Supporting Information

for

1,2-Benzothiazines from Sulfoximines and Allyl Methyl Carbonate by Rhodium-Catalyzed Cross Coupling and Oxidative Cyclization

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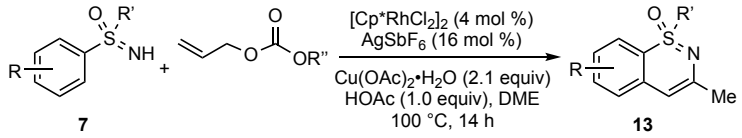
1. General information

^{1}H NMR spectra were recorded at 400 MHz or 600 MHz. The solvent for the NMR spectroscopy was $CDCl_3$ unless noted otherwise. Chemical shifts are reported in delta (δ) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = single, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. Chemical shifts are reported in ppm relative to 77.0 ppm for $CDCl_3$. High resolution mass spectra (HRMS) were measured on a Thermo Scientific LTQ Orbitrap XL spectrometer with positive ion mode. Melting points were determined in open-end capillary tubes on a Büchi B-540 melting point apparatus.

Flash column chromatography purifications were performed using silica gel 60 (63-200 μm) from Merck. All other reagents were purchased from Sigma-Aldrich, Acros or Alfa Aesar and used without further purification. All solvents were dried according to known methods and distilled prior to use. Sulfoximines **7a-q**[1] and allyl carbonates **12a-c**[2] were synthesized according to literature procedures.

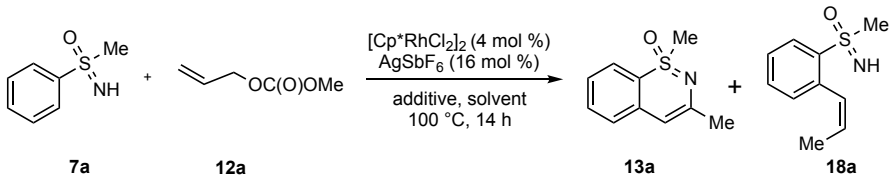
2. General experimental procedure



A sealed tube (15 mL) was charged with sulfoximine **7** (0.30 mmol), the allyl carbonate (0.9 mmol), $[Cp^*RhCl_2]_2$ (7.4 mg, 0.012 mmol, 4 mol %), $AgSbF_6$ (16.5 mg, 0.048 mmol), $Cu(OAc)_2 \cdot H_2O$ (125 mg, 0.63 mmol) and AcOH (18 mg, 0.3 mmol) Under an argon atmosphere, dry dimethoxyethane (1.5 mL) was added by syringe. After stirring the reaction mixture at 100 °C for 14 h, it was cooled to room temperature and extracted with dichloromethane (3 x 10 mL). The combined organic layers were extracted with brine (15 mL), dried over $MgSO_4$ and concentrated in vacuo. The product was purified by column chromatography on silica gel with n-pentane/ethyl acetate (4:1 to 2:1) as eluent to afford product **13**.

Scale-up experiment: Use of sulfoximine **7a** (155.0 mg, 1 mmol), allyl carbonate **12a** (348.1 mg, 3 mmol), $[Cp^*RhCl_2]_2$ (24.7 mg, 0.04 mmol), $AgSbF_6$ (55.0 mg, 0.16 mmol), $Cu(OAc)_2 \cdot H_2O$ (418 mg, 2.1 mmol) and AcOH (60 mg, 1 mmol), and dry dimethoxyethane (5 mL) in a 25 mL sized sealed tube under argon (for 14 h at 100 °C) followed by work-up (as detailed above) with DCM (3 x 10 mL) and brine (15 mL) gave 112 mg (58%) of product **13a**.

Table S1: Optimization of the reaction conditions[a,b]



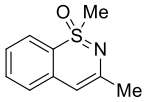
7a **12a** **13a** **18a**

Entry	Solvent	Additive (equiv)	Yield of **13a** (%)	Yield of **18a** (%, *Z*/*E*)
1	MeOH	$Cu(OAc)_2 \cdot H_2O$ (2.1)	20	0
2	*t*-BuOH	$Cu(OAc)_2 \cdot H_2O$ (2.1)	32	0
3	*t*-AmOH	$Cu(OAc)_2 \cdot H_2O$ (2.1)	35	0
4	DME	$Cu(OAc)_2$ (2.1)	52	0
5	DME	—	0	40 (9:1)
6	DCE	—	0	38 (10:1)
7	DME	Ag(OAc) (1.0)	0	39 (10:1)
8	DME	Ag_2CO_3 (1.0)	0	37 (9:1)
9	DME	Ag_2O (1.0)	0	31 (8:1)
10	DME	HOAc (1.0)	0	50 (11:1)
11	DME	HOAc (2.0)	0	48 (11:1)
12	DME	PivOH (1.0)	0	44 (6:1)
13	DME	$Fe(OAc)_2$ (0.2)	0	40 (10:1)
14	DCE	HOAc (1.0)	0	42 (10:1)
15	MeOH	HOAc (1.0)	0	25 (3:1)
16	*t*-AmOH	HOAc (1.0)	0	31 (4:1)
17	toluene	HOAc (1.0)	0	36 (9:1)

[a]Reaction conditions: sulfoximine **7a** (0.3 mmol), carbonate **12a** (0.9 mmol, 3.0 equiv), $[Cp^*RhCl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), additive and solvent (1.5 mL) at 100 °C for 14 h in a sealed tube under argon. [b]The *Z*/*E* ratios were determined by ^1H NMR spectroscopy.

Characterization data of products

1,3-Dimethylbenzo[*e*][1,2]thiazine 1-oxide (13a)[3]



Yellow solid, 41.7 mg, 72% yield, melting point: 93-95 °C.

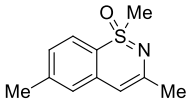
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.71 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 8.1 Hz, 1H), 5.94 (s, 1H), 3.50 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 148.1, 136.7, 132.5, 125.9, 125.5, 123.3, 117.2, 99.1, 45.1, 25.1.

MS (EI): m/z = 193 (55, M^+), 178 (8), 162 (5), 139 (6), 77 (27).

IR (KBr): ν = 3003, 2919, 1739, 1590, 1476, 1365, 1194, 970, 821, 748 (cm^{-1}).

HRMS m/z: Calcd for $[C_{10}H_{11}NOS+Na]^+$: 216.0459. Found: 216.0454

1,3,6-Trimethylbenzo[*e*][1,2]thiazine 1-oxide (13b)



Yellow solid, 40.5 mg, 65% yield, melting point: 128-130 °C.

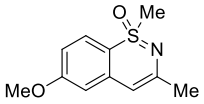
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.60 (d, J = 8.2 Hz, 1H), 7.12 (d, J = 8.2, 1H), 6.99 (s, 1H), 5.86 (s, 1H), 3.46 (s, 3H), 2.38 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.1, 143.2, 136.9, 126.9, 125.6, 123.3, 114.9, 98.9, 45.4, 25.1, 21.7.

MS (EI): m/z = 207 (64, M^+), 191 (2), 192 (9), 193 (1), 153 (5), 77 (29).

IR (KBr): ν = 3021, 2922, 1740, 1594, 1473, 1353, 1190, 1049, 951, 774 (cm^{-1}).

HRMS m/z: Calcd for $[C_{11}H_{13}NOS+Na]^+$: 230.0616 Found: 230.0611.

6-Methoxy-1,3-dimethylbenzo[*e*][1,2]thiazine 1-oxide (13c)



Yellow solid, 42.1 mg, 63% yield, melting point: 137-139 °C.

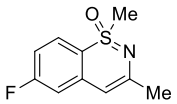
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.63 (d, J = 8.8 Hz, 1H), 6.88 (dd, J = 8.8, 2.5 Hz, 1H), 6.58 (d, J = 2.5 Hz, 1H), 5.85 (s, 1H), 3.85 (s, 3H), 3.44 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 165.3, 149.0, 139.4, 125.6, 114.9, 110.2, 106.7, 98.9, 55.5, 46.0, 25.1.

MS (EI): m/z = 223 (98, M^+), 208 (17), 192 (7), 77 (15).

IR (KBr): ν = 2923, 2855, 1737, 1590, 1469, 1350, 1191, 1055, 902, 779 (cm^{-1}).

HRMS m/z: Calcd for $[C_{11}H_{13}NO_2S+H]^+$: 224.0745. Found: 224.0740.

6-Fluoro-1,3-dimethylbenzo[*e*][1,2]thiazine 1-oxide (13d)



Yellow solid, 35.5 mg, 56% yield, melting point: 111-113 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.73 (dd, J = 8.8, 5.3 Hz, 1H), 7.02 (td, J = 8.5, 2.5 Hz, 1H), 6.85 (dd, J = 9.9, 2.5 Hz, 1H), 5.89 (s, 1H), 3.48 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.8 (d, $J_{C\text{-}F}$ = 256 Hz), 149.9, 139.8 (d, $J_{C\text{-}F}$ = 11 Hz), 126.5 (d, $J_{C\text{-}F}$ = 10 Hz), 114.0 (d, $J_{C\text{-}F}$ = 25 Hz), 113.4, 110.7 (d, $J_{C\text{-}F}$ = 22 Hz), 98.8 (d, $J_{C\text{-}F}$ = 2 Hz), 45.7, 25.1.

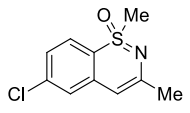
^{19}F NMR (376 MHz, $CDCl_3$) δ –105.2 (m, 1F).

MS (EI): *m/z* = 211 (62, M^+), 196 (15), 157 (5), 134 (4), 107 (20),77 (3).

IR (KBr): ν = 3018, 2926, 1740, 1586, 1472, 1350, 1196, 1062, 952, 777 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{10}H_{10}NOSF+Na]^+$: 234.0365. Found: 234.0359.

6-Chloro-1,3-dimethylbenzo[*e*][1,2]thiazine 1-oxide (13e)



Yellow solid, 42.2 mg, 62% yield, melting point: 143-145 °C.

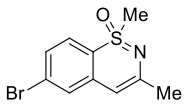
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.57 (d, *J* = 8.5 Hz, 1H), 7.40 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.38 (d, *J* = 1.8 Hz, 1H), 5.87 (s, 1H), 3.48 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 150.0, 138.8, 138.3, 125.8, 125.1, 125.0, 115.1, 98.4, 45.4, 25.1.

MS (EI): *m/z* = 229 (29), 227 (81, M^+), 212 (19), 192 (2), 173 (38), 123 (15), 77(16).

IR (KBr): ν = 3007, 2927, 2309, 1739, 1574, 1459, 1356, 1195, 1064, 896, 781 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{10}H_{10}NOSCl+Na]^+$: 250.0069. Found: 250.0064.

6-Bromo-1,3-dimethylbenzo[*e*][1,2]thiazine 1-oxide (13f)



Yellow solid, 44.6 mg, 55% yield, melting point: 166-168 °C.

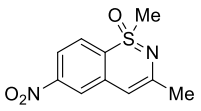
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.57 (d, *J* = 8.5 Hz, 1H), 7.40 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.38 (d, *J* = 1.8 Hz, 1H), 5.87 (s, 1H), 3.48 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 150.0, 138.4, 128.5, 128.2, 127.3, 125.0, 115.5, 98.3, 45.4, 25.2.

MS (EI): *m/z* = 273 (28), 271 (31, M^+), 256 (8), 231 (7), 194 (4), 192 (6), 77 (31).

IR (KBr): ν = 3005, 2924, 1737, 1571, 1459, 1339, 1188, 1065, 960, 781 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{10}H_{10}NOSBr+H]^+$: 271.9745. Found: 271.9739.

1,3-Dimethyl-6-nitrobenzo[*e*][1,2]thiazine 1-oxide (13g)



Yellow solid, 27.1 mg, 38% yield, melting point: 132-134 °C.

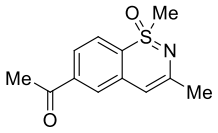
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.11 (d, *J* = 2.1 Hz, 1H), 8.06 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.87 (d, *J* = 8.7 Hz, 1H), 6.14 (s, 1H), 3.59 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 151.5, 149.8, 137.7, 125.1, 121.5, 119.8, 119.1, 99.8, 45., 25.2.

MS (EI): *m/z* = 238 (94, M^+), 223 (12), 192 (13), 184 (5), 161 (12), 77 (15).

IR (KBr): ν = 3095, 2922, 1739, 1588, 1513, 1347, 1197, 1064, 826, 728 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{10}H_{10}N_2O_3S+H]^+$: 239.0490. Found: 239.0485.

1-(1,3-Dimethyl-1-oxidobenzo[*e*][1,2]thiazin-6-yl)ethanone (13h)



Yellow solid, 36.7 mg, 52% yield, melting point: 131-133 °C.

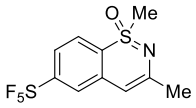
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.83 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.79 - 7.77 (m, 2H), 6.06 (s, 1H), 3.55 (s, 3H), 2.63 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 197.2, 149.5, 139.7, 136.8, 126.8, 124.1, 123.7, 119.3,99.7, 44.9, 26.8, 25.1.

MS (EI): *m/z* = 235 (100, M^+), 220 (4), 192 (4), 158 (2), 77 (10).

IR (KBr): ν = 2917, 1675, 1590, 1533, 1348, 1210, 1065, 894, 774 (cm^{-1}).

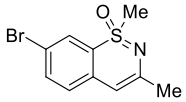
HRMS *m/z*: Calcd for $[C_{12}H_{13}NO_2S+Na]^+$: 258.0565. Found: 258.0560.

1-(1,3-Dimethyl-1-oxidobenzo[*e*][1,2]thiazin-6-yl)ethanone (13i)



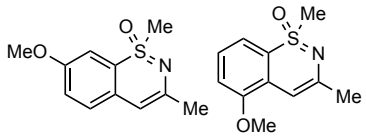
Yellow solid, 43.1 mg, 45% yield, melting point: 138-140 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.79 (d, *J* = 8.6 Hz, 1H), 7.66 - 7.62 (m, 2H), 6.05 (s, 1H), 3.55 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 156.6-156.1 (m, *C*-SF_5), 150.8, 137.2, 124.2, 124.0 (t, $J_{C\text{-}F}$ = 4.5 Hz), 122.3 (t, $J_{C\text{-}F}$ = 4.5 Hz),118.2, 99.5, 45.0, 25.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ 83.2-81.6 (m, 1F), 60.1 (d, *J* = 150 Hz).
MS (EI): *m*/*z* = 319 (38, M^+), 265 (5), 192 (21), 127 (82), 77 (19).
IR (KBr): ν = 3029, 2929, 1740, 1584, 1472, 1355, 1206, 1064, 812 (cm^{-1}).
HRMS *m/z*: Calcd for $[C_{10}H_{10}NOS_2F_5+H]^+$: 320.0202. Found: 320.0197.

7-Bromo-1,3-dimethylbenzo[*e*][1,2]thiazine 1-oxide (13j)



Yellow solid, 43.9 mg, 54% yield, melting point: 147-149 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.16 (d, *J* = 1.5 Hz, 1H), 7.91 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 6.28 (s, 1H), 3.86 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 148.9, 135.7, 135.4, 127.7, 125.7, 118.0, 117.3, 98.8, 45.2, 25.1.
MS (EI): *m*/*z* = 273 (45), 271 (63, M^+), 256 (5), 217 (86), 192 (6), 77 (14).
IR (KBr): ν = 2920, 1743, 1587, 1469, 1369, 1194, 1076, 965, 772 (cm^{-1}).
HRMS *m/z*: Calcd for $[C_{10}H_{10}NOSBr+Na]^+$: 293.9564. Found: 293.9559.

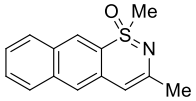
7-Methoxy-1,3-dimethylbenzo[*e*][1,2]thiazine 1-oxide (13k, major) and 5-methoxy-1,3-dimethylbenzo[*e*][1,2]thiazine 1-oxide (13k', minor)



13k + 13k'

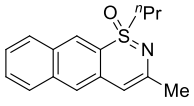
Yellow syrup, 24.2 mg, 36% yield (as isomeric mixture).
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.31 (d, *J* = 8.0 Hz, 1H), 7.25 (dd, *J* = 9.5, 6.5 Hz, 1H), 7.16 – 7.11 (m, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.31 (s, 1H), 5.88 (s, 1H), 3.89 (s, 3H), 3.83 (s, 1H), 3.50 (s, 3H), 3.49 (s, 1H), 2.22 (s, 3H), 2.16 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 157.5, 153.0, 147.8, 145.3, 130.5, 127.6, 125.4, 122.1, 117.4, 117.0, 114.7, 111.6, 104.8, 98.7, 92.8, 92.7, 55.8, 55.7, 45.1, 45.0, 25.3, 24.7.
MS (EI): *m*/*z* = 223 (45, M^+), 169 (5), 117 (7).
IR (KBr): ν = 2934, 1729, 1457, 1345, 1209, 1037, 764 (cm^{-1}).
HRMS *m/z*: Calcd for $[C_{10}H_{10}NOSBr+H]^+$: 223.0667. Found: 223.0662.

1,3-Dimethylnaphtho[2,3-*e*][1,2]thiazine 1-oxide (13l)



Yellow solid, 45.9 mg, 63% yield, melting point: 184-186 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.34 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.62 (s, 1H), 7.55 – 7.52 (m, 1H), 7.44 – 7.41 (m, 1H), 6.08 (s, 1H), 3.50 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 146.5, 135.6, 132.2, 131.2, 128.8, 128.7, 127.6, 125.5, 124.6, 122.8, 120.2, 99.3, 45.2, 25.2.
MS (EI): *m*/*z* = 243 (72, M^+), 189 (5), 166 (3), 139 (9), 126 (9), 77 (4).
IR (KBr): ν = 3019, 2919, 1739, 1592, 1369, 1197, 1050, 882, 744 (cm^{-1}).
HRMS *m/z*: Calcd for $[C_{14}H_{13}NOS+Na]^+$: 266.0616. Found: 266.0610.

3-Methyl-1-propylnaphtho[2,3-*e*][1,2]thiazine 1-oxide (13m)



Yellow solid, 47.2 mg, 58% yield, melting point: 112-114 °C.

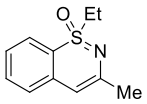
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.30 (s, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.60 (s, 1H), 7.58 – 7.50 (m, 1H), 7.43 – 7.40 (m, 1H), 6.00 (s, 1H), 3.68 – 3.65 (m, 1H), 3.49 – 3.44 (m, 1H), 2.22 (s, 3H), 1.81 – 1.67 (m, 1H), 1.59 – 1.52 (m, 1H), 0.96 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 147.2, 135.8, 133.3, 131.2, 128.8, 128.7, 127.6, 125.5, 125.4, 122.6, 118.0, 98.4, 59.0, 25.3, 17.2, 12.6.

MS (EI): *m*/*z* = 271 (40, M^+), 166 (3), 126 (15), 77 (5).

IR (KBr): ν = 3050, 2959, 1738, 1587, 1371, 1182, 1034, 872, 742 (cm^{-1}).

HRMS *m*/*z*: Calcd for $[C_{16}H_{17}NOS+H]^+$: 272.1109. Found: 272.1104.

1-Ethyl-3-methylbenzo[*e*][1,2]thiazine 1-oxide (13n)



Yellow oil. 44.1 mg, 71% yield.

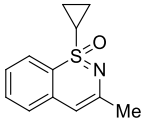
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.65 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 5.87 (s, 1H), 3.71 (dq, *J* = 14.5, 7.2 Hz, 1H), 3.49 (dq, *J* = 14.8, 7.4 Hz, 1H), 2.21 (s, 3H), 1.17 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 149.0, 136.7, 138.1, 132.6, 125.9, 125.4, 123.7, 114.1, 98.3, 51.1, 25.1, 8.7.

MS (EI): *m*/*z* = 207 (82, M^+), 178 (12), 131 (14), 116 (2), 77 (18).

IR (KBr): ν = 2925, 1736, 1584, 1467, 1365, 1190, 1057, 749 (cm^{-1}).

HRMS *m*/*z*: Calcd for $[C_{11}H_{13}NOS+H]^+$: 208.0796. Found: 208.0791.

