Hypervalent iodine-promoted twofold oxidative coupling of amines with amides and thioamides: chemoselective entryway to oxazoles and thiazoles

Jiang Nan,[a]* Xin Ren[a], Qiang Yan[a], Shilei Liu[a], Jing Wang[a], Yangmin Ma[a], Michal Szostak*[b]

[a] Key Laboratory of Chemical Additives for China National Light Industry, College of Chemistry and Chemical Engineering, Shaanxi University of Science and Technology, Xi'an 710021, China

[b] Department of Chemistry, Rutgers University, 73 Warren Street, Newark, New Jersey 07102, United States

Email: nanjiang@sust.edu.cn

Supporting Information

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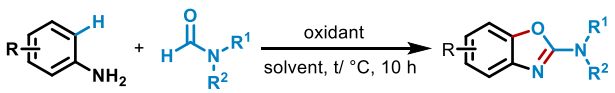
A. General information

All reagents were used as received unless otherwise noted. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F_{254}); visualization of the developed chromatogram was performed by fluorescence. Flash Chromatography was performed with silica gel (300-400 mesh). Proton-1 nuclear magnetic resonance (^{1}H NMR) data were acquired at 400 MHz on a Bruker Ascend 400 (400 MHz) spectrometer, and chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, coupling constants *J* are quoted in Hz. Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were acquired at 100 MHz on a Bruker Ascend 400 spectrometer, chemical shifts are reported in ppm relative to the center line of a triplet at 77.0 ppm for $CDCl_3$. Fluorine-19 nuclear magnetic resonance (^{19}F NMR) data were acquired at 376 MHz on a Bruker Ascend 400 spectrometer. Infrared spectra (IR) data were recorded on a TENSOR 27 FT-IR spectrometer and recorded in wave numbers (cm^{-1}). High resolution mass spectra were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer. Partial naphthylamine **1**[1,2], **12**[3], **13**[4], **14**[5], **15**[6], **4h'**[7], **6**[8], **7**[9], **10**[10] were prepared according to literature methods.

B. Complementary reaction optimization



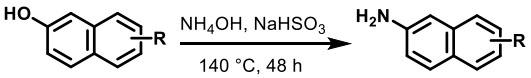
1 2′ 4

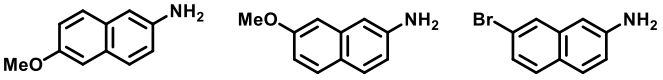
entry	oxidant	additive	solvent	t (℃)	yield (%)[a]
1	**PIDA**	\	\	**80**	**47**
2	PIFA	\	\	80	23
3	DMP	\	\	80	n.d.
4	PhIO	\	\	80	trace
5	IBX	\	\	80	20
6[b]	PhI + *m*-CPBA	\	\	80	n.d.
7	$Cu(OAc)_2•H_2O$	\	\	80	n.d.
8	$Cu(OTf)_2$	\	\	80	n.d.
9	DDQ	\	\	80	n.d.
10	1,4-benzoquinone	\	\	80	n.d.
11[c]	PIDA	\	\	80	61
12[d]	PIDA	\	\	80	53
13[e]	PIDA	\	\	80	52
14[f]	PIDA	\	\	80	21
15[g]	PIDA	\	\	80	19
16[h]	PIDA	\	\	80	trace
17[c]	PIDA	\	\	rt	trace

18[c]	PIDA	\	\	40	27
19[c]	PIDA	\	\	60	39
20[c]	PIDA	\	\	100	58
21[c]	PIDA	\	\	120	68
22[c,i]	PIDA	\	\	120	59
23[c,j]	PIDA	\	\	120	74
24[c,k]	PIDA	\	\	120	79
25[c,l]	**PIDA**	****	****	**120**	**81**
26[c,l,m]	PIDA	K_2CO_3	\	120	60
27[c,l,m]	PIDA	K_3PO_4	\	120	44
28[c,l,m]	PIDA	tBuOK	\	120	19
29[c,l,m]	PIDA	CH_3OK	\	120	57
30[c,l,m]	PIDA	Et_3N	\	120	48
31[c,l,m]	PIDA	DBU	\	120	n.d.
32[c,l,n]	PIDA	TFA	\	120	trace
33[c,l,n]	PIDA	CH_3COOH	\	120	66
34[c,l]	PIDA	\	1,4-dioxane	120	37
35[c,l]	PIDA	\	MeCN	120	47
36[c,l]	PIDA	\	toluene	120	40
37[c,l]	PIDA	\	THF	120	40
38[c,l]	PIDA	\	DCE	120	38
39[c,l]	PIDA	\	CH_3CH_2OH	120	28
40[c,l]	PIDA	\	DME	120	39
41[c,l]	PIDA	\	H_2O	120	trace
42[c,l]	PIDA	\	DMSO	120	trace
43[c,l,o]	PIDA	\	\	120	78

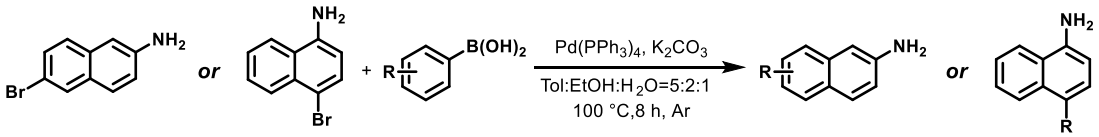
Reaction conditions: **1** (0.2 mmol), **2'** (80.0 equiv) and oxidant (1.0 equiv) for 10 h under air atmosphere. [a]H NMR yields using 1,3,5-trimethoxybenzene as an internal standard. [b]**PhI** (20 mol%), ***m*-CPBA** (1.5 equiv). [c]**2'** (25.0 equiv). [d]**2'** (20.0 equiv). [e]**2'** (15.0 equiv). [f]**2'** (8.0 equiv). [g]**2'** (5.0 equiv). [h]**2'** (2.0 equiv). [i]**PIDA** (3.0 equiv). [j]**PIDA** (2.5 equiv). [k]**PIDA** (2.0 equiv). [l]**PIDA** (1.5 equiv). [m]**additive** (3.0 equiv). [n]**additive** (2.0 equiv). [o]Ar condition.

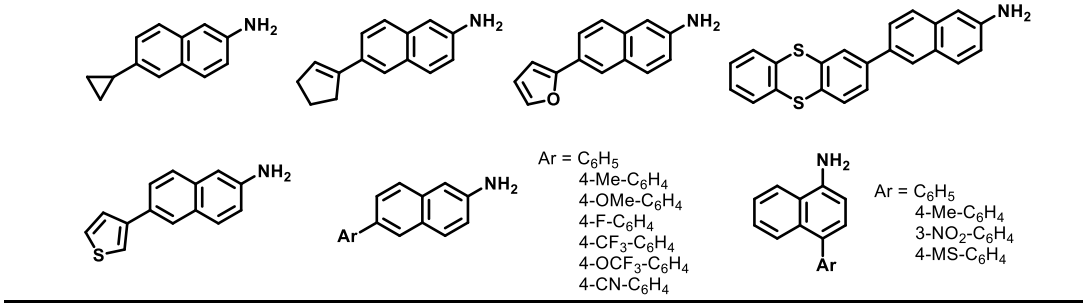
C. Preparation of substrates



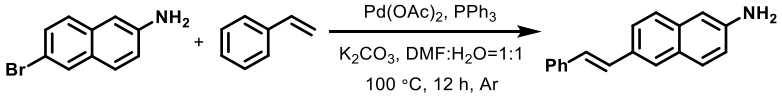


A pressure tube (capacity: 75.0 mL, outside diameter: 46.0 mm, length: 90.0 mm) was charged with naphthalen-2-ol (1.0 mmol) and $NaHSO_3$ (5 mmol). Then, NH_4OH (28-30%) was added slowly. The reaction mixture was stirred sharply at 140 ℃. After stirring for 48 h, the mixture was cooled to room temperature. The mixture was extracted with DCM (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Then the residue was separated and purified on a silica gel column using PE/EA eluent to obtain part of the corresponding products[1].



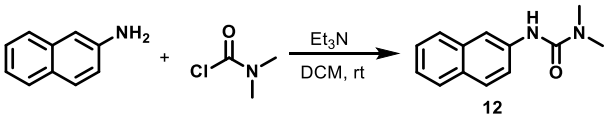


A pressure tube (capacity: 75.0 mL, outside diameter: 46.0 mm, length: 90.0 mm) was charged with naphthylamine (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2.0 eq.), $Pd(PPh_3)_4$ (4 mol%) and solvent (toluene: EtOH: H_2O = 5: 2: 1, 8.0 mL). The reaction mixture was stirred at 100 °C in an oil bath for 8 h under Ar condition. After cooling to room temperature, the residue was carefully dissolved in cold water and basified with ammonium chloride solution, then extracted with DCM (3 × 10.0 mL) and dried with Na_2SO_4, the solvent was removed under reduced pressure and purified by silica gel column chromatography using PE/EA to afford part of the corresponding products[2].



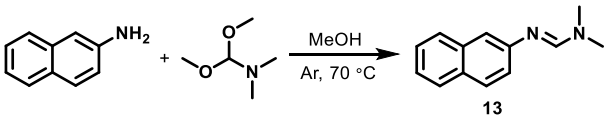
A pressure tube (capacity: 75.0 mL, outside diameter: 46.0 mm, length: 90.0 mm) was charged with 6-bromonaphthalen-2-amine (2.0 mmol), vinylbenzene(2.4 mmol), K_2CO_3 (2.0 eq.),

$Pd(OAc)_2$ (5 mol%), PPh_3 (20 mol%) and solvent (DMF:H_2O = 1:1, 7.0 mL). The reaction mixture was stirred at 100 °C in an oil bath for 12 h under Ar condition. After cooling to room temperature, the residue was carefully dissolved in cold water and basified with ammonium chloride solution, then extracted with DCM (3 × 15 mL) and dried with Na_2SO_4, the solvent was removed under reduced pressure and purified by silica gel column chromatography using PE/EA to afford the product (*E*)-6-styrylnaphthalen-2-amine[2].



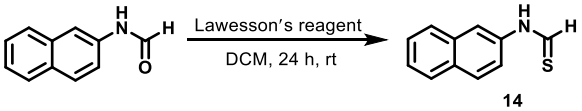
12

A pressure tube (capacity: 75.0 mL, outside diameter: 46.0 mm, length: 90.0 mm) was charged with naphthalen-2-amine (2.0 mmol) and solvent (Et_3N:DCM = 2:1, 6.0 mL), Then, dimethylcarbamic chloride (2.0 equiv) was added slowly at 0 °C. The mixture was stirred at room temperature overnight. After completion as indicated by TLC, the reaction mixture was poured onto crushed ice and extracted with ethyl acetate (8.0 mL). The reaction mixture was washed with 2N HCl (4.0 mL), then extracted with DCM (3 × 15 mL) and dried with Na_2SO_4, the solvent was removed under reduced pressure and purified by silica gel column chromatography using PE/EA to afford the product **12**[3].



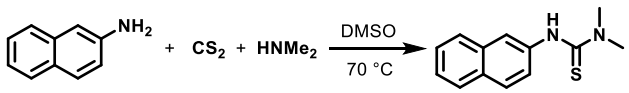
13

A pressure tube (capacity: 75.0 mL, outside diameter: 46.0 mm, length: 90.0 mm) was charged with naphthalen-2-amine (2.0 mmol), 1,1-dimethoxy-*N*,*N*-dimethylmethanamine (1.5 equiv) and solvent MeOH 3.0 mL. The reaction mixture was stirred at 70 °C in an oil bath for 12 h under Ar condition. After cooling to room temperature, the residue was carefully dissolved in cold water and basified with ammonium chloride solution, then extracted with DCM (3 × 15 mL) and dried with Na_2SO_4, the solvent was removed under reduced pressure and purified by silica gel column chromatography using PE/EA to afford the product **13**[4].



14

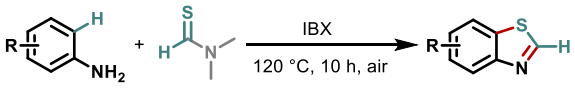
A pressure tube (capacity: 75.0 mL, outside diameter: 46.0 mm, length: 90.0 mm) was charged with *N*-(naphthalen-2-yl)formamide (2.0 mmol) , Lawesson's reagent (0.5 equiv) and solvent DCM 4.0 mL. The mixture was stirred at room temperature for 24 h. After completion as indicated by TLC, the mixture was filtered through a short Celite pad and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography using PE/EA eluent to afford the product **14**[5].



15

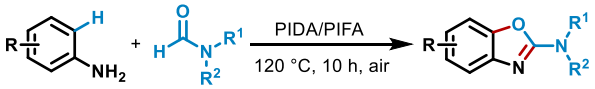
A pressure tube (capacity: 75.0 mL, outside diameter: 46.0 mm, length: 90.0 mm) was charged with naphthalen-2-amine (2.0 mmol), CS_2 (1.2 equiv), $HNMe_2$ (1.2 equiv) and solvent DMSO 10.0 mL. The reaction mixture was stirred at 70 °C in an oil bath for 2 h under air condition. After cooling to room temperature, the residue was carefully dissolved in cold water and basified with ammonium chloride solution, then extracted with DCM (3 × 15 mL) and dried with Na_2SO_4, the solvent was removed under reduced pressure and purified by silica gel column chromatography using PE/EA to afford the product **15**[6].

D. Reaction results



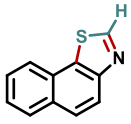
1 2 3

A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with aniline derivatives **1** (0.2 mmol), *N*,*N*-dimethylmethanethioamide **2** (5.0 equiv), and IBX (1.5 equiv). The reaction mixture was stirred at 120 °C for 10 h under air in an oil bath. After cooling to room temperature, the mixture was filtered through a short Celite pad and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography using PE/EA eluent to afford the product **3** and the excess of **2** could be easily recycled.



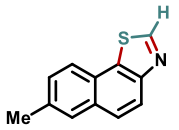
1 2′ 4

A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with aniline derivatives **1** (0.2 mmol), *N*,*N*-dialkylformamide **2'** (25.0 equiv), and PIDA or PIFA (1.5 equiv). The reaction mixture was stirred at 120 °C for 10 h under air in an oil bath. After cooling to room temperature, the reaction mixture was diluted with 15.0 mL aqueous saturated $NaHCO_3$ and extracted with DCM (5.0 mL × 3). The combined organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography using PE/EA eluent to afford the product **4**.



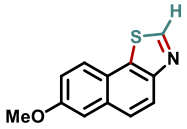
Naphtho[2,1-*d*]thiazole (3a)

White solid (25.9 mg, 70% yield). PE/EA = 10:1, R_f = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 8.19 (d, *J* = 8.8 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.68–7.56 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 151.6, 131.4, 131.3, 128.9, 128.2, 127.3, 127.0, 126.2, 125.2, 121.9. IR (KBr): 3025, 1686, 1534, 1445, 1006, 852, 794 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{11}H_8NS$ $[M+H]^+$ 186.0377, found 186.0371.



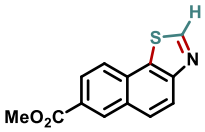
7-Methylnaphtho[2,1-*d*]thiazole (3b)

Yellow solid (25.9 mg, 65% yield). PE/EA = 10:1, R_f = 0.39. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.14 (d, *J* = 8.9 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.78 (s, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 151.2, 136.1, 131.5, 131.4, 129.1, 128.2, 126.9, 126.2, 125.1, 121.9, 21.6. IR (KBr): 2962, 1634, 1544, 1459, 1018, 837, 821 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{12}H_{10}NS$ $[M+H]^+$ 200.0534, found 200.0529.



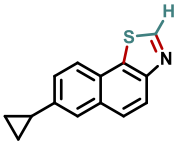
7-Methoxynaphtho[2,1-*d*]thiazole (3c)

Yellow solid (35.7 mg, 83% yield). PE/EA = 10:1, R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 7.99 (d, *J* = 8.9 Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.35 (s, 1H), 7.30 (d, *J* = 243.0 Hz, 1H), 4.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 151.3, 150.3, 132.7, 131.6, 126.7, 126.4, 123.0, 122.3, 119.0, 107.8, 55.4. IR (KBr): 2972, 1638, 1524, 1435, 1073, 855, 828 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{12}H_{10}NOS$ $[M+H]^+$ 216.0483, found 216.0477.



Methyl naphtho[2,1-*d*]thiazole-7-carboxylate (3d)

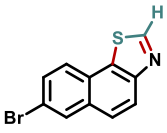
White solid (29.2 mg, 60% yield). PE/EA = 10:1, R_f = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.77 (s, 1H), 8.24 (d, *J* = 8.8 Hz, 2H), 8.12 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 4.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 153.8, 153.0, 131.7, 131.2, 130.5, 130.5, 128.3, 127.8, 126.8, 125.4, 122.8, 52.3. IR (KBr): 2974, 1713, 1609, 1555, 1425, 1063, 915, 835 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{13}H_{10}NO_2S$ $[M+H]^+$ 244.0432, found 244.0426.



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

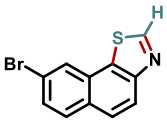
Yellow solid (30.6 mg, 68% yield). PE/EA = 10:1, R_f = 0.36. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.70 (s, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 2.22–2.04 (m, 1H), 1.15–1.06 (m, 2H), 0.91–0.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 151.1, 142.2, 131.5, 131.3, 126.9, 126.3, 125.8, 125.2, 125.0,

121.9, 15.7, 9.3. IR (KBr): 3074, 1678, 1586, 1474, 1053, 840 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{14}H_{12}NS$ $[M+H]^+$ 226.0690, found 226.0683.



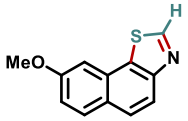
7-Bromonaphtho[2,1-*d*]thiazole (3f)

Yellow solid (26.9 mg, 51% yield). PE/EA = 10:1, R_f = 0.36. ^1H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.25–8.13 (m, 2H), 7.95 (d, *J* = 8.7 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 151.8, 132.5, 131.4, 131.1, 130.3, 126.8, 126.7, 126.4, 123.0, 120.1. IR (KBr): 3068, 1618, 1568, 1446, 1013, 785, 543 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{11}H_7BrNS$ $[M+H]^+$ 263.9483, found 263.9490.



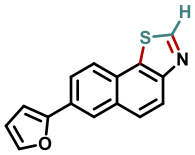
8-Bromonaphtho[2,1-*d*]thiazole (3g)

Yellow solid (27.5 mg, 52% yield). PE/EA = 10:1, R_f = 0.36. ^1H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.23 (s, 1H), 8.18 (d, *J* = 8.8 Hz, 1H), 7.87 (dd, *J* = 8.8, 2.2 Hz, 2H), 7.67 (d, *J* = 8.7, 1.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 152.2, 130.5, 130.4, 129.7, 129.6, 129.4, 127.4, 127.1, 122.4, 121.1. IR (KBr): 3058, 1625, 1529, 1443, 1019, 788, 546 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{11}H_7BrNS$ $[M+H]^+$ 263.9483, found 263.9490.



8-Methoxynaphtho[2,1-*d*]thiazole (3h)

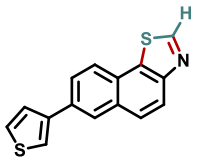
Yellow solid (36.6 mg, 85% yield). PE/EA = 10:1, R_f = 0.28. ^1H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.05 (d, *J* = 8.7 Hz, 1H), 7.90 (d, *J* = 8.9 Hz, 1H), 7.85 (d, *J* = 8.7 Hz, 1H), 7.32 (s, 1H), 7.25 (d, *J* = 8.9, 2.4 Hz, 1H), 4.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 152.3, 152.0, 130.5, 130.3, 129.4, 127.0, 126.2, 119.6, 118.1, 104.6, 55.5. IR (KBr): 2960, 1629, 1496, 1519, 1281, 1039, 792, cm^{-1}. HRMS (ESI) m/z Calcd for $C_{12}H_{10}NOS$ $[M+H]^+$ 216.0483, found 216.0477.



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

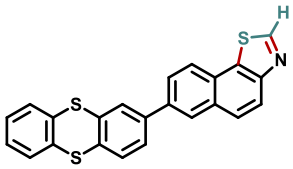
Yellow solid (22.6 mg, 45% yield). PE/EA = 10:1, R_f = 0.35. ^1H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.27 (s, 1H), 8.17 (d, *J* = 8.8 Hz, 1H), 8.03 (d, *J* = 8.6 Hz, 1H), 7.90 (t, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 3.3 Hz, 1H), 6.57 (d, *J* = 3.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 152.3, 151.7, 142.5, 131.5, 131.4, 128.8, 127.5, 127.1, 125.6, 123.3, 123.1,

122.4, 111.9, 105.9. IR (KBr): 3057, 1724, 1637, 1502, 1153, 1012, 832, 733 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{10}NOS$ $[M+H]^+$ 252.0483, found 252.0478.



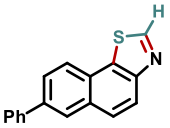
7-(Thiophen-3-yl)naphtho[2,1-*d*]thiazole (3j)

Yellow solid (29.4 mg, 55% yield). PE/EA = 10:1, R_f = 0.33. ^1H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 8.19 (d, *J* = 9.0 Hz, 2H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.92 (dd, *J* = 20.3, 8.6 Hz, 2H), 7.64 (s, 1H), 7.58 (d, *J* = 4.2 Hz, 1H), 7.50 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 151.7, 141.8, 133.8, 131.7, 131.4, 127.5, 127.1, 126.6, 126.3, 126.1, 125.9, 125.8, 122.4, 121.0. IR (KBr): 3034, 1746, 1628, 1532, 1137, 1022, 842, 735 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{10}NS_2$ $[M+H]^+$ 268.0255, found 268.0249.



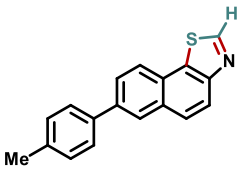
7-(Thianthren-2-yl)naphtho[2,1-*d*]thiazole (3k)

White solid (39.2 mg, 49% yield). PE/EA = 10:1, R_f = 0.24. ^1H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.33–8.18 (m, 2H), 8.12–7.96 (m, 2H), 7.81–7.72 (m, 1H), 7.60 (d, *J* = 23.8 Hz, 2H), 7.47–7.35 (m, 3H), 7.31–7.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 152.0, 141.9, 138.3, 136.3, 135.8, 135.8, 135.3, 131.4, 131.1, 129.5, 129.4, 128.8, 128.7, 128.6, 128.5, 127.8, 127.6, 127.6, 127.5, 127.2, 125.1, 122.5. IR (KBr): 3055, 1619, 1552, 1403, 1024, 747 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{23}H_{14}NS_3$ $[M+H]^+$ 400.0288, found 400.0281.



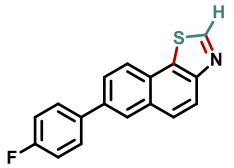
7-Phenylnaphtho[2,1-*d*]thiazole (3l)

Yellow solid (34.5 mg, 66% yield). PE/EA = 10:1, R_f = 0.33. ^1H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.26–8.19 (m, 2H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.9 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 1.6 Hz, 2H), 7.55 (t, *J* = 8.2 Hz, 2H), 7.49–7.42 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 151.7, 140.6, 139.2, 131.6, 131.3, 128.9, 127.6, 127.4, 127.2, 126.8, 126.6, 125.7, 122.3. IR (KBr): 3049, 1692, 1569, 1458, 1065, 965, 697 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{12}NS$ $[M+H]^+$ 262.0690, found 262.0683.



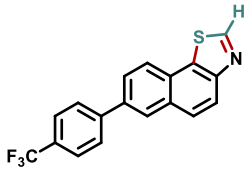
7-(p-tolyl)naphtho[2,1-*d*]thiazole (3m)

White solid (36.9 mg, 67% yield). PE/EA = 10:1, R_f = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.20 (d, *J* = 9.3 Hz, 2H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.7 Hz, 2H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 151.6, 139.1, 137.7, 137.5, 131.6, 131.3, 129.7, 127.6, 127.2, 127.1, 126.5, 126.5, 125.7, 122.2, 21.1. IR (KBr): 2989, 1670, 1539, 1450, 1043, 831 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{14}NS$ $[M+H]^+$ 276.0847, found 276.0841.



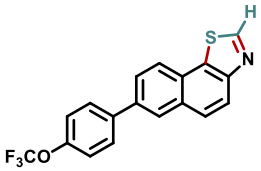
7-(4-Fluorophenyl)naphtho[2,1-*d*]thiazole (3n)

White solid (35.2 mg, 63% yield). PE/EA = 10:1, R_f = 0.32. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.21 (d, *J* = 8.8 Hz, 1H), 8.14 (d, *J* = 9.0 Hz, 2H), 7.97 (d, *J* = 8.9 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.72 (t, *J* = 8.2 Hz, 2H), 7.22 (t, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6 (d, *J* = 265 Hz), 152.5, 151.8, 138.2, 136.8 (d, *J* = 3.0 Hz), 131.6, 131.3, 129.0 (d, *J* = 8.0 Hz), 127.5, 127.2, 126.6 (d, *J* = 27 Hz), 125.9, 122.5, 116.0, 115.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ -115.0. IR (KBr): 3031, 1721, 1548, 1452, 1143, 1058, 823, 744 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{11}FNS$ $[M+H]^+$ 280.0596, found 280.0590.



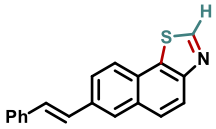
7-(4-(Trifluoromethyl)phenyl)naphtho[2,1-*d*]thiazole (3o)

Yellow solid (40.2 mg, 61% yield). PE/EA = 10:1, R_f = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.25 (d, *J* = 7.5 Hz, 2H), 8.20 (d, *J* = 8.6 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.89 (dd, *J* = 9.0, 7.2 Hz, 3H), 7.80 (d, *J* = 8.1 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 152.1, 144.2, 137.6, 131.6, 131.3, 129.8 (q, *J* = 32 Hz), 127.8, 127.7, 127.6, 127.4, 126.3, 126.1, 125.9 (q, *J* = 4 Hz), 124.3 (q, *J* = 270 Hz), 122.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.4. IR (KBr): 3051, 1730, 1417, 1328, 1124, 1069, 890, 843 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{11}F_3NS$ $[M+H]^+$ 330.0564, found 330.0559.



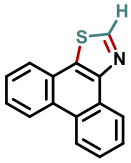
7-(4-(Trifluoromethoxy)phenyl)naphtho[2,1-*d*]thiazole (3p)

Yellow solid (41.4 mg, 60% yield). PE/EA = 10:1, R_f = 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.21 (d, *J* = 8.8 Hz, 1H), 8.15 (d, *J* = 11.3 Hz, 2H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.84 (d, *J* = 7.3 Hz, 1H), 7.76 (d, *J* = 6.4 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 151.9, 149.0, 139.4, 137.7, 131.6, 131.3, 128.7, 127.6, 127.4, 127.0, 126.4, 126.0, 122.6, 121.4, 120.6 (q, *J* = 256 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -57.8. IR (KBr): 2986, 1758, 1503, 1343, 1168, 841 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{11}F_3NOS$ $[M+H]^+$ 346.0513, found 346.0508.



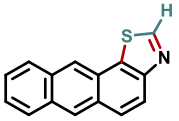
(*E*)-7-Styrylnaphtho[2,1-*d*]thiazole (3q)

Yellow solid (28.7 mg, 50% yield). PE/EA = 10:1, R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.19 (d, *J* = 8.8 Hz, 1H), 8.07 (d, *J* = 10.1 Hz, 2H), 7.91 (dd, *J* = 17.4, 8.6 Hz, 2H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.47–7.40 (m, 2H), 7.34 (d, *J* = 13.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 151.7, 137.2, 135.5, 131.7, 131.5, 129.7, 128.8, 128.3, 127.9, 127.5, 127.4, 127.3, 126.6, 125.7, 124.9, 122.4. IR (KBr): 2922, 1669, 1585, 1436, 1068, 964, 693 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{19}H_{14}NS$ $[M+H]^+$ 288.0847, found 288.0838.



Phenanthro[9,10-*d*]thiazole (3r)

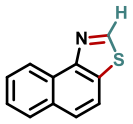
Yellow solid (32.9 mg, 70% yield). PE/EA = 10:1, R_f = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.90 (d, *J* = 7.9 Hz, 1H), 8.65 (d, *J* = 8.1 Hz, 2H), 7.97 (d, *J* = 8.6 Hz, 1H), 7.81–7.68 (m, 2H), 7.68–7.57 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 149.1, 130.1, 129.8, 129.2, 128.2, 127.5, 127.3, 127.0, 126.8, 126.0, 124.6, 123.7, 123.0. IR (KBr): 3015, 1627, 1514, 1418, 1052, 748 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{10}NS$ $[M+H]^+$ 236.0534, found 236.0526.



Anthra[2,1-*d*]thiazole (3s)

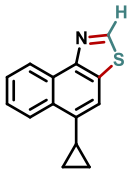
Yellow solid (36.7 mg, 78% yield). PE/EA = 10:1, R_f = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 8.52 (d, *J* = 18.6 Hz, 2H), 8.14–7.94 (m, 4H), 7.62–7.52 (m, 2H). ^{13}C NMR (100

MHz, $CDCl_3$) δ 152.0, 151.3, 132.0, 131.7, 131.1, 129.6, 128.2, 127.9, 127.7, 126.3, 125.8, 123.3, 121.8. IR (KBr): 3011, 1631, 1535, 1424, 1026, 820, 757 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{10}NS$ $[M+H]^+$ 236.0534, found 236.0526.



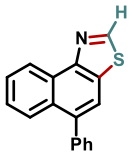
Naphtho[1,2-*d*]thiazole (3aa)

Yellow oil (20.7 mg, 56% yield). PE/EA = 10:1, R_f = 0.40. ^1H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.92 (d, *J* = 8.3 Hz, 1H), 8.03 (t, *J* = 8.5 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 149.9, 132.0, 130.7, 128.9, 128.1, 127.2, 126.4, 126.3, 123.7, 119.0. IR (KBr): 3023, 1683, 1537, 1448, 1014, 856, 799 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{11}H_8NS$ $[M+H]^+$ 186.0377, found 186.0371.



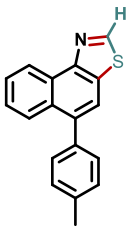
5-Cyclopropylnaphtho[1,2-*d*]thiazole (3ab)

Brown solid (27.0 mg, 60% yield). PE/EA = 10:1, R_f = 0.36. ^1H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.95 (d, *J* = 8.0 Hz, 1H), 8.59 (d, *J* = 8.2 Hz, 1H), 7.83 (s, 1H), 7.82–7.70 (m, 2H), 2.56–2.41 (m, 1H), 1.26–1.15 (m, 2H), 0.89 (d, *J* = 5.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 148.9, 138.0, 132.2, 130.5, 128.7, 126.9, 126.1, 124.9, 124.2, 117.0, 14.0, 6.6. IR (KBr): 3064, 1671, 1576, 1483, 1041, 743cm^{-1}. HRMS (ESI) m/z Calcd for $C_{14}H_{12}NS$ $[M+H]^+$ 226.0690, found 226.0683.



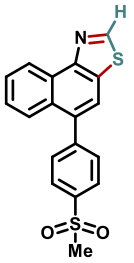
5-Phenylnaphtho[1,2-*d*]thiazole (3ac)

Brown solid (33.5 mg, 64% yield). PE/EA = 10:1, R_f = 0.33. ^1H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 9.00 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.6 Hz, 1H), 7.93 (s, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.61–7.49 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 149.4, 140.3, 139.0, 130.7, 130.3, 130.1, 129.0, 128.4, 127.6, 127.0, 126.7, 126.3, 124.1, 119.7. IR (KBr): 3059, 1682, 1563, 1468, 1055, 739, 699 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{12}NS$ $[M+H]^+$ 262.0690, found 262.0683.



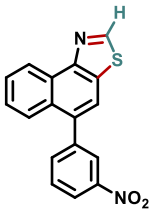
5-(*p*-Tolyl)naphtho[1,2-*d*]thiazole (3ad)

Brown solid (36.9 mg, 67% yield). PE/EA = 10:1, R_f = 0.32. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.99 (d, *J* = 8.2 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.93 (s, 1H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 2H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 149.3, 139.0, 137.4, 137.3, 130.7, 130.3, 130.0, 129.1, 129.0, 127.0, 126.8, 126.2, 124.0, 119.5, 21.2. IR (KBr): 2997, 1680, 1538, 1457, 1033, 761 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{14}NS$ $[M+H]^+$ 276.0847, found 276.0841.



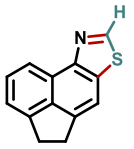
5-(4-(Methylsulfonyl)phenyl)naphtho[1,2-d]thiazole (3ae)

White solid (29.0 mg, 55% yield). PE/EA = 5:1, R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 9.02 (d, *J* = 8.2 Hz, 1H), 8.16 (d, *J* = 7.8 Hz, 2H), 7.95 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 7.7 Hz, 3H), 7.63 (t, *J* = 7.6 Hz, 1H), 3.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 150.1, 146.2, 139.9, 136.7, 131.2, 130.2, 130.0, 129.1, 127.6, 127.5, 126.8, 126.0, 124.4, 120.2, 44.7. IR (KBr): 2922, 1722, 1633, 1500, 1397, 1307, 1147, 1084, 954, 838, 769 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{14}NO_2S_2$ $[M+H]^+$ 340.0466, found 340.0457.



5-(3-Nitrophenyl)naphtho[1,2-*d*]thiazole (3af)

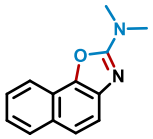
Brown solid (39.8 mg, 65% yield). PE/EA = 10:1, R_f = 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 9.02 (d, *J* = 8.2 Hz, 1H), 8.45 (s, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.96 (s, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.81–7.71 (m, 2H), 7.66–7.59 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 150.1, 148.5, 142.0, 136.2, 136.1, 130.1, 130.0, 129.4, 129.1, 127.5, 126.9, 125.7, 124.9, 124.4, 122.6, 120.2. IR (KBr): 3072, 1734, 1526, 1345, 822, 771, 691 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{11}N_2O_2S$ $[M+H]^+$ 307.0541, found 307.0531.



4,5-Dihydroacenaphtho[5,4-*d*]thiazole (3ah)

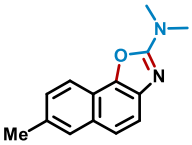
Yellow solid (23.7 mg, 56% yield). PE/EA = 10:1, R_f = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.43 (d, *J* = 8.1 Hz, 1H), 7.82–7.65 (m, 2H), 7.48 (d, *J* = 7.1 Hz, 1H), 3.62–3.43 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 146.9, 145.7, 144.7, 138.5, 133.7, 128.9, 126.7, 120.3,

119.0, 112.0, 31.2, 29.8. IR (KBr): 2922, 1640, 1533, 1428, 833, 765 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{13}H_{10}NS$ $[M+H]^+$ 212.0534, found 212.0530.



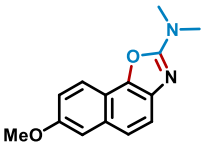
_N_,_N_-Dimethylnaphtho[2,1-_d_]oxazol-2-amine (4a)

Brown solid (34.4 mg, 81% yield). PE/EA = 4:1, R_f = 0.25. ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 3.31 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 143.1, 139.9, 129.3, 128.7, 126.3, 124.3, 123.3, 119.7, 118.7, 116.9, 37.9. IR (KBr): 2957, 1632, 1547, 1463, 1283, 829, 731 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{13}H_{13}N_2O$ $[M+H]^+$ 213.1028, found 213.1021.



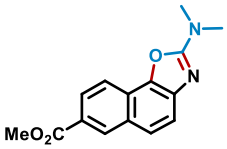
_N_,_N_,7-Trimethylnaphtho[2,1-_d_]oxazol-2-amine (4b)

Brown solid (31.9 mg, 71% yield). PE/EA = 4:1, R_f = 0.24. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 1H), 7.69 (s, 1H), 7.64–7.56 (m, 2H), 7.40 (d, *J* = 8.5 Hz, 1H), 3.30 (s, 6H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 143.2, 139.1, 132.8, 129.6, 128.6, 127.6, 123.6, 118.6, 117.9, 116.9, 37.9, 21.7. IR (KBr): 2961, 1679, 1556, 1442, 1253, 839 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{14}H_{15}N_2O$ $[M+H]^+$ 227.1184, found 227.1176.



7-Methoxy-_N_,_N_-dimethylnaphtho[2,1-_d_]oxazol-2-amine (4c)

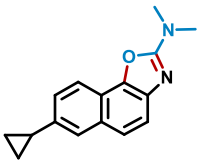
Brown solid (37.5 mg, 78% yield). PE/EA = 4:1, R_f = 0.23. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.62 (d, J = 5.6 Hz, 2H), 7.28 (d, J = 5.7 Hz, 2H), 3.98 (s, 3H), 3.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 155.9, 143.6, 138.1, 130.4, 122.9, 120.4, 119.1, 117.4, 115.2, 106.9, 55.4, 37.9. IR (KBr): 2959, 1668, 1581, 1485, 1243, 825 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{14}H_{15}N_2O_2$ $[M+H]^+$ 243.1134, found 243.1128.



Methyl 2-(dimethylamino)naphtho[2,1-_d_]oxazole-7-carboxylate (4d)

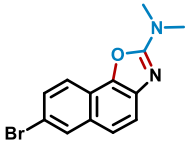
Brown solid (32.7 mg, 61% yield). PE/EA = 1:1, R_f = 0.33. ^1H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.13 (d, *J* = 8.7 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 4.02 (s, 3H), 3.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 163.6, 142.9, 142.5, 132.0, 128.1, 126.1, 125.9, 124.7, 121.3, 118.7, 117.7, 52.1, 37.8. IR (KBr): 2947, 1714,

1644, 1566, 1465, 1428, 1286, 1193, 809, 741 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{15}N_2O_3$ $[M+H]^+$ 271.1083, found 271.1075.



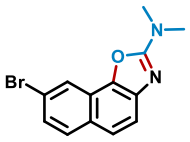
7-Cyclopropyl-*N*,*N*-dimethylnaphtho[2,1-*d*]oxazol-2-amine (4e)

Yellow solid (33.5 mg, 67% yield). PE/EA = 4:1, R_f = 0.24. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.6 Hz, 1H), 7.63–7.55 (m, 3H), 7.29 (d, *J* = 43.1 Hz, 1H), 3.29 (s, 6H), 2.15–2.03 (m, 1H), 1.04 (dd, *J* = 7.9, 5.6 Hz, 2H), 0.83 (d, *J* = 5.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 143.3, 139.1, 138.8, 129.6, 125.4, 124.7, 123.6, 118.7, 118.1, 117.0, 37.9, 15.6, 8.8. IR (KBr): 3075, 2956, 1642, 1553, 1467, 1247, 834 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{16}H_{17}N_2O$ $[M+H]^+$ 253.1341, found 253.1336.



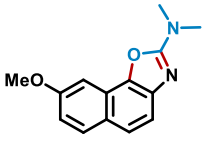
7-Bromo-*N*,*N*-dimethylnaphtho[2,1-*d*]oxazol-2-amine (4f)

Brown solid (34.9 mg, 60% yield). PE/EA = 4:1, R_f = 0.21. ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.93 (d, *J* = 8.7 Hz, 1H), 7.64 (dd, *J* = 10.6, 7.5 Hz, 3H), 3.33 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 143.1, 140.4, 130.6, 130.2, 129.5, 123.5, 120.5, 118.0, 118.0, 116.8, 37.9. IR (KBr): 2925, 1640, 1558, 1426, 1291, 1113, 827 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{13}H_{12}BrN_2O$ $[M+H]^+$ 291.0133, found 291.0125.



8-Bromo-*N*,*N*-dimethylnaphtho[2,1-*d*]oxazol-2-amine (4g)

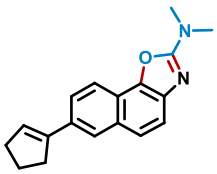
Brown solid (34.4 mg, 59% yield). PE/EA = 4:1, R_f = 0.21. ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 1.9 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.66 (s, 2H), 7.47 (dd, *J* = 8.8, 1.9 Hz, 1H), 3.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 141.5, 138.7, 130.4, 127.8, 127.1, 124.8, 120.9, 120.3, 116.6, 38.0. IR (KBr): 2928, 1645, 1566, 1432, 1298, 1194, 830 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{13}H_{12}BrN_2O$ $[M+H]^+$ 291.0133, found 291.0125.



8-Methoxy-*N*,*N*-dimethylnaphtho[2,1-*d*]oxazol-2-amine (4h)

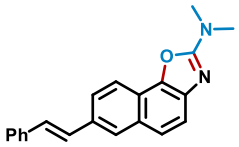
Brown solid (37.5 mg, 78% yield). PE/EA = 4:1, R_f = 0.23. ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.9 Hz, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.27 (s, 1H), 7.05 (d, *J* = 9.1 Hz, 1H), 4.01 (s, 3H), 3.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 158.2, 142.8, 140.4, 130.4, 124.8, 124.1, 120.5, 116.1, 114.3, 97.1, 55.4, 37.9. IR (KBr): 2955, 1662, 1578,

1481, 1240, 819 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{14}H_{15}N_2O_2$ $[M+H]^+$ 243.1134, found 243.1128.



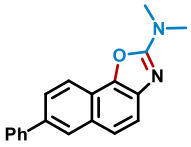
7-(Cyclopent-1-en-1-yl)-*N*,*N*-dimethylnaphtho[2,1-*d*]oxazol-2-amine (4i)

Yellow solid (30.5 mg, 55% yield). PE/EA = 3:1, R_f = 0.32. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.7 Hz, 1H), 7.80 (s, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 6.32 (s, 1H), 3.30 (s, 6H), 2.91–2.82 (m, 2H), 2.67–2.57 (m, 2H), 2.16–2.05 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 143.3, 142.5, 139.9, 131.9, 129.4, 126.0, 125.0, 124.7, 124.5, 118.6, 118.5, 117.0, 37.9, 33.5, 33.2, 23.4. IR (KBr): 2949, 1681, 1561, 1470, 1246, 805 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{19}N_2O$ $[M+H]^+$ 279.1497, found 279.1490.



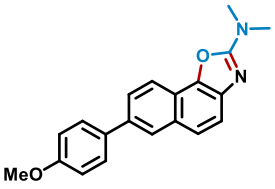
(*E*)-*N*,*N*-Dimethyl-7-styrylnaphtho[2,1-*d*]oxazol-2-amine (4j)

Yellow solid (35.6 mg, 57% yield). PE/EA = 2:1, R_f = 0.30. ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.7 Hz, 1H), 7.94 (s, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.65–7.57 (m, 3H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.30 (dd, *J* = 18.9, 10.0 Hz, 3H), 3.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 143.3, 140.3, 137.6, 132.5, 129.5, 128.9, 128.7, 128.1, 127.5, 126.4, 124.5, 124.1, 119.2, 118.9, 117.3, 37.9. IR (KBr): 2969, 1658, 1541, 1431, 1251, 715 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{21}H_{19}N_2O$ $[M+H]^+$ 315.1497, found 315.1491.



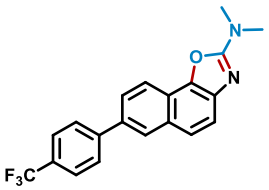
***N*,*N*-Dimethyl-7-phenylnaphtho[2,1-*d*]oxazol-2-amine (4k)**

Brown solid (44.1 mg, 77% yield). PE/EA = 2:1, R_f = 0.29. ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.08 (m, 2H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.79–7.73 (m, 3H), 7.66 (d, *J* = 8.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 3.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 143.1, 141.2, 140.2, 136.1, 129.6, 128.8, 127.2, 127.1, 126.6, 126.0, 124.7, 119.3, 118.7, 117.4, 37.9. IR (KBr): 2963, 1657, 1547, 1434, 1255, 713 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{19}H_{17}N_2O$ $[M+H]^+$ 289.1341, found 289.1333.



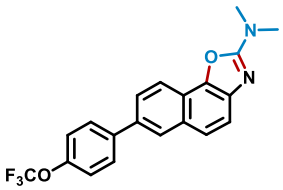
7-(4-Methoxyphenyl)-*N*,*N*-dimethylnaphtho[2,1-*d*]oxazol-2-amine (4l)

Brown solid (47.5 mg, 75% yield). PE/EA = 2:1, R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 11.9 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.76 (dd, *J* = 8.5, 2.8 Hz, 1H), 7.71 (dd, *J* = 8.4, 2.7 Hz, 2H), 7.66 (dd, *J* = 8.6, 2.8 Hz, 1H), 7.08 (dd, *J* = 8.5, 3.1 Hz, 2H), 3.93 (s, 3H), 3.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 159.1, 139.9, 135.7, 133.8, 129.7, 128.3, 125.9, 124.5, 119.2, 118.4, 117.3, 114.3, 55.4, 37.9. IR (KBr): 2959, 1665, 1548, 1430, 1241, 815 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{20}H_{19}N_2O_2$ $[M+H]^+$ 319.1447, found 319.1441.



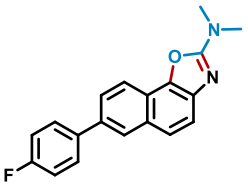
_N_,_N_-Dimethyl-7-(4-(trifluoromethoxy)phenyl)naphtho[2,1-*d*]oxazol-2-amine (4m)

Yellow solid (53.4 mg, 75% yield). PE/EA = 2:1, R_f = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.2 Hz, 2H), 7.87–7.74 (m, 6H), 7.68 (d, *J* = 8.7 Hz, 1H), 3.34 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 144.7, 143.0, 140.6, 134.4, 129.3, 129.1 (q, *J* = 32 Hz), 127.4, 127.2, 125.8 (q, *J* = 4 Hz), 125.6, 124.9, 124.4 (q, *J* = 270 Hz), 119.6, 119.0, 117.7, 37.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.4. IR (KBr): 2966, 1738, 1543, 1423, 1252, 1162, 1070 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{20}H_{16}F_3N_2O$ $[M+H]^+$ 357.1215, found 357.1208.



_N_,_N_-Dimethyl-7-(4-(trifluoromethoxy)phenyl)naphtho[2,1-*d*]oxazol-2-amine (4n)

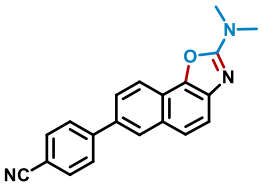
Yellow solid (56.3 mg, 76% yield). PE/EA = 2:1, R_f = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15–8.07 (m, 2H), 7.77 (dd, *J* = 9.5, 7.1 Hz, 4H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 3.34 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 148.6, 143.1, 140.5, 140.0, 134.6, 129.5, 128.5, 126.7, 125.7, 125.6 (q, *J* = 281 Hz), 121.2, 119.4, 119.3, 118.9, 117.6, 37.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ -57.8. IR (KBr): 2961, 1766, 1542, 1437, 1256, 1165, 1066 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{20}H_{16}F_3N_2O_2$ $[M+H]^+$ 373.1164, found 373.1159.



7-(4-Fluorophenyl)-_N_,_N_-dimethylnaphtho[2,1-*d*]oxazol-2-amine (4o)

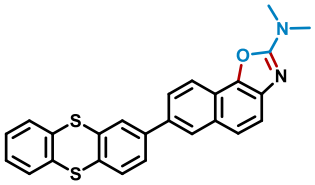
Brown solid (42.6 mg, 70% yield). PE/EA = 2:1, R_f = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.6 Hz, 1H), 8.07 (s, 1H), 7.79–7.65 (m, 5H), 7.21 (t, *J* = 8.6 Hz, 2H), 3.34 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.4 (d, *J* = 244 Hz), 143.1, 140.2, 137.4 (d, *J* = 3 Hz), 135.1, 129.5, 128.7 (d, *J* = 8 Hz), 126.4, 125.8, 124.6, 119.3, 118.7, 117.5, 115.6 (d, *J* = 21 Hz),

37.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ -116.0. IR (KBr): 2979, 1731, 1546, 1421, 1242, 1164, 1067 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{19}H_{16}FN_2O$ $[M+H]^+$ 307.1247, found 307.1241.



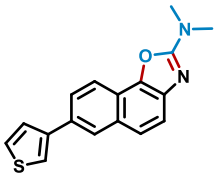
4-(2-(Dimethylamino)naphtho[2,1-*d*]oxazol-7-yl)benzonitrile (4p)

Brown solid (37.3 mg, 60% yield). PE/EA = 2:1, R_f = 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (t, *J* = 4.2 Hz, 2H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.82–7.76 (m, 4H), 7.68 (d, *J* = 8.6 Hz, 1H), 3.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 145.7, 143.0, 141.0, 133.8, 132.6, 129.3, 127.7, 127.4, 125.3, 125.0, 119.8, 119.2, 119.0, 117.9, 110.7, 37.9. IR (KBr): 2923, 2224, 1644, 1564, 1505, 1427, 1294, 1193, 900, 814 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{20}H_{16}N_3O$ $[M+H]^+$ 314.1293, found 314.1285.



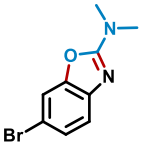
***N*,*N*-Dimethyl-7-(thianthren-2-yl)naphtho[2,1-*d*]oxazol-2-amine (4q)**

Yellow solid (51.0 mg, 60% yield). PE/EA = 2:1, R_f = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.5 Hz, 1H), 7.94 (s, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.43–7.32 (m, 3H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.20 (dd, *J* = 8.3, 6.7 Hz, 1H), 3.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.24, 143.23, 142.55, 140.53, 136.37, 136.02, 135.50, 135.30, 135.18, 129.44, 129.22, 128.93, 128.79, 128.47, 128.13, 128.00, 127.70, 127.49, 127.07, 124.69, 118.92, 118.48, 117.48, 37.89. IR (KBr): 3054, 1643, 1562, 1433, 1292, 1025, 901, 746 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{25}H_{19}N_2OS_2$ $[M+H]^+$ 427.0939, found 427.0930.



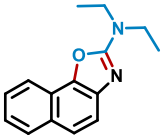
***N*,*N*-Dimethyl-7-(thiophen-3-yl)naphtho[2,1-*d*]oxazol-2-amine (4r)**

Yellow solid (38.6 mg, 66% yield). PE/EA = 4:1, R_f = 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.57 (d, *J* = 9.1 Hz, 2H), 7.48 (s, 1H), 3.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 143.2, 142.4, 140.1, 130.8, 129.5, 126.4, 126.3, 125.7, 125.5, 124.5, 120.0, 119.3, 118.6, 117.4, 37.9. IR (KBr): 2925, 1649, 1567, 1401, 1297, 818, 775 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{15}N_2OS$ $[M+H]^+$ 295.0905, found 295.0900.



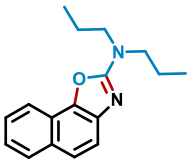
6-Bromo-*N*,*N*-dimethylbenzo[*d*]oxazol-2-amine[7] (4s)

Brown solid (11.6 mg, 24% yield). PE/EA = 5:1, R_f = 0.29. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.32 (d, *J* = 4.6 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 3.25 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 149.6, 143.0, 127.0, 116.9, 112.2, 112.1, 77.3, 77.0, 76.7, 37.7.



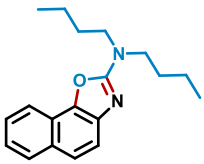
***N*,*N*-Diethylnaphtho[2,1-*d*]oxazol-2-amine (4a')**

Brown oil (39.6 mg, 83% yield). PE/EA = 5:1, R_f = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.55 (t, *J* = 8.1 Hz, 1H), 7.38 (t, *J* = 8.3 Hz, 1H), 3.71 (d, *J* = 6.8 Hz, 4H), 1.39 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 142.8, 139.9, 129.1, 128.7, 126.3, 124.2, 123.2, 119.6, 118.7, 116.8, 43.1, 13.5. IR (KBr): 2943, 1687, 1537, 1449, 1214, 736 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{17}N_2O$ $[M+H]^+$ 241.1341, found 241.1337.



***N*,*N*-Dipropylnaphtho[2,1-*d*]oxazol-2-amine (4b')**

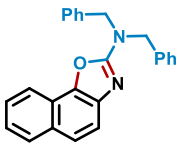
Brown oil (40.5 mg, 76% yield). PE/EA = 5:1, R_f = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 3.62 (t, *J* = 7.5 Hz, 4H), 1.84 (h, *J* = 7.5 Hz, 4H), 1.07 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 142.7, 140.0, 129.1, 128.6, 126.2, 124.1, 123.1, 119.7, 118.6, 116.9, 50.5, 21.3, 11.3. IR (KBr): 2963, 1677, 1549, 1439, 1224, 729 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{21}N_2O$ $[M+H]^+$ 269.1654, found 269.1645.



***N*,*N*-Dibutylnaphtho[2,1-*d*]oxazol-2-amine (4c')**

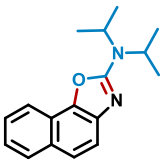
Brown oil (43.0 mg, 73% yield). PE/EA = 5:1, R_f = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 3.65 (t, *J* = 7.4 Hz, 4H), 1.86–1.72 (m, 4H), 1.56–1.42 (m, 4H), 1.05 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 142.7, 140.1, 129.1, 128.6, 126.2, 124.1, 123.1, 119.7, 118.6, 116.9, 48.5, 30.2, 20.1, 13.9. IR (KBr): 2958,

1628, 1564, 1454, 1373, 1290, 1051, 901, 809, 738 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{19}H_{25}N_2O$ $[M+H]^+$ 297.1967, found 297.1961.



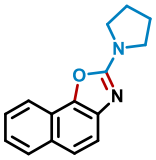
_N_,_N_-Dibenzylnaphtho[2,1-_d_]oxazol-2-amine (4d')

Yellow solid (52.9 mg, 73% yield). PE/EA = 4:1, R_f = 0.31. ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.60–7.53 (m, 1H), 7.45–7.34 (m, 10H), 4.85 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 143.0, 139.8, 136.5, 129.5, 128.7, 128.7, 128.1, 127.7, 126.4, 124.4, 123.5, 119.8, 118.7, 117.1, 50.7. IR (KBr): 2948, 1673, 1559, 1440, 1221, 1028, 737, 687 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{25}H_{21}N_2O$ $[M+H]^+$ 365.1654, found 365.1648.



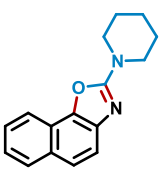
_N_,_N_-Diisopropylnaphtho[2,1-_d_]oxazol-2-amine (4e')

Brown oil (41.0 mg, 77% yield). PE/EA = 5:1, R_f = 0.25. ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 4.39–4.30 (m, 2H), 1.50 (d, *J* = 8.4 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 142.6, 139.4, 129.1, 128.6, 126.2, 124.0, 123.0, 119.6, 118.7, 116.8, 47.8, 20.9. IR (KBr): 2941, 1674, 1540, 1453, 1367, 1233, 1037, 758 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{21}N_2O$ $[M+H]^+$ 269.1654, found 269.1645.4.



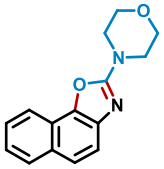
2-(Pyrrolidin-1-yl)naphtho[2,1-_d_]oxazole (4f')

Yellow solid (35.4 mg, 75% yield). PE/EA = 5:1, R_f = 0.24. ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 3.77 (t, *J* = 6.3 Hz, 4H), 2.17–2.07 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 143.1, 140.0, 129.2, 128.6, 126.2, 124.2, 123.2, 119.7, 118.7, 117.0, 47.5, 25.6. IR (KBr): 2951, 1684, 1551, 1461, 1223, 1047, 754 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{15}N_2O$ $[M+H]^+$ 239.1184, found 239.1179.



