Supporting Information

Rhodium-Catalyzed [4+3] Annulations of Sulfoximines with α,β-Unsaturated Ketones Leading to 1,2-Benzothiazepine 1-Oxides

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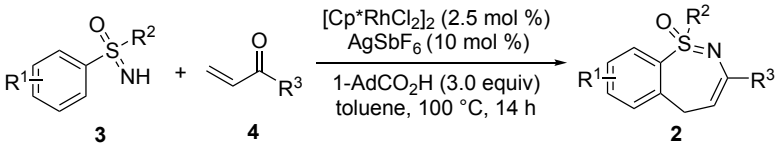
1. General information

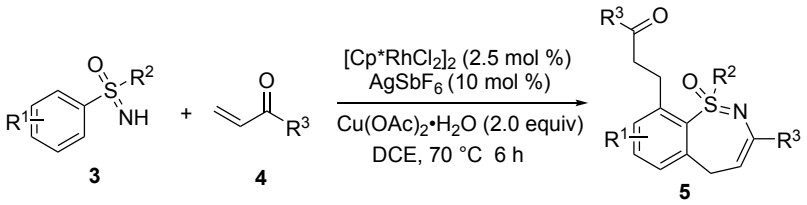
^{1}H NMR spectra were recorded at 400 MHz or 600 MHz. The solvent for the NMR spectroscopy was $CDCl_3$ unless noted otherwise. Chemical shifts are reported in delta (δ) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data were reported as follows: chemical 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 and α,β-unsaturated ketones were synthesized according to literature procedures.[1,2]

2. General experimental procedures



Procedure A: A sealed tube (15 mL) was charged with sulfoximine **3** (0.90 mmol), α,β-unsaturated ketone **4** (0.30 mmol), $[Cp^*RhCl_2]_2$ (4.7 mg, 0.0075 mmol,), $AgSbF_6$ (10.3 mg, 0.03 mmol), 1-$AdCO_2H$ (162.2 mg, 0.90 mmol) under an argon atmosphere. Then, dry toluene (3 mL) was added by syringe. After stirring the reaction mixture at 100 °C for 14 h, it was cooled to room temperature 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 **2**.

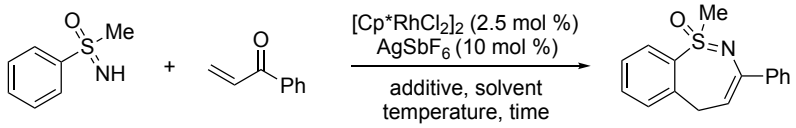
Scale-up experiment: A sealed tube (45 mL) was charged with sulfoximine **3a** (465.0 mg**,** 3.0 mmol), α,β-unsaturated ketone **4a** (132.0 mg**,** 1.0 mmol), $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol,), $AgSbF_6$ (34.4 mg, 0.1 mmol), 1-$AdCO_2H$ (540.7 mg, 3.0 mmol) under an argon atmosphere. Then, dry toluene (10 mL) was added by syringe. After stirring the reaction mixture at 100 °C for 14 h, it was cooled to room temperature 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 **2aa** (172.2 mg, 64%).



Procedure B: A sealed tube (15 mL) was charged with sulfoximine **3** (0.30 mmol), α,β-unsaturated ketone **4** (0.90 mmol), $[Cp^*RhCl_2]_2$ (4.7 mg, 0.0075 mmol,), $AgSbF_6$ (10.3 mg, 0.03 mmol), $Cu(OAc)_2 \cdot H_2O$ (119.8 mg, 0.60 mmol) under an argon atmosphere. Then, dry DCE (3 mL) was added by syringe. After stirring the reaction mixture at 70 °C for 6 h, it was cooled to room temperature and extracted with dichloromethane (3 x 10 mL). The combined organic lays were extracted with brine (15 mL), dried over Na_2SO_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 **5**.

Scale-up experiment: A sealed tube (45 mL) was charged with sulfoximine **3a** (155.0 mg, 1.0 mmol), α,β-unsaturated ketone **4a** (396.2 mg, 3.0 mmol), $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol,), $AgSbF_6$ (34.4 mg, 0.1 mmol), $Cu(OAc)_2 \cdot H_2O$ (399.3 mg, 2.0 mmol) under an argon atmosphere. Then, dry DCE (10 mL) was added by syringe. After stirring the reaction mixture at 70 °C for 6 h, it was cooled to room temperature and extracted with dichloromethane (3 x 30 mL). The combined organic lays were extracted with brine (45 mL), dried over Na_2SO_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 **5aa** (324.8 mg, 81%).

Table S1. Optimization of the reaction conditions[a]

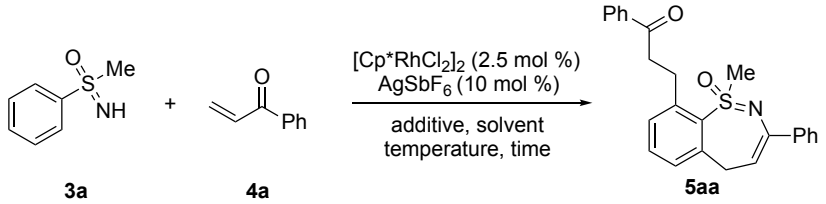


3a **4a** **2aa**

Entry	**3a**/**4a**	Solvent	Temp (°C)	t (h)	Additive (equiv)	**2aa** (%)
1	1:3	DCE	100	14	PivOH (3)	15
2	1:3	THF	100	14	PivOH (3)	5
3	1:3	MeOH	100	14	PivOH (3)	trace
4	1:3	chlorobenzene	100	14	PivOH (3)	25
5	1:3	toluene	100	14	PivOH (3)	28
6	1:2	toluene	100	14	PivOH (3)	30
7	2:1	toluene	100	14	PivOH (3)	52
8	3:1	toluene	100	14	PivOH (3)	56
9	4:1	toluene	100	14	PivOH (3)	57
10	5:1	toluene	100	14	PivOH (3)	55
11	3:1	toluene	100	14	1-AdCO_2H (3)	73
12	3:1	toluene	100	14	AcOH	41
13	3:1	toluene	100	14	Benzoic Acid	33
14	3:1	toluene	100	20	1-AdCO_2H (3)	61
15	3:1	toluene	100	8	1-AdCO_2H (3)	63
16	3:1	toluene	110	14	1-AdCO_2H (3)	64
17	3:1	toluene	90	14	1-AdCO_2H (3)	67
18	3:1	toluene	90	20	1-AdCO_2H (3)	65

[a]All reactions were conducted on a scale of 0.3 mmol for **3a** or **4a**.

Table S2. Optimization of the reaction conditions[a]



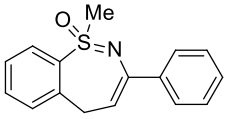
3a **4a** **5aa**

Entry	**3a**/**4a**	Solvent	Temp (°C）	t (h)	Additive (equiv)	**5aa** (%)
1	1:3	DCE	100	14	$Cu(OAc)_2·H_2O$ (2)	72
2	1:3	DCE	100	6	$Cu(OAc)_2·H_2O$ (2)	80
3	1:3	DCE	80	6	$Cu(OAc)_2·H_2O$ (2)	85
4	1:3	DCE	70	6	$Cu(OAc)_2·H_2O$ (2)	89
5	1:3	DCE	60	6	$Cu(OAc)_2·H_2O$ (2)	82
6	1:2	DCE	70	6	$Cu(OAc)_2·H_2O$ (2)	83
7	1:1	DCE	70	6	$Cu(OAc)_2·H_2O$ (2)	71
8	1:3	THF	70	6	$Cu(OAc)_2·H_2O$ (2)	53
9	1:3	toluene	70	6	$Cu(OAc)_2·H_2O$ (2)	55
10	1:3	MeOH	70	6	$Cu(OAc)_2·H_2O$ (2)	35
11	1:3	DCE	70	6	$Cu(OAc)_2$ (2)	78

[a]All reactions were conducted on a scale of 0.3 mmol for **3a** or **4a**.

3. Characterization data of products

1-Methyl-3-phenylbenzo[*f*][1,2]thiazepine 1-oxide (2aa)



Light yellow syrup (59.0 mg, 73%).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.97 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.73 – 7.71 (m, 2H), 7.50 – 7.41 (m, 2H), 7.32 – 7.21 (m, 4H), 6.14 (dd, *J* = 7.2, 6.3 Hz, 1H), 4.16 (dd, *J* = 13.7, 6.1 Hz, 1H), 3.38 (s, 3H), 3.16 (dd, *J* = 13.7, 7.4 Hz, 1H).

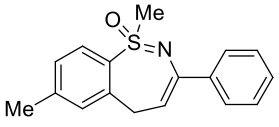
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ (ppm) 144.6, 142.5, 138.1, 136.4, 133.0, 130.7, 129.1, 128.0, 127.9, 127.5, 125.7, 114.4, 46.7, 32.4.

MS (CI): *m*/*z* = 270 ($[M+H]^+$, 100), 269 (32, M^+).

IR (ATR): ν = 3027, 2325, 1679, 1441, 1321, 1216, 1066, 971, 749 (cm^{-1}).

HRMS *m*/*z*: Calcd. for $[C_{16}H_{15}NOS+H]^+$: 270.0953. Found: 270.0952.

1,7-Dimethyl-3-phenylbenzo[*f*][1,2]thiazepine 1-oxide (2ba)



Yellow syrup (52.8 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.85 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 7.1 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.22 (d, *J* = 7.4 Hz, 2H), 7.07 (s, 1H), 6.12 (dd, *J* = 7.3, 6.2 Hz, 1H), 4.12 (dd, *J* = 13.6, 6.1 Hz, 1H), 3.35 (s, 3H), 3.08 (dd, *J* = 13.7, 7.4 Hz, 1H), 2.38 (s, 3H).

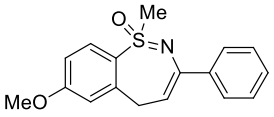
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 144.6, 144.0, 142.6, 138.3, 133.3, 131.1, 129.8, 128.7, 127.9, 127.5, 125.8, 114.5, 47.0, 32.6, 21.4.

MS (EI): *m*/*z* = 283 (M^+, 78), 268 (4), 206 (4), 167 (3), 116 (9), 77 (30).

IR (ATR): ν = 3053, 2925, 2087, 1682, 1598, 1445, 1328, 1222, 1128, 966, 818, 757 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{17}H_{17}NOS+H]^+$: 284.1109. Found: 284.1106.

7-Methoxy-1-methyl-3-phenylbenzo[*f*][1,2]thiazepine 1-oxide (2ca)



Light yellow syrup (53.8 mg, 60%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.91 (d, *J* = 8.8 Hz, 1H), 7.72 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.23 (dd, *J* = 4.8, 3.6 Hz, 1H), 6.89 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.74 (d, *J* = 2.6 Hz, 1H), 6.12 (dd, *J* = 7.4, 6.1 Hz, 1H), 4.13 (dd, *J* = 13.5, 6.1 Hz, 1H), 3.84 (s, 3H), 3.35 (s, 3H), 3.05 (dd, *J* = 13.6, 7.4 Hz, 1H).

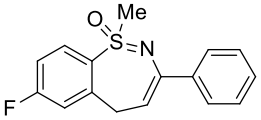
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 162.9, 147.1, 142.8, 138.2, 133.4, 127.9, 127.6, 127.5, 125.8, 114.3, 114.2, 113.0, 55.5, 47.4, 33.0.

MS (EI): *m*/*z* = 299 (M^+, 81), 268 (3), 222 (5), 77 (40).

IR (ATR): ν = 3022, 2928, 1724, 1587, 1471, 1321, 1229, 1062, 965, 752 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{17}H_{17}NO_2S+H]^+$: 300.1058. Found: 300.1056.

7-Fluoro-1-methyl-3-phenylbenzo[*f*][1,2]thiazepine 1-oxide (2da)



Light yellow syrup (38.7 mg, 45%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97 (dd, *J* = 8.8, 5.6 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.09 (td, *J* = 8.4, 2.6 Hz, 1H), 6.97 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.11 (dd, *J* = 7.3, 6.2 Hz, 1H), 4.13 (dd, *J* = 13.7, 6.1 Hz, 1H), 3.36 (s, 3H), 3.08 (dd, *J* = 13.7, 7.4 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 164.8 (d, $J_{C\text{-}F}$ = 255 Hz), 148.0 (d, $J_{C\text{-}F}$ = 9 Hz), 142.9, 137.8, 133.9 (d, $J_{C\text{-}F}$ = 9 Hz), 132.2, 128.0, 127.7, 125.8, 116.0 (d, $J_{C\text{-}F}$ = 22 Hz), 115.1 (d, $J_{C\text{-}F}$ = 22 Hz), 113.9, 47.0, 32.6.

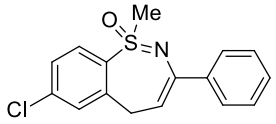
^{19}F NMR (376 MHz, $CDCl_3$) δ -104.87 (dd, *J* = 14.2, 7.8 Hz).

MS (EI): *m*/*z* = 287 (M^+, 70), 268 (2), 77 (20).

IR (ATR): ν = 3042, 2929, 1731, 1686, 1599, 1498, 1318, 1216, 1129, 967, 750 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{16}H_{14}NOSF+H]^+$: 288.0858. Found: 288.0858.

7-Chloro-1-methyl-3-phenylbenzo[*f*][1,2]thiazepine 1-oxide (2ea)



Light yellow syrup (46.4 mg, 51%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.90 (d, *J* = 8.5 Hz, 1H), 7.70 (d, *J* = 7.1 Hz, 2H), 7.40 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.26 – 7.21 (m, 1H), 6.11 (dd, *J* = 7.3, 6.2 Hz, 1H), 4.12 (dd, *J* = 13.7, 6.2 Hz, 1H), 3.37 (s, 3H), 3.09 (dd, *J* = 13.8, 7.4 Hz, 1H).

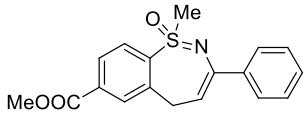
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 146.4, 142.9, 139.4, 137.8, 134.8, 132.5, 129.1, 128.2, 128.1, 127.8, 125.8, 113.9, 46.9, 32.4.

MS (EI): *m*/*z* = 303 (M^+, 71), 186 (3), 116 (4), 77 (50).

IR (ATR): ν = 3016, 2921, 1735, 1575, 1450, 1329, 1224, 1132, 964, 747 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{16}H_{14}NOSCl+H]^+$: 304.0563. Found: 304.0562.

Methyl-1-methyl-3-phenylbenzo[*f*][1,2]thiazepine-7-carboxylate 1-oxide (2fa)



Light yellow syrup (68.7 mg, 70%)

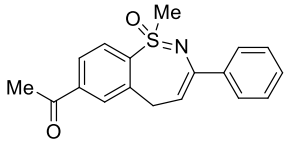
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.04 (dt, *J* = 15.3, 4.9 Hz, 2H), 7.94 (d, *J* = 0.9 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 1H), 6.11 (dd, *J* = 7.1, 6.4 Hz, 1H), 4.14 (dd, *J* = 13.9, 6.2 Hz, 1H), 3.95 (s, 3H), 3.39 (s, 3H), 3.27 (dd, *J* = 13.9, 7.3 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 165.6, 144.6, 142.7, 140.5, 137.9, 133.9, 130.7, 130.2, 128.8, 128.0, 127.7, 125.8, 113.7, 52.6, 46.4, 32.4.

MS (EI): *m*/*z* = 327 (M^+, 65), 225 (4), 211 (5), 116 (8), 102 (16), 77 (58).

IR (ATR): ν = 3021, 2927, 1719, 1609, 1438, 1278, 1116, 974, 907, 743 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{18}H_{17}NO_3S+H]^+$: 328.1007. Found: 328.1003.

1-(1-Methyl-1-oxido-3-phenylbenzo[*f*][1,2]thiazepin-7-yl)ethanone (2ga)



Yellow syrup (61.6 mg, 66%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.04 (d, *J* = 8.2 Hz, 1H), 7.94 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.82 (s, 1H), 7.70 (d, *J* = 7.1 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 1H), 6.11 (dd, *J* = 7.2, 6.3 Hz, 1H), 4.15 (dd, *J* = 13.9, 6.3 Hz, 1H), 3.40 (s, 3H), 3.28 (dd, *J* = 13.9, 7.3 Hz, 1H), 2.63 (s, 3H).

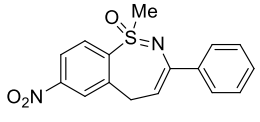
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 196.9, 145.0, 142.8, 140.6, 140.1, 137.9, 131.0, 128.8, 128.1, 127.8, 127.6, 125.8, 113.7, 46.5, 32.5, 26.9.

MS (EI): *m*/*z* = 311 (M^+, 70), 195 (3), 116 (4), 102 (10), 77 (37).

IR (ATR): ν = 3018, 2929, 1739, 1687, 1569, 1408, 1224, 1130, 962, 752 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{18}H_{17}NO_2S+H]^+$: 312.1058. Found: 312.1058.

1-Methyl-7-nitro-3-phenylbenzo[*f*][1,2]thiazepine 1-oxide (2ha)



Orange solid, melting point: 168-170 °C (42.4 mg, 45%)

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.22 (dd, *J* = 8.6, 2.3 Hz, 1H), 8.11

(dd, *J* = 7.5, 5.5 Hz, 2H), 7.70 – 7.69 (m, 2H), 7.33 – 7.31 (m, 2H), 7.27 (dt, *J* = 9.1, 4.4 Hz, 1H), 6.12 – 6.09 (m, 1H), 4.17 (dd, *J* = 14.0, 6.3 Hz, 1H), 3.43 (s, 3H), 3.34 (dd, *J* = 14.0, 7.2 Hz, 1H).

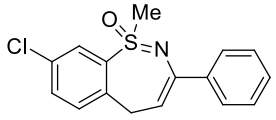
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ (ppm) 149.8, 146.2, 143.0, 142.4, 137.5, 131.9, 128.2, 128.1, 125.8, 123.9, 122.7, 112.9, 46.3, 32.4.

MS (EI): *m*/*z* = 314 (M^+, 78), 268 (3), 237 (3), 102 (13), 77 (38).

IR (ATR): ν = 2913, 1738, 1611, 1519, 1336, 1229, 1133, 974, 895, 748 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{16}H_{14}N_2O_3S+H]^+$: 315.0803. Found: 315.0803.

8-Chloro-1-methyl-3-phenylbenzo[*f*][1,2]thiazepine 1-oxide (2ia)



Light yellow syrup (46.4 mg, 51%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (d, *J* = 2.2 Hz, 1H), 7.69 (d, *J* = 7.3 Hz, 2H), 7.42 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 6.10 (dd, *J* = 7.3, 6.2 Hz, 1H), 4.08 (dd, *J* = 13.8, 6.1 Hz, 1H), 3.37 (s, 3H), 3.11 (dd, *J* = 13.8, 7.4 Hz, 1H).

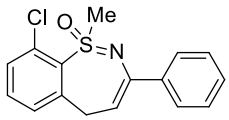
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 143.0, 142.5, 137.8, 137.7, 133.7, 133.1, 130.5, 128.0, 127.7, 125.7, 114.2, 46.6, 31.8.

MS (EI): *m*/*z* = 303 (M^+, 96), 226 (2), 187 (6), 77 (9).

IR (ATR): ν = 3058, 2926, 2086, 1737, 1617, 1471, 1328, 1226, 1133, 974, 856, 759 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{16}H_{14}NOSCl+H]^+$: 304.0563. Found: 304.0560.

9-Chloro-1-methyl-3-phenylbenzo[*f*][1,2]thiazepine 1-oxide (2ja)



Light yellow solid, melting point:179-181 °C (68.2 mg, 75%)

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.78 (dd, *J* = 8.3, 1.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.34 (dt, *J* = 11.1, 7.8 Hz, 3H), 7.28 – 7.24 (m, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 6.20 (dd, *J* = 7.4, 5.9 Hz, 1H), 4.30 (dd, *J* = 13.7, 5.8 Hz, 1H), 3.58 (s, 3H), 3.17 (dd, *J* = 13.7, 7.5 Hz, 1H).

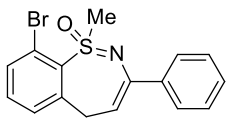
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ (ppm) 146.4, 142.3, 137.3, 136.6, 134.9, 132.7, 131.3, 129.1, 128.0, 127.8, 126.0, 115.2, 43.8, 33.8.

MS (CI): *m*/*z* = 304 ($[M+H]^+$, 100), 303 (M^+, 2).

IR (ATR): ν = 3023, 2927, 2323, 1567, 1440, 1316, 1219, 1130, 973, 755 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{16}H_{14}NOSCl+Na]^+$: 326.0382. Found: 326.0377.

9-Bromo-1-methyl-3-phenylbenzo[*f*][1,2]thiazepine 1-oxide (2ka)



Light yellow solid, melting point: 190-192 °C (70.8 mg, 68%)

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.77 (d, *J* = 8.1 Hz, 2H), 7.69 (t, *J* = 4.6 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.25 (dd, *J* = 12.1, 3.0 Hz, 3H), 6.20 (t, *J* = 6.6 Hz, 1H), 4.33 (dd, *J* = 13.6, 5.8 Hz, 1H), 3.59 (s, 3H), 3.15 (dd, *J* = 13.5, 7.5 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ (ppm) 146.8, 142.3, 138.0, 137.2, 135.2, 132.9, 129.8, 128.0,

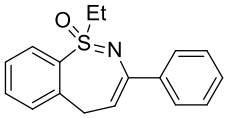
127.8, 126.0, 123.7, 115.4, 43.5, 34.2.

MS (EI): *m/z* = 347 (M^+, 57), 231 (21), 116 (9), 102 (41), 77 (61).

IR (ATR): ν = 3019, 2929, 2116, 1621, 1550, 1439, 1324, 1218, 1134, 978, 789 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{16}H_{14}NOSBr+Na]^+$: 369.9877. Found: 369.9874.

1-Ethyl-3-phenylbenzo[*f*][1,2]thiazepine 1-oxide (2la)



Light yellow syrup (60.3 mg, 71%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.74 – 7.72 (m, 2H), 7.49 – 7.40 (m, 2H), 7.32 – 7.20 (m, 4H), 6.14 (dd, *J* = 7.4, 6.1 Hz, 1H), 4.20 (dd, *J* = 13.6, 6.0 Hz, 1H), 3.52 – 3.41 (m, 2H), 3.07 (dd, *J* = 13.7, 7.5 Hz, 1H), 1.43 (t, *J* = 7.4 Hz, 3H).

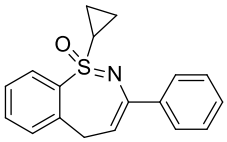
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 145.8, 142.4, 138.3, 134.6, 133.0, 131.8, 129.2, 128.0, 127.9, 127.5, 125.9, 114.5, 53.3, 32.7, 8.6.

MS (EI): *m/z* = 283 (M^+, 85), 206 (17), 77 (14).

IR (ATR): ν = 3056, 2938, 1735, 1617, 1444, 1325, 1219, 1131, 1066, 906, 734 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{17}H_{17}NOS+H]^+$: 284.1109. Found: 284.1104.

1-Cyclopropyl-3-phenylbenzo[*f*][1,2]thiazepine 1-oxide (2ma)



Light yellow syrup (62.0 mg, 70%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 7.3 Hz, 2H), 7.46 (td, *J* = 7.4, 1.1 Hz, 1H), 7.39 (t, *J* = 7.1 Hz, 1H), 7.28 (q, *J* = 7.3 Hz, 3H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.06 (t, *J* = 6.8 Hz, 1H), 4.08 (dd, *J* = 13.8, 6.5 Hz, 1H), 3.27 (dd, *J* = 13.9, 7.1 Hz, 1H), 2.89 – 2.83 (m, 1H), 1.66 – 1.53 (m, 1H), 1.51 – 1.46 (m, 1H), 1.23 – 1.15 (m, 1H) 1.13 – 1.04 (m, 1H).

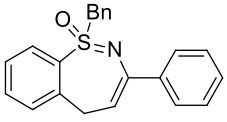
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 144.0, 142.3, 138.7, 136.9, 132.7, 129.9, 129.0, 127.9, 127.7, 127.4, 125.8, 112.4, 34.2, 32.4, 5.9, 5.8.

MS (EI): *m/z* = 295 (M^+, 100), 218 (1), 179 (2), 116 (2), 77 (15).

IR (ATR): ν = 3056, 2110, 1735, 1619, 1443, 1225, 1135, 1065, 884, 732 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{18}H_{17}NOS+H]^+$: 296.1109. Found: 296.1104.

1-Benzyl-3-phenylbenzo[*f*][1,2]thiazepine 1-oxide (2na)



Light yellow syrup (71.4 mg, 69%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.76 – 7.73 (m, 3H), 7.41 (td, *J* = 7.5, 1.4 Hz, 1H), 7.34 – 7.30 (m, 4H), 7.25 – 7.20 (m, 3H), 7.07 (t, *J* = 7.0 Hz, 3H), 6.01 (dd, *J* = 7.5, 6.1 Hz, 1H), 4.71 (d, *J* = 13.7 Hz, 1H), 4.56 (d, *J* = 13.7 Hz, 1H), 3.37 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.64 (dd, *J* = 13.6, 7.6 Hz, 1H).

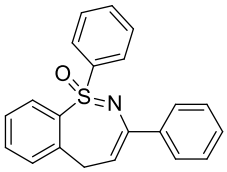
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 146.8, 142.1, 138.2, 133.5, 133.2, 132.4, 131.4, 129.2, 128.7, 128.5, 128.1, 127.9, 127.6, 127.4, 125.9, 114.5, 65.1, 31.9.

MS (EI): *m*/*z* = 345 (M^+, 58), 254 (24), 91 (100), 77 (10).

IR (ATR): ν = 3058, 2925, 1729, 1591, 1444, 1324, 1226, 1126, 1070, 912, 736 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{22}H_{19}NOS+H]^+$: 346.1266. Found: 346.1265.

1,3-Diphenylbenzo[*f*][1,2]thiazepine 1-oxide (2oa)



Light yellow syrup (54.6 mg, 55%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.26 (d, *J* = 7.0 Hz, 2H), 7.79 (d, *J* = 7.7 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.63 – 7.52 (m, 3H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.24 (dd, *J* = 11.2, 7.6 Hz, 2H), 6.15 (t, *J* = 6.8 Hz, 1H), 4.19 (dd, *J* = 14.0, 6.5 Hz, 1H), 3.35 (dd, *J* = 14.0, 7.2 Hz, 1H).

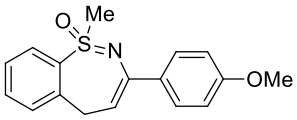
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 143.8, 142.3, 141.6, 138.6, 138.0, 132.9, 132.7, 130.4, 129.1, 129.0, 128.5, 128.0, 127.8, 127.5, 125.9, 112.2, 32.3.

MS (EI): *m*/*z* = 331 (M^+, 9), 229 (2), 228 (6), 103 (9), 102 (6), 77 (44).

IR (ATR): ν = 3060, 2089, 1724, 1683, 1593, 1444, 1326, 1229, 1137, 904, 752 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{21}H_{17}NOS+H]^+$: 332.1109. Found: 332.1104.

3-(4-Methoxyphenyl)-1-methylbenzo[*f*][1,2]thiazepine 1-oxide (2ab)



Yellow syrup (58.3 mg, 65%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96 (d, *J* = 8.3 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.44 (dt, *J* = 20.8, 7.3 Hz, 2H), 7.25 (d, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.02 (t, *J* = 6.7 Hz, 1H), 4.13 (dd, *J* = 13.7, 6.1 Hz, 1H), 3.78 (s, 3H), 3.36 (s, 3H), 3.11 (dd, *J* = 13.8, 7.4 Hz, 1H).

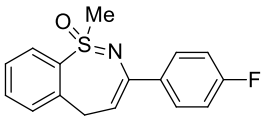
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 159.3, 145.0, 142.1, 136.5, 133.1, 131.0, 130.9, 129.1, 128.0, 127.1, 113.4, 112.8, 55.2, 46.8, 32.5.

MS (EI): *m*/*z* = 299 (M^+, 67), 192 (5), 153 (3), 146 (2), 103 (6).

IR (ATR): ν = 3017, 2940, 2105, 1738, 1600, 1505, 1309, 1228, 1122, 969, 753 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{17}H_{17}NO_2S+H]^+$: 300.1058. Found: 300.1055.

3-(4-Fluorophenyl)-1-methylbenzo[*f*][1,2]thiazepine 1-oxide (2ac)



Light yellow syrup (62.0 mg, 72%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.98 (dd, *J* = 8.7, 5.6 Hz, 1H), 7.71 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.10 (td, *J* = 8.4, 2.5 Hz, 1H), 6.97 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.11 (t, *J* = 6.7 Hz, 1H), 4.13 (dd, *J* = 13.7, 6.0 Hz, 1H), 3.36 (s, 3H), 3.08 (dd, *J* = 13.7, 7.4 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 164.8 (d, $J_{C\text{-}F}$ = 255 Hz), 148.0 (d, $J_{C\text{-}F}$ = 44 Hz), 142.9, 137.8, 133.9 (d, $J_{C\text{-}F}$ = 10 Hz), 132.2 (d, $J_{C\text{-}F}$ = 3 Hz), 128.0, 127.7, 125.8, 116.0 (d, $J_{C\text{-}F}$ = 22 Hz), 115.1 (d, $J_{C\text{-}F}$ = 22 Hz), 113.9, 47.0, 32.6.

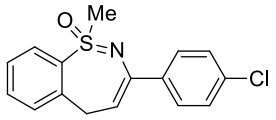
^{19}F NMR (376 MHz, $CDCl_3$) δ –104.86 (dd, *J* = 13.9, 7.8 Hz).

MS (EI): *m/z* = 287 (M^+, 83), 153 (4), 134 (2), 95(3).

IR (ATR): ν = 3062, 2111, 1739, 1599, 1470, 1330, 1223, 1132, 965, 828, 752 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{16}H_{14}NOSF+H]^+$: 288.0858. Found: 288.0556.

3-(4-Chlorophenyl)-1-methylbenzo[*f*][1,2]thiazepine 1-oxide (2ad)



Light yellow syrup (70.0 mg, 77%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.50 – 7.39 (m, 2H), 7.27 – 7.23 (m, 3H), 6.11 (dd, *J* = 7.3, 6.2 Hz, 1H), 4.12 (dd, *J* = 13.7, 6.1 Hz, 1H), 3.36 (s, 3H), 3.14 (dd, *J* = 13.7, 7.4 Hz, 1H).

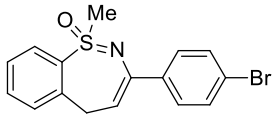
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 144.5, 141.6, 136.8, 136.4, 133.3, 133.2, 130.8, 129.3, 128.2, 128.1, 127.2, 114.9, 46.8, 32.5.

MS (EI): *m/z* = 303 (M^+, 72), 192 (2), 153 (3), 150 (2), 111 (8).

IR (ATR): ν = 3018, 2927, 1731, 1589, 1483, 1277, 1217, 1128, 970, 831, 752 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{16}H_{14}NOSCl+H]^+$: 304.0563. Found: 304.0560.

3-(4-Bromophenyl)-1-methylbenzo[*f*][1,2]thiazepine 1-oxide (2ae)



Light yellow syrup (71.8 mg, 69%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.47 – 7.39 (m, 4H), 7.25 (d, *J* = 6.7 Hz, 1H), 6.12 (t, *J* = 6.8 Hz, 1H), 4.12 (dd, *J* = 13.7, 6.1 Hz, 1H), 3.36 (s, 3H), 3.14 (dd, *J* = 13.8, 7.4 Hz, 1H).

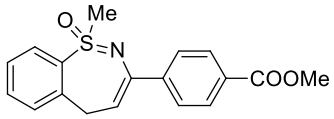
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 144.4, 141.6, 137.2, 136.3, 133.2, 131.0, 130.8, 129.3, 128.2, 127.5, 121.5, 115.0, 46.8, 32.5.

MS (EI): *m/z* = 346 (M^+, 68), 268 (9), 192 (2), 155 (3).

IR (ATR): ν = 3057, 2926, 1732, 1588, 1479, 1321, 1223, 1134, 970, 830, 751 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{16}H_{14}NOSBr+H]^+$: 348.0058. Found: 348.0056.

Methyl 4-(1-methyl-1-oxidobenzo[*f*][1,2]thiazepin-3-yl)benzoate (2af)



Light yellow syrup (69.7 mg, 71%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96 – 7.93 (m, 3H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.39 (m, 2H), 7.25 (d, *J* = 6.9 Hz, 1H), 6.24 (t, *J* = 6.8 Hz, 1H), 4.14 (dd, *J* = 13.7, 6.2 Hz, 1H), 3.87 (s, 3H), 3.37 (s, 3H), 3.17 (dd, *J* = 13.7, 7.4 Hz, 1H).

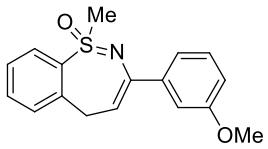
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 167.0, 144.1, 142.6, 141.8, 136.3, 133.3, 130.7, 129.4, 129.3, 128.9, 128.2, 125.6, 116.7, 51.9, 46.8, 32.5.

MS (EI): *m/z* = 327 (M^+, 80), 268 (72), 192 (3), 135 (14).

IR (ATR): ν = 3069, 2952, 2097, 1705, 1607, 1441, 1283, 1148, 957, 746 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{18}H_{17}NO_3S+H]^+$: 328.1007. Found: 328.1000.

