Electronic Supplementary Information

Sulfur-Silicon Bond Activation Catalysed by Cl/Br Ions: Waste-Free Synthesis of Unsymmetrical Thioethers by Replacing Fluoride Catalysis and Fluorinated Substrates in S_NAr Reactions

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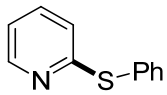
Contents

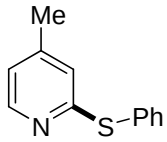
Experimental

General. Unless otherwise noted, substrates, catalysts, and solvents were all purchased and used without further purification. Except $PhSSiMe_3$, other S-Si reagents were prepared according to the reported literature procedure (*Bull. Chem. Soc. Jpn.* **1978**, *51*, 2183; *Org. Lett.* **2012**, *14*, 1846). Small scale reactions were carried out in sealed Schlenk tubes under nitrogen atmosphere using degassed commercial solvents and then monitored by TLC and/or GC-MS. Products were purified by column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent. Unless otherwise noted, ^1H and ^{13}C NMR spectra were measured on a Bruker Avance-III 500 instrument (500 MHz for ^1H, 125.4 MHz for ^{13}C NMR spectroscopy) using $CDCl_3$ as the solvent. Dry $CDCl_3$ was obtained by distillation under nitrogen after dried over $CaCl_2$, and then stored in a sealed Schlenk tube over dry molecular sieves under nitrogen protection. Chemical shifts for ^1H and ^{13}C NMR were referred to internal Me_4Si (0 ppm) as the standard. Mass spectra were measured on a Shimadzu GC-MS-QP2010 Plus spectrometer (EI). HRMS (ESI) analysis was measured on a Bruker micrOTOF-Q II instrument.

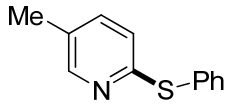
Typical Procedure of TBAB-Catalysed S_NAr Reaction of 2-Chloropyridine with Phenylthiotrimethylsilane for Heteroaryl Aryl Thioether Synthesis. The mixture of 2-chloropyridine **3a** (0.047 ml, 0.5 mmol), phenylthiotrimethylsilane **1a** (0.104 ml, 0.55 mmol, 1.1 equiv.), and TBAB (0.0161 g, 10 mol%) in acetonitrile (0.5 mL) was sealed under nitrogen in a Schlenk tube (10 mL, see the picture below for the apparatus) and then stirred at 100 ^oC for 48 h. The reaction was monitored by TLC and/or GC-MS. After completion of the reaction, solvent was evaporated under vacuum. The residue was then purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent. The target product **6aa** was obtained in 96% isolated yield.



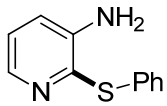
2-(Phenylthio)pyridine (6aa). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43 (dd, J = 5.0 Hz, J = 1.0 Hz, 1H), 7.61-7.58 (m, 2H), 7.46 (dd, J = 8.0 Hz, J = 2.0 Hz, 1H), 7.44-7.41 (m, 3H), 6.99 (ddd, J = 7.5 Hz, J = 5.0 Hz, J = 1.0 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 161.5, 149.6, 136.7, 134.9, 131.1, 129.6, 129.0, 121.4, 119.9. MS (EI): m/z (%) 187 (25), 186 (100), 154 (1), 115 (5), 109 (2), 93 (5), 78 (7), 65 (4), 52 (3), 51 (12). This compound was known: S. Yasuike, M. Nishioka, N. Kakusawa, J. Kurita, *Tetrahedron Lett.* **2011**, *52*, 6403-6406.



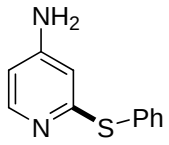
4-Methyl-2-(phenylthio)pyridine (6ab). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28 (d, J = 5.0 Hz, 1H), 7.59-7.56 (m, 2H), 7.43-7.38 (m, 3H), 6.82 (d, J = 5.0 Hz, 1H), 6.74 (s, 1H), 2.20 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 160.9, 149.3, 148.0, 134.7, 131.4, 129.5, 128.8, 122.2, 121.3, 20.9. MS (EI): m/z (%) 201 (26), 200 (100), 186 (4), 115 (2), 109 (3), 100 (4), 77 (4), 65 (19), 51 (6). This compound was known: B. Sreedhar, P. S. Reddy, M. A. Reddy, *Synthesis* **2009**, 1732-1738.



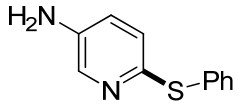
5-Methyl-2-(phenylthio)pyridine (6ac). Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (d, J = 2.0 Hz, 1H), 7.56-7.54 (m, 2H), 7.40-7.36 (m, 3H), 7.28 (dd, J = 8.0 Hz, J = 2.0 Hz, 1H), 6.85 (d, J = 8.5 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 157.5, 149.9, 137.5, 134.2, 132.0, 129.7, 129.4, 128.6, 121.7, 17.8. MS (EI): m/z (%) 201 (27), 200 (100), 185 (2), 156 (1), 109 (3), 93 (2), 77 (4), 65 (18), 51 (6). This compound was known: S. Arai, M. Yamazaki, M. Hida, *J. Heterocyclic.Chem.***1990**, *27*, 1073-1078.



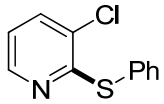
2-(Phenylthio)pyridin-3-amine (6ad). Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, J = 3.5 Hz, 1H), 7.28-7.24 (m, 4H), 7.21-7.17 (m, 1H), 7.07 (dd, J = 8.0 Hz, J = 4.5 Hz,1H), 7.00 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H), 4.23 (b, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 144.2, 140.3, 139.0, 134.0, 129.4, 129.1, 126.6, 124.2, 122.0. MS (EI): m/z (%) 202 (46), 201 (100), 186 (7), 168 (5), 140 (1), 115 (2), 101 (6), 77 (4), 66 (10), 51 (4). This compound was known: X. Xu, S. Guo, Q. Dang, J. Chen, X. Bai, *J. Comb. Chem.* **2007**, *9*, 773-782.



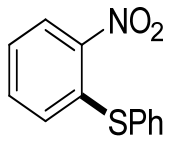
2-(Phenylthio)pyridin-4-amine (6ae). Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, J = 5.5 Hz, 1H), 7.59-7.57 (m, 2H), 7.40-7.39 (m, 3H), 6.27 (dd, J = 5.5 Hz, J = 2.0 Hz, 1H), 6.09 (d, J = 2.0 Hz, 1H), 4.07 (b, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 161.7, 153.4, 149.8, 134.9, 131.5, 129.5, 128.9, 107.0, 106.4. MS (EI): m/z (%) 202 (26), 201 (100), 184 (6), 140 (3), 108 (2), 93 (3), 77 (3), 66 (9), 52 (3), 51 (4). HRMS Calcd for $C_{11}H_{11}N_2S$ (M+H): 203.0604; found: 203.0637.



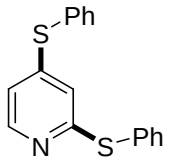
6-(Phenylthio)pyridin-3-amine (6af). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, J = 2.5 Hz, 1H), 7.42-7.41 (m, 1H), 7.40-7.39 (m, 1H), 7.33-7.29 (m, 2H), 7.27-7.24 (m, 1H), 7.02 (d, J = 8.5 Hz, 1H), 6.88 (dd, J = 8.0 Hz, J = 2.5 Hz, 1H), 3.22 (b, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 146.6, 141.0, 137.5, 134.9, 131.8, 129.2, 127.3, 125.9, 123.1. MS (EI): m/z (%) 203 (10), 202 (46), 201 (100), 184 (5), 174 (8), 173 (4), 147 (3), 101 (3), 77 (4), 66 (7). This compound was known: H. C. Winter, F. E. Reinhart. *J. Am. Chem. Soc.* **1940**, *62* (12), 3508–3511.



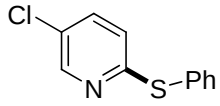
3-Chloro-2-(phenylthio)pyridine (6ag). Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (dd, J = 4.5 Hz, J = 1.5 Hz, 1H), 7.57-7.54 (m, 3H), 7.43-7.40 (m, 3H), 6.95 (dd, (dd, J = 8.0 Hz, J = 4.5 Hz, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 157.5, 147.4, 136.2, 135.4, 129.7, 129.1, 129.0, 128.7, 120.6. MS (EI): m/z (%) 221 (29), 220 (100), 185 (15), 140 (2), 115 (5), 85 (2), 76 (7), 65 (6), 52 (1), 51 (9). This compound was known: X. Zhang, X. Zhang, S. Guo, *J. Sulfur Chem.* **2011**, *32*, 23-35.



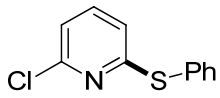
4-Chloro-2-(phenylthio)pyridine (6ah). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, J = 5.0 Hz, 1H), 7.57-7.55 (m, 2H), 7.52-7.46 (m, 3H), 6.90 (d, J = 1.0 Hz, 1H), 6.85 (dd, J = 5.5Hz, J = 2.0 Hz, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 153.8, 151.9, 148.9, 135.4, 130.19, 130.16, 128.4, 120.2, 119.4. MS (EI): m/z (%) 221 (100), 186 (44), 158 (6), 140 (14), 115 (25), 109 (19), 93 (7), 85 (10), 77 (21) 65 (22), 51 (34). HRMS Calcd for $C_{11}H_9ClNS$ (M+H): 222.0139; found:222.0116.



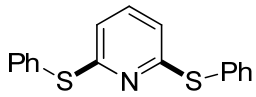
2,4-Bis(phenylthio)pyridine (6ah'). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (d, J = 5.5 Hz, 1H), 7.49-7.47 (m, 2H), 7.42-7.40 (m, 2H), 7.39-7.37 (m, 1H), 7.36-7.31 (m, 5H), 6.66 (dd, J = 5.5 Hz, J = 2.0 Hz, 1H), 6.40 (d, J = 1.5 Hz, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 161.9, 151.4, 148.8, 135.2, 135.0, 130.4, 129.8, 129.64, 129.57, 129.1, 128.9, 117.3, 117.1. MS (EI): m/z (%) 295 (36), 294 (100), 260 (1), 217 (4), 185 (12), 173 (4), 147 (5), 115 (10), 77 (8), 51 (7). HRMS Calcd for $C_{17}H_{14}NS_2$ (M+H): 296.0562; found: 296.0531.



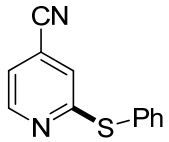
5-Chloro-2-(phenylthio)pyridine (6ai). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.37 (d, J = 2.5 Hz, 1H), 7.59-7.57 (m, 2H), 7.43-7.40 (m, 4H), 6.83 (d, J = 8.5 Hz, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 159.6, 148.2, 136.4, 134.9, 130.7, 129.7, 129.3, 128.3, 122.1. MS (EI): m/z (%) 221 (28), 220 (100), 185 (13), 158 (1), 140 (4), 93 (11), 76 (12), 65 (10), 51 (12). This compound was known: R. E. Tenbrink, S. W. Kortum, W. O. Patent, 2003072548, 2003.



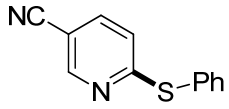
2-Chloro-6-(phenylthio)pyridine (6aj). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61-7.59 (m, 2H), 7.45-7.43 (m, 3H), 7.38-7.35 (m, 1H), 6.99 (d, J = 7.5 Hz, 1H), 6.69 (d, J = 8.0 Hz, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 162.8, 150.8, 138.8, 135.1, 130.0, 129.8, 129.6, 119.8, 119.1. MS (EI): m/z (%) 221 (54), 220 (100), 186 (20), 153 (4), 140 (8), 115 (10), 109 (10), 93 (9), 76 (15), 65 (13), 51 (17). This compound was known: S. Kato, A. Masui, S. Ishida, *Nippon Noyaku Gakkaishi* **1989**, *14*, 11-22.



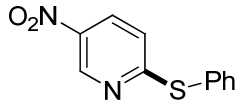
2,6-Bis(phenylthio)pyridine (6aj'). White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58-7.55 (m, 4H), 7.39-7.38 (m, 6H), 7.17 (m, 1H), 6.51 (d, J = 8.1 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 161.5, 136.9, 135.0, 130.7, 129.5, 129.0, 117.0. MS (EI): m/z (%) 296 (24), 295 (88), 294 (100), 216 (16), 186 (58), 185 (36), 115 (22), 109 (16), 77 (17), 65 (11), 51 (11). This compound was known: Y. G. Zhang, K. C. Ngeow, J. Y. Ying, *Org. Lett.* **2007**, *9*, 3495-3498.



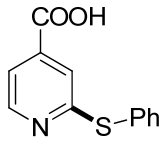
2-(Phenylthio)isonicotinonitrile (6ak). White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.55 (d, J = 5.0 Hz, 1H), 7.62-7.60 (m, 2H), 7.51-7.47 (m, 3H), 7.17 (dd, J = 5.0 Hz, J = 1.0 Hz, 1H), 6.98 (s, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 164.4, 150.2, 135.4, 130.12, 130.09, 128.8, 121.9, 121.0, 120.5, 116.2. MS (EI): m/z (%) 212 (26), 211 (100), 184 (2), 109 (4), 92 (2), 82 (1), 77 (5), 65 (6), 51 (9). HRMS Calcd for $C_{12}H_9N_2S$ (M+H): 213.0481; found: 213.0439.



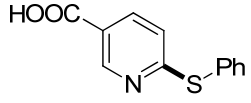
6-(Phenylthio)nicotinonitrile (6al). White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.62 (d, J = 2.0 Hz, 1H), 7.65-7.63 (m, 1H), 7.61-7.59 (m, 2H), 7.51-7.49 (m, 3H), 6.90 (d, J = 8.5 Hz, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 167.8, 152.0, 138.8, 135.4, 130.1, 130.0, 128.4, 120.0, 116.7, 104.9. MS (EI): m/z (%) 212 (29), 211 (100), 179 (1), 140 (7), 109 (4), 92 (2), 82 (2), 77 (7), 69 (4), 51 (10). HRMS Calcd for $C_{12}H_9N_2S$ (M+H): 213.0481; found: 213.0438.



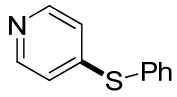
5-Nitro-2-(phenylthio)pyridine (6am). White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.19 (d, J = 2.5 Hz, 1H), 8.18 (dd, J = 9.0 Hz, J = 3.0 Hz, 1H), 7.63-7.61 (m, 2H), 7.63-7.49 (m, 3H), 6.94 (d, J = 9.0 Hz, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 170.2, 145.0, 141.0, 135.5, 131.1, 130.3, 130.1, 128.4, 119.7. MS (EI): m/z (%) 232 (38), 231 (100), 201 (11), 185 (49), 173 (5), 115 (11), 109 (29), 77 (10), 65 (17), 52 (1), 51 (8). This compound was known: E. A. Hamed, A. A. El-Bardan, E. F. Saad, G. A. Gohar, G. A. Hassan, *J. Chem. Soc., Perkin Trans. 2.* **1997**, 2415-2422.



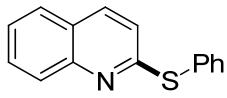
2-(Phenylthio)isonicotinic acid (6an). White solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 8.58 (dd, J = 5.0 Hz, J = 1.0 Hz, 1H), 7.64-7.62 (m, 2H), 7.54-7.53 (m, 4H), 7.29 (s, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 165.6, 161.5, 150.4, 139.8, 134.8, 130.0, 129.7, 129.4, 119.4, 119.2. This compound was known: M. Ryozo, H. Katsumi, Patent, 19730515, 1973.



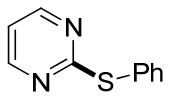
6-(Phenylthio)nicotinic acid (6ao). White solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 8.85 (s, 1H), 8.06 (d, J = 8.5 Hz, 1H), 7.63-7.61 (m, 2H), 7.53-7.52 (m, 3H), 6.95 (d, J = 8.5 Hz, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 163.9, 150.3, 137.7, 134.92, 134.89, 130.01, 129.98, 129.71, 129.67, 129.3, 119.9. This compound was known: M. Ryozo, H. Katsumi. Patent, 19730515, 1973.



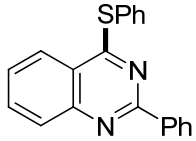
4-(Phenylthio)pyridine (6ap). Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34 (dd, J = 4.5 Hz, J = 1.5 Hz, 2H), 7.56-7.54 (m, 2H), 7.46-7.44 (m, 3H), 6.94 (dd, J = 4.5 Hz, J = 1.5 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 150.3, 149.3, 135.1, 129.9, 129.6, 129.5, 120.8. MS (EI): m/z (%) 187 (100), 186 (68), 160 (7), 154 (7), 134 (2), 128 (3), 115 (14), 65 (7), 52 (2), 51 (28). This compound was known: G. R. Alfonso, F. I. M. Angeles, R. G. Arrayas, J. C. Carretero, *Chem. Eur. J.* **2011**, *17*, 3567-3570.



2-(Phenylthio)quinoline (6aq). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 9.0 Hz, 1H), 7.68-7.63 (m, 4H), 7.45-7.41 (m, 4H), 6.97 (d, J = 8.5 Hz, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 161.5, 148.0, 136.4, 135.1, 130.8, 129.9, 129.6, 129.1, 128.3, 127.5, 125.8, 125.7, 119.5. MS (EI): m/z (%) 237 (44), 236 (100), 204 (3), 165 (2), 128 (13), 119 (5), 101 (17), 65 (3), 51 (6). This compound was known: R. Saari, J. C. Toermae, T. Nevalainen, *Bioorg. Med. Chem.* **2011**, *19*, 939-950.

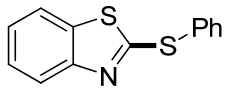


2-(Phenylthio)pyrimidine (6ar). Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.48 (d, J = 5.0 Hz, 2H), 7.64-7.62 (m, 2H), 7.45-7.42 (m, 3H), 6.95 (t, J = 5.0 Hz, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 172.8, 157.5, 135.2, 129.4, 129.3, 129.2, 116.9. MS (EI): m/z (%) 188 (35), 187 (100), 160 (3), 135 (4), 109 (10), 77 (16), 65 (9), 63 (4), 51 (11). This compound was known: M. Egi, L. S. Liebeskind, *Org. Lett.* **2003**, *5*, 801-802.

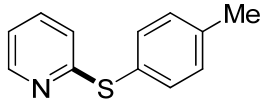


2-Phenyl-4-(phenylthio)quinazoline (6as). White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24-8.21 (m, 2H), 8.19-8.18 (m, 1H), 8.02 (d, J = 8.5 Hz, 1H), 7.86-7.83 (m, 1H), 7.73-7.69 (m, 2H), 7.59-7.51 (m, 4H), 7.41-7.34 (m, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 171.0, 159.0, 149.4, 137.7,

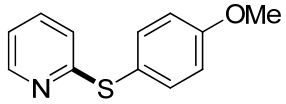
136.2, 133.7, 130.4, 129.5, 129.14, 129.10, 128.4, 128.3, 127.7, 126.8, 123.7, 122.0. This compound was known: B. Sreedhar, P. S. Reddy, M. A. Reddy, *Synthesis* **2009**, 1732-1738.



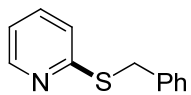
2-(Phenylthio)benzo[d]thiazole (6at). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, J = 8.0 Hz, 1H), 7.74-7.72 (m, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.52-7.44 (m, 3H), 7.40-7.37 (m, 1H), 7.26-7.23 (m, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 169.5, 153.9, 135.5, 135.2, 130.4, 130.0, 129.8, 126.1, 124.3, 121.9, 120.7. MS (EI): m/z (%) 243 (56), 242 (100), 209 (2), 121 (8), 108 (9), 82 (4), 77 (6), 65 (8), 51 (8). This compound was known: C. Dai, Z. Xu, F. Huang, Z. Yu, Y. Gao, *J. Org. Chem.* **2012**, *77*, 4414-4419.



2-(*p*-Tolythio)pyridine (6ba). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.39 (d, J = 4.5 Hz, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.42-7.39 (m, 1H), 7.22 (d, J = 8.0 Hz, 2H), 6. 95 (dd, J = 7.0 Hz, J = 5.0 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 162.1, 149.3, 139.3, 136.5, 135.1, 130.4, 127.1, 120.7, 119.5, 21.2. MS (EI): m/z (%) 202 (7), 201 (30), 200 (100), 199 (8), 100 (9), 91 (5), 79 (5), 78 (10), 77 (6), 65 (5), 63 (5), 51 (11). This compound was known: A. K. Verma, R. R. Jha, R. Chaudhary, R. K. Tiwari, A. K. Danodia, *Adv. Synth. Catal.* **2013**, *355*, 421-438.



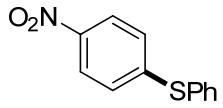
2-(4-Methoxyphenylthio)pyridine (6ca). Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.40 (d, J = 5.0 Hz, 1H), 7.55-7.52 (m, 2H), 7.44-7.41 (m, 1H), 6.98-6.94 (m, 3H), 6.79 (d, J = 8.0 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 162.8, 160.7, 149.4, 137.2, 136.6, 121.2, 120.5, 119.4, 115.3, 55.4. MS (EI): m/z (%) 218 (11), 217 (53), 216 (100), 202 (8), 201 (23), 186 (5), 174 (7), 173 (12), 78 (17), 73 (5), 70 (12), 63 (6), 61 (11), 51 (6). This compound was known: C. Robert Lucas. *Can. J. Chem.* **1986**, *64,* 1758-1763.



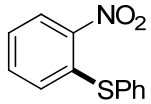
2-(Benzylthio)pyridine. (6da). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45-8.43 (m, 1H), 7.44-7.39 (m, 3H), 7.29-7.26 (m, 2H), 7.23-7.21 (m, 1H), 7.13 (d, J = 8.0 Hz, 1H), 6.97-6.94 (m, 1H), 4.43 (s, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 158.8, 149.3, 137.9, 135.9, 128.9, 128.4, 127.0,

122.0, 119.5, 34.4. MS (EI): m/z (%) 202 (9), 201 (65), 200 (5), 169 (14), 168 (100), 167 (23), 124 (8), 92 (5), 91 (49), 79 (13), 78 (4), 65 (17), 52 (4), 51 (5). This compound was known: K. Mai, G. Patil, *J. Org. Chem.* **1986**, *51*, 3545-3548.

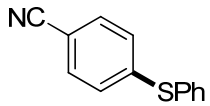
Typical Procedure of TBAC-Catalysed S_NAr Reaction of *p*-Chloronitrobenzene with Phenylthiotrimethylsilane for Diaryl Thioether Synthesis. The mixture of *p*-chloronitrobenzene **7a** (0.0788g, 0.5 mmol.), phenylthiotrimethylsilane **1a** (0.104 ml, 0.55 mmol, 1.1 equiv.), and TBAC (0.0417 g, 30 mol%) in DMF (0.5 mL) was sealed under nitrogen in a Schlenk tube (10 mL, the same apparatus as in the above picture) and then stirred at 150 ^oC for 43 h. The reaction was monitored by TLC and/or GC-MS. After completion of the reaction, solvent was evaporated under vacuum. The residue was then purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent. The target product **8a** was obtained in 95% isolated yield.



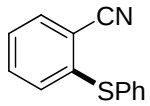
4-(Phenylthio)nitrobenzene (8a). Yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, J = 9.0 Hz, 2H), 7.55-7.52 (m, 2H), 7.47-7.44 (m, 3H), 7.16 (d, J = 9.0 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 148.4, 145.2, 134.7, 130.3, 129.9, 129.6, 126.5, 124.0. MS (EI): m/z (%) 233 (9), 232 (34), 231 (100), 186 (10), 185 (55), 173 (5), 115 (14), 109 (37), 93 (7), 77 (13), 69 (6), 65 (18), 51 (12). This compound was known: P. Guan, C. S. Cao, Y. Liu, Y. F. Li, P. He, Q. Chen, G. Liu, Y. H. Shi, *Tetrahedron Lett.* **2012**, *53*, 5987-5992.



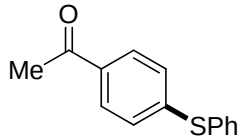
2-(Phenylthio)nitrobenzene (8b). Yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ 8.20 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H), 7.58-7.56 (m, 2H), 7.50-7.46 (m, 3H), 7.35-7.32 (m, 1H), 7.22-7.19 (m, 1H), 8.36 (dd, J = 8.0 Hz, J = 1.0 Hz, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 144.8, 139.4, 135.8, 133.4, 130.8, 130.05, 129.97, 128.3, 125.7, 124.9. MS (EI): m/z (%) 231 (13), 202 (11), 184 (26), 183 (6), 168 (15), 167 (100), 166 (39), 152 (16), 140 (10), 139 (19), 78 (8), 77 (20), 69 (7), 51 (13). This compound was known: A. Ivachtchenko, E. Golovina, M. Kadieva, O. Mitkin, S. Tkachenko, *Bioorg. Med. Chem.* **2013**, *21*, 4614-4627.



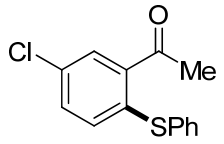
4-(Phenylthio)benzonitrile (8c). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52-7.49 (m, 2H), 7.46 (d, J = 6.5 Hz, 2H), 7.44-7.42 (m, 3H), 7.16 (d, J = 6.5 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 145.7, 134.5, 132.3, 130.7, 129.9, 129.3, 127.2, 118.7, 108.6. MS (EI): m/z (%) 213 (6), 212 (18), 211 (100), 210 (67), 209 (13), 184 (8), 183 (12), 171 (5), 109 (8), 92 (11), 77 (21), 69 (6), 65 (9), 51 (26), 50 (6). This compound was known: P. Guan, C. S. Cao, Y. Liu, Y. F. Li, P. He, Q. Chen, G. Liu, Y. H. Shi, *Tetrahedron Lett.* **2012**, *53*, 5987-5992.



2-(Phenylthio)benzonitrile (8d). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (dd, J = 7.5 Hz, J = 1.0 Hz, 1H), 7.47-7.45 (m, 2H), 7.42-7.37 (m, 4H), 7.27-7.24 (m, 1H), 7.12 (d, J = 8.0 Hz, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 142.2, 133.6, 133.5, 132.9, 131.7, 129.8, 129.7, 128.8, 126.4, 116.9, 112.7. MS (EI): m/z (%) 212 (17), 211 (100), 210 (50), 209 (9), 185 (8), 184 (41), 183 (9), 109 (8), 108 (6), 92 (10), 77 (26), 69 (7), 65 (10), 51 (28), 50 (6). This compound was known: P. Guan, C. S. Cao, Y. Liu, Y. F. Li, P. He, Q. Chen, G. Liu, Y. H. Shi, *Tetrahedron Lett.* **2012**, *53*, 5987-5992.

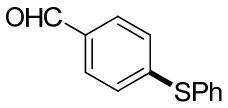


4-(Phenylthio)acetophenone (8e). Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, J = 8.5 Hz, 1H), 7.50-7.48 (m, 2H), 7.42-7.36 (m, 3H), 7.20 (d, J = 8.5 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 197.1, 144.9, 134.4, 133.8, 132.0, 129.6, 128.9, 128.7, 127.4, 26.4. MS (EI): m/z (%) 229 (13), 228 (76), 214 (15), 213 (100), 185 (19), 184 (69), 152 (14), 109 (7), 107 (7), 92 (6), 91 (6), 77 (7), 65 (9), 51 (10). This compound was known: S. G. Babu, R. Karvembu, *Tetrahedron Lett.* **2013**, *54*, 1677-1680.



5-Chloro-2-(phenylthio)acetophenone (8f). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, J = 2.5 Hz, 1H), 7.52-7.49 (m, 2H), 7.43-7.41 (m, 3H), 7.20 (dd, J = 8.5 Hz, J = 2.5 Hz, 1H), 6.82 (d, J = 8.5 Hz, 1H), 2.65 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 198.0, 140.2, 135.9, 134.8, 132.8, 131.9, 130.3, 130.1, 129.8, 129.1, 28.2. MS (EI): m/z (%) 264 (35), 263 (17), 262 (100), 249 (22), 247 (57), 212 (52), 185 (31), 184 (67), 183 (17), 173 (22), 171 (60), 152 (17), 139 (33), 77 (13), 69 (11), 51 (20). This compound was known: M. Rajsner, F. Miksik, M. Protiya, *Collection Czechoslov.*

Chern. Commun. **1978**, *43*, 1276-1284.



4-(Phenylthio)benzaldehyde (8g). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.91 (s, 1H), 7.72 (d, J = 8.5 Hz, 2H), 7.54-7.52 (m, 2H), 7.44-7.41 (m, 3H), 7.23 (d, J = 8.0 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 191.1, 147.2, 134.3, 133.7, 131.4, 130.1, 129.8, 129.1, 127.3. MS (EI): m/z (%) 216 (6), 215 (18), 214 (100), 213 (53), 186 (9), 185 (37), 184 (57), 152 (14), 109 (8), 77 (12), 69 (7), 65 (10), 51 (19), 50 (7). This compound was known: S. G. Babu, R. Karvembu, *Tetrahedron Lett.* **2013**, *54*, 1677-1680.

Detailed Procedure for Large Scale Reaction of 2-Chloropyridine and Phenylthiotrimethylsilane Catalysed by TBAC (eq. 1 in the text). A normal distillation apparatus was installed by equipping pre-dried glasswares, such as 50 mL round-bottomed flask with a stirrer, distillation head, condenser, receiving flask, etc. To the round-bottomed flask was added dry TBAC (1.3896 g, 10 mol%). The apparatus was then degassed and charged with nitrogen. Under a flow of nitrogen, 2-chloropyridine **3a** (4.7 mL, 50 mmol) and phenylthiotrimethylsilane **1a** (9.5 mL, 50 mmol, 1 equiv.) was successively added via syringes with long needles to the round-bottomed flask. The solvent-free mixture was firstly stirred and heated under nitrogen at 100 ^{o}C for 2 h. The mixture was then heated to 120 ^{o}C to distill out the byproduct trimethylchlorosilane (Me_3SiCl). In another 4 h at 120 ^{o}C, Me_3SiCl was obtained as colorless liquid, and the distillation ceased to finally give a recovery yield of 4.89g (90%) of Me_3SiCl, which was then characterized by ^{1}H and ^{13}C NMR analysis in dry $CDCl_3$. The residue of the reaction mixture in the round-bottomed flask was monitored by TLC and GC-MS, showing complete conversion of 2-chloropyridine and phenylthiotrimethylsilane. Column chromatography of the reaction residue gave 8.60 g (92% isolated yield) of **6aa**. See Figure S1 in the next page for the distillation apparatus and the freshly collected Me_3SiCl.

