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Construction of cyclopenta[*b*]dihydronaphthofurans via TsOH-catalyzed consecutive biscyclization

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Supporting Information

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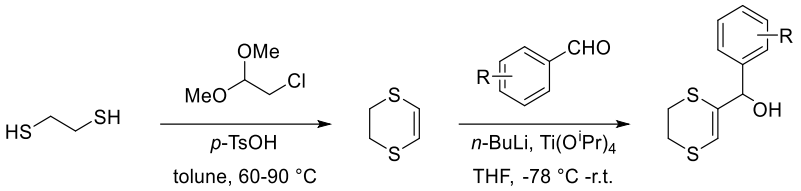
1. General methods

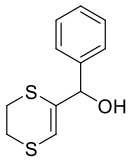
Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ on Bruker 600, 700 MHz, or JEOL 600 NMR instrument (at 600 or 700 MHz for ^1H, and at 150, or 175 MHz for ^{13}C). Proton chemical shifts were reported in parts per million (δ scale). Chemical shifts were reported in δ value (ppm) relative to $CDCl_3$ (^1H NMR: 7.26 ppm, ^{13}C NMR: 77.16 ppm) or TMS (0.00 ppm). ^{19}F NMR spectra were recorded at 658 MHz. High-resolution mass spectra (HRMS) were obtained using Agilent P/N G1969-90010 or Bruker TIMS-TOF-MS. High resolution mass spectra were reported for the molecular ion $[M+Na]^+$ or $[M+H]^+$. Melting points were recorded on BUCHI Melting Point M-565 instrument. X-ray diffraction experiment was carried out on an Agilent D8 QUEST and the data obtained were deposited at the Cambridge Crystallographic Data Centre. UV detection was performed at 254 nm. TLC was performed on glass-backed silica plates; products were visualized using UV light (λ = 254 nm). All the reactions were set up under air and using commercial AR solvents, without any precautions to exclude moisture unless otherwise noted. All reagents and solvents were obtained from commercial sources and used without further purification. Oil baths were used as the heat source. Column chromatography was performed on silica gel (200-300 mesh) using an eluent of ethyl acetate (EA) and petroleum ether (PE). 1-styrylnaphthols **1** and (5,6-dihydro-1,4-dithiin-2-yl)methanol **2a** were prepared according to the literature procedures.[1-2]

2. General procedure for the synthesis of 2b–2e

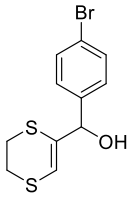


The preparation of 2,3-dihydro-1,4-dithiine:[3] Chloroacetaldehyde dimethyl acetal (50 mmol, 1 equiv.) was added to a solution of ethane dithiol (50 mmol, 1 equiv.) in toluene. The mixture was stirred and heated to 60 ℃, then *p*-TsOH (5 mmol, 0.1 equiv.) was added. The solution was stirred and heated to 90 ℃ to distill the azeotrope toluene/methanol. The reaction was monitored by checking the volume of distilled azeotrope and the formation of HCl (pH paper). After no azeotrope was formed anymore and the mixture was allowed to cool to r.t. and was then quenched with saturated aqueous solution of sodium carbonate. The formed salts are removed via filtration, and the filtrate is washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. Reactive vacuum distillation afforded 2,3-dihydro-1,4-dithiine as a pale-yellow oil.

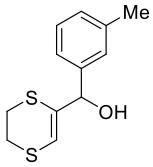
The preparation of 2: To a solution of 2,3-dihydro-1,4-dithiine (1 equiv) in 2 mL anhydrous THF which was cooled to -78 ℃, a solution of *n*-BuLi in hexane (2 equiv.) is added dropwise. The resulting mixture was kept at -78 ℃ over a period of 30 min. Then benzaldehydes (1.5 equiv.) and $Ti(O^iPr)_4$ (0.2 equiv.) were added dropwise. The reaction was let to warm to room temperature and monitored via TLC. The reaction was quenched by adding saturated aqueous solution of ammonium chloride. The mixture was extracted with methyl tert-butyl ether. The collected organic phases were washed with brine, dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.



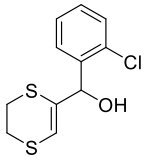
(5,6-dihydro-1,4-dithiin-2-yl)(phenyl)methanol (2b): the reaction was conducted at 2.0 mmol scale, 67% yield, yellow oil, R_f = 0.52 (PE/EA 5/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41-7.43 (m, 2H), 7.35-7.38 (m, 2H), 7.29-7.32 (m, 1H), 6.33 (s, 1H), 5.23 (s, 1H), 3.16-3.17 (m, 2H), 3.11-3.13 (m, 2H), 2.27 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.9, 130.8, 128.5, 128.2, 126.6, 113.4, 78.1, 27.3, 26.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{13}OS_2^+$ 225.0403, found 225.0401.



(4-bromophenyl)(5,6-dihydro-1,4-dithiin-2-yl)methanol (2c): the reaction was conducted at 2.0 mmol scale, 66% yield, yellow oil, R_f = 0.52 (PE/EA 5/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47-7.49 (m, 2H), 7.29-7.30 (m, 2H), 6.34 (s, 1H), 5.19 (s, 1H), 3.15-3.17 (m, 2H), 3.10-3.13 (m, 2H), 2.29 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.9, 131.6, 130.4, 128.3, 122.0, 114.0, 77.6, 27.3, 26.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{12}BrOS_2^+$ 302.9508, found 302.9505.



(5,6-dihydro-1,4-dithiin-2-yl)(m-tolyl)methanol (2d): the reaction was conducted at 2.0 mmol scale, 58% yield, yellow oil, R_f = 0.63 (PE/EA 5/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, J = 6.7 Hz, 1H), 7.22-7.24 (m, 2H), 7.14 (d, J = 7.3 Hz, 1H), 6.35 (s, 1H), 5.21 (s, 1H), 3.16-3.19 (m, 2H), 3.13-3.15 (m, 2H), 2.39 (s, 3H), 2.33 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.8, 138.2, 130.8, 128.9, 128.4, 127.2, 123.7, 113.2, 78.1, 27.2, 26.8, 21.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{15}ClOS_2^+$ 239.0559, found 239.0564.



(2-chlorophenyl)(5,6-dihydro-1,4-dithiin-2-yl)methanol (2e): the reaction was conducted at 2.0 mmol scale, 62% yield, yellow oil, R_f = 0.50 (PE/EA 5/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (dd, J = 7.7, 1.7 Hz, 1H), 7.35 (dd, J = 7.9, 1.4 Hz, 1H), 7.30-7.33 (m, 1H), 7.24-7.26 (m, 1H), 6.27 (s, 1H), 5.60 (s, 1H), 3.12-3.17 (m, 4H), 2.40 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.0, 132.9, 129.7, 129.3, 128.7, 128.3, 126.9, 114.7, 74.6, 27.2, 26.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{11}ClNaOS_2^+$ 280.9833, found 280.9840.

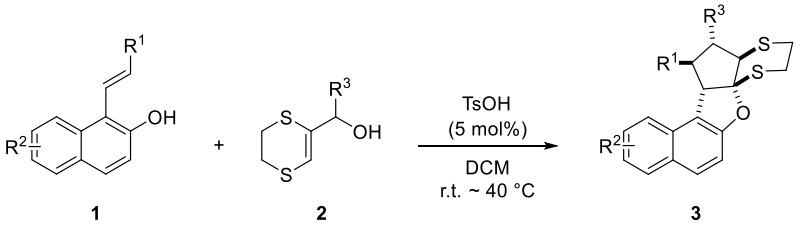
3. Reference

1. (a) Kshirsagar, U. A.; Regev, C.; Parnes, R.; Pappo, D. Iron-Catalyzed Oxidative Cross-Coupling of Phenols and Alkenes. *Org. Lett.* **2013,** *15*, 3174-3177. (b)Yang, D.; Zhu, Y.; Yang, N.; Jiang, Q.; Liu, R. One-Step Synthesis of Substituted Benzofurans from *ortho*-Alkenylphenols via Palladium-Catalyzed C−H Functionalization. *Adv. Synth. Catal.* **2016,** *358*, 1731-1735.

2. Hullaert, J.; Winne, J. M. (5,6-Dihydro-1,4-dithiin-2-yl)methanol as a Versatile Allyl-Cation Equivalent in (3+2) Cycloaddition Reactions. *Angew. Chem. Int. Ed.* **2016,** *55*, 13254-13258.

3. Christiaens, M.; Hullaert, J.; Van Hecke, K.; Laplace, D.; Winne, J. M. Stereoselective and Modular Assembly Method for Heterocycle-Fused Daucane Sesquiterpenoids. *Chem. – Eur. J.* **2018,** *24*, 13783-13787.

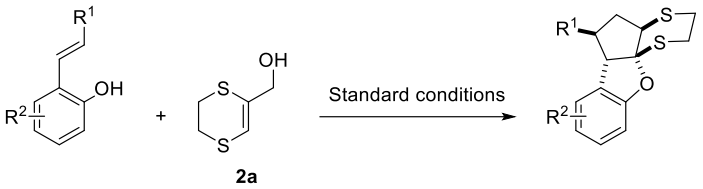
4. Synthesis of Compound 3

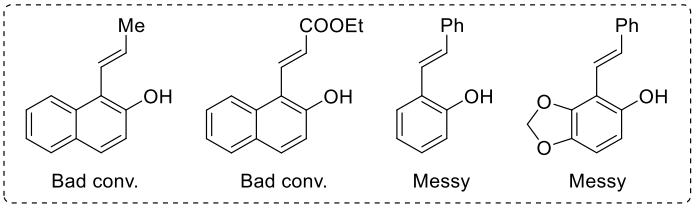


A mixture of 1-styrylnaphthols **1** (0.2 mmol), allylic alcohols **2** (0.3 mmol), and *p*-toluenesulfonic acid (0.01 mmol) was stirred in DCM (2.0 mL) at room temperature for 10 h. Then the reaction was heated to 40 ℃ and monitored via TLC. After the reaction finished, the reaction mixture was purified by column chromatography to afford the desired product **3**.

