Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Catalyst- and additive-free annulation/aromatization leading to benzothiazoles and naphthothiazoles

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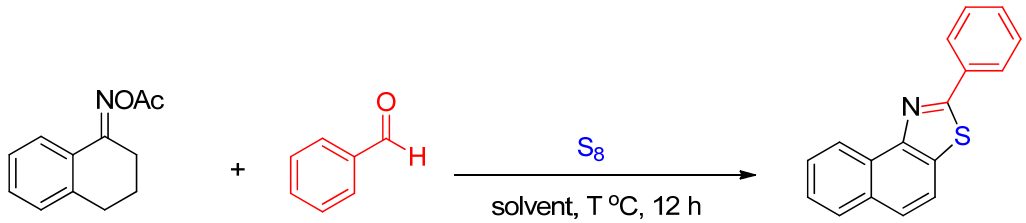
General information

All reactions were carried out under air atmosphere unless otherwise noted. Column chromatography was performed using aluminum oxide (neutral) (100-200 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 chloroform signals. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra were recorded at the 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 were prepared according previously reported method. All other 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.

Optimization of reaction conditions

Table S1.[a]



1a **2a** **3a**

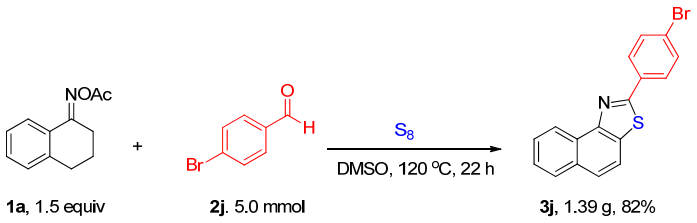
entry	catalyst	base	solvent	T/°C	yield (%)[b]
1	CuI	Li_2CO_3	DMSO	120	43
2	CuBr	Li_2CO_3	DMSO	120	80
3	CuCl	Li_2CO_3	DMSO	120	31
4	$CuBr_2$	Li_2CO_3	DMSO	120	25
5	$CuCl_2$	Li_2CO_3	DMSO	120	20
6	$Cu(OAc)_2$	Li_2CO_3	DMSO	120	trace
7	--	Li_2CO_3	DMSO	120	65
8	--	Na_2CO_3	DMSO	120	47
9	--	K_2CO_3	DMSO	120	40
10	--	Cs_2CO_3	DMSO	120	25
11	--	Et_3N	DMSO	120	44
12	--	LiOH	DMSO	120	49
13	--	BzOH	DMSO	120	54
14	--	--	**DMSO**	**120**	**85 (83)**[c]
15	--	--	toluene	120	trace
16	--	--	CH_3CN	120	trace
17	--	--	DMF	120	34
18	--	--	1,4-dioxane	120	trace
19	--	--	DMSO	110	70
20	--	--	DMSO	130	82
21[d]	--	--	DMSO	120	70
22[e]	--	--	DMSO	120	trace

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), S_8 (0.6 mmol), catalyst (15 mol %), base (50 mol %), solvent (1.0 mL), air, 12 h. [b] Yields determined by GC analysis based on **2a** with dodecane as the internal standard. [c] Isolated yield. [d] N_2 atmosphere. [e] O_2 atmosphere.

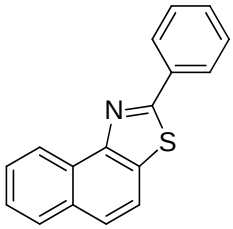
General procedure for the synthesis of fused thiazoles

General procedure A: Oxime acetate **1** (0.3 mmol), aldehyde **2** (0.2 mmol), S_8 (19.2 mg, 0.6 mmol) and DMSO (1.0 mL) were added successfully to a 10 mL oven-dried reaction vessel. The sealed reaction vessel was stirred at 120 °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/ethyl acetate) to yield the desired product **3**,**4**.

Gram-scale experiment for the synthesis of **3j**: 3,4-dihydronaphthalen-1(2H)-one-O-acetyl oxime **1a** (1.53 g, 7.5 mmol), 4-bromobenzaldehyde **2j** (0.93 g, 5.0 mmol), S_8 (480 mg, 15 mmol) and DMSO (25 mL) were added successfully to a 100 mL ovendried reaction flask. The sealed reaction flask was stirred at 120 °C for 22 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: 50/1) to yield the desired product **3j** (1.39 g, 82%) as a light yellow solid.



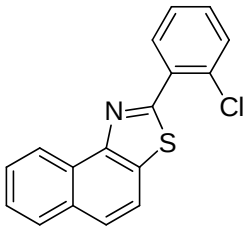
Characterization data of products



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

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), benzaldehyde (**2a**, 21 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 100/1) yielded **3a** (43.3 mg, 83%) as a green solid. mp: 99–101 °C.

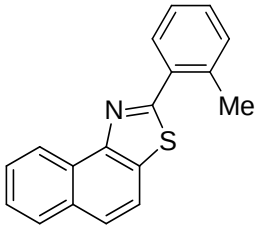
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.96 (d, *J* = 8.2 Hz, 1H), 8.21 (dt, *J* = 8.5, 2.3 Hz, 2H), 7.94 (dd, *J* = 15.9, 8.4 Hz, 2H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.73–7.68 (m, 1H), 7.63–7.56 (m, 1H), 7.55–7.47 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 150.4, 134.0, 132.1, 131.7, 130.6, 129.0, 128.8, 128.1, 127.3, 126.9, 126.1, 125.9, 124.0, 119.0. HRMS (ESI) m/z calcd for $C_{17}H_{12}NS^+$ $(M+H)^+$ 262.0685, found 262.0689.



2-(2-Chlorophenyl)naphtho[1,2-*d*]thiazole (3b)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), 2-chlorobenzaldehyde (**2b**, 23 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 100/1) yielded **3b** (51.9 mg, 88%) as a brown solid. mp: 199–201 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.93 (d, *J* = 8.2 Hz, 1H), 8.48 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.95 (t, *J* = 8.9 Hz, 2H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.73–7.66 (m, 1H), 7.63–7.57 (m, 1H), 7.55 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.47–7.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 148.8, 132.9, 132.4, 132.3, 132.0, 131.7, 130.8, 130.7, 128.7, 128.1, 127.1, 127.0, 126.2, 126.2, 123.9, 118.7. HRMS (ESI) m/z calcd for $C_{17}H_{11}ClNS^+$ $(M+H)^+$ 296.0295, found 296.0299.

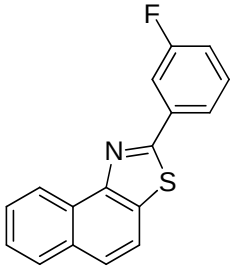


2-(*o*-Tolyl)Naphtho[1,2-*d*]thiazole (3c)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), 2-methylbenzaldehyde (**2c**, 24 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 70/1) yielded **3c**

(44.0 mg, 80%) as a gray solid. mp: 88–90 °C.

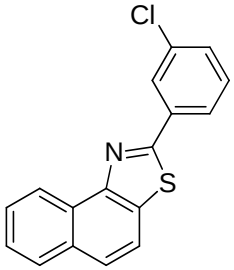
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.88 (d, *J* = 8.2 Hz, 1H), 7.94 (dd, *J* = 12.0, 8.4 Hz, 2H), 7.86 (d, *J* = 7.3 Hz, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.71–7.64 (m, 1H), 7.61-7.55 (m, 1H), 7.40–7.29 (m, 3H), 2.78 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 150.0, 137.3, 133.1, 132.0, 131.7, 130.5, 129.8, 128.8, 128.0, 126.9, 126.2, 126.1, 125.8, 124.0, 118.8, 21.8. HRMS (ESI) m/z calcd for $C_{18}H_{14}NS^+$ $(M+H)^+$ 276.0842, found 276.0845.



2-(3-Fluorophenyl)naphtho[1,2-*d*]thiazole (3d)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), 3-fluorobenzaldehyde (**2d**, 22 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 100/1) yielded **3d** (50.2 mg, 90%) as a dark blue solid. mp: 138–140 °C.

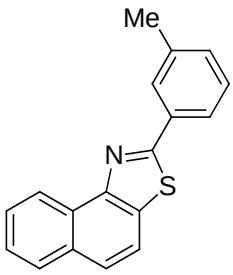
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.89 (d, *J* = 8.2 Hz, 1H), 7.97–7.84 (m, 4H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.72–7.65 (m, 1H), 7.58 (td, *J* = 7.6, 7.0, 1.2 Hz, 1H), 7.44 (td, *J* = 8.0, 5.8 Hz, 1H), 7.20–7.12 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3 (d, *J* = 3.1 Hz), 163.1 (d, *J* = 245.3 Hz), 150.3, 136.1(d, *J* = 8.0 Hz), 132.1, 131.8, 130.6 (d, *J* = 8.2 Hz), 128.8, 128.1, 127.1, 126.3 (d, *J* = 3.1 Hz), 124.0, 123.0, 123.0, 118.8, 117.4 (d, *J* = 21.3 Hz), 114.0 (d, *J* = 23.4 Hz). HRMS (ESI) m/z calcd for $C_{17}H_{11}FNS^+$ $(M+H)^+$ 280.0591, found 280.0591.



2-(3-Chlorophenyl)naphtho[1,2-*d*]thiazole (3e)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), 3-chlorobenzaldehyde (**2e**, 23 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 100/1) yielded **3e** (50.2 mg, 85%) as a dark blue solid. mp: 156–158 °C.

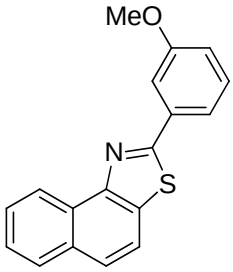
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.86 (d, *J* = 8.2 Hz, 1H), 8.17 (s, 1H), 7.95 (d, *J* = 7.2 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.67 (t, *J* = 7.3 Hz, 1H), 7.61–7.53 (m, 1H), 7.46–7.30 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 150.3, 135.5, 135.0, 132.0, 131.8, 130.3, 130.2, 128.7, 128.0, 127.1, 127.0, 127.0, 126.3, 126.2, 125.3, 124.0, 118.8. HRMS (ESI) m/z calcd for $C_{17}H_{11}ClNS^+$ $(M+H)^+$ 296.0295, found 296.0299.



2-(*m*-Tolyl)naphtho[1,2-*d*]thiazole (3f)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), 3-methylbenzaldehyde (**2f**, 24 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 100/1) yielded **3f** (37.4 mg, 68%) as a dark blue solid. mp: 121–123 °C.

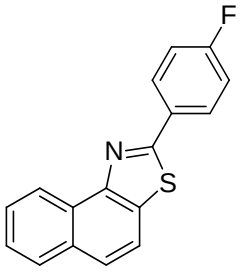
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.94 (d, *J* = 8.2 Hz, 1H), 8.04 (s, 1H), 8.01–7.89 (m, 3H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.73–7.65 (m, 1H), 7.63–7.55 (m, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 2.49 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 150.4, 138.8, 133.9, 132.1, 131.6, 131.4, 128.9, 128.8, 128.1, 127.8, 126.9, 126.1, 125.8, 124.6, 124.1, 119.0, 21.4. HRMS (ESI) m/z calcd for $C_{18}H_{14}NS^+$ $(M+H)^+$ 276.0842, found 276.0845.



2-(3-Methoxyphenyl)naphtho[1,2-*d*]thiazole (3g)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), 3-methoxybenzaldehyde (**2g**, 25 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 50/1) yielded **3g** (53.5 mg, 92%) as a brownish green solid. mp: 95–97 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.92 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.83–7.75 (m, 2H), 7.75–7.63 (m, 2H), 7.58 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.02 (ddd, *J* = 8.3, 2.6, 0.8 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 160.1, 150.3, 135.2, 132.0, 131.7, 130.0, 128.8, 128.1, 126.9, 126.1, 125.9, 124.0, 120.0, 118.9, 116.7, 112.1, 55.5. HRMS (ESI) m/z calcd for $C_{18}H_{14}NOS^+$ $(M+H)^+$ 292.0791, found 292.0794.

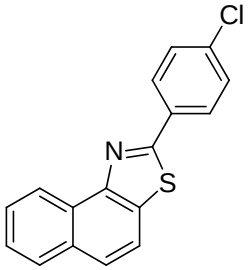


2-(4-Fluorophenyl)naphtho[1,2-*d*]thiazole (3h)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime

(**1a**, 60.9 mg, 0.3 mmol), 4-fluorobenzaldehyde (**2h**, 22 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 100/1) yielded **3h** (51.9 mg, 93%) as a white solid. mp: 105–107 °C.

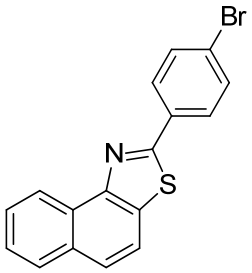
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.89 (d, *J* = 8.1 Hz, 1H), 8.23–8.10 (m, 2H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.72–7.65 (m, 1H), 7.62–7.56 (m, 1H), 7.23–7.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6 (d, *J* = 24.7 Hz), 163.0, 150.4, 132.1, 131.6, 130.3 (d, *J* = 3.3 Hz), 129.3 (d, *J* = 8.5 Hz), 128.7, 128.1, 127.0, 126.1 (d, *J* = 22.0 Hz), 124.0, 118.9, 116.2, 116.0. HRMS (ESI) m/z calcd for $C_{17}H_{11}FNS^+$ $(M+H)^+$ 280.0591, found 280.0591.



2-(4-Chlorophenyl)naphtho[1,2-*d*]thiazole (3i)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), 4-chlorobenzaldehyde (**2i**, 28.1 mg, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 100/1) yielded **3i** (47.8 mg, 81%) as a beige solid. mp: 156–158 °C.

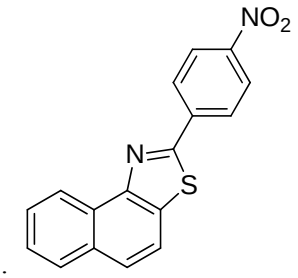
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.87 (d, *J* = 8.2 Hz, 1H), 8.14–8.01 (m, 2H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.71–7.63 (m, 1H), 7.61–7.52 (m, 1H), 7.49–7.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 150.4, 136.5, 132.4, 132.1, 131.7, 129.2, 128.7, 128.4, 128.1, 127.0, 126.2, 126.1, 123.9, 118.8. HRMS (ESI) m/z calcd for $C_{17}H_{11}ClNS^+$ $(M+H)^+$ 296.0295, found 296.0299.



2-(4-Bromophenyl)naphtho[1,2-*d*]thiazole (3j)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), 4-bromobenzaldehyde (**2j**, 37.0 mg, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 50/1) yielded **3j** (51.0 mg, 75%) as a light yellow white solid. mp: 159–161 °C.

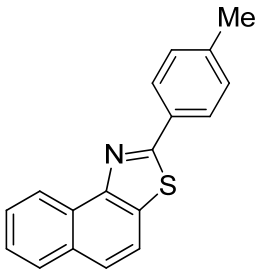
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.86 (d, *J* = 8.2 Hz, 1H), 8.03–7.95 (m, 2H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.71–7.64 (m, 1H), 7.62–7.53 (m, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 150.4, 132.8, 132.1, 132.0, 131.7, 128.7, 128.6, 128.1, 127.0, 126.2, 126.1, 124.9, 123.9, 118.8. HRMS (ESI) m/z calcd for $C_{17}H_{11}BrNS^+$ $(M+H)^+$ 339.9790, found 339.9793.



2-(4-Nitrophenyl)naphtho[1,2-*d*]thiazole (3k)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), 4-nitrobenzaldehyde (**2k**, 30.2 mg, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1) yielded **3k** (27.5 mg, 45%) as a dark green solid. mp: 211–213 °C.

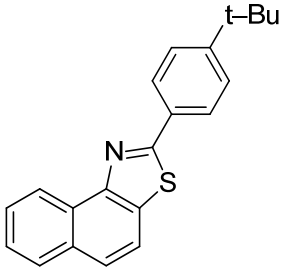
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.89 (d, *J* = 8.2 Hz, 1H), 8.37–8.24 (m, 4H), 7.94 (dd, *J* = 17.6, 8.4 Hz, 2H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.72 (t, *J* = 7.1 Hz, 1H), 7.65–7.59 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 150.7, 148.7, 139.4, 132.6, 132.2, 128.9, 128.2, 127.8, 127.4, 127.2, 126.6, 124.3, 123.9, 118.8. HRMS (ESI) m/z calcd for $C_{17}H_{11}N_2O_2S^+$ $(M+H)^+$ 307.0536, found 307.0537.



2-(*p*-Tolyl)naphtho[1,2-*d*]thiazole (3l)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), 4-methylbenzaldehyde (**2l**, 24 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc:100/1) yielded **3l** (47.9 mg, 87%) as a ink-blue solid. mp:106–108 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.92 (d, *J* = 8.2 Hz, 1H), 8.07 (d, *J* = 8.1 Hz, 2H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.71–7.64 (m, 1H), 7.57 (td, *J* = 7.6, 7.0, 1.2 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 150.3, 141.0, 132.0, 131.4, 131.3, 129.7, 128.7, 128.0, 127.2, 126.8, 126.0, 125.7, 124.0, 118.9, 21.5. HRMS (ESI) m/z calcd for $C_{18}H_{14}NS^+$ $(M+H)^+$ 276.0842, found 276.0845.

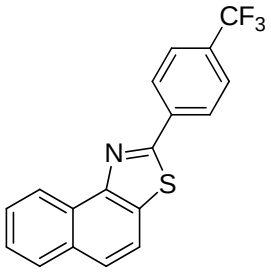


2-(4-(*tert*-Butyl)phenyl)naphtho[1,2-*d*]thiazole (3m)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), 4-(tert-butyl)benzaldehyde (**2m**, 34 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc:100/1) yielded **3m**

(43.1 mg, 68%) as a white solid. mp:110–112 °C.

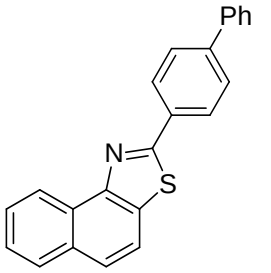
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.93 (d, *J* = 8.2 Hz, 1H), 8.11 (d, *J* = 8.3 Hz, 2H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.60–7.54 (m, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 154.1, 150.4, 132.0, 131.5, 131.2, 128.7, 128.0, 127.1, 126.9, 126.0, 126.0, 125.7, 124.1, 119.0, 35.0, 31.2. HRMS (ESI) m/z calcd for $C_{21}H_{20}NS^+$ $(M+H)^+$ 318.1311, found 318.1316.



2-(4-(Trifluoromethyl)phenyl)naphtho[1,2-*d*]thiazole (3n)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), 4-(trifluoromethyl)benzaldehyde (**2n**, 28 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc:70/1) yielded **3n** (57.2 mg, 87%) as a white solid. mp:147–149 °C.

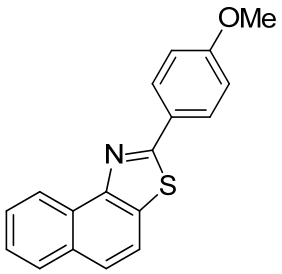
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.89 (d, *J* = 8.2 Hz, 1H), 8.26 (d, *J* = 8.1 Hz, 2H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.71 (dd, *J* = 17.7, 8.1 Hz, 3H), 7.60 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 150.5, 137.1, 132.1, 132.1, 132.0 (q, *J* = 32.4 Hz), 128.8, 128.1, 127.4, 127.2, 126.6, 126.4, 126.0 (q, *J* = 3.8 Hz), 124.0, 123.8 (q, *J* = 270.6 Hz), 118.8. HRMS (ESI) m/z calcd for $C_{18}H_{11}F_3NS^+$ $(M+H)^+$ 330.0559, found 330.0562.



2-([1,1'-Biphenyl]-4-yl)naphtho[1,2-*d*]thiazole (3o)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), [1,1'-biphenyl]-4-carbaldehyde (**2o**, 36.4 mg, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc:60/1) yielded **3o** (44.5 mg, 66%) as a light yellow solid. mp:183–185 °C.

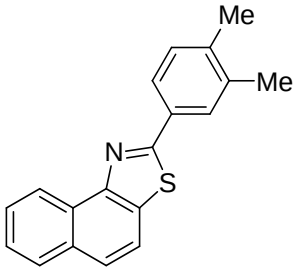
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.94 (d, *J* = 8.2 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.75–7.64 (m, 5H), 7.59 (td, *J* = 7.6, 7.0, 1.2 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.42–7.35 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 150.5, 143.3, 140.2, 132.9, 132.1, 131.7, 128.9, 128.7, 128.1, 127.9, 127.7, 127.6, 127.1, 126.9, 126.1, 125.9, 124.1, 118.9. HRMS (ESI) m/z calcd for $C_{23}H_{16}NS^+$ $(M+H)^+$ 338.0998, found 338.0997.



2-(4-Methoxyphenyl)naphtho[1,2-*d*]thiazole (3p)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), 4-methoxybenzaldehyde (**2p**, 25 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc:50/1) yielded **3p** (44.8 mg, 77%) as a gray solid. mp:128–130 °C.

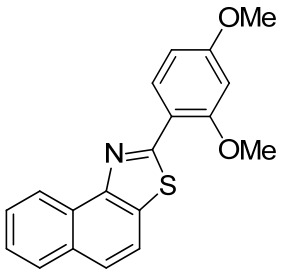
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.91 (d, *J* = 8.2 Hz, 1H), 8.13 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.71–7.64 (m, 1H), 7.61–7.53 (m, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 161.7, 150.3, 132.1, 131.2, 128.9, 128.6, 128.0, 126.8, 126.8, 126.0, 125.5, 124.0, 118.9, 114.4, 55.5. HRMS (ESI) m/z calcd for $C_{18}H_{14}NOS^+$ $(M+H)^+$ 292.0791, found 292.0794.



2-(3,4-Dimethylphenyl)naphtho[1,2-*d*]thiazole (3q)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), 3,4-dimethylbenzaldehyde (**2q**, 27 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1) yielded **3q** (53.8 mg, 93%) as a gray solid. mp: 152–154 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.92 (d, *J* = 8.2 Hz, 1H), 7.97 (s, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.91–7.84 (m, 2H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.71–7.63 (m, 1H), 7.60–7.53 (m, 1H), 7.27–7.21 (m, 1H), 2.37 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 150.4, 139.7, 137.3, 132.0, 131.6, 131.4, 130.2, 128.7, 128.3, 128.0, 126.8, 126.0, 125.6, 124.8, 124.1, 118.9, 19.8, 19.8. HRMS (ESI) m/z calcd for $C_{19}H_{16}NS^+$ $(M+H)^+$ 290.0998, found 290.1000.

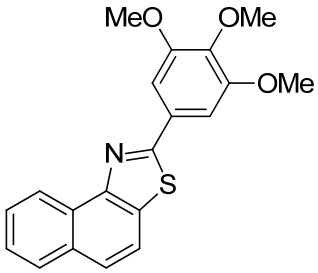


2-(2,4-Dimethoxyphenyl)naphtho[1,2-*d*]thiazole (3r)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), 2,4-dimethoxybenzaldehyde (**2r**, 33.3 mg, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded

3r (57.8 mg, 90%) as a dark green solid. mp: 145–147 °C.

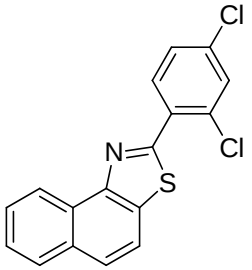
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.94 (d, *J* = 8.2 Hz, 1H), 8.67 (d, *J* = 8.8 Hz, 1H), 7.90 (dd, *J* = 13.8, 8.4 Hz, 2H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.69–7.63 (m, 1H), 7.60–7.48 (m, 1H), 6.67 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.53 (d, *J* = 2.3 Hz, 1H), 3.99 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 162.0, 158.2, 148.3, 131.9, 131.9, 130.5, 128.4, 128.0, 126. 5, 125.7, 124.7, 123.9, 118.9, 116.0, 106.0, 98.3, 55.6, 55.5. HRMS (ESI) m/z calcd for $C_{19}H_{16}NO_2S^+$ $(M+H)^+$ 322.0896, found 322.0897.



2-(3,4,5-Trimethoxyphenyl)naphtho[1,2-*d*]thiazole (3s)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), 3,4,5-trimethoxybenzaldehyde (**2s**, 39.3 mg, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **3s** (51.9 mg, 74%) as a ink-blue colour solid. mp: 183–185 °C.

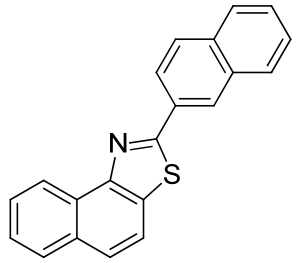
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.93 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.62–7.56 (m, 1H), 7.42 (s, 2H), 4.02 (s, 6H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 153.6, 150.3, 140.4, 132.1, 131.6, 129.4, 128.6, 128.1, 126.9, 126.1, 125.8, 124.0, 118.9, 104.6, 61.0, 56.3. HRMS (ESI) m/z calcd for $C_{20}H_{18}NO_3S^+$ $(M+H)^+$ 352.1002, found 352.1005.



2-(2,4-Dichlorophenyl)naphtho[1,2-*d*]thiazole (3t)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), 2,4-dichlorobenzaldehyde (**2t**, 35.0 mg, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 50/1) yielded **3t** (51.5 mg, 74%) as a light green solid. mp: 187–189 °C.

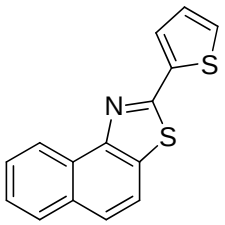
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.90 (d, *J* = 8.1 Hz, 1H), 8.48 (d, *J* = 8.5 Hz, 1H), 7.94 (dd, *J* = 14.4, 8.4 Hz, 2H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.56 (s, 1H), 7.42 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 148.7, 136.2, 133.0, 132.9, 132.4, 132.1, 131.0, 130.5, 128.7, 128.2, 127.6, 127.1, 126.5, 126.3, 123.9, 118.6. HRMS (ESI) m/z calcd for $C_{17}H_{10}Cl_2NS^+$ $(M+H)^+$ 329.9906, found 329.9909.



2-(Naphthalen-2-yl)naphtho[1,2-*d*]thiazole (3u)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), 2-naphthaldehyde (**2u**, 31.2 mg, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 50/1) yielded **3u** (56.0 mg, 90%) as a bright green solid. mp: 159–161 °C.

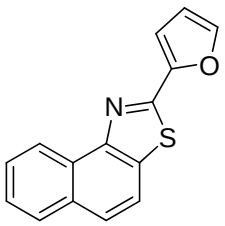
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.98 (d, *J* = 8.2 Hz, 1H), 8.63 (s, 1H), 8.32 (d, *J* = 8.5 Hz, 1H), 8.01–7.84 (m, 5H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.54 (dd, *J* = 6.1, 3.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 150.4, 134.5, 133.3, 132.1, 131.7, 131.3, 128.8, 128.8, 128.8, 128.1, 127.9, 127.3, 127.1, 127.0, 126.8, 126.2, 126.0, 124.5, 124.1, 118.9. HRMS (ESI) m/z calcd for $C_{21}H_{14}NS^+$ $(M+H)^+$ 312.0842, found 312.0843.



2-(Thiophen-2-yl)naphtho[1,2-*d*]thiazole (3v)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), thiophene-2-carbaldehyde (**2v**, 19 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 50/1) yielded **3v** (43.8 mg, 82%) as a gray solid. mp: 105–107 °C.

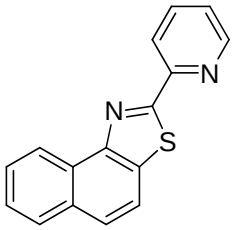
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.86 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.70–7.62 (m, 2H), 7.56 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 1H), 7.47 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.12 (dd, *J* = 5.0, 3.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 150.0, 137.8, 132.0, 131.2, 128.7, 128.4, 128.0, 128.0, 127.8, 126.9, 126.1, 125.9, 124.1, 118.7. HRMS (ESI) m/z calcd for $C_{15}H_{10}NS_2^+$ $(M+H)^+$ 268.0249, found 268.0252.



2-(Furan-2-yl)naphtho[1,2-*d*]thiazole (3w)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), furan-2-carbaldehyde (**2w**, 17 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 50/1) yielded **3w** (42.2 mg, 84%) as a dark green solid. mp: 106–108 °C.

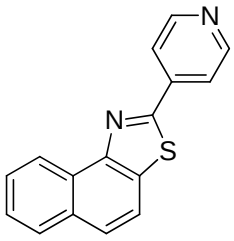
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.88 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.70–7.64 (m, 1H), 7.62–7.54 (m, 2H), 7.28–7.23 (m, 1H), 6.61 (dd, *J* = 3.5, 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 150.1, 149.1, 144.3, 132.1, 130.9, 128.5, 128.0, 126.9, 126.2, 126.0, 124.0, 118.8, 112.5, 110.8. HRMS (ESI) m/z calcd for $C_{15}H_{10}NOS^+$ $(M+H)^+$ 252.0478, found 252.0481.



2-(Pyridin-2-yl)naphtho[1,2-*d*]thiazole (3x)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), picolinaldehyde (**2x**, 19 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 50/1) yielded **3x** (33.5 mg, 64%) as a dark green solid. mp: 127–129 °C.

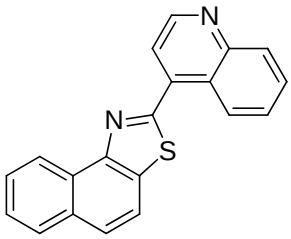
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.91 (d, *J* = 8.2 Hz, 1H), 8.68 (d, *J* = 7.9 Hz, 1H), 8.52 (d, *J* = 7.9 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.87 (td, *J* = 7.8, 1.7 Hz, 1H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.73–7.67 (m, 1H), 7.62–7.56 (m, 1H), 7.41–7.33 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 151.7, 150.6, 149.5, 137.1, 133.2, 132.0, 128.9, 128.1, 127.0, 126.5, 126.2, 124.9, 123.7, 120.6, 119.3. HRMS (ESI) m/z calcd for $C_{16}H_{11}N_2S^+$ $(M+H)^+$ 263.0638, found 263.0641.



2-(Pyridin-4-yl)naphtho[1,2-*d*]thiazole (3y)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), isonicotinaldehyde (**2y**, 19 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 3/1) yielded **3y** (38.8 mg, 74%) as a dark green solid. mp: 151–153 °C.

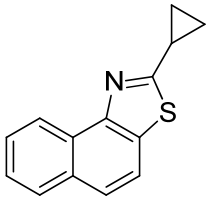
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.91 (d, *J* = 8.2 Hz, 1H), 8.78 (d, *J* = 6.0 Hz, 2H), 8.08–8.00 (m, 2H), 8.00–7.90 (m, 2H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.78–7.69 (m, 1H), 7.66–7.59 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 150.6, 150.4, 140.6, 132.2, 132.0, 128.7, 128.1, 127.3, 127.0, 126.5, 123.8, 120.8, 118.7. HRMS (ESI) m/z calcd for $C_{16}H_{11}N_2S^+$ $(M+H)^+$ 263.0636, found 263.0640.



2-(Quinolin-4-yl)naphtho[1,2-*d*]thiazole (3z)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), quinoline-4-carbaldehyde (**2y**, 31.5 mg, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **4a** (45.6 mg, 73%) as a dark green solid. mp: 140–142 °C.

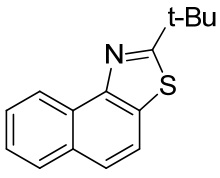
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.42–9.18 (m, 1H), 9.03 (d, *J* = 4.5 Hz, 1H), 8.95 (d, *J* = 8.2 Hz, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 8.05–7.94 (m, 2H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.88–7.79 (m, 2H), 7.74 (m, 2H), 7.68–7.61 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 150.7, 149.5, 148.9, 138.5, 132.4, 132.1, 130.1, 129.7, 128.9, 128.2, 128.2, 127.4, 127.2, 126.6, 126.4, 125.0, 124.0, 121.9, 118.6. HRMS (ESI) m/z calcd for $C_{20}H_{13}N_2S^+$ $(M+H)^+$ 313.0794, found 313.0797.



2-Cyclopropylnaphtho[1,2-*d*]thiazole (3aa)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), cyclopropanecarbaldehyde (**2z**, 15 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 100/1) yielded **4b** (33.8 mg, 75%) as an ink blue liquid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.75 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.65–7.60 (m, 1H), 7.57–7.50 (m, 1H), 2.57–2.46 (m, 1H), 1.25 (d, *J* = 6.5 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 149.3, 131.9, 130.2, 128.2, 127.9, 126.6, 125.8, 124.9, 123.9, 118.8, 15.4, 11.8. HRMS (ESI) m/z calcd for $C_{14}H_{12}NS^+$ $(M+H)^+$ 226.0685, found 226.0686.

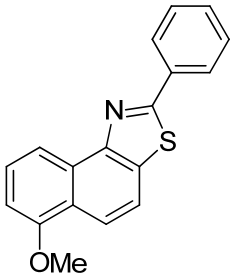


2-(*tert*-Butyl)naphtho[1,2-*d*]thiazole (3ab)

The general procedure **A** was followed using 3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1a**, 60.9 mg, 0.3 mmol), pivalaldehyde (**2aa**, 22 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatographyb on silica gel (*n*-hexane/EtOAc: 100/1) yielded **3aa** (28.9 mg, 60%) as an ink blue liquid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.82 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 1.57 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 149.2, 131.8, 131.2, 128.6, 127.9, 126.6, 125.7, 125.0,

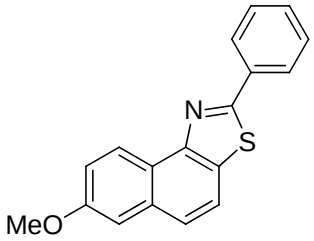
124.0, 119.0, 38.4, 31.0. HRMS (ESI) m/z calcd for $C_{15}H_{16}NS^+$ $(M+H)^+$ 242.0998, found 242.1000.



6-Methoxy-2-phenylnaphtho[1,2-*d*]thiazole (4a)

The general procedure **A** was followed using 5-methoxy-3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1b**, 69.9 mg, 0.3 mmol), benzaldehyde (**2a**, 21 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1) yielded **4a** (52.4 mg, 90%) as a light green solid. mp: 107–109 °C.

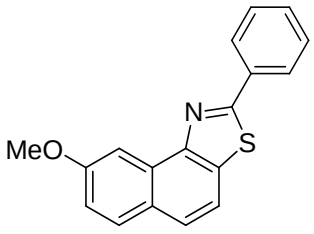
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.50 (d, *J* = 8.3 Hz, 1H), 8.23 (d, *J* = 9.0 Hz, 1H), 8.17 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.85 (d, *J* = 9.0 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.51–7.44 (m, 3H), 6.91 (d, *J* = 7.7 Hz, 1H), 4.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 155.6, 150.1, 133.9, 132.3, 130.5, 129.8, 128.9, 127.2, 127.1, 123.7, 119.8, 118.0, 116.2, 104.6, 55.5. HRMS (ESI) m/z calcd for $C_{18}H_{14}NOS^+$ $(M+H)^+$ 292.0791, found 292.0794.



7-Methoxy-2-phenylnaphtho[1,2-*d*]thiazole (4b)

The general procedure **A** was followed using 6-methoxy-3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1c**, 69.9 mg, 0.3 mmol), benzaldehyde (**2a**, 21 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1) yielded **4b** (53.0 mg, 91%) as a yellow solid. mp: 158–160 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.80 (d, *J* = 9.0 Hz, 1H), 8.18–8.10 (m, 2H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.51–7.43 (m, 3H), 7.32 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.23 (d, *J* = 2.4 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 157.8, 150.5, 134.0, 133.4, 130.5, 129.5, 128.9, 127.2, 125.6, 125.0, 123.9, 119.5, 118.7, 106.9, 55.3. HRMS (ESI) m/z calcd for $C_{18}H_{14}NOS^+$ $(M+H)^+$ 292.0791, found 292.0794.

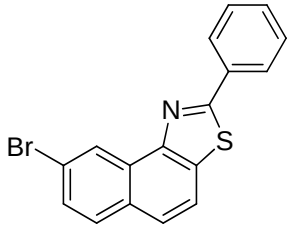


8-Methoxy-2-phenylnaphtho[1,2-*d*]thiazole (4c)

The general procedure **A** was followed using 7-methoxy-3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1d**, 69.9 mg, 0.3 mmol), benzaldehyde (**2a**, 21 μL, 0.2 mmol), and S_8 (19.2 mg,

0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1) yielded **4c** (54.1 mg, 93%) as a yellow solid. mp: 150–152 °C.

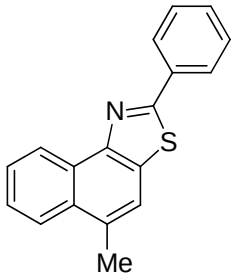
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.23 (d, *J* = 2.6 Hz, 1H), 8.19 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.76–7.69 (m, 2H), 7.53–7.47 (m, 3H), 7.25–7.19 (m, 1H), 4.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 158.6, 149.7, 133.9, 132.2, 130.5, 130.0, 129.7, 129.0, 127.3, 127.2, 125.7, 118.4, 116.4, 102.7, 55.6. HRMS (ESI) m/z calcd for $C_{18}H_{14}NOS^+$ $(M+H)^+$ 292.0791, found 292.0794.



8-Bromo-2-phenylnaphtho[1,2-*d*]thiazole (4d)

The general procedure **A** was followed using 7-bromo-3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1e**, 84.6 mg, 0.3 mmol), benzaldehyde (**2a**, 21 μL, 0.2 mmol) and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 50/1) yielded **4d** (61.2 mg, 90%) as a light green solid. mp: 180–182 °C.

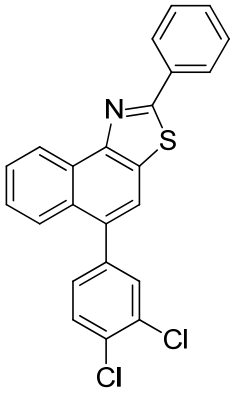
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.02 (s, 1H), 8.21–8.10 (m, 2H), 7.86 (d, *J* = 8.7 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.65–7.57 (m, 1H), 7.50 (d, *J* = 5.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 149.4, 133.7, 132.5, 130.8, 130.4, 129.7, 129.6, 129.4, 129.0, 127.3, 126.5, 125.4, 121.1, 119.4. HRMS (ESI) m/z calcd for $C_{17}H_{11}BrNS^+$ $(M+H)^+$ 339.9790, found 339.9793.



5-Methyl-2-phenylnaphtho[1,2-*d*]thiazole (4e)

The general procedure **A** was followed using 4-methyl-3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1f**, 65.1 mg, 0.3 mmol), benzaldehyde (**2a**, 21 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 50/1) yielded **4e** (50.6 mg, 92%) as a dark green solid. mp: 139–141 °C.

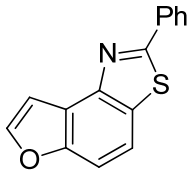
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.95 (d, *J* = 7.5 Hz, 1H), 8.16 (dd, *J* = 7.9, 1.5 Hz, 2H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.77–7.65 (m, 2H), 7.64–7.54 (m, 1H), 7.55 – 7.39 (m, 3H), 2.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 149.4, 134.0, 132.5, 131.4, 131.3, 130.3, 129.0, 128.6, 127.2, 126.6, 126.0, 124.5, 124.5, 119.0, 20.0. HRMS (ESI) m/z calcd for $C_{18}H_{14}NS^+$ $(M+H)^+$ 276.0842, found 276.0847.



5-(3,4-Dichlorophenyl)-2-phenylnaphtho[1,2-*d*]thiazole (4f)

The general procedure **A** was followed using 4-(3,4-dichlorophenyl)-3,4-dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**1g**, 104.4 mg, 0.3 mmol), benzaldehyde (**2a**, 21 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 30/1) yielded **4f** (74.7 mg, 92%) as a yellow solid. mp: 165–167 °C.