1-Cyclopropyl-3-methylbenzo[*e*][1,2]thiazine 1-oxide (13o)



Yellow oil. 46.0 mg, 70% yield.

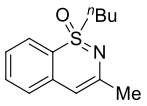
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.79 (d, *J* = 8.1 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.32 – 7.27 (m, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 5.95 (s, 1H), 2.82 – 2.78 (m, 1H), 2.21 (s, 3H), 1.75 – 1.71 (m, 1H), 1.41– 1.37 (m, 1H), 1.35 – 1.28 (m, 1H), 1.22 – 1.17 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 148.3, 136.9, 132.2, 125.7, 125.3, 123.5, 117.9, 99.1, 32.4, 6.8, 4.5.

MS (EI): *m*/*z* = 219 (58, M^+), 178 (4), 130 (10), 116 (3), 103 (13), 89 (14), 77 (25)

IR (KBr): ν = 3047, 2918, 2325, 1738, 1589, 1471, 1367, 1208, 1051, 886, 740 (cm^{-1}).

HRMS *m*/*z*: Calcd for $[C_{12}H_{13}NOS+H]^+$: 220.0796. Found: 220.0791.

1-Butyl-3-methylbenzo[*e*][1,2]thiazine 1-oxide (13p)



Yellow oil. 45.8 mg, 65% yield.

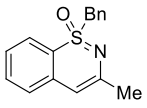
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.65 (d, *J* = 8.1 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.30 – 7.27 (m, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 5.95 (s, 1H), 3.68 – 3.63 (m, 1H), 3.50 – 3.45 (m, 1H), 2.21 (s, 3H), 1.65 – 1.61 (m, 1H), 1.45– 1.35 (m, 4H), 0.89 – 0.86(m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 148.8, 137.8, 132.6, 125.9, 125.4, 123.7, 114.8, 98.3, 56.4, 25.9, 25.2, 21.2, 13.5.

MS (EI): *m*/*z* = 235 (30, M^+), 178 (6), 159 (3), 119 (2), 116 (5), 77 (22), 76 (13), 57 (51).

IR (KBr): ν = 2955, 2096, 1732, 1588, 1470, 1370, 1199, 1067, 789 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{13}H_{17}NOS+H]^+$: 236.1109. Found: 236.1104

1-Benzyl-3-methylbenzo[*e*][1,2]thiazine 1-oxide (13q)



Yellow oil. 48.4 mg, 60% yield.

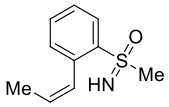
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.20 – 7.17 (m, 3H), 7.11 (d, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 5.57 (s, 1H), 4.67 (d, *J* = 14.1 Hz, 1H), 4.48 (d, *J* = 14.1 Hz, 1H), 2.11 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 149.4, 138.9, 133.0, 131.0, 128.6, 128.3, 128.1, 125.3, 125.1, 125.0, 113.9, 98.0, 64.6, 25.0.

MS (EI): *m/z* = 269 (4, M^+), 178 (9), 153 (2), 91 (100), 89 (3), 77 (4).

IR (KBr): ν = 3047, 2918, 1738, 1585, 1473, 1367, 1205, 1062, 778 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{16}H_{15}NOS+H]^+$: 270.0953. Found: 270.0947.

(*Z*)-1-(*S*-Methylsulfonimidoyl)-2-(prop-1-en-1-yl)benzene (18a)



Z/*E* = 11:1

Yellow oil. 29.3 mg, 50% yield.

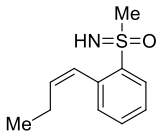
^{1}H NMR (600 MHz, $CDCl_3$) ***Z* isomer**: δ (ppm) 8.04 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.55 – 7.53 (m, 1H), 7.51 –7.48 (m, 2H), 7.36 – 7.33 (m, 1H), 6.20 (dq, *J* = 15.6, 6.7 Hz, 1H), 3.09 (s, 3H), 2.88 (bs, 1H), 1.93 (dd, *J* = 6.7, 1.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) ***Z* isomer**: δ (ppm) 139.3, 137.9, 133.0, 131.5, 128.6, 128.3, 127.6, 127.0, 44.3, 18.8.

MS (EI): *m/z* = 195 (33, M^+), 180 (100), 117 (49), 78 (12), 77 (23).

IR (KBr): ν = 3269, 2923, 2111, 1643, 1460, 1316, 1218, 1065, 995, 750 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{10}H_{13}NOS+H]^+$: 196.0796. Found: 196.0791.

(*Z*)-1-(But-1-en-1-yl)-2-(*S*-methylsulfonimidoyl)benzene (18b)



Z/*E* = 7:1

Yellow oil. 30.1 mg, 48% yield.

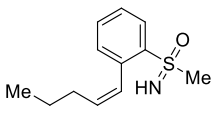
^{1}H NMR (600 MHz, $CDCl_3$) ***Z* isomer**: δ 8.04 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 6.22 (dt, *J* = 15.7, 6.6 Hz, 1H), 3.08 (s, 3H), 2.73 (bs, 1H), 2.35 – 2.21 (m, 2H), 1.09 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) ***Z* isomer**: δ (ppm) 139.6, 138.3, 137.9, 132.9, 128.6, 128.3, 127.0, 125.6, 44.2, 26.3, 13.4.

MS (EI): *m/z* = 209 (13, M^+), 194 (14), 180 (100), 131 (10), 78 (11), 77 (25).

IR (KBr): ν = 3273, 2964, 2116, 1642, 1460, 1221, 1065, 993, 749 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{11}H_{15}NOS+H]^+$: 210.0953. Found: 210.0947.

(*Z*)-1-(*S*-Methylsulfonimidoyl)-2-(pent-1-en-1-yl)benzene (18c)



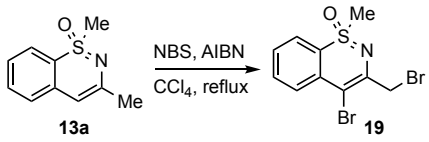
Z/*E* = 4:1

Yellow oil. 32.1 mg, 45% yield.

^{1}H NMR (600 MHz, $CDCl_3$) ***Z* isomer**: δ 8.09 (d, *J* = 7.9 Hz, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.52 – 7.49 (m, 2H), 7.35 (t, *J* = 7.7 Hz, 1H), 6.22 – 6.17 (m, 1H), 3.10 (s, 3H),2.30 – 2.26 (m, 2H), 1.49 – 1.44 (m, 2H), 1.38 – 1.33 (m, 3H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) ***Z* isomer**: δ (ppm) 139.6,

138.0, 137.1, 133.0, 128.7, 128.4, 127.0, 126.5, 44.2, 33.0, 31.3, 22.3, 13.9.
MS (EI): *m*/*z* = 237 (12, M^+), 222 (23), 180 (100), 159 (3), 78 (4), 77 (7).
IR (KBr): ν = 3274, 2926, 2111, 1693, 1461, 1222, 1066, 995, 751 (cm^{-1}).
HRMS *m/z*: Calcd for $[C_{13}H_{19}NOS+H]^+$: 238.1266. Found: 238.1261.

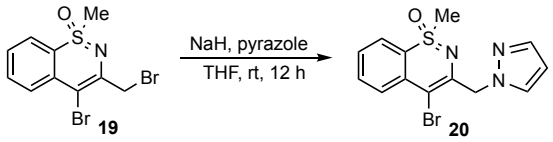
Procedure for the synthesis of 4-bromo-3-(bromomethyl)-1-methylbenzo[*e*][1,2]-thiazine 1-oxide (19)



13a **19**

A mixture of **13a** (0.4 mmol, 77.2 mg), NBS (0.8 mmol, 143 mg) and AIBN (0.08 mmol, 13.2 mg) in CCl_4 (8 mL) was heated to reflux for 12 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was washed with saturated $NaHCO_3$ and brine, and the organic layer was dried over $MgSO_4$, filtered, and concentrated. The product was purified by flash column chromatography on silica gel with n-pentane/ethyl acetate (3:1) as eluent to give product **19** as a yellow solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.95 (d, *J* = 8.5 Hz, 1H), 7.76 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.71 – 7.68 (m, 1H), 7.54 – 7.51 (m, 1H), 4.54 (d, *J* = 9.6 Hz, 1H), 4.47 (d, *J* = 9.6 Hz, 1H), 3.56 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 144.2, 134.0, 133.5, 128.0, 127.7, 123.3, 121.3, 98.2, 44.5, 35.9.
MS (EI): *m*/*z* = 353 (50), 351 (100, M^+), 270 (23).
IR (KBr): ν = 2925, 2329, 1744, 1454, 1321, 1200, 1050, 907, 753 (cm^{-1}).
HRMS *m/z*: Calcd for $[C_{10}H_9Br_2NOS+H]^+$: 351.8829. Found: 351.8825.

Procedure for the synthesis of 3-[(1*H*-pyrazol-1-yl)methyl]-4-bromo-1-methyl-benzo[*e*][1,2]thiazine 1-oxide (20)

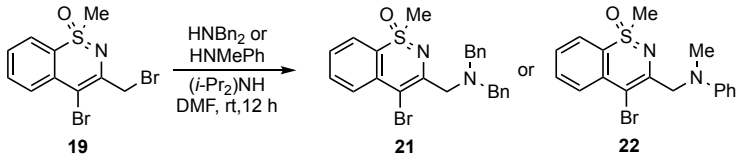


19 **20**

To a solution of pyrazole (0.36 mmol, 24.9 mg) in THF (1.0 mL) was added NaH (60%, 0.45 mmol, 18 mg) portionwise. Then, the suspension was stirred at room temperature for 30 min and **19** (0.3 mmol, 105.3 mg) was added. After stirring at room temperature for 12 h, the mixture was quenched with H_2O (10 mL) and extracted with EtOAc (3 x 10 mol). The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The product was purified by silica gel column chromatography to afford product **20.**
Yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.96 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 7.9, 1H), 7.70 – 7.67 (m, 1H), 7.60 (d, *J* = 2.2 Hz, 1H), 7.52 – 7.49 (m, 2H), 6.25 (t, *J* = 2.0 Hz, 1H), 5.45 (d, *J* = 14.5 Hz, 1H), 5.31 (d, *J* = 14.5 Hz, 1H), 3.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 143.0, 139.4, 134.1, 133.4, 130.1, 127.9, 127.6, 123.2, 121.1, 105.6, 97.6, 57.7, 44.4.

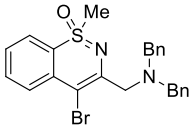
MS (EI): *m*/*z* =339 (10), 337 (8, M^+), 258 (100).
IR (KBr): ν = 2917, 2329, 1741, 1557, 1455, 1308, 1203, 1045, 753 (cm^{-1}).
HRMS *m/z*: Calcd for $[C_{13}H_{12}BrN_3OS+Na]^+$: 359.9782. Found: 359.9777.

Procedure for the synthesis of 4-bromo-3-[(dibenzylamino)methyl]-1-methyl-benzo[*e*][1,2]thiazine 1-oxide (21) and 4-bromo-1-methyl-3-[(methyl(phenyl)-amino]-methyl)benzo[*e*][1,2]thiazine 1-oxide (22)



A mixture of **19** (0.3 mmol, 105.3 mg), (*i*-Pr)$_2$NEt (0.45 mmol, 58 mg) and dibenzylamine or methyl phenyl amine (0.36 mmol) in DMF (1 mL) was stirred at room temperature for 12 h. Then, the reaction mixture was extracted with DCM (3 x 10 mL), and the combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The product was purified by silica gel column chromatography to afford product **21** or **22**.

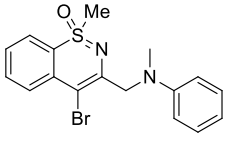
4-Bromo-3-[(dibenzylamino)methyl]-1-methylbenzo[*e*][1,2]thiazine 1-oxide (21)



Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.96 (d, *J* = 8.4 Hz, 1H), 7.71 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.67 – 7.64 (m, 1H), 748 – 7.45 (m, 5H), 7.30 (t, *J* = 7.6 Hz, 4H), 7.22 (t, *J* = 7.3 Hz, 2H), 3.84 – 3.78 (m, 6H), 3.52 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 147.3, 139.5, 134.5, 133.0, 129.0, 127.9, 127.2, 126.9, 126.6, 123.0, 120.3, 98.1, 59.5, 57.8, 44.5.

MS (EI): *m*/*z* = 468 (3), 466 (4, M^+), 387 (19).
IR (KBr): ν = 3032, 2913, 2334, 1462, 1329, 1214, 1058, 734 (cm^{-1}).
HRMS *m/z*: Calcd for $[C_{24}H_{23}BrN_2OS+H]^+$: 467.0793. Found: 467.0789.

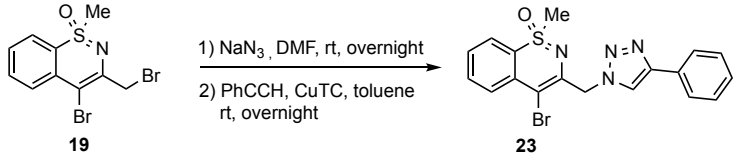
4-Bromo-1-methyl-3-[(methyl(phenyl)amino]methyl)benzo[*e*][1,2]thiazine 1-oxide (22)



Yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.92 (d, *J* = 8.3 Hz, 1H), 7.70 – 7.66 (m, 2H), 7.45 (t, *J* = 7.1 Hz, 1H), 7.22 – 7.19 (m, 2H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.68 (t, *J* = 7.2 Hz, 1H), 4.79 (d, *J* = 16.7 Hz, 1H), 4.36 (d, *J* = 16.7 Hz, 1H), 3.19 (s, 3H), 3.16 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 149.6, 147.5, 134.5, 133.3, 128.9, 127.0, 126.5, 123.3, 120.4, 116.2, 112.5, 96.0, 58.1, 44.5, 39.9.

MS (EI): *m*/*z* = 378 (86), 376 (79, M^+), 297 (100), 120 (97).
IR (KBr): ν = 2913, 2338, 2106, 1475, 1327, 1199, 1019, 741 (cm^{-1}).
HRMS *m/z*: Calcd for $[C_{17}H_{17}BrN_2OS+H]^+$: 377.0323. Found: 377.0319.

Procedure for the synthesis of 4-bromo-1-methyl-3-[(4-phenyl-1*H*-1,2,3-triazol--1-yl)methyl]benzo[*e*][1,2]thiazine 1-oxide (23)



19 **23**

A mixture of **19** (0.3 mmol, 105.3 mg) and NaN_3 (0.45 mmol, 29.3 mg) in DMF (1 mL) was stirred overnight at room temperature. Then reaction mixture was extracted with DCM (3 x 10 mL), and then, the combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated. The crude azidomethyl product (0.3 mmol, 93 mg), phenylacetylene (0.45 mmol, 46 mg) and CuTC (0.03 mmol, 5.75 mg) were dissolved in toluene (1 mL), and the mixture was stirred overnight at room temperature. Then, the solution was extracted with DCM (3 x 10 mL). The combined organic layers were washed with brine, dried over MgSO4, filtered, and concentrated. The product was purified by flash column chromatography on silica gel with n-pentane/ethyl acetate (3:1 to 1:1) as eluent to give **23** as a white solid.

^{1}H NMR (400 MHz, DMSO) δ (ppm) 8.55 (s, 1H), 8.22 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.93 – 7.82 (m, 4H), 7.69 – 7.65 (m, 1H), 7.43 (dd, *J* = 10.4, 4.8 Hz, 2H), 7.34 – 7.29 (m, 1H), 5.69 (d, *J* = 15.1 Hz, 1H), 5.61 (d, *J* = 15.1 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ (ppm) 146.2, 141.8, 133.7, 132.3, 130.8, 128.9, 128.3, 127.9, 126.5, 125.3, 124.2, 122.1, 121.5, 96.3, 55.2, 42,6.

MS (EI): *m*/*z* = 416 (4), 414 (4, M^+), 335 (54).

IR (KBr): ν = 2925, 2664, 2326, 1740, 1557, 1456, 1323, 1201, 1049, 753 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{18}H_{15}BN_4OS + H]^+$: 415.0228. Found: 415.0224.

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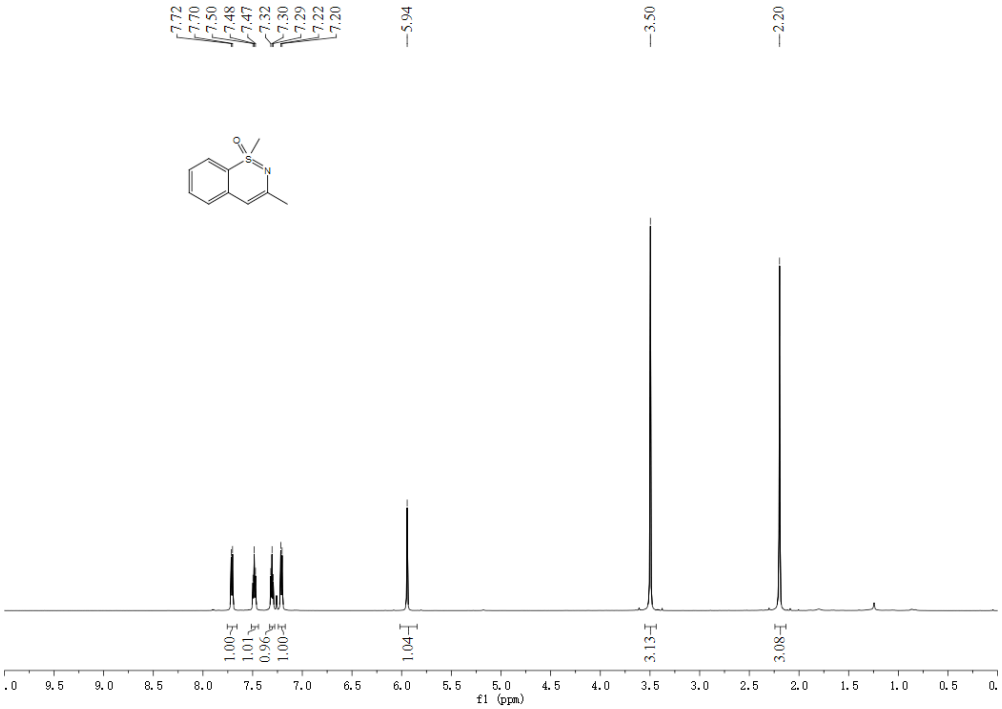
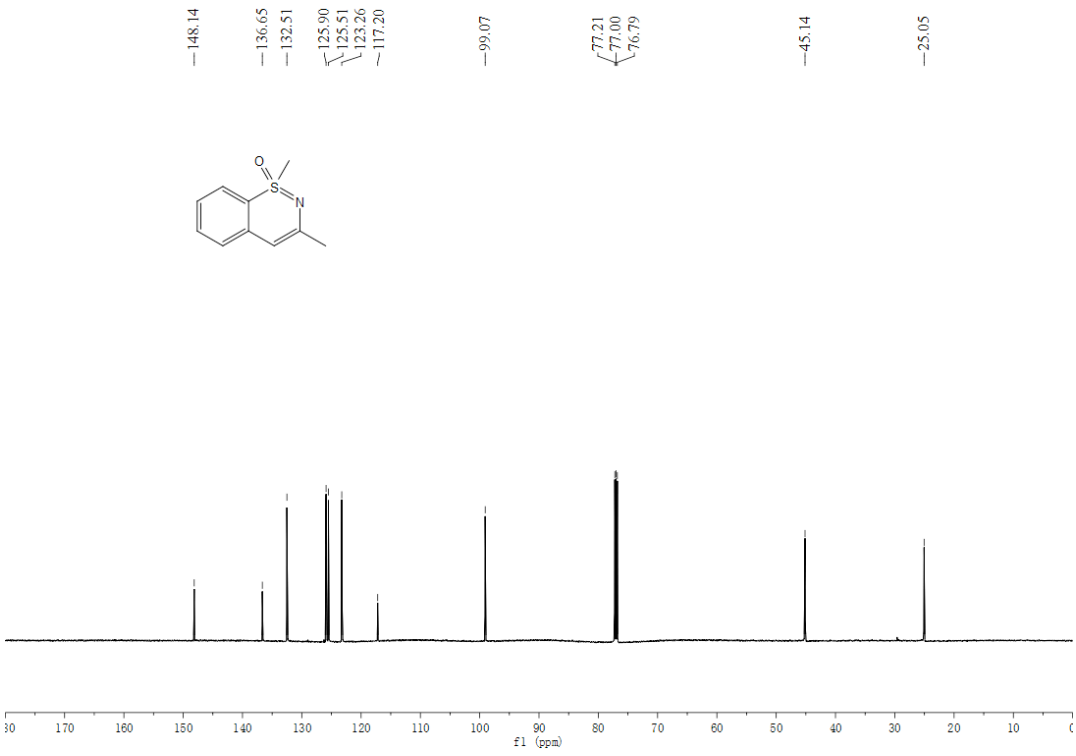
2. (a) Bongini, A.B.;Cardillo, G.; Orena, M.; Porzi, G.; Sandri, S. *J. Org. Chem*. **1982**, *47*, 4626. [b] Vrieze, D. C.; Hoge, G. S.; Hoerter, P. Z.; Van Haitsma, J. T.; Samas, B. M. *Org. Lett*. **2009**, *11*, 3140.

