Supporting Information

Double C-S Bonds Formation *via* C-H Bonds Functionalization: Synthesis of Benzothiazoles from N-Substituted Arylamines and Elemental Sulfur

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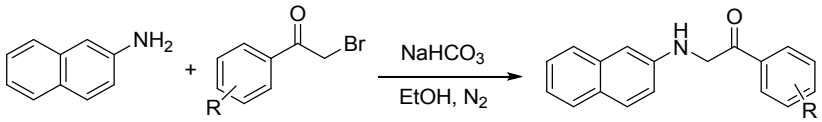
1) General Information

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance-500 instrument (500 MHz for ^{1}H; 125 MHz for ^{13}C) at room temperature, unless otherwise noted. High-resolution mass spectra (HRMS) were recorded on a Thermo Scientific LTQ Orbitrap XL mass spectrometer using ESI (electrospray ionization). Low-resolution mass spectra (LRMS) data were measured on GCMS-QP2010 Ultra. GC analyses were recorded on Hunan Huasi Instrument Co. Ltd GC 8010 gas chromstograph spectrometer using FID. Reactions were monitored by thin-layer chromatography. Column chromatography was performed on silica gel (200-300 mesh) using petroleum ether (PE)/ethyl acetate (EA).

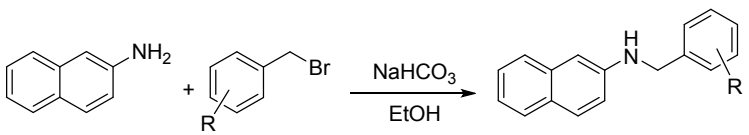
2) Synthesis of Starting Materials

Method A: Substrates **1u – 1x** were prepared according to literature.[1]



To a mixture of *β*-naphthylamine (2 mmol) and $NaHCO_3$ (3 mmol) in ethanol was added the appropriately substituted *a*-bromoacetophenone (2 mmol) at 25 ^{o}C under a nitrogen atmosphere. The mixture was stirred until complete consumption of starting material indicated by TLC, then diluted with water (10 mL). The mixture was extracted with ethyl acetate, the organic layers were combined, washed with water, dried over anhydrous Na_2SO_4 and concentrated in vacuum. The resulting residue was purified by column chromatography (petroleum ether/ethyl acetate) to afford the pure product.

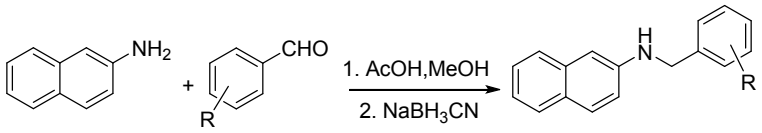
Method B: Substrates **1d, 1f, 1g-1h, 1j, 1y, 3b-3e** were prepared according to literature.[1]



An oven-dried flask was charged with arylamine (2.6 mmol), the corresponding

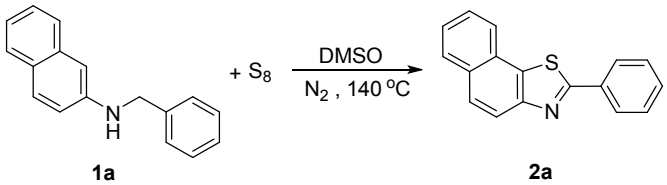
benzyl bromide (2 mmol), $NaHCO_3$ (4 mmol), and EtOH (5 mL). The mixture was stirred at 50 °C, until complete consumption of starting material indicated by TLC. Then cooled to room temperature, the mixture was quenched with water and the organic layer was extracted with ethyl acetate. The combined extracts were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure and purified by column chromatography (petroleum ether/ethyl acetate) to afford the pure product.

Method C: Substrates **1a-1c, 1e, 1i, 1k-1t, 1z, 3g, 5a- 5b** were prepared according to literature.[2]



A solution of arylamine (2 mmol) and corresponding benzaldehyde (2 mmol) in methanol (15 mL) were added acetic acid (3 mmol). The reaction mixture was stirred at rt for 2 h. The solution was cooled down to 0 °C and sodium cyanoborohydride (3 mmol) was added in two portions over 30 min. The reaction mixture was stirred at rt until the complete consumption of the starting material indicated by TLC. The reaction was quenched with the addition of saturated aqueous Na_2CO_3 (15 mL). The aqueous layer was extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4. After the evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/ethyl acetate) to give the pure product.

3) Typical Procedures



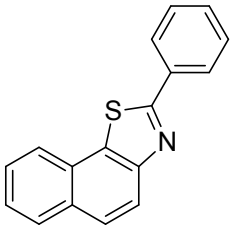
1a **2a**

The sealed Schlenk tube was charged with N-Benzyl-2-naphthylamine **1a** (0.3 mmol), S_8 (0.075 mmol), and DMSO (2 mL). Then under the protection of nitrogen atmosphere, the mixture was stirred at 140 °C for 22 h. After the completion of the

reaction (monitored by TLC), the reaction mixture was cooled to room temperature, quenched by water and extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4, and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the pure product (**2a**).

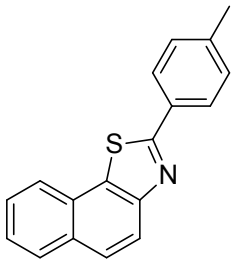
4) Characterization Data of Products

2-phenylnaphtho[2,1-*d*]thiazole (2a)[3]



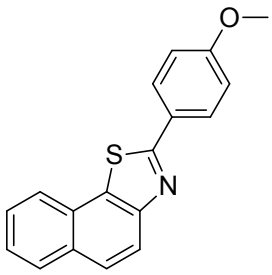
Light yellow solid (75 mg, 95%); mp: 109-110 ^oC; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.13 (dd, J = 7.5 Hz, J = 1.5 Hz, 2H), 8.10 (d, J = 8.5 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8 Hz, 1H), 7.85 (d, J = 8.5 Hz, 1H), 7.56 (t, J = 6.5 Hz, 1H), 7.53 - 7.46 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.03, 152.11, 133.59, 132.09, 130.93, 130.59, 128.93, 128.85, 127.97, 127.30, 127.22, 126.87, 125.85, 125.04, 121.59.

2-(*p*-tolyl)naphtho[2,1-*d*]thiazole (2b)[4]



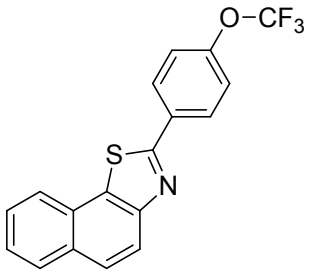
Yellow solid (79 mg, 95%); mp: 137-139 ^oC; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.08 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.5 Hz, 1H), 7.53 (t, J = 7.0 Hz, 1H), 7.48 (td, J = 8.0 Hz, J = 1.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.23, 152.11, 140.93, 131.85, 130.92, 130.86, 129.58, 128.81, 127.98, 127.17, 127.10, 126.78, 125.69, 124.99, 121.51, 21.37.

2-(4-methoxyphenyl)naphtho[2,1-*d*]thiazole (2c)



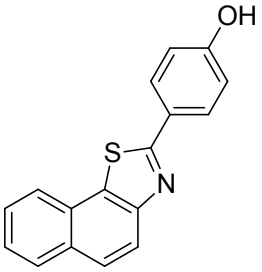
Yellow solid (79 mg, 91%); mp: 106-108 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.06 (d, J = 8.5 Hz, 1H), 8.03 (d, J = 8.5 Hz, 2H), 7.94 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 9.0 Hz, 1H), 7.54 (t, J = 6.5 Hz, 1H), 7.49 (t, J = 6.5 Hz, 1H), 6.96 (d, J = 8.5 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.93, 161.58, 152.14, 131.63, 130.77, 128.81, 128.71, 127.98, 127.12, 126.77, 126.41, 125.58, 124.95, 121.40, 114.24, 55.26; HRMS (ESI) m/z calcd. for $C_{18}H_{14}NOS^{+}$ $(M+H)^{+}$ 292.0791, found 292.0792.

2-(4-(trifluoromethoxy)phenyl)naphtho[2,1-*d*]thiazole (2d)



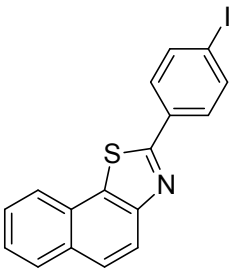
Light yellow solid (90 mg, 86%); mp: 141-143 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.14 (d, J = 9.0 Hz, 2H), 8.08 (d, J = 9.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 9.0 Hz, 1H), 7.59 (t, J = 7.0 Hz, 1H), 7.54 (d, J = 7.0 Hz, 1H), 7.34 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.24, 152.23, 150.84, 132.39, 132.28, 131.14, 128.99, 128.78, 128.01, 127.61, 127.10, 126.16, 125.13, 121.68, 121.23, 120.41 (q, J = 256.75); HRMS (ESI) m/z calcd. for $C_{18}H_{11}F_3NOS^{+}$ $(M+H)^{+}$ 346.0508, found 346.0506.

4-(naphtho[2,1-*d*]thiazol-2-yl)phenol (2e)



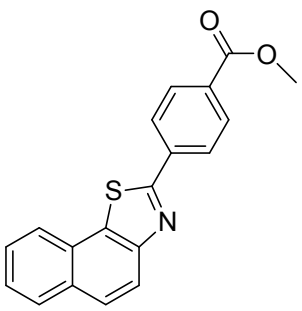
Light yellow solid (57 mg, 69%); mp: >250 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.25 (s, 1H), 8.04 (dd, J = 9.0 Hz, J = 2.5 Hz, 1H), 8.00 - 7.95 (m, 4H), 7.62 (t, J = 8.0 Hz, 1H), 7.56 (t, J = 8.0 Hz, 1H), 6.97 (d, J = 8.5 Hz, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 167.33, 160.89, 152.31, 131.18, 130.91, 129.48, 129.33, 127.93, 127.90, 127.88, 126.47, 125.35, 124.65, 121.71, 116.64; HRMS (ESI) m/z calcd. for $C_{17}H_{12}NOS^+$ $(M+H)^+$ 278.0634, found 278.0642.

2-(4-iodophenyl)naphtho[2,1-*d*]thiazole (2f)



Ivory-white solid (89 mg, 78%); mp: 211-223 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.09 (d, J = 9.0 Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.90 - 7.85 (m, 5H), 7.62 (t, J =7.5 Hz, 1H), 7.56 (d, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.94, 152.24, 138.22, 133.23, 132.29, 131.18, 129.04, 128.71, 128.05, 127.64, 127.13, 126.18, 125.18, 121.68, 97.10; HRMS (ESI) m/z calcd. for $C_{17}H_{11}INS^+$ $(M+H)^+$ 387.9651, found 387.9653.

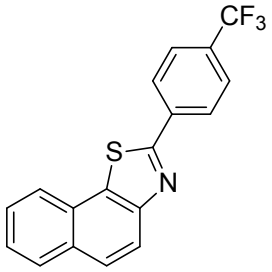
methyl 4-(naphtho[2,1-*d*]thiazol-2-yl)benzoate (2g)



White solid (0.088 mg, 92%); mp: 195-197 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.15 (q,

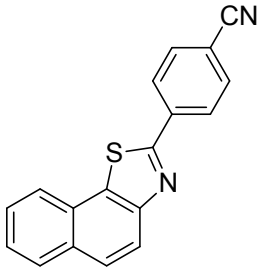
J = 8.5 Hz, 4H), 8.08 (d, *J* = 9.0 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.38, 165.52, 152.27, 137.47, 132.69, 131.69, 131.20, 130.24, 128.99, 127.97, 127.72, 127.13, 127.08, 126.29, 125.19, 121.75, 52.29. HRMS (ESI) m/z calcd. for $C_{19}H_{14}NO_2S^+$ $(M+H)^+$ 320.0740, found 320.0736.

2-(4-(trifluoromethyl)phenyl)naphtho[2,1-*d*]thiazole (2h)



Light yellow solid (92 mg, 93%); mp: 173-175 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.13 (d, *J* = 8.0 Hz, 2H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.92 (t, *J* = 9.0 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.57 - 7.51 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.97, 152.18, 136.74, 132.62, 132.14(d, *J* = 32.63 Hz), 131.22, 129.02, 127.94, 127.79, 127.42, 127.18, 126.36, 125.98(d, *J* = 3.5 Hz), 125.15, 123.84(d, *J* = 270.75 Hz), 121.72; HRMS (ESI) m/z calcd. for $C_{18}H_{11}F_3NS^+$ $(M+H)^+$ 330.0559, found 330.0559.

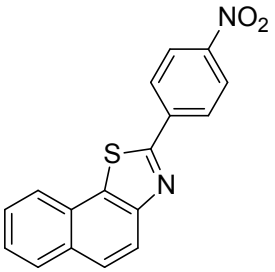
4-(naphtho[2,1-*d*]thiazol-2-yl)benzonitrile (2i)



Yellow solid (81 mg, 95%); mp: 216-218 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.21 (d, *J* = 8.5 Hz, 2H), 8.10 (d, *J* = 9.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H),7.91 (d, *J* = 8.5 Hz, 1H),7.77 (d, *J* = 8.5 Hz, 2H), 7.63 (t, *J* =7.0 Hz, 1H), 7.59 (t, *J* = 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.14, 152.18, 137.35, 132.85, 132.64, 131.26, 129.03, 127.94, 127.81, 127.44, 127.25, 126.55, 125.13, 121.71, 118.26, 113.65; HRMS (ESI) m/z calcd. for $C_{18}H_{11}N_2S^+$ $(M+H)^+$ 287.0638, found

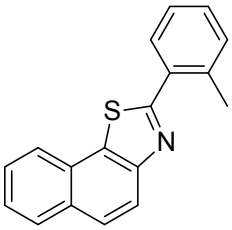
287.0635.

2-(4-nitrophenyl)naphtho[2,1-*d*]thiazole (2j)[5]



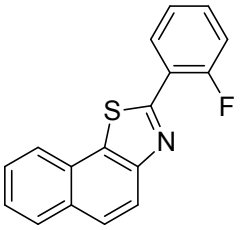
Yellow solid (61 mg, 66%); mp: 220-222 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.33 (d, J = 8.5 Hz, 2H), 8.27 (d, J = 8.5 Hz, 2H), 8.11 (d, J = 8.5 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 9.0 Hz, 1H), 7.64 (t, J = 7.5Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.75, 152.42, 148.78, 139.21, 133.23, 131.41, 129.12, 128.14, 127.91, 127.86, 127.39, 126.72, 125.27, 124.34, 121.84.

2-(*o*-tolyl)naphtho[2,1-*d*]thiazole (2k)



White solid (83 mg, 98%); mp: 69-71 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.17 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.90 - 7.88 (m, 2H), 7.60 (t, J = 7.0 Hz, 1H), 7.56 (t, J = 7.0 Hz, 1H), 7.42 - 7.34 (m, 3H), 2.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.04, 151.90, 137.22, 133.19, 132.81, 131.67, 131.06, 130.61, 129.94, 129.02, 128.08, 127.28, 127.01, 126.23, 126.02, 125.35, 121.94, 21.62; HRMS (ESI) m/z calcd. for $C_{18}H_{14}NS^+$ $(M+H)^+$ 276.0842, found 276.0844.

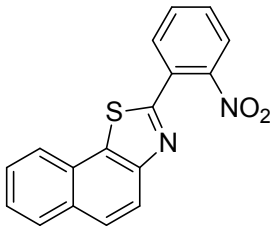
2-(2-fluorophenyl)naphtho[2,1-*d*]thiazole (2l)



Yellow solid (60 mg, 72%); mp: 155-157 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.45 (t, J

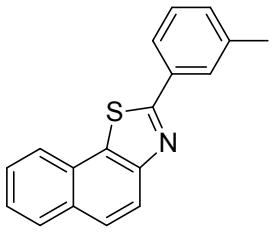
= 7.5 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.58 (d, *J* = 7.0 Hz, 1H), 7.53 (d, *J* = 7.0 Hz, 1H), 7.40 (dd, *J* = 8.0 Hz, *J* = 7.0 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.23 (dd, *J* = 10.5 Hz, *J* = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.52 (d, *J* = 202.13 Hz), 159.54 (d, *J* = 55.50 Hz), 150.70, 133.01 (d, *J* = 8.13 Hz), 131.74 (d, *J* = 8.5Hz), 131.01, 129.40 (d, *J* = 2.25 Hz), 128.90, 127.97, 127.40, 126.94, 126.05, 125.02, 124.65 (d, *J* = 3.5Hz), 121.59, 121.46 (d, *J* = 11 Hz), 116.28 (d, *J* = 21.75); HRMS (ESI) m/z calcd. for $C_{17}H_{11}FNS^+$ $(M+H)^+$ 280.0591, found 280.0590.

2-(2-nitrophenyl)naphtho[2,1-*d*]thiazole (2m)



Yellow solid (58 mg, 63%); mp: 153-155 ^{o}C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 8.12 - 8.00 (m, 6H), 7.87 (t, *J* = 7.5 Hz, 1H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 161.56, 151.83, 148.89, 133.50, 133.06, 132.31, 132.19, 131.22, 129.53, 128.48, 128.21, 127.63, 127.32, 126.53, 125.62, 125.07, 121.93; HRMS (ESI) m/z calcd. for $C_{17}H_{11}N_2O_2S^+$ $(M+H)^+$ 307.0536, found 307.0536.

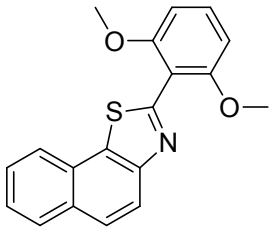
2-(*m*-tolyl)naphtho[2,1-*d*]thiazole (2n)



Yellow solid (78 mg, 96%); mp: 102-104 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.10 (d, *J* = 9.0 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.91 (t, *J* = 7.5 Hz, 2H), 7.84 (d, *J* = 9.0 Hz, 1H),7.55 (td, *J* = 7.0 Hz, *J* = 1.0 Hz, 1H), 7.50 (td, *J* = 7.0 Hz, *J* = 1.0 Hz, 1H), 7.37 (t, *J* =7.5 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.26, 152.06, 138.69, 133.46, 132.00, 131.40, 130.88, 128.81, 128.79, 127.94, 127.62, 127.22, 126.80, 125.76, 124.98, 124.48, 121.53, 21.25; HRMS (ESI) m/z calcd. for

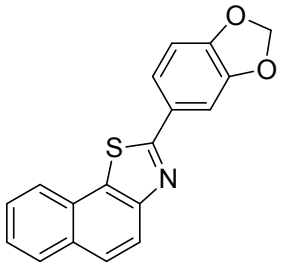
$C_{18}H_{14}NS^+$ $(M+H)^+$ 276.0842, found 276.0842.

2-(2,6-dimethoxyphenyl)naphtho[2,1-*d*]thiazole (2o)



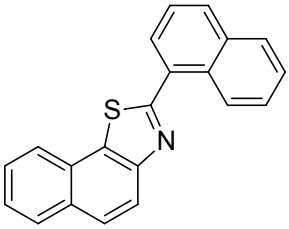
Light yellow solid (92 mg, 94%); mp: 175-177 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.17 (d, J = 3.0 Hz, 1H), 8.14 - 8.12 (m, 2H), 7.95 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 9.0 Hz, 1H), 7.59 (td, J = 7.0 Hz, J = 1.0 Hz, 1H), 7.52 (td, J = 7.0 Hz, J = 1.0 Hz, 1H),7.02 - 6.96 (m, 2H), 4.02 (s, 3H), 3.92 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.58, 153.83, 151.47, 150.16, 133.14, 130.77, 128.83, 128.16, 126.92, 126.62, 125.57, 124.86, 122.73, 121.50, 118.32, 113.21, 112.30, 56.23, 55.87; HRMS (ESI) m/z calcd. for $C_{19}H_{16}NO_2S^+$ $(M+H)^+$ 322.0896, found 322.0898.

2-(benzo[*d*][1,3]dioxol-5-yl)naphtho[2,1-*d*]thiazole (2p)



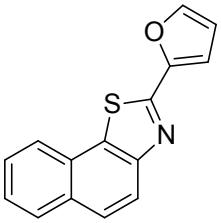
Light yellow solid (80 mg, 88%); mp: 161-163 ºC; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.03 (d, J = 8.5 Hz, 1H), 7.92 (t, J = 9.0 Hz, 2H), 7.82 (d, J = 8.5 Hz, 1H), 7.60 - 7.58 (m, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 7.5 Hz, 1H), 6.00 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.62, 152.01, 149.75, 148.25, 131.70, 130.86, 128.85, 128.01, 127.95, 127.21, 126.82, 125.69, 124.96, 122.05, 121.45, 108.53, 107.21, 101.59; HRMS (ESI) m/z calcd. for $C_{18}H_{12}NO_2S^+$ $(M+H)^+$ 306.0583, found 306.0584.

2-(naphthalen-1-yl)naphtho[2,1-*d*]thiazole (2q)



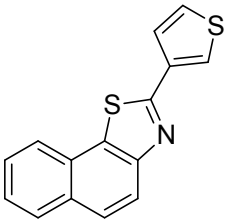
Yellow solid (92 mg, 93%); mp: 95-97 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.08 (d, J = 8.5 Hz, 1H), 8.25 (d, J = 8.5 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 7.0 Hz,3H), 7.94 (t, J = 8.0 Hz, 2H), 7.67 (td, J = 7.0 Hz, J = 1.0 Hz, 1H), 7.62 - 7.55 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.57, 152.16, 133.97, 132.62, 130.99, 130.86, 130.78, 130.59, 129.30, 128.90, 128.34, 127.90, 127.54, 127.28, 126.92, 126.41, 125.98, 125.89, 125.29, 124.95, 121.87; HRMS (ESI) m/z calcd. for $C_{21}H_{14}NS^+$ $(M+H)^+$ 312.0842, found 312.0843.

2-(furan-2-yl)naphtho[2,1-*d*]thiazole (2r)



Yellow solid (65 mg, 83%); mp: 109-110 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.05 (d, J = 8.5 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 9.0 Hz, 1H), 7.58 (s, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.19 (d, J = 3.5 Hz, 1H), 6.58 (dd, J = 3.0 Hz, J = 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.60, 151.74, 148.72, 144.36, 131.30, 130.91, 128.86, 127.87, 127.52, 126.96, 125.90, 124.85, 121.40, 112.45, 110.78; HRMS (ESI) m/z calcd. for $C_{15}H_{10}NOS^+$ $(M+H)^+$ 252.0478, found 252.0478.

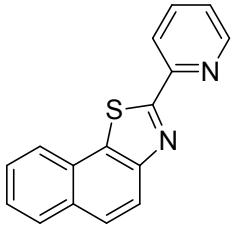
2-(thiophen-3-yl)naphtho[2,1-*d*]thiazole (2s)



Yellow solid (61 mg, 77%); mp: 105-106 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.08 (d, J = 9.0 Hz, 1H), 8.05 (d, J = 2.0 Hz, 1H), 7.99 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 8.5 Hz,

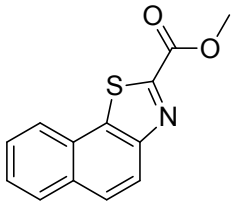
1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.74 (d, *J* = 5.0 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.45 (dd, *J* = 5.0 Hz, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.77, 151.84, 135.89, 131.61, 130.94, 128.87, 127.95, 127.32, 126.88, 126.81, 126.43, 125.80, 125.39, 124.95, 121.46; HRMS (ESI) m/z calcd. for $C_{15}H_{10}NS_2^+$ $(M+H)^+$ 268.0249, found 268.0252.