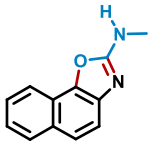
2-(Piperidin-1-yl)naphtho[2,1-*d*]oxazole (4g')

Yellow solid (39.1 mg, 78% yield). PE/EA = 5:1, R_f = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 3.77 (s, 4H), 1.76 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 142.8, 139.7, 129.4, 128.6, 126.3, 124.2, 123.3, 119.7, 118.7, 116.9, 46.8, 25.3, 24.1. IR (KBr): 2946, 1663, 1554, 1447, 1362, 1236, 1035, 768 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{16}H_{17}N_2O$ $[M+H]^+$ 253.1341, found 253.1336.



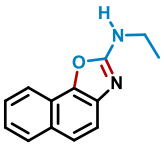
2-Morpholinonaphtho[2,1-*d*]oxazole[8] (4h')

Brown solid (37.8 mg, 75% yield). PE/EA = 5:1, R_f = 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.68–7.61 (m, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 3.92 (t, *J* = 4.8 Hz, 4H), 3.81 (t, *J* = 4.9 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 143.0, 139.1, 129.6, 128.6, 126.4, 124.5, 123.6, 119.7, 118.6, 117.0, 66.2, 45.9.



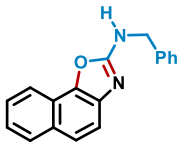
***N*-Methylnaphtho[2,1-*d*]oxazol-2-amine (4i')**

Yellow solid (29.4 mg, 75% yield). PE/EA = 5:1, R_f = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.63 (d, *J* = 8.7 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 5.11 (s, 1H), 3.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 142.9, 139.3, 129.7, 128.6, 126.4, 124.3, 123.6, 119.7, 118.7, 117.0, 29.7. IR (KBr): 2967, 1648, 1641, 1567, 1415, 1291, 1154, 801, 726 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{12}H_{11}N_2O$ $[M+H]^+$ 199.0871, found 199.0864.



***N*-Ethylnaphtho[2,1-*d*]oxazol-2-amine (4j')**

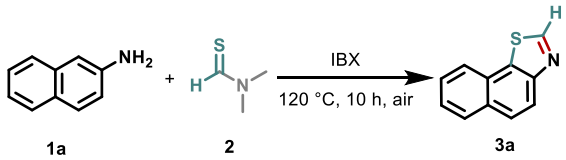
Yellow solid (34.1 mg, 81% yield). PE/EA = 5:1, R_f = 0.29. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 5.07 (s, 1H), 3.74–3.58 (m, 2H), 1.42 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 142.7, 139.4, 129.6, 128.6, 126.3, 124.3, 123.5, 119.7, 118.7, 117.1, 38.3, 15.2. IR (KBr): 2987, 1676, 1623, 1536, 1429, 1284, 1169, 806 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{13}H_{13}N_2O$ $[M+H]^+$ 213.1028, found 213.1023.



_N_-Benzylnaphtho[2,1-_d_]oxazol-2-amine (4k')

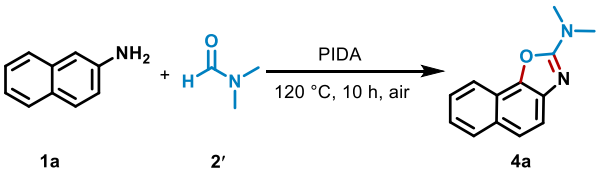
Yellow solid (40.3 mg, 74% yield). PE/EA = 5:1, R_f = 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 8.3 Hz, 1H), 7.73 (d, J = 8.6 Hz, 1H), 7.63 (d, J = 8.6 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 7.2 Hz, 2H), 7.46–7.40 (m, 3H), 7.37 (t, J = 7.2 Hz, 1H), 5.46 (s, 1H), 4.80 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 142.9, 139.2, 137.8, 129.7, 128.9, 128.7, 127.9, 127.7, 126.4, 124.4, 123.7, 119.8, 118.8, 117.1, 47.5. IR (KBr): 1697, 1666, 1588, 1454, 1231, 1021, 737, 687 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{15}N_2O$ $[M+H]^+$ 275.1184, found 275.1179.

E. Large-scale transformation and further derivatization



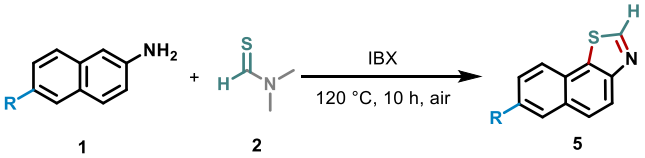
1a 2 3a

A pressure tube (capacity: 75.0 mL, outside diameter: 46.0 mm, length: 90.0 mm) was charged with naphthalen-2-amine **1a** (5.0 mmol), *N*,*N*-dimethylmethanethioamide **2** (5.0 equiv), and IBX (1.5 equiv). The reaction mixture was stirred at 120 °C for 10 h under air in an oil bath. After cooling to room temperature, the mixture was filtered through a short Celite pad and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography using PE/EA eluent to afford the product **3a** (602.1 mg, 65% yield).



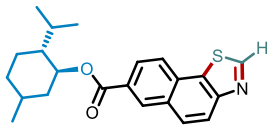
1a 2′ 4a

A pressure tube (capacity: 75.0 mL, outside diameter: 46.0 mm, length: 90.0 mm) was charged with naphthalen-2-amine **1a** (5.0 mmol), *N*,*N*-dimethylformamide **2'** (25.5 equiv), and PIDA (1.5 equiv). The reaction mixture was stirred at 120 °C for 10 h under air in an oil bath. After cooling to room temperature, a saturated aqueous solution (45 mL) of $NaHCO_3$ was added, followed by an extraction with DCM (10 mL × 3). The combined organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography using PE/EA eluent to afford the product **4a** (805.6 mg, 76% yield).



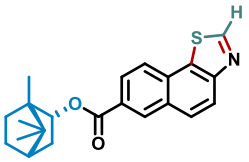
1 2 5

A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with naphthylamine derivatives **1** (0.2 mmol), *N*,*N*-dimethylmethanethioamide **2** (5.0 equiv), and IBX (1.5 equiv). The reaction mixture was stirred at 120 °C for 10 h under air in an oil bath. After cooling to room temperature, the mixture was filtered through a short Celite pad and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography using PE/EA eluent to afford the product **5**.



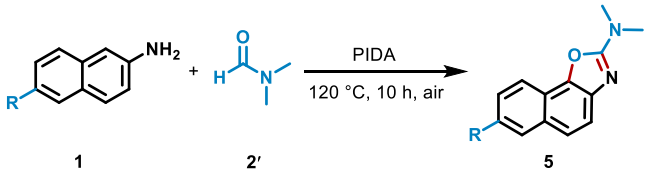
(1S,2S)-2-Isopropyl-5-methylcyclohexyl naphtho[2,1-*d*]thiazole-7-carboxylate (5a)

Yellow solid (52.2 mg, 71% yield). PE/EA = 5:1, R_f = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.76 (s, 1H), 8.25 (t, *J* = 8.3 Hz, 2H), 8.08 (dd, *J* = 29.9, 8.7 Hz, 2H), 5.12‑5.01 (m, 1H), 2.23 (d, *J* = 11.7 Hz, 1H), 2.06 (t, *J* = 7.4 Hz, 1H), 1.79 (d, *J* = 12.1 Hz, 2H), 1.72‑1.58 (m, 2H), 1.28‑1.14 (m, 2H), 0.99 (d, *J* = 6.8 Hz, 7H), 0.87 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 153.9, 152.9, 131.6, 131.2, 130.5, 130.5, 128.5, 128.4, 126.9, 125.4, 122.7, 47.3, 41.1, 34.3, 31.5, 26.6, 23.7, 22.1, 20.8, 16.6. IR (KBr): 2951, 1707, 1643, 1566, 1463, 1430, 1358, 1282, 1191, 1099, 974, 906, 809 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{24}H_{31}N_2O_3$ $[M+H]^+$ 395.2335, found 395.2328.



(1R,2R,4R)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl naphtho[2,1-*d*]thiazole-7-carboxylate (5b)

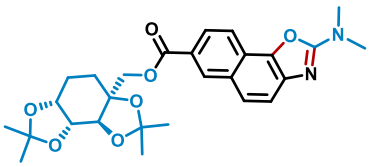
Yellow solid (50.4 mg, 69% yield). PE/EA = 10:1, R_f = 0.29. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.80 (s, 1H), 8.35–8.25 (m, 2H), 8.13 (dd, *J* = 26.8, 9.3 Hz, 2H), 5.29 (d, *J* = 9.8 Hz, 1H), 2.69–2.52 (m, 1H), 2.37–2.22 (m, 1H), 1.86 (s, 1H), 1.71 (s, 1H), 1.60–1.39 (m, 2H), 1.27 (d, *J* = 14.8 Hz, 1H), 1.10–0.99 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 153.8, 153.0, 131.5, 131.2, 130.5, 128.6, 128.4, 126.9, 125.4, 122.7, 81.0, 49.2, 48.0, 45.1, 37.0, 28.2, 27.5, 19.8, 18.9, 13.7. IR (KBr): 2954, 1721, 1463, 1380, 1283, 1190, 1101, 980, 838, 748 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{22}H_{23}NO_2S$ $[M+H]^+$ 366.1528, found 366.1519.



1 2′ 5

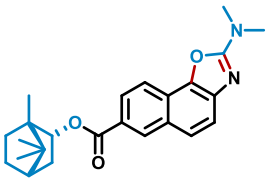
A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with naphthylamine derivatives **1** (0.2 mmol), *N*,*N*-dimethylformamide **2'** (25.5 equiv), and PIDA (1.5 equiv). The reaction mixture was stirred at 120 °C for 10 h under air in an oil bath. After cooling to room temperature, a saturated aqueous solution (15 mL) of $NaHCO_3$ was added, followed by an extraction with DCM (10 mL × 3). The combined organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel

chromatography using PE/EA eluent to afford the product **5**.



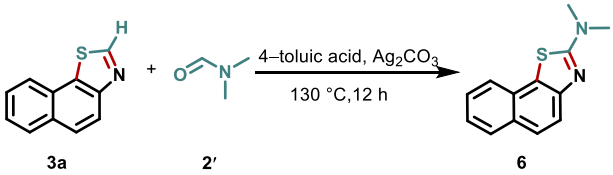
((3aS,5aR,8aR,8bS)-2,2,7,7-Tetramethyltetrahydrobenzo[1,2-*d*:3,4-*d*']bis([1,3]dioxole)-3a(4H)-yl)methyl 2-(dimethylamino)naphtho[2,1-d]oxazole-7-carboxylate (5c)

Yellow solid (76.5 mg, 77% yield). PE/EA = 2:1, R_f = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.18 (d, *J* = 8.8 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 8.7 Hz, 1H), 4.78 (d, *J* = 11.8 Hz, 1H), 4.71 (d, *J* = 8.0 Hz, 1H), 4.58 (s, 1H), 4.45 (d, *J* = 11.8 Hz, 1H), 4.31 (d, *J* = 8.2 Hz, 1H), 4.02 (d, *J* = 13.0 Hz, 1H), 3.86 (d, *J* = 13.0 Hz, 1H), 3.34 (s, 6H), 1.60 (s, 3H), 1.54–1.39 (m, 11H).^{13}C NMR (151 MHz, $CDCl_3$) δ 166.2, 163.6, 142.8, 132.4, 128.0, 126.2, 126.1, 124.4, 121.4, 118.8, 117.8, 109.2, 108.9, 101.8, 70.8, 70.6, 70.2, 65.3, 61.4, 37.9, 26.6, 25.9, 25.6, 24.1. IR (KBr): 2926, 1720, 1645, 1565, 1463, 1379, 1252, 1197, 1071, 898, 750 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{27}H_{33}N_2O_7$ $[M+H]^+$ 497.2288, found 497.2281.



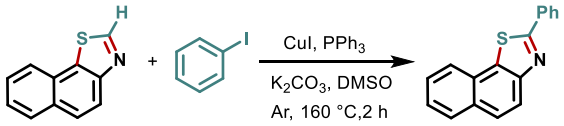
(1R,2R,4R)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 2-(dimethylamino)naphtho[2,1-*d*]oxazole-7-carboxylate (5d)

Yellow solid (58.9 mg, 75% yield). PE/EA = 3:1, R_f = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.17 (d, *J* = 8.8 Hz, 1H), 8.05 (d, *J* = 8.7 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 5.24 (d, *J* = 9.9 Hz, 1H), 3.33 (s, 6H), 2.57 (t, *J* = 12.3 Hz, 1H), 2.34–2.22 (m, 1H), 1.89 (s, 1H), 1.51 (t, *J* = 14.0 Hz, 1H), 1.42 (t, *J* = 12.9 Hz, 1H), 1.34–1.17 (m, 2H), 1.06–0.96 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 163.6, 142.9, 142.4, 131.8, 128.1, 126.1, 126.0, 125.5, 121.3, 118.7, 117.7, 80.5, 49.2, 47.9, 45.1, 37.8, 37.0, 28.2, 27.5, 19.7, 18.9, 13.7. IR (KBr): 2951, 1709, 1644, 1566, 1464, 1379, 1286, 1191, 1103, 982, 904, 810 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{24}H_{29}N_2O_3$ $[M+H]^+$ 393.2178, found 383.2170.



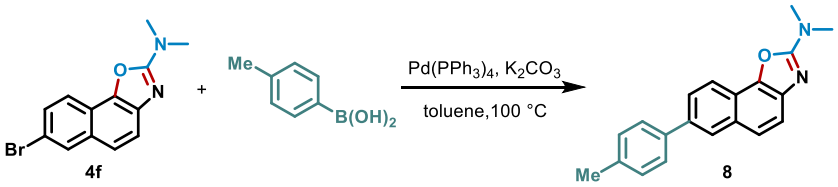
3a **2′** **6**

A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with **3a** (0.2 mmol), *N*,*N*-dimethylformamide **2'** (2.0 mL), 4-toluic acid (5.0 equiv) and Ag_2CO_3 (2.0 equiv). The reaction mixture was stirred at 130 °C for 12 h under air in an oil bath. After cooling to room temperature, the reaction mixture was diluted with 30 mL aqueous saturated $NaHCO_3$ and extracted with DCM (10 mL × 3). The combined organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography using PE/EA eluent to afford the product **6**[9](19.6 mg, 43% yield).



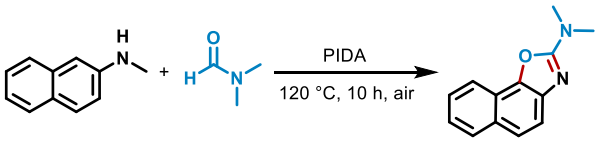
3a 7

A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with naphtho[2,1-*d*]thiazole **3a** (0.2 mmol),PhI (1.0 equiv), CuI (1.0 equiv), PPh_3 (0.2 equiv), and K_2CO_3 (2.0 equiv) was dissolved in 0.6 mL DMSO under Ar condition. The reaction mixture was stirred at 160 °C for 2 h under air in an oil bath. After cooling to room temperature, a saturated aqueous solution (15 mL) of $NaHCO_3$ was added, followed by an extraction with DCM (10 mL × 3). The combined organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography using PE/EA eluent to afford the product **7**[10]. Yellow solid (33.5 mg, 64% yield). PE/EA = 20:1, R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 16.8, 7.6 Hz, 3H), 8.09 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 8.9 Hz, 1H), 7.69–7.50 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 152.3, 133.7, 132.3, 131.1, 130.8, 129.1, 129.0, 128.1, 127.5, 127.4, 127.1, 126.1, 125.2, 121.8.



4f 8

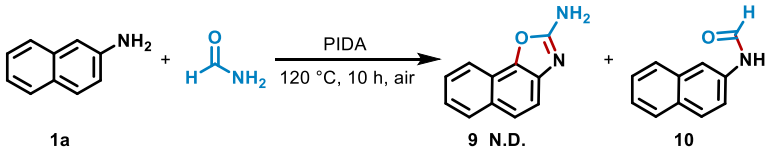
A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with **4f** (0.2mmol), *p*-tolylboronic acid (1.2 equiv), $Pd(PPh_3)_4$ (4 mmol%) and K_2CO_3 (2.0 equiv) was dissolved in 0.6 mL toluene under Ar condition. The reaction mixture was stirred at 100 °C for 12 h under air in an oil bath. After cooling to room temperature, the mixture was filtered through a short Celite pad and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography using PE/EA eluent to afford the product **8**. Brown solid (53.8 mg, 89% yield). PE/EA = 5:1, R_f = 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 9.1 Hz, 2H), 7.82 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.66 (dd, *J* = 8.3, 3.4 Hz, 3H), 7.33 (d, *J* = 7.9 Hz, 2H), 3.32 (s, 6H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 143.2, 140.0, 138.3, 136.9, 136.1, 129.7, 129.6, 127.1, 126.3, 126.0, 124.7, 119.2, 118.7, 117.3, 37.9, 21.1. IR (KBr): 2988, 1661, 1587, 1402, 1272, 831 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{20}H_{19}N_2O$ $[M+H]^+$ 303.1497, found 303.1490.



1′ 2′ 4a

A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with *N*-methylnaphthalen-2-amine **1'** (0.2 mmol), *N*,*N*-dimethylformamide **2'** (25.5 equiv), and PIDA (1.5 equiv). The reaction mixture was stirred at 120 °C for 10 h under air in an oil bath. After cooling to room temperature, a saturated aqueous solution (15 mL) of $NaHCO_3$ was added, followed by an extraction with DCM (10 mL × 3). The combined organic phase was dried over

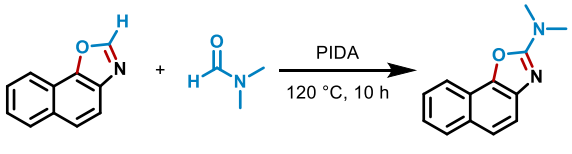
$MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography using PE/EA eluent to afford the product **4a** (22.5 mg ,53% yield).



1a 9 N.D. 10

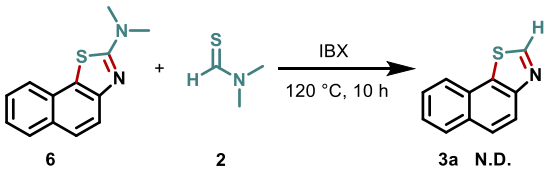
A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with naphthalen-2-amine **1** (0.2 mmol), formamide (25.5 equiv), and PIDA (1.5 equiv). The reaction mixture was stirred at 120 °C for 10 h under air in an oil bath. After cooling to room temperature, a saturated aqueous solution (15 mL) of $NaHCO_3$ was added, followed by an extraction with DCM (10 mL × 3). The combined organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography using PE/EA eluent to afford the product **10**[11]. Yellow oil (26.7 mg, 78% yield). PE/EA = 2:1, R_f = 0.29. ^{1}H NMR (400 MHz, DMSO) δ 10.37 (s, 1H), 8.42 (s, 1H), 8.32 (s, 1H), 7.95–7.83 (m, 3H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 160.3, 136.3, 133.9, 130.4, 129.0, 127.9, 127.7, 127.0, 125.2, 120.2, 116.0.

F. Mechanistic study



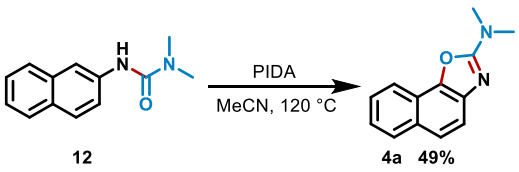
11 2′ 4a N.D.

A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with naphtho[2,1-*d*]oxazole **11** (0.2 mmol), *N*,*N*-dimethylformamide **2'** (25.5 equiv) and PIDA (1.5 equiv). The reaction mixture was stirred at 120 °C for 10 h under air in an oil bath. After cooling to room temperature, a saturated aqueous solution (15 mL) of $NaHCO_3$ was added, followed by an extraction with DCM (10 mL × 3). The combined organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield the crude product, which was further detected by NMR spectroscopy and showed no desired product **4a**.



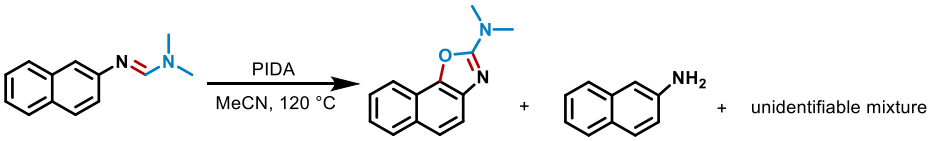
6 2 3a N.D.

A pressure tube (capacity: 75.0 mL, outside diameter: 46.0 mm, length: 90.0 mm) was charged with *N*,*N*-dimethylnaphtho[2,1-*d*]thiazol-2-amine **6** (5.0 mmol), *N*,*N*-dimethylmethaneth-ioamide **2** (5.0 equiv), and IBX (1.5 equiv). The reaction mixture was stirred at 120 °C for 10 h under air in an oil bath. After cooling to room temperature, filtered and concentrated under reduced pressure to yield the crude product, which was further detected by NMR spectroscopy and showed no desired product **3a**.



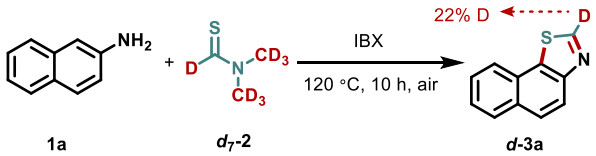
12 4a 49%

A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with 1,1-dimethyl-3-(naphthalen-2-yl)urea **12** (0.2 mmol), and PIDA (1.5 equiv) was dissolved in 0.8 mL MeCN. The reaction mixture was stirred at 120 °C for 10 h under air in an oil bath. After cooling to room temperature, a saturated aqueous solution (15 mL) of $NaHCO_3$ was added, followed by an extraction with DCM (10 mL × 3). The combined organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield the crude product, which was further purified by silica gel chromatography to afford the product **4a** (20.8 mg, 49% yield).



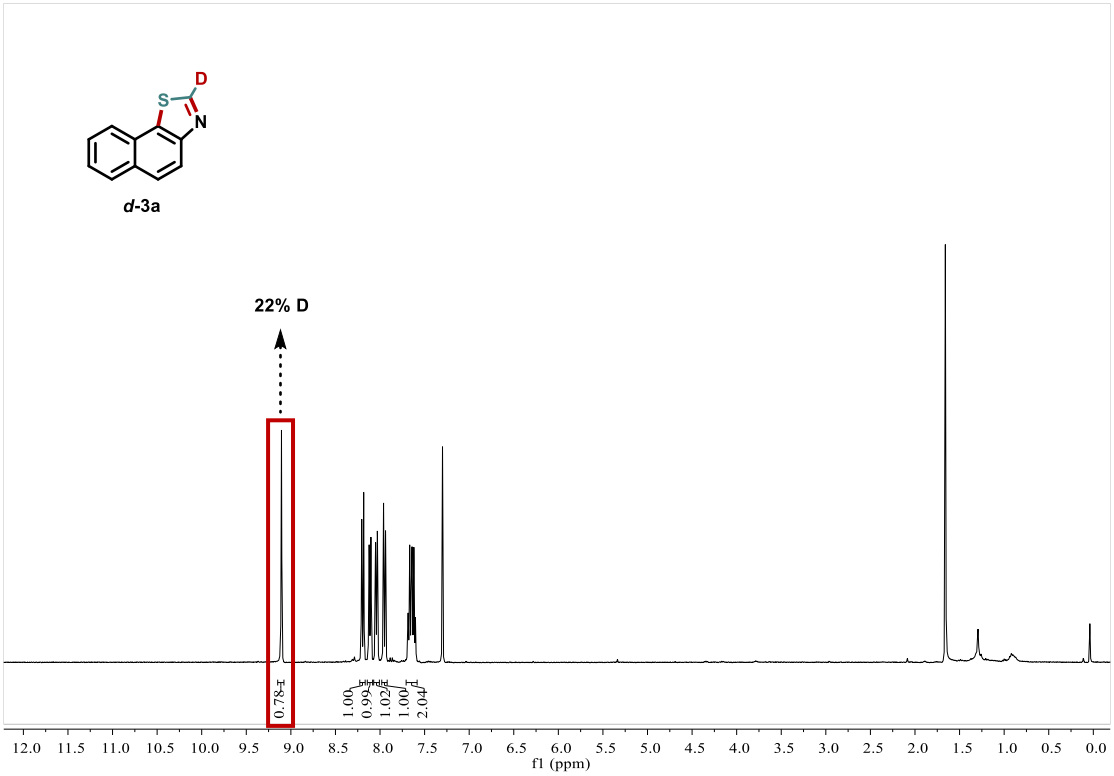
13 4a trace 1a

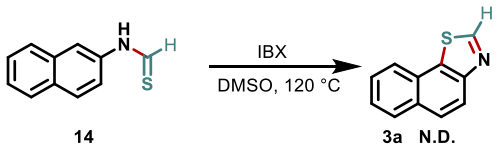
A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with 1,1-dimethyl-3-(naphthalen-2-yl)urea **12** (0.2 mmol), and PIDA (1.5 equiv) was dissolved in 0.8 mL MeCN. The reaction mixture was stirred at 120 °C for 10 h under air in an oil bath. After cooling to room temperature, a saturated aqueous solution (15 mL) of $NaHCO_3$ was added, followed by an extraction with DCM (10 mL × 3). The combined organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield the crude product, which was further detected by NMR spectroscopy and showed trace amount of product **4a** and 2-naphthylamine, accompanied with some unidentifiable mixture.



1a d_7-2 *d*-3a

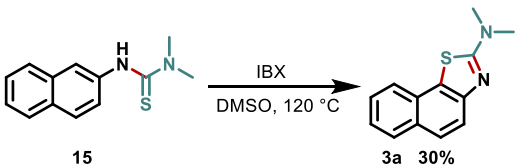
A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with naphthalen-2-amine **1a** (0.2 mmol), ***d*$_7$-2** (5.0 equiv) and IBX (1.5 equiv). The reaction mixture was stirred at 120 °C for 10 h under air in an oil bath. After cooling to room temperature, all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography using PE/EA eluent to afford the products ***d*-3a** (22% yield).





14 3a N.D.

A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with *N*-(naphthalen-2-yl)methanethioamide **14** (0.2 mmol), and IBX (1.5 equiv) was dissolved in 0.8 mL DMSO. The reaction mixture was stirred at 120 °C for 10 h under air in an oil bath. After cooling to room temperature, a saturated aqueous solution (15 mL) of $NaHCO_3$ was added, followed by an extraction with DCM (10 mL × 3). The combined organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield the crude product, which was further detected by NMR spectroscopy and showed no desired product **3a**.



15 3a 30%

A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with 1,1-dimethyl-3-(naphthalen-2-yl)thiourea **15** (0.2 mmol), and IBX (1.5 equiv) was dissolved in 0.8 mL DMSO. The reaction mixture was stirred at 120 °C for 10 h under air in an oil bath. After cooling to room temperature, a saturated aqueous solution (15 mL) of $NaHCO_3$ was added, followed by an extraction with DCM (10 mL × 3). The combined organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield the crude product, which was further detected by NMR spectroscopy and showed no desired product **3a** (13.7 mg, 30% yield).

G. References

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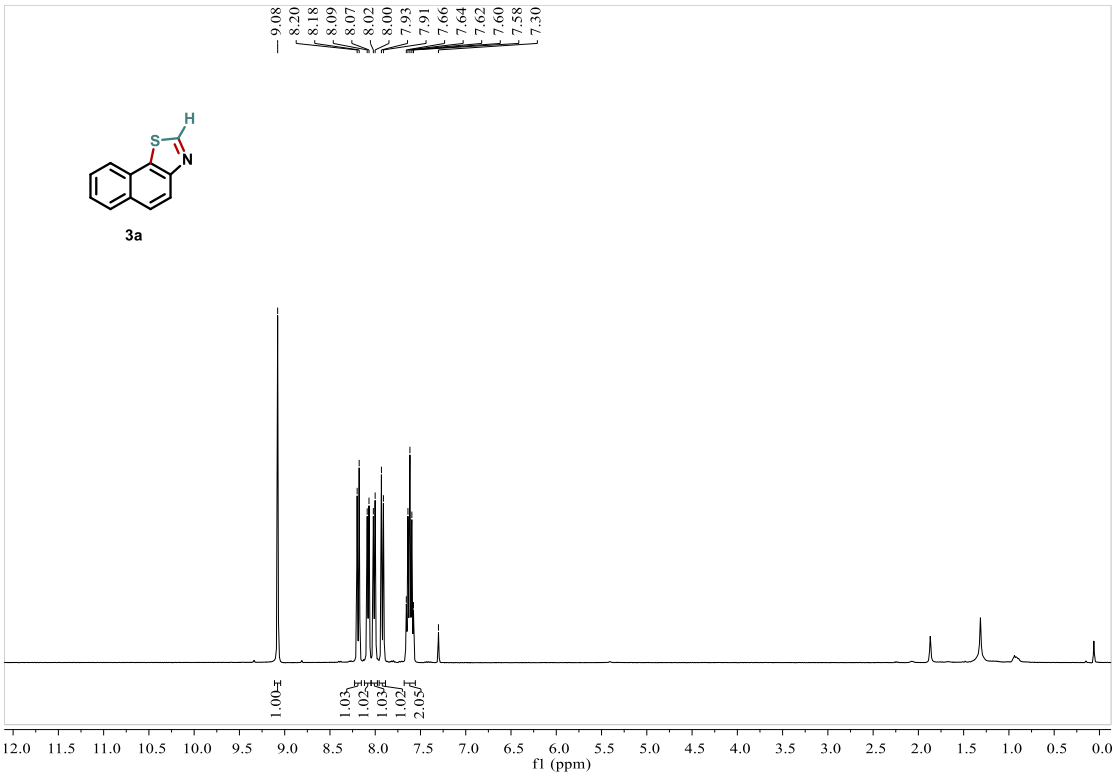
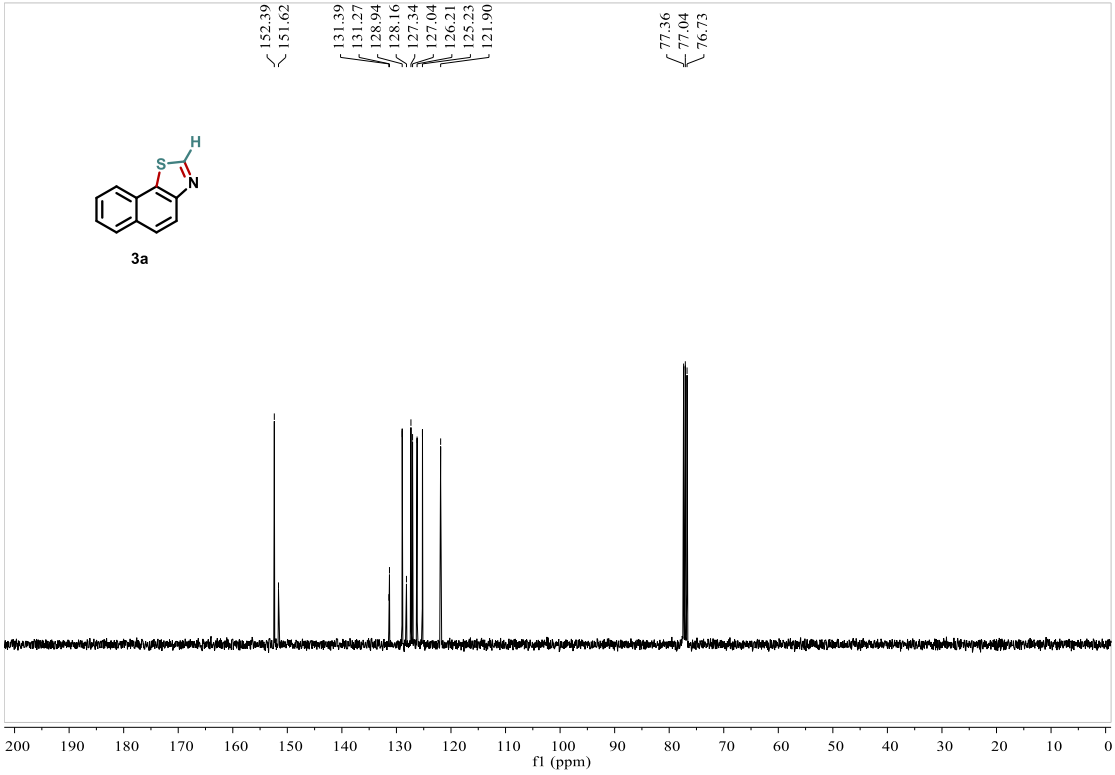
11) J. W. Yin, J. Y. Zhang, C. Q. Cai, G.-J. Deng, H. Gong, *Org. Lett.* **2019**, 21, 387-392.

H. NMR spectra

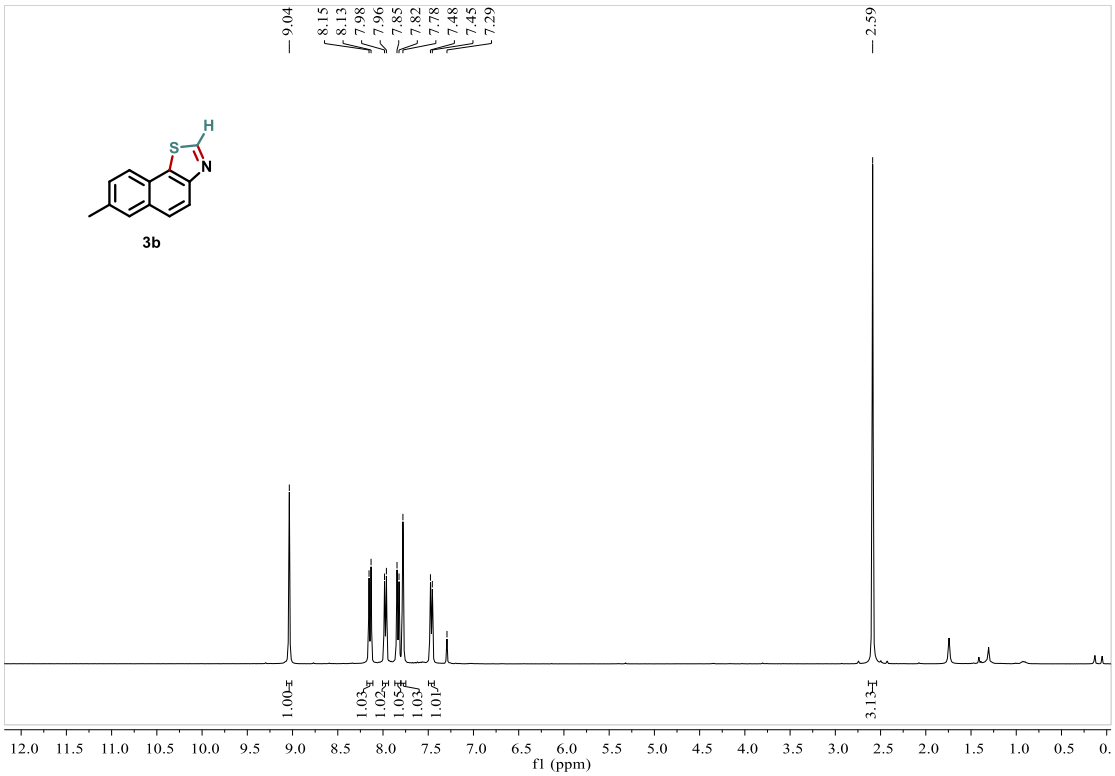
^{1}H NMR of **3a** (400 MHz, $CDCl_3$)



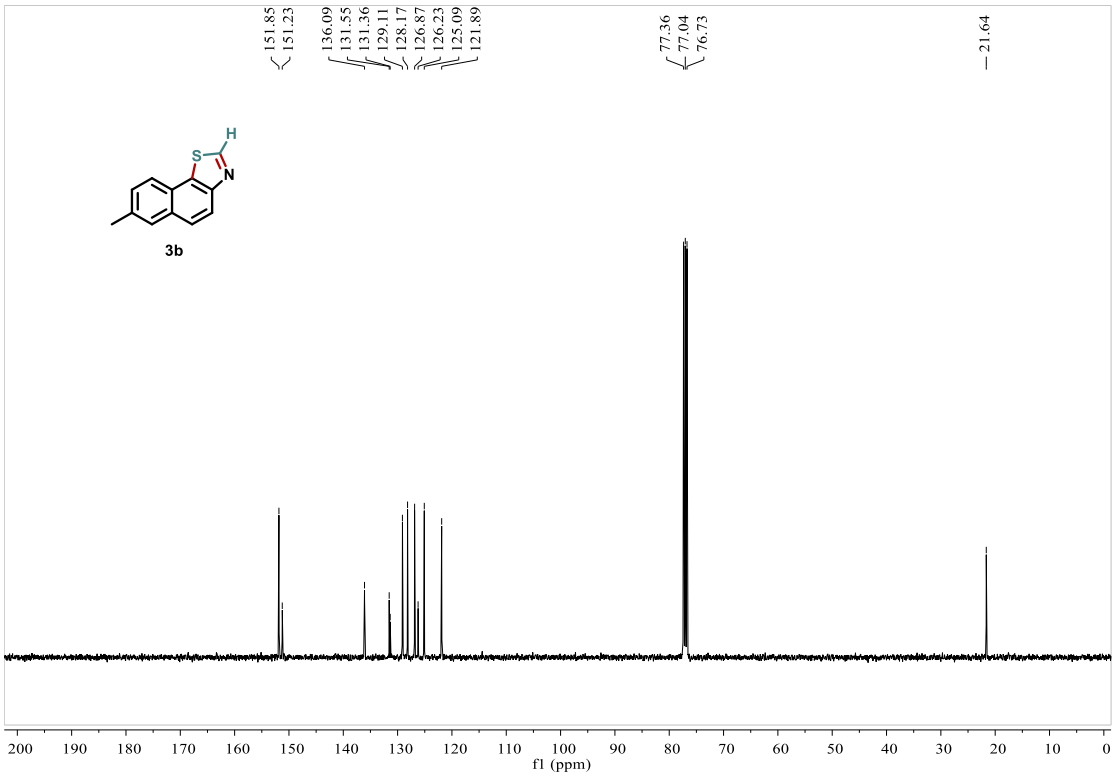
^{13}C NMR of **3a** (100 MHz, $CDCl_3$)



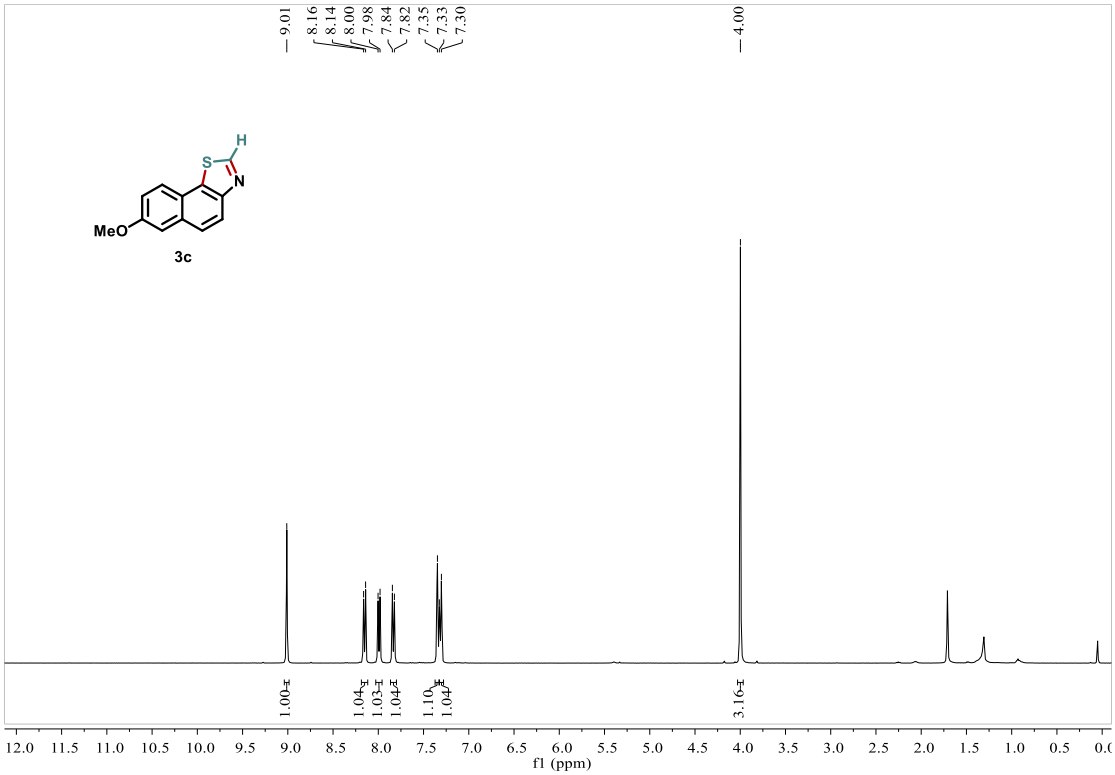
^{1}H NMR of **3b** (400 MHz, $CDCl_3$)



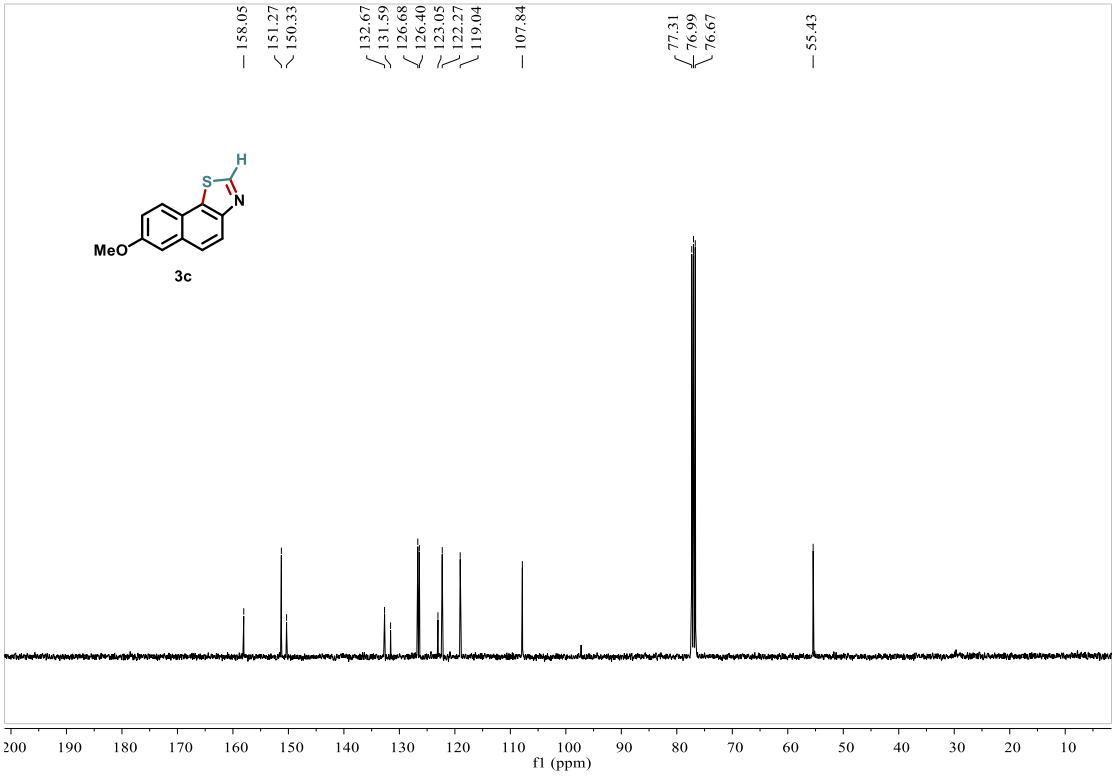
^{13}C NMR of **3b** (100 MHz, $CDCl_3$)



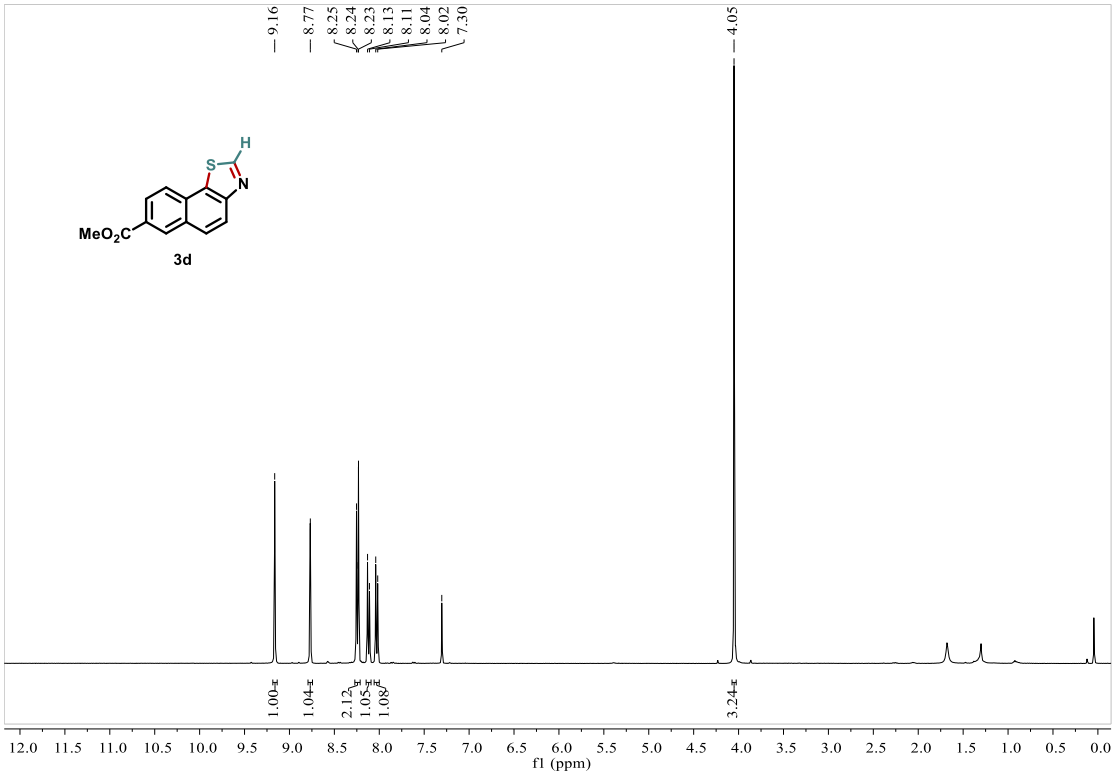
^{1}H NMR of **3c** (400 MHz, $CDCl_3$)



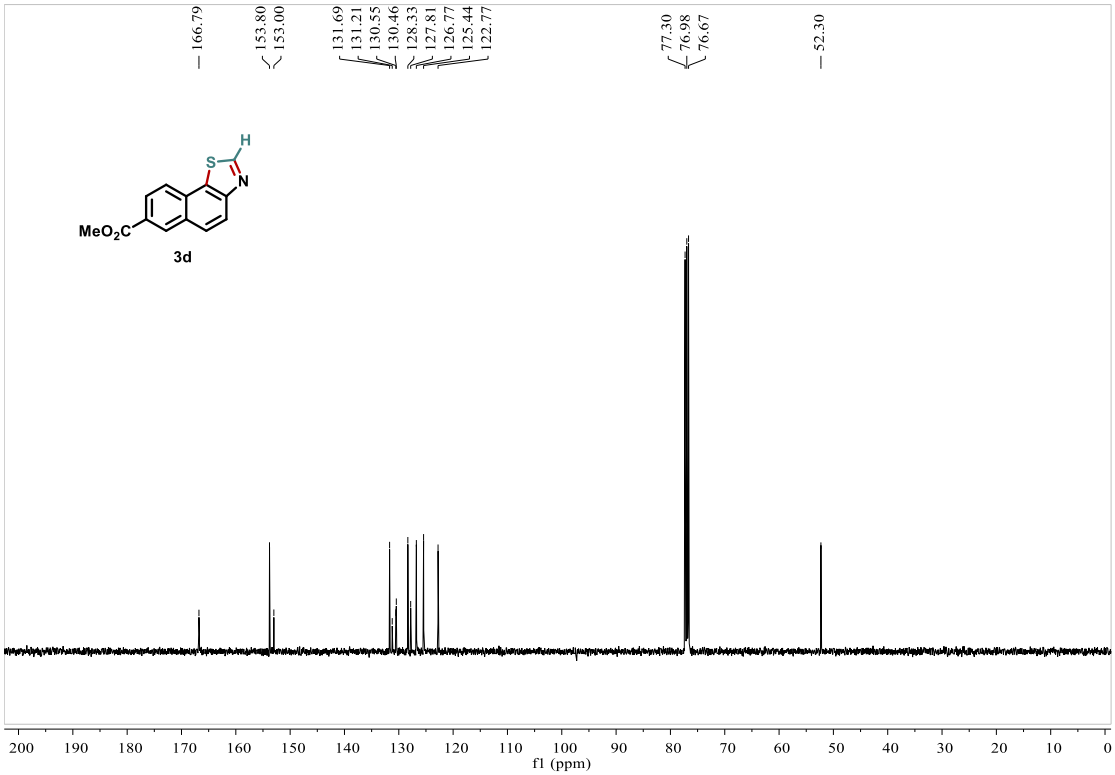
^{13}C NMR of **3c** (100 MHz, $CDCl_3$)



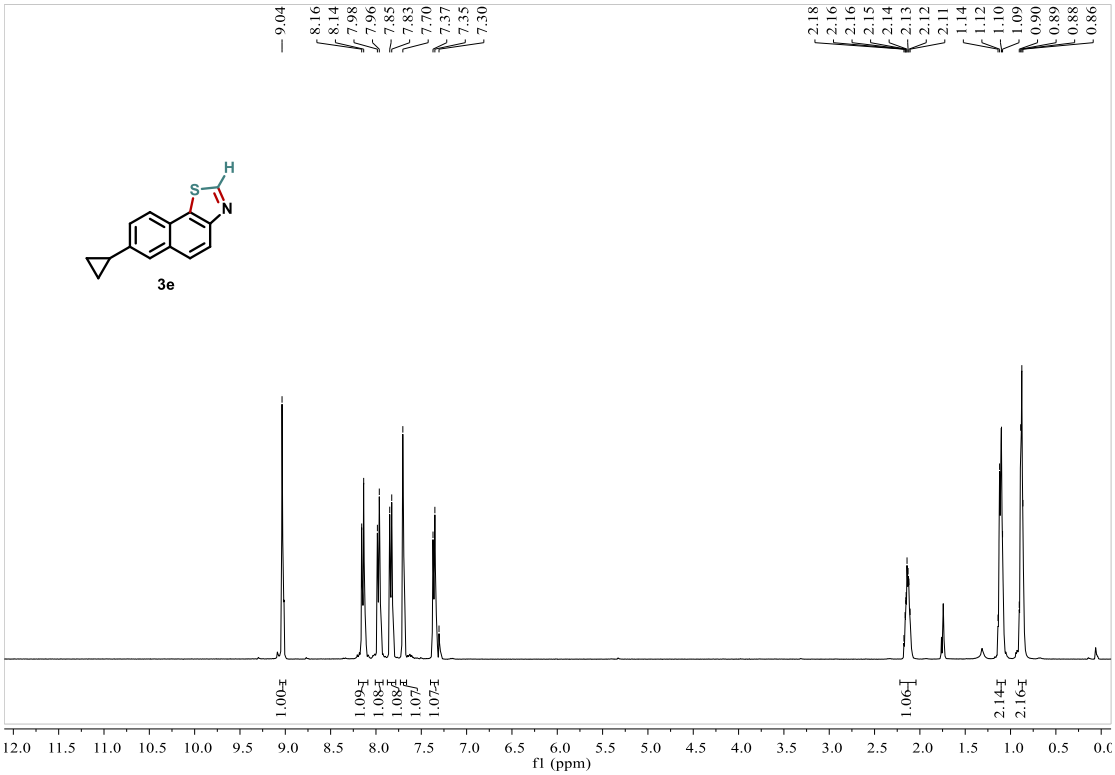
^{1}H NMR of **3d** (400 MHz, $CDCl_3$)



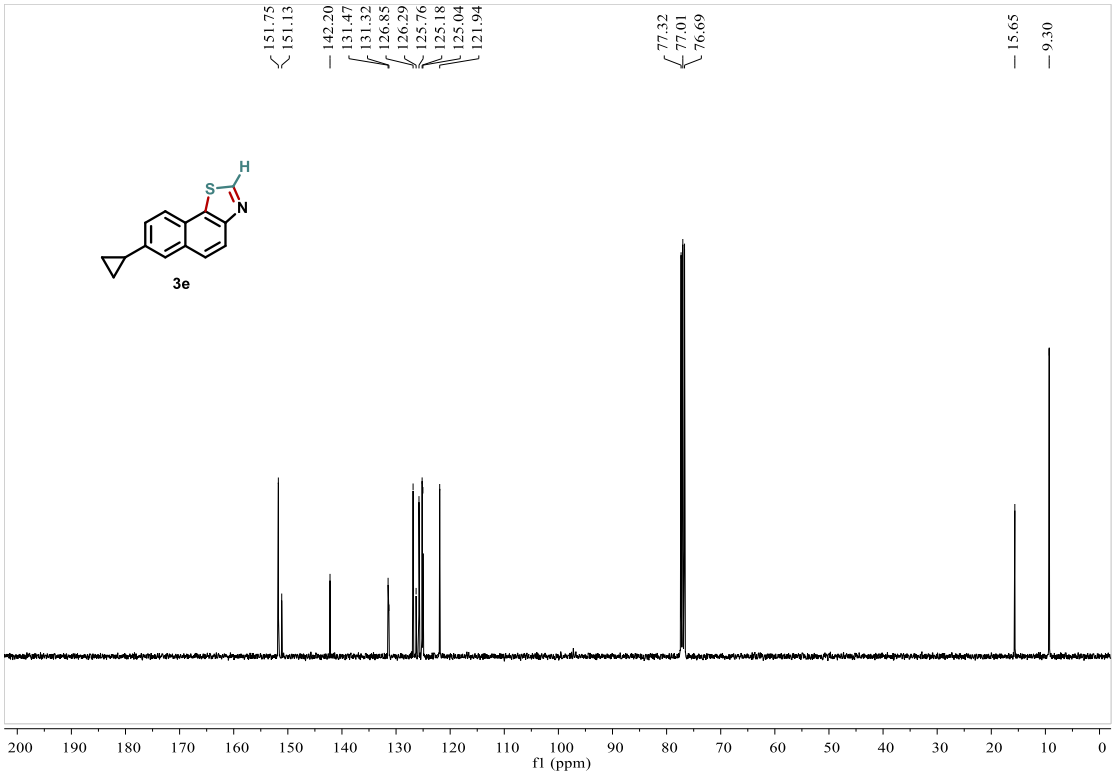
^{13}C NMR of **3d** (100 MHz, $CDCl_3$)



