Supporting Information

Transition-Metal-Free Decarboxylative Halogenation of 2-Picolinic Acids with Dihalomethane under Oxygen Conditions

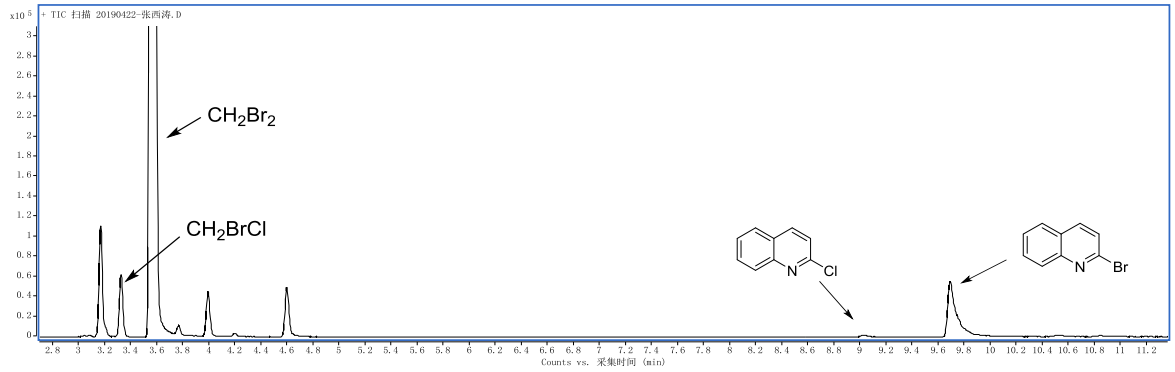
Xitao Zhang,[a] Xiujuan Feng,*[a] Haixia Zhang,[a] Yoshinori Yamamoto,[a,b] and Ming Bao*[a]

[a] *State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116023, China*

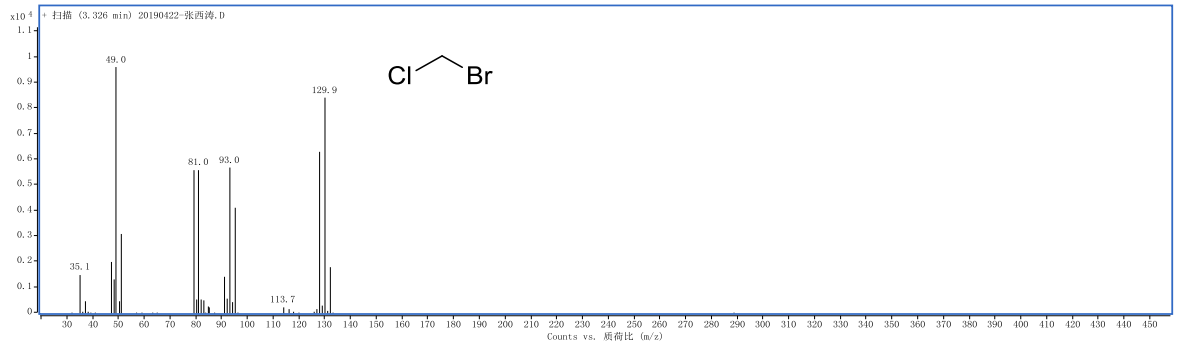
[b] *Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan and Research Organization of Science and Technology, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan*

Table of Contents

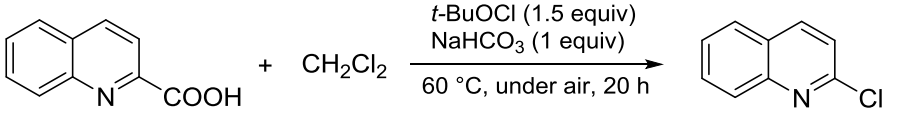
1. GC spectrum for CH_2BrCl capture



Mass spectrum for CH_2BrCl

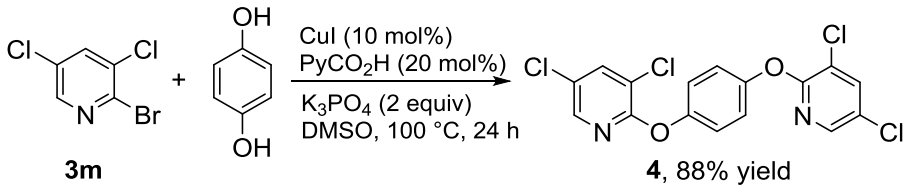


2. Procedure for Gram-Scale Synthesis and Further Transformations



1a, 10 mmol 66 mL **2a**, 1.24 g, 76% yield

A reaction flask was charged with a mixture of quinoline-2-carboxylic acid (**1a**, 1.73 g, 10 mmol), $NaHCO_3$ (840 mg, 10 mmol), *t*-BuOCl (1.7 mL, 15 mmol), and dichloromethane (100 mL). The reaction mixture was stirred at 60 ℃ for 20 h, and then was cooled to room temperature. The solvent was removed under reduced pressure, and the residue obtained was purified via silica gel chromatography (eluent: ethyl acetate : petroleum ether = 1 : 10) to afford 2-chloroquinoline (**2a**) as a white solid (1.24 g, 76%).

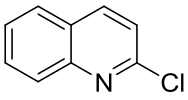


A reaction flask was charged with a mixture of 2-bromo-3,5-dichloropyridine (272.3 mg, 1.2 mmol), hydroquinone (50.1 mg, 0.5 mmol), K_3PO_4 (424.5 mg, 2 mmol), CuI (19.0 mg, 0.1 mmol), and picolinic acid (24.6 mg, 0.2 mmol). After the flask was evacuated and back-filled with N_2, DMSO (2 mL) were added, and then the mixture was heated at 100 ℃ for 24 h. EtOAc (10 mL) and H_2O (10 mL) were added and the mixture was filtered through a Celite pad. The organic layer was separated and the aqueous layer was extracted twice with EtOAc (2 × 10 mL). The combined organic layers were washed with H_2O (2 × 10 mL), dried over Na_2SO_4, and filtered through a pad of silica gel. The filtrate was concentrated and the residue was purified by column chromatography (eluent: ethyl acetate : petroleum ether = 1 : 10) to afford 1,4-bis((3,5-dichloropyridin-2-yl)oxy)benzene (**4**) as a white solid (176.8 mg, 88%).

3. Characterization Data of Products

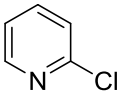
The spectroscopic data of all the products are presented. All the known compounds were in accordance with the data reported in the literatures.

2-chloroquinoline (2a)[1]



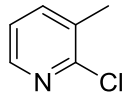
White solid (43.2 mg, 88% yield), mp 37–39 ℃, (lit.[1] mp 36–38 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.74–7.69 (m, 1H), 7.55–7.51 (m, 1H), 7.34 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 147.9, 138.9, 130.6, 128.6, 127.6, 127.0, 126.8, 122.3.

2-chloropyridine (2b)[1]



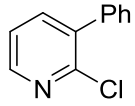
Colorless oil (73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (dd, J = 4.8, 1.6 Hz, 1H), 7.68–7.63 (m, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.24–7.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.6, 149.8, 138.7, 124.5, 122.2.

2-chloro-3-methylpyridine (2c)[2]



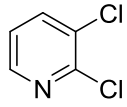
Colorless oil (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 4.0 Hz, 1H), 7.55 (d, J = 7.2 Hz, 1H), 7.14 (dd, J = 7.2, 4.8 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.6, 147.0, 139.3, 132.5, 122.5, 19.6.

2-chloro-3-phenylpyridine (2d)[2]



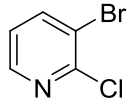
White solid (50.1 mg, 91% yield), mp 52–54 ℃, (lit.[2] mp 46–47 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 7.67–7.64 (m, 1H), 7.45–7.43 (m, 5H), 7.32–7.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 148.4, 139.7, 137.5, 137.0, 129.3, 128.4, 122.6.

2,3-dichloropyridine (2e)[2]



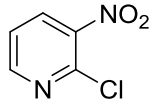
White solid (35.5 mg, 80% yield), mp 46–48 ℃, (lit.[2] mp 45–46 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, J = 4.4 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.23 (dd, J = 7.8, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 147.3, 138.8, 130.7, 123.2.

3-bromo-2-chloropyridine (2f)[2]



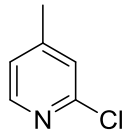
Light yellow solid (47.9 mg, 83% yield), mp 55–57 ℃, (lit.[2] mp 55–56 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (dd, J = 4.8, 1.6 Hz, 1H), 7.95 (dd, J = 7.6, 1.6 Hz, 1H), 7.14 (dd, J = 8.0, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 148.0, 142.3, 123.4, 120.4.

2-chloro-3-nitropyridine (2g)[2]



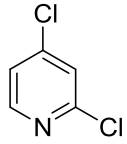
colorless solid (22.4 mg, 47% yield), mp 100–102 ℃, (lit.[2] mp 99–101 ℃) ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (dd, J = 4.8, 1.6 Hz, 1H), 8.24 (dd, J = 8.0, 1.6 Hz, 1H), 7.48 (dd, J = 8.0, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 148.9, 143. 6, 134.2, 122.9.

2-chloro-4-methylpyridine (2h)[3]



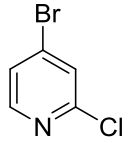
Colorless oil (74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, J = 5.2 Hz, 1H), 7.16 (s, 1H), 7.03 (d, J = 5.2 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5, 150.4, 149.3, 124.9, 20.8.

2,4-dichloropyridine (2i)[4]



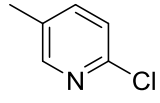
Light yellow oil (27.1 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 5.2 Hz, 1H), 7.38 (d, J = 1.6 Hz, 1H), 7.34–7.17 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 150.2, 145.9, 124.5, 123.0.

4-bromo-2-chloropyridine (2j)[4]



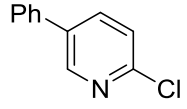
Light yellow oil (30.0 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, J = 5.2 Hz, 1H), 7.55 (d, J = 1.6 Hz, 1H), 7.41 (dd, J = 5.2, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 150.1, 134.23, 127.4, 125.9.

2-chloro-5-methylpyridine (2k)[3]



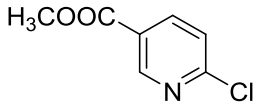
Colorless oil (72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.46 (dd, J = 8.4, 1.6 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 148.7, 139.4, 132.0, 123.7, 17.7.

2-chloro-5-phenylpyridine (2l)[5]



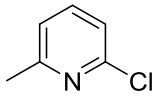
White solid (31.9 mg, 56% yield), mp 55–56 ℃, (lit.[5] mp 53–54 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.46 (dd, J = 8.4, 1.6 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 148.7, 139.4, 132.0, 123.7, 17.7.

2-methyl-6-phenylpyridine (3m)[6]



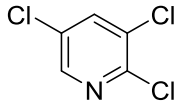
White solid (35.4 mg, 59% yield), mp 86–87 ℃, (lit.[6] mp 86–88 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.46 (dd, J = 8.4, 1.6 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 148.7, 139.4, 132.0, 123.7, 17.7.

2-chloro-6-methylpyridine (2n)[7]



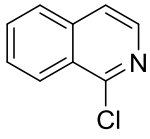
Colorless oil (65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (dd, J = 7.6, 7.6 Hz, 1H), 7.13 (d, J = 8.0 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 150.6, 138.8, 121.7, 121.2, 24.1.

2,3,5-trichloropyridine (2o)[8]



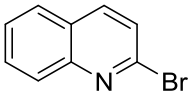
White solid (22.9 mg, 42% yield), mp 49–51 ℃, (lit.[8] mp 49–50 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 2.0 Hz, 1H), 7.80 (d, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 146.1, 138.2, 131.1, 130.9.

1-chloroisoquinoline (2p)[9]



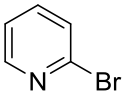
Light yellow solid (45.2 mg, 92%), mp 34–36 ℃, (lit.[9] mp 30.1 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J = 8.4 Hz, 1H), 8.25 (d, J = 5.6 Hz, 1H), 7.82 (d, J = 8.10 Hz, 1H), 7.74–7.71 (m, 1H), 7.68–7.65 (m, 1H), 7.58 (d, J = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 141.3,137.7, 131.2, 128.5, 126.9, 126.8, 126.3, 120.8.

2-Bromoquinoline (3a)[1]



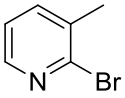
White solid (47.5 mg, 76% yield), mp 49–50 ℃, (lit.[10] mp 50–51 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.8 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.74–7.71 (m, 1H), 7.58–7.54 (m, 1H), 7.50 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 141.8, 138.4, 130.5, 128.7, 127.7, 127.1, 127.0, 125.8.

2-bromopyridine (3b)[11]



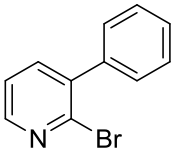
Colorless oil (65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (dd, J = 4.8, 1.2 Hz, 1H), 7.59–7.35 (m, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.28–7.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 142.3, 138.5, 128.3, 122.6.

2-bromo-3-methylpyridine (3c)[12]



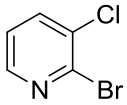
Light yellow oil (70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 4.4 Hz, 1H), 7.51 (d, J = 7.2 Hz, 1H), 7.17–7.14 (m, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 144.7, 138.8, 125.3, 122.8, 22.0.

2-bromo-3-phenylpyridine (3d)[13]



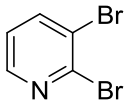
Light yellow oil (64.6 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (dd, J = 4.8, 1.6 Hz, 1H), 7.61 (dd, J = 7.6, 2.0 Hz, 1H), 7.47–7.40 (m, 5H), 7.33 (dd, J = 7.6, 4.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7, 142.4, 139.8, 139.1, 138.9, 129.3, 128.4, 128.3, 122.7.

2-bromo-3-chloropyridine (3e)[14]



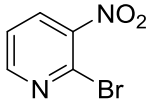
White solid (46.1 mg, 80% yield), mp 57–58 ℃, (lit.[13] mp 50–53 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (dd, J = 4.8, 1.6 Hz, 1H), 7.51 (dd, J = 8.0, 1.6 Hz, 1H), 7.20 (dd, J = 7.6, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 141.8, 138.2, 133.5, 123.5.

2,3-dibromopyridine (3f)[15]



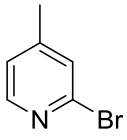
White solid (55.4 mg, 78% yield), mp 58–60 ℃, (lit.[15] mp 60.5 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (dd, J = 4.4 Hz, 1.6 Hz, 1H), 7.89 (dd, J = 8.0, 1.6 Hz, 1H), 7.14 (dd, J = 8.0, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 143.7, 141.7, 123.9, 123.6.

2-bromo-3-nitropyridine (3g)[16]



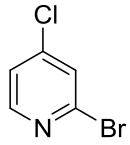
White solid (37.6 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63–8.59 (m, 1H), 8.23–8.13 (m, 1H), 7.49–7.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152,6, 133.9, 133.7, 123.1.

2-bromo-4-methylpyridine (3h)[13]



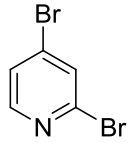
Light yellow oil (55% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 5.2 Hz, 1H), 7.32 (s, 1H), 7.06 (d, J = 4.4 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 149.7, 142.3, 128.7, 123.8, 20.7.

2-bromo-4-chloropyridine (3i)[17]



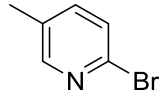
Yellow oil (32.4 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 5.6 Hz, 1H), 7.53 (d, J = 1.6 Hz, 1H), 7.27 (dd, J = 5.2, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 145.5, 142.6, 128.1, 123.3.

2,4-dibromopyridine (3j)[18]



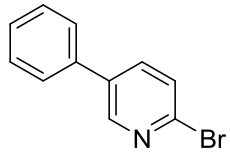
Yellow oil (32.1 mg, 45 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 5.2 Hz, 1H), 7.69 (s, 1H), 7.42 (d, J = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 142.6, 140.0, 131.0, 126.2.

2-bromo-5-methylpyridine(3k)[12]



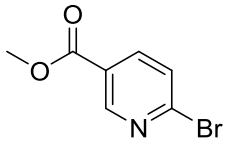
Light yellow oil (40% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.35 (d, J = 1.2 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 139.3, 139.0, 132.5, 127.5, 17.8.

2-bromo-5-phenylpyridine (3l)[19]



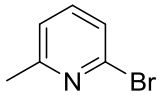
White solid (37.2 mg, 53% yield), mp 73–75 ℃, (lit.[19] mp 76–77 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, J = 2.4 Hz, 1H), 7.75 (dd, J = 8.4, 2.8 Hz, 1H), 7.58–7.55 (m, 3H), 7.52–7.48 (m, 2H), 7.46–7.42 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 140.9, 137.0, 136.5, 136.0, 129.3, 128.5, 128.0, 127.0.

methyl-6-bromonicotinate (3m)[20]



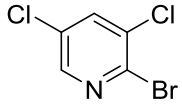
Light yellow solid (29.1 mg, 45% yield), mp 107–109 ℃, (lit.[21] mp 108–110 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.94 (d, J = 2.4 Hz, 1H), 8.11 (dd, J = 8.4, 2.4 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 151.4, 146.8, 139.2, 128.1, 125.3, 52.6.

2-bromo-6-methylpyridine (3n)[12]



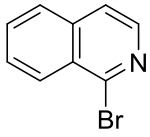
Colorless oil (35% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.33 (m, 1H), 7.22 (d, J = 8.0 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 141.3, 138.6, 125.0, 122.1, 24.1.

2-bromo-3,5-dichloropyridine (3o)[22]



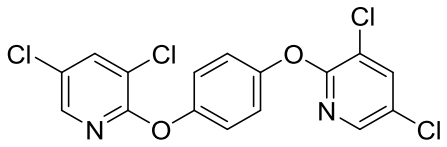
White solid (41.5 mg, 61% yield), mp 39–40 ℃, (lit.[22] mp 40–41 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 2.4 Hz, 1 H), 7.75 (d, J = 2.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 139.4, 137.7, 133.9, 131.4.

4-Phenylstyrene (3p)[10]



White solid (53.0 mg, 85% yield), mp 42–44 ℃, (lit.[10] mp 41–43 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 5.6 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.74–7.70 (m, 1H), 7.68–7.64, 7.58 (d, J = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 142.0, 137.4, 131.2, 129.0, 128.8, 128.7, 127.1, 121.2.

1,4-bis((3,5-dichloropyridin-2-yl)oxy)benzene (4)



White solid (176.8 mg, 88% yield), mp 156–158 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 5.6 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.74–7.70 (m, 1H), 7.68–7.64, 7.58 (d, J = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 142.0, 137.4, 131.2, 129.0, 128.8, 128.7, 127.1, 121.2. IR (KBr): ν 3061, 1575, 1501, 1288, 1178, 842, 734 cm^{-1}. HRMS (ESI) calcd for $[C_{16}H_9Cl_4N_2O_2, M+H]^+$: 402.9389, found: 402.9390.

3. References

[1] W. Kijrungphaiboon, O. Chantarasriwong, W. Chavasiri, *Tetrahedron Letter.* **2012**, *53*, 674–677.

[2] H. Yamanaka, T. Araki, T. Sakamoto, *Chem. Pharm. Bull*. **1988**, *36*, 2244–2247.

[3] P. Narendar, B. Gangadasu, Ch. Ramesh, B. C. Raju, V. J. Rao, *Synthetic Commun*. **2004**, *34*, 1097–1113.

[4] A. Honraedt, T. Gallagher, *Synlett* **2016**, *27*, 67–69.

[5] E. Zhang, J. Tang, S. Li, P. Wu, J. E. Moses, K. B. Sharpless, *Chem. Eur. J*. **2016**, *22*, 5692–5697.

[6] Z. Li, W. Zhu, J. Bao, X, Zou, *Chem. Commun*. **2014**, *44*, 1155–1164.

[7] A. Puszko, *Mang. Reson. Chem*. **1992**, *30*, 271–271.

[8] P. Zhong, H. Hu, S. Guo, *Synthetic Commun*. **2004**, *34*, 4301–4311.

[9] O. Sugimoto, Y. Harada, K. Tanji, *Heterocycles* **2012**, *86*, 1583–1590.

[10] M. Schlosser, F. Cottet, *Eur. J. Org. Chem.* **2002**, 4181–4184.

[11] H. P. Kokatla, P. F. Thomson, S. Bae, V. R. Doddi, M. K. Lakshman, *J. Org. Chem*. **2011**, *76*, 7842–7848.

[12] K. K. Bhasin, P. Venugopalan, J. Singh, *Phosphorus Sulfur*. **2002**, *177*, 2579–2587.

[13] J. Kan, S. Huang, J. Lin, M. Zhang, W. Su, *Angew. Chem. Int. Ed*. **2015**, *54*, 2199 –2203.

[14] M. Schlosser, F. Cottet, *Eur. J. Org. Chem.* **2002**, 4181–4184.

[15] K. Menzel, E. L. Fisher, L. DiMichele, D. E. Frantz, T. D. Nelson, M. H. Kress, *J. Org. Chem*. **2006**, *71*, 2188–2191.

[16] Y. Loidreau, P. Marchand, C. Dubouilh-Benard, M. Nourrisson, M. Duflos, O. Lozach, N. Loa ëc, L. Meijer, T. Besson, *Eur. J. Med. Chem.* **2012**, *58*, 171–183.

[17] S. Choppin. P. Gros, Y. Fourt, *Eur. J. Org. Chem.* **2001**, 603–606.

[18] C. Sicre, M. Magdalena Cid, *Org. Lett.* **2005**, *7*, 5735–5739.

[19] Q. Zhou, B. Zhang, L. Su, T. Jiang, R. Chen, T. Du, Y. Ye, J. Shen, G. Dai, D. Han, H. Jiang, *Tetrahedron* **2013**, *69*, 10996–11003.

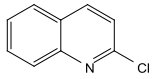
[20] N. D. Bogdan, M. Matache, V. M. Meier, C. Dobrota, I. Dumitru, G. D. Roiban, D. P. Funeriu, *Chem. Eur. J*. **2010**, *16*, 2170–2180.

[21] H. L. Bradlow, C. A. Vanderwerf, *J. Org. Chem*. **1949**, *14*, 509–513.