5. More screening studies on the substrate scope

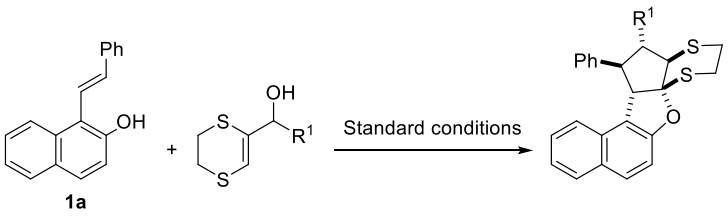
5.1 More screening studies on other phenols

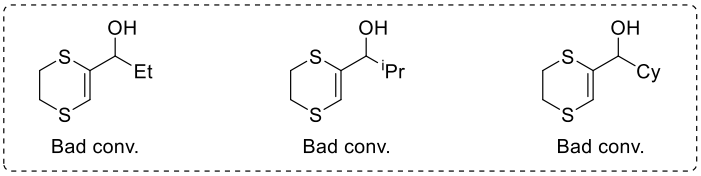




Reactions were performed with phenols (0.1 mmol), **2a** (0.15 mmol), *p*-TsOH (5 mol%), DCM, and at room temperature to 40 ℃. Bad conv. means phenols could not be transformed into corresponding products under the optimal catalytic reaction conditions. Messy means the conversation was too messy to separate or identify as pure compounds.

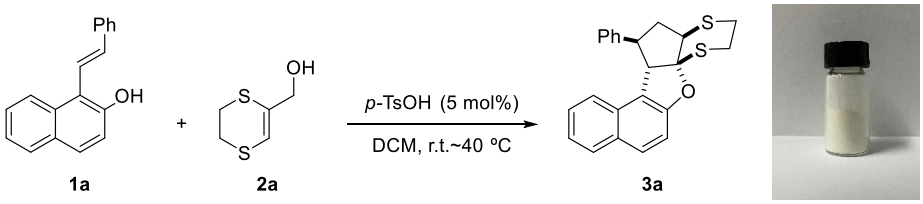
5.2 More screening studies on other allylic alcohols





Reactions were performed with **1a** (0.1 mmol), allylic alcohols (0.15 mmol), *p*-TsOH (5 mol%), DCM, and at room temperature to 40 ℃. Bad conv. means **1a** could not be transformed into corresponding products under the optimal catalytic reaction conditions.

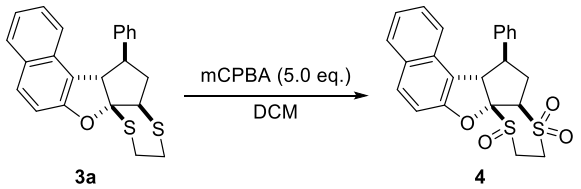
6. Gram-scale synthesis of compound 3a



A mixture of 1-styrylnaphthols **1a** (4.06 mmol, 1.00 g), allylic alcohol **2a** (6.09 mmol, 0.90 g), and *p*-toluenesulfonic acid (0.20 mmol, 34.96 mg) was stirred in DCM at room temperature for 30 h. Then the reaction was heated to 40 ℃ and monitored via TLC. After completion of the reaction, the reaction mixture was concentrated and directly

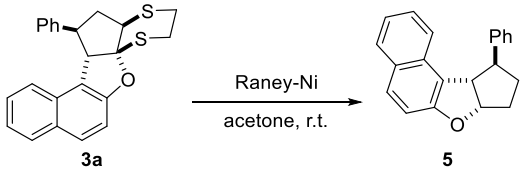
purified by flash column chromatography on silica gel to afford the pure products **3a** as a white solid in 82% yield (1.25 g).

7. Synthesis of compound 4



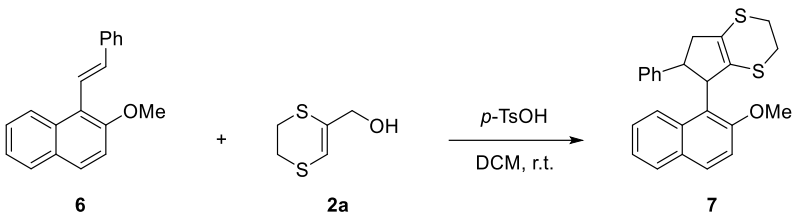
m-chloroperoxybenzoic acid (*m*CPBA) (0.744 mmol, 128.3 mg) was dissolved in DCM, and the dissolved solution was added to **3a** (0.186 mmol, 70.0 mg) solution in DCM, and then the mixture was stirred in ice water bath for 1 hour. The mixture after reaction was extracted with saturated sodium bicarbonate solution. The organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The product was obtained after column chromatography. The product was isolated as a white solid in 66% yield (52.1 mg).

8. Synthesis of compound 5



A suspension of 1.0 g (wet) Raney-Nickel (washed three times with water) in acetone was heavily stirred at room temperature, and then a solution of **3a** (0.2 mmol, 75.3 mg) in acetone was added to this mixture. After two hours of stirring at room temperature, the reaction mixture was filtered over a pad of celite and the residue was washed extensively with acetone. This filtrate is concentrated in vacuo, redissolved in diethyl ether and washed with brine, dried over anhydrous sodium sulfate and again concentrated in vacuo. The resulting product was purified by flash chromatography over silica yielding the product of **5** as a white solid in 61% yield (35.0 mg).

9. Control experiments

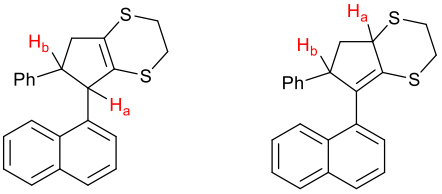


6 2a 7

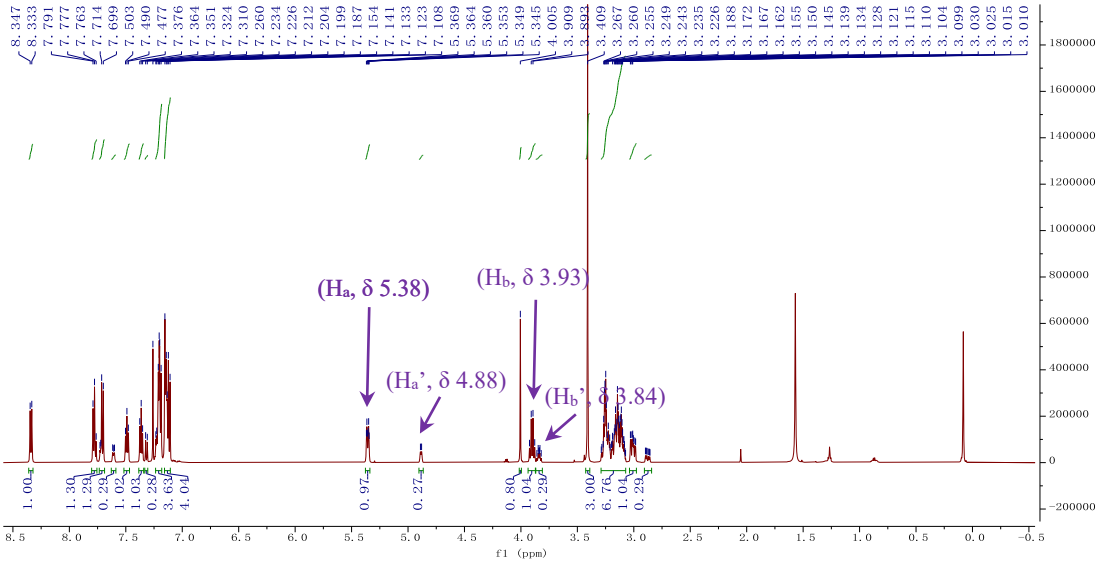
A mixture of **6** (0.2 mmol, 52.07 mg), allylic alcohol **2a** (0.3 mmol, 44.07 mg), and *p*-toluenesulfonic acid (0.01 mmol, 1.72 mg) was stirred in DCM at room temperature for 10 h. Then the reaction was heated to 40 ℃ and monitored via TLC. When substrate **6** was no longer converted, the reaction mixture was concentrated and directly purified by flash column chromatography on silica gel to afford the products **7** as a white solid in 39% yield (30.4 mg), 3.3:1 dr.

Compound 7: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, J = 8.6 Hz, 1.0 H), 7.76-7.79 (m, 1.3 H), 7.70-7.73 (m, 1.3 H), 7.60-7.62 (m, 0.3 H), 7.48-7.50 (m, 1.0 H), 7.35-7.38 (m, 1.0 H), 7.32 (d, J = 9.0 Hz, 0.3 H), 7.19-7.23 (m, 3.6 H), 7.11-7.15 (m, 4.0 H), 5.34-5.37 (m, 1.0 H), 4.88-4.89 (m, 0.3 H), 4.01 (s, 0.8 H), 3.88-3.92 (m, 1.0 H), 3.82-3.86 (m, 0.3 H), 3.41 (s, 3.0 H), 3.07-3.29 (m, 6.8 H), 2.98-3.03 (m, 1.0 H), 2.86-2.90 (m, 0.3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.4, 144.0, 133.1, 130.2, 129.4, 129.1, 128.2, 127.8, 126.3, 126.1, 125.7 124.3, 123.5, 121.21, 119.2, 115.0, 57.7, 54.7, 49.4, 45.4, 27.2, 27.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{23}OS_2^+$ 391.1185, found 391.1188.

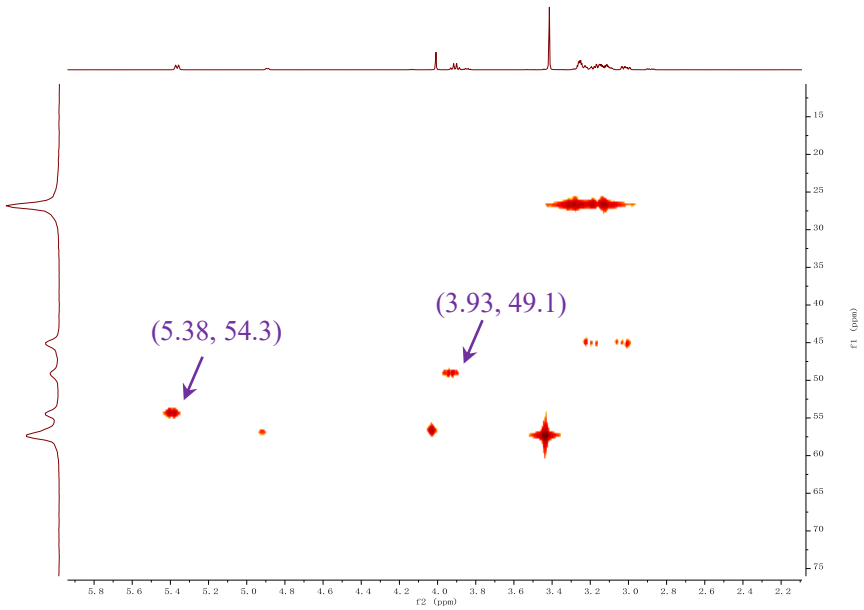
We further confirmed the structure of **7** by H-H COSY and HMQC spectra. From ^{1}H NMR and HMQC spectra, the major proton signal of ‘Ha’ and ‘Hb’ were assigned to 5.38 and 3.93. The H-H COSY spectrum showed cross peaks at (5.38, 3.93), indicating that proton Ha and Hb are intercoupling. These results were in accordance with the structure of **7** rather than another positional alkene isomers **7’**. The proton Ha’ and Hb’ in minor products were also intercoupling (cross peak at 4.88, 3.84). Therefore, according to these results and analysis, we could probably confirm that the double bond existed between the two ring sulfur atoms and the compound **7** was obtained in 3.3:1 dr.



