Supporting Information

Pd-Catalyzed Multicomponent Reactions Toward Medium-sized Sulfoximine Heterocycles *via* Double Carbopalladation/*syn*-Insertion Cascades

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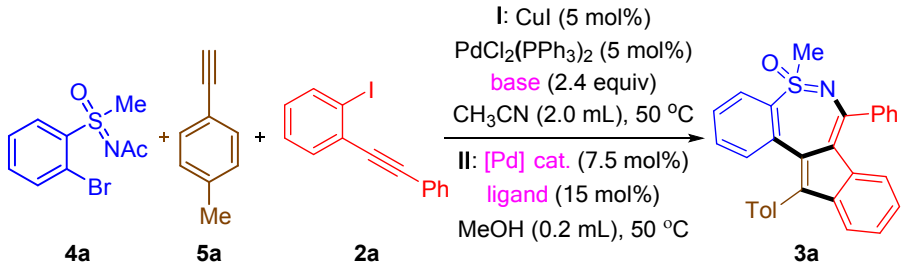
Contents

1. General remarks.

Unless otherwise noted, commercial reagents were purchased from commercial suppliers and were used as received. All solvents were dried and distilled according to standard procedures before use. The Flash column chromatography was performed using silica gel (60 Å pore size, 32-63 μm, standard grade). Analytical thin-layer chromatography (TLC) was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25-35 °C. Nuclear magnetic resonance (NMR) spectra were recorded in parts per million (ppm) from internal trimethylsilane (TMS) on the δ scale. High resolution mass spectrometry (HRMS) spectra analysis was performed by electrospray ionization (ESI-micrOTOF).

Table S1. Optimization of the reaction conditions.[a]



4a **5a** **2a** **3a**

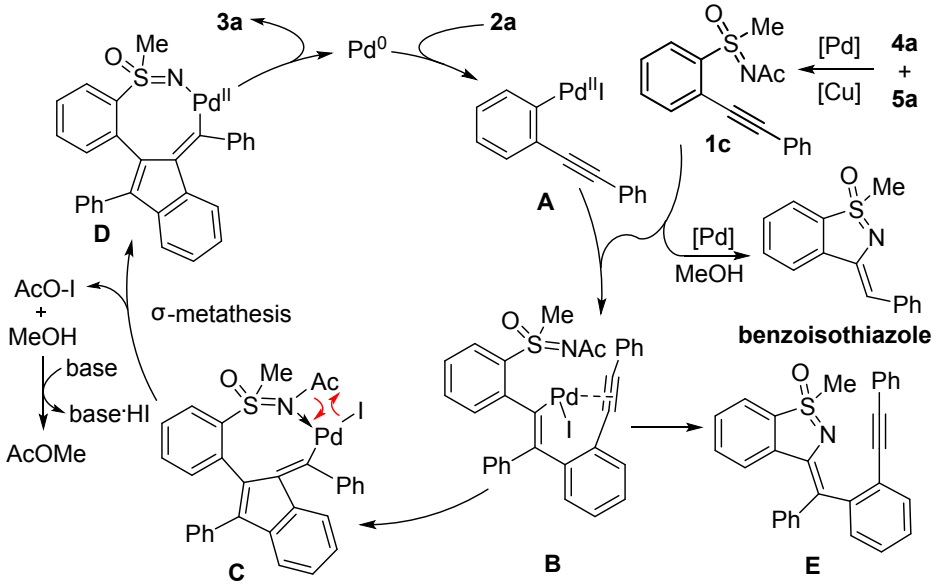
entry	[Pd] *cat.*	ligand	base	**3a** [%][a]
1	-	$P(4\text{-}MeC_6H_4)_3$	Cs_2CO_3	20
2	-	$P(4\text{-}MeOC_6H_4)_3$	Cs_2CO_3	trace
3	-	$P(4\text{-}FC_6H_4)_3$	Cs_2CO_3	23
4	-	$P(4\text{-}ClC_6H_4)_3$	Cs_2CO_3	31
5	-	Sphos	Cs_2CO_3	39
6	-	Mephos	Cs_2CO_3	60
7	-	PCy_3	Cs_2CO_3	41
8	$Pd(PPh_3)_2Cl_2$	Mephos	Cs_2CO_3	53
9	$Pd(OAc)_2$	Mephos	Cs_2CO_3	42
10	$Pd(OCOCF_3)_2$	Mephos	Cs_2CO_3	50
11	$Pd(dba)_2$	Mephos	Cs_2CO_3	59
12	**$Pd(MeCN)_2Cl_2$**	**Mephos**	**Cs_2CO_3**	**77**
13	$Pd(PhCN)_2Cl_2$	Mephos	Cs_2CO_3	70
14	$Pd(MeCN)_2Cl_2$	Mephos	Cs_2CO_3	30[b]
15	$Pd(MeCN)_2Cl_2$	Mephos	TEA	trace
16	$Pd(MeCN)_2Cl_2$	Mephos	Py	trace
17	$Pd(MeCN)_2Cl_2$	Mephos	K_2CO_3	20
18	$Pd(MeCN)_2Cl_2$	Mephos	MeONa	30
19	$Pd(MeCN)_2Cl_2$	Mephos	*t*BuONa	34
20	$Pd(MeCN)_2Cl_2$	Mephos	toluene	53[c]
21	$Pd(MeCN)_2Cl_2$	Mephos	1,4-dioxane	51[d]

[a] Reaction conditions, step I: NAc-sulfoximine **4a** (0.26 mmol), terminal alkyne **5a** (0.26 mmol) and $Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (5 mol%), base (2.4 equiv) in 2.0 mL of CH_3CN at 50 °C for 2-4 h, then step II: *ortho*-alkynyl aryl iodide **2a** (0.20 mmol), [Pd] *cat.* (7.5 mol%), ligand (15 mol%), and MeOH (0.20 mL), 50 °C, 2-4 h. [b] $Pd(MeCN)_2Cl_2$ was used instead of $Pd(PPh_3)_2Cl_2$. [c] toluene instead of CH_3CN. [d]1,4-dioxane instead of CH_3CN. MePhos = 2-(dicyclohexylphosphino)-2'-methylbiphenyl.

In a first stage, various different phosphine ligands were evaluated in the three-component reaction in the absence of extra [Pd] additive in CH_3CN. Phosphine ligands PAr_3 only resulted in low yield of product **3a** (Table S1, entries 1-4). Pleasingly, when Buchwald-type ligand was added, the reaction was drastically accelerated within only 2-2.5 h, and **3a** was formed in 60% yield when MePhos was utilized (entries 5-6). Variation of extra [Pd] catalyst (entries 8-13) showed that $Pd(MeCN)_2Cl_2$ gave the best yield of the desired product (entry 12). The use of a Pd^0 catalyst did not offer any improvement (entry 11). Nevertheless, $Pd(MeCN)_2Cl_2$ and

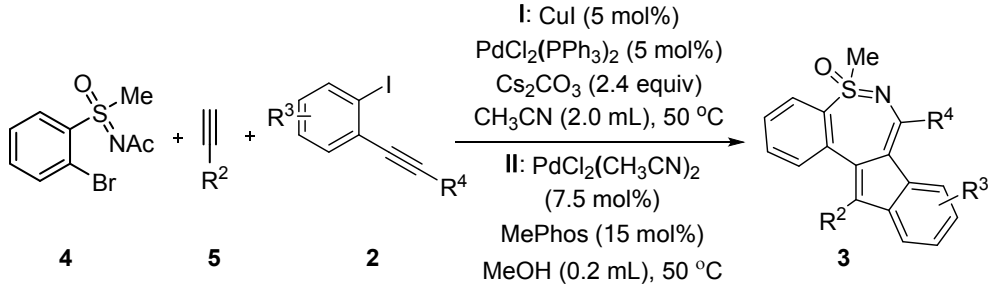
$Pd(PhCN)_2Cl_2$ exhibited satisfied catalytic efficiency, affording the product **3a** in 77% and 70% yields, respectively (entries 12-13). The importance of $Pd(PPh_3)_2Cl_2$ in the first step was confirmed as only low yield of **3a** was formed by replacing it with $Pd(MeCN)_2Cl_2$ as the sole catalyst (entry 14). The reaction did not proceed when organic base was used (entries 15-16), and the other bases, such as K_2CO_3, MeONa, and *t*BuONa, were inferior than Cs_2CO_3 (entries 17-19). The solvent screening indicated that CH_3CN was an optimal medium for this reaction (entries 20-21).

Scheme S1. Proposed mechanism.

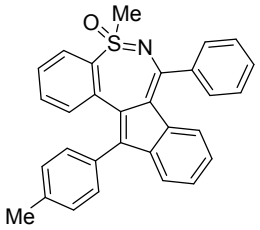


Oxidative addition of Pd^0 to 2-alkynyliodobenzene **2a** firstly occurred to generate a Pd^{II} intermediate **A**, which underwent intermolecular coordination and *syn*-insertion into a triple bond of **1c** to give Pd^{II}-complex **B**. Subsequently, the second intramolecular coordination and *syn*-insertion of Pd^{II} species in **B** with the adjacent triple bond would be expected to give a new Pd^{II}-complex **C**. The N atom could coordinate with electrophilic Pd-center in **C** species. And an intramolecular σ-metathesis of ArPd-I with *N*-Ac could be facilitated through this coordination to generate the octa-palladacycle **D** and Ac-I. The reaction of Ac-I with MeOH under the assistance of base would deliver the byproduct AcOMe. And the reductive elimination reaction of **D** could be realized to give the desired product **3a**, and meanwhile re-generate the active Pd^0 species to complete the catalytic cycle. It should be noted that several competitive reactions were observed in this protocol: (1) Pd-catalyzed cyclizations of **1c** would give the undesired compound 1,2-benzothiazine; and (2), direct annulation of **B** would give the un-cyclized 1,2-benzoisothiazole derivative **E**.

2. Three-component synthesis of medium-sized sulfoximines.



To a screw capped schlenk tube equipped with a stir bar was charged with *ortho*-bromophenylsulfoximine **4** (0.26 mmol), $PdCl_2(PPh_3)_2$ (7.0 mg, 5 mol%), CuI (2.9 mg, 5 mol%), Cs_2CO_3 (156 mg) in anhydrous CH_3CN (2.0 mL) was added terminal alkyne **5** (0.26 mmol) dropwise slowly at 50°C. The reaction was stirred at 50°C for an additional 4 h. The reaction was allowed to cool to room temperature, and then 2-ethynyl iodobenzene **2** (0.20 mmol), $Pd(MeCN)_2Cl_2$ (10 mol%), Mephos (15 mol%), CH_3OH (0.20 mL) were added subsequently. The resulting yellow solution was stirred at 50 °C for an additional 2-3 h under N_2. Upon completion of the reaction as indicated by TLC, the reaction was cooled to room temperature, diluted with ethyl acetate (5.0 mL), then filtered through a short pad of silica. The solid residue was washed with ethyl acetate (~15 mL) unless otherwise noted. The concentrated crude residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether/dichloromethane = 1: 20:2, *v/v/v.*) to afford the product **3** .



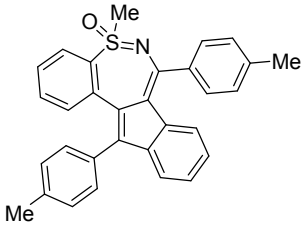
5-Methyl-7-phenyl-12-(*p*-tolyl)-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3a**.

Yield 77%, 68.6 mg; red solid; mp: 241-243 °C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.79-7.73 (m, 2H), 7.53-7.49 (m, 3H), 7.39-7.35 (m, 1H), 7.30-7.24 (m, 5H), 7.19-7.12 (m, 3H), 6.95-6.91 (m, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 3.29 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.3, 140.5, 139.1, 138.5, 137.9, 137.8, 137.1, 136.3, 134.9, 134.4, 133.2, 133.0, 130.5, 130.5, 130.2, 130.0, 127.2, 124.4, 124.3, 124.0, 122.1, 120.0, 100.0, 36.5, 21.4.

HRMS (ESI) calculated for $C_{30}H_{24}NOS$ $[M+H]^+$: 446.1573, found: 446.1570.

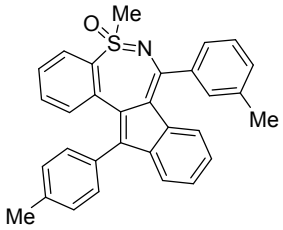


5-Methyl-7,12-di-p-tolyl-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3b**.

Yield 78%, 71.6 mg; red solid; mp: 245-247 ^oC.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 1H), 7.71-7.62 (m, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.39-7.35 (m, 2H), 7.30-7.24 (m, 4H), 7.19-7.12 (m, 4H), 6.96-6.93 (m, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 3.26 (s, 3H), 2.45 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.7, 140.8, 138.0, 137.9, 137.7, 137.7, 137.0, 136.4, 135.0, 134.4, 133.3, 132.9, 130.5, 130.2, 129.6, 127.1, 124.4, 124.1, 123.9, 122.1, 119.9, 119.6, 36.6, 21.6, 21.4. **HRMS (ESI)** calculated for $C_{31}H_{26}NOS$ $[M+H]^+$: 460.1730, found: 460.1737.

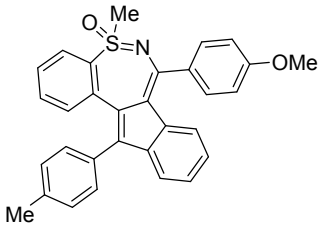


5-Methyl-7-(*m*-tolyl)-12-(*p*-tolyl)-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3c**.

Yield 66%, 60.6 mg; red solid; mp: 267-269 ^oC.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.63-7.50 (m, 3H), 7.40-7.36 (m, 1H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.29-7.13 (m, 8H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 3.29 (s, 3H), 2.49-2.30 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.6, 140.5, 138.3, 137.8, 137.0, 136.4, 135.0, 134.4, 133.3, 132.9, 131.2, 130.6, 130.5, 130.2, 129.6, 127.2, 124.4, 124.2, 124.0, 122.1, 119.9, 36.5, 34.7, 21.4. **HRMS (ESI)** calculated for $C_{31}H_{26}NOS$ $[M+H]^+$: 460.1730, found: 460.1735.

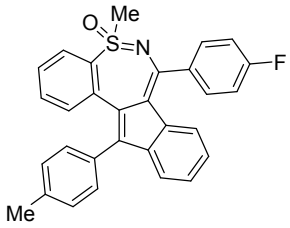


7-(4-Methoxyphenyl)-5-methyl-12-(*p*-tolyl)-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3d**.

Yield 80%, 76.1 mg; red solid; mp: 267-269 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.82-7.68 (m, 2H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.39-7.35 (m, 1H), 7.30-7.25 (m, 5H), 7.19-7.13 (m, 3H), 7.07 (s, 1H), 6.98-6.94 (m, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 3.89 (s, 3H), 3.25 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.9, 156.4, 138.0, 137.6, 137.5, 136.9, 136.4, 135.0, 134.4, 133.4, 132.9, 132.8, 130.5, 130.2, 129.5, 127.0, 124.3, 124.0, 123.8, 122.0, 119.8, 55.5, 36.6, 21.4. **HRMS (ESI)** calculated for $C_{31}H_{26}NO_2S$ $[M+H]^+$: 476.1679, found: 476.1679.

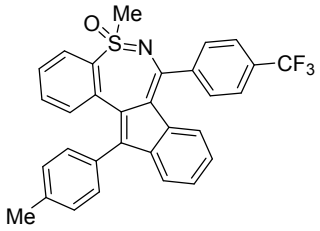


7-(4-Fluorophenyl)-5-methyl-12-(*p*-tolyl)-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3e**.

Yield 67%, 62.7 mg; red solid; mp: 251-253 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.73 (m, 1H), 7.82-7.73 (m, 2H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.41-7.35 (m, 1H), 7. 29-7.25 (m, 4H), 7.20-7.14 (m, 4H), 7.03-6.95 (m, 2H), 6.70 (d, *J* = 8.1 Hz, 1H), 3.28 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4 (d, ^1J = 251 Hz), 155.0, 139.8, 139.1, 138.6, 138.5, 137.9, 137.8, 137.1, 136.6, 136.2, 134.8, 134.4, 133.1, 133.0, 130.4, 130.2, 129.6, 127.2, 124.4, 124.2 (d, ^2J = 27 Hz), 121.9, 120.4, 36.6, 21.4. **HRMS (ESI)** calculated for $C_{30}H_{23}FNOS$ $[M+H]^+$: 464.1479, found: 464.1484.

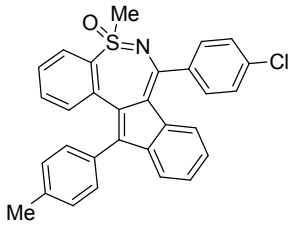


5-Methyl-12-(*p*-tolyl)-7-(4-(trifluoromethyl)phenyl)-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3f**.

Yield 59%, 60.5 mg; red solid; mp: 260-262 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.90-7.88 (m, 2H), 7.71-7.62 (m, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.39-7.37 (m, 1H), 7.30-7.15 (m, 8H), 6.98-6.94 (m, 1H), 6.61 (d, *J* = 8.1 Hz, 1H), 3.32 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.9, 144.1, 139.5, 138.2, 137.7, 137.4, 135.9, 134.7, 134.4, 133.1, 132.9, 132.2, 131.9, 130.3, 130.1, 129.7, 127.4, 125.5, 124.8, 124.4 (q, $^1J_{C\text{-}F}$ = 271 Hz), 122.8, 121.9, 120.5, 120.3, 36.6, 21.4. **HRMS (ESI)** calculated for $C_{31}H_{23}F_3NOS$ $[M+H]^+$: 514.1447, found: 514.1443. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.43 (s).

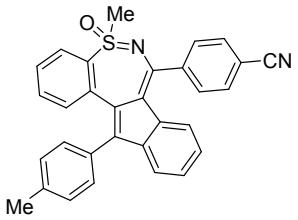


7-(4-Chlorophenyl)-5-methyl-12-(*p*-tolyl)-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3g**.

Yield 66%, 63.4 mg; red solid; mp: 255-257 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.75-7.71 (m, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.39-7.36 (m, 1H), 7.28-7.14 (m, 9H), 6.99-6.96 (m, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 3.28 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.6, 139.1, 138.9, 138.8, 138.6, 138.0, 137.7, 137.2, 136.6, 136.1, 134.8, 134.4, 133.0, 130.4, 130.2, 129.6, 127.3, 124.5, 124.4, 124.2, 121.9, 120.1, 36.6, 21.4. **HRMS (ESI)** calculated for $C_{30}H_{23}ClNOS$ $[M+H]^+$: 480.1183, found: 480.1180.

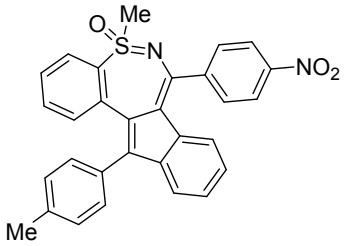


4-(5-Methyl-5-oxido-12-(*p*-tolyl)-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepin-7-yl)benzonitrile **3h**.

Yield 48%, 45.1 mg; red solid; mp: 220-222 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.89-7.85 (m, 2H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.42-7.37 (m, 1H), 7.32-7.16 (m, 9H), 6.98-6.94 (m, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 3.32 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.0, 145.0, 139.9, 138.4, 137.6, 137.5, 135.7, 134.5, 134.4, 133.2, 132.8, 131.1, 130.2, 130.1, 129.7, 129.3, 127.5, 125.0, 124.5, 121.8, 120.4, 118.6, 113.7, 36.6, 21.4. **HRMS (ESI)** calculated for $C_{31}H_{23}N_2OS$ $[M+H]^+$: 471.1526, found: 471.1525.

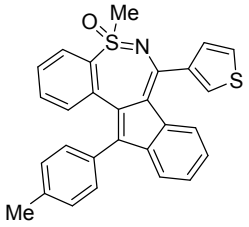


5-Methyl-7-(4-nitrophenyl)-12-(*p*-tolyl)-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3i**.

Yield 55%, 53.9 mg; brownness solid; mp: 218-220 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39-8.21 (m, 2H), 8.02-7.96 (m, 3H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.43-7.39 (m, 1H), 7.30-7.25 (m, 4H), 7.21-7.16 (m, 3H), 6.97-6.94 (m, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 3.34 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.4, 148.9, 146.8, 140.2, 138.4, 137.6, 135.7, 134.5, 134.4, 133.2, 132.7, 130.3, 130.2, 130.1, 129.7, 127.5, 125.1, 124.6, 124.5, 121.8, 121.2, 120.5, 36.7, 21.4. **HRMS (ESI)** calculated for $C_{30}H_{23}N_2O_3S$ $[M+H]^+$: 491.1424, found: 491.1420.

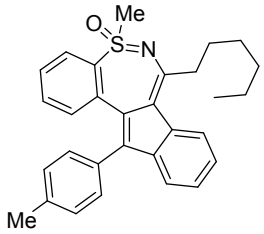


7-(4,5-Dihydrothiophen-3-yl)-5-methyl-12-(*p*-tolyl)-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3j**.

Yield 32%, 28.8 mg; red solid; mp: 288-290 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 1H), 7.84 (s, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 4.5 Hz, 1H), 7.39-7.34 (m, 2H), 7.29-7.25 (m, 4H), 7.19-7.15 (m, 3H), 7.03 (d, *J* = 3.7 Hz, 2H), 3.26 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.2, 138.0, 137.7, 137.0, 136.0, 134.9, 134.4, 133.2, 132.9, 130.2, 130.0, 129.6, 127.1, 125.4, 124.3, 124.0, 121.9, 120.0, 36.6, 21.4. **HRMS (ESI)** calculated for $C_{28}H_{22}NOS_2$ $[M+H]^+$: 452.1137, found: 452.1142.

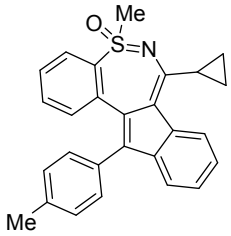


7-Hexyl-5-methyl-12-(*p*-tolyl)-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3k**.

Yield 64%, 58.4 mg; red solid; mp: 219-221 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.37-7.34 (m, 2H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.21-7.16 (m, 6H), 3.27-3.20 (m, 1H), 3.17 (s, 3H), 2.95-2.88 (m, 1H), 2.39 (s, 3H), 1.95-1.89 (m, 2H), 1.57-1.50 (m, 2H), 1.40-1.37 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.9, 138.2, 138.1, 137.6, 136.9, 135.1, 134.9, 134.8, 133.5, 132.7, 130.4, 129.6, 128.8, 127.1, 124.8, 124.2, 124.1, 121.9, 120.5, 119.3, 39.4, 36.0, 31.8, 29.6, 28.1, 22.7, 21.4, 14.1. **HRMS (ESI)** calculated for $C_{30}H_{32}NOS$ $[M+H]^+$: 454.2199, found: 454.2199.

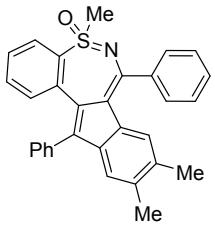


7-Cyclopropyl-5-methyl-12-(*p*-tolyl)-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3l**.

Yield 80%, 65.4 mg; yellow solid; mp: 228-230 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.35-7.31 (m, 2H), 7.28-7.26 (m, 1H), 7.24-7.18 (m, 6H), 3.07 (s, 3H), 2.75-2.73 (m, 1H), 2.39 (s, 3H), 1.76-1.75 (m, 1H), 1.34-1.29 (m, 1H), 0.95-0.92 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.4, 137.9, 137.6, 136.7, 136.1, 135.3, 135.0, 134.6, 133.7, 132.8, 130.4, 129.5, 129.4, 126.9, 124.3, 123.8, 122.1, 120.4, 119.3, 35.8, 21.4, 19.7, 11.4, 7.4. **HRMS (ESI)** calculated for $C_{27}H_{24}NOS$ $[M+H]^+$: 410.1573, found: 410.1579.

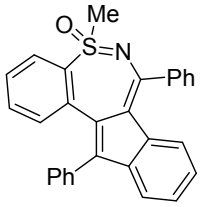


5,9,10-Trimethyl-7,12-diphenyl-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3m**.

Yield 82%, 74.3 mg; red solid; mp: 308-310 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 1H), 7.76 (s, 2H), 7.54-7.52 (m, 2H), 7.38-7.25 (m, 6H), 7.24-7.23 (m, 4H), 6.38 (s, 1H), 3.28 (d, *J* = 4.0 Hz, 3H), 2.24 (s, 3H), 2.05-2.04 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.3, 140.7, 138.6, 137.7, 136.6, 136.4, 134.9, 134.8, 134.7, 134.4, 133.3, 132.8, 130.3, 130.3, 130.1, 128.8, 127.3, 127.1, 124.4, 123.1, 120.4, 120.0, 36.4, 29.7, 20.5, 20.1. **HRMS (ESI)** calculated for $C_{31}H_{26}NOS$ $[M+H]^+$: 460.1730, found: 460.1739.

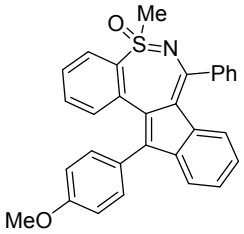


5-Methyl-7,12-diphenyl-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3n**.

Yield 77%, 66.5 mg; red solid; mp: 230-232 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 1H), 7.78-7.73 (m, 2H), 7.54-7.49 (m, 3H), 7.37-7.34 (m, 7H), 7.27-7.23 (m, 2H), 7.16-7.13 (m, 1H), 6.95-6.91 (m, 1H), 6.65 (d, *J* = 8.1 Hz, 1H), 3.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.7, 140.5, 138.4, 138.3, 137.8, 137.8, 136.4, 136.3, 134.7, 134.5, 133.0, 130.8, 130.7, 130.5, 130.4, 128.9, 127.3, 124.4, 124.3, 124.1, 122.1, 119.9, 36.5. **HRMS (ESI)** calculated for $C_{29}H_{22}NOS$ $[M+H]^+$: 432.1417, found: 432.1420.

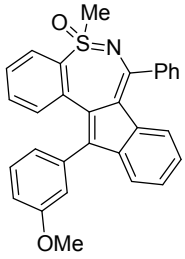


12-(4-Methoxyphenyl)-5-methyl-7-phenyl-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3o**.

Yield 76%, 70.2 mg; red solid; mp: 215-217 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 1H), 7.79-7.70 (m, 2H), 7.53-7.49 (m, 3H), 7.38-7.23 (m, 6H), 7.16-7.13 (m, 1H), 6.95-6.91 (m, 3H), 6.64 (d, *J* = 8.1 Hz, 1H), 3.84 (s, 3H), 3.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.0, 156.1, 140.6, 138.1, 138.0, 137.8, 136.3, 135.0, 134.4, 133.0, 131.5, 130.4, 130.2, 128.5, 127.1, 124.4, 124.3, 124.1, 122.1, 119.9, 114.4, 55.3, 36.5. **HRMS (ESI)** calculated for $C_{30}H_{24}NO_2S$ $[M+H]^+$: 462.1522, found: 462.1528.

