

Supporting Information

Rhodium-catalyzed C–H activation/cyclization of aryl sulfoximines with iodonium ylides towards polycyclic 1,2-benzothiazines

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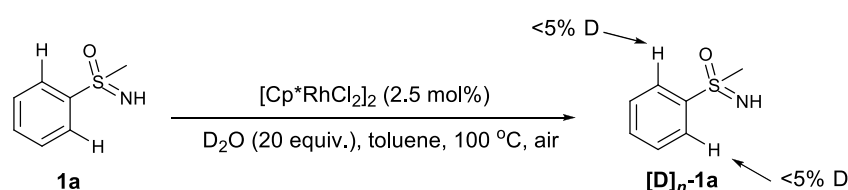
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1. General Considerations

Unless otherwise noted, all chemicals were purchased and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a 300 or 400 MHz NMR spectrometer (75 or 100 MHz for ^{13}C). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to CDCl_3 (d 7.26 or 77.0 ppm) as the internal standard. The coupling constants J are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). *S*-Aryl sulfoximines¹ and iodonium ylides² were prepared according to the previous reports.

2. Mechanism Studies

(1) The H/D exchange experiment



To an oven-dried Schlenk tube was sequentially added **1a** (0.2 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (2.5 mol%), D_2O (20 equiv.) in toluene (2 mL). Under the atmosphere of air, the mixture was heated to 100 °C in an oil bath and stirred for 5 h. After removing of volatile materials from the reaction mixture under vacuum, the crude residue was purified by silica gel column chromatography to give a mixture of deuterated **1a** and **1a**. The deuterated ratio was calculated from ^1H NMR analysis. The ^1H NMR analysis showed that <5% hydrogen of the **1a** was deuterated.

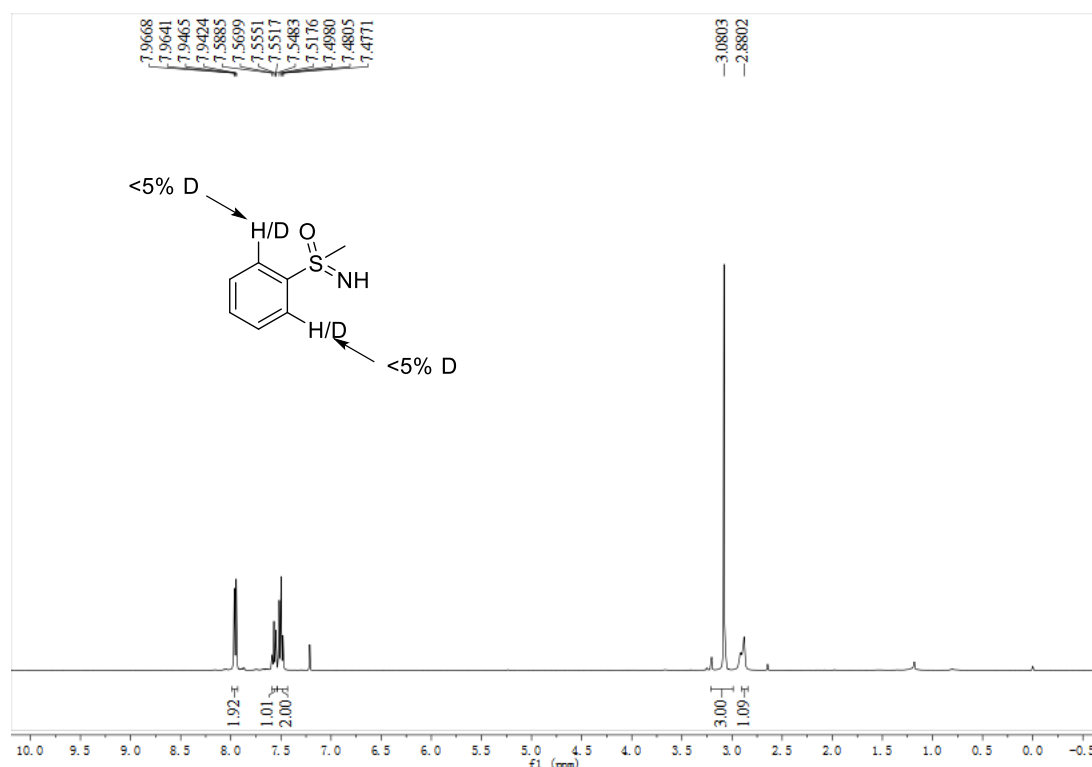
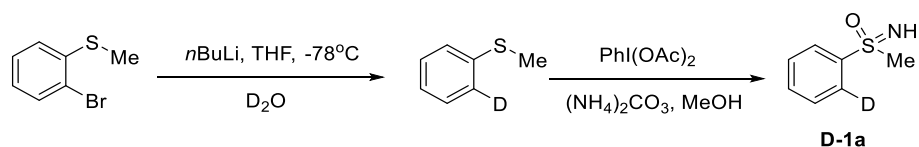


Figure S1 The ^1H NMR spectrum for the H/D exchange experiment

(2) Intramolecular competitive kinetic isotope experiment

¹ S. Li, L. Liu, R. Wang, Y. Yang, J. Li and J. Wei, *Org. Lett.*, 2020, **22**, 7470.

² Y. Jiang, P. Li, J. Zhao, B. Liu and X. Li, *Org. Lett.*, 2020, **22**, 7475.



2-Bromothioanisole (2.03 g, 10 mmol) was dissolved in dry THF (20 mL), the solution was cooled to $-78\text{ }^{\circ}\text{C}$, and *n*BuLi (6.25 mL, 1.6 M, 10 mmol) was added dropwise. After stirring for 1 h at $-78\text{ }^{\circ}\text{C}$, D_2O (4.0 mL) was added dropwise. Then the mixture was stirred for additional 4 h at room temperature. Next, H_2O (20 mL) was added, the phases were separated, and the aqueous layer was extracted by DCM. The combined organic layers were dried over anhydrous Na_2SO_4 , filtered, concentrated, and the crude product was purified by distillation under reduced pressure to give a colorless oil. The subsequent two steps (oxidation of the sulfide to the sulfoxide and subsequent imination of sulfoxide to the sulfoximine) were carried out according to the literature procedure.³ ^1H NMR (300 MHz, CDCl_3) δ 8.00-7.98 (m, 1H), 7.63-7.58 (m, 1H), 7.56-7.51 (m, 2H), 3.09 (s, 3H).

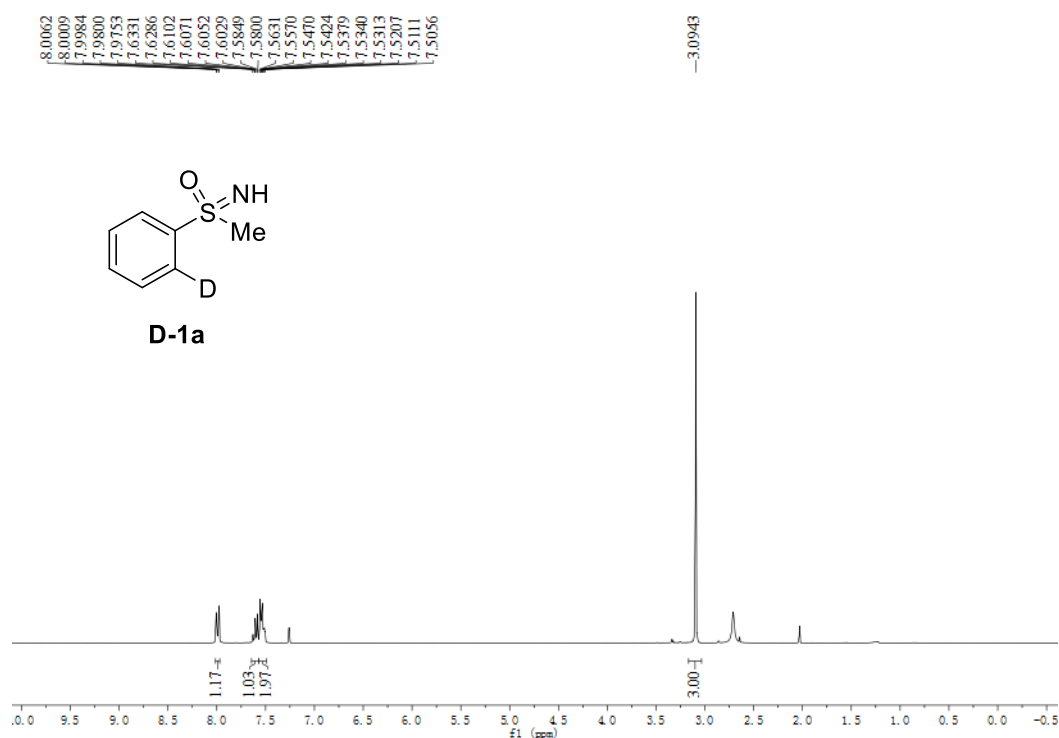
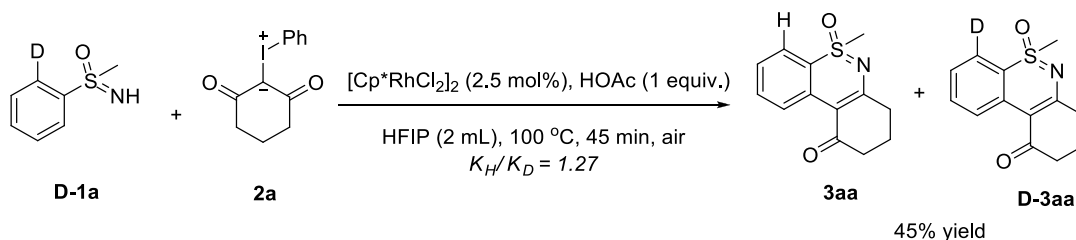


Figure S2 The ^1H NMR spectrum for **D-1a**.



To an oven-dried Schlenk tube was sequentially added **D-1a** (0.2 mmol), **2a** (0.24 mmol, 1.2 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (2.5 mol%), HOAc (1.0 equiv), HFIP (2 mL). Under air atmosphere, the reaction mixture was heated to $100\text{ }^{\circ}\text{C}$ in an oil bath and stirred for 45 min. After removing of volatile materials from the reaction mixture under vacuum, the crude residue was purified by silica

³ W. Dong, L. Wang, K. Parthasarathy, F. Pan and C. Bolm, *Angew. Chem. Int. Ed.*, 2013, **52**, 11573.

gel column chromatography to give a mixture of **[D]-3aa** and **3aa**. The deuterated ratio was calculated from ^1H NMR analysis. The ^1H NMR analysis showed that 56% hydrogen was deuterated. ^1H NMR (300 MHz, CDCl_3) δ 9.02 (dd, $J = 8.6, 1.1$ Hz, 1H), 7.61 (dd, $J = 8.0, 1.5$ Hz, 0.44H), 7.42-7.36 (m, 1H), 3.34 (s, 3H), 2.72 (td, $J = 6.1, 1.5$ Hz, 2H), 2.52 (t, $J = 6.2$ Hz, 2H), 1.99-1.90 (m, 2H).

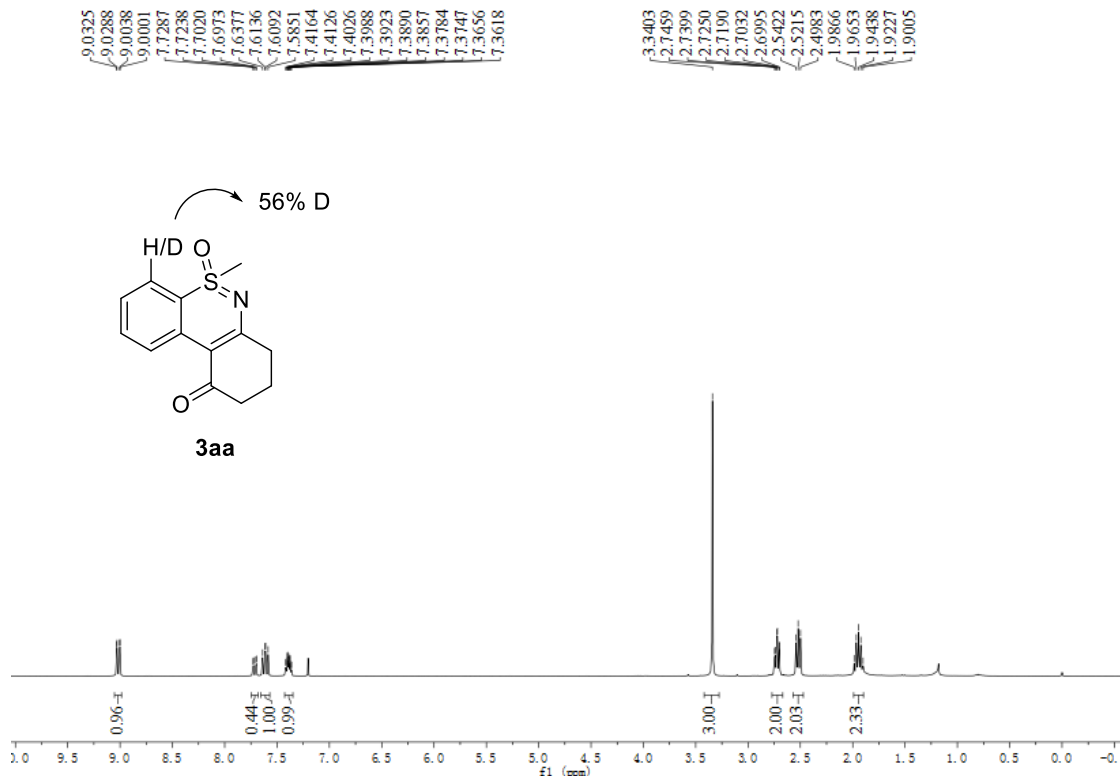
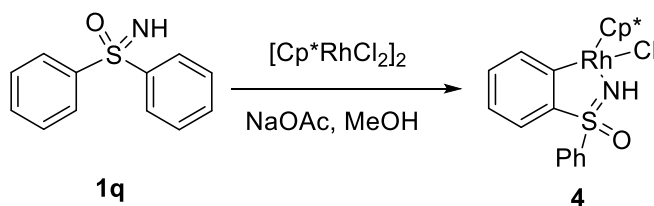


Figure S3 The ^1H NMR spectrum for the mixture of **[D]-3aa** and **3aa**.

(2) Synthesis and application of Rh(III) complex **4**.



According to the literature,⁴ **1q** (0.2 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (0.1 mmol, 61.8 mg), and NaOAc (0.8 mmol) were stirred overnight in MeOH (4 mL) at room temperature. The solvent was then removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 , and filtered to remove NaOAc. Column chromatography was performed on silica gel using ethyl acetate (EA)/petroleum ether (PE) to afford complex **4**. ^1H NMR (300 MHz, CDCl_3) δ 8.12 (d, $J = 7.2$ Hz, 2H), 7.77 (d, $J = 7.6$ Hz, 1H), 7.55-7.50 (m, 1H), 7.47-7.42 (m, 2H), 7.32-7.29 (m, 1H), 7.00-6.94 (m, 2H), 5.29 (s, 1H), 1.69 (s, 15H).

⁴ B. Shen, B. Wan and X. Li, *Angew. Chem. Int. Ed.*, 2018, **57**, 15534.

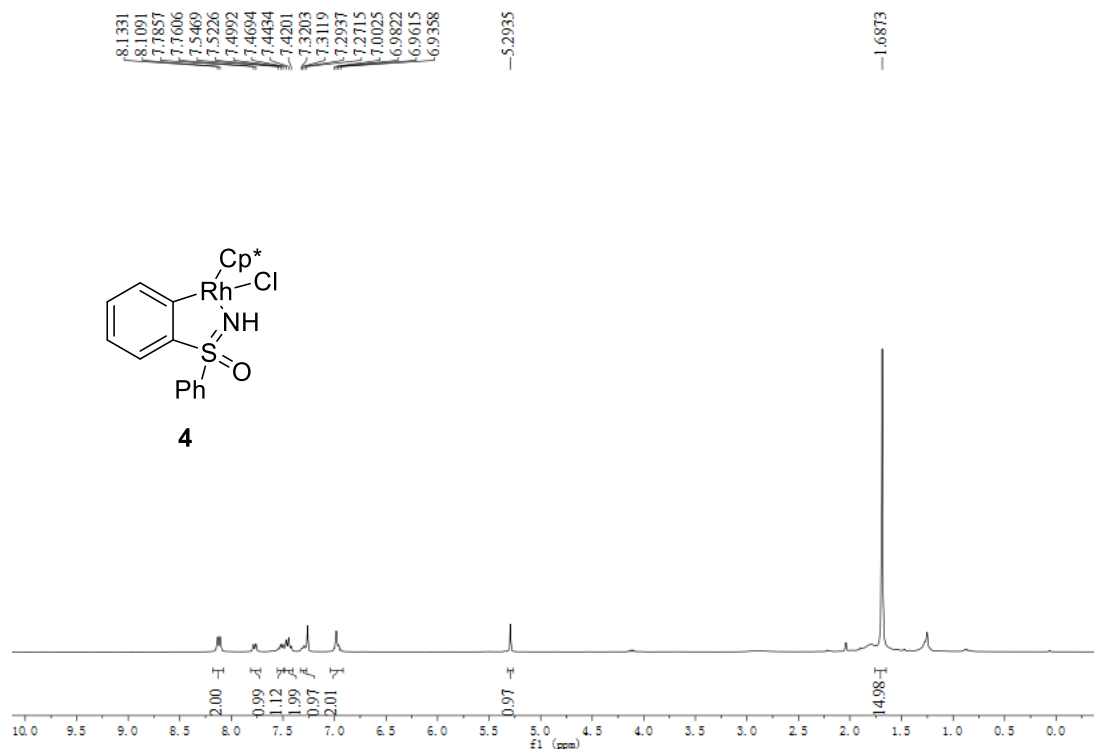
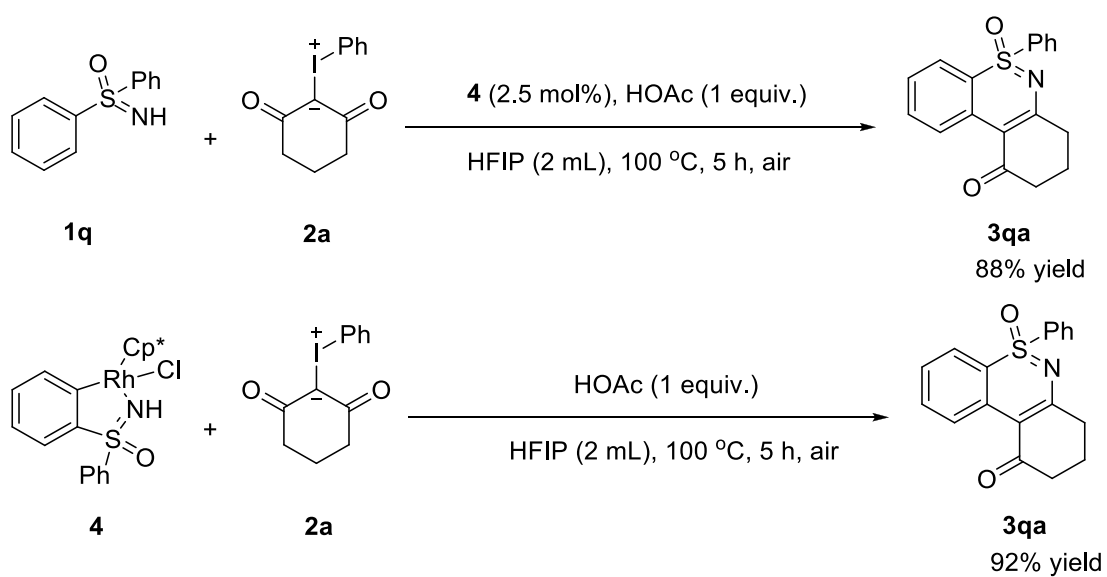


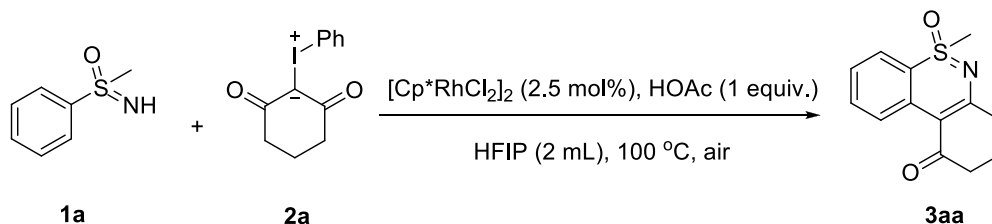
Figure S4 The ^1H NMR for complex **4**.



Rh(III) complex **4** was used as the catalyst or reagent to obtain the target product **3qa** in 88% and 92%, respectively.

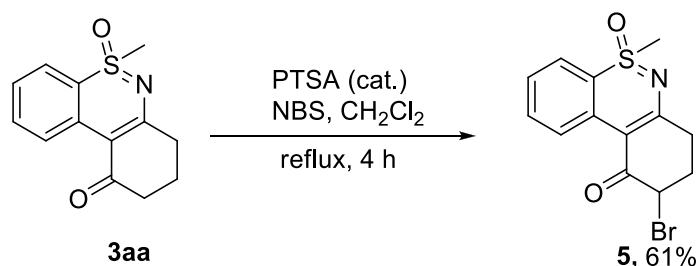
3. General synthetic procedures

(1) Typical procedure for the Rh(III)-catalyzed cyclization reaction of *S*-aryl sulfoximines and iodonium ylides



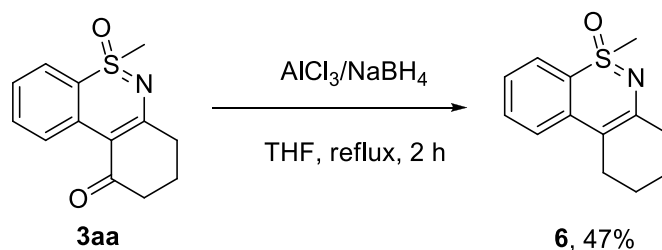
Under air, a 20 mL Schlenk tube equipped with a stir bar was charged with **1a** (31 mg, 0.2 mmol), **2a** (0.24 mmol, 1.2 equiv), [Cp^{*}RhCl₂]₂ (2.5 mol%), HOAc (1.0 equiv), HFIP (2 mL) and sealed with a Teflon lined cap. The reaction mixture was stirred at 100 °C for 5 h in oil bath. After removing of volatile materials from the reaction mixture under vacuum, the resulted residue was purified by silica gel (300–400 mesh) column chromatography using petroleum ether and ethyl acetate as eluents to obtain **3aa** in 89% yield.

(2) Synthesis 9-Bromo-5-methyl-8,9-dihydrodibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide ⁵



Under air, a 20 mL Schlenk tube equipped with a stir bar was charged with **3aa** (49.4 mg, 0.2 mmol), PTSA (20 mol%, 0.02 mmol), NBS (35.6 mg, 0.2 mmol), CH₂Cl₂ (2.0 mL) and sealed with a Teflon lined cap. The reaction mixture was stirred at reflux temperature for 4 h in oil bath. The mixture was allowed to warm to room temperature. Then, the mixture was extracted with CH₂Cl₂ (5 mL×3). The combined organic layer was dried over anhydrous Na₂SO₄ and then filtered. After evaporation of the volatile materials under vacuum, the resulting residue was purified by flash chromatography using a mixture of ethyl acetate and hexanes (hexanes/ethyl acetate = 3:1) to afford 9-bromo-5-methyl-8,9-dihydrodibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide **5** (38.9 mg, 61%).

(3) Synthesis 5-Methyl-7,8,9,10-tetrahydro-dibenzo[c,e][1,2]thiazine 5-oxide ⁶



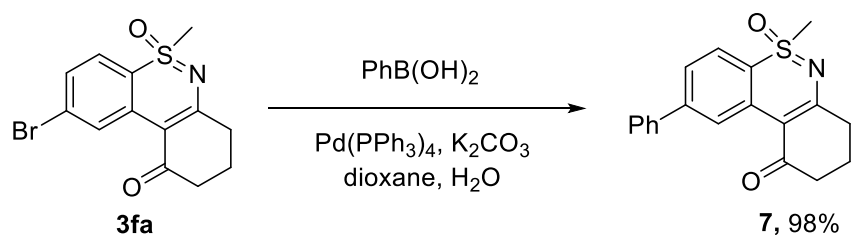
Under air, a 20 mL Schlenk tube equipped with a stir bar was charged with **3aa** (49.4 mg, 0.2

⁵ T. A. Salama and Z. Novák, *Tetrahedron Lett.*, 2011, **2**, 4026.