2-(pyridin-2-yl)naphtho[2,1-*d*]thiazole (2t)[6]



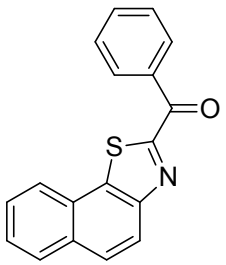
Light yellow solid (65 mg, 82%); mp: 146-147 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.66 (d, *J* = 4.5 Hz, 1H), 8.34 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 9.0 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 9.0 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.33 - 7.30 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.13, 152.29, 151.30, 149.52, 136.90, 133.62, 131.11, 128.82, 128.15, 127.38, 126.96, 126.17, 125.22, 124.88, 121.72, 120.32.

methyl naphtho[2,1-*d*]thiazole-2-carboxylate (2u)[7]



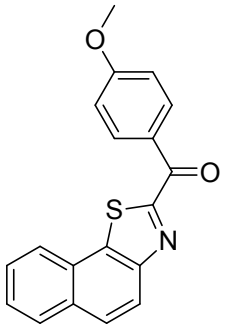
Yellow solid (39 mg, 53%); mp: 110-112 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.16 (d, *J* = 9.0 Hz, 1H), 8.09 - 8.07 (m, 1H), 7.98 - 7.97 (m, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.65 - 7.61 (m, 2H), 4.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.02, 156.47, 151.61, 135.53, 131.91, 129.09, 128.55, 127.75, 127.50, 125.42, 122.62, 53.55.

naphtho[2,1-*d*]thiazol-2-yl(phenyl)methanone (2v)



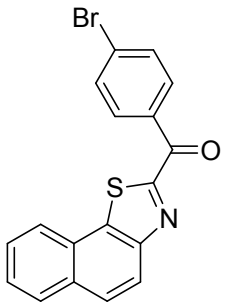
Yellow solid (56 mg, 64%); mp: 144-146 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.61 (d, J = 8.0 Hz, 2H), 8.13 (d, J = 9.0 Hz, 1H), 8.11 - 8.09 (m, 1H), 7.94 - 7.92 (m, 1H), 7.88 (d, J = 9.0 Hz, 1H), 7.67 (d, J = 7.5 Hz, 1H), 7.62 - 7.55 (m, 4H);^{13}C NMR ($CDCl_3$, 125 MHz) δ 184.69, 165.87, 152.08, 135.95, 134.97, 133.69, 131.77, 131.20, 128.92, 128.38, 128.26, 127.72, 127.43, 127.33, 125.80, 122.70; HRMS (ESI) m/z calcd. for $C_{18}H_{12}NOS^+$ $(M+H)^+$ 290.0634, found 290.0632.

(4-methoxyphenyl)(naphtho[2,1-*d*]thiazol-2-yl)methanone (2w)



Yellow solid (75 mg, 78%); mp: 173-175 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.69 (d, J = 8.5 Hz, 2H), 8.17 - 8.13 (m, 2H), 7.96 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 8.5 Hz, 1H), 7.64 - 7.59 (m, 2H), 7.05 (d, J = 9.0 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 182.91, 166.78, 164.29, 152.14, 135.78, 133.81, 131.78, 128.98, 128.19, 127.87, 127.84, 127.35, 125.87, 122.73, 113.83, 55.51; HRMS (ESI) m/z calcd. for $C_{19}H_{14}NO_2S^+$ $(M+H)^+$ 320.0740, found 320.0739.

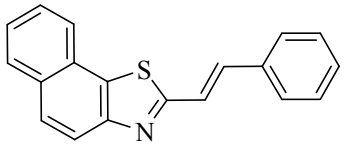
(4-bromophenyl)(naphtho[2,1-*d*]thiazol-2-yl)methanone (2x)



Yellow solid (35 mg, 32%); mp: 179-181 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.59 (d, J = 8.5Hz, 2H), 8.14 - 8.12 (m, 2H), 7.97 - 7.96 (m, 1H), 7.91 (d, J = 9.0 Hz, 1H), 7.63 (t, J = 4.0 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 183.40, 165.61, 152.14, 140.46, 136.17, 133.31, 132.68, 131.91, 129.04, 128.78, 128.48, 127.78, 127.63, 127.49, 125.91, 122.72; HRMS (ESI) m/z calcd. for $C_{18}H_{11}BrNOS^+$

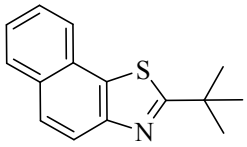
$(M+H)^+$ 367.9739, found 367.9735.

(*E*)-2-styrylnaphtho[2,1-*d*]thiazole (2y)[8]



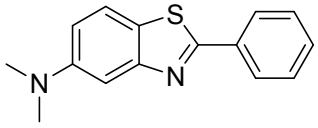
Yellow solid (40 mg, 48%); mp: 138-140 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.04 (d, J = 9.0Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.5 Hz, 1H), 7.62 - 7.59 (m, 4H), 7.55 (t, J = 7.5 Hz, 1H), 7.48 - 7.41 (m, 3H), 7.37 (t, J = 6.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.12, 151.93, 136.88, 135.52, 131.52, 131.17, 129.33, 129.01, 128.96, 128.00, 127.51, 127.35, 127.06, 126.05, 125.16, 121.98, 121.43.

2-(tert-butyl)naphtho[2,1-d]thiazole (2z)



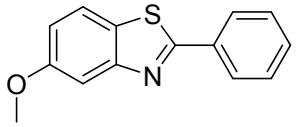
Yellow oily liquid (40 mg, 55%);^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.04 (d, J = 9.0 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.57 (d, J = 7.5 Hz, 1H), 7.51 (d, J = 7.5 Hz, 1H), 1.59 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 180.97, 151.14, 131.71, 130.72, 128.87, 128.17, 126.75, 125.55, 124.99, 121.45, 38.33, 30.90; HRMS (ESI) m/z calcd. for $C_{15}H_{16}NS^+$ $(M+H)^+$ 242.0998, found 242.0998.

N,N-dimethyl-2-phenylbenzo[*d*]thiazol-5-amine (4a)



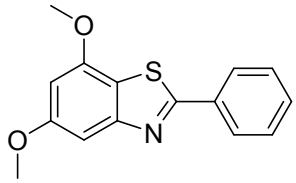
Yellow solid (70 mg, 92%); mp: 87-90 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.08 - 8.06 (m, 2H), 7.70 (d, J = 9.0 Hz, 1H), 7.48 - 7.46 (m, 3H), 7.43 (d, J = 2.0 Hz, 1H), 6.96 (dd, J = 8.5 Hz, J = 2.0 Hz, 1H), 3.03 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.62, 155.68, 149.84, 133.83, 130.61, 128.86, 127.27, 121.47, 113.33, 105.99, 41.26. HRMS (ESI) m/z calcd. for $C_{15}H_{15}N_2S^+$ $(M+H)^+$ 255.0951, found 255.0958.

5-methoxy-2-phenylbenzo[*d*]thiazole (4b)[9]



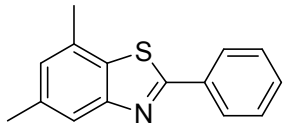
Light yellow solid (49 mg, 68%); mp: 75-77 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.09 - 8.07 (m, 2H), 7.74 (d, J = 9.0 Hz, 1H), 7.59 (d, J = 2.5 Hz, 1H), 7.49 - 7.48 (m, 3H), 7.04 (dd, J = 9.0 Hz, J = 2.5 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.32, 159.16, 155.22, 133.60, 130.92, 129.00, 127.39, 126.81, 121.81, 115.56, 105.44, 55.61.

5,7-dimethoxy-2-phenylbenzo[*d*]thiazole (4c)



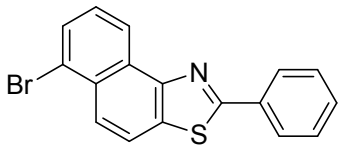
Yellow solid (72 mg, 88%); mp: 84-85 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.08 - 8.06 (m, 2H), 7.49 - 7.46 (m, 3H), 7.19 (d, J = 1.5 Hz, 1H), 6.49 (d, J = 1.5 Hz, 1H), 3.94 (s, 3H), 3.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.16, 160.31, 155.76, 154.26, 133.66, 130.71, 128.91, 127.24, 116.20, 97.52, 96.84, 55.83, 55.67; HRMS (ESI) m/z calcd. for $C_{15}H_{14}NO_2S^+$ $(M+H)^+$ 272.0740, found 272.0740.

5,7-dimethyl-2-phenylbenzo[*d*]thiazole (4d)



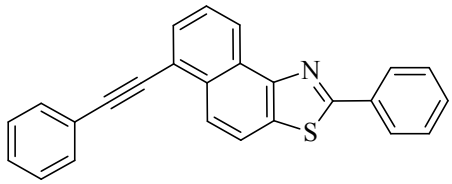
yellow solid (13 mg, 18%); mp: 79-82 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 - 8.09 (m, 2H), 7.73 (s, 1H), 7.51 - 7.48 (m, 3H), 7.04 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.59, 154.27, 136.50, 133.81, 132.50, 131.05, 130.71, 128.92, 127.42, 127.10, 120.65, 21.41, 21.29; HRMS (ESI) m/z calcd. for $C_{15}H_{14}NS^+$ $(M+H)^+$ 240.0842, found 240.0842.

6-bromo-2-phenylnaphtho[1,2-*d*]thiazole (4e)



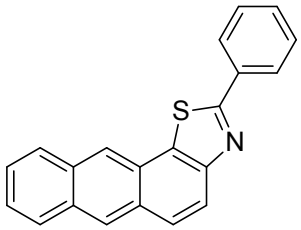
Cadmium green pale solid (52 mg, 50%); mp: 187-189 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.91 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 9.0 Hz, 1H), 8.17 (d, J = 5.5 Hz, 2H), 7.97 (d, J = 9.0 Hz, 1H), 7.86 (d, J = 7.5 Hz, 1H), 7.52 - 7.48 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.82, 150.38, 133.74, 132.35, 130.81, 130.62, 130.24, 130.00, 129.04, 127.35, 127.21, 124.73, 124.00, 122.98, 120.23; HRMS (ESI) m/z calcd. for $C_{17}H_{11}BrNS^+$ $(M+H)^+$ 339.9790, found 339.9794.

2-phenyl-6-(phenylethynyl)naphtho[1,2-*d*]thiazole (4f)



Pale solid (27 mg, 25%); mp:139-141 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.95 (d, J = 8.0 Hz, 1H), 8.44 (d, J = 8.5 Hz, 1H), 8.20 (d, J = 6.5 Hz, 1H), 8.02 (d, J = 8.5 Hz, 1H), 7.87 (d, J = 7.0 Hz, 1H), 7.69 - 7.66 (m, 3H), 7.55 - 7.49 (m, 3H), 7.47 - 7.38 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.45,150.66, 133.90, 132.22, 132.02, 131.69, 130.71, 130.58, 129.05, 128.70, 128.49, 128.46, 127.36, 126.34, 124.78, 124.04, 123.30, 121.18, 119.76, 94.47, 87.69. HRMS (ESI) m/z calcd. for $C_{25}H_{16}NS^+$ $(M+H)^+$ 362.0998, found 362.1001.

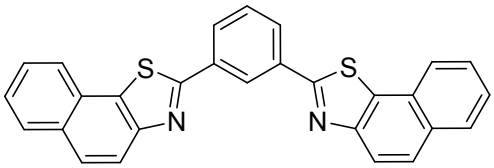
2-phenylanthra[2,1-*d*]thiazole (4g)



Yellow solid (92 mg, 98%); mp:167-170 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.42 (s, 1H), 8.39 (s, 1H), 8.11 (d, J = 6.5 Hz, 2H), 8.0 - 7.95 (m, 3H), 7.90 (d, J = 9.0 Hz, 1H), 7.51 - 7.46 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.73, 151.69, 133.64, 131.89, 131.60, 131.39, 130.47, 129.32, 128.95, 128.16, 127.80, 127.63, 127.09, 126.14, 126.07, 125.48, 122.95, 121.58; HRMS (ESI) m/z calcd. for $C_{21}H_{14}NS^+$

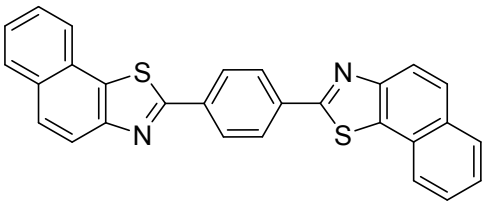
$(M+H)^+$ 312.0842, found 312.0842.

1,3-bis(naphtho[2,1-*d*]thiazol-2-yl)benzene (6a)



white solid (65 mg, 50%); mp: >250 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.91 (s, 1H), 8.28 (d, J = 7.5 Hz,2H), 8.16 (d, J = 9.0 Hz, 2H), 8.09 (d, J = 8.5 Hz, 2H), 7.99 (d, J = 7.5Hz, 2H), 7.92 (d, J = 8.5 Hz, 2H), 7.69 - 7.63 (m, 3H), 7.58 (t, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.07, 152.39, 134.79, 132.56, 131.27, 129.85, 129.27, 129.07, 128.19, 127.64, 127.15, 126.20, 126.13, 125.27, 121.87; HRMS (ESI) m/z calcd. for $C_{28}H_{17}N_2S_2^+$ $(M+H)^+$ 445.0828, found 445.0830.

1,4-bis(naphtho[2,1-*d*]thiazol-2-yl)benzene (6b)



Yellow solid (50 mg, 42%); mp: >250 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.31 (s, 4H), 8.15 (d, J = 8.5 Hz, 2H), 8.08 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 9.0 Hz, 2H), 7.64 (t, J = 7.5 Hz, 2H), 7.58 (t, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.96, 152.45, 135.63, 132.59, 131.25, 129.08, 128.12, 127.93, 127.73, 127.18, 126.26, 125.27, 121.80; HRMS (ESI) m/z calcd. for $C_{28}H_{17}N_2S_2^+$ $(M+H)^+$ 445.0828, found 445.0828.

5) References.

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6) X-ray Crystallographic Studies for 2h

The single crystals of **2h** suitable for X-ray analysis were grown in chloroform-d solution. Crystallographic data of **2h** were collected at 296(2) K on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromatic Mo-*Kα* radiation (λ = 0.71073 Å) using a φ-ω mode. Suitable single crystal with approximate dimensions of 0.23 mm × 0.21 mm × 0.20 mm for **2h** was selected for data collection. All the data were corrected by *Lp* factors and empirical absorbance. The structure was solved by direct methods. All non-hydrogen atoms were determined in successive difference Fourier synthesis, and all hydrogen atoms were added according to theoretical models. All hydrogen and non-hydrogen atoms were refined by their isotropic and anisotropic thermal parameters through full-matrix least-squares techniques. All calculations were completed by the SHELXTL-97 program. Crystal data, data collection and processing parameters for compound **2h** are summarized in Table S1. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1570797 (**2h**).

Table S1. Crystal data and structure refinement for **2h**.

Empirical formula	$C_{18}H_{10}F_3NS$	D_c / (Mg·m^{-3})	1.503
Formula weight	329.33	Absorption coefficient / mm^{-1}	0.253
Temperature / K	296(2) K	F(000)	672
Wavelength / nm	0.071073	Crystal size / mm	0.23 × 0.21 × 0.20
Crystal system	Triclinic	θ range for date collection / (°)	2.66 to 27.44
Space group	*P***Error!**	Limiting indices	-7≤h≤7, -18≤k≤19, -20≤l≤20
a / nm	0.59106(15)	Reflections collected / unique(R_{int})	17722 / 6551 [R_{int} = 0.0313]
b / nm	1.5410(4)	Completeneness to ≤ θ / %	98.5
c / nm	1.6103(4)	Data / restraints /parameters	6551 / 0 / 416
α / (°)	93.706(3)	Goodness-of-fit on F^2	1.059

β / (°)	90.347(3)	Final R indices [$I>2\delta(I)$]	$R_1 = 0.0471$, $wR_2 = 0.1341$
γ / (°)	96.046(3)	R indices(all data)	$R_1 = 0.0565$, $wR_2 = 0.1420$
Volume / nm^3	1.4554(7)	Largest diff. peak and hole(e·nm^{-3})	461 and -362
Z	4		

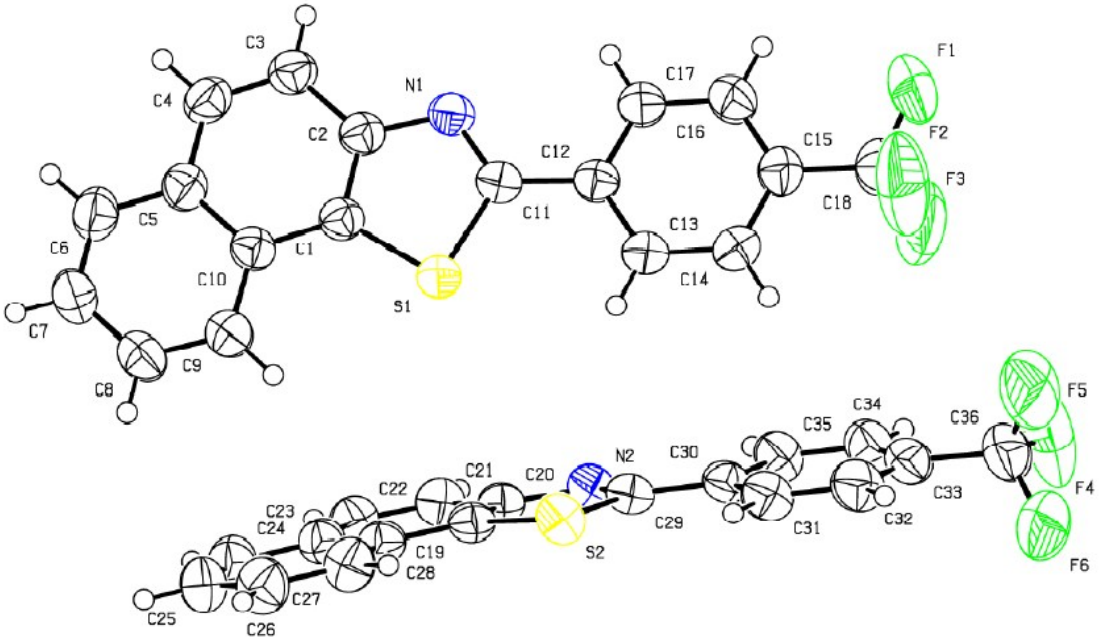


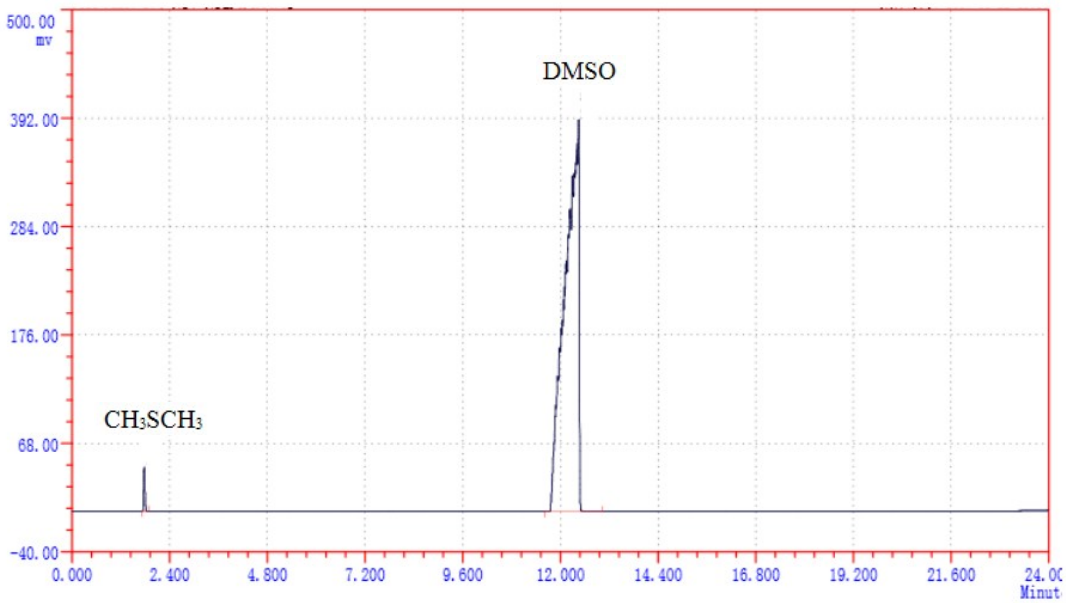
Figure S1. OPTEP structure of **2h**

7) Mechanism Study

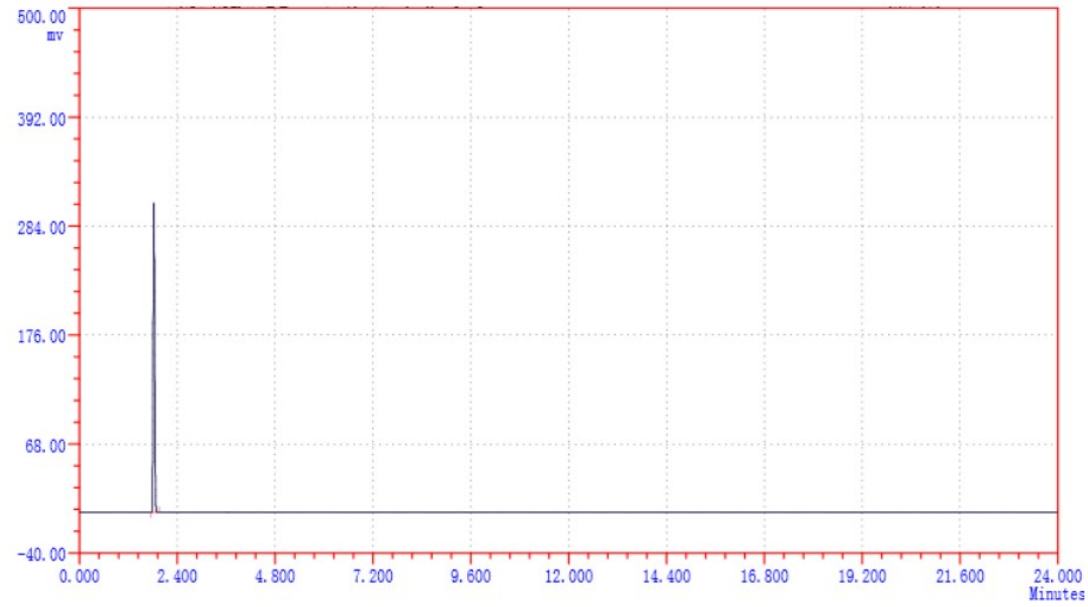
GC and GC-MS Analyses of the Composition of the Reactions

Experiment 1: The sealed Schlenk tube was charged with N-benzyl-2-naphthylamine **1a** (0.3 mmol), S_8 (0.075 mmol), and DMSO (2 mL). Then, under the protection of nitrogen atmosphere, the mixture was stirred at 140 ^oC for 4 h. After cooling to room temperature, 0.8 μL of the mixed liquid of the reaction mixture A was taken using a syringe and GC analysis of the composition was carried out (Figure S2).

