Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Copper-catalyzed direct amination of benzylic hydrocarbons and inactive aliphatic alkanes with arylamines

Hua Yao, Bo Xie, Xiaoyang Zhong, Shengzhou Jin, Sen Lin*, and Zhaohua Yan*

College of Chemistry, Nanchang University, Nanchang 330031, PR China

*To whom correspondence should be addressed. Email: senlin@ncu.edu.cn

Table of Contents

1. General information

^{1}H and ^{13}C NMR spectra were recorded on Bruker Ascend™ 400 (400 MHz) using tetramethylsilane as an internal reference. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, m = multiplet, br = broad signal. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. The rest of chemicals were purchased from the Sinopharm Chemical Reagent Co., Adamas, Aladdin and TCI used as received. Q-TOF were used for the HRMS and GC-MS measurement. HRMS (ESI) data were obtained using electron spray ionization and GC-MS data were obtained using electron impact ionization.

2. General procedure for for the synthesis of 3, 5, 7, and 8

Without other special notes, all products of **3, 5, 7, and 8** were synthesized according to the following procedure: A 50 mL Schlenk tube was added amines **1, 4, or 6** (0.5 mmol), benzylic hydrocarbons **2** (or aliphatic alkanes) (2 mL), Cu powder (60 mol %) and DTBP (2 equiv). The tube was then charged with N_2 (1 atm), and was stirred at 120°C for 12 h. After the reaction mixture was cooled to room temperature, the reaction mixture was extracted with ethyl acetate (3×10 mL). The combined organic layer was washed with brine (10 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by flash chromatography on silica gel with a mixture of petroleum ether and ethyl acetate as eluent to afford various target compounds (PE/EA = 20/1--4/1).

3. Characterization data for amination products

N-benzyl-5-chloropyridin-2-amine **(3a)** [1]

Purified by using a flash column chromatography；isolated yield = 75%, 82.0 mg; white solid; mp: 114 – 115 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.34 – 7.31 (m, 5H), 7.26 (ddd, *J* = 7.9, 4.6, 3.2 Hz, 1H), 6.30 (d, *J* = 8.9 Hz, 1H), 5.09 (s, 1H), 4.46 (d, *J* = 5.8 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.96, 146.46, 138.73, 137.21, 128.82, 128.67, 127.36, 119.90, 107.57, 46.42.

N-benzyl-6-fluoropyridin-2-amine **(3b)**

Purified by using a flash column chromatography；isolated yield = 77%, 78.15 mg; white solid; mp: 101 – 102 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 3.0 Hz, 1H), 7.35 – 7.31 (m, 4H), 7.29 – 7.24 (m, 1H), 7.16 (ddd, *J* = 9.1, 7.9, 3.0 Hz, 1H), 6.30 (dd, *J* = 9.0, 3.4 Hz, 1H), 5.00 (s, 1H), 4.45 (d, *J* = 5.8 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.055(d, *J*=71.71 Hz), 152.29, 139.07, 134.71 (d, *J*=26.40 Hz), 128.63, 127.38, 127.28, 125.20 (d, *J*=20.20 Hz), 107.01 (d, *J*=4.04 z), 46.81. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}FN_2$ 203.0979; Found: 203.0970.

6-(benzylamino)nicotinonitrile **(3c)**

Purified by using a flash column chromatography；isolated yield = 72%, 75.24 mg; white solid; mp: 114 – 115 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 7.49 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.31 (t, *J* = 4.3 Hz, 5H), 6.36 (d, *J* = 8.8 Hz, 1H), 6.30 – 6.07 (m, 1H), 4.51 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.84, 153.03, 139.73, 137.66, 128.85, 127.76, 127.53, 118.57, 96.91, 45.92. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}N_3$ 210.1025; Found: 210.1015.

N-benzyl-5-bromopyridin-2-amine **(3d)**

Purified by using a flash column chromatography；isolated yield = 71%, 93.3mg; white solid; mp: 124 – 125℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 7.44 (d, *J* = 8.6 Hz, 1H), 7.32 (m, 5H), 6.27 (d, *J* = 8.8 Hz, 1H), 5.01 (s, 1H), 4.46 (d, *J* = 5.4 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.84, 153.03, 139.73, 137.66, 128.85, 127.76, 127.53, 118.57, 96.91, 45.92. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}BrN_2$ 263.0178; Found: 263.0166.

N-benzyl-5-iodopyridin-2-amine **(3e)**

Purified by using a flash column chromatography；isolated yield = 68%, 105.4 mg; white solid; mp: 128 – 129 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (s, 1H), 7.55 (d, *J* = 8.7 Hz, 1H), 7.30 – 7.25 (m, 5H), 6.19 (d, *J* = 8.7 Hz, 1H), 5.06 (s, 1H), 4.43 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.35, 153.73, 144.91, 138.56, 128.68, 127.39, 127.34, 109.08, 76.69, 46.18. HRMS (ESI-TOF) m/z: [M+H] $^{+}$ Calcd for $C_{12}H_{11}IN_2$ 311.0039; Found: 311.0028.

N-benzylpyridin-2-amine (3f) [1]

Purified by using a flash column chromatography；isolated yield = 51%, 47.0 mg; white solid; mp: 93 – 94 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 4.1 Hz, 1H), 7.40 – 7.30 (m, 5H), 7.27 – 7.24 (m, 1H), 6.59 – 6.55 (m, 1H), 6.35 (d, *J* = 8.4 Hz, 1H), 4.90 (s, 1H), 4.48 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.59, 148.17, 139.12, 137.49, 128.62, 127.37, 127.22, 113.15, 106.77, 46.30.

N-benzyl-3-methylpyridin-2-amine **(3g)**

Purified by using a flash column chromatography；isolated yield = 32%, 31.7 mg; white solid; mp: 92 – 93℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 4.0 Hz, 1H), 7.41 – 7.31 (m, 4H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.23 (d, *J* = 7.0 Hz, 1H), 6.55 (dd, *J* = 7.1, 5.1 Hz, 1H), 4.68 (d, *J* = 5.3 Hz, 2H), 4.36 (s, 1H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.64, 145.45, 139.96, 136.86, 128.60, 127.88, 127.19, 116.52, 112.91, 45.84, 17.01. HRMS (ESI-TOF) m/z: [M+H] $^{+}$ Calcd for $C_{13}H_{14}IN_2$ 199.1229; Found: 199.1223.

N-benzyl-4-methylpyridin-2-amine **(3h)**

Purified by using a flash column chromatography；isolated yield = 31%, 30.7 mg; white solid; mp: 98 – 99 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 5.2 Hz, 1H), 7.32 (d, *J* = 7.3 Hz, 4H), 7.25 (d, *J* = 7.0 Hz, 1H), 6.41 (d, *J* = 5.1 Hz, 1H), 6.18 (s, 1H), 4.93 (s, 1H), 4.47 (d, *J* = 5.6 Hz, 2H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.87, 148.51, 147.77, 139.30, 128.59, 127.37, 127.16, 114.74, 106.98, 46.29, 21.20. HRMS (ESI-TOF) m/z: [M+H] $^{+}$ Calcd for $C_{13}H_{14}IN_2$ 199.1229; Found: 199.1221.

N-benzyl-5-methylpyridin-2-amine **(3i)**

Purified by using a flash column chromatography；isolated yield = 33%, 32.7 mg; white solid; mp: 95 – 96℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.36 – 7.28 (m, 4H), 7.25 (d, *J* = 6.9 Hz, 1H), 7.20 (s, 1H), 6.29 (d, *J* = 8.4 Hz, 1H), 4.78 (s, 1H), 4.46 (d, *J* = 5.7 Hz, 2H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.83, 147.71, 139.36, 138.49, 128.57, 127.33, 127.13, 121.90, 106.42, 46.54, 17.40. HRMS (ESI-TOF) m/z: [M+H] $^{+}$ Calcd for $C_{13}H_{14}IN_2$ 199.1229; Found: 199.1222.

N-benzylpyridin-3-amine **(3j)** [1]

Purified by using a flash column chromatography；isolated yield = 29%, 26.7 mg; white solid; mp: 86 – 88 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.94 (d, *J* = 4.7 Hz, 1H), 7.34 – 7.33 (m, 4H), 7.27 (q, *J* = 4.2 Hz, 1H), 7.04 (dd, *J* = 8.4, 4.7 Hz, 1H), 6.86 – 6.82 (m, 1H), 4.32 (d, *J* = 5.0 Hz, 2H), 4.13 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.03, 138.71, 138.43, 135.97, 128.76, 127.51, 127.39, 123.77, 118.66, 47.83.

N-benzylpyrazin-2-amine **(3k)**

Purified by using a flash column chromatography；isolated yield =3 8%, 35.2 mg; white solid; mp: 69 – 71 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 2.6 Hz, 1H), 7.88 (s, 1H), 7.81 (d, *J* = 2.8 Hz, 1H), 7.34 – 7.33 (m, 4H), 7.29 – 7.26 (m, 1H), 4.89 (s, 1H), 4.55 (d, *J* = 5.8 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.37, 141.98, 138.38, 133.14, 132.08, 128.76, 127.56, 127.54, 45.55. HRMS (ESI-TOF) m/z: [M+H] $^{+}$ Calcd for $C_{11}H_{11}N_3$ 186.1025; Found: 186.1018.

N-benzylquinolin-8-amine (**3l)**

Purified by using a flash column chromatography；isolated yield = 46%, 53.9 mg; white solid; mp: 136 - 137 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.71 – 8.69 (m, 1H), 8.05 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.34 (dt, *J* = 7.9, 5.3 Hz, 4H), 7.27 (d, *J* = 7.4 Hz, 1H), 7.06 – 7.03 (m, 1H), 6.63 (d, *J* = 7.7 Hz, 1H),

6.59 (s, 1H), 4.55 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.88, 144.57, 139.22, 135.99, 129.38, 128.61, 128.58, 127.73, 127.39, 127.10, 121.36, 114.12, 105.11, 47.69. HRMS (ESI-TOF) m/z: [M+H] $^+$ Calcd for $C_{16}H_{14}N_2$ 235.1229; Found: 235.1219.

N-benzyl-4-nitroaniline **(5a)** [2]

Purified by using a flash column chromatography；isolated yield = 71%, 81.1 mg; yellow solid; mp: 147 – 148 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 9.0 Hz, 2H), 7.37 – 7.31 (m, 5H), 6.55 (d, *J* = 9.0 Hz, 2H), 4.92 (s, 1H), 4.42 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.05, 138.27, 137.34, 128.94, 127.85, 127.33, 126.40, 111.32, 47.61.

N-benzyl-4-(trifluoromethyl) aniline **(5b)** [3]

Purified by using a flash column chromatography；isolated yield = 70%, 88.1 mg; white solid; mp: 53 –54 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.31 (m, 4H), 7.31 – 7.27 (m, 1H), 6.62 (d, *J* = 8.4 Hz, 2H), 4.39 (s, 1H), 4.36 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.43, 138.42, 128.74, 127.48, 127.32, 126.58 (q, *J*=4.04 Hz), 126.28, 111.95, 112.75, 47.79.

4-(benzylamino) benzonitrile **(5c)** [4]

Purified by using a flash column chromatography；isolated yield = 66%, 68.7 mg; white solid; mp: 66 – 67 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 1.4 Hz, 1H), 7.33 (d, *J* = 3.9 Hz, 3H), 7.31 (s, 1H), 6.57 (d, *J* = 8.5 Hz, 2H), 4.71 (s, 1H), 4.36 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.18, 137.86, 133.69, 128.85, 127.65, 127.28, 120.42, 112.42, 98.93, 47.44.

3-(benzylamino) benzonitrile **(5d)** [5]

Purified by using a flash column chromatography；isolated yield = 64%, 66.6 mg; white solid; mp: 69 – 70 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 7.5 Hz, 1H), 7.36 – 7.33 (m, 4H), 7.21 (d, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.4 Hz, 1H), 6.81 – 6.78 (m, 2H), 4.32 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.19, 138.11, 129.88, 128.78, 127.59, 127.33, 120.94, 119.38, 117.24, 115.05, 112.95, 47.87.

N-benzyl-4-bromoaniline **(5e)** [6]

Purified by using a flash column chromatography；isolated yield = 54%, 70.7 mg; white solid; mp: 51 – 52℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 4.4 Hz, 4H), 7.27 (dd, *J* = 4.9, 3.7 Hz, 1H), 7.23 (d, *J* = 4.2 Hz, 2H), 6.48 (d, *J* = 8.7 Hz, 2H), 4.28 (s, 2H), 4.08 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.00, 138.81, 131.90, 128.69, 127.36, 127.34, 114.37, 109.07, 48.17.

N-benzyl-3-bromoaniline **(5f)**

Purified by using a flash column chromatography；isolated yield = 52%, 68.2 mg; white solid; mp: 112 – 113 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.30 (m, 4H), 7.27 (q, *J* = 4.1 Hz, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.76 (s, 1H), 6.51 (d, *J* = 6.8 Hz, 1H), 4.28 (s, 2H), 4.09 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.33, 138.67, 130.45, 128.69, 127.43, 127.40, 123.23, 120.31, 115.39, 111.49, 48.07. HRMS (ESI-TOF) m/z: [M+H] $^+$ Calcd for $C_{13}H_{12}BrN$ 262.0225; Found: 262.0213.

N-benzyl-3,5-dibromoaniline **(5g)**

Purified by using a flash column chromatography；isolated yield = 57%, 96.6 mg; white solid; mp: 108 – 109 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (q, *J* = 7.0 Hz, 5H), 6.95 (s, 1H), 6.67 (d, *J* = 1.6 Hz, 2H), 4.26 (s, 2H), 4.14 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.00, 137.99, 128.81, 127.64, 127.43, 123.46, 122.63, 114.26, 47.90. HRMS (ESI-TOF) m/z: [M+H] $^+$ Calcd for $C_{13}H_{11}Br_2N$ 339.9331; Found: 339.9327.

N-benzyl-4-iodoaniline **(5h)**

Purified by using a flash column chromatography；isolated yield = 45%, 69.8 mg; white solid; mp: 54 – 55 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (s, 2H), 7.33 (d, *J* = 4.3 Hz, 4H), 7.29 – 7.26 (m, 1H), 6.41 (s, 2H), 4.28 (s, 2H), 4.08 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.62, 138.80, 137.77, 128.68, 127.35, 127.33, 115.04, 78.08, 48.04. HRMS (ESI-TOF) m/z: [M+H] $^+$ Calcd for $C_{13}H_{12}IN$ 310.0087; Found: 310.0076

N-benzylaniline **(5i)** [7]

Purified by using a flash column chromatography；isolated yield = 26%, 23.9 mg; white solid; mp: 37 – 38 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 3H), 7.26 – 7.21 (m, 4H), 7.16 (s, 1H), 6.70 (dd, *J* = 19.6, 7.7 Hz, 2H), 4.64 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.17, 138.59, 129.17, 128.59, 126.84, 126.64, 116.70, 112.46, 54.18.

5-chloro-N-(4-methylbenzyl) pyridin-2-amine **(7a)**

Purified by using a flash column chromatography；isolated yield = 80%, 93.1 mg; white solid; mp: 156 – 157 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.22 (d, *J* = 7.3 Hz, 2H), 7.14 (d, *J* = 6.9 Hz, 2H), 6.29 (d, *J* = 8.9 Hz, 1H), 5.15 (s, 1H), 4.40 (d, *J* = 5.7 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.97, 146.44, 137.21, 137.08, 135.55, 129.37, 127.41, 119.73, 107.45, 46.23, 21.13. HRMS (ESI-TOF) m/z: [M+H] $^{+}$ Calcd for $C_{13}H_{13}ClN_2$ 233.0840; Found: 233.0846.

5-fluoro-N-(4-methylbenzyl) pyridin-2-amine **(7b)**

Purified by using a flash column chromatography；isolated yield = 82%, 88.7 mg; white solid; mp: 119 – 120 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.18 (s, 1H), 7.13 (s, 2H), 6.29 (d, *J* = 8.6 Hz, 1H), 4.97 (s, 1H), 4.39 (d, *J* = 5.6 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.04 (d, *J*=79.79), 152.22, 136.99, 1365.88, 134.70(d, *J*=25.25), 129.34, 127.41, 125.26(d, J=21.21), 106.95, 46.59, 26.11. HRMS (ESI-TOF) m/z: [M+H] $^{+}$ Calcd for $C_{13}H_{13}FN_2$ 217.1136; Found: 217.1143.

5-bromo-N-(4-methylbenzyl) pyridin-2-amine **(7c)**

Purified by using a flash column chromatography；isolated yield = 76%, 105.3 mg; white solid; mp: 169 – 170 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.21 (d, *J* = 7.3 Hz, 2H), 7.13 (d, *J* = 7.2 Hz, 2H), 6.26 (d, *J* = 8.7 Hz, 1H), 5.08 (s, 1H), 4.40 (d, *J* = 5.6 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.16, 148.69, 139.72, 137.08, 135.51, 129.36, 127.37, 108.15, 107.12, 46.15, 21.10. HRMS (ESI-TOF) m/z: [M+H] $^{+}$ Calcd for $C_{13}H_{13}BrN_2$ 277.0349; Found: 277.0346.

N-(4-methylbenzyl) pyridin-2-amine **(7d)** [8]

Purified by using a flash column chromatography；isolated yield = 61%, 60.5 mg; white solid; mp: 73 – 74 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 5.0 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 2H), 6.60 – 6.52 (m, 1H), 6.35 (d, *J* = 8.4 Hz, 1H), 4.97 (s, 1H), 4.44 (d, *J* = 5.6 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.66, 148.13, 137.46, 136.84, 136.04, 129.29, 127.37, 113.01, 106.71, 46.08, 21.10.

N-(2-methylbenzyl) pyridin-2-amine **(7e)**

Purified by using a flash column chromatography；isolated yield = 58%, 57.6 mg; white solid; mp: 90 – 91 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 4.9 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 6.7 Hz, 1H), 7.18 (s, 3H), 6.60 – 6.53 (m, 1H), 6.35 (d, *J* = 8.3 Hz, 1H), 4.86 (s, 1H), 4.44 (d, *J* = 5.4 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.66, 148.15, 137.45, 136.74, 136.32, 130.41, 127.98, 127.40, 126.13, 112.95, 106.73, 44.42, 19.02. HRMS (ESI-TOF) m/z: [M+H] $^{+}$ Calcd for $C_{13}H_{14}N_2$ 199.1229; Found: 199.1220.

5-chloro-N-(4-chlorobenzyl) pyridin-2-amine **(7f)**

Purified by using a flash column chromatography；isolated yield = 39%, 38.6 mg; yellow solid; mp: 110 – 111 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.33 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.26 (d, *J* = 6.3 Hz, 4H), 6.28 (d, *J* = 8.9 Hz, 1H), 4.91 (s, 1H), 4.44 (d, *J* = 5.9 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.61, 146.48, 137.31, 137.26, 133.02, 128.77, 128.61, 120.19, 107.76, 45.62. HRMS (ESI-TOF) m/z: [M+H] $^{+}$ Calcd for $C_{12}H_{10}Cl_2N_2$ 253.0294; Found: 253.0297.

5-chloro-N-(3,5-dimethylbenzyl) pyridin-2-amine **(7h)**

Purified by using a flash column chromatography；isolated yield = 69%, 85.1 mg; white solid; mp: 128 – 129 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 6.93 – 6.90 (m, 3H), 6.30 (d, *J* = 8.6 Hz, 1H), 4.88 (s, 1H), 4.37 (d, *J* = 5.5 Hz, 2H), 2.28 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.92, 150.96，146.44, 138.51, 138.30, 137.21, 129.00, 125.15, 107.54, 46.39, 21.27. HMS (ESI-TOF) m/z: [M+H] $^+$ Calcd for $C_{14}H_{15}ClN_2$ 247.0996; Found: 247.0994.

N-(3,5-dimethylbenzyl) pyridin-2-amine **(7i)**

Purified by using a flash column chromatography；isolated yield = 54%, 57.3 mg; white solid; mp: 98 – 99 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 5.0 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 6.97 (s, 2H), 6.90 (s, 1H), 6.57 (t, *J* = 6.1 Hz, 1H), 6.36 (d, *J* = 8.4 Hz, 1H), 4.91 (s, 1H), 4.40 (d, *J* = 5.5 Hz, 2H), 2.29 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.67, 148.13, 138.97, 138.20, 137.47, 128.87, 125.22, 113.01, 106.71, 46.31, 21.28. HRMS (ESI-TOF) m/z: [M+H] $^+$ Calcd for $C_{14}H_{16}N_2$ 213.1386; Found: 213.1395.

5-chloro-N-(1-phenylethyl) pyridin-2-amine **(7j)**

Purified by using a flash column chromatography；isolated yield = 58%, 67.5 mg; white solid; mp: 132 – 133 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.36 – 7.28 (m, 4H), 7.24 (d, *J* = 6.3 Hz, 2H), 6.12 (d, *J* = 8.9 Hz, 1H), 5.11 (d, *J* = 6.3 Hz, 1H), 4.66 (q, *J* = 6.7 Hz, 1H), 1.53 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.32, 146.50, 144.16, 137.17, 128.72, 127.17, 125.77, 119.78, 107.40, 52.14, 24.33. HRMS (ESI-TOF) m/z: [M+H] $^+$ Calcd for $C_{13}H_{13}ClN_2$ 233.0840; Found: 233.0832.

5-bromo-N-(1-phenylethyl) pyridin-2-amine **(7k)**

Purified by using a flash column chromatography；isolated yield = 55%, 76.2mg; white solid; mp: 141 – 142 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.38 – 7.27 (m, 6H), 6.09 (d, *J* = 8.0 Hz, 1H), 5.28 (s, 1H), 4.70 – 4.65 (m, 1H), 1.53 (d, *J* = 4.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.61, 148.71, 144.13, 139.73, 128.74, 127.18, 125.79, 108.11, 107.12, 52.07, 24.26. HRMS (ESI-TOF) m/z: [M+H] $^+$ Calcd for $C_{13}H_{13}BrN_2$ 277.0334; Found: 277.0330.

N-(1-phenylethyl) pyridin-2-amine **(7l)** [8]

Purified by using a flash column chromatography；isolated yield = 43%, 42.6 mg; yellow oil; mp: 87 – 89 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 3.9 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 3H), 7.22 (t, *J* = 7.1 Hz, 1H), 6.55 – 6.49 (m, 1H), 6.18 (d, *J* = 8.4 Hz, 1H), 5.30 (s, 1H), 4.69 (q, *J* = 6.6 Hz, 1H), 1.53 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.01, 147.96, 144.66, 137.56, 128.64, 126.99, 125.83, 112.95, 106.68, 51.95, 24.44.

5-chloro-N-(1-phenylpropyl) pyridin-2-amine **(7m)**

Purified by using a flash column chromatography；isolated yield = 47%, 58.0 mg; white solid; mp: 128 – 130 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 7.30 – 7.26 (m, 4H), 7.24 – 7.23 (m, 1H), 7.22 – 7.21 (m, 1H), 6.11 (d, *J* = 8.8 Hz, 1H), 5.06 (d, *J* = 6.6 Hz, 1H), 4.39 (d, *J* = 6.7 Hz, 1H), 1.83 (q, *J* = 6.9 Hz, 2H), 0.95 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.56, 146.50, 142.84, 137.16, 128.58, 127.17, 126.37, 119.71, 107.22, 58.32, 31.15, 10.72. HRMS (ESI-TOF) m/z: [M+H] $^+$ Calcd for $C_{14}H_{15}ClN_2$ 247.0996; Found: 247.0996.

N-(1-phenylpropyl) pyridin-2-amine **(7n)**

Purified by using a flash column chromatography；isolated yield = 33%, 35.1 mg; white solid; mp:80 – 81℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 3.3 Hz, 1H), 7.36 – 7.26 (m, 5H), 7.22 (d, *J* = 7.0 Hz, 1H), 6.52 – 6.47 (m, 1H), 6.17 (d, *J* = 8.4 Hz, 1H), 5.39 (d, *J* = 6.5 Hz, 1H), 4.43 (q, *J* = 6.8 Hz, 1H), 1.84 (dt, *J* = 14.1, 7.2 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.40, 148.17, 143.48, 137.49, 128.52, 127.00, 126.45, 112.90, 106.40, 58.17, 31.33, 10.87. HRMS (ESI-TOF) m/z: [M+H] $^+$ Calcd for $C_{14}H_{16}N_2$ 213.1386; Found: 213.1395.

5-chloro-N-cyclohexylpyridin-2-amine **(7o)**

Purified by using a flash column chromatography；isolated yield = 46%, 48.5 mg; white solid; mp: 71 – 72 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 6.27 (d, *J* = 8.9 Hz, 1H), 4.46 (s, 1H), 3.44 (d, *J* = 11.8 Hz, 1H), 1.99 (d, *J* = 11.1 Hz, 2H), 1.75 – 1.69 (m, 2H), 1.61 (d, *J* = 9.8 Hz, 1H), 1.35 (d, *J* = 11.3 Hz, 2H), 1.17 (t, *J* = 11.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.37, 146.47, 137.08, 118.93, 107.49, 50.38, 33.17, 25.69, 24.82. HRMS (ESI-TOF) m/z: [M+H] $^+$ Calcd for $C_{11}H_{15}ClN_2$ 211.0097; Found: 211.1007.

5-bromo-N-cyclohexylpyridin-2-amine **(7p)**

Purified by using a flash column chromatography；isolated yield = 42%, 53.8 mg; white solid; mp: 62 – 63 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.41 (d, *J* = 8.7 Hz, 1H), 6.24 (d, *J* = 8.5 Hz, 1H), 4.47 (d, *J* = 8.1 Hz, 1H), 3.48 – 3.40 (m, 1H), 1.98 (d, *J* = 11.1 Hz, 2H), 1.72 (d, *J* = 12.3 Hz, 2H), 1.61 (d, *J* = 11.7 Hz, 1H), 1.34 (t, *J* = 12.4 Hz, 2H), 1.17 (t, *J* = 11.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.56, 148.70, 139.60, 108.16, 106.21, 50.32, 33.13, 25.68, 24.81. HRMS (ESI-TOF) m/z: [M+H] $^+$ Calcd for $C_{11}H_{15}BrN_2$ 255.0491; Found: 255.0498.

N-cyclohexylpyridin-2-amine **(7q)** [9]

Purified by using a flash column chromatography；isolated yield = 35%, 30.8 mg; white solid; mp: 125 – 126 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 5.0 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 6.49 (t, *J* = 6.1 Hz, 1H), 6.32 (d, *J* = 8.5 Hz, 1H), 4.43 (d, *J* = 8.2 Hz, 1H), 3.52 – 3.44 (m, 1H), 2.01 (d, *J* = 12.4 Hz, 2H), 1.72 (d, *J* = 10.8 Hz, 2H), 1.61 (d, *J* = 12.3 Hz, 1H), 1.35 (t, *J* = 12.5 Hz, 2H), 1.23 – 1.14 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.97, 148.04, 137.41, 112.27, 106.69, 50.11, 33.29, 25.75, 24.87.

N-(4-methylbenzyl)-5-nitropyridin-2-amine **(8a)**

Purified by using a flash column chromatography；isolated yield = 75%, 91.2 mg; yellow solid; mp: 175 – 176 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.77 (s, 1H), 7.21 – 7.08 (m, 4H), 6.61 (d, *J* = 8.9 Hz, 2H), 4.32 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.82, 136.60, 136.25, 135.82, 129.49, 127.63, 126.58, 121.54, 46.01, 21.08. HRMS (ESI-TOF) m/z: [M+H] $^+$ Calcd for $C_{14}H_{14}N_2O_2$ 243.1128 Found: 243.1117.

N-(2-methylbenzyl)-4-nitroaniline **(8b)**

Purified by using a flash column chromatography；isolated yield = 72%, 87.5 mg; yellow solid; mp: 179 – 180 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 8.8 Hz, 2H), 7.25 – 7.20 (m, 4H), 6.55 (d, *J* = 8.8 Hz, 2H), 4.66 (s, 1H), 4.35 (d, *J* = 5.2 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.05, 138.15, 136.28, 134.92, 130.75, 128.09, 128.06, 126.45, 126.41, 111.14, 45.79, 18.96. HRMS (ESI-TOF) m/z: [M+H] $^+$ Calcd for $C_{14}H_{14}N_2O_2$ 243.1128 Found: 243.1116.

N-(2-methylbenzyl)-4-(trifluoromethyl) aniline **(8c)**

Purified by using a flash column chromatography；isolated yield =7 0%, 92.8 mg; yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.24 – 7.17 (m, 3H), 6.62 (d, *J* = 8.4 Hz, 2H), 4.29 (s, 2H), 4.18 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.53, 136.28, 135.99, 130.57, 128.07, 127.72, 126,63 (q, *J*=4.04 Hz), 126.30, 126.26, 123.61, 111.77, 45.89, 18.91. HRMS (ESI-TOF) m/z: [M+H] $^+$ Calcd for $C_{15}H_{14}F_3N$ 266.1151; Found: 266.1143.

N-(4-chlorobenzyl)-4-nitroaniline **(8d)**

Purified by using a flash column chromatography；isolated yield = 18%, 23.7 mg; yellow solid; mp: 185 – 186 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 (d, *J* = 9.0 Hz, 2H), 7.82 (t, *J* = 5.5 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 8.7 Hz, 2H), 4.38 (d, *J* = 5.9 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.65, 138.10, 136.48, 132.01, 129.48, 128.90, 126.61, 121.51, 45.47. HRMS (ESI-TOF) m/z: [M+H] $^+$ Calcd for $C_{13}H_{11}ClN_2O_2$ 263.0582; Found: 263.0583.

N-(3,5-dimethylbenzyl)-4-nitroaniline **(8e)**

Purified by using a flash column chromatography；isolated yield = 66%, 84.6 mg; yellow solid; mp: 136 – 137 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.7 Hz, 2H), 6.93 (s, 3H), 6.55 (d, *J* = 8.7 Hz, 2H), 4.86 (s, 1H), 4.32 (d, *J* = 5.4 Hz, 2H), 2.30 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.16, 138.59, 138.09, 137.24, 129.44, 126.41, 125.17, 111.24, 47.60, 21.29. HRMS (ESI-TOF) m/z: [M+H] $^{+}$ Calcd for $C_{15}H_{16}N_2O_2$ 257.1284; Found: 257.1274.

N-(3,5-dimethylbenzyl)-4-(trifluoromethyl) aniline **(8f)**

Purified by using a flash column chromatography；isolated yield = 63%, 88.1 mg; yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.3 Hz, 2H), 6.95 – 6.92 (m, 3H), 6.61 (d, *J* = 8.3 Hz, 2H), 4.31 (s, 1H), 4.26 (d, *J* = 4.3 Hz, 2H), 2.30 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.53, 138.40, 138.32, 129.14, 126.58(q, *J*=4.04 Hz) 126.30, 125.22, 123.61, 111.87, 47.49, 21.28. HRMS (ESI-TOF) m/z: [M+H] $^{+}$ Calcd for $C_{16}H_{16}F_3N$ 280.1307; Found: 280.1294.

4-nitro-N-(1-phenylethyl) aniline **(8g)** [10]

Purified by using a flash column chromatography；isolated yield = 32%, 38.8 mg; yellow solid; mp: 95 – 96 ℃ ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01-7.96 (m, 2H), 7.35 – 7.25 (m, 5H), 6.44 (d, *J* = 9.2 Hz, 2H), 4.83 (s, 1H), 4.61 – 4.55 (m, 1H), 1.57 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.19, 143.19, 128.96, 127.51, 126.21, 125.59, 111.82, 53.28, 24.57.

REFERENCE

(1) X.-C. Yu, C.-Z. Liu, L. Jiang, Q. Xu, Manganese Dioxide Catalyzed N-Alkylation of Sulfonamides and Amines with Alcohols under Air. *Organic Letters*., 2011, **13**, 23, 6184-6187.

(2) R.-J. He, P.-H. Toy, Y.-L. Lam, Polymer-supported Hantzsch 1,4-dihydropyridine ester: an efficient biomimetic hydrogen source. *Adv. Synth. Catal*., 2008, **350**, 54-60.

(3) J.-W. Xie, X.-H. Zhu, M.-N. Huang, F. Meng, W.-W. Chen, Y.-Q. Wan, Pyrrole-2-carbohydrazides as Ligands for Cu-Catalyzed Amination of Aryl Halides with Amines in Pure Water. *Eur. J. Org., Chem*., 2010, 3219–3223.

(4) P.-R. Likhar, R. Arundhathi, M.-L. Kantam, P.-S. Prathima, Amination of Alcohols Catalyzed by Copper-Aluminum Hydrotalcite: A Green Synthesis of Amines. *Eur. J. Org. Chem*., 2009, **31**, 5383-5389.

(5) Y.-S. Zhao, S. W. Foo, S. Saito, Iron/Amino Acid Catalyzed Direct N-Alkylation of Amines with Alcohols. *Angew. Chem. Int. Ed*., 2011, **50**, 3006-3009.

(6) H. Zhang, Q. Cai, D.-W. Ma, Amino Acid Promoted CuI-Catalyzed C-N Bond Formation between Aryl Halides and Amines or N-Containing Heterocycles. *J. Org. Chem*., 2005, **70**, 5164-5173.

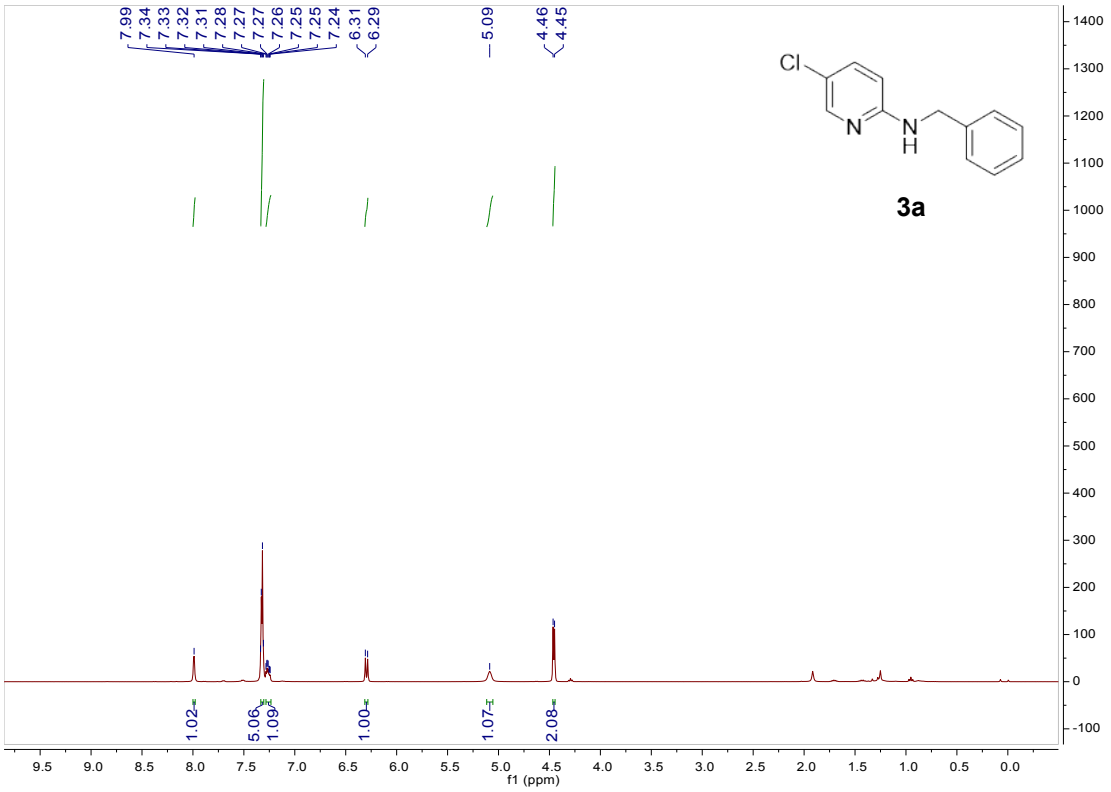
(7) D. B. Bagal, R. A. Watile, M. V. Khedkar, K. P. Dhake, B. M. Bhanage, Amino Acid Promoted CuI-Catalyzed C-N Bond Formation between Aryl Halides and Amines or N-Containing Heterocycles. *Catal. Sci. Technol*., 2012, **2**, 2, 354-358.