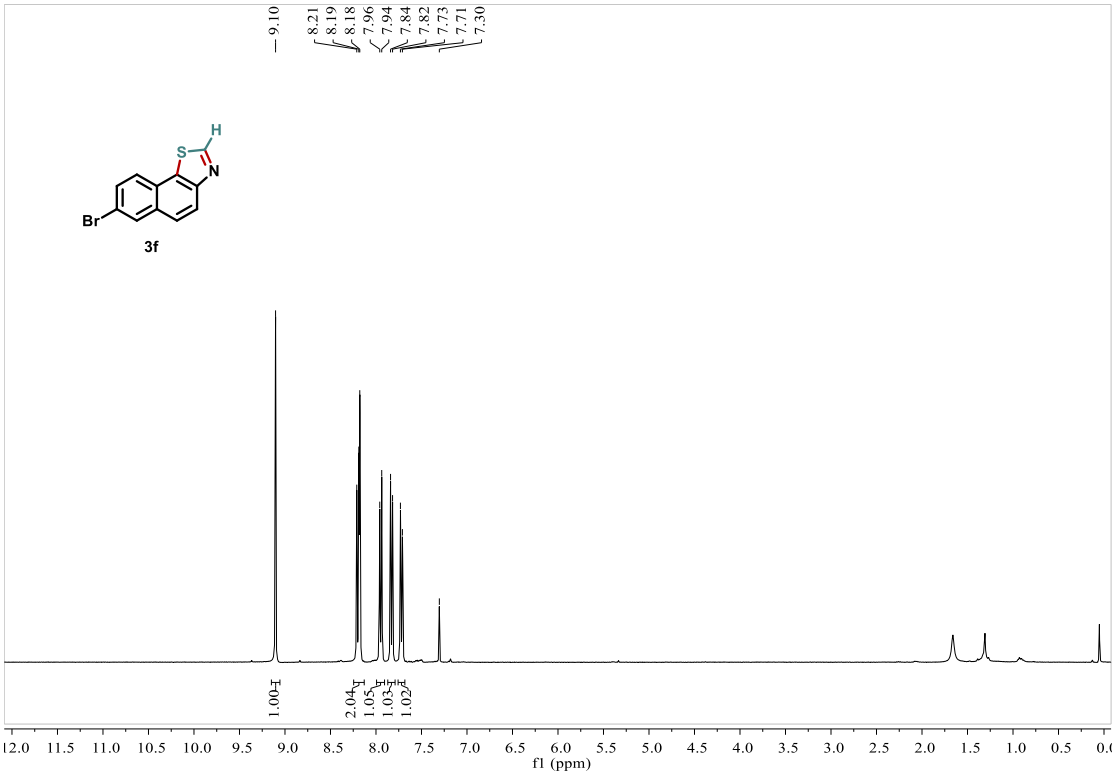
^{1}H NMR of **3e** (400 MHz, $CDCl_3$)



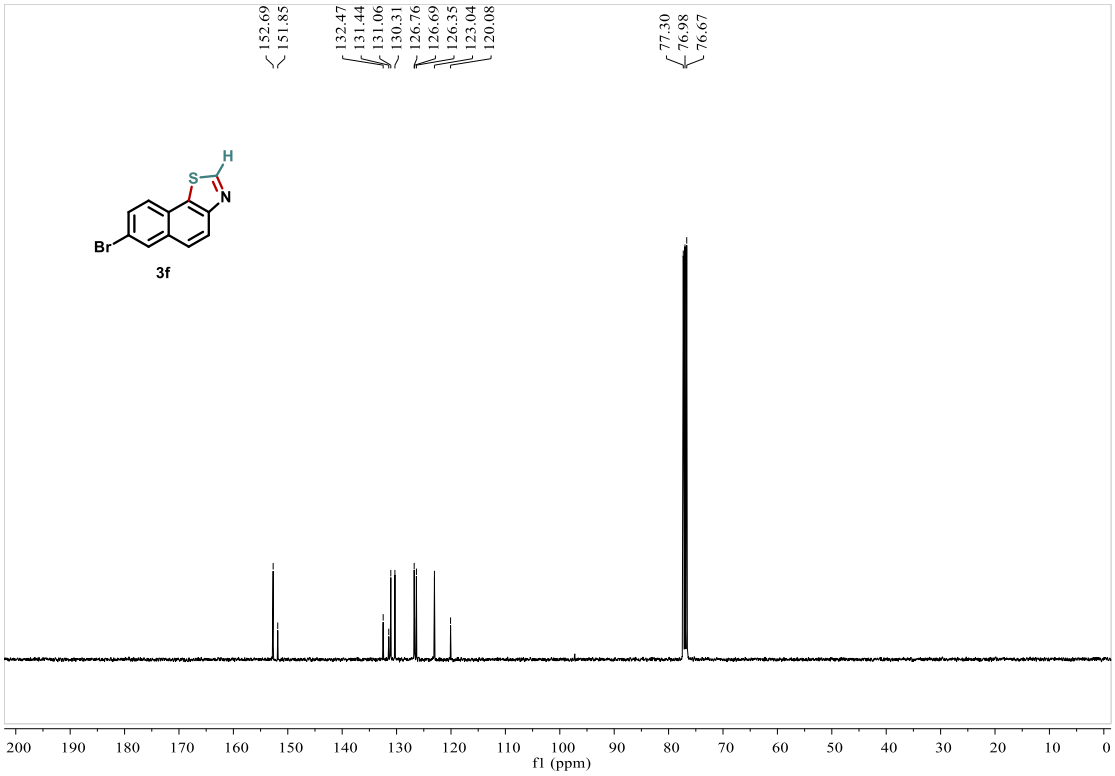
^{13}C NMR of **3e** (100 MHz, $CDCl_3$)



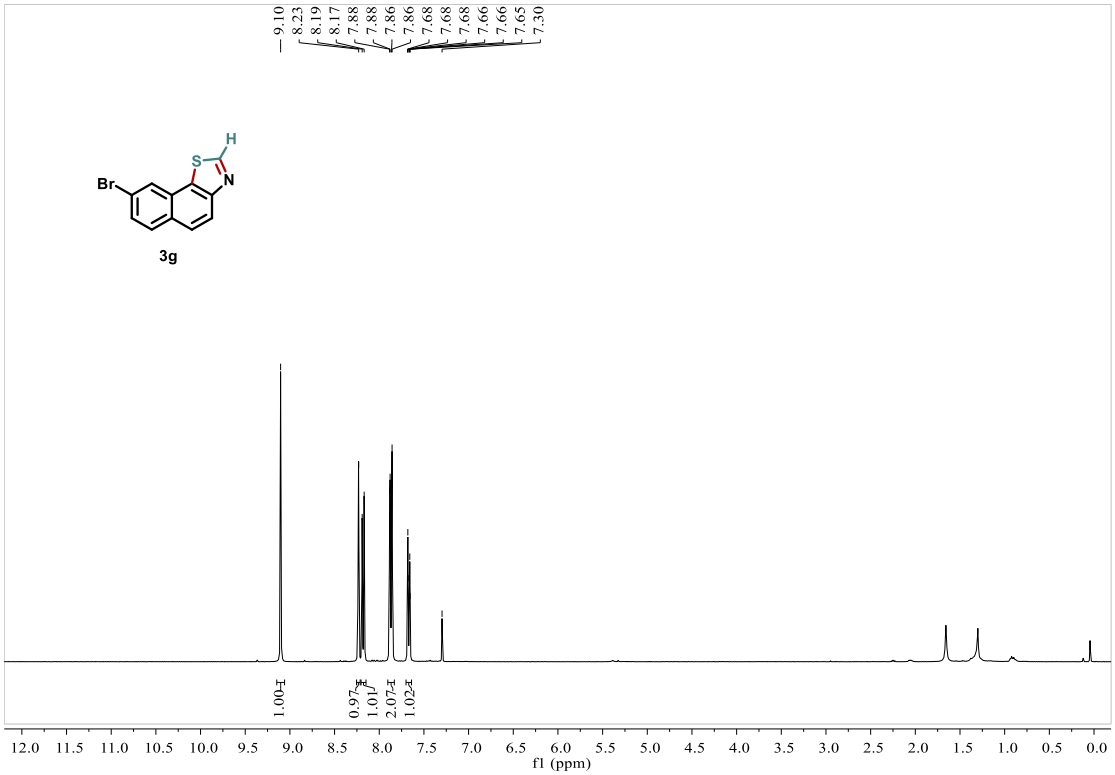
^{1}H NMR of **3f** (400 MHz, $CDCl_3$)



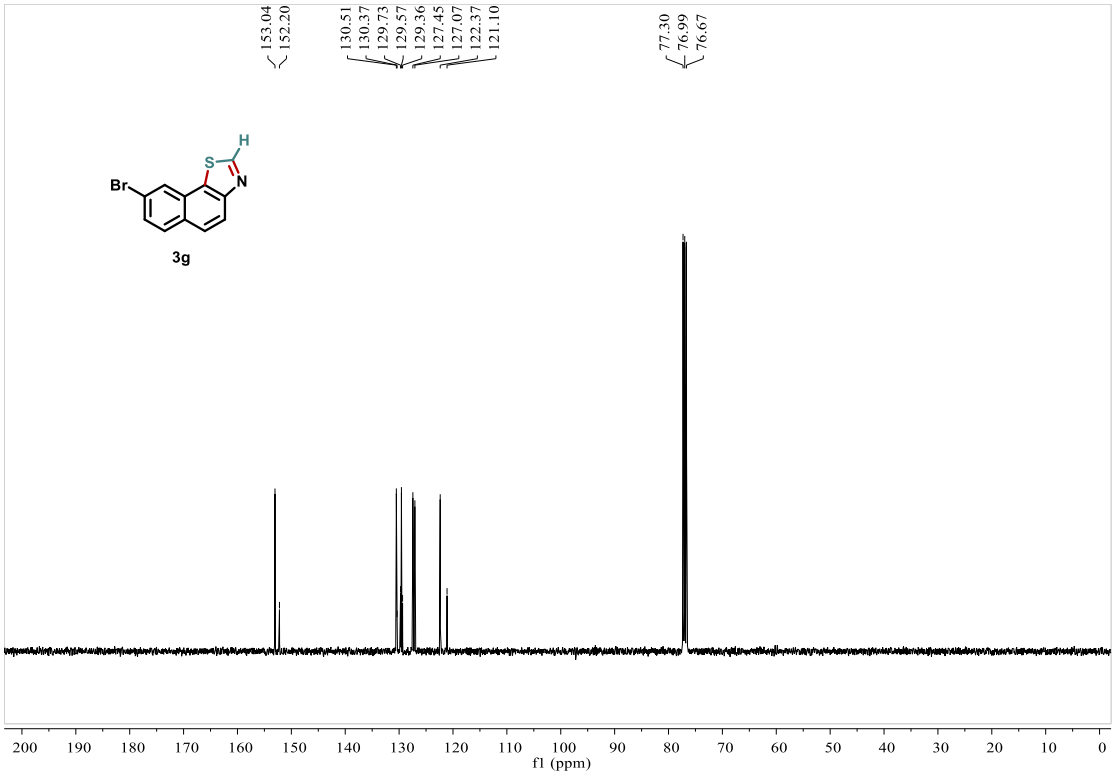
^{13}C NMR of **3f** (100 MHz, $CDCl_3$)



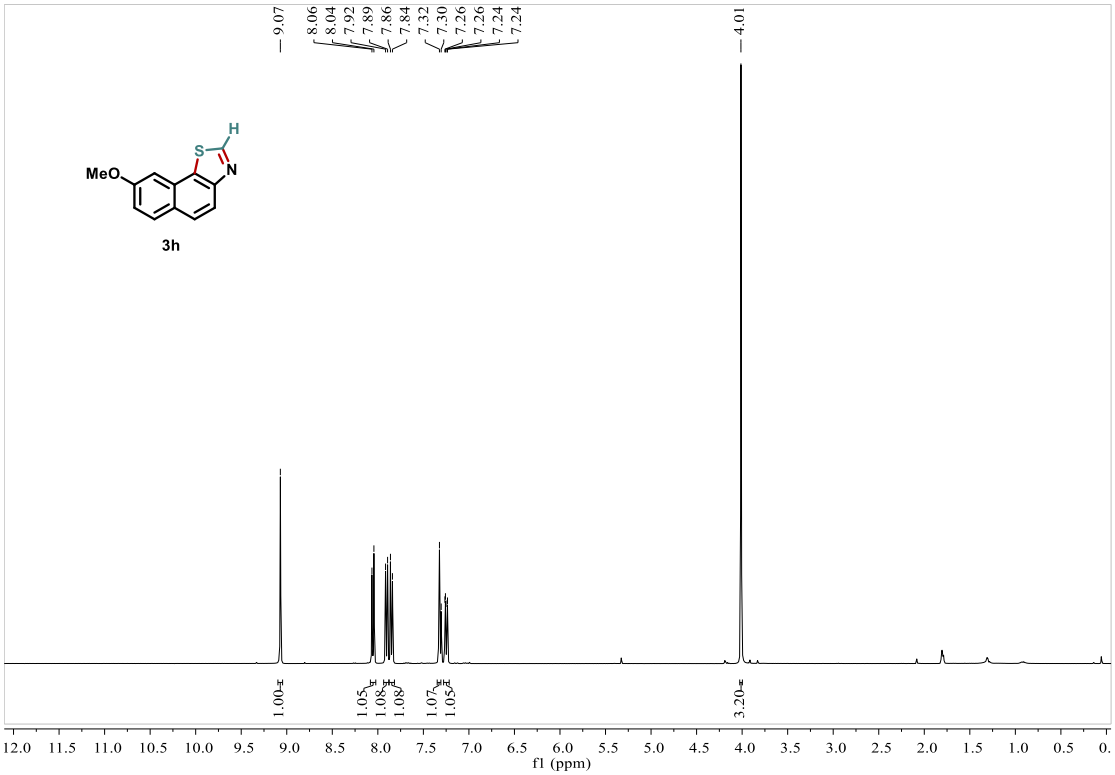
^{1}H NMR of **3g** (400 MHz, $CDCl_3$)



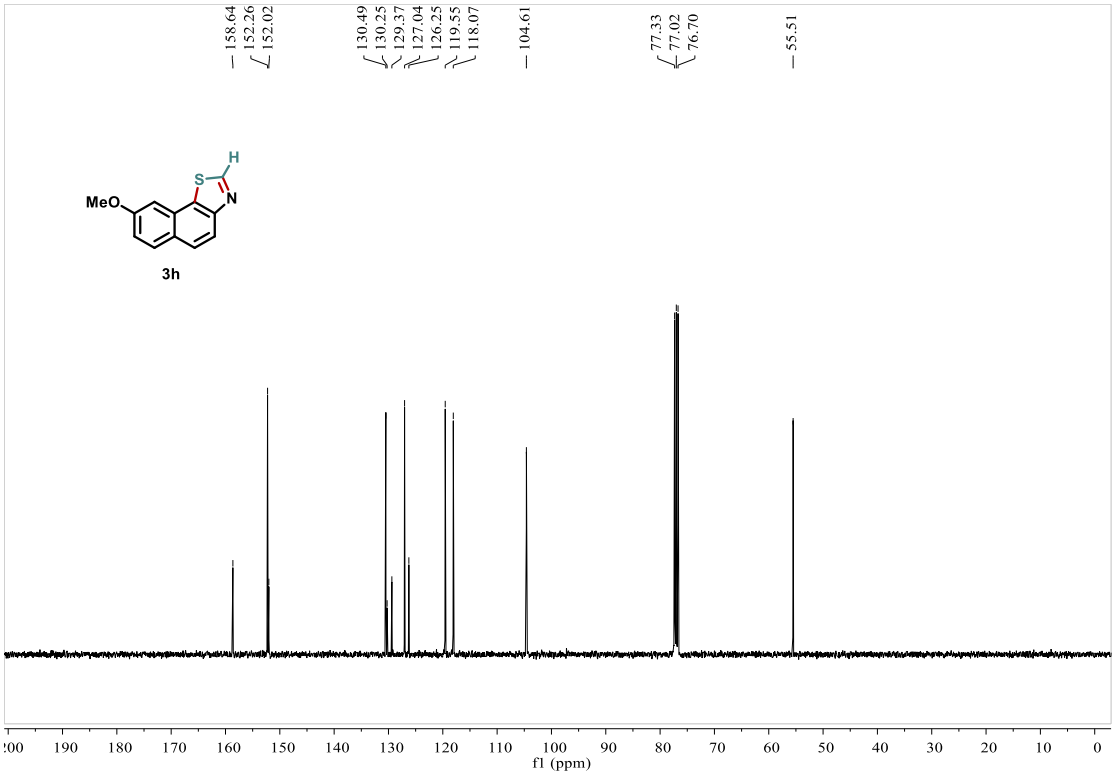
^{13}C NMR of **3g** (100 MHz, $CDCl_3$)



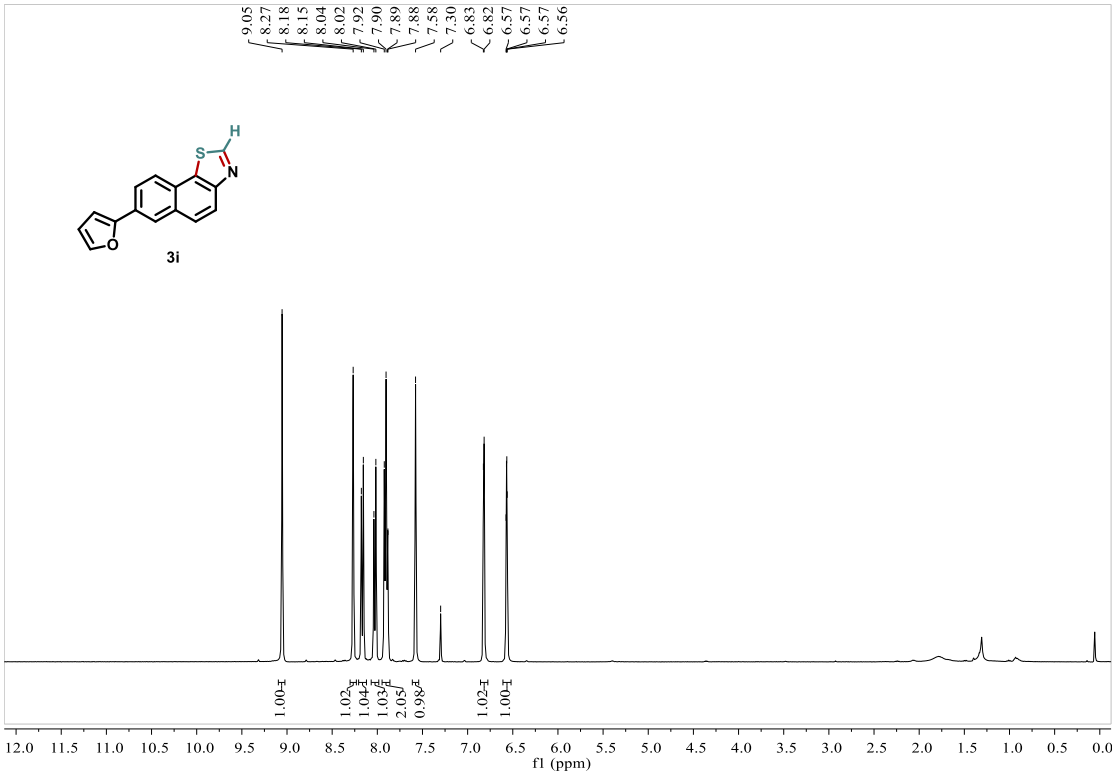
^{1}H NMR of **3h** (400 MHz, $CDCl_3$)



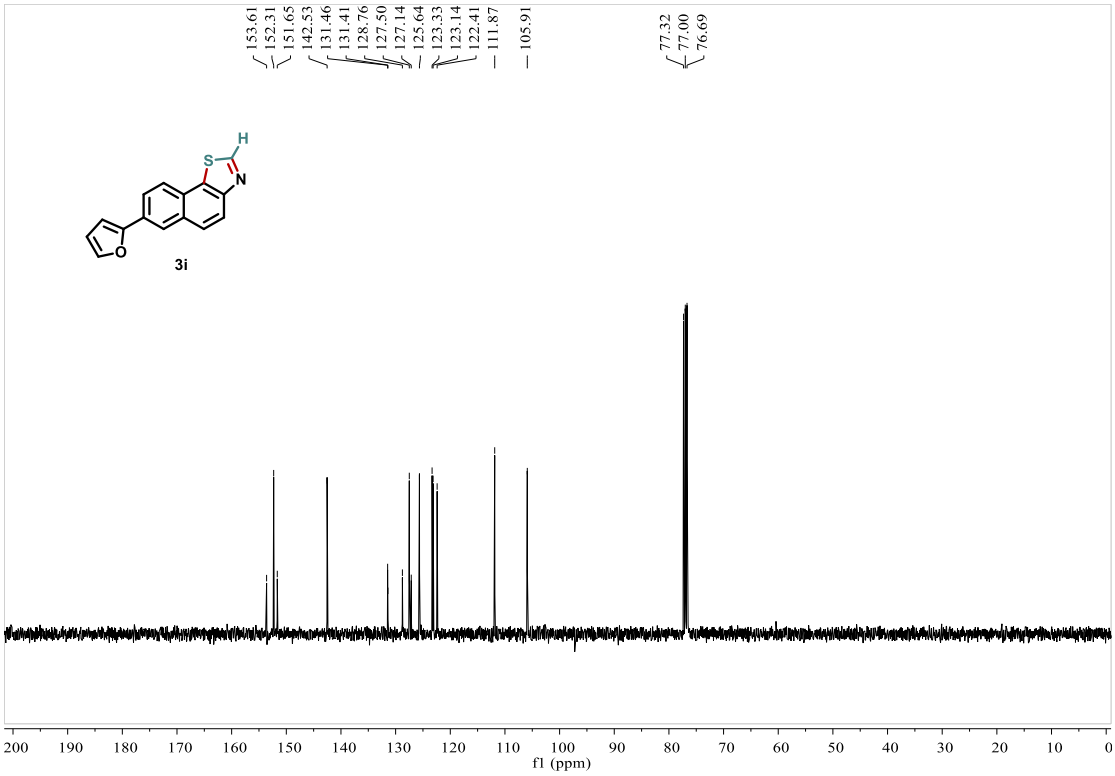
^{13}C NMR of **3h** (100 MHz, $CDCl_3$)



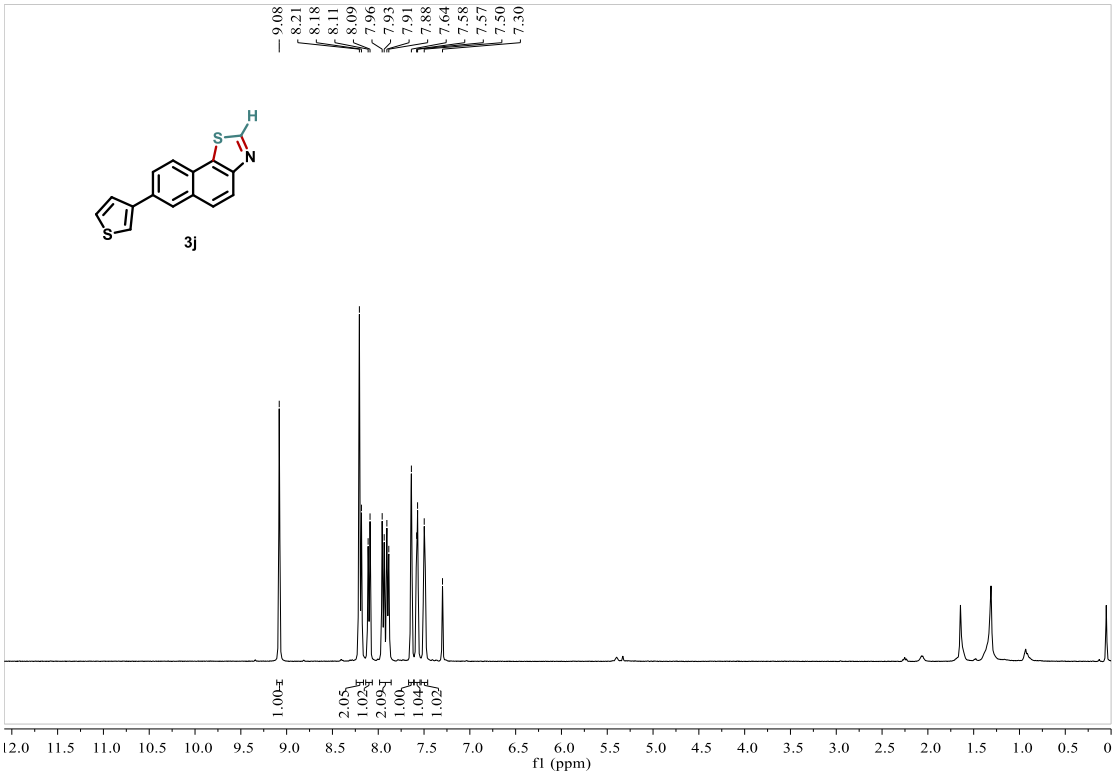
^{1}H NMR of **3i** (400 MHz, $CDCl_3$)



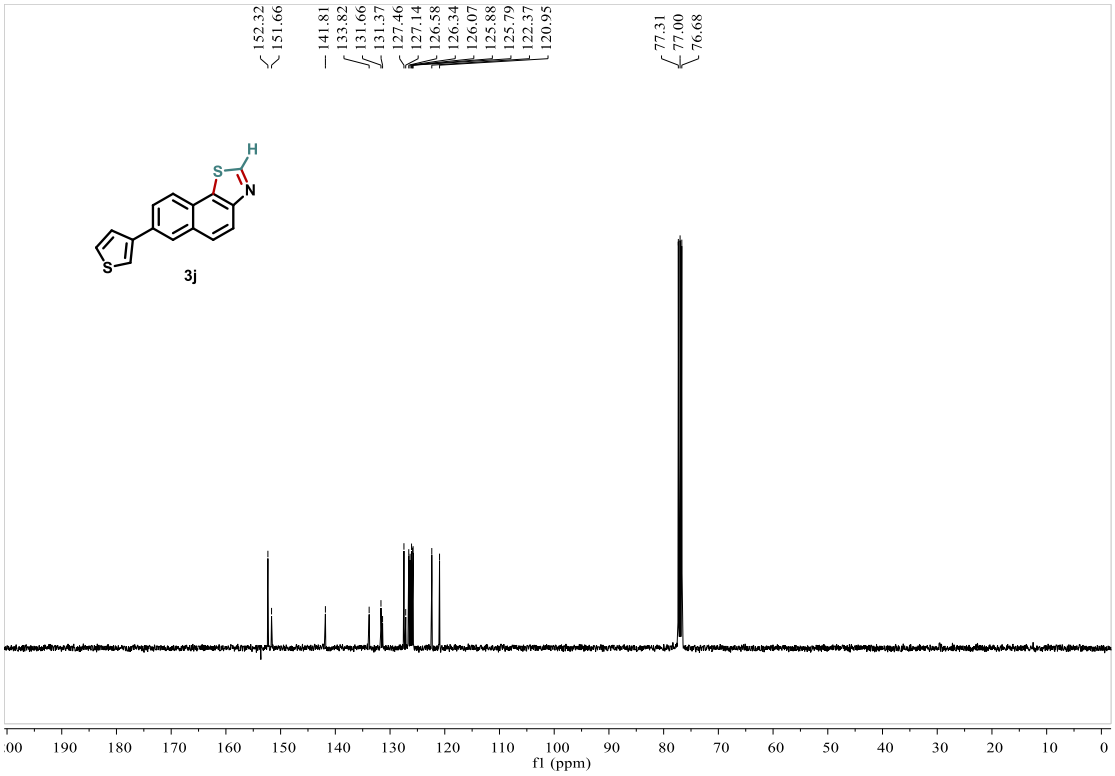
^{13}C NMR of **3i** (100 MHz, $CDCl_3$)



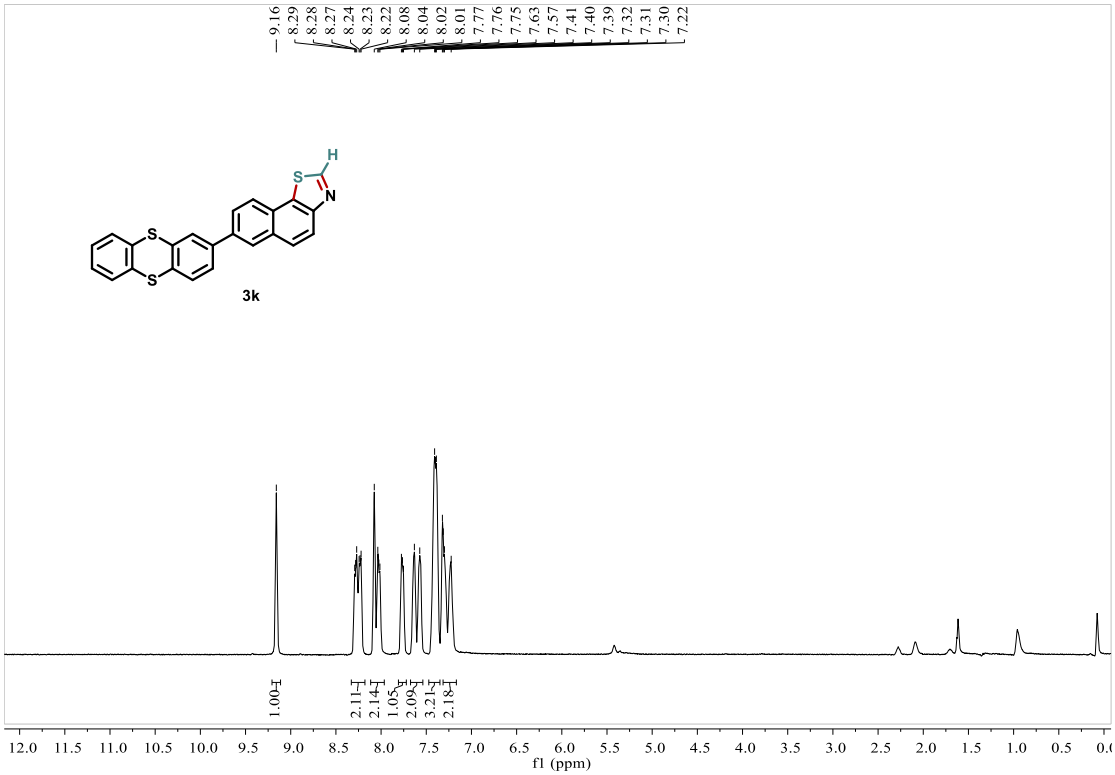
^{1}H NMR of **3j** (400 MHz, $CDCl_3$)



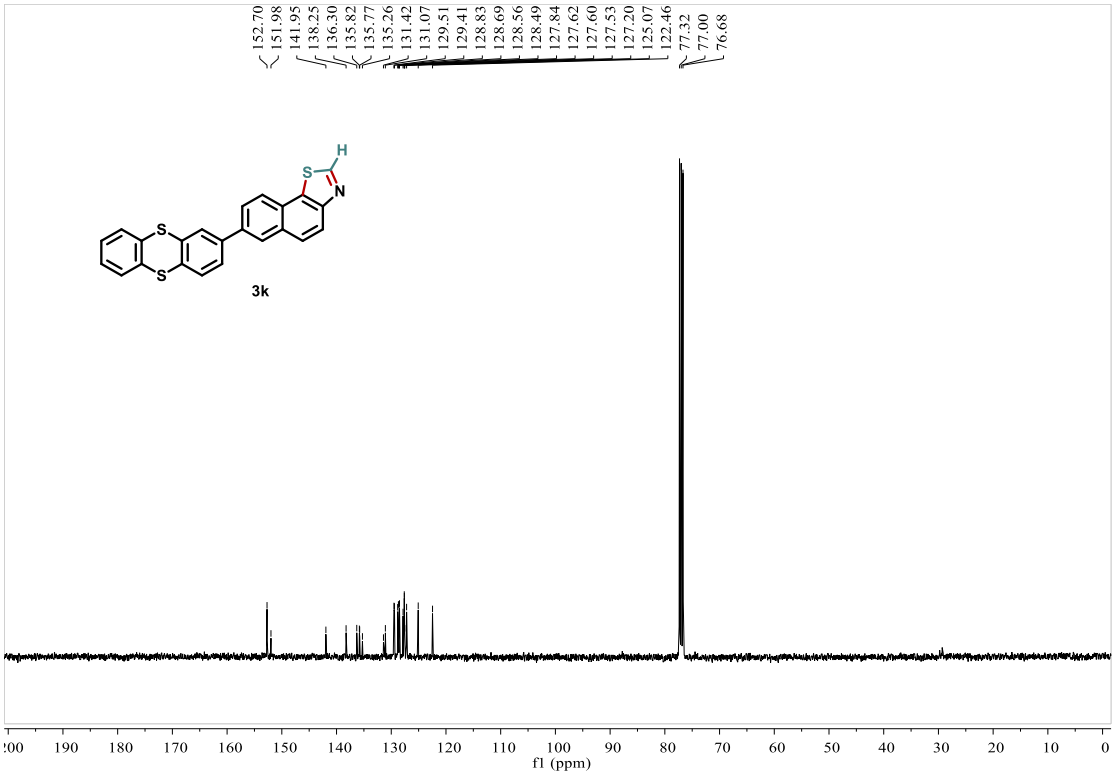
^{13}C NMR of **3j** (100 MHz, $CDCl_3$)



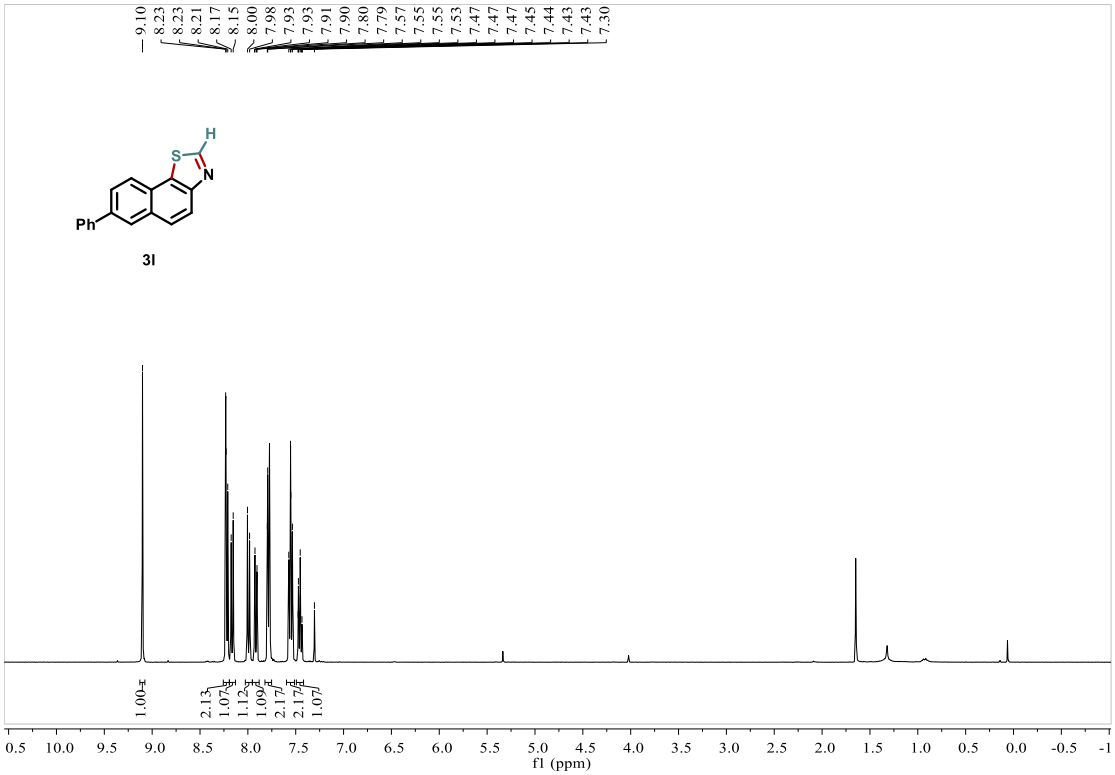
^{1}H NMR of **3k** (400 MHz, $CDCl_3$)



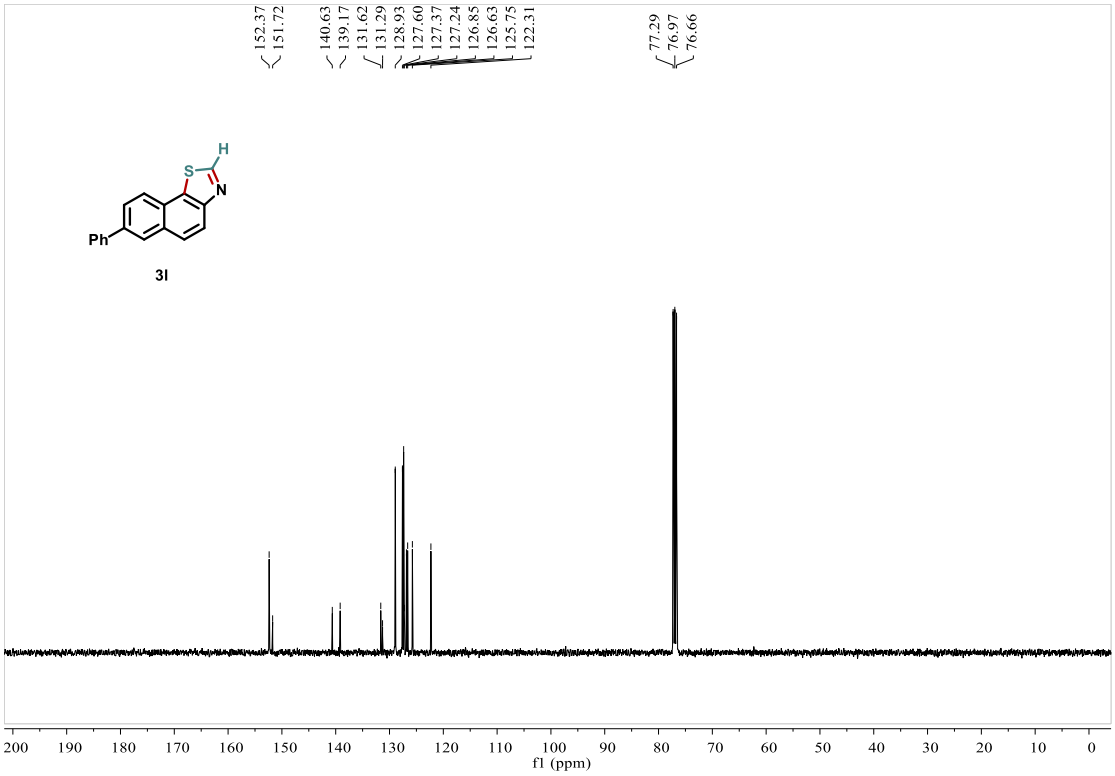
^{13}C NMR of **3k** (100 MHz, $CDCl_3$)



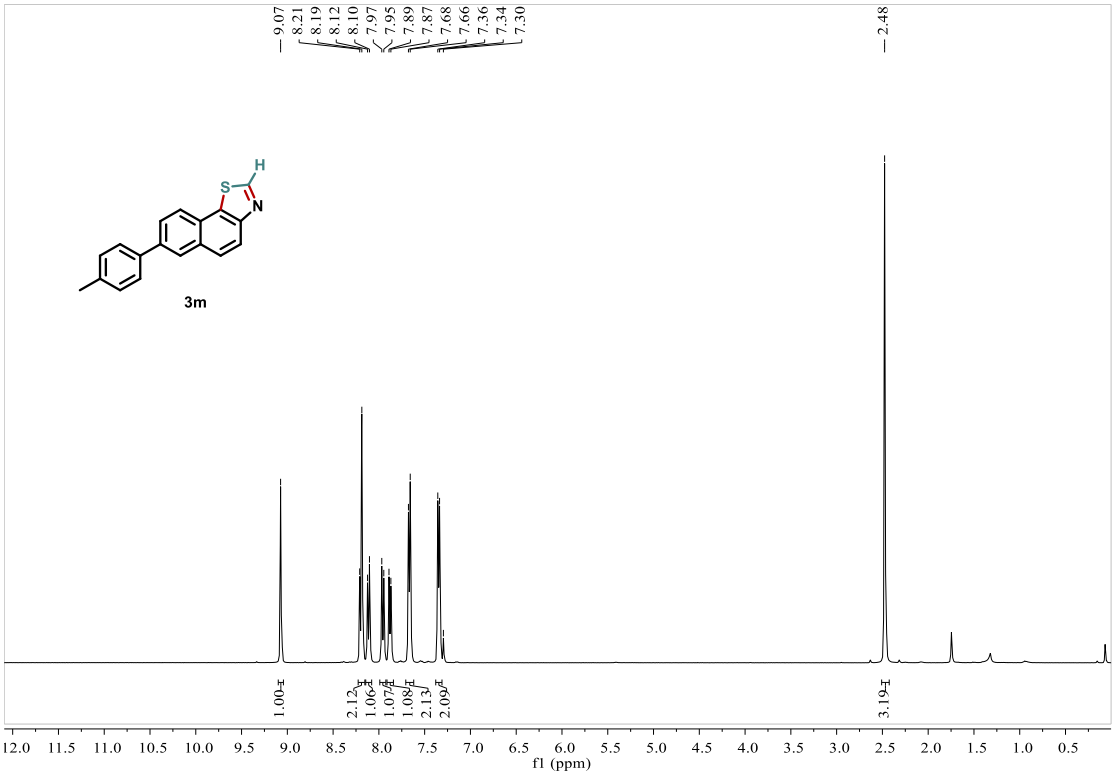
^{1}H NMR of **3l** (400 MHz, $CDCl_3$)



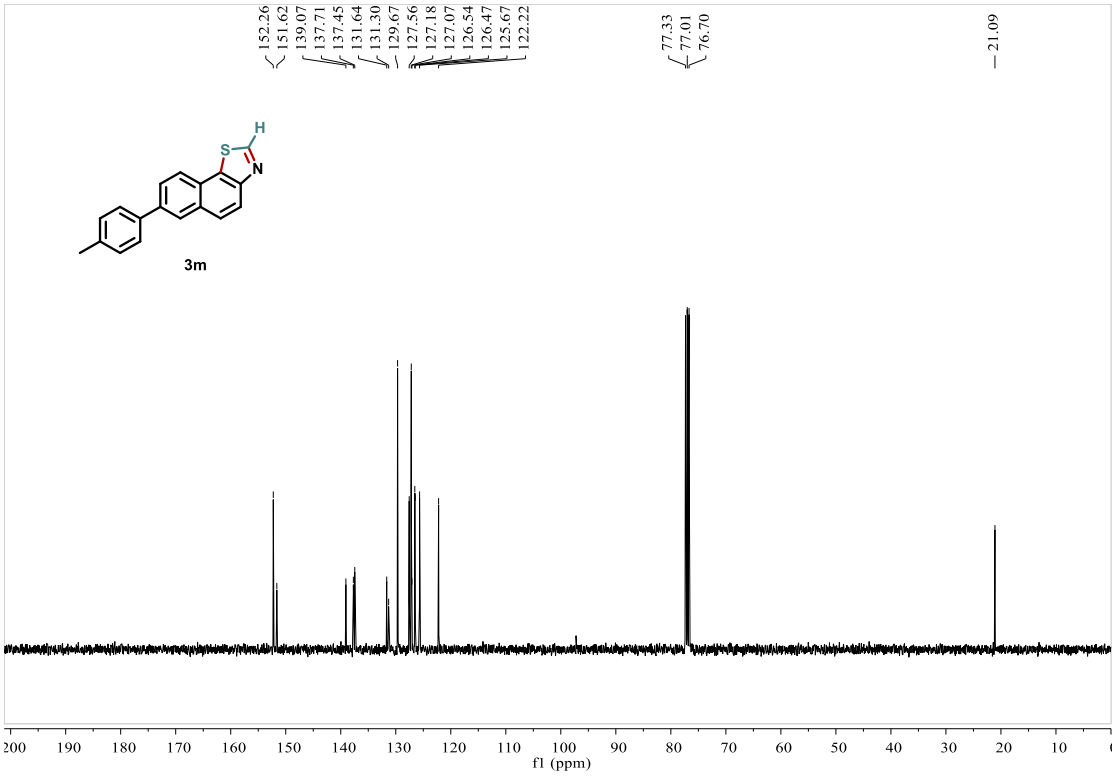
^{13}C NMR of **3l** (100 MHz, $CDCl_3$)



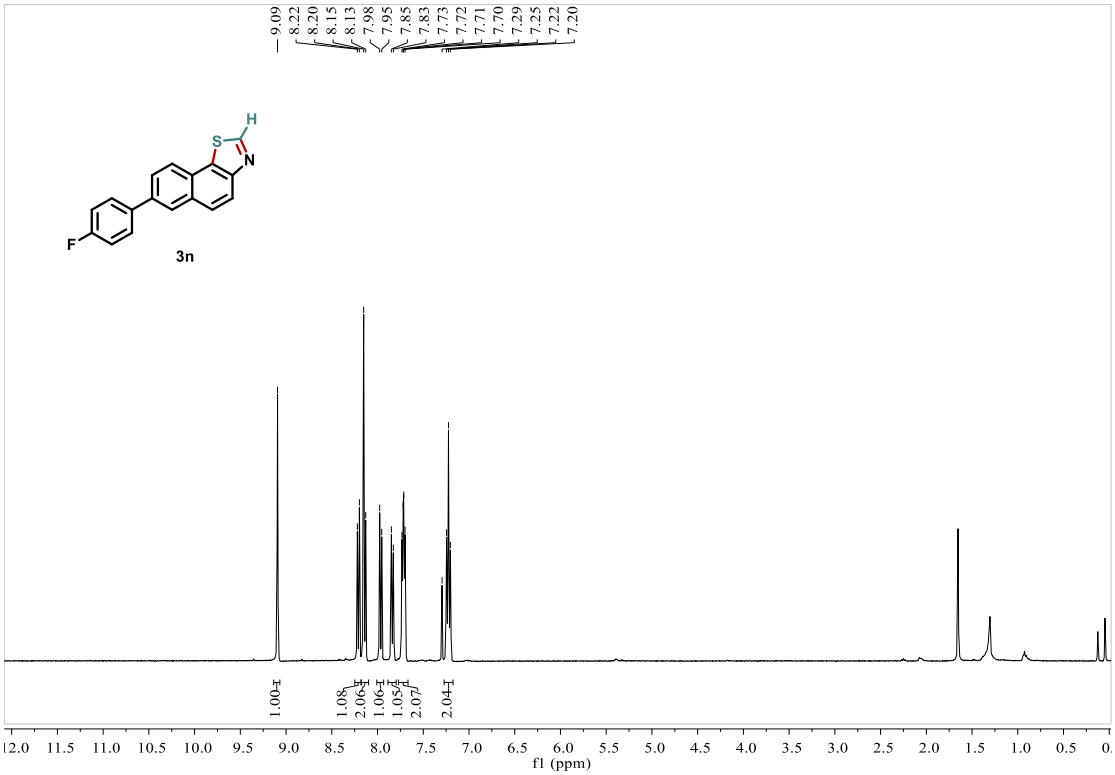
^{1}H NMR of **3m** (400 MHz, $CDCl_3$)



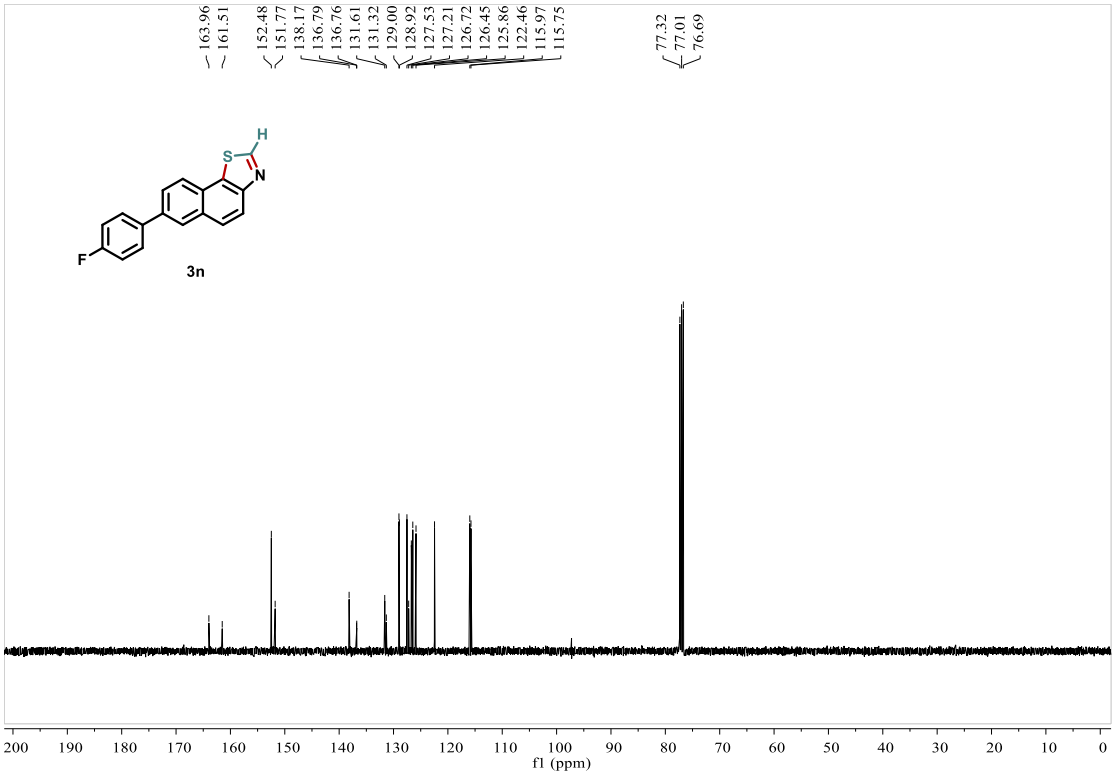
^{13}C NMR of **3m** (100 MHz, $CDCl_3$)



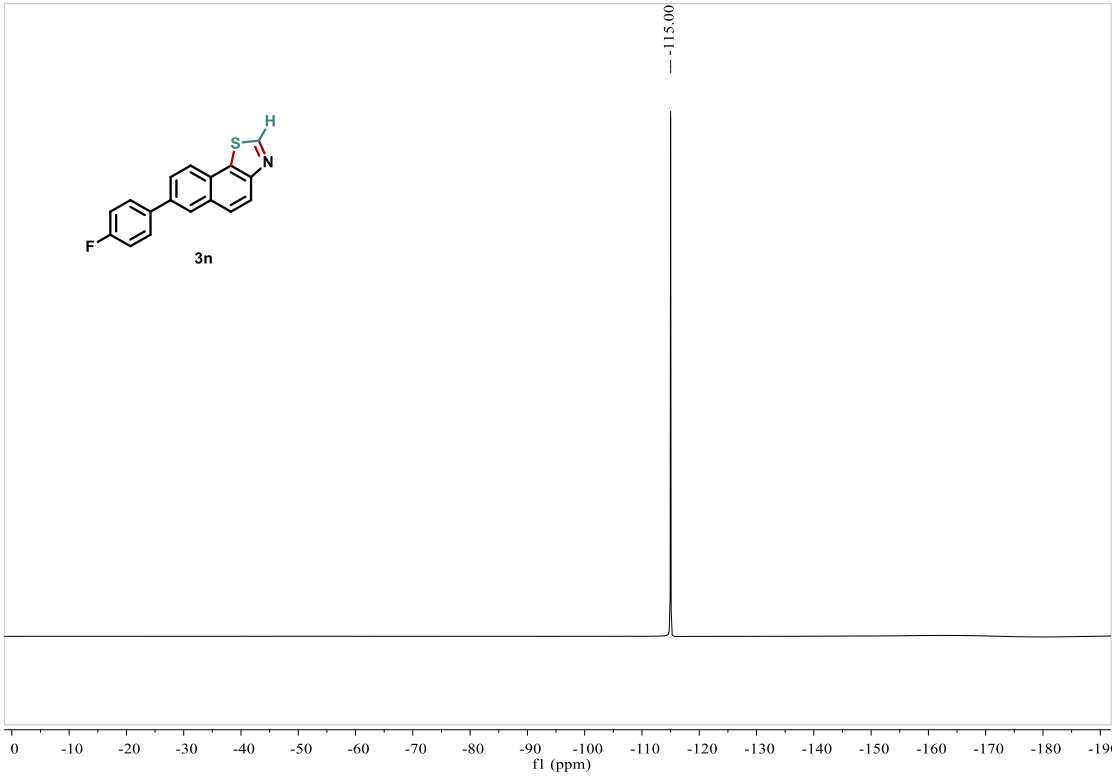
^{1}H NMR of **3n** (400 MHz, $CDCl_3$)



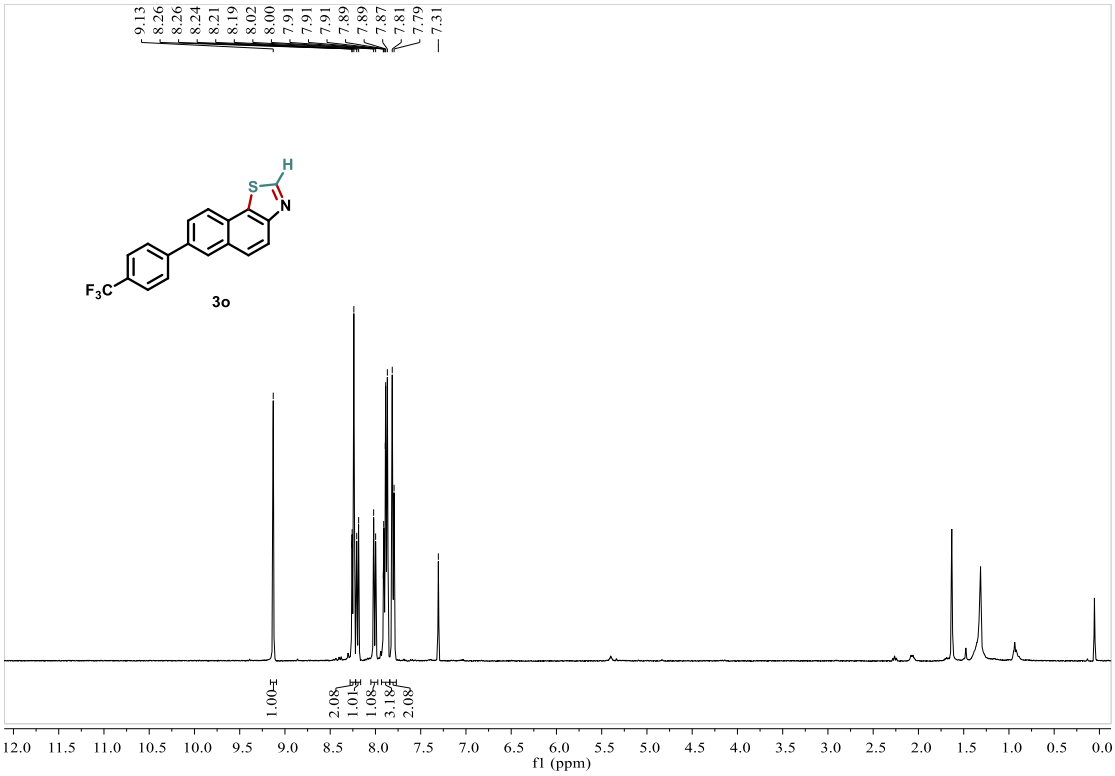
^{13}C NMR of **3n** (100 MHz, $CDCl_3$)



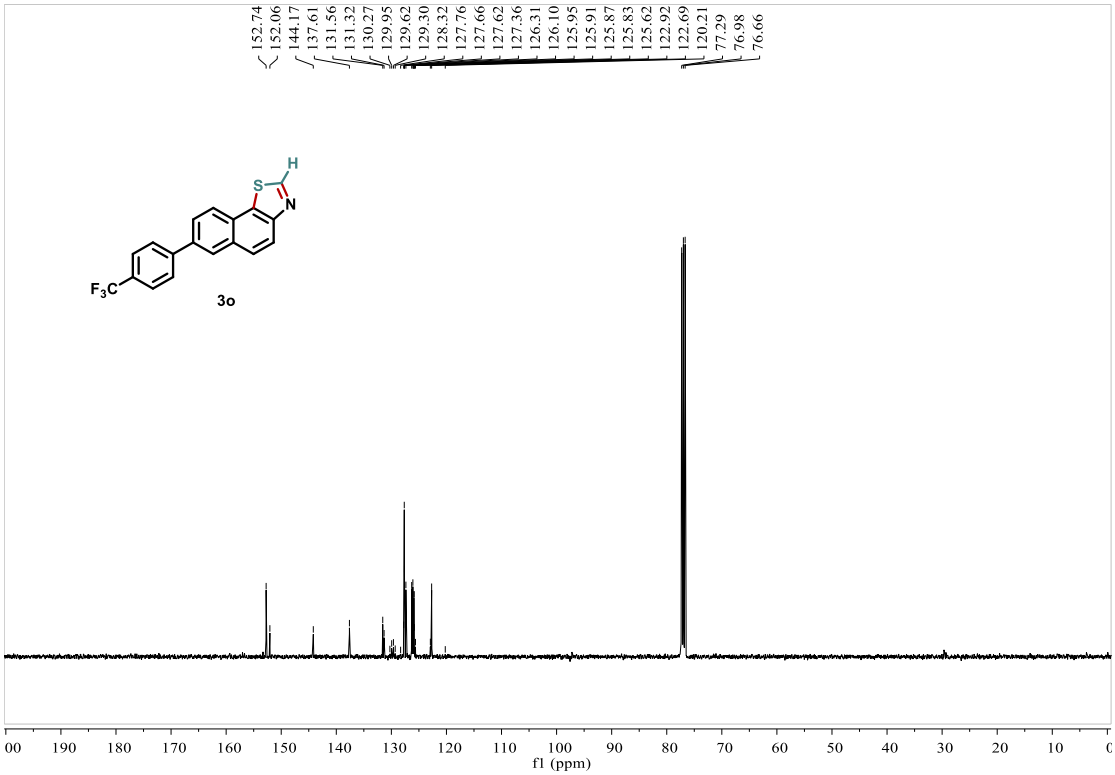
^{19}F NMR of **3n** (376 MHz, $CDCl_3$)