3. (a) Cheng, Y.; Bolm, C. *Angew. Chem., Int. Ed.* **2015**, *127*, 12526. (b) Yu, D.-G.; Azambuja, F. de.; Glorius, F. *Angew. Chem., Int. Ed.* **2014**, *53*, 2754.

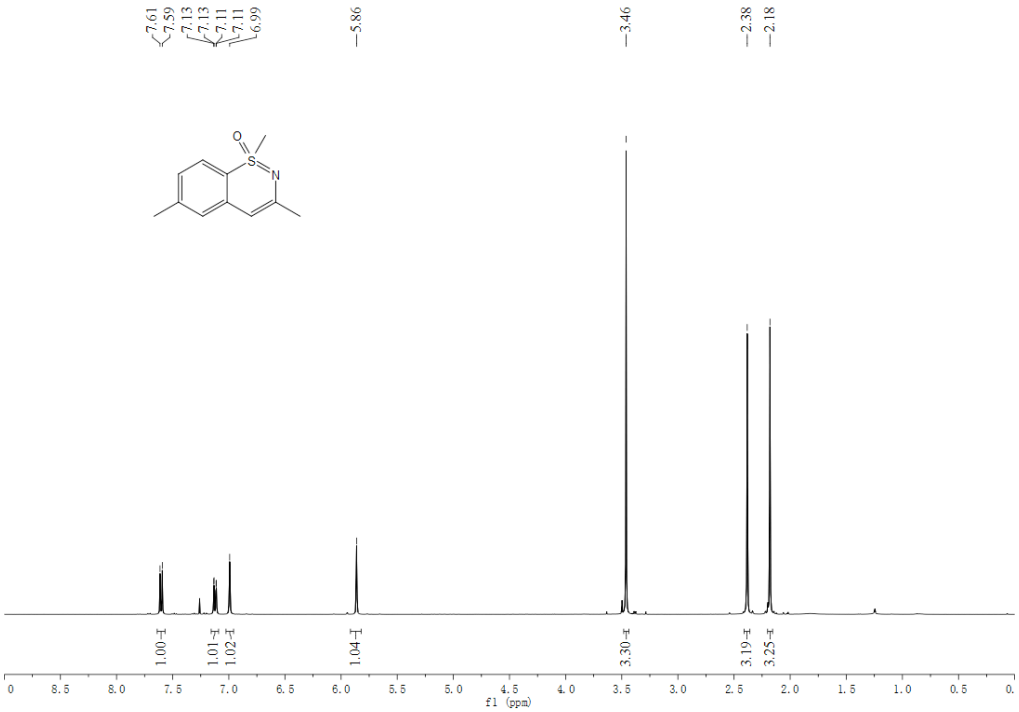
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 13a



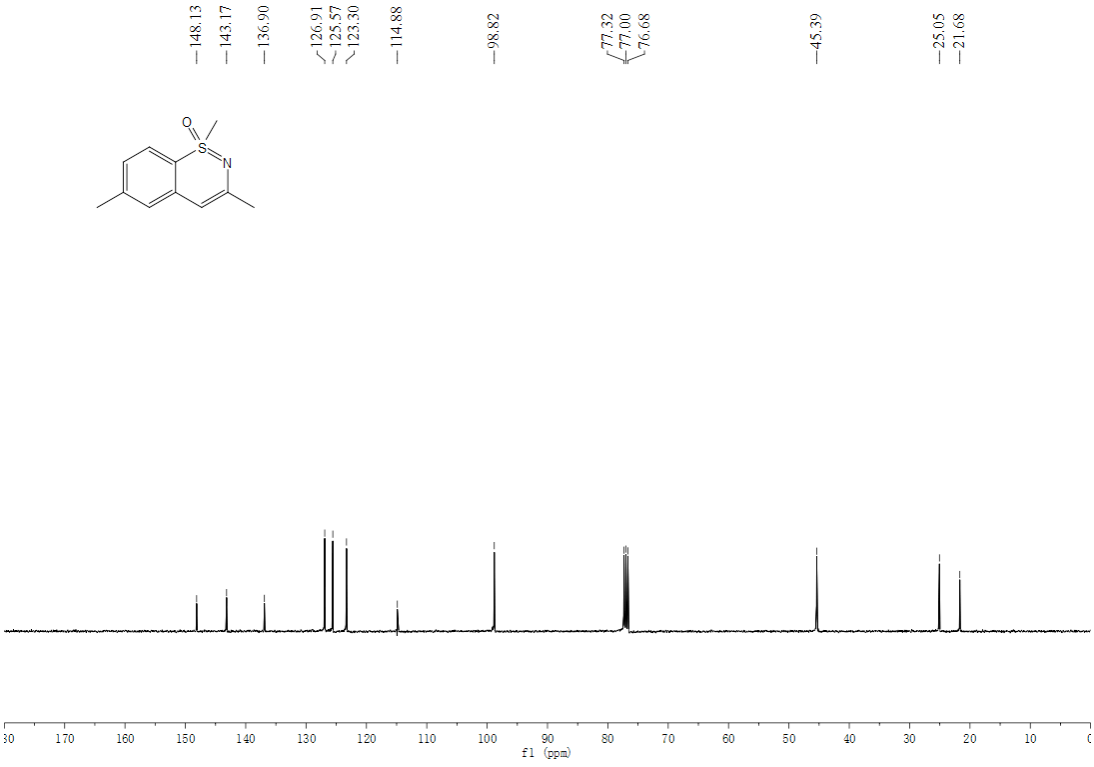
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 13a



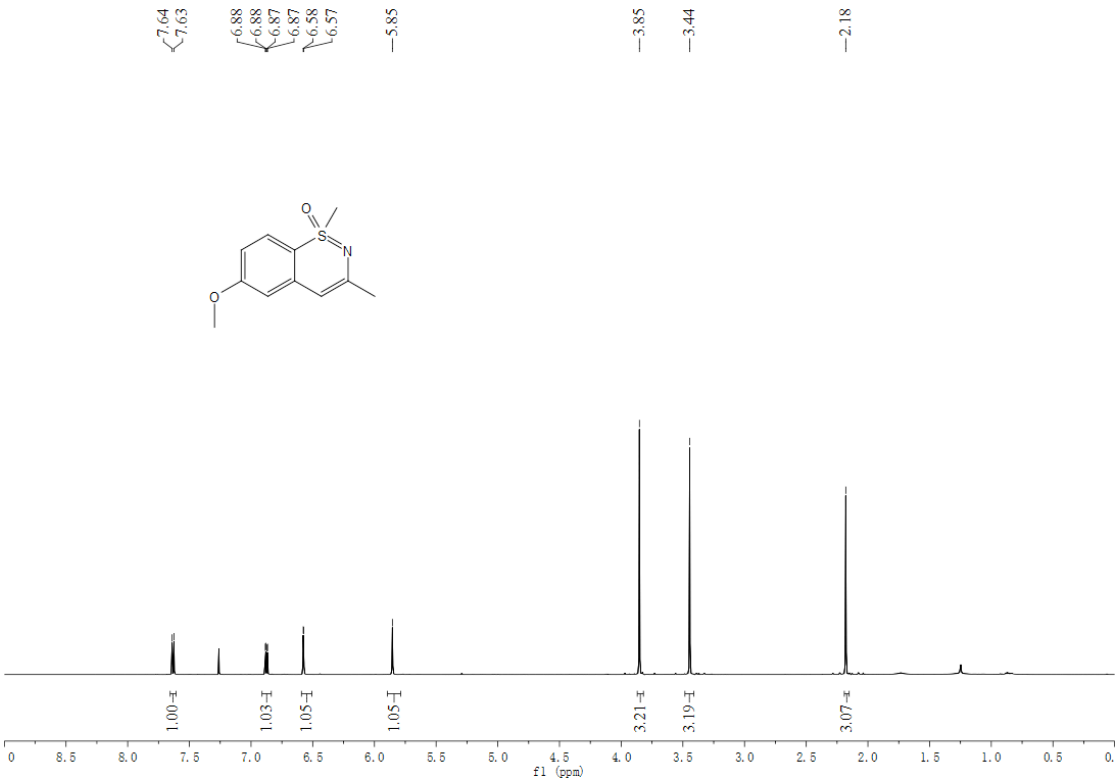
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 13b



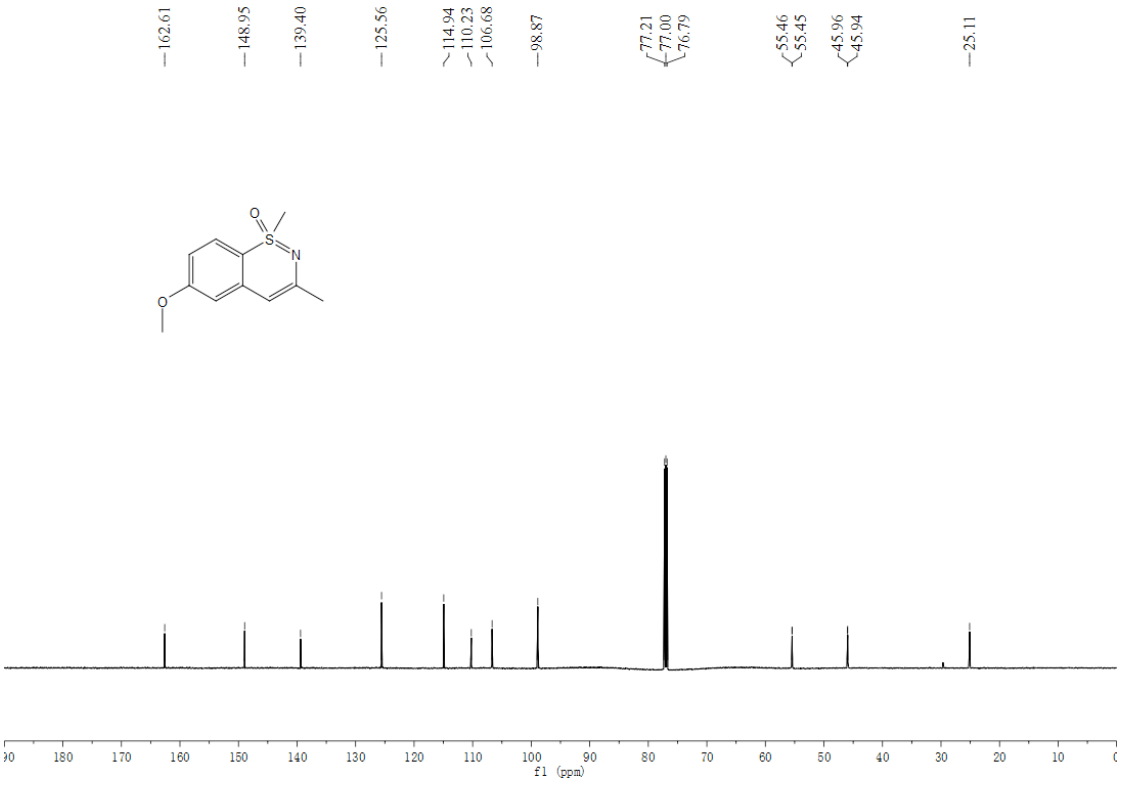
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 13b



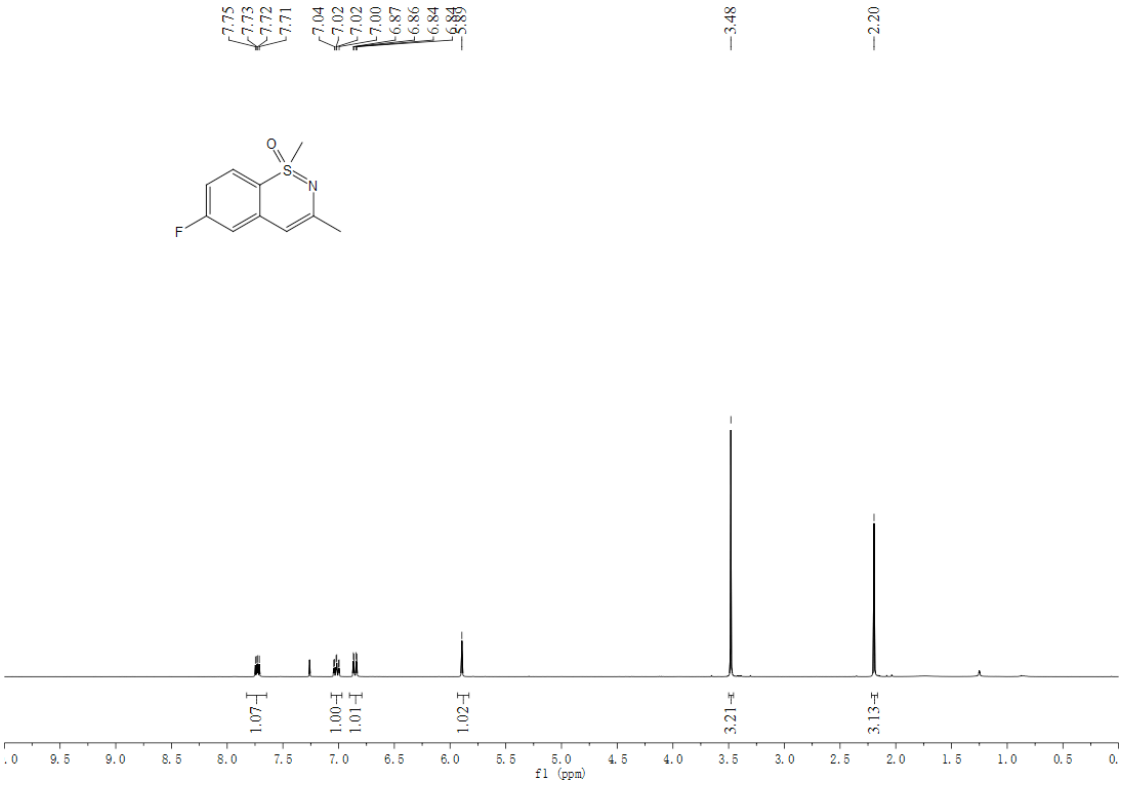
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 13c



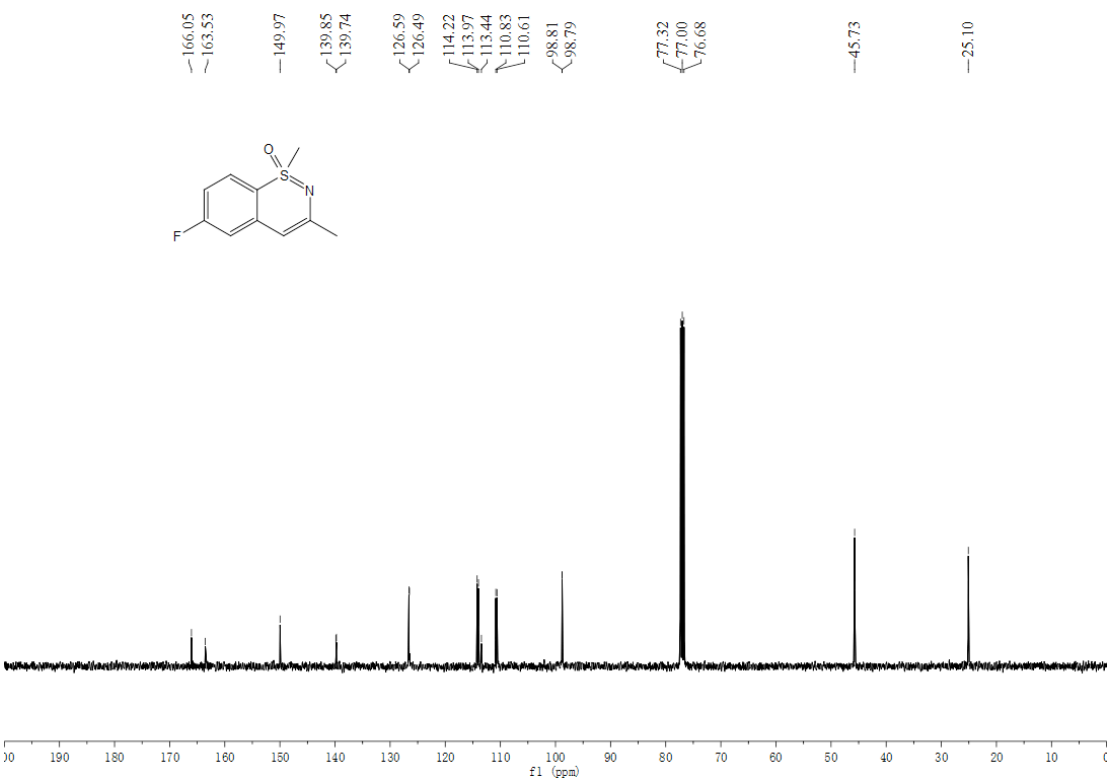
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 13c



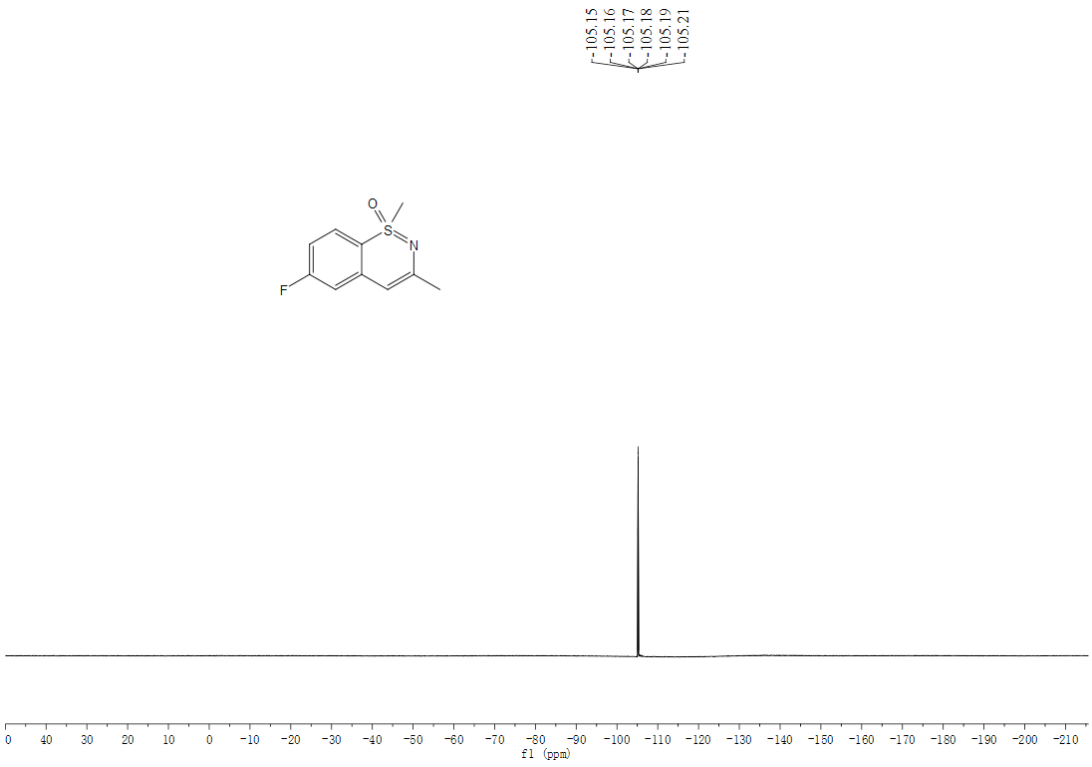
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 13d



