Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Three-component 2-aryl substituted benzothiophene formation under transition-metal free conditions

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A. General information

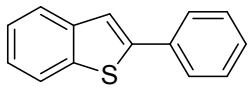
All experiments were carried out under an atmosphere of air. Flash column chromatography was performed over silica gel (48-75 μm). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to $SiMe_4$ or chloroform signals. MS analyses were performed on Agilent 5975 GC-MS instrument (EI). The new compounds were characterized by ^{1}H NMR, ^{13}C NMR, MS and HRMS. The structure of known compounds was further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those of literature. All reagents were used as received from commercial sources without further purification.

B. General procedure of the reaction

A 10 mL oven-dried reaction vessel was charged with sulphur powder (25.6 mg, 0.8 mmol), K_2CO_3 (82.8 mg, 0.6 mmol), methyl 2-phenylacetate (**1a**, 45 mg, 0.3 mmol), 2-bromobenzaldehyde (**2a**, 37.0 mg, 0.2 mmol). The reaction vessel was added DMF (0.5 mL) by syringe. The sealed vessel was stirred at 110 ^{o}C for 16 h. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether) to give **3a** (37.4 mg) as white solid in 89% yield.

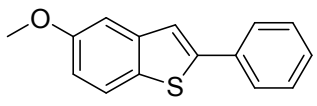
C. Characterization data of products

2-Phenylbenzo[b]thiophene (3a, CAS: 1207-95-0) [1]



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.83 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 7.2 Hz, 1H), 7.73-7.71 (m, 2H), 7.55 (s, 1H), 7.45-7.41 (m, 2H), 7.35-7.29 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.2, 140.7, 139.5, 134.3, 128.9, 128.2, 126.5, 124.5, 124.3, 123.5, 122.2, 119.4; MS (EI) m/z (%) 210 (100), 178, 165, 139, 77.

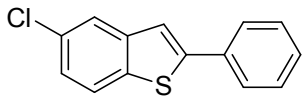
5-Methoxy-2-phenylbenzo[b]thiophene (3b) [2]



The reaction was conducted with **1a** (45 mg, 0.3 mmol) and 2-bromo-5-methoxybenzaldehyde (**2b**, 43.0 mg, 0.2 mmol) under the standard conditions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, PE : EA = 50 : 1) to give **3b** (35.1 mg) as white solid in 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.69 (m, 3H), 7.47 (s, 1H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 6.97 (dd, *J* = 10.4, *J* = 1.6 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.7, 145.5, 141.7, 134.4, 132.0, 128.9, 128.2, 126.4, 122.9, 119.3, 114.5, 105.8, 55.5; MS (EI) m/z (%) 240 (100), 197, 165, 152, 120.

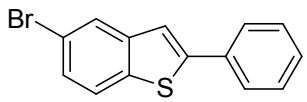
5-Chloro-2-phenylbenzo[b]thiophene (3c, CAS: 101219-31-2) [1]



The reaction was conducted with **1a** (45 mg, 0.3 mmol) and 2-bromo-5-chlorobenzaldehyde (**2c**, 43.8 mg, 0.2 mmol) under the standard conditions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether) to give **3c** (41.0 mg) as white solid in 84% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.74-7.69 (m, 4H), 7.47-7.36 (m, 4H), 7.28-7.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 146.4, 141.8, 137.6, 133.9, 130.7, 129.0, 128.7, 126.6, 124.7, 123.2, 123.0, 118.6; MS (EI) m/z (%) 244 (100), 208, 165, 122, 104.

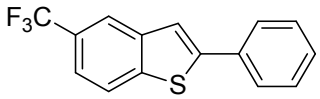
5-Bromo-2-phenylbenzo[b]thiophene (3d, CAS: 7312-09-6) [2]



The reaction was conducted with **1a** (45 mg, 0.3 mmol) and 5-bromo-2-fluorobenzaldehyde (**2e**, 40.6 mg, 0.2 mmol) under the standard conditions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether) to give **3d** (43.4 mg) as white solid in 74% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.91 (s, 1H), 7.69 (m, 3H), 7.46-7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 146.2, 142.3, 138.1, 133.8, 129.0, 128.7, 127.3, 126.6, 126.1, 123.6, 118.52, 118.48; MS (EI) m/z (%) 290 (100), 208, 165, 145, 104.

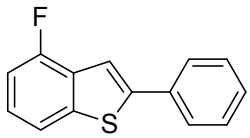
2-Phenyl-5-(trifluoromethyl)benzo[b]thiophene (3e)



The reaction was conducted with **1a** (45 mg, 0.3 mmol) and 2-fluoro-5-(trifluoromethyl) benzaldehyde (**2f**, 38.4 mg, 0.2 mmol) under the standard conditions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether) to give **3e** (48.4 mg) as white solid in 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.04 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.59 (s, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.40-7.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 146.6, 142.5, 140.2, 133.6, 129.1, 128.8, 127.2 (d, *J* = 32.0 Hz), 126.6, 124.6 (q, *J* = 270 Hz), 122.7, 120.6 (d, *J* = 4.2 Hz), 120.5 (d, *J* = 3.6 Hz), 119.3; HRMS (ESI) calcd. for: $C_{15}H_{10}F_3S$ $[M+H]^+$ 279.04498, found 279.04525.

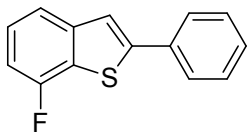
4-Fluoro-2-phenylbenzo[b]thiophene (3f)



The reaction was conducted with **1a** (45 mg, 0.3 mmol) and 2,6-difluorobenzaldehyde (**2g**, 28.4 mg, 0.2 mmol) under the standard conditions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether) to give **3f** (13.7 mg) as white solid in 30% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) *δ* 7.72 (d, *J* = 7.6 Hz, 2H), 7.65 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.29-7.24 (m, 1H), 7.04-7.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) *δ* 157.7 (d, *J* = 250 Hz), 144.7, 141.8, 133.8, 129.8 (d, *J* = 15 Hz), 129.0, 128.6, 126.6, 125.1 (d, *J* = 7.2 Hz), 118.0 (d, *J* = 3.9 Hz), 114.2 (d, *J* = 1 Hz), 109.5 (d, *J* = 18.8 Hz); HRMS (ESI) calcd. for: $C_{14}H_{10}FS$ $[M+H]^+$ 229.04818, found 229.04726.

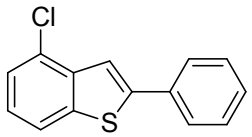
7-Fluoro-2-phenylbenzo[b]thiophene (3g)



The reaction was conducted with **1a** (45 mg, 0.3 mmol) and 2,3-difluorobenzaldehydel (**2h**, 28.4 mg, 0.2 mmol) under the standard conditions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether) to give **3g** (27.8 mg) as white solid in 61% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.56-7.55 (m, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.39-7.28 (m, 2H), 7.01 (t, *J* = 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.5 (d, *J* = 245 Hz), 145.6, 145.0, 133.8, 129.0, 128.7, 126.6, 125.8 (d, *J* = 6.7 Hz), 122.8, 119.5 (d, *J* = 2.2 Hz), 119.3 (d, *J* = 3.3 Hz), 109.4 (d, *J* = 18.4 Hz); HRMS (ESI) calcd. for: $C_{14}H_{10}FS$ $[M+H]^+$ 229.04818, found 229.04829.

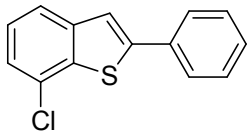
4-Chloro-2-phenylbenzo[b]thiophene (3h) [2]



The reaction was conducted with **1a** (45 mg, 0.3 mmol) and 2,6-dichlorobenzaldehyde (**2j**, 35.0 mg, 0.2 mmol) under the standard conditions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether) to give **3h** (18.5 mg) as white solid in 38% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.75-7.71 (m, 4H), 7.46-7.42 (m, 2H), 7.39-7.34 (m, 2H), 7.26-7.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.3, 140.5, 138.9, 133.8, 129.0, 128.7, 128.5, 126.6, 124.9, 124.5, 120.7, 117.6; MS (EI) m/z (%) 244 (100), 208, 165, 122, 104.

7-Chloro-2-phenylbenzo[b]thiophene (3i)

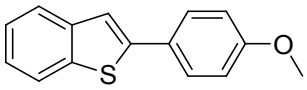


The reaction was conducted with **1a** (45 mg, 0.3 mmol) and 2,3-dichlorobenzaldehyde (**2k**, 35.0 mg, 0.2 mmol) under the standard conditions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether) to give **3i** (40.0 mg) as white solid in 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.68-7.66 (m, 1H), 7.57 (s, 1H),

7.44 (t, J = 7.4 Hz, 2H), 7.38 (d, J = 7.2 Hz, 1H), 7.31-7.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.3, 141.9, 138.6, 133.8, 129.0, 128.6, 127.5, 126.5, 125.7, 123.9, 121.9, 119.9; HRMS (ESI) calcd. for: $C_{14}H_{10}ClS$ $[M+H]^+$ 245.01863, found 245.01816..

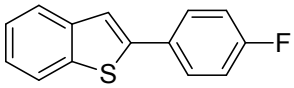
2-(4-Methoxyphenyl)benzo[b]thiophene (3j, CAS: 27884-09-9) [1]



The reaction was conducted with methyl 2-(4-methoxyphenyl)acetate (**1b**, 54.0 mg, 0.3 mmol) and **2a** (37.0 mg, 0.2 mmol) under the standard conditions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, PE : EA = 50 : 1) to give **3j** (13.4 mg) as yellow solid in 28% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.81 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.43 (s, 1H), 7.35-7.26 (m, 2H), 6.96 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 159.8, 144.2, 140.9, 139.2, 127.8, 127.1, 124.4, 123.9, 123.2, 122.2 118.2, 114.4, 55.4; MS (EI) m/z (%) 240 (100), 225, 207, 197, 120.

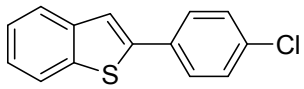
2-(4-Fluorophenyl)benzo[b]thiophene (3k, CAS: 936734-96-2) [1]



The reaction was conducted with methyl 2-(4-fluorophenyl)acetate (**1c**, 50.4 mg, 0.3 mmol) and **2a** (37.0 mg, 0.2 mmol) under the standard conditions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether) to give **3k** (23.3 mg) as white solid in 51% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.82 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.69-7.66 (m, 2H), 7.46 (s, 1H), 7.37-7.29 (m, 2H), 7.12 (t, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 162.8 (d, J = 247 Hz), 143.1, 140.7, 139.5, 130.6 (d, J = 3.4 Hz), 128.2 (d, J = 8.1 Hz), 124.6, 124.4, 123.5, 122.2, 119.4 (d, J = 1.4 Hz), 115.9 (d, J = 21.6 Hz); MS (EI) m/z (%) 228 (100), 207, 196, 183, 114.

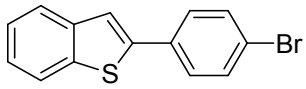
2-(4-Chlorophenyl)benzo[b]thiophene (3l, CAS: 63676-27-7) [3]



The reaction was conducted with methyl 2-(4-chlorophenyl)acetate (**1d**, 55.2 mg, 0.3 mmol) and **2a** (37.0 mg, 0.2 mmol) under the standard conditions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether) to give **3l** (21.0 mg) as white solid in 43% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.51 (s, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.36-7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.8, 140.6, 139.5, 134.1, 132.9, 129.1, 127.6, 124.7, 124.6, 123.7, 122.3, 119.9; MS (EI) m/z (%) 244(100), 208, 165, 122, 104.

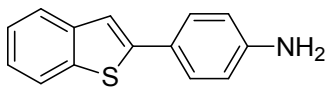
2-(4-Bromophenyl)benzo[b]thiophene (3m)



The reaction was conducted with methyl 2-(4-bromophenyl)acetate (**1e**, 68.7 mg, 0.3 mmol) and **2a** (37.0 mg, 0.2 mmol) under the standard conditions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether) to give **3m** (27.7 mg) as white solid in 48% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 1H),7.59-7.56 (m, 4H), 7.53 (s, 1H), 7.38-7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.9, 140.6, 139.5, 133.3, 132.1, 127.9, 124.7, 124.6, 123.7, 122.3, 122.2, 119.9; HRMS (ESI) calcd. for: $C_{14}H_{10}BrS$ $[M+H]^+$ 288.96762, found 288.96811.

4-(Benzo[b]thiophen-2-yl)aniline (3n)

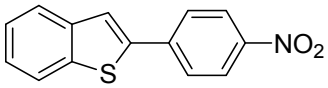


The reaction was conducted with methyl 2-(4-aminophenyl)acetate (**1f**, 49.5 mg, 0.3 mmol) and **2a** (37.0 mg, 0.2 mmol) under the standard conditions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography

(silica gel, EA : PE = 10:1) to give **3n** (13.5 mg) as yellow solid in 30% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.37 (s, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.27-7.23 (m, 1H), 6.72 (d, *J* = 8.0 Hz, 2H), 3.80 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 146.7, 141.0, 138.9, 136.2, 127.7, 124.8, 124.3, 123.6, 123.0, 122.1, 117.2, 115.2; HRMS (ESI) calcd. for: $C_{14}H_{12}NS$ $[M+H]^+$ 226.06850, found 226.06831.

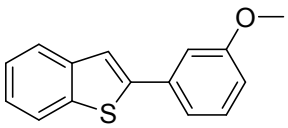
2-(4-Nitrophenyl)benzo[b]thiophene (3o, CAS : 54492-94-3) [1]



The reaction was conducted with methyl 2-(4-nitrophenyl)acetate (**1g**, 58.5 mg, 0.3 mmol) and **2a** (37.0 mg, 0.2 mmol) under the standard conditions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, PE : EA = 10 : 1) to give **3o** (25.5 mg) as yellow solid in 50% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.28 (d, *J* = 8.8 Hz 2H), 7.86-7.83 (m, 4H), 7,71 (s, 1H), 7.40-7.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 147.2, 141.2, 140.6, 140.3, 140.2, 126.8, 125.5, 125.0, 124.4, 124.3, 122.43, 122.41; MS (EI) m/z (%) 225 (100), 209, 133, 122, 77.

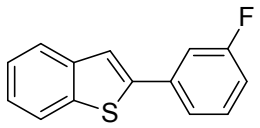
2-(3-Methoxyphenyl)benzo[b]thiophene (3p) [3]



The reaction was conducted with methyl 2-(3-methoxyphenyl)acetate (**1h**, 54.0 mg, 0.3 mmol) and **2a** (37.0 mg, 0.2 mmol) under the standard conditions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, PE : EA = 50 : 1) to give **3p** (37.0 mg) as yellow solid in 77% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.54 (s, 1H), 7.37-7.25 (m, 5H), 6.89 (d, *J* = 7.2 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.0, 144.1, 140.6, 139.5, 135.6, 129.9, 124.5, 124.3, 123.6, 122.2, 119.7, 119.1, 113.8, 112.2, 55.3; MS (EI) m/z (%) 240 (100), 197, 165, 152, 120.

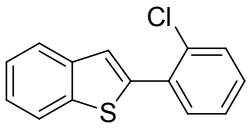
2-(3-Fluorophenyl)benzo[b]thiophene (3q) [4]



The reaction was conducted with methyl 2-(3-fluorophenyl)acetate (**1i**, 50.4 mg, 0.3 mmol) and **2a** (37.0 mg, 0.2 mmol) under the standard conditions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether) to give **3q** (27.8 mg) as white solid in 61% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.83 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 7.2 Hz, 1H), 7.56 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.43-7.32 (m, 4H), 7.04 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 163.1 (d, *J* = 245 Hz), 142.6 (d, *J* = 2.4 Hz), 140.4, 139.5, 136.4 (d, *J* = 7.9 Hz), 130.4 (d, *J* = 8.5 Hz), 124.7, 124.6, 123.8, 122.3, 122.1 (d, *J* = 2.8 Hz), 120.3, 115.0 (d, *J* = 21.1 Hz), 113.2 (d, *J* = 22.7 Hz); MS (EI) m/z (%) 232, 123, 109 (100), 83, 77. MS (EI) m/z (%) 228 (100), 207, 196, 183, 114.

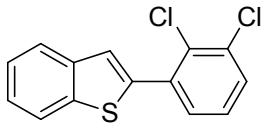
2-(2-Chlorophenyl)benzo[b]thiophene (3r, CAS: 936734-94-0) [5]



The reaction was conducted with methyl 2-(2-chlorophenyl)acetate (**1j**, 55.2 mg, 0.3 mmol) and **2a** (37.0 mg, 0.2 mmol) under the standard conditions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether) to give **3r** (35.6 mg) as yellow solid in 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.87-7.81 (m, 2H), 7.61-7.59 (m, 1H), 7.58 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.40-7.28 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 140.3, 140.2, 139.9, 133.2, 132.8, 131.9, 130.6, 129.2, 126.9, 124.53, 124.46, 124.43, 123.9, 122.0; MS (EI) m/z (%) 244 (100), 208, 165, 122, 104.

