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Supporting Information

Synthesis of Dibenzothiazines from Sulfides by One-Pot N,O-Transfers and Intramolecular C-H Amination

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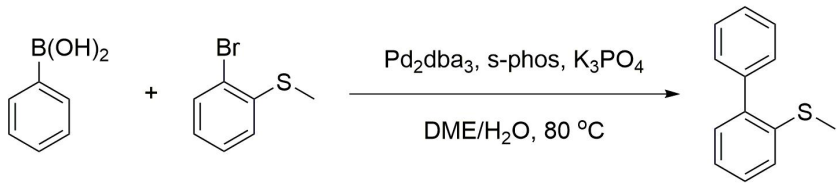
General Methods and Materials

^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance III 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) in $CDCl_3$ with TMS as internal standard. Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for ^{1}H, or to chloroform δ = 77.0 for ^{13}C as internal standard. ^{19}F NMR were recorded on the same instrument. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants, *J*, are reported in hertz. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals Adamas-beta or TCI and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm).

Experimental Details

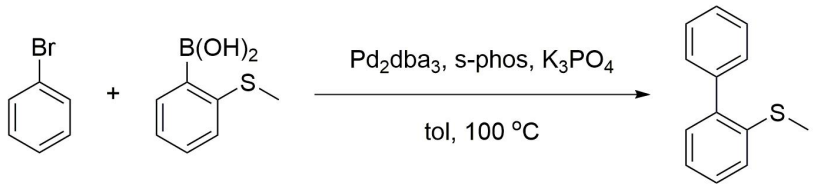
General procedure for the synthesis of substrates

Method A



An oven-dried one-neck flask was charged with (2-bromophenyl)(methyl)sulfane (5 mmol, 1.0 equiv), $PhB(OH)_2$ (7.5 mmol, 1.5 equiv), S-Phos (4.8 mol %), Pd_2dba_3 (2 mol %), and K_3PO_4 (15 mmol, 3.0 equiv) in glovebox, then 25 mL of DME/H_2O (8:1) were injected into the flask, and the reaction was stirred at 80°C for 24 hours. After the reaction was completed, water was added and the organic layer was separated. The aq. layer was extracted with dichloromethane. The combined organic layers were dried over Na_2SO_4. The crude reaction mixture was purified by flash chromatography on silica gel plug to give the coupling product.[1]

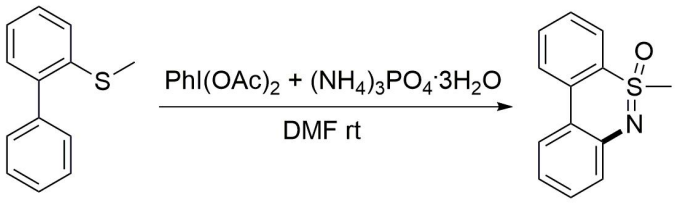
Method B



An oven-dried one-neck flask was charged with bromobenzene (5 mmol, 1.0 equiv), Pd_2dba_3 (2 mol %), S-Phos (4.8 mol %), (2-(methylthio)phenyl)boronic acid (7.5 mmol, 1.5 equiv), and K_3PO_4 (15 mmol, 3.0 equiv) in glovebox, then 25 mL of toluene were injected into the flask, and

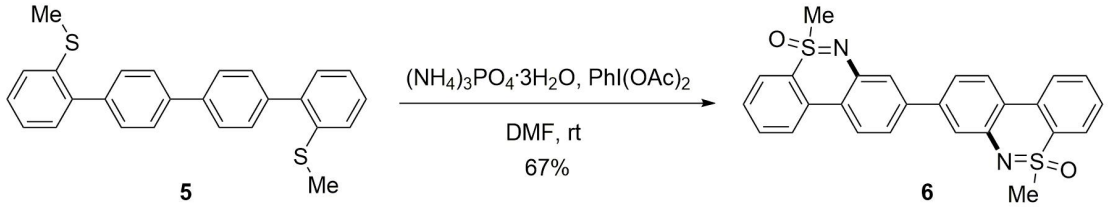
the reaction was stirred at 100 ℃ for 24 hours. After the reaction was completed, water was added and the organic layer was separated. The aq. layer was extracted with dichloromethane. The combined organic layers were dried over Na_2SO_4. The crude reaction mixture was purified by flash chromatography on silica gel.[2]

General procedure for the synthesis of benzothiazines



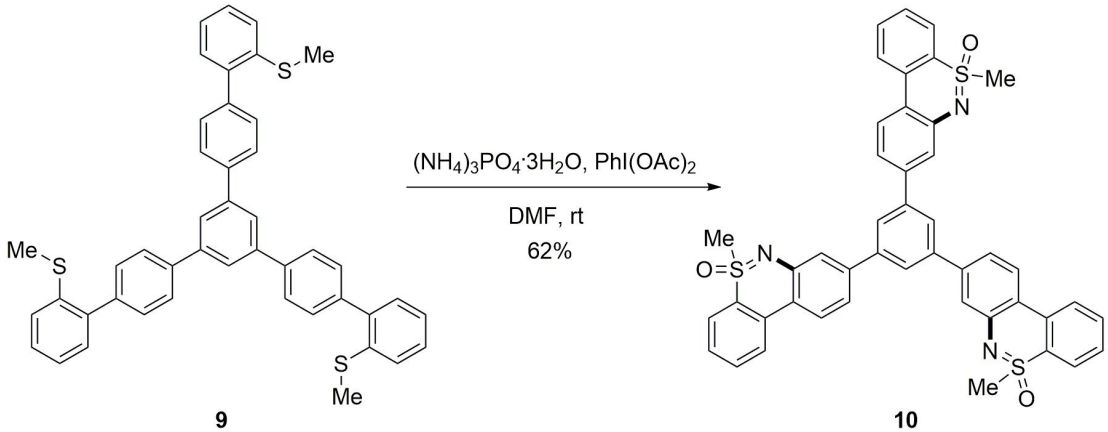
1a **2a**

$PhI(OAc)_2$ (1.5 mmol, 3.0 equiv), was added to the solution of **1a** (0.5 mmol, 1.0 equiv) and $(NH_4)_3PO_4 \bullet 3H_2O$ (0.25 mmol, 0.5 equiv) in DMF (2 mL). Then the reaction mixture was allowed to room temperature and stirred for 24 hours. After the reaction was completed, the solvent was removed under reduced pressure. The crude reaction mixture was purified by flash chromatography on silica gel to give the product **2a**.



5 **6**

$PhI(OAc)_2$ (3 mmol, 6.0 equiv), was added to the solution of **5** (0.5 mmol, 1.0 equiv) and $(NH_4)_3PO_4 \bullet 3H_2O$ (0.5 mmol, 1.0 equiv) in DMF (5 mL). Then the reaction mixture was allowed to room temperature and stirred for 24 hours. After the reaction was completed, the solvent was removed under reduced pressure. The crude reaction mixture was purified by flash chromatography on silica gel to give the product **6**.



9 **10**

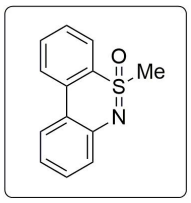
$PhI(OAc)_2$ (4.5 mmol, 9.0 equiv), was added to the solution of **9** (0.5 mmol, 1.0 equiv) and $(NH_4)_3PO_4 \bullet 3H_2O$ (0.75 mmol, 1.5 equiv) in DMF (7 mL). Then the reaction mixture was allowed to room temperature and stirred for 24 hours. After the reaction was completed, the solvent was

removed under reduced pressure. The crude reaction mixture was purified by flash chromatography on silica gel to give the product **10**.

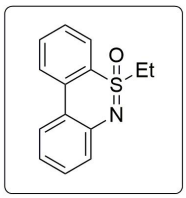
References

1. (a) H. Wang, L. Jiang, T. Chen and Y. Li, *Eur. J. Org. Chem.,* **2010**, 2324; (b) M. Tobisu, Y. Masuya, K. Baba and N. Chatani, *Chem. Sci.,* 2016, **7**, 2587; (c) J. Song, L. M. Jones, G. D. K. Kumar, E. S. Conner, L. Bayeh, G. E. Chavarria, A. K. Charlton-Sevcik, S.-E. Chen, D. J. Chaplin, M. L. Trawick and K. G. Pinney, *ACS Med. Chem. Lett.,* 2012, **3**, 450.
2. Y.-N. Ma and S.-D. Yang, *Chem. Eur. J.* 2015, **21**, 6673.

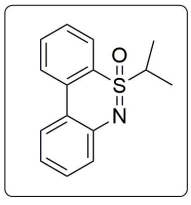
Characterization of the Products



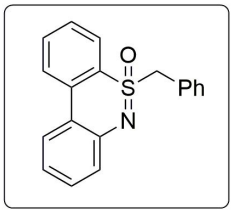
2a： white solid, mp 147-149 ℃; 90%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.13 (d, *J* = 8.4 Hz, 1 H), 7.96 (d, *J* = 8.0 Hz, 1 H), 7.85 (d, *J* = 8.0 Hz, 1 H), 7.66 (t, *J* = 7.8 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 1 H), 7.35 (t, *J* = 7.6 Hz, 1 H), 7.24 (d, *J* = 8.4 Hz, 1 H), 7.05 (t, *J* = 7.6 Hz, 1 H), 3.47 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 142.65, 133.68, 132.75, 130.52, 127.77, 124.63, 123.70, 123.66, 123.41, 120.67, 117.24, 44.43; **HRMS** calc. for $C_{13}H_{11}NOS$ $[M + Na]^+$, 252.0454; found, 252.0458.



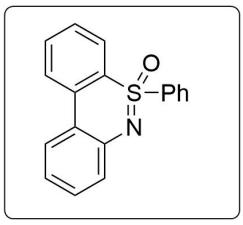
2b: white solid, mp 126-128 ℃; 94%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.19 (d, *J* = 8.0 Hz, 1 H), 7.99 (d, *J* = 8.0 Hz, 1 H), 7.84 (d, *J* = 8.0 Hz, 1 H), 7.71 (t, *J* = 7.8 Hz, 1 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.37 (t, *J* = 7.6 Hz, 1 H), 7.27 (d, *J* = 8.0 Hz, 1 H), 7.05 (d, *J* = 7.6 Hz, 1 H), 3.75-3.66 (m, 1 H), 3.59-3.50 (m, 1 H), 1.21 (t, *J* = 7.4 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 143.39, 135.01, 132.95, 130.55, 127.76, 124.75, 124.33, 123.63, 123.36, 121.53, 120.40, 116.65, 50.63, 8.47; **HRMS** calc. for $C_{14}H_{13}NOS$ $[M + Na]^+$, 266.0610; found, 266.0613.



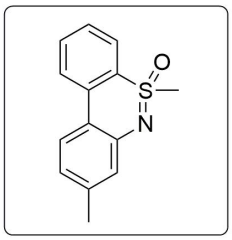
2c: white solid, mp 108-110 ℃; 92%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.16 (d, *J* = 8.4 Hz, 1 H), 7.94 (d, *J* = 8.0 Hz, 1 H), 7.85 (d, *J* = 8.0 Hz, 1 H), 7.72-7.68 (m, 1 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.35-7.31 (m, 1 H), 7.26-7.24 (m, 1 H), 7.02-6.98 (m, 1 H), 3.76-3.66 (m, 1 H), 1.49 (d, *J* = 6.8 Hz, 3 H), 1.15 (d, *J* = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 144.21, 135.82, 133.11, 130.57, 127.64, 125.07, 124.74, 123.36, 123.33, 120.78, 119.99, 116.68, 57.32, 16.76, 13.73; **HRMS** calc. for $C_{15}H_{15}NOS$ $[M + H]^+$, 258.0947; found, 258.0948.



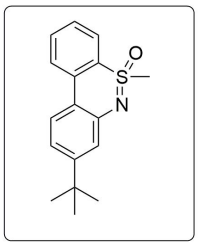
2d: white solid, mp 142-144 ℃; 78%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 8.0 Hz, 1 H), 7.78 (d, *J* = 8.0 Hz, 1 H), 7.64-7.59 (m, 2 H), 7.40 (t, *J* = 7.6 Hz, 1 H), 7.30 (t, *J* = 7.6 Hz, 1 H), 7.22-7.07 (m, 6 H), 6.94 (t, *J* = 7.6 Hz, 1 H), 4.59-4.45 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 144.05, 135.70, 133.40, 130.98, 130.56, 128.58, 128.19, 127.49, 127.35, 125.60, 124.51, 123.29, 123.11, 121.41, 120.15, 116.89, 64.01; **HRMS** calc. for $C_{19}H_{15}NOS$ $[M + Na]^+$, 328.0767; found, 328.0771.



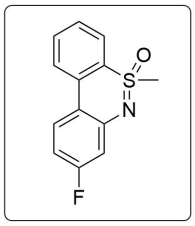
2e: white solid, mp 125-127 ℃; 83%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.19 (d, *J* = 8.4 Hz, 1 H), 8.07 (d, *J* = 8.0 Hz, 1 H), 8.02 (d, *J* = 7.6 Hz, 2 H), 7.64-7.58 (m, 2 H), 7.54 (t, *J* = 8.0 Hz, 2 H), 7.44-7.33 (m, 4 H), 7.14-7.10 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 142.92, 139.31, 133.59, 133.53, 132.20, 130.48, 129.39, 129.03, 127.60, 125.63, 125.45, 125.34, 123.34, 123.26, 120.93, 117.00; **HRMS** calc. for $C_{18}H_{13}NOS$ $[M + H]^+$, 292.0791; found, 292.0791.



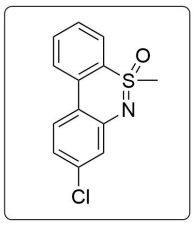
2f： white solid, mp 176-178 ℃; 85%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.12 (d, *J* = 8.4 Hz, 1 H), 7.87 (d, *J* = 8.0 Hz, 2 H), 7.68 (t, *J* = 7.6 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 1 H), 7.06 (s, 1 H), 6.89 (d, *J* = 8.4 Hz, 1 H), 3.49 (s, 3 H), 2.37 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 142.56, 141.02, 133.95, 132.78, 127.31, 124.80, 124.21, 123.78, 123.47, 123.30, 122.08, 114.75, 44.54, 21.34; **HRMS** calc. for $C_{14}H_{13}NOS$ $[M + H]^+$, 244.0791; found, 244.0793.



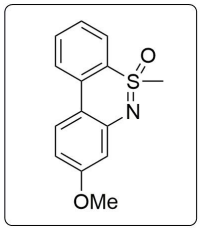
2g: white solid, mp 146-147 ℃; 85%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.15 (d, *J* = 8.0 Hz, 1 H), 7.93 (d, *J* = 8.4 Hz, 1 H), 7.87 (d, *J* = 8.0 Hz, 1 H), 7.69 (t, *J* = 7.6 Hz, 1 H), 7.51 (t, *J* = 7.6 Hz, 1 H), 7.28 (s, 1 H), 7.13 (d, *J* = 8.4 Hz, 1 H), 3.52 (s, 3 H), 1.35 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 154.23, 142.27, 133.79, 132.78, 127.37, 124.25, 123.78, 123.52, 123.11, 121.32, 118.52, 114.61, 44.61, 34.70, 31.03; **HRMS** calc. for $C_{17}H_{19}NOS$ $[M + H]^+$, 286.1260; found, 286.1255.



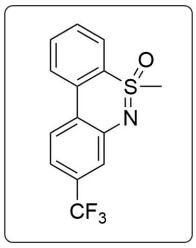
2h: white solid, mp 129-132 ℃; 90%; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -110.29; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.08 (d, *J* = 8.4 Hz, 1 H), 7.96-7.92 (m, 1 H), 7.88 (d, *J* = 7.6 Hz, 1 H), 7.71 (t, *J* = 7.6 Hz, 1 H), 7.55 (t, *J* = 7.6 Hz, 1 H), 6.92 (dd, *J* = 10.4 Hz, *J* = 2.0 Hz, 1 H), 6.80-6.76 (m, 1 H), 3.51 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 164.14 (d, *J* = 246.9 Hz), 144.79 (d, *J* = 2.6 Hz), 133.44, 133.09, 127.70, 125.26 (d, *J* = 5.3 Hz), 123.95, 123.59, 113.89, 110.51 (d, *J* = 22.5 Hz),, 108.68 (d, *J* = 22.6 Hz), 44.65; **HRMS** calc. for $C_{13}H_{10}FNOS$ $[M + Na]^+$, 270.0359; found, 270.0357.



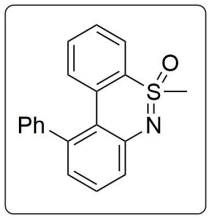
2i: white solid, mp 192-194 ℃; 75%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.12 (d, *J* = 8.0 Hz, 1 H), 7.90 (d, *J* = 8.4 Hz, 2 H), 7.76-7.72 (m, 1 H), 7.59 (t, *J* = 7.2 Hz, 1 H), 7.27-7.23 (m, 1 H), 7.03 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1 H), 3.52 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 143.83, 136.04, 133.21, 133.14, 128.16, 124.63, 124.38, 124.25, 123.97, 123.71, 121.09, 115.88, 44.65; **HRMS** calc. for $C_{13}H_{10}ClNOS$ $[M + Na]^+$, 286.0064; found, 286.0070.



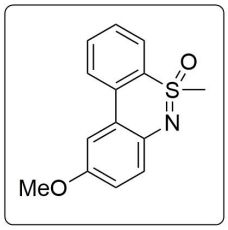
2j: white solid, mp 163-164 ℃; 73%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.04 (d, *J* = 8.4 Hz, 1 H), 7.88-7.83 (m, 2 H), 7.67-7.63 (m, 1 H), 7.45 (t, *J* = 7.6 Hz, 1 H), 6.74 (d, *J* = 2.4 Hz, 1 H), 6.66 (dd, *J* = 8.8 Hz, *J* = 2.8 Hz, 1 H), 3.83 (s, 3 H), 3.50 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 161.54, 144.35, 133.94, 132.85, 126.63, 124.71, 123.80, 123.09, 123.04, 110.55, 109.55, 106.97, 55.21, 44.55; **HRMS** calc. for $C_{14}H_{13}NO_2S$ [M + Na]$^+$, 282.0559; found, 282.0558.



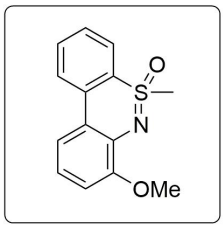
2k: white solid, mp 161-163 ℃; 84%; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -62.98; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.22 (d, *J* = 8.4 Hz, 1 H), 8.10 (d, *J* = 8.4 Hz, 1 H), 7.95 (d, *J* = 8.0 Hz, 1 H), 7.80 (t, *J* = 7.8 Hz, 1 H), 7.67 (t, *J* = 7.6 Hz, 1 H), 7.52 (s, 1 H), 7.29 (d, *J* = 8.4 Hz, 1H), 3.56 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 142.84, 133.21, 132.57, 132.20, 131.87, 129.04, 123.83 (q, *J* = 269.8 Hz), 124.16, 123.95, 121.85, 119.94, 116.78, 44.56; **HRMS** calc. for $C_{14}H_{10}F_3NOS$ [M + H]$^+$, 298.0508; found, 298.0513.



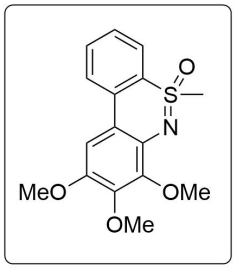
2l: white solid, mp 201-202 ℃; 71%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 8.0 Hz, 1 H), 7.49-7.25 (m, 8 H), 7.21 (m, 1 H), 7.19-7.13 (m, 1 H), 7.02 (d, *J* = 7.2 Hz, 1 H), 3.48 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 144.47, 143.29, 141.05, 133.53, 130.41, 130.33, 129.80, 128.83, 127.59, 127.16, 127.01, 124.81, 124.24, 121.32, 118.45, 41.56; **HRMS** calc. for $C_{19}H_{15}NOS$ [M + Na]$^+$, 328.0767; found, 328.0762.



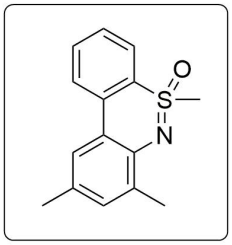
2ma: white solid, mp 185-187 ℃; 41%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.12 (d, *J* = 8.0 Hz, 1 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.71 (t, *J* = 7.8 Hz, 1 H), 7.55 (t, *J* = 7.6 Hz, 1 H), 7.48 (d, *J* = 2.4 Hz, 1 H), 7.20 (d, *J* = 8.8 Hz, 1 H), 7.02 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1 H), 3.85 (s, 3 H), 3.51 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 153.91, 136.51, 133.46, 132.67, 127.94, 125.68, 125.12, 123.91, 123.61, 117.92, 107.55, 55.74, 44.71; **HRMS** calc. for $C_{14}H_{13}NO_2S$ [M + Na]$^+$, 282.0559; found, 282.0553.



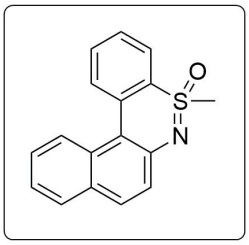
2mb: white solid, mp 205-207 ℃; 42%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.19 (d, *J* = 8.0 Hz, 1 H), 7.91 (d, *J* = 8.0 Hz, 1 H), 7.73 (t, *J* = 7.6 Hz, 1 H), 7.65 (d, *J* = 8.0 Hz, 1 H), 7.58 (t, *J* = 7.4 Hz, 1 H), 7.05 (t, *J* = 7.8 Hz, 1 H), 6.97 (d, *J* = 7.6 Hz, 1 H), 3.97 (s, 3 H), 3.64 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 152.70, 133.74, 132.70, 127.90, 124.86, 124.37, 123.56, 120.35, 118.22, 115.55, 111.17, 56.12, 44.31; **HRMS** calc. for $C_{14}H_{13}NO_2S$ $[M + Na]^+$, 282.0559; found, 282.0562.



2n: white solid, mp 156-158 ℃; 82%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.05 (d, *J* = 8.4 Hz, 1 H), 7.87-7.85 (m, 1 H), 7.70-7.66 (m, 1 H), 7.51 (t, *J* = 7.4 Hz, 1 H), 7.26 (s, 1 H), 4.02 (s, 3 H), 3.99 (s, 3 H), 3.92 (s, 3 H), 3.58 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 147.42, 146.22, 144.95, 133.24, 132.43, 131.97, 127.28, 124.54, 123.60, 123.40, 113.15, 101.65, 61.10, 61.01, 56.37, 43.87; **HRMS** calc. for $C_{16}H_{17}NO_4S$ $[M + Na]^+$, 342.0770; found, 342.0773.

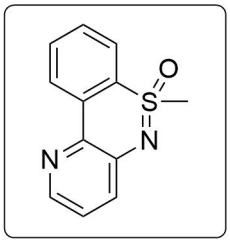


2o: white solid, mp 166-168 ℃; 36%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.17 (d, *J* = 8.0 Hz, 1 H), 8.87 (d, *J* = 8.0 Hz, 1 H), 7.71-7.67 (m, 2 H), 7.53 (t, *J* = 7.6 Hz, 1 H), 7.13 (s, 1 H), 3.47 (s, 3 H), 2.42 (s, 3 H), 2.37 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 139.17, 134.37, 132.75, 132.59, 132.23, 129.12, 127.45, 124.69, 124.09, 123.58, 121.22, 116.85, 44.44, 21.00, 18.22; **HRMS** calc. for $C_{15}H_{15}NOS$ $[M + Na]^+$, 280.0767; found, 280.0766.

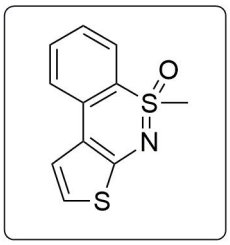


2p: white solid, mp 160-162 ℃; 42%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.47 (d, *J* = 8.8 Hz, 1 H),

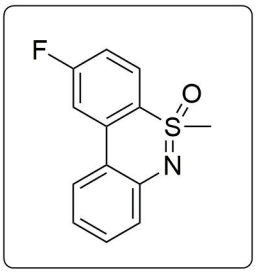
8.40 (d, *J* = 8.0 Hz, 1 H), 7.88-7.80 (m, 3 H), 3.66 (t, *J* = 7.8 Hz, 1 H), 7.56-7.48 (m, 2 H), 7.43-7.37 (m, 2 H), 3.39 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 142.51, 131.64, 131.13, 128.90, 128.70, 127.31, 126.67, 124.75, 123.71, 121.70, 114.56, 40.63; **HRMS** calc. for $C_{17}H_{13}NOS$ [M + Na]$^+$, 302.0610; found, 302.0605.



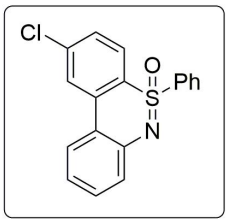
2q: white solid, mp 157-159 ℃;40%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.88 (d, *J* = 8.4 Hz, 1 H), 8.37-8.36 (m, 1 H), 7.89 (d, *J* = 8.0 Hz, 1 H), 7.81 (t, *J* = 7.6 Hz, 1 H), 7.66 (t, *J* = 7.6 Hz, 1 H), 7.50 (d, *J* = 8.4 Hz, 1 H), 7.31-7.27 (m, 1 H), 3.56 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 141.93, 139.06, 135.14, 134.46, 133.16, 131.31, 129.46, 126.08, 125.36, 125.05, 123.50, 45.43; **HRMS** calc. for $C_{12}H_{10}N_2OS$ [M + H]$^+$, 231.0587; found, 231.0595.



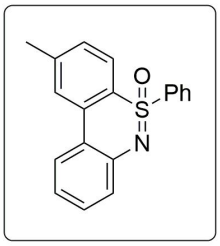
2r: white solid, mp 138-140 ℃; 58%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.85 (d, *J* = 8.0 Hz, 1 H), 7.76 (d, *J* = 8.0 Hz, 1 H), 7.66 (t, *J* = 7.6 Hz, 1 H), 7.44 (t, *J* = 7.6 Hz, 1 H), 7.29-7.26 (m, 1 H), 6.70 (d, *J* = 5.6 Hz, 1 H), 3.59 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 152.62, 133.22, 132.44, 126.05, 124.01, 123.22, 120.33, 119.06, 113.54, 113.52, 45.05; **HRMS** calc. for $C_{11}H_9NOS_2$ [M + Na]$^+$, 258.0018; found, 258.0007.



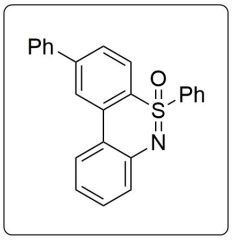
2s: white solid, mp 175-177 ℃; 41%; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -103.30; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.84-7.87 (m, 2 H), 7.81 (dd, *J* = 10.8 Hz, *J* = 2.4 Hz, 1 H), 7.42-7.38 (m, 1 H), 7.29-7.23 (m, 2 H), 7.07 (t, *J* = 7.4 Hz, 1 H), 3.49 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 165.07 (d, *J* = 252.2 Hz), 143.14, 137.33 (d, *J* = 9.3 Hz), 131.42, 126.99 (d, *J* = 9.8 Hz), 124.89, 123.66, 120.98 (d, *J* = 2.8 Hz), 120.91, 116.64 (d, *J* = 2.5 Hz), 115.98 (d, *J* = 23.7 Hz), 110.04 (d, *J* = 23.5 Hz), 45.12; **HRMS** calc. for $C_{13}H_{10}FNOS$ [M + H]$^+$, 248.0540; found, 248.0536.