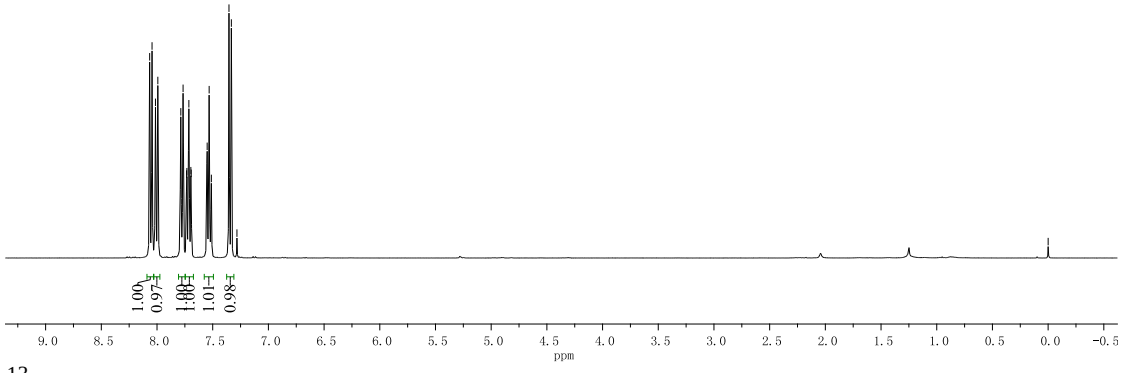
[22] E. Marzi, A. Bigi, M. Schlosser, *Eur. J. Org. Chem.* **2001**, 1371–1376.