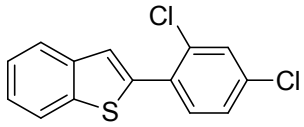
2-(2,3-Dichlorophenyl)benzo[b]thiophene (3s)



The reaction was conducted with methyl 2-(2,3-dichlorophenyl)acetate (**1k** 65.7 mg, 0.3 mmol) and **2a** (37.0 mg, 0.2 mmol) under the standard condtions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether) to give **3s** (45.8 mg) as yellow solid in 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.86-7.82 (m, 1H), 7.71-7.69 (m, 1H), 7.50-7.41 (m, 5H), 7.30-7.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 138.7, 134.6, 133.7, 130.5, 128.7, 128.6, 128.0, 126.4, 126.3, 125.9, 125.5, 125.0, 121.4, 120.0; HRMS (ESI) calcd. for: $C_{14}H_9Cl_2S$ $[M+H]^+$ 278.97965, found 278.97809.

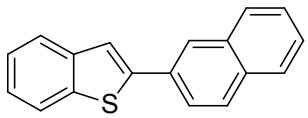
2-(2,4-Dichlorophenyl)benzo[b]thiophene (3t)



The reaction was conducted with methyl 2-(2,4-dichlorophenyl)acetate (**1l** 65.7 mg, 0.3 mmol) and **2a** (37.0 mg, 0.2 mmol) under the standard condtions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether) to give **3t** (44.1 mg) as yellow solid in 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.86-7.81 (m, 2H), 7.56-7.52 (m, 3H), 7.43-7.30 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 140.2, 139.8, 139.1, 134.5, 133.5, 132.5, 131.9, 130.4, 127.3, 124.8, 124.7, 124.6, 123.9, 122.0; HRMS (ESI) calcd. for: $C_{14}H_9Cl_2S$ $[M+H]^+$ 278.97965, found 278.97947.

2-(Naphthalen-2-yl)benzo[b]thiophene (3u, CAS: 17164-77-1) [2]

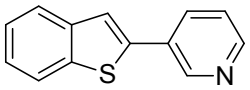


The reaction was conducted with methyl 2-(naphthalen-2-yl)acetate (**1m** 60.0 mg, 0.3 mmol) and

2a (37.0 mg, 0.2 mmol) under the standard conditions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether) to give **3u** (32.8 mg) as white solid in 63% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.15 (s, 1H), 7.91-7.84 (m, 5H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.68 (s, 1H), 7.52-7.49 (m, 2H), 7.35 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.3, 140.8, 139.6, 133.6, 133.1, 131.7, 128.6, 128.2, 127.7, 126.7, 126.4, 125.4, 124.6, 124.43, 124.36, 123.6, 122.3, 119.9; MS (EI) m/z (%) 260 (100), 133, 127, 115, 77.

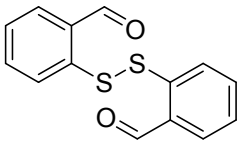
3-(Benzo[b]thiophen-2-yl)pyridine (3v) [6]



The reaction was conducted with methyl 2-(pyridin-3-yl)acetate (**1n** 45.3 mg, 0.3 mmol) and **2a** (37.0 mg, 0.2 mmol) under the standard conditions. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, PE : EA = 4 : 1) to give **3v** (35.9 mg) as yellow solid in 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.99 (s, 1H), 8.57 (d, *J* = 4.0 Hz 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 7.2Hz 1H), 7.81 (s, *J* = 8.0 Hz 1H), 7.60 (s, 1H), 7.40-7.33 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 149.0, 147.3, 140.4, 140.1, 139.7, 133.6, 130.4, 124.9, 124.8, 123.8, 123.7, 122.3, 120.8; MS (EI) m/z (%) 221 (100), 179, 167, 139, 79.

2,2'-Dithiodibenzaldehyde (A, CAS: 55164-16-4)[7]



^{1}H NMR (400 MHz, $CDCl_3$, ppm) *δ* 10.22 (s, 2H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H); MS (EI) m/z (%) 274, 137(100), 109, 76, 65.

D. References

[1] P. H. Durga, H. Thea, K. Burkhard, *Org. Lett.*, 2012, **14**, 5334–5337.

[2] H. Yu, M. Zhang, Y. Li, *J. Org. Chem.*, 2013, **78**, 8898−8903.

[3] B. Liégault, D. Lapointe, L. Caron, A. Vlassova, K. Fagnou, *J. Org. Chem.*, 2009, **74**, 1826–1834.

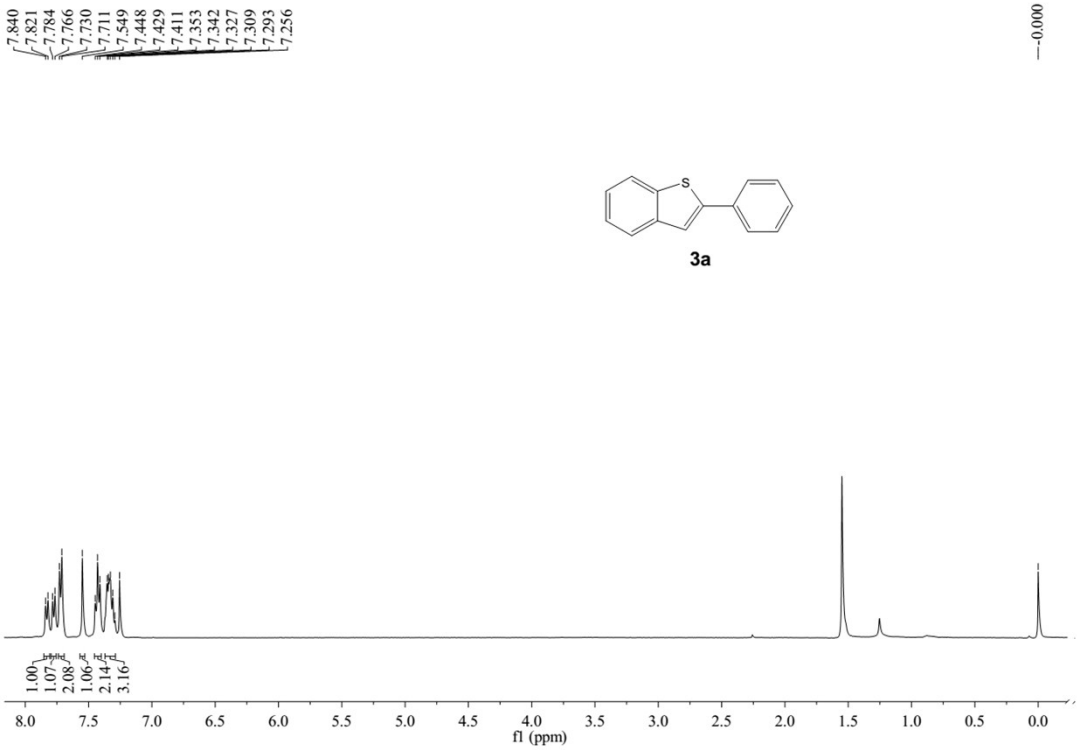
[4] V. Guilarte, M. A. Fernández-Rodríguez, P. García-García, E. Hernando, R. Sanz, *Org. Lett.*, 2011, **13**, 5100–5103.

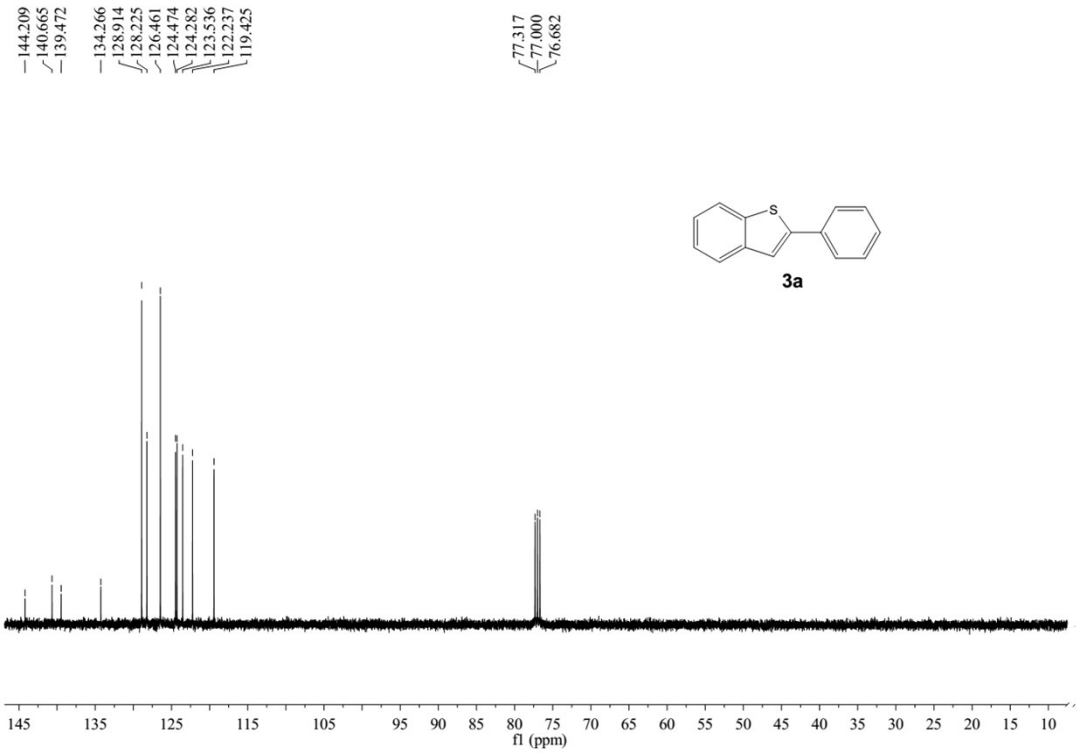
[5] T. Truong, M. Mesgar, K. K. A. Le, O. Daugulis, *J. Am. Chem. Soc.*, 2014, **136**, 8568−8576.

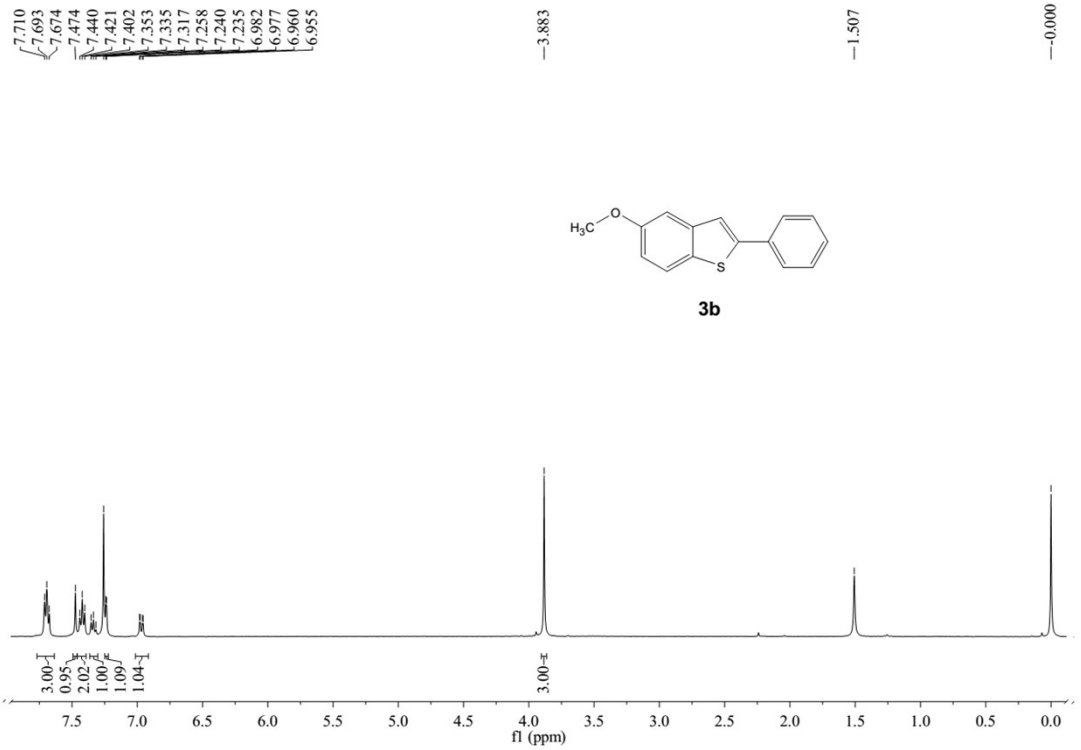
[6] S. Ge, J. F. Hartwig, *Angew. Chem. Int. Ed.*, 2012, **51**, 12837-12841.

[7] M. Raj, H. Wu, S. L. Blosser, M. A. Vittoria, P. S. Arora, *J. Am. Chem. Soc.*, 2015, **137**, 6932–6940.