GC analysis of the reaction mixture A



GC analysis of standard sample methyl sulfide

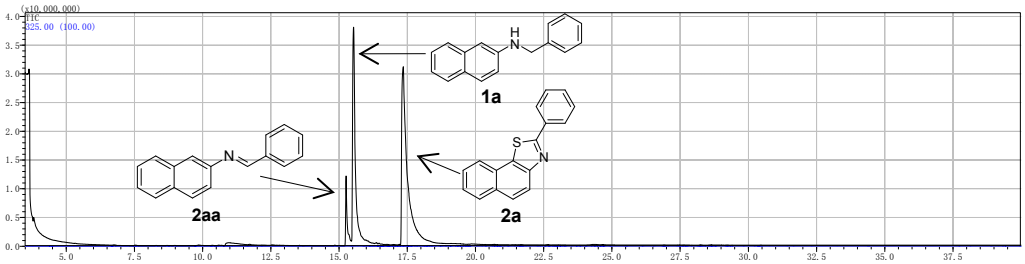


GC analysis of standard sample DMSO

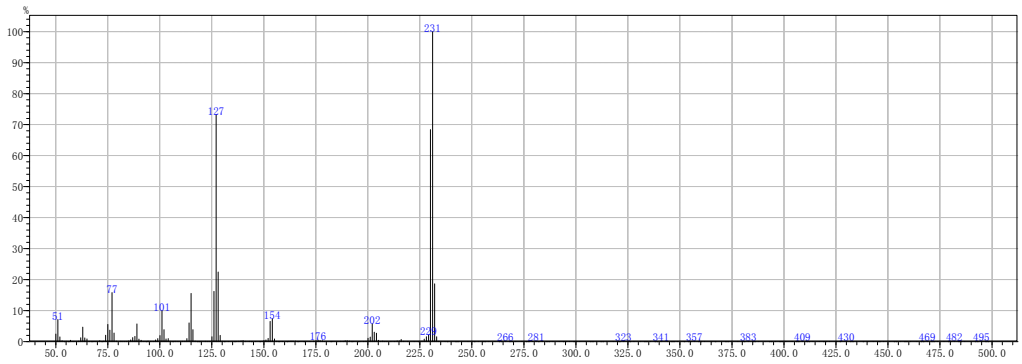
Figure S2. GC-MS analysis of the reaction mixtures A

Experiment 2: The sealed Schlenk tube was charged with N-Benzyl-2-naphthylamine **1a** (0.3 mmol), S_8 (0.075 mmol), and DMSO (2 mL). Then, under the protection of nitrogen atmosphere, the mixture was stirred at 140 °C for 4 h. After cooling to room temperature, the reaction mixture B was detected by GC-MS, and the results revealed that the reaction mixture contained N-Benzyl-2-naphthylamine (**1a)**, imine (**2aa**) and 2-phenylnaphtho[2,1-*d*]thiazole **2a** (Figure S3).

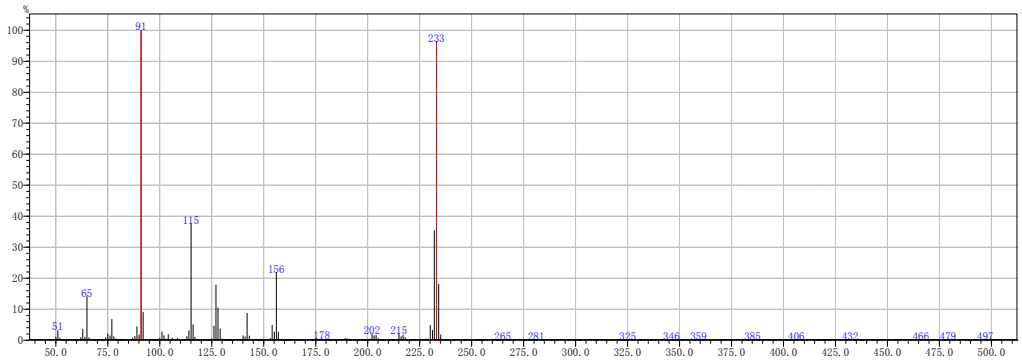
(a) GC of the reaction mixtures B



(b) MS of **2aa**



(c) MS of **1a**



(d) MS of **2a**

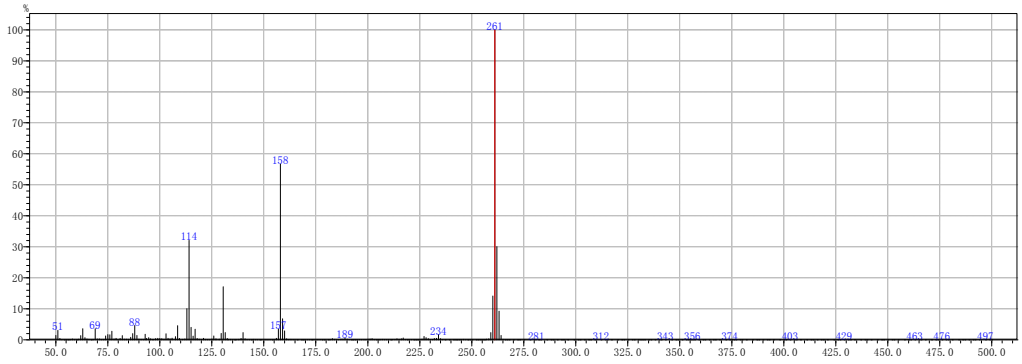
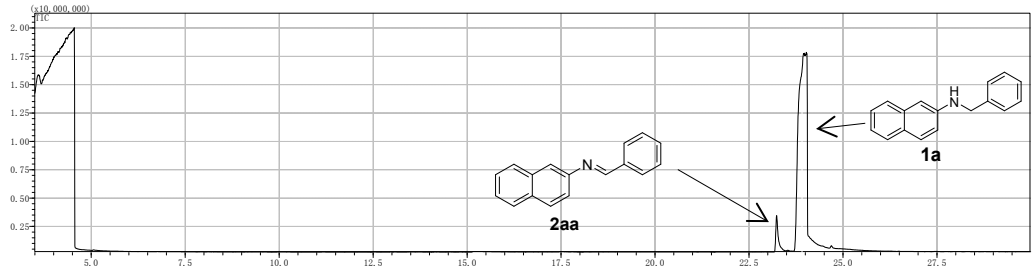


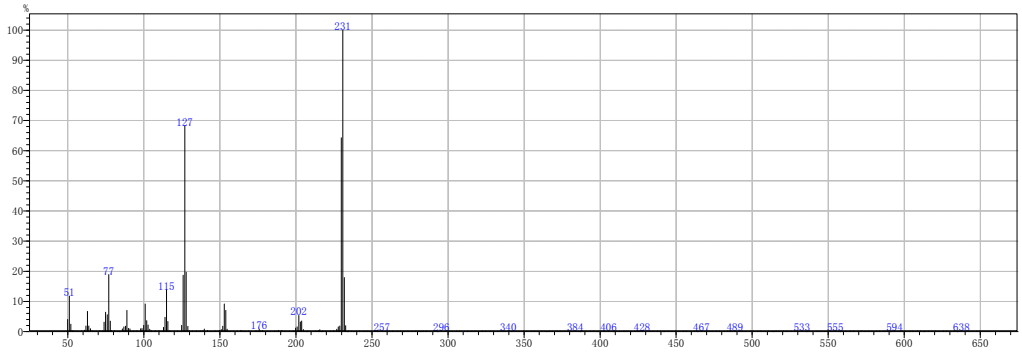
Figure S3. GC-MS analysis of the reaction mixture B

Experiment 3: The sealed Schlenk tube was charged with N-Benzyl-2-naphthylamine **1a** (0.3 mmol), and DMSO (2 mL). Then under the protection of nitrogen atmosphere, the mixture was stirred at 140 °C for 22 h. After cooling to room temperature, the reaction mixture C was detected by GC-MS, and the results revealed that the reaction mixture contained N-Benzyl-2-naphthylamine (**1a)**, imine (**2aa**) (Figure S4).

(a) GC of the reaction mixture C



(b) MS of **2aa**



(c) MS of **1a**

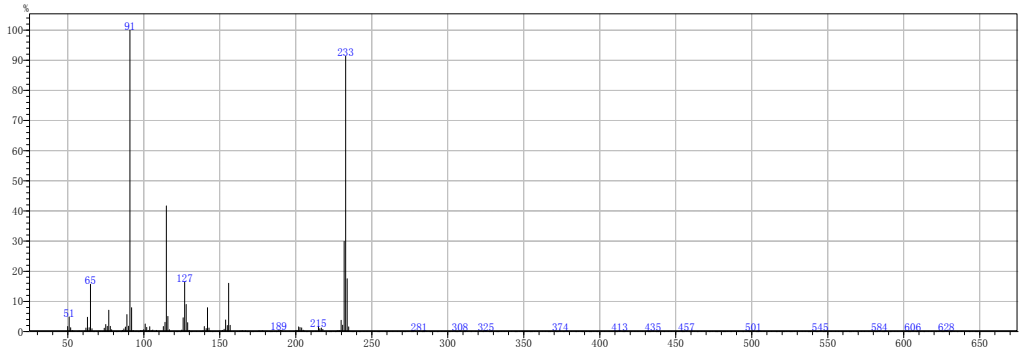
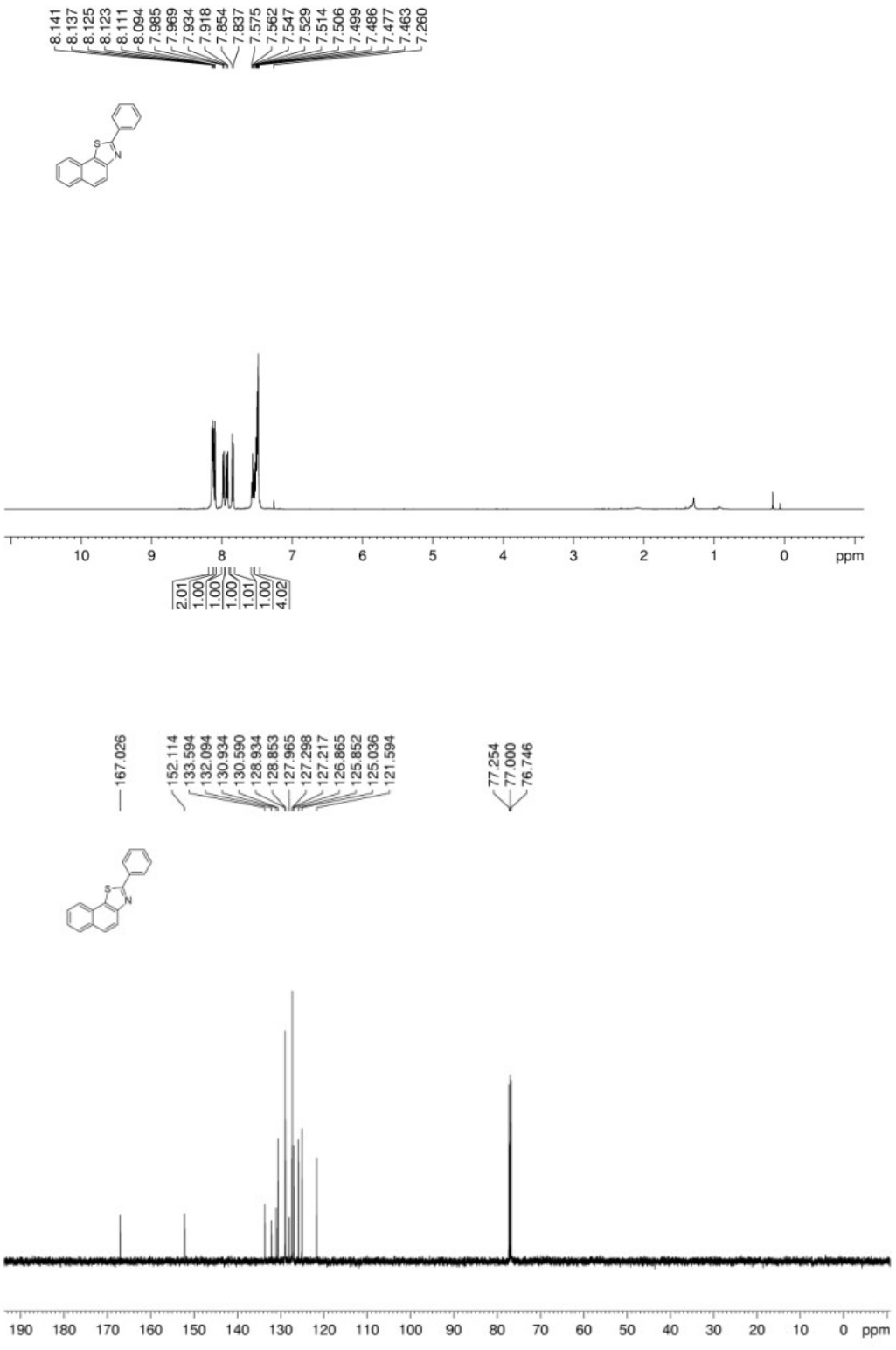


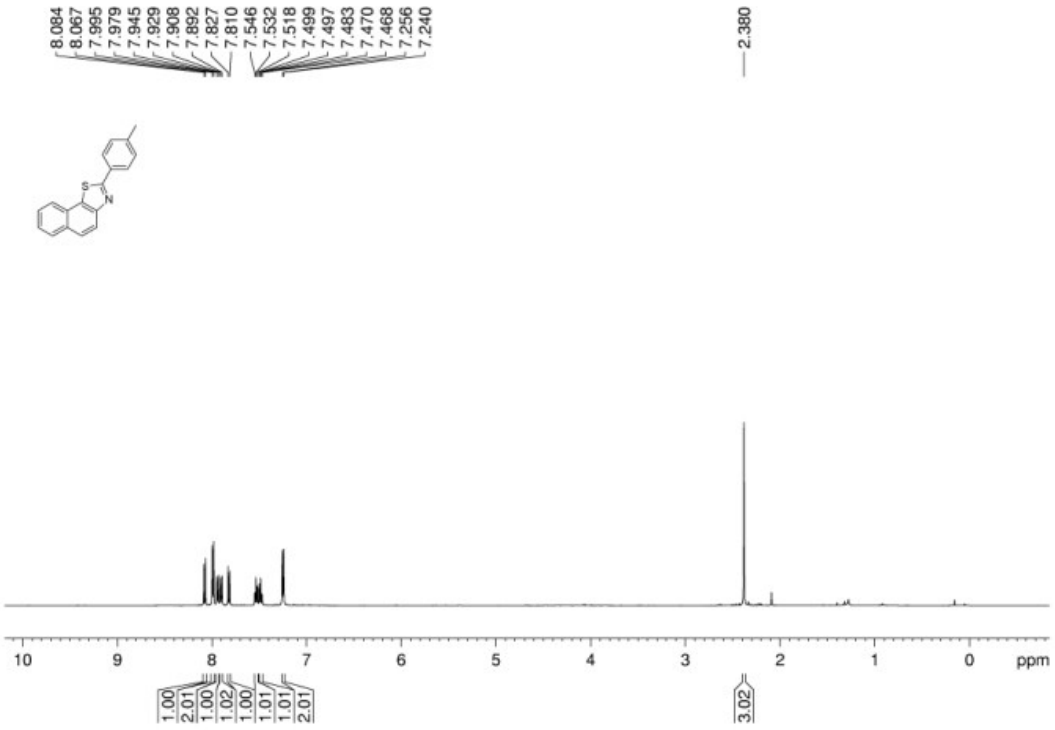
Figure S4. GC-MS analysis of the reaction mixture C

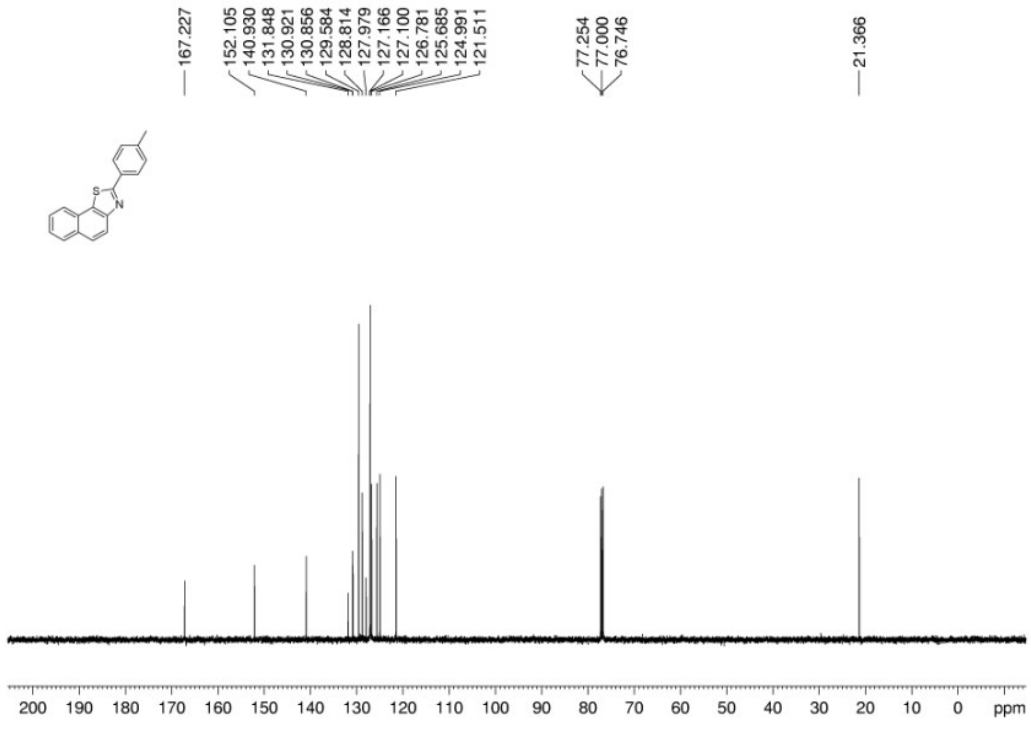
8) ^{1}H NMR and ^{13}C NMR Spectra of Products

^{1}H and ^{13}C Spectrum of Compound **2a**

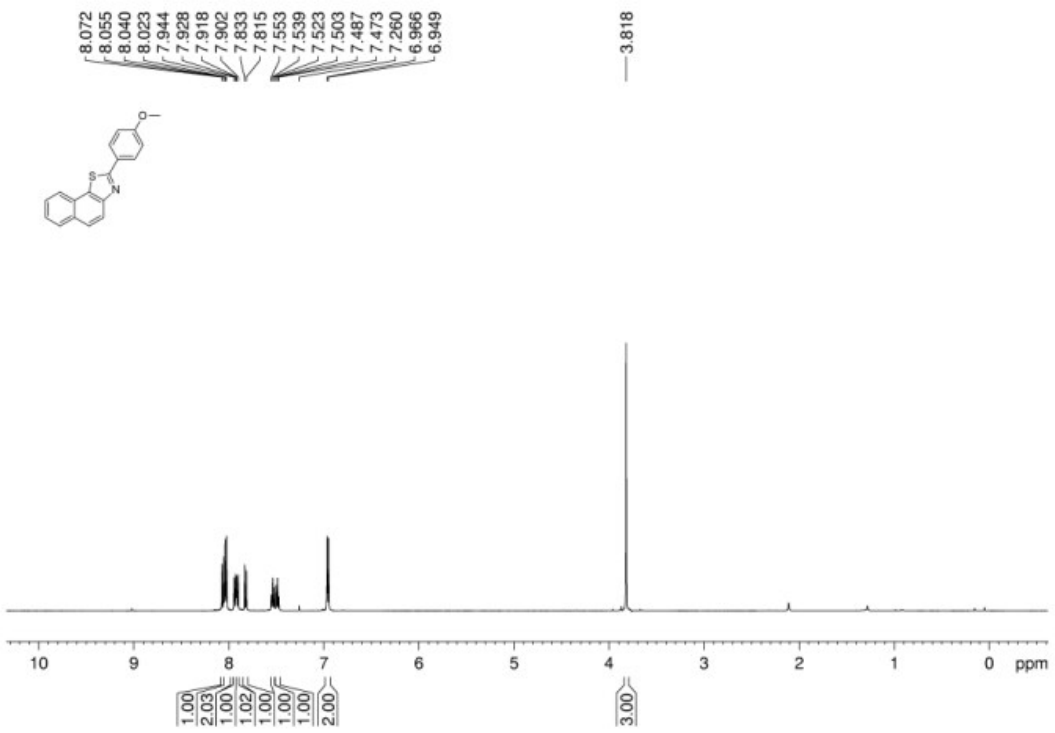


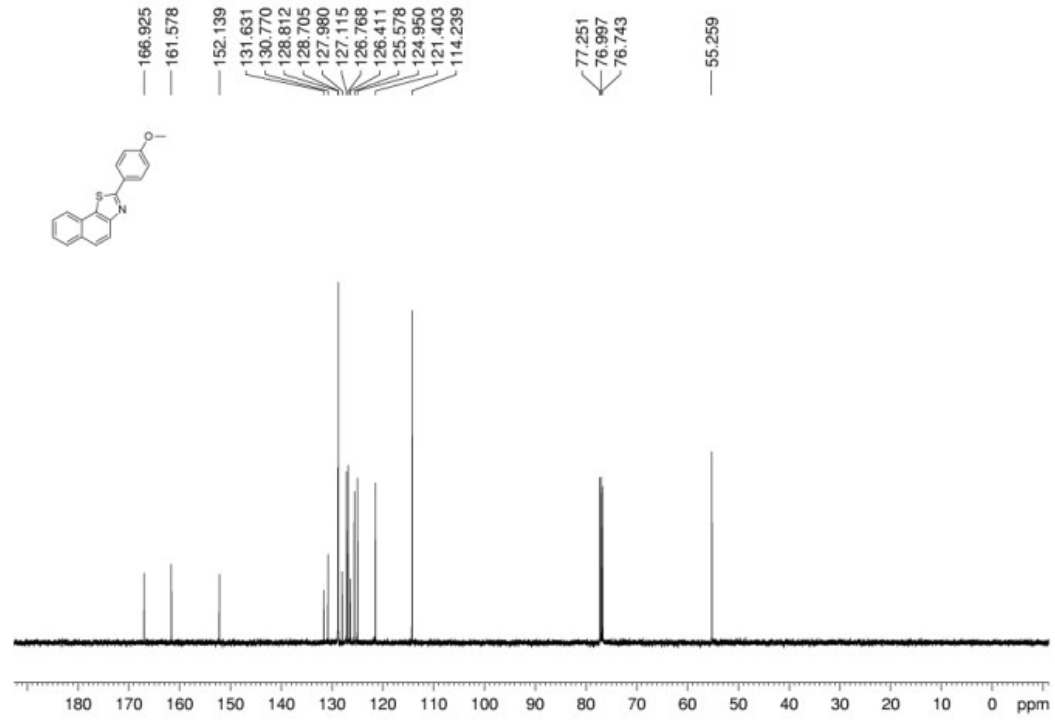
^{1}H and ^{13}C Spectrum of Compound **2b**