7. Copies of ^{1}H and ^{13}C NMR Spectra of Products

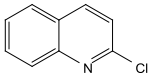
^{1}H NMR, 400 MHz, $CDCl_3$



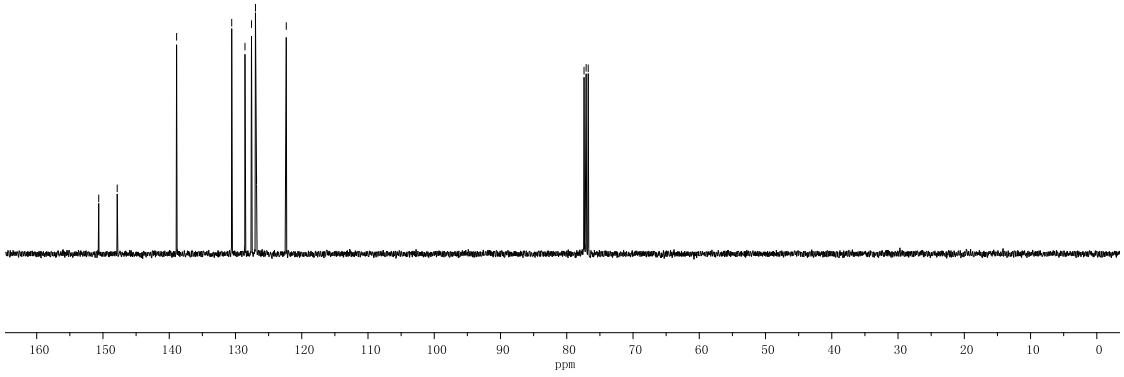
2a



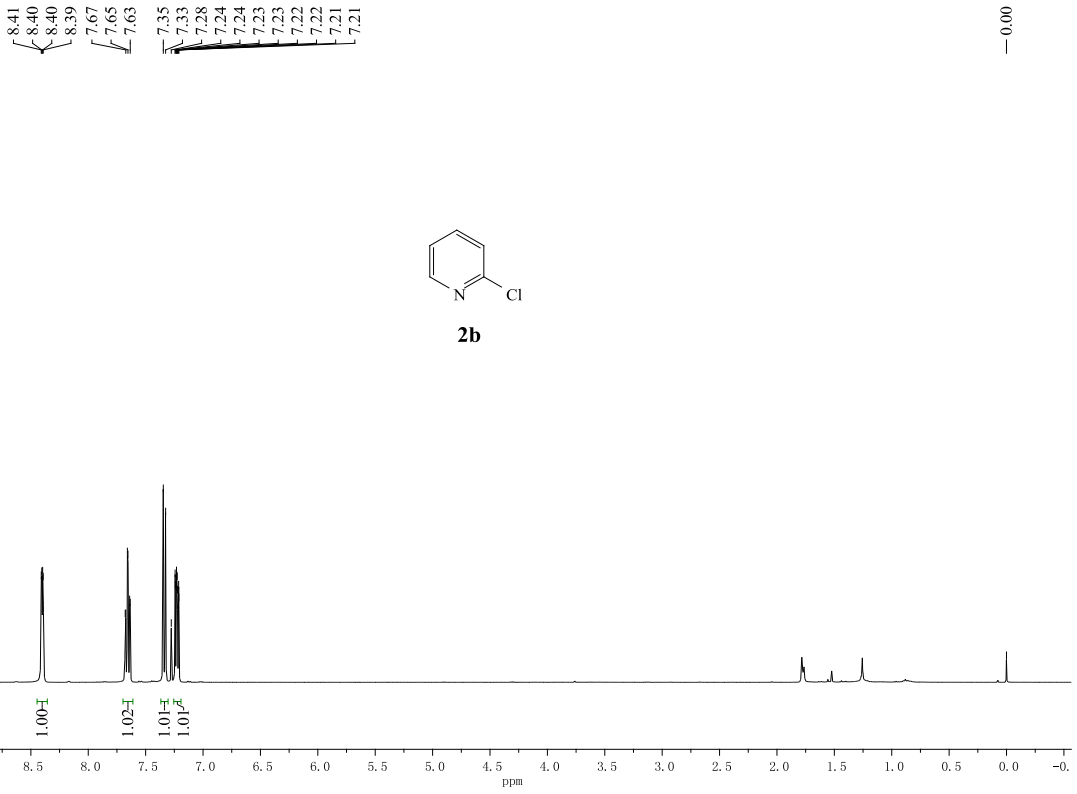
^{13}C NMR, 100 MHz, $CDCl_3$



2a

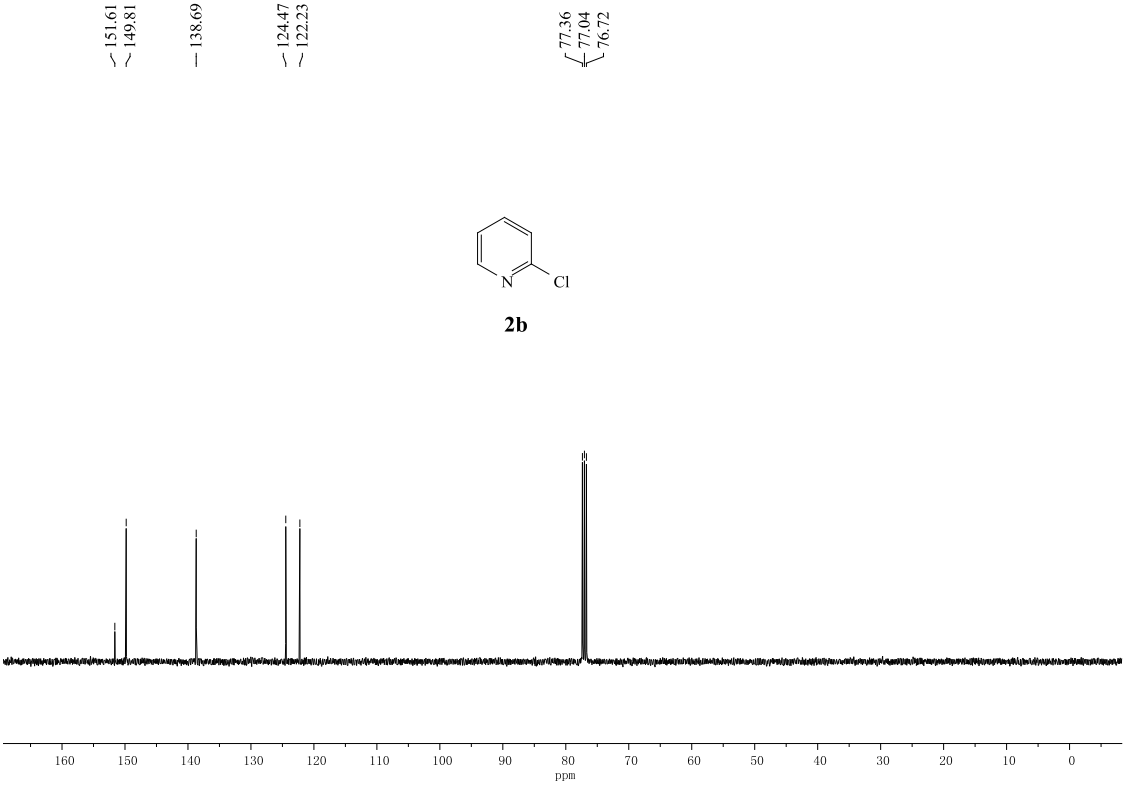


^{1}H NMR, 400 MHz, $CDCl_3$



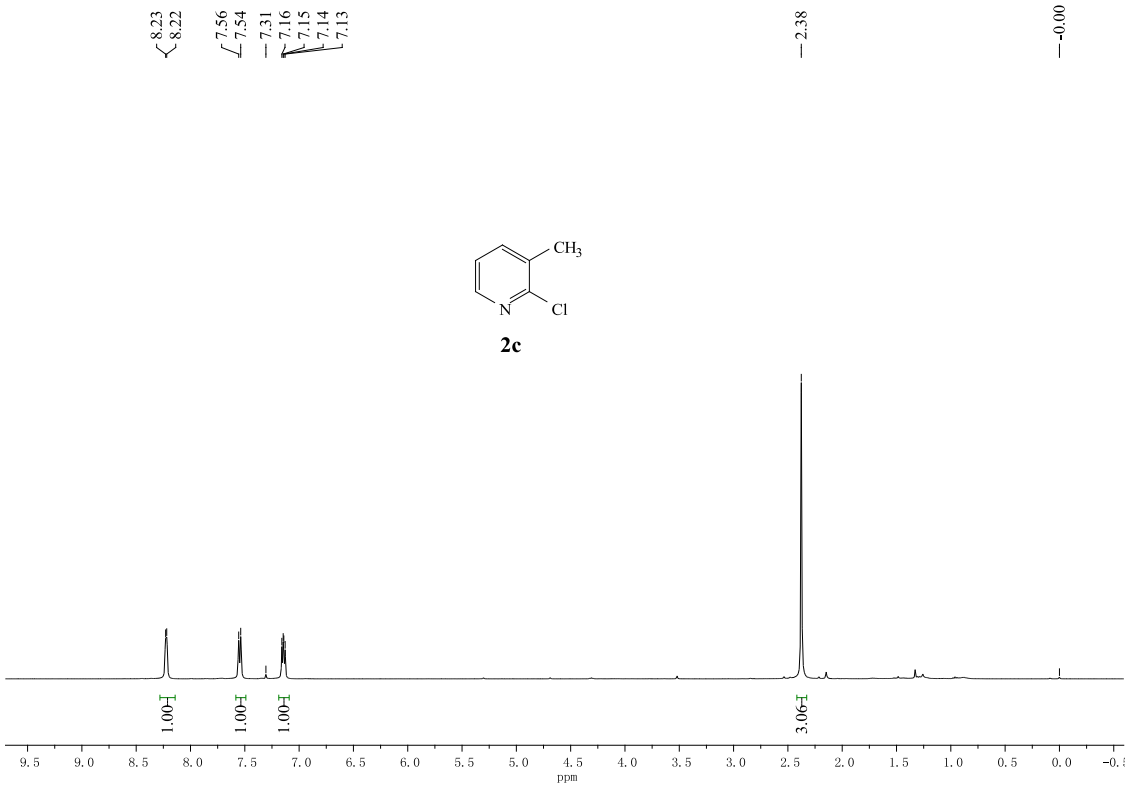
2b

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



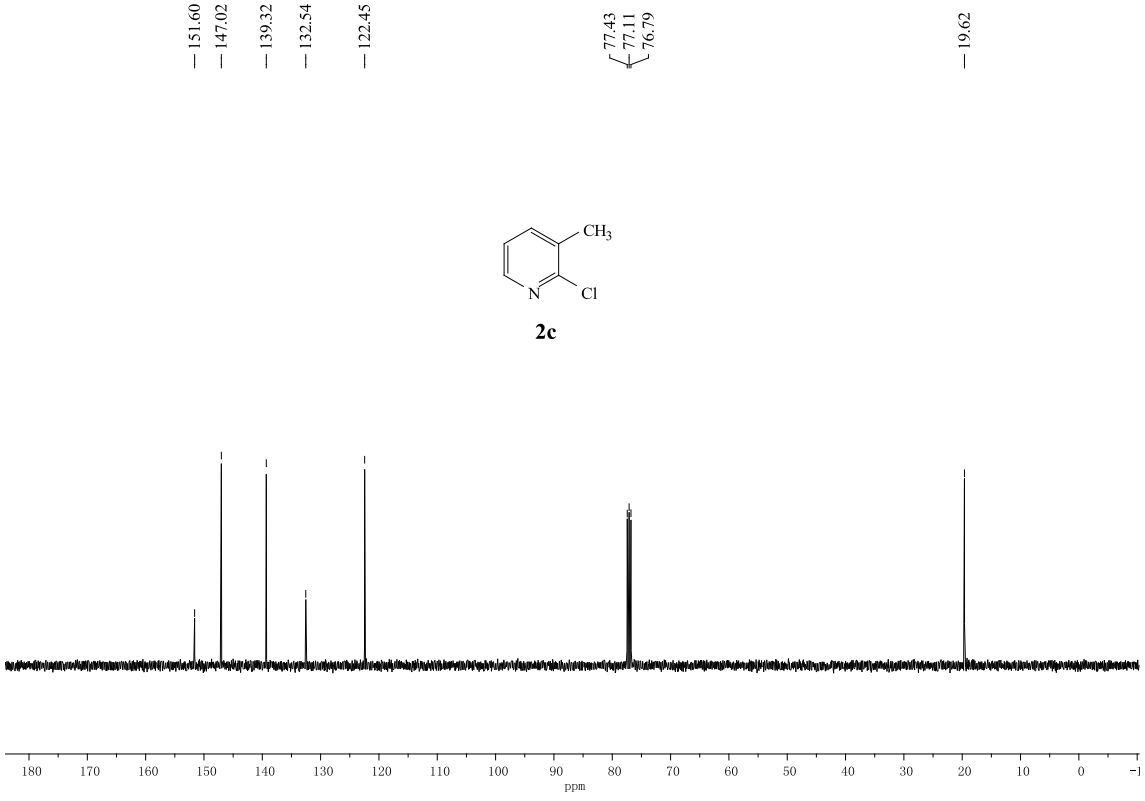
2b

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



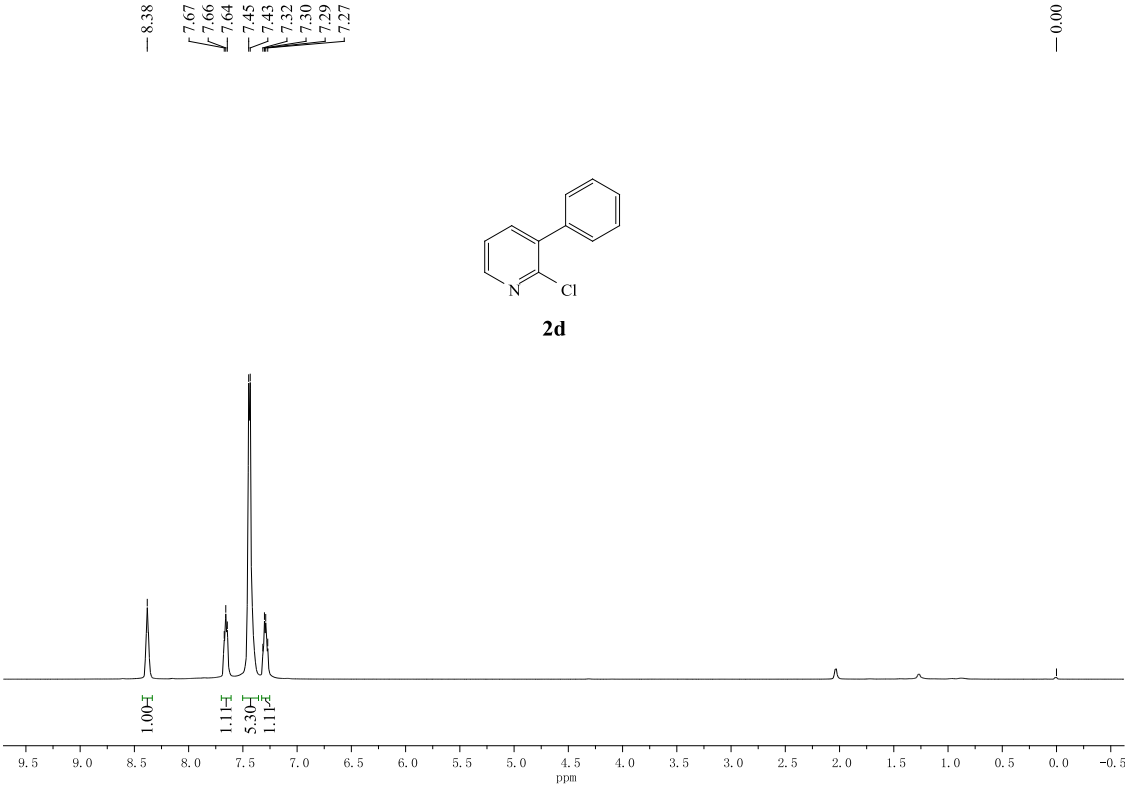
2c

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



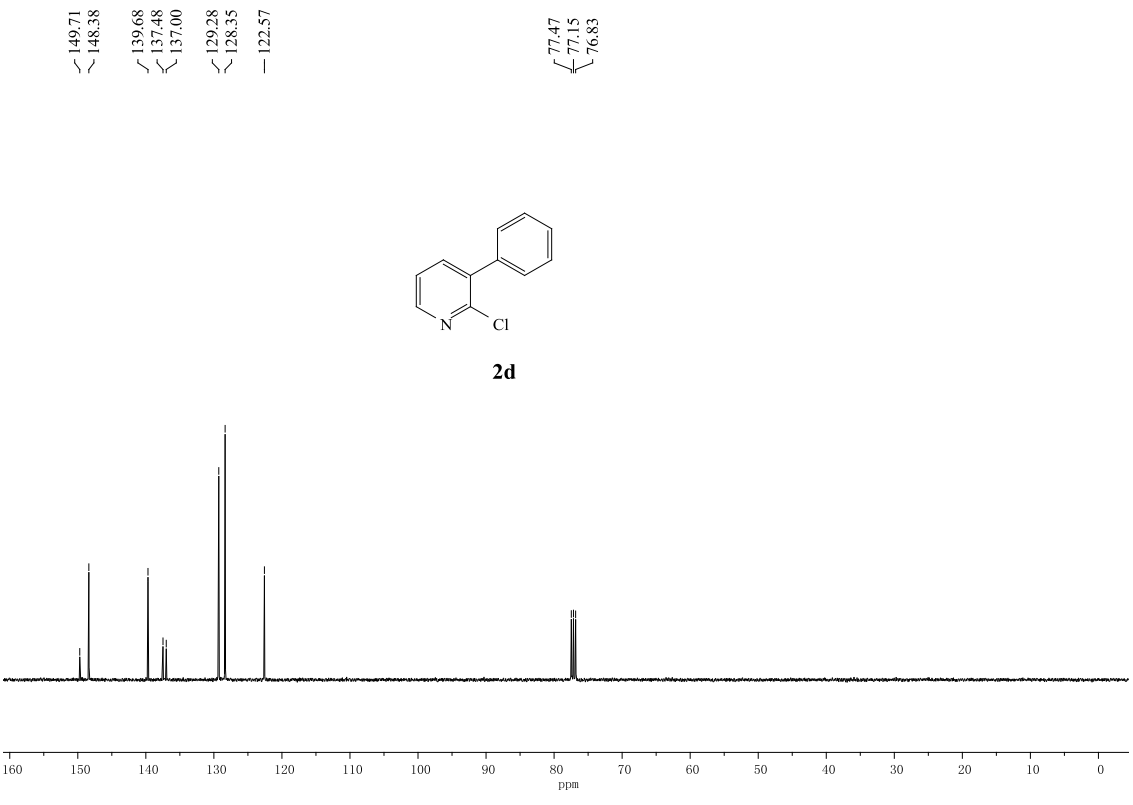
2c

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



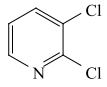
2d

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

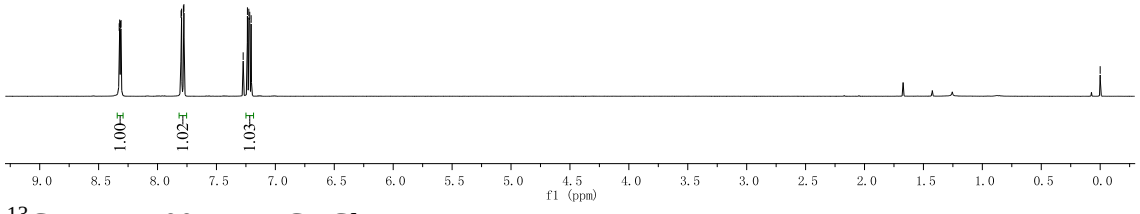


2d

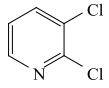
^{1}H NMR, 400 MHz, $CDCl_3$



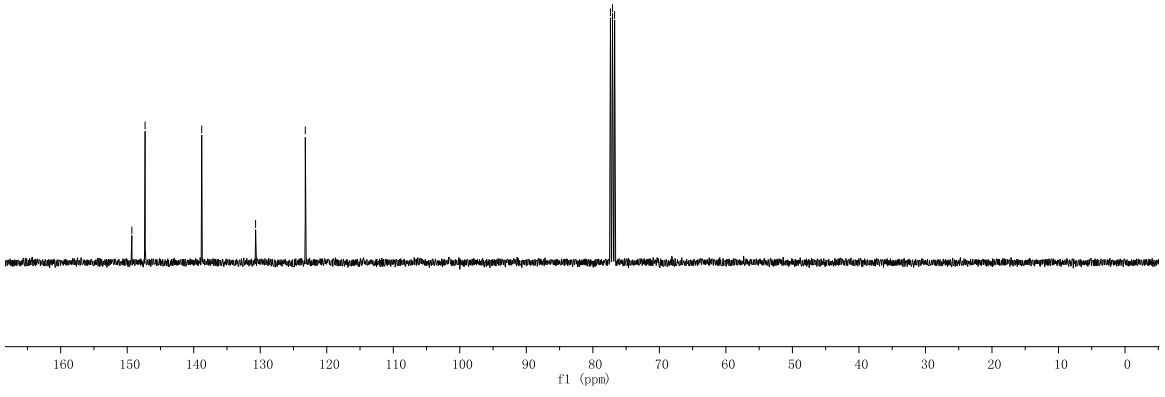
2e



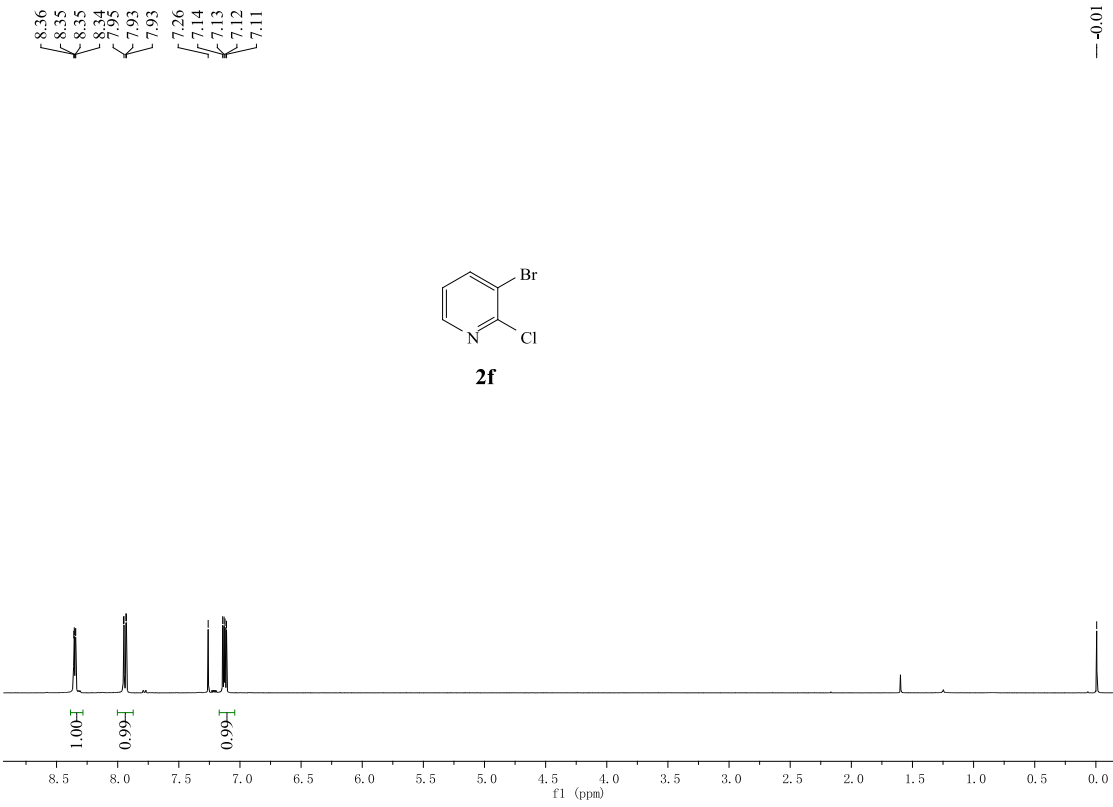
^{13}C NMR, 100 MHz, $CDCl_3$



2e

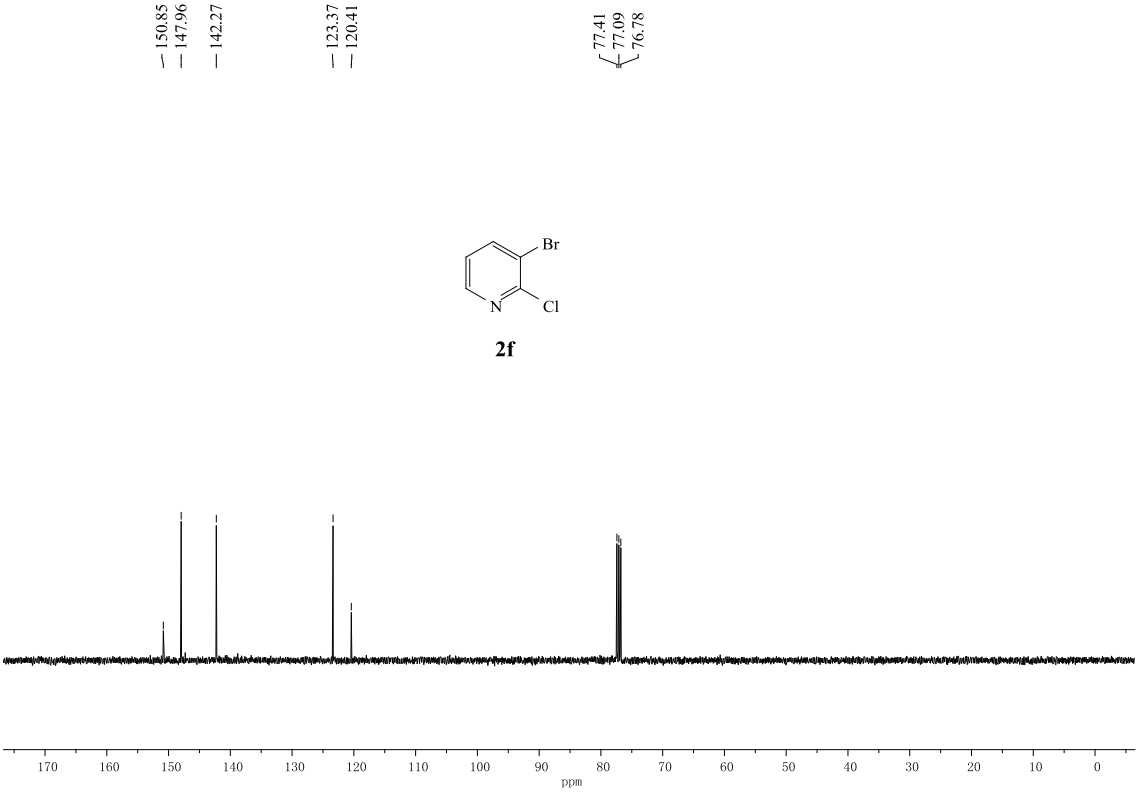


^{1}H NMR, 400 MHz, $CDCl_3$



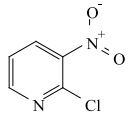
2f

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