E. Copies of ^{1}H and ^{13}C NMR spectra of the products



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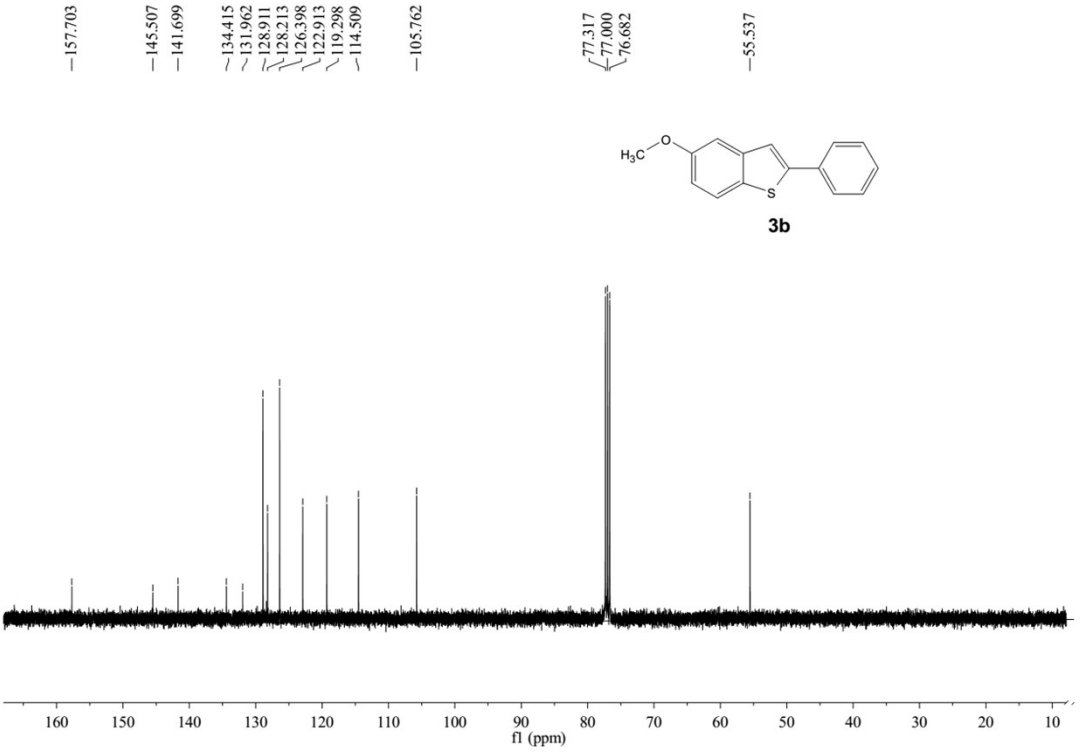
7.674
7.474
7.440
7.421
7.402
7.353
7.335
7.317
7.258
7.240
7.235
6.982
6.977
6.960
6.955
3.883
1.507
0.000
H3C
O
S
3b
3.00
0.95
2.02
1.00
1.09
1.04
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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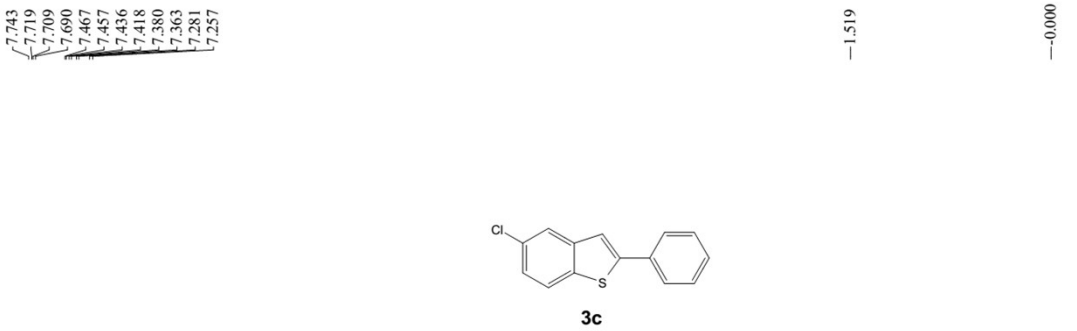
145.507
141.699
134.415
131.962
128.911
128.213
126.398
122.913
119.298
114.509
105.762
77.317
77.000
76.682
55.537
H3C
O
S
3b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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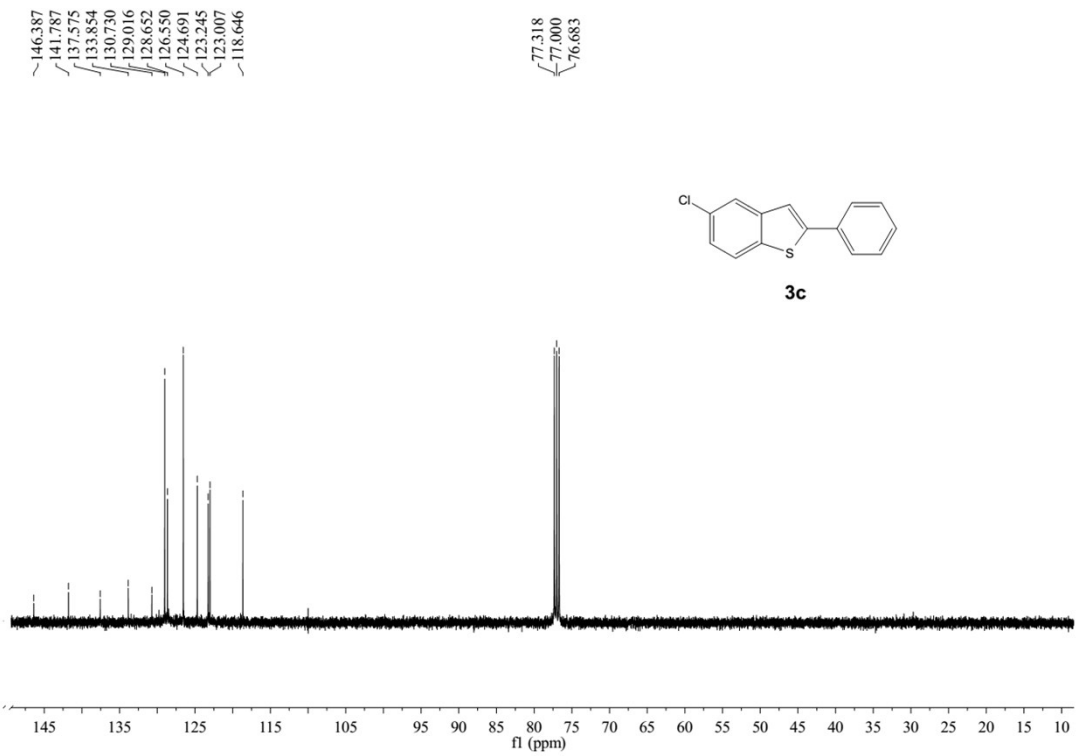
7.719
7.709
7.690
7.467
7.457
7.436
7.418
7.380
7.363
7.281
7.257
1.519
0.000
Cl
S
3c
4.00
3.99
0.90
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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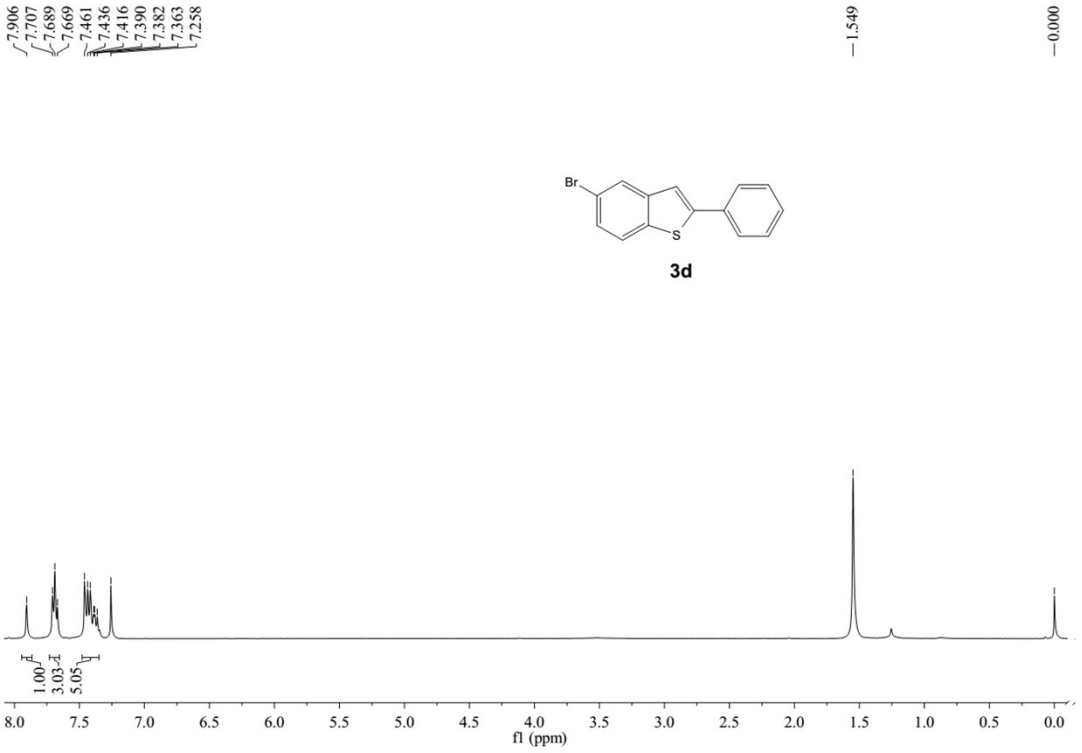
137.575
133.854
130.730
129.016
128.652
126.550
124.691
123.245
123.007
118.646
77.318
77.000
76.683
Cl
S
3c
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)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7.689
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7.416
7.390
7.382
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7.258
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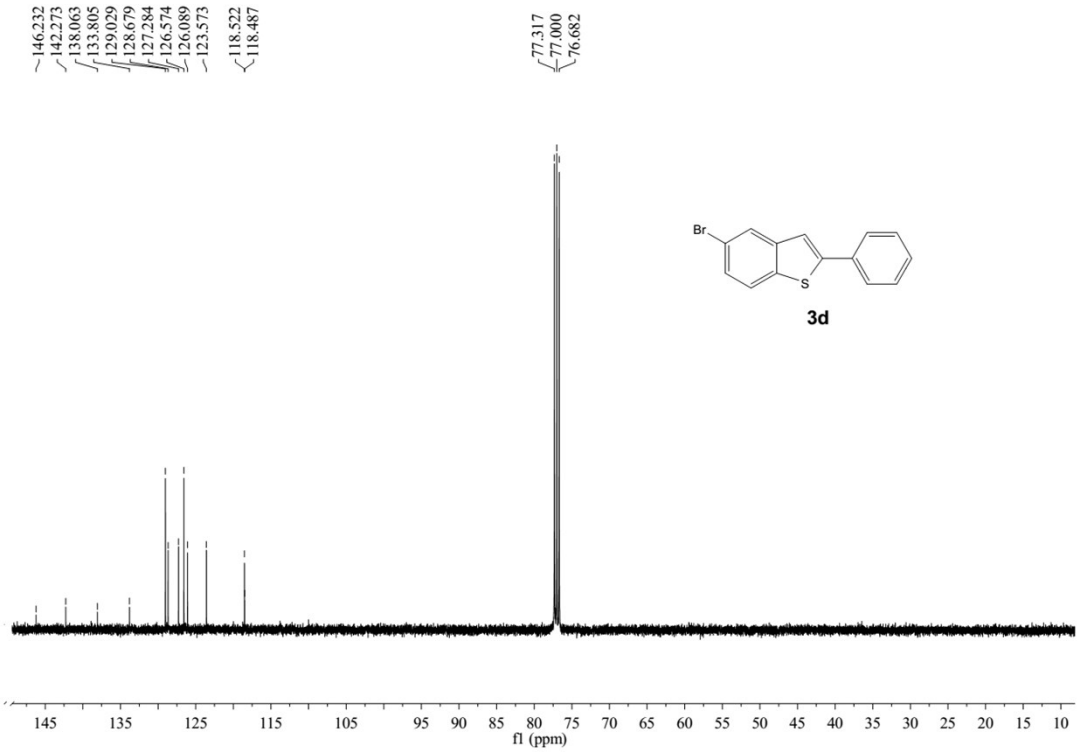
0.000
Br
S
3d
1.00
3.03
5.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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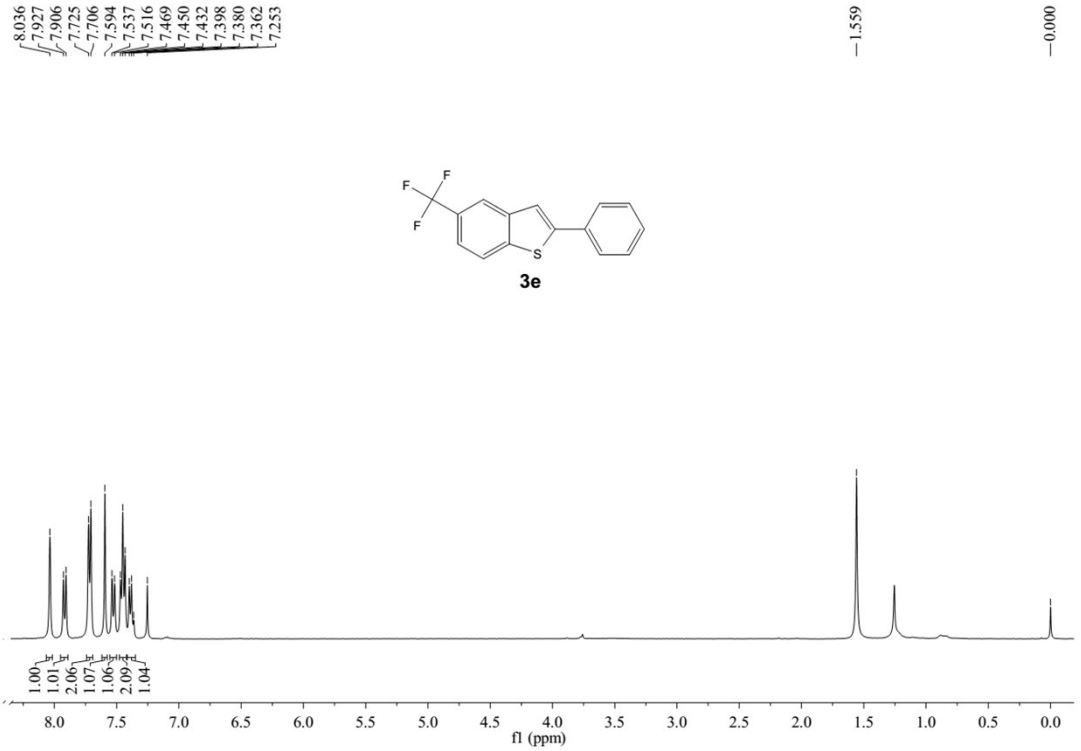
129.029
128.679
127.284
126.574
126.089
123.573
118.522
118.487
77.317
77.000
76.682
Br
S
3d
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)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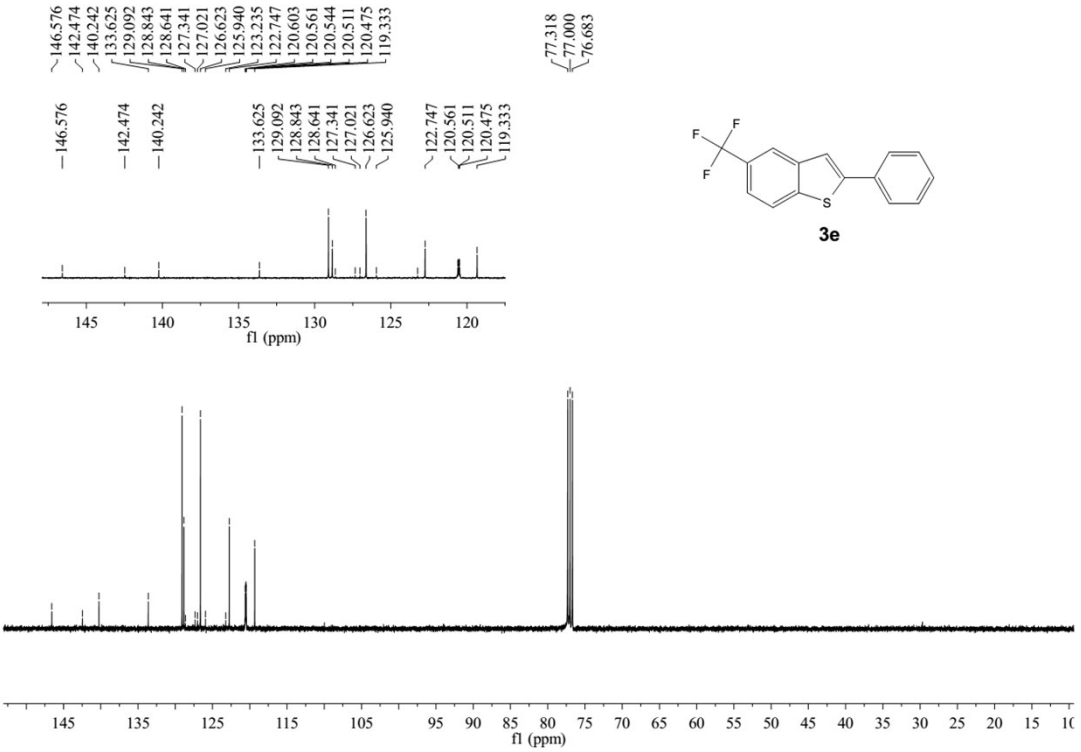
7.906
7.725
7.706
7.594
7.537
7.516
7.469
7.450
7.432
7.398
7.380
7.362
7.253
1.559
0.000
3e
1.00
1.01
2.06
1.07
1.06
2.09
1.04
fl (ppm)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122.747
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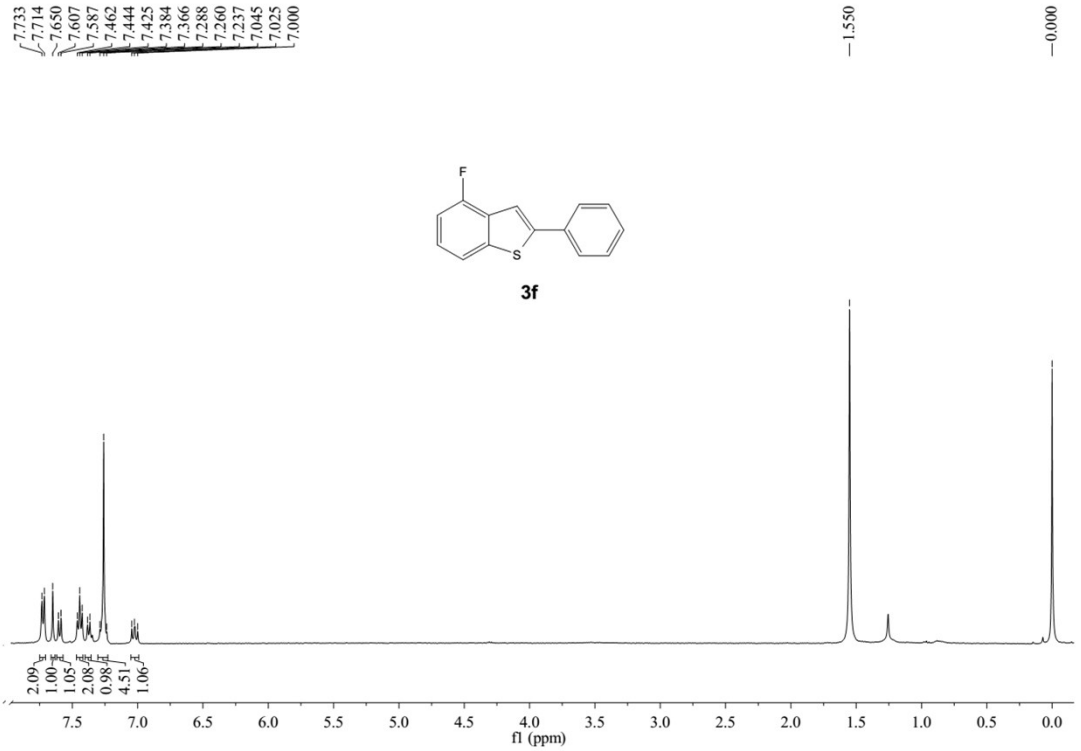
3e
fl (ppm)