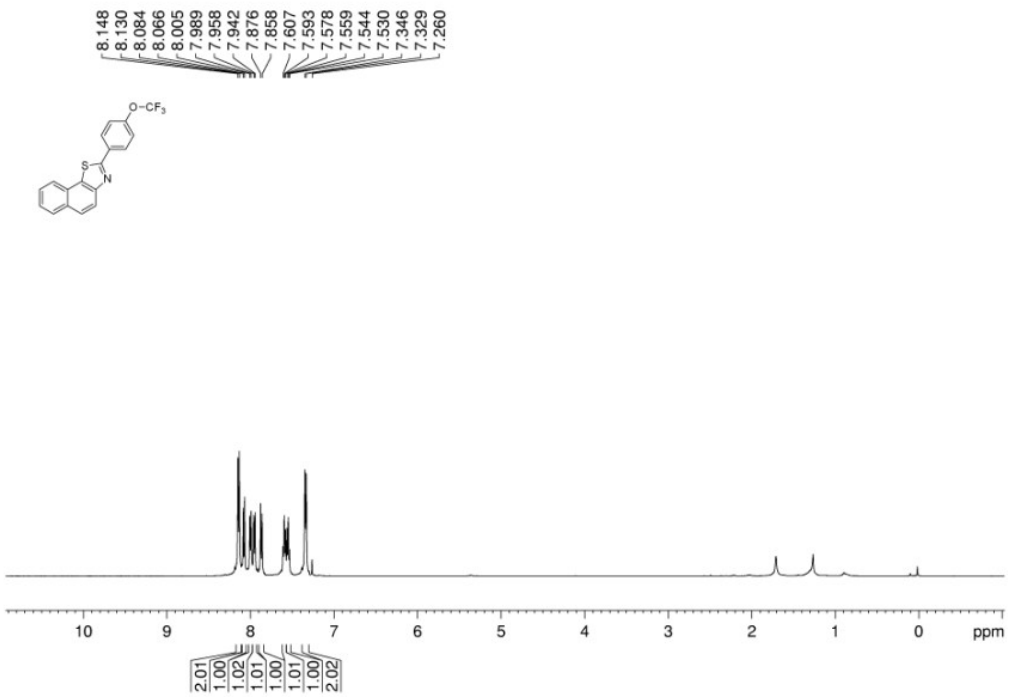


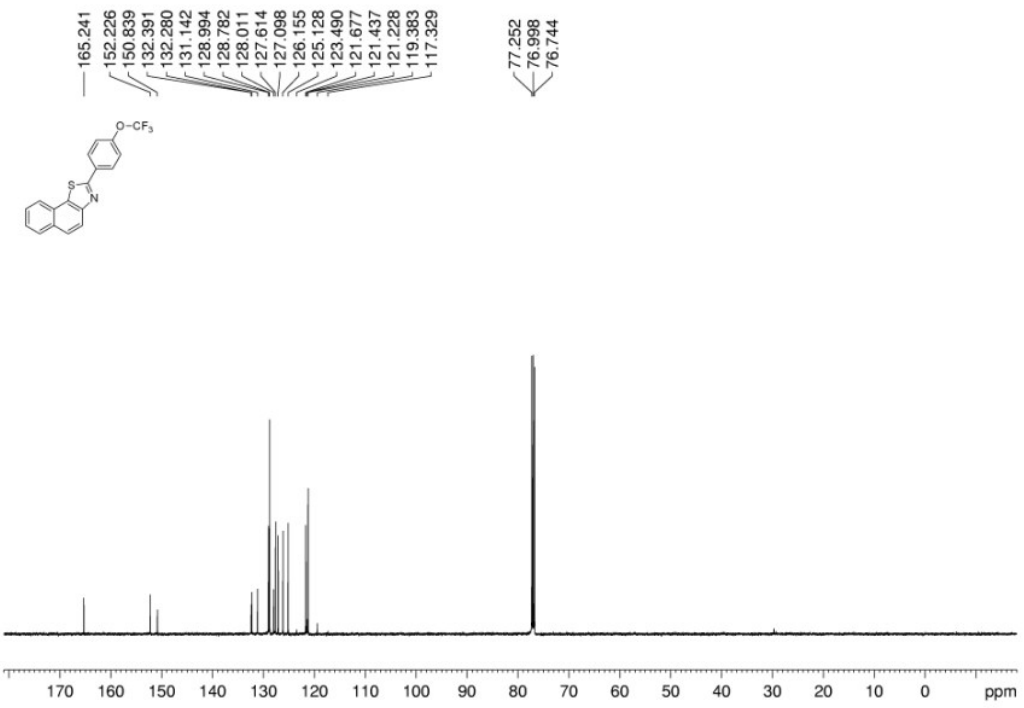
^{1}H and ^{13}C Spectrum of Compound **2c**



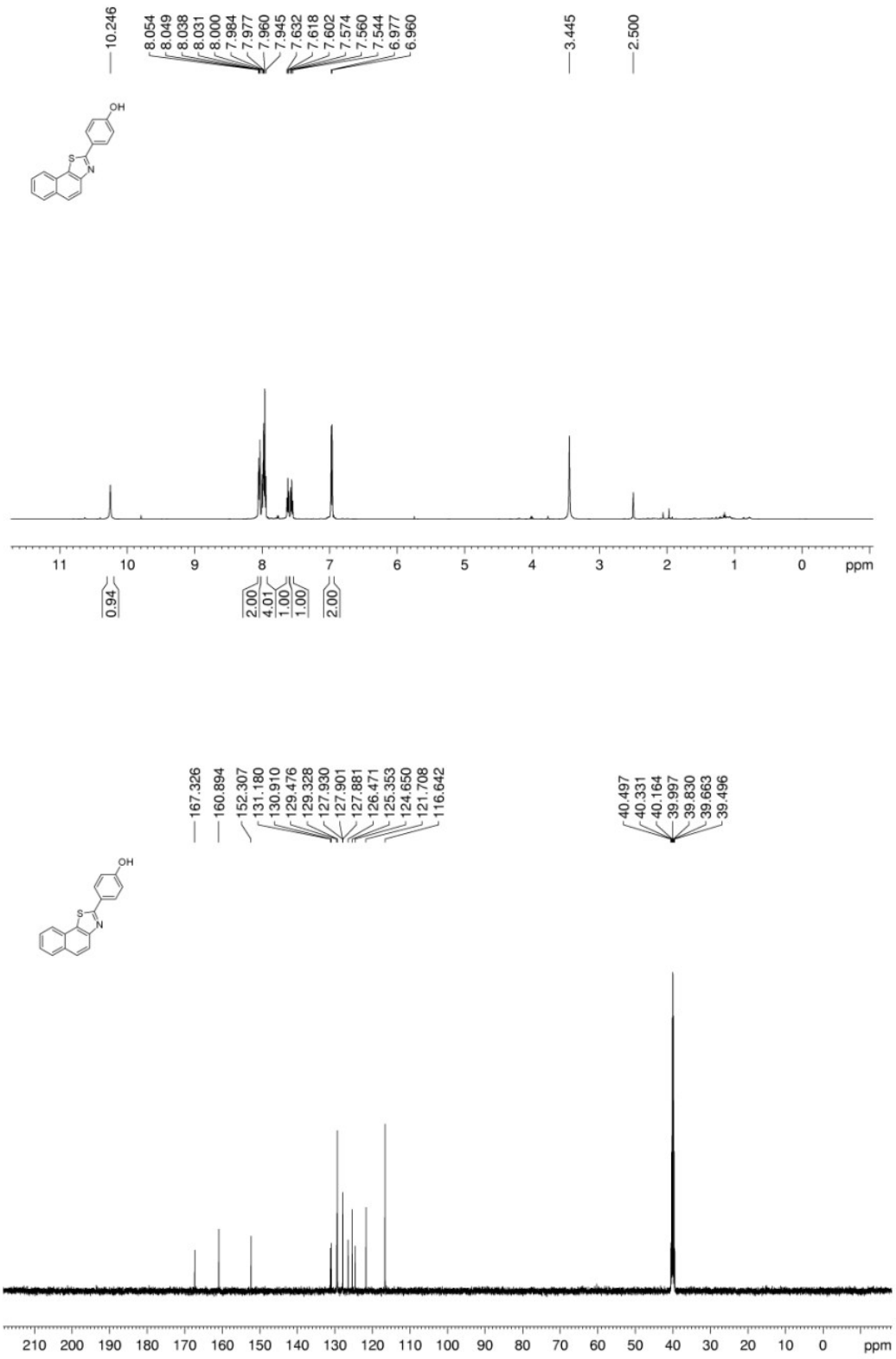


^{1}H and ^{13}C Spectrum of Compound **2d**

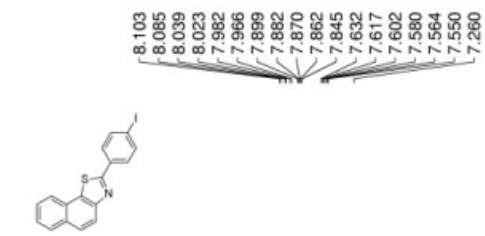


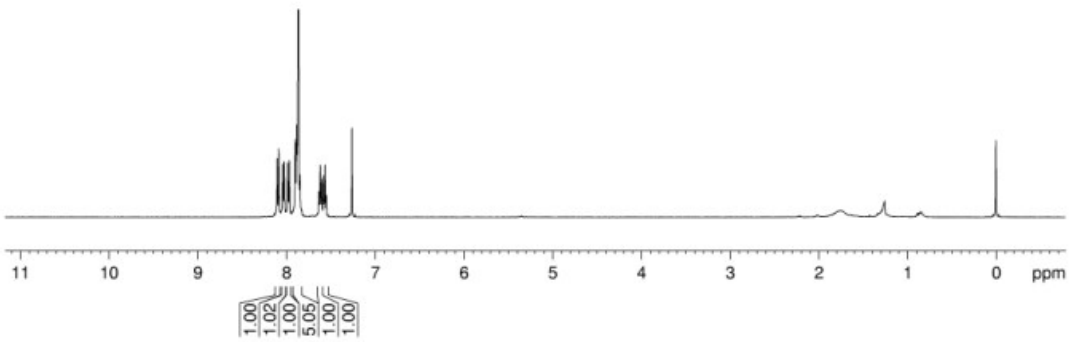


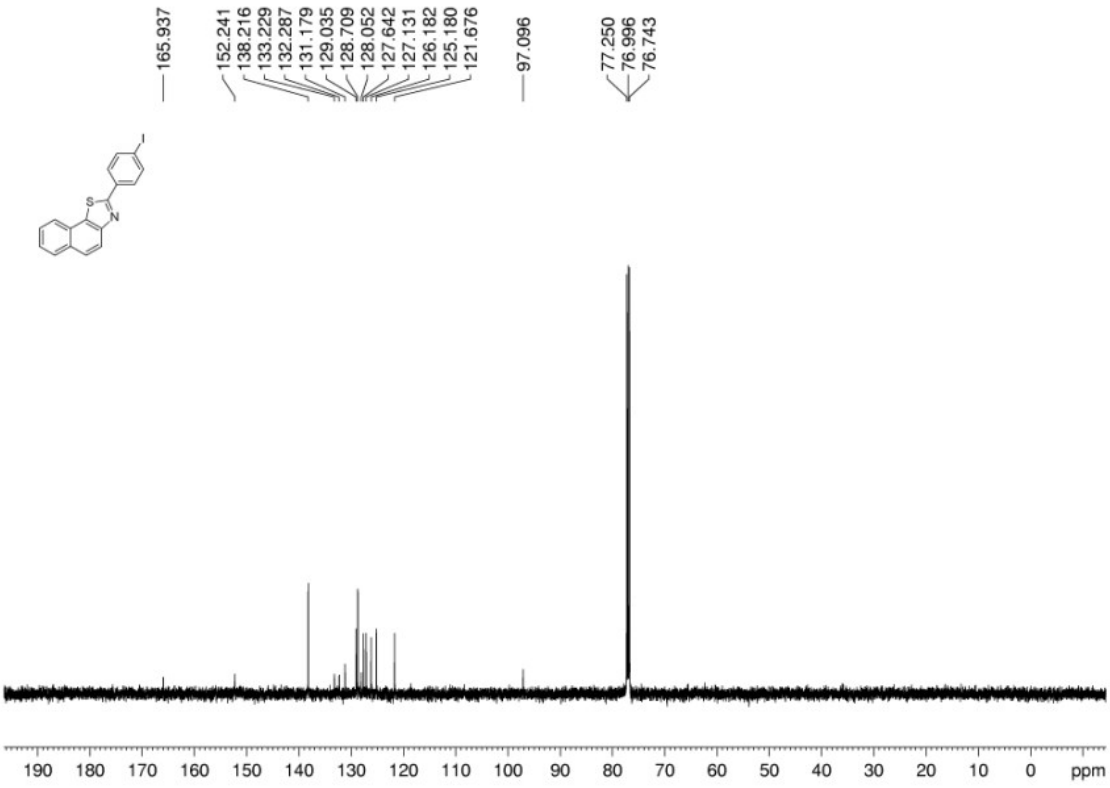
^{1}H and ^{13}C Spectrum of Compound **2e**



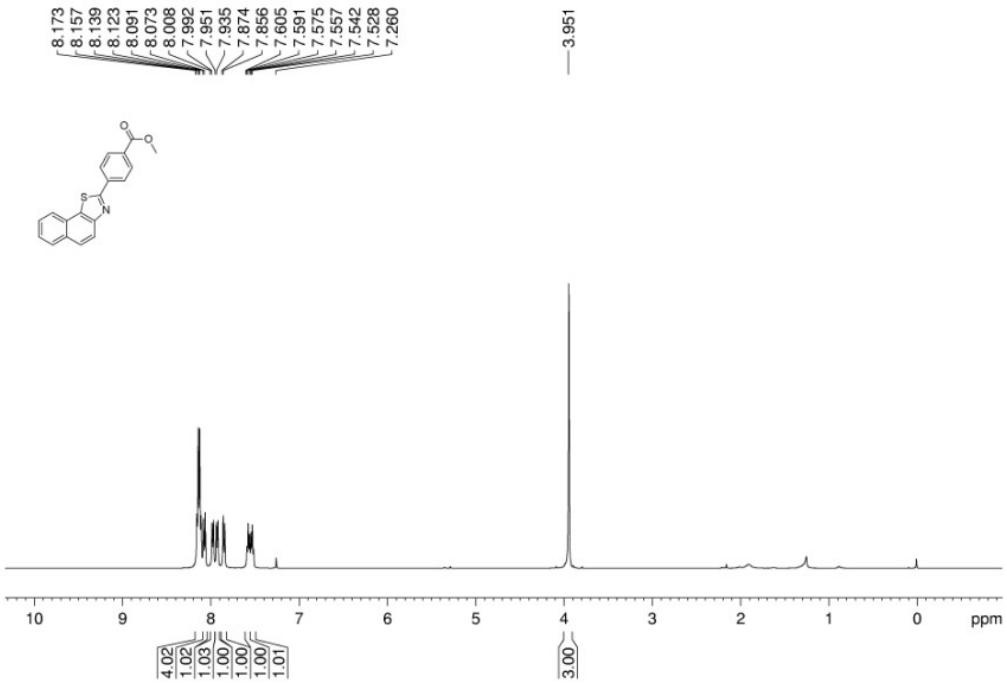
^{1}H and ^{13}C Spectrum of Compound **2f**

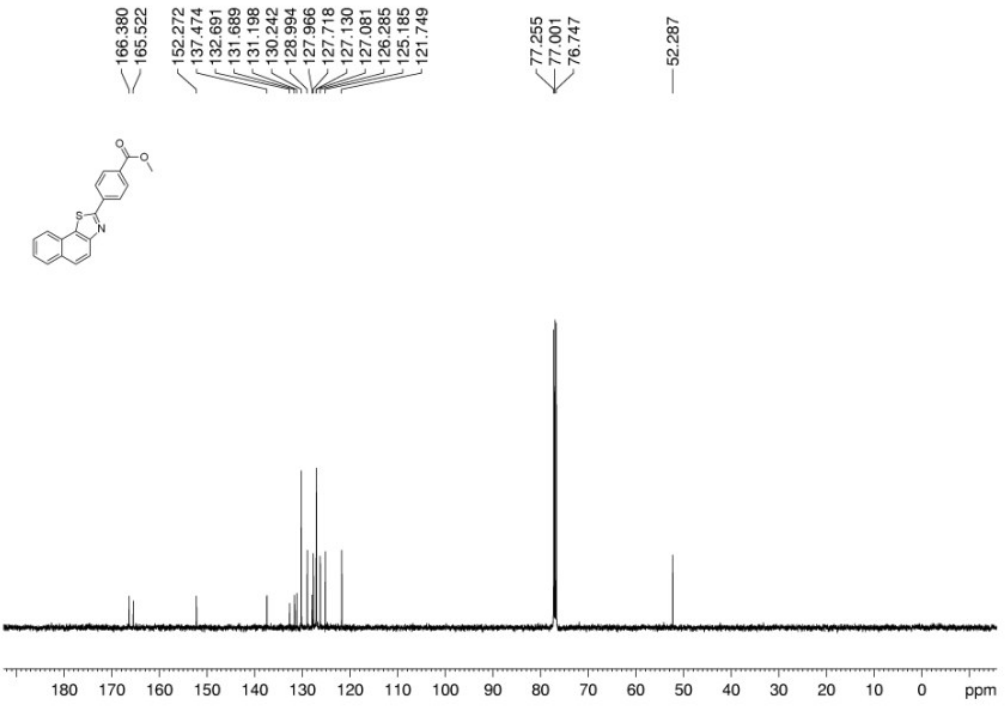




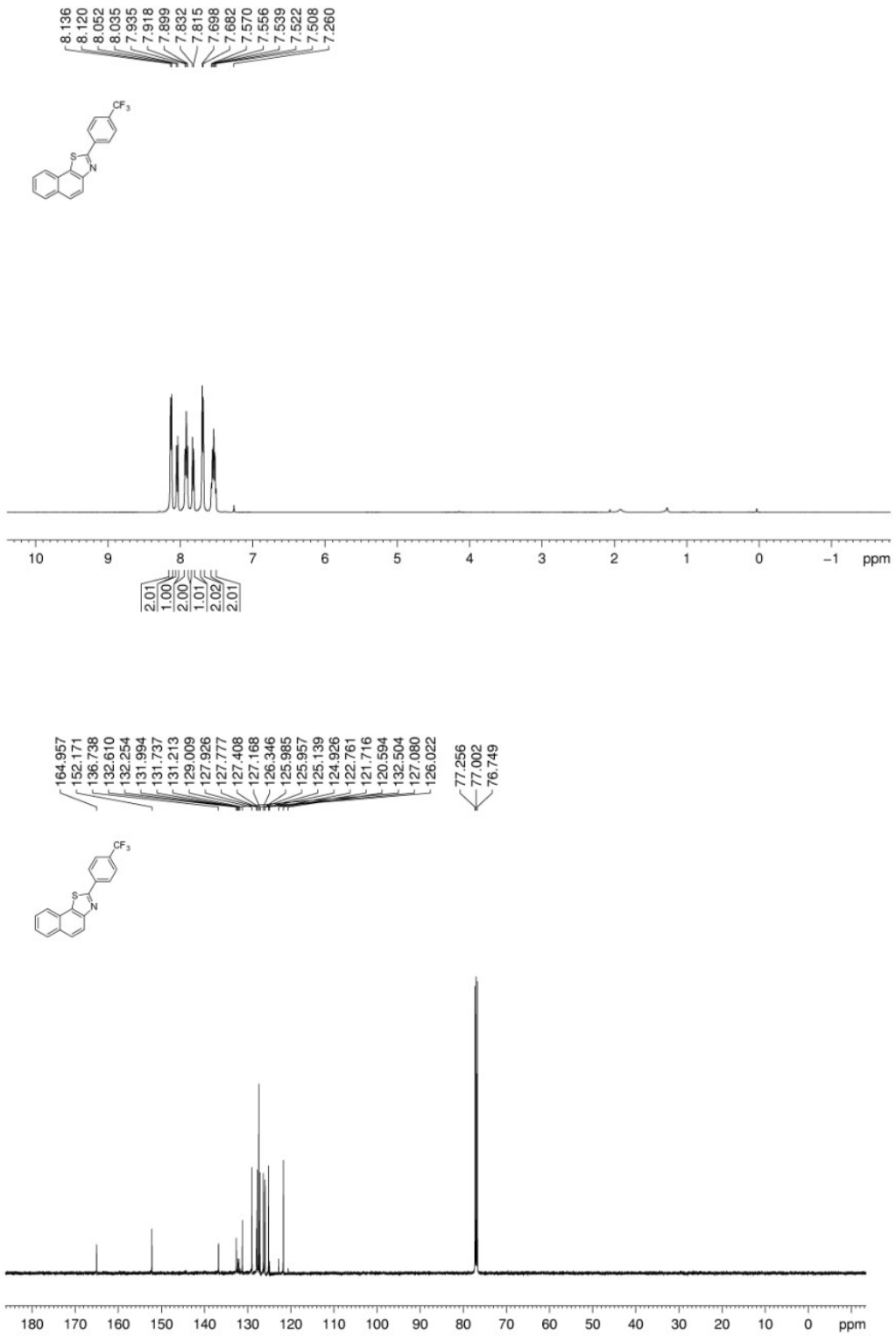


^{1}H and ^{13}C Spectrum of Compound **2g**

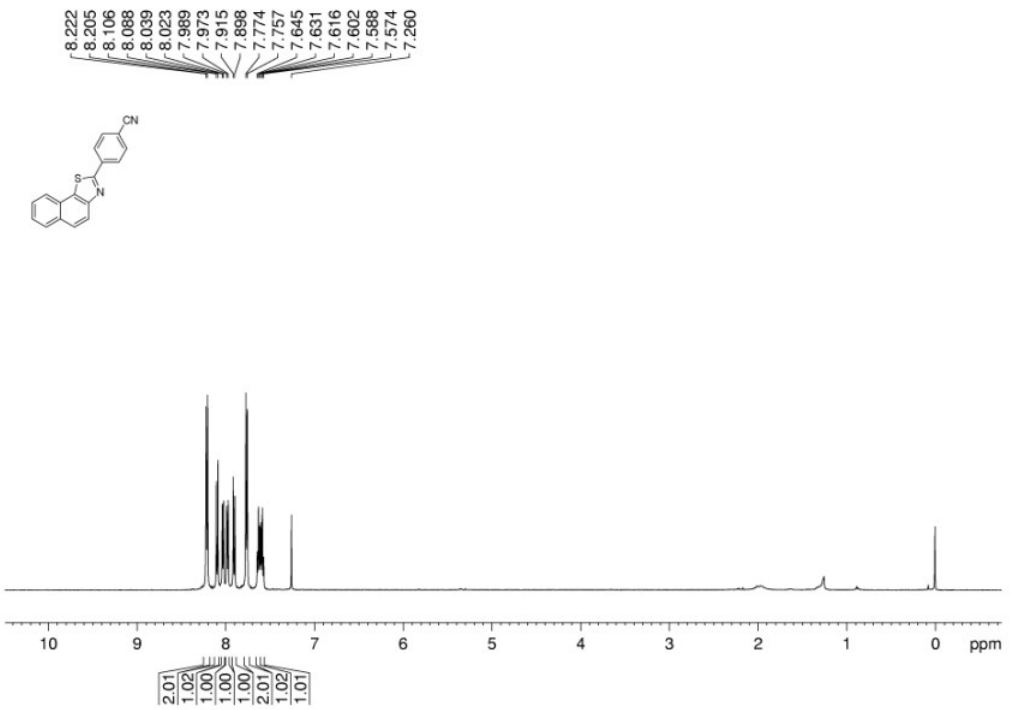


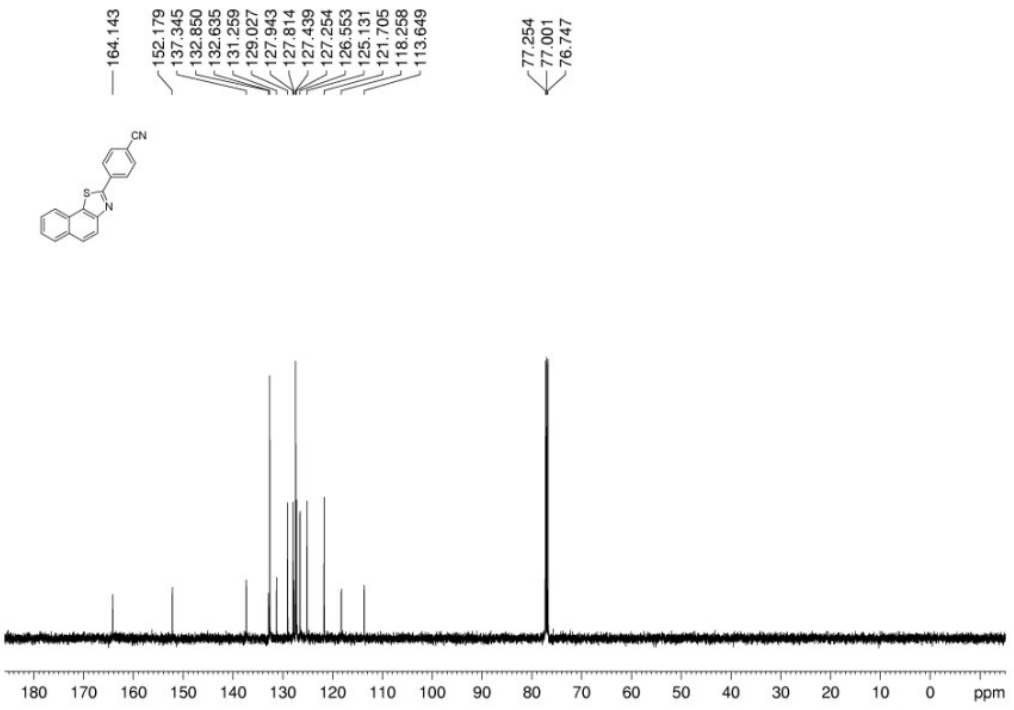


^{1}H and ^{13}C Spectrum of Compound **2h**

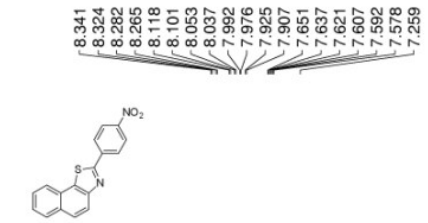


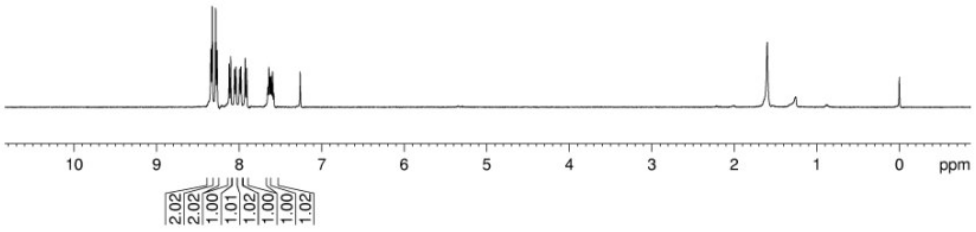
^{1}H and ^{13}C Spectrum of Compound **2i**