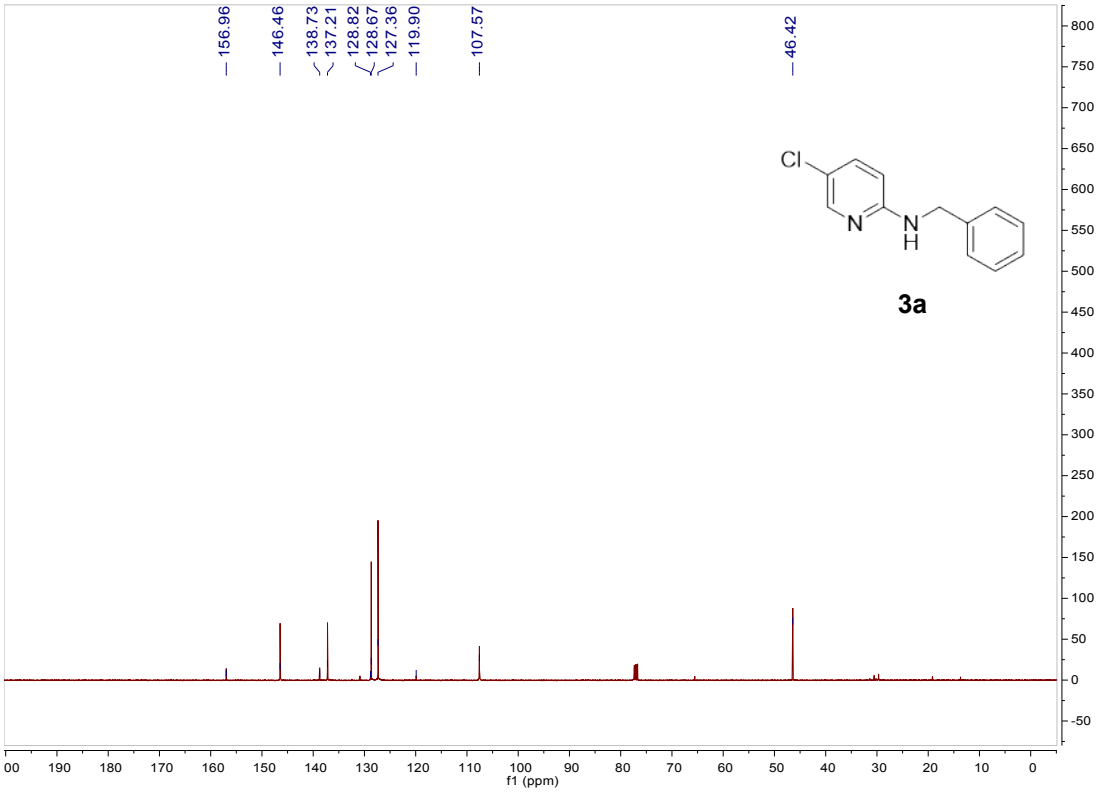
(8) M. A. Ana; D. J. Ramon, M. Yus, N-Alkylation of poor nucleophilic amines and derivatives with alcohols by a hydrogen autotransfer process catalyzed by copper (II) acetate: Scope and mechanistic considerations. *Tetrahedron*., 2011, **67**, 17, 3140-3149.

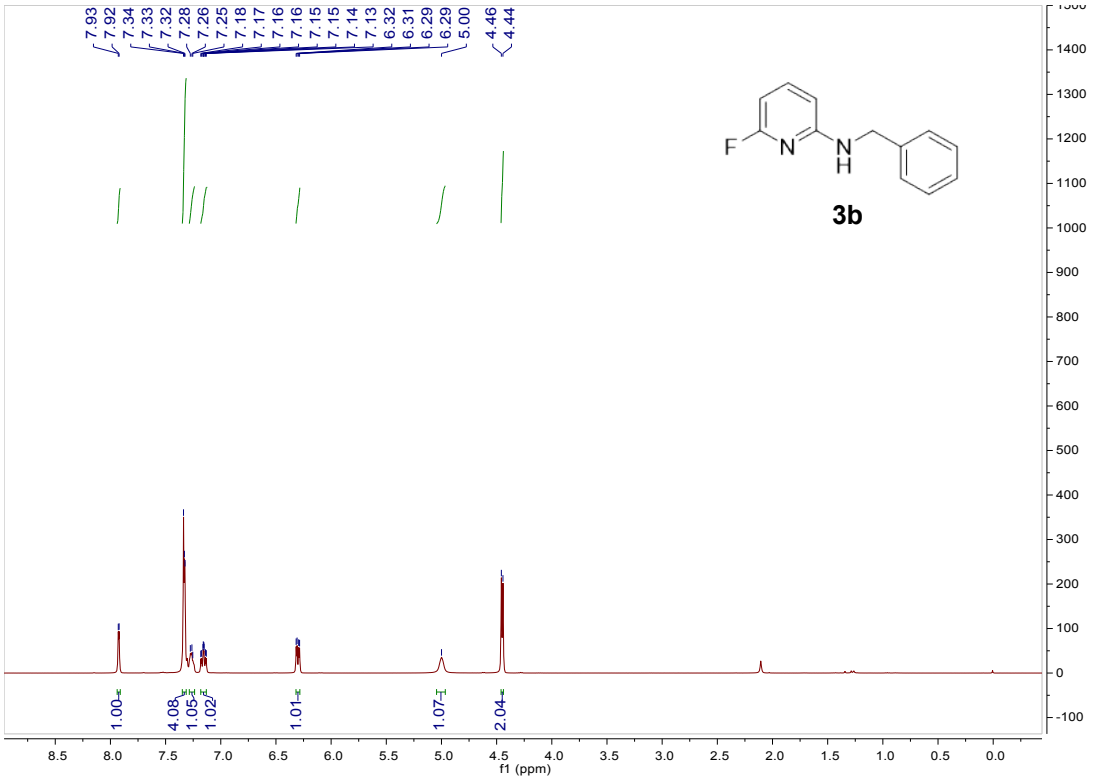
(9) Z.-Q. Wu, L. Zhou, Z.-Q. Jiang, D. Wu, Z.-K. Li, X.-G. Zhou, Sulfonato-Cu (salen) complex catalyzed N-arylation of aliphatic amines with aryl halides in water. *Eur. J. Org. Chem.,* 2010**, 26**, 4971-4975.

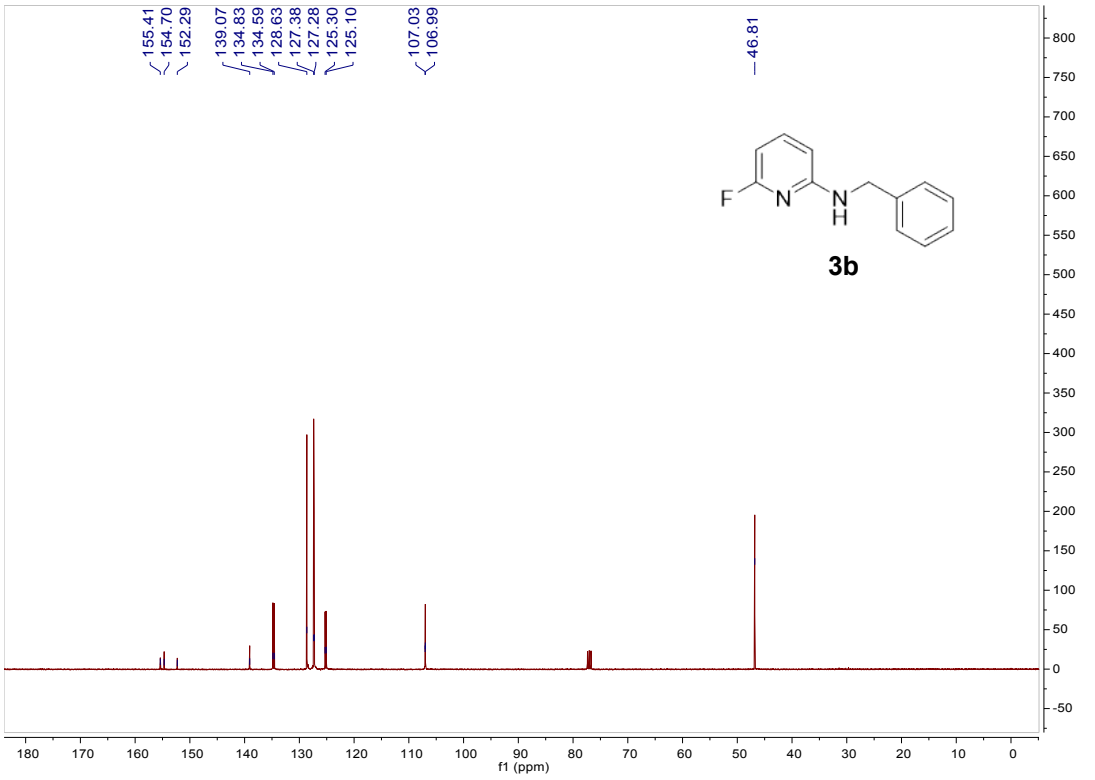
(10) S. Haubenreisser, M. Niggemann, Calcium-Catalyzed Direct Amination of π-Activated Alcohols. *Adv. Synth. Catal.,* 2011, **353,** 469-474.

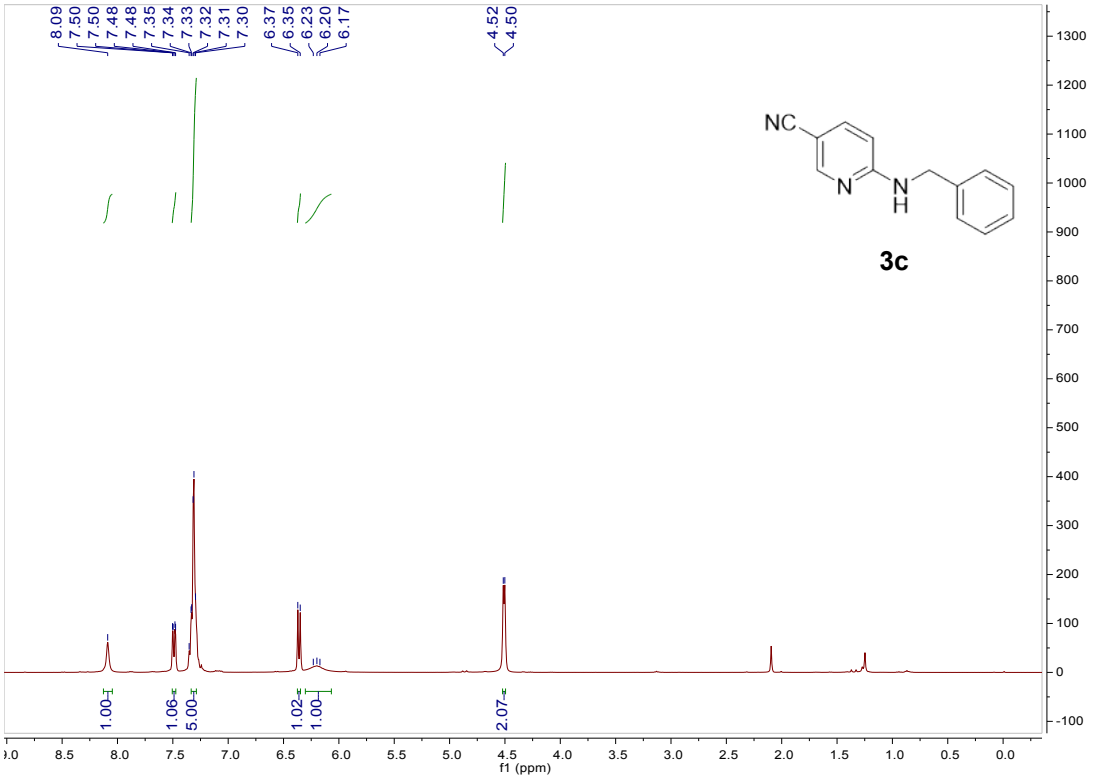
4.^{1}H NMR and ^{13}C NMR for all compounds

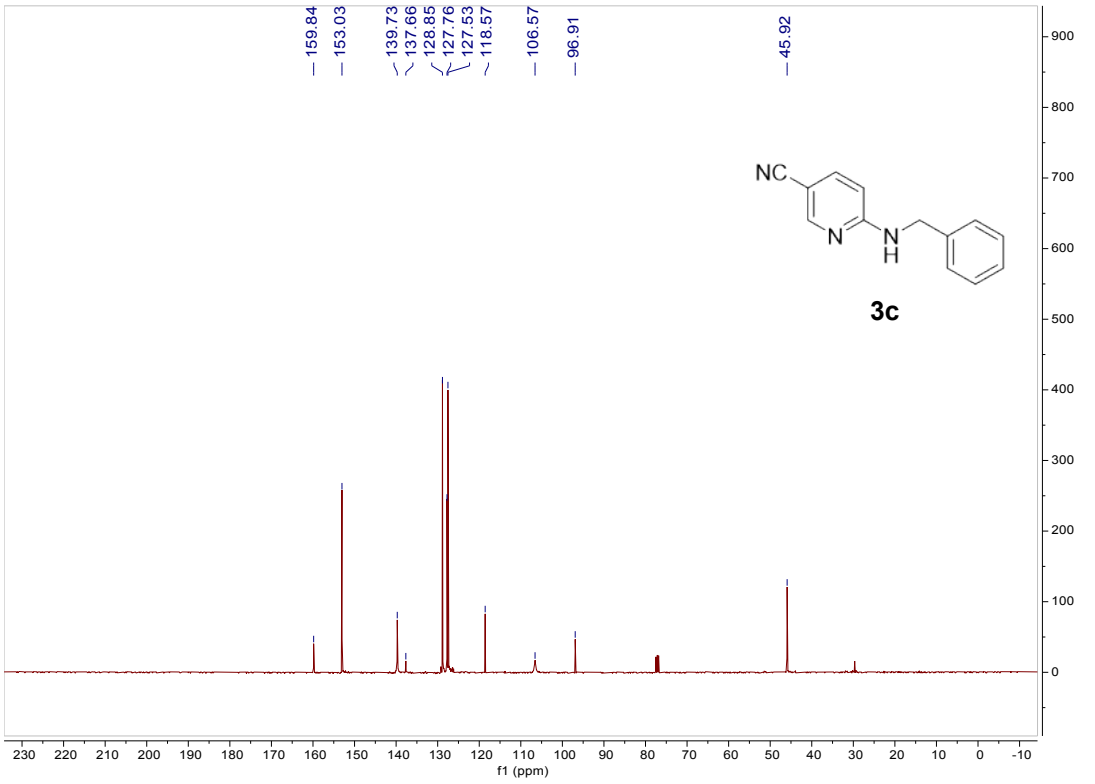


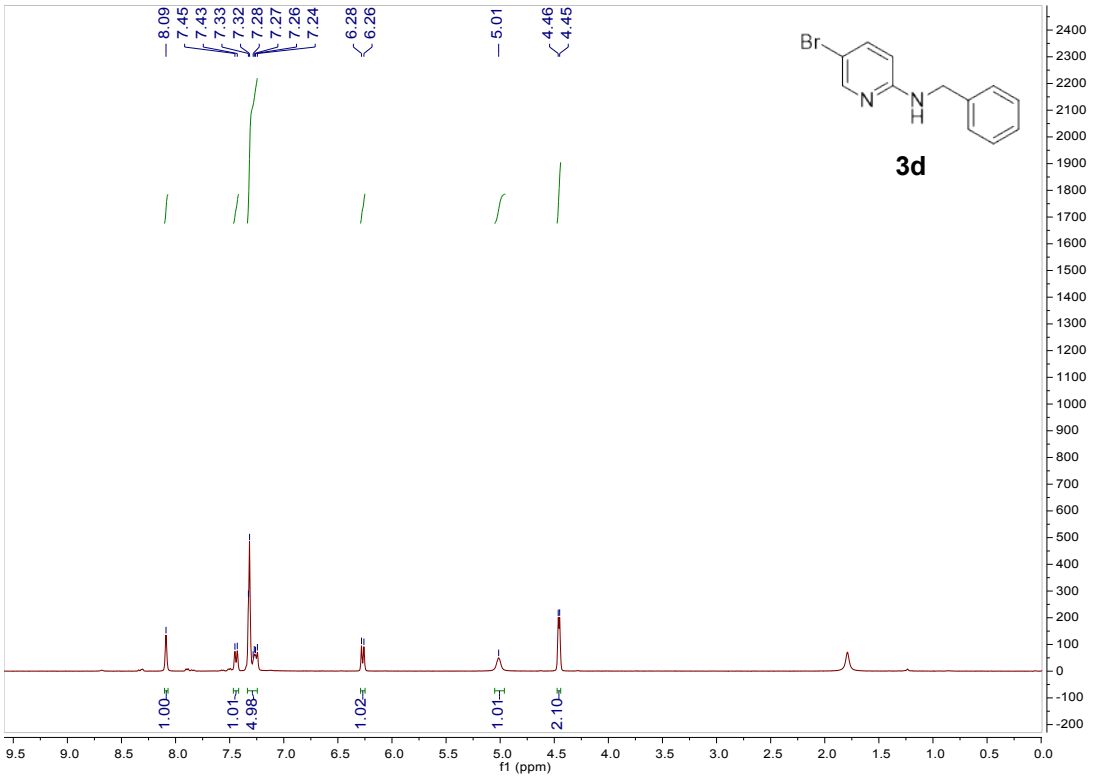


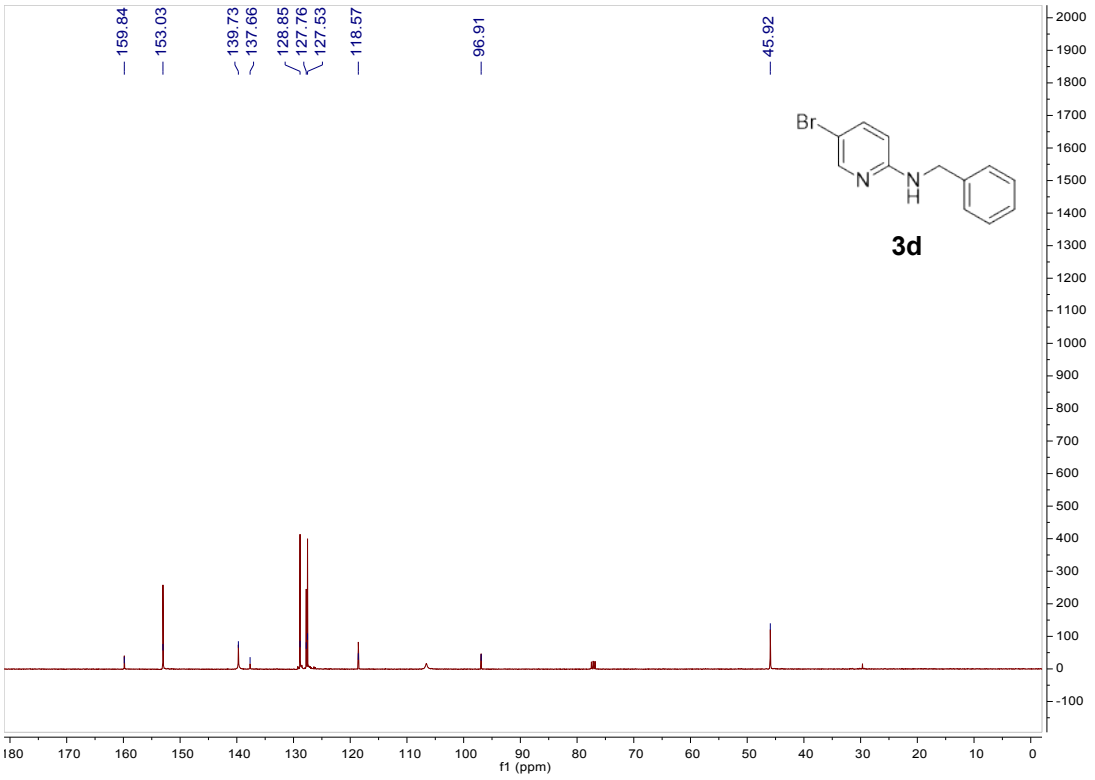

7.93
7.92
7.34
7.33
7.32
7.28
7.26
7.25
7.18
7.17
7.16
7.16
7.15
7.15
7.14
7.13
6.32
6.31
6.29
6.29
5.00
4.46
4.44
F
N
N
H
3b
1.00
4.08
1.05
1.02
1.01
1.07
2.04
f1 (ppm)

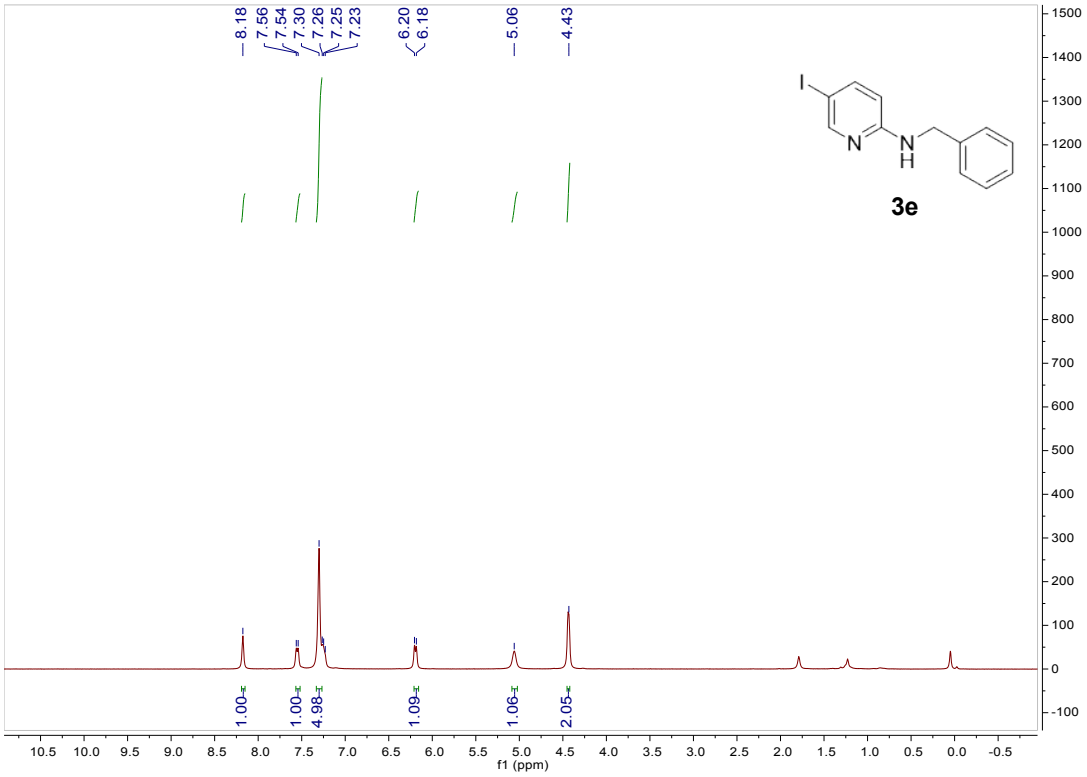

155.41
154.70
152.29
139.07
134.83
134.59
128.63
127.38
127.28
125.30
125.10
107.03
106.99
46.81
F
N
N
H
3b
f1 (ppm)

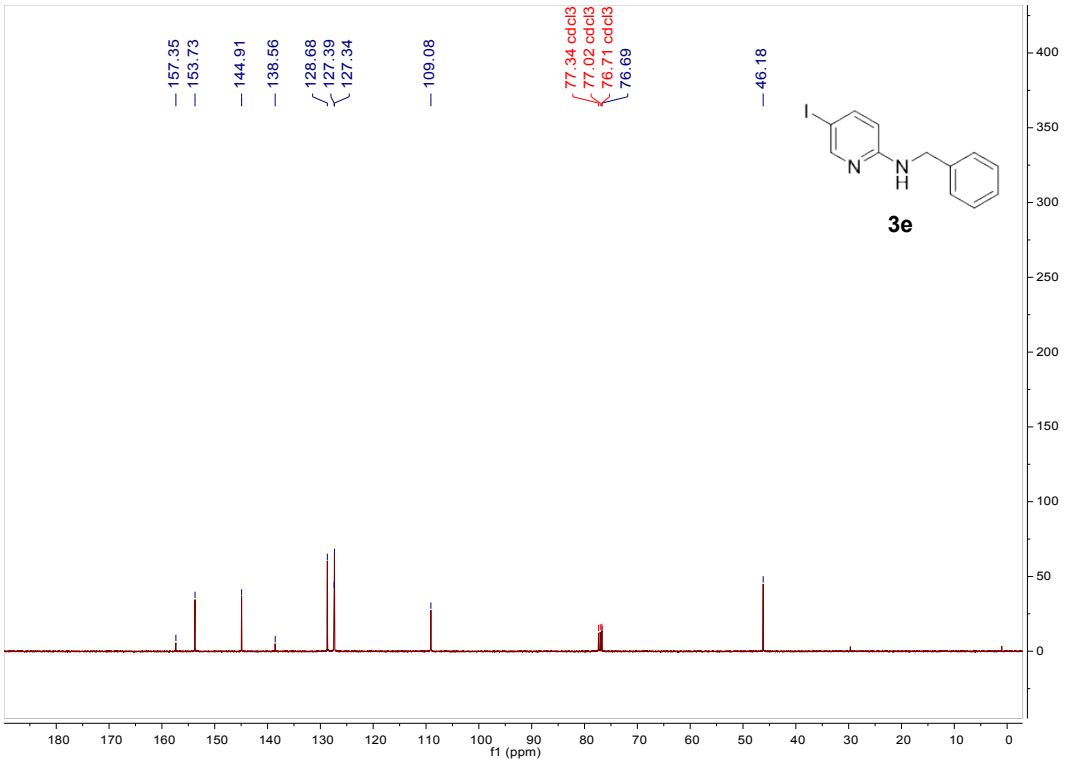

8.09
7.50
7.50
7.48
7.48
7.35
7.34
7.33
7.32
7.31
7.30
6.37
6.35
6.23
6.20
6.17
4.52
4.50
NC
N
N
H
3c
1.00
1.06
5.00
1.02
1.00
2.07
f1 (ppm)

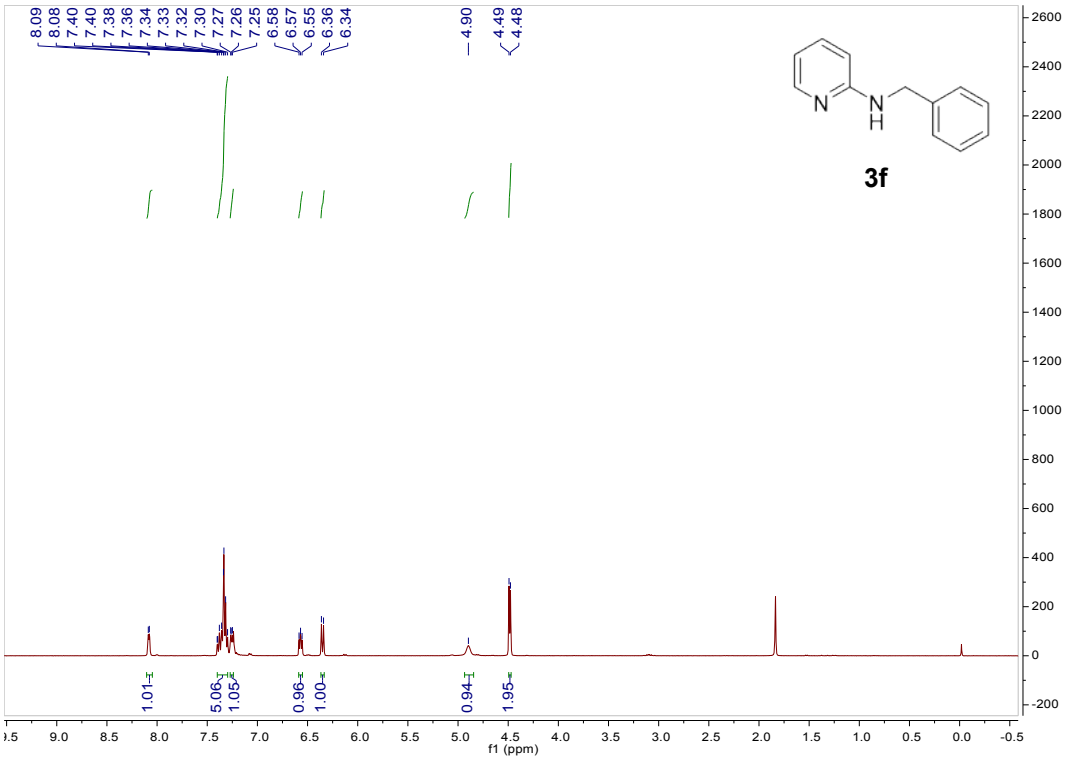

159.84
153.03
139.73
137.66
128.85
127.76
127.53
118.57
106.57
96.91
45.92
NC
N
N
H
3c
f1 (ppm)

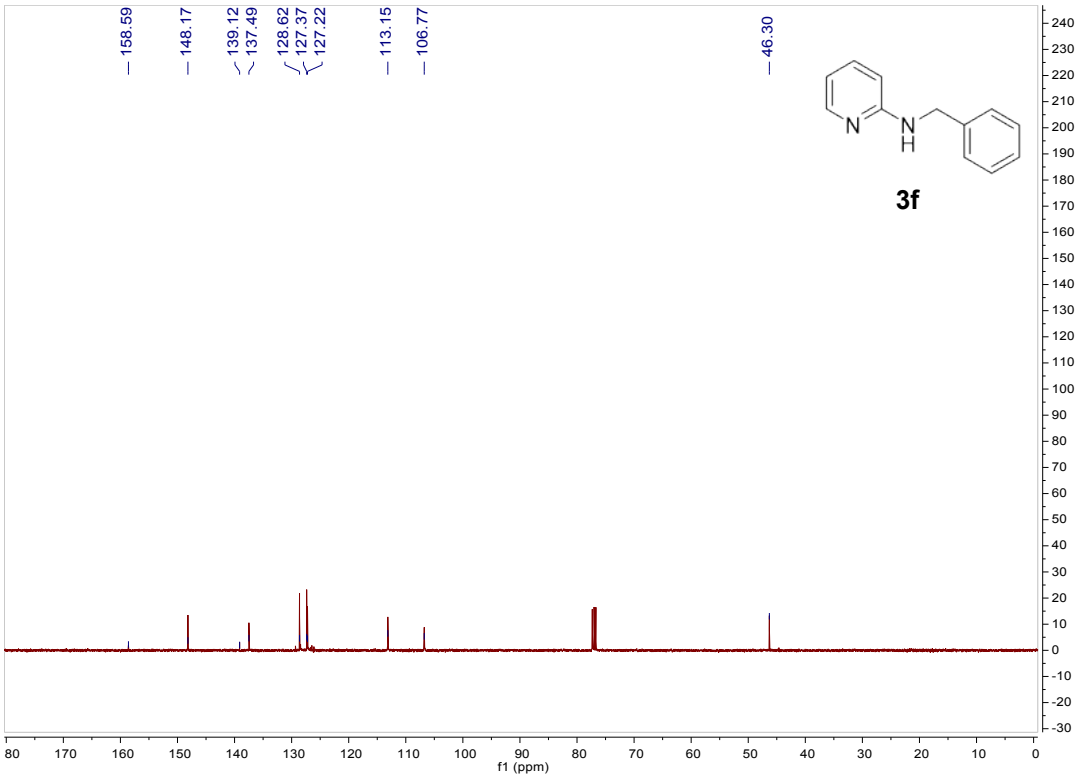

8.09
7.45
7.43
7.33
7.32
7.28
7.27
7.26
7.24
6.28
6.26
5.01
4.46
4.45
Br
N
H
3d
1.00
1.01
4.98
1.02
1.01
2.10
f1 (ppm)

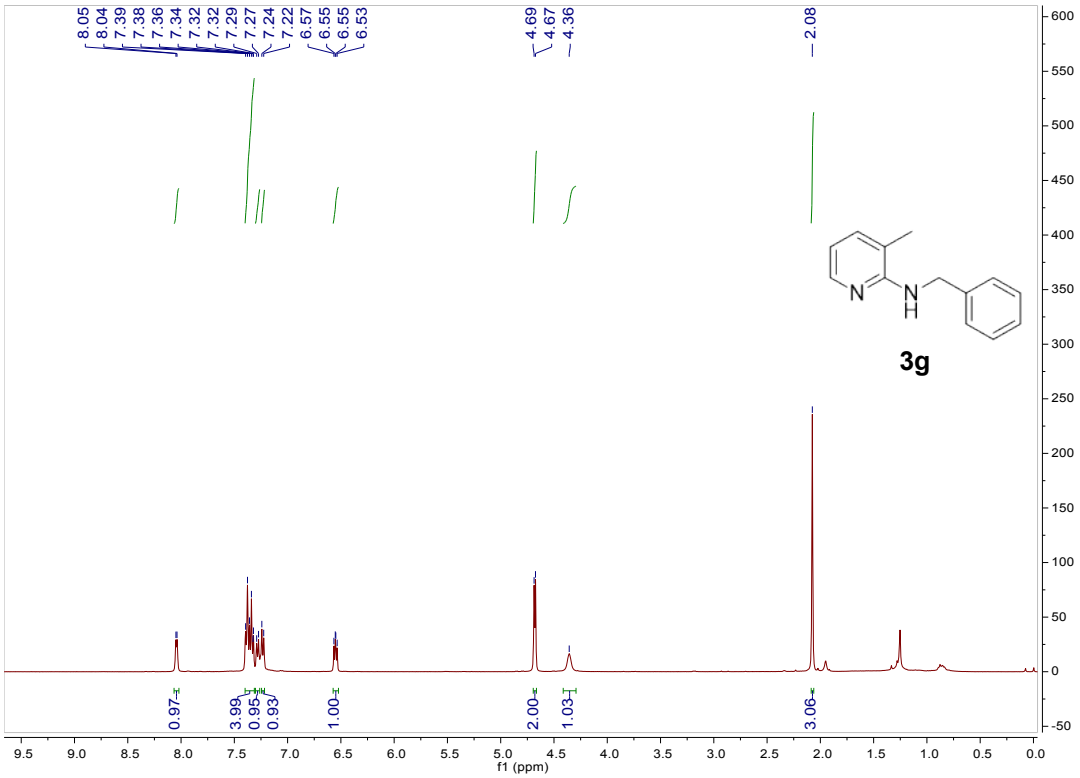

159.84
153.03
139.73
137.66
128.85
127.76
127.53
118.57
96.91
45.92
Br
N
H
3d
f1 (ppm)