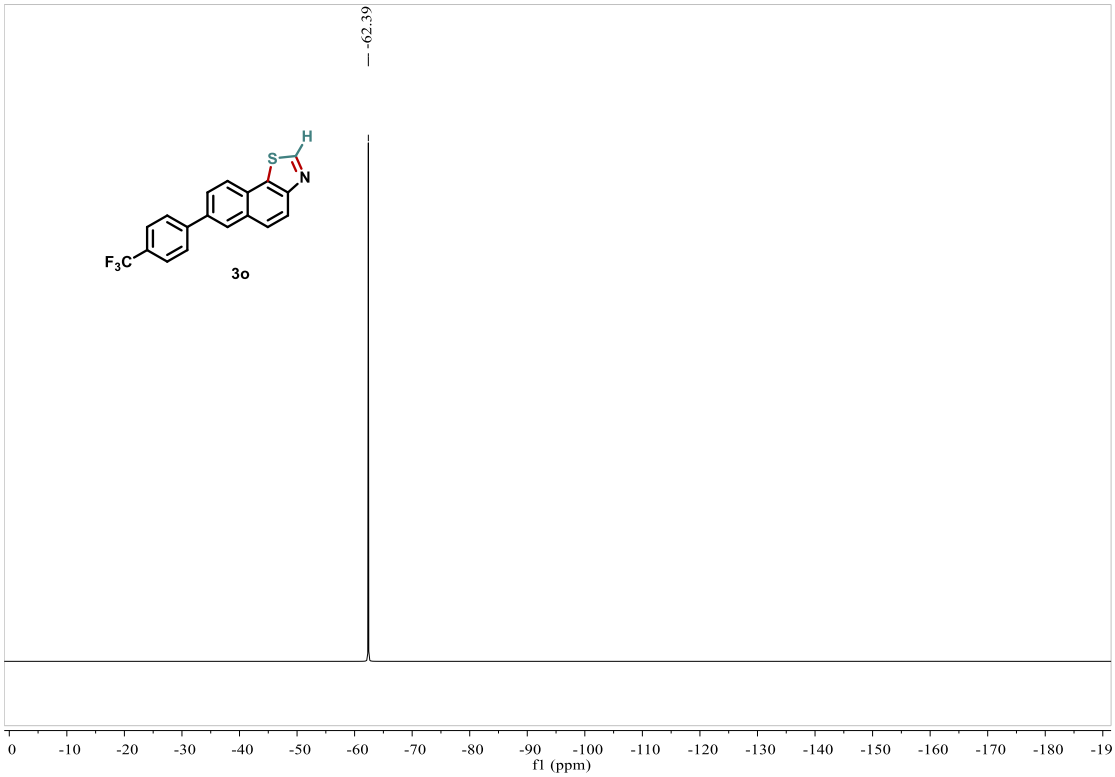
^{1}H NMR of **3o** (400 MHz, $CDCl_3$)



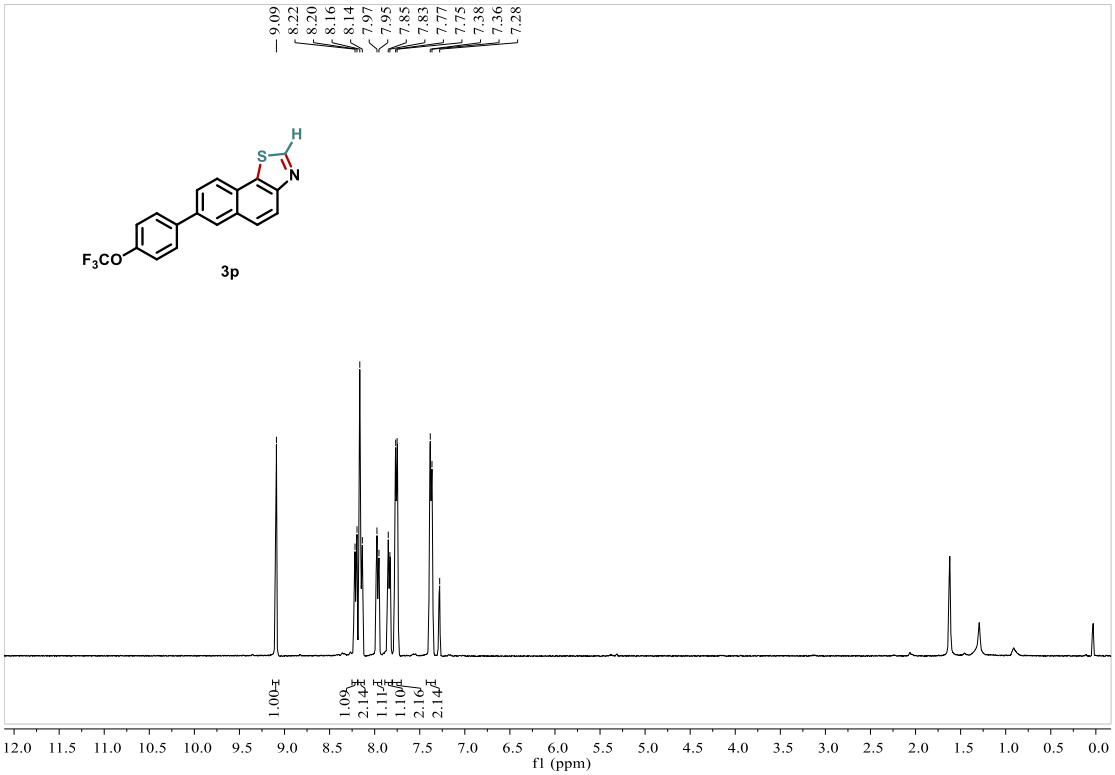
^{13}C NMR of **3o** (100 MHz, $CDCl_3$)



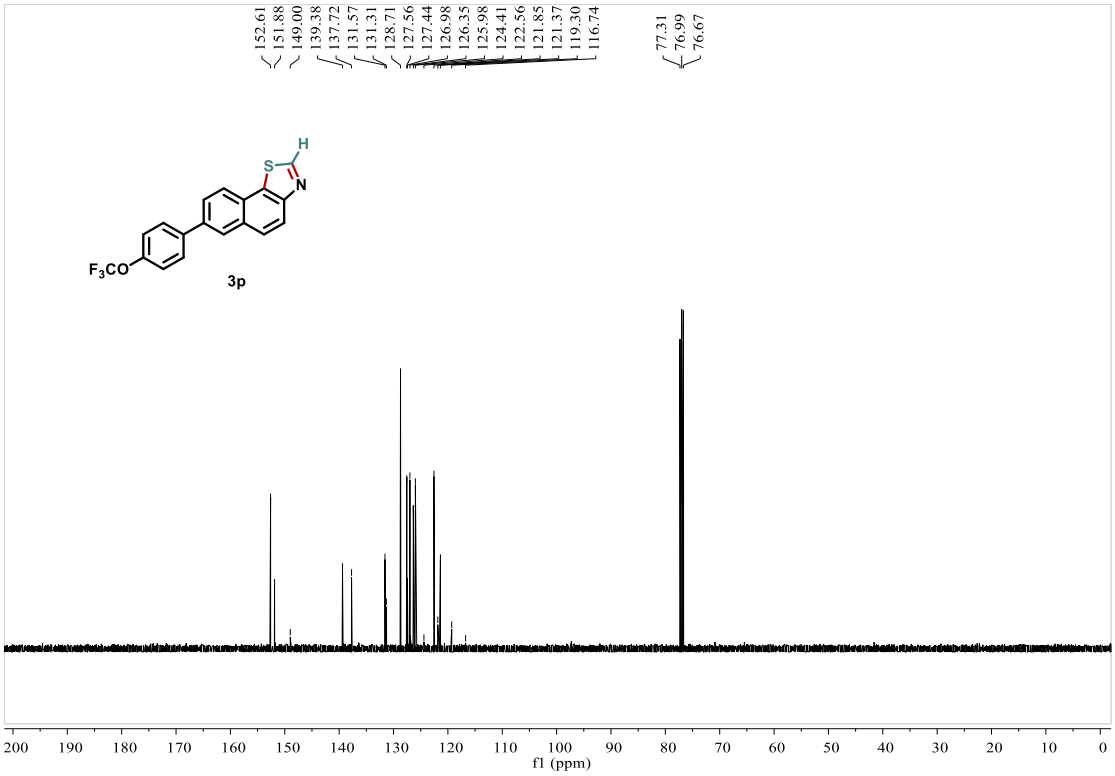
^{19}F NMR of **3o** (376 MHz, $CDCl_3$)



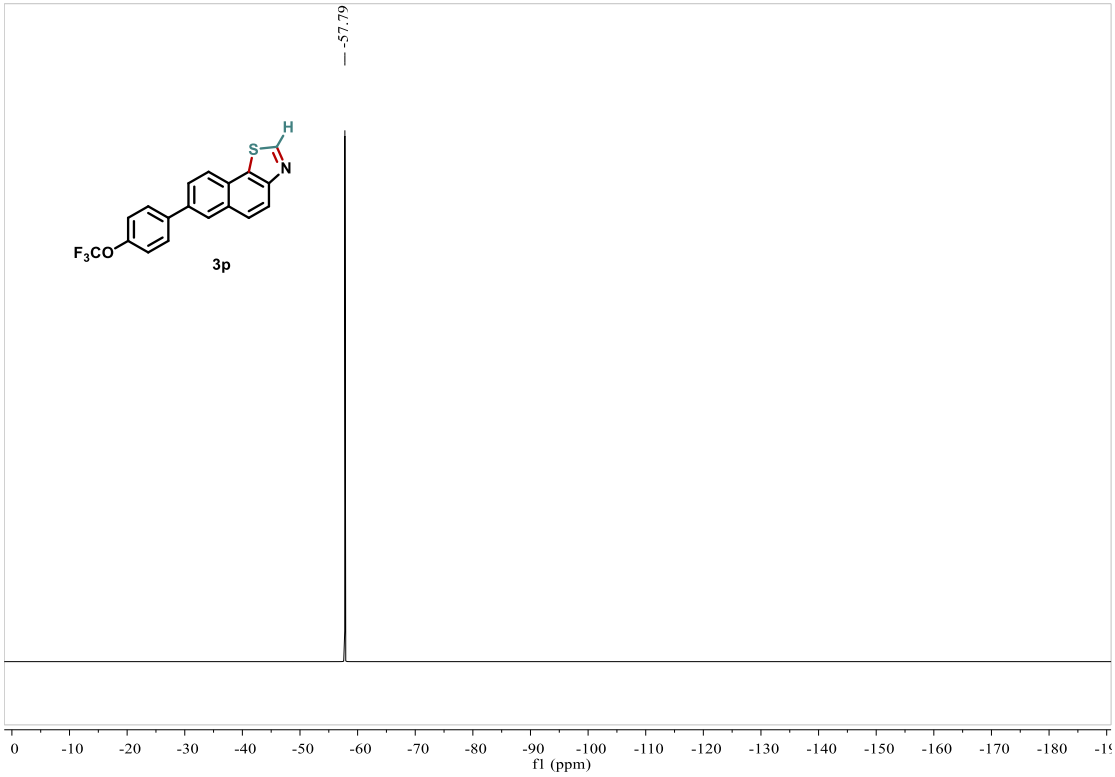
^{1}H NMR of **3p** (400 MHz, $CDCl_3$)



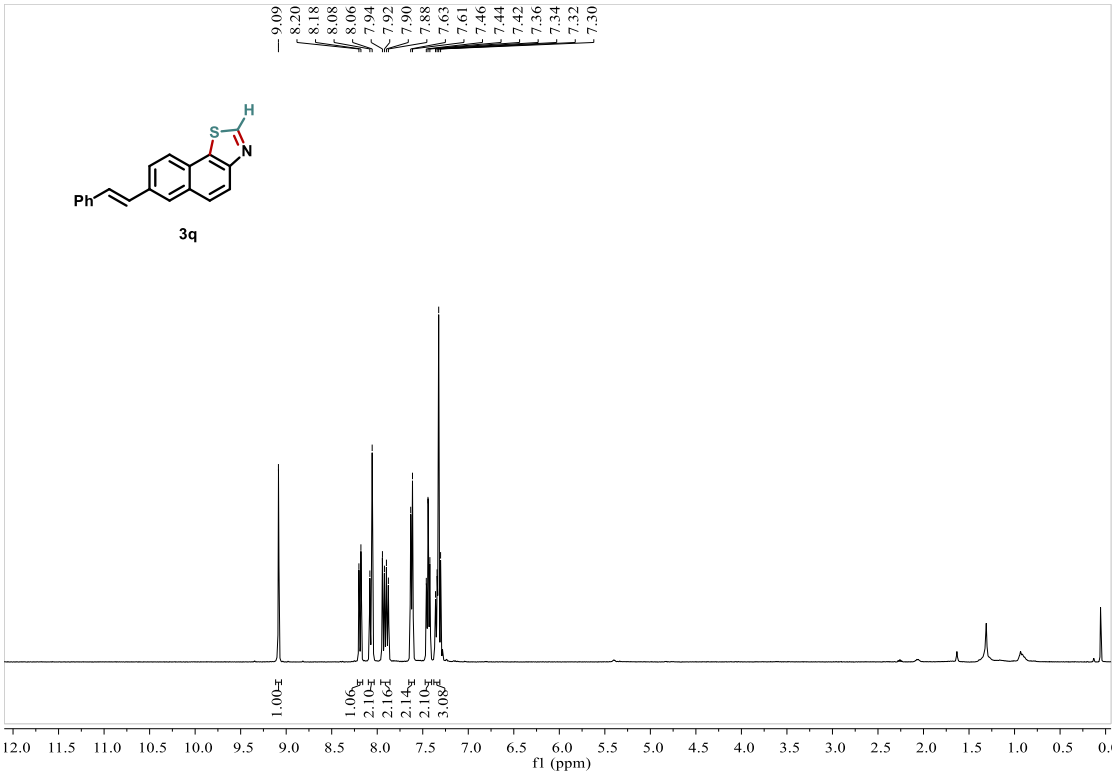
^{13}C NMR of **3p** (100 MHz, $CDCl_3$)



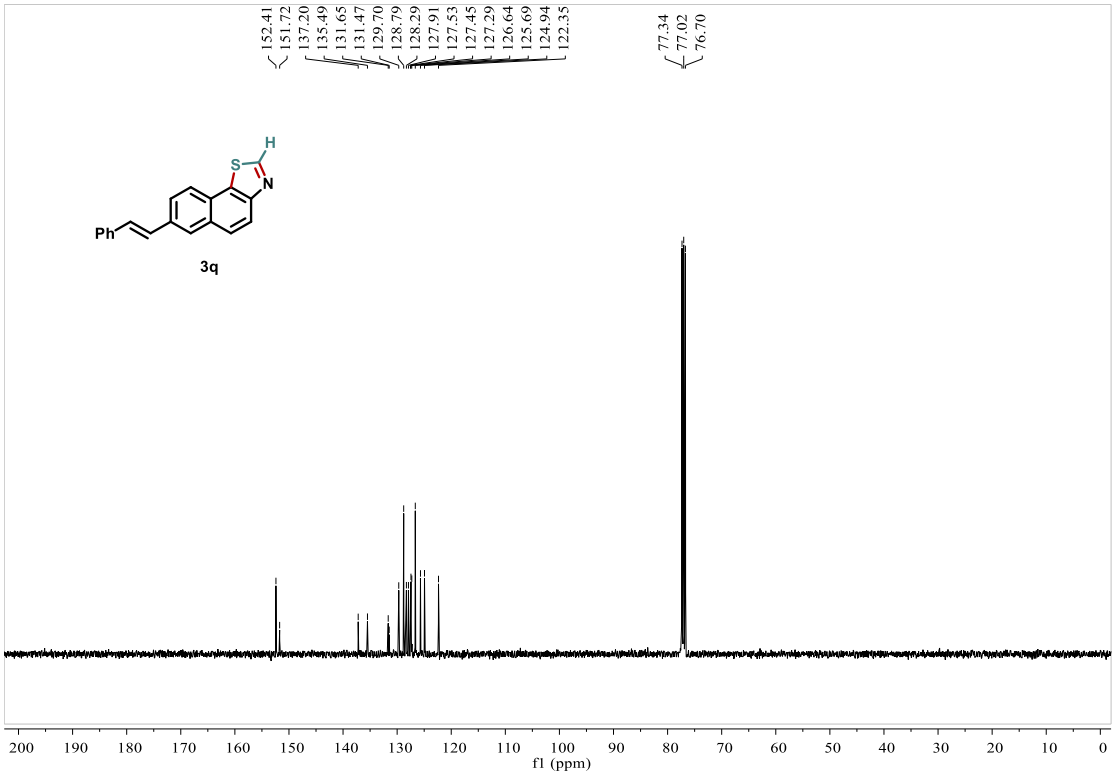
^{19}F NMR of **3p** (376 MHz, $CDCl_3$)



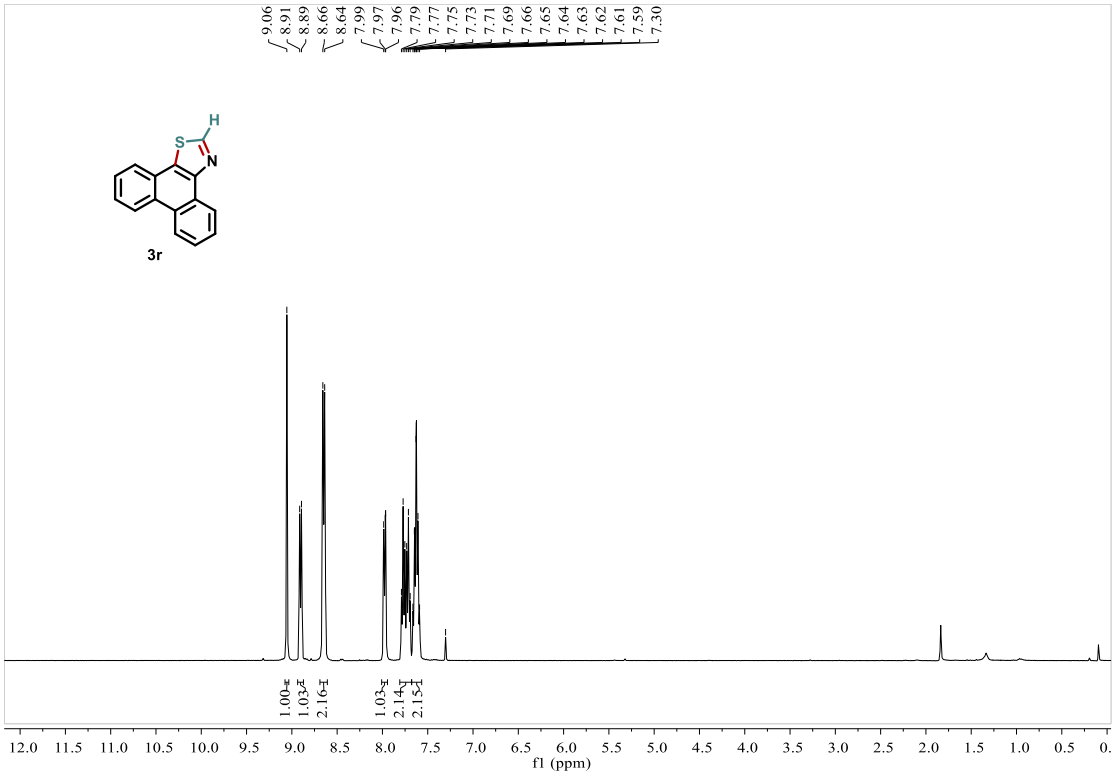
^{1}H NMR of **3q** (400 MHz, $CDCl_3$)



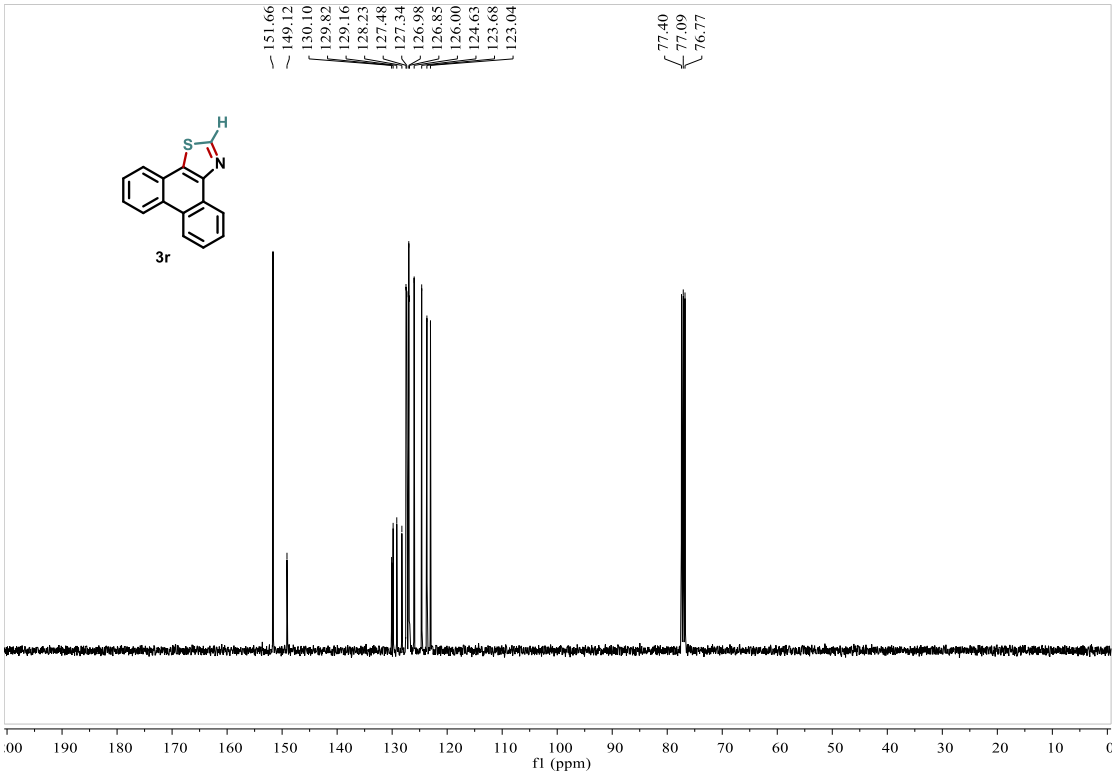
^{13}C NMR of **3q** (100 MHz, $CDCl_3$)



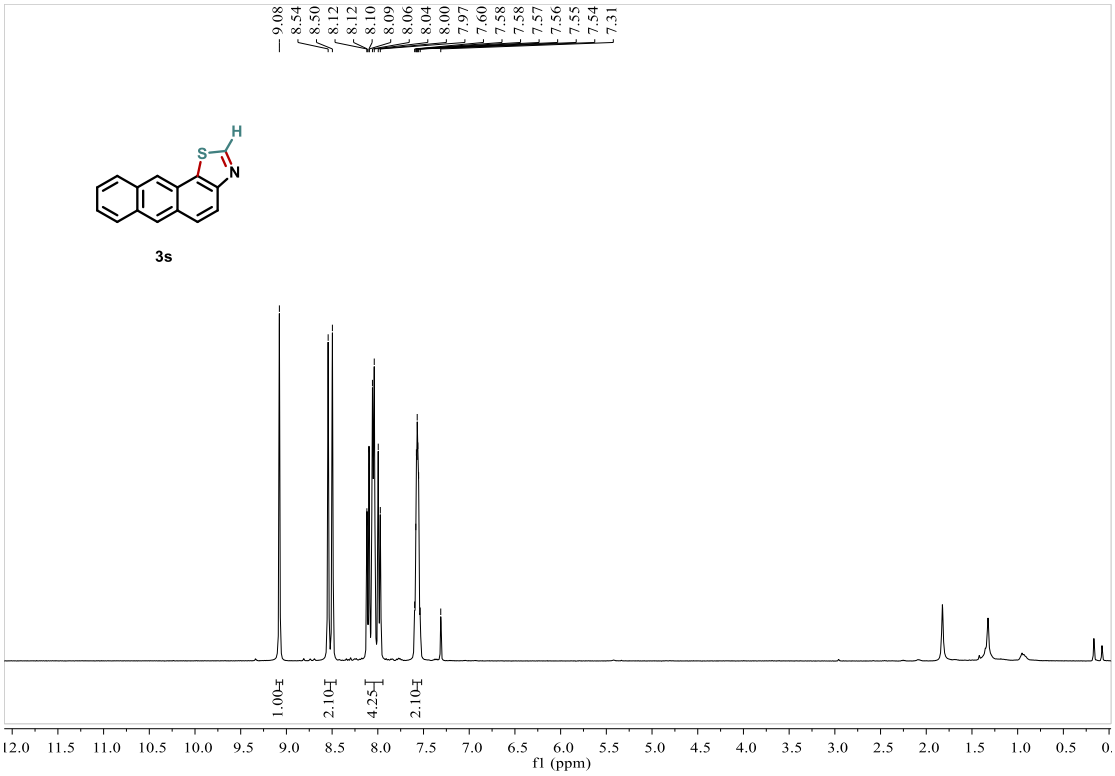
^{1}H NMR of **3r** (400 MHz, $CDCl_3$)



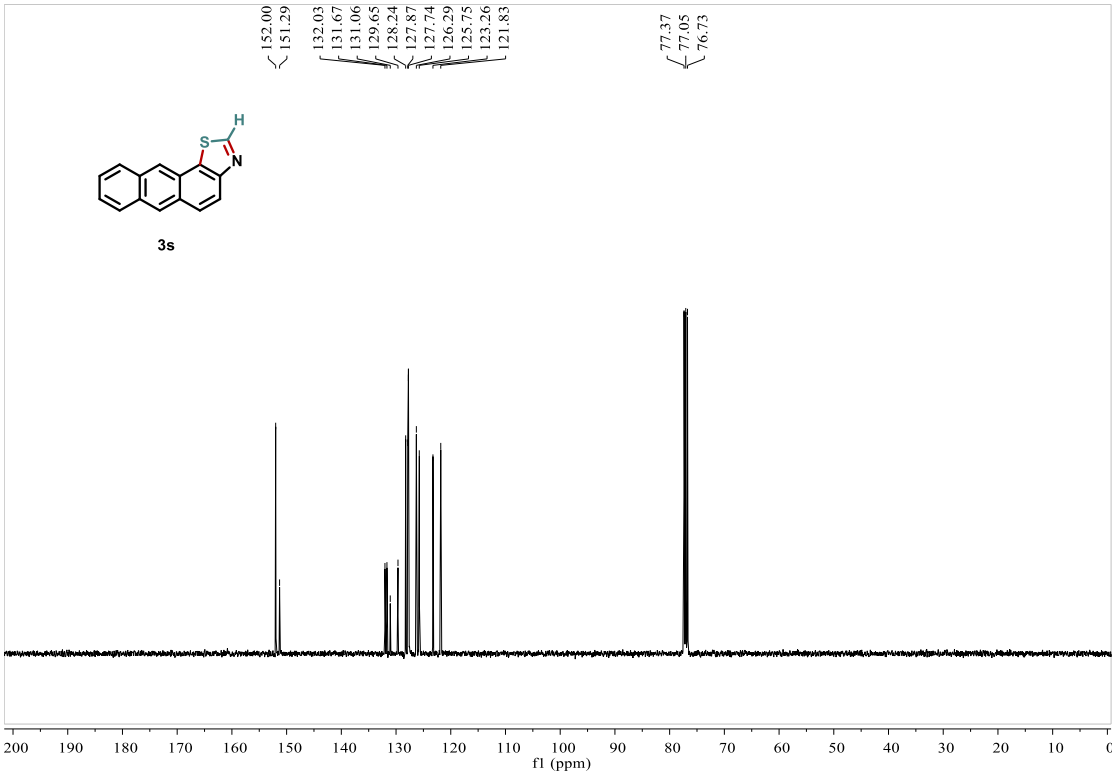
^{13}C NMR of **3r** (100 MHz, $CDCl_3$)



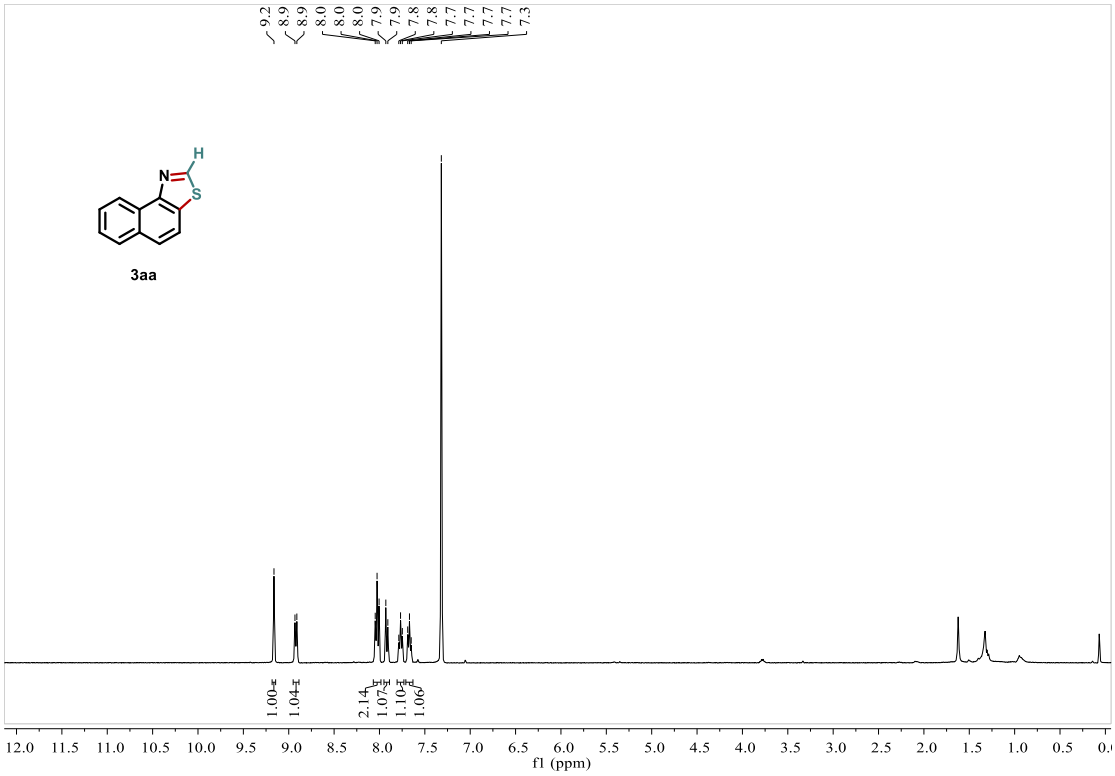
^{1}H NMR of **3s** (400 MHz, $CDCl_3$)



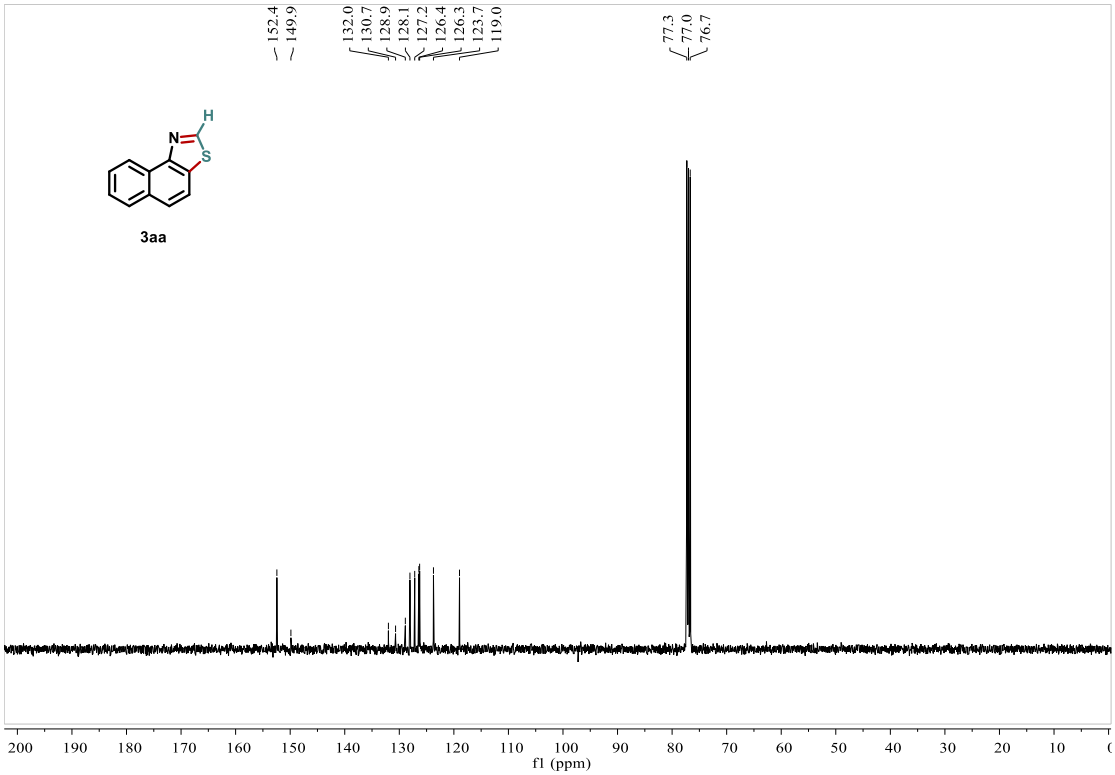
^{13}C NMR of **3s** (100 MHz, $CDCl_3$)



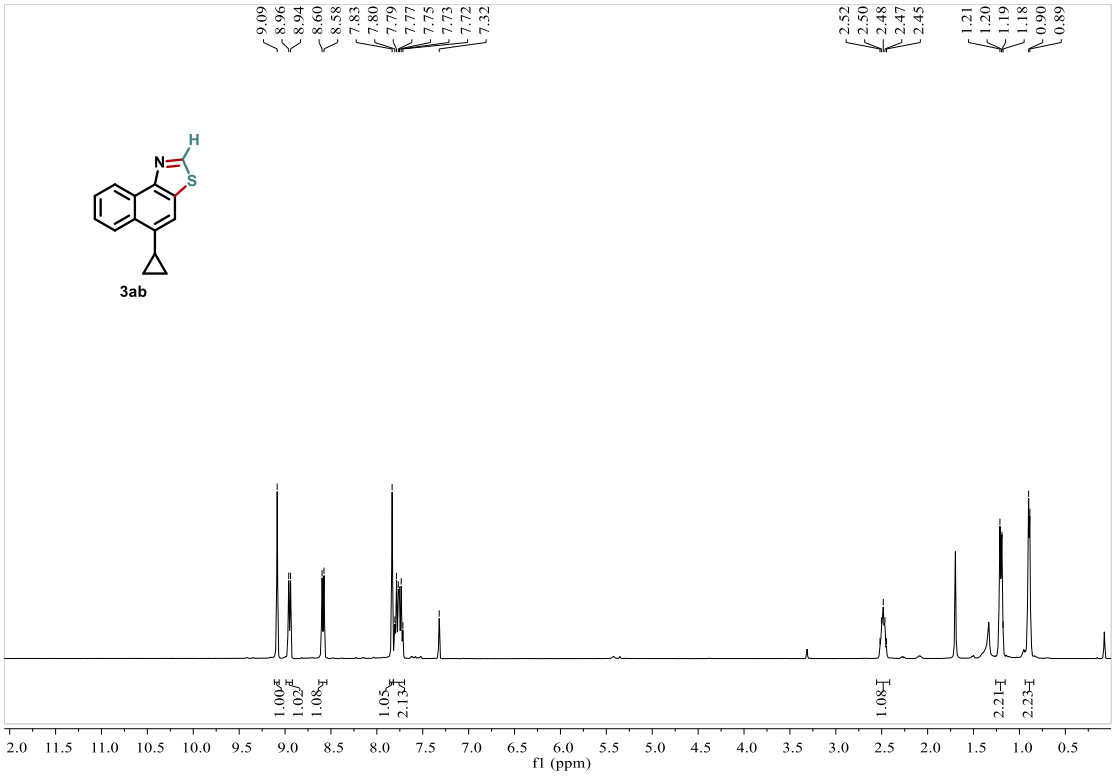
^{1}H NMR of **3aa** (400 MHz, $CDCl_3$)



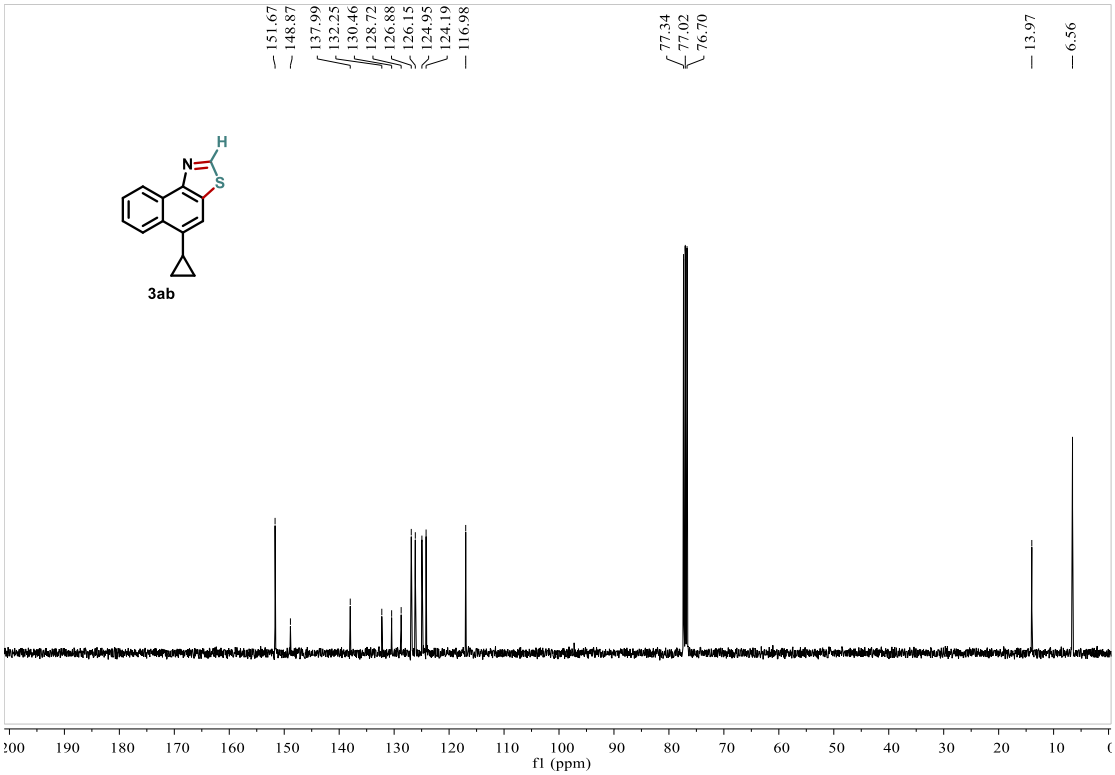
^{13}C NMR of **3aa** (100 MHz, $CDCl_3$)



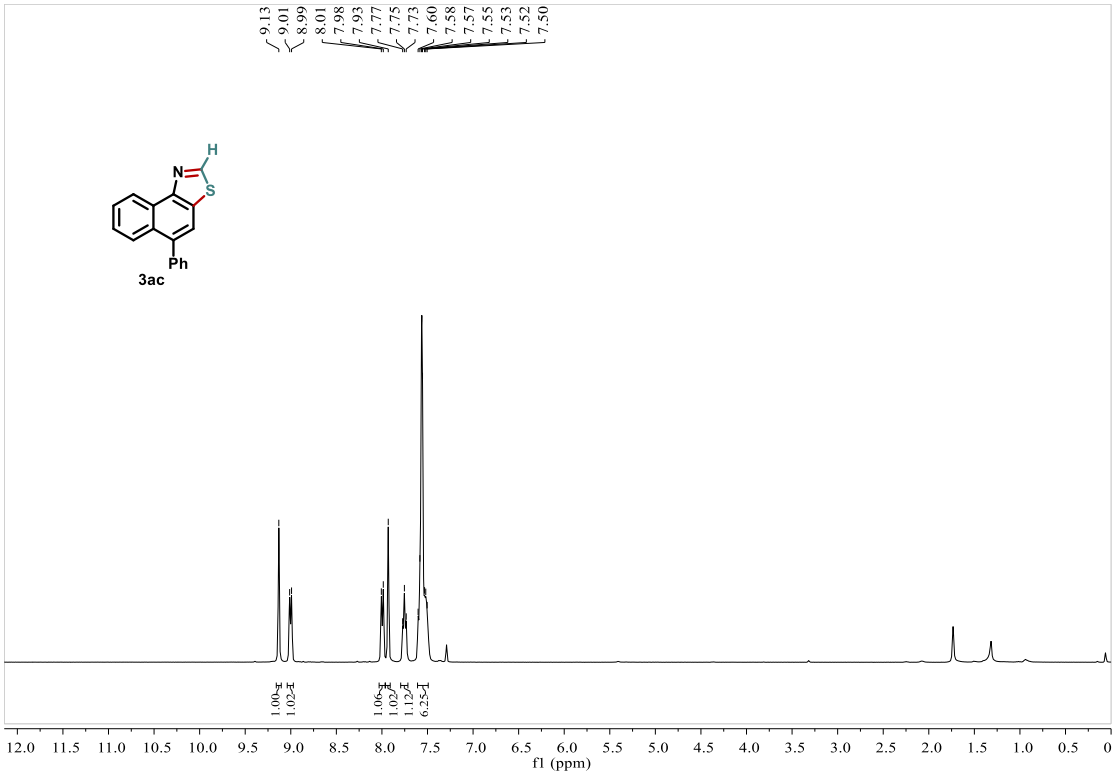
^{1}H NMR of **3ab** (400 MHz, $CDCl_3$)



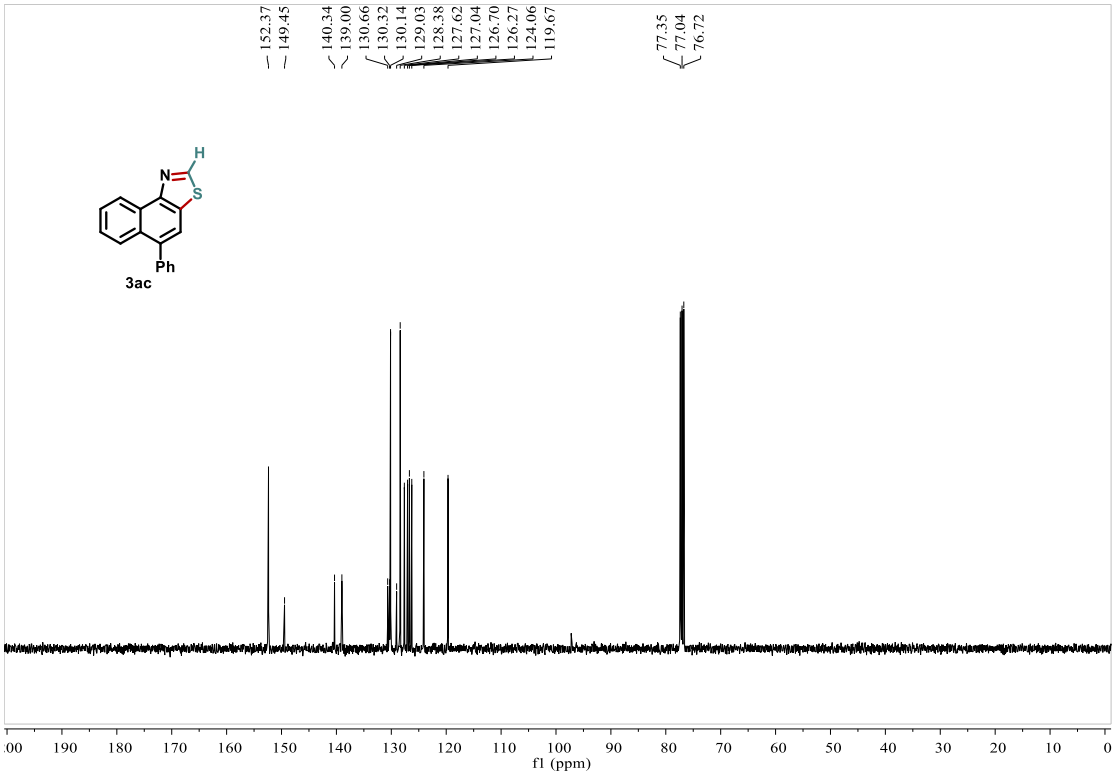
^{13}C NMR of **3ab** (100 MHz, $CDCl_3$)



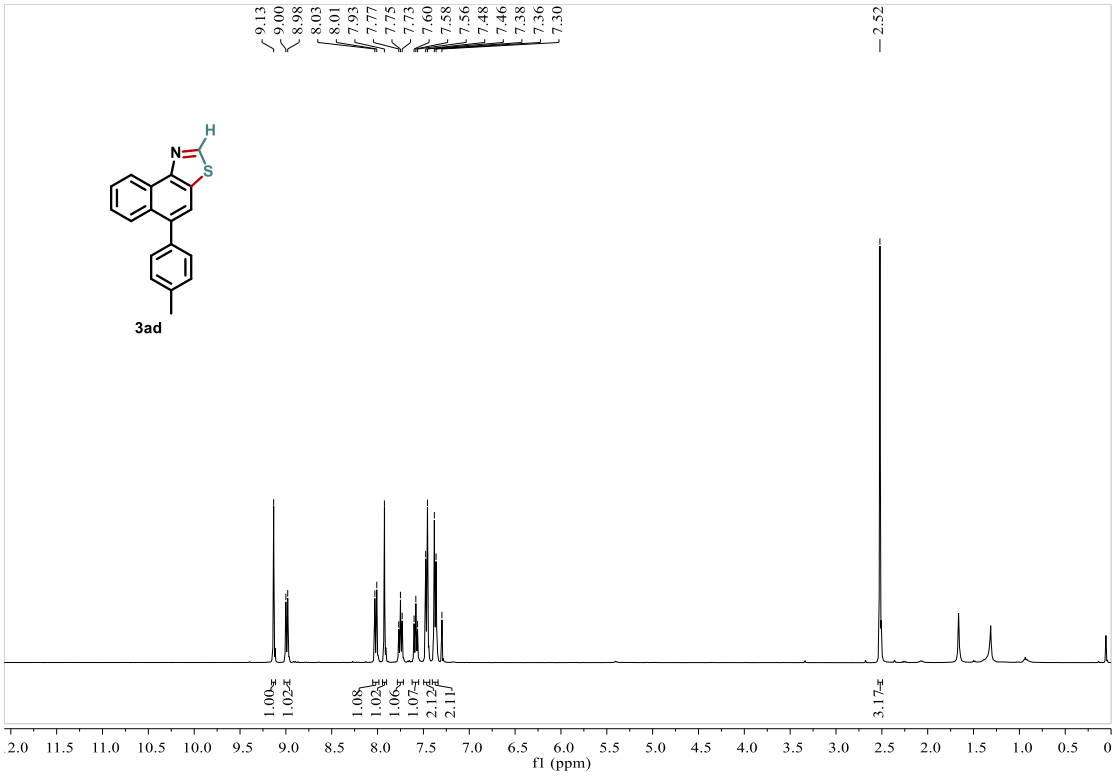
^{1}H NMR of **3ac** (400 MHz, $CDCl_3$)



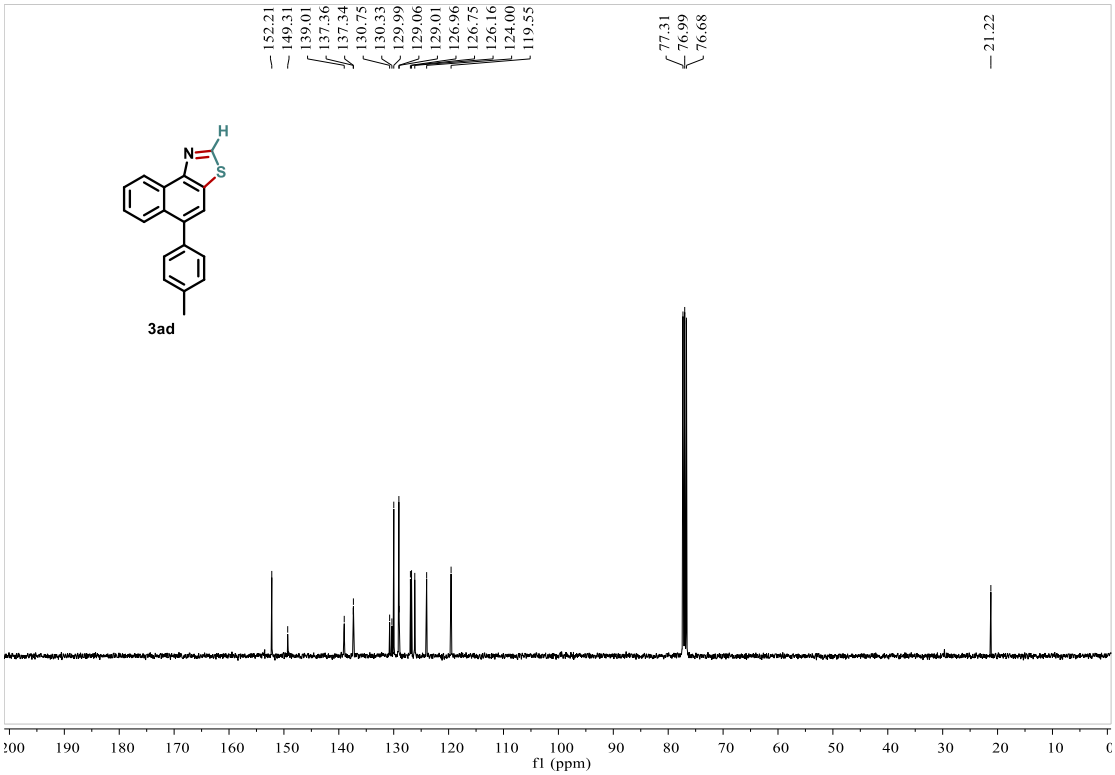
^{13}C NMR of **3ac** (100 MHz, $CDCl_3$)



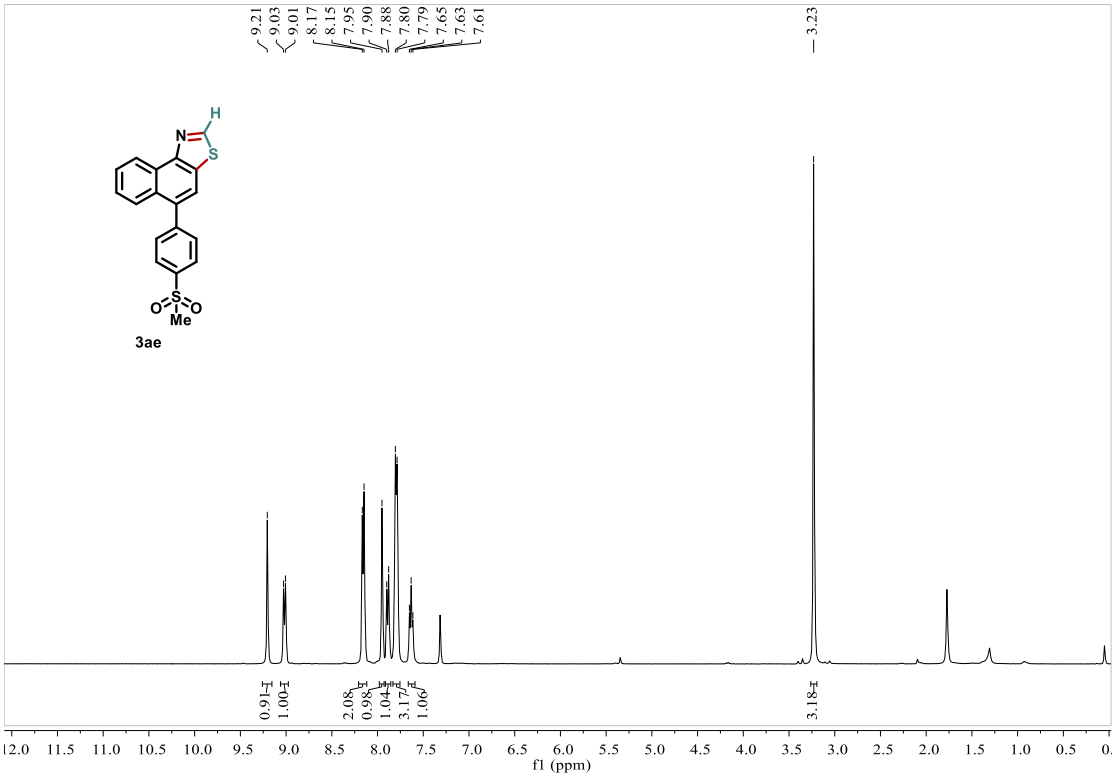
^{1}H NMR of **3ad** (400 MHz, $CDCl_3$)



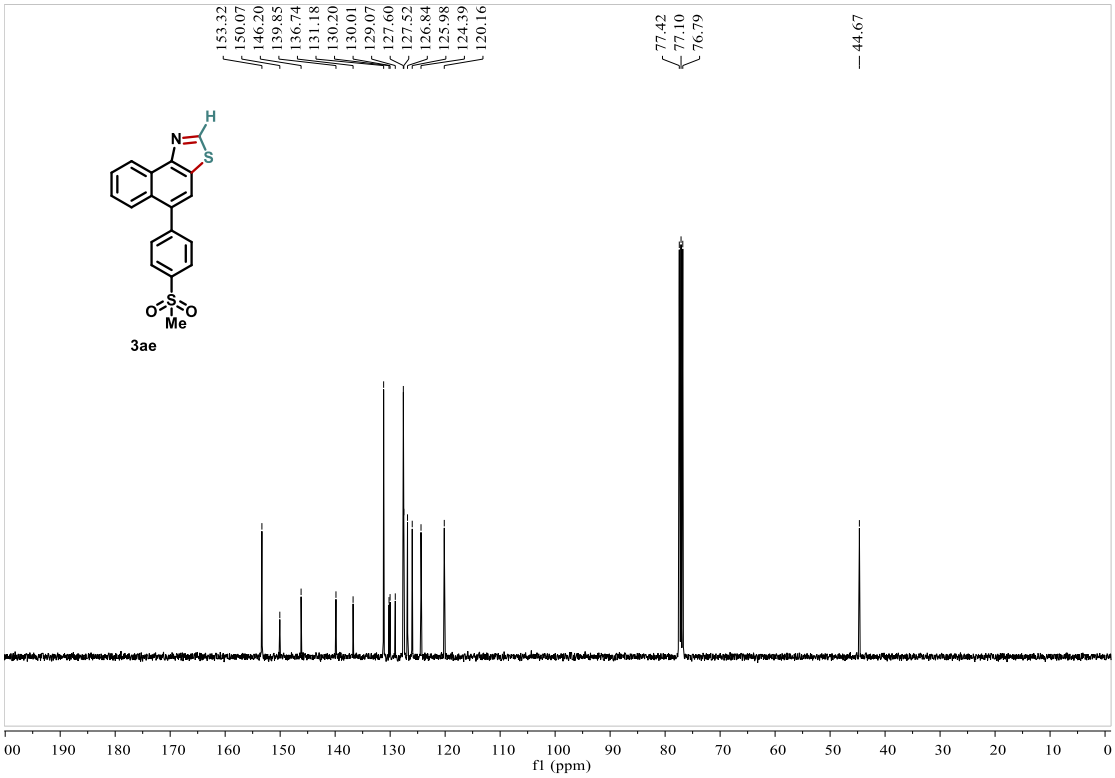
^{13}C NMR of **3ad** (100 MHz, $CDCl_3$)



