Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis of Biaryl Sultams Using Visible-Light-Promoted Denitrogenative Cyclization of 1,2,3,4-Benzothiatriazine-1,1-dioxide **

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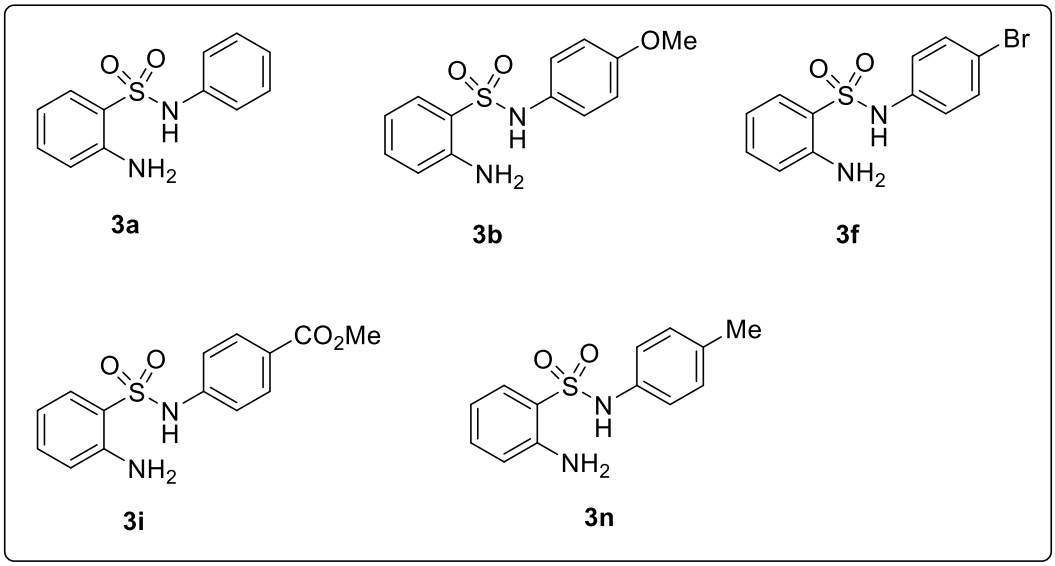
Contents

1. General methods.

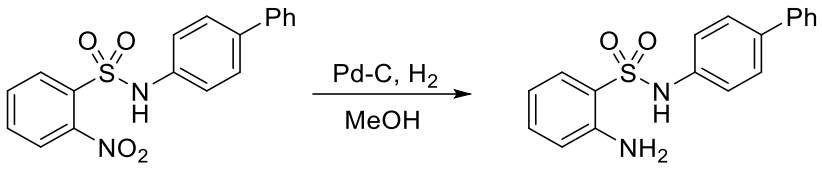
DMSO was dried according to Purification of Common Laboratory Chemicals. Other reagents were used without further purification. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light and by staining with phosphomolybdic acid or potassium permanganate, respectively. Column chromatography was performed on EMD Silica Gel 60 (300–400 Mesh) using a forced flow of 0.5–1.0 bar. ^{1}H NMR (400 MHz), ^{13}C NMR (100MHz) and ^{19}F (376MHz) were measured on a Bruker AVANCE III–400 spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to the residual solvent peak. Coupling constants are reported as Hertz (Hz), signal shapes and splitting patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared (IR) spectra were recorded on a Nicolet 6700 spectrophotometer and are reported as wavenumber (cm^{-1}).

The 2-amino-N-phenylbenzenesulfonamide derivatives **3a**[1], **3b**[1], **3f**[1], **3i**[2], **3n**[3] were synthetized according to the corresponding literature.



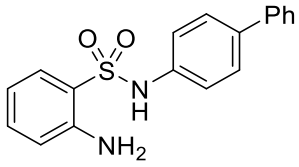
[1] J. F. Ramirez-Martinez, R. Gonzalez-Chavez, R. Guerrero-Alba, P. E. Reyes-Gutierrez, R. Martinez, M. Miranda-Morales, R. Espinosa-Luna, M. M. Gonzalez-Chavez, C. Barajas-Lopez, *Molecules* **2013**, *18*, 894-913.
[2] C. V. Kumar, K. R. Gopidas, K. Bhattacharyya, P. K. Das, M. V. George, *J. Org. Chem.* **1986**, 51, 1967-1972.
[3] T. Miura, M. Yamauchi, A. Kosaka, M. Murakami, *Angew. Chem., Int. Edit.* **2010**, *49*, 4955-4957.

2. The synthesis of 3d, 3g, 3l, 3o.



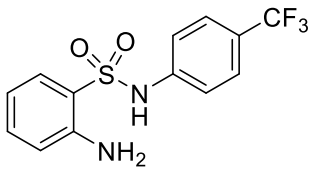
S1 **3d**

Add Pd-C (141.8mg) to the solution of **S1** (2.0 mmol) in MeOH (20 mL) slowly. The mixture was stired at ambient temperature in hydrogen atmosphere for 30 min. Progress of the reaction was monitored by TLC. After the reaction was complete (as judged by TLC analysis), the reaction mixture was filtered through celite. The filtrate was collected, concentrated in vacuo, and get the pure product **3d** (95% yield).



3d

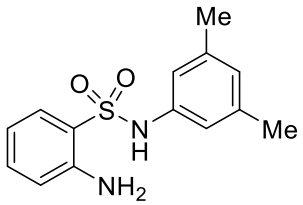
N-([1,1'-biphenyl]-4-yl)-2-aminobenzenesulfonamide (3d): 95% yield. IR (film, cm^{-1}): 3483, 3384，3269，1620，1595，1515，1481，844，760 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.46 – 7.36 (m, 4H), 7.34 – 7.28 (m, 1H), 7.28 – 7.24 (m, 1H), 7.14 – 7.08 (m, 2H), 6.97 (s, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 6.72 – 6.66 (m, 1H), 4.89 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 140.1, 138.7, 135.5, 134.5, 130.0, 128.8, 127.8, 127.4, 126.9, 123.0, 121.10, 118.01, 117.8. HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{18}H_{17}O_2N_2S$: 325.1005; found: 325.1001.



3g

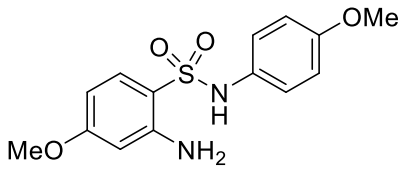
2-amino-N-(4-(trifluoromethyl)phenyl)benzenesulfonamide (3g): 83% yield. IR (film, cm^{-1}): 3445, 3370, 3267, 1617, 1597, 1517, 1482, 846, 754 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.38 (s, 1H),

7.32 – 7.27 (m, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.78 – 6.69 (m, 2H), 4.91 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.29 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 139.8, 134.9, 129.9, 127.1(q, *J* = 33.3 Hz), 126.5 (q, *J* = 3.8 Hz), 123.9(q, *J* = 272.7 Hz), 120.8, 120.6, 118.2, 118.0. HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{13}H_{12}O_2N_2F_3S$: 317.0566; found: 317.0567.



3l

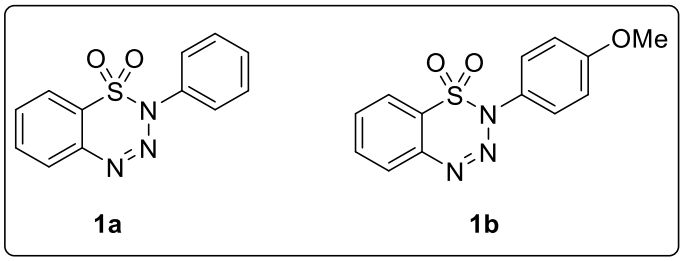
2-amino-N-(3,5-dimethylphenyl)benzenesulfonamide (3l): 91% yield. IR (film, cm^{-1}): 3444, 3363, 3250, 1618, 1598, 1481, 1454, 1385, 762, 696 cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.28 – 7.21 (m, 1H), 7.04 (s, 1H), 6.72 (dd, *J* = 8.1, 0.7 Hz, 1H), 6.70 (s, 1H), 6.69 – 6.64 (m, 1H), 6.64 (s, 2H), 4.92 (s, 2H), 2.16 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 138.8, 136.1, 134.4, 130.0, 127.3, 121.0, 120.0, 117.8, 117.7, 21.2. HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{14}H_{17}O_2N_2S$: 277.1005; found: 277.1005.



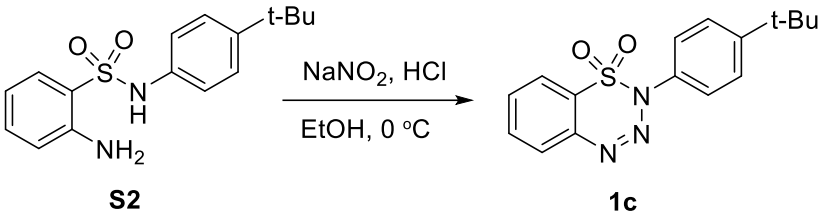
3o

2-amino-4-methoxy-N-(4-methoxyphenyl)benzenesulfonamide (3o): 80% yield. IR (film, cm^{-1}): 3459, 3370, 3282, 1598, 1575, 1508, 1495, 1321, 1132, 834, 673 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.7 Hz, 1H), 6.98 – 6.93 (m, 2H), 6.89 (s, 1H), 6.73 – 6.67 (m, 2H), 6.20 – 6.14 (m, 2H), 4.95 (s, 2H), 3.73 (s, 3H), 3.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 158.0, 147.1, 132.1, 129.0, 126.0, 114.3, 113.1, 104.6, 101.3, 55.38, 55.36. HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{14}H_{17}O_4N_2S$: 309.0904; found: 309.0904.

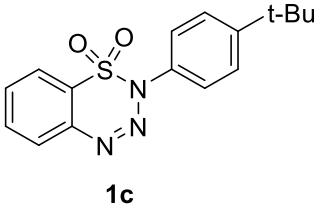
The 1,2,3,4-benzothiatriazine-1,1-dioxide derivatives **1a**[4], **1b**[5] were synthetized according to the corresponding literature.



3. The synthesis of 1c-m.



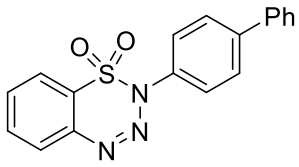
To a solution of **S2** (2.0 mmol) in EtOH (10 mL) and HCl (8.0 mmol) was slowly added a solution of $NaNO_2$ (2.4 mmol) in water (5 mL) at 0℃. After being stired at 0 ℃ for 45 min, the reation mixture was diluted with H_2O (10 mL)and extracted with CH_2Cl_2 (5×10 mL). The combined organic layers were dried over $MgSO_4$. The solvents were removed under reduced pressure and the residue was purified by flash chromatography (Petroleum ether: EtOAc = 10:1) to give the product **1c** (63% yield).



2-(4-(tert-butyl)phenyl)-2H-benzo[e][1,2,3,4]thiatriazine 1,1-dioxide (1c): 63% yield. IR (film, cm^{-1}): 2967, 1505, 1477, 1448, 1394, 1339, 1184, 865, 773, 758 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.09 (m, 2H), 7.93 (td, *J* = 8.0, 1.3 Hz, 1H), 7.83 (td, *J* = 7.7, 1.0 Hz, 1H), 7.56 (s, 4H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 141.3, 134.3, 133.0, 132.0, 129.6, 127.6, 126.6, 126.4, 121.0, 34.9, 31.3. HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{16}H_{18}O_2N_3S$: 316.1114; found:

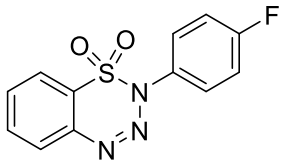
[4] F. Ullmann, C. Gross, *Ber. Dtsch. Chem. Ges.* **1910,** *43*, 2694-2704.
[5] K. S. Burmistrov, S. I. Burmistrov, M. S. Malinovskii, *Chem. Heterocycl. Compd.* **1977**, *13*, 1201-1204.

316.1113.



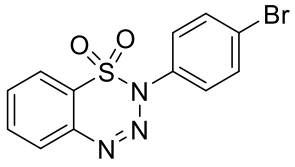
1d

2-([1,1'-biphenyl]-4-yl)-2H-benzo[e][1,2,3,4]thiatriazine 1,1-dioxide (1d): 77% yield. IR (film, cm^{-1}): 3078, 1621, 1594, 1476, 1448, 1337, 1186, 862, 761, 683 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.10 (m, 2H), 7.94 (td, *J* = 7.9, 1.3 Hz, 1H), 7.84 (td, *J* = 7.7, 1.1 Hz, 1H), 7.79 – 7.69 (m, 4H), 7.66 – 7.60 (m, 2H), 7.51 – 7.44 (m, 2H), 7.43 – 7.36 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 141.3, 139.9, 134.4, 133.9, 133.1, 129.7, 129.0, 128.3, 128.2, 128.0, 127.3, 126.5, 121.0. HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{18}H_{14}O_2N_3S$: 336.0801; found: 336.0801.



1e

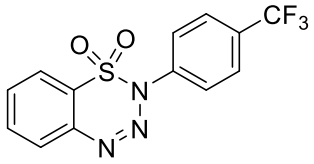
2-(4-fluorophenyl)-2H-benzo[e][1,2,3,4]thiatriazine 1,1-dioxide (1e): 60% yield. IR (film, cm^{-1}): 3080, 1621, 1597, 1569, 1489, 1328, 1183, 829, 775 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.7 Hz, 2H), 7.95 (t, *J* = 7.5 Hz, 1H), 7.85 (t, *J* = 7.5 Hz, 1H), 7.70 – 7.55 (m, 2H), 7.24 (t, *J* = 8.3 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.23 (s, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5 (d, *J* = 251.5 Hz), 141.2, 134.5, 133.3, 130.6 (d, *J* = 3.0 Hz), 130.3 (d, *J* = 9.1 Hz), 129.8, 126.4, 121.0, 116.6 (d, *J* = 23.2 Hz). HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{12}H_9O_2N_3FS$: 278.0394; found: 278.0394.



1f

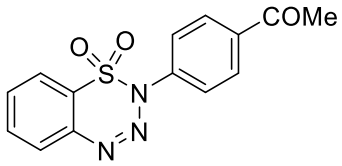
2-(4-bromophenyl)-2H-benzo[e][1,2,3,4]thiatriazine 1,1-dioxide (1f): 64% yield. IR (film, cm^{-1}): 3085, 3063, 1615, 1593, 1574, 1472, 1448, 1338, 1186, 860, 775 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 5.6 Hz, 2H), 7.95 (t, *J* = 7.3 Hz, 1H), 7.85 (t, *J* = 7.2 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 134.5, 133.9, 133.3, 132.8, 129.8, 129.4, 126.4, 124.2, 121.0. HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{12}H_9O_2N_3BrS$: 337.9593; found: 337.9593.



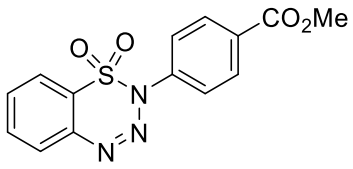
1g

2-(4-(trifluoromethyl)phenyl)-2H-benzo[e][1,2,3,4]thiatriazine 1,1-dioxide (1g): 88% yield. IR (film, cm^{-1}): 3080, 1613, 1594, 1570, 1448, 1327, 1185, 882, 775 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (t, *J* = 6.4 Hz, 2H), 7.96 (t, *J* = 7.4 Hz, 1H), 7.87 (t, *J* = 7.7 Hz, 1H), 7.84 – 7.86 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.68 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 138.3, 134.6, 133.5, 131.6 (q, *J* = 32.9 Hz), 129.9, 127.6, 126.7 (q, *J* = 3.7 Hz), 126.5, 123.6(q, *J* = 273.7 Hz), 121.0. HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{13}H_9O_2N_3F_3S$: 328.0362; found: 328.0362.



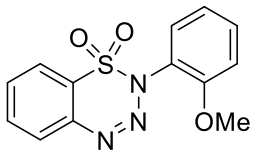
1h

1-(4-(1,1-dioxido-2H-benzo[e][1,2,3,4]thiatriazin-2-yl)phenyl)ethan-1-one (1h): 60% yield. IR (film, cm^{-1}): 3082, 1688, 1598, 1570, 1502, 1450, 1339, 1183, 863, 780 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.07 (m, 4H), 7.97 (t, *J* = 7.4 Hz, 1H), 7.87 (t, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 2H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 141.0, 139.1, 137.5, 134.6, 133.5, 129.9, 129.5, 127.1, 126.5, 121.0, 26.8. HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{14}H_{12}O_3N_3S$: 302.0594; found: 302.0594.



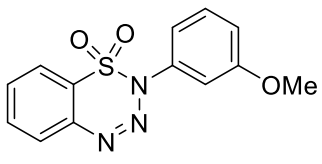
1i

methyl 4-(1,1-dioxido-2H-benzo[e][1,2,3,4]thiatriazin-2-yl)benzoate (1i): 55% yield. IR (film, cm^{-1}): 3086, 1721, 1596, 1574, 1507, 1448, 1382, 1336, 896, 761 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.6 Hz, 2H), 8.18 – 8.11 (m, 2H), 7.97 (td, *J* = 7.8, 1.3 Hz, 1H), 7.87 (td, *J* = 7.7, 1.1 Hz, 1H), 7.74 (d, *J* = 8.6 Hz, 2H), 3.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 141.1, 139.1, 134.5, 133.4, 131.1, 130.8, 129.8, 126.9, 126.6, 121.0, 52.5. HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{14}H_{12}O_4N_3S$: 318.0543; found: 318.0543.



1j

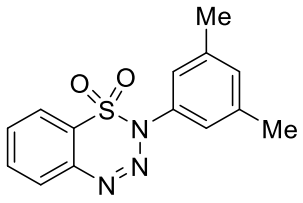
2-(2-methoxyphenyl)-2H-benzo[e][1,2,3,4]thiatriazine 1,1-dioxide (1j): 79% yield. IR (film, cm^{-1}): 3077, 3014, 1596, 1501, 1465, 1445, 1341, 1182, 757 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.01 (m, 2H), 7.90 (t, *J* = 7.3 Hz, 1H), 7.79 (t, *J* = 7.2 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.16 – 7.00 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 141.4, 134.1, 132.9, 132.4, 131.5, 129.6, 126.9, 122.9, 120.9, 120.8, 112.8, 56.2. HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{13}H_{12}O_3N_3S$: 290.0594; found: 290.0593.



1k

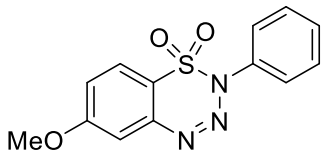
2-(3-methoxyphenyl)-2H-benzo[e][1,2,3,4]thiatriazine 1,1-dioxide (1k): 66% yield. IR (film, cm^{-1}): 3086, 1606, 1589, 1574, 1481, 1448, 1334, 1185, 878, 755 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.94 (td, *J* = 7.8, 1.3 Hz, 1H), 7.87 – 7.80 (m, 1H), 7.44 (t, *J* = 8.1 Hz, 1H), 7.24 (d, *J* = 1.1 Hz, 1H), 7.17 (t, *J* = 2.2

Hz, 1H), 7.08 (dd, *J* = 8.4, 1.9 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 141.2, 135.8, 134.3, 133.1, 130.1, 129.7, 126.5, 121.0, 120.2, 116.2, 113.4, 55.6. HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{13}H_{12}O_3N_3S$: 290.0594; found: 290.0594.



1l

2-(3,5-dimethylphenyl)-2H-benzo[e][1,2,3,4]thiatriazine 1,1-dioxide (1l): 88% yield. IR (film, cm^{-1}): 3075, 1615, 1594, 1573, 1448, 1339, 1187, 896, 872, 768 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.07 (m, 2H), 7.95 – 7.89 (m, 1H), 7.82 (td, *J* = 7.7, 1.0 Hz, 1H), 7.26 (s, 2H), 7.16 (s, 1H), 2.40 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 139.4, 134.6, 134.2, 133.0, 131.8, 129.6, 126.5, 125.8, 120.9, 21.2. HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{14}H_{14}O_2N_3S$: 288.0801; found: 288.0801.



1m

6-methoxy-2-phenyl-2H-benzo[e][1,2,3,4]thiatriazine 1,1-dioxide (1m): 93% yield. IR (film, cm^{-1}): 3088, 3014, 1595, 1566, 1466, 1448, 1336, 1180, 889, 751, 691 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.8 Hz, 1H), 7.68 – 7.60 (m, 2H), 7.58 – 7.48 (m, 4H), 7.31 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 143.3, 135.0, 130.0, 129.5, 128.0, 122.8, 120.7, 118.7, 112.2, 56.2. HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{13}H_{12}O_3N_3S$: 290.0594; found: 290.0594.

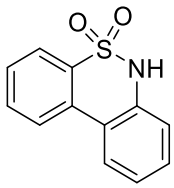
4. General procedure: synthesis of biaryl sultams.

General Procedure A: A 10 mL round bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with 1,2,3,4-benzothiatriazine-1,1-dioxides **1a** (0.2 mmol, 1.0 equiv) and $Ru(bpy)_3Cl_2$ (0.002 mmol, 0.01 equiv). The flask was evacuated and backfilled with nitrogen for 3 times. DMSO (2.0 mL, 0.1 M) were added with a syringe under nitrogen. The mixture was then irradiated by blue LED strips. After the reaction was complete (as judged by TLC analysis), the mixture was poured into a separatory funnel containing 20 mL of H_2O and 20 mL of EtOAc. The layers were separated and the organic layers were extracted with H_2O (2×20 mL). The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude product was purified by flash chromatography on silica gel to afford the desired product **2a**.

General Procedure B: One-pot synthesis of biaryl sultams.

A 10 mL round bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with 2-amino-N-phenylbenzenesulfonamide **3a** (0.2 mmol, 1.0 equiv) and $Ru(bpy)_3Cl_2$ (0.002 mmol, 0.01 equiv). The flask was evacuated and backfilled with nitrogen for 3 times. DMSO (2.0 mL, 0.1 M) and *t*-BuONO (0.3 mmol, 1.5 equiv) were added with syringes under nitrogen. The mixture was then irradiated by blue LED strips. After the reaction was complete (as judged by TLC analysis), the mixture was poured into a separatory funnel containing 20 mL of H_2O and 20 mL of EtOAc. The layers were separated and the organic layers were extracted with H_2O (2×20 mL). The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude product was purified by flash chromatography on silica gel to afford the desired product **2a**.

5. Data for annulated biaryl sultams.

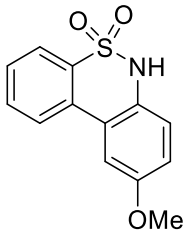


2a

6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2a):[6] According to the general procedure A: **1a** (0.2 mmol, 51.8 mg), $Ru(bpy)_3Cl_2$ (0.002 mmol, 1.5 mg) in DMSO (2.0 mL) afforded **2a** (45.1 mg, 98%) as a white solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 2 h.

According to the general procedure B: **3a** (0.2 mmol, 1.0 equiv), $Ru(bpy)_3Cl_2$ (0.002 mmol, 0.01 equiv), *t*-BuONO (0.3 mmol, 1.5 equiv) in DMSO (2.0 mL) afforded **2a** (39.3 mg, 85%) as a white solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 1.5 h.

^{1}H NMR (400 MHz, d_6-DMSO) δ 11.43 (s, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.22 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.97 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.82 (ddd, *J* = 8.8, 7.8, 1.4 Hz, 1H), 7.68 (td, *J* = 7.7, 0.9 Hz, 1H), 7.49 (td, *J* = 8.0, 1.3 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.24 (dd, *J* = 8.0, 1.0 Hz, 1H).^{13}C NMR (101 MHz, d_6-DMSO) δ 136.5, 134.4, 132.5, 131.7, 130.4, 128.5, 125.6, 125.3, 123.9, 121.4, 121.1, 119.6.



2b

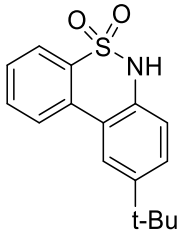
9-methoxy-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2b):[5] According to the general procedure A: **1b** (0.2 mmol, 57.9 mg), $Ru(bpy)_3Cl_2$ (0.002 mmol, 1.5 mg) in DMSO (2.0 mL) afforded **2b** (49.9 mg, 96%) as a white solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 2h.

According to the general procedure B: **3b** (0.2 mmol, 1.0 equiv), $Ru(bpy)_3Cl_2$ (0.002 mmol, 0.01 equiv), *t*-BuONO (0.3 mmol, 1.5 equiv) in DMSO (2.0 mL) afforded **2b**

[6] Laha, J. K.; Jethava, K. P.; Dayal, N. *J. Org. Chem.* **2014,** *79*, 8010-8019.

(35.3 mg, 68%) as a white solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 1.5 h.

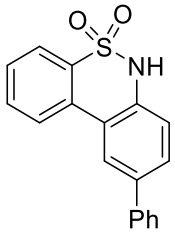
^{1}H NMR (400 MHz, *d*$_6$-DMSO) δ 11.02 (s, 1H), 8.30 (d, *J* = 7.9 Hz, 1H), 7.94 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.81 (td, *J* = 7.9, 1.3 Hz, 1H), 7.72 (d, *J* = 2.7 Hz, 1H), 7.68 (td, *J* = 7.7, 0.8 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 1H), 7.10 (dd, *J* = 8.8, 2.7 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, *d*$_6$-DMSO) δ 156.1, 134.8, 132.4, 131.7, 129.7, 128.6, 126.0, 123.1, 121.8, 121.2, 117.1, 109.5, 55.6.



2c

9-(tert-butyl)-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2c): According to the general procedure A: **1c** (0.2 mmol, 63.0 mg), Ru(bpy)$_3$Cl$_2$ (0.002 mmol, 1.5 mg) in DMSO (2.0 mL) afforded **2c** (55.3 mg, 96%) as a white solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 2 h.

IR (film, cm^{-1}): 3160, 2954, 1610, 1594, 1567, 1486, 1387, 1161, 819, 747 cm^{-1}. ^{1}H NMR (400 MHz, *d*$_6$-DMSO) δ 11.26 (s, 1H), 8.33 (d, *J* = 7.9 Hz, 1H), 8.14 (s, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.82 (t, *J* = 7.4 Hz, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 1H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, *d*$_6$-DMSO) δ 146.4, 134.6, 134.1, 132.4, 132.1, 128.3, 127.6, 125.7, 121.6, 121.1, 121.0, 119.5, 34.4, 31.1. HRMS (DART-Positive) ([M+H]$^+$) Calcd. For $C_{16}H_{18}O_2NS$: 288.1053; found: 288.1053.



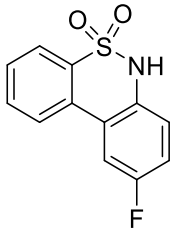
2d

9-phenyl-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2d): According to the general procedure A: **1d** (0.2 mmol, 67.1 mg), Ru(bpy)$_3$Cl$_2$ (0.002 mmol, 1.5 mg) in DMSO

(2.0 mL) afforded **2d** (51.3 mg, 84%) as a white solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 2 h.

According to the general procedure B: **3d** (0.2 mmol, 1.0 equiv), $Ru(bpy)_3Cl_2$ (0.002 mmol, 0.01 equiv), *t*-BuONO (0.3 mmol, 1.5 equiv) in DMSO (2.0 mL) afforded **2d** (46.5 mg, 76%) as a white solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 1.5 h.

IR (film, cm^{-1}): 3167, 2972, 1599, 1567, 1559, 1480, 1387, 1163, 764, 743, 696 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 1.9 Hz, 1H), 8.08 – 8.01 (m, 2H), 7.73 (td, *J* = 7.8, 1.3 Hz, 1H), 7.64 – 7.56 (m, 4H), 7.51 – 7.45 (m, 2H), 7.43 – 7.37 (m, 1H), 7.27 (s, 1H), 7.21 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 138.5, 135.0, 134.5, 132.6, 132.5, 129.3 , 129.0, 128.4, 127.7, 127.1, 125.5, 124.1, 123.3, 122.2, 121.1. HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{18}H_{14}O_2NS$: 308.0740; found: 308.0740.

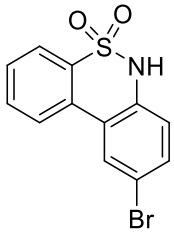


2e

9-fluoro-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2e): According to the general procedure A: **1e** (0.2 mmol, 55.4 mg), $Ru(bpy)_3Cl_2$ (0.002 mmol, 1.5 mg) in DMSO (2.0 mL) afforded **2e** (40.6 mg, 82%) as a white solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 2 h.

IR (film, cm^{-1}): 3166, 2917, 1597, 1567, 1496, 1430, 1171, 866, 770 cm^{-1}. ^1H NMR (400 MHz, d_6-DMSO) δ 11.41 (s, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 8.14 (dd, *J* = 10.2, 2.8 Hz, 1H), 7.97 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.84 (td, *J* = 7.8, 1.3 Hz, 1H), 7.76 – 7.69 (m, 1H), 7.37 (td, *J* = 8.5, 2.8 Hz, 1H), 7.30 – 7.23 (m, 1H). ^{19}F NMR (376 MHz, DMSO) δ -118.07 (s, 1F). ^{13}C NMR (101 MHz, d_6-DMSO) δ 158.6(d, *J* = 240.4 Hz), 134.5, 132.8 (d, *J* = 2.0 Hz), 132.6, 130.9 (d, *J* = 2.0 Hz), 129.2, 126.1, 123.2 (d, *J* = 8.1 Hz), 121.8 (d, *J* = 9.1 Hz), 121.2, 117.5 (d, *J* = 23.2 Hz), 111.8 (d, *J* = 24.2 Hz).

HRMS (DART-Positive) ([M+H]$^+$) Calcd. For $C_{12}H_9O_2NFS$: 250.0333; found: 250.0332.

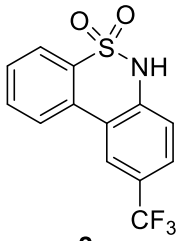


2f

9-bromo-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2f): According to the general procedure A: **1f** (0.2 mmol, 44.6 mg), $Ru(bpy)_3Cl_2$ (0.002 mmol, 1.5 mg) in DMSO (2.0 mL) afforded **2f** (32.9 mg, 82%) as a white solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 2 h.