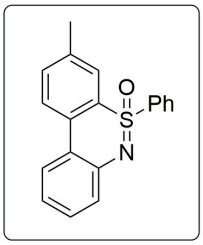
2t: white solid, mp 192-194 ℃; 83%; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 8.19 (s, 1 H), 8.02-8.01 (m, 3 H), 7.66 (t, *J* = 7.8 Hz, 1 H), 7.58 (t, *J* = 7.8 Hz, 2 H), 7.47-7.44 (m, 1 H), 7.39 (dd, *J* = 7.8 Hz, *J* = 0.6 Hz, 1 H), 7.34-7.31 (m, 2 H), 7.16-7.14 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 143.27, 139.01, 138.79, 135.34, 133.82, 131.24, 129.50, 129.21, 127.91, 127.15, 125.55, 123.98, 123.47, 123.25, 121.24, 116.12; **HRMS** calc. for $C_{13}H_{10}FNOS$ $[M + Na]^+$, 348.0220; found, 348.0227.



2u: white solid, mp 208-210 ℃; 79%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.08 (d, *J* = 8.4 Hz, 1 H), 8.01-7.99 (m, 3 H), 7.63-7.60 (m, 1 H), 7.54 (t, *J* = 7.6 Hz, 2 H), 7.43-7.36 (m, 2 H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 1 H), 7.14-7.10 (m, 1 H), 2.47 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 143.19, 142.94, 139.97, 133.79, 133.39, 130.40, 129.25, 129.02, 128.85, 125.64, 125.31, 123.30, 123.09, 120.81, 116.93, 22.03; **HRMS** calc. for $C_{19}H_{15}NOS$ $[M + Na]^+$, 328.0767; found, 328.0773.

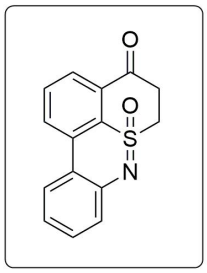


2v: white solid, mp 201-203 ℃; 40%; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 8.43 (s, 1 H), 8.22 (d, *J* = 5.6 Hz, 1 H), 8.11 (d, *J* = 5.2 Hz, 2 H), 7.70-7.66 (m, 3 H), 7.63-7.60 (m, 3 H), 7.53-7.45 (m, 6 H), 7.20 (t, *J* = 4.8 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 145.20, 143.22, 139.63, 139.50, 134.04, 133.55, 130.61, 129.41, 128.08, 128.97, 128.44, 127.38, 126.68, 126.07, 125.43, 124.26, 123.37, 121.77, 120.96, 117.08; **HRMS** calc. for $C_{24}H_{17}NOS$ $[M + H]^+$, 368.1104; found, 368.1106.

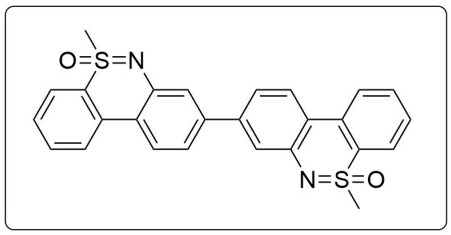


2w: white solid, mp 162-164 ℃; 82%; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 8.12-8.10 (m, 1 H), 8.06 (d,

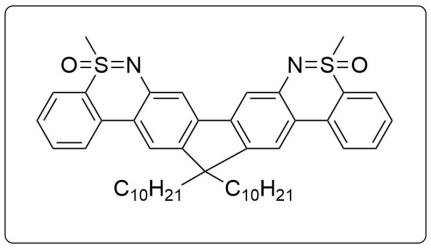
J = 8.1 Hz, 1 H), 8.03-8.02 (m, 2 H), 7.66-7.63 (m, 1 H), 7.58-7.56 (m, 2 H), 7.46-7.45 (m, 1 H), 7.42-7.36 (m, 2 H), 7.18 (s, 1 H), 7.14-7.11 (m, 1 H), 2.32 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 142.65, 139.75, 138.10, 133.71, 133.49, 131.30, 130.10, 129.41, 129.09, 125.42, 125.28, 125.20, 123.25, 123.10, 120.89, 117.07, 21.09; **HRMS** calc. for $C_{19}H_{15}NOS$ $[M + Na]^+$, 328.0767; found, 328.0760.



2x: yellow solid, mp 200-202 ℃; 24%; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 8.29 (d, *J* = 8.4 Hz, 1 H), 8.07 (d, *J* = 7.8 Hz, 1 H), 7.99 (d, *J* = 7.8 Hz, 1 H), 7.74 (t, *J* = 7.8 Hz, 1 H), 7.39 (t, *J* = 7.8 Hz, 1 H), 7.29 (d, *J* = 7.8 Hz, 1 H), 7.09 (t, *J* = 7.2 Hz, 1 H), 4.00-3.96 (m, 2 H), 3.71-3.65 (m, 1 H), 3.27 (dd, *J* = 18.0 Hz, *J* = 2.4 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 190.08, 142.22, 132.45, 132.26, 131.25, 129.88, 127.30, 127.21, 125.28, 123.94, 123.70, 121.75, 118.29, 48.76, 35.31; **HRMS** calc. for $C_{15}H_{11}NO_2S$ $[M + Na]^+$, 292.0403; found, 292.0412.

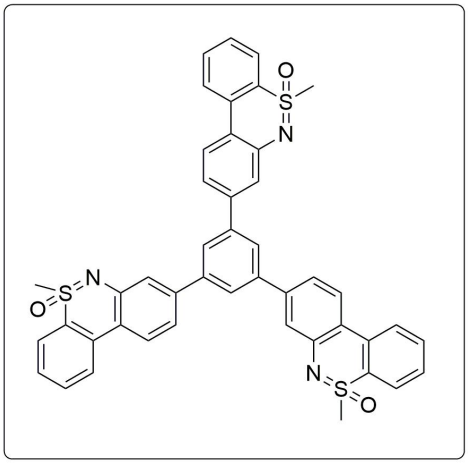


6: white solid, 63%; mp >330 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.246 (d, *J* = 8.4 Hz, 1 H), 8.10 (d, *J* = 8.4 Hz, 1 H), 7.94 (d, *J* = 8.0 Hz, 1 H), 7.77 (t, *J* = 7.6 Hz, 1 H), 7.62-7.58 (m, 2 H), 3.56 (s, 3 H), 1.54 (s, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 142.51, 133.88, 133.04, 127.91, 124.71, 124.10, 124.01, 123.93, 122.96, 119.76, 116.77, 29.71; **HRMS** calc. for $C_{26}H_{20}N_2O_2S_2$ $[M + Na]^+$, 479.0858; found, 479.0875.



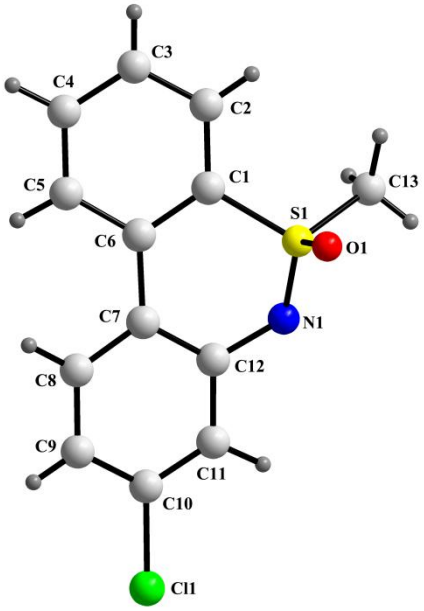
8: white solid, mp 98-100 ℃; 30%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.24 (d, *J* = 8.0 Hz, 1 H), 8.10 (d, *J* = 8.4 Hz, 1 H), 7.96-7.91 (m, 2 H), 7.84-7.82 (m, 2 H), 7.67 (t, *J* = 7.6 Hz, 1 H), 7.61 (t, *J* = 7.2 Hz, 1 H), 7.53 (s, 1 H), 7.48-7.42 (m, 2 H), 7.39 (d, *J* = 8.4 Hz, 1 H), 3.50 (s, 3 H), 3.34 (s, 3 H), 2.86-2.78 (m, 2 H), 1.99-1.89 (m, 2 H), 1.08-0.92 (m, 28 H), 0.70 (td, *J* = 6.8 Hz, *J* = 2.4 Hz, 6

H), 0.58-0.49 (m, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 145.12, 143.77, 143.24, 142.02, 141.83, 139.85, 134.43, 132.88, 132.69, 127.35，127.32, 124.46, 124.27, 124.13, 124.02, 123.82, 123.34, 116.98, 116.60，116.64，115.39, 112.86, 56.71, 44.69, 44.67, 44.44, 38.07, 37.99, 37.73, 31.72, 30.12, 30.05, 29.96, 29.54, 29.50, 29.45, 29.28, 29.24, 29.16, 29.15, 29.13, 24.01, 23.95, 22.50, 14.00; **HRMS** calc. for $C_{47}H_{60}N_2O_2S_2$ $[M + Na]^+$, 771.3988; found, 771.3965.



10: white solid, mp >330 ℃; 57%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.22 (d, J = 8.4 Hz, 1 H), 8.08 (d, J = 8.4 Hz, 1 H), 7.98 (s, 1 H), 7.96 (s, J = 7.6 Hz, 1 H), 7.73 (t, J = 7.2 Hz, 1 H), 7.65 (s, 1 H), 7.56 (t, J = 7.6 Hz, 1 H), 7.44 (dd, J = 8.0 Hz, J = 1.2 Hz, 1 H), 3.56 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 143.22, 142.97, 141.27, 133.78, 132.99, 127.87, 125.09, 124.65, 124.12, 123.99, 123.91, 123.04, 119.85, 116.65, 44.83; **HRMS** calc. for $C_{45}H_{33}N_3O_3S_3$ $[M + Na]^+$, 782.1576; found, 782.1572.

The X-ray crystallographic analysis data



2i

CCDC 1834056

Table S1 Crystal data and structure refinement for **2i**.

Empirical formula	$C_{13}H_{10}ClNOS$
Formula weight	263.73
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.4863(2)
b/Å	9.6208(2)
c/Å	12.3830(2)
α/°	90
β/°	111.484(2)
γ/°	90
Volume/Å^3	1162.48(4)
Z	4
ρ_{calc}g/cm^3	1.507
μ/mm^{-1}	4.426
F(000)	544.0
Crystal size/mm^3	0.62 × 0.48 × 0.45
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.492 to 144.782
Index ranges	$-12 \le h \le 11$, $-11 \le k \le 7$, $-15 \le l \le 15$
Reflections collected	6586
Independent reflections	2269 [R_{int} = 0.0365, R_{sigma} = 0.0349]
Data/restraints/parameters	2269/0/194
Goodness-of-fit on F^2	1.155
Final R indexes [I>=2σ (I)]	R_1 = 0.0454, wR_2 = 0.1406
Final R indexes [all data]	R_1 = 0.0528, wR_2 = 0.1462
Largest diff. peak/hole / e Å^{-3}	0.23/-0.52

Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2i**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Cl1	3202.7(7)	9521.1(7)	5606.9(7)	51.3(2)
S1	7960.5(5)	5581.5(5)	5274.0(4)	27.6(2)
O1	8957.7(16)	6603.7(18)	5223.5(15)	37.7(4)
N1	6885.2(19)	6014(2)	5786.7(16)	34.3(4)
C1	7072(2)	4956(2)	3871.8(18)	28.4(4)
C2	7611(2)	3922(3)	3378(2)	37.6(5)
C3	6898(3)	3527(3)	2248(2)	43.7(6)
C4	5664(3)	4182(3)	1616(2)	41.6(6)
C5	5138(2)	5208(3)	2105(2)	35.5(5)
C6	5823(2)	5624(2)	3268.7(19)	28.0(5)
C7	5253(2)	6663(2)	3834.1(18)	27.7(4)
C8	4148(2)	7515(3)	3192(2)	35.0(5)
C9	3534(2)	8414(3)	3719(2)	38.3(5)
C10	4009(2)	8444(2)	4925(2)	35.8(5)
C11	5103(2)	7647(2)	5593(2)	34.3(5)
C12	5765(2)	6774(2)	5056.4(18)	28.4(4)
C13	8856(3)	4209(3)	6160(2)	41.2(6)

Table S3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **2i**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Cl1	47.0(4)	54.0(4)	57.6(5)	-10.0(3)	24.7(3)	9.4(3)
S1	23.8(3)	31.5(3)	23.2(3)	1.64(17)	3.4(2)	-0.90(17)
O1	30.9(8)	39.4(9)	38.0(9)	1.1(7)	7.0(7)	-9.1(7)
N1	30.3(9)	46.6(10)	22.0(9)	0.9(8)	5.0(8)	3.5(8)
C1	27.5(10)	31.5(10)	24.3(10)	-0.5(8)	7.3(8)	-4.8(8)
C2	34.3(11)	38.6(12)	38.4(13)	-3.2(10)	11.7(10)	0.9(9)
C3	50.5(14)	39.9(13)	43.7(14)	-11.5(11)	20.8(12)	-1.4(11)
C4	47.9(14)	44.8(12)	29.7(12)	-9.9(10)	11.2(11)	-9.3(11)
C5	33.7(11)	40.5(12)	26.4(11)	-2.1(9)	4.3(10)	-3.1(9)
C6	27.7(10)	30(1)	25.3(11)	0.6(7)	8.3(9)	-5.2(7)
C7	25.6(9)	30.6(10)	24.9(10)	1.4(7)	6.8(8)	-3.2(7)
C8	31.2(11)	40.6(11)	28.5(11)	2.2(9)	5.1(9)	0.9(9)
C9	30.8(10)	40.7(12)	40.0(13)	3.6(10)	8.9(10)	4.5(9)
C10	31.3(10)	36.4(11)	42.3(13)	-4.8(10)	16.7(10)	-0.6(9)
C11	33.1(11)	40.7(11)	28.5(11)	-4.0(9)	10.6(9)	-2.6(9)
C12	24.4(9)	34(1)	24.2(10)	-1.1(8)	5.9(8)	-3.1(8)
C13	39.2(13)	43.5(13)	34.9(13)	10.5(10)	6.3(11)	4.8(11)

Table S4 Bond Lengths for **2i.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C10	1.739(2)	C4	C5	1.375(4)
S1	O1	1.4534(16)	C5	C6	1.413(3)
S1	N1	1.5401(19)	C6	C7	1.467(3)
S1	C1	1.749(2)	C7	C8	1.404(3)
S1	C13	1.754(3)	C7	C12	1.413(3)
N1	C12	1.398(3)	C8	C9	1.377(3)
C1	C2	1.391(3)	C9	C10	1.391(3)
C1	C6	1.403(3)	C10	C11	1.376(3)
C2	C3	1.376(4)	C11	C12	1.403(3)
C3	C4	1.394(4)			

Table S5 Bond Angles for 2i.

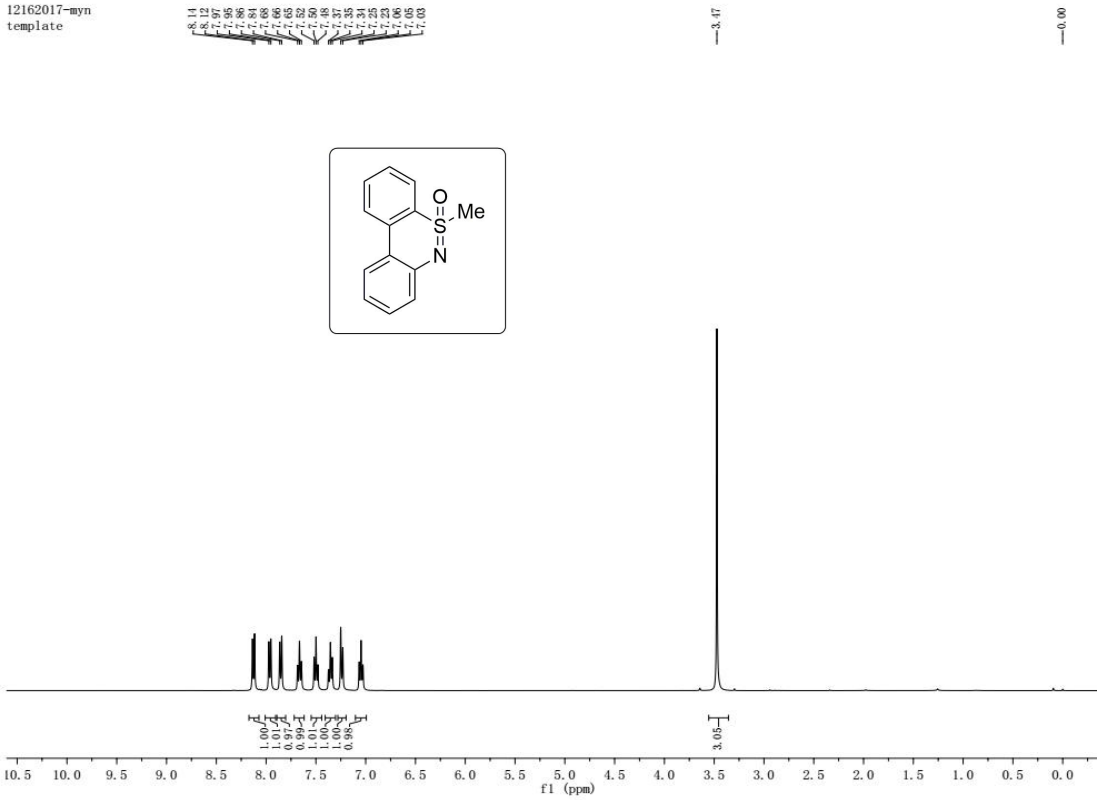
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	N1	118.81(11)	C1	C6	C7	121.5(2)
O1	S1	C1	108.66(10)	C5	C6	C7	122.4(2)
O1	S1	C13	107.92(12)	C8	C7	C6	121.6(2)
N1	S1	C1	107.33(10)	C8	C7	C12	118.3(2)
N1	S1	C13	104.52(12)	C12	C7	C6	120.08(19)
C1	S1	C13	109.29(13)	C9	C8	C7	122.0(2)
C12	N1	S1	116.29(15)	C8	C9	C10	118.4(2)
C2	C1	S1	121.85(17)	C9	C10	Cl1	119.17(19)
C2	C1	C6	122.9(2)	C11	C10	Cl1	119.16(19)
C6	C1	S1	115.13(17)	C11	C10	C9	121.7(2)
C3	C2	C1	119.2(2)	C10	C11	C12	119.9(2)
C2	C3	C4	119.6(2)	N1	C12	C7	123.6(2)
C5	C4	C3	121.1(2)	N1	C12	C11	116.8(2)
C4	C5	C6	121.1(2)	C11	C12	C7	119.5(2)
C1	C6	C5	116.1(2)				

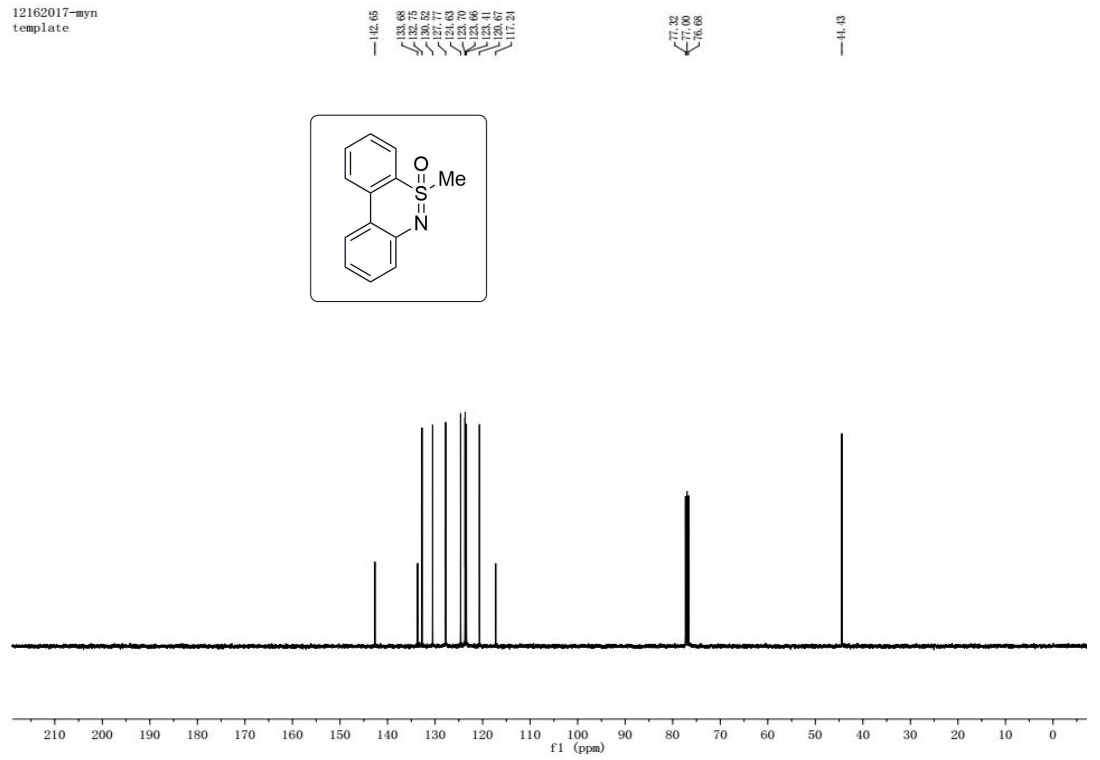
Table S6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **2i**.

Atom	***x***	***y***	***z***	**U(eq)**
H2	8450(40)	3510(40)	3760(30)	65(11)
H3	7270(30)	2840(40)	1940(30)	60(10)
H4	5170(30)	3950(30)	800(30)	44(8)
H5	4330(40)	5650(30)	1620(30)	55(10)
H8	3830(30)	7500(40)	2340(30)	54(9)
H9	2810(30)	8970(40)	3280(30)	52(9)
H11	5460(30)	7620(30)	6460(30)	51(8)
H13A	9180(40)	4550(40)	6880(40)	66(12)
H13B	9580(30)	3870(30)	5850(30)	51(9)
H13C	8290(40)	3480(40)	6100(30)	59(10)