⁶ A. Ono, T. Maruyama and N. Suzuki, *Synth. Commun.*, 1987, **17**, 1001.

mmol), NaBH₄ (19.0 mg, 0.5 mmol), AlCl₃ (40 mg, 0.3 mmol) and THF (2.0 mL) sealed with a Teflon lined cap. The reaction mixture was stirred at reflux temperature for 2 h in oil bath. The mixture was cooled to room temperature. Then, H₂O (2.0 mL) was added to the mixture, and the mixture was extracted with EtOAc (5 mL×3). The combined organic layer was dried over anhydrous Na₂SO₄ and then filtered. After evaporation of the volatile materials under vacuum, the resulting residue was purified by flash chromatography using a mixture of ethyl acetate and hexanes (hexanes/ethyl acetate = 4:1) to afford 5-methyl-7,8,9,10-tetrahydro-dibenzo[c,e][1,2]thiazine 5-oxide **6** (21.9 mg, 47%).

(4) Synthesis 5-Methyl-2-phenyl-8,9-dihydro-5-dibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide⁷

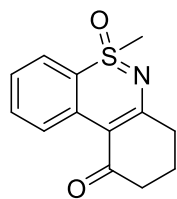


Under N₂, a 20 mL Schlenk tube was equipped with a stir bar and charged with **3fa** (32.5 mg, 0.1 mmol), PhB(OH)₂ (14.6 mg, 0.12 mmol), K₂CO₃ (45.5 mg, 0.66 mmol), Pd(PPh₃)₄ (5.8 mg, 5 mol%), 0.5 mL of dioxane and 0.5 mL of H₂O, sealed with a Teflon lined cap. The mixture was stirred at 100 °C for 3 h. Upon the completion of the reaction, the mixture was poured into ethyl acetate (5 mL×3). The organic layer was separated and dried over Na₂SO₄ and then filtered. The resulting residue was purified by flash chromatography using a mixture of ethyl acetate and hexanes (hexanes/ethyl acetate = 2:1) to afford 5-methyl-2-phenyl-8,9-dihydro-5-dibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide **7** (31.6 mg, 98%).

⁷ H. Xiong, X. Wu, H. Wang, S. Sun, J-T. Yu and J. Cheng, *Adv. Synth. Catal.*, 2019, **361**, 3538.

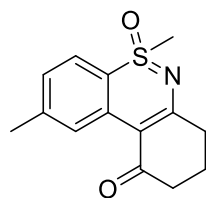
4. Characterization data for the products

5-Methyl-8,9-dihydrodibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide (3aa)⁸



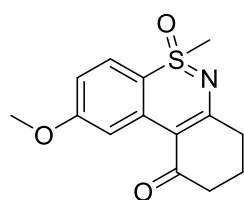
Purification by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 2:1) gave **3aa** (43.9 mg, 89% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 9.05 (dd, *J* = 8.6, 3.6 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.66-7.62 (m, 1H), 7.44-7.39 (m, 1H), 3.38 (s, 3H), 2.76-2.74 (m, 2H), 2.57-2.53 (m, 2H), 2.00-1.94 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 196.3, 166.3, 134.1, 133.9, 127.3, 126.8, 123.3, 118.7, 108.5, 44.7, 39.4, 35.2, 20.8.

2,5-Dimethyl-8,9-dihydrodibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide (3ba)



Purification by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 2:1) gave **3ba** (44.4 mg, 85% yield) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 8.90 (s, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.29-7.27 (m, 1H), 3.38 (s, 3H), 2.80-2.76 (m, 2H), 2.59 (t, *J* = 6.4 Hz, 2H), 2.48 (s, 3H), 2.02-1.99 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 196.4, 166.4, 145.0, 134.2, 128.0, 127.2, 123.3, 116.1, 108.4, 45.0, 39.5, 35.3, 22.4, 20.9. HRMS (ESI) *m/z* calcd for C₁₄H₁₅NNaO₂S⁺ [M+Na]⁺: 284.0716, found 284.0718.

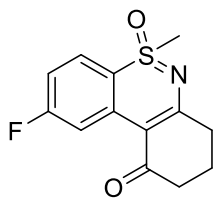
2-Methoxy-5-methyl-8,9-dihydrodibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide (3ca)



Purification by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 1:1) gave **3ca** (50.9 mg, 92% yield) as a yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 8.75 (d, *J* = 2.5 Hz, 1H), 7.67 (d, *J* = 8.9 Hz, 1H), 6.98 (dd, *J* = 8.9, 2.6 Hz, 1H), 3.90 (s, 3H), 3.34 (s, 3H), 2.77 (td, *J* = 6.1, 1.8 Hz, 2H), 2.57 (t, *J* = 6.4 Hz, 2H), 2.02-1.96 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 196.6, 167.2, 163.8, 136.9, 125.4, 116.1, 110.7, 108.7, 107.7, 55.7, 45.7, 39.6, 35.5, 20.9. HRMS (ESI) *m/z* calcd for C₁₄H₁₅NNaO₃S⁺ [M+Na]⁺: 300.0665, found 300.0666.

2-Fluoro-5-methyl-8,9-dihydrodibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide (3da)

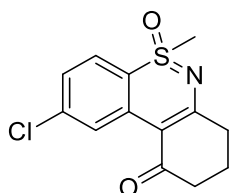
⁸ Y. Cheng and C. Bolm, *Angew. Chem. Int. Ed.*, 2015, **54**, 12349.



Purification by flash column chromatography on silica gel (petroleum ether:

ethyl acetate, 2:1) gave **3da** (38.2 mg, 72% yield) as a yellow liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.93 (dd, $J = 12.8, 2.6$ Hz, 1H), 7.79 (dd, $J = 8.8, 5.6$ Hz, 1H), 7.19-7.14 (m, 1H), 3.40 (s, 3H), 2.79 (td, $J = 6.1, 1.6$ Hz, 2H), 2.58 (t, $J = 6.6$ Hz, 2H), 2.04-1.98 (m, 2H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 196.2, 167.3, 165.8 (d, $J_{\text{C-F}} = 251.6$ Hz), 137.3 (d, $J_{\text{C-F}} = 12.0$ Hz), 126.3 (d, $J_{\text{C-F}} = 10.4$ Hz), 115.3 (d, $J_{\text{C-F}} = 24.7$ Hz), 114.6 (d, $J_{\text{C-F}} = 2.3$ Hz), 113.5 (d, $J_{\text{C-F}} = 26.5$ Hz), 107.7 (d, $J_{\text{C-F}} = 2.9$ Hz), 45.5, 39.40, 35.3, 20.8. HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{12}\text{FNNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 288.0465, found 288.0461.

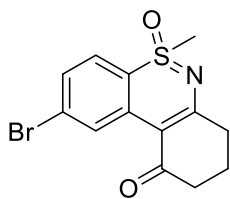
2-Chloro-5-methyl-8,9-dihydrodibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide (3ea)



Purification by flash column chromatography on silica gel (petroleum ether:

ethyl acetate, 2:1) gave **3ea** (50.0 mg, 89% yield) as a white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.19 (d, $J = 2.1$ Hz, 1H), 7.70 (d, $J = 8.5$ Hz, 1H), 7.41 (dd, $J = 8.6, 2.1$ Hz, 1H), 3.40 (s, 3H), 2.80-2.76 (m, 2H), 2.57 (t, $J = 6.2$ Hz, 2H), 2.03-1.96 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 196.1, 167.2, 140.8, 135.6, 127.2, 127.0, 124.8, 116.6, 107.7, 45.1, 39.4, 35.3, 20.8. HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{12}\text{ClNNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 304.0169, found 304.0175.

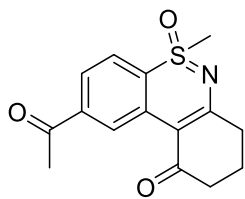
2-Bromo-5-methyl-8,9-dihydrodibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide (3fa)



Purification by flash column chromatography on silica gel (petroleum ether:

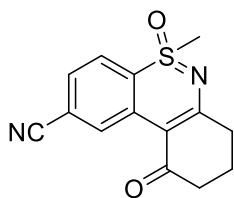
ethyl acetate, 2:1) gave **3fa** (59.2 mg, 91% yield) as a white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.34 (t, $J = 1.8$ Hz, 1H), 7.62 (d, $J = 8.5$ Hz, 1H), 7.57-7.54 (m, 1H), 3.39 (s, 3H), 2.78 (t, $J = 6.4$ Hz, 2H), 2.58-2.55 (m, 2H), 2.02-1.96 (m, 2H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 196.0, 167.2, 135.6, 130.0, 130.0, 129.5, 124.7, 117.0, 107.6, 45.0, 39.4, 35.3, 20.7. HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{12}\text{BrNNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 347.9664, found 347.9656.

2-Acetyl-5-methyl-8,9-dihydrodibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide (3ga)



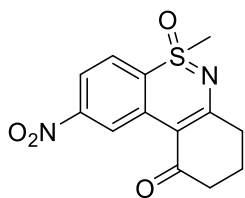
Purification by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 1:1) gave **3ga** (50.3 mg, 87% yield) as a yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 9.78 (d, $J = 1.6$ Hz, 1H), 7.99 (dd, $J = 8.3, 1.7$ Hz, 1H), 7.84 (d, $J = 8.4$ Hz, 1H), 3.48 (s, 3H), 2.83-2.80 (m, 2H), 2.69 (s, 3H), 2.62-2.58 (m, 2H), 2.06-1.99 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 198.0, 196.5, 167.0, 140.7, 134.6, 128.6, 125.2, 123.5, 120.9, 108.5, 44.5, 39.4, 35.2, 27.0, 20.8. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 312.0665, found 312.0668.

5-Methyl-10-oxo-7,8,9,10-tetrahydrodibenzo[c,e][1,2]thiazine-2-carbonitrile 5-oxide (3ha)



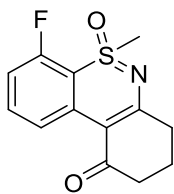
Purification by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 1:1) gave **3ha** (34.3 mg, 63% yield) as a yellow liquid. ^1H NMR (300 MHz, CDCl_3) δ 9.54 (d, $J = 1.4$ Hz, 1H), 7.86 (d, $J = 8.2$ Hz, 1H), 7.66 (dd, $J = 8.2, 1.5$ Hz, 1H), 3.49 (s, 3H), 2.82 (t, $J = 6.1$ Hz, 2H), 2.62-2.57 (m, 2H), 2.07-2.00 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 196.1, 167.6, 134.6, 132.1, 128.8, 124.2, 120.8, 117.7, 117.5, 107.8, 44.5, 39.2, 35.3, 20.7. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{NaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 295.0512, found 295.0513.

5-Methyl-2-nitro-8,9-dihydrodibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide (3ia)



Purification by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 1:1) gave **3ia** (23.4 mg, 40% yield) as a yellow liquid. ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 9.92 (d, $J = 2.3$ Hz, 1H), 8.50 (d, $J = 8.8$ Hz, 1H), 8.31 (dd, $J = 8.8, 2.3$ Hz, 1H), 4.03 (s, 3H), 2.86-2.78 (m, 2H), 2.58-2.53 (m, 2H), 2.00-1.92 (m, 2H). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ 196.0, 168.0, 150.4, 133.9, 126.6, 123.4, 121.7, 121.1, 107.7, 42.7, 39.1, 35.1, 20.9. HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{NaO}_4\text{S}^+$ $[\text{M}+\text{Na}]^+$: 315.0410, found 315.0415.

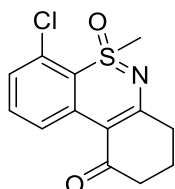
4-Fluoro-5-methyl-8,9-dihydrodibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide (3ja)



Purification by flash column chromatography on silica gel (petroleum ether: ethyl

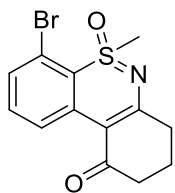
acetate, 2:1) gave **3ja** (37.6 mg, 71% yield) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 9.03 (d, $J = 8.6$ Hz, 1H), 7.68-7.62 (m, 1H), 7.14 (t, $J = 8.4$ Hz, 1H), 3.67 (s, 3H), 2.85-2.81 (m, 2H), 2.65-2.52 (m, 2H), 2.07-1.97 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 196.3, 166.3, 159.2 (d, $J_{\text{C-F}} = 248.4$ Hz), 136.1, 134.8 (d, $J_{\text{C-F}} = 9.2$ Hz), 123.3 (d, $J_{\text{C-F}} = 3.5$ Hz), 112.3 (d, $J_{\text{C-F}} = 19.7$ Hz), 108.6 (d, $J_{\text{C-F}} = 16.4$ Hz), 107.5 (d, $J_{\text{C-F}} = 2.4$ Hz), 47.2 (d, $J_{\text{C-F}} = 6.7$ Hz), 39.7, 35.4, 20.8. HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{12}\text{FNNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 288.0465, found 288.0461.

4-Chloro-5-methyl-8,9-dihydrodibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide (3ka)



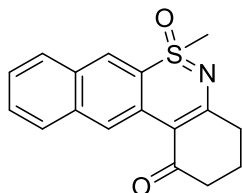
Purification by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 2:1) gave **3ka** (46.1 mg, 82% yield) as a colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ 9.18 (dd, $J = 8.6, 1.1$ Hz, 1H), 7.58 (t, $J = 7.8$ Hz, 1H), 7.44 (dd, $J = 7.8, 1.1$ Hz, 1H), 3.73 (s, 3H), 2.81 (t, $J = 6.3$ Hz, 2H), 2.65-2.51 (m, 2H), 2.03-1.98 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 196.2, 165.6, 137.1, 133.8, 130.08, 128.5, 126.4, 117.6, 107.2, 48.9, 39.7, 35.2, 20.7. HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{12}\text{ClNNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 304.0169, found 304.0175.

4-Bromo-5-methyl-8,9-dihydrodibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide (3la)



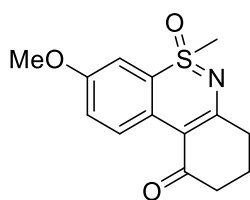
Purification by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 2:1) gave **3la** (52.0 mg, 80% yield) as a white solid. ^1H NMR (300 MHz, CDCl_3) δ 9.19 (dd, $J = 8.6, 1.1$ Hz, 1H), 7.63 (dd, $J = 7.7, 1.1$ Hz, 1H), 7.48 (t, $J = 8.6$ Hz, 1H), 3.74 (s, 3H), 2.79 (t, $J = 5.9$ Hz, 2H), 2.60-2.54 (m, 2H), 2.00 (t, $J = 6.2$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 196.1, 165.3, 137.5, 134.0, 132.5, 127.0, 118.9, 118.2, 107.2, 48.8, 39.7, 35.2, 20.6. HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{12}\text{BrNNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 347.9664, found 347.9656.

6-Methyl-3,4-dihydrobenzo[c]naphtho[2,3-e][1,2]thiazin-1(2H)-one 6-oxide (3ma)



Purification by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 2:1) gave **3ma** (36.2 mg, 61% yield) as a brown liquid. ^1H NMR (300 MHz, CDCl_3) δ 9.54 (s, 1H), 8.39 (s, 1H), 7.97 (d, $J = 8.4$ Hz, 1H), 7.88 (d, $J = 8.2$ Hz, 1H), 7.62-7.56 (m, 1H), 7.52-7.46 (m, 1H), 3.35 (s, 3H), 2.79 (td, $J = 6.0, 1.7$ Hz, 2H), 2.63 (td, $J = 6.2, 1.9$ Hz, 2H), 2.06-2.00 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 196.4, 166.0, 136.2, 130.9, 129.3, 129.2, 128.4, 128.3, 126.8, 126.4, 124.8, 120.5, 108.9, 44.9, 39.5, 35.3, 20.8. HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{15}\text{NNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 320.0716, found 320.0722.

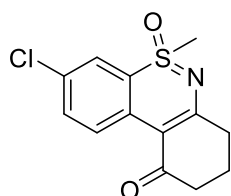
3-Methoxy-5-methyl-8,9-dihydrodibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide (3na)



Purification by flash column chromatography on silica gel (petroleum ether:

ethyl acetate, 1:1) gave **3na** (35.5 mg, 64% yield) as a brown liquid. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 9.05 (d, $J = 9.3$ Hz, 1H), 7.29-7.24 (m, 1H), 7.18 (d, $J = 2.8$ Hz, 1H), 3.88 (s, 3H), 3.38 (s, 3H), 2.76 (td, $J = 6.0, 1.3$ Hz, 2H), 2.57 (t, $J = 6.2$ Hz, 2H), 2.04-1.96 (m, 2H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 196.4, 164.3, 158.1, 129.4, 127.7, 122.1, 119.3, 108.5, 105.5, 55.8, 44.9, 39.4, 34.9, 20.9. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 300.0665, found 300.0666.

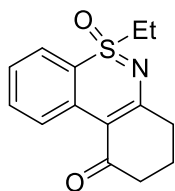
3-Chloro-5-methyl-8,9-dihydrodibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide (3oa)



Purification by flash column chromatography on silica gel (petroleum ether:

ethyl acetate, 2:1) gave **3oa** (34.3 mg, 61% yield) as a colorless liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.11 (d, $J = 9.2$ Hz, 1H), 7.73 (d, $J = 2.4$ Hz, 1H), 7.61 (dd, $J = 9.2, 2.4$ Hz, 1H), 3.43 (s, 3H), 2.81-2.77 (m, 2H), 2.59 (t, $J = 6.6$ Hz, 2H), 2.01 (t, $J = 6.4$ Hz, 2H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 196.3, 166.3, 134.2, 132.6, 132.2, 129.3, 122.6, 119.6, 108.2, 44.9, 39.4, 35.2, 20.7. HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{12}\text{ClNNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 304.0169, found 304.0175.

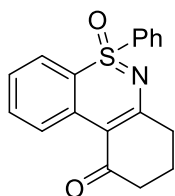
5-Ethyl-8,9-dihydrodibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide (3pa)



Purification by flash column chromatography on silica gel (petroleum ether: ethyl

acetate, 2:1) gave **3pa** (47 mg, 90% yield) as a yellow liquid. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 9.12 (d, $J = 8.2$ Hz, 1H), 7.73-7.64 (m, 2H), 7.46-7.40 (m, 1H), 3.62-3.37 (m, 2H), 2.80 (t, $J = 6.2$ Hz, 2H), 2.58 (t, $J = 6.2$ Hz, 2H), 2.04-1.96 (m, 2H), 1.19 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 196.3, 167.3, 135.5, 134.0, 127.4, 126.7, 123.8, 115.7, 107.9, 51.3, 39.5, 35.4, 20.9, 7.6. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{NNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 284.0716, found 284.0718.

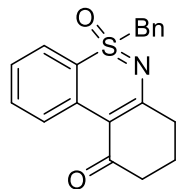
5-phenyl-8,9-dihydrodibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide (3qa)



Purification by flash column chromatography on silica gel (petroleum ether: ethyl

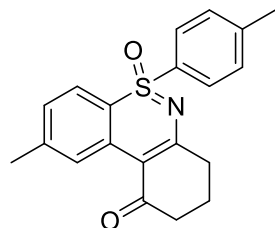
acetate, 2:1) gave **3qa** (58.1 mg, 94% yield) as a yellow liquid. ^1H NMR (300 MHz, CDCl_3) δ 9.12 (d, $J = 8.6$ Hz, 1H), 7.81 (d, $J = 7.5$ Hz, 2H), 7.64-7.50 (m, 4H), 7.25-7.22 (m, 2H), 2.84 (t, $J = 6.2$ Hz, 2H), 2.64-2.49 (m, 2H), 2.05-1.97 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.7, 166.3, 138.7, 134.1, 133.3, 129.4, 128.7, 127.0, 126.7, 124.8, 119.7, 108.3, 39.6, 35.6, 21.0. HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{15}\text{NNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 332.0716, found 332.0721.

5-benzyl-8,9-dihydrodibenzo[*c,e*][1,2]thiazin-10(7*H*)-one 5-oxide (3ra)



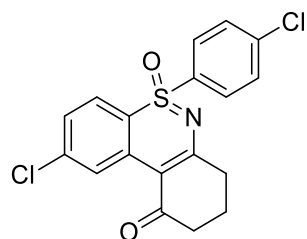
Purification by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 2:1) gave **3ra** (56.8 mg, 88% yield) as a yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.89 (dd, $J = 8.5, 1.1$ Hz, 1H), 7.64-7.62 (m, 1H), 7.57 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.38-7.34 (m, 1H), 7.29-7.27 (m, 1H), 7.19 (t, 7.8, 2H), 6.99 (d, $J = 7.2$ Hz, 2H), 4.51 (d, $J = 13.8$ Hz, 1H), 4.38 (d, $J = 13.8$ Hz, 1H), 2.75-2.63 (m, 2H), 2.52-2.45 (m, 1H), 2.37-2.29 (m, 1H), 1.92-1.85 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.7, 167.7, 136.3, 134.5, 131.1, 129.5, 128.5, 126.9, 126.5, 126.2, 124.8, 115.4, 108.3, 64.5, 39.3, 35.1, 20.7. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{17}\text{NNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 346.0872, found 346.0866.

2-Methyl-5-(*p*-tolyl)-8,9-dihydrodibenzo[*c,e*][1,2]thiazin-10(7*H*)-one 5-oxide (3sa)



Purification by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 2:1) gave **3sa** (61.4 mg, 91% yield) as a yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.99 (s, 1H), 7.71 (d, $J = 8.1$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 8.2$ Hz, 1H), 7.09 (d, $J = 8.1$ Hz, 1H), 2.87 (t, $J = 5.6$ Hz, 2H), 2.67-2.59 (m, 2H), 2.44 (s, 3H), 2.42 (s, 3H), 2.08-2.02 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.7, 166.4, 145.2, 144.1, 136.0, 134.2, 129.9, 128.6, 127.8, 126.8, 124.8, 117.4, 108.1, 39.7, 35.6, 22.4, 21.7, 21.1. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{19}\text{NNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 360.1029, found 360.1032.

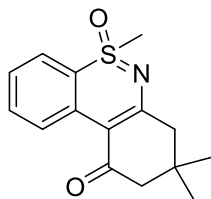
2-Chloro-5-(4-chlorophenyl)-8,9-dihydrodibenzo[*c,e*][1,2]thiazin-10(7*H*)-one 5-oxide (3ta)



Purification by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 2:1) gave **3ta** (60.3 mg, 80% yield) as a yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 9.35 (d, $J = 1.9$ Hz, 1H), 7.83 (d, $J = 8.7$ Hz, 2H), 7.62 (d, $J = 8.7$ Hz, 2H), 7.33-7.28 (m,

2H), 2.96-2.93 (m, 2H), 2.71-2.66 (m, 2H), 2.15-2.10 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.5, 167.0, 141.4, 140.4, 137.1, 135.52, 130.0, 129.8, 127.3, 126.7, 126.3, 117.4, 107.6, 39.6, 35.6, 20.9. HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{13}\text{Cl}_2\text{NNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 399.9936, found 399.9925.

5,8,8-Trimethyl-8,9-dihydrodibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide (3ab)⁹



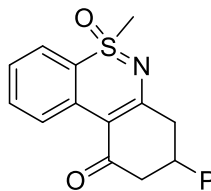
Purification by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 3:1) gave **3ab** (47.3 mg, 86% yield) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 9.19 (dd, $J = 8.5, 1.1$ Hz, 1H), 7.78 (dd, $J = 8.0, 1.4$ Hz, 1H), 7.69-7.65 (m, 1H), 7.47-7.43 (m, 1H), 3.41 (s, 3H), 2.72-2.61 (m, 2H), 2.49-2.40 (m, 2H), 1.08 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 196.5, 164.8, 134.0, 134.0, 127.1, 126.8, 123.3, 118.3, 107.2, 53.2, 48.8, 45.0, 31.6, 28.4, 27.8.

