Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Three-component bis-heterocycliation for synthesis of 2-aminobenzo[4,5]thieno[3,2-*d*]thiazoles

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1. General information

All reactions were carried out under an atmosphere of air unless otherwise noted. Column chromatography was performed over silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or dimethyl sulfoxide signals. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra were recorded at Institute of Chemistry, Chinese Academy of Sciences. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those of literature. Ketoxime acetates and isothiocyanate were prepared according previously reported method. All reagents were obtained from commercial suppliers and used without further purification. The molecular weight of S_8 is determined to be 32 g/mol unless otherwise noted.

2. General procedure for the synthesis of thiophere-fused heterocycles

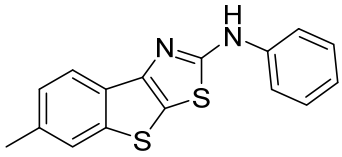
General procedure A: A 10 mL oven-dried reaction vessel was charged with oxime acetates **1** (0.2 mmol) isothiocyanate **2** (0.6 mmol), S_8 (19.2 mg, 0.6 mmol), KSCN (5.0 mg, 0.05 mmol, 25 mol%), Li_2CO_3 (3.7 mg, 0.05 mmol, 25 mol%), and DMSO (1.6 mL) under air. The reaction vessel was stirred at 120 ^{o}C for 12 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (10 mL) and water (10 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL) for three times. The combined organic layer was brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether (PE)/EtOAc (EA)) to give the pure product.

Gram-scale experiment for the synthesis of 3a: A 100 mL oven-dried reaction vessel was charged with oxime acetates **1a** (1.91 g, 10 mmol) phenyl isothiocyanate **2a** (3.6 mL, 30 mmol), S_8 (960 mg, 30 mmol), KSCN (250 mg, 2.5 mmol, 25 mol%), Li_2CO_3 (185 mg, 2.5 mmol, 25 mol%), and DMSO (60 mL) under air. The reaction vessel was stirred at 120 ^{o}C for 24 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (100 mL) and water (100 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (100 mL) for three times. The combined organic layer was brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 10/1) to give the pure product **3a** (1.33 g, 45%) as a

yellow white solid.

3. Characterization data of products

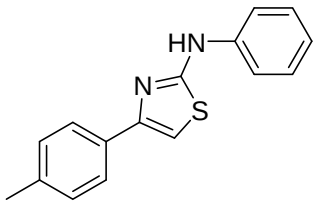
6-methyl-*N*-phenylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3a)



The general procedure A was followed using 1-(*p*-tolyl)ethanone *O*-acetyl oxime (**1a**, 38.2 mg, 0.2 mmol), phenyl isothiocyanate (**2a**, 72 μL, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3a** (39.6 mg, 67%) as a yellow solid. mp: 211 – 213 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.43 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 7.1 Hz, 3H), 7.34 (t, J = 7.7 Hz, 2H), 7.26 (d, J = 8.1 Hz, 1H), 6.97 (t, J = 7.2 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.4, 150.4, 142.1, 141.3, 134.1, 129.5, 128.5, 126.7, 123.9, 122.0, 120.8, 119.2, 117.6, 21.5. HRMS (ESI) m/z calcd for $C_{16}H_{13}N_2S_2^+$ $(M+H)^+$ 297.0515, found 297.0518.

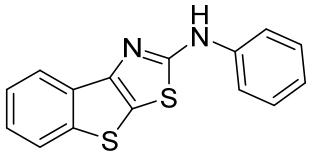
***N*-Phenyl-4-(*p*-tolyl)thiazol-2-amine (3a')[1]**



The general procedure A was followed using 1-(*p*-tolyl)ethanone *O*-acetyl oxime (**1a**, 38.2 mg, 0.2 mmol), phenyl isothiocyanate (**2a**, 72 μL, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 8/1) yielded **3a'** (16.0 mg, 30%) as a red solid. mp: 93 – 95 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 6.5 Hz, 2H), 7.38 – 7.32 (m, 4H), 7.22 (d, J = 6.5 Hz, 2H), 7.07 (t, J = 5.8 Hz, 1H), 6.78 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 151.4, 140.4, 137.7, 131.8, 129.4, 129.4, 1261, 122.9, 118.2, 101.0, 21.3.

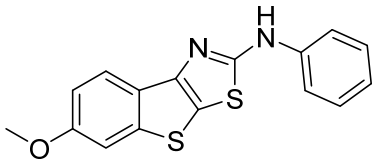
***N*-phenylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3b)**



The general procedure A was followed using 1-phenylethanone *O*-acetyl oxime (**1b**, 35.4 mg, 0.2 mmol), phenyl isothiocyanate (**2a**, 72 μL, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3b** (23.7 mg, 42%) as a yellow solid. mp: 232 – 234 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.51 (s, 1H), 7.99 – 7.96 (m, 2H), 7.76 (d, J = 7.9 Hz, 2H), 7.44 (t, J = 7.4 Hz, 1H), 7.38 – 7.32 (m, 3H), 6.98 (t, J = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.5, 150.5, 141.8, 141.3, 130.6, 129.5, 125.3, 124.5, 124.2, 122.1, 121.1, 120.5, 117.6. HRMS (ESI) m/z calcd for $C_{15}H_{11}N_2S_2^+$ $(M+H)^+$ 283.0358, found 283.0361.

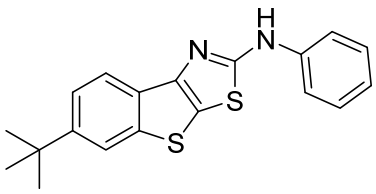
6-methoxy-*N*-phenylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3c)



The general procedure A was followed using 1-(4-methoxyphenyl)ethanone *O*-acetyl oxime (**1c**, 41.4 mg, 0.2 mmol), phenyl isothiocyanate (**2a**, 72 μL, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3c** (41.2 mg, 66%) as a yellow solid. mp: 192 – 194 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.41 (s, 1H), 7.84 (d, J = 8.7 Hz, 1H), 7.74 (dd, J = 8.6, 1.1 Hz, 2H), 7.59 (d, J = 2.3 Hz, 1H), 7.34 (m, 2H), 7.05 (dd, J = 8.7, 2.3 Hz, 1H), 6.97 (t, J = 7.3 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.5, 157.3, 150.1, 143.4, 141.4, 129.5, 124.7, 122.0, 121.6, 117.5, 117.3, 114.4, 107.6, 56.0. HRMS (ESI) m/z calcd for $C_{16}H_{13}N_2OS_2^+$ $(M+H)^+$ 313.0464, found 313.0467.

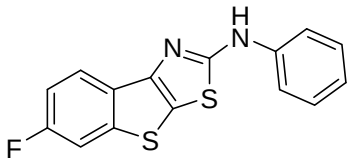
6-(*tert*-butyl)-*N*-phenylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3d)



The general procedure A was followed using 1-(4-(*tert*-butyl)phenyl)ethanone *O*-acetyl oxime (**1d**, 46.6 mg, 0.2 mmol), phenyl isothiocyanate (**2a**, 72 μL, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3d** (41.9 mg, 62%) as a yellow solid. mp: 48 – 50 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.42 (s, 1H), 7.96 (d, J = 3.4 Hz, 1H), 7.88 (d, J = 8.3 Hz, 1H), 7.74 (d, J = 7.9 Hz, 2H), 7.51 – 748 (m, 1H), 7.35 (t, J = 7.8 Hz, 2H), 6.98 (t, J = 7.2 Hz, 1H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.3, 150.3, 147.5, 142.1, 141.3, 129.5, 128.4, 123.1, 122.0, 120.6, 120.4, 119.7, 117.6, 35.2, 31.8. HRMS (ESI) m/z calcd for $C_{19}H_{19}N_2S_2^+$ $(M+H)^+$ 339.0984, found 339.0986.

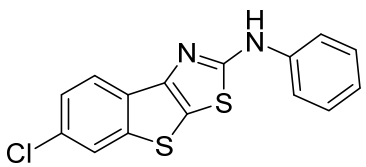
6-fluoro-*N*-phenylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3e)



The general procedure A was followed using 1-(4-fluorophenyl)ethanone *O*-acetyl oxime (**1e**, 39 mg, 0.2 mmol), phenyl isothiocyanate (**2a**, 72 μL, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3e** (32.4 mg, 54%) as a yellow solid. mp: 160 – 162 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.47 (s, 1H), 7.99 – 7.93 (m, 2H), 7.75 (d, J = 7.8 Hz, 2H), 7.38 – 7.29 (m, 3H), 6.99 (t, J = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.82, 160.0 (d, J = 240.1 Hz), 149.6, 143.0, 142.1 (d, J = 10.3 Hz), 129.6, 127.56, 122.1, 122.1 (d, J = 8.5 Hz), 120.0 (d, J = 3.4 Hz), 117.6, 113.7 (d, J = 23.9 Hz), 110.7 (d, J = 26.0 Hz); ^{19}F NMR (376 MHz, DMSO-d_6) δ -117.9. HRMS (ESI) m/z calcd for $C_{15}H_{10}FN_2S_2^+$ $(M+H)^+$ 301.0264, found 301.0268.

6-chloro-*N*-phenylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3f)

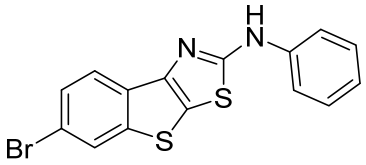


The general procedure A was followed using 1-(4-chlorophenyl)ethanone *O*-acetyl oxime (**1f**, 42.2

mg, 0.2 mmol), phenyl isothiocyanate (**2a**, 72 μL, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3f** (27.8 mg, 44%) as a light yellow white solid. mp: 204 – 206 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.48 (s, 1H), 8.15 (d, J = 1.7 Hz, 1H), 7.94 (d, J = 8.5 Hz, 1H), 7.74 (d, J = 7.8 Hz, 2H), 7.46 (dd, J = 8.5, 1.9 Hz, 1H), 7.35 (t, J = 7.9 Hz, 2H), 6.98 (t, J = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.8, 149.7, 143.1, 141.2, 129.5, 129.3, 129.0, 125.6, 123.7, 122.2, 122.1, 121.6, 117.7. HRMS (ESI) m/z calcd for $C_{15}H_{10}ClN_2S_2^+$ $(M+H)^+$ 316.9968, found 316.9971.

6-bromo-*N*-phenylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3g)

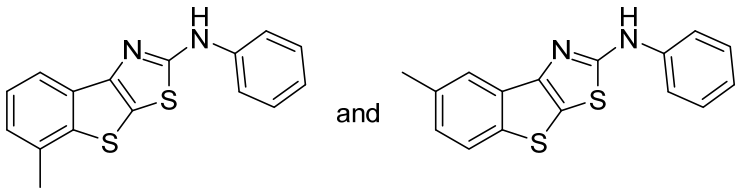


The general procedure A was followed using 1-(4-bromophenyl)ethanone *O*-acetyl oxime (**1g**, 51.2 mg, 0.2 mmol), phenyl isothiocyanate (**2a**, 72 μL, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3g** (39.7 mg, 55%) as a yellow solid. mp: 199 – 201 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.47 (s, 1H), 8.29 (d, J = 1.7 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.76 – 7.72 (m, 2H), 7.58 (dd, J = 8.4, 1.8 Hz, 1H), 7.35 (m, 2H), 6.98 (t, J = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.8, 149.7, 143.5, 141.2, 129.5, 128.2, 126.5, 122.4, 122.15, 121.7, 117.6, 117.1. HRMS (ESI) m/z calcd for $C_{15}H_{10}BrN_2S_2^+$ $(M+H)^+$ 360.9463, found 360.9466.

5-methyl-*N*-phenylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3i)

7-methyl-*N*-phenylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3i′)



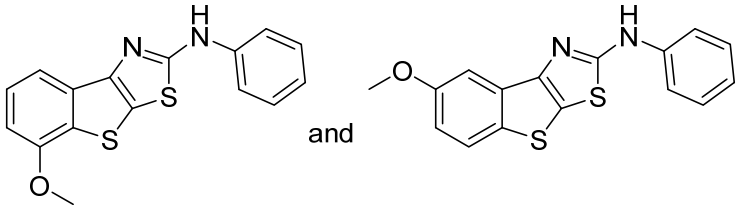
The general procedure A was followed using 1-(*m*-tolyl)ethanone *O*-acetyl oxime (**1i**, 38.2 mg, 0.2 mmol), phenyl isothiocyanate (**2a**, 72 μL, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by

column chromatography on silica gel (PE/EA = 10/1) yielded **3i** and **3i′** (40.0 mg, 54%) as a light yellow white solid. mp: 176 – 178 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.46 (s, 0.8H), 10.44 (s, 0.2H), 7.84 – 7.81 (m, 1H), 7.78 – 7.74 (m, 2H), 7.40 – 7.33 (m, 3H), 7.21 – 7.16 (m, 1H), 6.98 (t, *J* = 7.3 Hz, 1H), 2.48 (s, 2.4H), 2.45 (s, 0.6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.4, 166.3, 151.3, 150.3, 141.5, 141.3, 141.3, 139.0, 134.7, 132.6, 130.8, 130.5, 129.5, 126.1, 125.6, 125.1, 123.8, 122.1, 122.0, 121.1, 120.6, 119.9, 118.9, 117.6, 117.5, 21.4, 19.7. HRMS (ESI) m/z calcd for $C_{16}H_{13}N_2S_2^+$ $(M+H)^+$ 297.0515, found 297.0518.

5-methoxy-*N*-phenylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3j)

7-methoxy-*N*-phenylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3j')

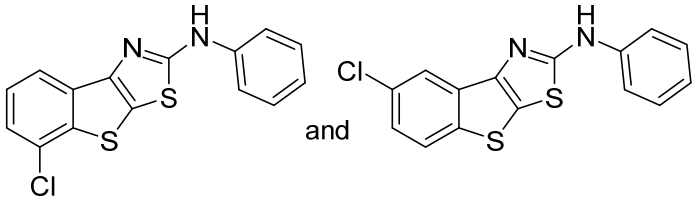


The general procedure A was followed using 1-(3-methoxyphenyl)ethanone *O*-acetyl oxime (**1j**, 41.4 mg, 0.2 mmol), phenyl isothiocyanate (**2a**, 72 μL, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3j** and **3j′** (26.2 mg, 42%) as a light yellow white solid. mp: 83 – 85 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.44 (s, 0.72H), 10.42 (s, 0.28H), 7.83 (d, *J* = 8.8 Hz, 0.28H), 7.80 – 7.69 (m, 2H), 7.58 (d, *J* = 7.7 Hz, 0.72H), 7.44 – 7.33 (m, 3H), 7.03 – 6.93 (m, 2H), 3.96 (s, 2H), 3.86 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.5 , 166.1, 158.0, 154.5, 151.0, 150.3, 141.3, 133.7, 132.1, 131.6, 129.6, 129.3, 126.9, 124.9, 122.0, 121.7, 120.7, 117.6, 114.2, 113.9, 105.5, 103.7, 56.2, 55.9. HRMS (ESI) m/z calcd for $C_{16}H_{13}N_2OS_2^+$ $(M+H)^+$ 313.0464, found 313.0467.

5-chloro-*N*-phenylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3k)

7-chloro-*N*-phenylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3k')

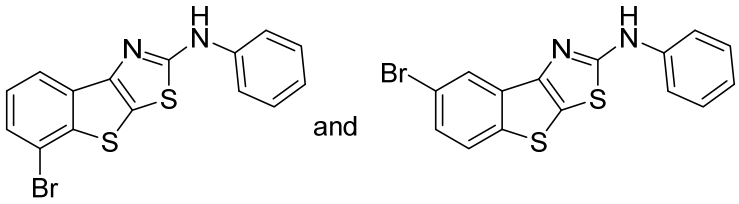


The general procedure A was followed using 1-(3-chlorophenyl)ethanone *O*-acetyl oxime (**1k**, 42.2 mg, 0.2 mmol), phenyl isothiocyanate (**2a**, 72 μL, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3k** and **3k′** (33.5 mg, 53%) as a white solid. mp: 205 – 207 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.51 (s, 0.7H), 10.49 (s, 0.3H), 8.02 (d, J = 8.6 Hz, 0.3H), 7.95 (dt, J = 5.4, 1.9 Hz, 1H), 7.78 – 7.74 (m, 2H), 7.47 (d, J = 1.4 Hz, 0.7H), 7.40 – 7.31 (m, 3H), 7.01 – 6.97 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.9, 166.6, 150.7, 149.4, 141.2, 141.2, 140.3, 140.0, 132.4, 131.7, 130.4, 129.6, 129.5, 127.4, 127.0, 125.8, 124.4, 124.1, 123.1, 122.2, 122.2, 121.7, 120.2, 120.0, 117.7, 117.3. HRMS (ESI) m/z calcd for $C_{15}H_{10}ClN_2S_2^+$ $(M+H)^+$ 316.9968, found 316.9971.

5-bromo-*N*-phenylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3l)

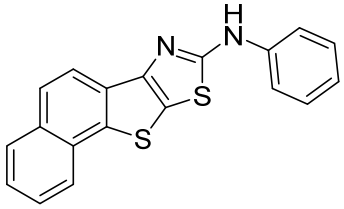
7-bromo-*N*-phenylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3l')



The general procedure A was followed using 1-(3-bromophenyl)ethanone *O*-acetyl oxime (**1l**, 50.8 mg, 0.2 mmol), phenyl isothiocyanate (**2a**, 72 μL, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3l** and **3l′** (31.8 mg, 44%) as a white solid. mp: 194 – 196 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.51 (s, 0.7H), 10.49 (s, 0.3H), 8.09 (d, J = 1.9 Hz, 0.3H), 8.01 – 7.94 (m, 1H), 7.76 (t, J = 7.3 Hz, 2H), 7.60 – 7.57 (m, 0.7H), 7.49 – 7.33 (m, 3H), 6.99 (t, J = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.7, 166.7, 150.8, 149.3, 142.6, 141.17, 140.8, 132.2, 132.1, 129.6, 127.2, 127.1, 127.0, 126.1, 123.2, 122.9, 122.2, 122.2, 121.6, 120.4, 118.5, 117.7, 117.7, 116.2. HRMS (ESI) m/z calcd for $C_{15}H_{10}BrN_2S_2^+$ $(M+H)^+$ 360.9463, found 360.9466.

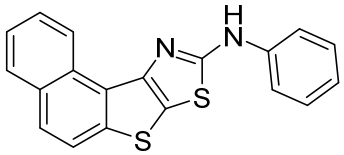
***N*-phenylnaphtho[2',1':4,5]thieno[3,2-*d*]thiazol-8-amine (3m)**



The general procedure A was followed using 1-(naphthalen-2-yl)ethanone *O*-acetyl oxime (**1m**, 45.4 mg, 0.2 mmol), phenyl isothiocyanate (**2a**, 72 μL, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3m** (47.9 mg, 72%) as a yellow solid. mp: 230 – 232 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.51 (s, 1H), 8.09 – 8.04 (m, 3H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.00 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.7, 152.0, 141.3, 138.4, 130.9, 129.6, 129.6, 129.3, 128.2, 127.7, 126.2, 126.2, 122.6, 122.1, 120.1, 119.7, 117.7. HRMS (ESI) m/z calcd for $C_{19}H_{13}N_2S_2^+$ $(M+H)^+$ 333.0515, found 333.0518.

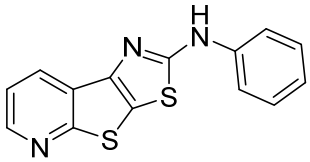
***N*-phenylnaphtho[1',2':4,5]thieno[3,2-*d*]thiazol-9-amine (3n)**



The general procedure A was followed using 1-(naphthalen-1-yl)ethanone *O*-acetyl oxime (**1n**, 45.4 mg, 0.2 mmol), phenyl isothiocyanate (**2a**, 72 μL, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3n** (46.5 mg, 70%) as a yellow solid. mp: 181 – 183 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.59 (s, 1H), 9.38 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.83 (t, *J* = 8.7 Hz, 3H), 7.75 (t, *J* = 7.3 Hz, 1H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.04 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.7, 151.7, 141.3, 139.2, 131.4, 129.7, 128.6, 128.3, 126.9, 126.1, 125.3, 124.8, 124.2, 122.3, 122.2, 121.1, 117.7. HRMS (ESI) m/z calcd for $C_{19}H_{13}N_2S_2^+$ $(M+H)^+$ 333.0515, found 333.0518.

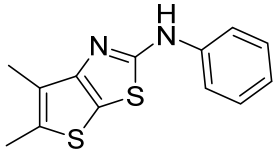
***N*-phenylthiazolo[4',5':4,5]thieno[2,3-*b*]pyridin-2-amine (3o)**



The general procedure A was followed using 1-(pyridin-3-yl)ethanone *O*-acetyl oxime (**1o**, 35.6 mg, 0.2 mmol), phenyl isothiocyanate (**2a**, 72 μL, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3o** (21.5 mg, 38%) as a light yellow white solid. mp: 227 – 229 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.55 (s, 1H), 8.52 – 8.51 (m, 1H), 8.33 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.75 (d, *J* = 7.7 Hz, 2H), 7.49 (dd, *J* = 8.0, 4.6 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.00 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.3, 163.1, 147.1, 146.1, 141.2, 129.6, 128.7, 124.9, 122.2, 120.7, 120.4, 117.7. HRMS (ESI) m/z calcd for $C_{14}H_{10}N_3S_2^+$ $(M+H)^+$ 284.0311, found 284.0319.

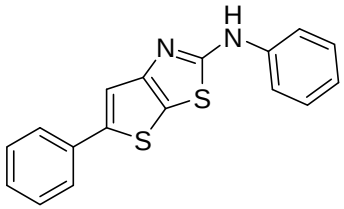
5,6-dimethyl-*N*-phenylthieno[3,2-*d*]thiazol-2-amine (3p)



The general procedure A was followed using (3*E*)-3-methylpent-3-en-2-one *O*-acetyl oxime (**1p**, 31.0 mg, 0.2 mmol), phenyl isothiocyanate (**2a**, 72 μL, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3p** (27.1 mg, 52%) as a yellow solid. mp: 30 – 32 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.22 (s, 1H), 7.67 – 7.65 (m, 2H), 7.32 – 7.28 (m, 2H), 6.93 (t, *J* = 7.3 Hz, 1H), 2.36 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.2, 157.2, 141.5, 133.8, 129.4, 124.0, 121.7, 117.3, 113.9, 14.3, 12.3. HRMS (ESI) m/z calcd for $C_{13}H_{13}N_2S_2^+$ $(M+H)^+$ 261.0515, found 261.0517.

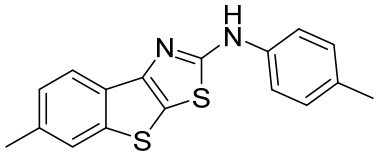
***N*,5-diphenylthieno[3,2-*d*]thiazol-2-amine (3q)**



The general procedure A was followed using (3*E*)-4-phenylbut-3-en-2-one *O*-acetyl oxime (**1q**, 40.6 mg, 0.2 mmol), phenyl isothiocyanate (**2a**, 72 μL, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3q** (50.5 mg, 82%) as a tan solid. mp: 229 – 231 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.35 (s, 1H), 7.72 (s, 1H), 7.70 – 7.63 (m, 4H), 7.42 – 7.38 (m, 2H), 7.34 – 7.27 (m, 3H), 6.96 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.9, 157.5, 144.5, 141.3, 134.7, 129.6, 129.5, 128.1, 125.3, 122.0, 119.8, 117.6, 115.1. HRMS (ESI) m/z calcd for $C_{17}H_{13}N_2S_2^+$ $(M+H)^+$ 309.0515, found 309.0518.

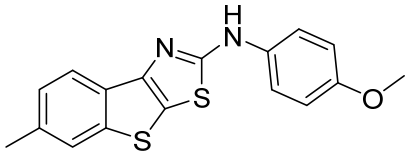
6-methyl-*N*-(*p*-tolyl)benzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3r)



The general procedure A was followed using 1-(p-tolyl)ethanone *O*-acetyl oxime (**1a**, 38.2 mg, 0.2 mmol), 4-methylphenyl isothiocyanate (**2r**, 78 μL, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3r** (37.8 mg, 61%) as a light yellow white solid. mp: 190 – 192 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.31 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.75 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.15 (d, *J* = 8.3 Hz, 2H), 2.42 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.6, 150.4, 142.1, 138.9, 134.0, 130.9, 129.9, 128.5, 126.7, 123.9, 120.7, 118.8, 117.7, 21.6, 20.9. HRMS (ESI) m/z calcd for $C_{17}H_{15}N_2S_2^+$ $(M+H)^+$ 311.0671, found 311.0675.

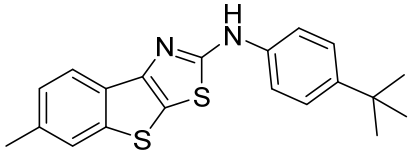
***N*-(4-methoxyphenyl)-6-methylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3s)**



The general procedure A was followed using 1-(p-tolyl)ethanone *O*-acetyl oxime (**1a**, 38.2 mg, 0.2 mmol), 4-methoxyphenyl isothiocyanate (**2s**, 83 μL, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3s** (33.9 mg, 52%) as a light yellow white solid. mp: 205 – 207 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.22 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.74 (s, 1H), 7.67 – 7.61 (m, 2H), 7.26-7.24 (m, 1H), 6.95 (t, J = 2.8 Hz, 1H), 6.93 (t, J = 2.8 Hz, 1H), 3.72 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.1, 154.8, 150.5, 142.1, 134.8, 134.0, 128.5, 126.7, 123.9, 120.7, 119.4, 118.4, 114.8, 55.7, 21.6. HRMS (ESI) m/z calcd for $C_{17}H_{15}N_2OS_2^+$ $(M+H)^+$ 327.0620, found 327.0623.

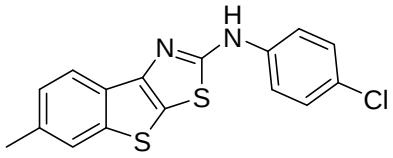
_N_-(4-(*tert*-butyl)phenyl)-6-methylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3t)



The general procedure A was followed using 1-(*p*-tolyl)ethanone *O*-acetyl oxime (**1a**, 38.2 mg, 0.2 mmol), 4-*tert*-butylphenyl isothiocyanate (**2t**, 114.6 mg, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3t** (37.4 mg, 53%) as a light yellow white solid. mp: 174 – 176 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.33 (s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.76 (s, 1H), 7.64 (dd, J = 9.1, 2.2 Hz, 2H), 7.36 (dd, J = 9.2, 2.3 Hz, 2H), 7.27 – 7.24 (m, 1H), 2.42 (s, 3H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.6, 150.5, 144.4, 142.1, 138.8, 134.0, 128.5, 126.7, 126.1, 123.9, 120.7, 118.8, 117.5, 34.4, 31.7, 21.6. HRMS (ESI) m/z calcd for $C_{20}H_{21}N_2S_2^+$ $(M+H)^+$ 353.1141, found 353.1143.

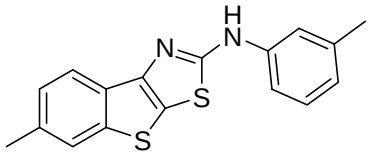
_N_-(4-chlorophenyl)-6-methylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3u)



The general procedure A was followed using 1-(*p*-tolyl)ethanone *O*-acetyl oxime (**1a**, 38.2 mg, 0.2 mmol), 4-chlorophenyl isothiocyanate (**2u**, 101.8 mg, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3u** (31.1 mg, 47%) as a white solid. mp: 260 – 262 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.59 (s, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.81 – 7.76 (m, 3H), 7.41 – 7.37 (m, 2H), 7.27 (d, J = 8.0 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.0, 150.3, 142.1, 140.2, 134.2, 129.3, 128.4, 126.7, 125.3, 123.9, 120.7, 119.6, 119.0, 21.6. HRMS (ESI) m/z calcd for $C_{16}H_{12}ClN_2S_2^+$ $(M+H)^+$ 331.0125, found 331.0128.

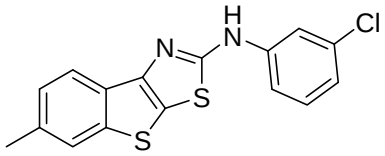
6-methyl-*N*-(*m*-tolyl)benzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3v)



The general procedure A was followed using 1-(*p*-tolyl)ethanone *O*-acetyl oxime (**1a**, 38.2 mg, 0.2 mmol), 3-methylphenyl isothiocyanate (**2v**, 89.4 mg, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3v** (34.8 mg, 56%) as a light yellow white solid. mp: 192 – 194 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.35 (s, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.75 (s, 1H), 7.57 (d, J = 8.1 Hz, 1H), 7.51 (s, 1H), 7.27 – 7.20 (m, 2H), 6.80 (d, J = 7.5 Hz, 1H), 2.42 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.4, 150.4, 142.1, 141.3, 138.7, 134.1, 129.4, 128.5, 126.7, 123.9, 122.8, 120.8, 119.1, 118.1, 114.8, 21.8, 21.6. HRMS (ESI) m/z calcd for $C_{17}H_{15}N_2S_2^+$ $(M+H)^+$ 311.0671, found 311.0675.