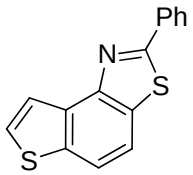
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.98 (d, *J* = 8.1 Hz, 1H), 8.22–8.07 (m, 2H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.73 (s, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 2.0 Hz, 1H), 7.56–7.45 (m, 5H), 7.31 (dd, *J* = 8.2, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 150.5, 140.3, 135.6, 133.8, 132.5, 131.9, 131.8, 131.1, 130.7, 130.3, 130.1, 129.5, 129.0, 128.8, 127.3, 127.0, 126.5, 125.9, 124.6, 119.8. HRMS (ESI) m/z calcd for $C_{23}H_{14}Cl_2NS^+$ $(M+H)^+$ 406.0219, found 406.0220.



2-Phenylbenzofuro[4,5-*d*]thiazole (4g)

The general procedure **A** was followed using 6,7-dihydrobenzofuran-4(5*H*)-one *O*-acetyl oxime (**1h**, 57.9 mg, 0.3 mmol), benzaldehyde (**2a**, 21 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 50/1) yielded a mixture of **4g** (40.2 mg, 80%) as a yellow solid. mp: 98–100 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.20–8.12 (m, 2H), 7.82–7.75 (m, 2H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.51 (d, *J* = 5.3 Hz, 3H), 7.43–7.37 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 154.5, 147.4, 145.1, 133.8, 130.8, 129.6, 129.0, 127.4, 121.9, 116.6, 109.9, 105.5. HRMS (ESI) m/z calcd for $C_{15}H_{10}NOS^+$ $(M+H)^+$ 252.0478, found 252.0481.

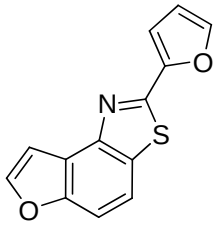


2-Phenylthieno[2',3':5,6]benzo[1,2-*d*]thiazole (4h)

The general procedure **A** was followed using 6,7-dihydrobenzo[*b*]thiophen-4(5*H*)-one *O*-acetyl oxime (**1i**, 62.7 mg, 0.3 mmol), benzaldehyde (**2a**, 21 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1) yielded **4h** (47.0 mg,

88%) as a green solid. mp: 116–118 °C.

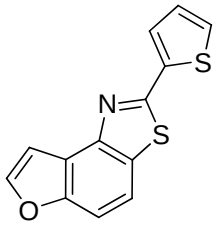
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.14 (dd, *J* = 7.2, 2.0 Hz, 2H), 8.07 (d, *J* = 5.4 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.59 (d, *J* = 5.4 Hz, 1H), 7.51–7.45 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 149.2, 138.4, 134.3, 133.8, 131.1, 130.7, 129.0, 127.4, 127.0, 122.2, 119.6, 117.3. HRMS (ESI) m/z calcd for $C_{15}H_{10}NS_2^+$ $(M+H)^+$ 268.0249, found 268.0251.



2-(Furan-2-yl)benzofuro[4,5-*d*]thiazole (4i)

The general procedure **A** was followed using 6,7-dihydrobenzofuran-4(5*H*)-one *O*-acetyl oxime (**1h**, 57.9 mg, 0.3 mmol), furan-2-carbaldehyde (**2w**, 17 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 40/1) yielded **4i** (39.5 mg, 82%) as a dark green solid. mp: 111–113 °C.

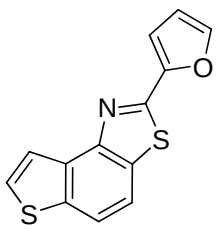
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.77–7.69 (m, 2H), 7.65–7.51 (m, 2H), 7.41–7.35 (m, 1H), 7.21 (d, *J* = 3.4 Hz, 1H), 6.60 (dd, *J* = 3.3, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 154.5, 148.9, 147.1, 145.1, 144.5, 128.8, 121.7, 116.5, 112.5, 111.2, 109.9, 105.5. HRMS (ESI) m/z calcd for $C_{13}H_8NO_2S^+$ $(M+H)^+$ 242.0270, found 242.0273.



2-(Thiophen-2-yl)benzofuro[4,5-*d*]thiazole (4j)

The general procedure **A** was followed using 6,7-dihydrobenzofuran-4(5*H*)-one *O*-acetyl oxime (**1h**, 57.9 mg, 0.3 mmol), thiophene-2-carbaldehyde (**2v**, 19 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1) yielded **4j** (45.7 mg, 89%) as a yellow solid. mp: 129–131 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.78–7.72 (m, 1H), 7.72–7.63 (m, 2H), 7.55 (d, *J* = 8.7 Hz, 1H), 7.49 (d, *J* = 5.0 Hz, 1H), 7.35 (s, 1H), 7.12 (t, *J* = 4.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 154.5, 146.9, 145.0, 137.5, 129.2, 129.0, 128.2, 128.0, 121.7, 116.4, 109.9, 105.6. HRMS (ESI) m/z calcd for $C_{13}H_8NOS_2^+$ $(M+H)^+$ 258.0042, found 258.0046.

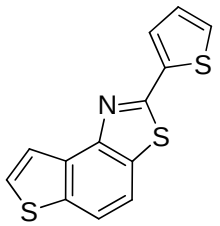


2-(Furan-2-yl)thieno[2',3':5,6]benzo[1,2-*d*]thiazole (4k)

The general procedure **A** was followed using 6,7-dihydrobenzo[b]thiophen-4(5*H*)-one *O*-acetyl oxime (**1i**, 62.7 mg, 0.3 mmol), furan-2-carbaldehyde (**2w**, 17 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6

mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1) yielded **4k** (41.1 mg, 80%) as a light green solid. mp: 161–163 °C.

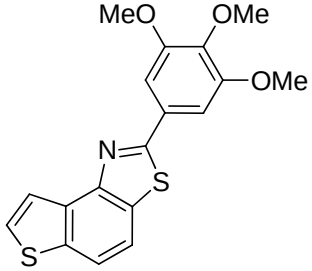
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.06 (d, *J* = 5.4 Hz, 1H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.63–7.57 (m, 2H), 7.23 (d, *J* = 3.4 Hz, 1H), 6.62–6.57 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 148.9, 148.9, 144.5, 138.6, 134.1, 130.3, 127.1, 122.2, 119.7, 117.2, 112.5, 111.2. HRMS (ESI) m/z calcd for $C_{13}H_8NOS_2^+$ $(M+H)^+$ 258.0042, found 258.0046.



2-(Thiophen-2-yl)thieno[2',3':5,6]benzo[1,2-*d*]thiazole (4l)

The general procedure **A** was followed using 6,7-dihydrobenzo[b]thiophen-4(5*H*)-one *O*-acetyl oxime (**1i**, 62.7 mg, 0.3 mmol), thiophene-2-carbaldehyde (**2v**, 19 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1) yielded a mixture of **4l** (50.8 mg, 93%) as a dark green solid. mp: 120–122 °C.

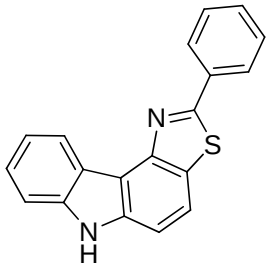
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.04 (d, *J* = 5.4 Hz, 1H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.68 (d, *J* = 3.5 Hz, 1H), 7.59 (d, *J* = 5.4 Hz, 1H), 7.49 (d, *J* = 5.0 Hz, 1H), 7.17–7.09 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 148.7, 138.5, 137.5, 134.0, 130.7, 128.9, 128.1, 128.0, 127.0, 122.2, 119.6, 117.1. HRMS (ESI) m/z calcd for $C_{13}H_8NS_3^+$ $(M+H)^+$ 273.9813, found 273.9816.



2-(3,4,5-Trimethoxyphenyl)thieno[2',3':5,6]benzo[1,2-*d*]thiazole (4m)

The general procedure **A** was followed using 6,7-dihydrobenzo[*b*]thiophen-4(5*H*)-one *O*-acetyl oxime (**1i**, 62.7 mg, 0.3 mmol), 3,4,5-trimethoxybenzaldehyde (**2s**, 39.3 mg, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **4m** (63.5 mg, 89%) as a dark white solid. mp: 195–197 °C.

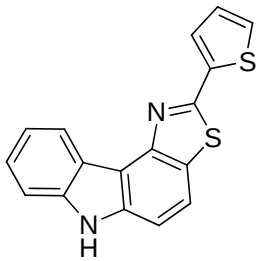
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.10 (d, *J* = 5.4 Hz, 1H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 8.6 Hz, 1H), 7.62 (d, *J* = 5.4 Hz, 1H), 7.39 (s, 2H), 4.02 (s, 6H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167. 5, 153.5, 149.0, 140.4, 138.5, 134.2, 131.0, 129.2, 127.1, 122.2, 119.6, 117.2, 104.6, 61.0, 56.3. HRMS (ESI) m/z calcd for $C_{18}H_{16}NO_3S_2^+$ $(M+H)^+$ 358.0566, found 358.0568.



2-Phenyl-6*H*-thiazolo[5,4-*c*]carbazole (4n)

The general procedure **A** was followed using 2,3-dihydro-1*H*-carbazol-4(9*H*)-one *O*-acetyl oxime (**1j**, 72.6 mg, 0.3 mmol), benzaldehyde (**2a**, 21 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **4n** (36.6 mg, 61%) as a yellow solid. mp: 212–215 °C.

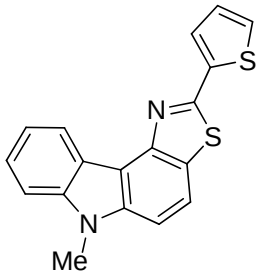
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.84 (d, *J* = 7.8 Hz, 1H), 8.32–8.18 (m, 3H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.55–7.45 (m, 6H), 7.41–7.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 148.8, 138.8, 138.4, 134.2, 130.6, 129.0, 127.5, 126.9, 125.7, 123.3, 122.5, 120.1, 118.3, 116.6, 110.5, 109.6. HRMS (ESI) m/z calcd for $C_{19}H_{13}N_2S^+$ $(M+H)^+$ 301.0794, found 301.0797.



10-Phenylphenanthro[2',1':4,5]thieno[3,2-*d*]thiazole (4o)

The general procedure **A** was followed using 2,3-dihydro-1*H*-carbazol-4(9*H*)-one *O*-acetyl oxime (**1j**, 72.6 mg, 0.3 mmol), thiophene-2-carbaldehyde (**2v**, 19 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **4o** (18.9 mg, 31%) as a dark green solid. mp: 223–225 °C.

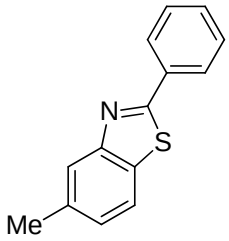
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.78 (d, *J* = 7.8 Hz, 1H), 8.28 (s, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 3.6 Hz, 1H), 7.49 (dt, *J* = 13.9, 6.7 Hz, 4H), 7.38 (t, *J* = 7.0 Hz, 1H), 7.16 (t, *J* = 4.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 148.4, 138.8, 138.4, 138.2, 128.8, 128.0, 127.9, 126.4, 125.7, 123.4, 122.4, 120.1, 118.1, 116.4, 110.4, 109.5. HRMS (ESI) m/z calcd for $C_{17}H_{11}N_2S_2^+$ $(M+H)^+$ 307.0358, found 307.0361.



6-Methyl-2-(thiophen-2-yl)-6*H*-thiazolo[5,4-*c*]carbazole (4p)

The general procedure **A** was followed using 9-methyl-2,3-dihydro-1*H*-carbazol-4(9*H*)-one *O*-acetyl oxime (**1k**, 76.8 mg, 0.3 mmol), thiophene-2-carbaldehyde (**2v**, 19 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1) yielded **4p** (32.6 mg, 51%) as a yellow solid. mp: 184–186 °C.

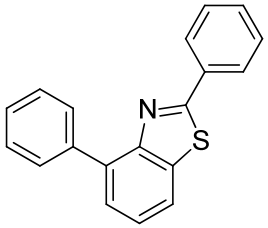
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.78 (d, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.69 (d, *J* = 3.4 Hz, 1H), 7.57–7.46 (m, 2H), 7.44–7.34 (m, 3H), 7.17–7.08 (m, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 148.4, 140.2, 139.9, 138.2, 128.8, 127.9, 127.8, 126.0, 125.4, 123.3, 121.7, 119.5, 117.8, 115.6, 108.3, 107.4, 29.5. HRMS (ESI) m/z calcd for $C_{18}H_{13}N_2S_2^+$ $(M+H)^+$ 321.0515, found 321.0517.



5-Methyl-2-phenylbenzo[*d*]thiazole (4q)

The general procedure **A** was followed using 3-methylcyclohex-2-enone *O*-acetyl oxime (**1l**, 50.1 mg, 0.3 mmol), benzaldehyde (**2a**, 21 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 60/1) yielded **4q** (25.6 mg, 57%) as a dark green solid. mp: 145–147 °C.

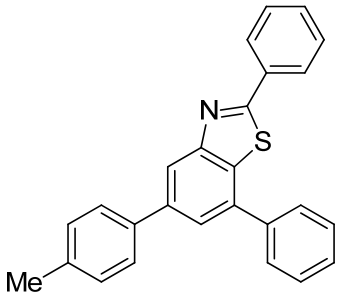
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.09 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.89 (s, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.51–7.47 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 154.3, 136.5, 133.6, 131.9, 130.9, 129.0, 127.5, 126.9, 123.2, 121.1, 21.5.



2,4-Diphenylbenzo[*d*]thiazole (4r)

The general procedure **A** was followed using 4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one *O*-acetyl oxime (**1m**, 68.7 mg, 0.3 mmol), benzaldehyde (**2a**, 21 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1) yielded **4r** (23.5 mg, 41%) as a yellow solid. mp: 102–104 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.06 (dd, *J* = 6.4, 3.1 Hz, 2H), 7.93 (d, *J* = 7.7 Hz, 2H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.46–7.37 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 151.7, 139.0, 136.3, 133.8, 130.9, 129.9, 129.0, 128.2, 127.7, 127.6, 126.5, 125.4, 120.7. HRMS (ESI) m/z calcd for $C_{19}H_{14}NS^+$ $(M+H)^+$ 288.0842, found 288.0844.

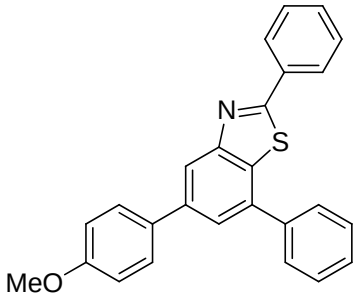


2,7-Diphenyl-5-(*p*-tolyl)benzo[*d*]thiazole (4s)

The general procedure **A** was followed using 4''-methyl-1',6'-dihydro-[1,1':3',1''-terphenyl]-5'(2'*H*)-one *O*-acetyl oxime (**1o**, 95.7 mg, 0.3 mmol), benzaldehyde (**2a**, 21 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1) yielded **4q** (70.1 mg, 93%) as a light yellow

white solid. mp: 159–161 °C.

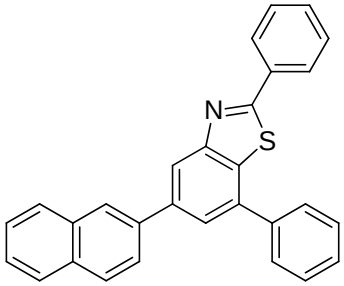
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.28 (s, 1H), 8.15–8.08 (m, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.69 (s, 1H), 7.64 (d, *J* = 7.7 Hz, 2H), 7.57–7.45 (m, 6H), 7.31 (d, *J* = 7.7 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 155.2, 140.6, 140.5, 137.7, 137.4, 136.4, 133.4, 133.0, 131.1, 129.7, 129.0, 129.0, 128.3, 127.9, 127.5, 127.2, 124.4, 120.1, 21.1. HRMS (ESI) m/z calcd for $C_{26}H_{20}NS^+$ $(M+H)^+$ 378.1311, found 378.1317.



5-(4-Methoxyphenyl)-2,7-diphenylbenzo[*d*]thiazole (4t)

The general procedure **A** was followed using 4''-methoxy-1',6'-dihydro-[1,1':3',1''-terphenyl]-5'(2'*H*)-one *O*-acetyl oxime (**1p**, 100.5 mg, 0.3 mmol), benzaldehyde (**2a**, 21 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **4r** (74.7 mg, 95%) as a light yellow white solid. mp: 149–151 °C.

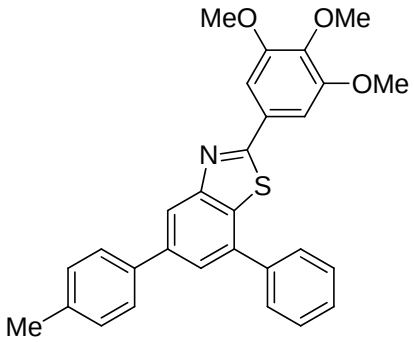
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.22 (s, 1H), 8.13–8.05 (m, 2H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 3H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.49–7.40 (m, 4H), 7.01 (d, *J* = 8.3 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 159.4, 155.4, 140.6, 140.1, 136.3, 133.5, 133.1, 132.8, 131.0, 129.0, 128.9, 128.4, 128.2, 127.8, 127.4, 124.1, 119.9, 114.4, 55.3. HRMS (ESI) m/z calcd for $C_{26}H_{20}NOS^+$ $(M+H)^+$ 394.1260, found 394.1264.



5-(Naphthalen-2-yl)-2,7-diphenylbenzo[*d*]thiazole (4u)

The general procedure **A** was followed using 5-(naphthalen-2-yl)-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one *O*-acetyl oxime (**1q**, 106.5 mg, 0.3 mmol), benzaldehyde (**2a**, 21 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1) yielded **4s** (76.8 mg, 93%) as a yellow solid. mp: 204–206 °C.

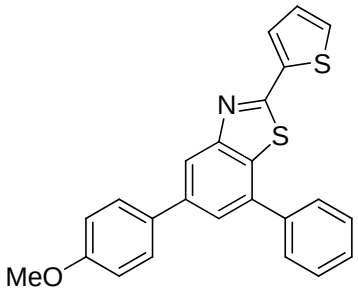
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.39 (s, 1H), 8.16 (s, 1H), 8.14–8.04 (m, 2H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.92–7.83 (m, 3H), 7.83–7.74 (m, 3H), 7.59–7.40 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 155.4, 140.5, 140.3, 137.8, 136.5, 133.6, 133.5, 133.4, 132.7, 131.1, 129.0, 129.0, 128.6, 128.3, 128.2, 127.9, 127.6, 127.5, 126.4, 126.1, 126.0, 125.6, 124.5, 120.6. HRMS (ESI) m/z calcd for $C_{29}H_{20}NS^+$ $(M+H)^+$ 414.1311, found 414.1314.



7-Phenyl-5-(*p*-tolyl)-2-(3,4,5-trimethoxyphenyl)benzo[*d*]thiazole (4v)

The general procedure **A** was followed using 4''-methyl-1',6'-dihydro-[1,1':3',1''-terphenyl]-5'(2'*H*)-one *O*-acetyl oxime (**1r**, 95.7 mg, 0.3 mmol), 3,4,5-trimethoxybenzaldehyde (**2s**, 39.3 mg, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **4t** (84.1 mg, 90%) as a gray white solid. mp: 212–214 °C.

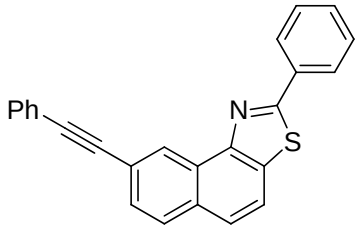
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.24 (s, 1H), 7.75 (d, *J* = 7.7 Hz, 2H), 7.66 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.46 (d, *J* = 6.9 Hz, 1H), 7.34 (s, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 3.96 (s, 6H), 3.93 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 155.2, 153.5, 140.6, 140.4, 137.6, 137.4, 136.3, 133.0, 129.6, 128.9, 128.9, 128.2, 127.8, 127.1, 124.2, 119.9, 104.5, 60.9, 56.3, 21.1. HRMS (ESI) m/z calcd for $C_{29}H_{26}NO_3S^+$ $(M+H)^+$ 468.1628, found 468.1628.



5-(4-Methoxyphenyl)-7-phenyl-2-(thiophen-2-yl)benzo[*d*]thiazole (4w)

The general procedure **A** was followed using 4''-methoxy-1',6'-dihydro-[1,1':3',1''-terphenyl]-5'(2'*H*)-one *O*-acetyl oxime (**1s**, 100.5 mg, 0.3 mmol), thiophene-2-carbaldehyde (**2v**, 19 μL, 0.2 mmol), and S_8 (19.2 mg, 0.6 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **4u** (72.6 mg, 91%) as a yellow solid. mp: 148–150 °C.

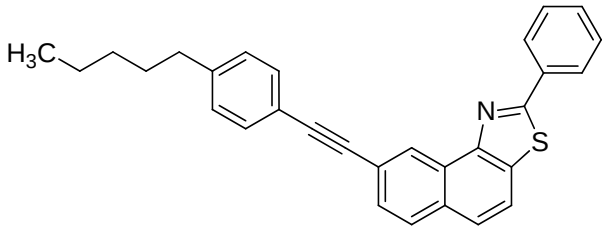
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.18 (s, 1H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.68–7.59 (m, 4H), 7.55–7.41 (m, 4H), 7.10 (t, *J* = 4.3 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 159.3, 154.9, 140.5, 140.2, 137.2, 136.2, 132.9, 132.3, 129.4, 129.0, 128.6, 128.3, 128.3, 128.1, 127.8, 124.1, 119.5, 114.3, 55.3. HRMS (ESI) m/z calcd for $C_{24}H_{18}NOS_2^+$ $(M+H)^+$ 400.0824, found 400.0828.



2-Phenyl-8-(phenylethynyl)naphtho[1,2-*d*]thiazole (5a)

To a stirred mixture of **4d** (68.2 mg, 0.2 mmol), $PdCl_2$ (1.8 mg, 5 mol%), PPh_3 (7.9 mg, 15 mol%) and CuI (1.9 mg, 5 mol%) in pressure tube (10 mL) was evacuated and purged with argon gas three times. To the tube was then added triethylamine (1.0 mL) via syringes. The mixture was stirred at room temperature for 30 min and then added phenylacetylene (33 μL, 0.30 mmol) via syringes. Thereafter, the reaction mixture was allowed to stir at 80 °C for 12 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 50/1) yielded **5c** (56.3 mg, 78%) as a yellow solid. mp: 218–220 °C.

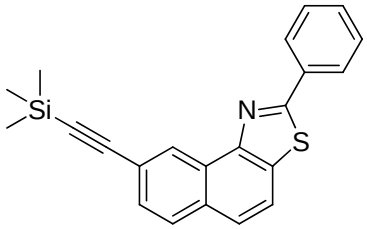
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.15 (s, 1H), 8.24 (d, *J* = 7.4 Hz, 2H), 7.94 (d, *J* = 8.7 Hz, 2H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 7.4 Hz, 2H), 7.55 – 7.46 (m, 3H), 7.44 – 7.33 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 150.0, 133.8, 132.2, 131.7, 131.3, 130.7, 129.1, 128.7, 128.4, 128.3, 128.1, 127.6, 127.4, 125.5, 123.3, 121.6, 119.7, 90.3, 90.0. HRMS (ESI) m/z calcd for $C_{25}H_{16}NS^+$ $(M+H)^+$ 362.0998, found 362.1000.



8-((4-Pentylphenyl)ethynyl)-2-phenylnaphtho[1,2-*d*]thiazole (5b)

To a stirred mixture of **4d** (68.2 mg, 0.2 mmol), $PdCl_2$ (1.8 mg, 5 mol%), PPh_3 (7.9 mg, 15 mol%) and CuI (1.9 mg, 5 mol%) in pressure tube (10 mL) was evacuated and purged with argon gas three times. To the tube was then added triethylamine (1.0 mL) via syringes. The mixture was stirred at room temperature for 30 min and then added 4-pentylphenylacetylene (59 μL, 0.30 mmol) via syringes. Thereafter, the reaction mixture was allowed to stir at 80 °C for 12 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 50/1) yielded **5d** (60.3 mg, 70%) as a yellow solid. mp: 136–138 °C.

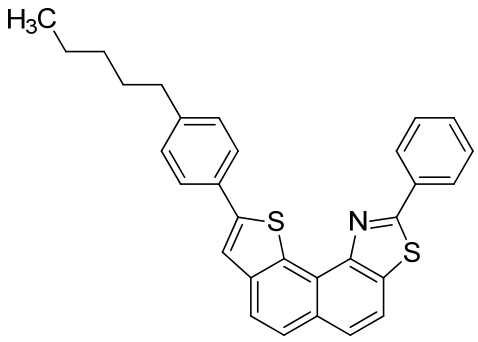
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.13 (s, 1H), 8.27–8.21 (m, 2H), 7.93 (dd, *J* = 8.5, 1.8 Hz, 2H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.71 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.55 (q, *J* = 6.9, 5.6 Hz, 5H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.68–2.62 (m, 2H), 1.66 (q, *J* = 7.3 Hz, 2H), 1.36 (dd, *J* = 8.2, 4.6 Hz, 4H), 0.93 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 149.9, 143.5, 133.8, 132.2, 131.6, 131.2, 130.7, 129.0, 128.7, 128.5, 128.3, 128.1, 127.4, 127.3, 125.5, 121.8, 120.4, 119.5, 90.6, 89.4, 35.9, 31.4, 30.9, 22.5, 14.0. HRMS (ESI) m/z calcd for $C_{30}H_{26}NS^+$ $(M+H)^+$ 432.1781, found 432.1785.



2-Phenyl-8-((trimethylsilyl)ethynyl)naphtho[1,2-*d*]thiazole (5c)

To a stirred mixture of **4d** (68.2 mg, 0.2 mmol), $PdCl_2$ (1.8 mg, 5 mol%), PPh_3 (7.9 mg, 15 mol%) and CuI (1.9 mg, 5 mol%) in pressure tube (10 mL) was evacuated and purged with argon gas three times. To the tube was then added triethylamine (1.0 mL) via syringes. The mixture was stirred at room temperature for 30 min and then added trimethylsilylacetylene (68 μL, 0.60 mmol) via syringes. Thereafter, the reaction mixture was allowed to stir at 80 °C for 12 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 50/1) yielded **5e** (59.3 mg, 83%) as a yellow solid. mp: 149–151 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.08 (s, 1H), 8.22 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.95–7.87 (m, 2H), 7.77 (dd, *J* = 8.7, 3.8 Hz, 1H), 7.64 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.56–7.50 (m, 3H), 0.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 149.9, 133.8, 132.2, 131.4, 130.7, 129.0, 128.9, 128.2, 128.1, 128.0, 127.3, 125.4, 121.4, 119.8, 105.5, 95.1, 0.0. HRMS (ESI) m/z calcd for $C_{22}H_{20}NSSi^+$ $(M+H)^+$ 358.1080, found 358.1087.



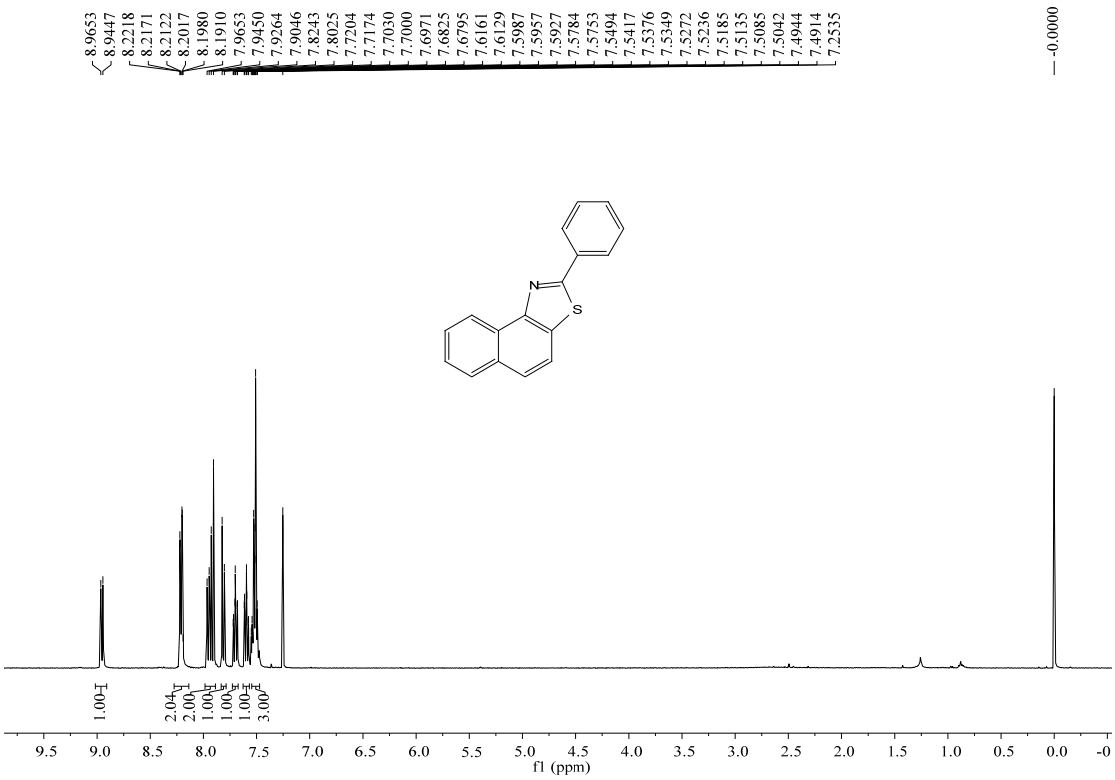
9-(4-Pentylphenyl)-2-phenylthieno[3',2':7,8]naphtho[1,2-*d*]thiazole (5d)

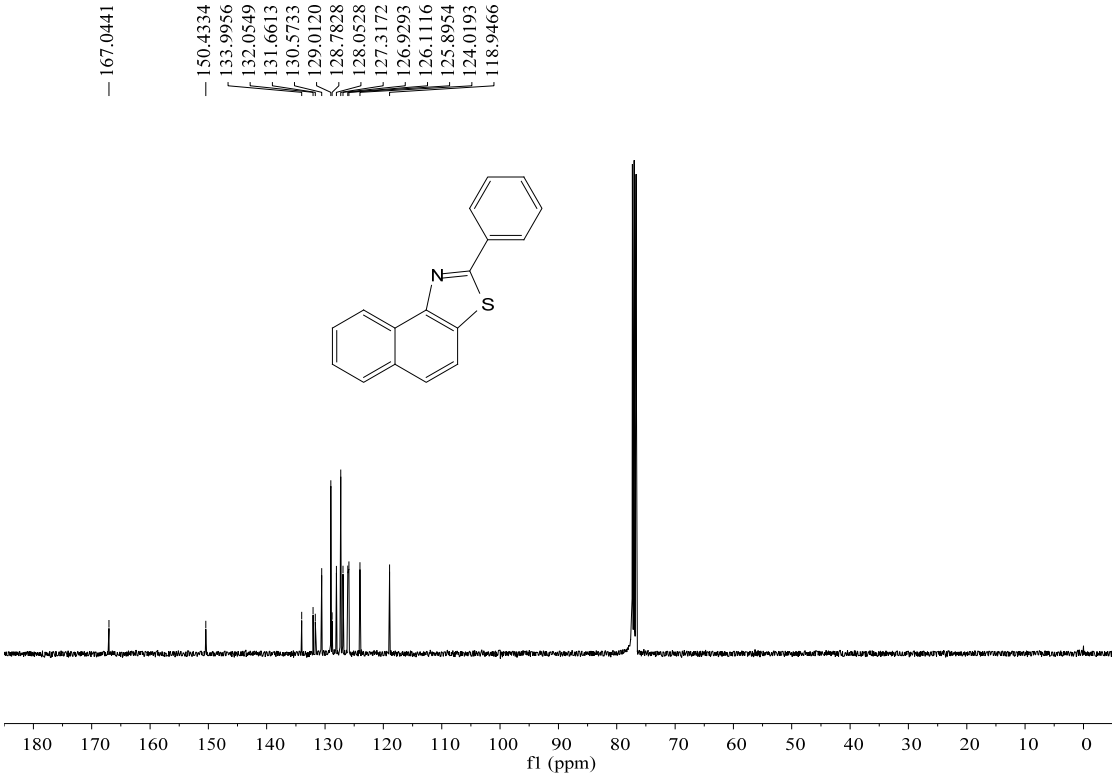
To a stirred mixture of **5d** (43.1 mg, 0.1 mmol) and S_8 (25.6 mg, 0.8 mmol) in pressure tube (10 mL) was evacuated and purged with argon gas three times. To the tube was then added DMF (1.0 mL) via syringes. Thereafter, the reaction mixture was allowed to stir at 140 °C for 48 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 50/1) yielded **5f** (21.6 mg, 50%) as a yellow solid. mp: 110–112 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.97 (s, 1H), 8.29–8.20 (m, 2H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 2.4 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 3H), 2.71–2.62 (m, 2H), 1.68 (q, *J* = 7.4 Hz, 2H), 1.42–1.32 (m, 4H), 0.94 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 150.3, 142.8, 136.1, 134.7, 133.9, 132.1, 131.4, 130.6, 129.4, 129.0, 129.0, 128.8, 128.4, 127.8, 127.3, 126.5, 125.6, 123.8, 122.3, 118.6, 35.7, 31.5, 31.1, 22.6, 14.1. HRMS (ESI) m/z calcd for $C_{30}H_{26}NS_2^+$ $(M+H)^+$ 464.1501, found 464.1502.

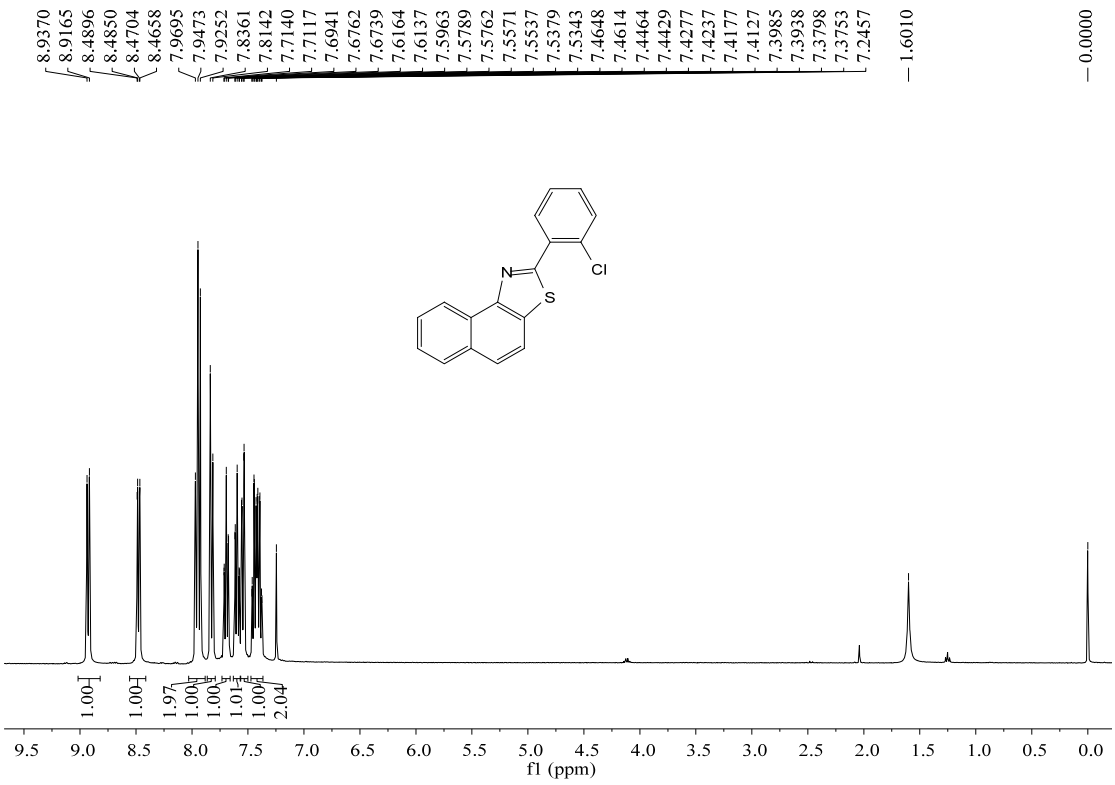
Copies of ^{1}H and ^{13}C NMR spectra of all products