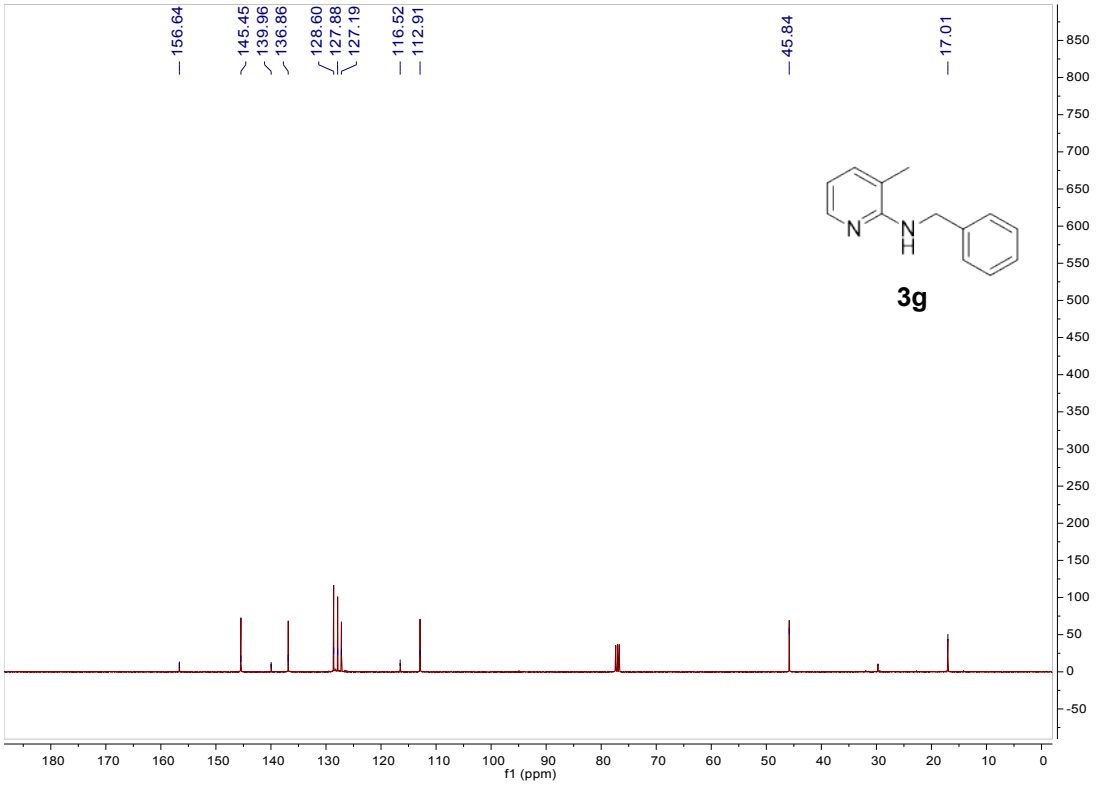

8.18
7.56
7.54
7.30
7.26
7.25
7.23
6.20
6.18
5.06
4.43
1.00
1.00
4.98
1.09
1.06
2.05
I
N
N
H
3e
f1 (ppm)

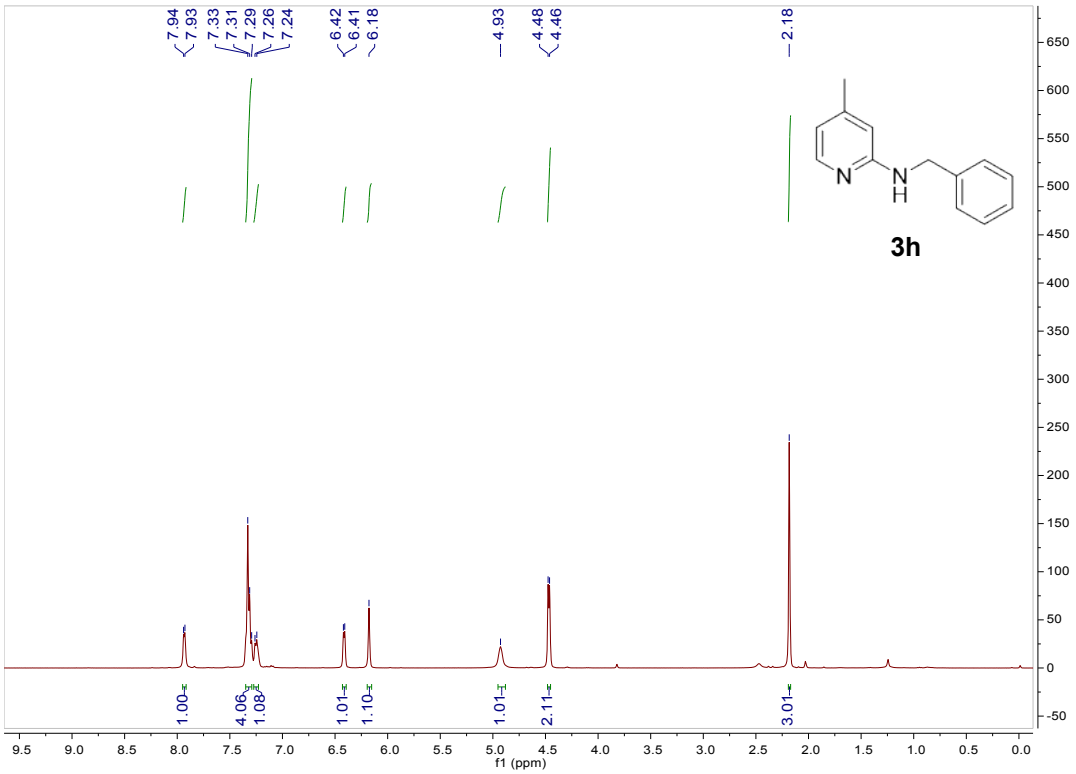

157.35
153.73
144.91
138.56
128.88
127.39
127.34
109.08
77.34 cdcl3
77.02 cdcl3
76.71 cdcl3
76.69
46.18
I
N
N
H
3e
f1 (ppm)

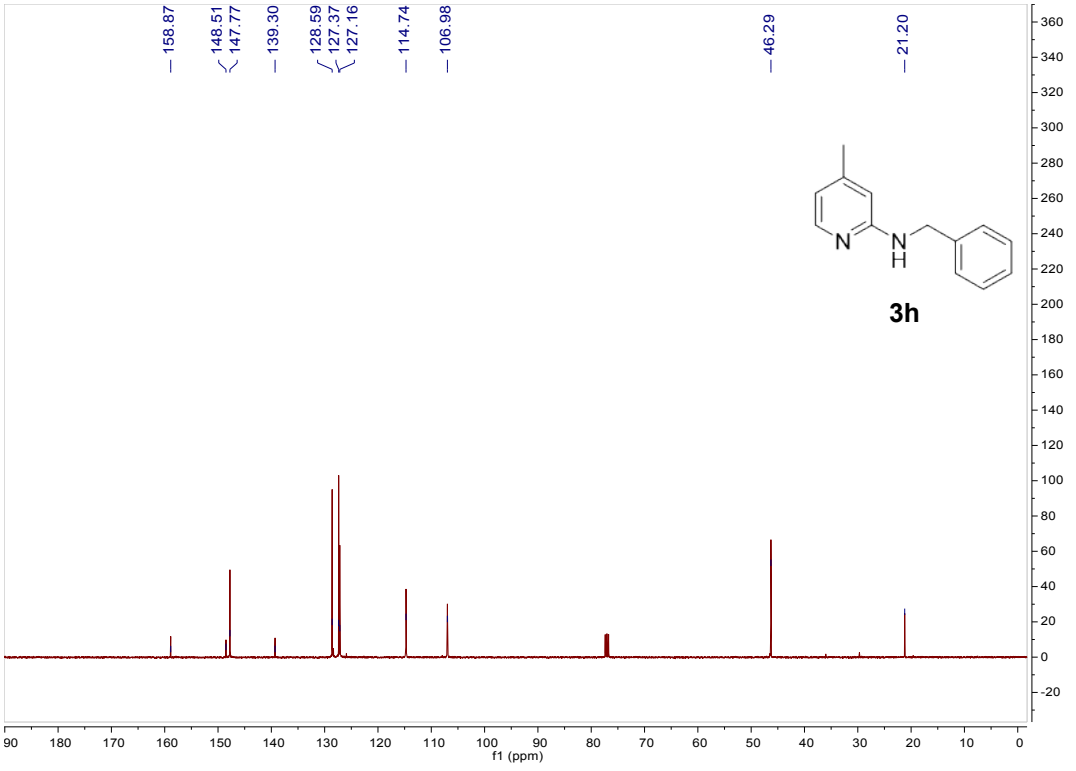

8.09
8.08
7.40
7.40
7.38
7.36
7.34
7.33
7.32
7.30
7.27
7.26
7.25
6.58
6.57
6.55
6.36
6.34
4.90
4.49
4.48
1.01
5.06
1.05
0.96
1.00
0.94
1.95
f1 (ppm)
3f

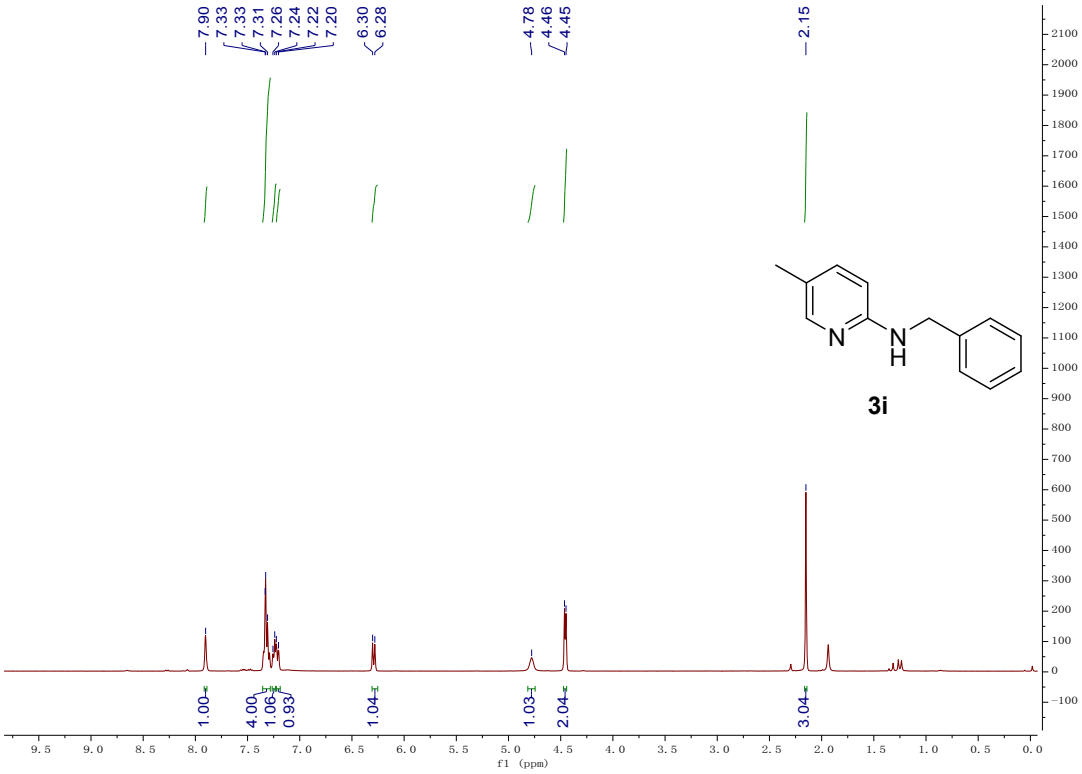

158.59
148.17
139.12
137.49
128.62
127.37
127.22
113.15
106.77
46.30
f1 (ppm)
3f

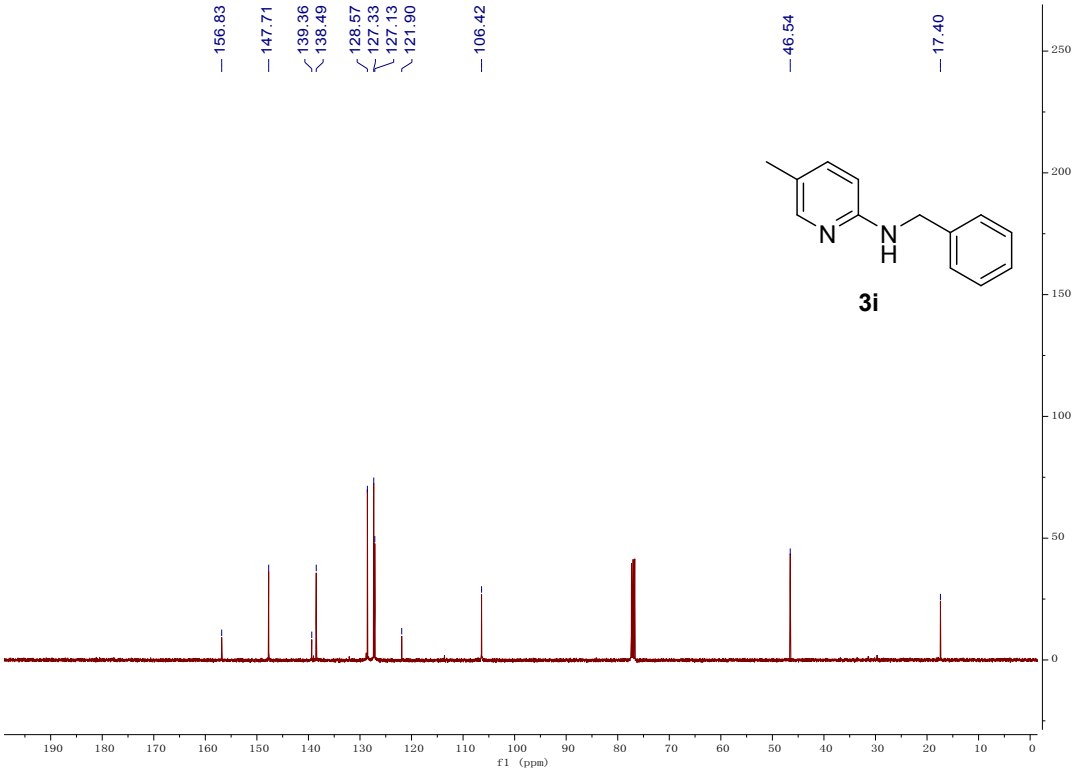

8.05
8.04
7.39
7.38
7.36
7.34
7.32
7.32
7.29
7.27
7.24
7.22
6.57
6.55
6.55
6.53
4.69
4.67
4.36
2.08
0.97
3.99
0.95
0.93
1.00
2.00
1.03
3.06
f1 (ppm)
3g

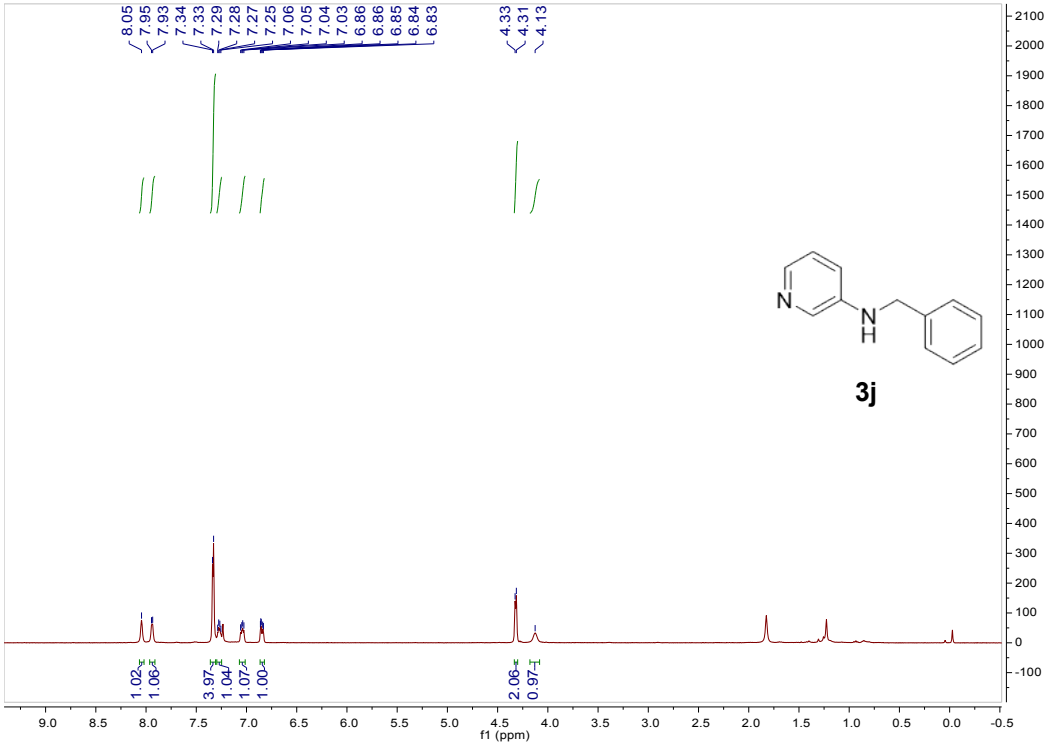

156.64
145.45
139.96
136.86
128.60
127.88
127.19
116.52
112.91
45.84
17.01
f1 (ppm)
3g

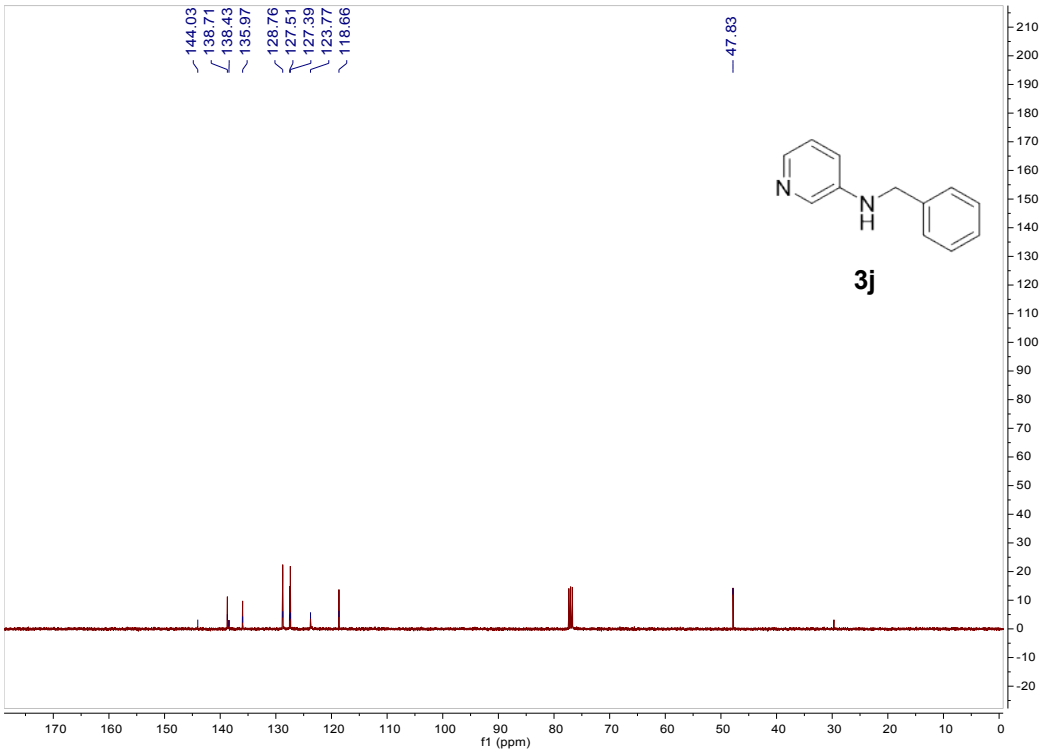

7.94
7.93
7.33
7.31
7.29
7.26
7.24
6.42
6.41
6.18
4.93
4.48
4.46
2.18
1.00
4.06
1.08
1.01
1.10
1.01
2.11
3.01
f1 (ppm)
3h

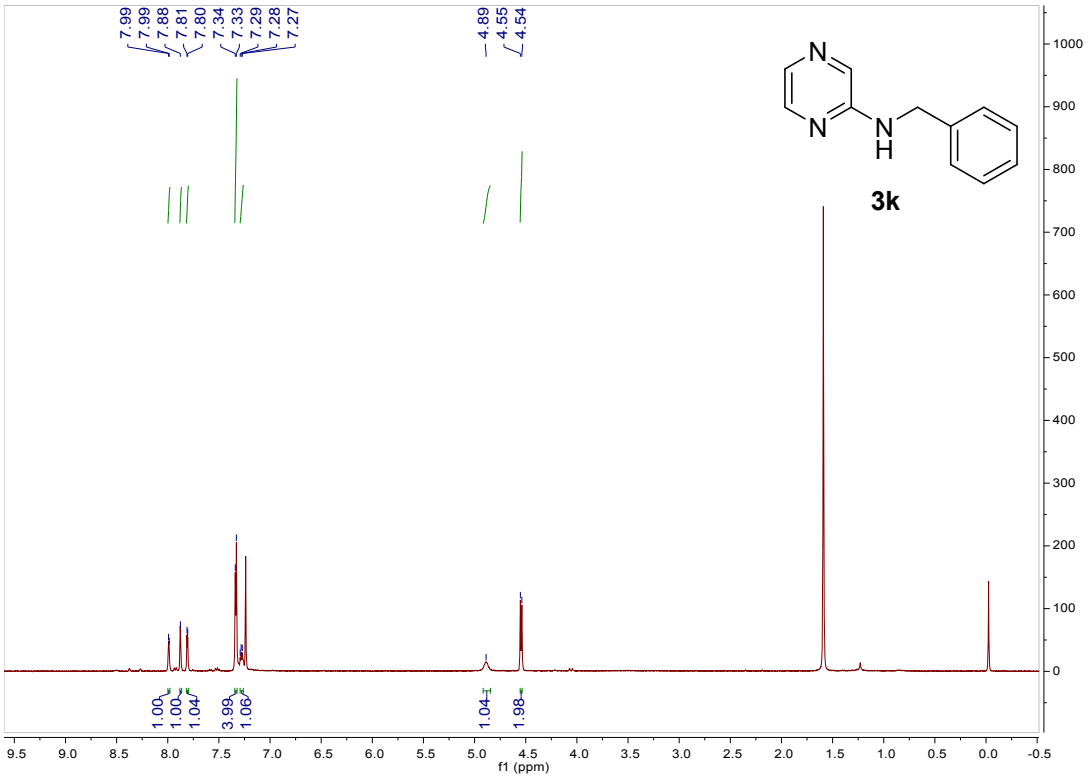

158.87
148.51
147.77
139.30
128.59
127.37
127.16
114.74
106.98
46.29
21.20
f1 (ppm)
3h

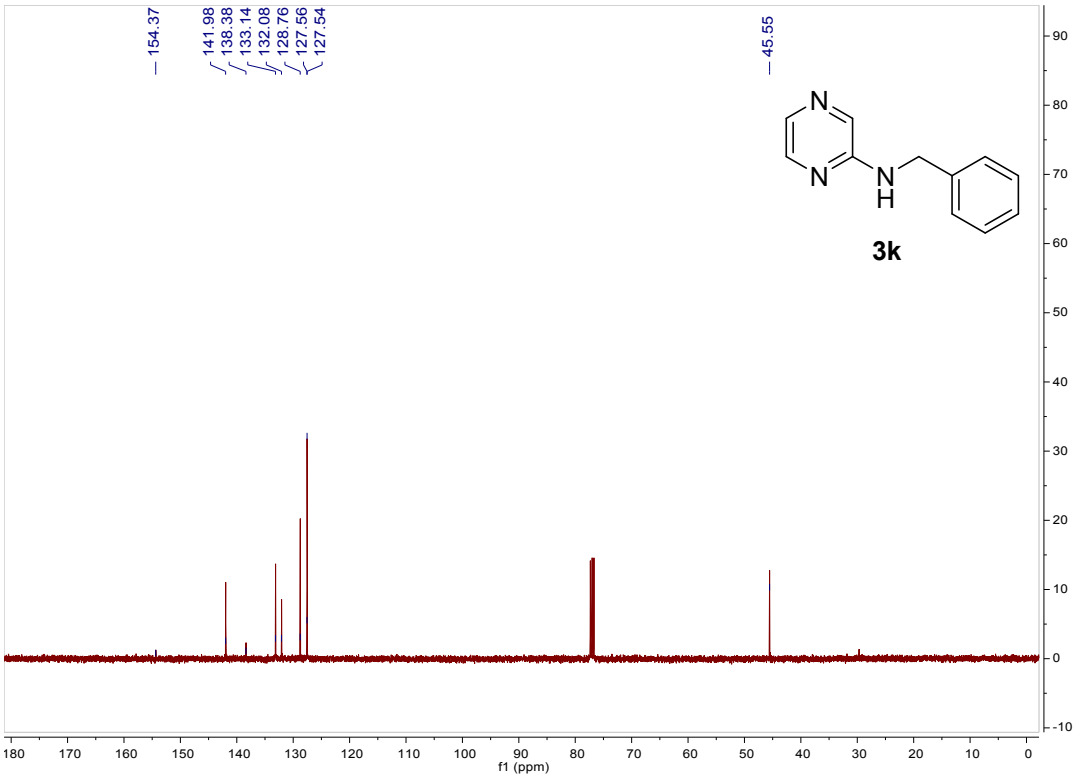

7.90
7.33
7.33
7.31
7.26
7.24
7.22
7.20
6.30
6.28
4.78
4.46
4.45
2.15
N
N
H
3i
1.00
4.00
1.06
0.93
1.04
1.03
2.04
3.04
f1 (ppm)

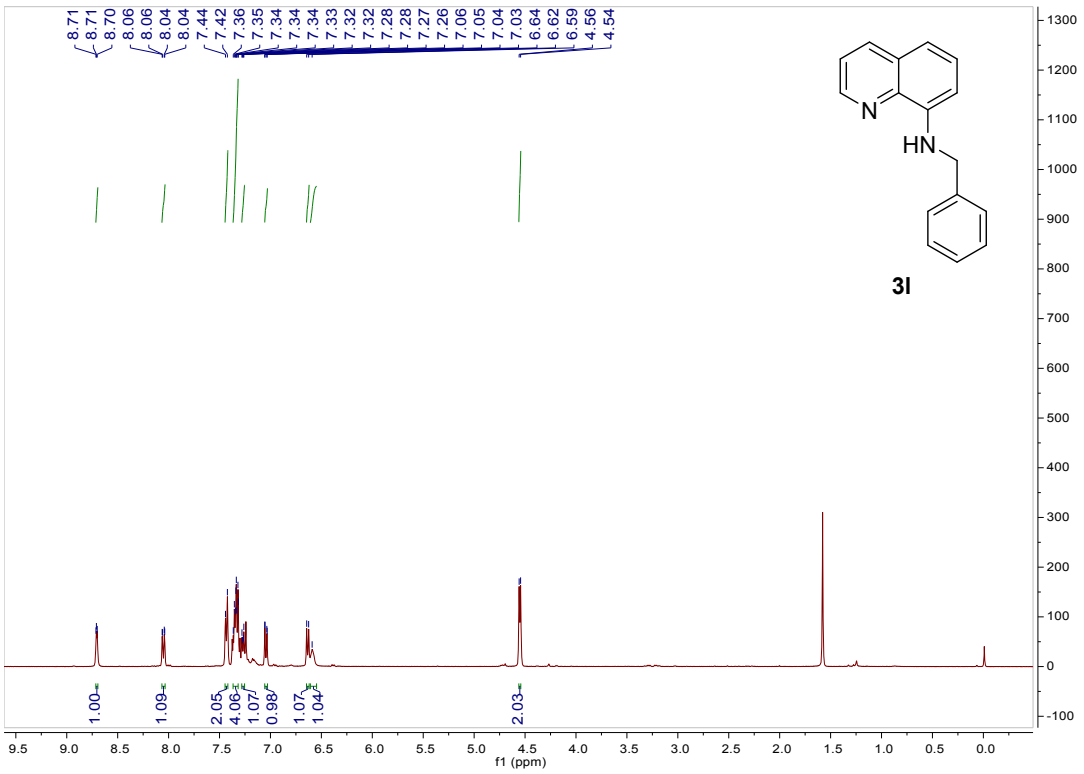

156.83
147.71
139.36
138.49
128.57
127.33
127.13
121.90
106.42
46.54
17.40
N
N
H
3i
f1 (ppm)

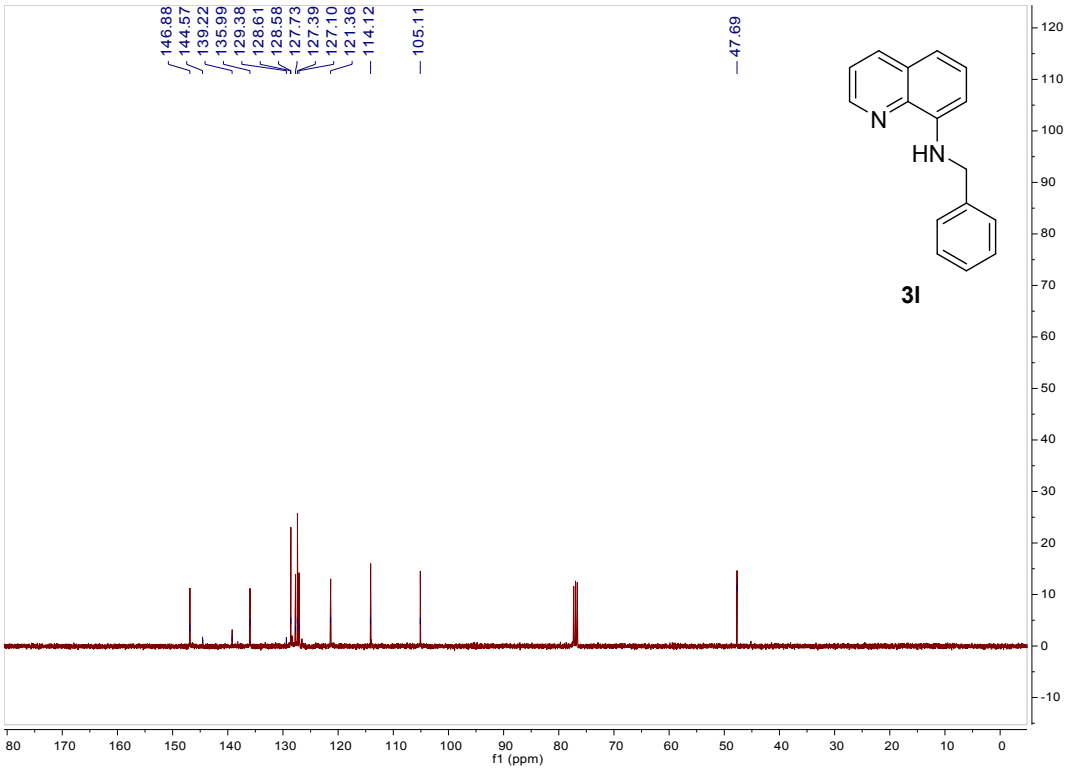

8.05
7.95
7.93
7.34
7.33
7.29
7.28
7.27
7.25
7.06
7.05
7.04
7.03
6.86
6.86
6.85
6.84
6.83
4.33
4.31
4.13
1.02
1.06
3.97
1.04
1.07
1.00
2.06
0.97
f1 (ppm)
N
N
H
3j

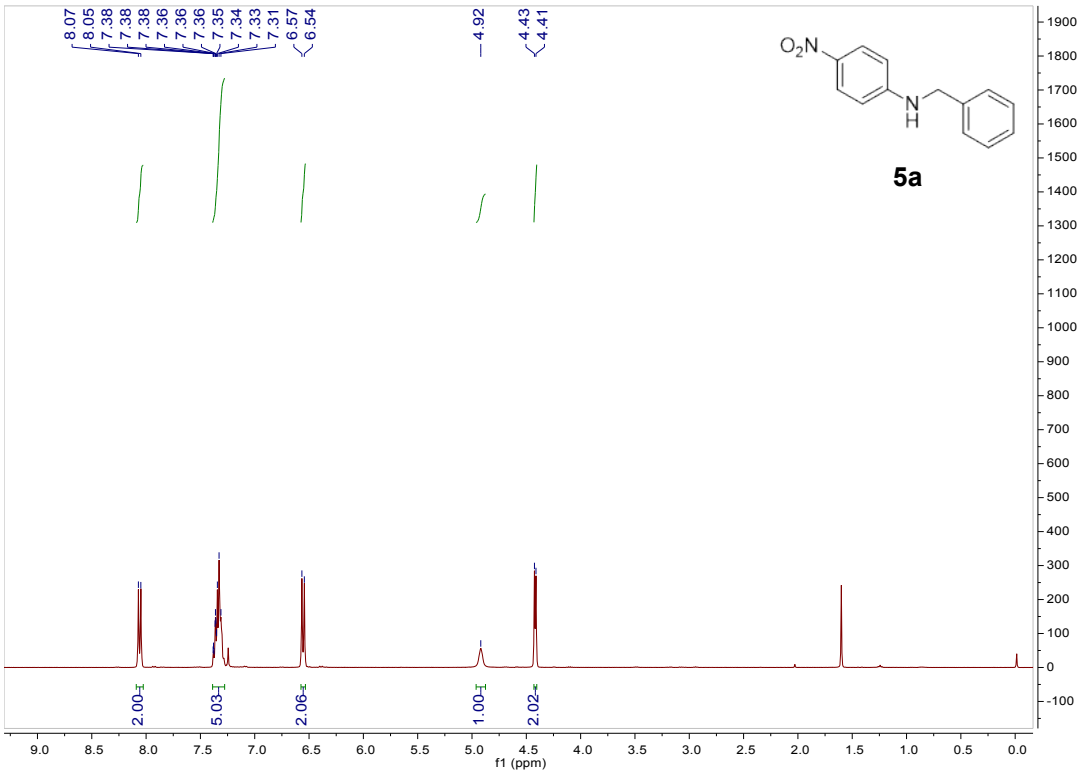

144.03
138.71
138.43
135.97
128.76
127.51
127.39
123.77
118.66
47.83
f1 (ppm)
N
N
H
3j

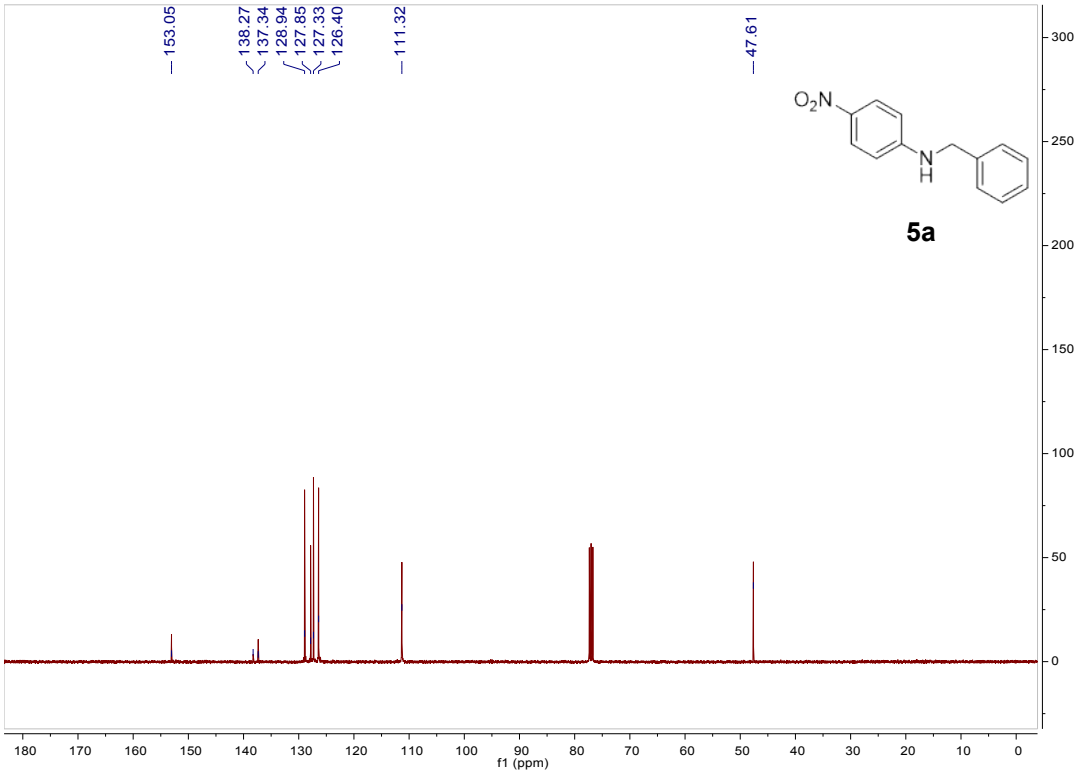

7.99
7.99
7.88
7.81
7.80
7.34
7.33
7.29
7.28
7.27
4.89
4.55
4.54
N
N
N
H
3k
1.00
1.00
1.04
3.99
1.06
1.04
1.98
f1 (ppm)