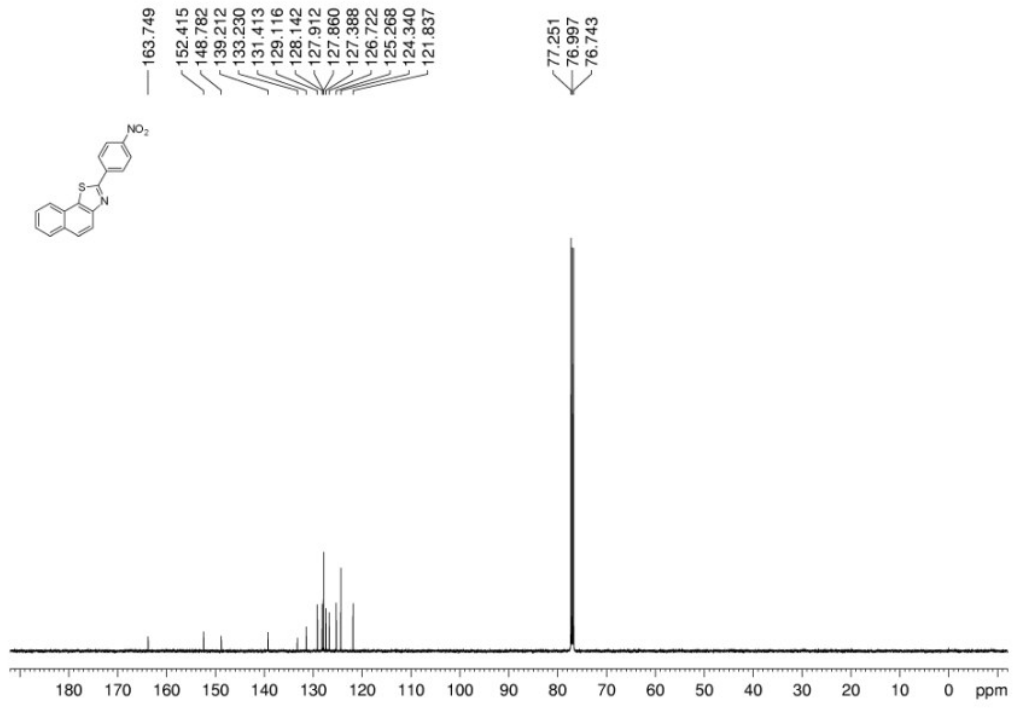




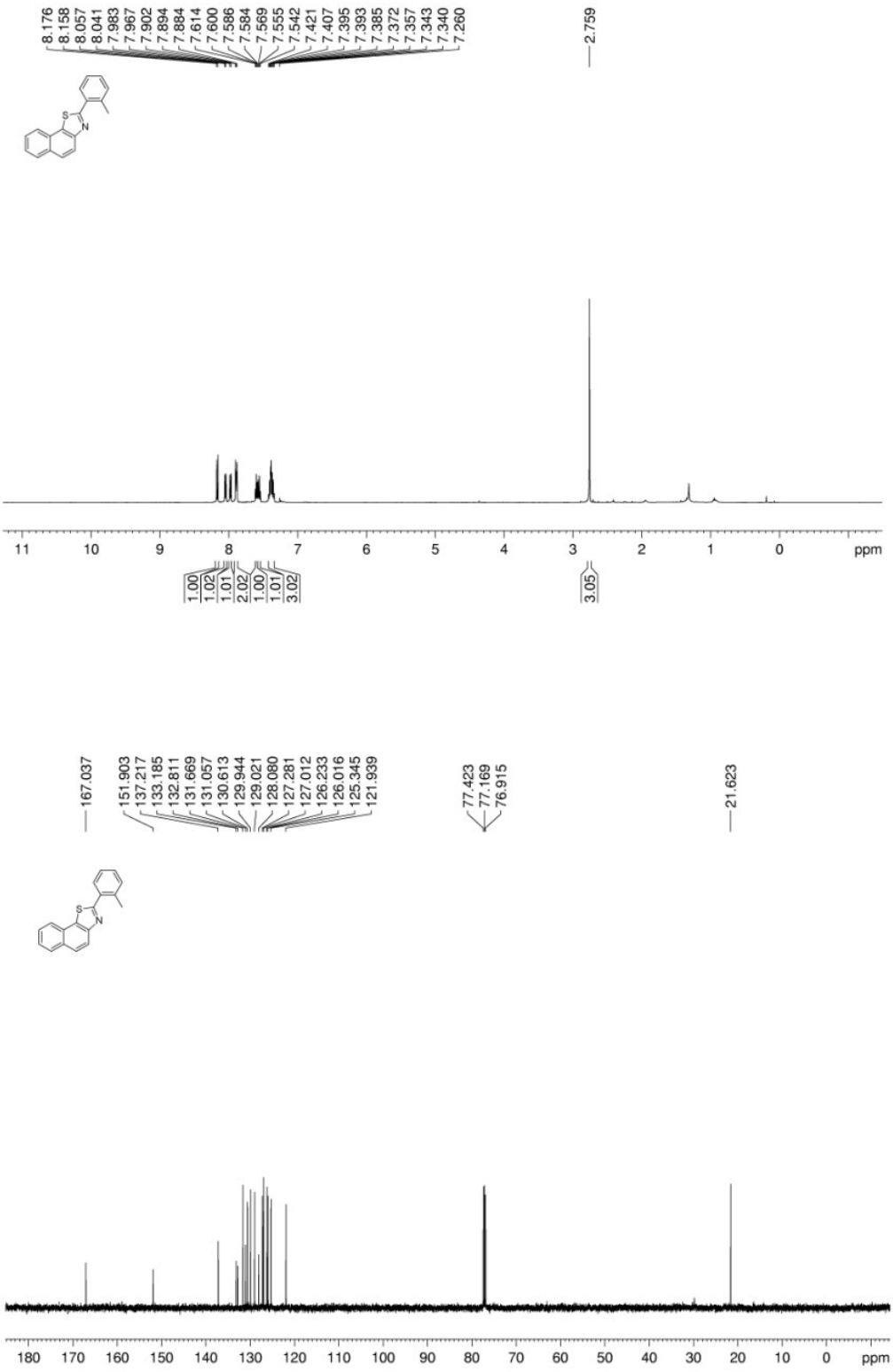
^{1}H and ^{13}C Spectrum of Compound **2j**



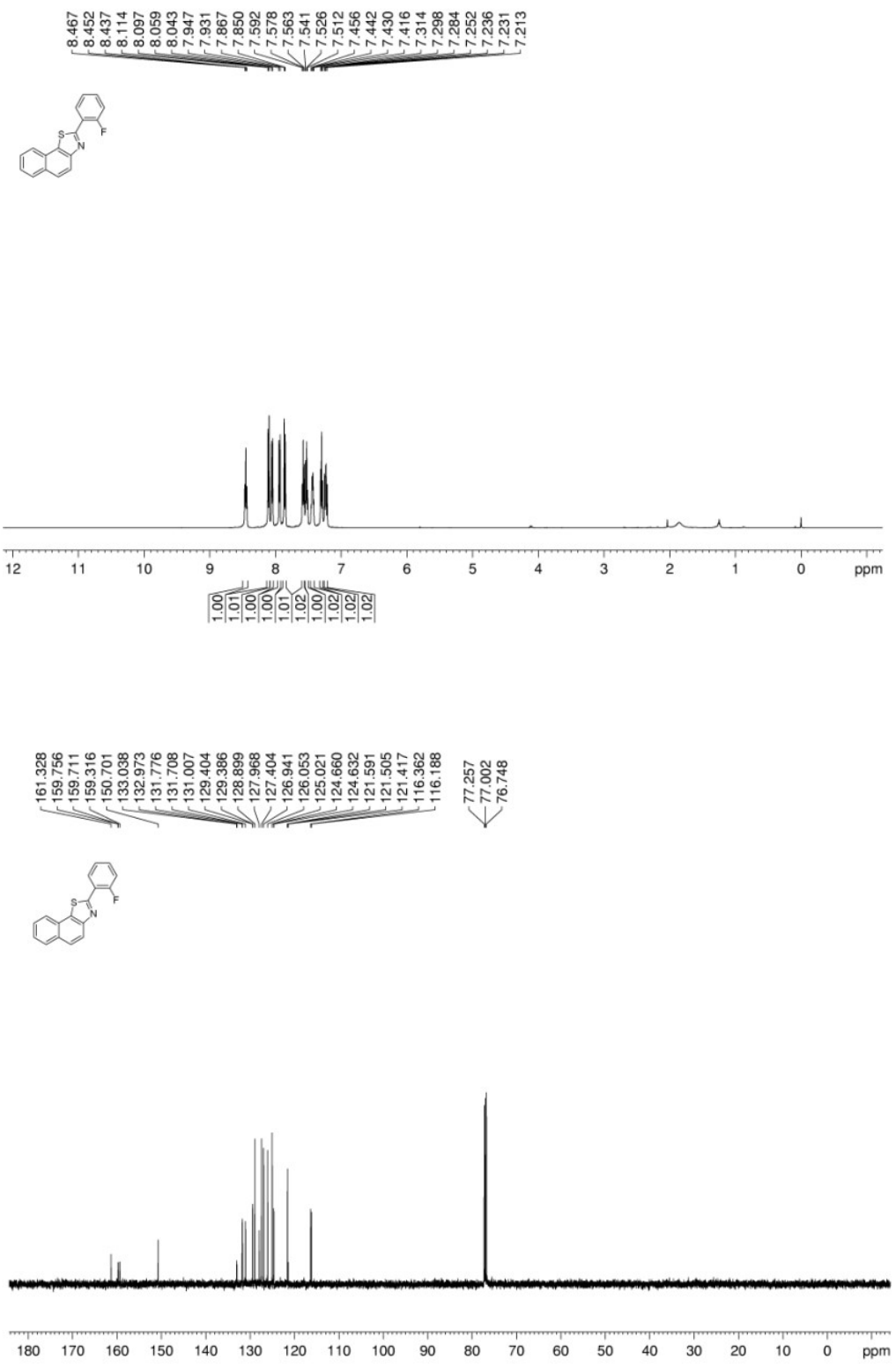




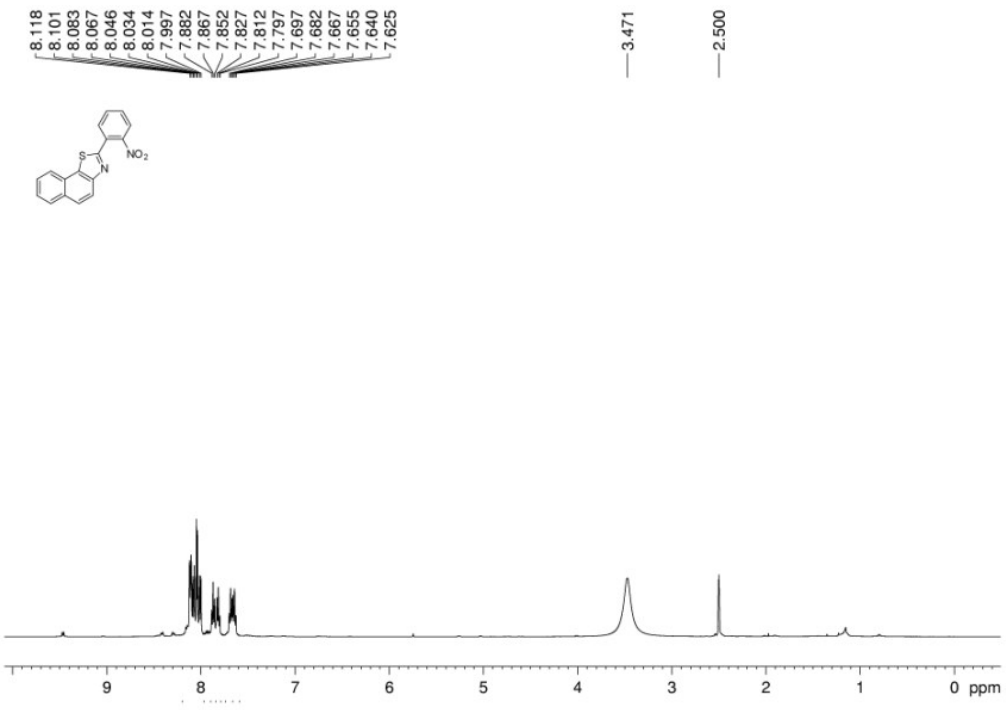
^{1}H and ^{13}C Spectrum of Compound **2k**

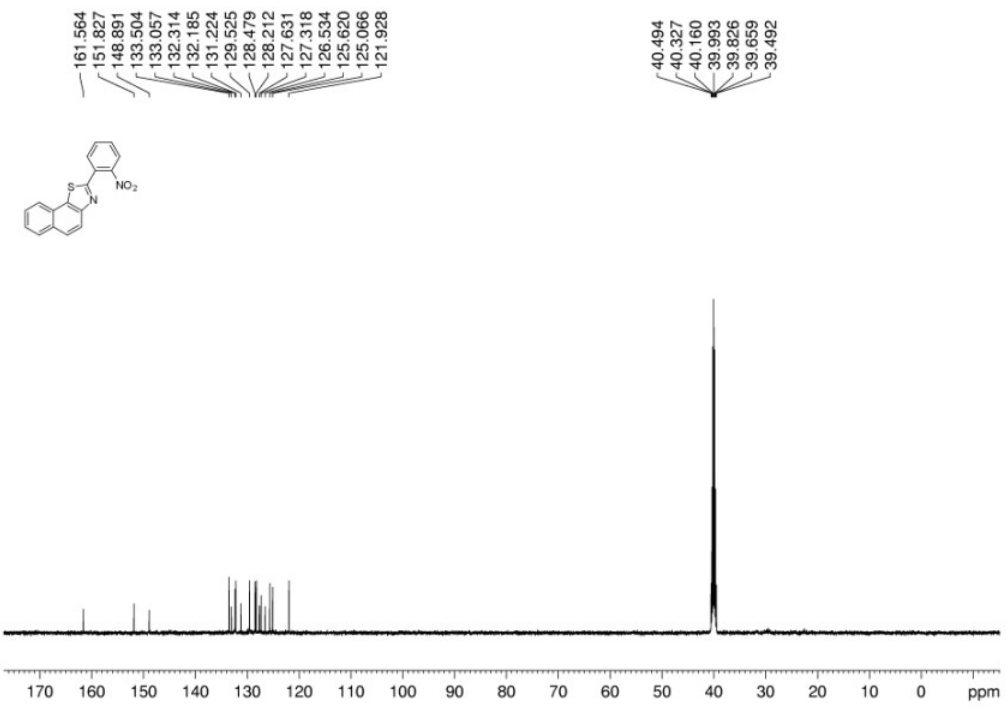


^{1}H and ^{13}C Spectrum of Compound **2l**

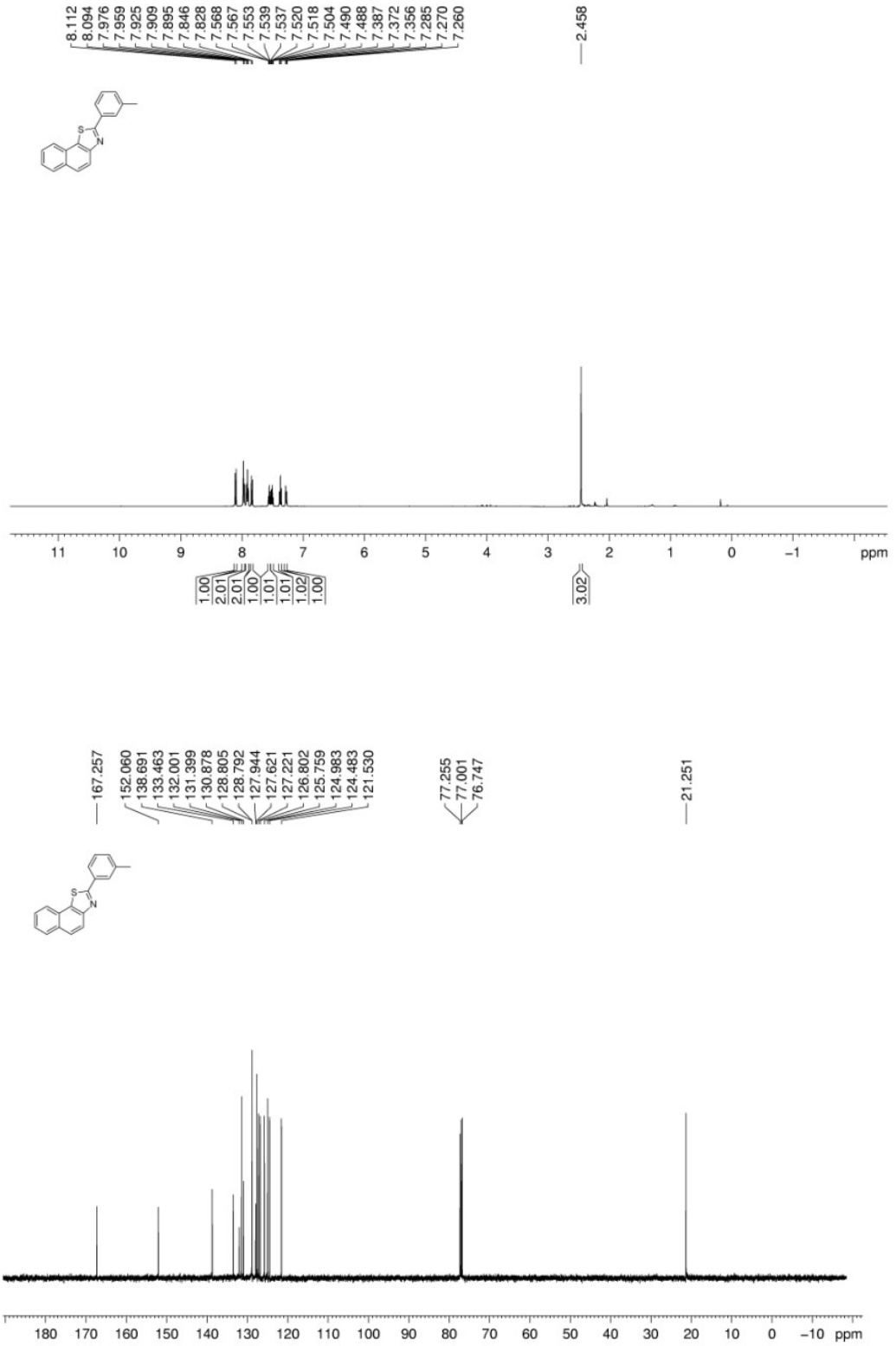


^{1}H and ^{13}C Spectrum of Compound **2m**

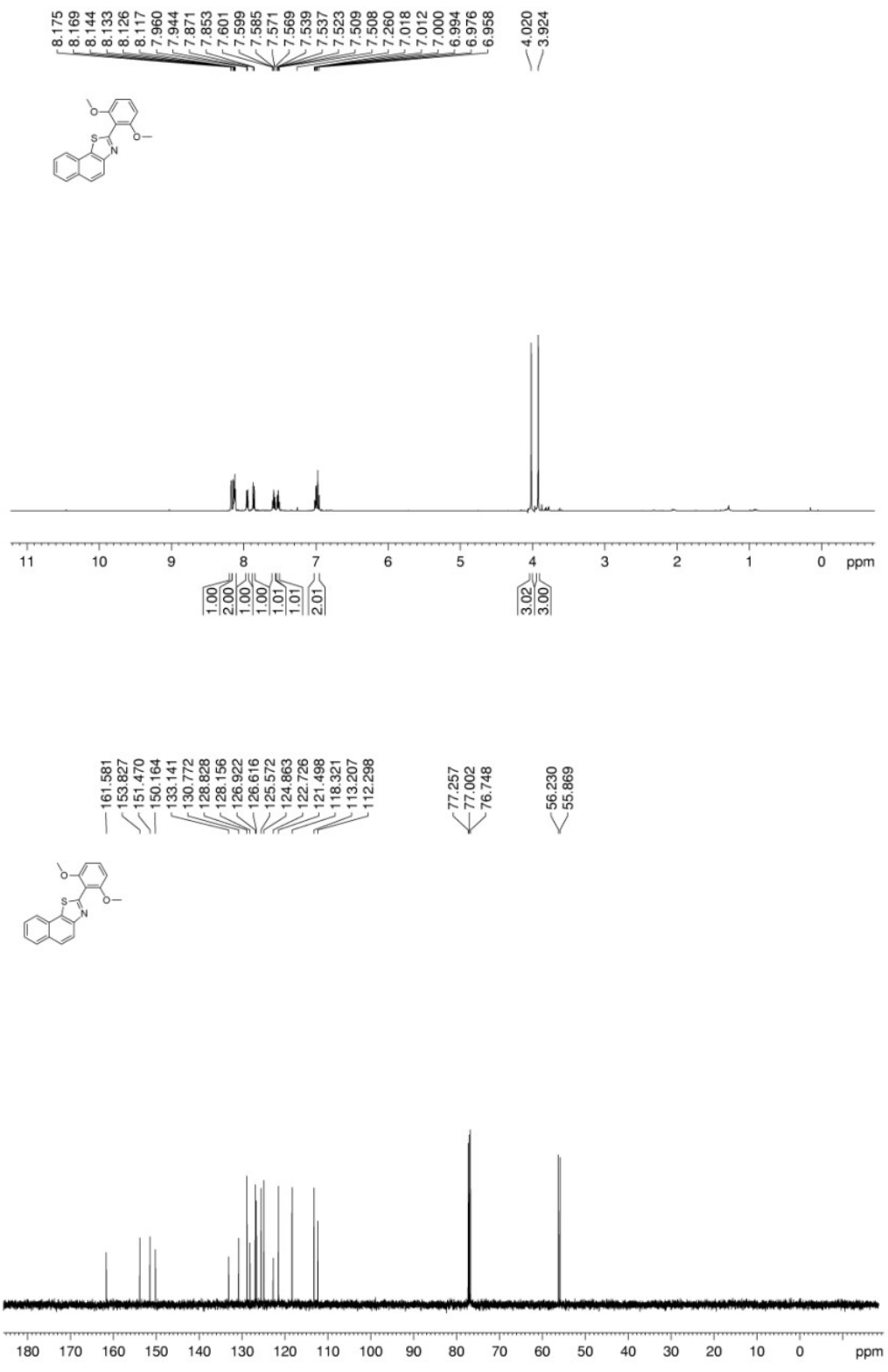




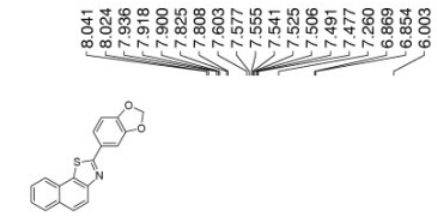
^{1}H and ^{13}C Spectrum of Compound **2n**