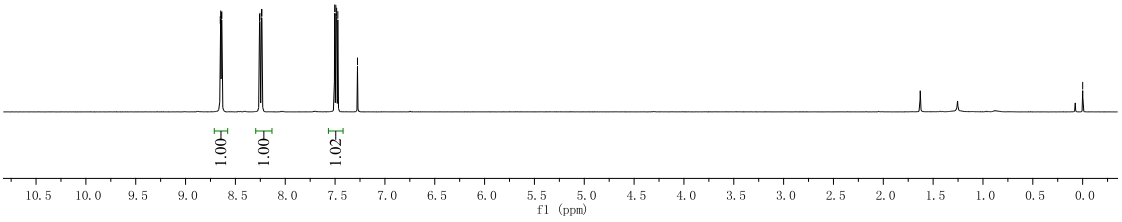


2f

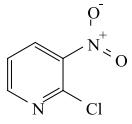
^{1}H NMR, 400 MHz, $CDCl_3$



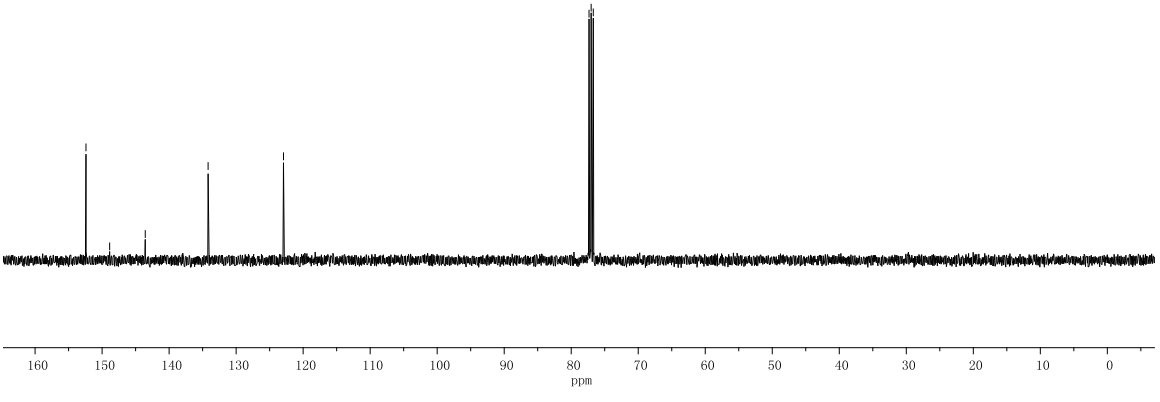
2g



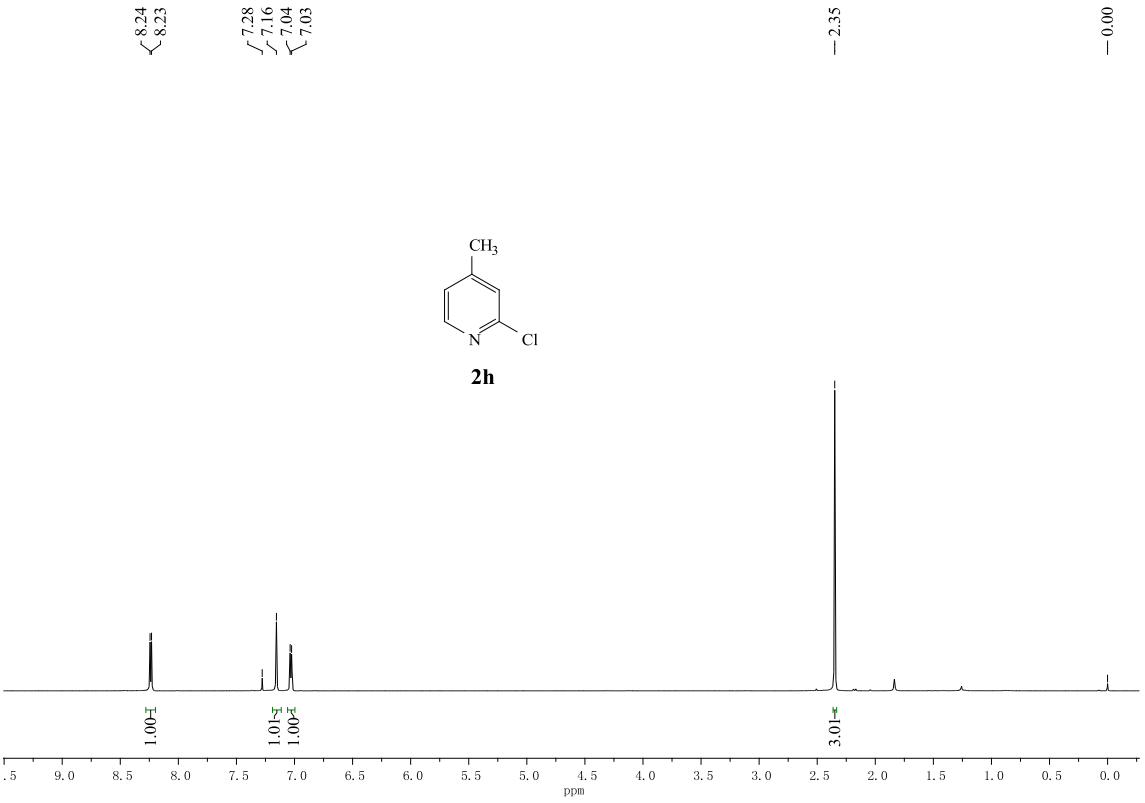
^{13}C NMR, 100 MHz, $CDCl_3$



2g

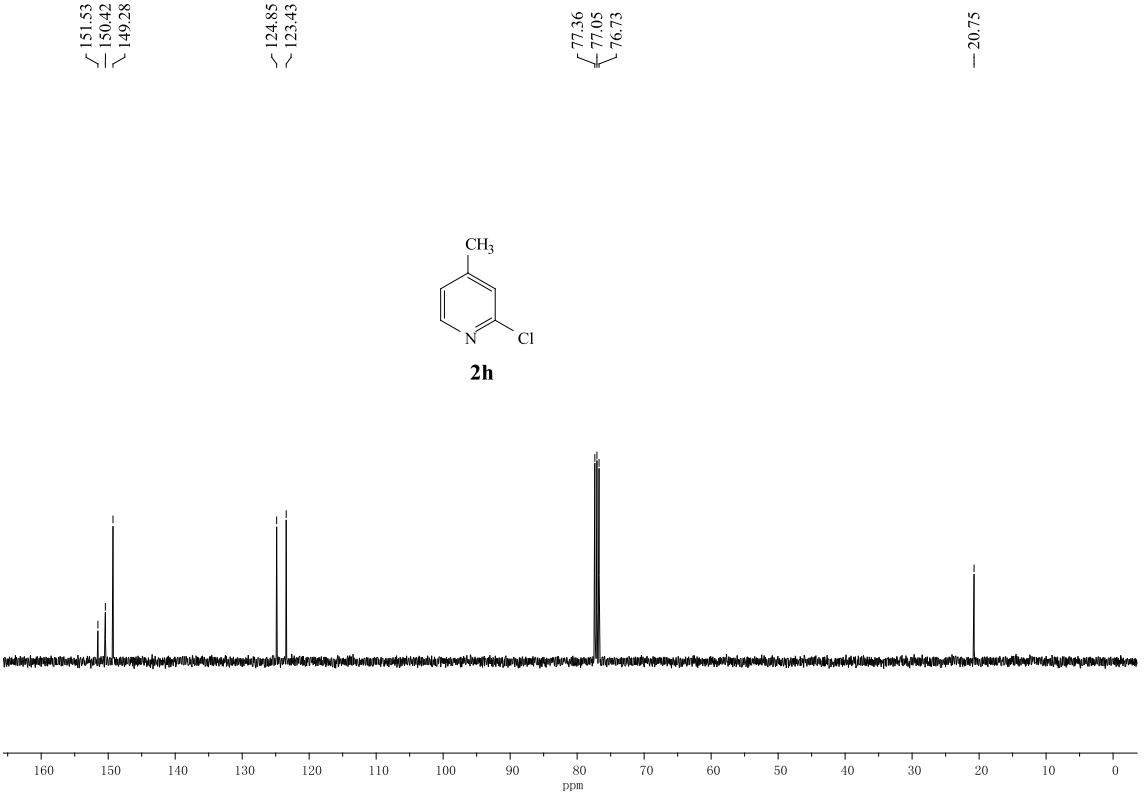


^{1}H NMR, 400 MHz, $CDCl_3$



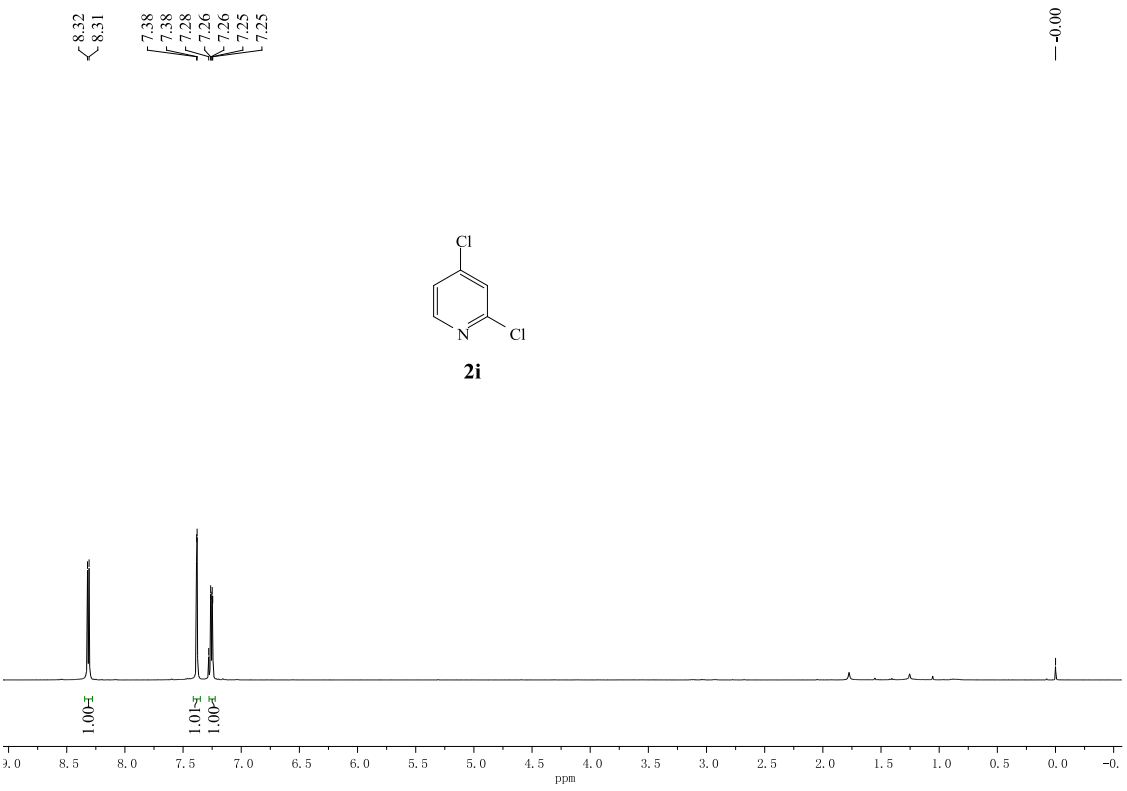
2h

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



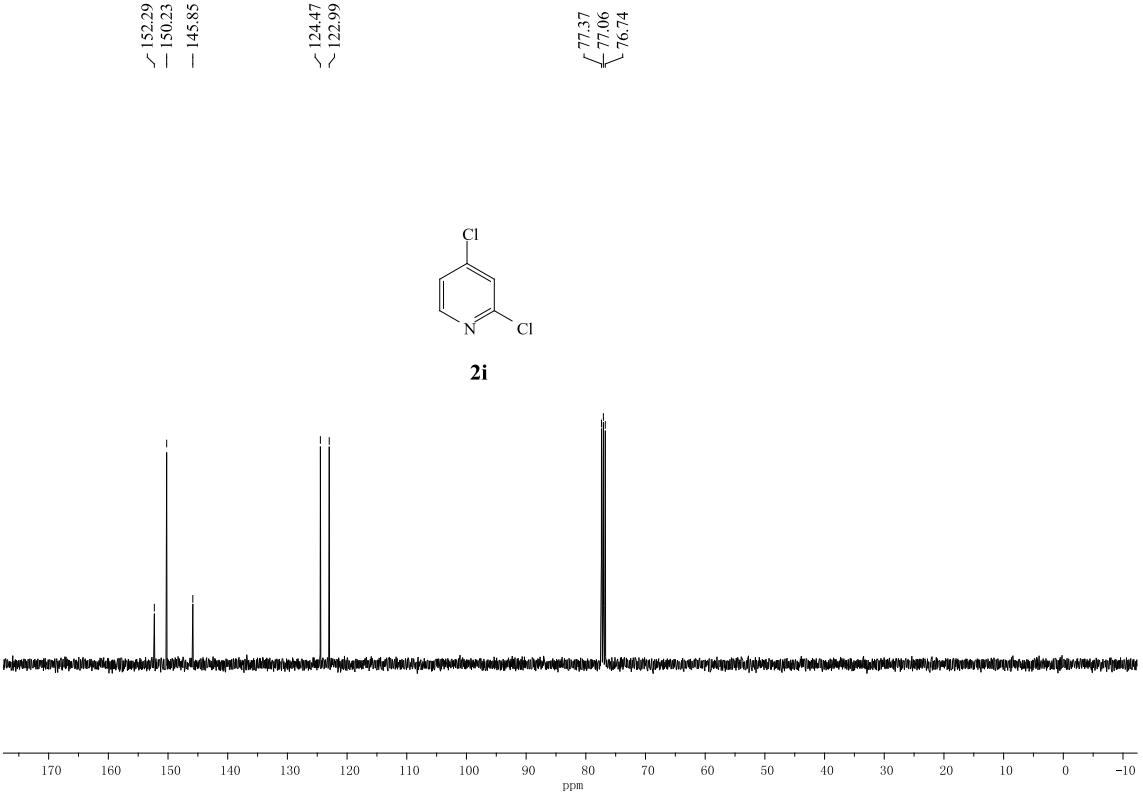
2h

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



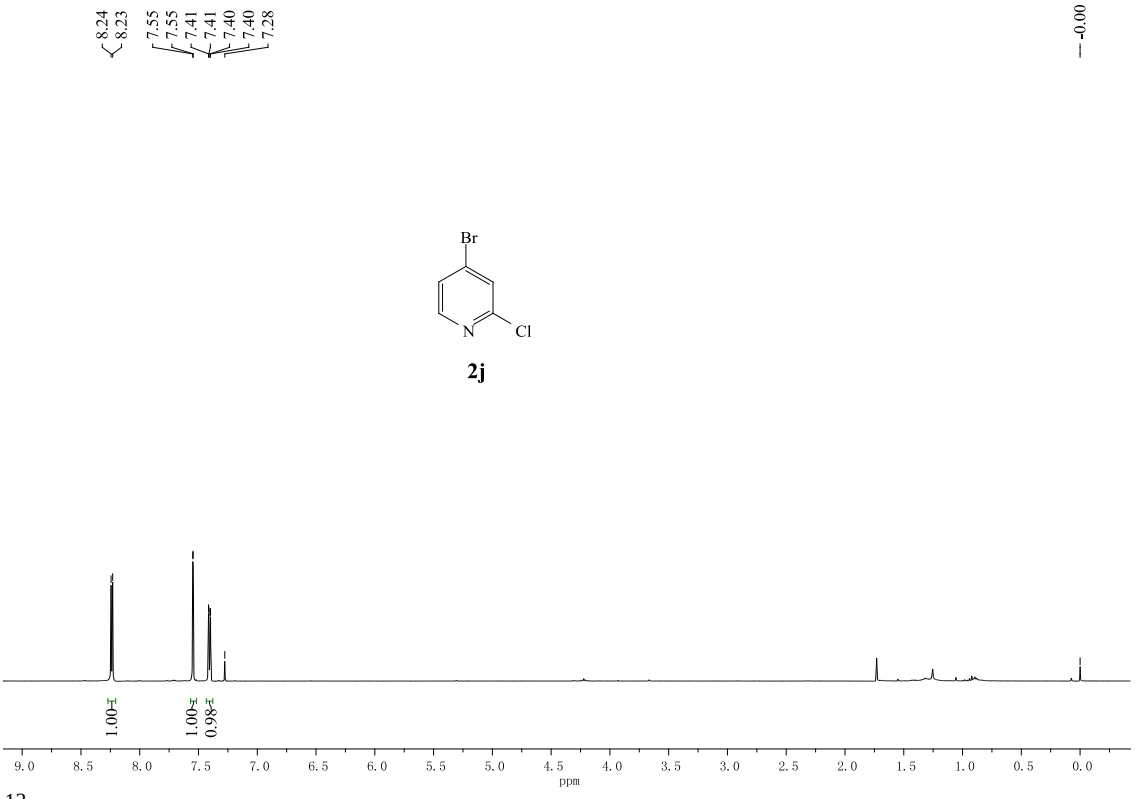
2i

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



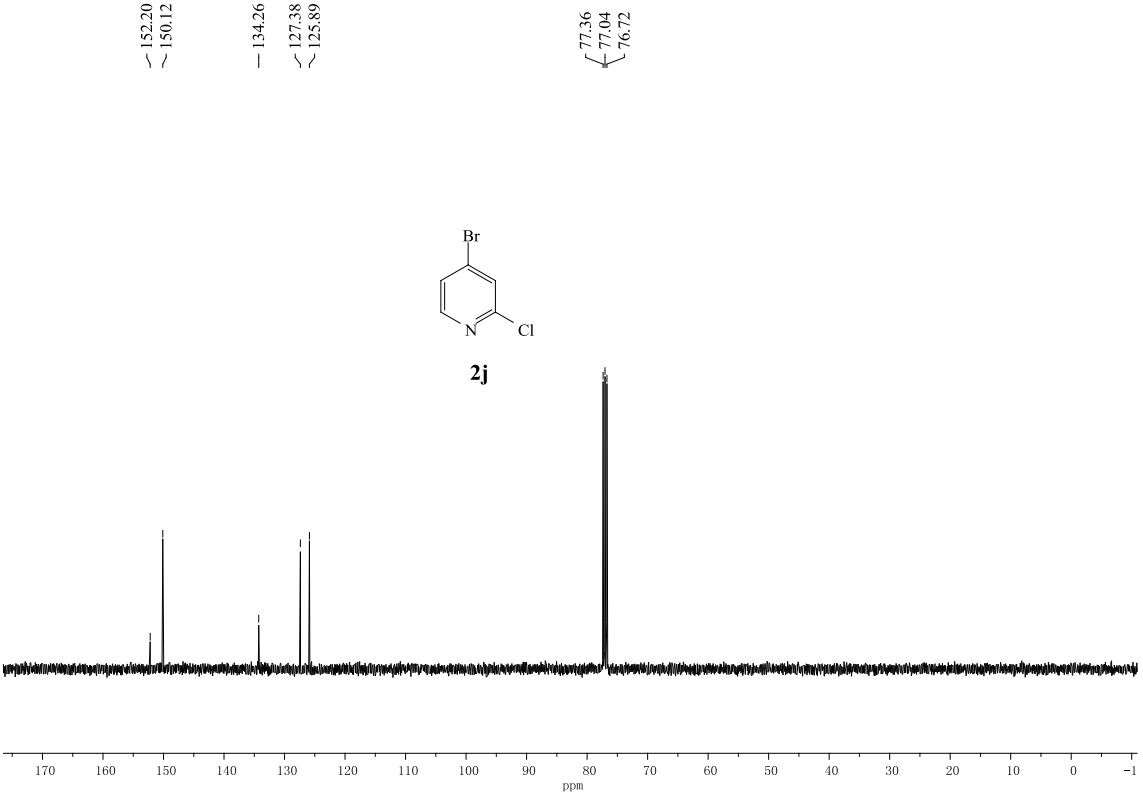
2i

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



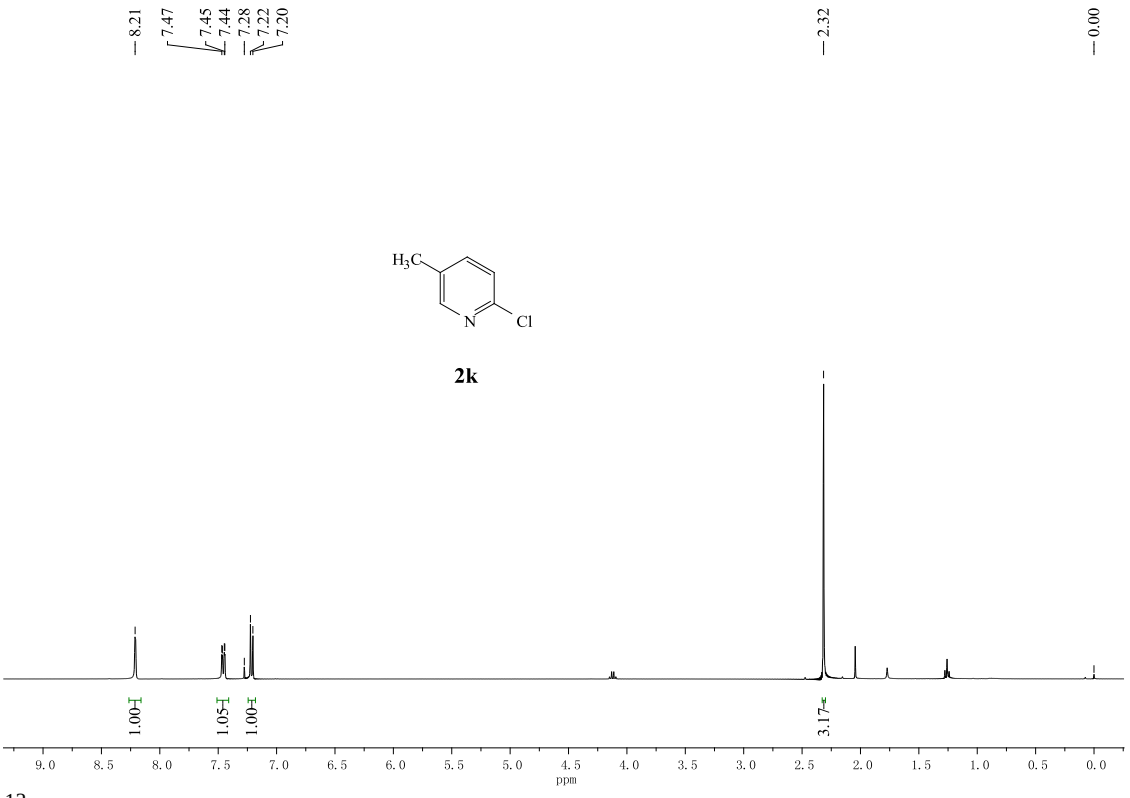
2j

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



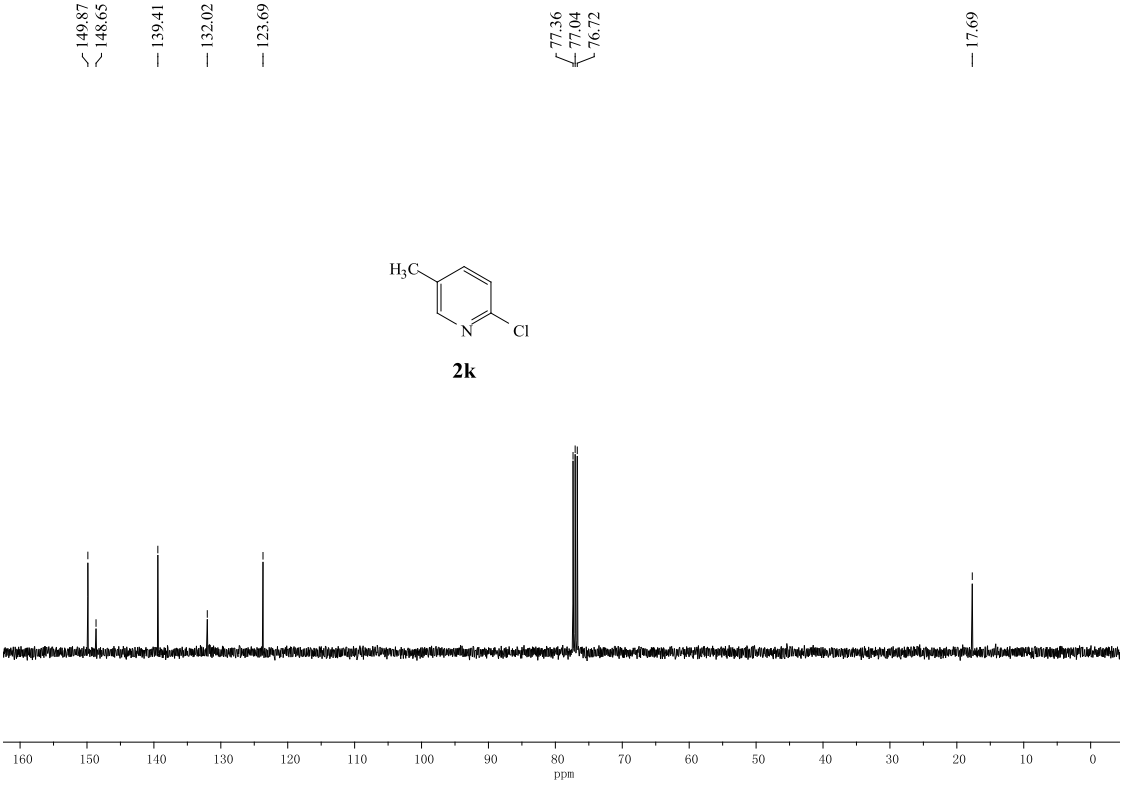
2j

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



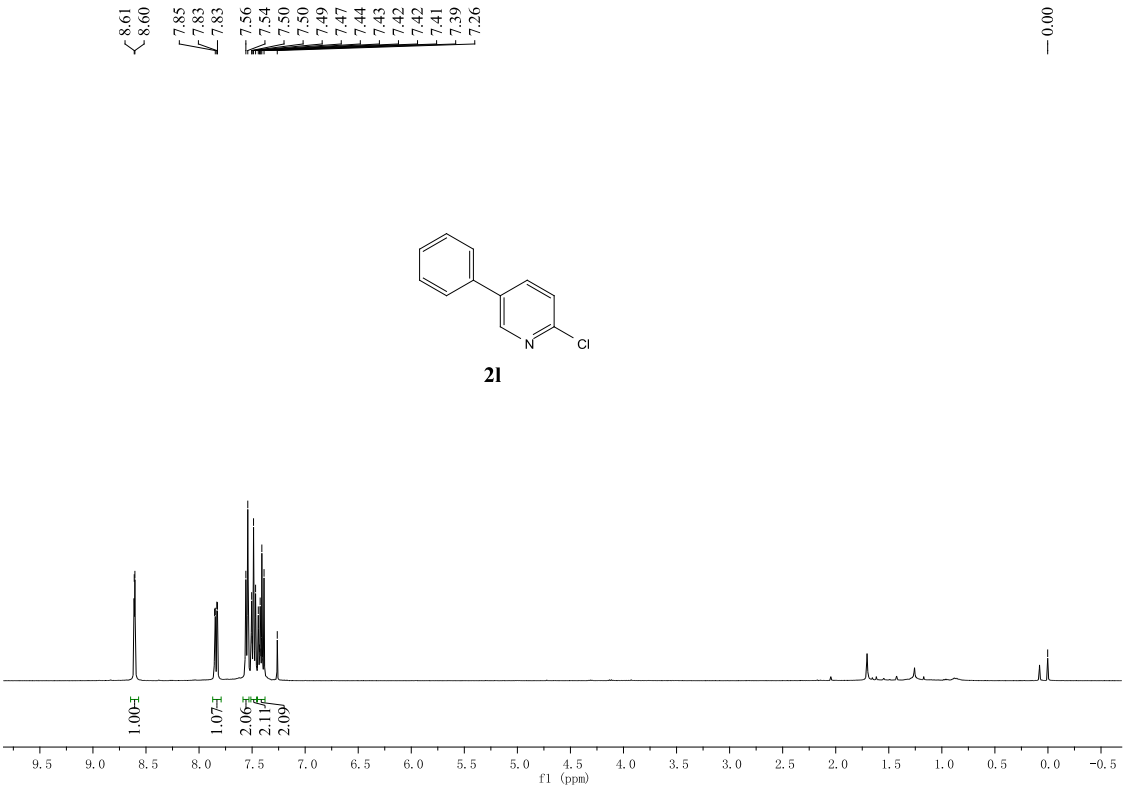
2k

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



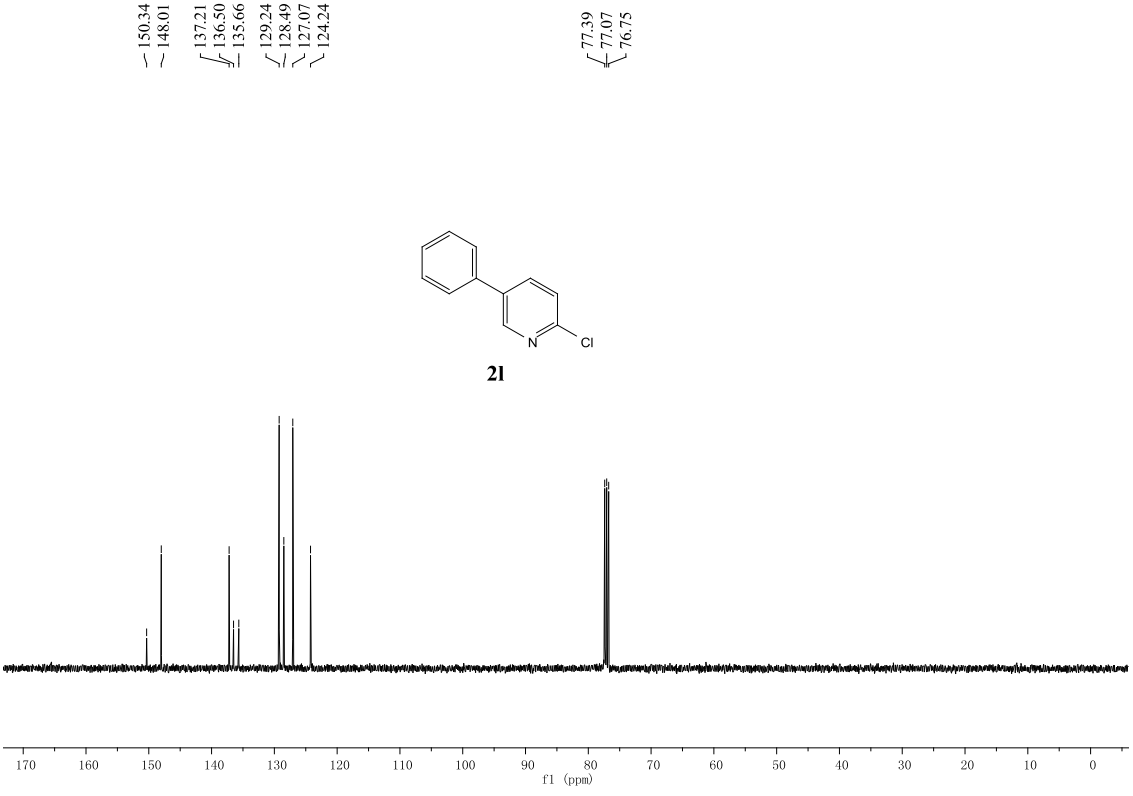
2k

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



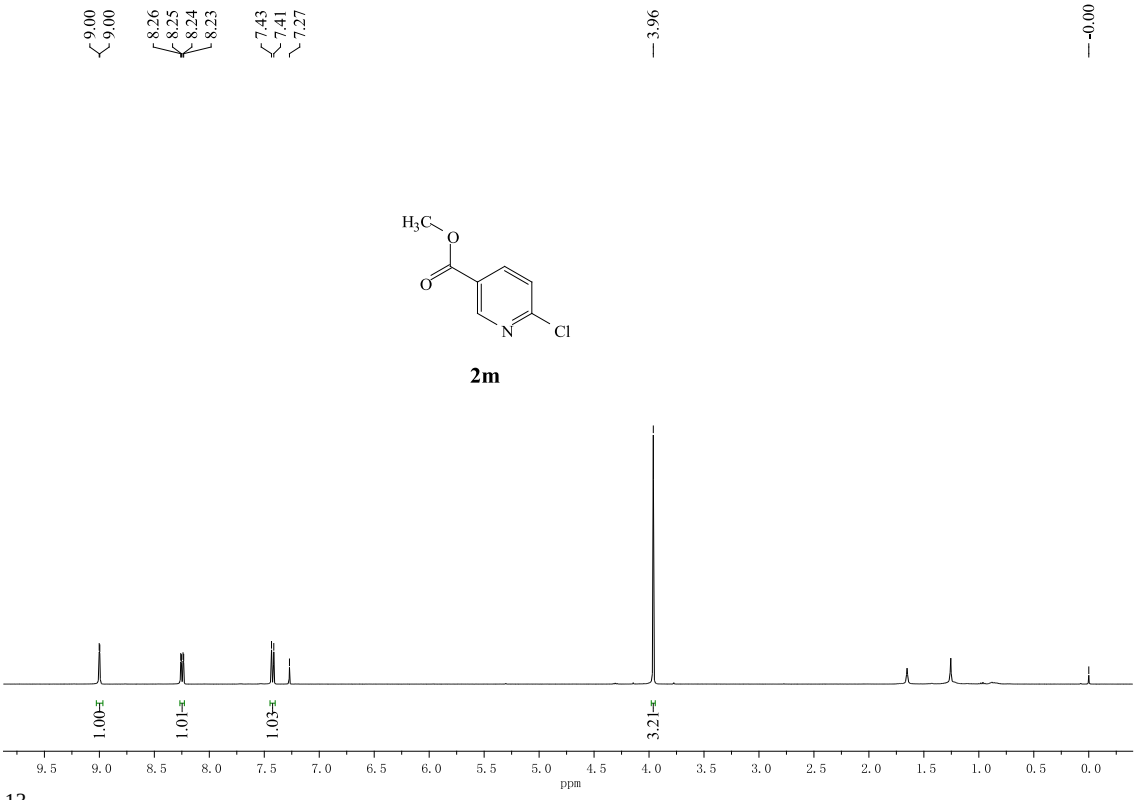
2l

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