According to the general procedure B: **3f** (0.2 mmol, 1.0 equiv), $Ru(bpy)_3Cl_2$ (0.002 mmol, 0.01 equiv), *t*-BuONO (0.3 mmol, 1.5 equiv) in DMSO (2.0 mL) afforded **2f** (52.1 mg, 84%) as a white solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 1.5 h.

IR (film, cm^{-1}): 3196, 3088, 1591, 1559, 1478, 1418, 1165, 891, 815, 782 cm^{-1}. ^{1}H NMR (400 MHz, d_6-DMSO) δ 11.62 (s, 1H), 8.43 (d, J = 2.1 Hz, 1H), 8.32 (d, J = 8.0 Hz, 1H), 7.97 (dd, J = 7.7, 0.8 Hz, 1H), 7.86 – 7.79 (m, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.65 (dd, J = 8.6, 2.1 Hz, 1H), 7.18 (d, J = 8.6 Hz, 1H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 135.8, 134.3, 133.0, 132.7, 130.4, 129.2, 127.8, 126.1, 123.4, 121.6, 121.2, 116.0. HRMS (DART-Positive) ([M+H]$^+$) Calcd. For $C_{12}H_9O_2NBrS$: 309.9532; found: 309.9532.



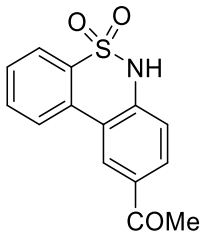
2g

9-(trifluoromethyl)-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2g): According to the general procedure A: **1g** (0.2 mmol, 65.4 mg), $Ru(bpy)_3Cl_2$ (0.002 mmol, 1.5 mg)

in DMSO (2.0 mL) afforded **2g** (52.2 mg, 87%) as a white solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 2 h.

According to the general procedure B: **3g** (0.2 mmol, 1.0 equiv), $Ru(bpy)_3Cl_2$ (0.002 mmol, 0.01 equiv), *t*-BuONO (0.3 mmol, 1.5 equiv) in DMSO (2.0 mL) afforded **2g** (52.2 mg, 87%) as a white solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 1.5 h.

IR (film, cm^{-1}): 3179, 2973, 1622, 1591, 1569, 1505, 1490, 1173, 820, 770, 748 cm^{-1}. ^1H NMR (400 MHz, d_6-DMSO) δ 12.08 (s, 1H), 8.60 (s, 1H), 8.45 (d, *J* = 8.0 Hz, 1H), 8.02 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.92 – 7.82 (m, 2H), 7.77 (t, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -55.47 (s, 3F). ^{13}C NMR (101 MHz, d_6-DMSO) δ 139.8, 134.2, 132.8, 130.4, 129.4, 128.0 (q, *J* = 3.0 Hz), 126.3, 124.2 (q, *J* = 32.4 Hz), 124.1(q, *J* =272.7 Hz), 122.7(q, *J* = 3.8 Hz), 121.24, 121.19, 120.0. HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{13}H_9O_2NF_3S$: 300.0301; found: 300.0300.

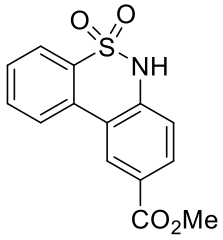


2h

1-(5,5-dioxido-6H-dibenzo[c,e][1,2]thiazin-9-yl)ethan-1-one (2h): According to the general procedure A: **1h** (0.2 mmol, 60.3 mg), $Ru(bpy)_3Cl_2$ (0.002 mmol, 1.5 mg) in DMSO (2.0 mL) afforded **2h** (51.8 mg, 95%) as a red solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 2 h.

IR (film, cm^{-1}): 3180, 3059, 1658, 1596, 1434, 1395, 1172, 830, 766, 772 cm^{-1}. ^1H NMR (400 MHz, d_6-DMSO) δ 11.97 (s, 1H), 8.76 (d, *J* = 1.7 Hz, 1H), 8.43 (d, *J* = 8.0 Hz, 1H), 8.05 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.99 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.91 – 7.85 (m, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 2.69 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 196.7, 140.6, 134.0, 132.8, 132.2, 131.0, 129.9, 129.0, 126.1,

126.0, 121.2, 120.4, 119.2, 26.7. HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{14}H_{12}O_3NS$: 274.0532; found:274.0533.

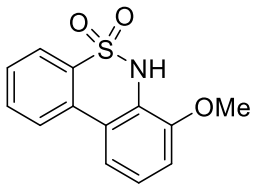


2i

methyl 6H-dibenzo[c,e][1,2]thiazine-9-carboxylate 5,5-dioxide (2i): According to the general procedure A: **1i** (0.2 mmol, 63.5 mg), $Ru(bpy)_3Cl_2$ (0.002 mmol, 1.5 mg) in DMSO (2.0 mL) afforded **2i** (47.2 mg, 82%) as a white solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 2 h.

According to the general procedure B: **3i** (0.2 mmol, 1.0 equiv), $Ru(bpy)_3Cl_2$ (0.002 mmol, 0.01 equiv), *t*-BuONO (0.3 mmol, 1.5 equiv) in DMSO (2.0 mL) afforded **2i** (45.7 mg, 79%) as a white solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 1.5 h.

IR (film, cm^{-1}): 3156, 1697, 1609, 1427, 1389, 1165, 844, 774, 766 cm^{-1}. ^1H NMR (400 MHz, d_6-DMSO) δ 11.98 (s, 1H), 8.73 (d, *J* = 1.7 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.06 (dd, *J* = 8.4, 1.8 Hz, 1H), 8.01 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.91 – 7.83 (m, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 165.6, 140.7, 134.0, 132.8, 131.0, 130.8, 129.1, 126.4, 125.7, 124.7, 121.2, 120.6, 119.4, 52.2. HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{14}H_{12}O_4NS$: 290.0482; found: 290.0482.

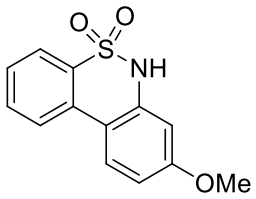


2j

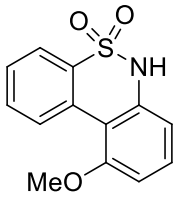
7-methoxy-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2j): According to the general procedure A: **1j** (0.2 mmol, 57.9 mg), $Ru(bpy)_3Cl_2$ (0.002 mmol, 1.5 mg) in DMSO (2.0 mL) afforded **2j** (23.8 mg, 46%) as a white solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 2 h.

According to the general procedure B: **3j** (0.2 mmol, 1.0 equiv), $Ru(bpy)_3Cl_2$ (0.002 mmol, 0.01 equiv), *t*-BuONO (0.3 mmol, 1.5 equiv) in DMSO (2.0 mL) afforded **2j** (30.4 mg, 58%) as a white solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 3 h.

IR (film, cm^{-1}): 3207, 2918, 2848, 1645, 1588, 1562, 1495, 1458, 1368, 1183, 759, 747 cm^{-1}. ^1H NMR (400 MHz, d_6-DMSO) δ 10.72 (s, 1H), 8.21 (d, *J* = 7.9 Hz, 1H), 7.92 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.84 – 7.75 (m, 2H), 7.67 (td, *J* = 7.7, 1.0 Hz, 1H), 7.29 (t, *J* = 8.1 Hz, 1H), 7.18 (dd, *J* = 8.2, 0.9 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 150.2, 134.9, 132.4, 131.9, 128.6, 126.0, 125.6, 124.3, 123.2, 121.2, 116.8, 111.9, 56.0. HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{13}H_{12}O_3NS$: 262.0532; found: 262.0532.



2k



2k'

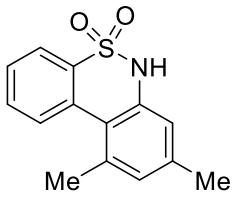
8-methoxy-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2k) and 10-methoxy-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2k'): According to the general procedure A: **1k** (0.2 mmol, 57.9 mg), $Ru(bpy)_3Cl_2$ (0.002 mmol, 1.5 mg) in DMSO (2.0 mL) afforded **2k** (22.3 mg, 43%) and **2k'** (22.8 mg, 44%) as white solids after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 2 h.

According to the general procedure B: **3k** (0.2 mmol, 1.0 equiv), $Ru(bpy)_3Cl_2$ (0.002 mmol, 0.01 equiv), *t*-BuONO (0.3 mmol, 1.5 equiv) in DMSO (2.0 mL) afforded **2k** (12.6 mg, 24%) and **2k'** (16.3 mg, 31%) as white solids after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 3 h.

2k: IR (film, cm^{-1}): 3180, 2973, 2920, 1645, 1594, 1578, 1489, 1449, 1385, 1172, 795, 781, 744 cm^{-1}. ^1H NMR (400 MHz, d_6-DMSO) δ 11.35 (s, 1H), 8.14 (d, *J* = 7.9 Hz, 1H), 8.13(d, *J* = 8.9 Hz, 1H), 7.90 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.81 – 7.73 (m, 1H), 7.62 – 7.55 (m, 1H), 6.90 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.73 (d, *J* = 2.6 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 160.7, 138.0, 133.2, 132.5, 131.9, 127.3, 126.8,

124.8, 121.1, 114.3, 110.7, 103.7, 55.4. HRMS (DART-Positive) ([M+H]$^+$) Calcd. For $C_{13}H_{12}O_3NS$: 262.0532; found: 262.0532.

2k': IR (film, cm^{-1}): 3248, 3004, 2973, 1615, 1591, 1559, 1517, 1452, 1373, 1155, 840, 759, 744 cm^{-1}. ^{1}H NMR (400 MHz, d_6-DMSO) δ 11.31 (s, 1H), 8.60 (dd, *J* = 8.2, 0.6 Hz, 1H), 7.92 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.77 – 7.70 (m, 1H), 7.61 (td, *J* = 7.7, 1.1 Hz, 1H), 7.41 (t, *J* = 8.2 Hz, 1H), 6.99 (dd, *J* = 8.4, 0.7 Hz, 1H), 6.85 (dd, *J* = 8.0, 0.9 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 157.6, 137.8, 134.8, 131.5, 130.6, 130.4, 129.1, 127.7, 120.6, 112.0, 111.1, 107.1, 56.0. HRMS (DART-Positive) ([M+H]$^+$) Calcd. For $C_{13}H_{12}O_3NS$: 262.0532; found: 262.0532.

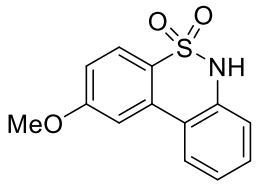


2l

8,10-dimethyl-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2l): According to the general procedure A: **1l** (0.2 mmol, 57.5 mg), $Ru(bpy)_3Cl_2$ (0.002 mmol, 1.5 mg) in DMSO (2.0 mL) afforded **2l** (47.4 mg, 86%) as a white solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 2 h.

According to the general procedure B: **3l** (0.2 mmol, 1.0 equiv), $Ru(bpy)_3Cl_2$ (0.002 mmol, 0.01 equiv), *t*-BuONO (0.3 mmol, 1.5 equiv) in DMSO (2.0 mL) afforded **2l** (50.4 mg, 91%) as a white solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 1.5 h.

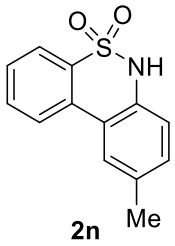
IR (film, cm^{-1}): 3194, 1615, 1594, 1578, 1463, 1366, 1173, 880, 775, 747 cm^{-1}. ^{1}H NMR (400 MHz, d_6-DMSO) δ 11.12 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.94 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.74 (td, *J* = 7.8, 1.4 Hz, 1H), 7.62 (td, *J* = 7.7, 0.9 Hz, 1H), 7.01 (s, 1H), 6.91 (s, 1H), 2.65 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 139.0, 137.0, 136.0, 139.9, 131.9, 131.3, 129.1, 128.5, 127.4, 121.0, 120.0, 117.7, 22.6, 20.7. HRMS (DART-Positive) ([M+H]$^+$) Calcd. For $C_{14}H_{14}O_2NS$: 260.0740; found: 260.0741.



2m

2-methoxy-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2m): According to the general procedure A: **1m** (0.2 mmol, 57.9 mg), $Ru(bpy)_3Cl_2$ (0.002 mmol, 1.5 mg) in DMSO (2.0 mL) afforded **2m** (52.2 mg, 86%) as a red solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 2 h.

IR (film, cm^{-1}): 3234, 3031, 1645, 1598, 1559, 1485, 1394, 1169, 874, 813, 766 cm^{-1}. ^1H NMR (400 MHz, d_6-DMSO) δ 11.28 (s, 1H), 8.25 (d, J = 7.1 Hz, 1H), 7.87 (d, J = 8.7 Hz, 1H), 7.69 (d, J = 2.3 Hz, 1H), 7.51 – 7.43 (m, 1H), 7.32 – 7.26 (m, 1H), 7.24 – 7.18 (m, 2H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 162.1, 136.9, 133.8, 130.4, 127.2, 125.7, 123.6, 123.3, 121.2, 119.4, 114.8, 109.8, 55.9. HRMS (DART-Positive) ($[M+H]^+$) Calcd. For $C_{13}H_{12}O_3NS$: 262.0532; found: 262.0533.

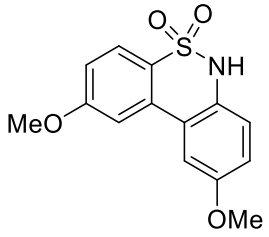


2n

9-methyl-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2n): According to the general procedure B: **1n** (0.2 mmol, 52.5 mg), $Ru(bpy)_3Cl_2$ (0.002 mmol, 1.5 mg) in DMSO (2.0 mL) afforded **2n** (40.9 mg, 83%) as a yellow solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 2 h.

IR (film, cm^{-1}): 3161, 1595, 1564, 1484, 1419, 1387, 1157, 808, 769, 763 cm^{-1}. ^1H NMR (400 MHz, d_6-DMSO) δ 11.20 (s, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.02 (s, 1H), 7.92 (dd, J = 7.8, 1.1 Hz, 1H), 7.79 (td, J = 8.0, 1.3 Hz, 1H), 7.65 (td, J = 7.8, 0.9 Hz, 1H), 7.28 (dd, J = 8.1, 1.3 Hz, 1H), 7.11 (d, J = 8.1 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 134.5, 134.1, 133.2, 132.4, 131.8, 131.1, 128.4, 125.5, 125.4,

121.4, 121.1, 119.7, 20.6. HRMS (DART-Positive) ([M+H]$^+$) Calcd. For $C_{13}H_{12}O_2NS$: 246.0583; found: 246.0584.

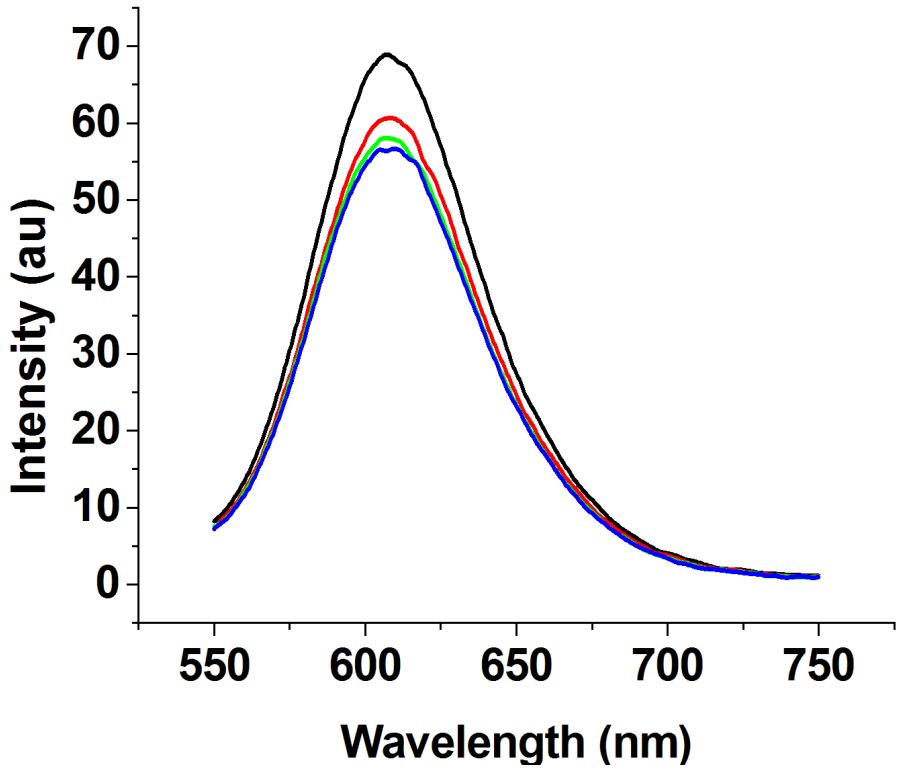


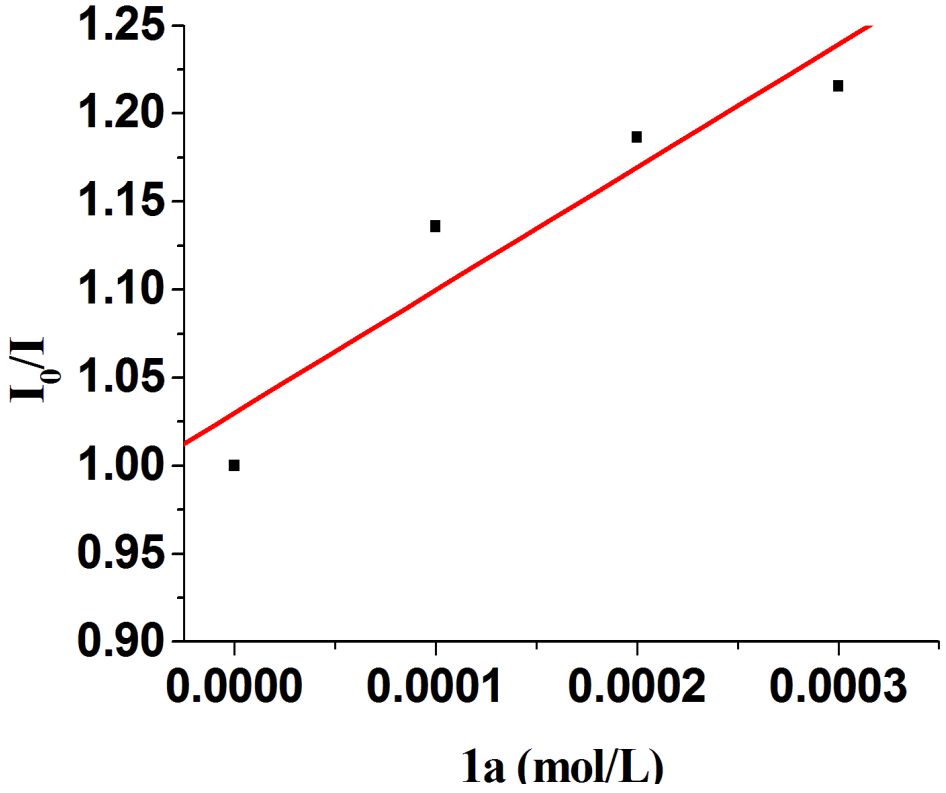
2o

2,9-dimethoxy-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2o): According to the general procedure B: **1o** (0.2 mmol, 61.6 mg), $Ru(bpy)_3Cl_2$ (0.002 mmol, 1.5 mg) in DMSO (2.0 mL) afforded **2o** (36.8 mg, 63%) as a yellow solid after purification on silica gel (Petroleum ether: EtOAc = 7:1). Reaction time: 1h. IR (film, cm^{-1}): 3192, 1602, 1564, 1503, 1487, 1420, 1386, 1129, 808, 656 cm^{-1}. ^{1}H NMR (400 MHz, d_6-DMSO) δ 10.85 (s, 1H), 7.84 (d, J = 8.7 Hz, 1H), 7.71 (dd, J = 6.1, 2.5 Hz, 2H), 7.21 (dd, J = 8.7, 2.4 Hz, 1H), 7.15 (d, J = 8.8 Hz, 1H), 7.09 (dd, J = 8.8, 2.7 Hz, 1H), 3.95 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 162.1, 156.0, 133.8, 130.1, 127.6, 123.3, 123.0, 121.6, 117.0, 114.6, 110.4, 110.0, 55.9, 55.7. HRMS (DART-Positive) ([M+H]$^+$) Calcd. For $C_{14}H_{14}O_4NS$: 292.0638; found: 292.0637.

6. Luminescence quenching by compound 1a

A Hitachi F-7000 fluoresence spectrometer was used to record the emission intensities. All the solutions were excited at 452 nm and the emission intensity at 607 nm was observed. DMSO was degassed with a stream of Ar for 30 min. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of $Ru(bpy)_3Cl_2$ in DMSO was collected. Then, appropriate amount of quencher **1a** was added to the measured solution in a quartz cuvette and the emission spectrum of the sample was collected. I_0 and I represent the intensities of the emission in the absence and presence of the quencher at 607 nm.



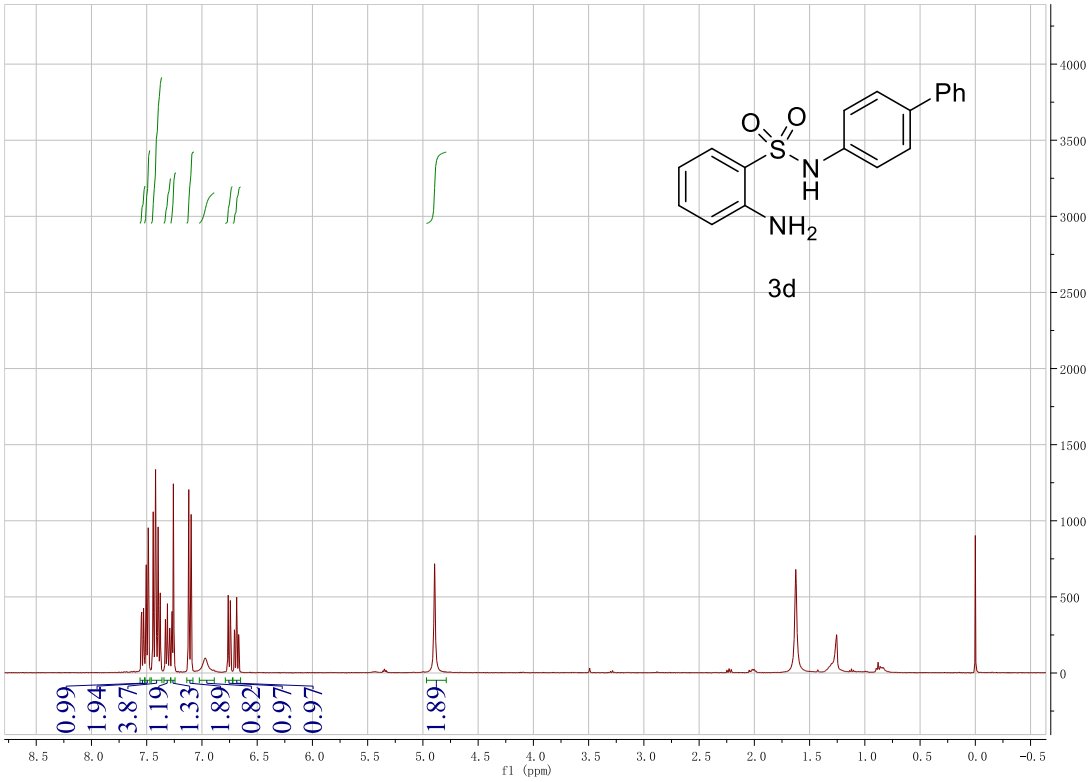


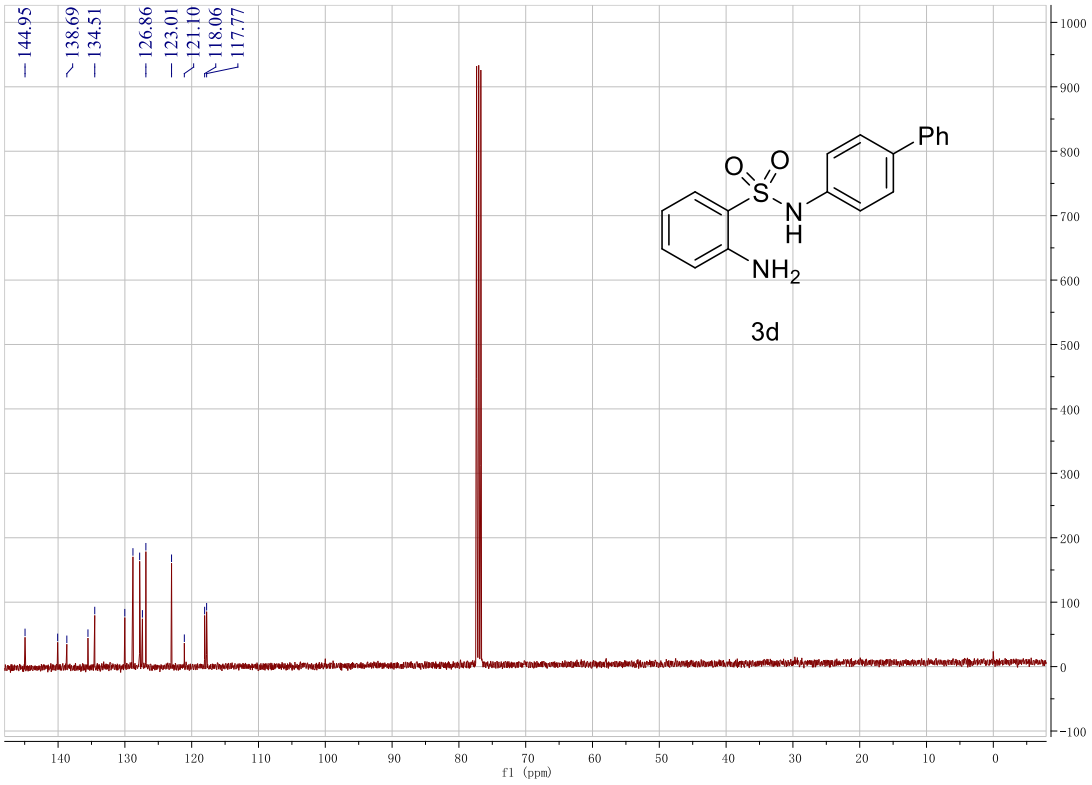
Y = A + B * X

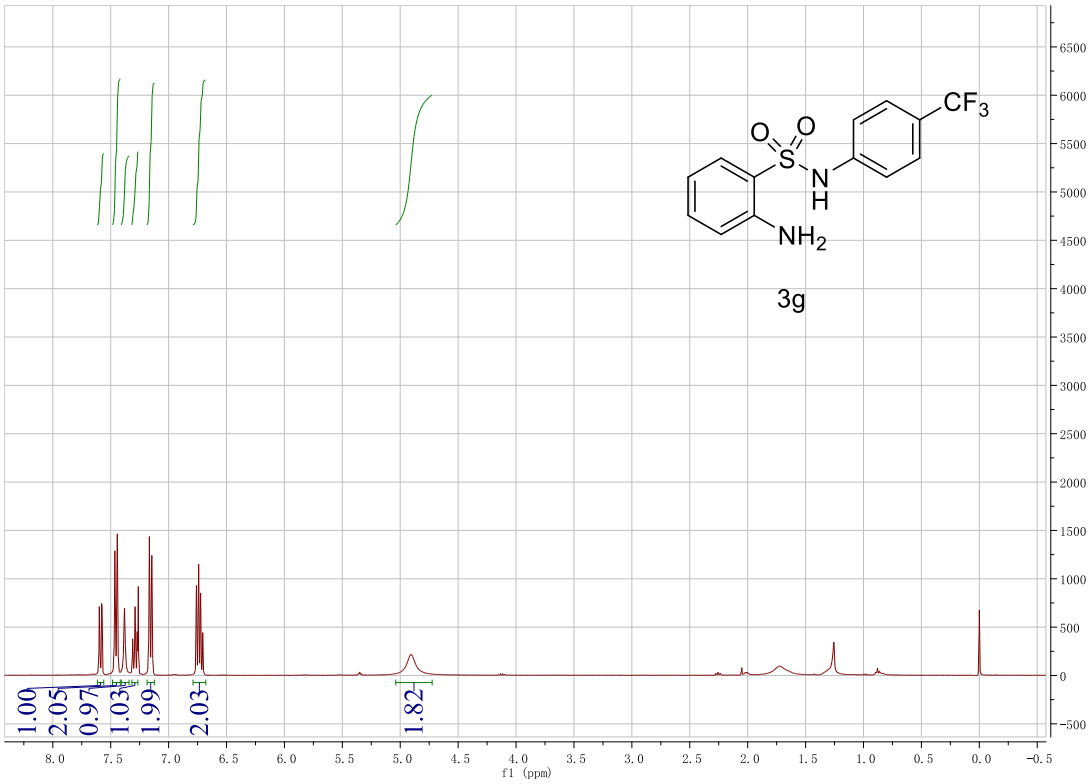
Parameter	Value	Error
A	1.02988	0.03268
B	698.06685	174.66321

