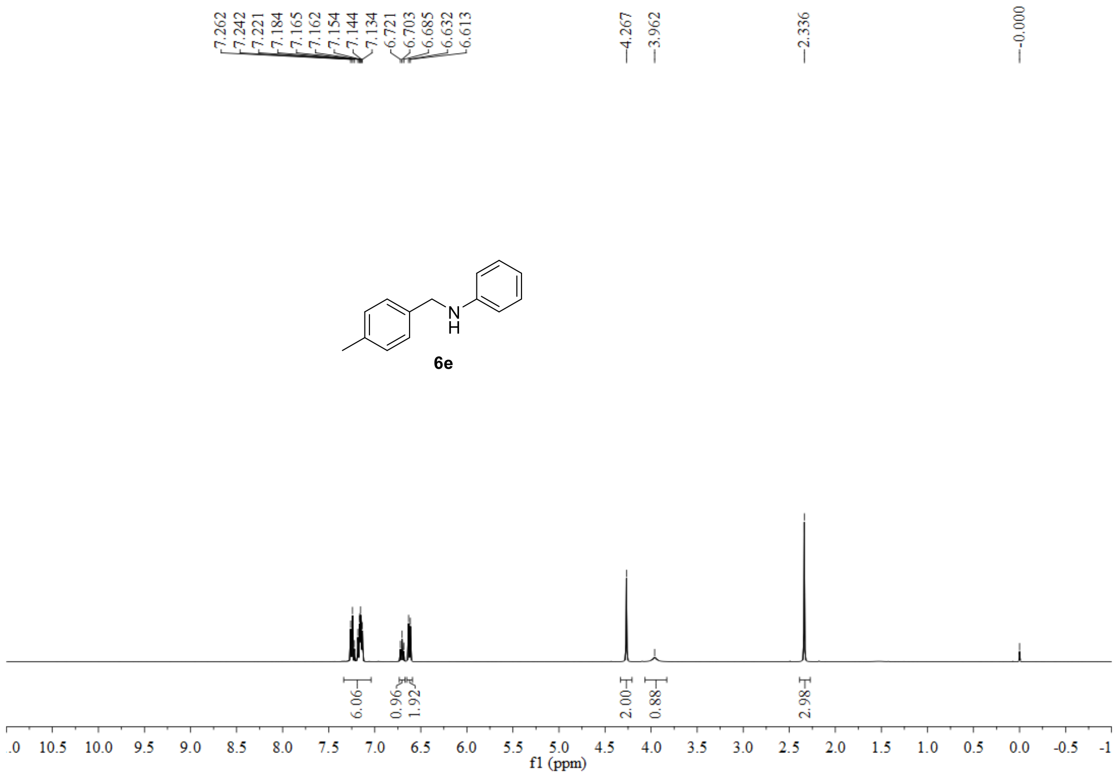
77.318
77.000
76.683
48.029
N
H
Cl
f1 (ppm)