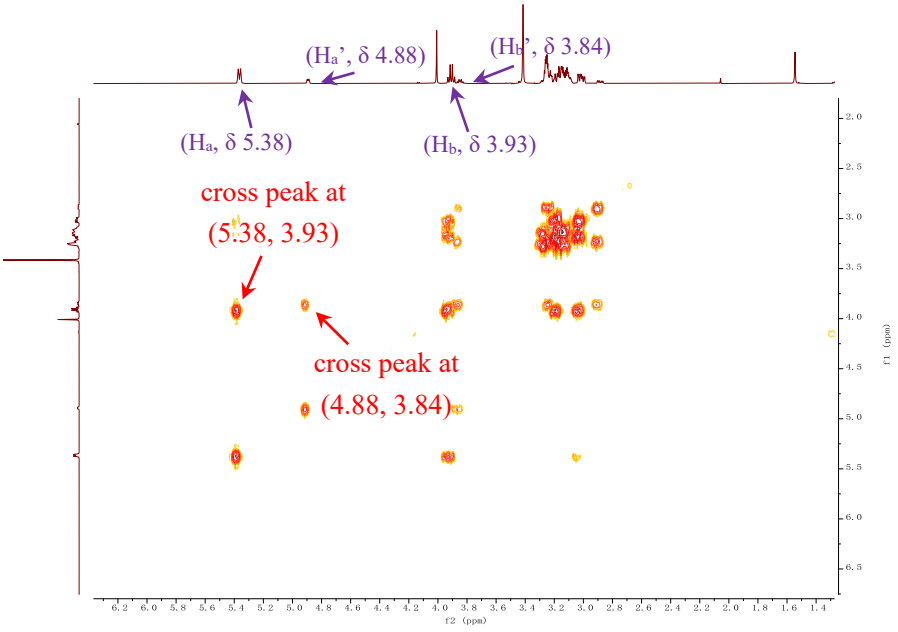
7 **7'**



^{1}H NMR spectra of **7**



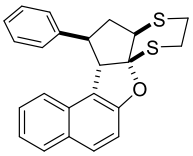
HMQC spectra of **7**



H-H COSY spectra of **7**

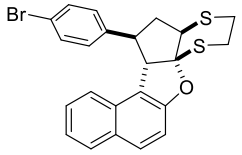
10. Analytical data of compounds 3–6

6-phenyl-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3a):



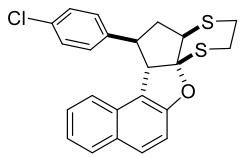
The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3a** as a white solid in 99% yield (74.6 mg), m.p. 144-146 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 6.0 Hz, 1H), 7.71 (d, *J* = 12.0 Hz, 1H), 7.48-7.50 (m, 2H), 7.43-7.45 (m, 2H), 7.33-7.36 (m, 1H), 7.23-7.25 (m, 1H), 7.16-7.23 (m, 2H), 6.97 (d, *J* = 6.0 Hz, 1H), 4.06 (d, *J* = 6.0 Hz, 1H), 3.50-3.54 (m, 1H), 3.29-3.36 (m, 2H), 3.14-3.19 (m, 1H), 2.86 (ddd, *J* = 13.2, 5.4, 3 Hz, 1H), 2.74 (ddd, *J* = 13.8, 5.4, 3 Hz, 1H), 2.52-2.58 (m, 1H), 2.32-2.36 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.2, 144.0, 130.4, 130.3, 130.0, 129.1, 128.9, 128.2, 127.2, 126.8, 124.0, 123.4, 121.2, 113.0, 96.1, 63.4, 50.8, 47.4, 42.5, 28.5, 22.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{20}NaOS_2^+$ 399.0848, found 399.0851.

6-(4-bromophenyl)-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3b):



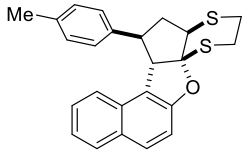
The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3b** as a white solid in 98% yield (89.0 mg), m.p. 140-142 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.55-7.58 (m, 2H), 7.36-7.38 (m, 2H), 7.22-7.25 (m, 2H), 7.16 (d, *J* = 8.8 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 3.99 (d, *J* = 6.7 Hz, 1H), 3.50-3.54 (m, 1H), 3.26-3.33 (m, 2H), 3.14-3.18 (m, 1H), 2.84-2.88 (m, 1H), 2.74 (ddd, *J* = 14.1, 5.7, 2.8 Hz, 1H), 2.46-2.53 (m, 1H), 2.31-2.35 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.3, 143.1, 132.2, 130.5, 130.3, 130.0, 129.9, 129.1, 127.0, 123.7, 123.5, 121.0, 120.8, 113.0, 95.8, 63.3, 50.1, 47.2, 42.4, 28.4, 22.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{19}BrNaOS_2^+$ 476.9953, found 476.9950.

6-(4-chlorophenyl)-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3c):



The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3c** as a white solid in 99% yield (81.5 mg), m.p. 134-136 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72-7.79 (m, 1H), 7.72 (d, *J* = 8.9 Hz, 1H), 7.40-7.44 (m, 4H), 7.21-7.28 (m, 2H), 7.16 (d, *J* = 8.8 Hz, 1H), 6.93-6.94 (m, 1H), 3.99 (d, *J* = 6.7 Hz, 1H), 3.50-3.54 (m, 1H), 3.27-3.34 (m, 2H), 3.14-3.18 (m, 1H), 2.84-2.88 (m, 1H), 2.74 (ddd, *J* = 14.1, 5.7, 2.9 Hz, 1H), 2.47-2.53 (m, 1H), 2.31-2.35 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.3, 142.6, 132.9, 130.5, 130.3, 130.0, 129.6, 129.3, 129.1, 126.9, 123.7, 123.4, 120.8, 113.0, 95.8, 63.4, 50.1, 47.2, 42.4, 28.4, 22.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{19}ClNaOS_2^+$ 433.0459, found 433.0460.

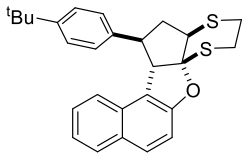
6-(p-tolyl)-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3d):



The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3d** as a white solid in 92% yield (72.0 mg), m.p. 138-140 ℃.^{1}H NMR (600 MHz, $CDCl_3$) δ

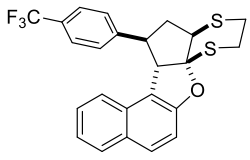
7.77 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.19-7.26 (m, 4H), 7.17 (d, *J* = 8.9 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 4.02 (d, *J* = 6.7 Hz, 1H), 3.49-3.54 (m, 1H), 3.26-3.33 (m, 2H), 3.14-3.19 (m, 1H), 2.85 (ddd, *J* = 13.7, 5.8, 3.2 Hz, 1H), 2.73 (ddd, *J* = 14.1, 5.8, 2.9 Hz, 1H), 2.50-2.56 (m, 1H), 2.42 (s, 3H), 2.29-2.33 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.2, 141.0, 136.7, 130.2, 130.0, 129.7, 128.9, 128.1, 126.8, 124.0, 123.3, 121.2, 113.0, 95.9, 63.3, 50.3, 47.3, 42.4, 28.5, 22.6, 21.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{22}NaOS_2^+$ 413.1005, found 413.1002.

6-(4-(tert-butyl)phenyl)-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3e):



The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3e** as a white solid in 87% yield (75.0 mg), m.p. 168-170 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 10.0 Hz, 1H), 7.43-7.47 (m, 4H), 7.25-7.27 (m, 1H), 7.20-7.23 (m, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 4.04 (d, *J* = 6.6 Hz, 1H), 3.51-3.55 (m, 1H), 3.30-3.36 (m, 2H), 3.15-3.20 (m, 1H), 2.85-2.89 (m, 1H), 2.75 (ddd, *J* = 14.1, 5.7, 2.9 Hz, 1H), 2.53-2.59 (m, 1H), 2.32-2.36 (m, 1H), 1.40 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.2, 150.1, 140.9, 130.4, 130.2, 130.0, 128.9, 127.8, 126.7, 125.9, 124.1, 123.3, 121.3, 113.0, 96.0, 63.4, 50.1, 47.3, 42.3, 34.7, 31.6, 28.4, 22.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{28}NaOS_2^+$ 455.1474, found 455.1473.

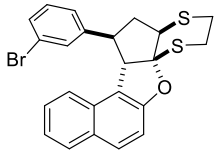
6-(4-(trifluoromethyl)phenyl)-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3f):



The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3f** as a white solid in 98% yield (87.0 mg), m.p. 169-171 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.71-7.75 (m, 3H), 7.62-7.63 (m, 2H), 7.26-7.29 (m, 1H), 7.22-7.24 (m, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 4.05 (d, *J* = 6.5 Hz,

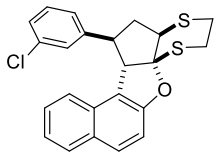
1H), 3.52-3.56 (m, 1H), 3.34-3.42 (m, 2H), 3.15-3.20 (m, 1H), 2.86-2.90 (m, 1H), 2.74-2.78 (m, 1H), 2.51-2.57 (m, 1H), 2.35-2.39 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ155.3, 148.2, 130.6, 130.2, 130.0, 129.5 (q, J_{CF} = 32.4 Hz), 129.1, 128.6, 127.0, 126.1 (q, J_{CF} = 3.8 Hz), 124.3 (q, J_{CF} = 270.1 Hz), 123.5, 123.4, 120.6, 113.0, 95.7, 63.2, 50.4, 47.2, 42.4, 28.4, 22.6; ^{19}F NMR (658 MHz, $CDCl_3$) δ -62.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}F_3OS_2^+$ 445.0903, found 445.0900.