R	SD	N	P
0.94272	0.03906	4	0.05728

7. NMR spectra for all compounds.



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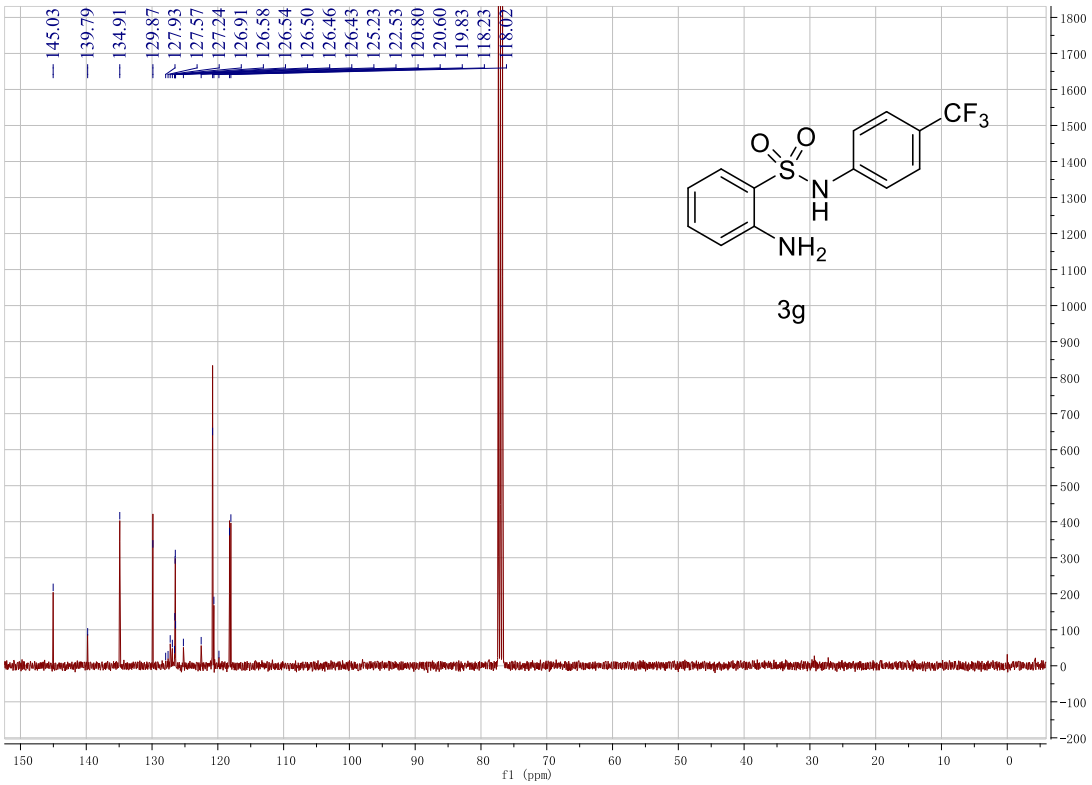
0.97
1.03
1.99
2.03
1.82
f1 (ppm)
3g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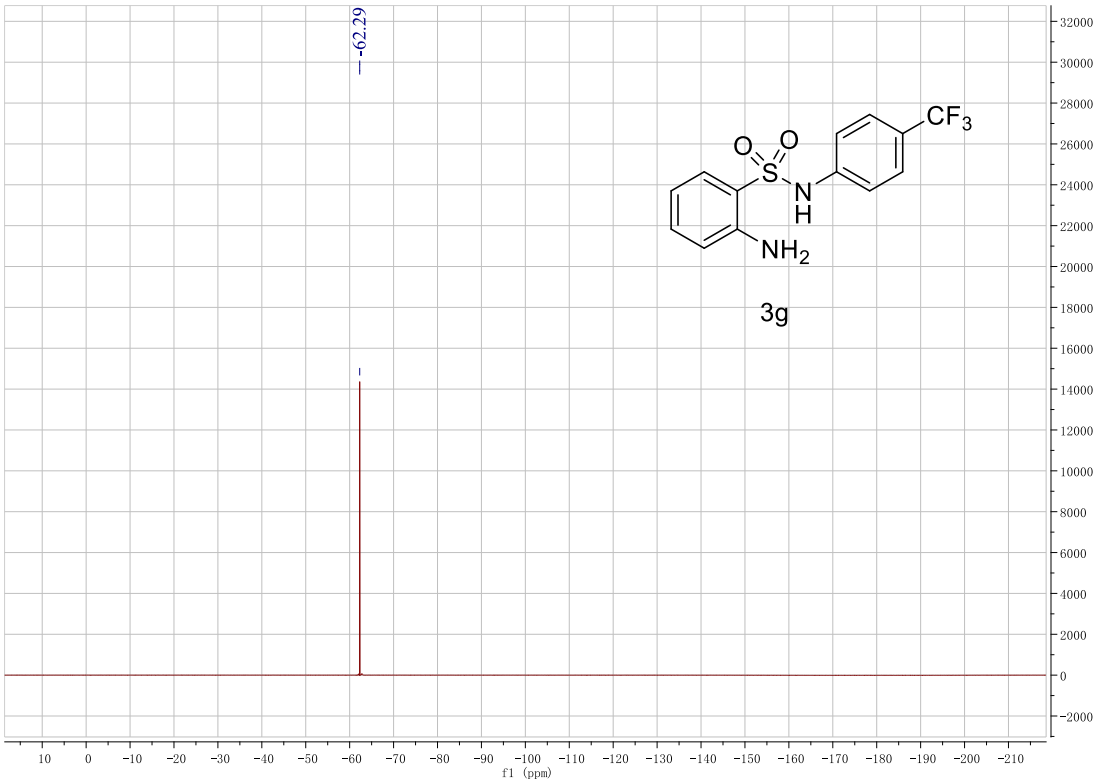
134.91
129.87
127.93
127.57
127.24
126.91
126.58
126.54
126.50
126.46
126.43
125.23
122.53
120.80
120.60
119.83
118.23
118.02
f1 (ppm)
3g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CF3
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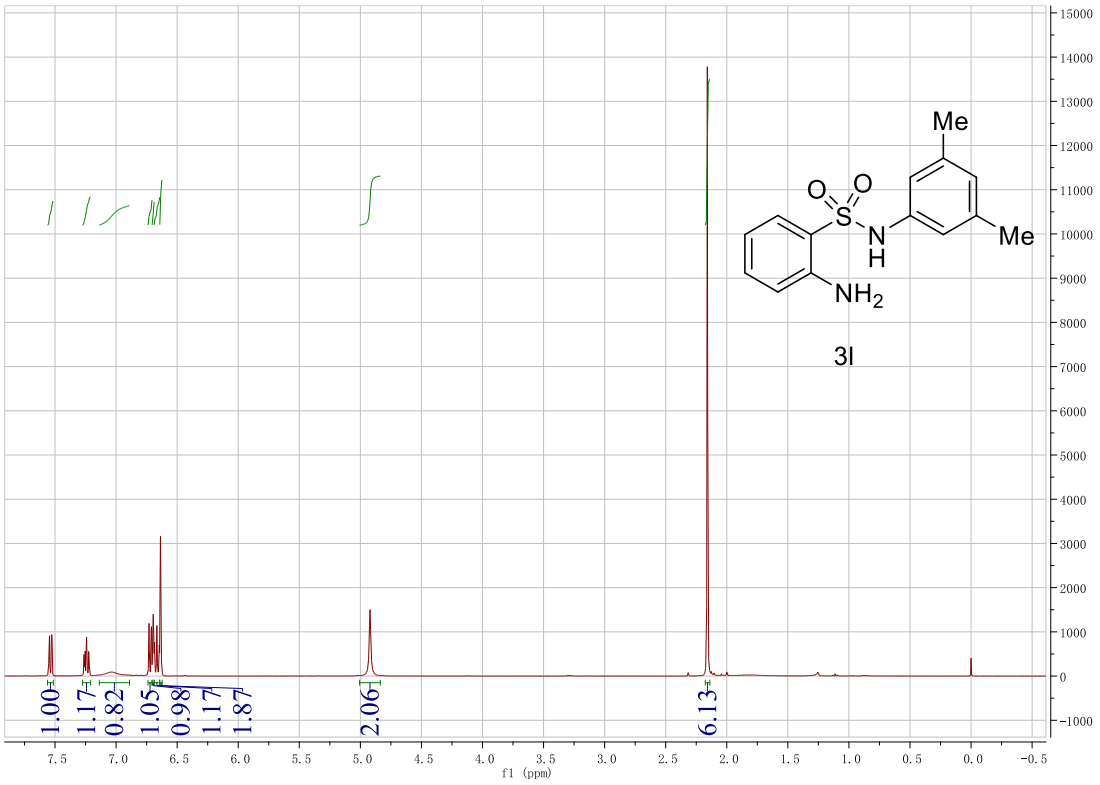
O
S
N
H
NH2
3g
f1 (ppm)