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

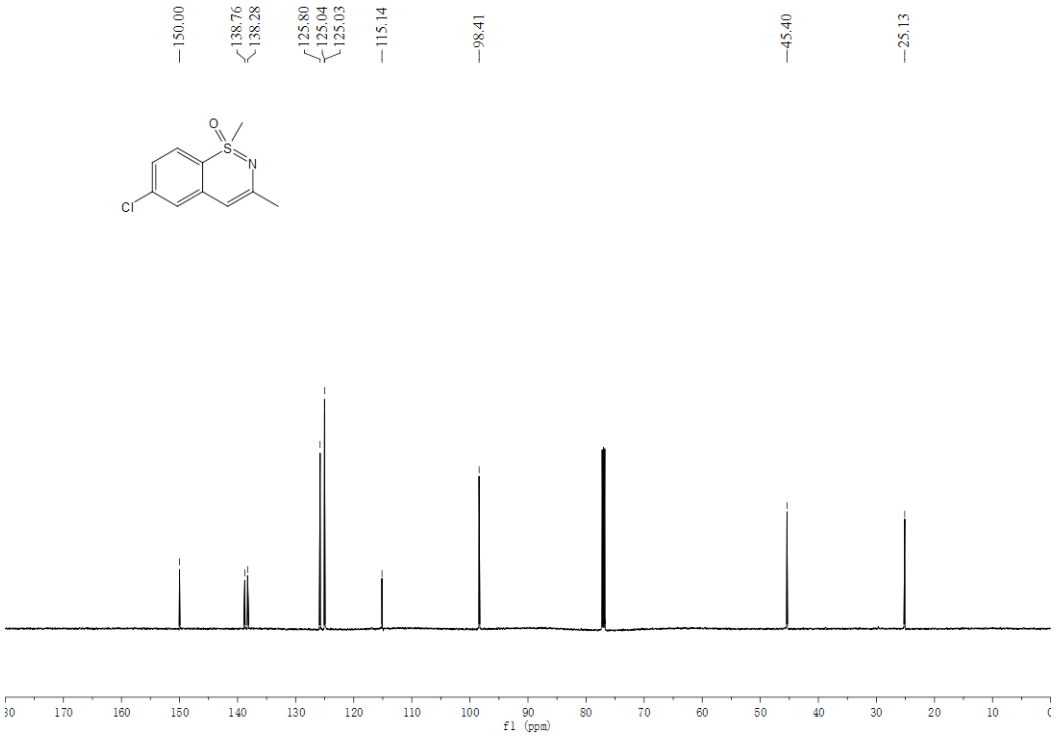


^{1}F NMR spectrum (376 MHz, $CDCl_3$) of 13d

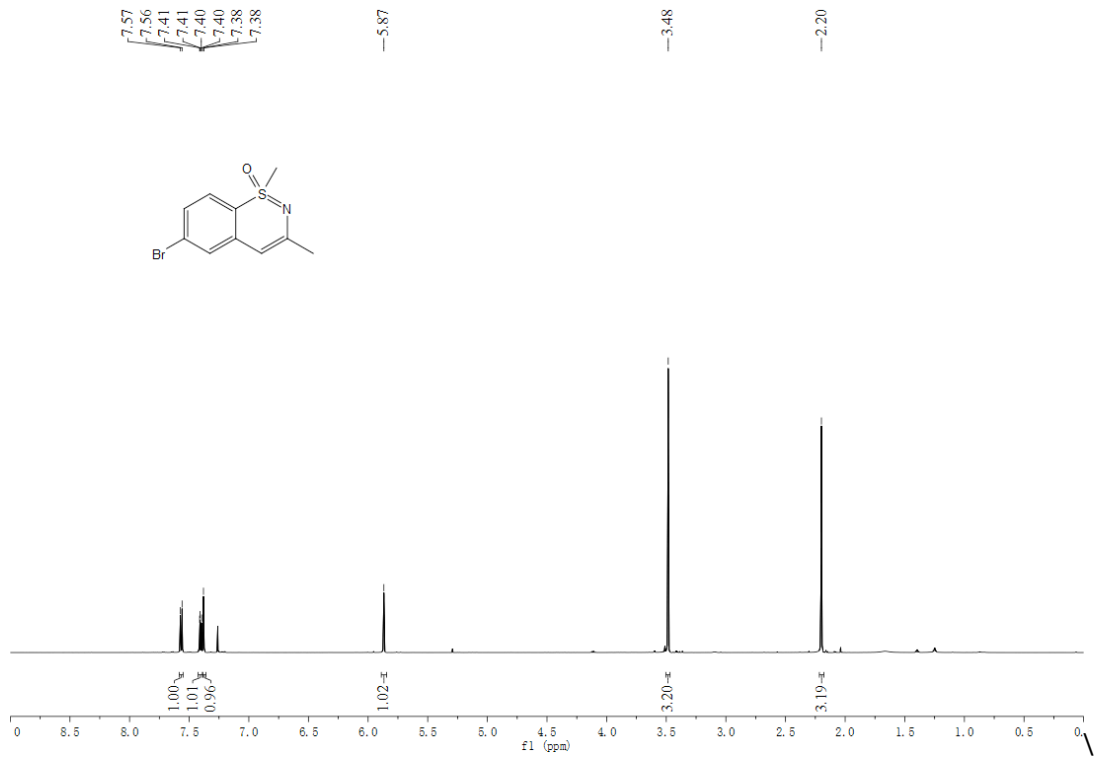


^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 13e

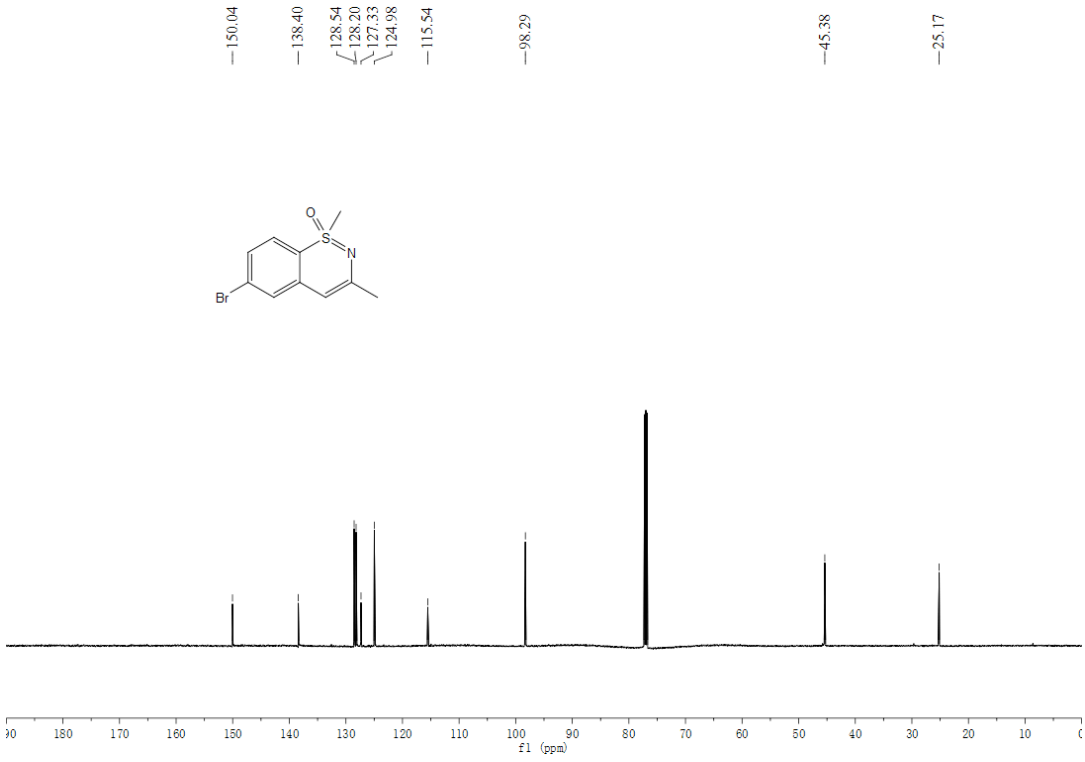
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 13e



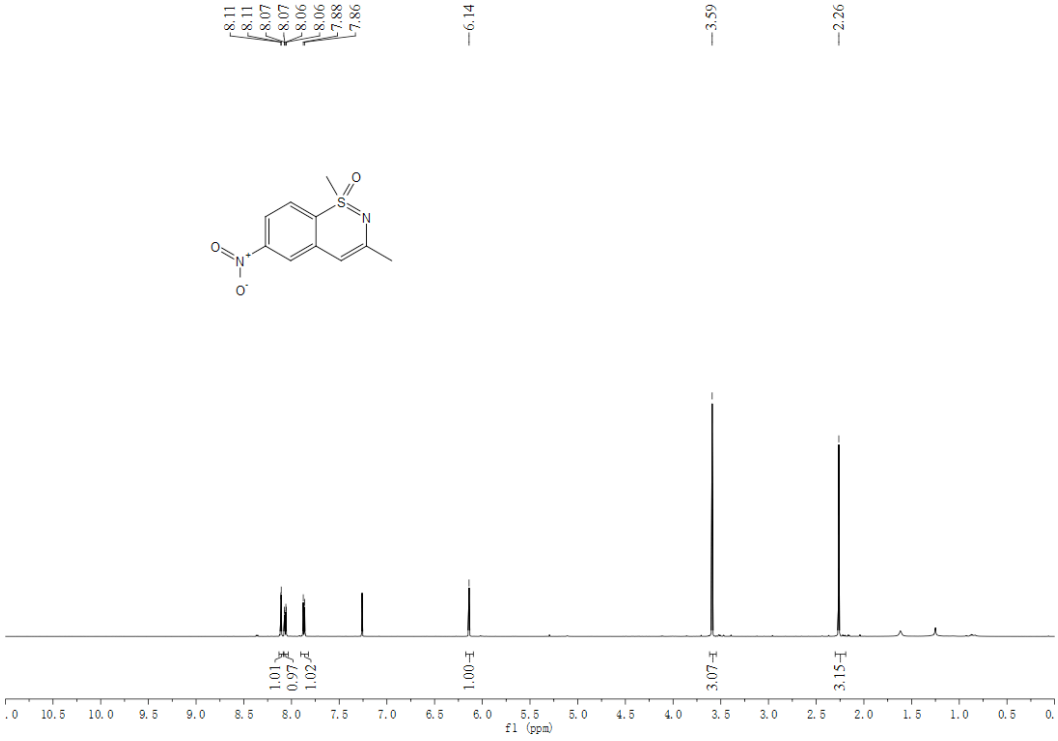
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 13f



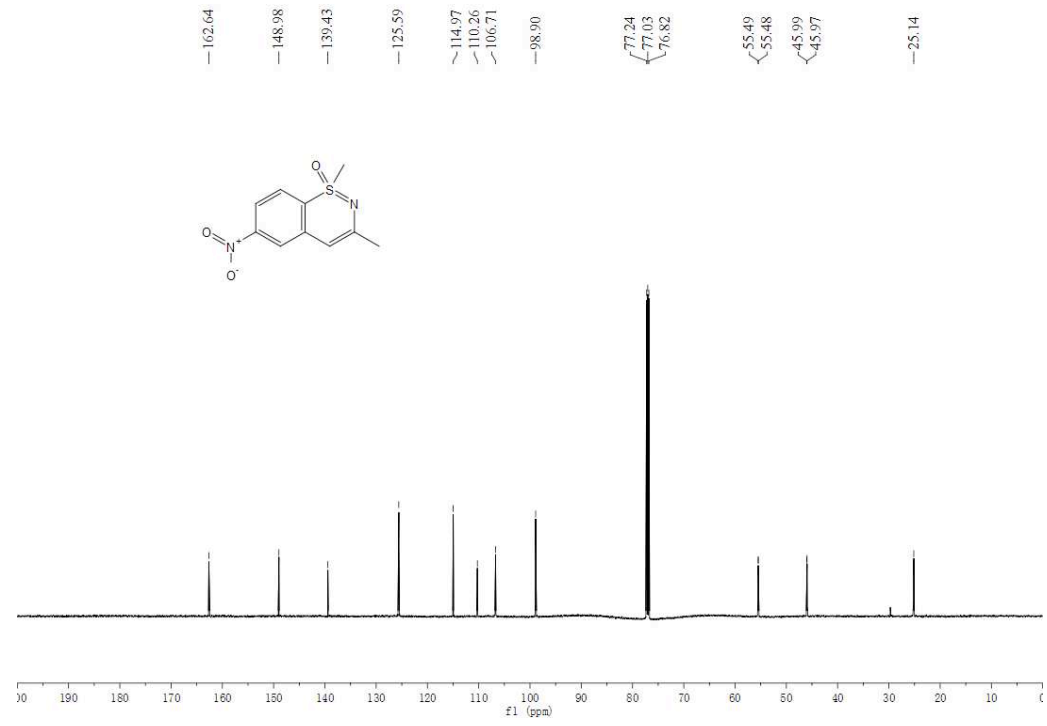
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 13f



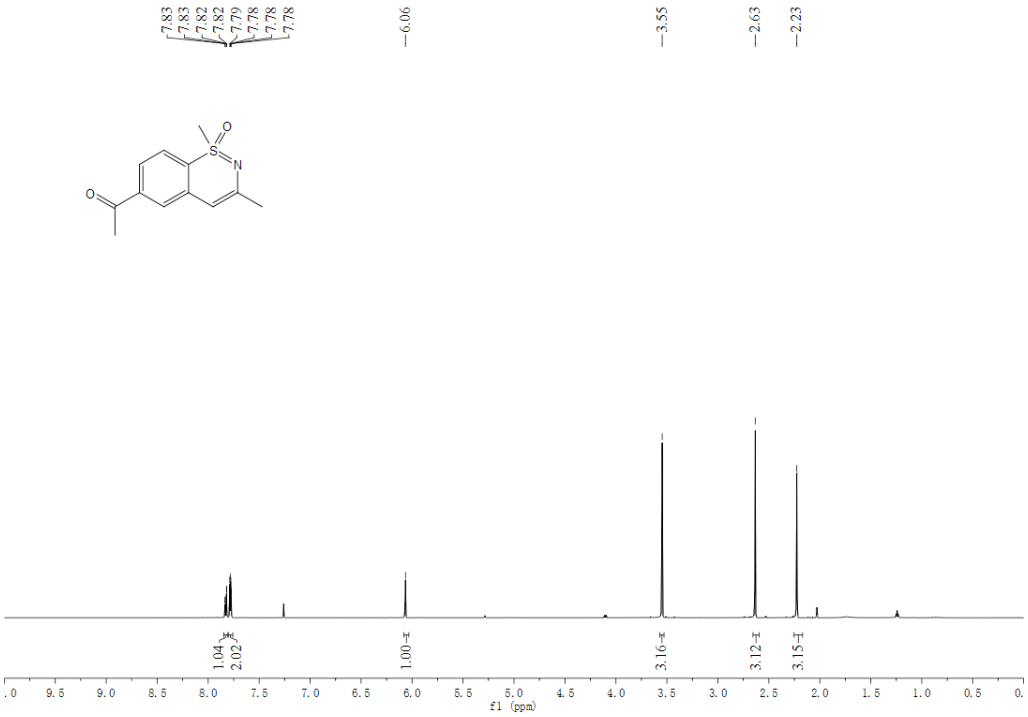
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 13g



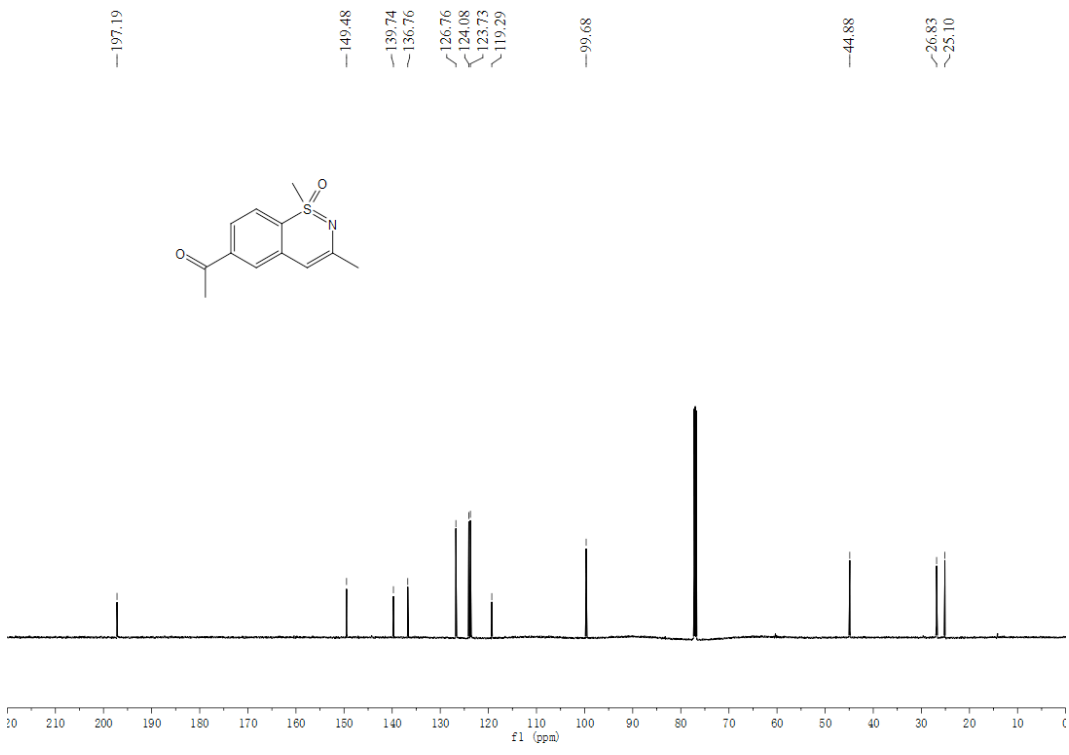
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 13g



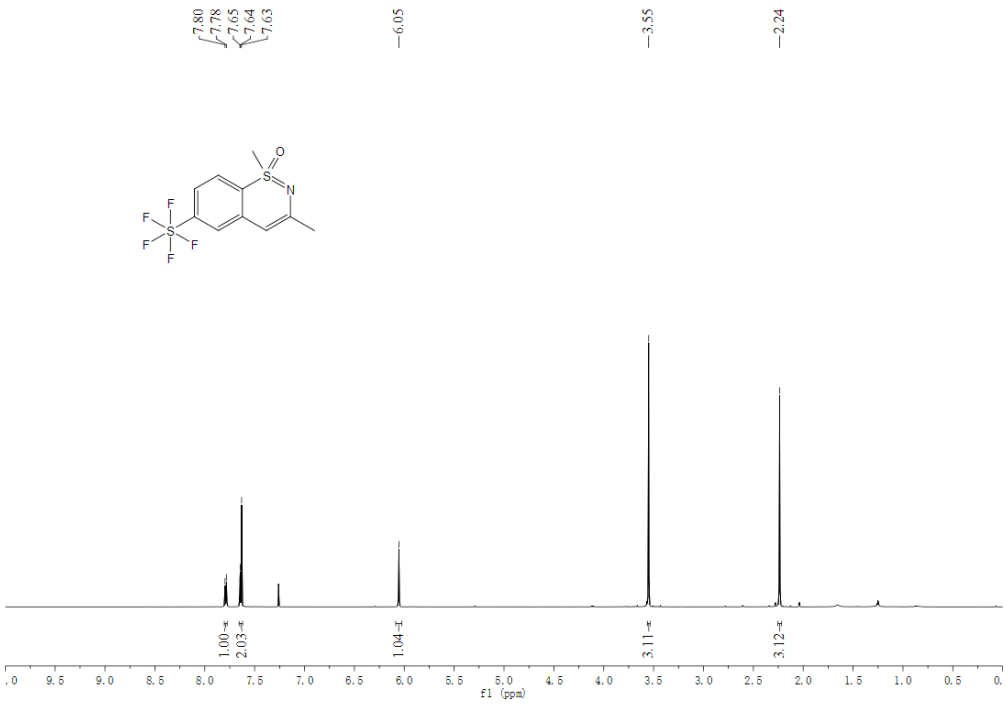
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 13h