6d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6.632
6.613
4.267
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H
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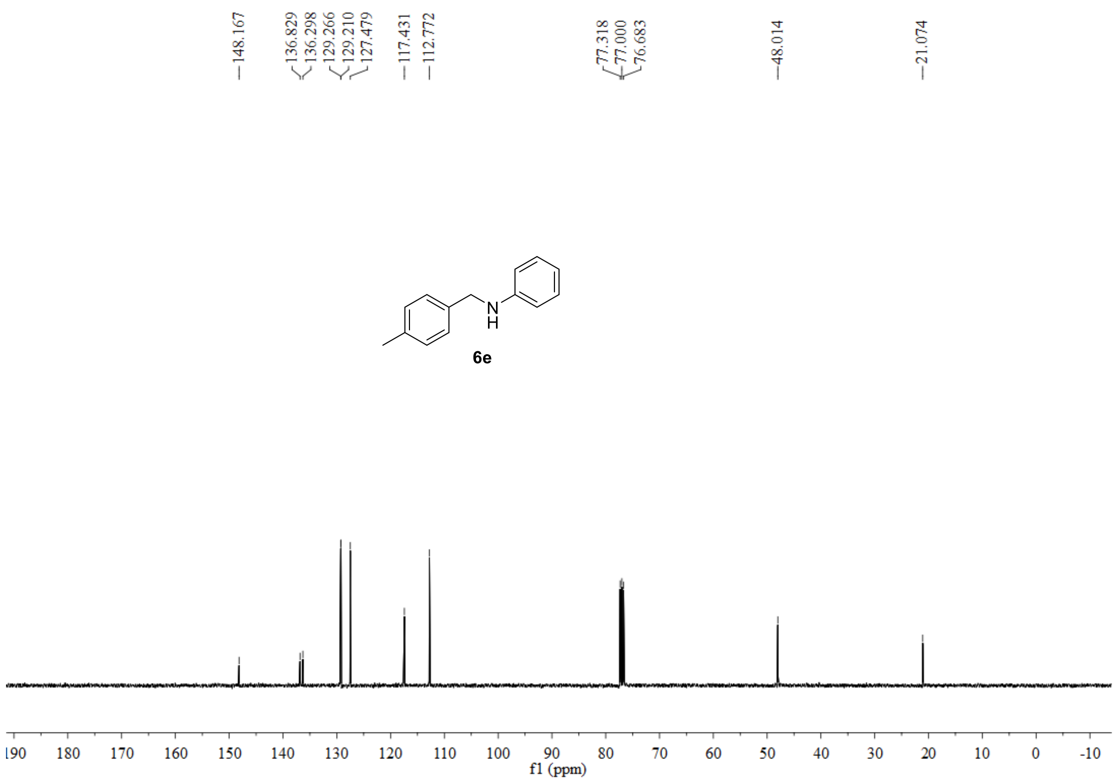
f1 (ppm)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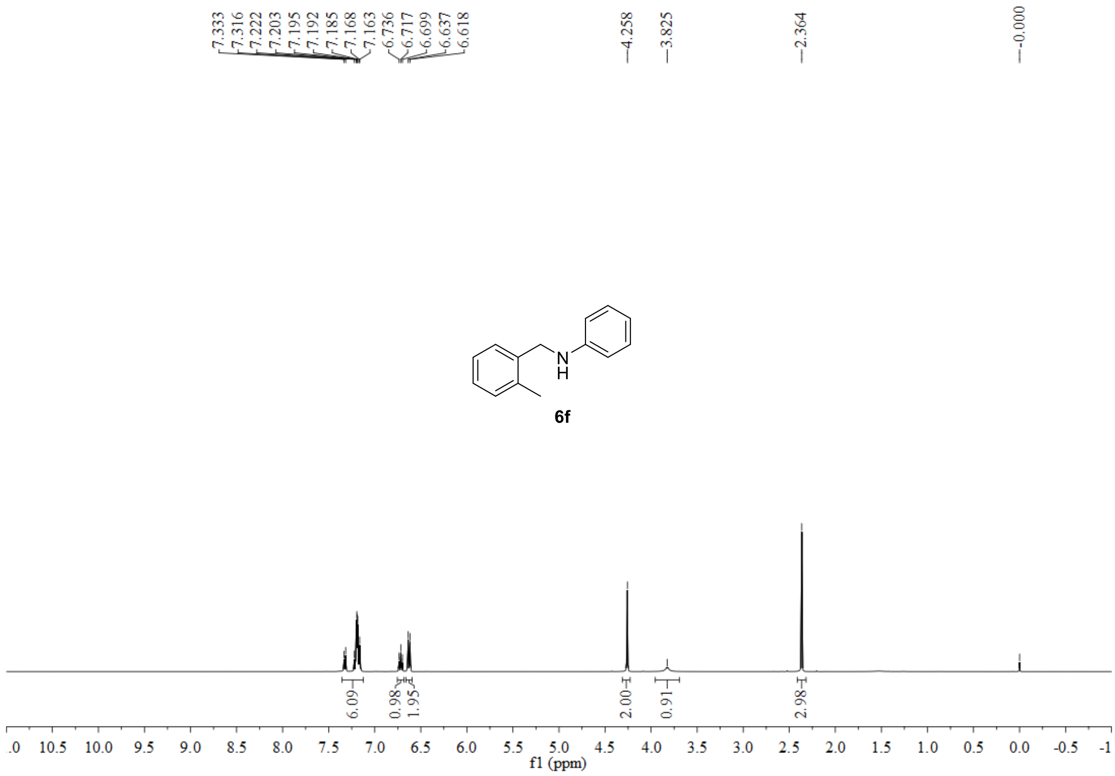
H
6e
f1 (ppm)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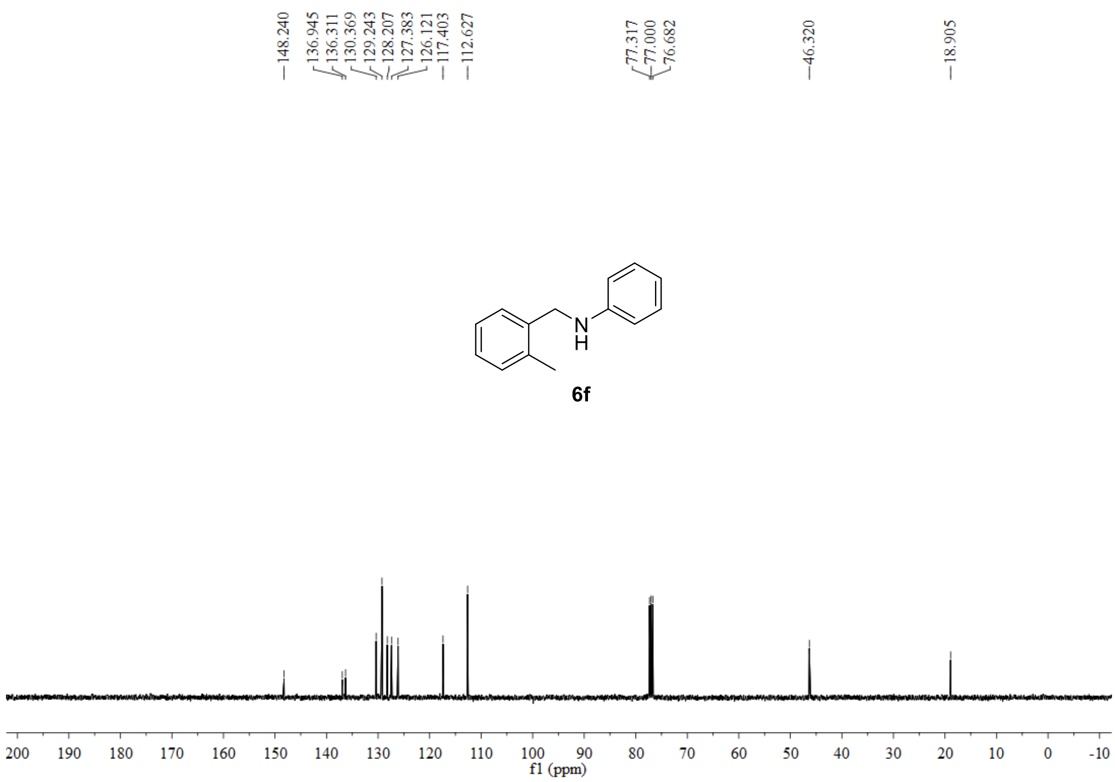
6.637
6.618
4.258
3.825
2.364
0.000
N
H
6f
6.09
0.98
1.95
2.00
0.91
2.98
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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126.121
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112.627
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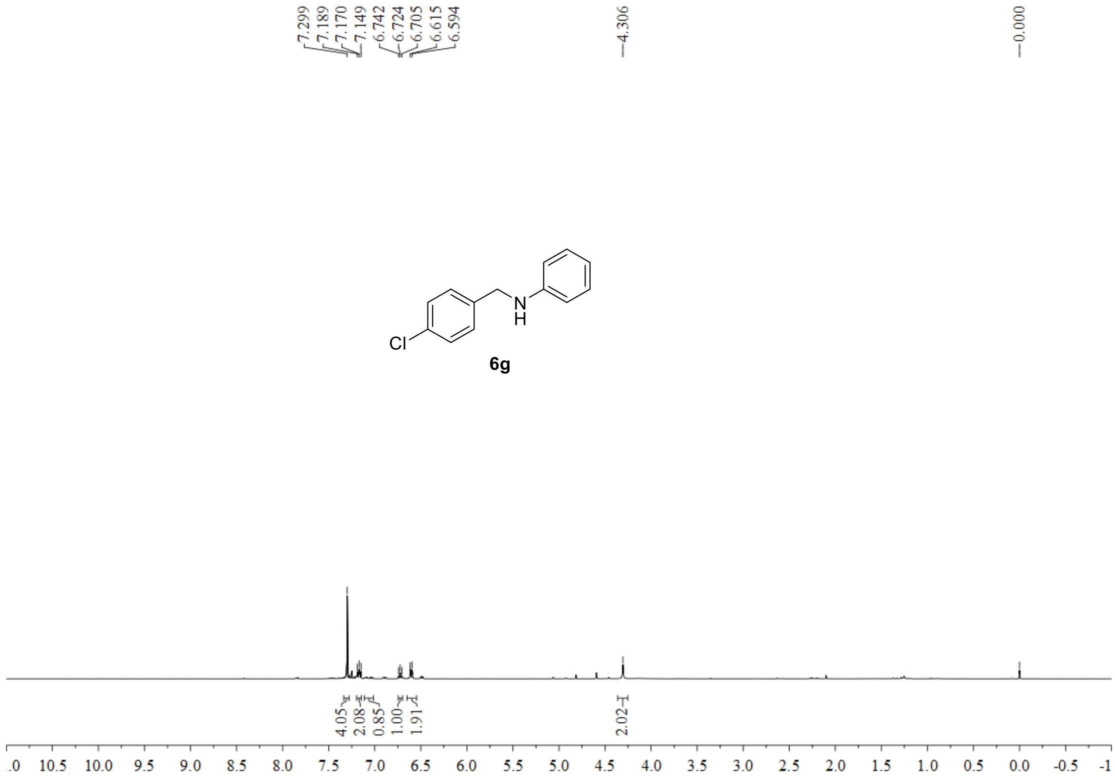
18.905
N
H
6f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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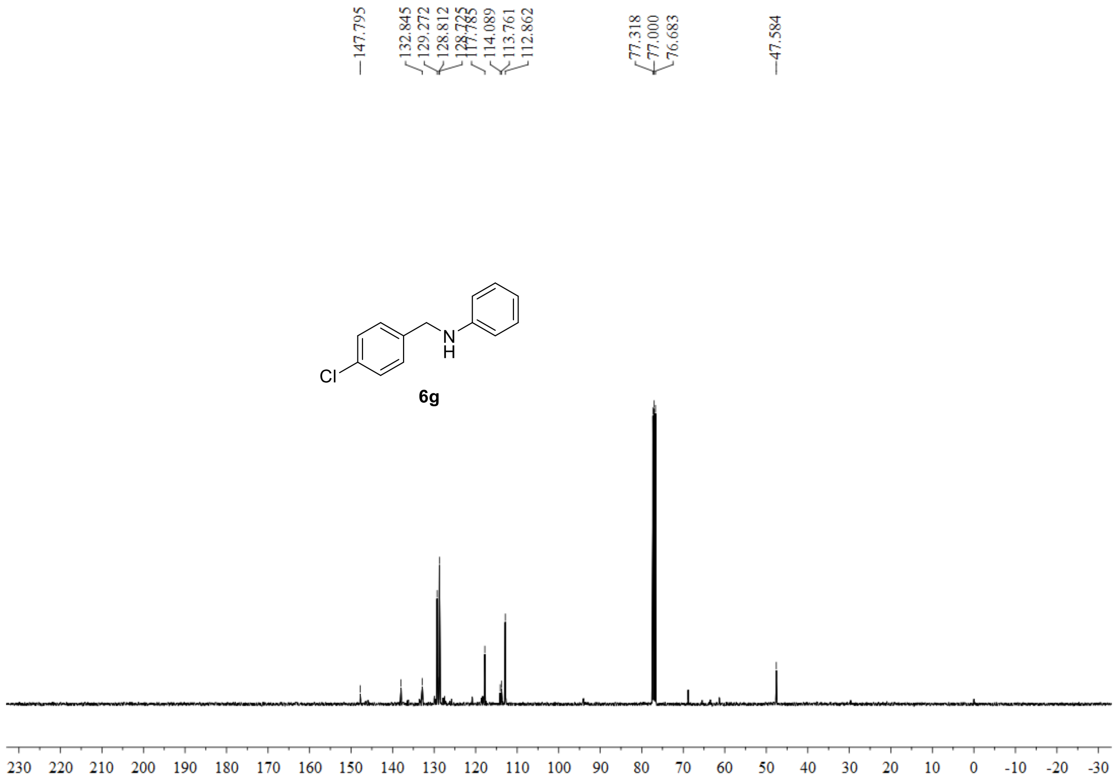
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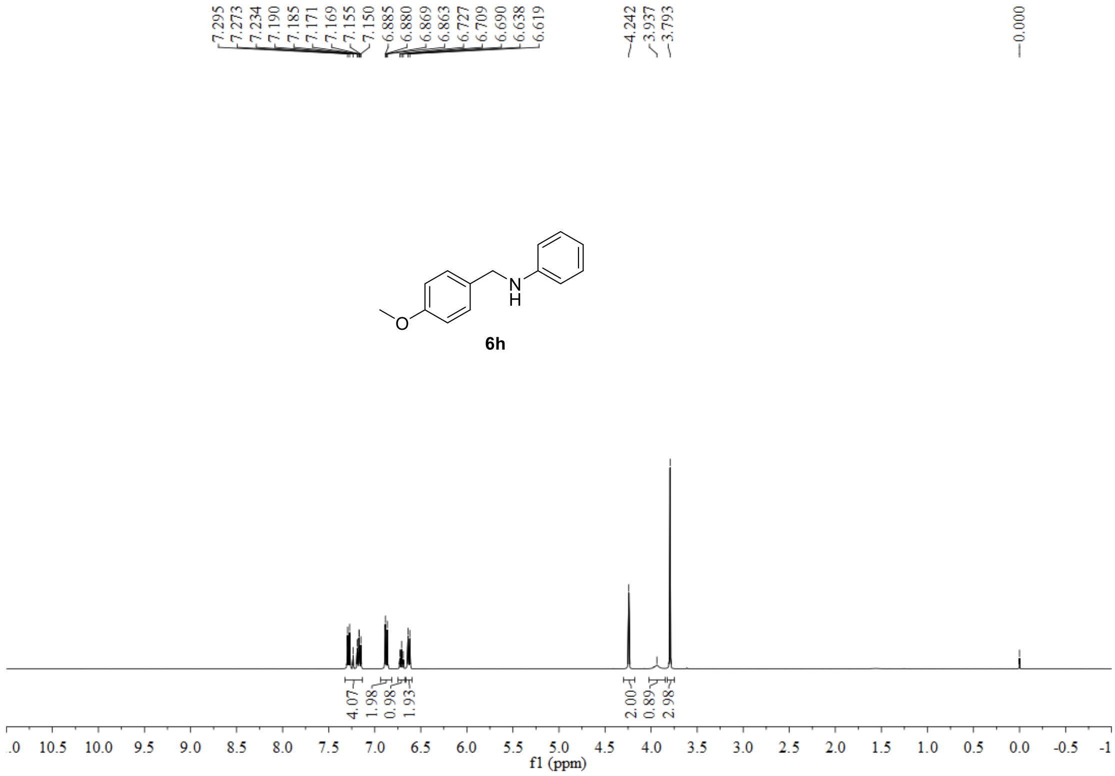
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6.863
6.727
6.709
6.690
6.638
6.619
4.242
3.937
3.793
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O
6h
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0.98
1.93
2.00
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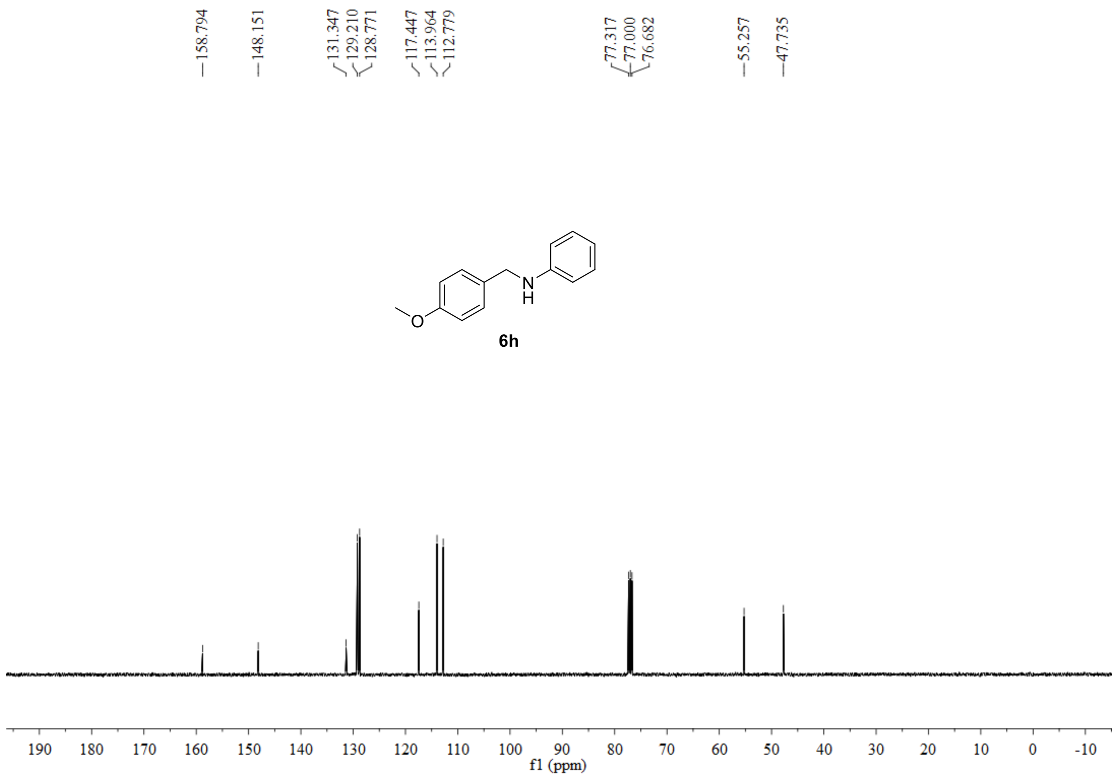
2.98
f1 (ppm)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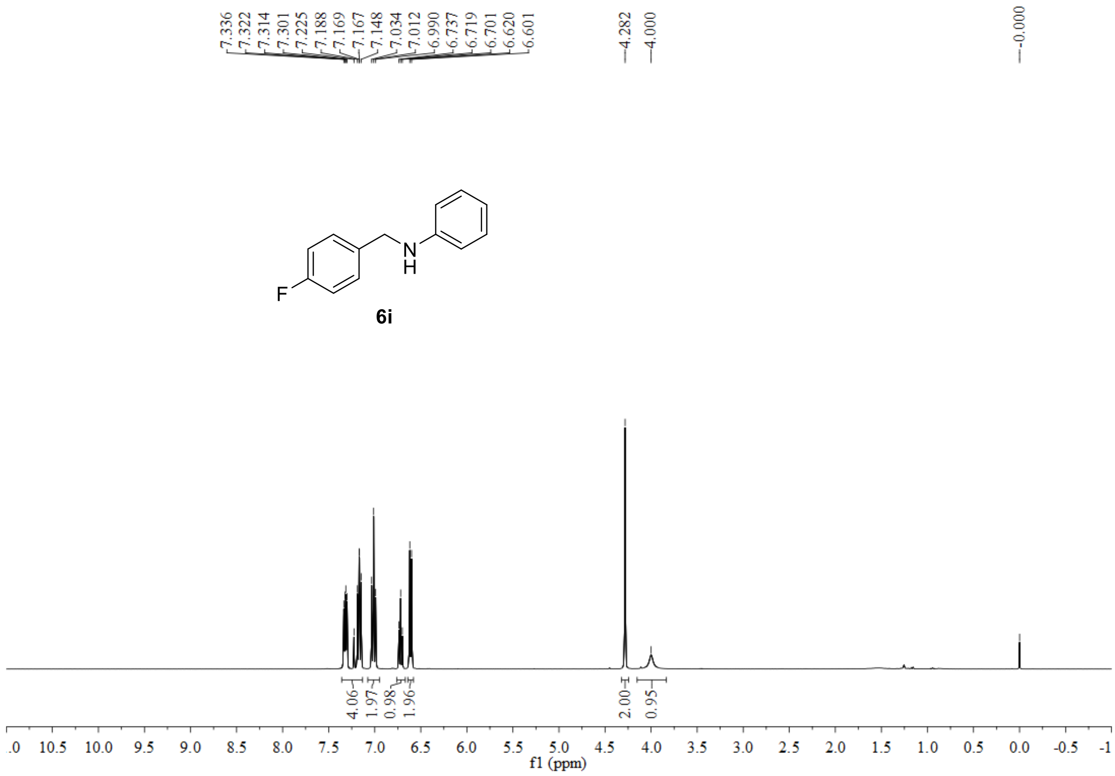
76.682
55.257
47.735
N
H
O
6h
f1 (ppm)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7.034
7.012
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6.719
6.701
6.620
6.601
4.282
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0.000
F
N
H
6i
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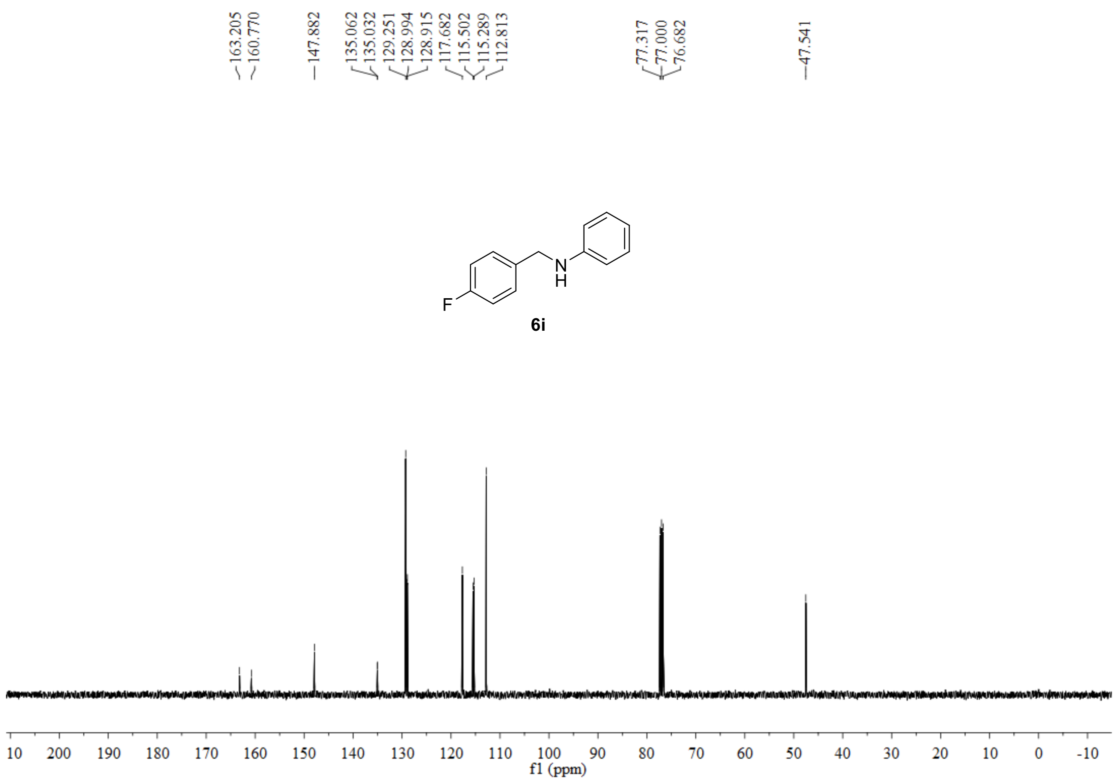
1.96
2.00
0.95
f1 (ppm)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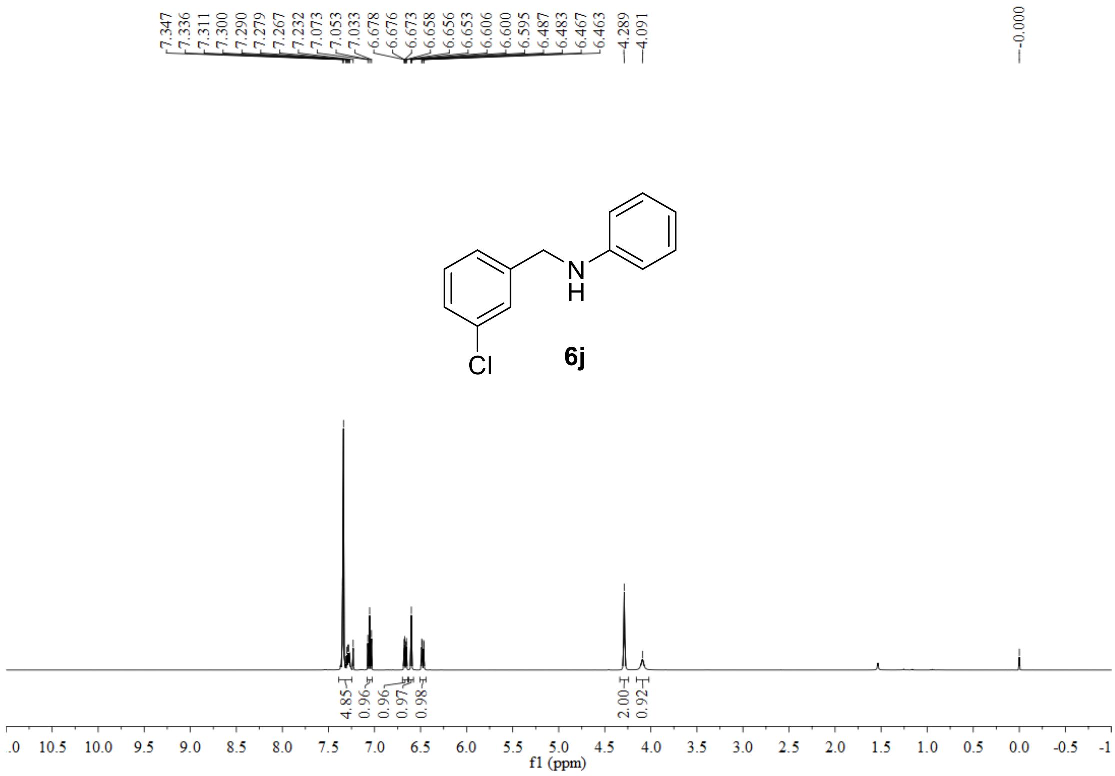
77.000
76.682
47.541
F
N
H
6i
f1 (ppm)