3-(3-Methoxyphenyl)-1-methylbenzo[*f*][1,2]thiazepine 1-oxide (2ag)



Yellow syrup (65.5 mg, 73%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.30 – 7.28 (m, 2H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.19 (t, *J* = 8.1 Hz, 1H), 6.80 – 6.75 (m, 1H), 6.11 (dd, *J* = 7.3, 6.3 Hz, 1H), 4.12 (dd, *J* = 13.7, 6.2 Hz, 1H), 3.80 (s, 3H), 3.35 (s, 3H), 3.13 (dd, *J* = 13.7, 7.4 Hz, 1H).

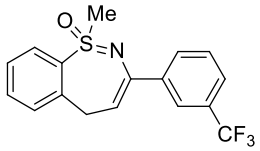
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 159.4, 144.5, 142.4, 139.8, 136.8, 133.1, 130.7, 129.2, 128.9, 128.0, 118.3, 114.7, 113.5, 111.2, 55.1, 46.7, 32.5.

MS (EI): *m*/*z* = 299 (M^+, 100), 268 (31), 192 (2), 107 (5).

IR (ATR): ν = 3056, 2935, 2107, 1681, 1581, 1431, 1234, 1129, 1043, 968, 736 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{17}H_{17}NO_2S+H]^+$: 300.1058. Found: 300.1055.

1-Methyl-3-(3-(trifluoromethyl)phenyl)benzo[*f*][1,2]thiazepine 1-oxide (2ah)



Light yellow syrup (72.8 mg, 72%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96 – 7.91 (m, 3H), 7.51 – 7.39 (m, 4H), 7.27 (d, *J* = 6.9 Hz, 1H), 6.20 (dd, *J* = 7.3, 6.3 Hz, 1H), 4.14 (dd, *J* = 13.8, 6.2 Hz, 1H), 3.39 (s, 3H), 3.20 (dd, *J* = 13.8, 7.3 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 144.2, 141.5, 139.2, 136.4, 133.3, 130.7, 129.3, 129.2 (d, $J_{C\text{-}F}$ = 1.1 Hz), 128.5, 128.2, 124.1 (q, $J_{C\text{-}F}$ = 7.4 Hz), 122.5 (q, $J_{C\text{-}F}$ = 7.8 Hz), 115.7, 46.7, 32.5.

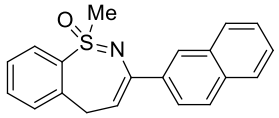
^{19}F NMR (376 MHz, $CDCl_3$) δ –62.6 (s, 3F).

MS (EI): *m*/*z* = 337 (M^+, 66), 268 (11), 192 (2), 145 (8).

IR (ATR): ν = 3007, 2926, 2108, 1739, 1617, 1435, 1334, 1221, 1105, 975, 752 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{17}H_{14}NOSF_3+H]^+$: 338.0826. Found: 338.0821.

1-Methyl-3-(naphthalen-2-yl)benzo[*f*][1,2]thiazepine 1-oxide (2ai)



Light yellow syrup (62.2 mg, 65%)

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.32 (s, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.81 (dd, *J* = 8.6, 1.3 Hz, 2H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.54 – 7.44 (m, 4H), 7.32 – 7.29 (m, 1H), 6.34 – 6.32 (m, 1H), 4.25 (dd, *J* = 13.7, 6.2 Hz, 1H), 3.46 (s, 3H), 3.24 (dd, *J* = 13.8, 7.4 Hz, 1H).

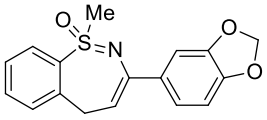
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ (ppm) 144.7, 142.5, 136.5, 135.5, 133.4, 133.2, 133.0, 130.9, 129.2, 128.6, 128.1, 127.4, 127.3, 125.8, 125.7, 125.3, 123.6, 115.2, 46.9, 32.7.

MS (CI): *m*/*z* = 320 ($[M+H]^+$, 100), 319 (M^+, 22), 192 (4), 153 (5), 127 (2).

IR (ATR): ν = 3050, 2929, 2321, 1727, 1605, 1464, 1312, 1226, 1127, 966, 750 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{20}H_{17}NOS+Na]^+$: 342.0929. Found: 342.0925.

3-(Benzo[*d*][1,3]dioxol-5-yl)-1-methylbenzo[*f*][1,2]thiazepine 1-oxide (2aj)



Yellow syrup (60.1 mg, 64%)

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.94 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.42 (dtd, *J* = 13.7, 7.5, 4.0 Hz, 2H), 7.25 (dt, *J* = 9.1, 4.6 Hz, 2H), 7.18 (d, *J* = 1.6 Hz, 1H), 6.73 (d, *J* = 8.2 Hz), 5.97 (dd, *J* = 7.3, 6.2 Hz, 1H), 5.89 (s, 2H), 4.10 (dd, *J* = 13.7, 6.1 Hz, 1H), 3.34 (s, 3H), 3.09 (dd, *J* = 13.8, 7.4 Hz, 1H.

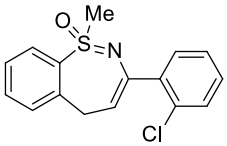
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ (ppm) 147.4, 147.2, 144.8, 142.1, 136.4, 133.1, 132.8, 130.8, 129.1, 128.0, 119.9, 113.3, 107.7, 106.3, 100.8, 46.7, 32.5.

MS (EI): *m*/*z* = 313 (M^+, 75), 192 (11), 167 (3), 146 (18), 121 (18).

IR (ATR): ν = 3061, 2891, 1601, 1484, 1308, 1234, 1121, 1036, 910, 727 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{17}H_{15}NO_3S+H]^+$: 314.0851. Found: 314.0847.

3-(2-Chlorophenyl)-1-methylbenzo[*f*][1,2]thiazepine 1-oxide (2ak)



Light yellow syrup (69.1 mg, 76%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.64 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.52 – 7.42 (m, 2H), 7.31 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.27 (d, *J* = 6.6 Hz, 1H), 7.21 (td, *J* = 7.5, 1.4 Hz, 1H), 7.15 – 7.10 (m, 1H), 5.91 (dd, *J* = 7.2, 6.4 Hz, 1H), 4.09 (dd, *J* = 13.9, 6.3 Hz, 1H), 3.36 (s, 3H), 3.28 (dd, *J* = 13.9, 7.2 Hz, 1H).

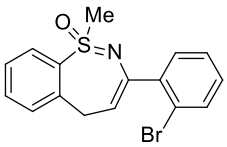
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 143.8, 140.0, 137.8, 136.4, 133.2, 131.9, 131.1, 129.9, 129.8, 129.2, 128.3, 128.0, 126.5, 118.8, 46.3, 32.3.

MS (EI): *m*/*z* = 303 (M^+, 88), 268 (26), 192 (2), 111 (3).

IR (ATR): ν = 3059, 2928, 1728, 1622, 1432, 1322, 1218, 1134, 964, 746 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{16}H_{14}NOSCl+H]^+$: 304.0563. Found: 304.0561.

3-(2-Bromophenyl)-1-methylbenzo[*f*][1,2]thiazepine 1-oxide (2al)



Light yellow syrup (78.1 mg, 75%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.56 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.45 (td, *J* = 7.6, 1.3 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.06 (td, *J* = 7.7, 1.7 Hz, 1H), 5.74 (t, *J* = 6.8 Hz, 1H), 4.01 (dd, *J* = 14.0, 6.5 Hz, 1H), 3.41 – 3.32 (m, 4H).

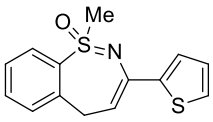
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 143.3, 142.0, 140.3, 136.5, 133.2, 133.0, 131.0, 129.3, 129.2, 128.6, 127.9, 127.1, 122.0, 117.2, 46.0, 32.0.

MS (EI): *m*/*z* = 346 (M^+, 63), 268 (81), 192 (5), 153 (9).

IR (ATR): ν = 3025, 2928, 1736, 1617, 1444, 1333, 1202, 1127, 960, 750 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{16}H_{14}NOSBr+Na]^+$: 369.9877. Found: 369.9872.

1-Methyl-3-(thiophen-2-yl)benzo[*f*][1,2]thiazepine 1-oxide (2am)



Yellow syrup (43.7 mg, 53%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.93 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.29 (d, *J* = 3.6 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 5.0 Hz, 1H), 6.93 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.02 (t, *J* = 6.8 Hz, 1H), 4.08 (dd, *J* = 14.0, 6.3 Hz, 1H), 3.34 (s, 3H), 3.14 (dd, *J* = 14.0, 7.3 Hz, 1H).

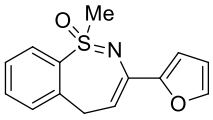
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 144.2, 143.9, 137.5, 136.8, 133.1, 130.4, 129.3, 128.0, 127.2, 124.4, 124.3, 113.0, 46.4, 32.2.

MS (EI): *m*/*z* = 275 (M^+, 100), 260 (12), 83 (31).

IR (ATR): ν = 3274, 3066, 2931, 2072, 1923, 1741, 1630, 1522,, 1319, 1229, 1124, 964, 706 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{14}H_{13}NOS_2+H]^+$: 276.0517. Found: 276.0512

3-(Furan-2-yl)-1-methylbenzo[*f*][1,2]thiazepine 1-oxide (2an)



Yellow syrup (47.4 mg, 61%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.93 (d, *J* = 7.7 Hz, 1H), 7.44 (ddd, *J* = 21.5, 10.8, 6.4 Hz, 2H), 7.28 – 7.24 (m, 2H), 6.60 (d, *J* = 3.2 Hz, 1H), 6.35 (dd, *J* = 3.0, 1.7 Hz, 1H), 6.11 (t, *J* = 6.9 Hz, 1H), 4.10 (dd, *J* = 13.7, 6.2 Hz, 1H), 3.34 (s, 3H), 3.17 (dd, *J* = 13.9, 7.4 Hz, 1H).

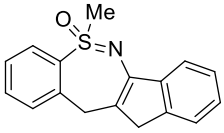
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 153.4, 144.5, 141.9, 136.9, 133.9, 133.1, 130.6, 129.4, 128.0, 113.2, 111.3, 107.8, 46.5, 31.9.

MS (EI): *m*/*z* = 259 (M^+, 100), 167 (10), 153 (2).

IR (ATR): ν = 2933, 1716, 1674, 1480, 1324, 1226, 1136, 971, 743 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{14}H_{13}NO_2S+H]^+$: 260.0745. Found: 260.0741.

5-Methyl-11,12-dihydrobenzo[*f*]indeno[1,2-c][1,2]thiazepine 5-oxide (2ao)



White solid, melting point: 60-62 °C (34.6 mg, 41%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.58 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.35 – 7.29 (m, 2H), 7.26 (t, *J* = 8.7 Hz, 2H), 7.13 (td, *J* = 7.4, 1.1 Hz, 1H), 4.43 (d, *J* = 15.8 Hz, 1H), 3.66 (d, *J* = 15.8 Hz, 1H), 3.59 (s, 3H), 3.40 (q, *J* = 22.4 Hz, 2H).

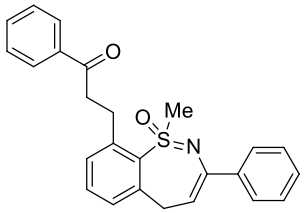
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 144.6, 141.0, 140.3, 138.0, 132.9, 129.5, 126.9, 126.1, 124.3, 123.0, 122.7, 117.9, 116.2, 42.2, 39.8, 33.4.

MS (CI): *m*/*z* = 282 ($[M+H]^+$, 65), 281 (M^+, 13), 153 (30).

IR (ATR): ν = 3025, 2925, 1818, 1709, 1593, 1464, 1308, 1202, 985, 725 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{17}H_{15}NOS+Na]^+$: 304.0772. Found: 304.0767.

3-(1-Methyl-1-oxido-3-phenylbenzo[*f*][1,2]thiazepin-9-yl)-1-phenylpropan-1-one (5aa)



Yellow solid, melting point: 182-184 °C (107.1 mg, 89%)

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.92 (d, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.32 (dd, *J* = 12.8, 5.3 Hz, 1H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 7.3 Hz, 1H), 6.27 (dd, *J* = 7.2, 6.1 Hz, 1H), 4.30 (dd, *J* = 13.5, 5.9 Hz, 1H), 3.69 – 3.63 (m, 1H), 3.58 – 3.53 (m, 1H), 3.48 (s, 3H), 3.25 – 3.20 (m, 1H), 3.14 – 3.08 (m, 2H).

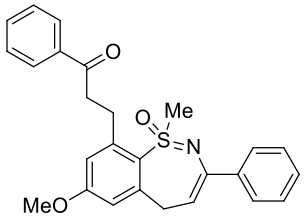
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ (ppm) 199.0, 145.5, 144.6, 142.1, 137.5, 136.9, 136.6, 132.9, 132.5, 131.7, 128.7, 128.4, 128.0, 127.6, 125.8, 115.8, 45.8, 41.3, 34.1, 29.8.

MS (EI): *m*/*z* = 401 (M^+, 39), 296 (72), 105 (100), 77 (93).

IR (ATR): ν = 3030, 2935, 2313, 1739, 1677, 1579, 1447, 1323, 1215, 1133, 1045, 971, 750 (cm^{-1}).

HRMS *m*/*z*: Calcd for $[C_{25}H_{23}NO_2S+H]^+$: 402.1528. Found: 402.1525.

3-(7-Methoxy-1-methyl-1-oxido-3-phenylbenzo[*f*][1,2]thiazepin-9-yl)-1-phenylpropan-1-one (5ca)



Yellow solid, melting point:82-84 °C (103.4 mg, 80%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.91 (d, *J* = 7.8 Hz, 2H), 7.77 (d, *J* = 7.9 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.22 (dd, *J* = 13.2, 6.2 Hz, 1H), 6.81 (s, 1H), 6.63 (s, 1H), 6.22 (t, *J* = 6.5 Hz, 1H), 4.25 (dd, *J* = 13.3, 5.7 Hz, 1H), 3.80 (s, 3H), 3.68 – 3.61 (m, 1H), 3.55 – 3.43 (m, 1H), 3.43 (s, 3H), 3.19 – 3.08 (m, 2H), 3.03 (dd, *J* = 13.5, 7.5 Hz, 1H).

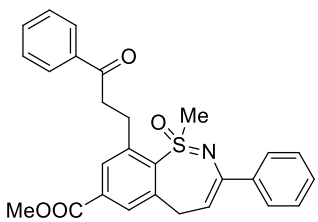
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 199.1, 161.7, 147.8, 147.1, 142.3, 137.6, 132.9, 128.4, 128.0, 127.9, 127.5, 125.8, 116.5, 115.2, 113.6, 55.3, 46.2, 41.3, 34.6, 30.1.

MS (EI): *m*/*z* = 431 (M^+, 5), 326 (15), 105 (100), 77 (60).

IR (ATR): ν = 3052, 2935, 2321, 1679, 1583, 1445, 1282, 1129, 1075, 966, 746 (cm^{-1}).

HRMS *m*/*z*: Calcd for $[C_{26}H_{25}NO_3S+Na]^+$: 432.1633. Found: 432.1628.

Methyl-1-methyl-9-(3-oxo-3-phenylpropyl)-3-phenylbenzo[f][1,2]thiazepine-7-carboxylate-1-oxide (5fa)



Yellow solid, melting point: 84-86 °C (108.8 mg, 79%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97 (s, 1H), 7.91 (d, *J* = 7.5 Hz, 2H), 7.80 (s, 1H), 7.76 (d, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.25 (t, *J* = 6.6 Hz, 1H), 4.31 (dd, *J* = 13.5, 5.8 Hz, 1H),

3.92 (s, 3H), 3.70 – 3.62 (m, 1H), 3.59 – 3.52 (m, 1H), 3.49 (s, 3H), 3.31 – 3.10 (m, 3H).

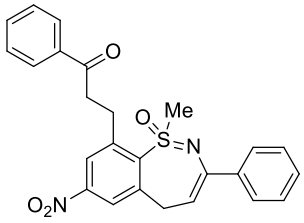
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 198.6, 165.4, 145.7, 145.0, 132.9, 132.8, 132.1, 129.3, 128.4, 128.0, 127.9, 127.7, 125.7, 115.4, 52.5, 45.5, 41.0, 34.0, 29.8.

MS (EI): *m*/*z* = 459 (M^+, 3), 354 (11), 105 (100), 77 (73).

IR (ATR): ν = 3018, 2946, 2316, 1725, 1681, 1572, 1441, 1293, 1128, 975, 749 (cm^{-1}).

HRMS *m*/*z*: Calcd for $[C_{22}H_{25}NO_4S+H]^+$: 460.1583. Found: 460.1582.

3-(1-Methyl-7-nitro-1-oxido-3-phenylbenzo[*f*][1,2]thiazepin-9-yl)-1-phenylpropan-1-one (5ha)



Orange solid, melting point: 87-89 °C (97.7 mg, 73%)

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.16 (d, *J* = 2.4 Hz, 1H), 7.98 (d, *J* = 2.4 Hz, 1H), 7.92 (d, *J* = 7.3 Hz, 2H), 7.75 (d, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.9 Hz, 1H), 6.26 (dd, *J* = 7.2, 6.0 Hz, 1H), 4.37 (dd, *J* = 13.7, 5.8 Hz, 1H), 3.67 – 3.63 (m, 1H), 3.61 – 3.58 (m, 1H), 3.55 (s, 3H), 3.38 – 3.34 (m, 1H), 3.25 (dd, *J* = 13.7, 7.3 Hz, 2H).

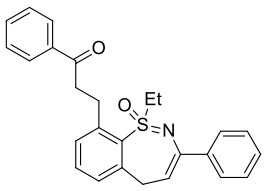
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ (ppm) 198.2, 148.7, 147.6, 147.2, 142.8, 142.5, 136.7, 136.3, 133.3, 128.8, 128.6, 128.1, 128.0, 125.8, 125.5, 122.8, 114.8, 48.6, 40.5, 34.2, 29.9.

MS (CI): *m*/*z* = 447 ($[M+H]^+$, 5), 133 (100).

IR (ATR): ν = 3021, 2936, 2326, 1740, 1680, 1524, 1347, 1220, 969, 746 (cm^{-1}).

HRMS *m*/*z*: Calcd for $[C_{25}H_{22}N_2O_4S+H]^+$: 447.1379. Found: 447.1379.

3-(1-Ethyl-1-oxido-3-phenylbenzo[*f*][1,2]thiazepin-9-yl)-1-phenylpropan-1-one (5la)



Yellow solid, melting point: 104-106 °C (99.6 mg, 80%)

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.92 (d, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.41 – 7.34 (m, 3H), 7.34 – 7.29 (m, 3H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 6.24 (dd, *J* = 7.0, 6.3 Hz, 1H), 4.32 (dd, *J* = 13.5, 5.8 Hz, 1H), 3.70 – 3.65 (m, 1H), 3.63 – 3.50 (m, 3H), 3.21 – 3.16 (m, 1H),, 3.12 – 3.04 (m, 2H), 1.50 (t, *J* = 7.4 Hz, 3H).

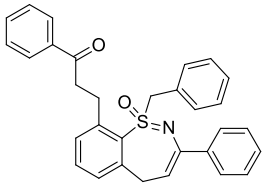
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ (ppm) 199.1, 146.6, 144.8, 141.8, 137.6, 136.6, 134.9, 132.9, 132.5, 131.9, 128.6, 128.4, 128.1, 128.0, 127.6, 125.8, 115.1, 52.3, 41.6, 34.2, 30.1, 8.8.

MS (EI): *m*/*z* = 415 (11, M^+), 338 (4), 310 (80), 105 (100), 77 (70).

IR (ATR): ν = 2941, 2112, 1739, 1680, 1580, 1449, 1369, 1210, 978, 743 (cm^{-1}).

HRMS *m*/*z*: Calcd for $[C_{26}H_{25}NO_2S+Na]^+$: 438.1504. Found: 438.1549.

3-(1-Benzyl-1-oxido-3-phenylbenzo[*f*][1,2]thiazepin-9-yl)-1-phenylpropan-1-one (5na)



Light yellow solid, melting point: 71-73 °C (113.1 mg, 79%)

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.94 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.28 (m, 5H), 7.24 – 7.17 (m, 5H), 6.92 (d, *J* = 6.9 Hz, 1H), 6.07 (t, *J* = 6.7 Hz, 1H), 4.73 (q, *J* = 13.5 Hz, 2H), 3.72 – 3.62 (m, 2H), 3.42 (dd, *J* = 13.4, 5.9 Hz, 1H), 3.22 – 3.18 (m, 1H), 3.11 (ddd, *J* = 16.3, 9.1, 5.1 Hz, 1H), 2.63 (dd, *J* = 13.5, 7.4 Hz, 1H).

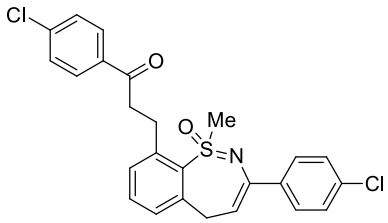
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ (ppm) 199.2, 147.5, 145.3, 141.6, 137.7, 136.6, 133.7, 132.9, 132.7, 131.7, 131.4, 129.3, 128.7, 128.4, 128.2, 128.1, 128.0, 127.5, 125.9, 114.7, 63.7, 41.6, 33.5, 30.3.

MS (EI): *m*/*z* = 477 (M^+, 3), 358 (2), 105 (100), 91(78), 77 (81).

IR (ATR): ν = 3059, 2931, 2327, 1679, 1580, 1449, 1278, 1217, 1122, 975, 745 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{31}H_{27}NO_2S+H]^+$: 478.1841. Found: 478.1837.

1-(4-Chlorophenyl)-3-(3-(4-chlorophenyl)-1-methyl-1-oxidobenzo[*f*][1,2]thiazepin-9-yl)propan-1-one (5ad)



Yellow solid, melting point: 186-188 °C (129.5 mg, 92%)

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.85 (d, *J* = 8.6 Hz, 2H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.39 – 7.32 (m, 3H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 7.4 Hz, 1H), 6.24 (dd, *J* = 7.2, 6.1 Hz, 1H), 4.27 (dd, *J* = 13.5, 5.9 Hz, 1H), 3.63 – 3.57 (m, 1H), 3.55 – 3.50 (m, 1H), 3.46 (s, 3H), 3.18 (ddd, *J* = 13.1, 10.3, 5.1 Hz, 1H), 3.10 (dd, *J* = 13.6, 7.4 Hz, 1H), 3.05 (ddd, *J* = 17.6, 9.9, 5.2 Hz, 1H).

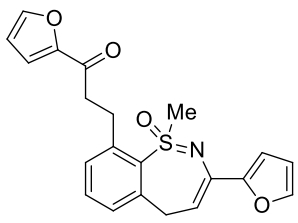
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ (ppm) 197.8, 145.4, 144.4, 141.1, 139.4, 136.7, 136.1, 134.8, 133.4, 132.6, 131.9, 129.5, 128.9, 128.8, 128.2, 127.1, 116.3, 45.8, 41.4, 34.1, 29.9.

MS (EI): *m*/*z* = 469 (M^+, 3), 139 (100), 111 (63).

IR (ATR): ν = 3016, 2936, 2048, 1739, 1582, 1478, 1368, 1216, 1093, 974, 774 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{25}H_{21}NO_2SCl_2+Na]^+$: 492.0568. Found: 492.0563.

1-(Furan-2-yl)-3-(3-(furan-2-yl)-1-methyl-1-oxidobenzo[*f*][1,2]thiazepin-9-yl)propan-1-one (5an)



Yellow solid, melting point: 90-92 °C (89.2 mg, 78%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.51 (d, *J* = 0.9 Hz, 1H), 7.36 – 7.29 (m, 3H), 7.16 (d, *J* = 3.6 Hz, 1H), 7.12 (dd, *J* = 7.0, 1.5 Hz, 1H), 6.62 (d, *J* = 3.2 Hz, 1H), 6.46 (dd, *J* = 3.5, 1.7 Hz, 1H), 6.36 (dd, *J* =

3.3, 1.8 Hz, 1H), 6.20 – 6.14 (m, 1H), 4.24 (dd, *J* = 13.7, 6.1 Hz, 1H), 3.49 – 3.42 (m, 2H), 3.42 (s, 3H), 3.23 – 3.16 (m, 1H), 3.09 (dd, *J* = 13.7, 7.5 Hz, 1H), 3.01 – 2.92 (m, 1H).

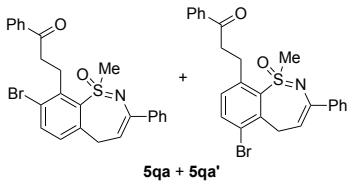
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 188.0, 153.1, 152.2, 146.3, 145.5, 144.1, 142.0, 137.2, 133.6, 132.5, 131.6, 128.9, 117.5, 114.9, 112.1, 111.3, 108.2, 45.6, 40.8, 33.5, 29.5.

MS (EI): *m*/*z* = 381 (M^+, 7), 286 (53), 95 (100).

IR (ATR): ν = 3133, 2934, 2053, 1739, 1668, 1567, 1463, 1318, 1224, 1151, 976, 735 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{21}H_{19}NO_4S+Na]^+$: 404.0932. Found: 404.0927.

3-(8-Bromo-1-methyl-1-oxido-3-phenylbenzo[f][1,2]thiazepin-9-yl)-1-phenylpropan-1-one (5qa) and 3-(6-Bromo-1-methyl-1-oxido-3-phenylbenzo[f][1,2]thiazepin-9-yl)-1-phenylpropan-1-one (5qa′)



5qa + 5qa'

Yellow solid, melting point: 80-82 °C (121.0 mg, 84%)

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.96 – 7.89 (m, 4H), 7.76 (t, *J* = 7.6 Hz, 4H), 7.68 (dd, *J* = 8.3, 3.9 Hz, 2H), 7.51 (dd, *J* = 12.5, 7.3 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 4H), 7.31 (q, *J* = 7.8 Hz, 4H), 7.24 (d, *J* = 7.3 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 6.29 – 6.19 (m, 2H), 4.26 (dd, *J* = 13.6, 5.8 Hz, 1H), 4.17 – 4.09 (m, 1H), 3.93 (dd, *J* = 13.7, 7.4 Hz, 1H), 3.67 – 3.59 (m, 3H), 3.53 – 3.42 (m, 8H), 3.29 – 3.23 (m, 1H), 3.22 – 3.14 (m, 1H), 3.14 – 3.04 (m, 2H).

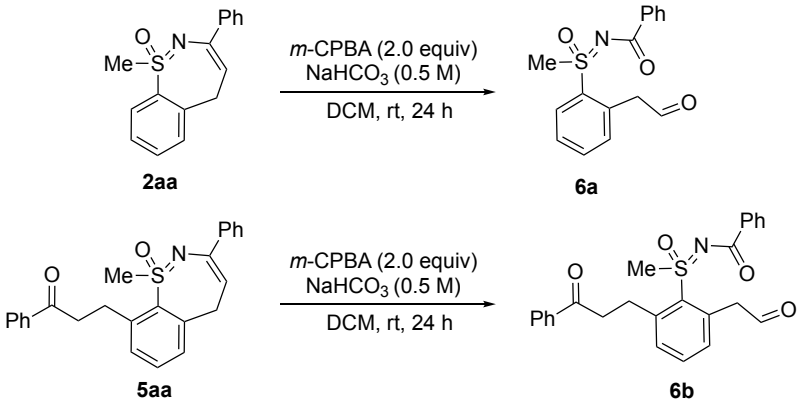
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ (ppm) 198.8, 198.7, 144.9, 144.3, 143.7, 142.7, 142.5, 137.2, 137.1, 136.7, 136.4, 133.1, 132.9, 132.3, 130.0, 128.5, 1284.4, 128.1, 128.0, 127.8, 127.7, 125.8, 125.7, 122.6, 115.3, 114.2, 45.8, 45.7, 41.1, 38.2, 33.9, 32.1, 30.2, 29.9.

MS (EI): *m*/*z* = 479 (M^+, 4), 374 (21), 105 (100), 77 (83).

IR (ATR): ν = 3015, 2219, 1739, 1681, 1441, 1366, 1218, 1131, 970, 746 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{25}H_{22}NO_2SBr+Na]^+$: 502.0452. Found: 502.0448.

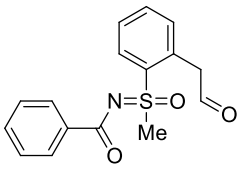
4. Oxidative cleavage of the products



In a round-bottom flask, compound **2aa** or **5aa** (0.2 mmol) was dissolved in DCM (10 mL), and the solution was stirred for 5 min. Then, an aqueous solution of $NaHCO_3$ (0.5 M, 10 mL) was added. To

the biphasic solution *m*-CPBA (69 mg, 0.4 mmol) was added, and the solution was stirred at rt for 24 h. Then, the mixture was poured into a separatory funnel. The organic layer was separated, and the aqueous layer was extracted with DCM. The combined organic layer was washed with an aq. solution of $NaHCO_3$ (0.5 M), brine, and dried over $MgSO_4$. The solvent was removed by the rotary evaporation. The residue was subjected to flash chromatography on silica gel using ethyl acetate/pentane (v/v, 1:2) as eluent to give product **6a** (from **2aa**) or **6b** (from **5aa**).

N-Bezoyl-*S*-methyl-*S*-[(2-oxoethyl)phenyl] sulfoximine (6a)



Light yellow syrup (68.6 mg, 76%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.82 (s, 1H), 8.12 (dd, *J* = 8.2, 1.0 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.49 (q, *J* = 7.2 Hz, 3H), 7.40 (t, *J* = 7.7 Hz, 3H), 7.29 (d, *J* = 7.6 Hz, 1H), 4.69 (d, *J* = 18.0 Hz, 1H), 4.08 (d, *J* = 18.0 Hz, 1H), 3.41 (s, 4H).

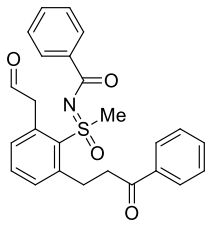
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 198.2, 173.9, 137.6, 135.3, 134.0, 133.7, 133.1, 132.2, 129.3, 128.9, 128.8, 128.0, 48.4, 44.2.

MS (EI): *m*/*z* = 302 ([M+H]$^+$, 8), 224 (6), 196 (4), 105 (100), 77 (36).

IR (ATR): ν = 3021, 2930, 1977, 1730, 1616, 1446, 1281, 1126, 967, 831, 713 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{16}H_{15}NO_3S+Na]^+$: 324.0670. Found: 324.0668.

N-Bezoyl-*S*-methyl-*S*-{(2-oxoethyl)-6-[(3-oxo-3-phenylpropyl)]phenyl} sulfoximine (6b)



White solid, melting point: 177-179 °C (96.1 mg, 74%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.88 (s, 1H), 7.99 (d, *J* = 6.8 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.36 (d, *J* = 6.7 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 2H), 7.18 – 7.08 (m, 4H), 5.12 (d, *J* = 18.3 Hz, 1H), 3.83 (d, *J* = 18.3 Hz, 1H), 3.65 – 3.57 (m, 1H), 3.45 (s, 3H), 3.39 – 3.31 (m, 1H), 3.09 – 2.98 (m, 2H).

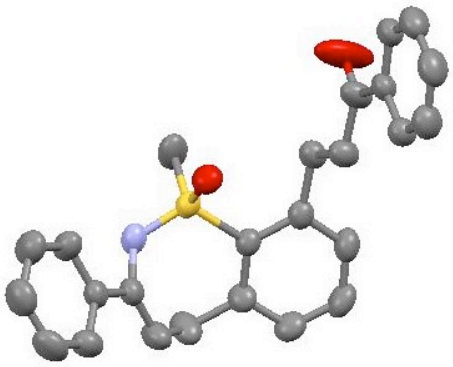
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 199.0, 197.8, 174.0, 141.4, 136.3, 135.9, 135.8, 134.7, 133.4, 133.1, 132.8, 132.4, 132.0, 129.0, 128.2, 127.9, 127.6, 50.5, 44.4, 40.7, 28.6.

MS (EI): *m*/*z* = 105 (100), 77 (46).

IR (ATR): ν = 3059, 2838, 2323, 1722, 1682, 1607, 1450, 1278, 1204, 1126, 974, 713 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{25}H_{23}NO_4S+Na]^+$: 456.1245. Found: 456.1240.