5,8-Dimethyl-8,9-dihydrodibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide (3ac)



Purification by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 3:1) gave **3ac** (41.8 mg, 80% yield) as a white solid. ^1H NMR (300 MHz, CDCl_3) δ 9.16 (d, $J = 8.6$ Hz, 0.64H), 9.08 (d, $J = 8.5$ Hz, 0.36H), 7.77 (td, $J = 7.8, 1.4$ Hz, 1H), 7.69-7.64 (m, 1H), 7.47-7.42 (m, 1H), 3.50 (s, 1.95H), 3.28 (s, 1.05H), 2.82-2.75 (m, 1H), 2.68-2.45 (m, 2H), 2.28-2.21 (m, 2H), 1.10-1.07 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 196.6, 196.4, 165.9, 165.7, 134.4, 134.2, 133.9, 133.7, 127.3, 127.0, 126.9, 126.7, 123.6, 123.0, 118.9, 118.0, 107.9, 47.7, 47.6, 45.2, 44.6, 43.5, 43.1, 28.1, 27.9, 20.9, 20.8. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{NNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 284.0716, found 284.0719.

5-Methyl-8-phenyl-8,9-dihydrodibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide (3ad)

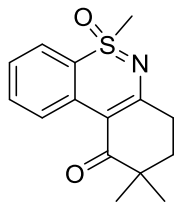


Purification by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 2:1) gave **3ad** (40.6 mg, 63% yield) as a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 9.21 (d, $J = 8.5$ Hz, 0.65H), 9.12 (d, $J = 8.4$ Hz, 0.35H), 7.83-7.78 (m, 1H), 7.71 (t, $J = 7.8$ Hz, 1H), 7.49 (t, $J = 7.5$ Hz, 1H), 7.38-7.33 (m, 2H), 7.30-7.26 (m, 3H), 3.56 (s, 1.95H), 3.47-3.38 (m, 1H), 3.29 (s, 1.05H), 3.07-2.99 (m, 2H), 2.94-2.78 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 195.6, 195.5, 165.6, 165.3, 142.8, 142.7, 134.4, 133.8, 133.8, 128.8, 128.8, 127.5, 127.2, 127.1, 127.0, 126.9, 126.9, 126.7, 123.7, 123.0, 119.1, 118.0, 108.0, 46.5, 46.2, 45.4, 44.6, 42.6,

⁹ Y. Aher, D. Lade and A. Pawar, *Chem. Commun.*, 2018, **54**, 6288.

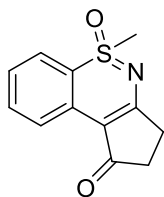
42.3, 38.6, 38.3. HRMS (ESI) m/z calcd for $C_{19}H_{17}NNaO_2S^+$ $[M+Na]^+$: 346.0872, found 346.0868.

5,9,9-Trimethyl-8,9-dihydrodibenzo[*c,e*][1,2]thiazin-10(7*H*)-one 5-oxide (3ae)



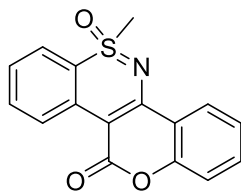
Purification by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 3:1) gave **3ae** (35.8 mg, 65% yield) as a colorless liquid. 1H NMR (300 MHz, $CDCl_3$) δ 9.02 (d, $J = 8.3$ Hz, 1H), 7.77 (dd, $J = 8.0, 1.4$ Hz, 1H), 7.68-7.62 (m, 1H), 7.47-7.42 (m, 1H), 3.39 (s, 3H), 2.83-2.78 (m, 2H), 1.88 (t, $J = 6.4$ Hz, 2H), 1.22 (s, 3H), 1.20 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.5, 164.3, 134.6, 133.7, 127.5, 126.8, 123.2, 119.0, 107.1, 44.8, 41.7, 34.3, 31.4, 25.5, 25.3. HRMS (ESI) m/z calcd for $C_{15}H_{17}NNaO_2S^+$ $[M+Na]^+$: 298.0872, found 298.0870.

5-Methyl-2,3-dihydro-1*H*-benzo[*e*]cyclopenta[*c*][1,2]thiazin-1-one 5-oxide (3af)



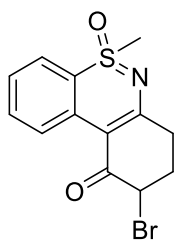
Purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate, 3:1) gave **3af** (36.3 mg, 78% yield) as a colorless liquid. 1H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, $J = 8.2$ Hz, 1H), 7.83 (d, $J = 7.5$ Hz, 1H), 7.72-7.68 (m, 1H), 7.49-7.45 (m, 1H), 3.51 (s, 3H), 2.84-2.81 (m, 2H), 2.57-2.54 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.4, 177.6, 134.6, 132.0, 127.5, 124.2, 123.8, 117.3, 107.9, 46.6, 34.3, 29.7. HRMS (ESI) m/z calcd for $C_{12}H_{11}NNaO_2S^+$ $[M+Na]^+$: 256.0403, found 256.0404.

6-Methylbenzo[*e*]chromeno[4,3-*c*][1,2]thiazin-11-one 6-oxide (3ag)



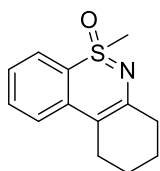
Purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate, 2:1) gave **3ag** (30.9 mg, 52% yield) as a colorless liquid. 1H NMR (300 MHz, $CDCl_3$) δ 9.31 (d, $J = 8.6$ Hz, 1H), 8.25 (dd, $J = 8.2, 1.7$ Hz, 1H), 7.85 (dd, $J = 7.9, 1.4$ Hz, 1H), 7.76-7.70 (m, 1H), 7.53 (d, $J = 7.3$ Hz, 1H), 7.48 (dd, $J = 7.0, 1.5$ Hz, 1H), 7.27-7.22 (m, 2H), 3.50 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5, 153.1, 152.9, 134.4, 133.7, 132.7, 128.0, 127.6, 125.7, 123.9, 123.9, 120.1, 118.6, 116.3, 96.9, 45.9. HRMS (ESI) m/z calcd for $C_{16}H_{11}NNaO_3S^+$ $[M+Na]^+$: 320.0352, found 320.0358.

10-Hydroxy-5-methyl-7,8,9,10-tetrahydrodibenzo[*c,e*][1,2]thiazine 5-oxide (5)



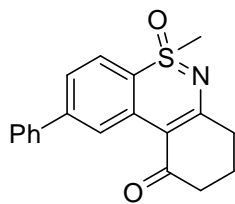
Purification by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 2:1) gave **5** (39.6 mg, 61% yield) as a brown liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.12 (d, $J = 6.5$ Hz, 0.07H), 8.94 (d, $J = 8.5$ Hz, 1H), 7.82 (dd, $J = 6.0, 1.1$ Hz, 1H), 7.73-7.69 (m, 1H), 7.56-7.52 (m, 1H), 7.43 (d, $J = 6.6$ Hz, 0.07H), 5.34 (t, $J = 3.6$ Hz, 0.07H), 5.05 (s, 1H), 3.59 (s, 0.21H), 3.25 (s, 2.79H), 3.08-2.99 (m, 1H), 2.68-2.61 (m, 1H), 2.52-2.43 (m, 1H), 2.39-2.33 (m, 1H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 194.9, 194.6, 162.0, 134.4, 133.8, 133.7, 128.7, 128.3, 128.2, 128.0, 127.8, 123.6, 123.0, 119.0, 108.4, 52.0, 51.8, 44.5, 44.3, 35.1, 35.0, 29.8, 29.7. HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{12}\text{BrNNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 347.9664, found 347.9659.

5-Methyl-7,8,9,10-tetrahydro-dibenzo[c,e][1,2]thiazine 5-oxide (6)



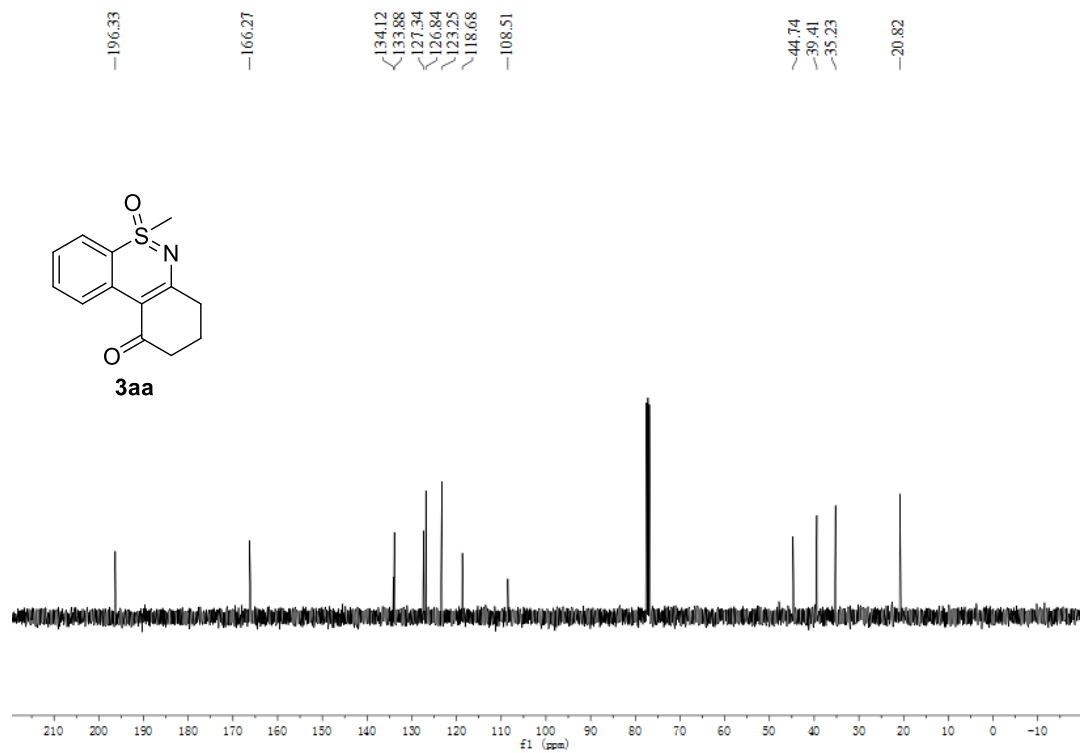
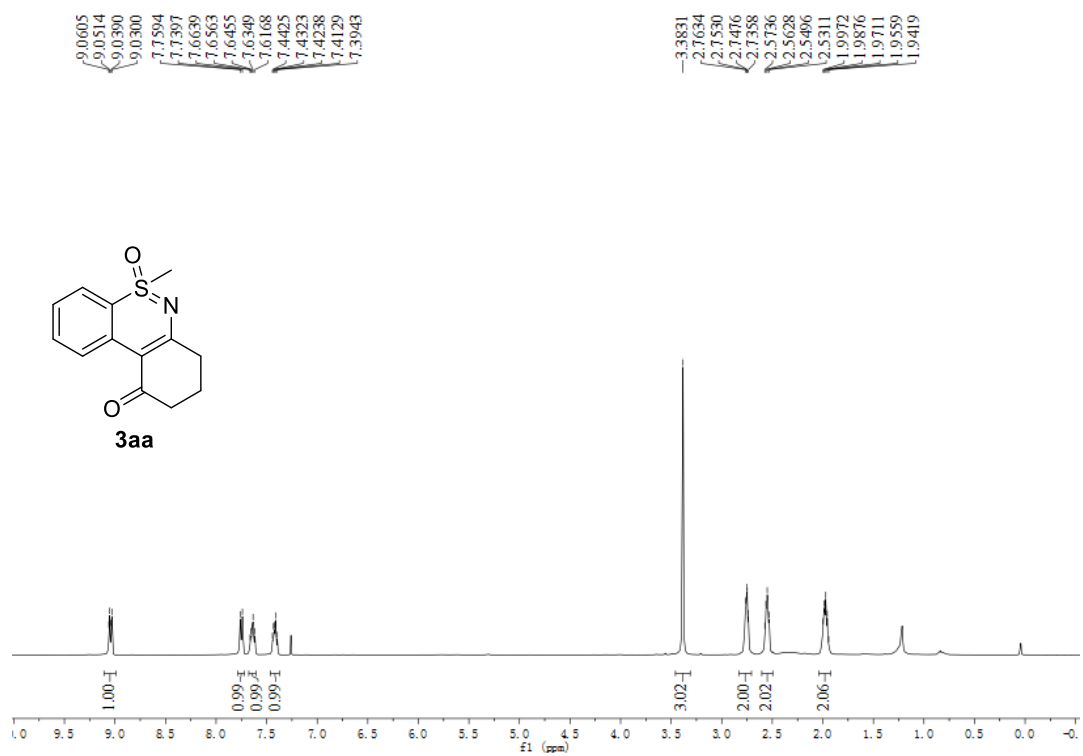
Purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate, 4:1) gave **6** (21.9 mg, 47% yield) as a yellow liquid. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.69 (d, $J = 8.0$ Hz, 1H), 7.54 (t, $J = 7.8$ Hz, 1H), 7.42 (d, $J = 8.6$ Hz, 1H), 7.32 (t, $J = 7.4$ Hz, 1H), 3.50 (s, 3H), 2.50-2.47 (m, 4H), 1.88-1.74 (m, 4H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 144.9, 136.3, 132.5, 125.3, 123.3, 122.3, 119.5, 104.8, 44.4, 33.3, 24.7, 23.0, 22.9. HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{NNaOS}^+$ $[\text{M}+\text{Na}]^+$: 256.0767, found 256.0768.

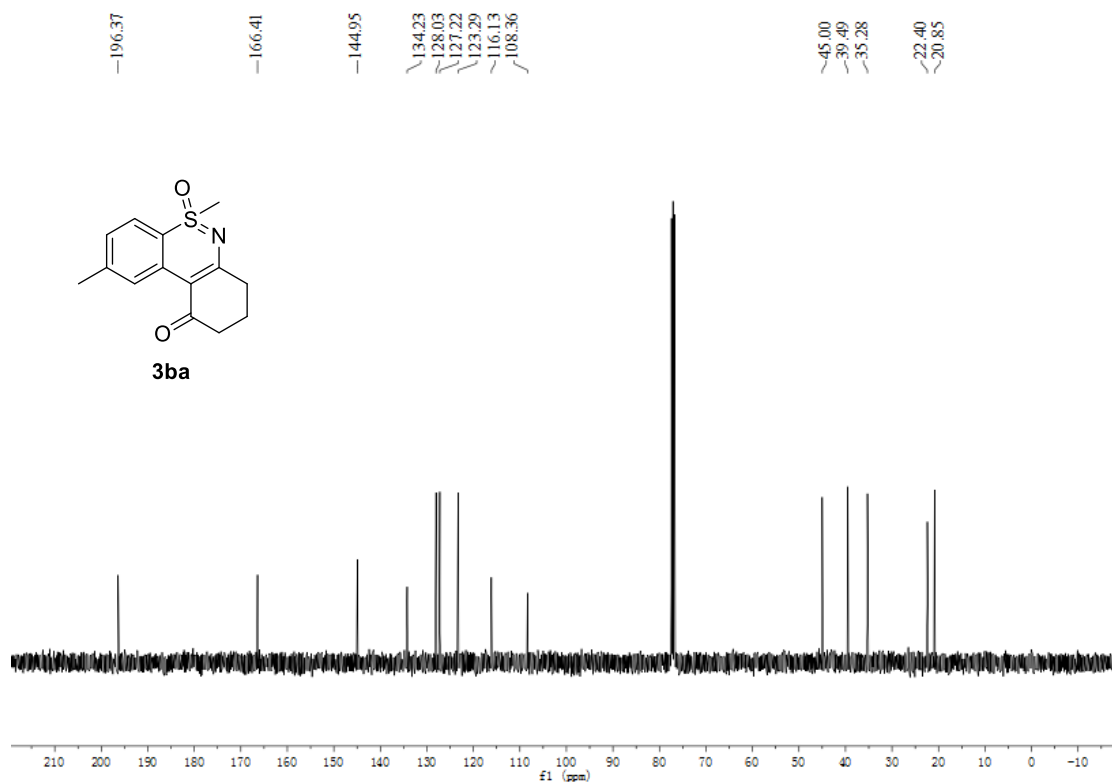
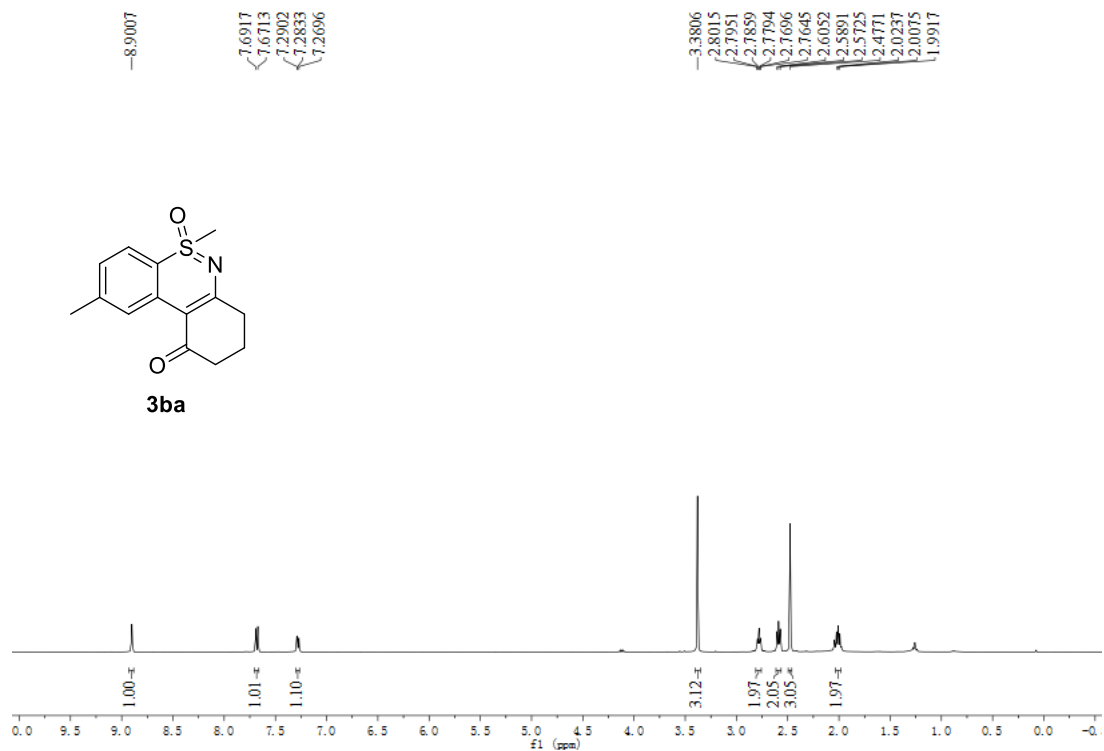
5-Methyl-2-phenyl-8,9-dihydro-5-dibenzo[c,e][1,2]thiazin-10(7H)-one 5-oxide (7)

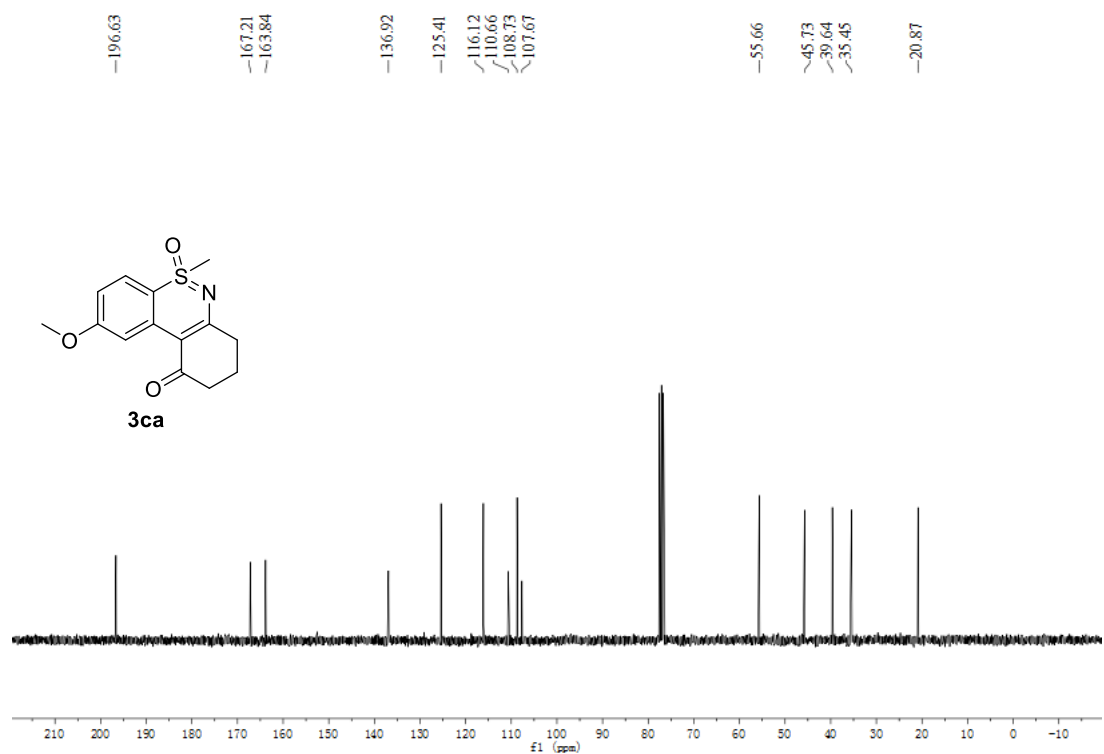
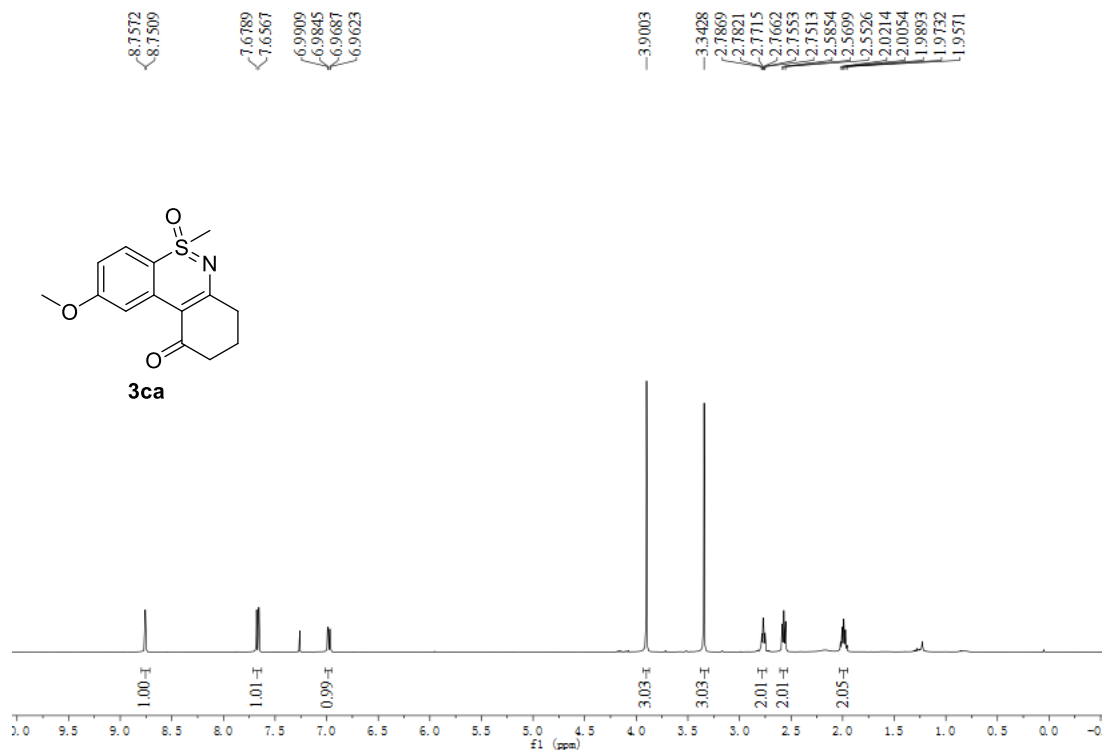