7.347
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7.311
7.300
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7.279
7.267
7.232
7.073
7.053
7.033
6.678
6.676
6.673
6.658
6.656
6.653
6.606
6.600
6.595
6.487
6.483
6.467
6.463
4.289
4.091
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Cl
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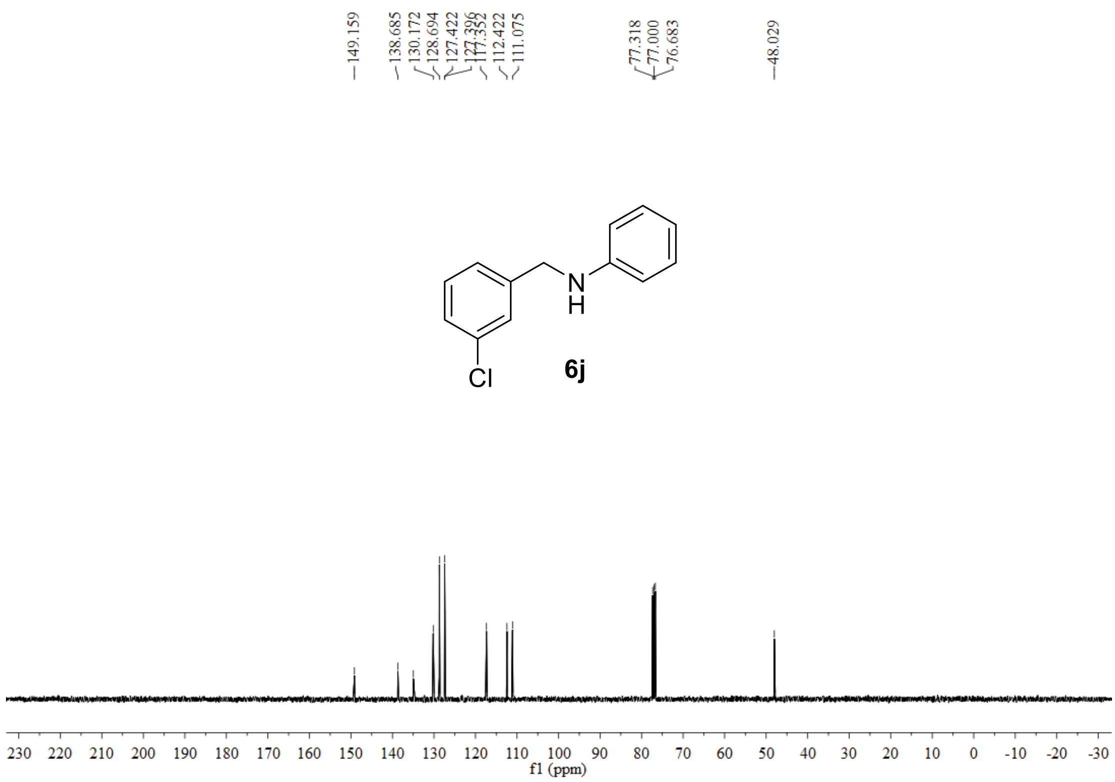
f1 (ppm)