Large Scale Reaction of 4-Chloronitrobenzene and Phenylthiotrimethylsilane Catalysed by TBAC (eq. 2 in the text). The same procedure as above was then applied to a neat large scale reaction of 4-chloronitrobenzene **7a** (3.94 g, 25 mmol) and phenylthiotrimethylsilane **1a** (4.75 mL, 25 mmol, 1 equiv.) in the presence of TBAC (2.09 g, 30 mol%). The mixture was firstly heated at 100 ^{o}C for 1 h and then 120 ^{o}C for 2 h under nitrogen to complete the distillation process, which finally gave 2.26 g (83%) of colourless Me_3SiCl. TLC analysis of the reaction residue showed

complete conversion of the reactants. Column chromatography of the reaction residue gave 5.31 g (92% isolated yield) of **8a**.

Large Scale Reaction of 2-Bromopyridine and Phenylthiotrimethylsilane Catalysed by TBAB (eq. 3 in the text). The same procedure as above was then applied to a neat large scale reaction of 2-bromopyridine **4a** (1.9 mL, 20 mmol) and phenylthiotrimethylsilane **1a** (3.8 mL, 20 mmol, 1 equiv.) in the presence of TBAB (0.645 g, 10 mol%). The mixture was firstly heated at 100-140 ^{o}C under nitrogen for 1 h, but no liquid could be distilled during the time. The mixture was then heated at more than 140 ^{o}C, at 140-150 ^{o}C. Small amounts of white crystal first appeared in the condenser pipe. A colourless liquid was then distilled as the heating continued. After heated at 140-150 ^{o}C for 4 h, the distillation stopped to finally gave 1.60 g (52%) of colourless Me_3SiBr. TLC analysis of the reaction residue showed complete conversion of the reactants. Column chromatography of the reaction residue gave 3.18 g (85% isolated yield) of **6aa**. Me_3SiBr is a highly moisture-sensitive chemical with pungent smell and easy to fog and decompose when exposed to air.

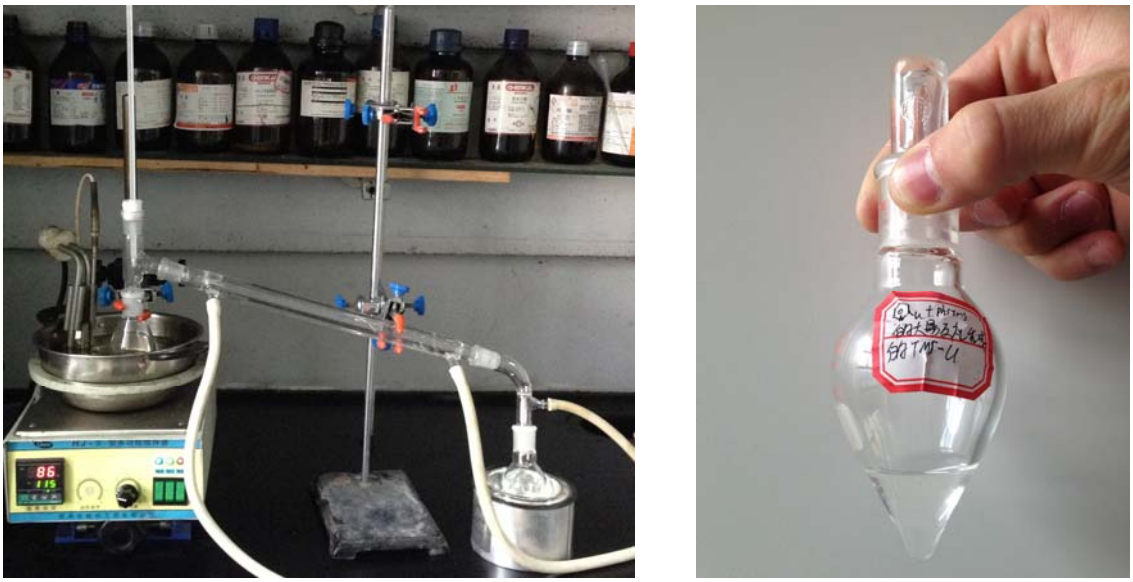


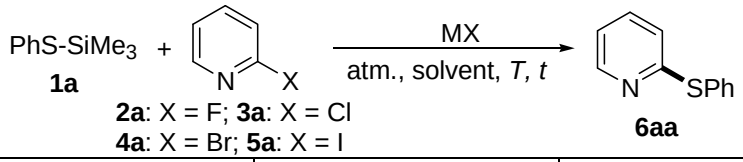
Figure S1. Left: the distillation apparatus; **Right:** freshly recovered Me_3SiCl

Trimethylcholorosilane (Me_3SiCl). Colorless liquid. ^{1}H NMR (500 MHz, dry $CDCl_3$): δ 0.44 (S, 9H). ^{13}C NMR (125.4 MHz, dry $CDCl_3$): δ 3.2. Consistent with the known data:

(a) http://www.sigmaaldrich.com/spectra/fnmr/FNMR009798.PDF.

(b) http://www.hanhonggroup.com/nmr/nmr_en/RB05010008.html.

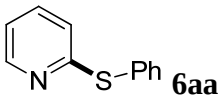
Table S1. Condition Optimization for TBAX-Catalysed S-Si Bond Activation in S_NAr Reaction of PhS-SiMe$_3$ (**1a**) and 2-Halopyridines (**2a**-**5a**).[a]



run	X	MX (mol%)	Solvent	*T, t*	**6aa**%[b]
1	F	TBAF (30)	CH_3CN	30 °C, 24 h	trace
2	F	TBAF (30)	CH_3CN	60 °C, 24 h	78
3	Cl	TBAF (30)	CH_3CN	60 °C, 24 h	30
4	Cl	TBAF (120)	CH_3CN	30 °C, 24 h	trace
5	Cl	TBAF (120)	CH_3CN	60 °C, 24 h	92
6	Cl	TBAF (30)	CH_3CN	80 °C, 24 h	(63)
7	Cl	TBAF (30)	CH_3CN	100 °C, 24 h	87 (96)
8	Cl	CsF (30)	CH_3CN	100 °C, 24 h	(23)
9	Cl	NaF (30)	CH_3CN	100 °C, 24 h	(8)
10	Cl	KF (30)	CH_3CN	100 °C, 24 h	(70)
11	Cl	—	CH_3CN	100 °C, 24 h	(0)
12	Cl	TBAF (30)	CH_3CN (under air)	100 °C, 24 h	trace
13	Br	TBAF (30)	CH_3CN	100 °C, 24 h	71
14	I	TBAF (30)	CH_3CN	100 °C, 24 h	76
15	Cl	TBAC (30)	CH_3CN	100 °C, 48 h	92
16	Cl	TBAB (30)	CH_3CN	100 °C, 48 h	94
17	Cl	TBAI (30)	CH_3CN	100 °C, 48 h	84
18	Cl	TBAB (20)	CH_3CN	100 °C, 48 h	96
19	Cl	TBAB (10)	CH_3CN	100 °C, 48 h	96
20	Cl	TBAB (10)	DMF	100 °C, 48 h	90
21	Cl	TBAB (10)	DMSO	100 °C, 48 h	15
22	Cl	TBAB (10)	Toluene	100 °C, 48 h	76
23	Cl	TBAB (10)	THF	100 °C, 48 h	78
24	Cl	TBAB (10)	Dioxane	100 °C, 48 h	84

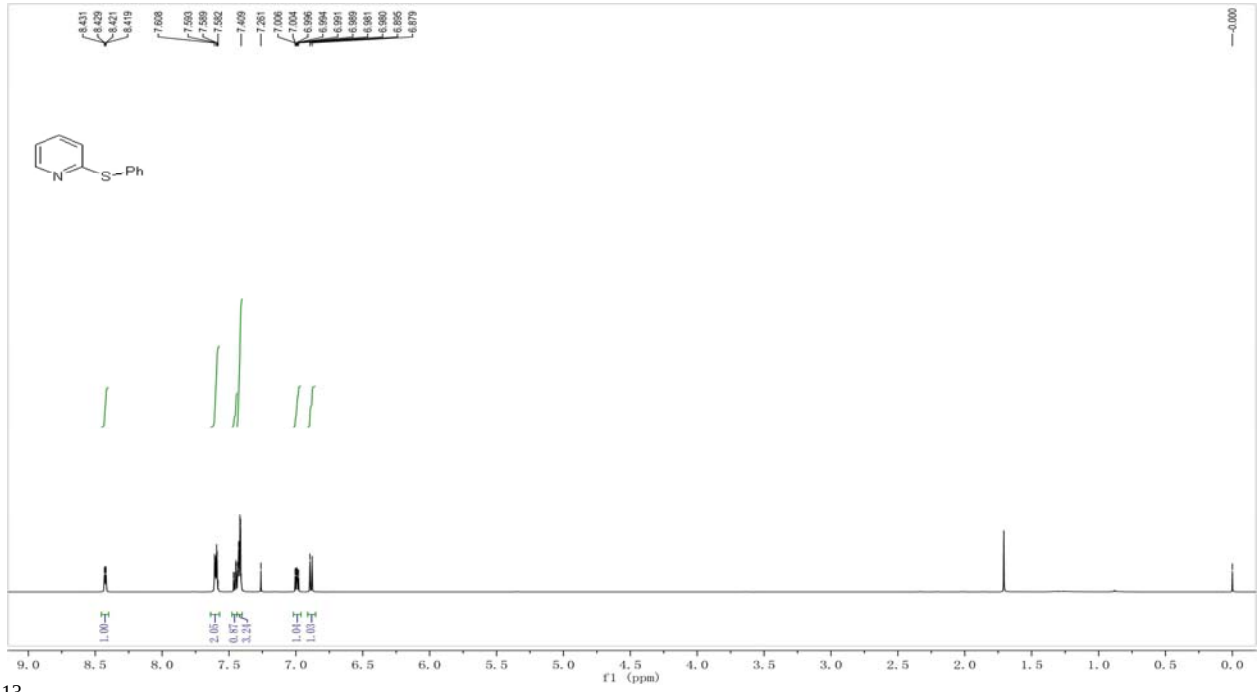
[a] The mixture of **1a** (0.55 mmol, 1.1 equiv.), **2a** (0.5 mmol), and MX salt in a solvent (0.5 mL) was sealed under air or N_2 in a 10 mL Schlenk tube and then heated and monitored by TLC and/or GC-MS. [b] Isolated yields (GC yields in parenthesis) are based on **2a**-**5a**.

^{1}H NMR and ^{13}C NMR Spectra of All Compounds

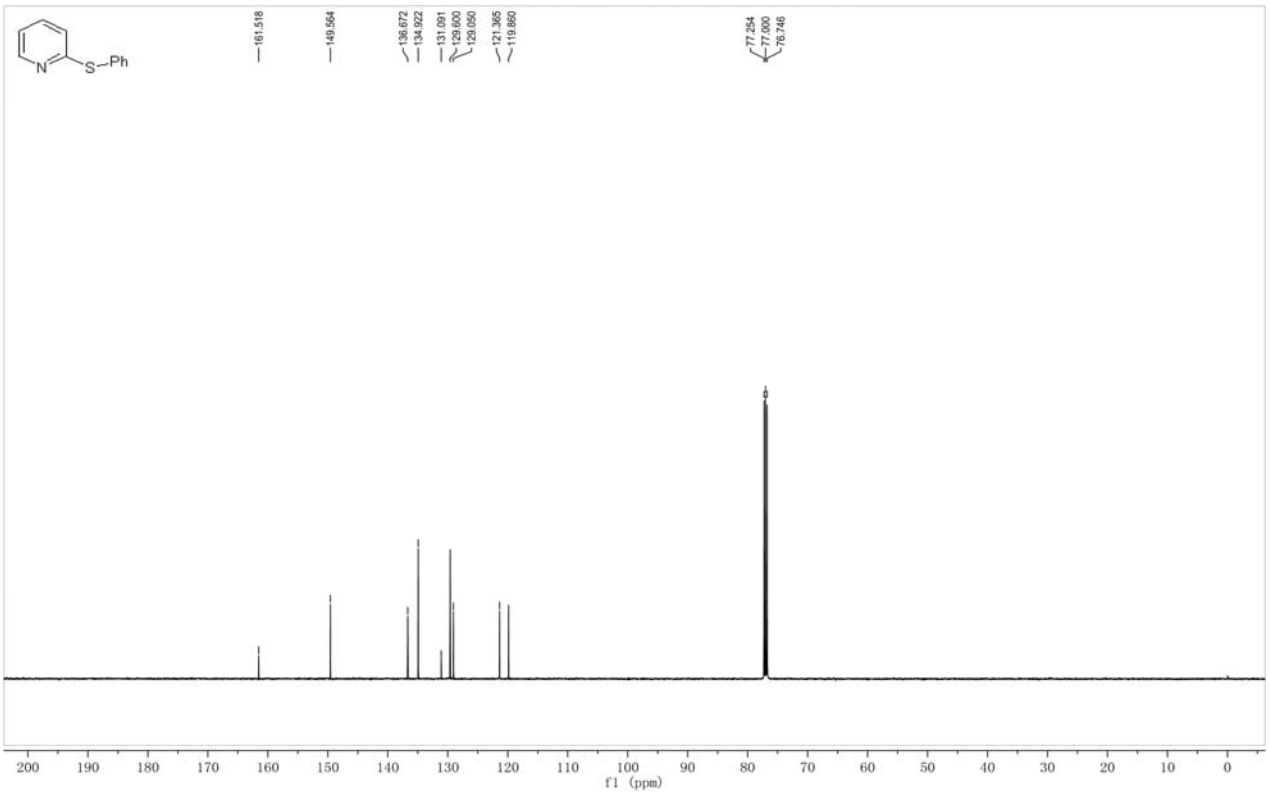


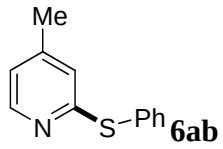
6aa

^{1}H NMR



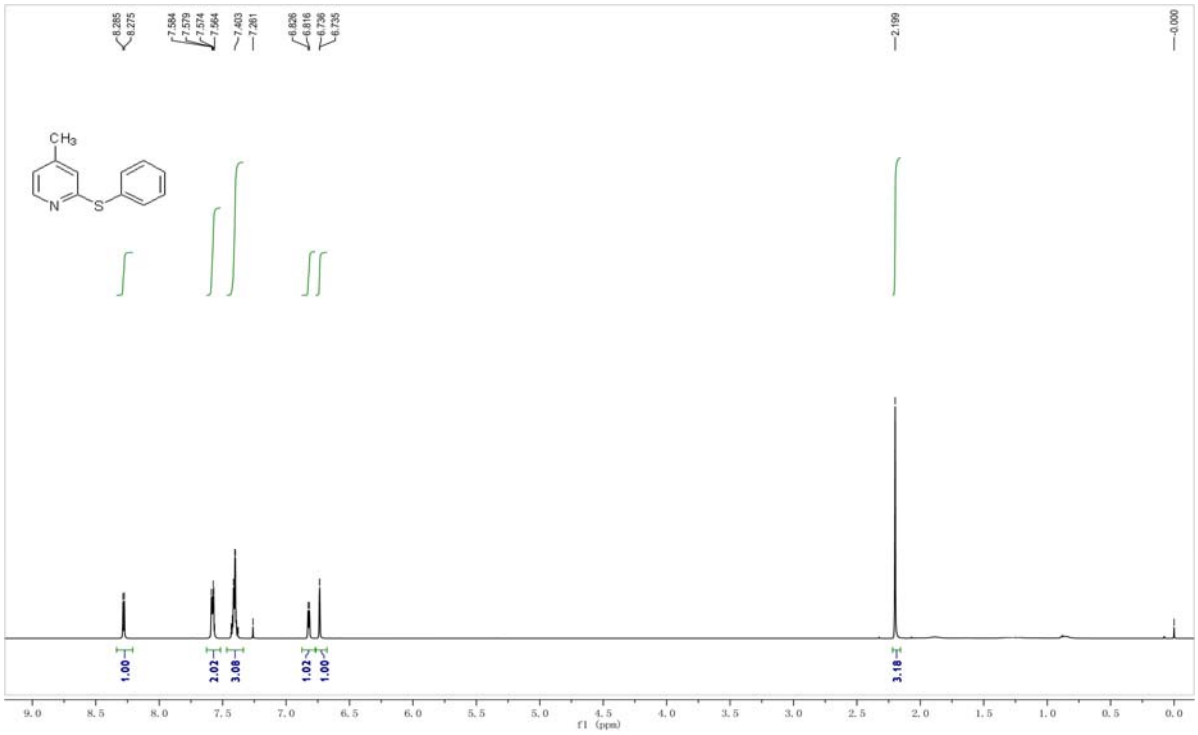
^{13}C NMR



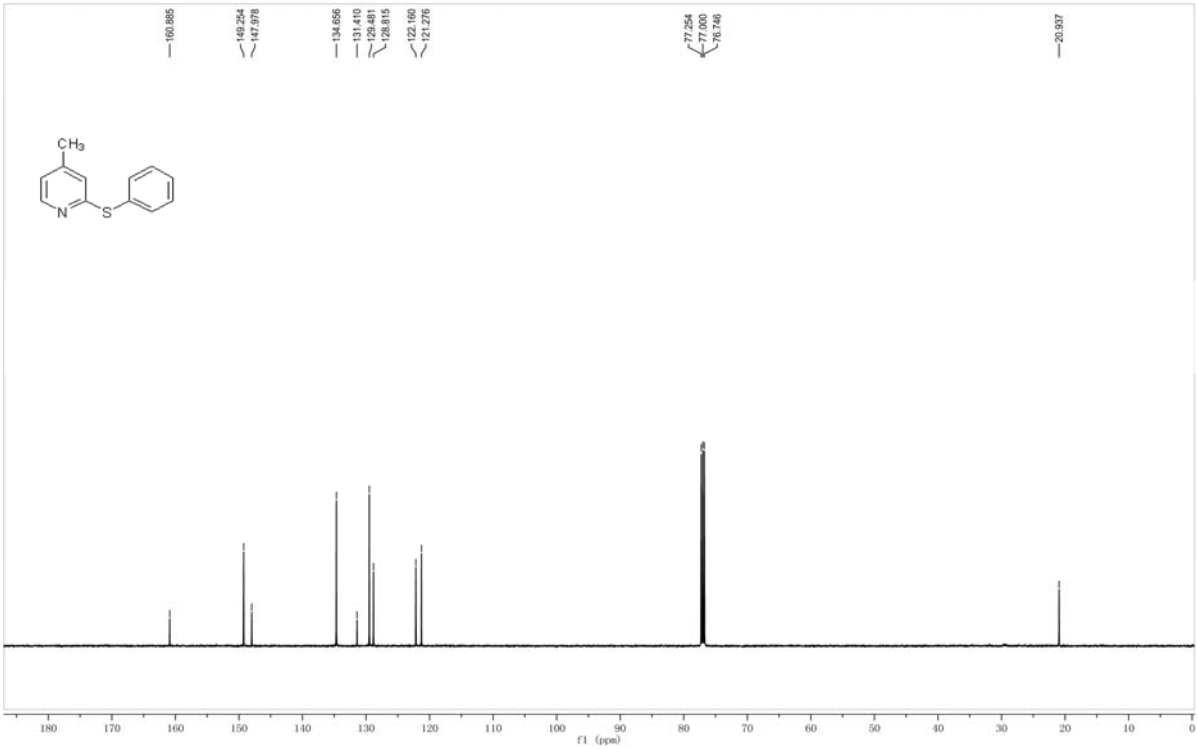


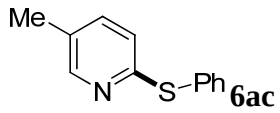
6ab

^{1}H NMR



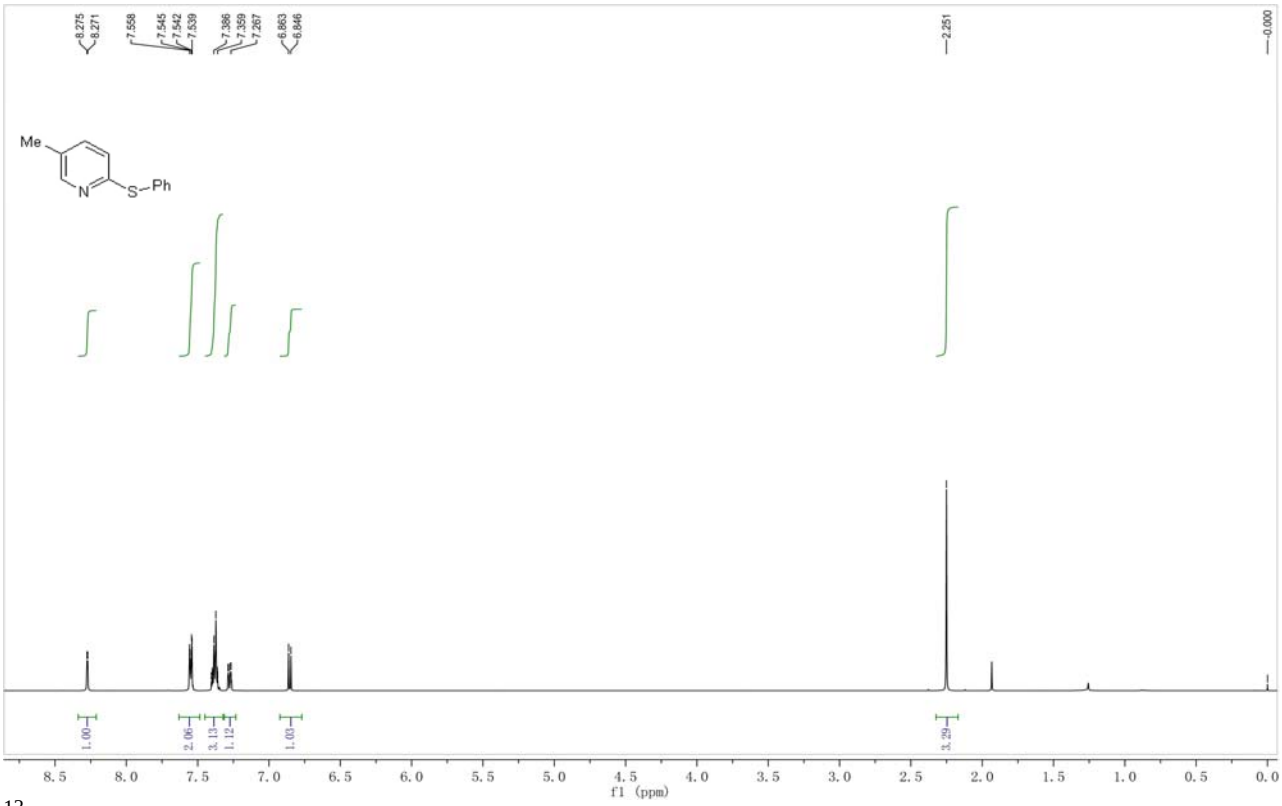
^{13}C NMR





6ac

^{1}H NMR



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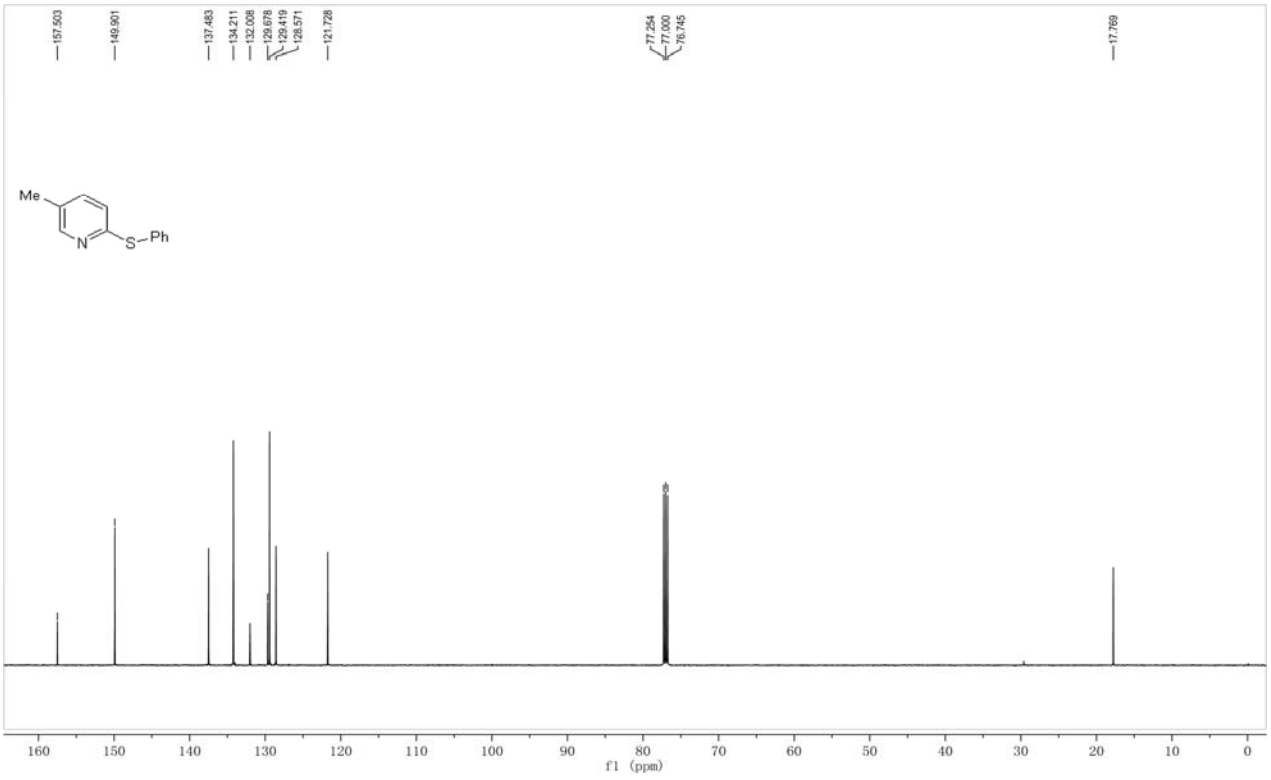
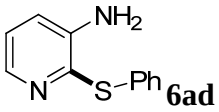
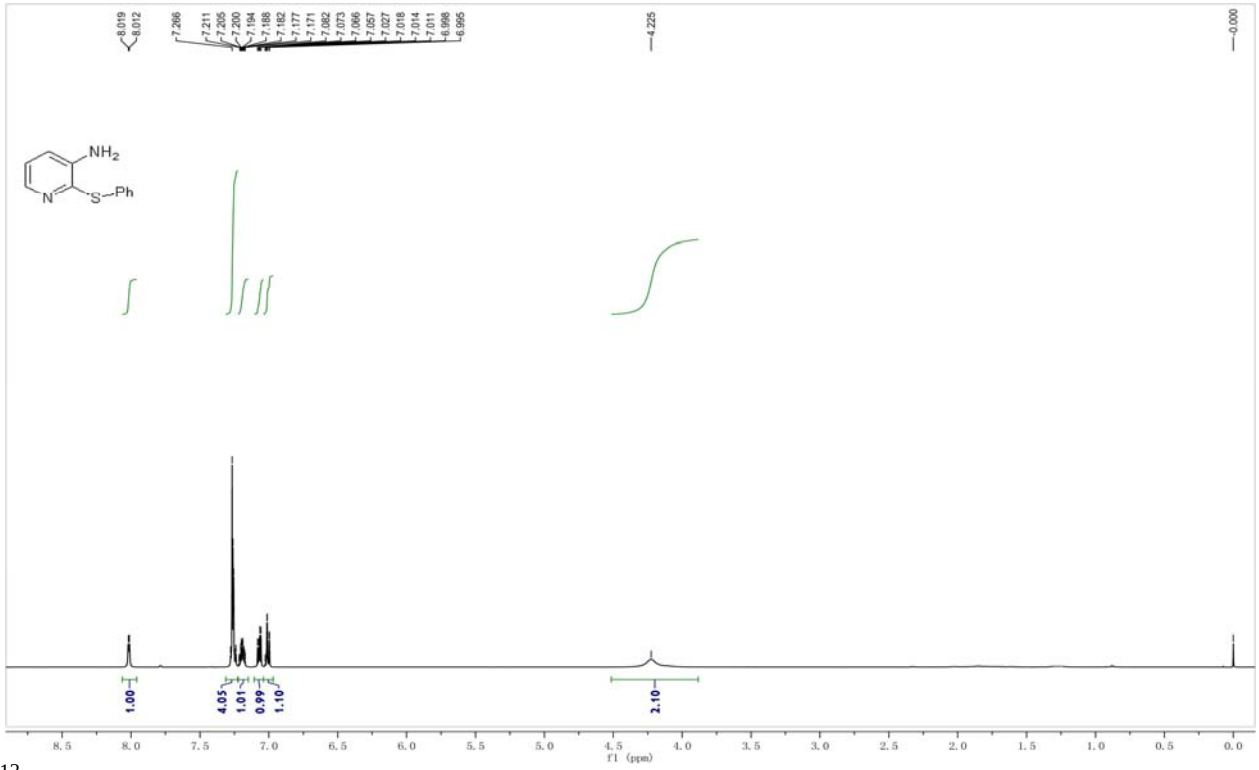