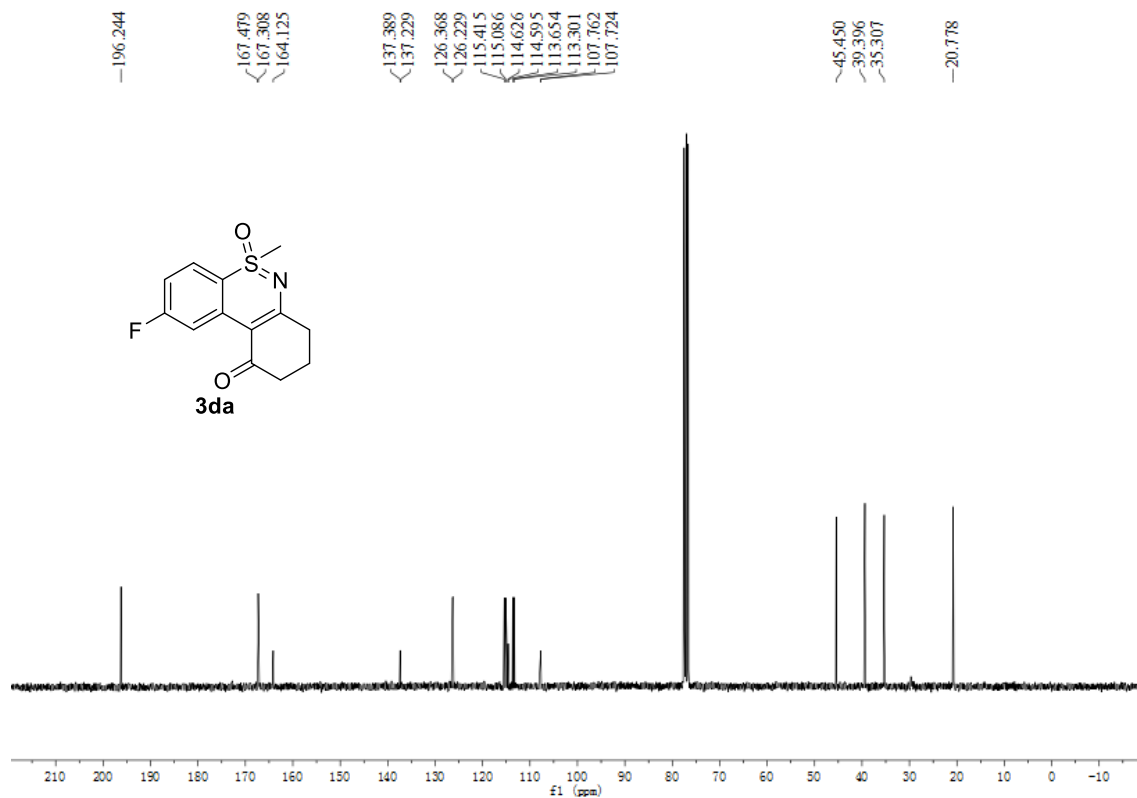
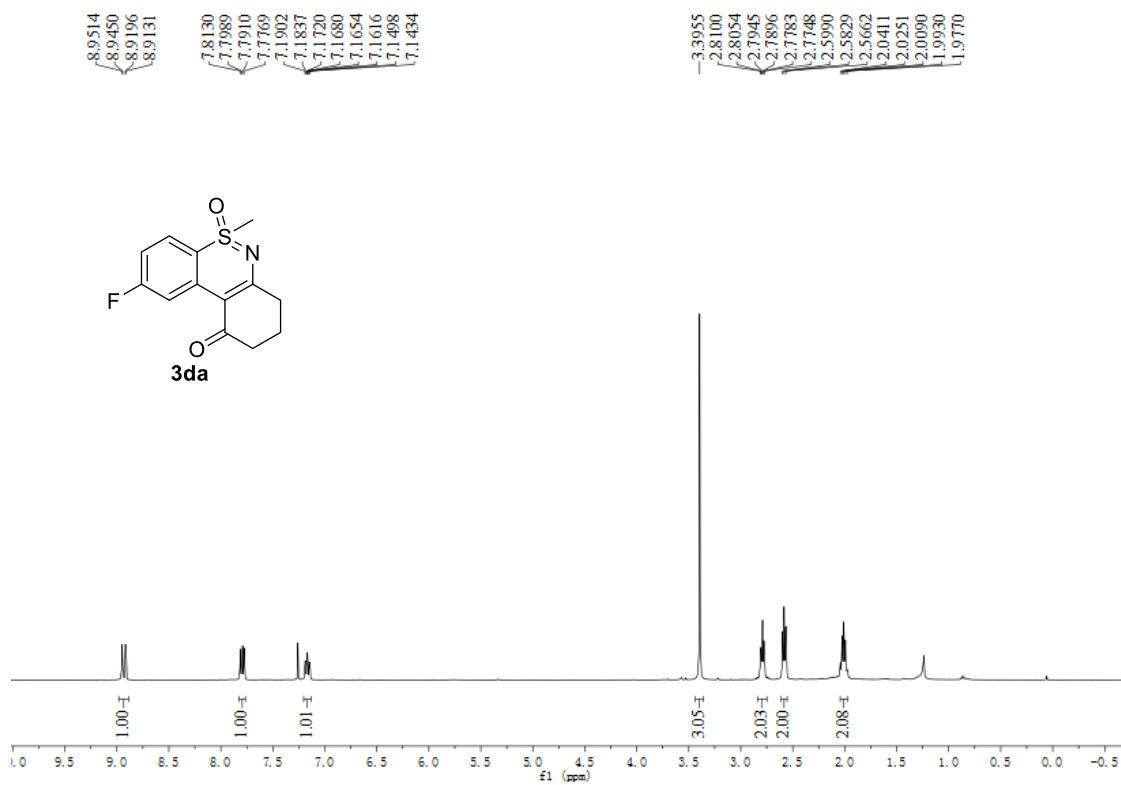
Purification by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 2:1) gave **7** (31.6 mg, 98% yield) as a yellow liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.39 (s, 1H), 7.84 (d, $J = 8.3$ Hz, 1H), 7.68 (d, $J = 7.2$ Hz, 3H), 7.46 (t, $J = 7.3$ Hz, 2H), 7.42-7.38 (m, 1H), 3.43 (s, 3H), 2.83-2.80 (m, 2H), 2.61 (t, $J = 6.5$ Hz, 2H), 2.06-1.99 (m, 2H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 196.5, 166.7, 146.7, 139.7, 134.7, 129.0, 128.6, 127.6, 125.8, 125.7, 123.9, 117.2, 108.6, 45.0, 39.5, 35.3, 20.9. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{17}\text{NNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 346.0872, found 346.0878.

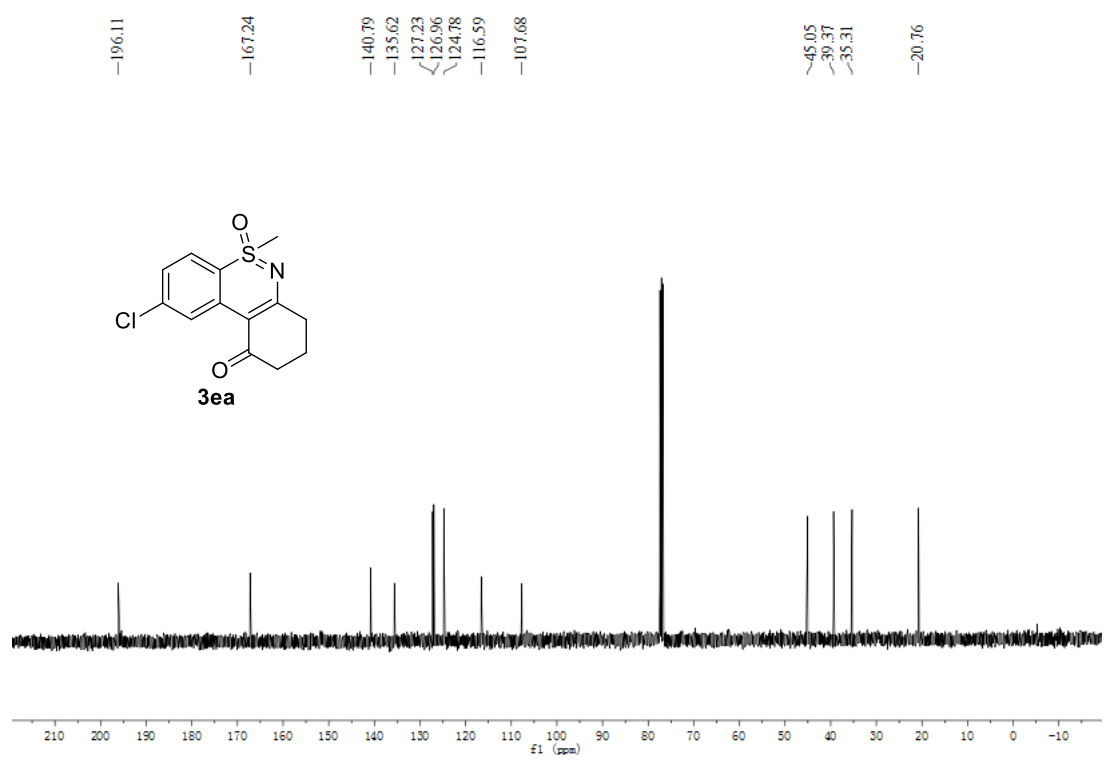
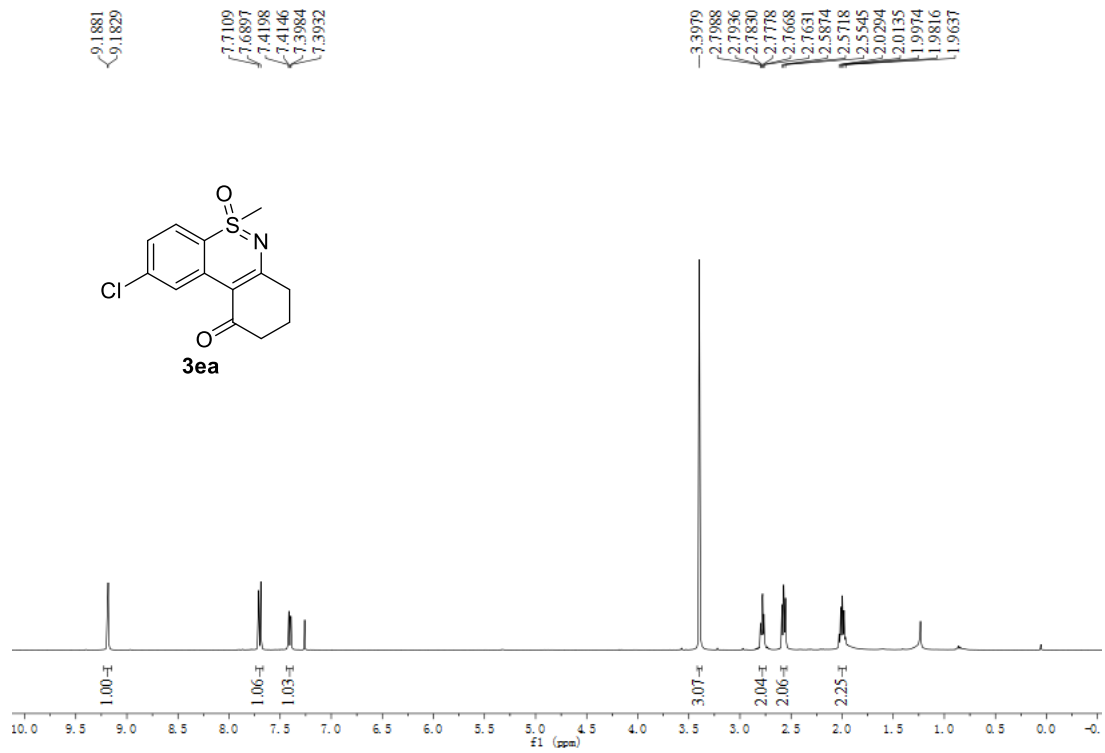
5. Copies of the ^1H NMR and ^{13}C NMR Spectra

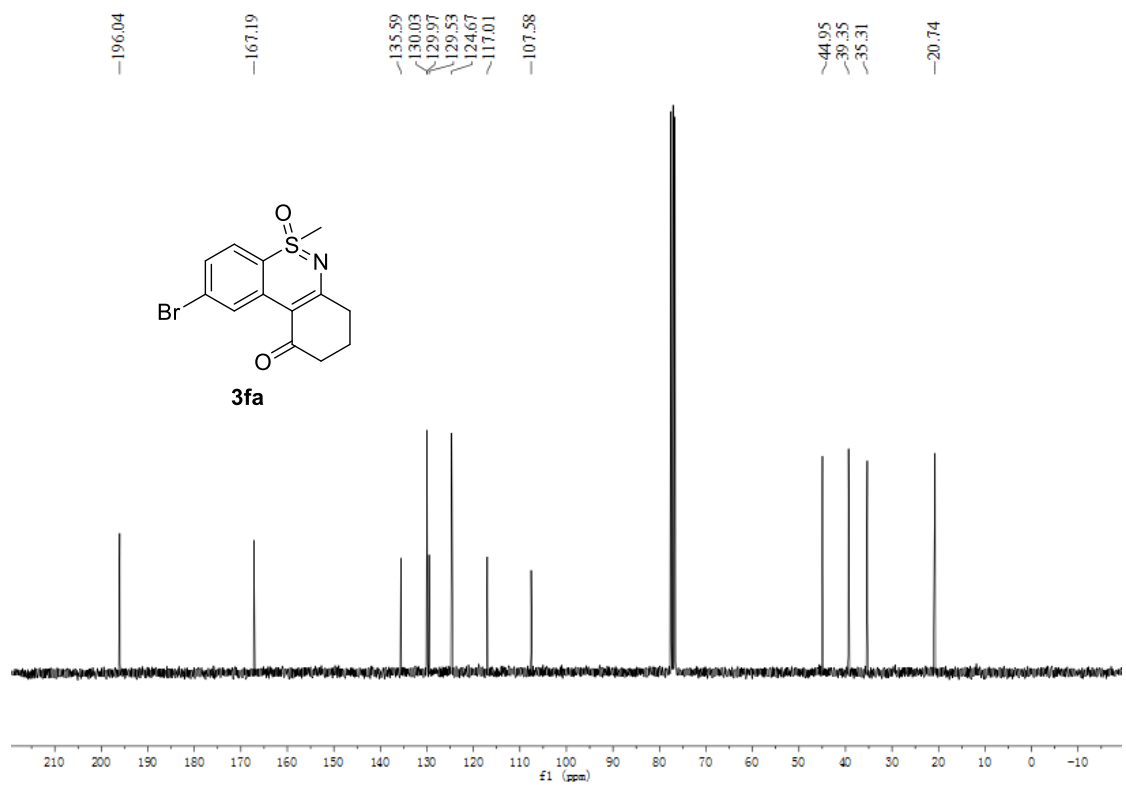
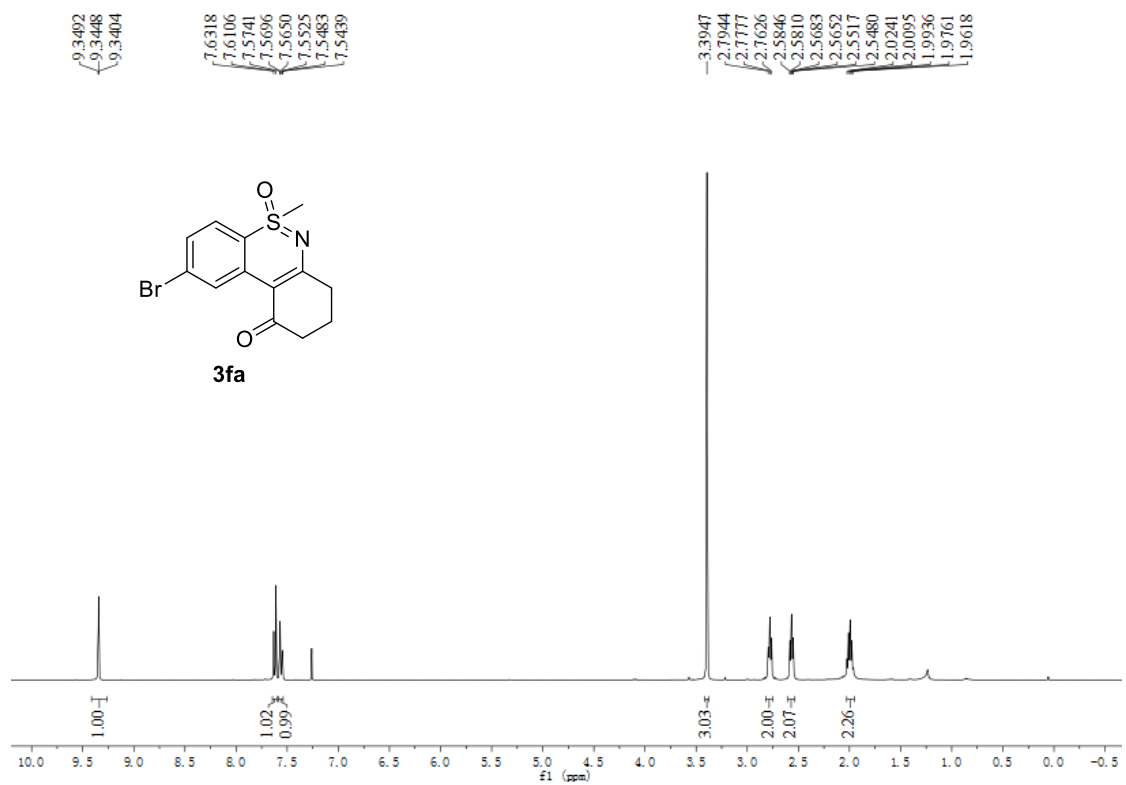


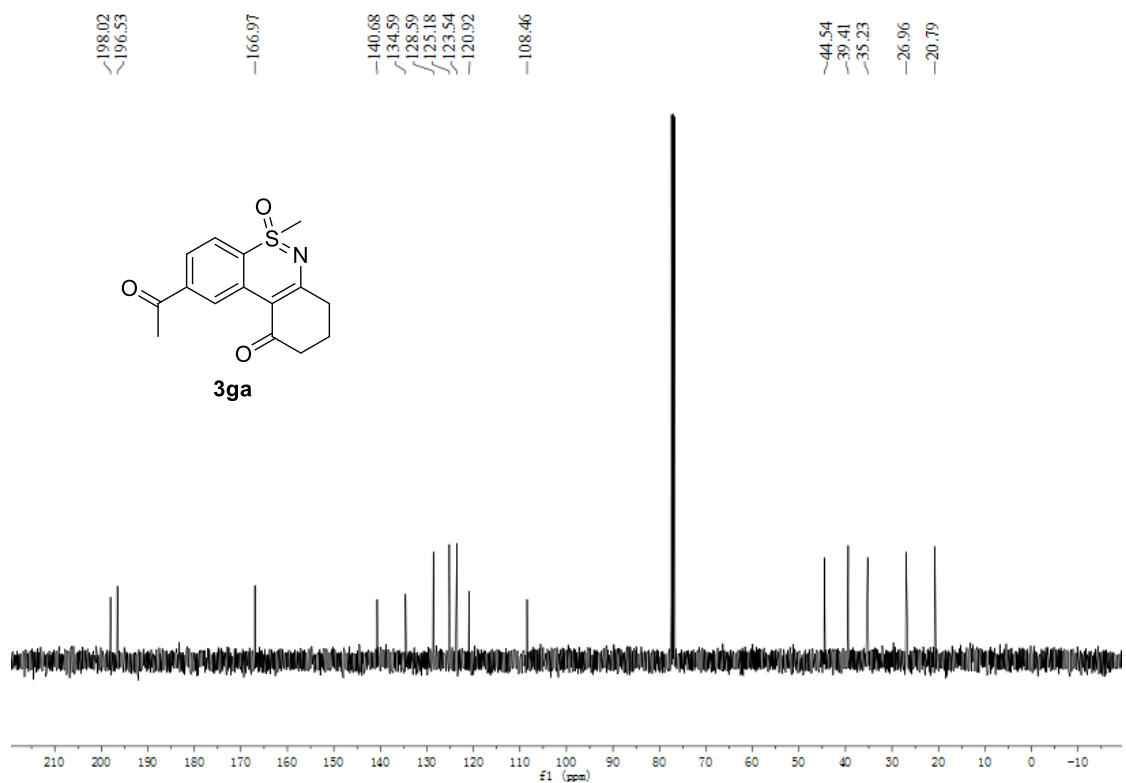
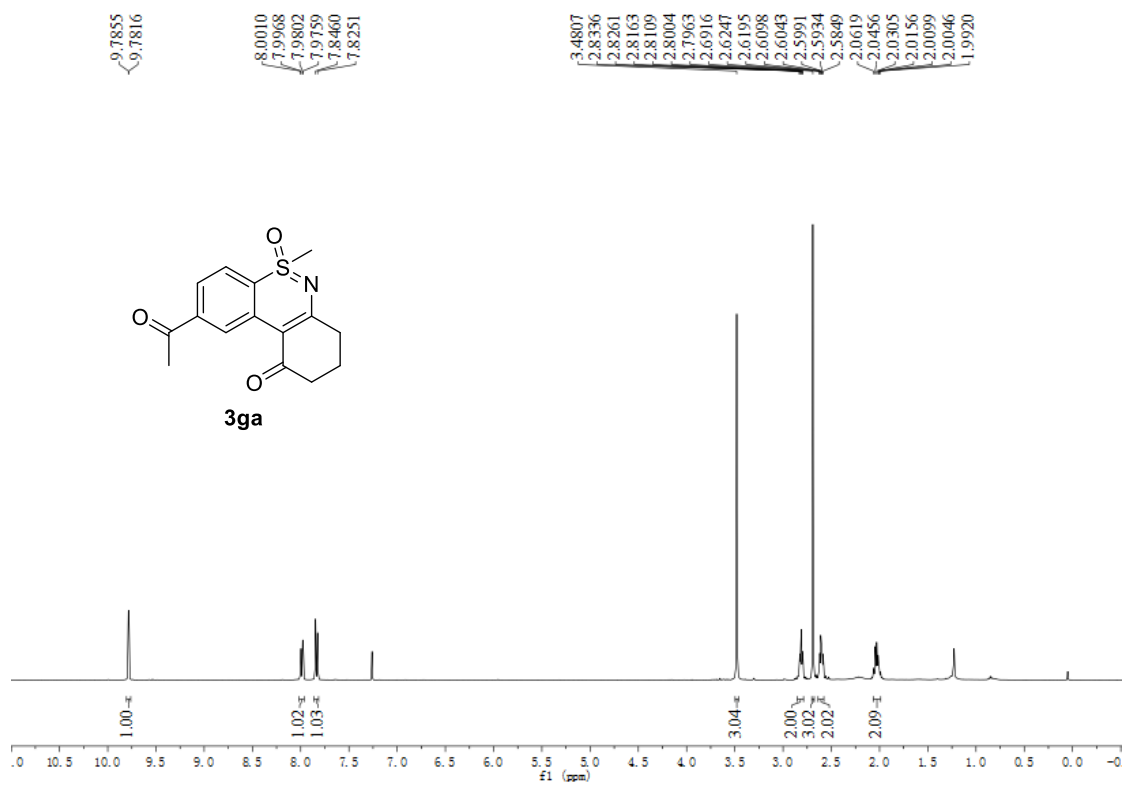