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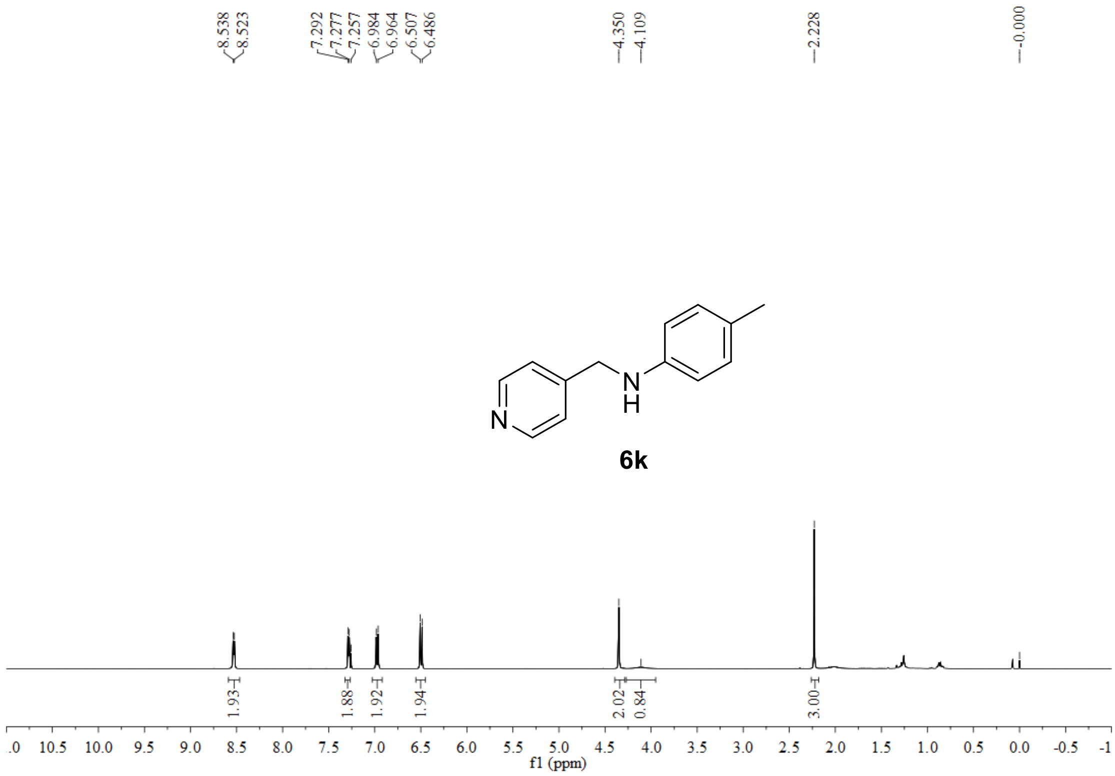
77.318
77.000
76.683
48.029
N
H
Cl
6j
f1 (ppm)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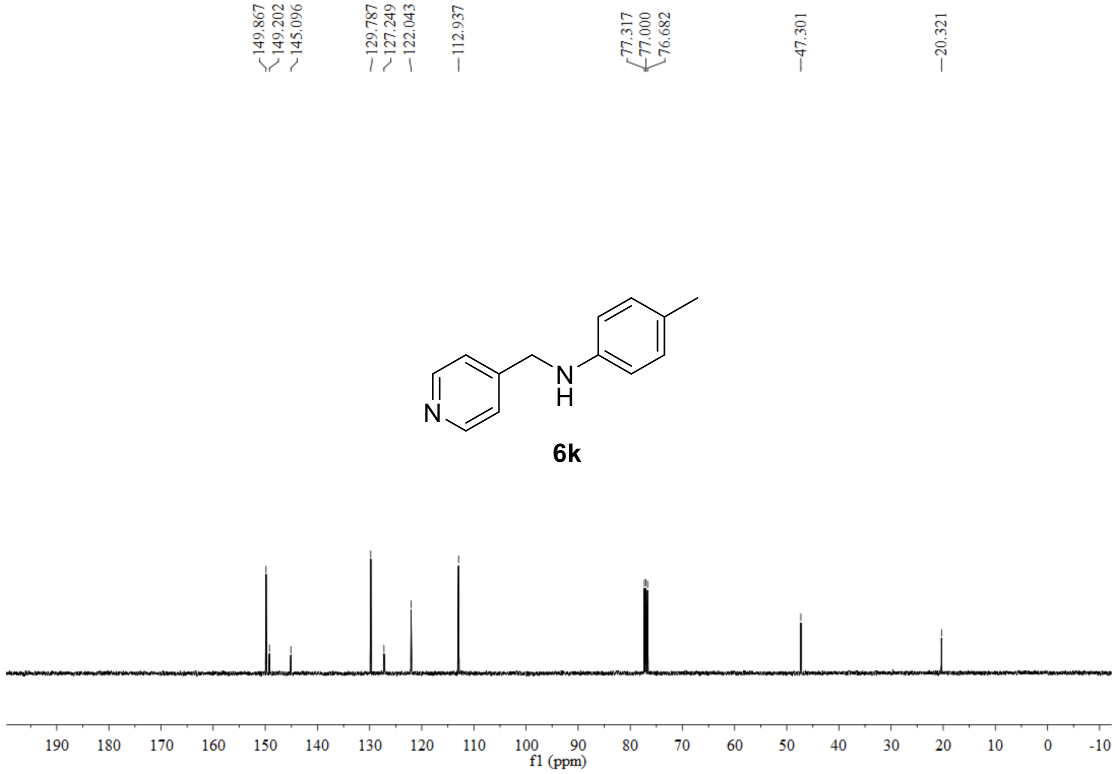
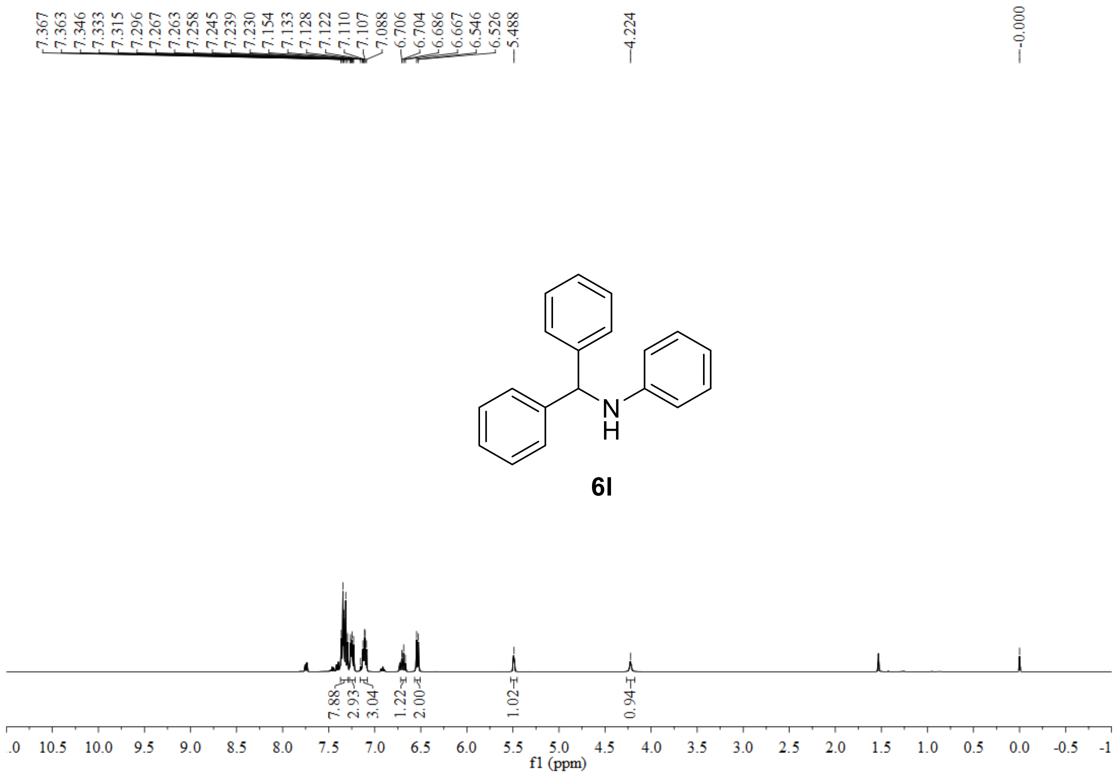
8.523
7.292
7.277
7.257
6.984
6.964
6.507
6.486
4.350
4.109
2.228
-0.000
N
N
H
6k
1.93
1.88
1.92
1.94
2.02
0.84
3.00
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