5. X-Ray crystal structure analysis of compound 5aa



Bond precision:	C-C = 0.0025 A		Wavelength=1.54178
Cell:	a=14.4968(8)	b=10.5034(6)	c=15.0275(8)
	alpha=90	beta=111.709(2)	gamma=90
Temperature:	296 K		

	Calculated	Reported
Volume	2125.9(2)	2125.9(2)
Space group	P 21/c	P_1_21/c_1
Hall group	-P 2ybc	-P_2ybc
Moiety formula	C25 H23 N O2 S	C25 H23 N1 O2 S1
Sum formula	C25 H23 N O2 S	C25 H23 N1 O2 S1
Mr	401.50	401.55
Dx,g cm-3	1.255	1.255
Z	4	4
Mu (mm-1)	1.508	1.508
F000	848.0	848.0
F000'	851.56	
h,k,lmax	17,12,17	17,12,17
Nref	3814	3751
Tmin,Tmax	0.467,0.572	0.559,0.753
Tmin'	0.155	

Correction method= # Reported T Limits: Tmin=0.559 Tmax=0.753 AbsCorr = MULTI-SCAN

Data completeness= 0.983 Theta(max)= 67.300

R(reflections)= 0.0450(3616) wR2(reflections)= wR= 0.0460(3616)

S = 1.011 Npar= 354

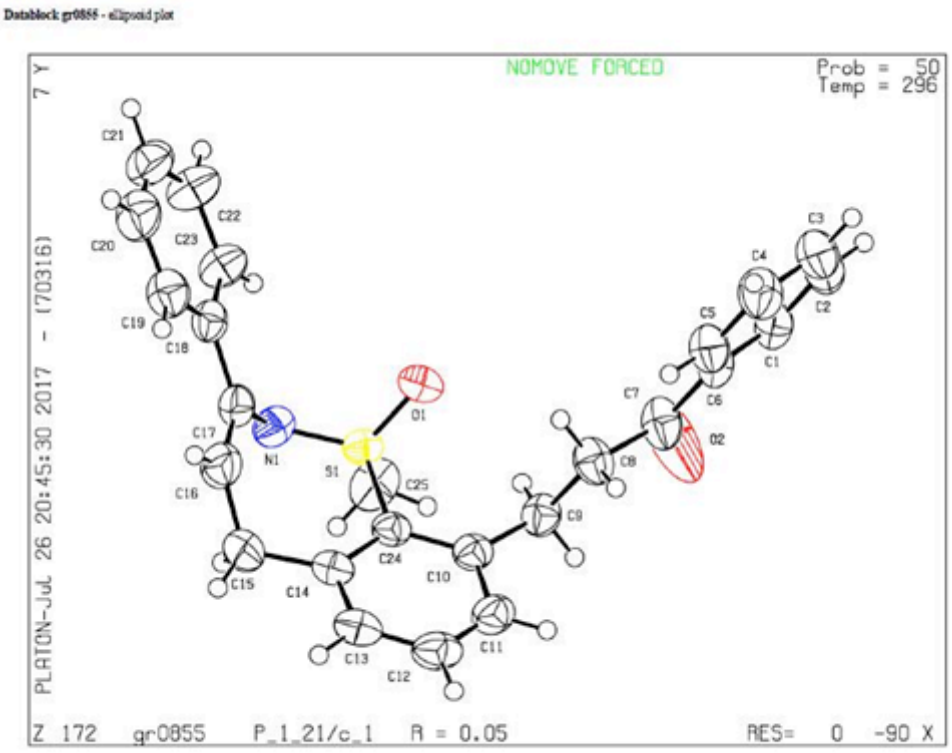


Figure S1. Solid state structure of **5aa** as determined by X-ray crystal structure analysis.

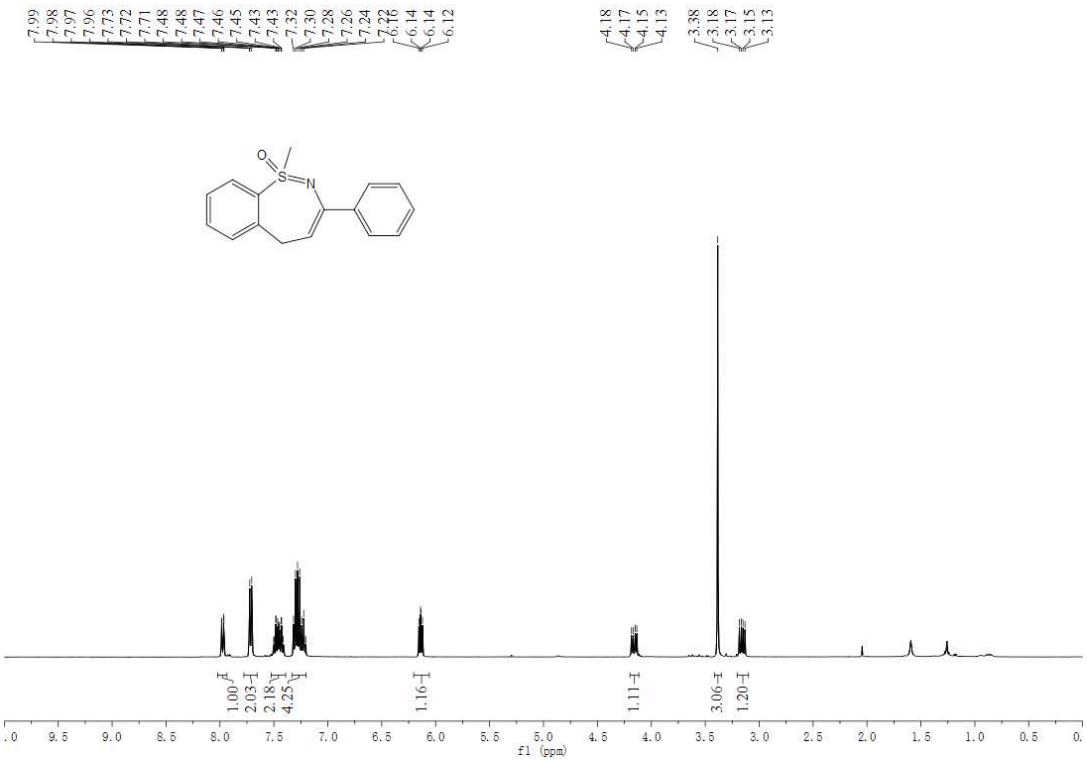
6. Reference

(1) (a) Johnson, C. R.; Haake, M.; Schroeck, C. W. *J. Am. Chem. Soc*. **1970**, *92*, 6594-6598; (b) Mancheño, O. García.; Bistri, O.; Bolm, C. *Org. Lett*. **2007**, *9*, 3809-3811; (c) Xie, Y.; Zhou, B.; Zhou, S.; Zhou, S.; Wei, W.; Liu, J.; Zhan, Y.; Cheng, D.; Chen, M.; Li, Y.; Wang, B.; Xue, X.-s.; Li, Z. *ChemistrySelect* **2017**, *2*, 1620-1624.

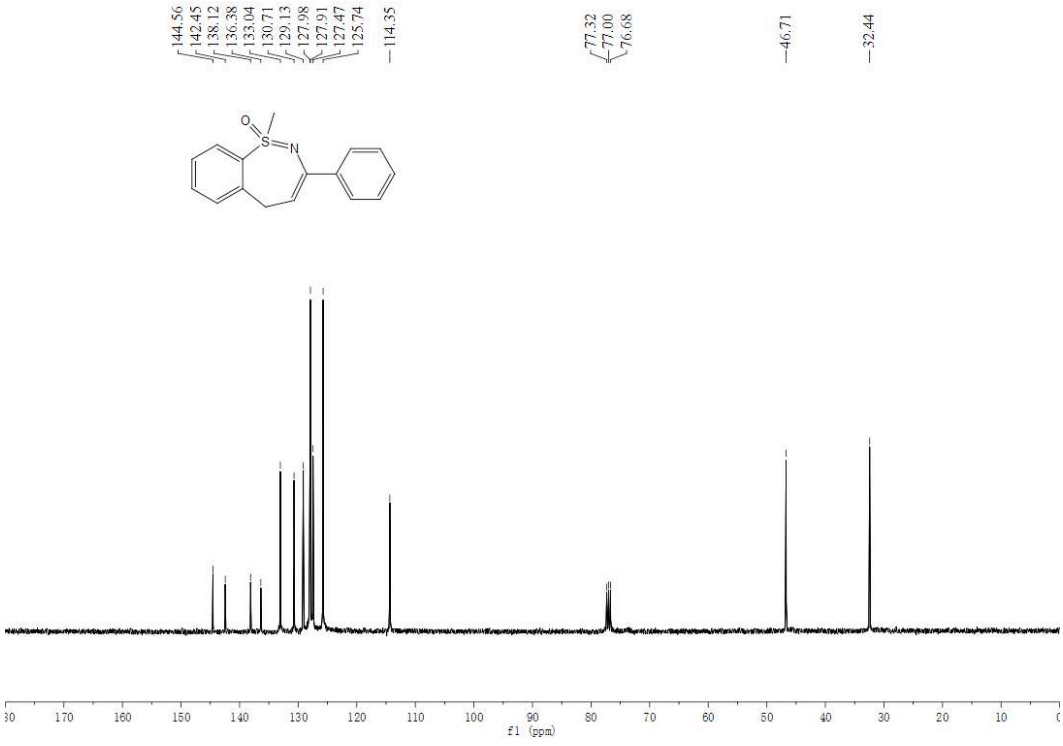
(2) (a) Bugarin, A.; Jones, K. D.; Connell, B. T. *Chem. Commun*. **2010**, *46*, 1715-1717. (b) Chanthamath, S.; Takaki, S.; Shibatomi, K.; Iwasa, S. *Angew. Chem., Int. Ed*. **2013**, *52*, 5818−5821. (c) Li, Y.-M.; Lou, S.-J.; Zhou, Q.-H.; Zhu, L.-W.; Zhu, L.-F.; Li, L. *Eur. J. Org. Chem*. **2015**, 3044-3047.

7. ^{1}H NMR, ^{13}C{^{1}H} NMR and ^{19}F NMR spectra of products

^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 2aa

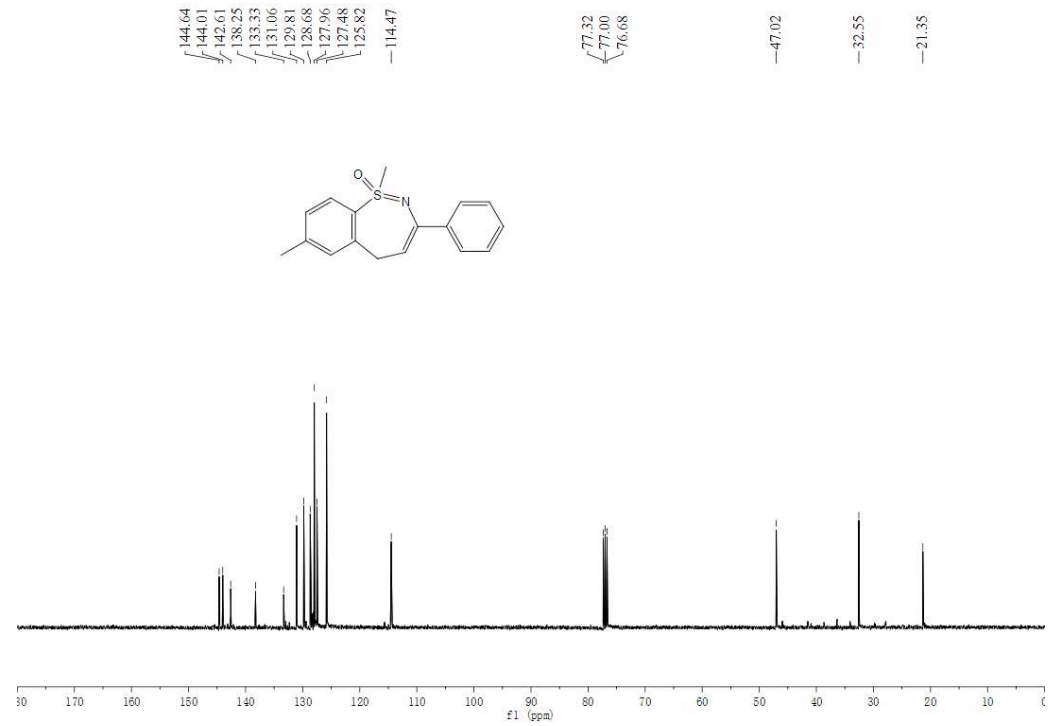


^{13}C{^{1}H} NMR spectrum (150 MHz, $CDCl_3$) of 2aa

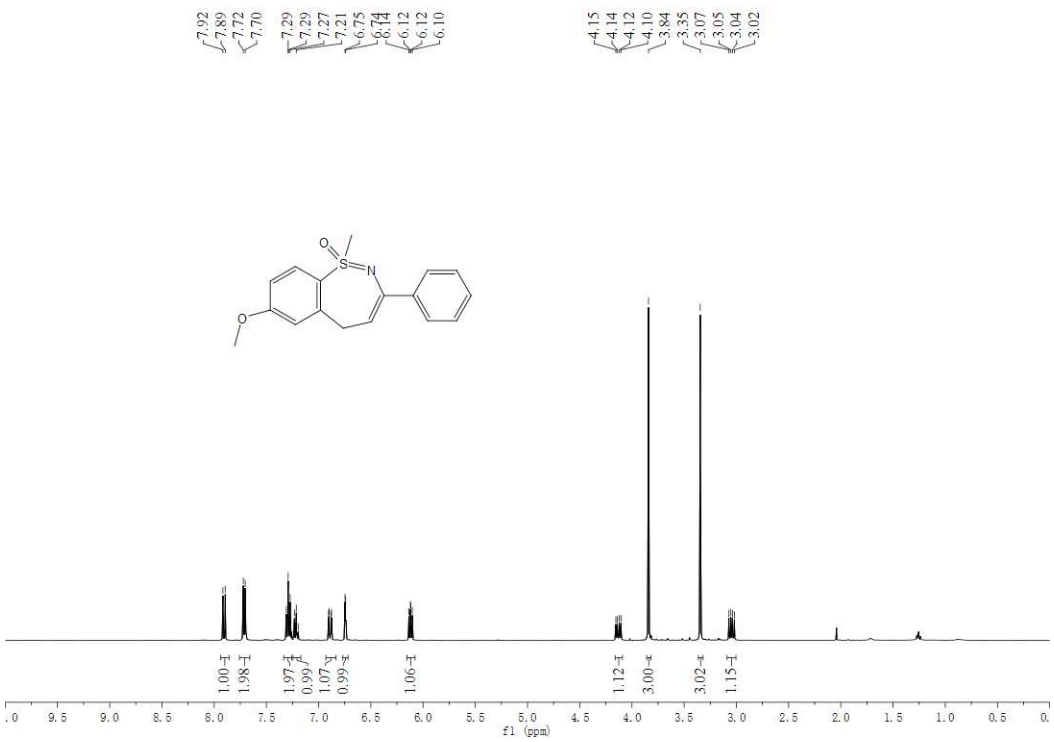


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2ba

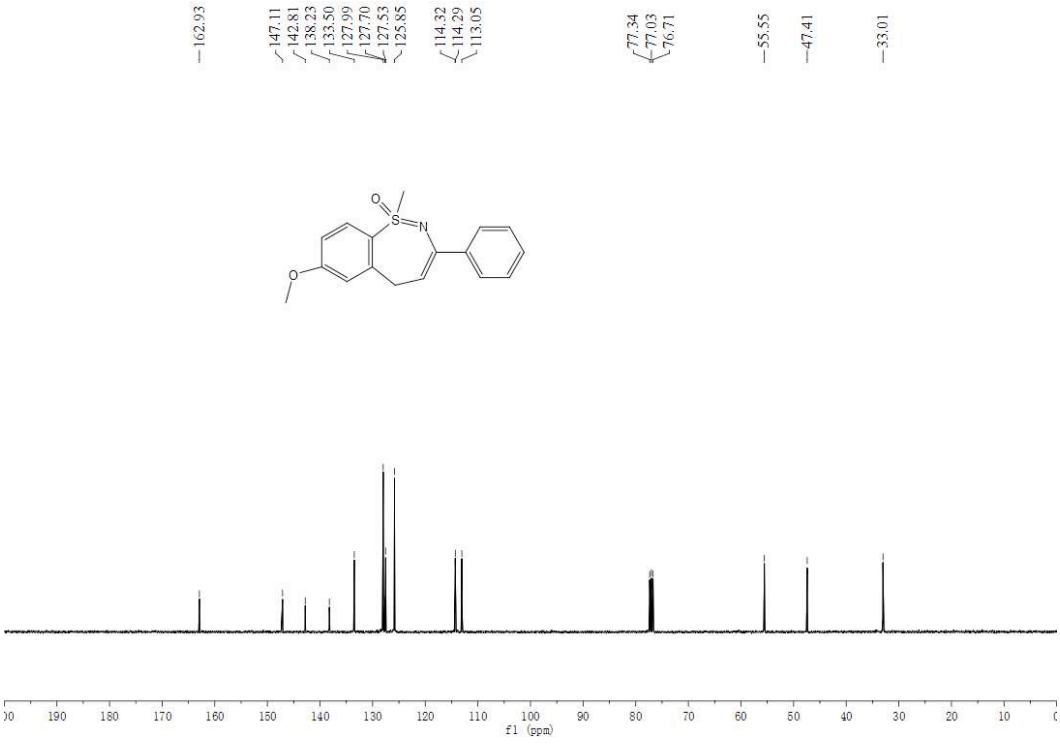
^{13}C{^{1}H}NMR spectrum (100 MHz, $CDCl_3$) of 2ba



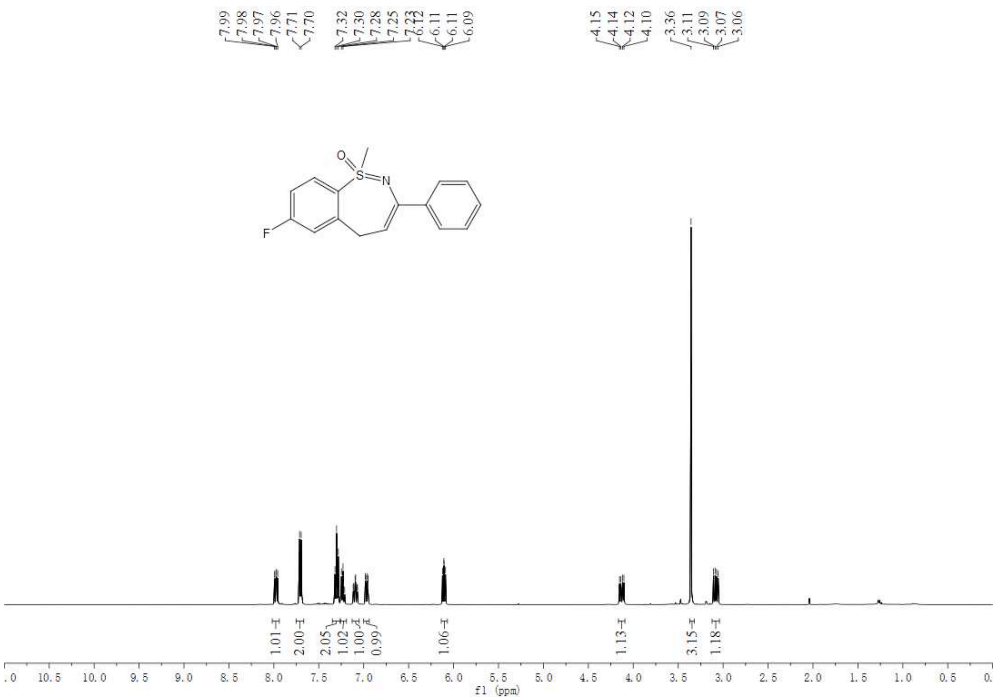
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2ca



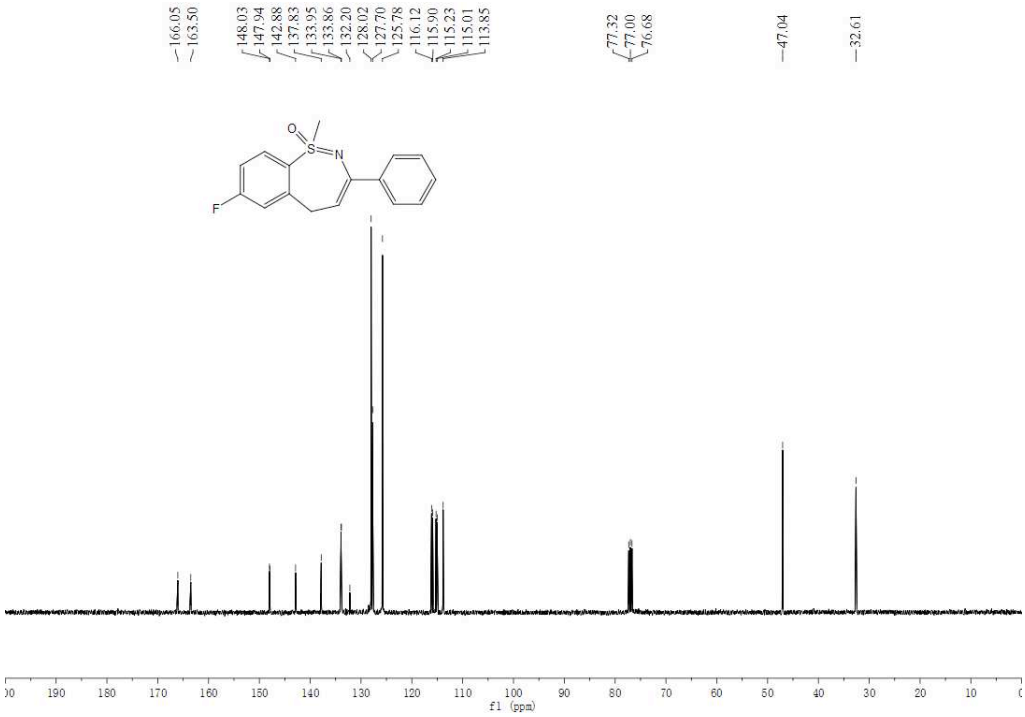
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2ca



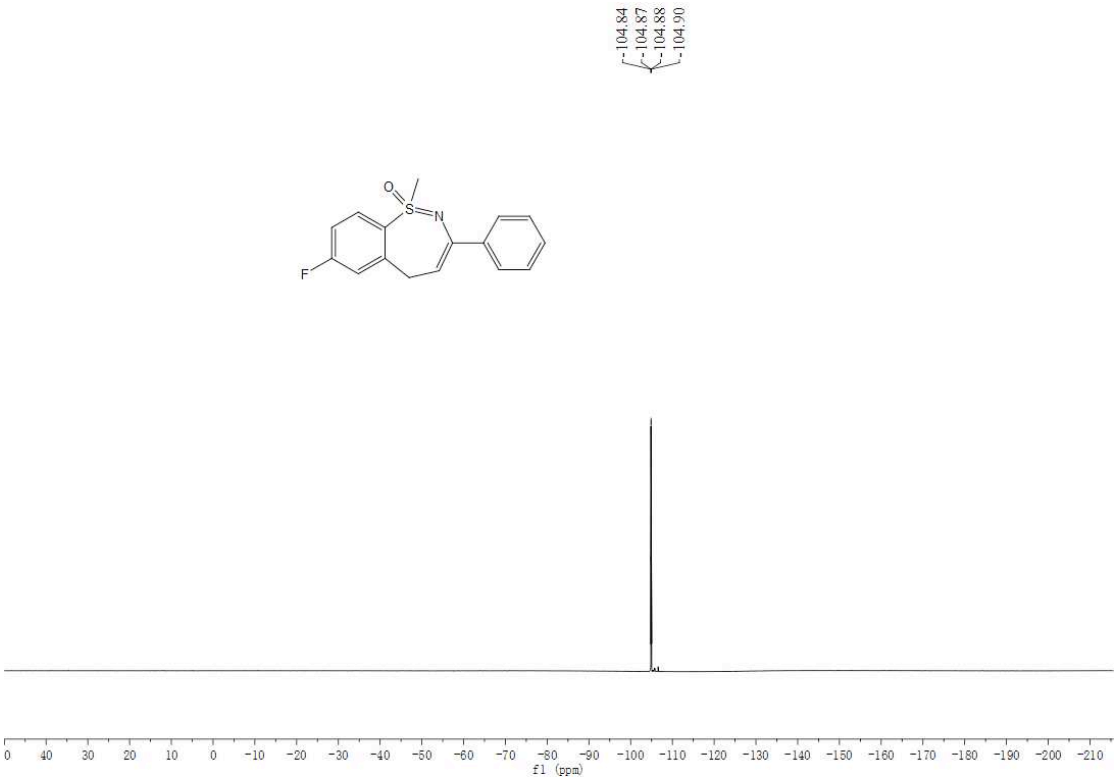
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2da



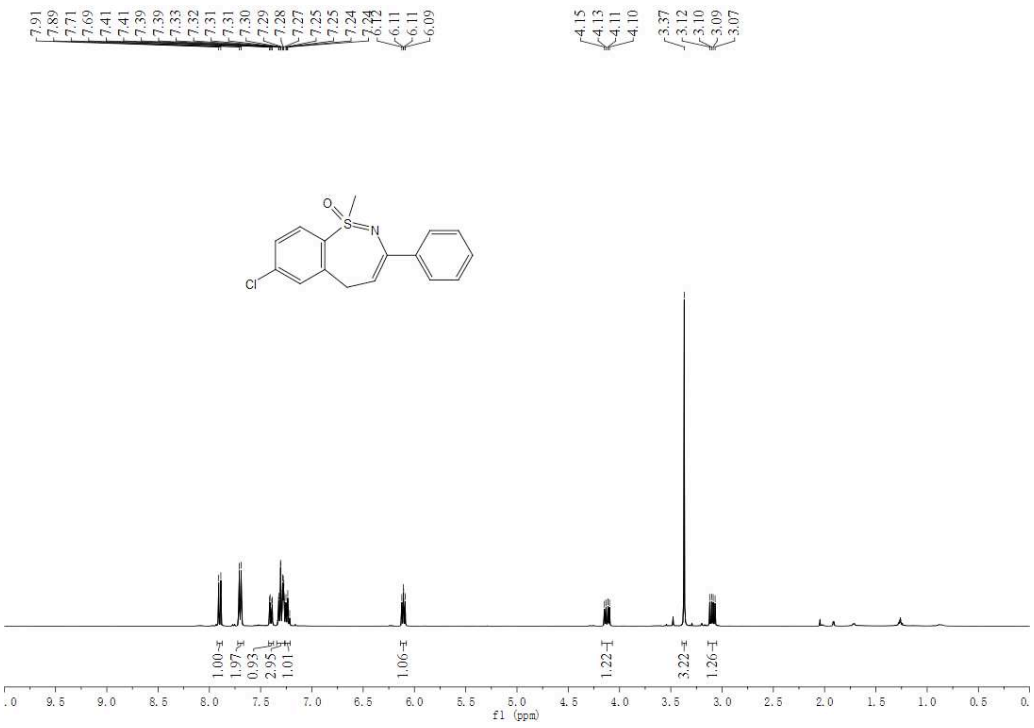
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2da



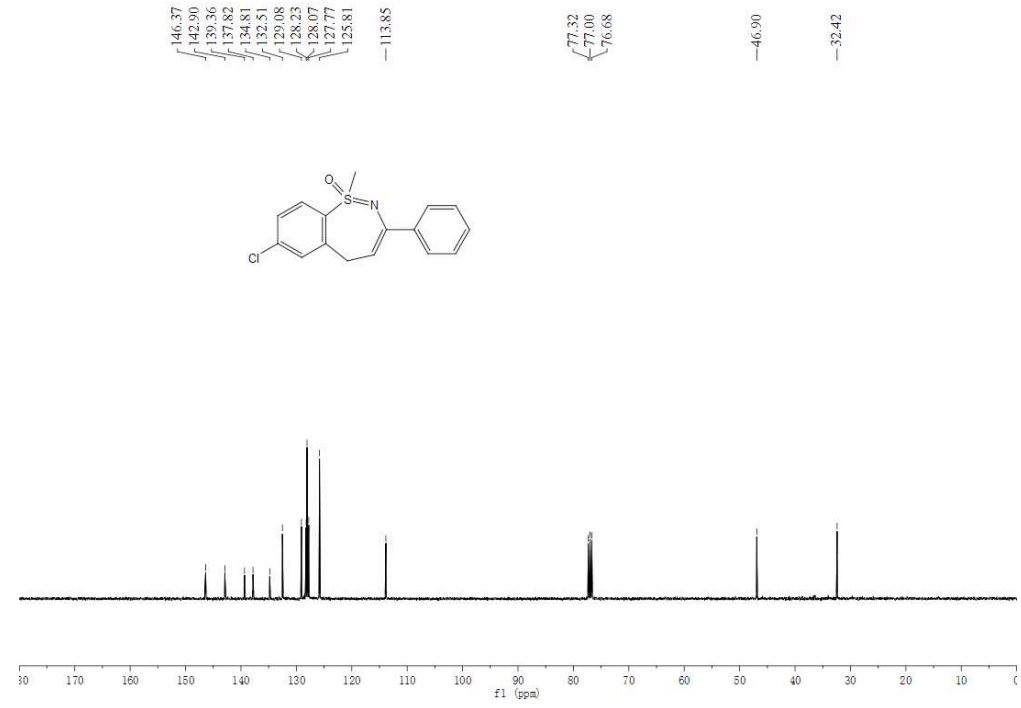
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of 2da



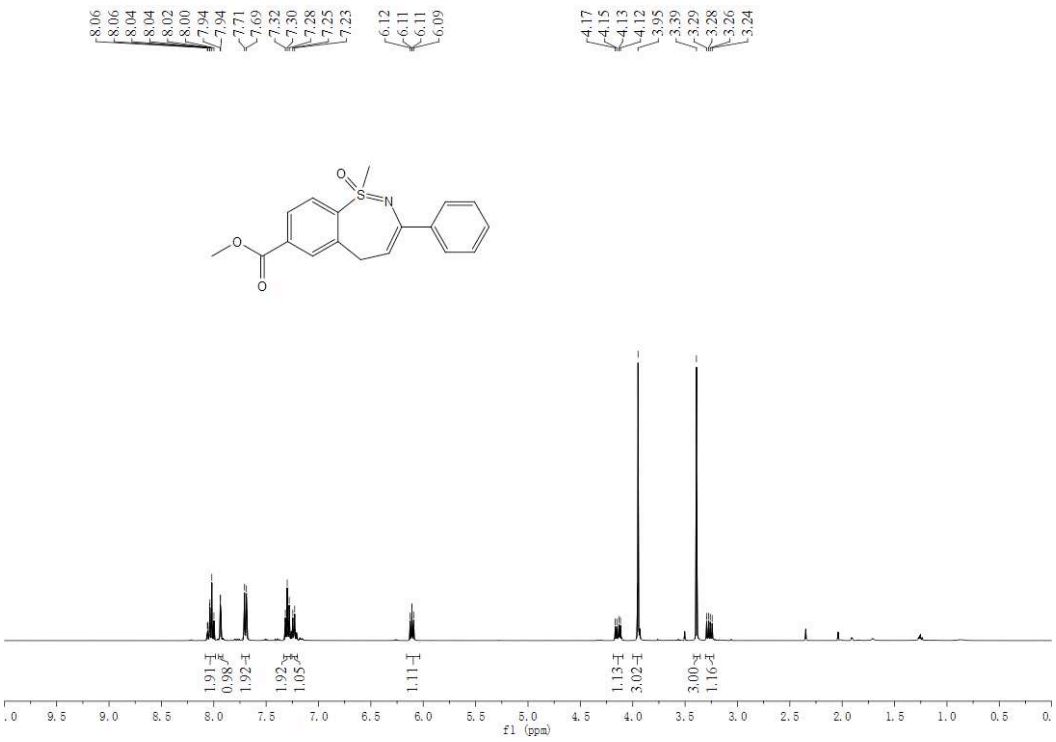
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2ea



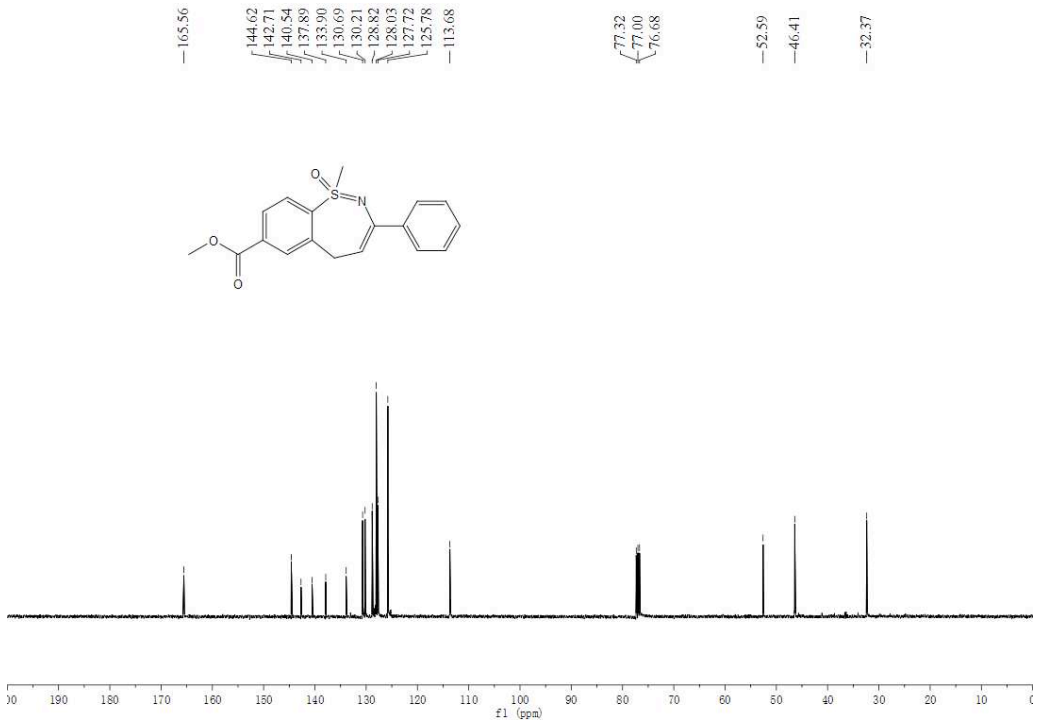
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2ea