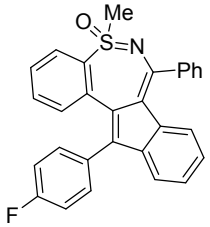


12-(3-Methoxyphenyl)-5-methyl-7-phenyl-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3p**.

Yield 48%, 44.3 mg; red solid; mp: 178-180 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 1H), 7.82-7.67 (m, 2H), 7.54-7.52 (m, 3H), 7.40-7.37 (m, 1H), 7.31-7.23 (m, 4H), 7.17-7.13 (m, 1H), 6.99-6.83 (m, 4H), 6.65 (d, *J* = 8.0 Hz, 1H), 3.79 (s, 3H), 3.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.9, 156.8, 140.5, 138.0, 137.8, 137.7, 136.3, 136.2, 134.7, 134.4, 133.1, 133.0, 130.9, 130.5, 129.9, 127.4, 124.4, 124.3, 124.0, 122.9, 122.8, 122.1, 119.9, 116.0, 112.6, 55.3, 36.4. **HRMS (ESI)** calculated for $C_{30}H_{24}NO_2S$ $[M+H]^+$: 462.1522, found: 462.1521.

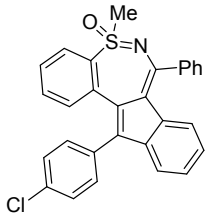


12-(4-Fluorophenyl)-5-methyl-7-phenyl-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3q**.

Yield 58%, 52.1 mg; red solid; mp: 240-242 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 1H), 7.79-7.72 (m, 2H), 7.55-7.51 (m, 2H), 7.47-7.45 (m, 1H), 7.42-7.38 (m, 2H), 7.34-7.28 (m, 3H), 7.25-7.23 (m, 1H), 7.18-7.14 (m, 1H), 7.11-7.07 (m, 2H), 6.96-6.92 (m, 1H), 6.66 (d, *J* = 8.1 Hz, 1H), 3.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.1 (d, ^1J = 246 Hz), 156.9, 140.4, 137.9, 137.6, 137.0, 136.2, 134.5, 134.3, 133.0, 132.3, 132.0, 131.9, 130.9, 130.6, 127.4, 124.5, 124.4, 124.2 (d, ^2J = 21 Hz), 122.1, 119.6, 116.1, 115.8 (d, ^2J = 21 Hz), 36.5. **HRMS (ESI)** calculated for $C_{29}H_{21}FNOS$ $[M+H]^+$: 450.1322, found: 450.1324. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.4.

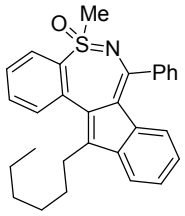


12-(4-Chlorophenyl)-5-methyl-7-phenyl-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3r**.

Yield 66%, 61.4 mg; red solid; mp: 216-218 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.73-7.59 (m, 2H), 7.54-7.51 (m, 2H), 7.47-7.35 (m, 5H), 7.32-7.29 (m, 3H), 7.24 (s, 1H), 7.17-7.14 (m, 1H), 6.96-6.93 (m, 1H), 6.66 (d, *J* = 8.1 Hz, 1H), 3.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.1, 140.3, 137.3, 136.6, 136.5, 136.2, 134.9, 134.8, 134.5, 134.4, 133.2, 133.1, 131.7, 131.6, 131.0, 130.7, 129.1, 127.5, 124.4, 124.2, 122.2, 119.5, 36.4. **HRMS (ESI)** calculated for $C_{29}H_{21}ClNOS$ $[M+H]^+$: 466.1027, found: 466.1023.

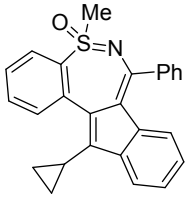


12-Hexyl-5-methyl-7-phenyl-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3s**.

Yield 78%, 68 mg; red solid; mp: 224-226 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.72-7.66 (m, 4H), 7.53-7.46 (m, 4H), 7.30 (s, 1H), 7.20-7.16 (m, 1H), 6.92-6.88 (m, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 3.06-3.04 (m, 3H), 3.03-2.98 (m, 1H), 2.94-2.87 (m, 1H), 1.90-1.82 (m, 1H), 1.74-1.67 (m, 1H), 1.48-1.42 (m, 2H), 1.34-1.30 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.3, 140.6, 138.7, 138.6, 138.2, 136.2, 135.0, 133.5, 132.4, 131.1, 130.2, 128.9, 127.9, 127.4, 124.7, 124.1, 123.9, 121.8, 120.2, 119.0, 36.9, 31.6, 30.5, 29.9, 26.9, 22.7, 14.2. **HRMS (ESI)** calculated for $C_{29}H_{30}NOS$ $[M+H]^+$: 440.2043, found: 440.2047.

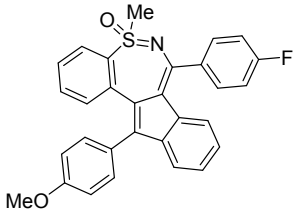


12-Cyclopropyl-5-methyl-7-phenyl-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3t**.

Yield 61%,48.2 mg; red solid; mp: 230-232 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.02 (m, 2H), 7.78-7.64 (m, 4H), 7.55-7.48 (m, 3H), 7.32 (s, 1H), 7.23-7.19 (m, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 3.03 (s, 3H), 2.19-2.17 (m, 1H), 1.23-1.16 (m, 2H), 0.84-0.82 (m, 1H), 0.55-0.52 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 140.6, 139.3, 139.1, 137.2, 135.8, 135.7, 134.4, 134.3, 133.8, 132.8, 132.7, 132.4, 130.2, 127.5, 124.2, 124.1, 123.9, 121.8, 119.4, 36.6, 9.5, 9.0, 7.8. **HRMS (ESI)** calculated for $C_{26}H_{22}NOS$ $[M+H]^+$: 396.1417, found: 396.1419.



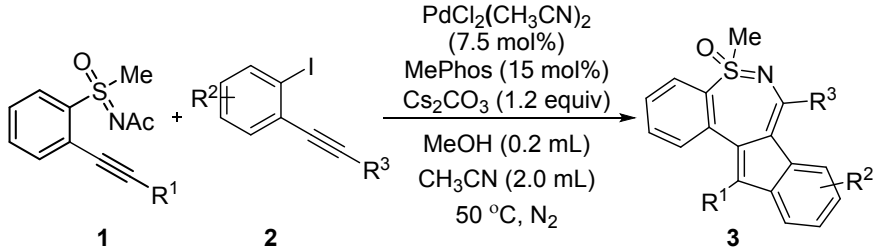
7-(4-Fluorophenyl)-12-(4-methoxyphenyl)-5-methyl-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3u**.

Yield 49%, 47.0 mg; red solid; mp: 287-289 ^{o}C.

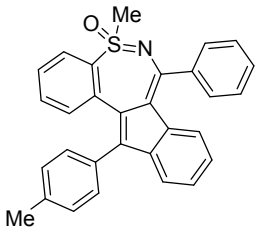
Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.83-7.71 (m, 2H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.40-7.36 (m, 1H), 7.29-7.15 (m, 6H), 7.03-6.92 (m, 4H), 6.70 (d, *J* = 8.1 Hz, 1H), 3.86 (s, 3H), 3.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3 (d, ^1J = 249 Hz), 159.0, 154.8, 138.2, 138.0, 137.9, 137.8, 136.6, 136.5, 136.2, 134.9, 134.3, 133.0, 131.4, 131.3, 130.1, 128.4, 127.2, 124.4, 124.3, 121. 0 (d, ^2J = 19 Hz), 114.4, 55.3, 36.6. **HRMS (ESI)** calculated for $C_{30}H_{23}FNO_2S$ $[M+H]^+$: 480.1428, found: 480.1425. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.0.

3. Two-component synthesis of medium-sized sulfoximine heterocycles.



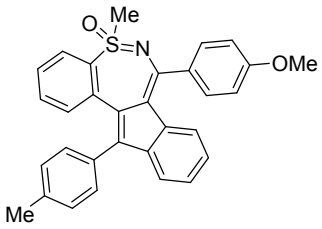
To a screw capped schlenk tube equipped with a stir bar was charged with *ortho*-alkynylphenylsulfoximine **1** (0.30 mmol) and 2-ethynyl iodobenzene **2** (0.36 mmol), $Pd(MeCN)_2Cl_2$ (7.5 mol%), Mephos (15 mol%), Cs_2CO_3 (1.2 equiv), CH_3OH (0.2 mL) and dry MeCN (2.0 mL). The reaction was purged with N_2 and stirred at 50℃ for 4 hours. The reaction was monitored by TLC. Upon completion, the reaction was allowed to cool to room temperature, diluted with ethyl acetate (5.0 mL), then filtered through a short pad of silica. The solid residue was washed with ethyl acetate (~15 mL) unless otherwise noted. Concentration of the filtrate under reduced pressure provided the crude product, which was purified by silica gel column chromatography (ethyl acetate/petroleum ether/ dichloromethane =1: 20: 2, *v/v/v*.) to afford the desired compound **3**.



5-Methyl-7-phenyl-12-(*p*-tolyl)-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3a**.

Yield 89%, 118.8 mg; red solid; mp: 241-243 °C.

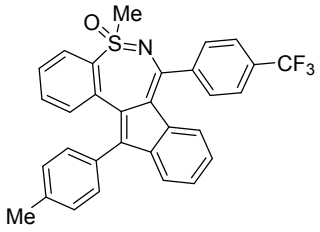
Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.



7-(4-Methoxyphenyl)-5-methyl-12-(*p*-tolyl)-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3d**.

Yield 90%, 126.8 mg; red solid; mp: 267-269 ^{o}C.

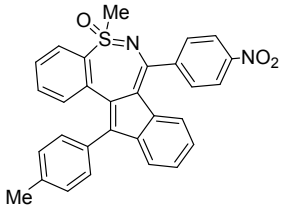
Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.



5-Methyl-12-(*p*-tolyl)-7-(4-(trifluoromethyl)phenyl)-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3f**.

Yield 70%, 107.7 mg; red solid; mp: 260-262 ^{o}C.

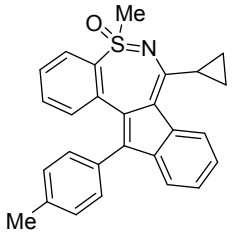
Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.



5-Methyl-7-(4-nitrophenyl)-12-(*p*-tolyl)-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3i**.

Yield 64%, 94 mg; brownness solid; mp: 218-220 ^{o}C.

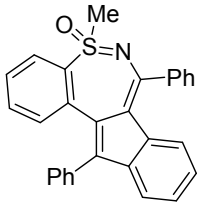
Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.



7-Cyclopropyl-5-methyl-12-(*p*-tolyl)-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3l**.

Yield 92%, 112.8 mg; yellow solid; mp: 228-230 ^{o}C.

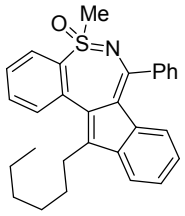
Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.



5-Methyl-7,12-diphenyl-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3n**.

Yield 95%, 122.8 mg; red solid; mp: 230-232 ^{o}C.

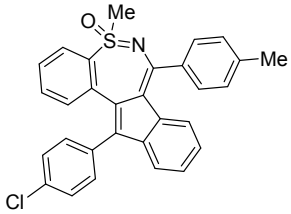
Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.



12-Hexyl-5-methyl-7-phenyl-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3s**.

Yield 93%, 122.4 mg; red solid; mp: 224-226 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

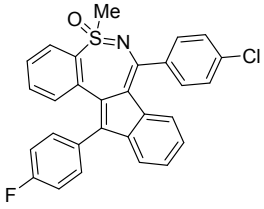


12-(4-Chlorophenyl)-5-methyl-7-(*p*-tolyl)-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3v**.

Yield 50%, 71.8 mg; red solid; mp: 280-282 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.7 Hz, 1H), 7.73-7.59 (m, 2H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.42-7.22 (m, 8H), 7.15 (t, *J* = 7.4 Hz, 2H), 6.98-6.94 (m, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 3.25 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 141.1, 137.9, 137.8, 137.4, 137.2, 136.3, 136.1, 135.0, 134.5, 134.4, 133.1, 133.0, 131.7, 131.6, 131.1, 129.1, 127.5, 124.5, 124.2, 124.0, 122.2, 119.5, 36.5, 21.7. **HRMS (ESI)** calculated for $C_{30}H_{23}ClNOS$ $[M+H]^+$: 480.1183, found: 480.1190.

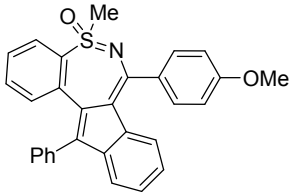


7-(4-Chlorophenyl)-12-(4-fluorophenyl)-5-methyl-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3w**.

Yield 60%, 86.9 mg; red solid; mp: 285-287 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.7 Hz, 1H), 7.78-7.67 (m, 2H), 7.53-7.39 (m, 4H), 7.32.7.28 (m, 3H), 7.22-7.16 (m, 2H), 7.11-7.07 (m, 2H), 7.01-6.97 (m, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 3.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2 (d, ^1J = 245 Hz), 155.3, 138.8, 137.9, 137.8, 137.7, 137.3, 137.2, 136.8, 135.9, 134.4, 134.3, 133.1, 132.2, 131.9, 130.7, 127.5, 127.6, 127.5, 124.4 (d, ^2J = 26 Hz), 122.0, 119.8, 116.0 (d, ^2J = 22 Hz), 36.5. **HRMS (ESI)** calculated for $C_{29}H_{20}ClFNOS$ $[M+H]^+$: 484.0933, found: 484.0929. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.1.

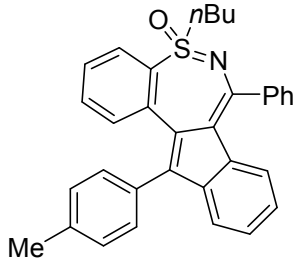


7-(4-Methoxyphenyl)-5-methyl-12-phenyl-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3x**.

Yield 92%, 127.2 mg; red solid; mp: 255-257 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.6 Hz, 1H), 7.77-7.74 (m, 2H), 7.52-7.50 (m, 1H), 7.37-7.22 (m, 8H), 7.17-7.12 (m, 1H), 7.06 (s, 1H), 6.99-6.95 (m, 1H), 6.86-6.84 (m, 2H), 3.88-3.87 (m, 3H), 3.24 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.9, 156.8, 138.0, 137.5, 137.4, 136.5, 136.4, 134.9, 134.5, 132.9, 132.8, 131.9, 130.8, 130.4, 128.8, 127.2, 124.4, 124.1, 123.8, 122.0, 119.8, 114.2, 113.3, 55.5, 36.6. **HRMS (ESI)** calculated for $C_{30}H_{24}NO_2S$ $[M+H]^+$: 462.1522, found: 462.1521.



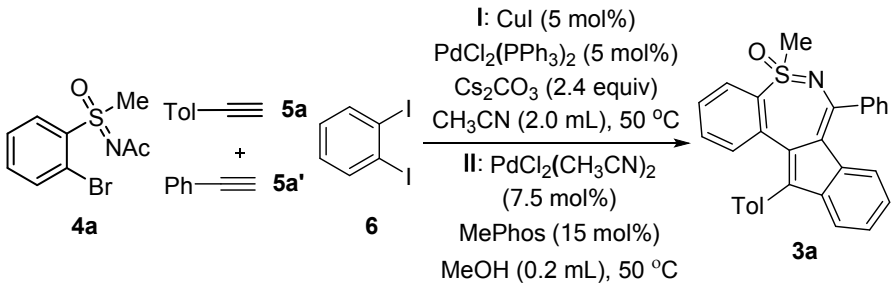
5-Butyl-7-phenyl-12-(*p*-tolyl)-5λ^4-benzo[*f*]indeno[1,2-*d*][1,2]thiazepine 5-oxide **3y**.

Yield 75%, 73.1 mg; red solid; mp: 256-258 ^{o}C.

Eluent: ethyl acetate/petroleum ether/ dichloromethane =1: 20:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.7 Hz, 1H), 7.83-7.69 (m, 2H), 7.55-7.69 (m, 3H), 7.38-7.35 (m, 1H), 7.29-7.18 (m, 7H), 7.15-7.11 (m, 1H), 6.93-6.90 (m, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 3.64-3.57 (m, 1H), 3.37-3.29 (m, 1H), 2.39 (s, 3H), 1.87-1.72 (m, 2H), 1.41-1.32 (m, 2H), 0.79 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.5, 140.7, 137.8, 137.0, 136.3, 135.0, 134.4, 133.4, 132.9, 132.6, 130.5, 130.5, 130.2, 129.9, 129.6, 128.9, 128.0, 127.3, 125.4, 124.1, 123.9, 122.1, 119.9, 119.8, 46.8, 23.8, 21.7, 21.4, 13.6. **HRMS (ESI)** calculated for $C_{33}H_{29}NOS$ $[M+H]^+$: 488.2043, found: 488.2048.

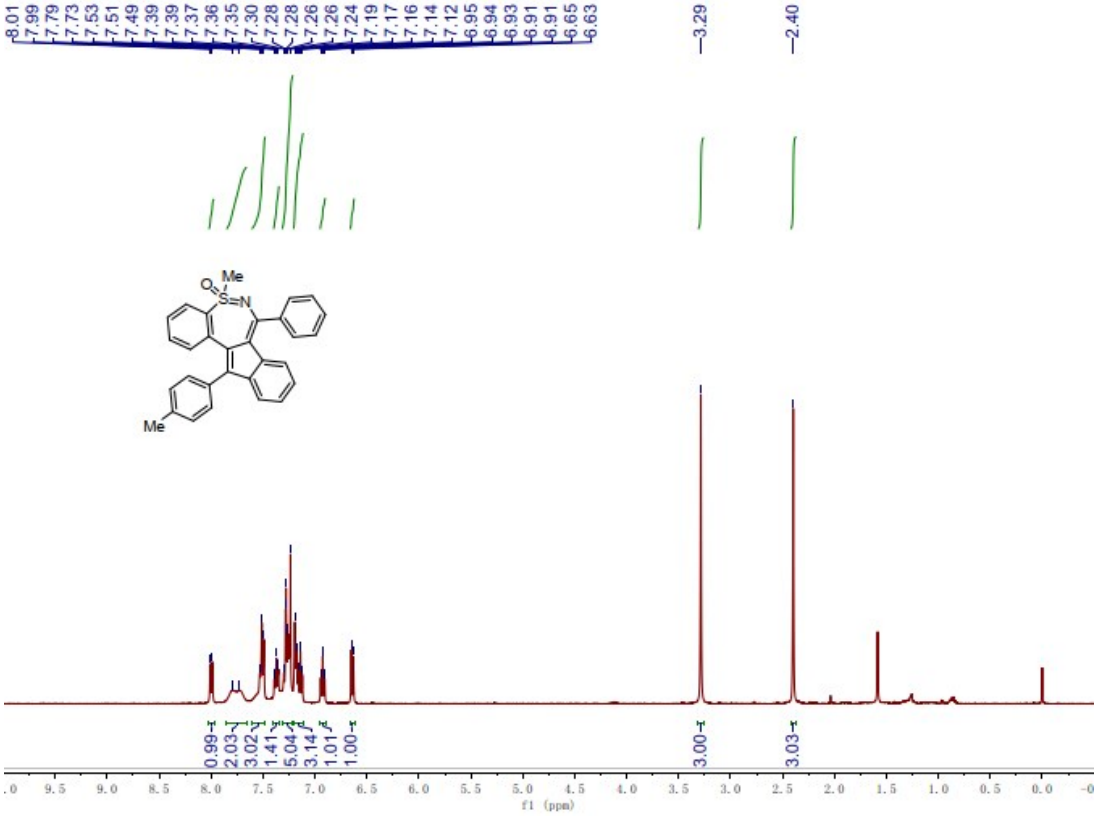
4. Four-component synthesis of medium-sized sulfoximine heterocycles.

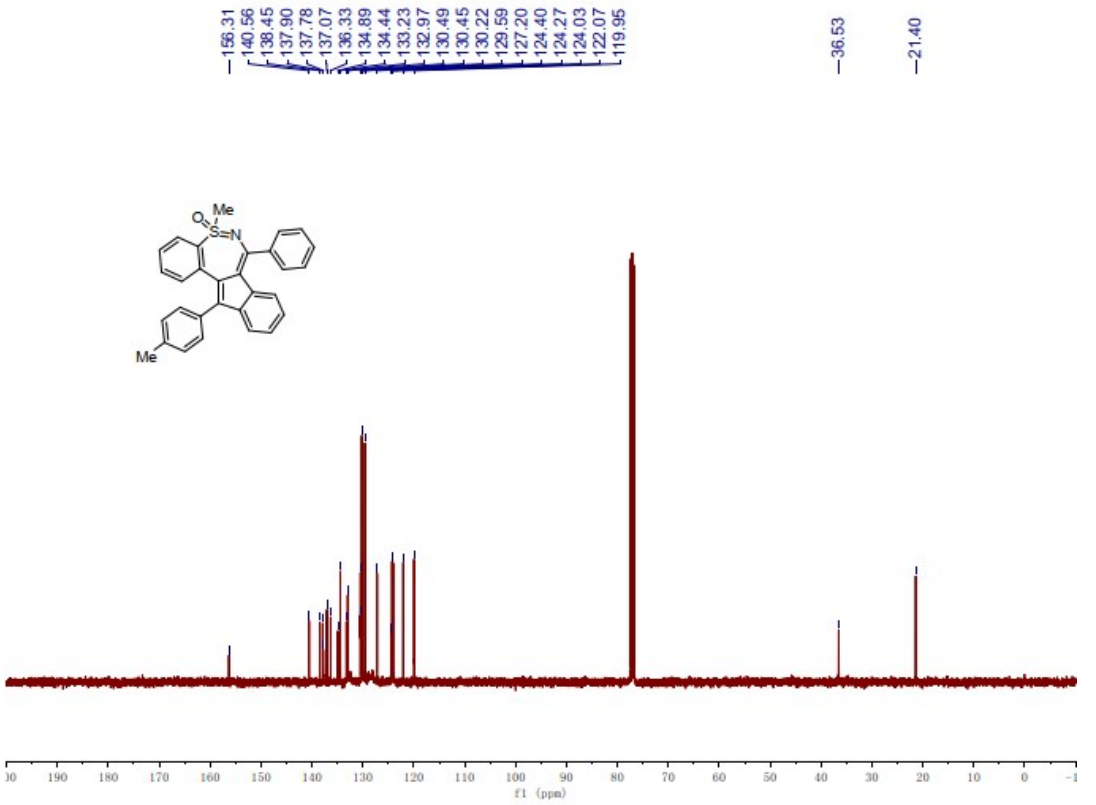


To a screw capped schlenk tube equipped with a stir bar was charged with ortho-bromophenylsulfoximine **4a** (0.30 mmol), $PdCl_2(PPh_3)_2$ (7.0 mg, 5 mol%), CuI (2.9 mg, 5 mol%), Cs_2CO_3 (156.7 mg, 2.4 equiv), dry CH_3CN (2.0 mL), and 1-ethynyl-4-methylbenzene **5a** (0.20 mmol) was added dropwise slowly at 50°C, and the stirred kept for an additional 4 h. Upon completion of the reaction as indicated by TLC, the reaction was allowed to cool to room temperature, then 1,2-diiodobenzene **6** (0.3 mmol), $Pd(MeCN)_2Cl_2$ (7.5 mol%), Mephos (15 mol%), CH_3OH (0.20 mL) were added subsequently, followed by the addition of ethynylbenzene **5a'** (0.3 mmol) drop wise slowly at 50°C. The reaction was stirred for 4 h under N_2. The reaction was monitored by TLC. Upon completion, the reaction was allowed to cool to room temperature, diluted with ethyl acetate (5.0 mL), then filtered through a short pad of silica. The solid residue was washed with ethyl acetate (~15 mL) unless otherwise noted. Concentration of the filtrate under reduced pressure provided the crude product, which was purified by silica gel column chromatography (ethyl acetate/petroleum ether/ dichloromethane =1: 20: 2, *v/v/v*.) to afford the desired compound **3a**, yield 31 mg, 35%.

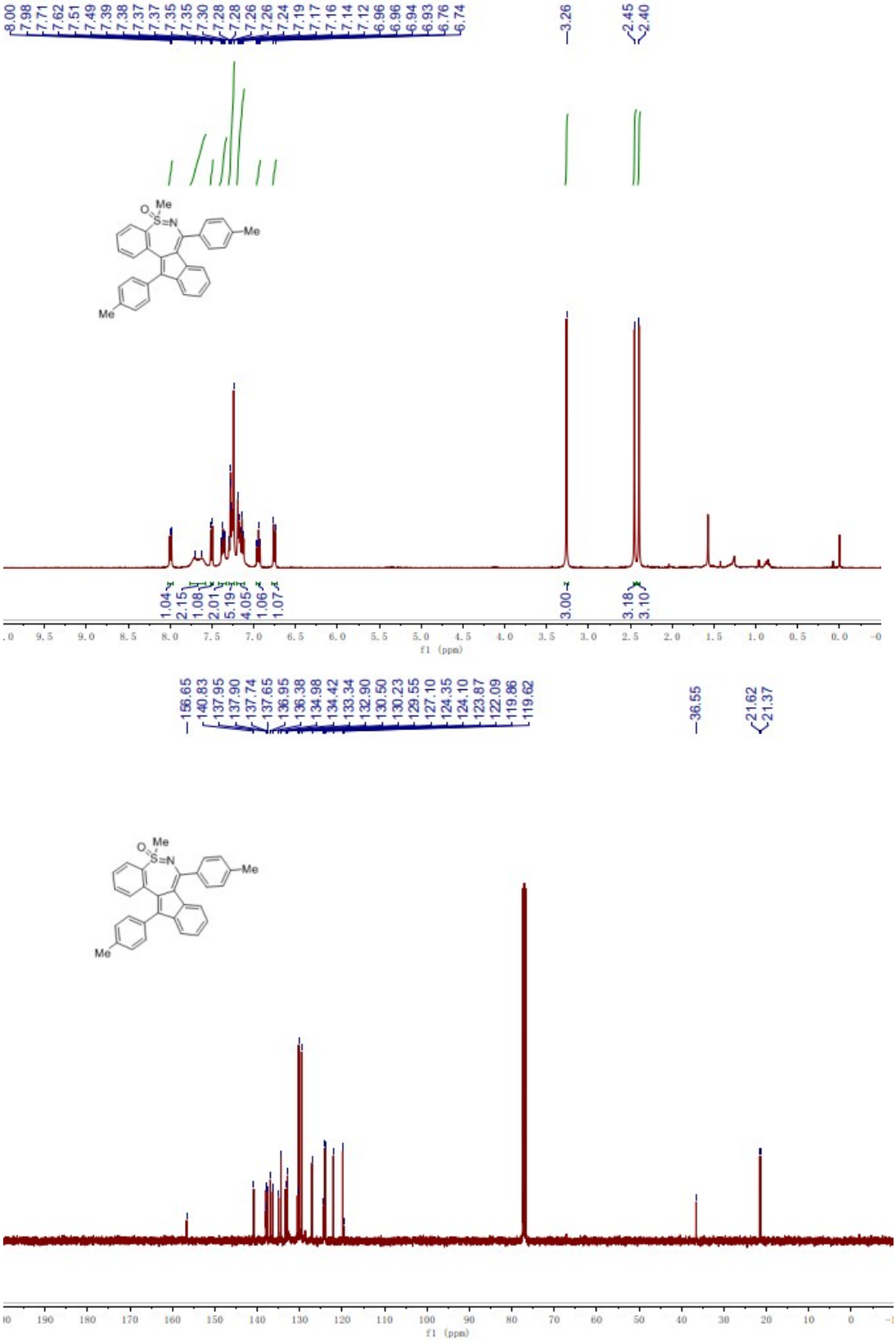
6. ^{1}H and ^{13}C NMR Spectra of all new compounds 3.