149.867
149.202
145.096
129.787
127.249
122.043
112.937
77.317
77.000
76.682
47.301
20.321
N
N
H
6k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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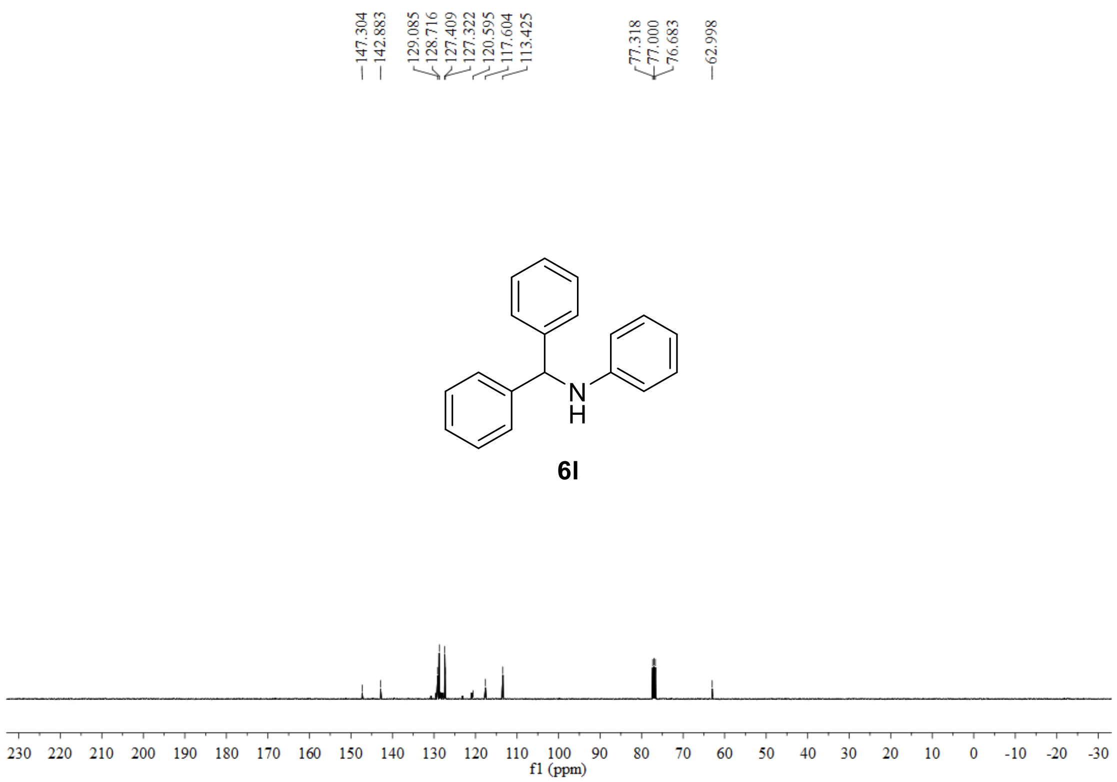
7.363
7.346
7.333
7.315
7.296
7.267
7.263
7.258
7.245
7.239
7.230
7.154
7.133
7.128
7.122
7.110
7.107
7.088
6.706
6.704
6.686
6.667
6.546
6.526
5.488
4.224
0.000
N
H
6l
7.88
2.93
3.04
1.22
2.00
1.02
0.94
f1 (ppm)