fl (ppm)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7.425
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7.366
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7.260
7.237
7.045
7.025
7.000
1.550
0.000
F
S
3f
2.09
1.00
1.05
2.08
0.98
4.51
1.06
7.5
7.0
6.5
6.0
5.5
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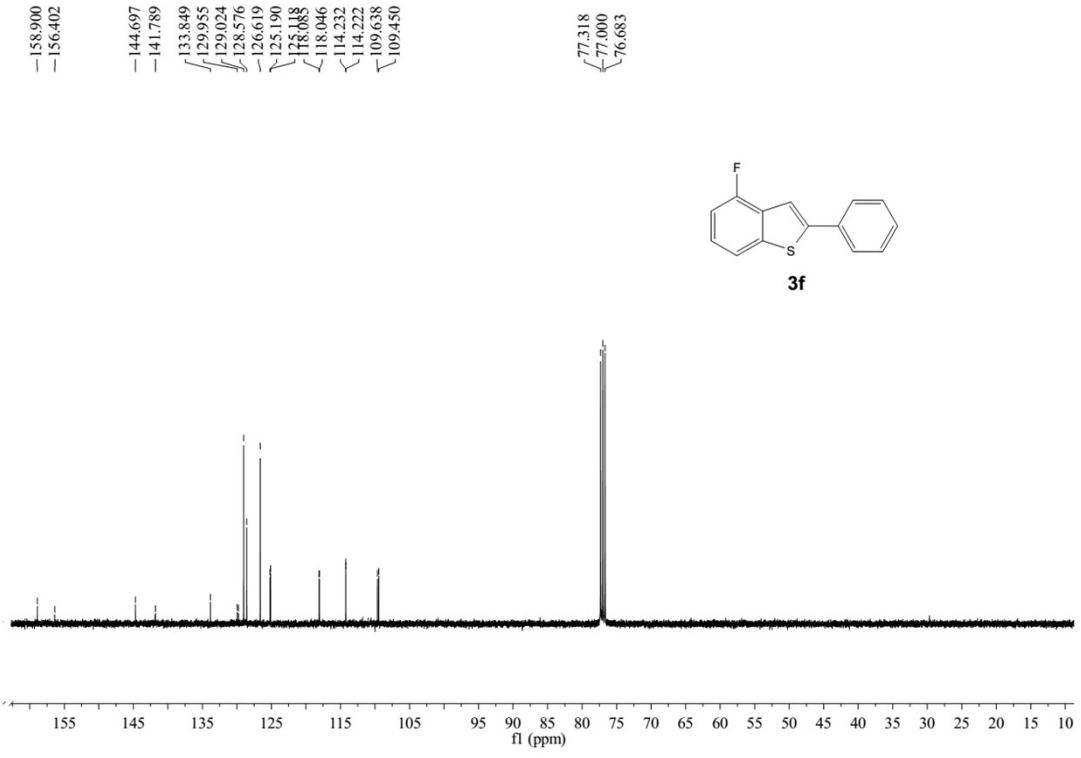
f1 (ppm)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114.232
114.222
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F
S
3f
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145
135
125
115
105
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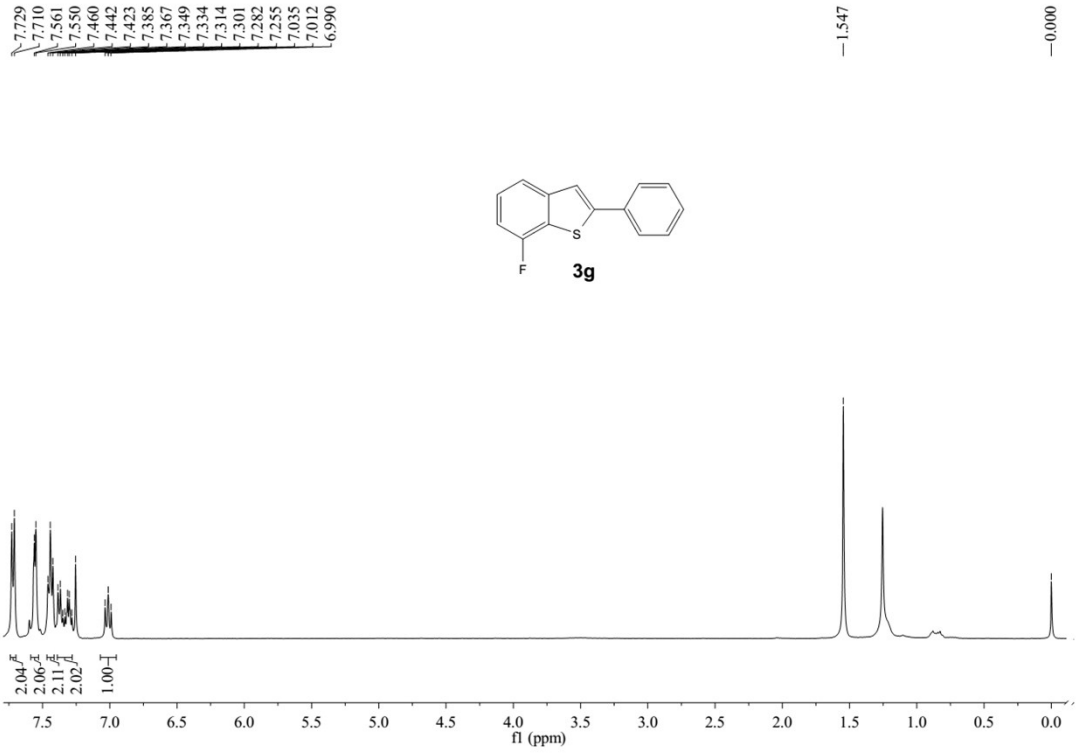
f1 (ppm)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7.349
7.334
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7.301
7.282
7.255
7.035
7.012
6.990
1.547
0.000
S
F
3g
2.04
2.06
2.11
2.02
1.00
7.5
7.0
6.5
6.0
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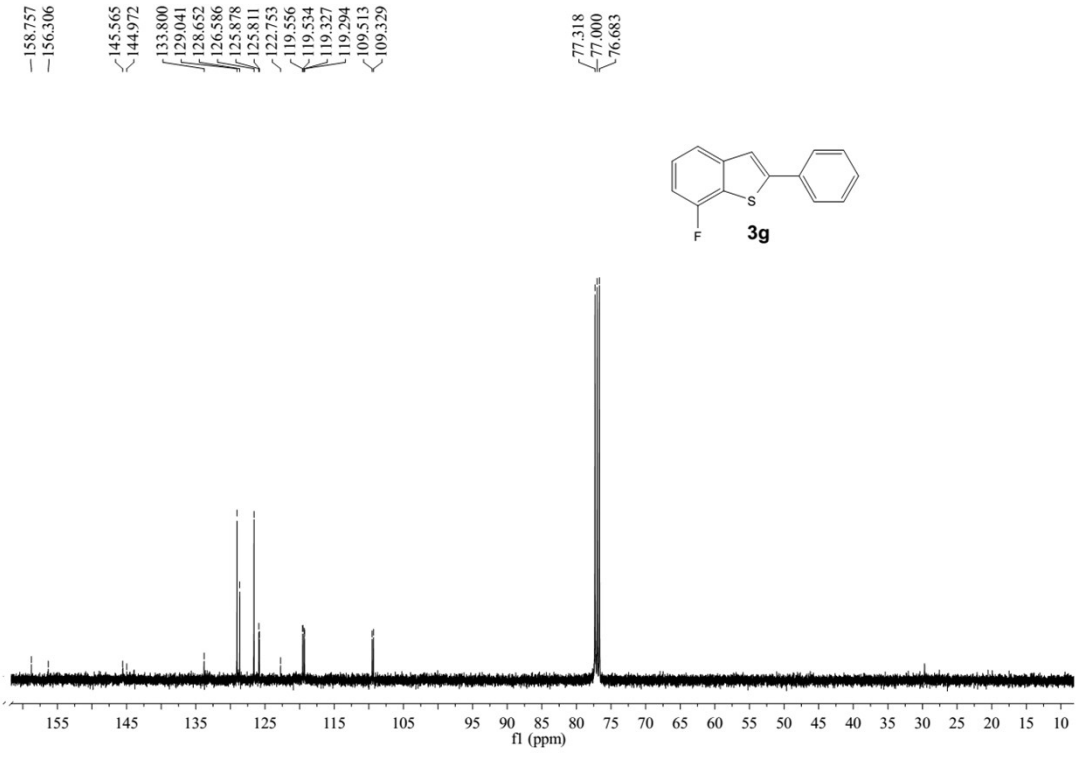
f1 (ppm)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F
3g
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135
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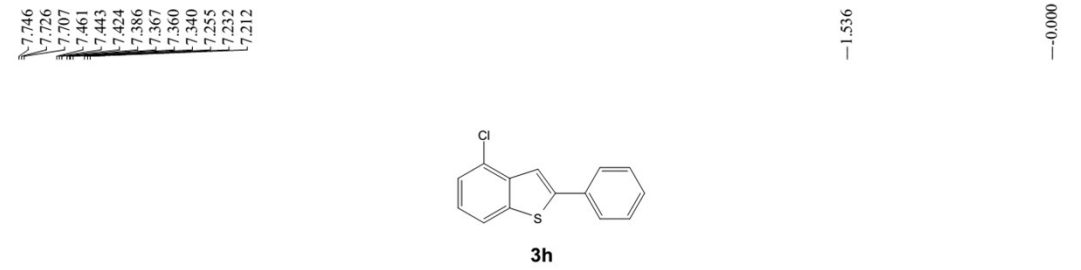
f1 (ppm)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Cl
S
3h
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2.10
2.09
1.00
7.5
7.0
6.5
6.0
5.5
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2.5
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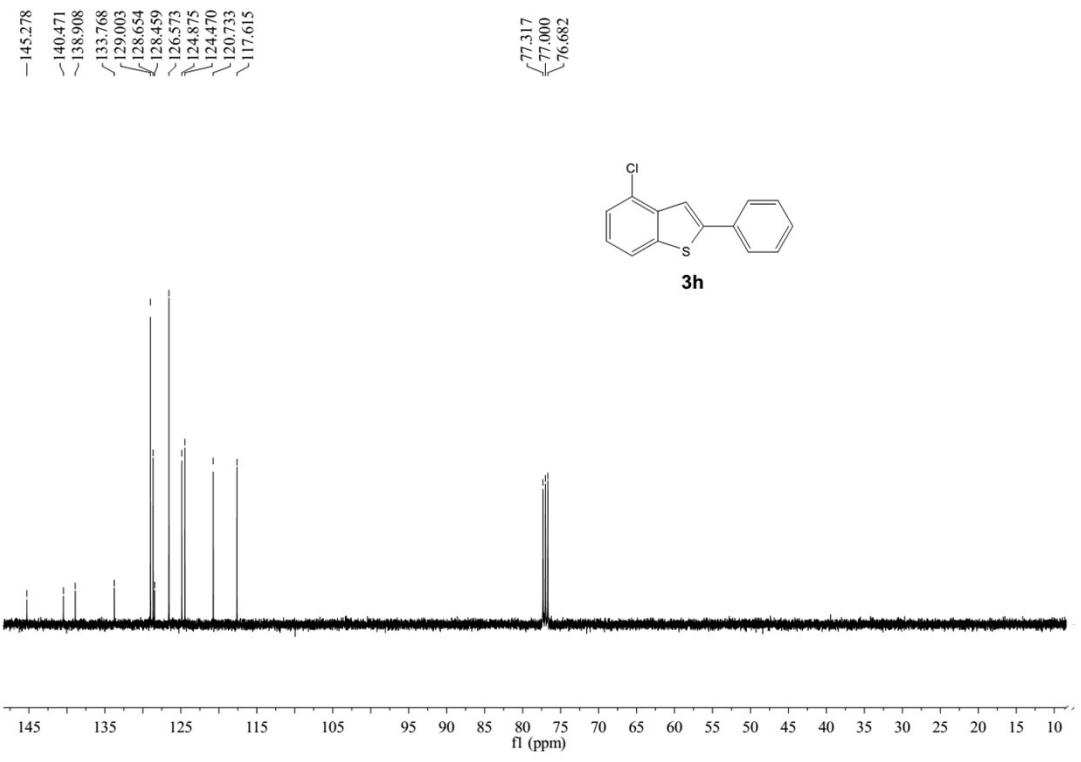
f1 (ppm)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77.000
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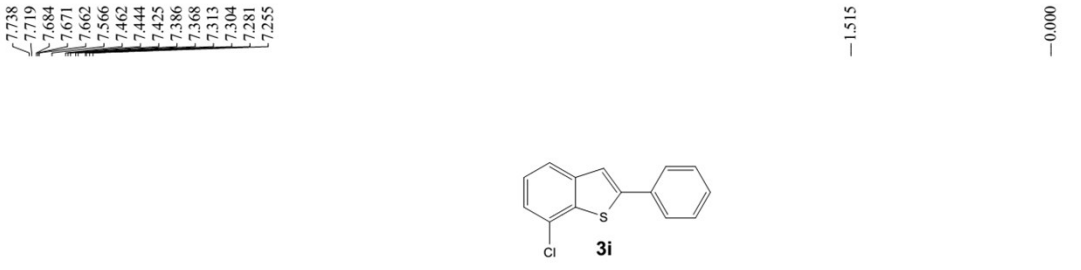
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)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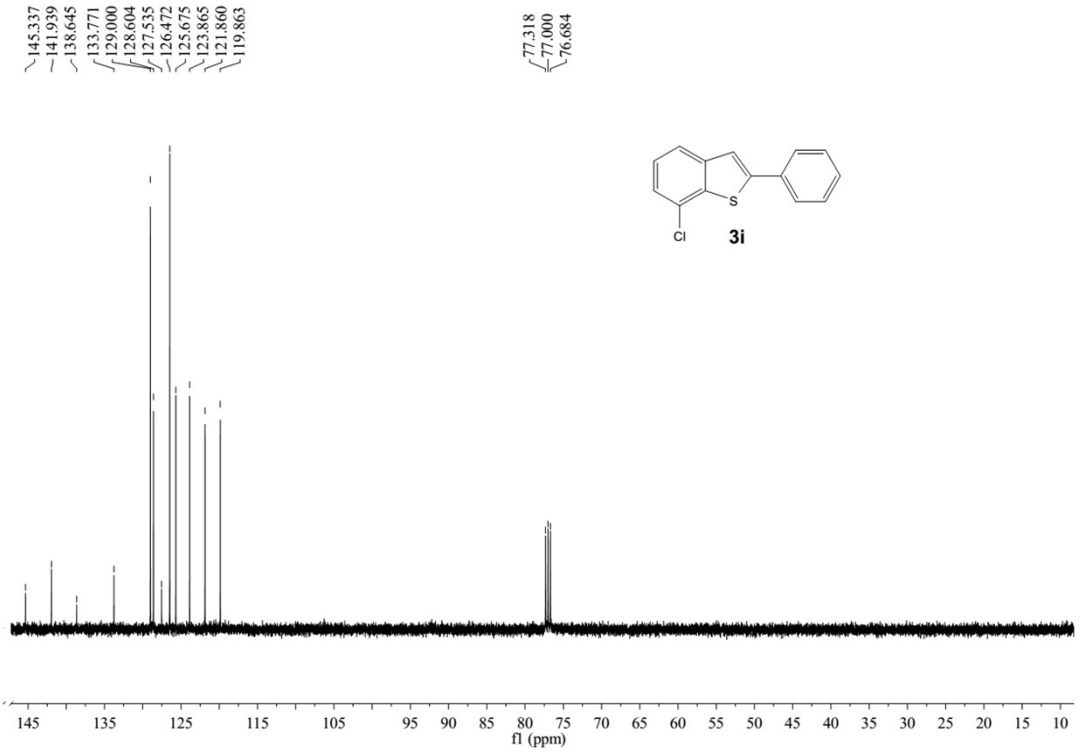
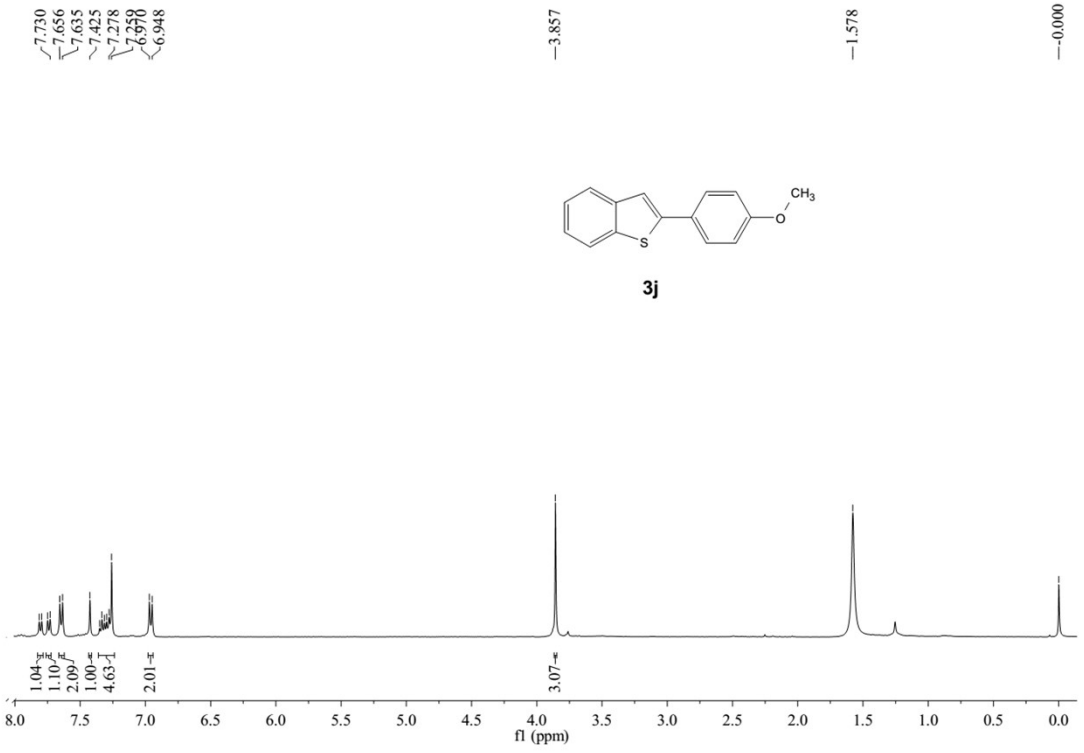
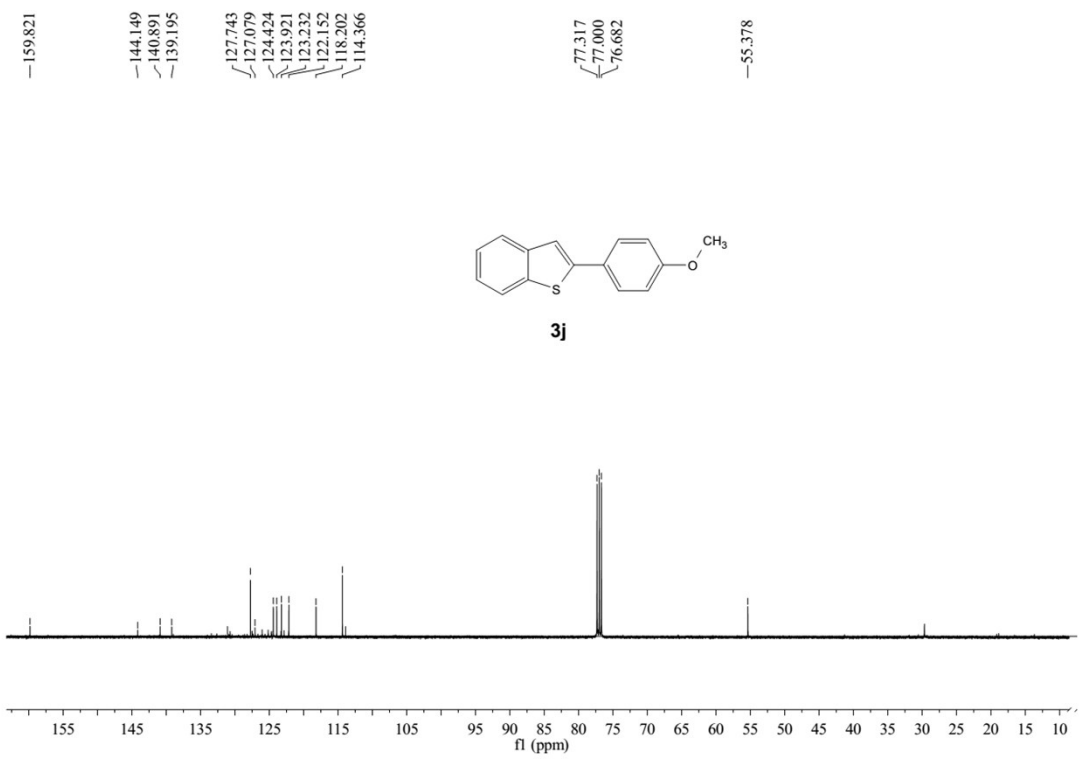
7.719
7.684
7.671
7.662
7.566
7.462
7.444
7.425
7.386
7.368
7.313
7.304
7.281
7.255
1.515
0.000
S
Cl
3i
2.05
1.04
1.00
2.06
0.98
1.99
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