3a.





3b.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7.16
7.14
7.12
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6.96
6.94
6.93
6.76
6.74
3.26
2.45
2.40
Me
Me
Me
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2.15
1.08
2.01
5.19
4.05
1.06
1.07
3.00
3.18
3.10
f1 (ppm)
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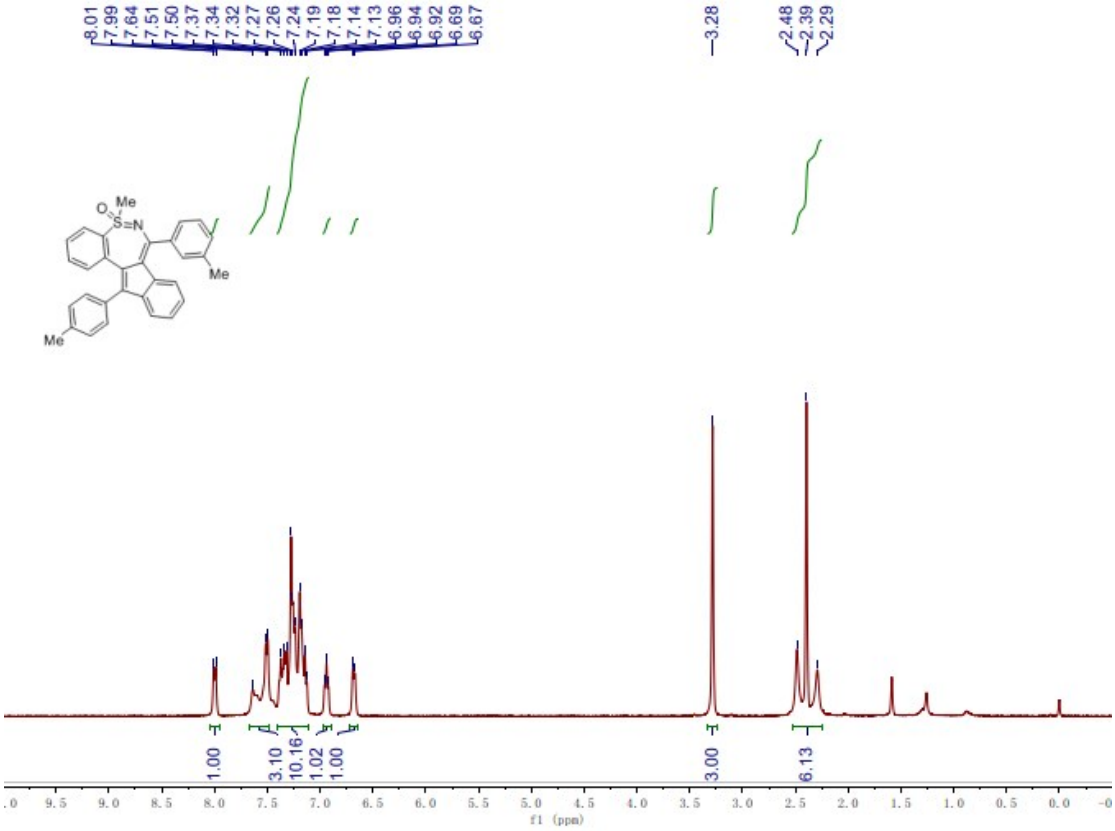
Me
f1 (ppm)

3c.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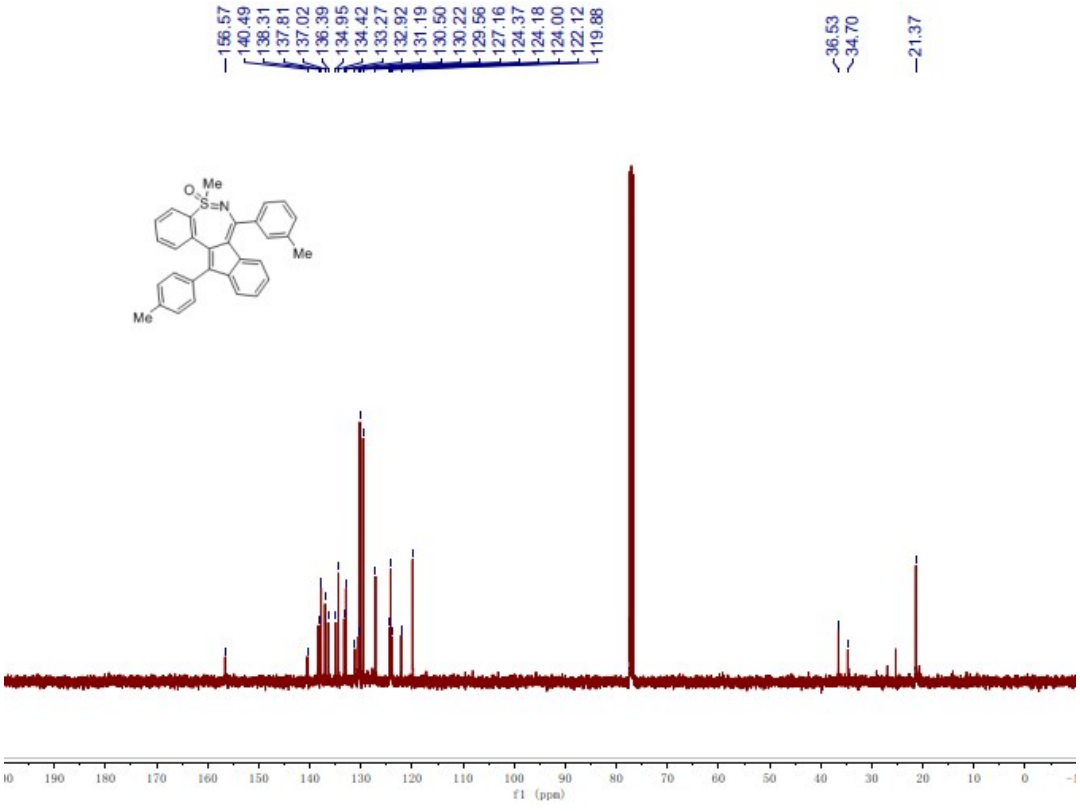
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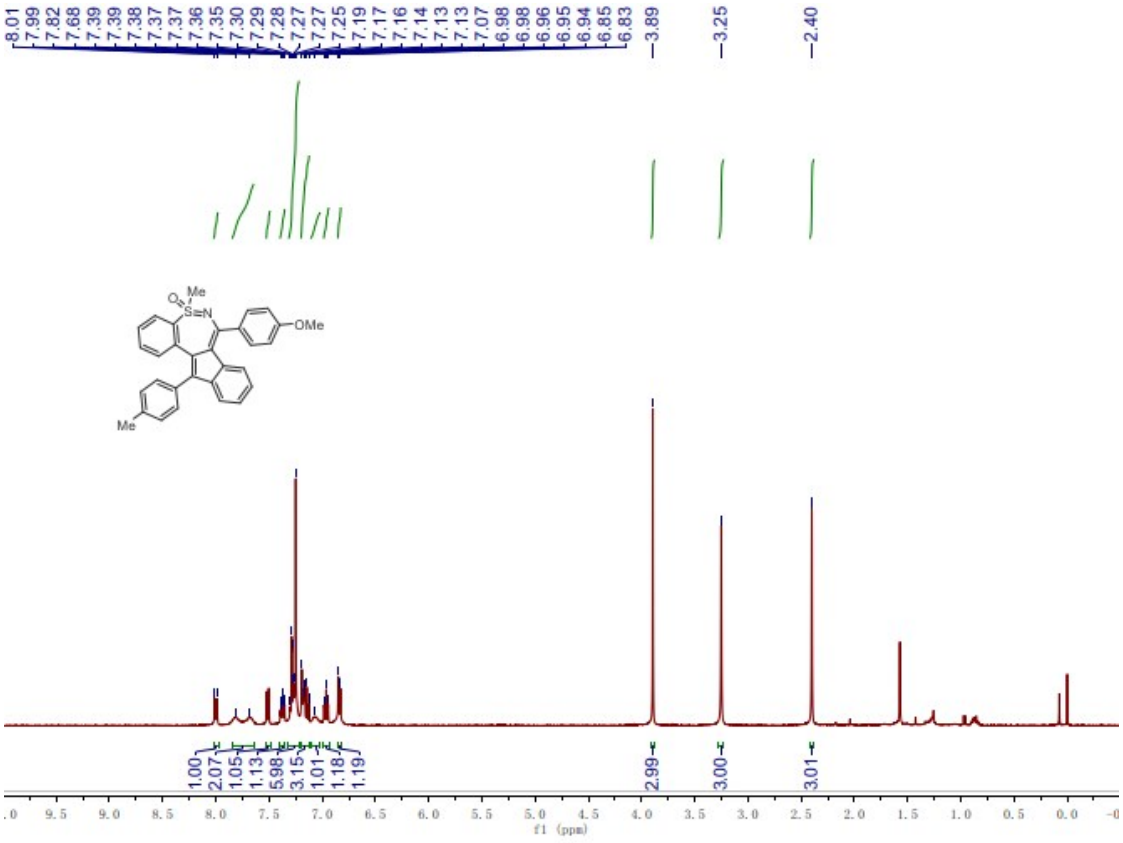
Me
f1 (ppm)

3d.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S
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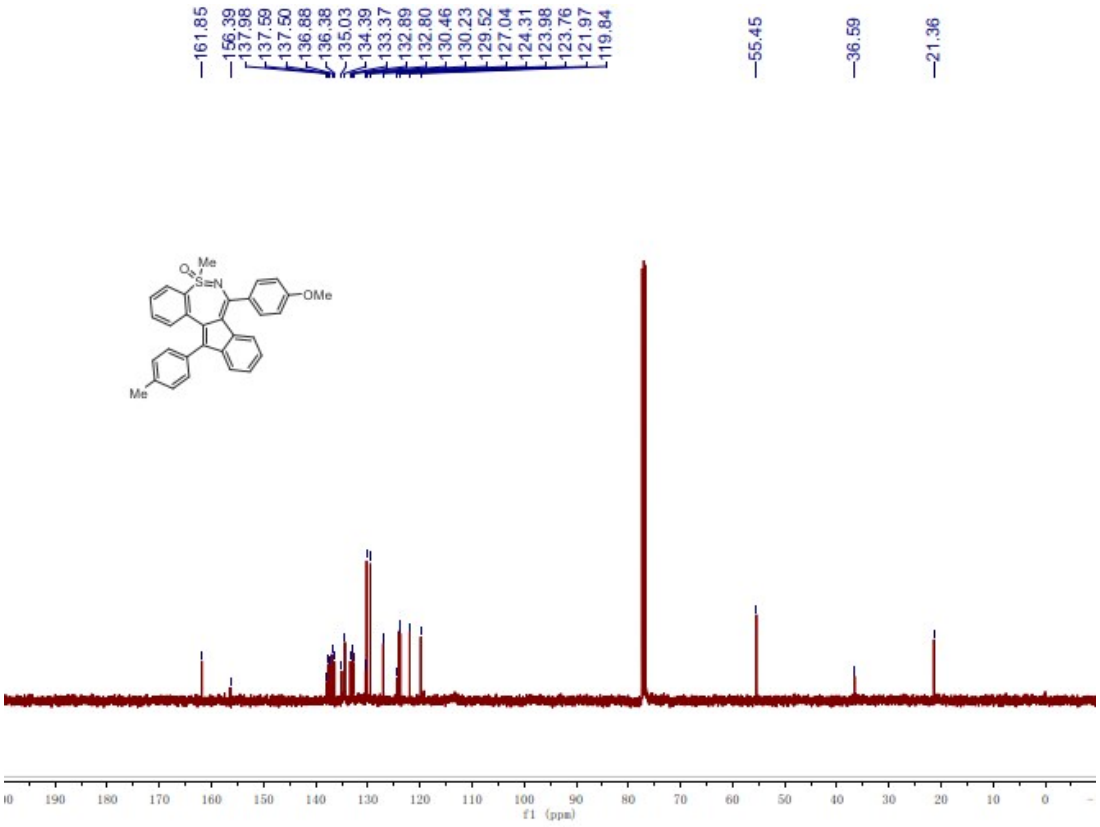
f1 (ppm)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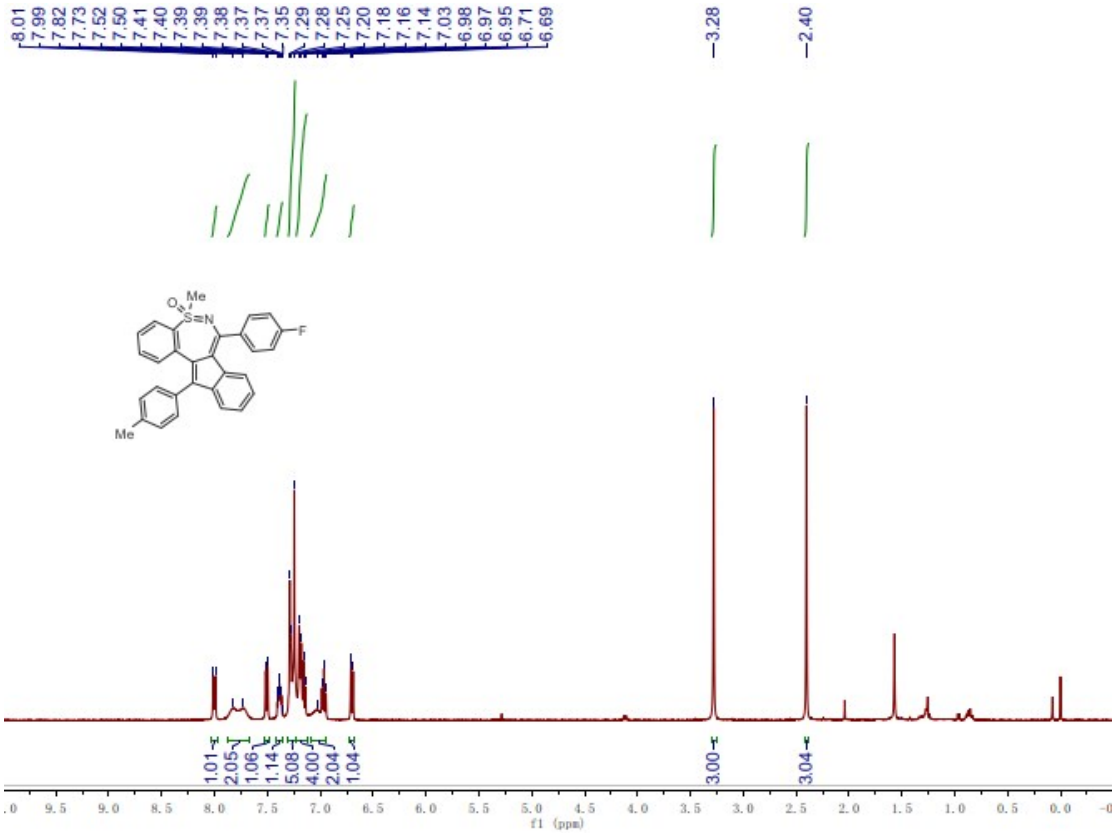
S
N
OMe
Me
f1 (ppm)

3e.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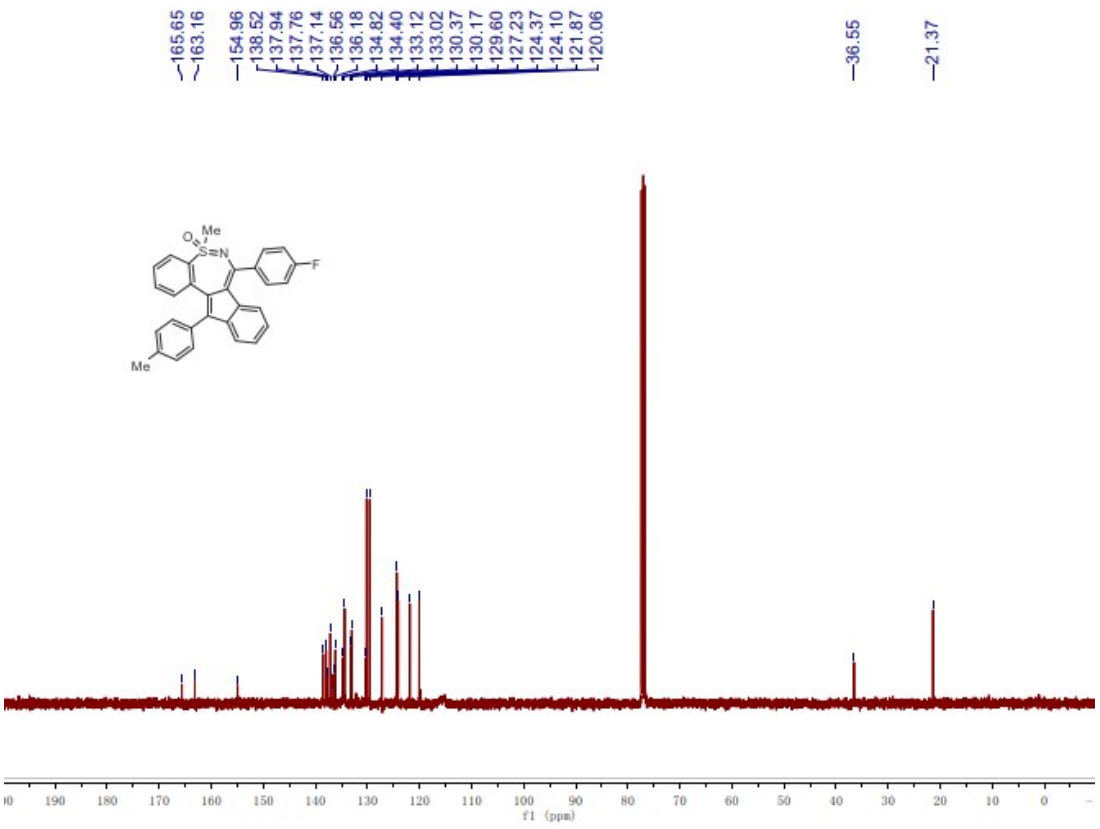
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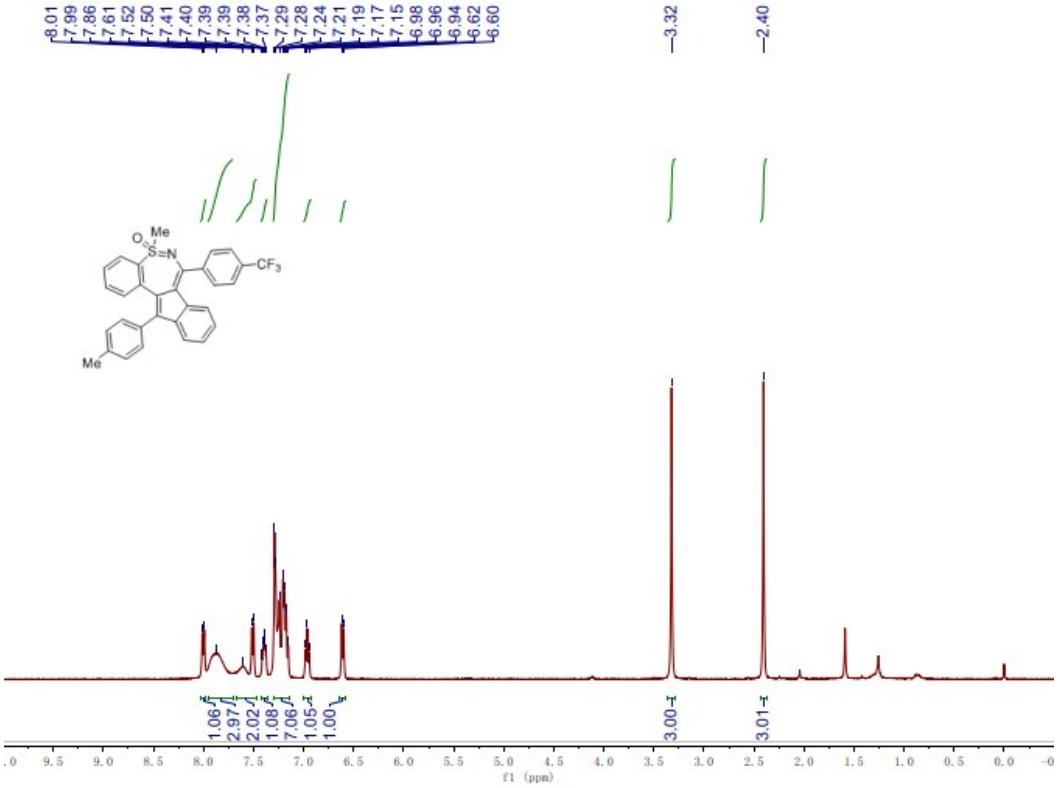
f1 (ppm)

3f.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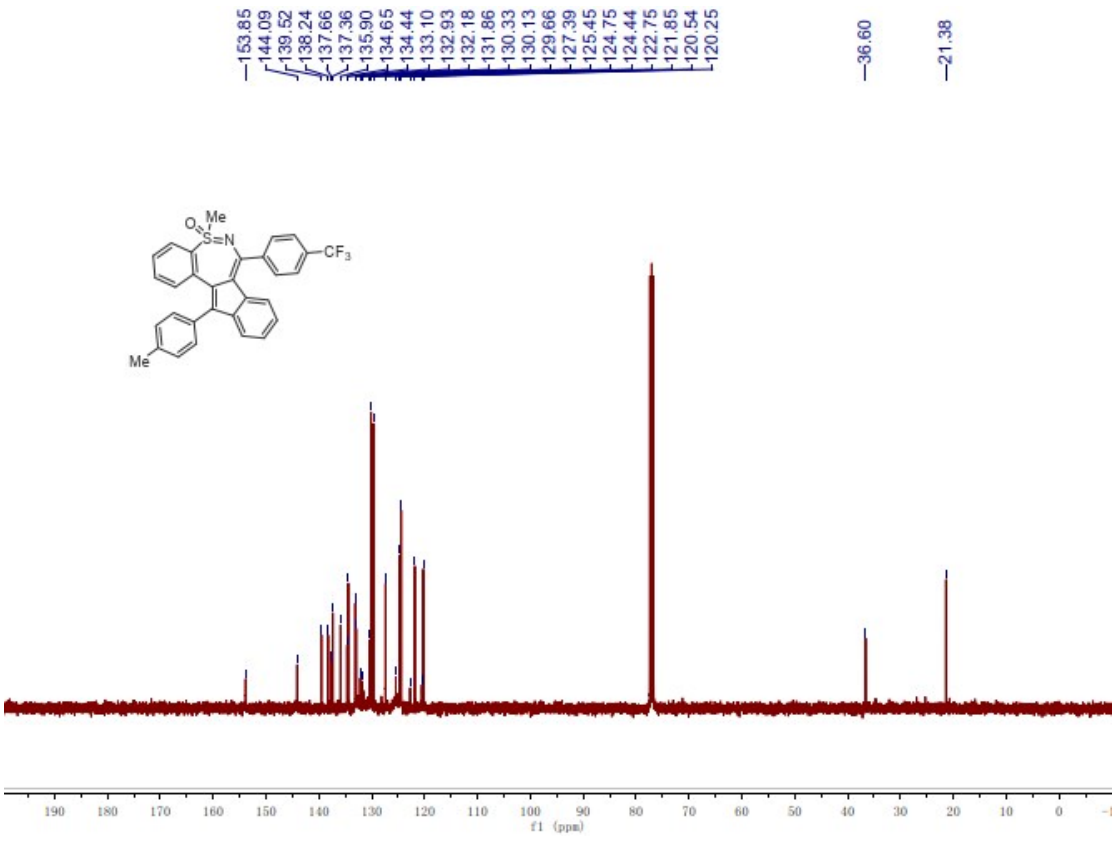
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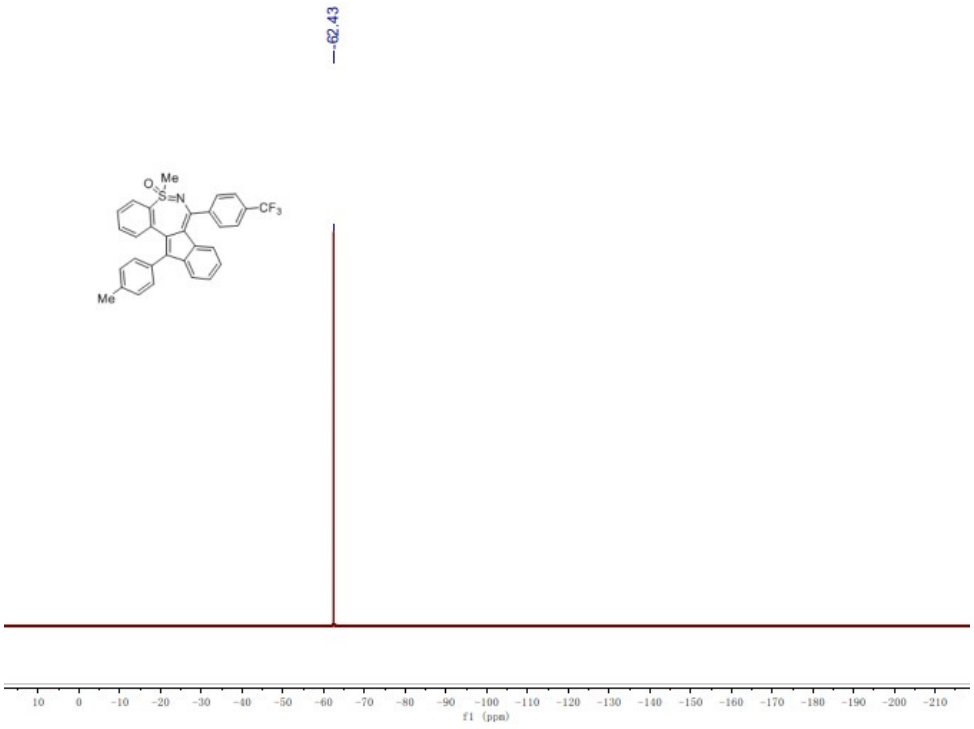
f1 (ppm)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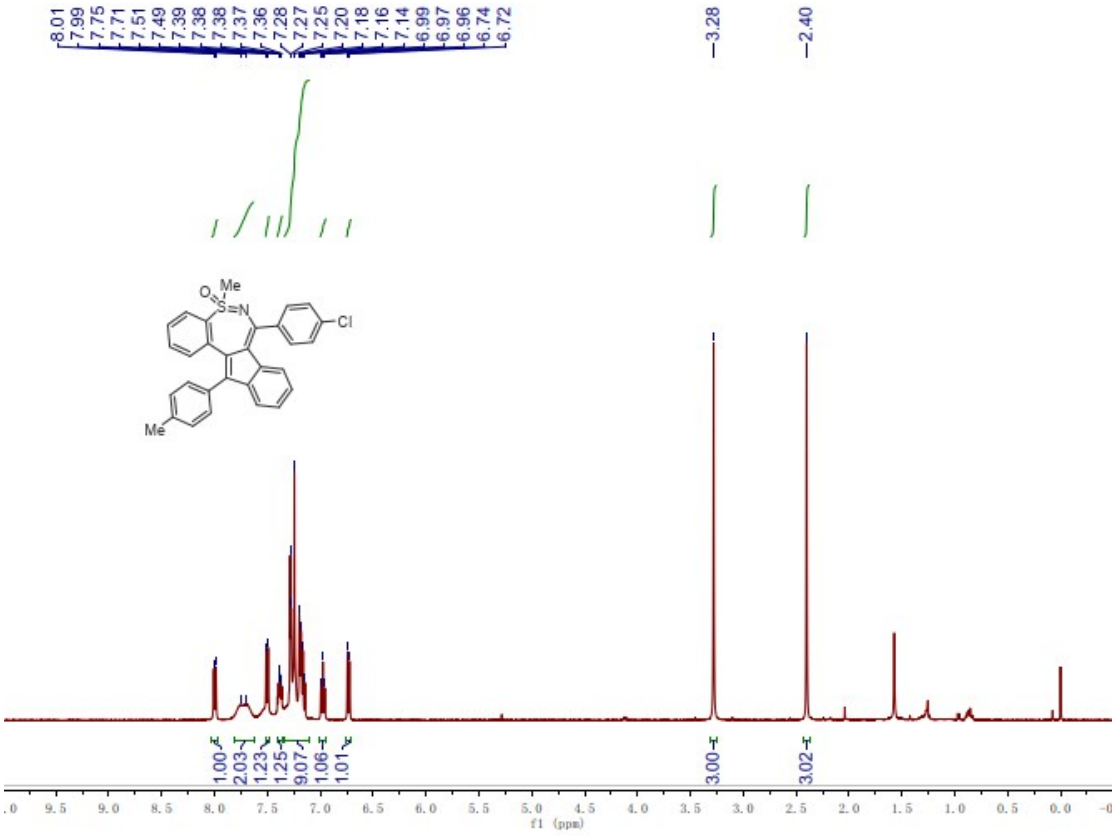
f1 (ppm)