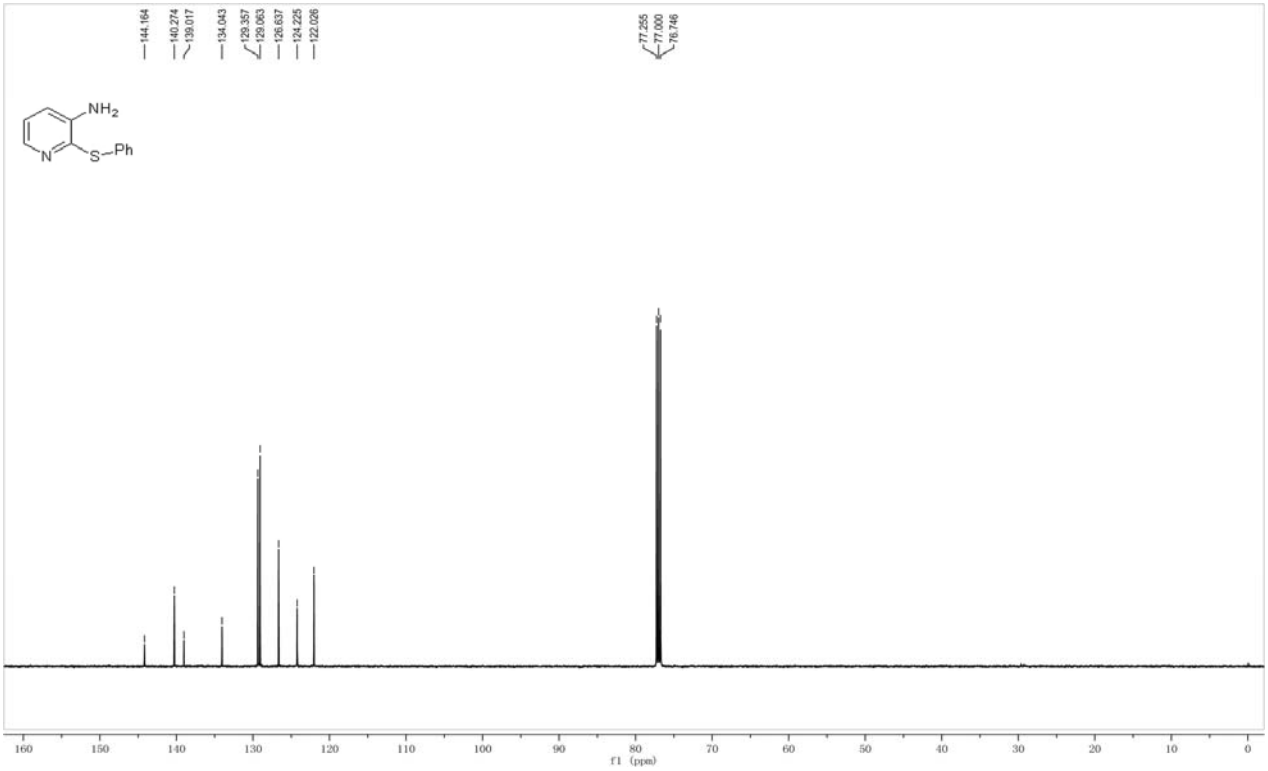


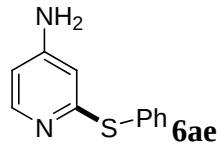
6ad

^{1}H NMR



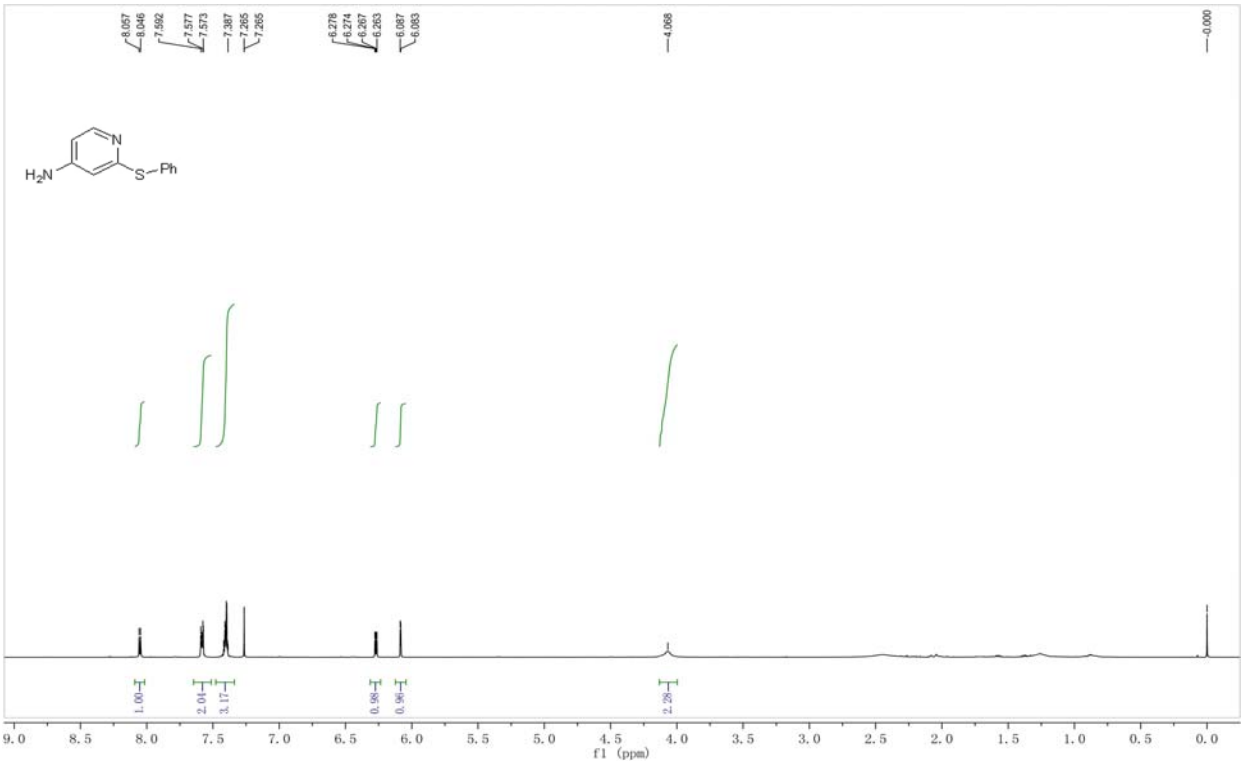
^{13}C NMR



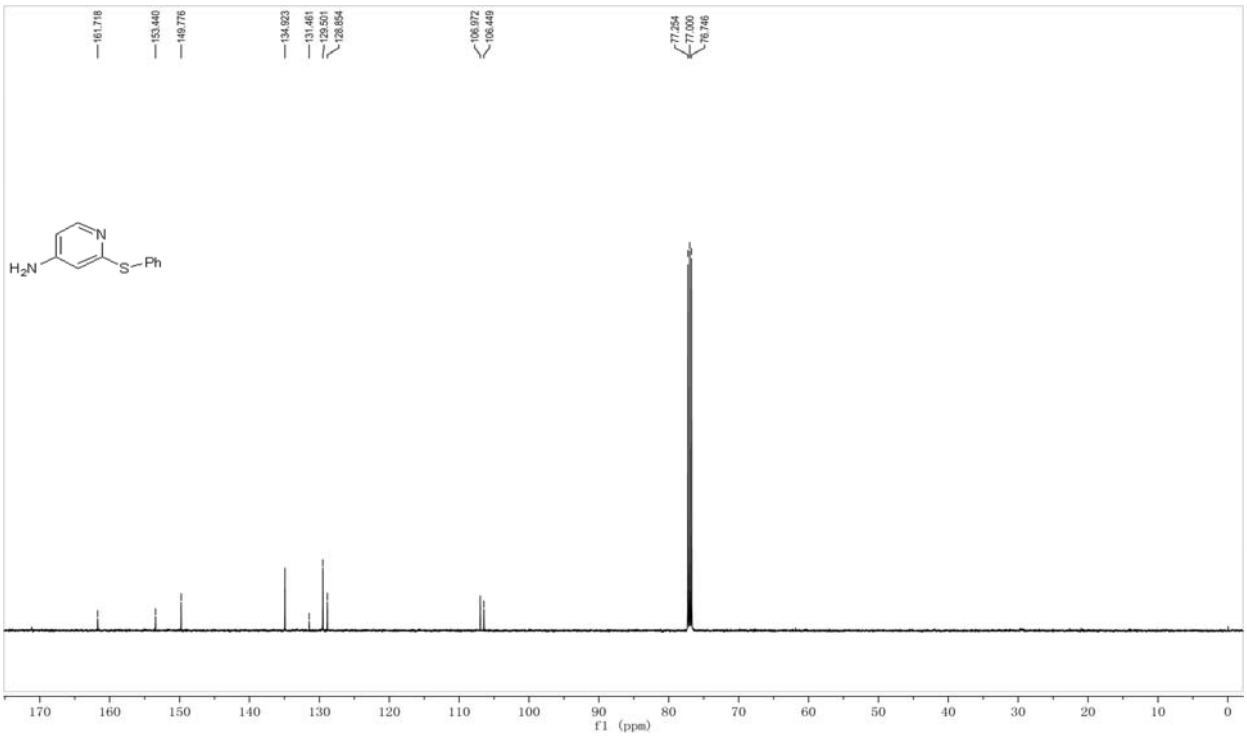


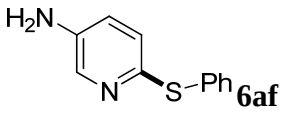
6ae

^{1}H NMR



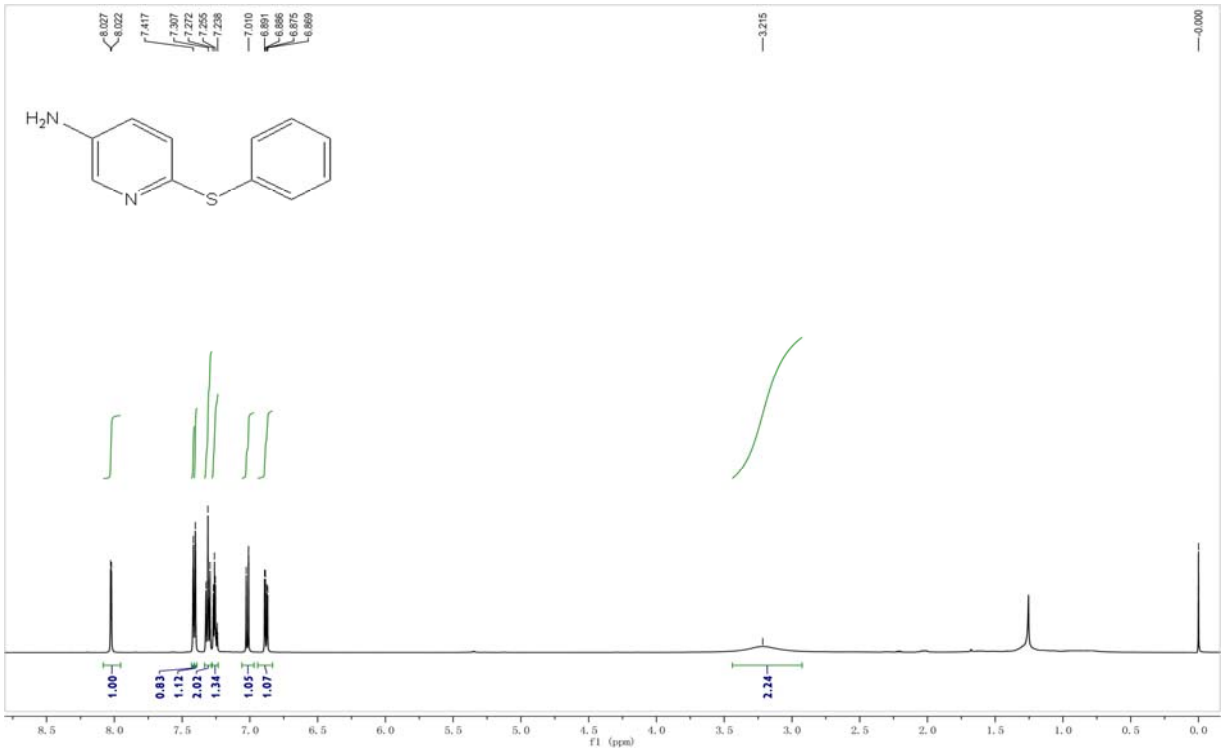
^{13}C NMR



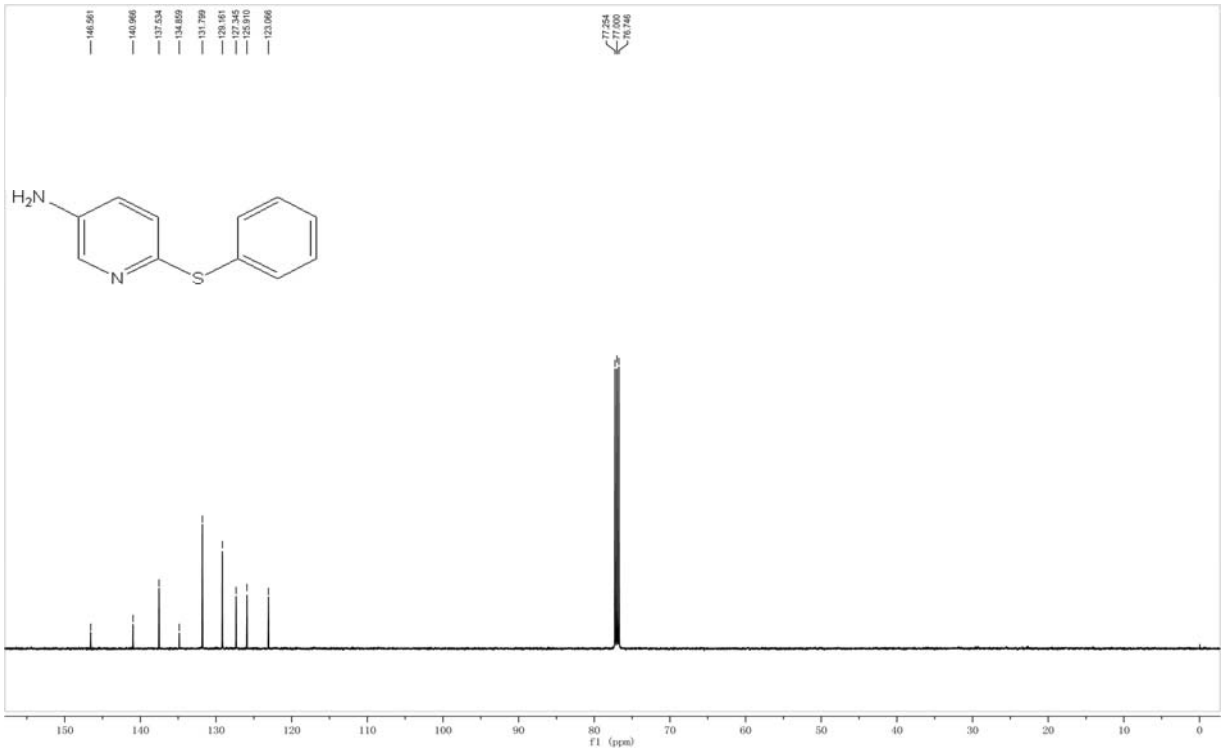


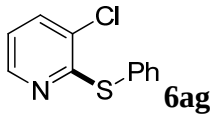
6af

^{1}H NMR



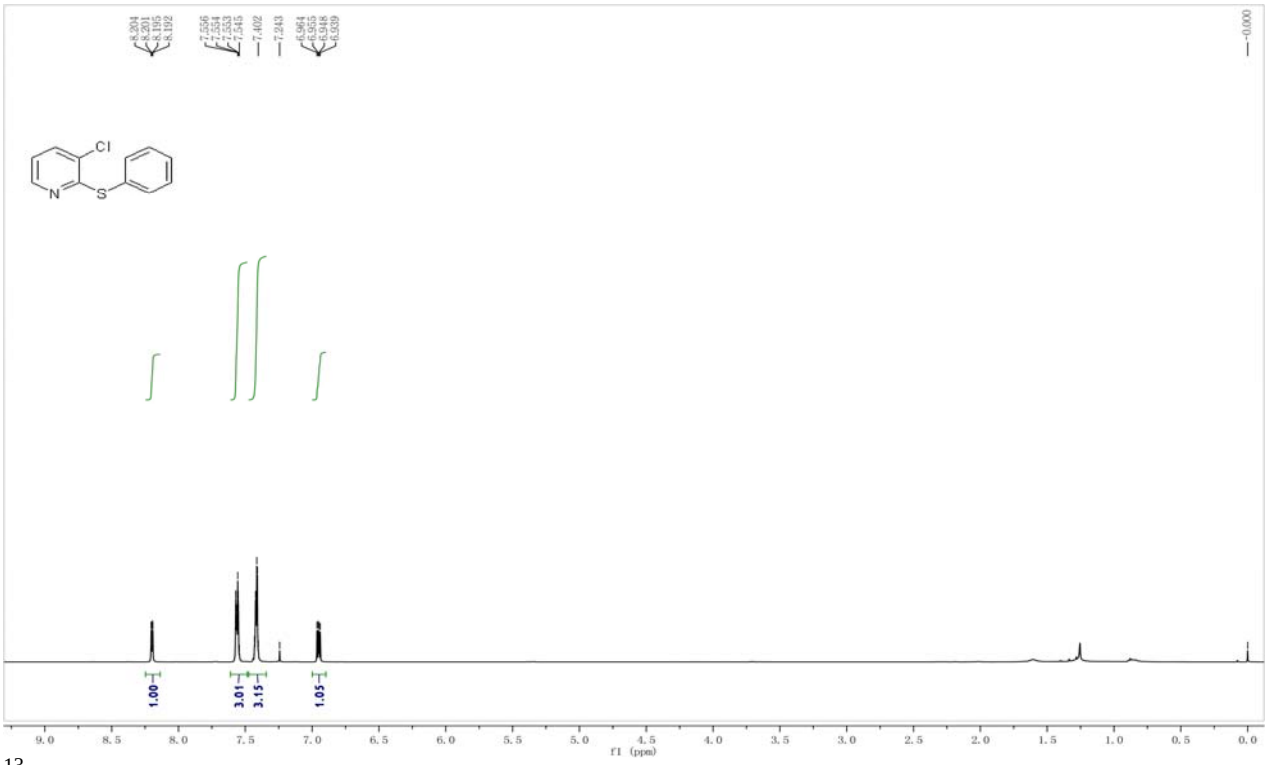
^{13}C NMR





6ag

^{1}H NMR



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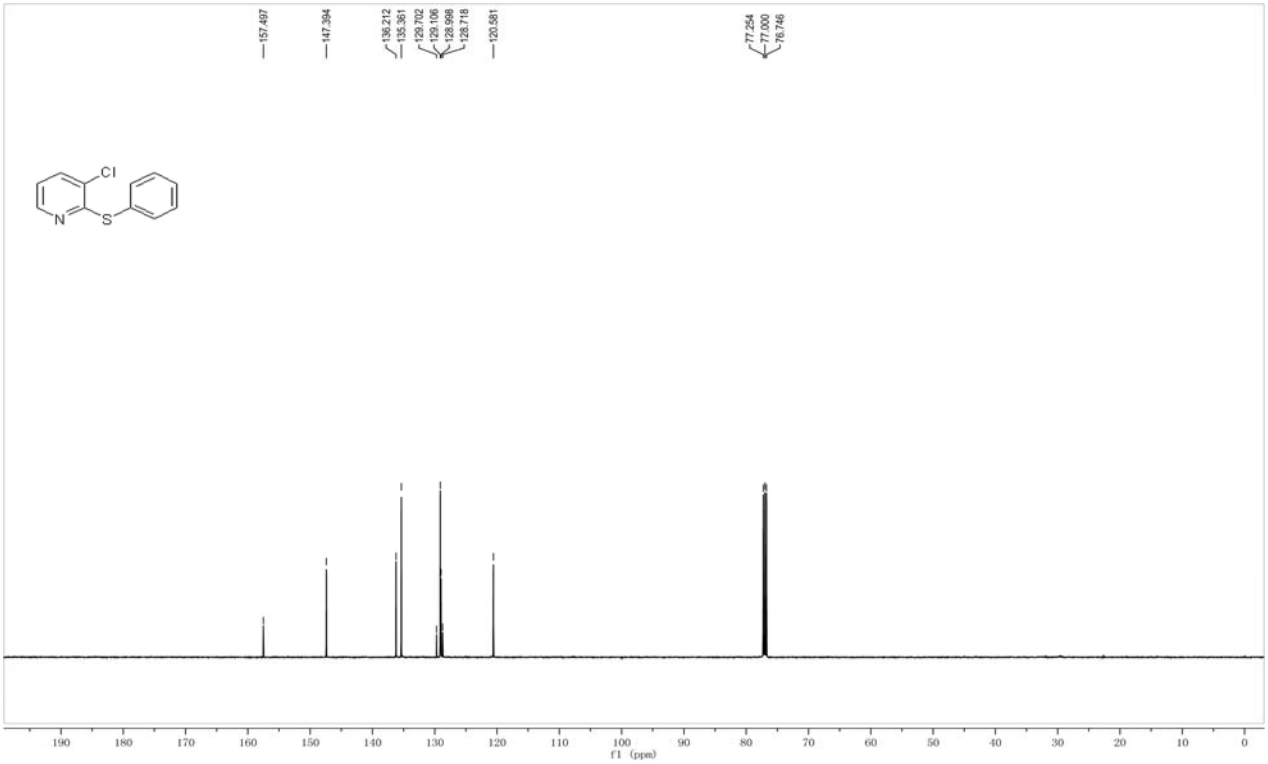

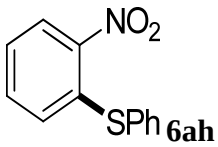

6ah

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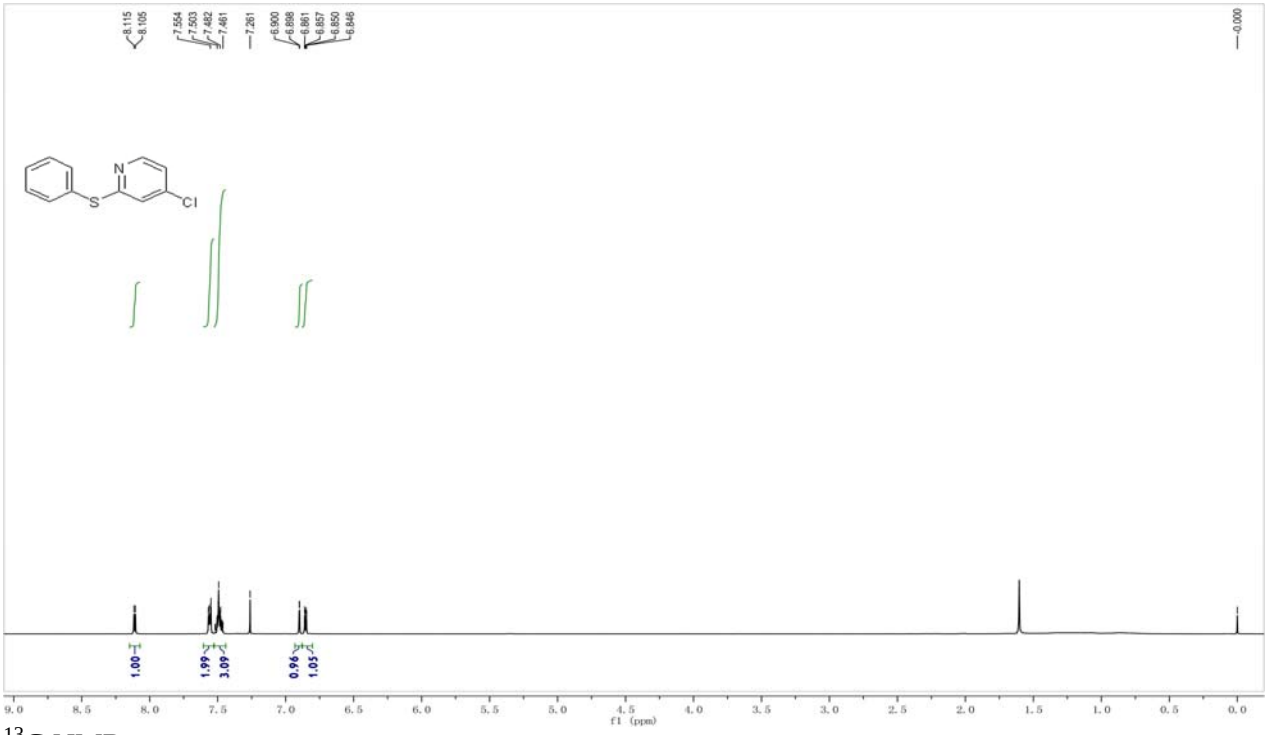

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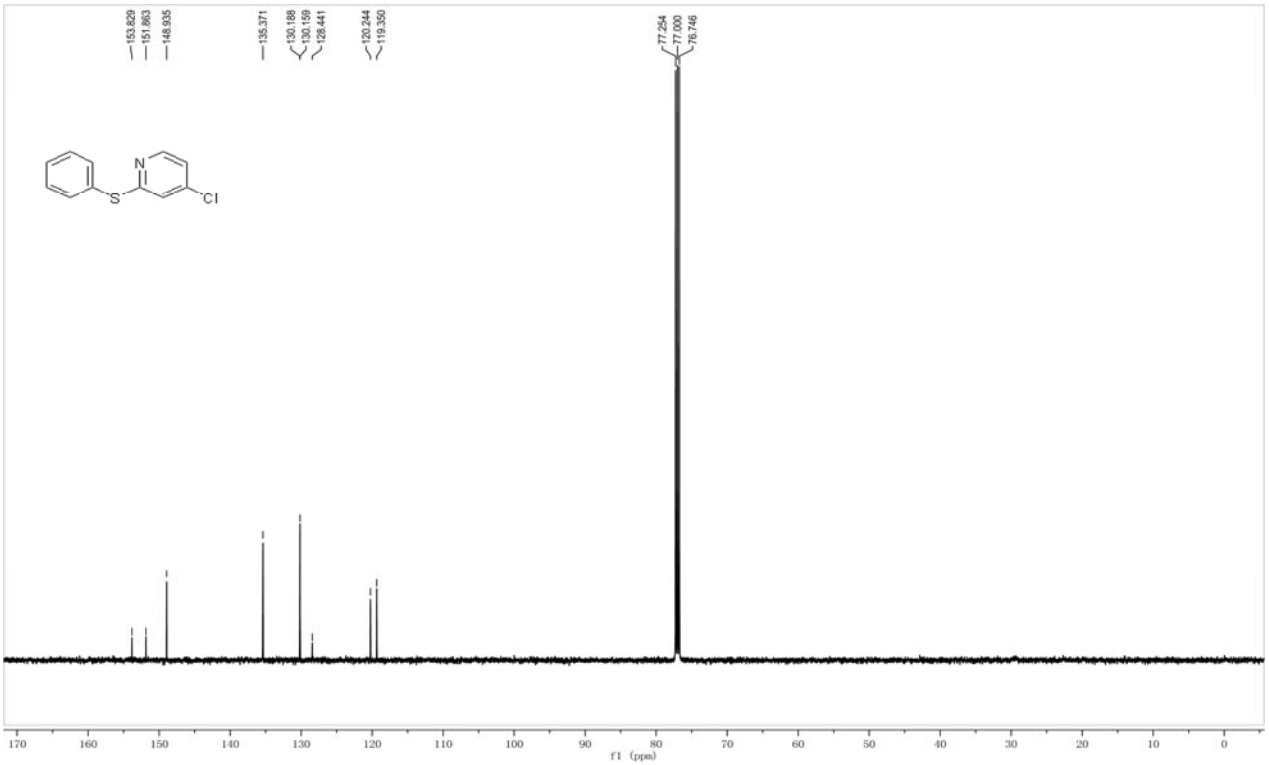

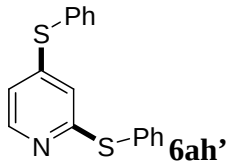

6ah'

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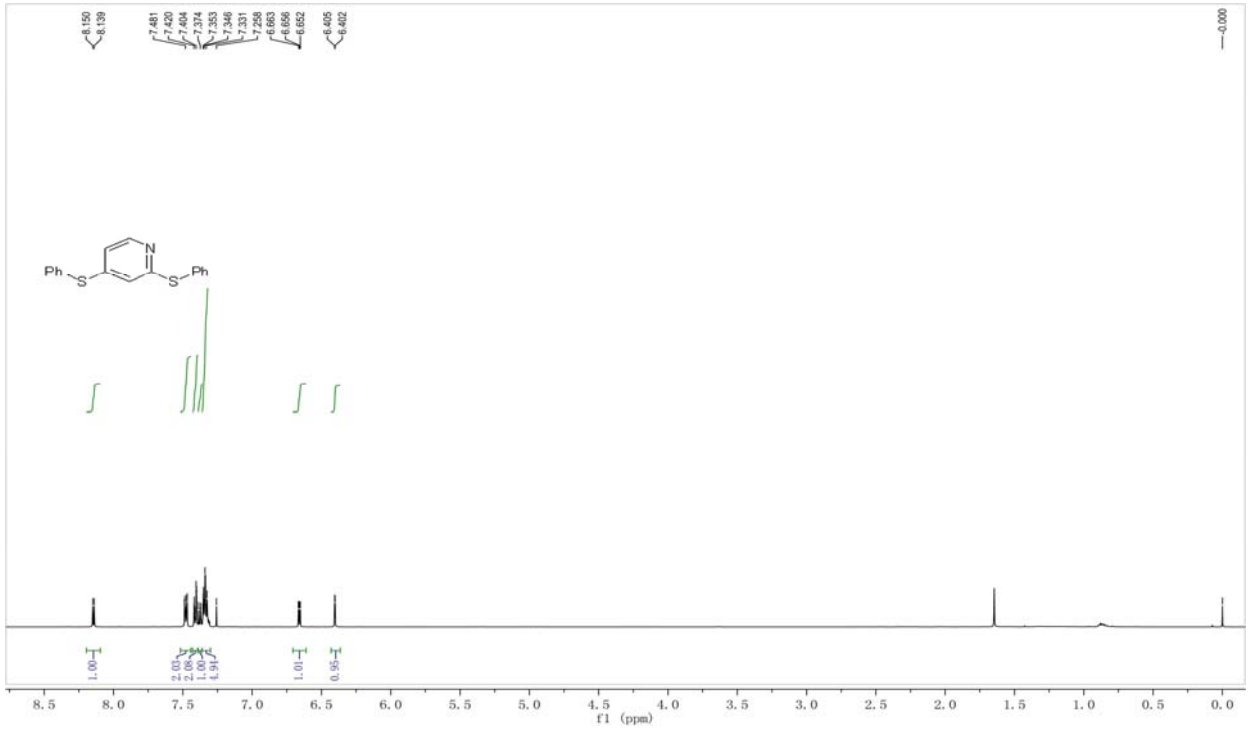