***N*-(3-chlorophenyl)-6-methylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3w)**

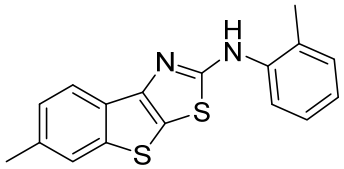


The general procedure A was followed using 1-(*p*-tolyl)ethanone *O*-acetyl oxime (**1a**, 38.2 mg, 0.2

mmol), 3-chlorophenyl isothiocyanate (**2w**, 101.8 mg, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3w** (21.2 mg, 32%) as a tan liquid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.66 (s, 1H), 7.99 (t, J = 1.9 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.78 (s, 1H), 7.59 (dd, J = 8.3, 1.5 Hz, 1H), 7.37 (t, J = 8.1 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.02 (dd, J = 7.8, 1.6 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.8, 150.2, 142.6, 142.2, 134.2, 133.9, 131.1, 128.4, 126.8, 123.9, 121.5, 120.7, 120.0, 116.8, 116.0, 21.6. HRMS (ESI) m/z calcd for $C_{16}H_{12}ClN_2S_2^+$ $(M+H)^+$ 331.0125, found 331.0128.

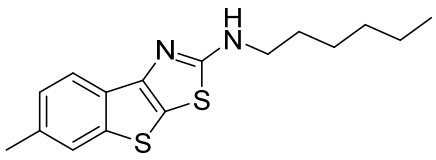
6-methyl-*N*-(*o*-tolyl)benzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3x)



The general procedure A was followed using 1-(*p*-tolyl)ethanone *O*-acetyl oxime (**1a**, 38.2 mg, 0.2 mmol), 3-methylphenyl isothiocyanate (**2x**, 89.4 mg, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3x** (34.1 mg, 55%) as a light yellow white solid. mp: 206 – 208 °C

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.56 (s, 1H), 7.99 (d, J = 8.2 Hz, 1H), 7.75 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 6.6 Hz, 3H), 7.03 (t, J = 7.3 Hz, 1H), 2.41 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.9, 150.3, 142.1, 139.5, 134.0, 131.2, 129.8, 128.5, 127.1, 126.7, 124.3, 123.9, 122.1, 120.7, 119.0, 21.5, 18.5. HRMS (ESI) m/z calcd for $C_{17}H_{15}N_2S_2^+$ $(M+H)^+$ 311.0671, found 311.0675.

***N*-hexyl-6-methylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3y)**

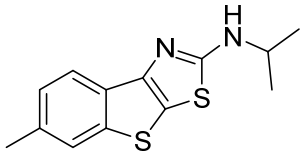


The general procedure A was followed using 1-(*p*-tolyl)ethanone *O*-acetyl oxime (**1a**, 38.2 mg, 0.2 mmol), *n*-hexyl isothiocyanate (**2y**, 92 μL, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3y** (18.2 mg, 30%) as a light yellow

white solid. mp: 154 – 156 °C

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.87 (t, J = 5.3 Hz, 1H), 7.69 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 8.3 Hz, 1H), 3.32 – 3.27 (m, 2H), 2.40 (s, 3H), 1.58 (p, J = 7.0 Hz, 2H), 1.38 – 1.26 (m, 6H), 0.86 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.9, 150.8, 141.9, 133.6, 128.5, 126.5, 123.8, 120.6, 116.5, 44.8, 31.4, 29.1, 26.6, 22.5, 21.5, 14.4. HRMS (ESI) m/z calcd for $C_{16}H_{21}N_2S_2^+$ $(M+H)^+$ 305.1141, found 305.1149.

_N_-isopropyl-6-methylbenzo[4,5]thieno[3,2-*d*]thiazol-2-amine (3z)



The general procedure A was followed using 1-(*p*-tolyl)ethanone *O*-acetyl oxime (**1a**, 38.2 mg, 0.2 mmol), isopropyl isothiocyanate (**2z**, 60.1 mg, 0.6 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (PE/EA = 10/1) yielded **3z** (14.1 mg, 27%) as a yellow solid. mp: 145 – 147 °C

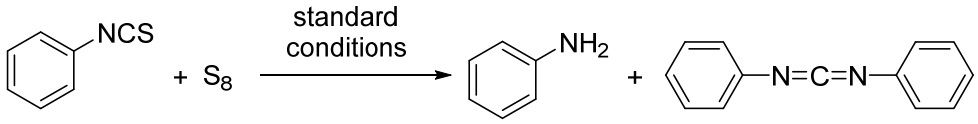
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.79 (d, J = 7.4 Hz, 1H), 7.75 – 7.67 (m, 2H), 7.20 (d, J = 8.3 Hz, 1H), 3.93 (dq, J = 13.2, 6.5 Hz, 1H), 2.41 (s, 3H), 1.22 (d, J = 6.5 Hz, 6H) ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.0, 150.8, 141.9, 133.6, 128.5, 126.5, 123.8, 120.6, 116.5, 46.6, 22.8, 21.5. HRMS (ESI) m/z calcd for $C_{13}H_{15}N_2S_2^+$ $(M+H)^+$ 263.0671, found 263.0674.

4. Reference

[1]. Tang X. D.; Zhu Z. Z.; Qi C. R.; Wu W. Q.; Jiang H. F. *Org. Lett.*, **2016**, *18*, 180.

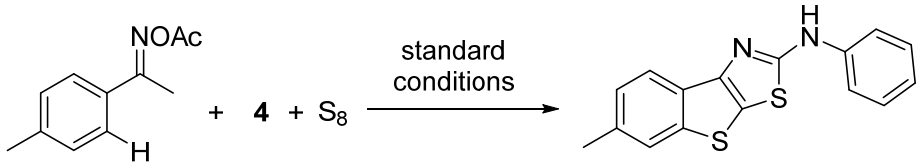
5. Control experiments

(a) Reaction of isothiocyanate 2a with sulfur powder: A mixture of **2a** (72 μL, 0.6 mmol), S_8 (19.2 mg, 0.6 mmol), KSCN (5.0 mg, 0.05 mmol, 25 mol%), Li_2CO_3 (3.7 mg, 0.05 mmol, 25 mol%), and DMSO (1.6 mL) under air. The reaction vessel was stirred at 120 ^oC for 12 h. Then, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (PE/ EA = 5/1) to give aniline in 38% (21.2 mg) and **4** in 18% (20.9 mg), respectively.



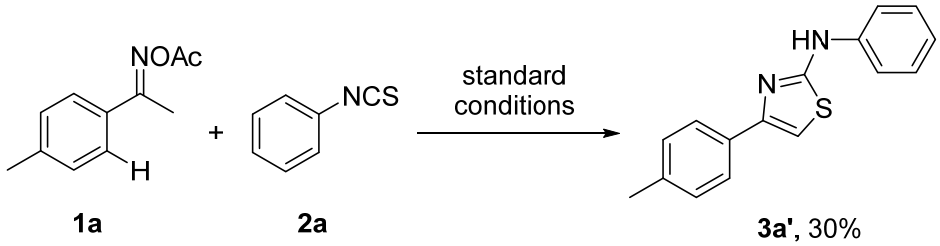
2a 38% **4**, 18%

(b) Reaction of oxime ester 1a with diamine 4: A mixture of **1a** (38.2 mg, 0.2 mmol), **4** (116.4 mg, 0.6 mmol), S_8 (19.2 mg, 0.6 mmol), KSCN (5.0 mg, 0.05 mmol, 25 mol%), Li_2CO_3 (3.7 mg, 0.05 mmol, 25 mol%), and DMSO (1.6 mL) under air. The reaction vessel was stirred at 120 ^oC for 12 h. Then, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (PE/ EA = 10/1) to give **3a** in 28% (16.6 mg).



1a **3a**, 28%

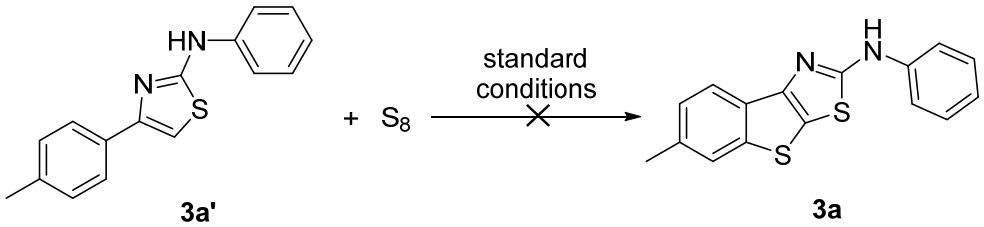
(c) Reaction of oxime ester 1a with isothiocyanate 2a: A mixture of **1a** (38.2 mg, 0.2 mmol), **2a** (72 μL, 0.6 mmol), KSCN (5.0 mg, 0.05 mmol, 25 mol%), Li_2CO_3 (3.7 mg, 0.05 mmol, 25 mol%), and DMSO (1.6 mL) under air. The reaction vessel was stirred at 120 ^oC for 12 h. Then, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (PE/ EA = 8/1) to give **3a'** in 30% (16.0 mg).



1a **2a** **3a'**, 30%

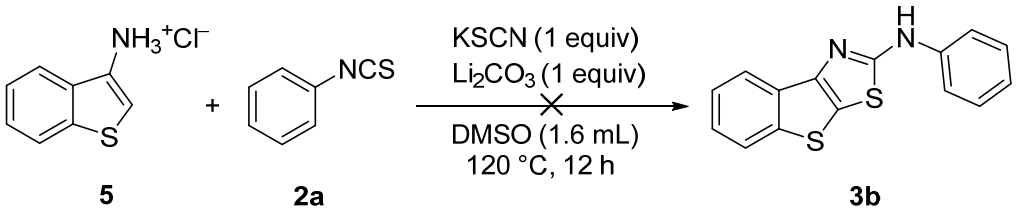
(d) Reaction of Thiazole 3a' with sulfur powder: A mixture of **3a'** (53.2 mg, 0.2 mmol), S_8

(19.2 mg, 0.6 mmol), KSCN (5.0 mg, 0.05 mmol, 25 mol%), Li_2CO_3 (3.7 mg, 0.05 mmol, 25 mol%), and DMSO (1.6 mL) under air. The reaction vessel was stirred at 120 °C for 12 h. Then, the mixture was flushed through a short column of silica gel with EtOAc. GC-MS analysis of the filtrate indicated that **3a** was not formed.



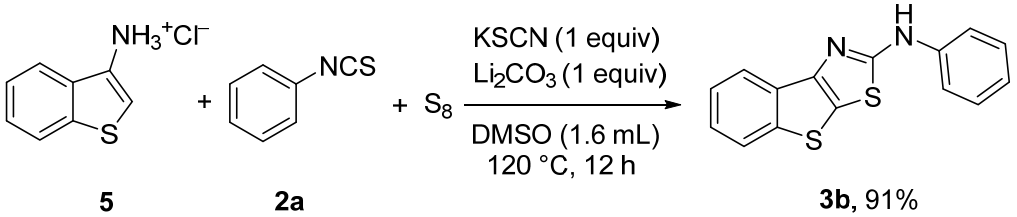
3a' **3a**

(e) Reaction of 3-Aminobenzothiophene 5 with isothiocyanate 2a: A mixture of **5** (37.0 mg, 0.2 mmol), **2a** (72 μL, 0.6 mmol), KSCN (20.0 mg, 0.1 mmol, 100 mol%), Li_2CO_3 (14.8 mg, 0.1 mmol, 100 mol%), and DMSO (1.6 mL) under air. The reaction vessel was stirred at 120 °C for 12 h. Then, the mixture was flushed through a short column of silica gel with EtOAc. GC-MS analysis of the filtrate indicated that **3b** was not formed.



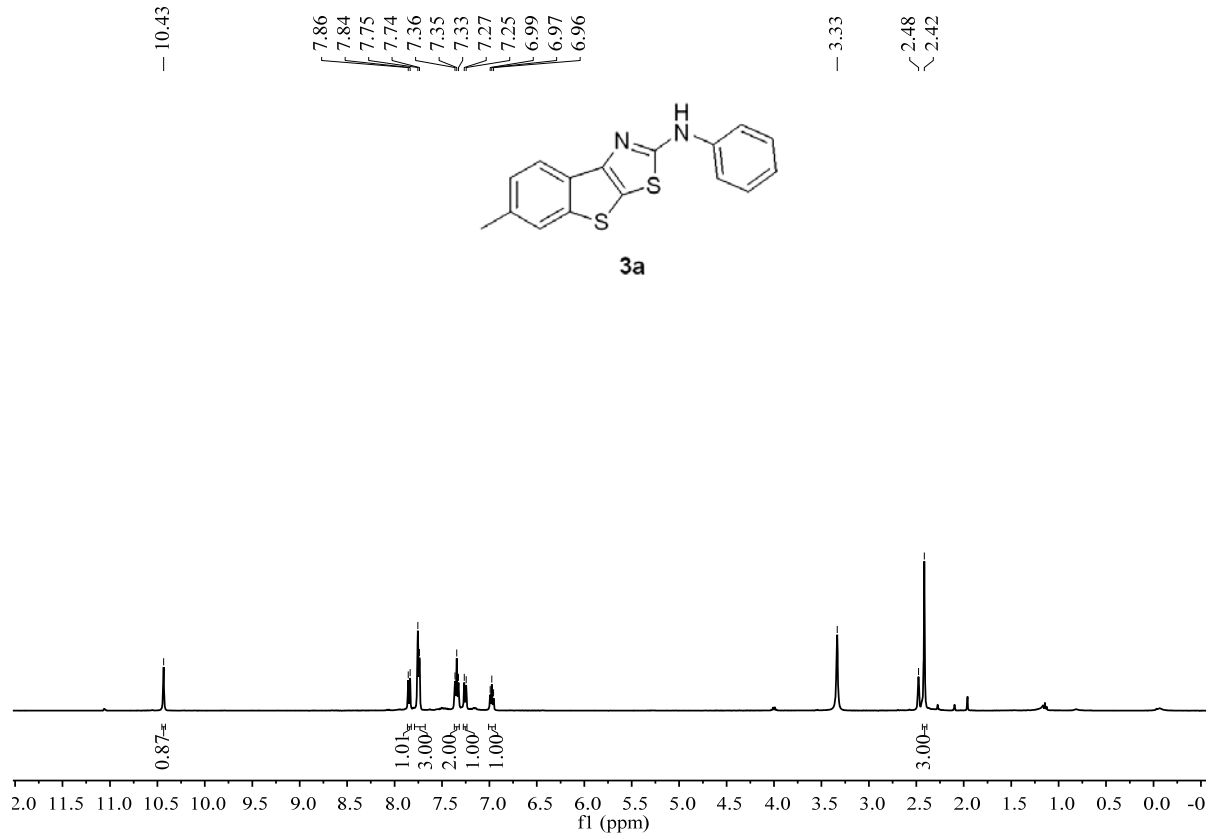
5 **2a** **3b**

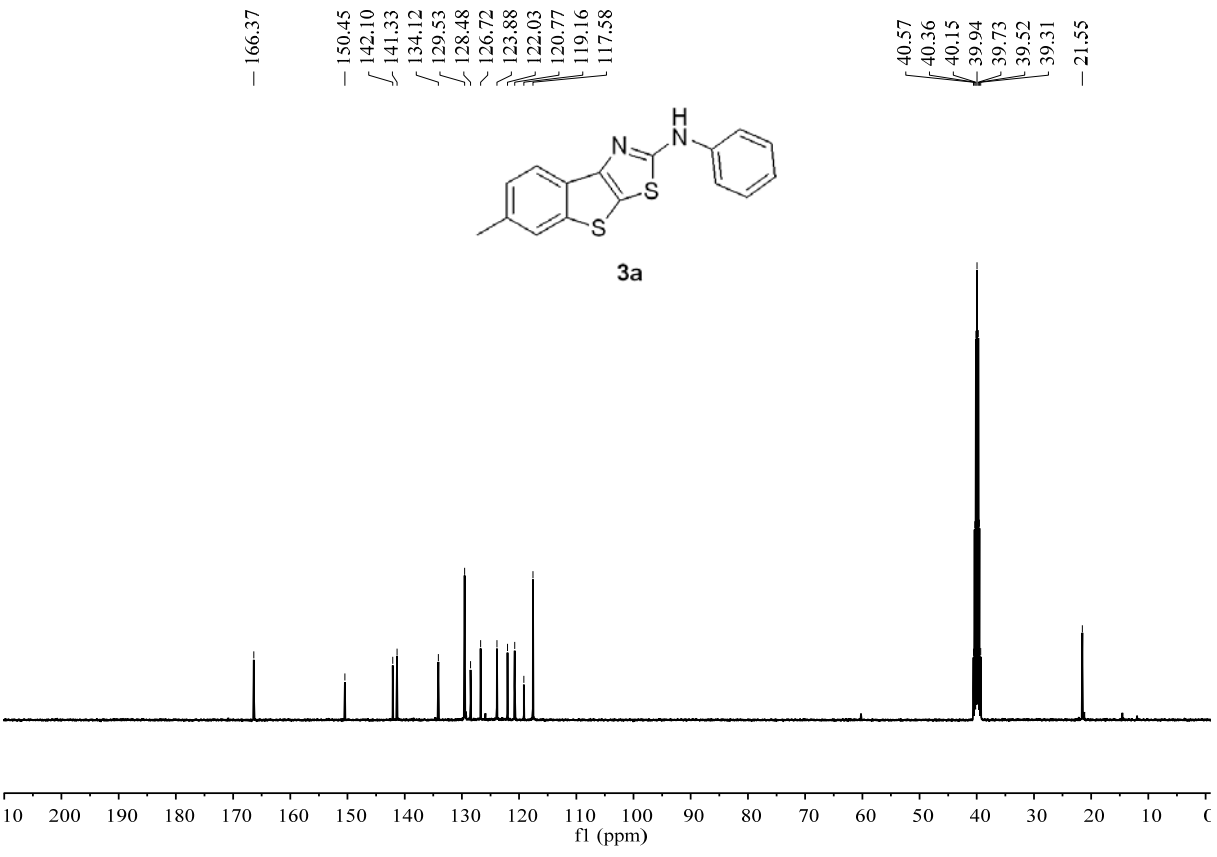
(f) Reaction of 3-Aminobenzothiophene 5 with isothiocyanate 2a: A mixture of **5** (37.0 mg, 0.2 mmol), **2a** (72 μL, 0.6 mmol), S_8 (19.2 mg, 0.6 mmol), KSCN (20.0 mg, 0.1 mmol, 100 mol%), Li_2CO_3 (14.8 mg, 0.1 mmol, 100 mol%), and DMSO (1.6 mL) under air. The reaction vessel was stirred at 120 °C for 12 h. Then, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (PE/ EA = 10/1) to give **3b** in 91% (51.3 mg).

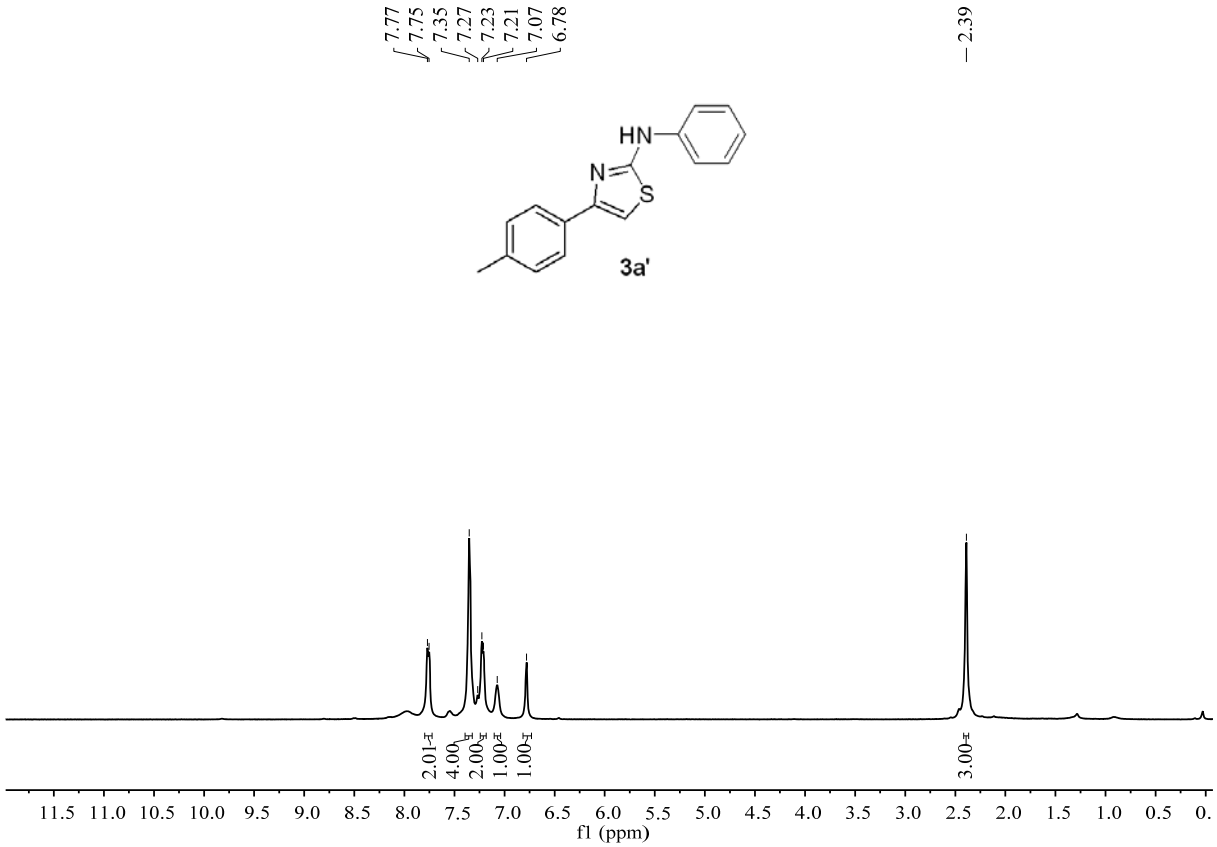


5 **2a** **3b**, 91%

6. ^{1}H NMR and ^{13}C NMR spectra of products



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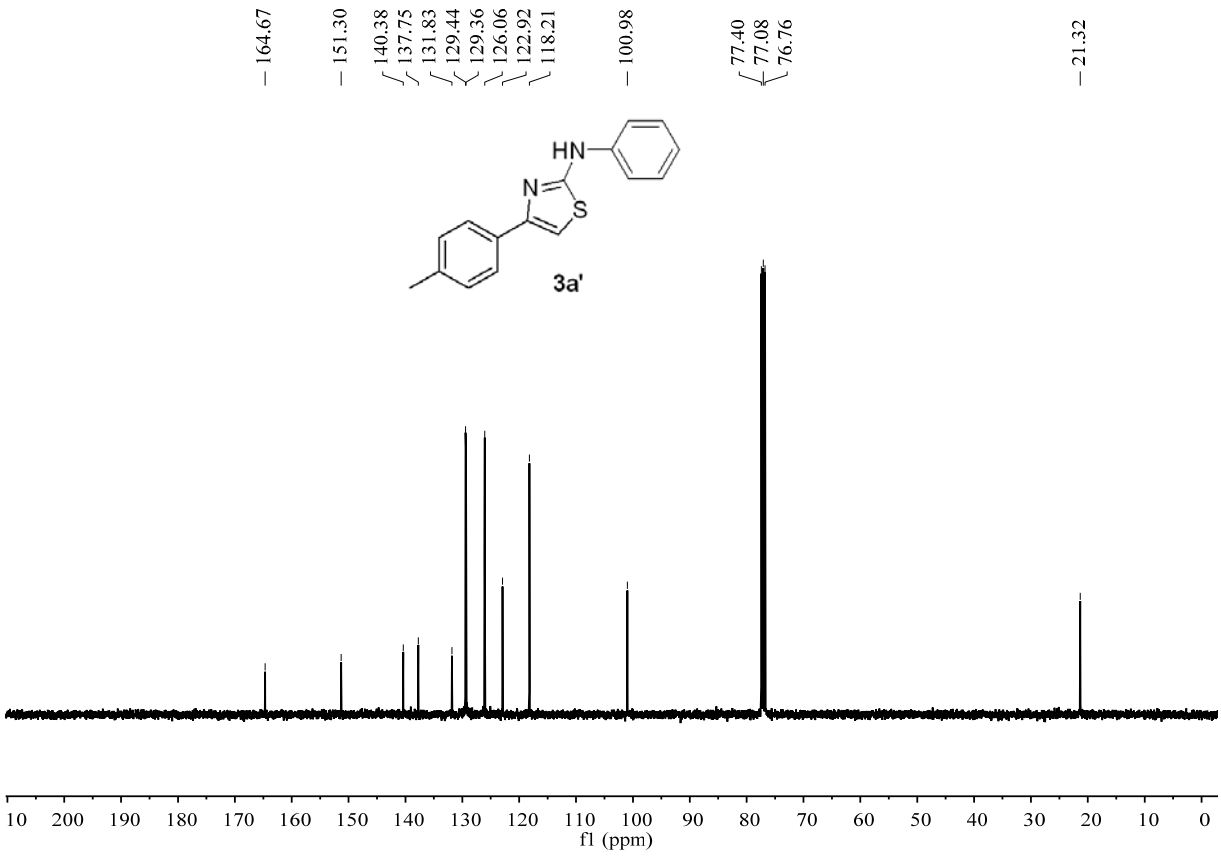
7.75
7.35
7.27
7.23
7.21
7.07
6.78
2.39
HN
N
S
3a'
2.01
4.00
2.00
1.00
1.00
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)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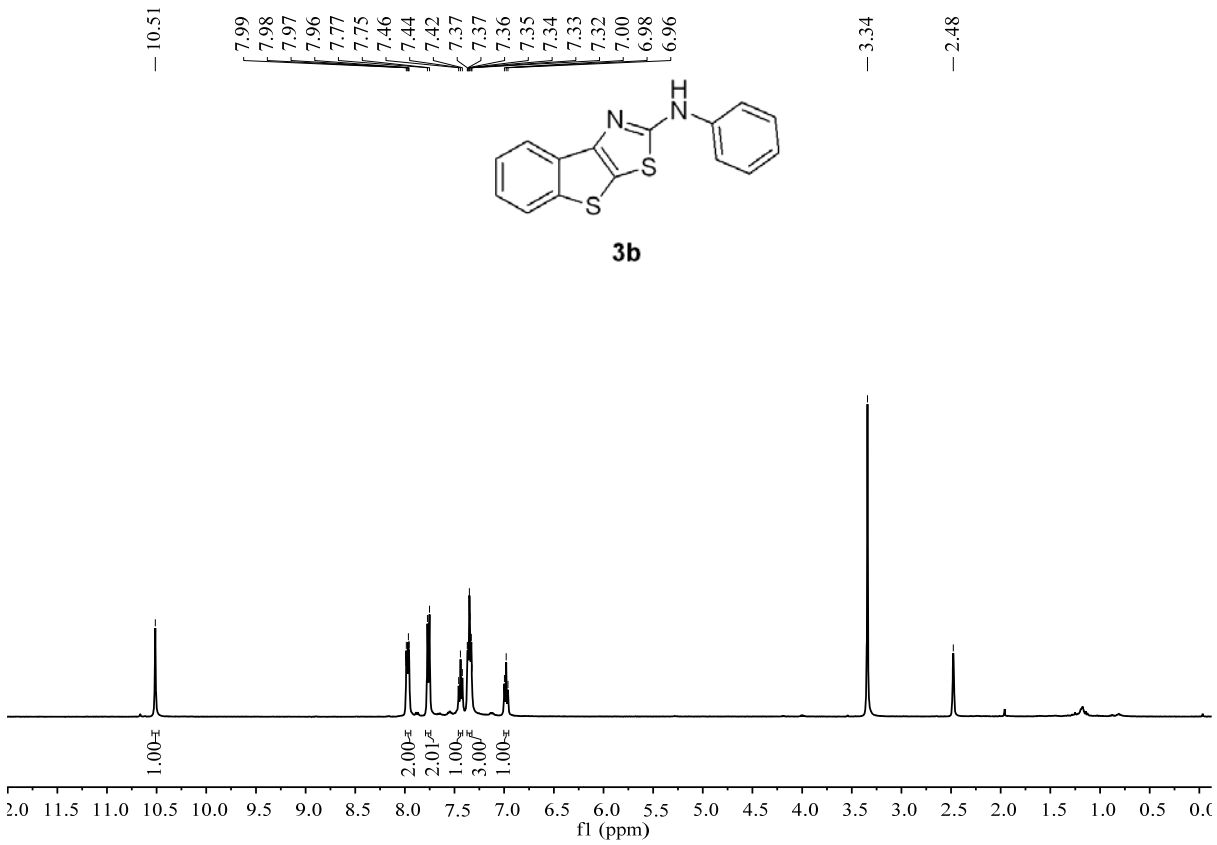
151.30
140.38
137.75
131.83
129.44
129.36
126.06
122.92
118.21
100.98
77.40
77.08
76.76
21.32
HN
N
S
3a'
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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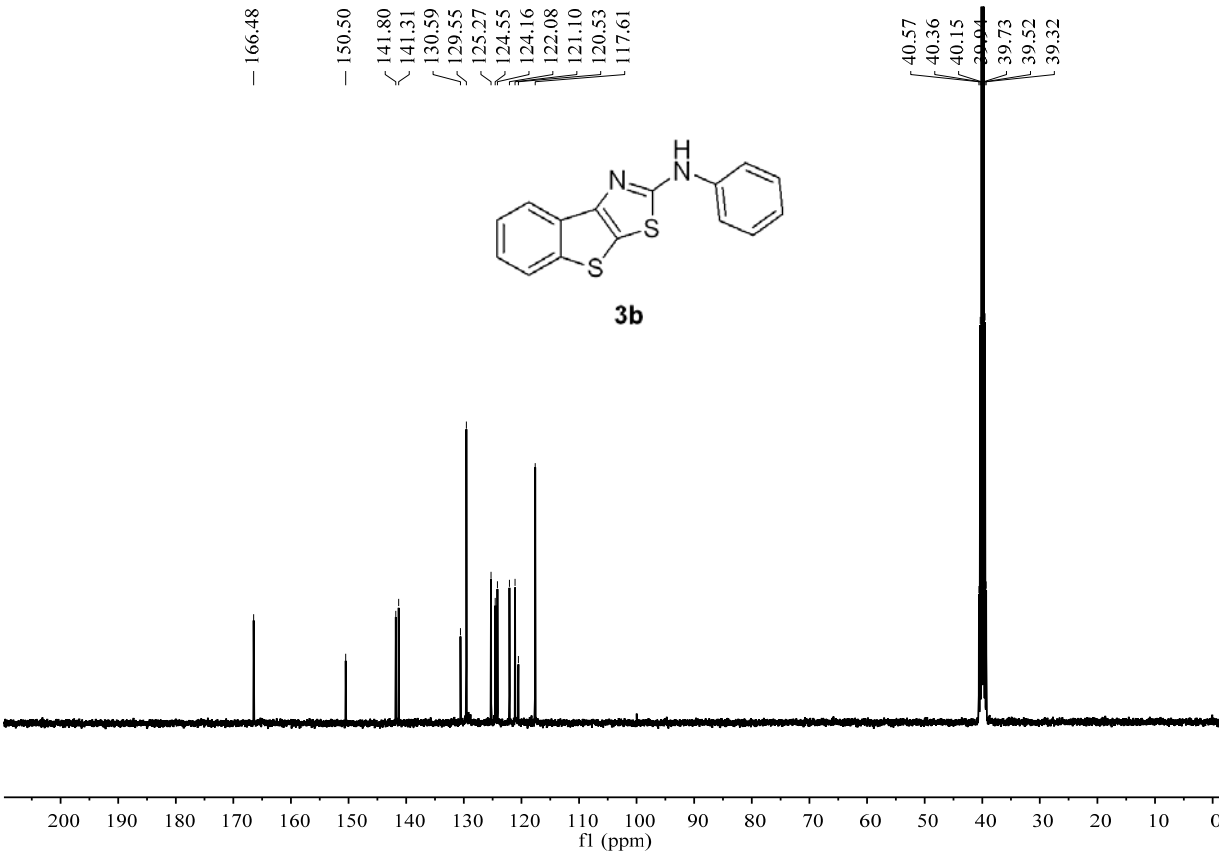
7.98
7.97
7.96
7.77
7.75
7.46
7.44
7.42
7.37
7.37
7.36
7.35
7.34
7.33
7.32
7.00
6.98
6.96
3.34
2.48
N
H
S
S
1.00
2.00
2.01
1.00
3.00
1.00
f1 (ppm)