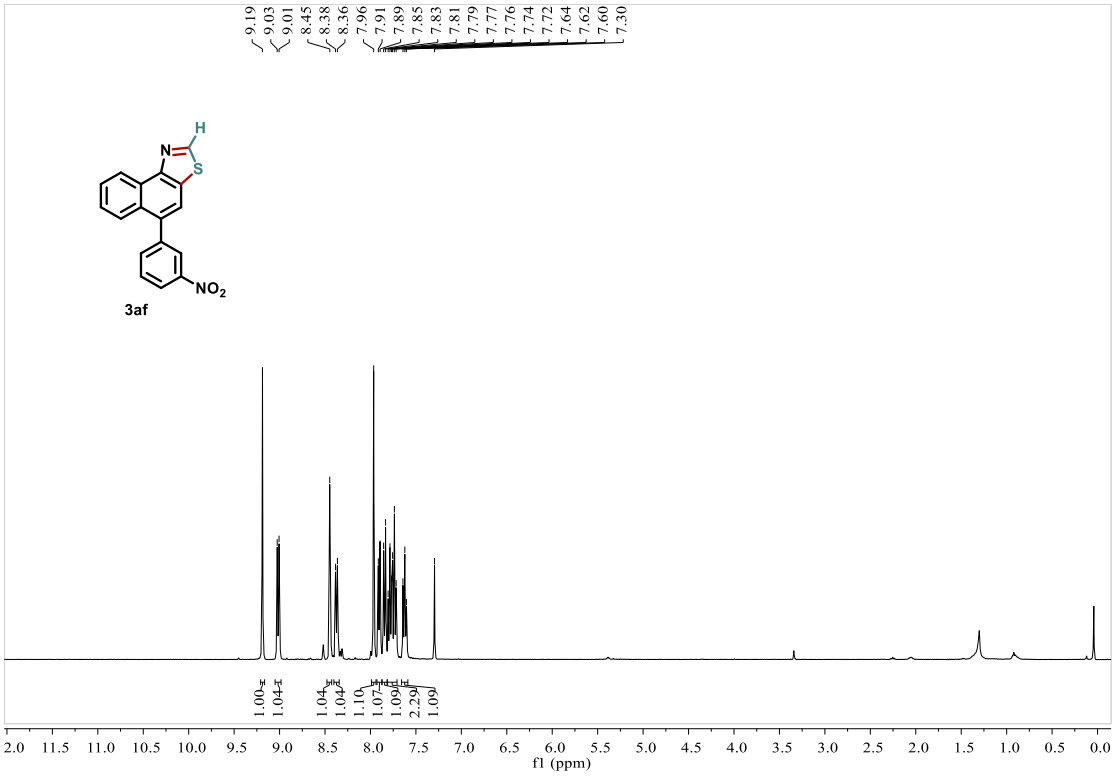
^{1}H NMR of **3ae** (400 MHz, $CDCl_3$)



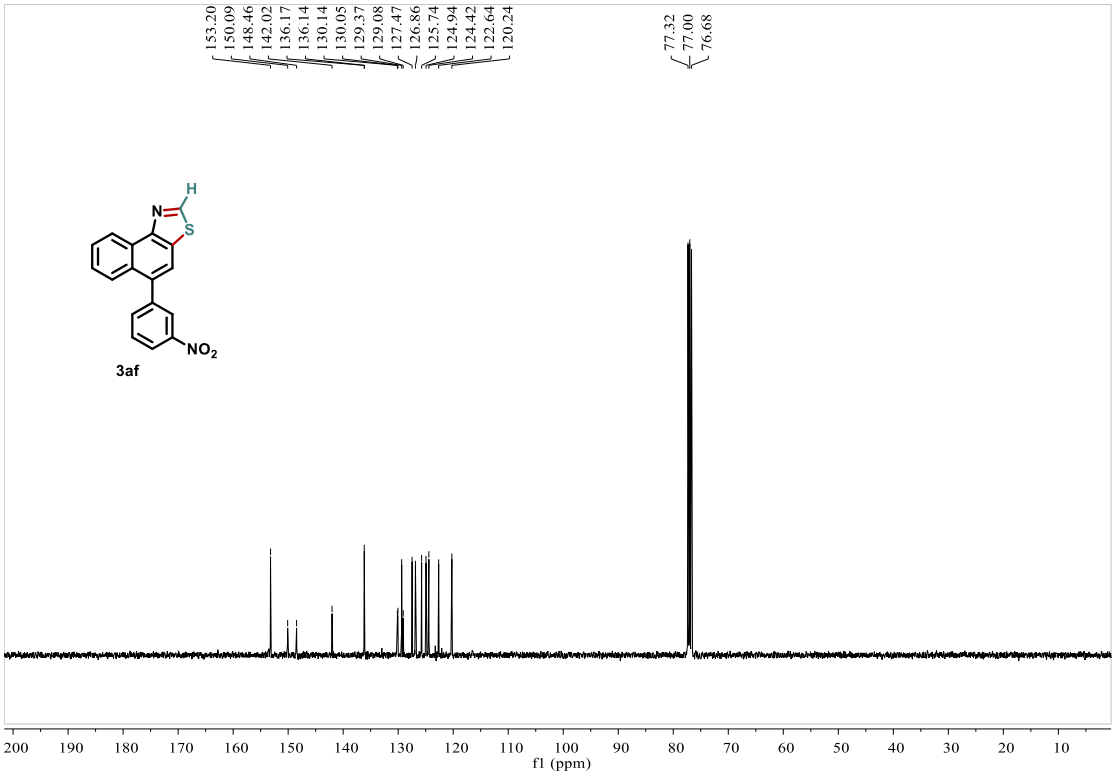
^{13}C NMR of **3ae** (100 MHz, $CDCl_3$)



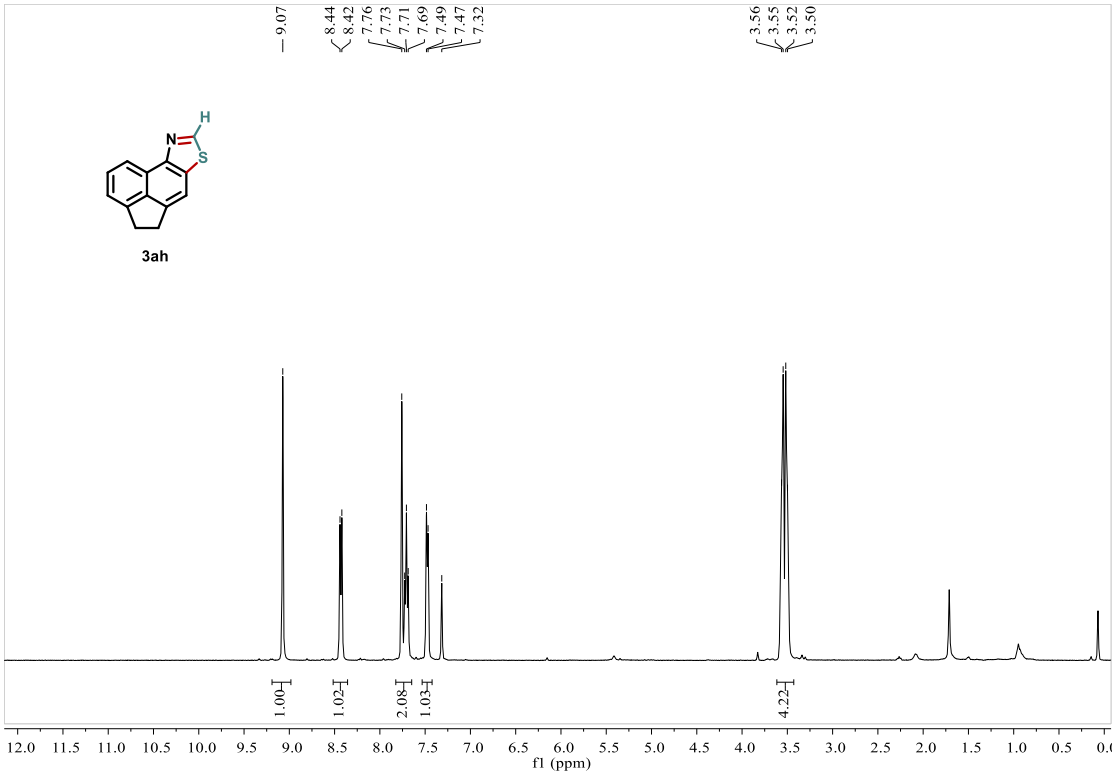
^{1}H NMR of **3af** (400 MHz, $CDCl_3$)



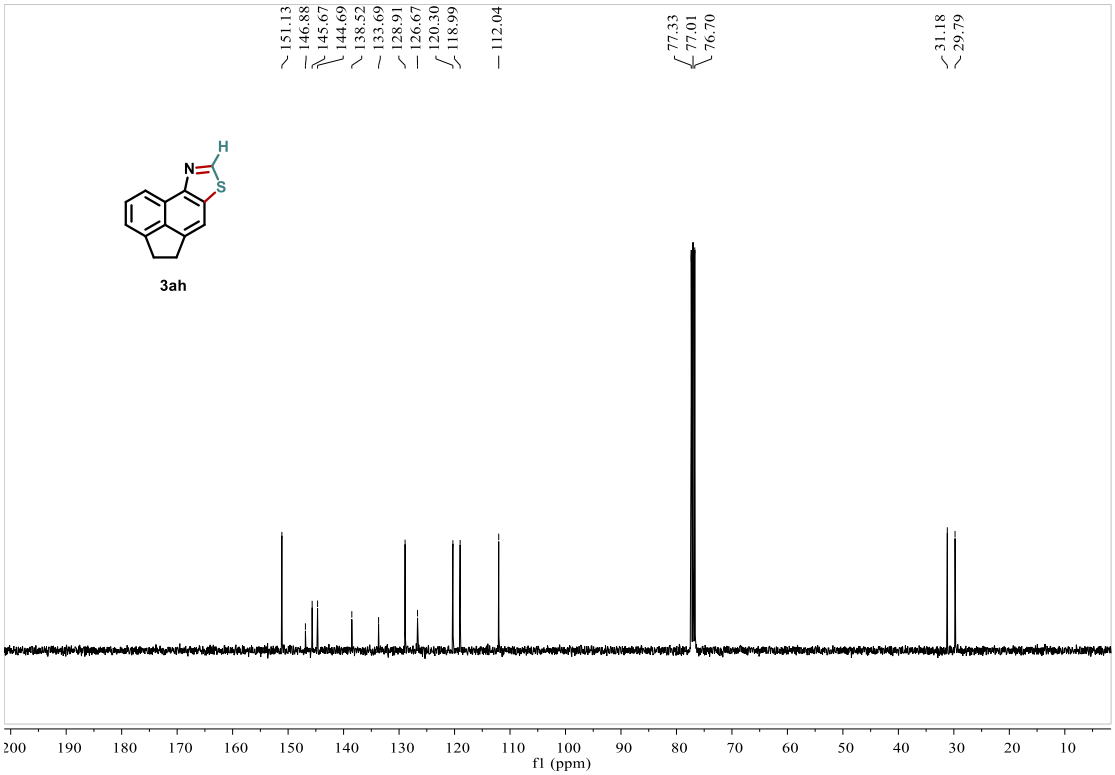
^{13}C NMR of **3af** (100 MHz, $CDCl_3$)



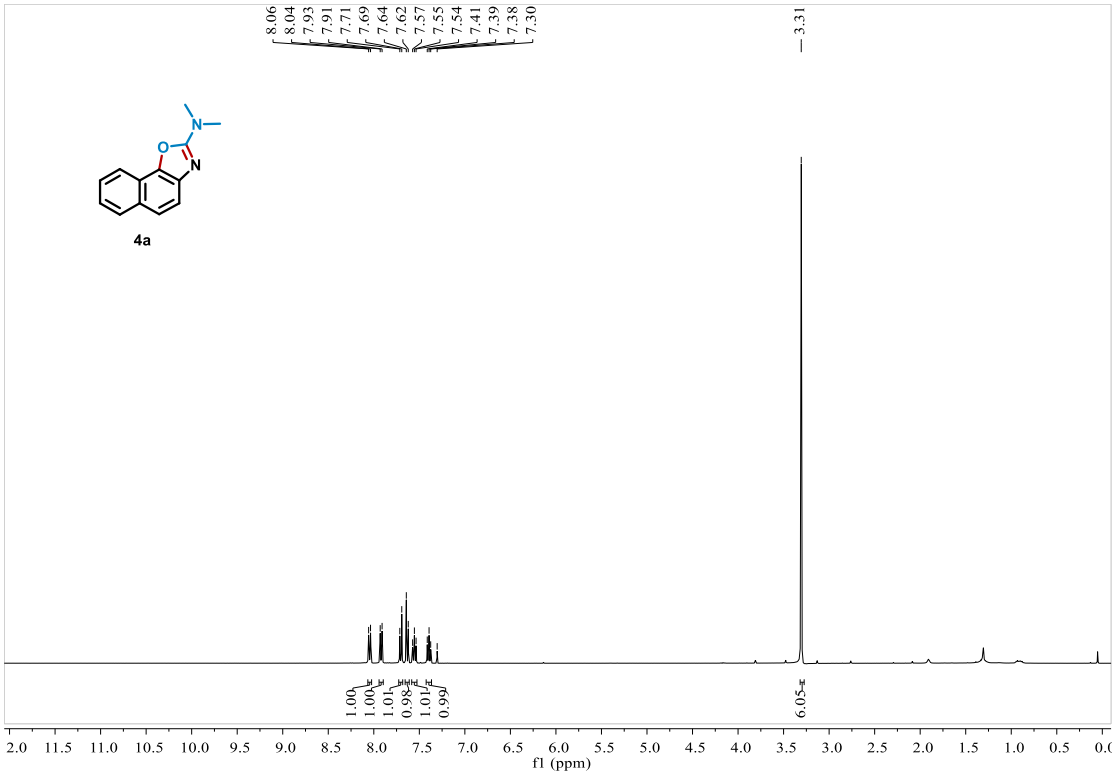
^{1}H NMR of **3ah** (400 MHz, $CDCl_3$)



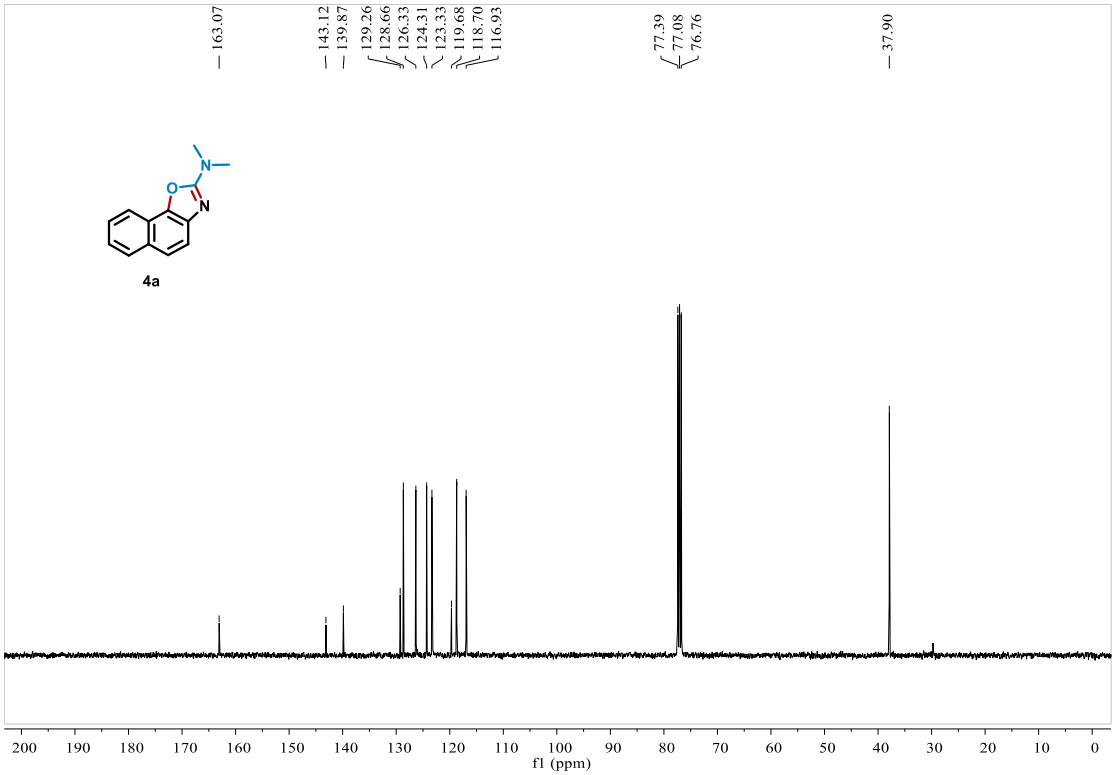
^{13}C NMR of **3ah** (100 MHz, $CDCl_3$)



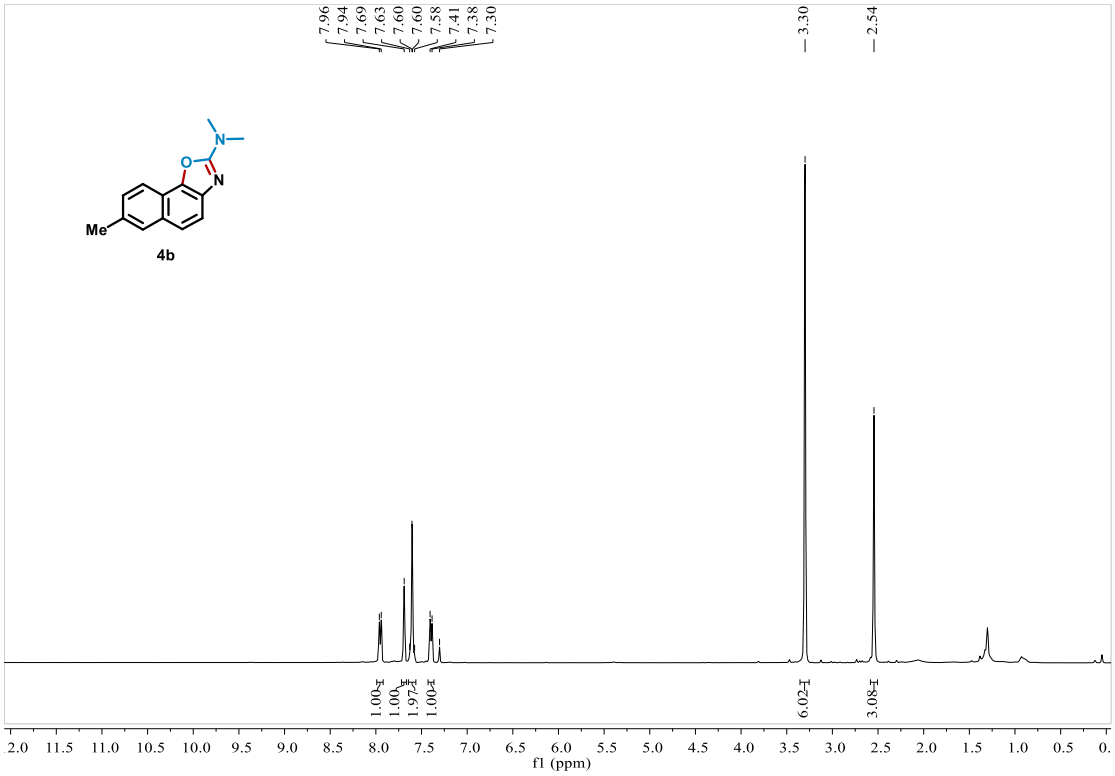
^{1}H NMR of **4a** (400 MHz, $CDCl_3$)



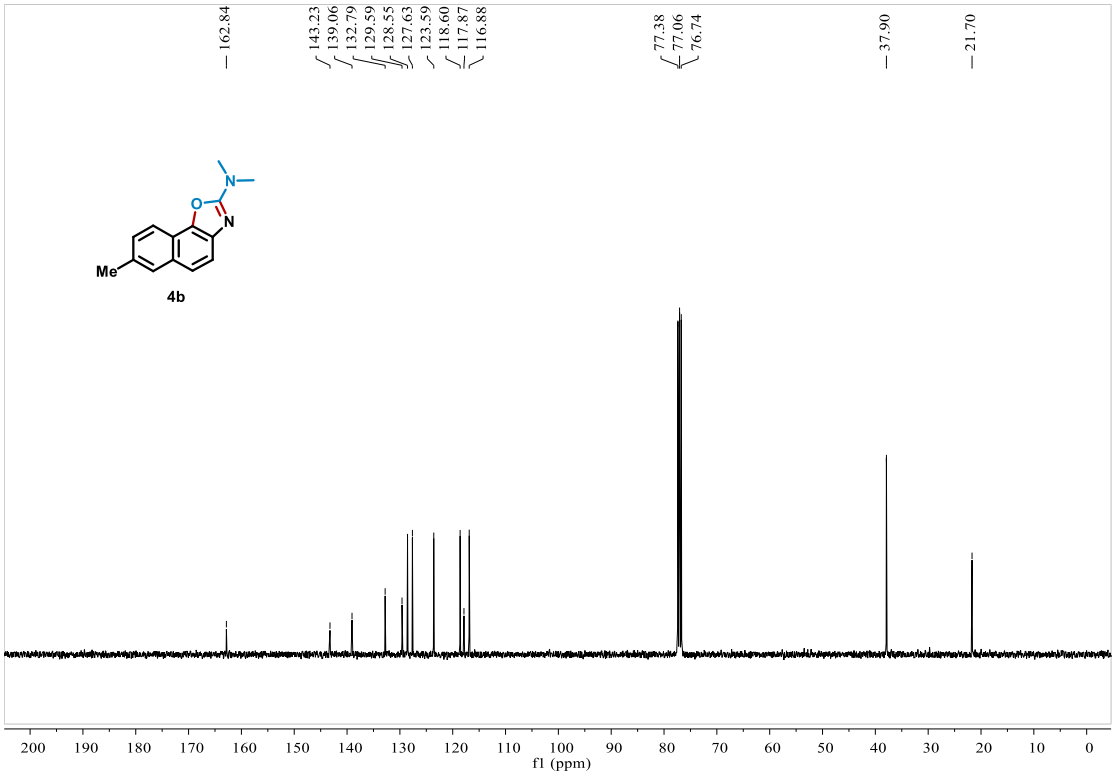
^{13}C NMR of **4a** (100 MHz, $CDCl_3$)



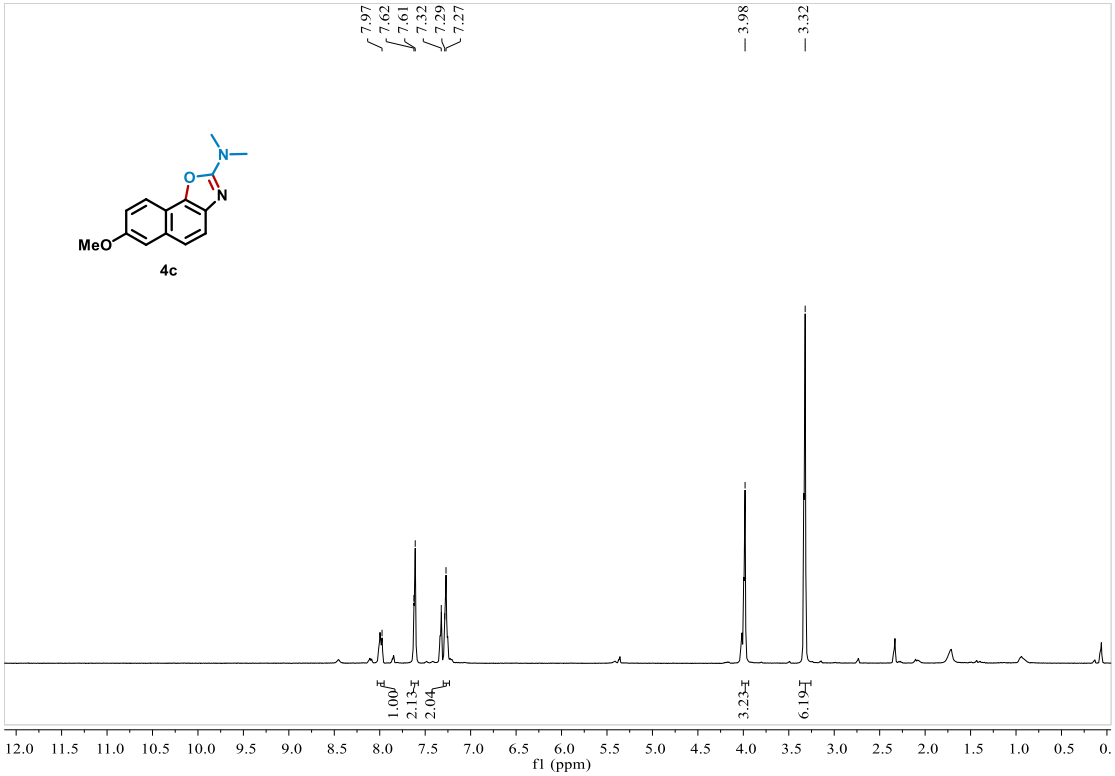
^{1}H NMR of **4b** (400 MHz, $CDCl_3$)



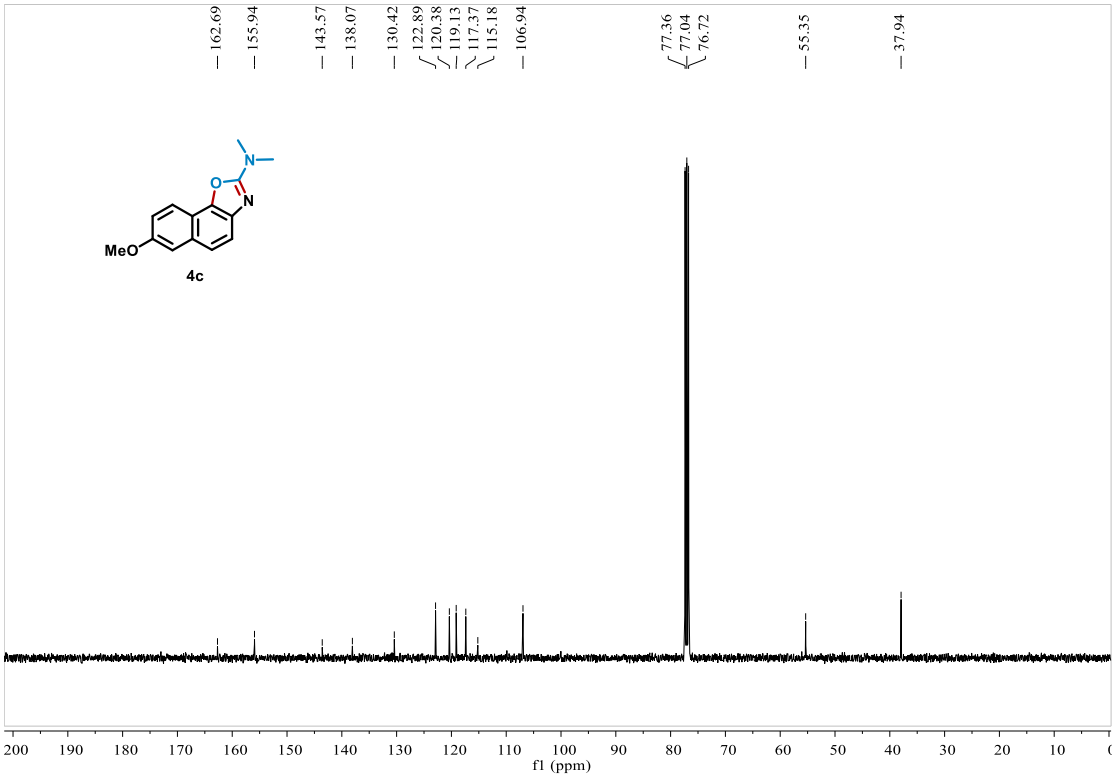
^{13}C NMR of **4b** (100 MHz, $CDCl_3$)



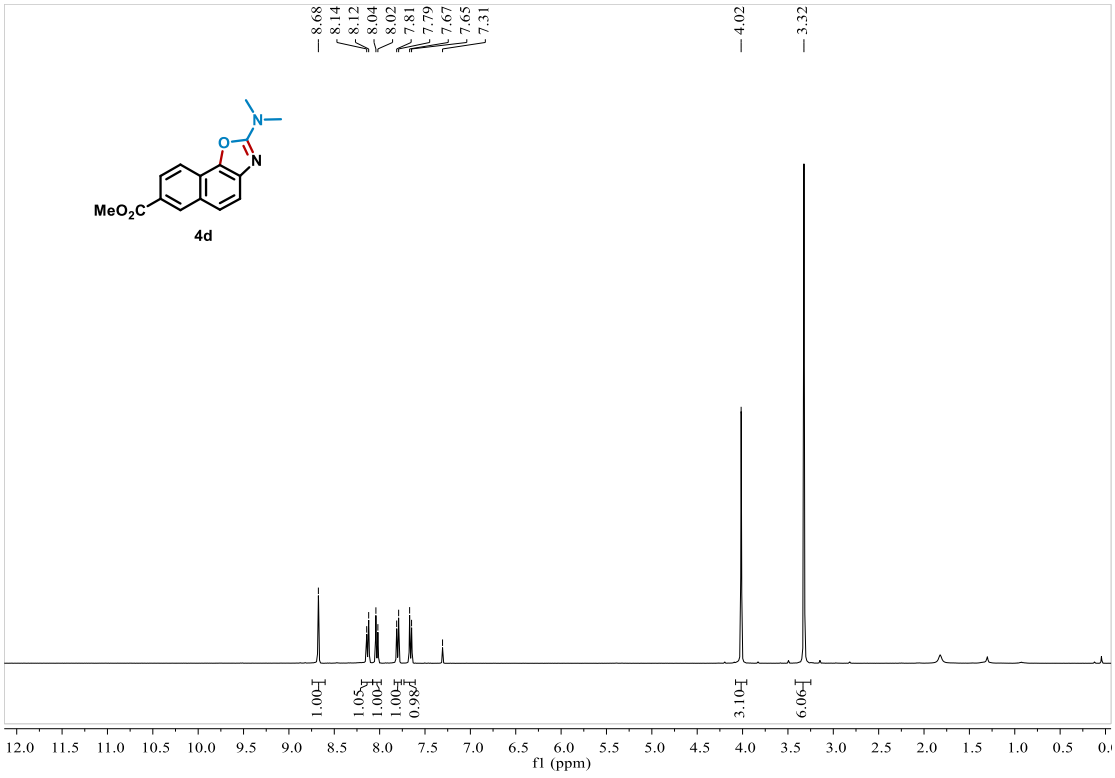
^{1}H NMR of **4c** (400 MHz, $CDCl_3$)



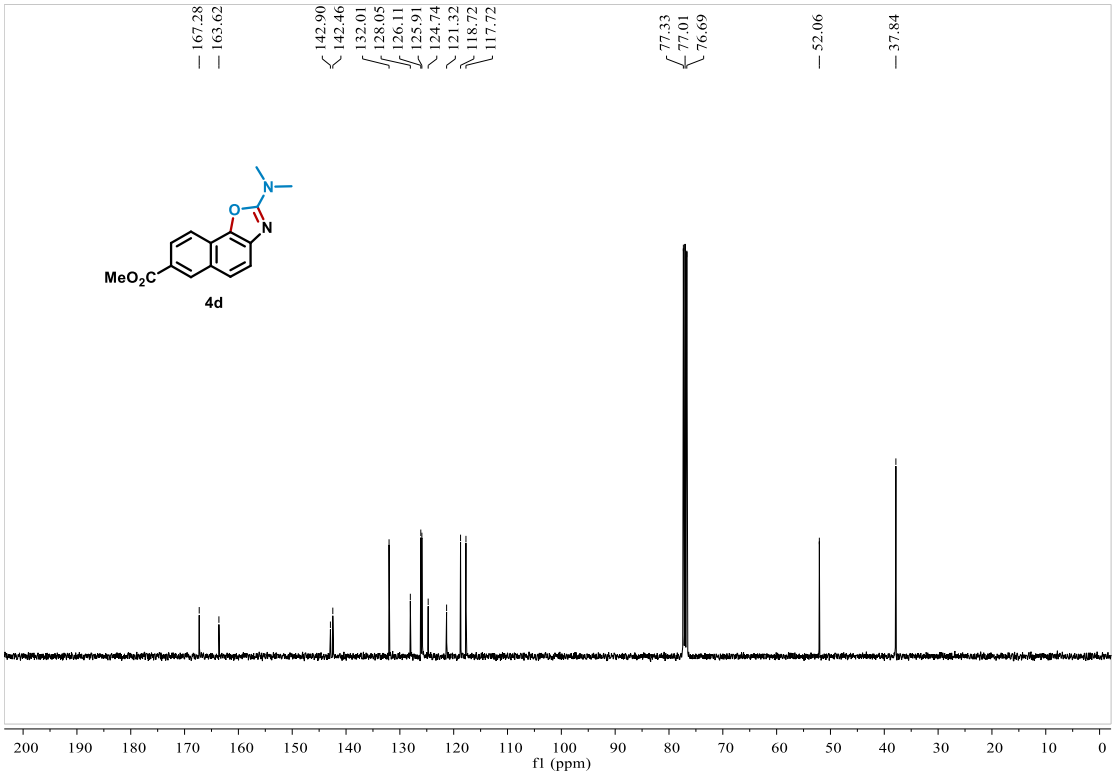
^{13}C NMR of **4c** (100 MHz, $CDCl_3$)



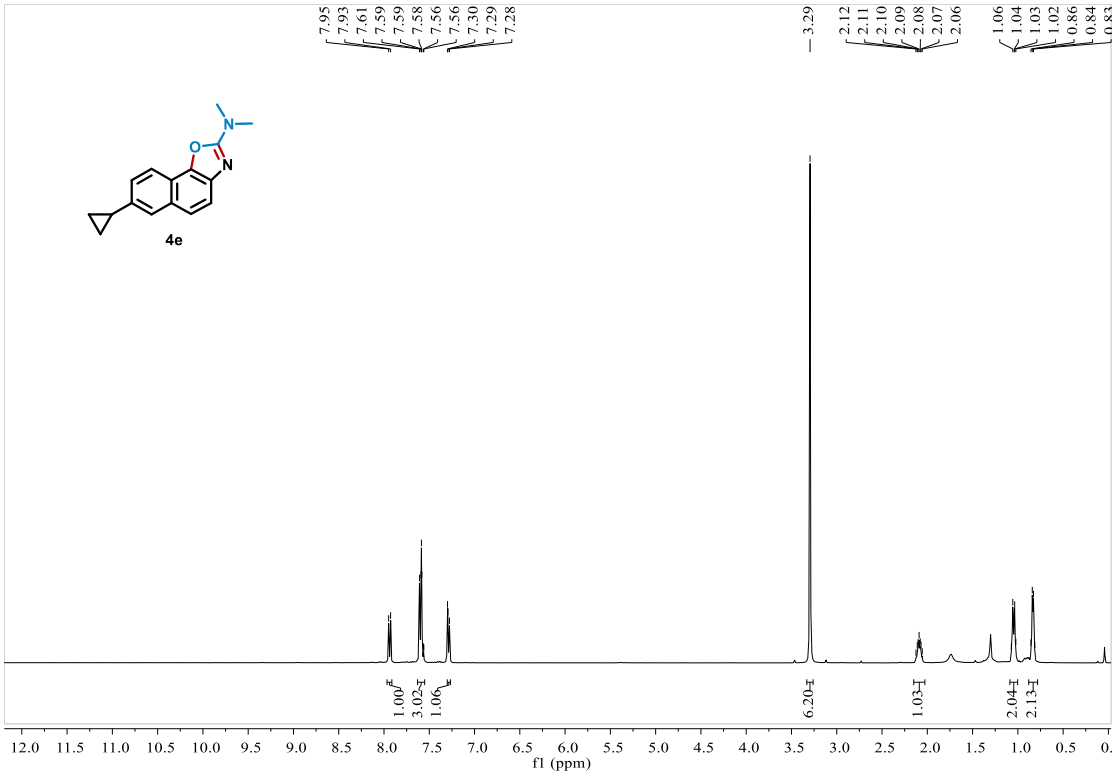
^{1}H NMR of **4d** (400 MHz, $CDCl_3$)



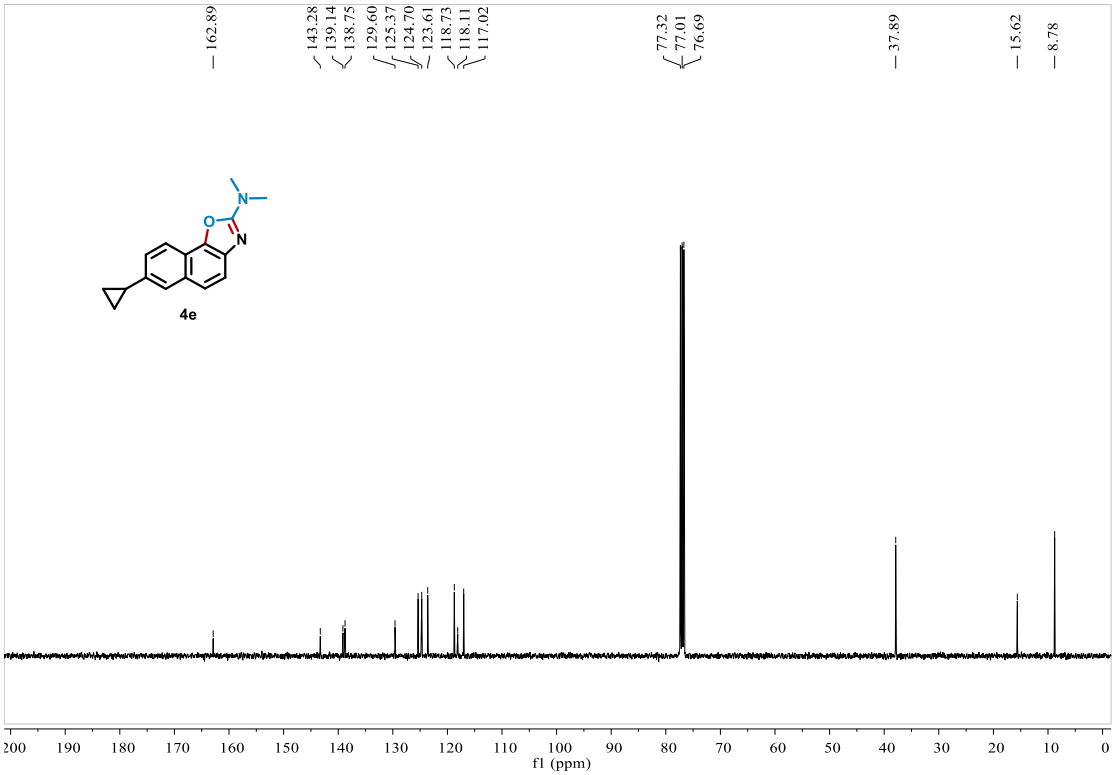
^{13}C NMR of **4d** (100 MHz, $CDCl_3$)



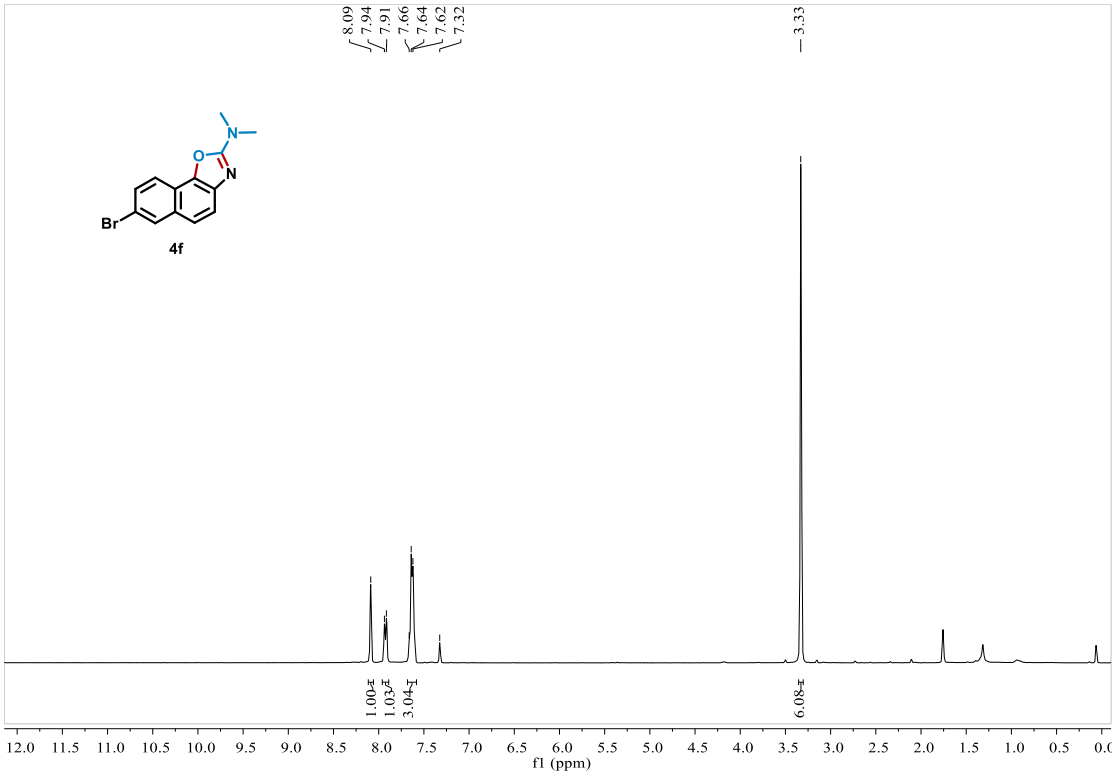
^{1}H NMR of **4e** (400 MHz, $CDCl_3$)



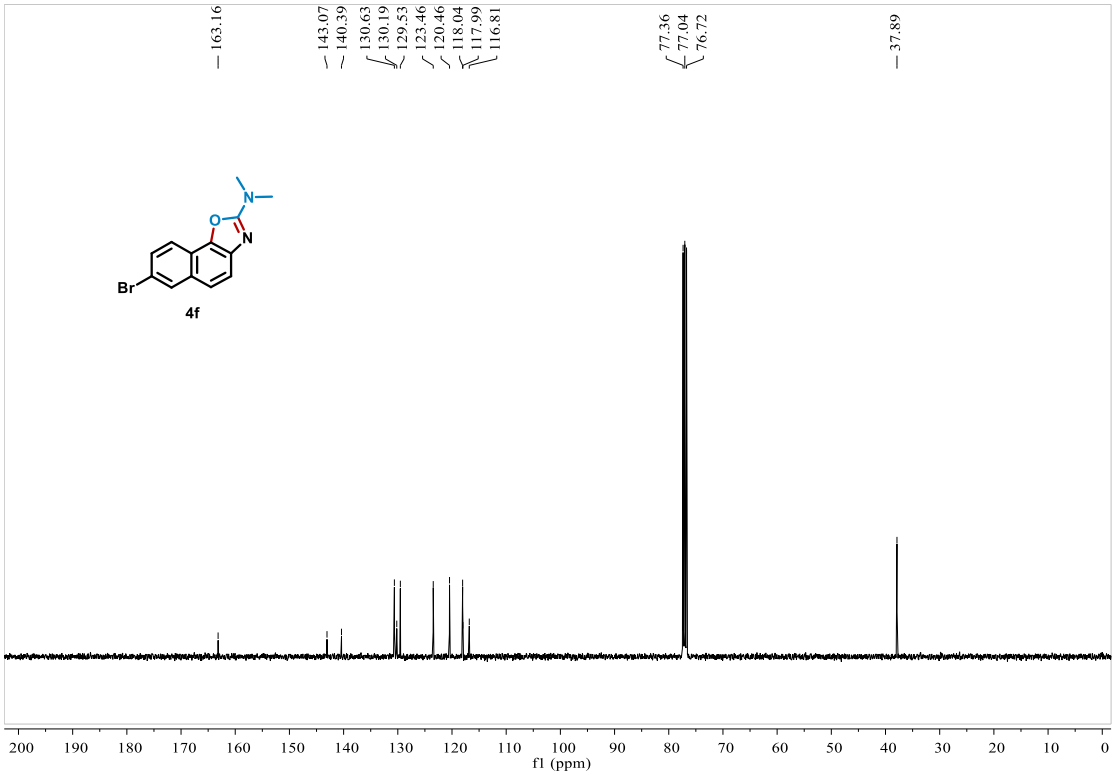
^{13}C NMR of **4e** (100 MHz, $CDCl_3$)



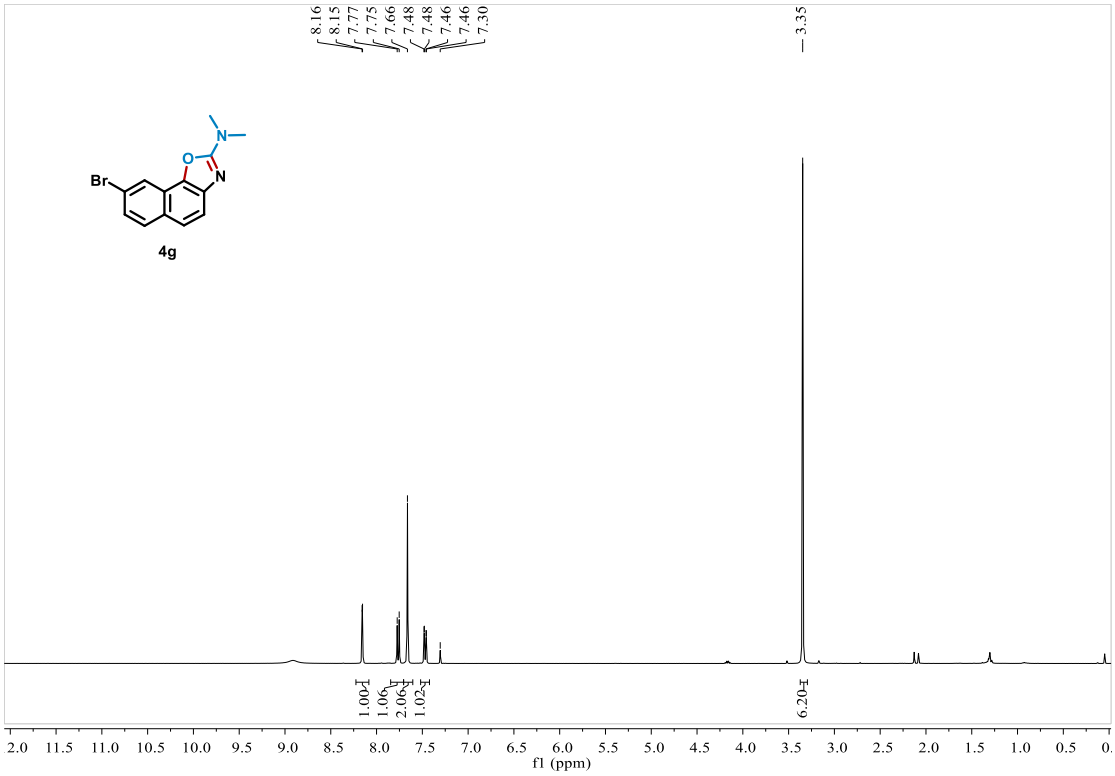
^{1}H NMR of **4f** (400 MHz, $CDCl_3$)



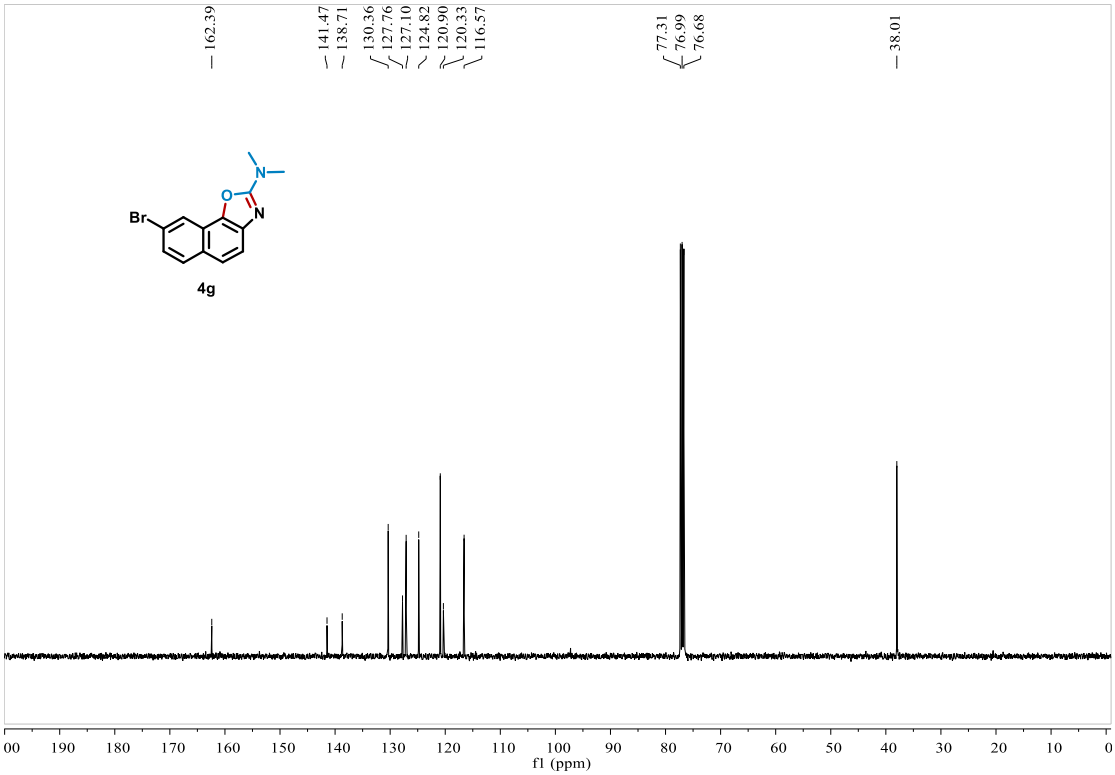
^{13}C NMR of **4f** (100 MHz, $CDCl_3$)



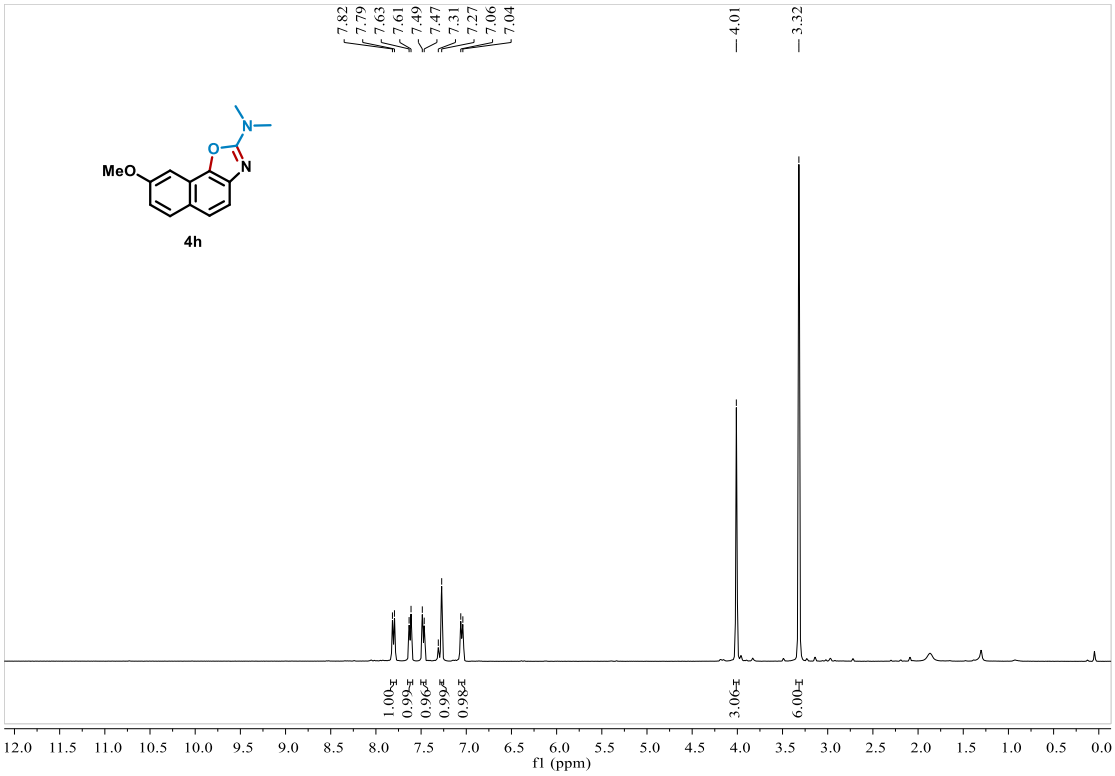
^{1}H NMR of **4g** (400 MHz, $CDCl_3$)



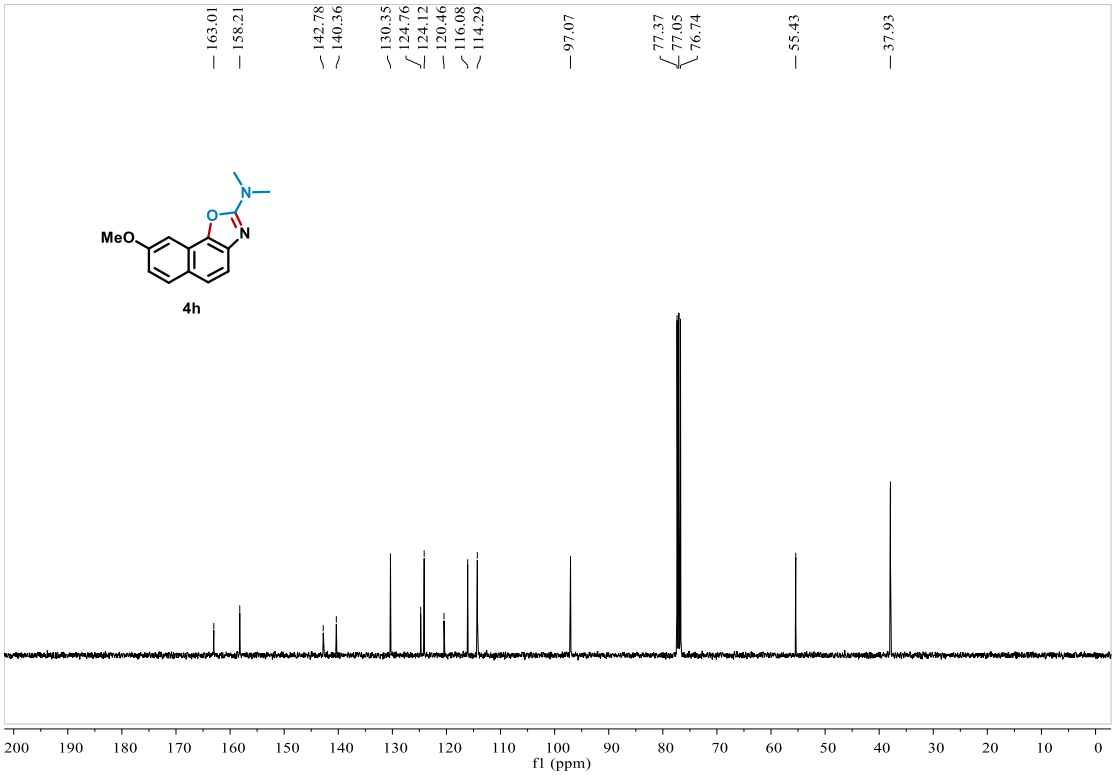
^{13}C NMR of **4g** (100 MHz, $CDCl_3$)