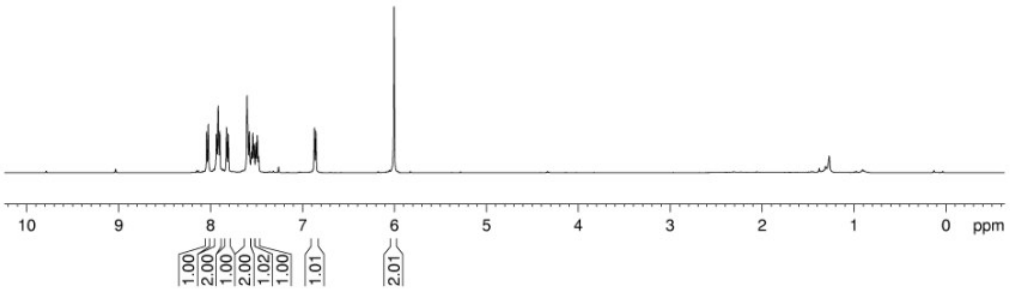


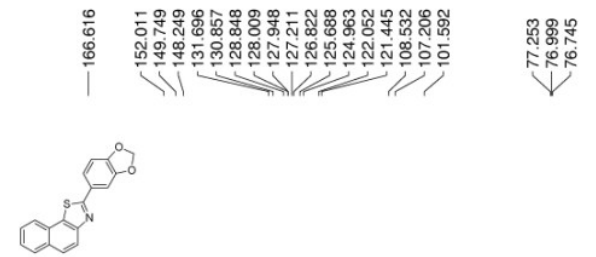
^{1}H and ^{13}C Spectrum of Compound **2o**

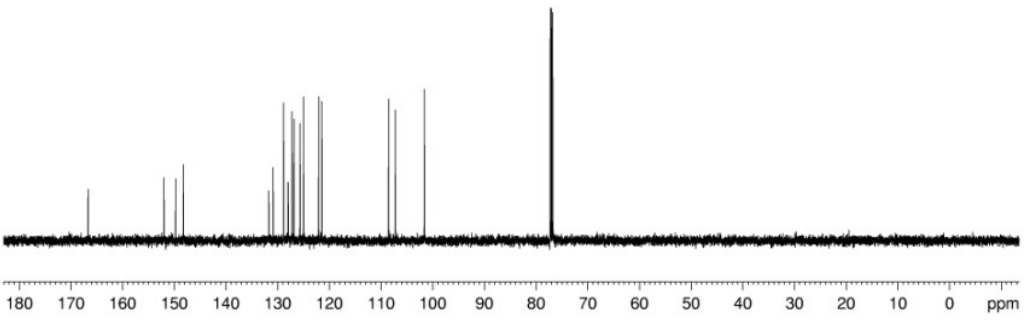


^{1}H and ^{13}C Spectrum of Compound **2p**

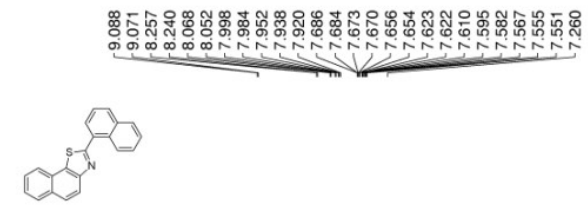


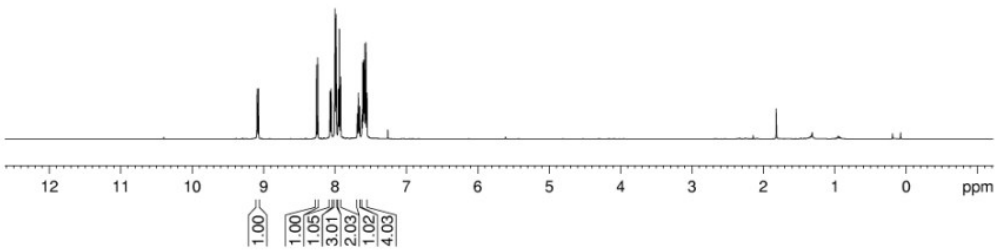


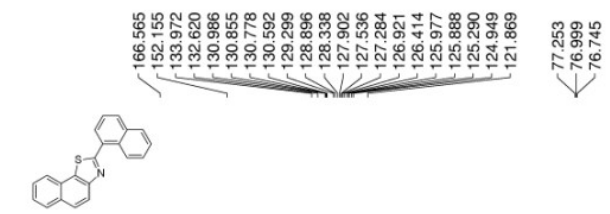


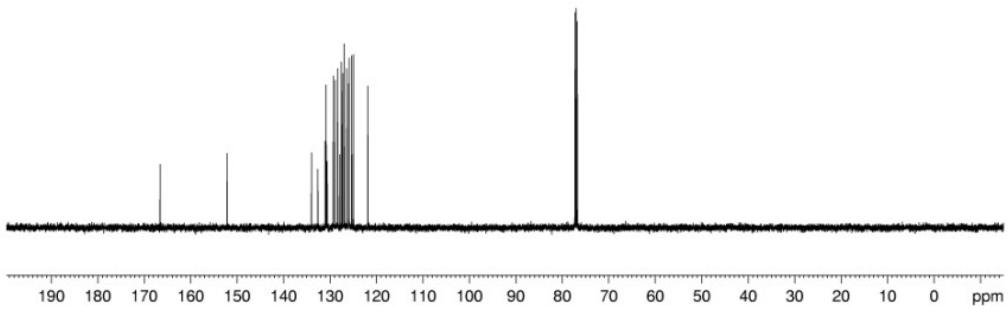


^{1}H and ^{13}C Spectrum of Compound **2q**

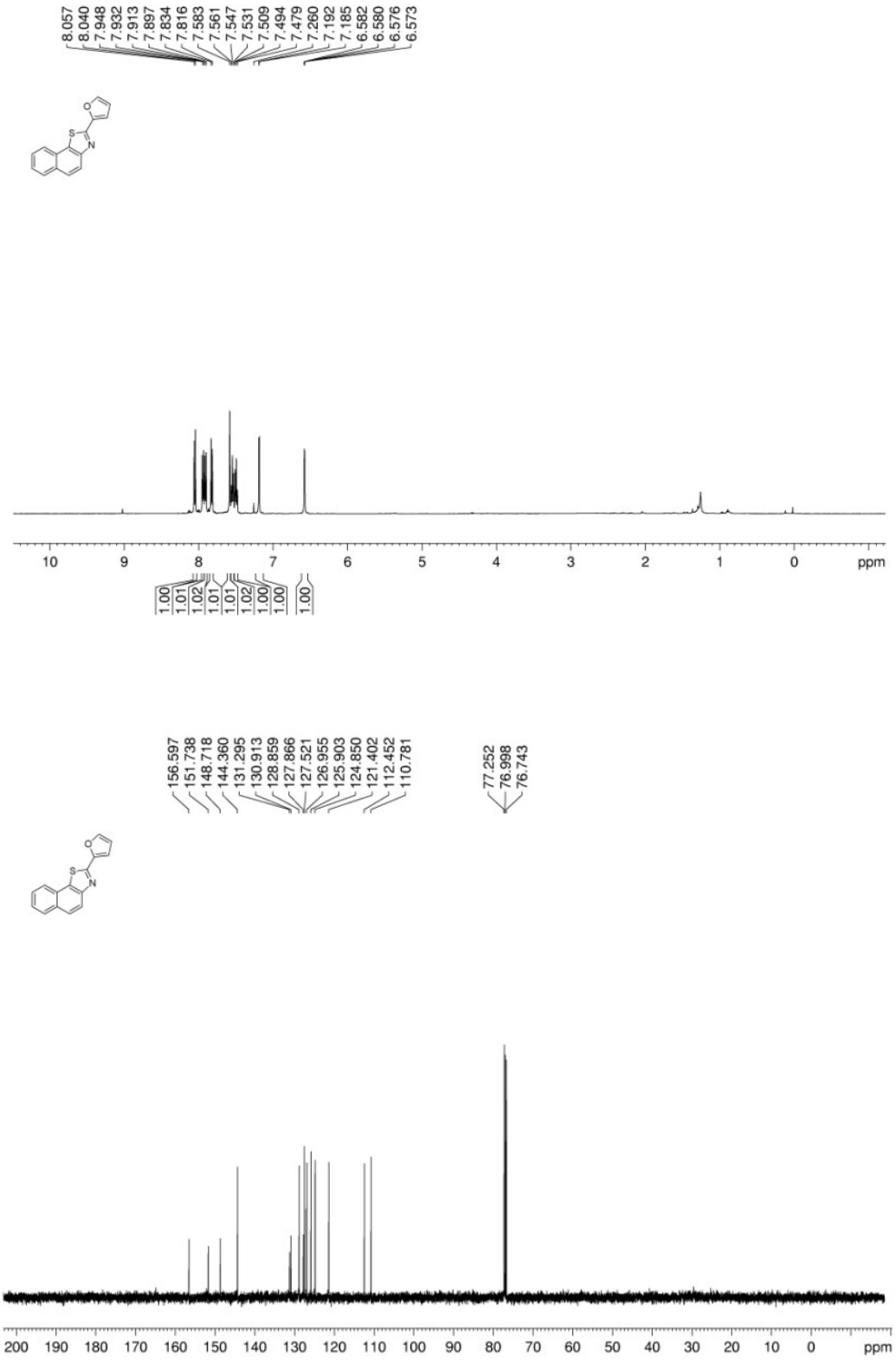




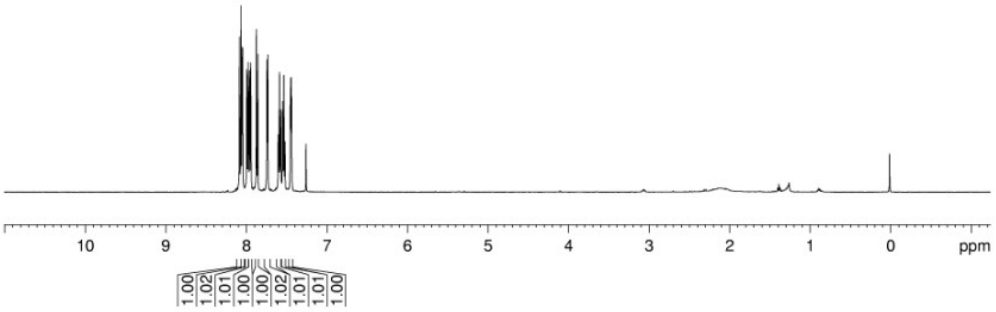


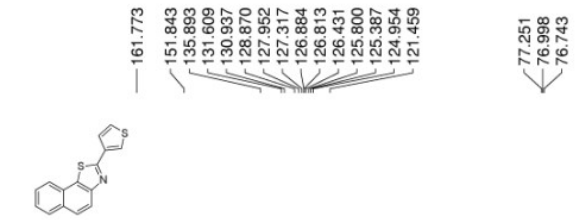


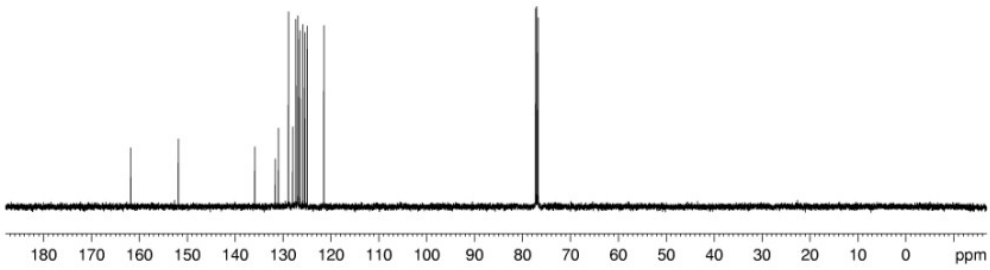
^{1}H and ^{13}C Spectrum of Compound **2r**



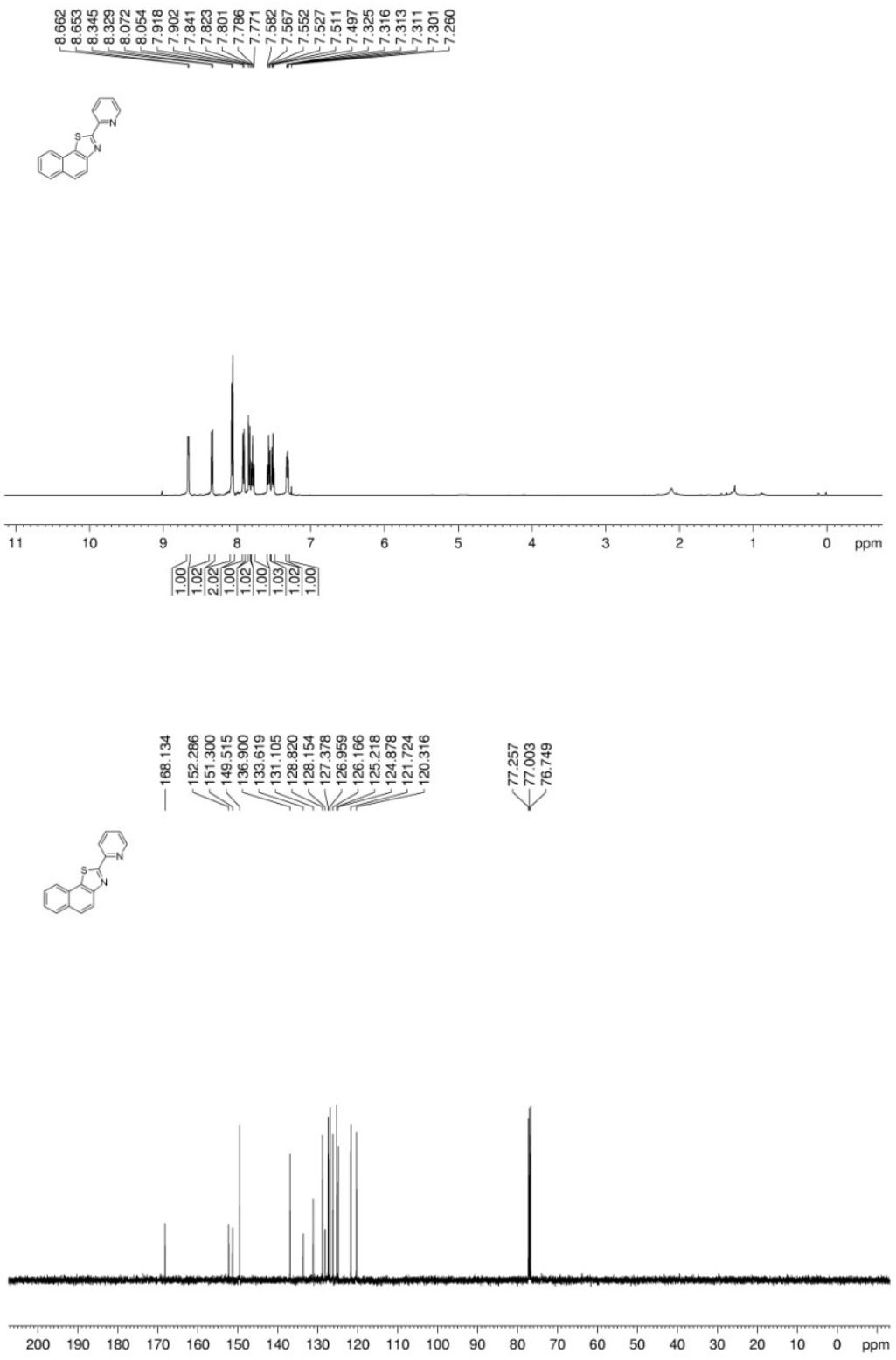
^{1}H and ^{13}C Spectrum of Compound **2s**



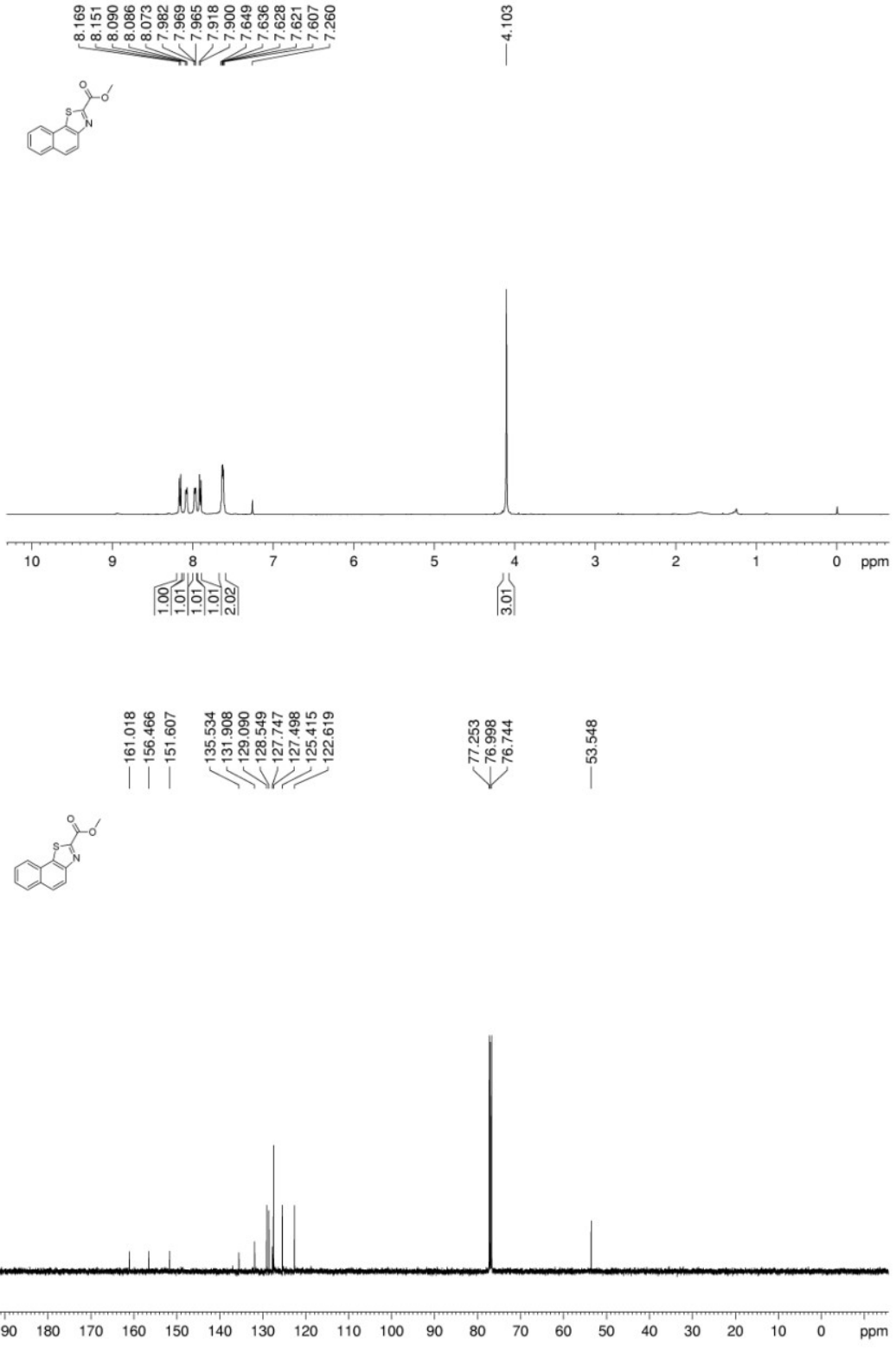




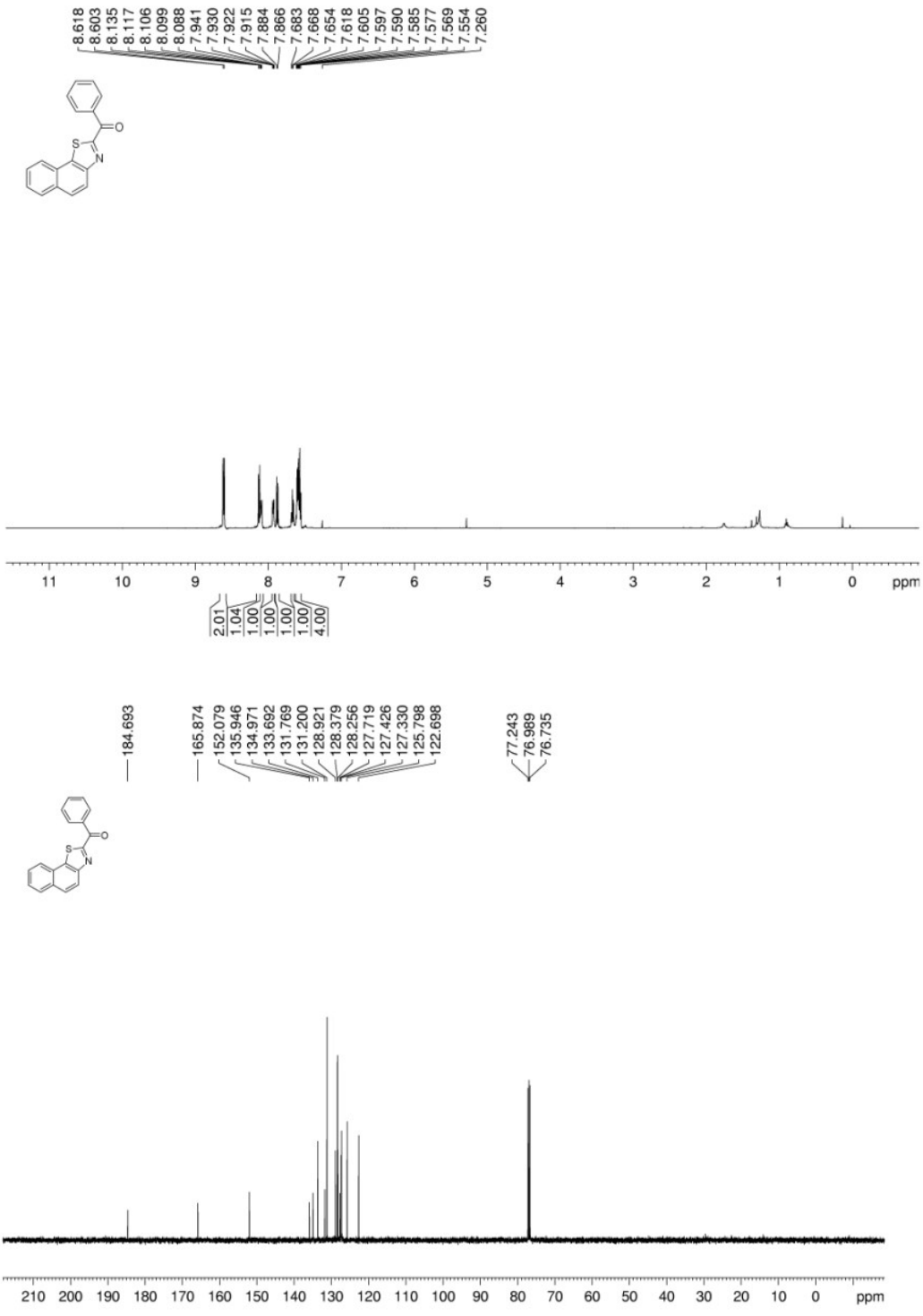
^{1}H and ^{13}C Spectrum of Compound **2t**