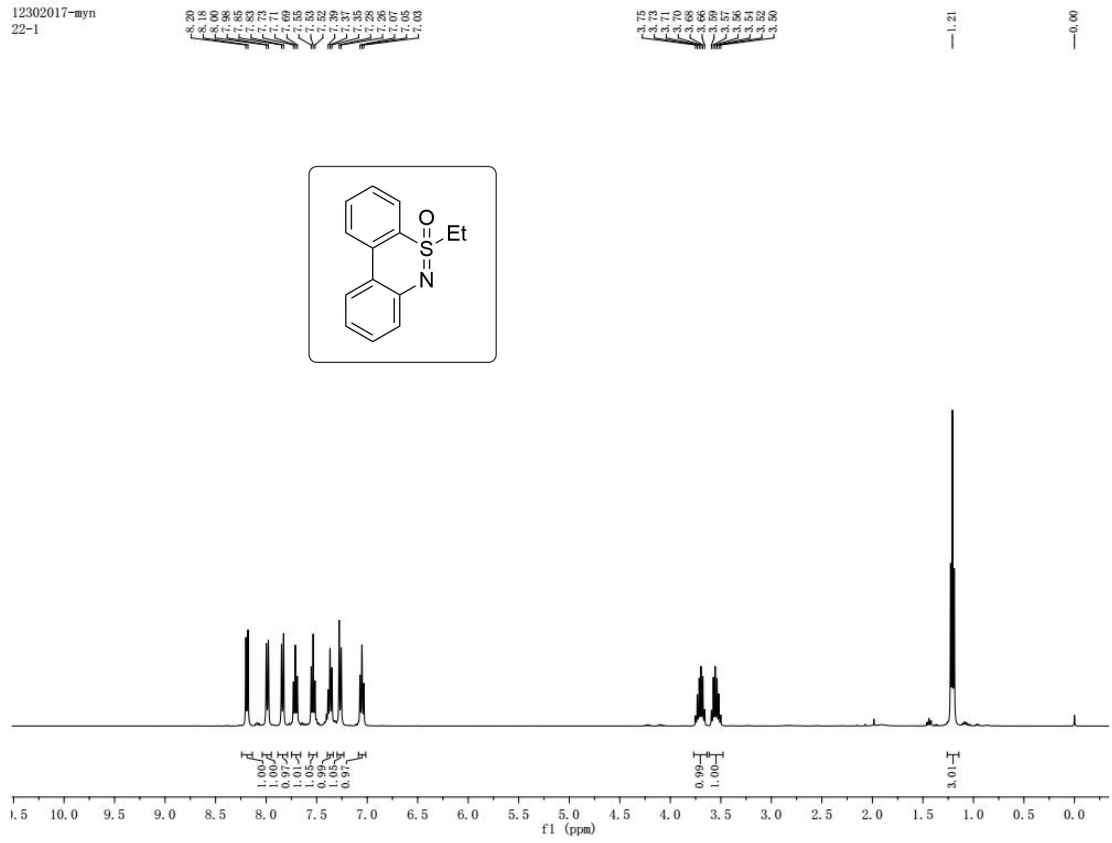
NMR charts

2a





2b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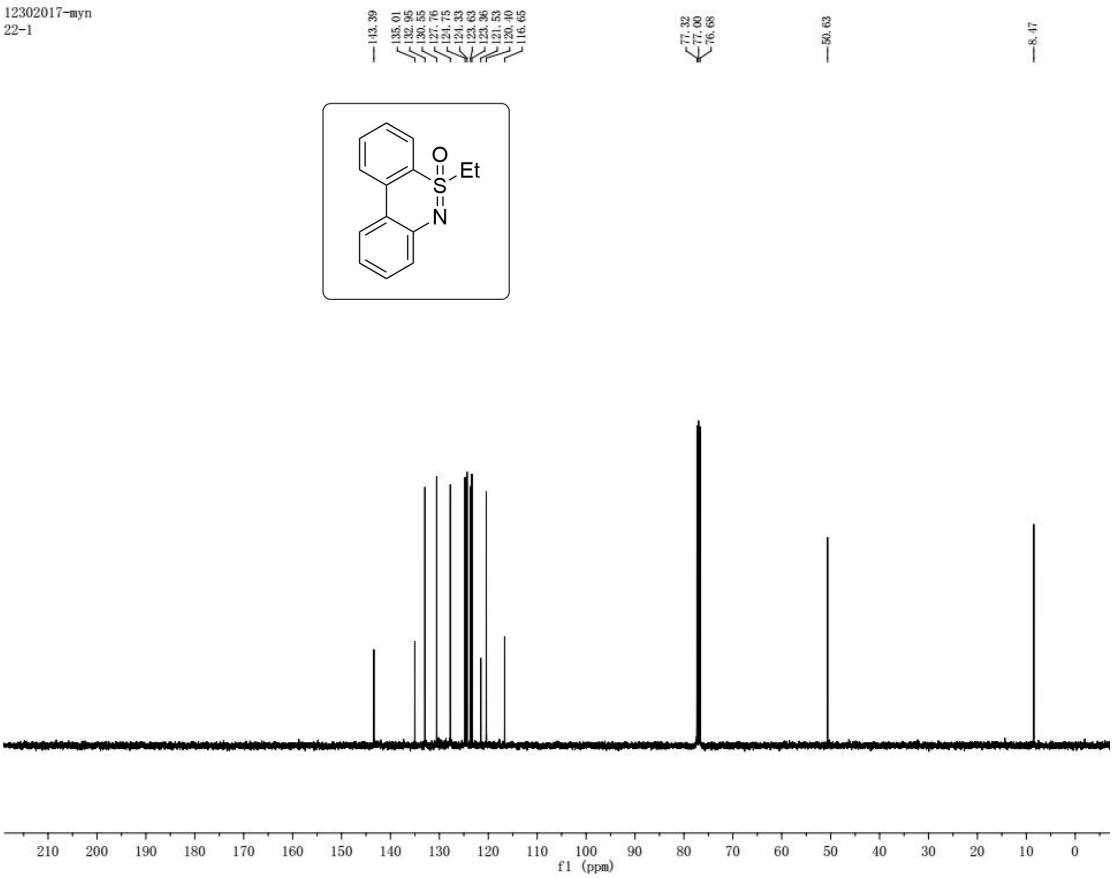
8.20
8.18
8.00
7.98
7.85
7.83
7.73
7.71
7.69
7.55
7.53
7.52
7.39
7.37
7.35
7.28
7.26
7.07
7.05
7.03
3.75
3.73
3.71
3.70
3.68
3.66
3.59
3.57
3.56
3.54
3.52
3.50
1.21
0.00
O
Et
S
N
1.00
1.00
0.97
1.01
1.05
0.99
1.05
0.97
0.99
1.00
3.01
f1 (ppm)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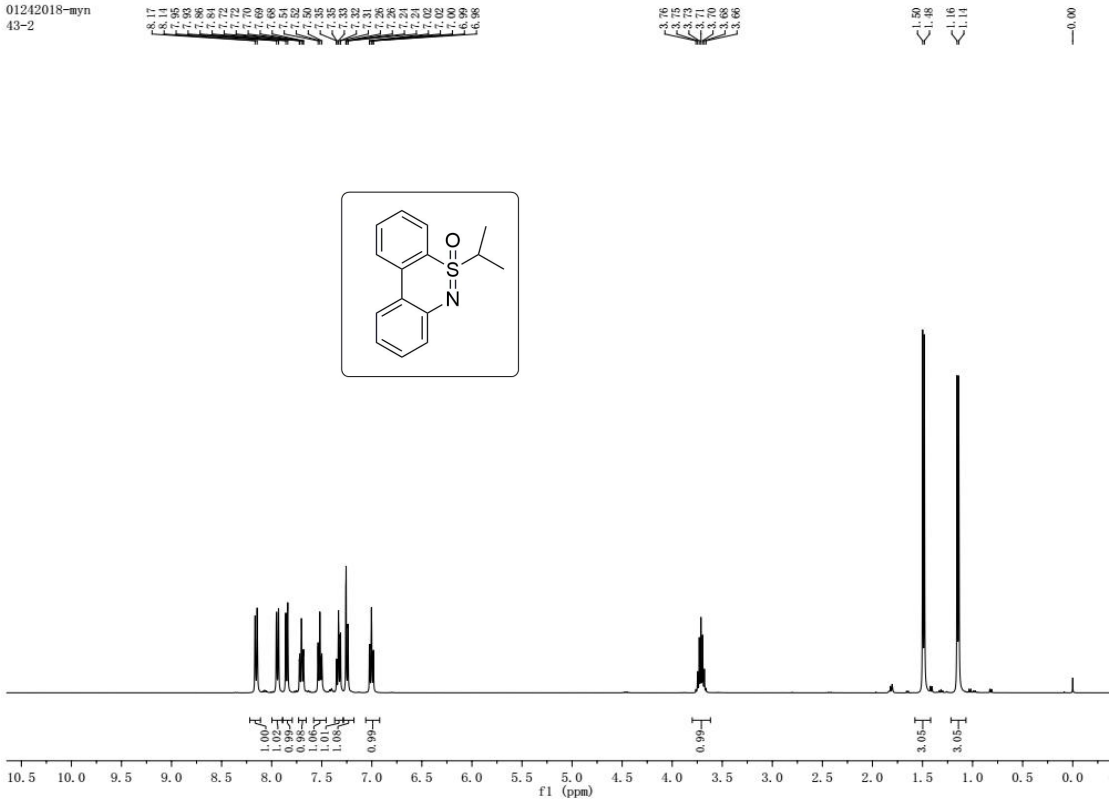
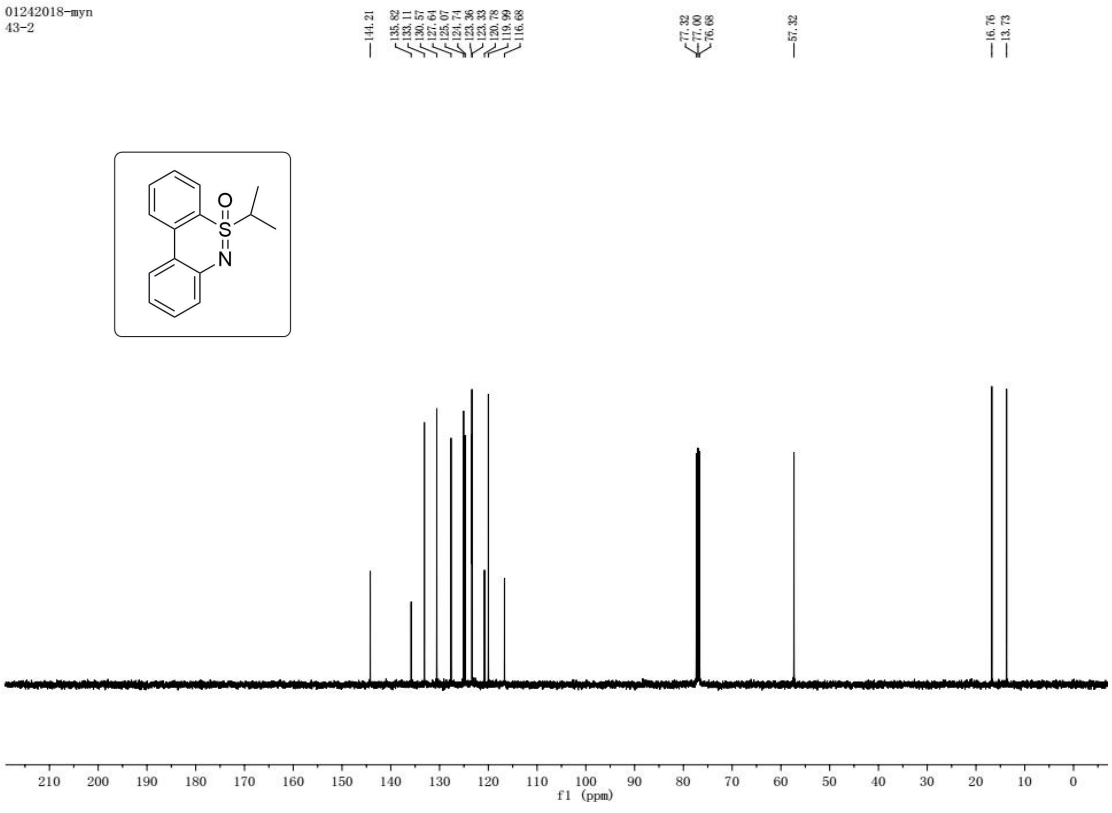
22-1
143.39
135.01
132.95
130.55
127.76
127.75
124.33
123.63
123.36
121.53
120.40
116.65
77.32
77.00
76.68
50.63
8.47
O
Et
S
N
f1 (ppm)

2c


01242018-myn
43-2
8.17
8.14
7.95
7.93
7.86
7.84
7.72
7.70
7.69
7.68
7.54
7.52
7.50
7.35
7.33
7.32
7.31
7.26
7.25
7.24
7.21
7.02
7.00
6.99
6.98
3.76
3.75
3.73
3.71
3.70
3.68
3.66
1.50
1.48
1.16
1.14
0.00
O
S
N
1.00
1.02
0.99
0.98
1.06
1.01
1.08
0.99
0.99
3.05
3.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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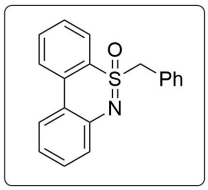
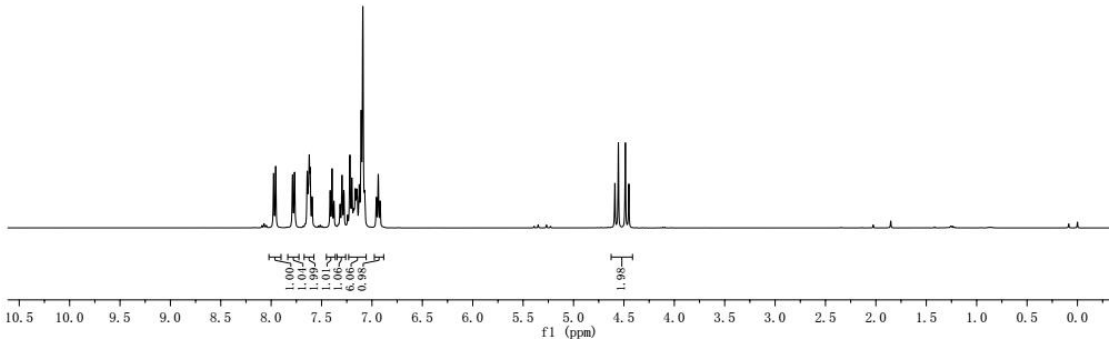
43-2
144.21
135.82
133.11
130.57
127.64
125.07
124.74
123.36
123.33
120.78
119.99
116.68
77.32
77.00
76.68
57.32
16.76
13.73
O
S
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

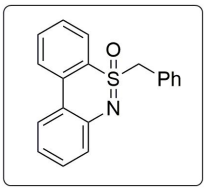
2d

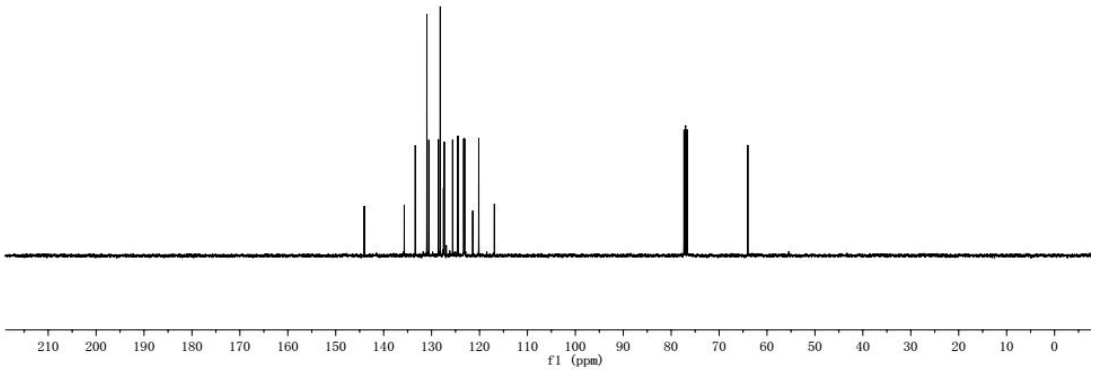
12312017-gcy
22-3



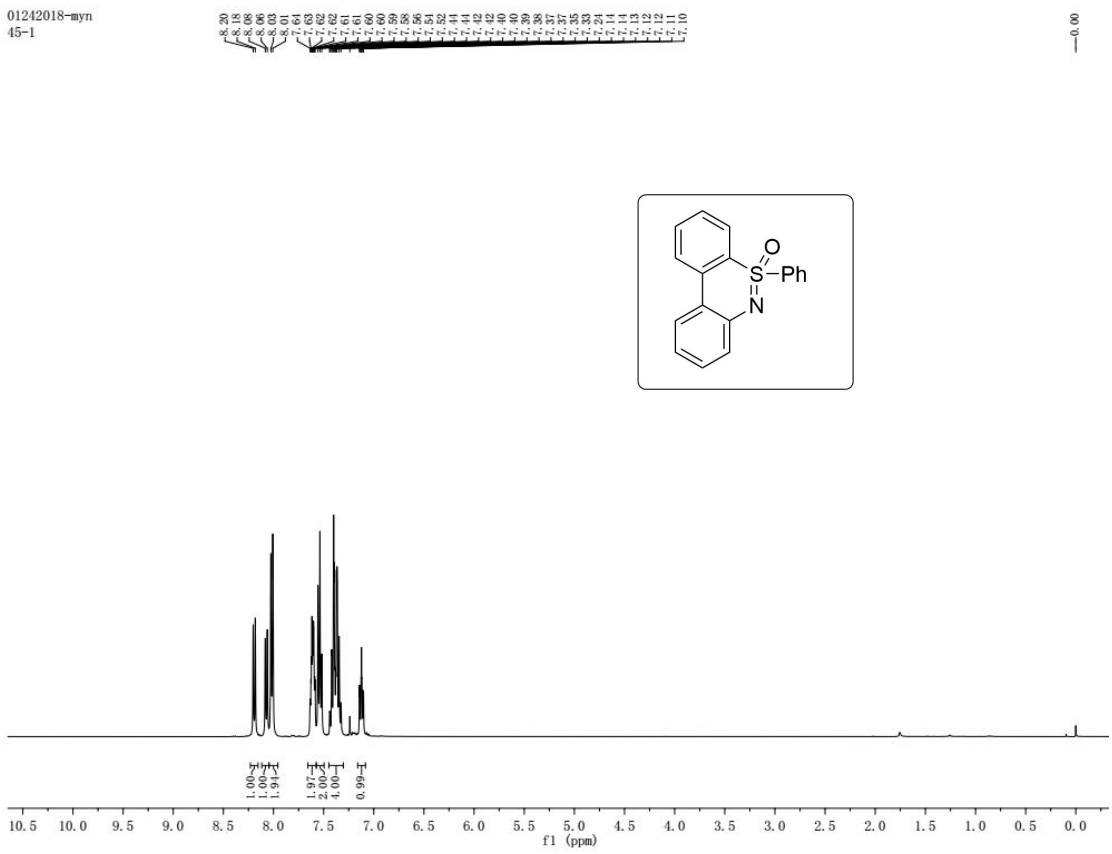


12312017-gcy
22-3





2e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45-1
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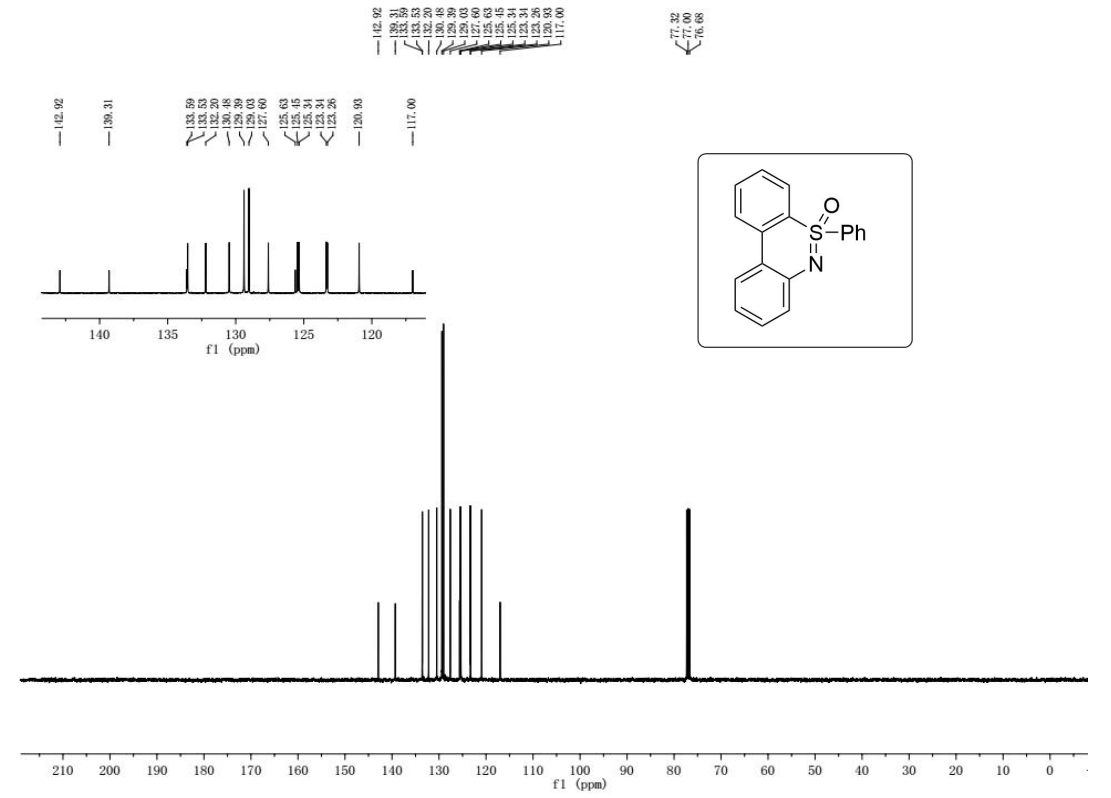
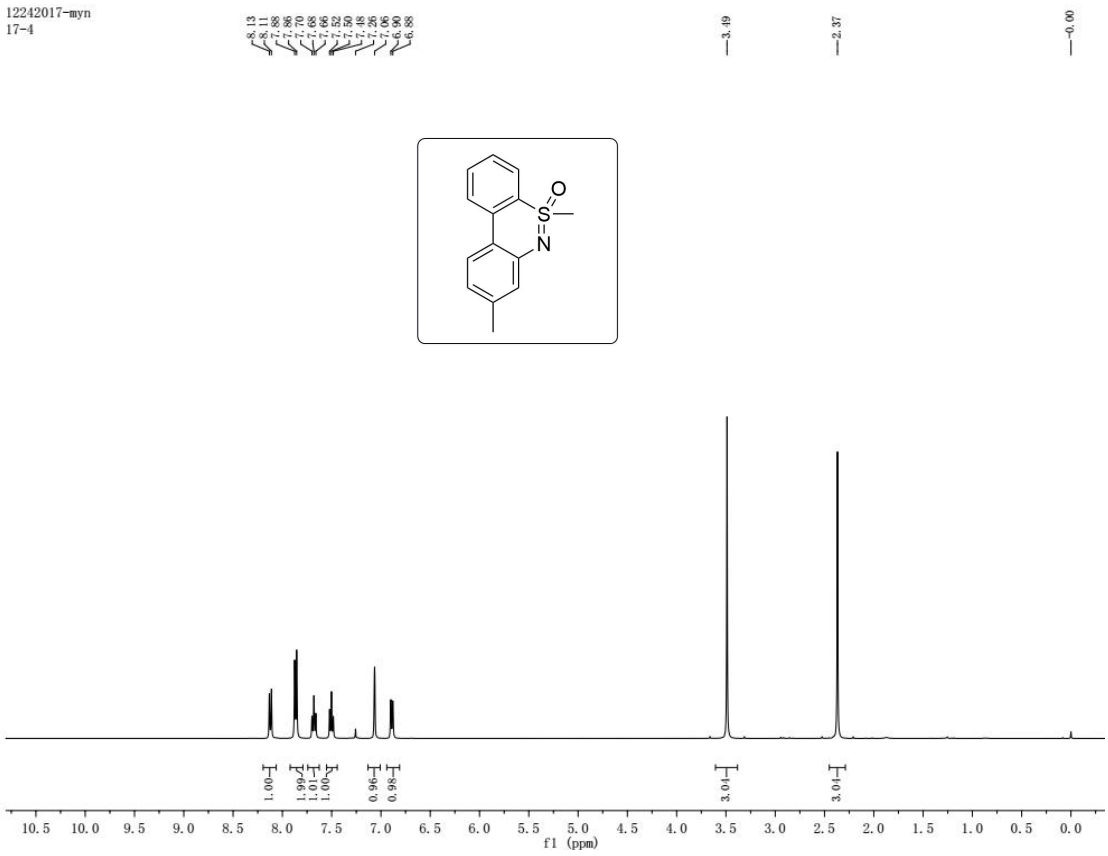
8.15
8.08
8.06
8.03
8.01
7.64
7.63
7.62
7.62
7.61
7.61
7.60
7.60
7.59
7.58
7.56
7.54
7.52
7.44
7.44
7.42
7.42
7.40
7.40
7.39
7.38
7.37
7.37
7.35
7.33
7.33
7.14
7.14
7.13
7.12
7.12
7.11
7.10
0.00
O
S
Ph
N
1.00
1.00
1.94
1.97
2.00
4.00
0.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.92
139.31
133.59
133.53
132.20
130.48
129.39
129.03
127.66
125.63
125.45
125.34
123.34
123.26
120.93
117.00
77.32
77.00
76.68
O
S
Ph
N
140 135 130 125 120
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2f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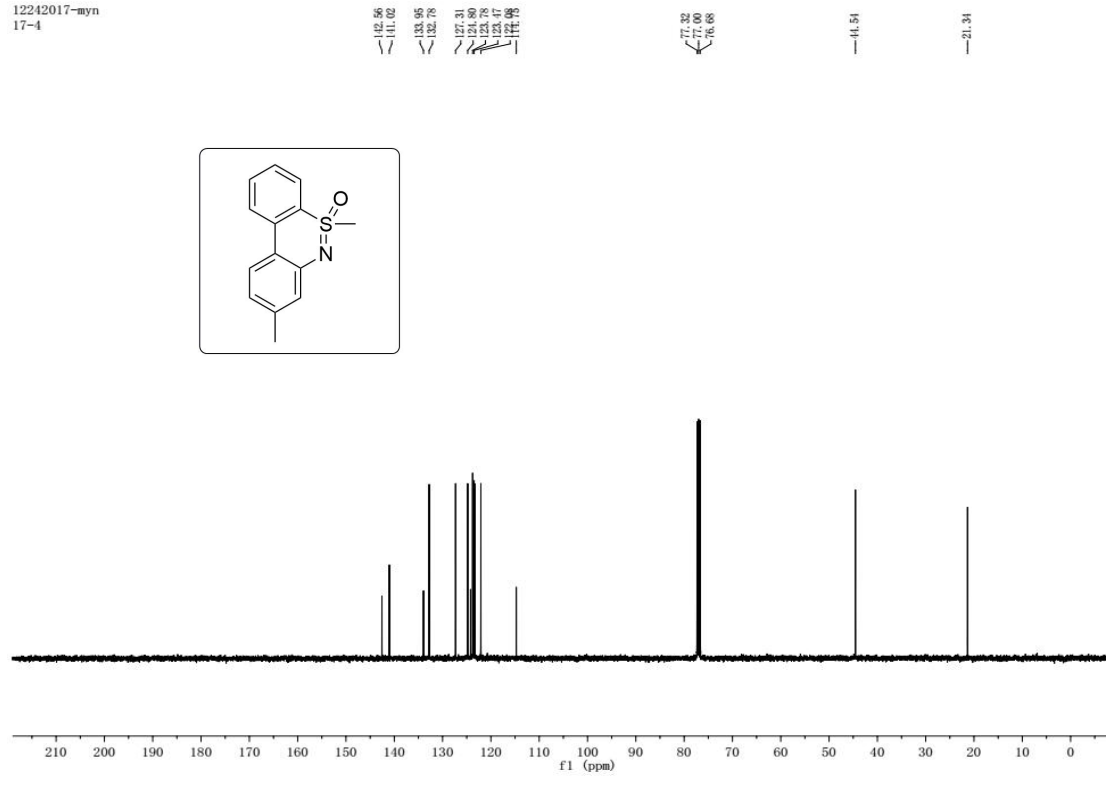
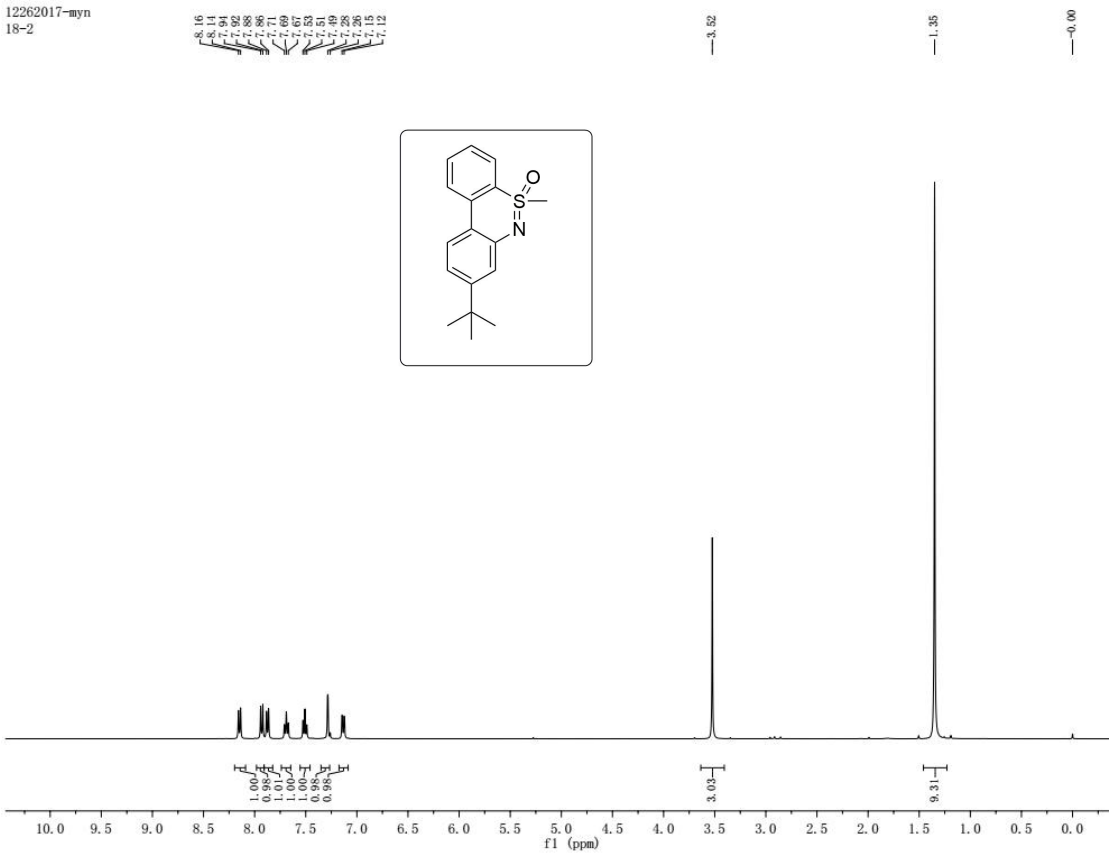
17-4
8.13
8.11
7.88
7.86
7.70
7.68
7.66
7.52
7.50
7.48
7.26
7.06
6.90
6.88
3.49
2.37
0.00
1.00
1.99
1.01
1.00
0.96
0.98
3.01
3.01
f1 (ppm)


12242017-myn
17-4
142.56
141.02
133.95
132.78
127.31
124.89
123.76
123.47
122.08
116.19
77.32
77.00
76.68
44.54
21.34
f1 (ppm)