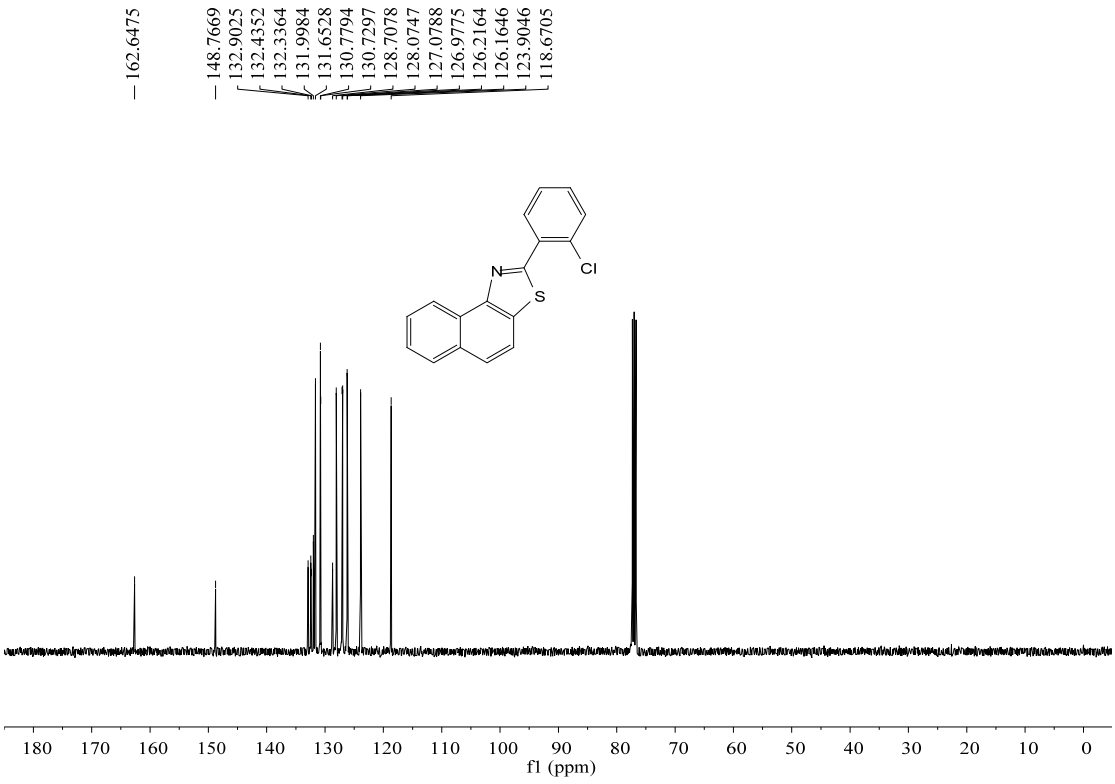
^{1}H and ^{13}C NMR spectra of **3a**



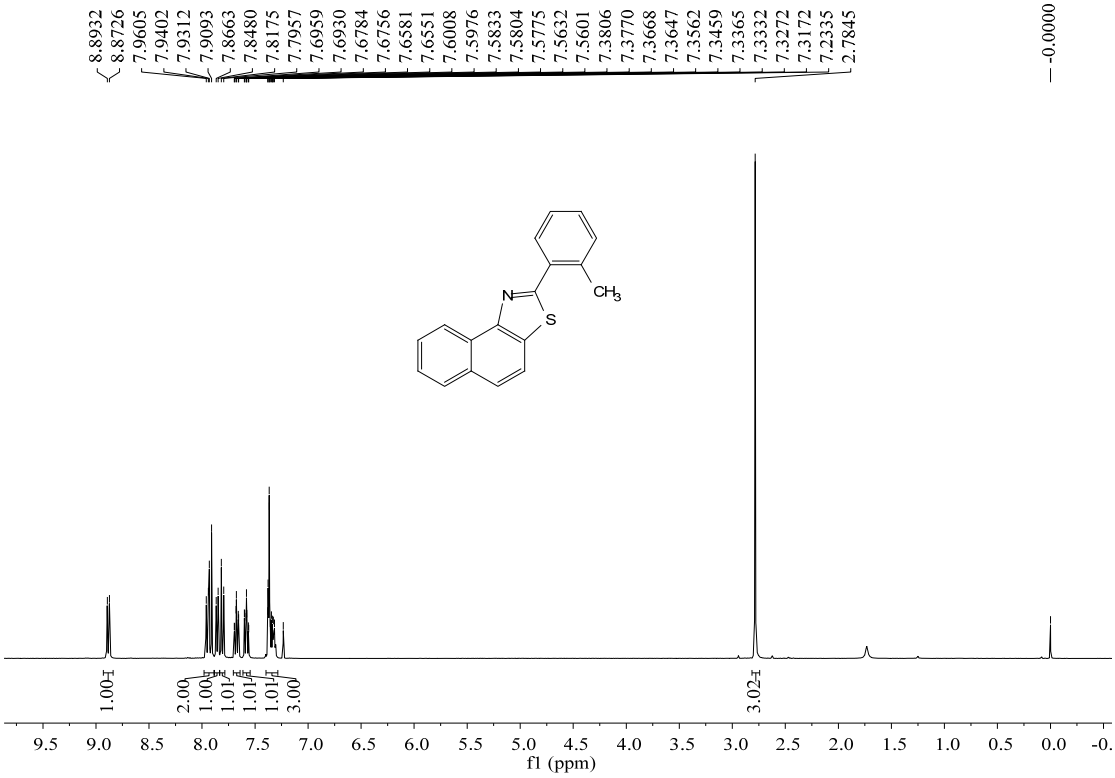


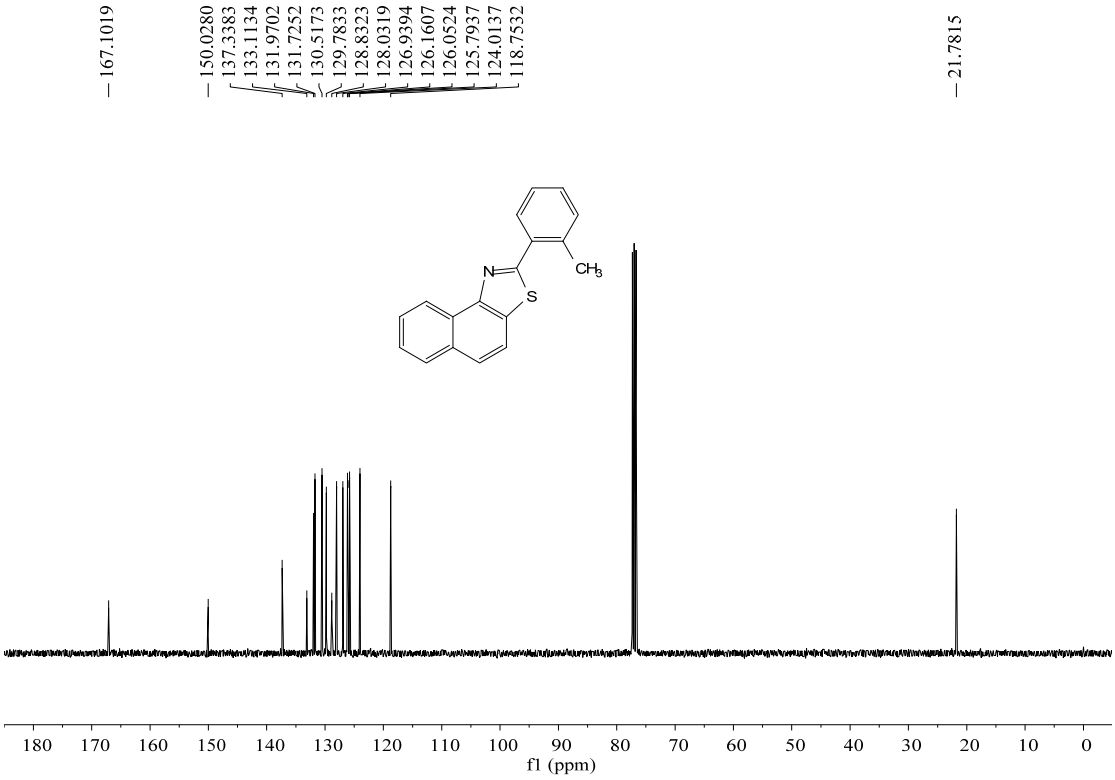
^{1}H and ^{13}C NMR spectra of **3b**



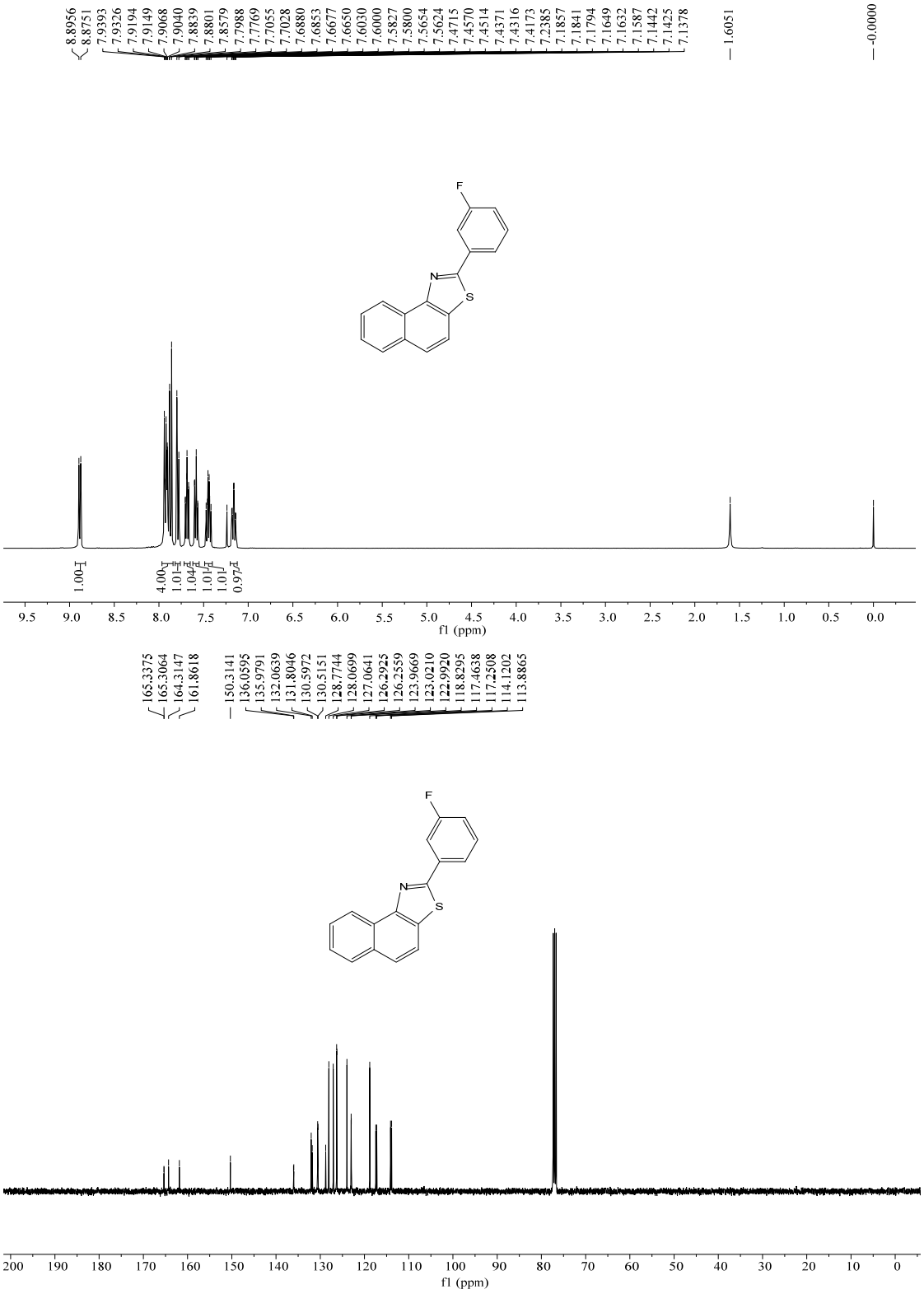


^{1}H and ^{13}C NMR spectra of **3c**

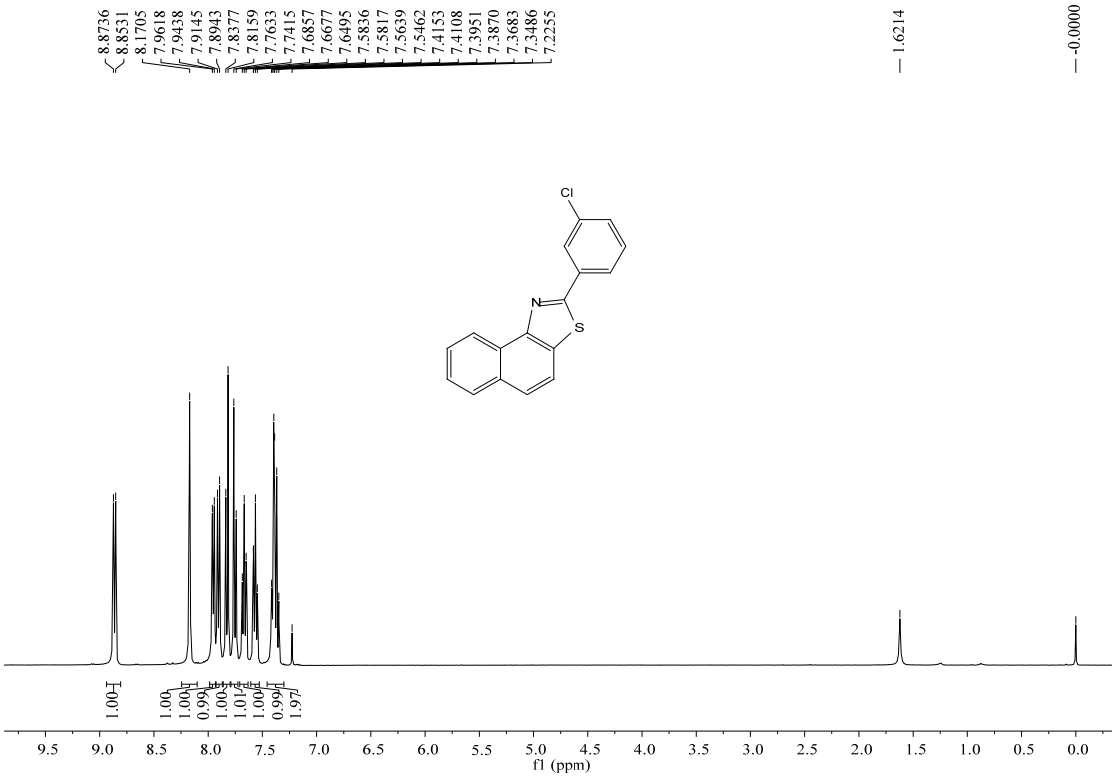


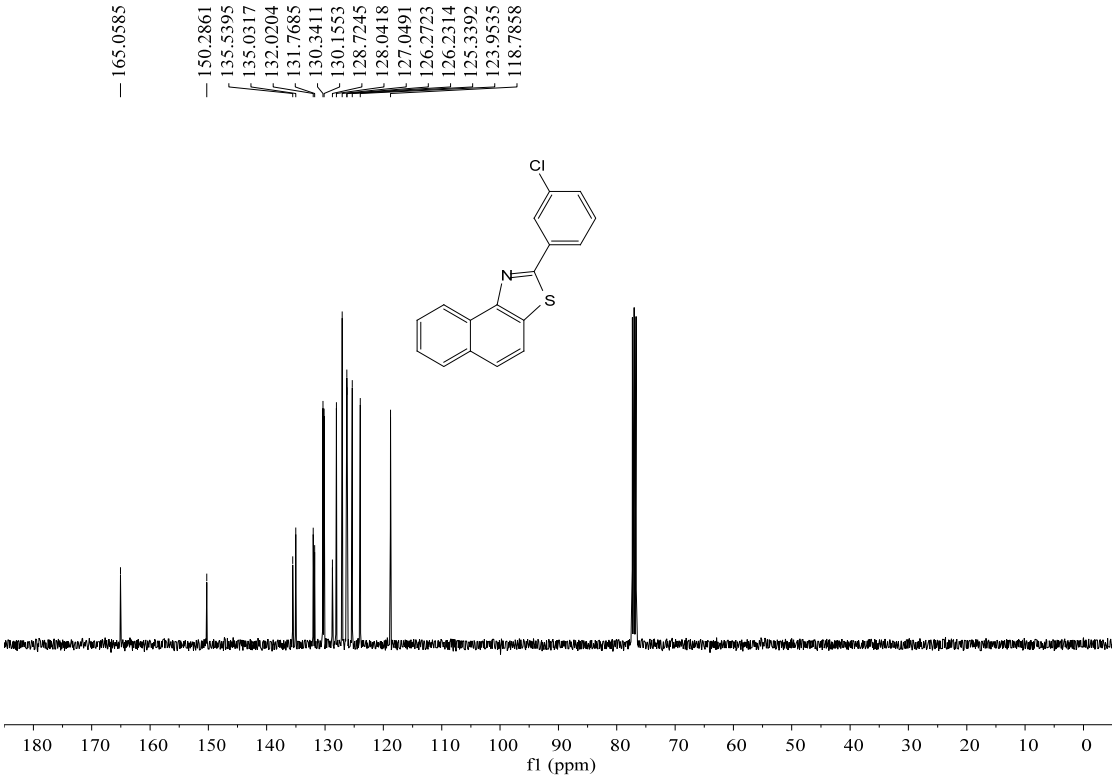


^{1}H and ^{13}C NMR spectra of **3d**

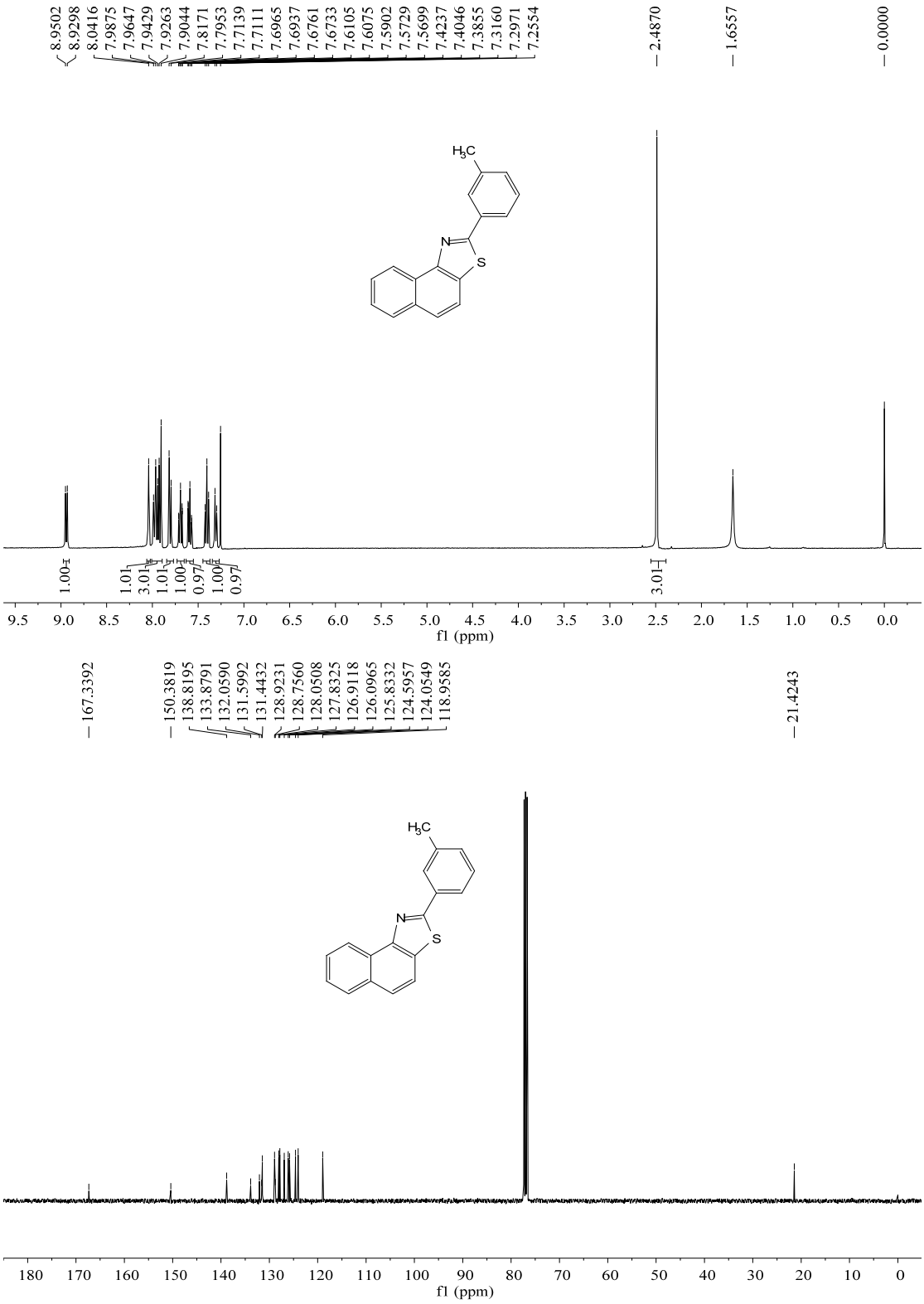


^{1}H and ^{13}C NMR spectra of **3e**

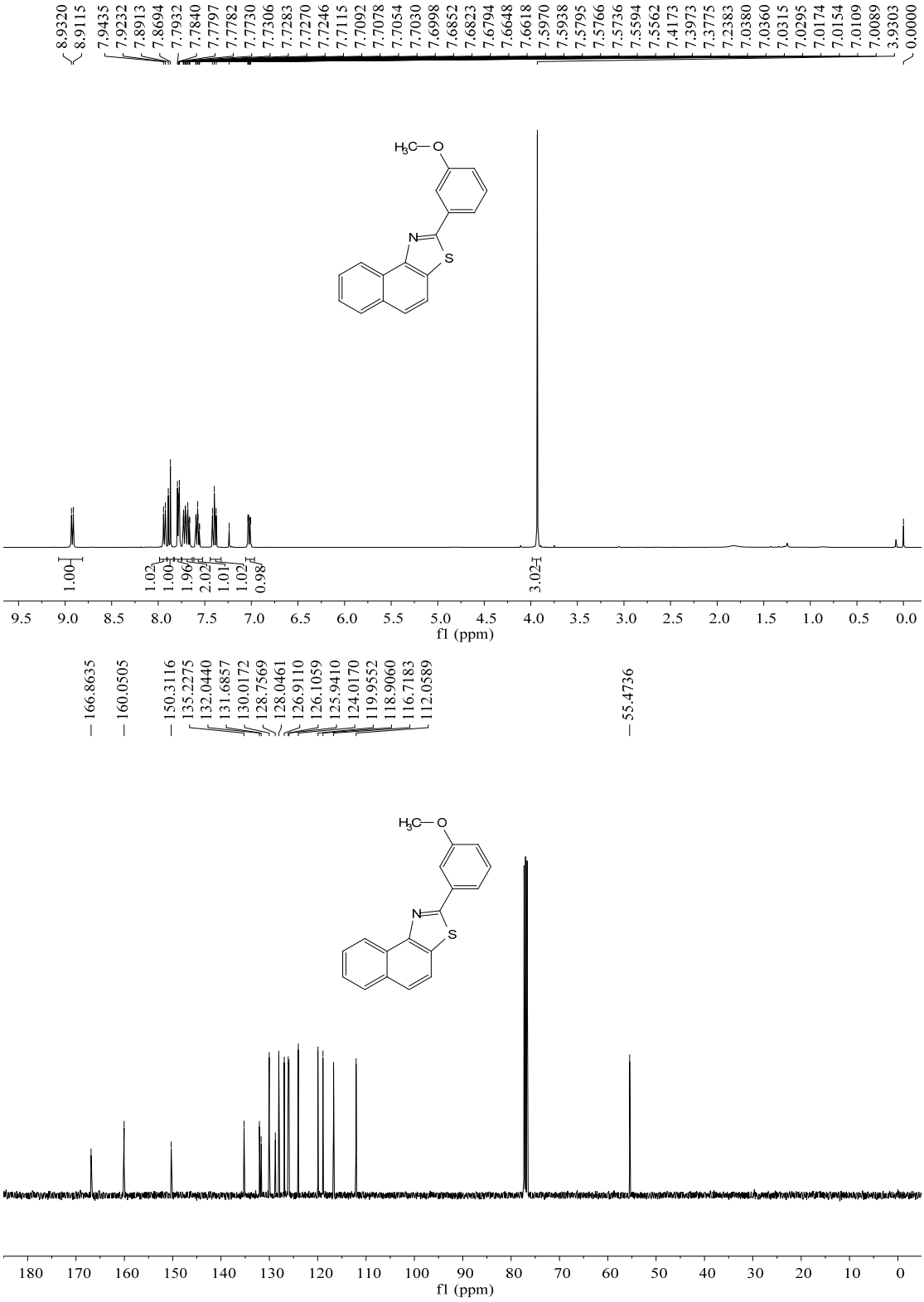




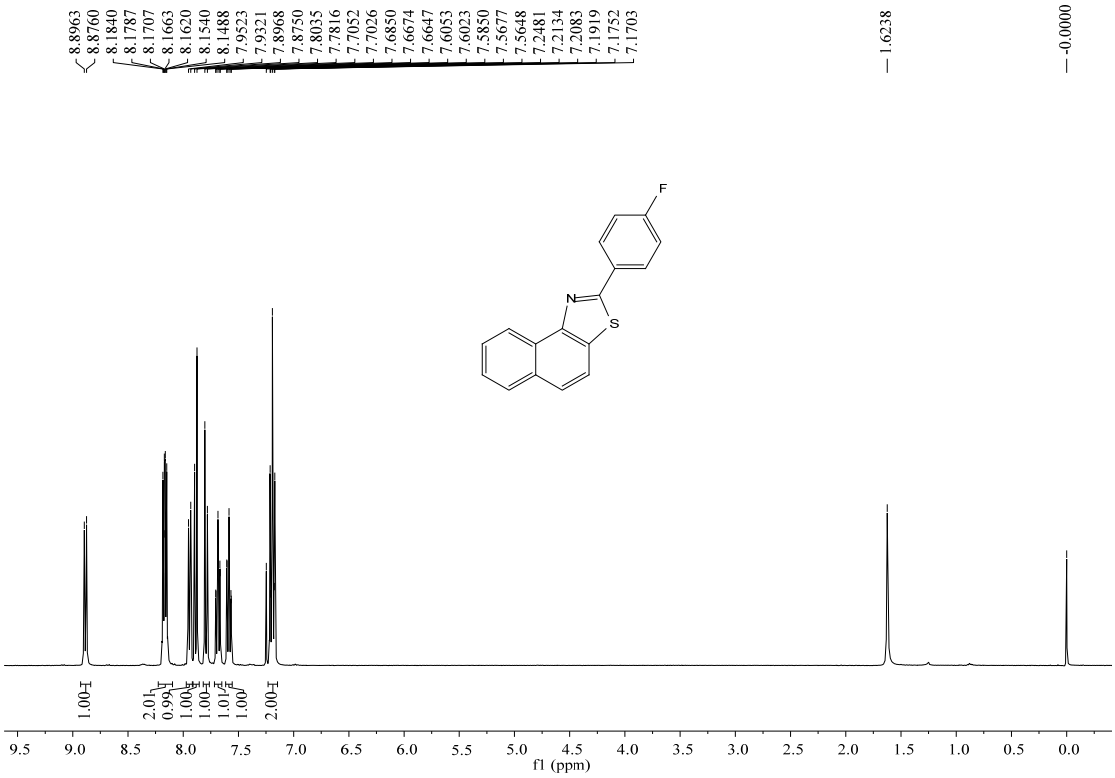
^{1}H and ^{13}C NMR spectra of **3f**

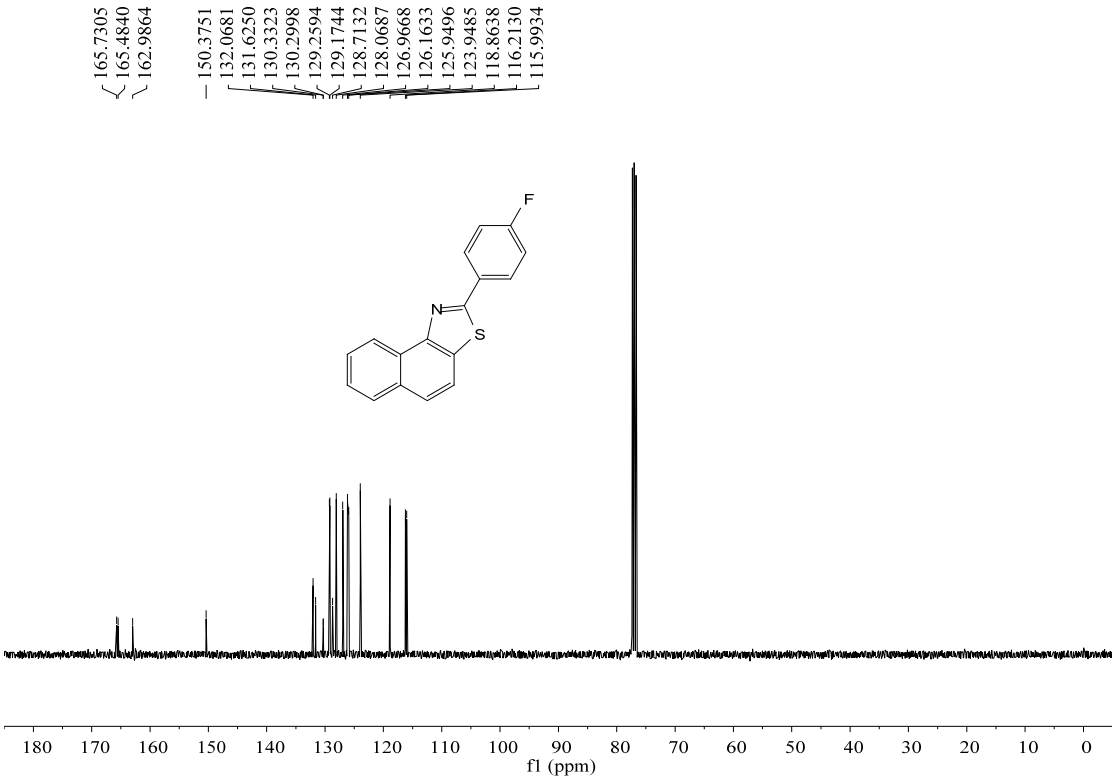


^{1}H and ^{13}C NMR spectra of **3g**

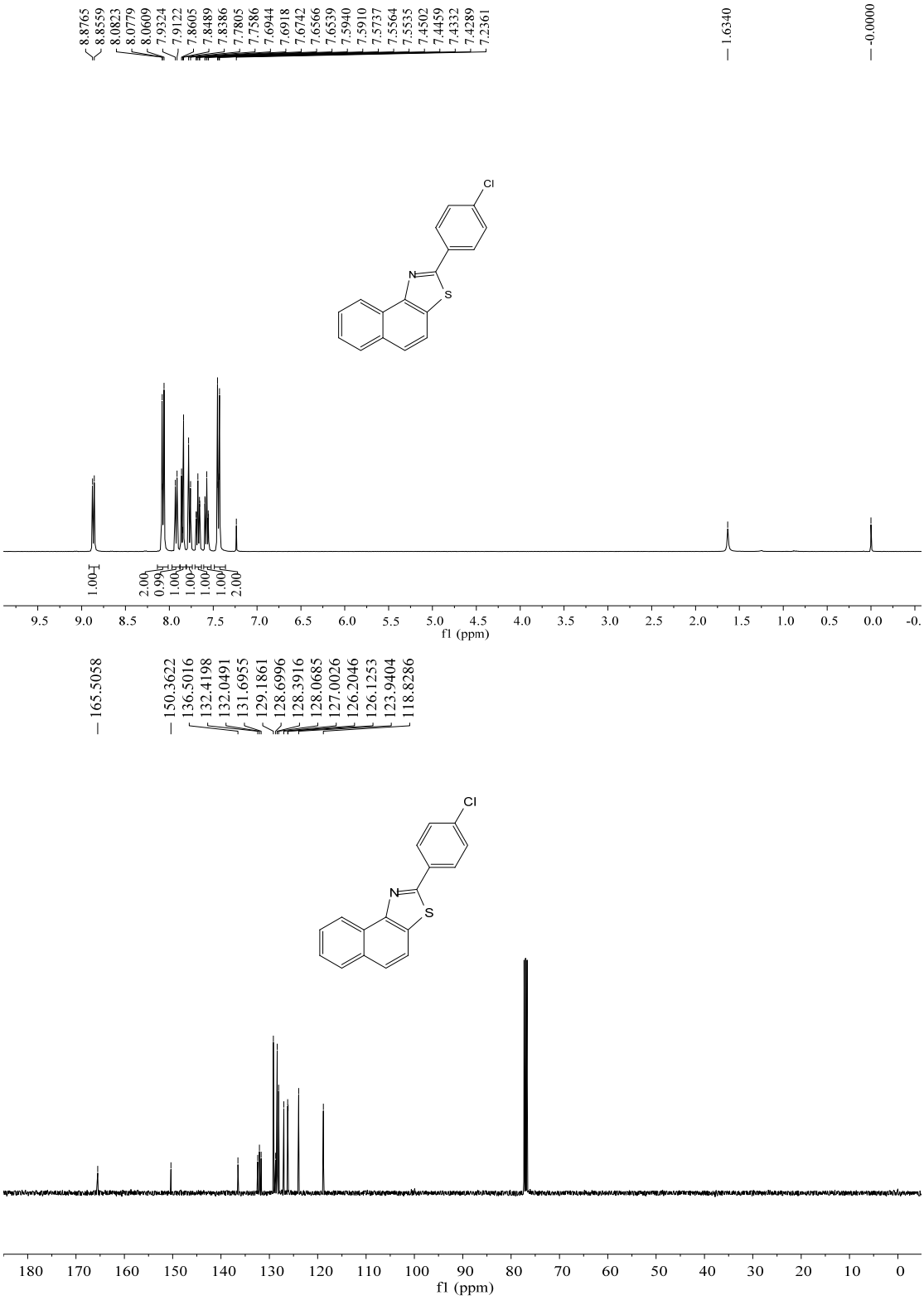


^{1}H and ^{13}C NMR spectra of **3h**

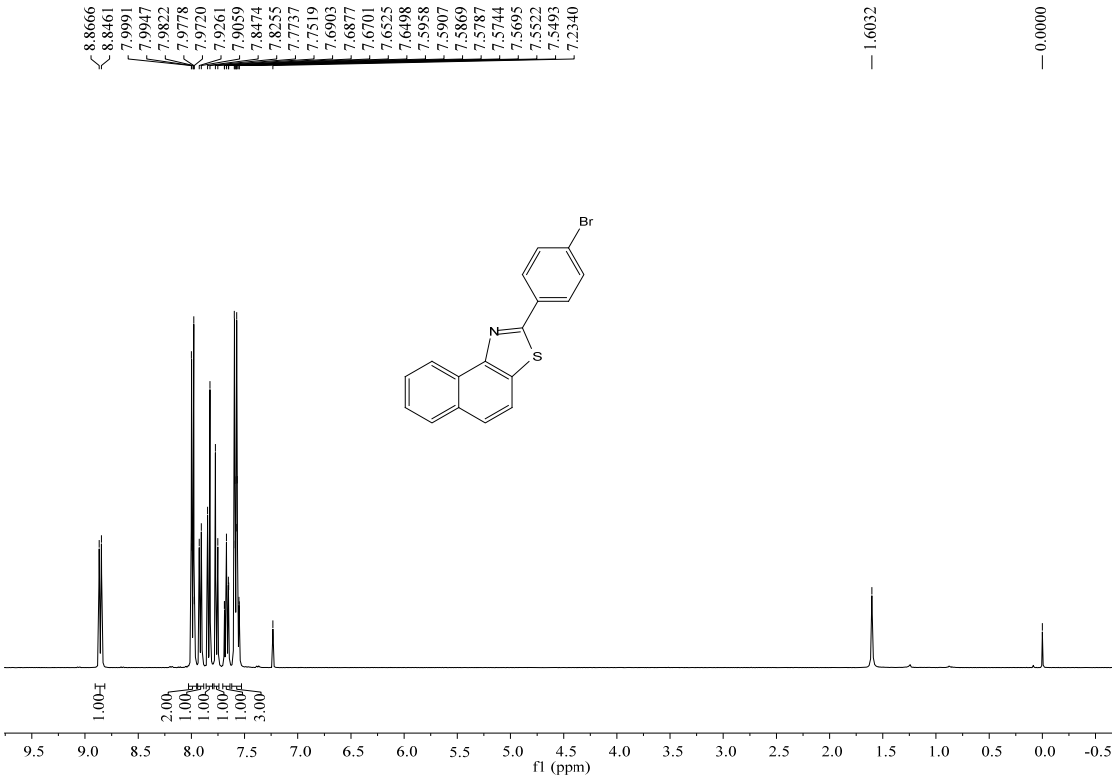


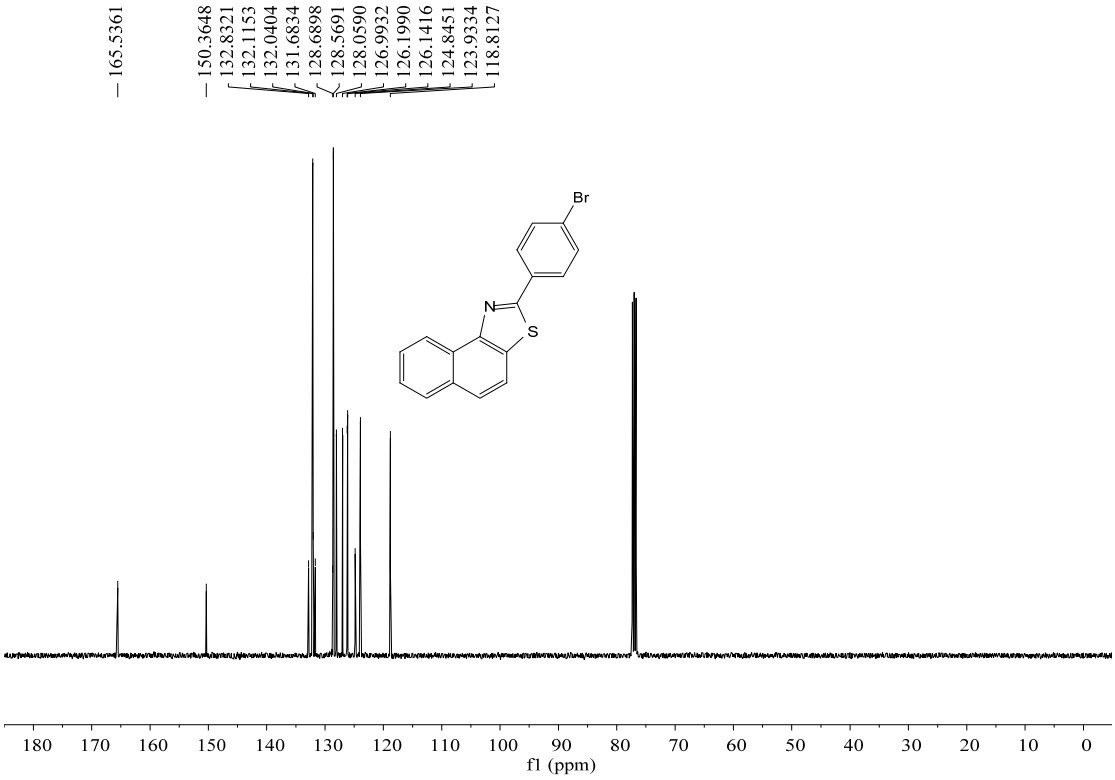


^{1}H and ^{13}C NMR spectra of **3i**

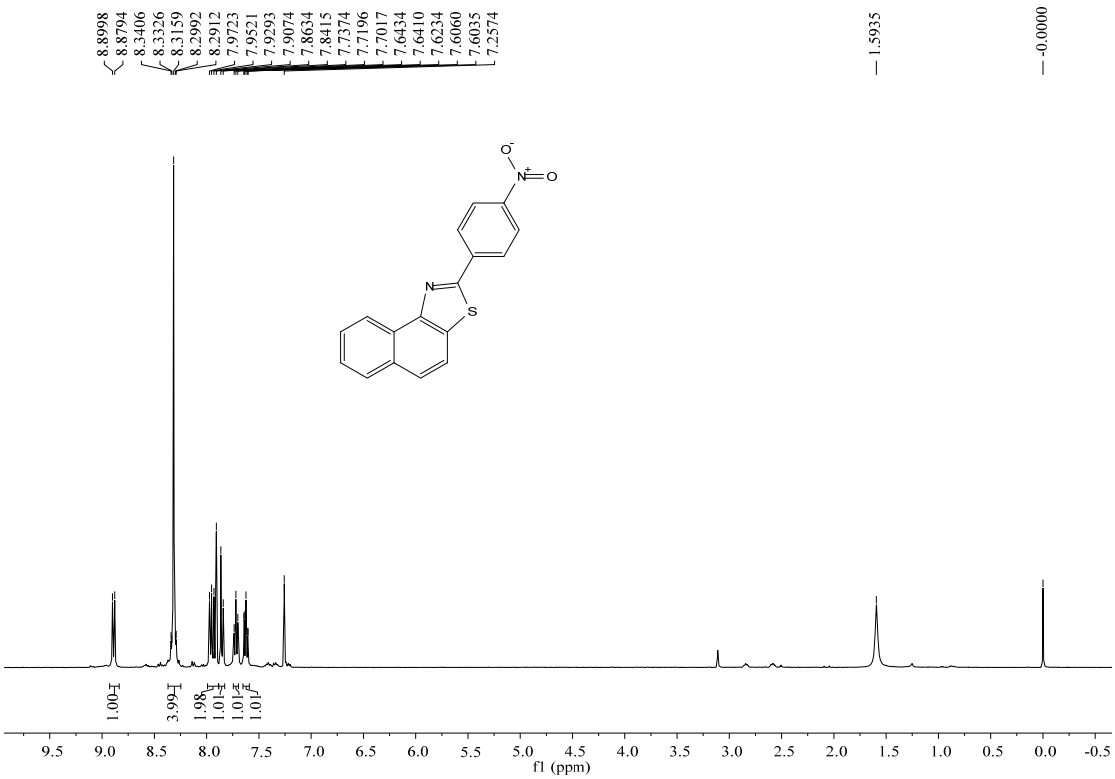