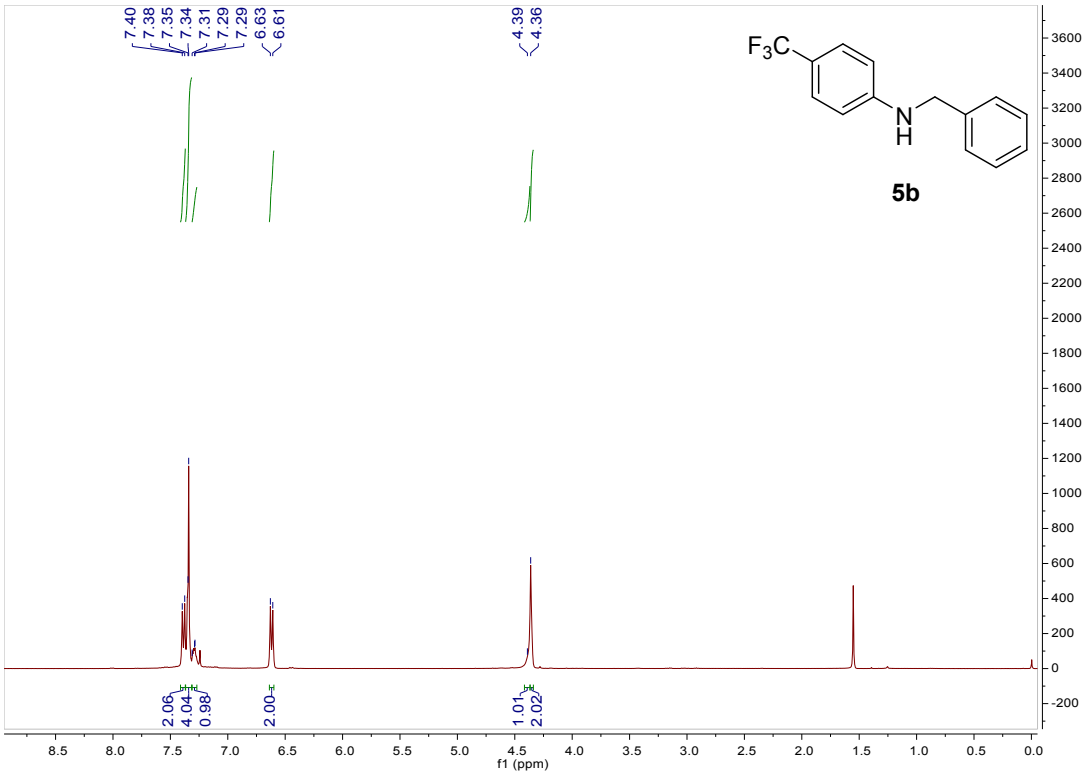

154.37
141.98
138.38
133.14
132.08
128.76
127.56
127.54
45.55
N
N
N
H
3k
f1 (ppm)

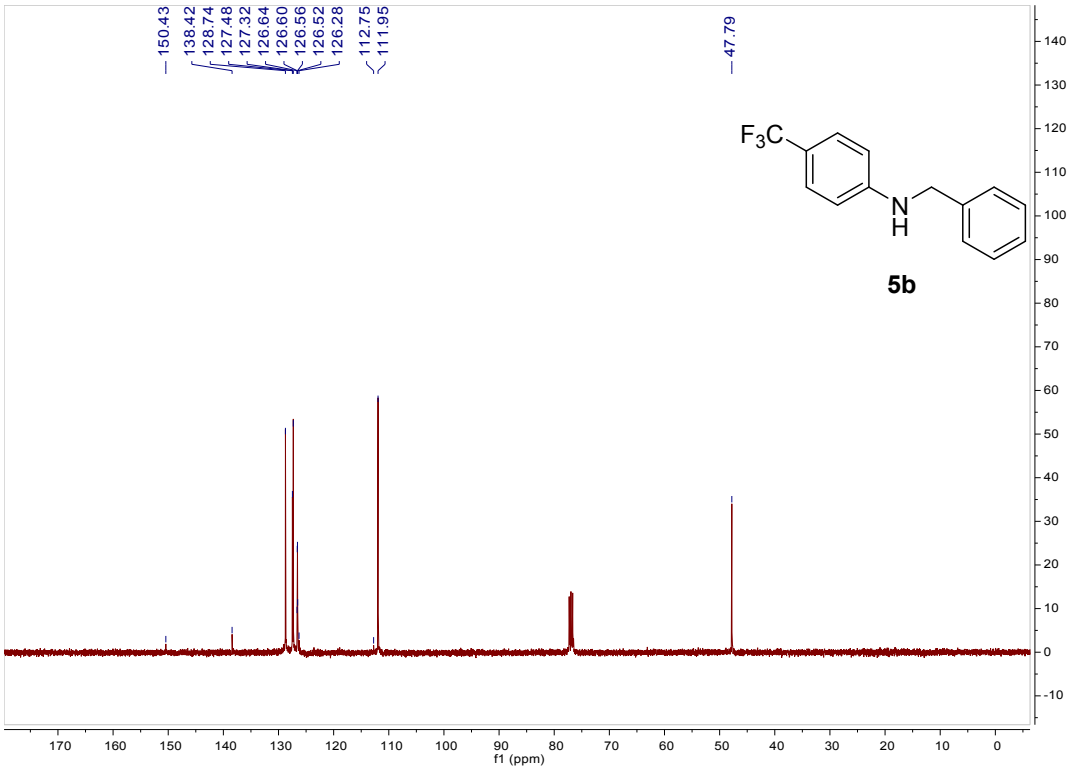

8.71
8.71
8.70
8.06
8.06
8.04
8.04
7.44
7.42
7.36
7.35
7.34
7.34
7.34
7.33
7.32
7.32
7.28
7.28
7.27
7.26
7.06
7.05
7.04
7.03
6.64
6.62
6.59
4.56
4.54
1.00
1.09
2.05
4.06
1.07
0.98
1.07
1.04
2.03
f1 (ppm)
N
HN
3l

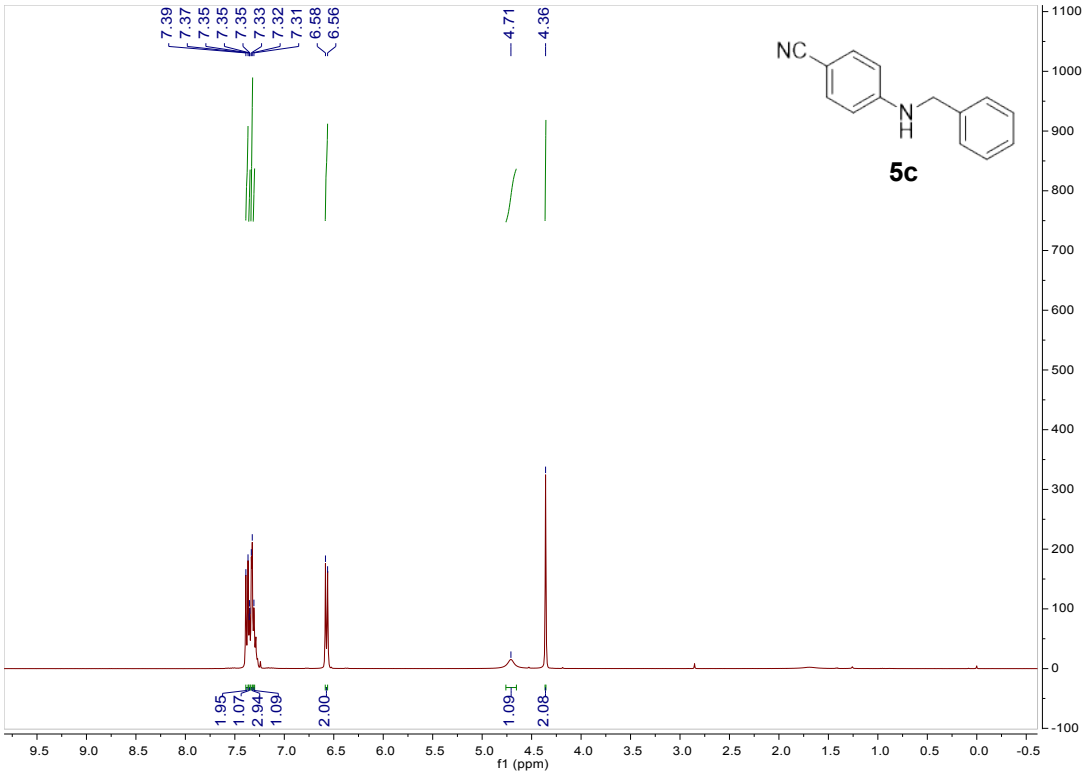

146.88
144.57
139.22
135.99
129.38
128.61
128.58
127.73
127.39
127.10
121.36
114.12
105.11
47.69
f1 (ppm)
N
HN
3l

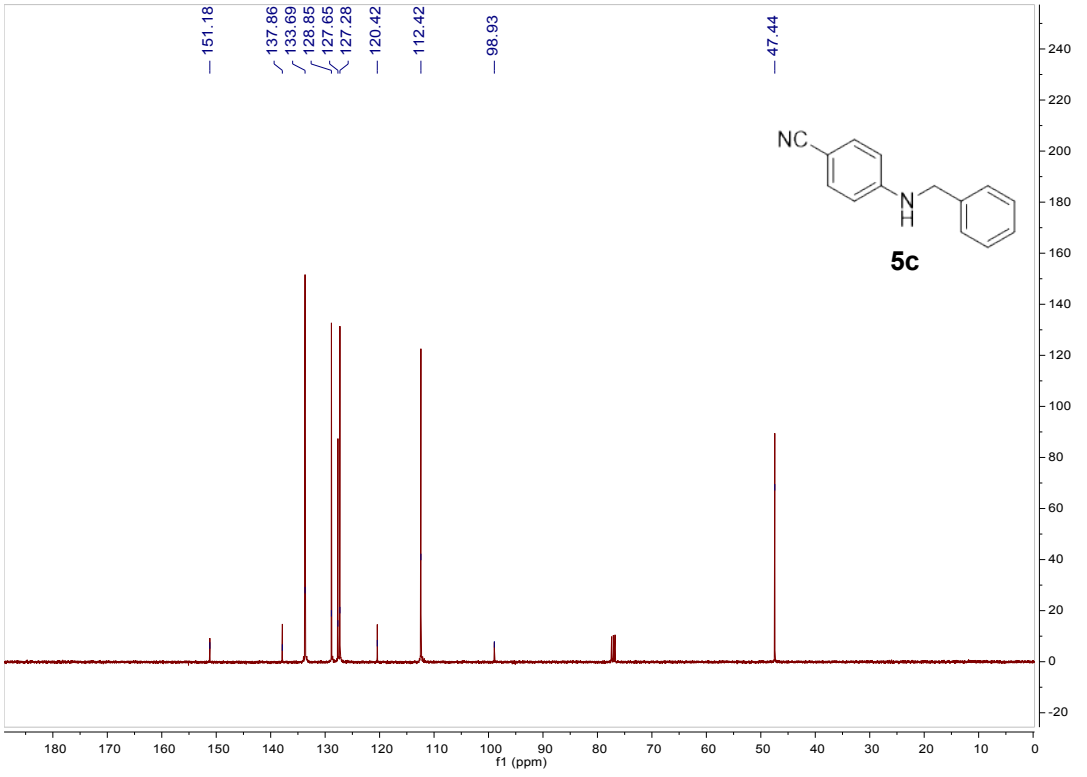

8.07
8.05
7.38
7.38
7.38
7.36
7.36
7.36
7.35
7.34
7.33
7.31
6.57
6.54
4.92
4.43
4.41
O2N
N
H
5a
2.00
5.03
2.06
1.00
2.02
f1 (ppm)

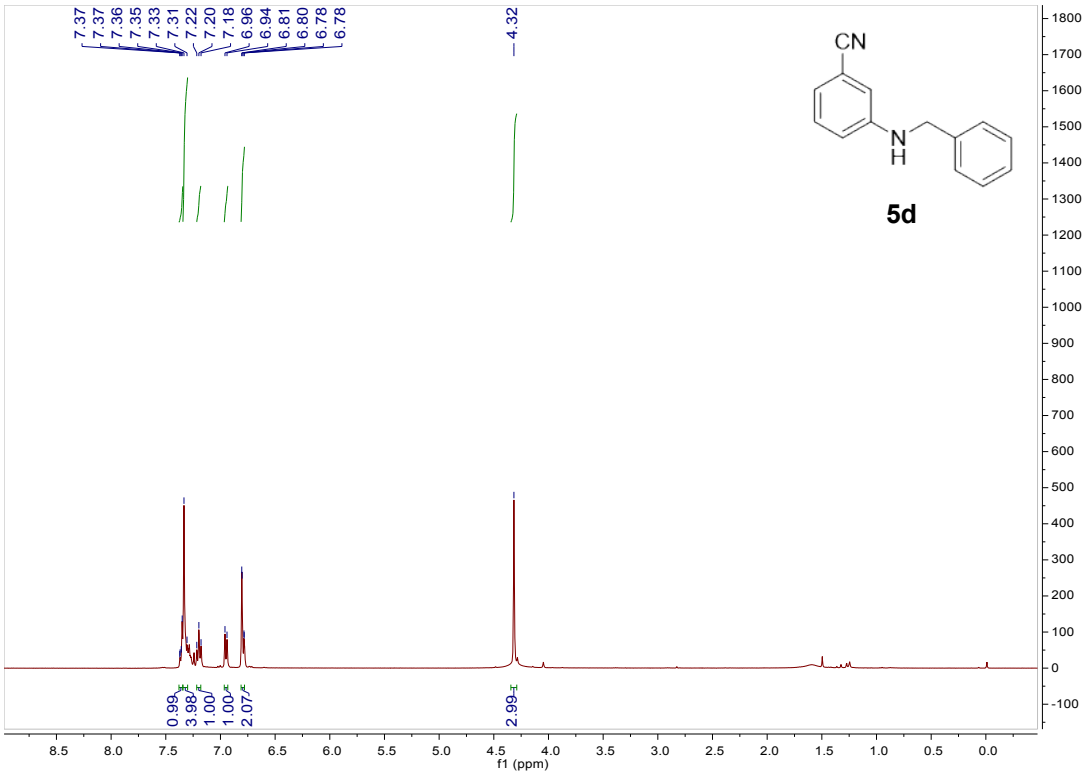

153.05
138.27
137.34
128.94
127.85
127.33
126.40
111.32
47.61
O2N
N
H
5a
f1 (ppm)

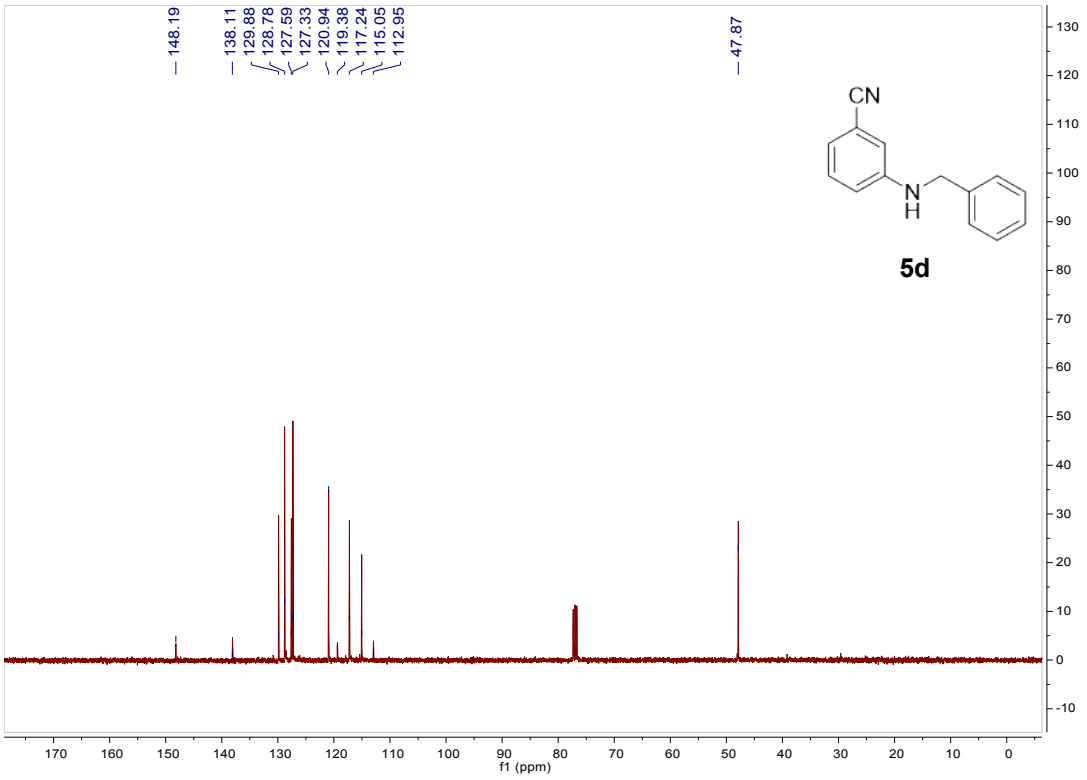

7.40
7.38
7.35
7.34
7.31
7.29
7.29
6.63
6.61
4.39
4.36
F3C
N
H
5b
2.06
4.04
0.98
2.00
1.01
2.02
f1 (ppm)

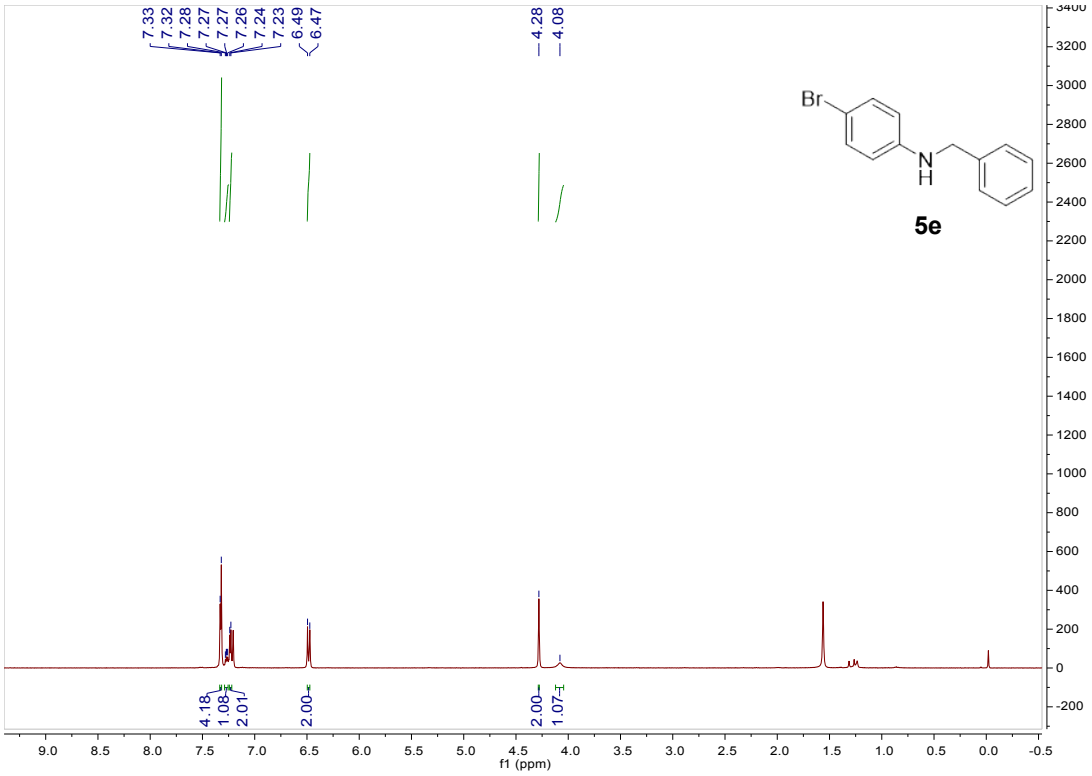

150.43
138.42
128.74
127.48
127.32
126.64
126.60
126.56
126.52
126.28
112.75
111.95
47.79
F3C
N
H
5b
f1 (ppm)

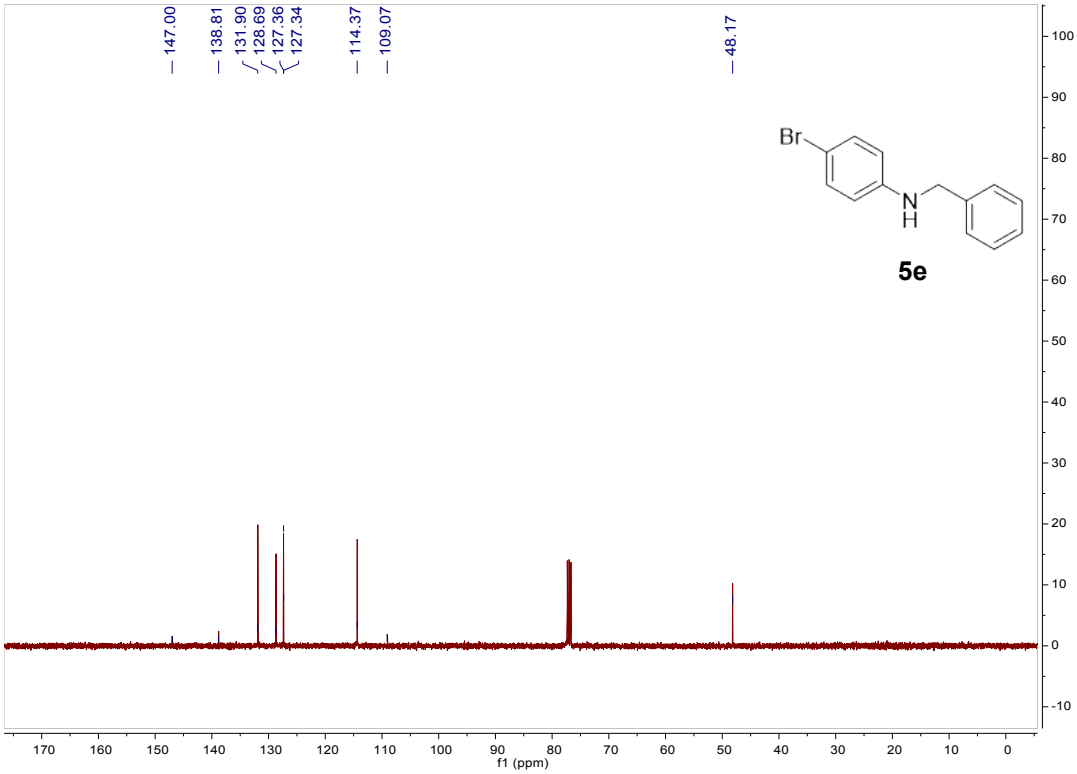

7.39
7.37
7.35
7.35
7.35
7.33
7.32
7.31
6.58
6.56
4.71
4.36
NC
N
H
5c
1.95
1.07
2.94
1.09
2.00
1.09
2.08
f1 (ppm)

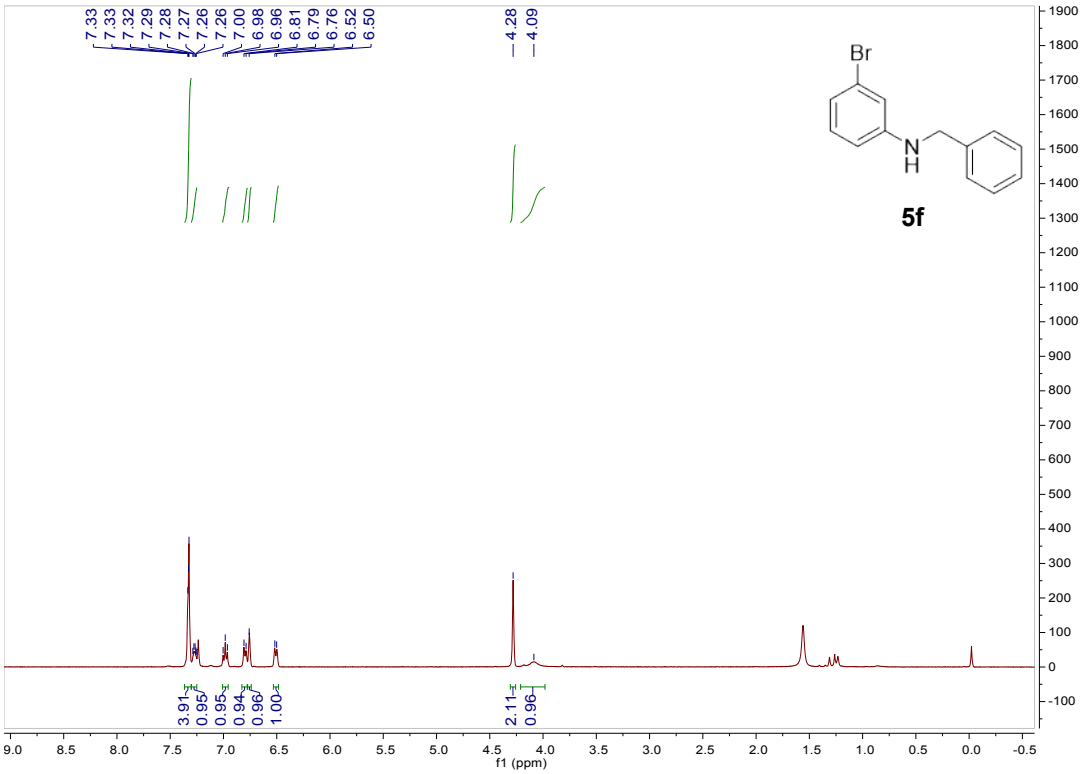

151.18
137.86
133.69
128.85
127.65
127.28
120.42
112.42
98.93
47.44
NC
N
H
5c
f1 (ppm)

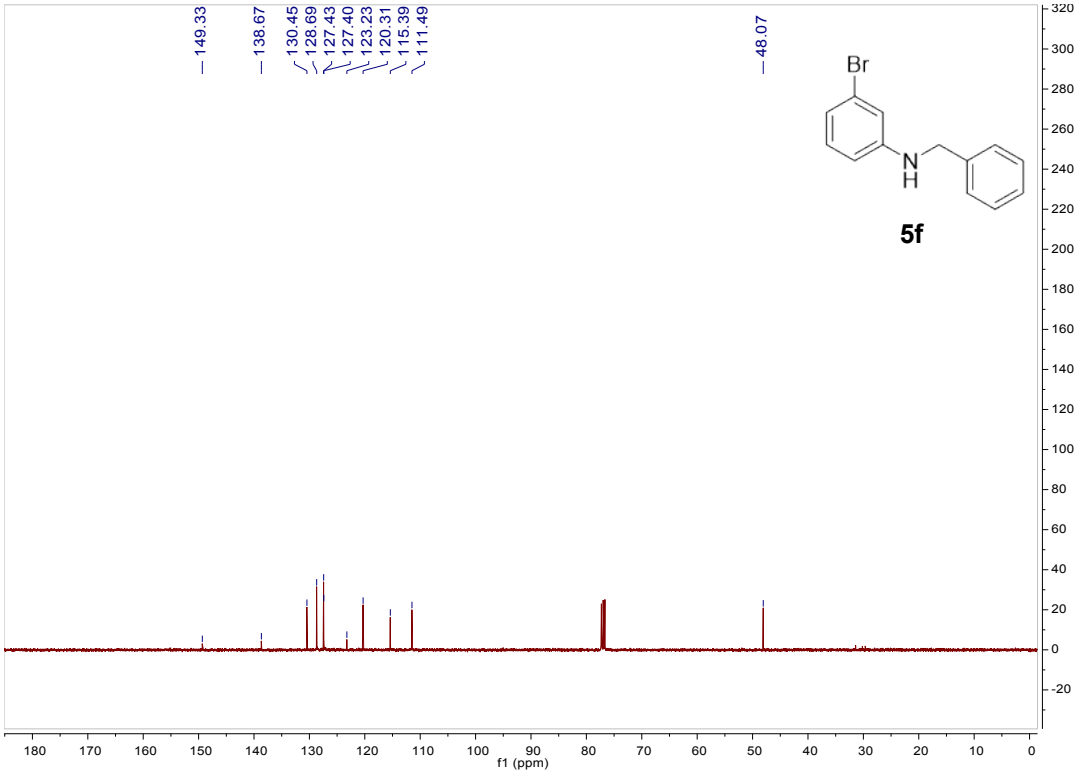

7.37
7.37
7.36
7.35
7.33
7.31
7.22
7.20
7.18
6.96
6.94
6.81
6.80
6.78
6.78
4.32
CN
N
H
5d
0.99
3.98
1.00
1.00
2.07
2.99
f1 (ppm)

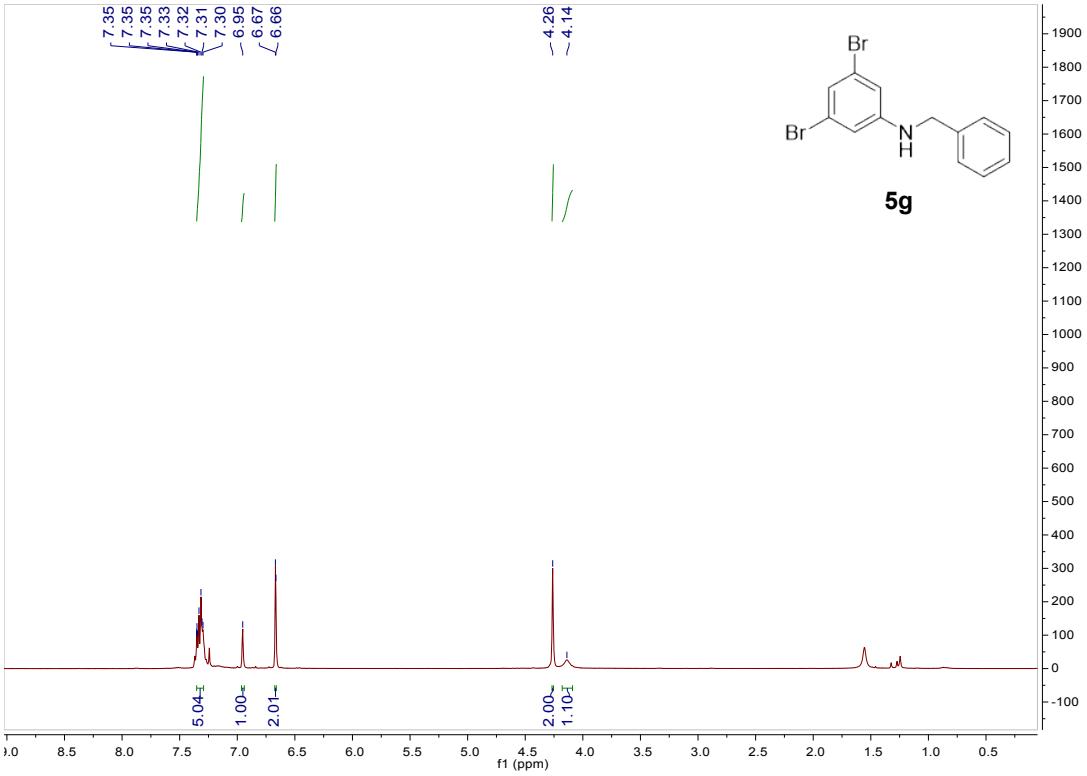

148.19
138.11
129.88
128.78
127.59
127.33
120.94
119.38
117.24
115.05
112.95
47.87
CN
N
H
5d
f1 (ppm)

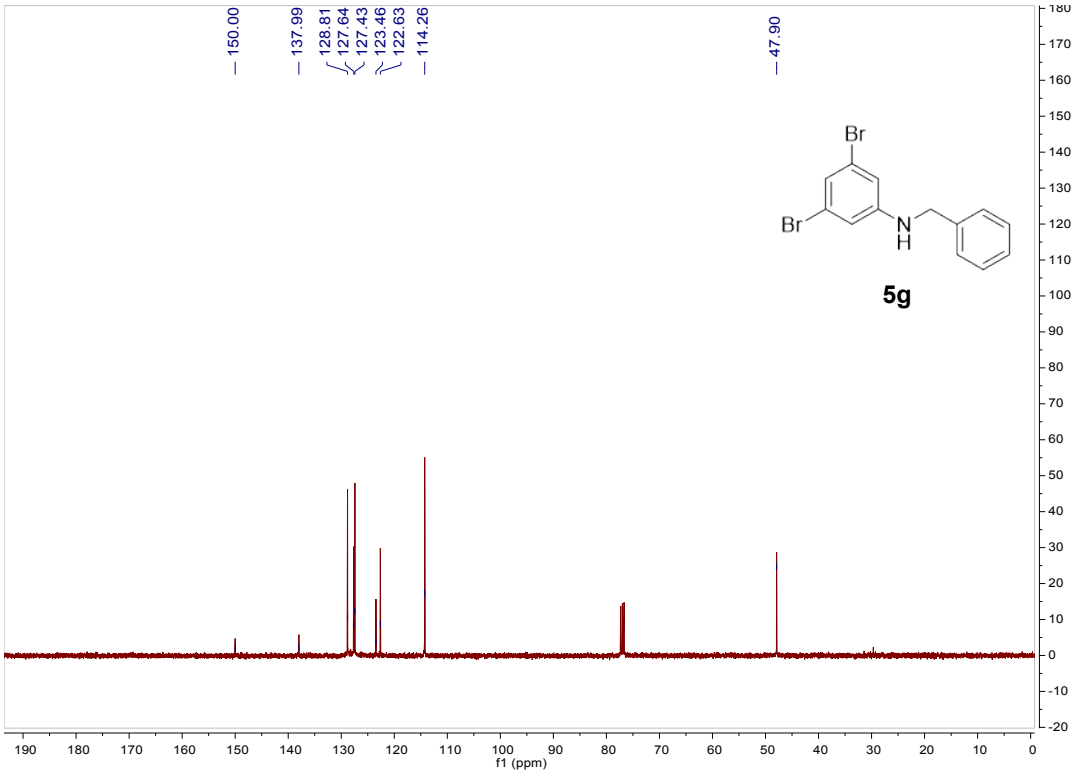

7.33
7.32
7.28
7.27
7.27
7.26
7.24
7.23
6.49
6.47
4.28
4.08
Br
N
H
5e
4.18
1.08
2.01
2.00
2.00
1.07
f1 (ppm)