Me
Me
O
O
S
N
H
NH2
3l
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1.17
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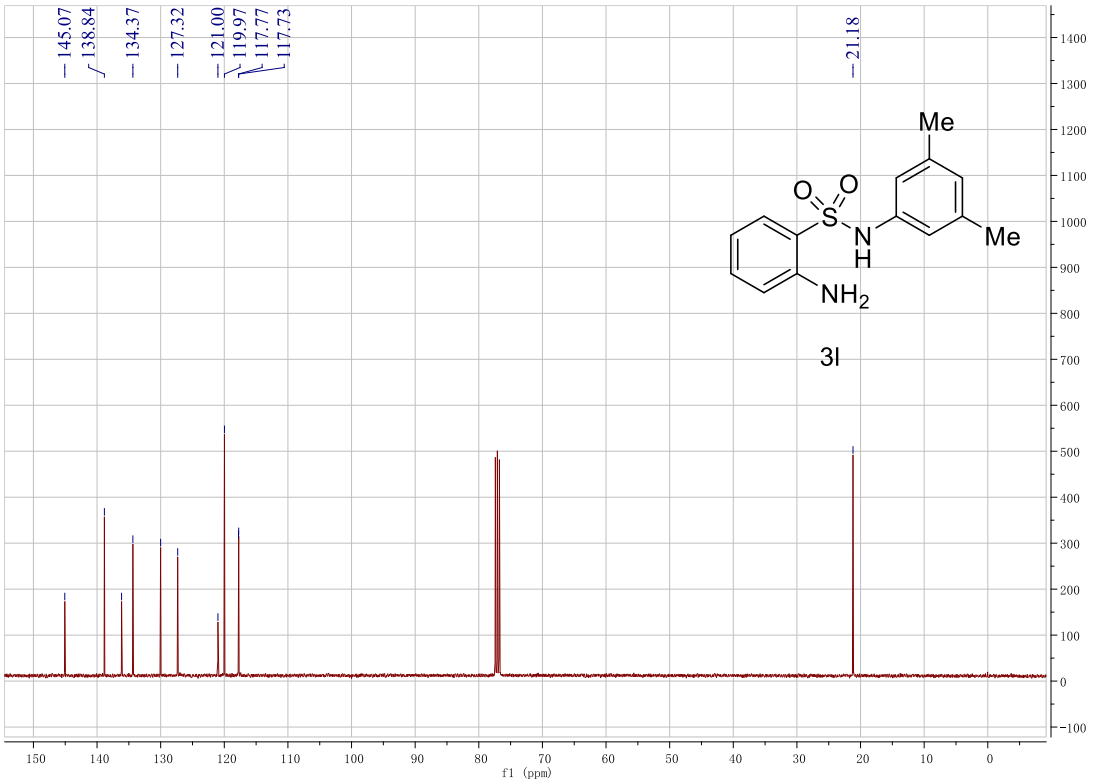
1.05
0.98
1.17
1.87
2.06
6.13
f1 (ppm)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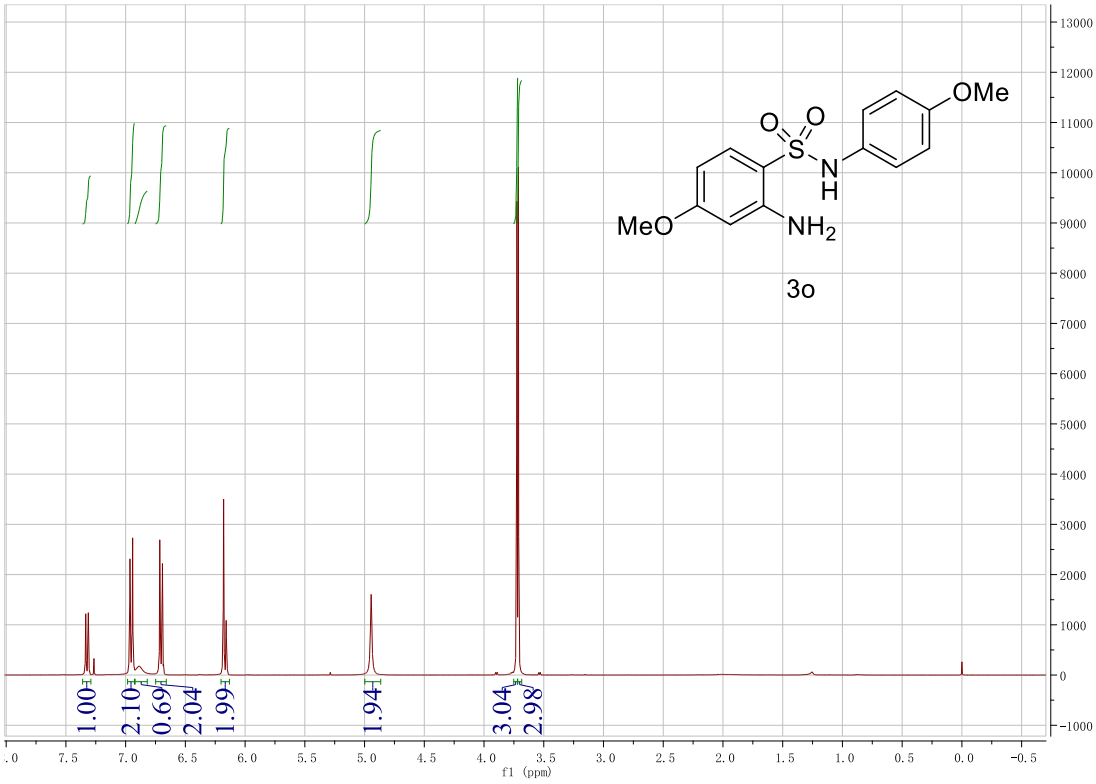
H
NH2
3l
f1 (ppm)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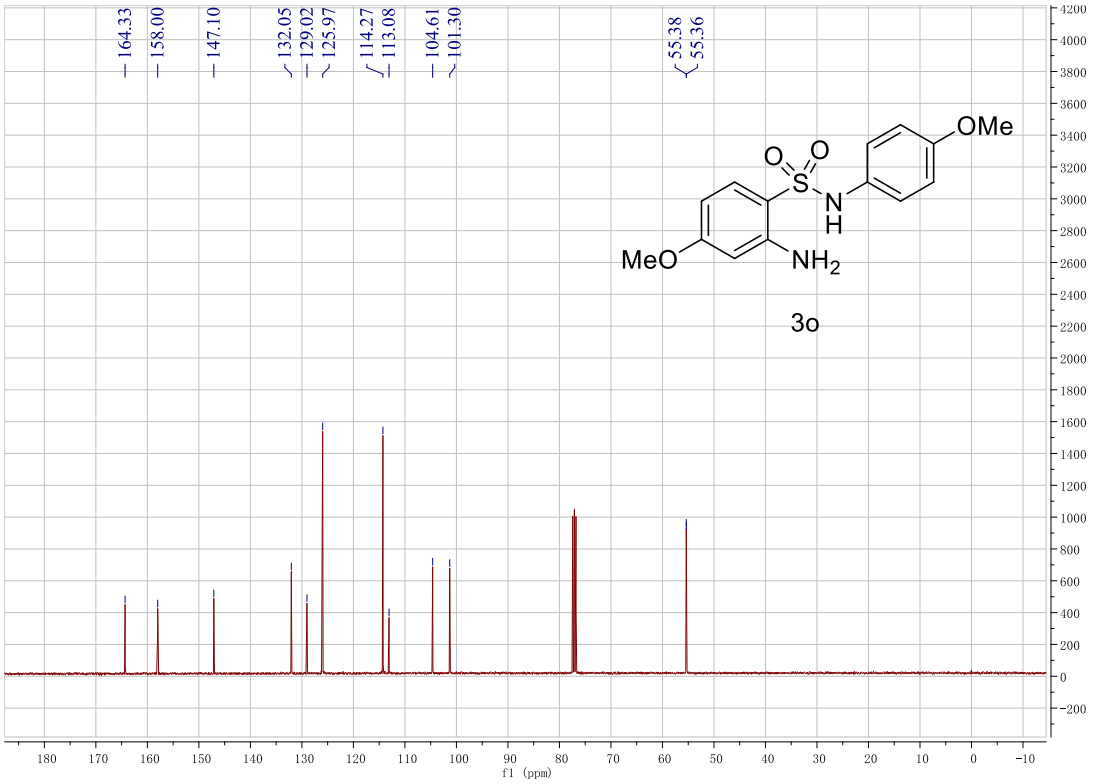
f1 (ppm)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132.05
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125.97
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113.08
104.61
101.30
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55.36
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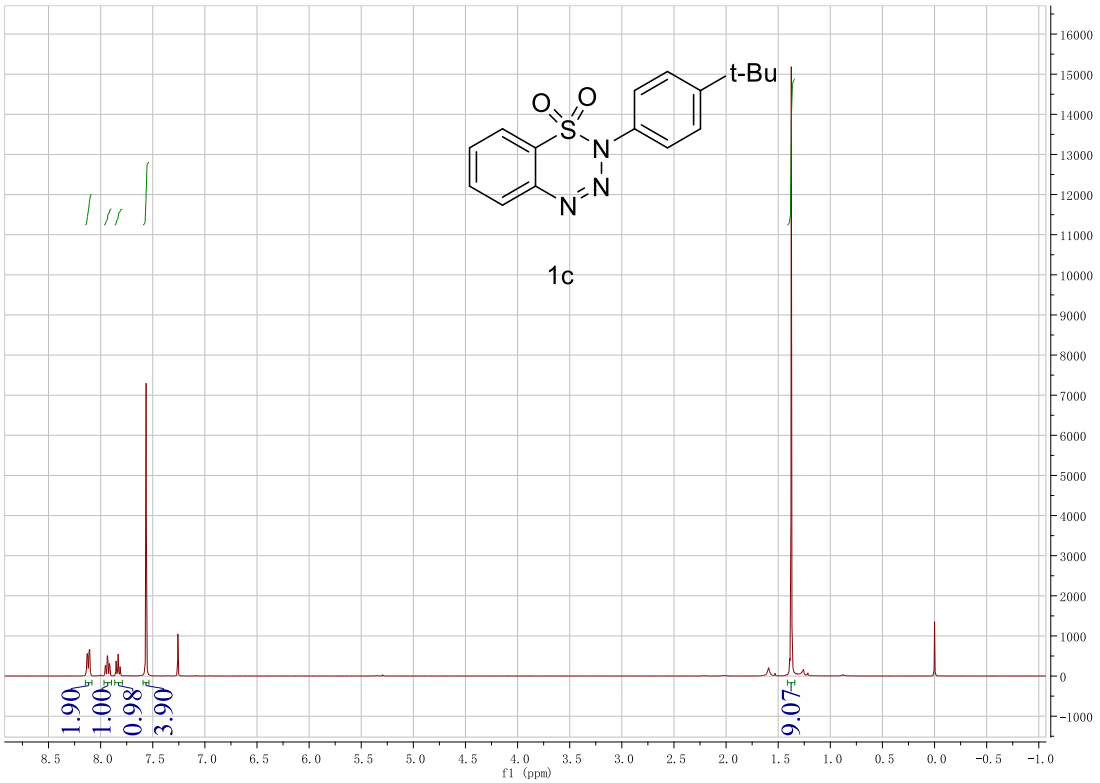
MeO
NH2
3o
f1 (ppm)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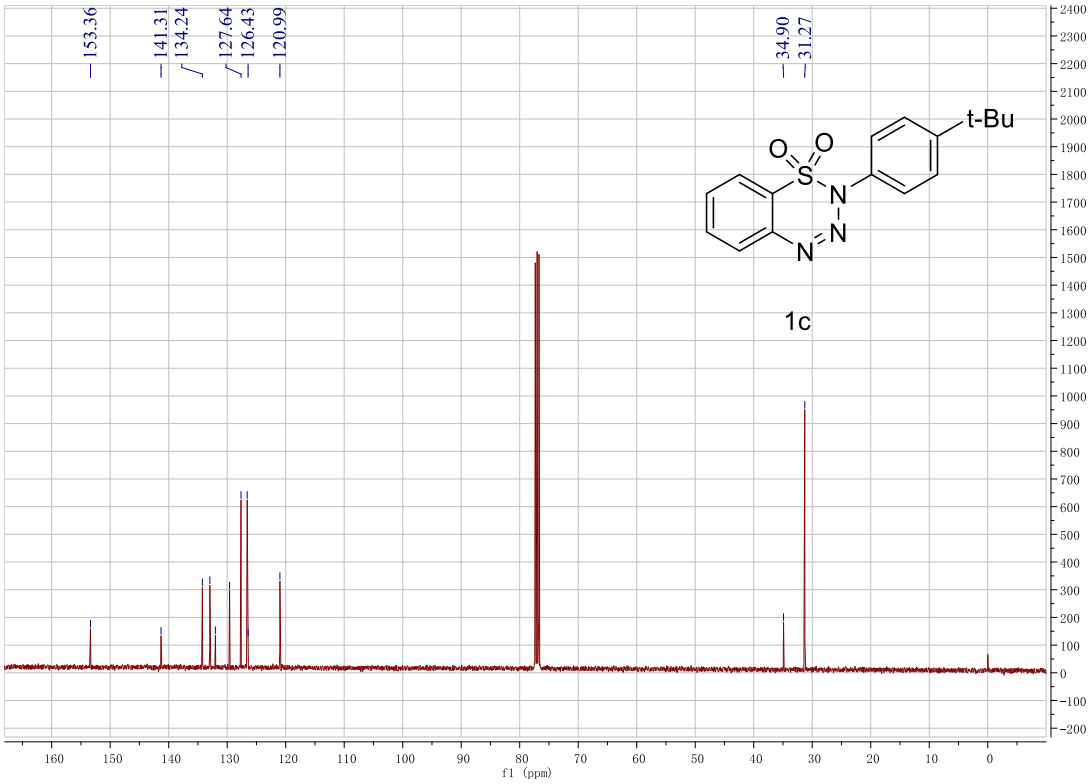
f1 (ppm)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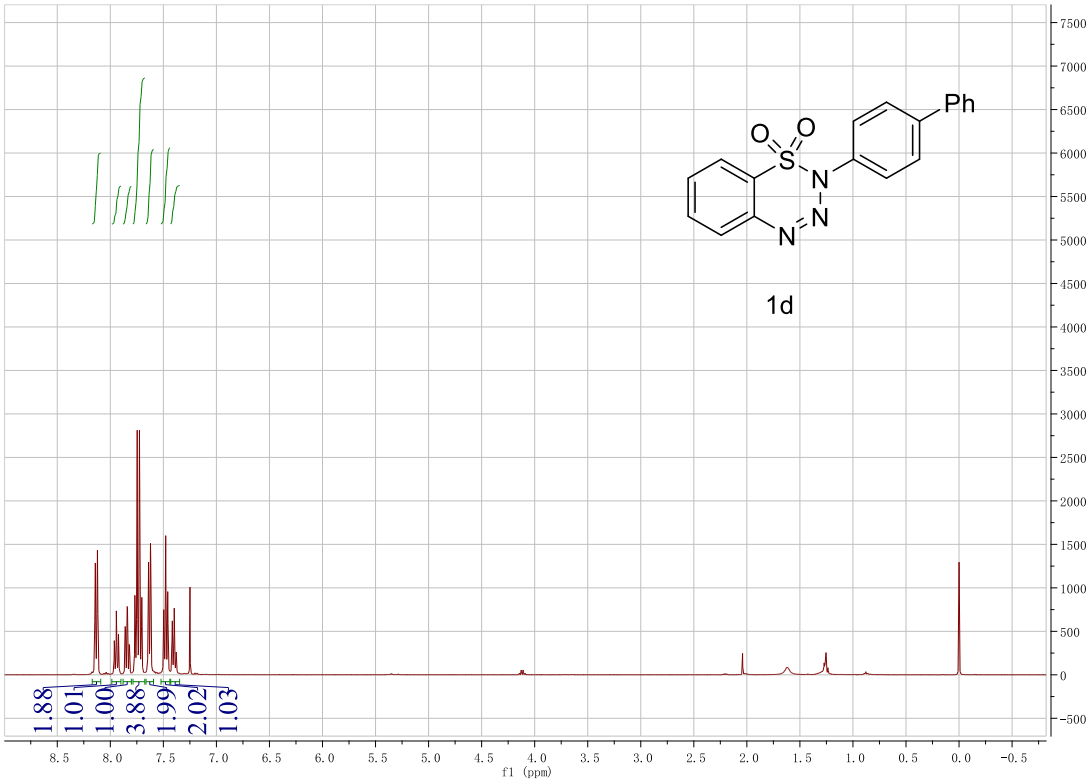
34.90
31.27
t-Bu
1c
f1 (ppm)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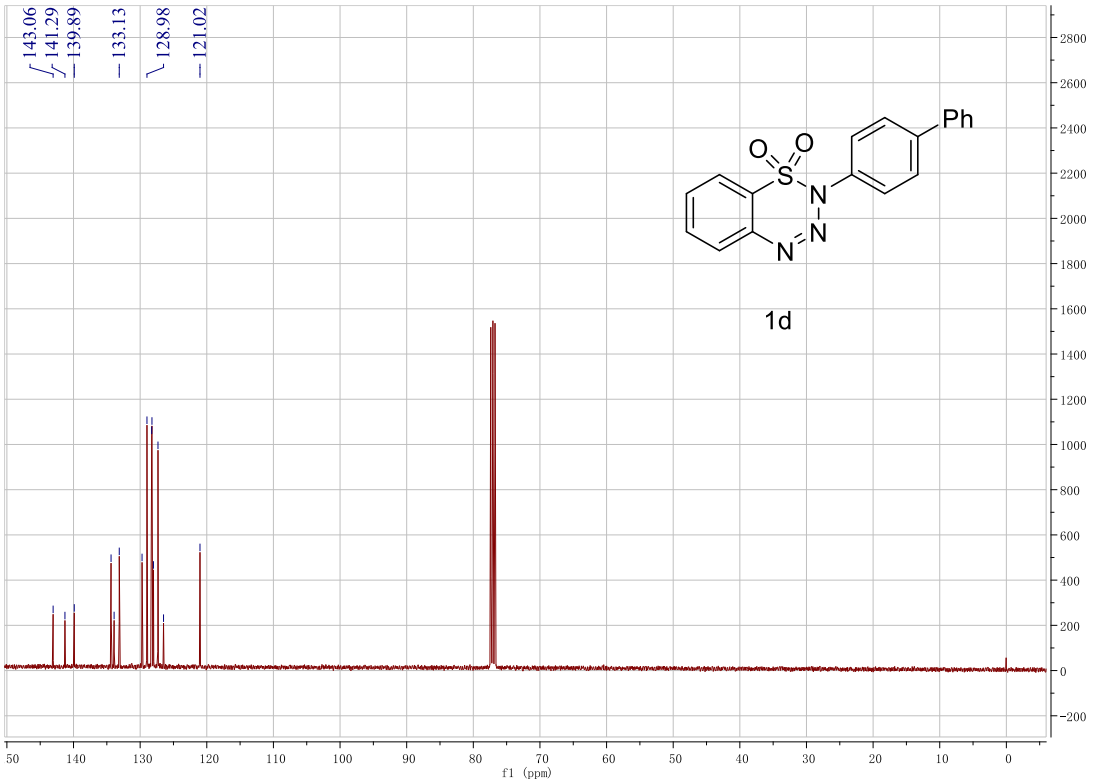
1.03
f1 (ppm)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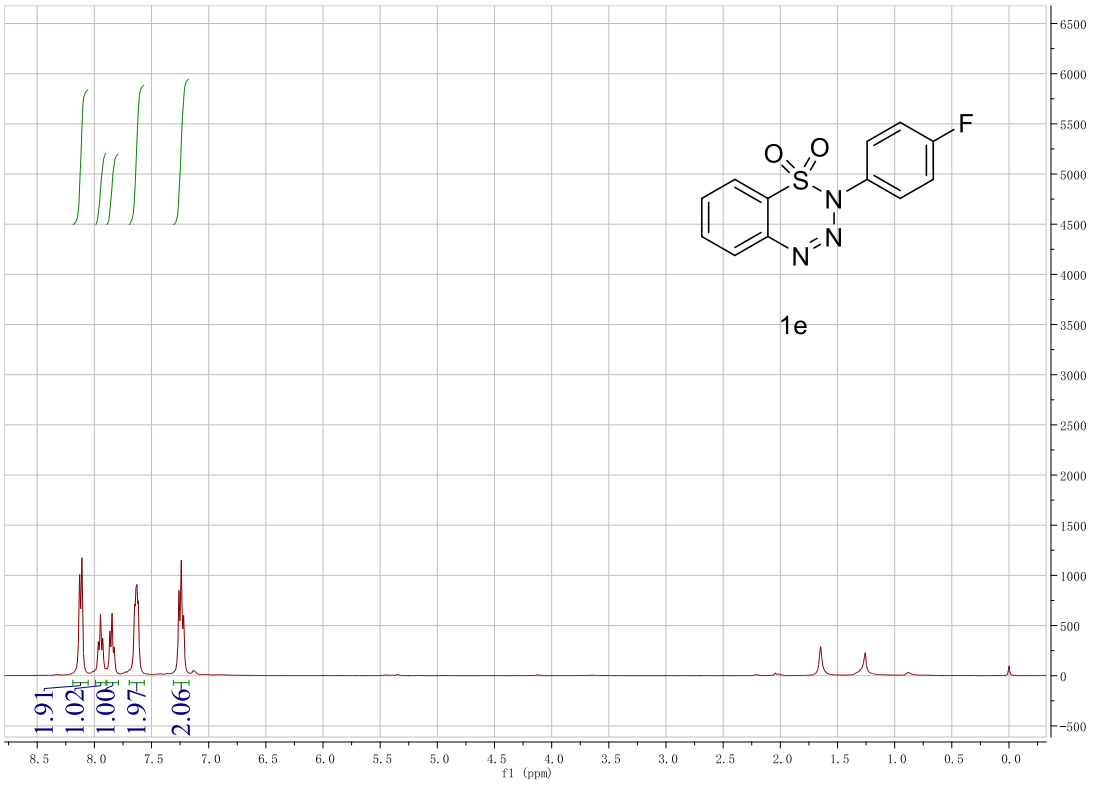
N
N
1d
f1 (ppm)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S
N
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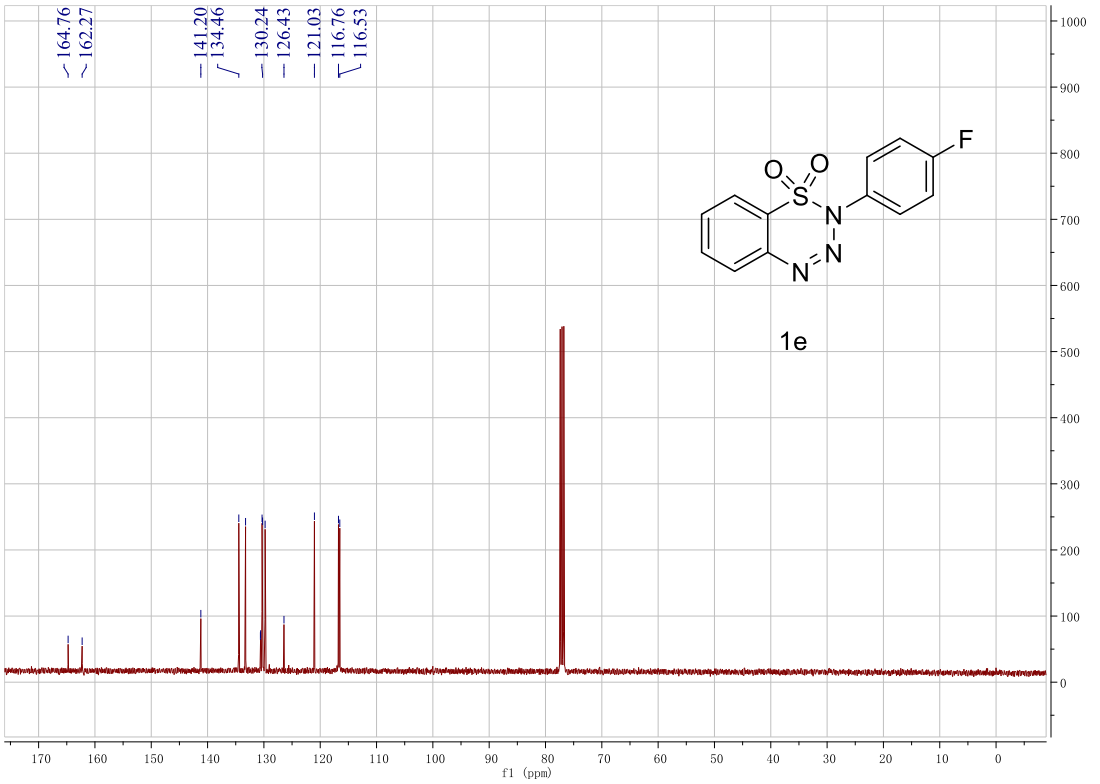
1.00
1.97
2.06
f1 (ppm)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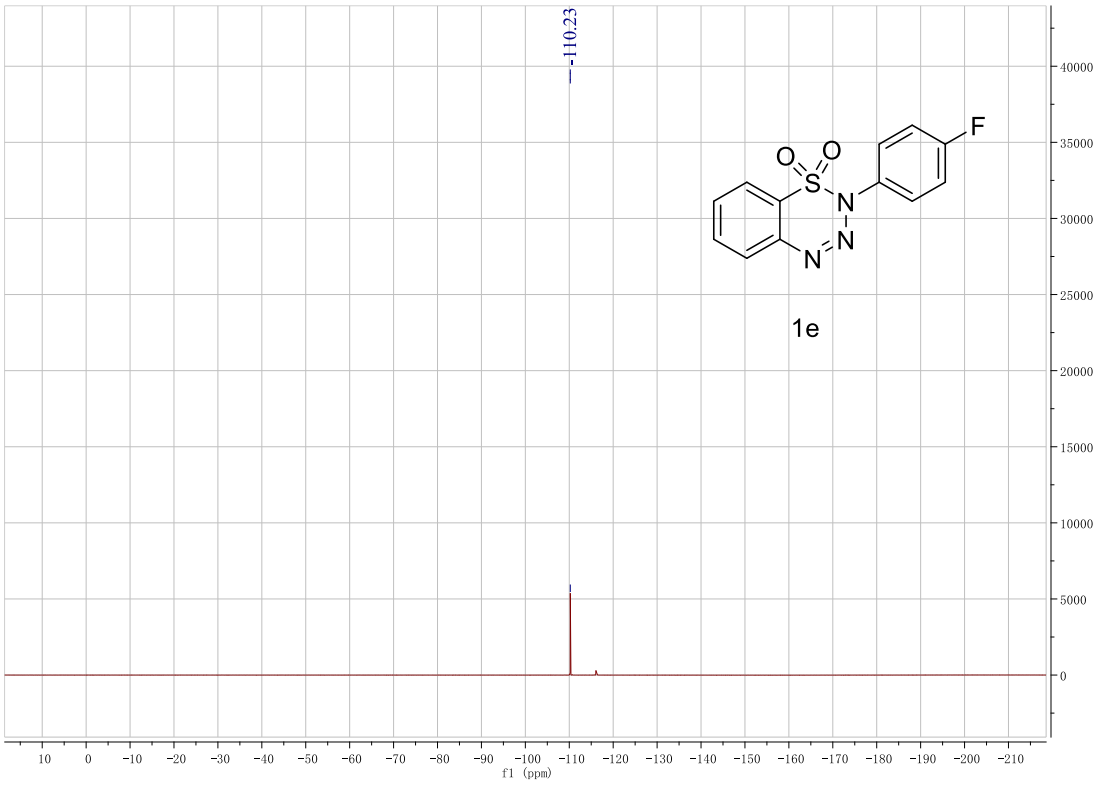
1e
f1 (ppm)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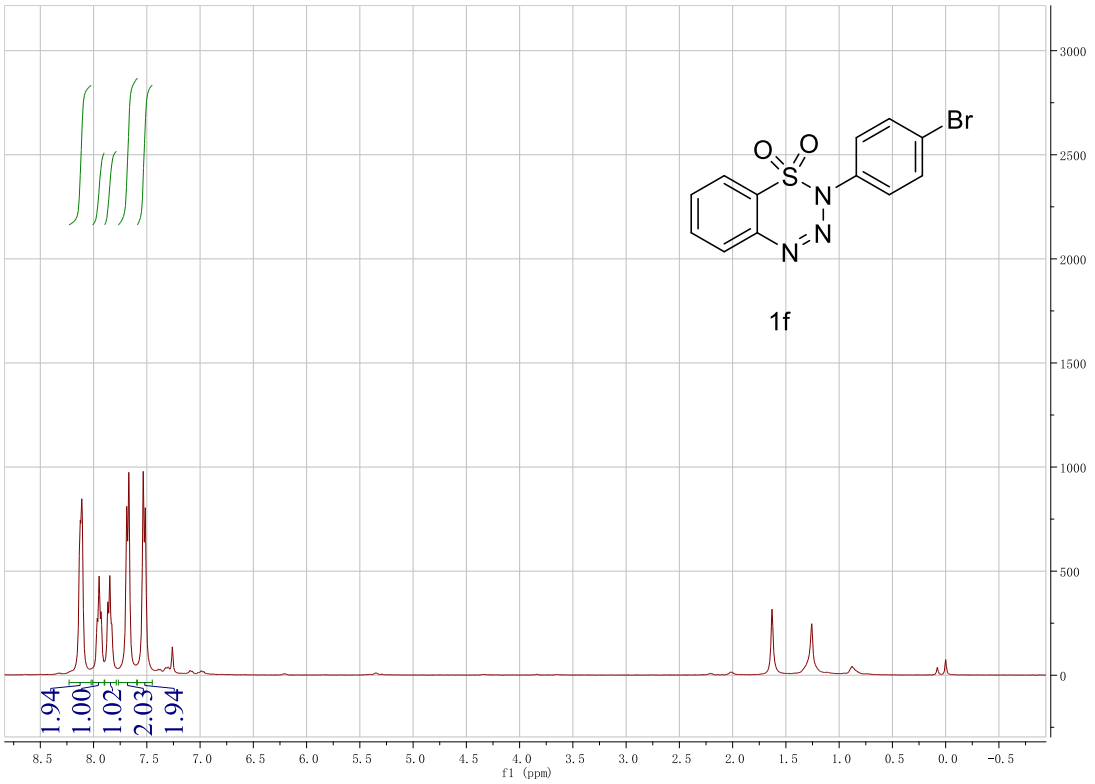
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1.94
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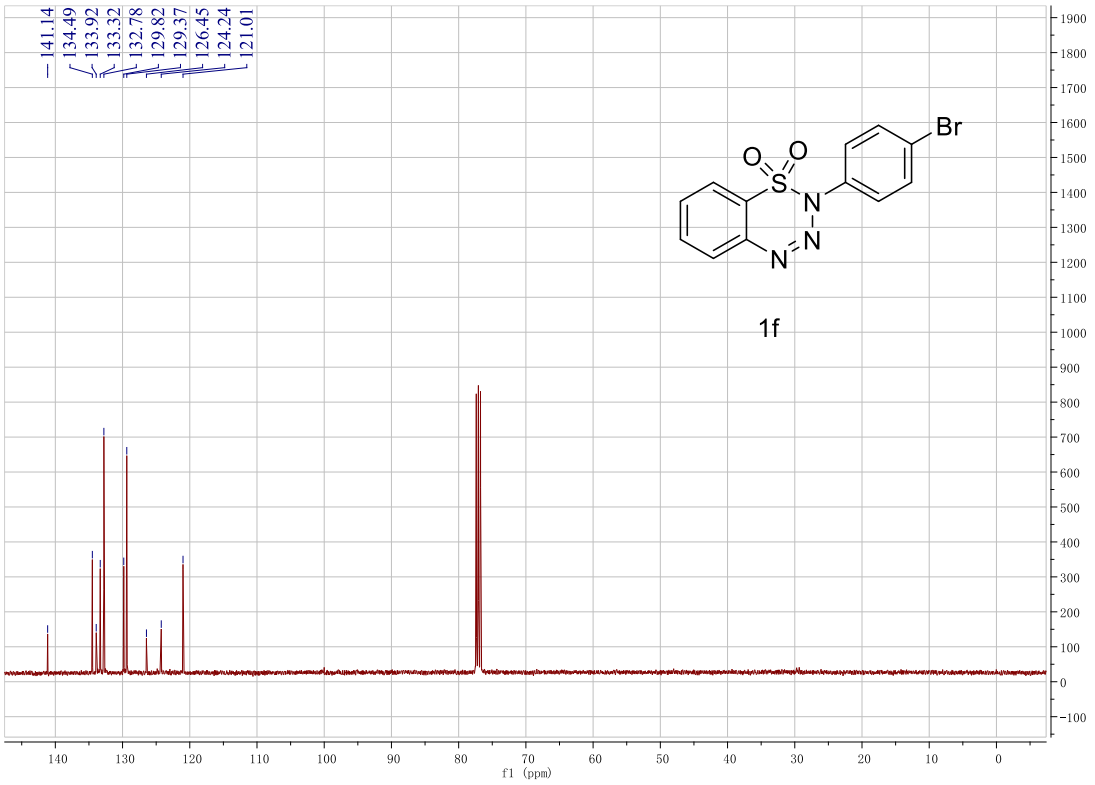
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O
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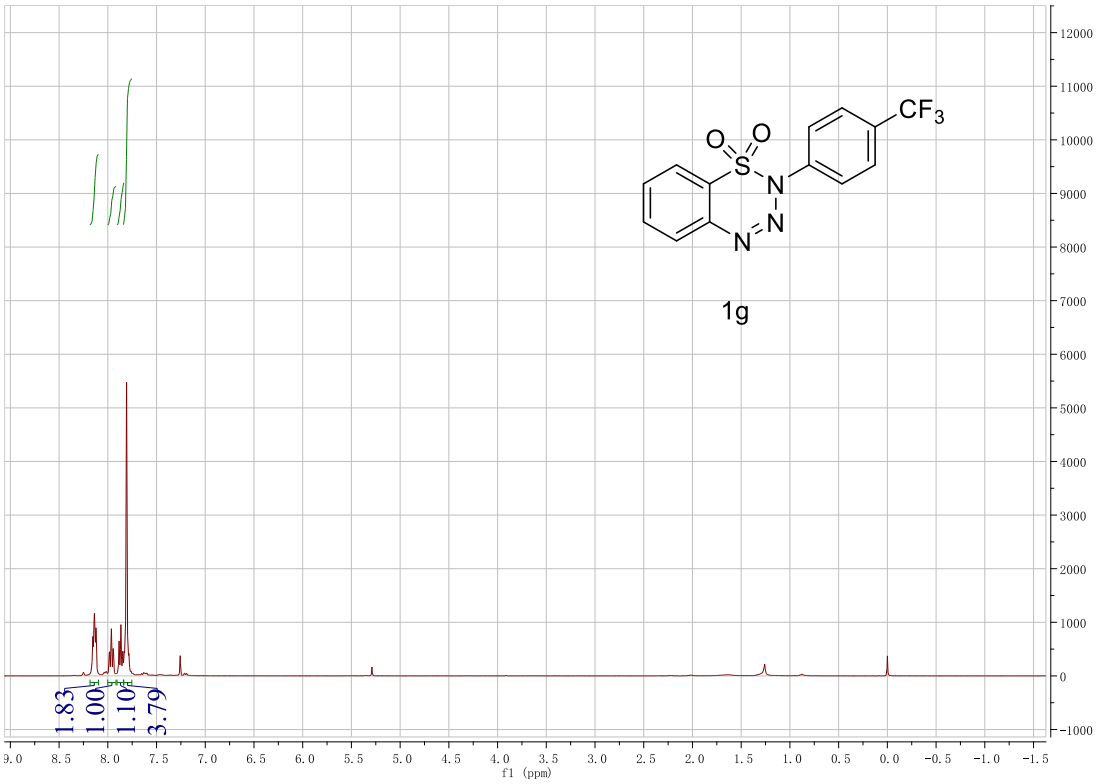
N
N
1f
f1 (ppm)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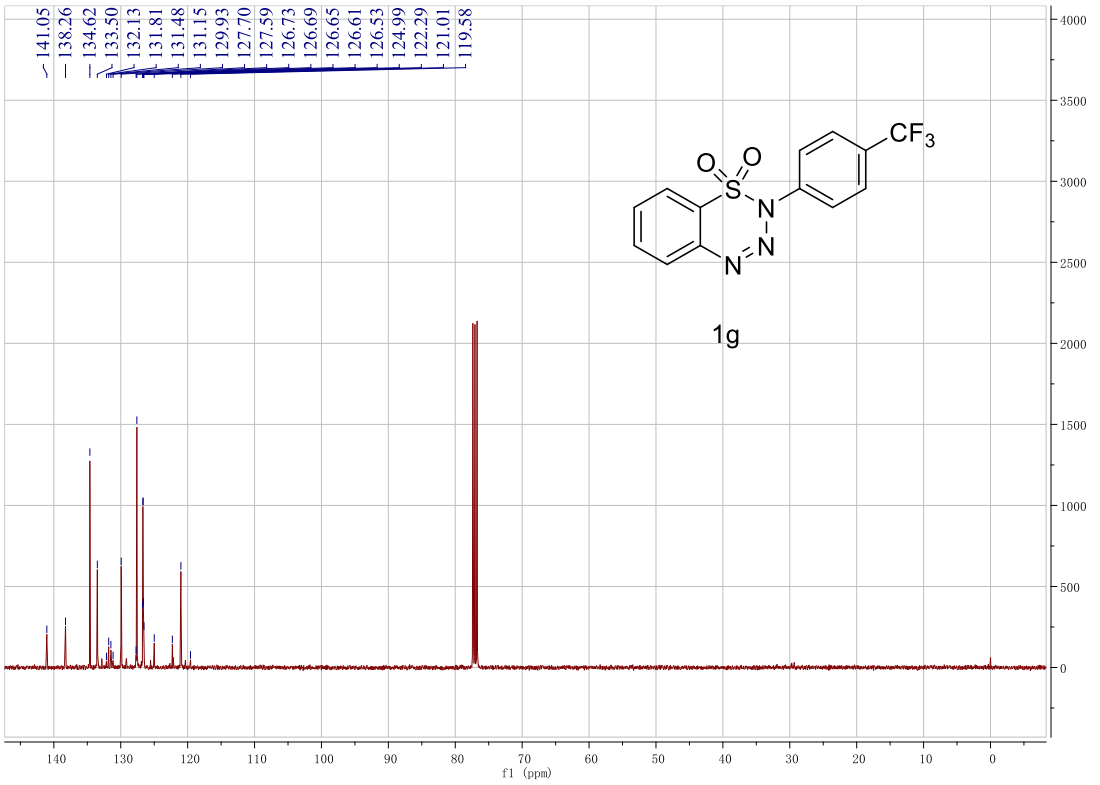
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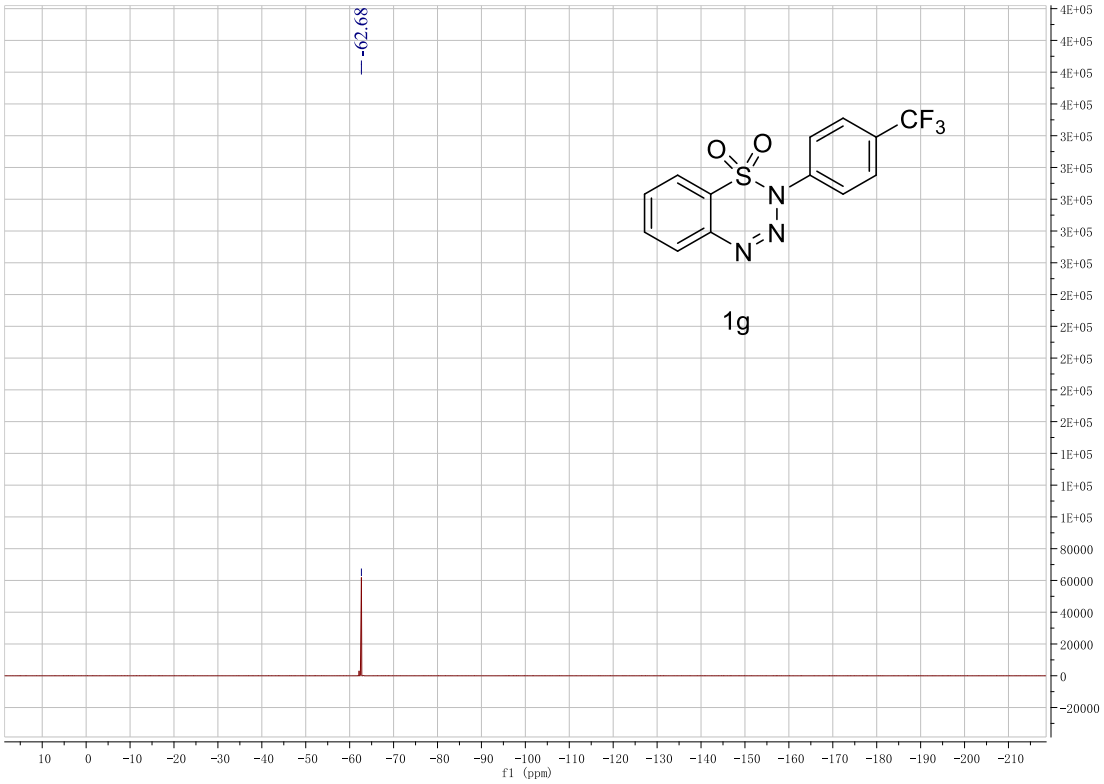
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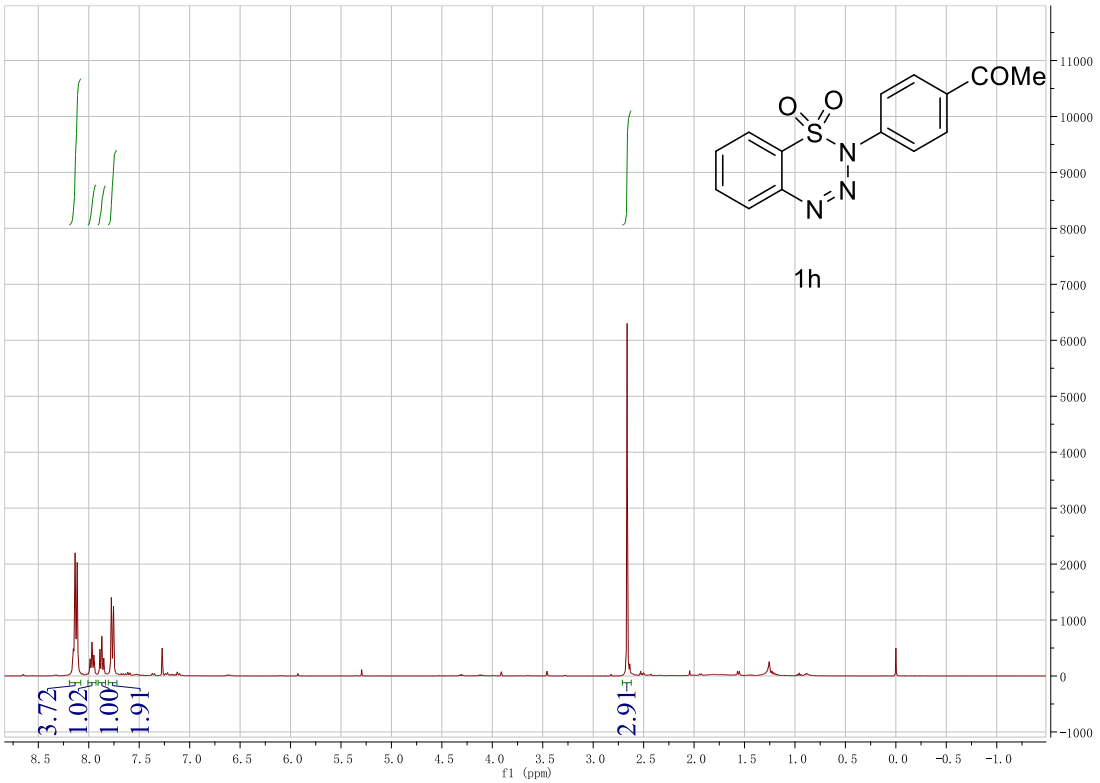
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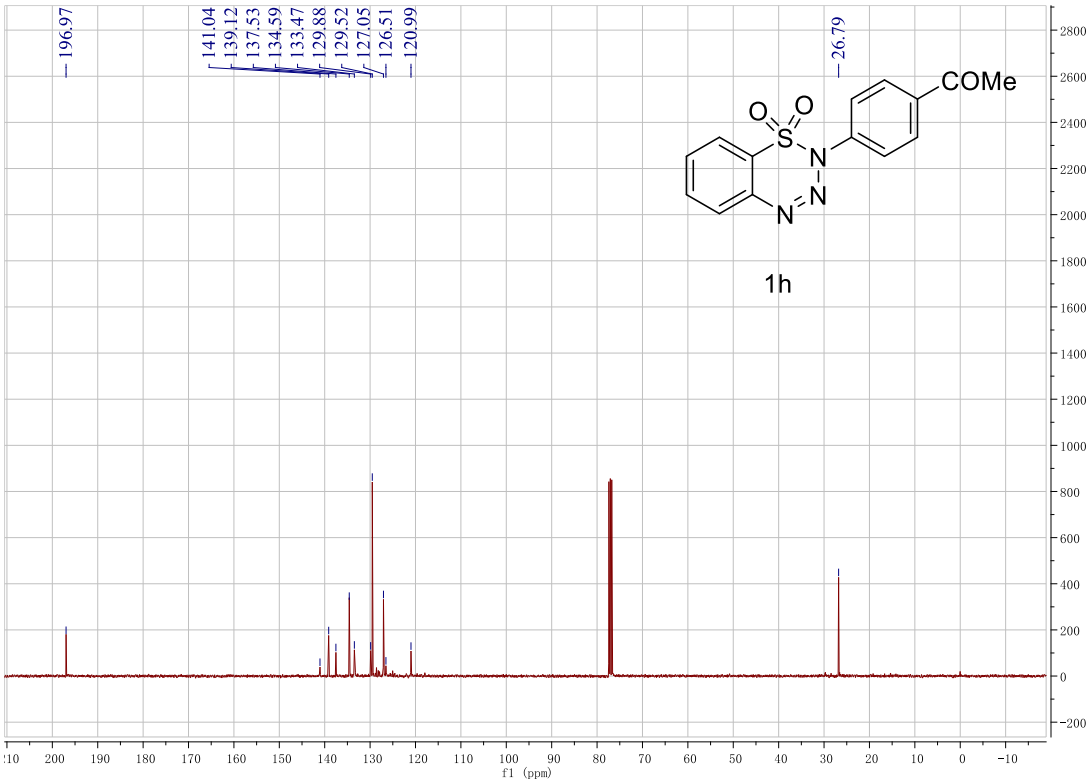
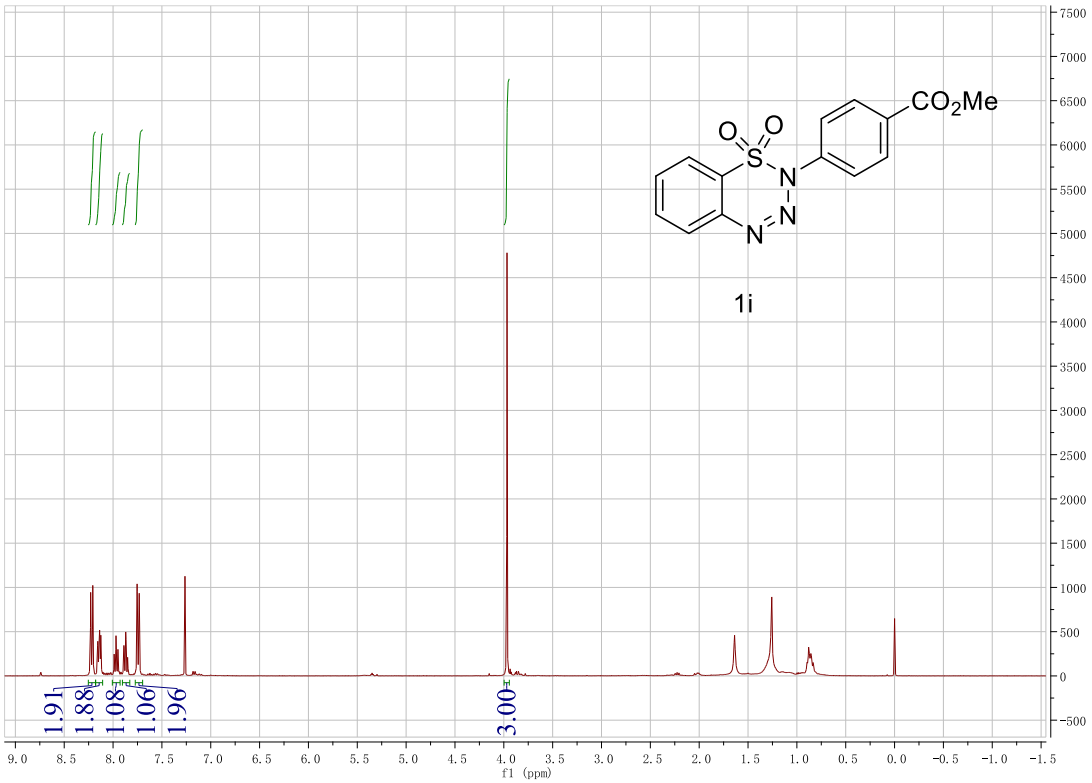
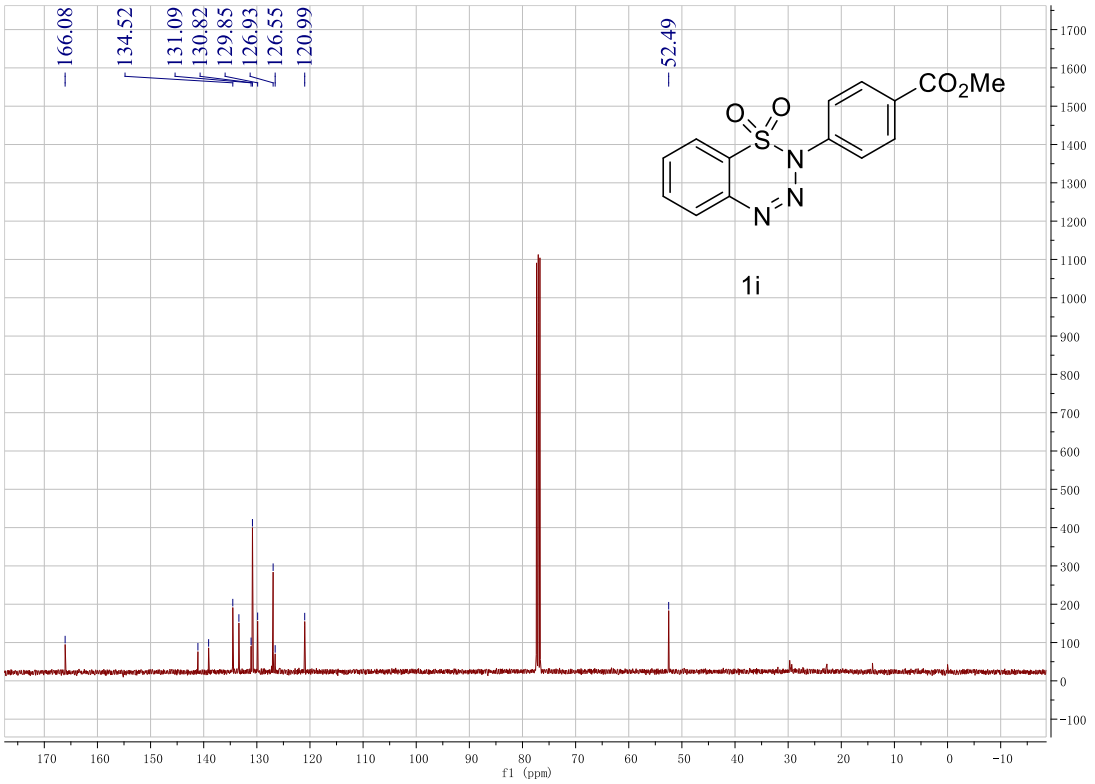
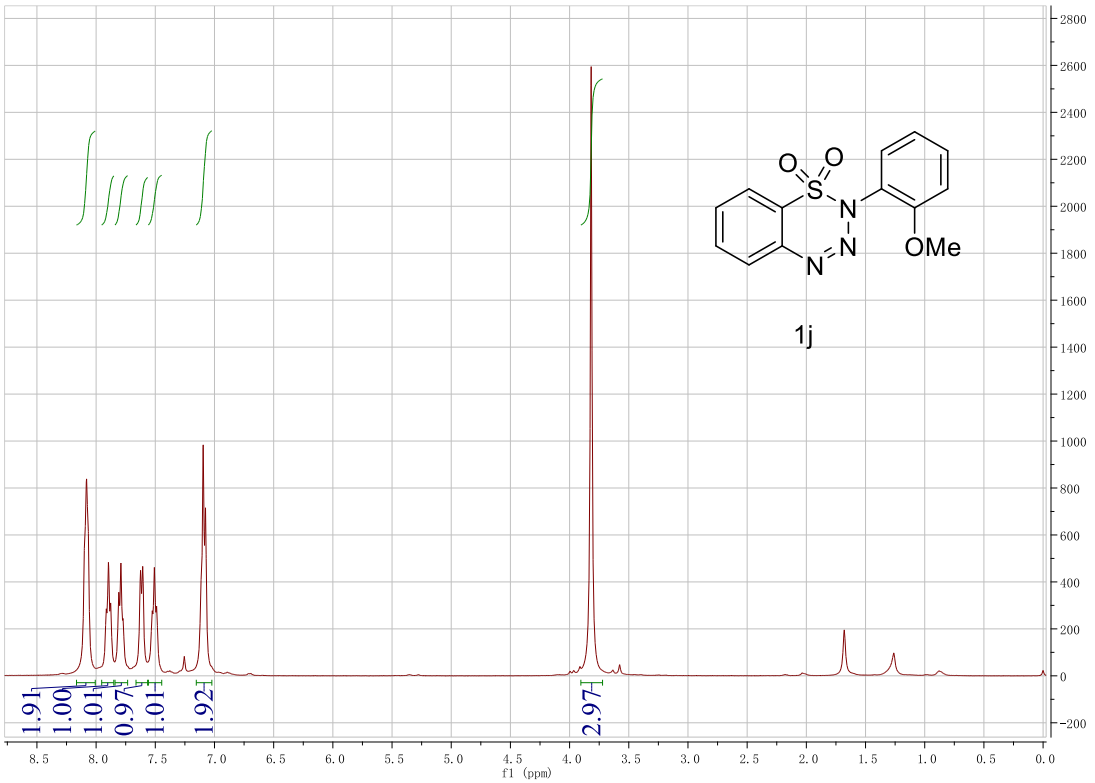
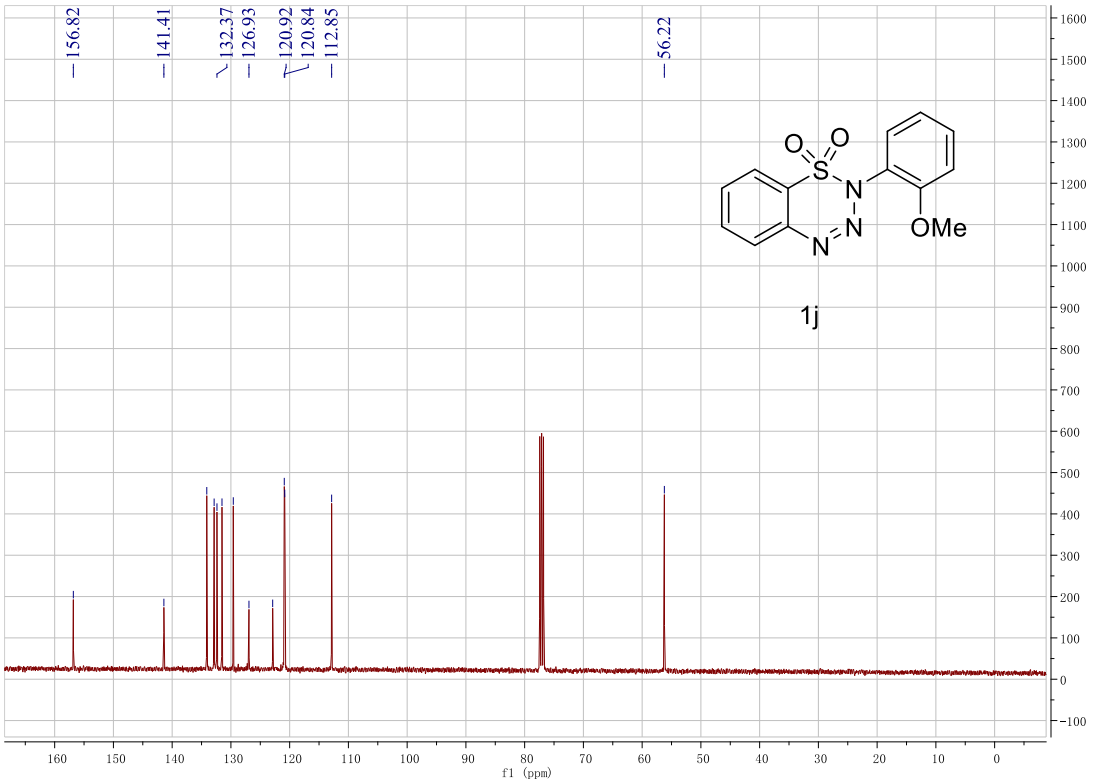
2.91
f1 (ppm)