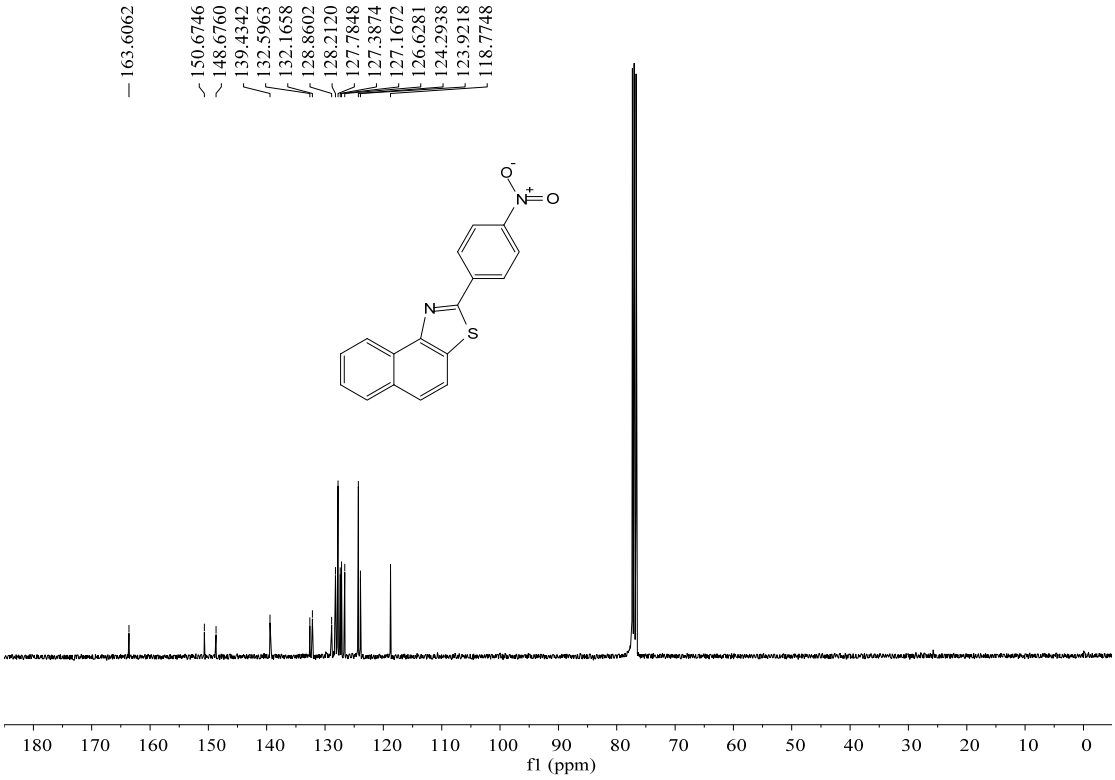
^{1}H and ^{13}C NMR spectra of **3j**



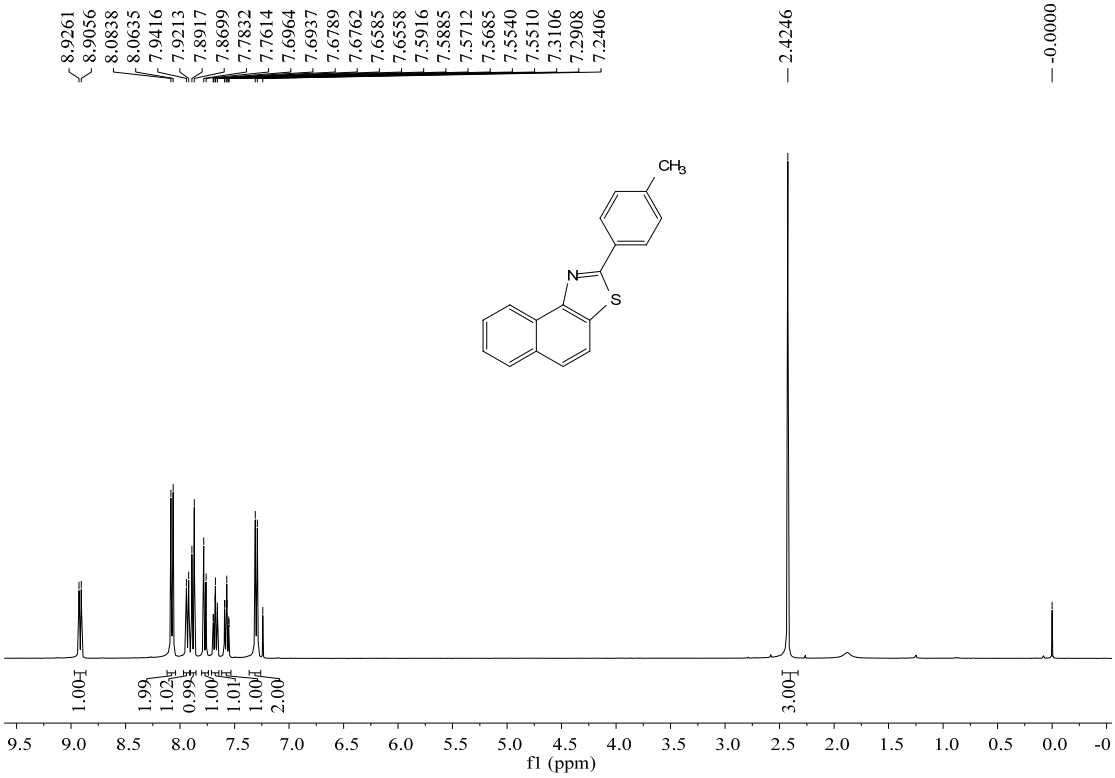


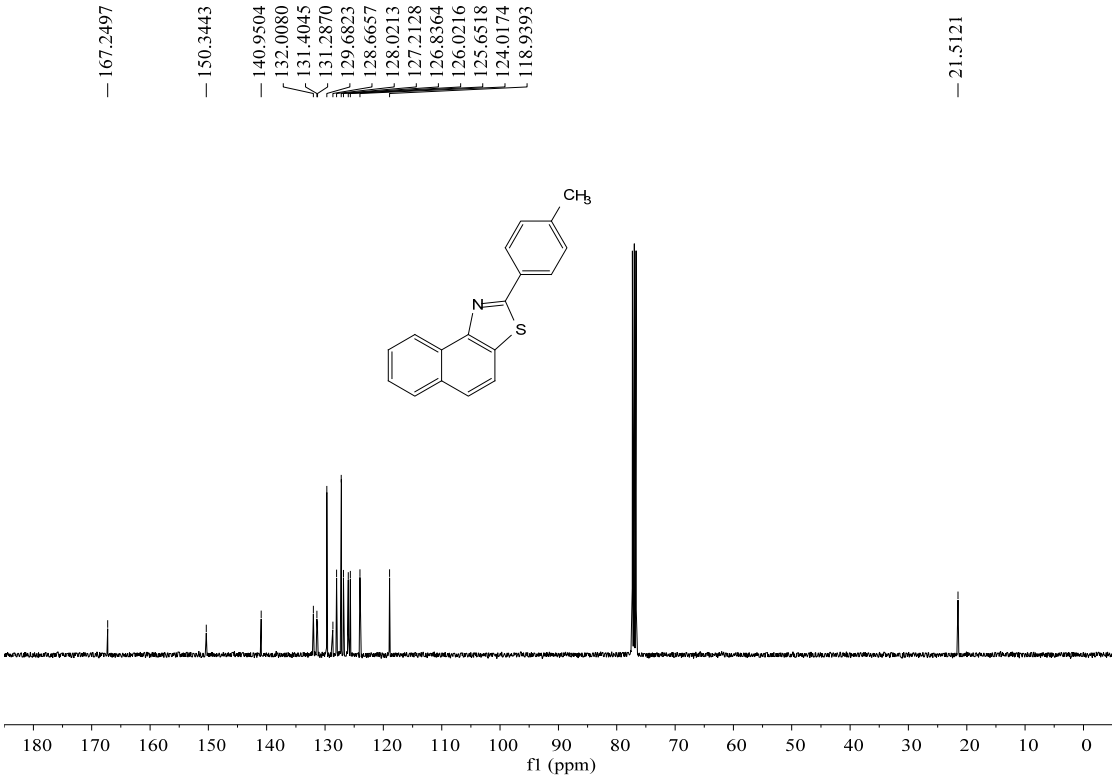
^{1}H and ^{13}C NMR spectra of **3k**



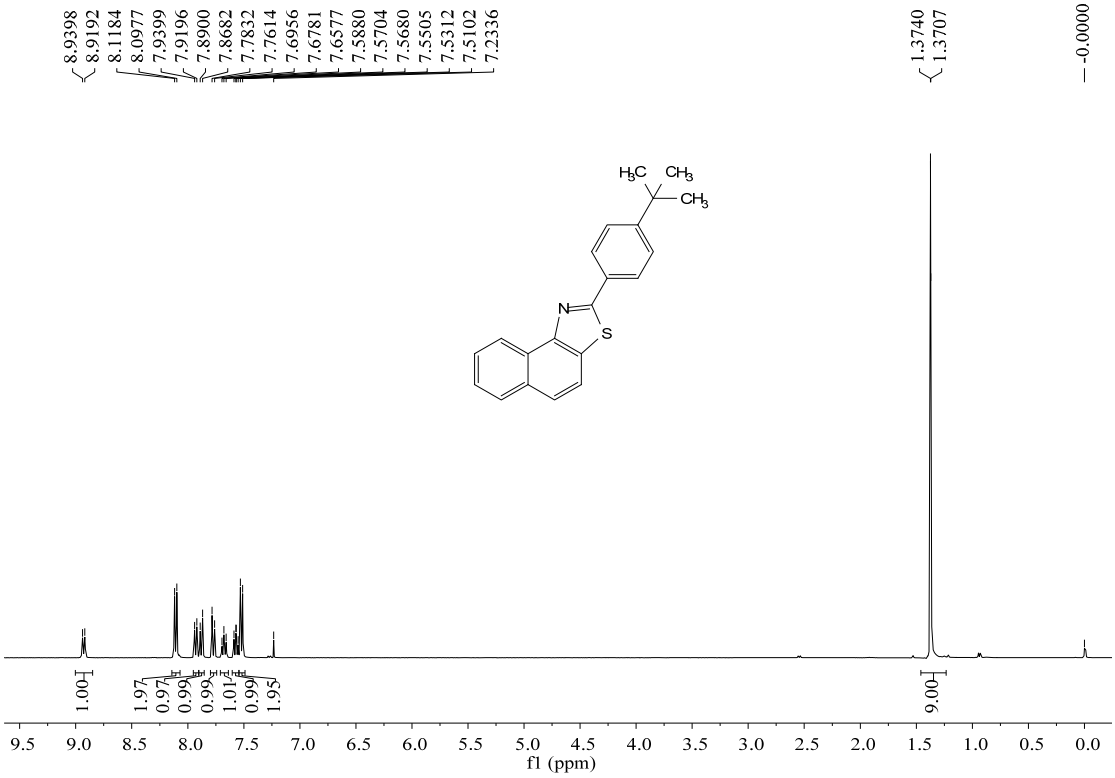


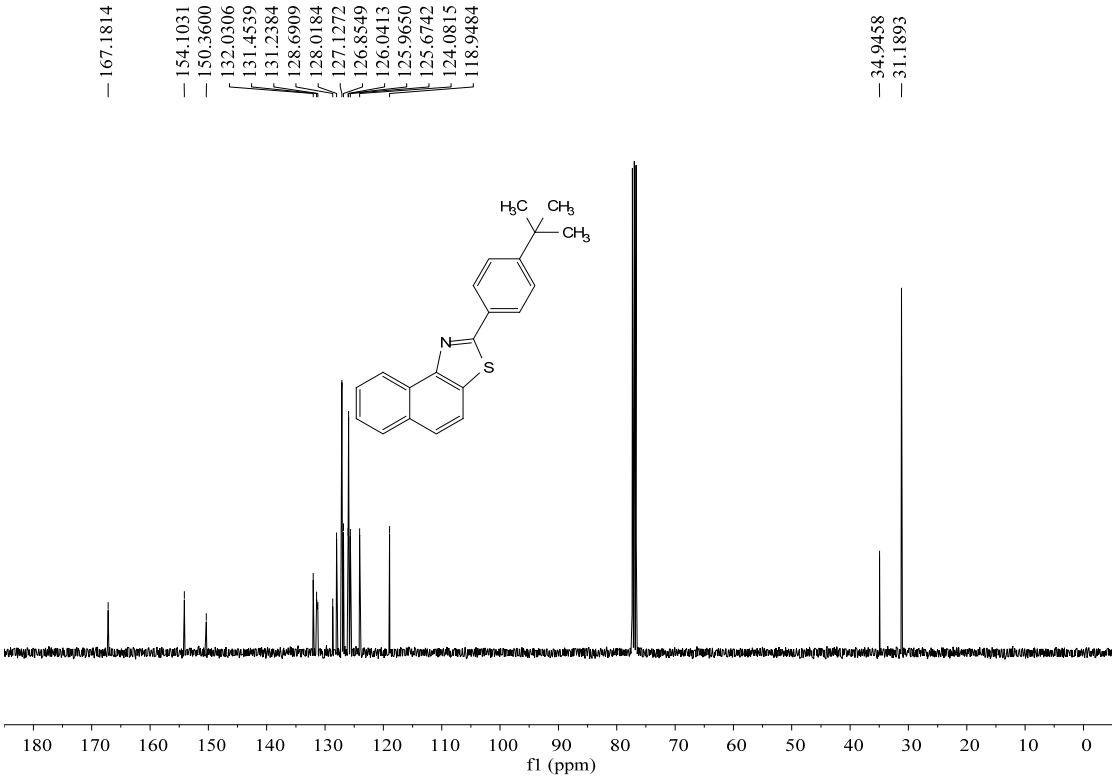
^{1}H and ^{13}C NMR spectra of **3l**



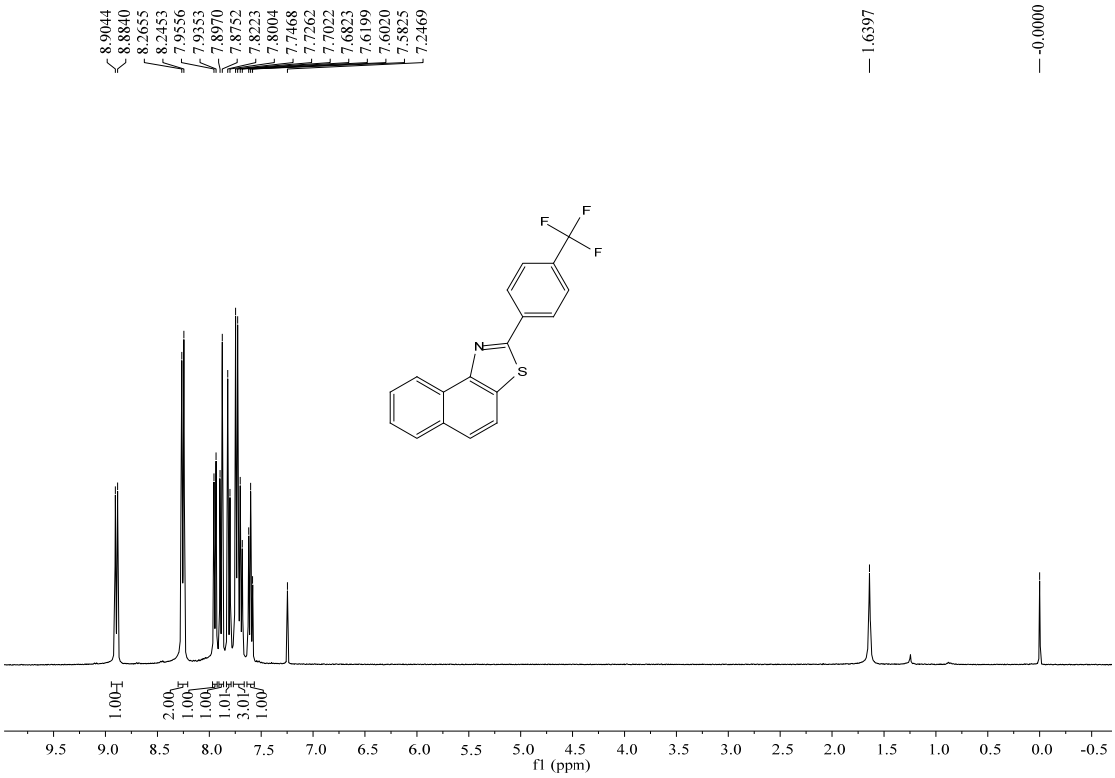


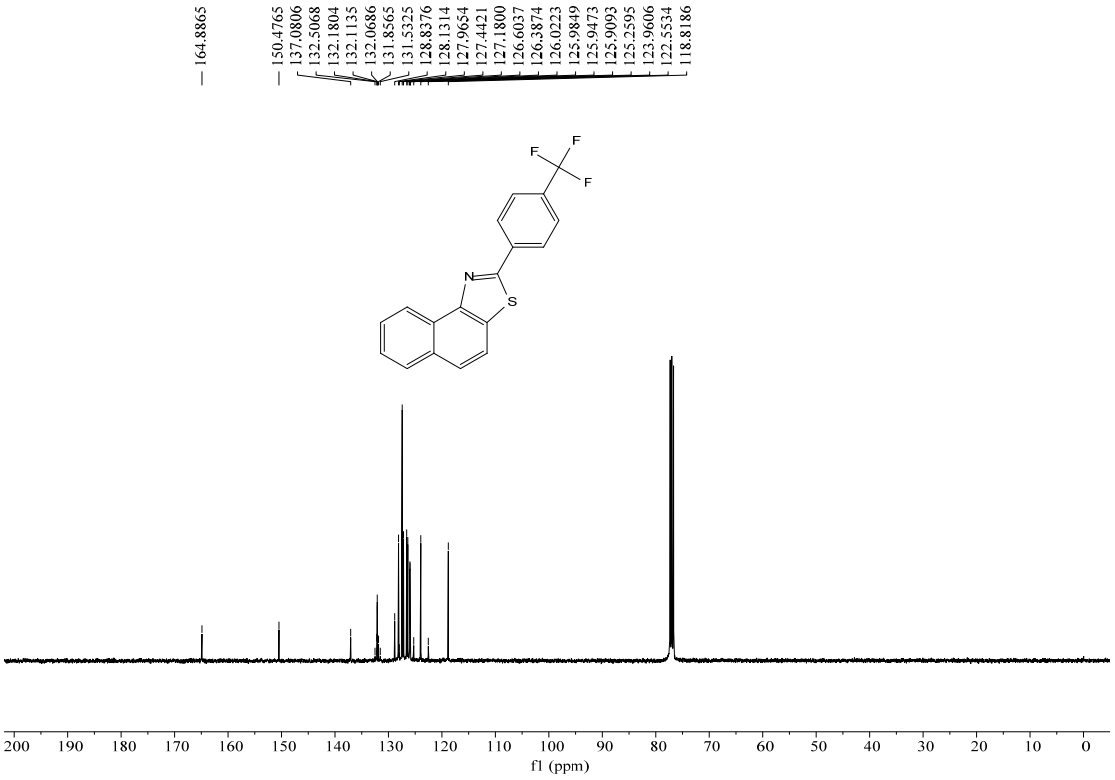
^{1}H and ^{13}C NMR spectra of **3m**



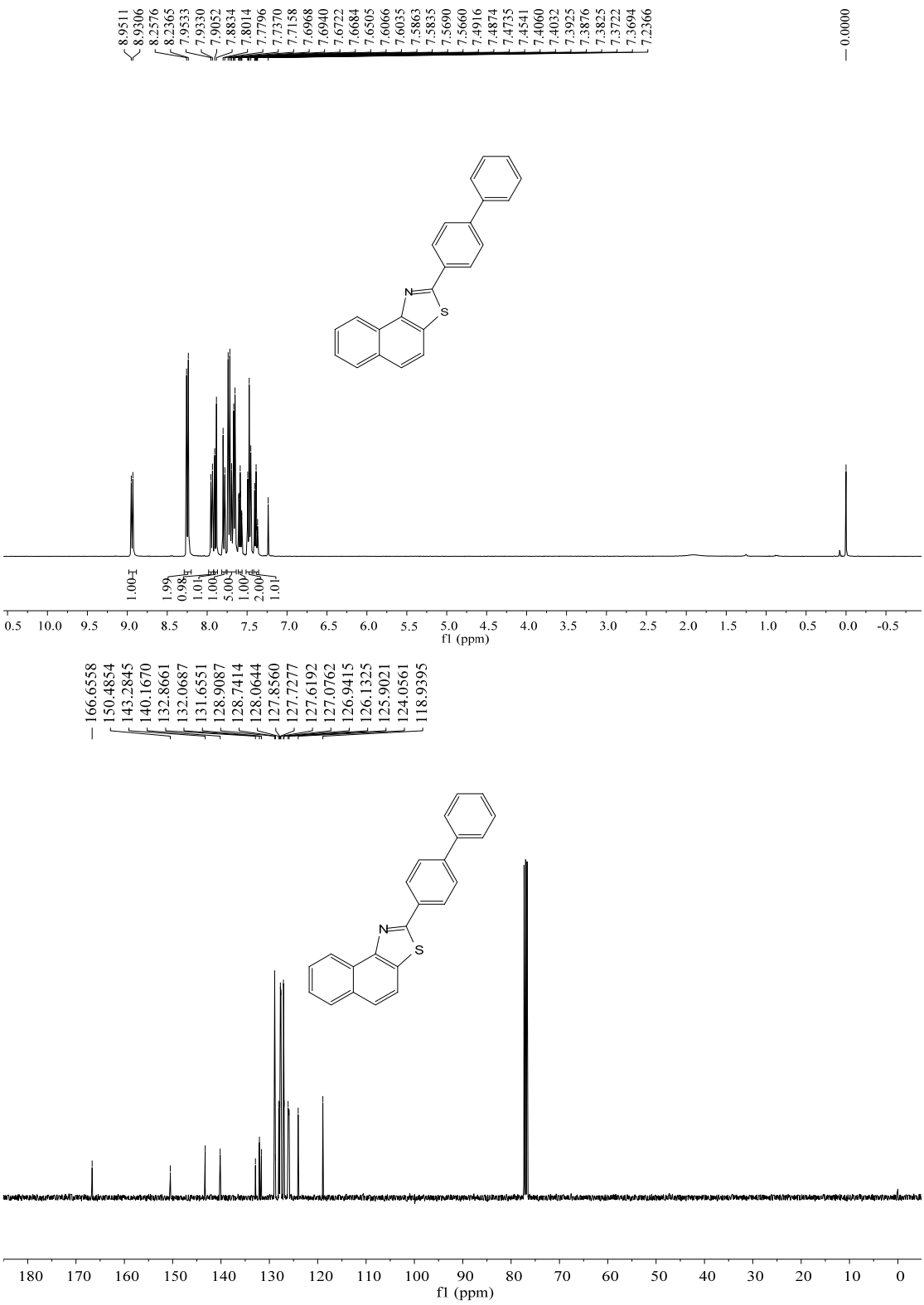


^{1}H and ^{13}C NMR spectra of **3n**

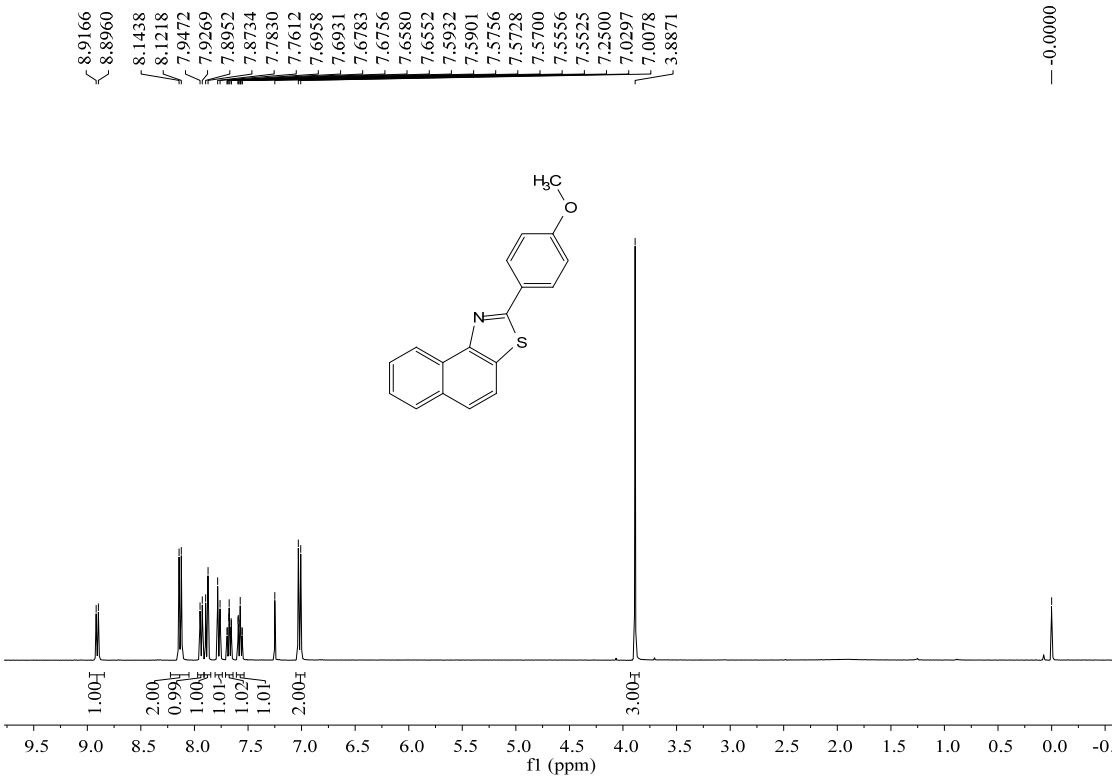


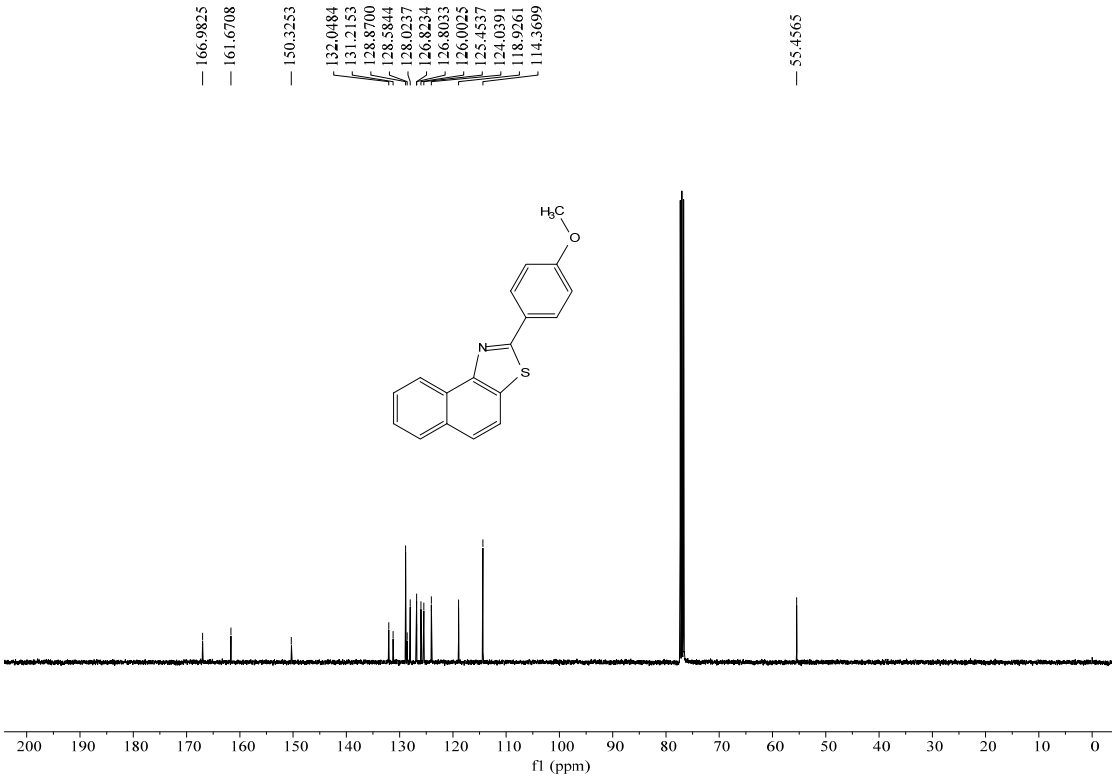


^{1}H and ^{13}C NMR spectra of **3o**

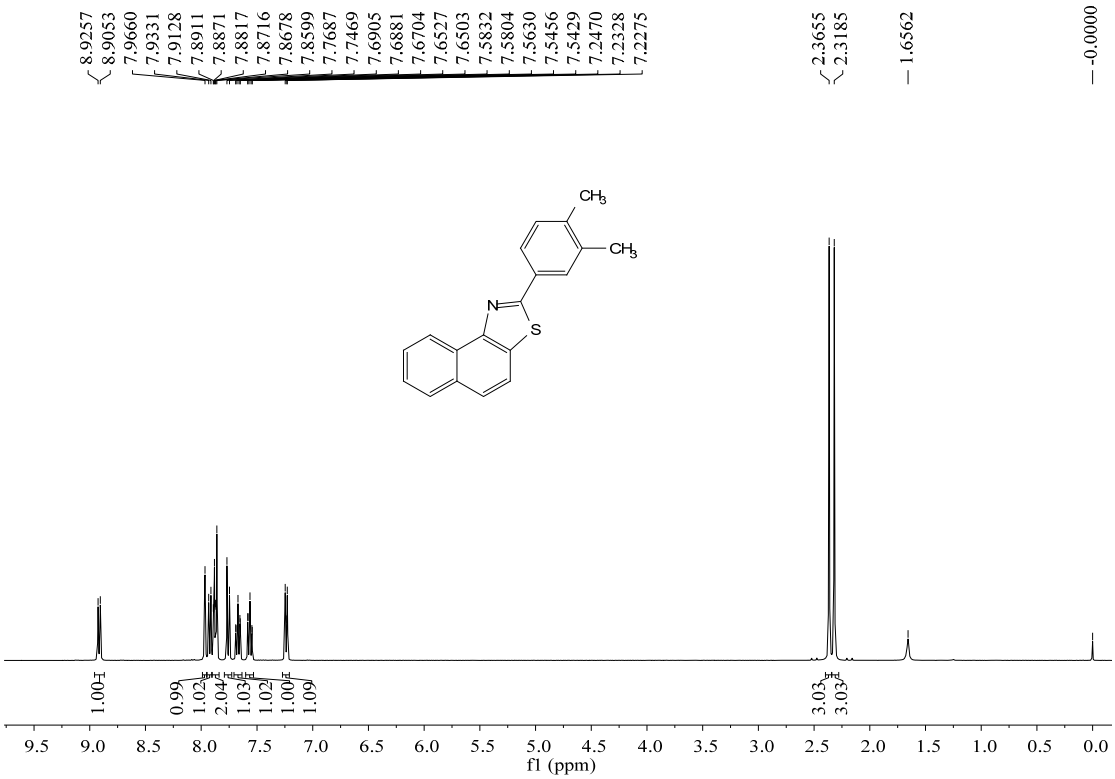


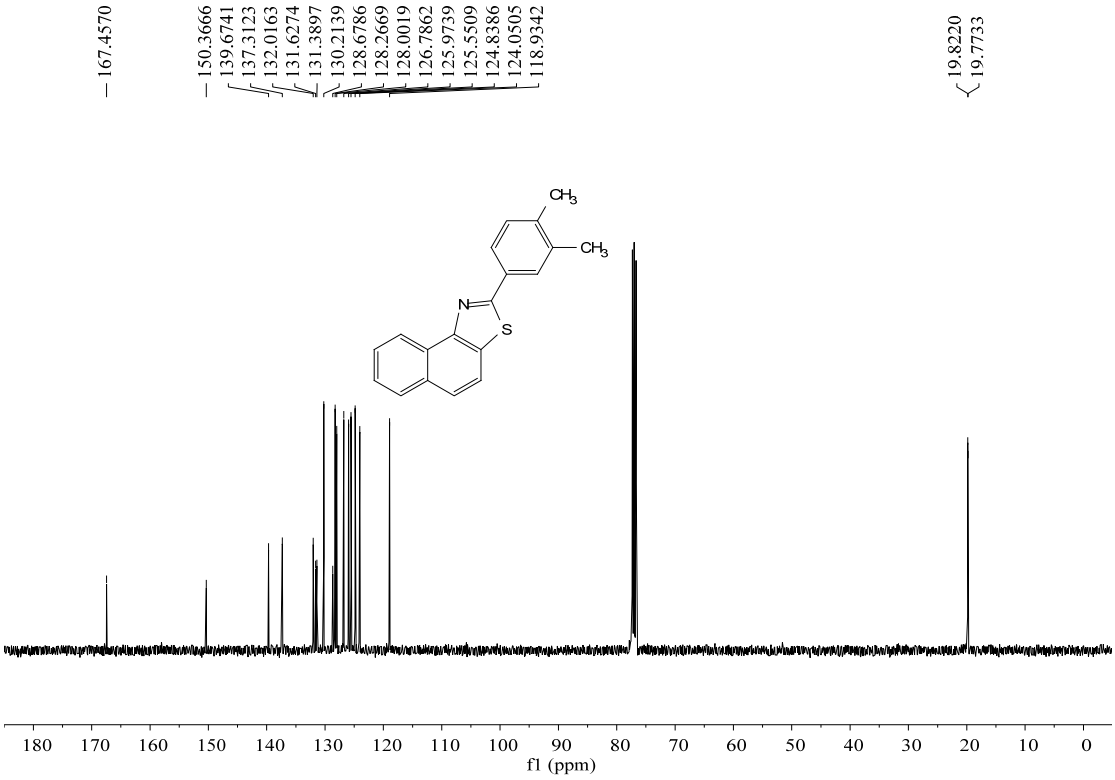
^{1}H and ^{13}C NMR spectra of **3p**



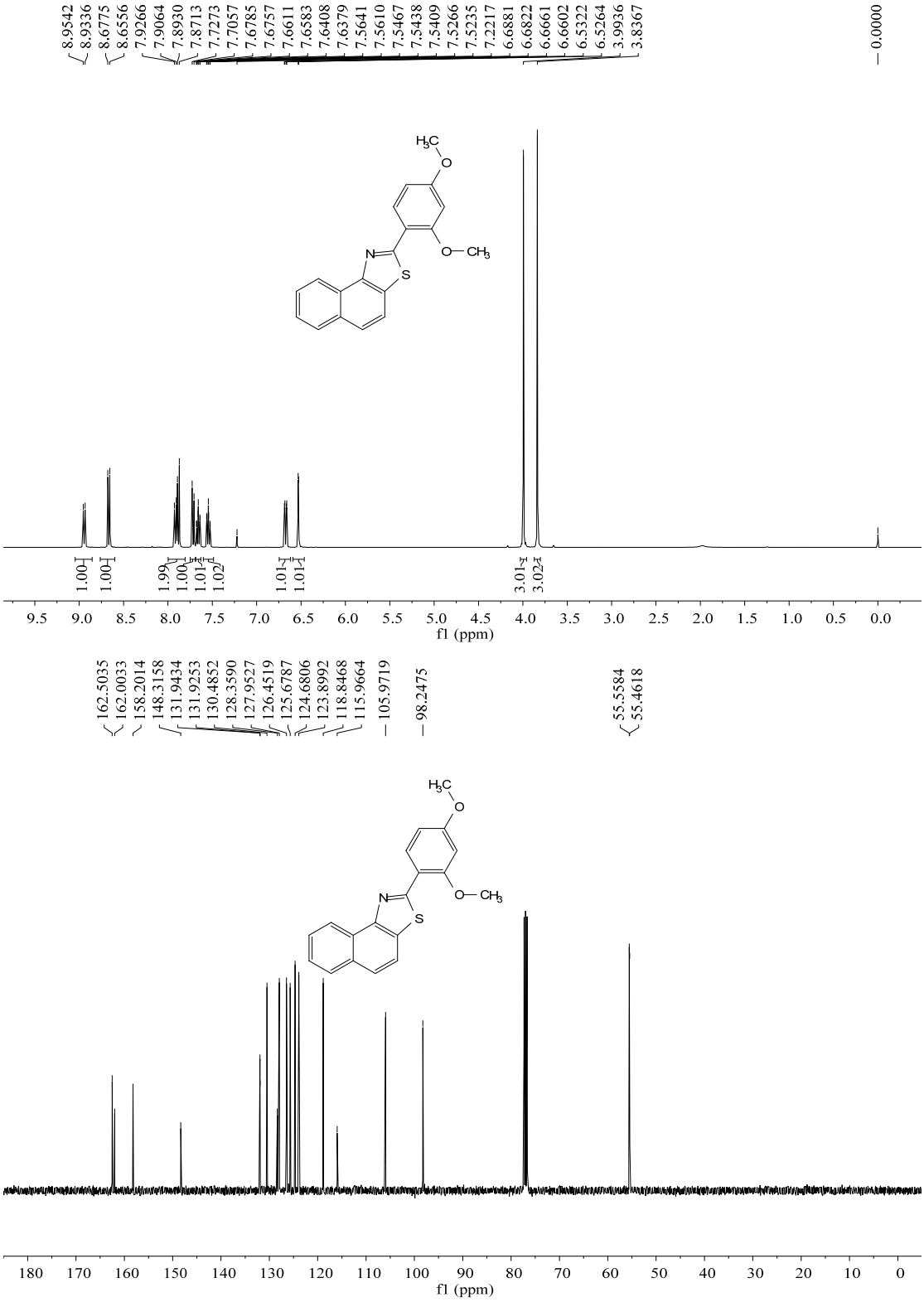


^{1}H and ^{13}C NMR spectra of **3q**

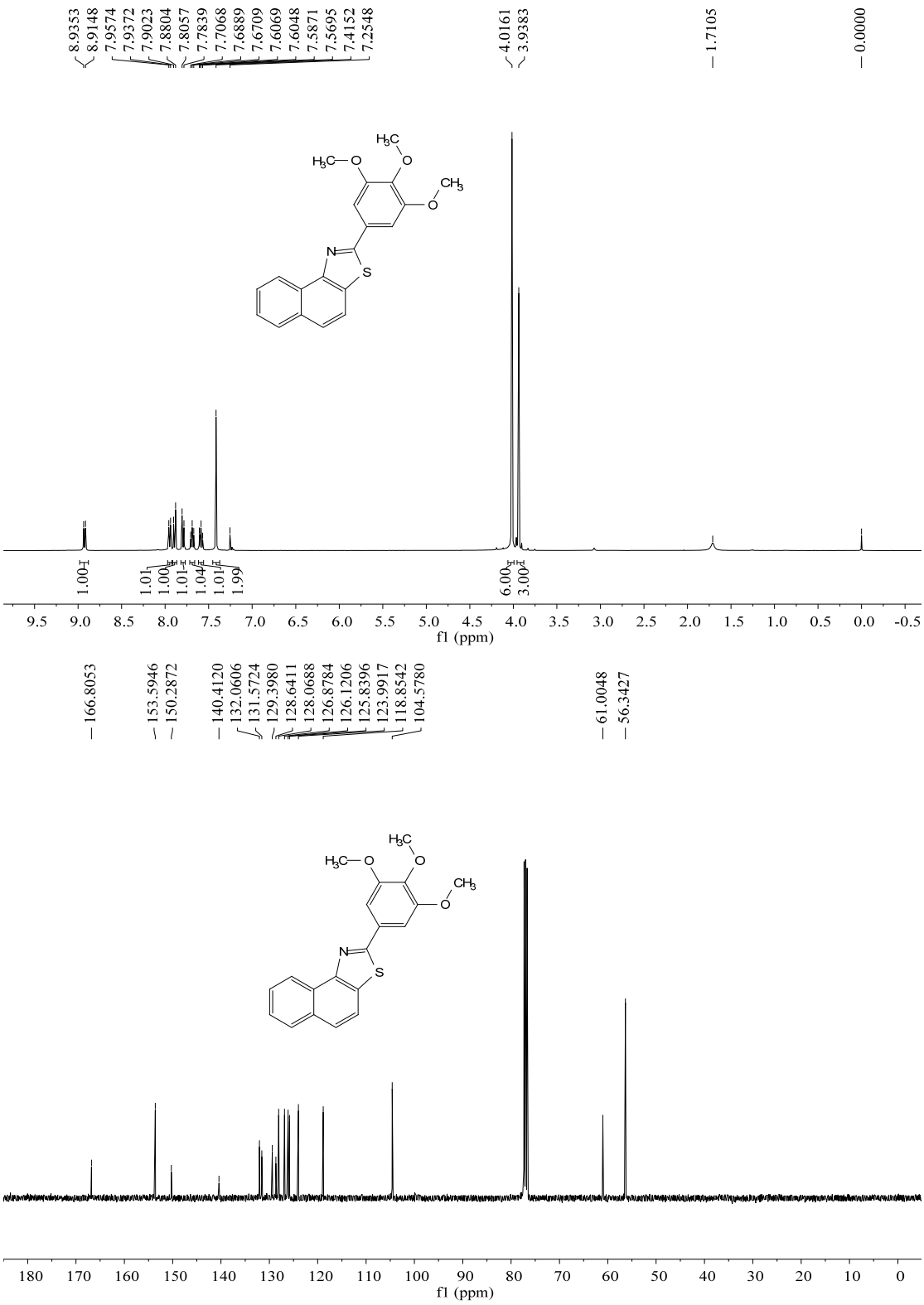