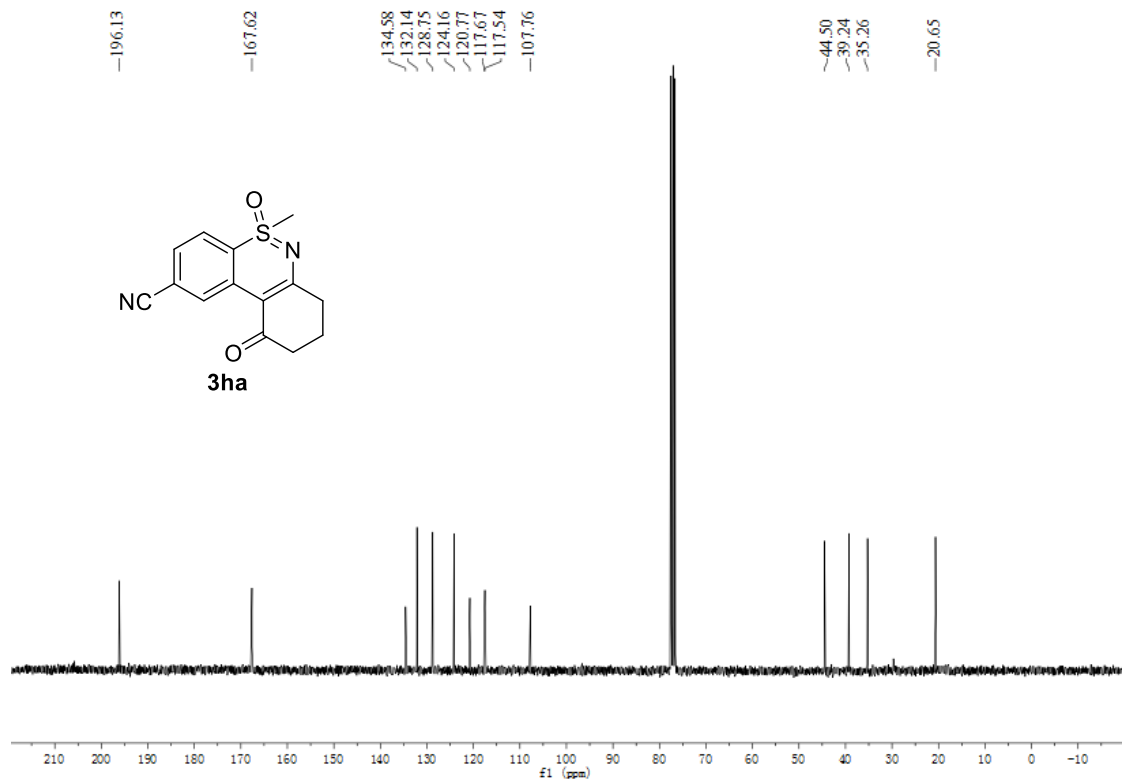
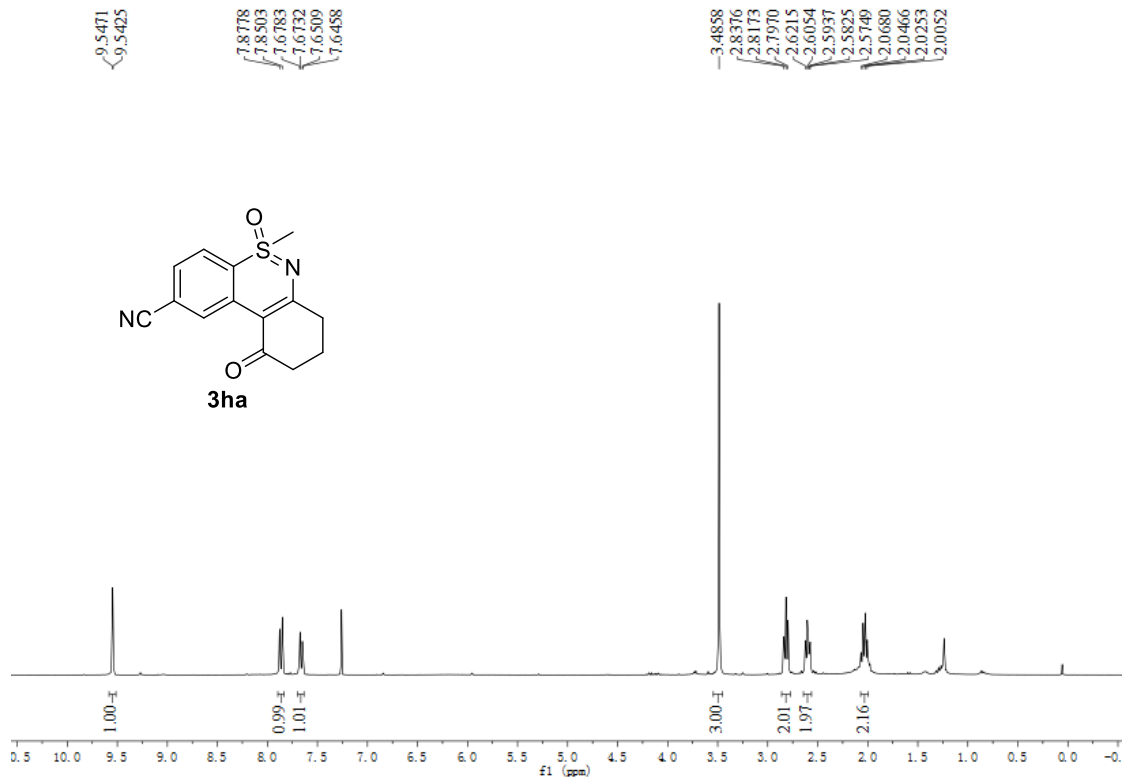


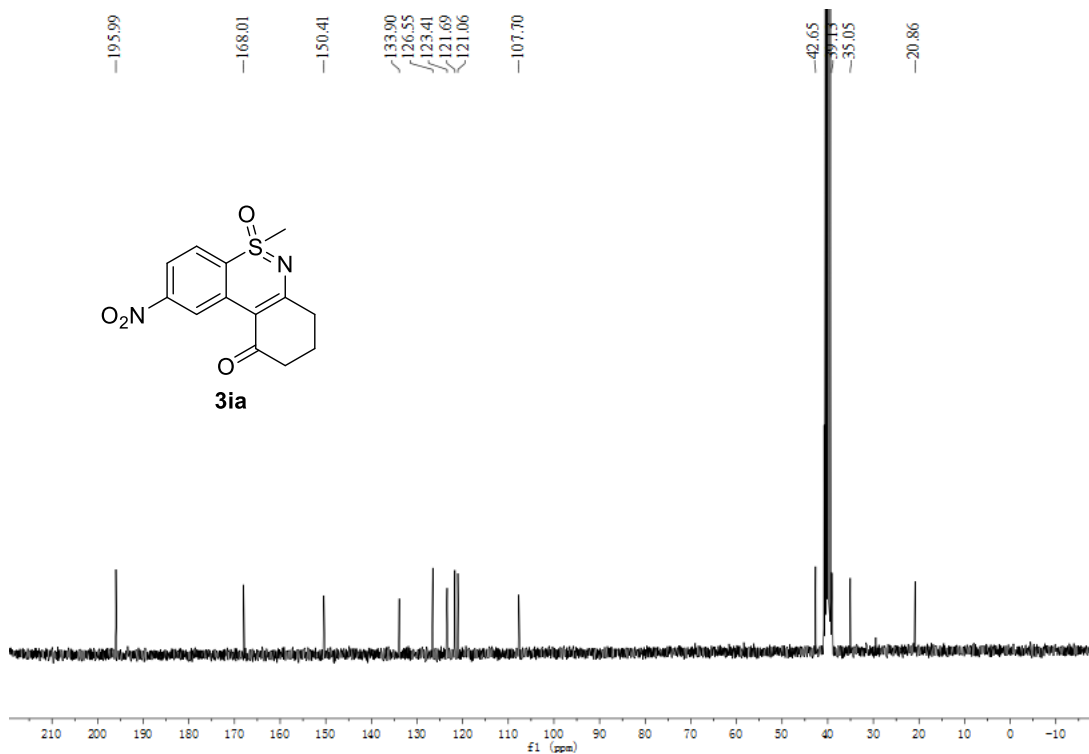
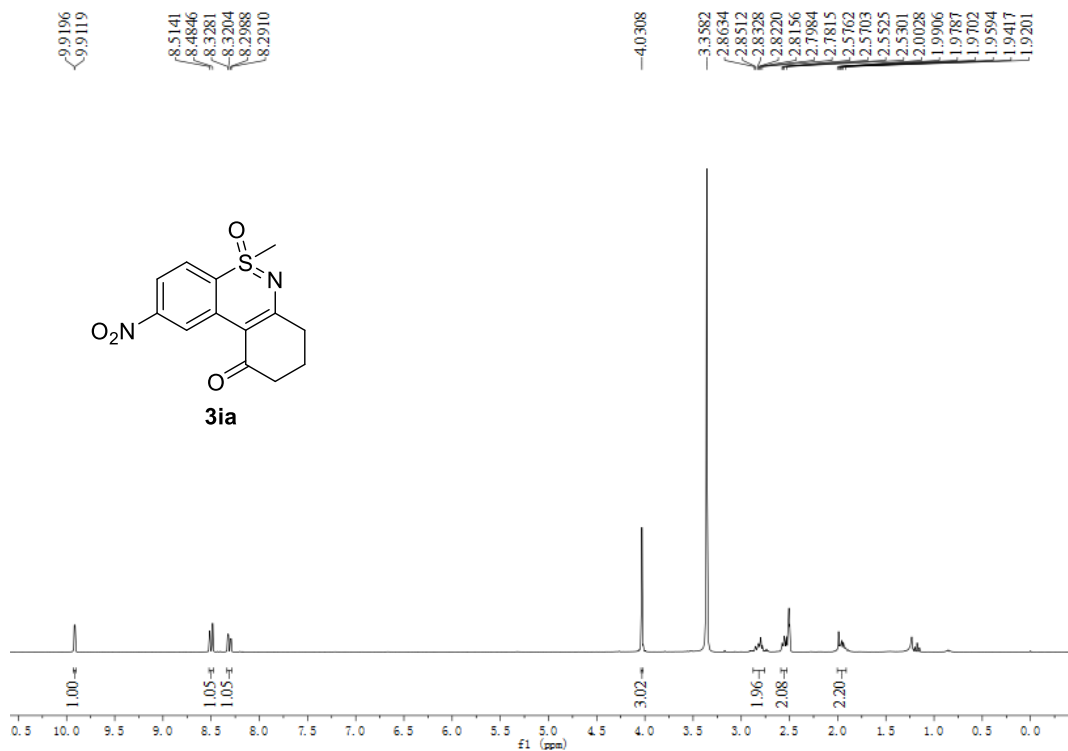


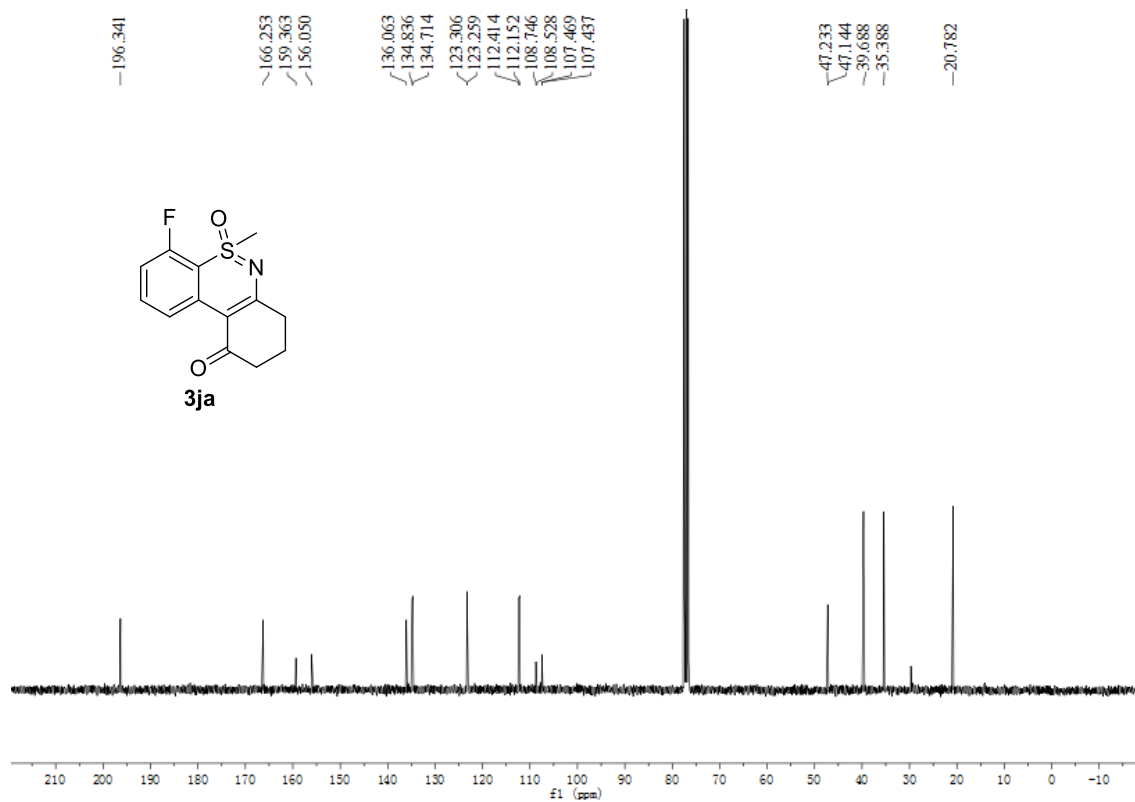
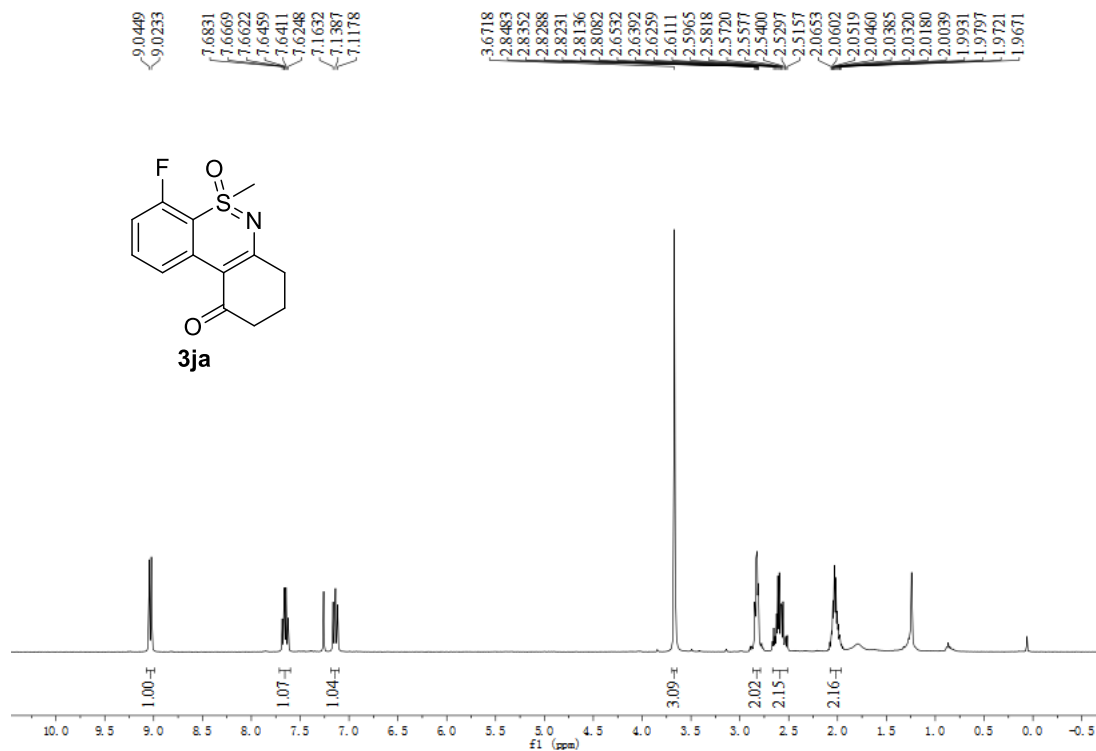


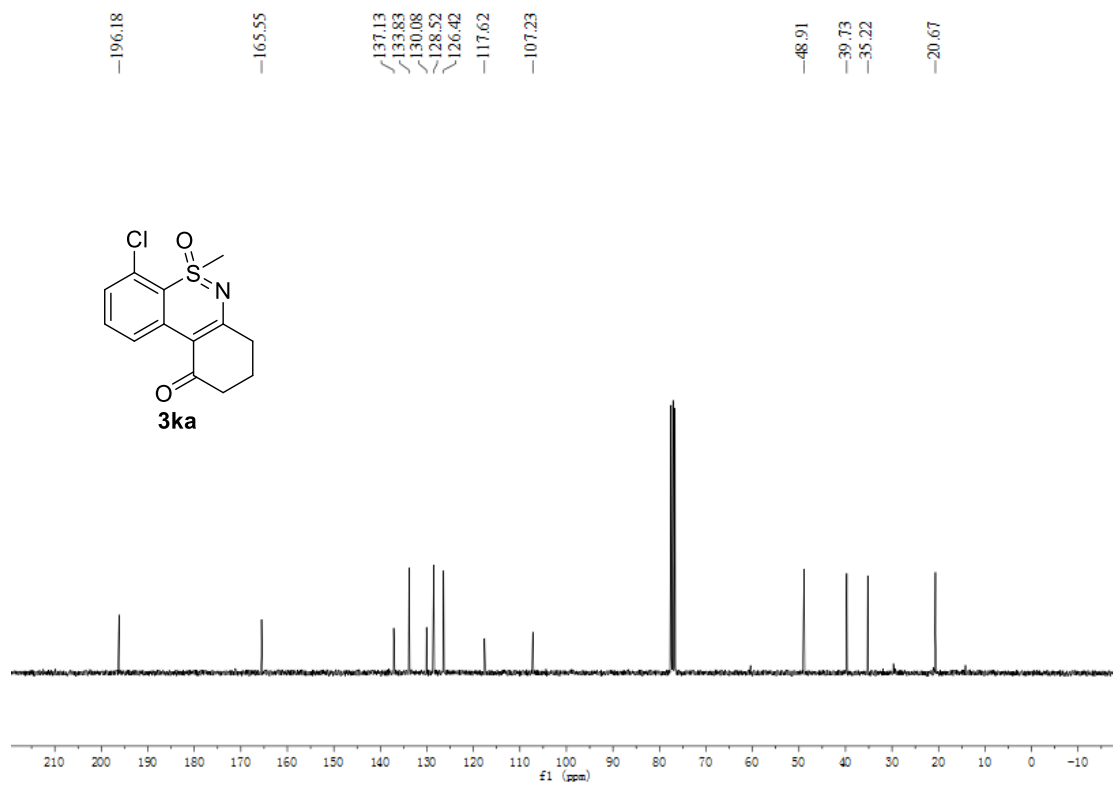
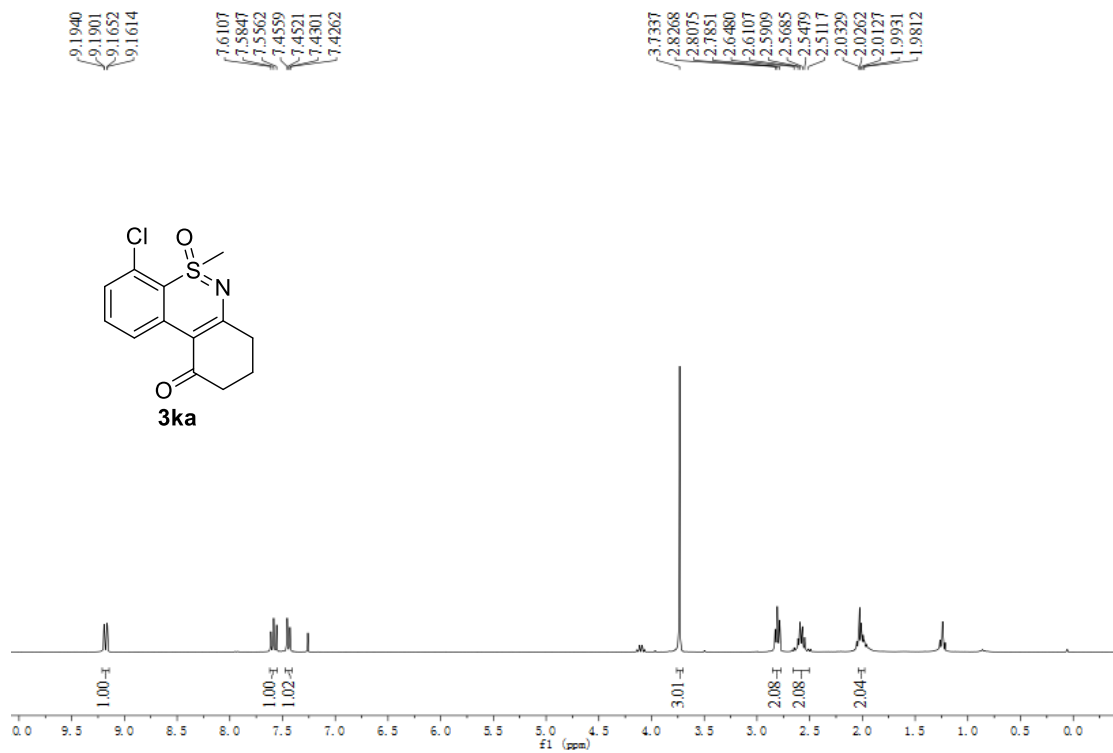








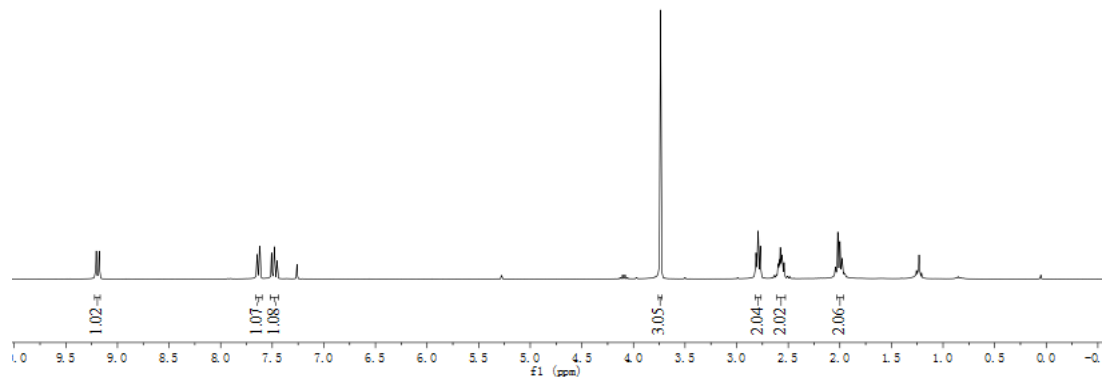
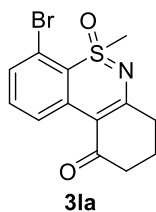