2g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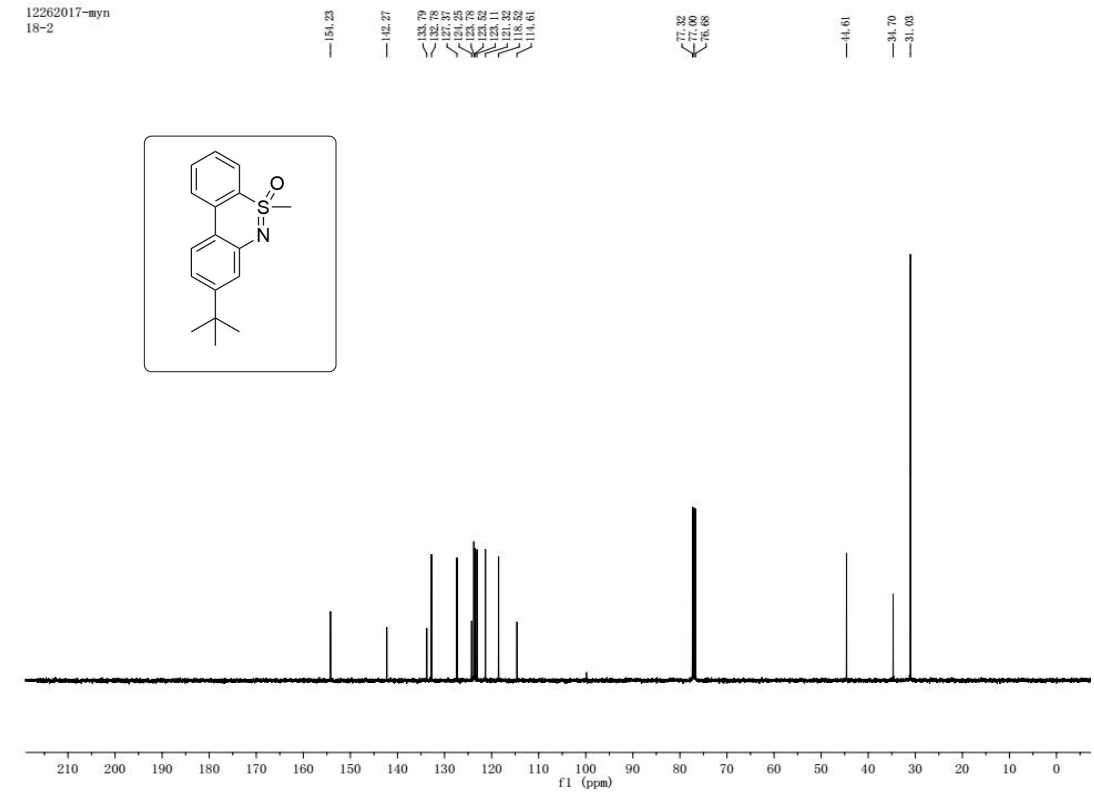
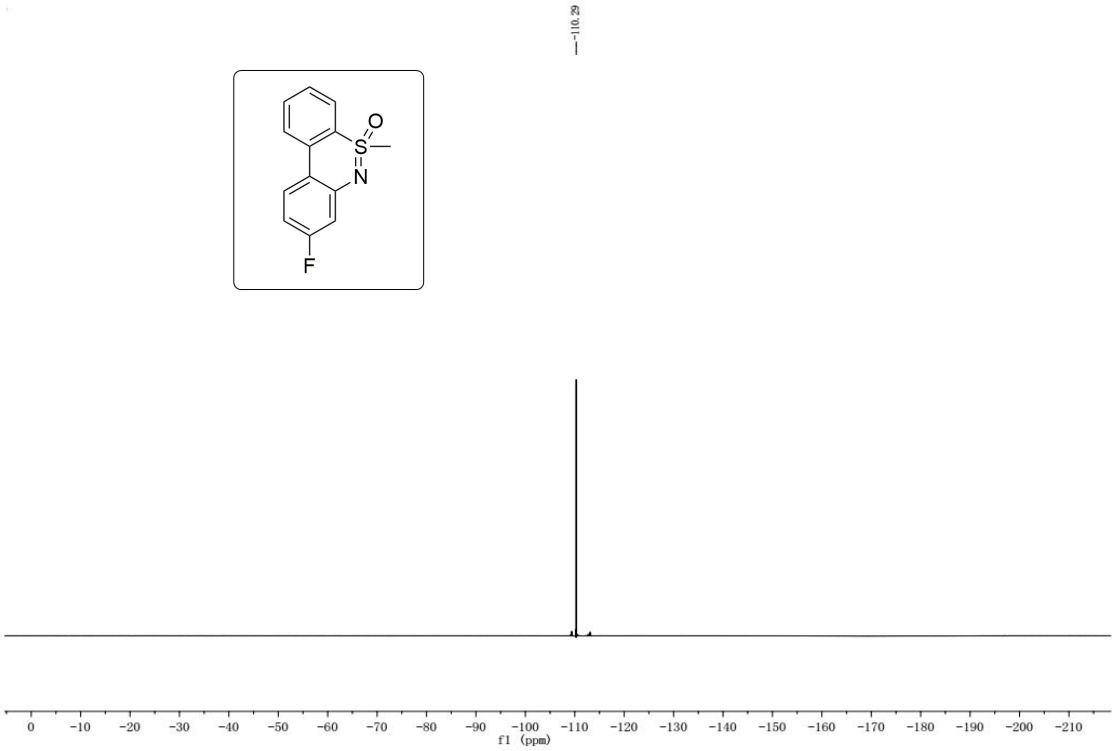
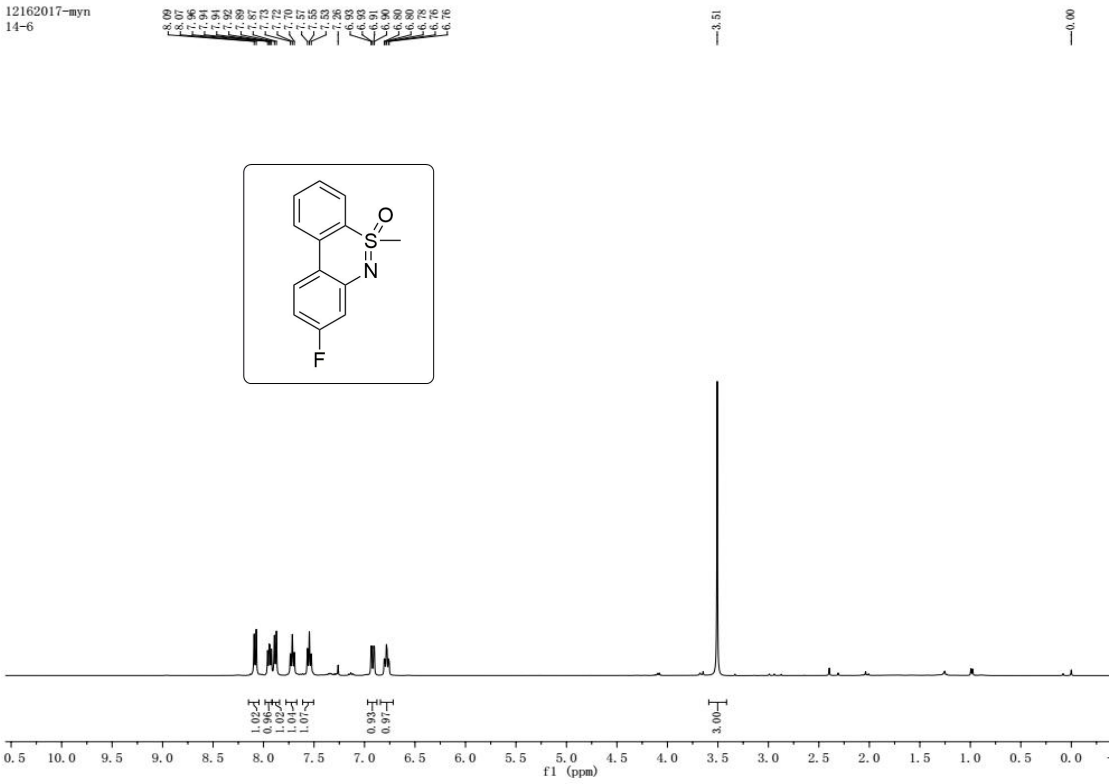
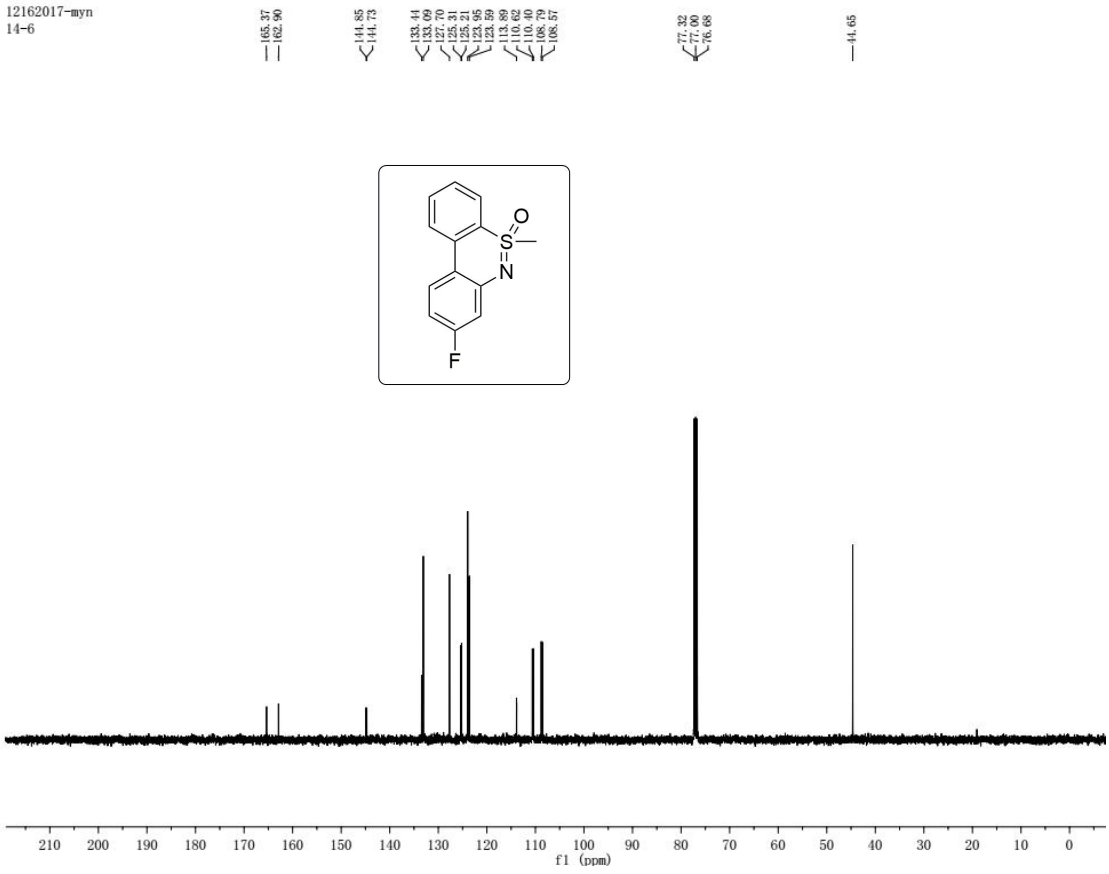
18-2
3.52
1.35
0.00
1.00
0.98
1.01
1.00
1.00
0.98
0.98
3.03
9.31
f1 (ppm)


12262017-myn
18-2
154.23
142.27
133.79
132.78
131.57
131.25
123.78
123.52
123.11
121.32
116.52
114.61
77.32
77.00
76.68
44.61
34.70
31.03
f1 (ppm)

2h


-110.29
O
S
N
F
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


12162017-myn
14-6
8.09
8.07
7.96
7.94
7.94
7.92
7.89
7.87
7.73
7.72
7.70
7.57
7.55
7.53
7.26
6.93
6.93
6.91
6.90
6.80
6.80
6.78
6.76
6.76
3.51
0.00
O
S
N
F
1.02
0.96
1.02
1.04
1.07
0.93
0.97
3.00
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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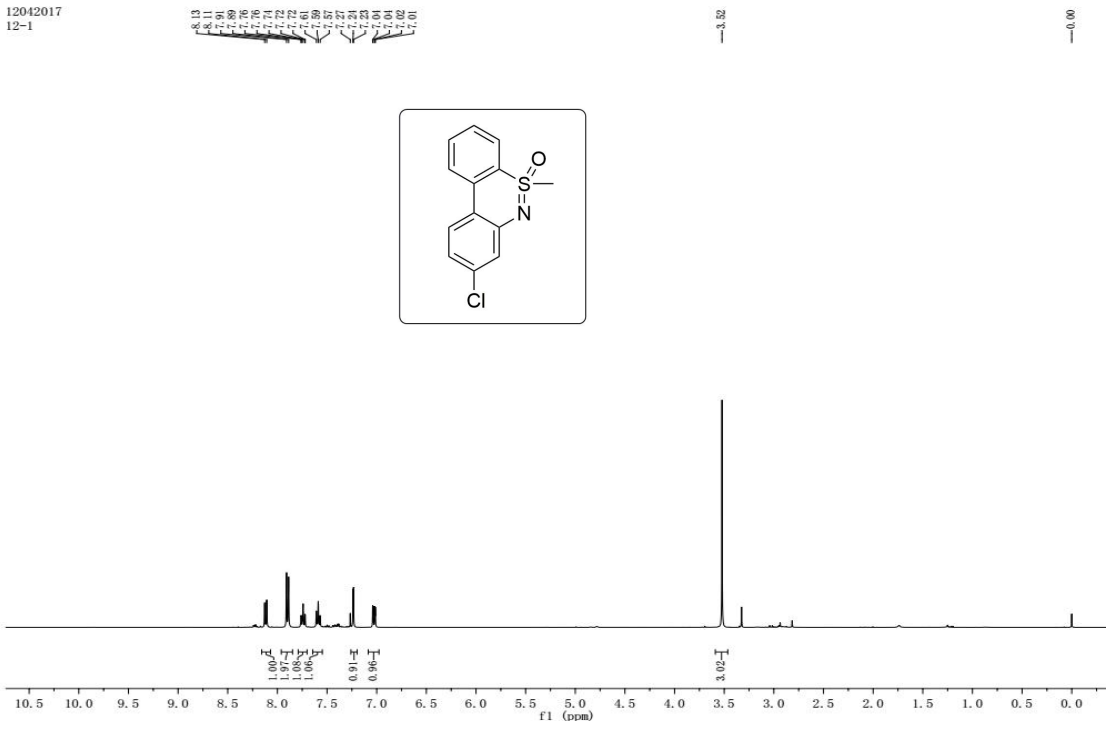
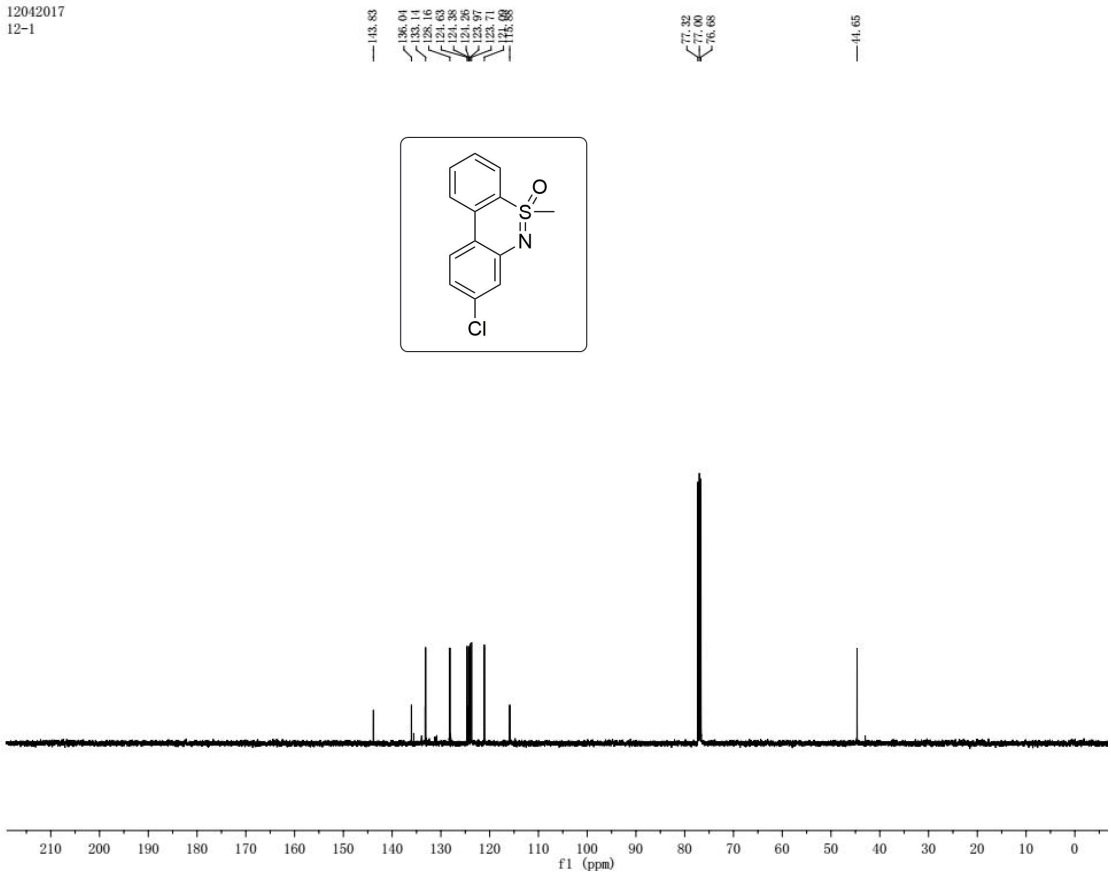
14-6
165.37
162.90
144.85
144.73
133.44
133.09
127.70
125.31
125.21
123.95
123.89
113.89
110.62
110.40
108.79
108.57
77.32
77.00
76.68
44.65
O
S
N
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2i


12042017
12-1
8.13
8.11
7.89
7.76
7.74
7.72
7.60
7.59
7.57
7.27
7.24
7.23
7.04
7.02
7.01
3.52
0.00
O
S
N
Cl
1.00
1.97
1.08
1.06
0.91
0.96
3.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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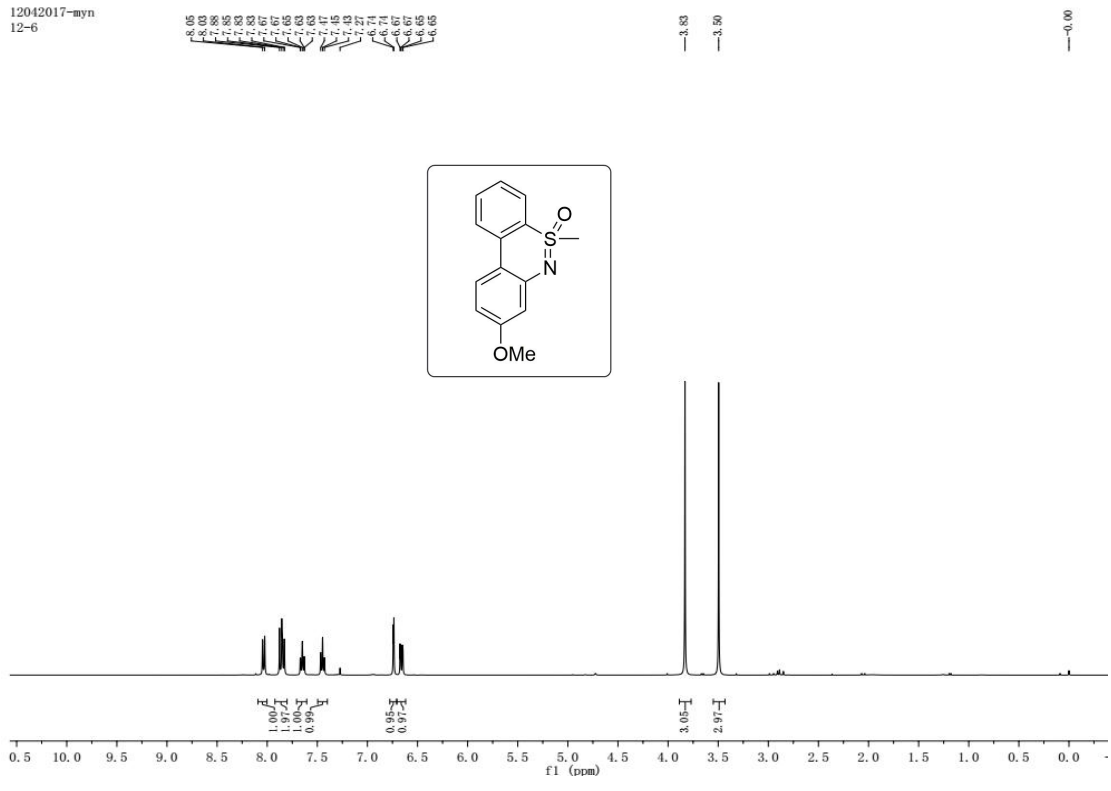
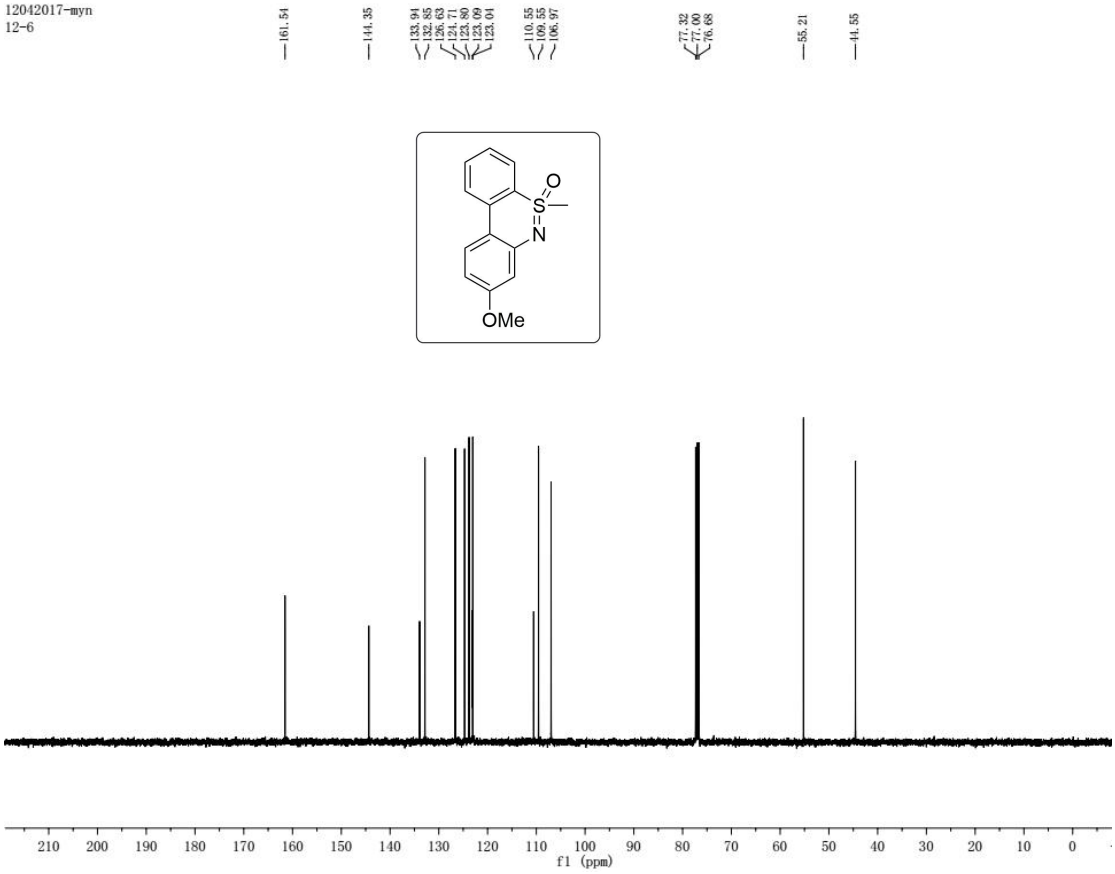
136.04
133.11
128.16
124.63
124.38
124.26
123.97
123.71
77.32
77.00
76.68
41.65
O
S
N
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2j


12042017-myn
12-6
8.05
8.03
7.88
7.85
7.83
7.67
7.65
7.63
7.47
7.45
7.43
7.27
6.74
6.67
6.65
3.83
3.50
0.00
O
S
N
OMe
1.00
1.97
1.00
0.99
0.95
0.97
3.05
2.97
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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12-6
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144.35
133.94
132.85
126.63
124.71
123.89
123.69
123.04
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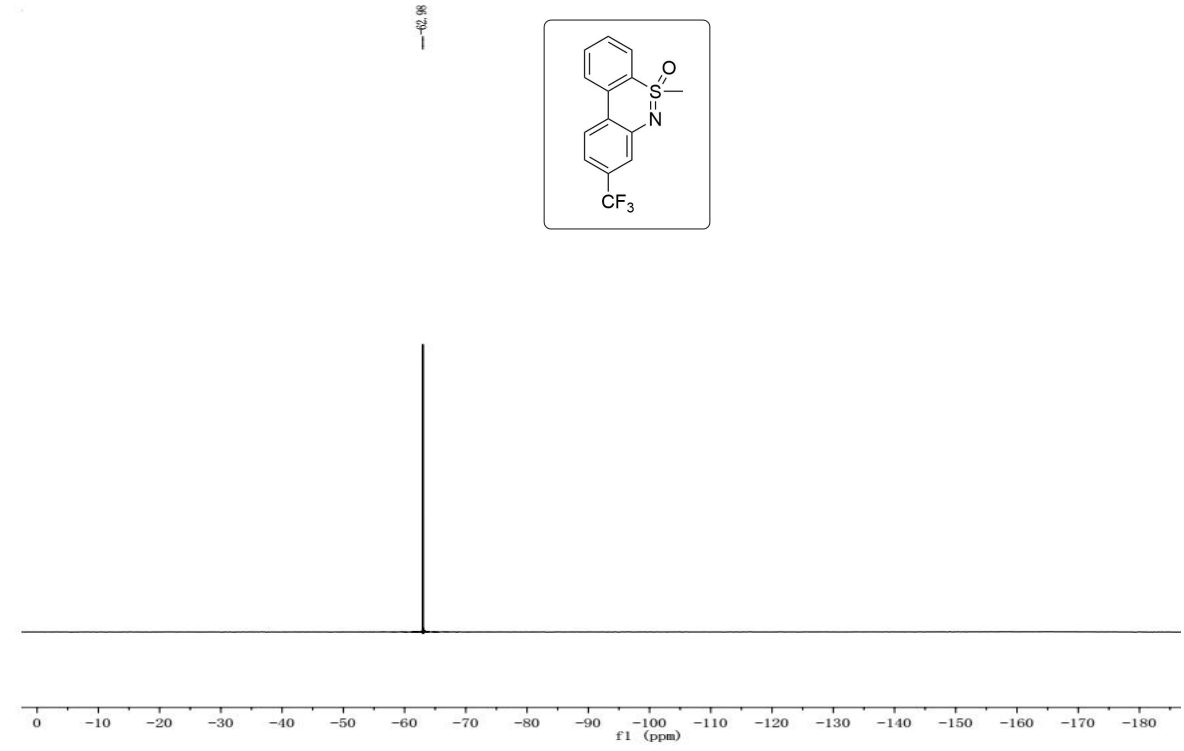
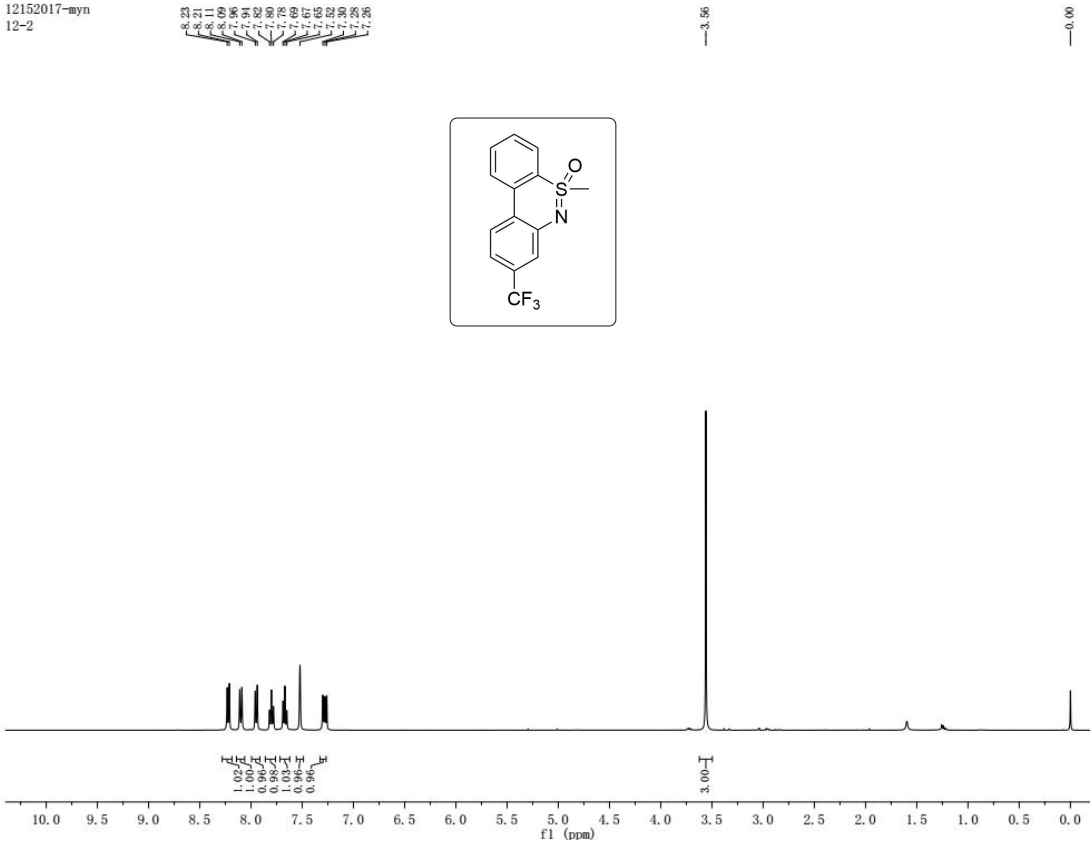
109.55
106.97
77.32
77.00
76.68
55.21
44.55
O
S
N
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