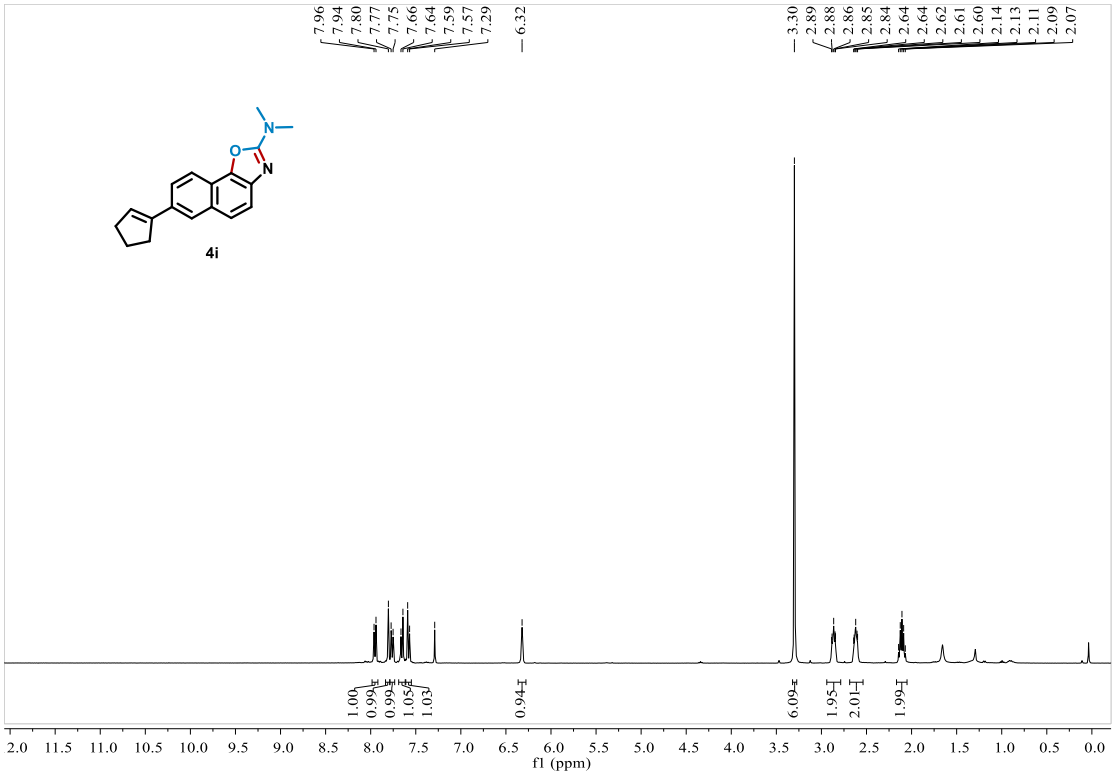
^{1}H NMR of **4h** (400 MHz, $CDCl_3$)



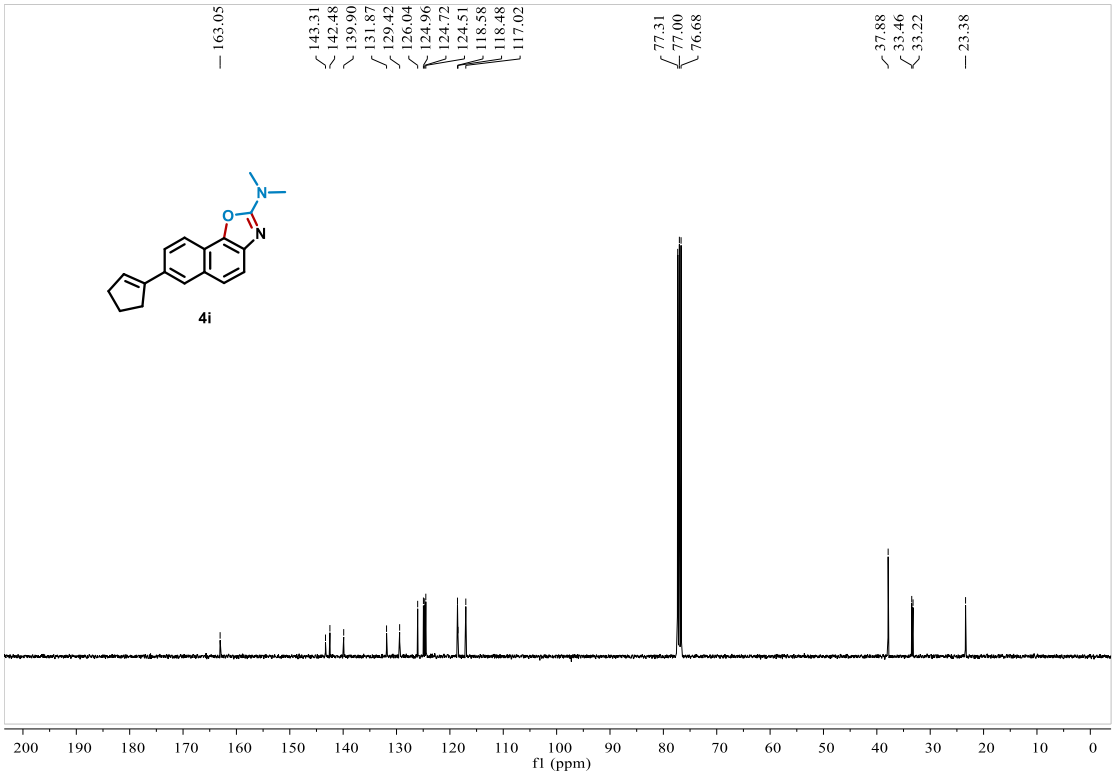
^{13}C NMR of **4h** (100 MHz, $CDCl_3$)



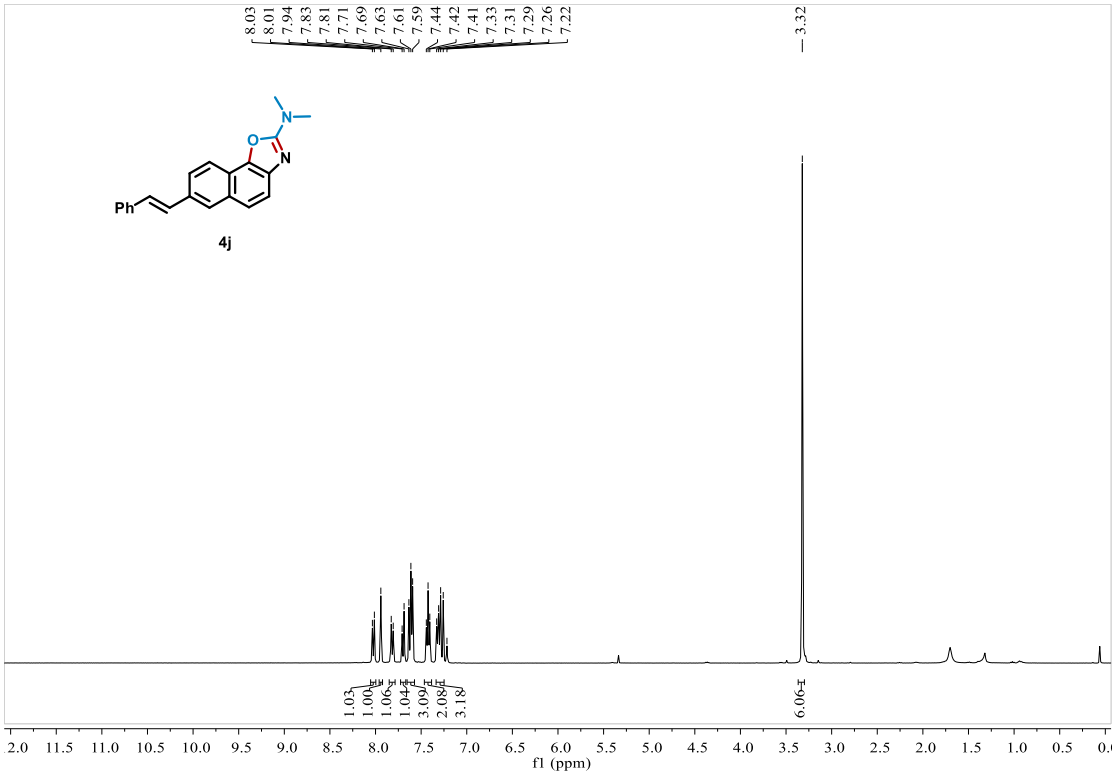
^{1}H NMR of **4i** (400 MHz, $CDCl_3$)



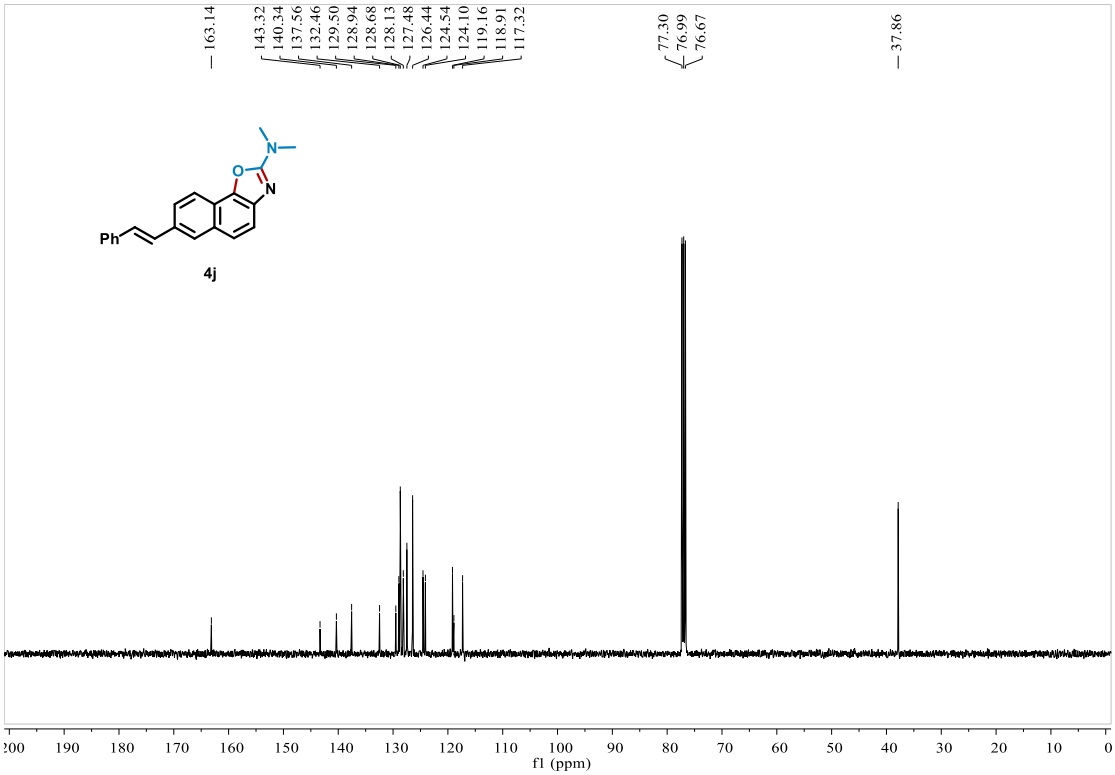
^{13}C NMR of **4i** (100 MHz, $CDCl_3$)



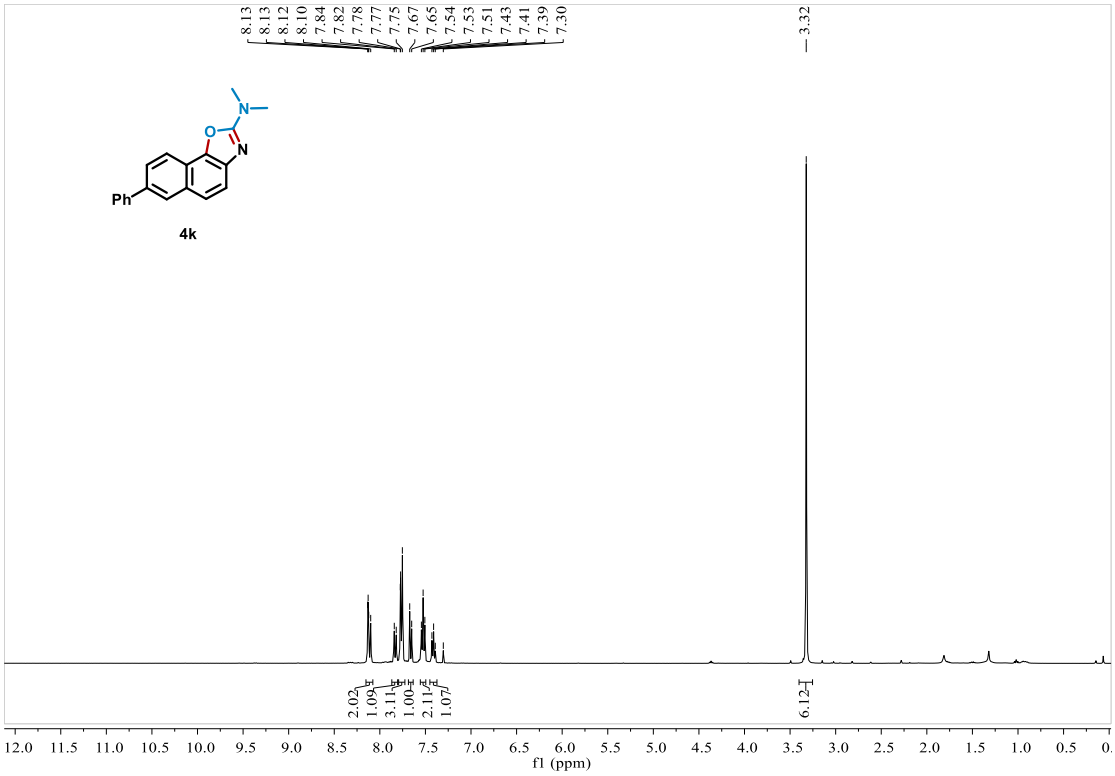
^{1}H NMR of **4j** (400 MHz, $CDCl_3$)



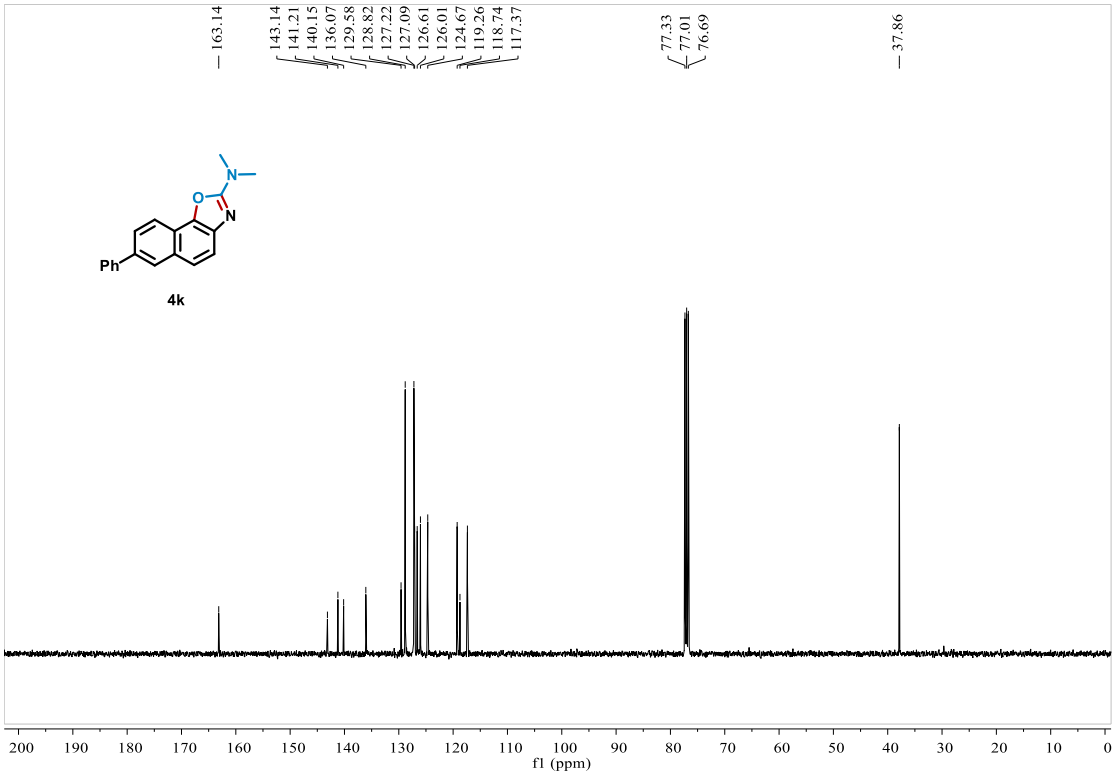
^{13}C NMR of **4j** (100 MHz, $CDCl_3$)



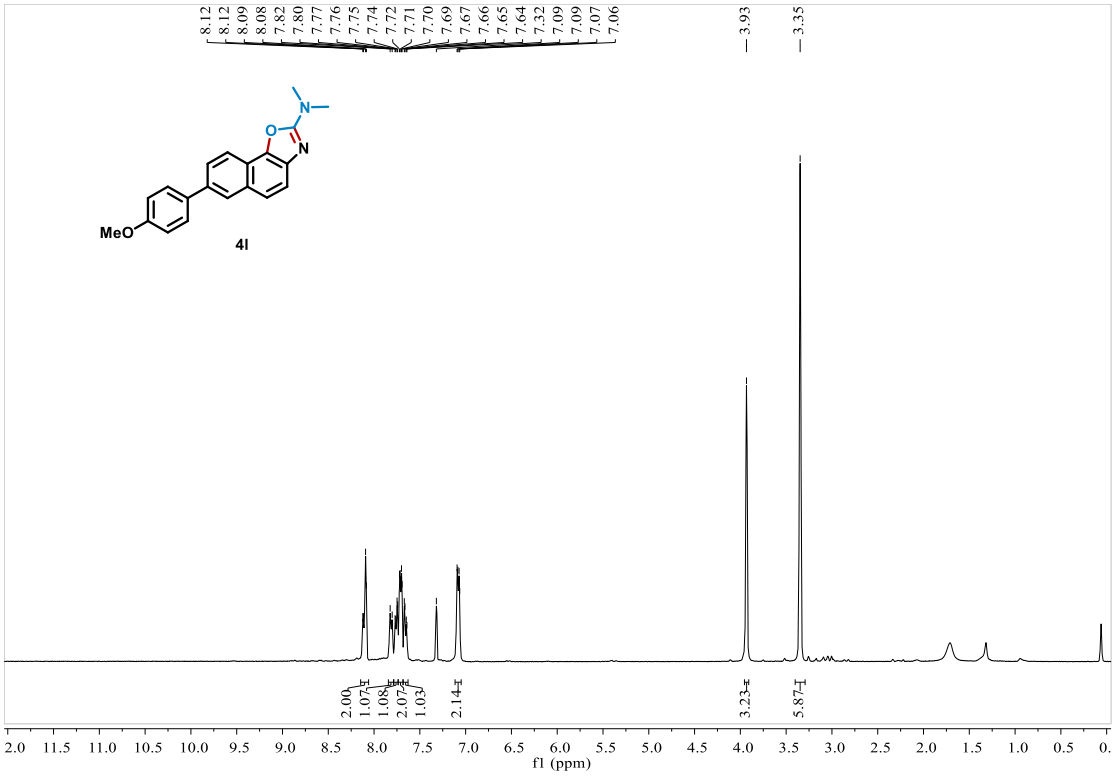
^{1}H NMR of **4k** (400 MHz, $CDCl_3$)



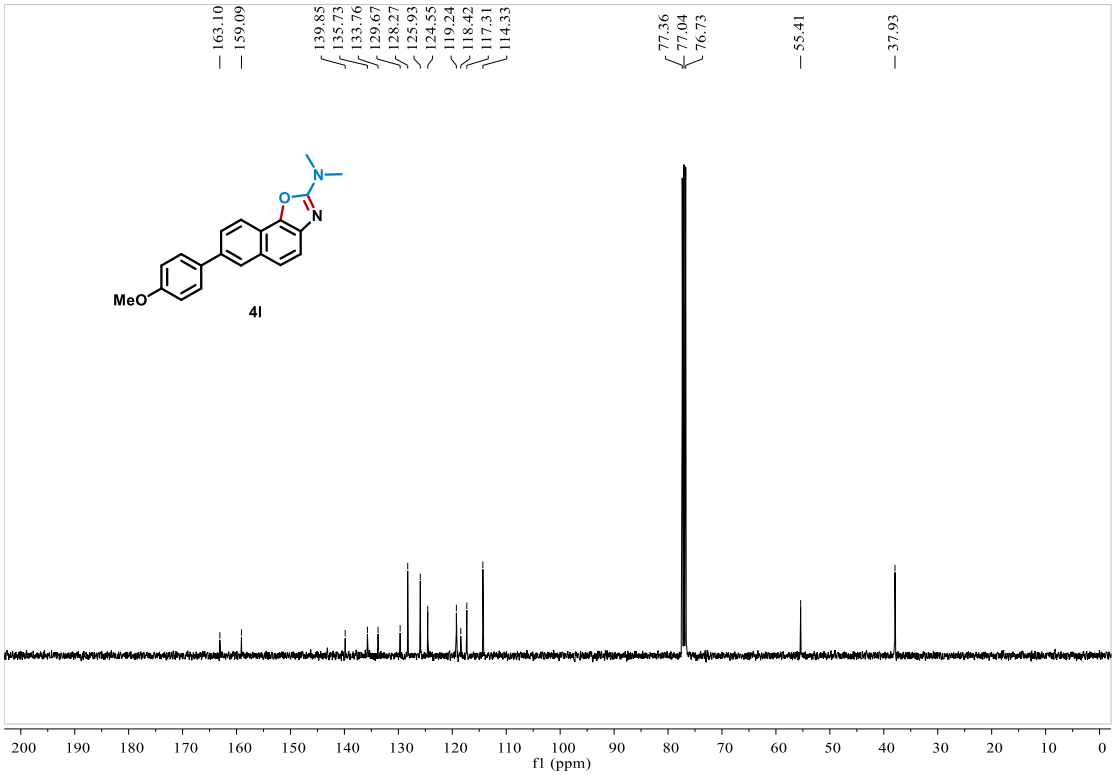
^{13}C NMR of **4k** (100 MHz, $CDCl_3$)



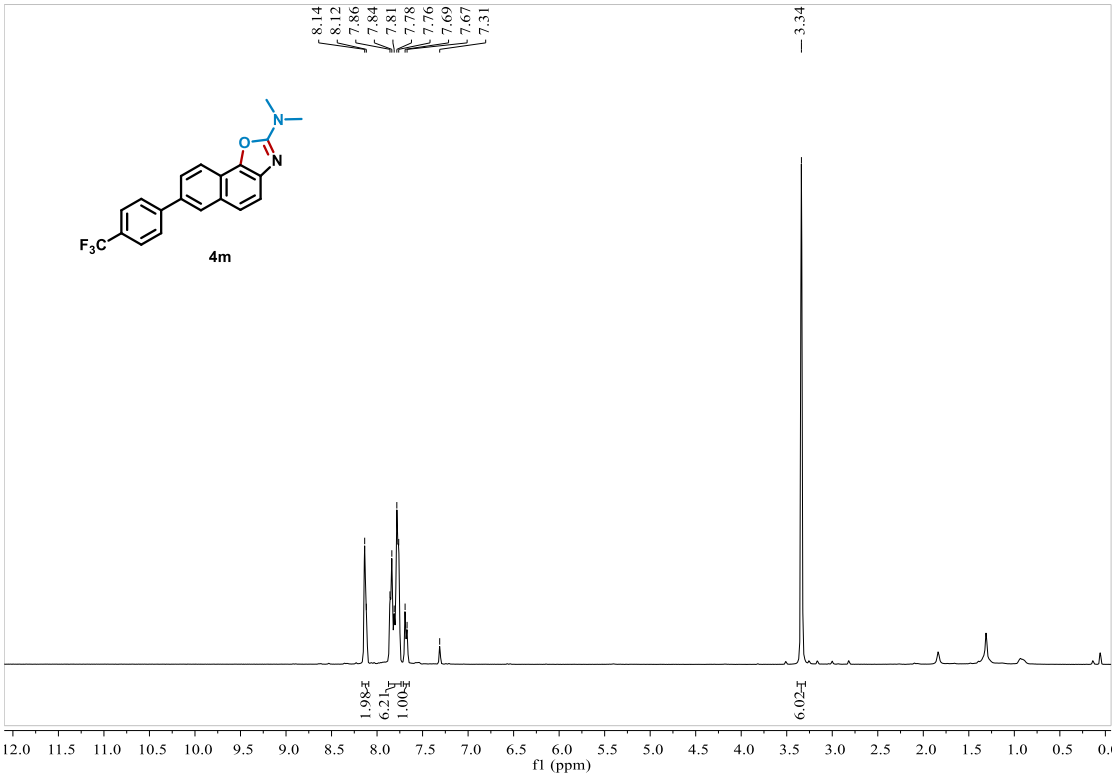
^{1}H NMR of **4l** (400 MHz, $CDCl_3$)



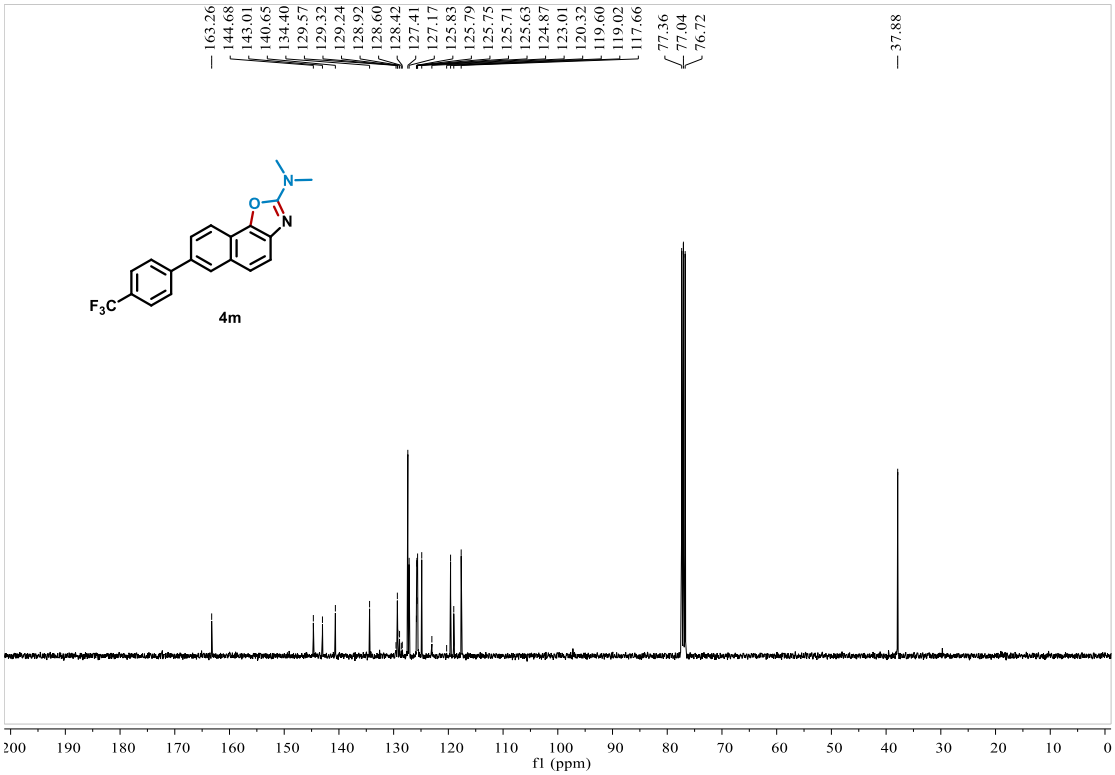
^{13}C NMR of **4l** (100 MHz, $CDCl_3$)



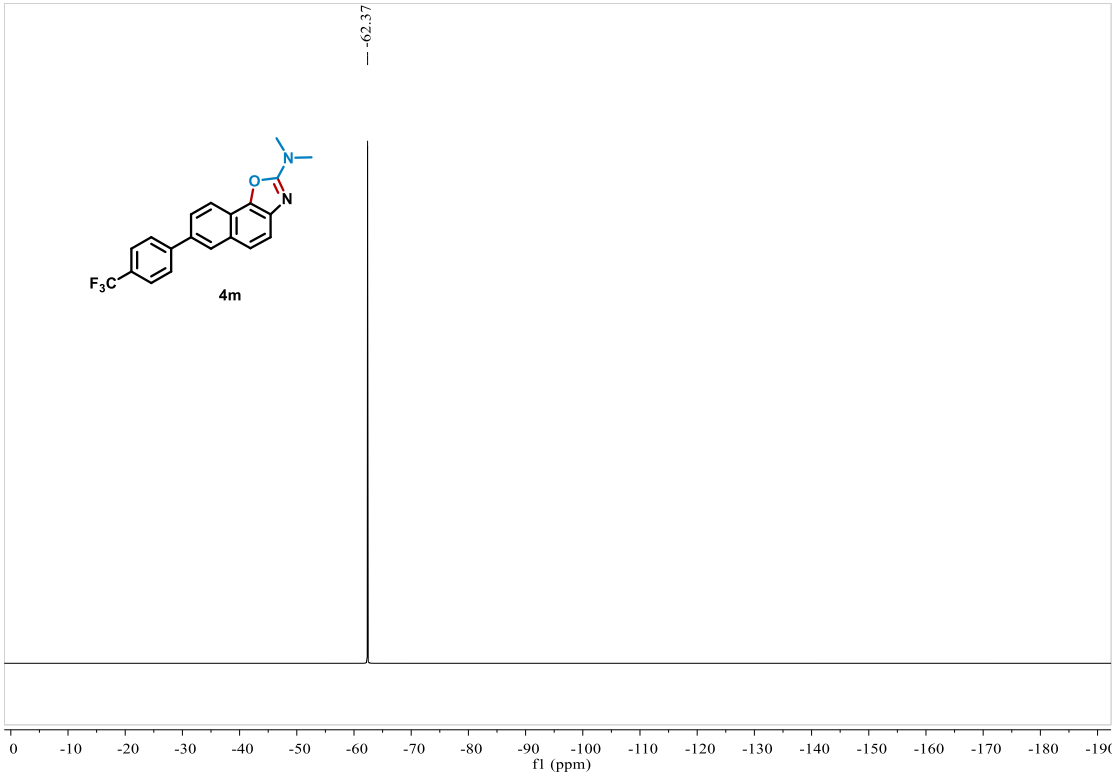
^{1}H NMR of **4m** (400 MHz, $CDCl_3$)



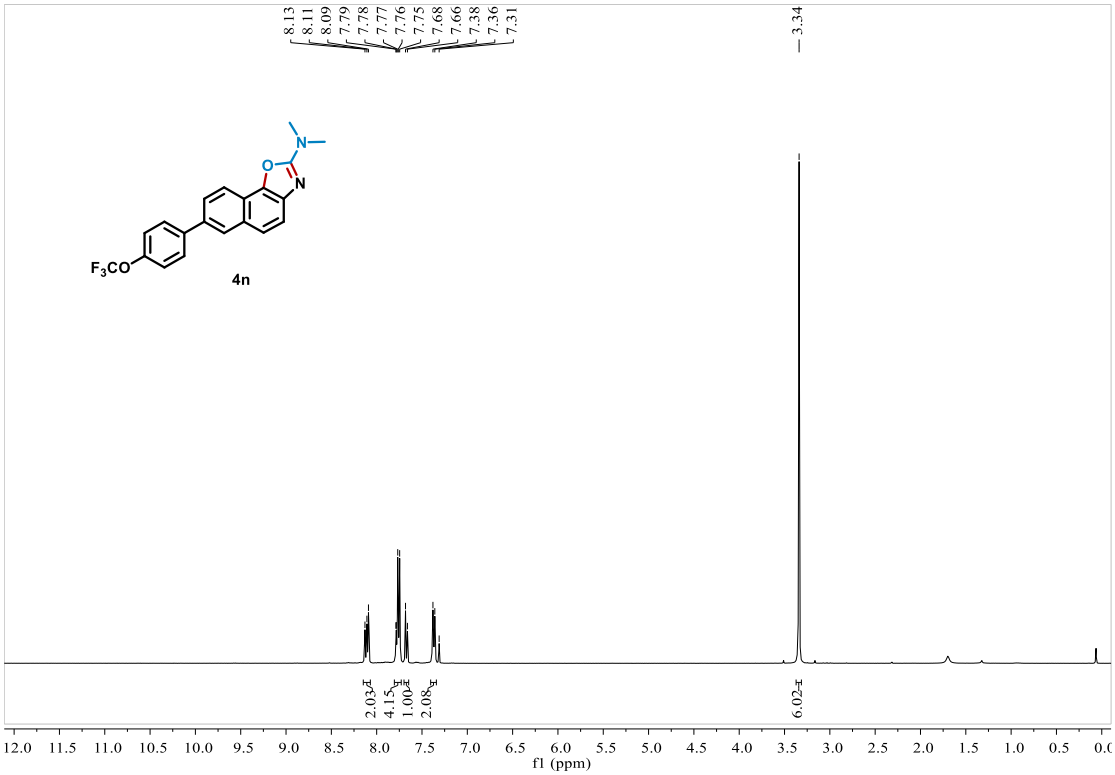
^{13}C NMR of **4m** (100 MHz, $CDCl_3$)



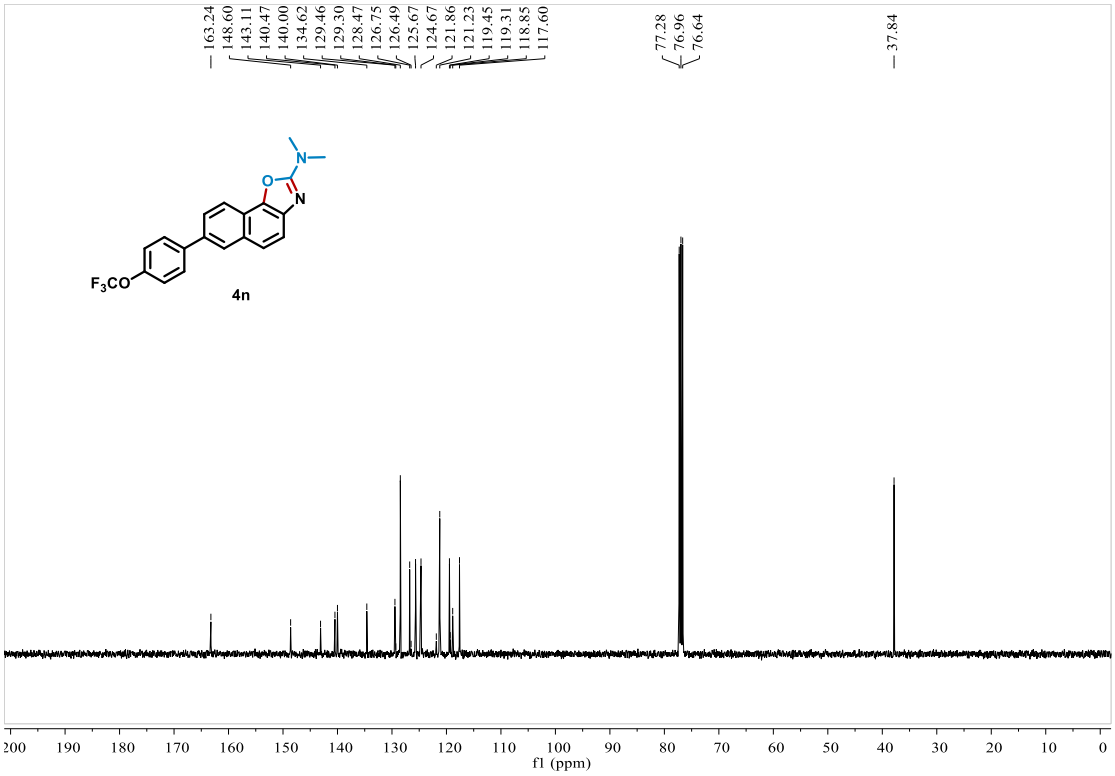
^{19}F NMR of **4m** (376 MHz, $CDCl_3$)



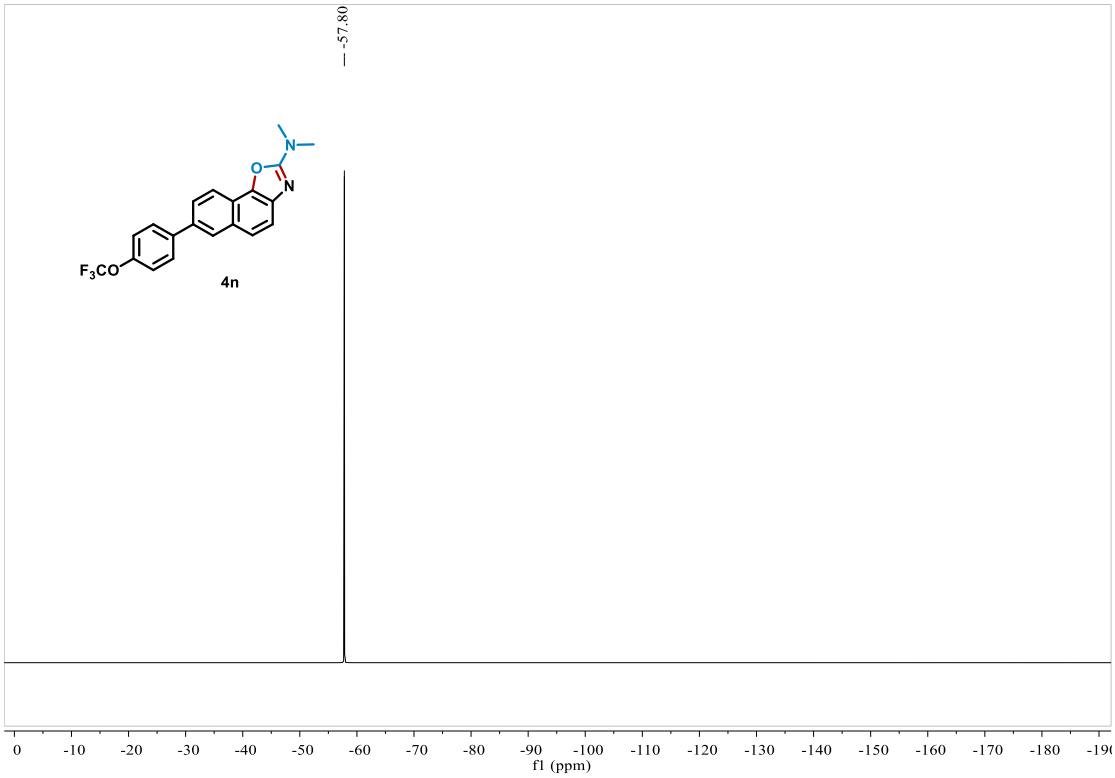
^{1}H NMR of **4n** (400 MHz, $CDCl_3$)



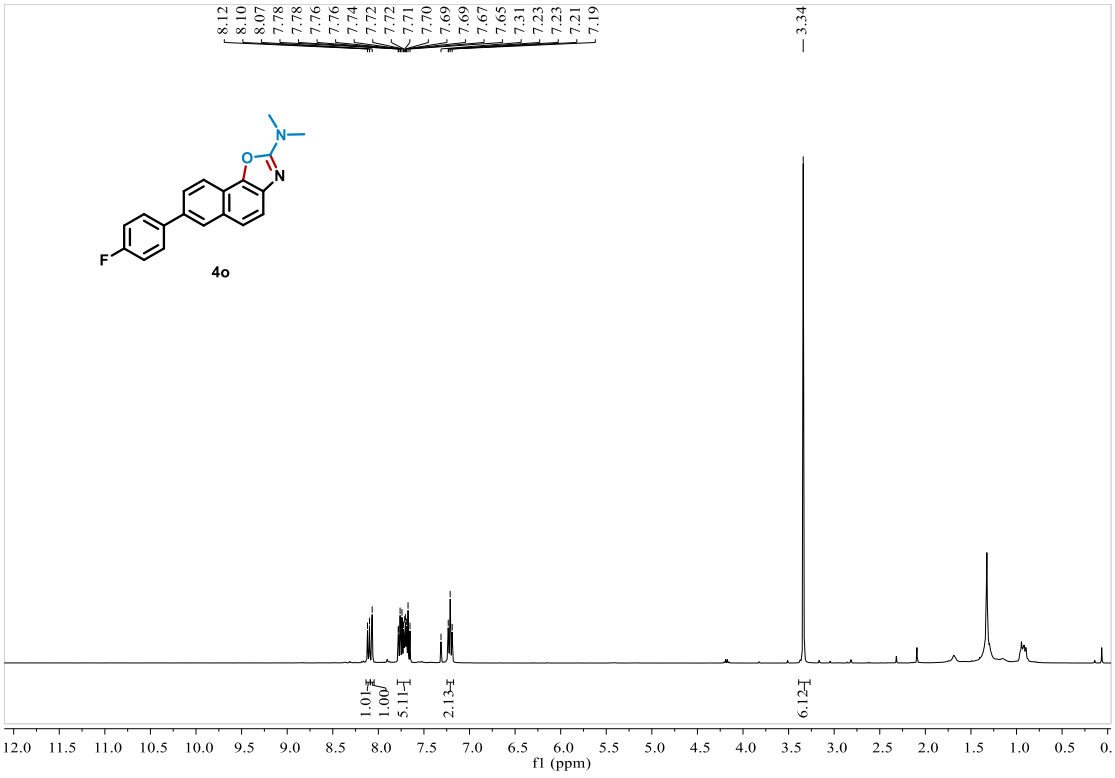
^{13}C NMR of **4n** (100 MHz, $CDCl_3$)



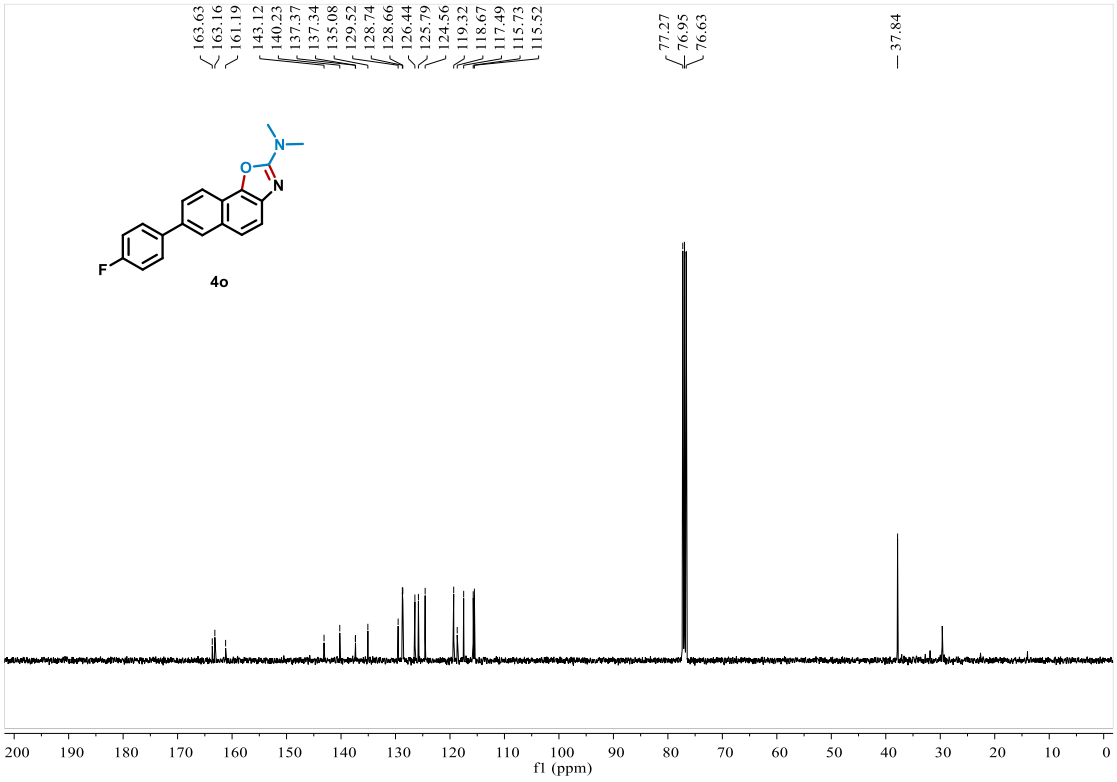
^{19}F NMR of **4n** (376 MHz, $CDCl_3$)



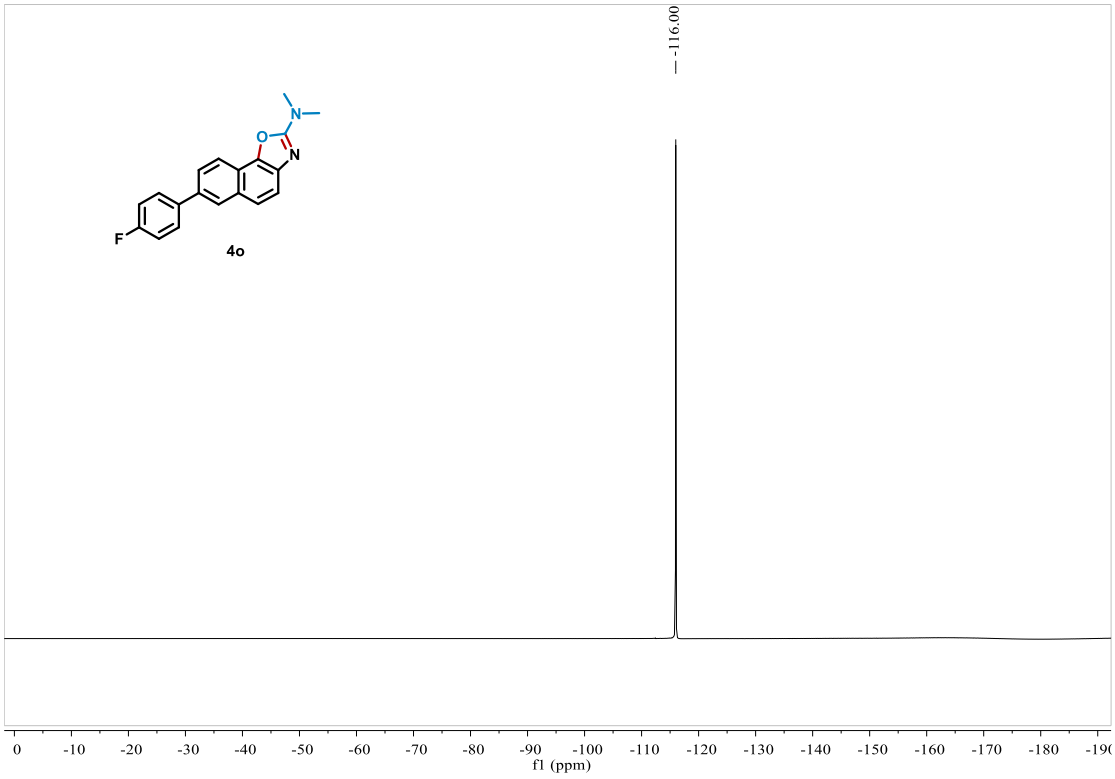
^{1}H NMR of **4o** (400 MHz, $CDCl_3$)



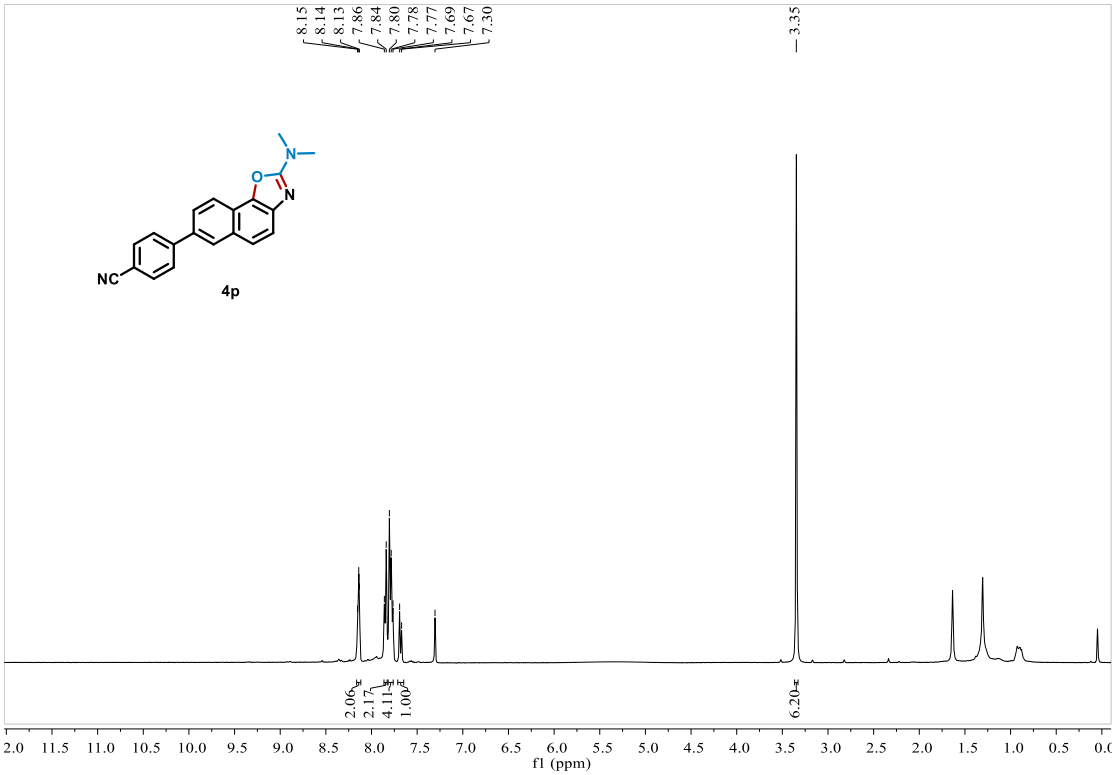
^{13}C NMR of **4o** (100 MHz, $CDCl_3$)



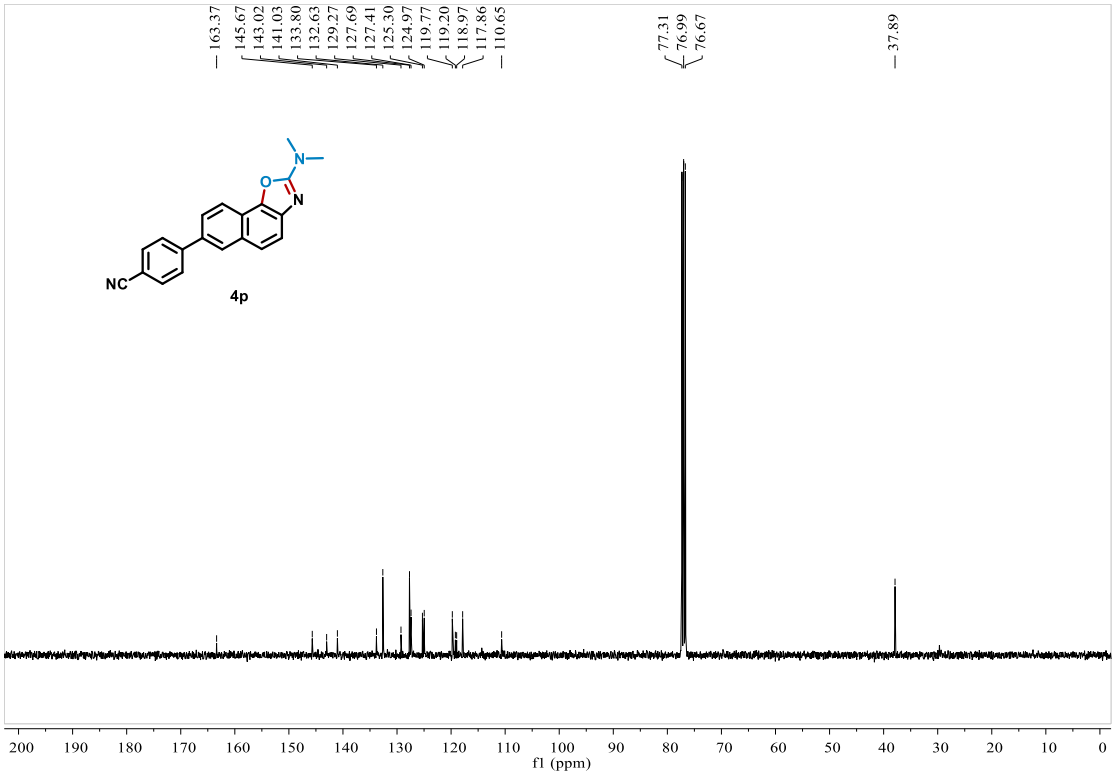
^{19}F NMR of **4o** (376 MHz, $CDCl_3$)



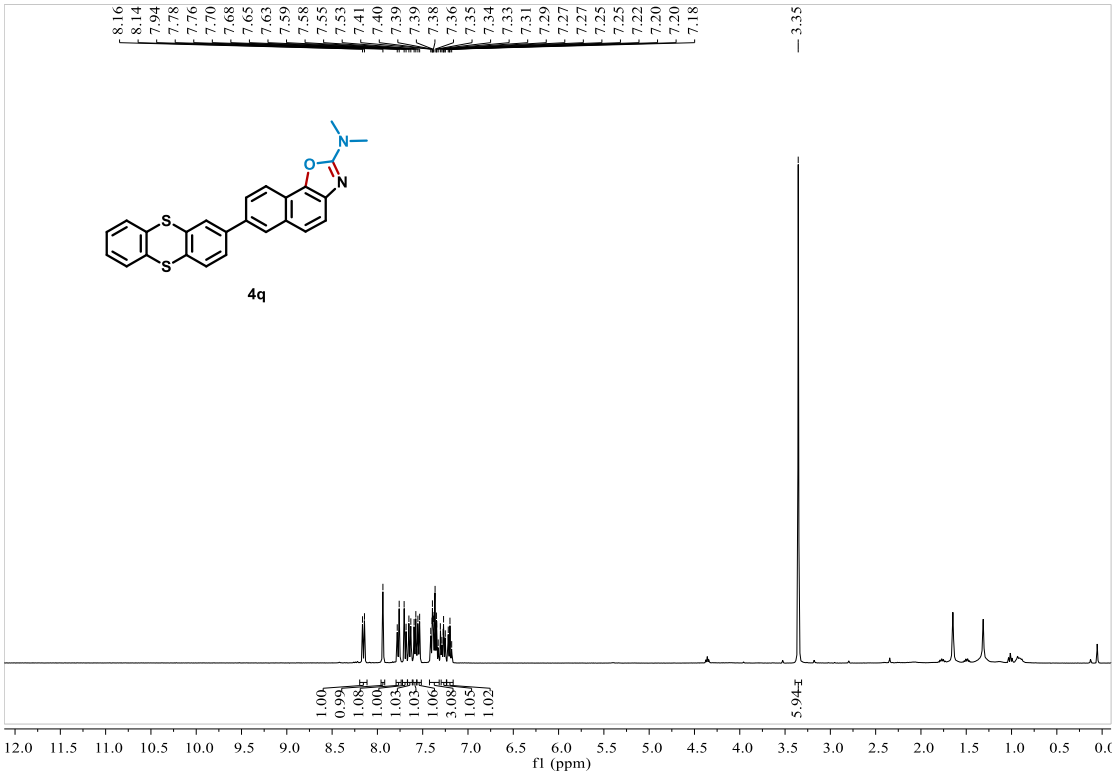
^{1}H NMR of **4p** (400 MHz, $CDCl_3$)