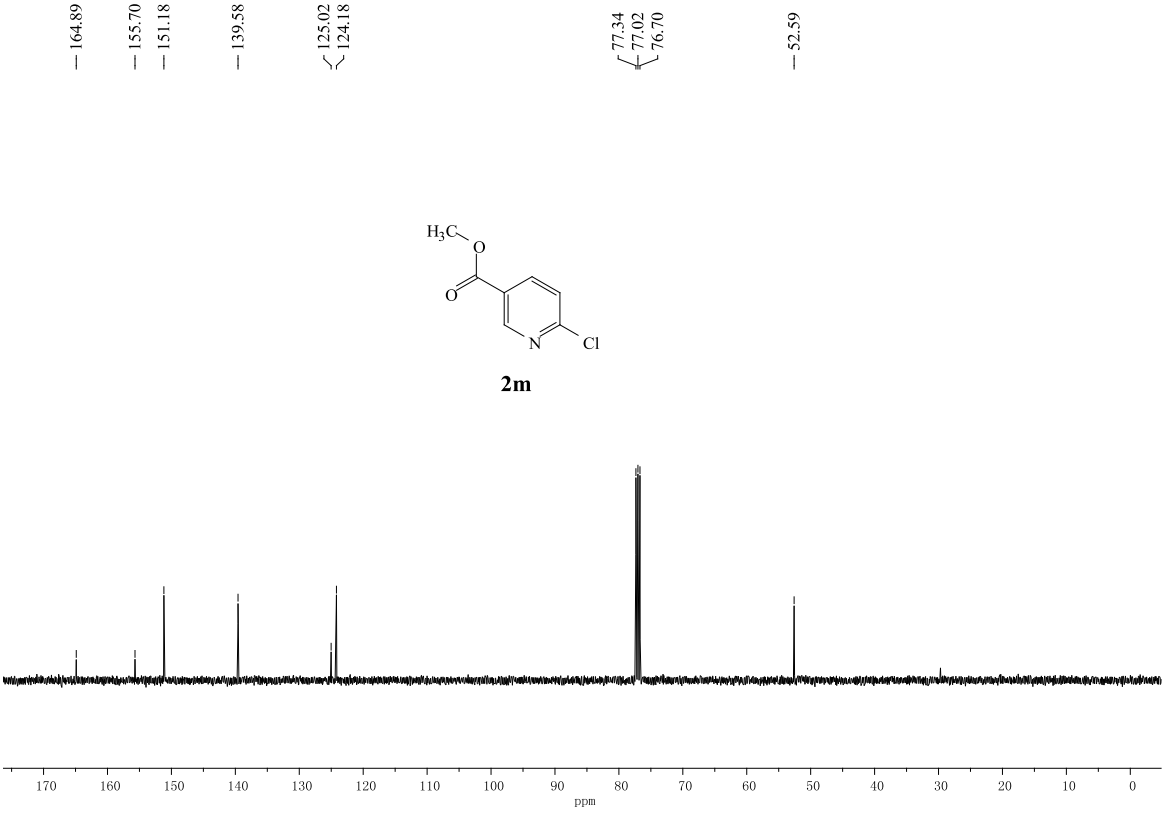
2l

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



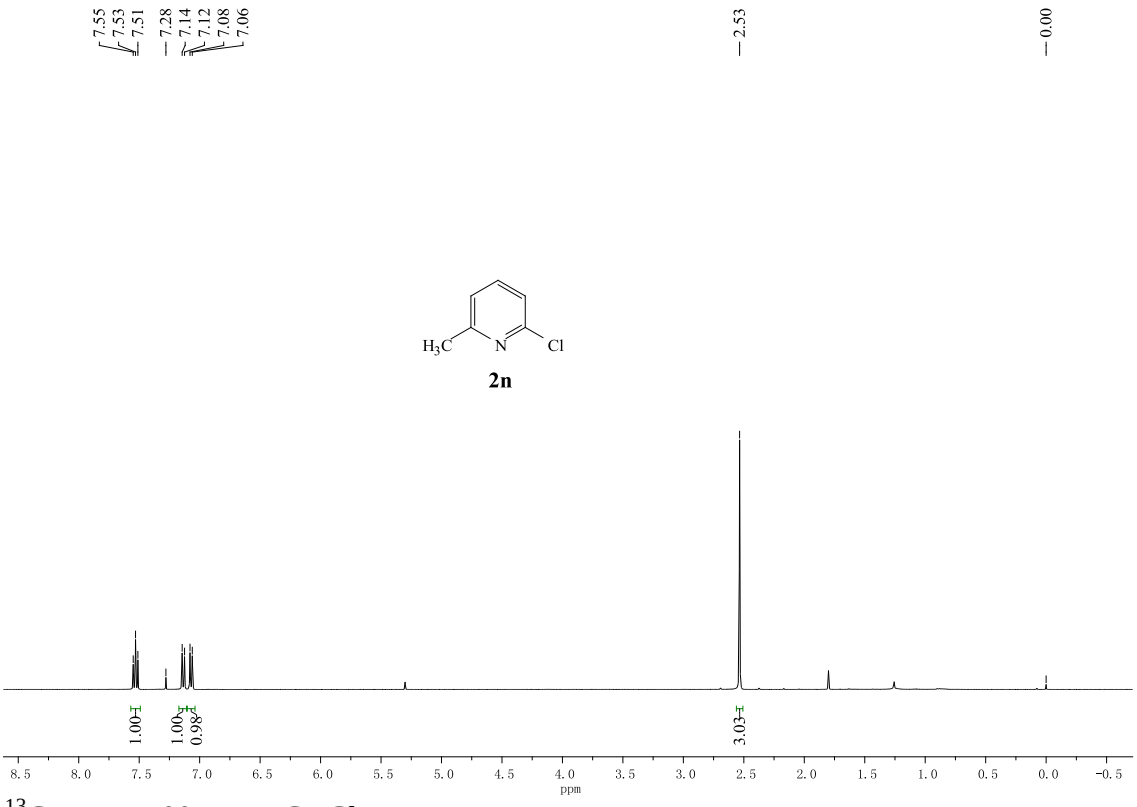
2m

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



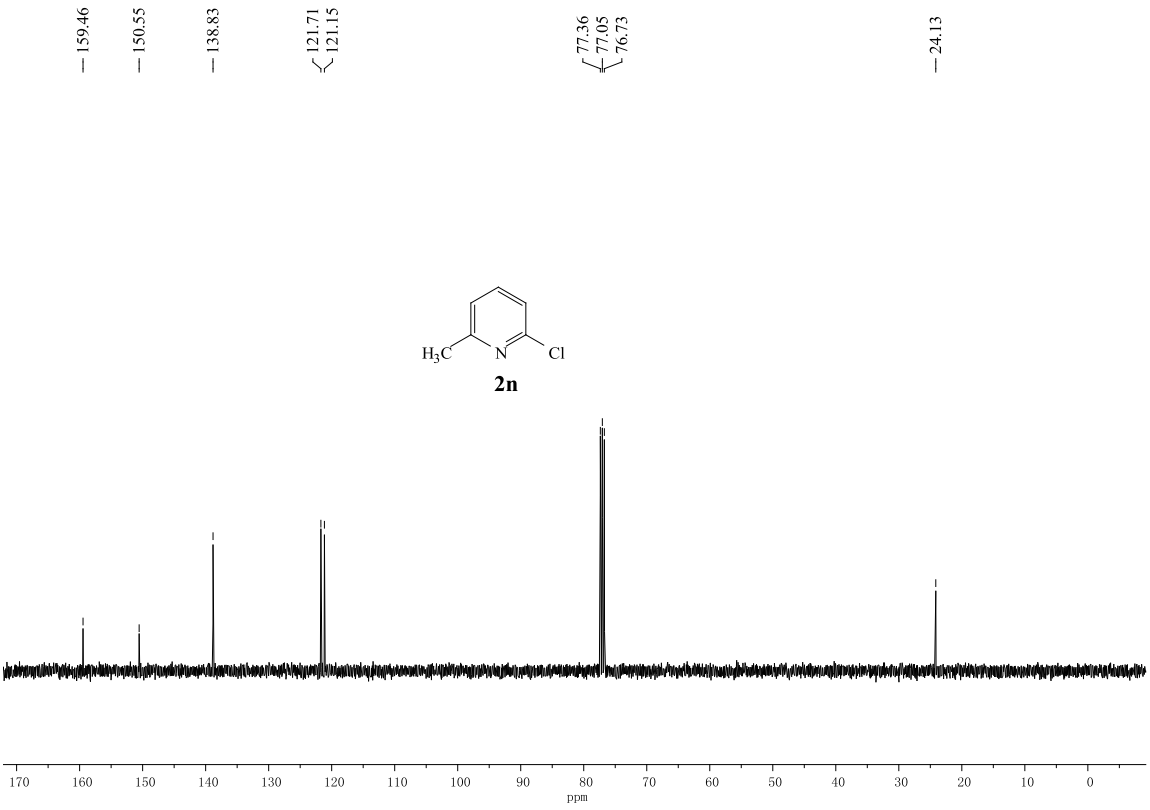
2m

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



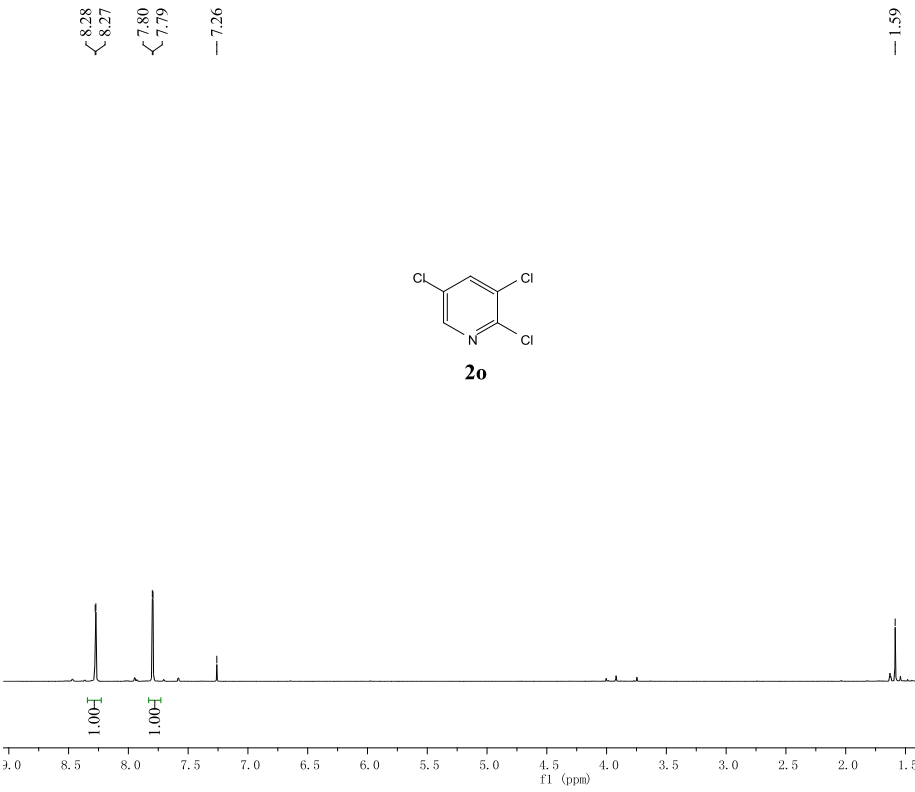
2n

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



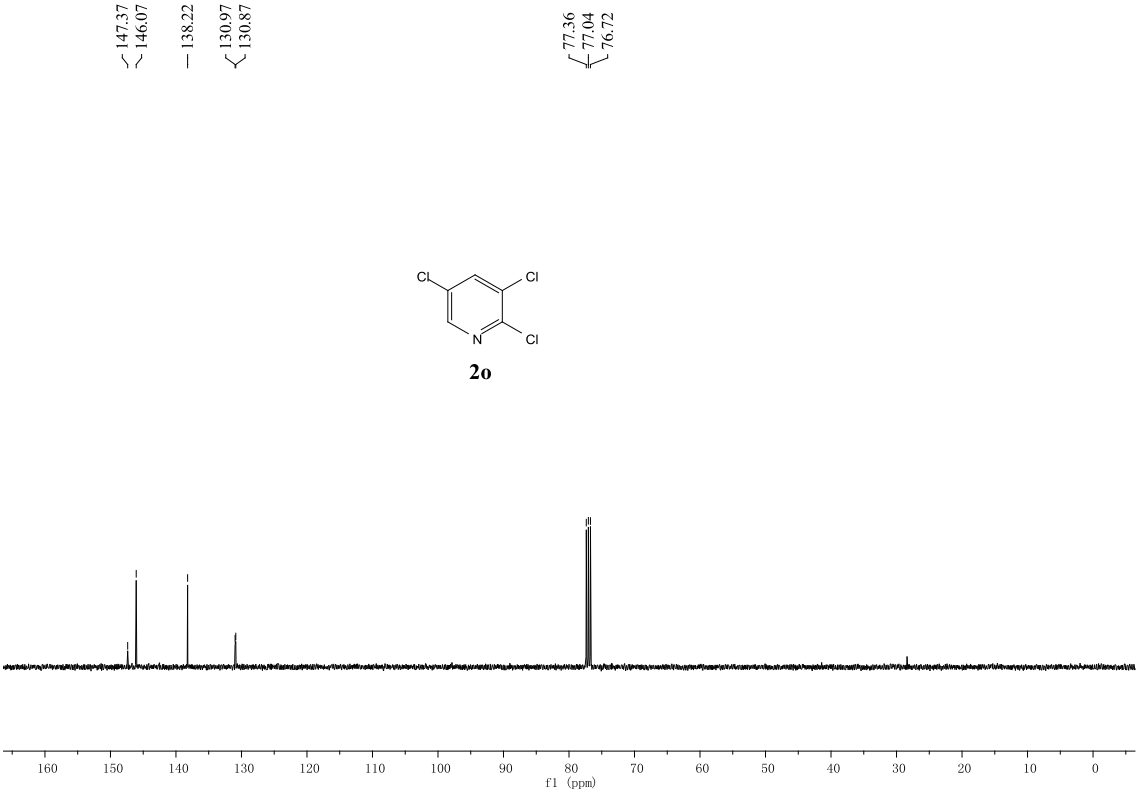
2n

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



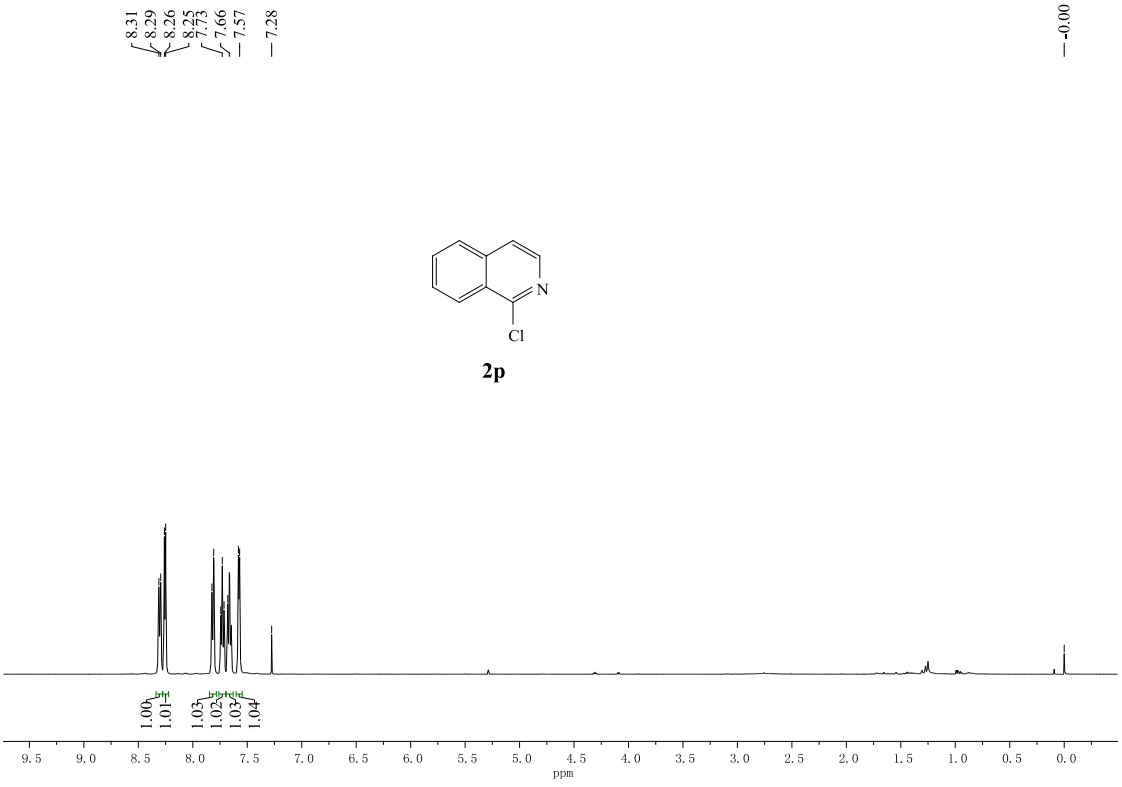
2o

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



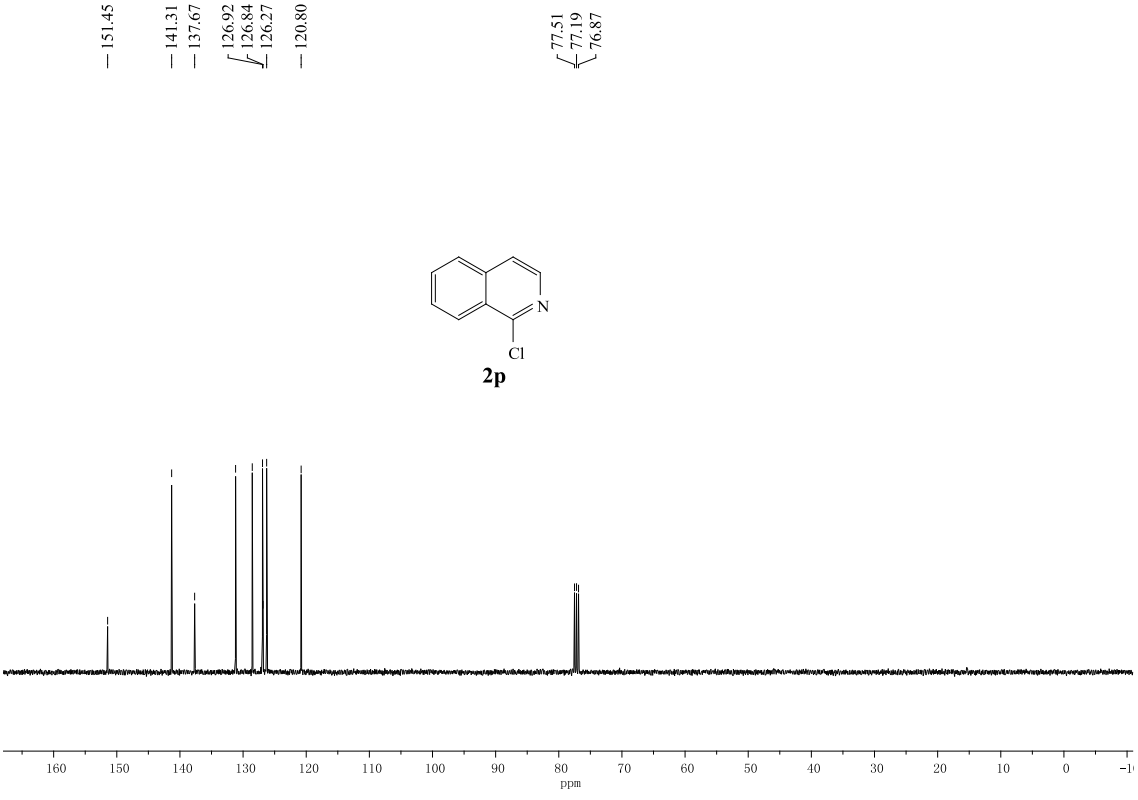
2o

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



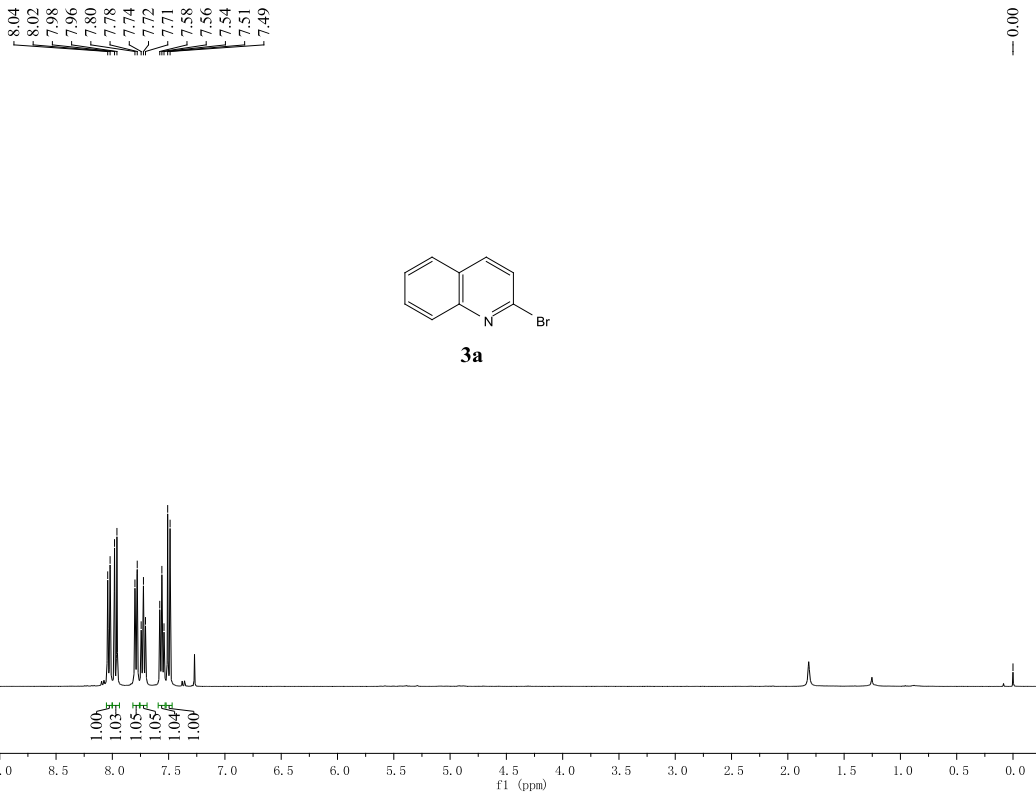
2p

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



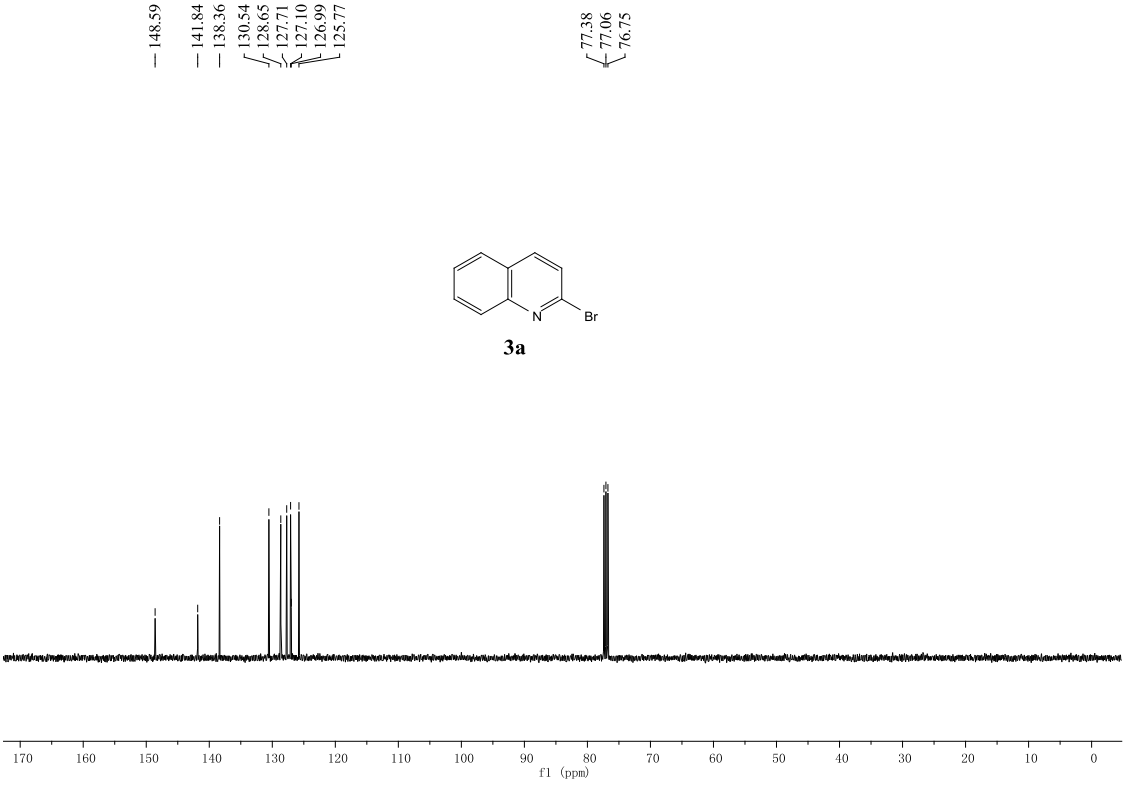
2p

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



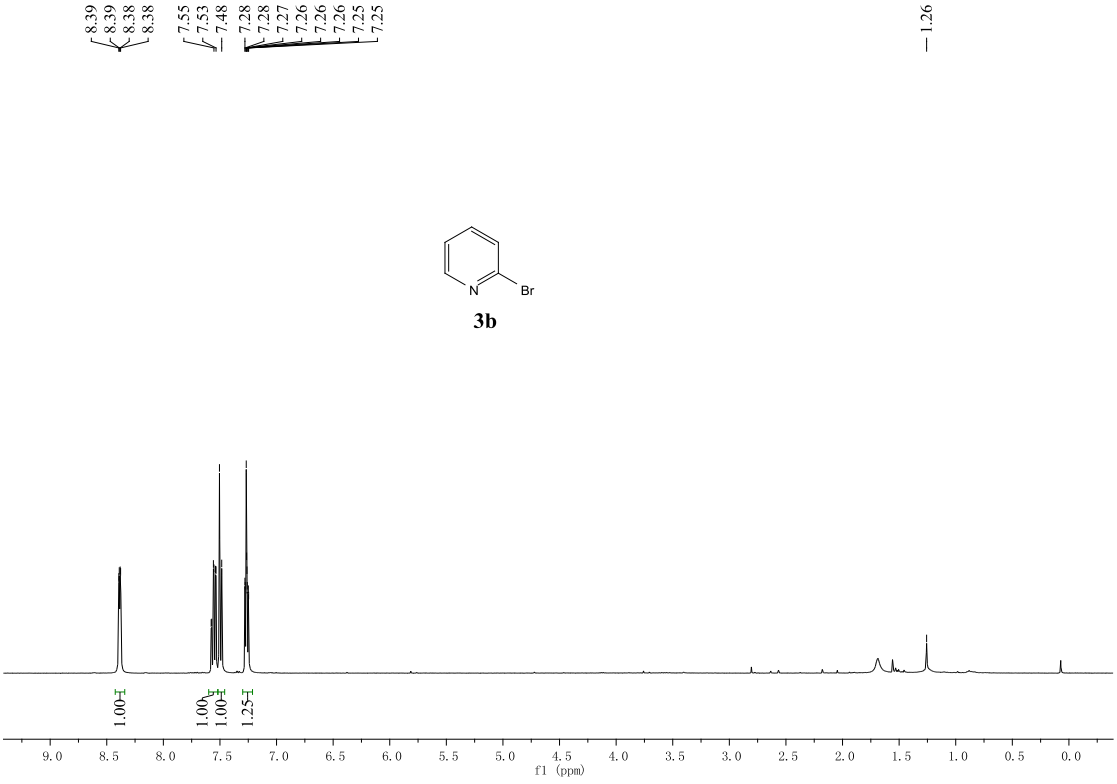
3a

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



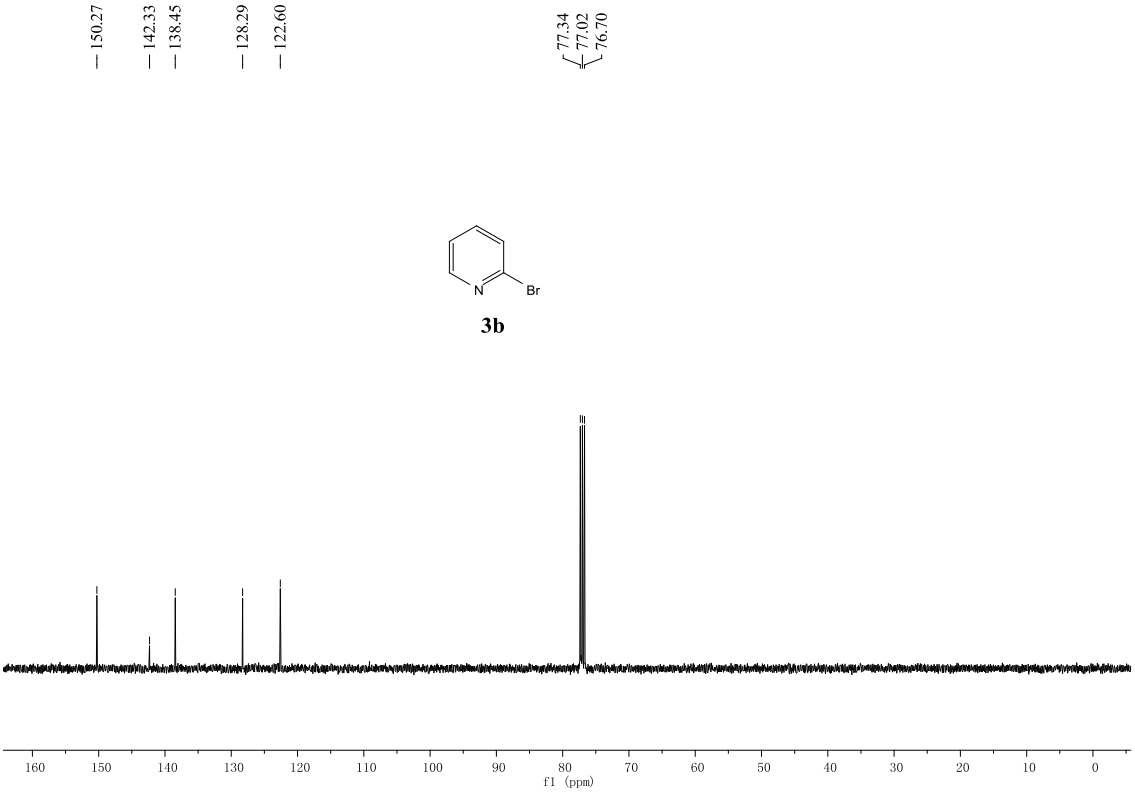
3a

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



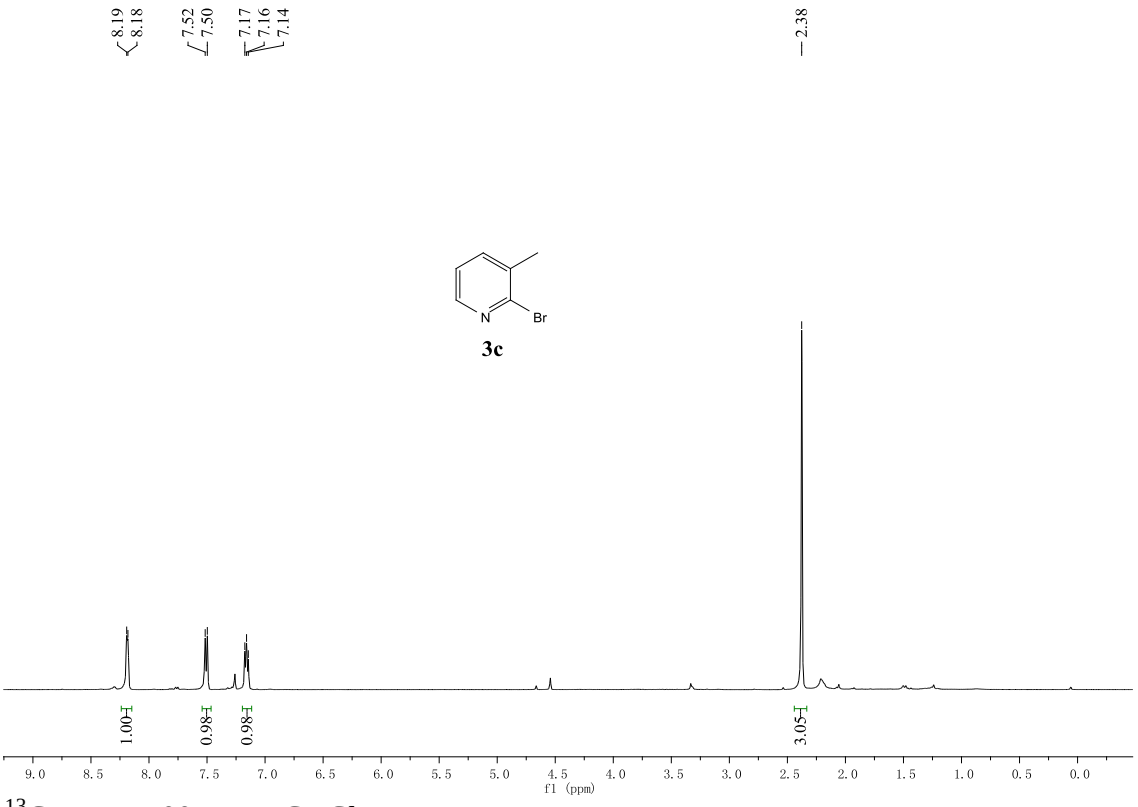
3b

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



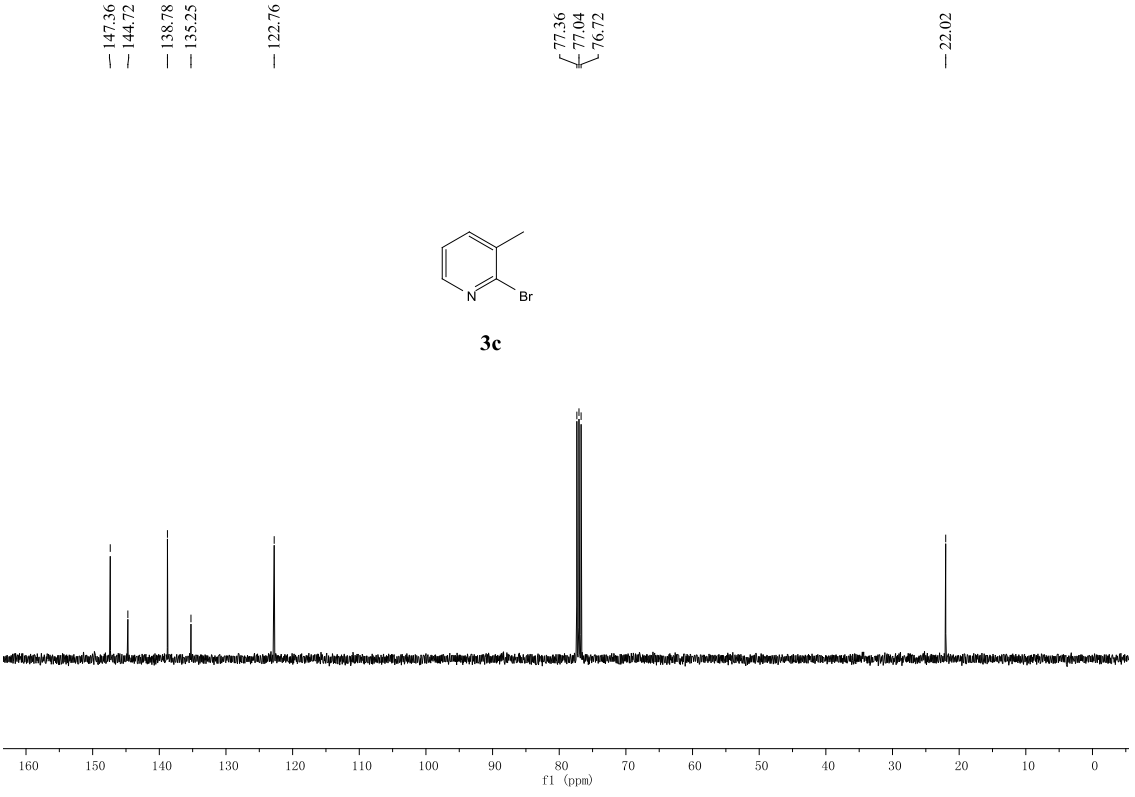