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2fa

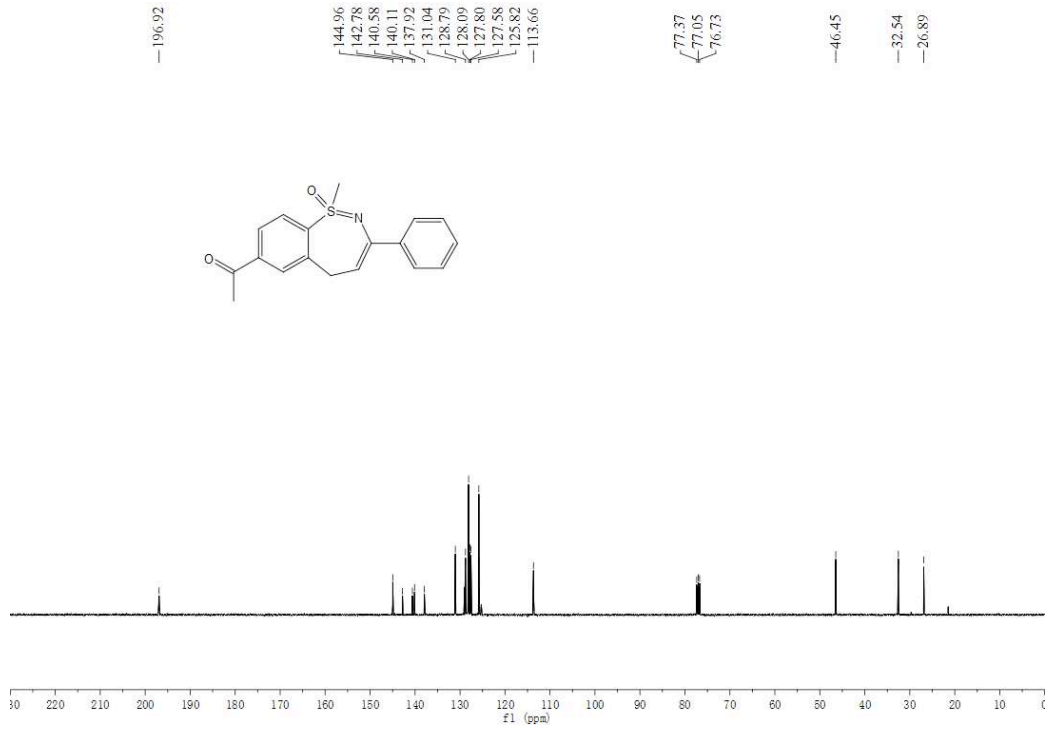


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2fa

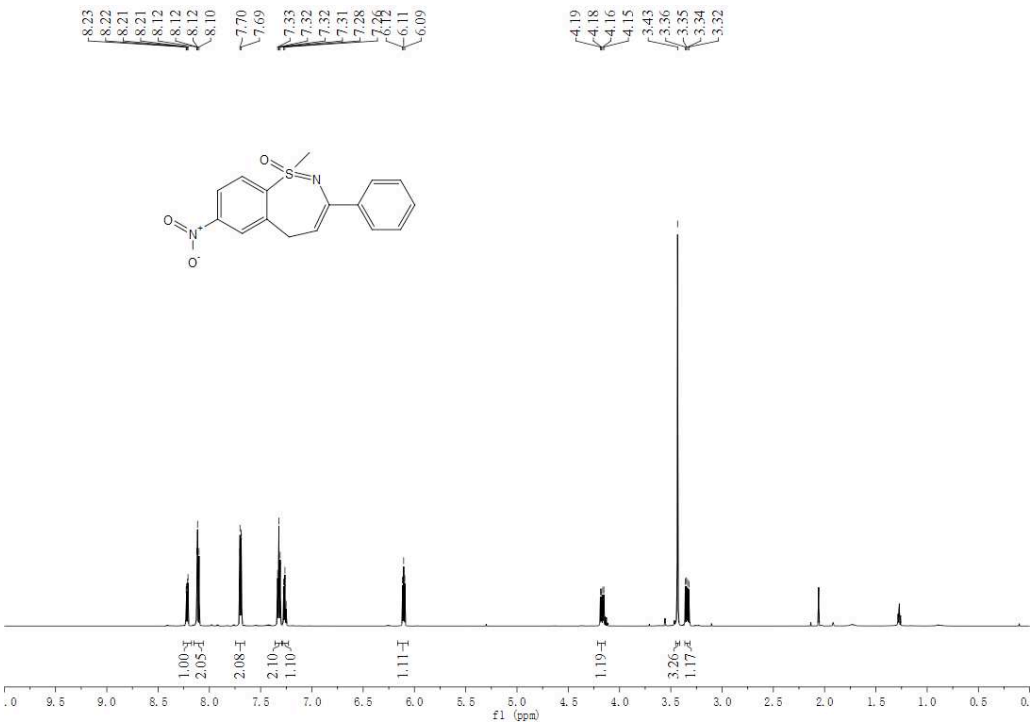


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2ga

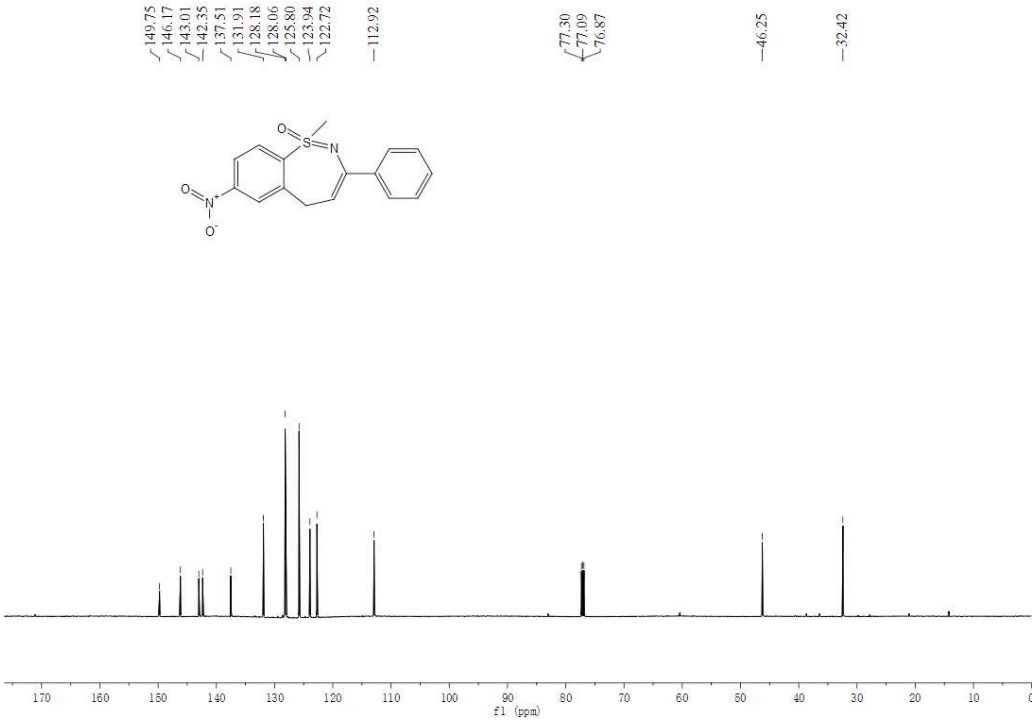
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2ga



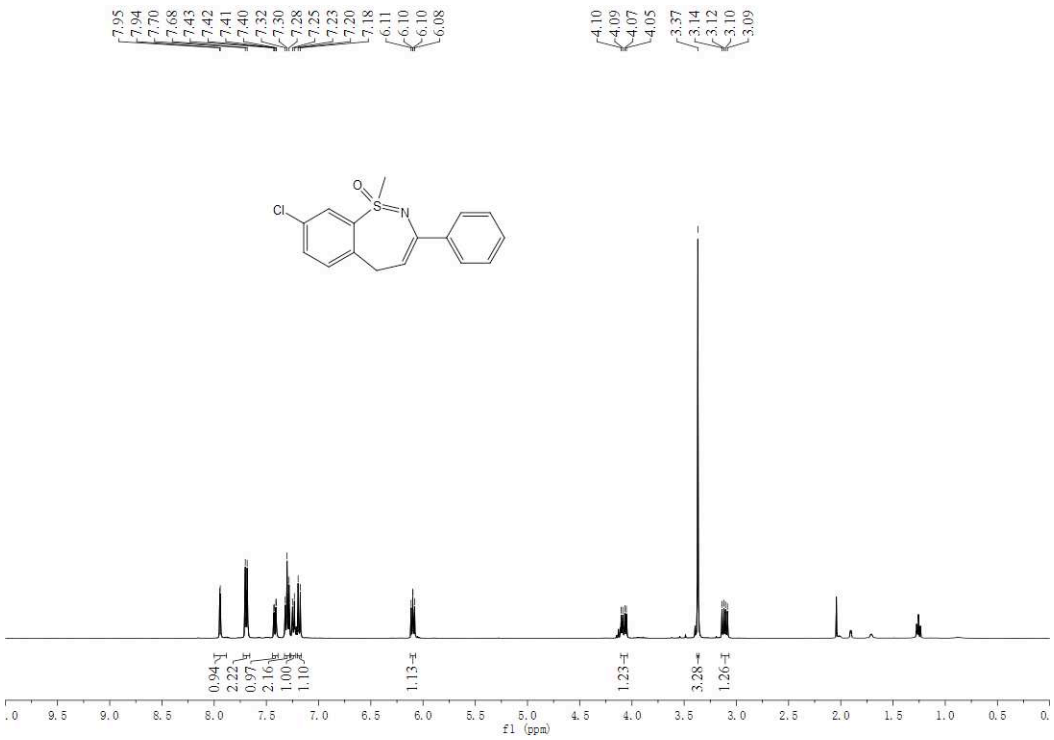
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 2ha



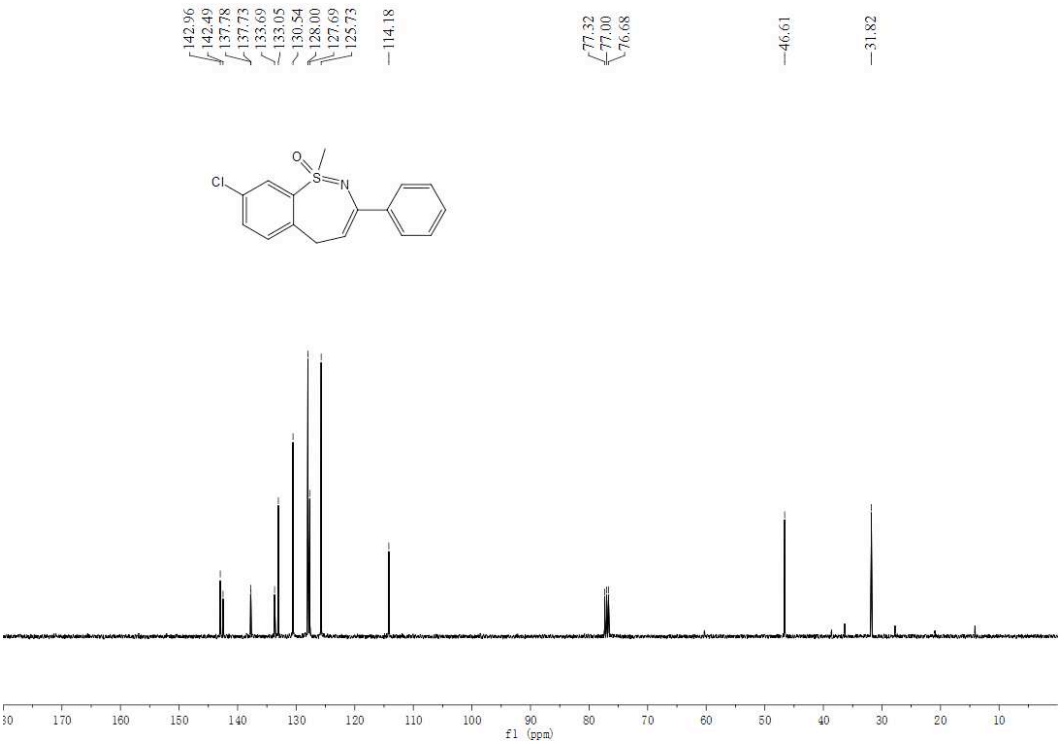
^{13}C{^{1}H} NMR spectrum (150 MHz, $CDCl_3$) of 2ha



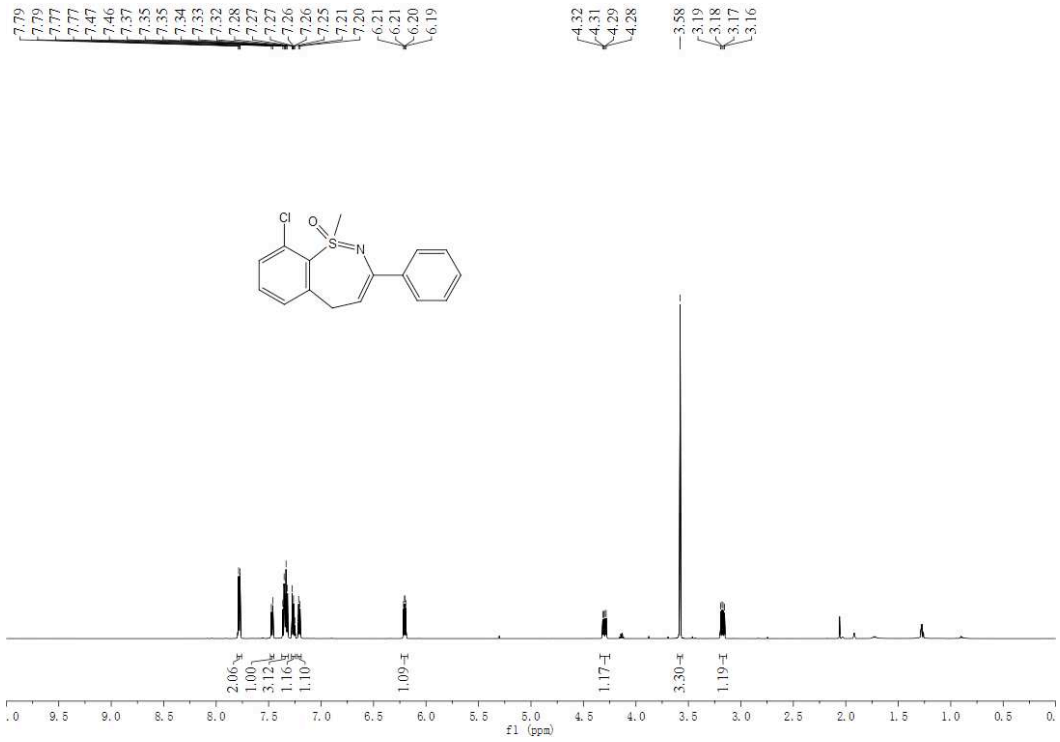
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2ia



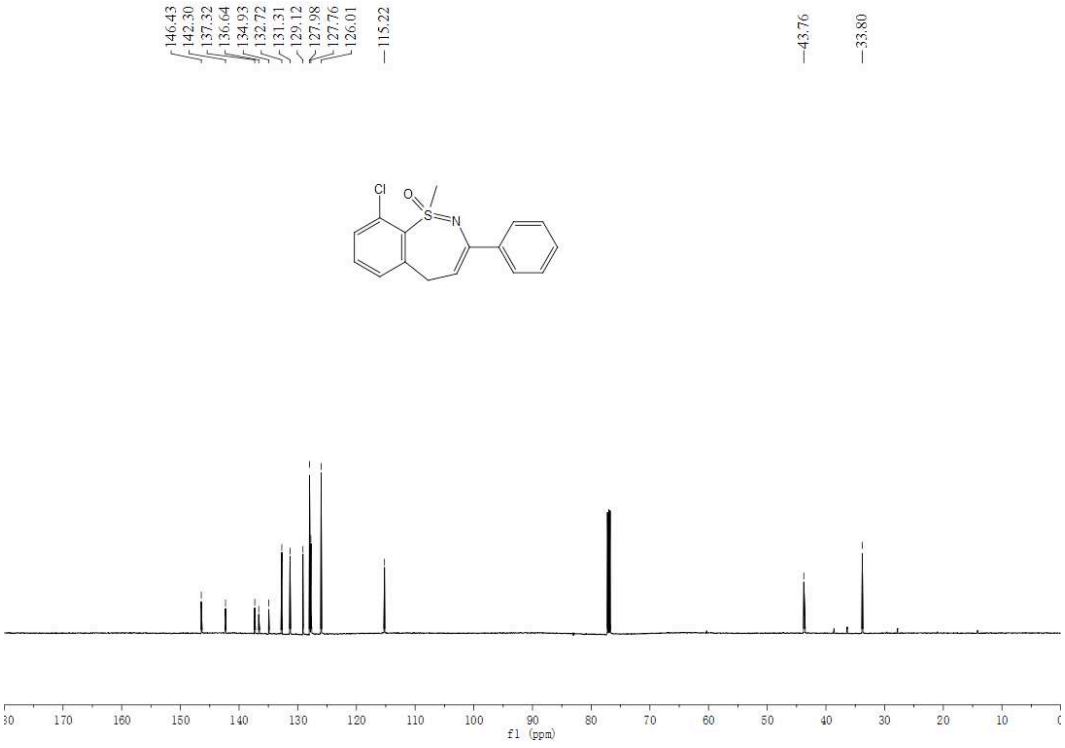
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2ia



^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 2ja

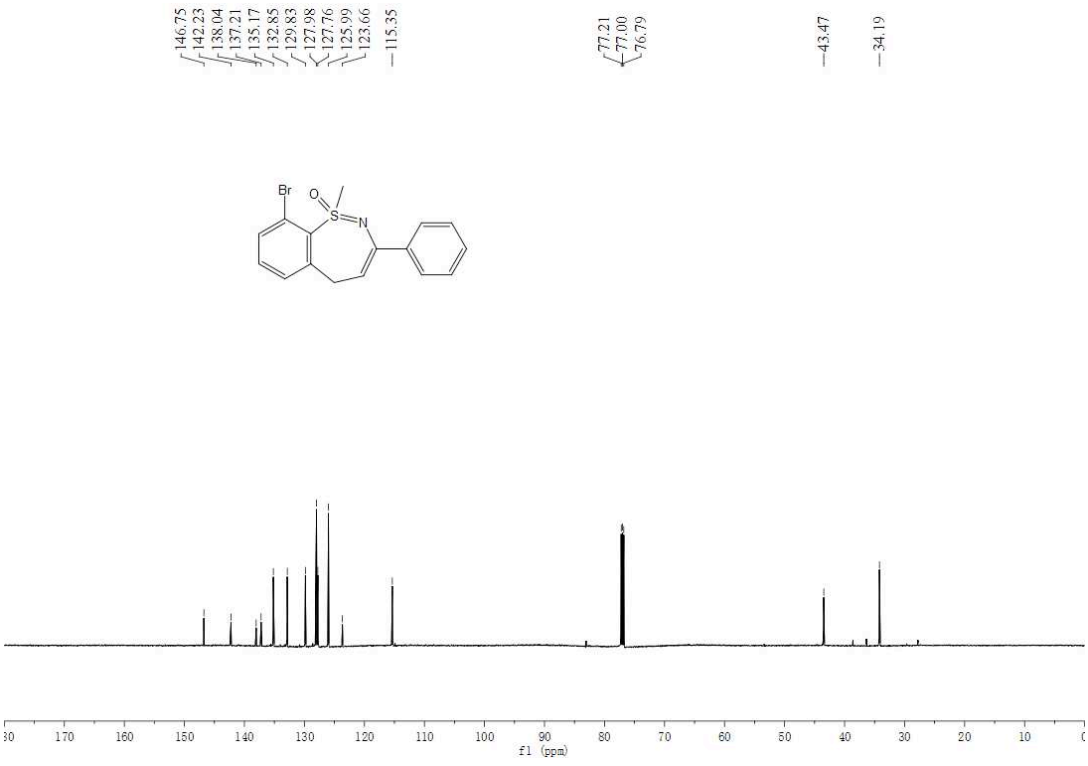


^{13}C{^{1}H} NMR spectrum (150 MHz, $CDCl_3$) of 2ja

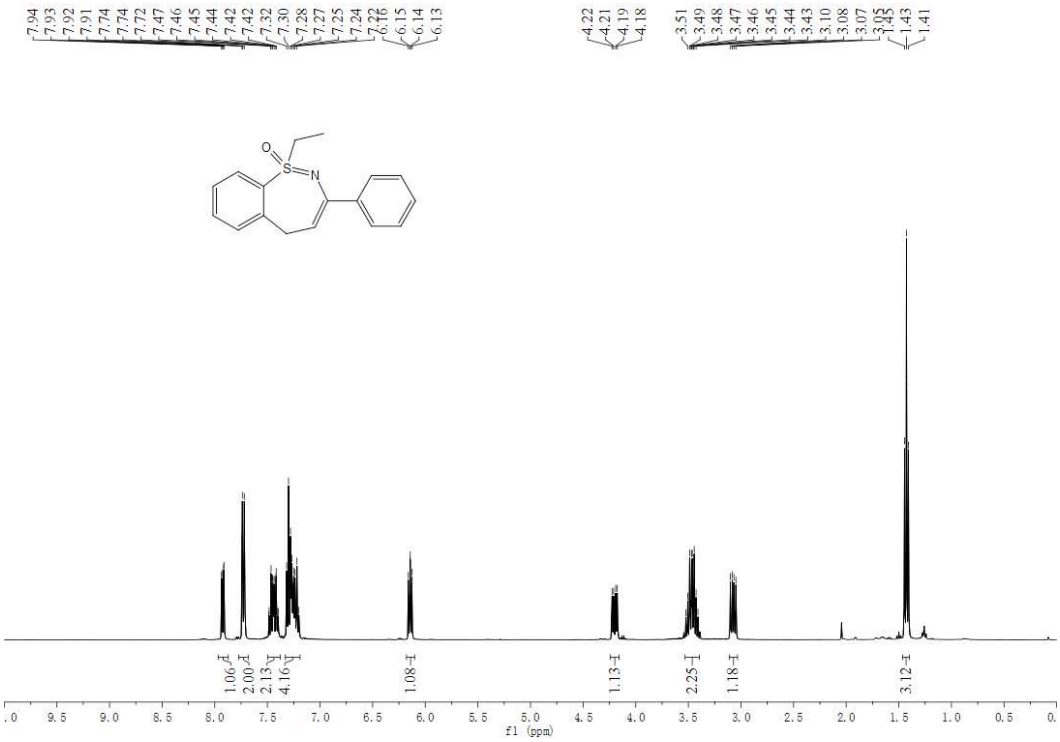


^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 2ka

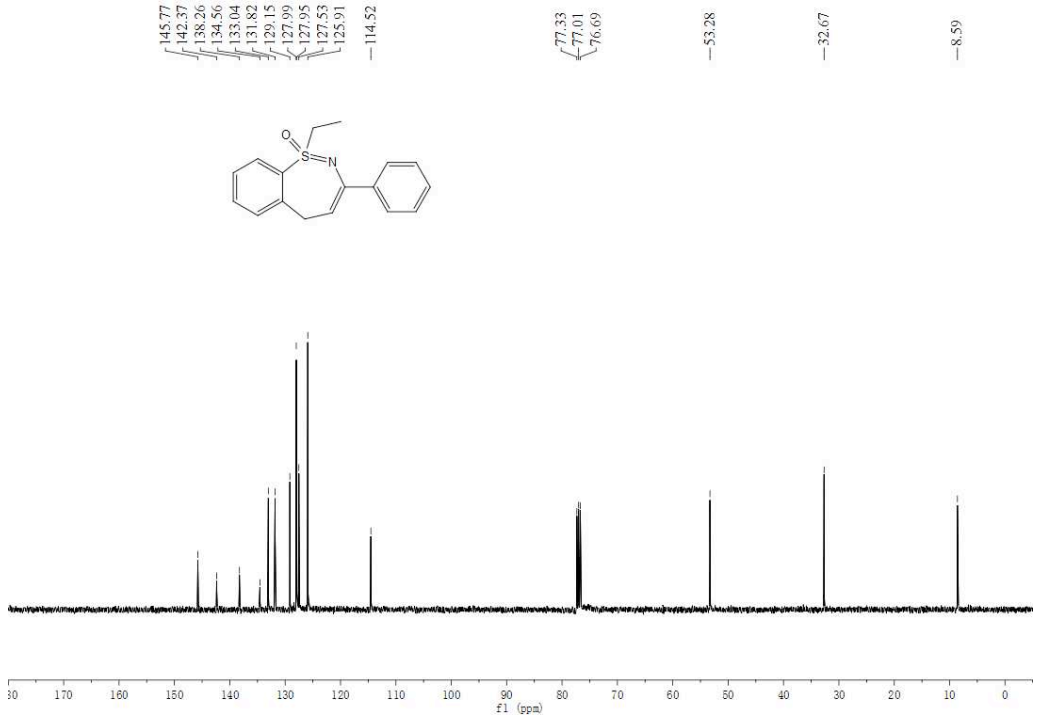
^{13}C{^{1}H} NMR spectrum (150 MHz, $CDCl_3$) of 2ka



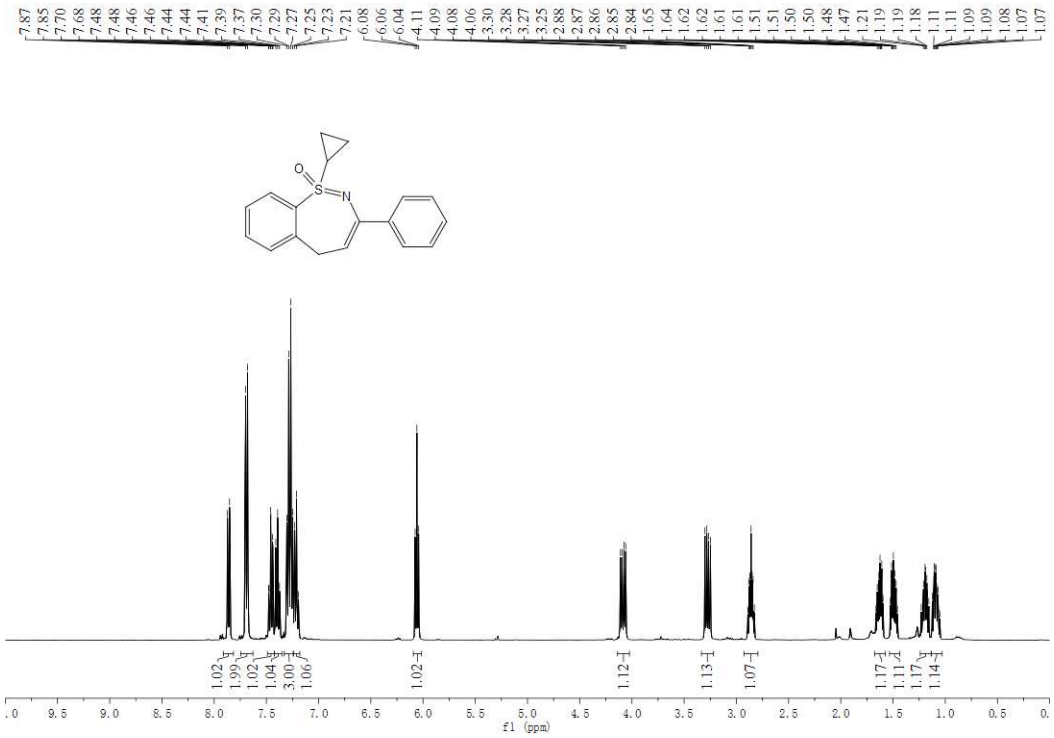
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2la



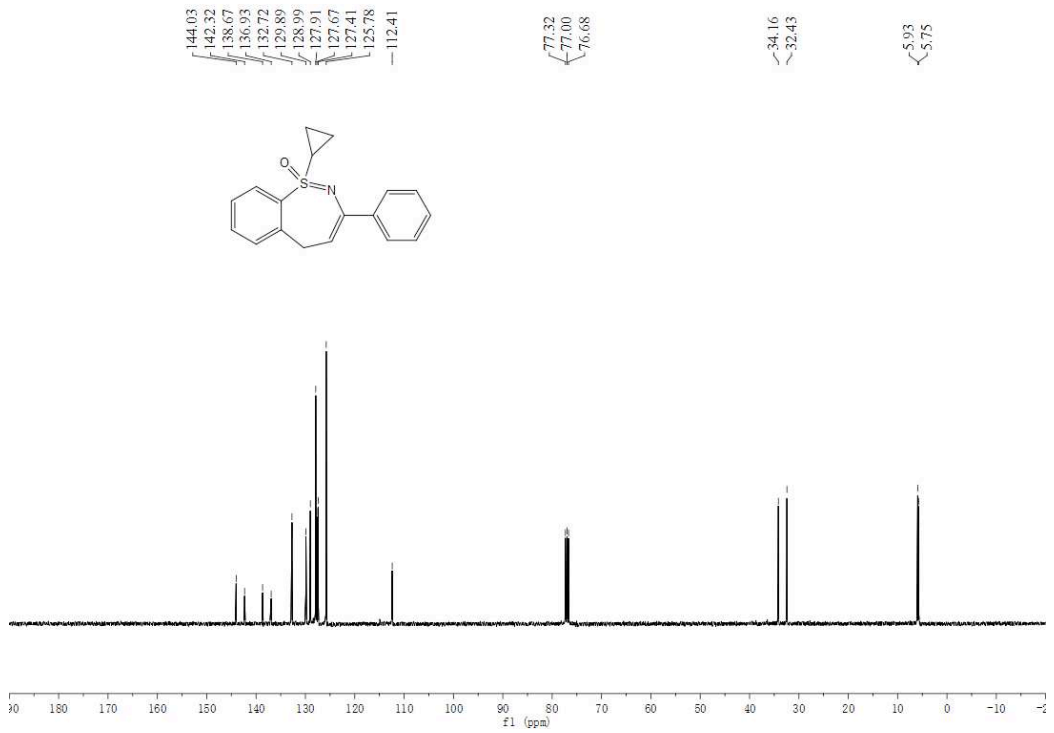
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2la



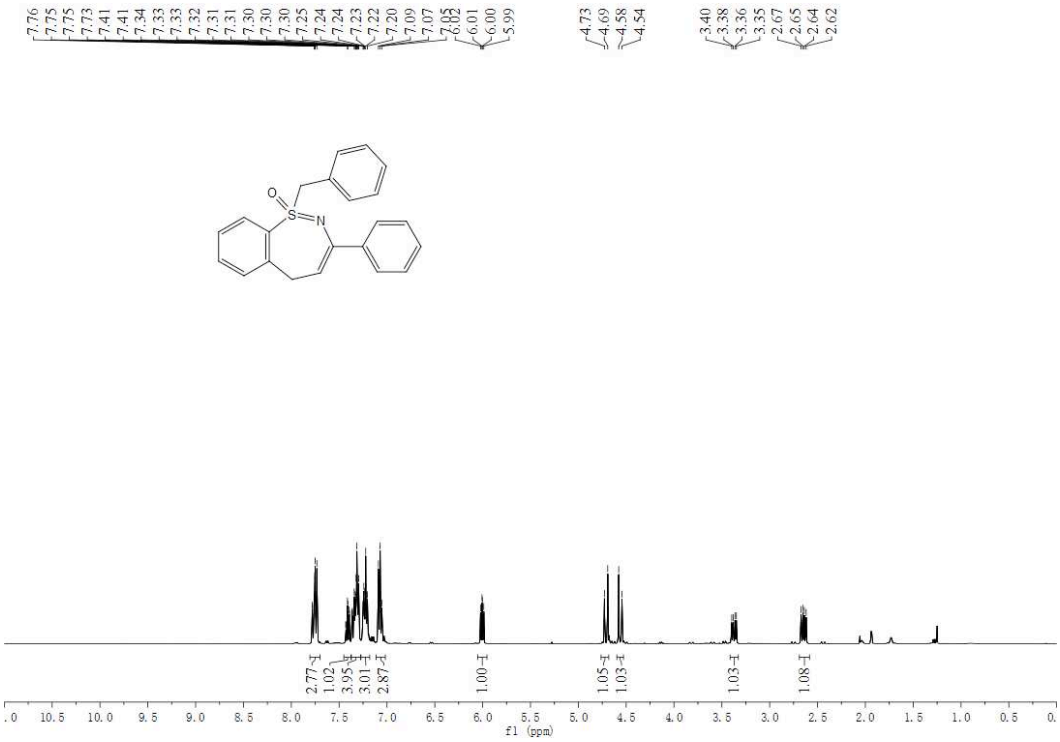
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2ma



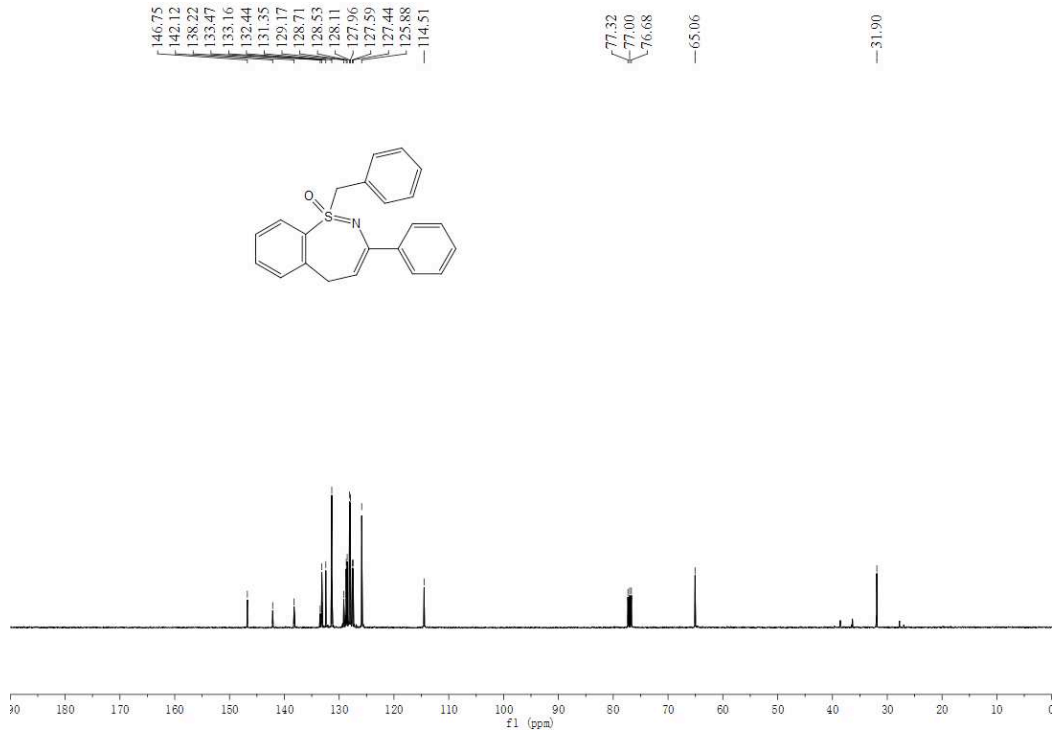
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2ma