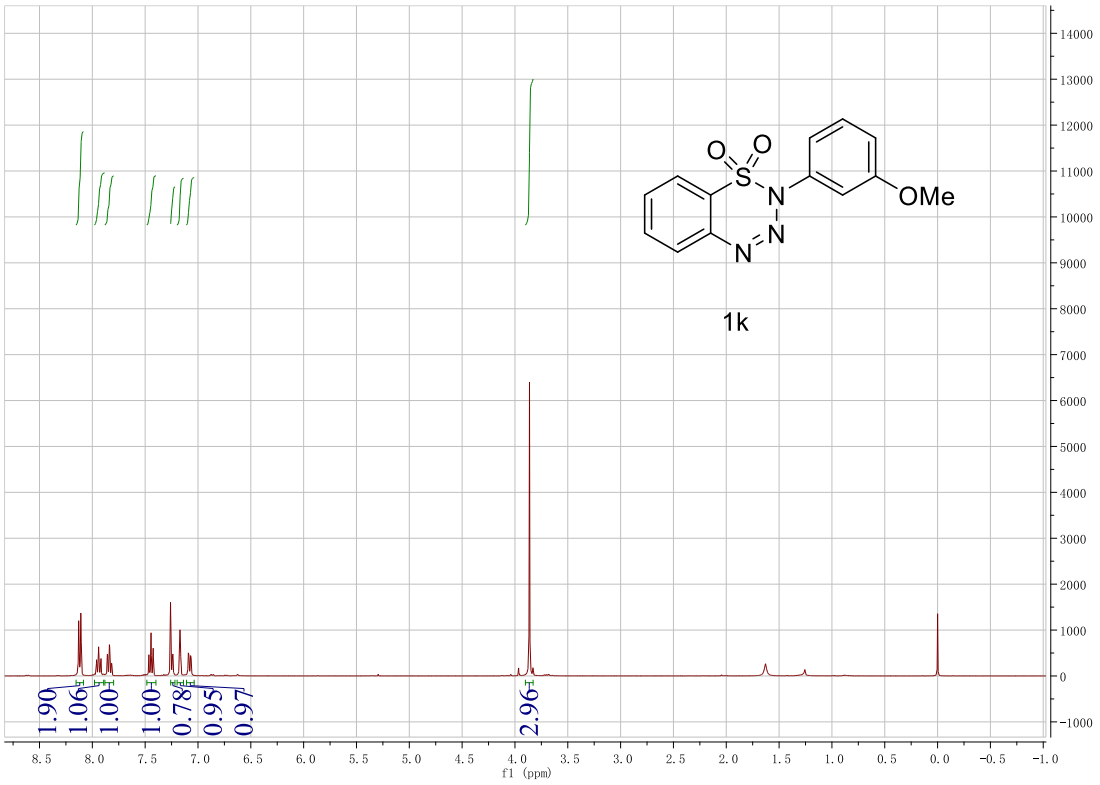

196.97
141.04
139.12
137.53
134.59
133.47
129.88
129.52
127.05
126.51
120.99
26.79
COMe
1h
f1 (ppm)

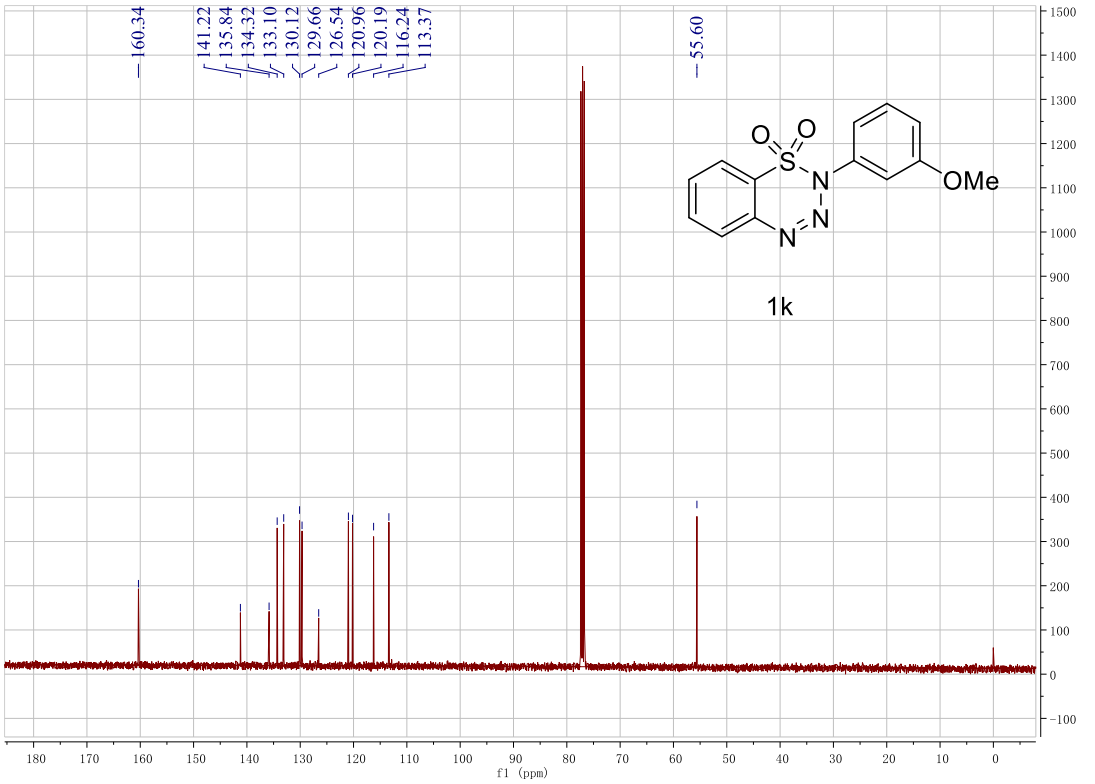

CO2Me
1i
1.91
1.88
1.08
1.06
1.96
3.00
f1 (ppm)

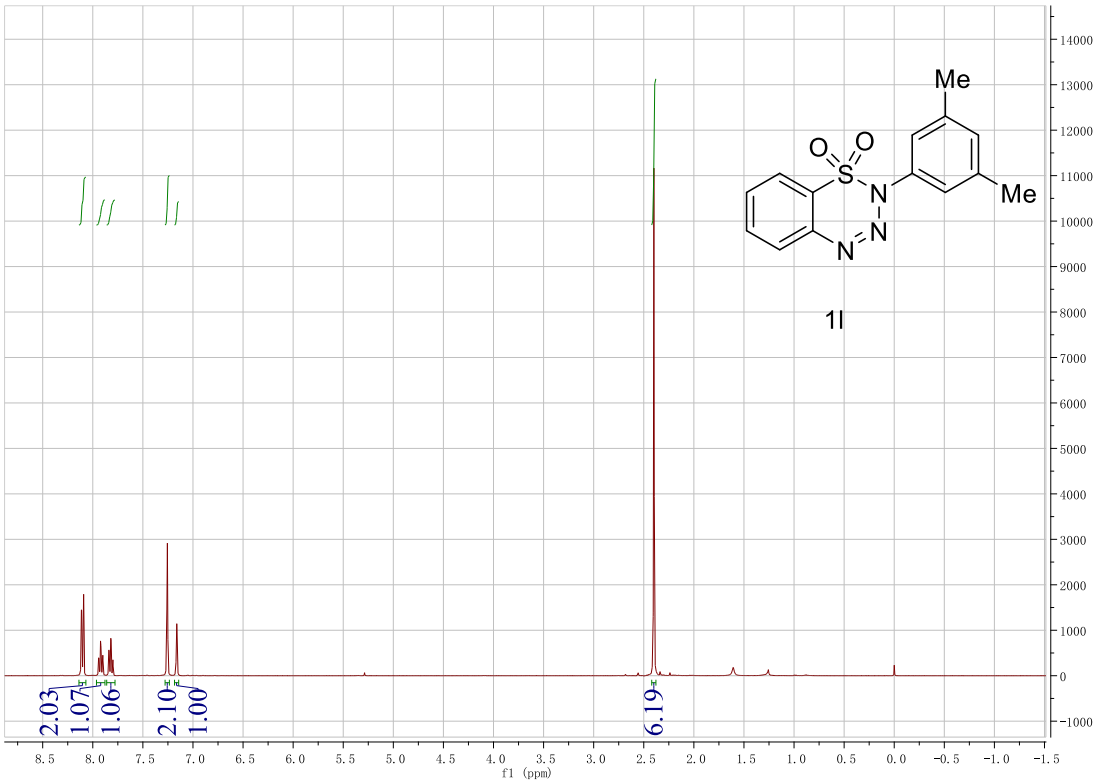

166.08
134.52
131.09
130.82
129.85
126.93
126.55
120.99
52.49
CO2Me
1i
f1 (ppm)

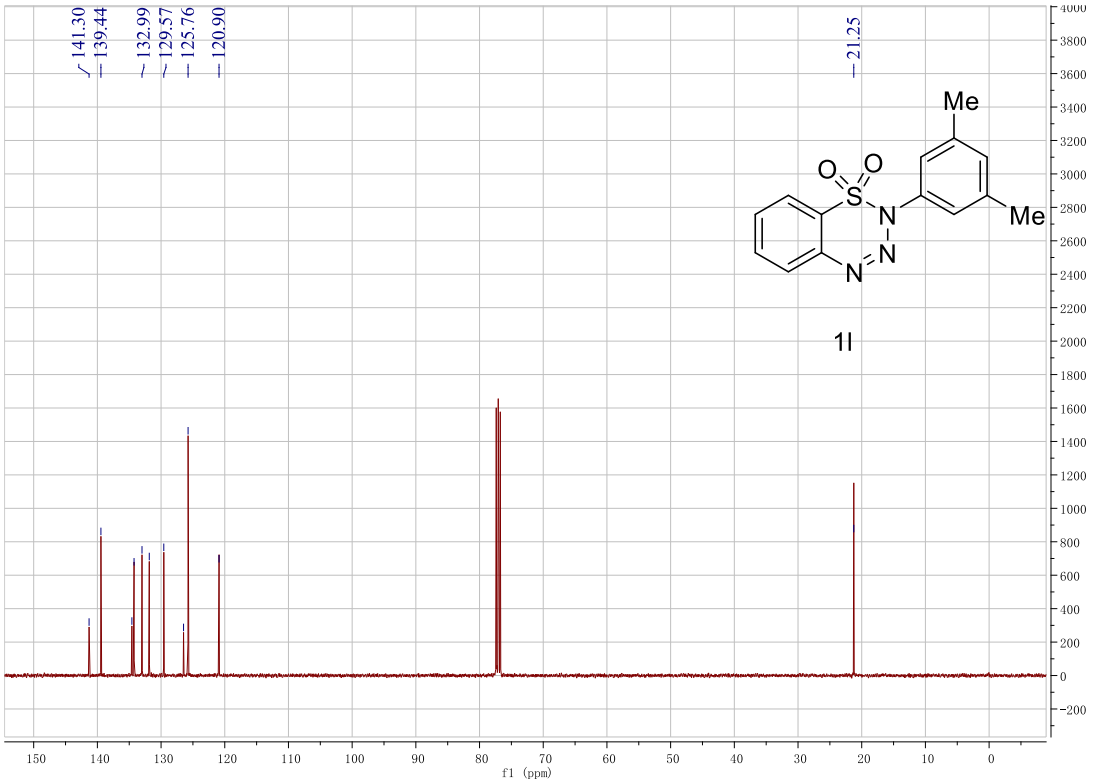

1.91
1.00
1.01
0.97
1.01
1.92
2.97
OMe
1j
f1 (ppm)

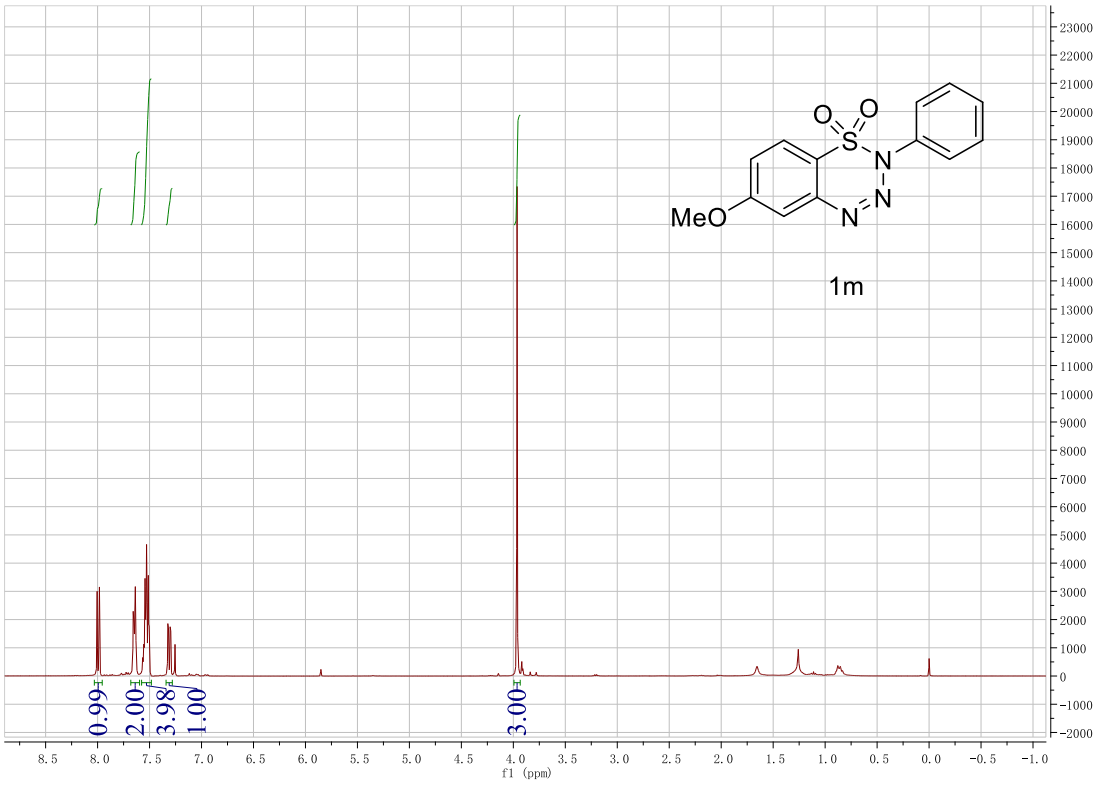

156.82
141.41
132.37
126.93
120.92
120.84
112.85
56.22
O
O
S
N
N
N
OMe
1j
f1 (ppm)

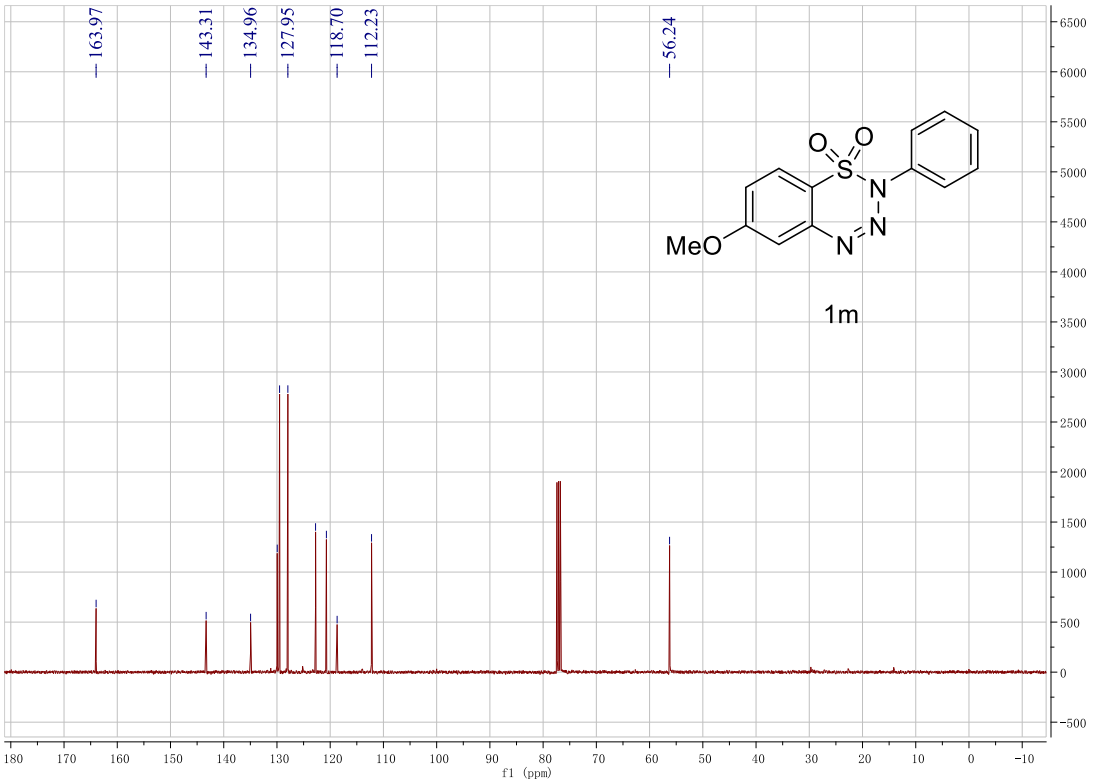

O
O
S
N
N
N
OMe
1k
1.90
1.06
1.00
1.00
0.78
0.95
0.97
2.96
f1 (ppm)

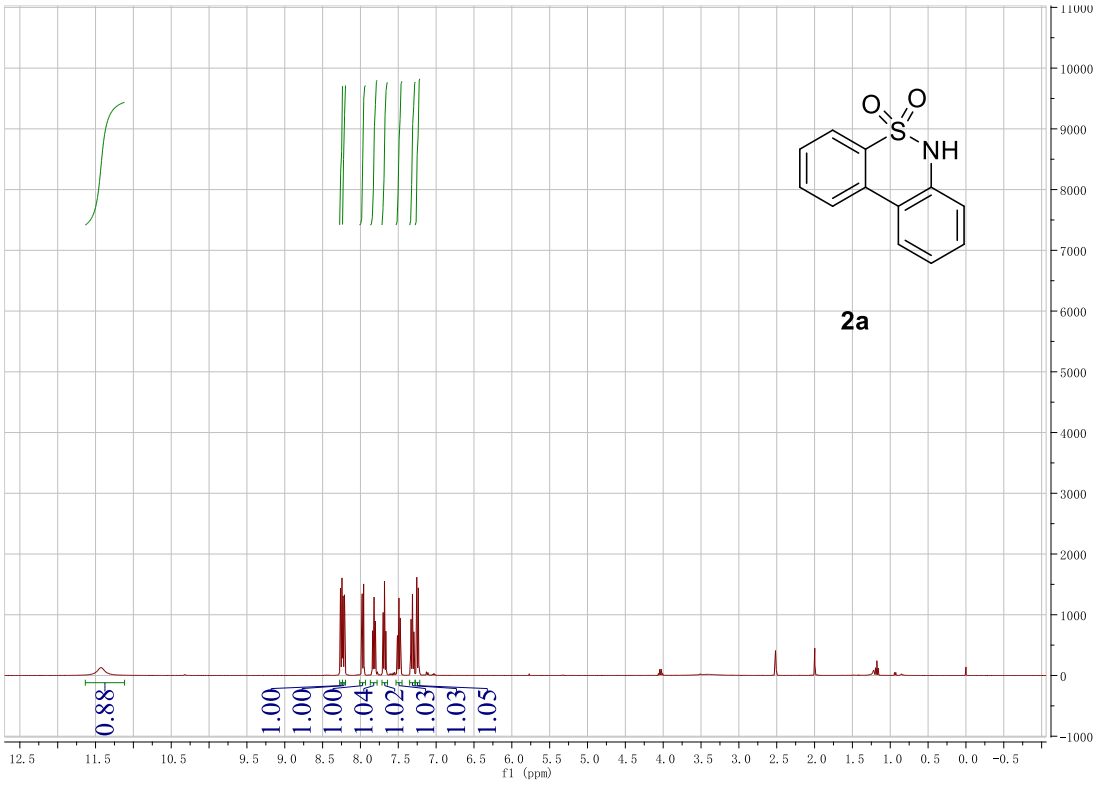

160.34
141.22
135.84
134.32
133.10
130.12
129.66
126.54
120.96
120.19
116.24
113.37
55.60
OMe
1k
f1 (ppm)

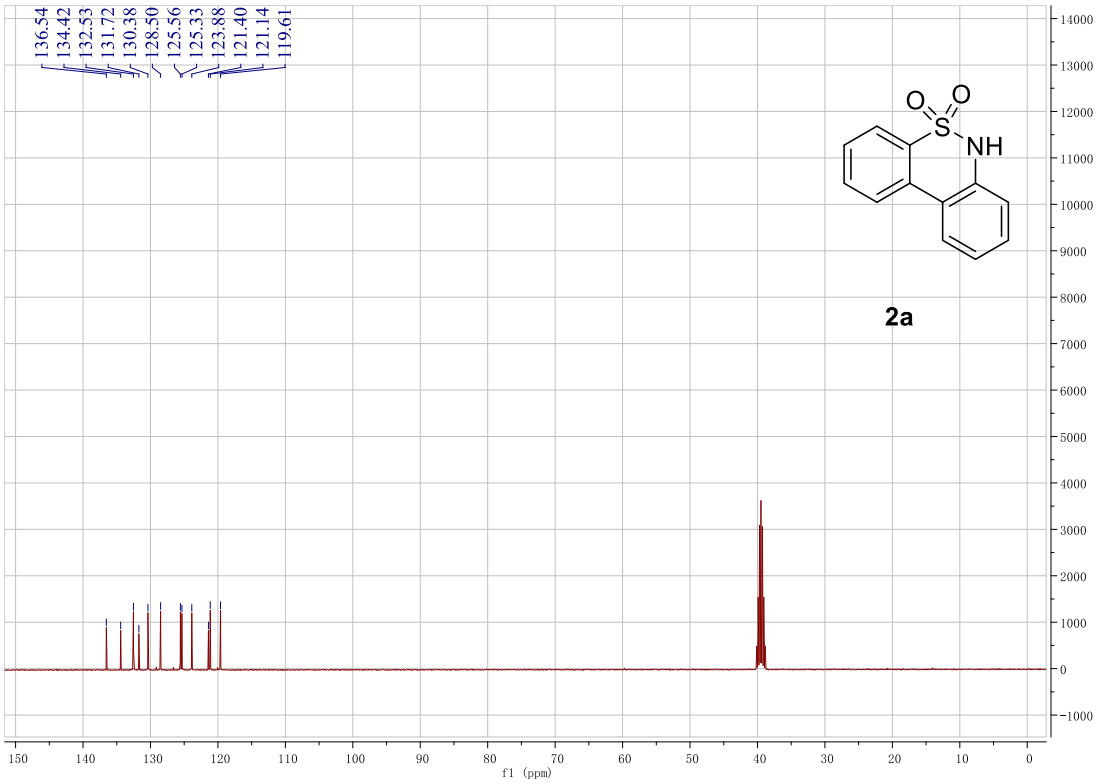

Me
Me
1l
2.03
1.07
1.06
2.10
1.00
6.19
f1 (ppm)

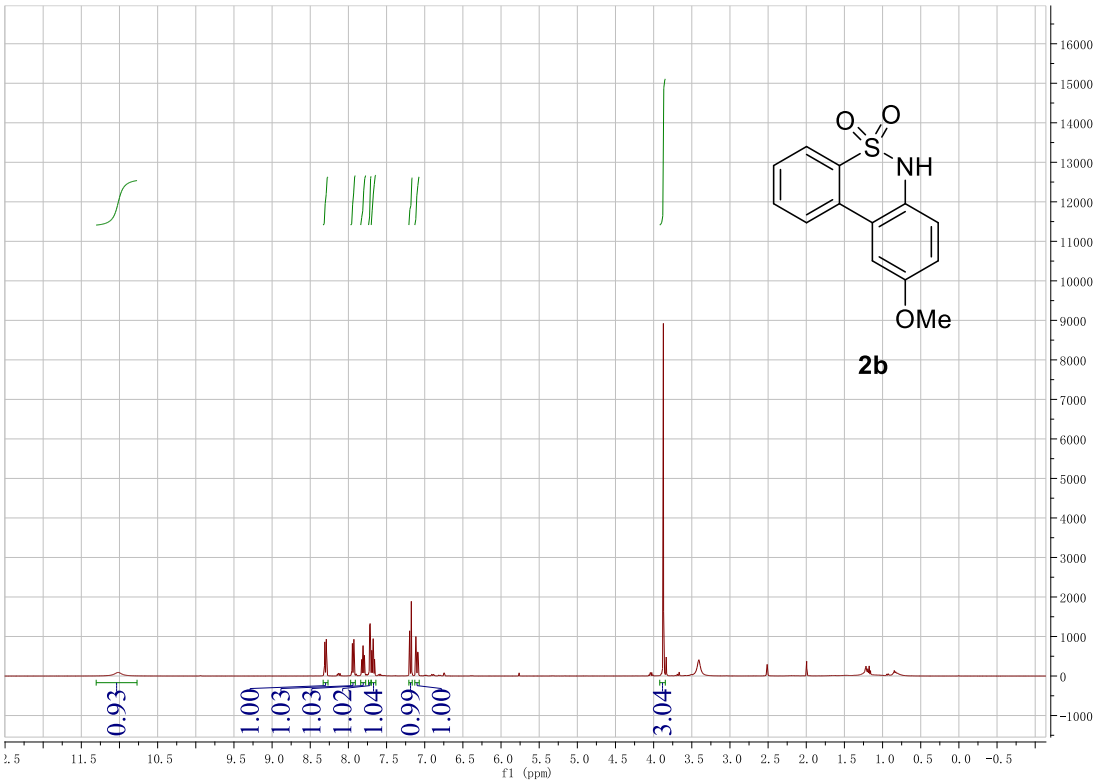

141.30
139.44
132.99
129.57
125.76
120.90
21.25
Me
Me
1l
f1 (ppm)