3b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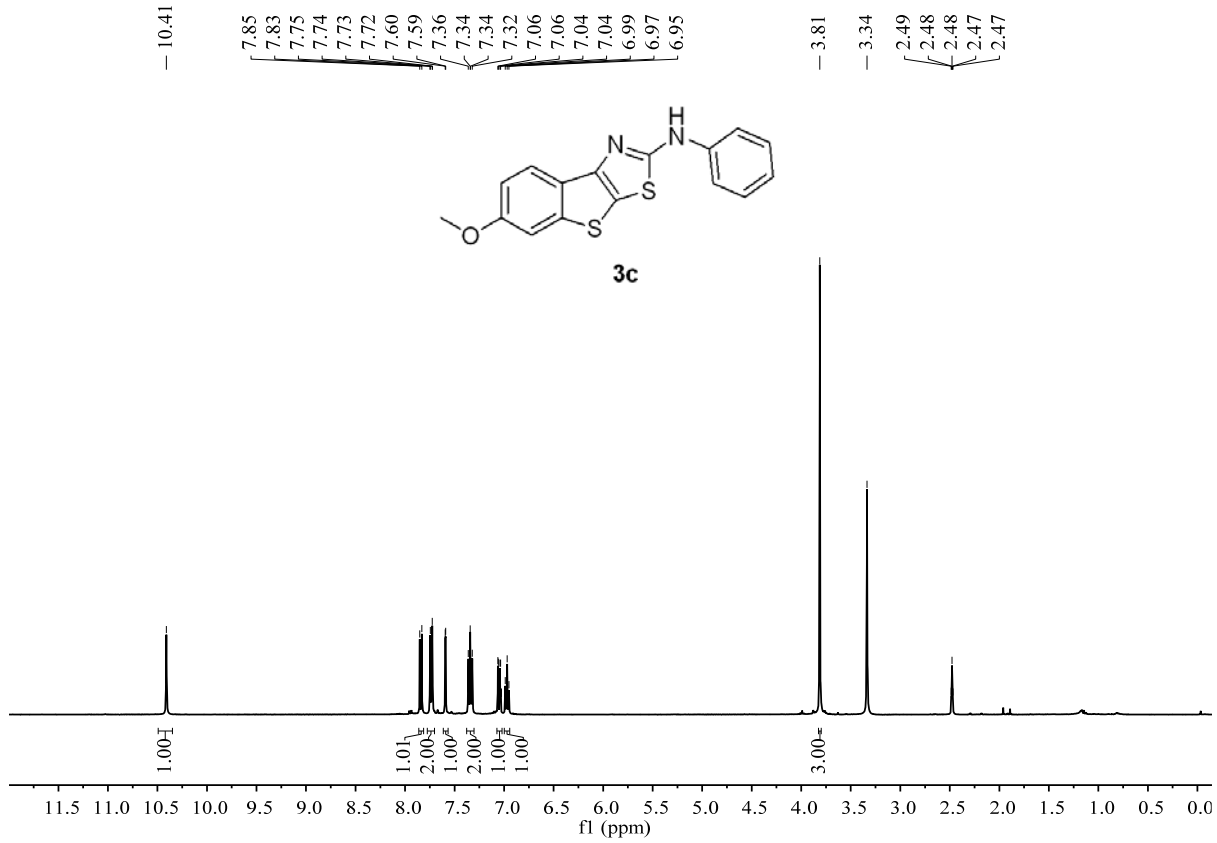
150.50
141.80
141.31
130.59
129.55
125.27
124.55
124.16
122.08
121.10
120.53
117.61
40.57
40.36
40.15
39.73
39.52
39.32
N
H
S
S
f1 (ppm)

3b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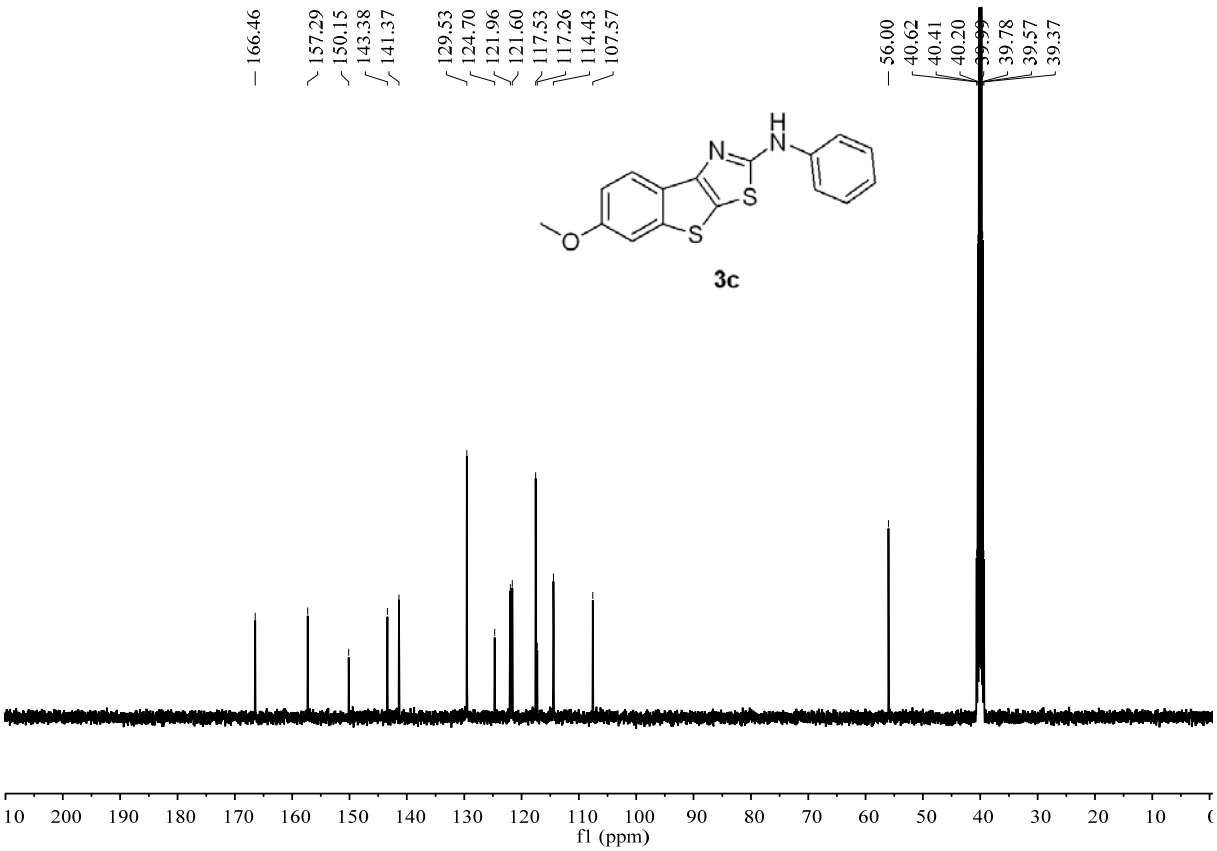
7.85
7.83
7.75
7.74
7.73
7.72
7.60
7.59
7.36
7.34
7.34
7.32
7.06
7.06
7.04
7.04
6.99
6.97
6.95
3.81
3.34
2.49
2.48
2.48
2.47
2.47
3c
1.00
1.01
2.00
1.00
2.00
1.00
1.00
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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157.29
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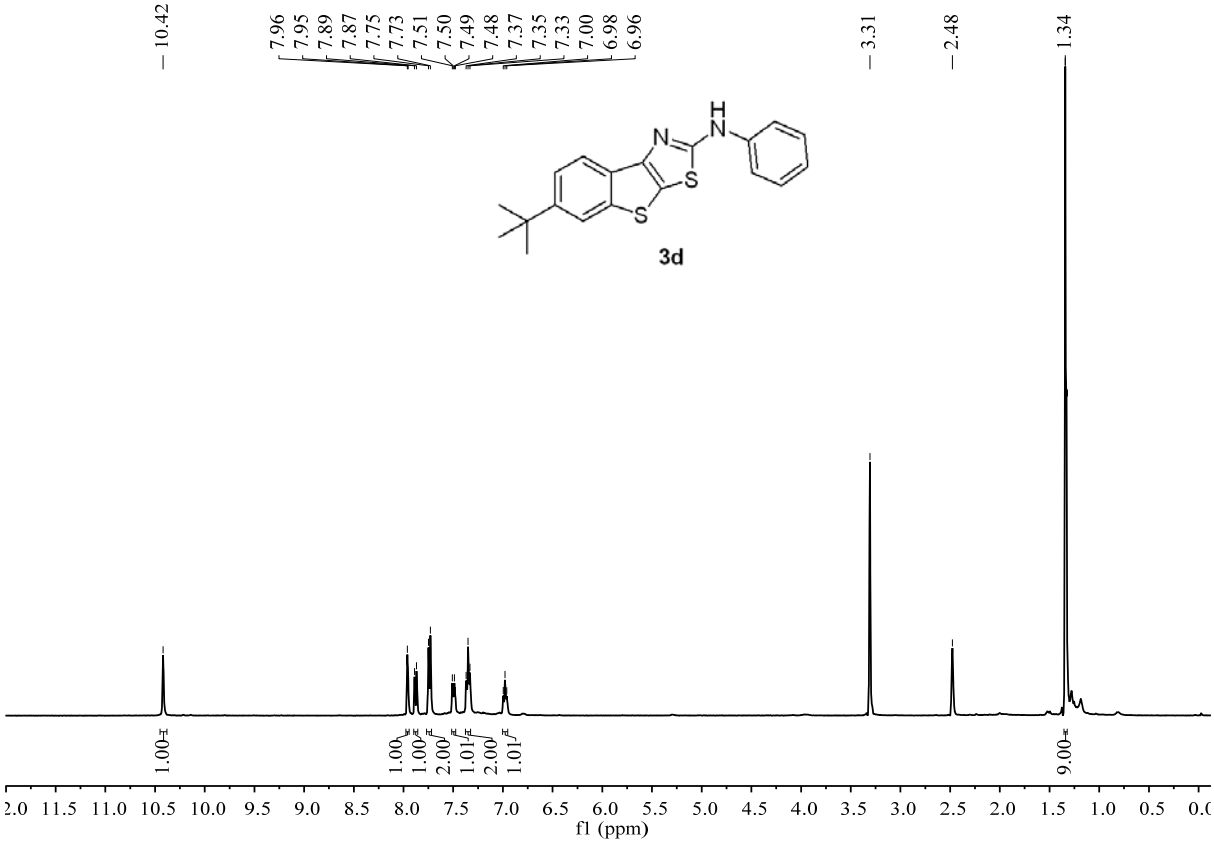
143.38
141.37
129.53
124.70
121.96
121.60
117.53
117.26
114.43
107.57
56.00
40.62
40.41
40.20
39.99
39.78
39.57
39.37
3c
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.95
7.89
7.87
7.75
7.73
7.51
7.50
7.49
7.48
7.37
7.35
7.33
7.00
6.98
6.96
3.31
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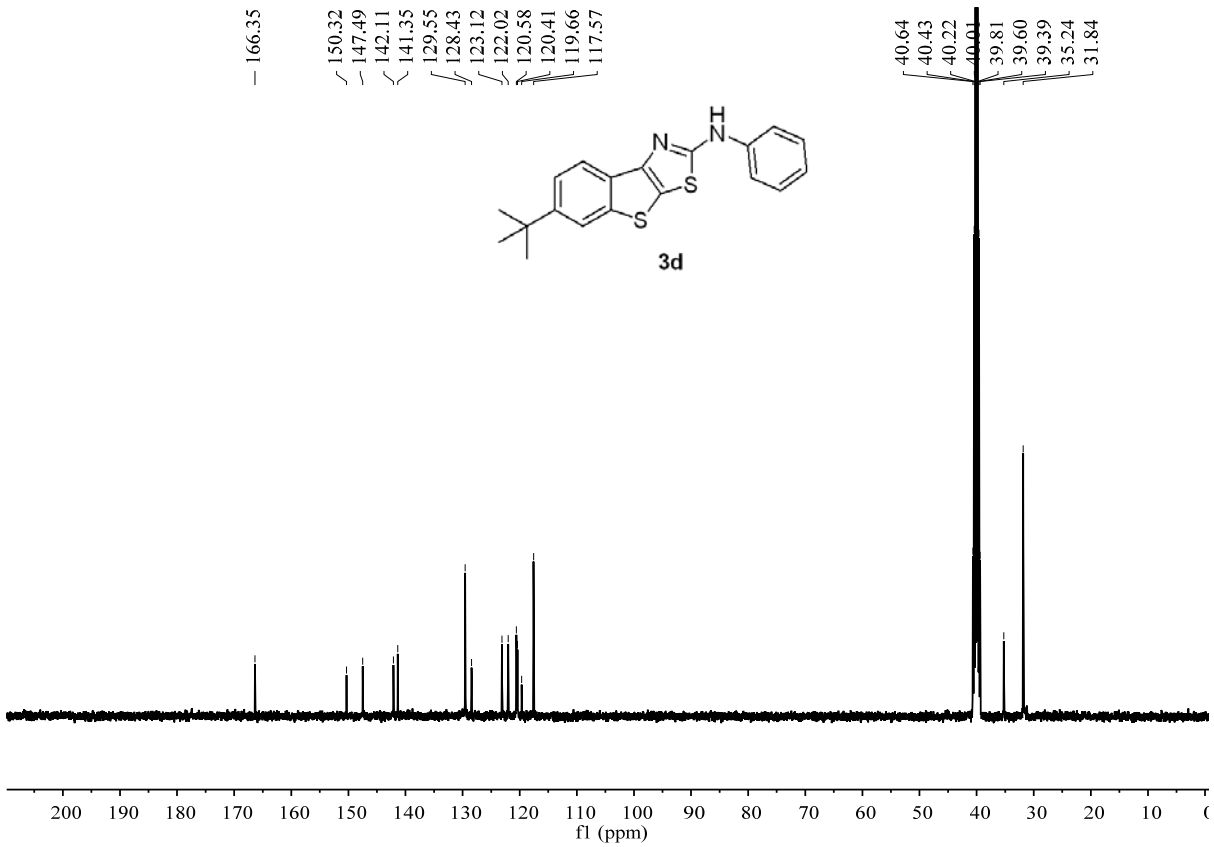
1.01
2.00
1.01
9.00
f1 (ppm)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150.32
147.49
142.11
141.35
129.55
128.43
123.12
122.02
120.58
120.41
119.66
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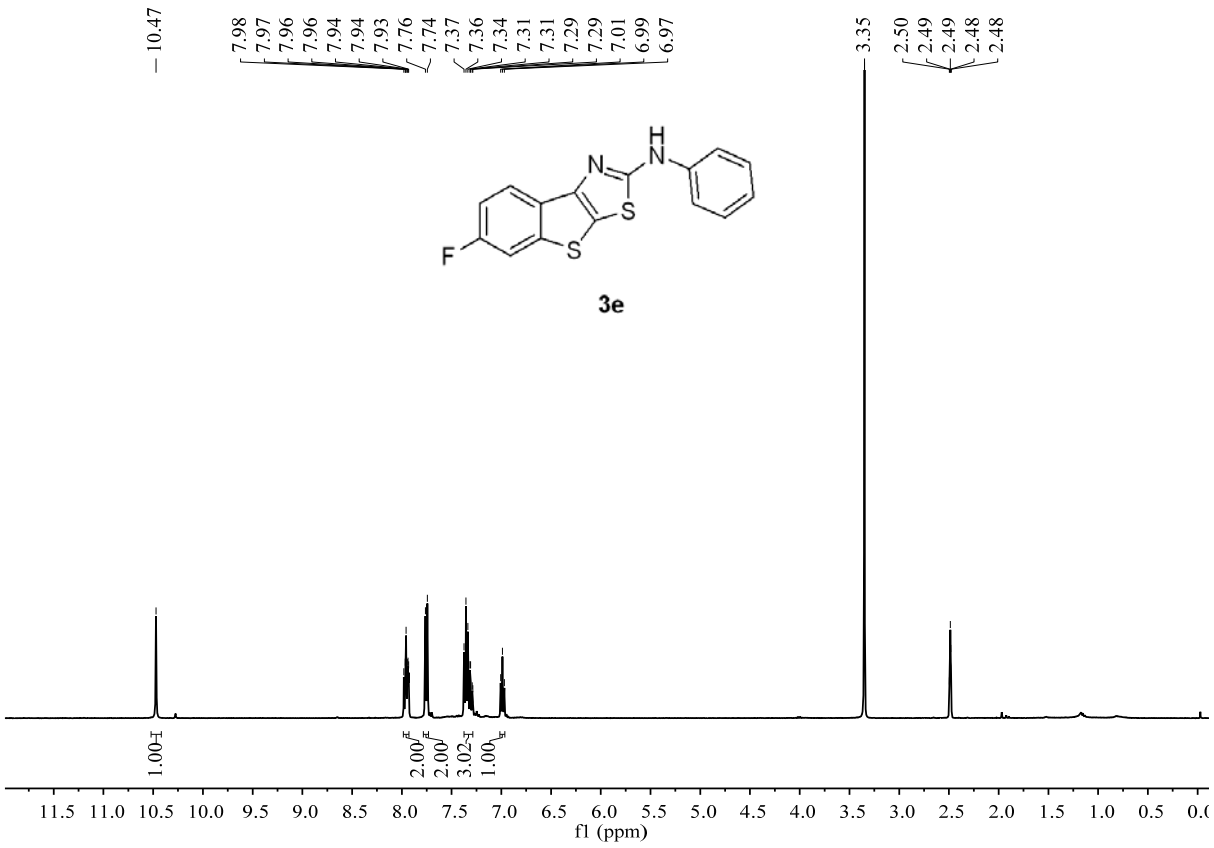
40.64
40.43
40.22
40.01
39.81
39.60
39.39
35.24
31.84
3d
f1 (ppm)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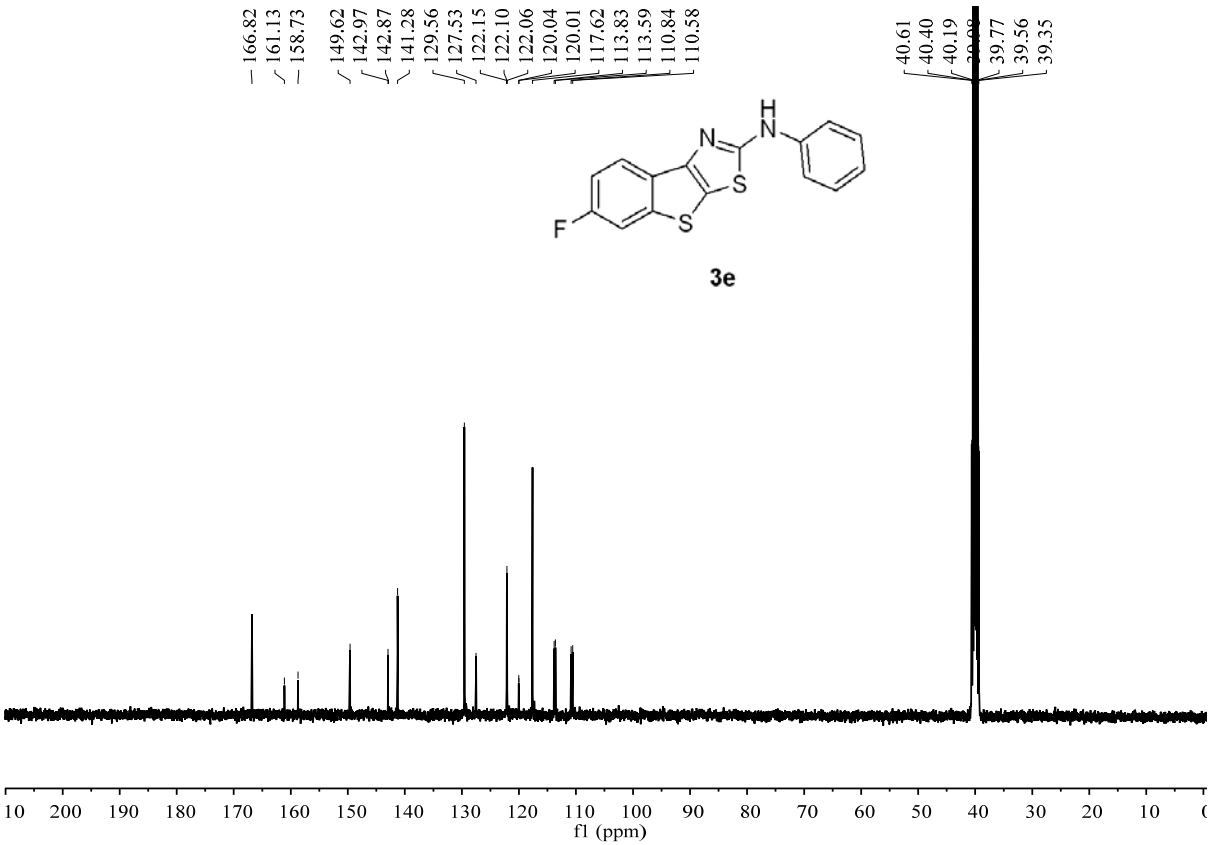
7.96
7.96
7.94
7.94
7.93
7.76
7.74
7.37
7.36
7.34
7.31
7.31
7.29
7.29
7.01
6.99
6.97
3.35
2.50
2.49
2.49
2.48
2.48
1.00
2.00
2.00
3.02
1.00
f1 (ppm)