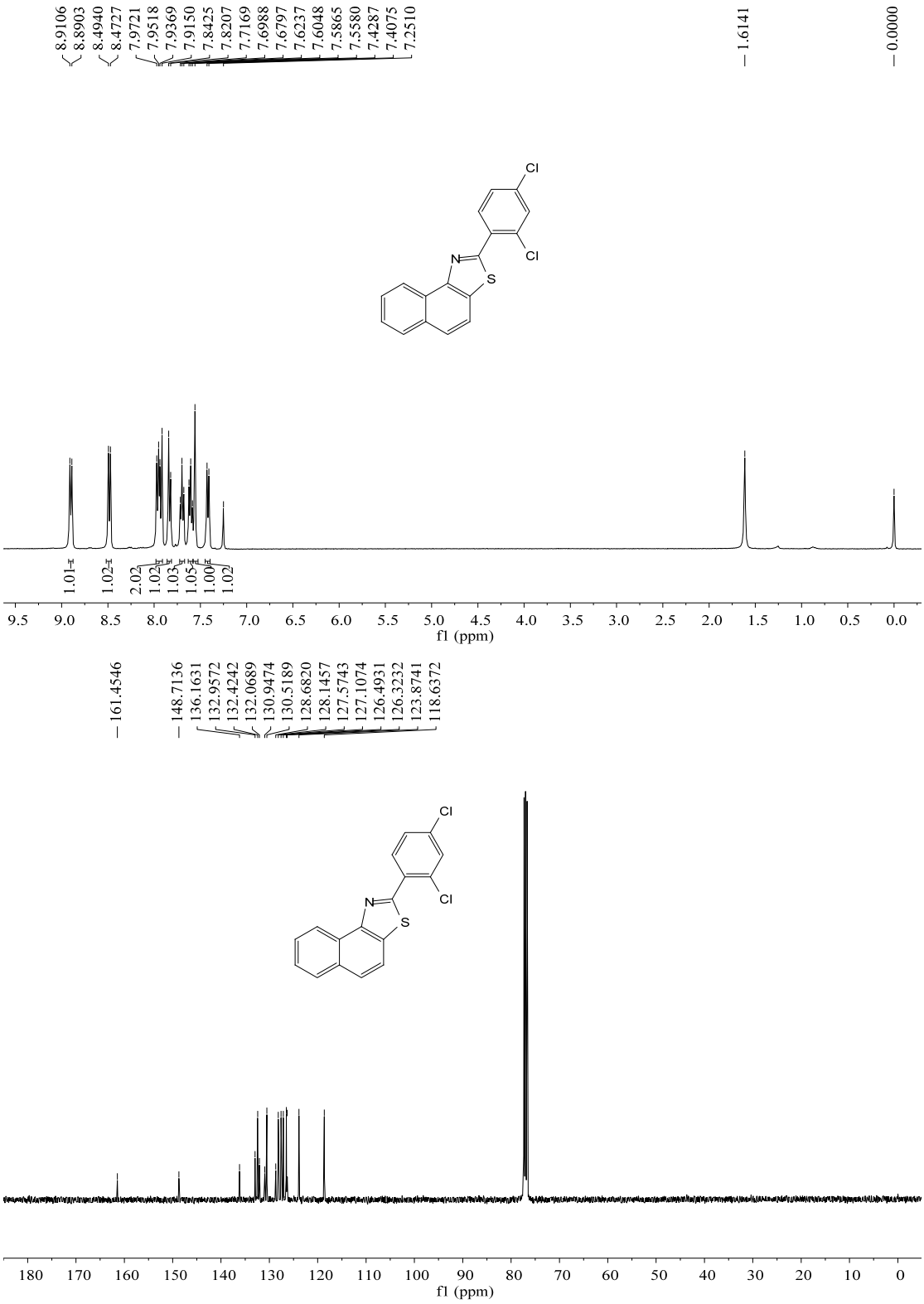
^{1}H and ^{13}C NMR spectra of **3r**



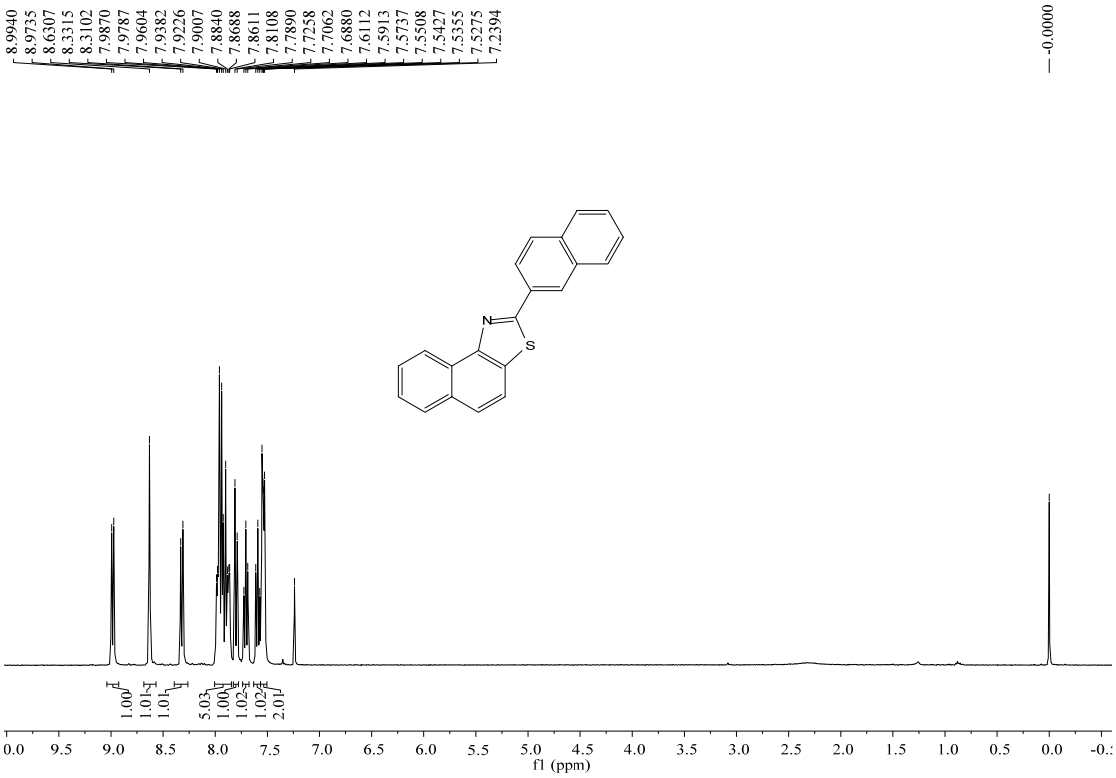
^{1}H and ^{13}C NMR spectra of **3s**

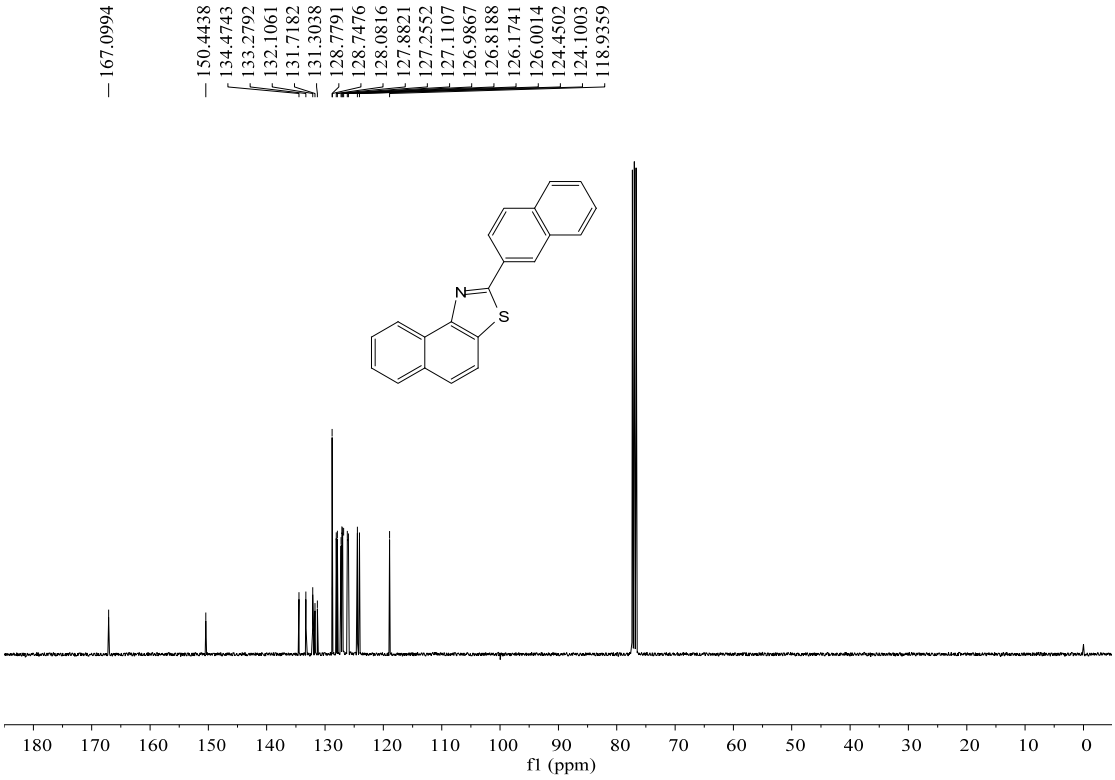


^{1}H and ^{13}C NMR spectra of **3t**

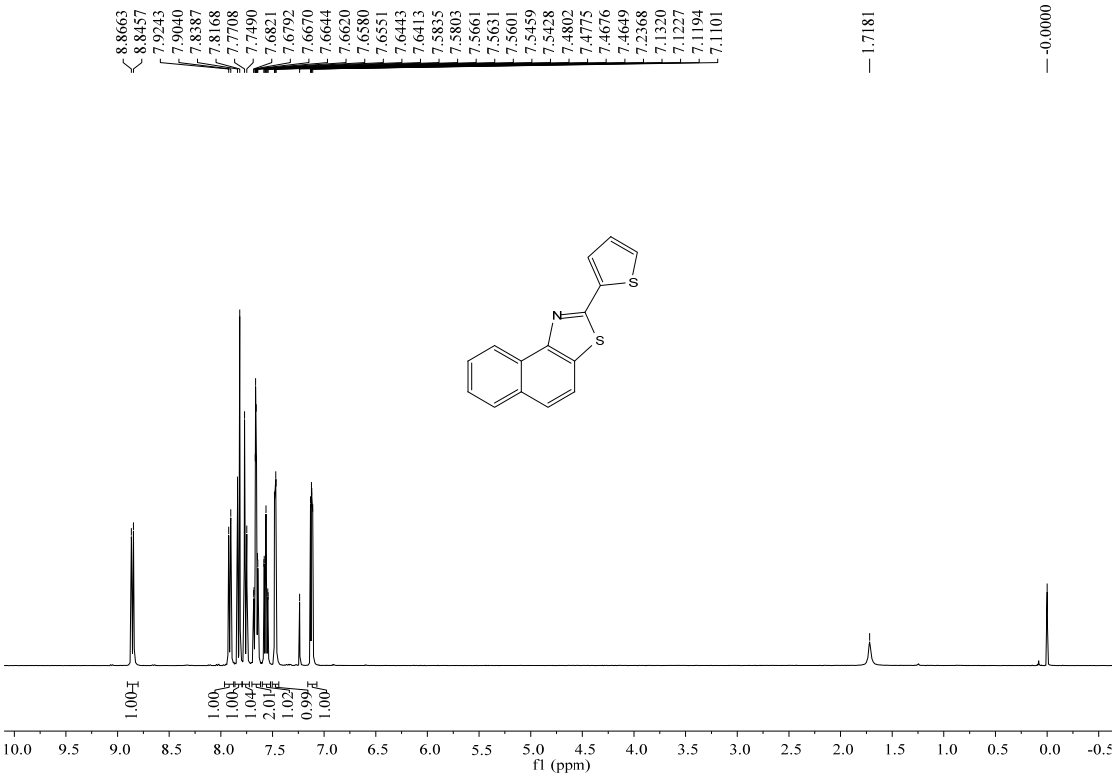


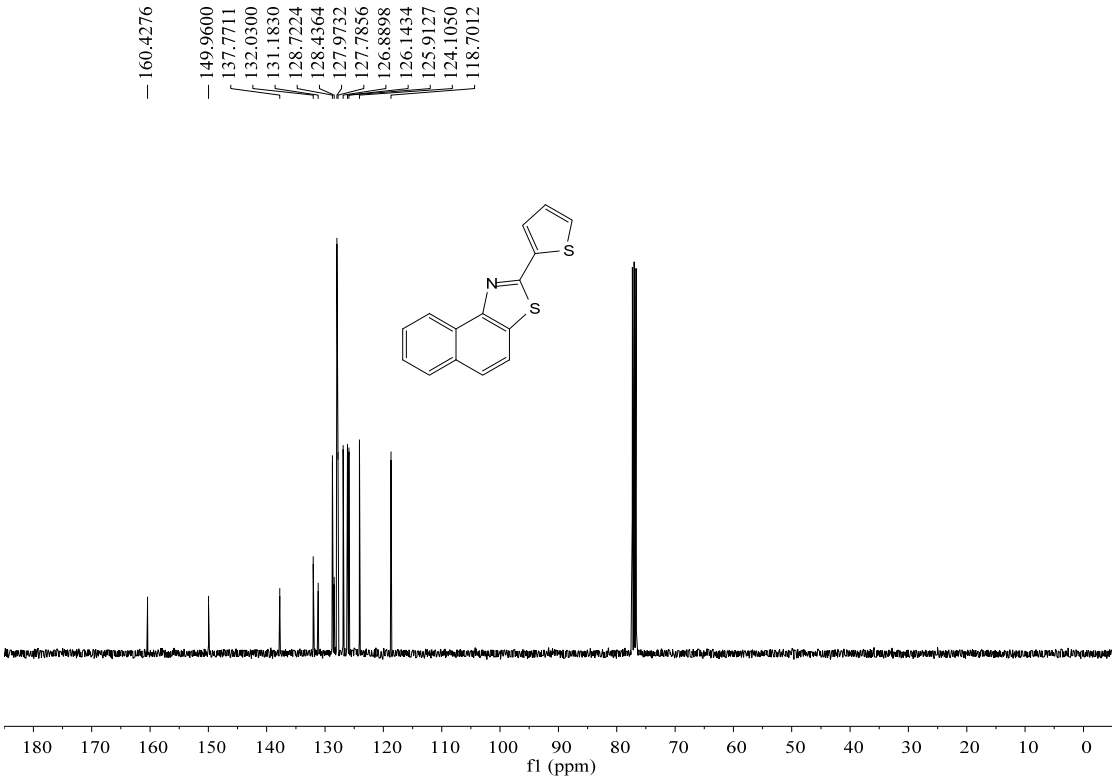
^{1}H and ^{13}C NMR spectra of **3u**



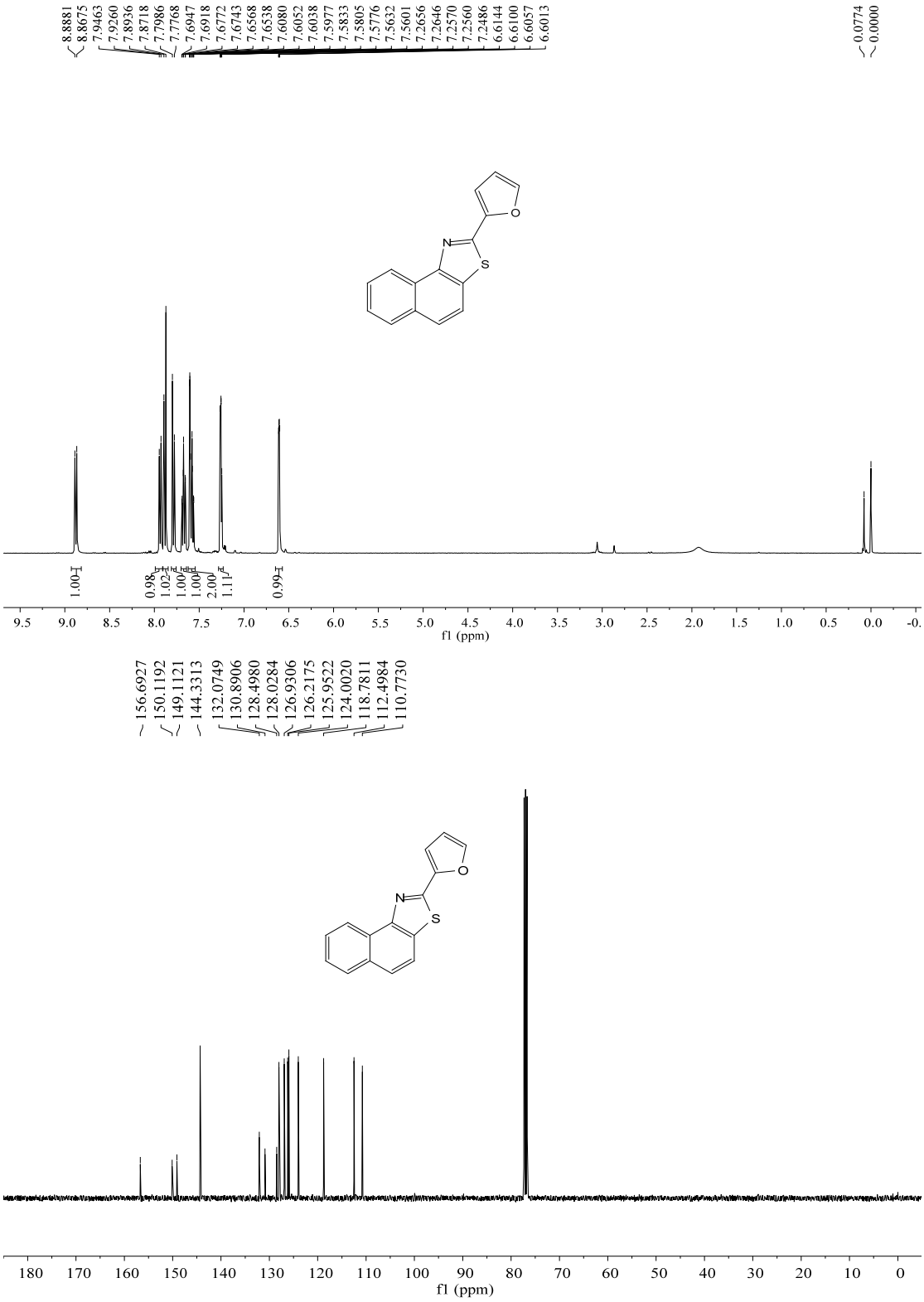


^{1}H and ^{13}C NMR spectra of **3v**

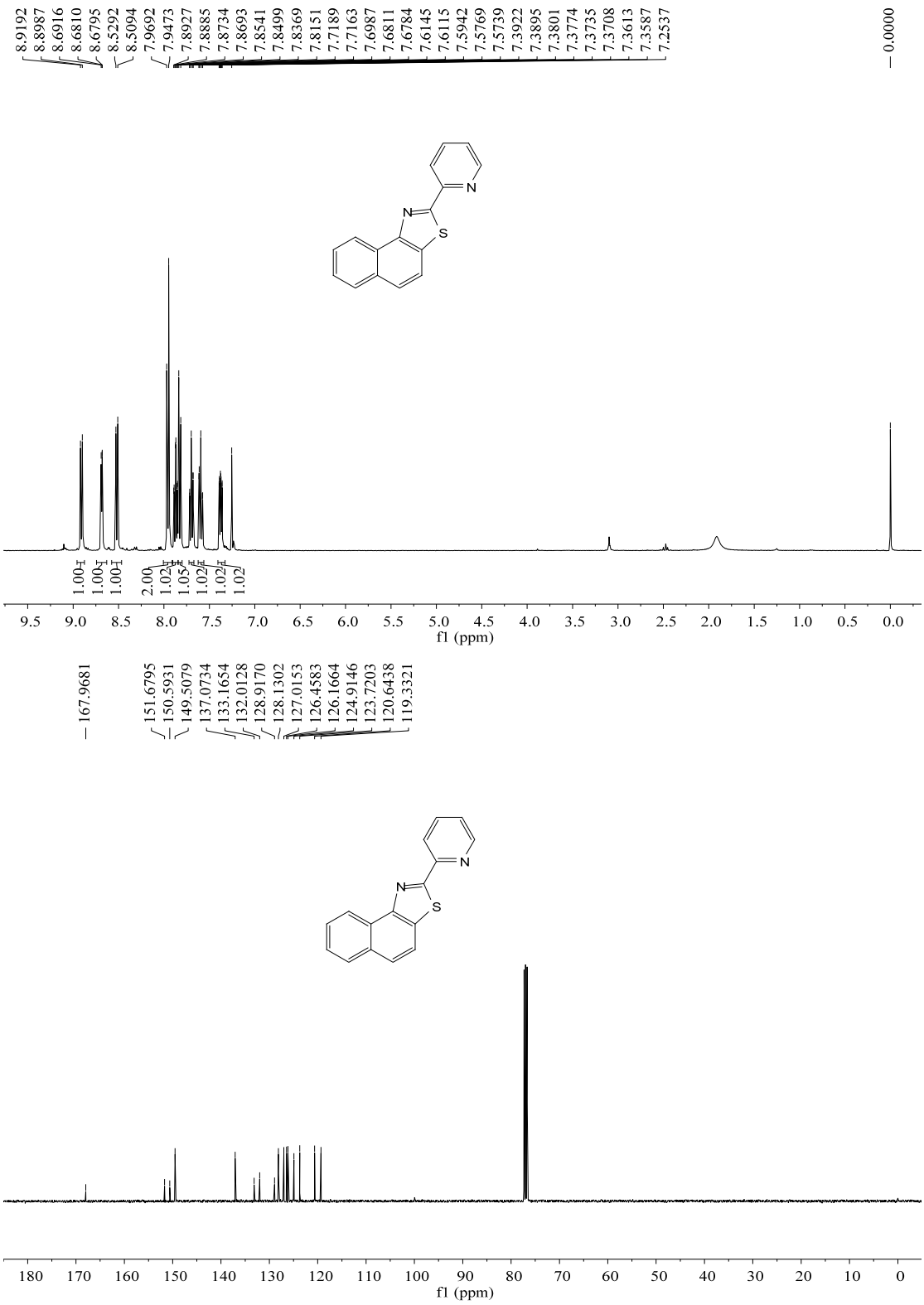




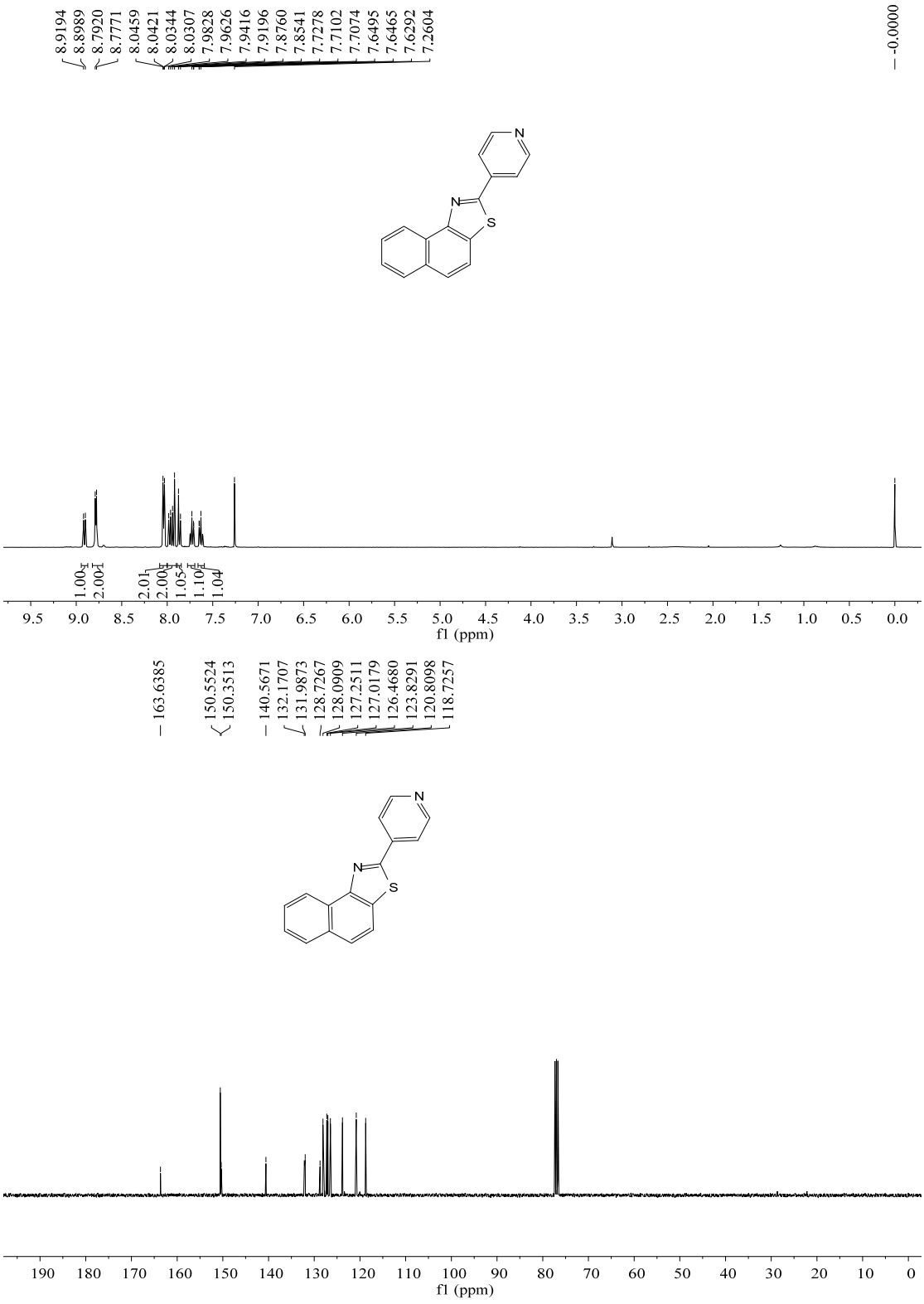
^{1}H and ^{13}C NMR spectra of **3w**



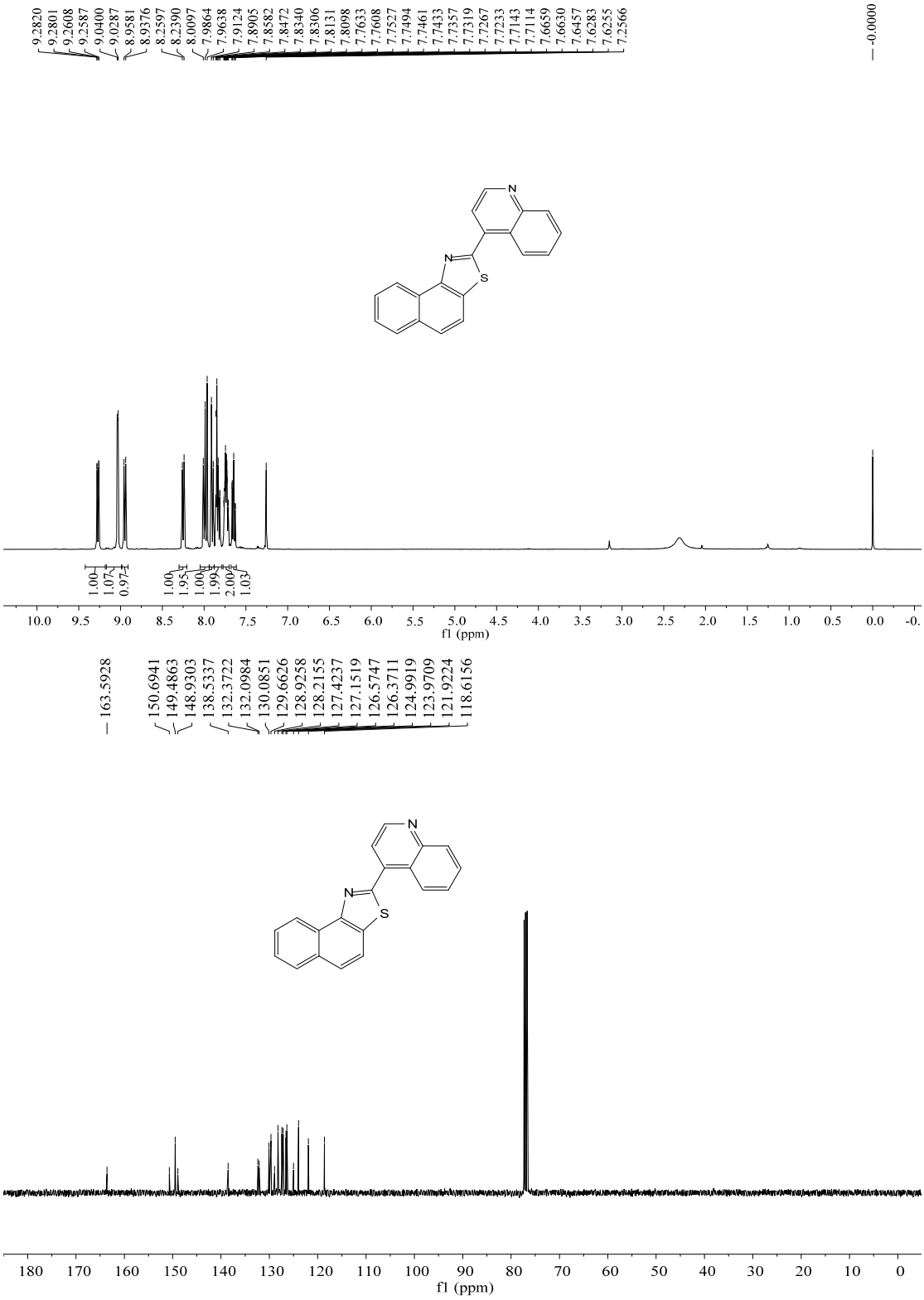
^{1}H and ^{13}C NMR spectra of **3x**



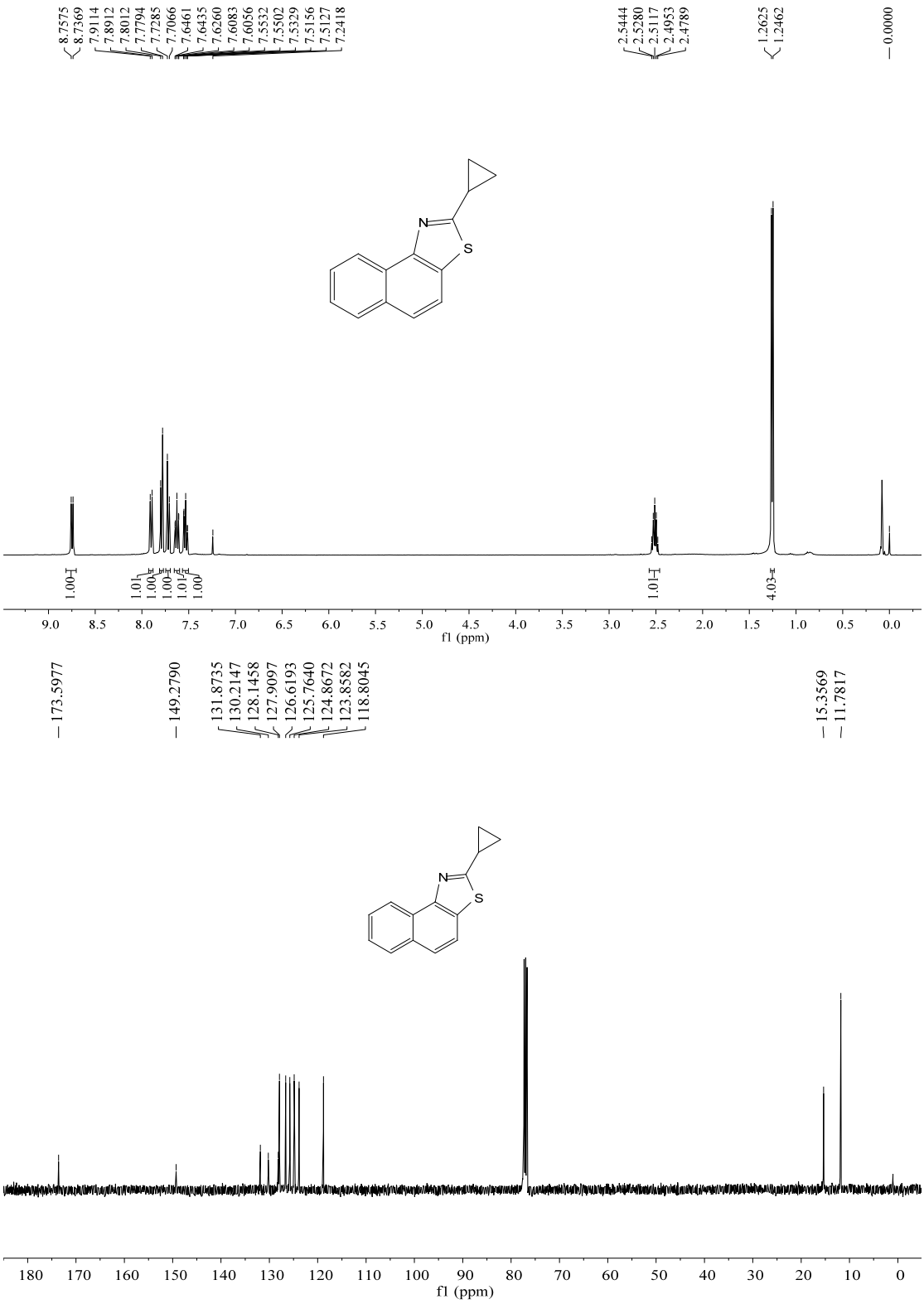
^{1}H and ^{13}C NMR spectra of **3y**



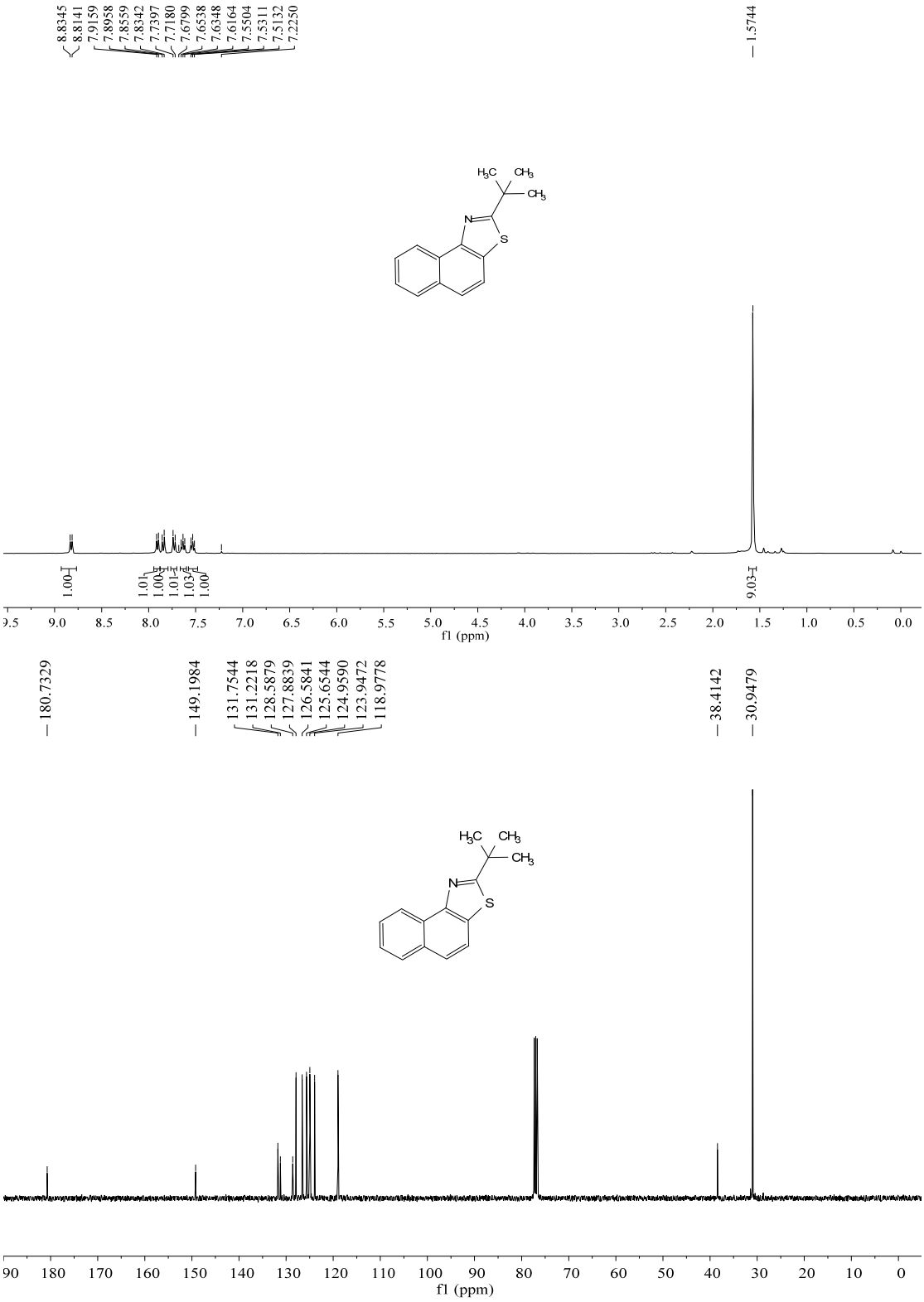
^{1}H and ^{13}C NMR spectra of **3z**



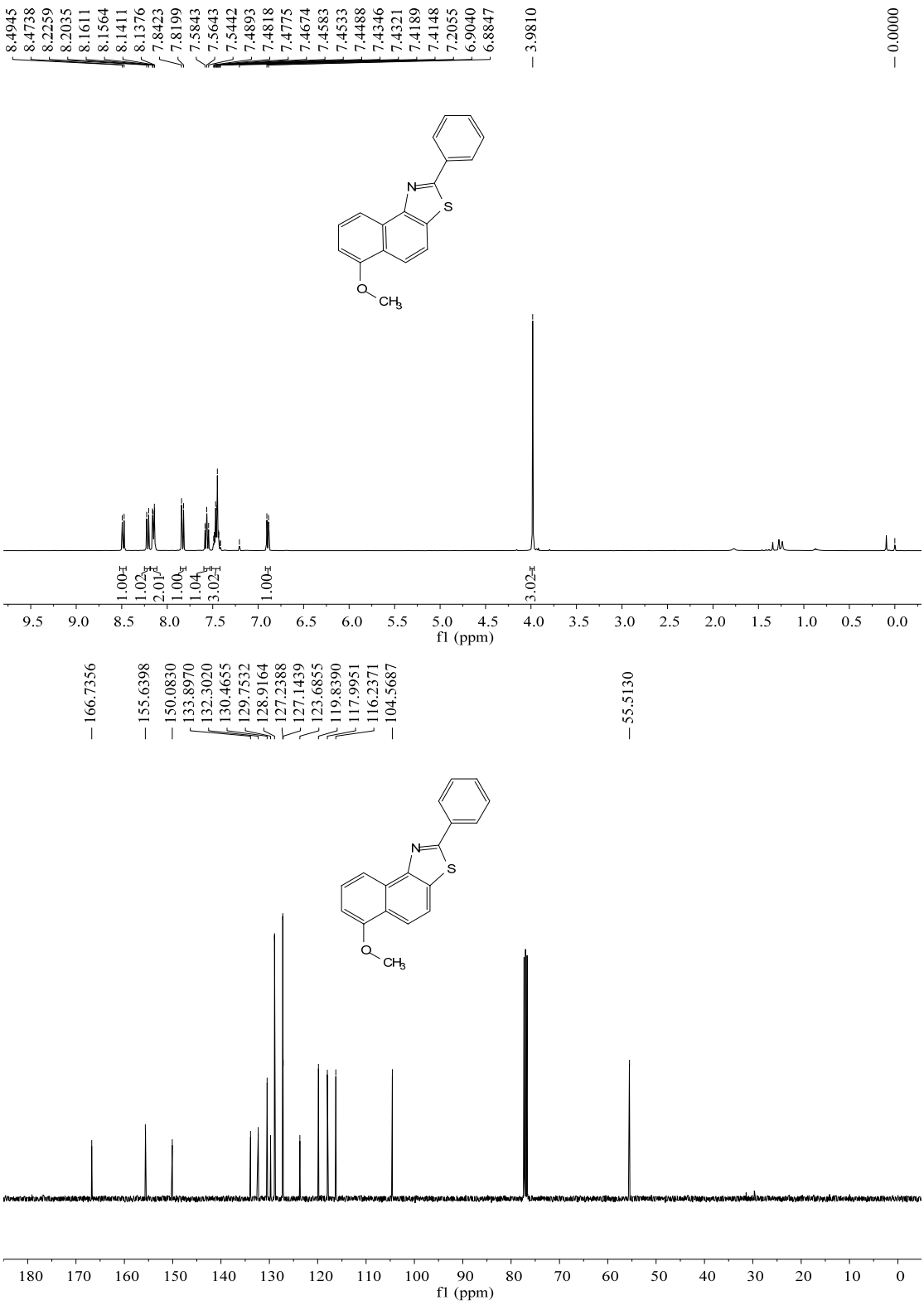
^{1}H and ^{13}C NMR spectra of **3aa**