147.304
142.883
129.085
128.716
127.409
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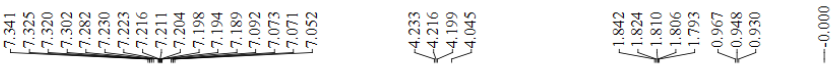
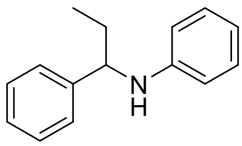
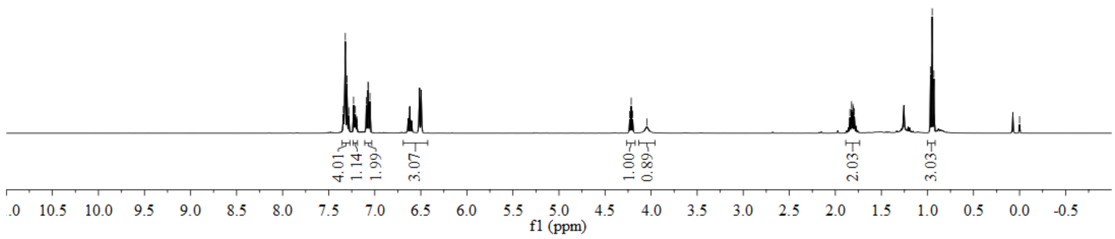
117.604
113.425
77.318
77.000
76.683
62.998
N
H
6l
f1 (ppm)