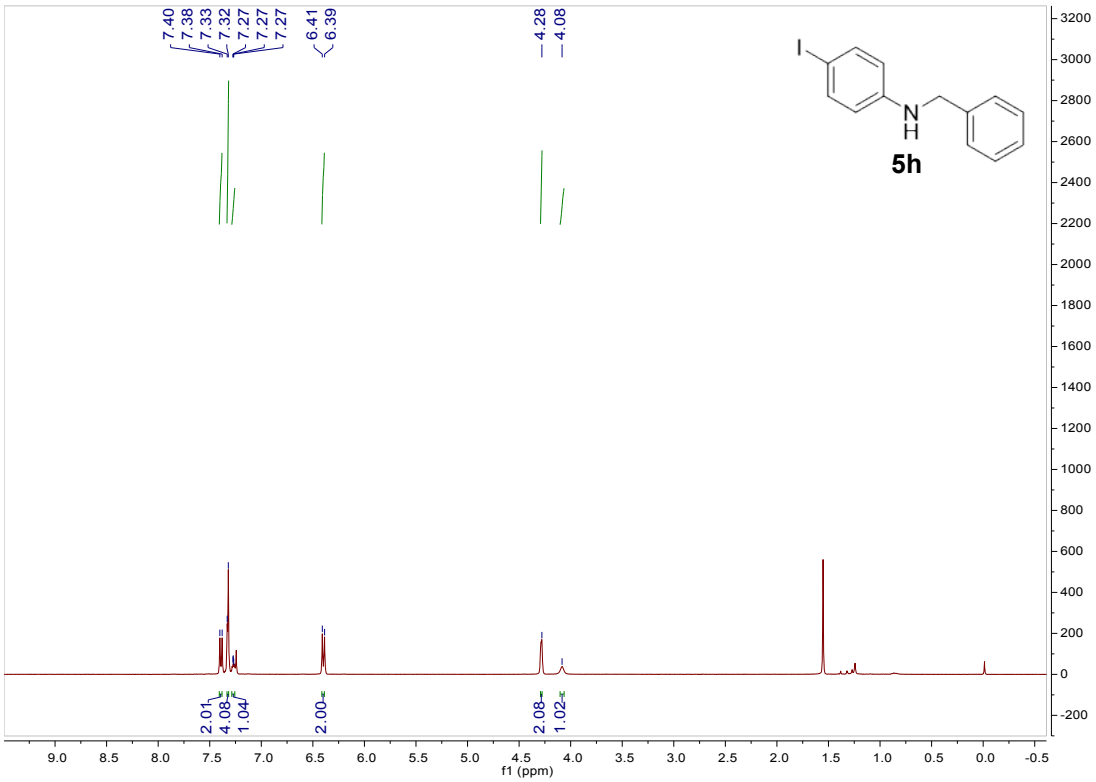

147.00
138.81
131.90
128.69
127.36
127.34
114.37
109.07
48.17
Br
N
H
5e
f1 (ppm)

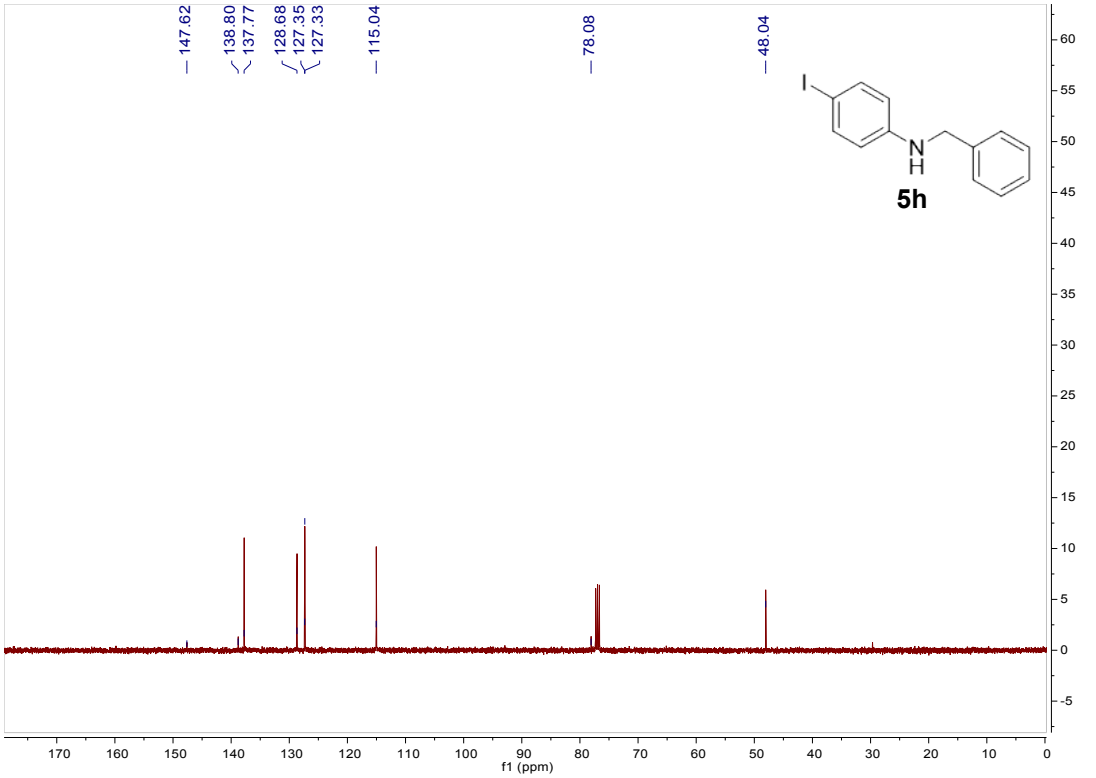

7.33
7.33
7.32
7.29
7.28
7.27
7.26
7.26
7.00
6.98
6.96
6.81
6.79
6.76
6.52
6.50
4.28
4.09
Br
N
H
5f
3.91
0.95
0.95
0.94
0.96
1.00
2.11
0.96
f1 (ppm)

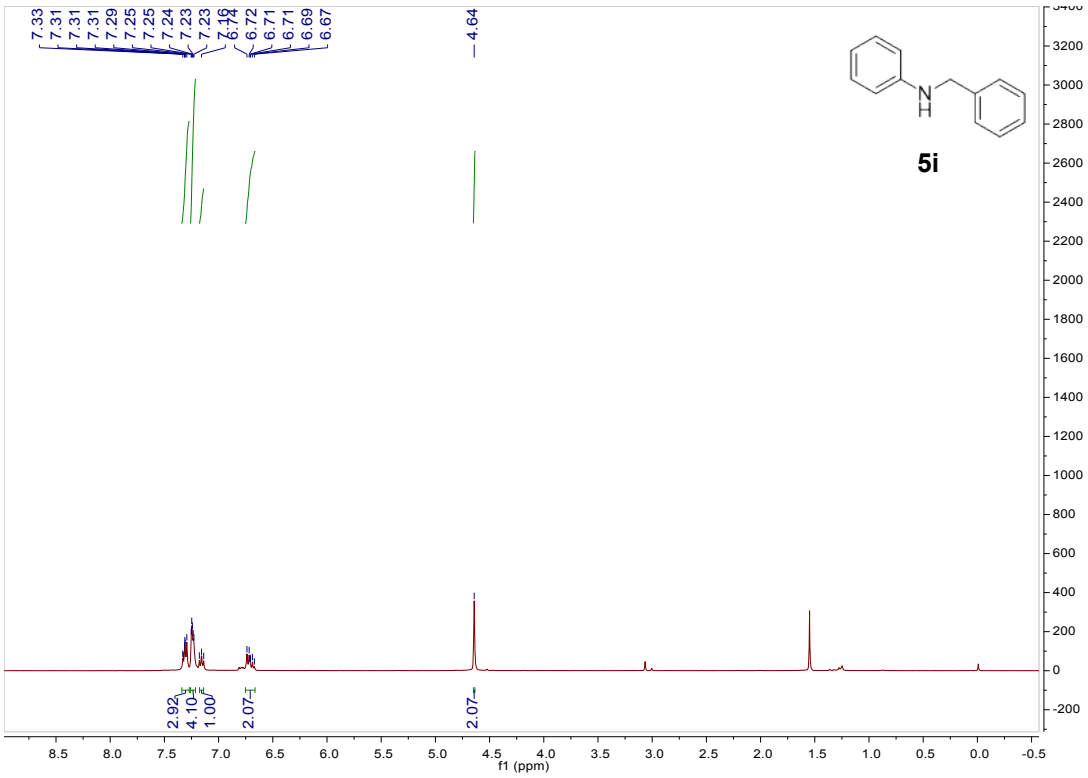

149.33
138.67
130.45
128.69
127.43
127.40
123.23
120.31
115.39
111.49
48.07
Br
N
H
5f
f1 (ppm)

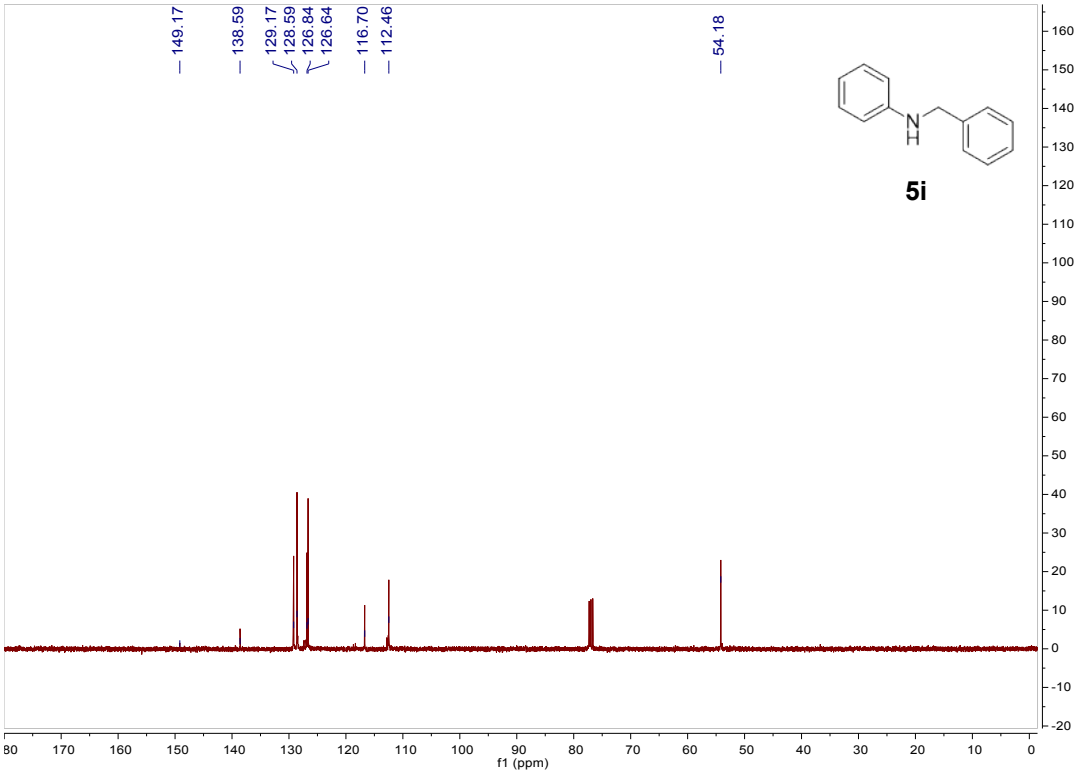

7.35
7.35
7.35
7.33
7.32
7.31
7.30
6.95
6.67
6.66
4.26
4.14
Br
Br
N
H
5g
5.04
1.00
2.01
2.00
1.10
f1 (ppm)

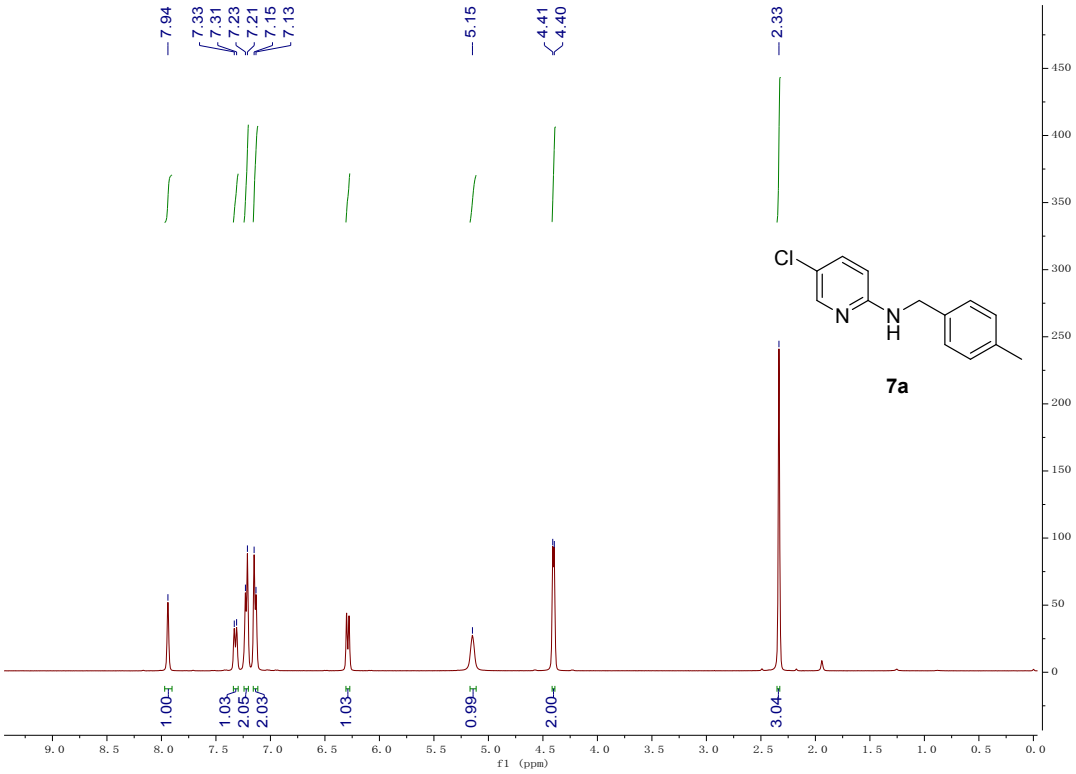

150.00
137.99
128.81
127.64
127.43
123.46
122.63
114.26
47.90
Br
Br
N
H
5g
f1 (ppm)

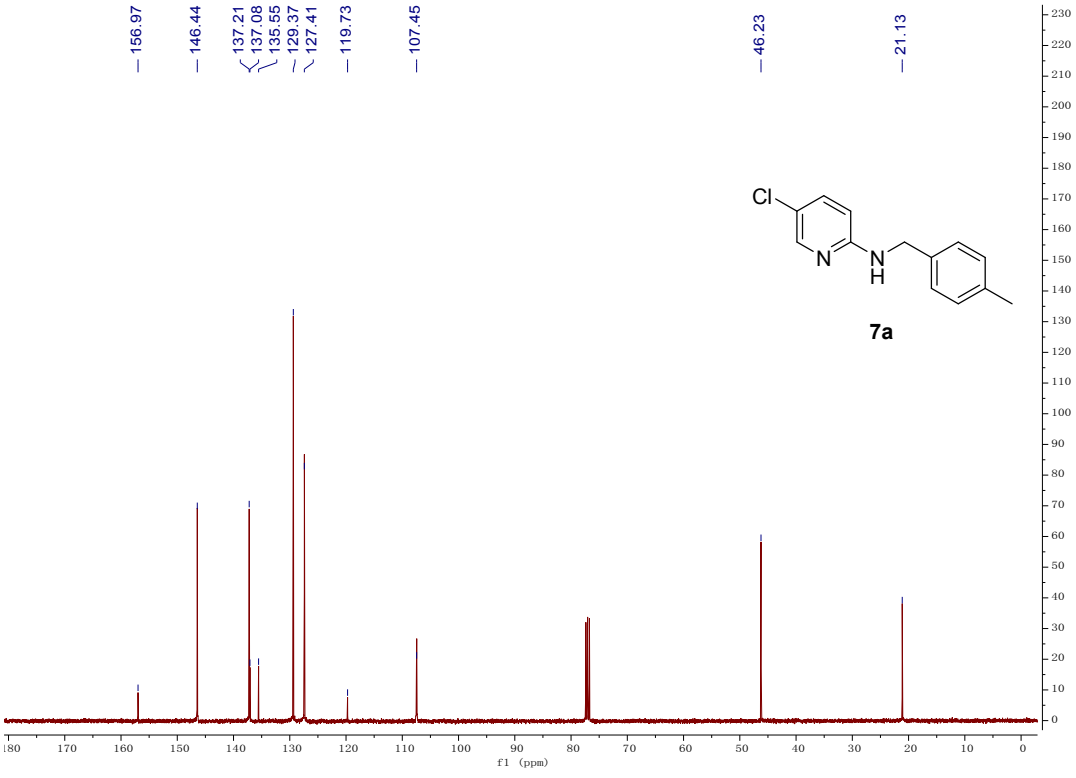

7.40
7.38
7.33
7.32
7.27
7.27
7.27
6.41
6.39
4.28
4.08
I
N
H
5h
2.01
4.08
1.04
2.00
2.08
1.02
f1 (ppm)

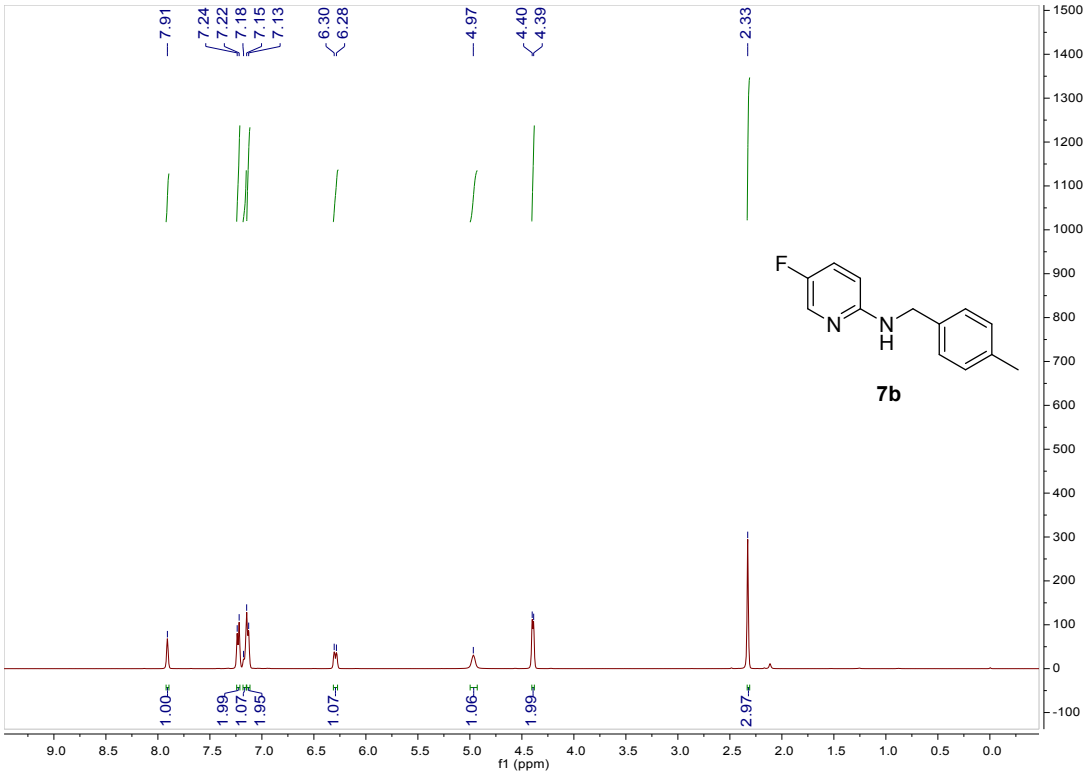

147.62
138.80
137.77
128.68
127.35
127.33
115.04
78.08
48.04
I
N
H
5h
f1 (ppm)

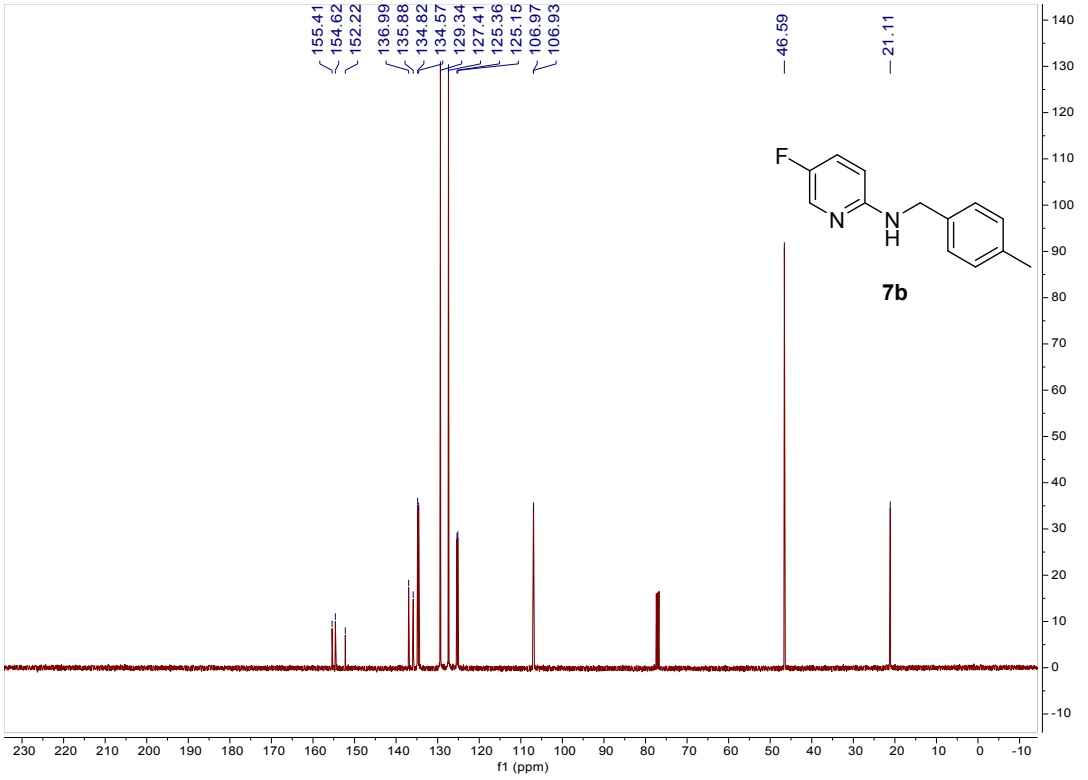

7.33
7.31
7.31
7.31
7.29
7.25
7.25
7.24
7.23
7.23
7.16
7.14
6.72
6.71
6.71
6.69
6.67
4.64
2.92
4.10
1.00
2.07
2.07
f1 (ppm)
5i

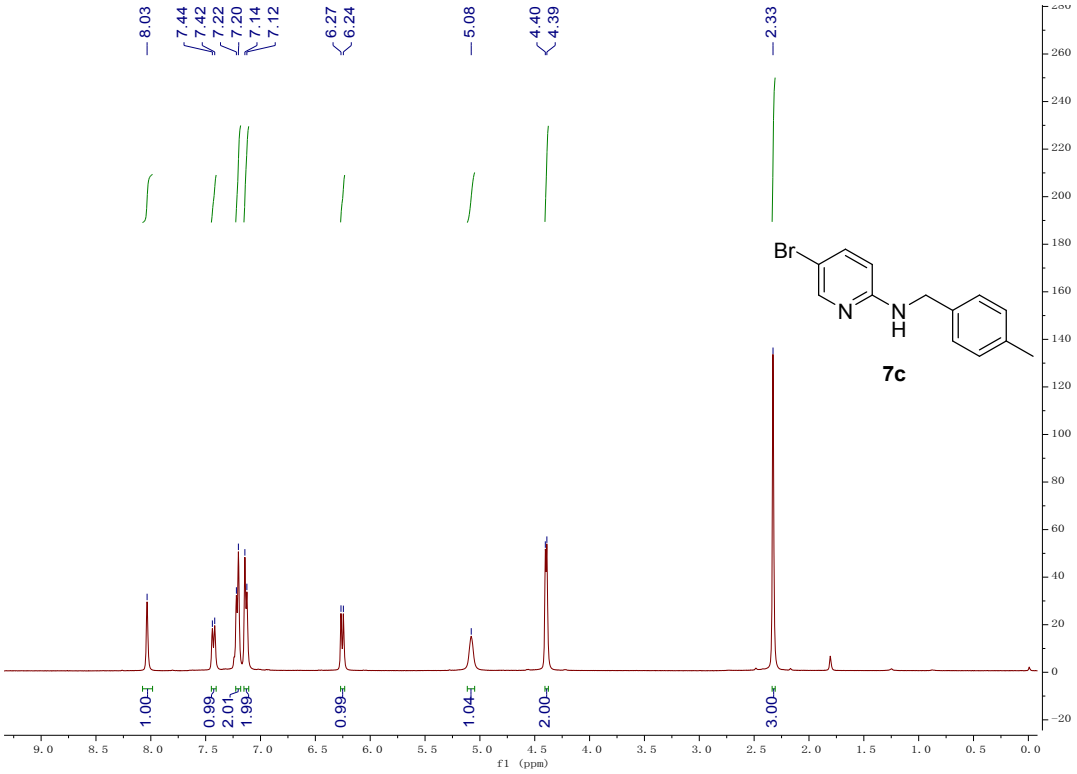

149.17
138.59
129.17
128.59
126.84
126.64
116.70
112.46
54.18
f1 (ppm)
5i

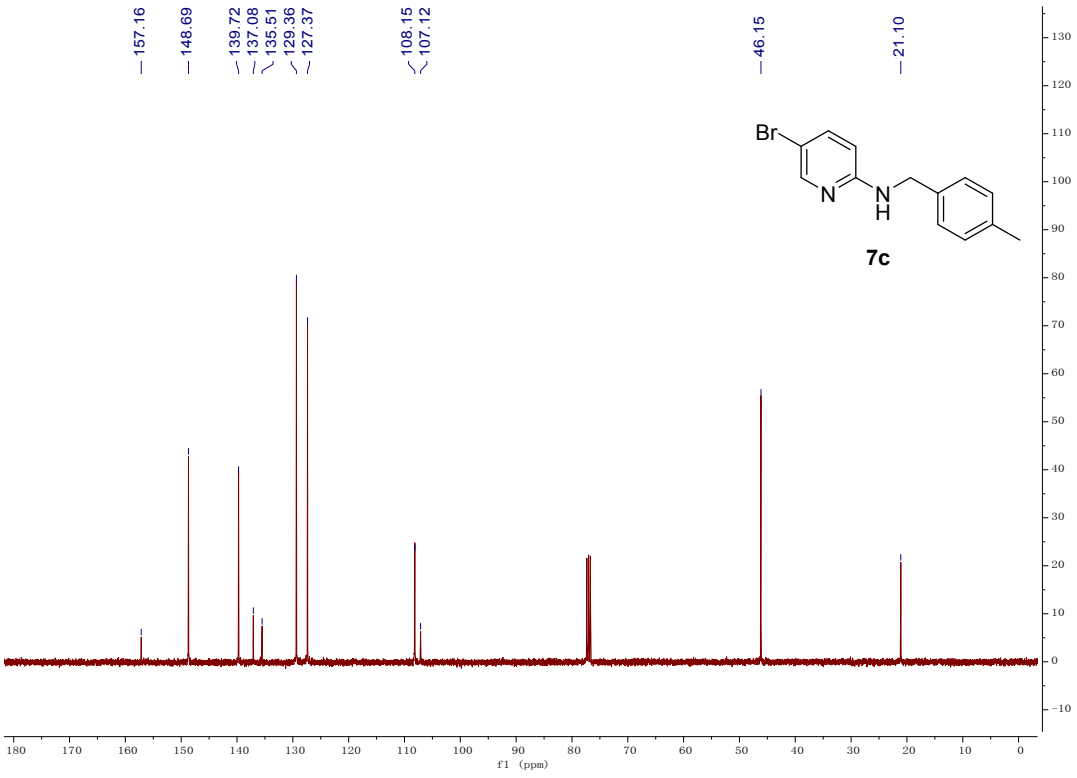

7.94
7.33
7.31
7.23
7.21
7.15
7.13
5.15
4.41
4.40
2.33
Cl
N
N
H
7a
1.00
1.03
2.05
2.03
1.03
0.99
2.00
3.04
f1 (ppm)

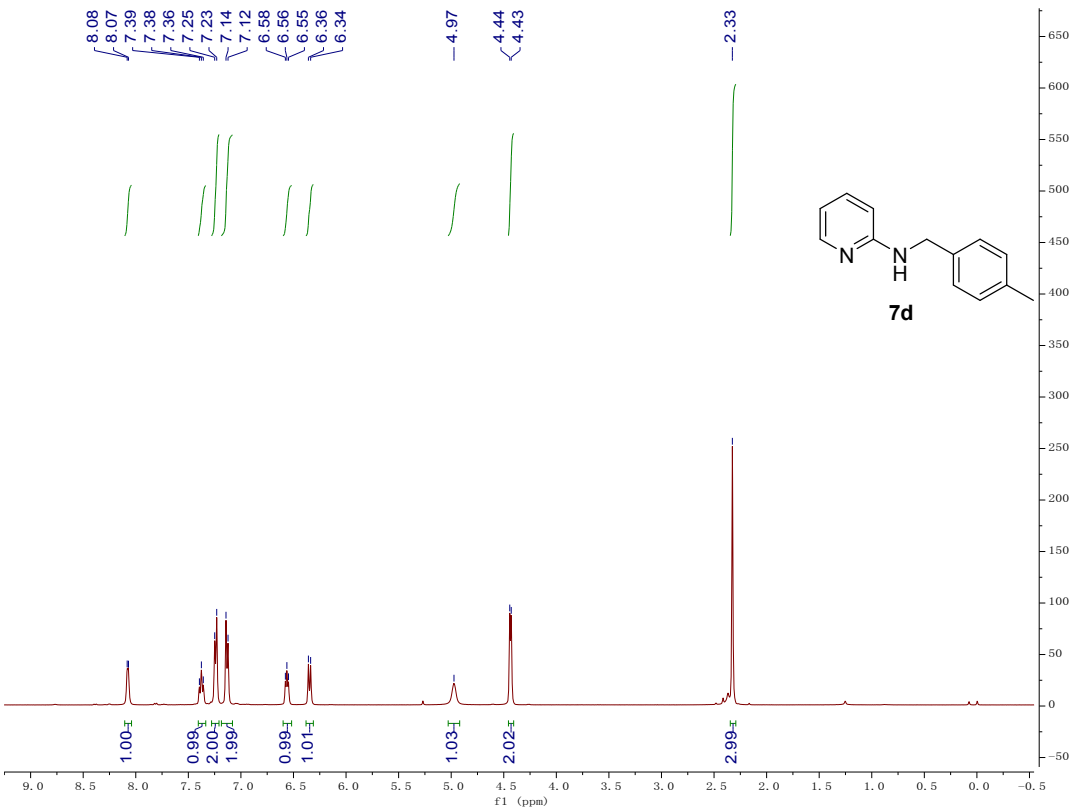

156.97
146.44
137.21
137.08
135.55
129.37
127.41
119.73
107.45
46.23
21.13
Cl
N
N
H
7a
f1 (ppm)


7.91
7.24
7.22
7.18
7.15
7.13
6.30
6.28
4.97
4.40
4.39
2.33
1.00
1.99
1.07
1.95
1.07
1.06
1.99
2.97
F
N
N
H
7b
f1 (ppm)

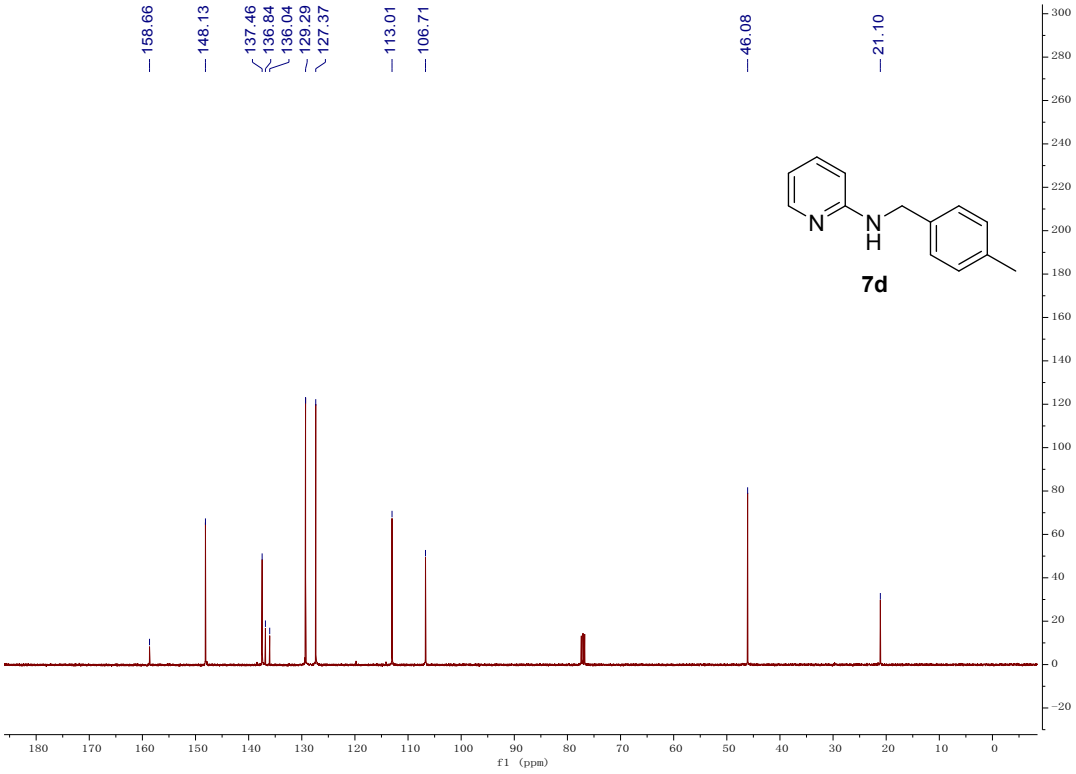

155.41
154.62
152.22
136.99
135.88
134.82
134.57
129.34
127.41
125.36
125.15
106.97
106.93
46.59
21.11
F
N
N
H
7b
f1 (ppm)


8.03
7.44
7.42
7.22
7.20
7.14
7.12
6.27
6.24
5.08
4.40
4.39
2.33
1.00
0.99
2.01
1.99
0.99
1.04
2.00
3.00
Br
N
N
H
7c
f1 (ppm)

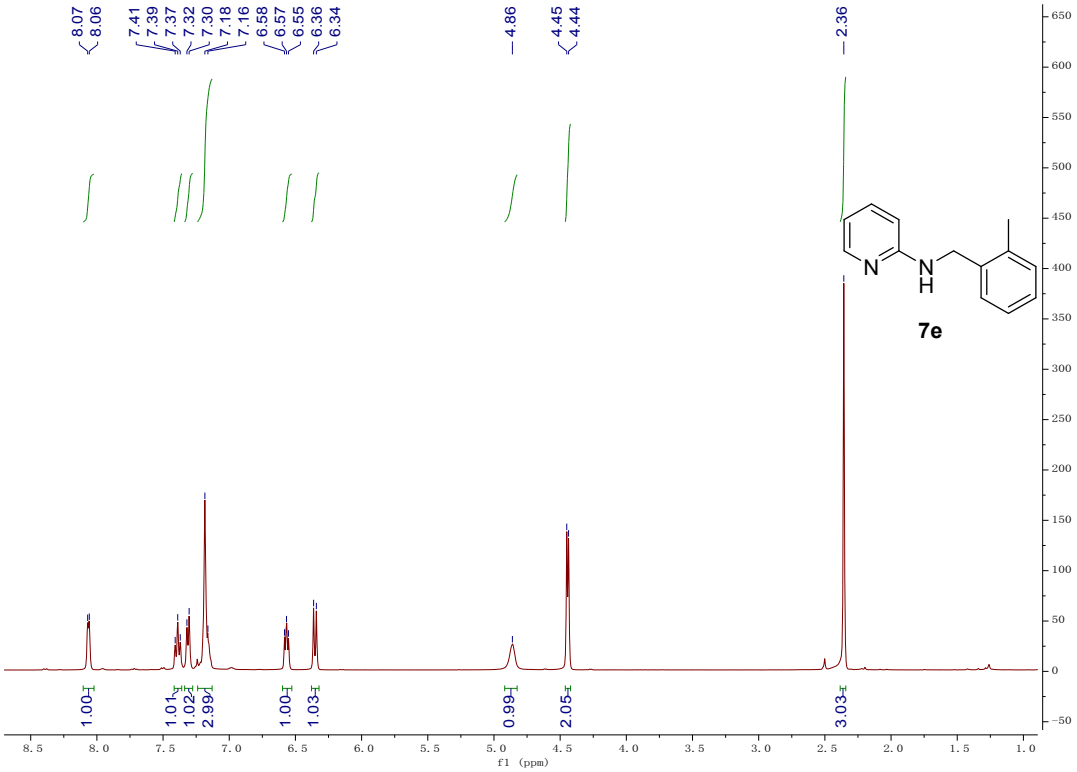

157.16
148.69
139.72
137.08
135.51
129.36
127.37
108.15
107.12
46.15
21.10
Br
N
N
H
7c
f1 (ppm)