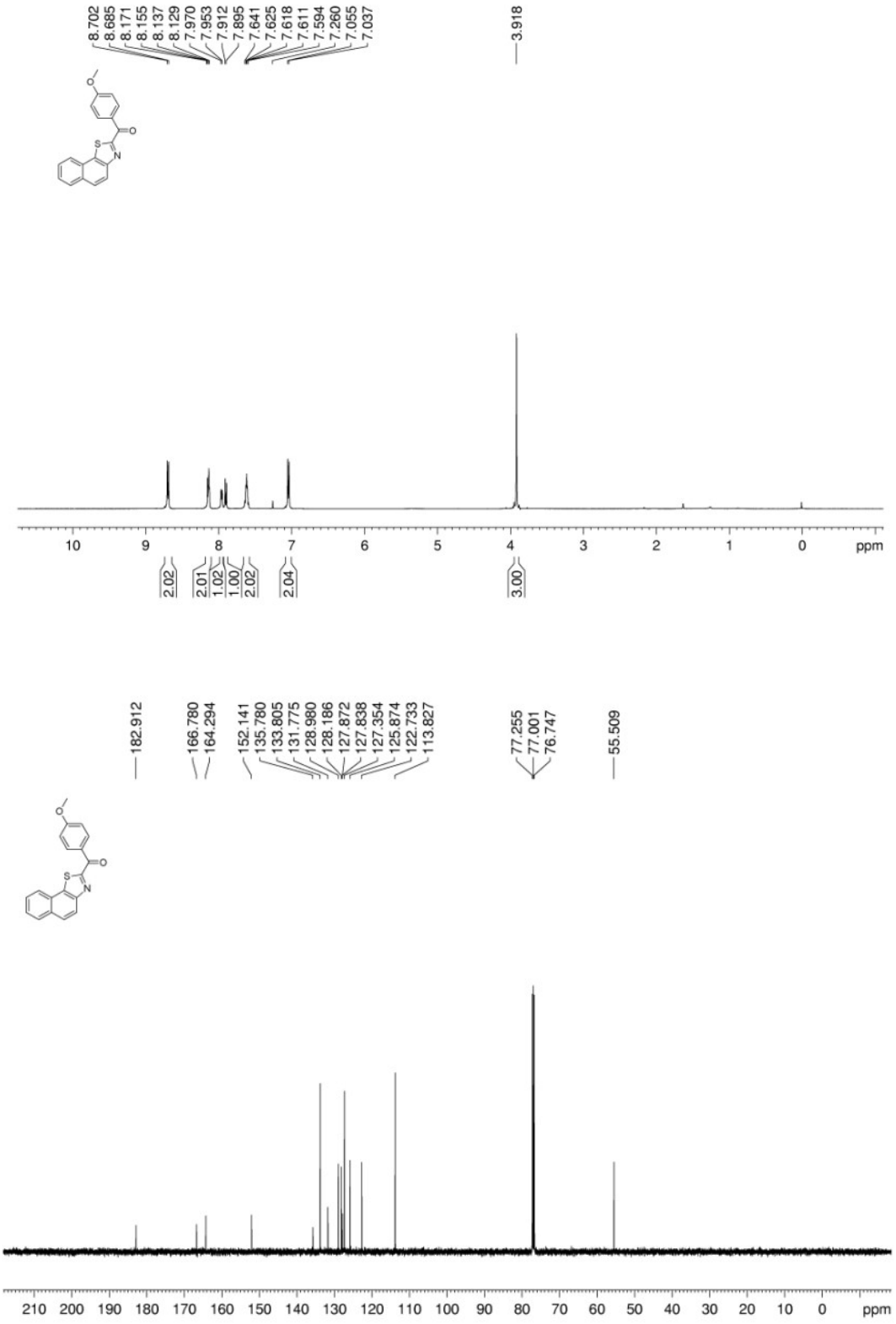
^{1}H and ^{13}C Spectrum of Compound **2u**



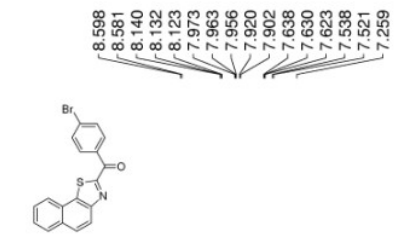
^{1}H and ^{13}C Spectrum of Compound **2v**

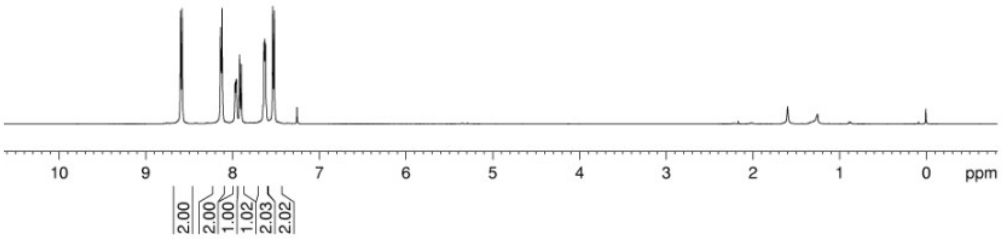


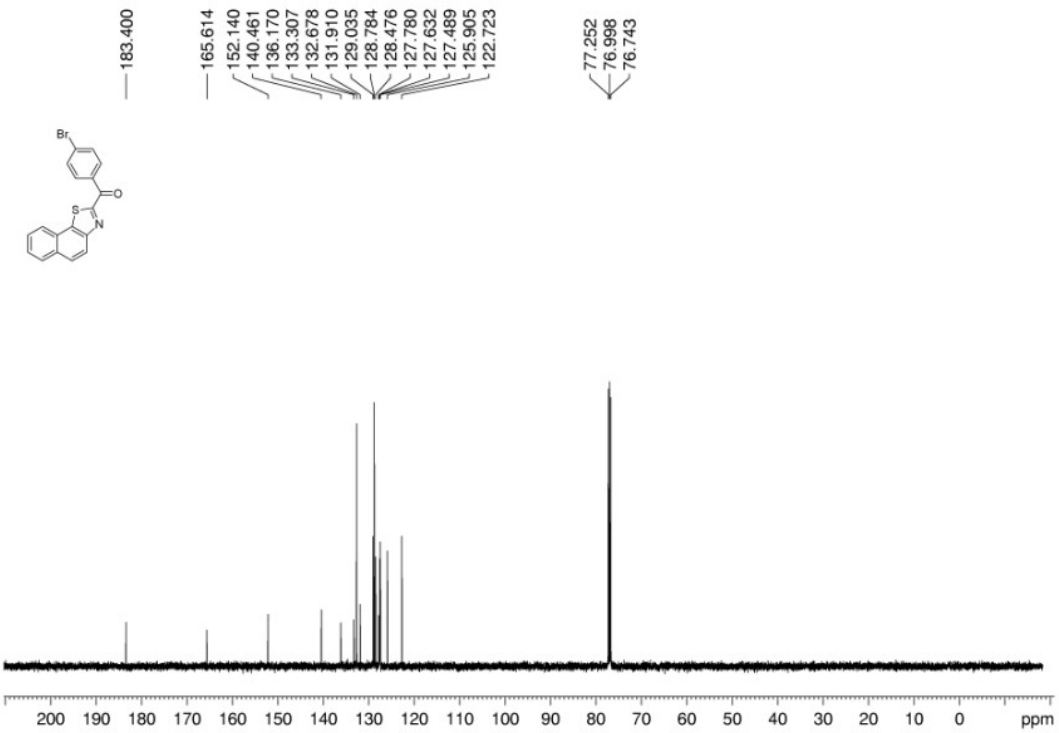
^{1}H and ^{13}C Spectrum of Compound **2w**



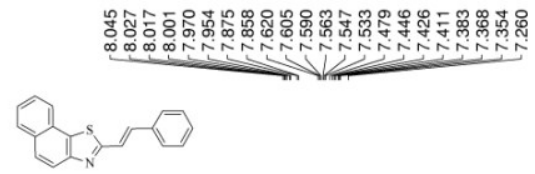
^{1}H and ^{13}C Spectrum of Compound **2x**

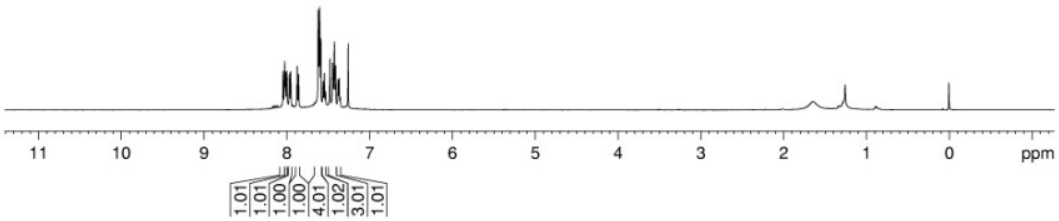


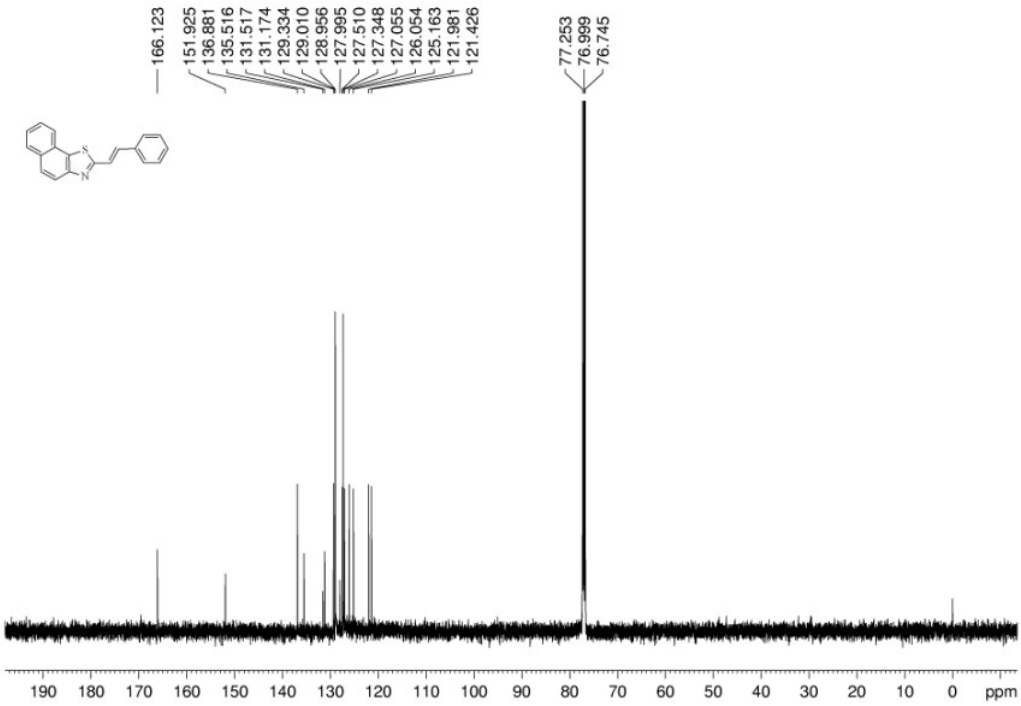




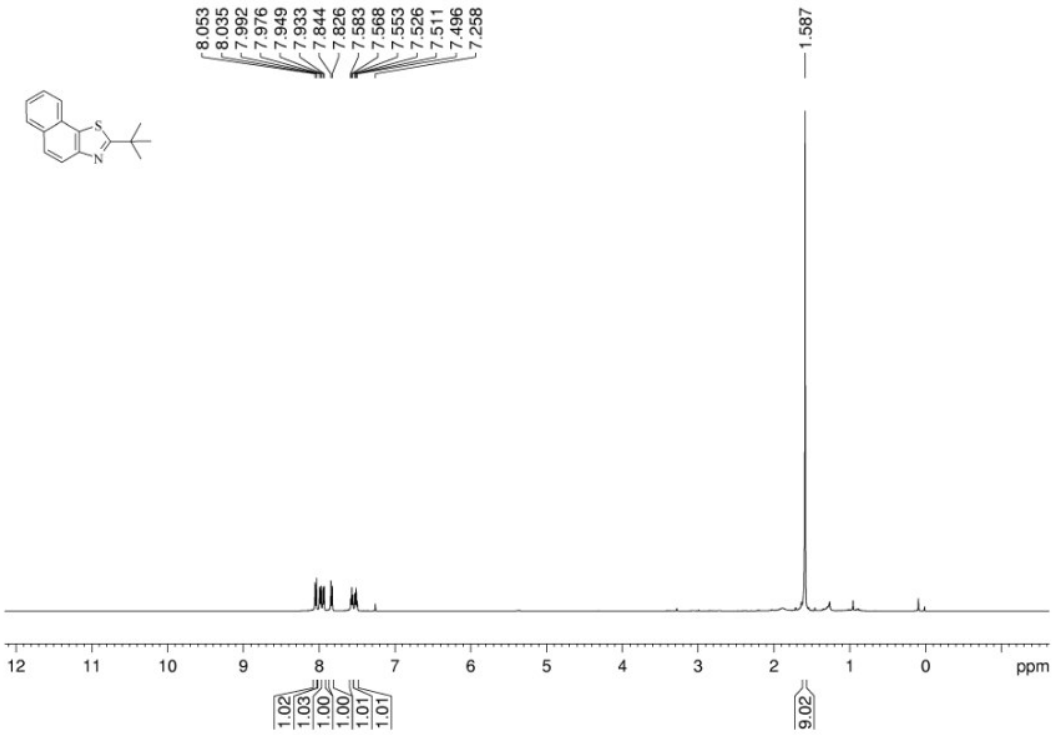
^{1}H and ^{13}C Spectrum of Compound **2y**

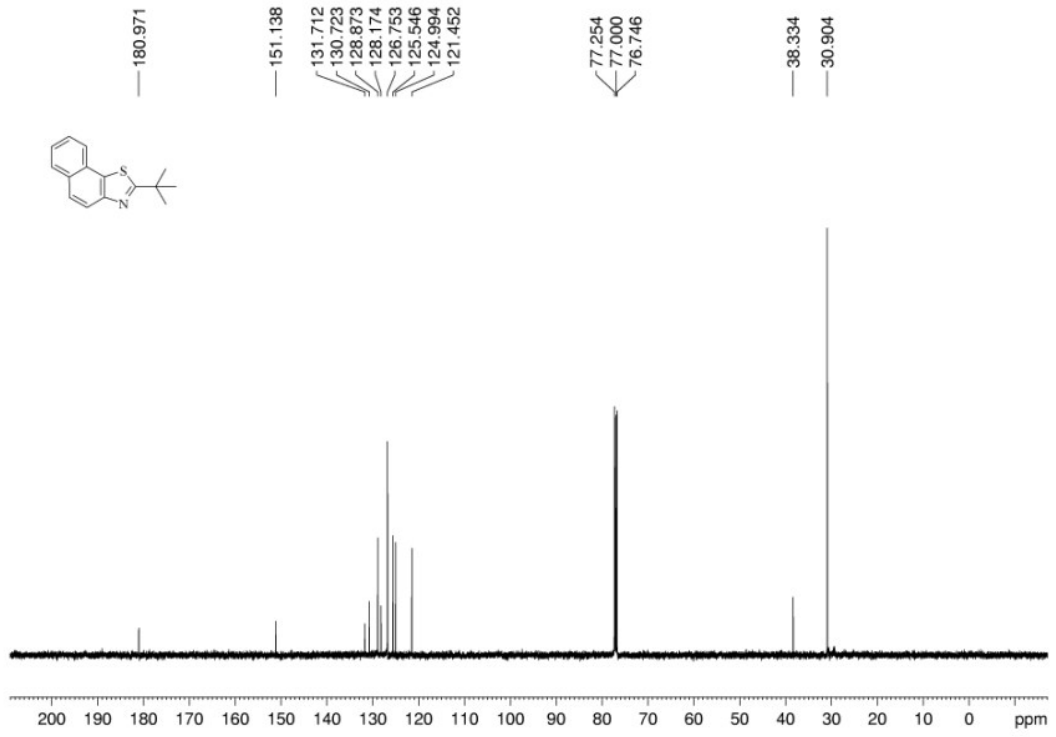




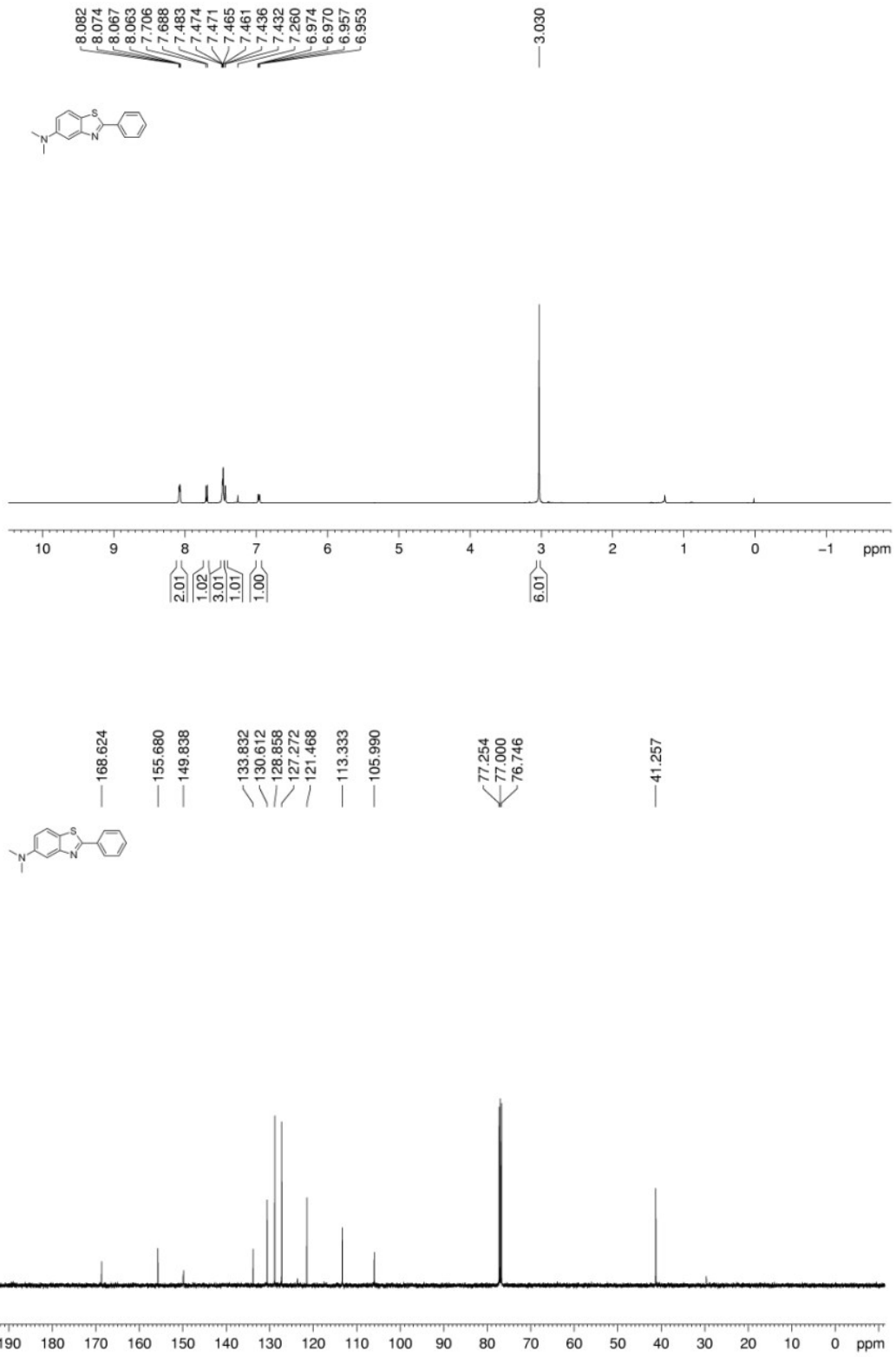


^{1}H and ^{13}C Spectrum of Compound **2z**

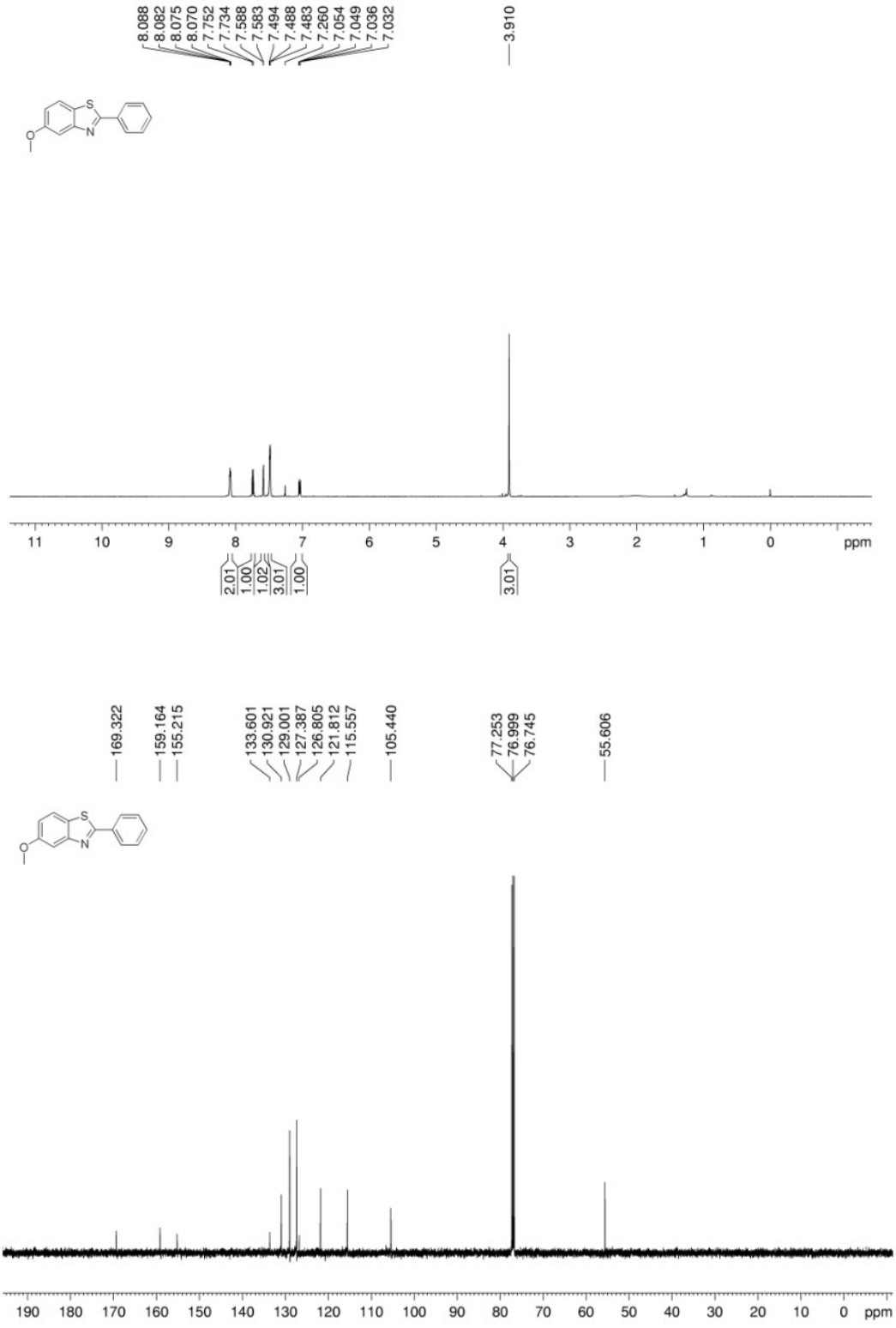




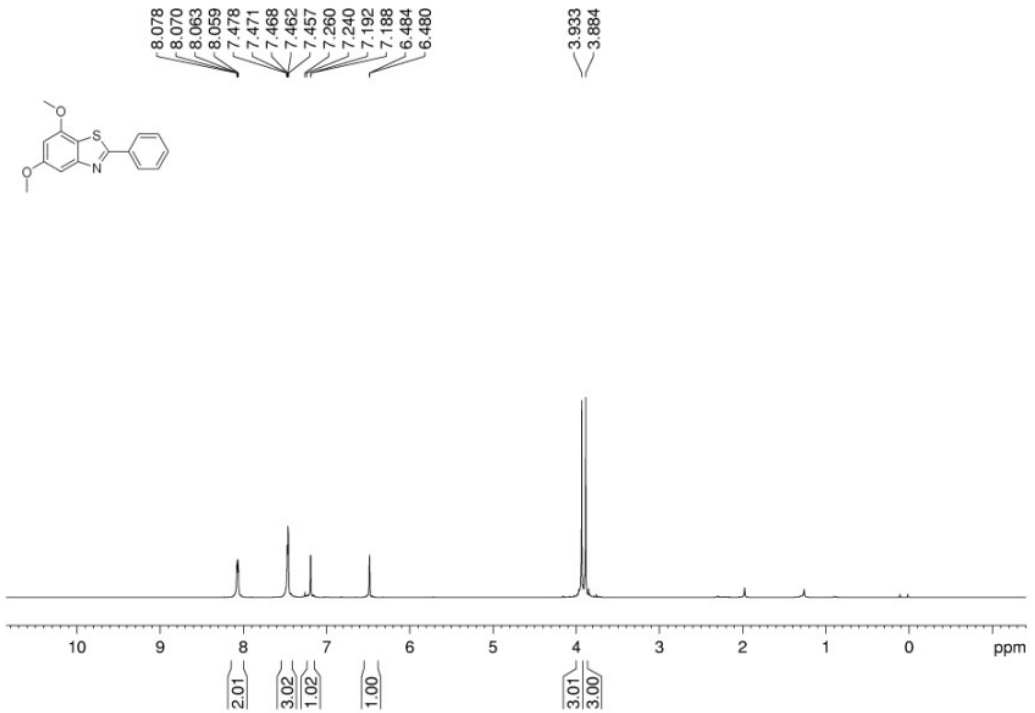
^{1}H and ^{13}C Spectrum of Compound **4a**