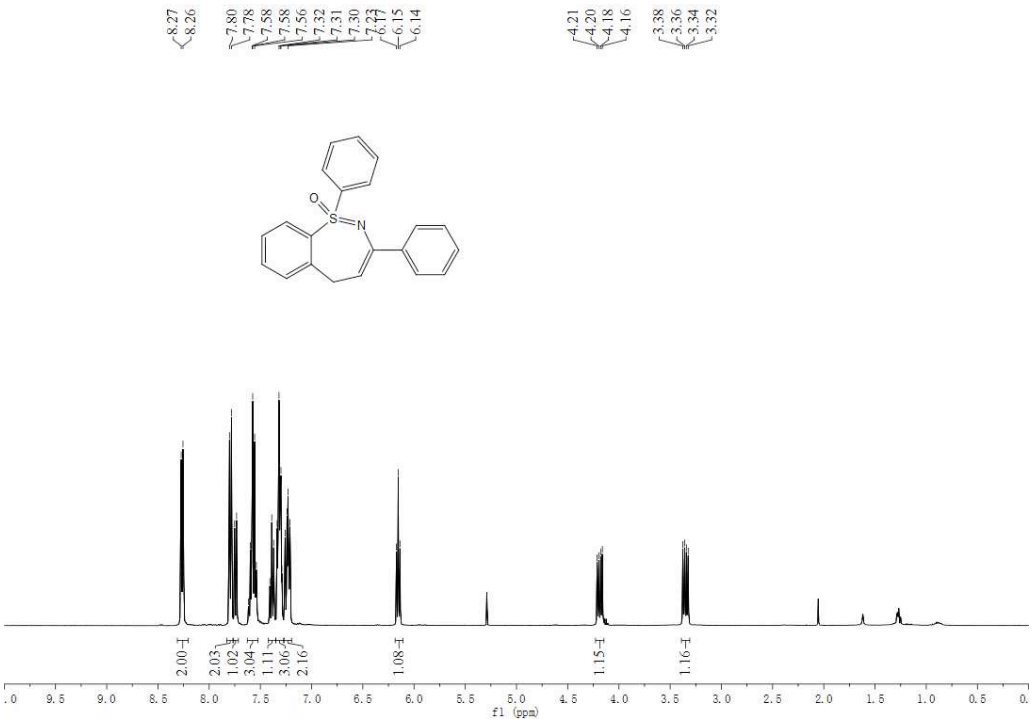
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2na



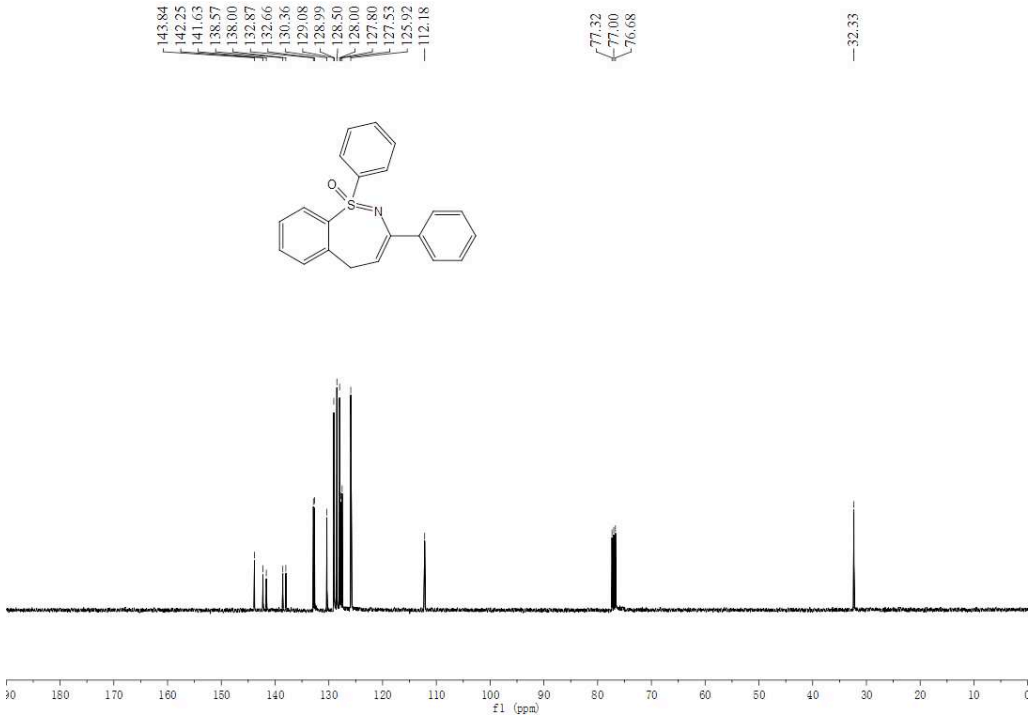
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2na



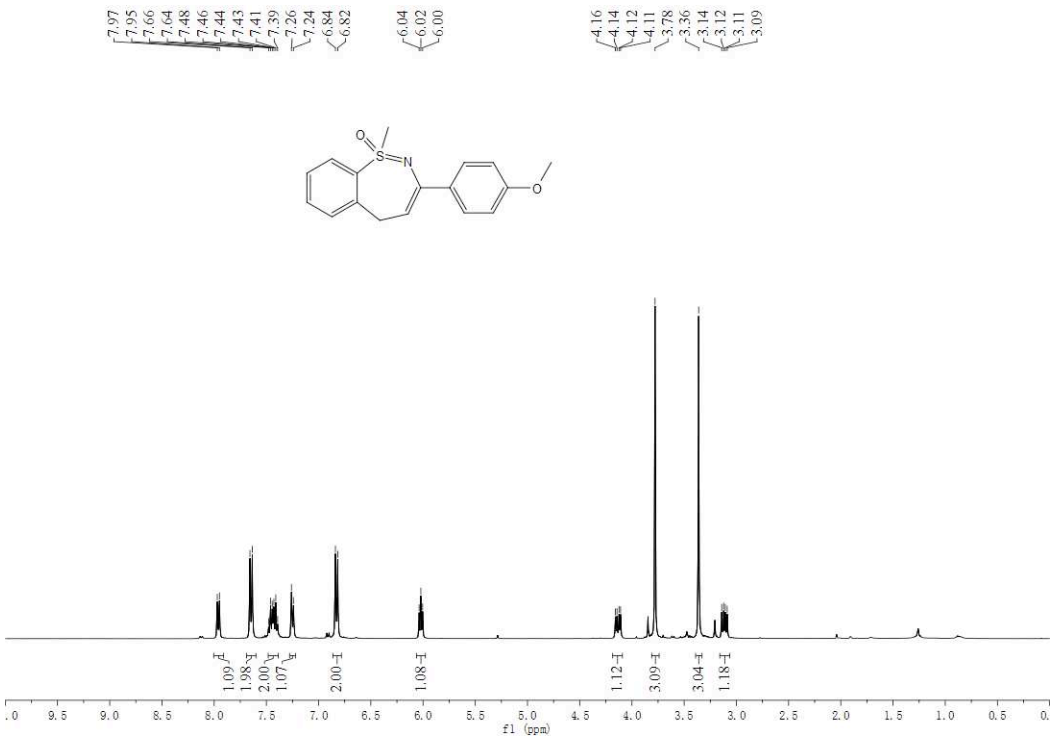
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2oa



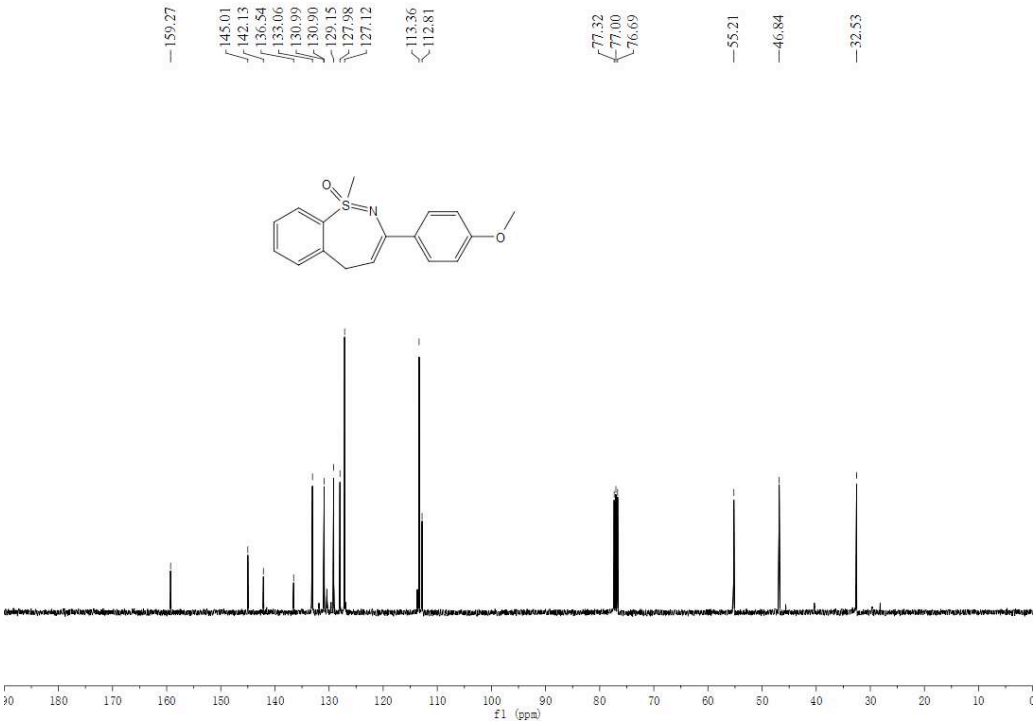
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2oa



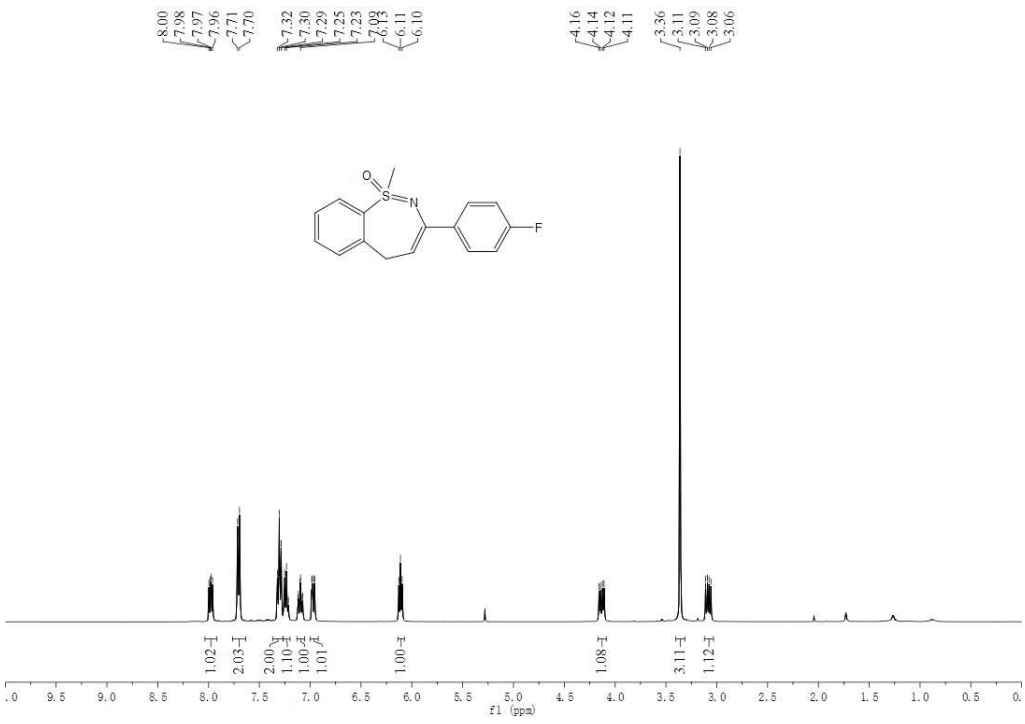
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2ab



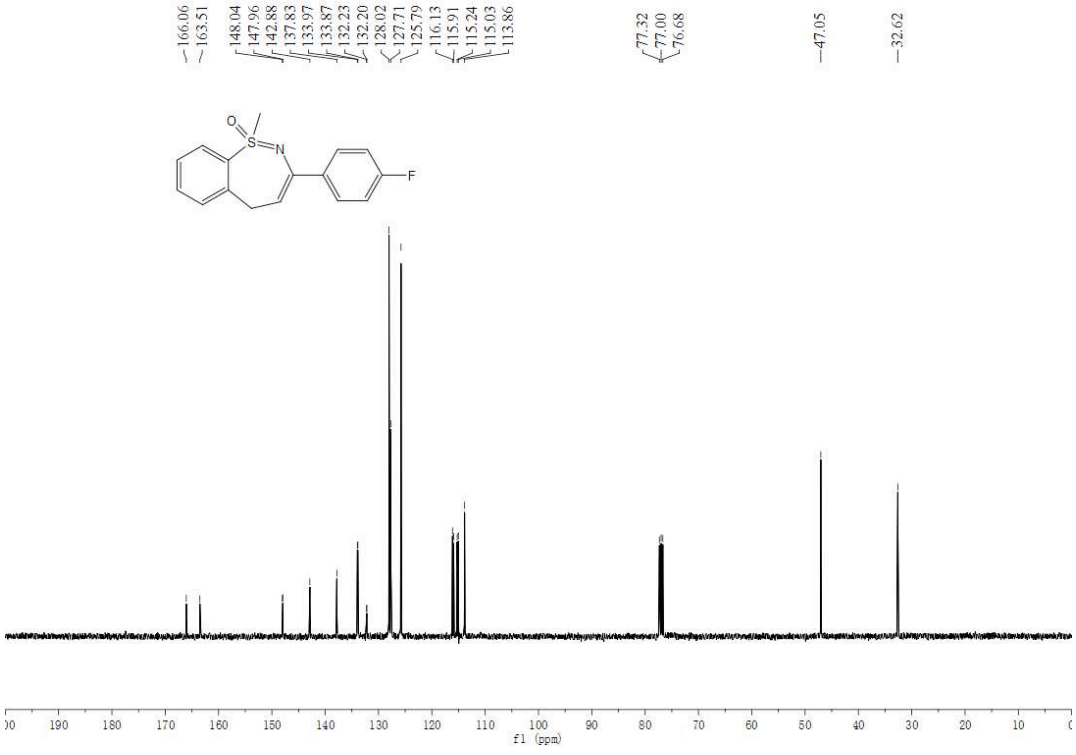
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2ab



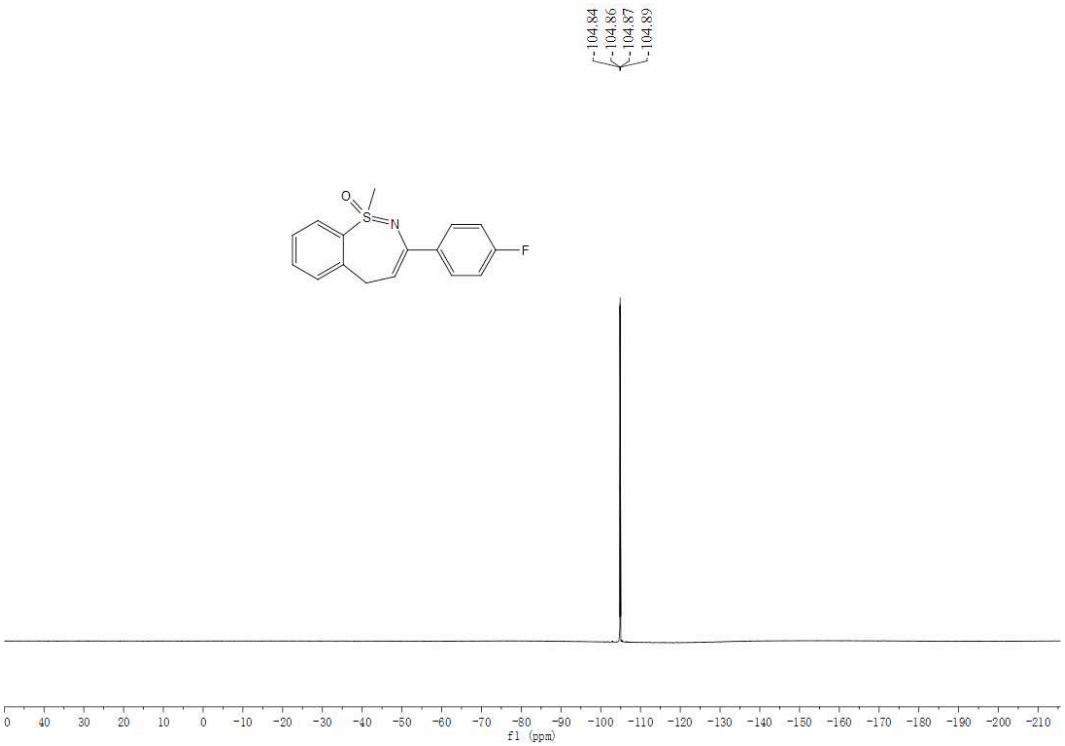
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2ac



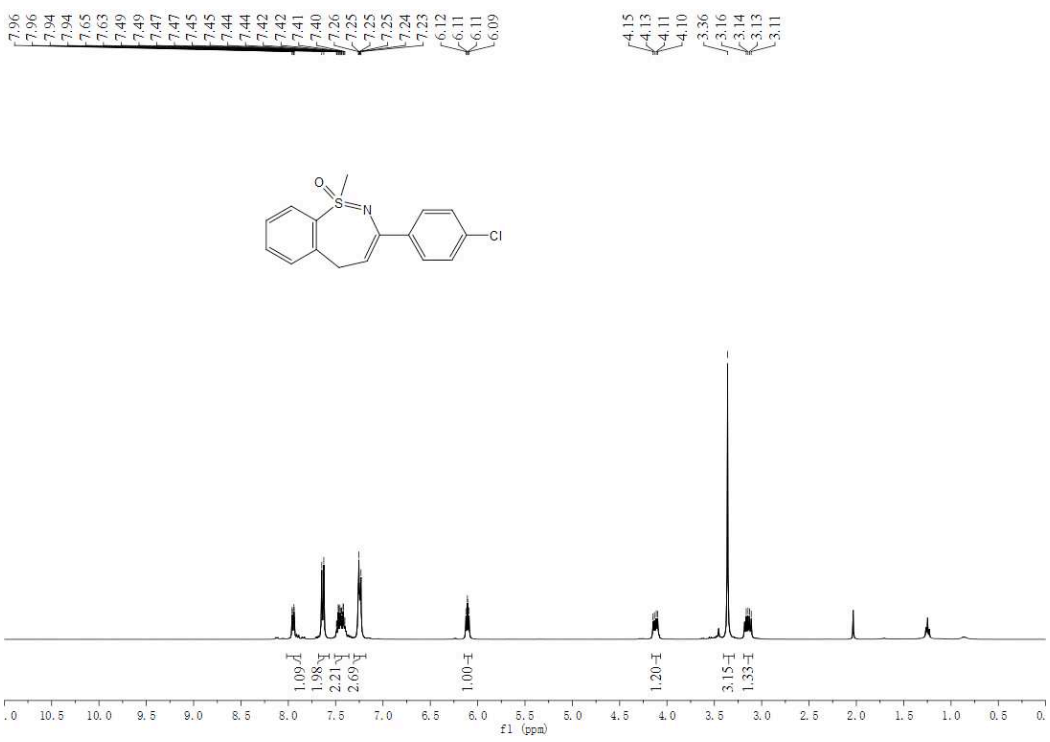
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2ac



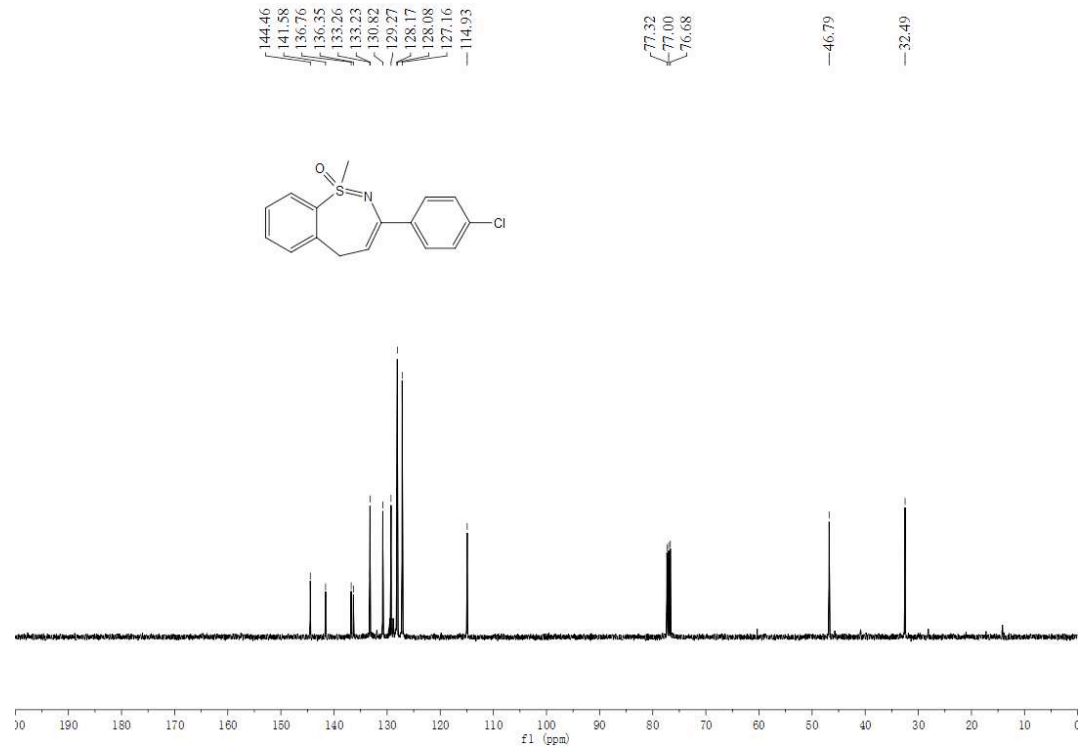
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of 2ac



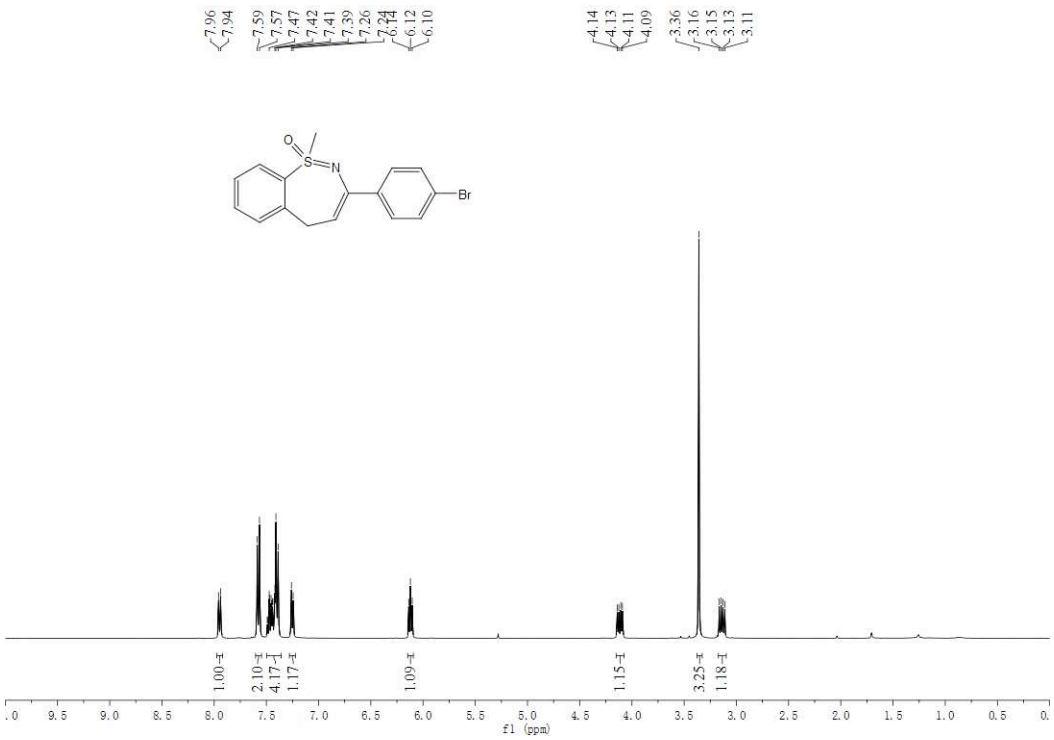
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2ad



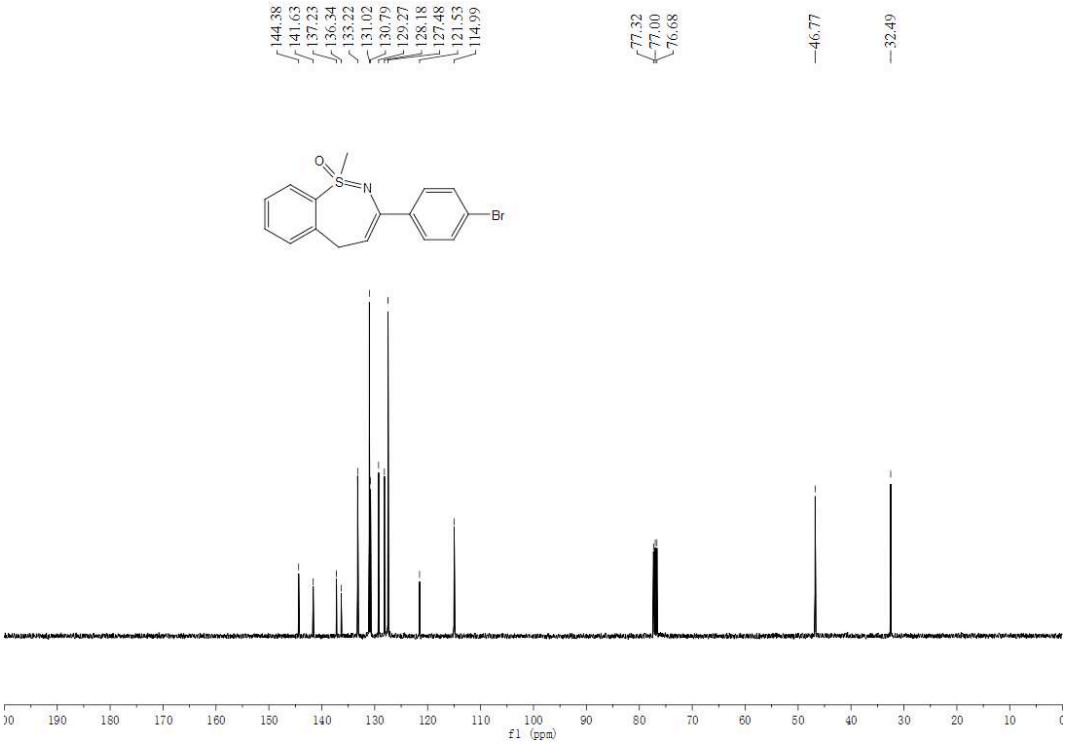
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2ad



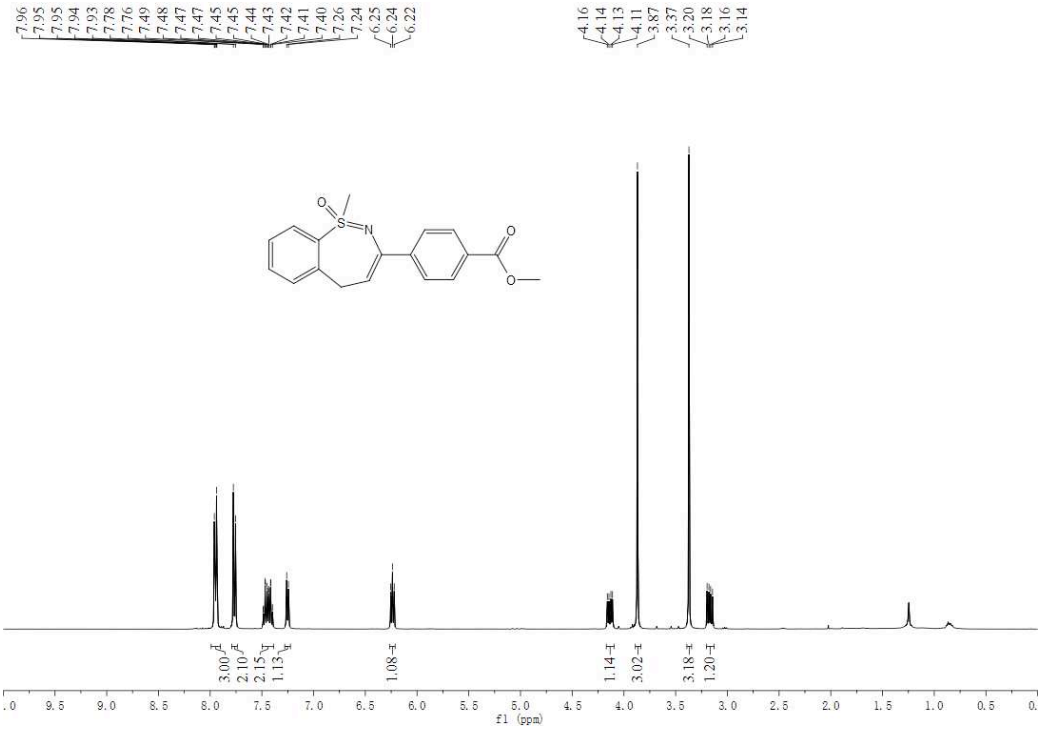
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2ae



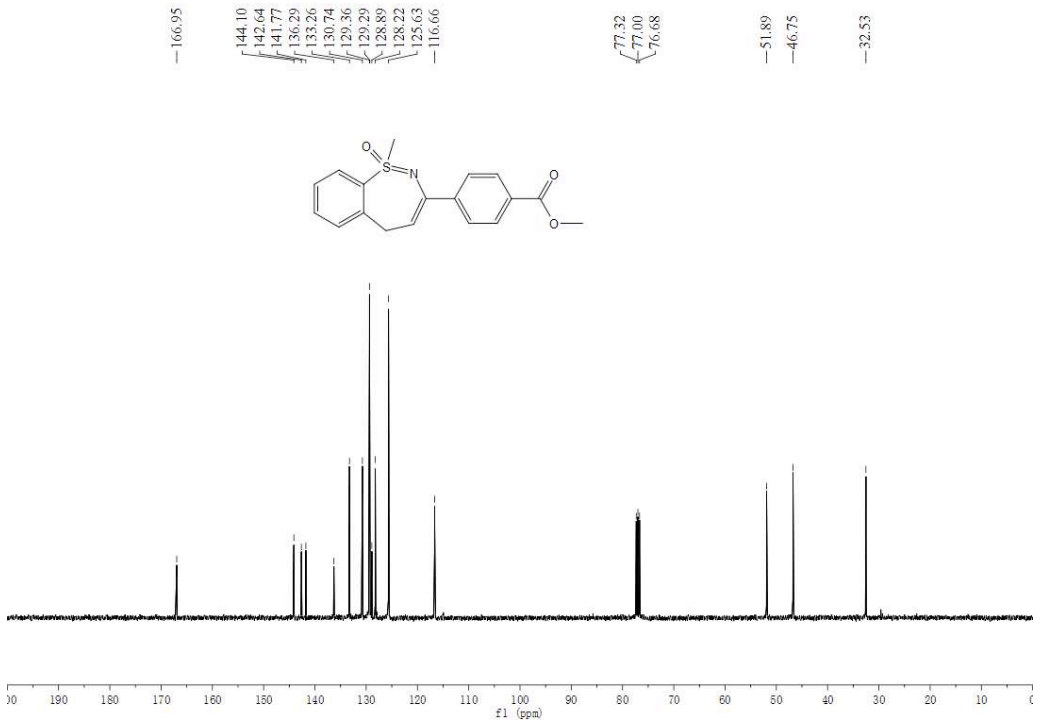
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2ae



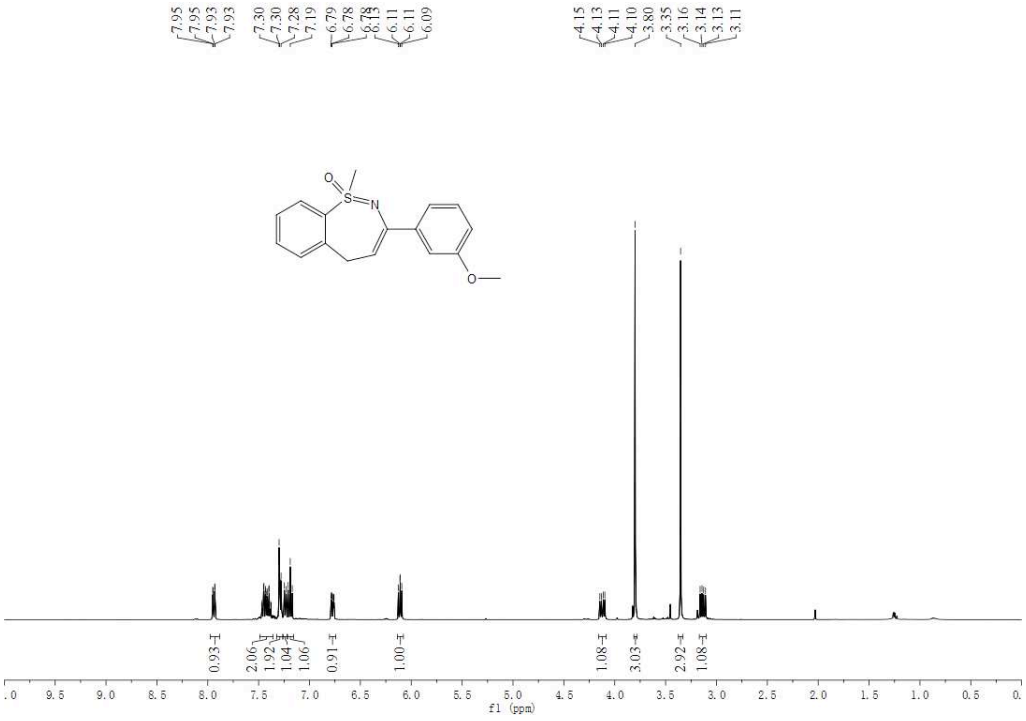
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2af