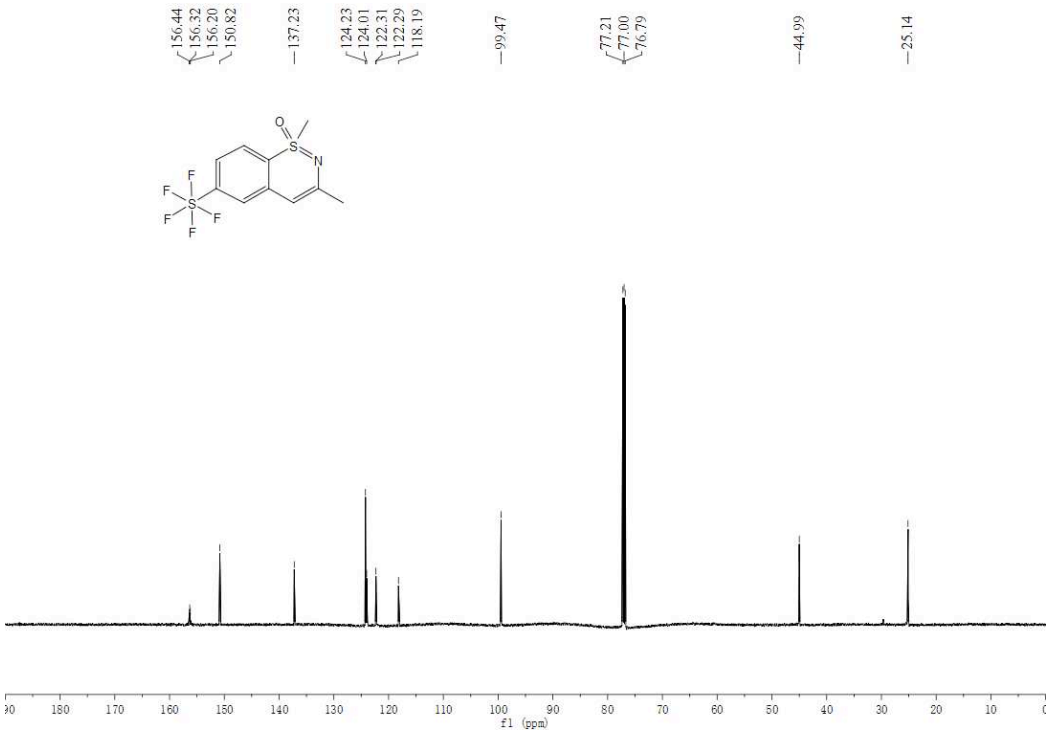
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 13h



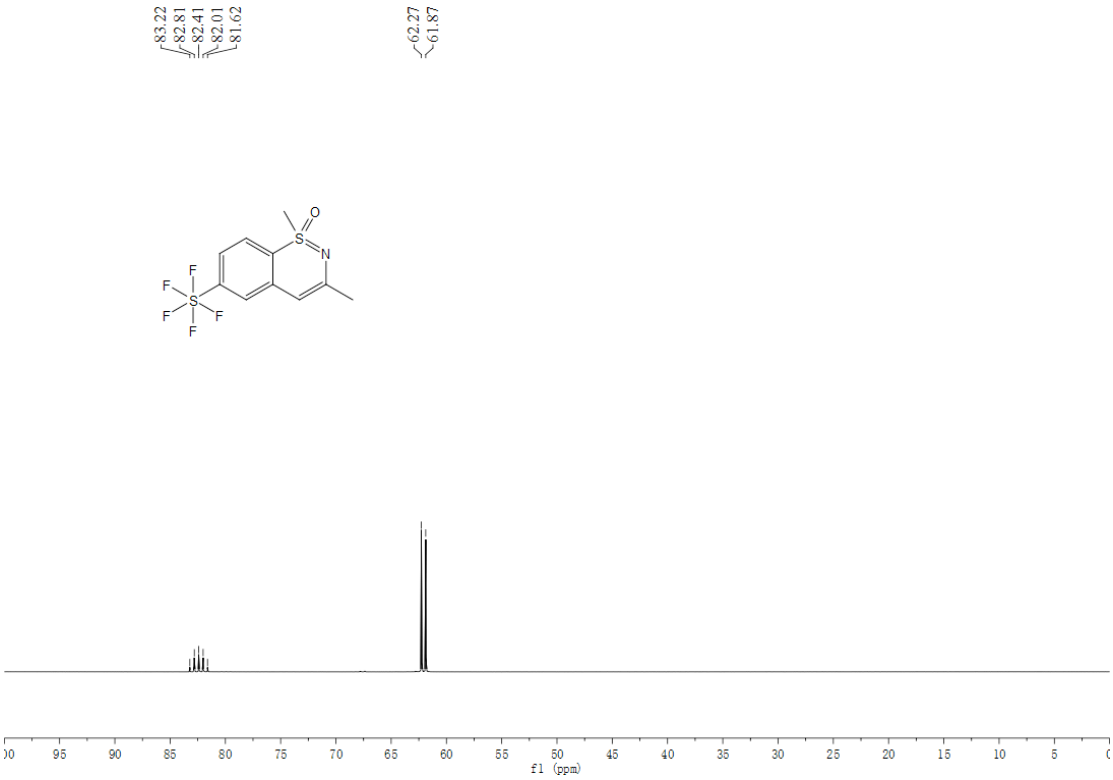
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 13i



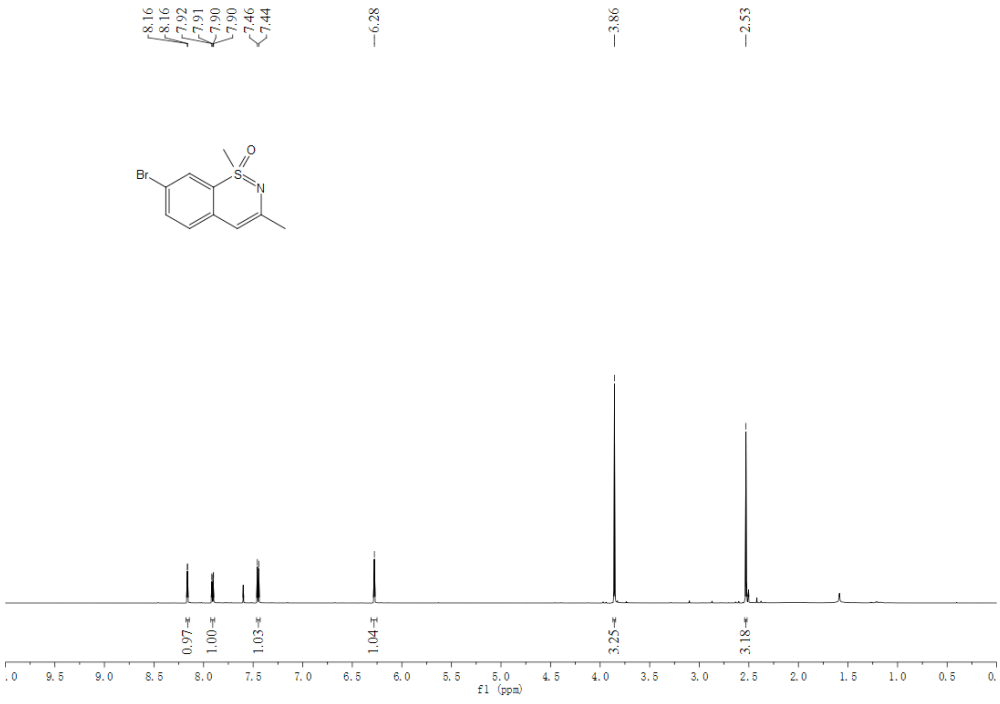
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 13i



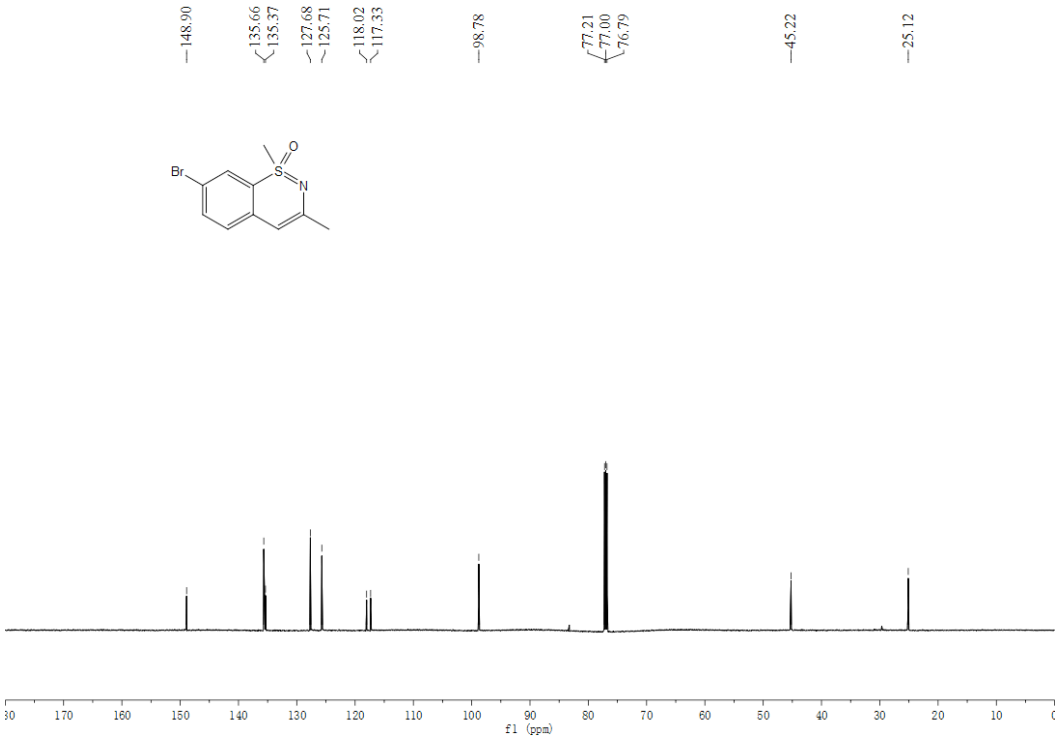
^{1}F NMR spectrum (376MHz, $CDCl_3$) of 13i



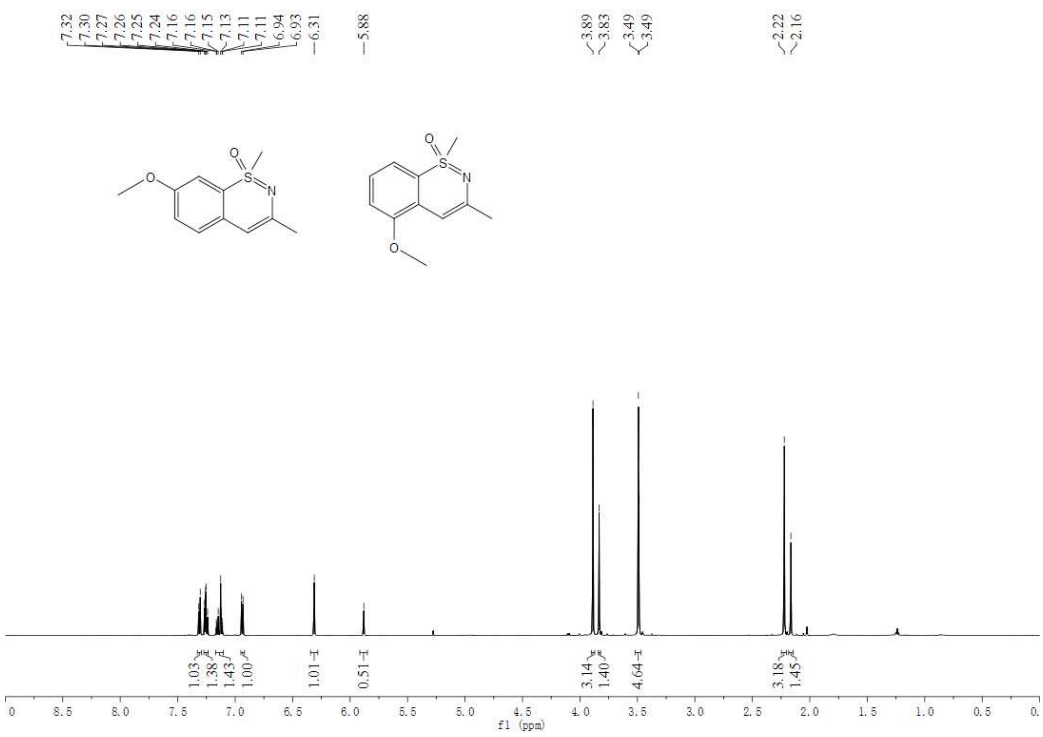
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 13j



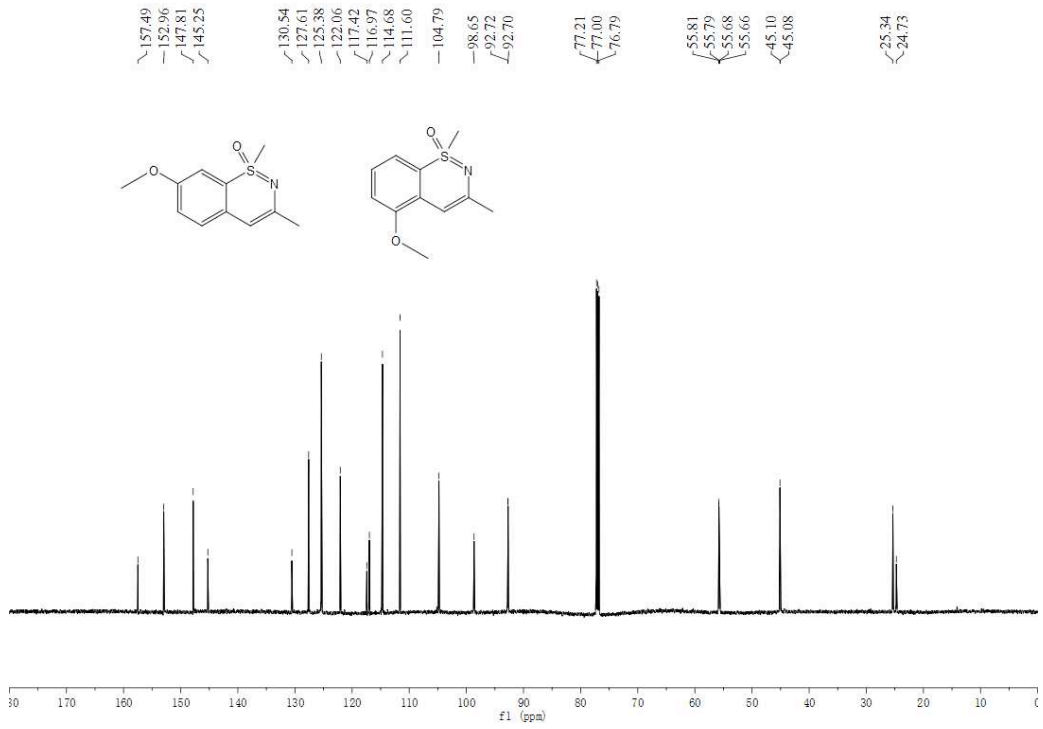
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 13j



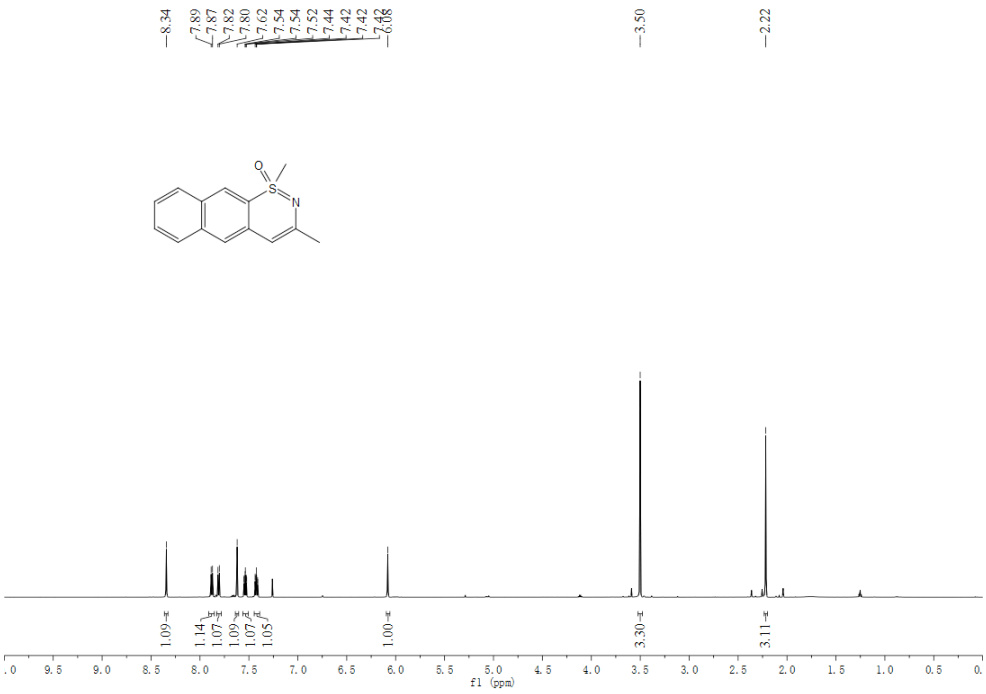
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 13k+13k'



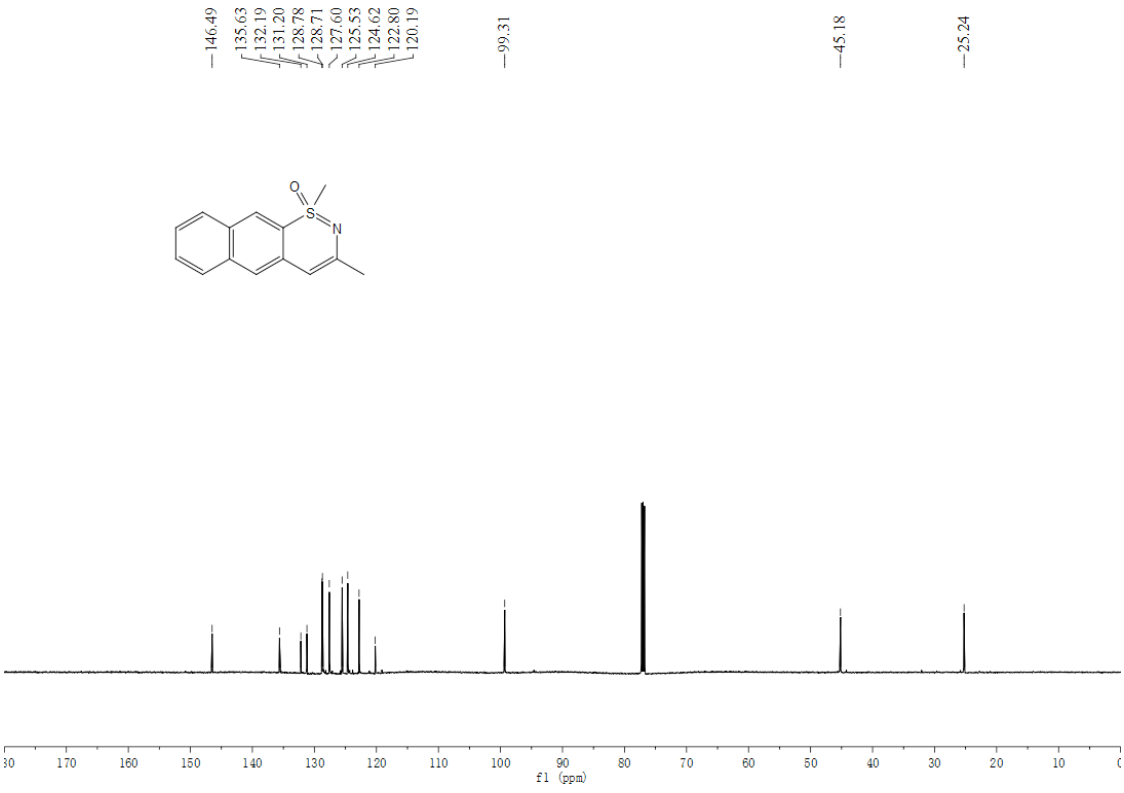
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 13k+13k'