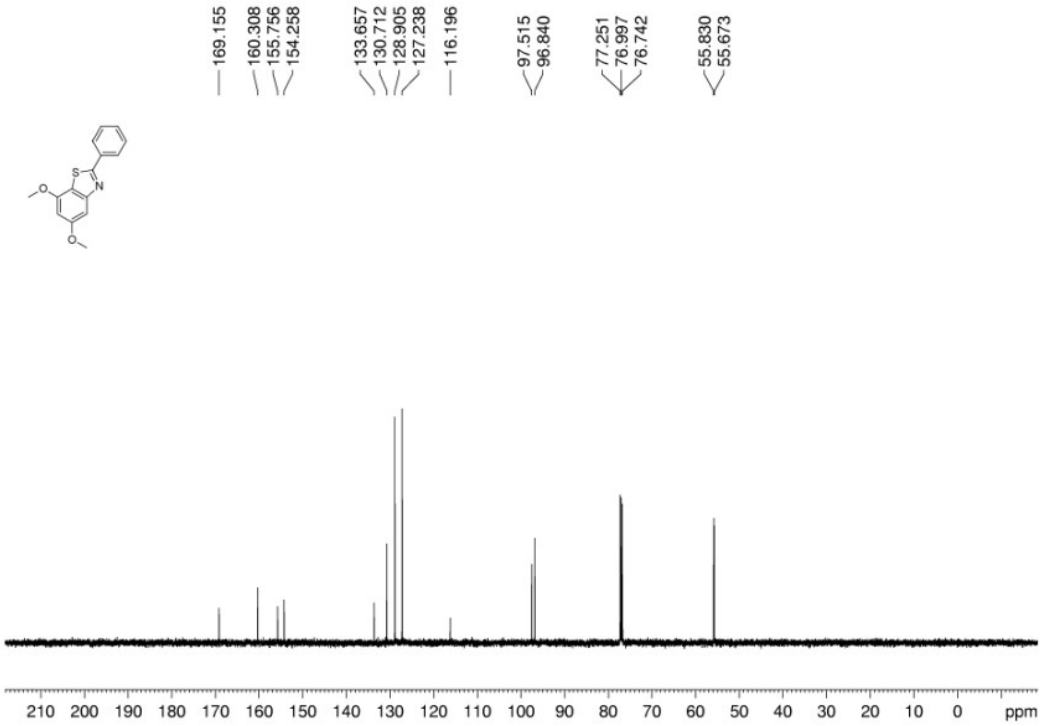


^{1}H and ^{13}C Spectrum of Compound **4b**

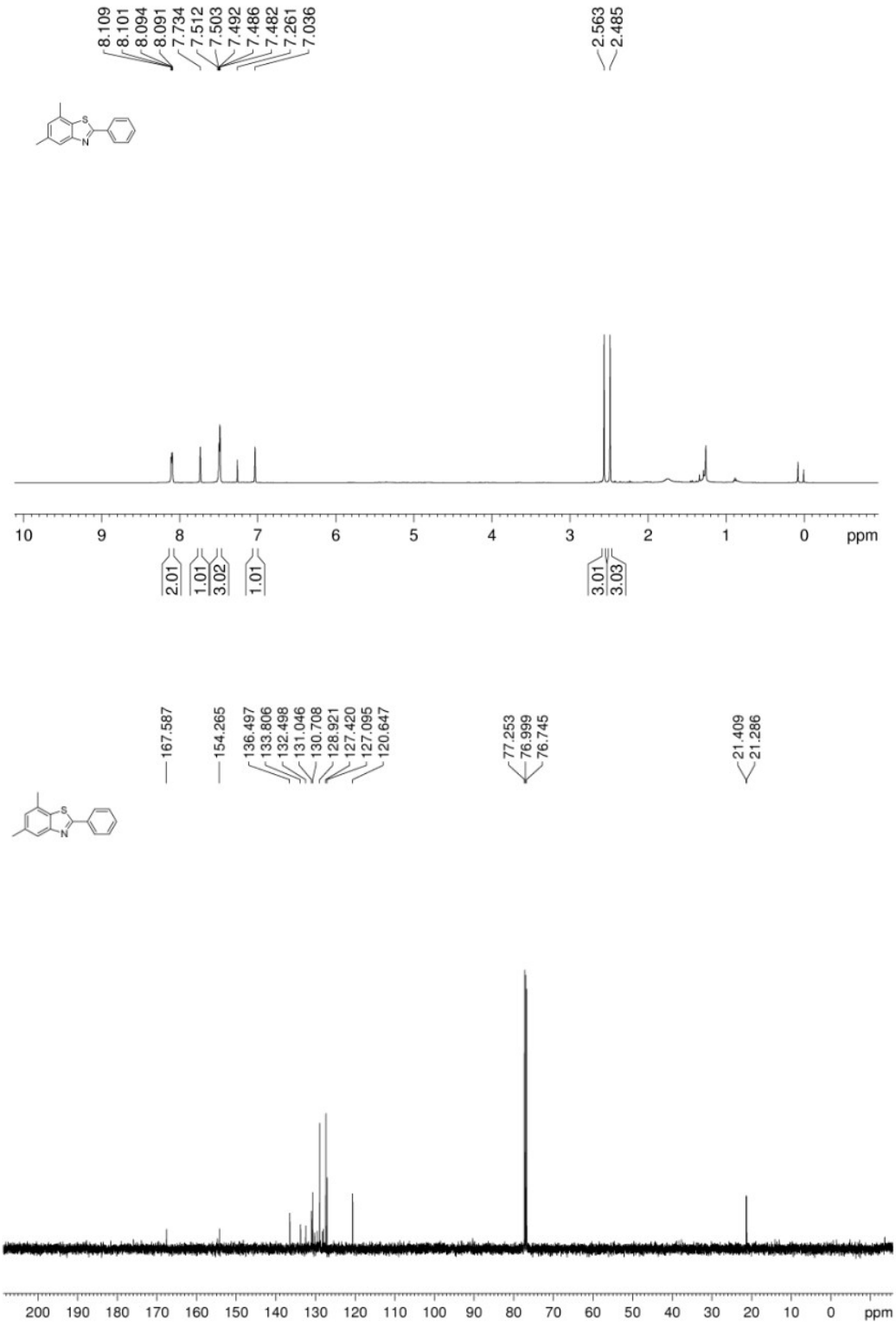


^{1}H and ^{13}C Spectrum of Compound **4c**

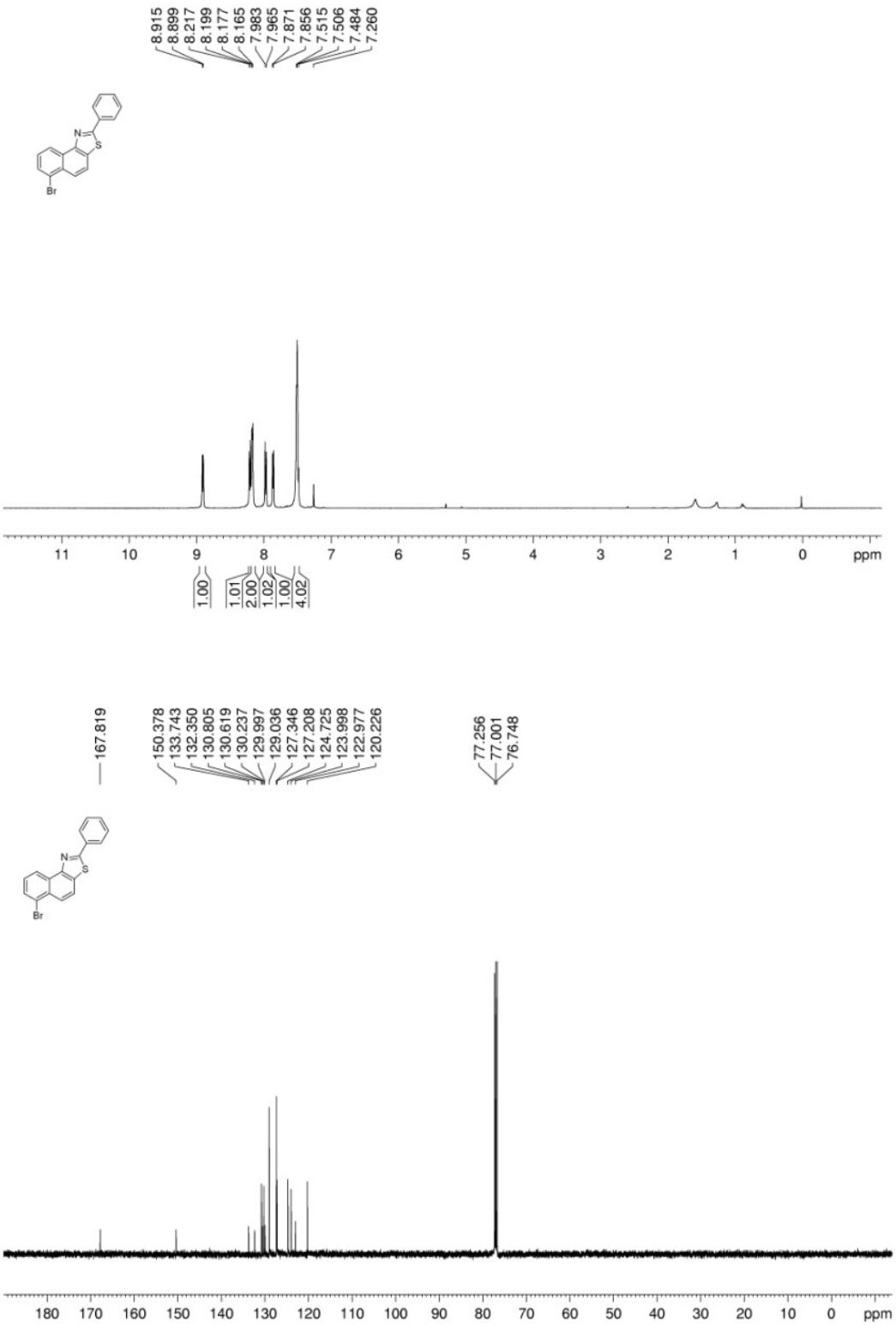




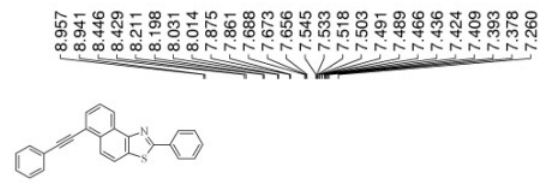
^{1}H and ^{13}C Spectrum of Compound **4d**

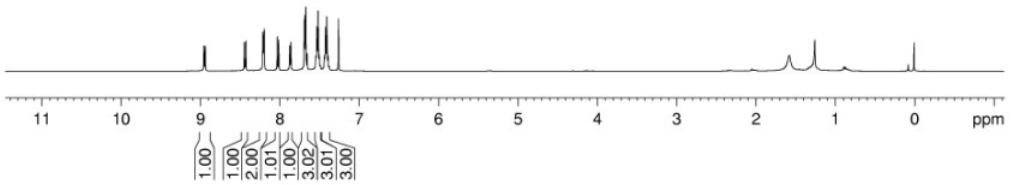


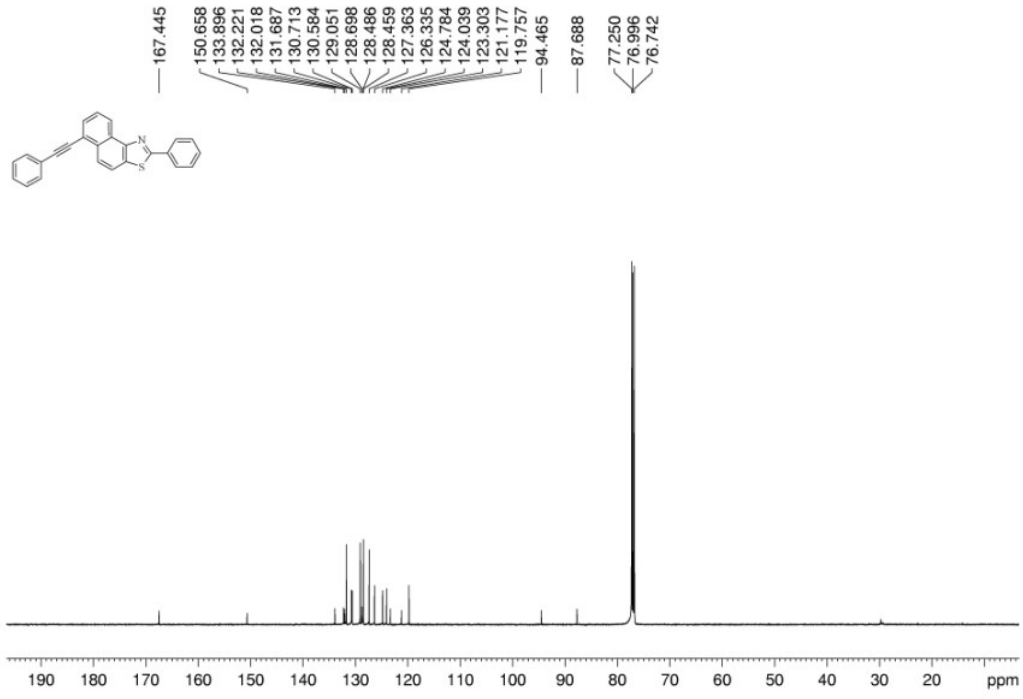
^{1}H and ^{13}C Spectrum of Compound **4e**



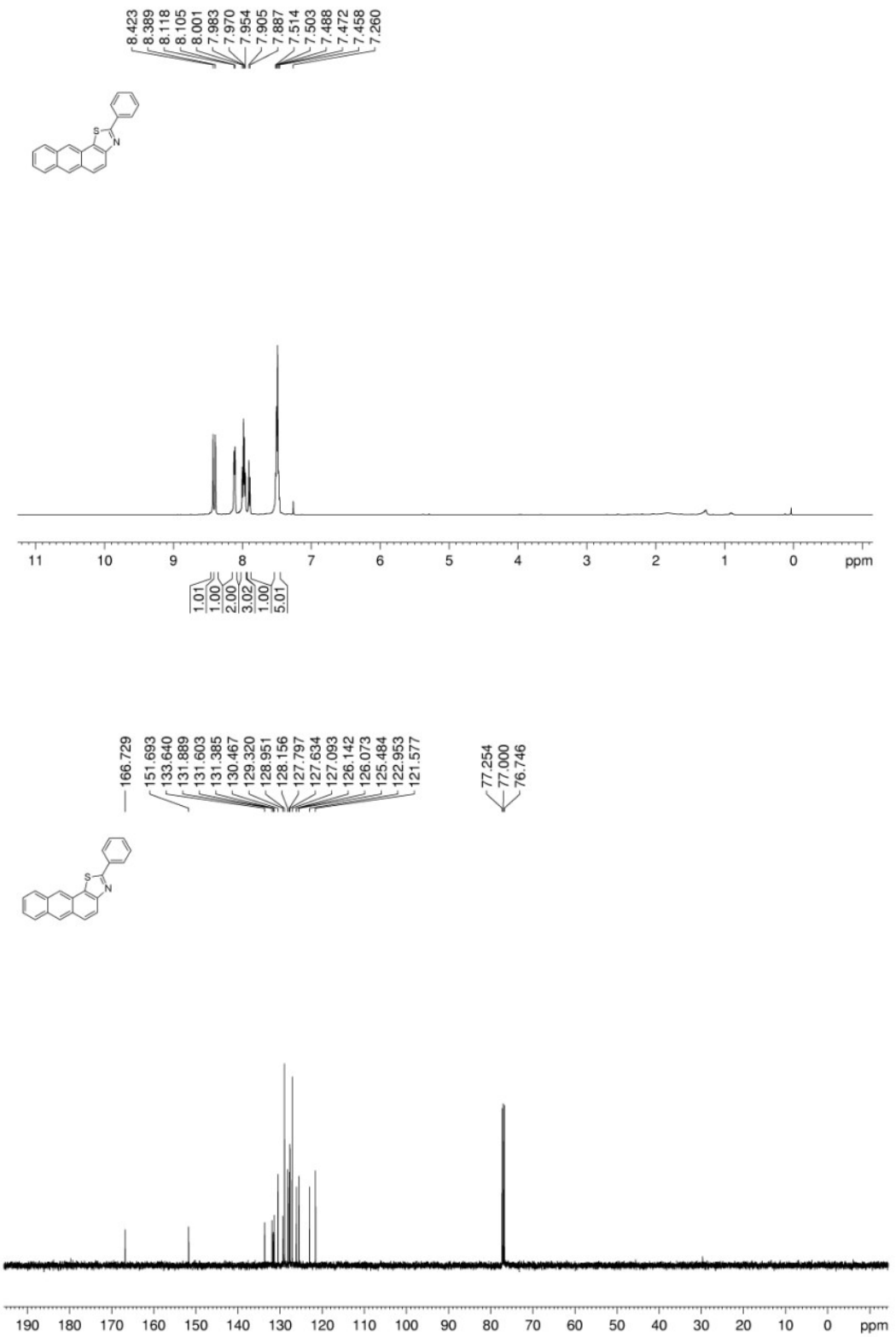
^{1}H and ^{13}C Spectrum of Compound **4f**



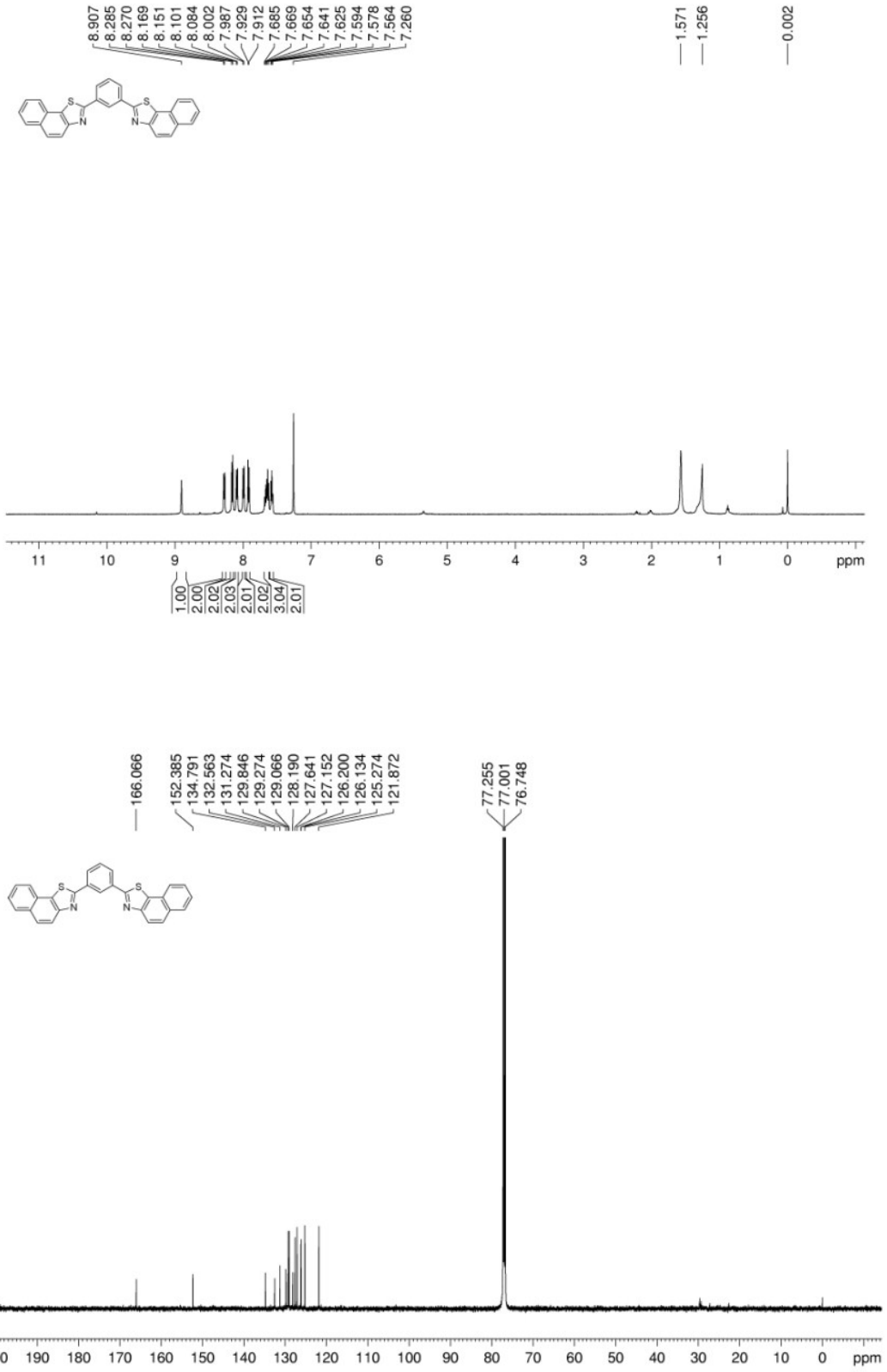




^{1}H and ^{13}C Spectrum of Compound **4g**



^{1}H and ^{13}C Spectrum of Compound **6a**



^{1}H and ^{13}C Spectrum of Compound **6b**