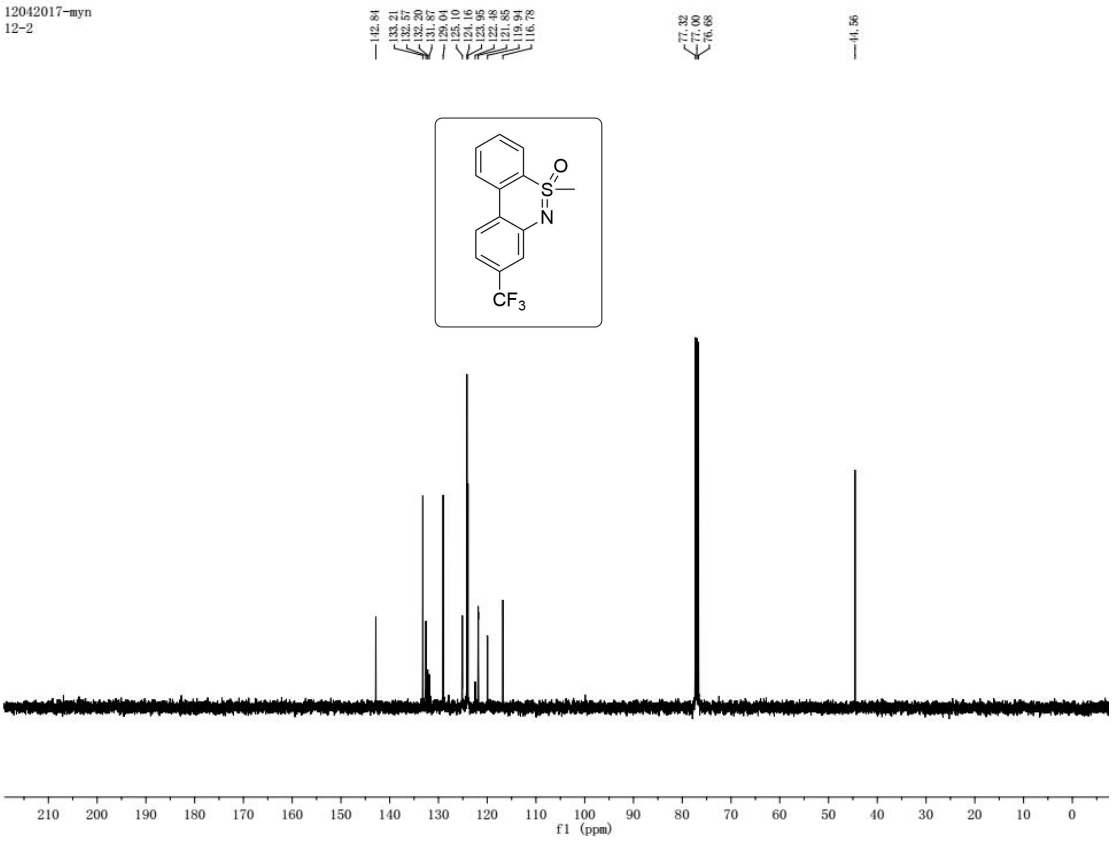
2k


-62.98
O
S
N
CF3
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

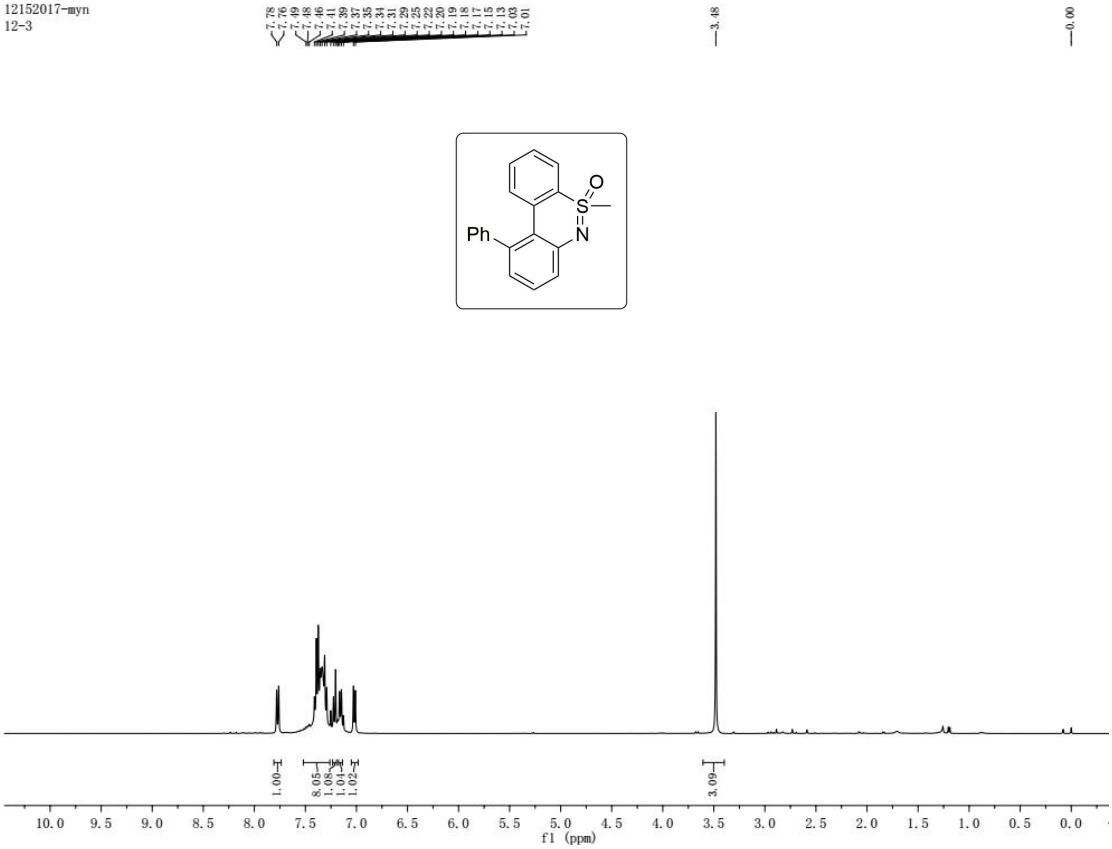
12152017-myn
12-2

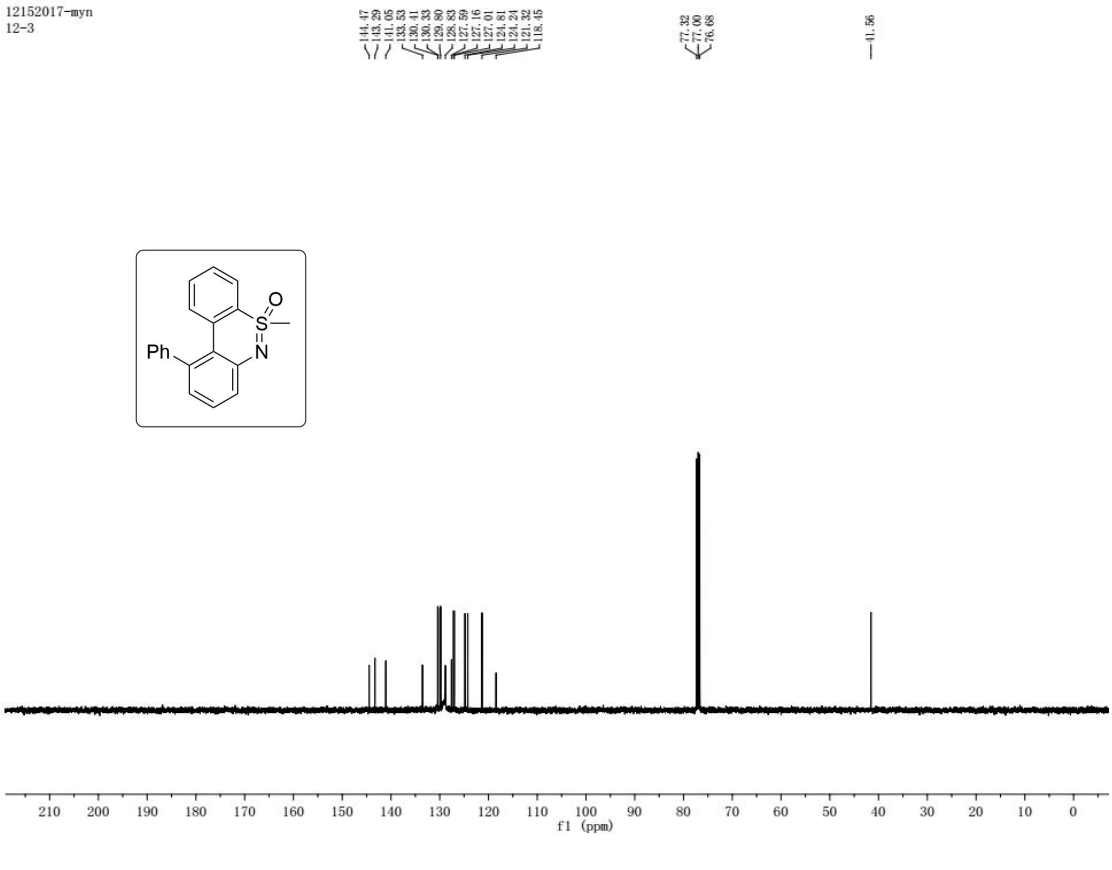


12042017-myn
12-2



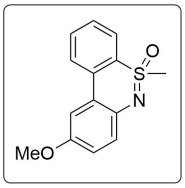
2l

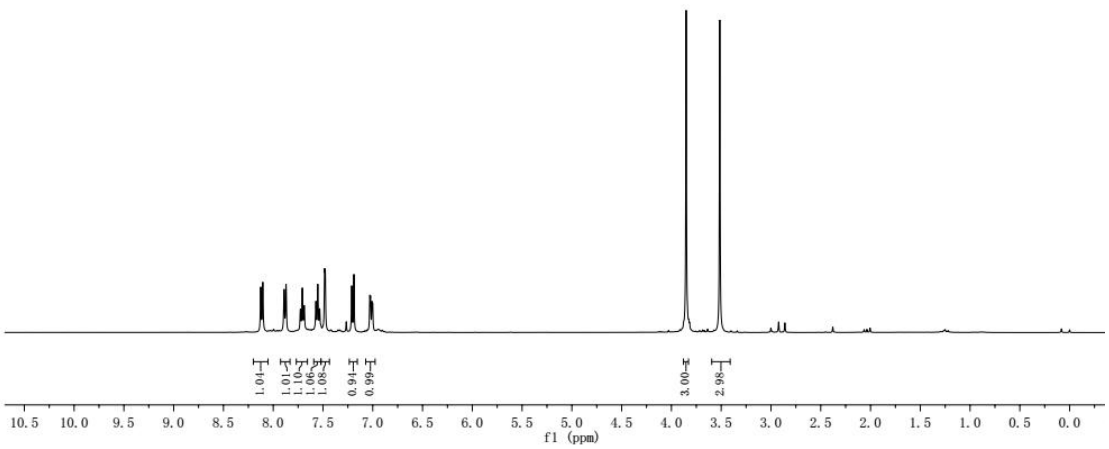

12152017-myn
12-3
7.78
7.76
7.49
7.48
7.46
7.41
7.39
7.37
7.35
7.34
7.31
7.29
7.25
7.22
7.20
7.19
7.18
7.17
7.15
7.13
7.03
7.01
3.48
0.00
Ph
O
S
N
1.00
8.05
1.08
1.04
1.02
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


12152017-myn
12-3
144.47
143.29
141.65
133.53
130.41
130.33
129.80
128.83
127.59
127.16
127.01
124.81
124.24
121.32
118.45
77.32
77.00
76.68
41.56
Ph
O
S
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

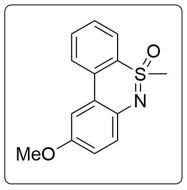
2ma

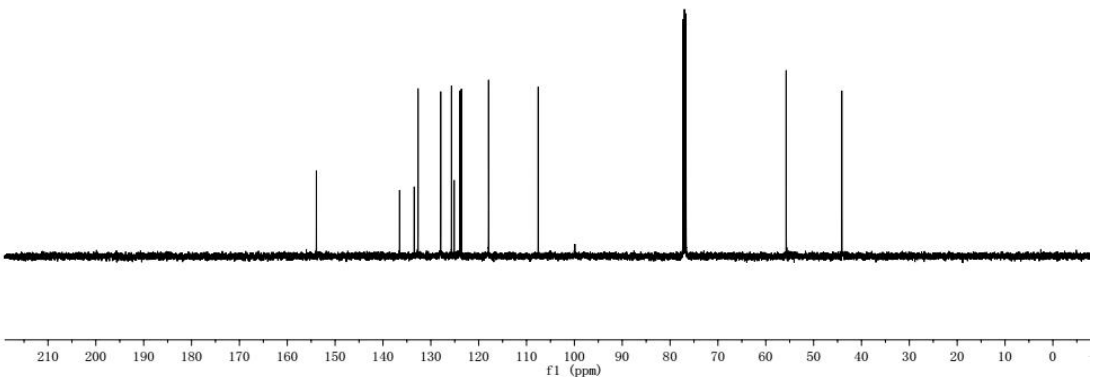
12162017-myn
14-8-up



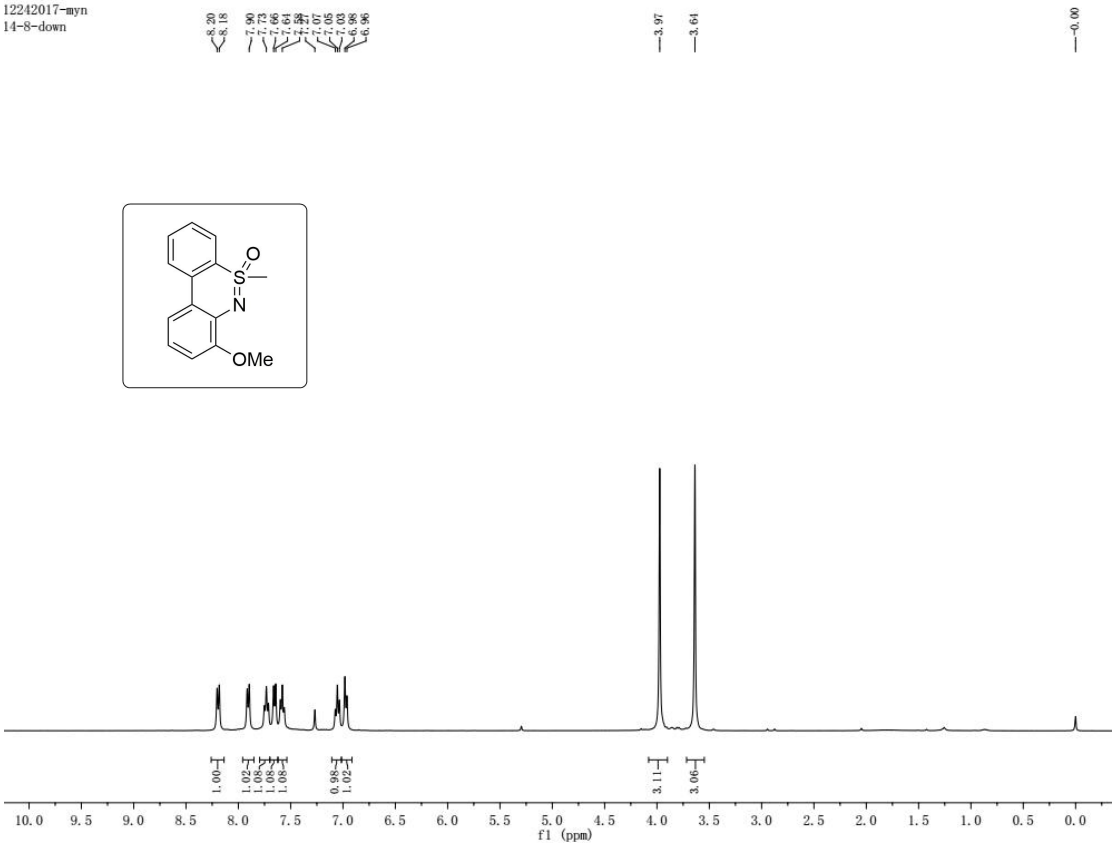


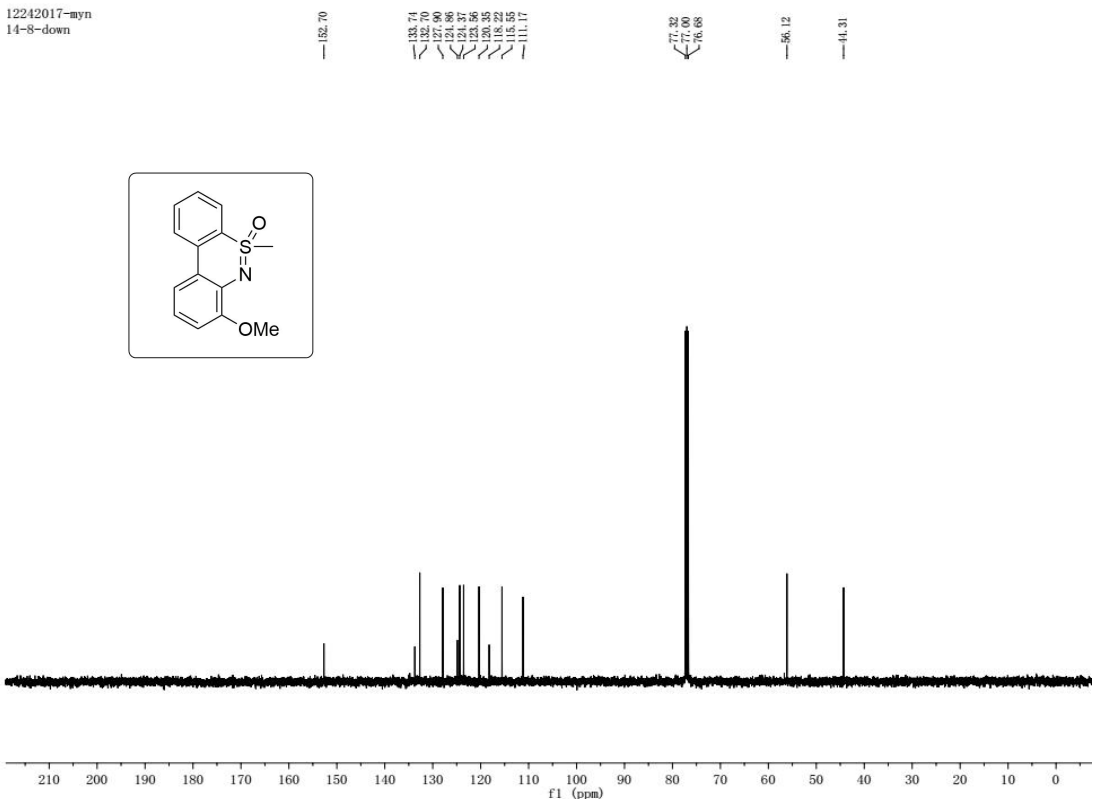
12162017-myn
14-8-up



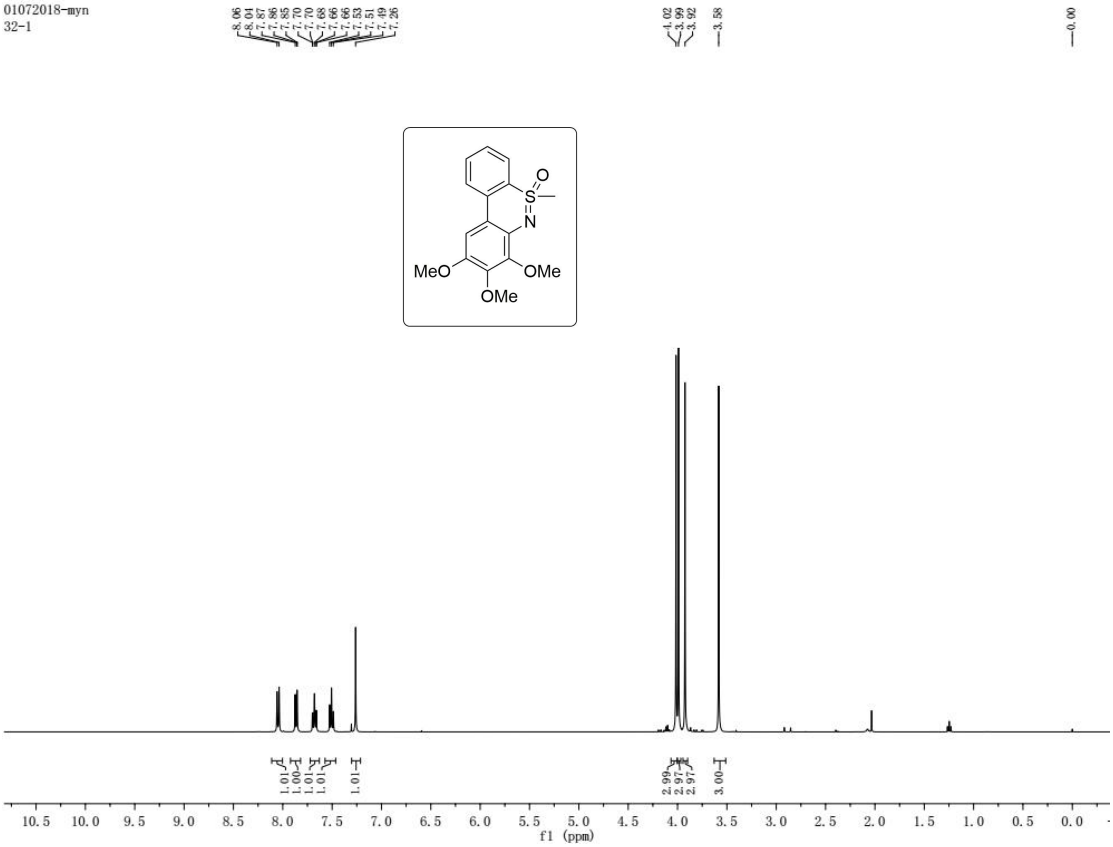


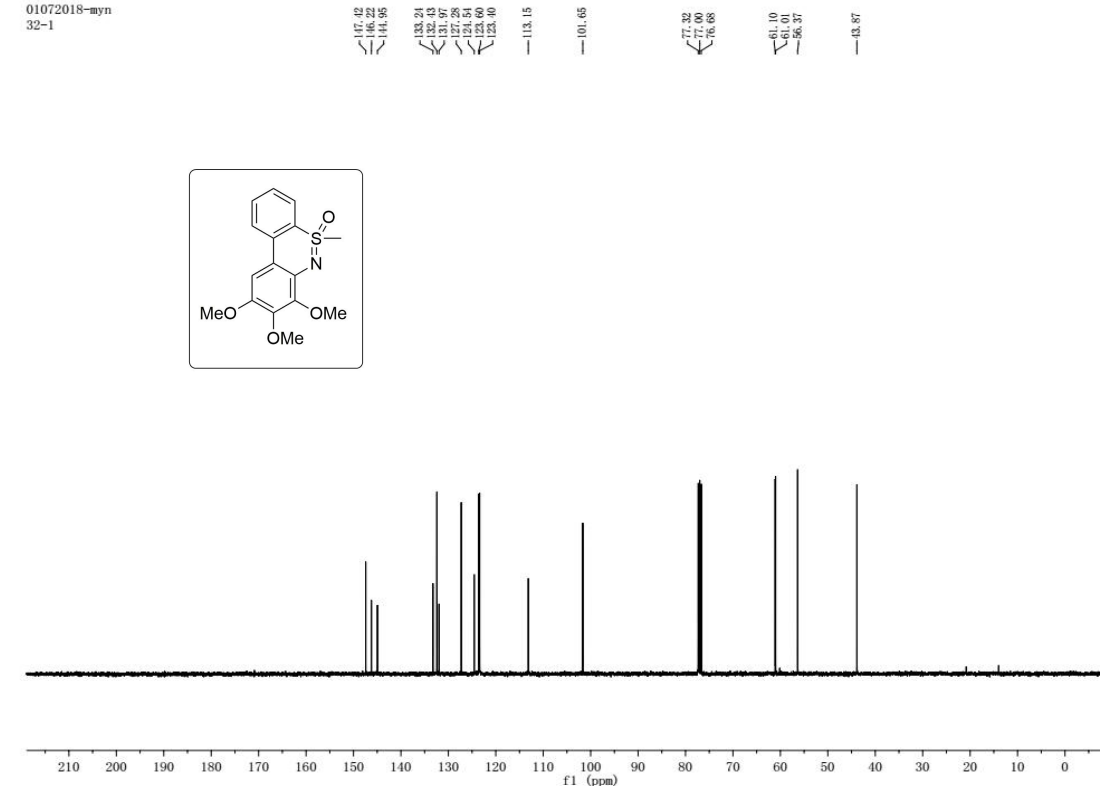
2mb


12242017-myn
14-8-down
8.20
8.18
7.90
7.73
7.66
7.64
7.07
7.05
7.03
6.98
6.96
3.97
3.64
0.00
O
S
N
OMe
1.00
1.02
1.08
1.08
1.08
0.98
1.02
3.11
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

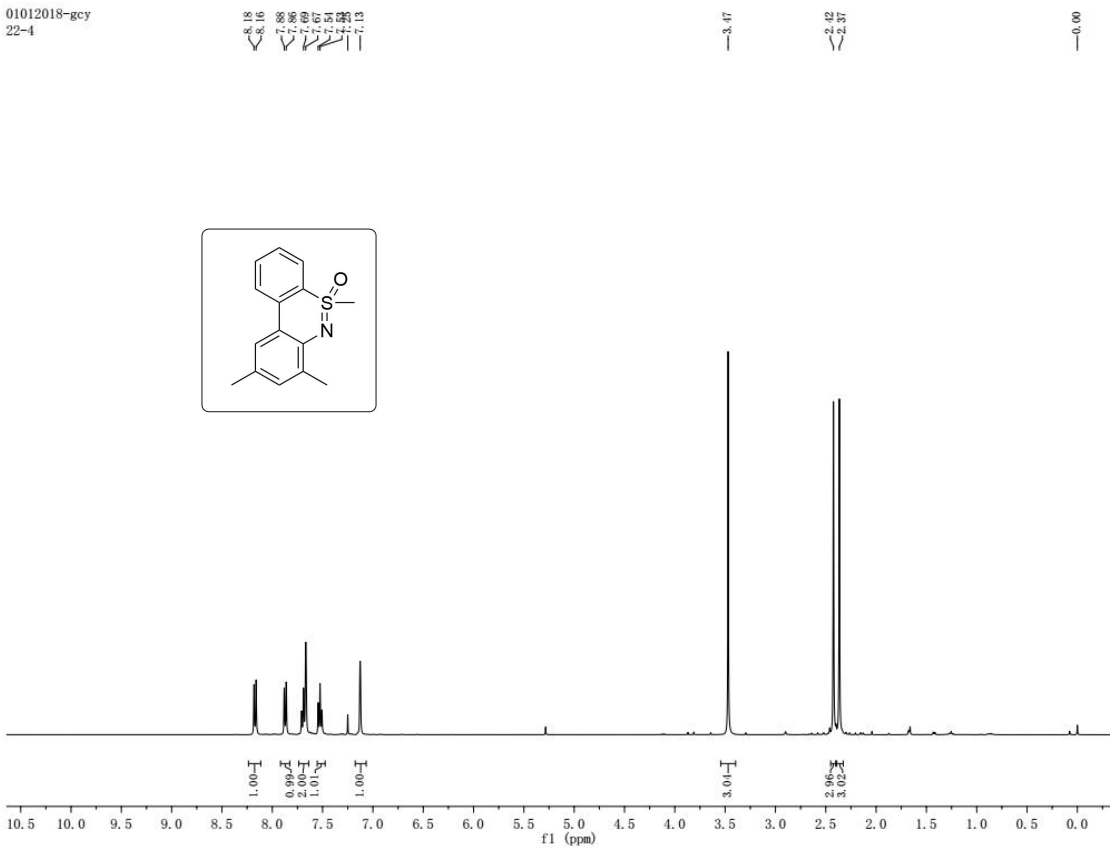

12242017-myn
14-8-down
152.70
133.74
132.70
127.90
124.86
124.37
123.56
120.35
118.22
115.55
111.17
77.32
77.00
76.68
56.12
44.31
O
S
N
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