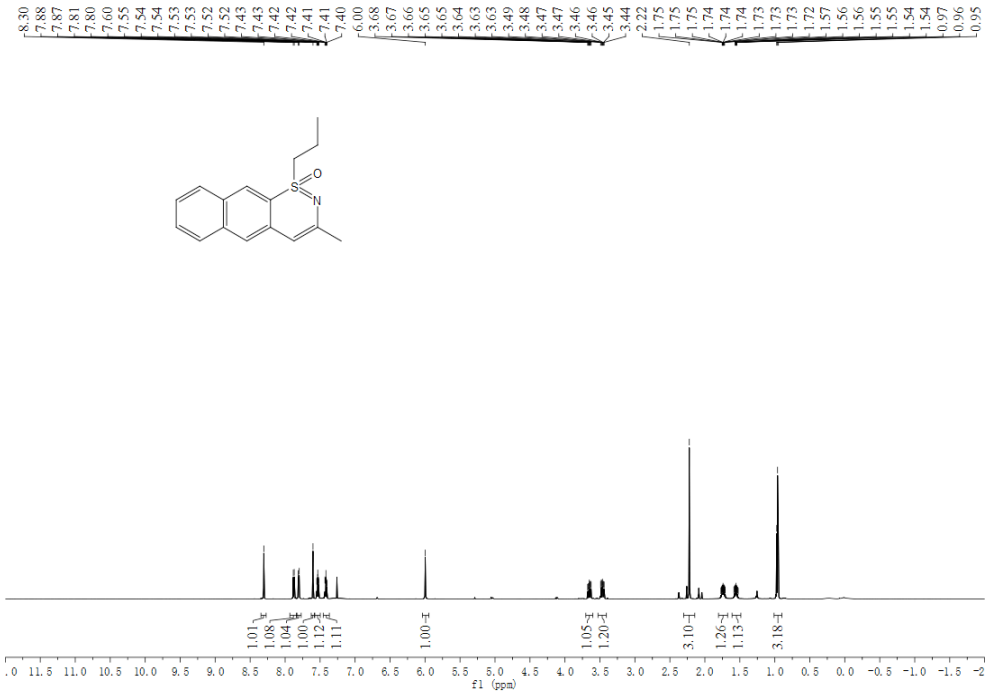
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 13l



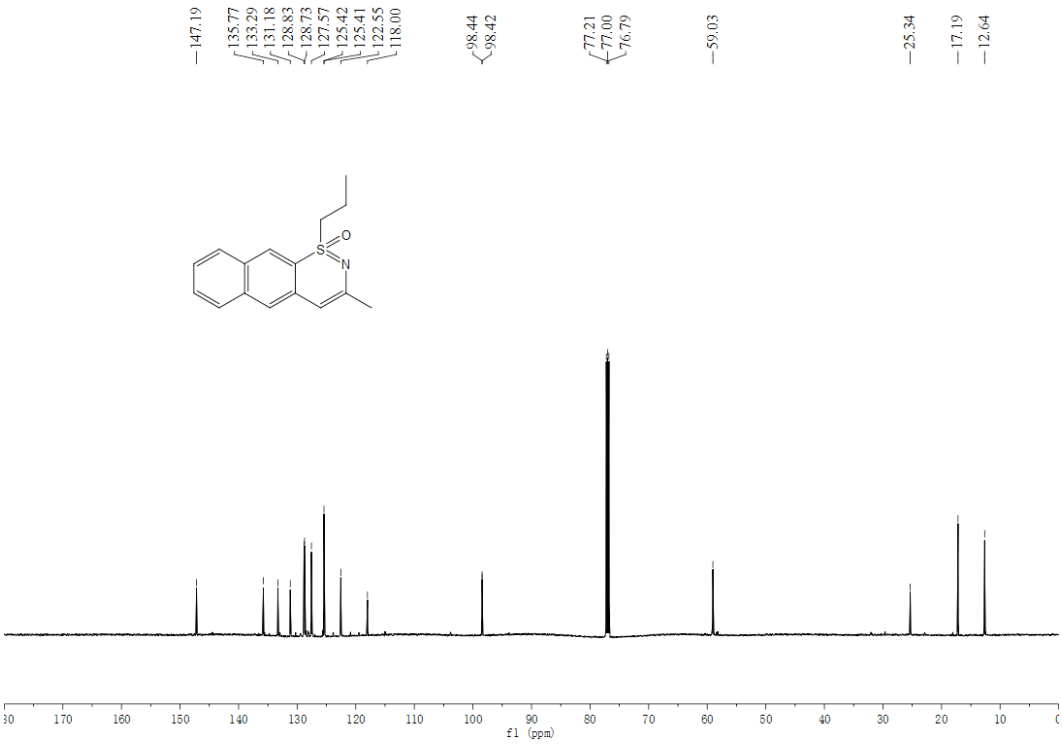
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 13l



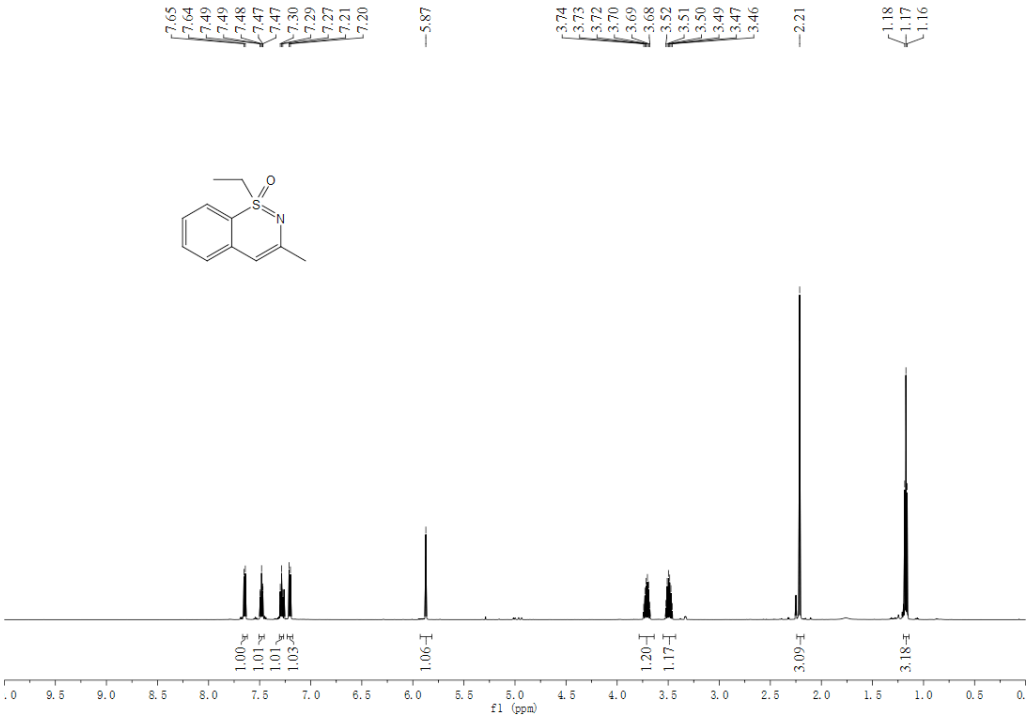
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 13m



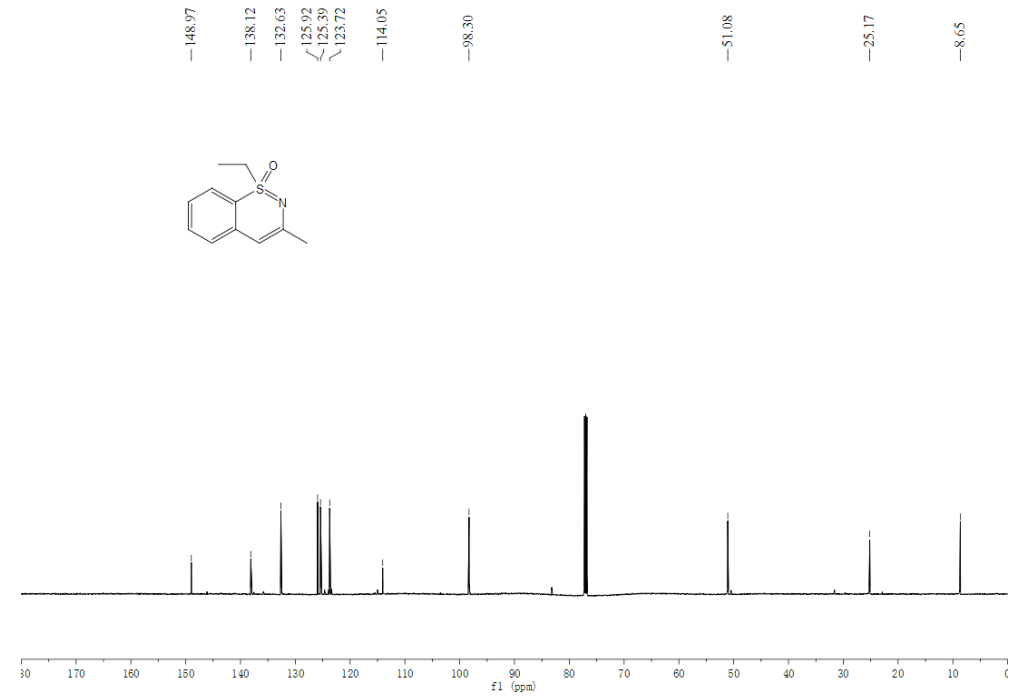
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 13m



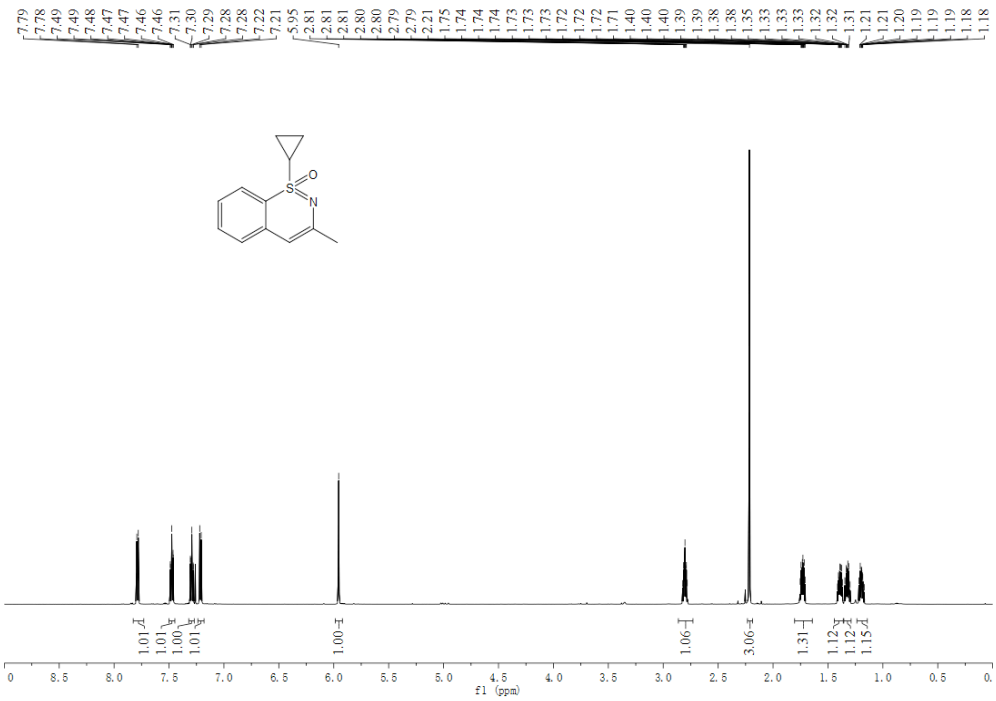
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 13n



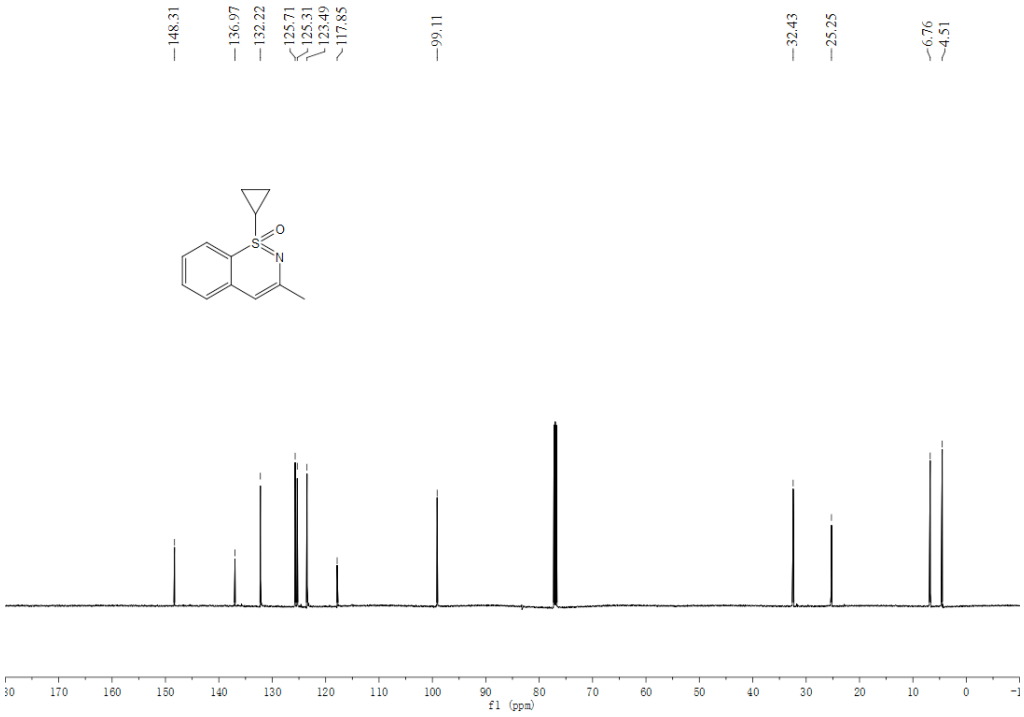
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 13n



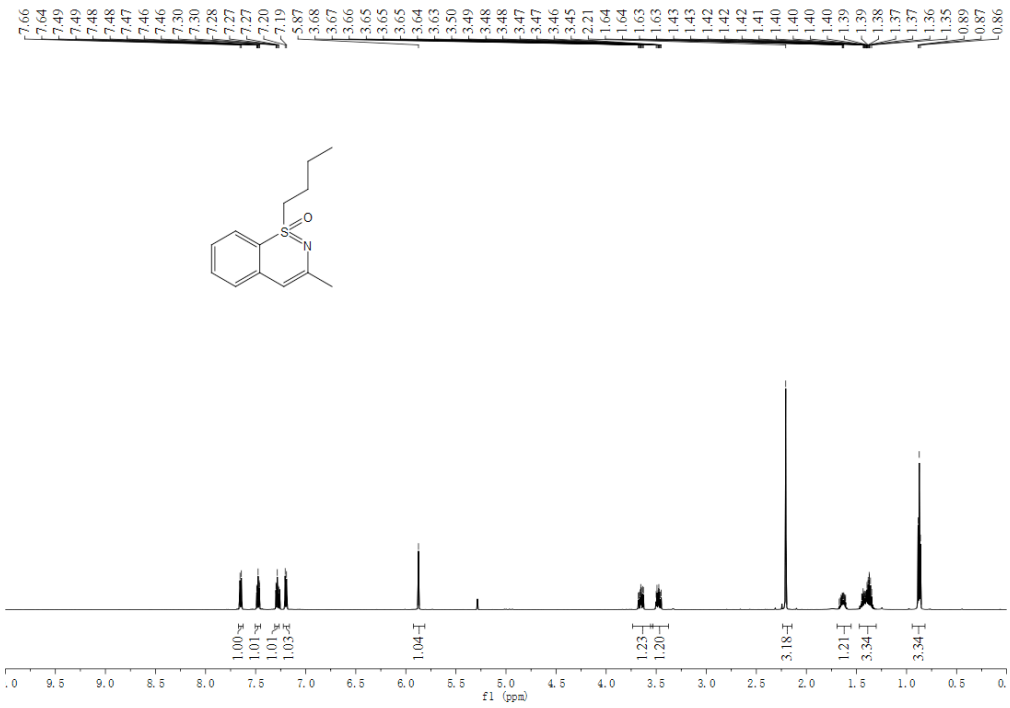
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 13o



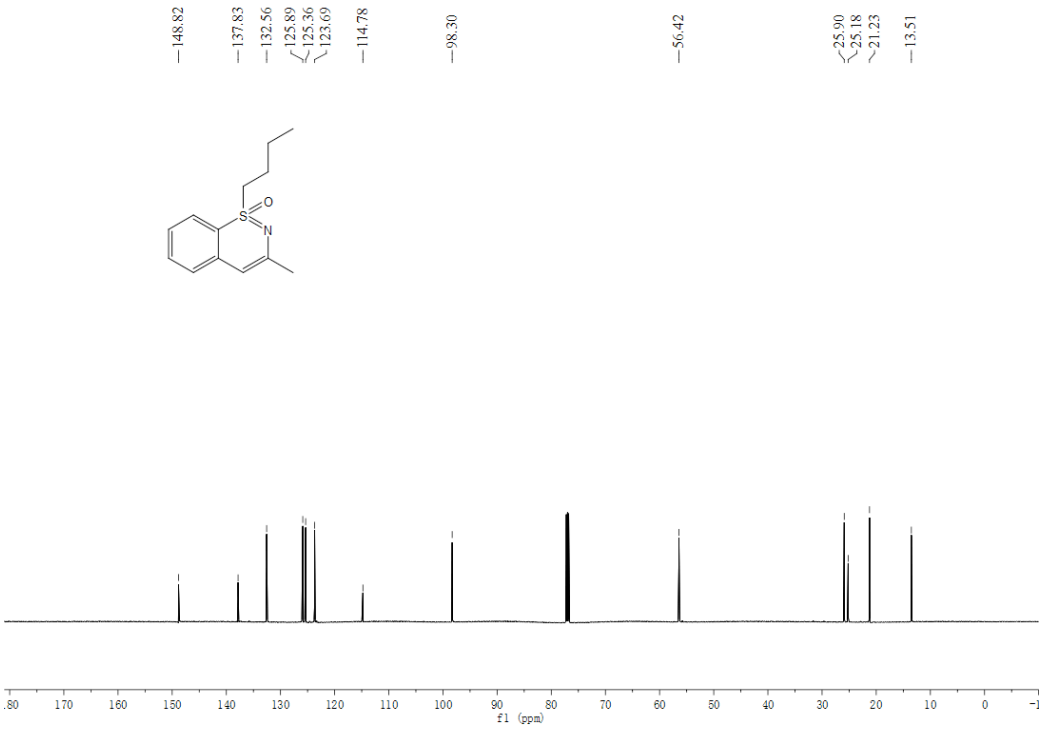
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 13o