3g.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6.96
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O
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Cl
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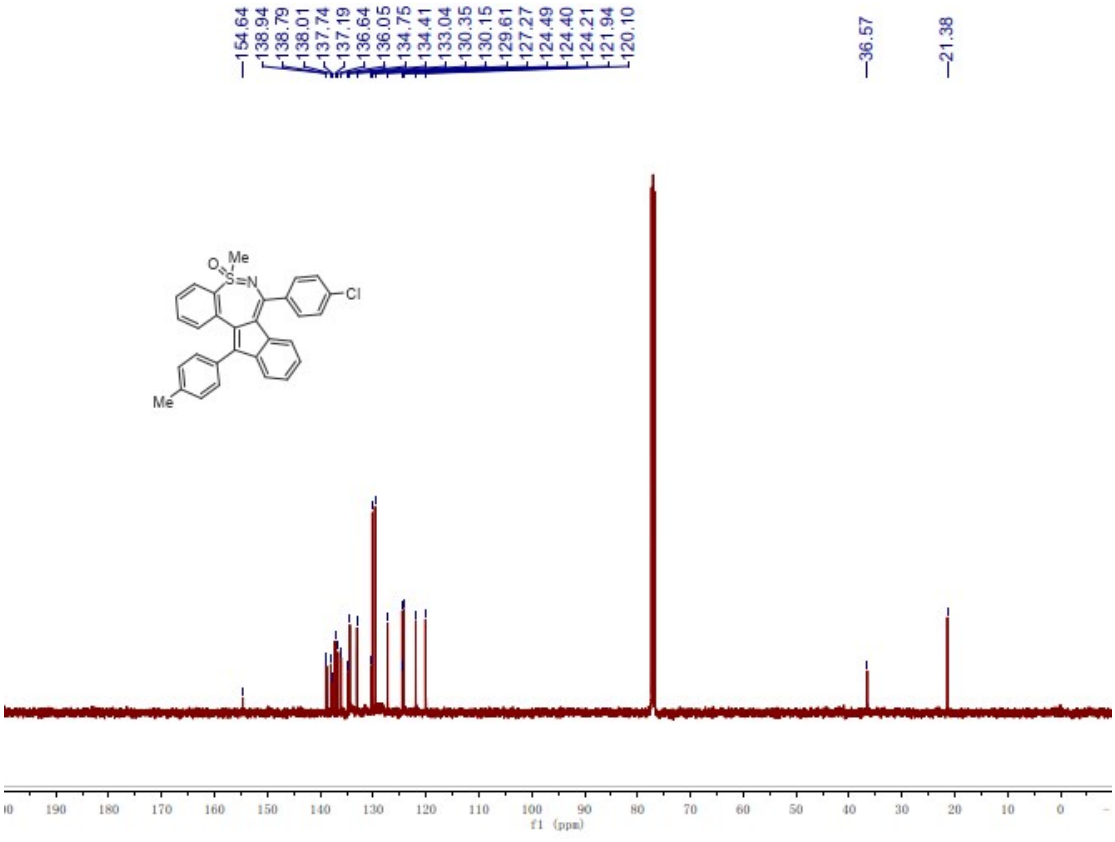
3.02
f1 (ppm)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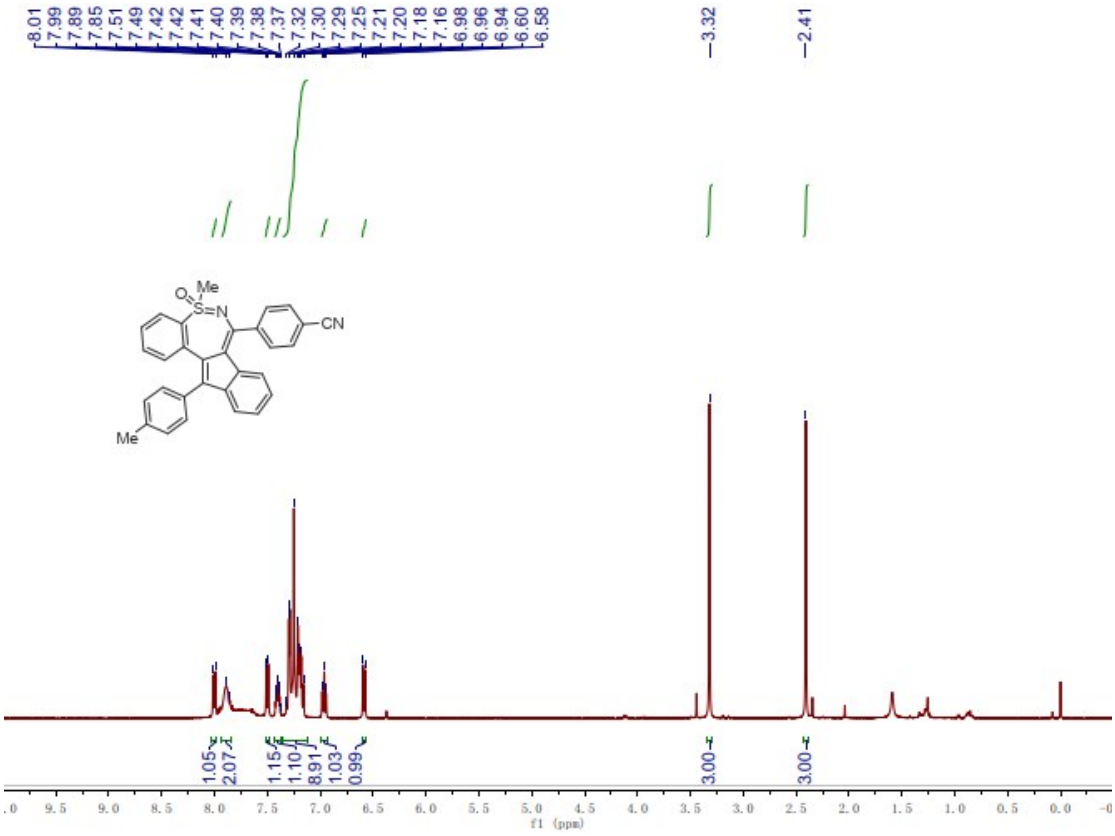
Me
O
S=N
Cl
Me
f1 (ppm)

3h.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7.18
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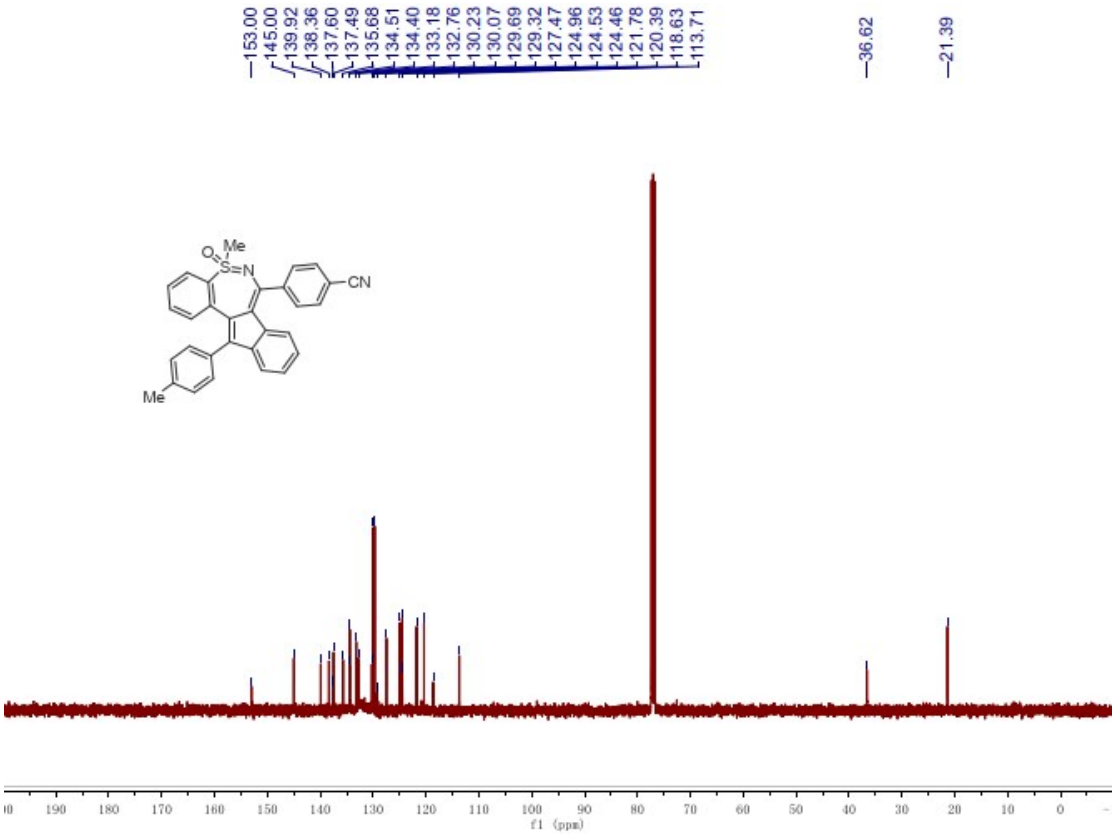
6.94
6.60
6.58
3.32
2.41
Me
O
S
N
CN
Me
1.05
2.07
1.15
1.10
8.91
1.03
0.99
3.00
3.00
f1 (ppm)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145.00
139.92
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137.49
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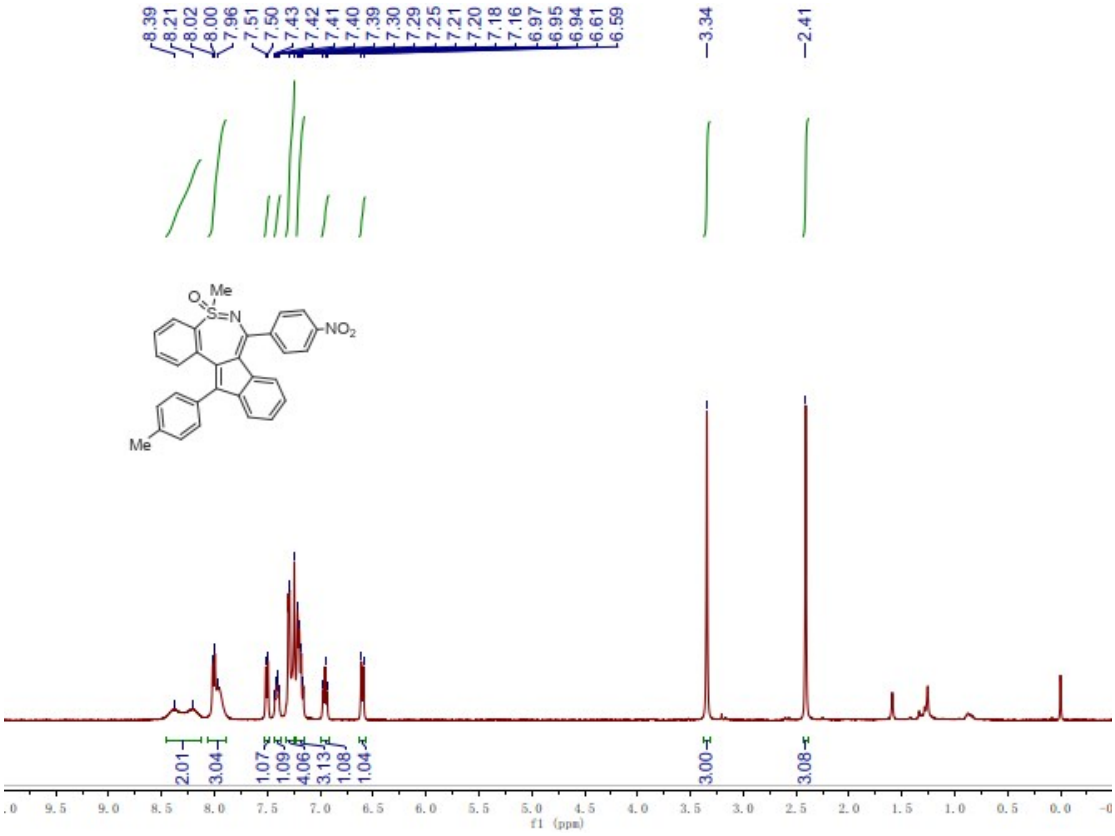
134.51
134.40
133.18
132.76
130.23
130.07
129.69
129.32
127.47
124.96
124.53
124.46
121.78
120.39
118.63
113.71
36.62
21.39
Me
O
S
N
CN
Me
f1 (ppm)

3i.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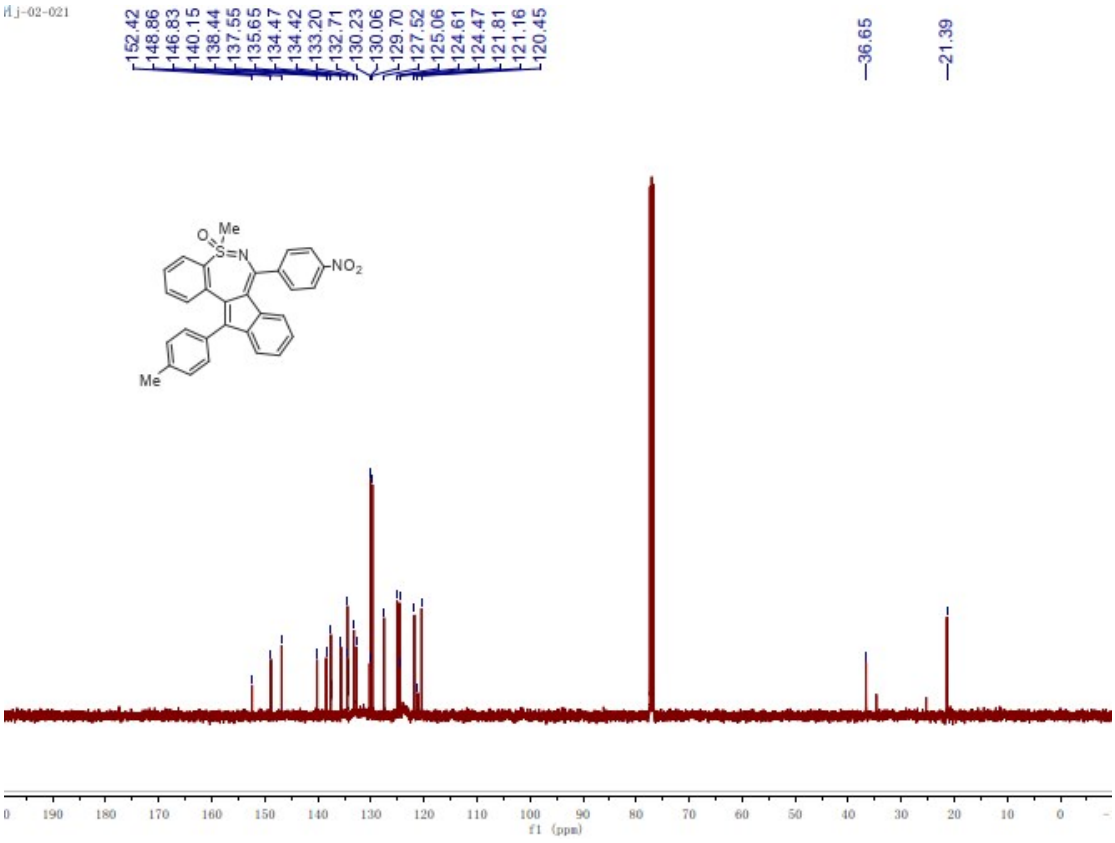
8.02
8.00
7.96
7.51
7.50
7.43
7.42
7.41
7.40
7.39
7.30
7.29
7.25
7.21
7.20
7.18
7.16
6.97
6.95
6.94
6.61
6.59
3.34
2.41
Me
O
S=N
NO2
Me
2.01
3.04
1.07
1.09
4.06
3.13
1.08
1.04
3.00
3.08
f1 (ppm)


Hj-02-021
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148.86
146.83
140.15
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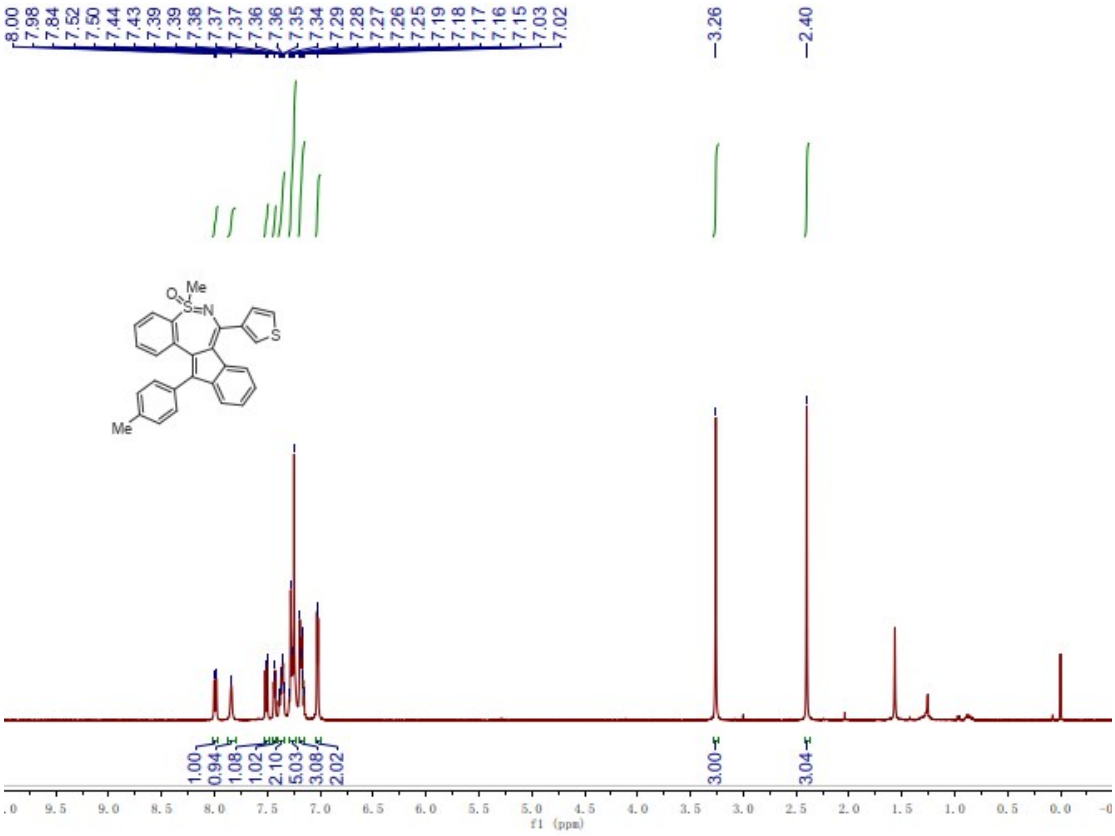
137.55
135.65
134.47
134.42
133.20
132.71
130.23
130.06
129.70
127.52
125.06
124.61
124.47
121.81
121.16
120.45
36.65
21.39
Me
O
S=N
NO2
Me
f1 (ppm)

3j.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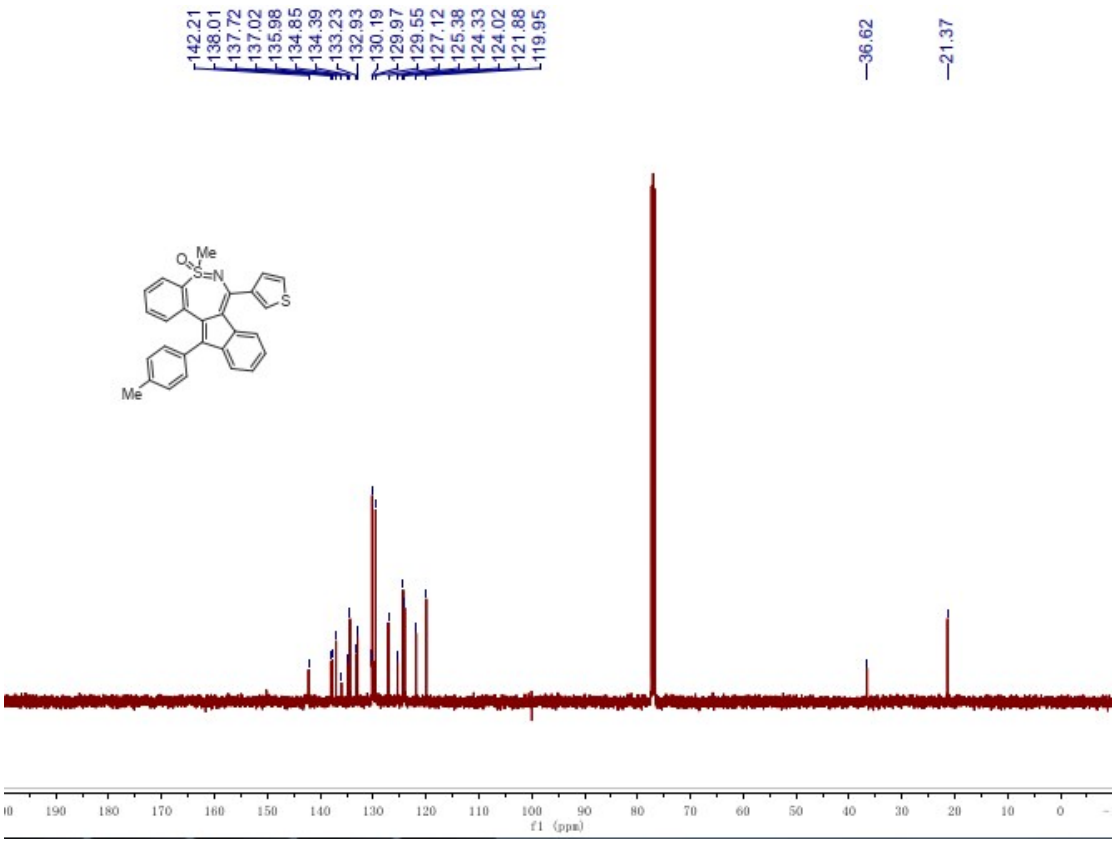
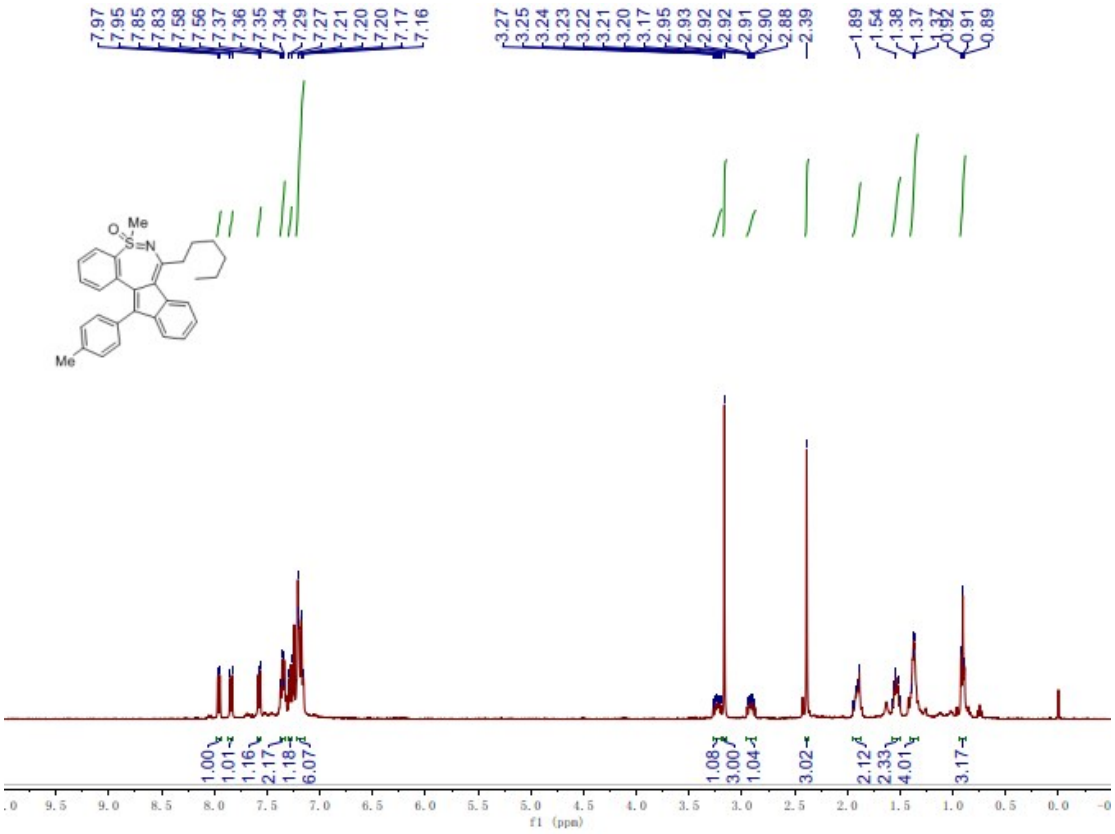
7.98
7.84
7.52
7.50
7.44
7.43
7.39
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.34
7.29
7.28
7.27
7.26
7.25
7.19
7.18
7.17
7.16
7.15
7.03
7.02
3.26
2.40
Me
O
S=N
S
Me
1.00
0.94
1.08
1.02
2.10
5.03
3.08
2.02
3.00
3.04
f1 (ppm)