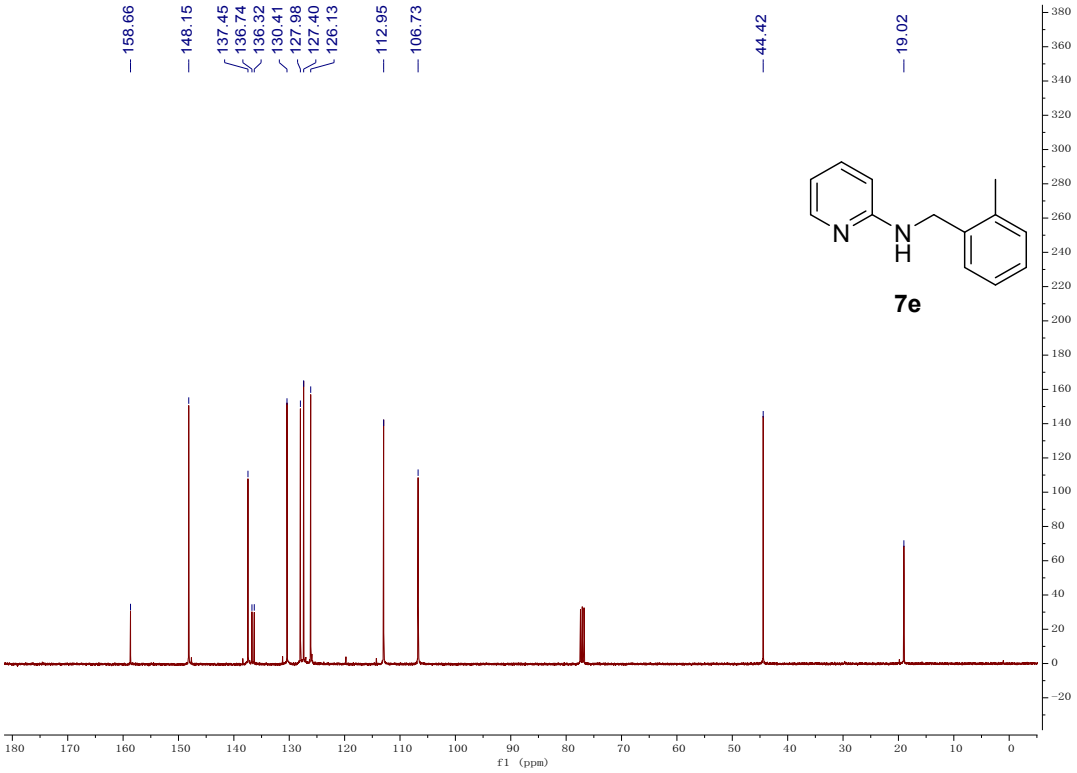

8.08
8.07
7.39
7.38
7.36
7.25
7.23
7.14
7.12
6.58
6.56
6.55
6.36
6.34
4.97
4.44
4.43
2.33
1.00
0.99
2.00
1.99
0.99
1.01
1.03
2.02
2.99
f1 (ppm)

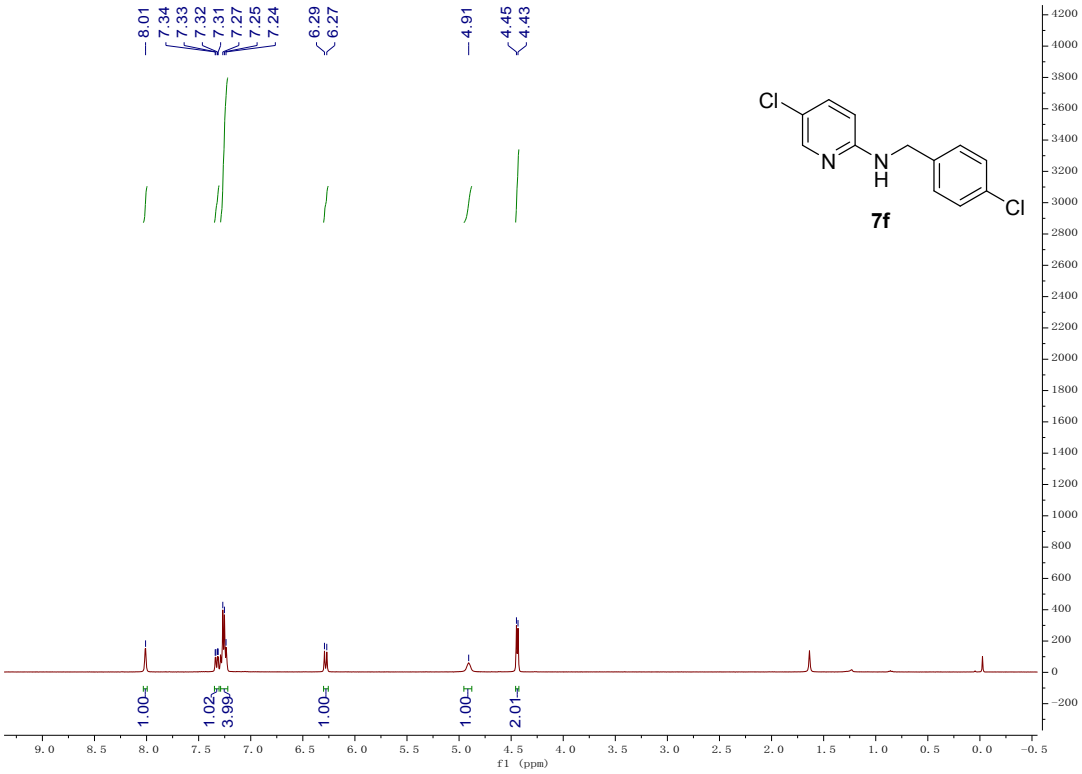
7d

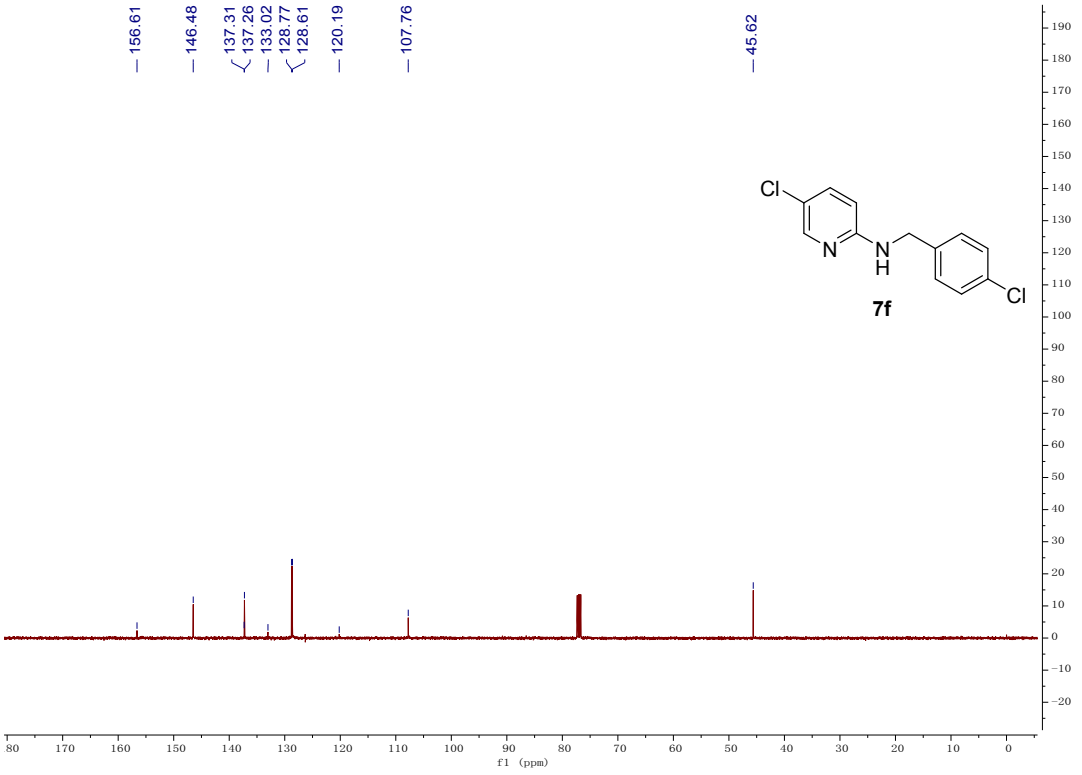

158.66
148.13
137.46
136.84
136.04
129.29
127.37
113.01
106.71
46.08
21.10
f1 (ppm)

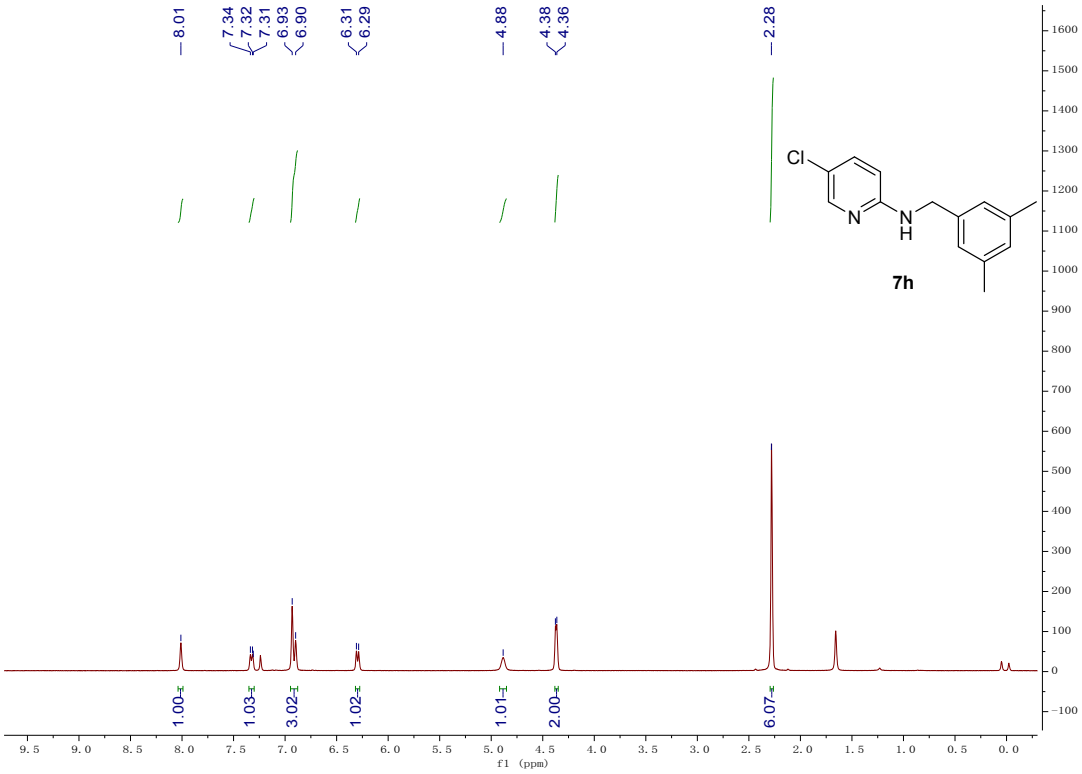
7d

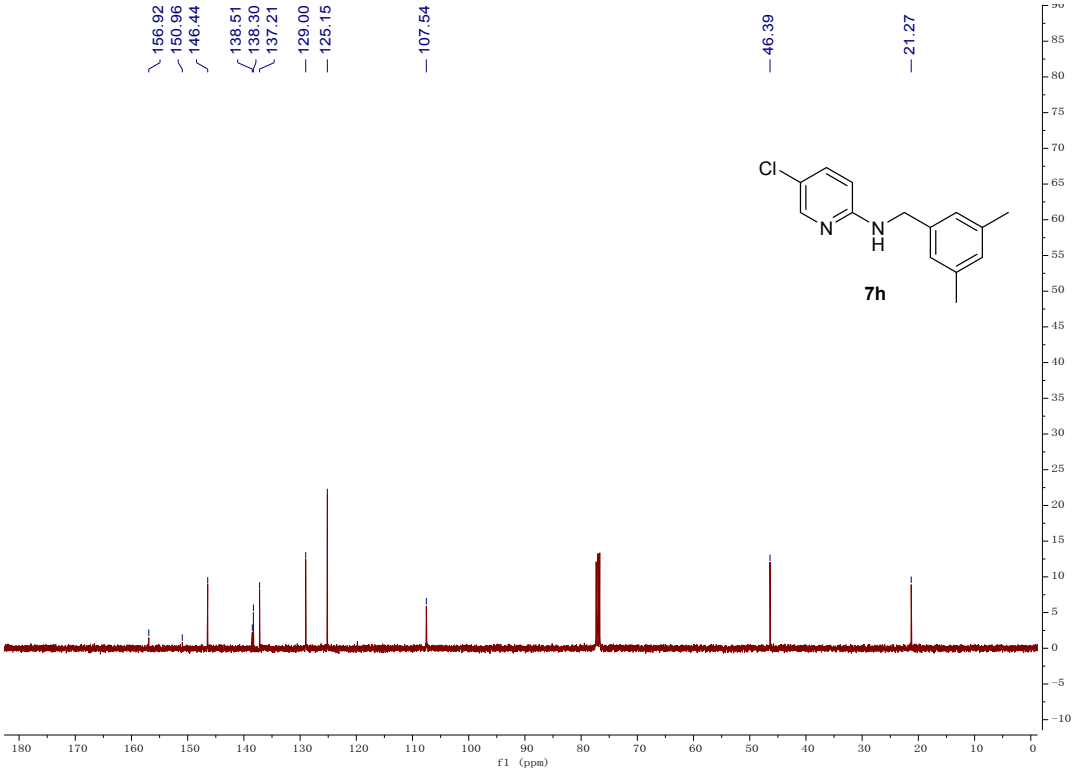

8.07
8.06
7.41
7.39
7.37
7.32
7.30
7.18
7.16
6.58
6.57
6.55
6.36
6.34
4.86
4.45
4.44
2.36
1.00
1.01
1.02
2.99
1.00
1.03
0.99
2.05
3.03
f1 (ppm)
7e

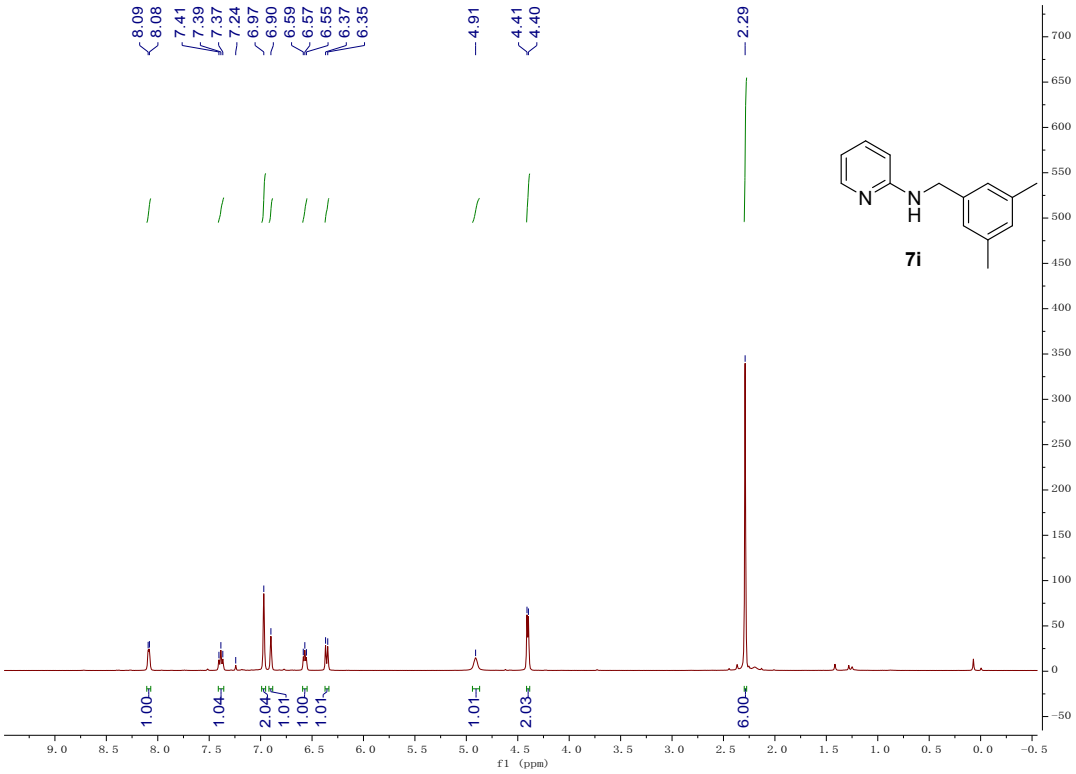

158.66
148.15
137.45
136.74
136.32
130.41
127.98
127.40
126.13
112.95
106.73
44.42
19.02
f1 (ppm)
7e

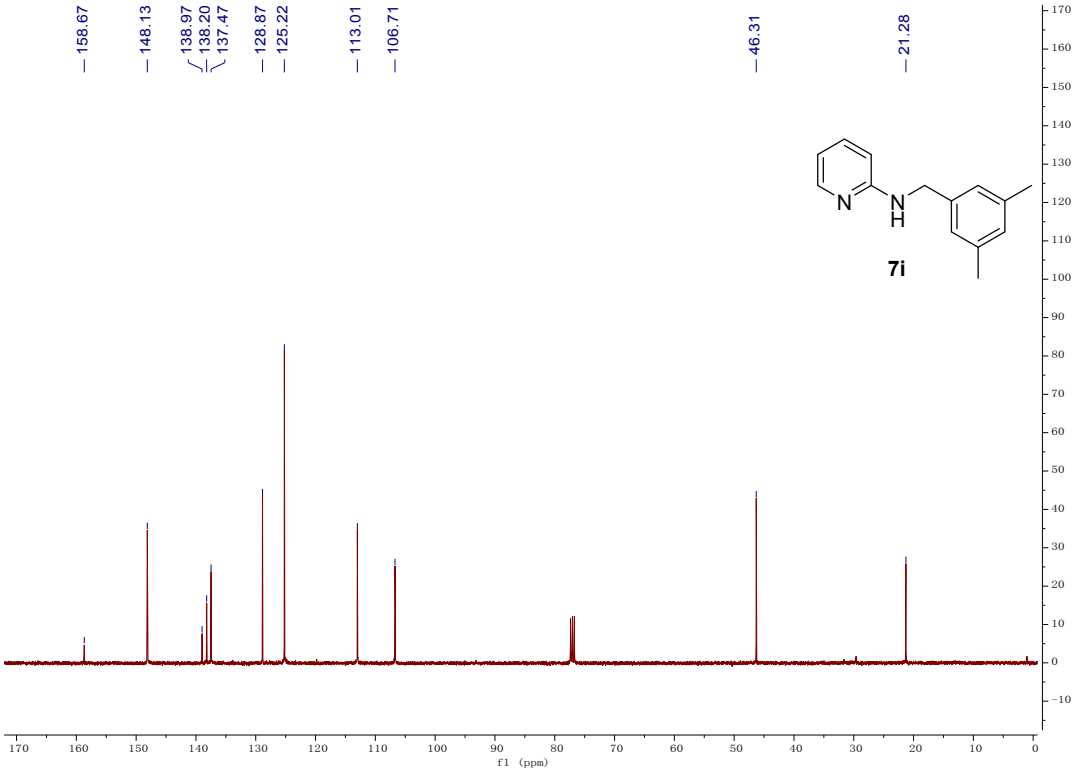

8.01
7.34
7.33
7.32
7.31
7.27
7.25
7.24
6.29
6.27
4.91
4.45
4.43
Cl
N
N
H
Cl
7f
1.00
1.02
3.99
1.00
1.00
2.01
f1 (ppm)

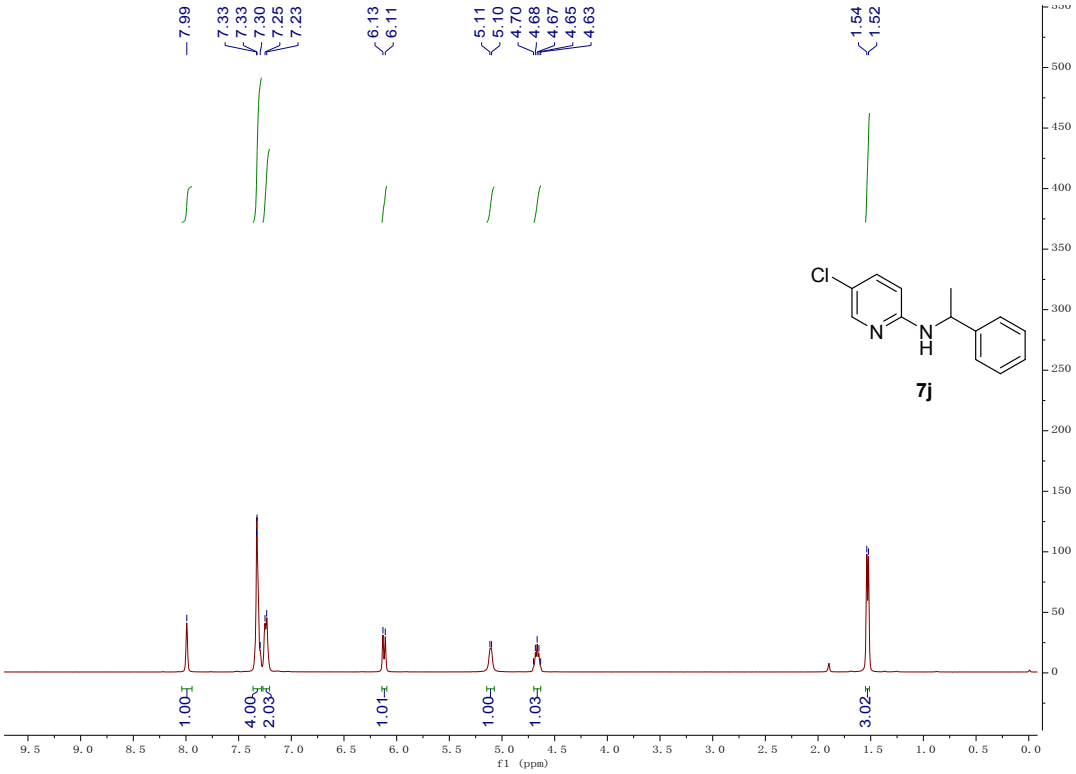

156.61
146.48
137.31
137.26
133.02
128.77
128.61
120.19
107.76
45.62
Cl
N
N
H
Cl
7f
f1 (ppm)

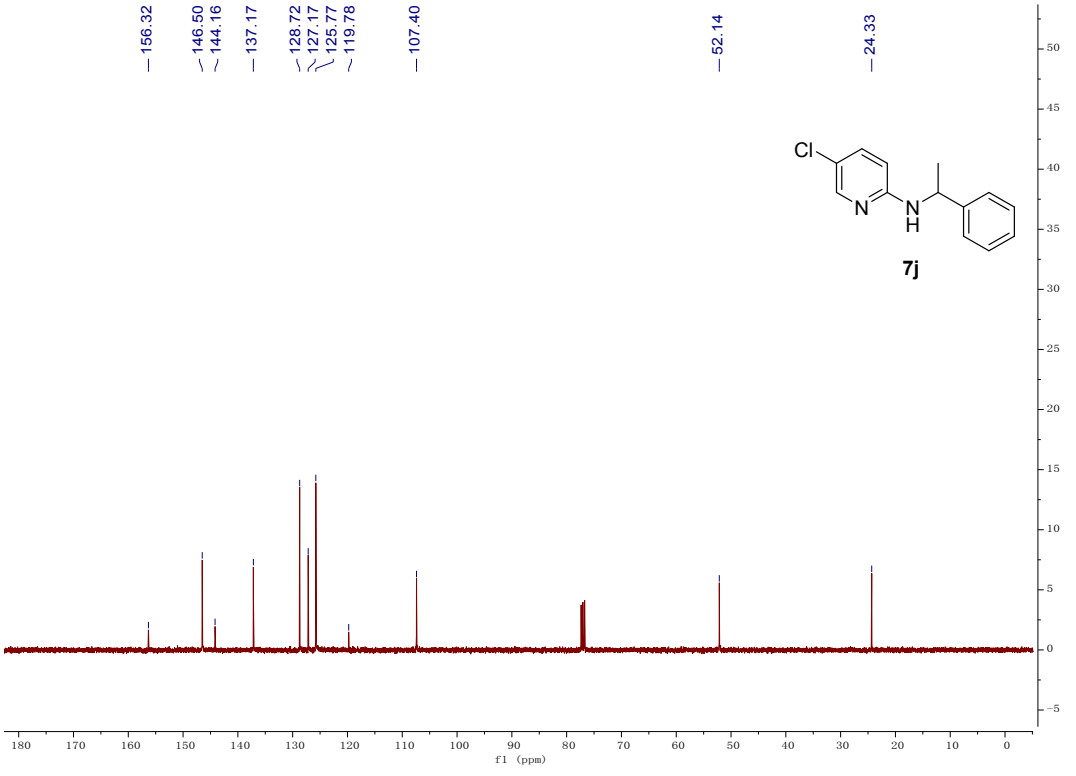

8.01
7.34
7.32
7.31
6.93
6.90
6.31
6.29
4.88
4.38
4.36
2.28
1.00
1.03
3.02
1.02
1.01
2.00
6.07
f1 (ppm)
Cl
N
N
H
7h

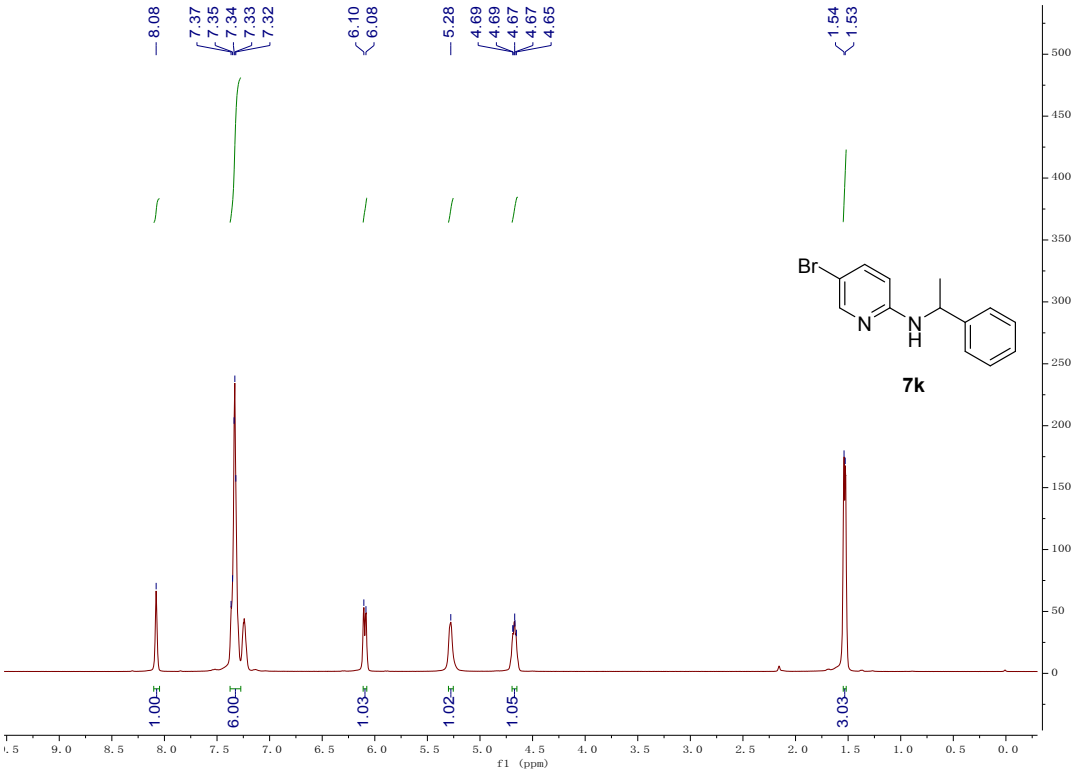

156.92
150.96
146.44
138.51
138.30
137.21
129.00
125.15
107.54
46.39
21.27
f1 (ppm)
Cl
N
N
H
7h

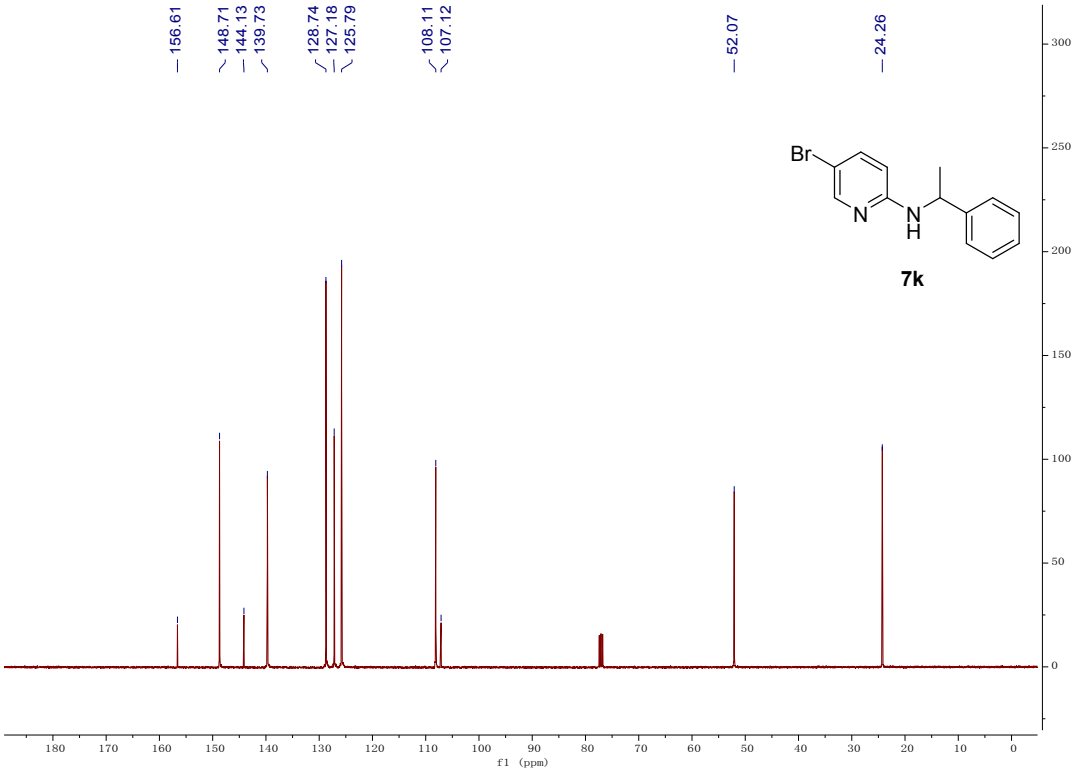

8.09
8.08
7.41
7.39
7.37
7.24
6.97
6.90
6.59
6.57
6.55
6.37
6.35
4.91
4.41
4.40
2.29
1.00
1.04
2.04
1.01
1.00
1.01
1.01
2.03
6.00
f1 (ppm)
7i

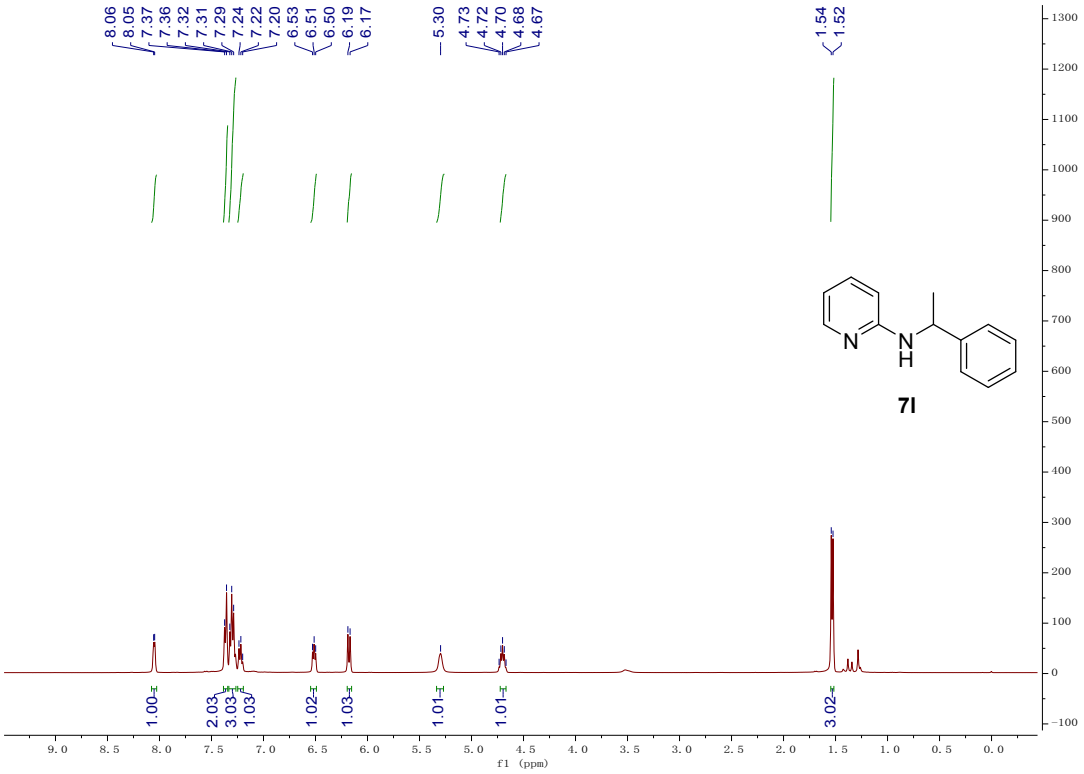

158.67
148.13
138.97
138.20
137.47
128.87
125.22
113.01
106.71
46.31
21.28
f1 (ppm)
7i


7.99
7.33
7.33
7.30
7.25
7.23
6.13
6.11
5.11
5.10
4.70
4.68
4.67
4.65
4.63
1.54
1.52
Cl
N
N
H
7j
1.00
4.00
2.03
1.01
1.00
1.03
3.02
f1 (ppm)