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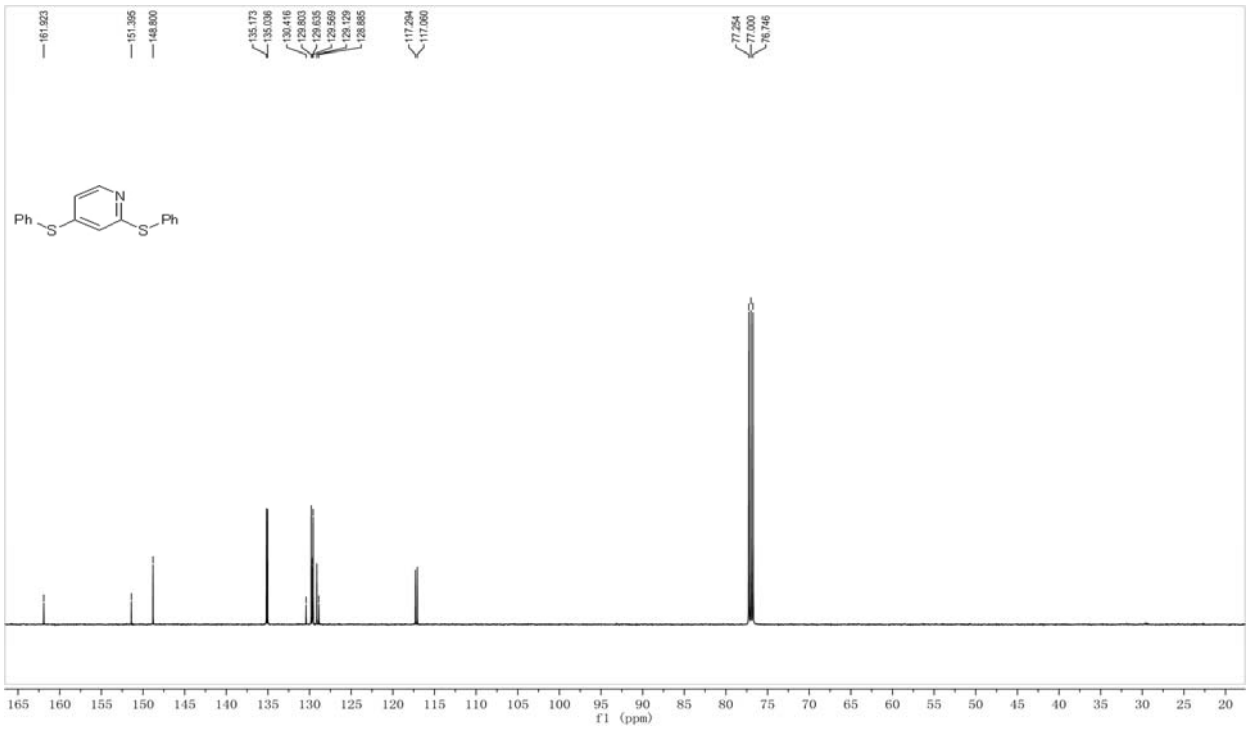

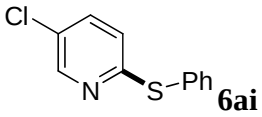

6ai

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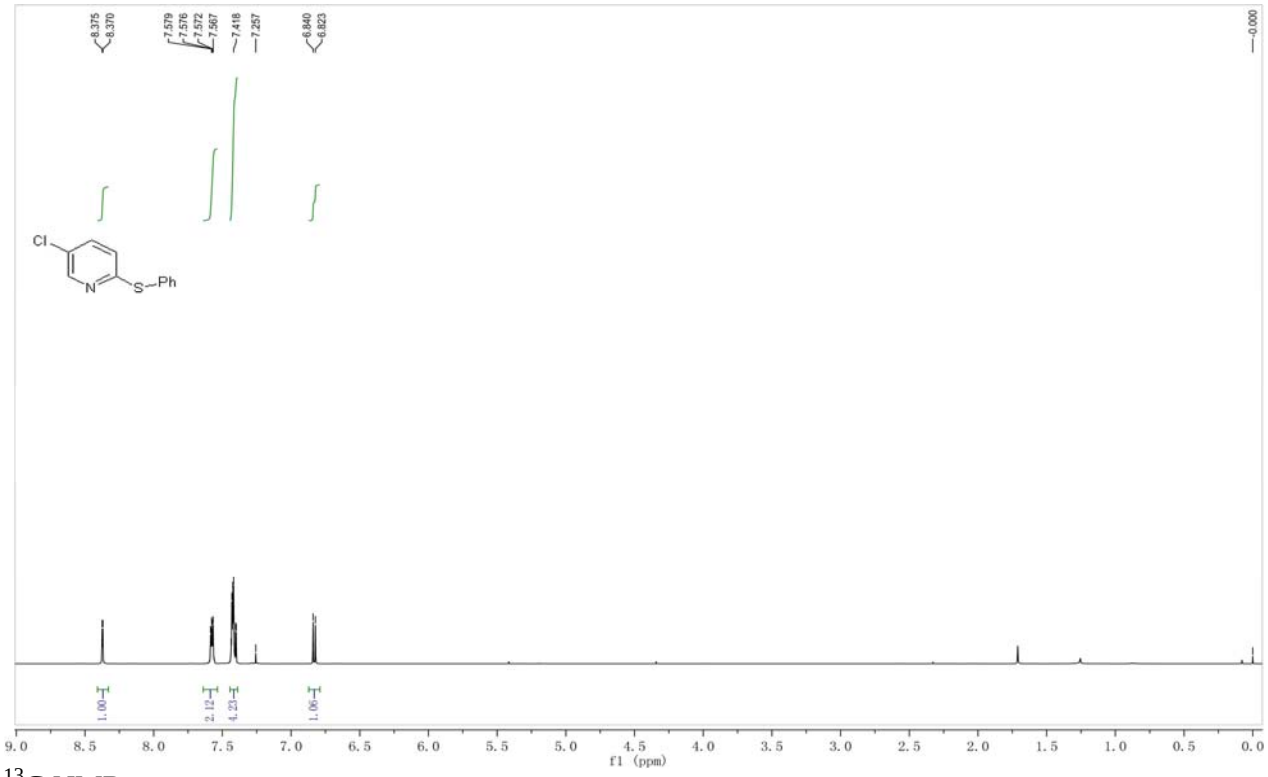

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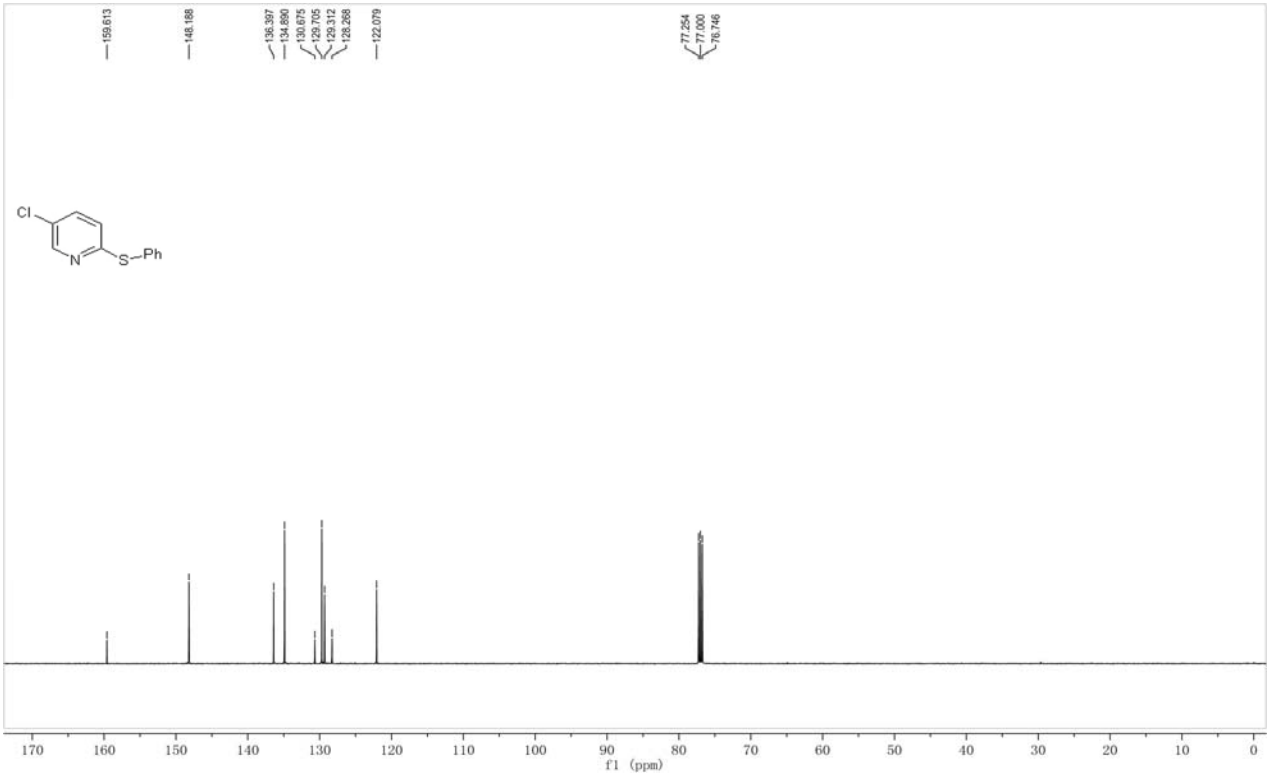
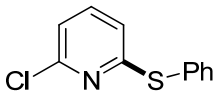
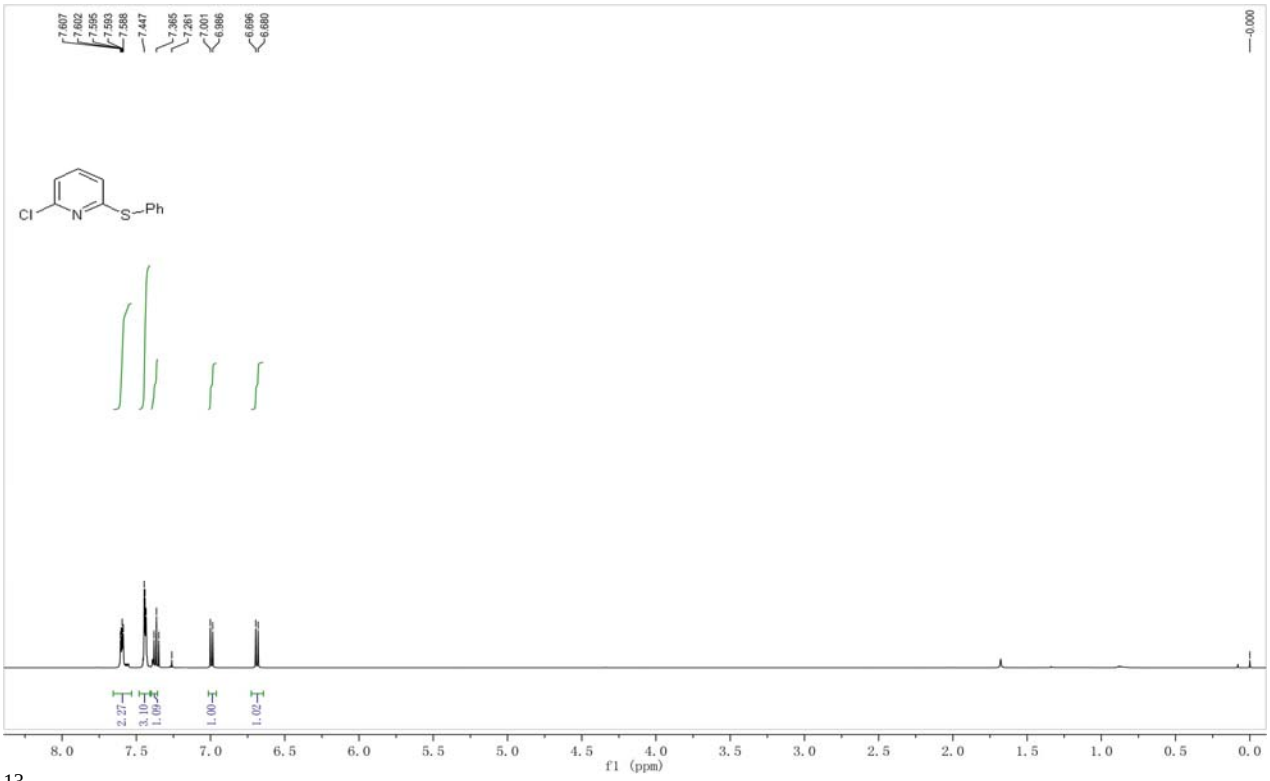




6aj

^{1}H NMR



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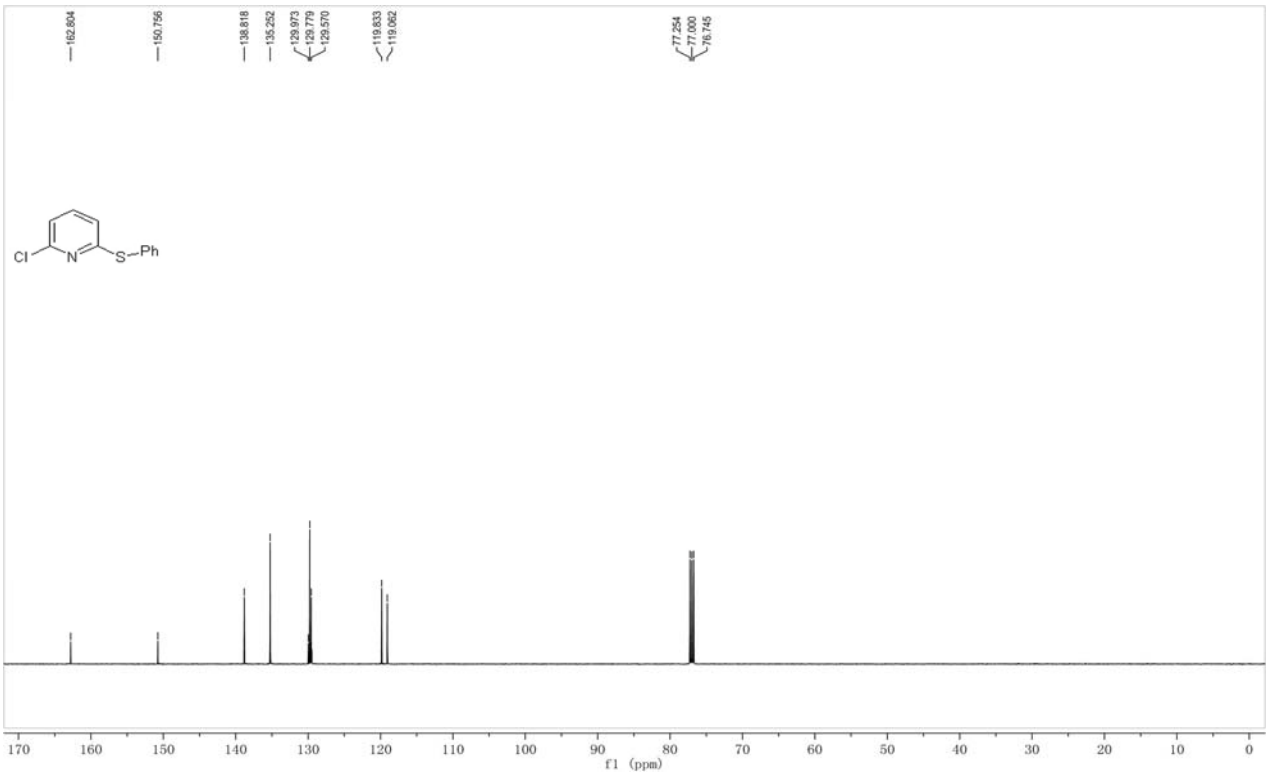

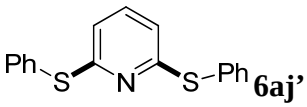

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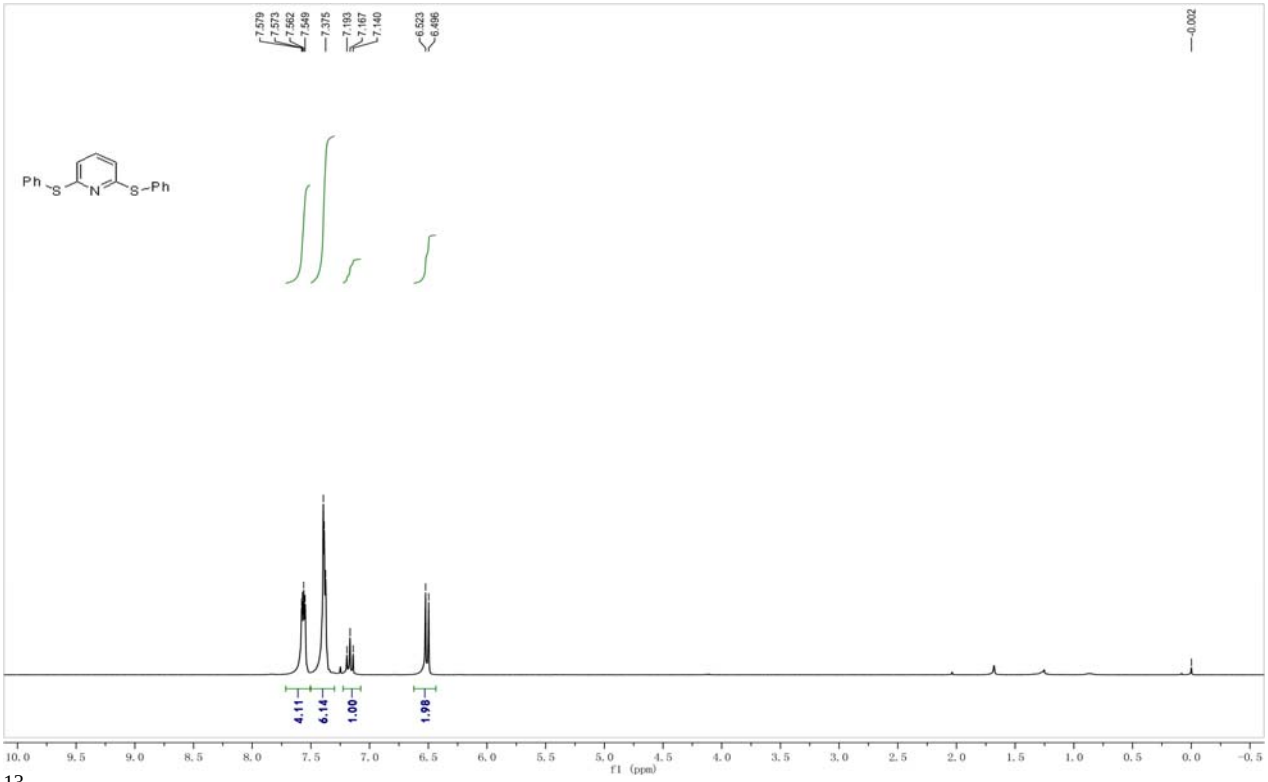

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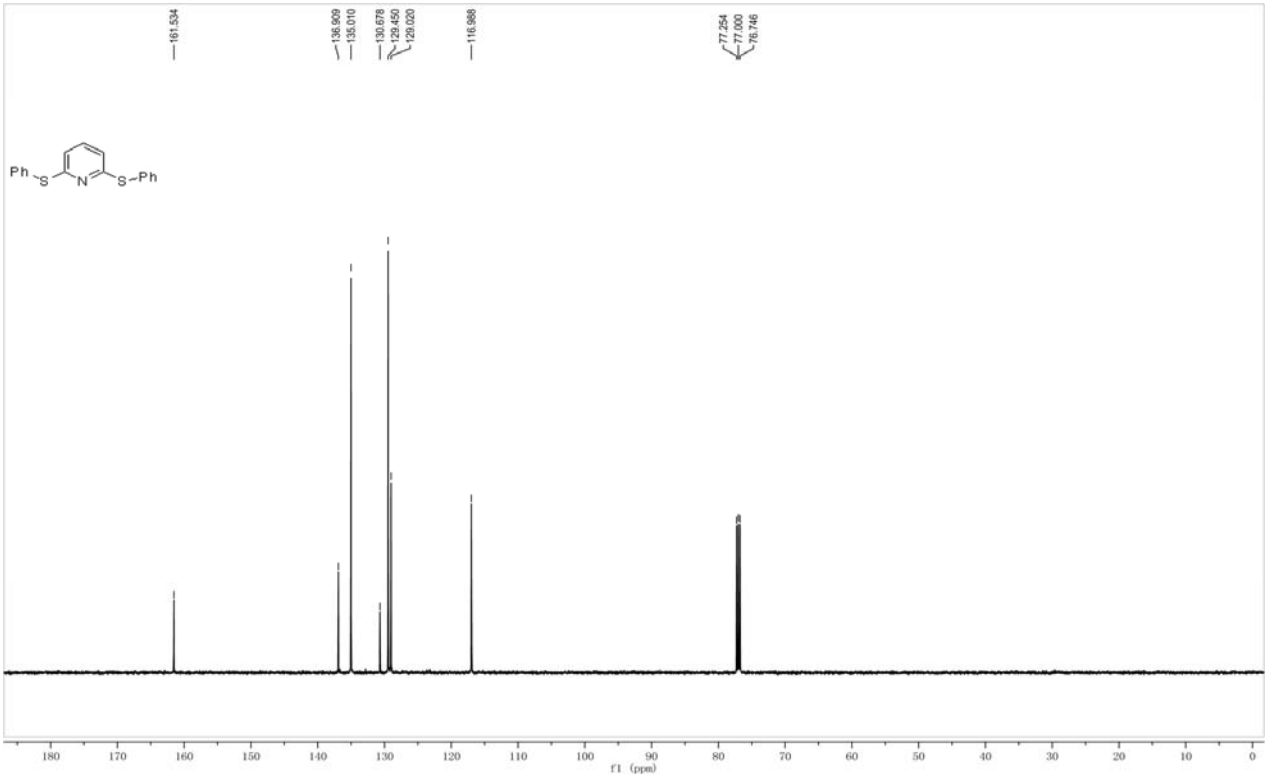

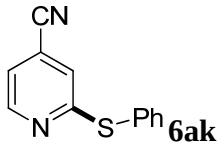

6ak

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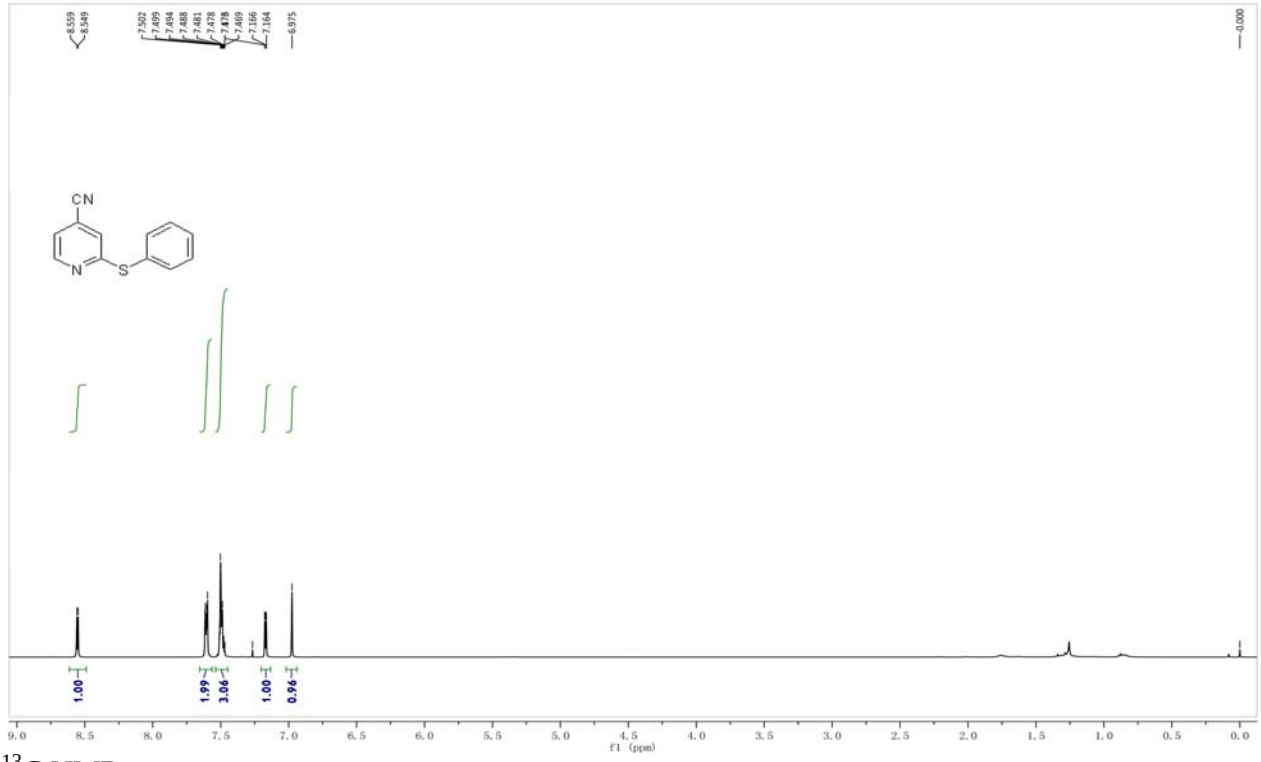

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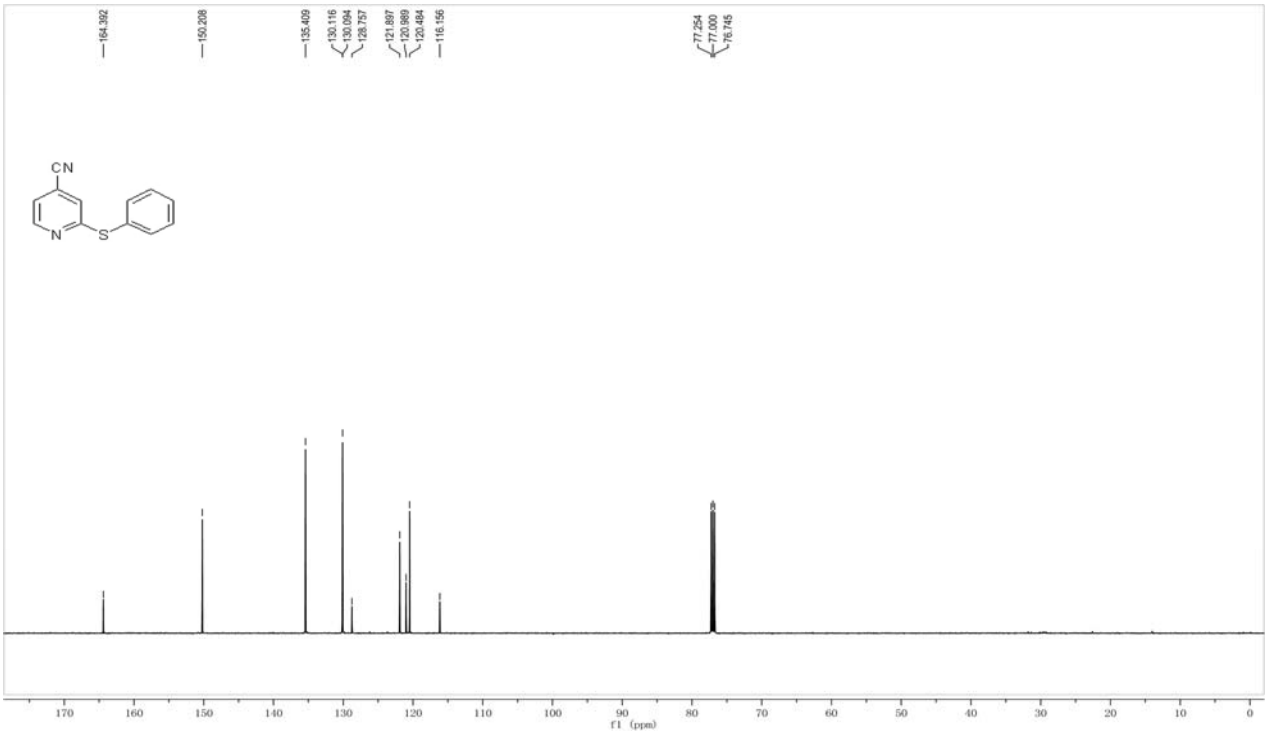

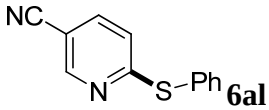

6al

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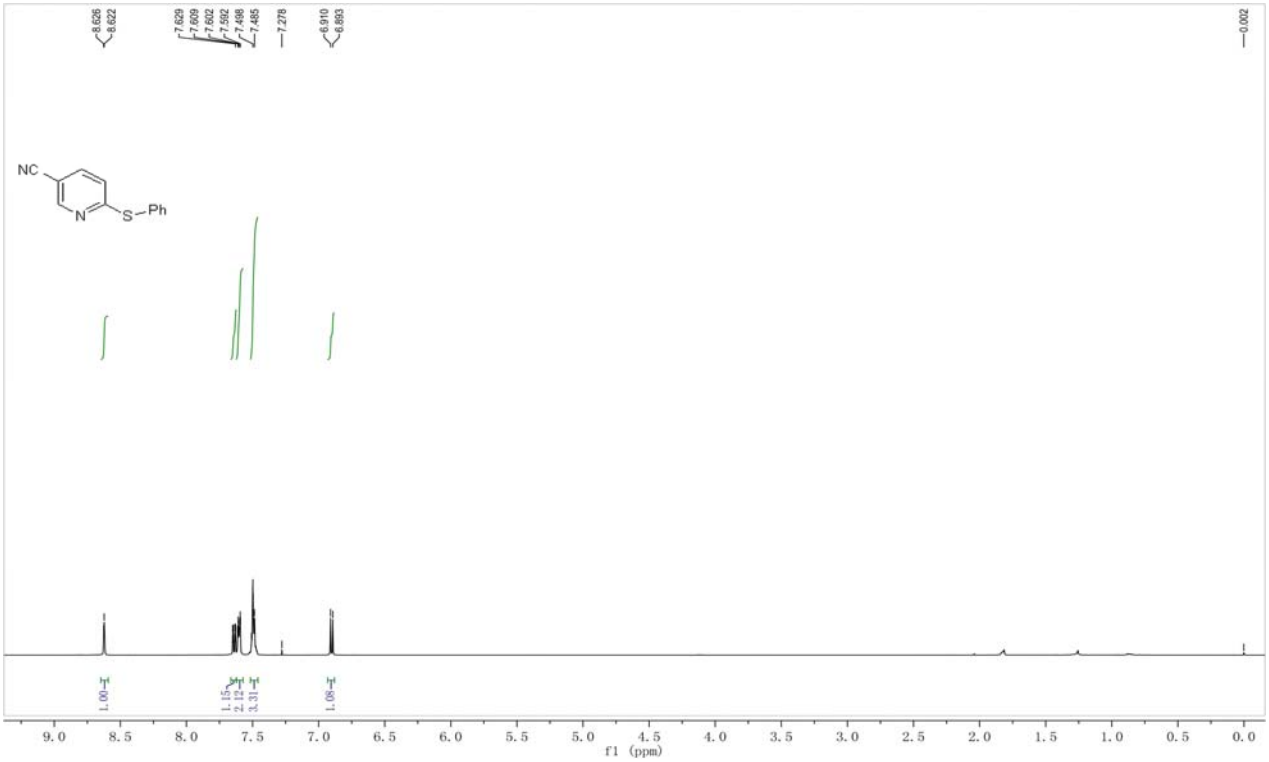