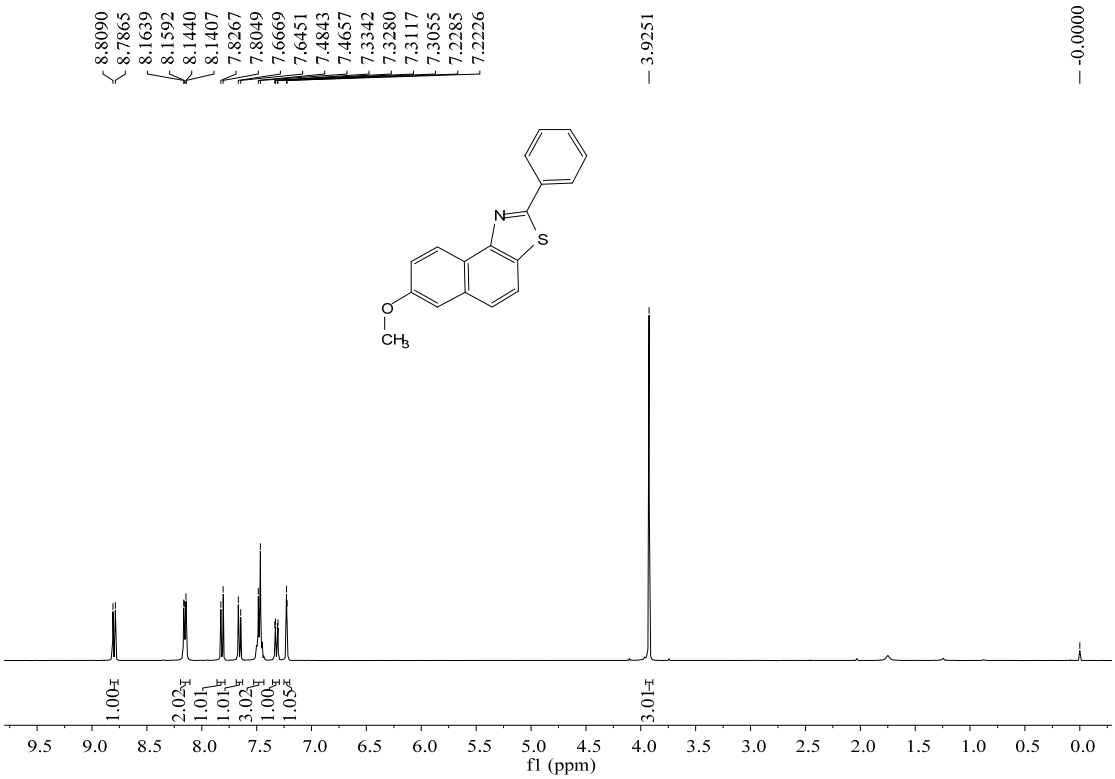
^{1}H and ^{13}C NMR spectra of **3ab**

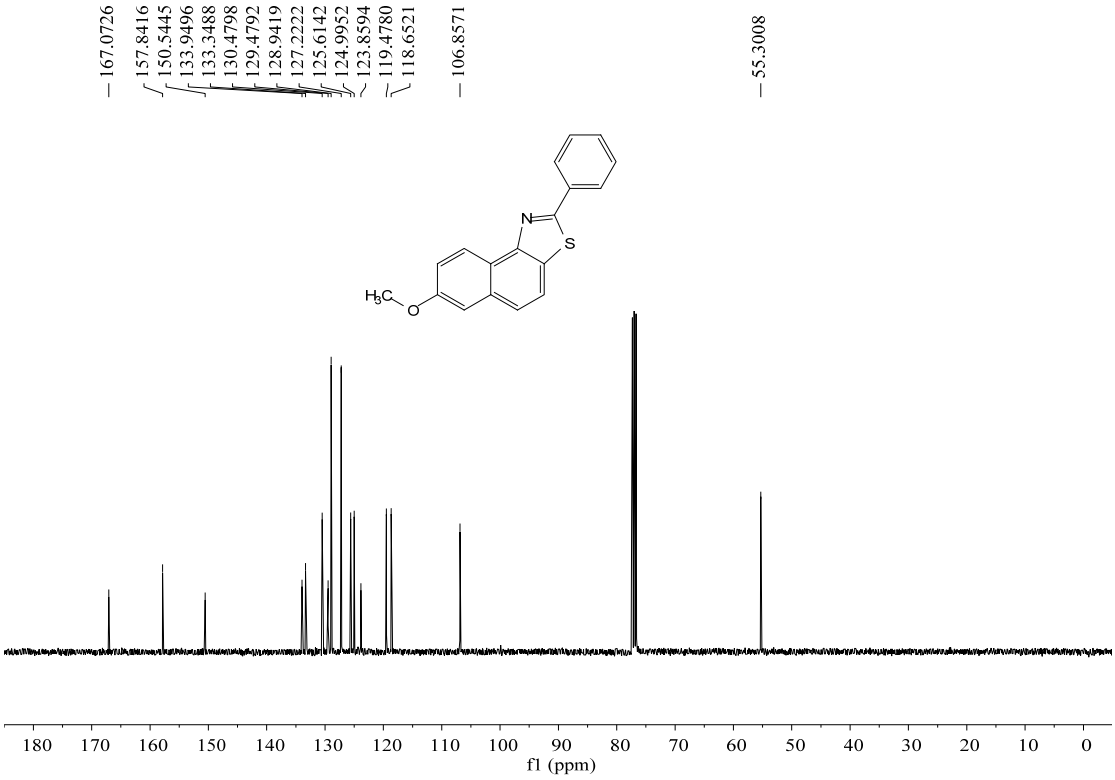


^{1}H and ^{13}C NMR spectra of **4a**

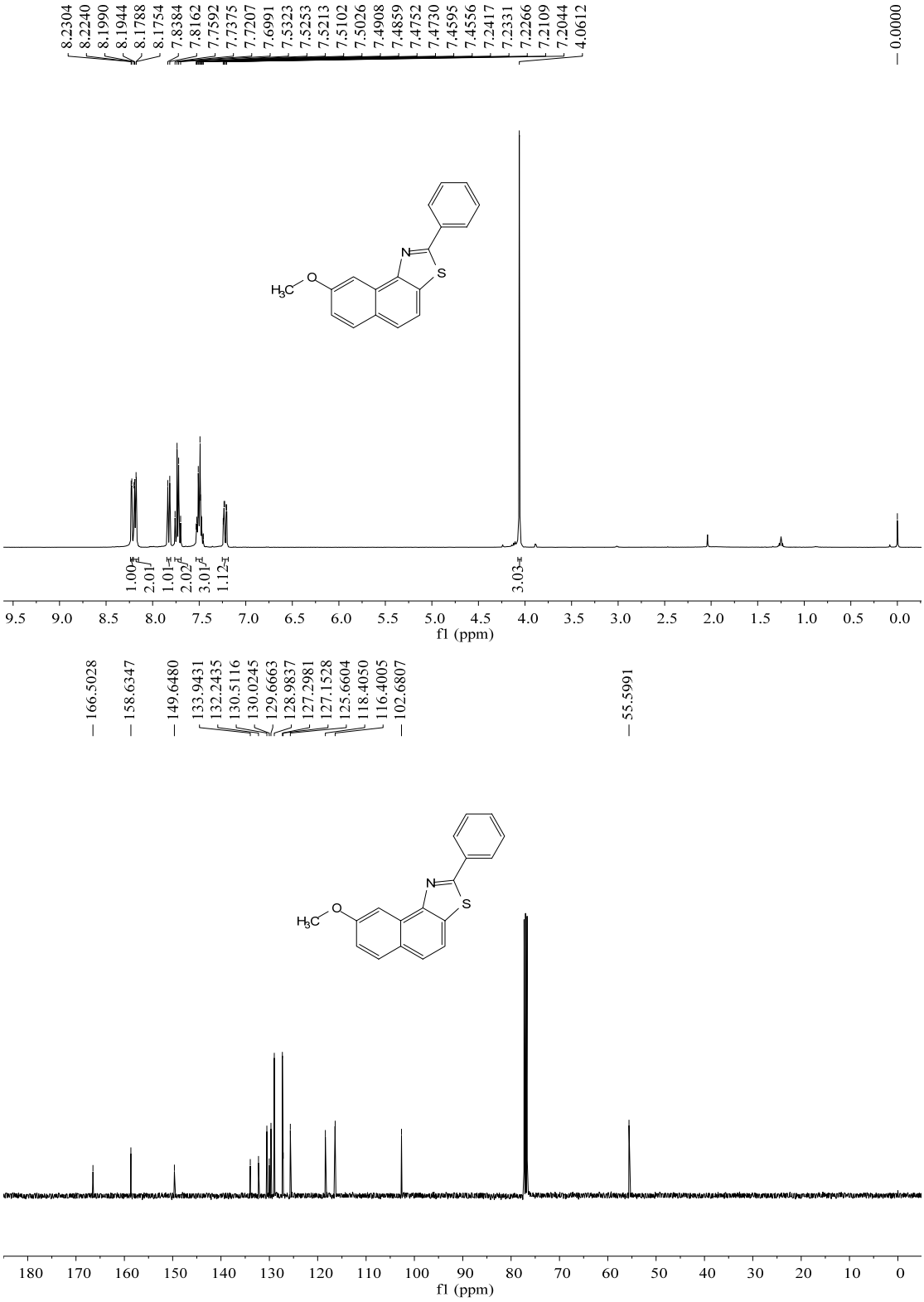


^{1}H and ^{13}C NMR spectra of **4b**

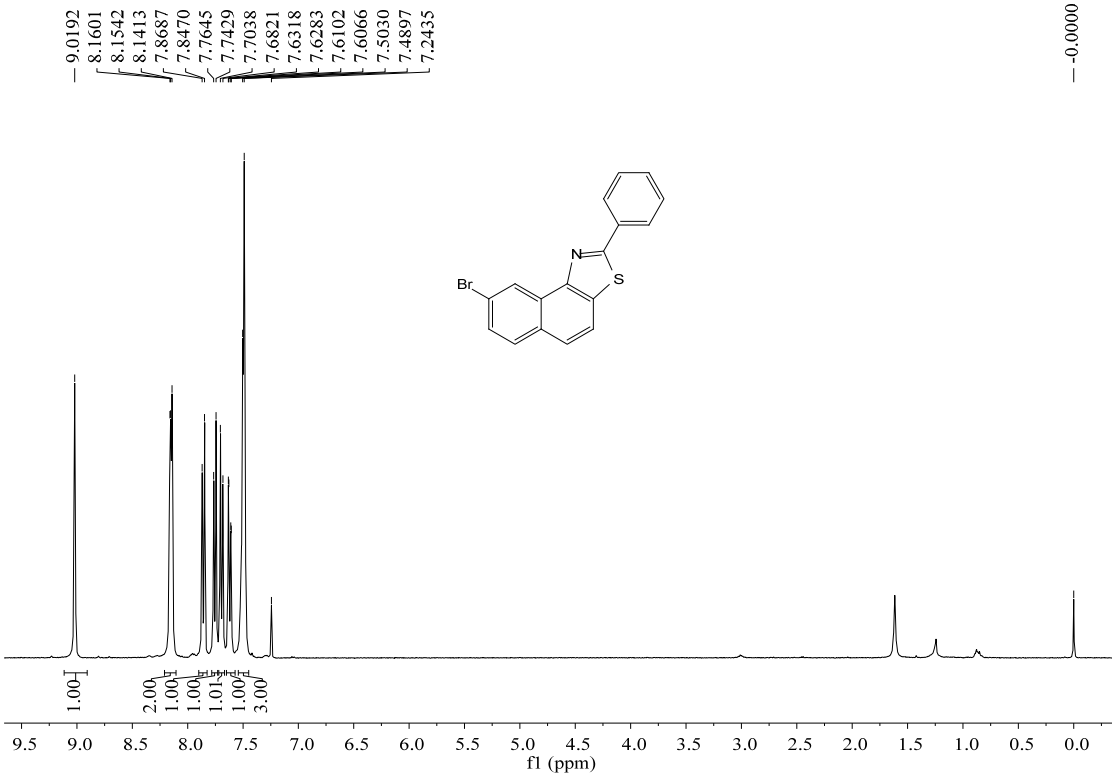


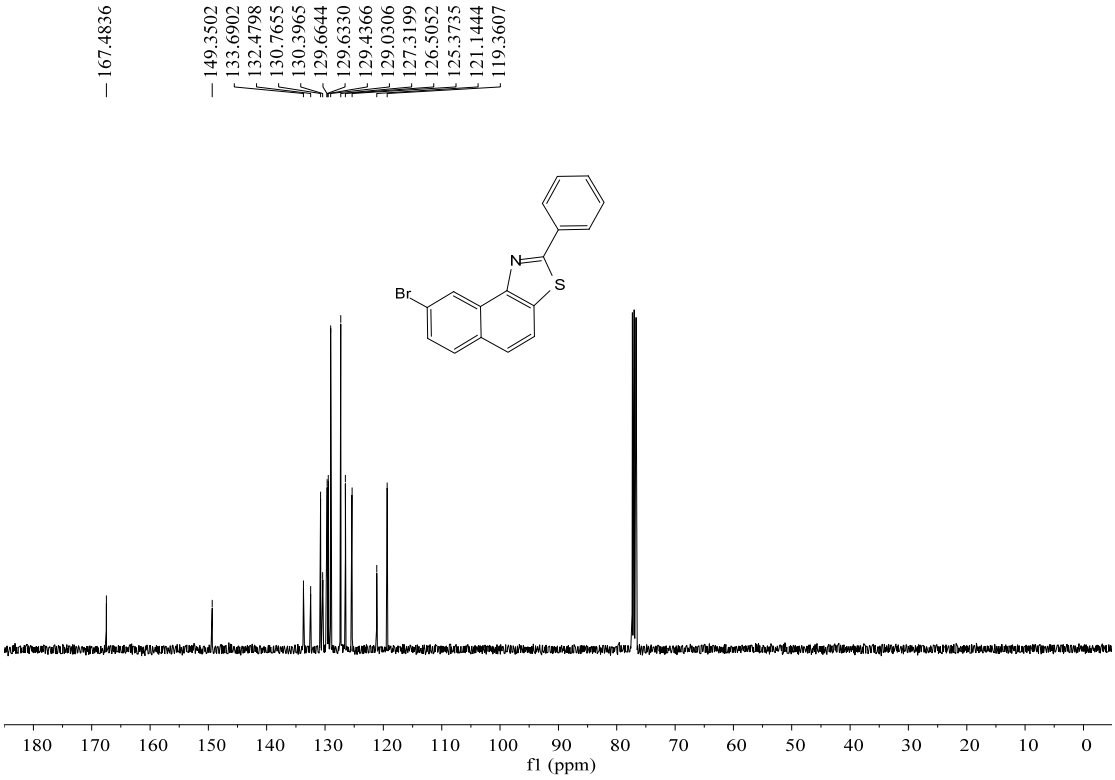


^{1}H and ^{13}C NMR spectra of **4c**

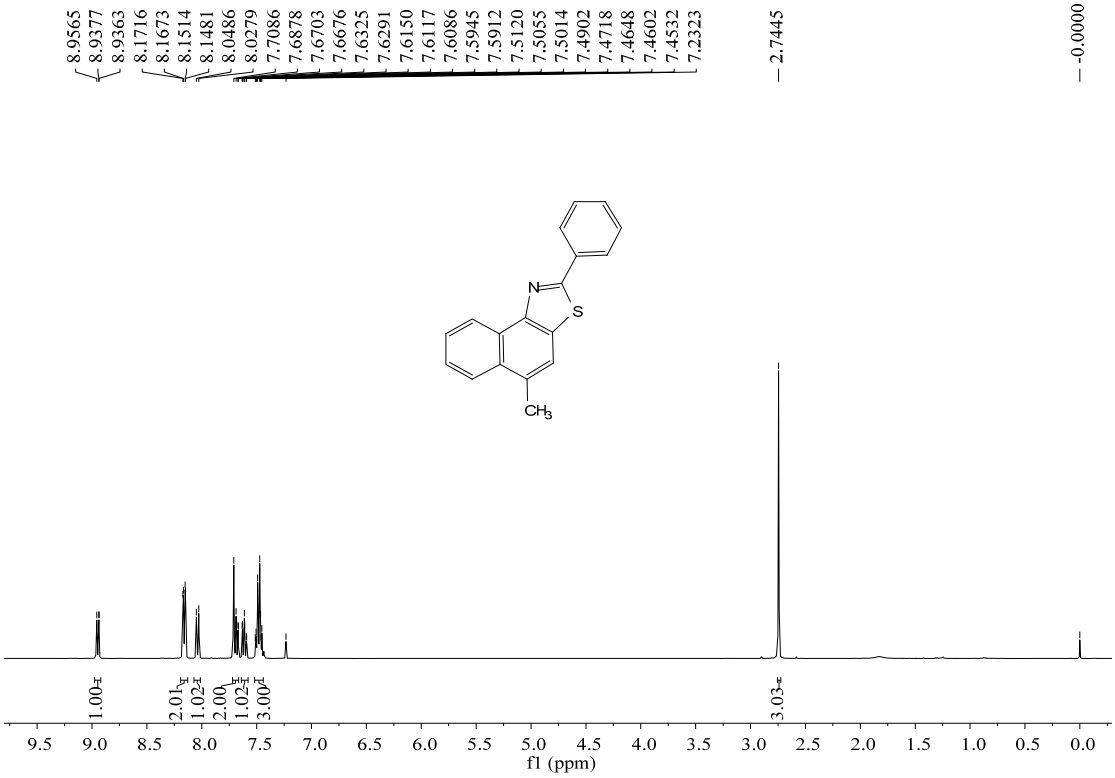


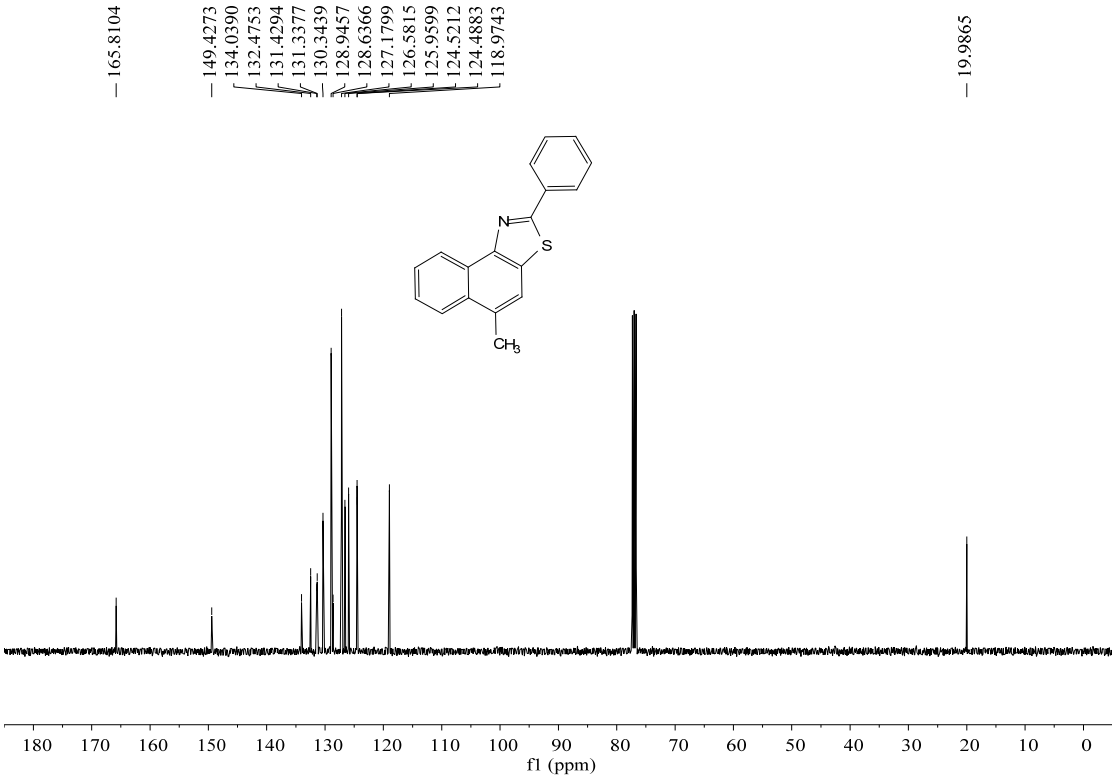
^{1}H and ^{13}C NMR spectra of **4d**



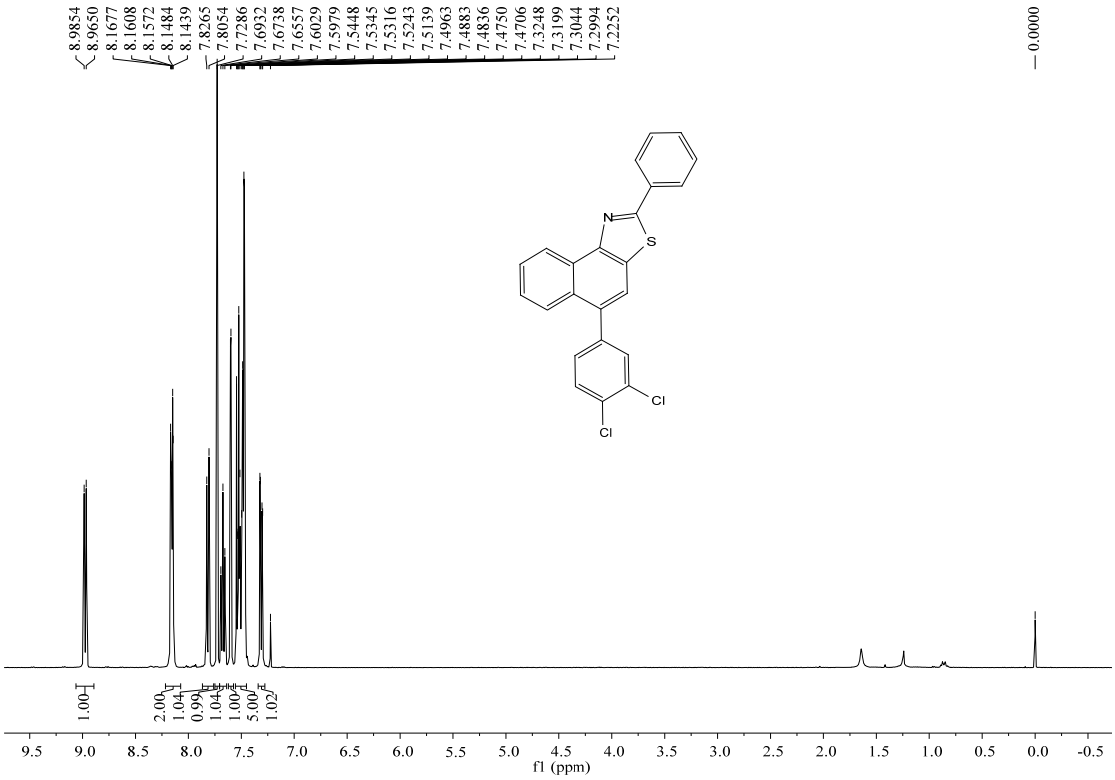


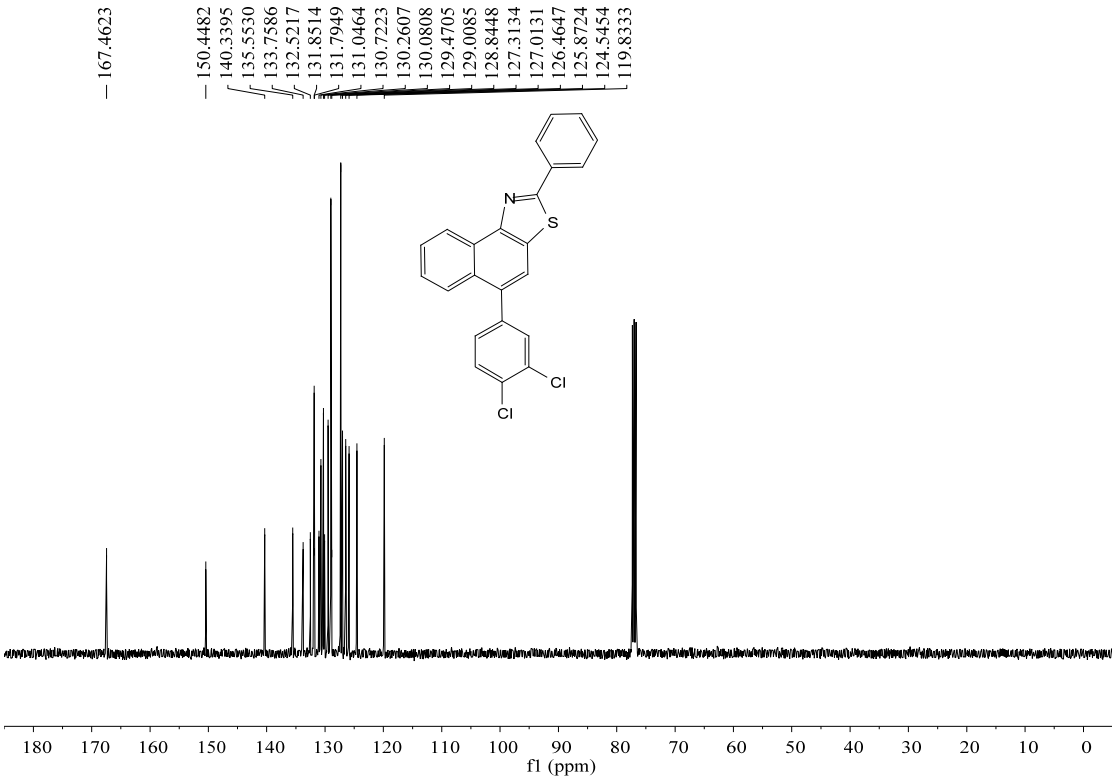
^{1}H and ^{13}C NMR spectra of **4e**



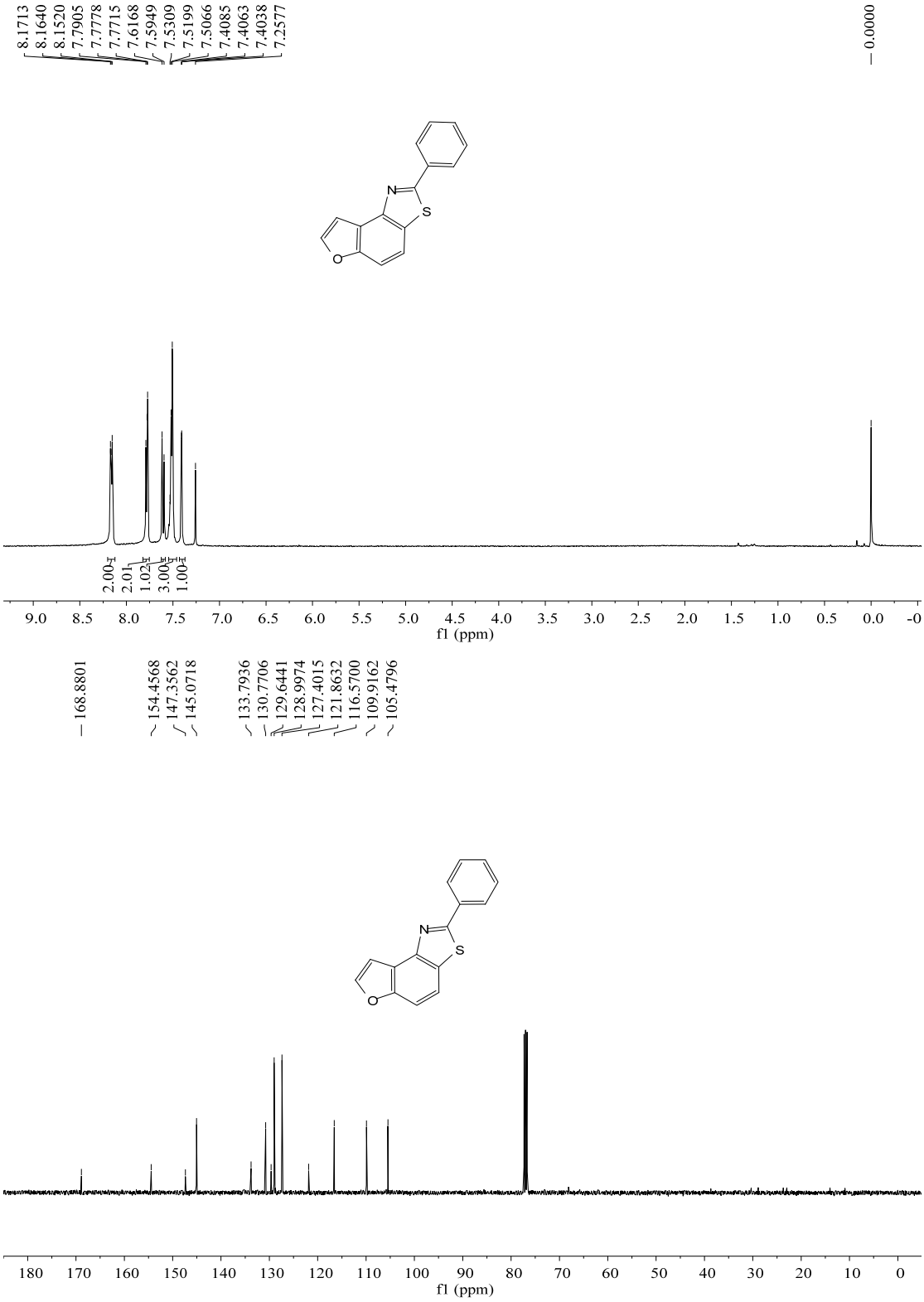


^{1}H and ^{13}C NMR spectra of **4f**

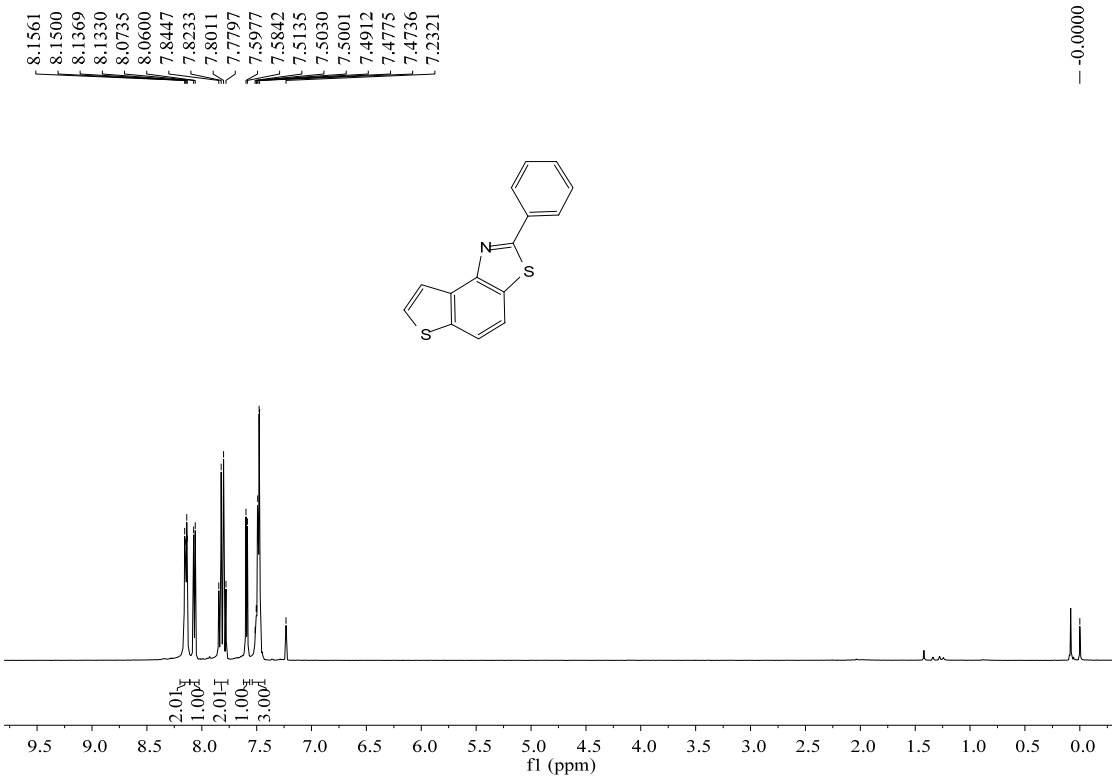


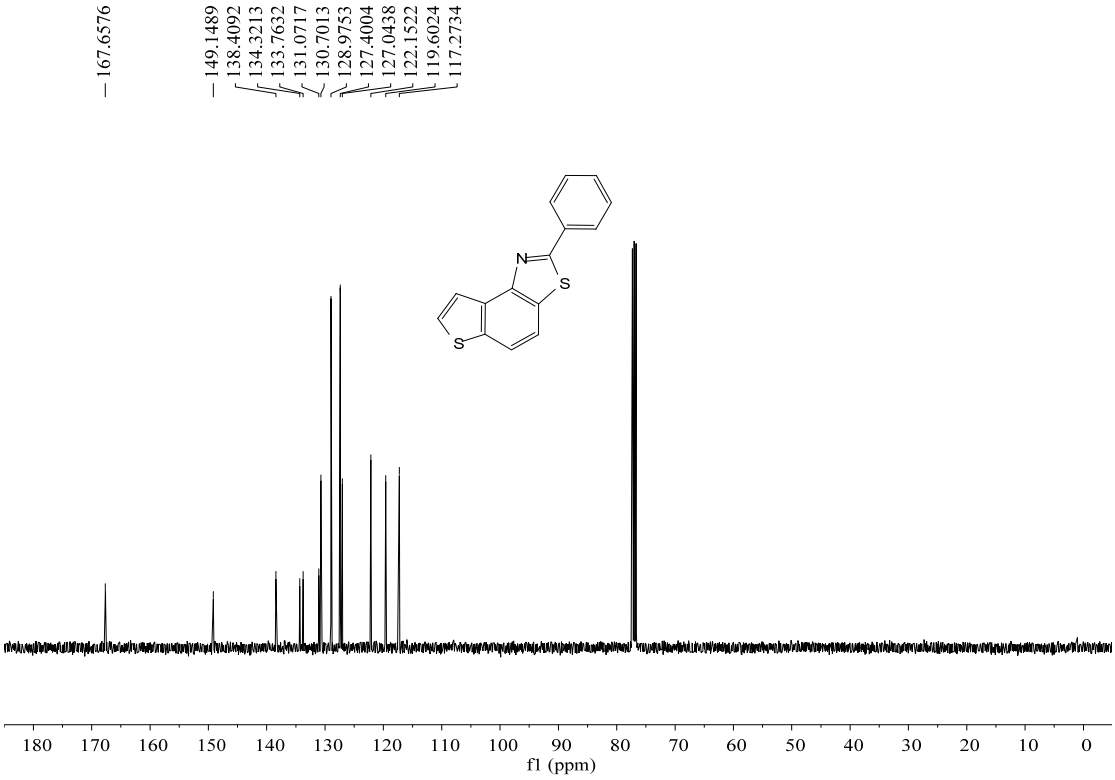


^{1}H and ^{13}C NMR spectra of **4g**

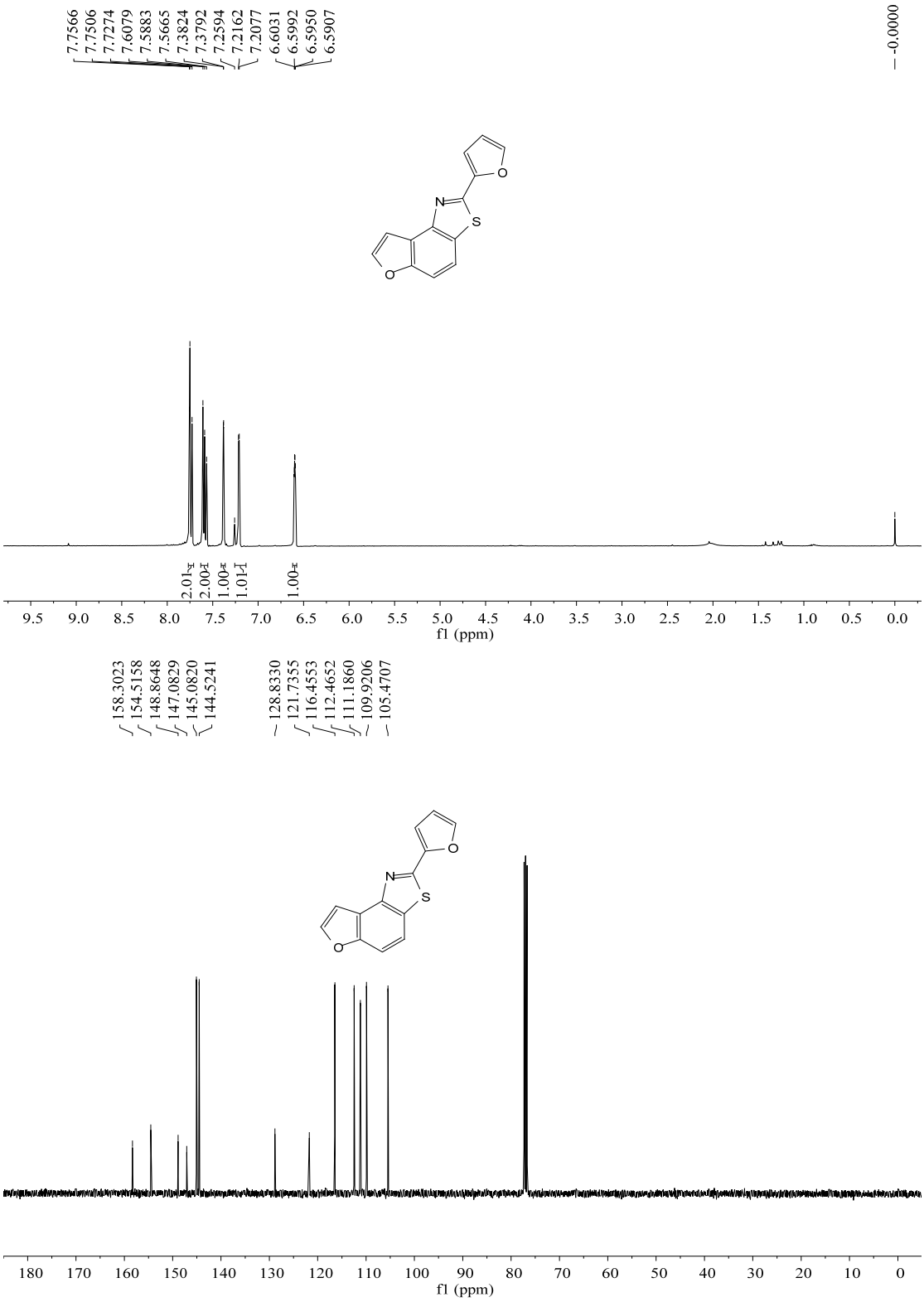


^{1}H and ^{13}C NMR spectra of **4h**

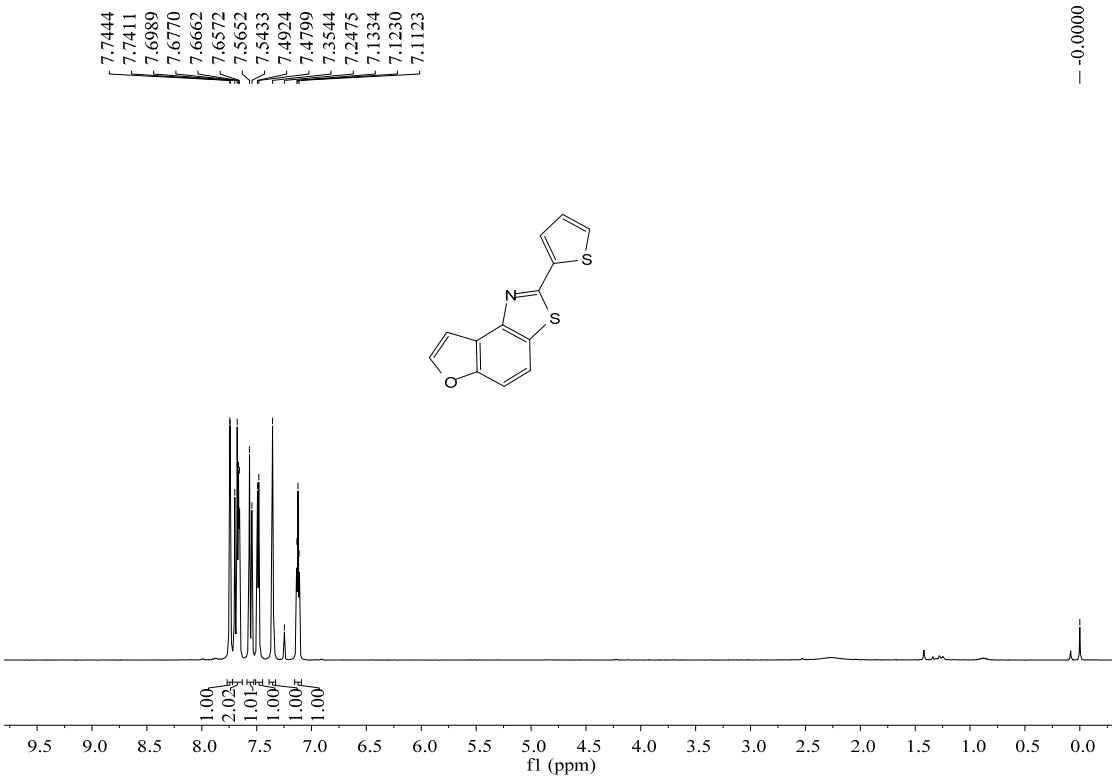