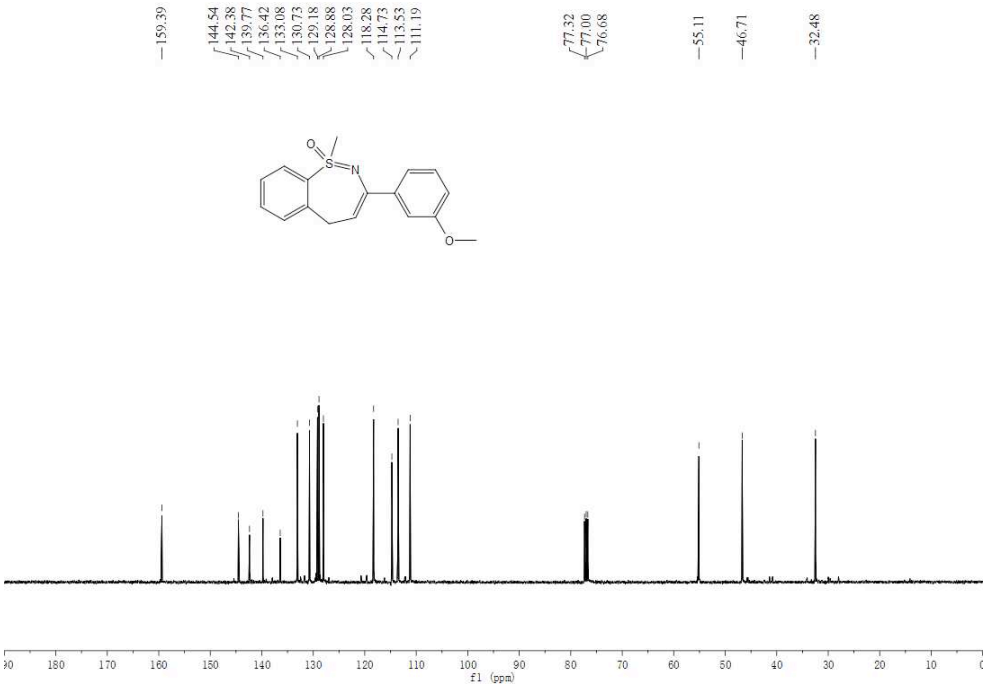
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2af



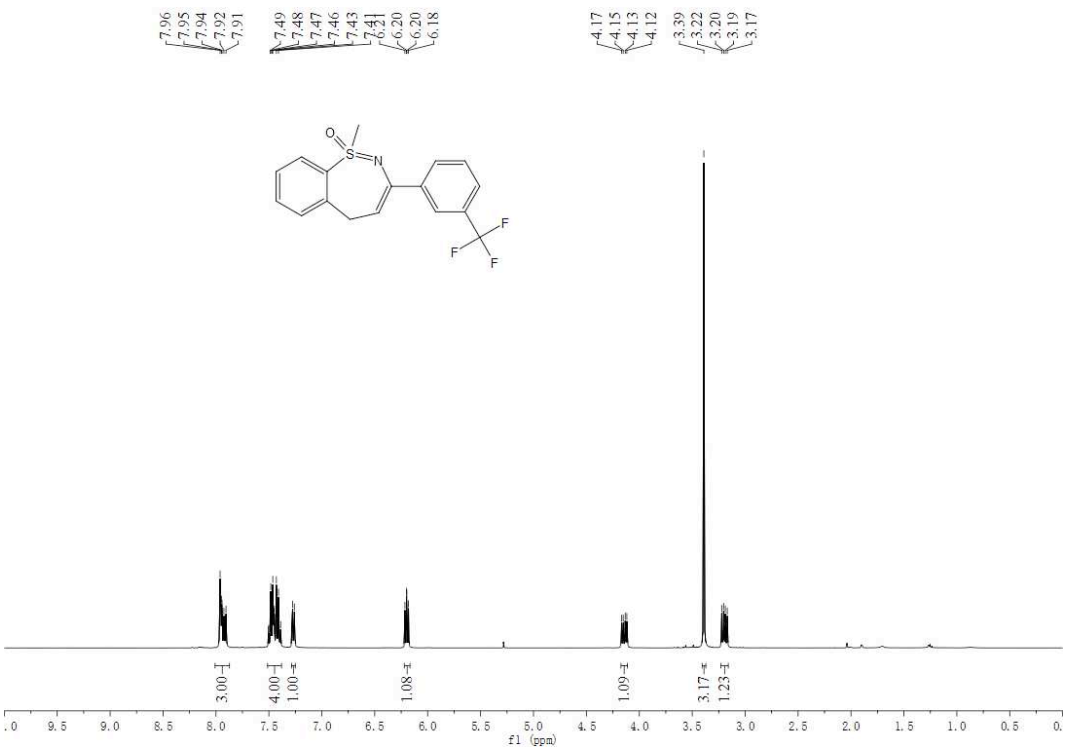
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2ag



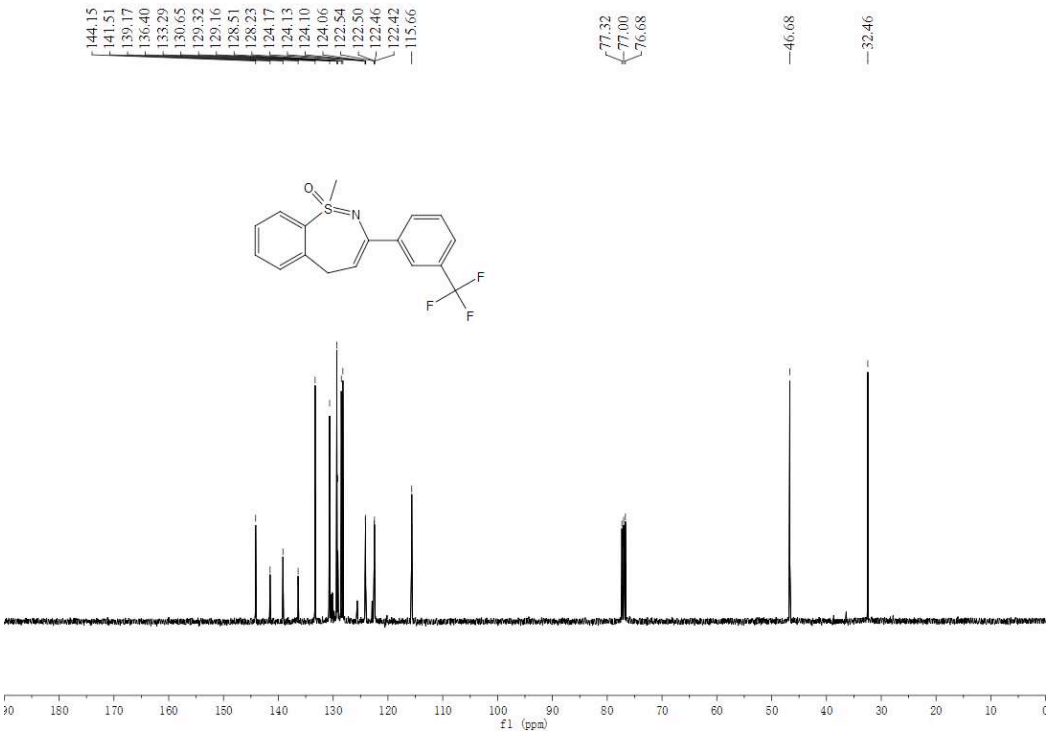
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2ag



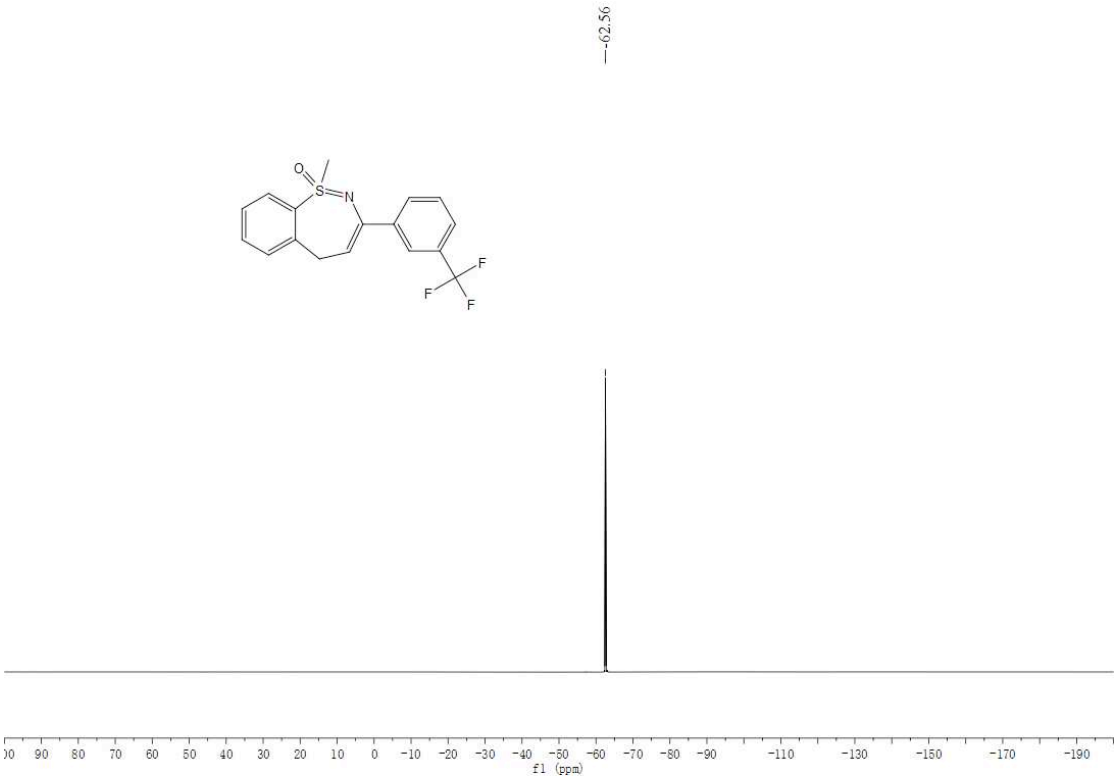
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2ah



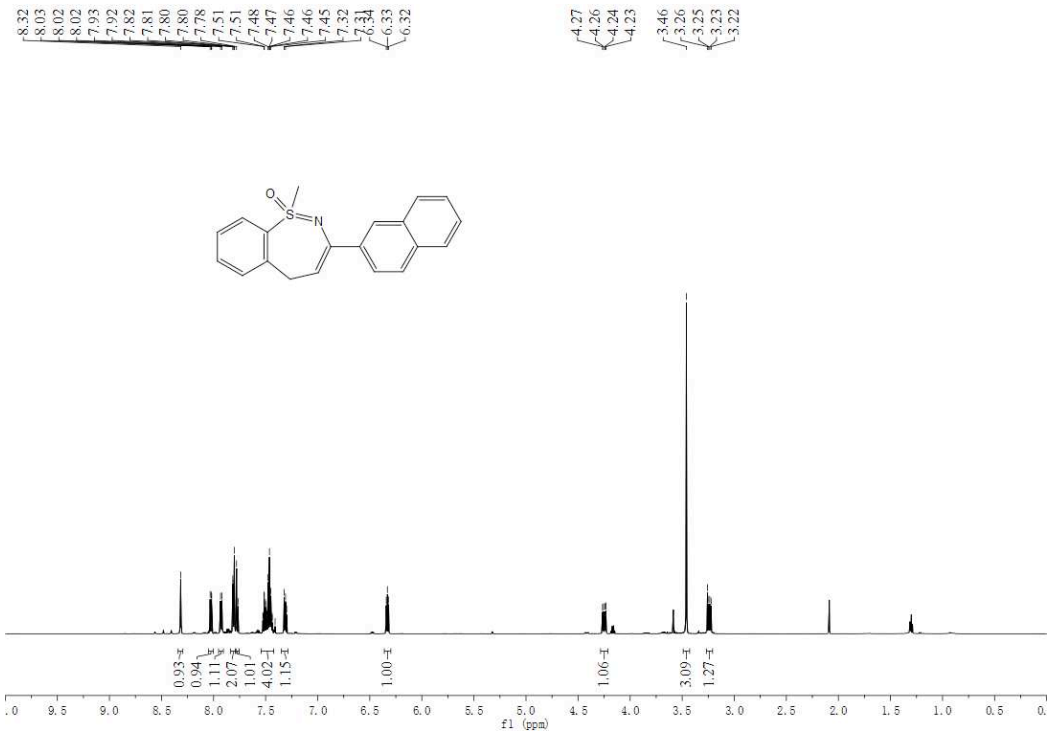
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2ah



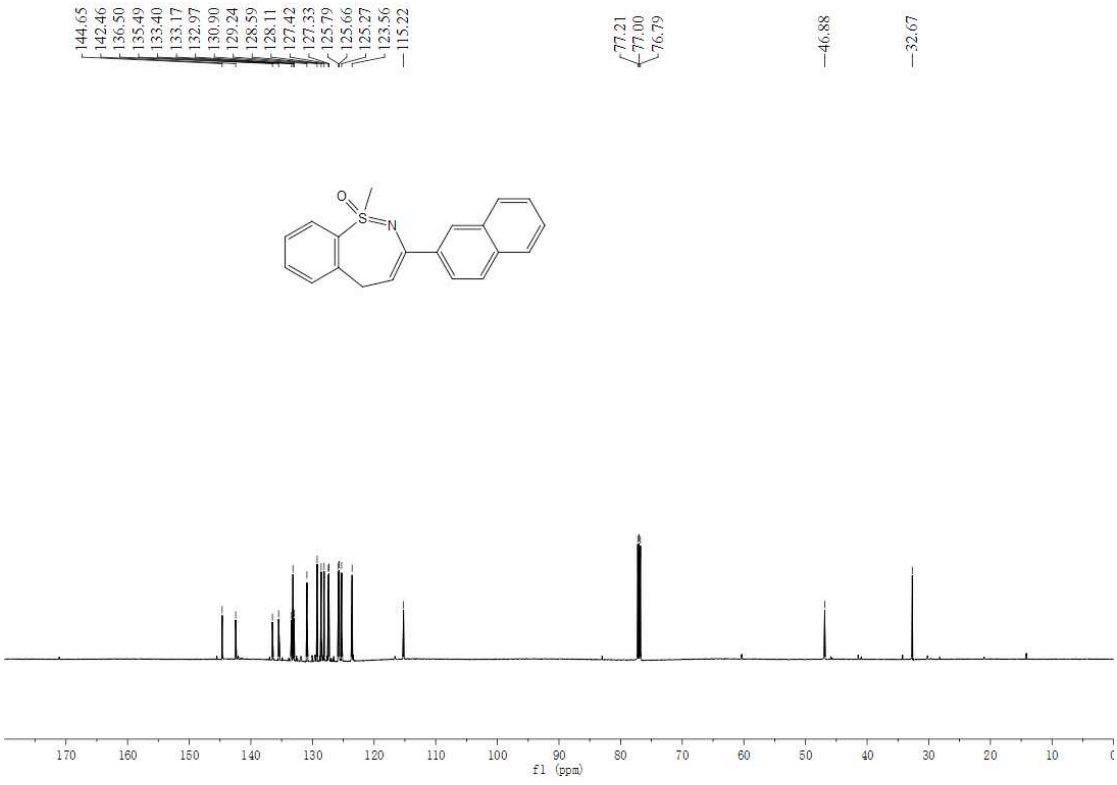
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of 2ah



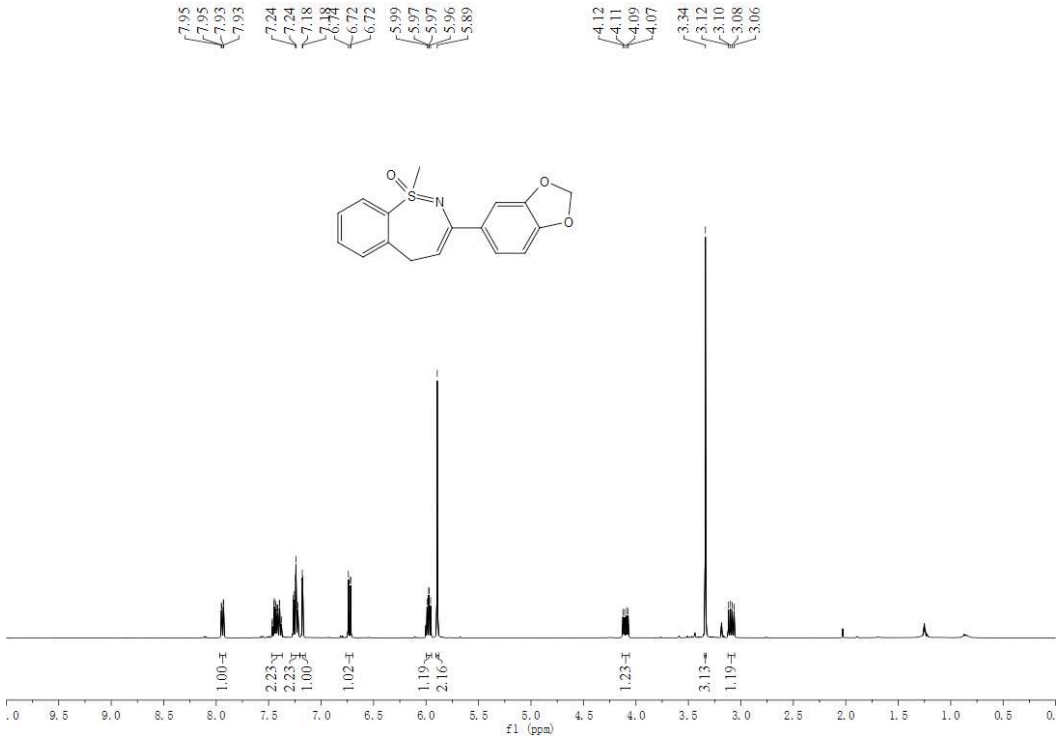
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 2ai



^{13}C{^{1}H} NMR spectrum (150 MHz, $CDCl_3$) of 2ai



^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 2aj



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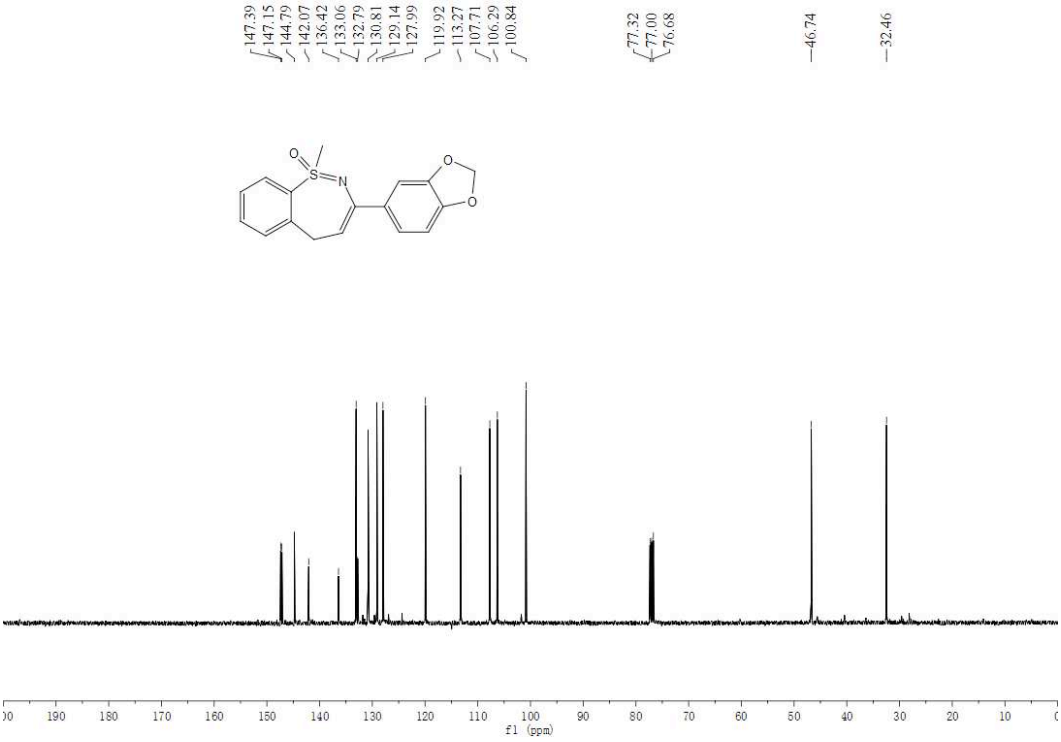
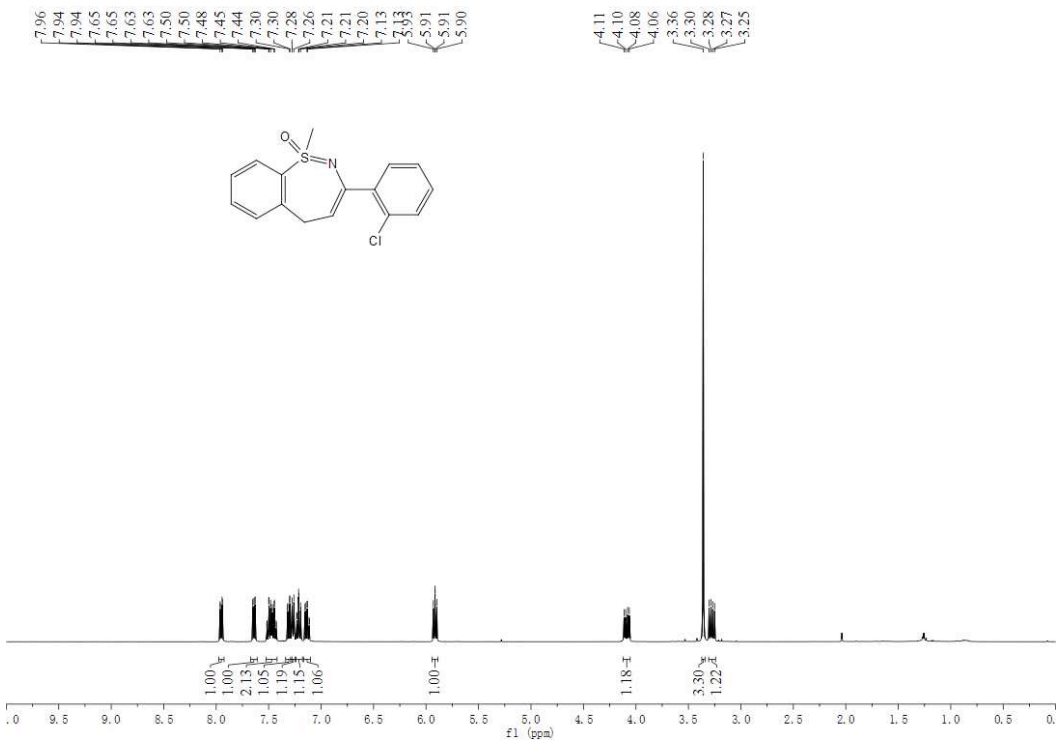
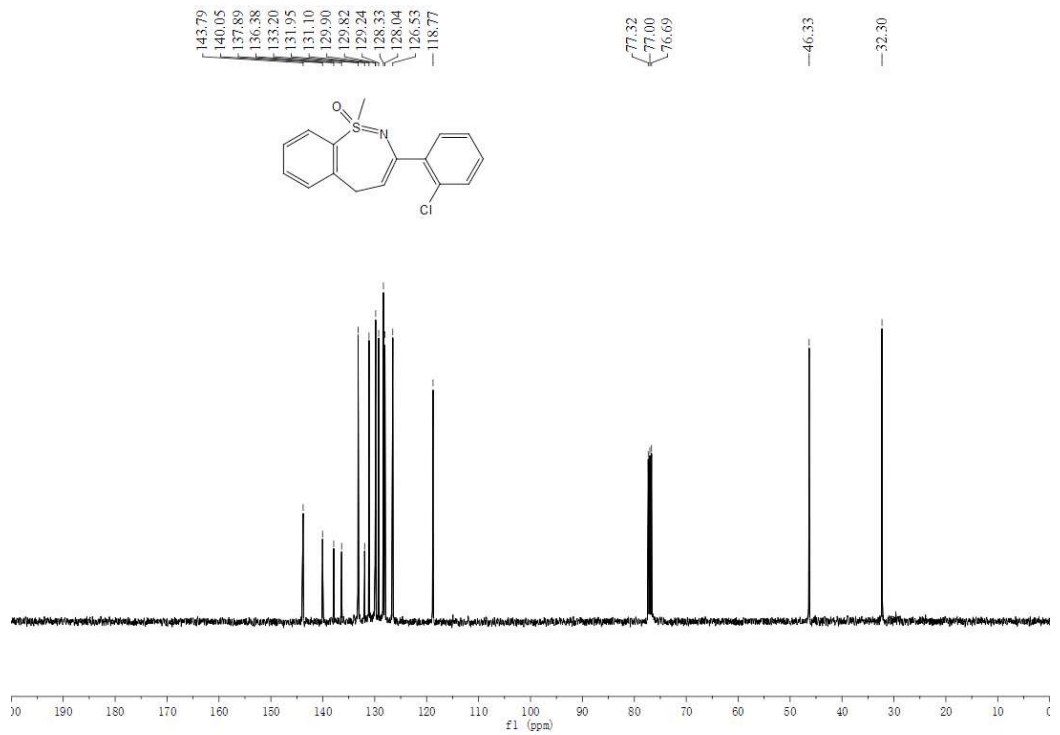
^{3}C{^{1}H} NMR spectrum (150 MHz, $CDCl_3$) of 2aj



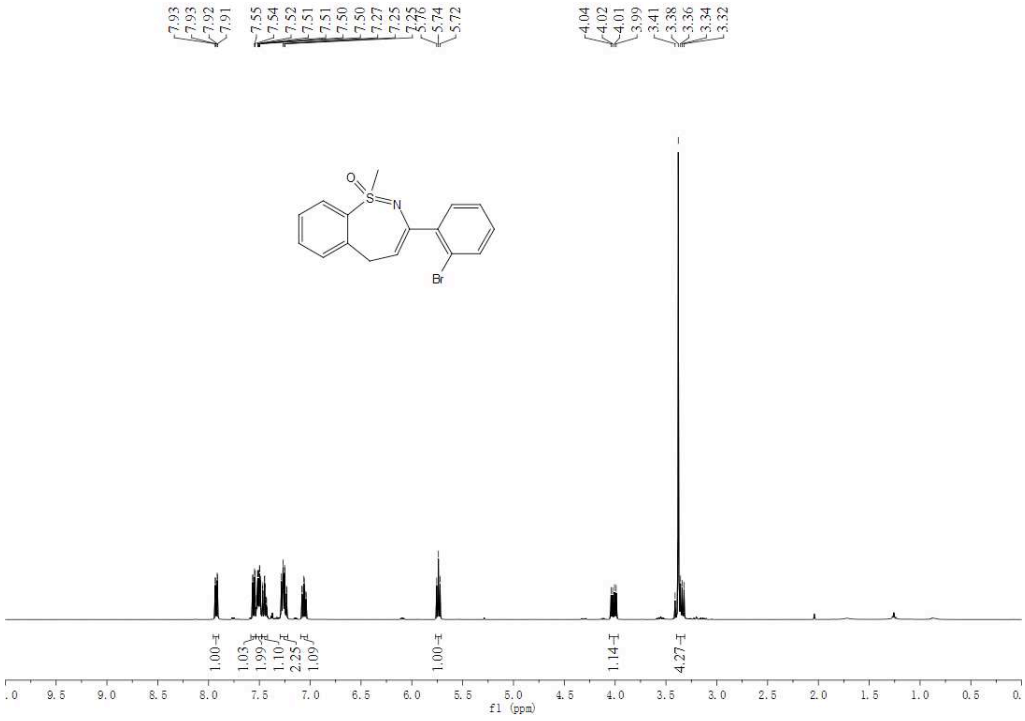
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2ak



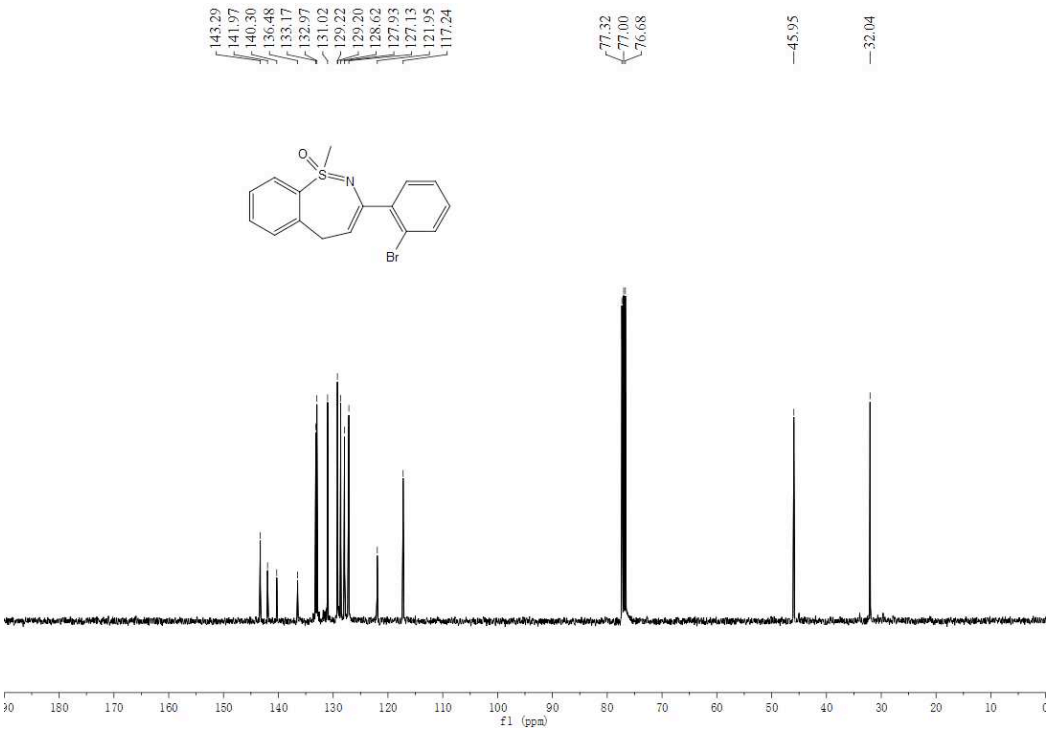
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2ak



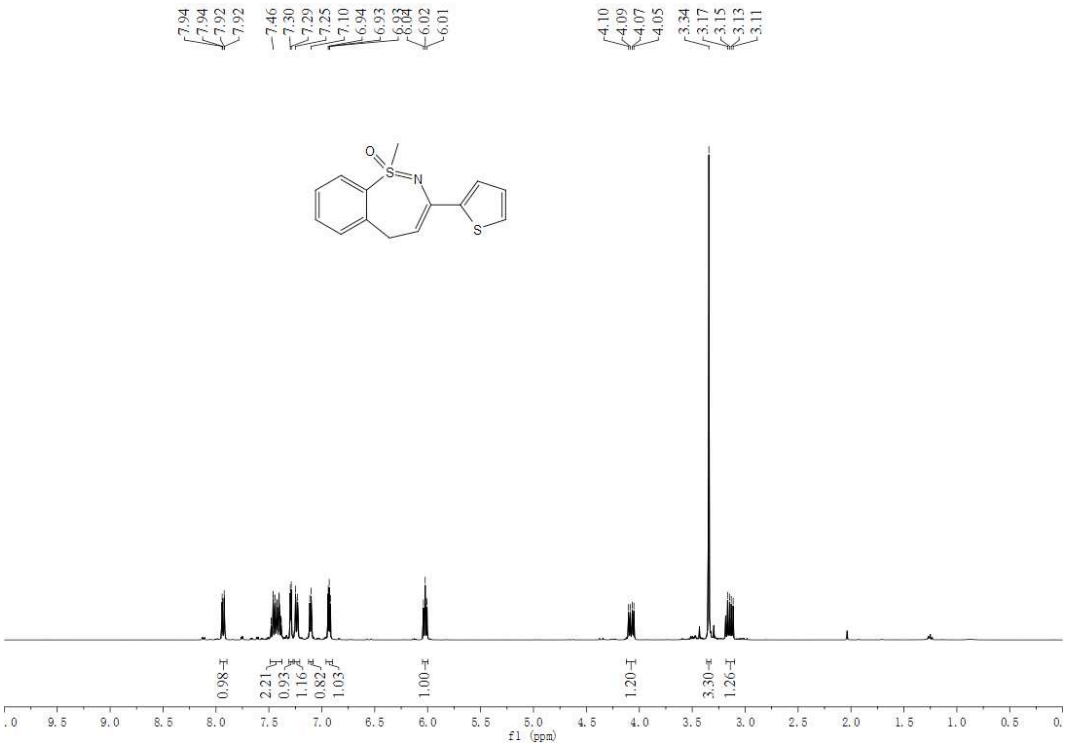
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2al