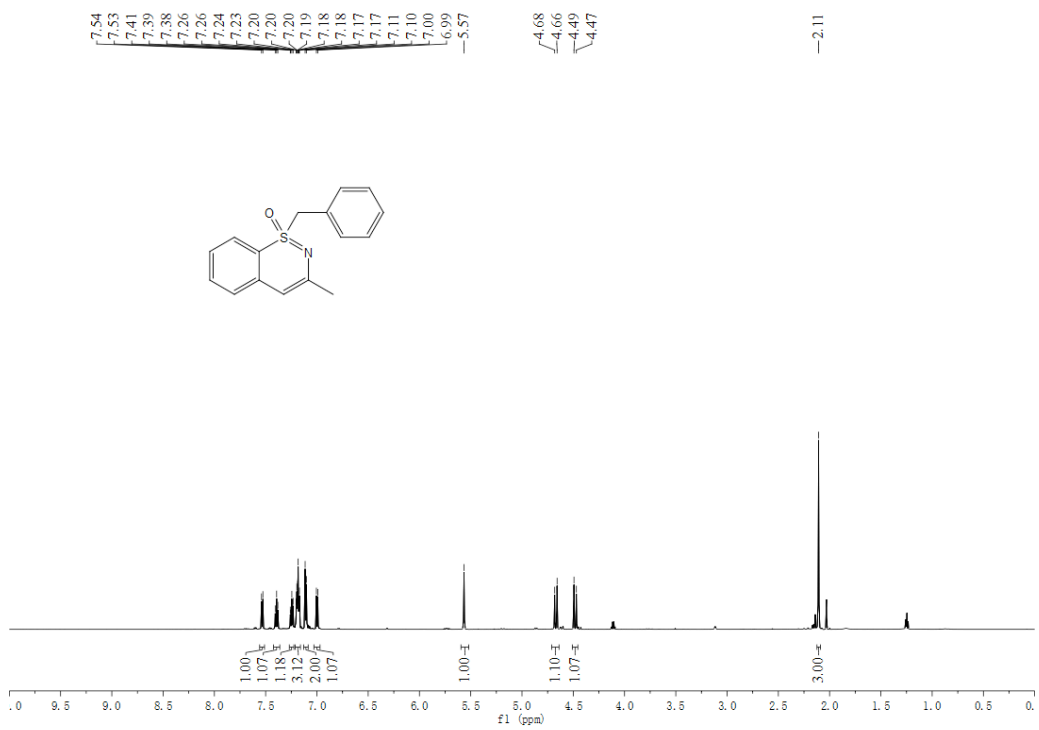
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 13p



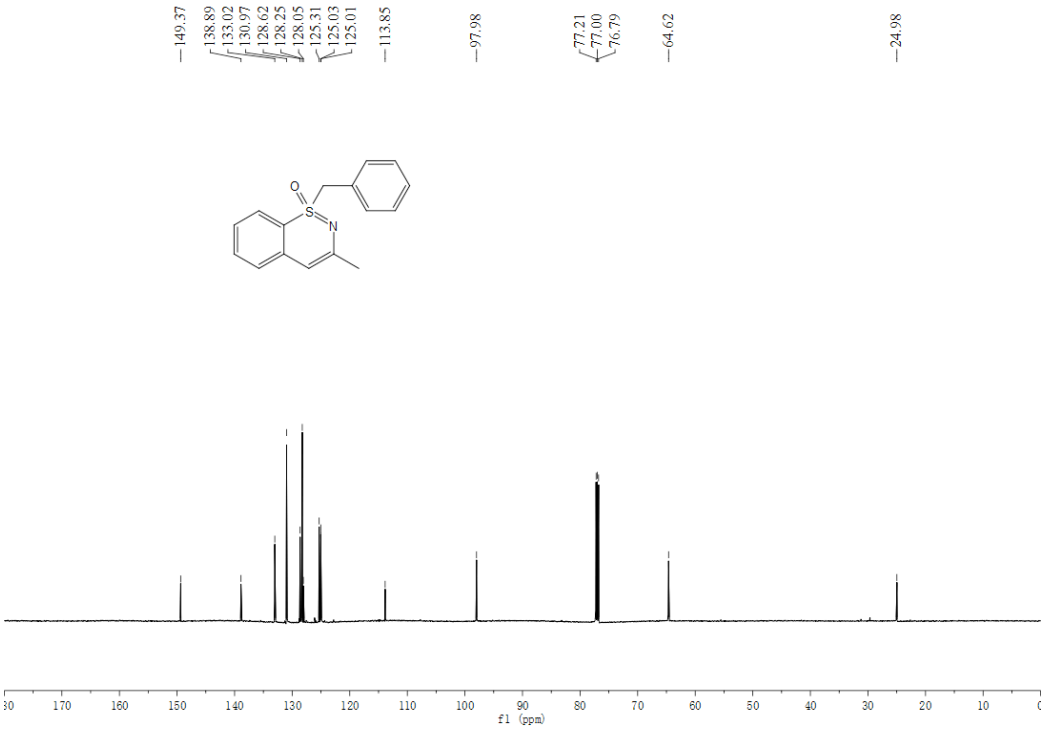
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 13p



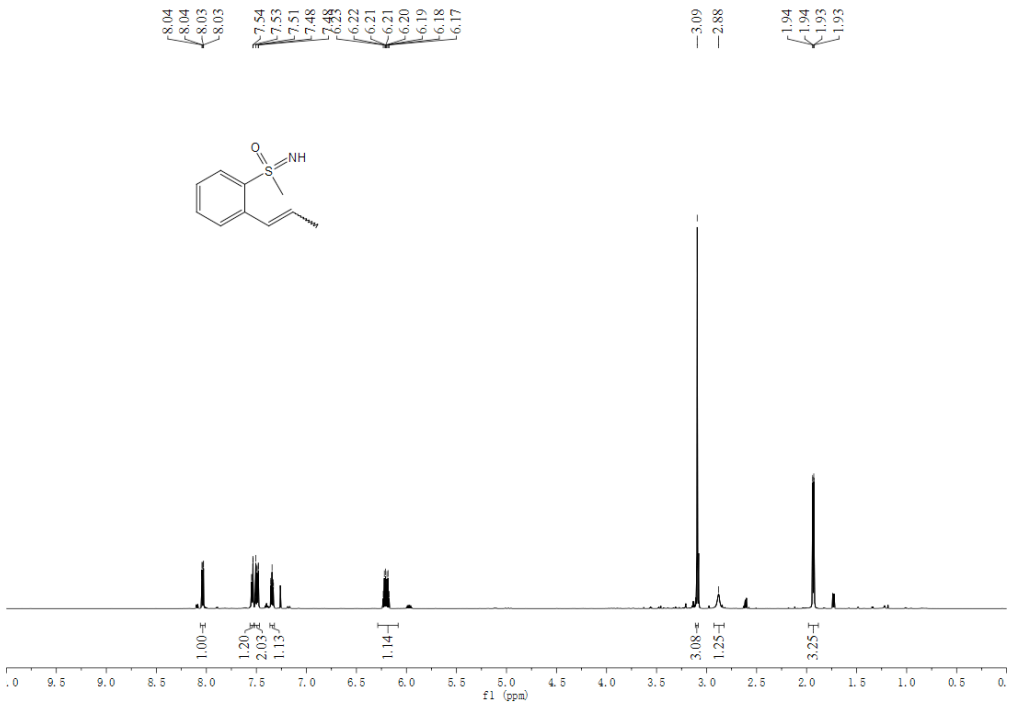
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 13q



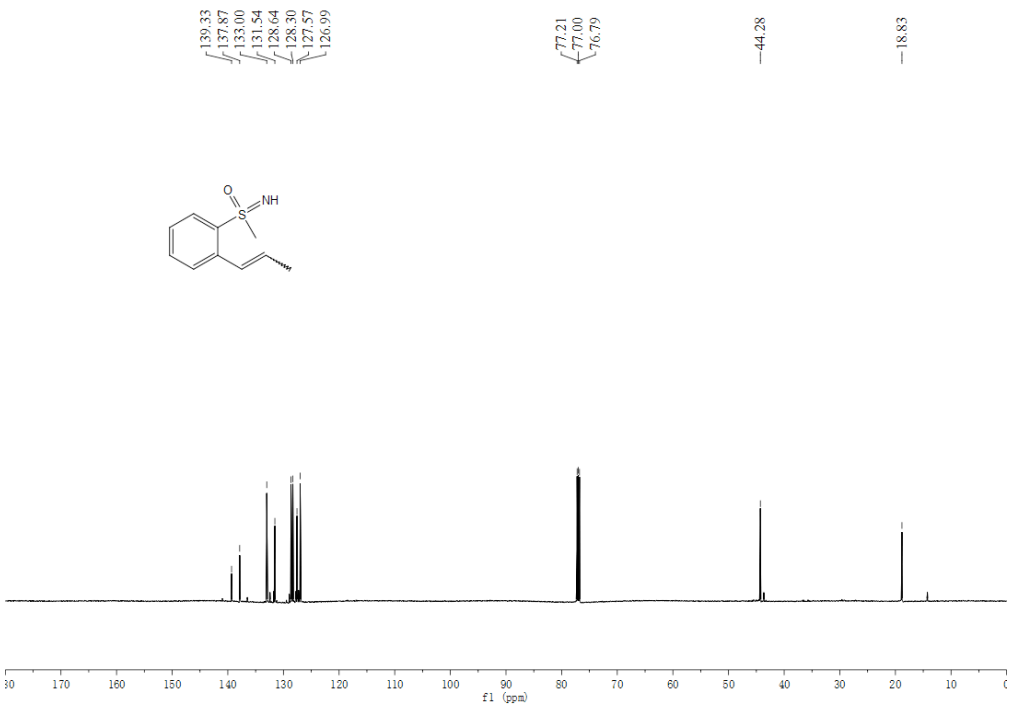
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 13q



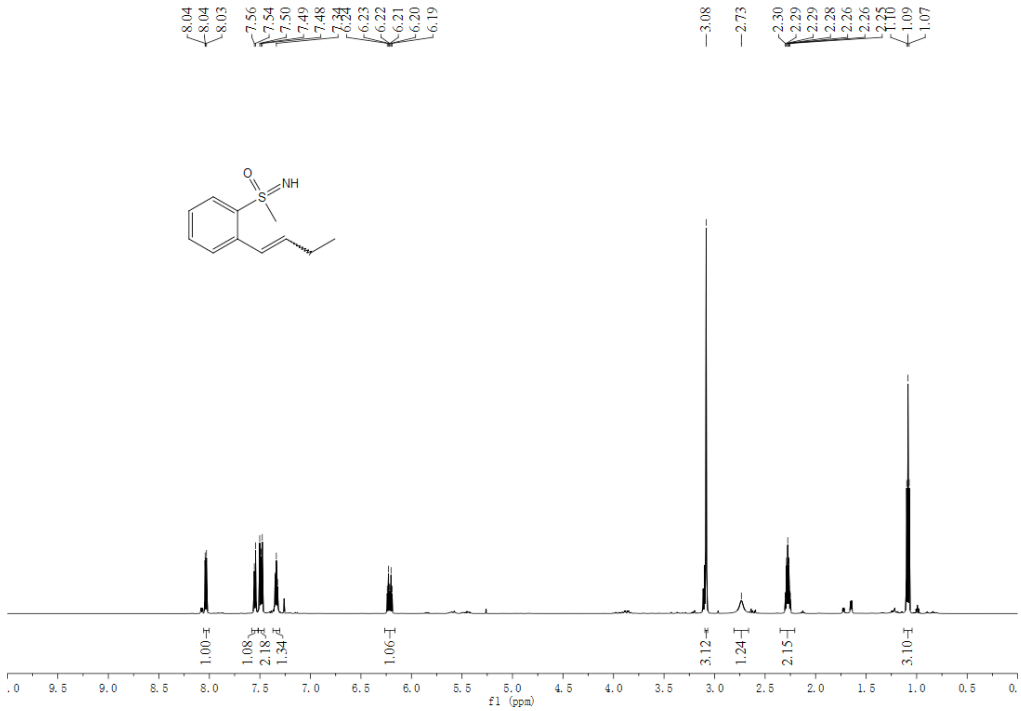
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 18a



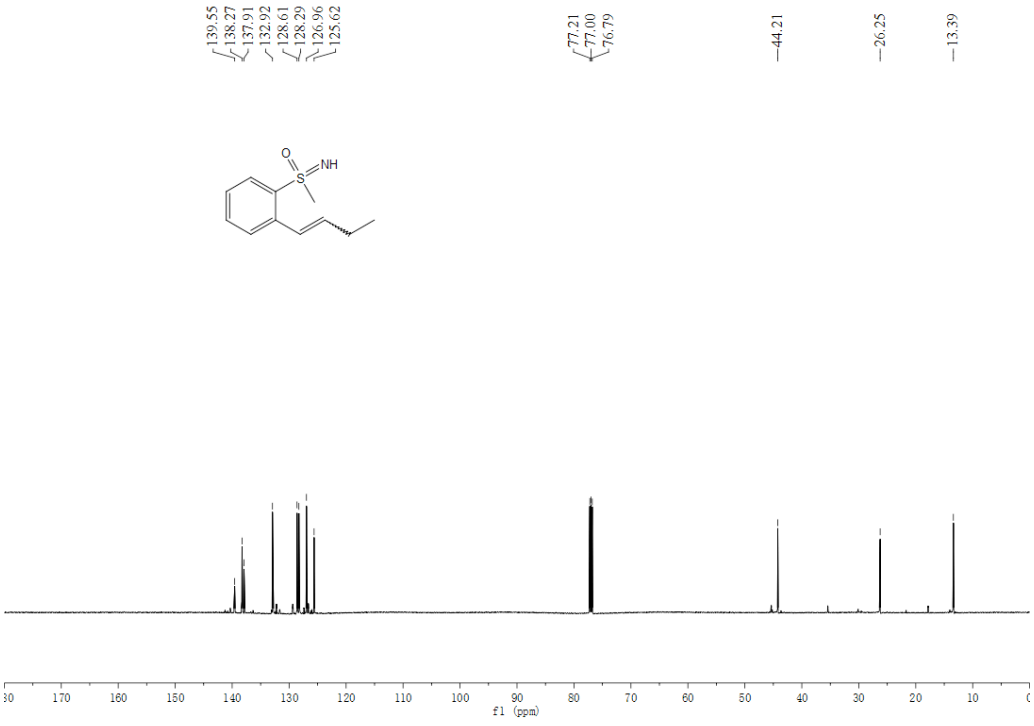
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 18a



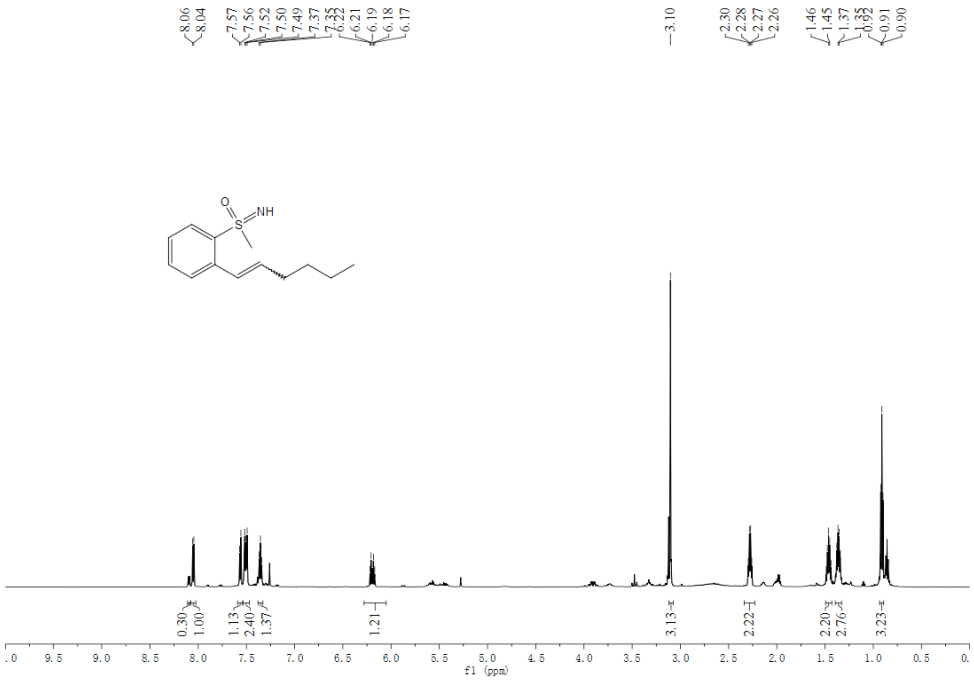
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 18b



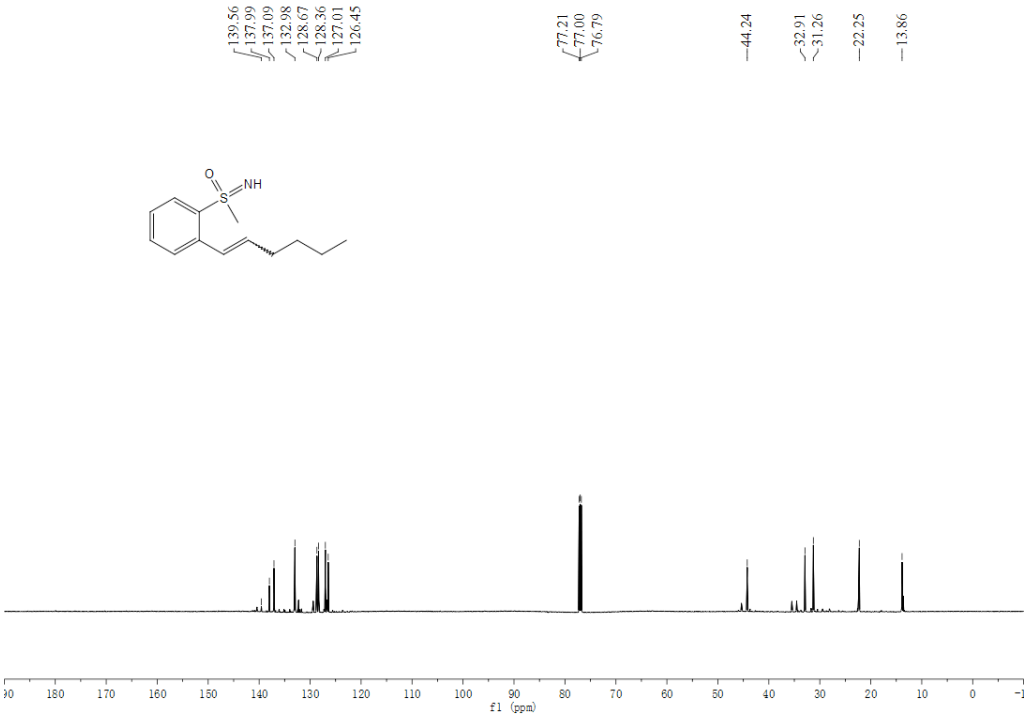
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 18b



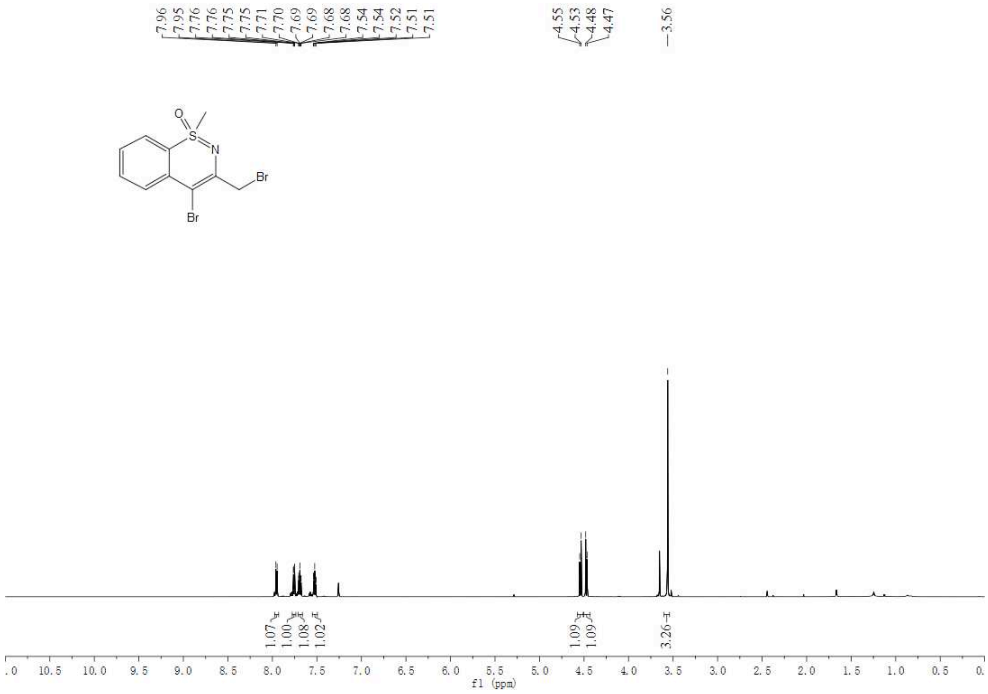
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 18c