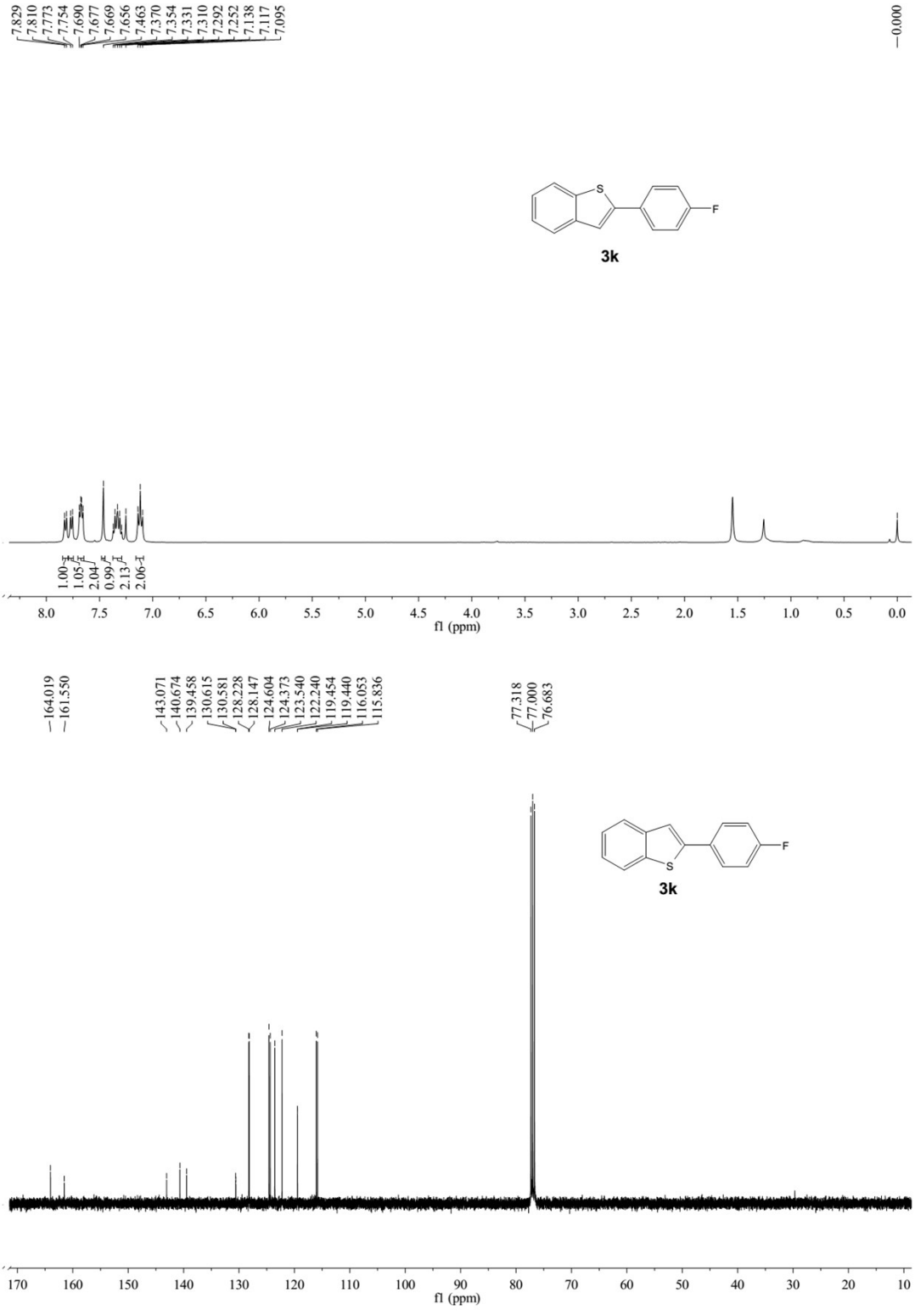

145.337
141.939
138.645
133.771
129.000
128.604
127.535
126.472
125.675
123.865
121.860
119.863
77.318
77.000
76.684
S
Cl
3i
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

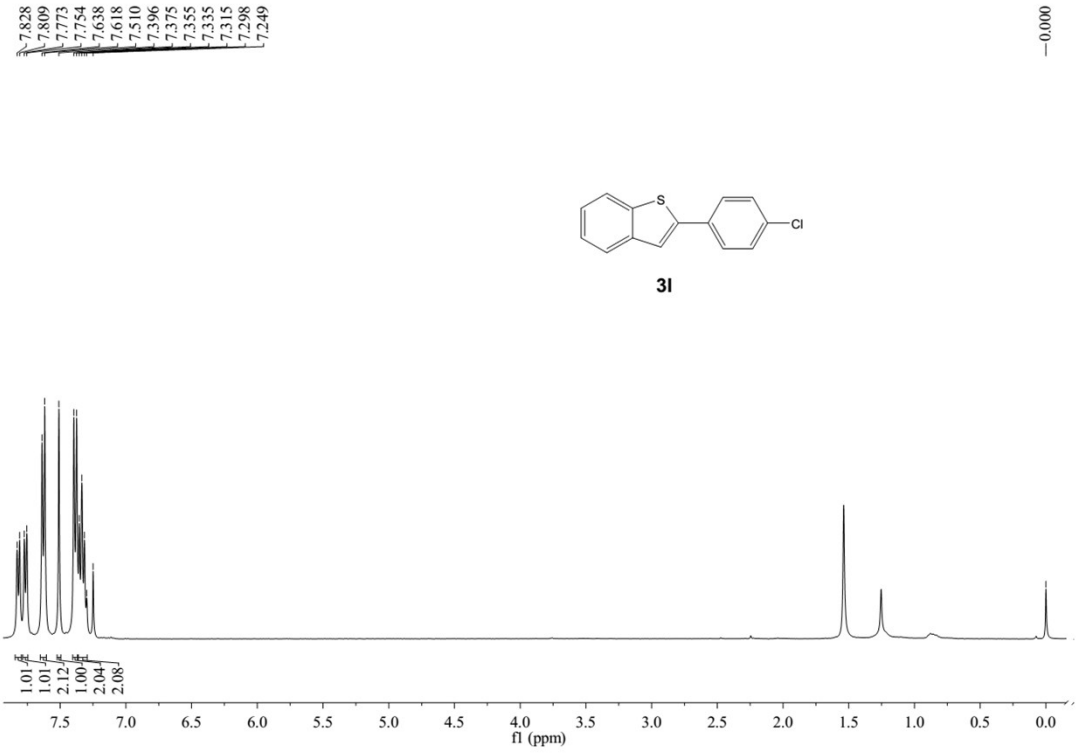

7.730
7.656
7.635
7.425
7.278
7.259
6.970
6.948
3.857
1.578
0.000
CH3
O
S
1.04
1.10
2.09
1.00
4.63
2.01
3.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

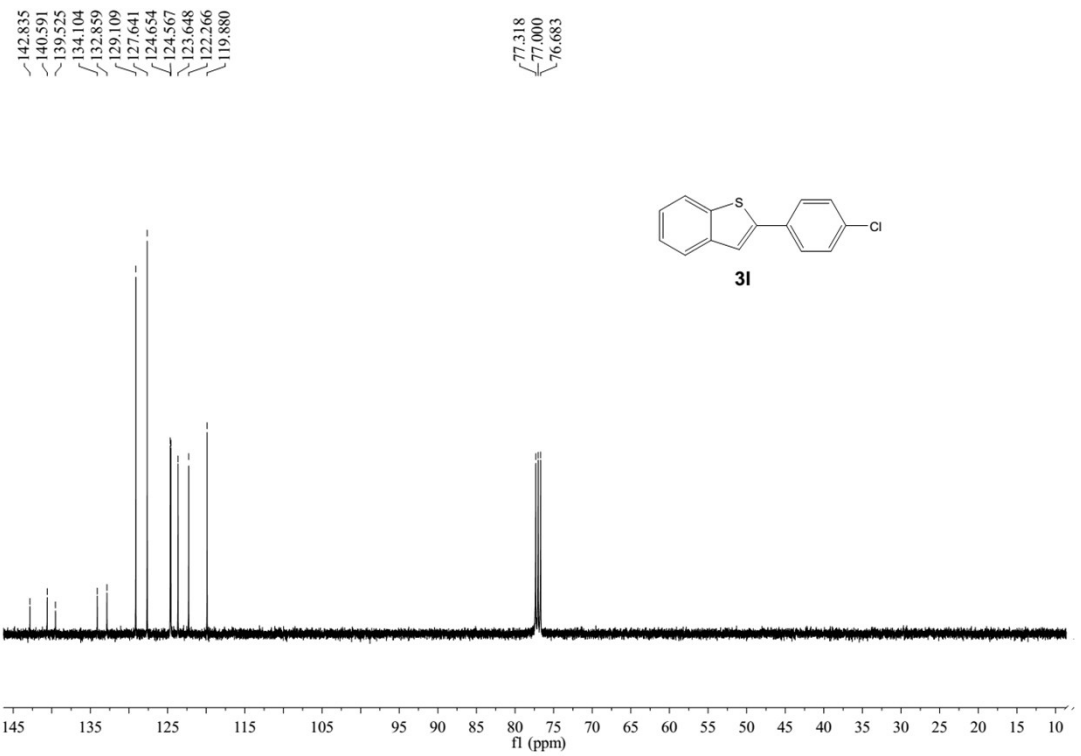
3j

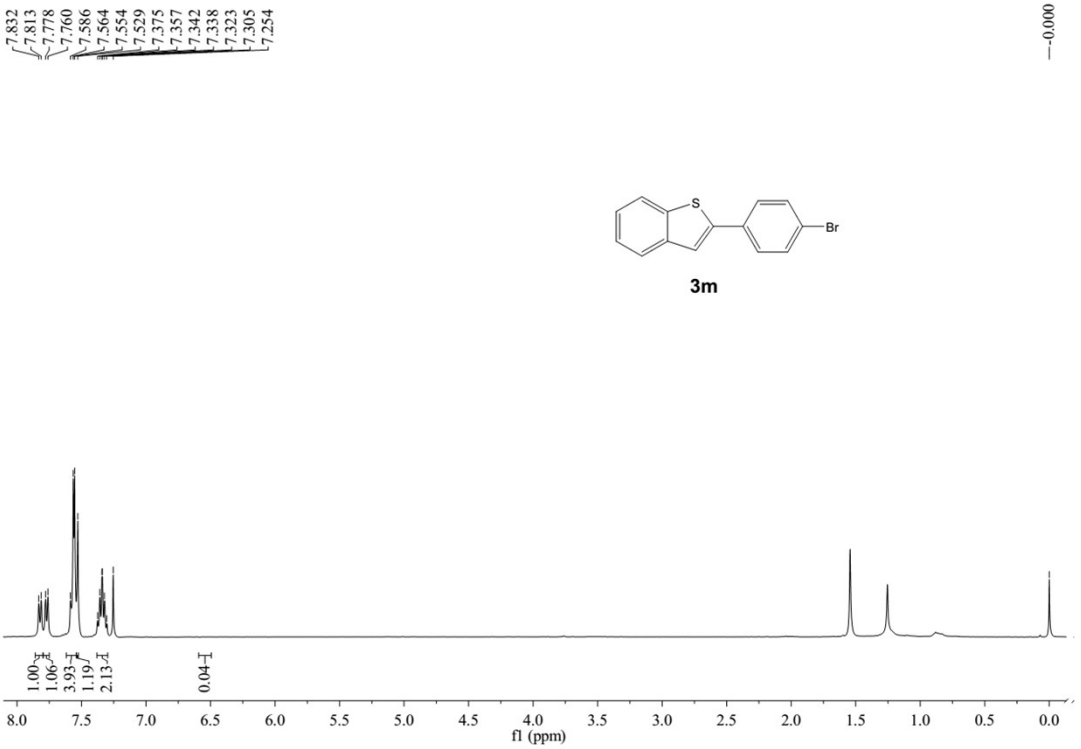

159.821
144.149
140.891
139.195
127.743
127.079
124.424
123.921
123.232
122.152
118.202
114.366
77.317
77.000
76.682
55.378
CH3
O
S
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