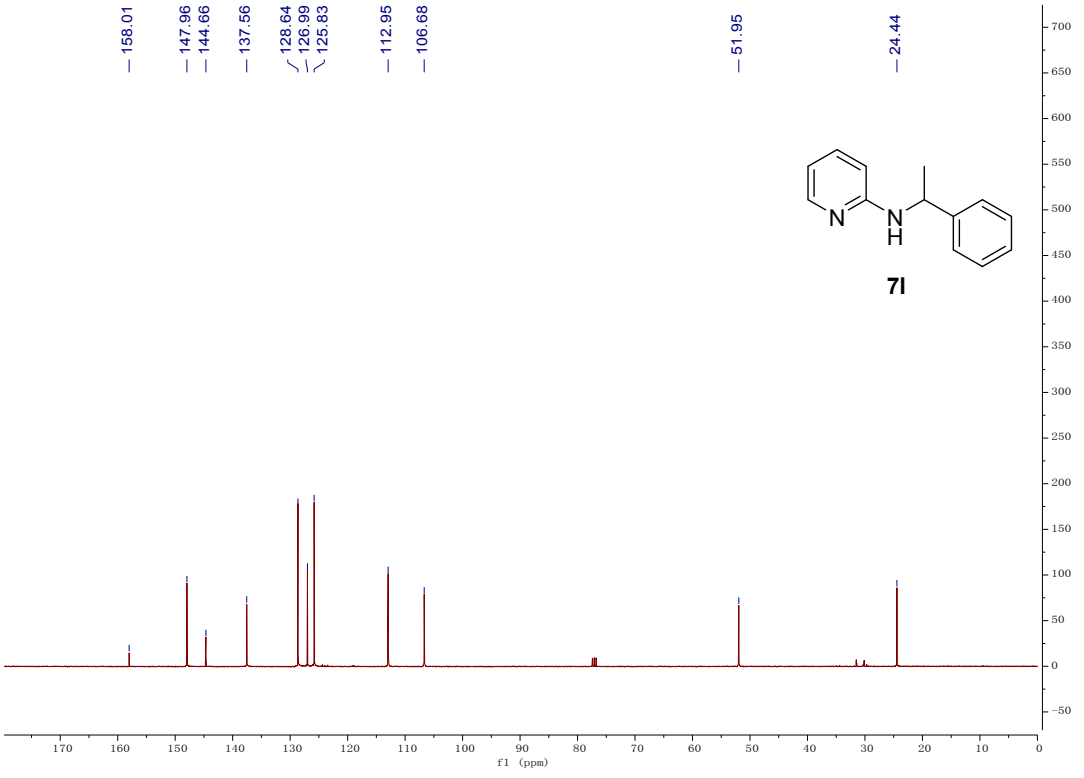

156.32
146.50
144.16
137.17
128.72
127.17
125.77
119.78
107.40
52.14
24.33
Cl
N
N
H
7j
f1 (ppm)


8.08
7.37
7.35
7.34
7.33
7.32
6.10
6.08
5.28
4.69
4.69
4.67
4.67
4.65
1.54
1.53
Br
N
N
H
7k
1.00
6.00
1.03
1.02
1.05
3.03
f1 (ppm)

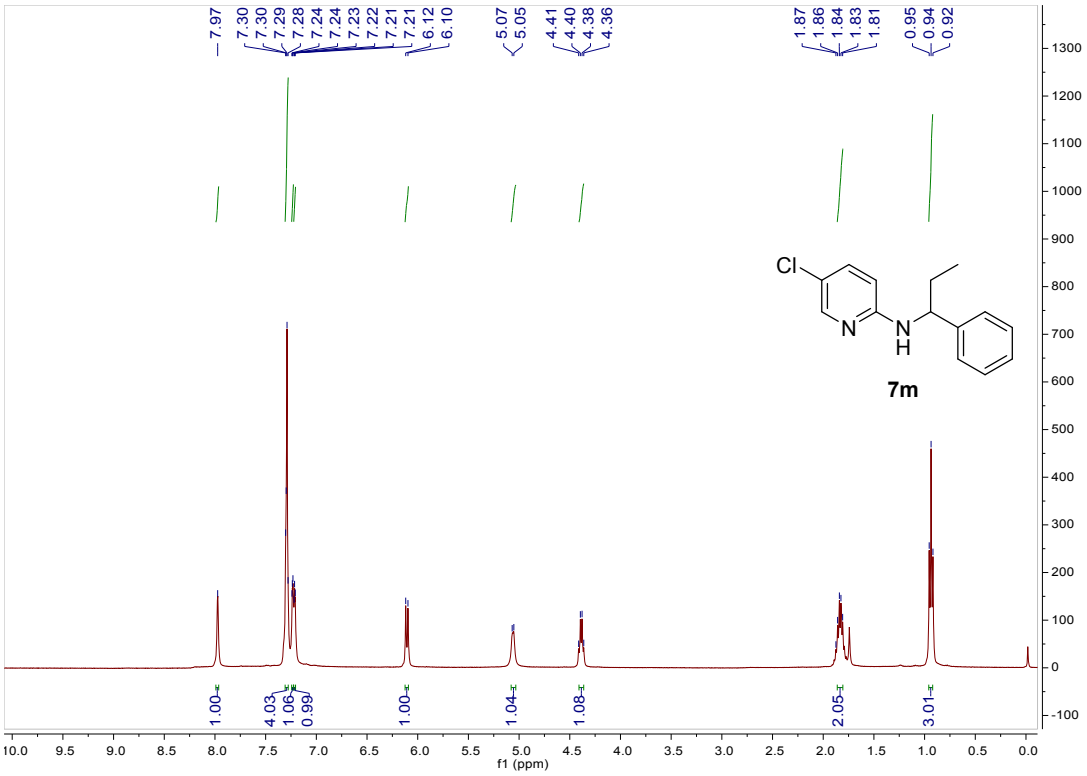

156.61
148.71
144.13
139.73
128.74
127.18
125.79
108.11
107.12
52.07
24.26
Br
N
N
H
7k
f1 (ppm)

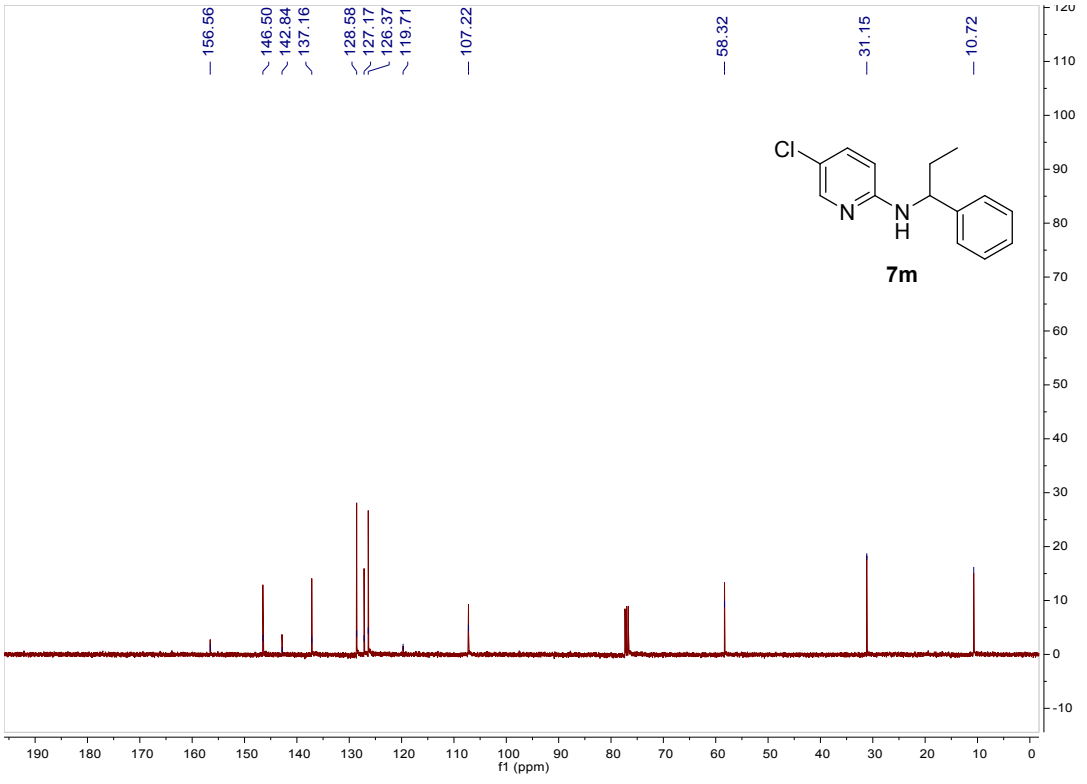

8.06
8.05
7.37
7.36
7.32
7.31
7.29
7.24
7.22
7.20
6.53
6.51
6.50
6.19
6.17
5.30
4.73
4.72
4.70
4.68
4.67
1.54
1.52
1.00
2.03
3.03
1.03
1.02
1.03
1.01
1.01
3.02
f1 (ppm)

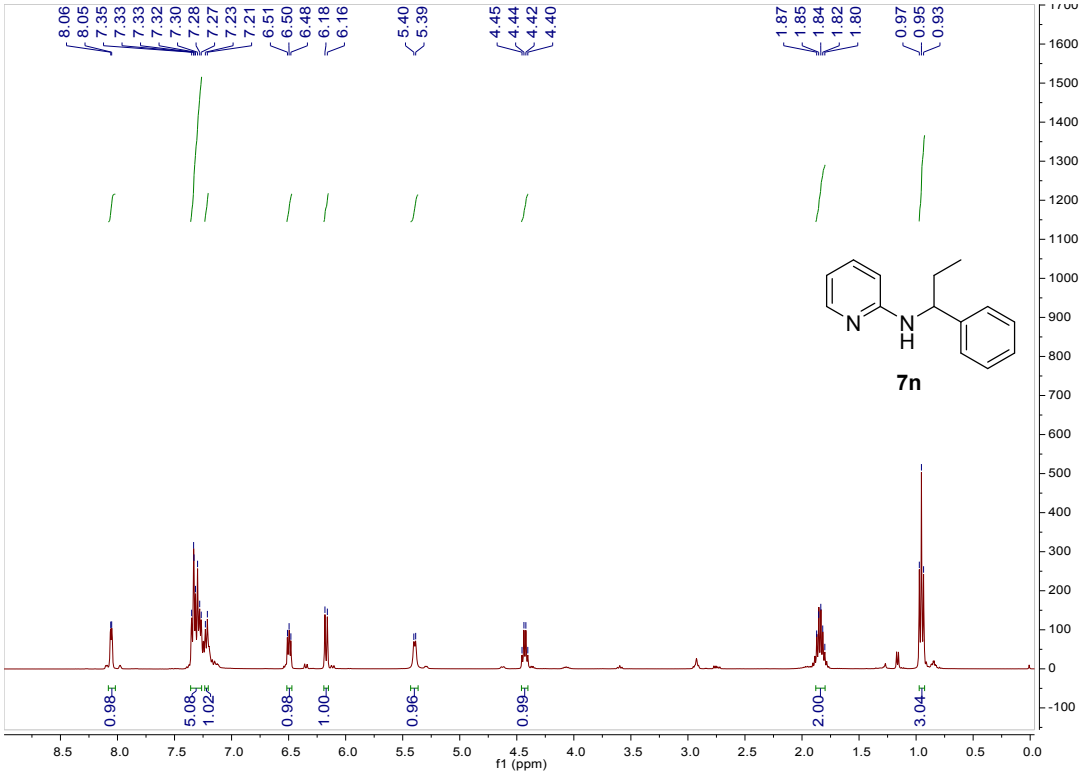
7l

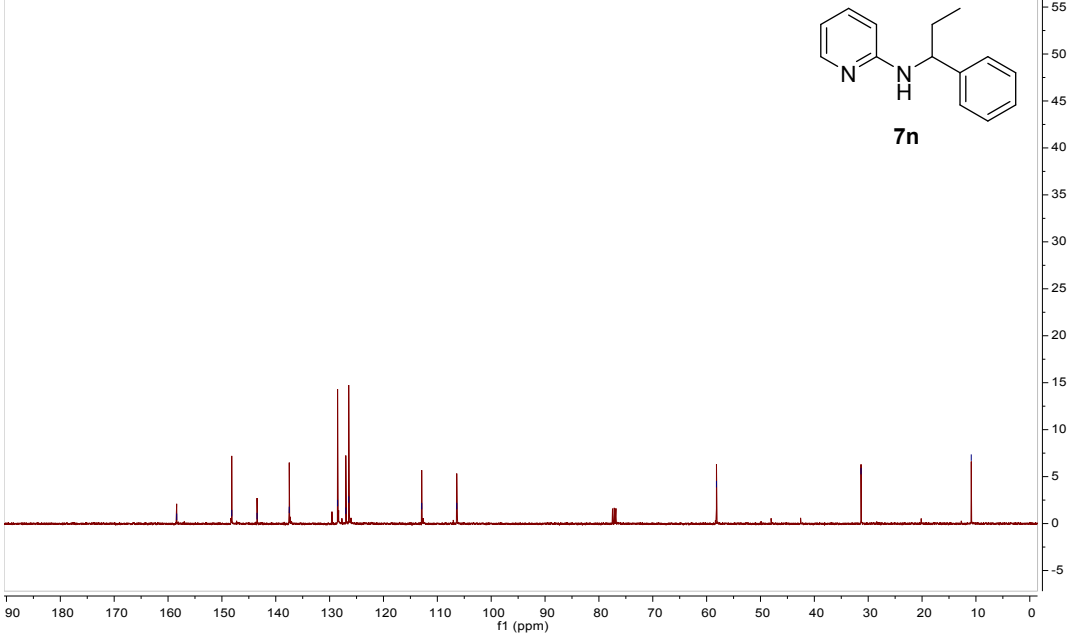

158.01
147.96
144.66
137.56
128.64
126.99
125.83
112.95
106.68
51.95
24.44
f1 (ppm)

7l

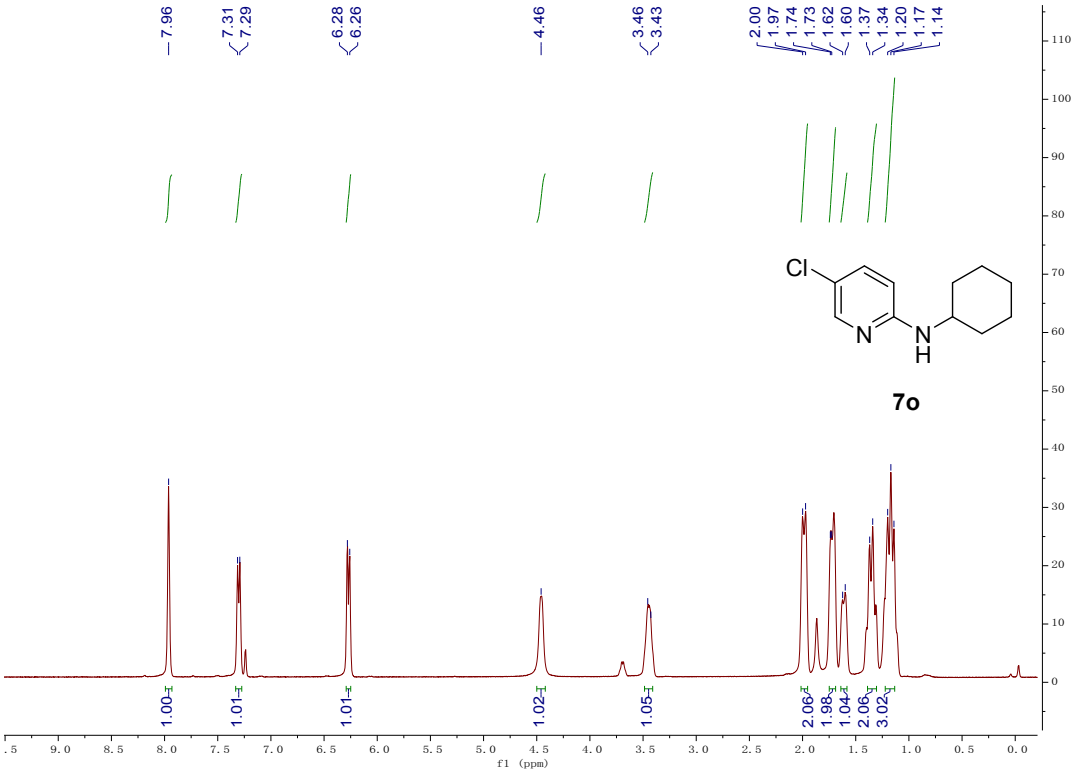

7.97
7.30
7.30
7.29
7.28
7.24
7.24
7.23
7.22
7.21
7.21
6.12
6.10
5.07
5.05
4.41
4.40
4.38
4.36
1.87
1.86
1.84
1.83
1.81
0.95
0.94
0.92
Cl
N
N
H
7m
1.00
4.03
1.06
0.99
1.00
1.04
1.08
2.05
3.01
f1 (ppm)


156.56
146.50
142.84
137.16
128.58
127.17
126.37
119.71
107.22
58.32
31.15
10.72
Cl
N
N
H
7m
f1 (ppm)

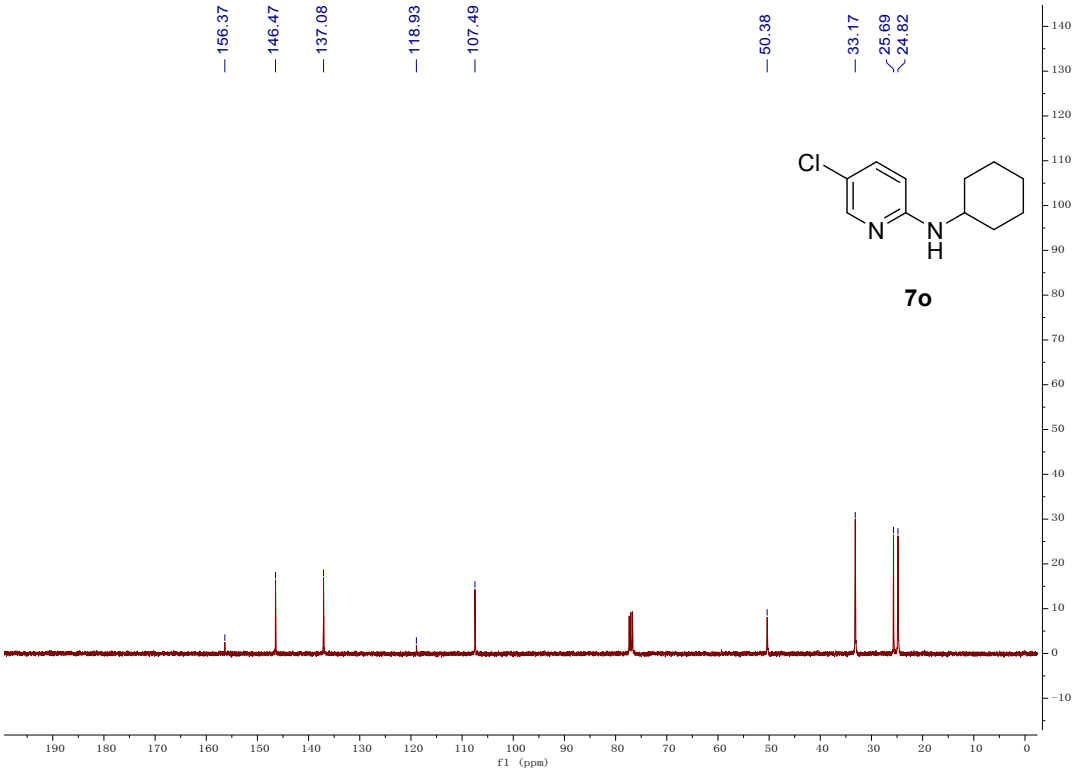

8.06
8.05
7.35
7.33
7.33
7.32
7.30
7.28
7.27
7.23
7.21
6.51
6.50
6.48
6.18
6.16
5.40
5.39
4.45
4.44
4.42
4.40
1.87
1.85
1.84
1.82
1.80
0.97
0.95
0.93
0.98
5.08
1.02
0.98
1.00
0.96
0.99
2.00
3.04
f1 (ppm)


158.40
148.17
143.48
137.49
128.52
127.00
126.45
112.90
106.40
58.17
31.33
10.87
f1 (ppm)

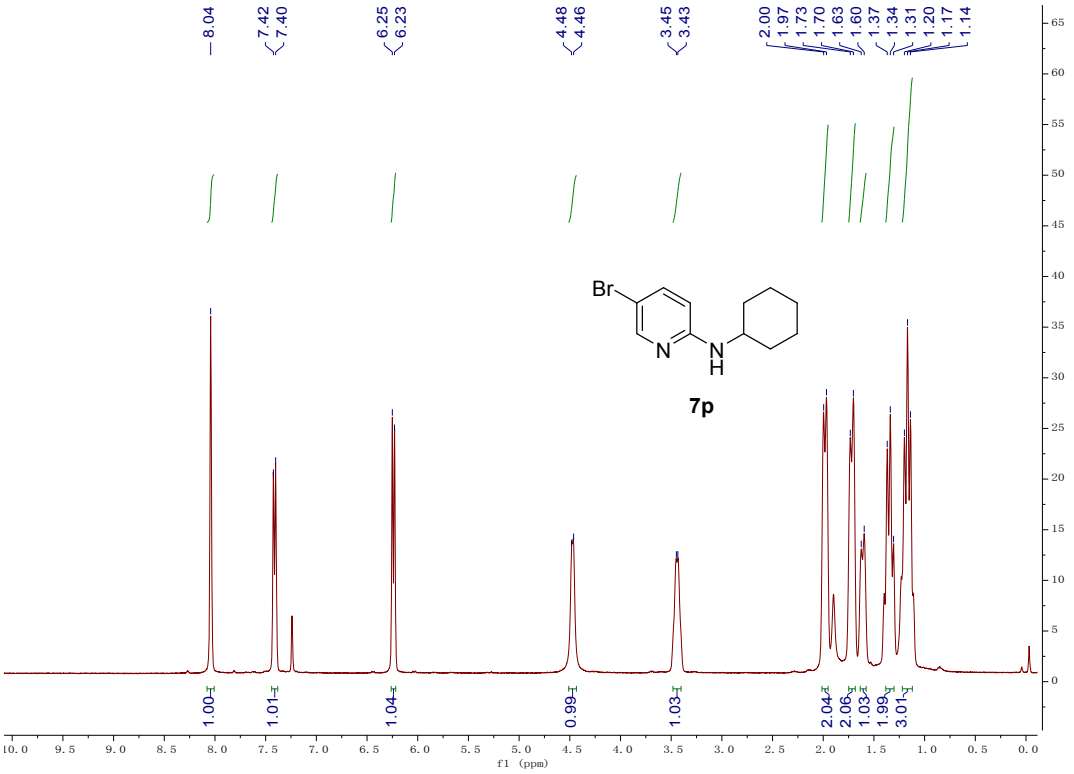
7n

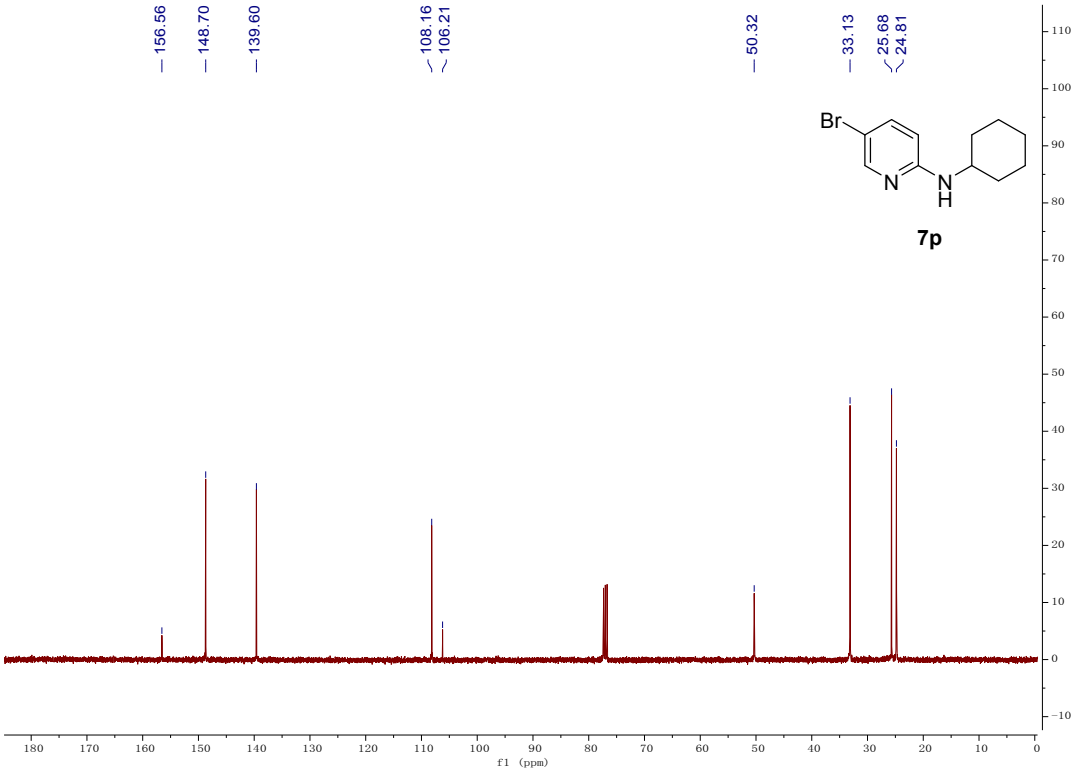

7.96
7.31
7.29
6.28
6.26
4.46
3.46
3.43
2.00
1.97
1.74
1.73
1.62
1.60
1.37
1.34
1.20
1.17
1.14
Cl
N
N
H
1.00
1.01
1.01
1.02
1.05
2.06
1.98
1.04
2.06
3.02
f1 (ppm)

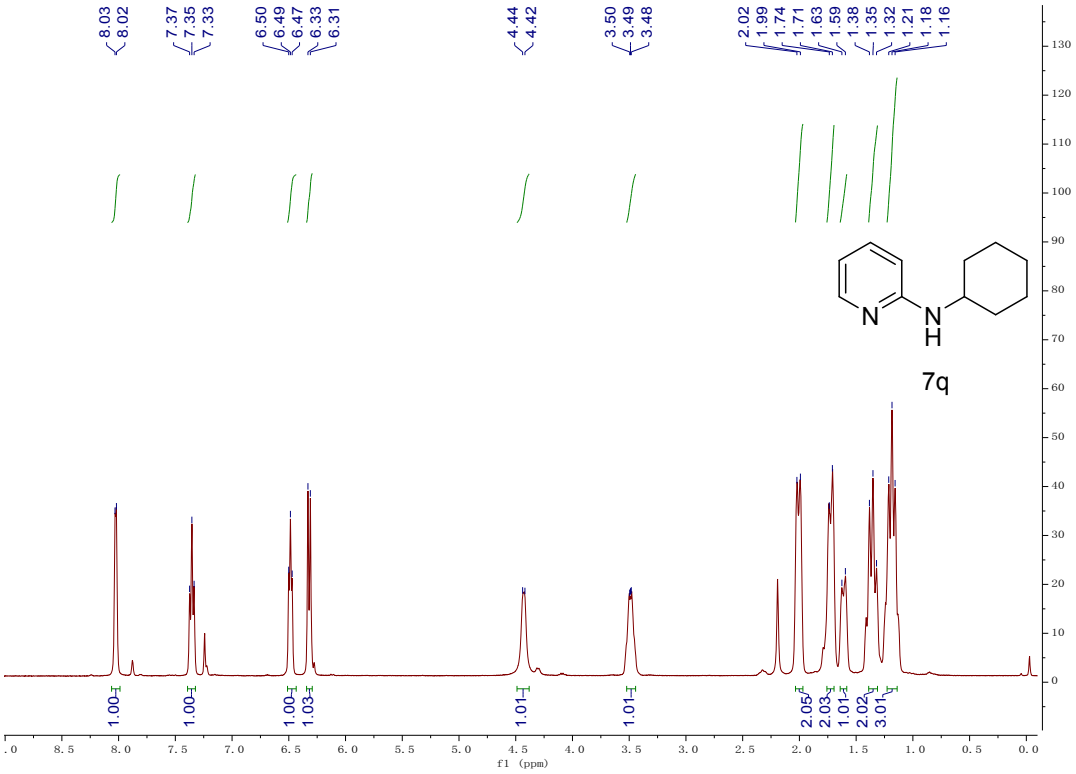
7o


156.37
146.47
137.08
118.93
107.49
50.38
33.17
25.69
24.82
Cl
N
N
H
f1 (ppm)

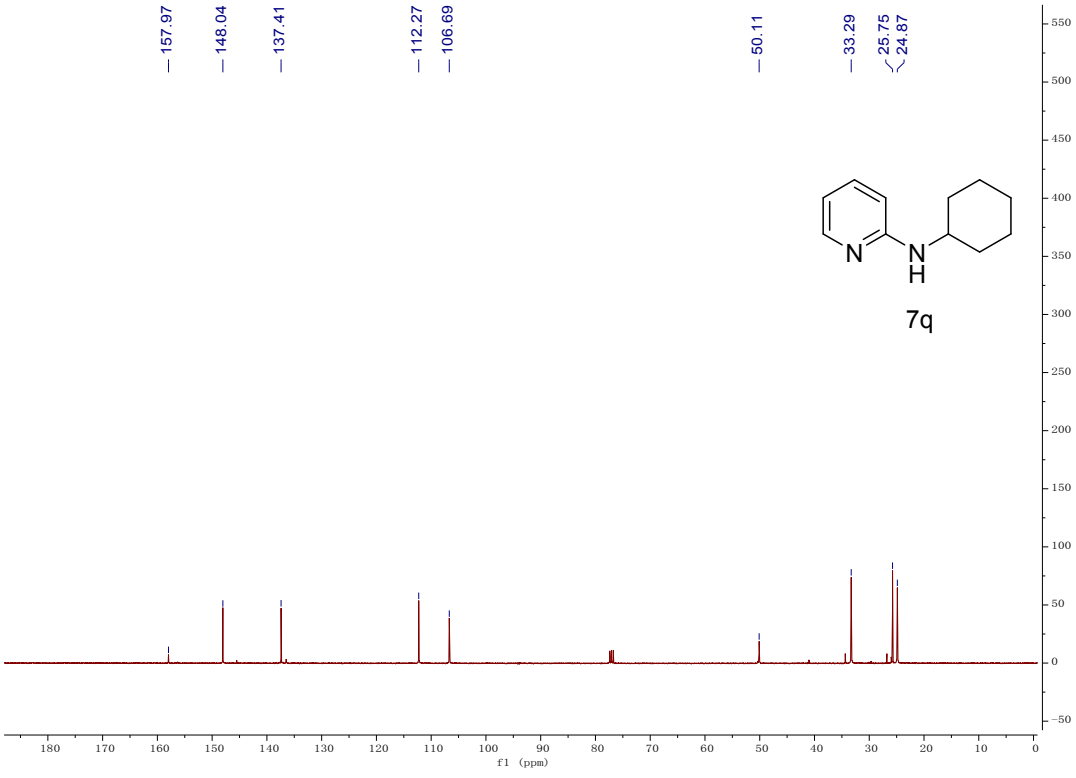
7o


8.04
7.42
7.40
6.25
6.23
4.48
4.46
3.45
3.43
2.00
1.97
1.73
1.70
1.63
1.60
1.37
1.34
1.31
1.20
1.17
1.14
Br
N
N
H
7p
1.00
1.01
1.04
0.99
1.03
2.04
2.06
1.03
1.99
3.01
f1 (ppm)

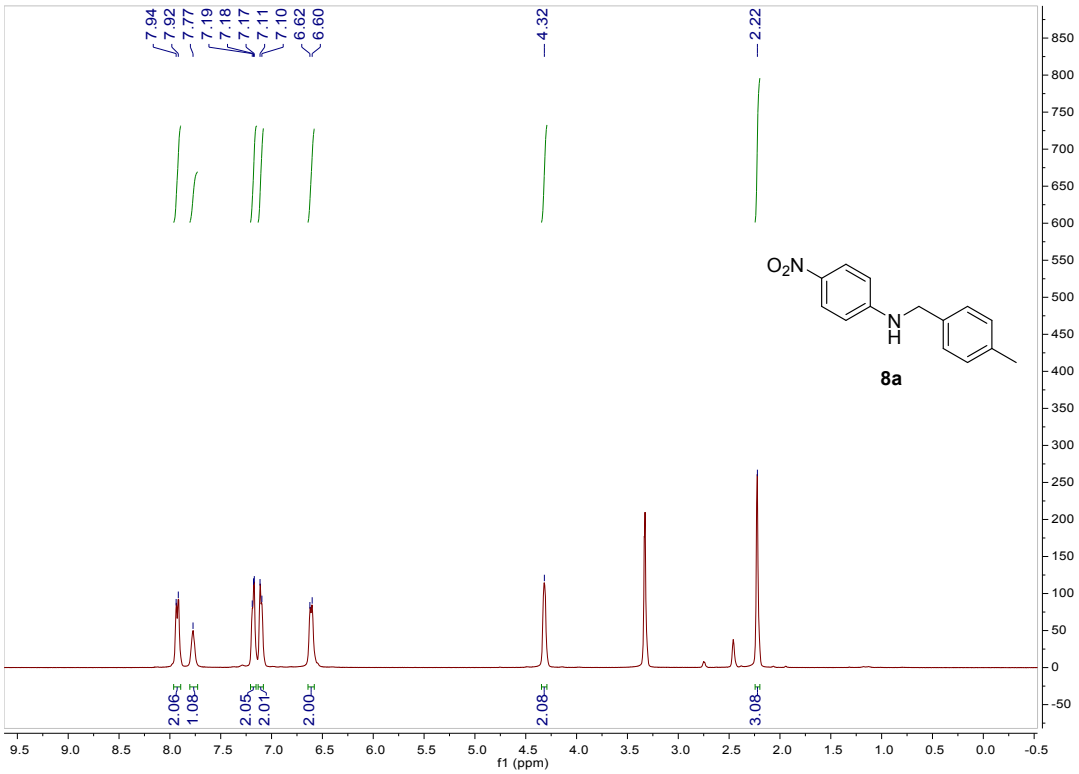

156.56
148.70
139.60
108.16
106.21
50.32
33.13
25.68
24.81
Br
N
N
H
7p
f1 (ppm)

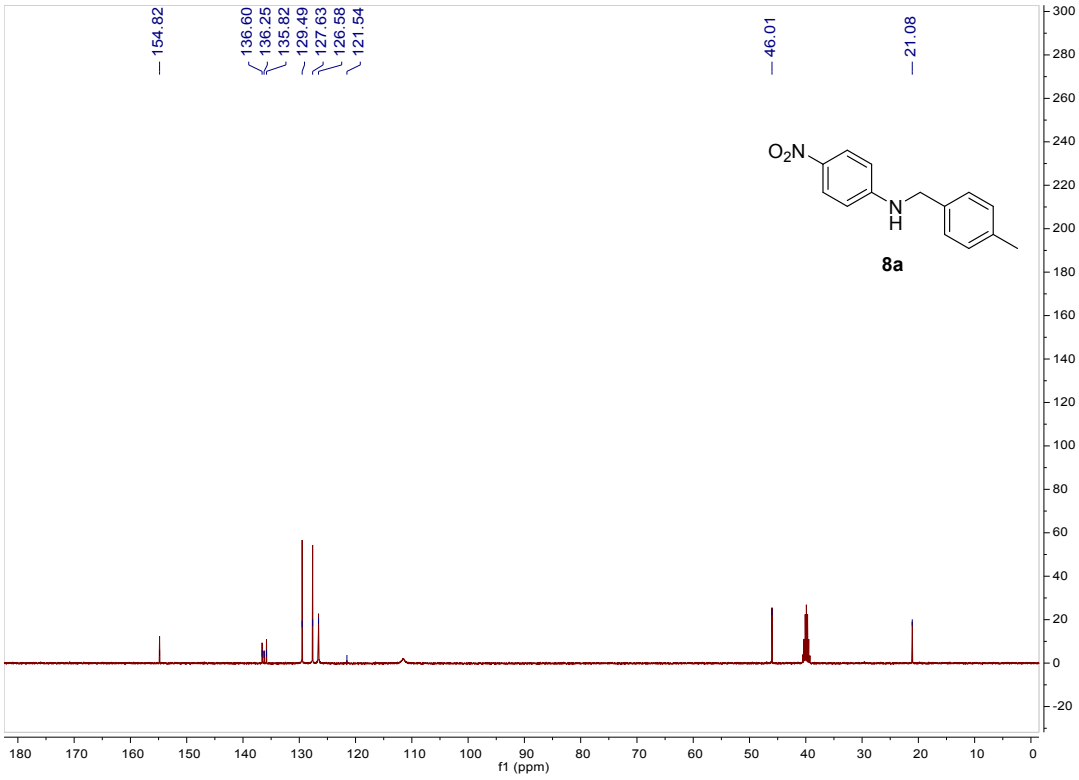

8.03
8.02
7.37
7.35
7.33
6.50
6.49
6.47
6.33
6.31
4.44
4.42
3.50
3.49
3.48
2.02
1.99
1.74
1.71
1.63
1.59
1.38
1.35
1.32
1.21
1.18
1.16
1.00
1.00
1.00
1.03
1.01
1.01
2.05
2.03
1.01
2.02
3.01
f1 (ppm)