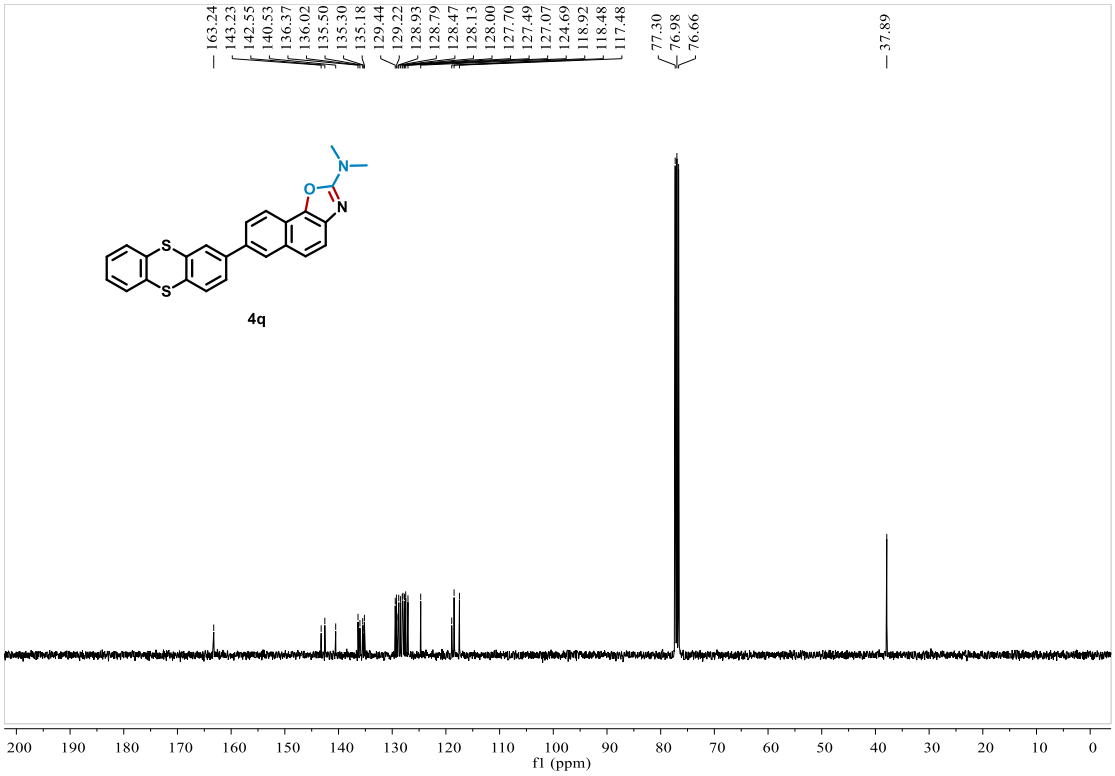
^{13}C NMR of **4p** (100 MHz, $CDCl_3$)



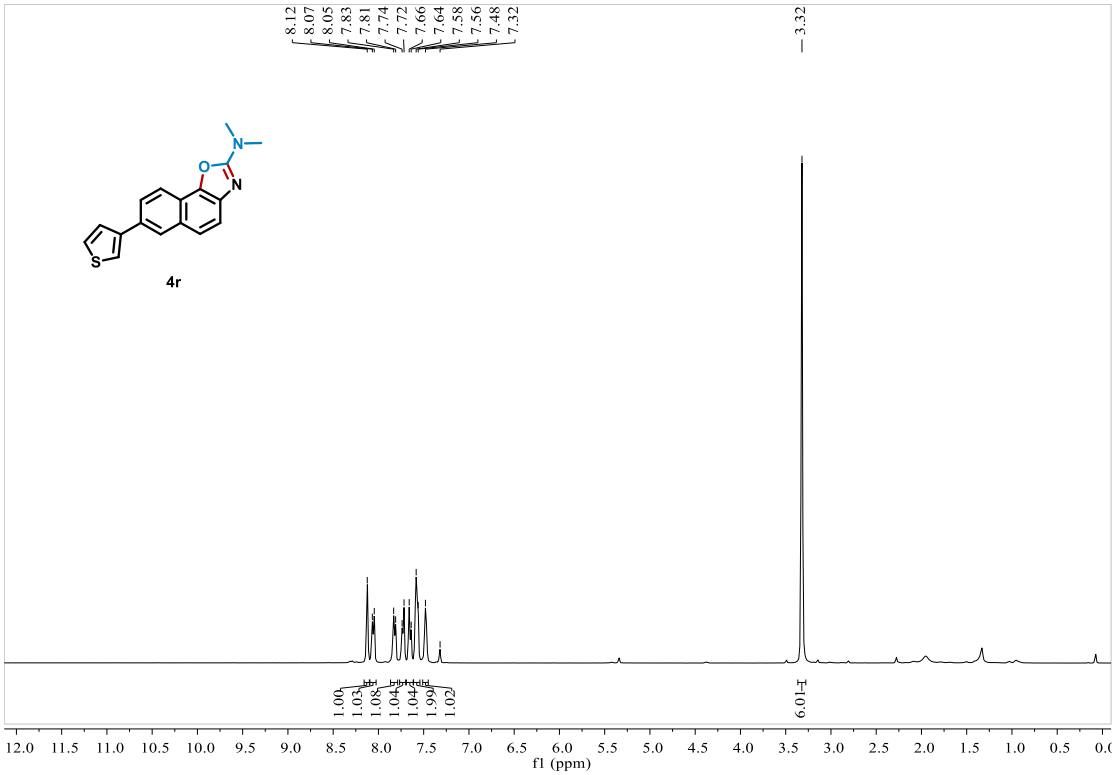
^{1}H NMR of **4q** (400 MHz, $CDCl_3$)



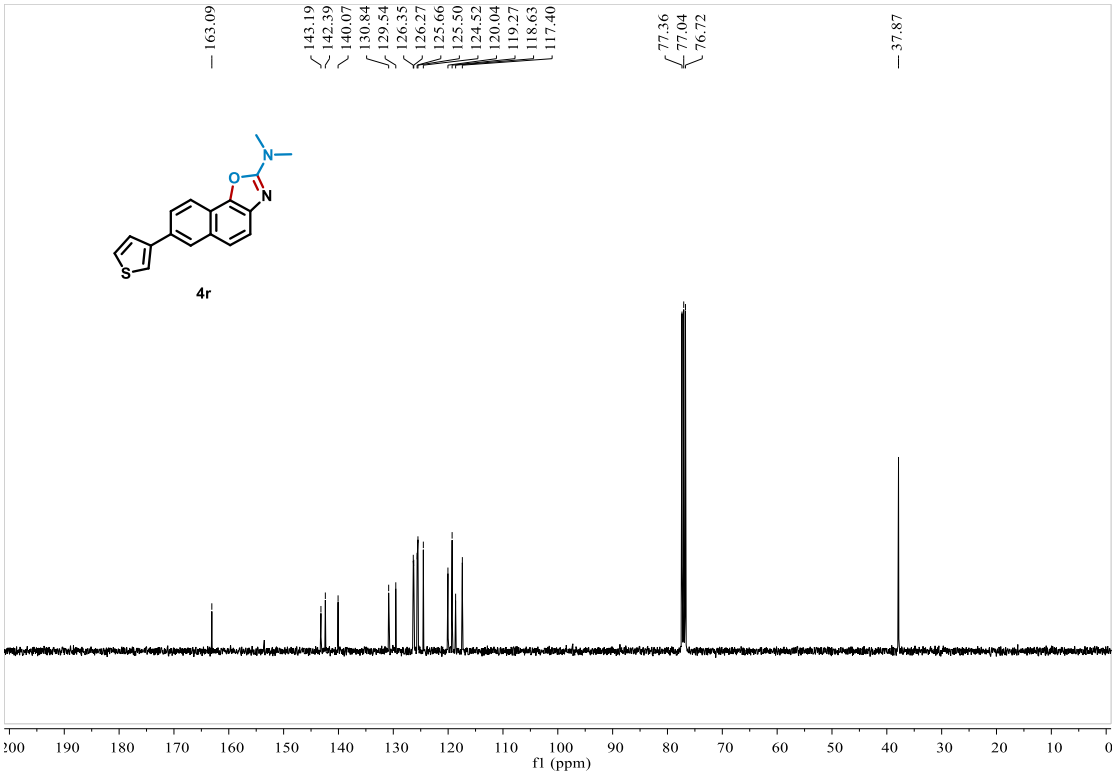
^{13}C NMR of **4q** (100 MHz, $CDCl_3$)



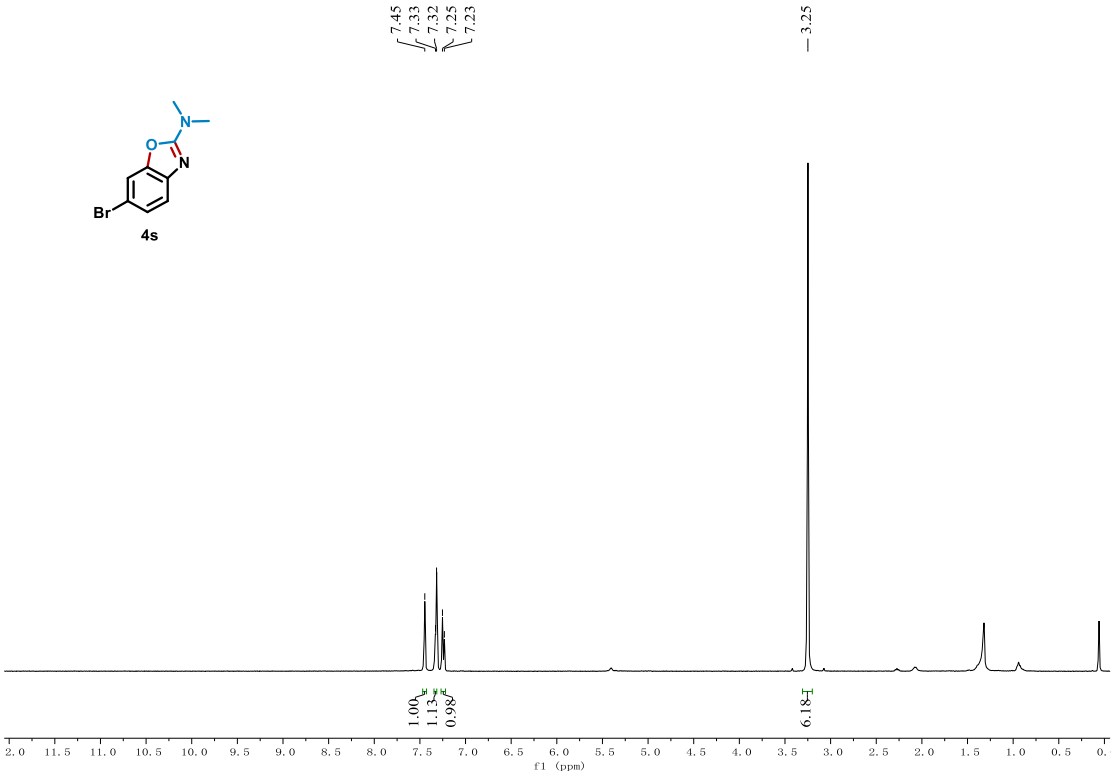
^{1}H NMR of **4r** (400 MHz, $CDCl_3$)



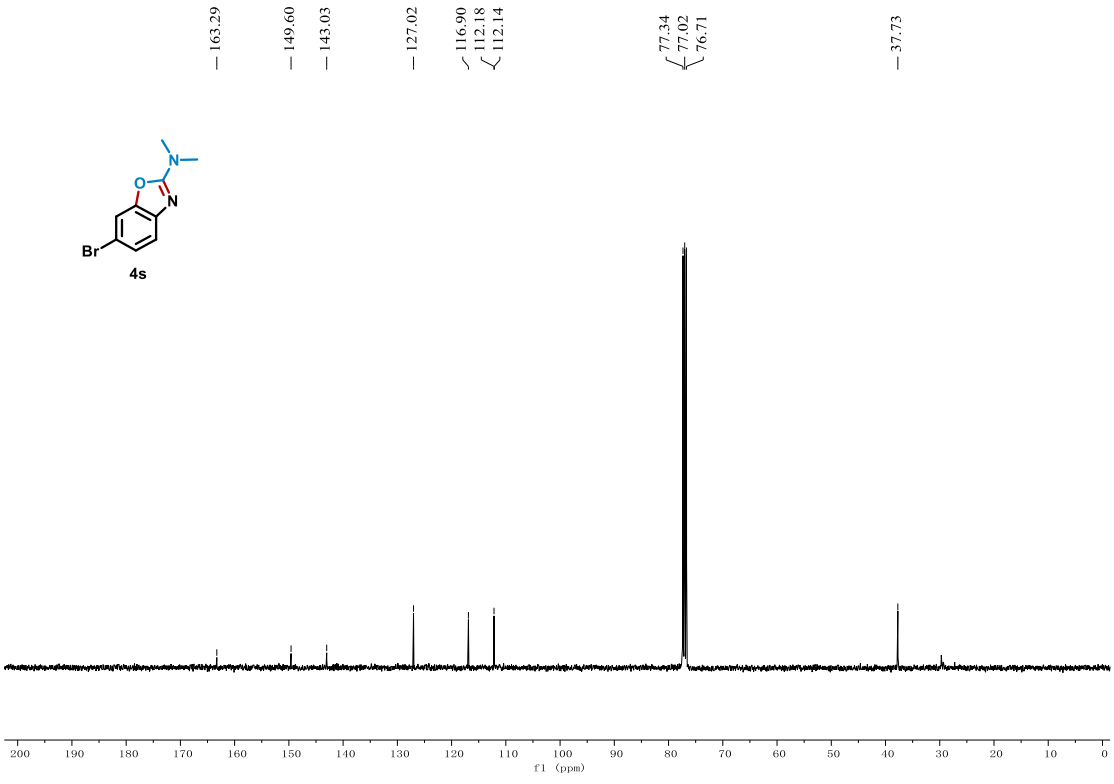
^{13}C NMR of **4r** (100 MHz, $CDCl_3$)



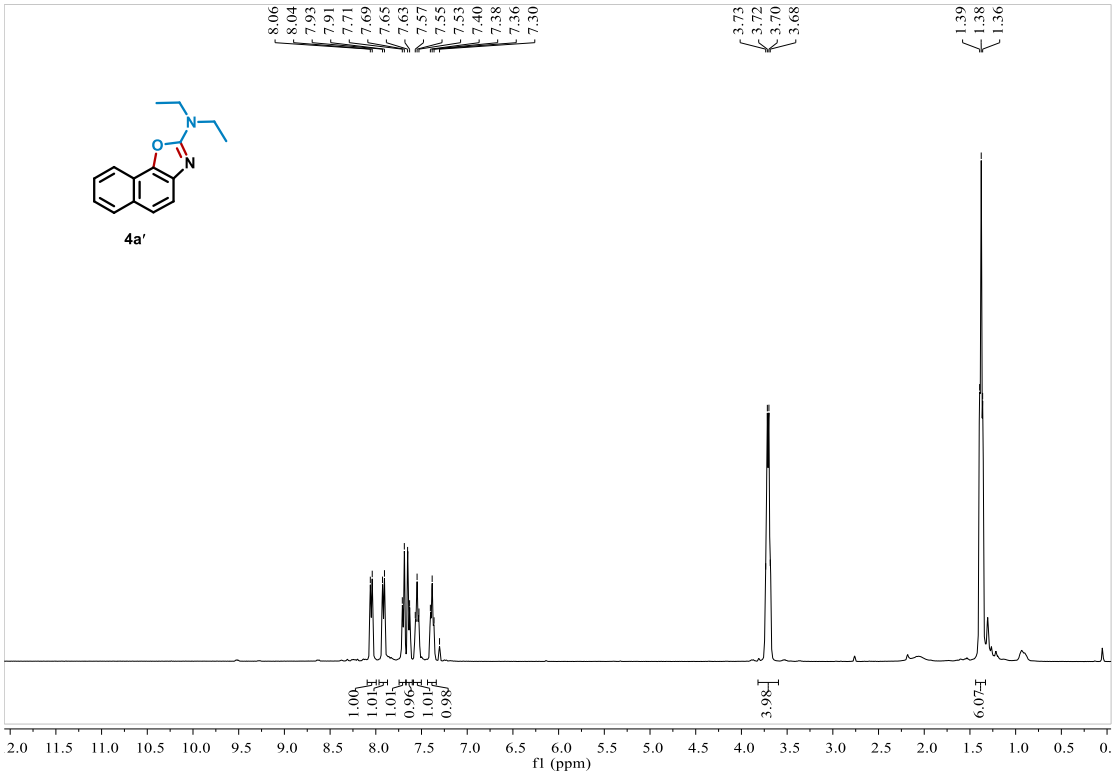
^{1}H NMR of **4s** (400 MHz, $CDCl_3$)



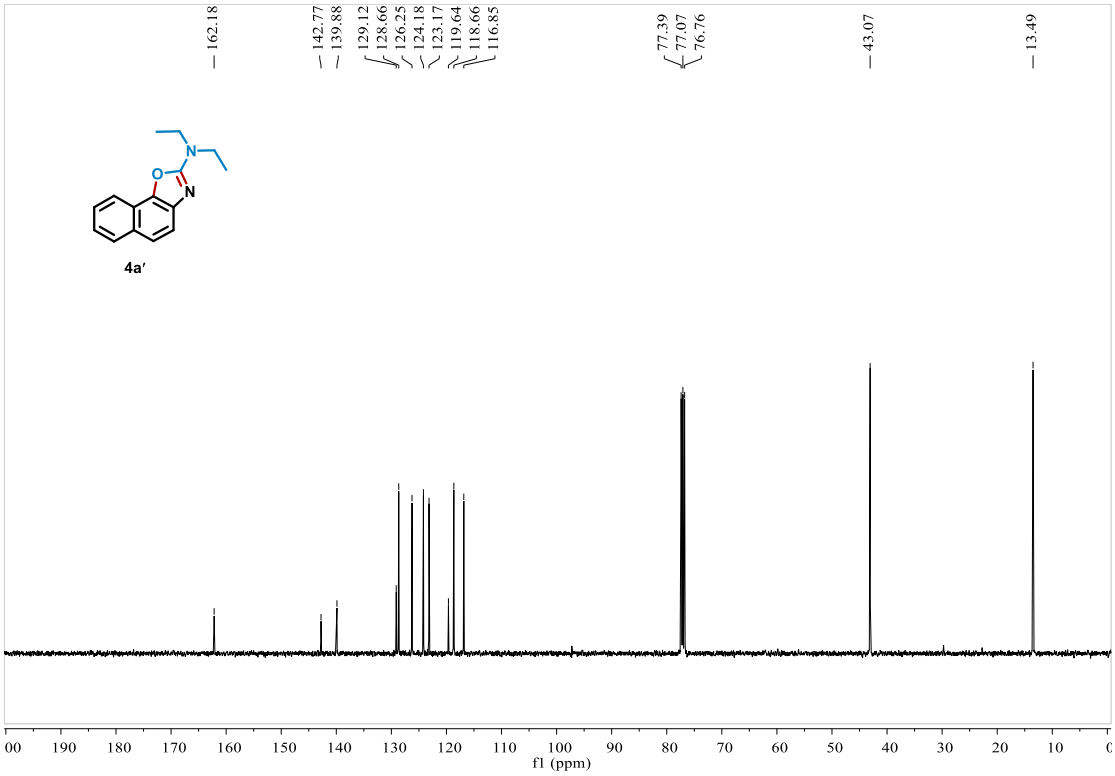
^{13}C NMR of **4s** (100 MHz, $CDCl_3$)



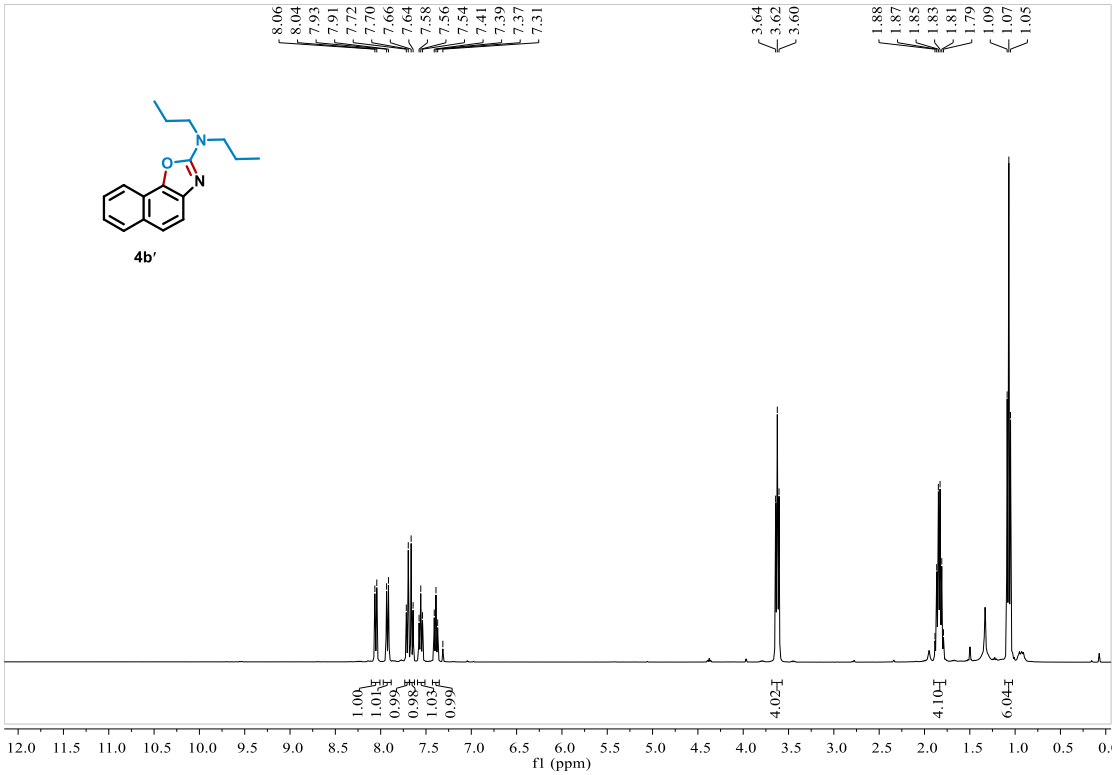
^{1}H NMR of **4a'** (400 MHz, $CDCl_3$)



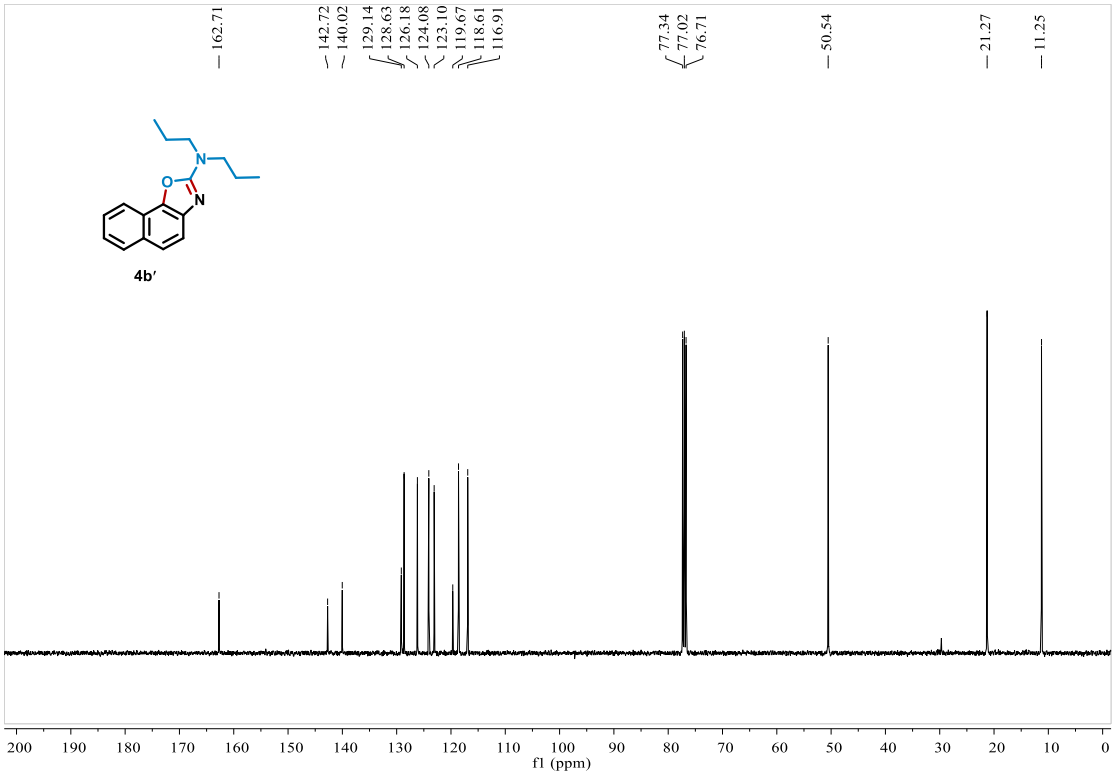
^{13}C NMR of **4a'** (100 MHz, $CDCl_3$)



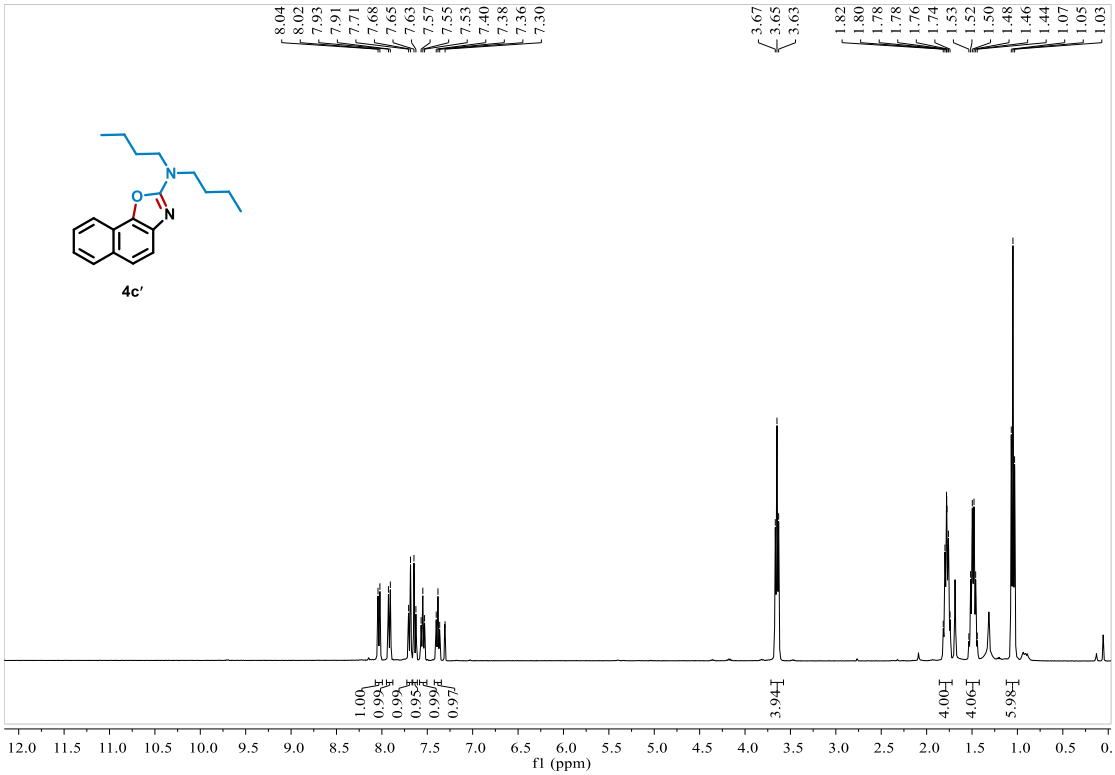
^{1}H NMR of **4b'** (400 MHz, $CDCl_3$)



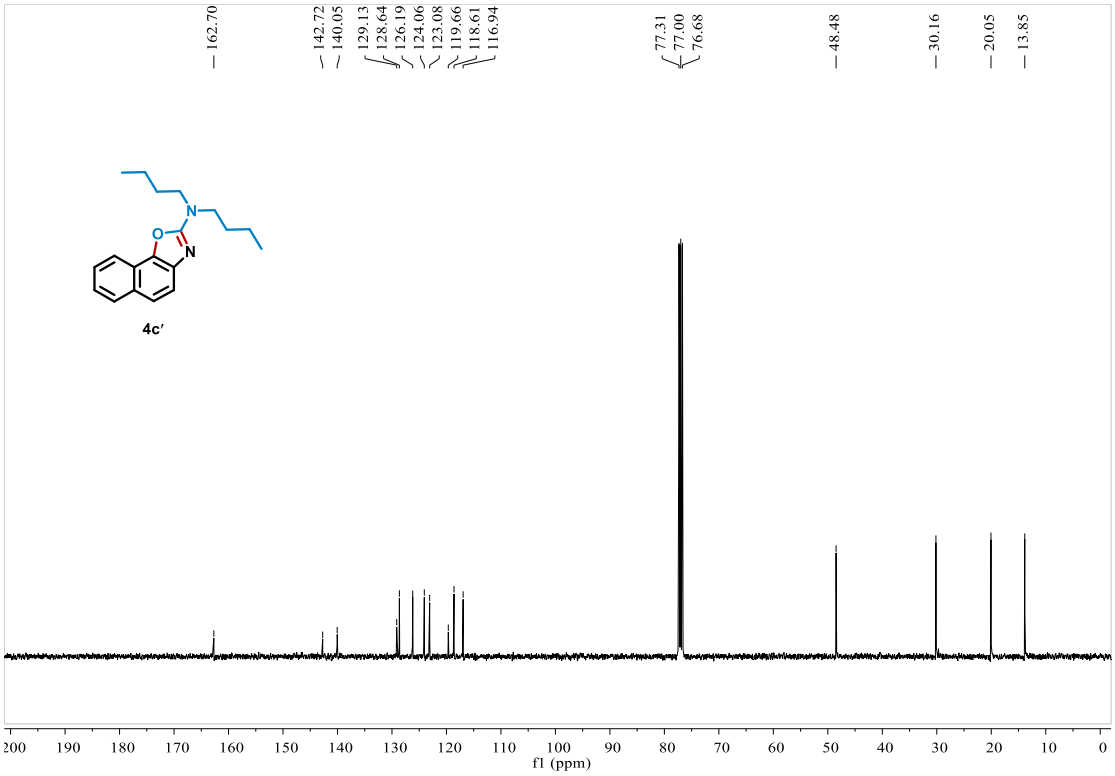
^{13}C NMR of **4b'** (100 MHz, $CDCl_3$)



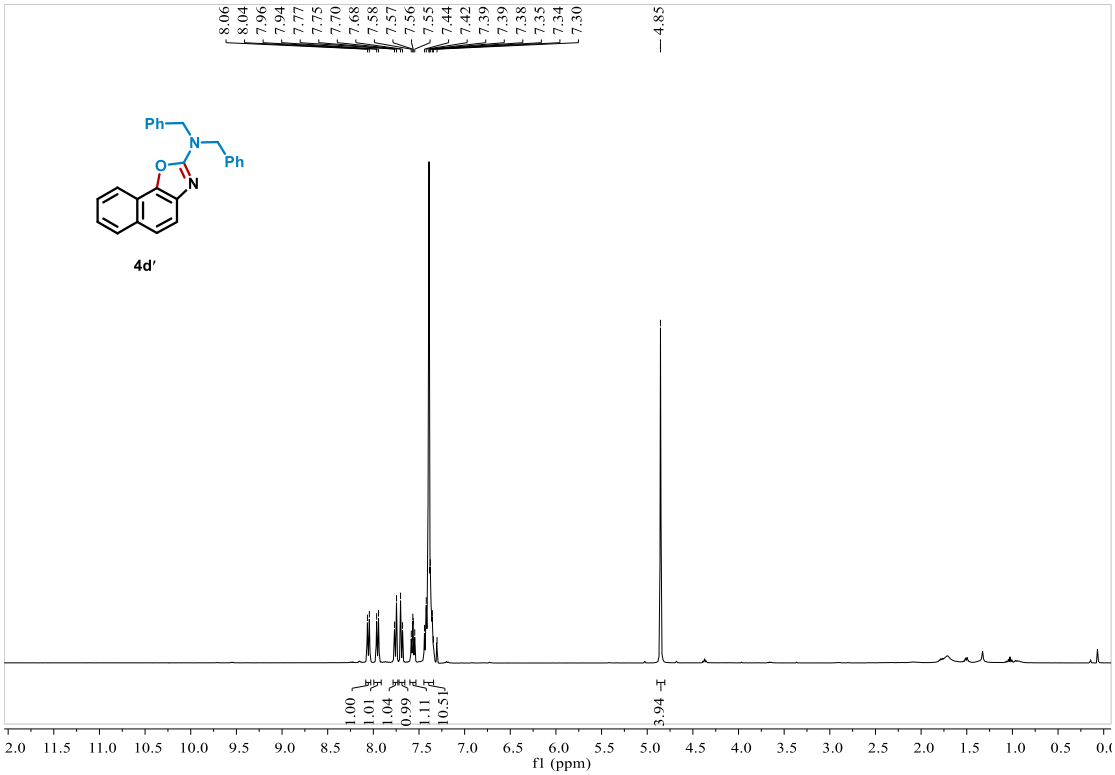
^{1}H NMR of **4c'** (400 MHz, $CDCl_3$)



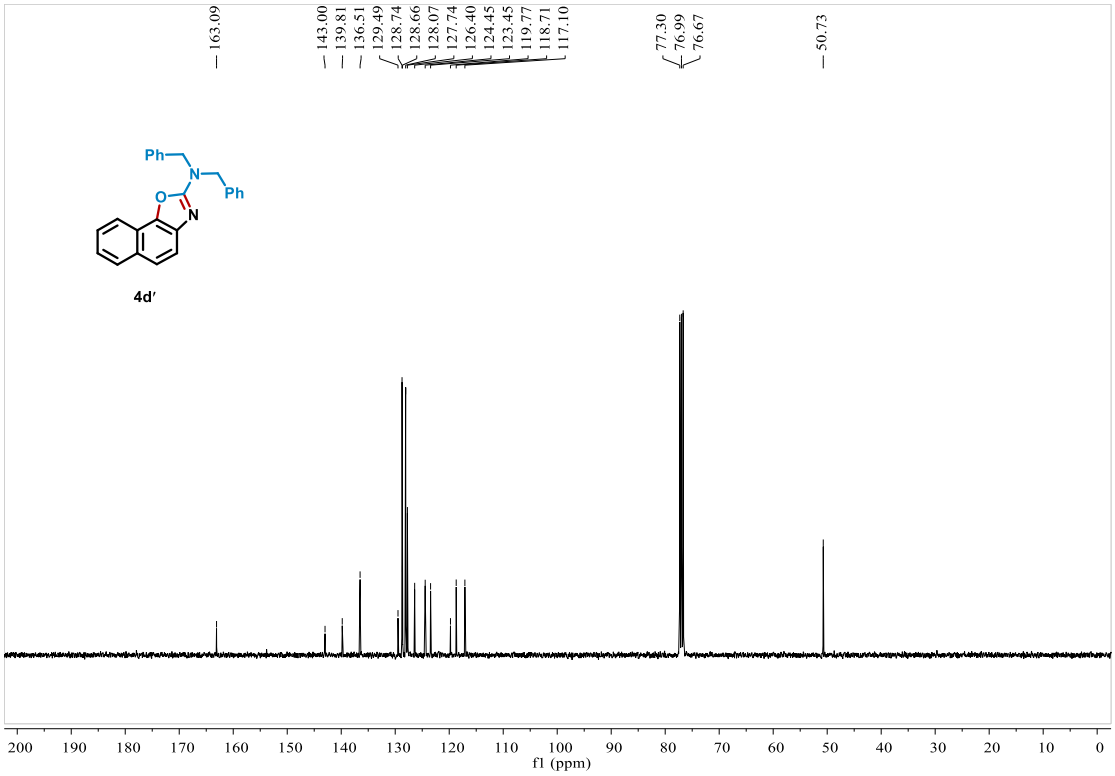
^{13}C NMR of **4c'** (100 MHz, $CDCl_3$)



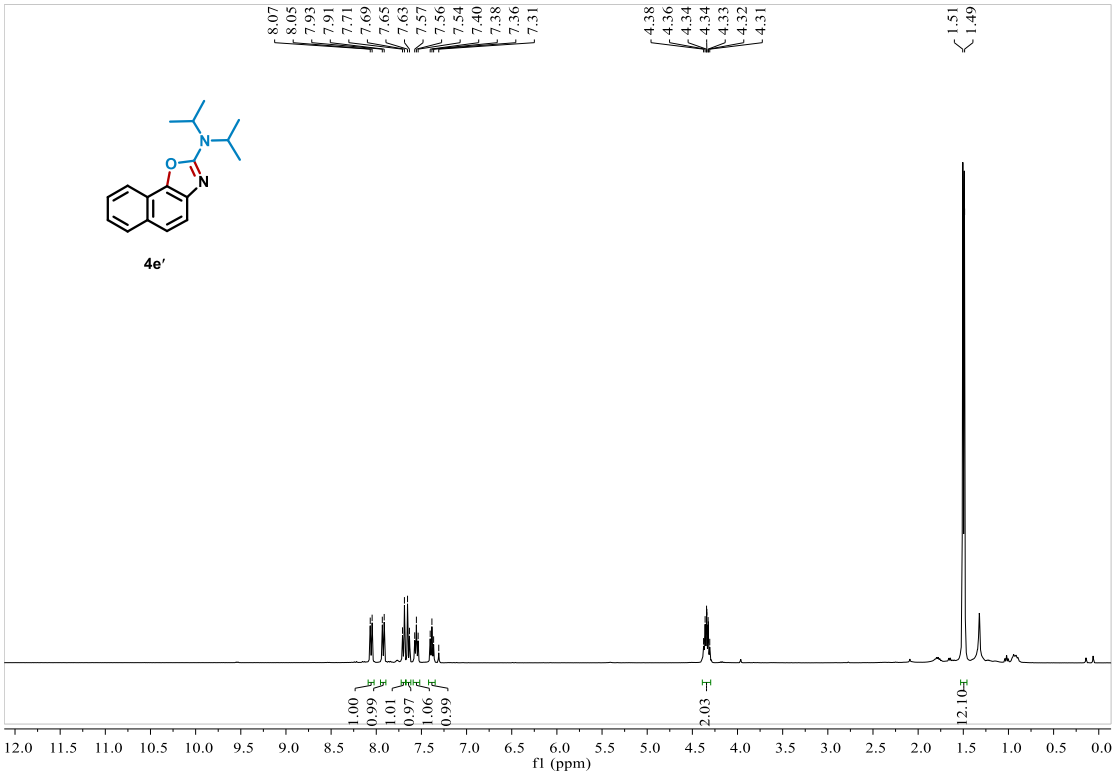
^{1}H NMR of **4d'** (400 MHz, $CDCl_3$)



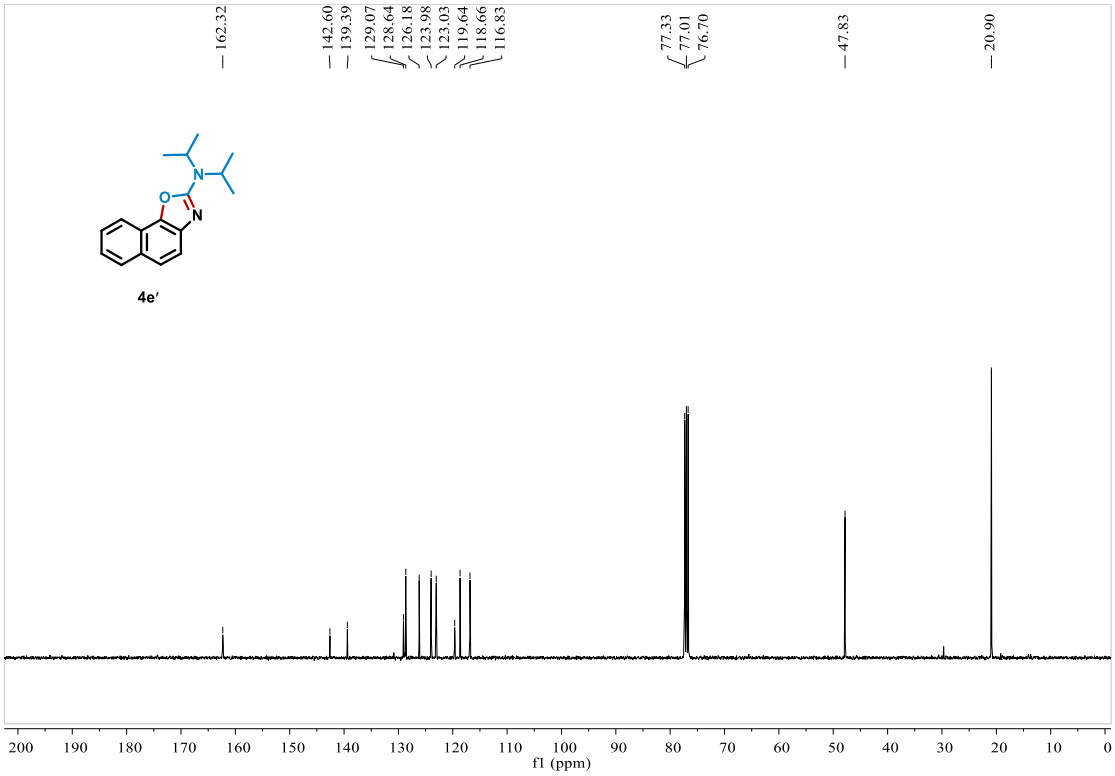
^{13}C NMR of **4d'** (100 MHz, $CDCl_3$)



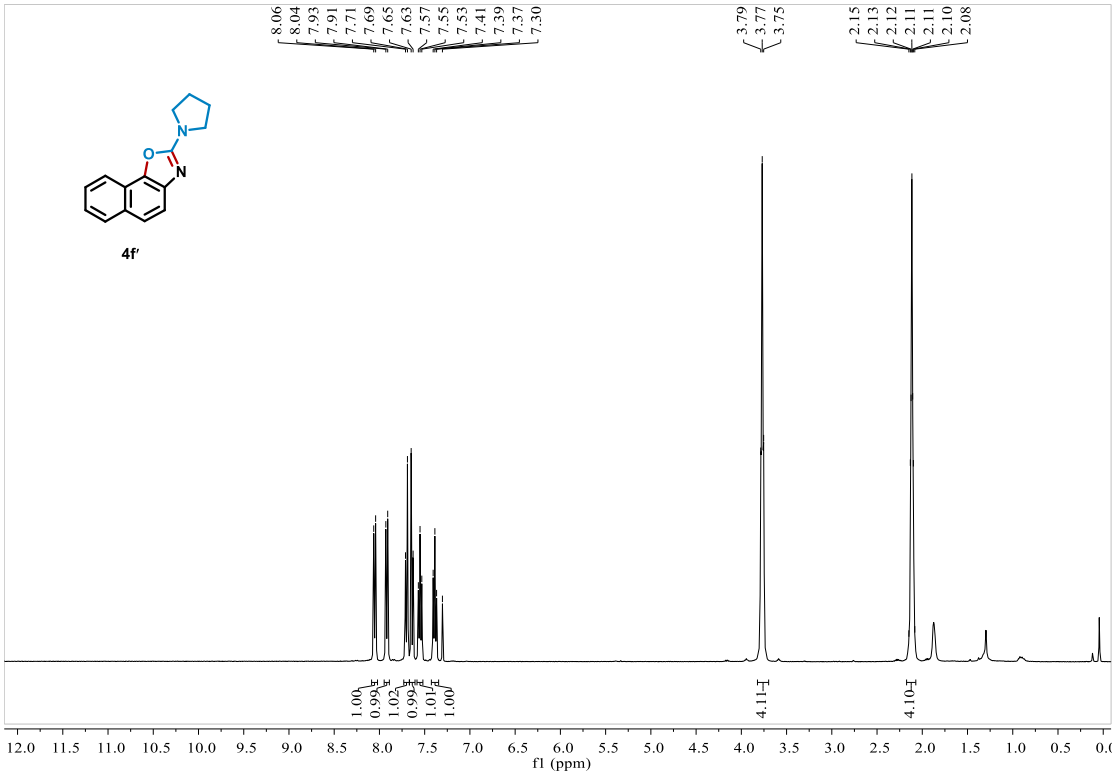
^{1}H NMR of **4e'** (400 MHz, $CDCl_3$)



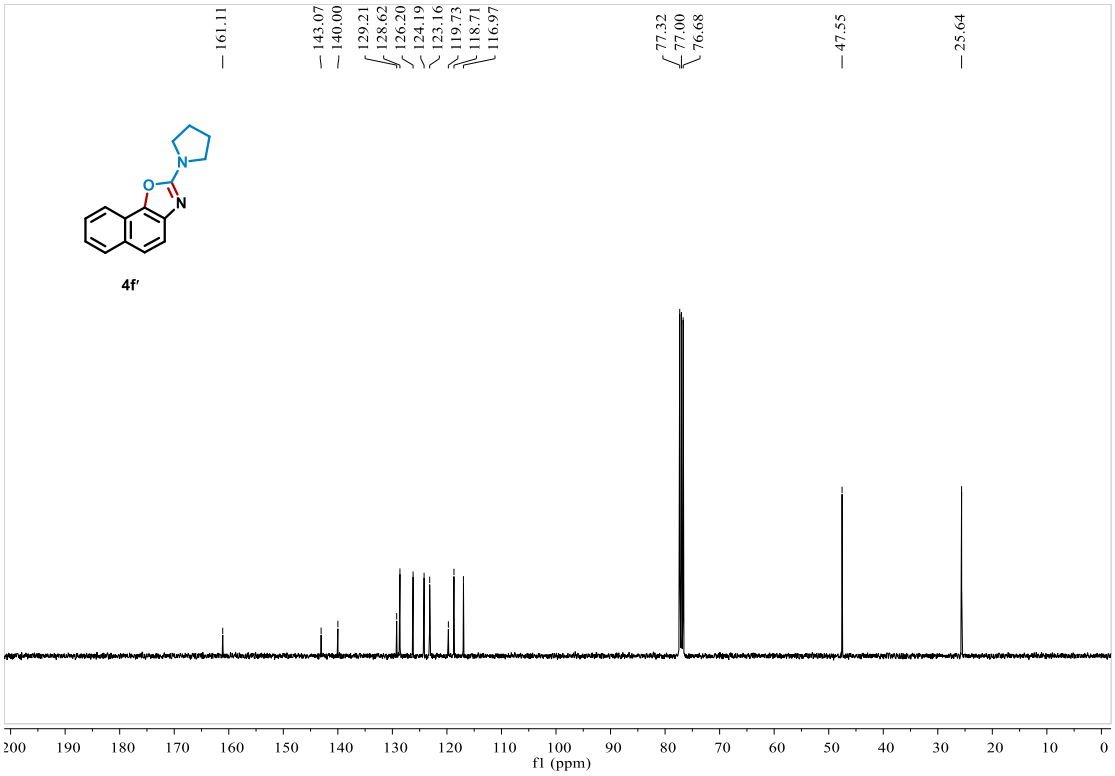
^{13}C NMR of **4e'** (100 MHz, $CDCl_3$)



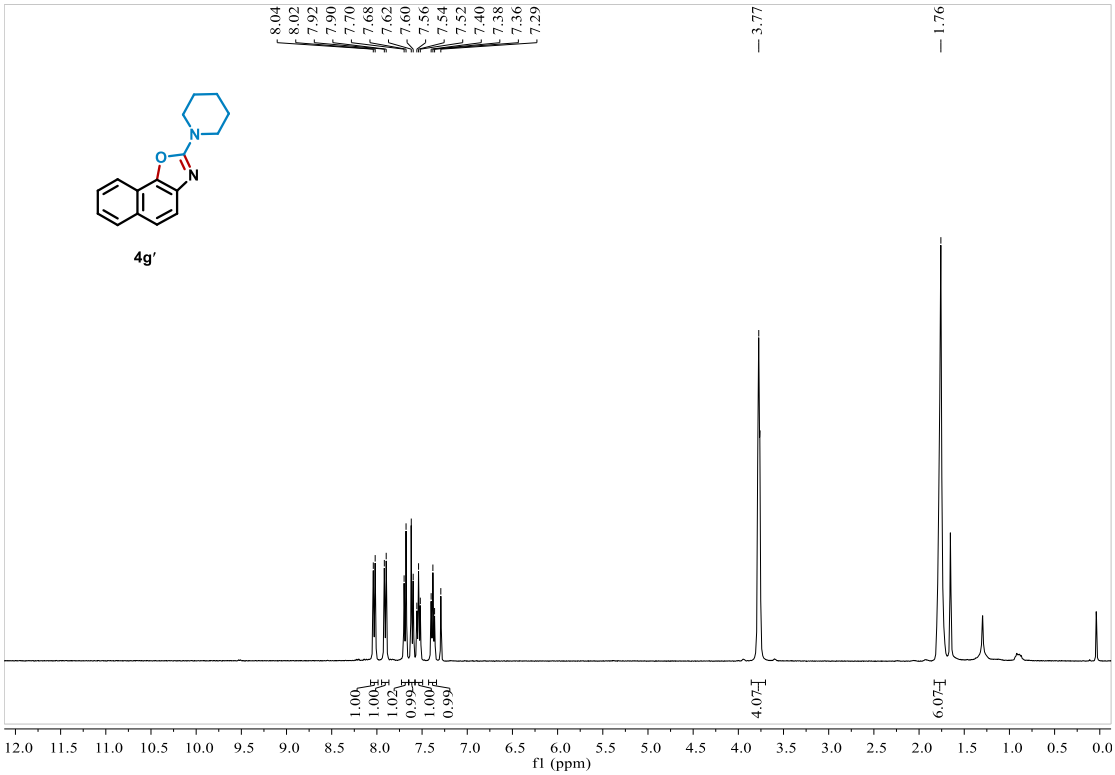
^{1}H NMR of **4f'** (400 MHz, $CDCl_3$)



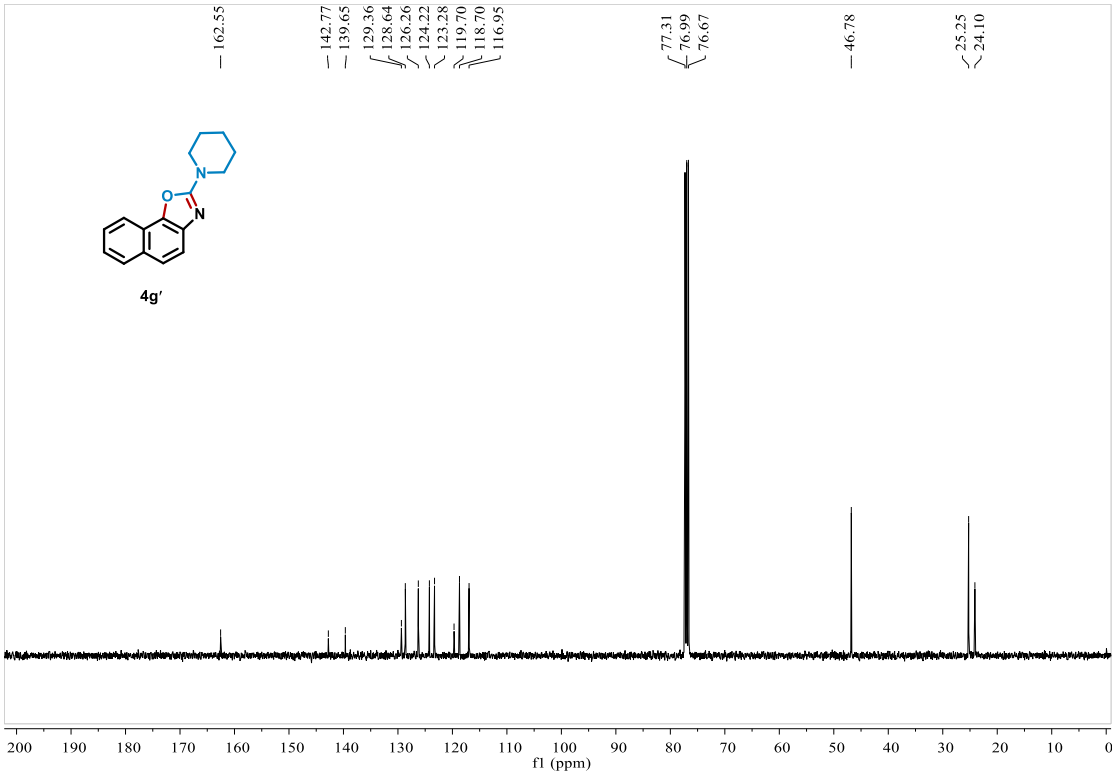
^{13}C NMR of **4f'** (100 MHz, $CDCl_3$)



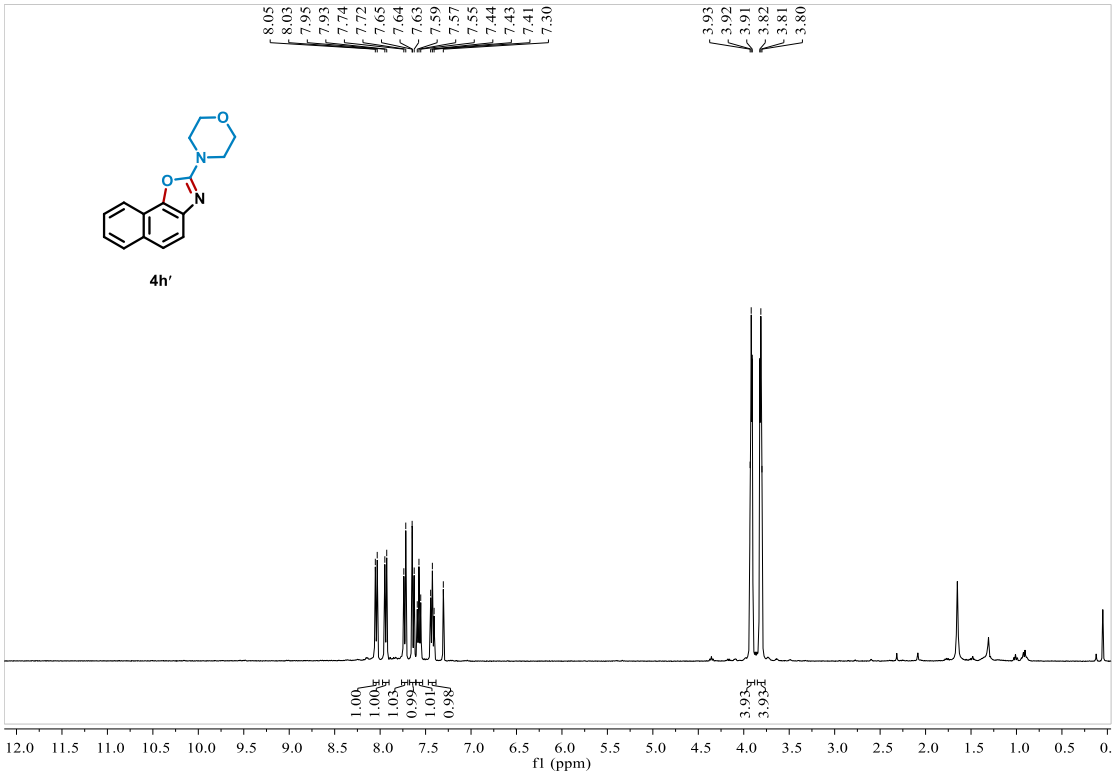
^{1}H NMR of **4g'** (400 MHz, $CDCl_3$)