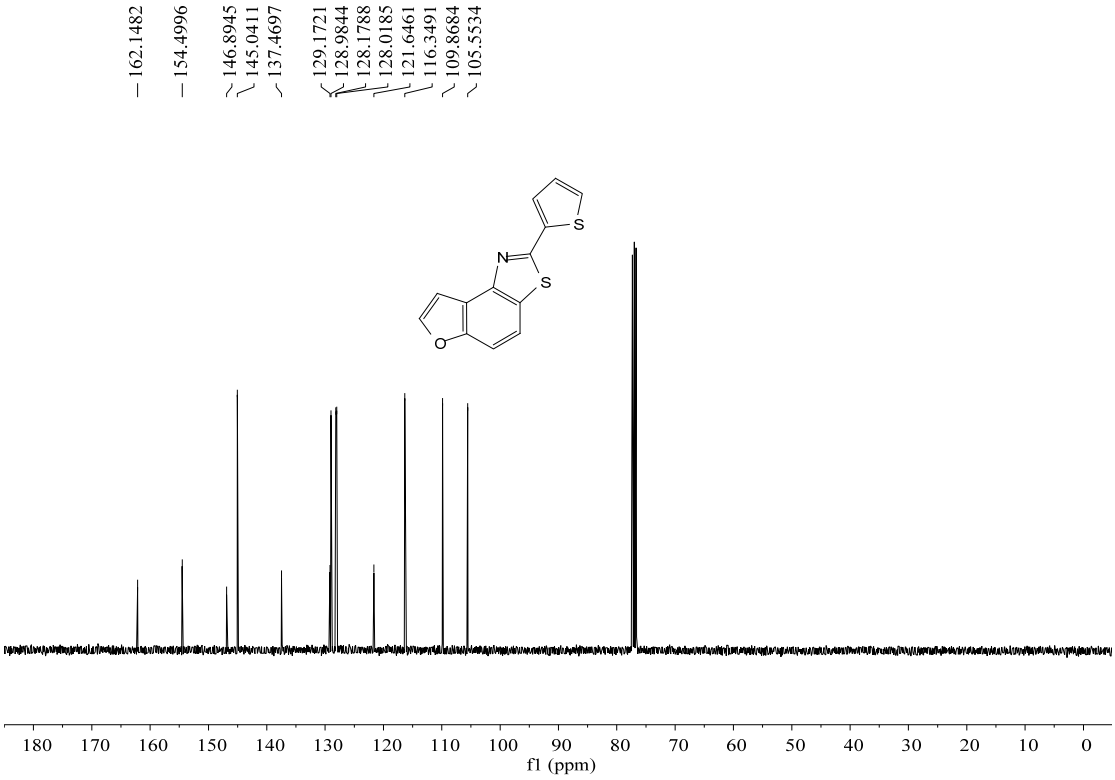


^{1}H and ^{13}C NMR spectra of **4i**

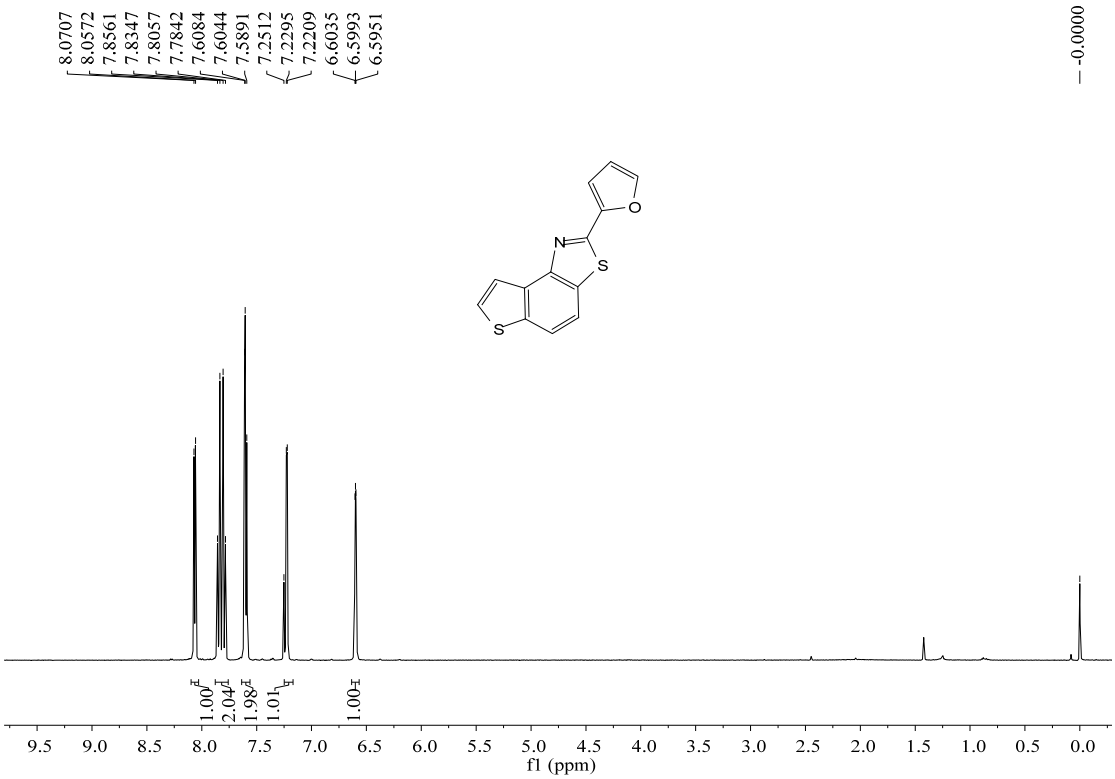


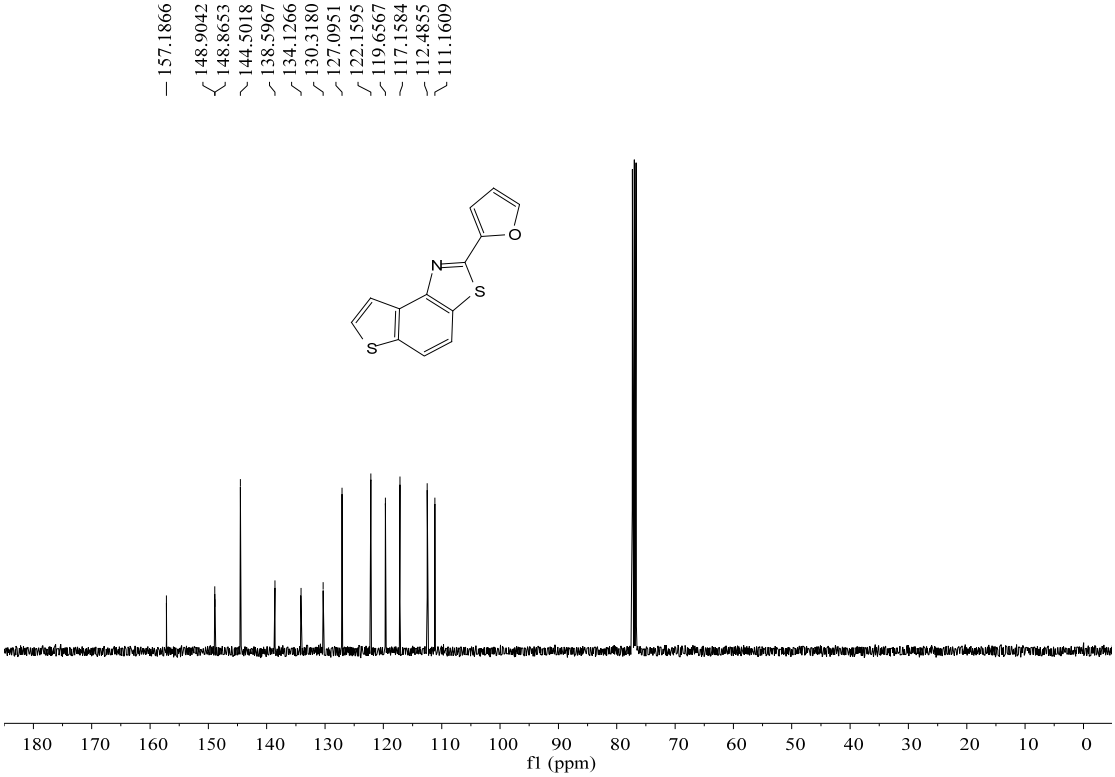
^{1}H and ^{13}C NMR spectra of **4j**



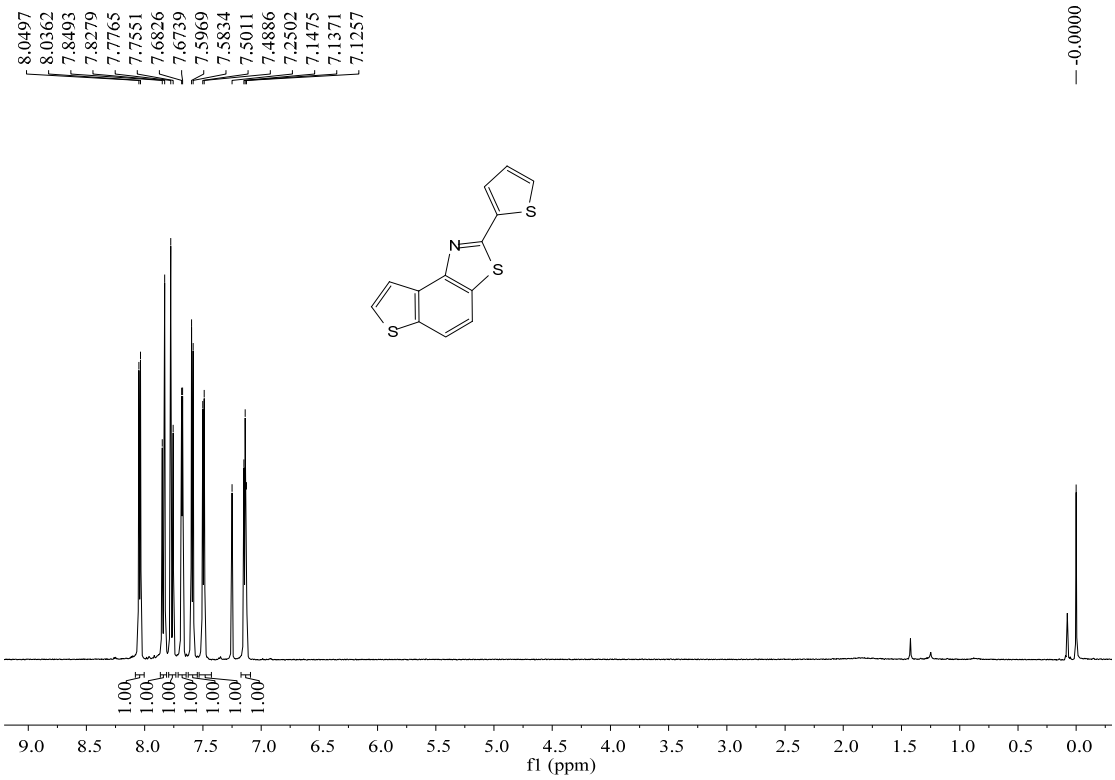


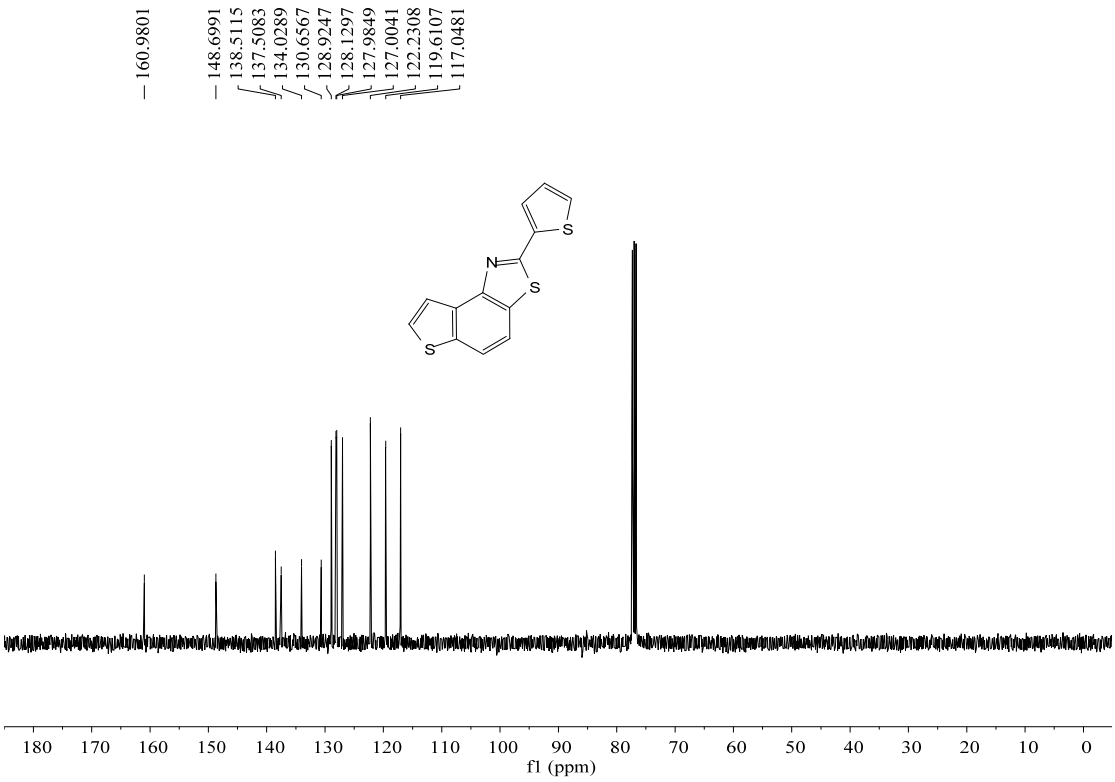
^{1}H and ^{13}C NMR spectra of **4k**



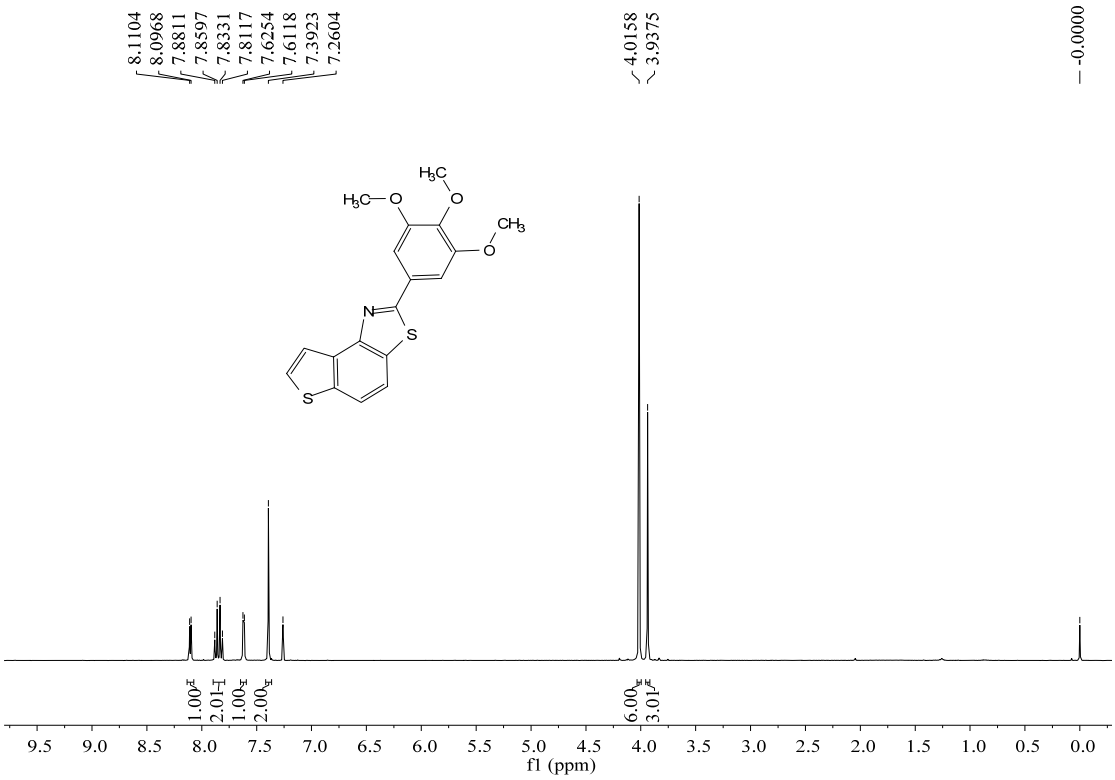


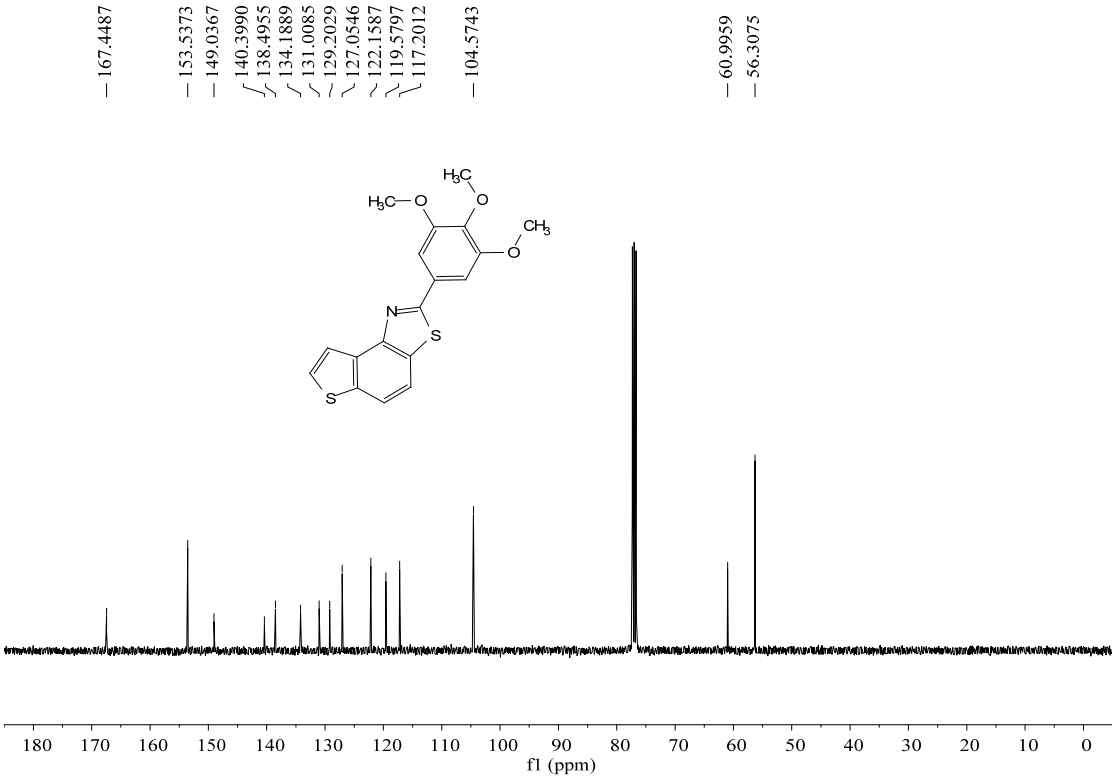
^{1}H and ^{13}C NMR spectra of **4l**



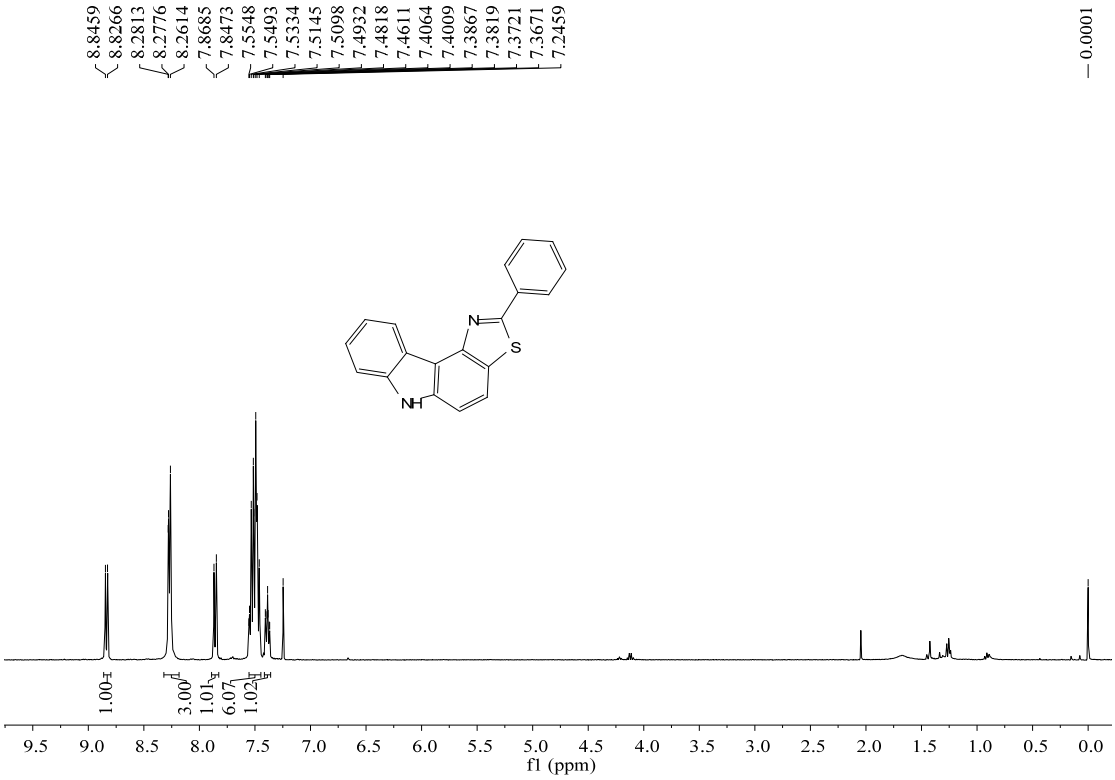


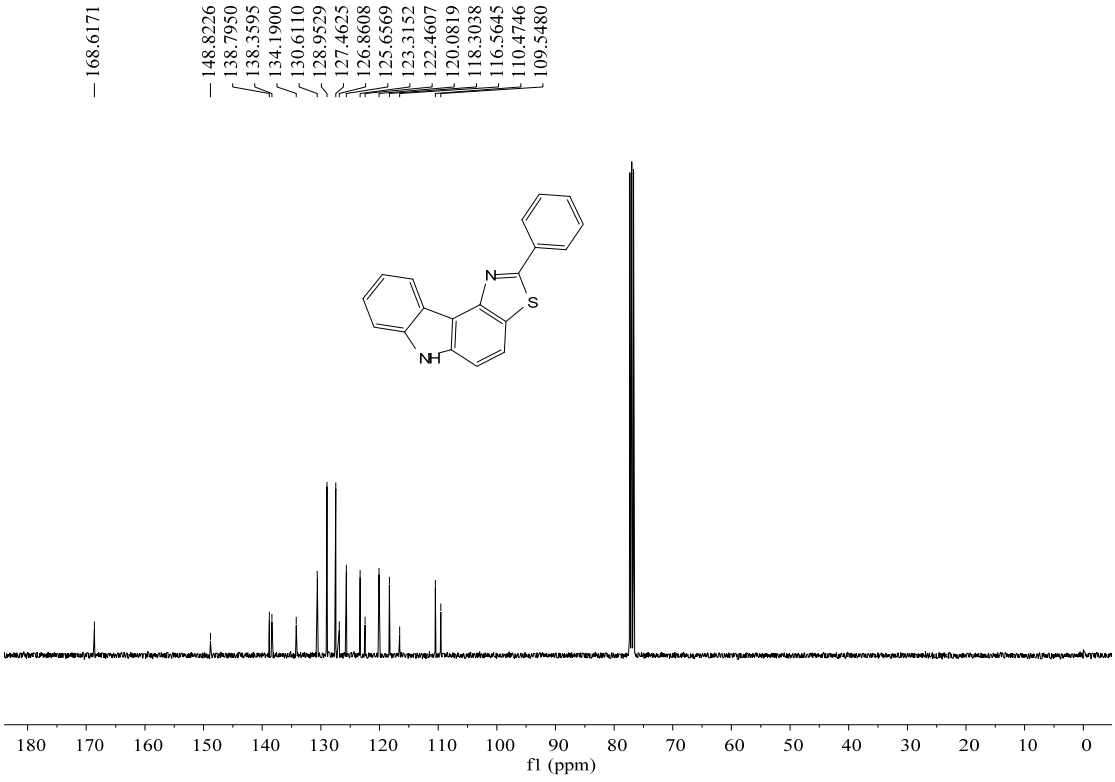
^{1}H and ^{13}C NMR spectra of **4m**



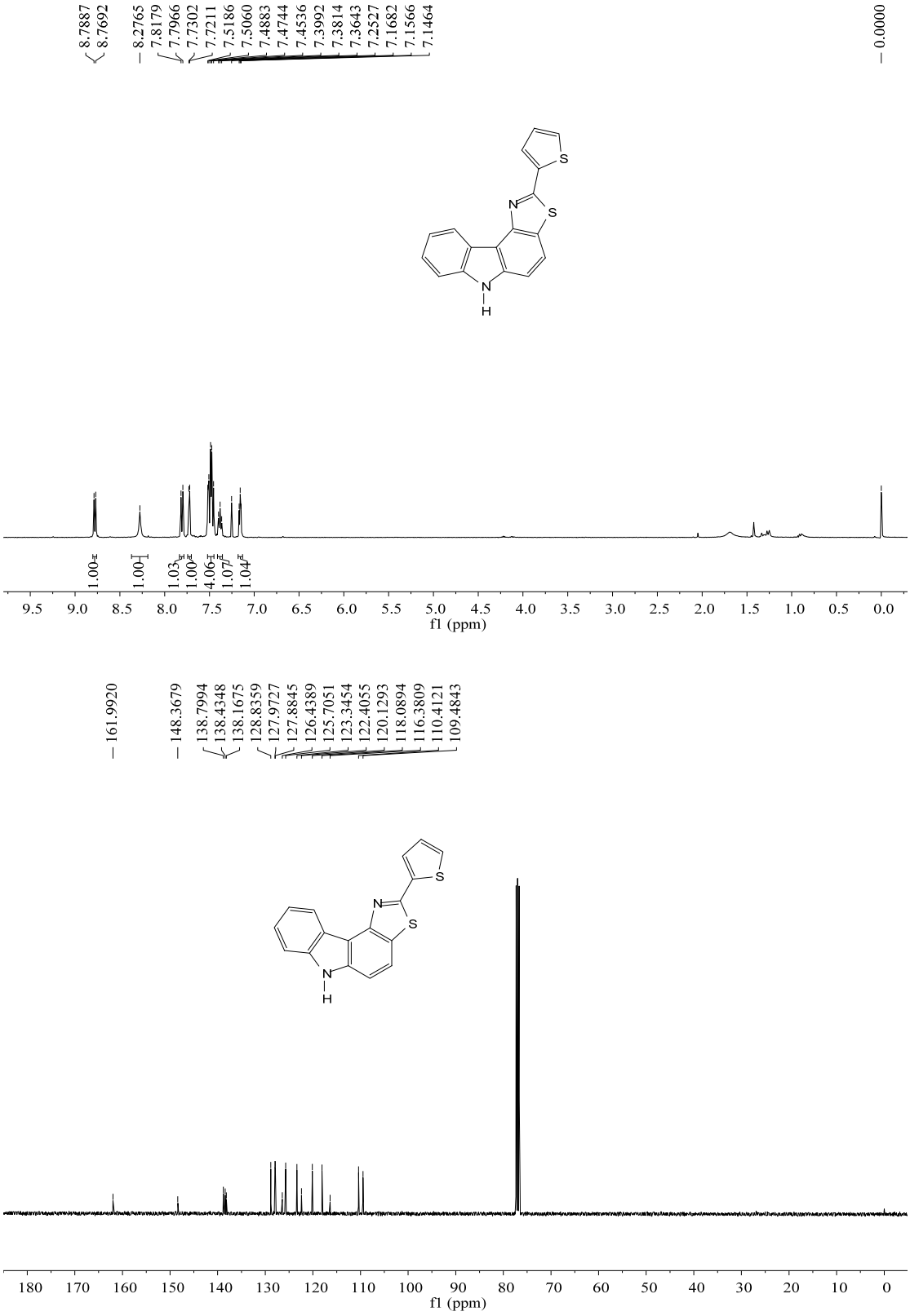


^{1}H and ^{13}C NMR spectra of **4n**

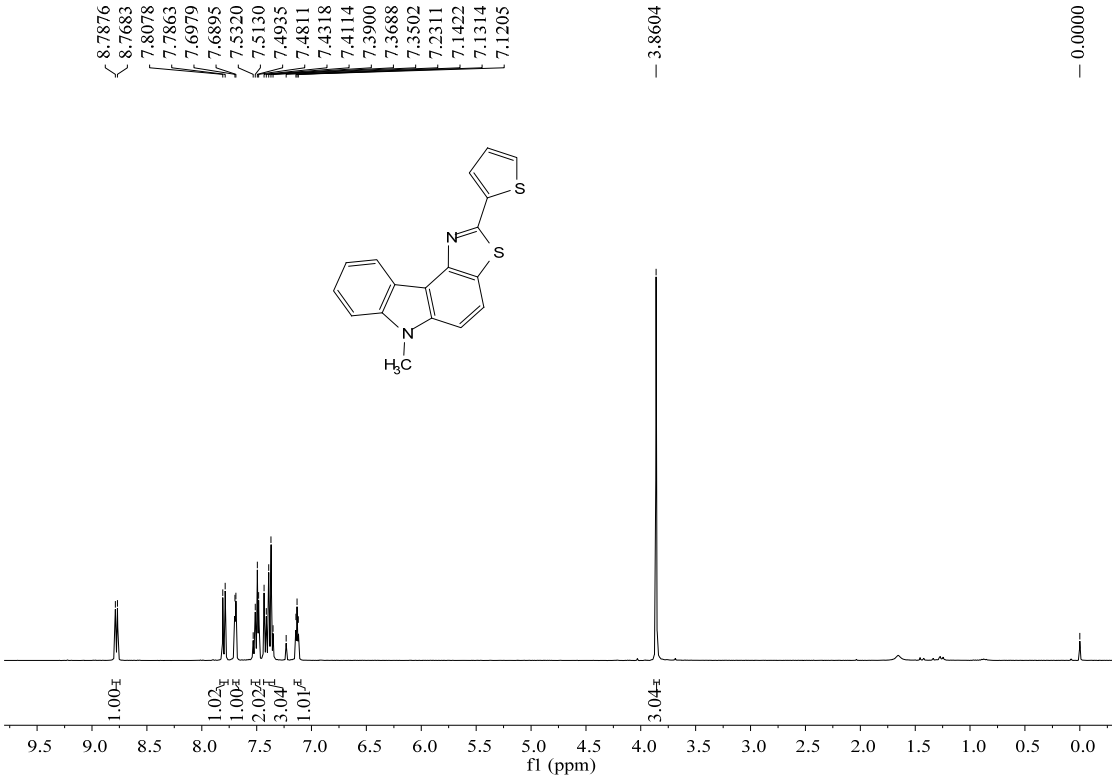


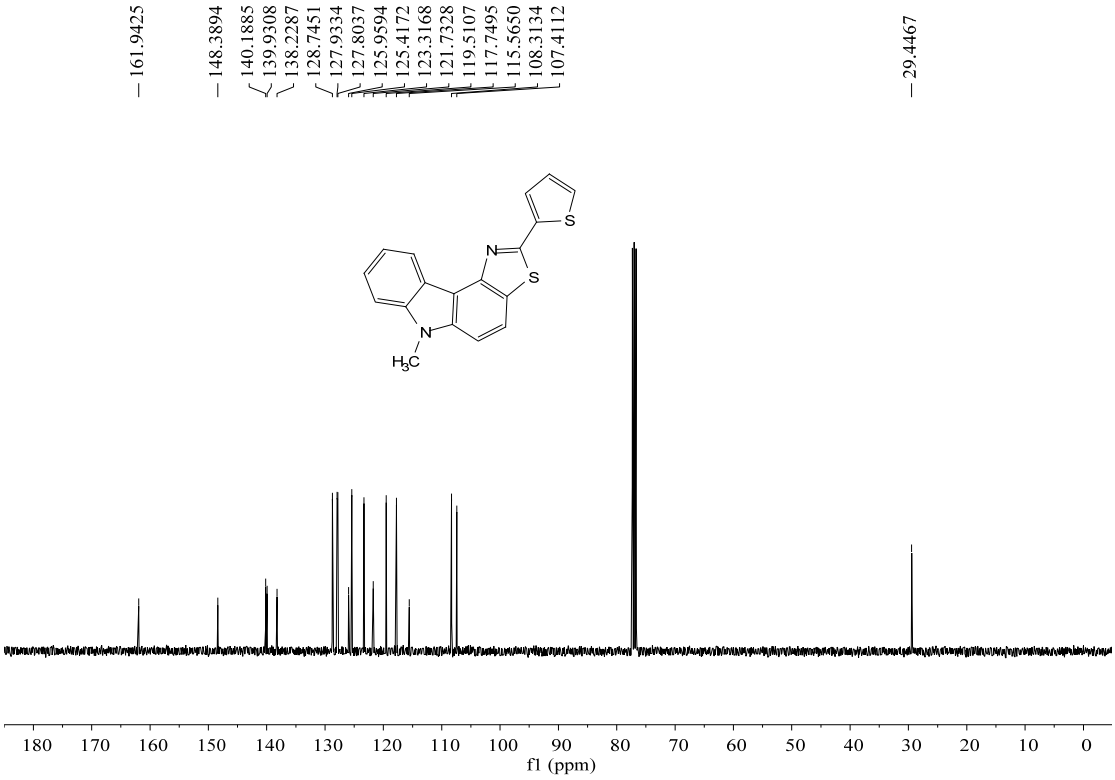


^{1}H and ^{13}C NMR spectra of **4o**

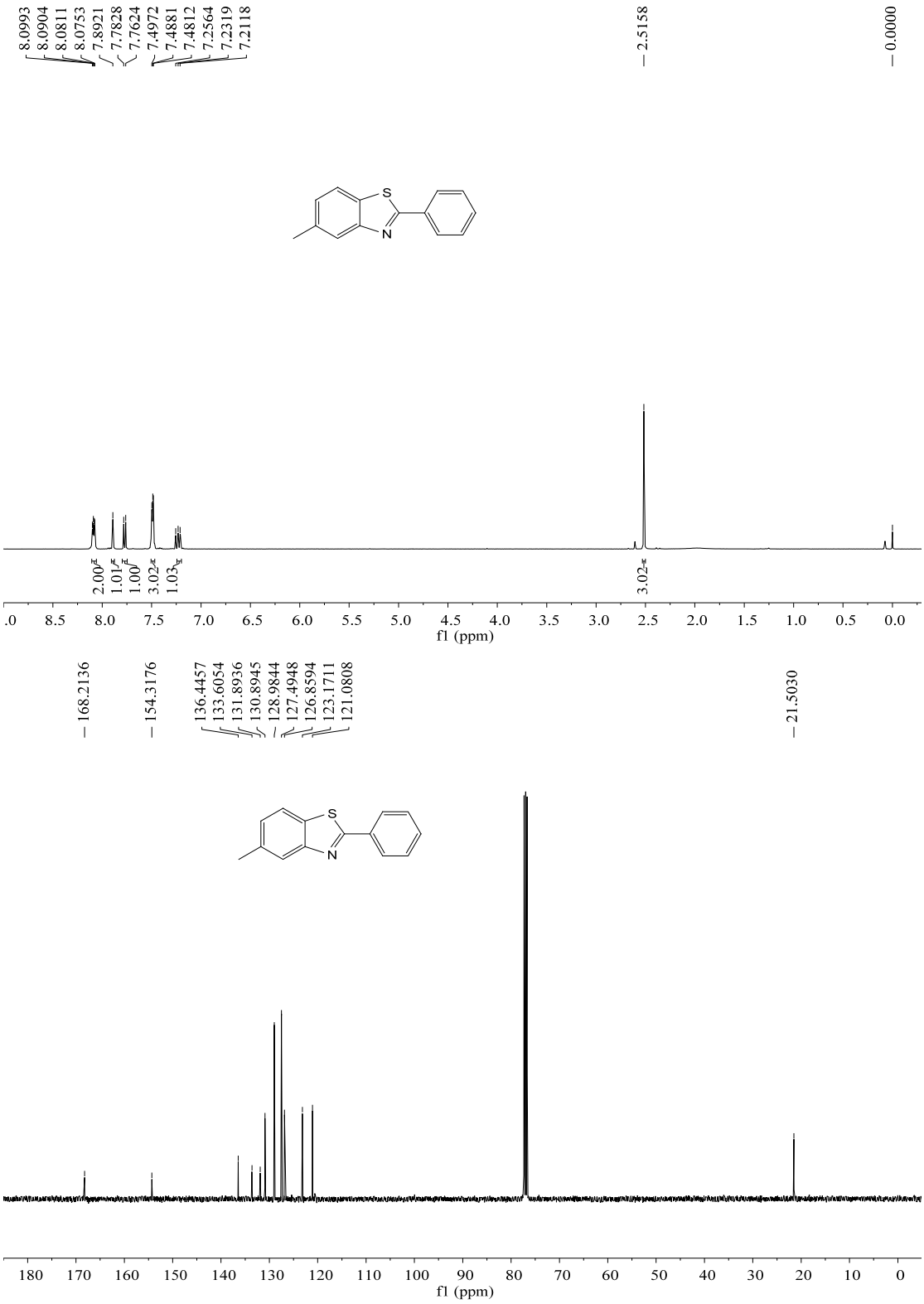


^{1}H and ^{13}C NMR spectra of **4p**

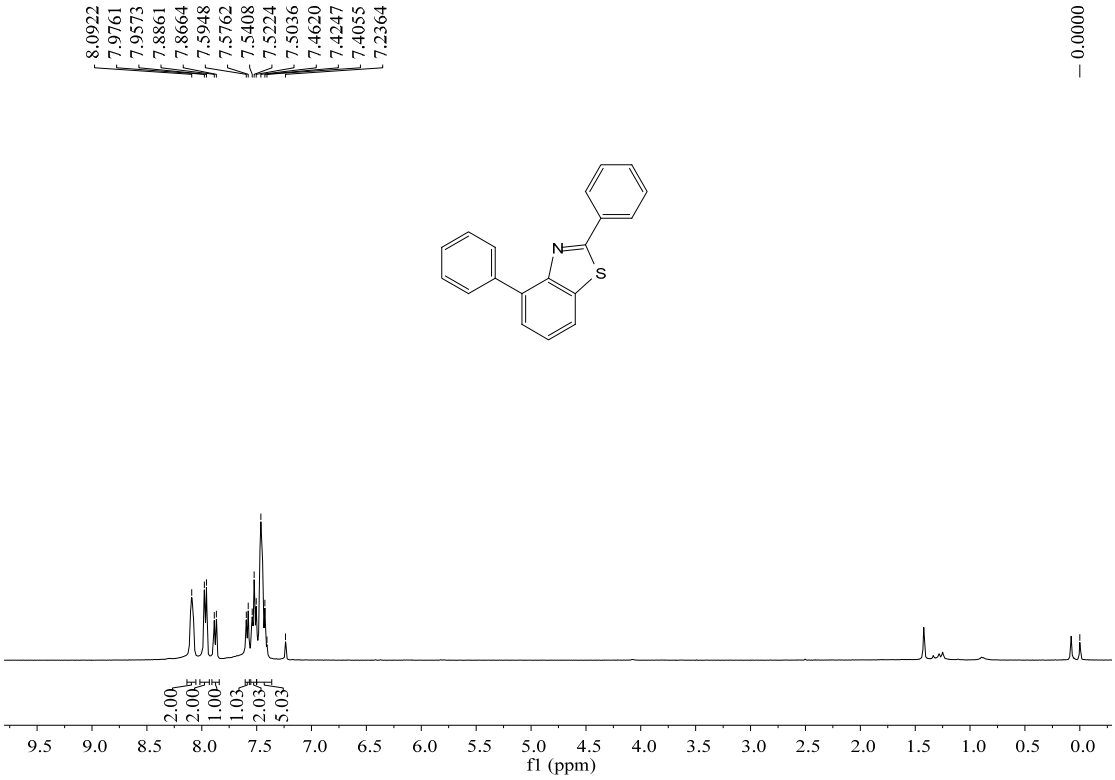