7.341
7.325
7.320
7.302
7.282
7.230
7.223
7.216
7.211
7.204
7.198
7.194
7.189
7.092
7.073
7.071
7.052
4.233
4.216
4.199
4.045
1.842
1.824
1.810
1.806
1.793
0.967
0.948
0.930
-0.000


N
H

6m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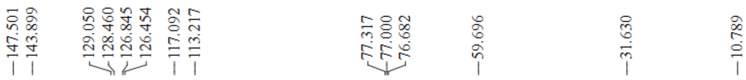
1.14
1.99
3.07
1.00
0.89
2.03
3.03
f1 (ppm)


147.501
143.899
129.050
128.460
126.845
126.454
117.092
113.217
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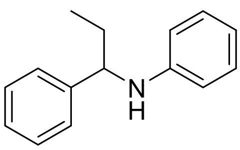
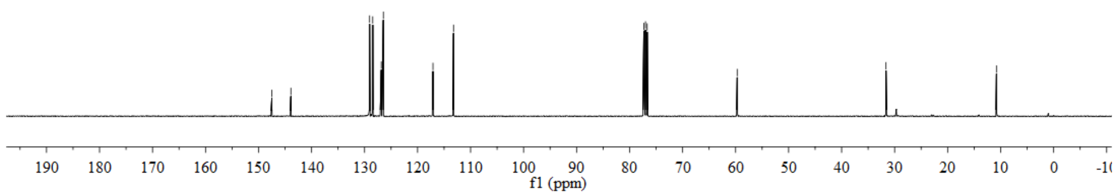
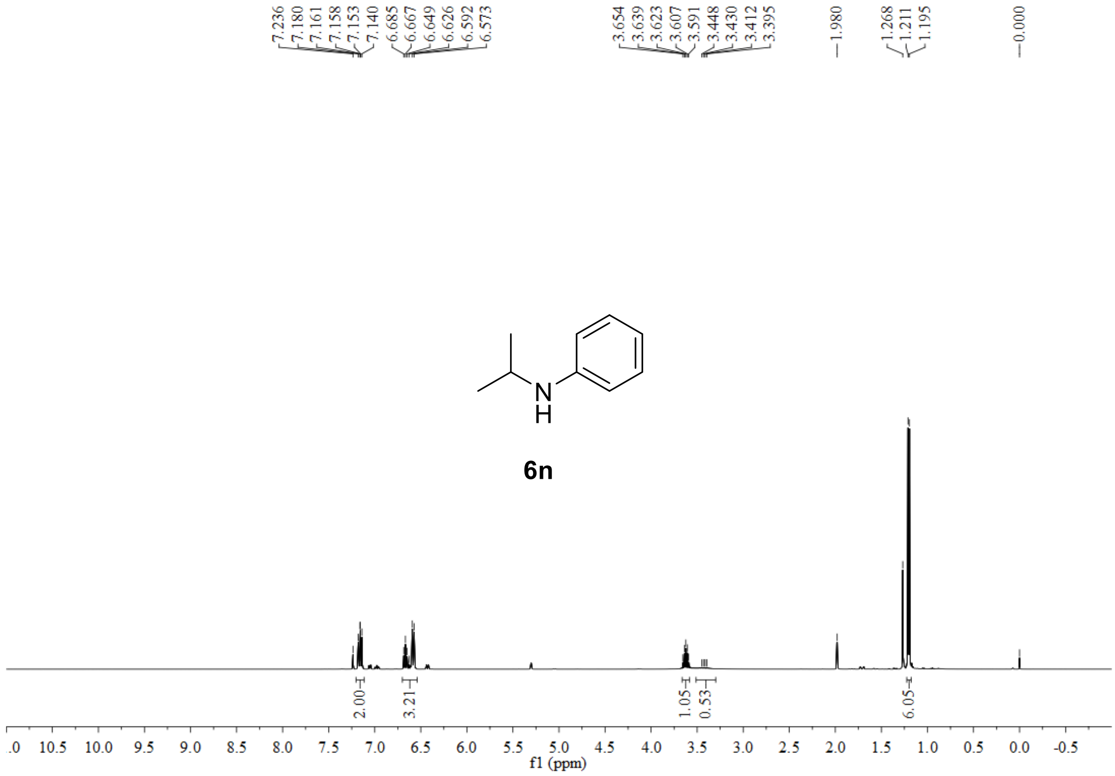
77.000
76.682
59.696
31.630
10.789