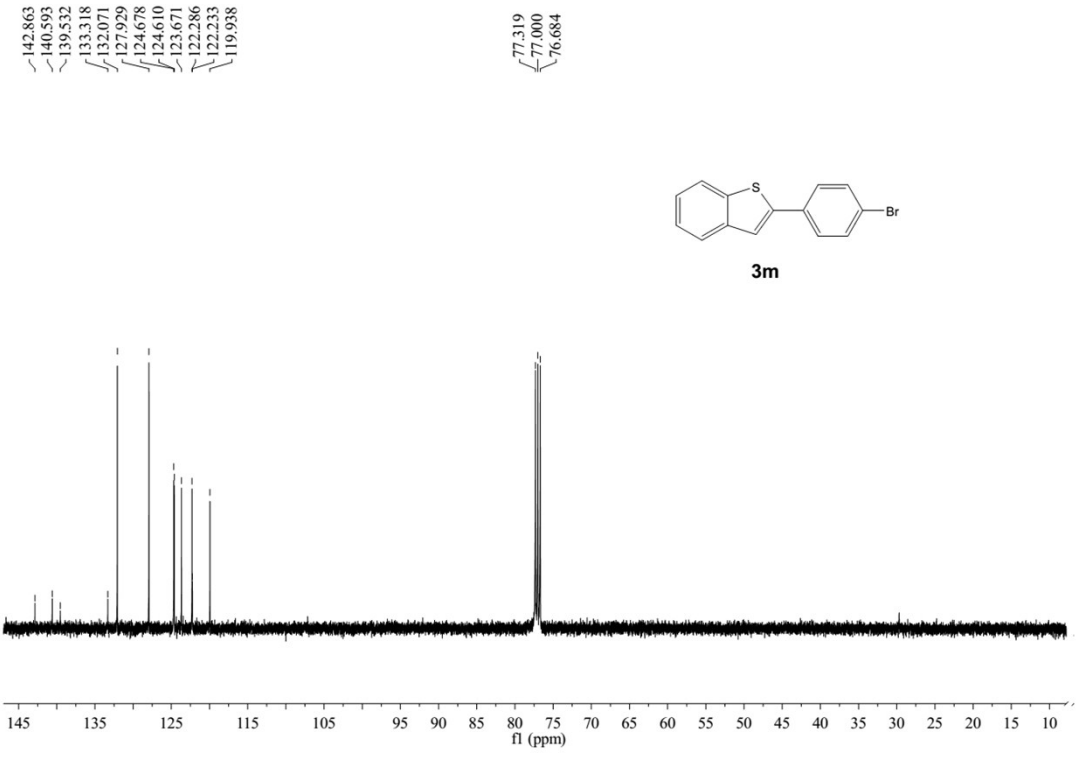
3j

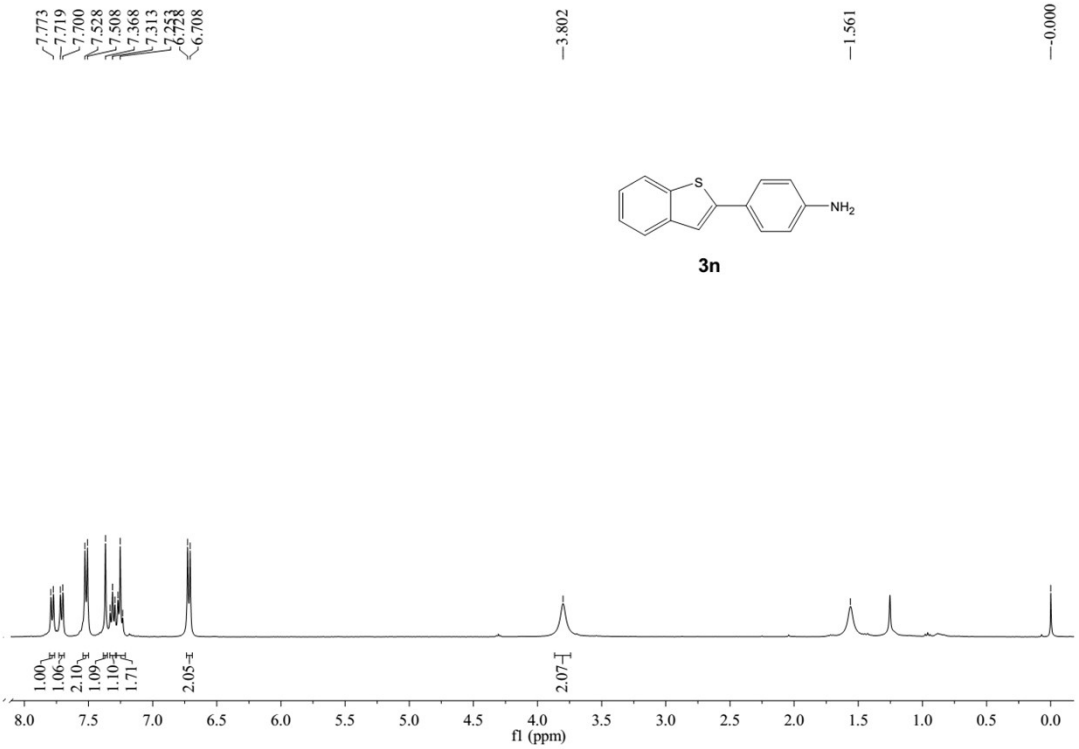

7.829
7.810
7.773
7.754
7.690
7.677
7.669
7.656
7.463
7.370
7.354
7.331
7.310
7.292
7.252
7.138
7.117
7.095
0.000
S
F
3k
1.00
1.05
2.04
0.99
2.13
2.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
164.019
161.550
143.071
140.674
139.458
130.615
130.581
128.228
128.147
124.604
124.373
123.540
122.240
119.454
119.440
116.053
115.836
77.318
77.000
76.683
S
F
3k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

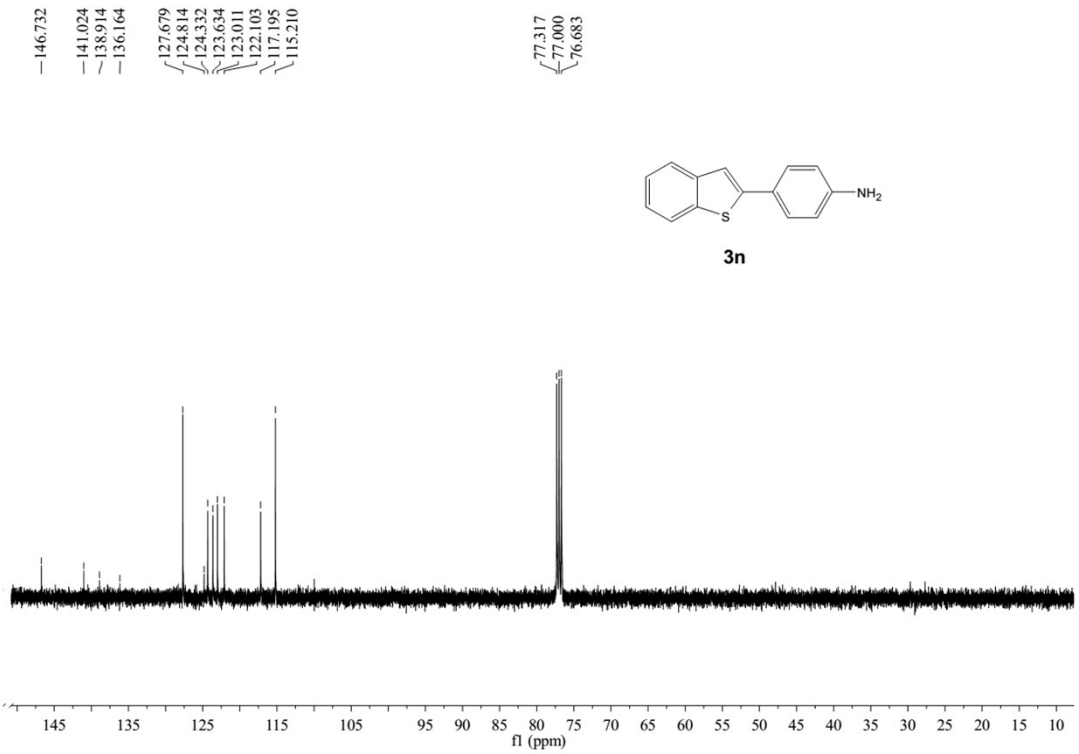

7.828
7.809
7.773
7.754
7.638
7.618
7.510
7.396
7.375
7.355
7.335
7.315
7.298
7.249
0.000
S
Cl
3l
1.01
1.01
2.12
1.00
2.04
2.08
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

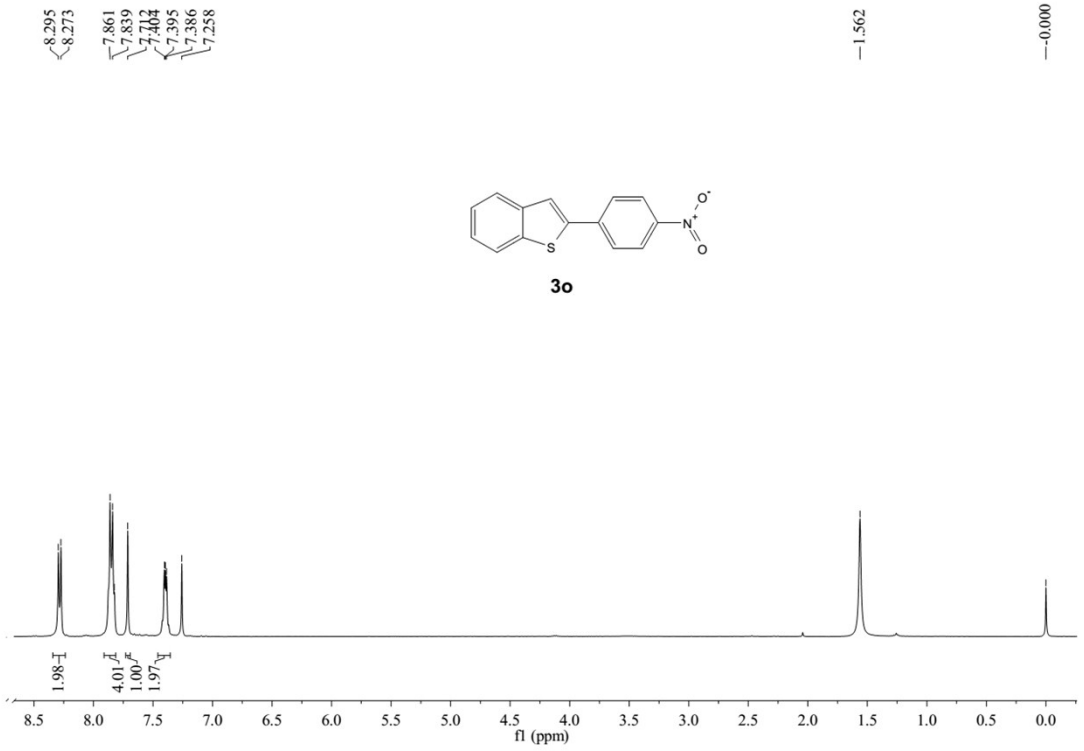

142.835
140.591
139.525
134.104
132.859
129.109
127.641
124.654
124.567
123.648
122.266
119.880
77.318
77.000
76.683
S
Cl
3l
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)


7.832
7.813
7.778
7.760
7.586
7.564
7.554
7.529
7.375
7.357
7.342
7.338
7.323
7.305
7.254
0.000
S
Br
3m
1.00
1.06
3.93
1.19
2.13
0.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

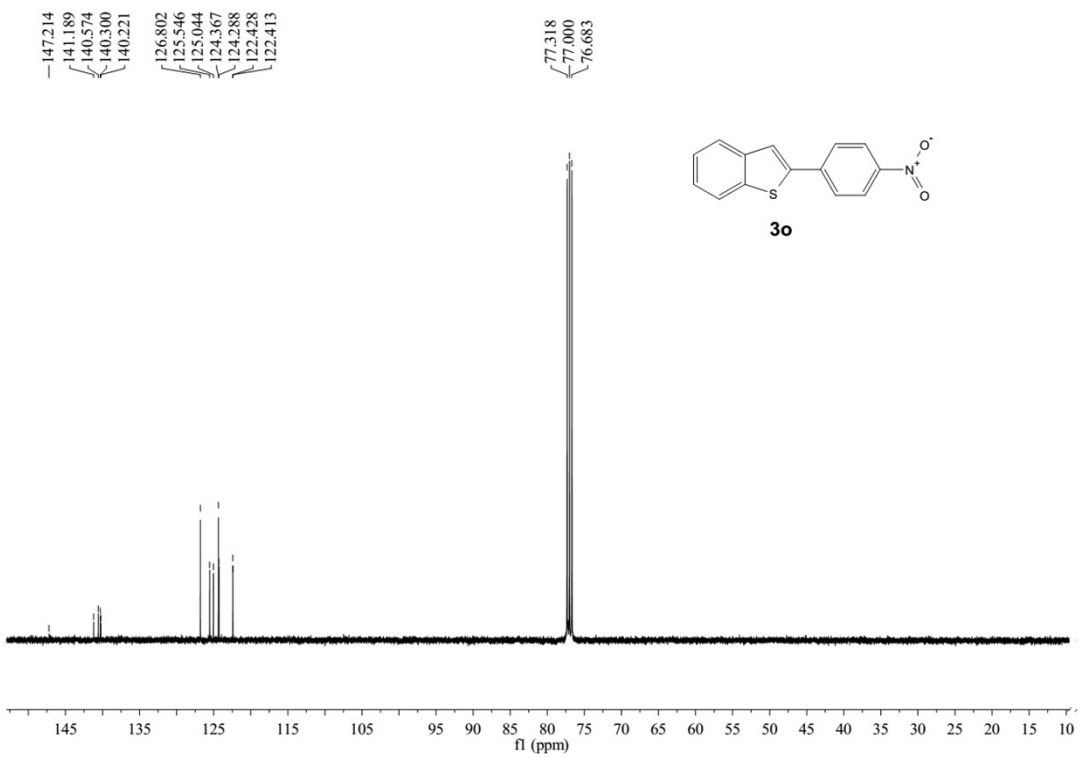

142.863
140.593
139.532
133.318
132.071
127.929
124.678
124.610
123.671
122.286
122.233
119.938
77.319
77.000
76.684
S
Br
3m
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)


7.773
7.719
7.700
7.528
7.508
7.368
7.313
6.728
6.708
3.802
1.561
0.000
NH2
3n
1.00
1.06
2.10
1.09
1.10
1.71
2.05
2.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

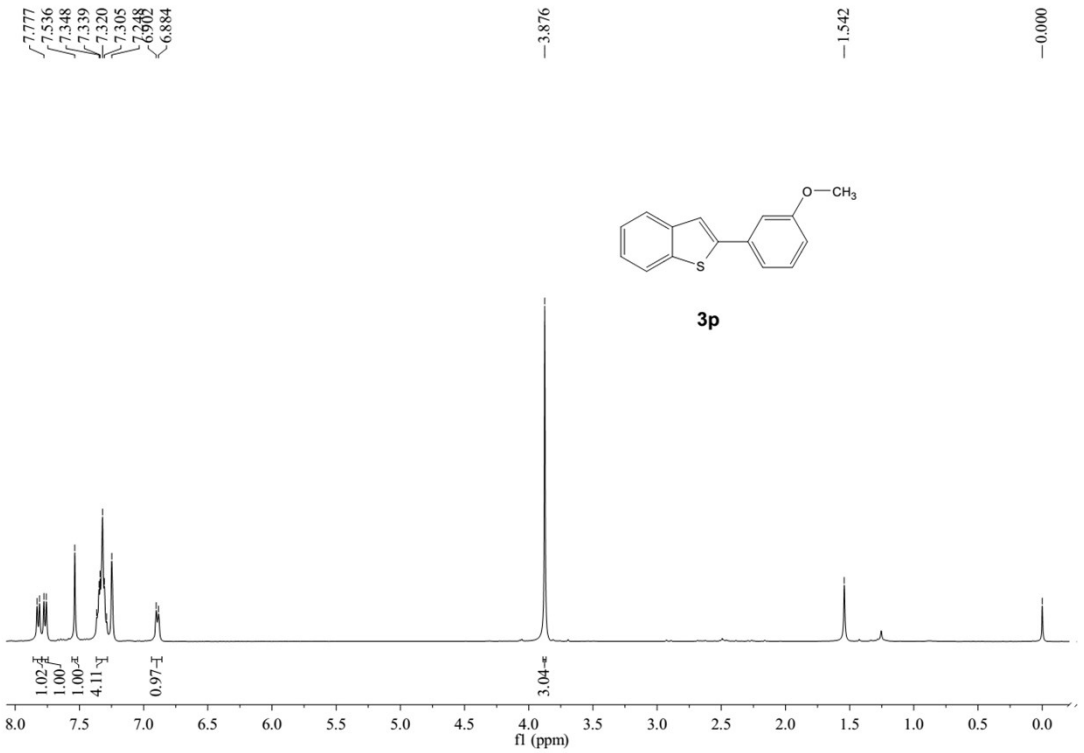

146.732
141.024
138.914
136.164
127.679
124.814
124.332
123.634
123.011
122.103
117.195
115.210
77.317
77.000
76.683
NH2
S
3n
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