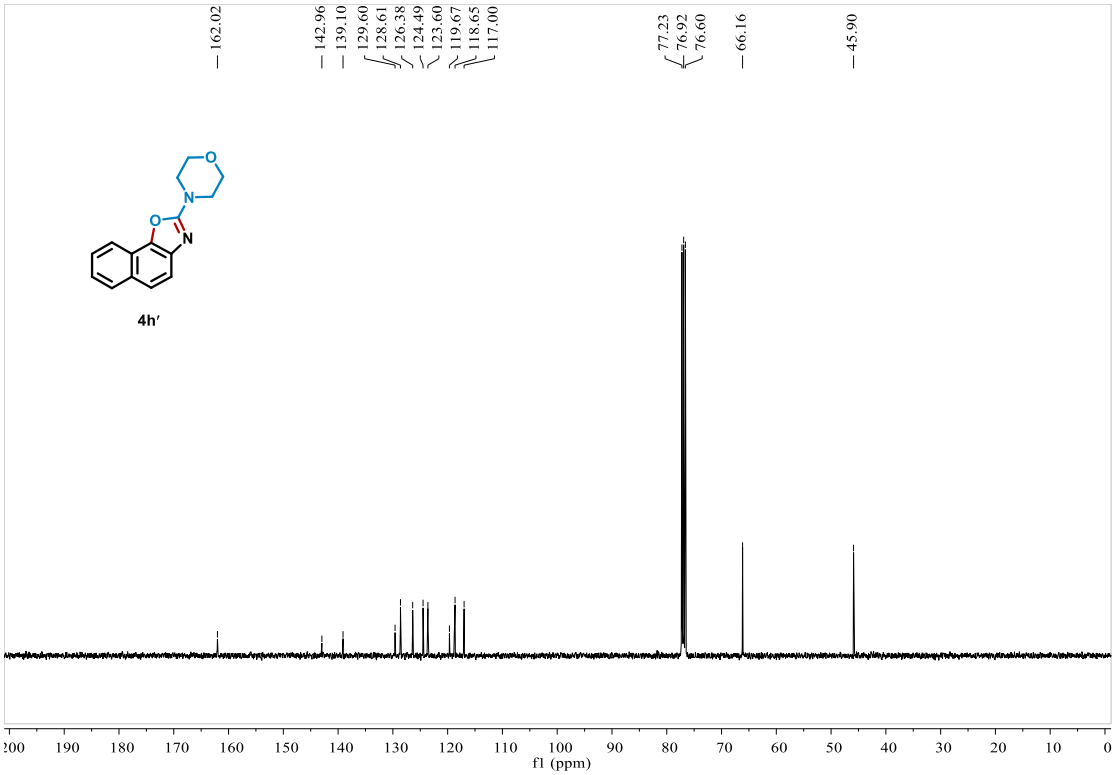
^{13}C NMR of **4g'** (100 MHz, $CDCl_3$)



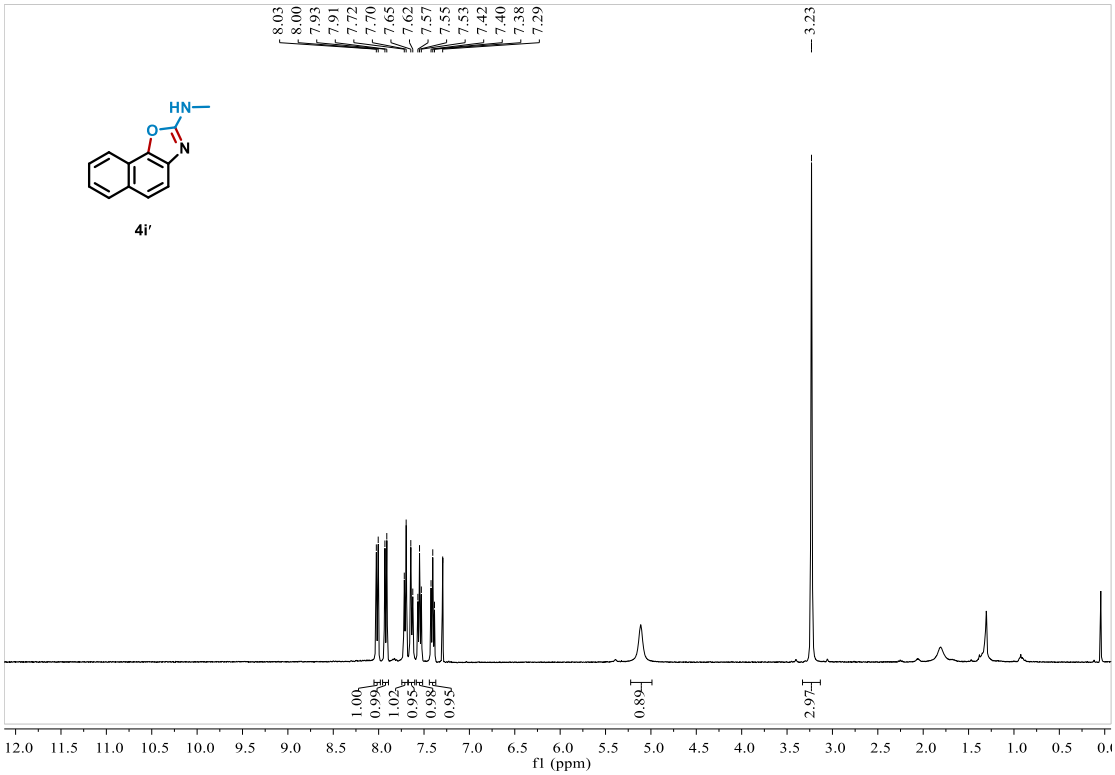
^{1}H NMR of **4h'** (400 MHz, $CDCl_3$)



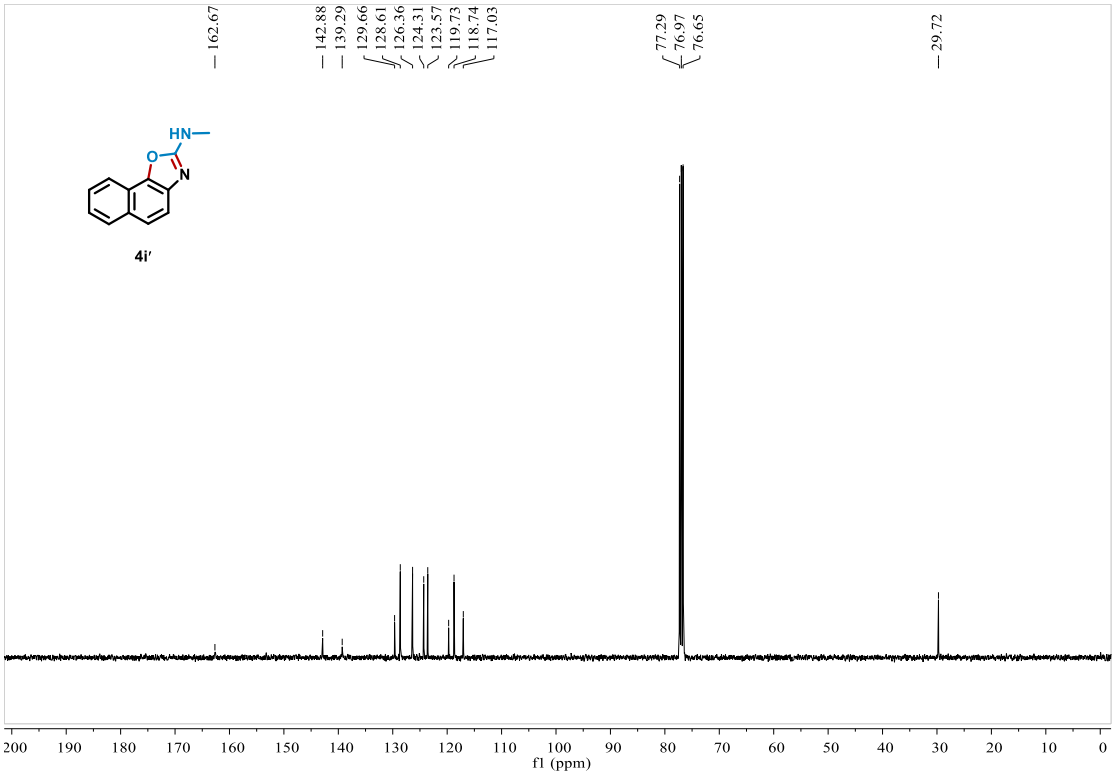
^{13}C NMR of **4h'** (100 MHz, $CDCl_3$)



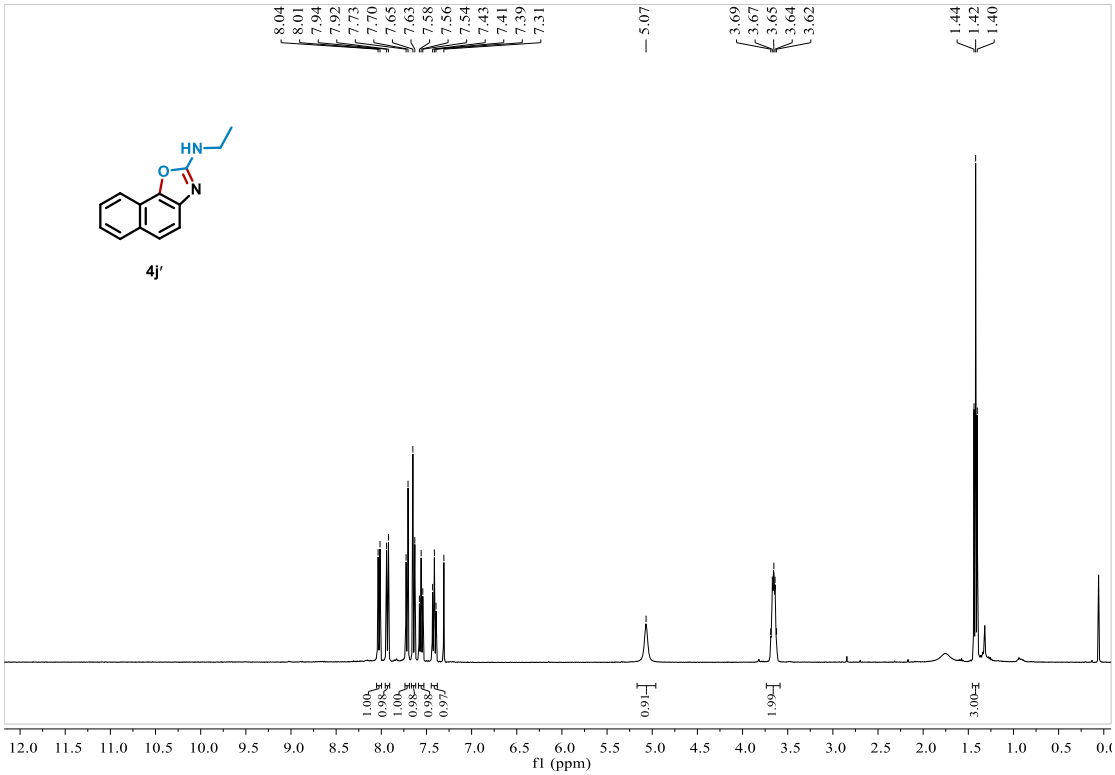
^{1}H NMR of **4i'** (400 MHz, $CDCl_3$)



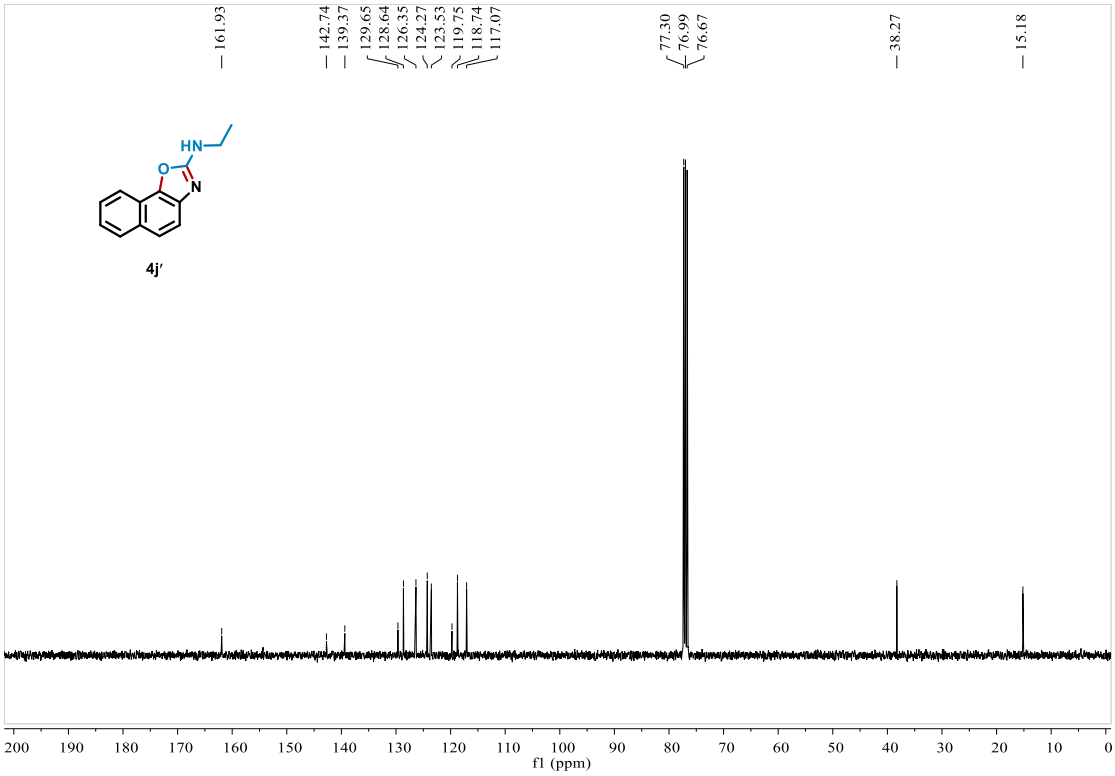
^{13}C NMR of **4i'** (100 MHz, $CDCl_3$)



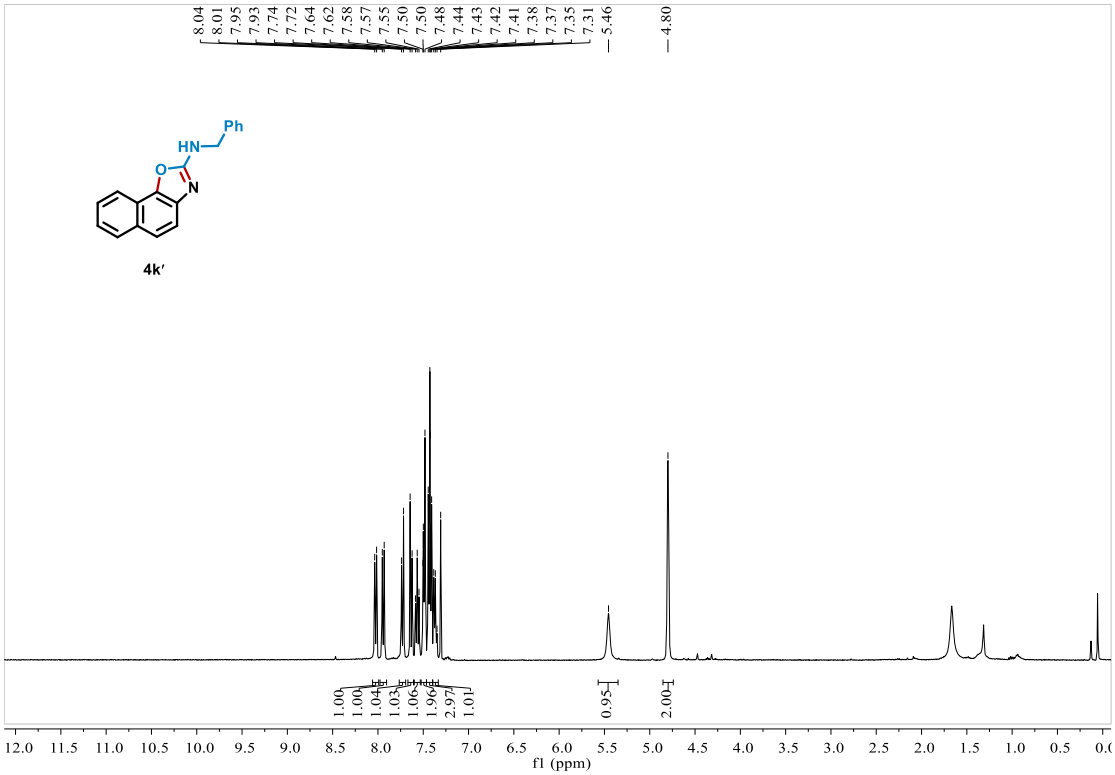
^{1}H NMR of **4j'** (400 MHz, $CDCl_3$)



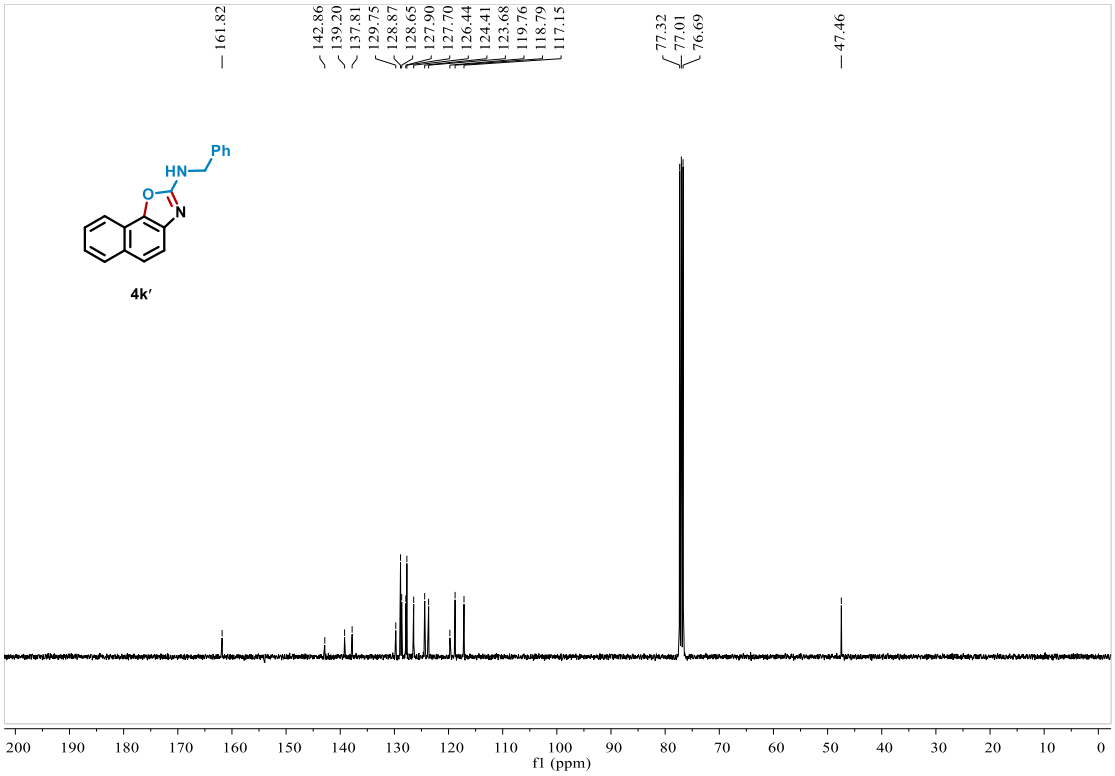
^{13}C NMR of **4j'** (100 MHz, $CDCl_3$)



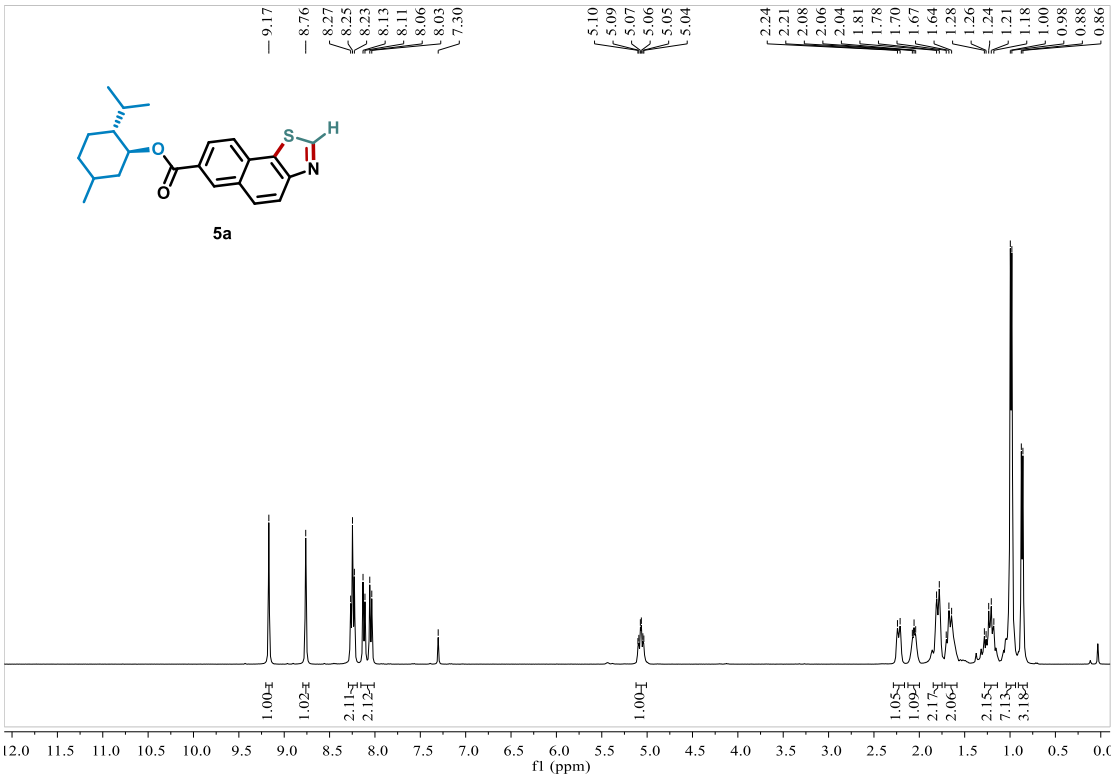
^{1}H NMR of **4k'** (400 MHz, $CDCl_3$)



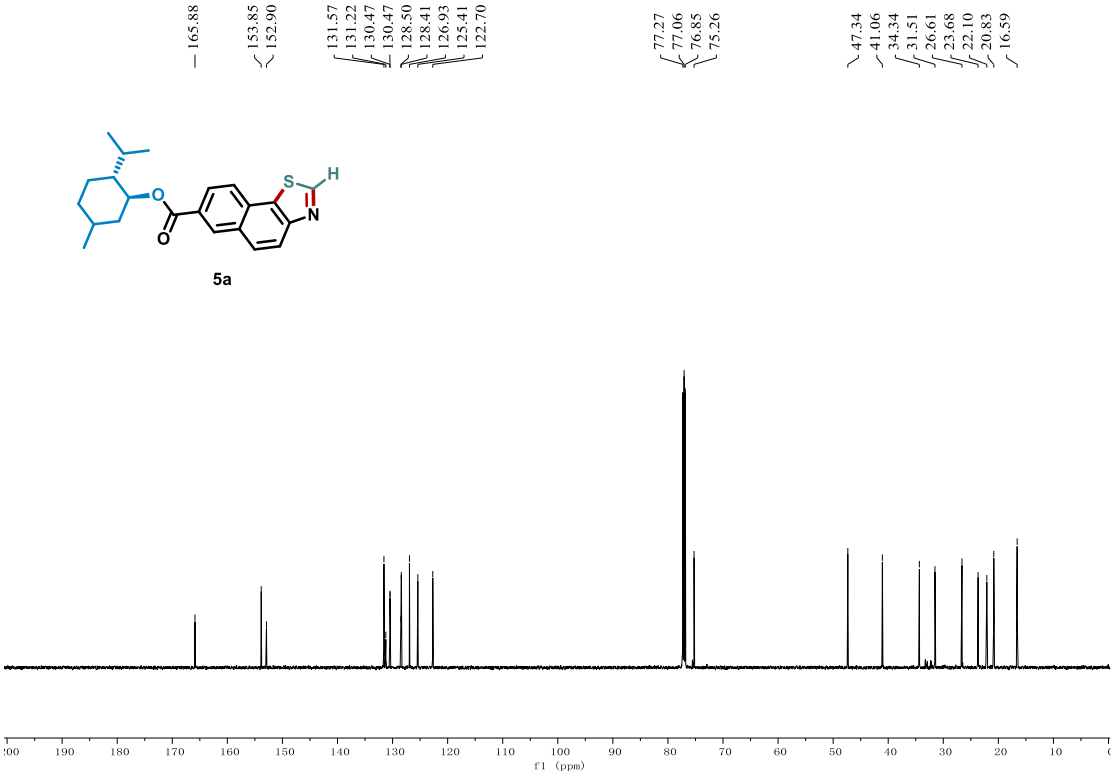
^{13}C NMR of **4k'** (100 MHz, $CDCl_3$)



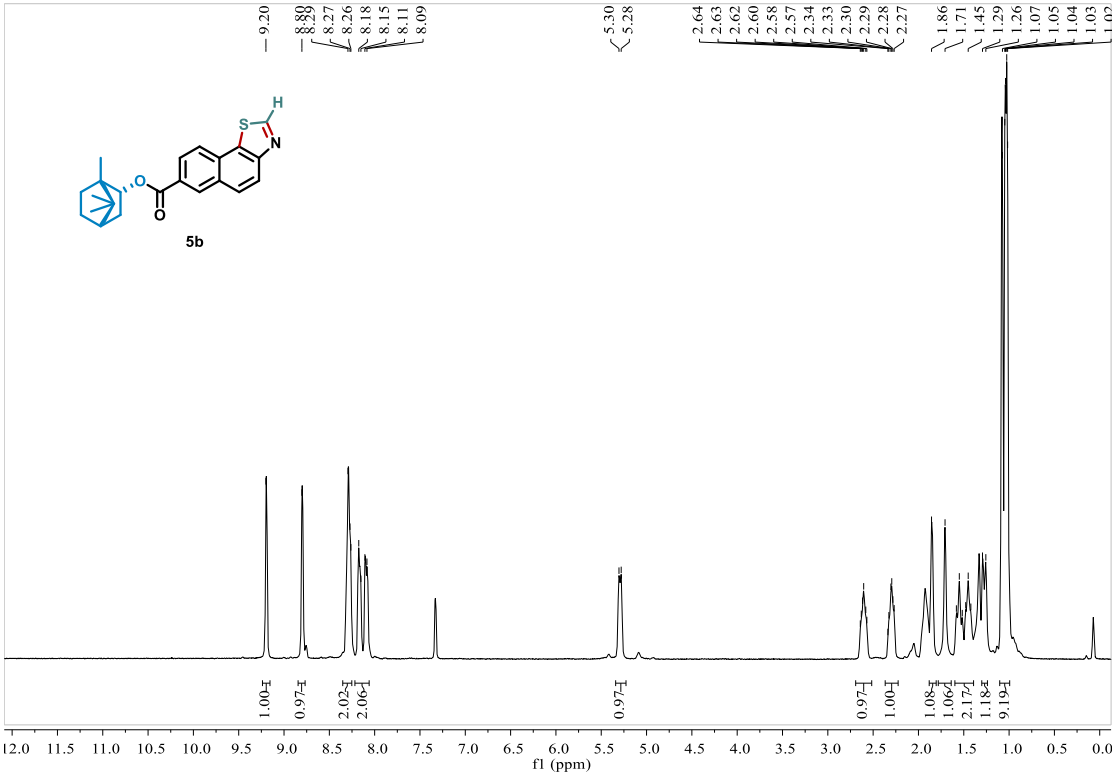
^{1}H NMR of **5a** (400 MHz, $CDCl_3$)



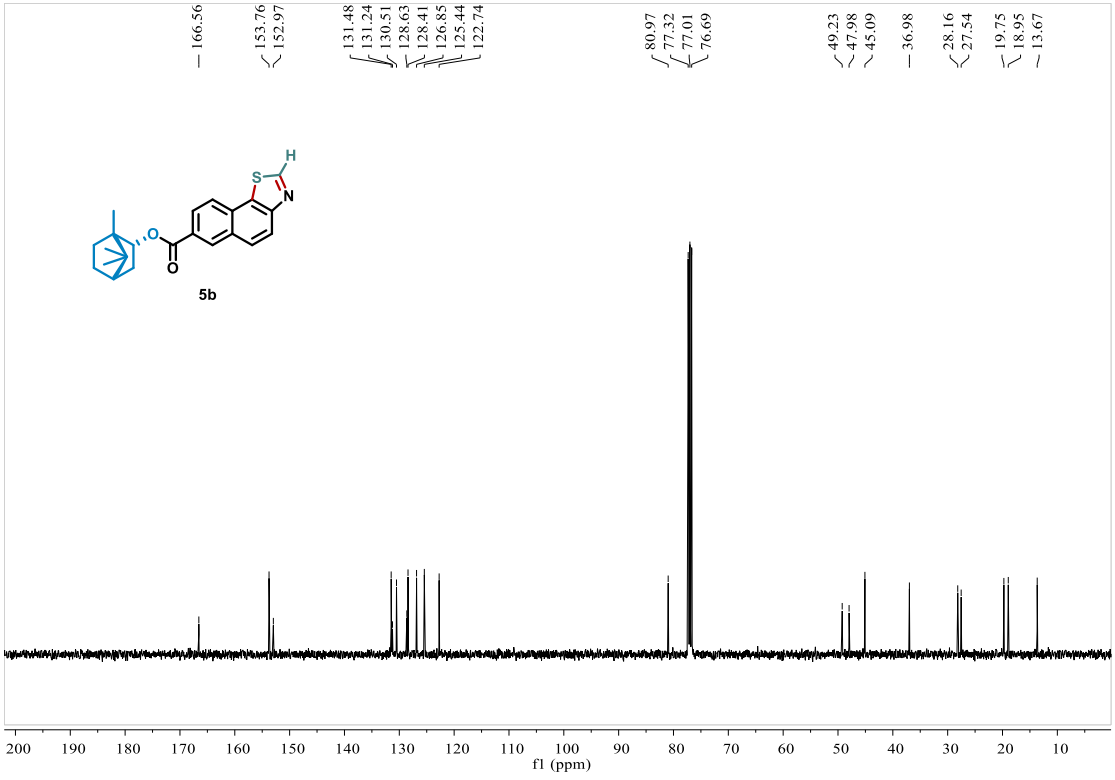
^{13}C NMR of **5a** (151 MHz, $CDCl_3$)



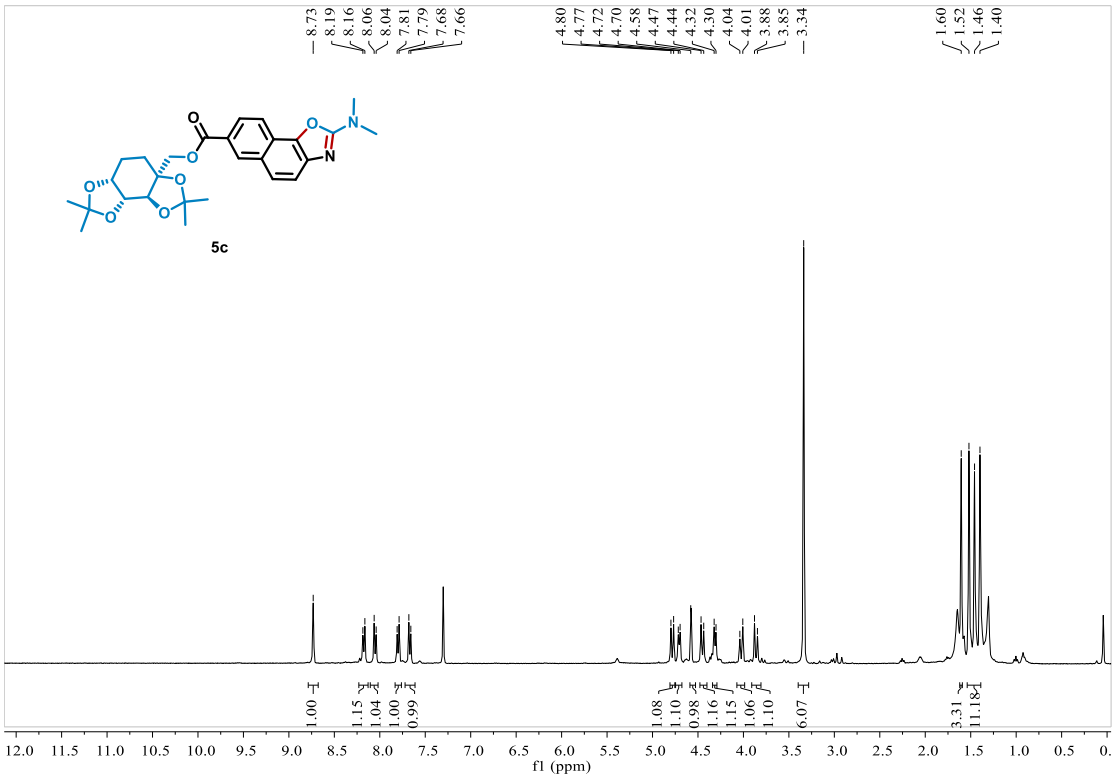
^{1}H NMR of **5b** (400 MHz, $CDCl_3$)



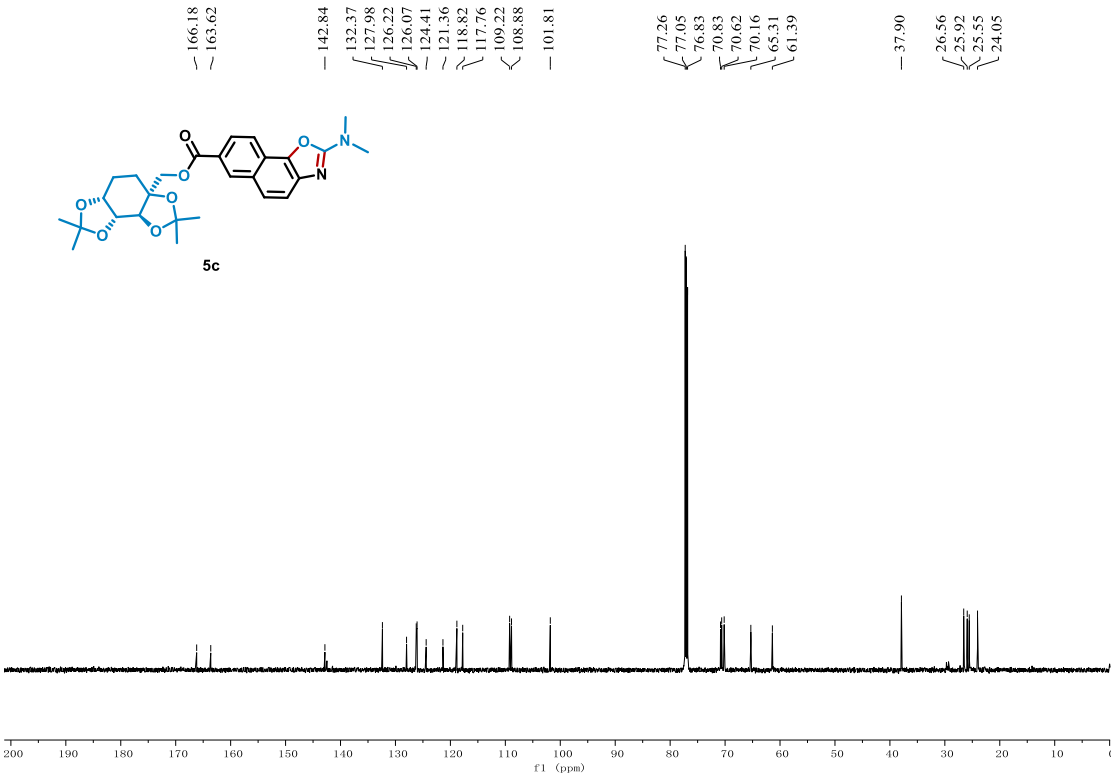
^{13}C NMR of **5b** (100 MHz, $CDCl_3$)



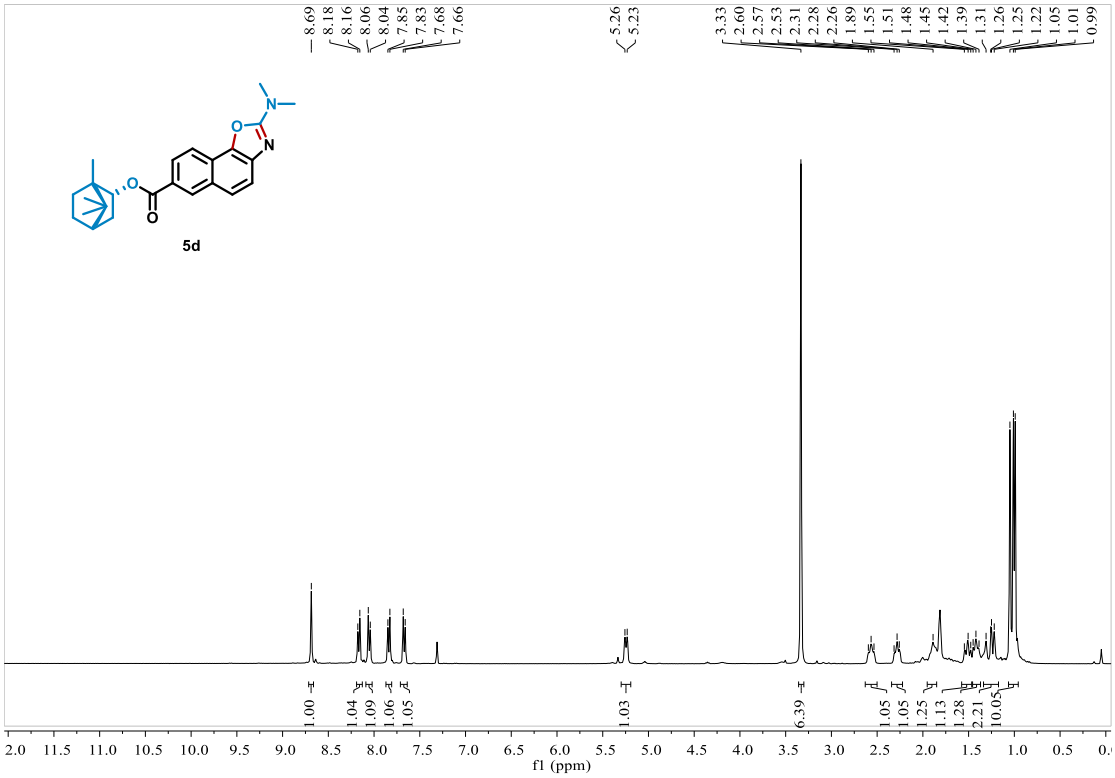
^{1}H NMR of **5c** (400 MHz, $CDCl_3$)



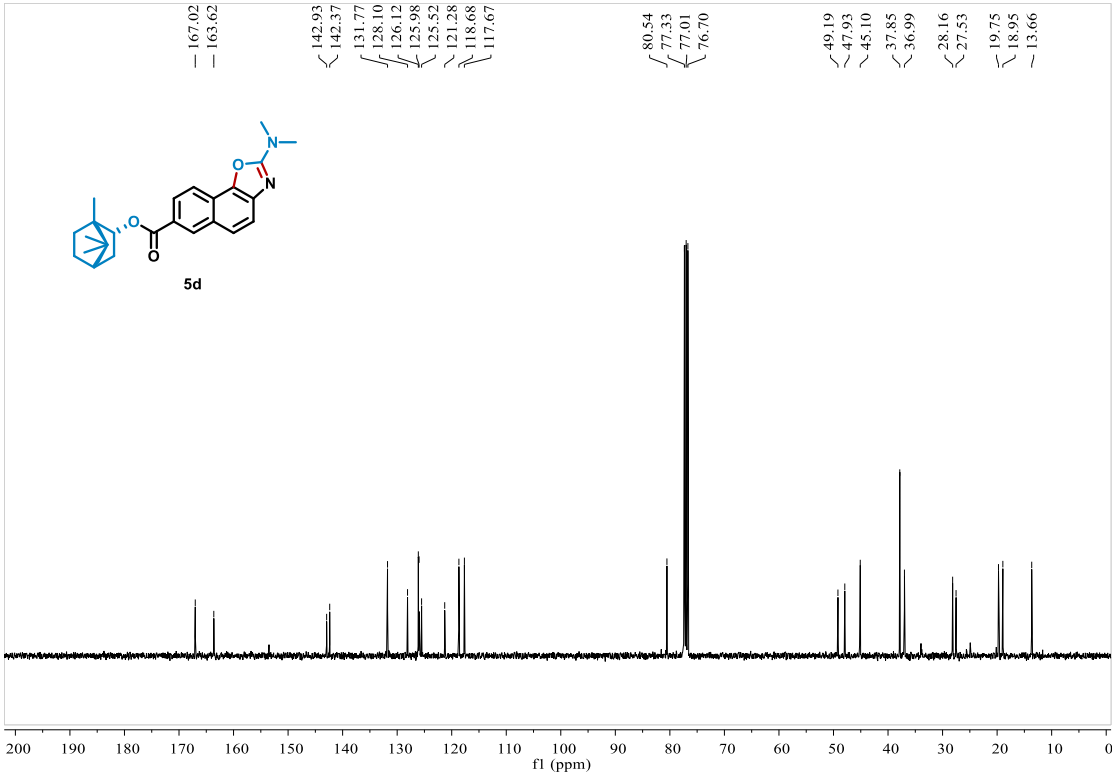
^{13}C NMR of **5c** (151 MHz, $CDCl_3$)



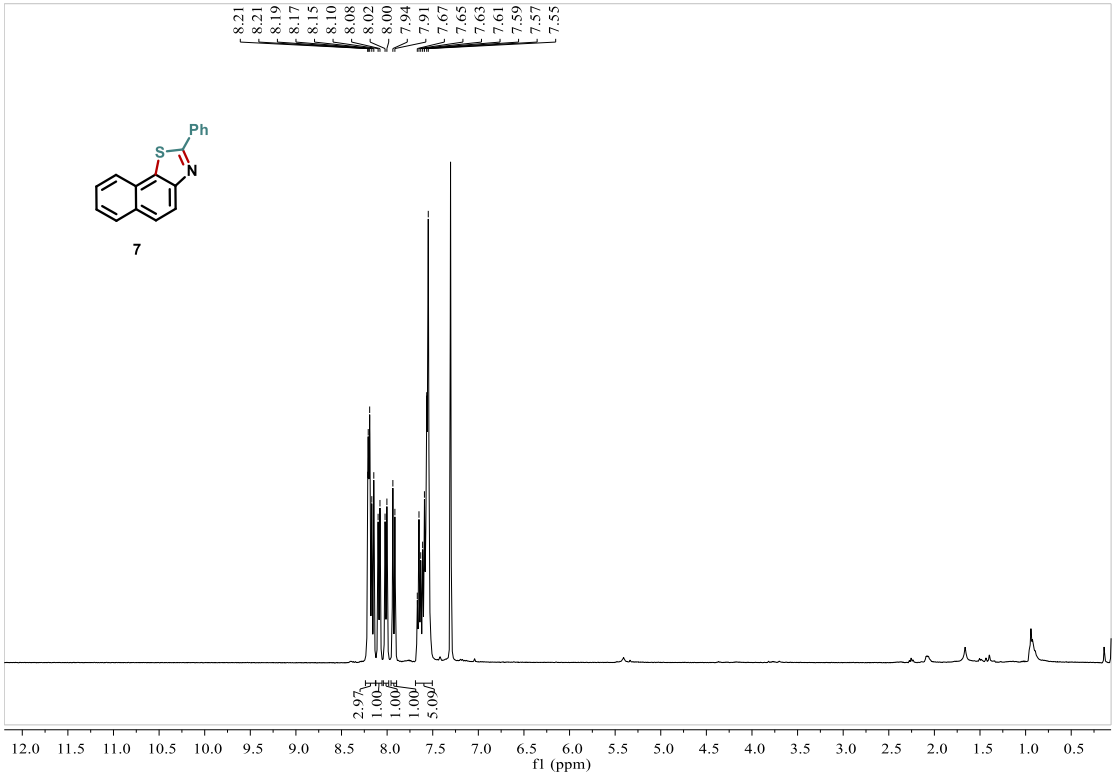
^{1}H NMR of **5d** (400 MHz, $CDCl_3$)



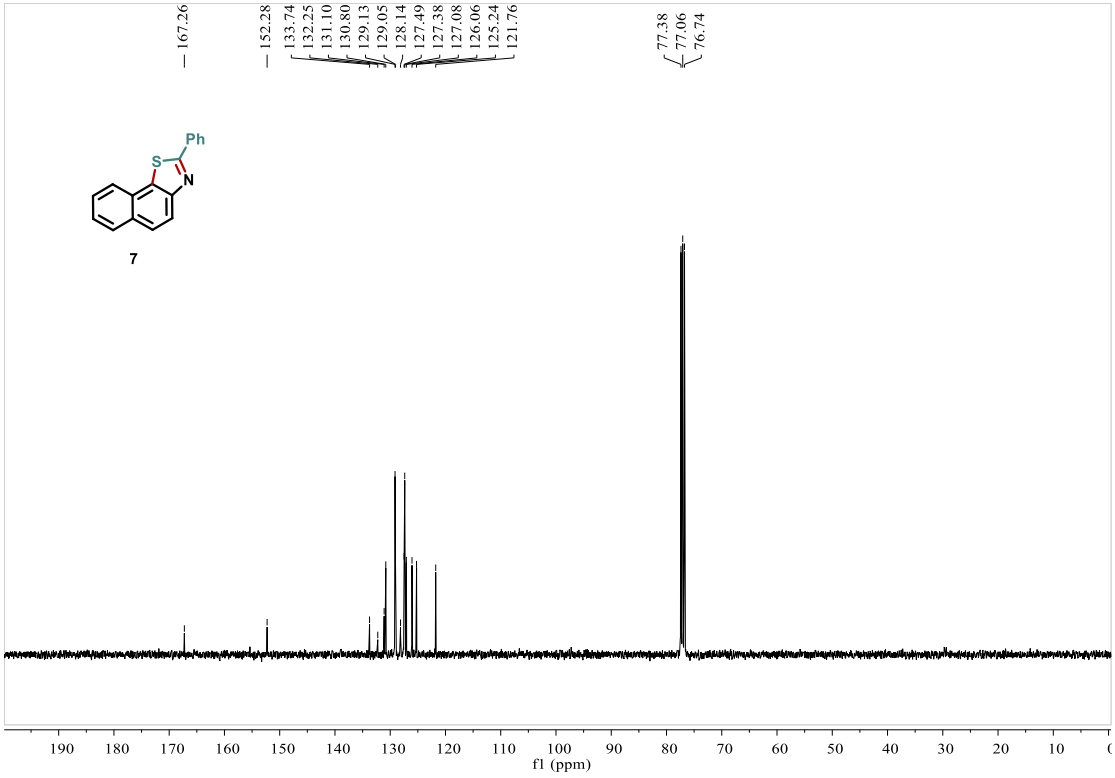
^{13}C NMR of **5d** (100 MHz, $CDCl_3$)



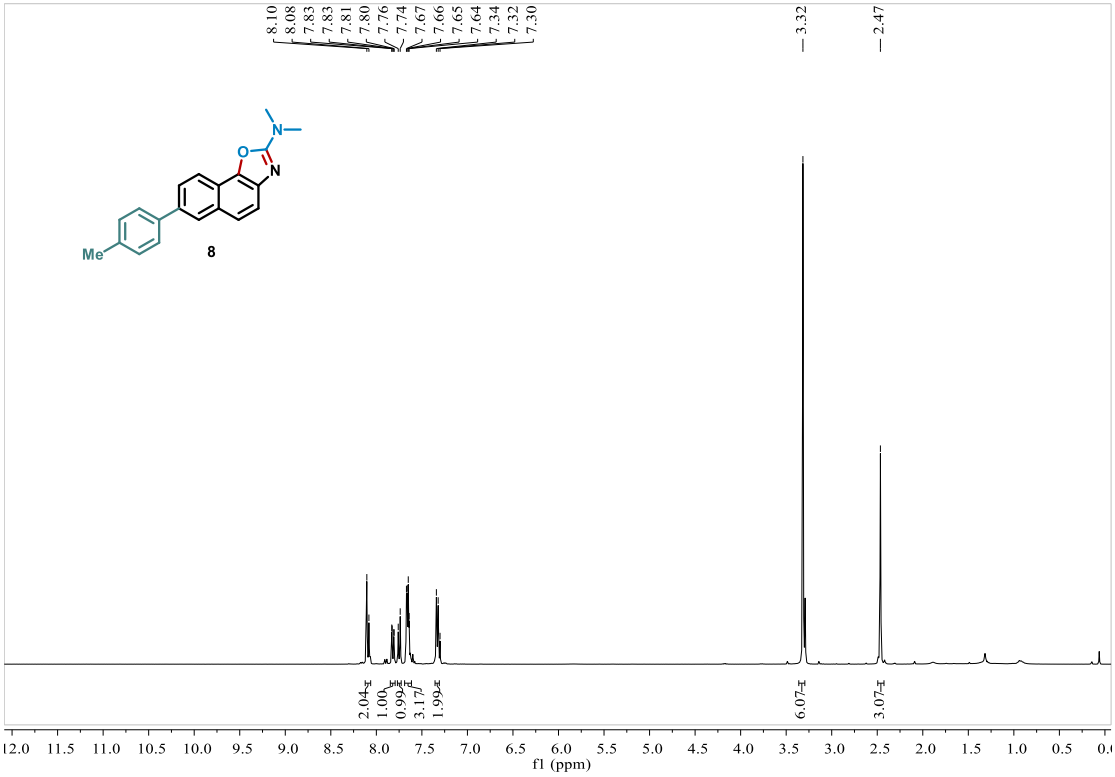
^{1}H NMR of **7** (400 MHz, $CDCl_3$)



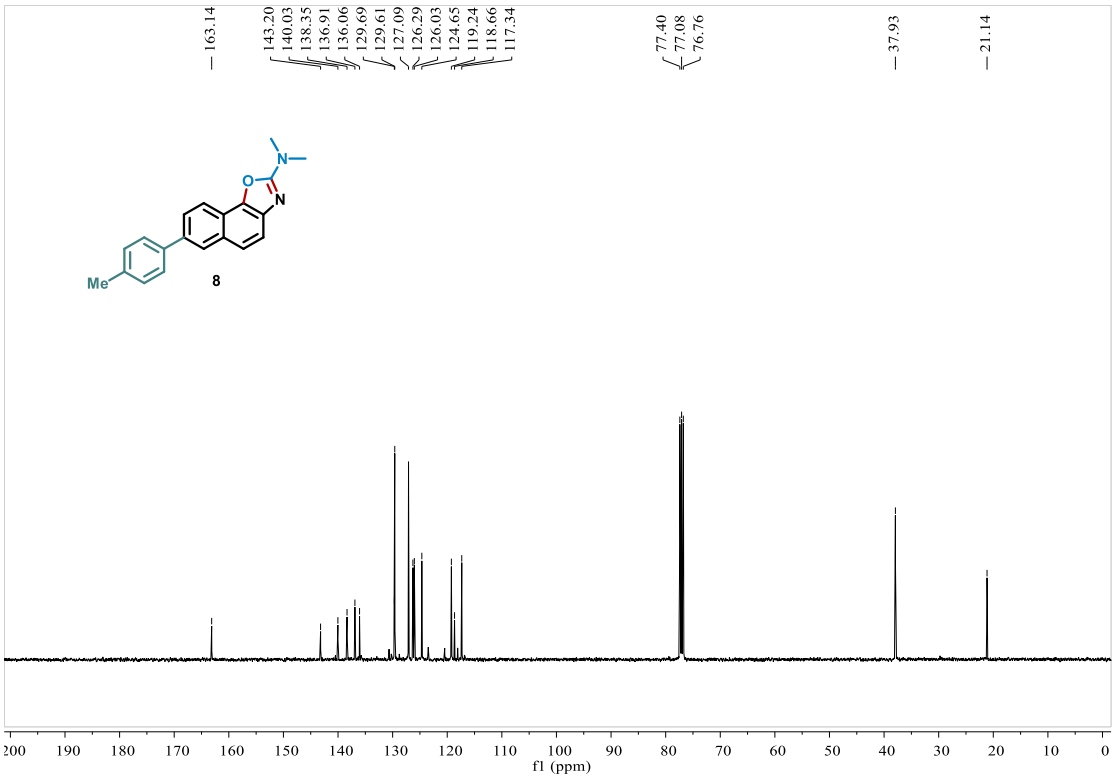
^{13}C NMR of **7** (100 MHz, $CDCl_3$)



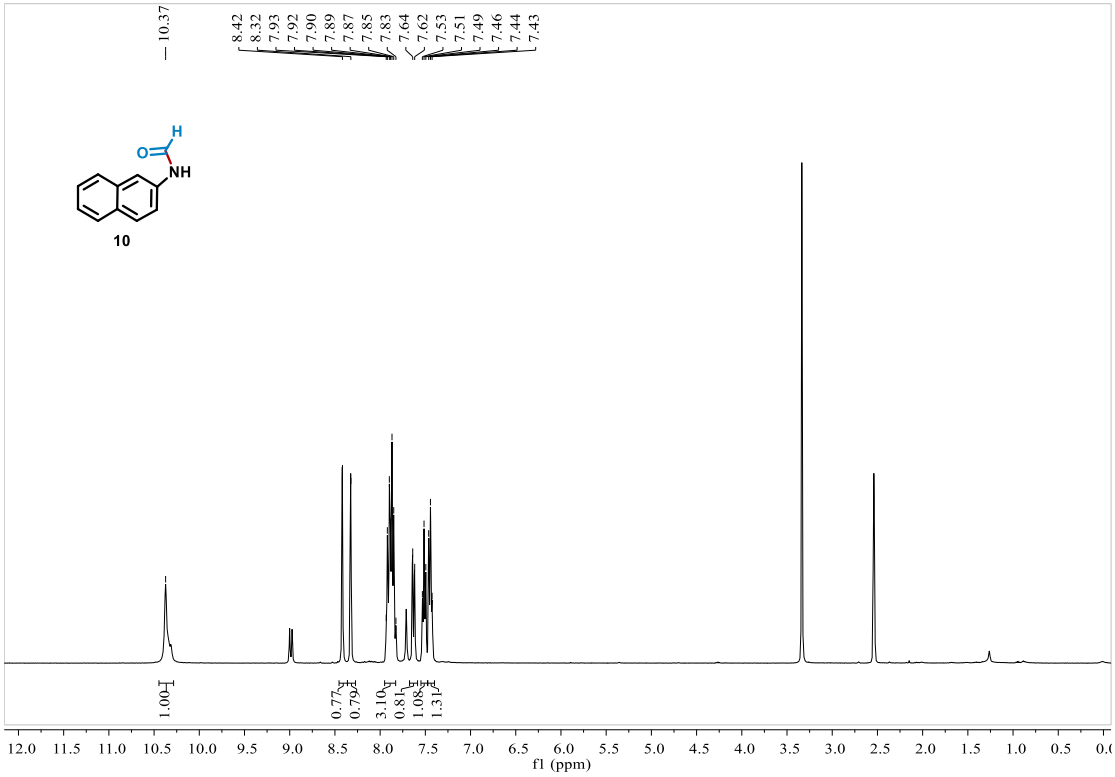
^{1}H NMR of **8** (400 MHz, $CDCl_3$)



^{13}C NMR of **8** (100 MHz, $CDCl_3$)



^{1}H NMR of **10** (400 MHz, DMSO)



^{13}C NMR of **10** (100 MHz, DMSO)