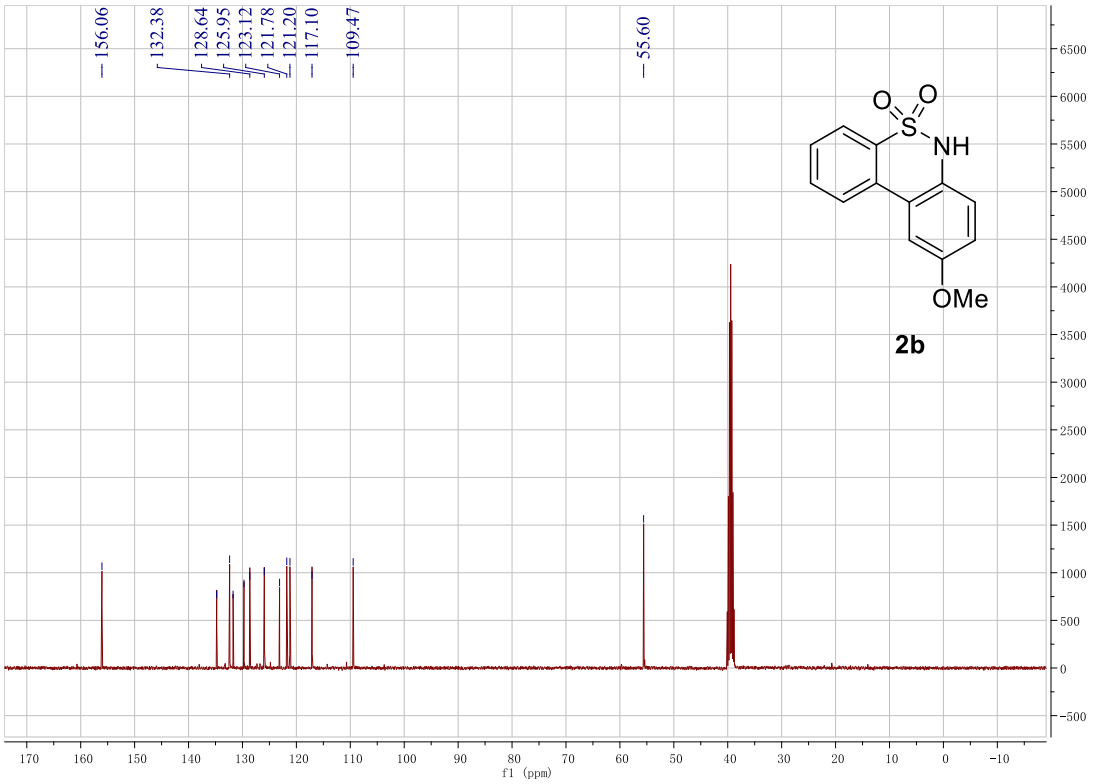

MeO
1m
0.99
2.00
3.98
1.00
3.00
f1 (ppm)

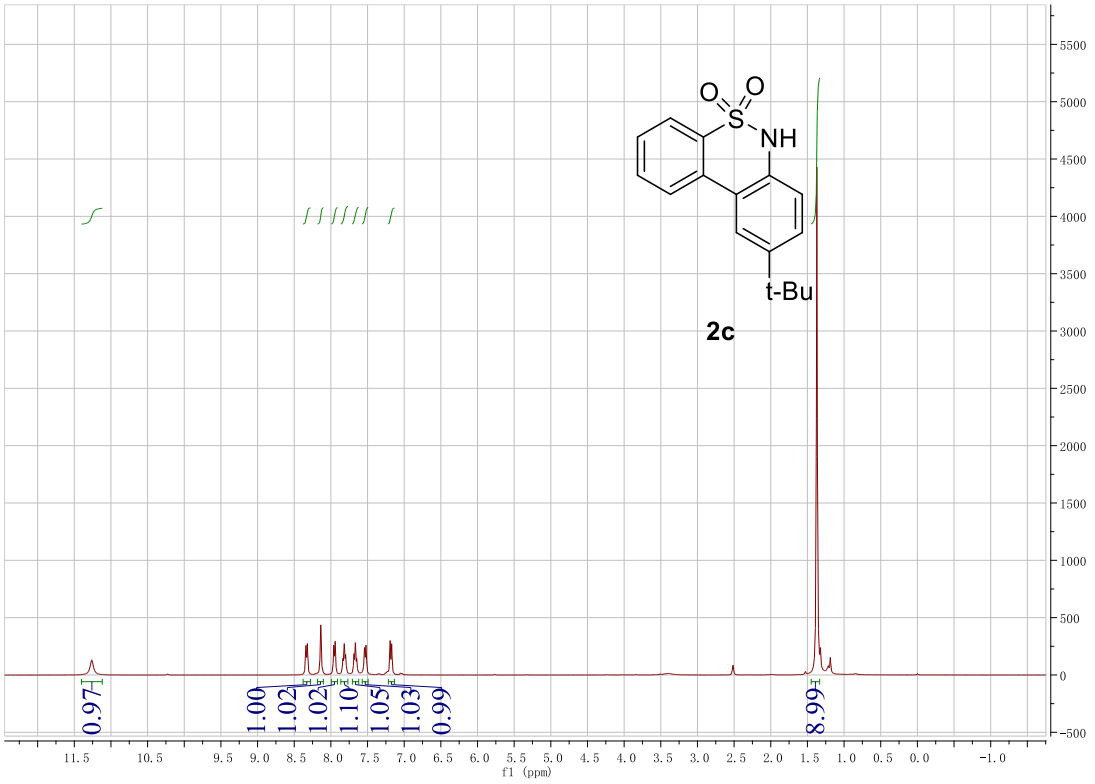

163.97
143.31
134.96
127.95
118.70
112.23
56.24
MeO
1m
f1 (ppm)

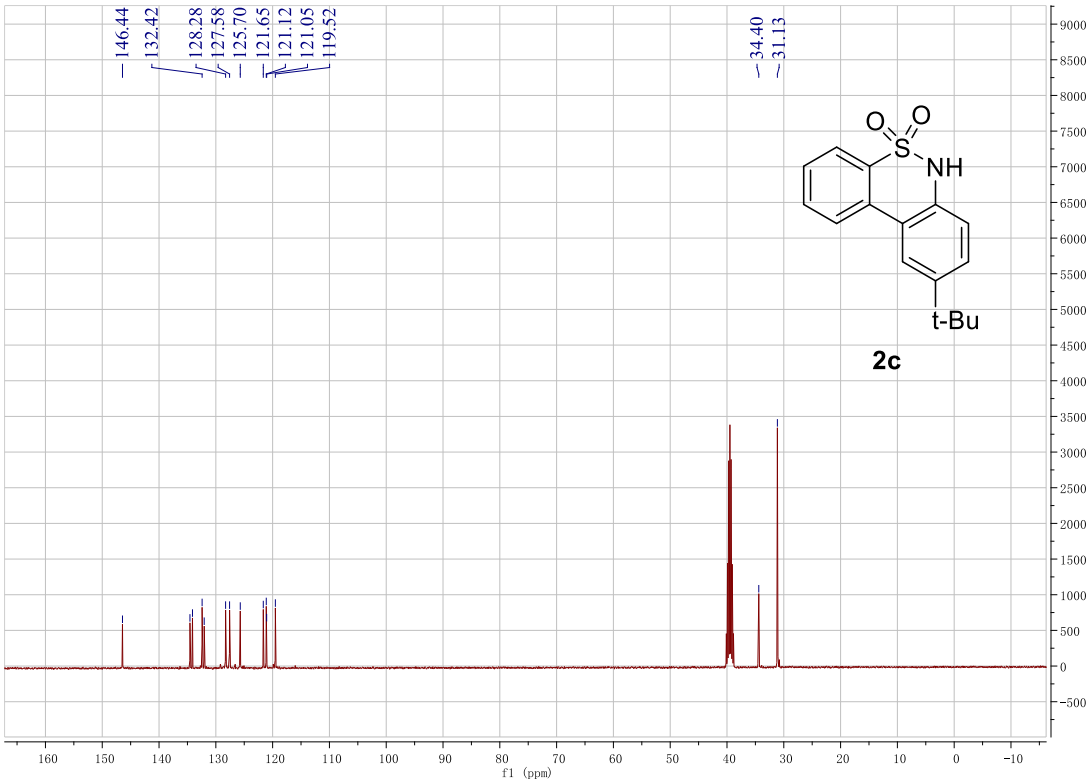

NH
2a
0.88
1.00
1.00
1.00
1.04
1.02
1.03
1.03
1.05
f1 (ppm)

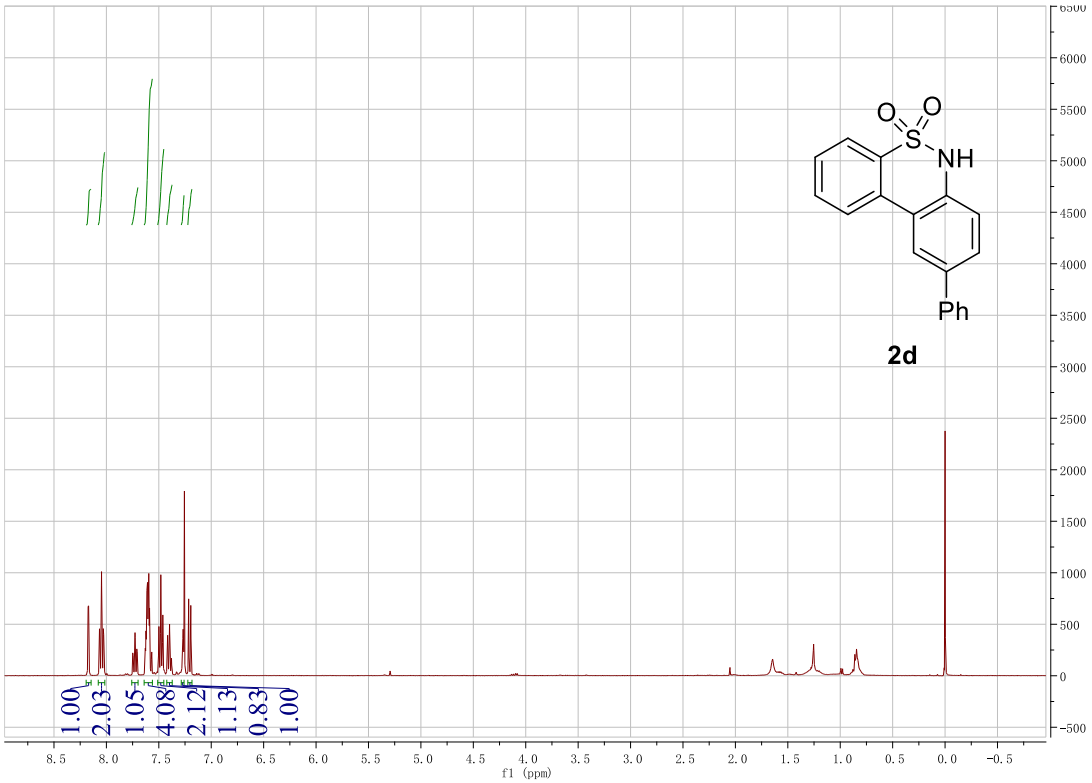

136.54
134.42
132.53
131.72
130.38
128.50
125.56
125.33
123.88
121.40
121.14
119.61
O
O
S
NH
2a
f1 (ppm)

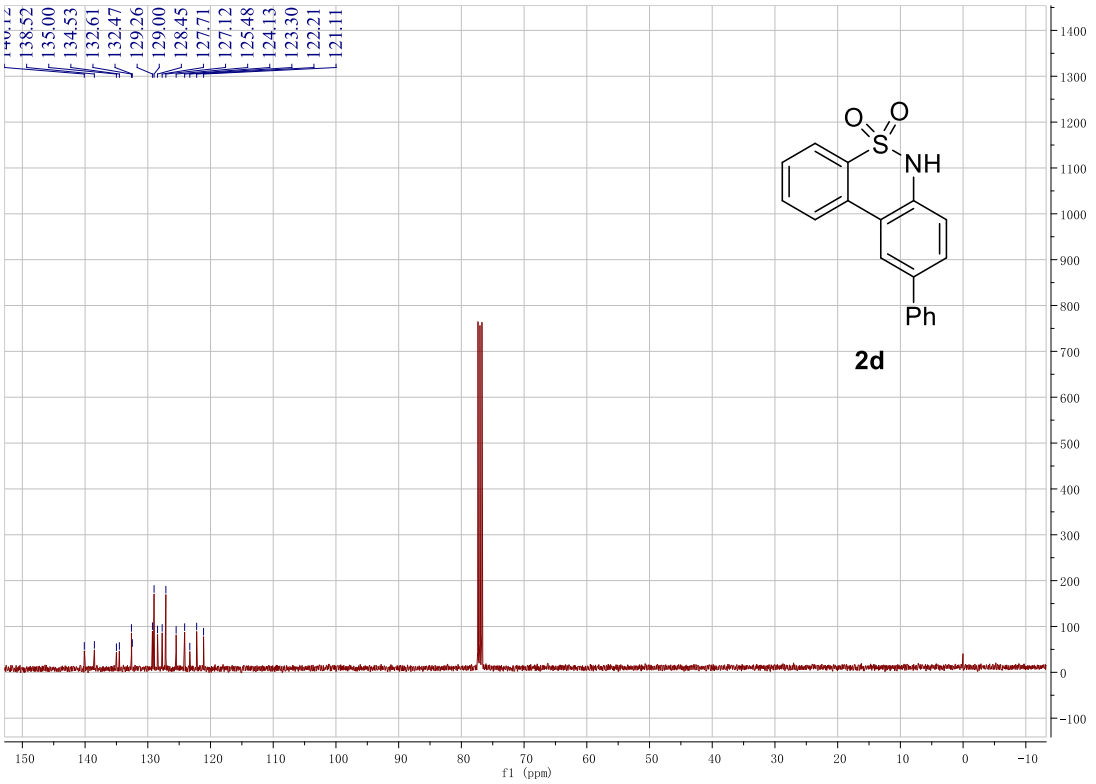

O
O
S
NH
OMe
2b
0.93
1.00
1.03
1.03
1.02
1.04
0.99
1.00
3.04
f1 (ppm)

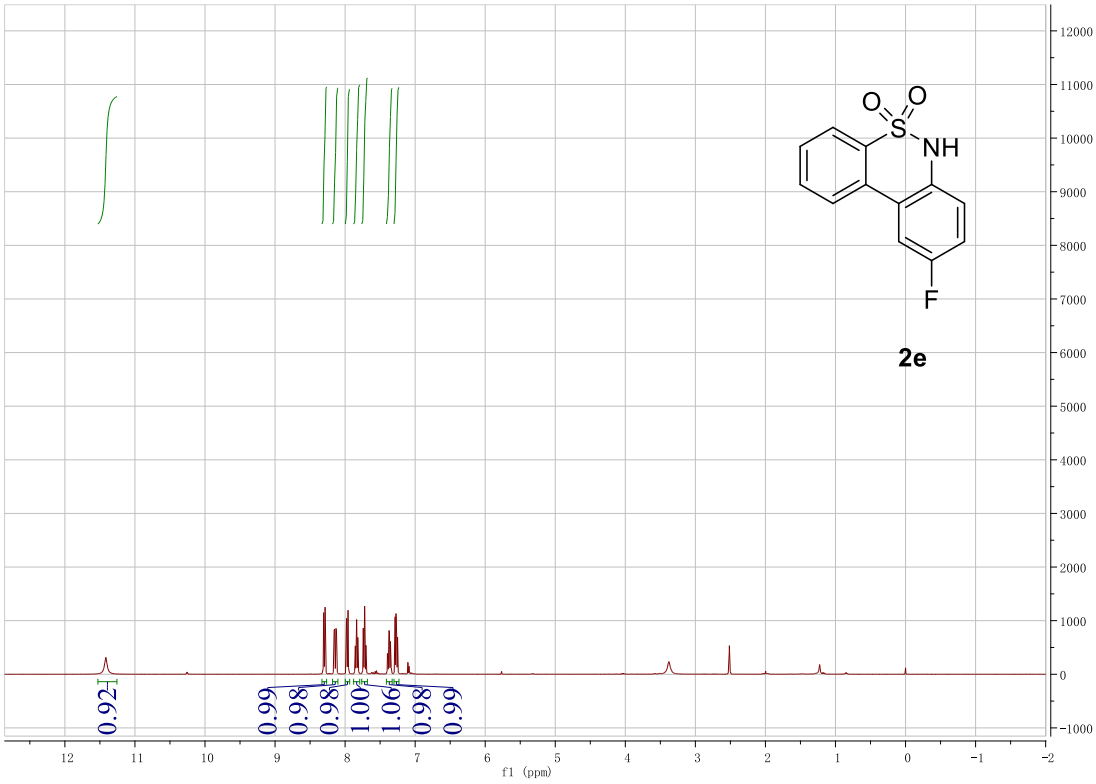

156.06
132.38
128.64
125.95
123.12
121.78
121.20
117.10
109.47
55.60
O
O
S
NH
OMe
2b
f1 (ppm)

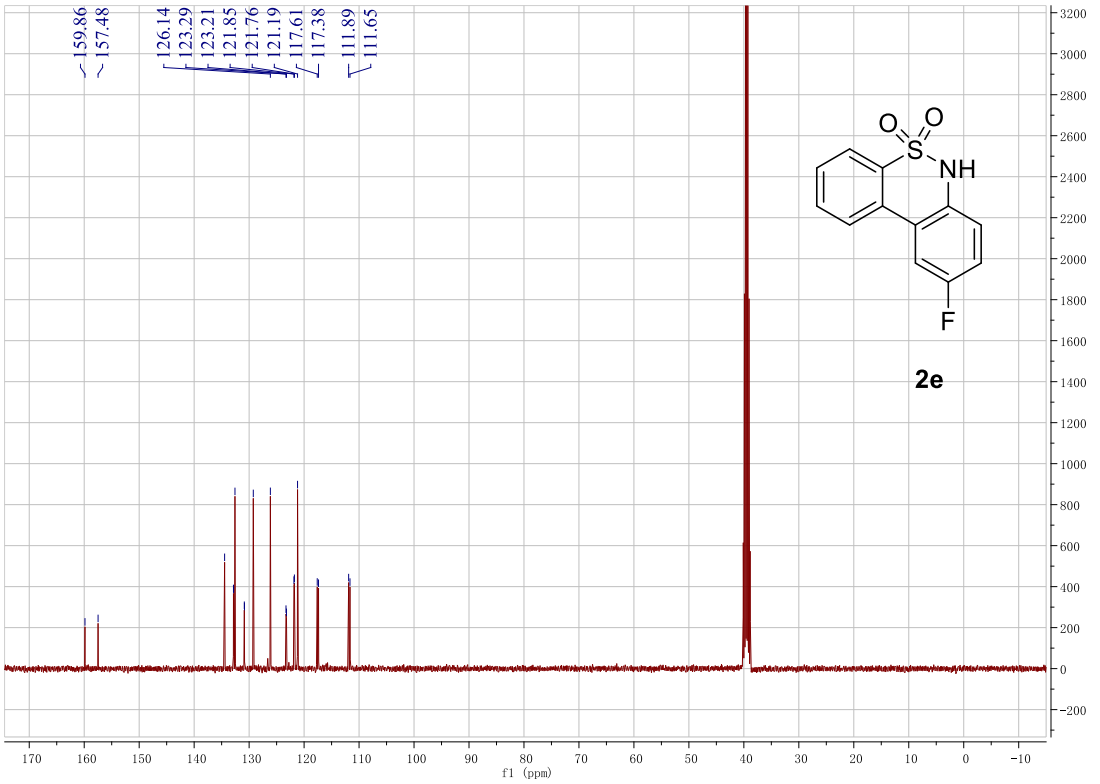

O
O
S
NH
t-Bu
2c
0.97
1.00
1.02
1.02
1.10
1.05
1.03
0.99
8.99
f1 (ppm)

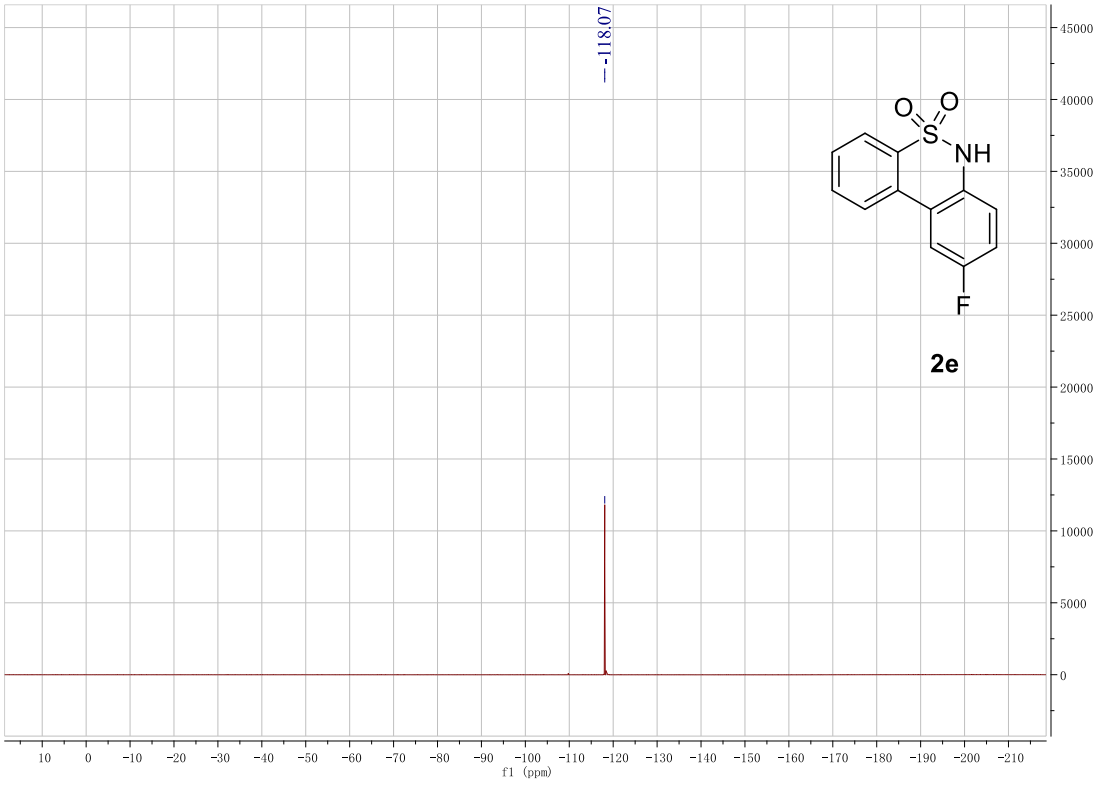

146.44
132.42
128.28
127.58
125.70
121.65
121.12
121.05
119.52
34.40
31.13
O
O
S
NH
t-Bu
2c
f1 (ppm)

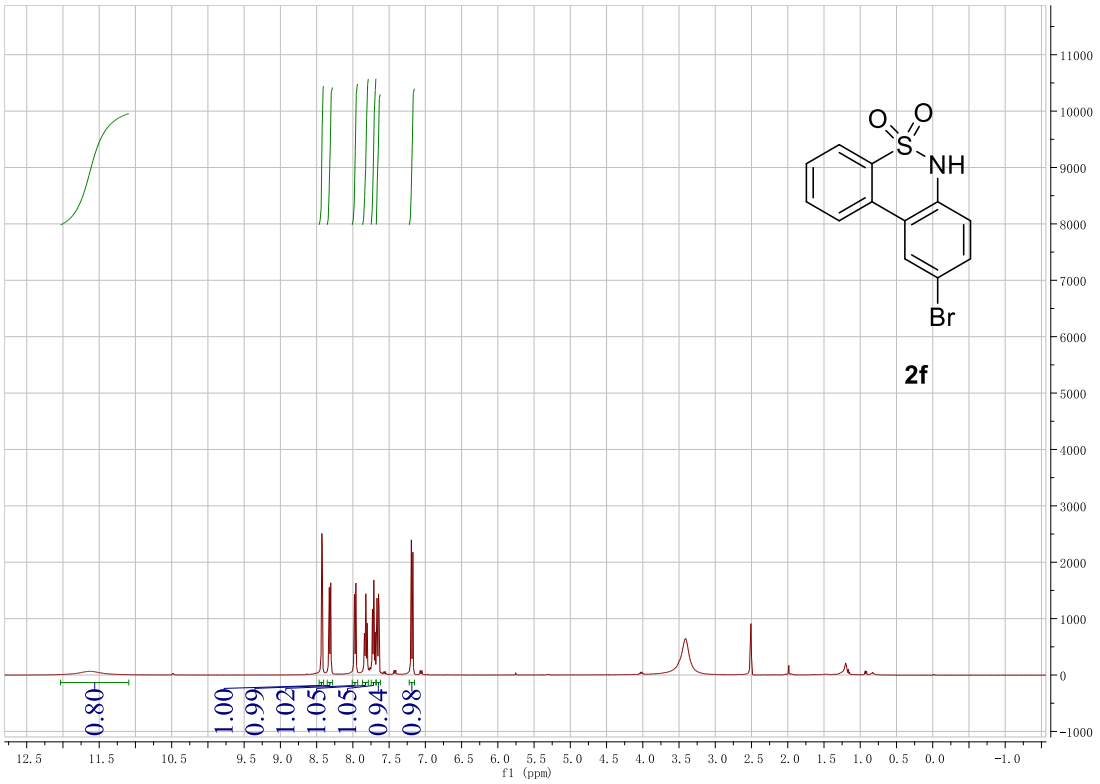

O
O
S
NH
Ph
2d
1.00
2.03
1.05
4.08
2.12
1.13
0.83
1.00
f1 (ppm)

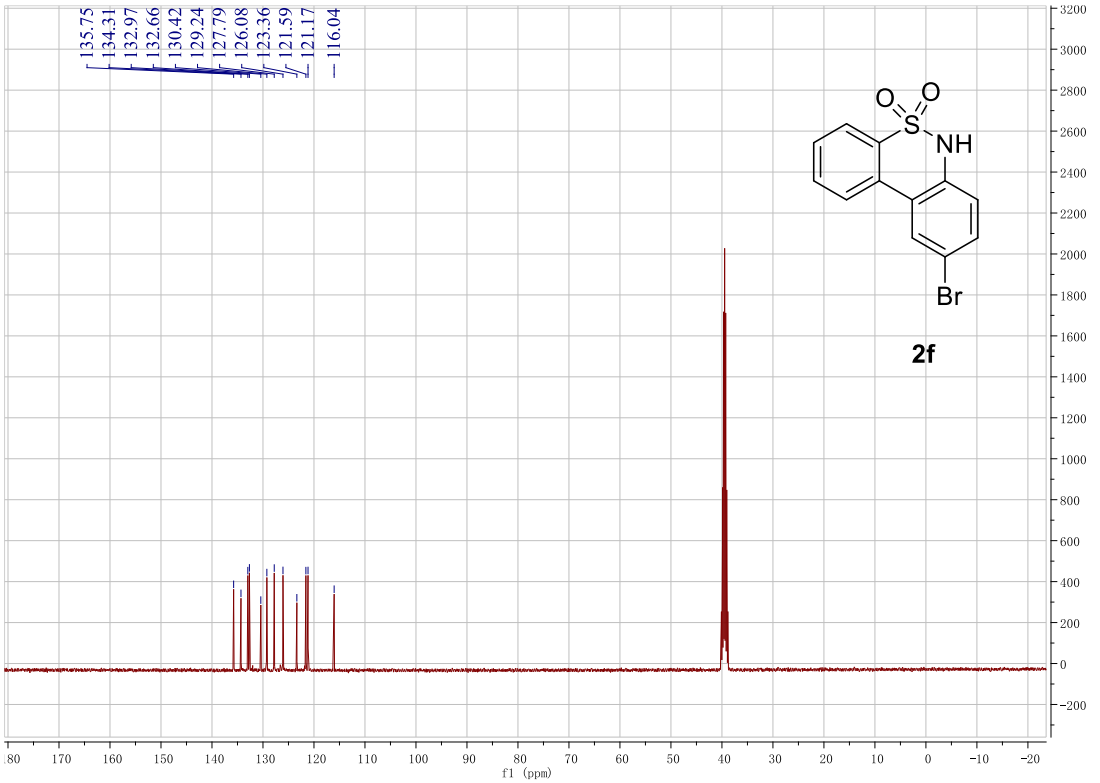

138.52
135.00
134.53
132.61
132.47
129.26
129.00
128.45
127.71
127.12
125.48
124.13
123.30
122.21
121.11
O
O
S
NH
Ph
2d
f1 (ppm)