3e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142.87
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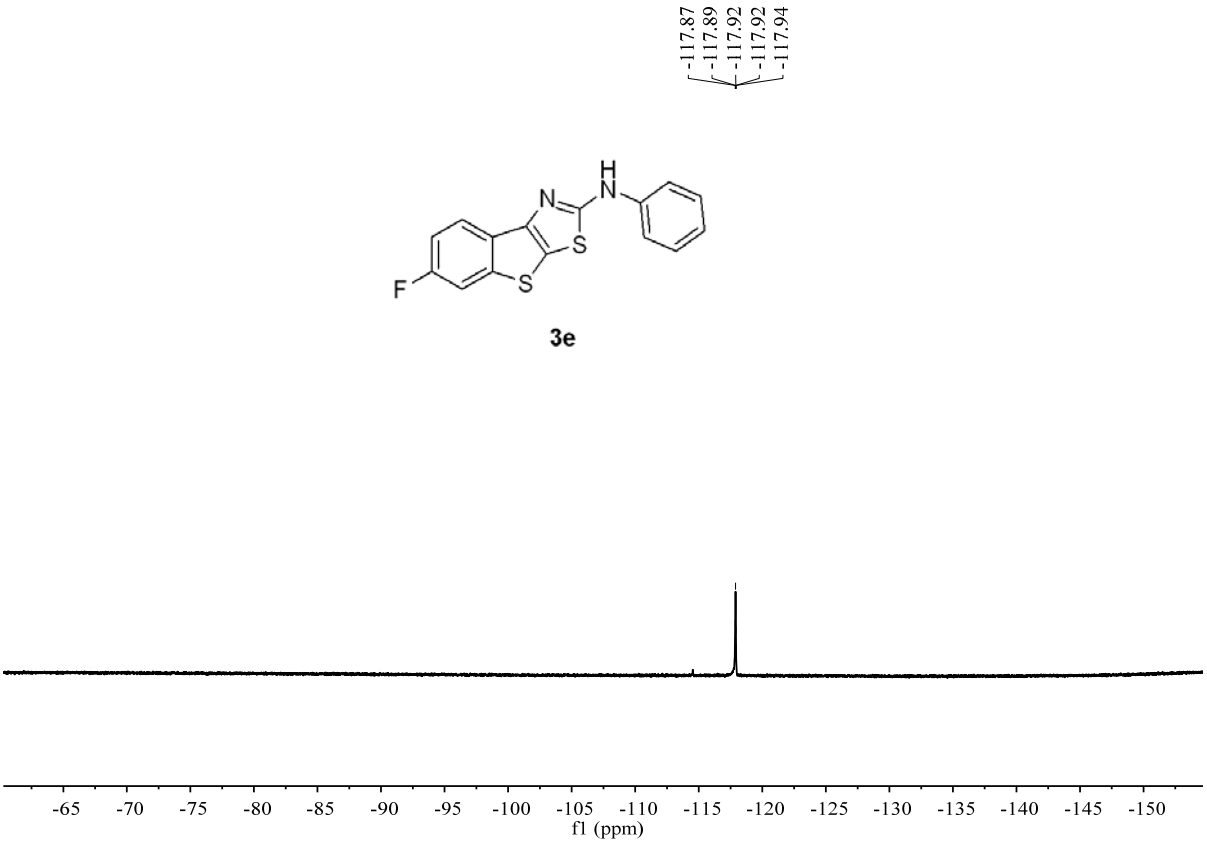
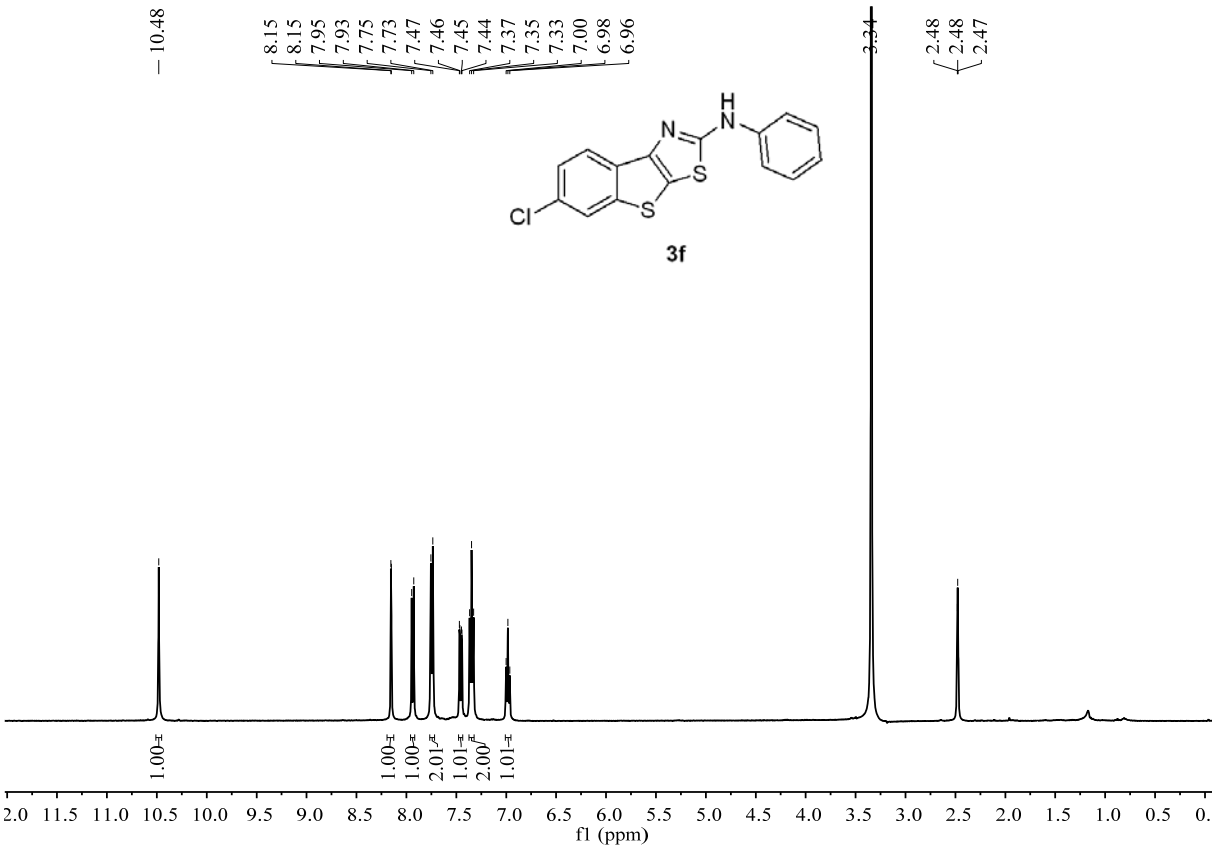
129.56
127.53
122.15
122.10
122.06
120.04
120.01
117.62
113.83
113.59
110.84
110.58
40.61
40.40
40.19
39.77
39.56
39.35
f1 (ppm)

3e


-117.87
-117.89
-117.92
-117.92
-117.94
H
N
N
S
S
F
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
f1 (ppm)

3e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8.15
7.95
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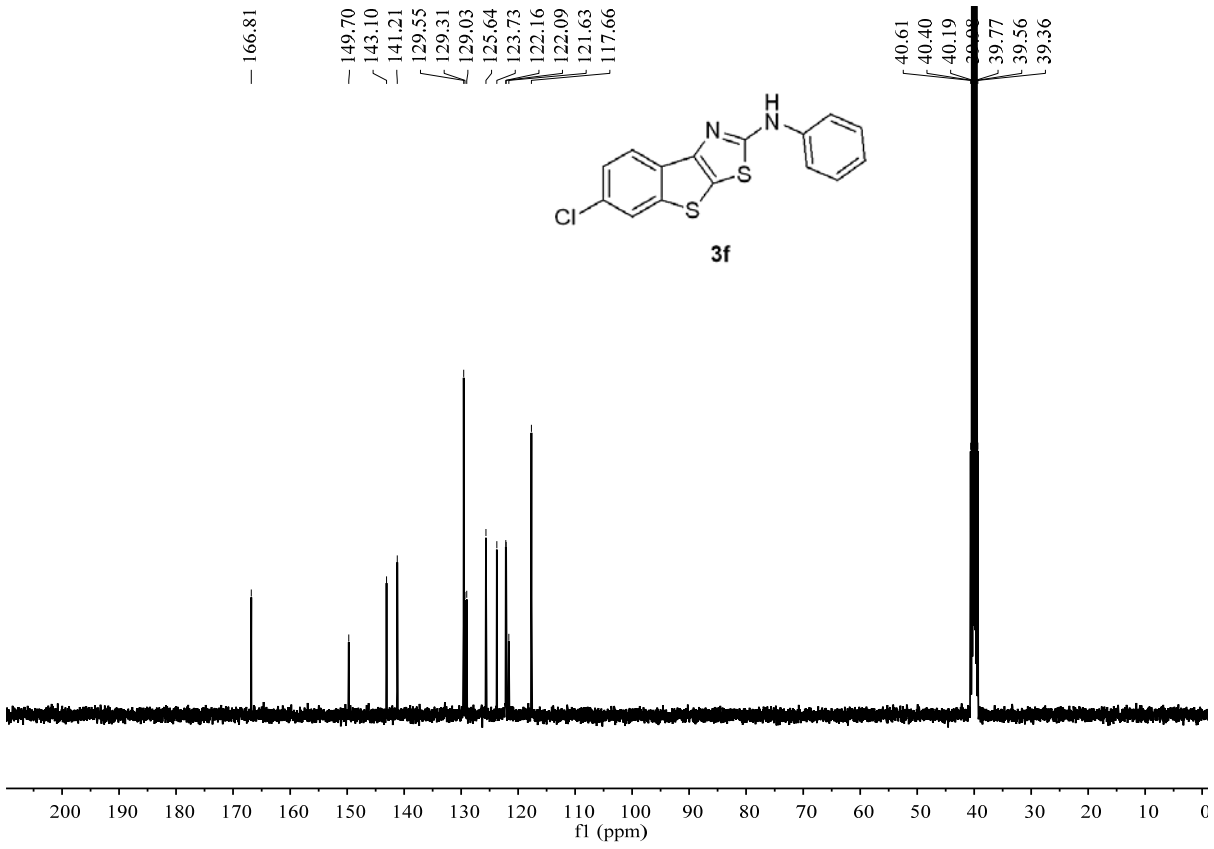
7.47
7.46
7.45
7.44
7.37
7.35
7.33
7.00
6.98
6.96
3.34
2.48
2.48
2.47
1.00
1.00
2.01
1.01
2.00
1.01
3f
f1 (ppm)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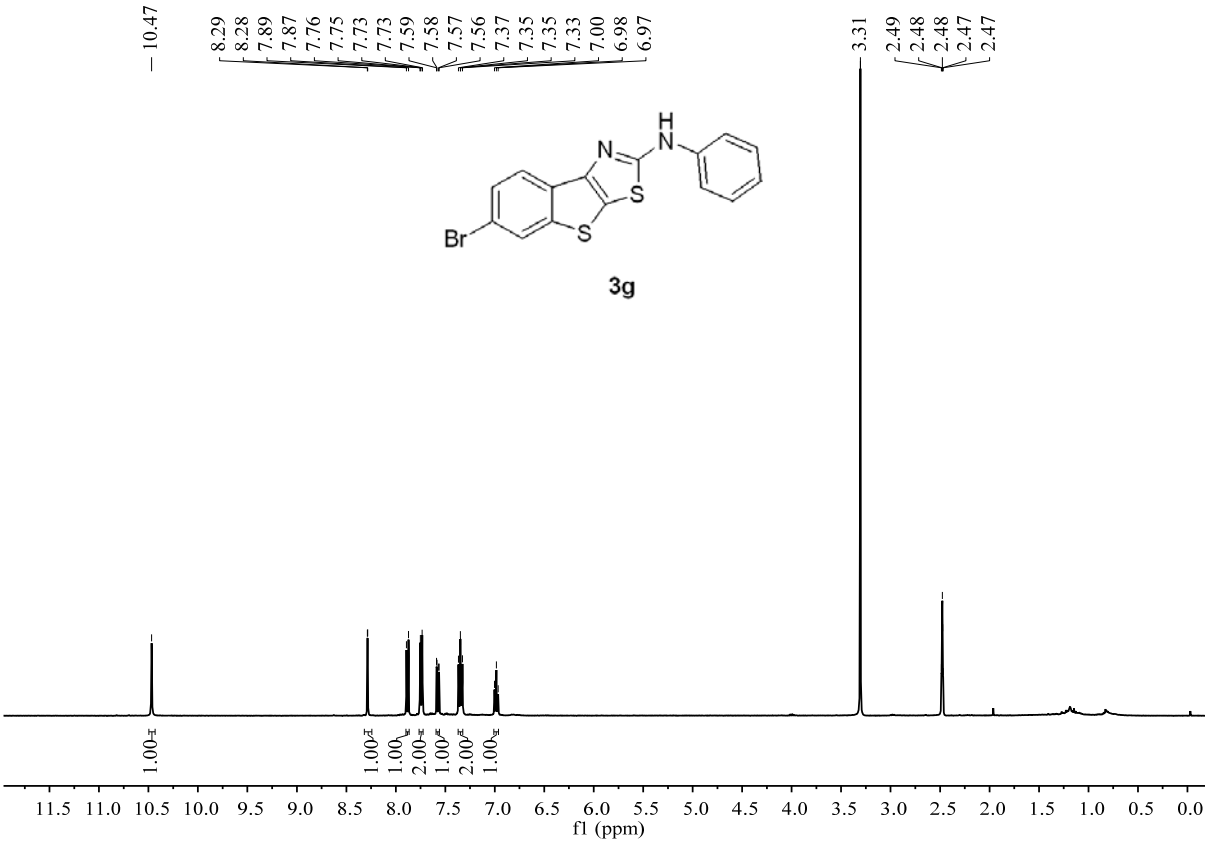
141.21
129.55
129.31
129.03
125.64
123.73
122.16
122.09
121.63
117.66
40.61
40.40
40.19
39.77
39.56
39.36
3f
f1 (ppm)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7.73
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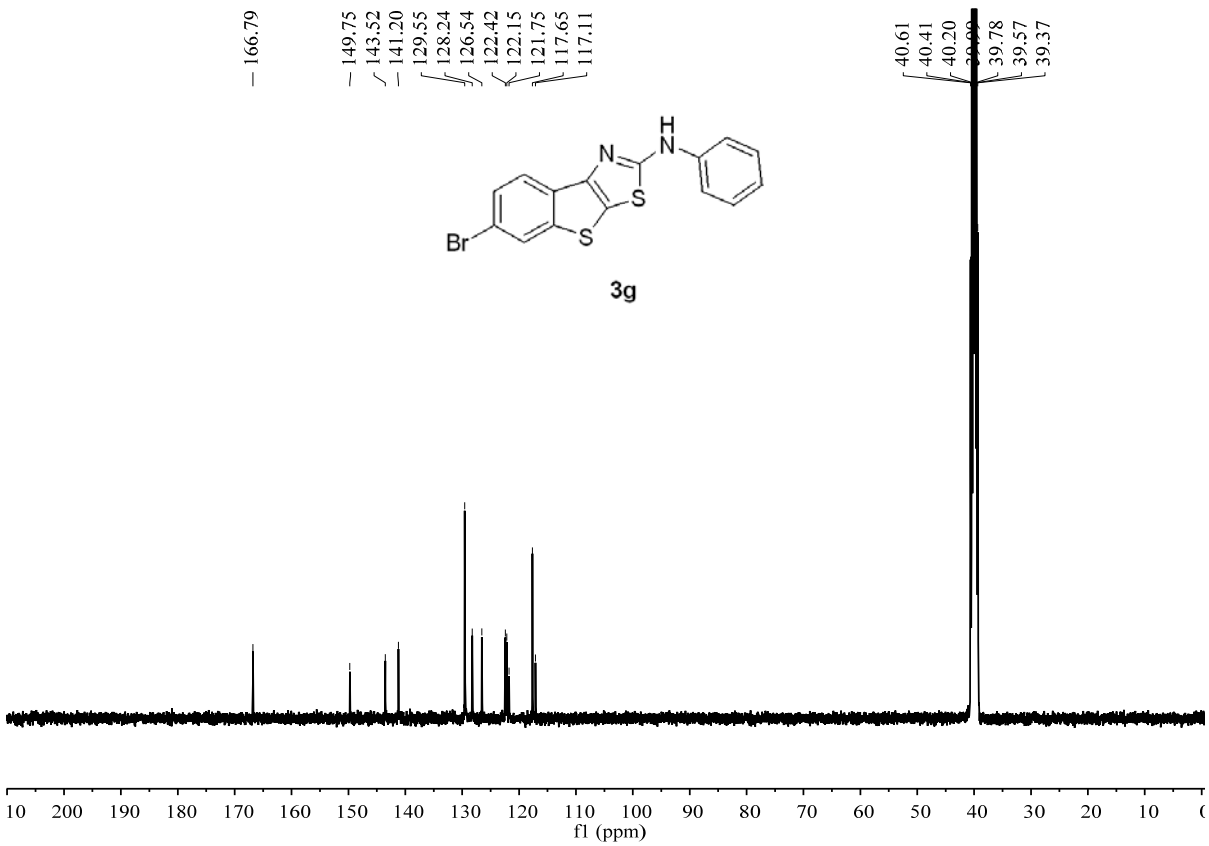
7.58
7.57
7.56
7.37
7.35
7.35
7.33
7.00
6.98
6.97
3.31
2.49
2.48
2.48
2.47
2.47
N
H
N
S
S
Br
3g
1.00
1.00
1.00
2.00
1.00
2.00
1.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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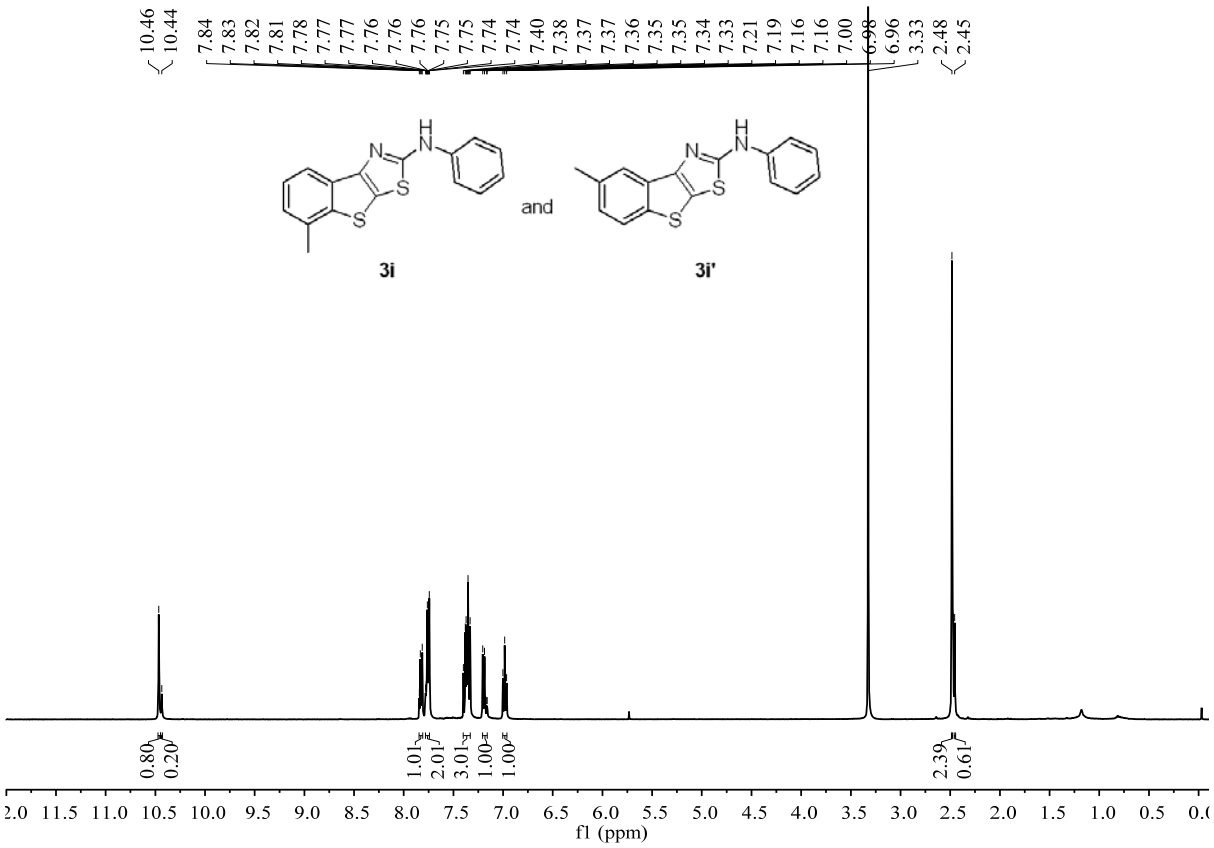
117.65
117.11
40.61
40.41
40.20
39.78
39.57
39.37
N
H
N
S
S
Br
3g
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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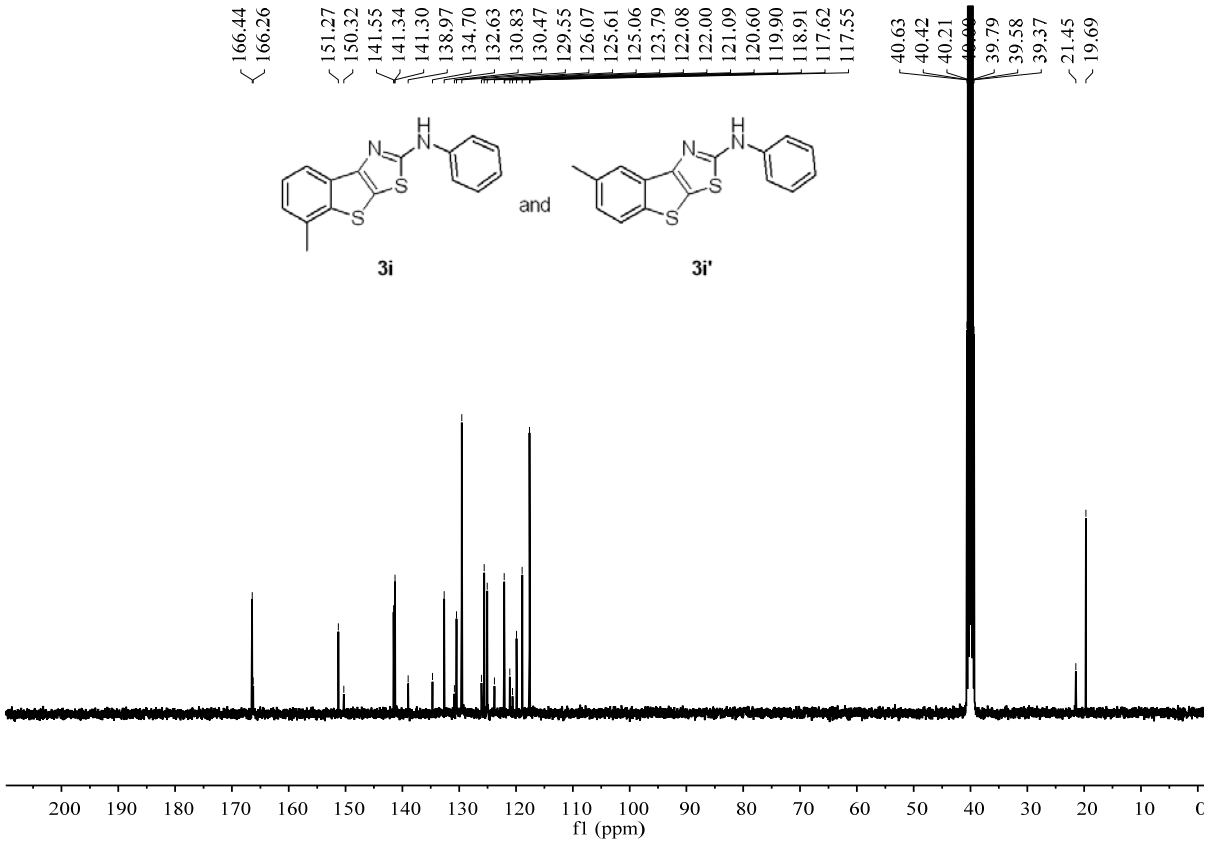
7.75
7.75
7.74
7.74
7.40
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.21
7.19
7.16
7.16
7.00
6.98
6.96
3.33
2.48
2.45
and
3i
3i'
0.80
0.20
1.01
2.01
3.01
1.00
1.00
2.39
0.61
fl (ppm)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132.63
130.83
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126.07
125.61
125.06
123.79
122.08
122.00
121.09
120.60
119.90
118.91
117.62
117.55
40.63
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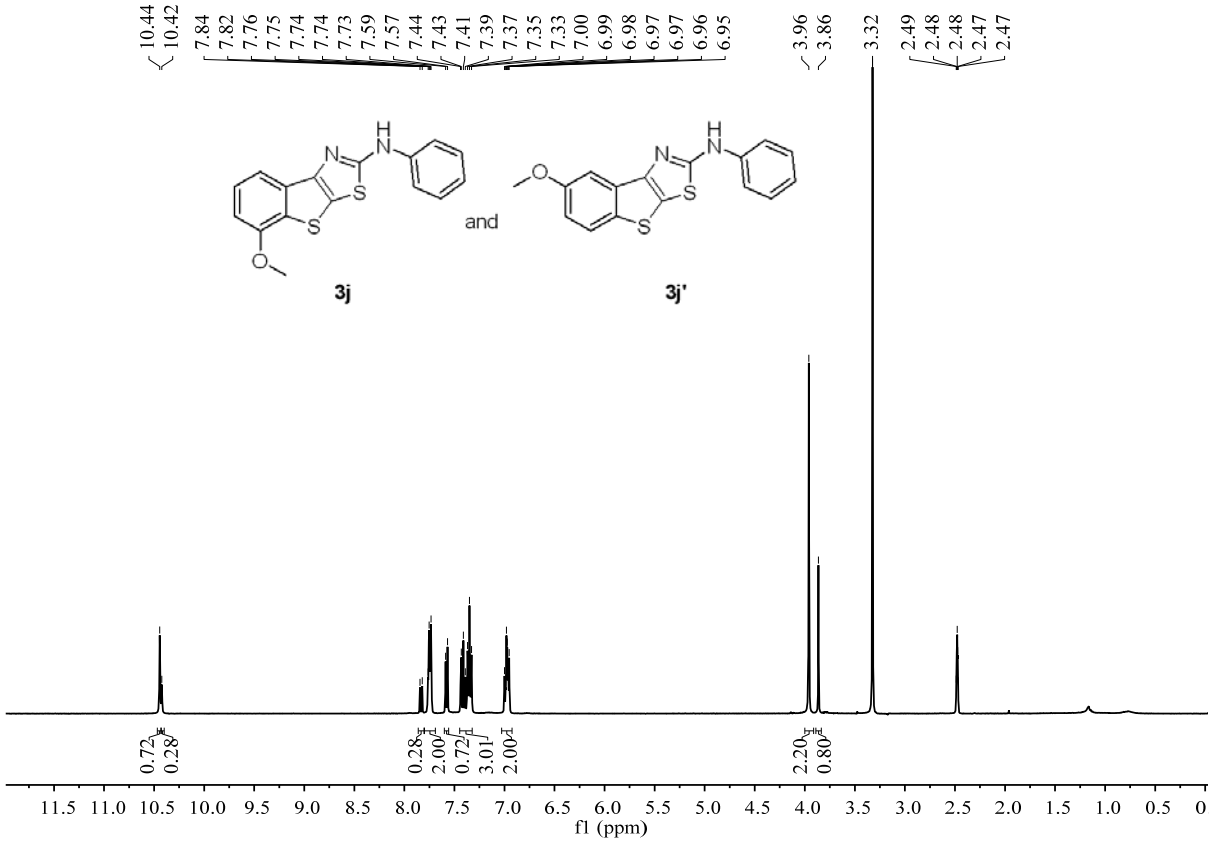
40.21
39.79
39.58
39.37
21.45
19.69
and
3i
3i'
fl (ppm)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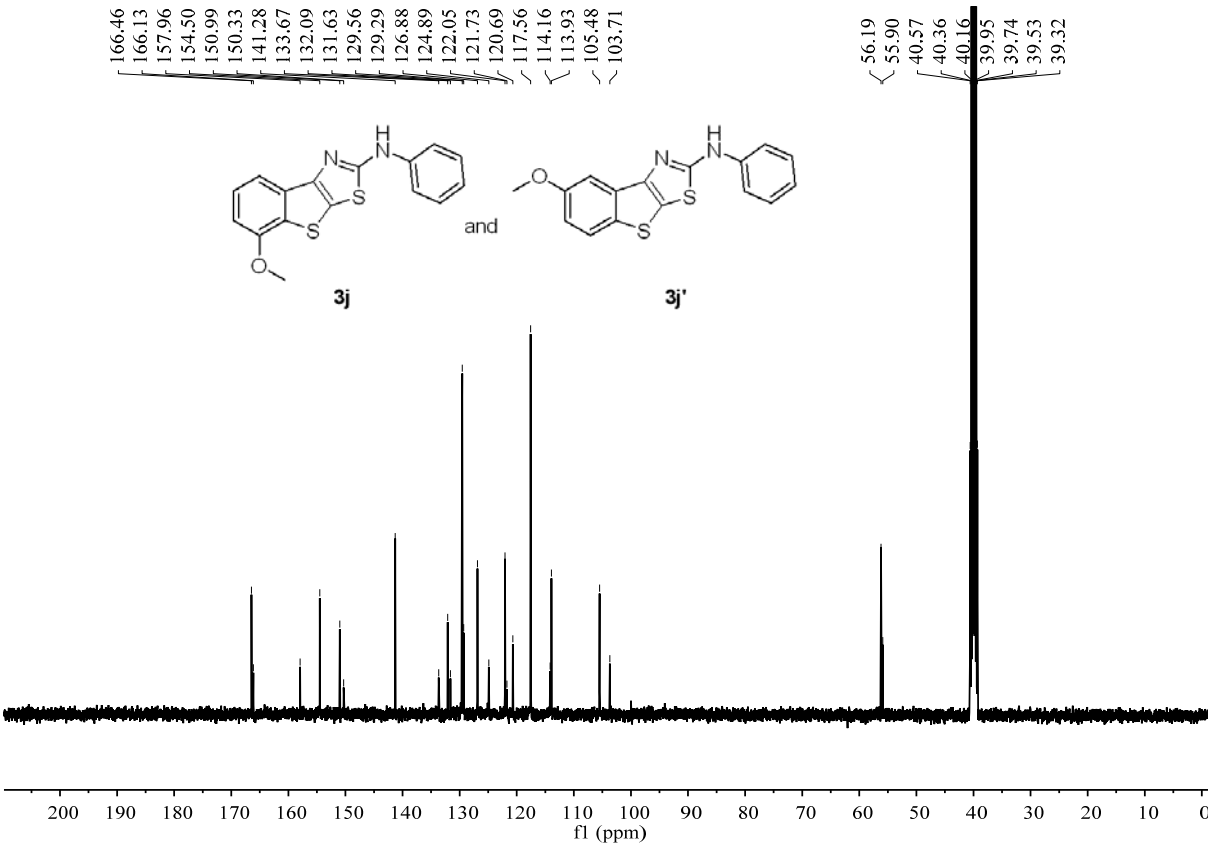
6.98
6.97
6.97
6.96
6.95
3.96
3.86
3.32
2.49
2.48
2.48
2.47
2.47
and
3j
3j'
0.72
0.28
0.28
2.00
0.72
3.01
2.00
2.20
0.80
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)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166.13
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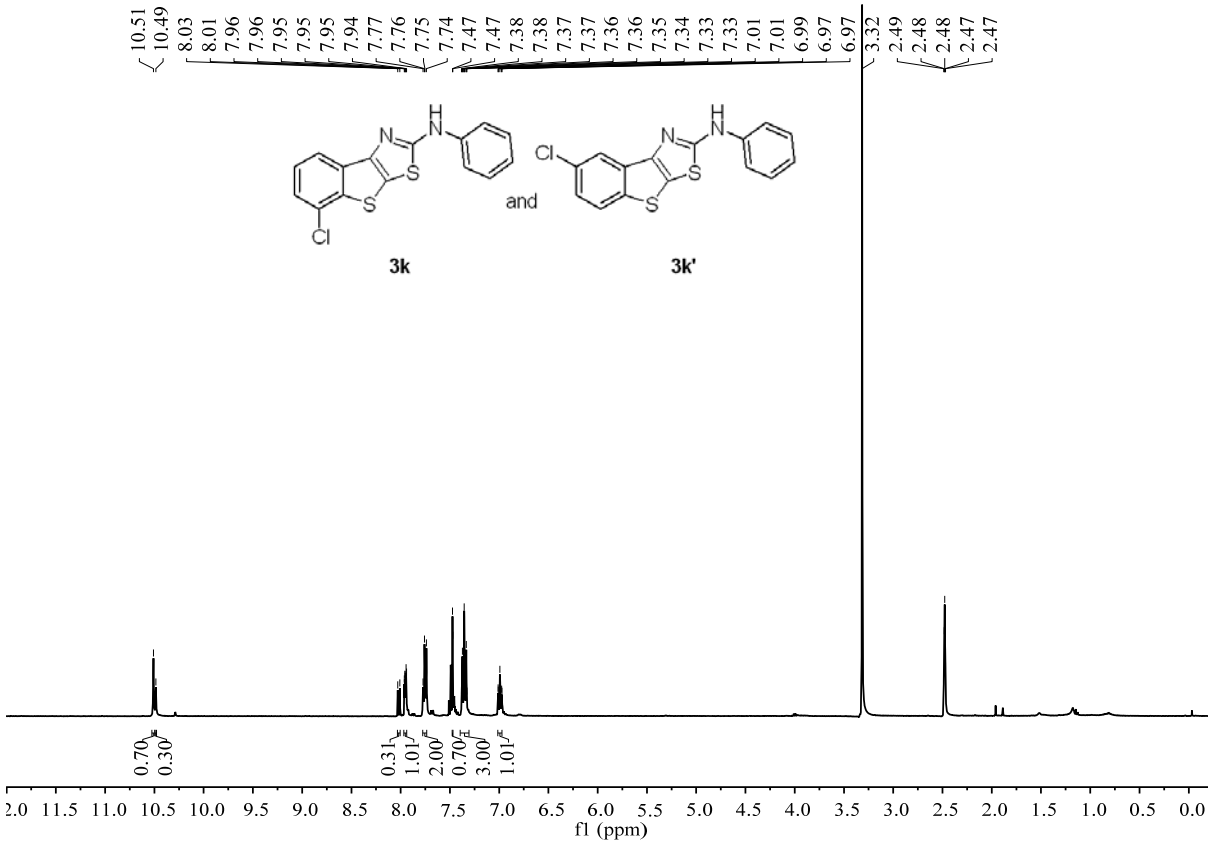
154.50
150.99
150.33
141.28
133.67
132.09
131.63
129.56
129.29
126.88
124.89
122.05
121.73
120.69
117.56
114.16
113.93
105.48
103.71
56.19
55.90
40.57
40.36
40.16
39.95
39.74
39.53
39.32
and
3j
3j'
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.01
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7.96
7.95
7.95
7.95
7.94
7.77
7.76
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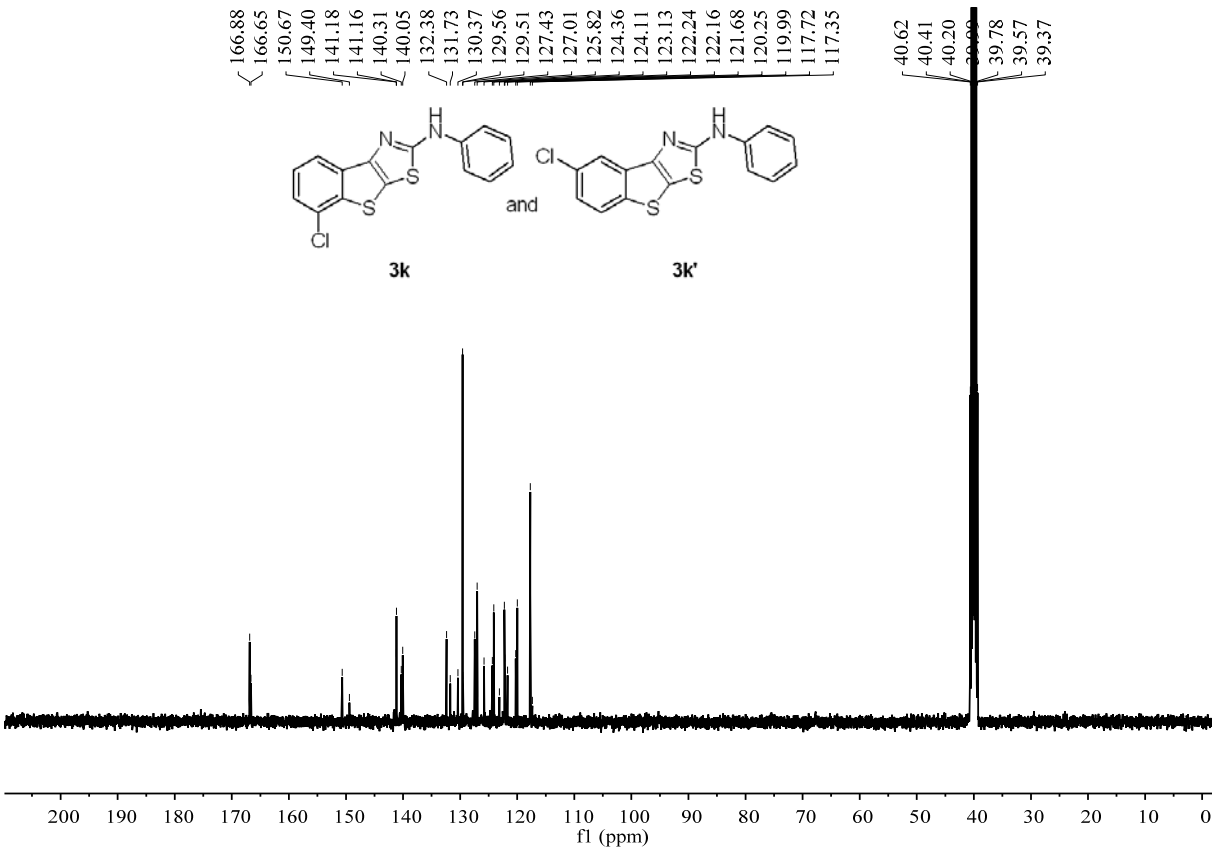
7.47
7.47
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.34
7.33
7.33
7.01
7.01
6.99
6.97
6.97
3.32
2.49
2.48
2.48
2.47
2.47
and
3k
3k'
0.70
0.30
0.31
1.01
2.00
0.70
3.00
1.01
f1 (ppm)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141.16
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140.05
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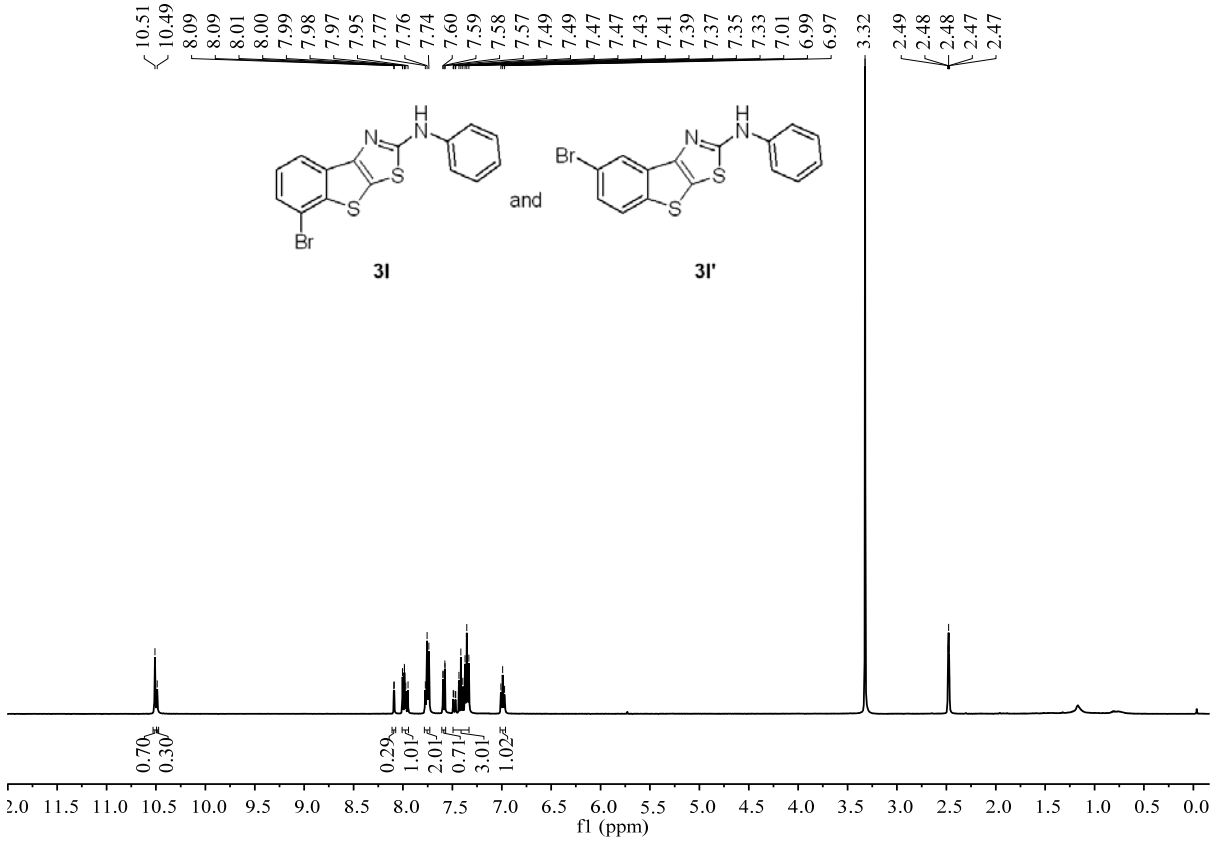
131.73
130.37
129.56
129.51
127.43
127.01
125.82
124.36
124.11
123.13
122.24
122.16
121.68
120.25
119.99
117.72
117.35
40.62
40.41
40.20
39.78
39.57
39.37
and
3k
3k'
f1 (ppm)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10.49
8.09
8.09
8.01
8.00
7.99
7.98
7.97
7.95
7.77
7.76
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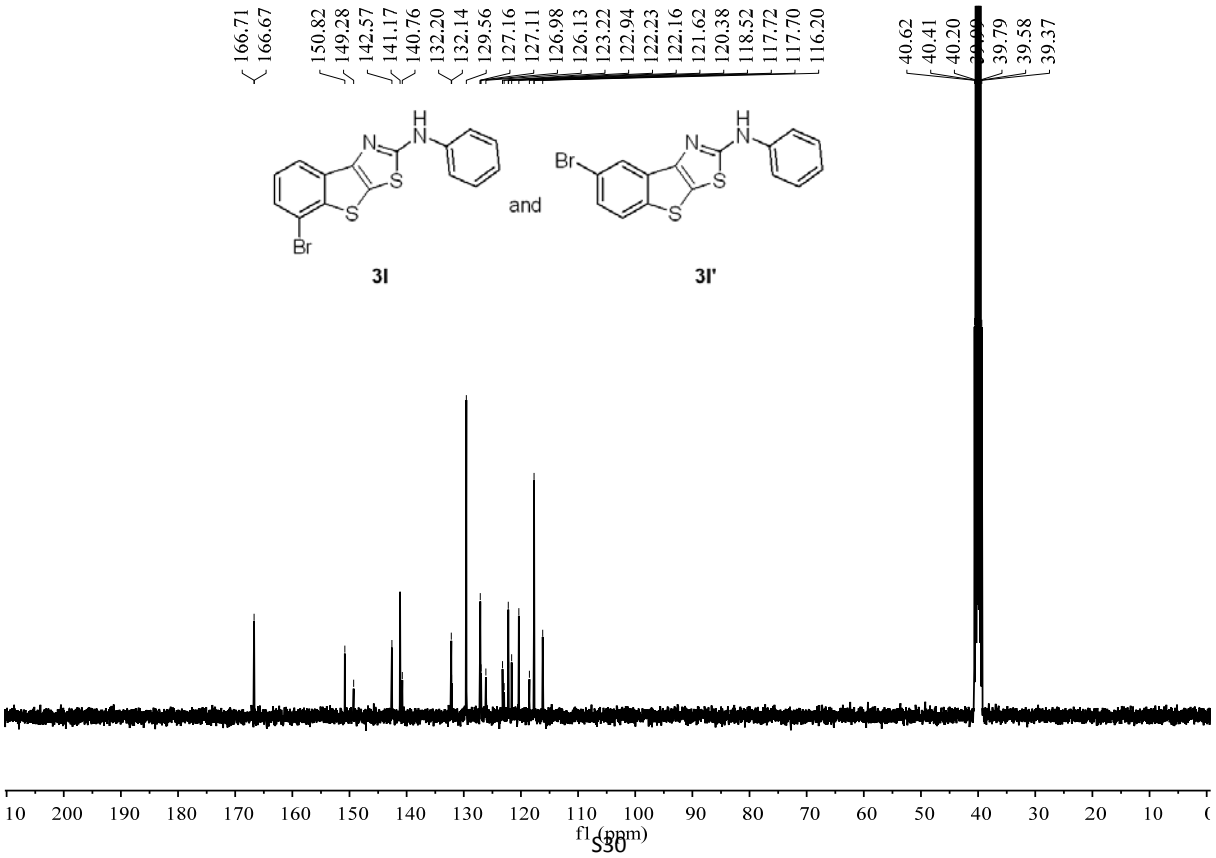
7.60
7.59
7.58
7.57
7.49
7.49
7.47
7.47
7.43
7.41
7.39
7.37
7.35
7.33
7.01
6.99
6.97
3.32
2.49
2.48
2.48
2.47
2.47
and
3l
3l'
0.70
0.30
0.29
1.01
2.01
0.71
3.01
1.02
f1 (ppm)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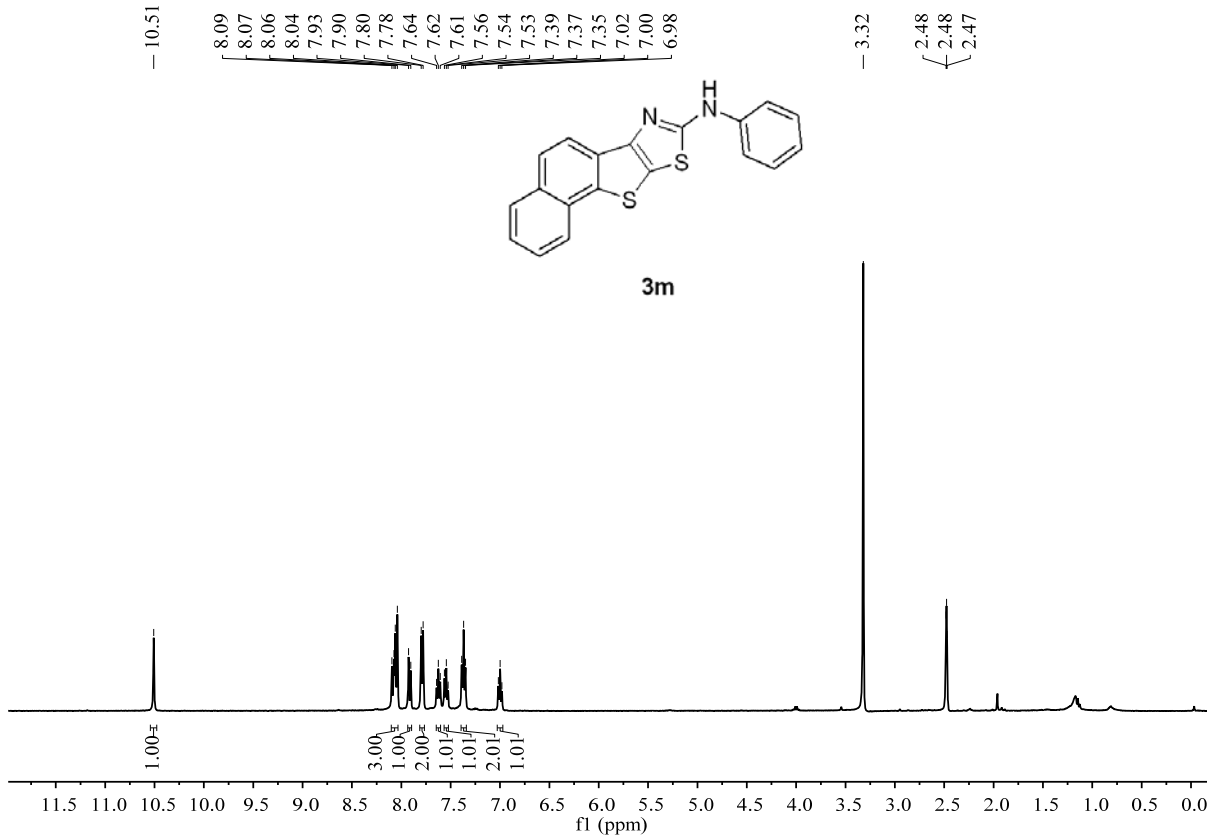
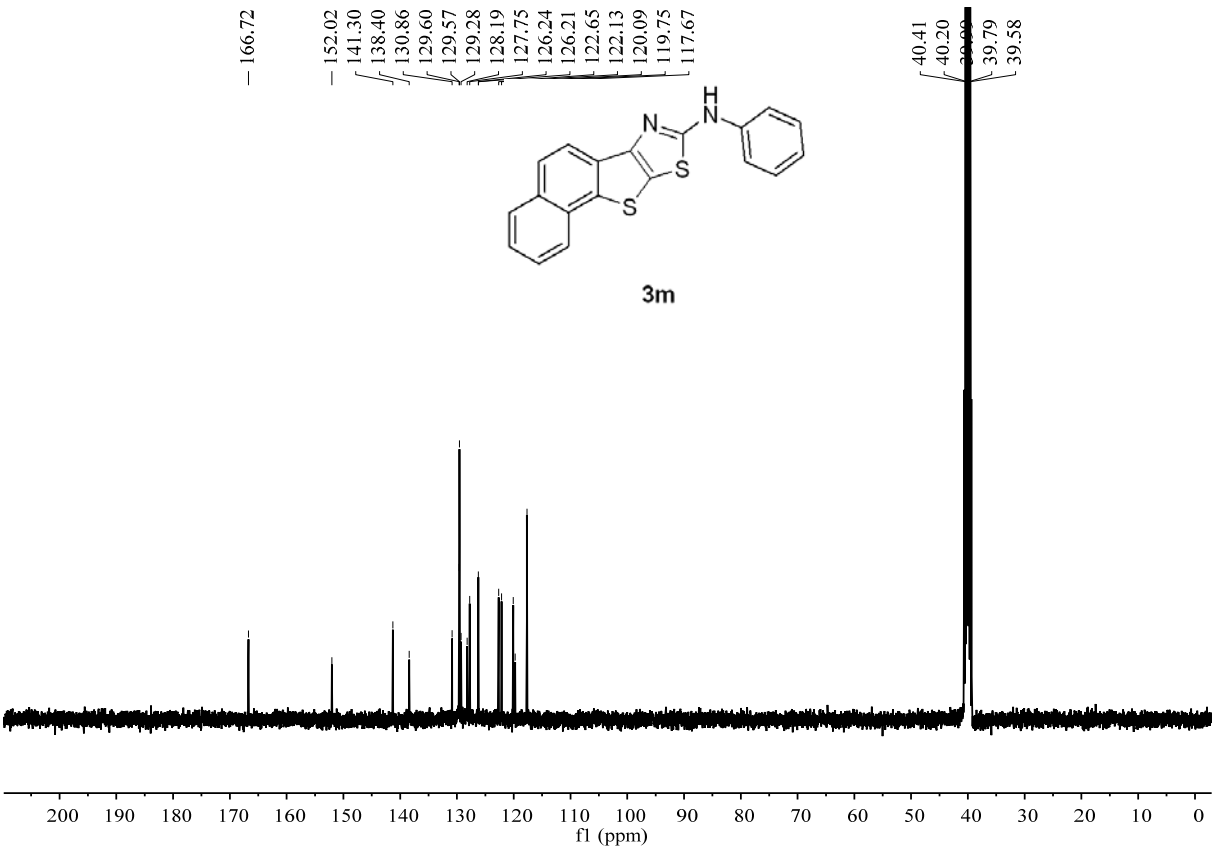
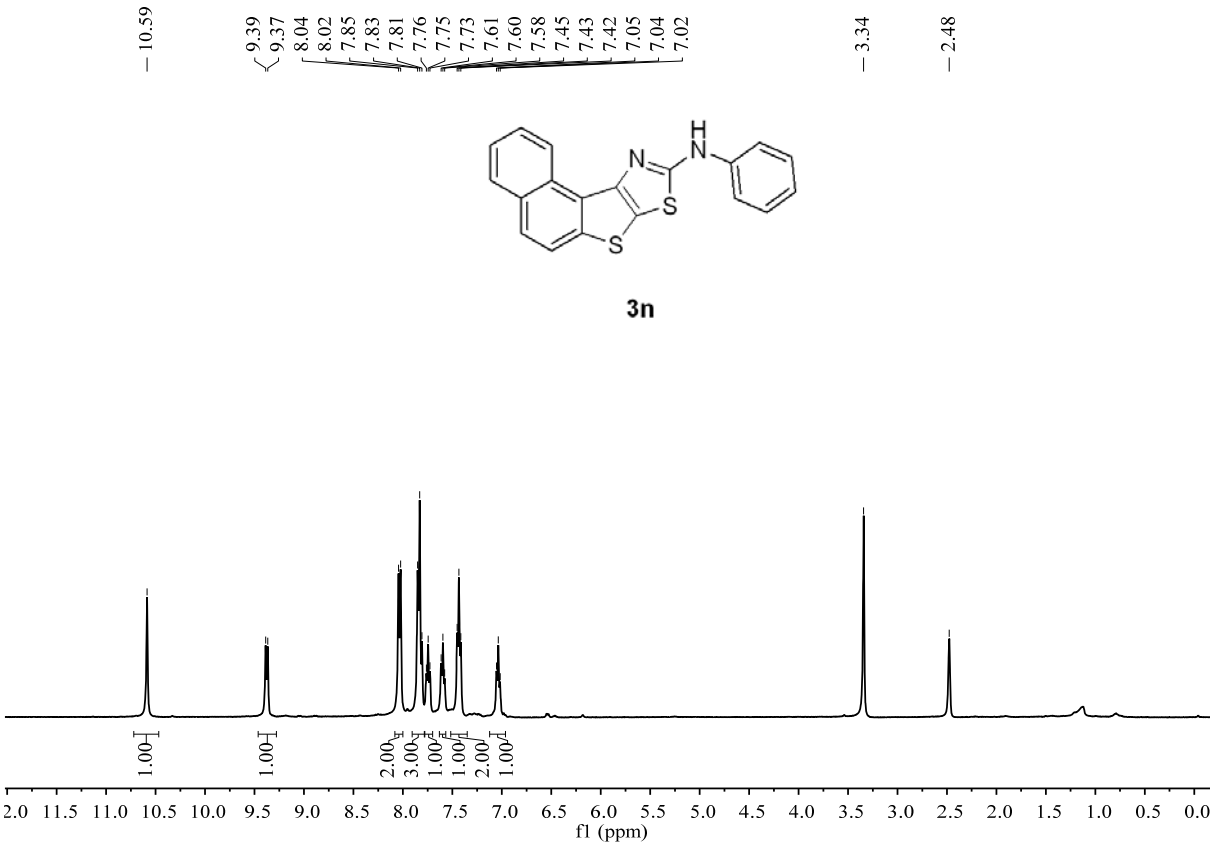
166.67
150.82
149.28
142.57
141.17
140.76
132.20
132.14
129.56
127.16
127.11
126.98
126.13
123.22
122.94
122.23
122.16
121.62
120.38
118.52
117.72
117.70
116.20
40.62
40.41
40.20
39.79
39.58
39.37
and
3l
3l'
f1 (ppm)