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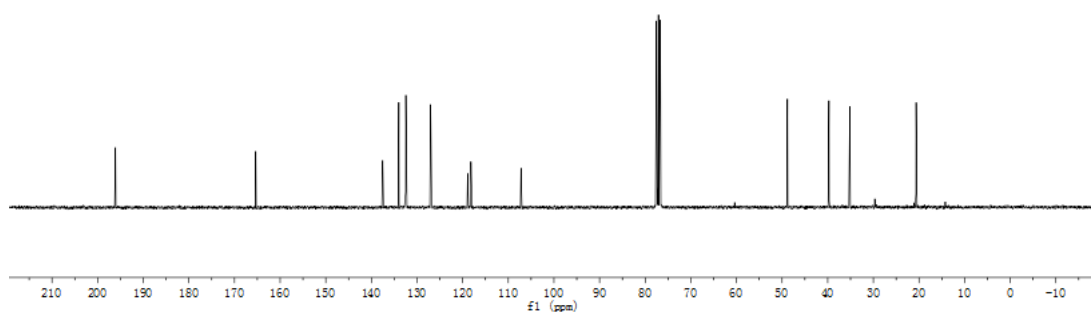
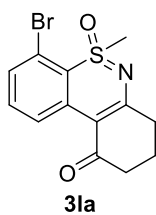
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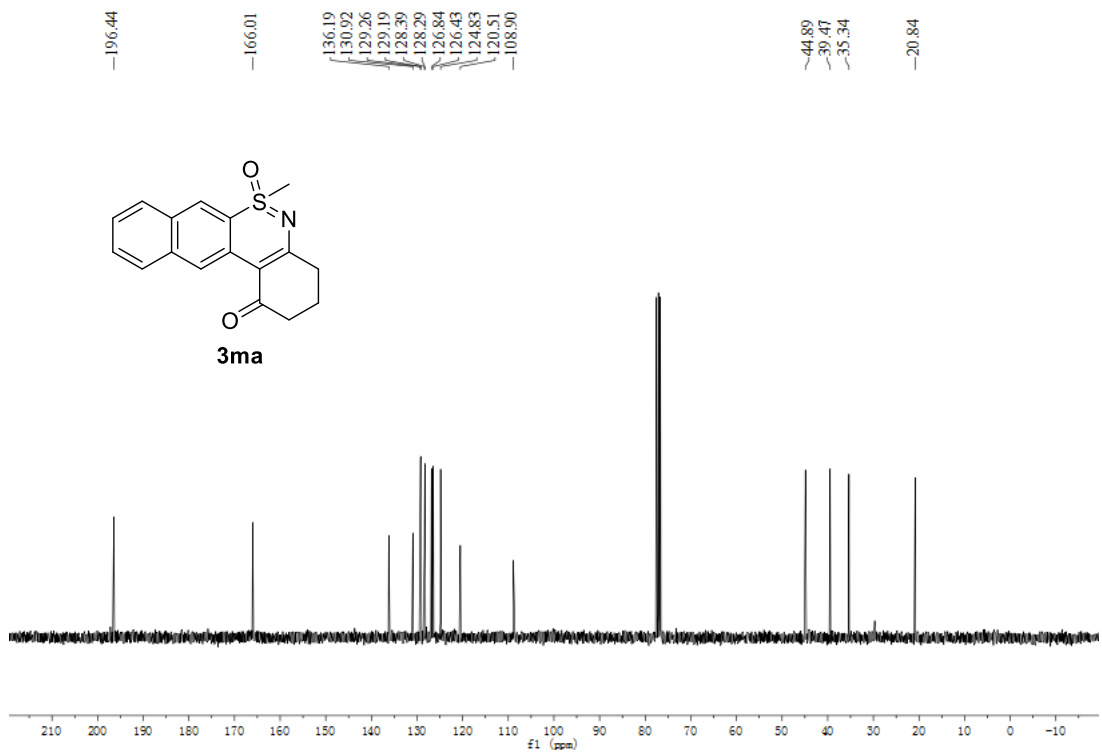
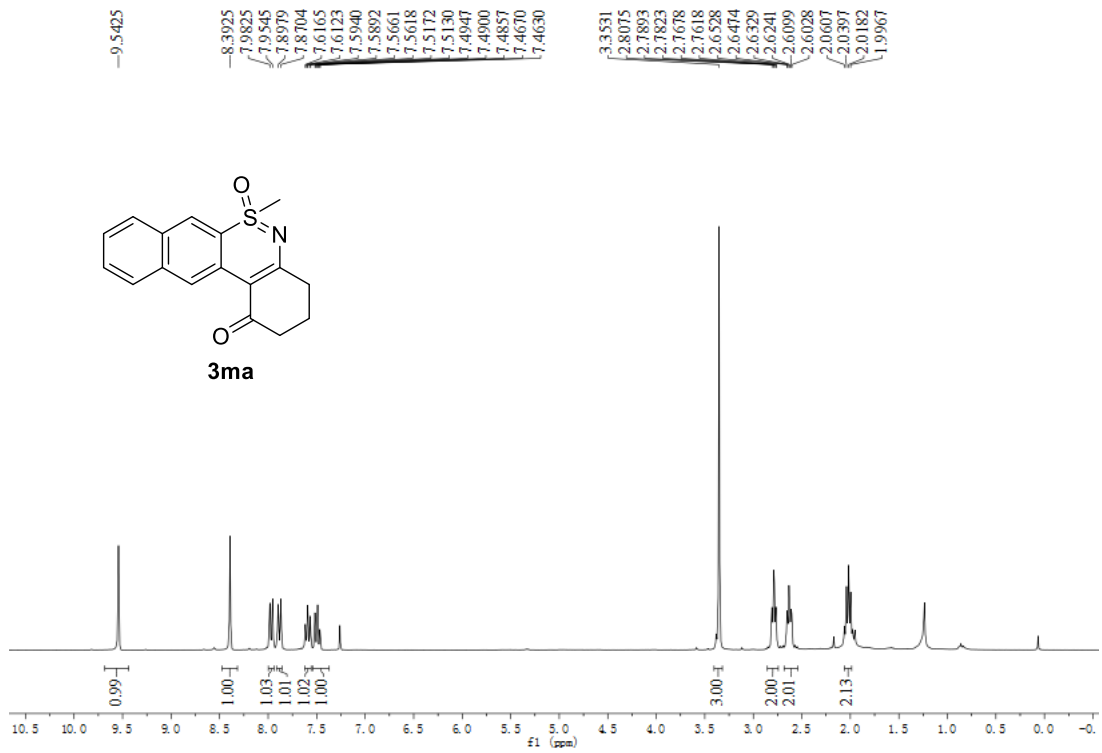
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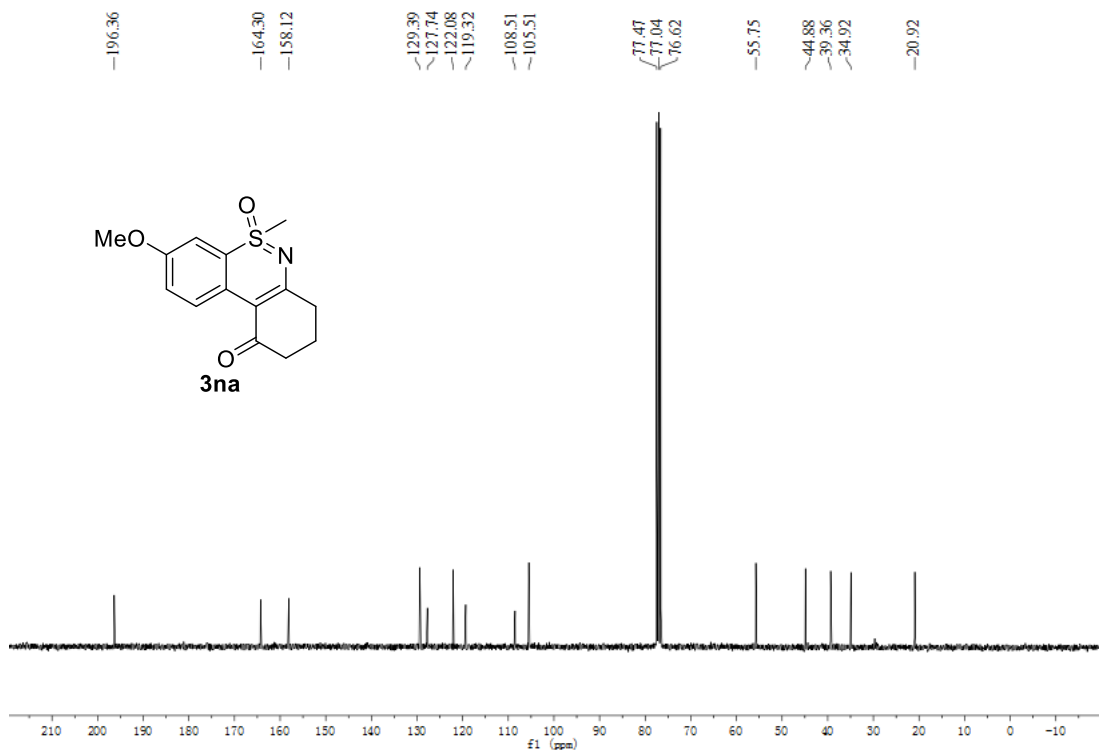
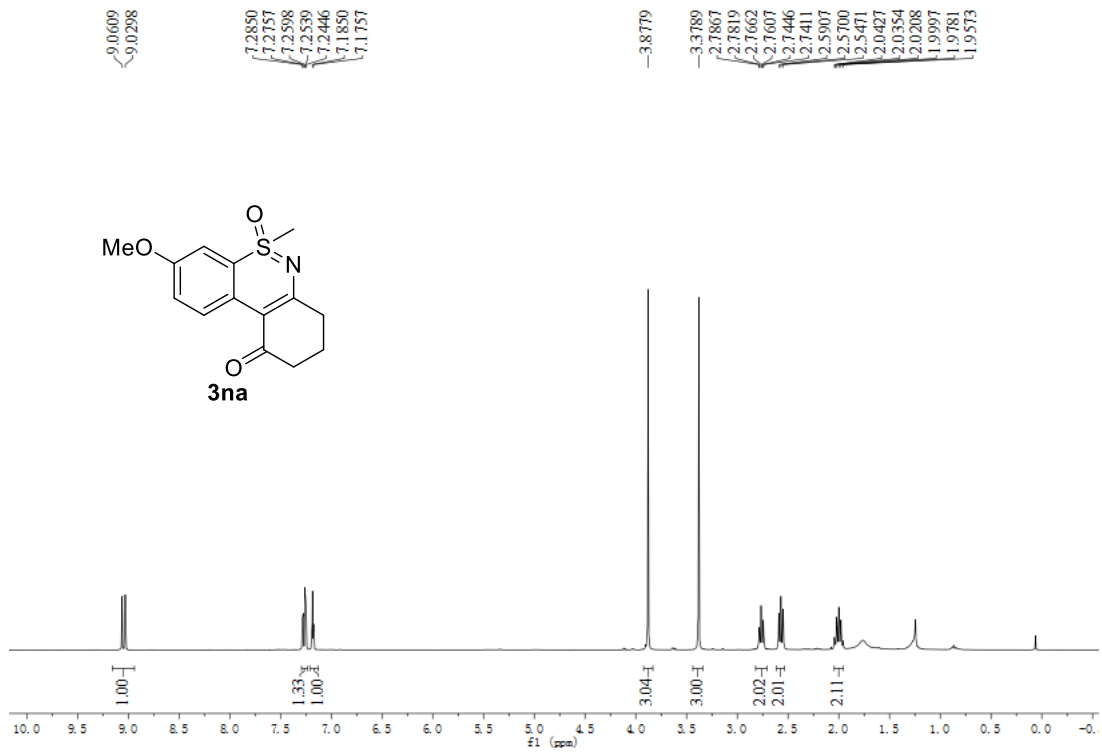
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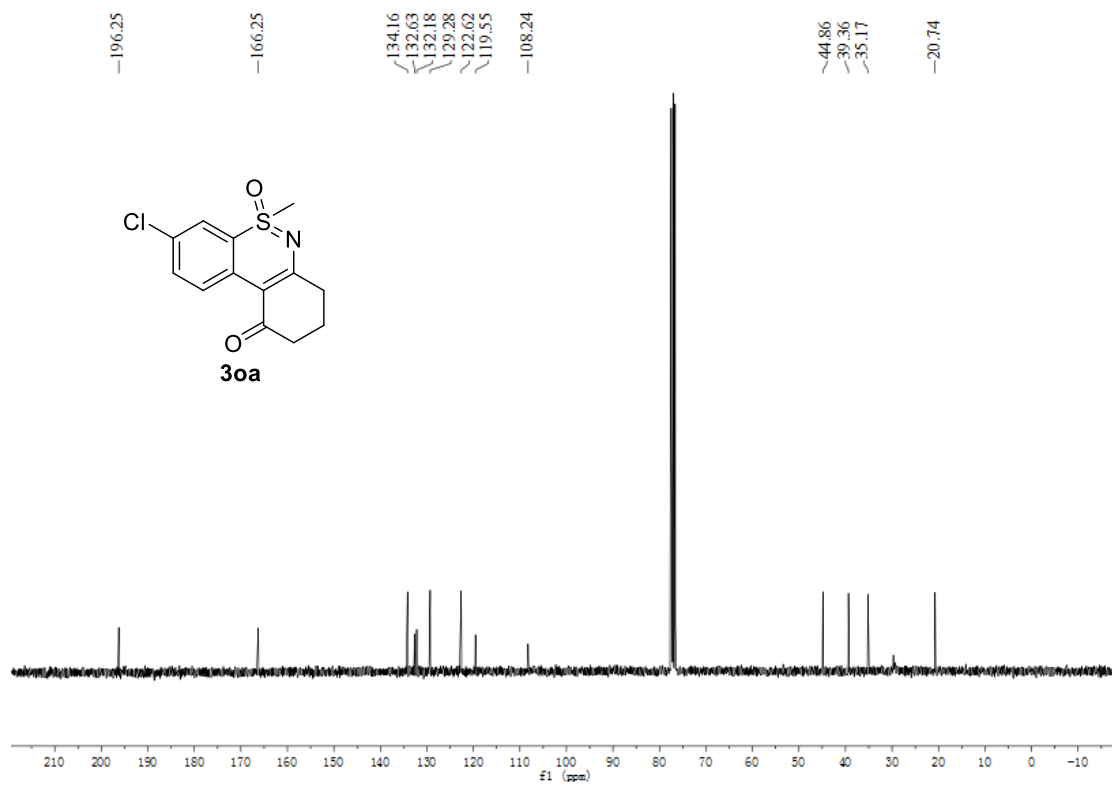
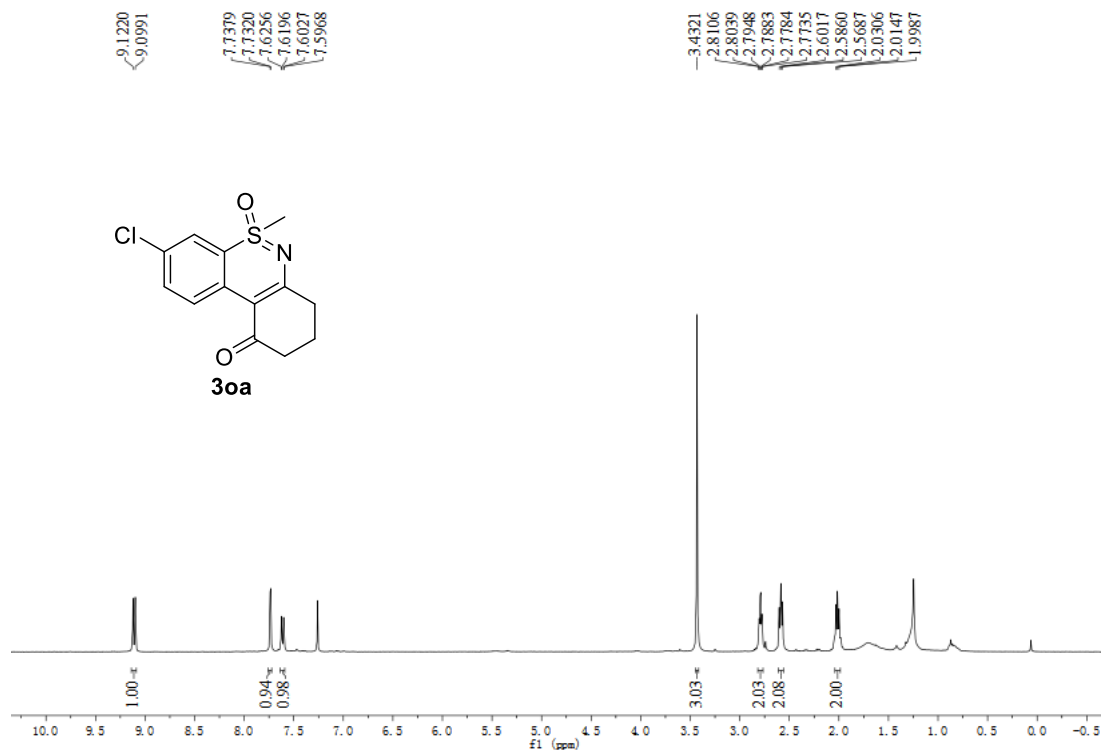
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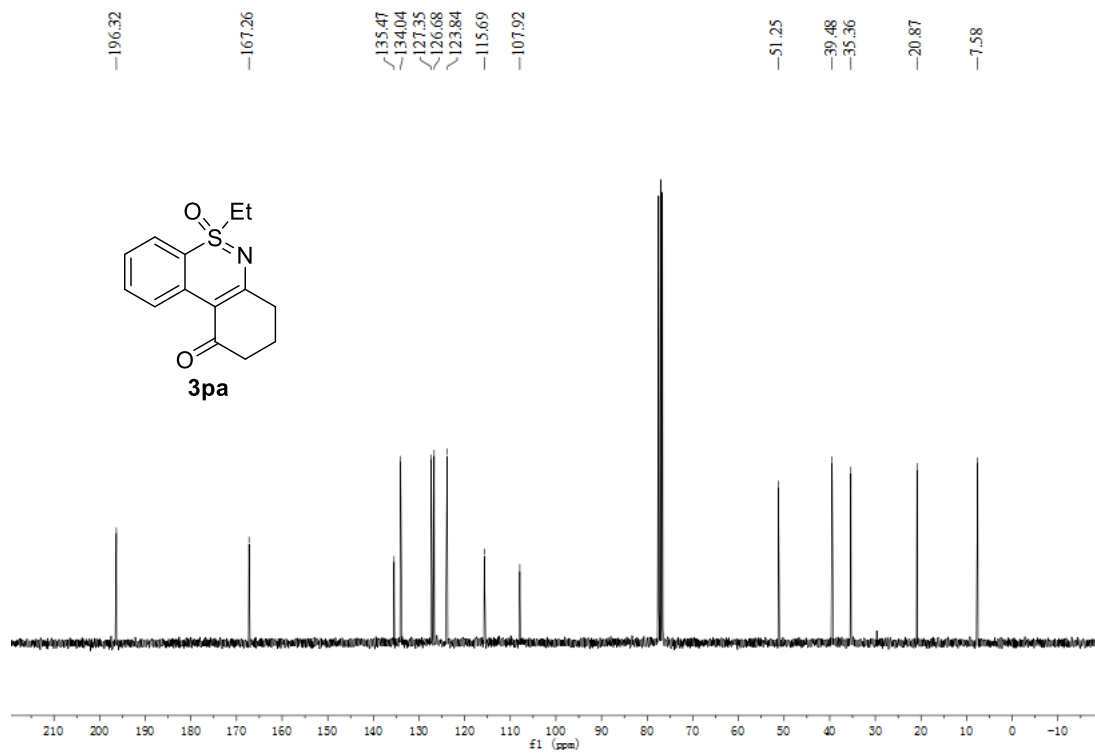
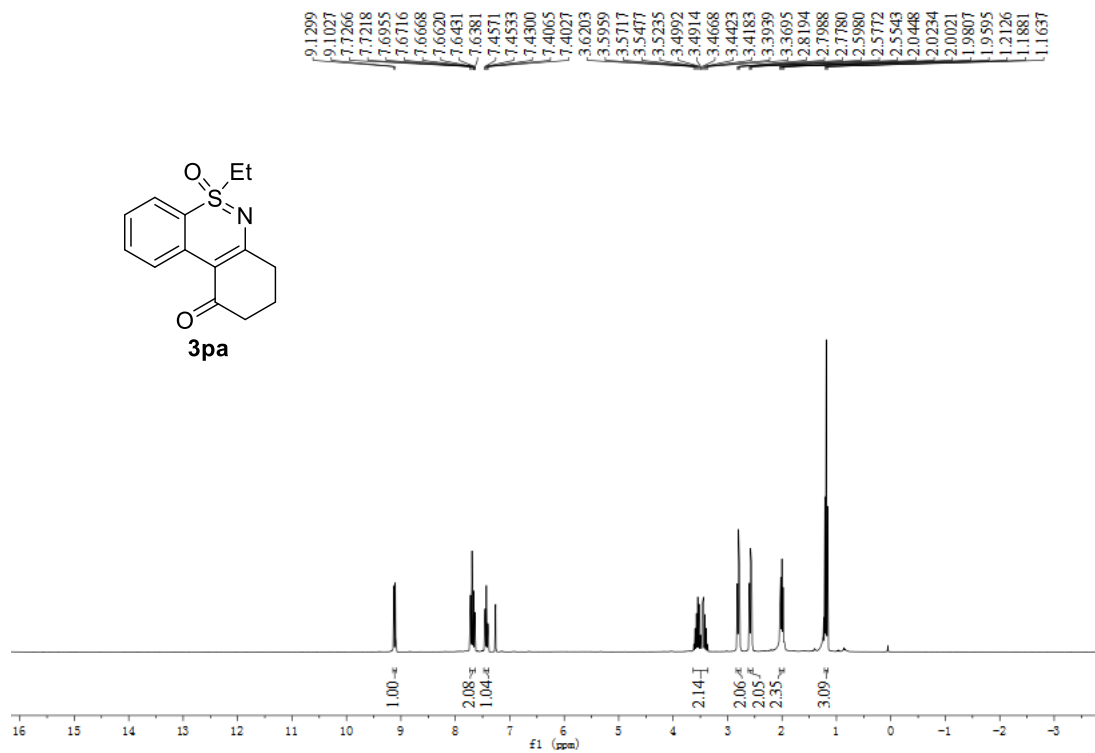
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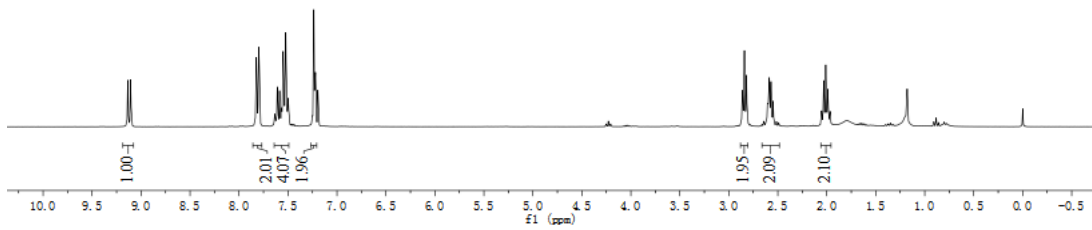
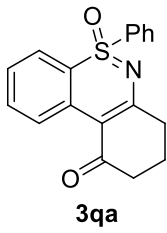




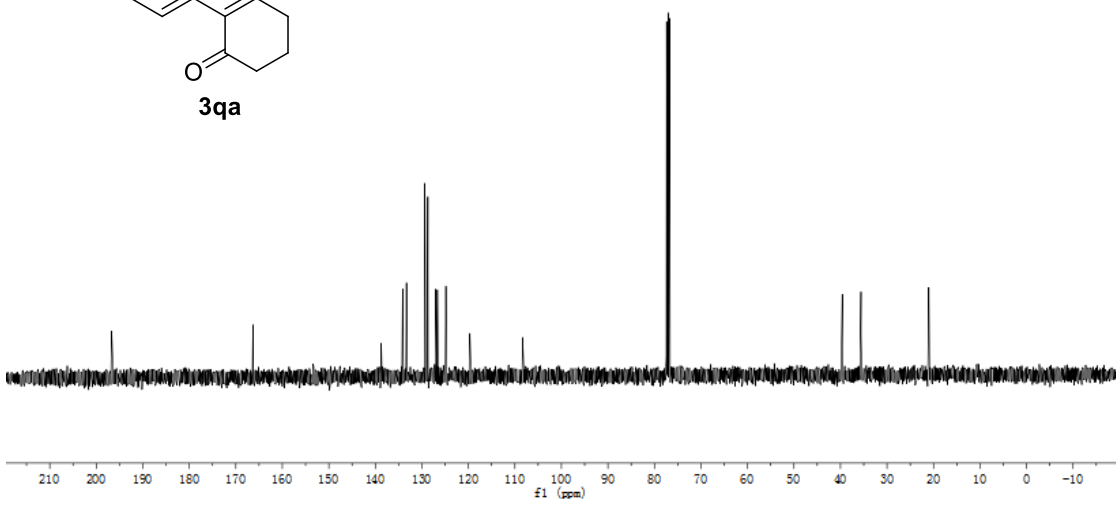
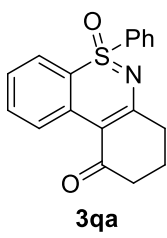