6-(3-bromophenyl)-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3g):



The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3g** as a white solid in 71% yield (58.2 mg), m.p. 178-180 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.78-7.79 (m, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.65-7.66 (m, 1H), 7.50 (ddd, *J* = 7.9, 2.0, 1.1 Hz, 1H), 7.41-7.43 (m, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.23-7.28 (m, 2H), 7.17 (d, *J* = 8.8 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 4.02 (d, *J* = 6.7 Hz, 1H), 3.51-3.55 (m, 1H), 3.33 (dd, *J* = 13.3, 5.5 Hz, 1H), 3.26-3.29 (m, 1H), 3.16-3.20 (m, 1H), 2.87 (ddd, *J* = 13.7, 5.8, 3.3 Hz, 1H), 2.75 (ddd, *J* = 14.1, 5.7, 2.9 Hz, 1H), 2.50-2.55 (m, 1H), 2.33-2.36 (m, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.3, 146.5, 131.2, 130.7, 130.5, 130.4, 130.2, 130.0, 129.1, 127.0, 126.9, 123.7, 123.5, 123.1, 120.7, 113.0, 95.8, 63.2, 50.4, 47.2, 42.3, 28.4, 22.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{19}BrNaOS_2^+$ 476.9953, found 476.9951.

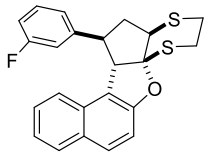
6-(3-chlorophenyl)-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3h):



The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3h** as a white solid in 71% yield (65.0 mg), m.p. 166-168 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.50-7.50 (m 1H), 7.36-7.38 (m, 2H), 7.33-7.35 (m, 1H), 7.22-7.28 (m, 2H), 7.17 (d, *J* = 8.8 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 4.02 (d, *J* = 6.6 Hz, 1H), 3.50-3.55 (m, 1H), 3.27-3.34 (m, 2H), 3.15-3.20 (m, 1H), 2.87 (ddd,

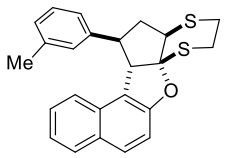
J = 13.6, 5.8, 3.2 Hz, 1H), 2.75 (ddd, *J* = 14.1, 5.7, 2.9 Hz, 1H), 2.50-2.56 (m, 1H), 2.32-2.37 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.3, 146.2, 134.9, 130.5, 130.4, 130.3, 130.0, 129.1, 128.3, 127.5, 127.0, 126.5, 123.7, 123.5, 120.7, 113.0, 95.8, 63.2, 50.4, 47.2, 42.3, 28.4, 22.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{19}ClNaOS_2^+$ 433.0459, found 433.0452.

6-(3-fluorophenyl)-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3i):



The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3i** as a white solid in 77% yield (61.1 mg), m.p. 159-161 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.39-7.43 (m, 1H), 7.22-7.27 (m, 4H), 7.17 (d, *J* = 8.8 Hz, 1H), 7.04-7.07 (m, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 4.03 (d, *J* = 6.6 Hz, 1H), 3.50-3.55 (m, 1H), 3.30-3.35 (m, 2H), 3.15-3.20 (m, 1H), 2.85-2.89 (m, 1H), 2.73-2.77 (m, 1H), 2.50-2.54 (m, 1H), 2.34-2.38 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.4 (d, J_{CF} = 244.9 Hz), 155.3, 146.7 (d, J_{CF} = 7.1 Hz), 130.6 (d, J_{CF} = 8.4 Hz), 130.4, 130.3, 130.0, 129.0, 126.9, 123.9 (d, J_{CF} = 2.7 Hz), 123.7, 123.4, 120.8, 115.0 (d, J_{CF} = 21.1 Hz), 114.2 (d, J_{CF} = 21.0 Hz), 113.0, 95.9, 63.2, 50.4, 47.2, 42.4, 28.4, 22.6; ^{19}F NMR (658 MHz, $CDCl_3$) δ -112.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{19}FNaOS_2^+$ 417.0754, found 417.0747.

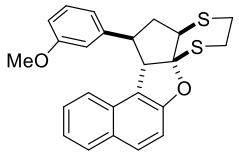
6-(m-tolyl)-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3j):



The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3j** as a white solid in 67% yield (52.3 mg), m.p. 158-160 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.32-7.35 (m, 1H), 7.28-7.31 (m, 2H), 7.24-7.27 (m, 1H), 7.19-7.21 (m, 1H), 7.17-7.19 (m, 2H), 6.99-7.01 (m, 1H), 4.06 (d, *J* = 6.8 Hz, 1H), 3.51-3.56 (m, 1H), 3.35 (dd, *J* = 13.3, 5.4 Hz, 1H), 3.26-3.30 (m, 1H), 3.16-3.21 (m, 1H), 2.87 (ddd, *J* = 13.6, 5.9, 3.3 Hz, 1H), 2.76 (ddd, *J* = 13.6, 5.8, 2.9 Hz,

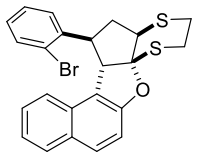
1H), 2.53-2.59 (m, 1H), 2.44 (s, 3H), 2.32-2.36 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.2, 143.9, 138.7, 130.4, 130.2, 130.0, 128.92, 128.89, 128.86, 128.0, 126.7, 125.3, 124.1, 123.3, 121.3, 113.0, 96.2, 63.3, 50.8, 47.5, 42.4, 28.5, 22.7, 21.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{22}NaOS_2^+$ 413.1005, found 413.1001.

6-(3-methoxyphenyl)-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3k):



The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3k** as a white solid in 68% yield (55.3 mg), m.p. 163-165 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.35-7.38 (m, 1H), 7.22-7.27 (m, 2H), 7.18 (d, *J* = 8.9 Hz, 1H), 7.05-7.10 (m, 3 H), 6.90-6.91 (m, 1H), 4.07 (d, *J* = 6.7 Hz, 1H), 3.87 (s, 3H), 3.51-3.55 (m, 1H), 3.30-3.35 (m, 2H), 3.16-3.20 (m, 1H), 2.86 (ddd, *J* = 13.7, 5.8, 3.2 Hz, 1H), 2.75 (ddd, *J* = 14.1, 5.7, 3.0 Hz, 1H), 2.55-2.60 (m, 1H), 2.33-2.35 (m, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 160.2, 155.2, 145.7, 130.4, 130.3, 130.1, 128.9, 126.8, 124.0, 123.4, 121.1, 120.6, 113.9, 113.0, 112.4, 95.9, 63.2, 55.4, 50.7, 47.3, 42.3, 28.5, 22.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{22}NaO_2S_2^+$ 429.0954, found 429.0955.

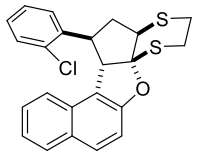
6-(2-bromophenyl)-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3l):



The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3l** as a white solid in 89% yield (81.0 mg), m.p. 143-145 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76-7.80 (m, 2H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.66 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.47-7.50 (m, 1H), 7.24-7.29 (m, 2H), 7.18-7.22 (m, 2H), 6.88-6.89 (m, 1H), 4.10 (d, *J* = 6.5 Hz, 1H), 3.95-3.99 (m, 1H), 3.52-3.57 (m, 1H), 3.38 (dd, *J* = 12.9, 5.8 Hz, 1H), 3.13-3.18 (m, 1H), 2.85-2.89 (m, 1H), 2.73 (ddd, *J* = 14.1, 5.5, 2.8 Hz, 1H), 2.38-2.48 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.2, 143.0, 133.2, 130.4, 130.3, 130.0, 128.9, 128.6, 128.5, 127.1, 124.8, 123.5, 123.4, 120.7, 112.9, 95.5, 62.6, 48.5, 47.1, 41.4, 28.5, 22.6. HRMS (ESI-TOF)

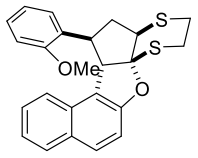
m/z: $[M+Na]^+$ Calcd for $C_{23}H_{19}BrNaOS_2^+$ 476.9953, found 476.9953.

6-(2-chlorophenyl)-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3m):



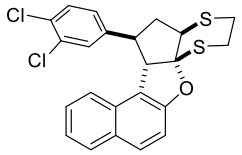
The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3m** as a white solid in 85% yield (70.1 mg), m.p. 139-141 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74-7.79 (m, 3H), 7.43-7.48 (m, 2H), 7.23-7.31 (m, 3H), 7.19 (d, *J* = 8.9 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 4.12 (d, *J* = 6.6 Hz, 1H), 3.97-4.01 (m, 1H), 3.52-3.57 (m, 1H), 3.37-3.40 (m, 1H), 3.14-3.18 (m, 1H), 2.85-2.89 (m, 1H), 2.72-2.76 (m, 1H), 2.42-2.46 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.2, 141.2, 134.0, 130.4, 130.3, 130.0, 129.9, 128.90, 128.87, 128.2, 128.0, 127.1, 123.5, 123.3, 120.7, 112.9, 95.6, 62.5, 47.2, 45.6, 41.3, 28.5, 22.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{19}ClNaOS_2^+$ 433.0459, found 433.0459.

6-(2-methoxyphenyl)-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3n):



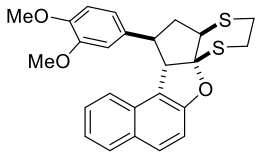
The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3n** as a white solid in 86% yield (67.0 mg), m.p. 158-160 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.32-7.35 (m, 1H), 7.22-7.25 (m, 1H), 7.14-7.18 (m, 2H), 7.08-7.11 (m, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 4.14 (d, *J* = 7.1 Hz, 1H), 3.82-3.87 (m, 1H), 3.75 (s, 3H), 3.51-3.55 (m, 1H), 3.37 (dd, *J* = 13.3, 5.5 Hz, 1H), 3.15-3.19 (m, 1H), 2.87 (ddd, *J* = 13.6, 5.9, 3.3 Hz, 1H), 2.76 (ddd, *J* = 14.0, 5.9, 2.9 Hz, 1H), 2.55-2.61 (m, 1H), 2.27-2.31 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.1, 155.1, 131.6, 130.4, 130.1, 129.9, 128.9, 128.7, 128.1, 126.4, 124.0, 123.2, 121.6, 121.3, 113.0, 110.9, 96.3, 61.8, 55.3, 47.6, 43.0, 40.5, 28.5, 22.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{22}NaO_2S_2^+$ 429.0954, found 429.0962.