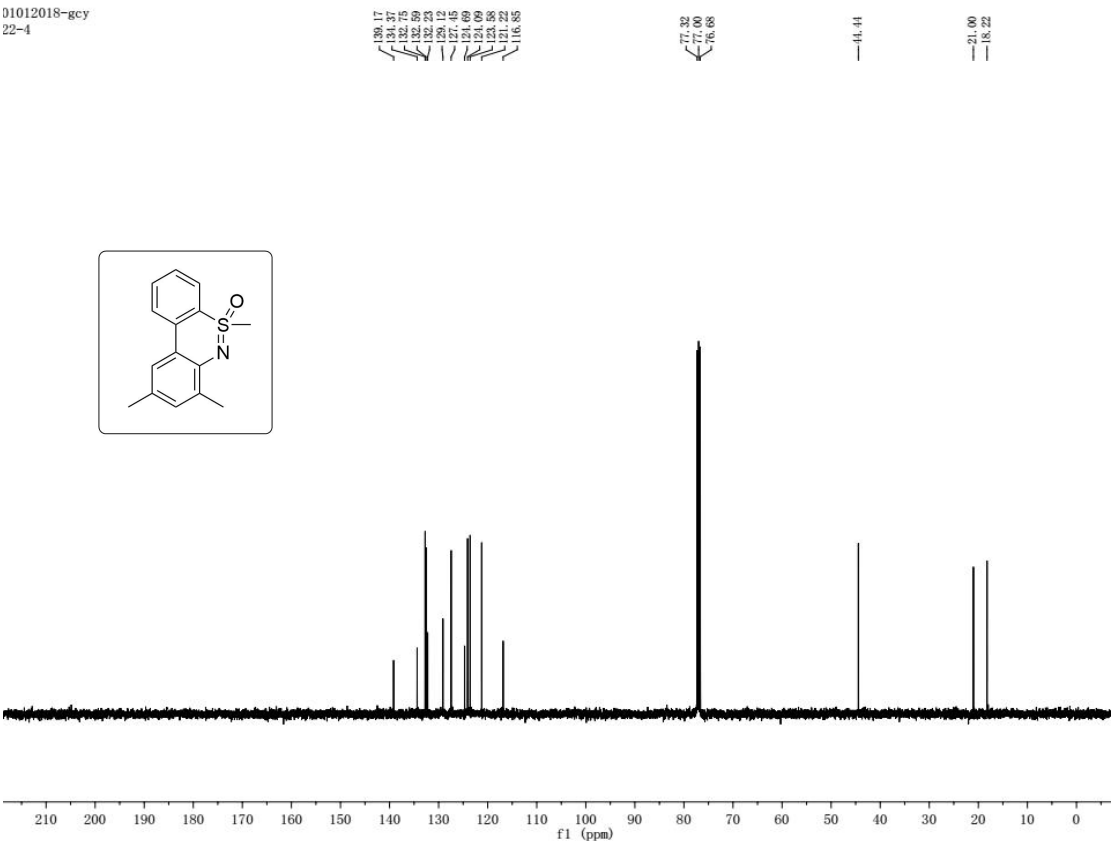
2n


01072018-myn
32-1
MeO
OMe
OMe
f1 (ppm)

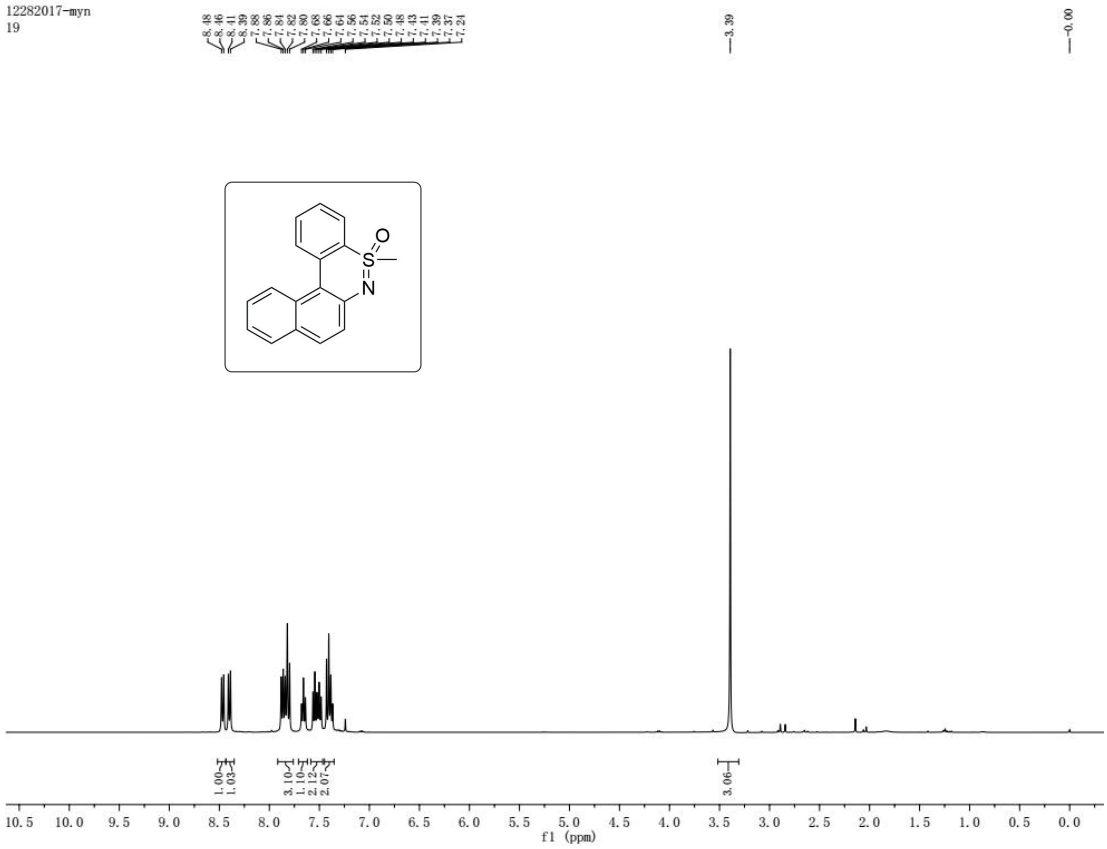

01072018-myn
32-1
MeO
OMe
OMe
f1 (ppm)

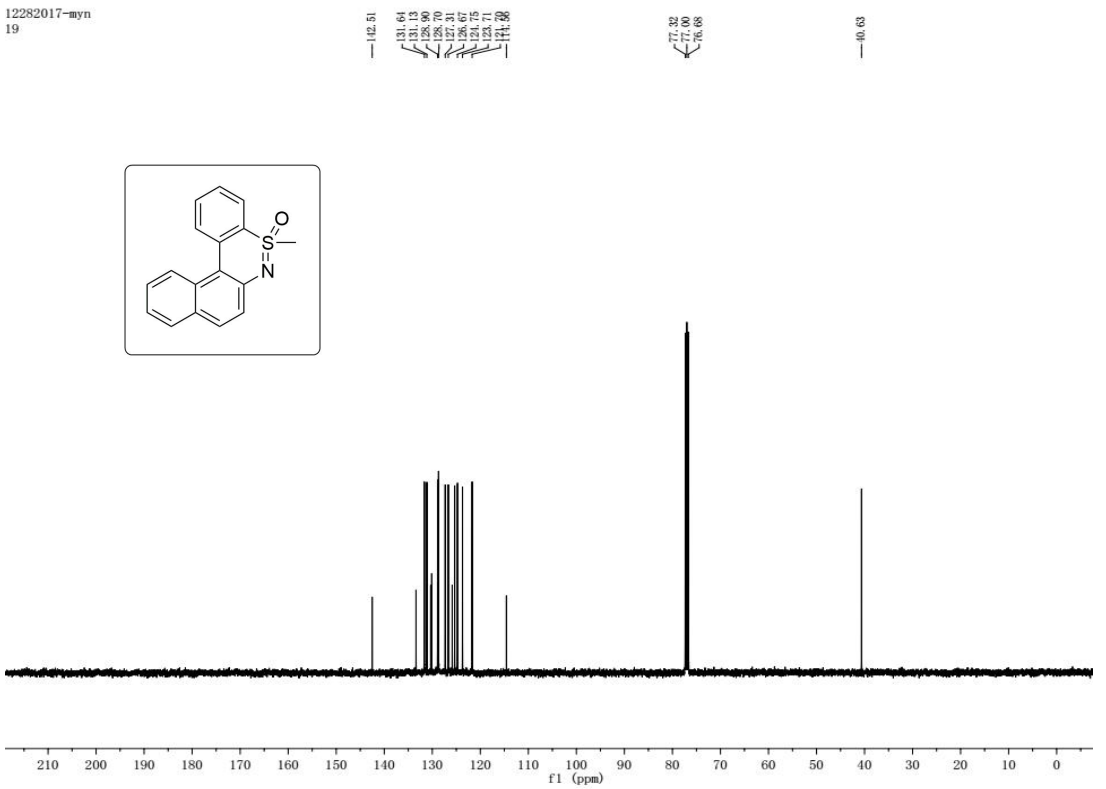
2o


01012018-gcy
22-4
8.18
8.16
7.88
7.69
7.67
7.54
7.13
3.47
2.42
2.37
0.00
1.00
0.99
2.00
1.01
1.00
3.04
2.96
3.02
f1 (ppm)

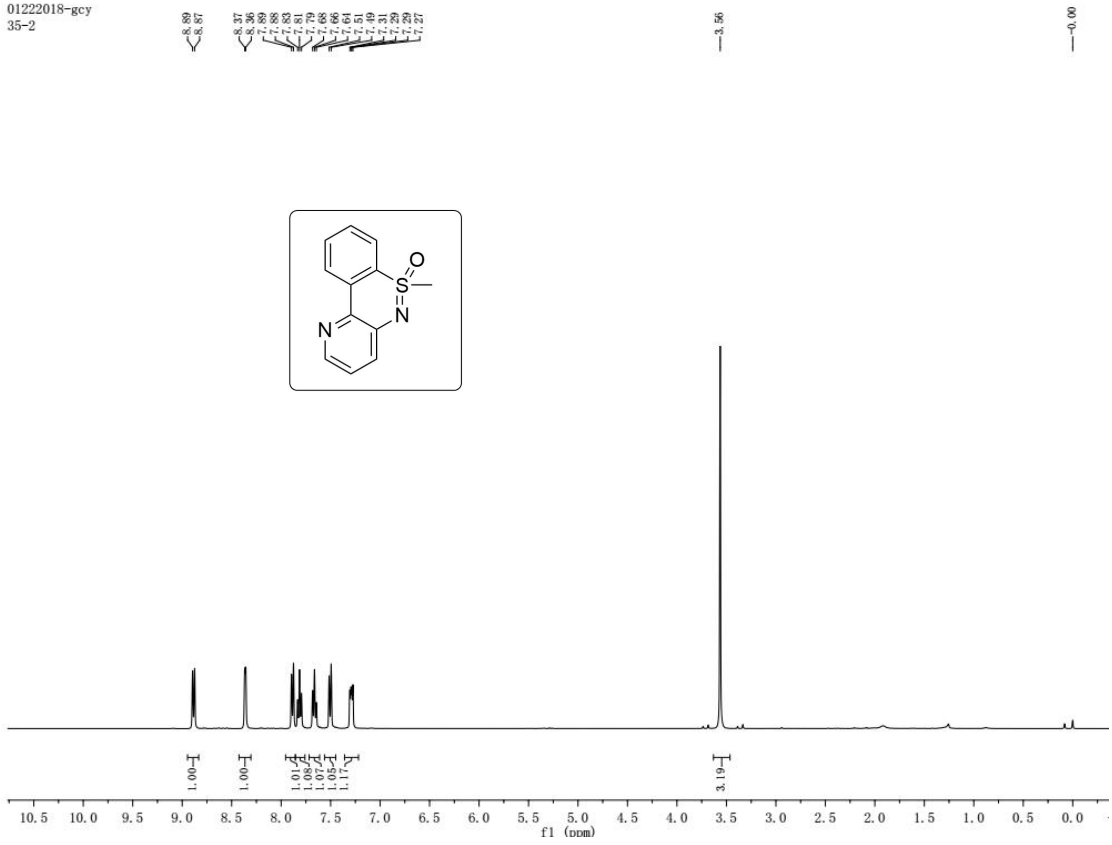

01012018-gcy
22-4
139.17
134.37
132.75
132.69
132.23
129.12
127.45
124.69
124.09
123.38
121.27
116.85
77.32
77.00
76.68
44.44
21.00
18.22
f1 (ppm)

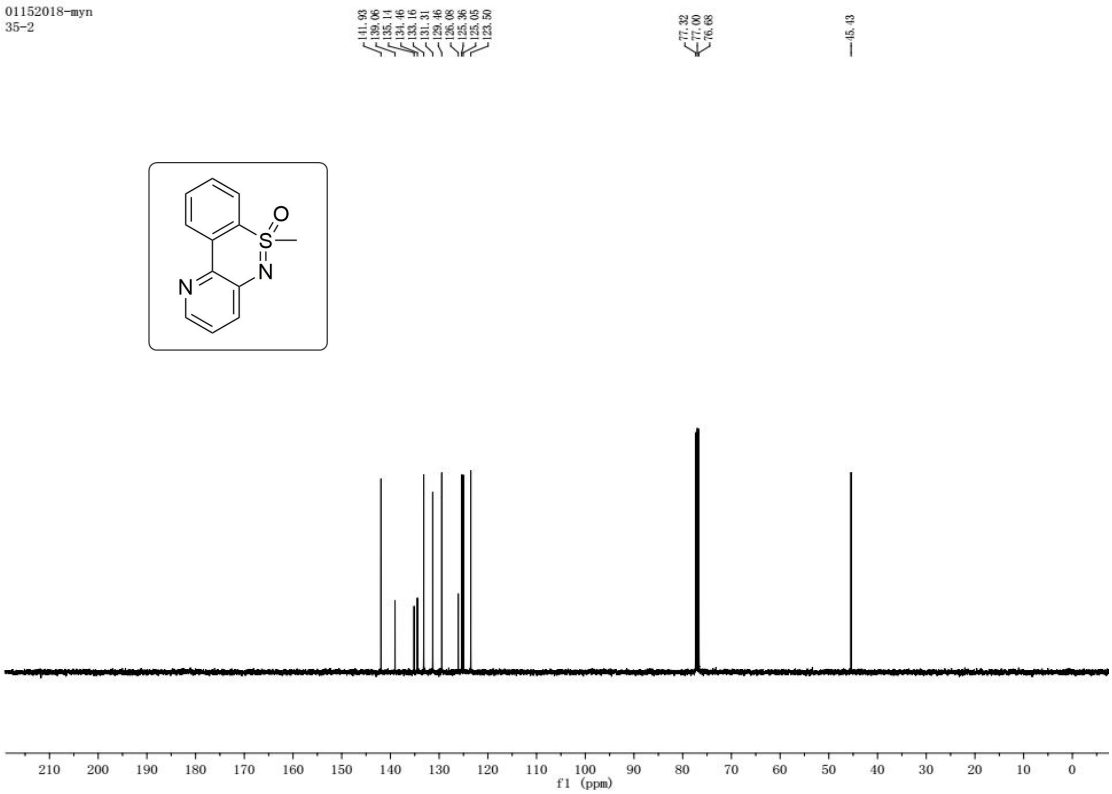
2p


12282017-myn
19
8.48
8.46
8.41
8.39
7.88
7.86
7.84
7.82
7.80
7.68
7.66
7.64
7.56
7.54
7.52
7.50
7.48
7.43
7.41
7.39
7.37
7.24
3.39
0.00
O
S
N
1.00
1.03
3.10
1.10
2.12
2.07
3.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

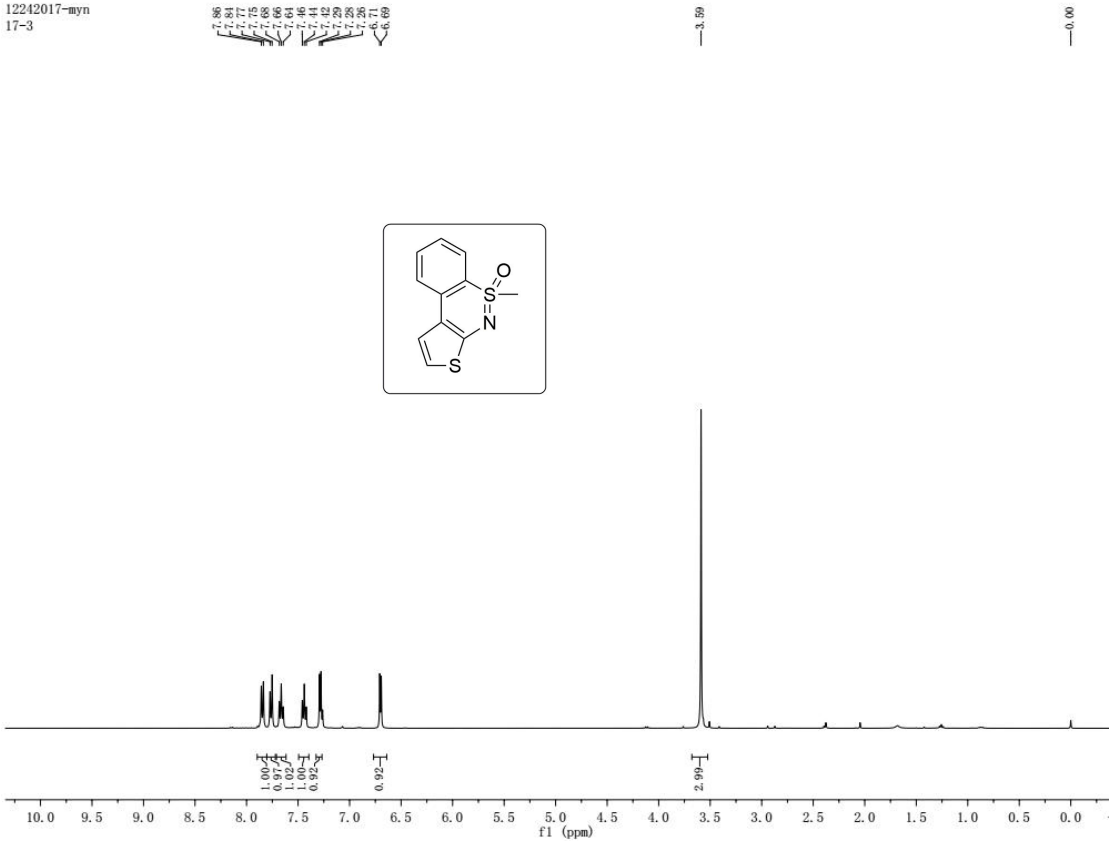

12282017-myn
19
142.51
131.64
131.13
128.90
128.70
127.31
126.67
124.75
123.71
111.58
77.32
77.00
76.68
40.63
O
S
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

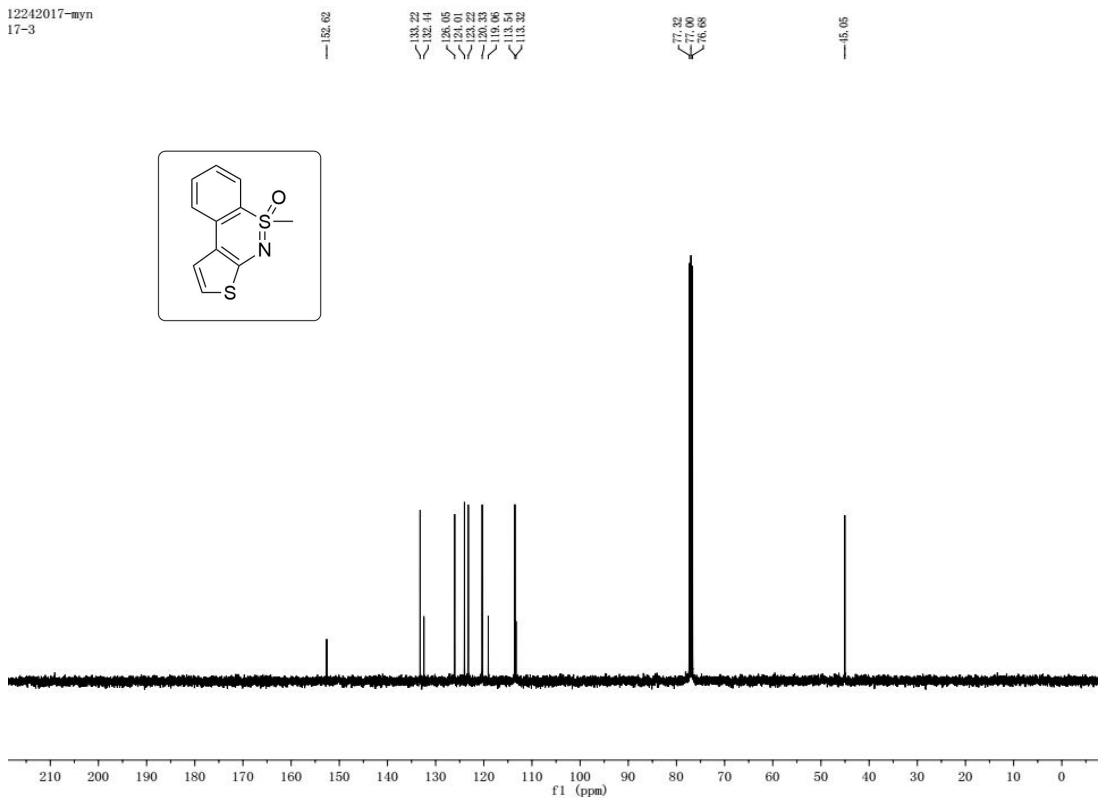
2q


01222018-gcy
35-2
8.89
8.87
8.37
8.36
7.89
7.88
7.83
7.81
7.79
7.68
7.66
7.64
7.51
7.49
7.31
7.29
7.29
7.27
3.56
0.00
1.00
1.00
1.01
1.09
1.07
1.05
1.17
3.19
f1 (ppm)

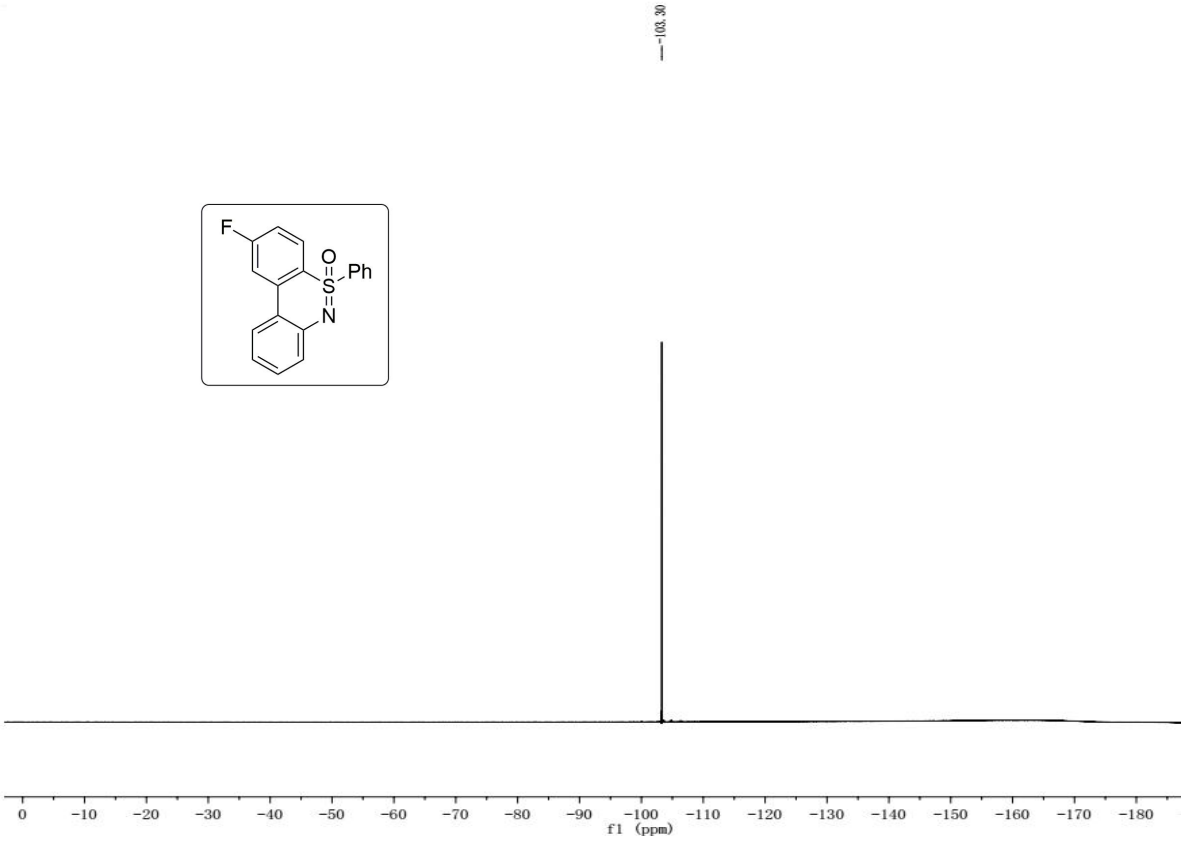

01152018-myn
35-2
141.93
139.06
135.14
134.46
133.16
131.31
129.46
126.08
125.36
123.45
123.09
77.32
77.00
76.68
45.43
f1 (ppm)