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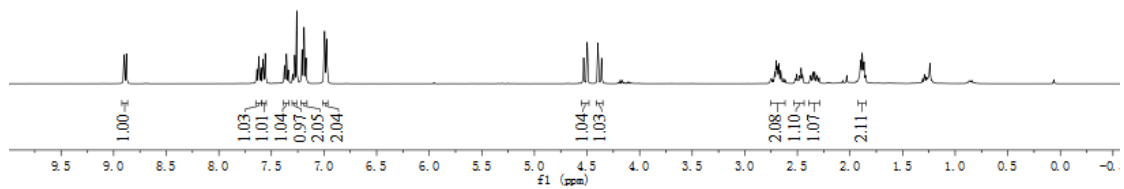
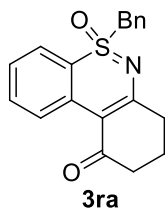
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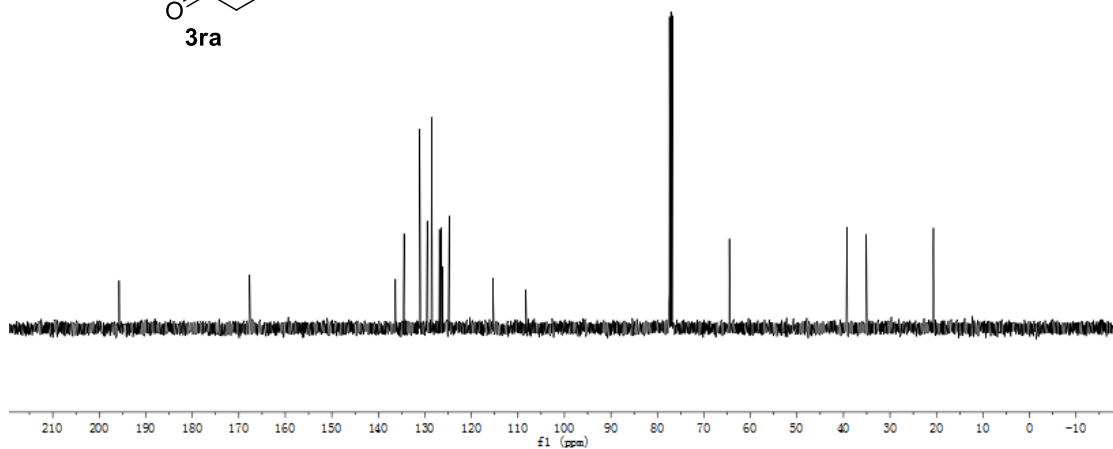
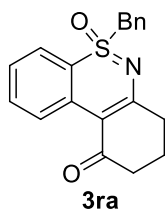
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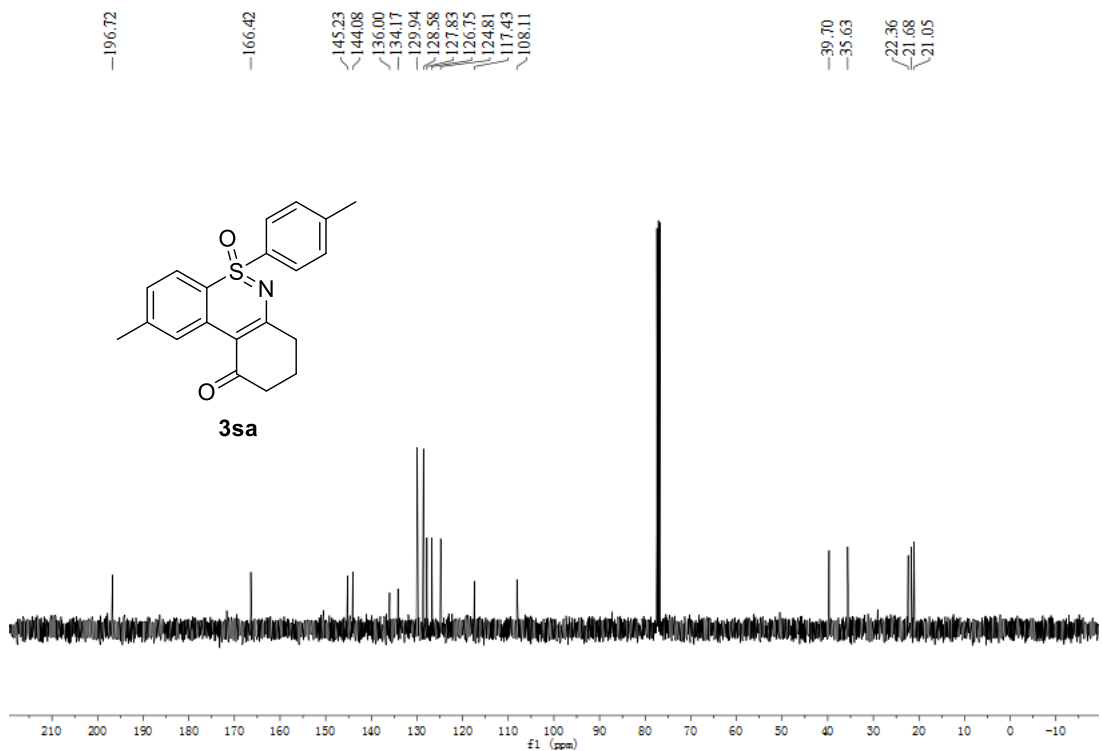
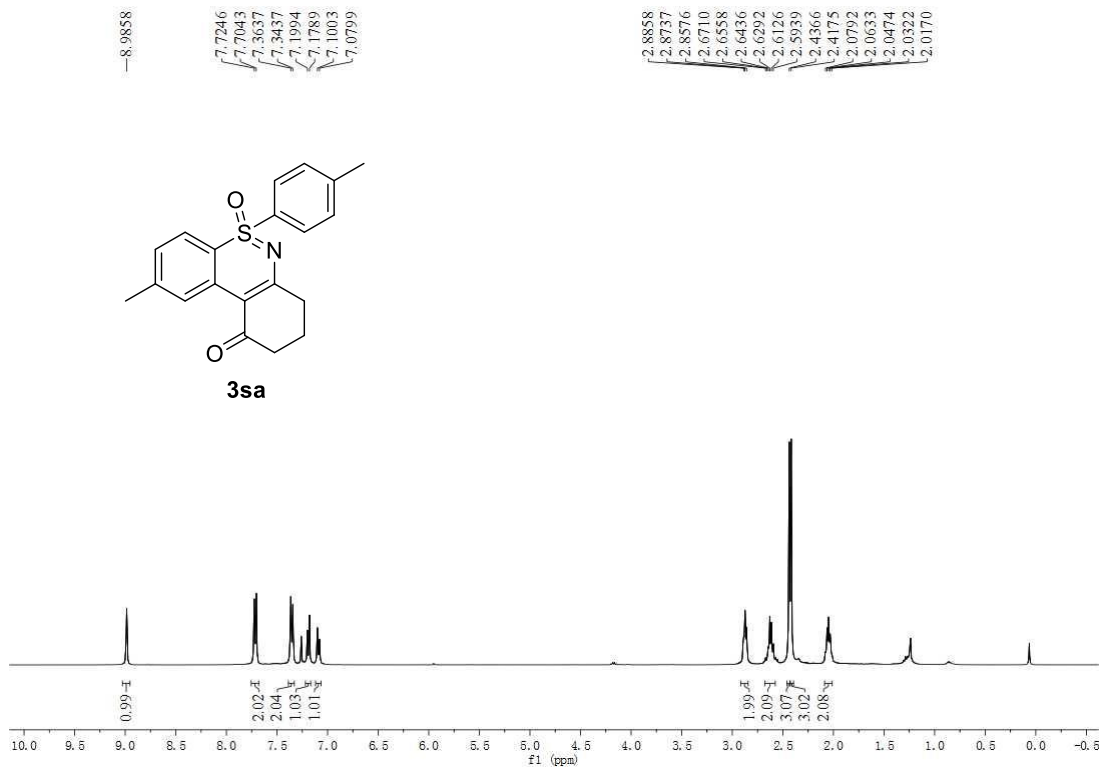


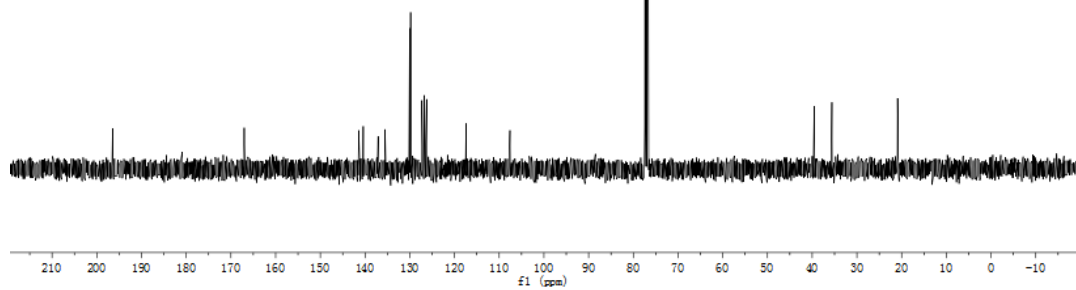
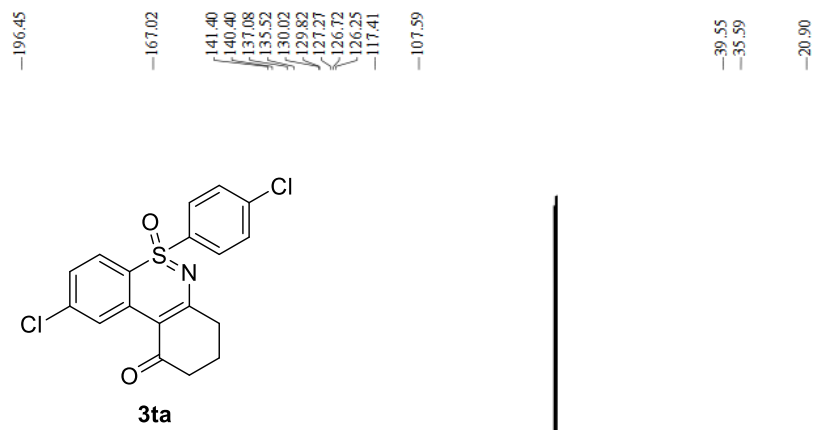
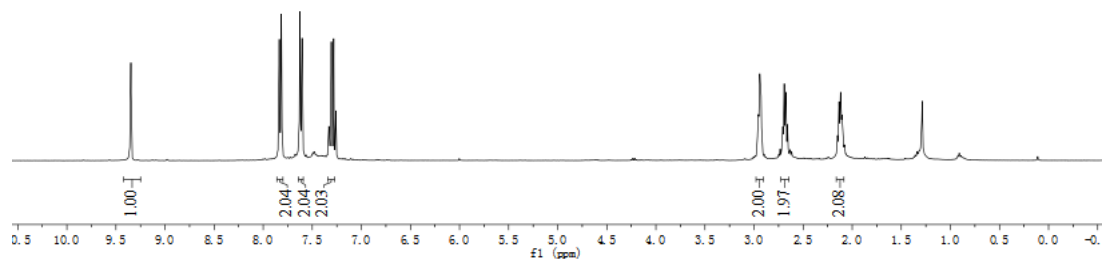
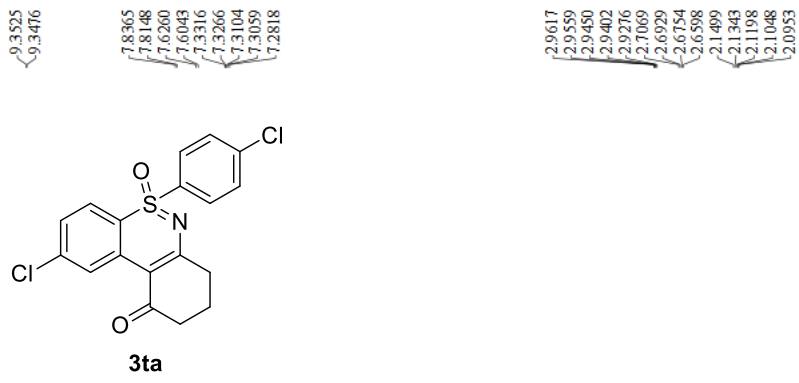
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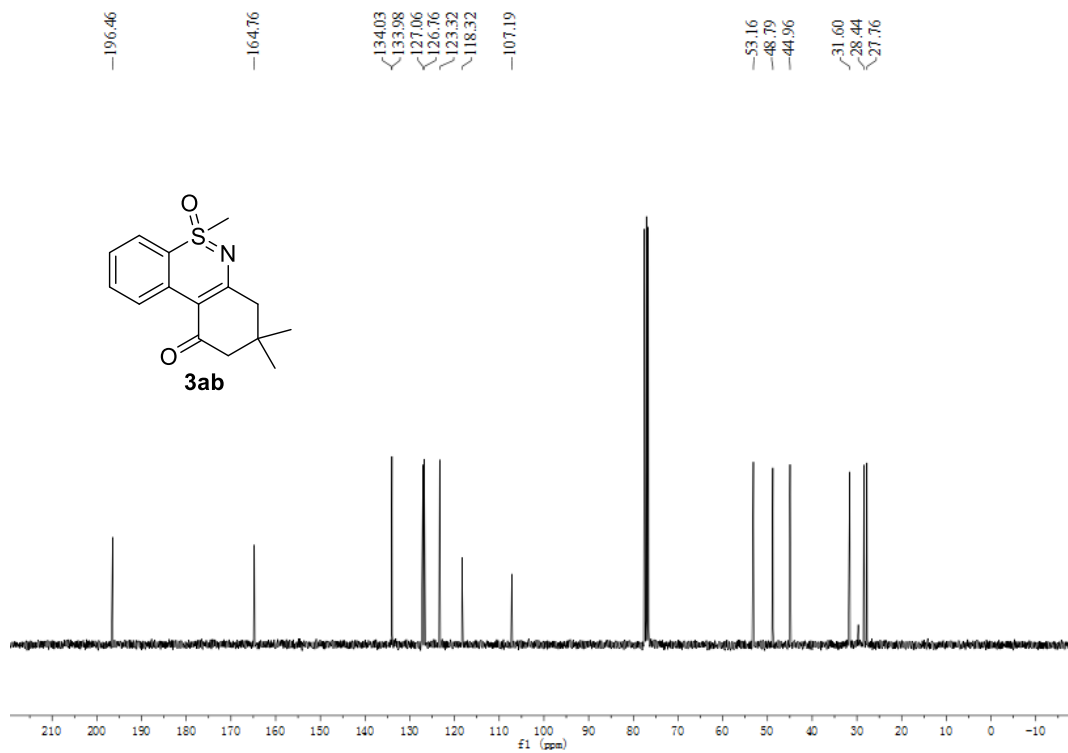
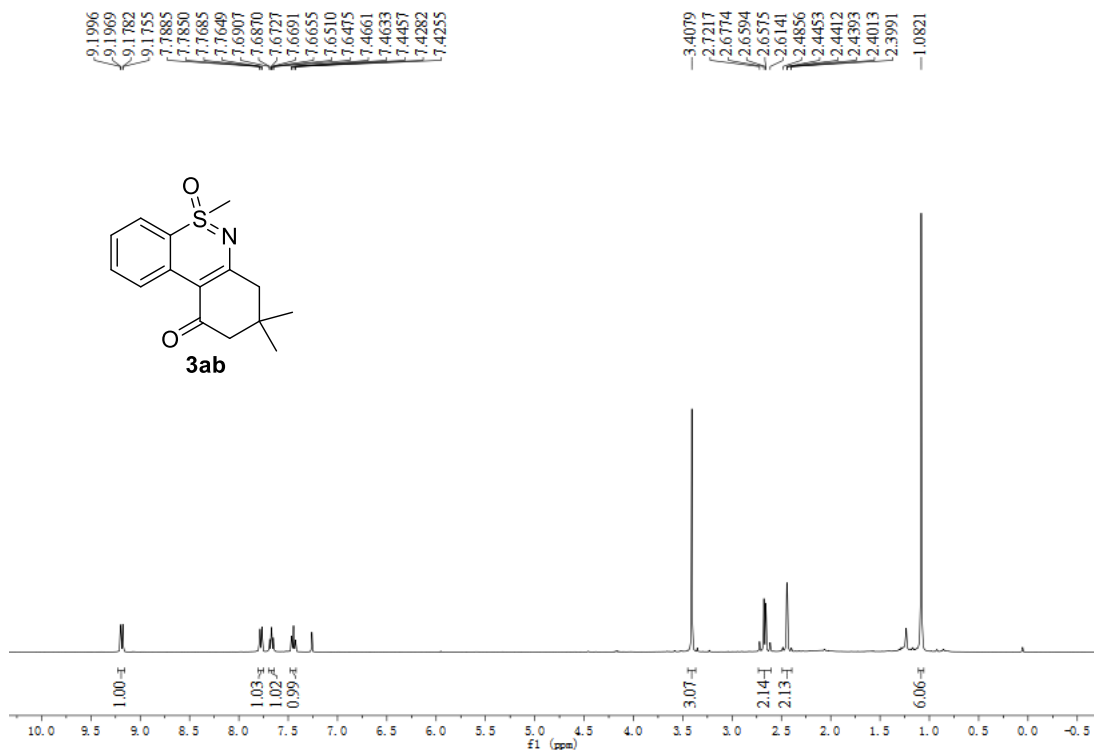


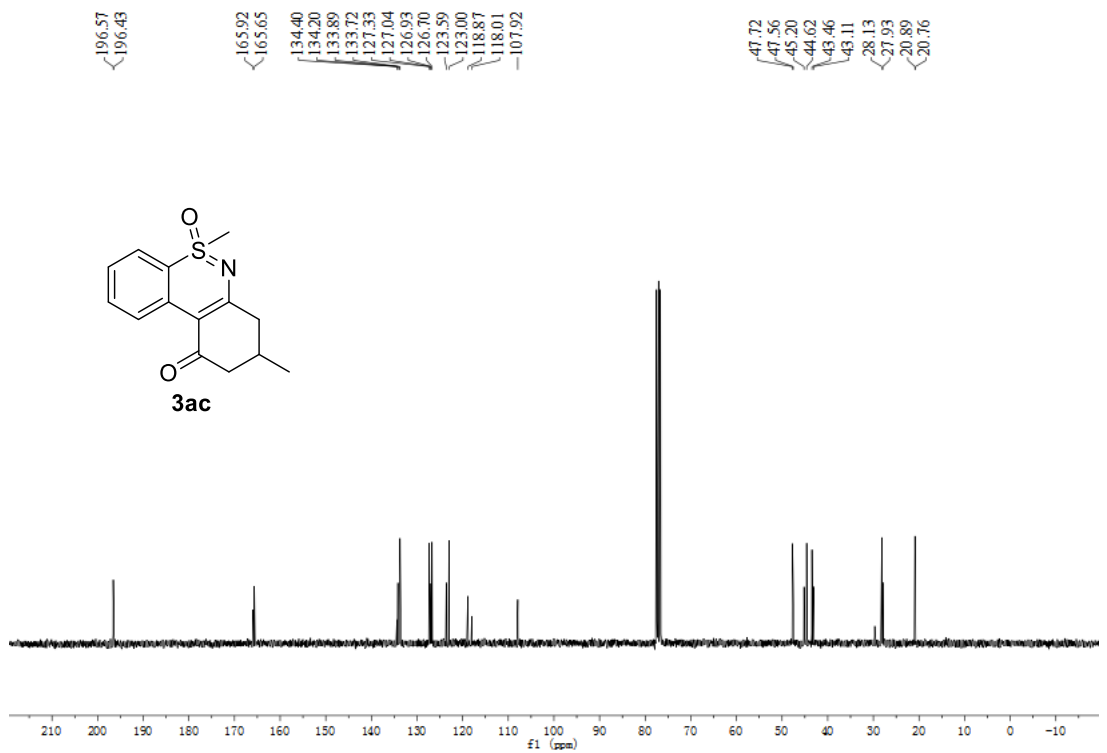
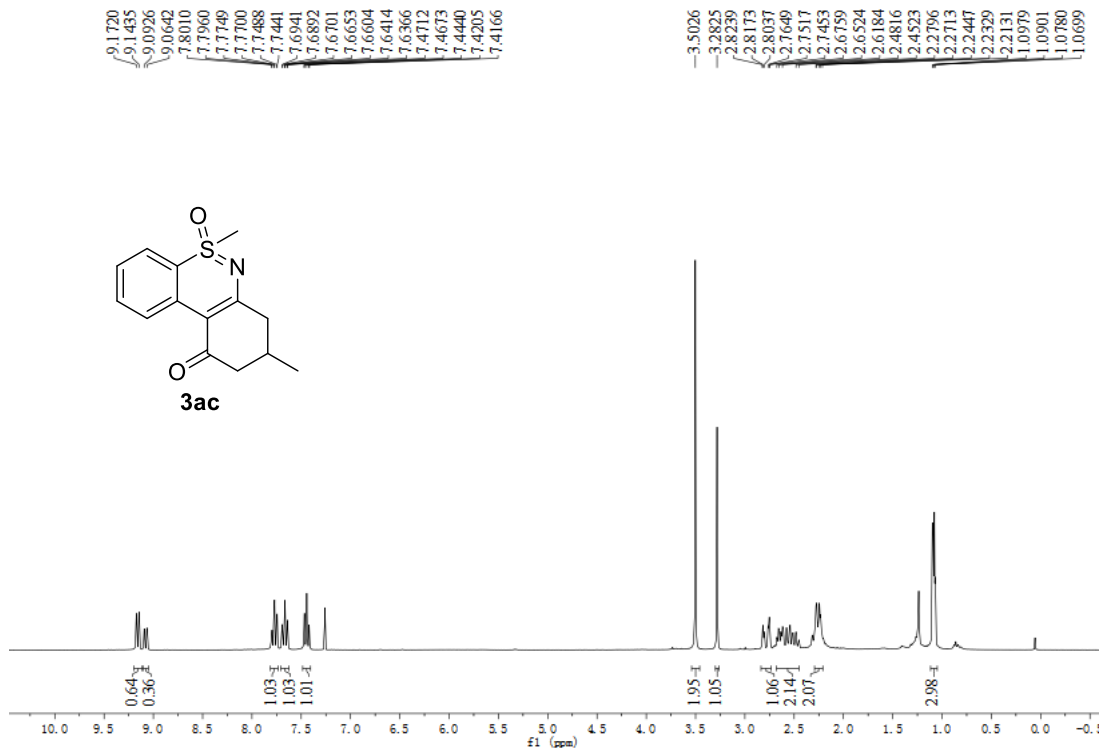
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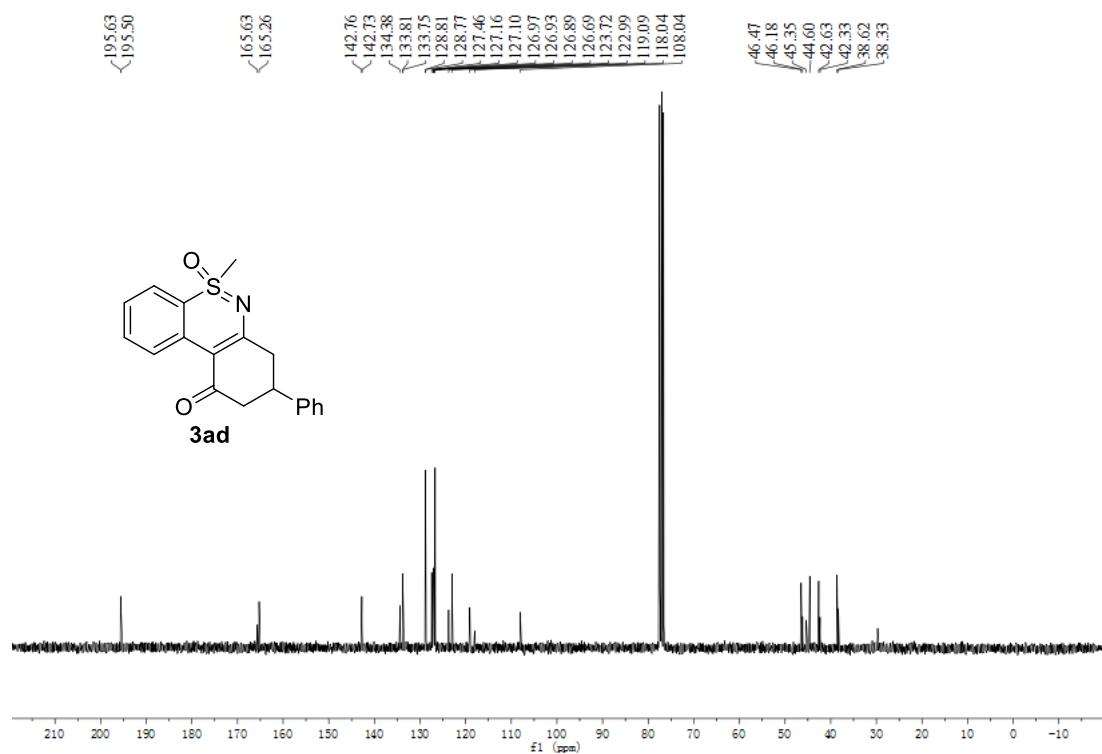
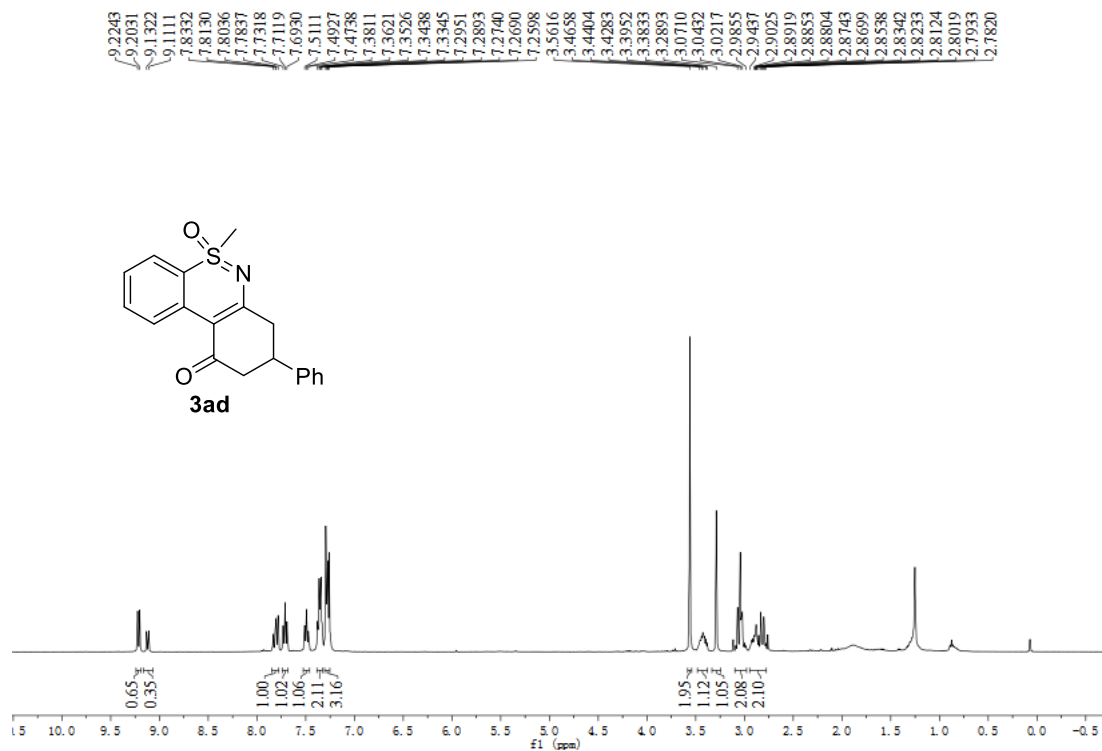