6-(3,4-dichlorophenyl)-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3o):



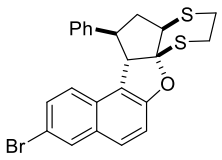
The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3o** as a white solid in 74% yield (66.0 mg), m.p. 156-158 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78-7.80 (m, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.59 (d, *J* = 2.2 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.33 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.25-7.30 (m, 2H), 7.17 (d, *J* = 8.9 Hz, 1H), 6.92-6.95 (m, 1H), 3.98 (d, *J* = 6.5 Hz, 1H), 3.50-3.55 (m, 1H), 3.25-3.32 (m, 2H), 3.15-3.19 (m, 1H), 2.85-2.89 (m, 1H), 2.73-2.77 (m, 1H), 2.46-2.52(m, 1H), 2.32-2.36 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.3, 144.5, 133.1, 131.2, 131.0, 130.6, 130.2, 130.1, 130.0, 129.2, 127.6, 127.1, 123.5, 123.4, 120.4, 113.0, 95.6, 63.2, 49.8, 47.0, 42.3, 28.4, 22.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{18}Cl_2NaOS_2^+$ 467.0069, found 467.0060.

6-(3,4-dimethoxyphenyl)-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3p):



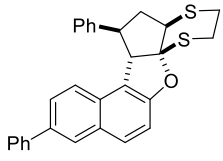
The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3p** as a white solid in 80% yield (70.0 mg), m.p. 201-203 ℃. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.25-7.28 (m, 1H), 7.22-7.24 (m, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 7.03-7.05 (m, 2H), 6.95 (d, *J* = 7.9 Hz, 1H), 4.03 (d, *J* = 6.8 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 3.51-3.55 (m, 1H), 3.33-3.36 (m, 1H), 3.26-3.29 (m, 1H), 3.16-3.20 (m, 1H), 2.86-2.89 (m, 1H), 2.75-2.79 (m, 1H), 2.53-2.58 (m, 1H), 2.33-2.36 (m, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.2, 149.3, 148.1, 136.5, 130.4, 130.3, 130.0, 128.9, 126.7, 124.1, 123.4, 121.2, 120.1, 113.0, 111.6, 111.3, 96.1, 63.6, 56.1, 50.4, 47.4, 42.3, 28.5, 27.0, 22.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{24}NaO_3S_2^+$ 459.1060, found 459.1061.

9-bromo-6-phenyl-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3q):



The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3q** as a white solid in 64% yield (58.4 mg), m.p. 175-177 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 2.0 Hz, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.43-7.47 (m, 4H), 7.34-7.37 (m, 1H), 7.24-7.26 (m, 1H), 7.18 (m, 1H), 6.79 (d, *J* = 8.9 Hz, 1H), 4.02 (d, *J* = 7.0 Hz, 1H), 3.49-3.54 (m, 1H), 3.35 (dd, *J* = 13.3, 5.5 Hz, 1H), 3.23-3.27 (m, 1H), 3.15-3.19 (m, 1H), 2.85-2.89 (m, 1H), 2.76 (ddd, *J* = 14.1, 5.9, 3.0 Hz, 1H), 2.51-2.58 (m, 1H), 2.33-2.37 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.5, 143.5, 131.1, 130.8, 130.0, 129.4, 129.2, 128.8, 128.1, 127.4, 125.7, 121.5, 116.9, 114.1, 96.5, 63.3, 51.0, 47.6, 42.4, 28.4, 22.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{19}BrNaOS_2^+$ 476.9953, found 476.9946.

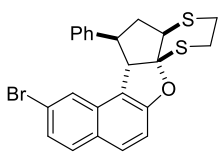
6,9-diphenyl-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3r):



The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3r** as a white solid in 77% yield (69.4 mg), m.p. 133-135 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.63-7.65 (m, 2H), 7.51-7.53 (m, 2H), 7.43-7.49 (m, 5H), 7.34-7.38 (m, 2H), 7.20 (d, *J* = 8.8 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 1H), 4.08 (d, *J* = 6.8 Hz, 1H), 3.52-3.56 (m, 1H), 3.32-3.39 (m, 2H), 3.16-3.21 (m, 1H), 2.86-2.90 (m, 1H), 2.75-2.79 (m, 1H), 2.55-2.61 (m, 1H), 2.35-2.39 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.4, 143.9, 141.1, 136.1, 130.6, 130.3, 129.5, 129.1, 129.0, 128.9, 128.2, 127.4, 127.28, 127.26, 127.2, 126.8, 126.5, 124.5, 121.2, 113.5, 96.3, 63.4, 50.9, 47.5, 42.5, 28.5, 22.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{24}NaOS_2^+$ 475.1161, found 475.1168.

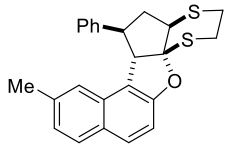
8-bromo-6-phenyl-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3s):

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3s** as a white solid in 74% yield (67.5 mg), m.p. 170-172 ℃. ^{1}H NMR (600



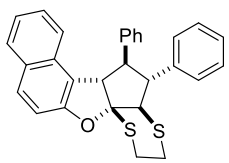
MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 1H), 7.46-7.50 (m, 4H), 7.36-7.39 (m, 1H), 7.31 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.16 (d, *J* = 8.8 Hz, 1H), 7.08-7.09 (m, 1H), 3.95 (d, *J* = 7.1 Hz, 1H), 3.49-3.54 (m, 1H), 3.35 (dd, *J* = 13.3, 5.4 Hz, 1H), 3.22-3.27 (m, 1H), 3.16-3.21 (m, 1H), 2.88 (ddd, *J* = 13.5, 6.1, 3.4 Hz, 1H), 2.77 (ddd, *J* = 14.0, 6.0, 3.0 Hz, 1H), 2.56-2.62 (m, 1H), 2.34-2.38 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.9, 143.3, 131.4, 130.4, 130.2, 129.2, 128.29, 128.27, 127.5, 126.7, 126.5, 121.3, 120.7, 113.4, 96.6, 63.7, 51.0, 47.6, 42.0, 28.4, 22.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{19}BrNaOS_2^+$ 476.9953, found 476.9954.

8-methyl-6-phenyl-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3t):



The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3t** as a white solid in 80% yield (62.5 mg), m.p. 188-190 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65-7.67 (m, 2H), 7.50-7.51 (m, 2H), 7.44-7.47 (m, 2H), 7.35-7.38 (m, 1H), 7.08-7.10 (m, 2H), 6.69 (s, 1H), 4.00 (d, *J* = 7.0 Hz, 1H), 3.50-3.55 (m, 1H), 3.35-3.38 (m, 1H), 3.25-3.29 (m, 1H), 3.16-3.20 (m, 1H), 2.87 (ddd, *J* = 13.6, 6.1, 3.4 Hz, 1H), 2.77 (ddd, *J* = 14.0, 6.0, 3.0 Hz, 1H), 2.55-2.61 (m, 1H), 2.33-2.38 (m, 1H), 2.17 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.2, 144.0, 136.6, 130.5, 129.9, 128.9, 128.6, 128.4, 128.1, 127.2, 125.6, 123.5, 120.6, 112.0, 96.2, 63.8, 51.0, 47.7, 42.2, 28.5, 22.8, 21.67, 21.65. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{22}NaOS_2^+$ 413.1005, found 413.1005.

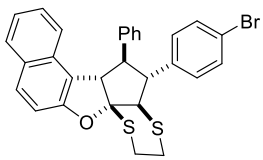
5,6-diphenyl-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3u):



The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3u** as a white solid in 55% yield (50.0 mg), m.p. 154-156 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.35-7.38 (m, 2H), 7.30-7.33 (m, 3H), 7.25-7.28 (m, 2H), 7.16-7.21 (m, 4H), 6.95-6.97 (m, 3H), 4.25 (d, *J* = 6.9 Hz, 1H), 3.76-3.80

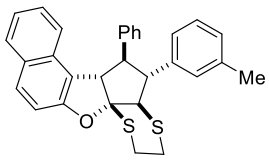
(m, 1H), 3.64 (d, *J* = 12.5 Hz, 1H), 3.57-3.61 (m, 1H), 3.37 (dd, *J* = 10.9, 7.1 Hz, 1H), 3.15-3.19 (m, 1H), 2.93 (ddd, *J* = 13.6, 6.1, 3.4 Hz, 1H), 2.75 (ddd, *J* = 14.1, 6.1, 3.0 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.2, 142.2, 138.0, 130.4, 130.3, 130.0, 128.9, 128.8, 128.5, 128.3, 128.0, 127.2, 127.1, 126.8, 123.8, 123.3, 121.1, 113.0, 95.5, 62.2, 58.9, 57.9, 53.5, 28.3, 22.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{24}NaOS_2^+$ 475.1161, found 475.1166.

5-(4-bromophenyl)-6-phenyl-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3v):



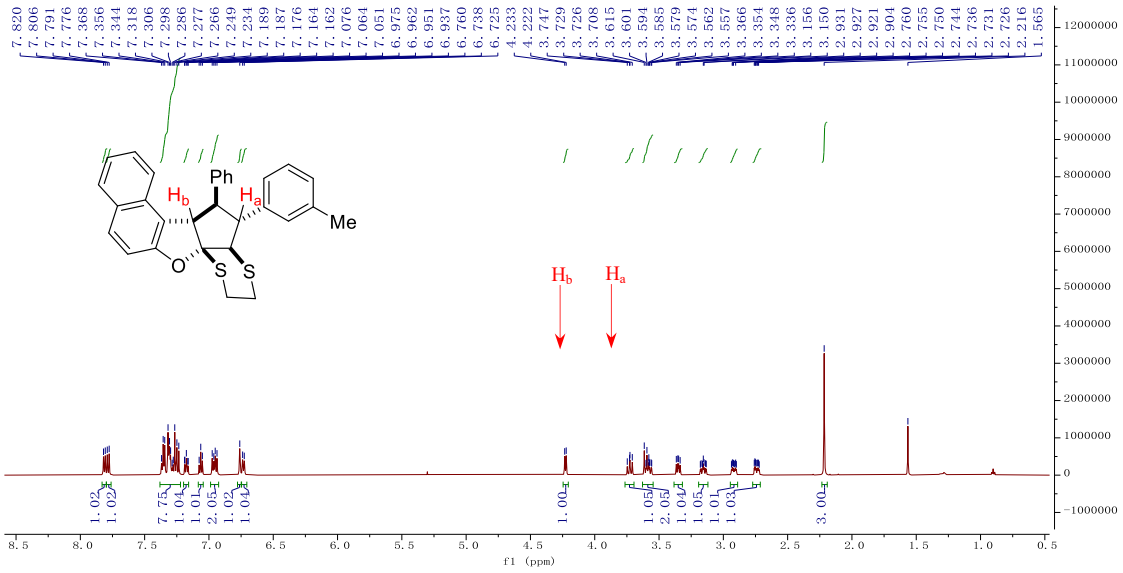
The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3v** as a white solid in 58% yield (61.9 mg), m.p. 150-152 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.9 Hz, 1H), 7.35-7.37 (m, 2H), 7.25-7.32 (m, 6H), 7.22 (d, *J* = 8.8 Hz, 1H), 7.15-7.18 (m, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.81-6.82 (m, 2H), 4.22 (d, *J* = 6.9 Hz, 1H), 3.73 (m, 1H), 3.54-3.59 (m, 2H), 3.28 (dd, *J* = 10.9, 7.0 Hz, 1H), 3.11-3.16 (m, 1H), 2.91 (ddd, *J* = 13.6, 6.1, 3.4 Hz, 1H), 2.74 (ddd, *J* = 14.1, 6.0, 3.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.2, 141.8, 137.1, 131.6, 130.5, 130.2, 130.0, 129.7, 128.90, 128.87, 128.2, 127.3, 126.8, 123.7, 123.4, 121.1, 120.9, 112.9, 95.2, 62.1, 57.4, 53.2, 31.6, 28.3, 22.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{23}BrNaOS_2^+$ 553.0266, found 553.0271.