10.51
8.09
8.07
8.06
8.04
7.93
7.90
7.80
7.78
7.64
7.62
7.61
7.56
7.54
7.53
7.39
7.37
7.35
7.02
7.00
6.98
3.32
2.48
2.48
2.47
3m
1.00
3.00
1.00
2.00
1.01
1.01
2.01
1.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.72
152.02
141.30
138.40
130.86
129.60
129.57
129.28
128.19
127.75
126.24
126.21
122.65
122.13
120.09
119.75
117.67
40.41
40.20
39.79
39.58
3m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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9.39
9.37
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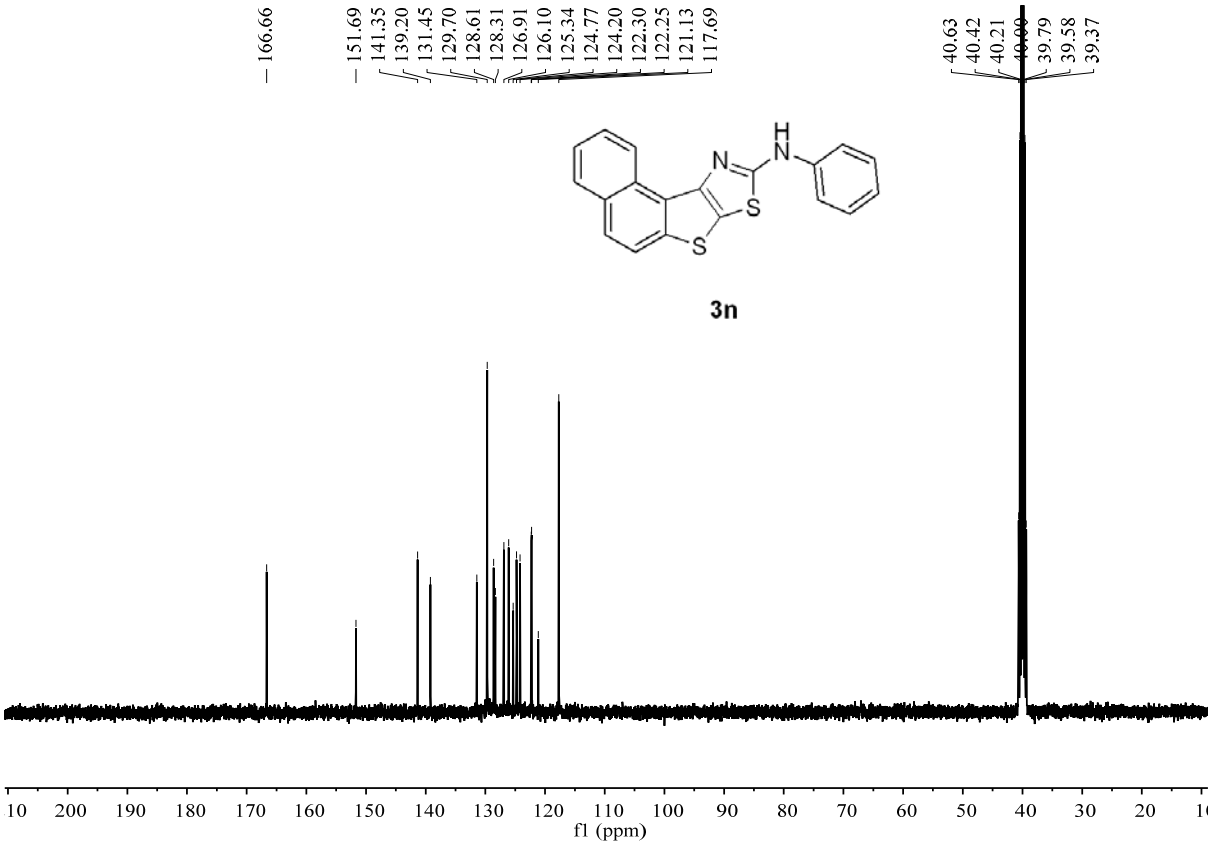
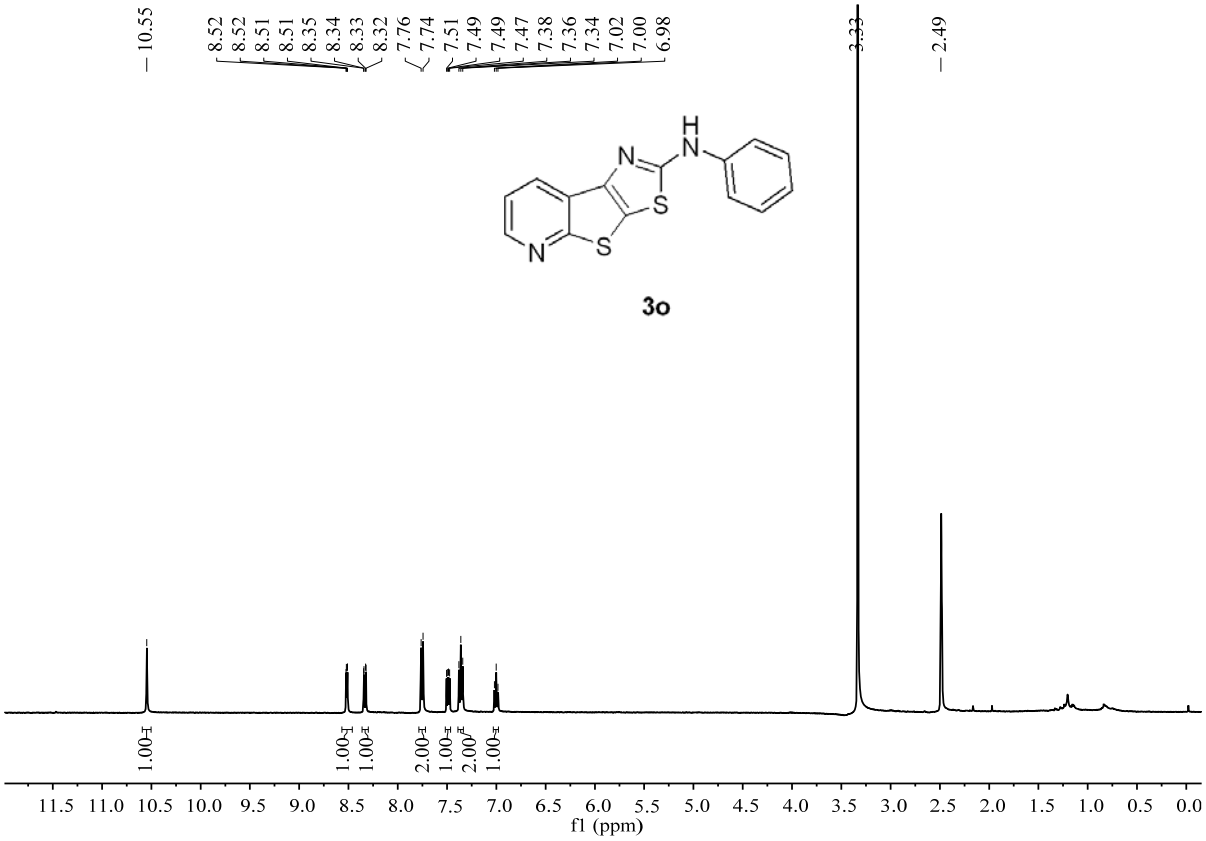
8.02
7.85
7.83
7.81
7.76
7.75
7.73
7.61
7.60
7.58
7.45
7.43
7.42
7.05
7.04
7.02
3.34
2.48
N
H
N
S
S
3n
1.00
1.00
2.00
3.00
1.00
1.00
2.00
1.00
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.66
151.69
141.35
139.20
131.45
129.70
128.61
128.31
126.91
126.10
125.34
124.77
124.20
122.30
122.25
121.13
117.69
40.63
40.42
40.21
40.00
39.79
39.58
39.37
N
H
N
S
S
3n
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 1
f1 (ppm)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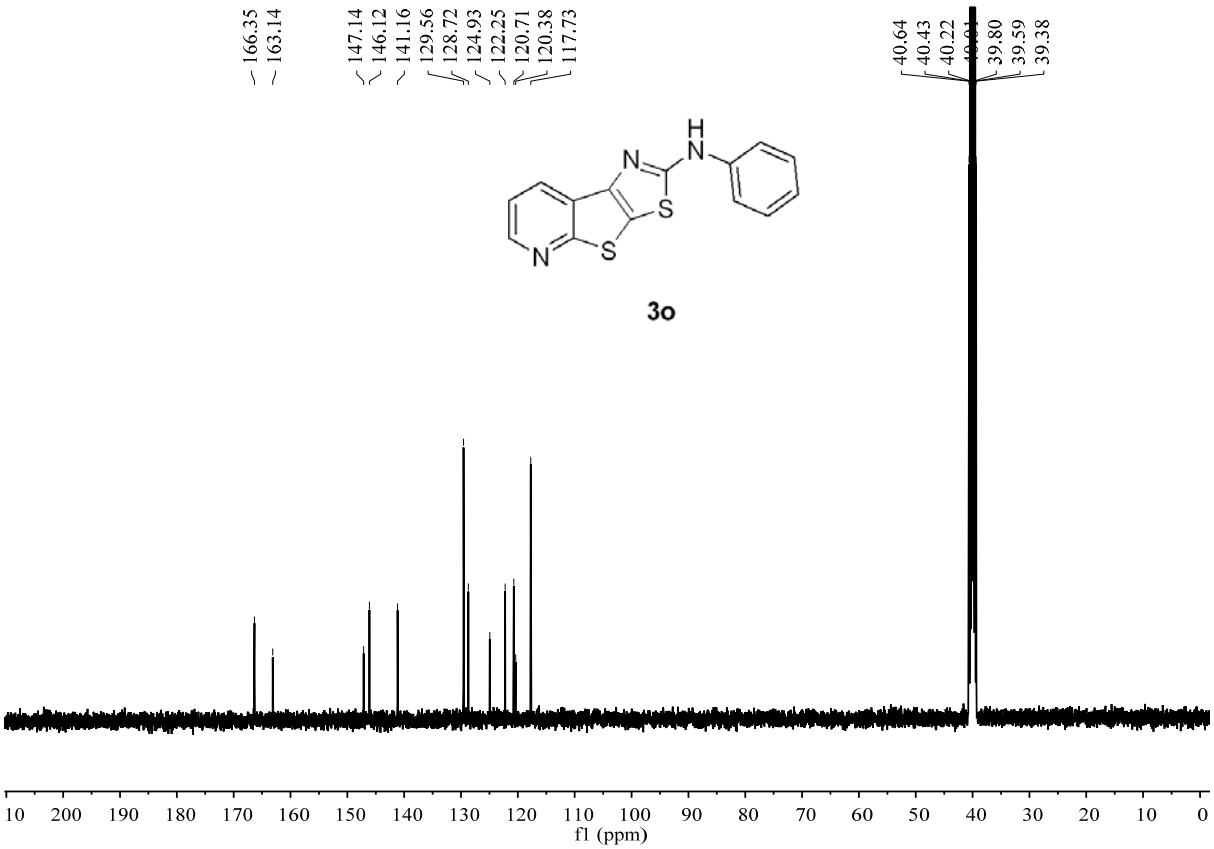
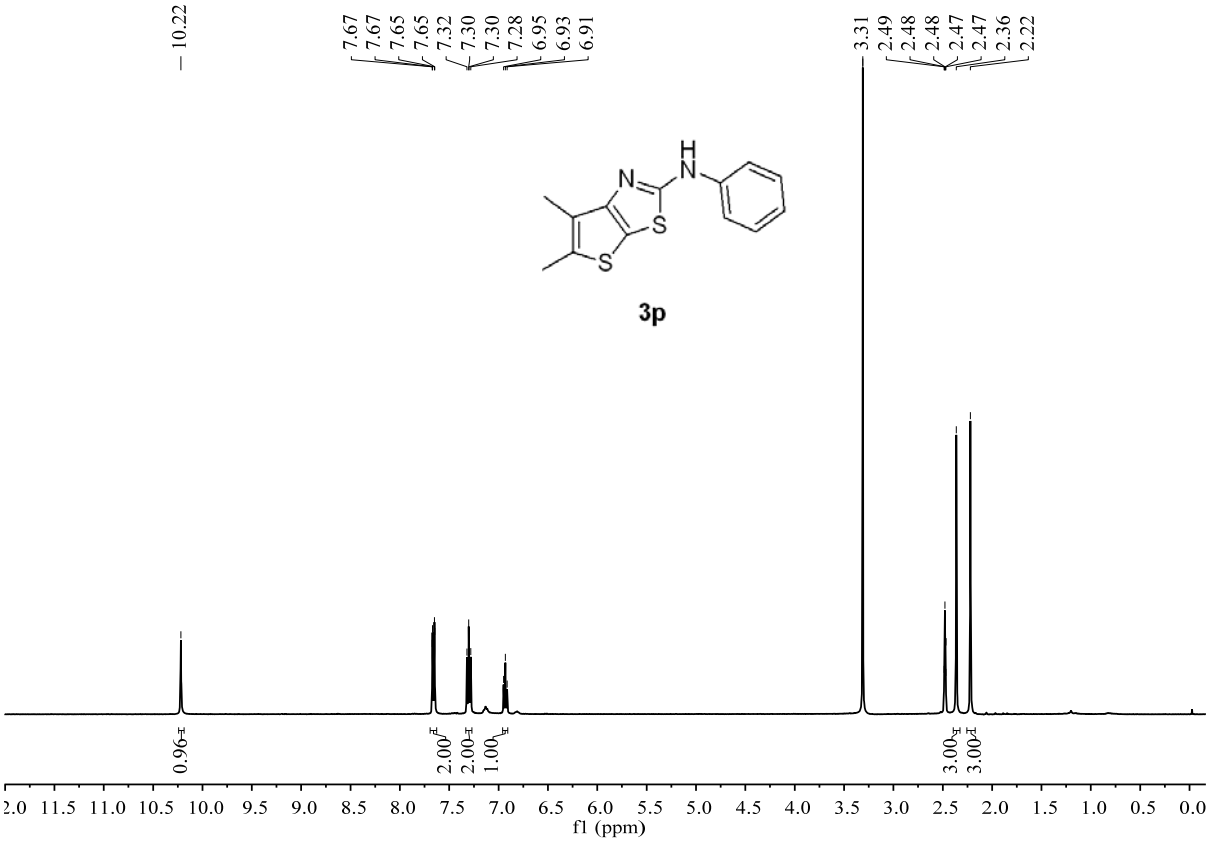
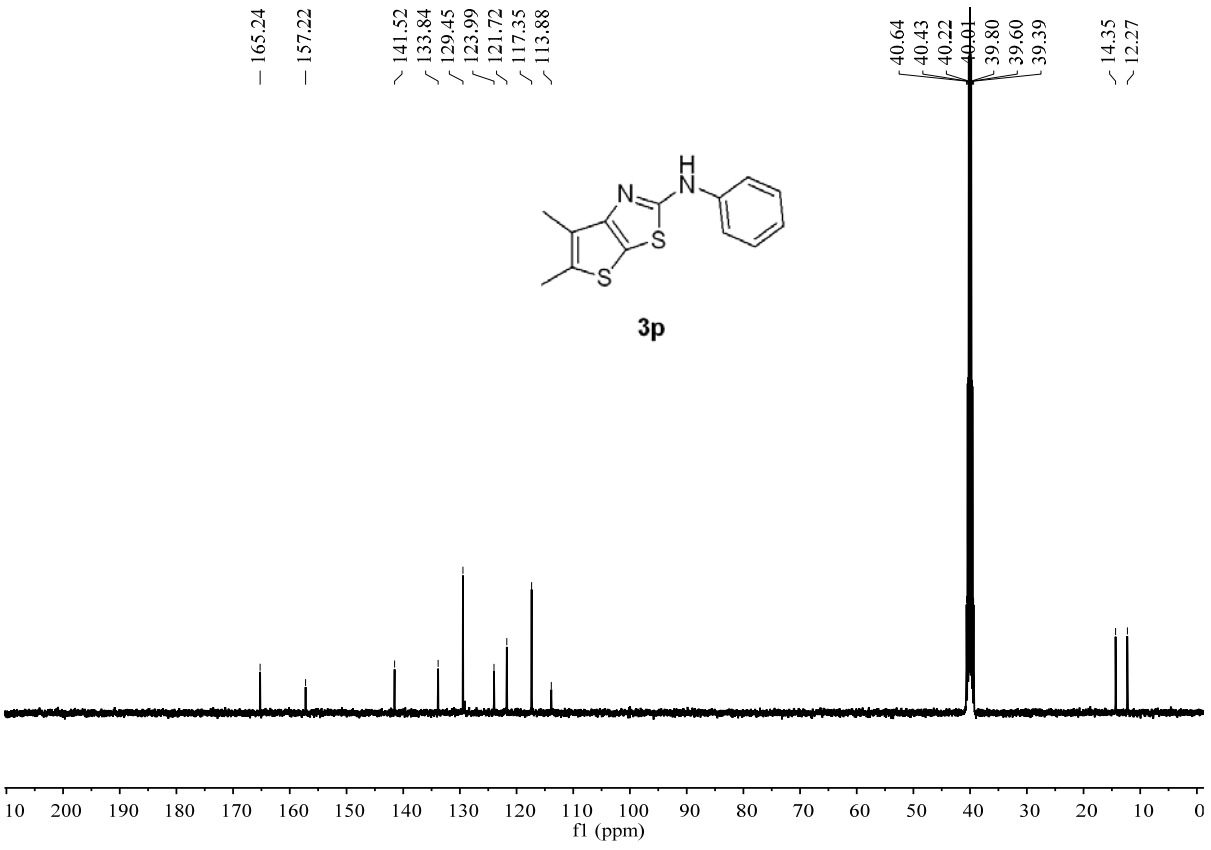
8.52
8.52
8.51
8.51
8.35
8.34
8.33
8.32
7.76
7.74
7.51
7.49
7.49
7.47
7.38
7.36
7.34
7.02
7.00
6.98
3.33
2.49
1.00
1.00
1.00
2.00
1.00
2.00
1.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3o