3b

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



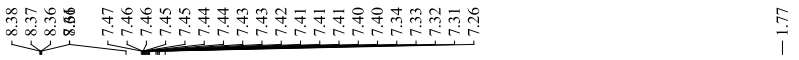
3c

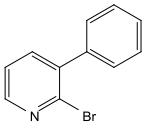
^{13}C NMR, 100 MHz, $CDCl_3$



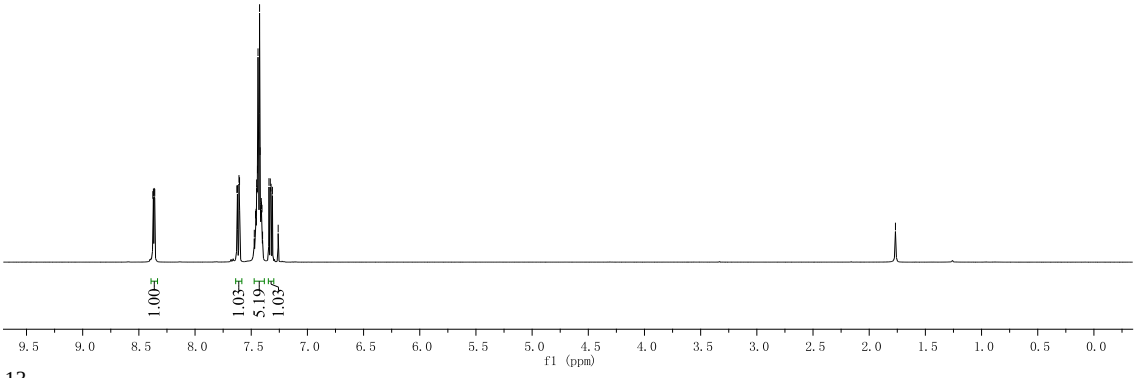
3c

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

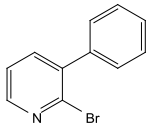




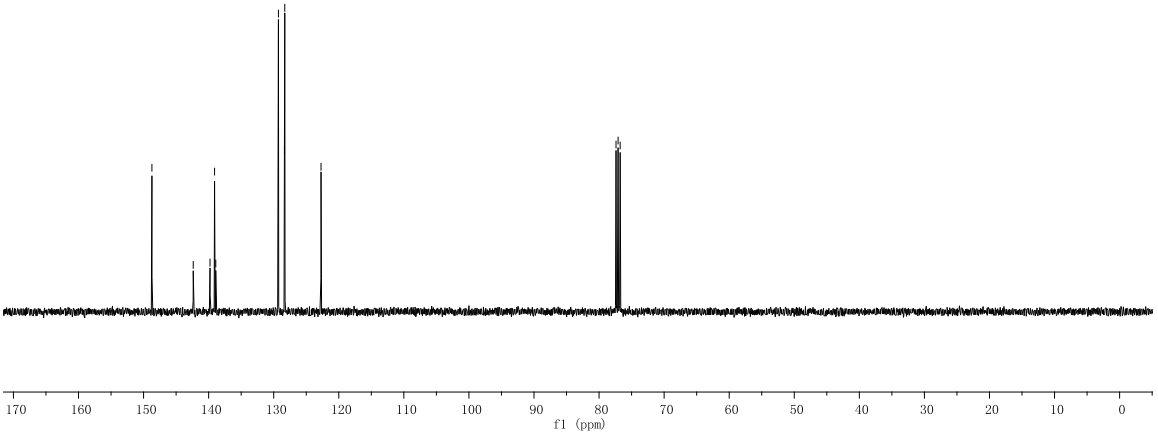
3d



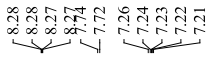
^{13}C NMR, 100 MHz, $CDCl_3$

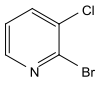


3d

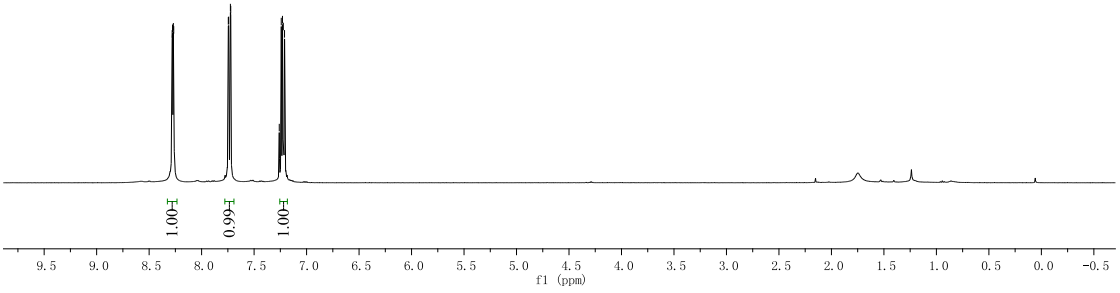


^{1}H NMR, 400 MHz, $CDCl_3$

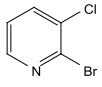




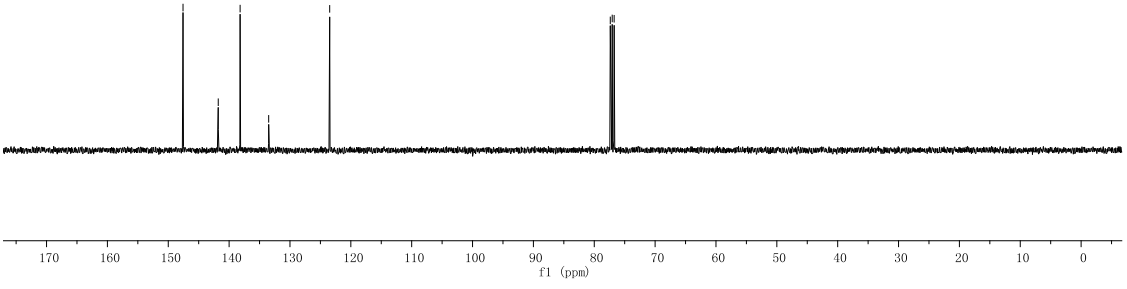
3e



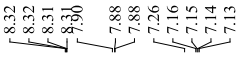
^{13}C NMR, 100 MHz, $CDCl_3$

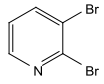


3e

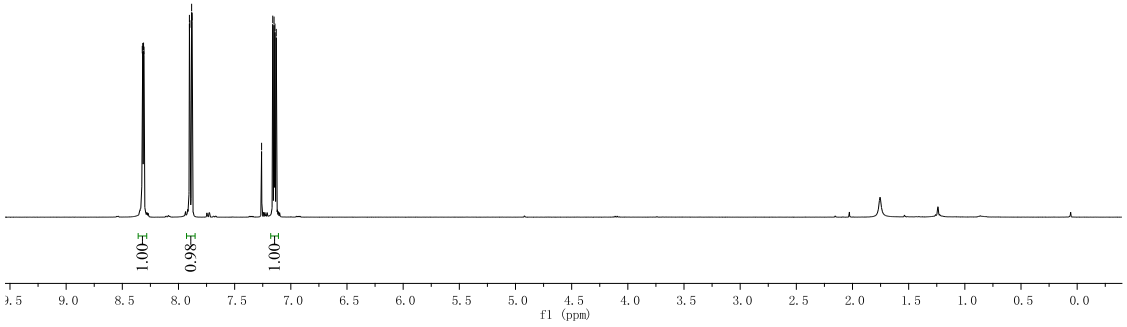


^{1}H NMR, 400 MHz, $CDCl_3$

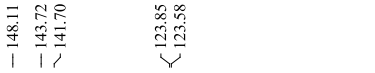


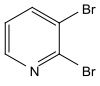


3f

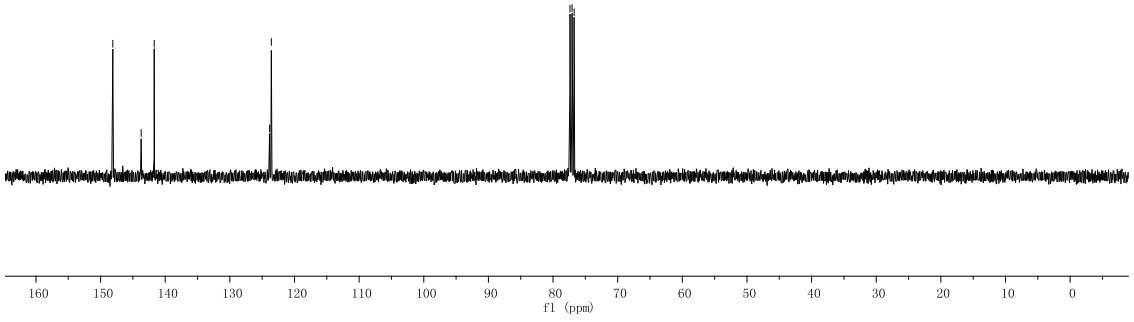


^{13}C NMR, 100 MHz, $CDCl_3$

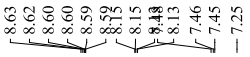


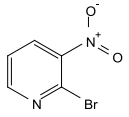


3f

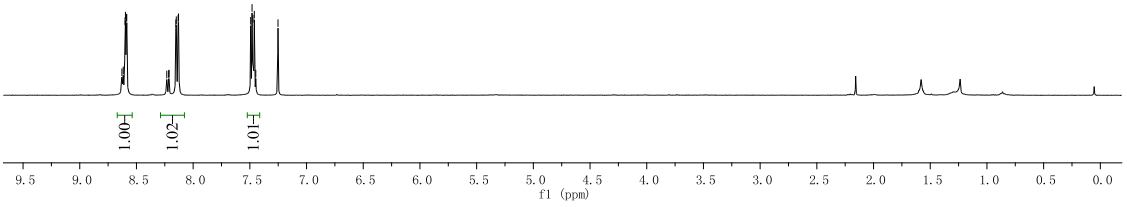


^{1}H NMR, 400 MHz, $CDCl_3$

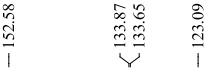