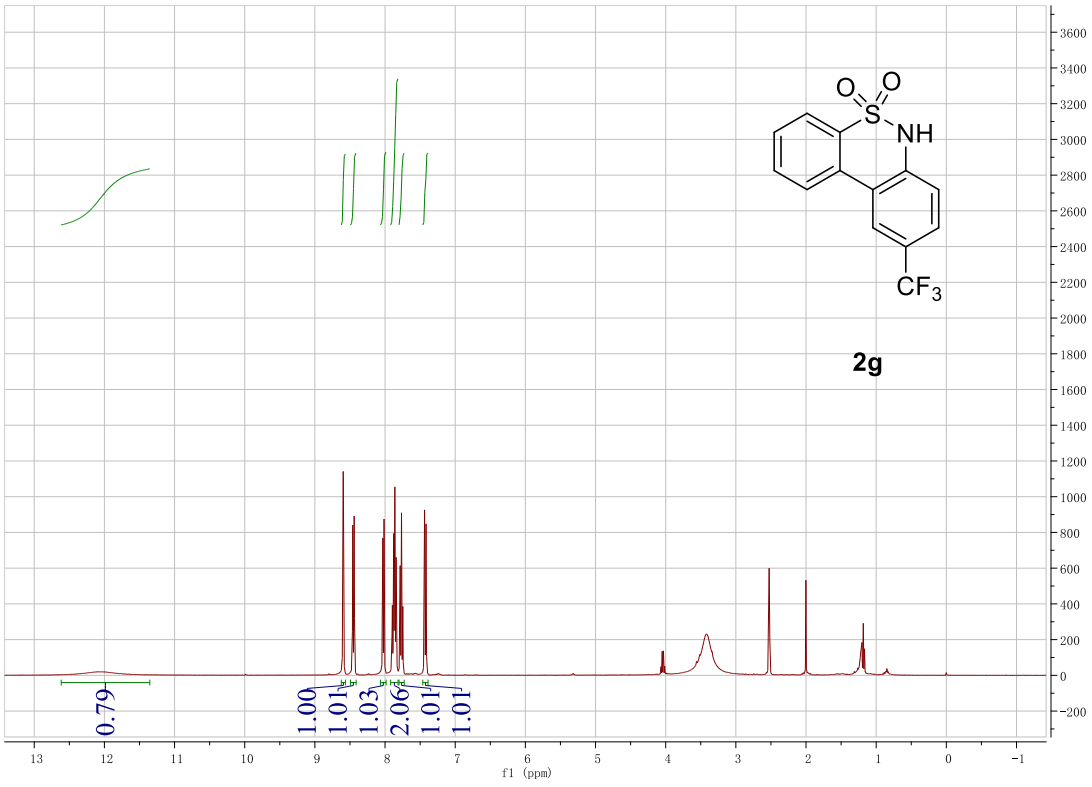

O
O
S
NH
F
2e
0.92
0.99
0.98
0.98
1.00
1.06
0.98
0.99
f1 (ppm)

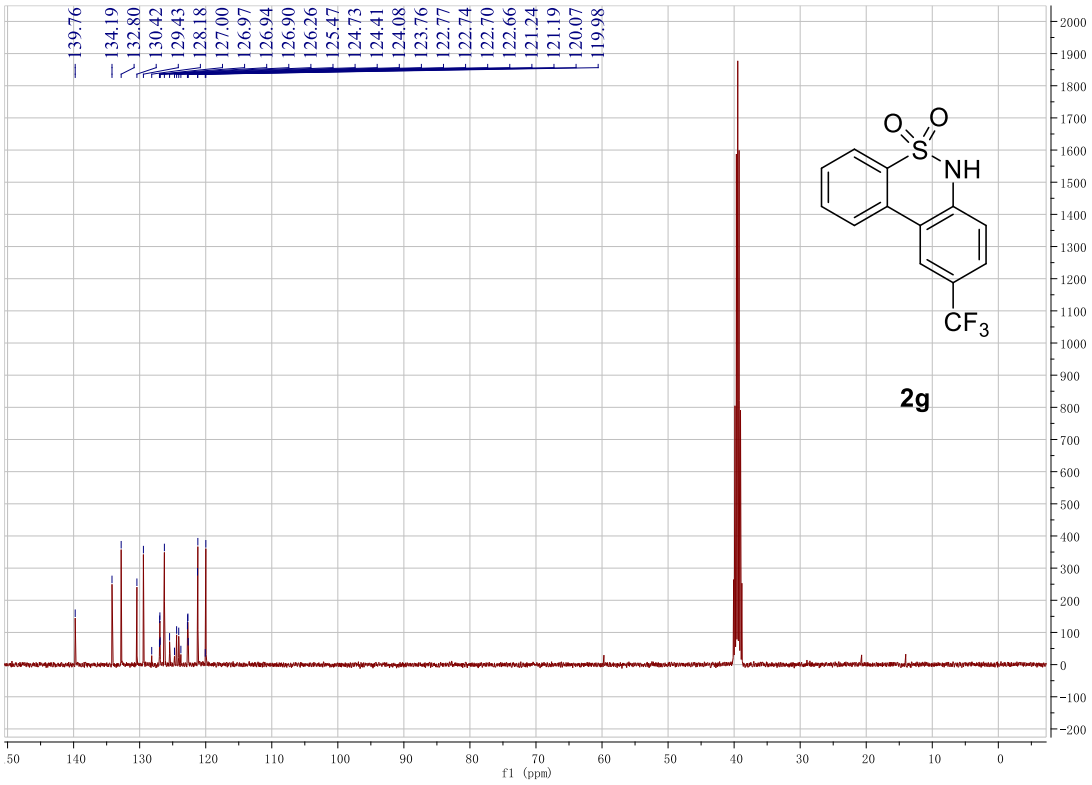

159.86
157.48
126.14
123.29
123.21
121.85
121.76
121.19
117.61
117.38
111.89
111.65
O
O
S
NH
F
2e
f1 (ppm)

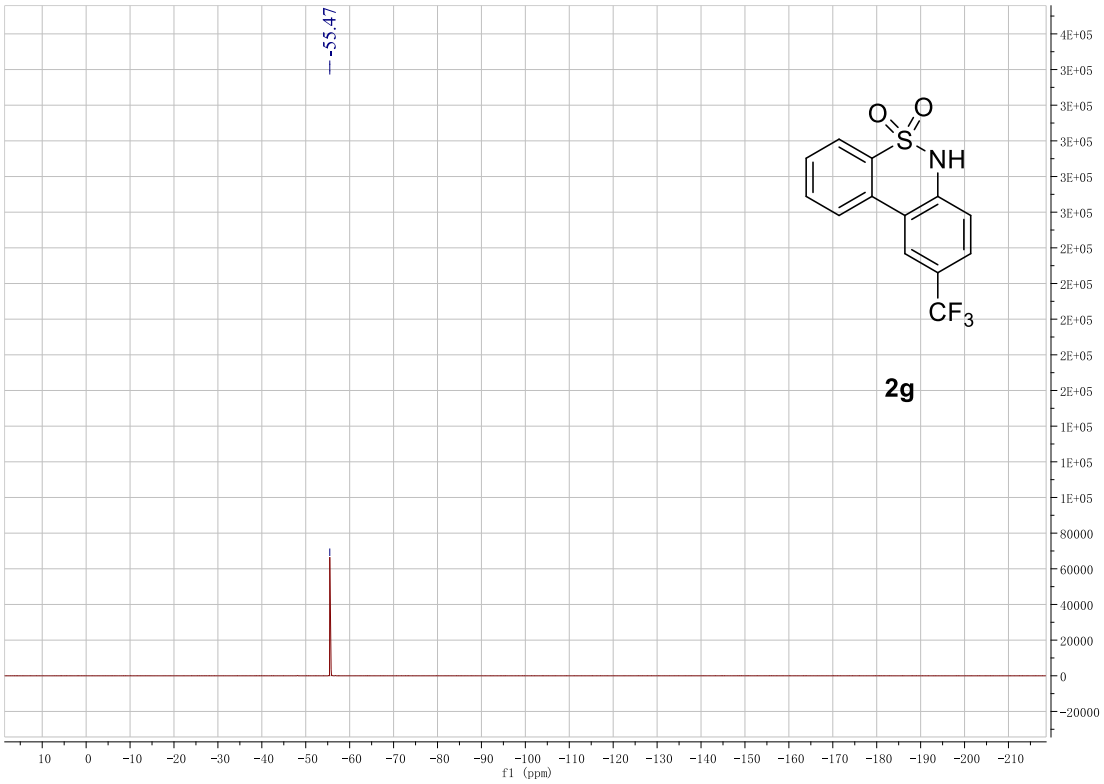

-118.07
O
O
S
NH
F
2e
f1 (ppm)

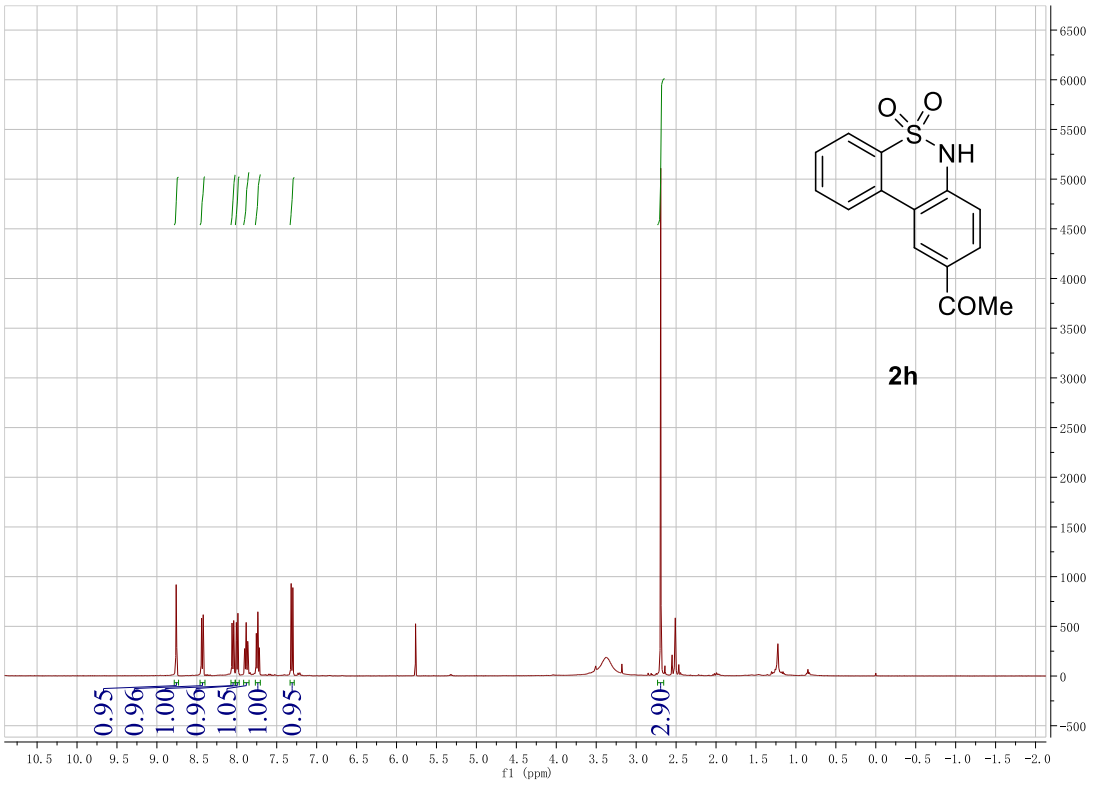

O
O
S
NH
Br
2f
0.80
1.00
0.99
1.02
1.05
1.05
0.94
0.98
f1 (ppm)

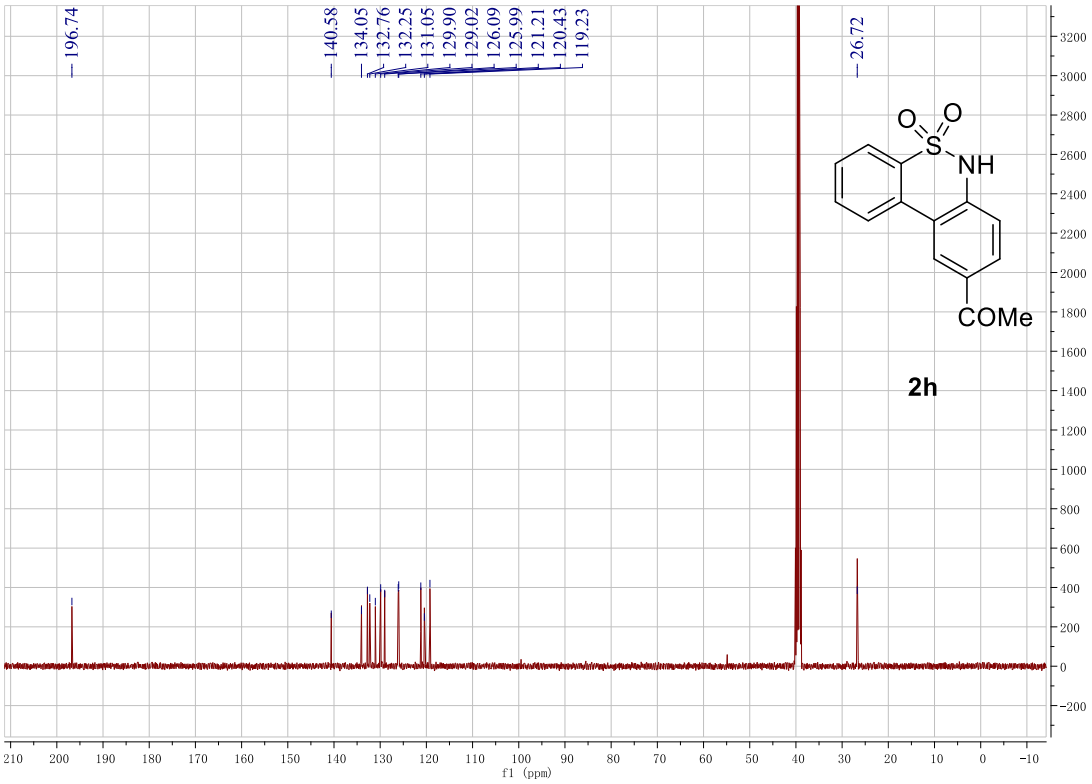

135.75
134.31
132.97
132.66
130.42
129.24
127.79
126.08
123.36
121.59
121.17
116.04
O
O
S
NH
Br
2f
f1 (ppm)

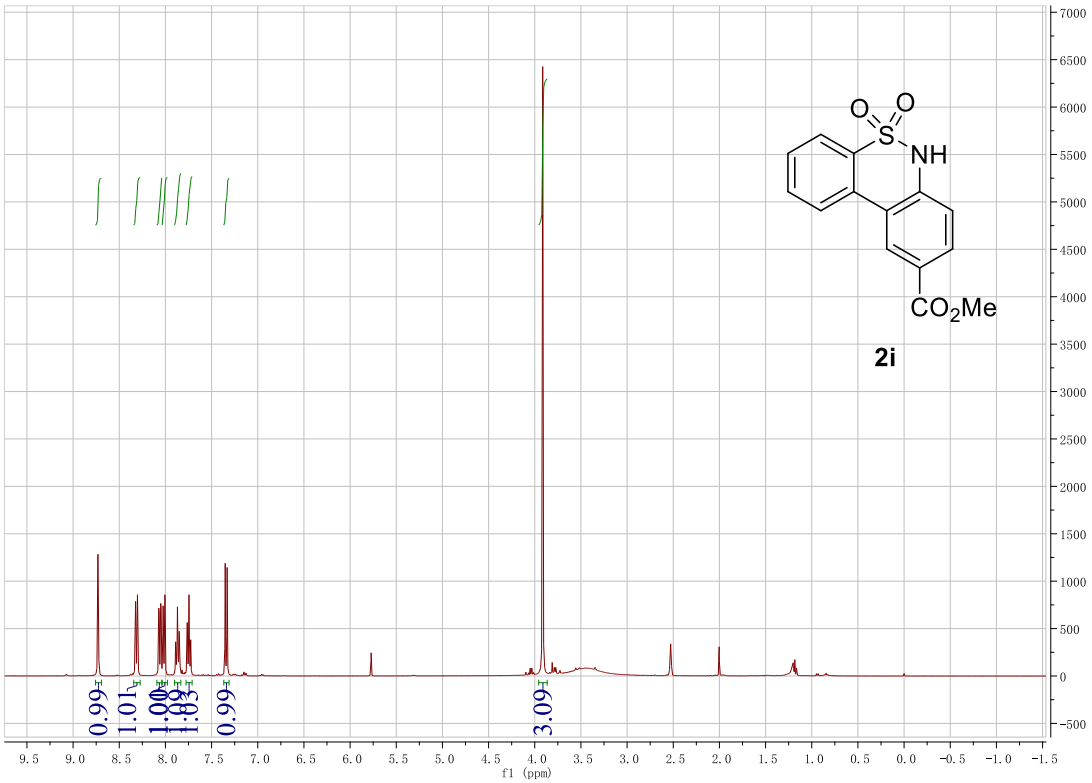

0.79
1.00
1.01
1.03
2.06
1.01
1.01
f1 (ppm)
2g

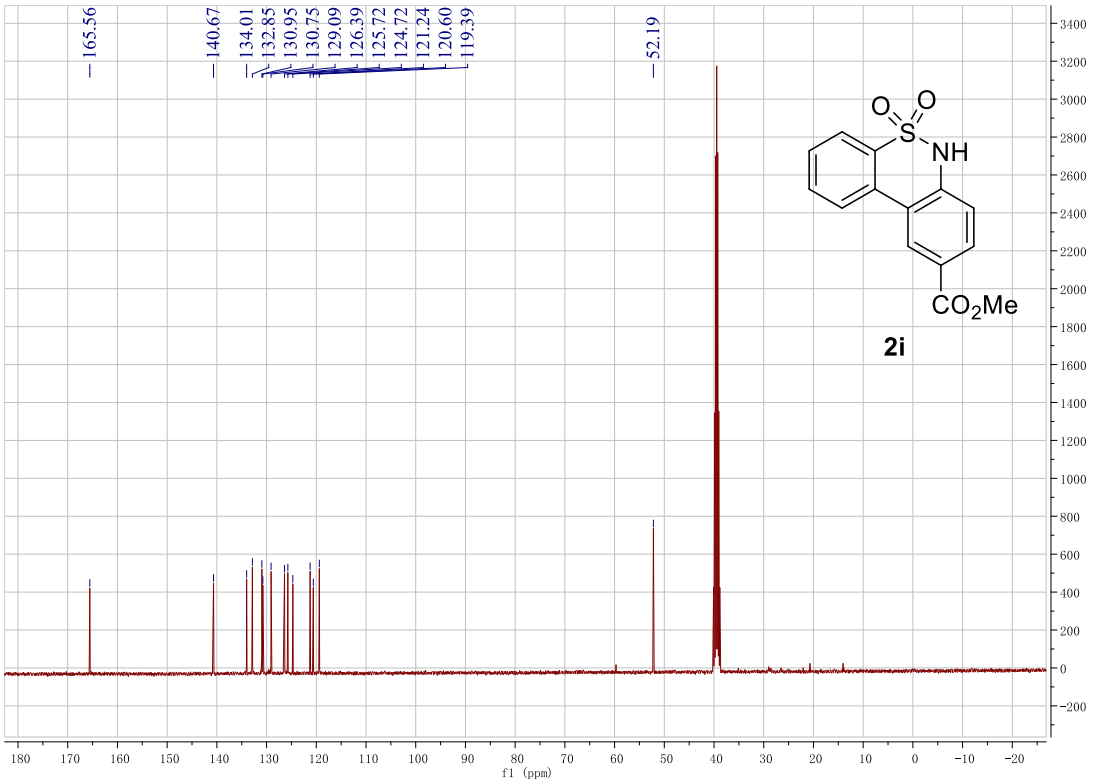

139.76
134.19
132.80
130.42
129.43
128.18
127.00
126.97
126.94
126.90
126.26
125.47
124.73
124.41
124.08
123.76
122.77
122.74
122.70
122.66
121.24
121.19
120.07
119.98
f1 (ppm)
2g

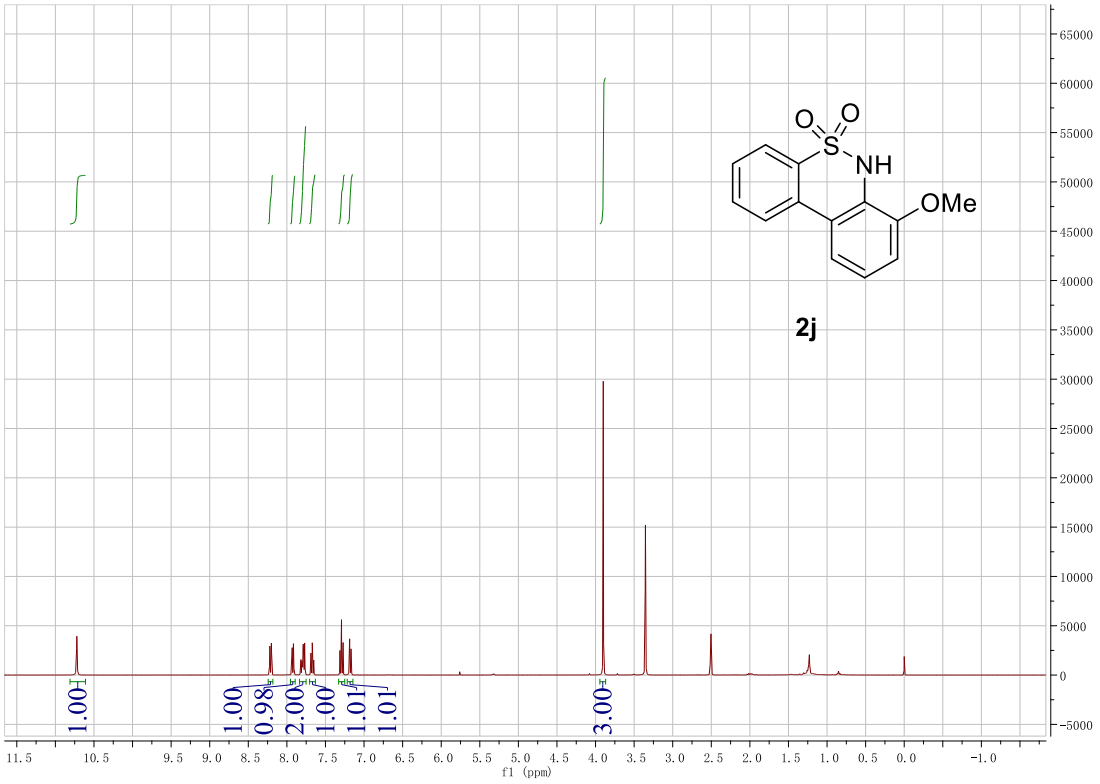

-55.47
O
O
S
NH
CF3
2g
f1 (ppm)

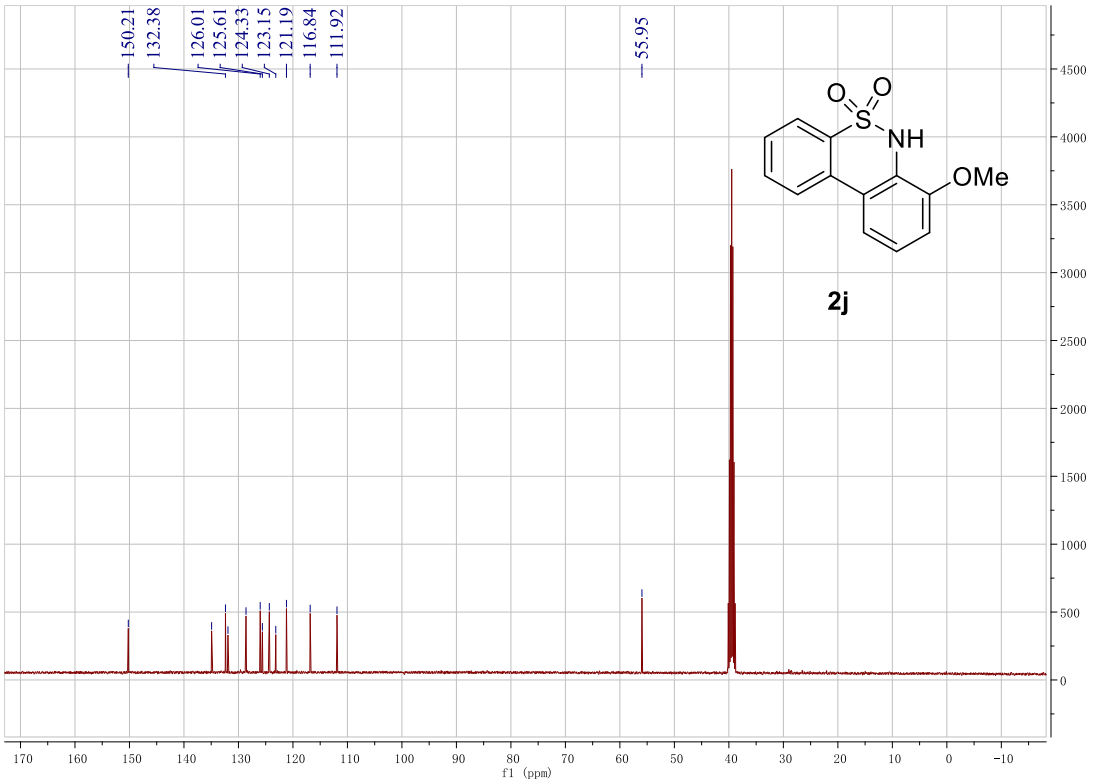

O
O
S
NH
COMe
2h
0.95
0.96
1.00
0.96
1.05
1.00
0.95
2.90
f1 (ppm)

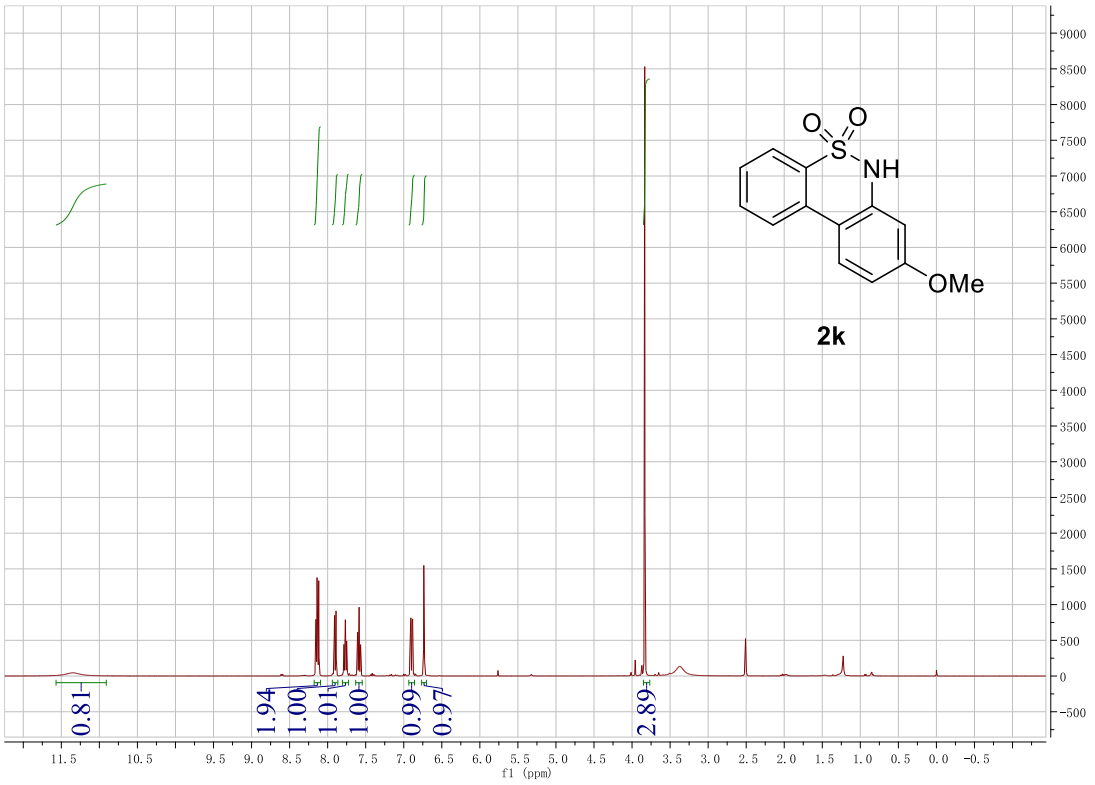

196.74
140.58
134.05
132.76
132.25
131.05
129.90
129.02
126.09
125.99
121.21
120.43
119.23
26.72
O
O
S
NH
COMe
2h
f1 (ppm)

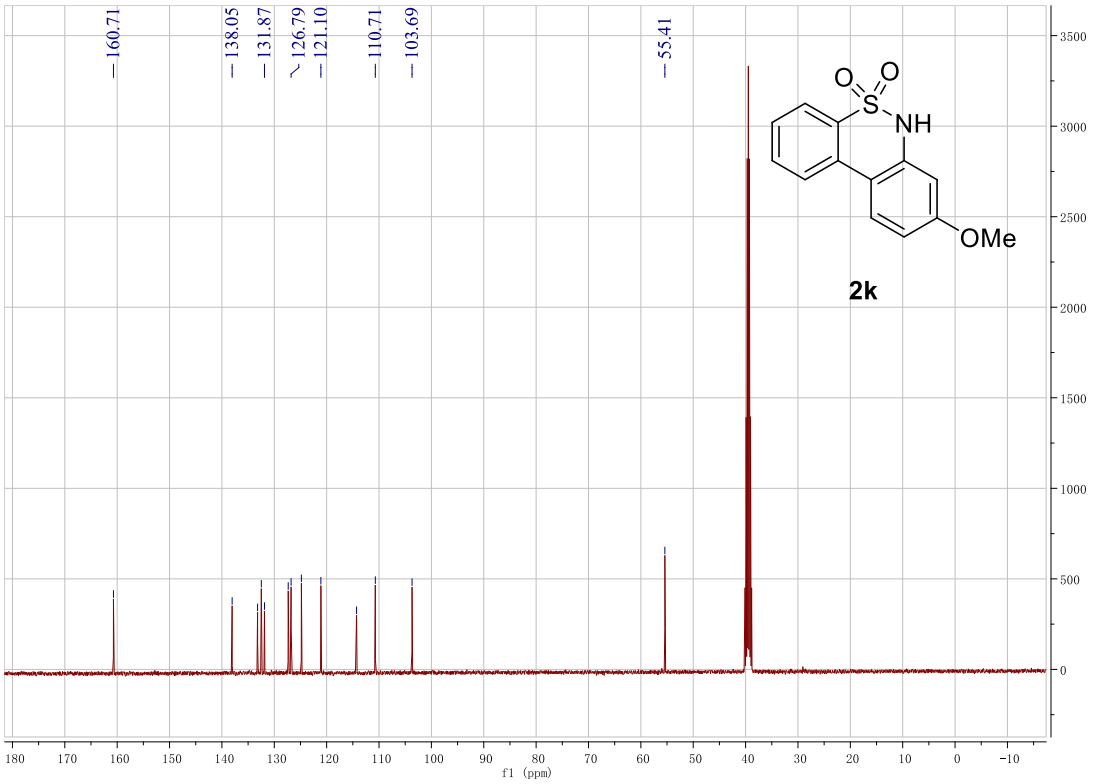

O
O
S
NH
CO2Me
2i
0.99
1.01
1.00
1.09
1.03
0.99
3.09
f1 (ppm)