166.35
163.14
147.14
146.12
141.16
129.56
128.72
124.93
122.25
120.71
120.38
117.73
40.64
40.43
40.22
40.01
39.80
39.59
39.38
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3o


10.22
7.67
7.67
7.65
7.65
7.32
7.30
7.30
7.28
6.95
6.93
6.91
3.31
2.49
2.48
2.48
2.47
2.47
2.36
2.22
3p
0.96
2.00
2.00
1.00
3.00
3.00
f1 (ppm)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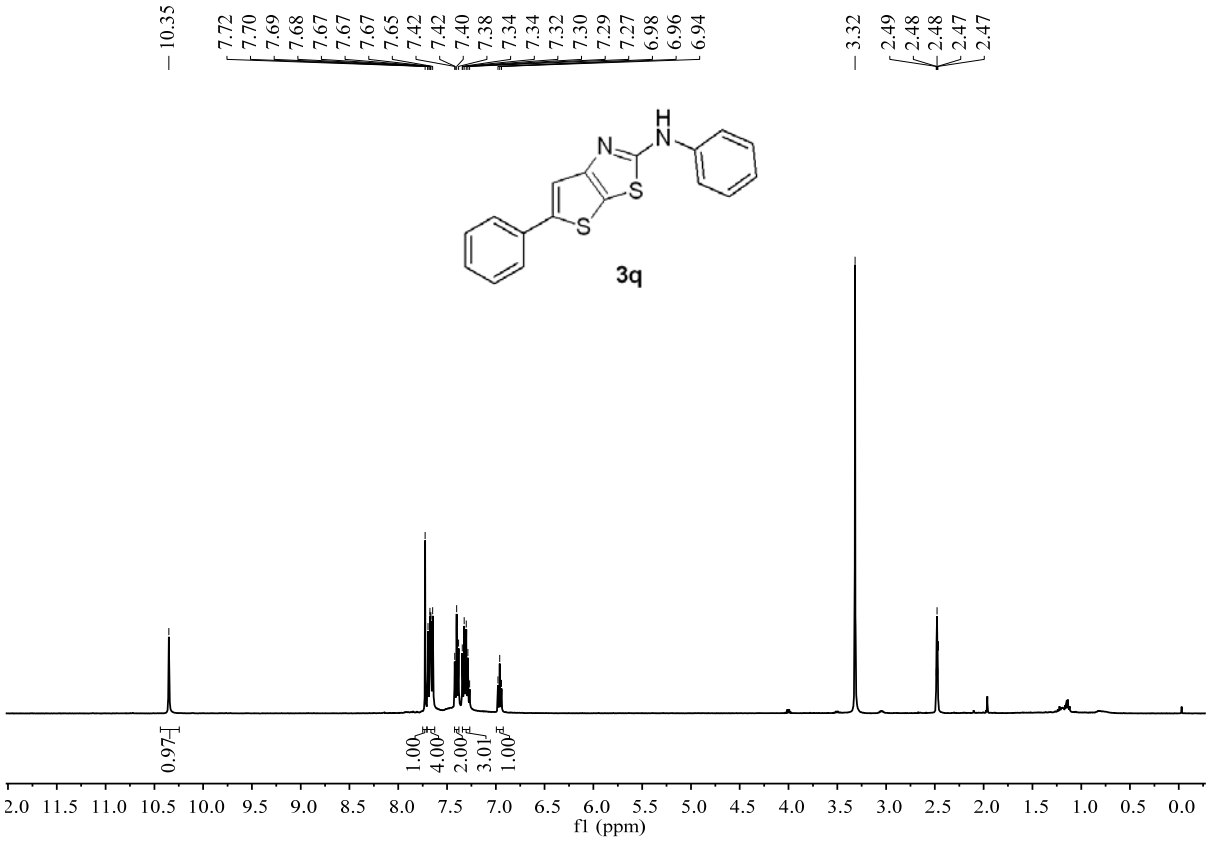
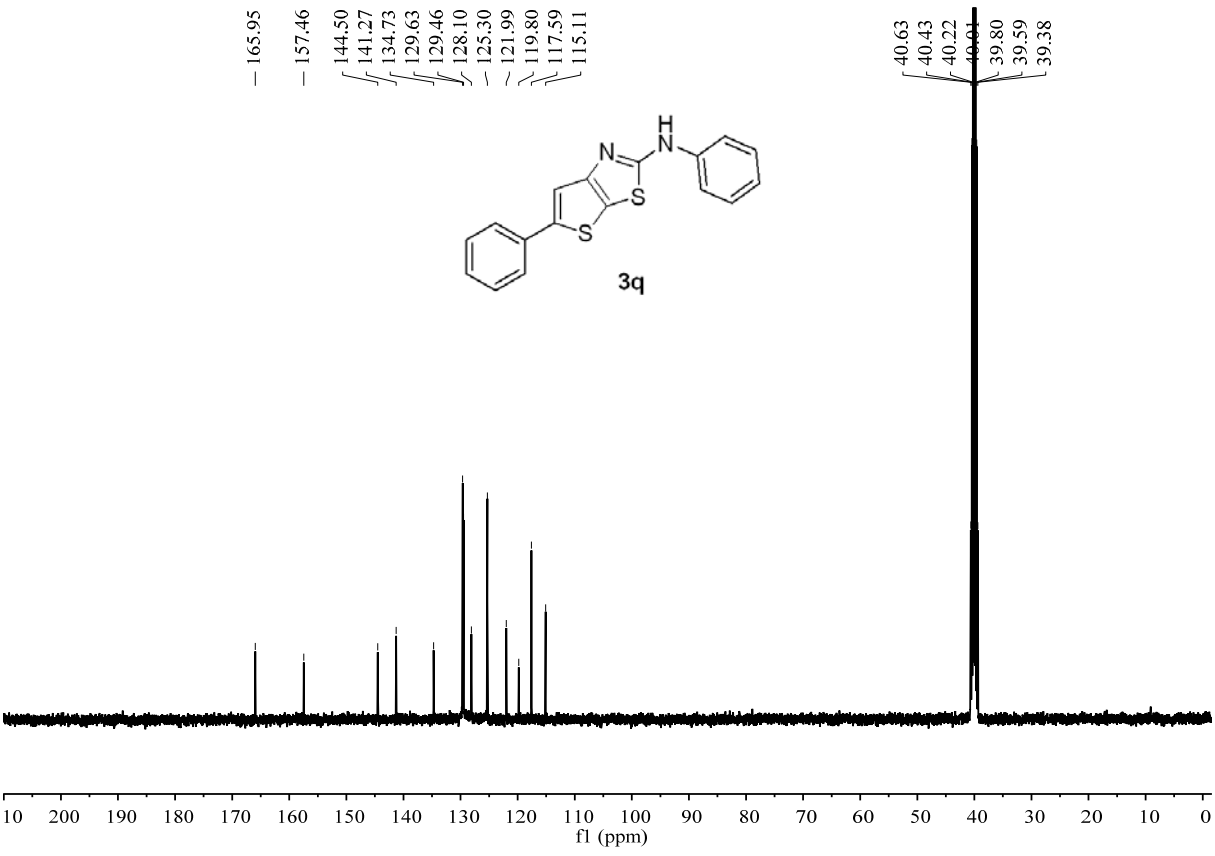
157.22
141.52
133.84
129.45
123.99
121.72
117.35
113.88
40.64
40.43
40.22
40.01
39.80
39.60
39.39
14.35
12.27
3p
f1 (ppm)