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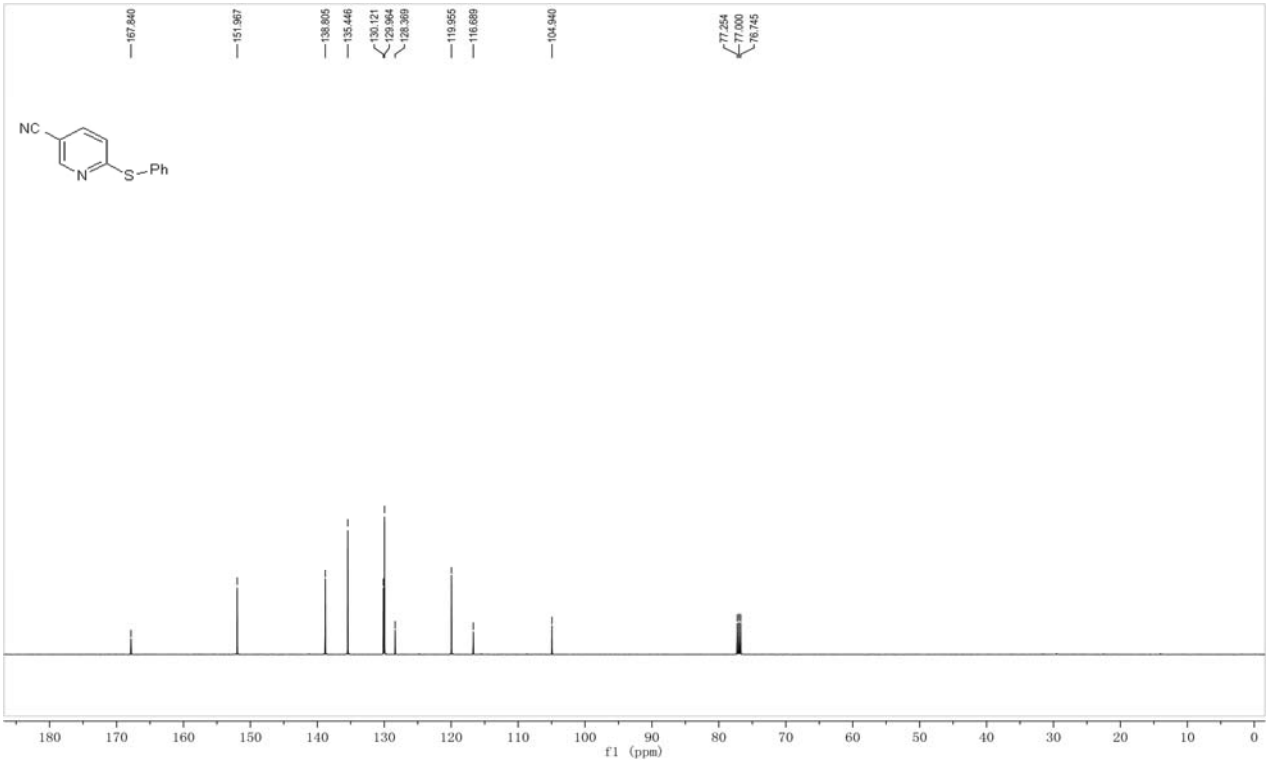

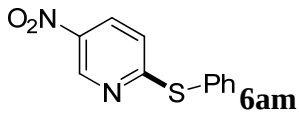

6am

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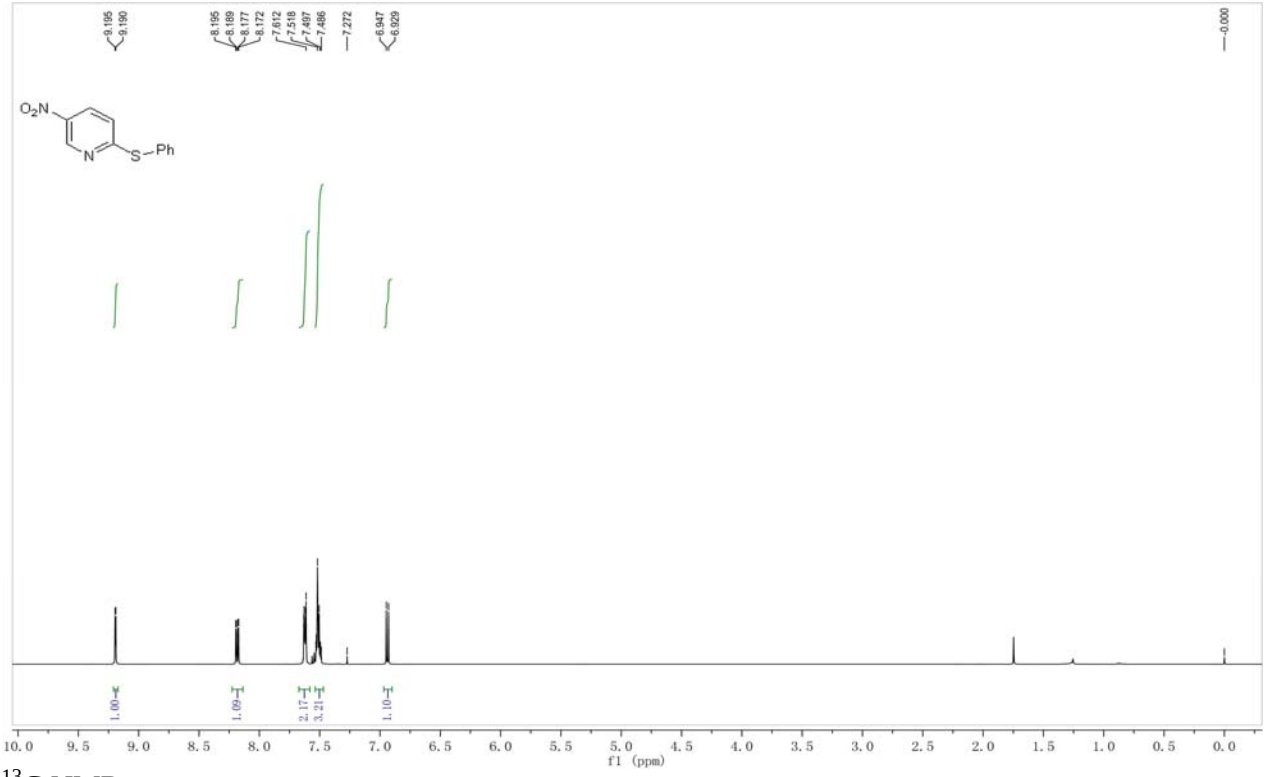

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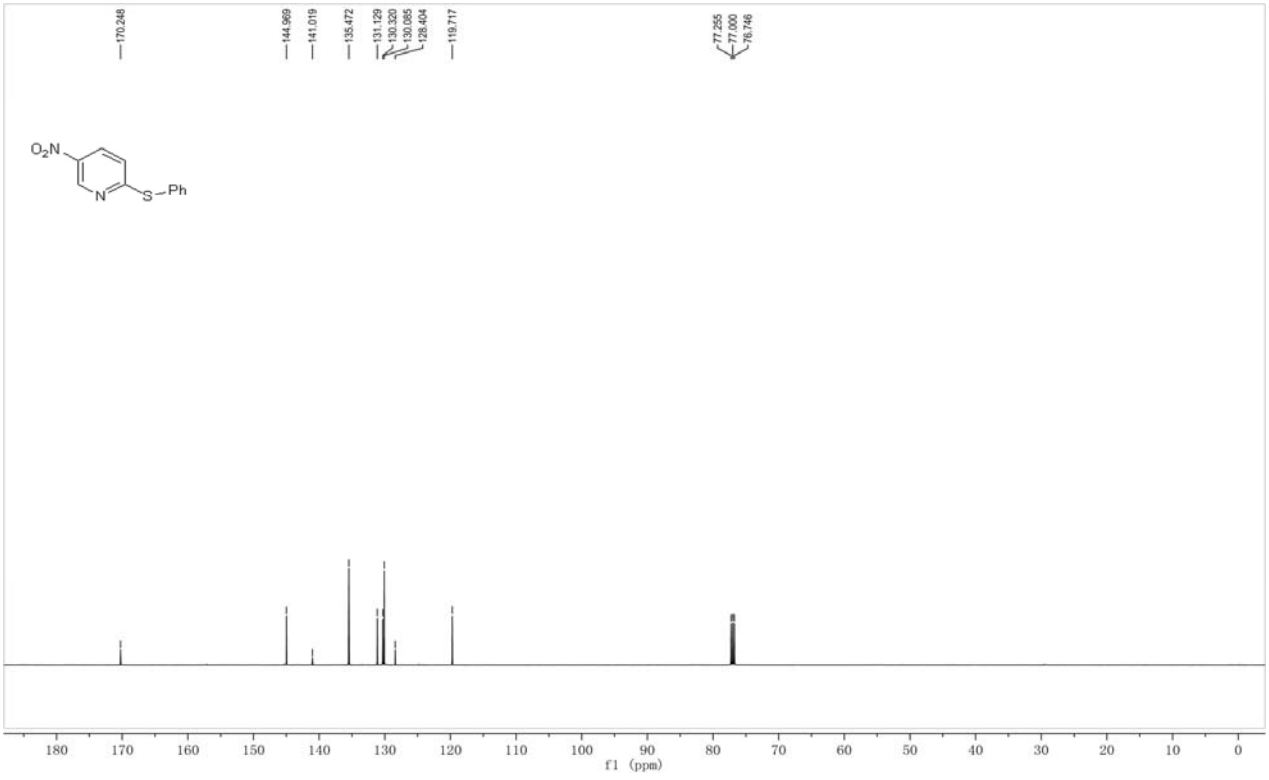

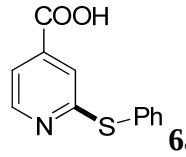

6an

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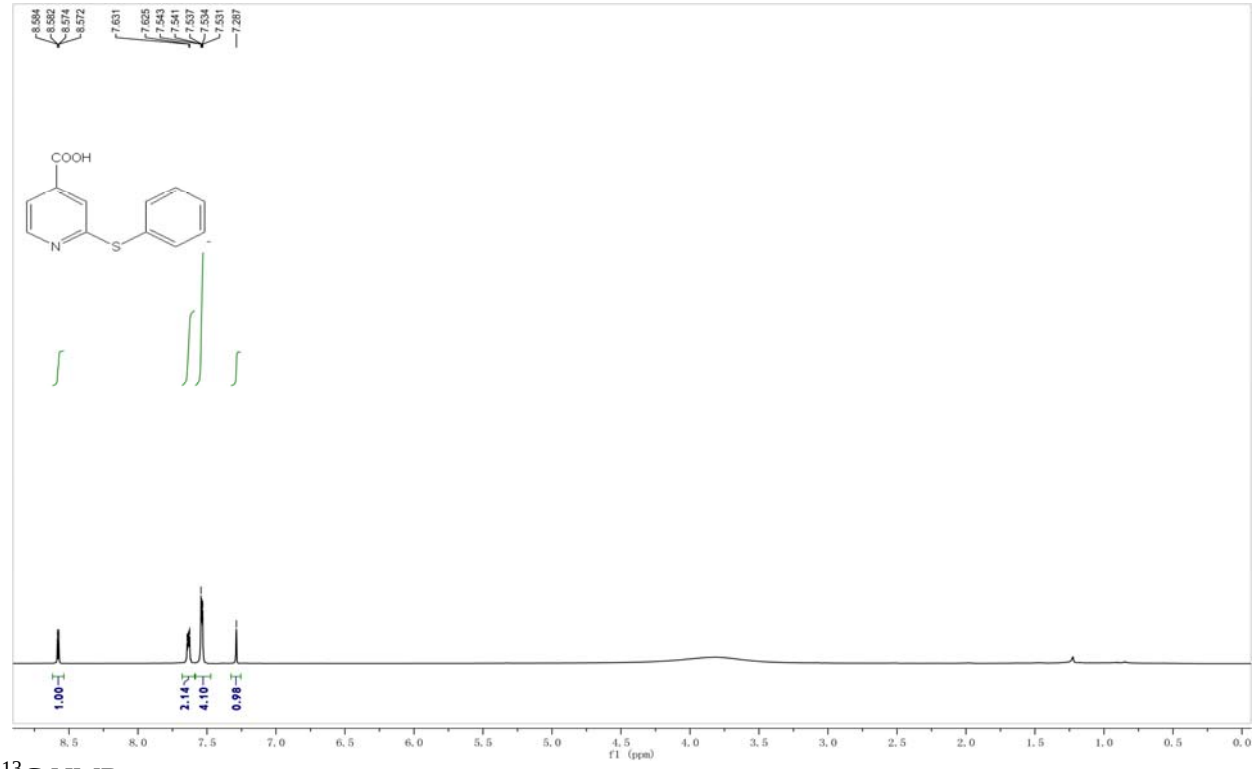

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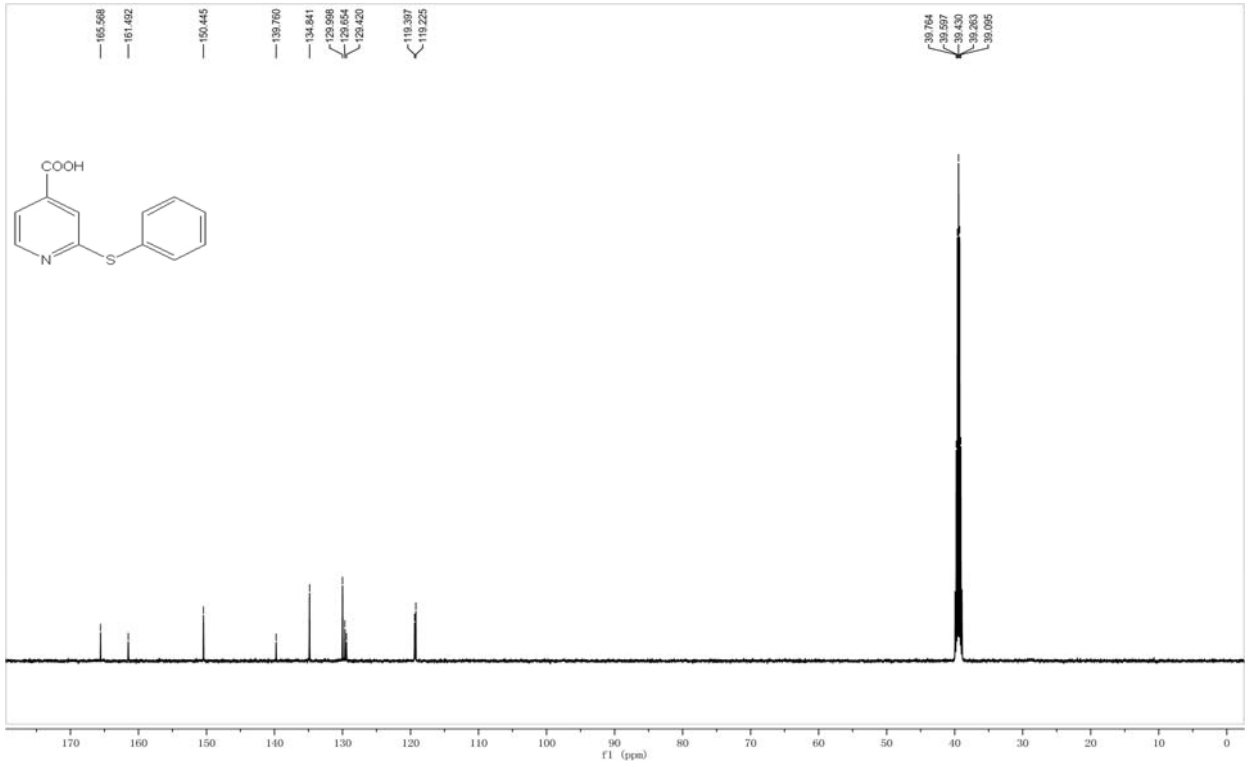
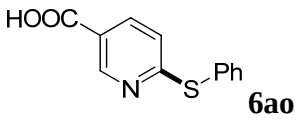
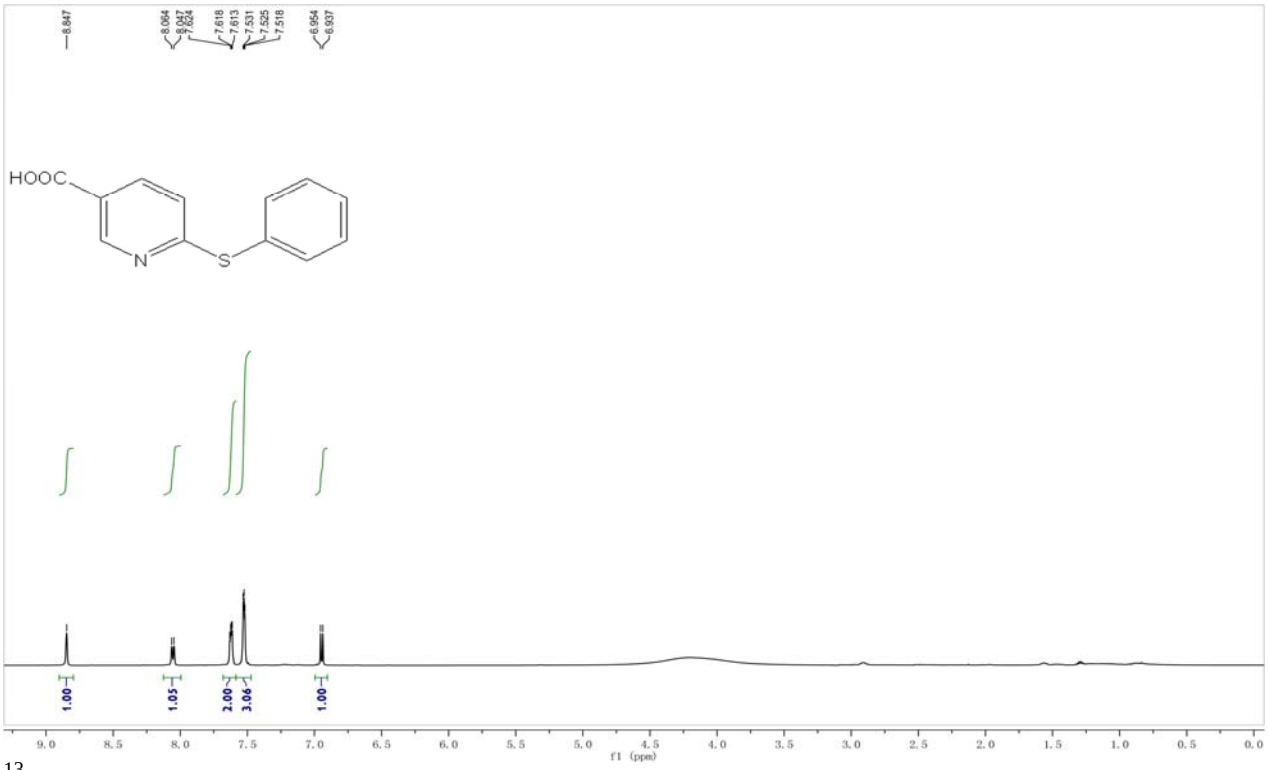


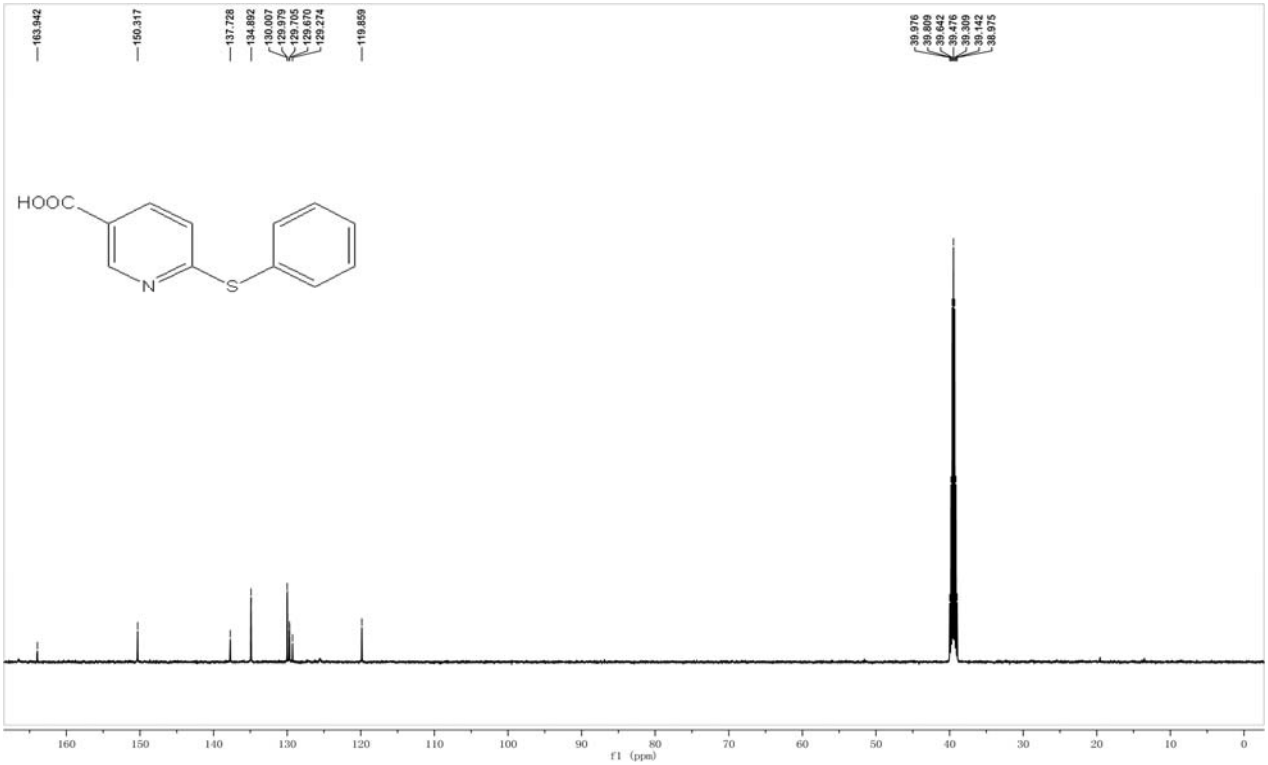


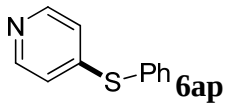
6ao

^{1}H NMR



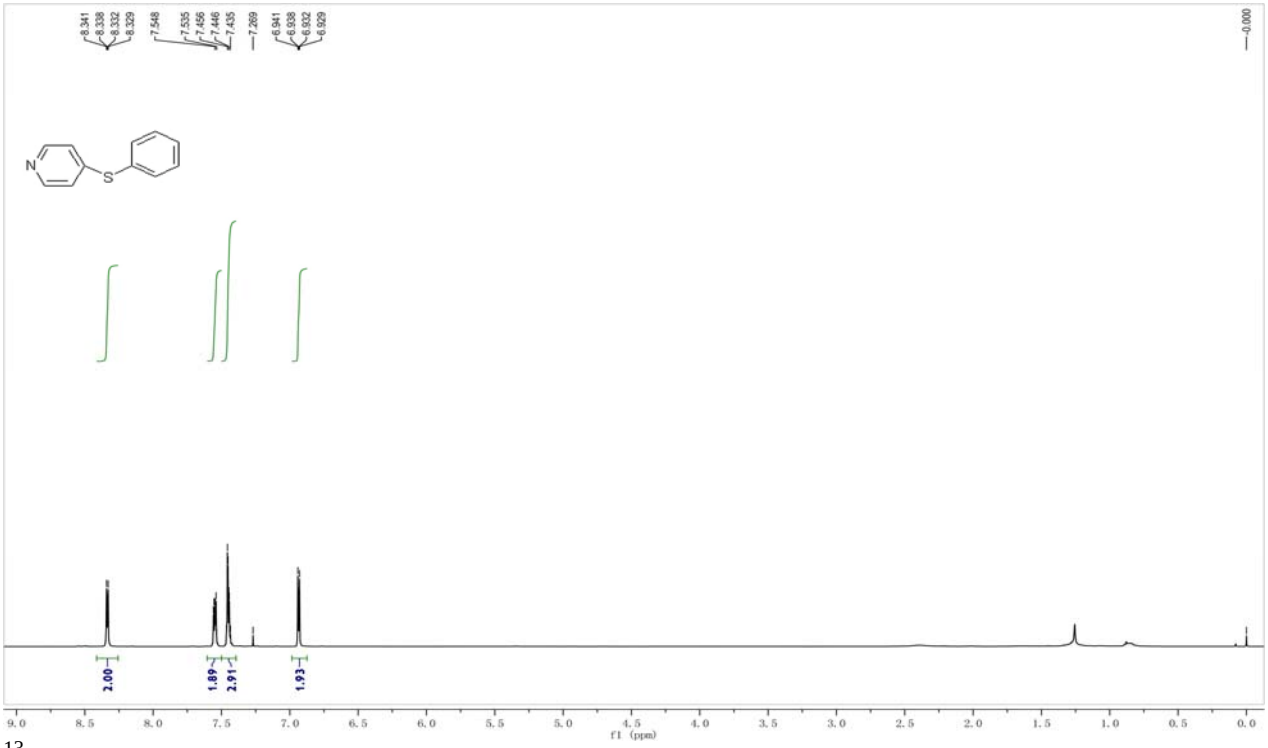
^{13}C NMR



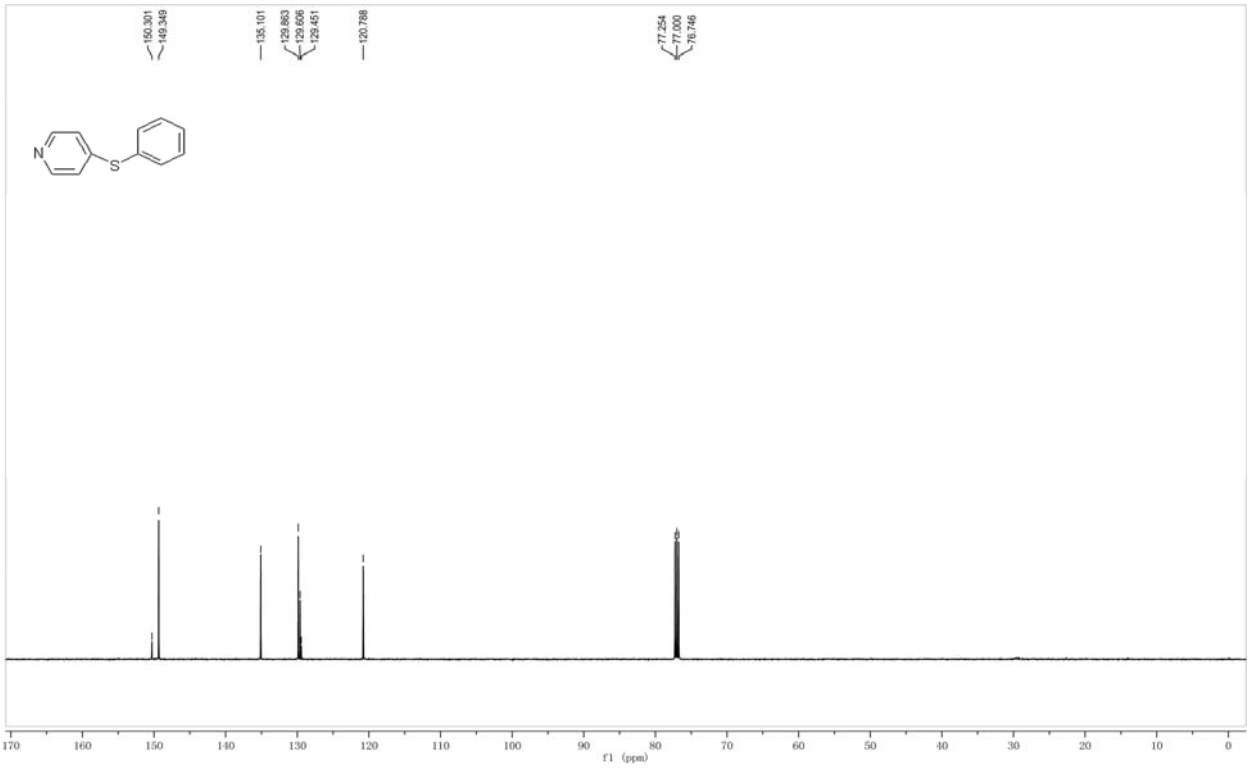


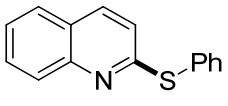
6ap

^{1}H NMR



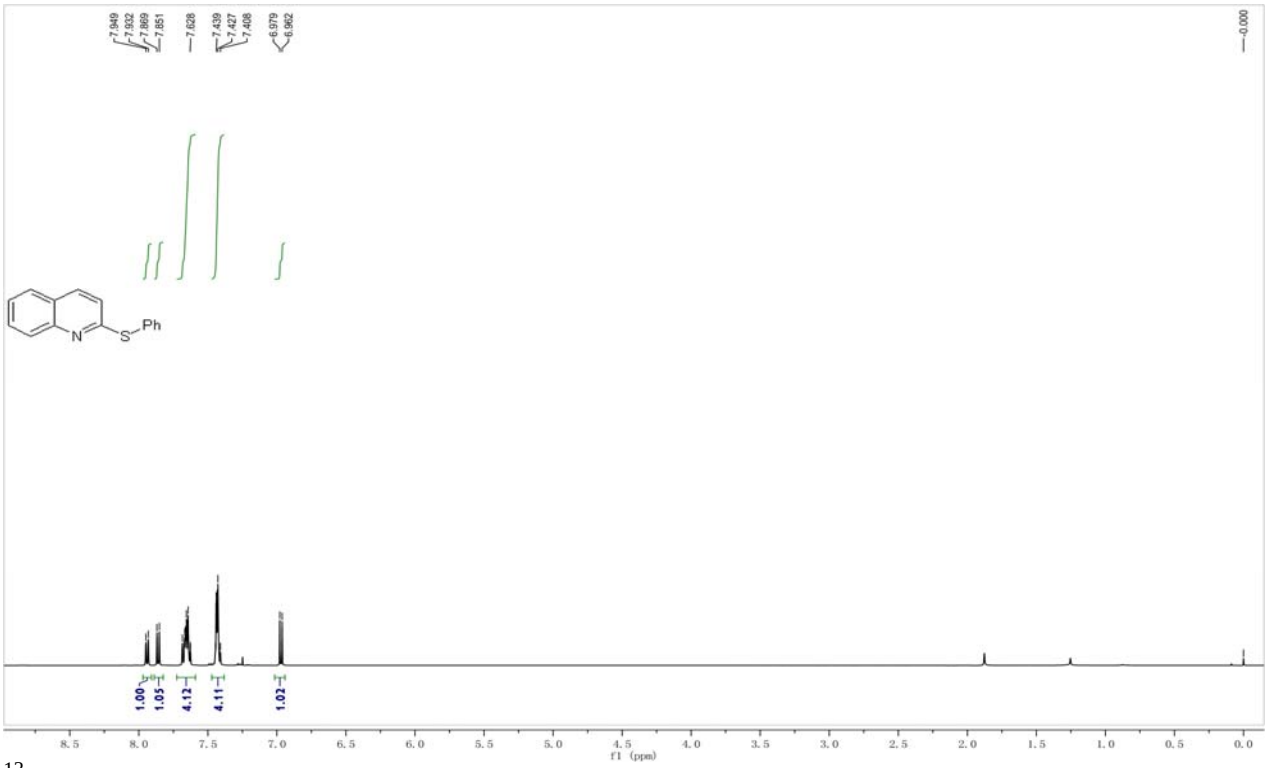
^{13}C NMR





6aq

^{1}H NMR



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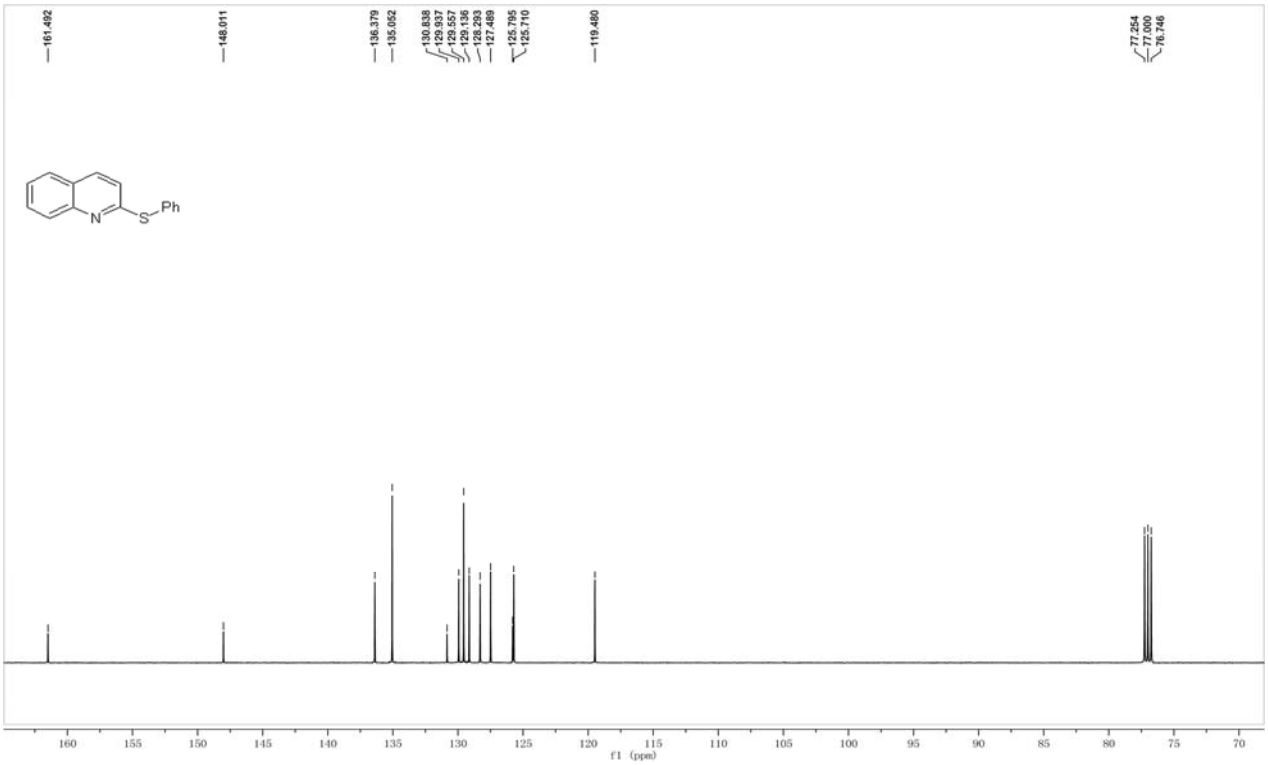