N
H

6m


f1 (ppm)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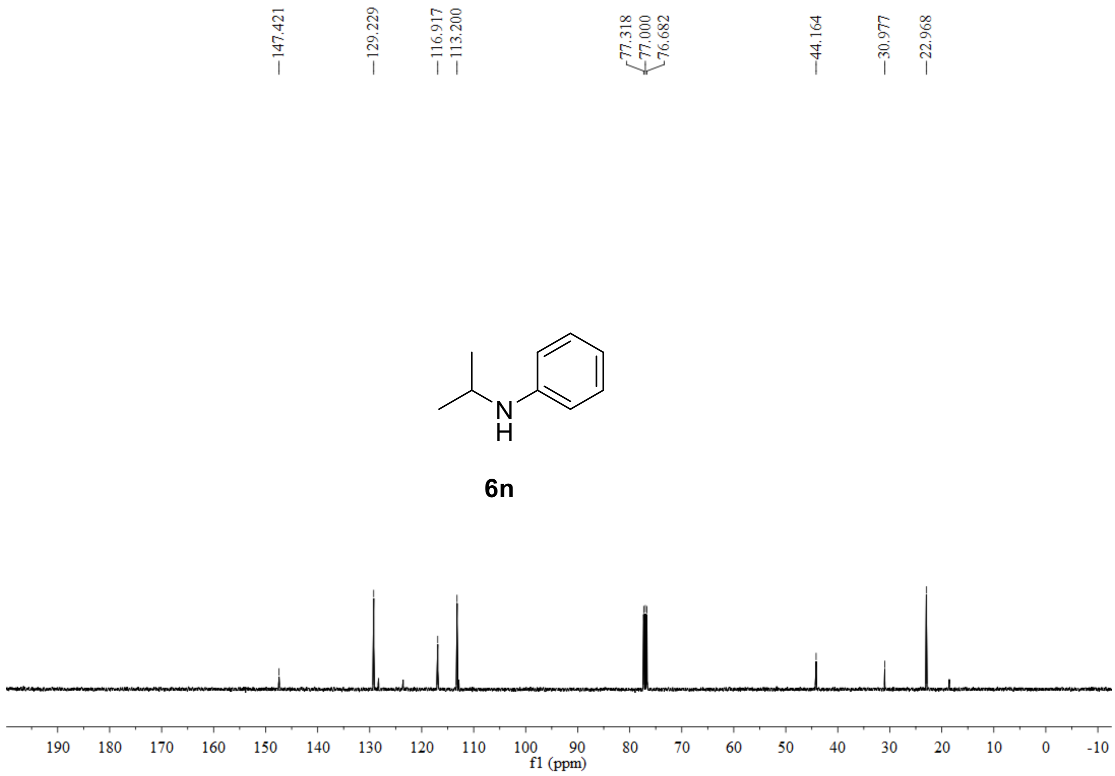
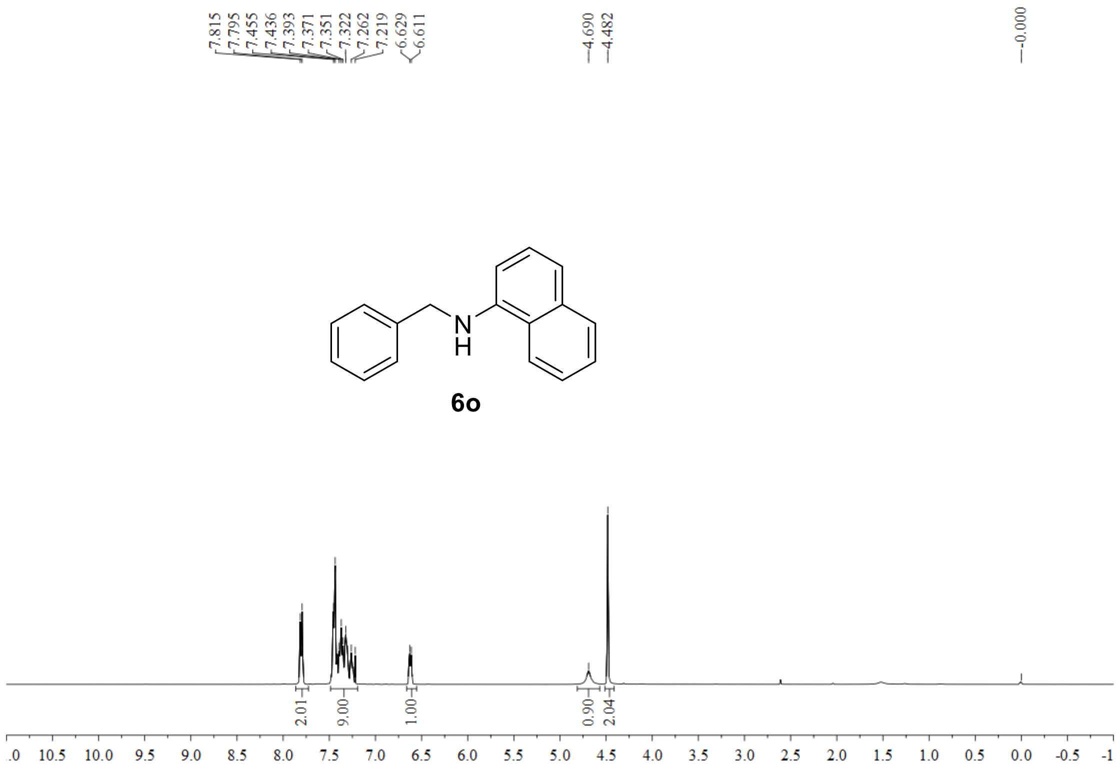
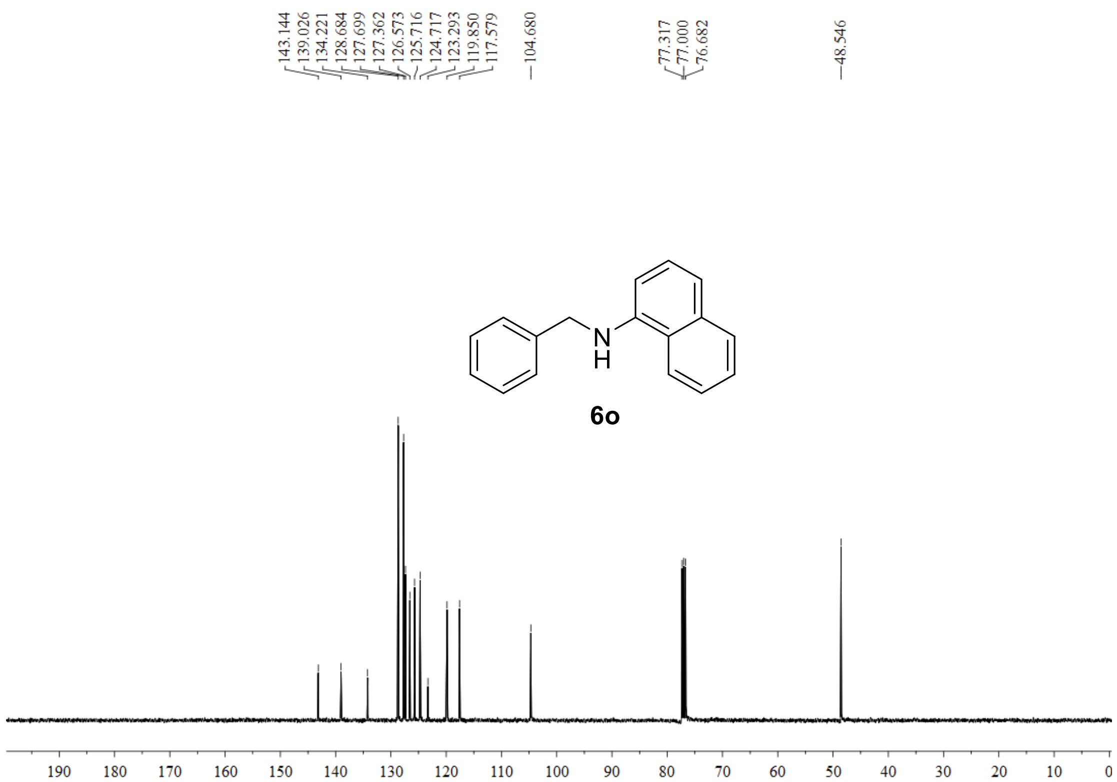
7.180
7.161
7.158
7.153
7.140
6.685
6.667
6.649
6.626
6.592
6.573
3.654
3.639
3.623
3.607
3.591
3.448
3.430
3.412
3.395
1.980
1.268
1.211
1.195
0.000
N
H
2.00
3.21
1.05
0.53
6.05
f1 (ppm)

6n


147.421
129.229
116.917
113.200
77.318
77.000
76.682
44.164
30.977
22.968
N
H
f1 (ppm)

6n


7.815
7.795
7.455
7.436
7.393
7.371
7.351
7.322
7.262
7.219
6.629
6.611
4.690
4.482
-0.000
N
H
6o
2.01
9.00
1.00
0.90
2.04


143.144
139.026
134.221
128.684
127.699
127.362
126.573
125.716
124.717
123.293
119.850
117.579
104.680
77.317
77.000
76.682
48.546
N
H
6o