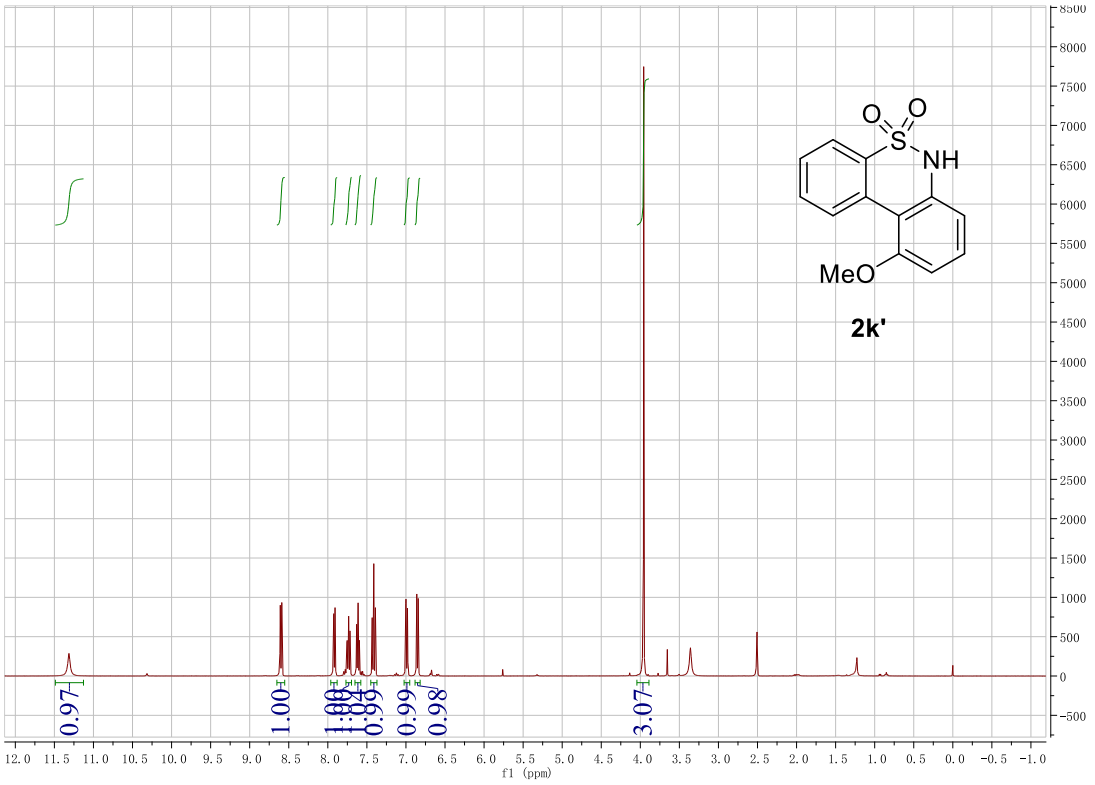

165.56
140.67
134.01
132.85
130.95
130.75
129.09
126.39
125.72
124.72
121.24
120.60
119.39
52.19
O
O
S
NH
CO2Me
2i
f1 (ppm)

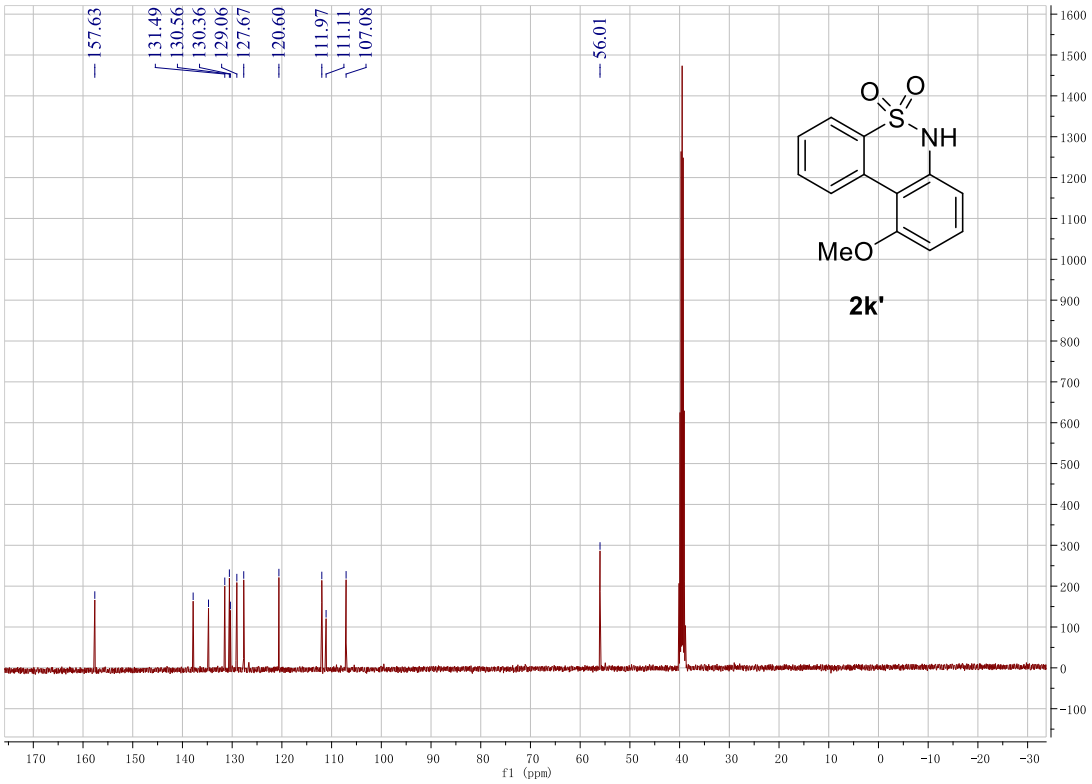

O
O
S
NH
OMe
2j
1.00
1.00
0.98
2.00
1.00
1.01
1.01
3.00
f1 (ppm)

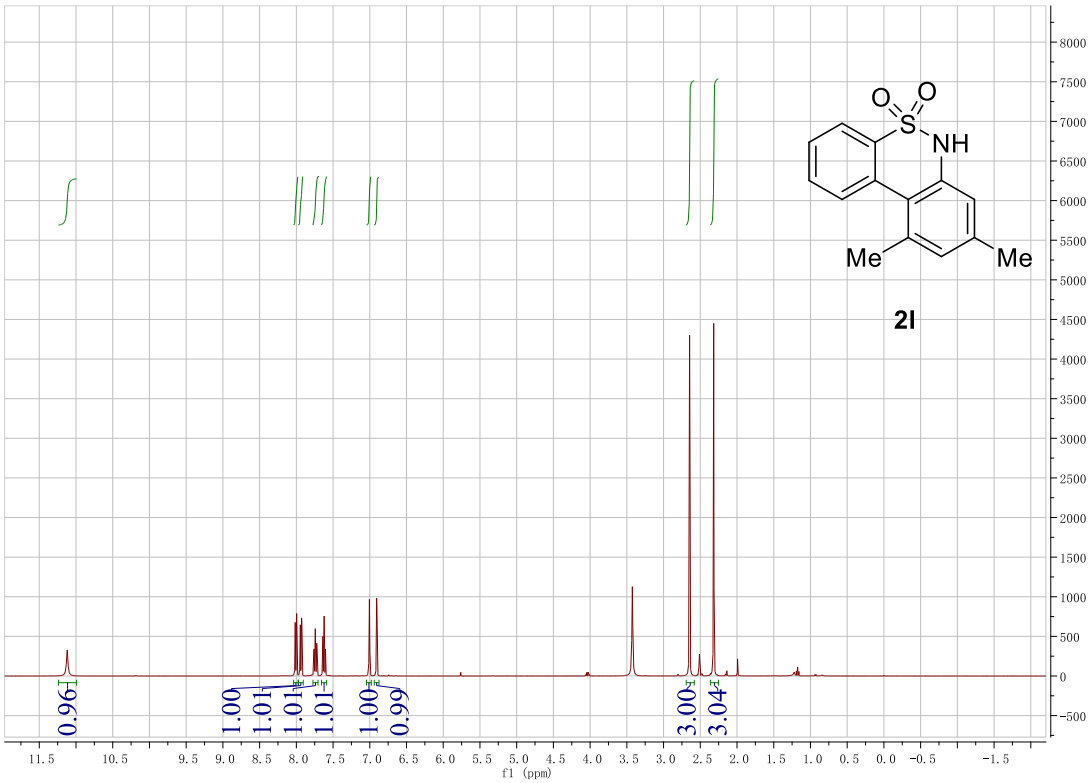

150.21
132.38
126.01
125.61
124.33
123.15
121.19
116.84
111.92
55.95
O
O
S
NH
OMe
2j
f1 (ppm)

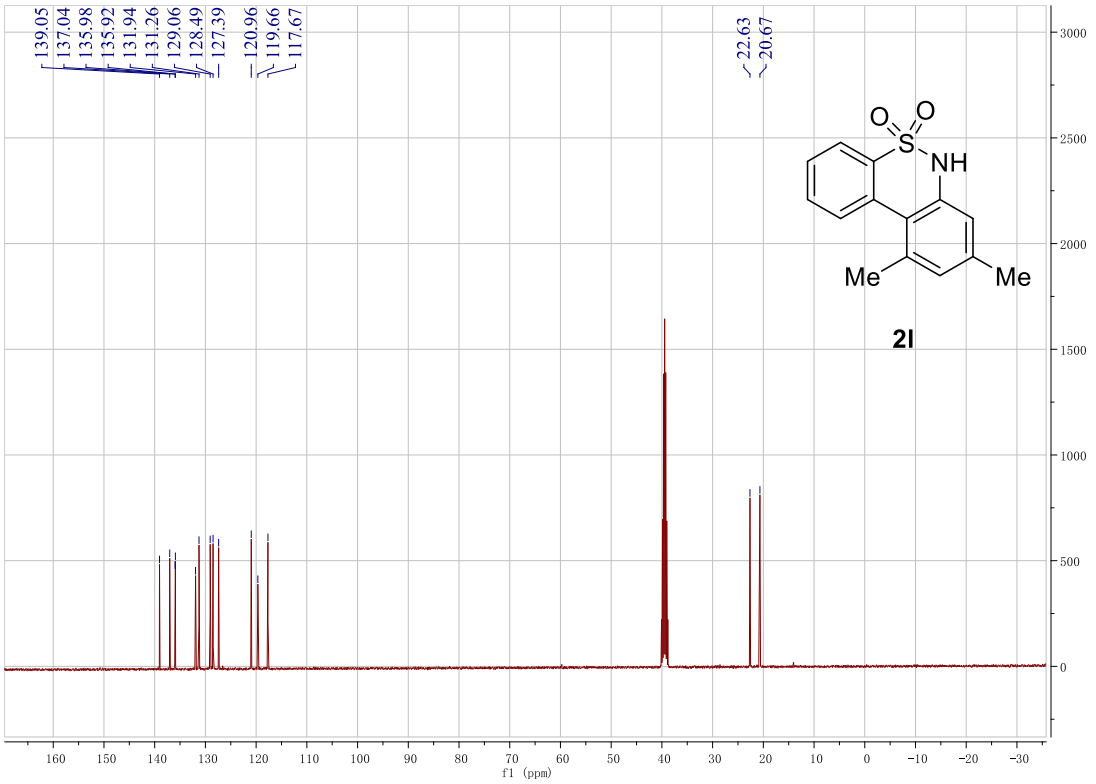

O
O
S
NH
OMe
2k
0.81
1.94
1.00
1.01
1.00
0.99
0.97
2.89
f1 (ppm)

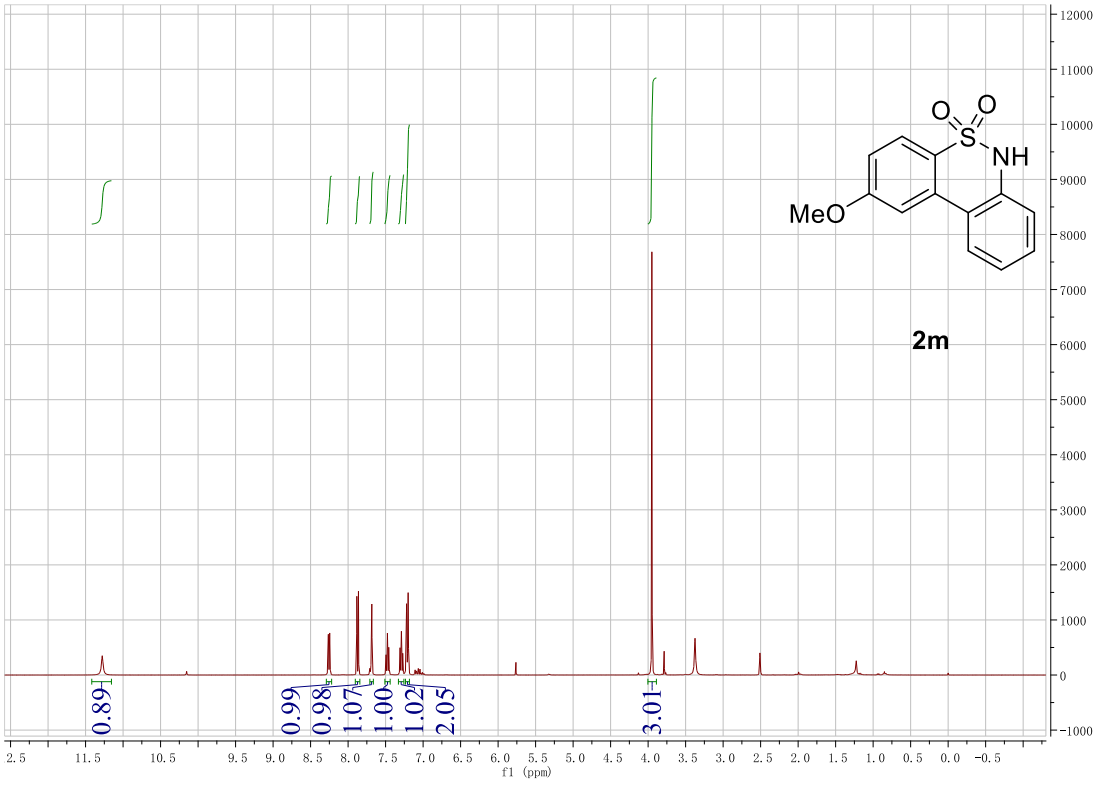

160.71
138.05
131.87
126.79
121.10
110.71
103.69
55.41
O
O
S
NH
OMe
2k
f1 (ppm)

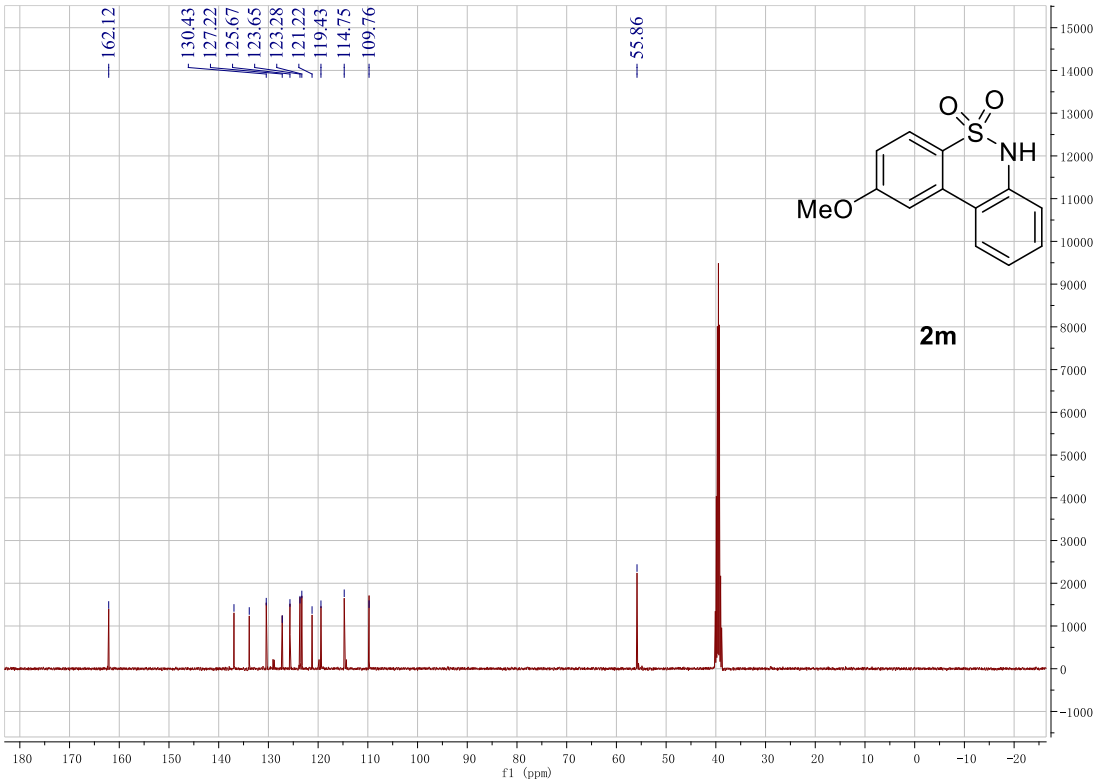

0.97
1.00
1.00
1.00
1.04
0.99
0.99
0.98
3.07
O
O
S
NH
MeO
2k'
f1 (ppm)

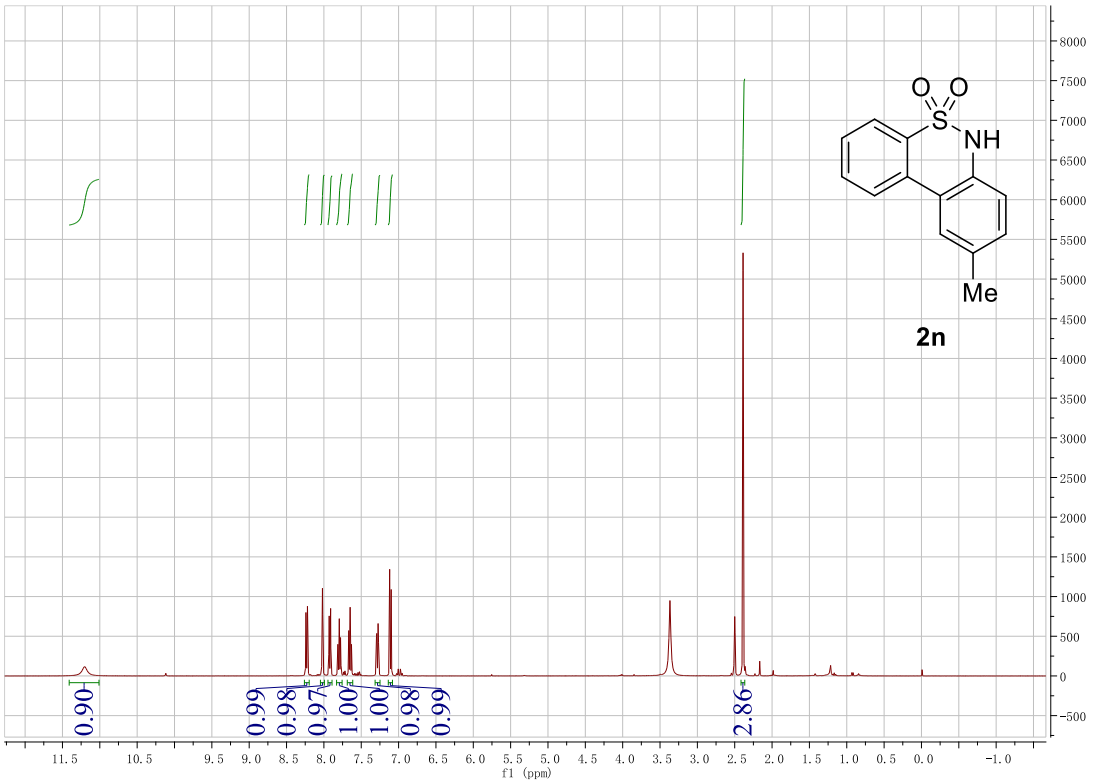

157.63
131.49
130.56
130.36
129.06
127.67
120.60
111.97
111.11
107.08
56.01
O
O
S
NH
MeO
2k'
f1 (ppm)

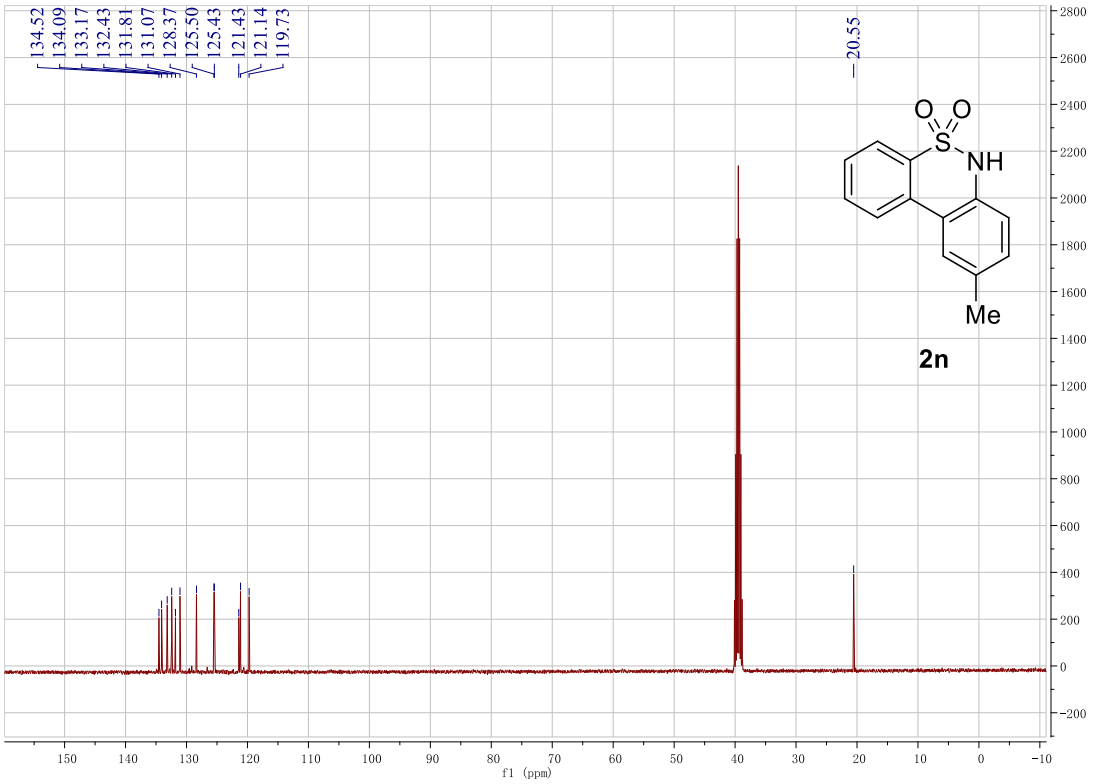

O
O
S
NH
Me
Me
2l
0.96
1.00
1.01
1.01
1.01
1.00
0.99
3.00
3.04
f1 (ppm)

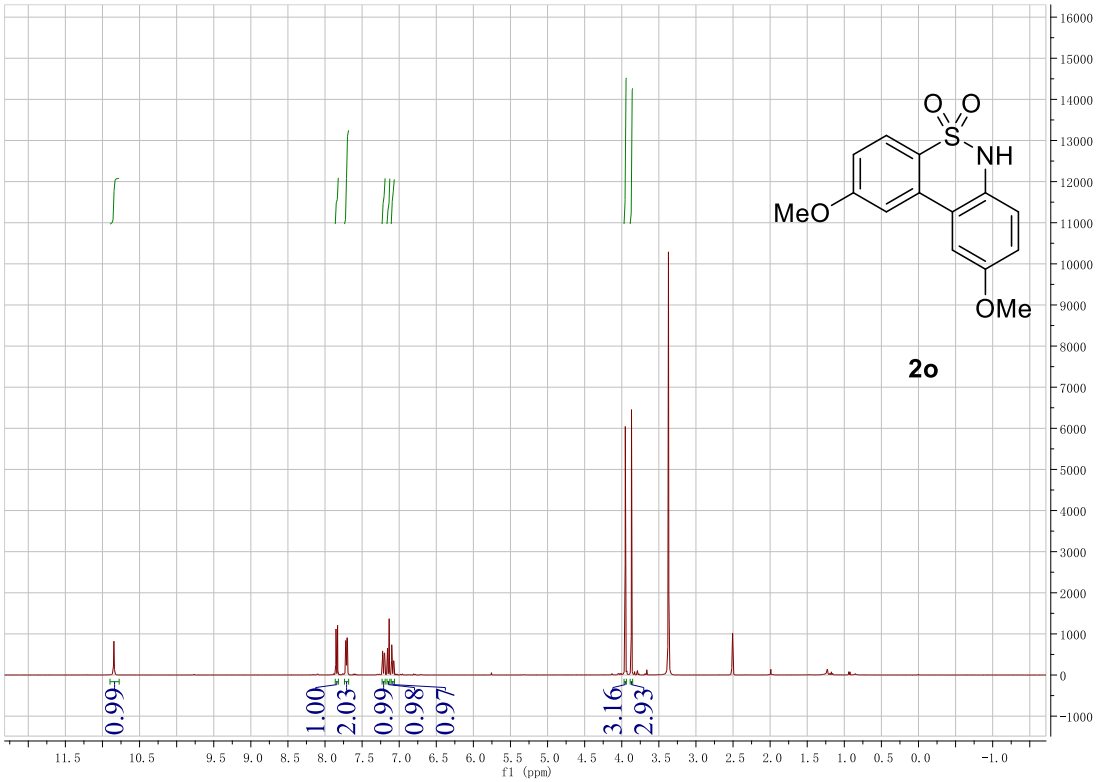

139.05
137.04
135.98
135.92
131.94
131.26
129.06
128.49
127.39
120.96
119.66
117.67
22.63
20.67
O
O
S
NH
Me
Me
2l
f1 (ppm)

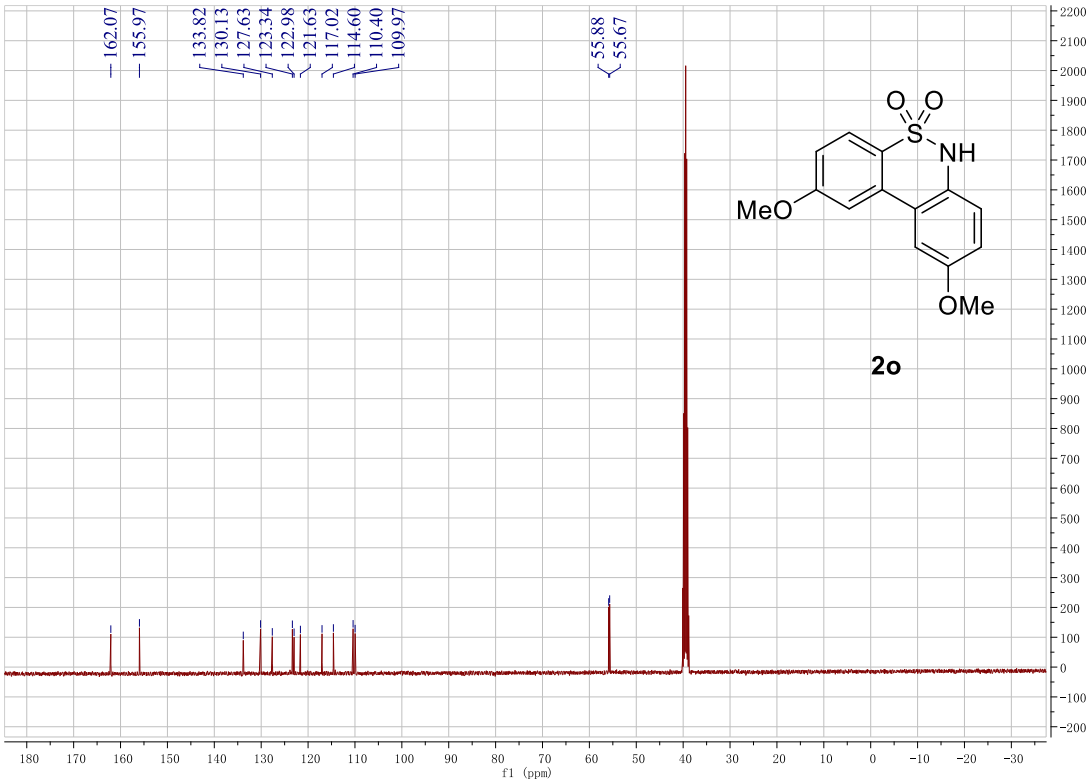

O
O
S
NH
MeO
2m
0.89
0.99
0.98
1.07
1.00
1.02
2.05
3.01
f1 (ppm)


162.12
130.43
127.22
125.67
123.65
123.28
121.22
119.43
114.75
109.76
55.86
O
O
S
NH
MeO
2m
f1 (ppm)


O
O
S
NH
Me
2n
0.90
0.99
0.98
0.97
1.00
1.00
0.98
0.99
2.86
f1 (ppm)


134.52
134.09
133.17
132.43
131.81
131.07
128.37
125.50
125.43
121.43
121.14
119.73
20.55
O
O
S
NH
Me
2n
f1 (ppm)


O
O
S
NH
MeO
OMe
2o
0.99
1.00
2.03
0.99
0.98
0.97
3.16
2.93
f1 (ppm)


162.07
155.97
133.82
130.13
127.63
123.34
122.98
121.63
117.02
114.60
110.40
109.97
55.88
55.67
O
O
S
NH
MeO
OMe
2o
f1 (ppm)