10.35
7.72
7.70
7.69
7.68
7.67
7.67
7.67
7.65
7.42
7.42
7.40
7.38
7.34
7.34
7.32
7.30
7.29
7.27
6.98
6.96
6.94
3.32
2.49
2.48
2.48
2.47
2.47
3q
0.97
1.00
4.00
2.00
3.01
1.00
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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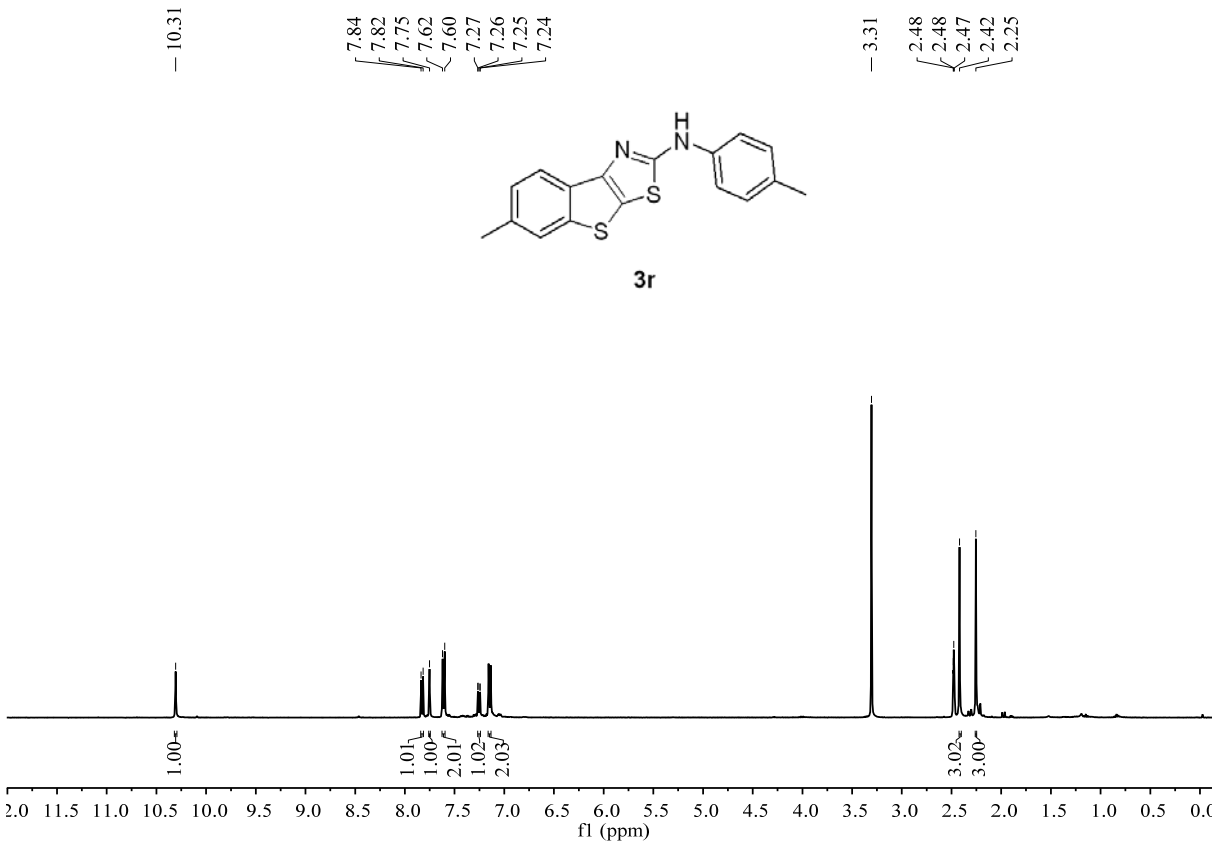
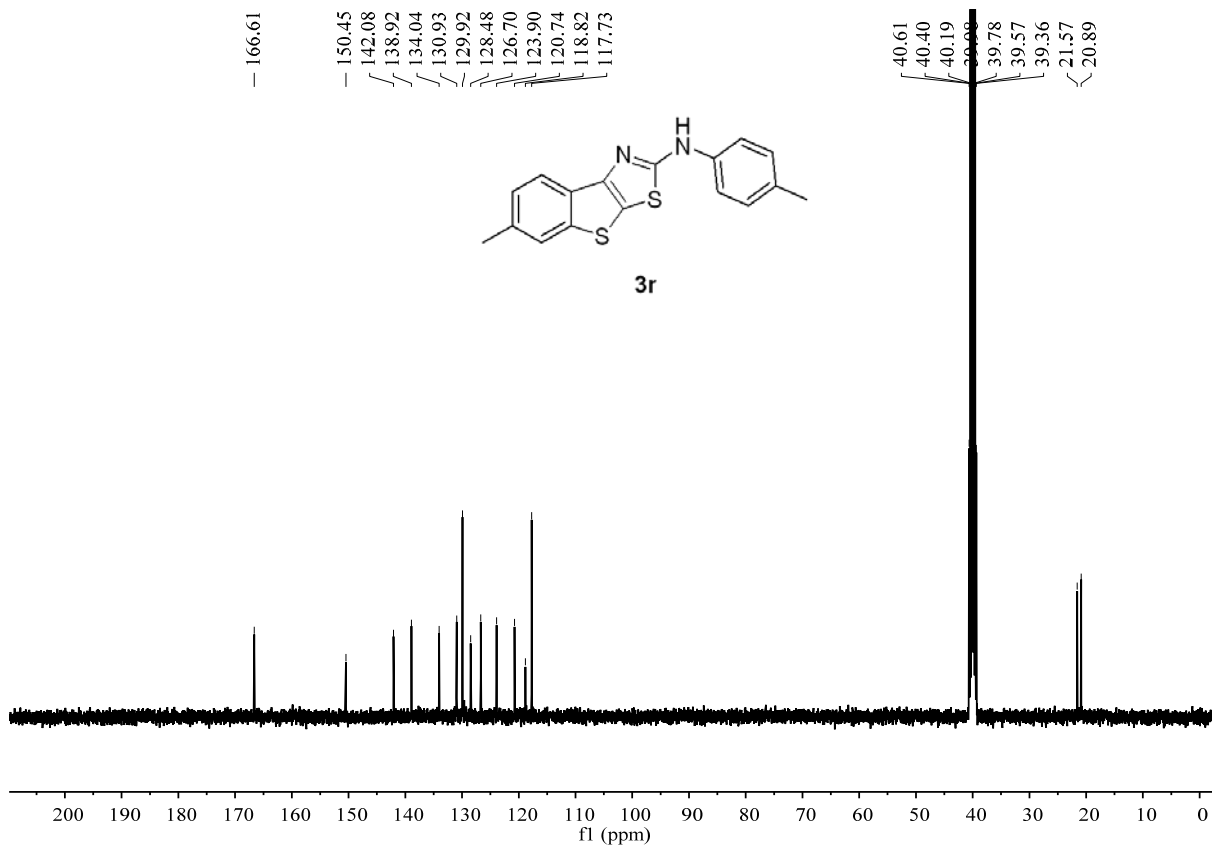
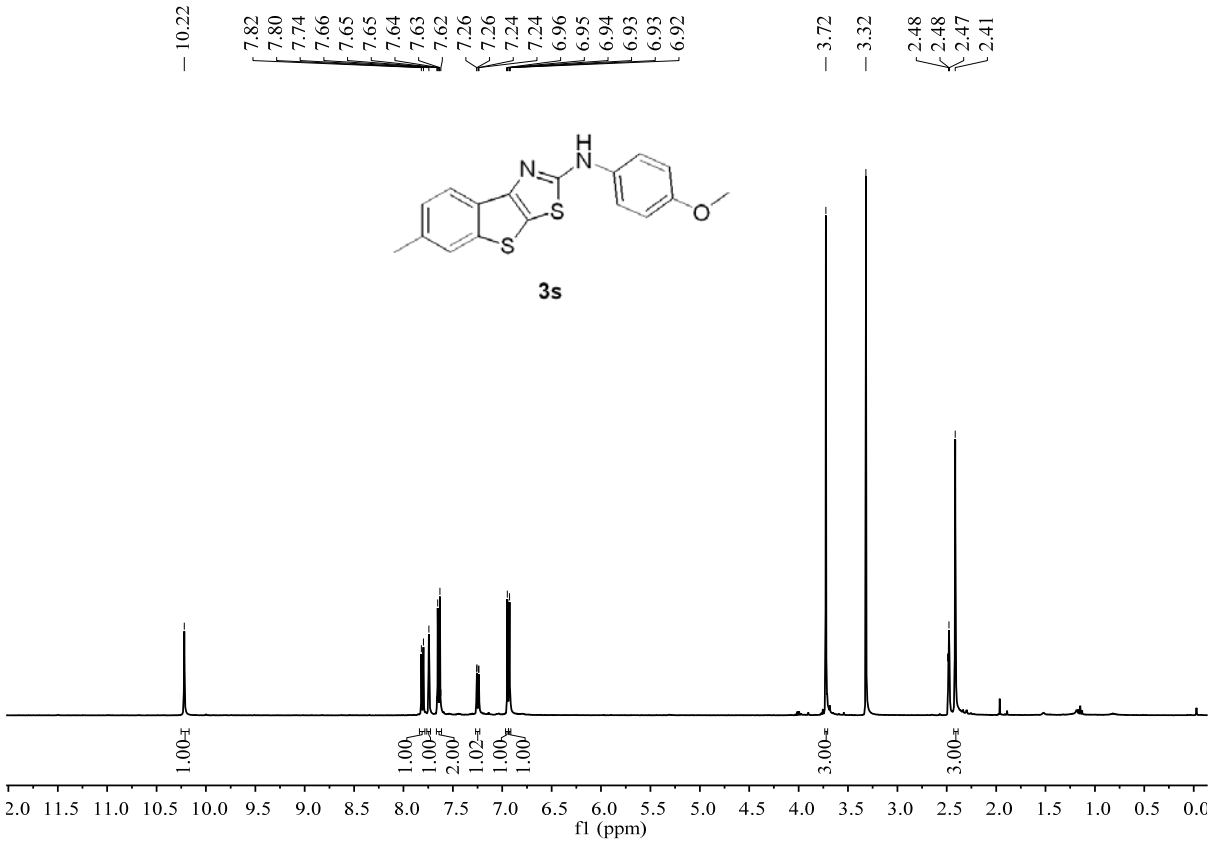
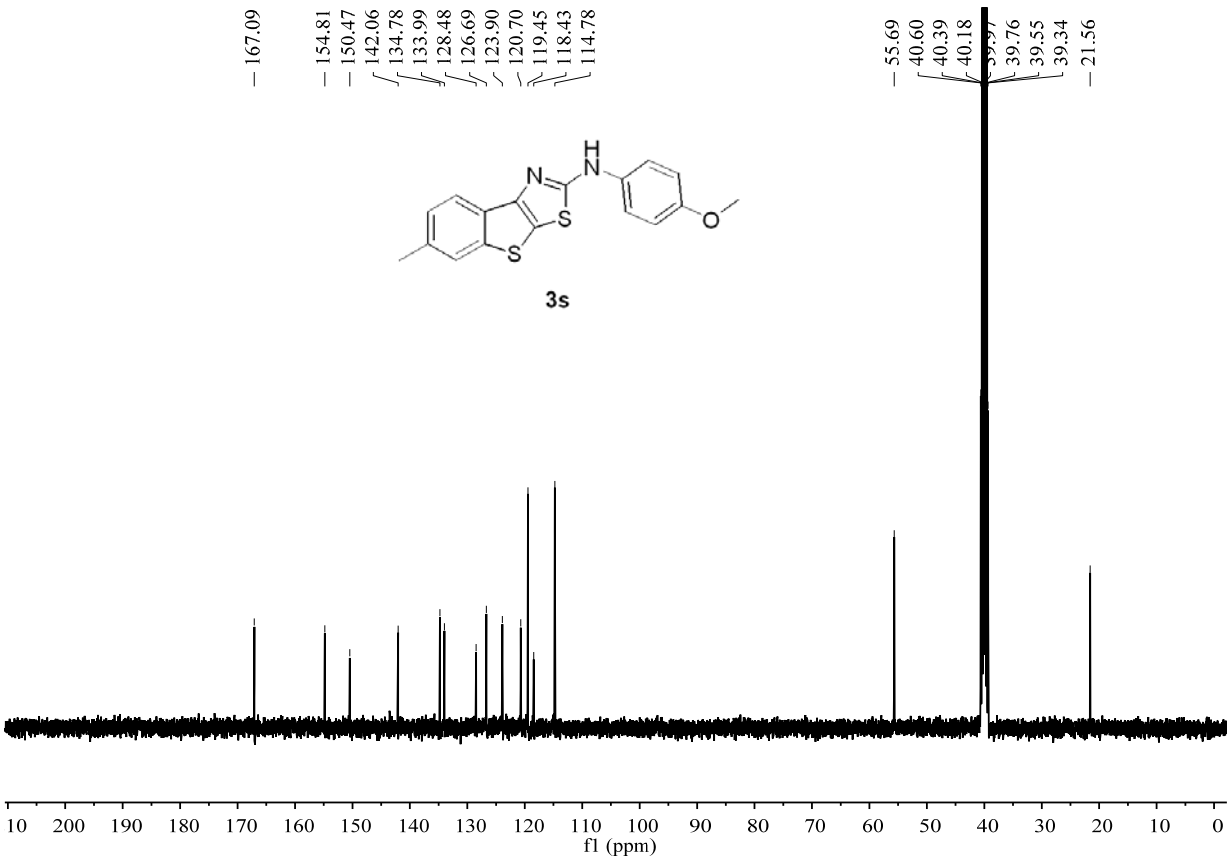
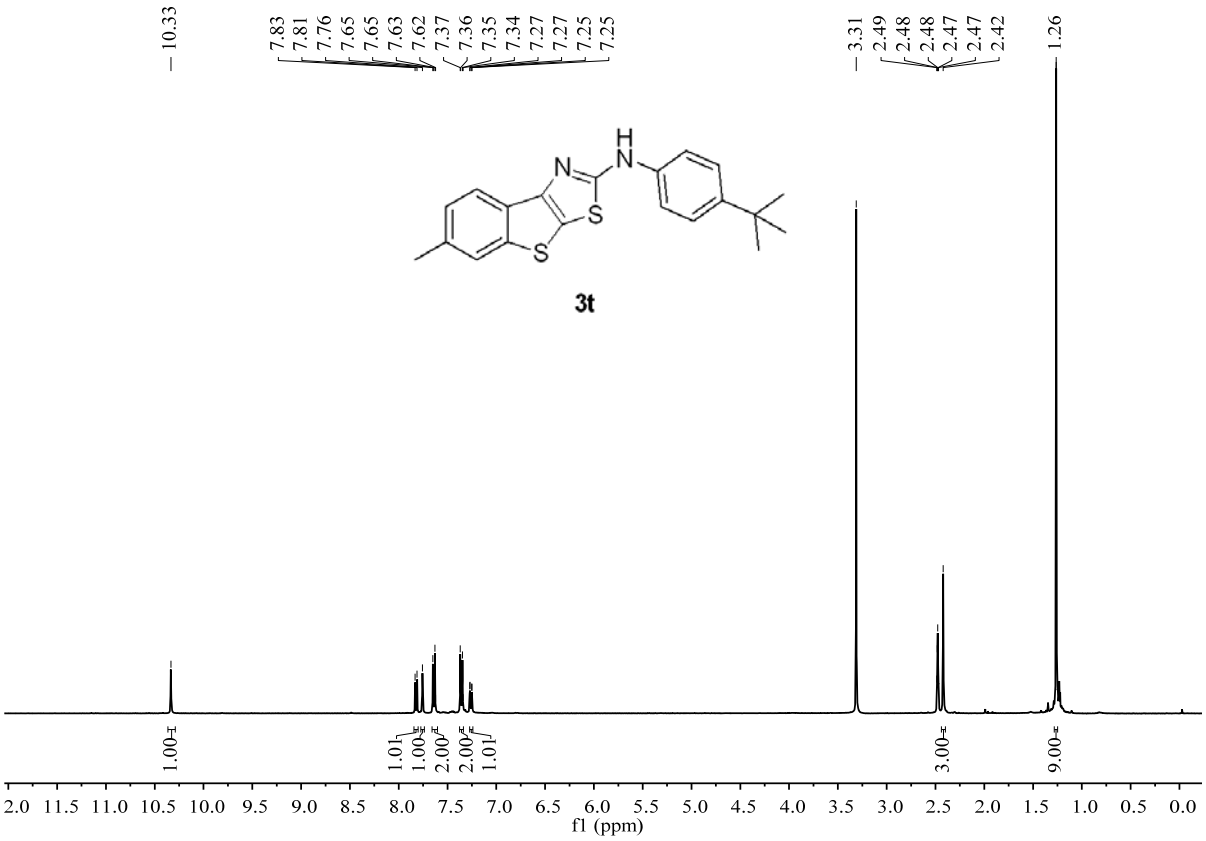
157.46
144.50
141.27
134.73
129.63
129.46
128.10
125.30
121.99
119.80
117.59
115.11
40.63
40.43
40.22
40.01
39.80
39.59
39.38
3q
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10.31
7.84
7.82
7.75
7.62
7.60
7.27
7.26
7.25
7.24
3.31
2.48
2.48
2.47
2.42
2.25
3r
1.00
1.01
1.00
2.01
1.02
2.03
3.02
3.00
f1 (ppm)


166.61
150.45
142.08
138.92
134.04
130.93
129.92
128.48
126.70
123.90
120.74
118.82
117.73
40.61
40.40
40.19
39.78
39.57
39.36
21.57
20.89
3r
f1 (ppm)


10.22
7.82
7.80
7.74
7.66
7.65
7.65
7.64
7.63
7.62
7.26
7.26
7.24
7.24
6.96
6.95
6.94
6.93
6.93
6.92
3.72
3.32
2.48
2.48
2.47
2.41
3s
1.00
1.00
1.00
2.00
1.02
1.00
1.00
3.00
3.00
f1 (ppm)


167.09
154.81
150.47
142.06
134.78
133.99
128.48
126.69
123.90
120.70
119.45
118.43
114.78
55.69
40.60
40.39
40.18
39.97
39.76
39.55
39.34
21.56
3s
f1 (ppm)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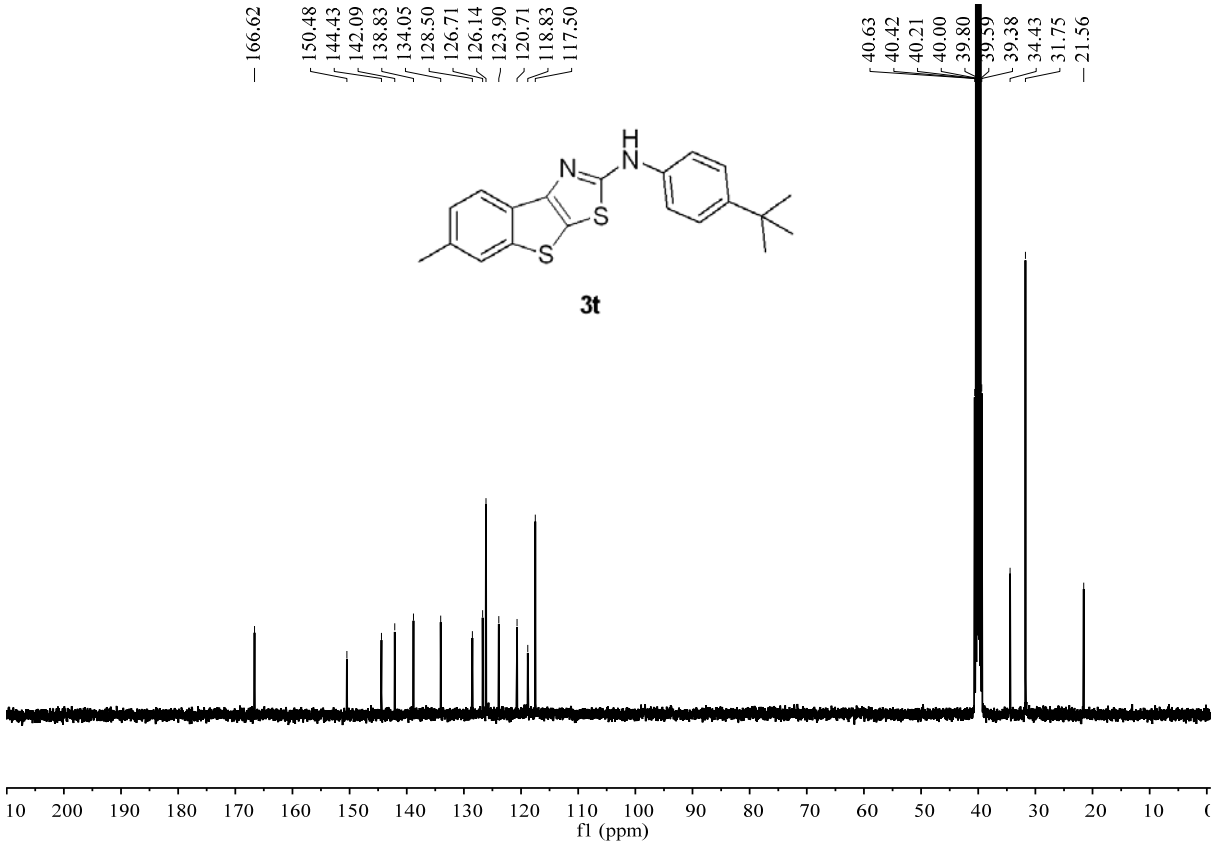
7.81
7.76
7.65
7.65
7.63
7.62
7.37
7.36
7.35
7.34
7.27
7.27
7.25
7.25
3.31
2.49
2.48
2.48
2.47
2.47
2.42
1.26
3t
1.00
1.01
1.00
2.00
2.00
1.01
3.00
9.00
fl (ppm)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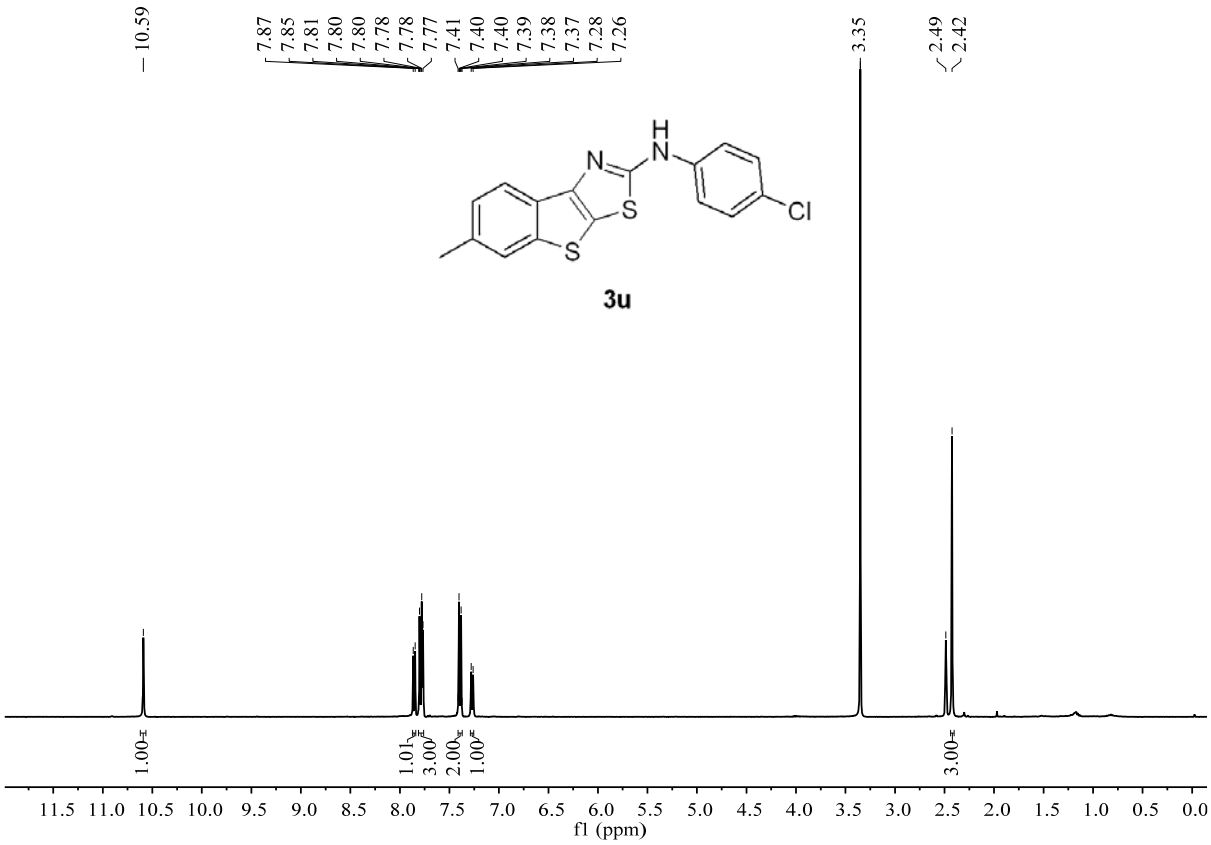
150.48
144.43
142.09
138.83
134.05
128.50
126.71
126.14
123.90
120.71
118.83
117.50
40.63
40.42
40.21
40.00
39.80
39.59
39.38
34.43
31.75
21.56
3t
fl (ppm)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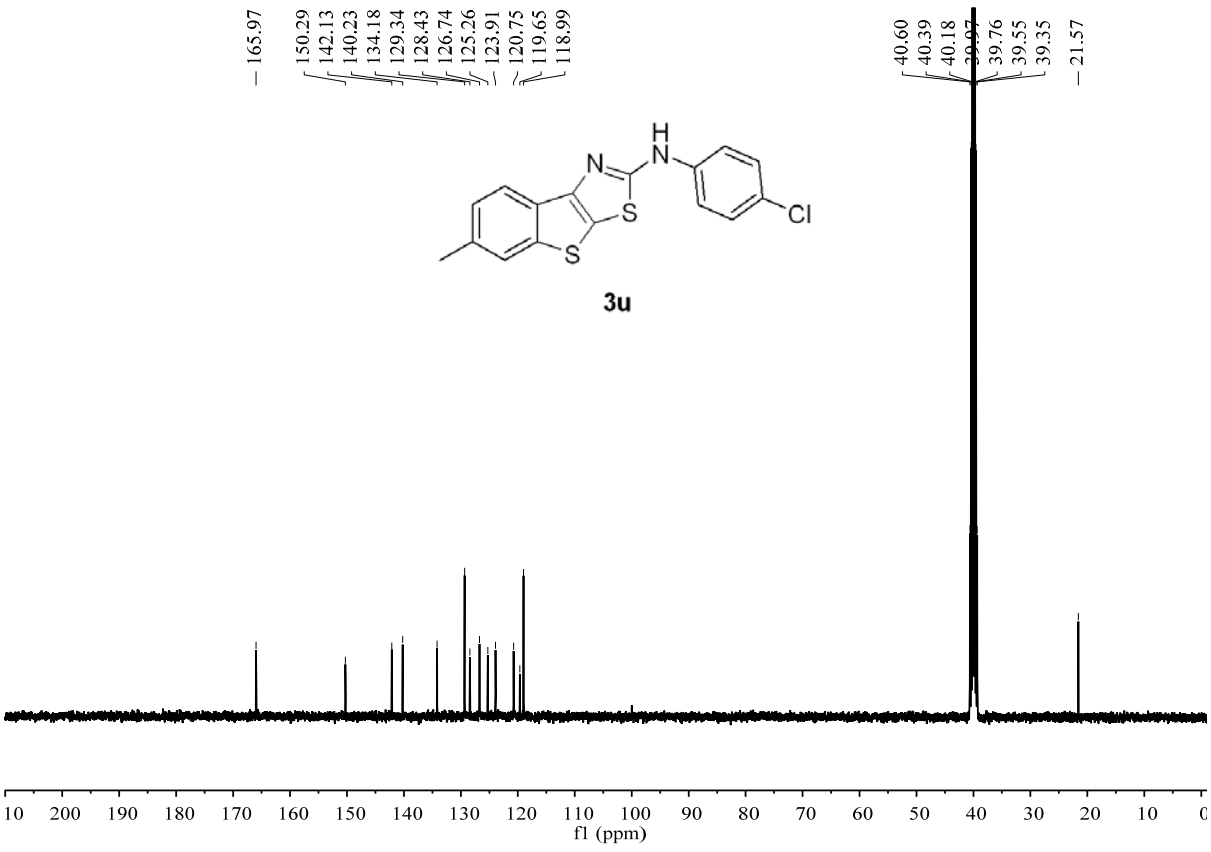
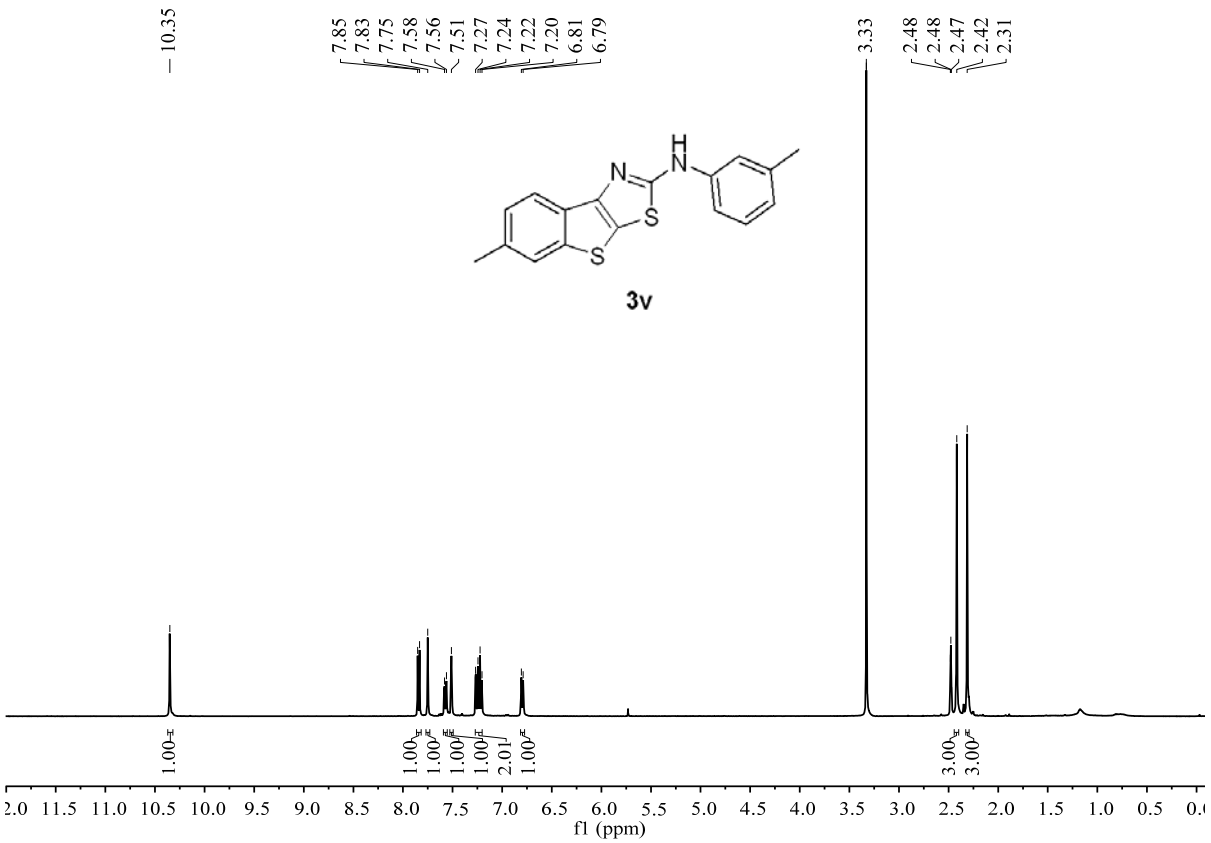
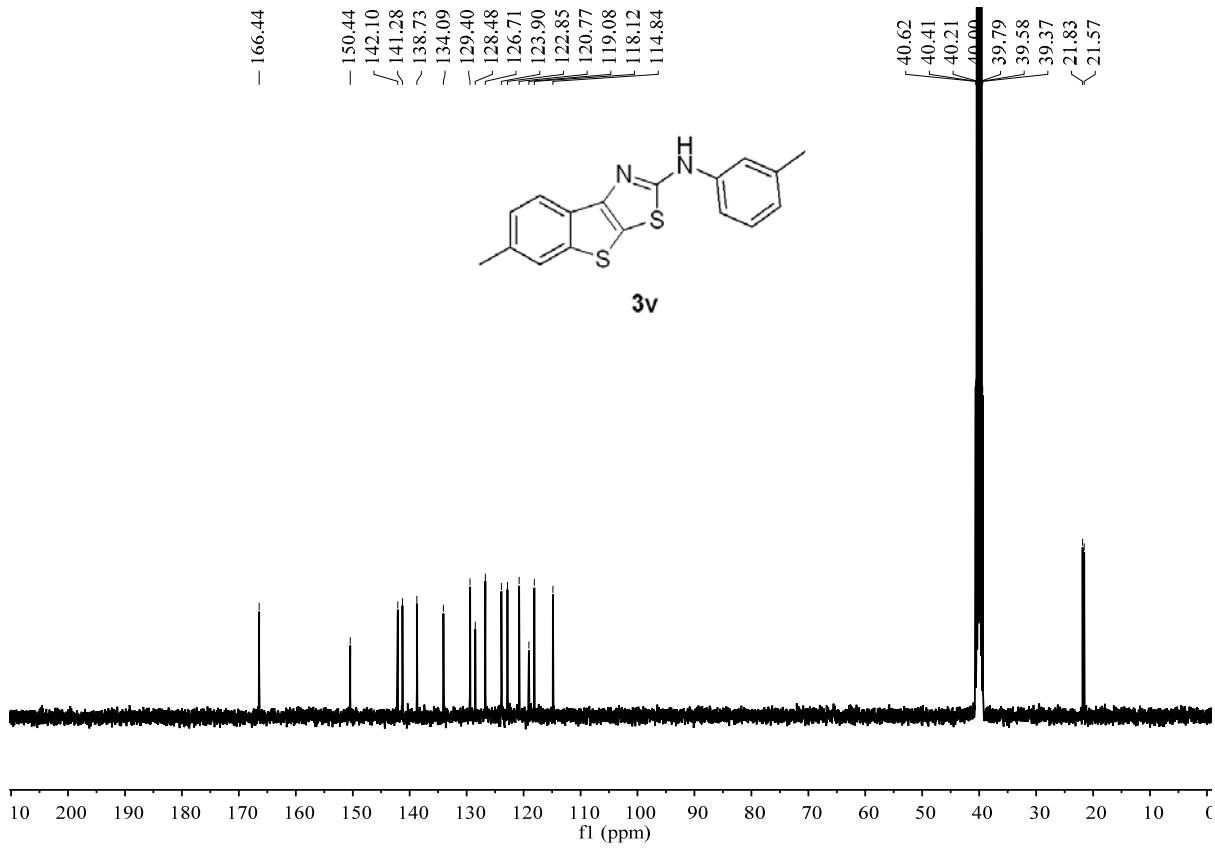
7.78
7.78
7.77
7.41
7.40
7.40
7.39
7.38
7.37
7.28
7.26
3.35
2.49
2.42
H
N
N
S
S
Cl
3u
1.00
1.01
3.00
2.00
1.00
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


165.97
150.29
142.13
140.23
134.18
129.34
128.43
126.74
125.26
123.91
120.75
119.65
118.99
40.60
40.39
40.18
39.97
39.76
39.55
39.35
21.57
H
N
N
S
S
Cl
3u
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10.35
7.85
7.83
7.75
7.58
7.56
7.51
7.27
7.24
7.22
7.20
6.81
6.79
3.33
2.48
2.48
2.47
2.42
2.31
1.00
1.00
1.00
1.00
2.01
1.00
3.00
3.00
f1 (ppm)