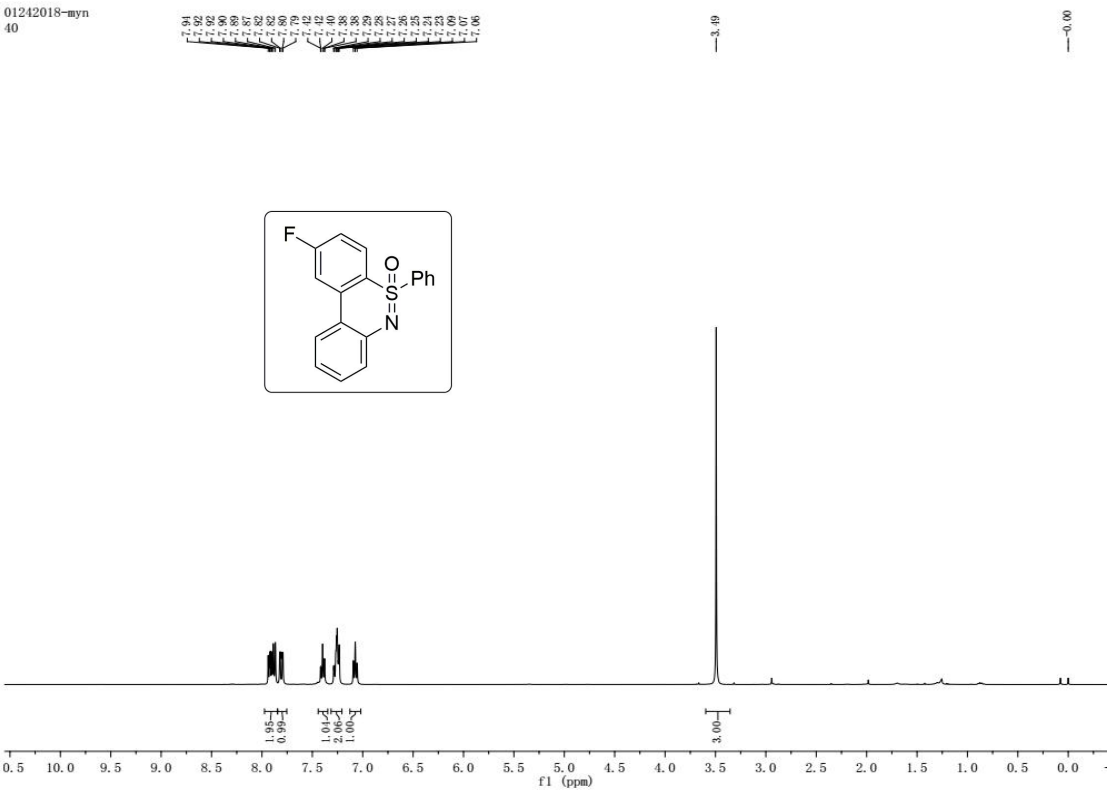
2r

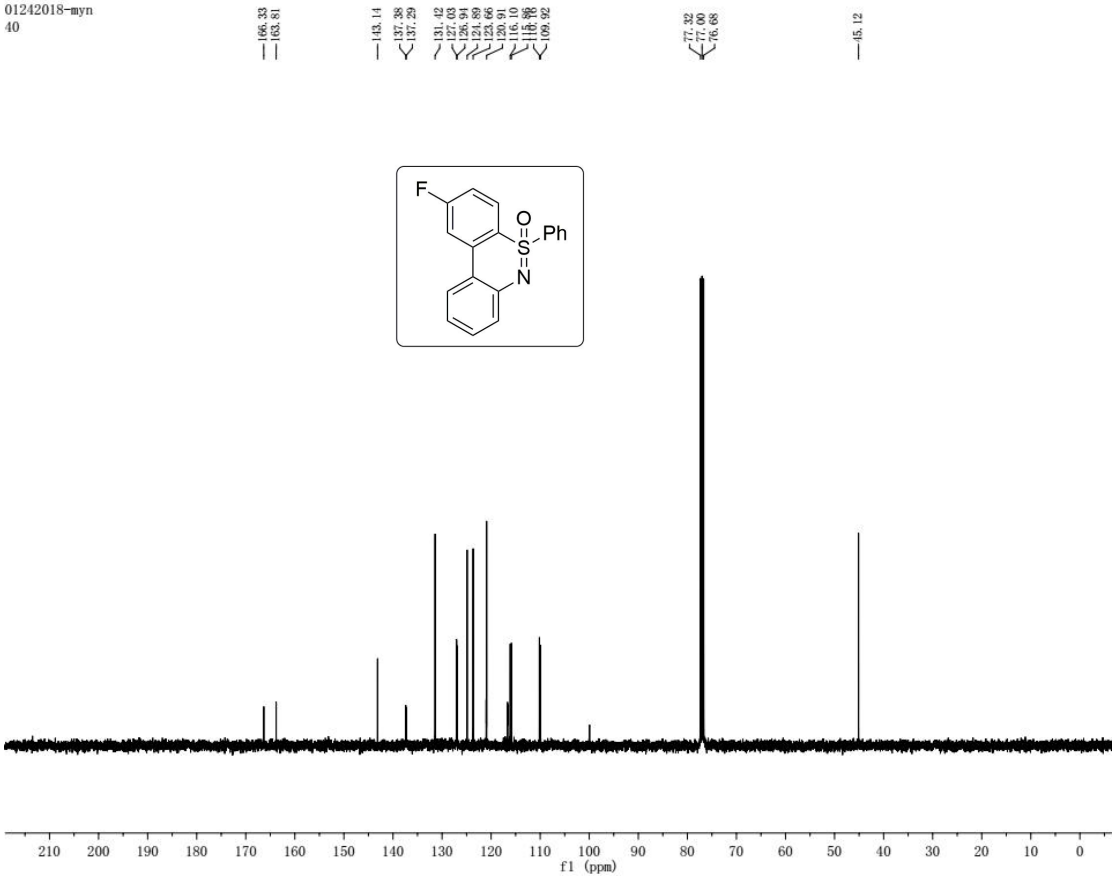

12242017-myn
17-3
7.86
7.84
7.77
7.75
7.68
7.66
7.64
7.46
7.44
7.42
7.29
7.28
6.71
6.69
3.59
0.00
1.00
0.97
1.02
1.00
0.92
0.92
2.99
f1 (ppm)


12242017-myn
17-3
152.62
133.22
132.44
126.05
124.01
123.22
120.33
119.06
113.54
113.32
77.32
77.00
76.68
45.05
f1 (ppm)

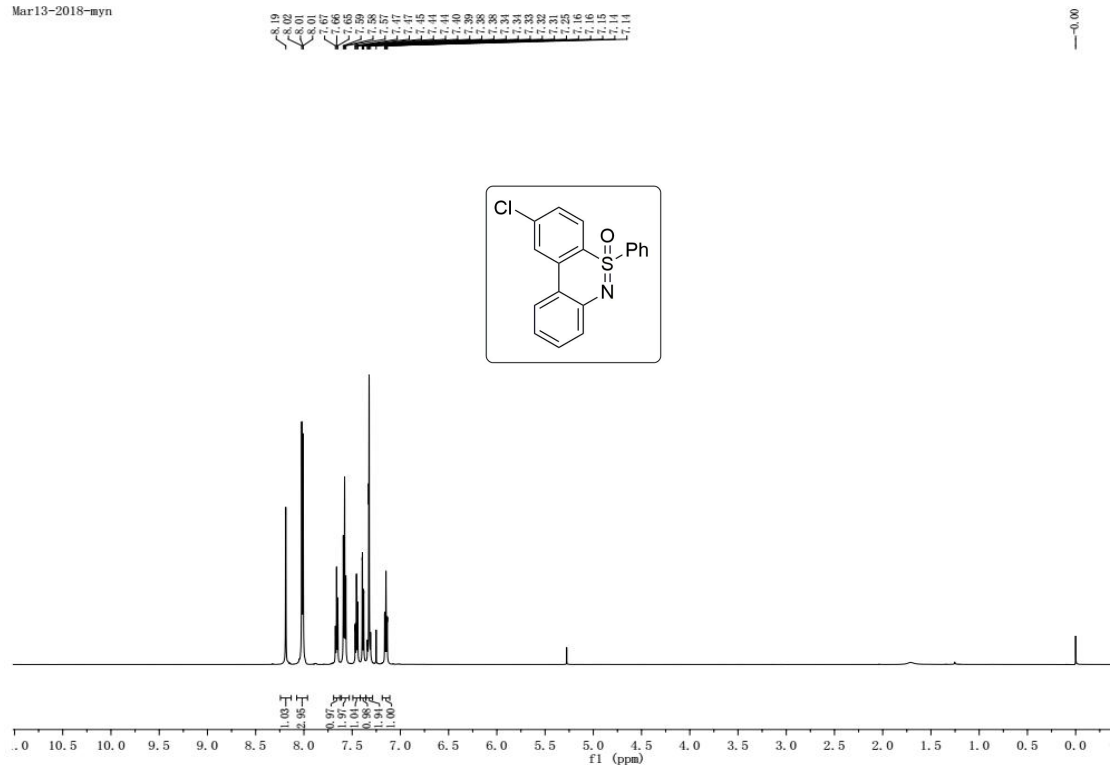
2s

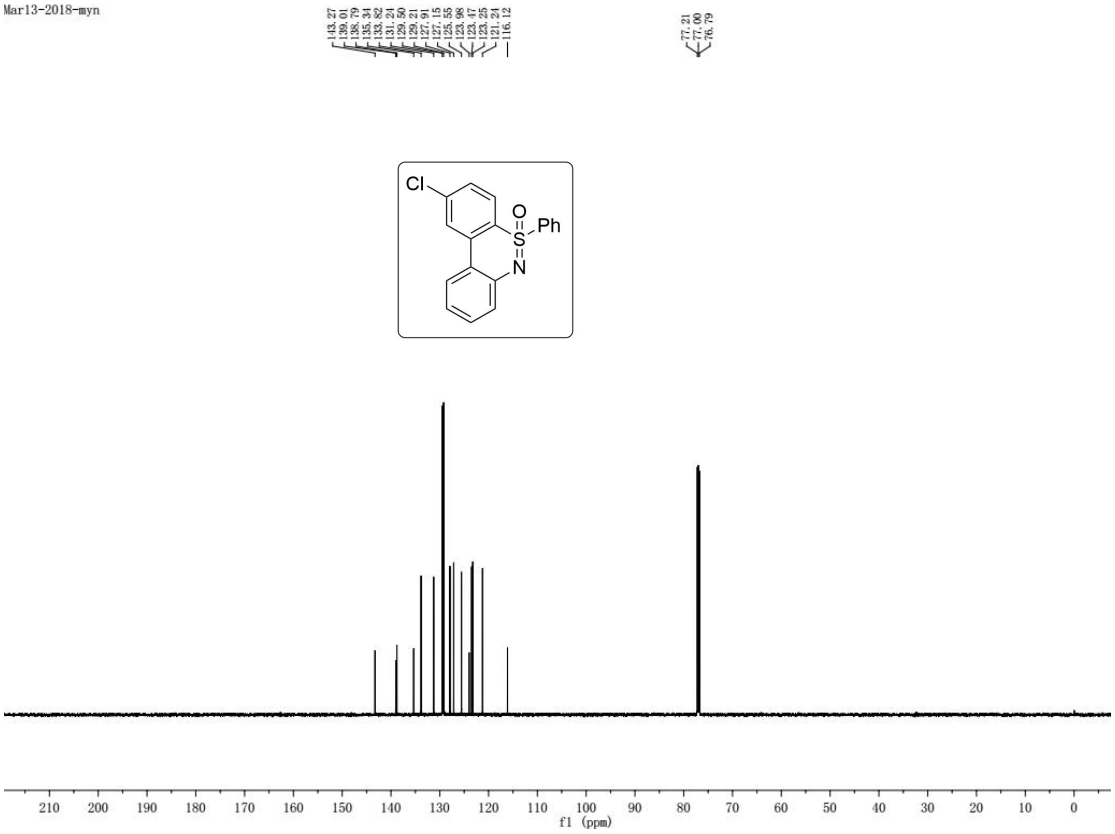

-103.30
F
O
S
Ph
N
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)


01242018-myn
40
7.94 7.92 7.92 7.90 7.89 7.87 7.82 7.80 7.79 7.42 7.40 7.38 7.38 7.29 7.28 7.27 7.26 7.25 7.24 7.23 7.09 7.07 7.06
3.49
0.00
F
O
S
Ph
N
1.95 0.99 1.04 2.06 1.00 3.00
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

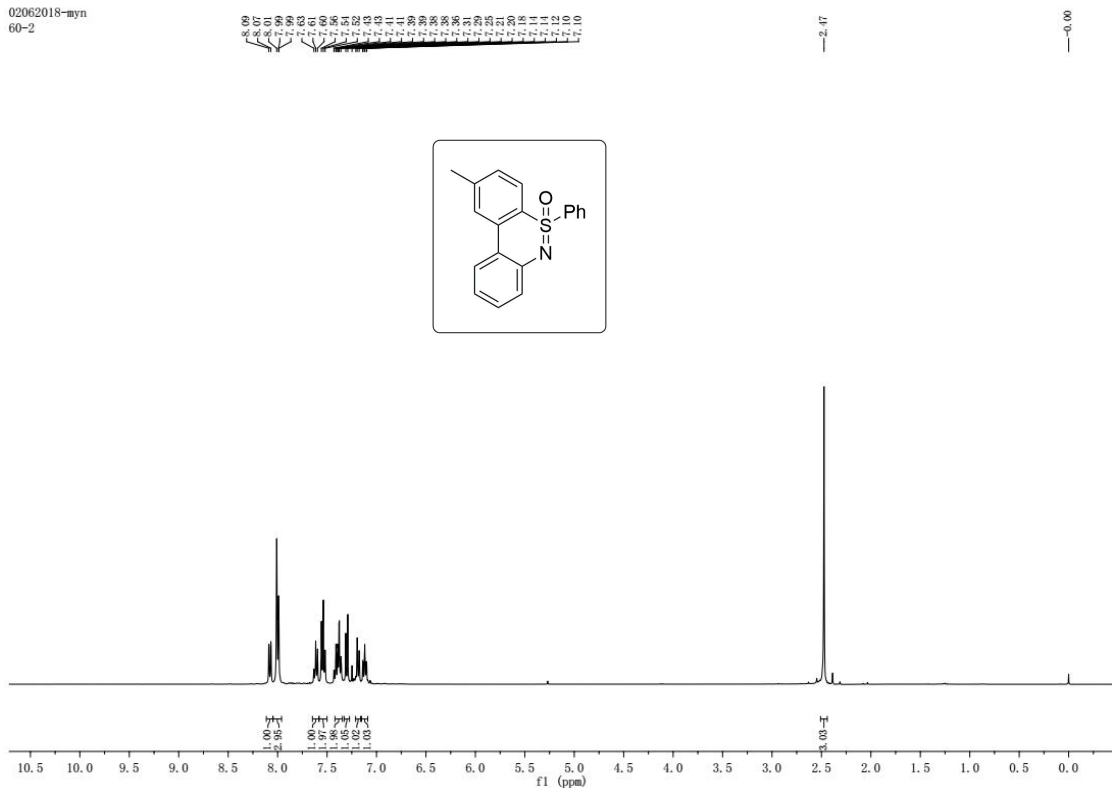

01242018-myn
40
166.33
163.81
143.14
137.38
137.29
131.42
127.03
126.94
126.89
123.66
120.91
116.10
109.92
77.32
77.00
76.68
45.12
F
O
S
N
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

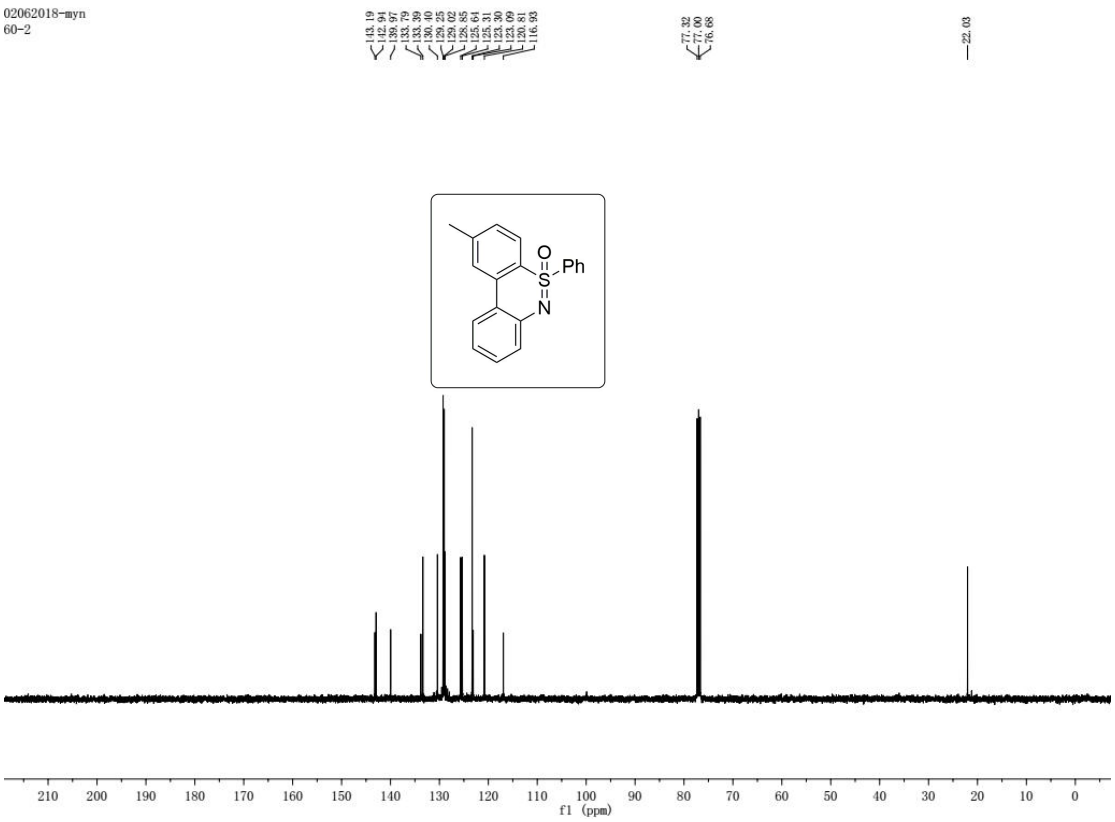
2t


Mar13-2018-myn
8.19
8.02
8.01
8.01
7.67
7.66
7.65
7.59
7.58
7.57
7.47
7.47
7.45
7.44
7.40
7.39
7.38
7.36
7.34
7.34
7.33
7.32
7.31
7.25
7.16
7.16
7.15
7.14
7.14
0.00
Cl
O
S
N
Ph
1.03
2.95
0.97
1.97
1.04
0.96
0.94
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

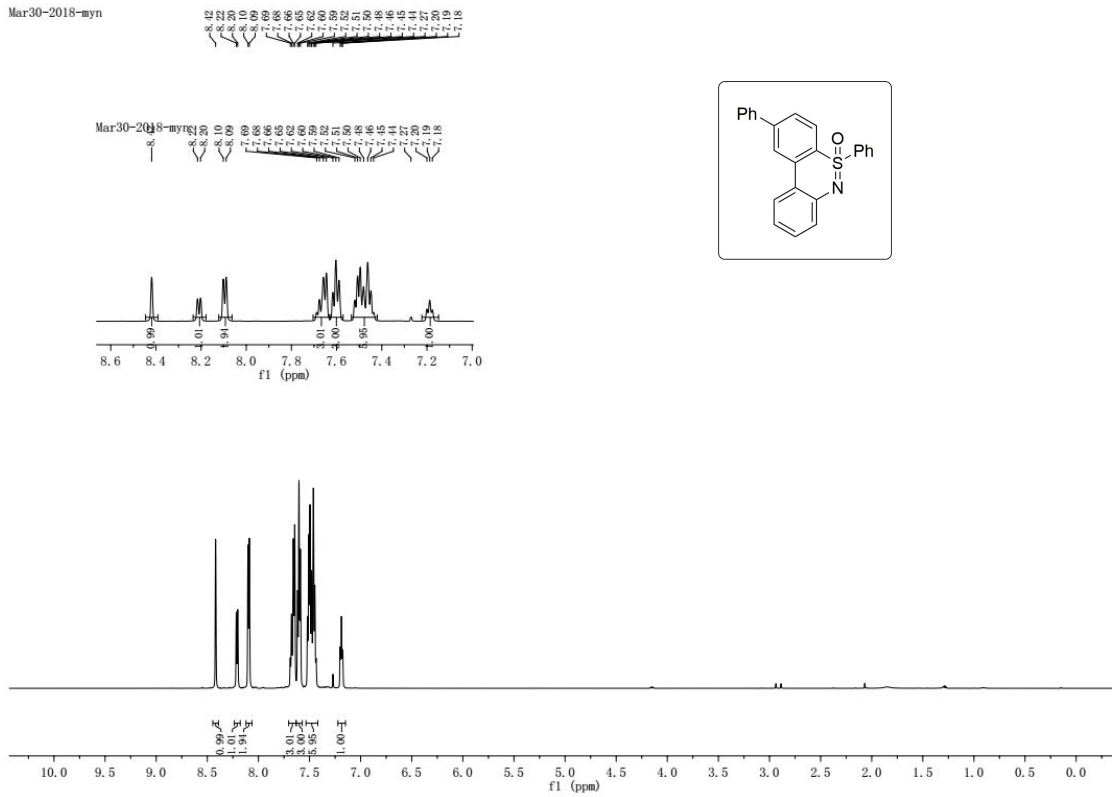

Mar13-2018-myn
143.27
139.01
138.79
135.84
133.82
131.24
129.50
129.21
127.91
127.15
125.55
123.98
123.47
123.25
121.24
116.12
77.21
77.00
76.79
Cl
O
S
N
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

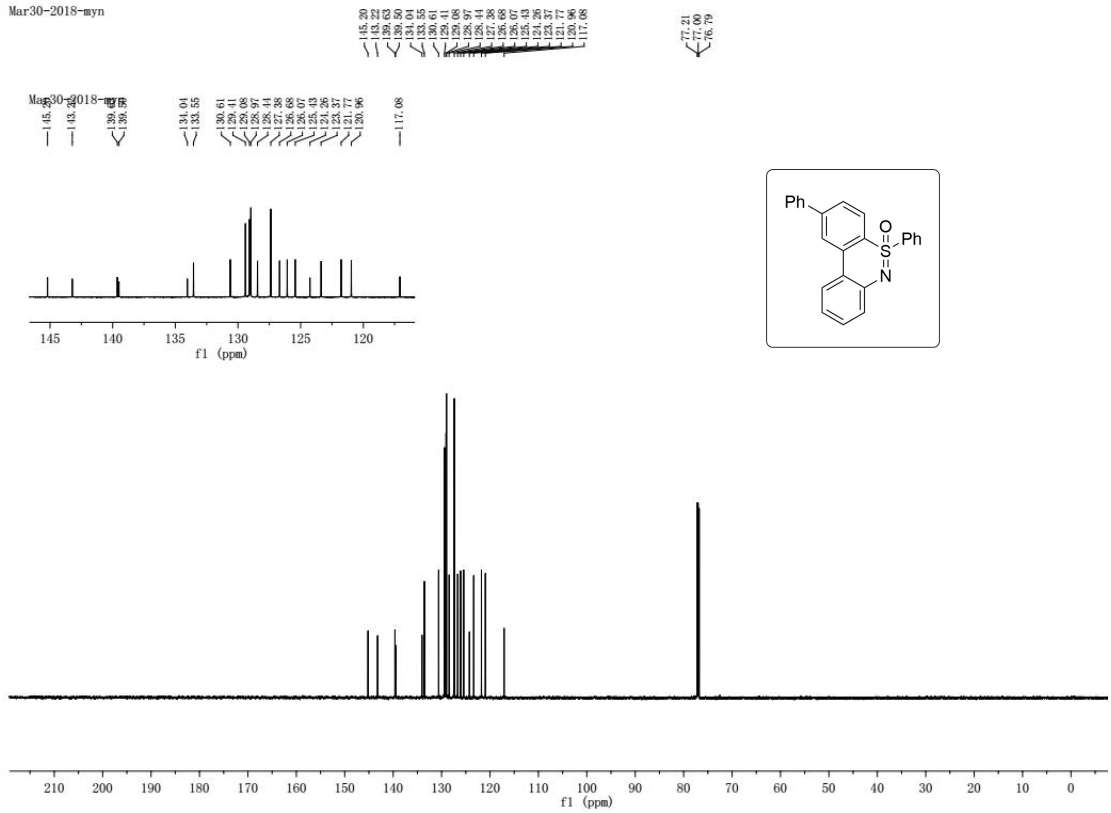
2u


02062018-myn
60-2
8.09
8.07
8.01
7.99
7.63
7.61
7.58
7.56
7.54
7.52
7.43
7.43
7.41
7.41
7.39
7.39
7.38
7.38
7.36
7.31
7.29
7.25
7.21
7.20
7.18
7.14
7.14
7.12
7.10
7.10
2.47
0.00
O
S
N
Ph
1.00
2.95
1.00
1.07
1.98
1.05
1.02
1.03
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

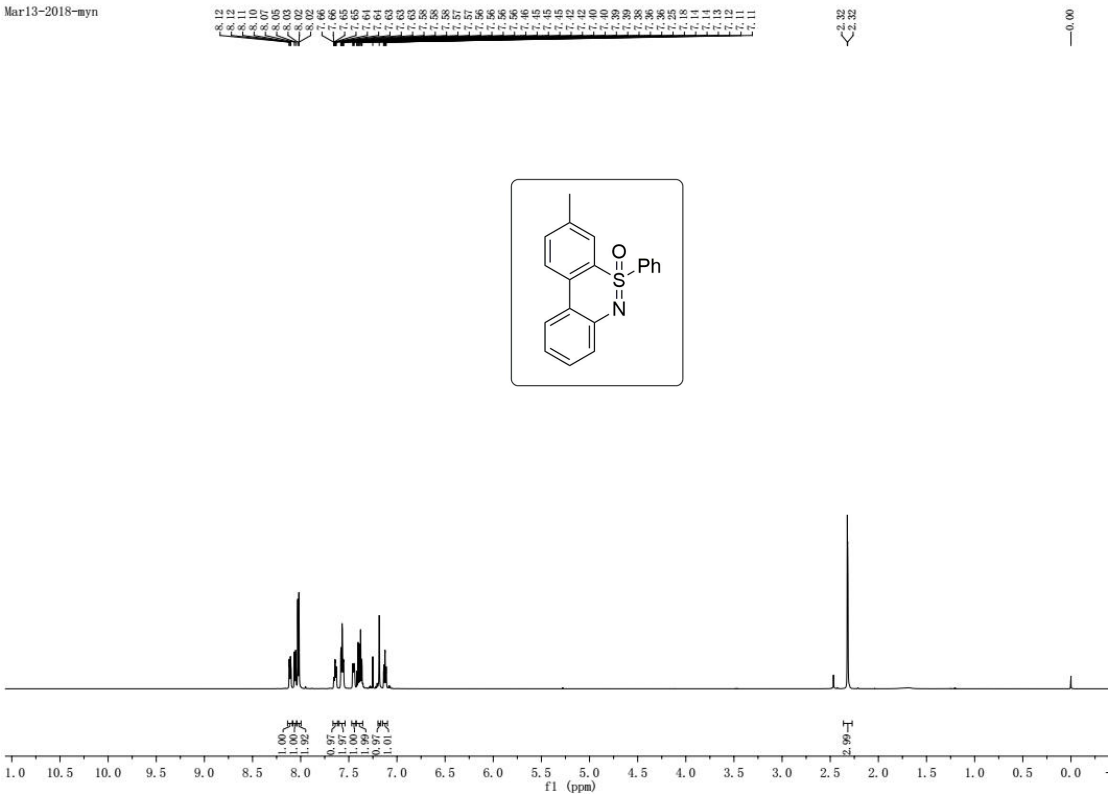

02062018-myn
60-2
143.19
142.94
139.57
133.79
133.39
130.10
129.25
129.02
128.55
125.61
125.31
123.30
123.09
120.81
116.93
77.32
77.00
76.68
22.03
O
Ph
S
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