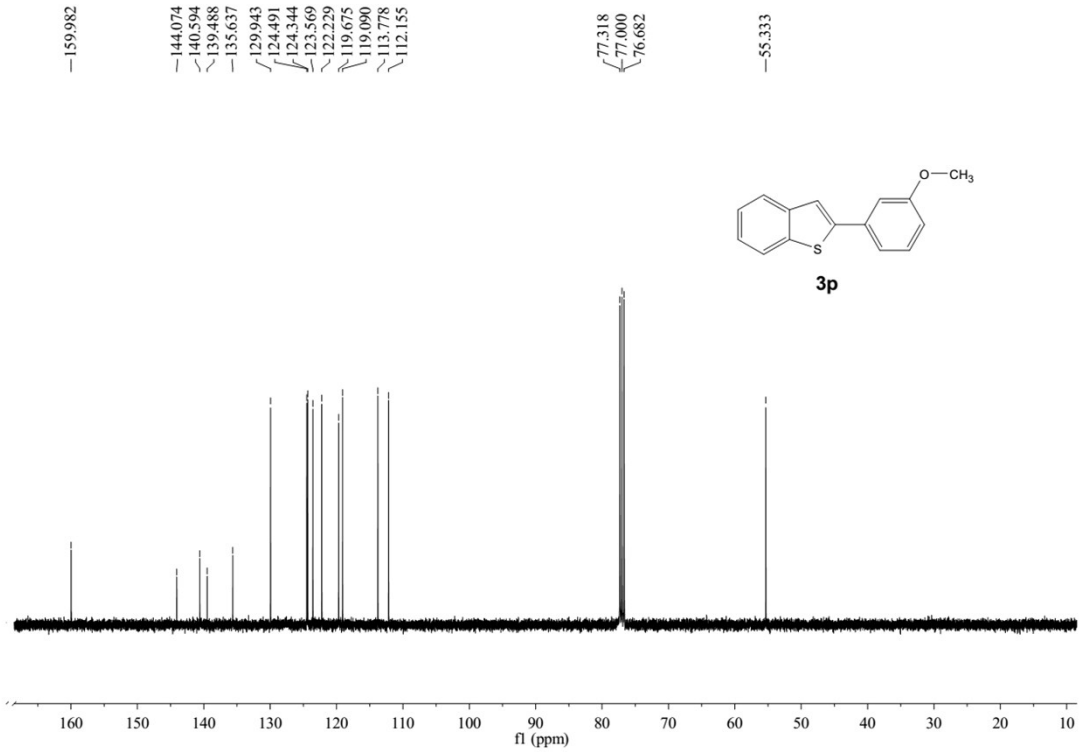

8.295
8.273
7.861
7.839
7.404
7.395
7.386
7.258
1.562
0.000
1.98
4.01
1.00
1.97
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

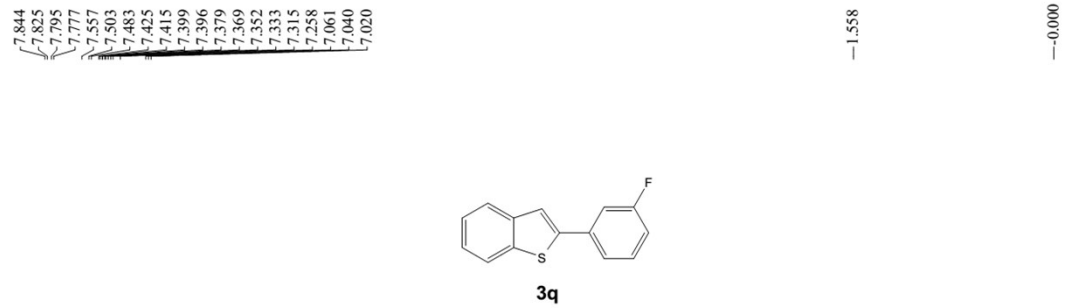
3o

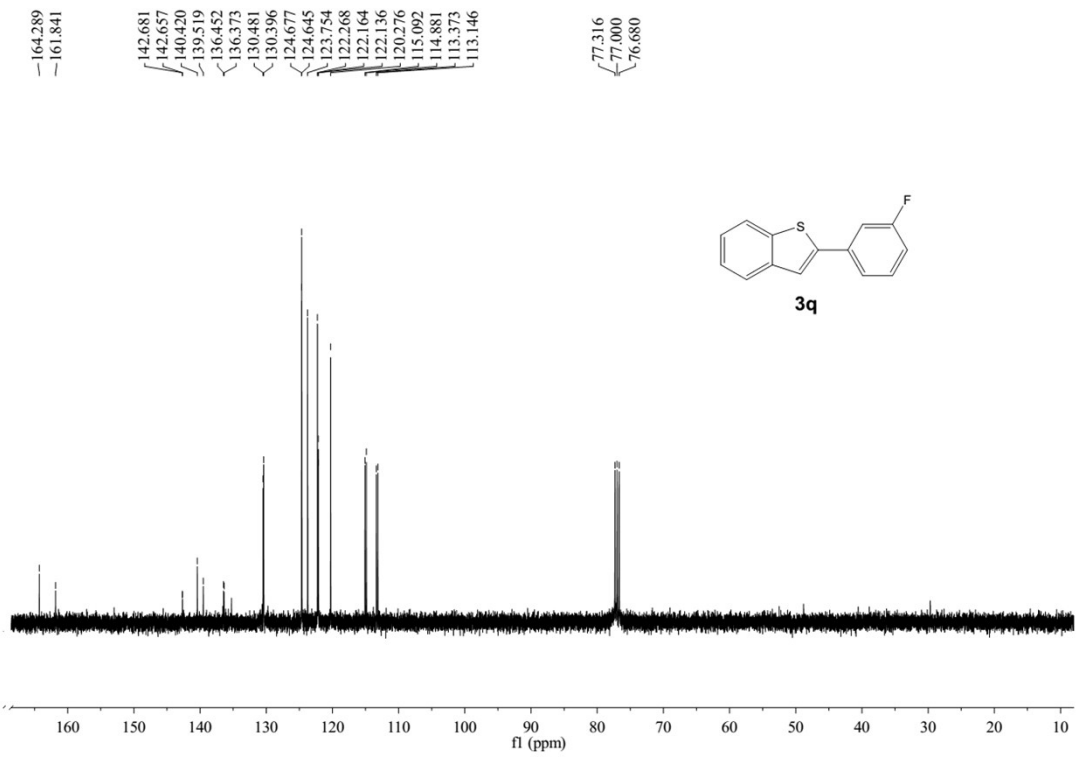

147.214
141.189
140.574
140.300
140.221
126.802
125.546
125.044
124.367
124.288
122.428
122.413
77.318
77.000
76.683
145 135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

3o


7.777
7.536
7.348
7.339
7.320
7.305
7.248
6.902
6.884
3.876
1.542
0.000
O—CH3
S
3p
1.02
1.00
1.00
4.11
0.97
3.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


159.982
144.074
140.594
139.488
135.637
129.943
124.491
124.344
123.569
122.229
119.675
119.090
113.778
112.155
77.318
77.000
76.682
55.333
O—CH3
S
3p
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.844
7.825
7.795
7.777
7.557
7.503
7.483
7.425
7.415
7.399
7.396
7.379
7.369
7.352
7.333
7.315
7.258
7.061
7.040
7.020
1.558
0.000
F
S
3q
0.99
1.06
1.00
1.08
4.13
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.289
161.841
142.681
142.657
140.420
139.519
136.452
136.373
130.481
130.396
124.677
124.645
123.754
122.268
122.164
122.136
120.276
115.092
114.881
113.373
113.146
77.316
77.000
76.680
F
S
3q
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.865
7.846
7.829
7.811
7.610
7.606
7.587
7.579
7.519
7.499
7.398
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7.362
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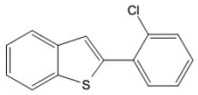
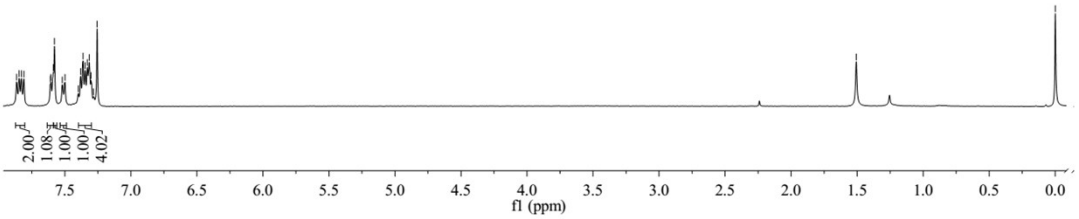
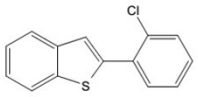
7.315
7.302
7.283
7.256
1.507
0.000


Cl
S

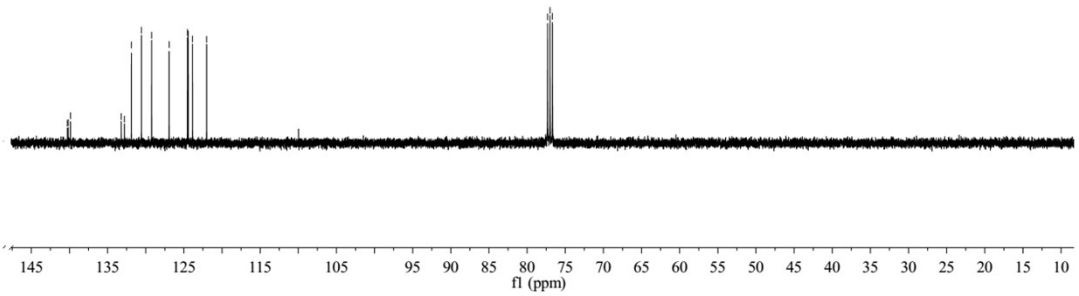
3r

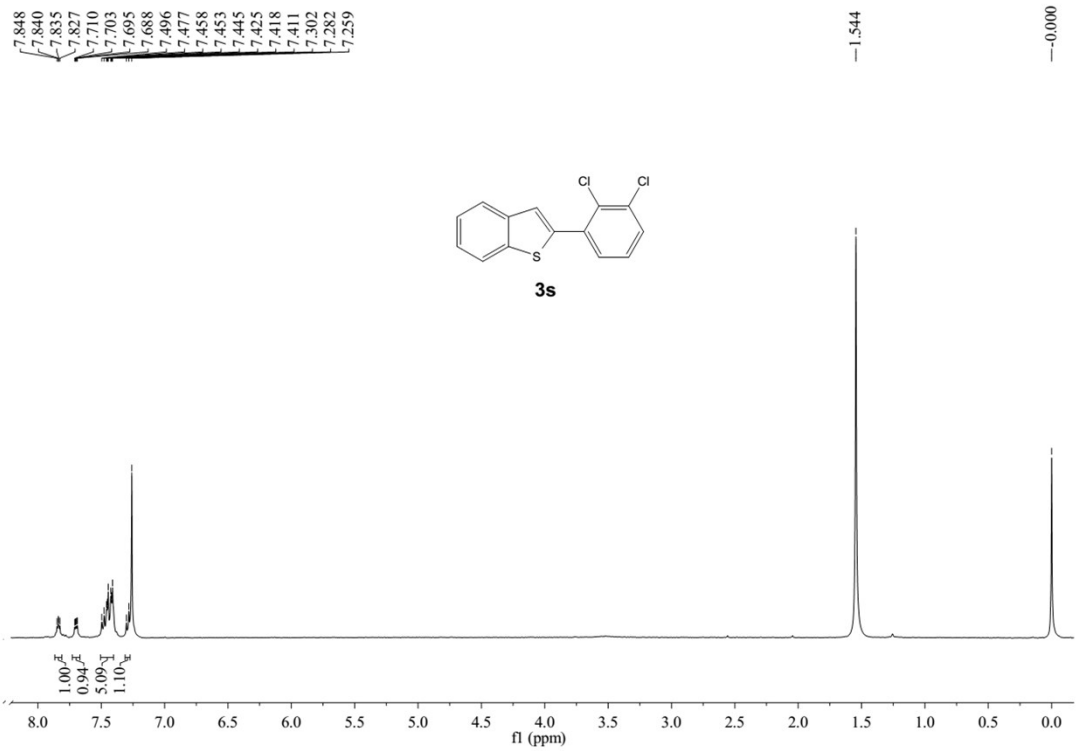

2.00
1.08
1.00
1.00
4.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

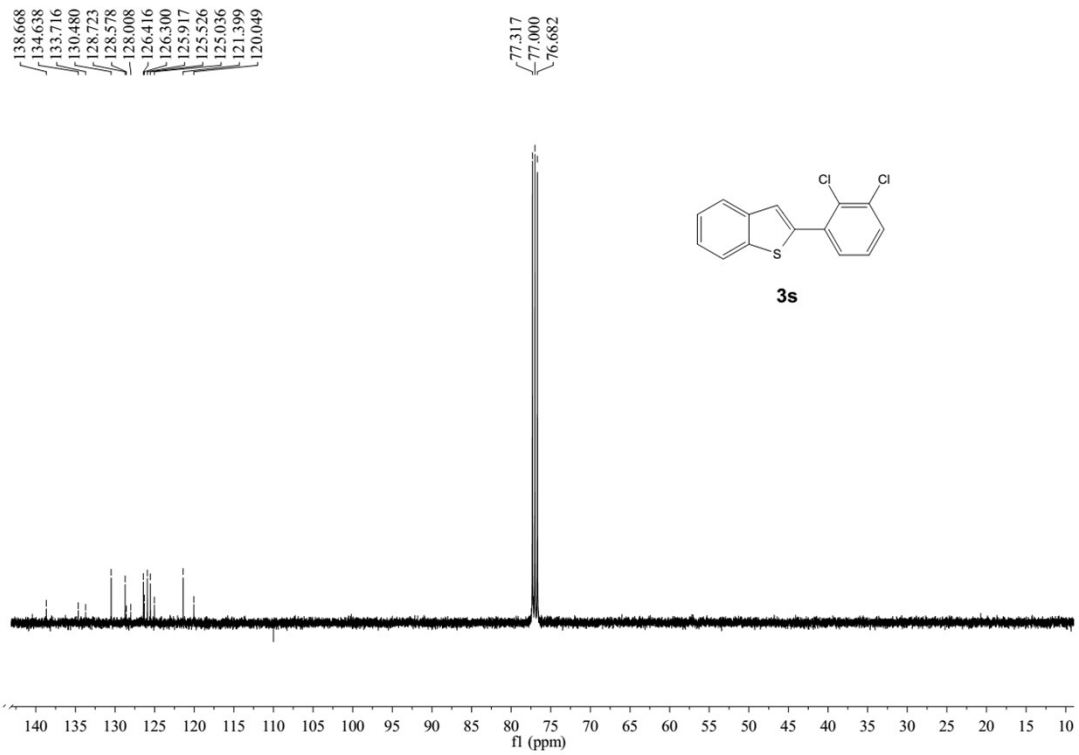

140.277
140.155
139.860
133.208
132.797
131.879
130.560
129.230
126.939
124.531
124.459
124.425
123.861
122.016
77.317
77.000
76.681