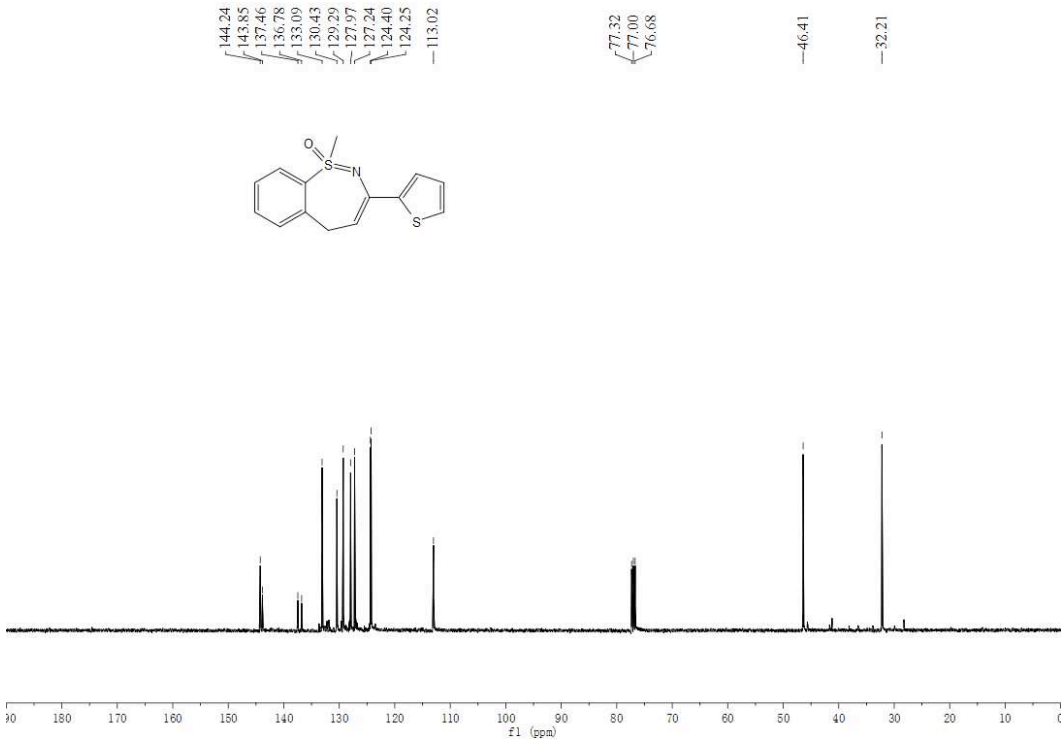
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2al



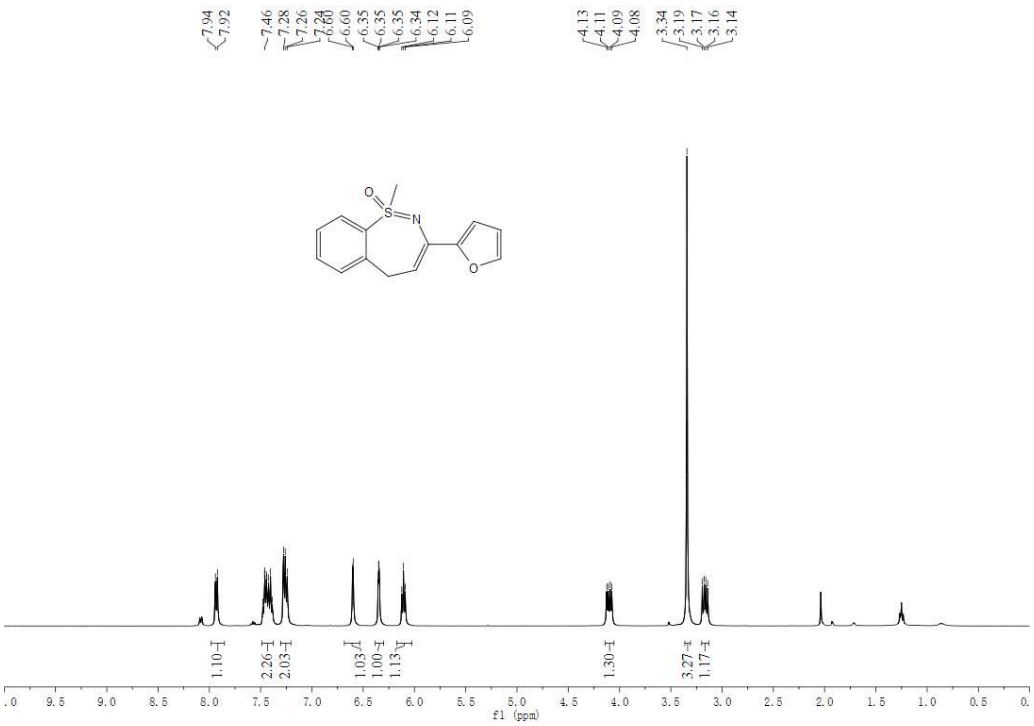
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2am



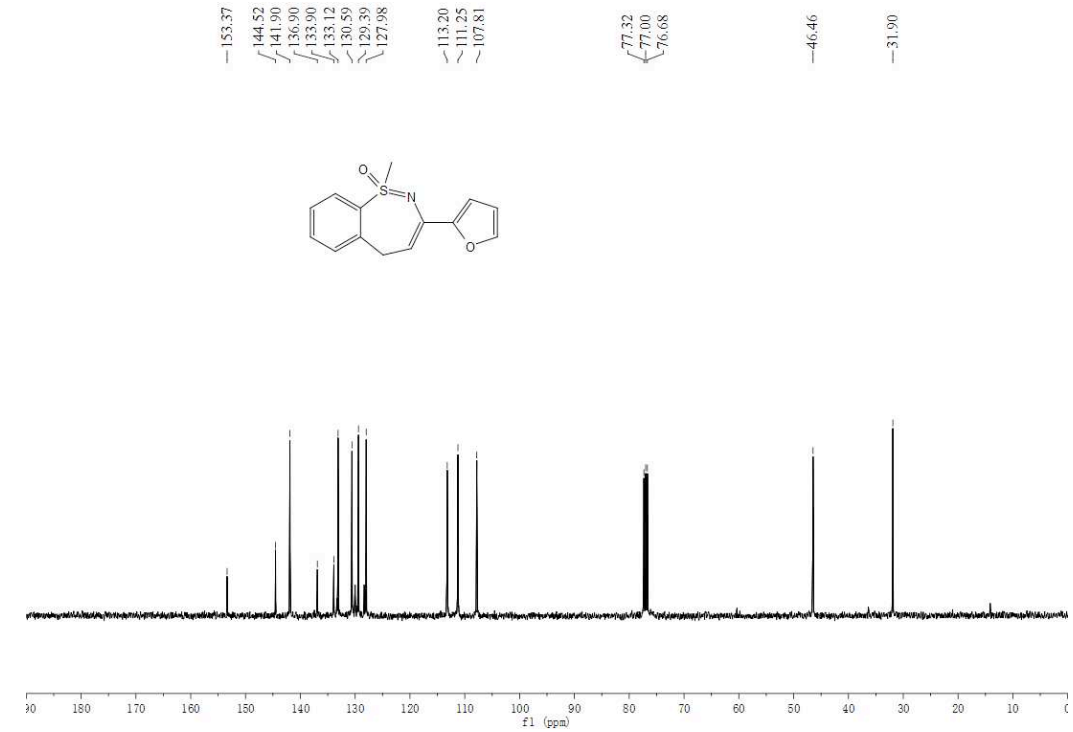
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2am



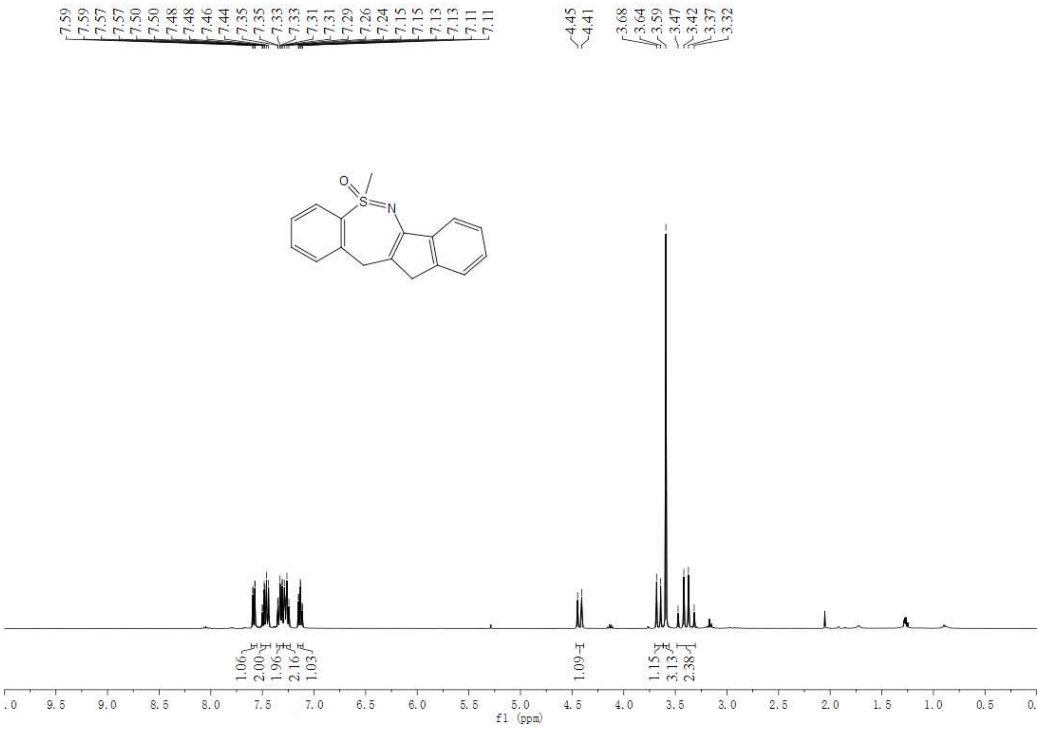
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2an



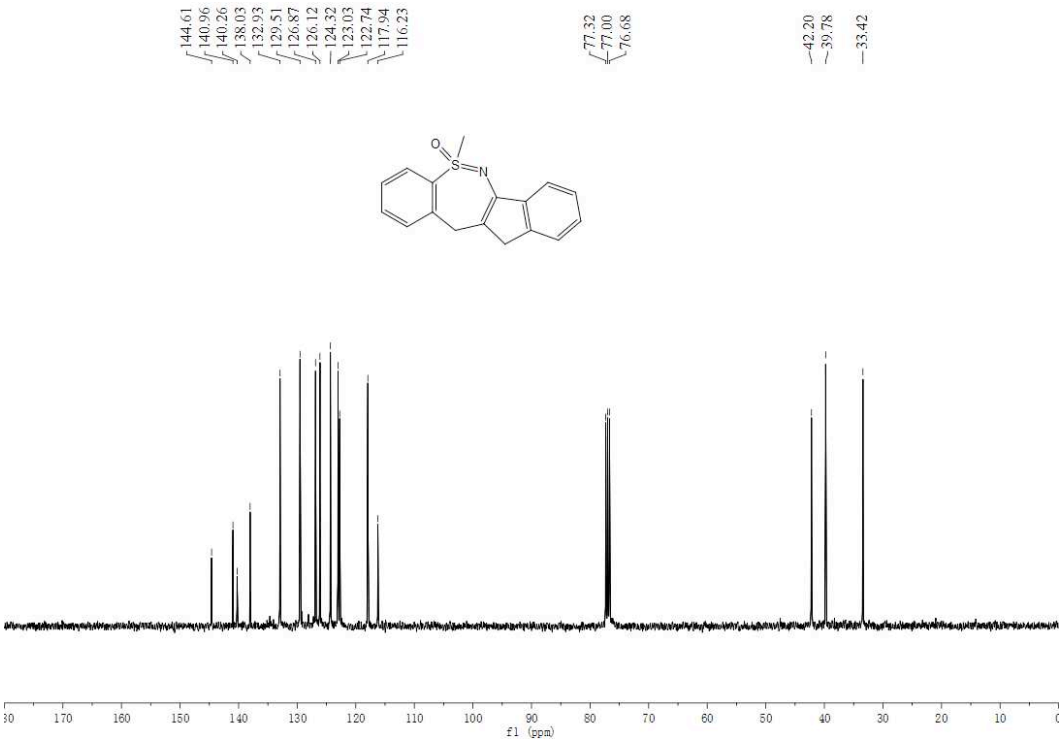
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2an



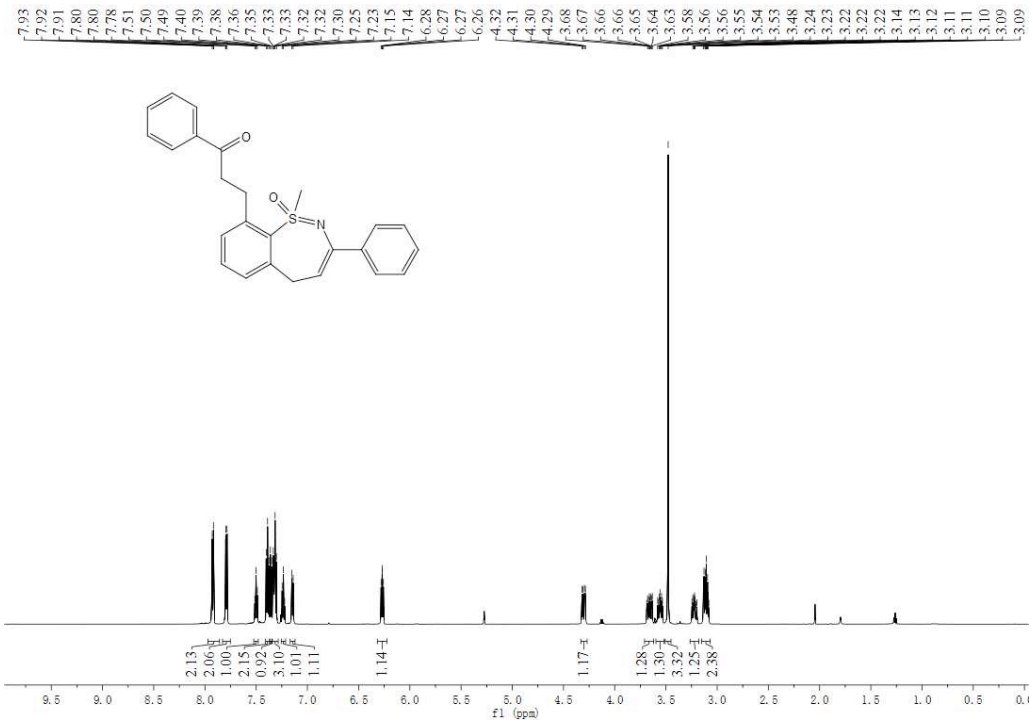
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2ao



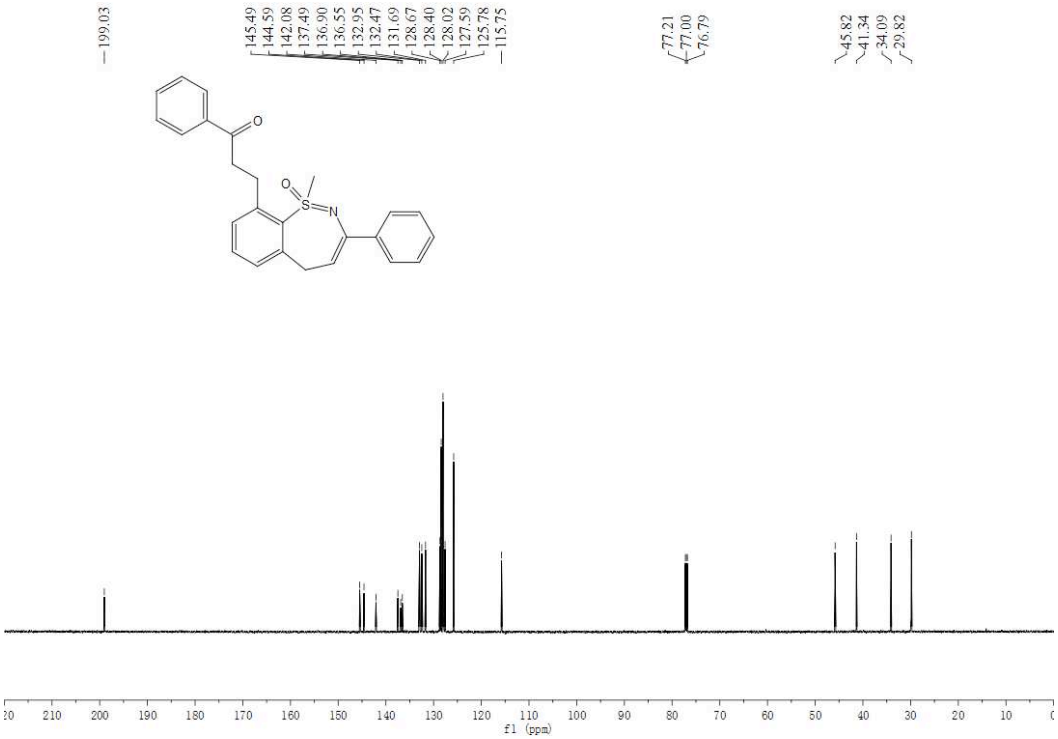
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2ao



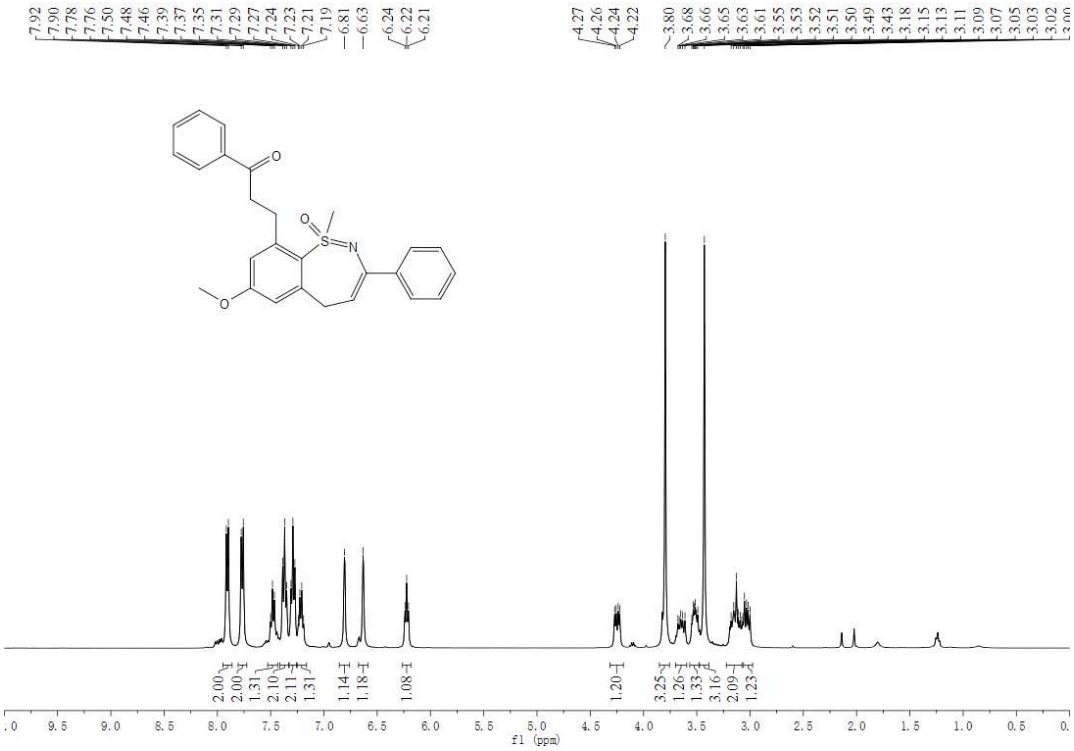
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 5aa



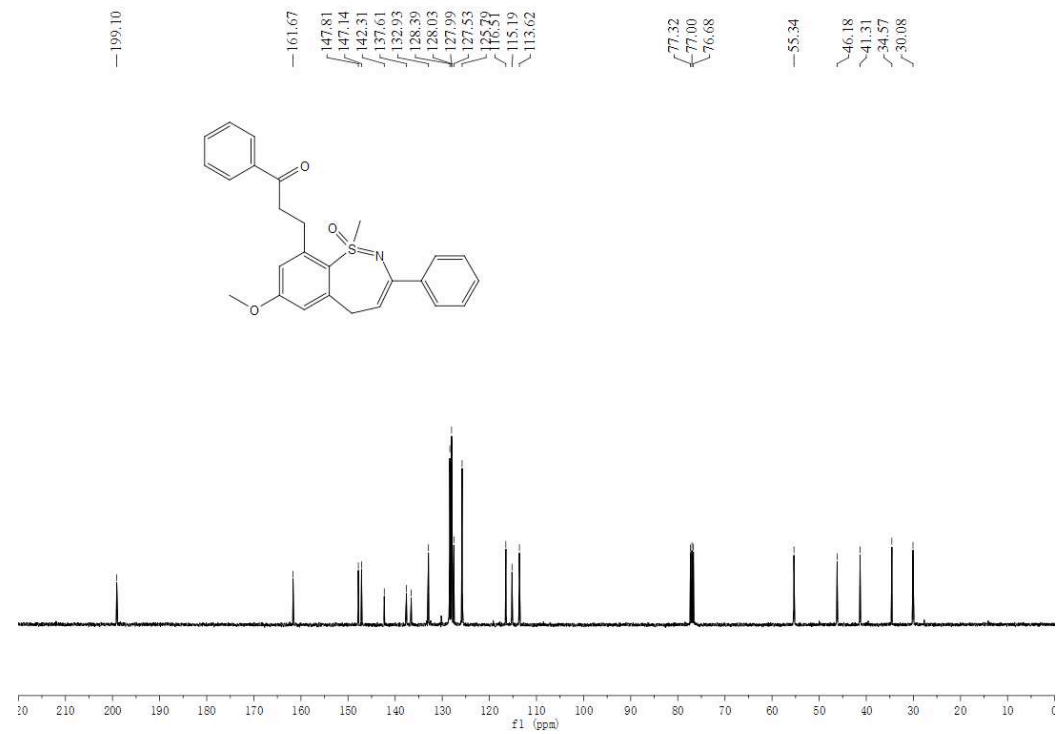
^{13}C{^{1}H} NMR spectrum (150 MHz, $CDCl_3$) of 5aa



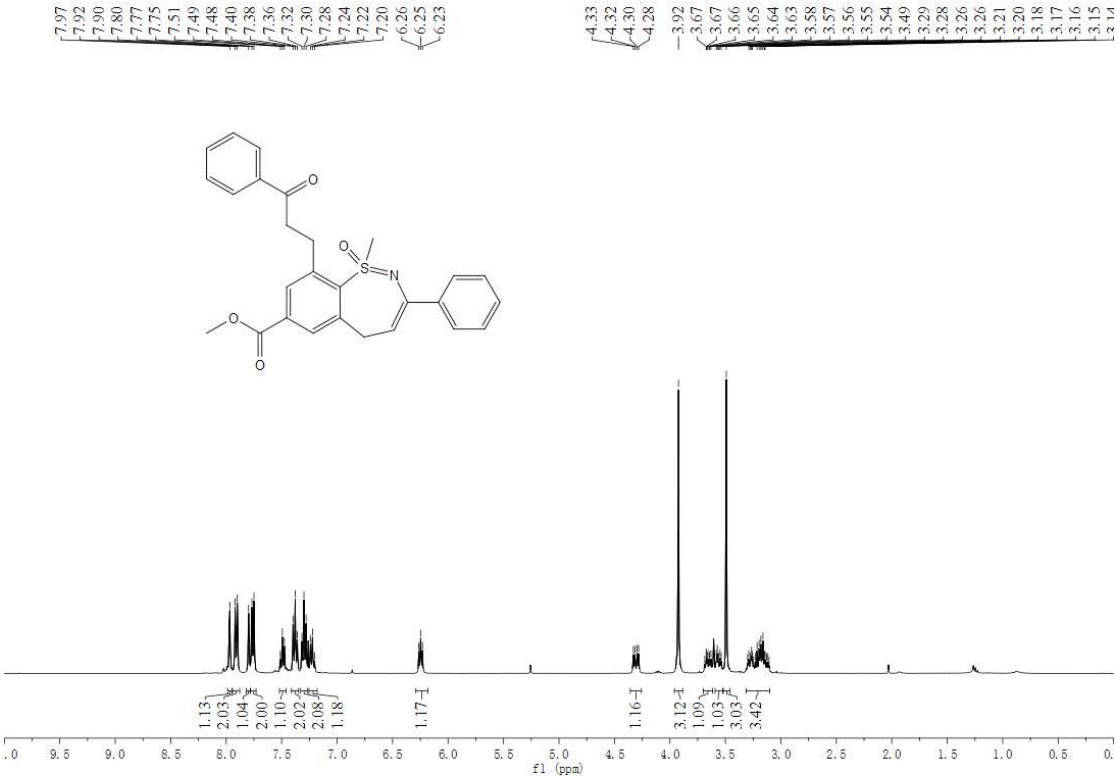
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 5ca



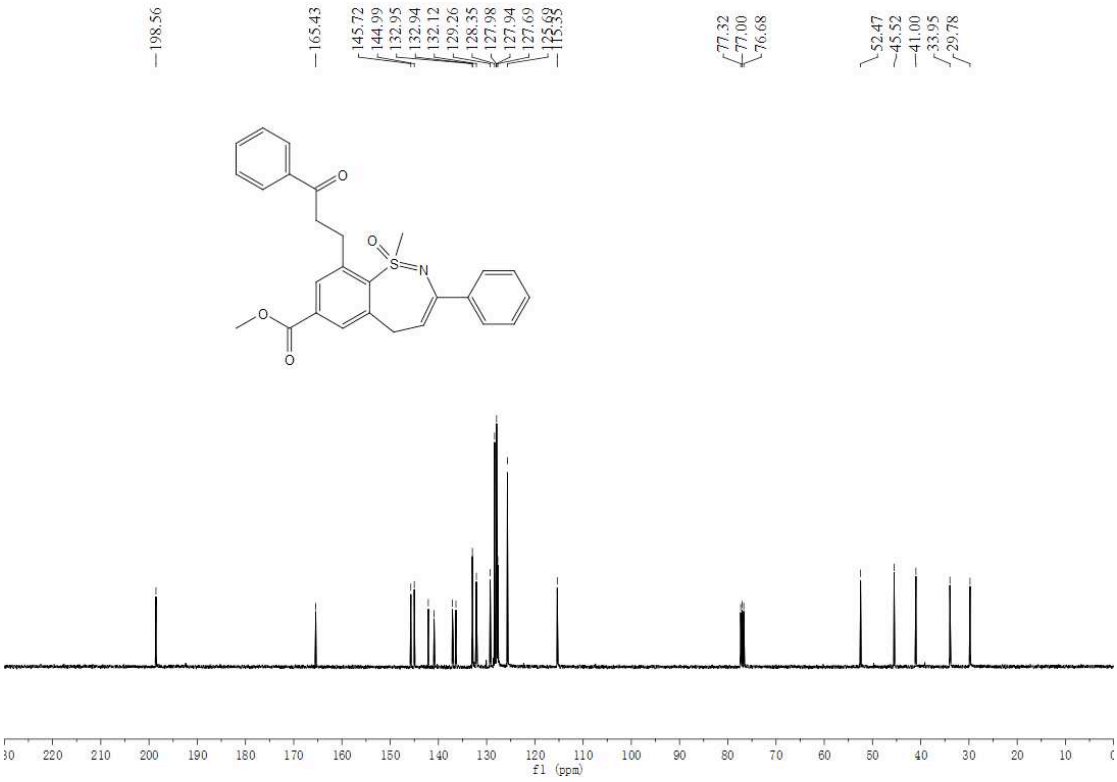
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 5ca



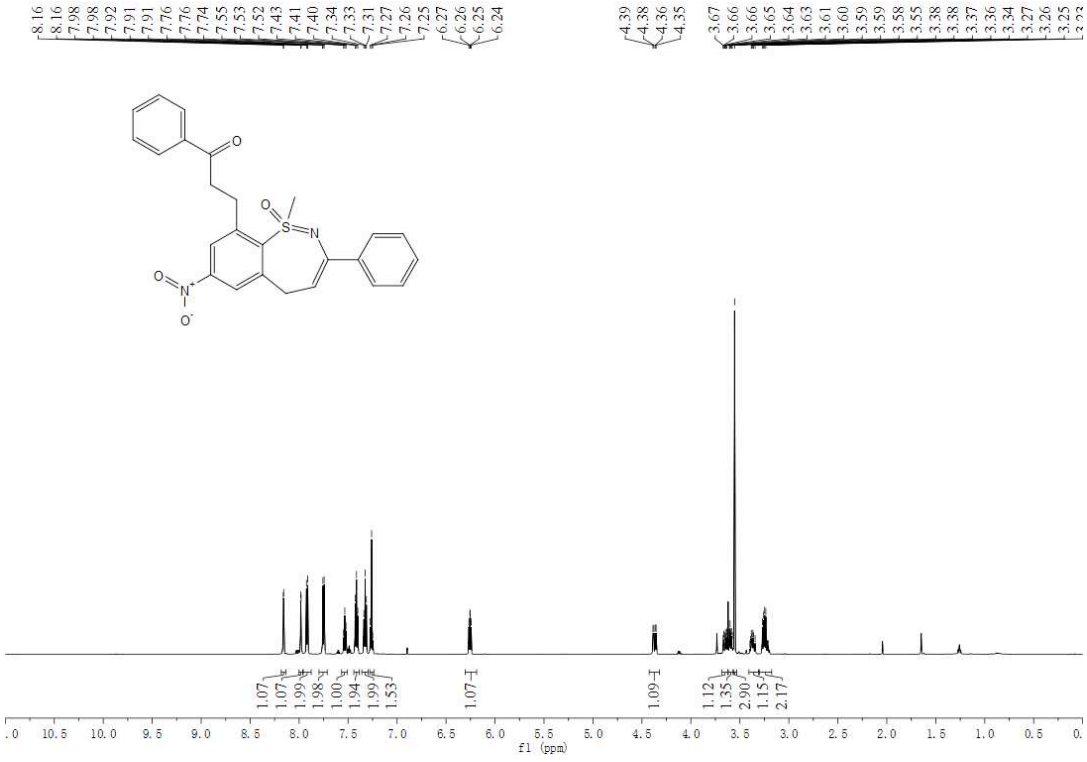
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 5fa



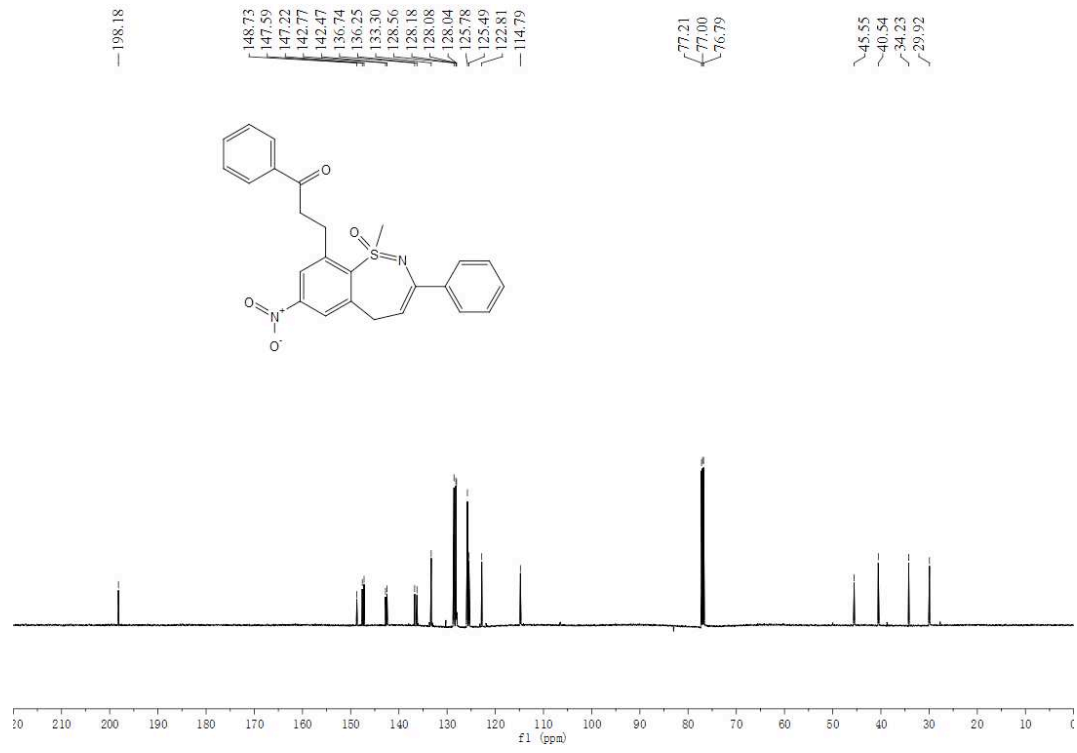
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 5fa