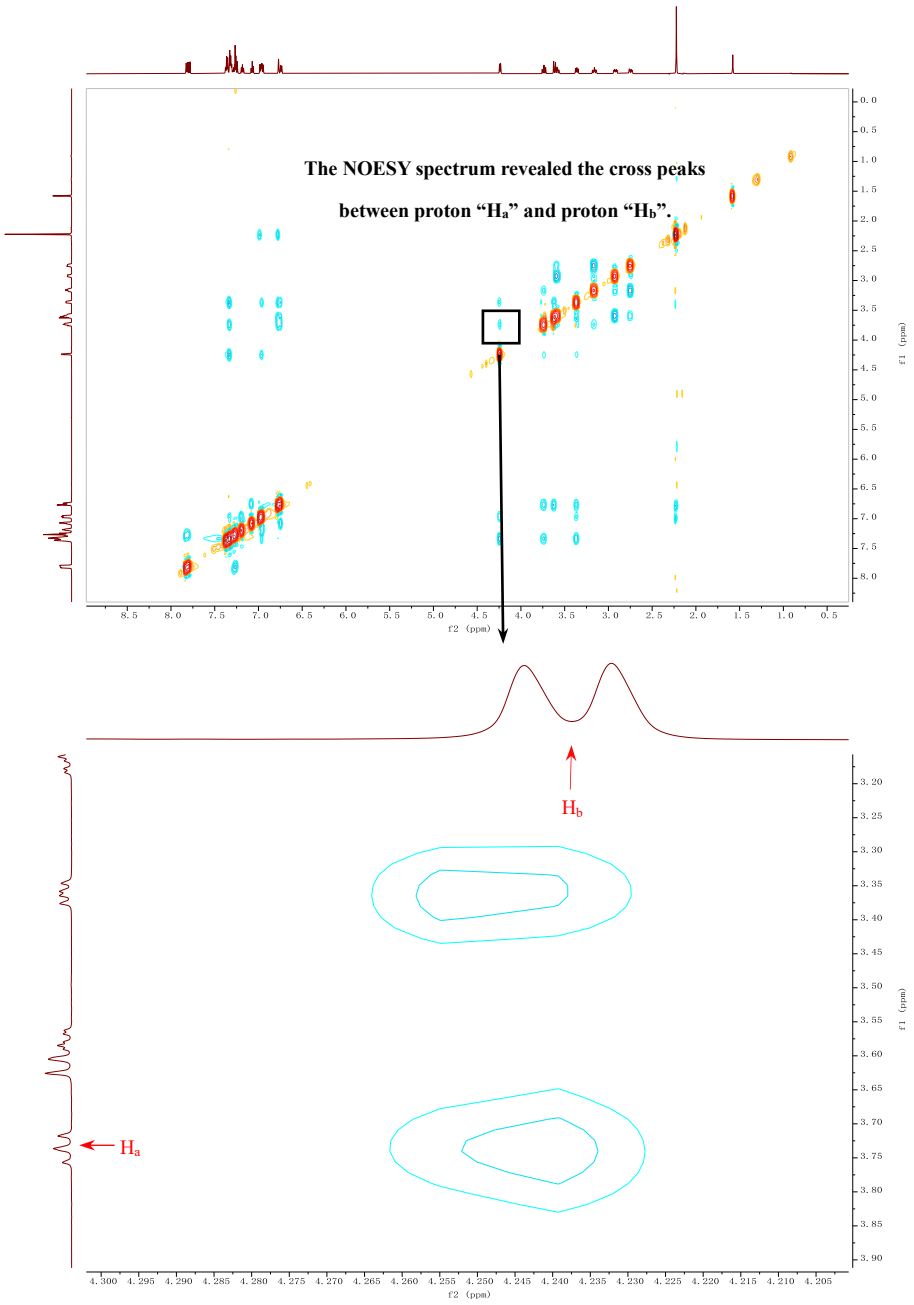
6-phenyl-5-(m-tolyl)-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3w):



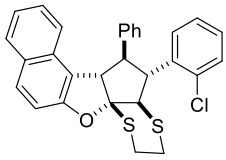
The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3w** as a white solid in 48% yield (45.1 mg), m.p. 175-177 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.9 Hz, 1H), 7.23-7.37 (m, 7H), 7.16-7.19 (m, 1H), 7.05-7.08 (m, 1H), 6.94-6.97 (m, 2H), 6.76 (s, 1H), 6.73 (d, *J* = 7.7 Hz, 1H), 4.23 (d, *J* = 7.0 Hz, 1H), 3.71-3.75 (m, 1H), 3.56-3.61 (m, 2H), 3.35 (dd, *J* = 10.9, 7.0 Hz, 1H), 3.13-3.18 (m, 1H), 2.90-2.94 (m, 1H), 2.72-2.76 (m, 1H), 2.22 (s, 3H); ^{13}C NMR

(150 MHz, $CDCl_3$) δ 155.2, 142.3, 137.9, 137.8, 130.32, 130.28, 129.9, 128.8, 128.7, 128.4, 128.3, 128.2, 128.1, 127.1, 126.8, 125.2, 123.9, 123.3, 121.2, 113.0, 95.5, 62.2, 58.9, 57.8, 53.5, 28.3, 22.6, 21.5. Important NOE signals: 4.14 × 3.74. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{26}NaOS_2^+$ 489.1318, found 489.1311.





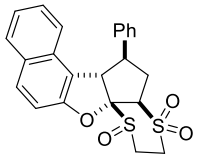
5-(2-chlorophenyl)-6-phenyl-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan (3x):



The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3x** as a white solid in 55% yield (53.8 mg), m.p. 138-140 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.33-7.37 (m, 4H), 7.27-7.31 (m, 2H), 7.23-7.25 (m, 2H), 7.14-7.21 (m, 3H), 7.06-7.09 (m, 1H), 6.98 (d, J = 8.3 Hz, 1H), 4.67-4.71

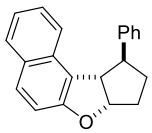
(m, 1H), 4.25 (d, *J* = 6.7 Hz, 1H), 3.55-3.60 (m, 1H), 3.40-3.43 (m, 2H), 3.30-3.34 (m, 1H), 2.90 (ddd, *J* = 13.8, 5.2, 2.8 Hz, 1H), 2.68 (ddd, *J* = 14.0, 5.2, 2.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.5, 141.6, 136.4, 130.5, 130.4, 130.1, 129.6, 129.0, 128.8, 128.4, 128.2, 127.33, 127.28, 127.2, 126.9, 123.9, 123.5, 121.1, 113.1, 94.1, 62.3, 58.7, 54.2, 52.1, 28.3, 23.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{23}ClNaOS_2^+$ 509.0772, found 509.0772.

6-phenyl-2,3,4a,5,6,6a-hexahydro-[1,4]dithiino[2',3':1,5]cyclopenta[1,2-b]naphtho[1,2-d]furan 1,4,4-trioxide (4):



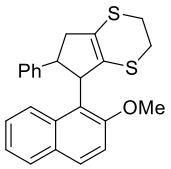
The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **4** as a white solid in 66% yield (52.1 mg), m.p. 170-172 ℃. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.9 Hz, 1H), 7.58-7.60 (m, 2H), 7.45-7.47 (m, 2H), 7.39-7.42 (m, 1H), 7.30-7.33 (m, 1H), 7.16-7.20 (m, 2H), 6.86 (*J* = 8.3 Hz, 1H), 5.30 (d, *J* = 7.8 Hz, 1H), 4.32-4.36 (m, 1H), 3.97-4.02 (m, 1H), 3.94 (ddd, *J* = 14.6, 6.4, 2.3 Hz, 1H), 3.71 (ddd, *J* = 15.2, 6.0, 1.9 Hz, 1H), 3.30-3.33 (m, 1H), 3.17-3.20 (m, 1H), 2.65-2.75 (m, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.0, 141.4, 131.2, 130.6, 130.0, 129.2, 128.8, 128.3, 127.9, 127.3, 124.37, 124.36, 119.7, 112.4, 104.9, 71.9, 59.7, 51.1, 41.7, 40.3, 36.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{20}NaO_4S_2^+$ 447.0696, found 447.0702.

10-phenyl-7a,9,10,10a-tetrahydro-8H-cyclopenta[b]naphtho[1,2-d]furan (5):



The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **5** as a white solid in 61% yield (35.0 mg), m.p. 102-104 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76-7.77 (m, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.36-7.38 (m, 1H), 7.27-7.30 (m, 3H), 7.21-7.25 (m, 3H), 7.21-7.25 (m, 3H), 7.08 (d, *J* = 8.8 Hz, 1H), 5.59-5.61 (m, 1H), 4.32 (dd, *J* = 8.6, 4.4 Hz, 1H), 3.39-3.42 (m, 1H), 2.31-2.38 (m, 1H), 2.07-2.13 (m, 2H), 1.76-1.80 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.2, 145.4, 130.8, 129.6, 128.9, 128.8, 127.6, 126.6, 123.6, 123.3, 122.8, 121.9, 112.1, 90.3, 54.0, 52.9, 34.1, 33.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}O^+$ 287.1431, found 287.1439.