142.21
138.01
137.72
137.02
135.98
134.85
134.39
133.23
132.93
130.19
129.97
129.55
127.12
125.38
124.33
124.02
121.88
119.95
36.62
21.37
Me
O
S=N
S
Me
f1 (ppm)

3k.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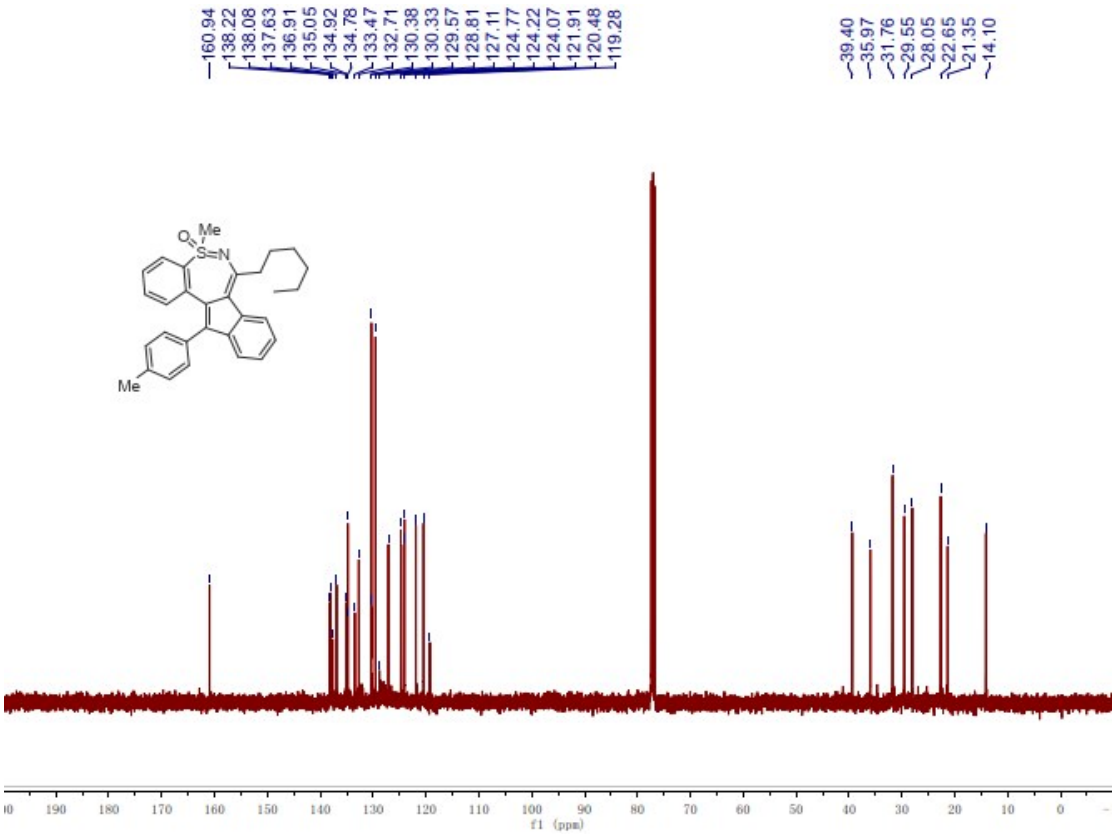
7.95
7.85
7.83
7.58
7.56
7.37
7.36
7.35
7.34
7.29
7.27
7.21
7.20
7.17
7.16
3.27
3.25
3.24
3.23
3.22
3.21
3.20
3.17
2.95
2.93
2.92
2.92
2.91
2.90
2.88
2.39
1.89
1.54
1.38
1.37
0.92
0.91
0.89
Me
Me
1.00
1.01
1.16
2.17
1.18
6.07
1.08
3.00
1.04
3.02
2.12
2.33
4.01
3.17
f1 (ppm)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138.22
138.08
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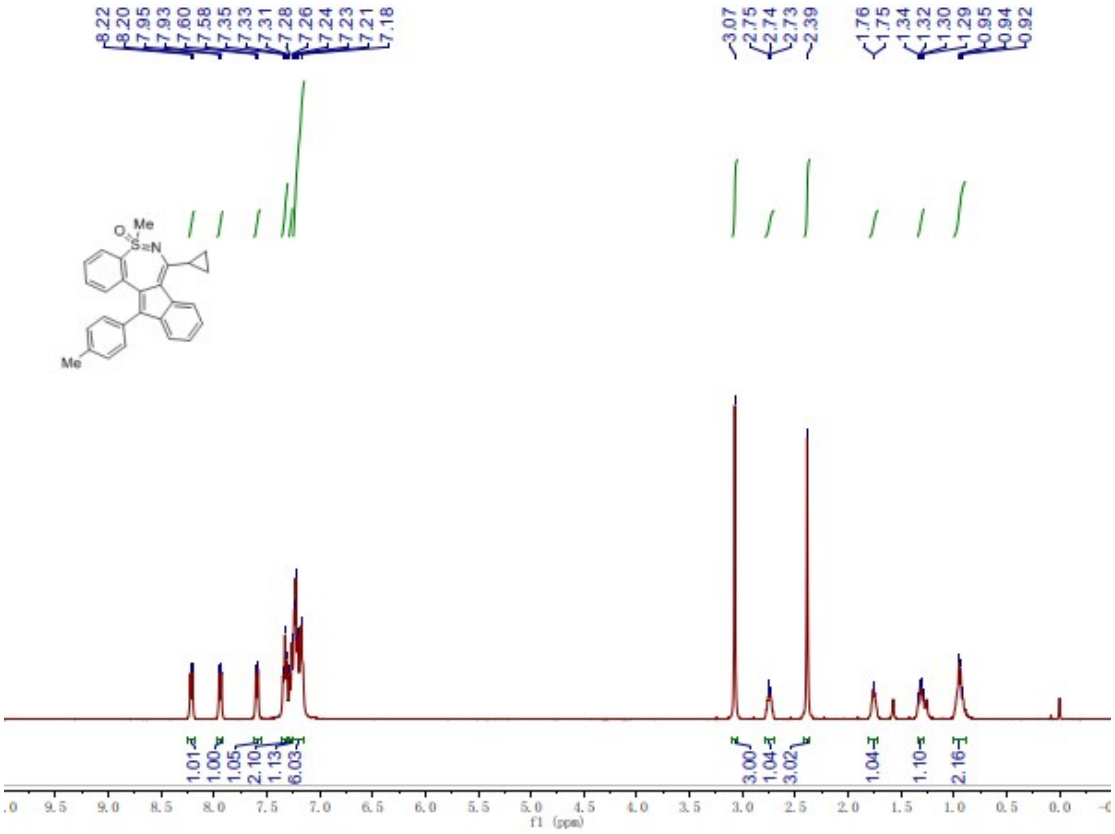
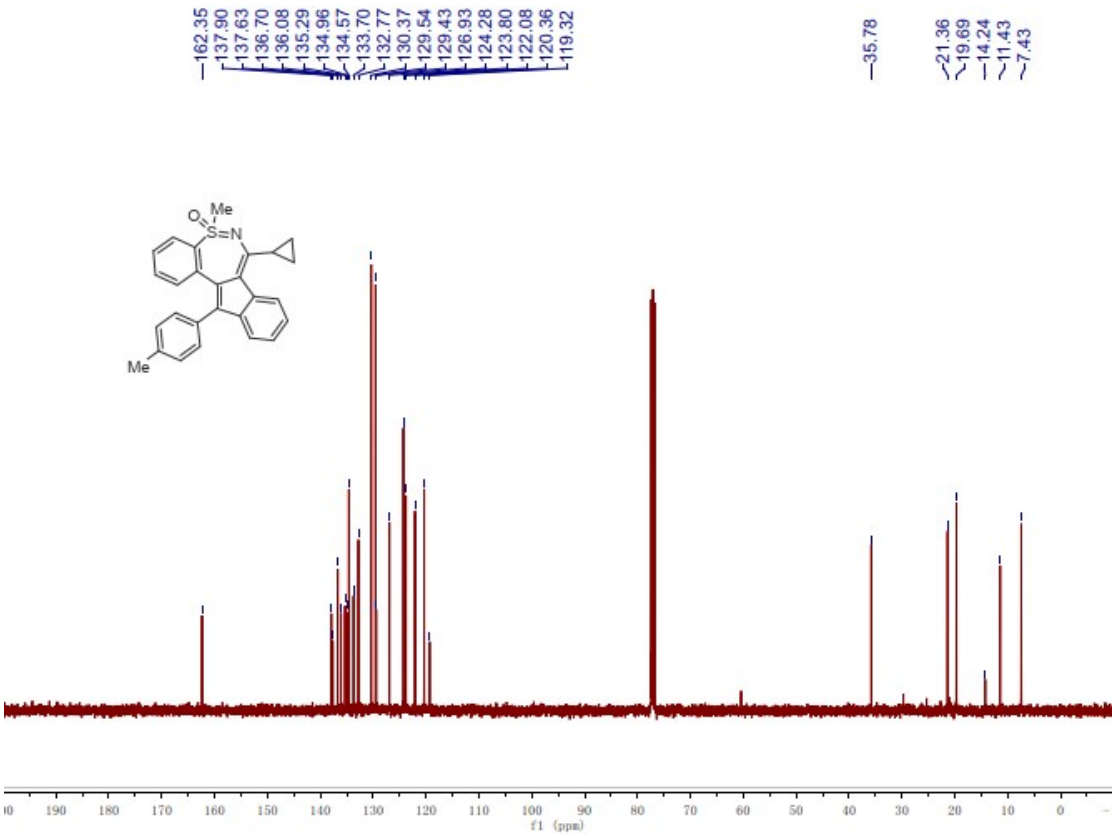
136.91
135.05
134.92
134.78
133.47
132.71
130.38
130.33
129.57
128.81
127.11
124.77
124.22
124.07
121.91
120.48
119.28
39.40
35.97
31.76
29.55
28.05
22.65
21.35
14.10
Me
Me
f1 (ppm)

3l.


8.22
8.20
7.95
7.93
7.60
7.58
7.35
7.33
7.31
7.28
7.26
7.24
7.23
7.21
7.18
3.07
2.75
2.74
2.73
2.39
1.76
1.75
1.34
1.32
1.29
0.95
0.94
0.92
Me
O
S=N
Me
1.01
1.00
1.05
2.10
1.13
6.03
3.00
1.04
3.02
1.04
1.10
2.16
f1 (ppm)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137.90
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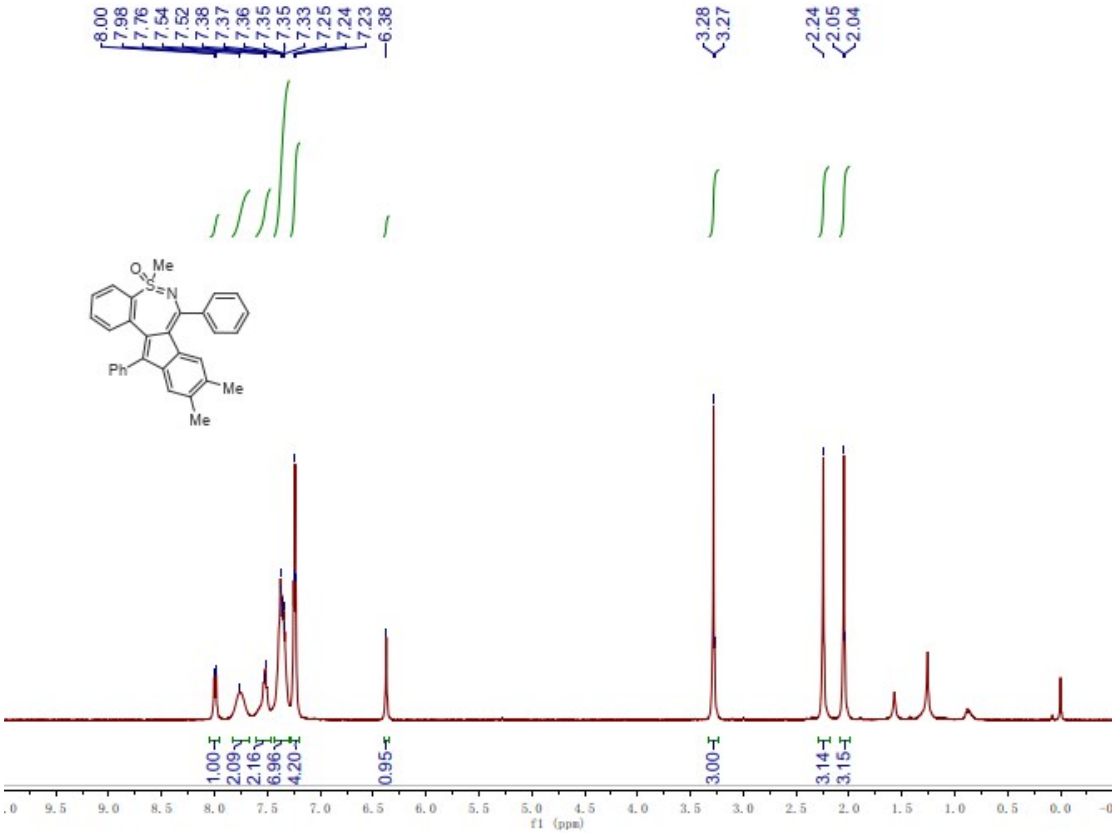
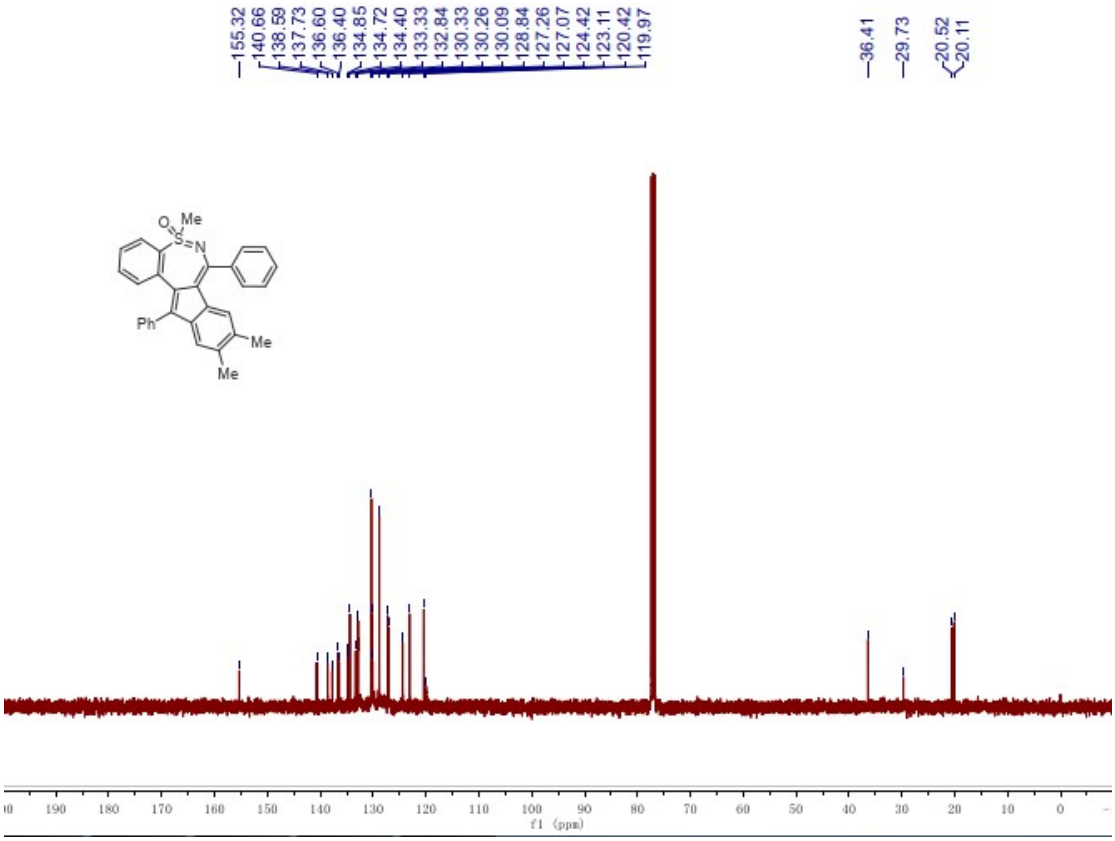
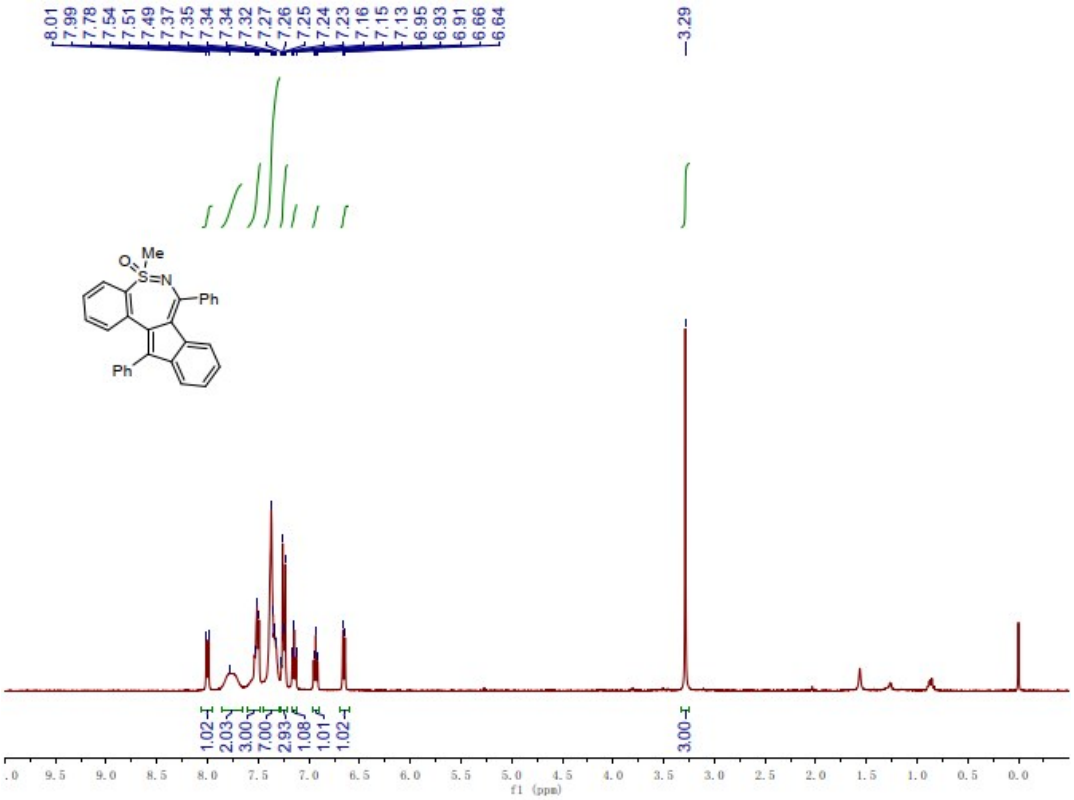
136.70
136.08
135.29
134.96
134.57
133.70
132.77
130.37
129.54
129.43
126.93
124.28
123.80
122.08
120.36
119.32
35.78
21.36
19.69
14.24
11.43
7.43
Me
O
S=N
Me
f1 (ppm)

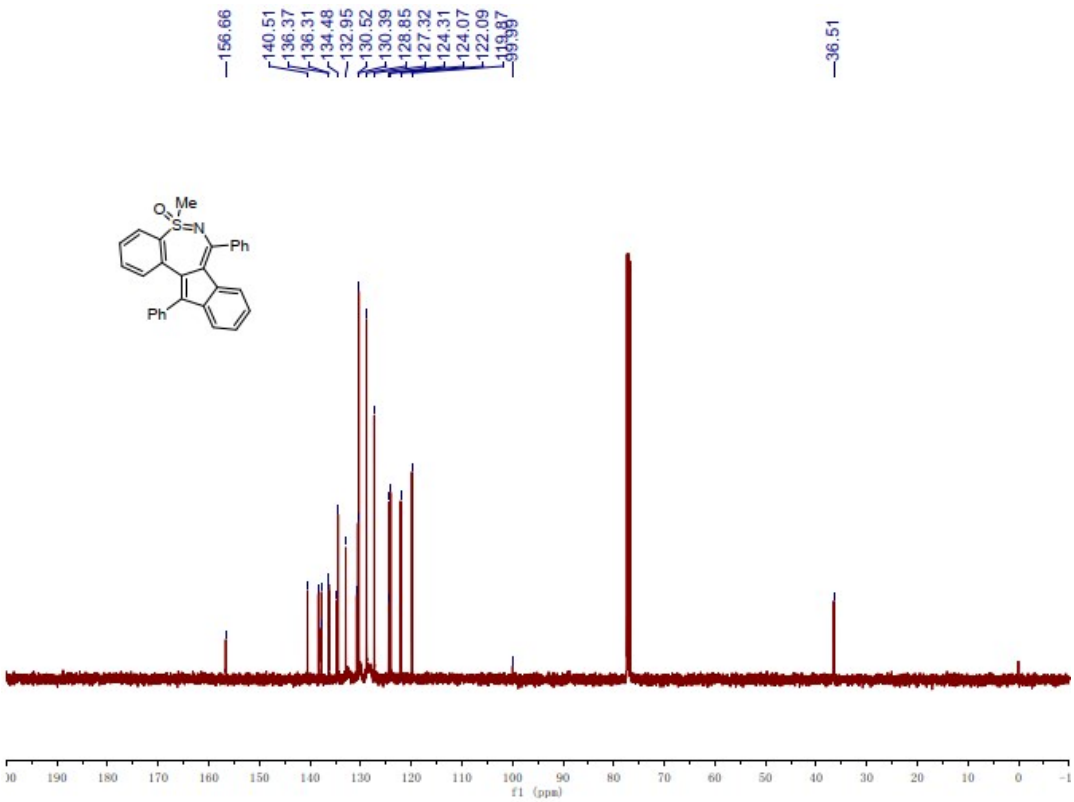
3m.


8.00
7.98
7.76
7.54
7.52
7.38
7.37
7.36
7.35
7.35
7.33
7.25
7.24
7.23
6.38
3.28
3.27
2.24
2.05
2.04
Me
Ph
Me
Me
1.00
2.09
2.16
6.96
4.20
0.95
3.00
3.14
3.15
f1 (ppm)

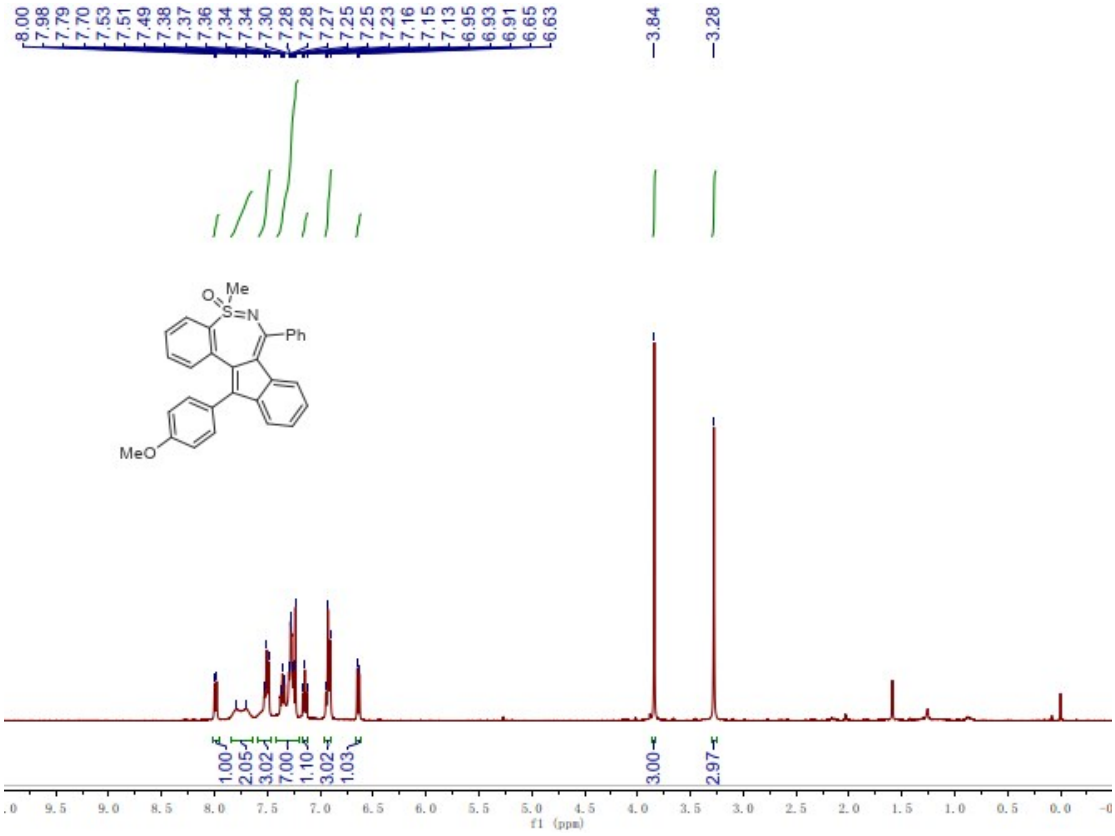

155.32
140.66
138.59
137.73
136.60
136.40
134.85
134.72
134.40
133.33
132.84
130.33
130.26
130.09
128.84
127.26
127.07
124.42
123.11
120.42
119.97
36.41
29.73
20.52
20.11
Me
Ph
Me
Me
f1 (ppm)

3n.