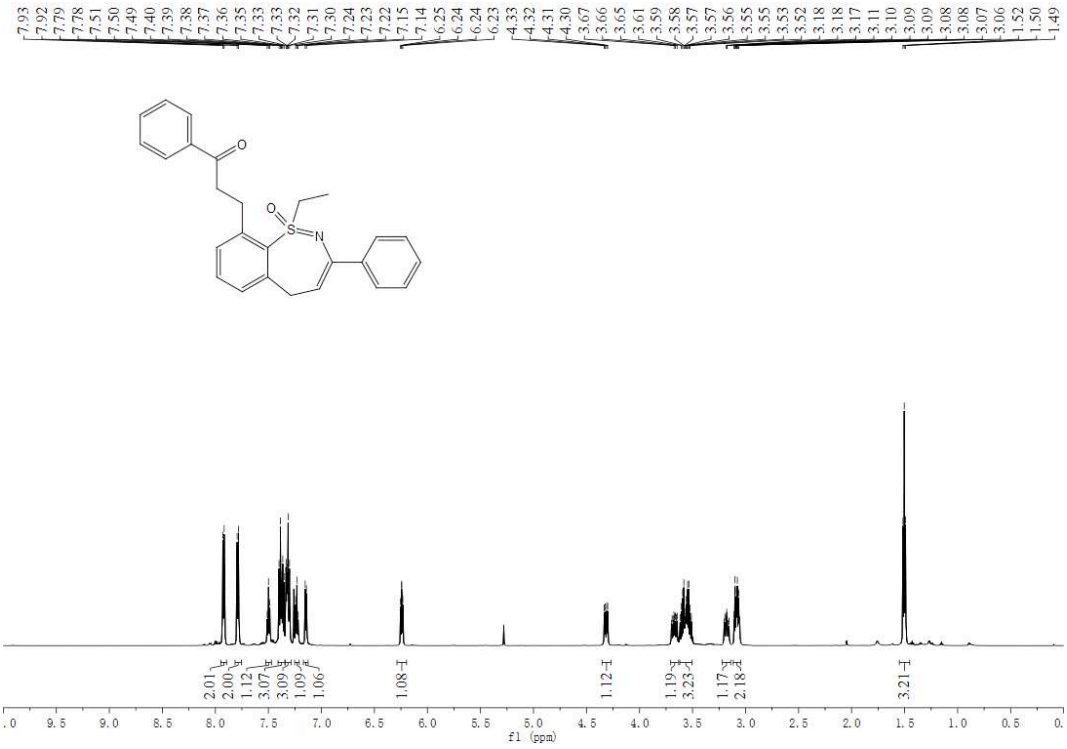
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 5ha



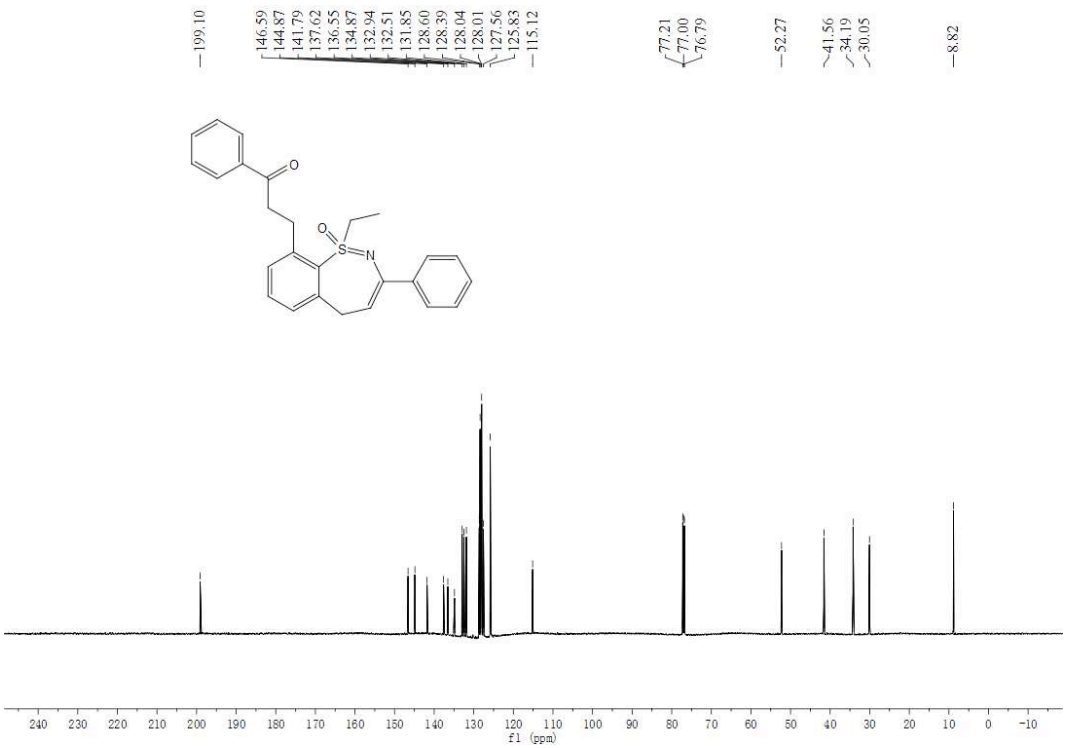
^{13}C{^{1}H} NMR spectrum (150 MHz, $CDCl_3$) of 5ha



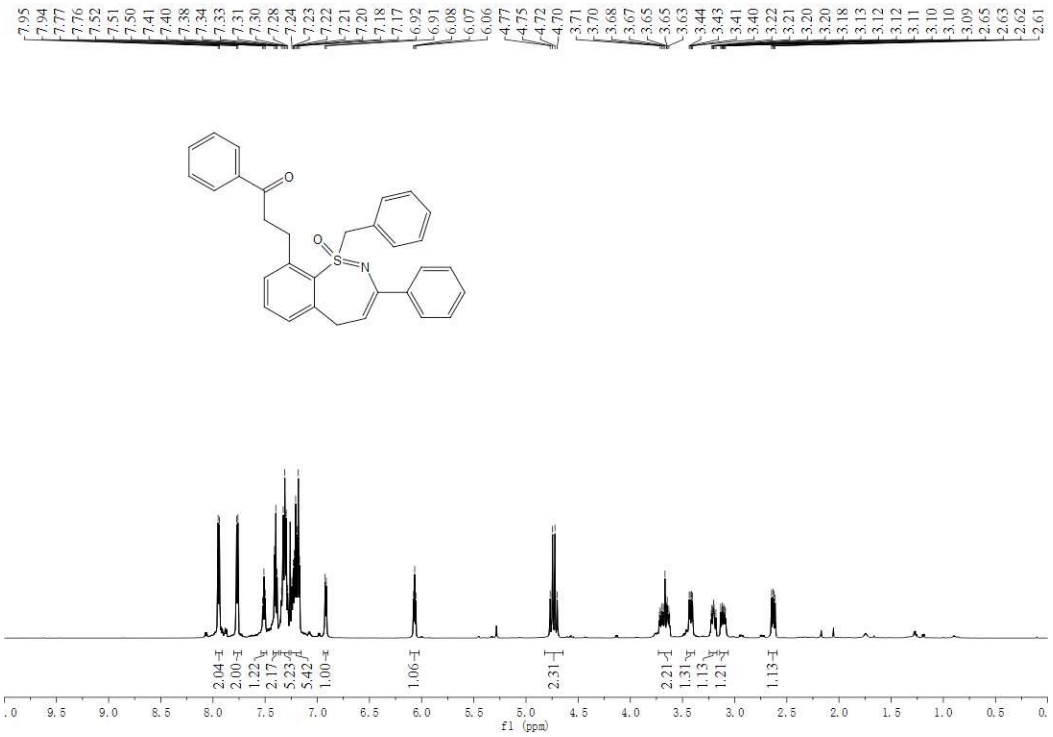
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 5la



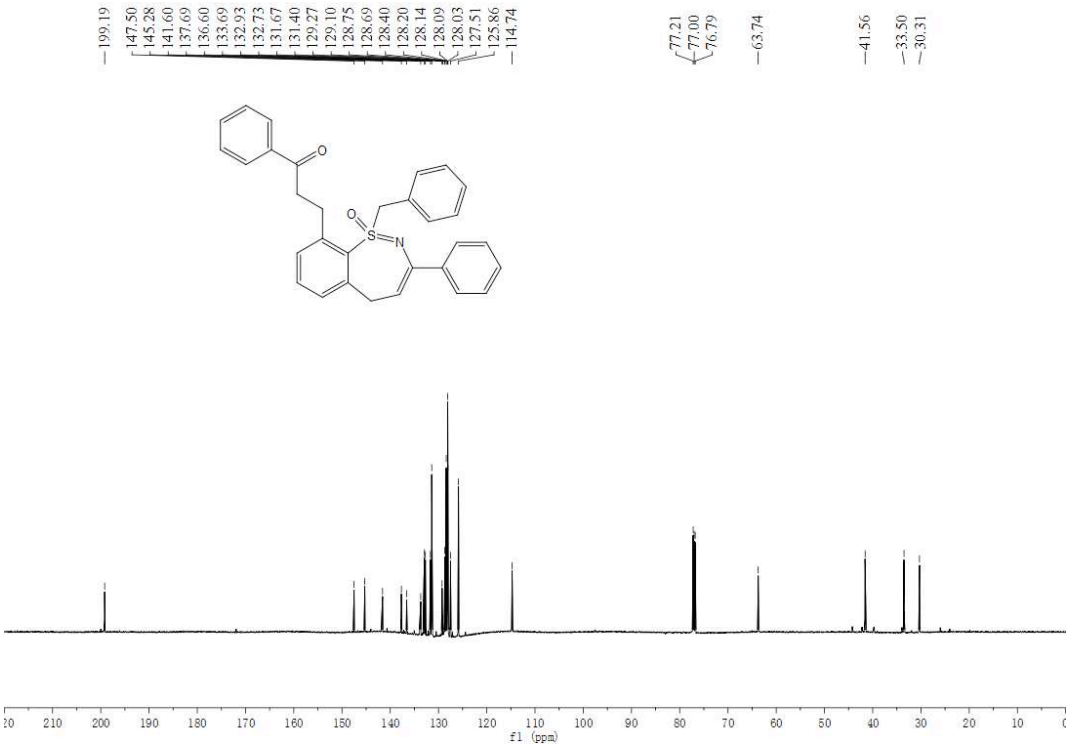
^{13}C{^{1}H} NMR spectrum (150 MHz, $CDCl_3$) of 5la



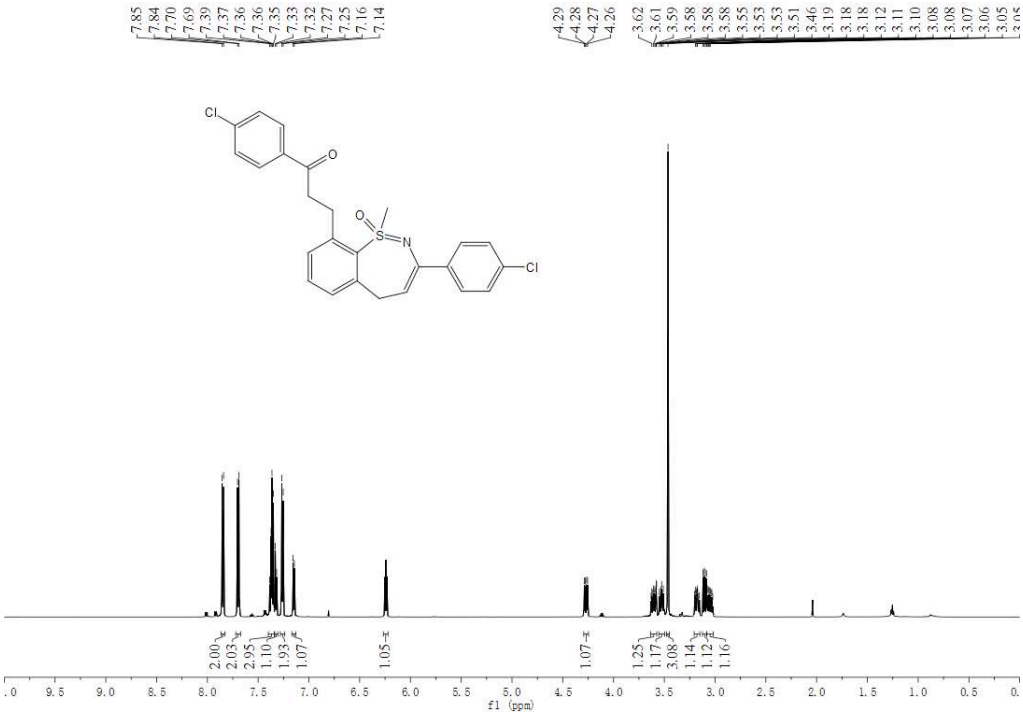
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 5na



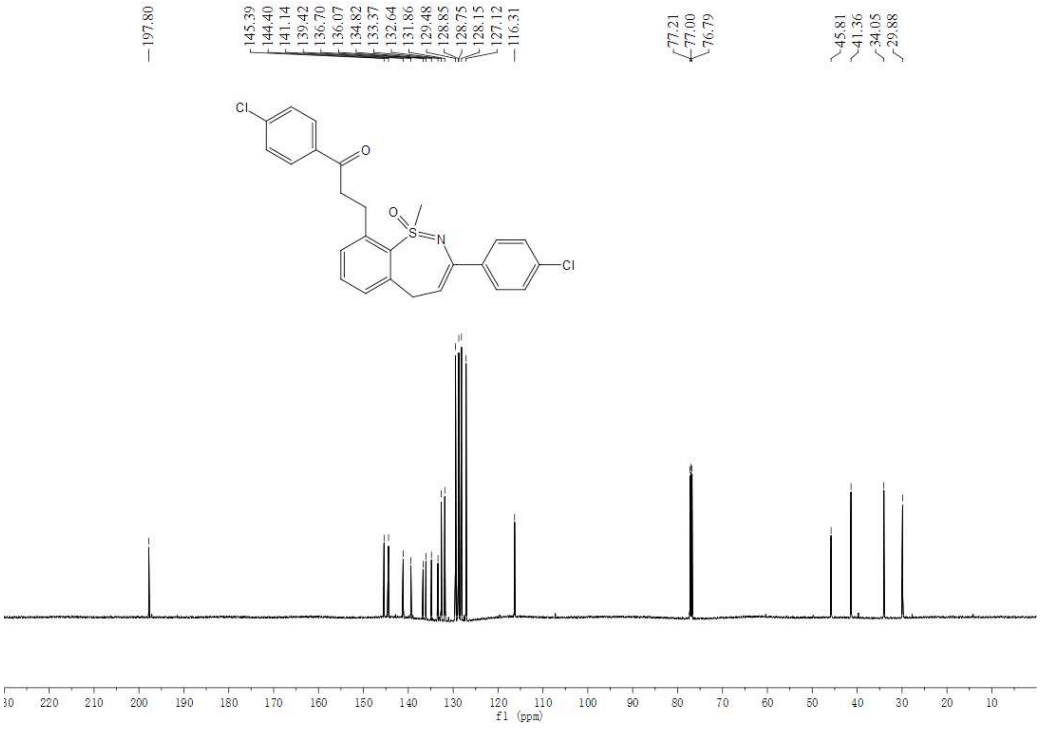
^{13}C{^{1}H} NMR spectrum (150 MHz, $CDCl_3$) of 5na



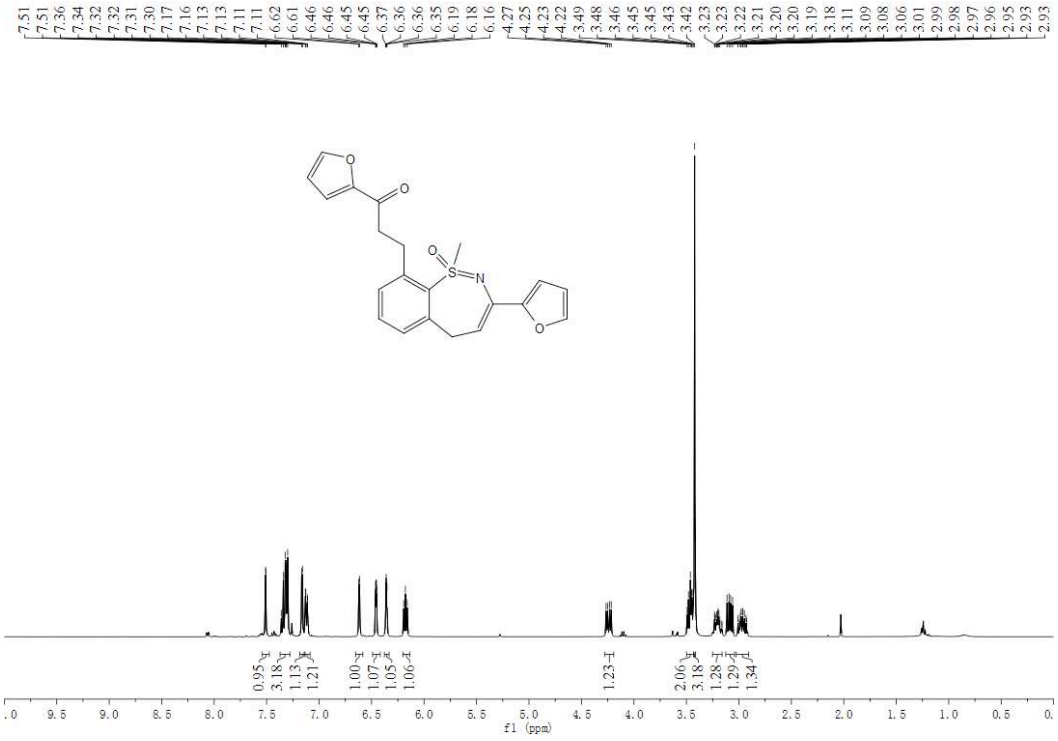
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 5ad



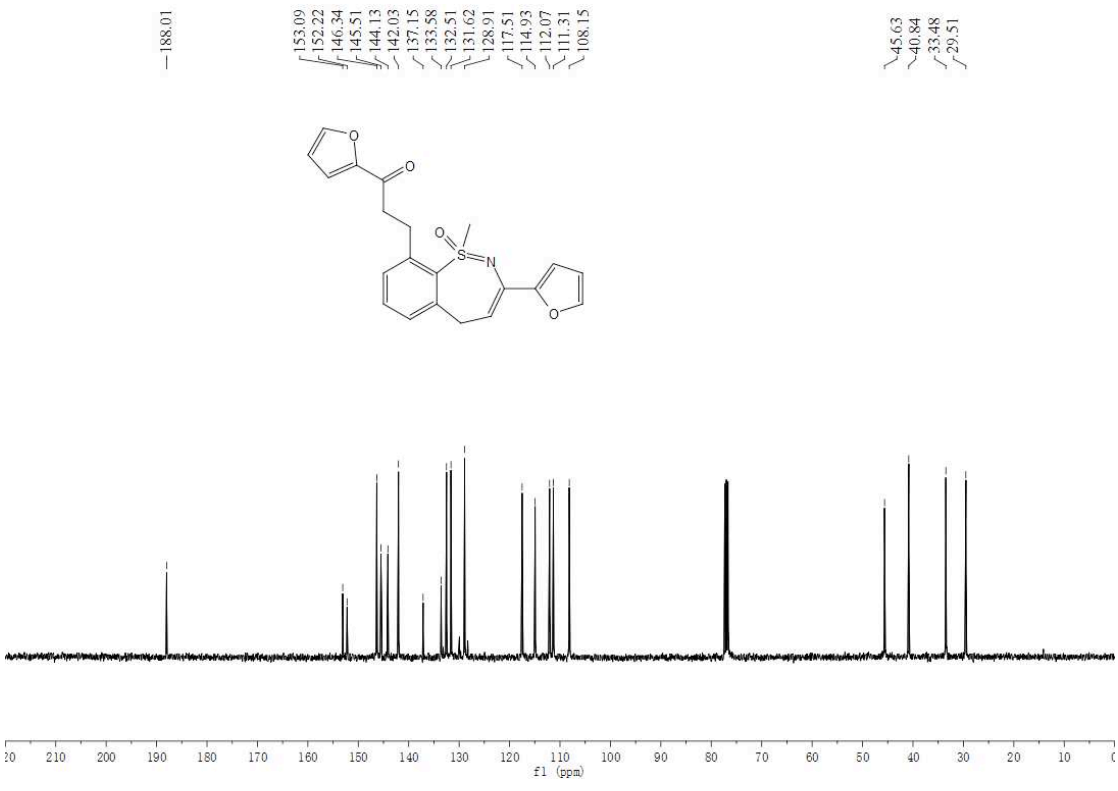
^{13}C{^{1}H} NMR spectrum (150 MHz, $CDCl_3$) of 4ad



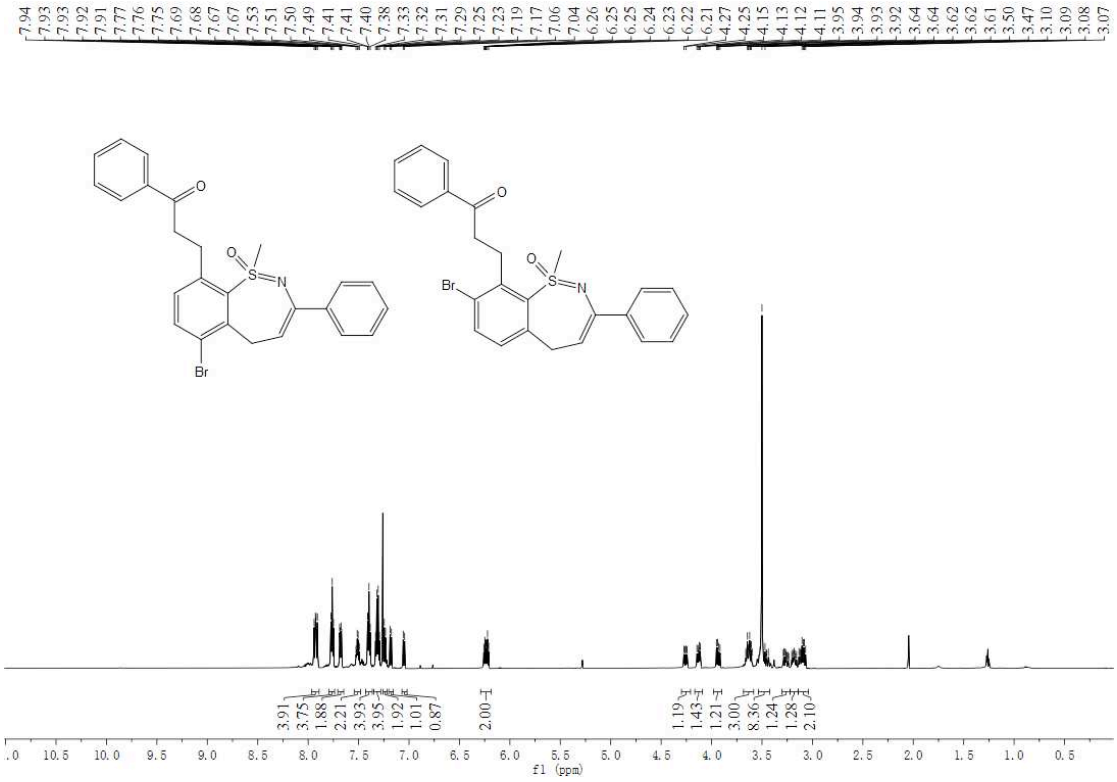
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 5an



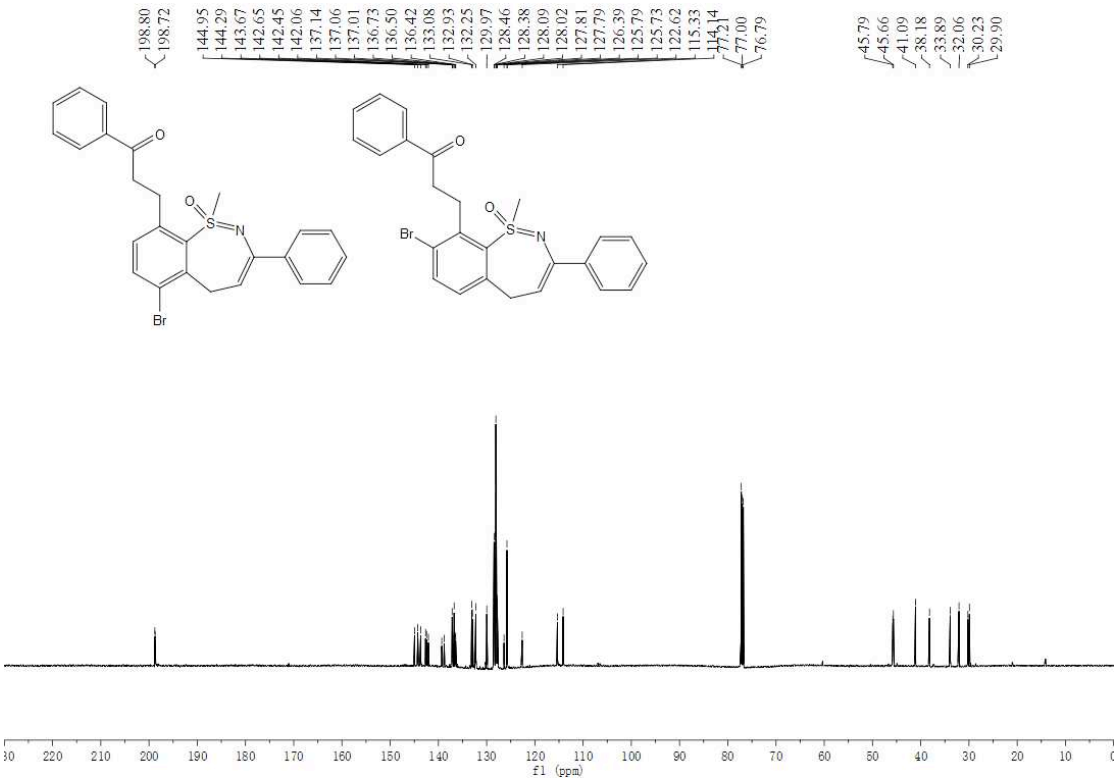
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 5an



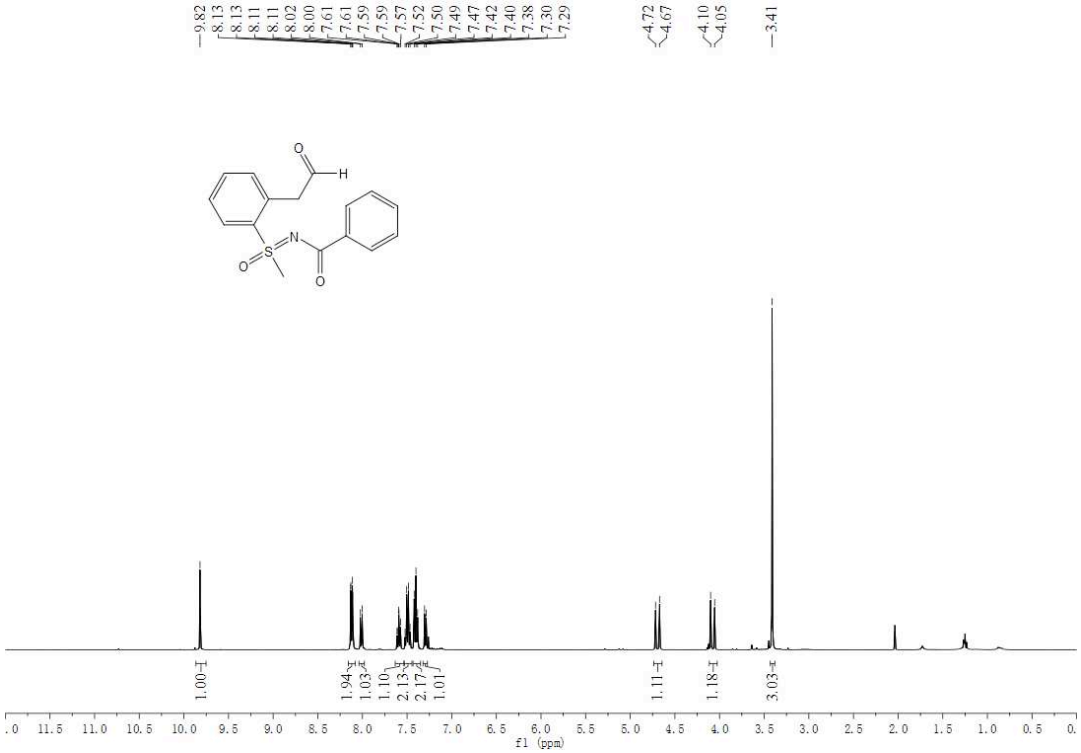
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 5qa



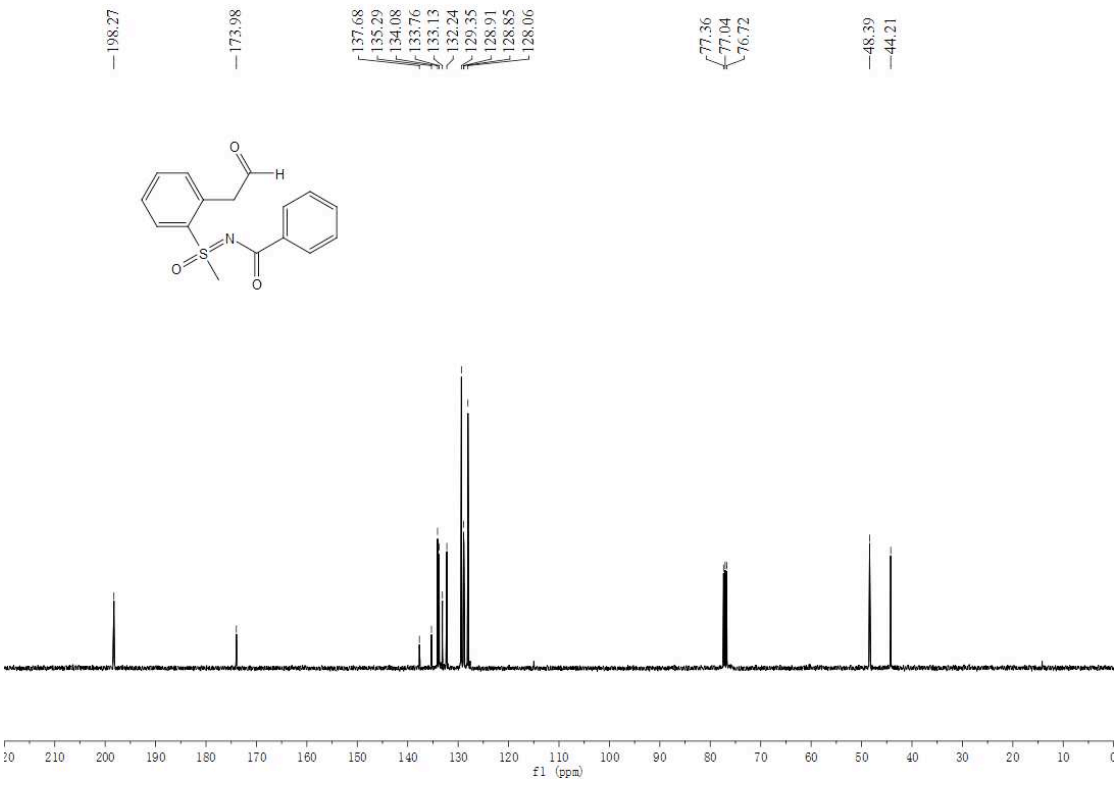
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of 5qa′



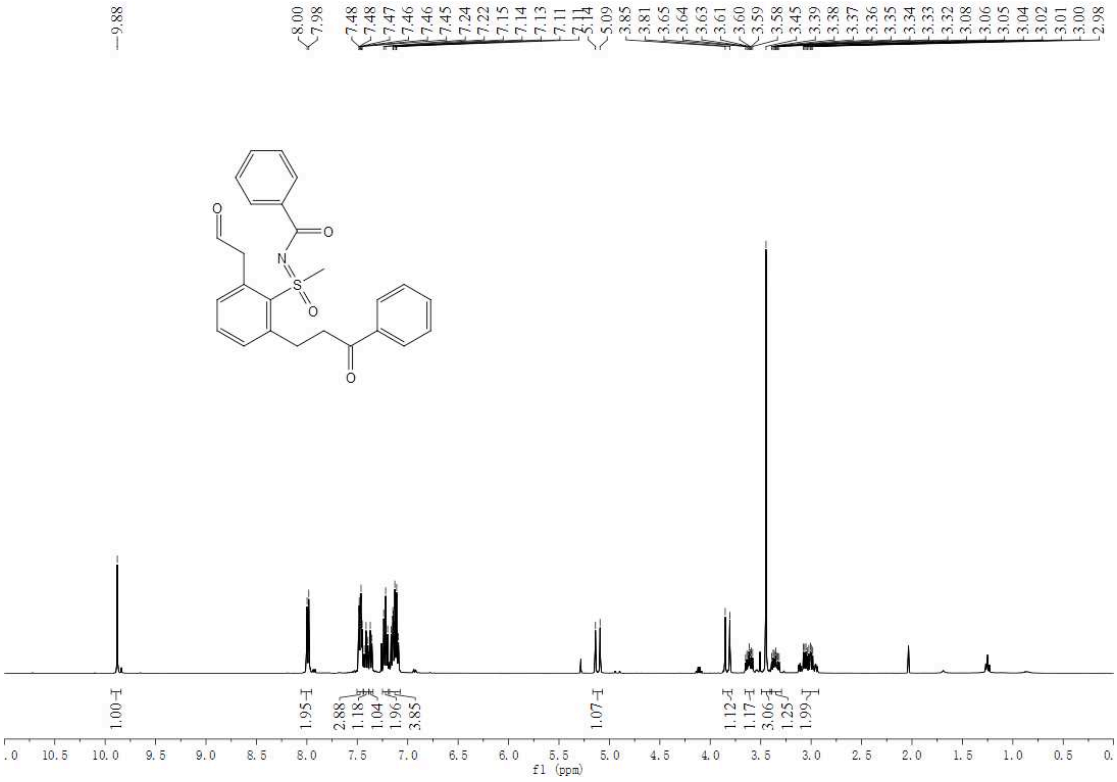
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 6a



^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 6a



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 6b



^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 6b