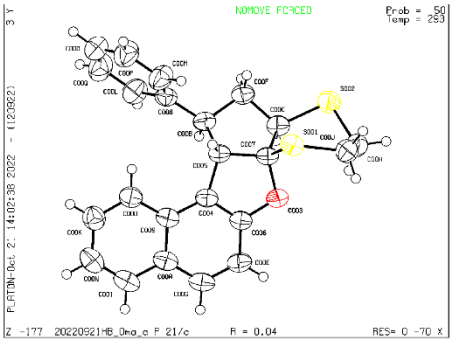
5-(2-methoxynaphthalen-1-yl)-6-phenyl-2,3,6,7-tetrahydro-5H-cyclopenta[b][1,4]dithiine (7):



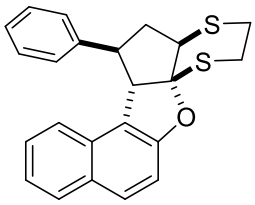
The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **7** as a white solid in 39% yield (30.4 mg), m.p. 150-152 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.6 Hz, 1.0 H), 7.76-7.79 (m, 1.3 H), 7.70-7.73 (m, 1.3 H), 7.60-7.62 (m, 0.3 H), 7.48-7.50 (m, 1.0 H), 7.35-7.38 (m, 1.0 H), 7.32 (d, *J* = 9.0 Hz, 0.3 H), 7.19-7.23 (m, 3.6 H), 7.11-7.15 (m, 4.0 H), 5.34-5.37 (m, 1.0 H), 4.88-4.89 (m, 0.3 H), 4.01 (s, 0.8 H), 3.88-3.92 (m, 1.0 H), 3.82-3.86 (m, 0.3 H), 3.41 (s, 3.0 H), 3.07-3.29 (m, 6.8 H), 2.98-3.03 (m, 1.0 H), 2.86-2.90 (m, 0.3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.4, 144.0, 133.1, 130.2, 129.4, 129.1, 128.2, 127.8, 126.3, 126.1, 125.7 124.3, 123.5, 121.21, 119.2, 115.0, 57.7, 54.7, 49.4, 45.4, 27.2, 27.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{23}OS_2^+$ 391.1185, found 391.1188.

11. X-ray crystal structures of 3a and 4

To a 10 mL tube containing **3a** (30.0 mg) was added a mixture of solvent (n-hexane/dichloromethane/isopropyl alcohol=1:1:1) (6.0 mL). A clear solution was obtained through ultrasound treatment and was kept at room temperature and the crystals were obtained after the solvent evaporated, which were characterized by X-ray single crystal diffraction. X-ray diffraction experiment was carried out on an Agilent Gemini and the data obtained were deposited at the Cambridge Crystallographic Data Centre.



(Ellipsoid contour probability 50%)

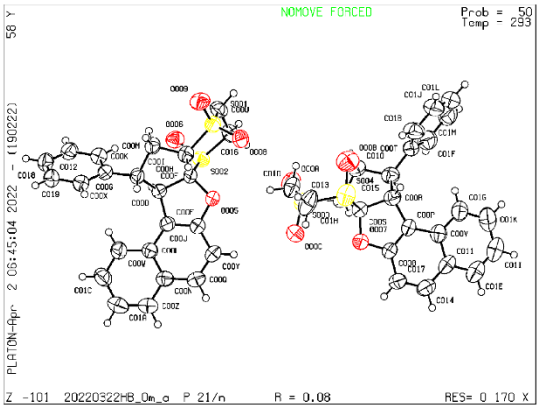


3a, CCDC 2214546

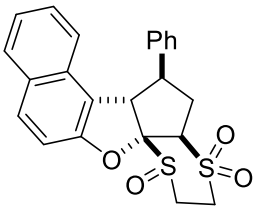
Identification code	20220921HB	
Chemical formula	$C_{23}H_{20}OS_2$	
Formula weight	376.51 g/mol	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 11.0348(9) Å	α = 90°
	b = 18.7940(17) Å	β = 111.244(4)°
	c = 9.6827(6) Å	γ = 90°
Volume	1871.6(3) $Å^3$	
Z	4	
Density (calculated)	1.336 g/cm^3	
Absorption coefficient	2.634 mm^{-1}	

F(000)	792
Theta range for data collection	4.30 to 68.47°
Index ranges	-13<=h<=13, -22<=k<=22, -11<=l<=10
Reflections collected	29693
Independent reflections	3447 [R(int) = 0.0648]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F2
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)
Function minimized	Σ w(Fo2 - Fc2)2
Data / restraints / parameters	3447 / 0 / 235
Goodness-of-fit on F2	1.031
Final R indices	2941 data; I>2 σ (I) R1 = 0.0414, wR2 = 0.1115
	all data R1 = 0.0489, wR2 = 0.1200
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0674P)^2+0.5196P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.173 and -0.338 $eÅ^{-3}$
R.M.S. deviation from mean	0.051 $eÅ^{-3}$

To a 10 mL tube containing **4** (30.0 mg) was added a mixture of solvent (dichloromethane/isopropyl alcohol=1:1) (6.0 mL). A clear solution was obtained through ultrasound treatment and was kept at room temperature and the crystals were obtained after the solvent evaporated, which were characterized by X-ray single crystal diffraction. X-ray diffraction experiment was carried out on an Agilent Gemini and the data obtained were deposited at the Cambridge Crystallographic Data Centre.



(Ellipsoid contour probability 50%)