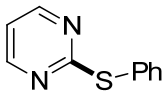

6ar

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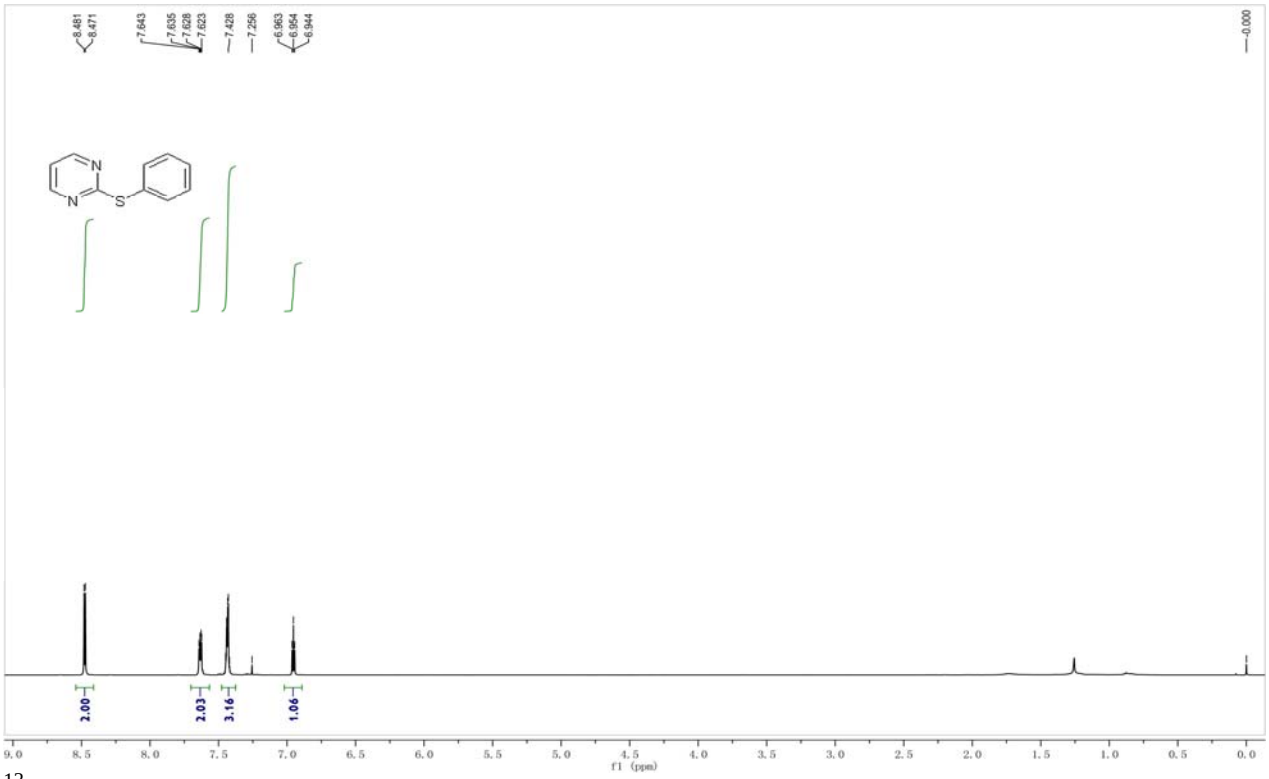
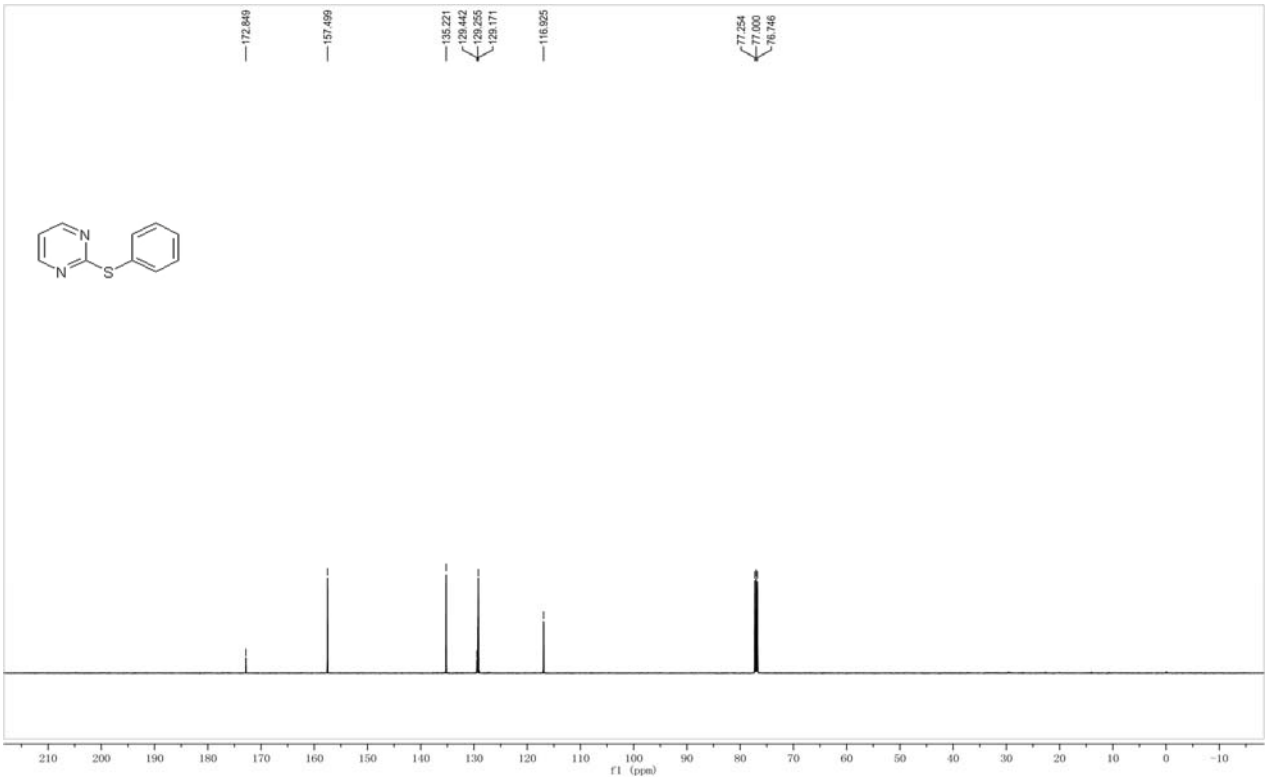
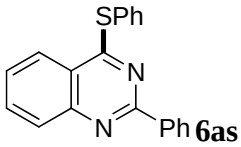


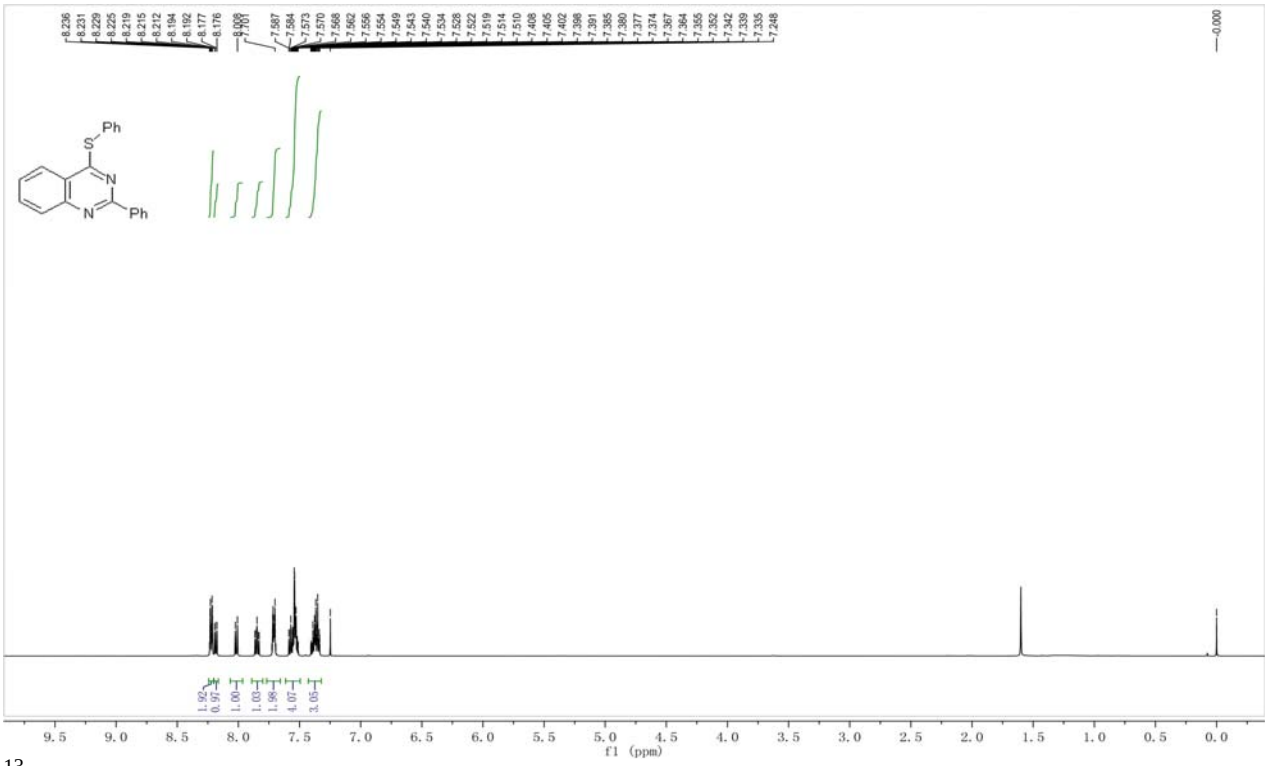
^{13}C NMR





6as

^{1}H NMR



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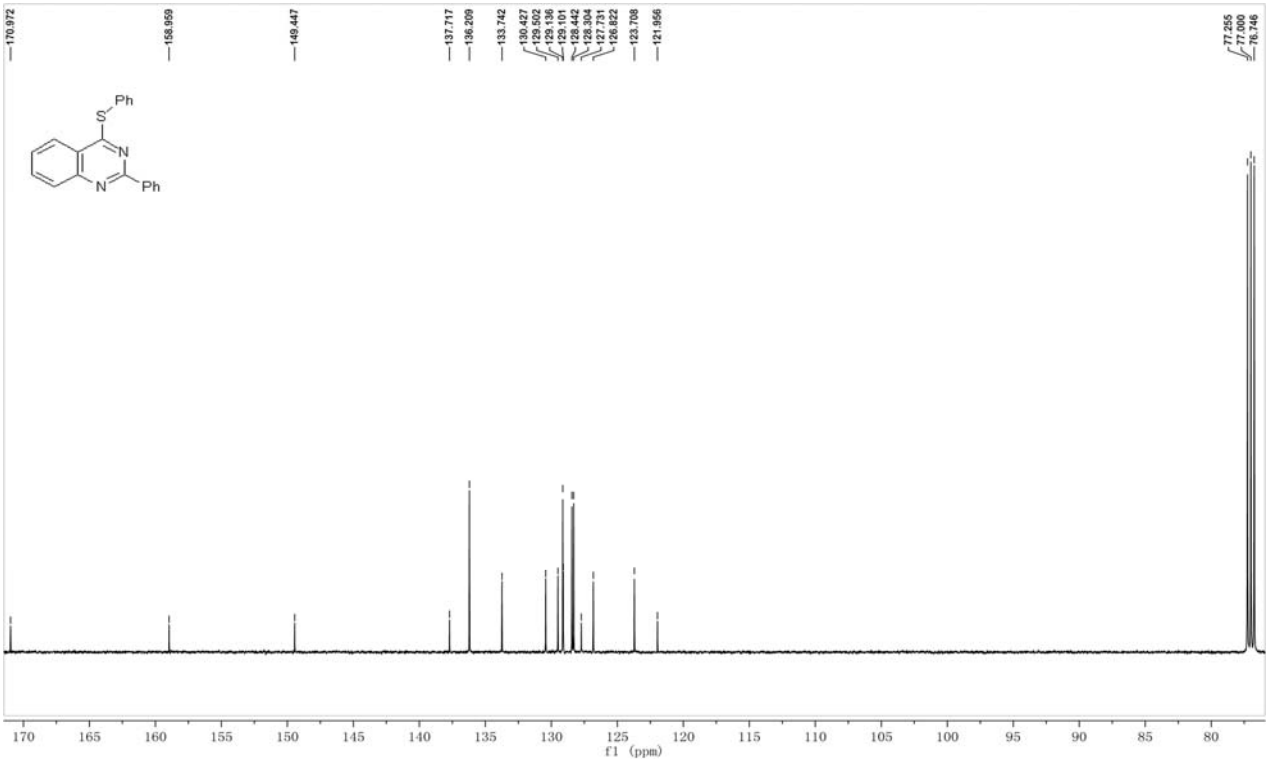

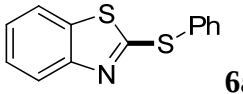

6at

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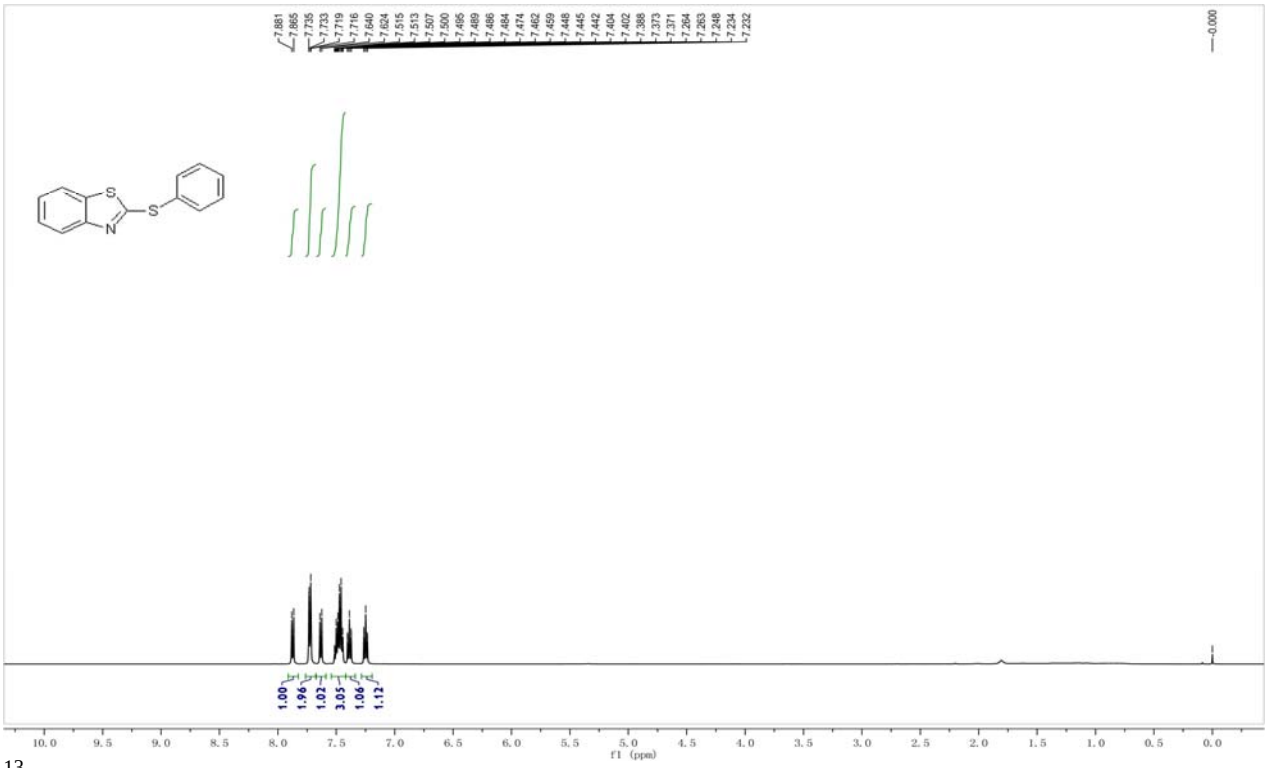

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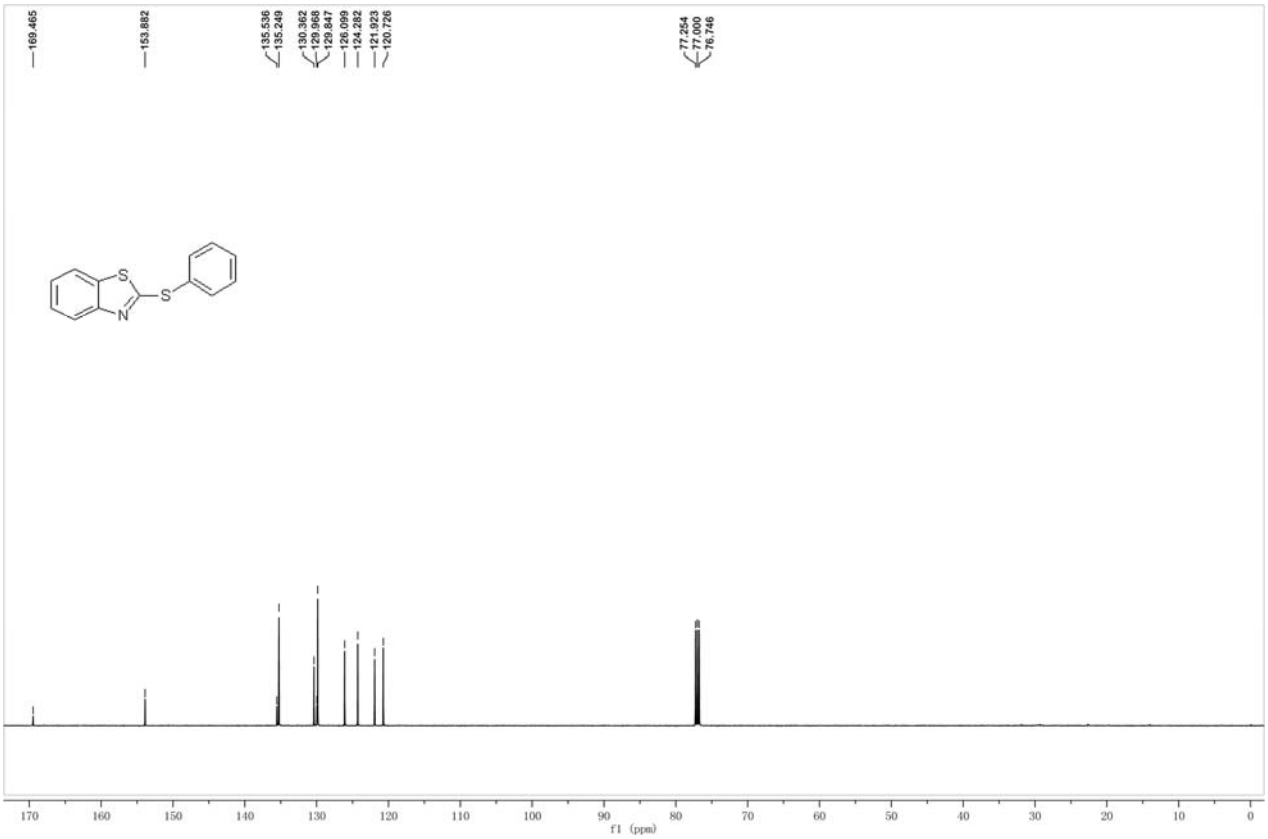

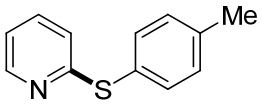

6ba

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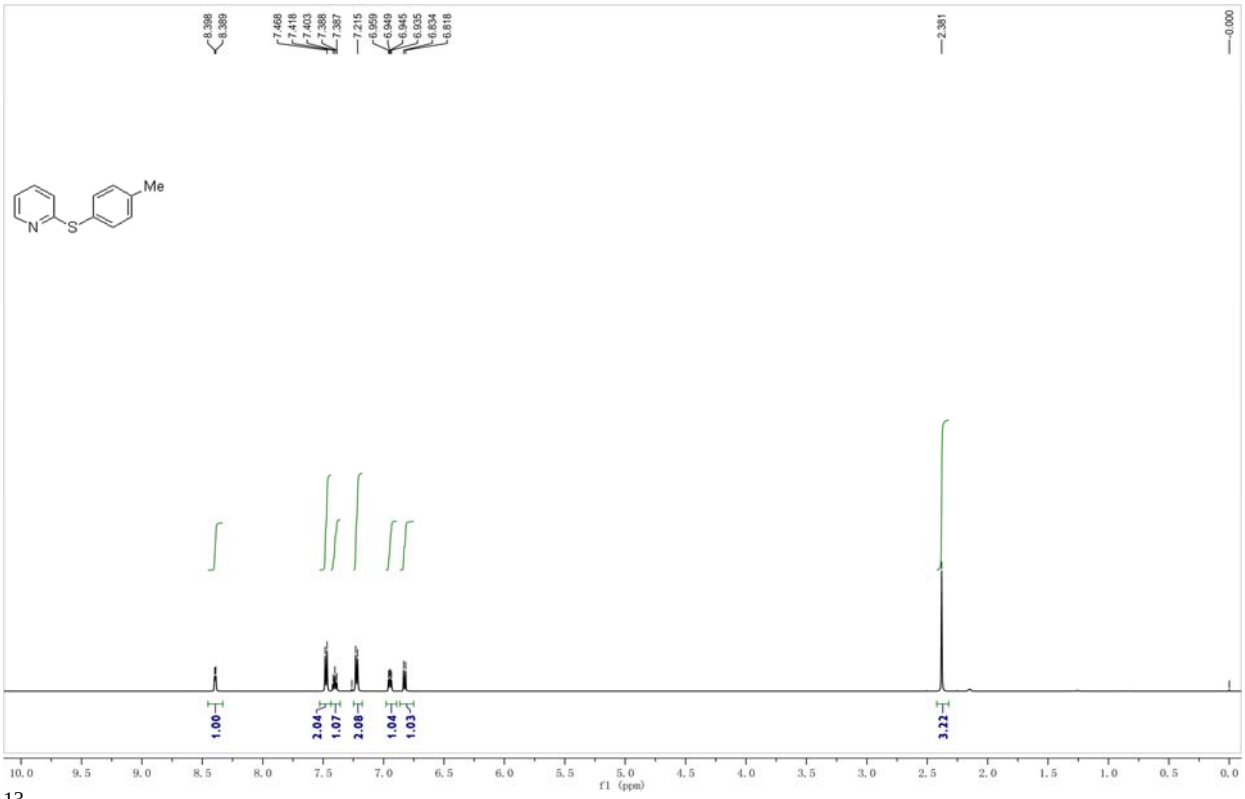
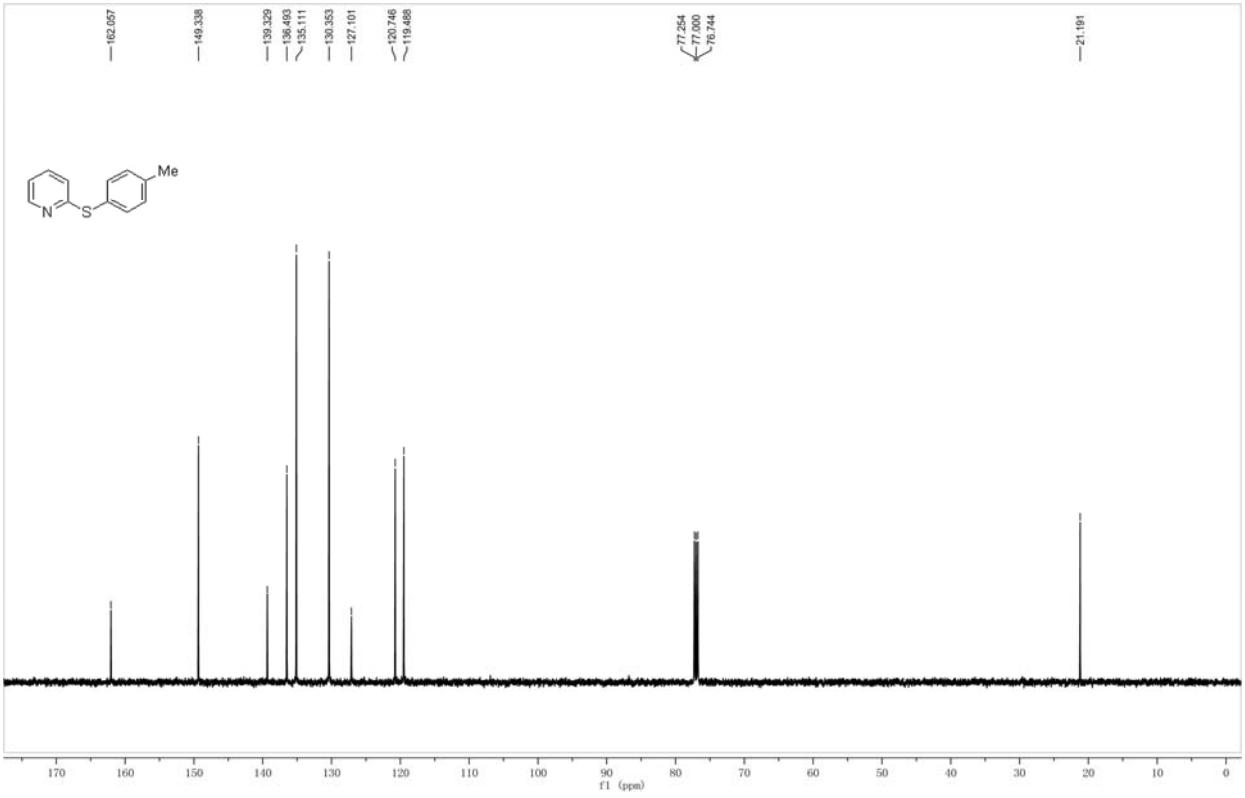
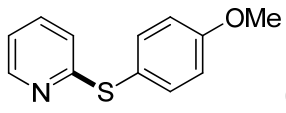