8.01
7.99
7.78
7.54
7.51
7.49
7.37
7.35
7.34
7.34
7.32
7.27
7.26
7.25
7.24
7.23
7.16
7.15
7.13
6.95
6.93
6.91
6.66
6.64
3.29
Me
O
S=N
Ph
Ph
1.02
2.03
3.00
7.00
2.93
1.08
1.01
1.02
3.00
f1 (ppm)


156.66
140.51
136.37
136.31
134.48
132.95
130.52
130.39
128.85
127.32
124.31
124.07
122.09
119.87
99.99
36.51
Me
O
S=N
Ph
Ph
f1 (ppm)

3o.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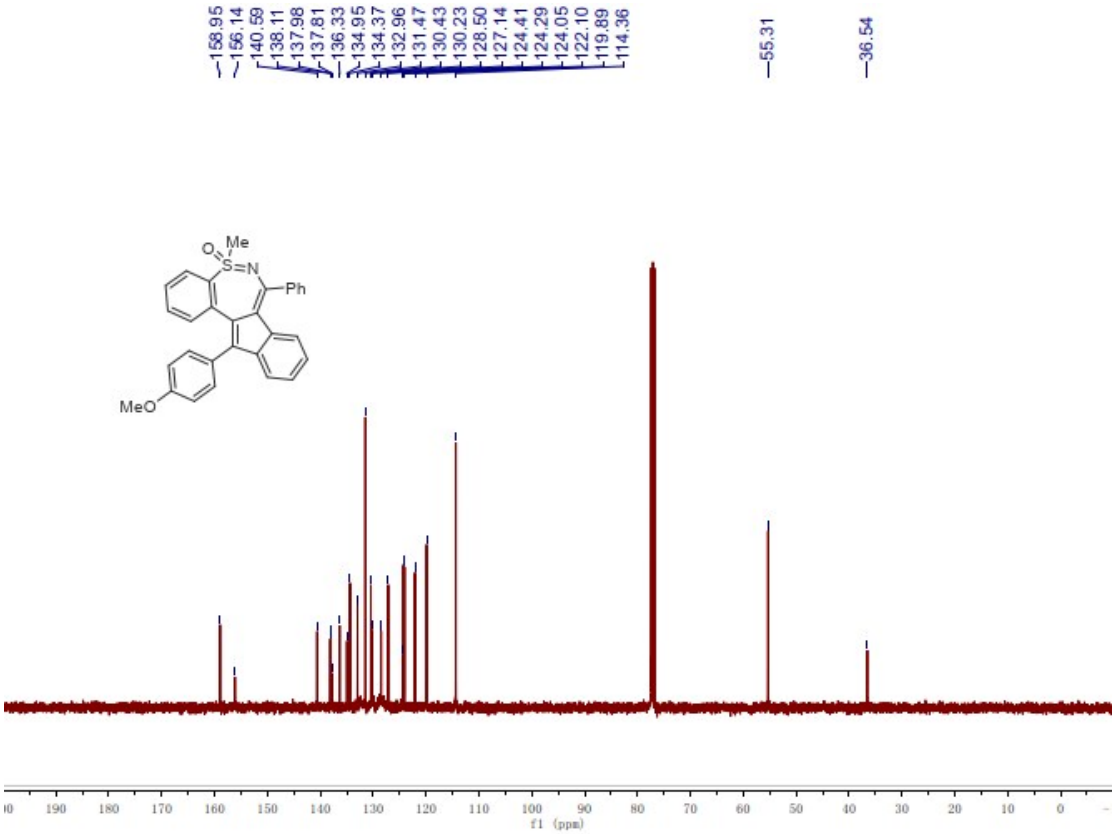
7.98
7.79
7.70
7.53
7.51
7.49
7.38
7.37
7.36
7.34
7.34
7.30
7.28
7.28
7.27
7.25
7.25
7.23
7.16
7.15
7.13
6.95
6.93
6.91
6.65
6.63
3.84
3.28
Me
O
S=N
Ph
MeO
1.00
2.05
3.02
7.00
1.10
3.02
1.03
3.00
2.97
f1 (ppm)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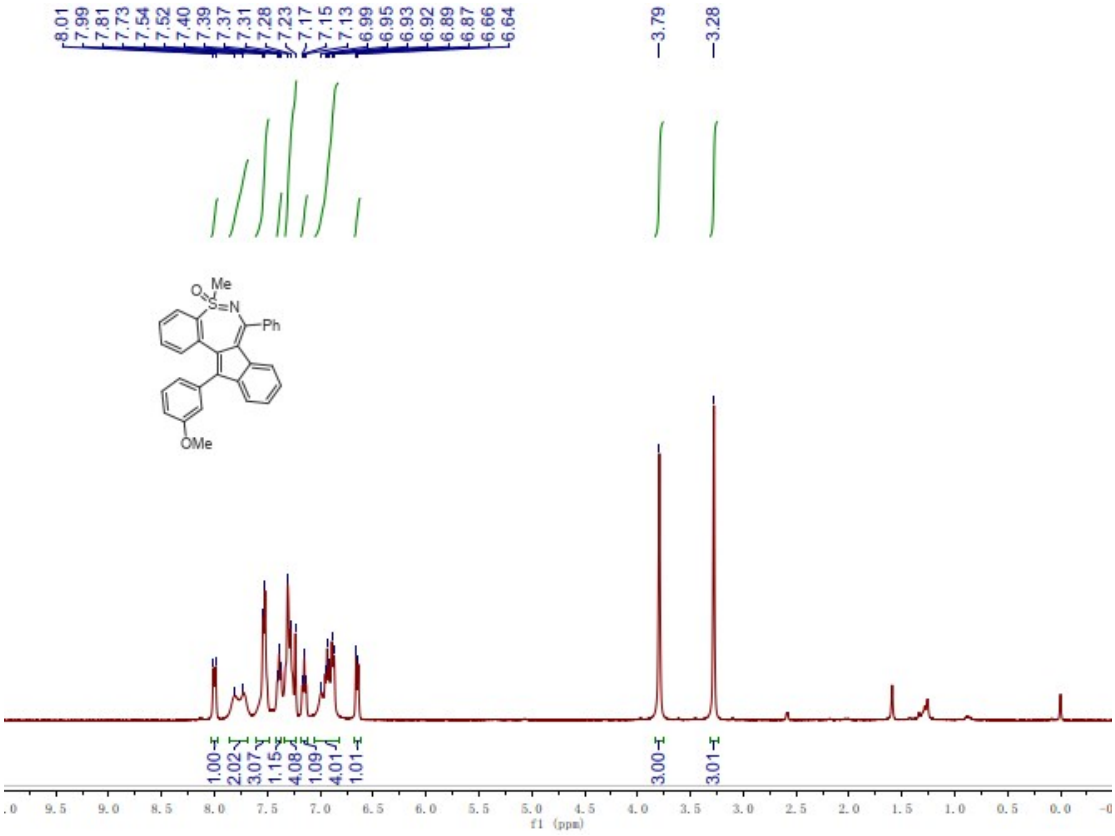
138.11
137.98
137.81
136.33
134.95
134.37
132.96
131.47
130.43
130.23
128.50
127.14
124.41
124.29
124.05
122.10
119.89
114.36
55.31
36.54
Me
O
S=N
Ph
MeO
f1 (ppm)

3p.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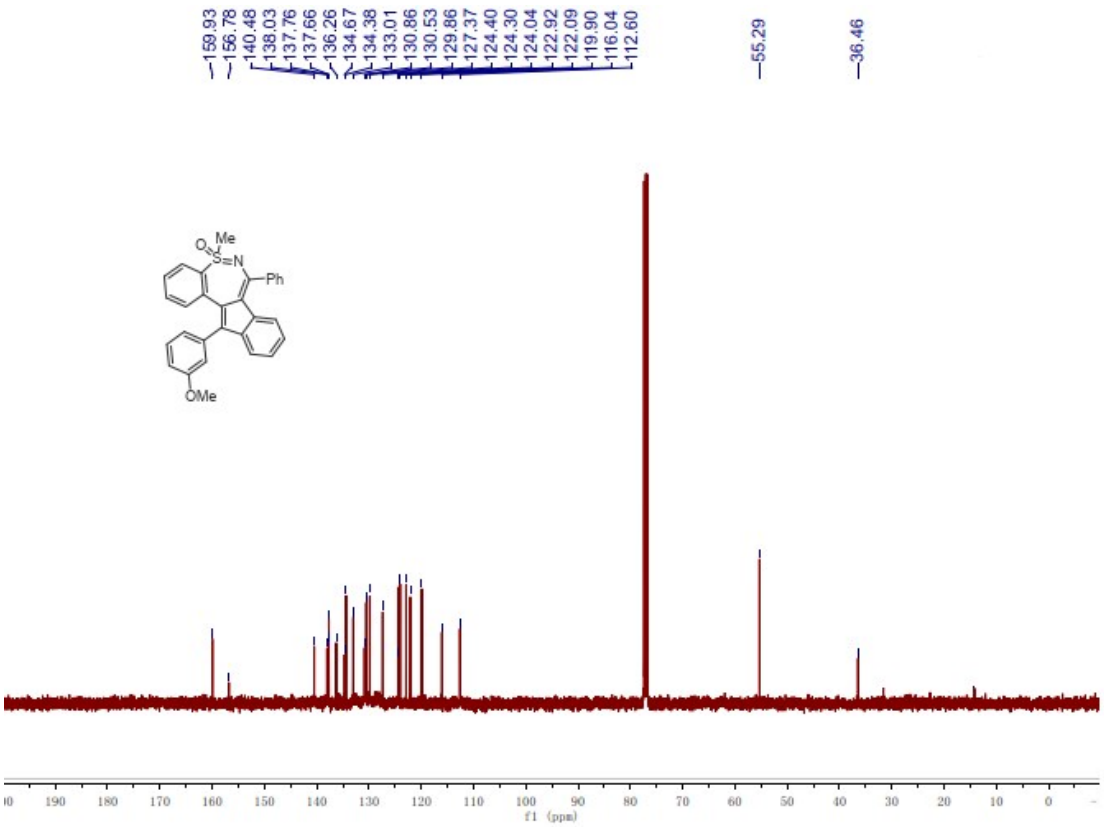
7.99
7.81
7.73
7.54
7.52
7.40
7.39
7.37
7.31
7.28
7.23
7.17
7.15
7.13
6.99
6.95
6.93
6.92
6.89
6.87
6.66
6.64
3.79
3.28
Me
O
S
N
Ph
OMe
1.00
2.02
3.07
1.15
4.08
1.09
4.01
1.01
3.00
3.01
f1 (ppm)


159.93
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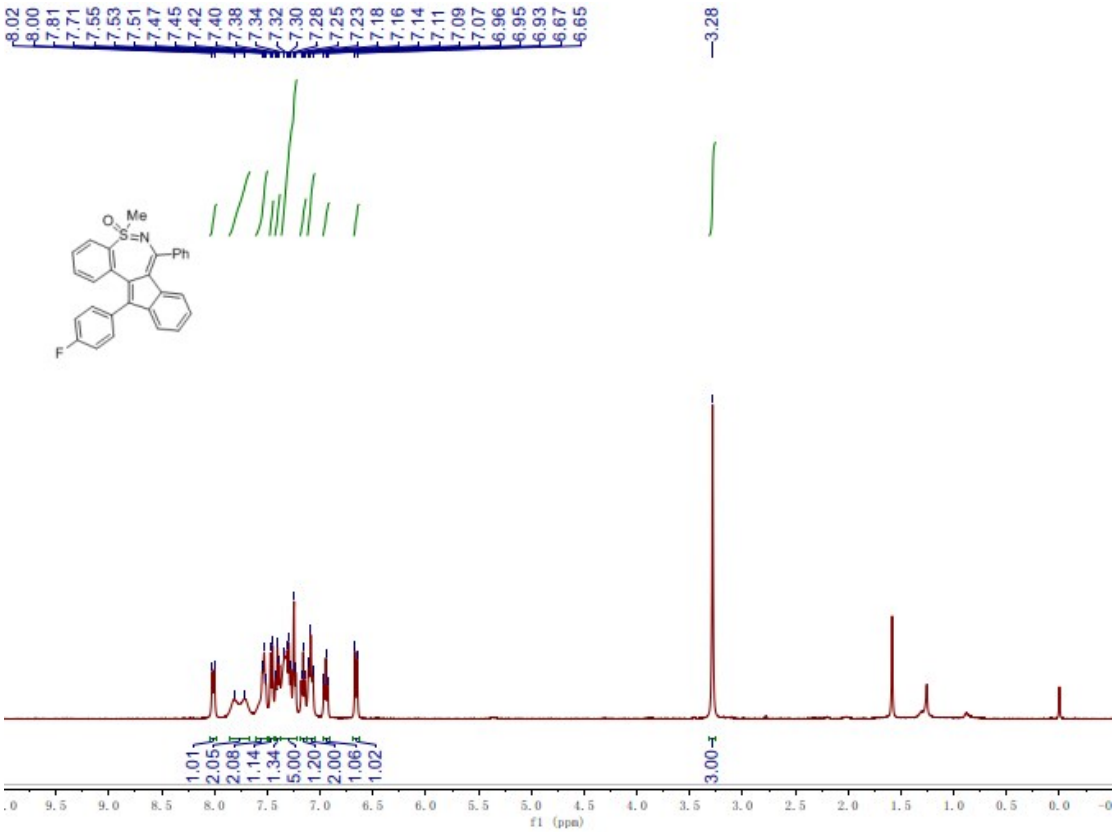
138.03
137.76
137.66
136.26
134.67
134.38
133.01
130.86
130.53
129.86
127.37
124.40
124.30
124.04
122.92
122.09
119.90
116.04
112.60
55.29
36.46
Me
O
S
N
Ph
OMe
f1 (ppm)

3q.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8.00
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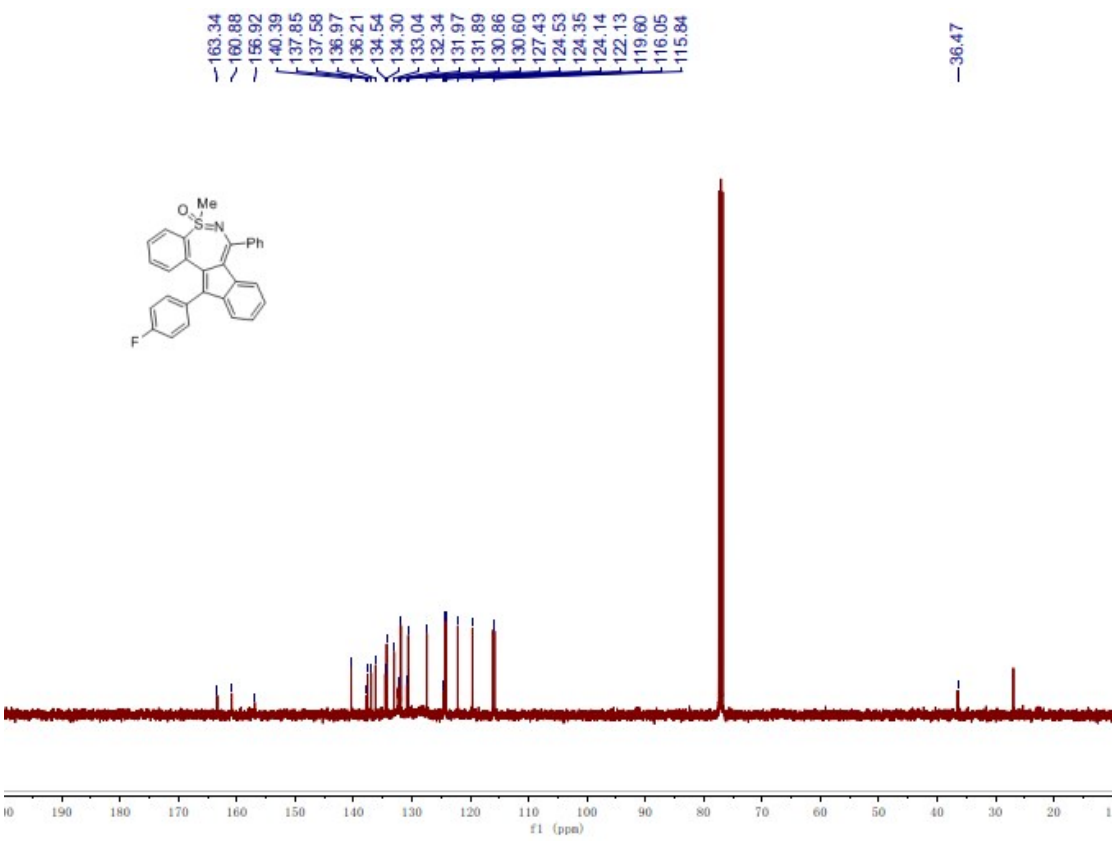
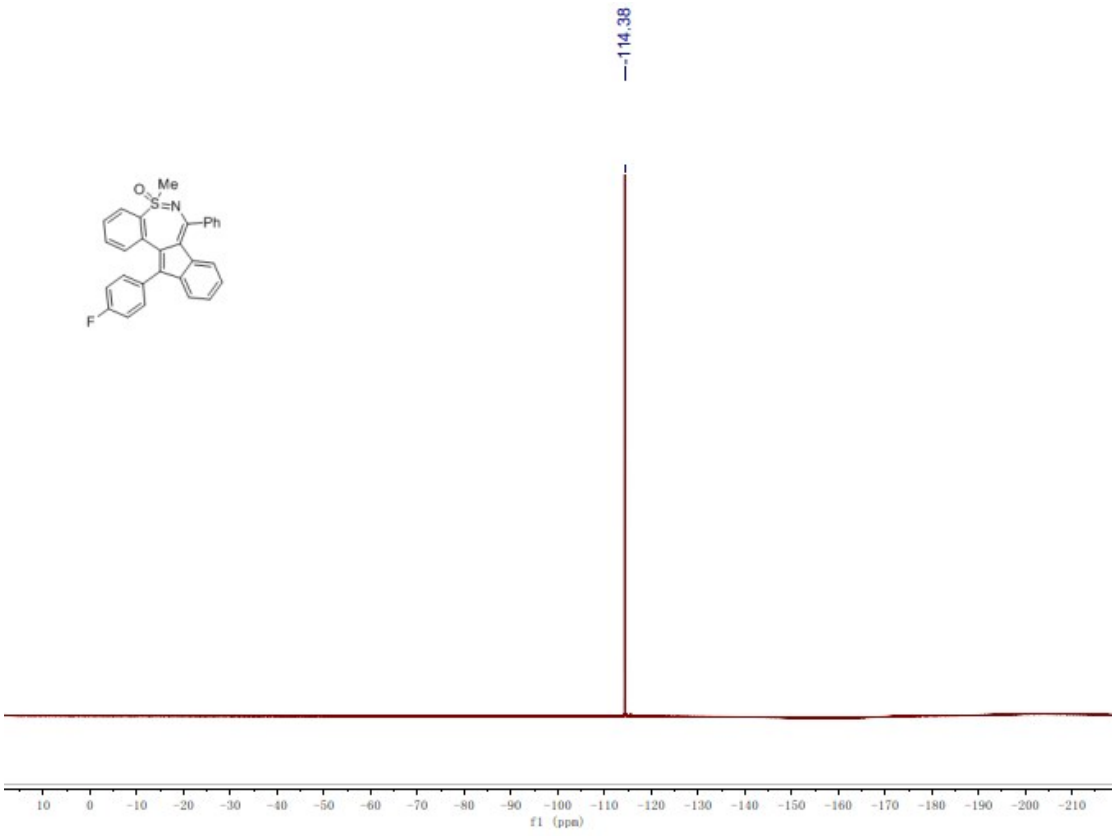
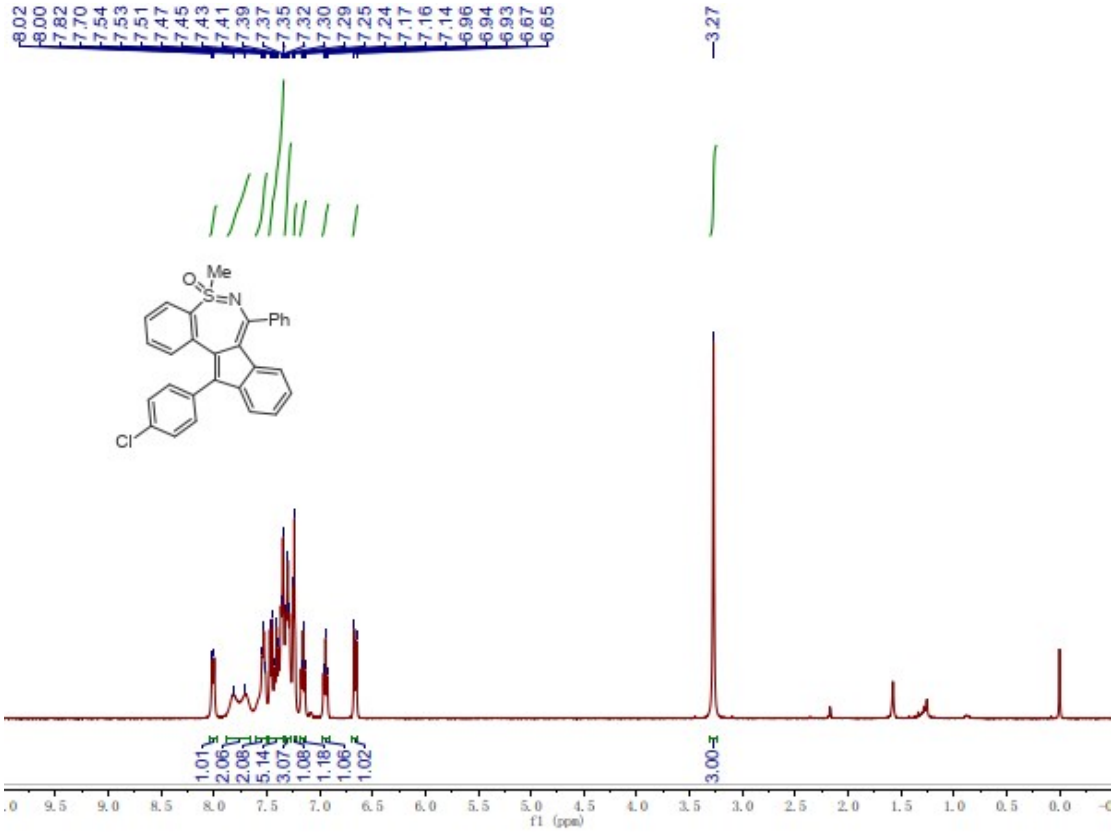
7.71
7.55
7.53
7.51
7.47
7.45
7.42
7.40
7.38
7.34
7.32
7.30
7.28
7.25
7.23
7.18
7.16
7.14
7.11
7.09
7.07
6.96
6.95
6.93
6.67
6.65
3.28
Me
O
S=N
Ph
F
1.01
2.05
2.08
1.14
1.34
5.00
1.20
2.00
1.06
1.02
3.00
f1 (ppm)


163.34
160.88
156.92
140.39
137.85
137.58
136.97
136.21
134.54
134.30
133.04
132.34
131.97
131.89
130.86
130.60
127.43
124.53
124.35
124.14
122.13
119.60
116.05
115.84
36.47
Me
O
S=N
Ph
F
f1 (ppm)