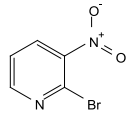


3g

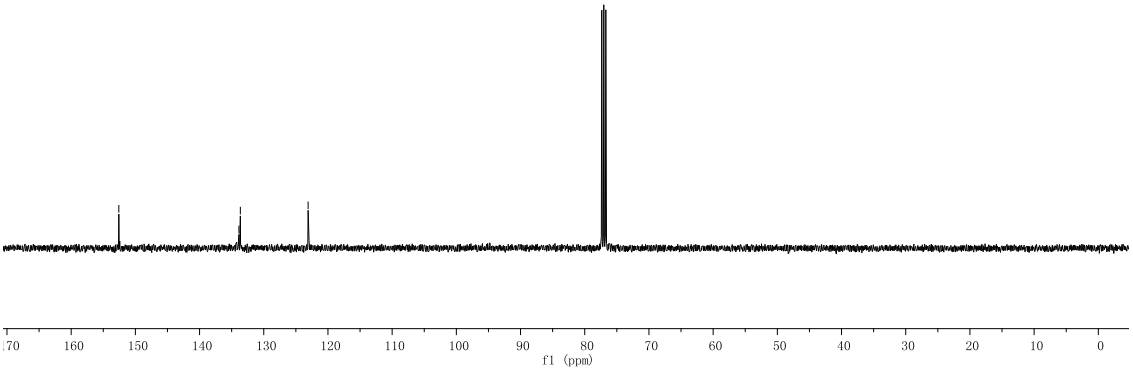


^{13}C NMR, 100 MHz, $CDCl_3$

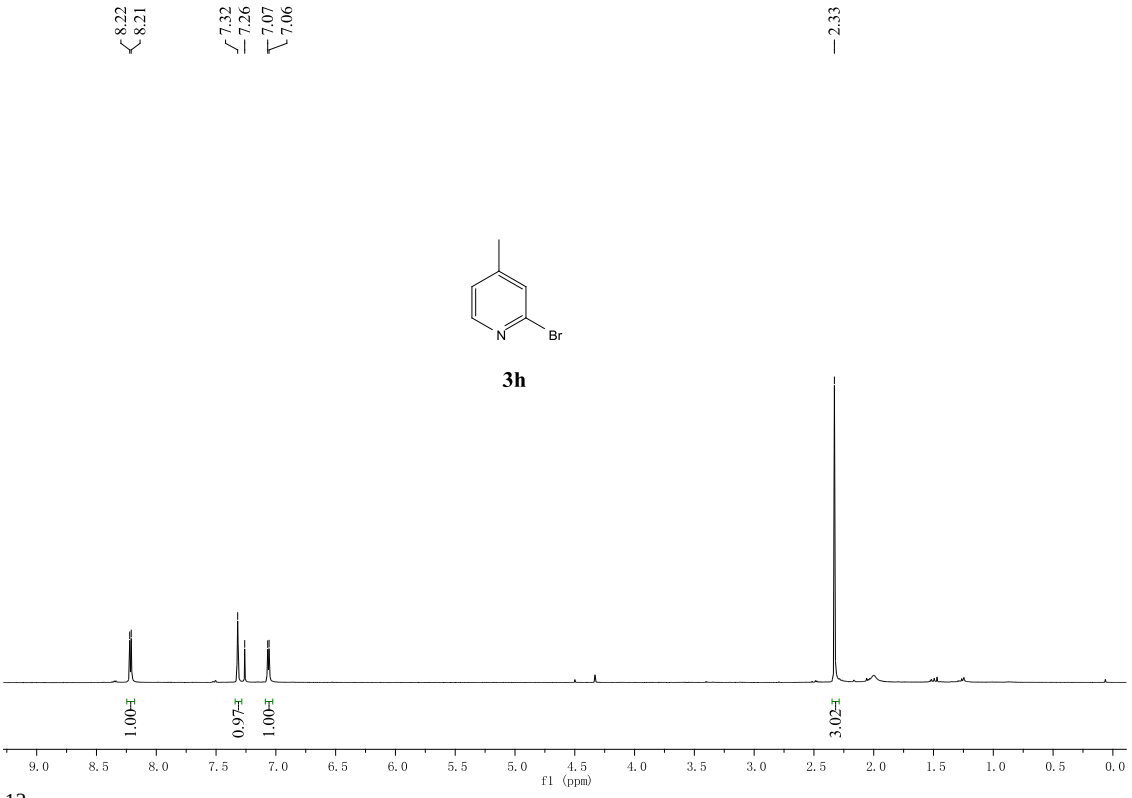




3g

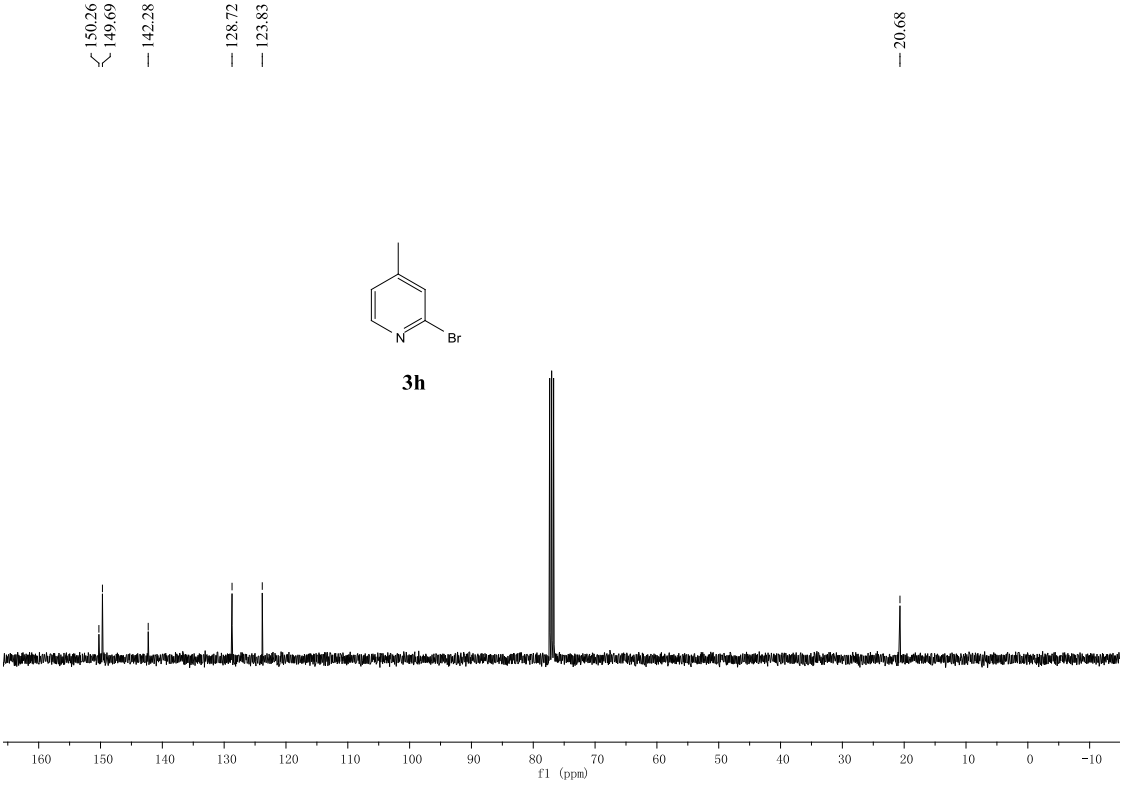


^{1}H NMR, 400 MHz, $CDCl_3$



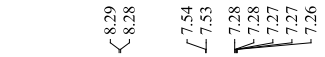
3h

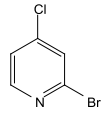
^{13}C NMR, 100 MHz, $CDCl_3$



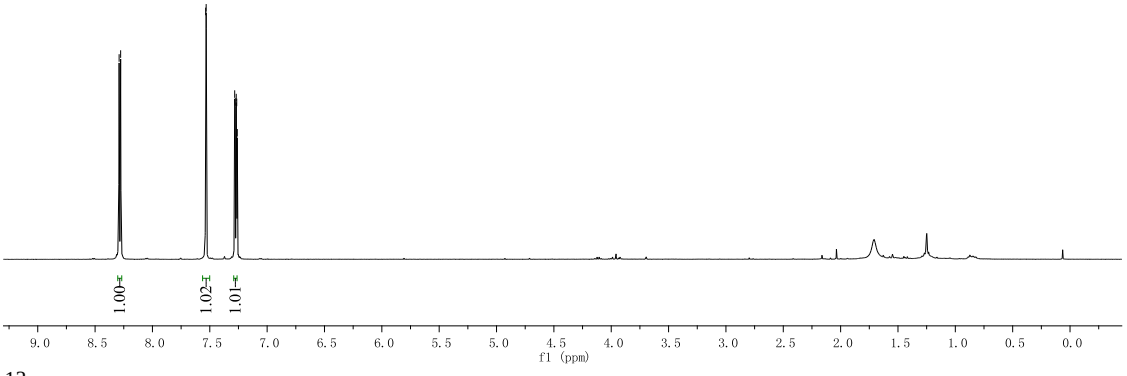
3h

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

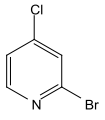




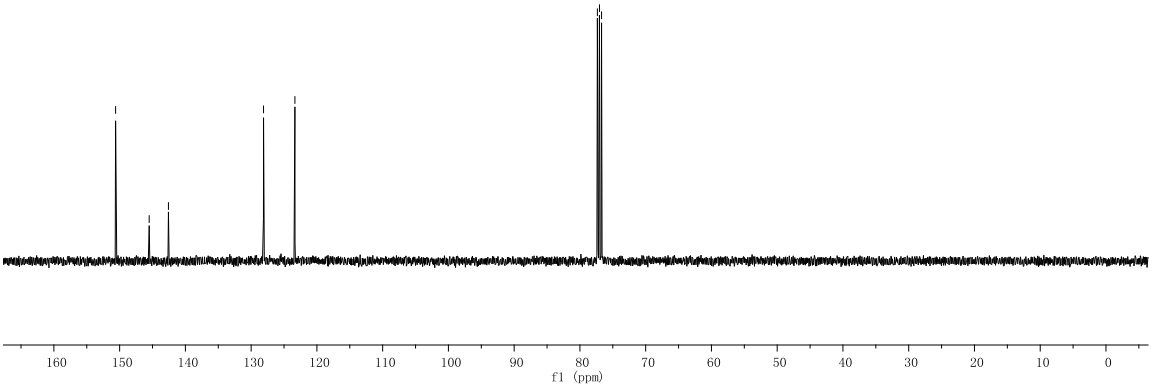
3i



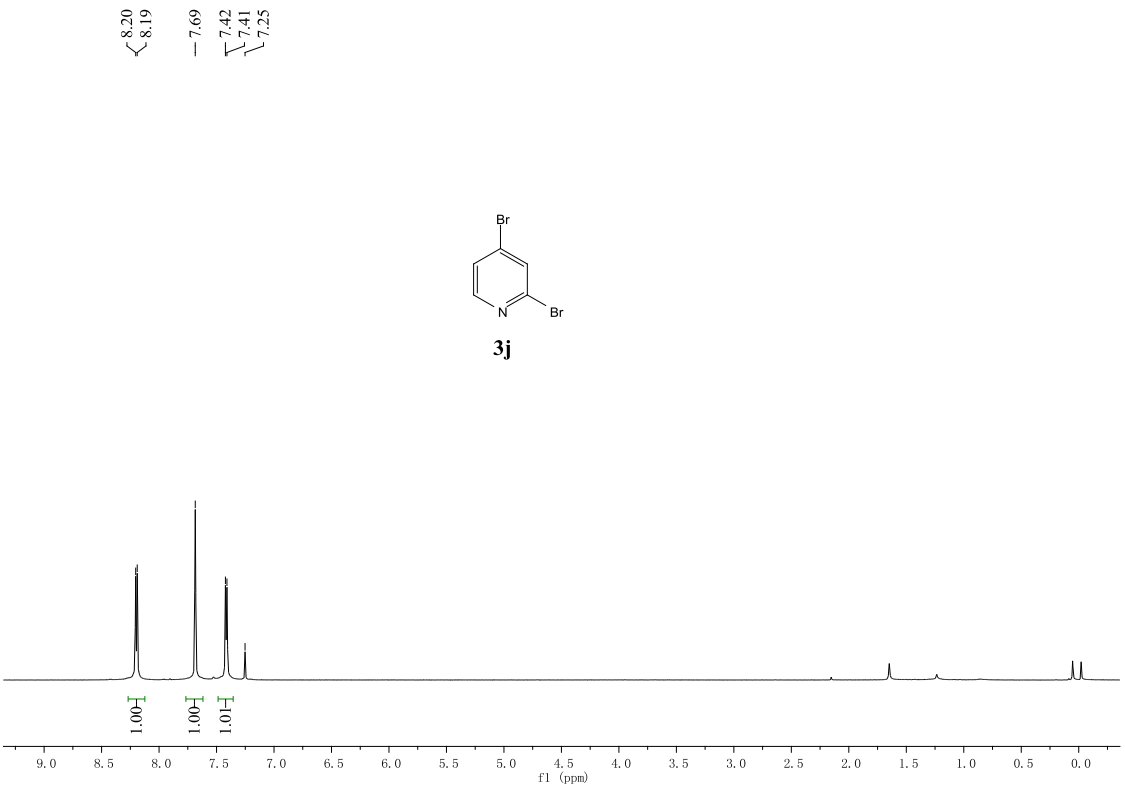
^{13}C NMR, 100 MHz, $CDCl_3$



3i

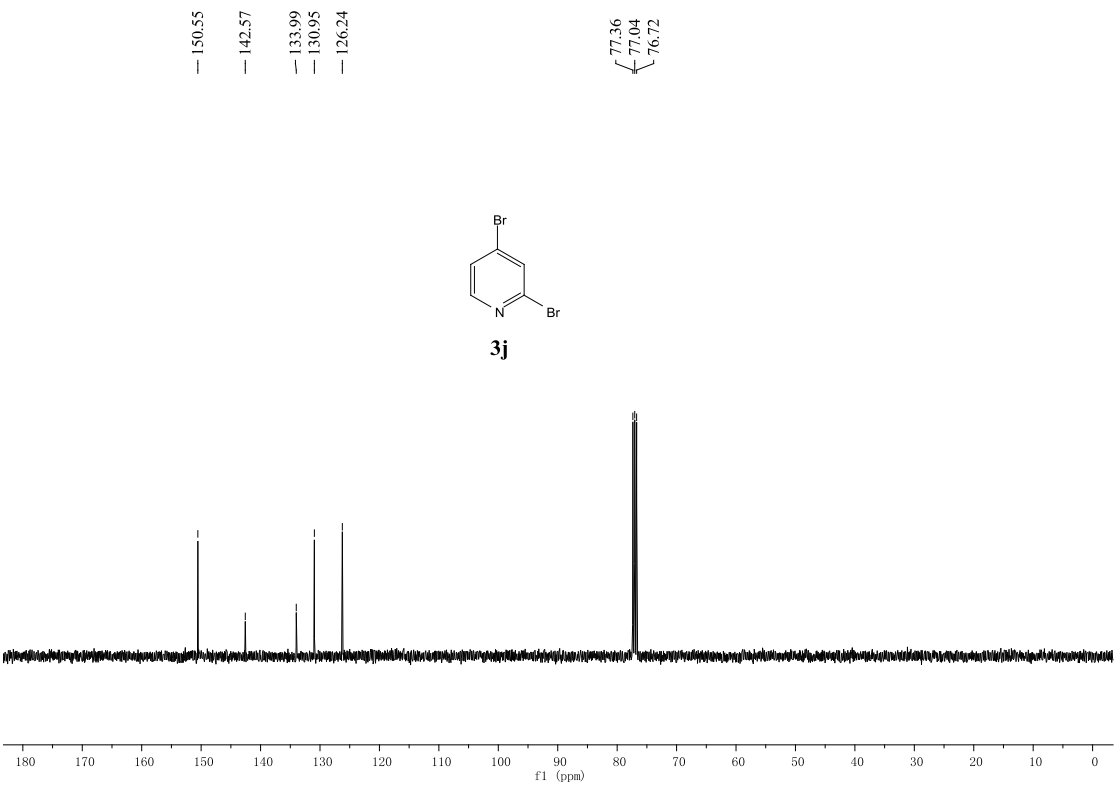


^{1}H NMR, 400 MHz, $CDCl_3$



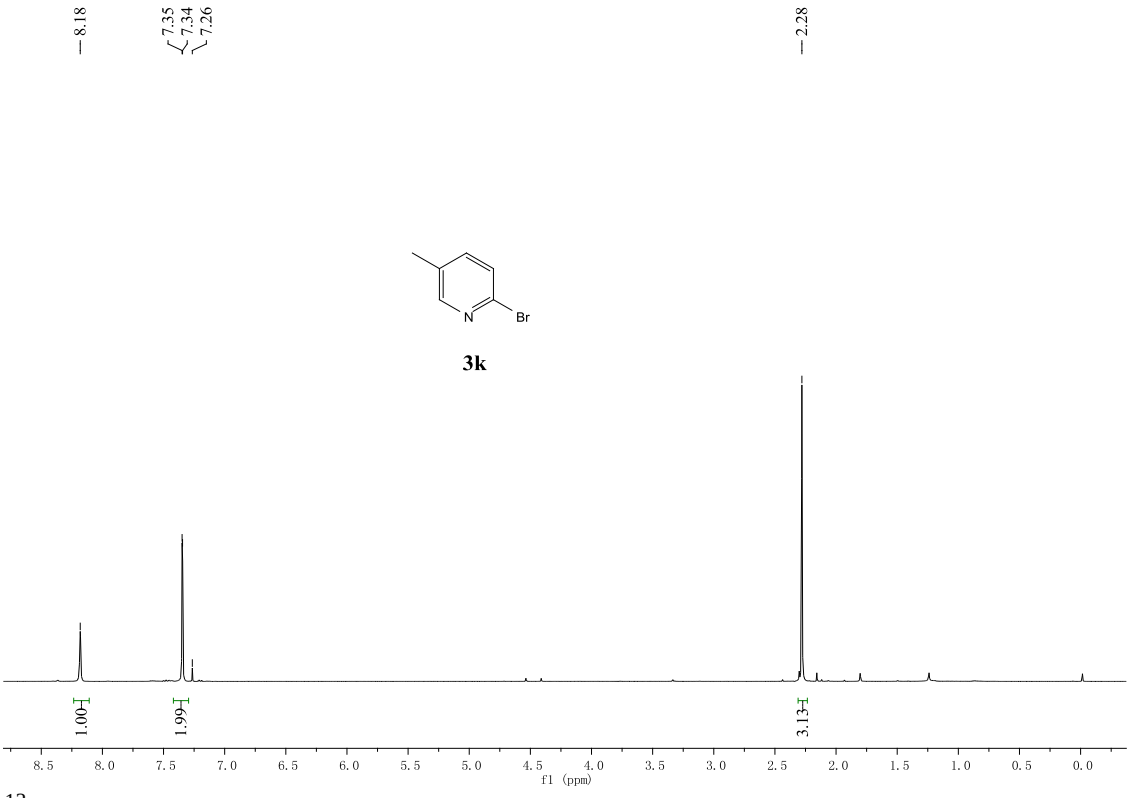
3j

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



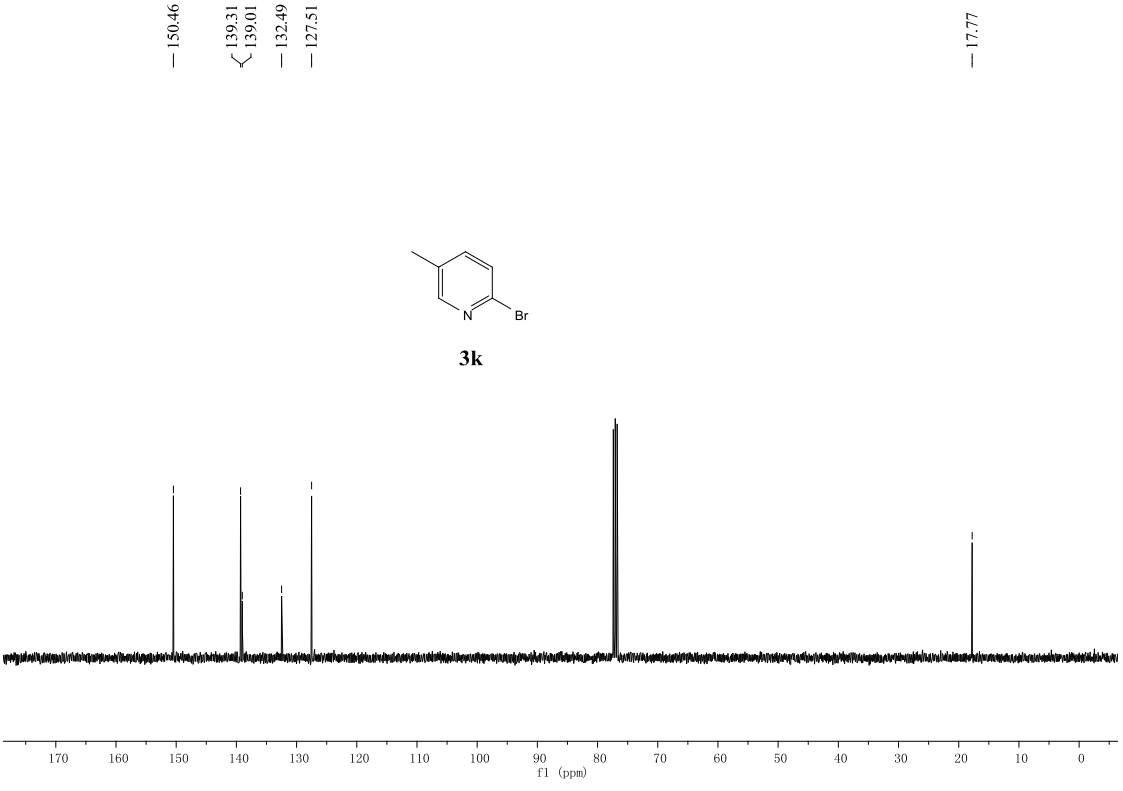
3j

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



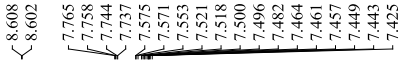
3k

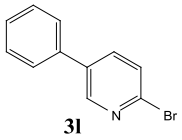
^{13}C NMR, 100 MHz, $CDCl_3$



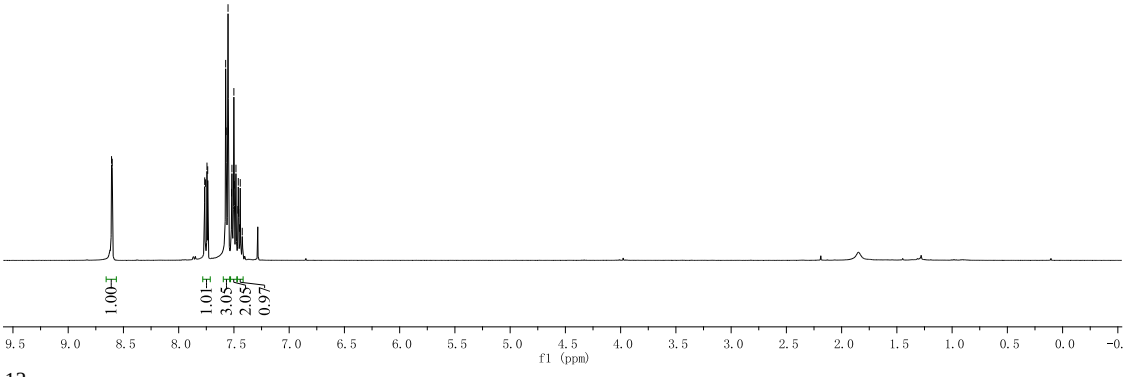
3k

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

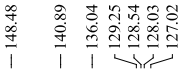


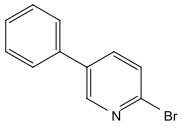


3l

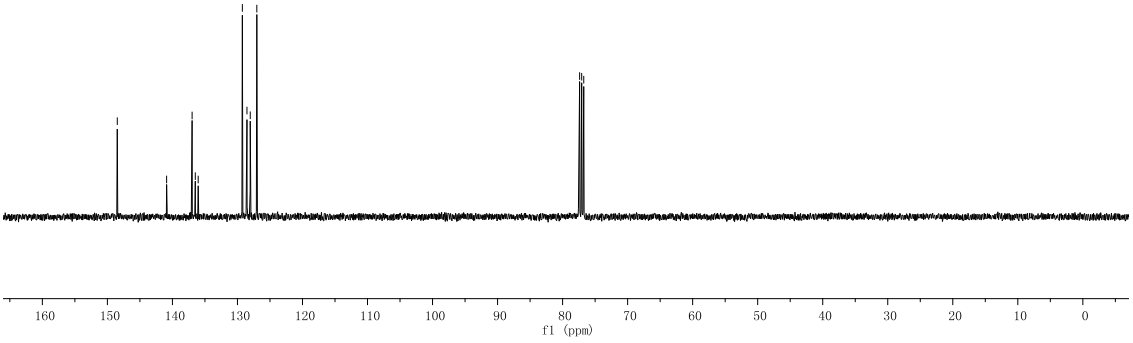