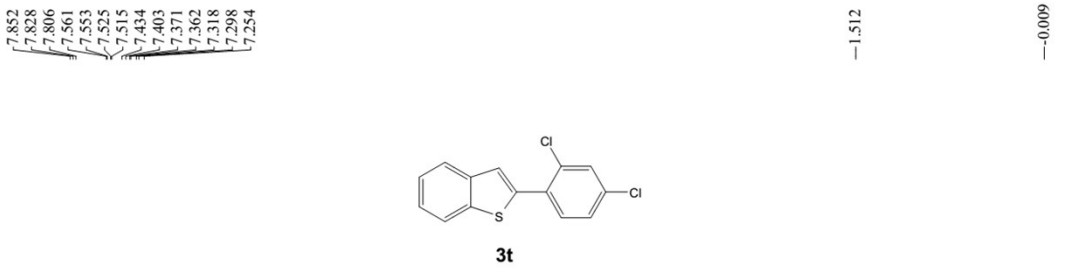

Cl
S

3r

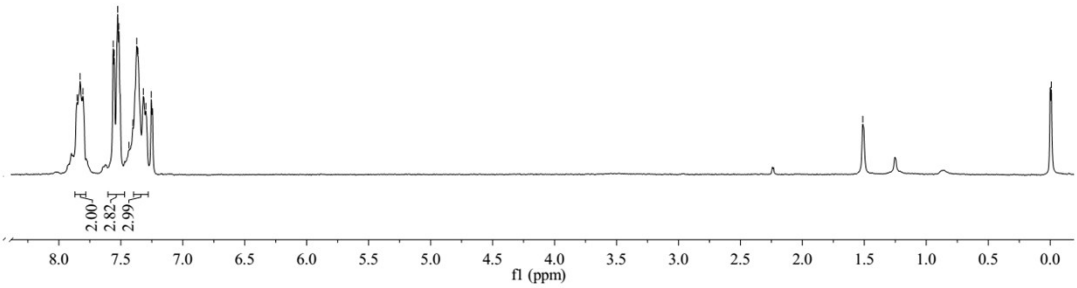

145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

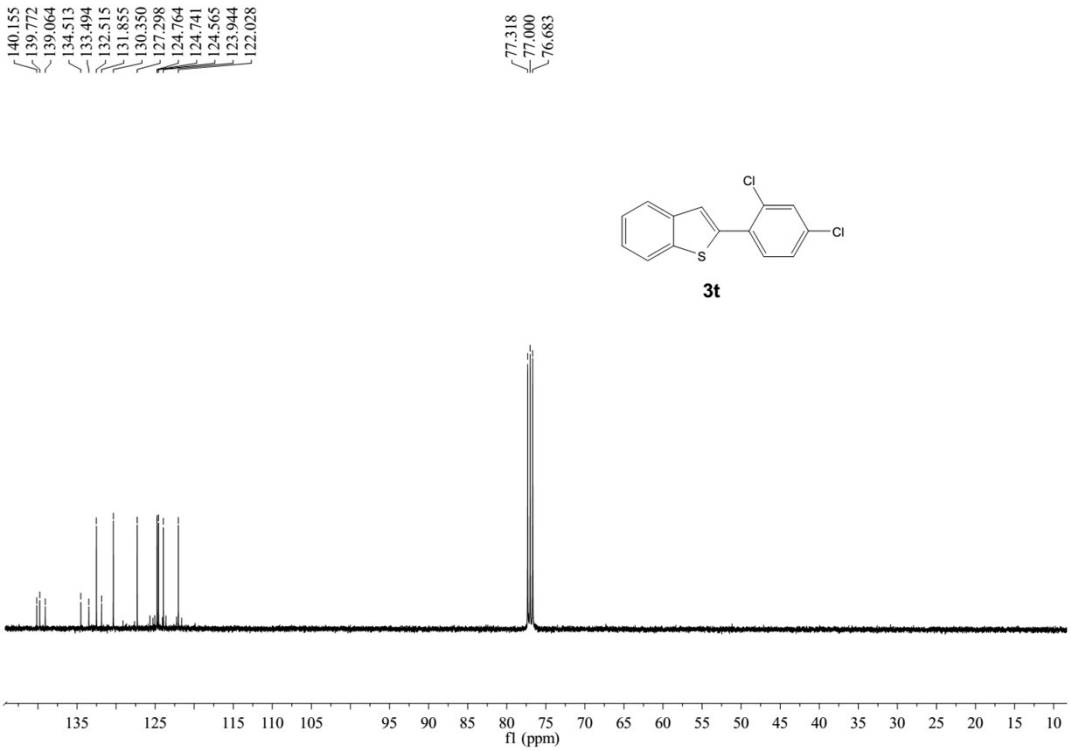

7.848
7.840
7.835
7.827
7.710
7.703
7.695
7.688
7.496
7.477
7.458
7.453
7.445
7.425
7.418
7.411
7.302
7.282
7.259
1.544
0.000
Cl
Cl
S
3s
1.00
0.94
5.09
1.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


138.668
134.638
133.716
130.480
128.723
128.578
128.008
126.416
126.300
125.917
125.526
125.036
121.399
120.049
77.317
77.000
76.682
Cl
Cl
S
3s
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

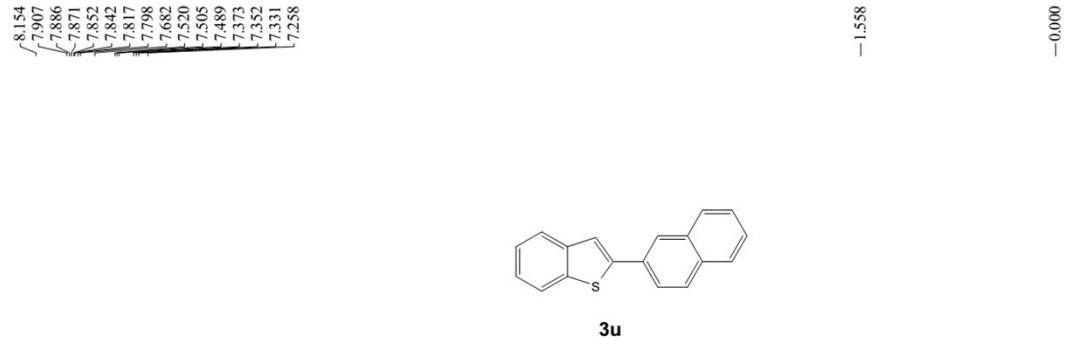

7.852
7.828
7.806
7.561
7.553
7.525
7.515
7.434
7.403
7.371
7.362
7.318
7.298
7.254
1.512
0.009
Cl
Cl
S

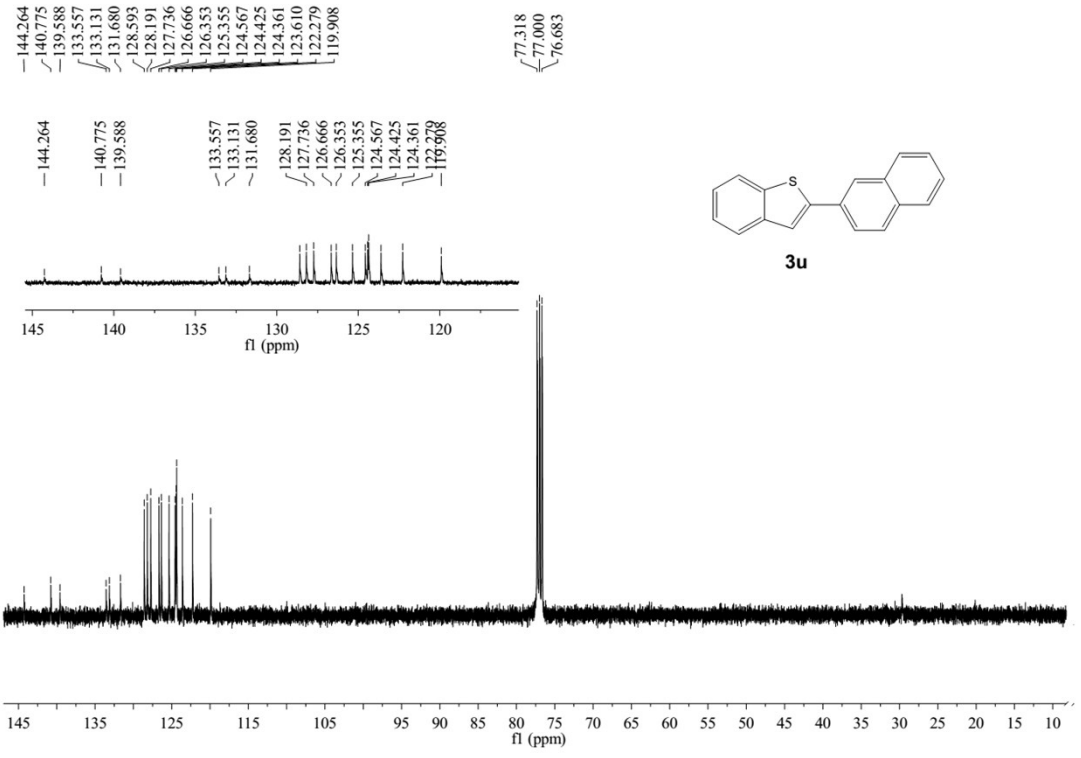
3t

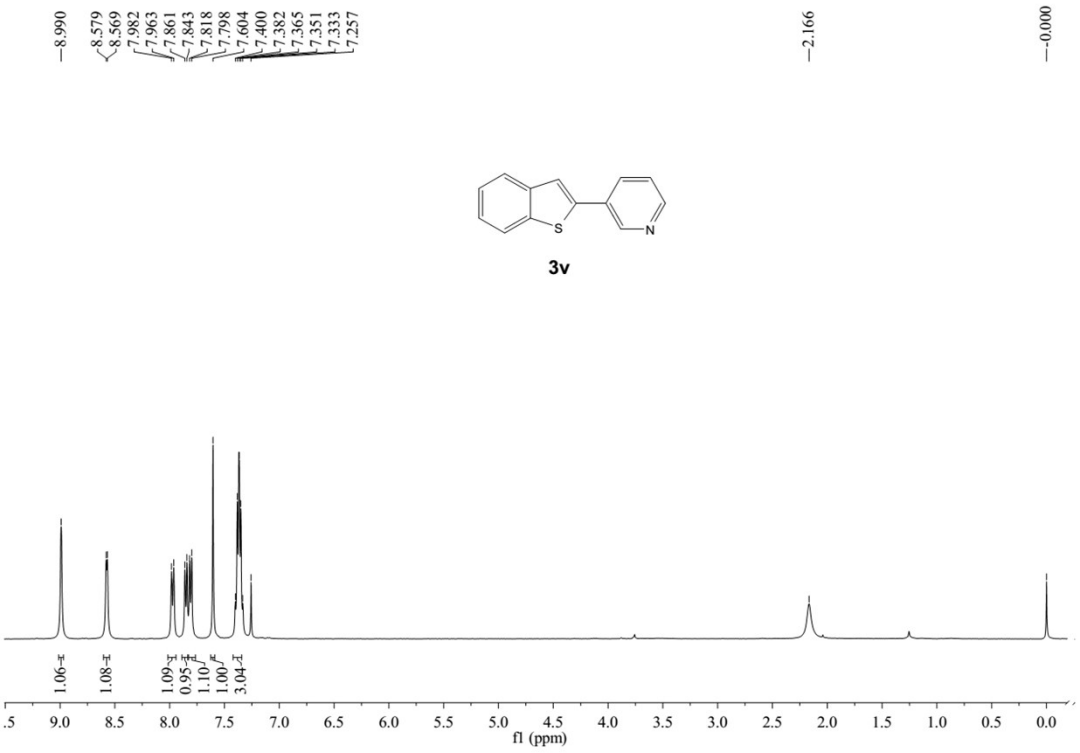

2.00
2.82
2.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

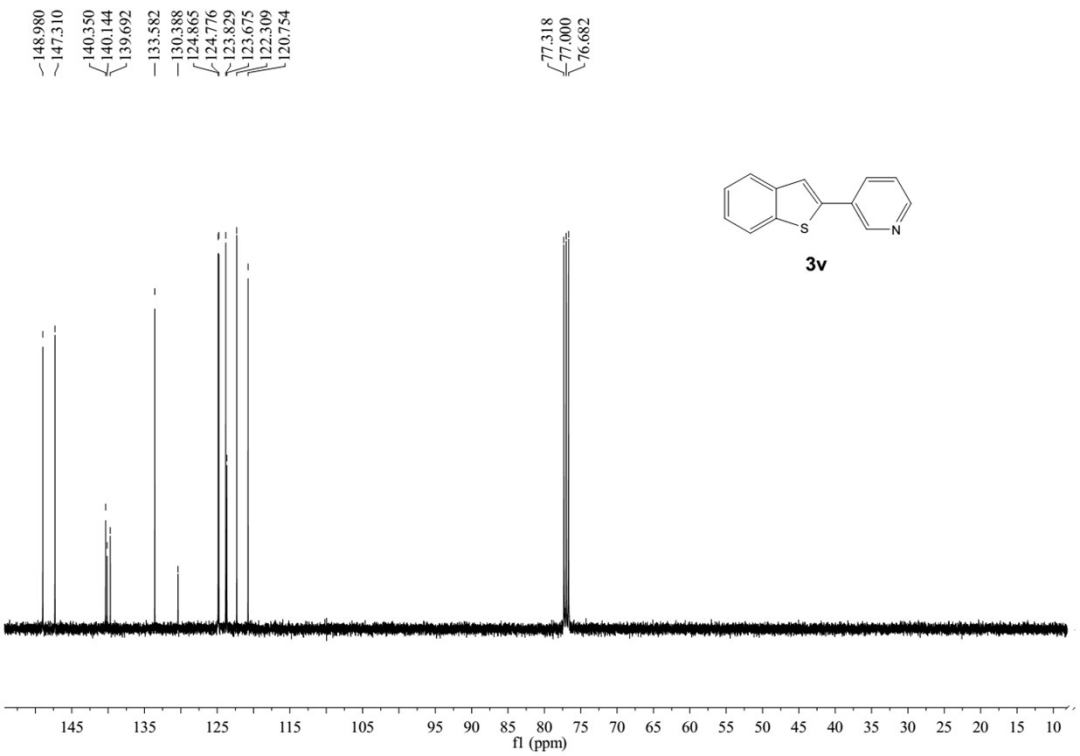

140.155
139.772
139.064
134.513
133.494
132.515
131.855
130.350
127.298
124.764
124.741
124.565
123.944
122.028
77.318
77.000
76.683
Cl
Cl
S
135
125
115
110
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

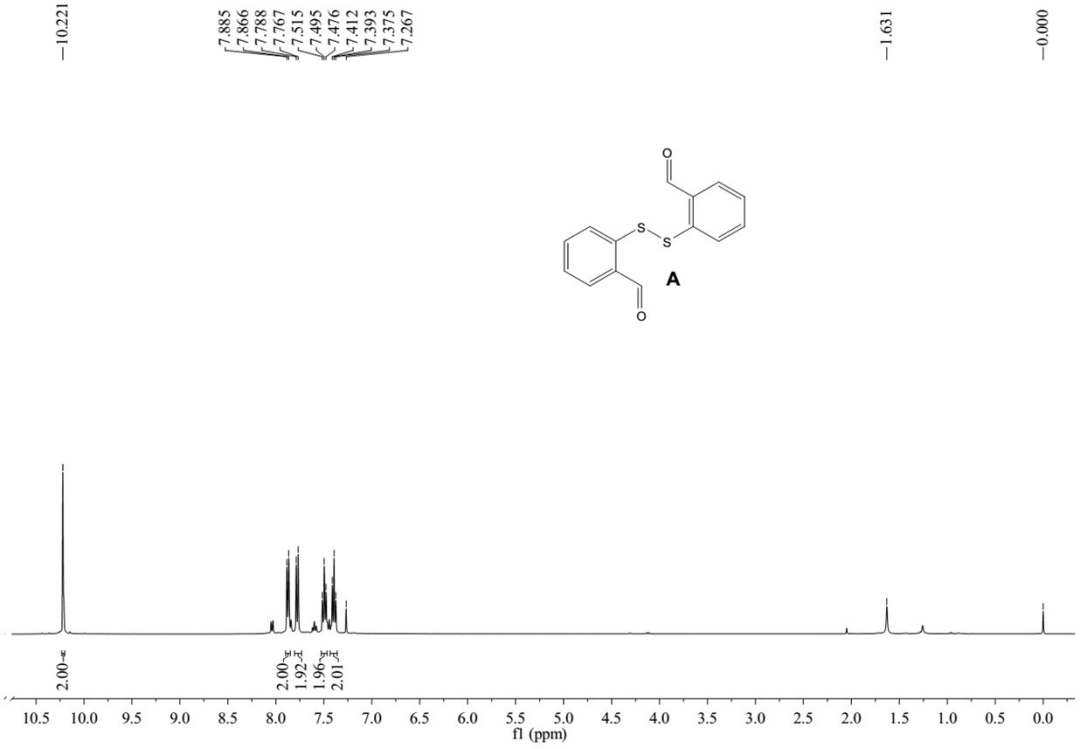
3t


8.154
7.907
7.886
7.871
7.852
7.842
7.817
7.798
7.682
7.520
7.505
7.489
7.373
7.352
7.331
7.258
1.558
0.000
S
3u
1.00
5.00
1.02
1.00
2.05
2.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


144.264
140.775
139.588
133.557
133.131
131.680
128.593
128.191
127.736
126.666
126.353
125.355
124.567
124.425
124.361
123.610
122.279
119.908
77.318
77.000
76.683
S
3u
145
140
135
130
125
120
f1 (ppm)
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)


8.990
8.579
8.569
7.982
7.963
7.861
7.843
7.818
7.798
7.604
7.400
7.382
7.365
7.351
7.333
7.257
2.166
0.000
S
N
3v
1.06
1.08
1.09
0.95
1.10
1.00
3.04
f1 (ppm)


148.980
147.310
140.350
140.144
139.692
133.582
130.388
124.865
124.776
123.829
123.675
122.309
120.754
77.318
77.000
76.682
S
N
3v
f1 (ppm)


10.221
7.885
7.866
7.788
7.767
7.515
7.495
7.476
7.412
7.393
7.375
7.267
1.631
0.000
A
2.00
2.00
1.92
1.96
2.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)