-114.38
Me
O
S
N
Ph
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

3r.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8.00
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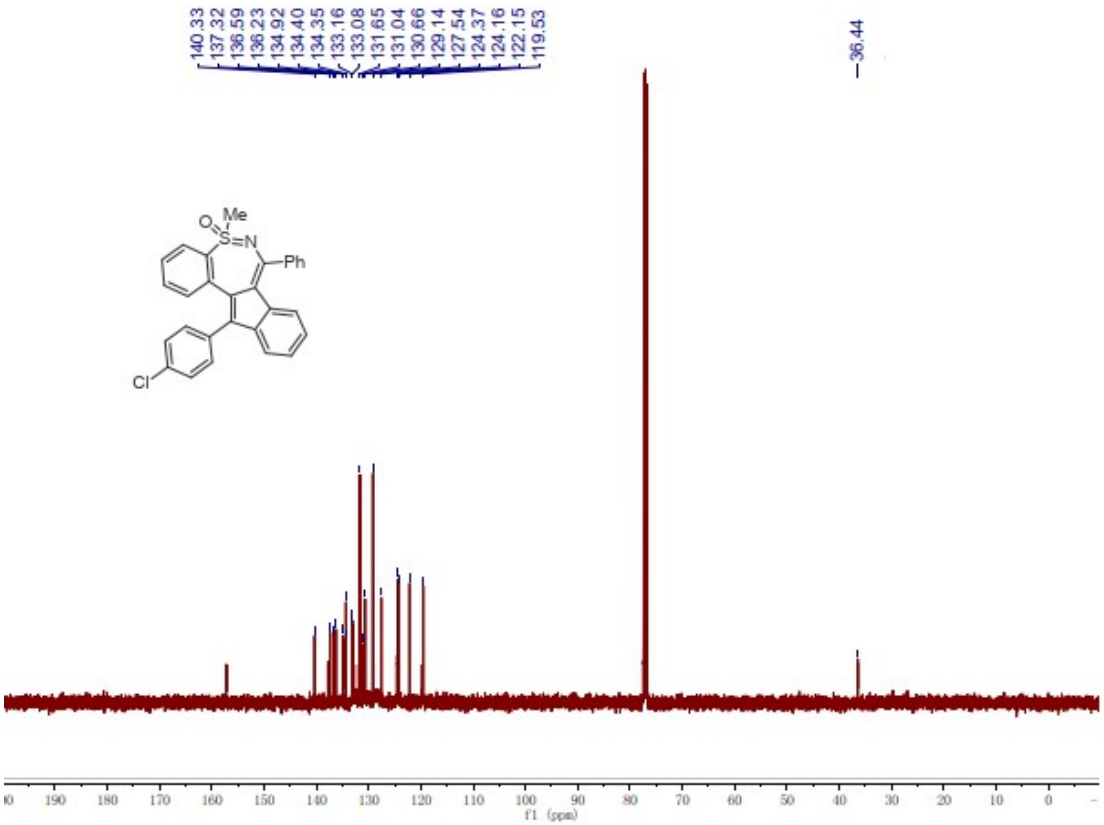
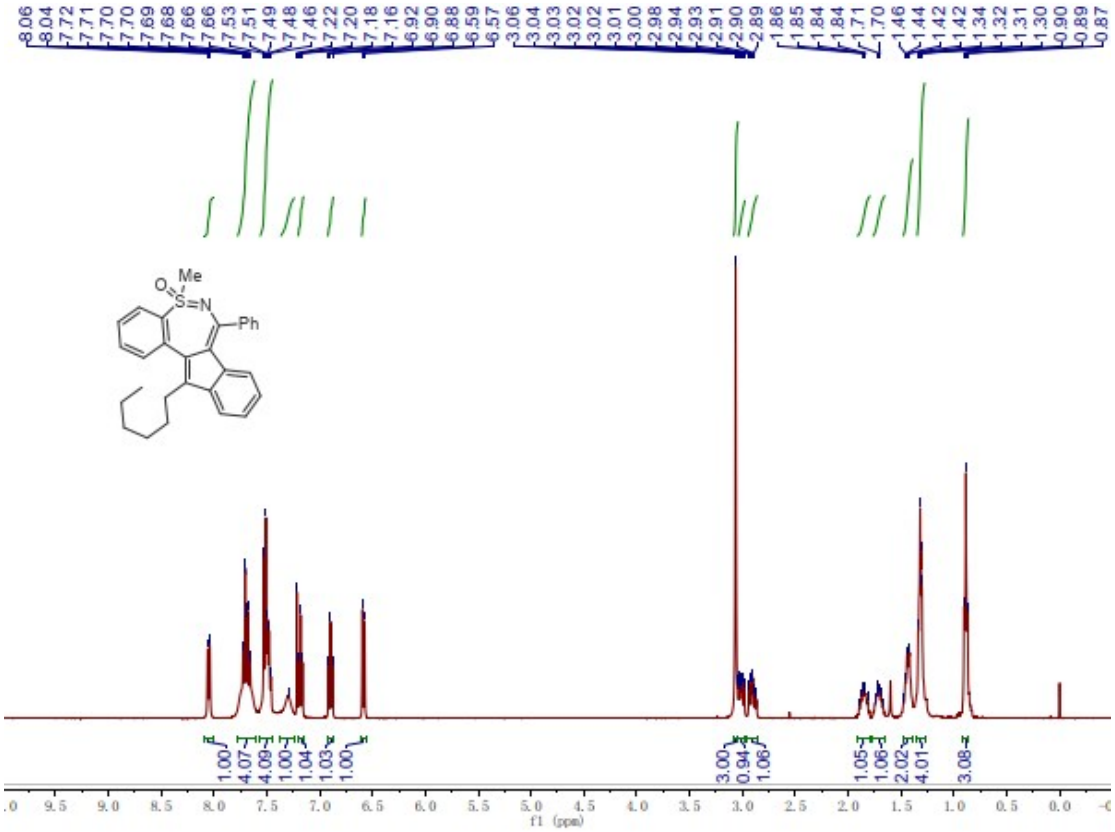
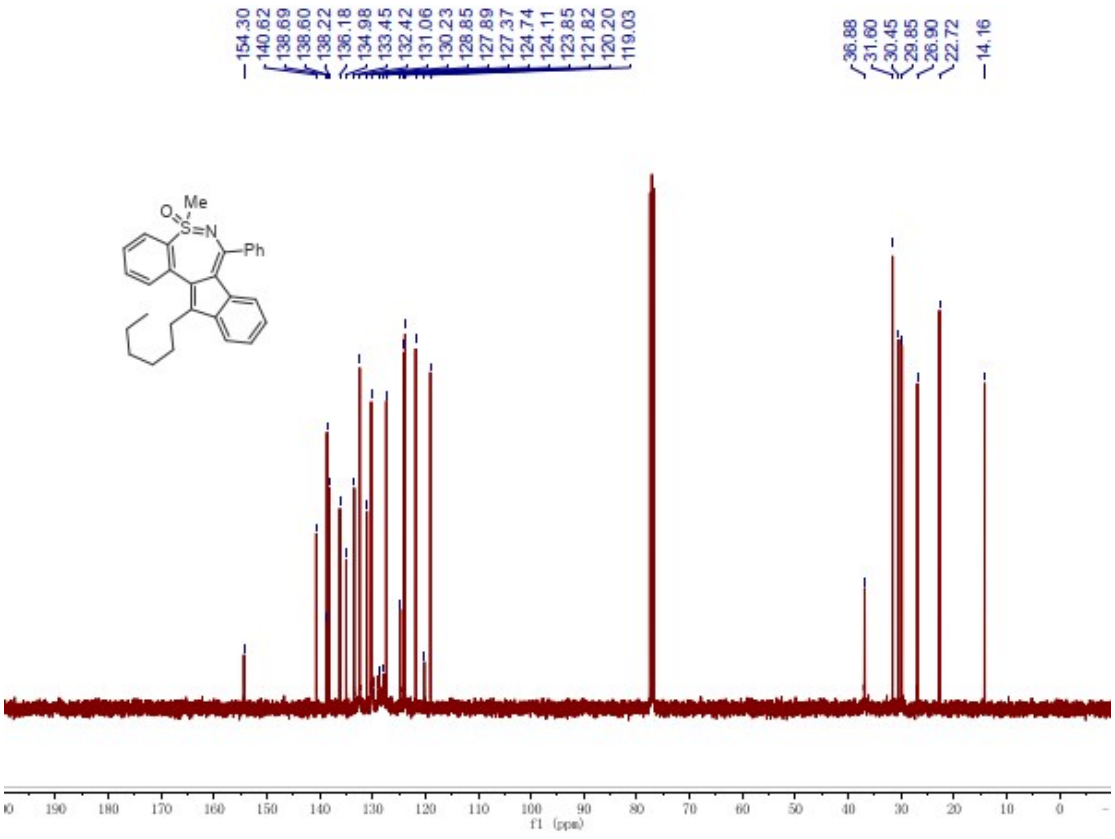
7.70
7.54
7.53
7.51
7.47
7.45
7.43
7.41
7.39
7.37
7.35
7.32
7.30
7.29
7.25
7.24
7.17
7.16
7.14
6.96
6.94
6.93
6.67
6.65
3.27
Me
O
S
N
Ph
Cl
1.01
2.06
2.08
5.14
3.07
1.08
1.18
1.06
1.02
3.00
f1 (ppm)


140.33
137.32
136.59
136.23
134.92
134.40
134.35
133.16
133.08
131.65
131.04
130.66
129.14
127.54
124.37
124.16
122.15
119.53
36.44
Me
O
S
N
Ph
Cl
f1 (ppm)

3s.


8.06
8.04
7.72
7.71
7.70
7.70
7.69
7.68
7.66
7.66
7.53
7.51
7.49
7.48
7.46
7.22
7.20
7.18
7.16
6.92
6.90
6.88
6.59
6.57
3.06
3.04
3.03
3.02
3.02
3.01
3.00
2.98
2.94
2.93
2.91
2.90
2.89
1.86
1.85
1.84
1.84
1.71
1.70
1.46
1.44
1.42
1.42
1.34
1.32
1.31
1.30
0.90
0.89
0.87
Me
O
S=N
Ph
1.00
4.07
4.09
1.00
1.04
1.03
1.00
3.00
0.94
1.06
1.05
1.06
2.02
4.01
3.08
f1 (ppm)


154.30
140.62
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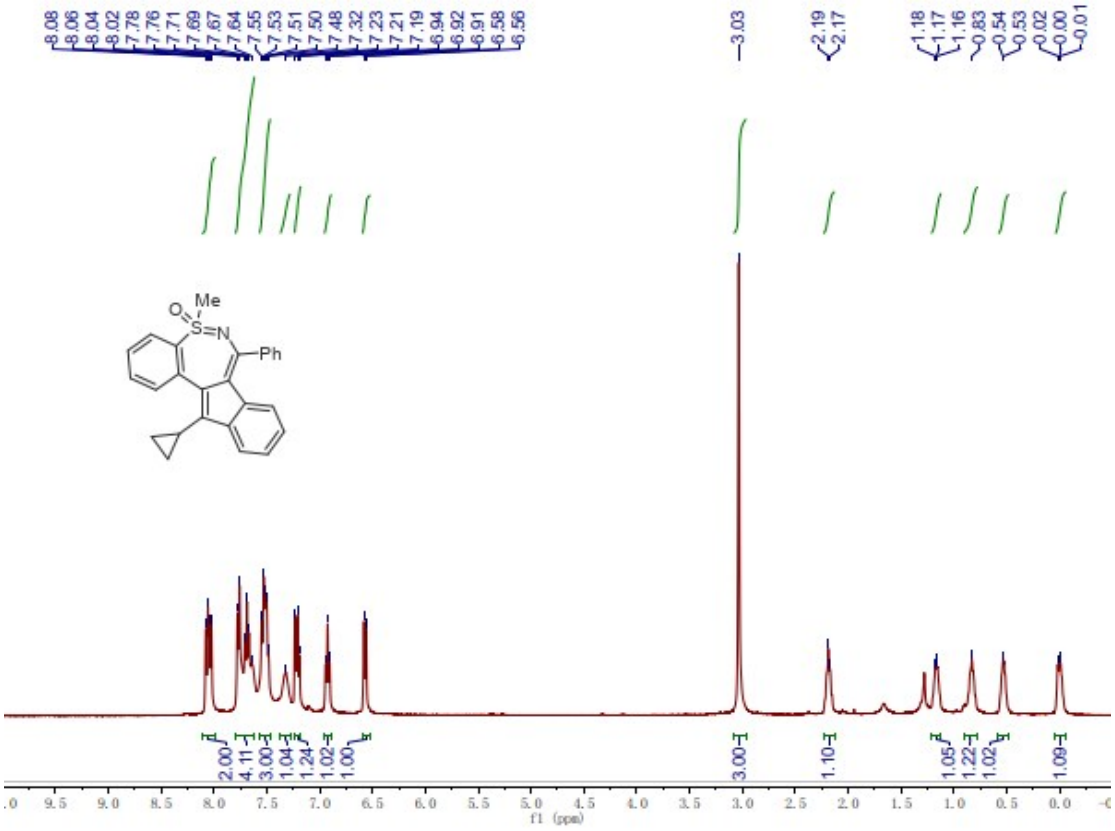
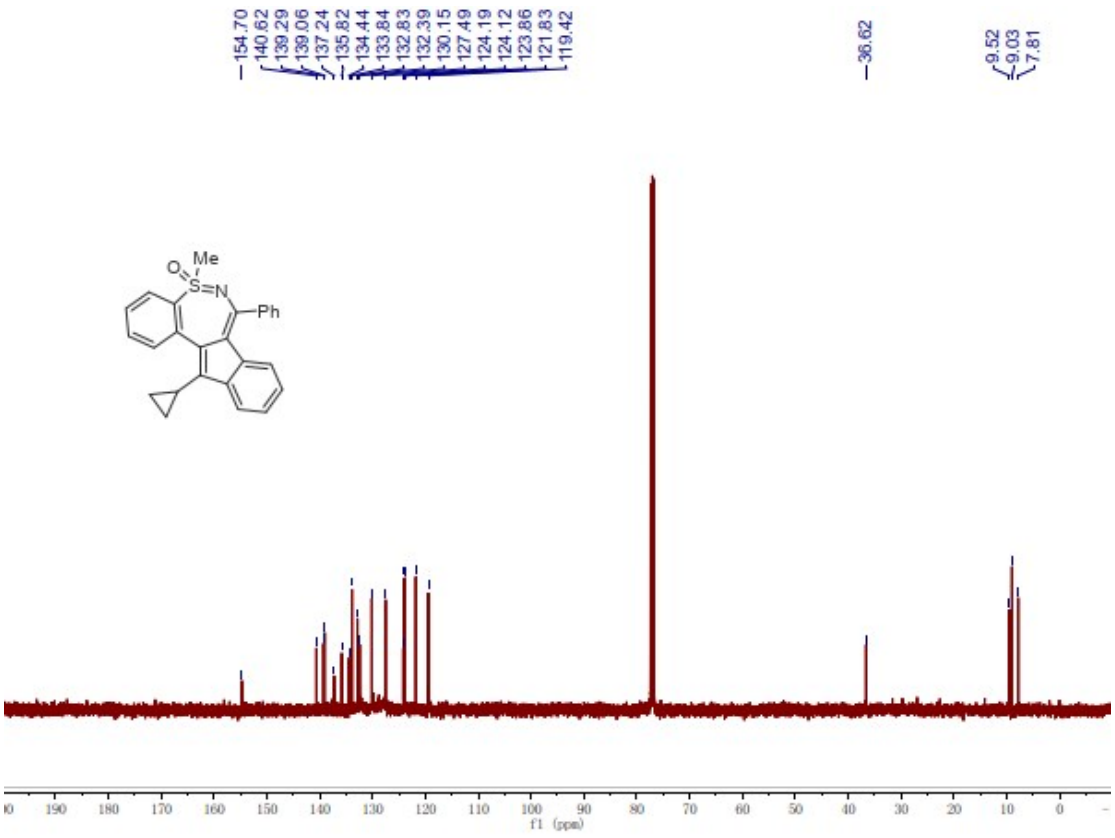
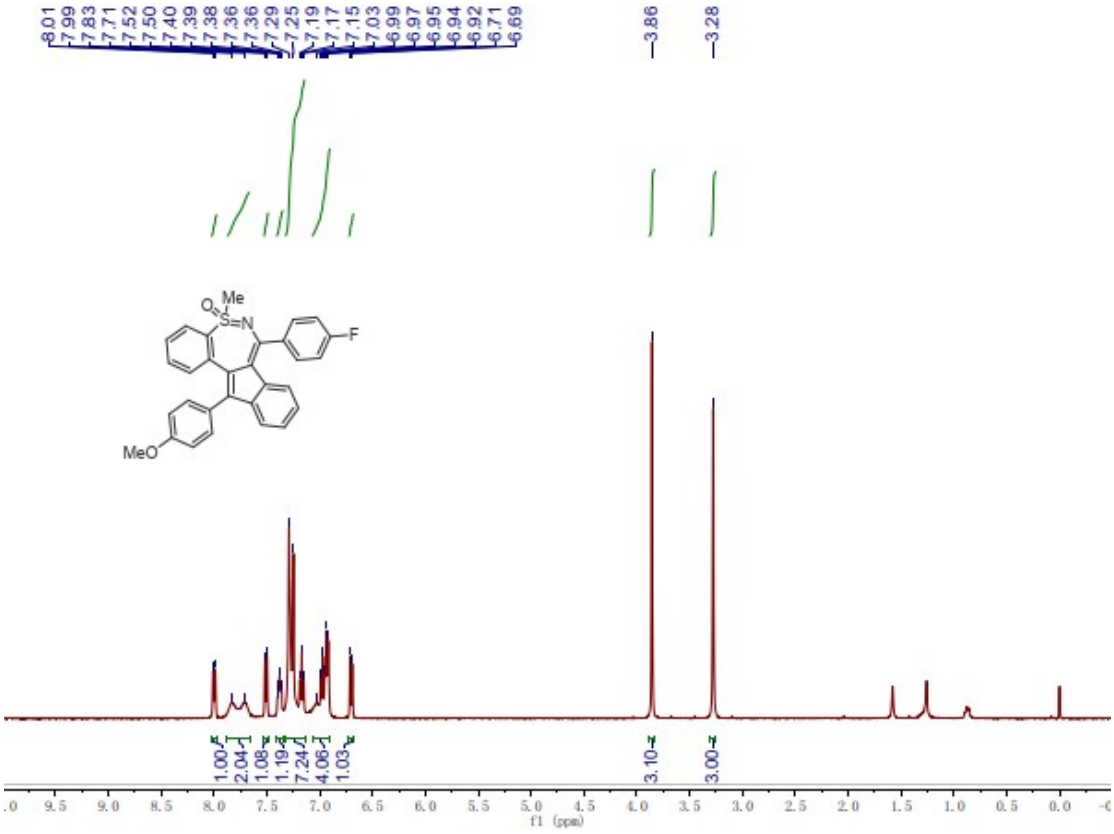
138.60
138.22
136.18
134.98
133.45
132.42
131.06
130.23
128.85
127.89
127.37
124.74
124.11
123.85
121.82
120.20
119.03
36.88
31.60
30.45
29.85
26.90
22.72
14.16
Me
O
S=N
Ph
f1 (ppm)

3t.


8.08
8.06
8.04
8.02
7.78
7.76
7.71
7.69
7.67
7.64
7.55
7.53
7.51
7.50
7.48
7.32
7.23
7.21
7.19
6.94
6.92
6.91
6.58
6.56
3.03
2.19
2.17
1.18
1.17
1.16
0.83
0.54
0.53
0.02
0.00
0.01
Me
O
S
N
Ph
2.00
4.11
3.00
1.04
1.24
1.02
1.00
3.00
1.10
1.05
1.22
1.02
1.09
f1 (ppm)


154.70
140.62
139.29
139.06
137.24
135.82
134.44
133.84
132.83
132.39
130.15
127.49
124.19
124.12
123.86
121.83
119.42
36.62
9.52
9.03
7.81
Me
O
S
N
Ph
f1 (ppm)

3u.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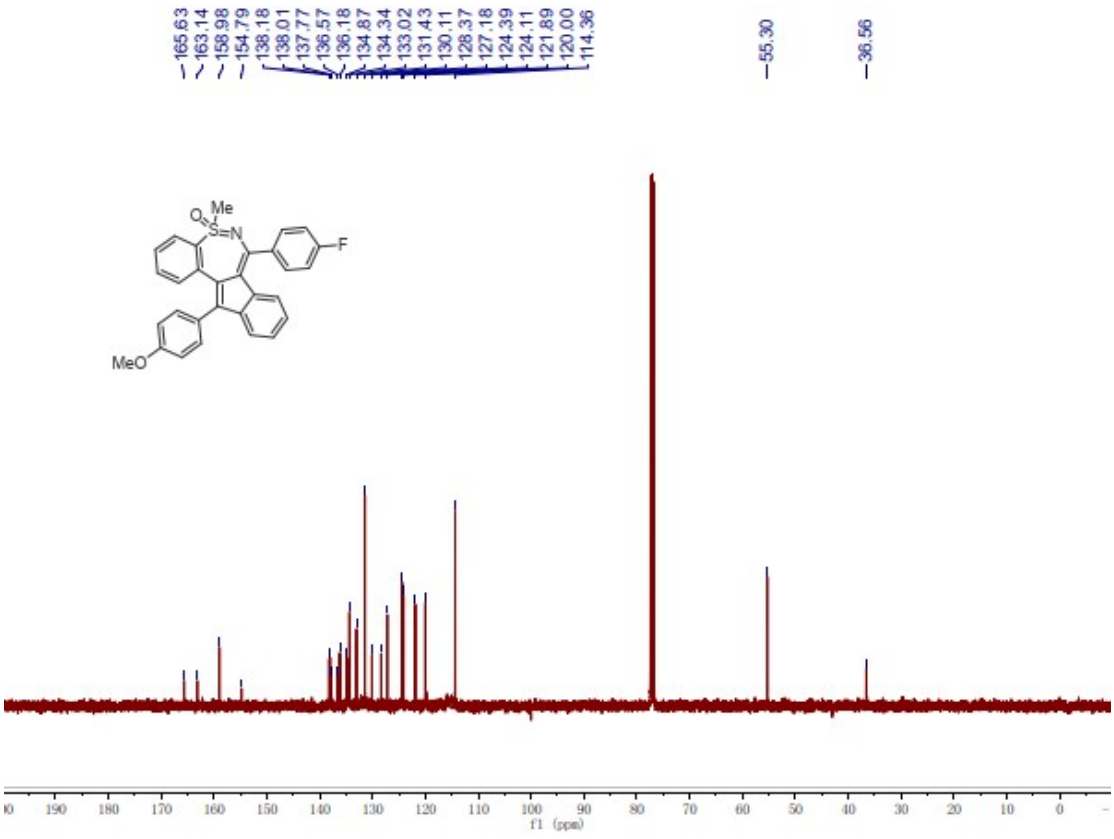
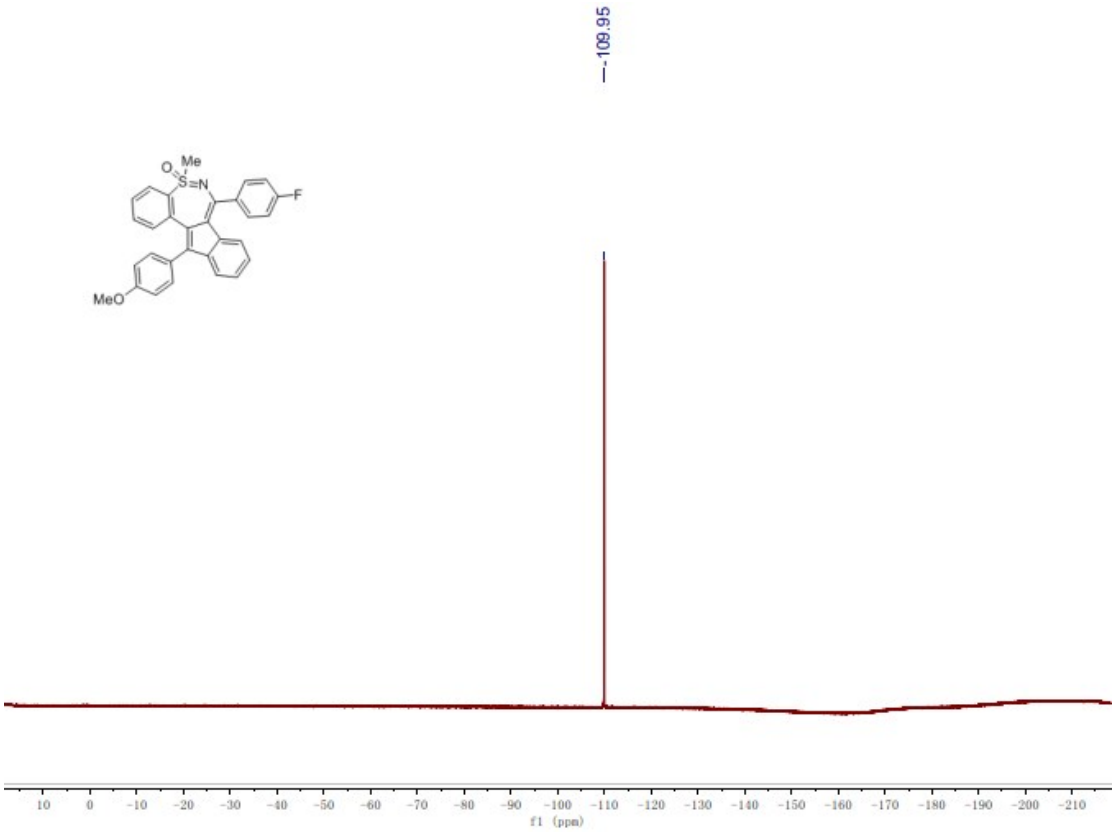
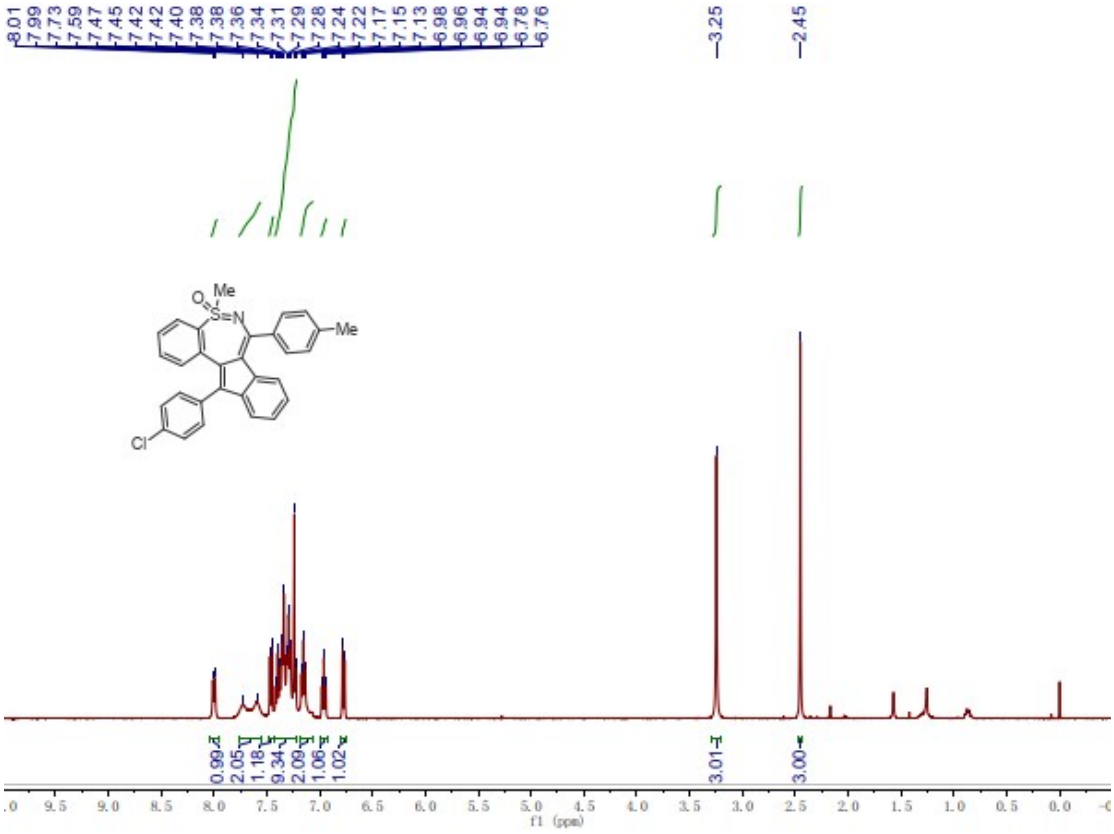
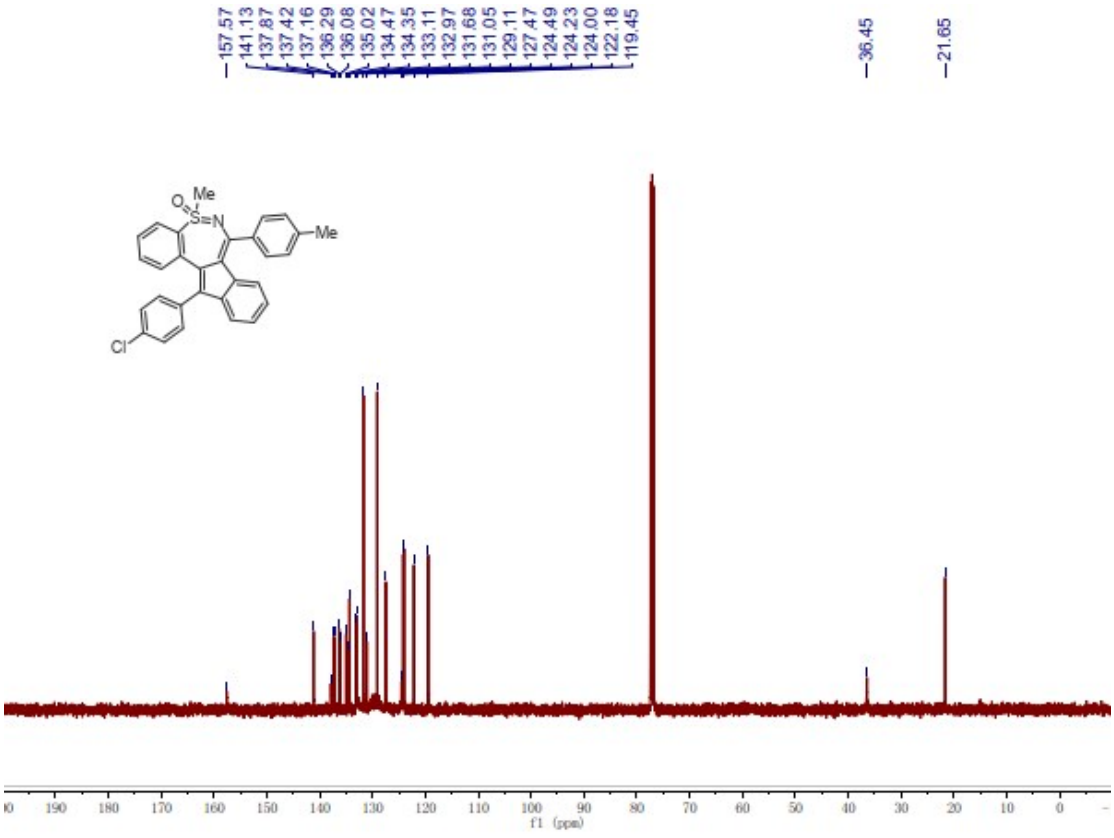
7.99
7.83
7.71
7.52
7.50
7.40
7.39
7.38
7.36
7.36
7.29
7.25
7.19
7.17
7.15
7.03
6.99
6.97
6.95
6.94
6.92
6.71
6.69
3.86
3.28
Me
O
S=N
F
MeO
1.00
2.04
1.08
1.19
7.24
4.06
1.03
3.10
3.00
f1 (ppm)