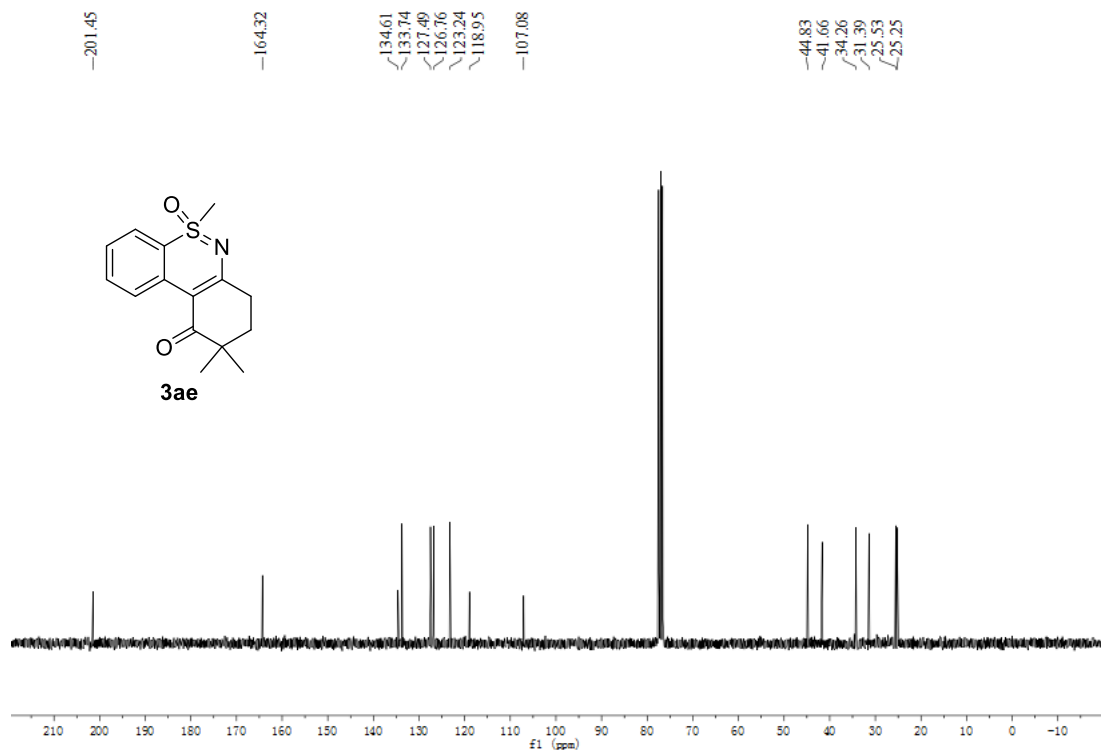
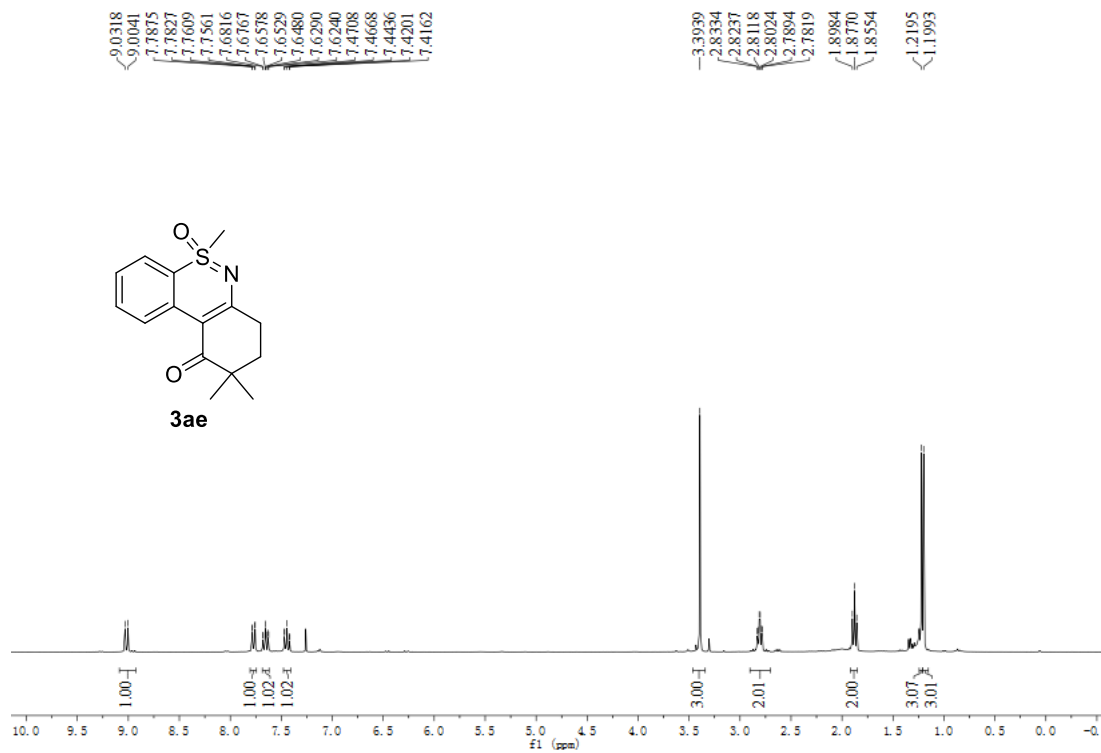


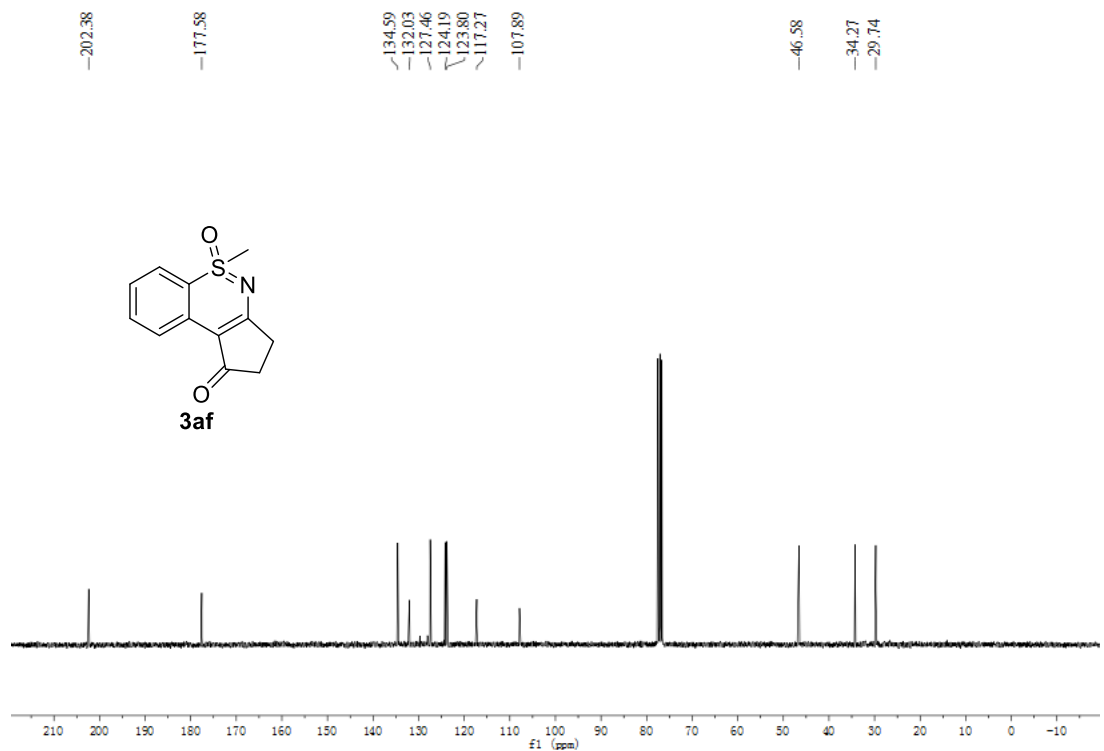
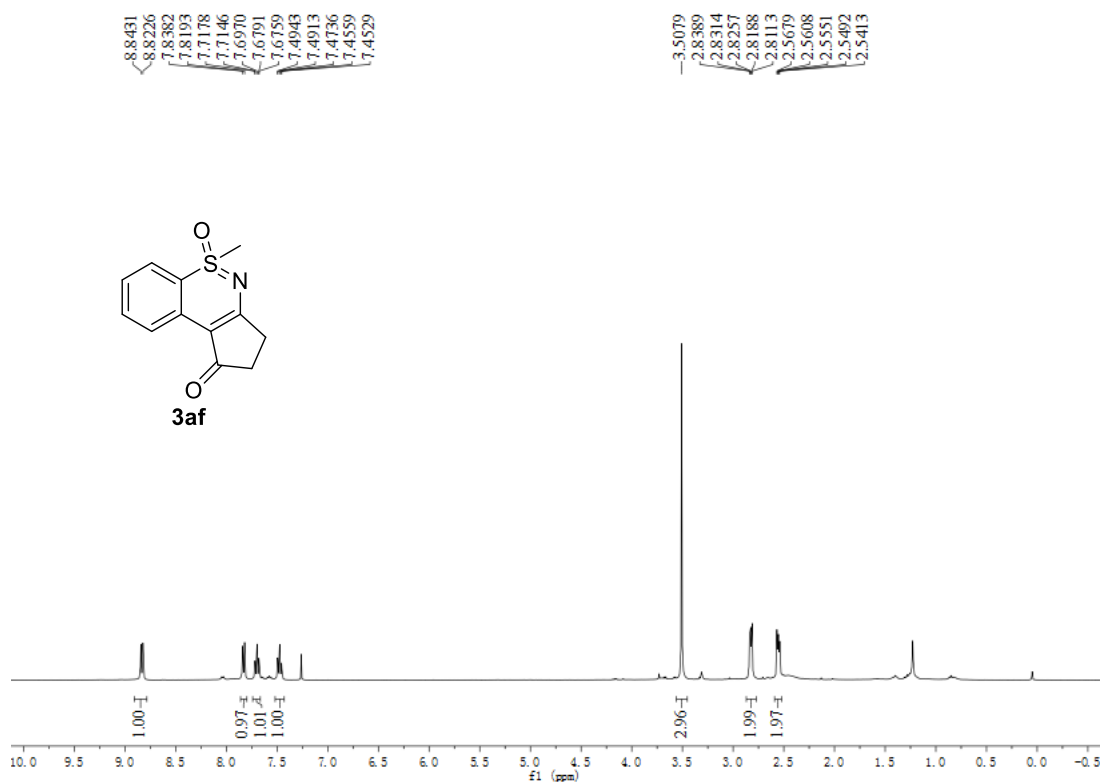


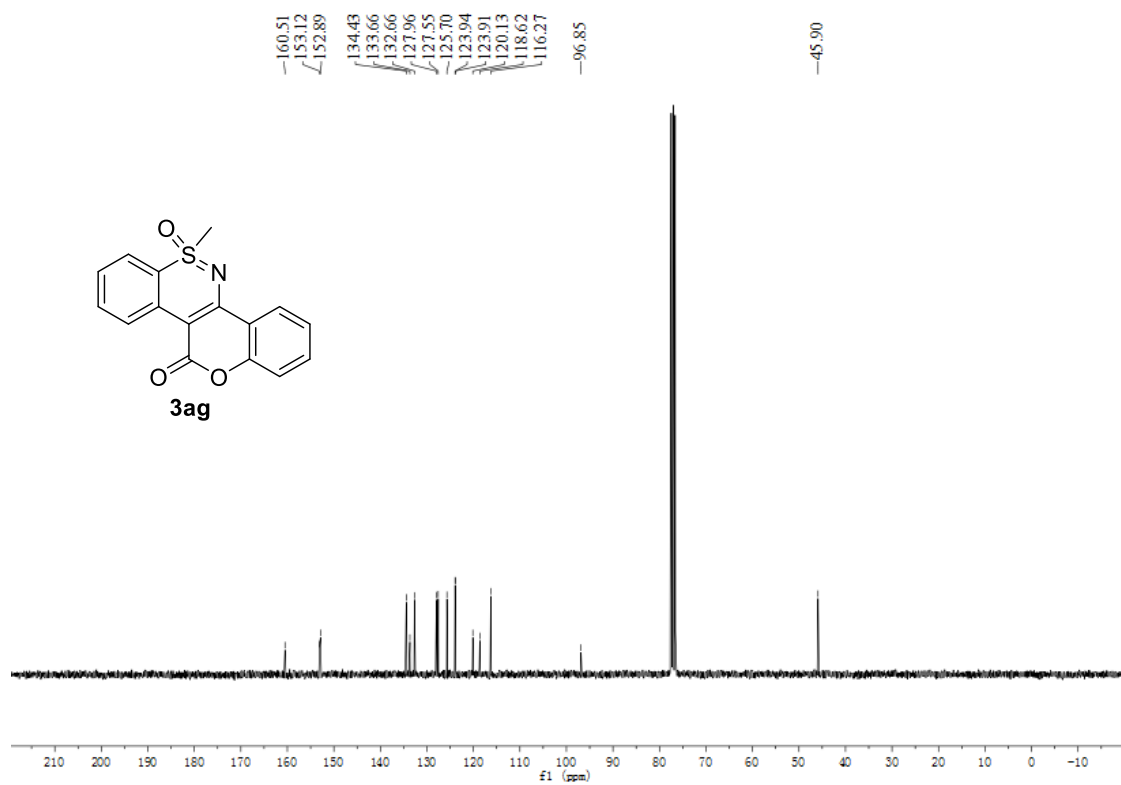
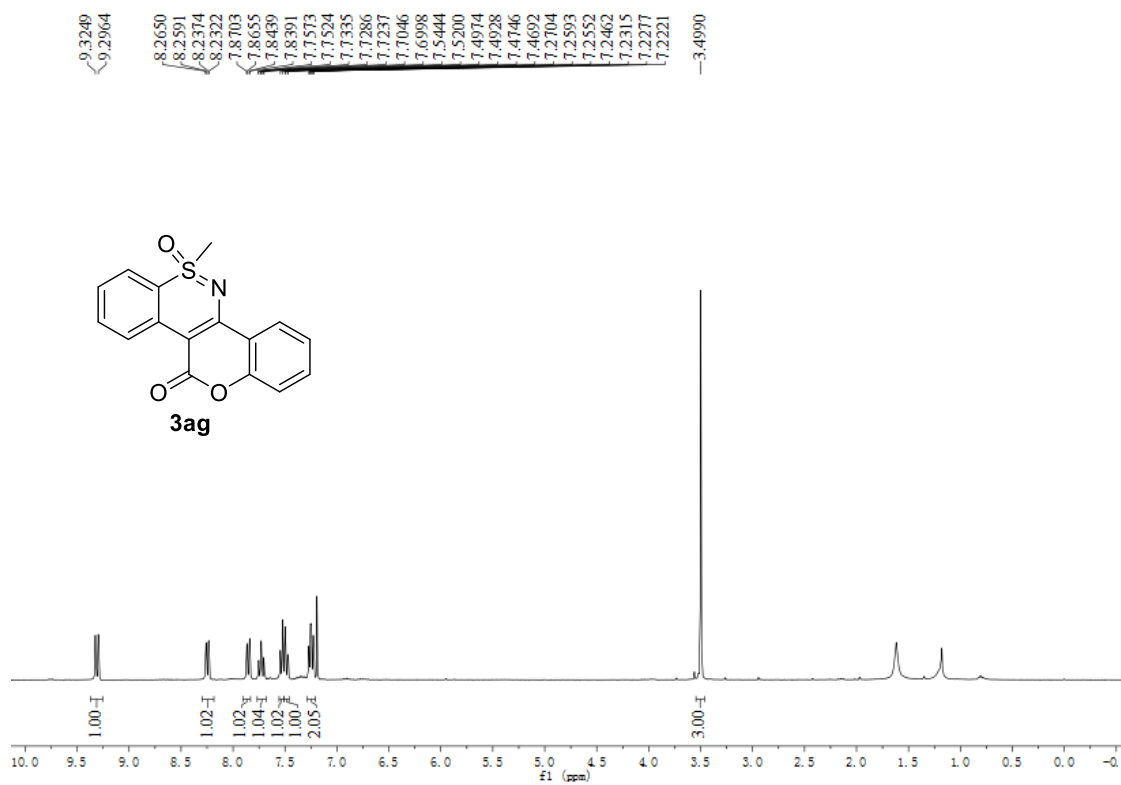


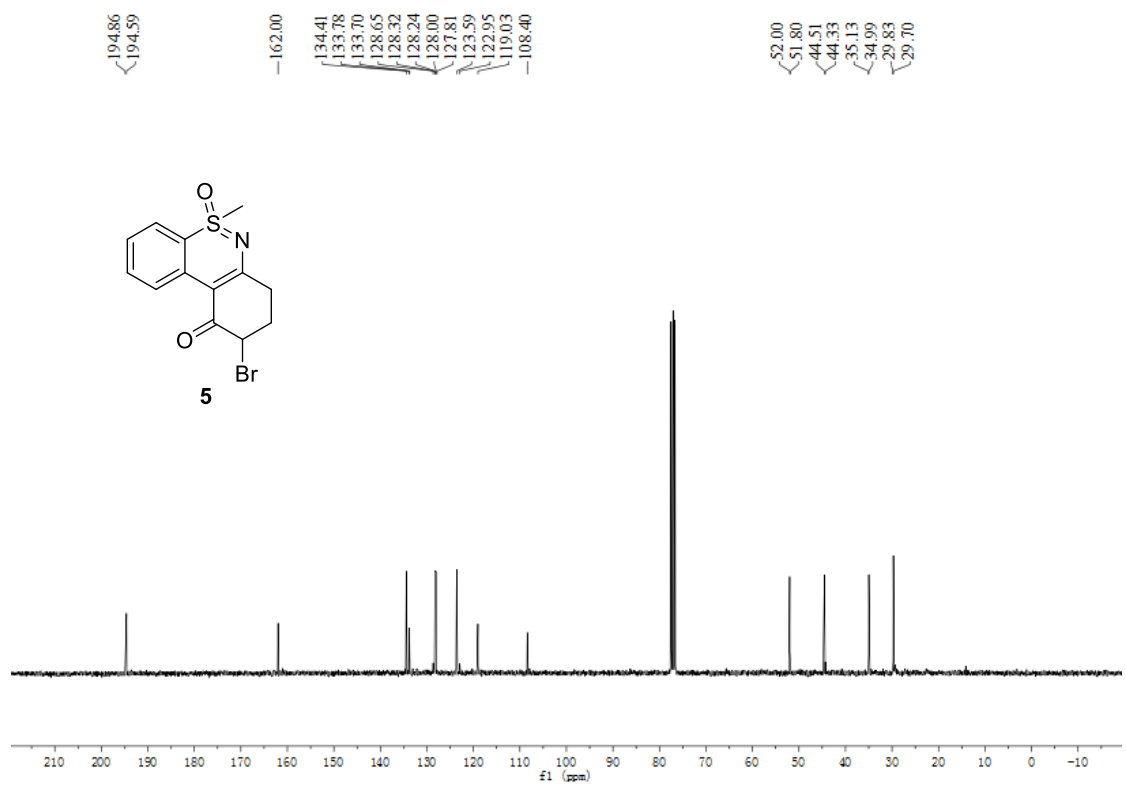
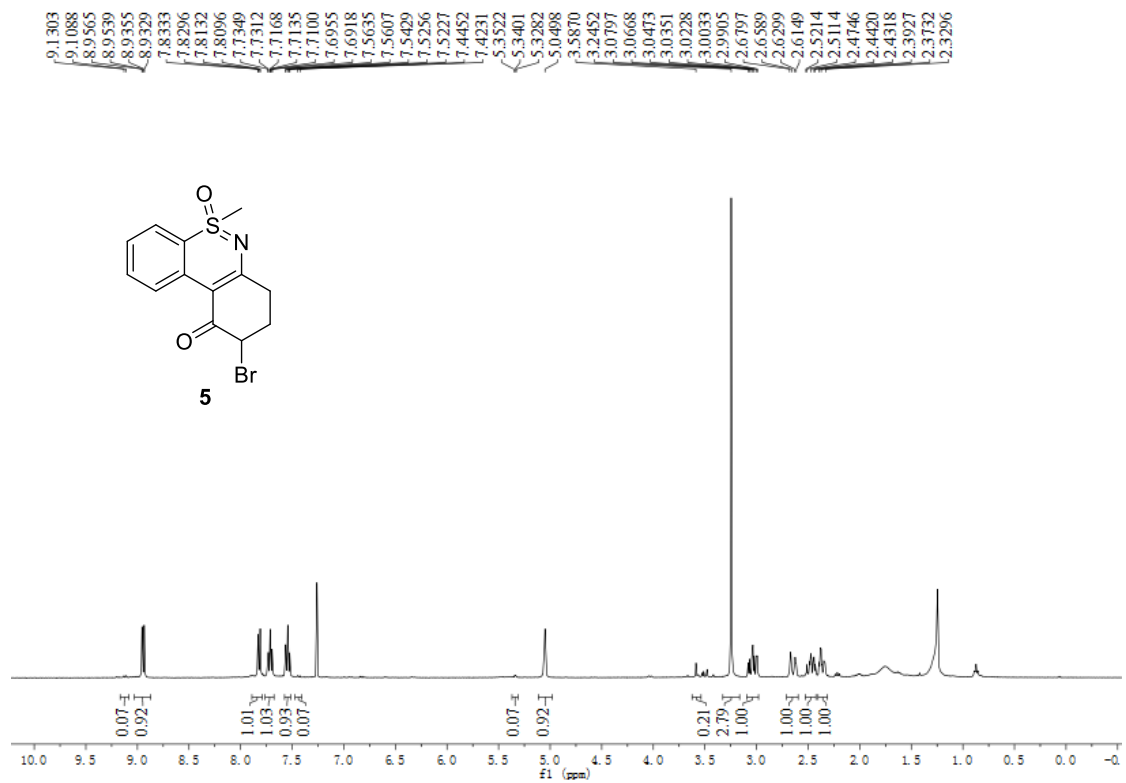








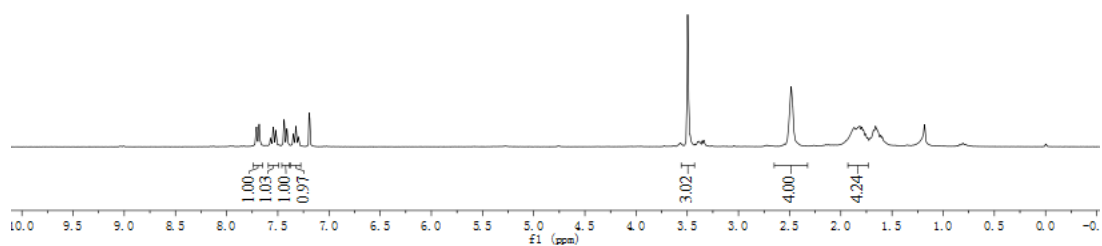
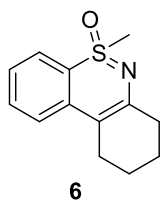




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