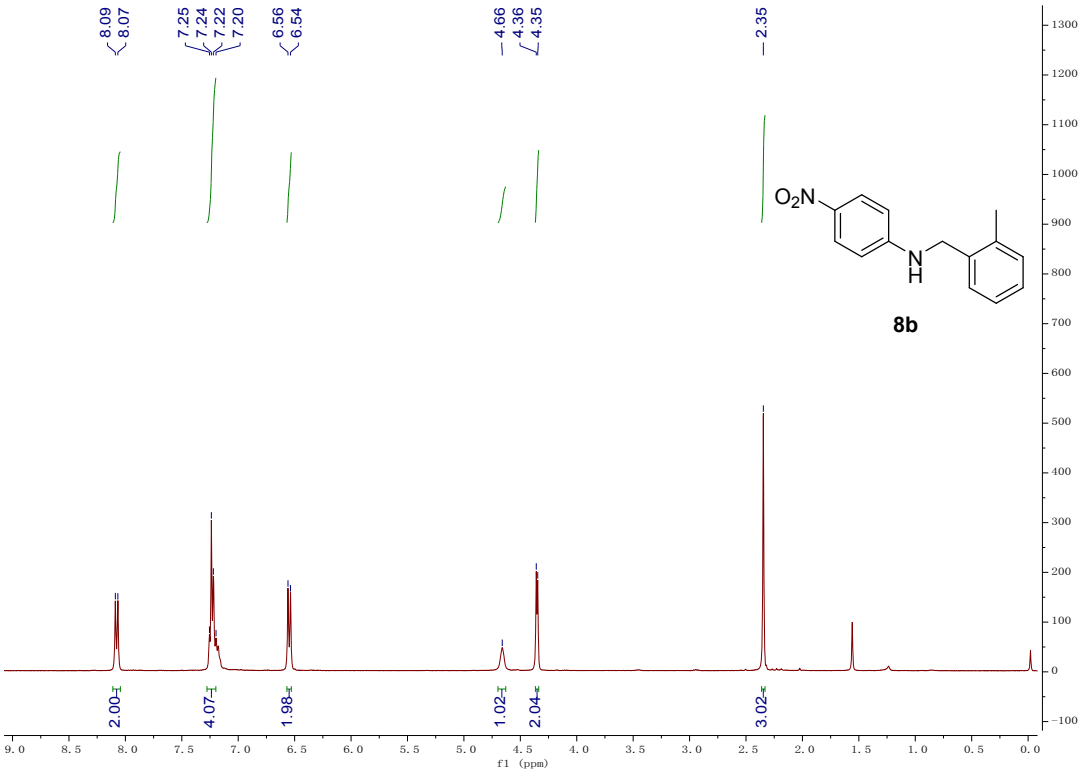
7q

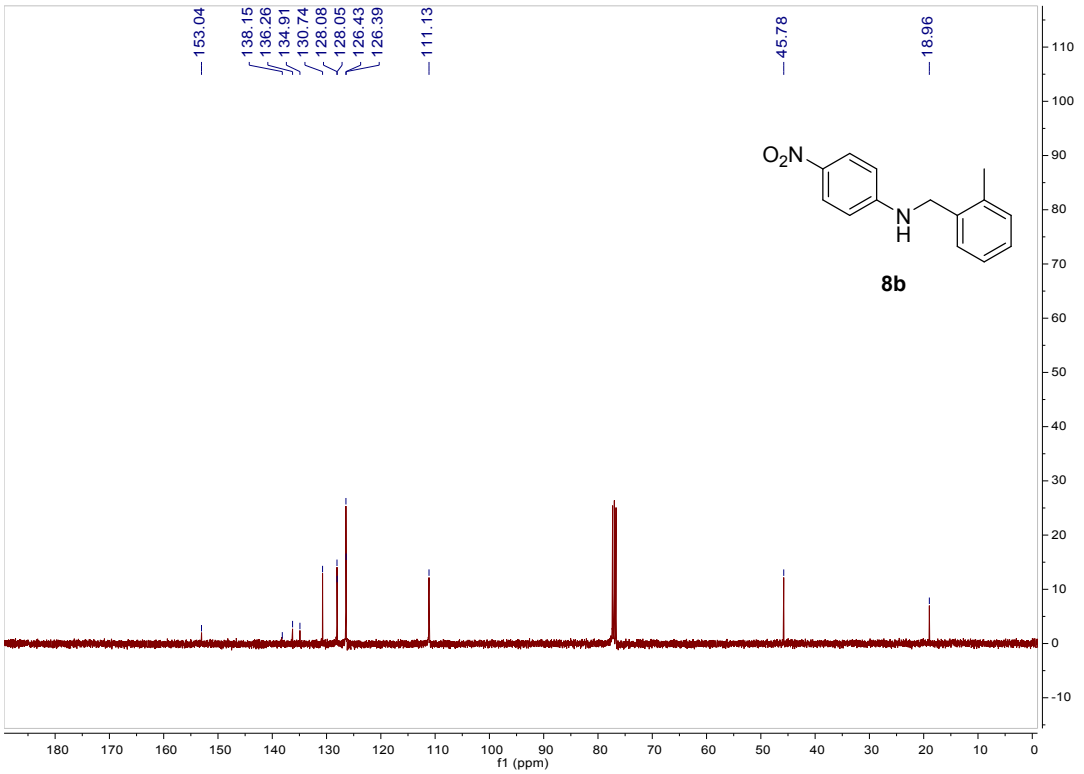

157.97
148.04
137.41
112.27
106.69
50.11
33.29
25.75
24.87
f1 (ppm)

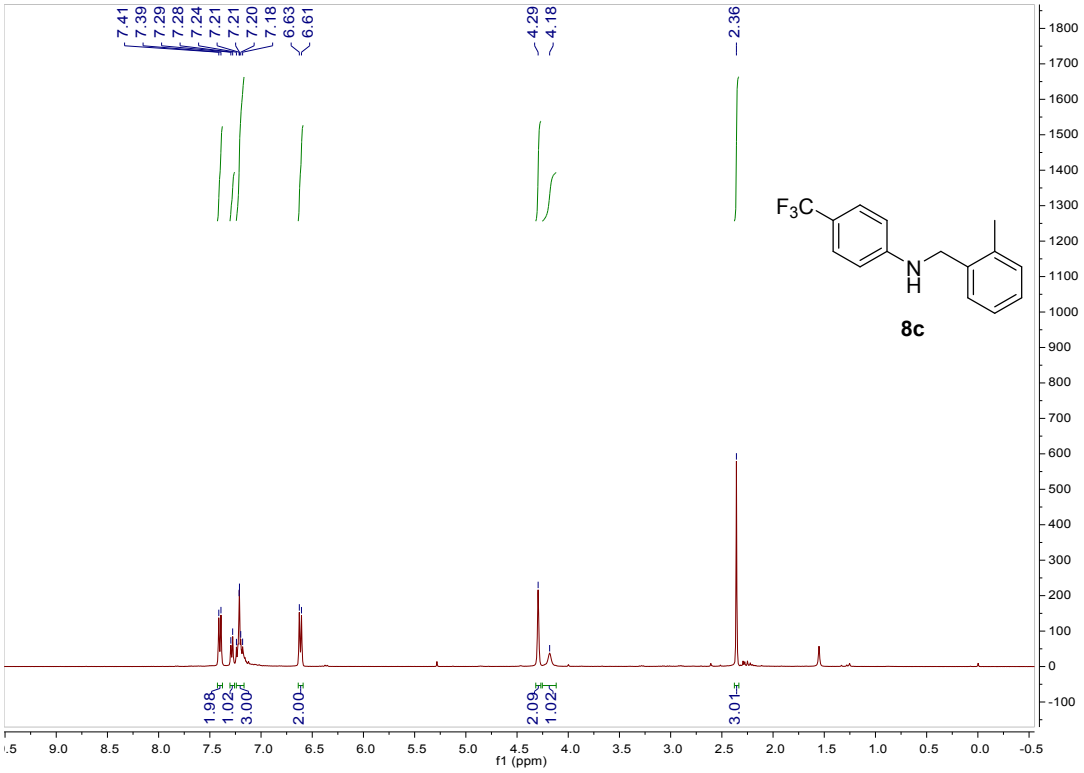
7q

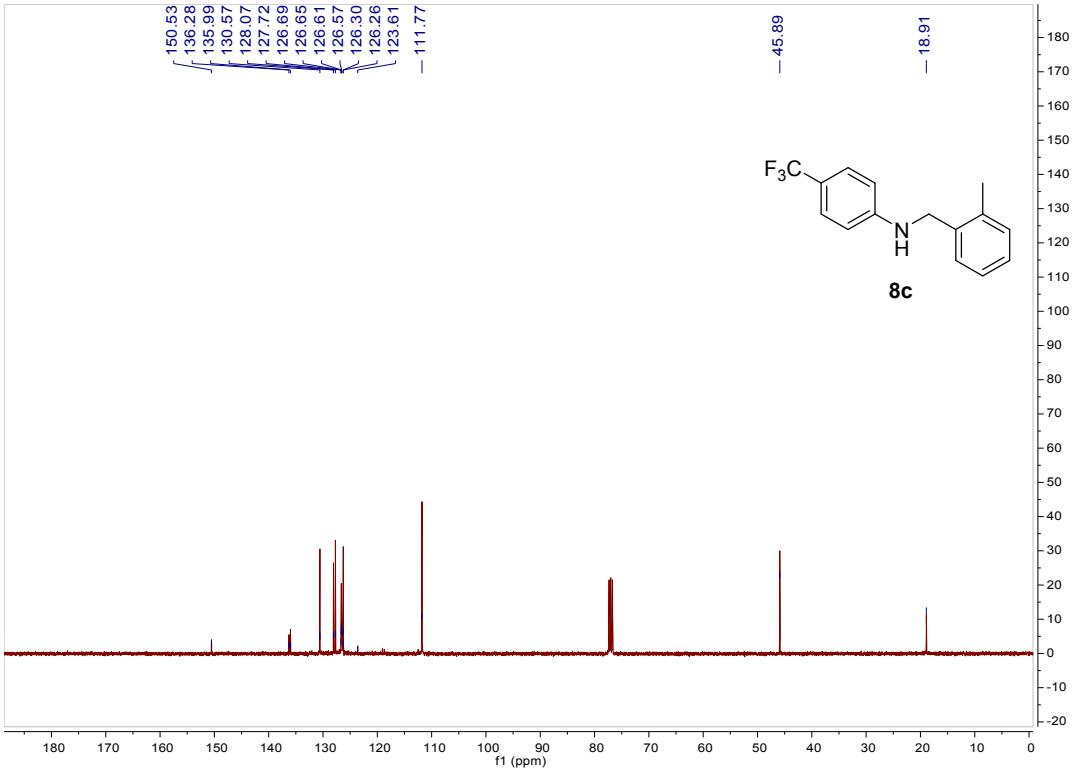

7.94
7.92
7.77
7.19
7.18
7.17
7.11
7.10
6.62
6.60
4.32
2.22
2.06
1.08
2.05
2.01
2.00
2.08
3.08
f1 (ppm)
O2N
N
H
8a

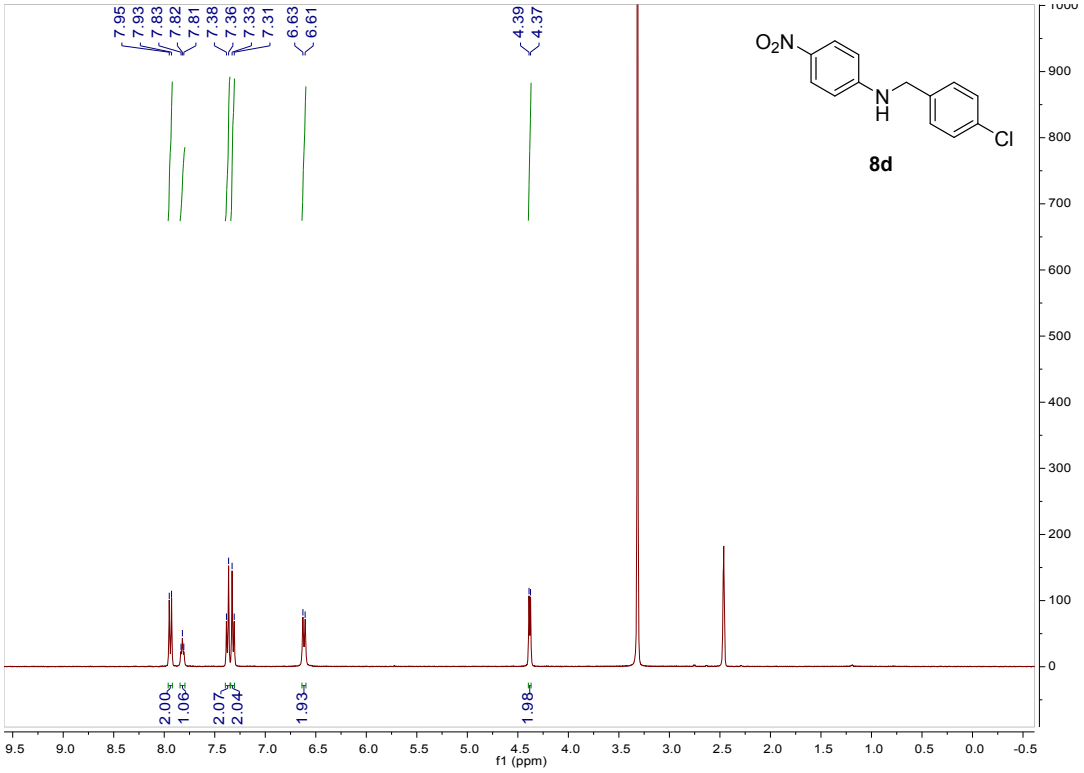

154.82
136.60
136.25
135.82
129.49
127.63
126.58
121.54
46.01
21.08
f1 (ppm)
O2N
N
H
8a

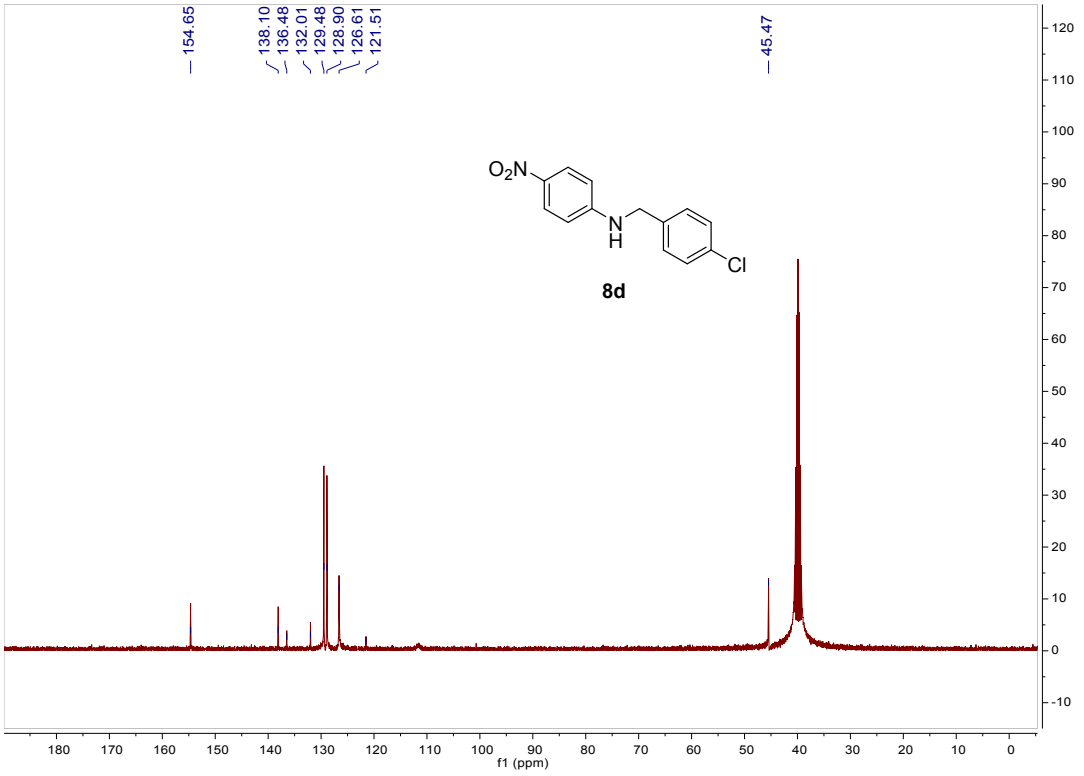

8.09
8.07
7.25
7.24
7.22
7.20
6.56
6.54
4.66
4.36
4.35
2.35
2.00
4.07
1.98
1.02
2.04
3.02
f1 (ppm)
O2N
N
H
8b

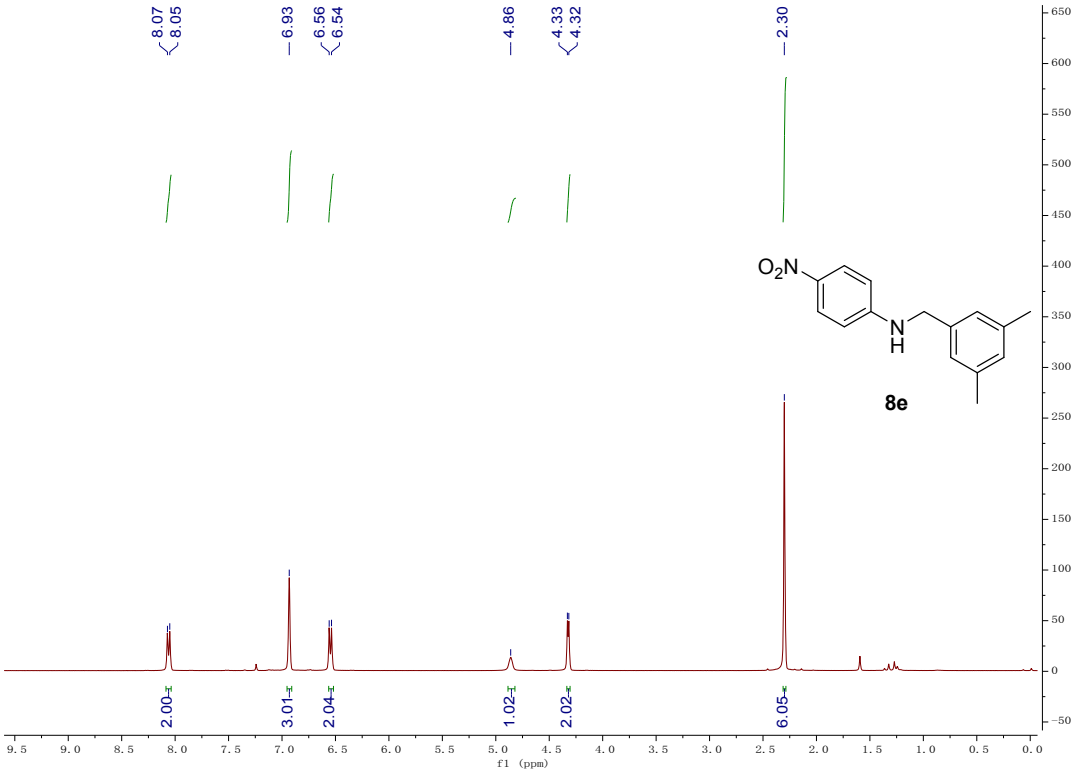

153.04
138.15
136.26
134.91
130.74
128.08
128.05
126.43
126.39
111.13
45.78
18.96
f1 (ppm)
O2N
N
H
8b

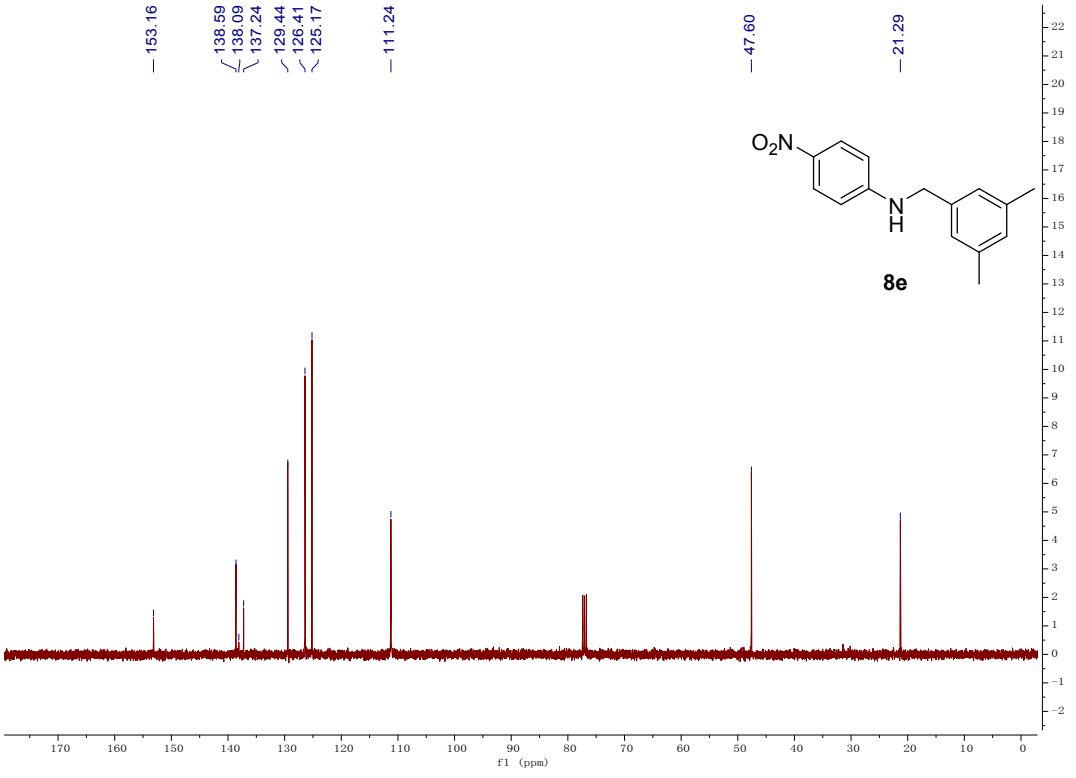

7.41
7.39
7.29
7.28
7.24
7.21
7.21
7.20
7.18
6.63
6.61
4.29
4.18
2.36
F3C
N
H
8c
1.98
1.02
3.00
2.00
2.09
1.02
3.01
f1 (ppm)

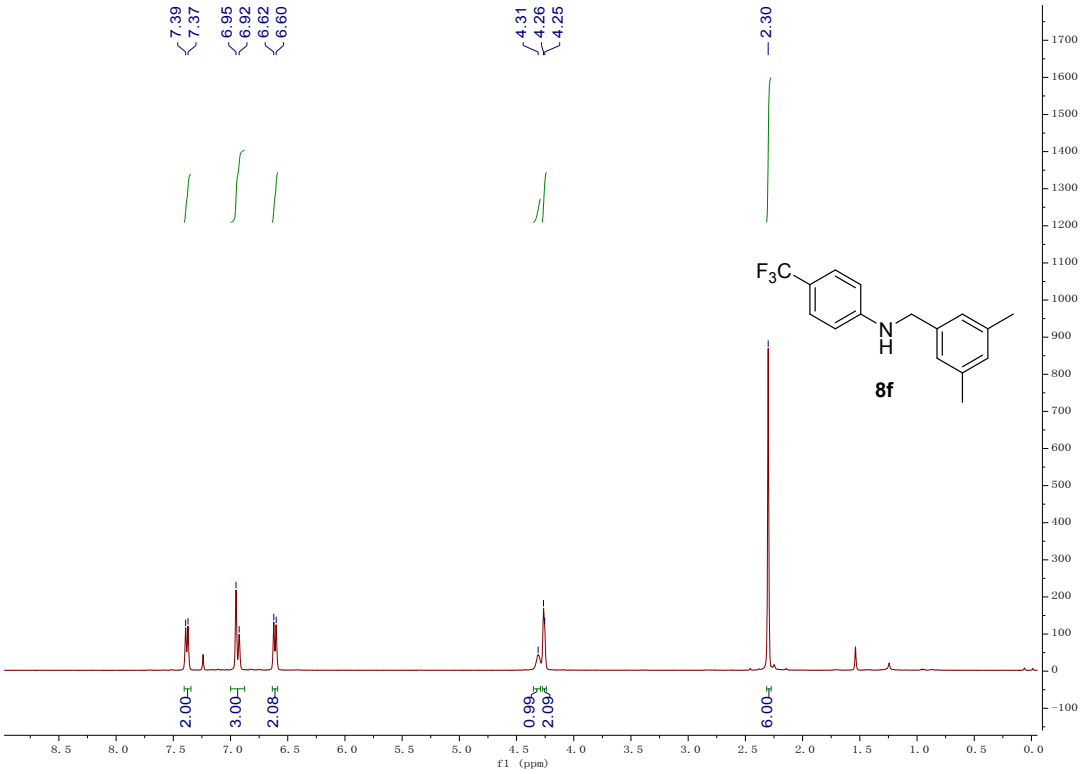

150.53
136.28
135.99
130.57
128.07
127.72
126.69
126.65
126.61
126.57
126.30
126.26
123.61
111.77
45.89
18.91
F3C
N
H
8c
f1 (ppm)

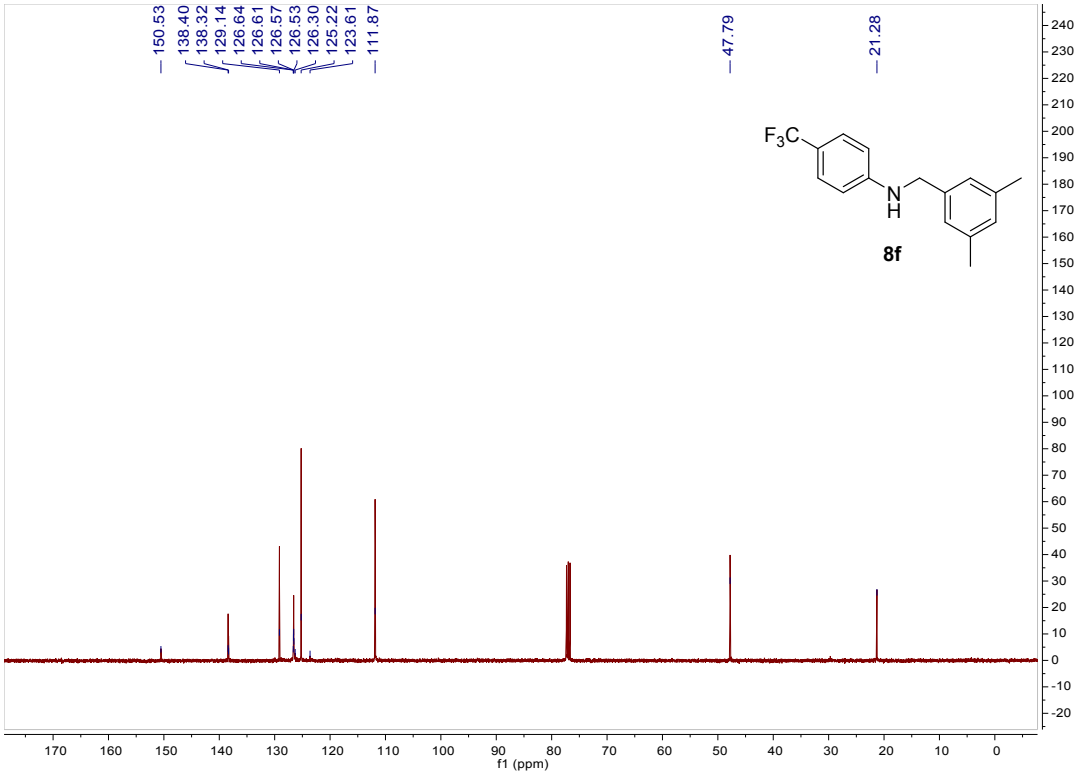

7.95
7.93
7.83
7.82
7.81
7.38
7.36
7.33
7.31
6.63
6.61
4.39
4.37
2.00
1.06
2.07
2.04
1.93
1.98
O2N
N
H
Cl
8d
f1 (ppm)

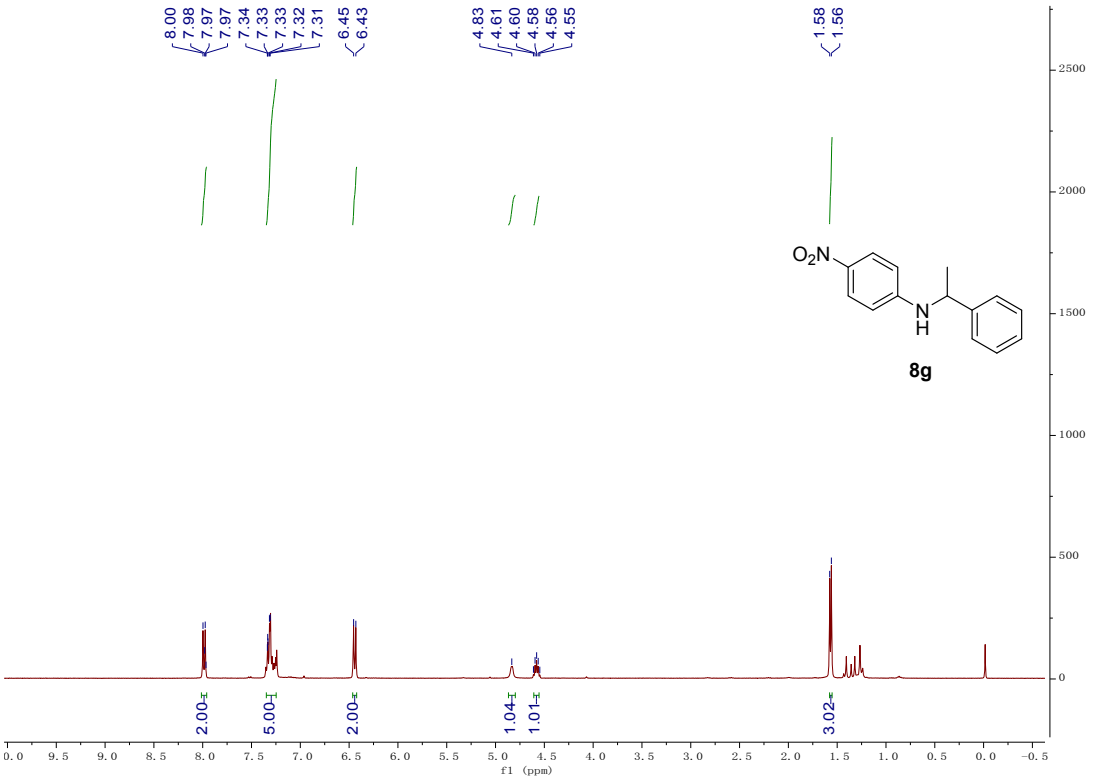

154.65
138.10
136.48
132.01
129.48
128.90
126.61
121.51
45.47
O2N
N
H
Cl
8d
f1 (ppm)

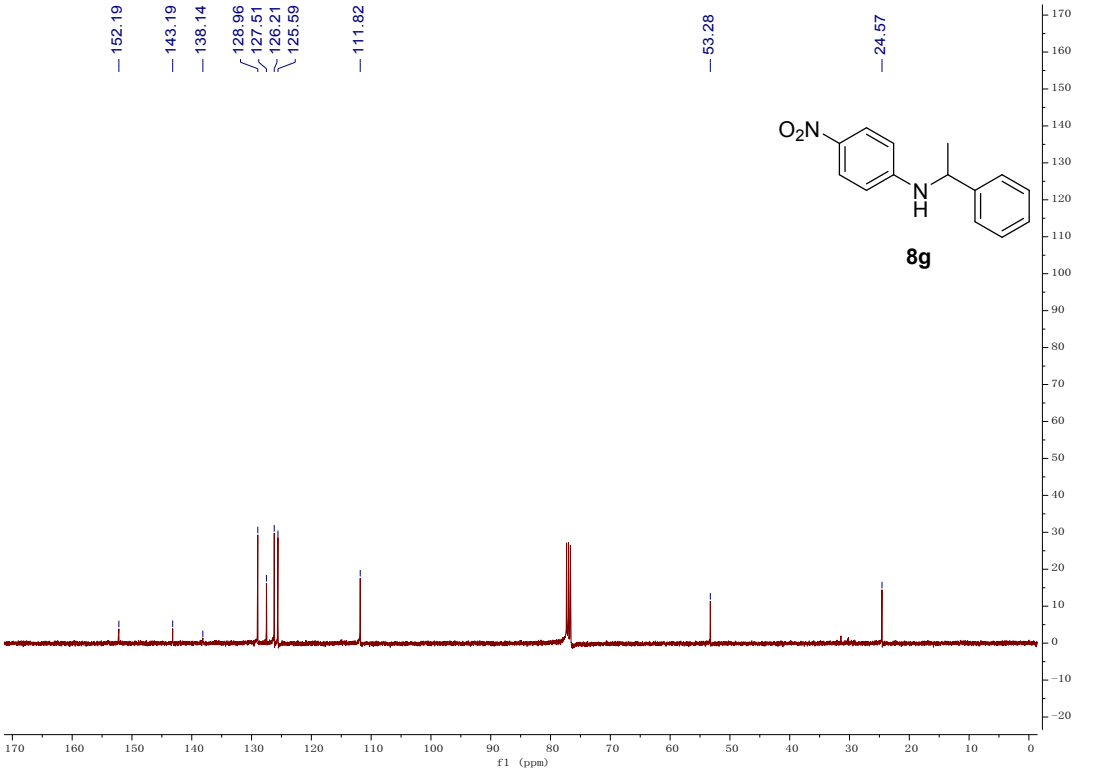

8.07
8.05
6.93
6.56
6.54
4.86
4.33
4.32
2.30
2.00
3.01
2.04
1.02
2.02
6.05
f1 (ppm)
O2N
N
H
8e


153.16
138.59
138.09
137.24
129.44
126.41
125.17
111.24
47.60
21.29
f1 (ppm)
O2N
N
H
8e


7.39
7.37
6.95
6.92
6.62
6.60
4.31
4.26
4.25
2.30
F3C
N
H
8f
2.00
3.00
2.08
0.99
2.09
6.00
f1 (ppm)


150.53
138.40
138.32
129.14
126.64
126.61
126.57
126.53
126.30
125.22
123.61
111.87
47.79
21.28
F3C
N
H
8f
f1 (ppm)


8.00
7.98
7.97
7.97
7.34
7.33
7.33
7.32
7.31
6.45
6.43
4.83
4.61
4.60
4.58
4.56
4.55
1.58
1.56
2.00
5.00
2.00
1.04
1.01
3.02
f1 (ppm)
O2N
N
H
8g


152.19
143.19
138.14
128.96
127.51
126.21
125.59
111.82
53.28
24.57
f1 (ppm)
O2N
N
H
8g