^{13}C NMR, 100 MHz, $CDCl_3$

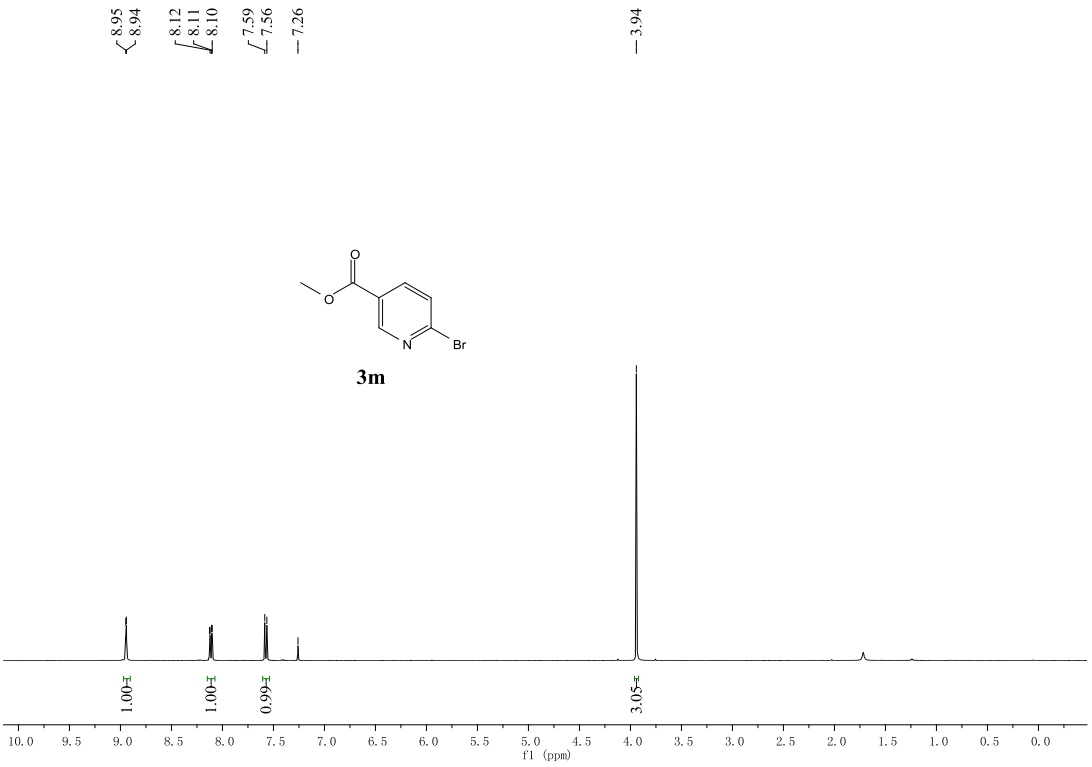




3l

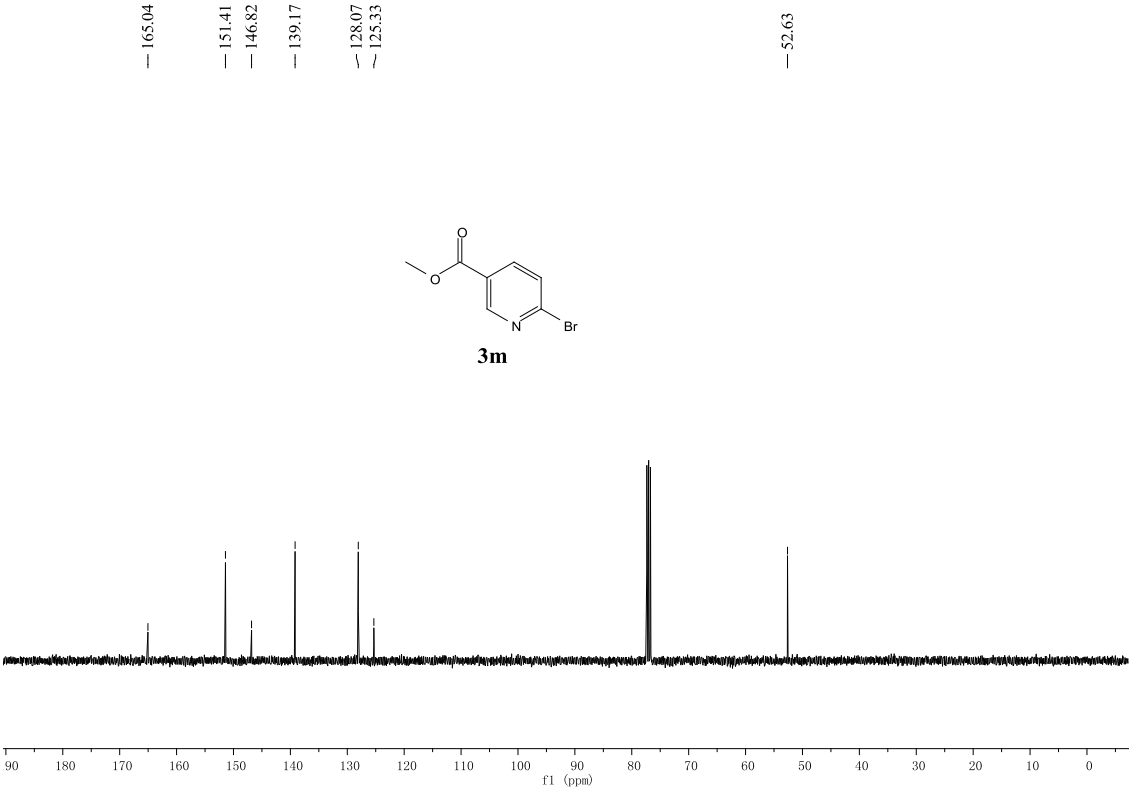


^{1}H NMR, 400 MHz, $CDCl_3$



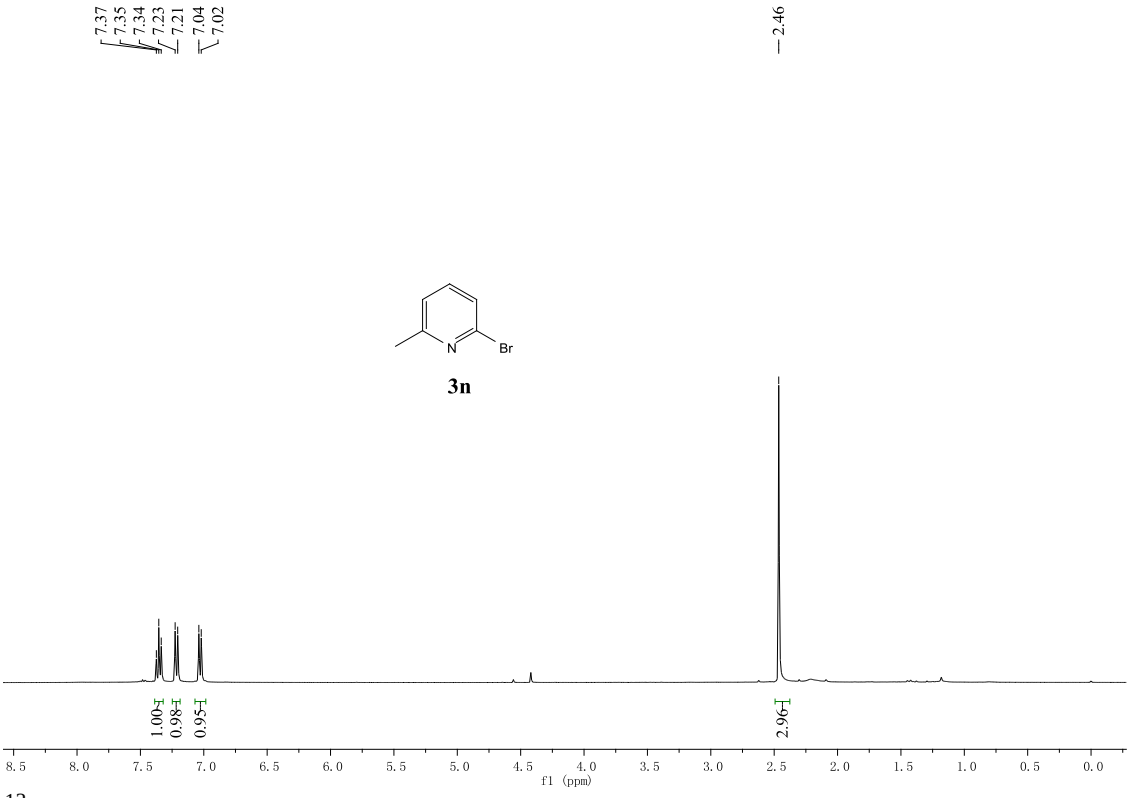
3m

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



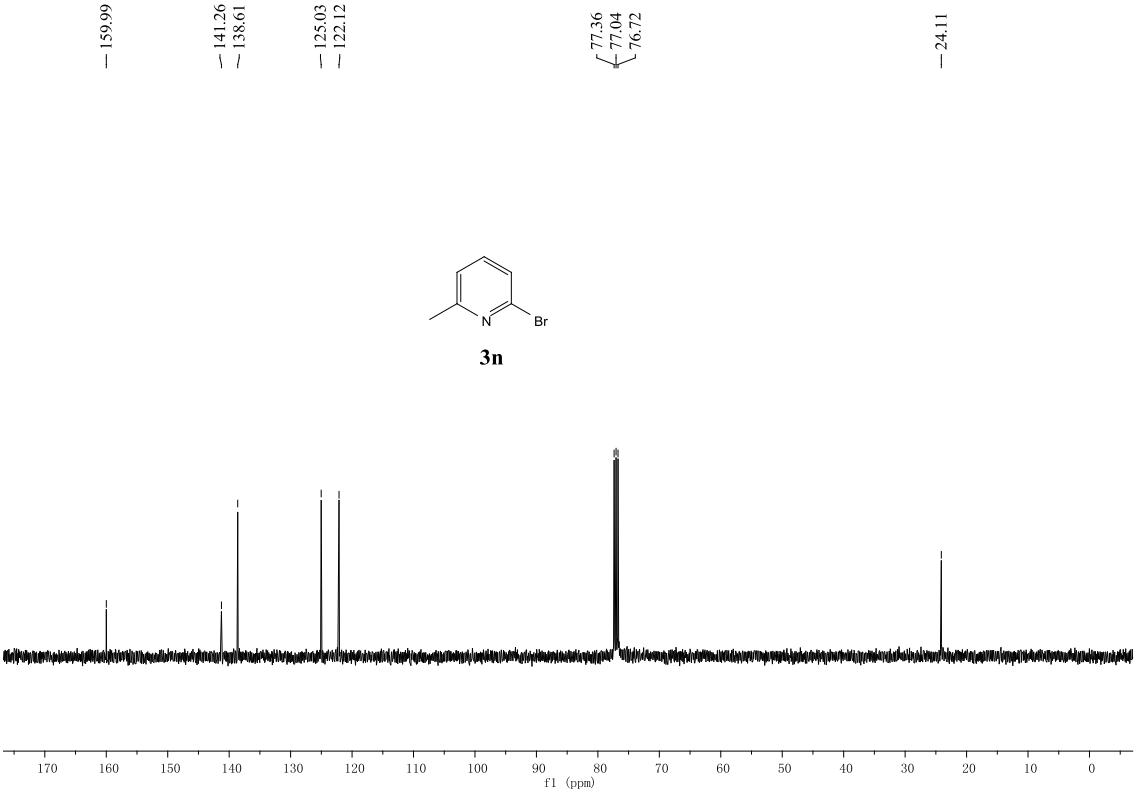
3m

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



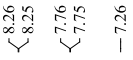
3n

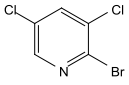
^{13}C NMR, 100 MHz, $CDCl_3$



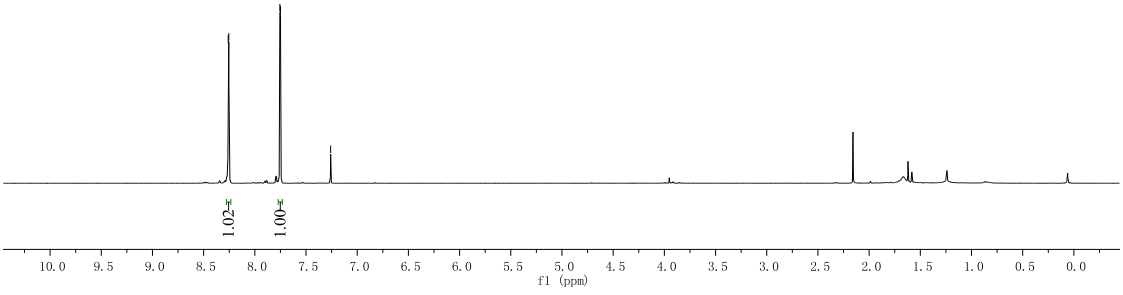
3n

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

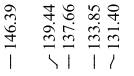


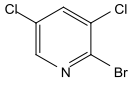


3o

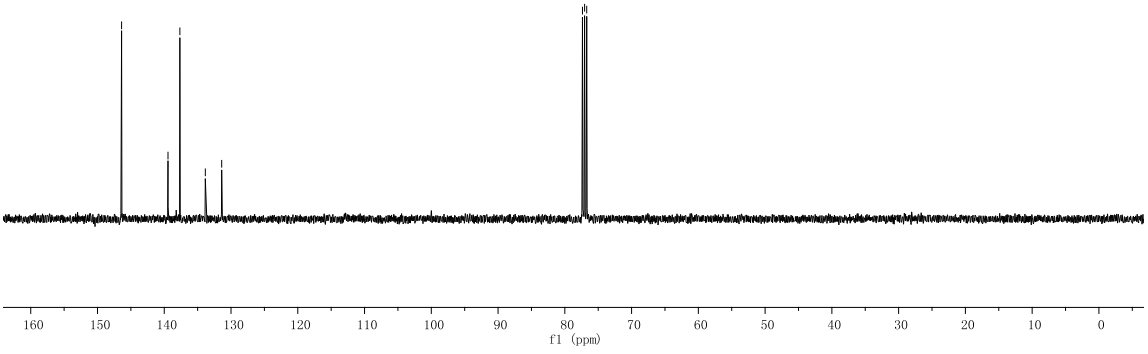


^{13}C NMR, 100 MHz, $CDCl_3$

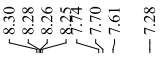


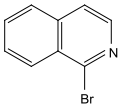


3o

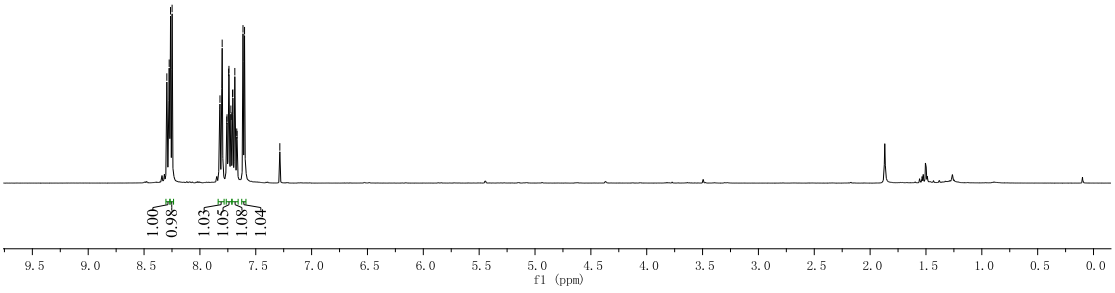


^{1}H NMR, 400 MHz, $CDCl_3$

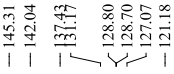


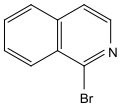


3p

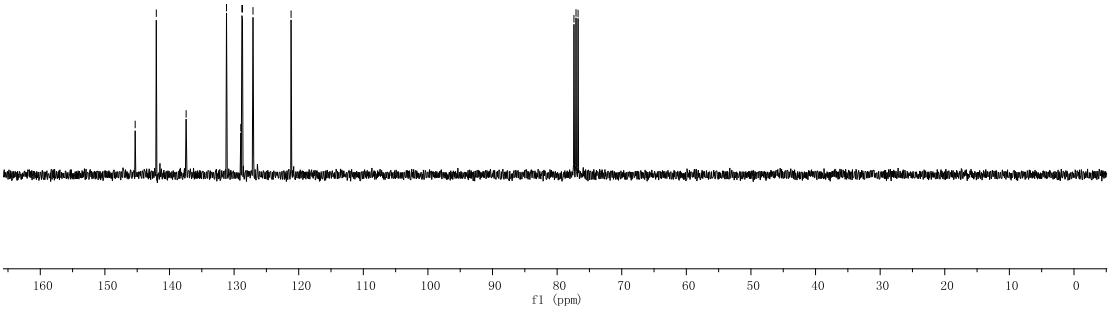


^{13}C NMR, 100 MHz, $CDCl_3$

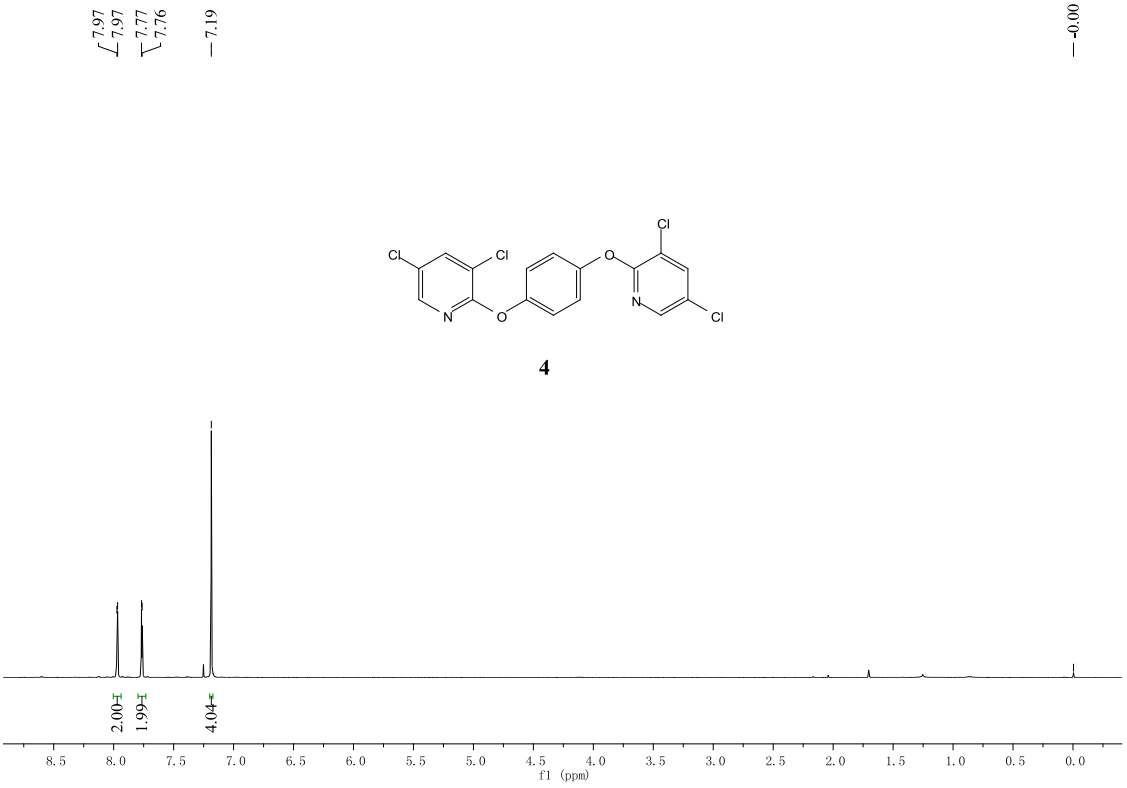




3p

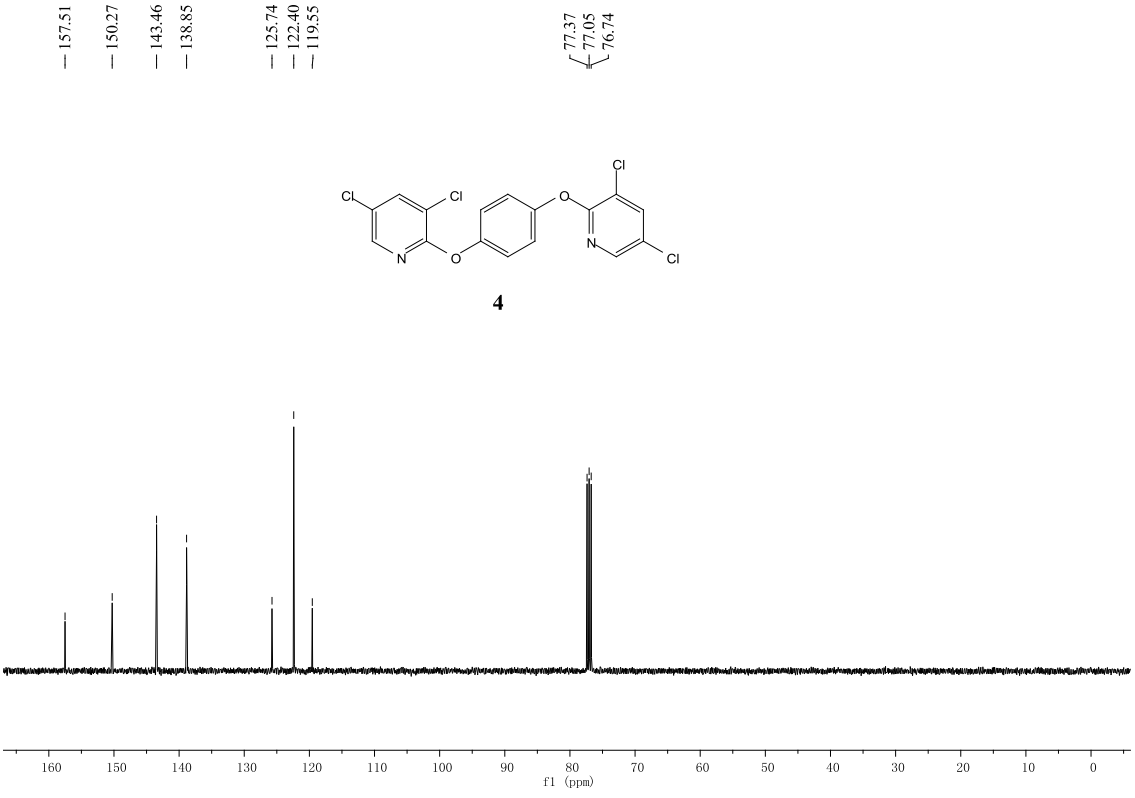


^{1}H NMR, 400 MHz, $CDCl_3$



4

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



4