165.63
163.14
158.98
154.79
138.18
138.01
137.77
136.57
136.18
134.87
134.34
133.02
131.43
130.11
128.37
127.18
124.39
124.11
121.89
120.00
114.36
55.30
36.56
Me
O
S=N
F
MeO
f1 (ppm)

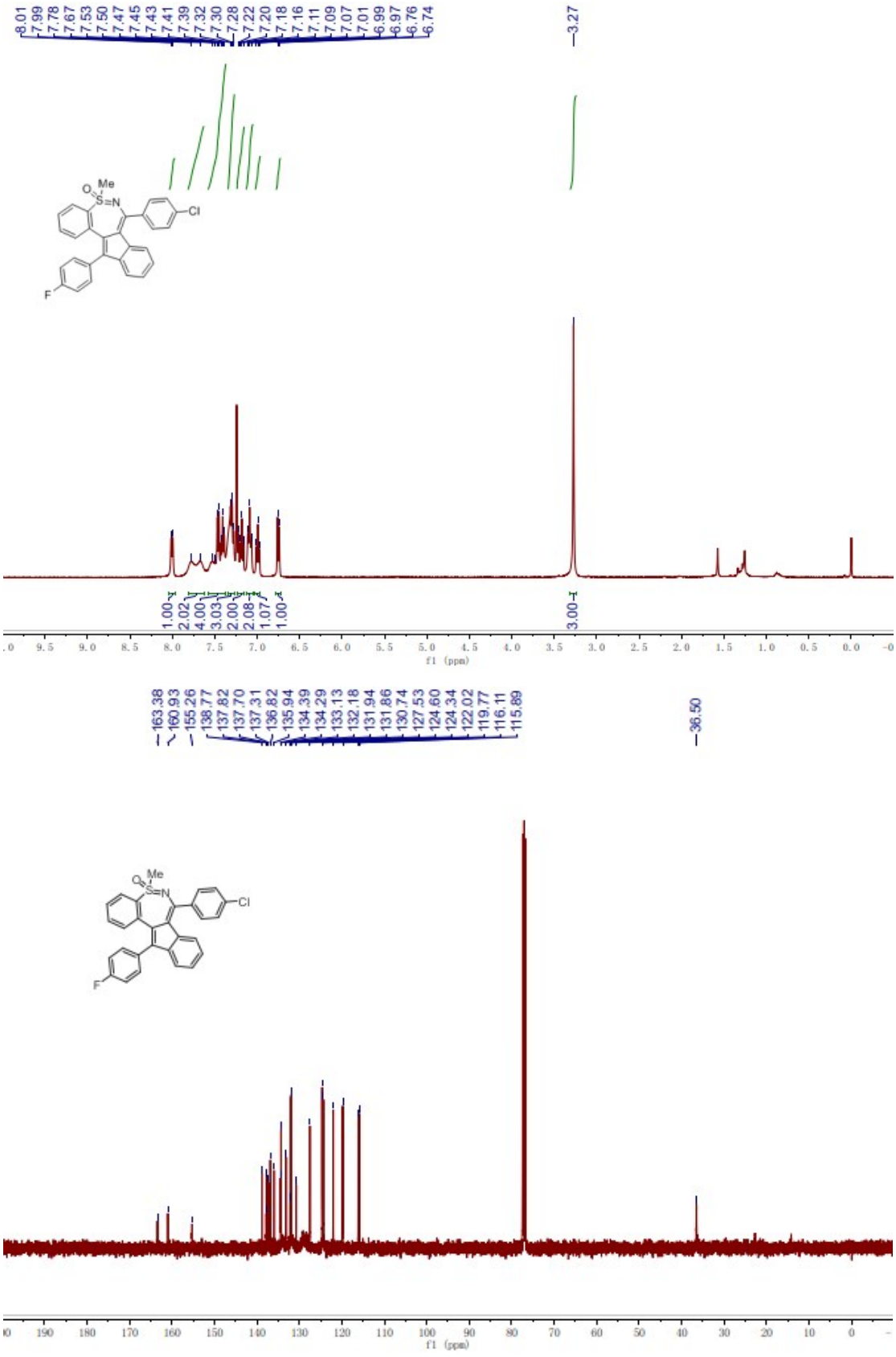

-109.95
Me
O
S=N
F
MeO
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

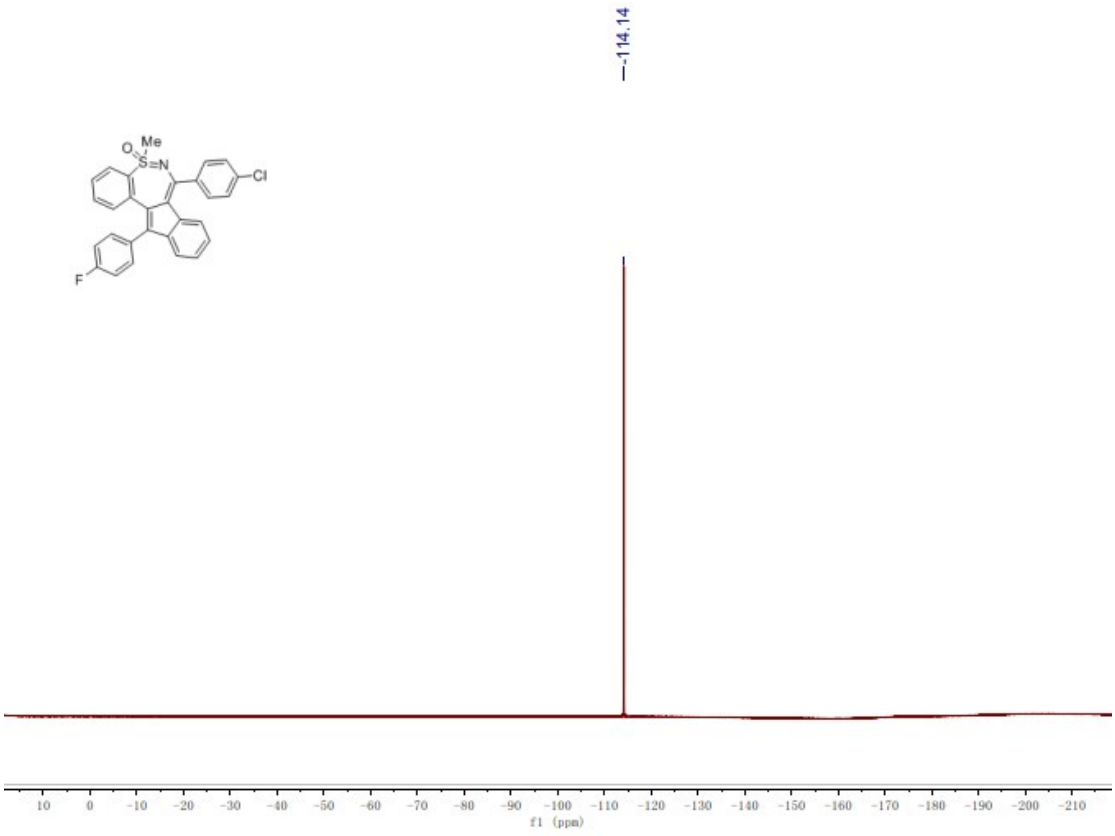
3v.


8.01
7.99
7.73
7.59
7.47
7.45
7.42
7.42
7.40
7.38
7.38
7.36
7.34
7.31
7.29
7.28
7.24
7.22
7.17
7.15
7.13
6.98
6.96
6.94
6.94
6.78
6.76
3.25
2.45
Me
O
S
N
Me
Cl
0.99
2.05
1.18
9.34
2.09
1.06
1.02
3.01
3.00
f1 (ppm)

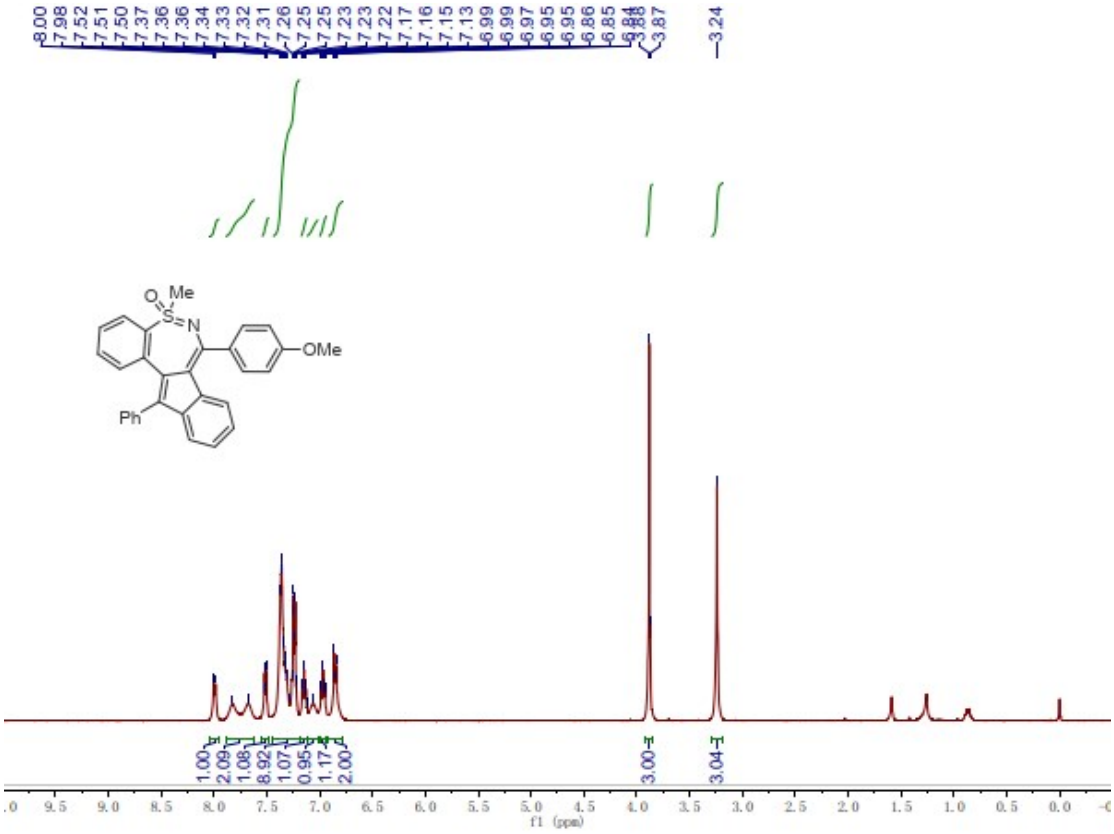

157.57
141.13
137.87
137.42
137.16
136.29
136.08
135.02
134.47
134.35
133.11
132.97
131.68
131.05
129.11
127.47
124.49
124.23
124.00
122.18
119.45
36.45
21.65
Me
O
S
N
Me
Cl
f1 (ppm)

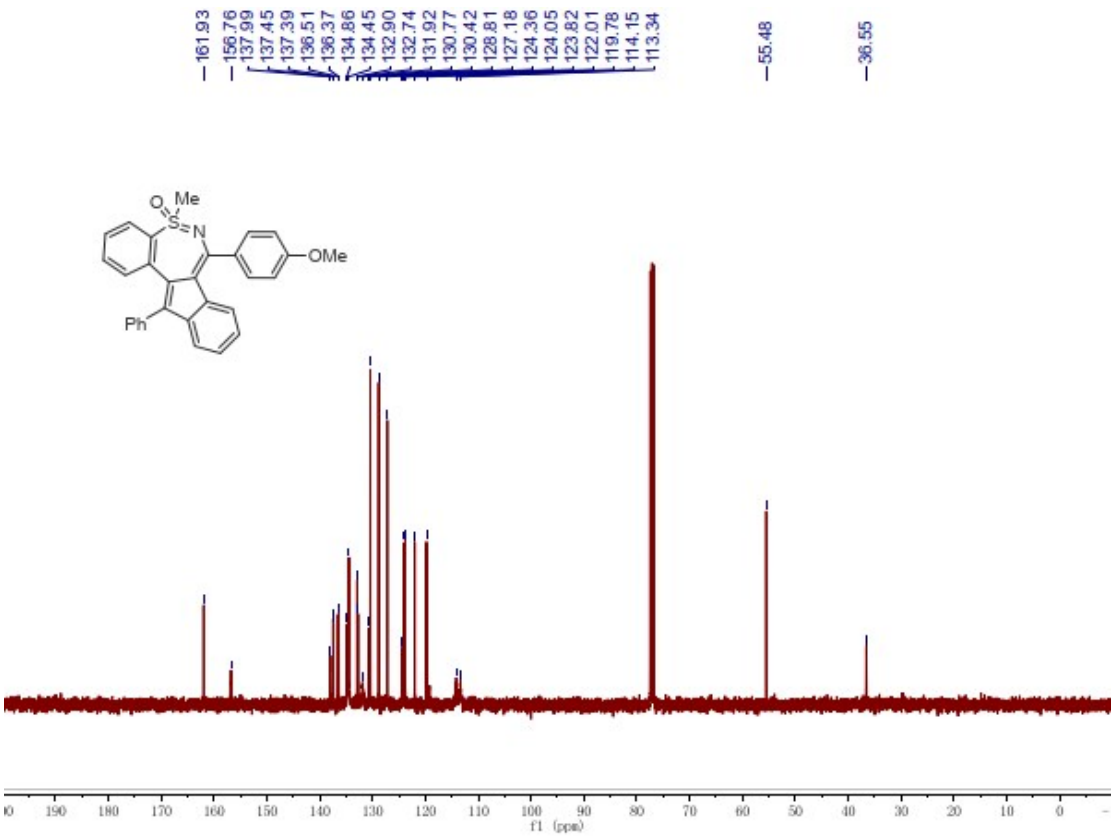
3w.


8.01
7.99
7.78
7.67
7.53
7.50
7.47
7.45
7.43
7.41
7.39
7.32
7.30
7.28
7.22
7.20
7.18
7.16
7.11
7.09
7.07
7.01
6.99
6.97
6.76
6.74
3.27
Me
O
S=N
Cl
F
1.00
2.02
4.00
3.03
2.00
2.08
1.07
1.00
3.00
f1 (ppm)
163.38
160.93
155.26
138.77
137.82
137.70
137.31
136.82
135.94
134.39
134.29
133.13
132.18
131.94
131.86
130.74
127.53
124.60
124.34
122.02
119.77
116.11
115.89
36.50
f1 (ppm)

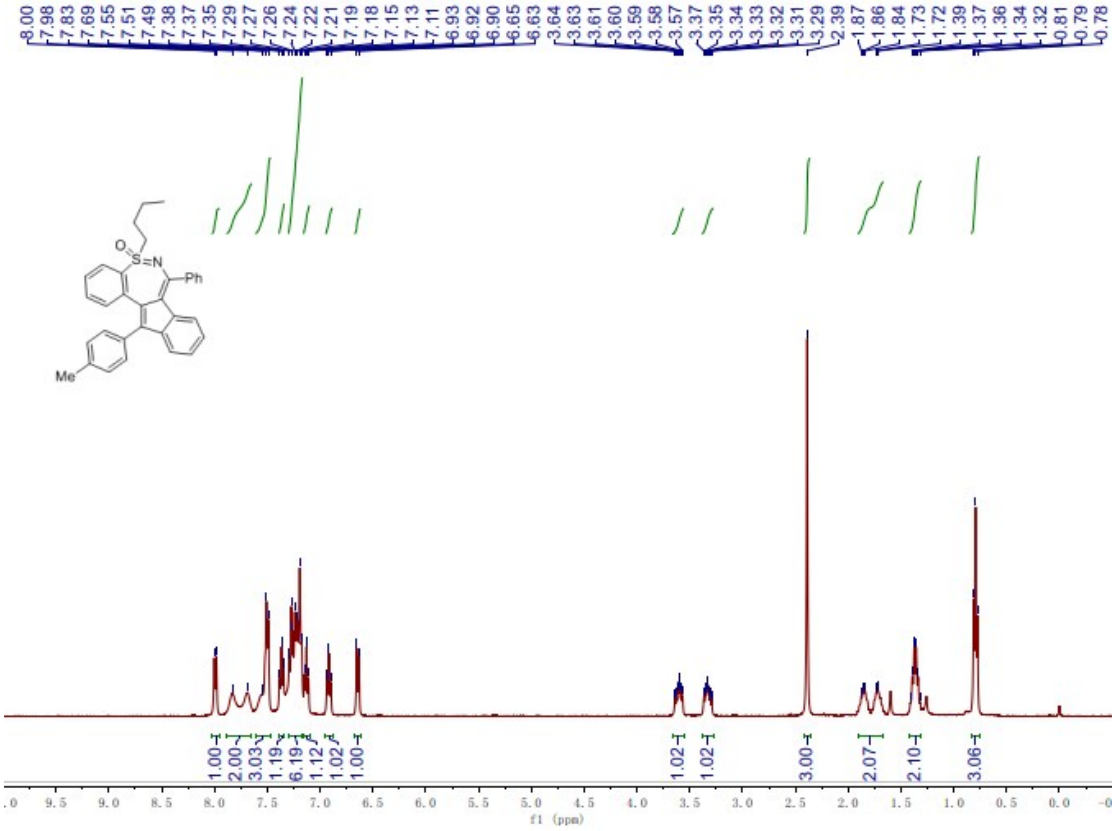

-114.14
Me
O
S=N
Cl
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

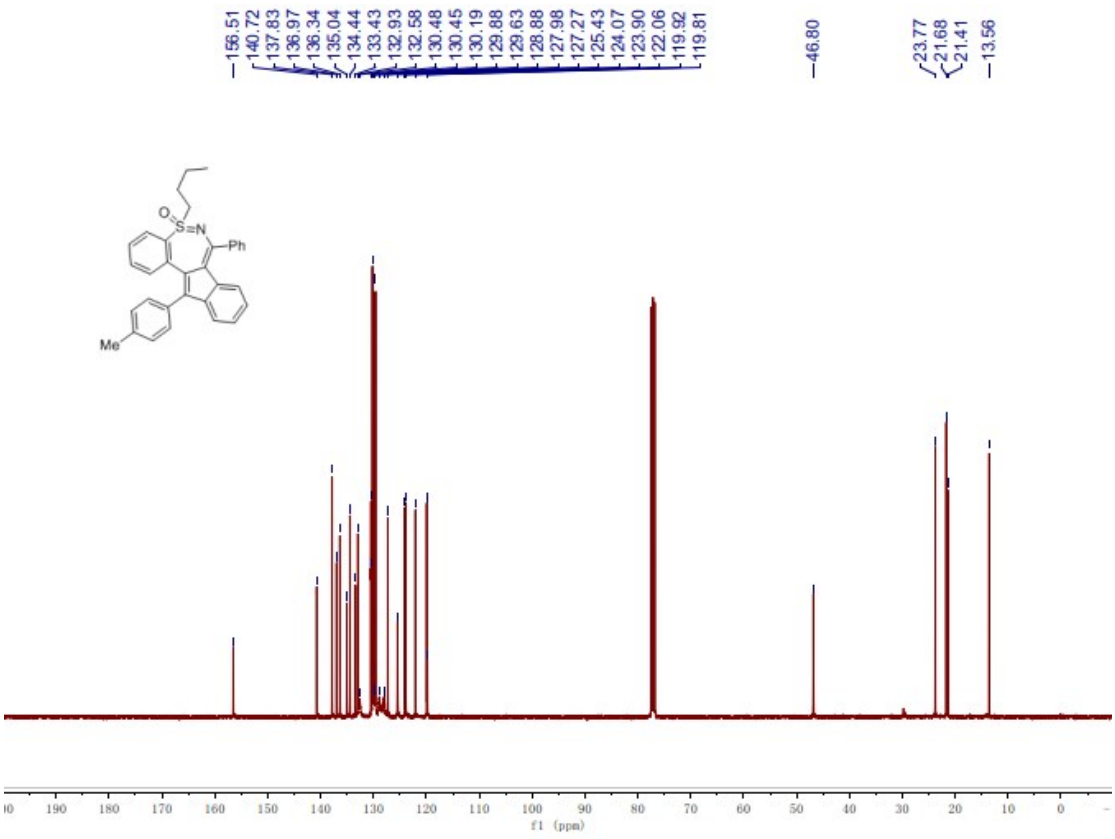
3x.


8.00
7.98
7.52
7.51
7.50
7.37
7.36
7.36
7.34
7.33
7.32
7.31
7.26
7.25
7.25
7.23
7.23
7.22
7.17
7.16
7.15
7.13
6.99
6.99
6.97
6.95
6.95
6.86
6.85
3.88
3.87
3.24
Me
O
S
N
OMe
Ph
1.00
2.09
1.08
8.92
1.07
0.95
1.17
2.00
3.00
3.04
f1 (ppm)

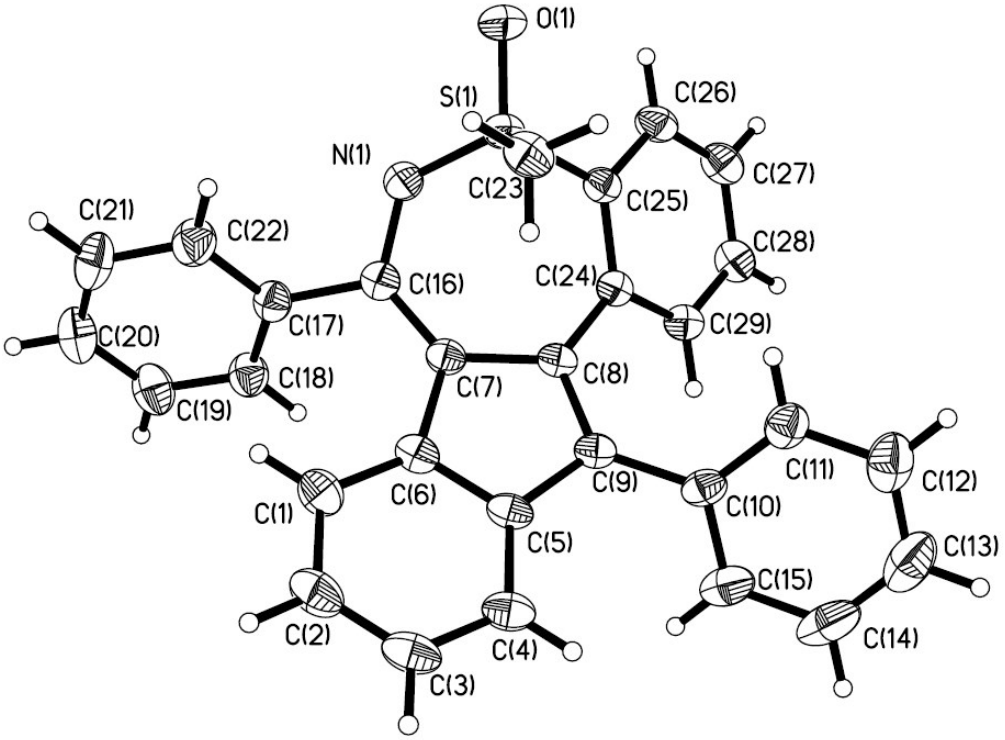

161.93
156.76
137.99
137.45
137.39
136.51
136.37
134.86
134.45
132.90
132.74
131.92
130.77
130.42
128.81
127.18
124.36
124.05
123.82
122.01
119.78
114.15
113.34
55.48
36.55
Me
O
S
N
OMe
Ph
f1 (ppm)

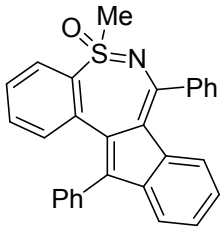
3y


8.00
7.98
7.83
7.69
7.55
7.51
7.49
7.38
7.37
7.35
7.29
7.27
7.26
7.24
7.22
7.21
7.19
7.18
7.15
7.13
7.11
6.93
6.92
6.90
6.65
6.63
3.64
3.63
3.61
3.60
3.59
3.58
3.57
3.37
3.35
3.34
3.33
3.32
3.31
3.29
2.39
1.87
1.86
1.84
1.73
1.72
1.39
1.37
1.36
1.34
1.32
0.81
0.79
0.78
O
S=N
Ph
Me
1.00
2.00
3.03
1.19
6.19
1.12
1.02
1.00
1.02
1.02
3.00
2.07
2.10
3.06
f1 (ppm)


156.51
140.72
137.83
136.97
136.34
135.04
134.44
133.43
132.93
132.58
130.48
130.45
130.19
129.88
129.63
128.88
127.98
127.27
125.43
124.07
123.90
122.06
119.92
119.81
46.80
23.77
21.68
21.41
13.56
O
S=N
Ph
Me
f1 (ppm)

7. X-ray crystal structure of compound 3n.





3n
CCDC 2059008

Bond precision: C-C = 0.0035 A Wavelength=0.71073

Cell: a=11.6422(5) b=10.9274(6) c=35.290(2)
alpha=90 beta=94.919(5) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	4473.0(4)	4473.0(4)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C29 H21 N O S	?
Sum formula	C29 H21 N O S	C58 H42 N2 O2 S2
Mr	431.53	863.05
Dx,g cm-3	1.282	1.282
Z	8	4
Mu (mm-1)	0.166	0.166
F000	1808.0	1808.0
F000'	1809.65	
h,k,lmax	13,12,41	13,12,41
Nref	7854	7834
Tmin,Tmax	0.951,0.956	0.522,1.000
Tmin'	0.951	

Correction method= # Reported T Limits: Tmin=0.522 Tmax=1.000
AbsCorr = NONE

Data completeness= 0.997 Theta(max)= 25.000

R(reflections)= 0.0526(6448) wR2(reflections)= 0.1319(7834)

S = 1.070 Npar= 577