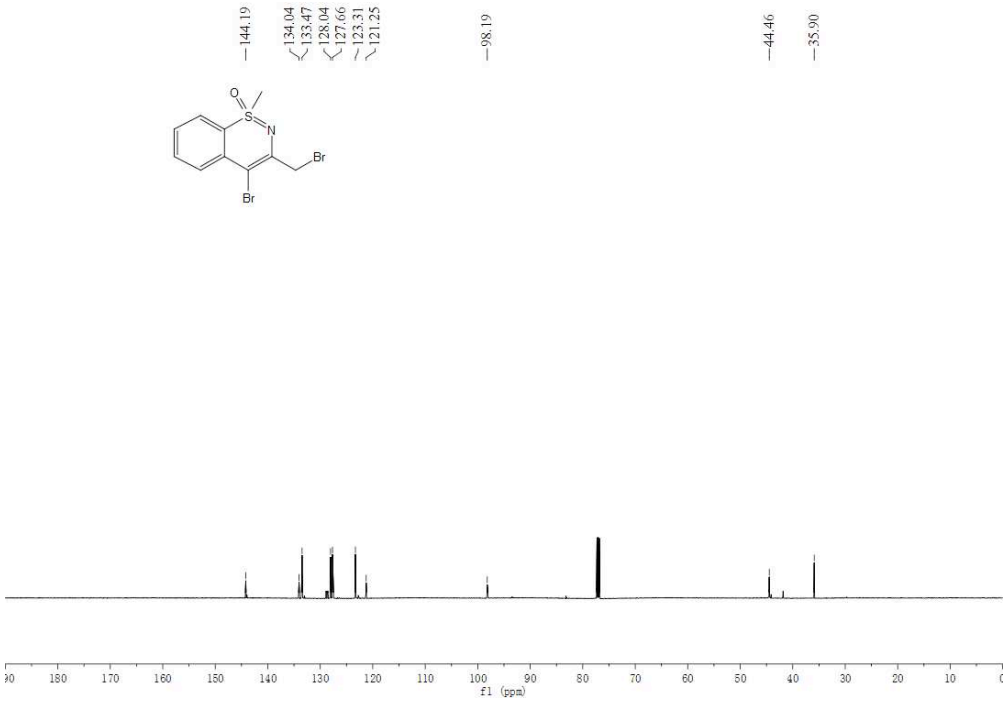
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 18c



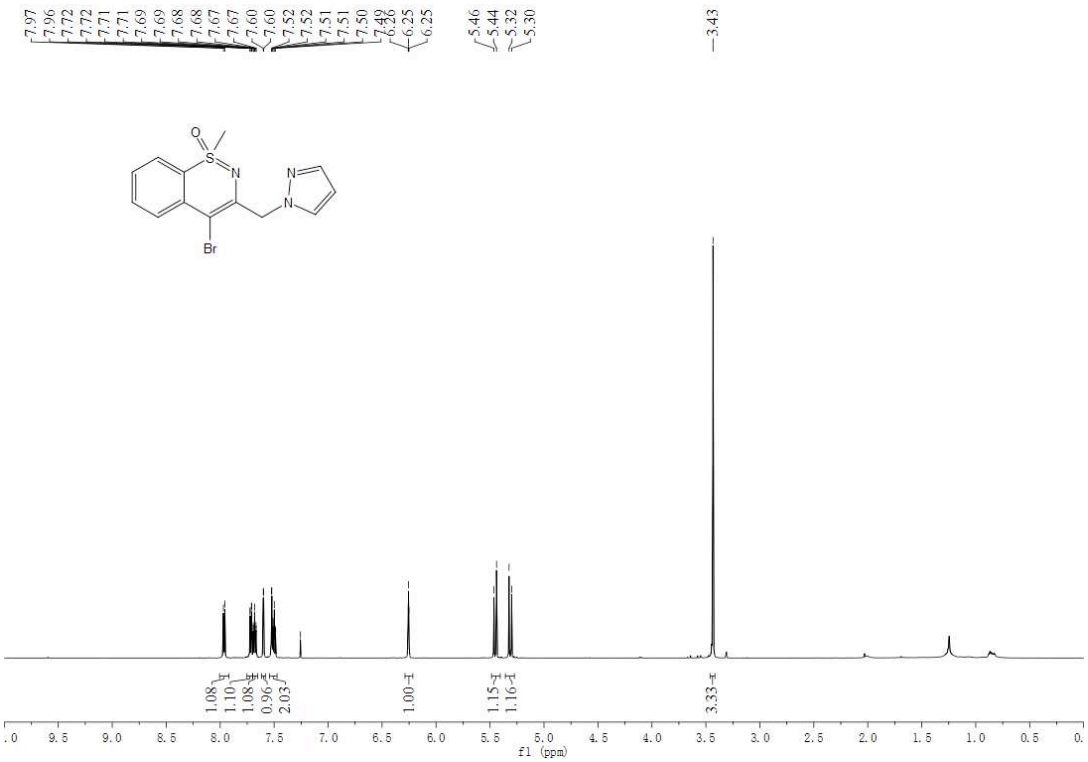
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 19



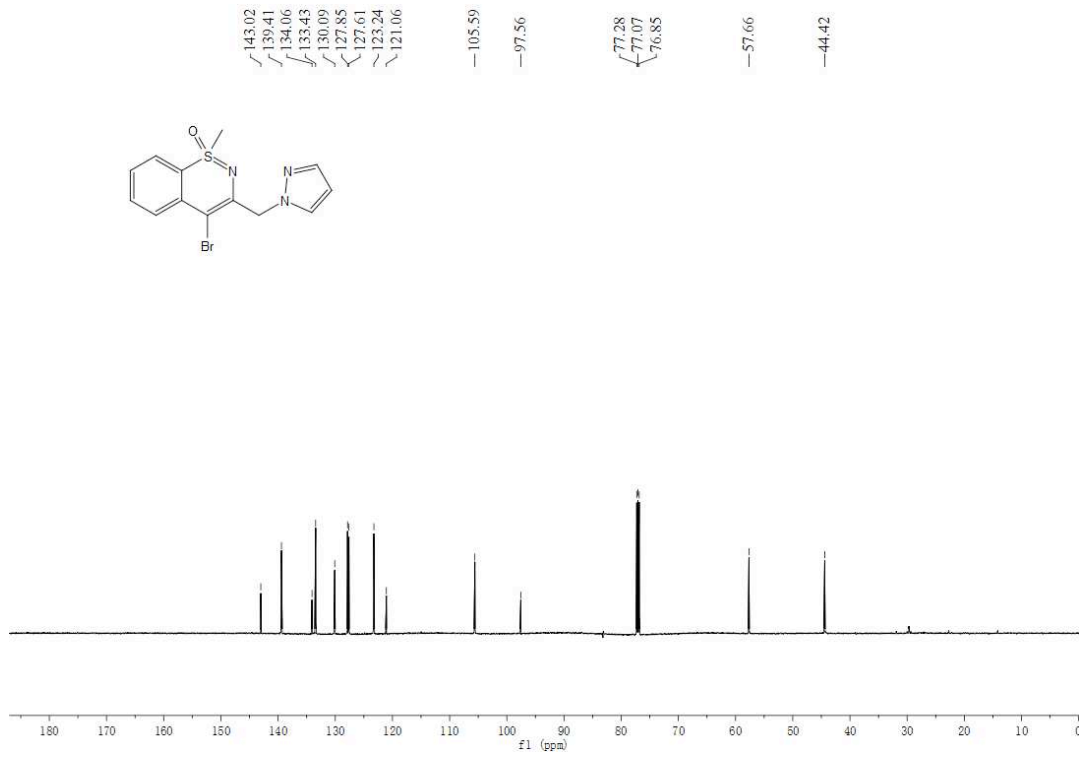
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 19



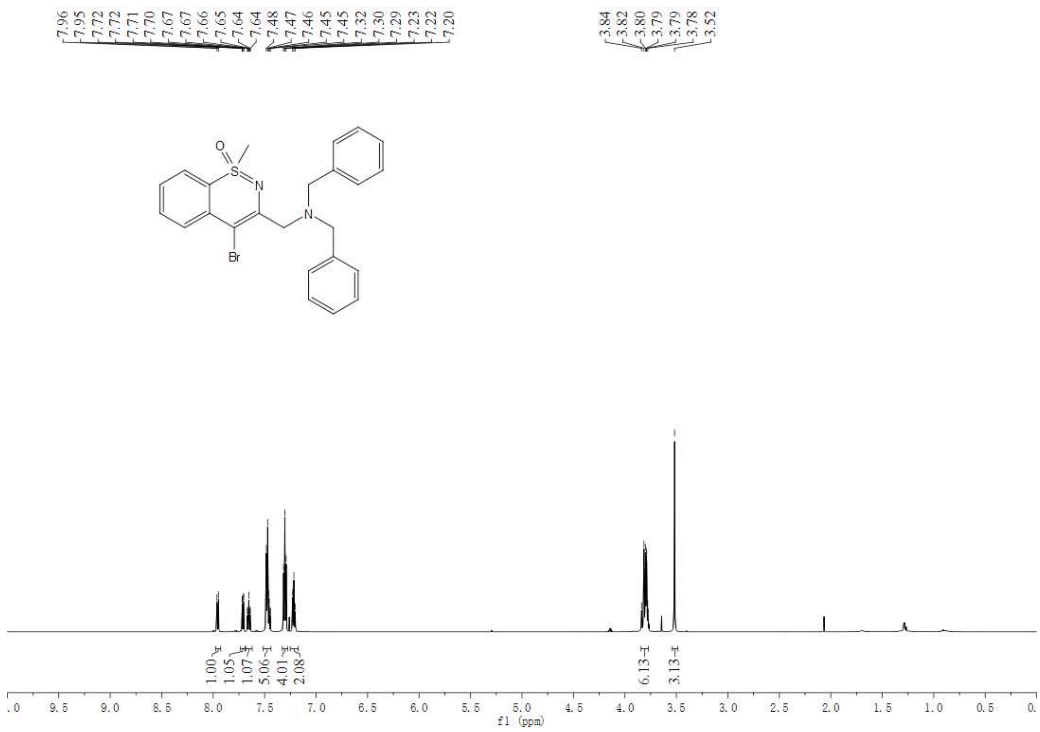
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 20



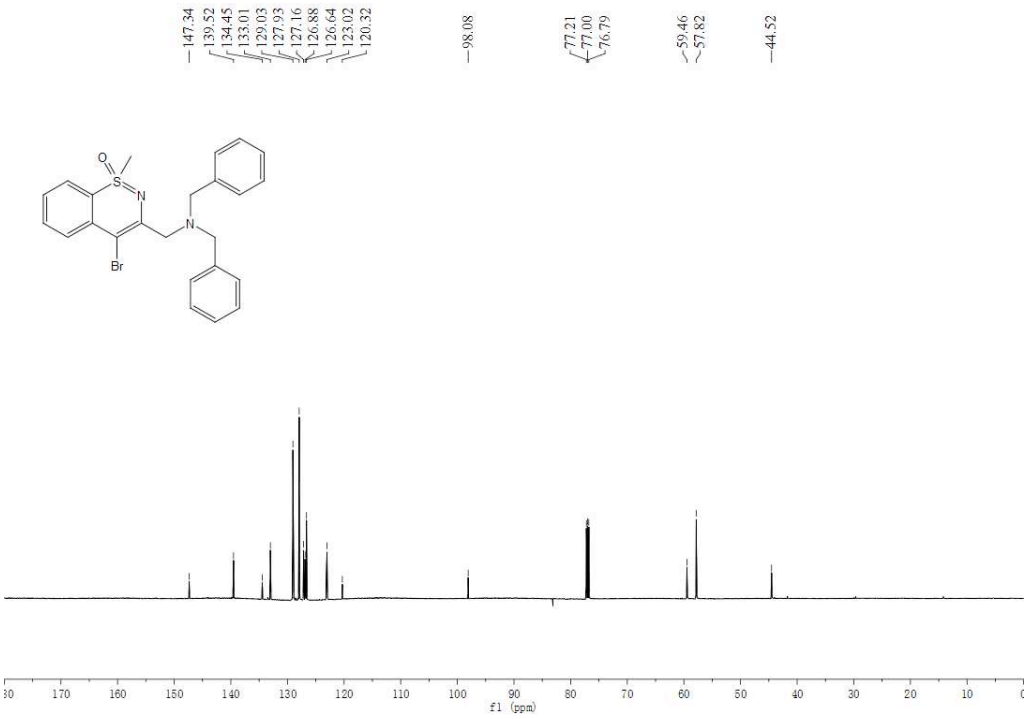
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 20



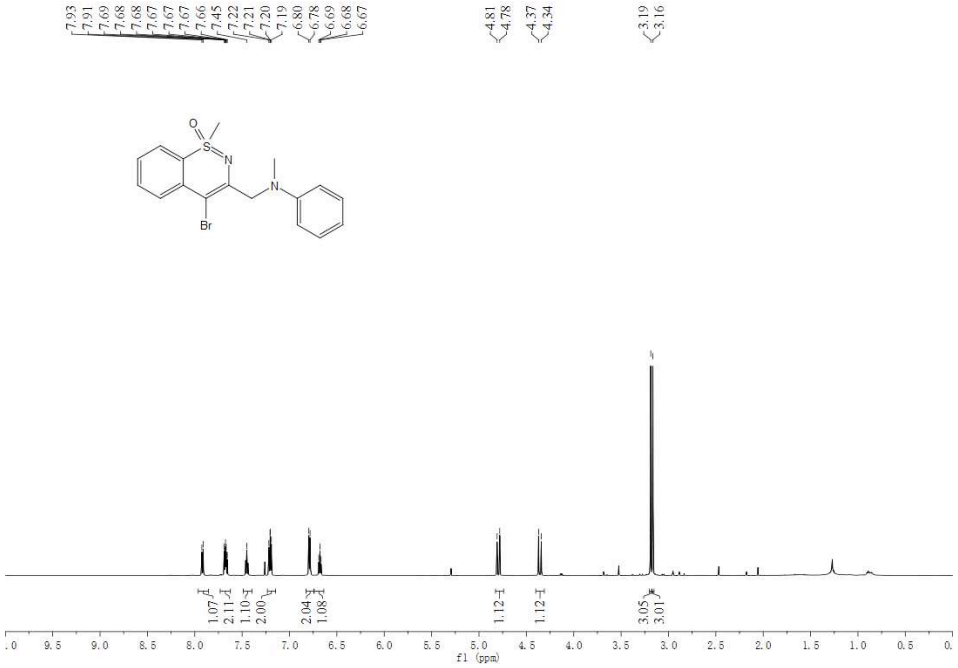
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 21



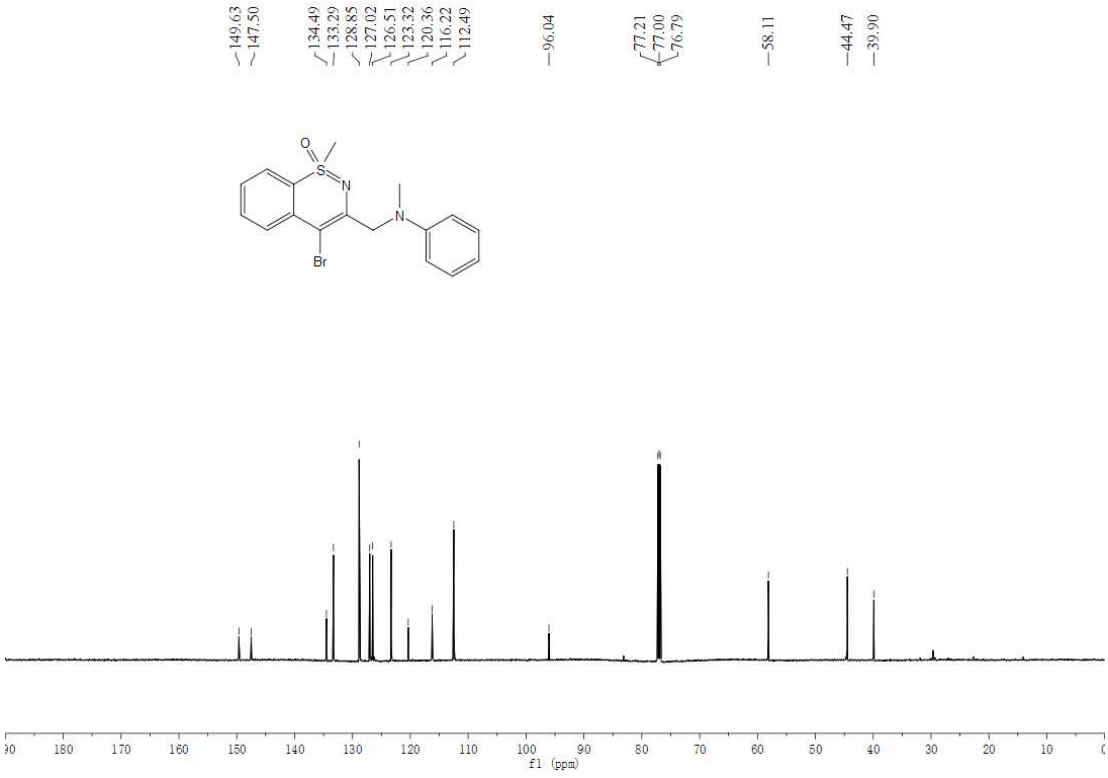
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 21



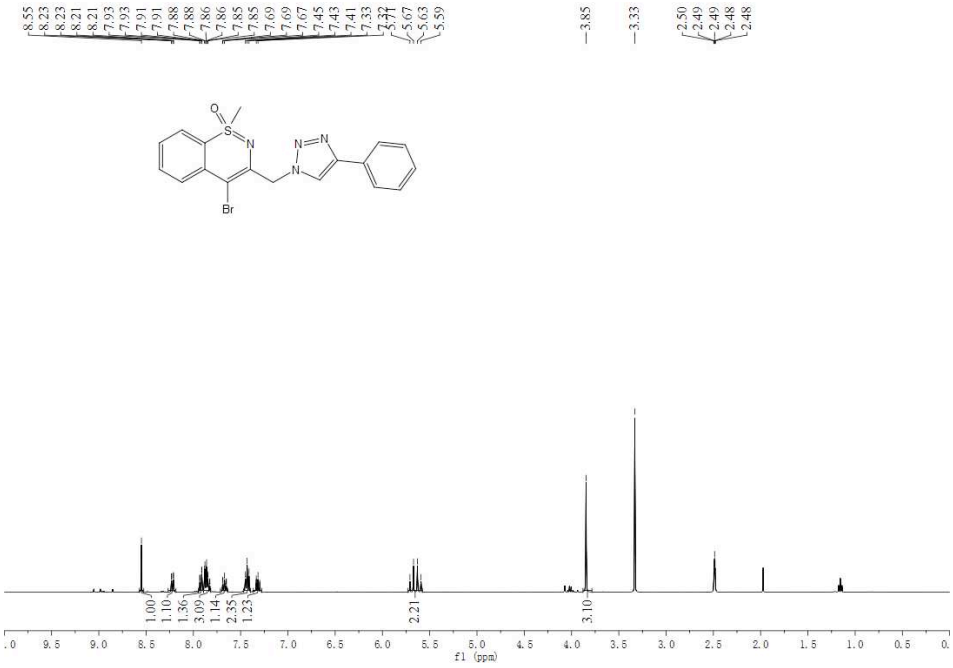
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 22



^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 22



^{1}H NMR spectrum (400 MHz, DMSO) of 23



^{13}C NMR spectrum (100 MHz, DMSO) of 23