3v


166.44
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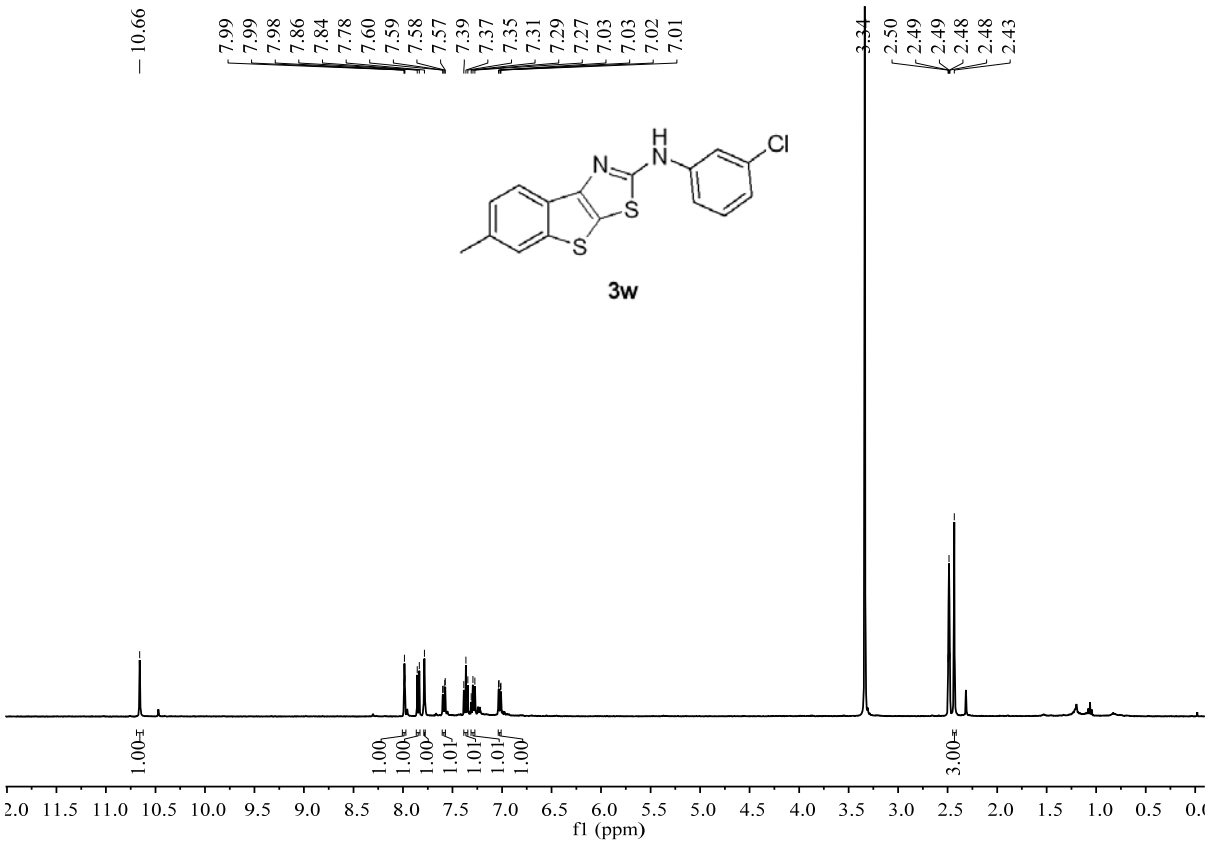
141.28
138.73
134.09
129.40
128.48
126.71
123.90
122.85
120.77
119.08
118.12
114.84
40.62
40.41
40.21
40.00
39.79
39.58
39.37
21.83
21.57
f1 (ppm)

3v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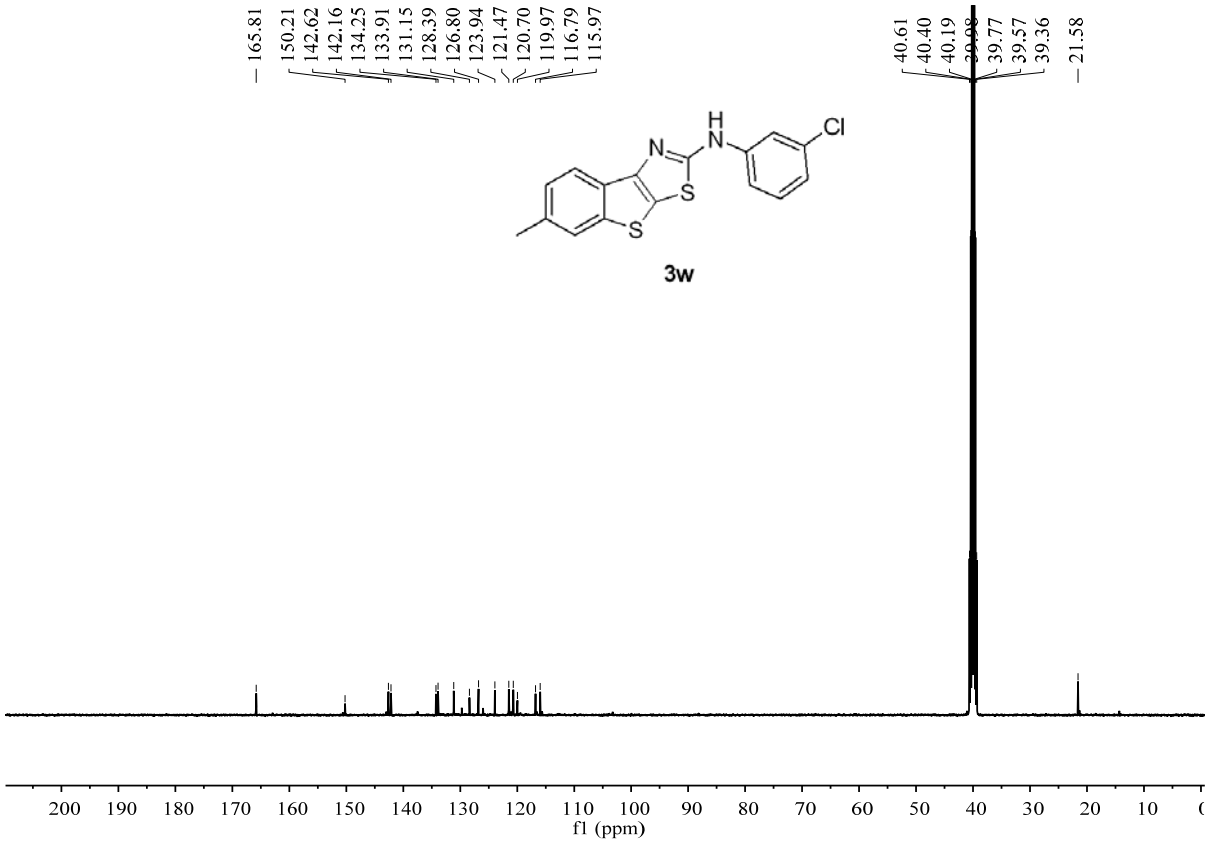
7.60
7.59
7.58
7.57
7.39
7.37
7.35
7.31
7.29
7.27
7.03
7.03
7.02
7.01
3.34
2.50
2.49
2.49
2.48
2.48
2.43
H
N
N
S
S
Cl
3w
1.00
1.00
1.00
1.01
1.01
1.01
1.00
3.00
f1 (ppm)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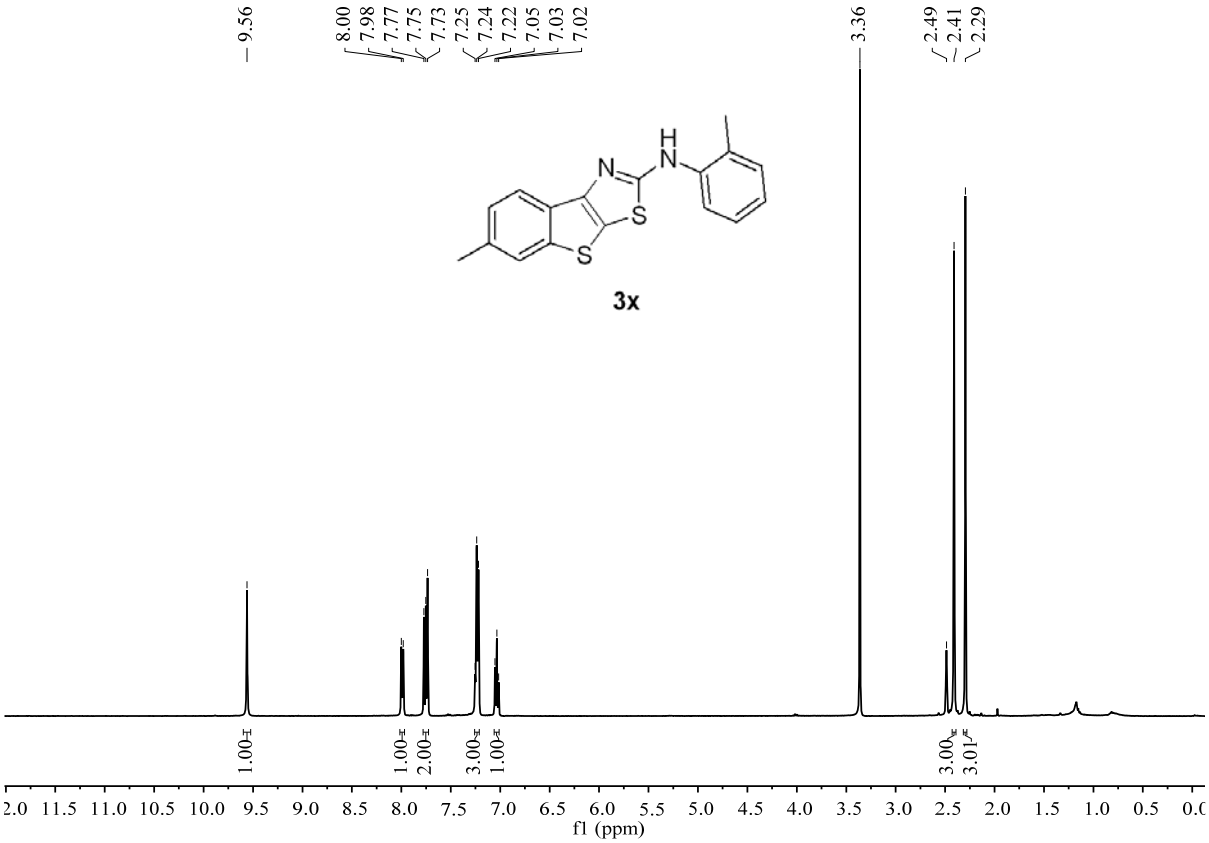
142.16
134.25
133.91
131.15
128.39
126.80
123.94
121.47
120.70
119.97
116.79
115.97
40.61
40.40
40.19
39.98
39.77
39.57
39.36
21.58
H
N
N
S
S
Cl
3w
f1 (ppm)


9.56
8.00
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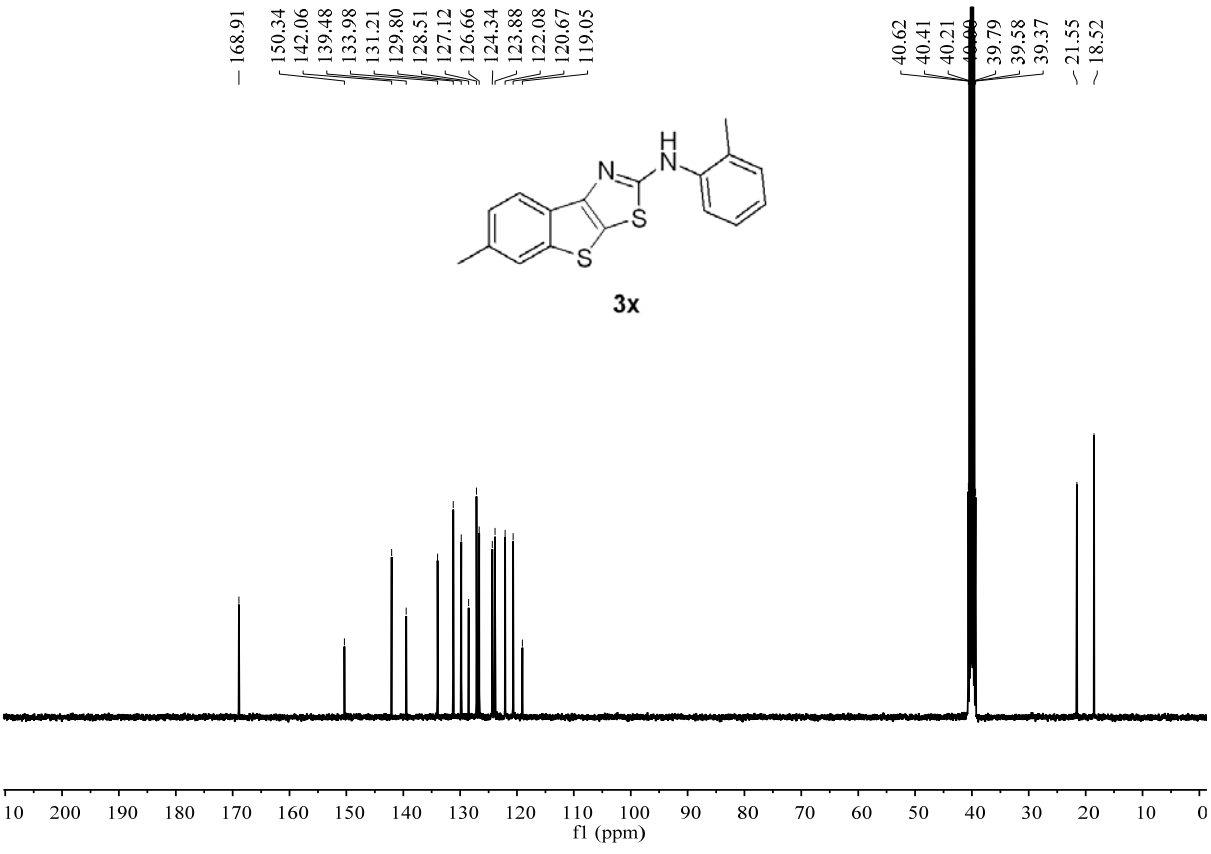
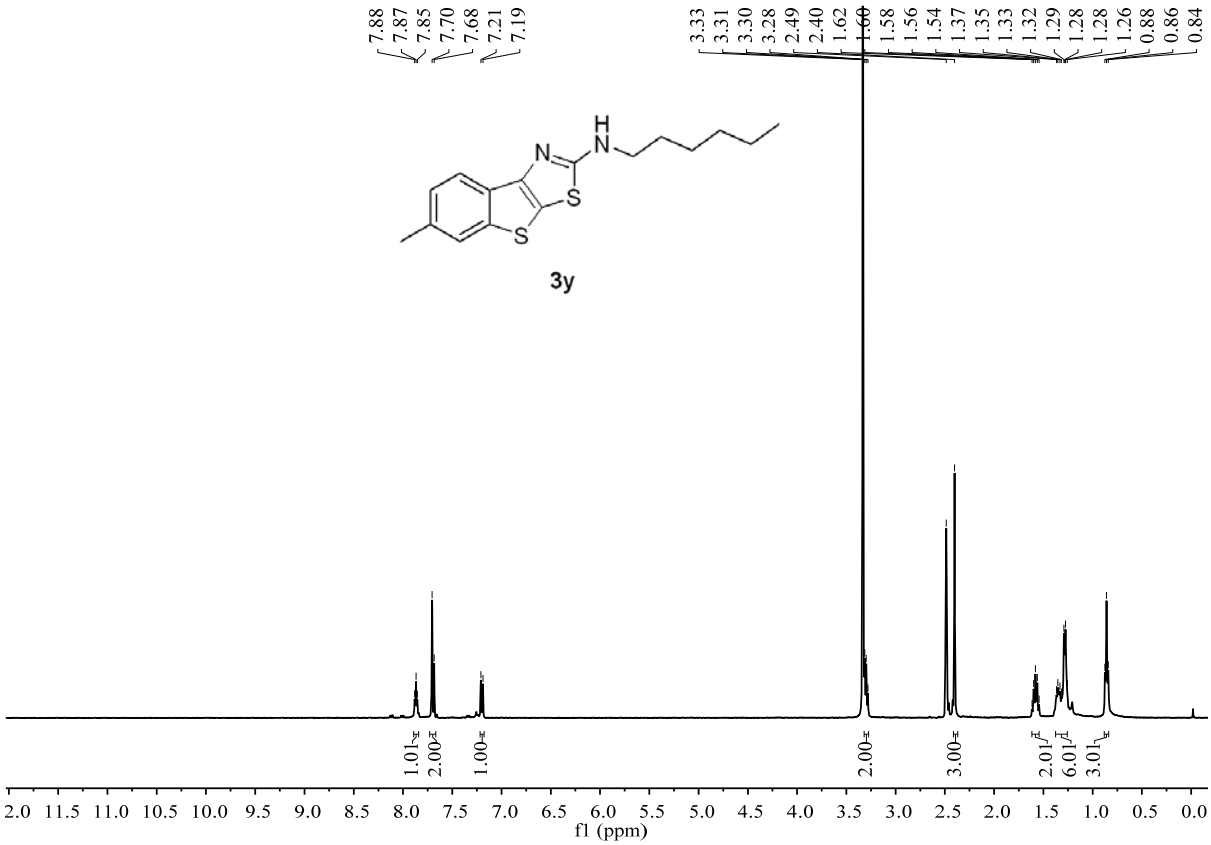
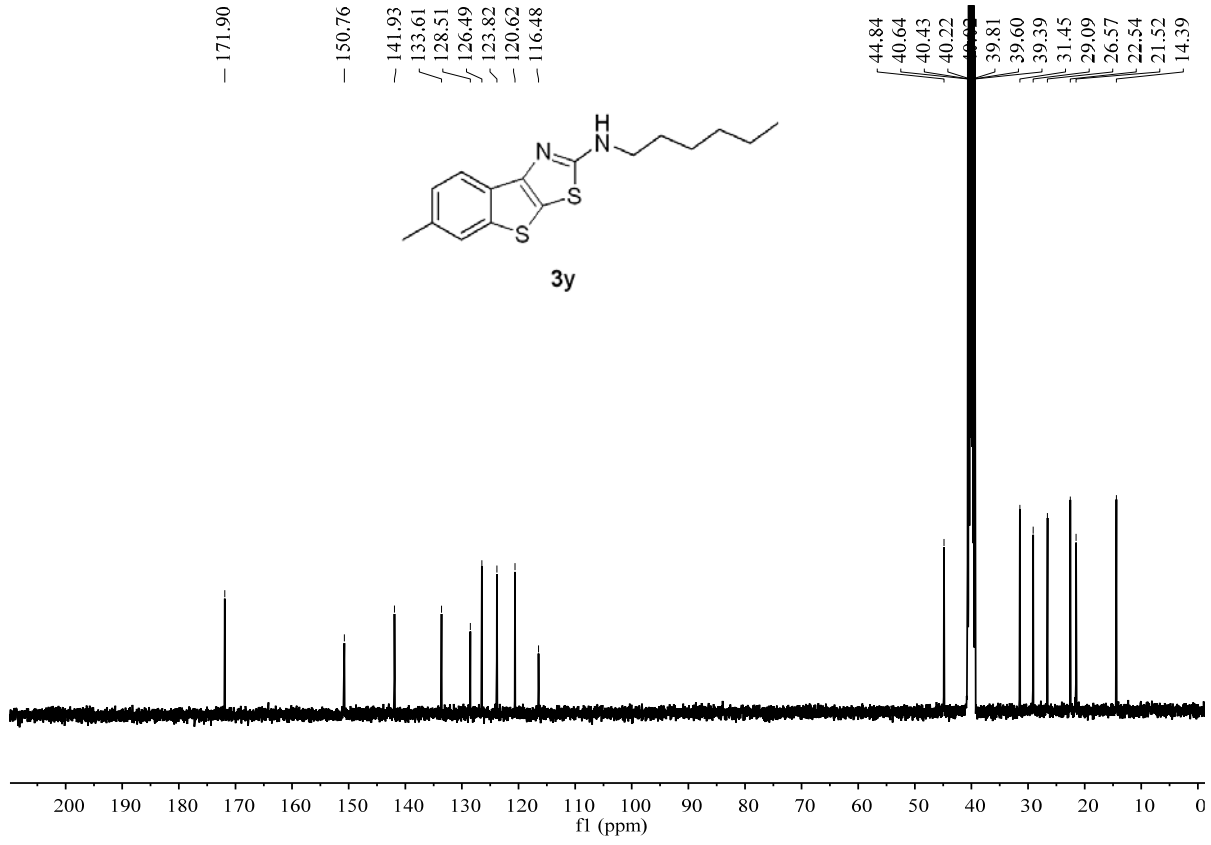
7.77
7.75
7.73
7.25
7.24
7.22
7.05
7.03
7.02
3.36
2.49
2.41
2.29
1.00
1.00
2.00
3.00
1.00
3.00
3.01
f1 (ppm)

3x


168.91
150.34
142.06
139.48
133.98
131.21
129.80
128.51
127.12
126.66
124.34
123.88
122.08
120.67
119.05
40.62
40.41
40.21
40.00
39.79
39.58
39.37
21.55
18.52
f1 (ppm)

3x


7.88
7.87
7.85
7.70
7.68
7.21
7.19
3.33
3.31
3.30
3.28
2.49
2.40
1.62
1.60
1.58
1.56
1.54
1.37
1.35
1.33
1.32
1.29
1.28
1.28
1.26
0.88
0.86
0.84
H
N
N
S
S
3y
1.01
2.00
1.00
2.00
3.00
2.01
6.01
3.01
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


171.90
150.76
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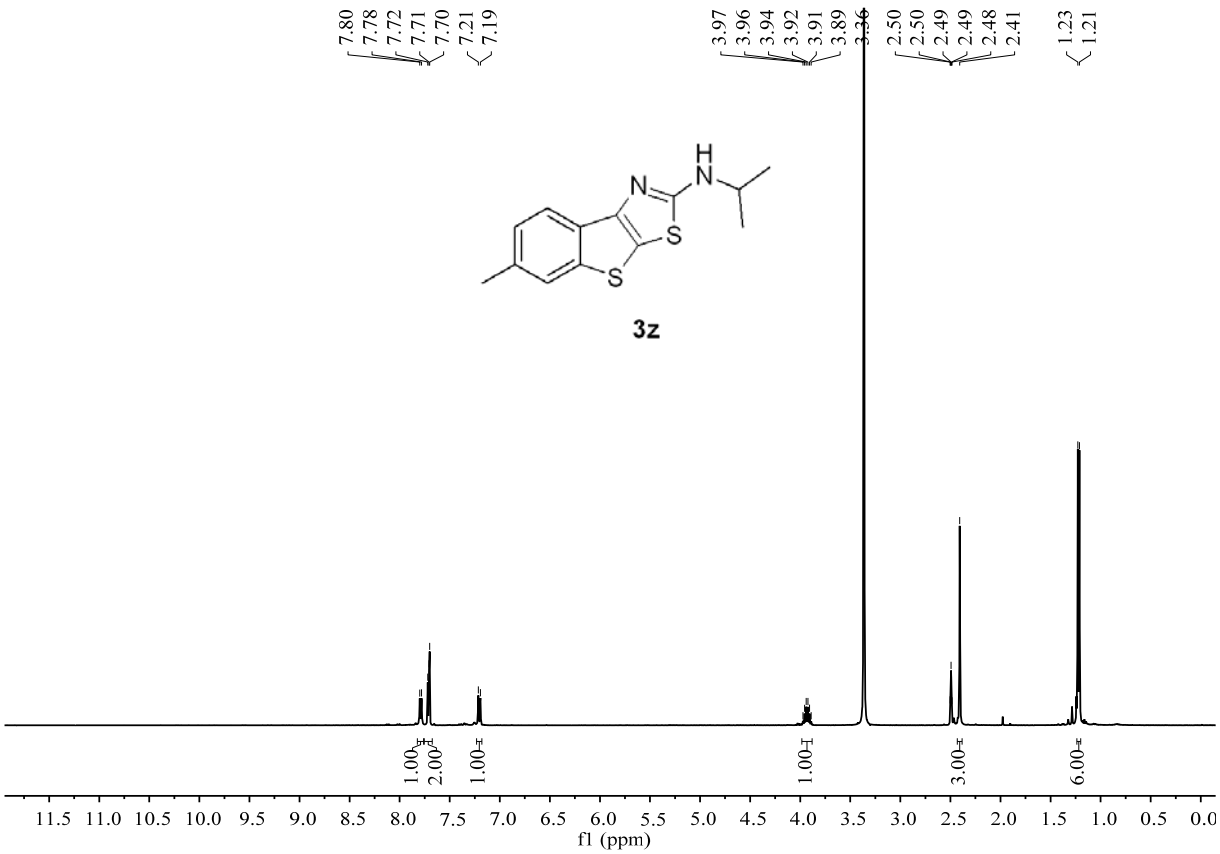
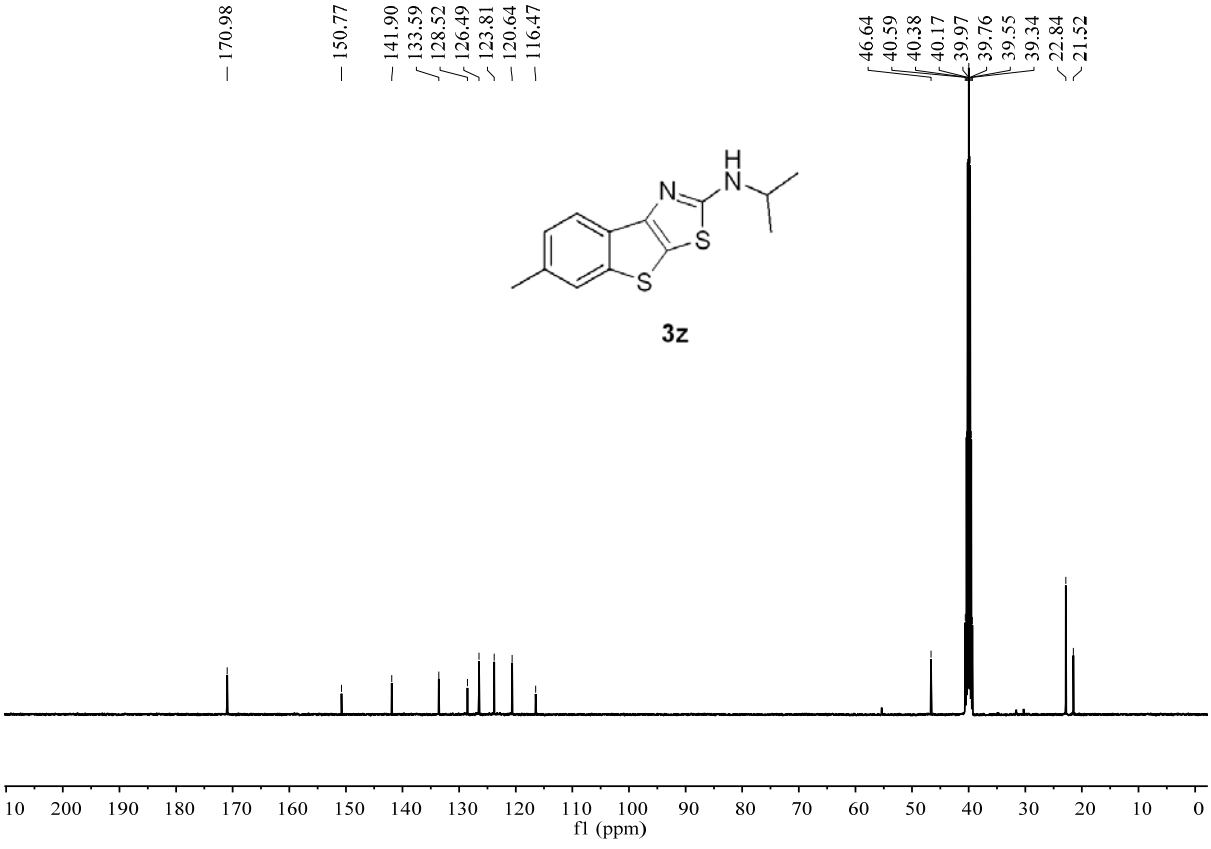
133.61
128.51
126.49
123.82
120.62
116.48
44.84
40.64
40.43
40.22
39.81
39.60
39.39
31.45
29.09
26.57
22.54
21.52
14.39
H
N
N
S
S
3y
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.80
7.78
7.72
7.71
7.70
7.21
7.19
3.97
3.96
3.94
3.92
3.91
3.89
3.36
2.50
2.50
2.49
2.49
2.48
2.41
1.23
1.21
H
N
N
S
S
3z
1.00
2.00
1.00
1.00
3.00
6.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


170.98
150.77
141.90
133.59
128.52
126.49
123.81
120.64
116.47
46.64
40.59
40.38
40.17
39.97
39.76
39.55
39.34
22.84
21.52
H
N
N
S
S
3z
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)