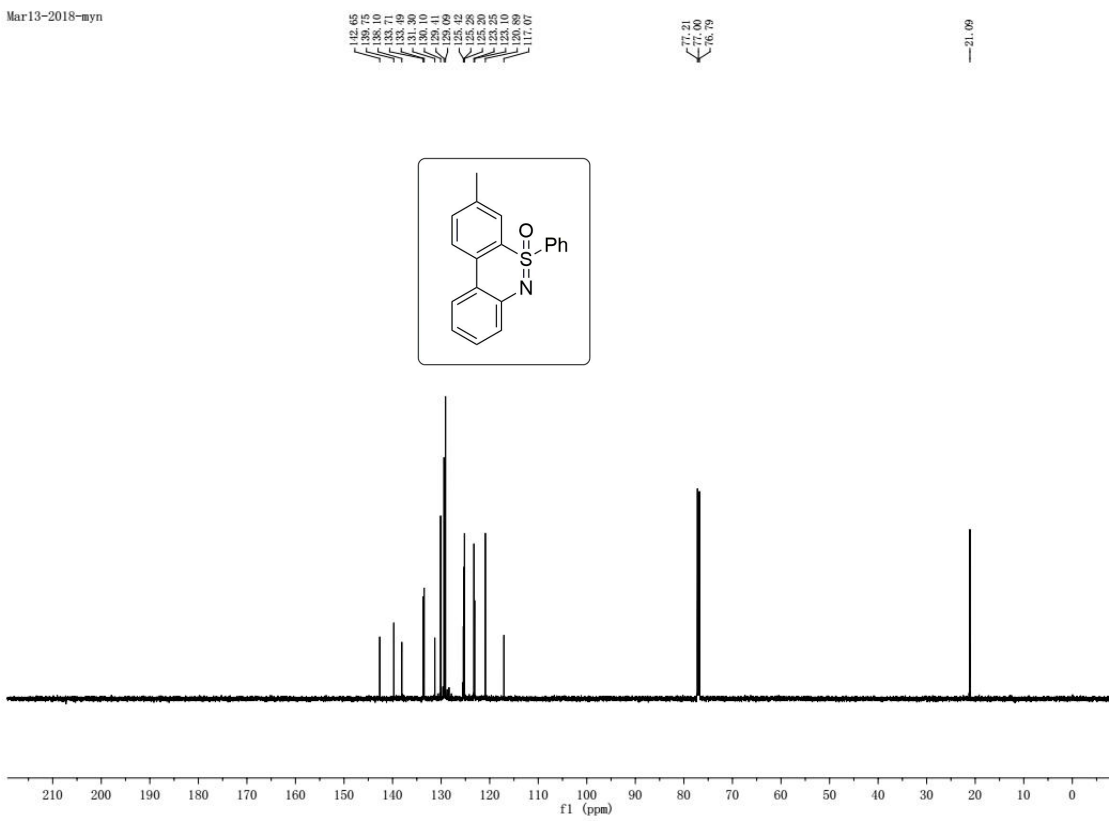
2v


Mar30-2018-myn
8.42
8.23
8.20
8.10
8.09
7.69
7.68
7.66
7.65
7.62
7.60
7.59
7.52
7.51
7.50
7.48
7.46
7.45
7.44
7.27
7.20
7.19
7.18
Mar30-2018-myn
0.99
1.01
0.94
3.01
3.00
5.95
1.00
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0
f1 (ppm)
Ph
O
Ph
S
N
0.99
1.01
1.94
3.01
3.00
5.95
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

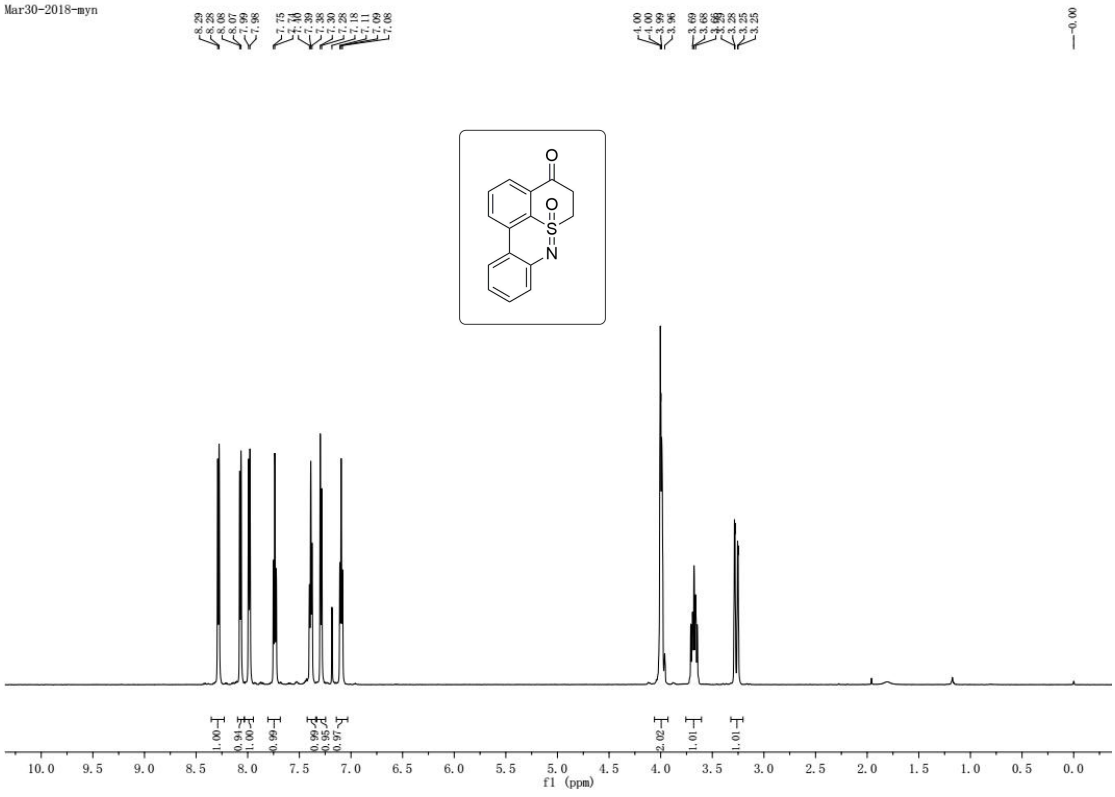

Mar30-2018-myn
145.20
145.22
139.63
139.50
134.04
133.55
130.61
129.08
128.97
128.44
127.38
127.08
126.07
125.43
124.26
123.37
121.77
120.96
117.08
77.21
77.00
76.79
Ph
O
S
N
Ph
f1 (ppm)

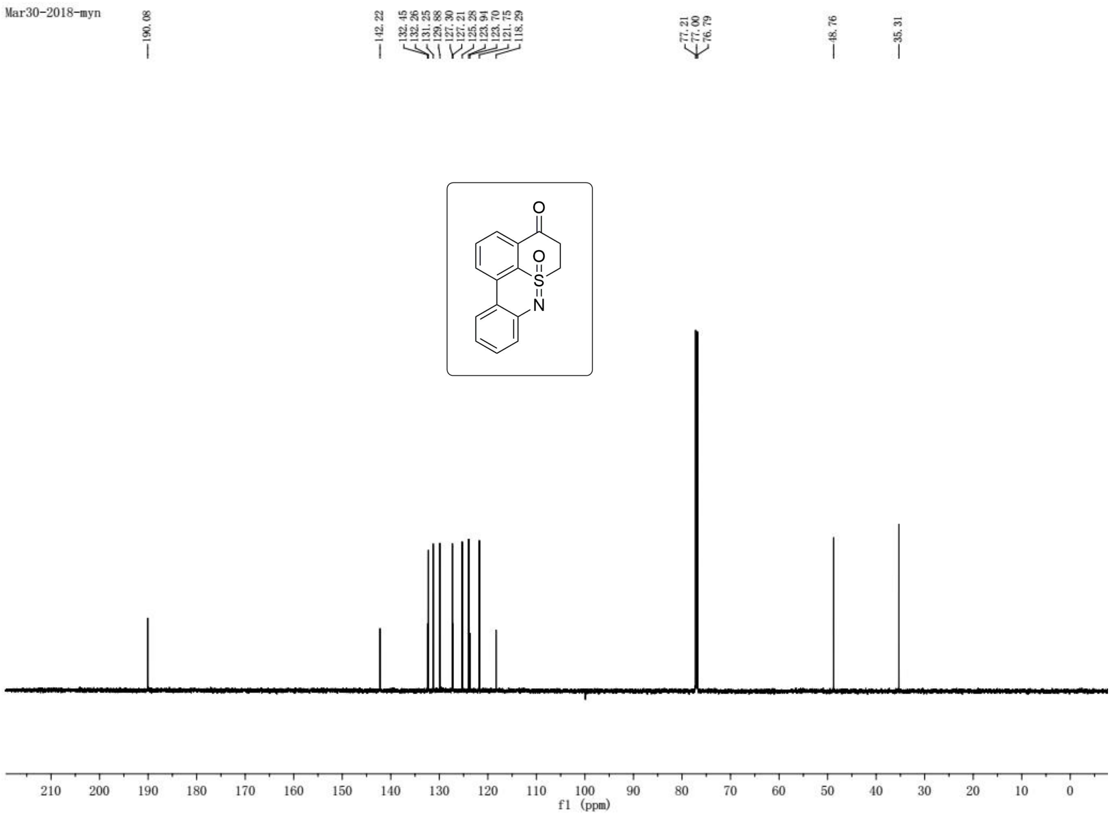
2w


Mar13-2018-myn
8.12
8.11
8.10
8.07
8.05
8.03
8.02
7.66
7.65
7.64
7.63
7.58
7.57
7.56
7.46
7.45
7.42
7.40
7.39
7.38
7.36
7.35
7.15
7.14
7.13
7.12
7.11
2.32
0.00
O
S
Ph
N
1.00
1.99
1.92
0.97
1.00
1.99
0.97
1.01
2.99
f1 (ppm)

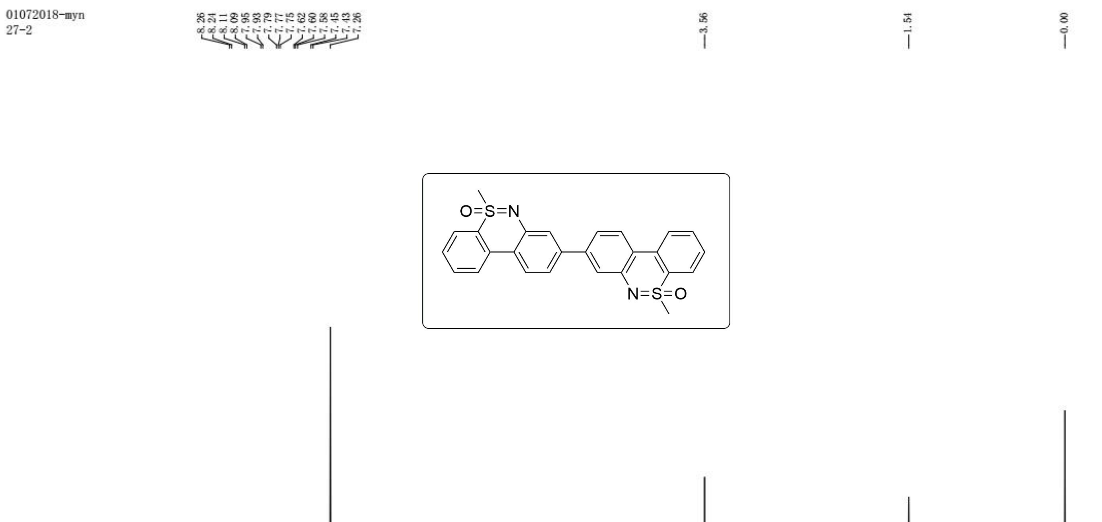

Mar13-2018-myn
142.65
139.75
138.10
133.71
133.49
131.30
130.10
129.41
128.89
125.42
125.28
125.20
123.25
123.10
120.99
117.07
77.21
77.00
76.79
21.09
O
Ph
S
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

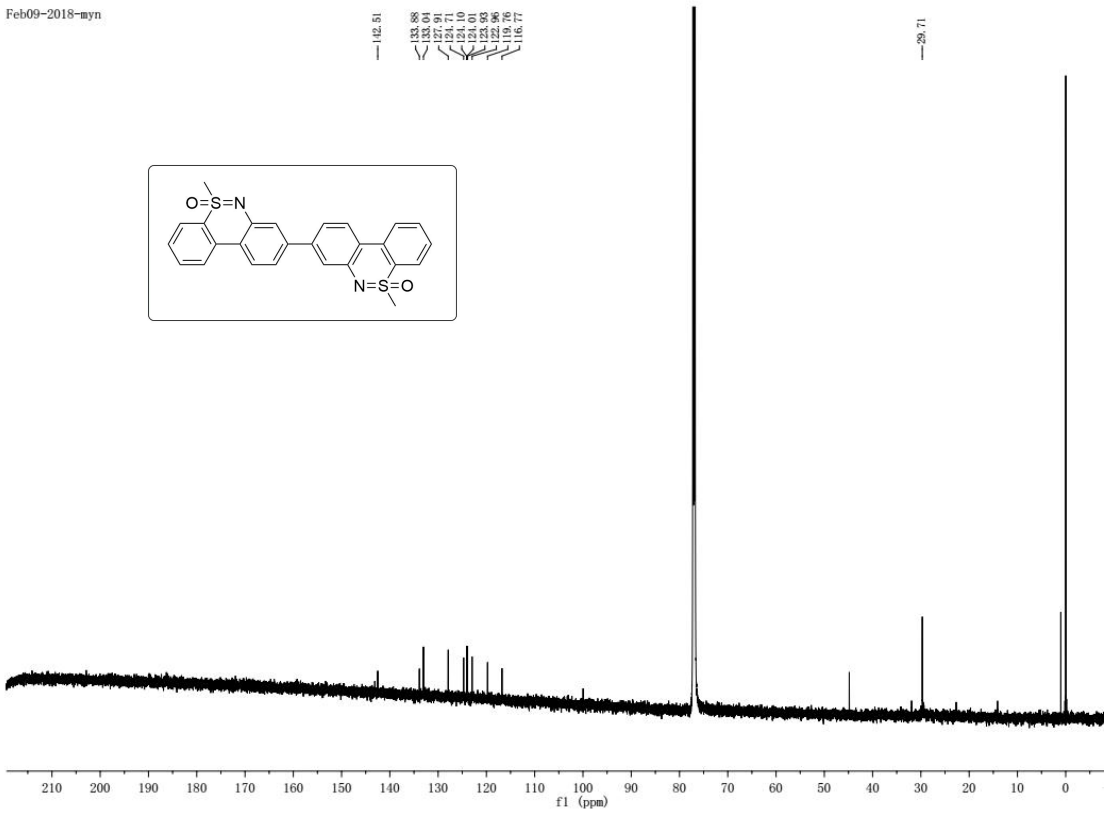
2x


Mar30-2018-myn
8.29
8.26
8.08
8.07
7.99
7.98
7.75
7.74
7.39
7.38
7.30
7.28
7.18
7.11
7.09
7.08
4.00
3.99
3.96
3.69
3.68
3.25
3.25
0.00
1.00
0.94
1.00
0.99
0.99
0.95
0.97
2.02
1.01
1.01
O
O
S
N
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

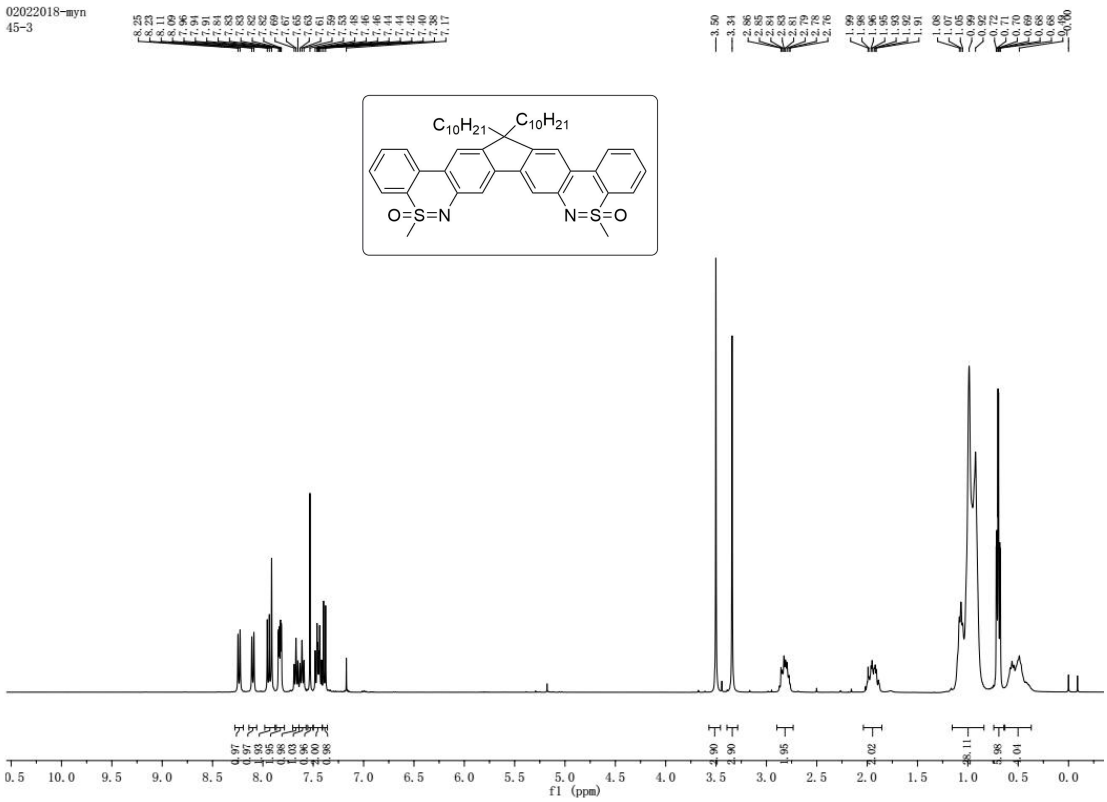

Mar30-2018-myn
190.08
142.22
132.45
132.26
131.25
129.88
127.30
127.21
125.28
123.94
123.70
121.75
118.29
77.21
77.00
76.79
48.76
35.31
O
S
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

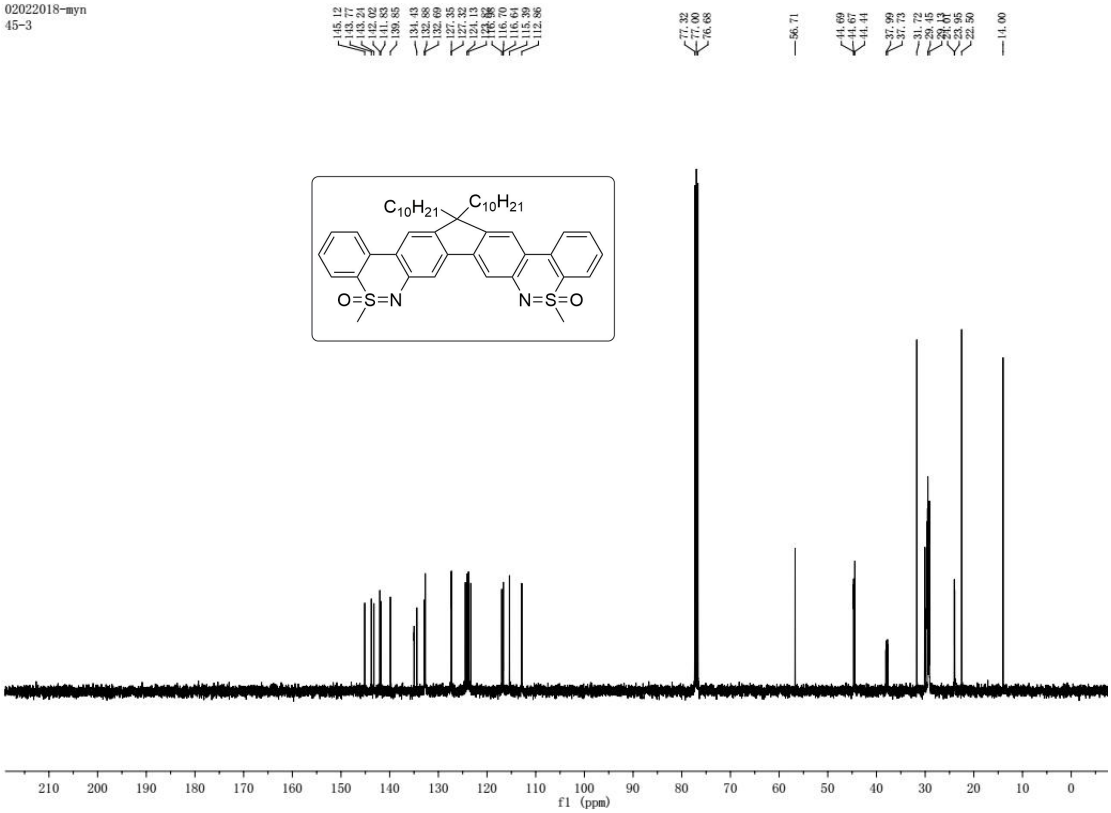
6


01072018-myn
27-2
8.26
8.24
8.11
8.09
7.95
7.93
7.79
7.77
7.75
7.62
7.60
7.58
7.45
7.43
7.26
3.56
1.54
0.00
O=S=N
N=S=O
1.10
1.06
0.98
1.04
1.94
1.06
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

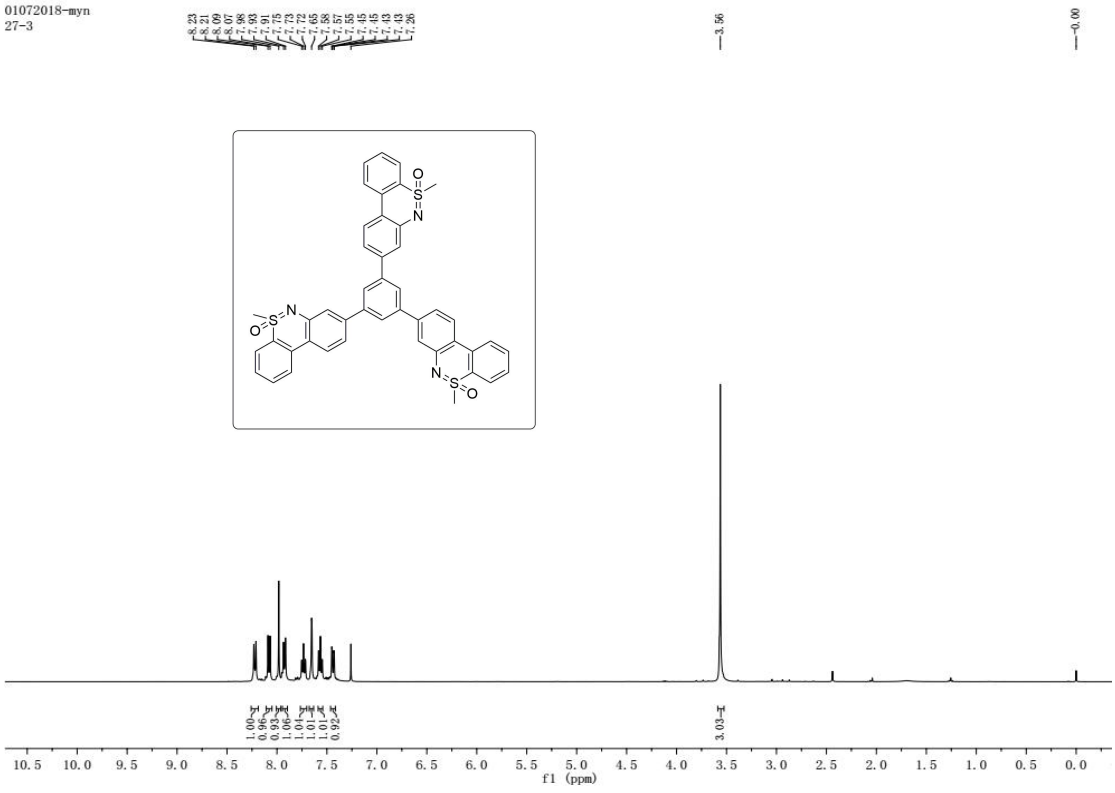

Feb09-2018-myn
142.51
133.88
133.05
127.91
124.71
124.10
124.01
123.68
122.96
119.76
116.77
29.71
O=S=N
N=S=O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

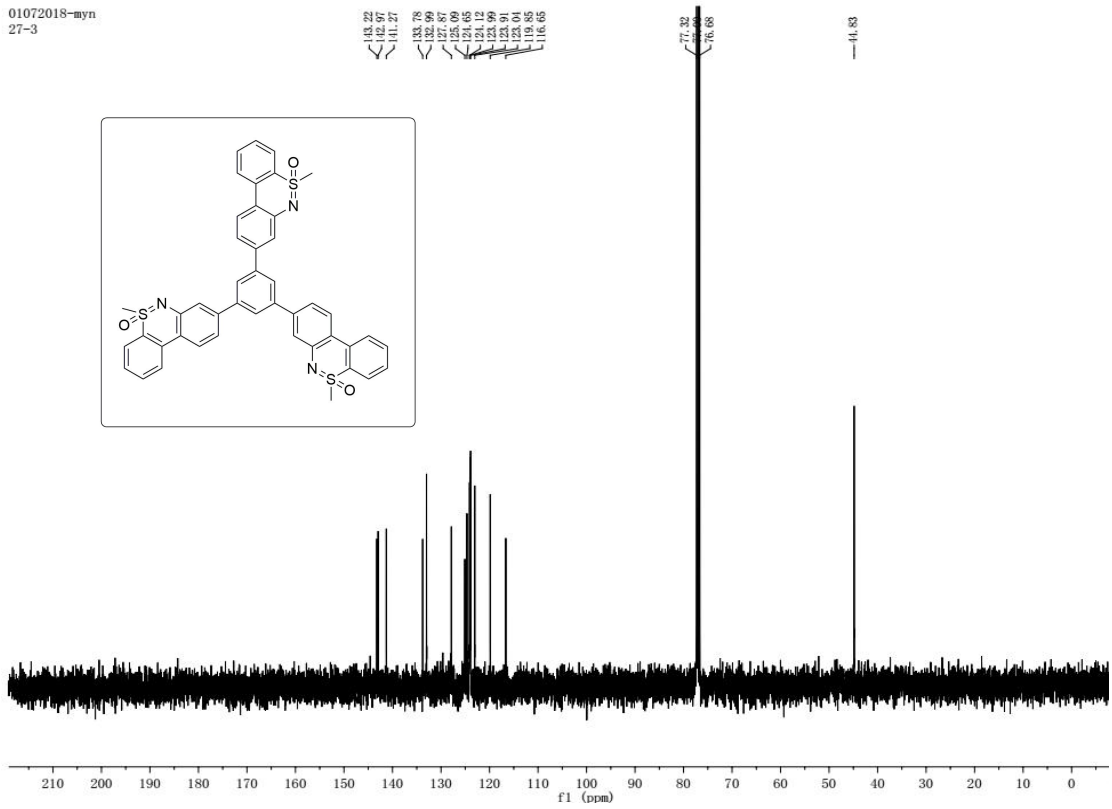
8


02022018-myn
45-3
8.25
8.23
8.11
8.09
7.96
7.94
7.91
7.84
7.83
7.82
7.82
7.69
7.67
7.65
7.63
7.61
7.59
7.53
7.48
7.46
7.44
7.42
7.40
7.38
7.17
3.50
3.34
2.86
2.85
2.84
2.83
2.81
2.79
2.78
2.76
1.99
1.98
1.96
1.95
1.93
1.92
1.91
1.08
1.07
1.05
0.99
0.92
0.72
0.71
0.70
0.69
0.68
0.68
0.00
C10H21
C10H21
O=S=N
N=S=O
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


02022018-myn
45-3
145.12
143.77
143.74
142.62
141.83
139.85
134.43
132.88
132.69
127.45
127.32
77.32
77.00
76.68
56.71
44.69
44.67
44.44
37.99
37.73
31.72
29.45
23.95
22.50
14.00
C10H21
C10H21
O=S=N
N=S=O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

10


01072018-myn
27-3
8.23
8.21
8.09
8.07
7.98
7.91
7.75
7.73
7.72
7.65
7.58
7.57
7.55
7.45
7.43
7.26
3.56
0.00
O
S
N
1.00
0.96
0.93
1.06
1.01
1.01
1.02
0.92
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


01072018-myn
27-3
143.22
142.97
141.27
133.78
132.99
127.87
125.09
124.65
124.12
123.99
123.91
123.04
119.85
116.65
77.32
77.00
76.68
41.83
O
S
N
O
S
N
N
S
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)