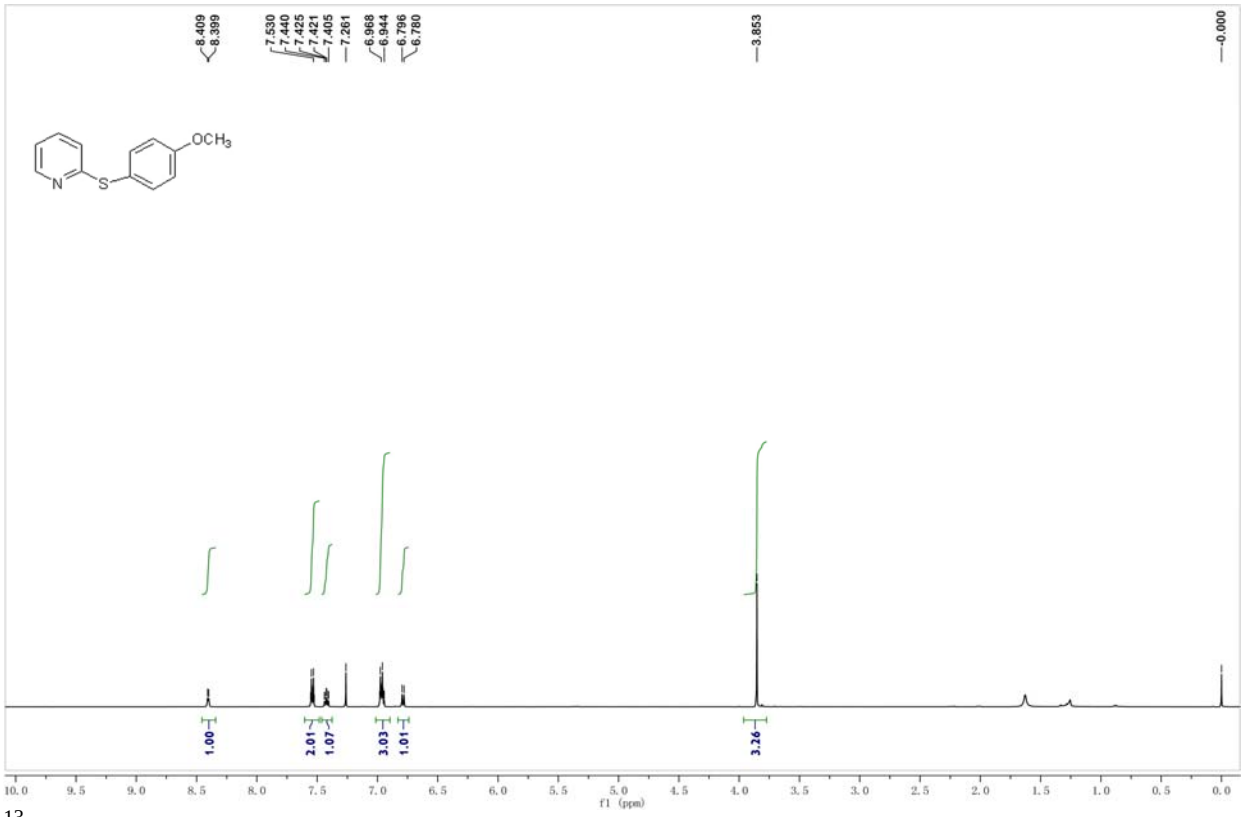
^{13}C NMR



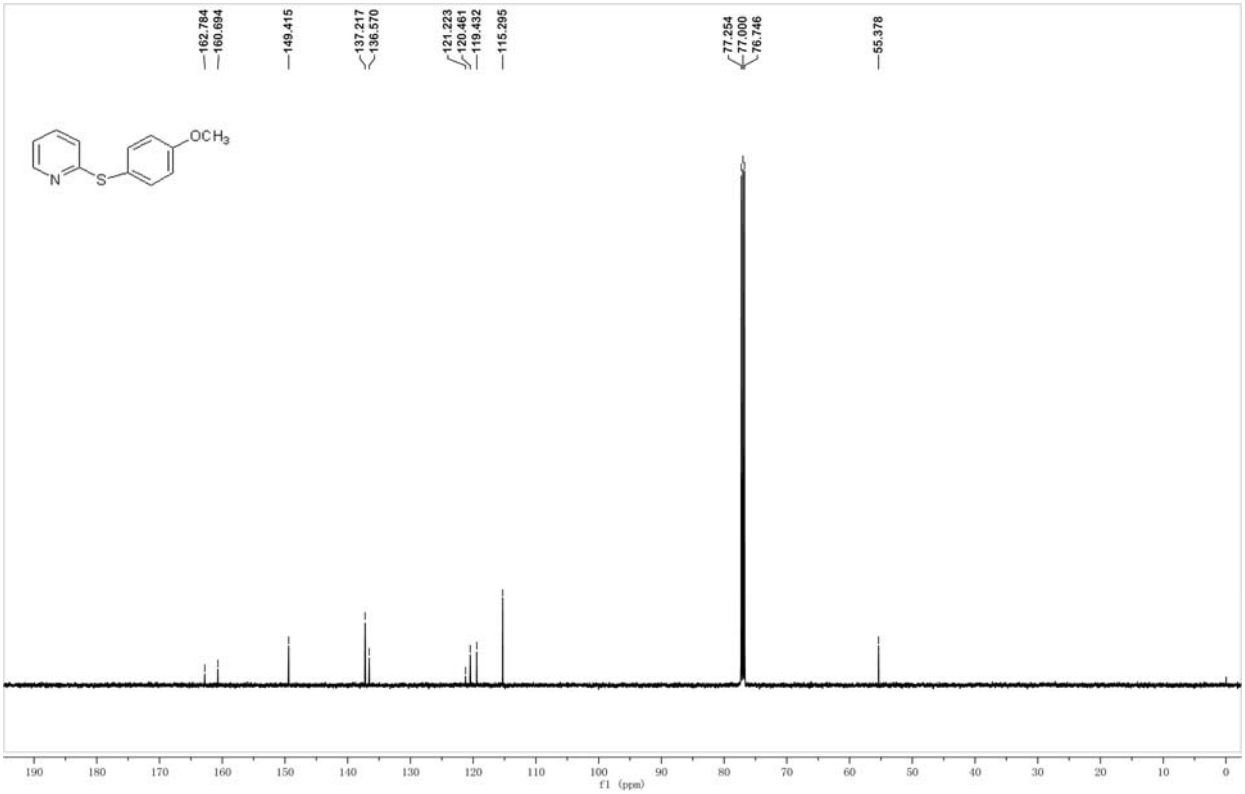


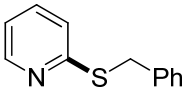
6ca

^{1}H NMR



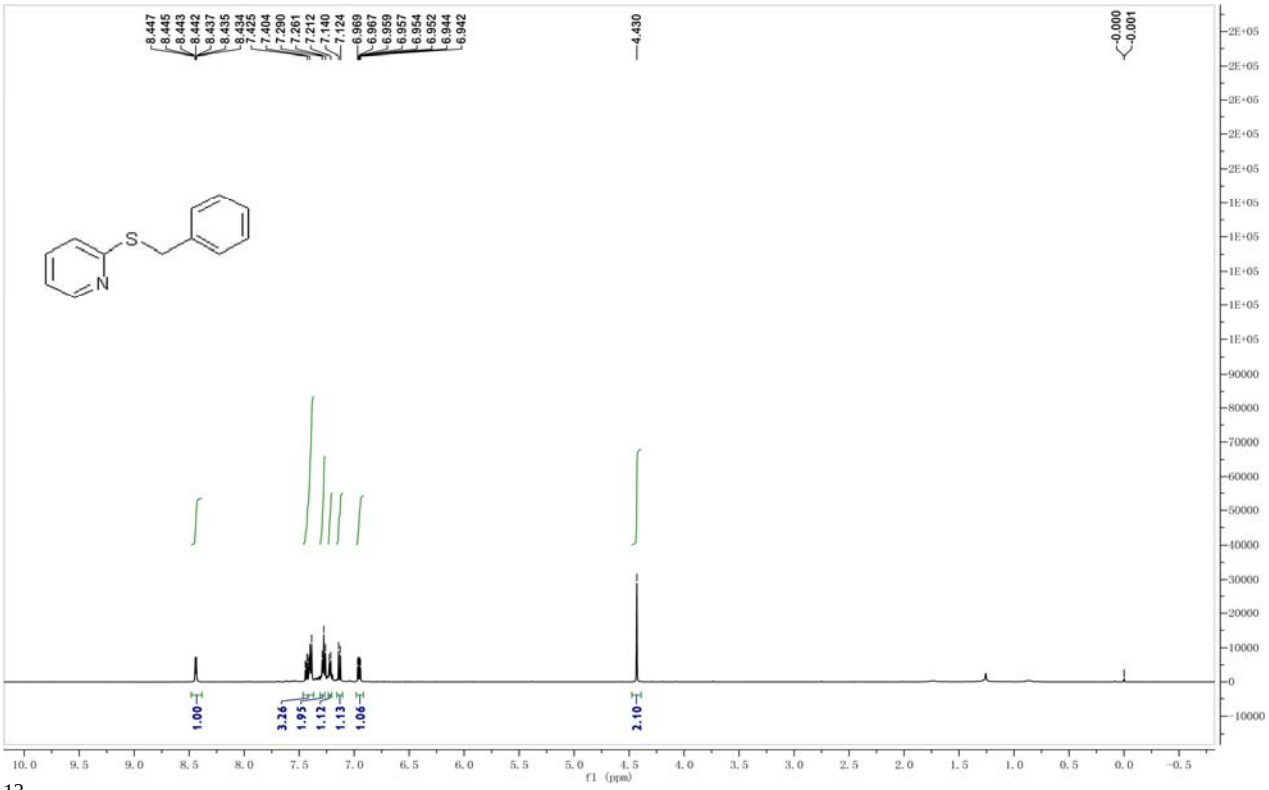
^{13}C NMR



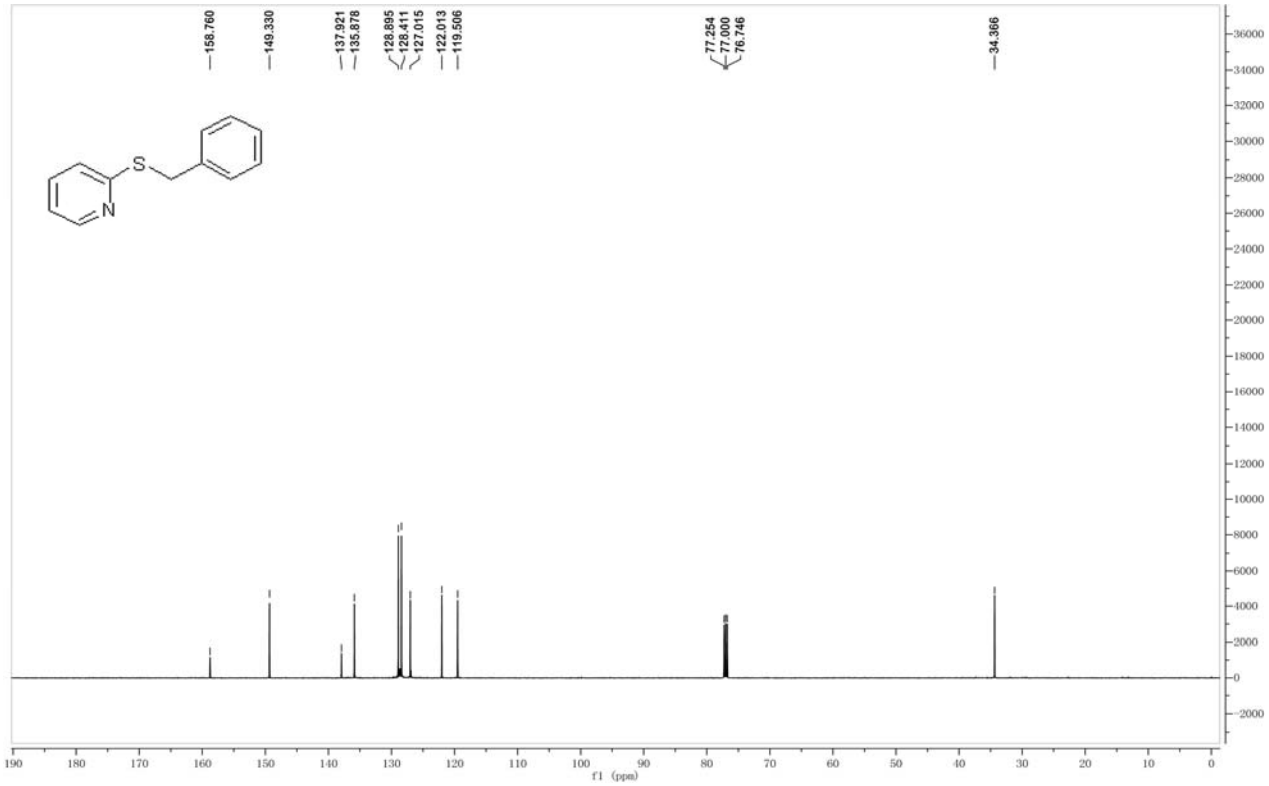


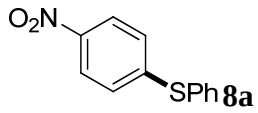
6da

^{1}H NMR



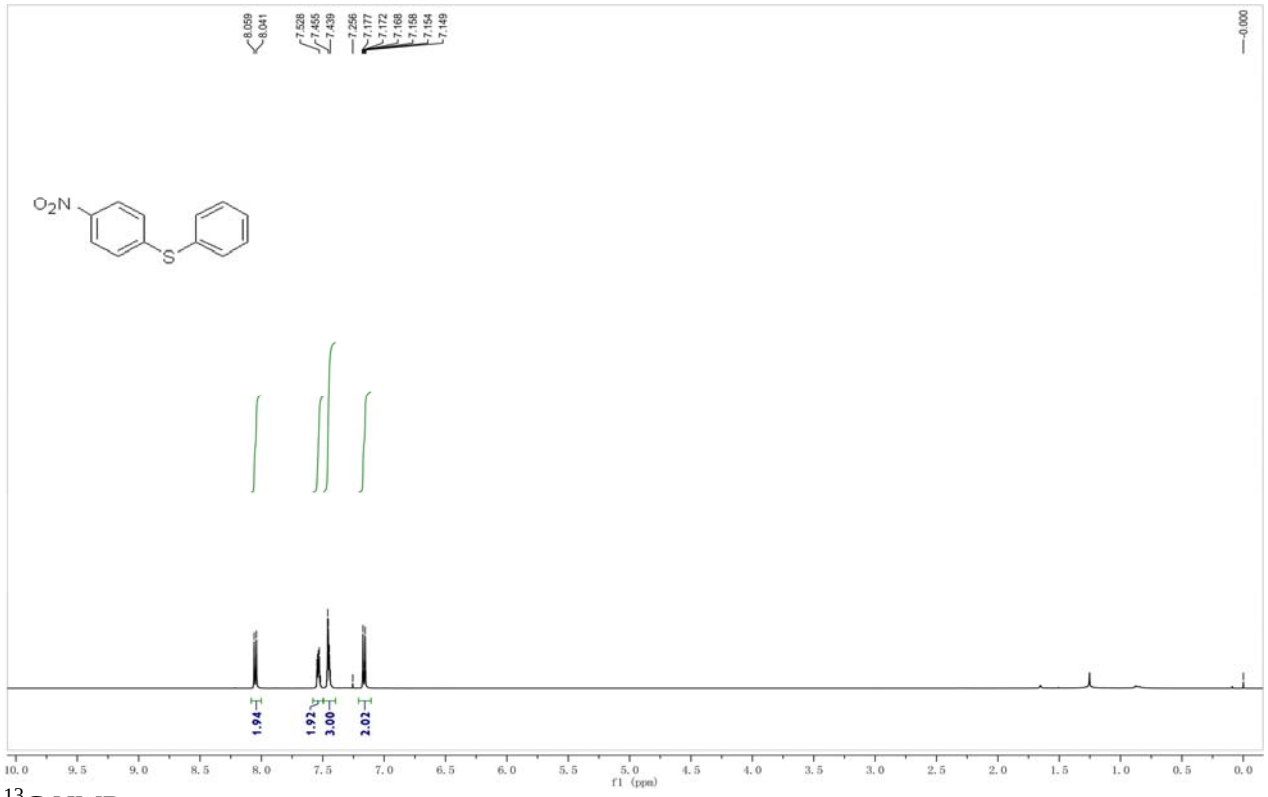
^{13}C NMR





8a

^{1}H NMR



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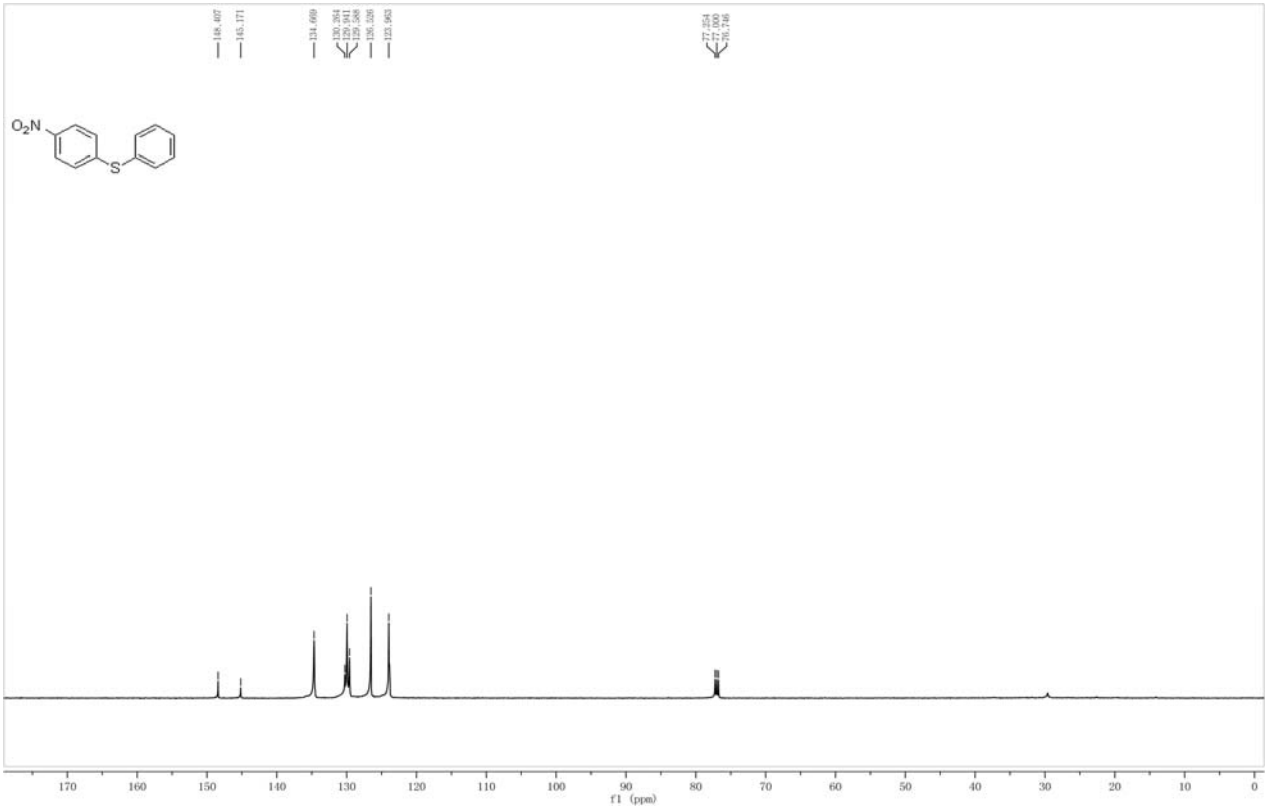

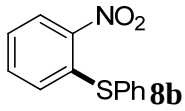

8b

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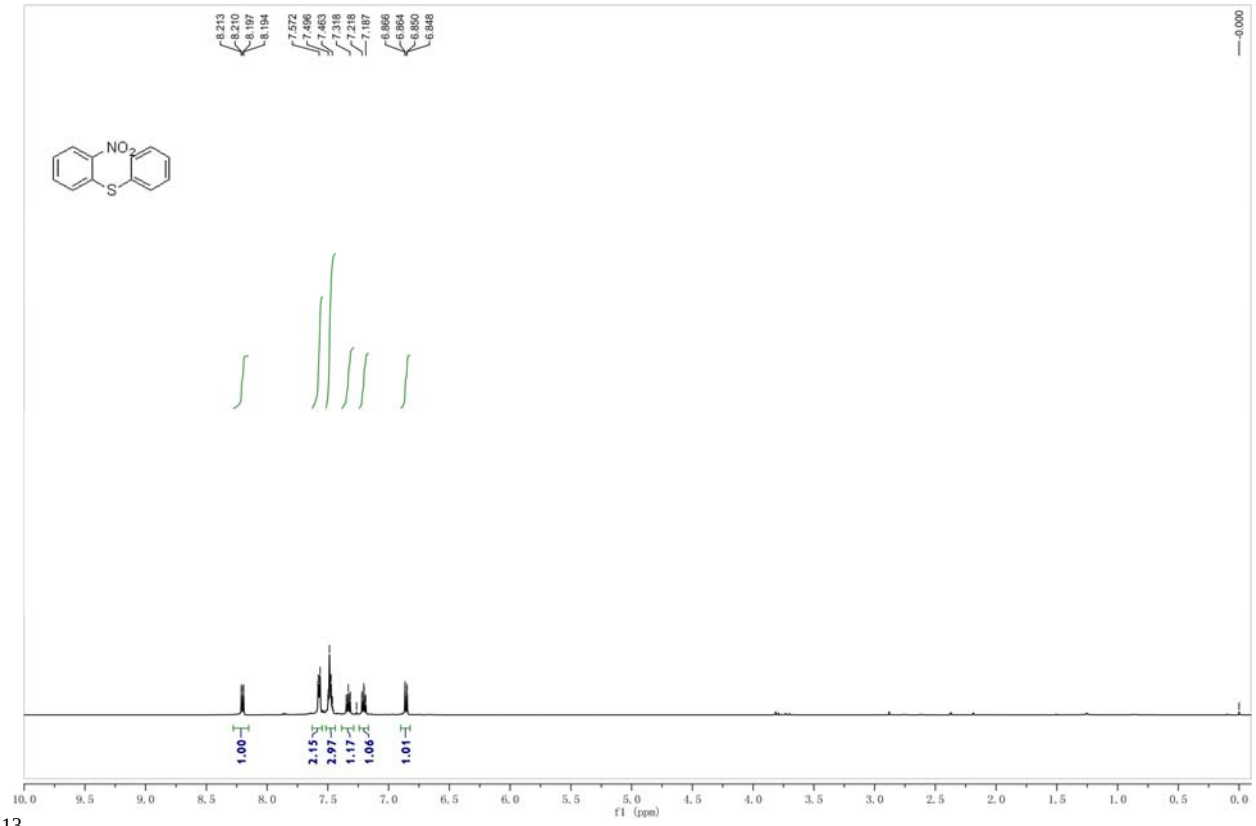

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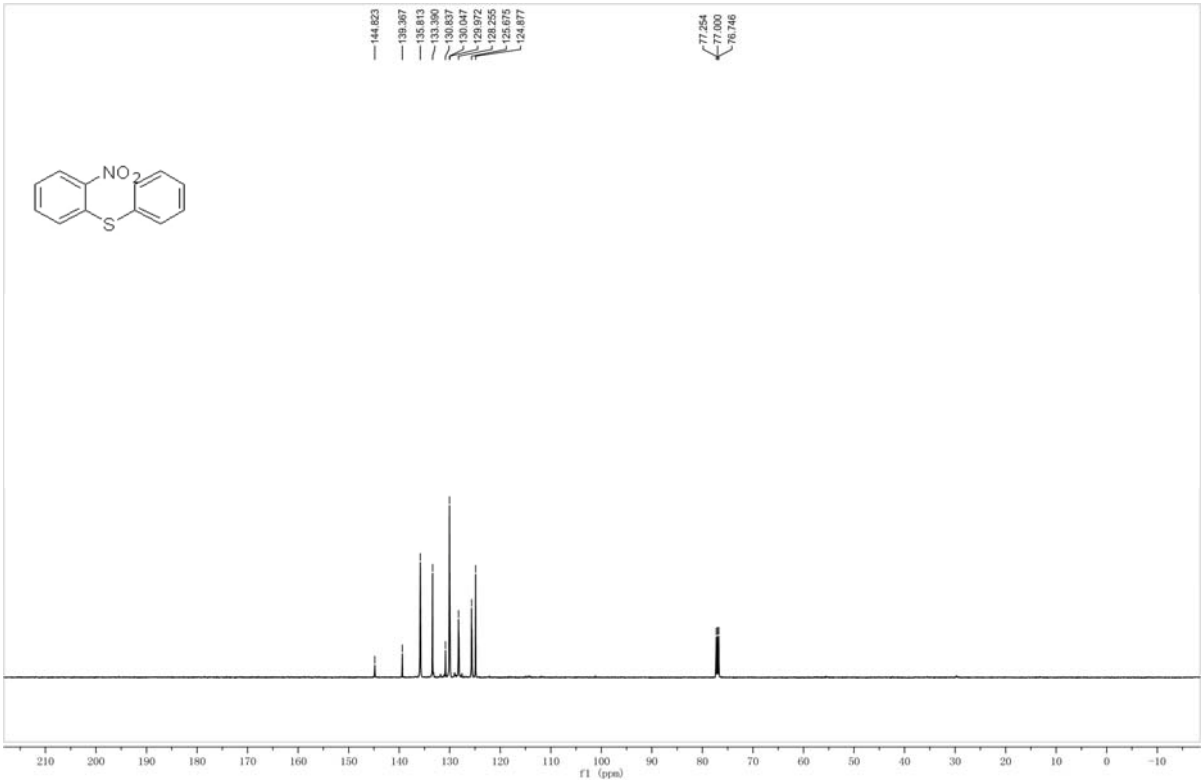
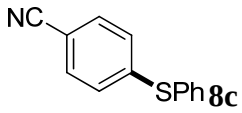
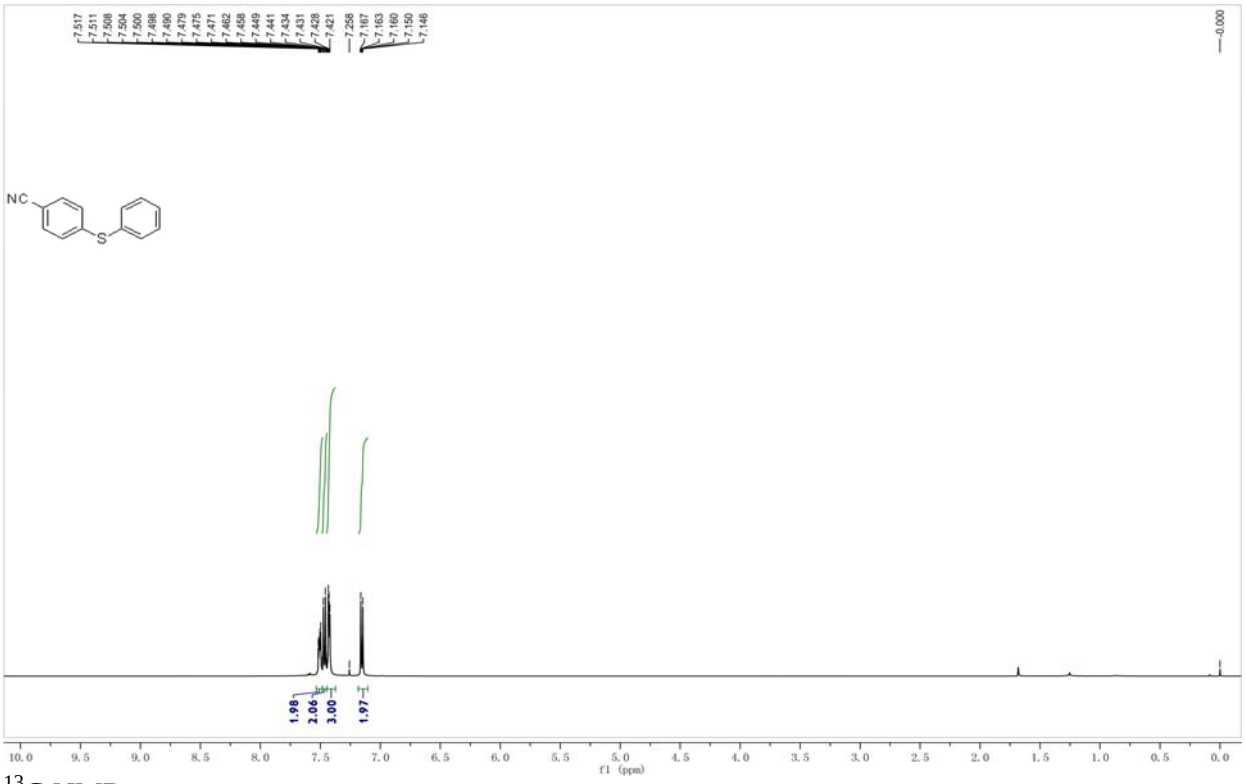