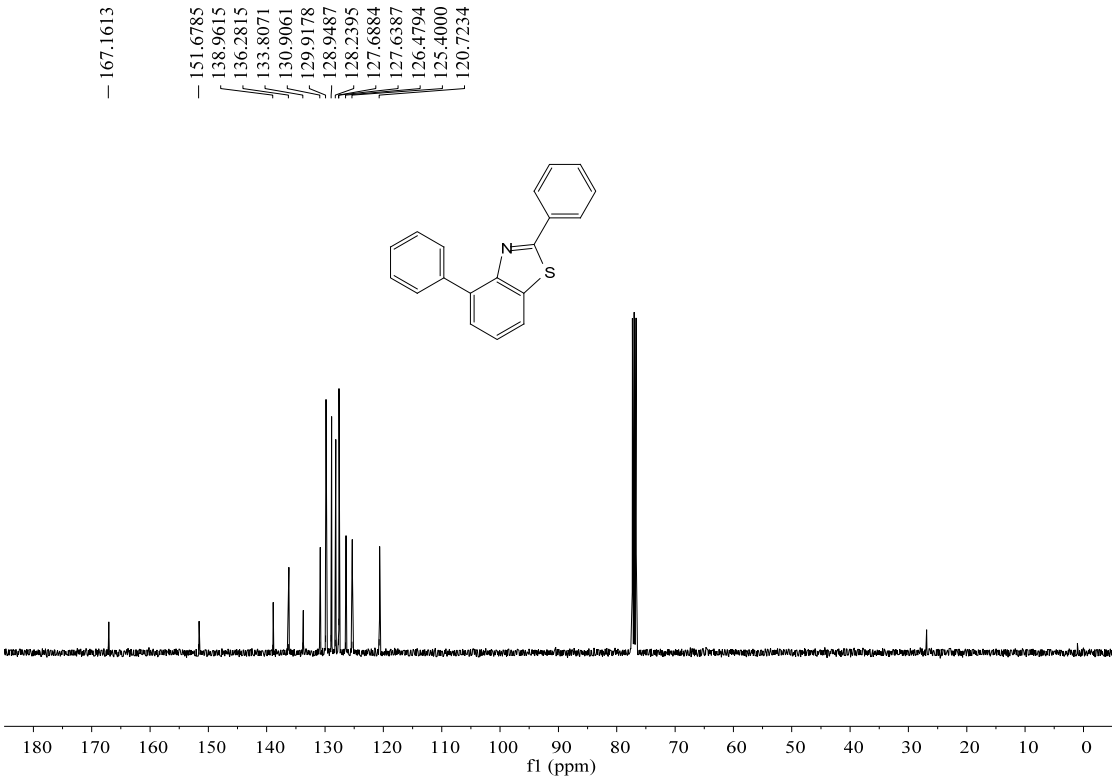


^{1}H and ^{13}C NMR spectra of **4q**

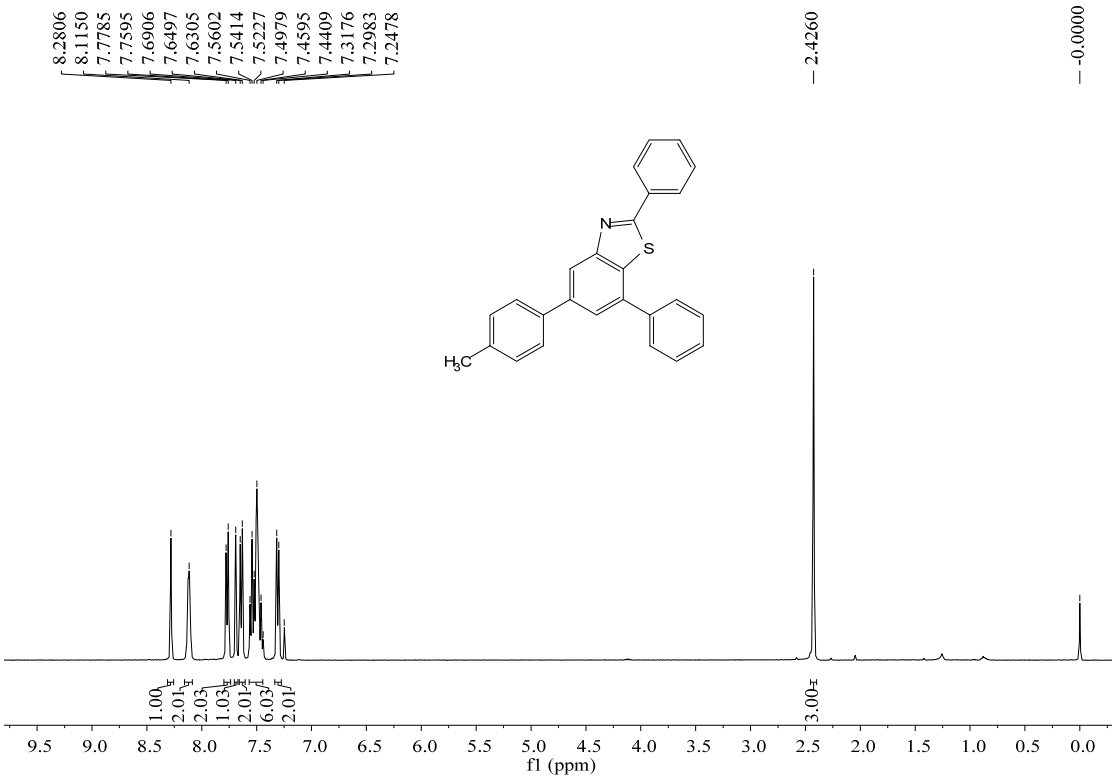


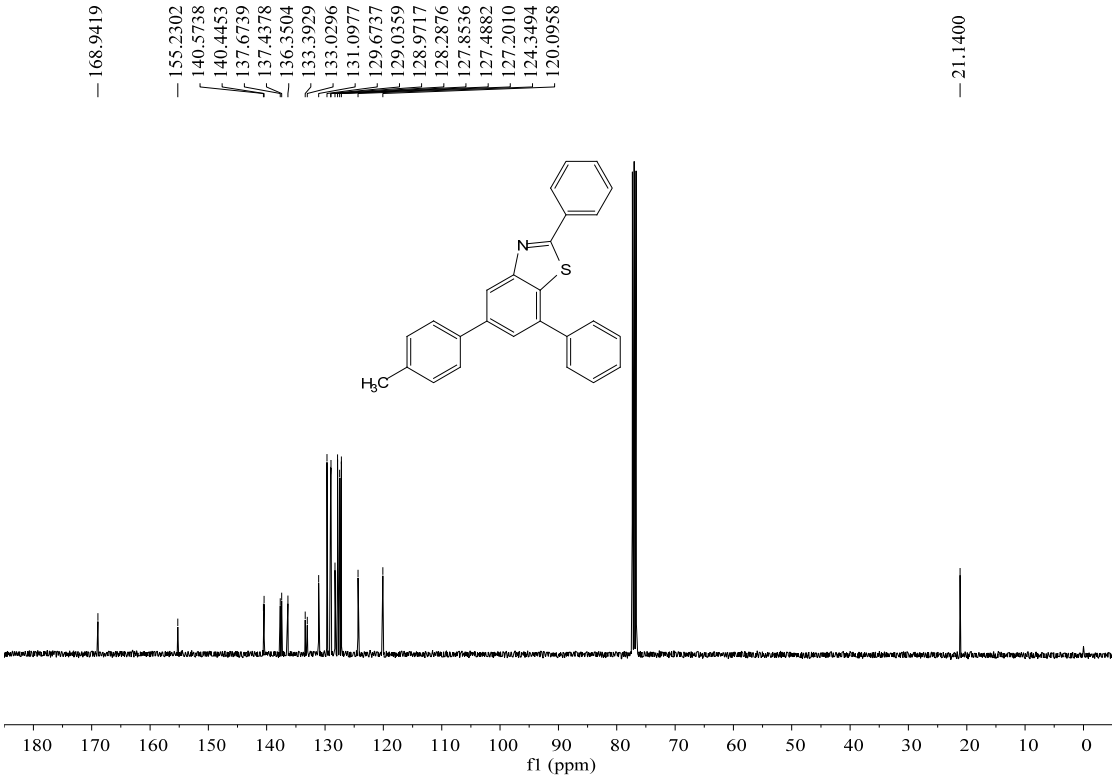
^{1}H and ^{13}C NMR spectra of **4r**



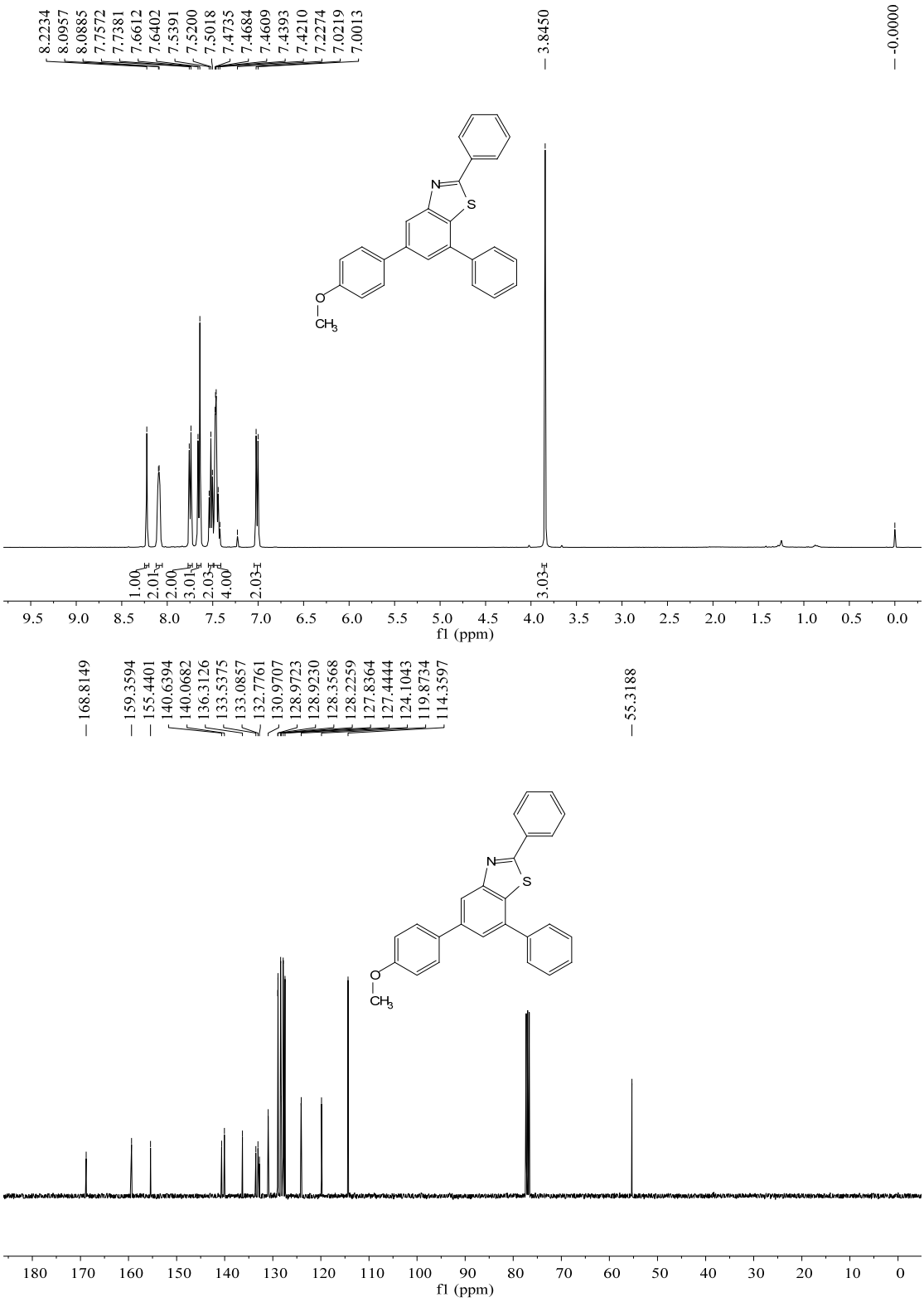


^{1}H and ^{13}C NMR spectra of **4s**

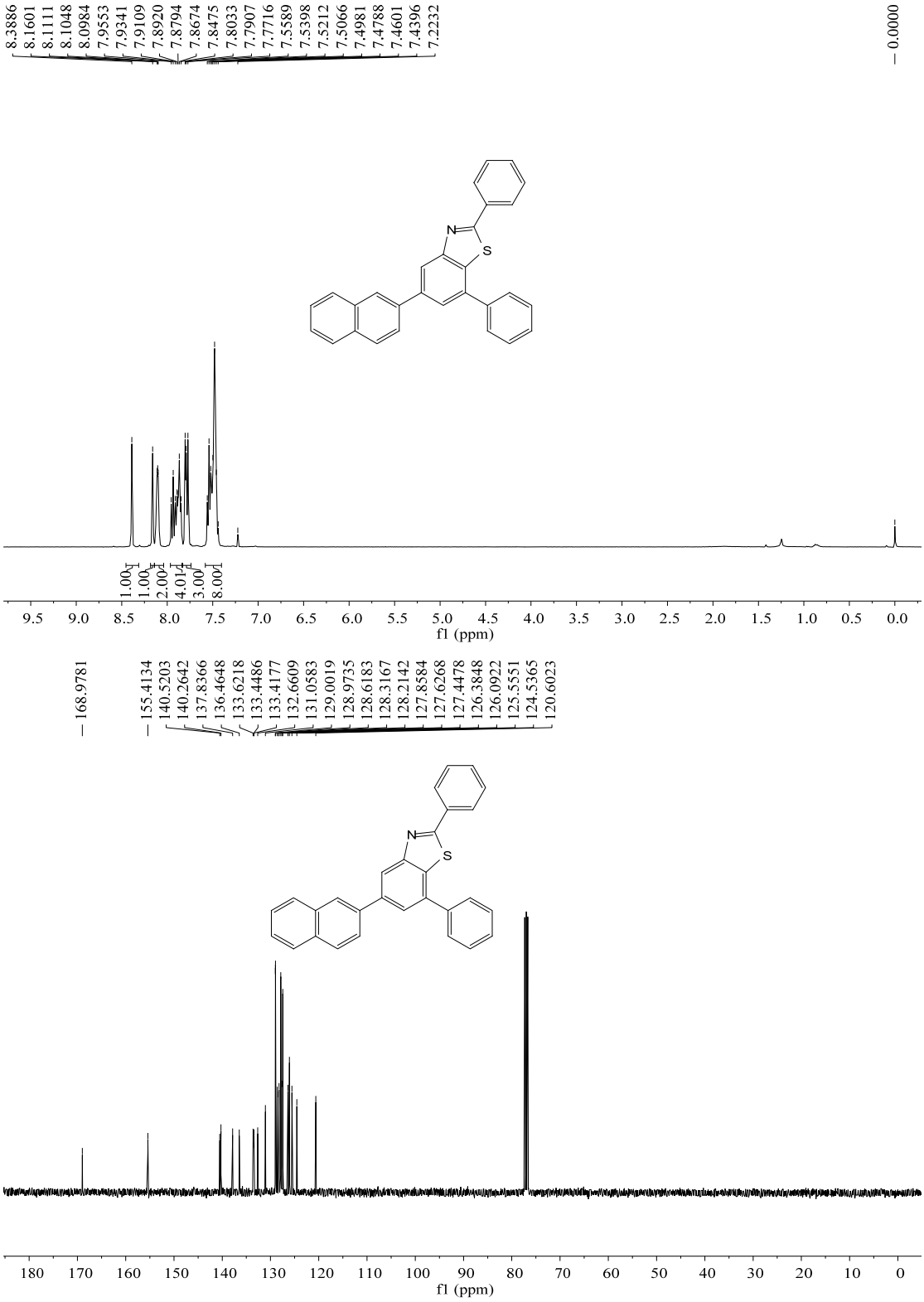




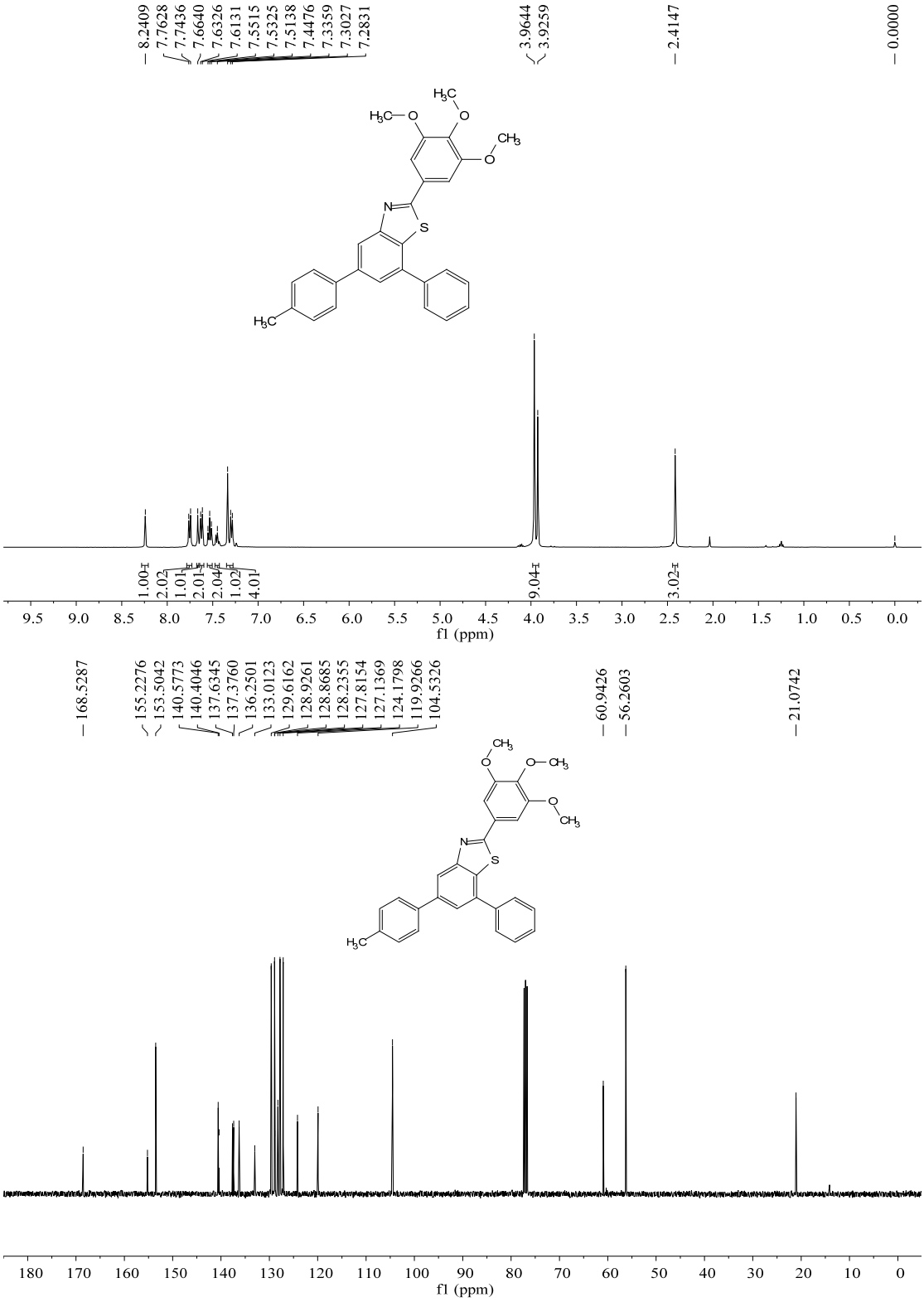
^{1}H and ^{13}C NMR spectra of **4t**



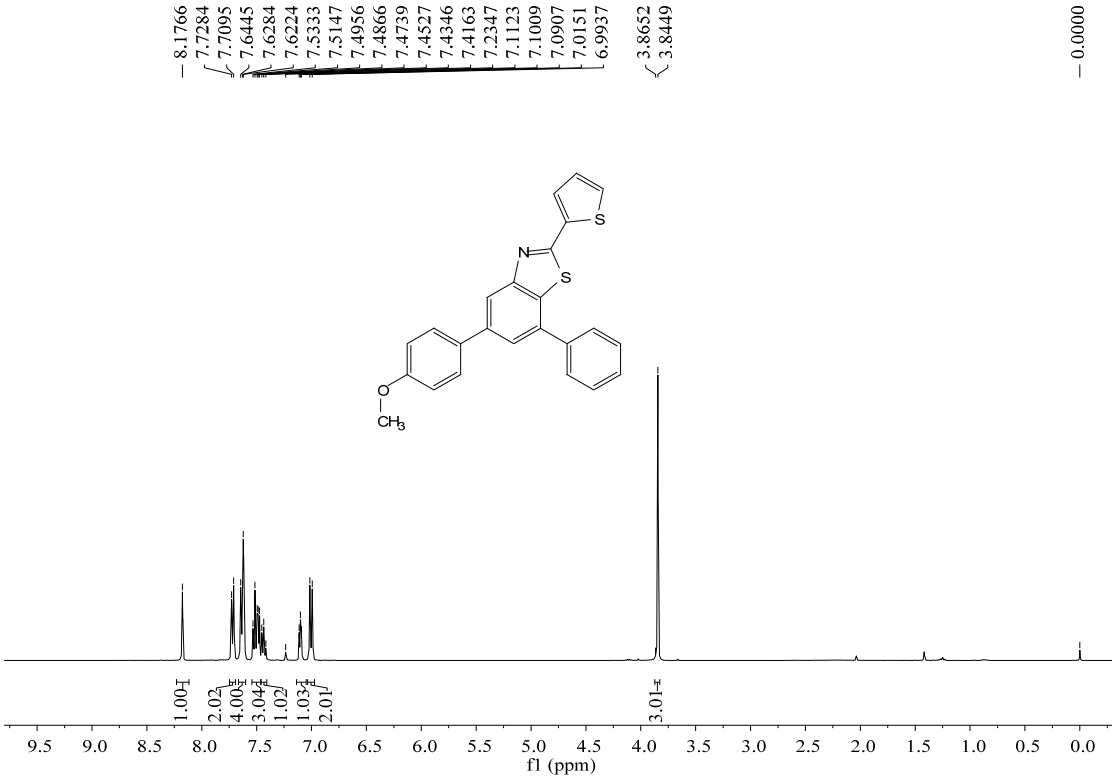
^{1}H and ^{13}C NMR spectra of **4u**

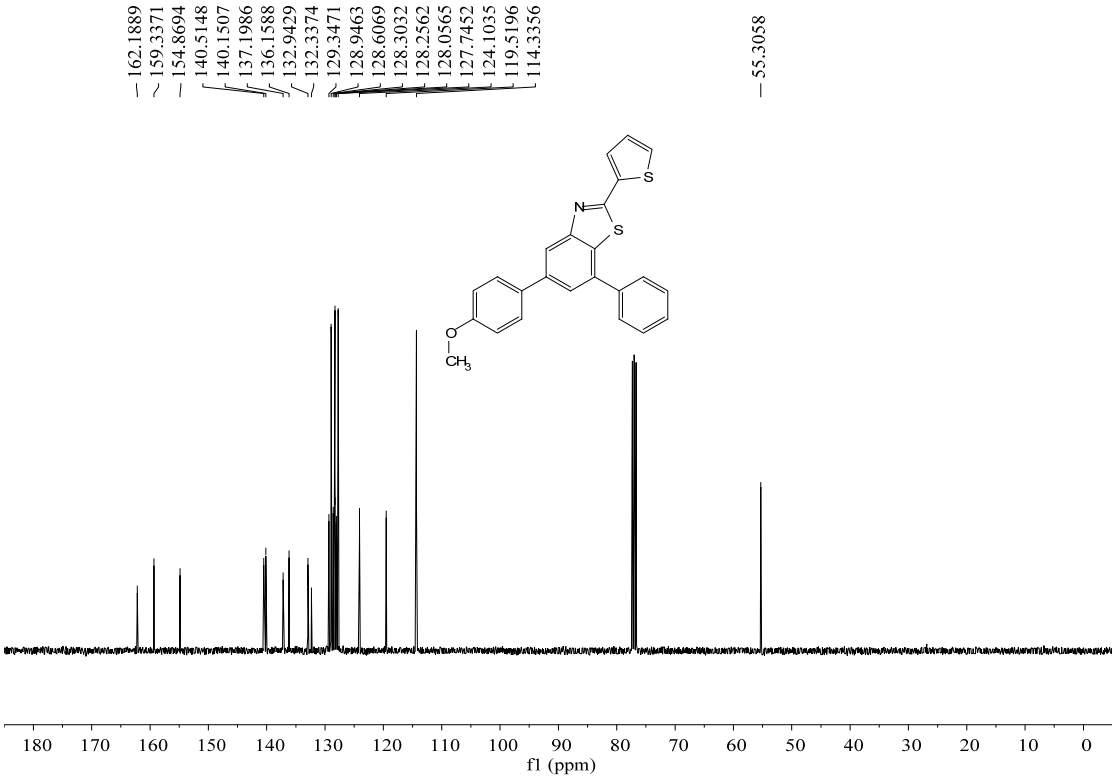


^{1}H and ^{13}C NMR spectra of **4v**

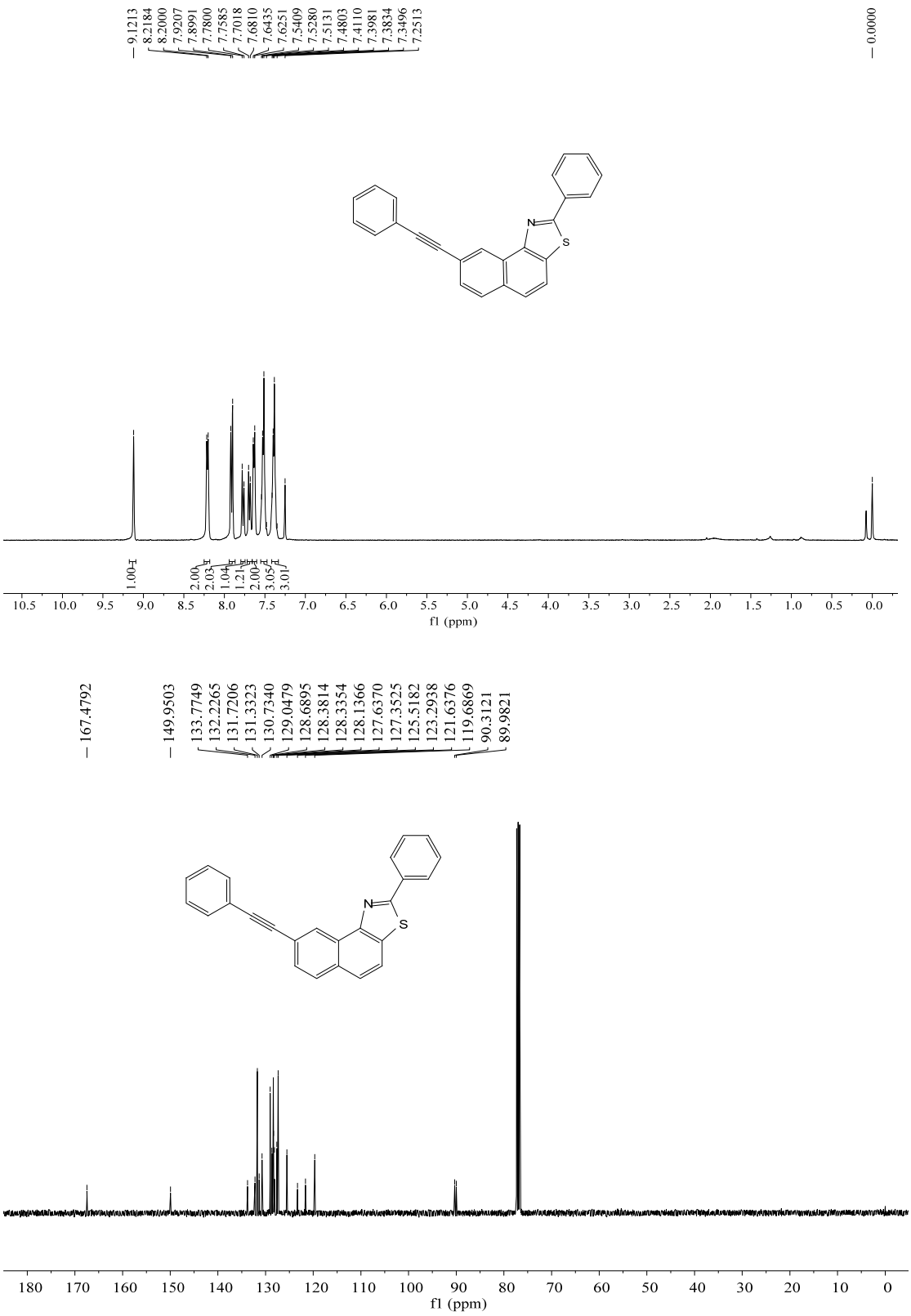


^{1}H and ^{13}C NMR spectra of **4w**

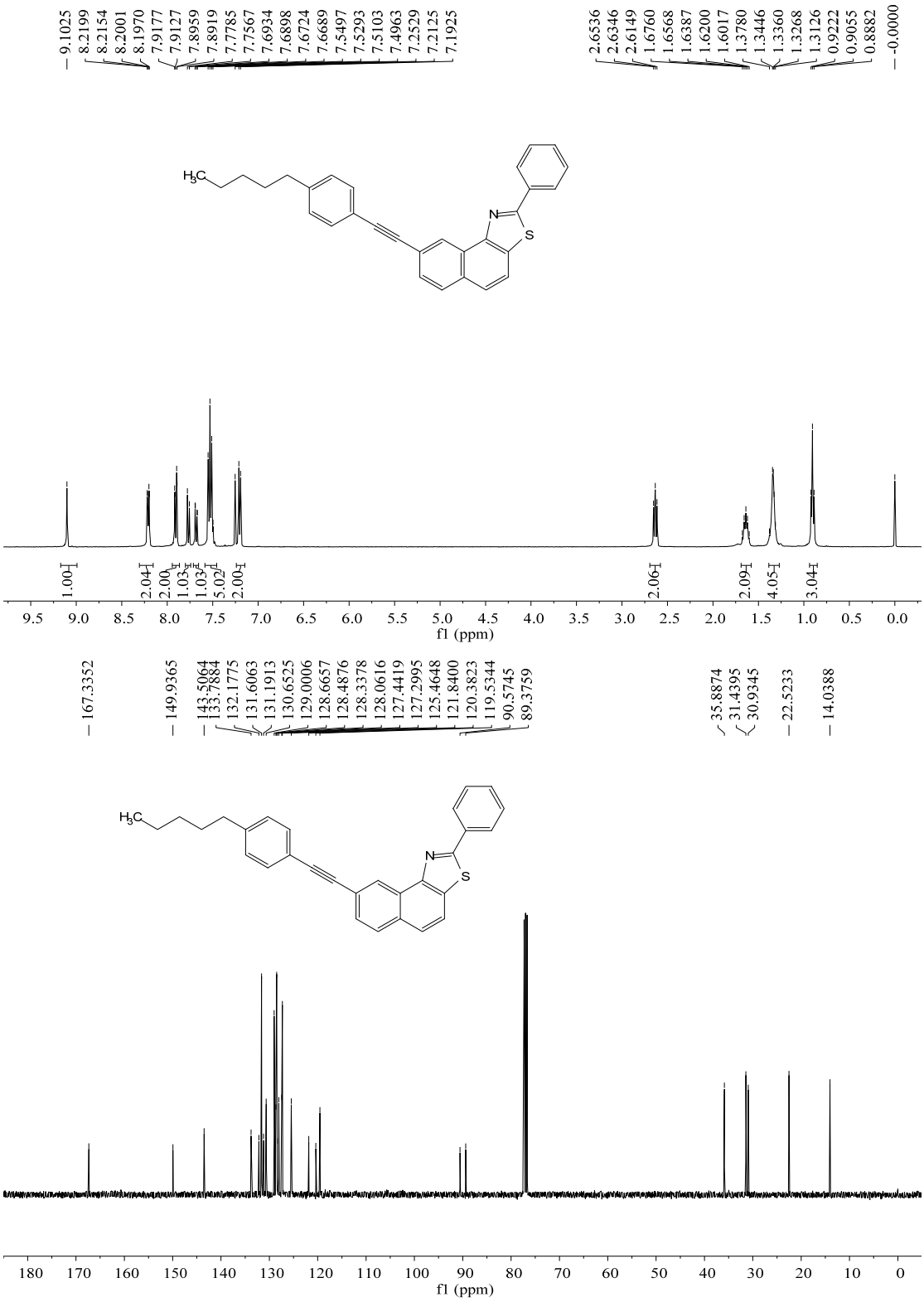




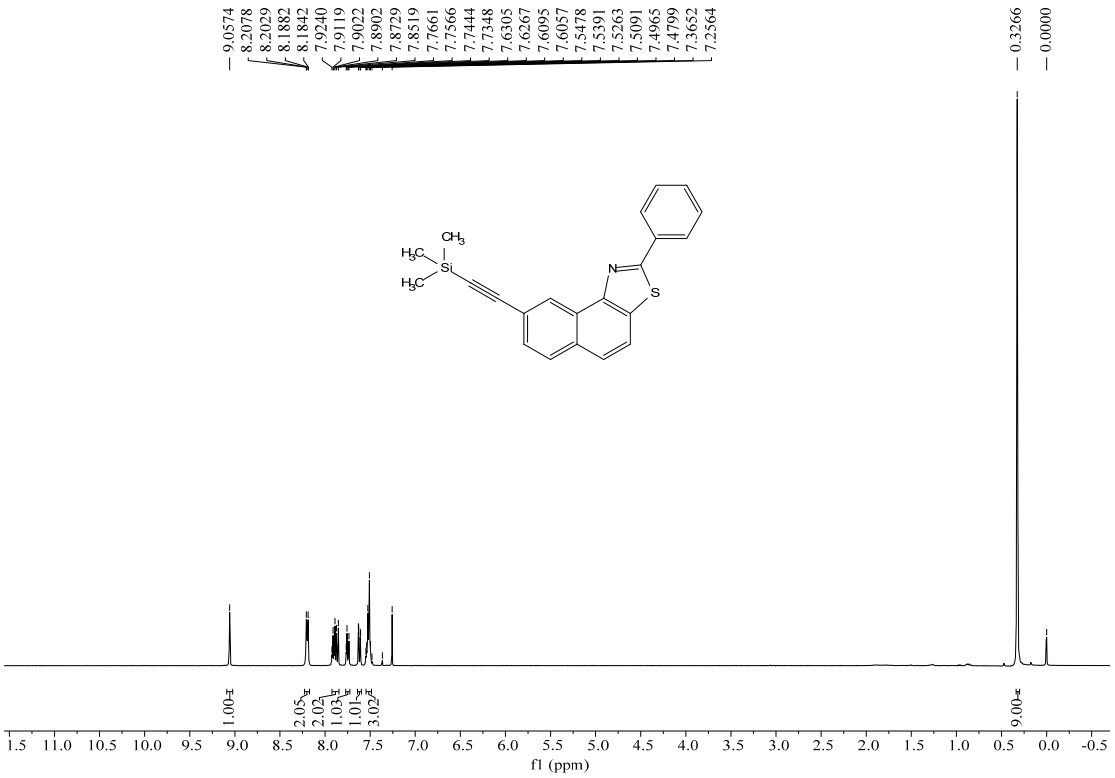
^{1}H and ^{13}C NMR spectra of **5a**

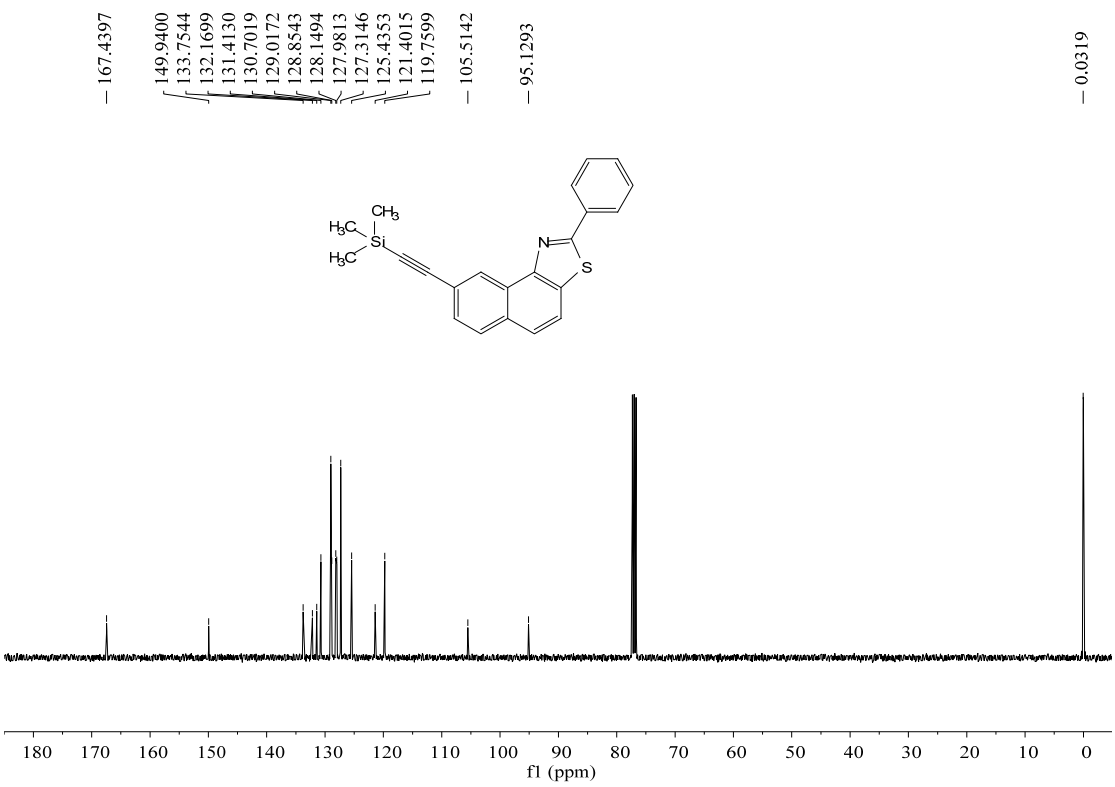


^{1}H and ^{13}C NMR spectra of **5b**



^{1}H and ^{13}C NMR spectra of **5c**





^{1}H and ^{13}C NMR spectra of **5d**