8c

^{1}H NMR



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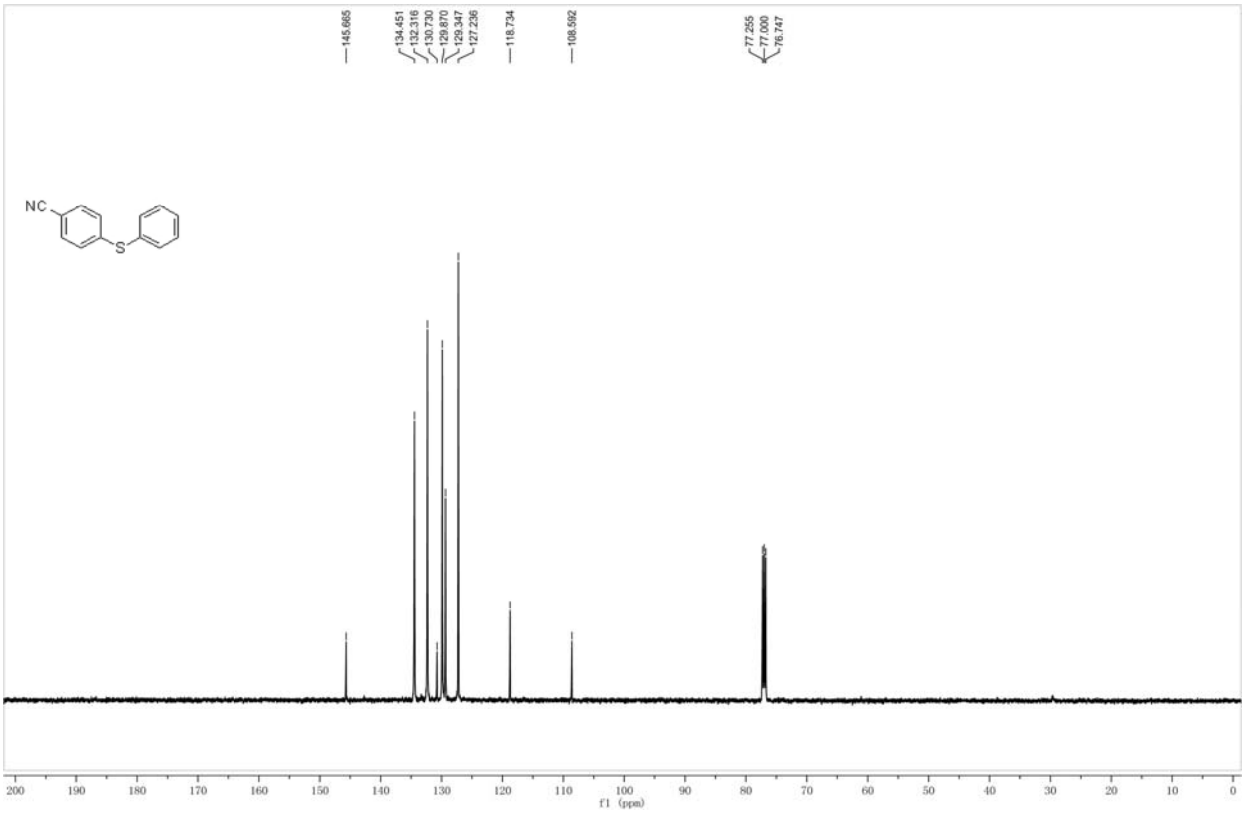

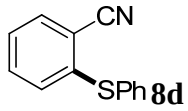

8d

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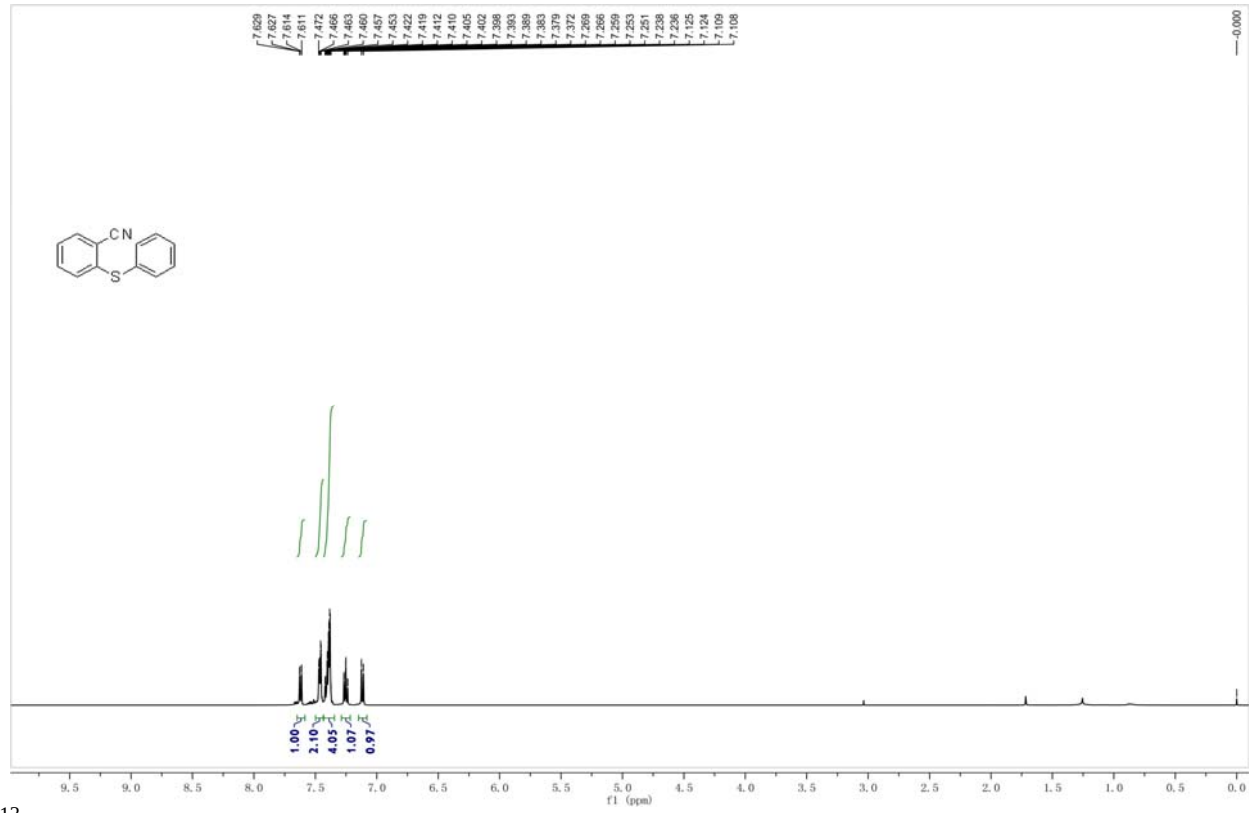

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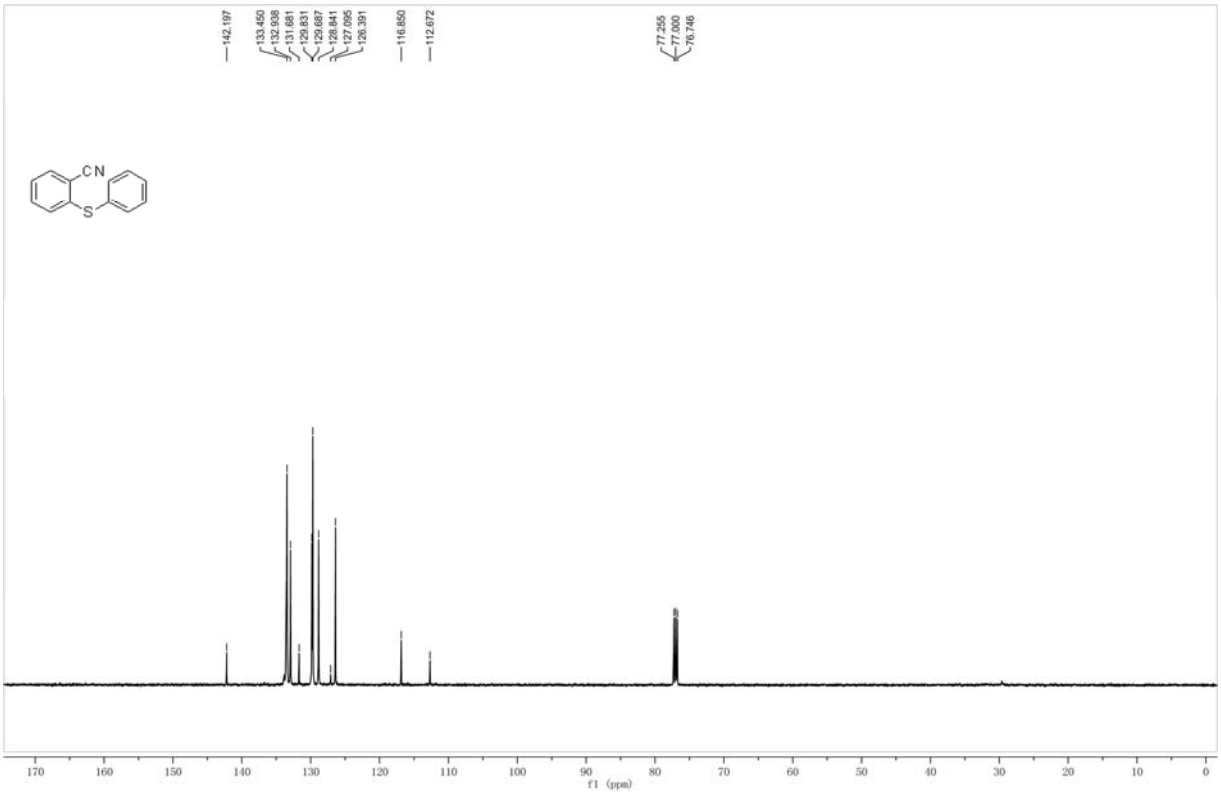

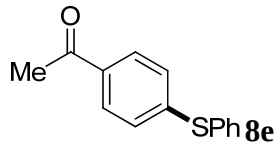

8e

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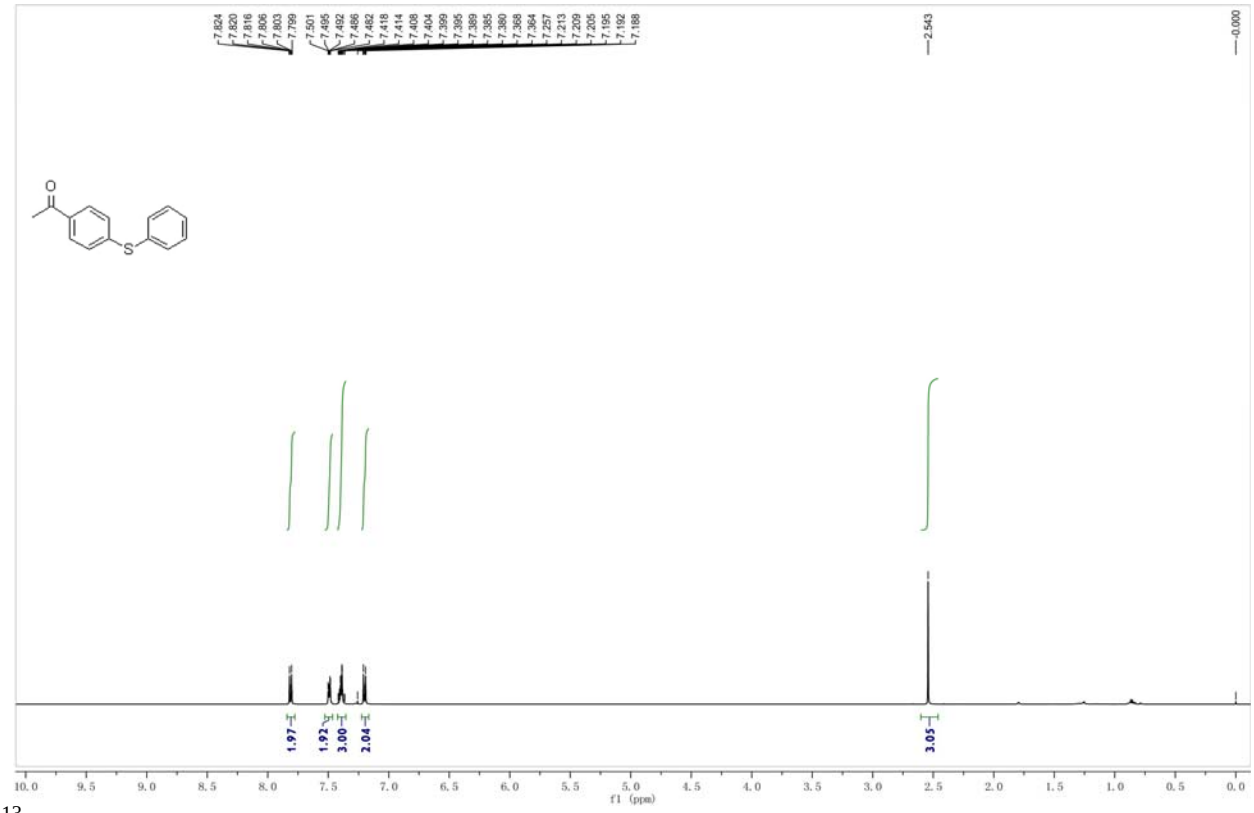

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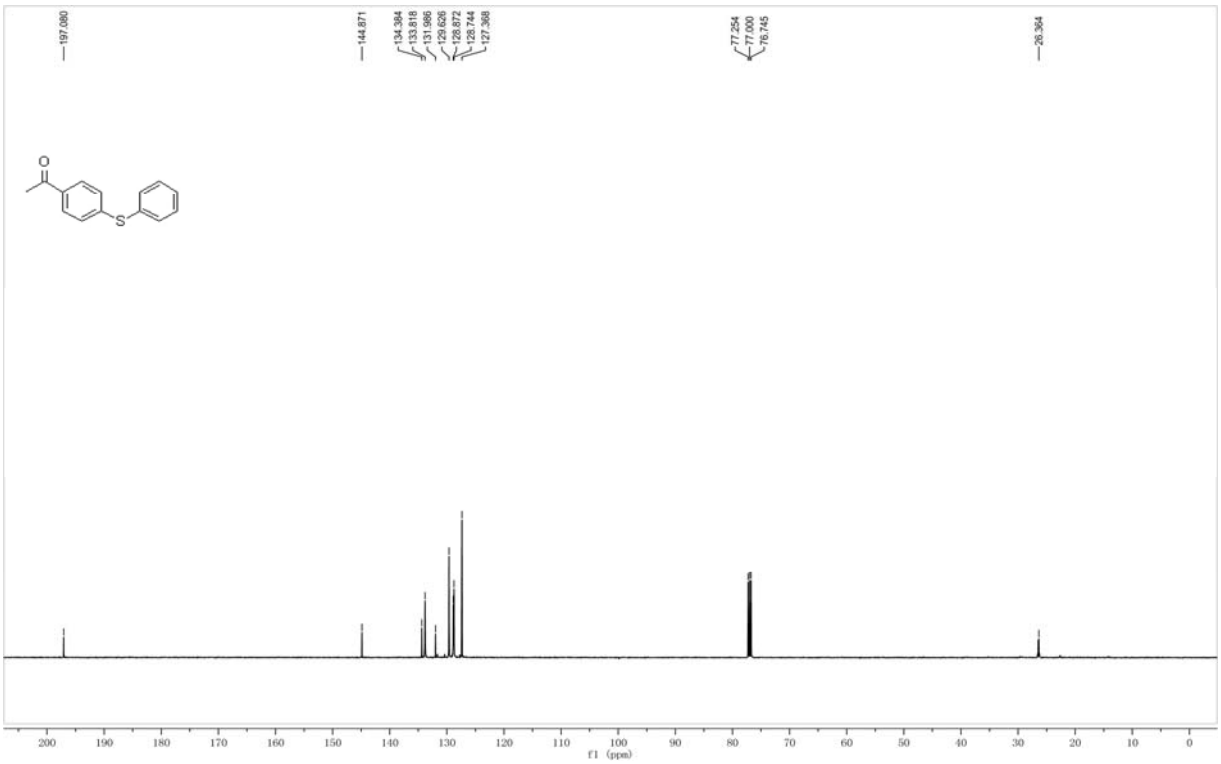
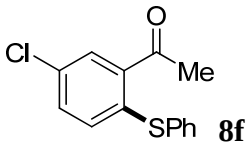
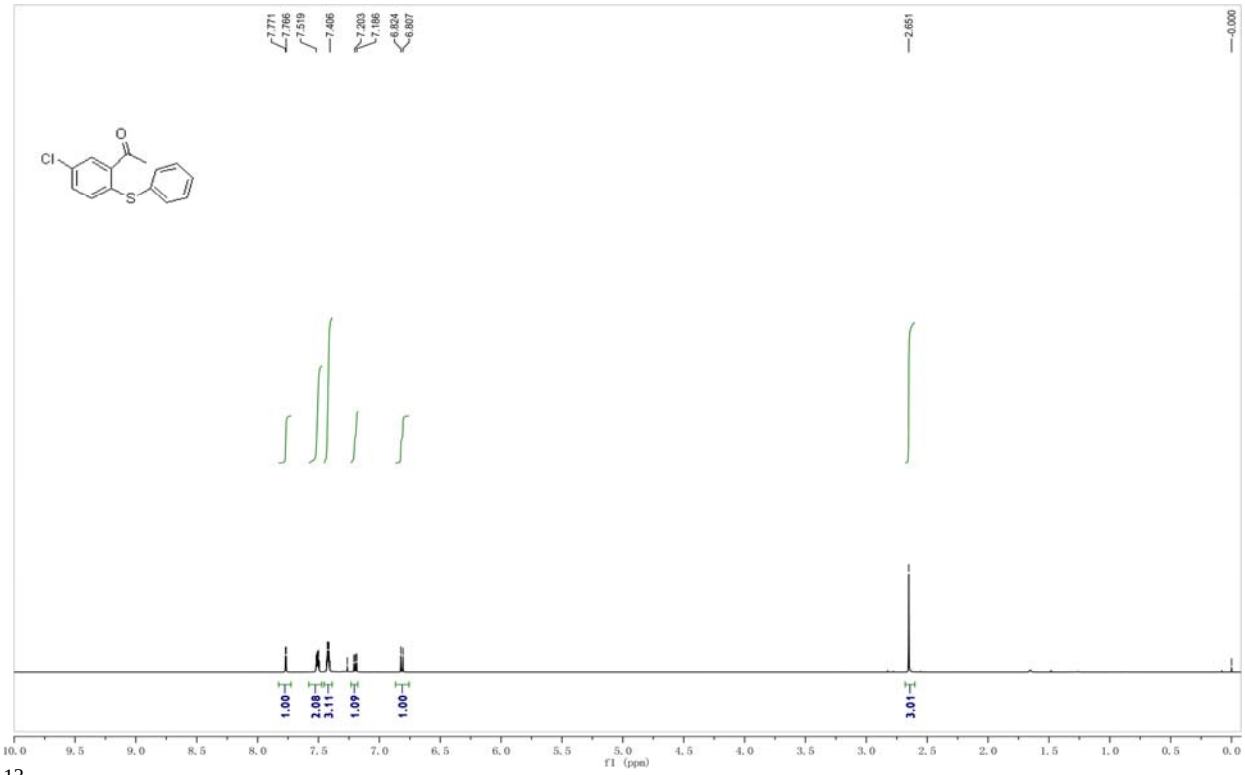


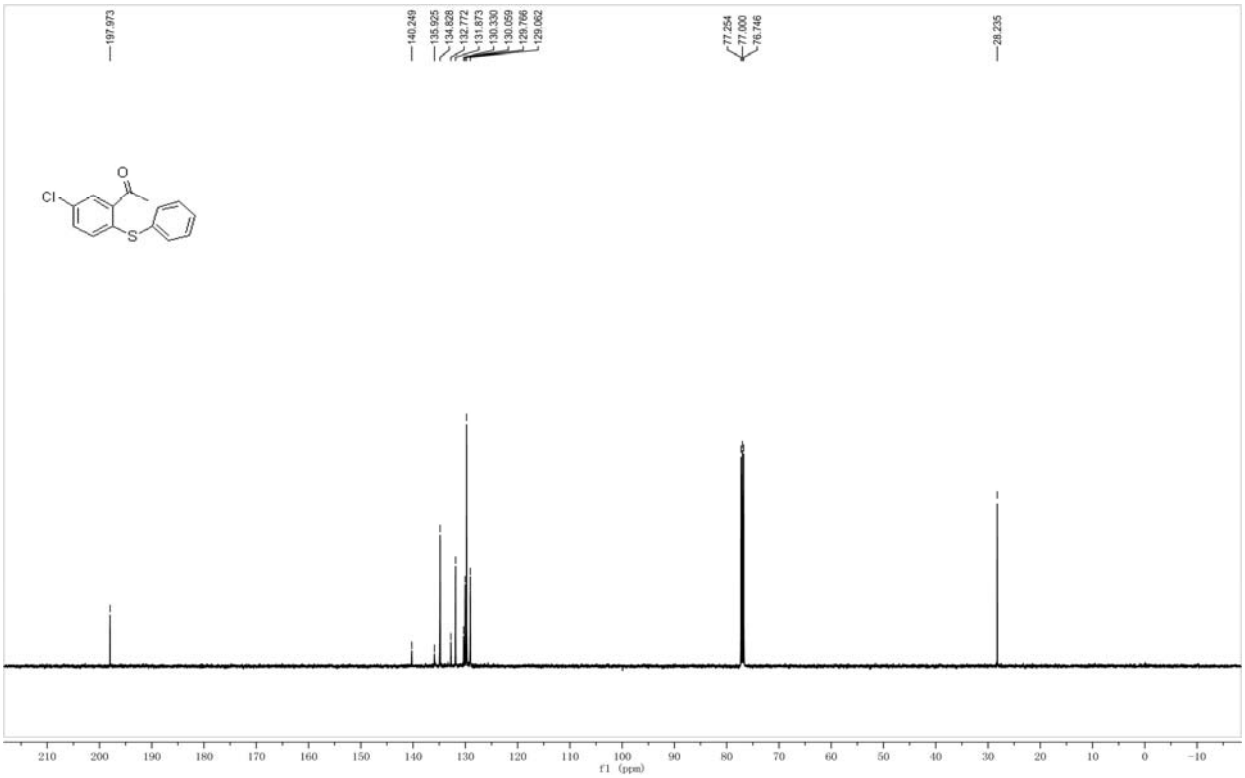


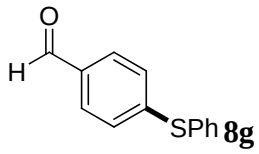
8f

^{1}H NMR



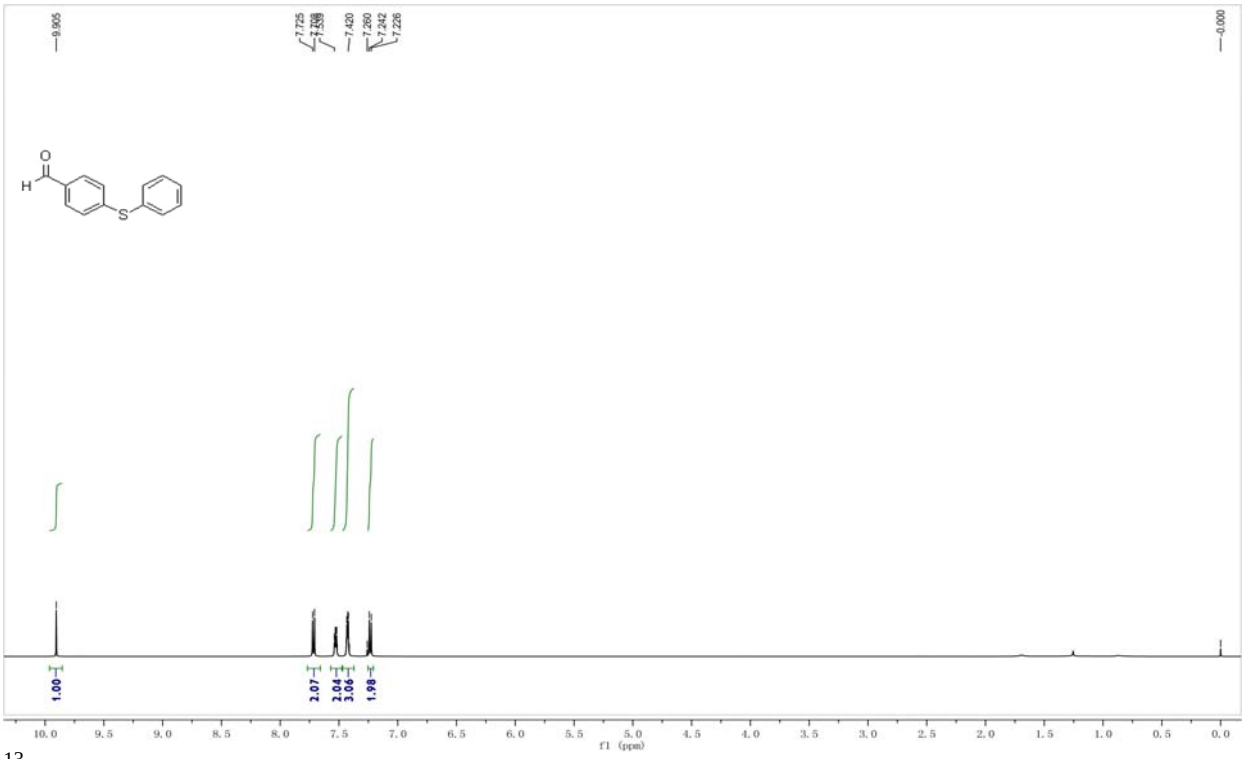
^{13}C NMR



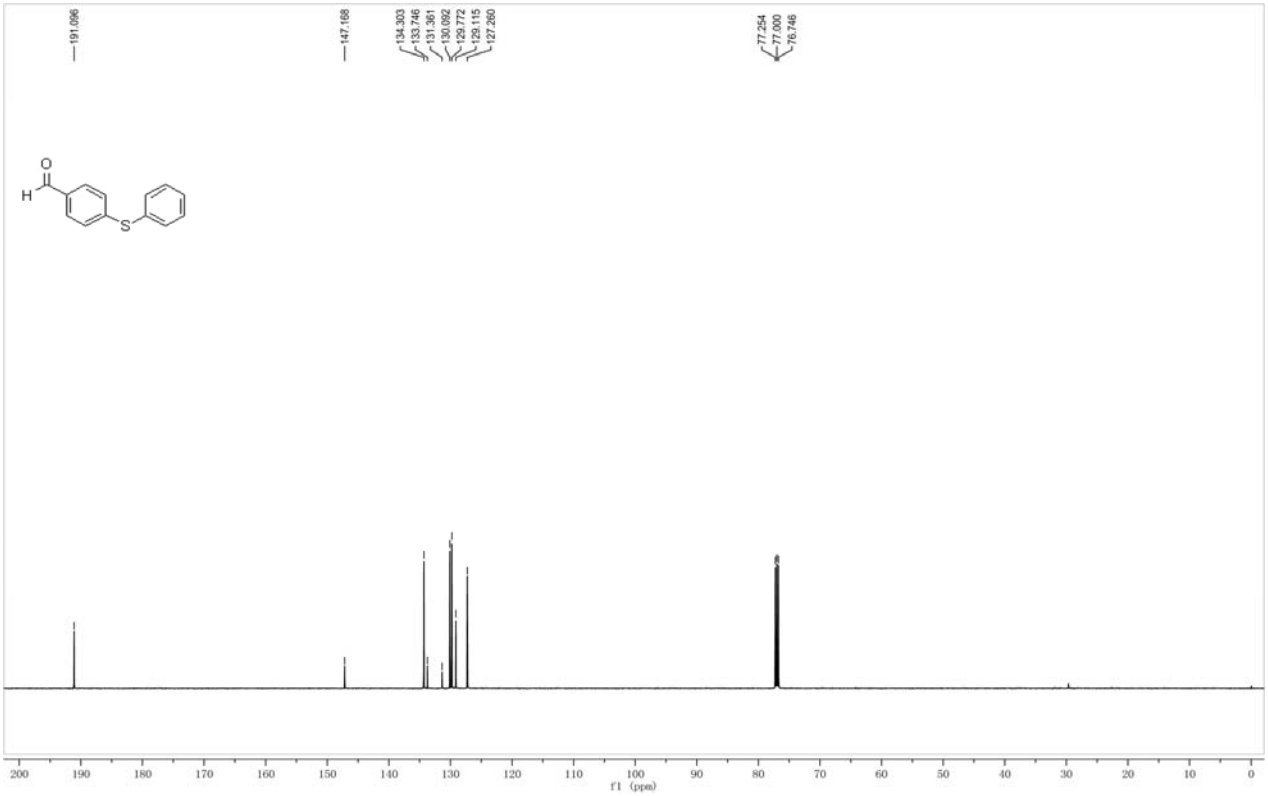


8g

^{1}H NMR

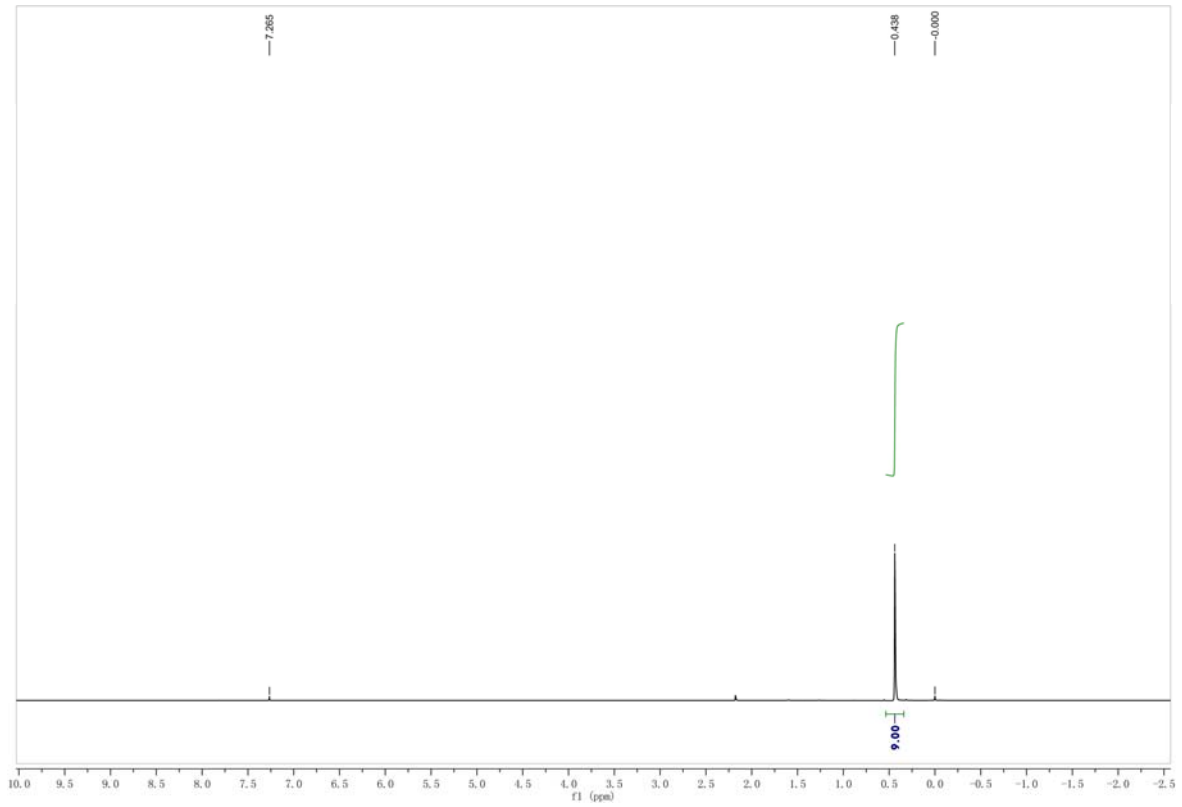


^{13}C NMR



Me_3Si-Cl

^{1}H NMR



^{13}C NMR