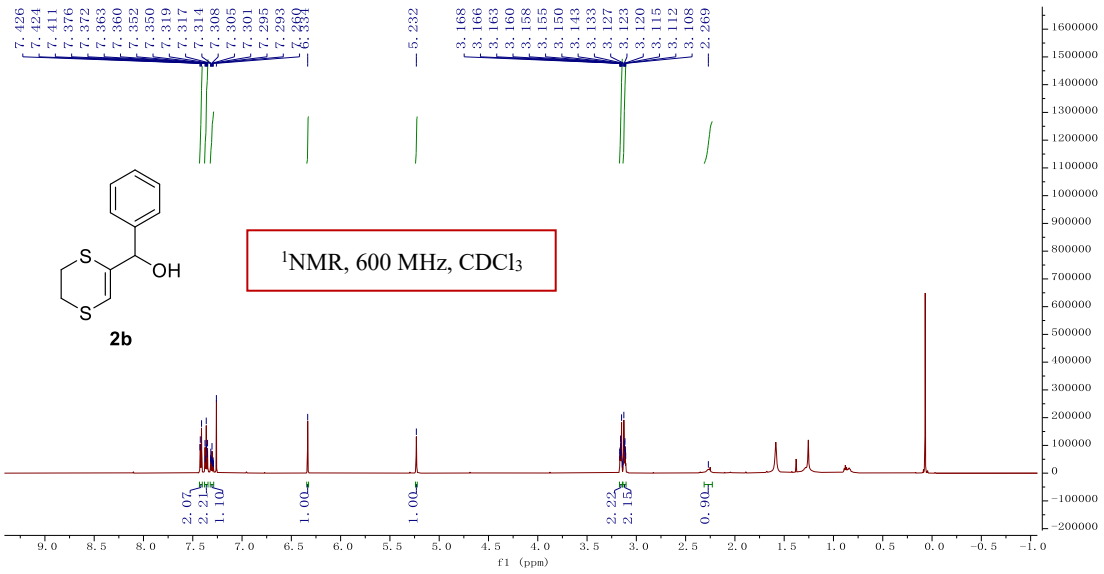


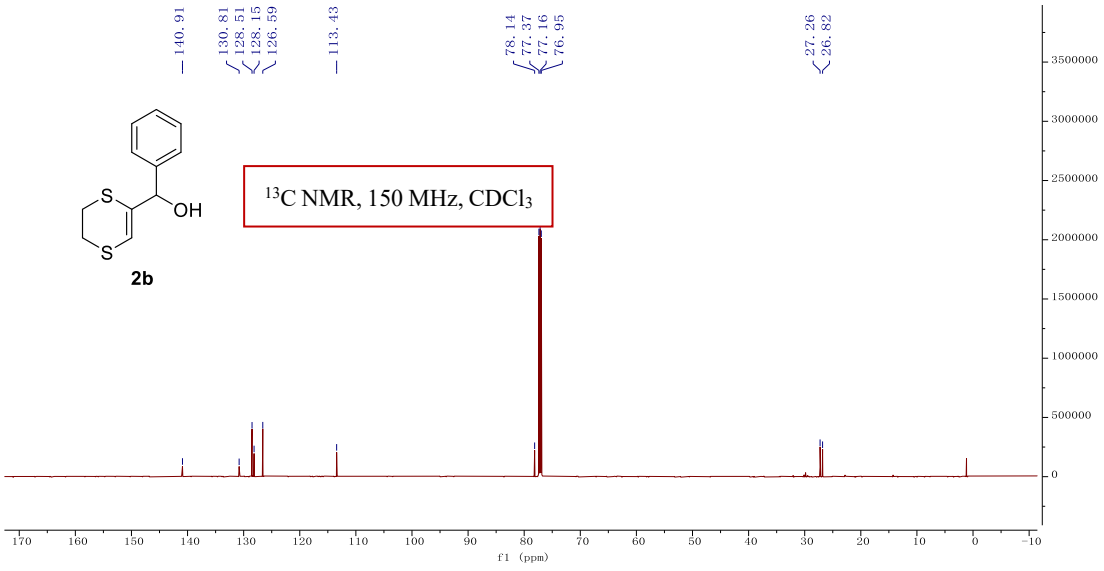
4, CCDC 2214538

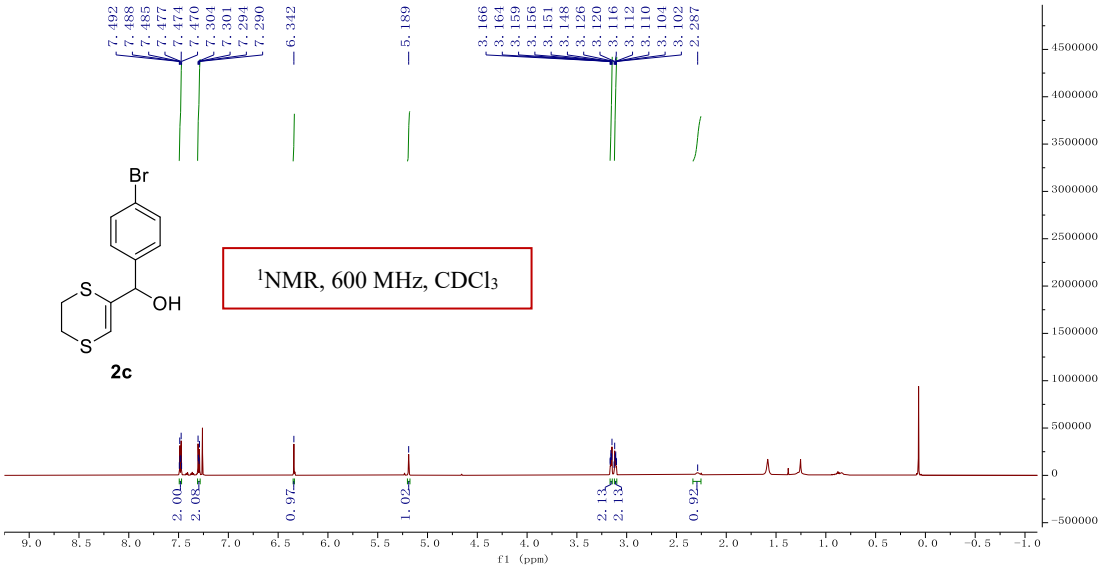
Identification code	20220322HB	
Chemical formula	$C_{46}H_{40}O_8S_4$	
Formula weight	849.02 g/mol	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 10.1975(5) Å	α = 90°
	b = 20.3322(11) Å	β = 101.235(3)°
	c = 19.3584(11) Å	γ = 90°
Volume	3936.8(4) $Å^3$	
Z	4	
Density (calculated)	1.432 g/cm^3	
Absorption coefficient	2.690 mm^{-1}	
F(000)	1776	
Theta range for data collection	3.18 to 68.65°	
Index ranges	-12<=h<=12, -21<=k<=20, -23<=l<=23	
Reflections collected	63099	
Independent reflections	7026 [R(int) = 0.1191]	
Coverage of independent reflections	96.4%	
Absorption correction	Multi-Scan	
Structure solution technique	direct methods	

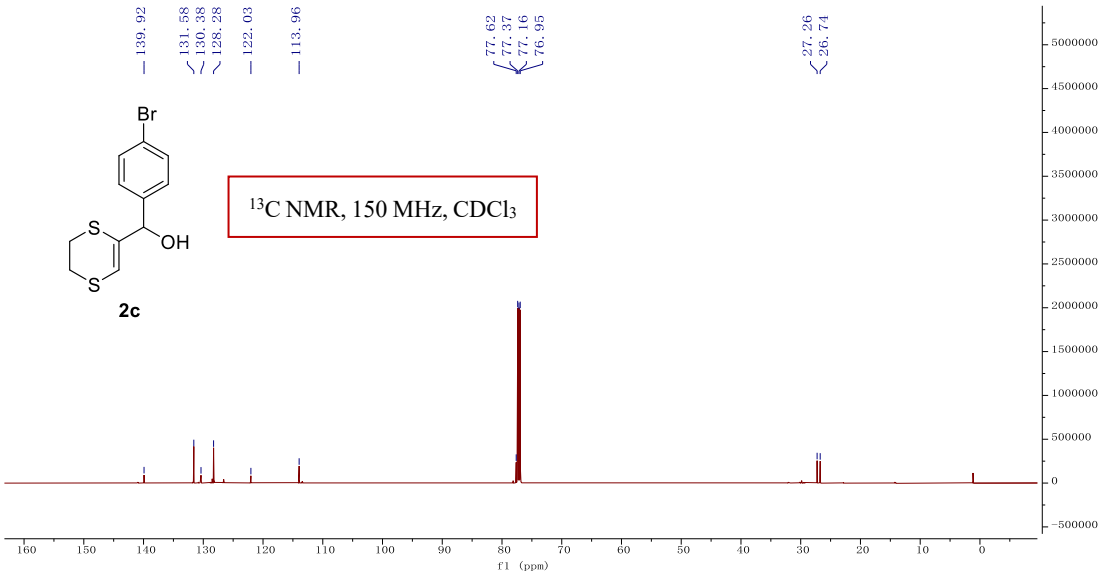
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F2
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)
Function minimized	Σ w(Fo2 - Fc2)2
Data / restraints / parameters	7026 / 0 / 524
Goodness-of-fit on F2	1.099
Final R indices	5048 data; I>2σ(I) R1 = 0.0760, wR2 = 0.1954
	all data R1 = 0.1010, wR2 = 0.2198
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1027P)^2+4.0054P]$ where $P=(F_o^2+2F_c^2)/3$
Extinction coefficient	0.0017(2)
Largest diff. peak and hole	1.166 and -0.459 eÅ^{-3}
R.M.S. deviation from mean	0.084 eÅ^{-3}

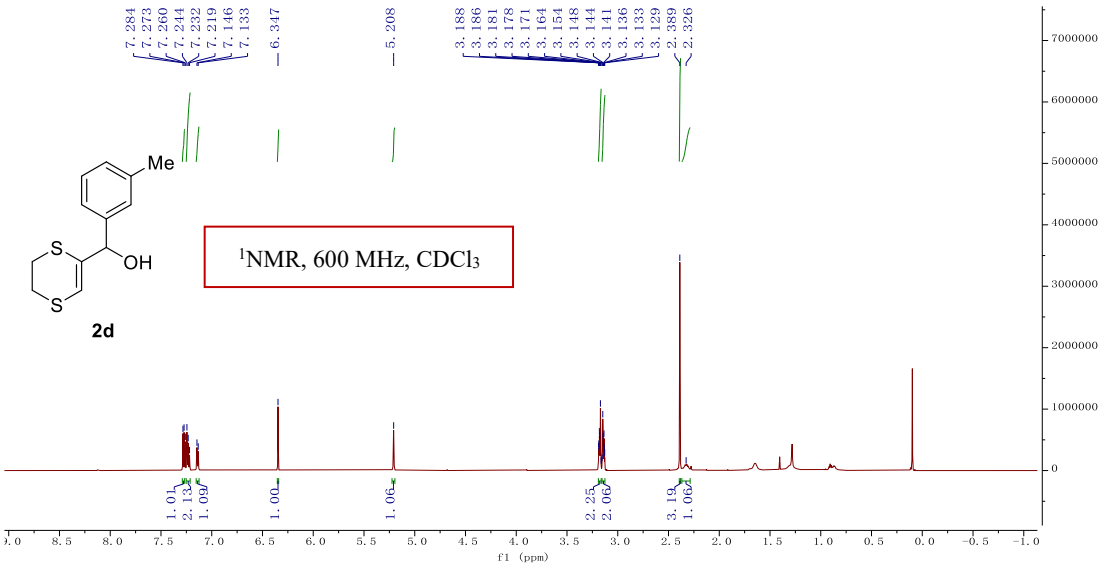
12. NMR spectra

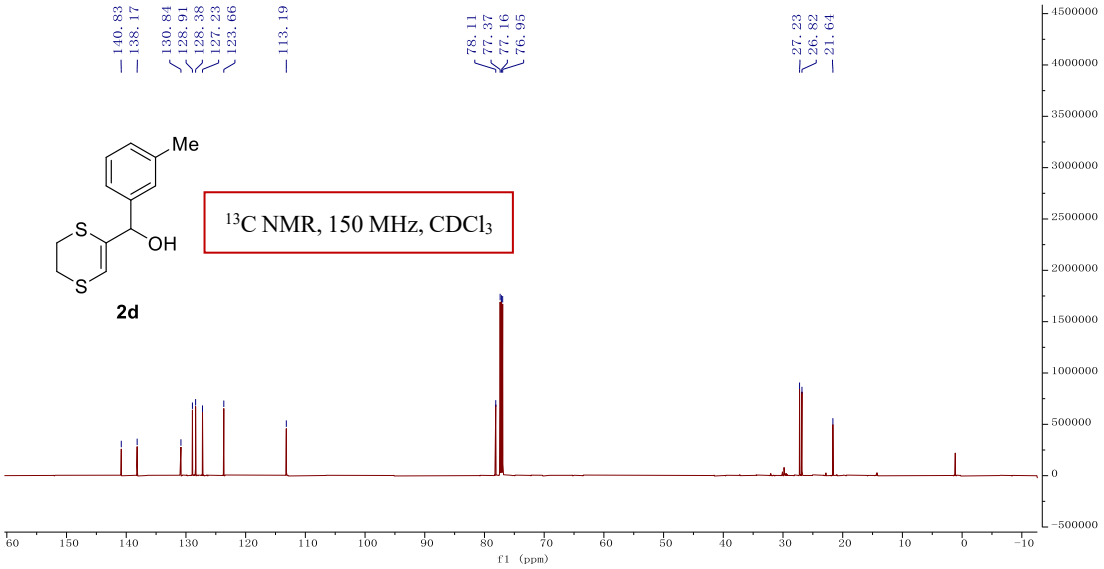


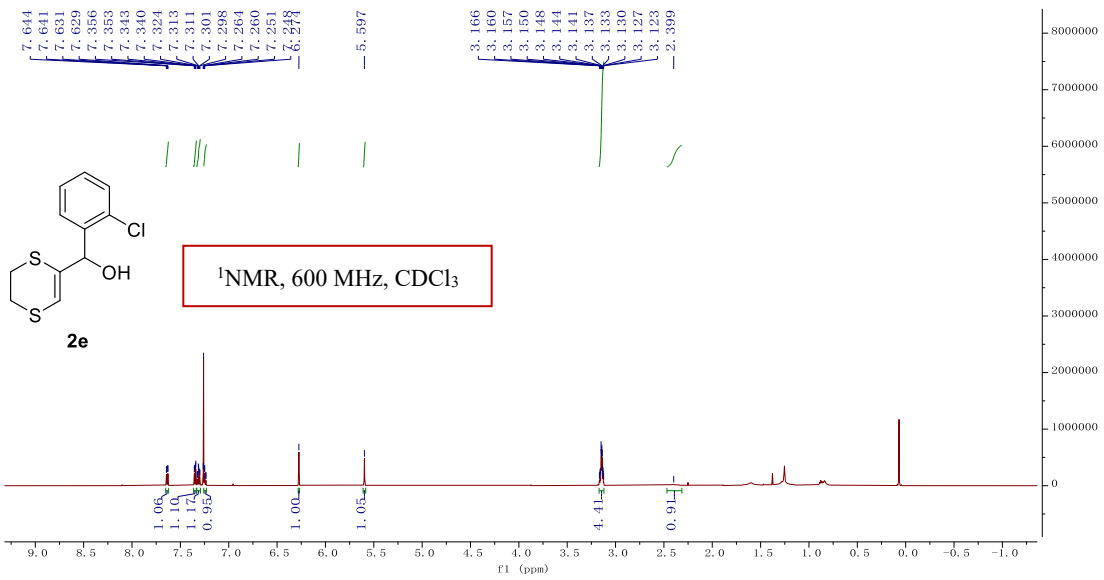


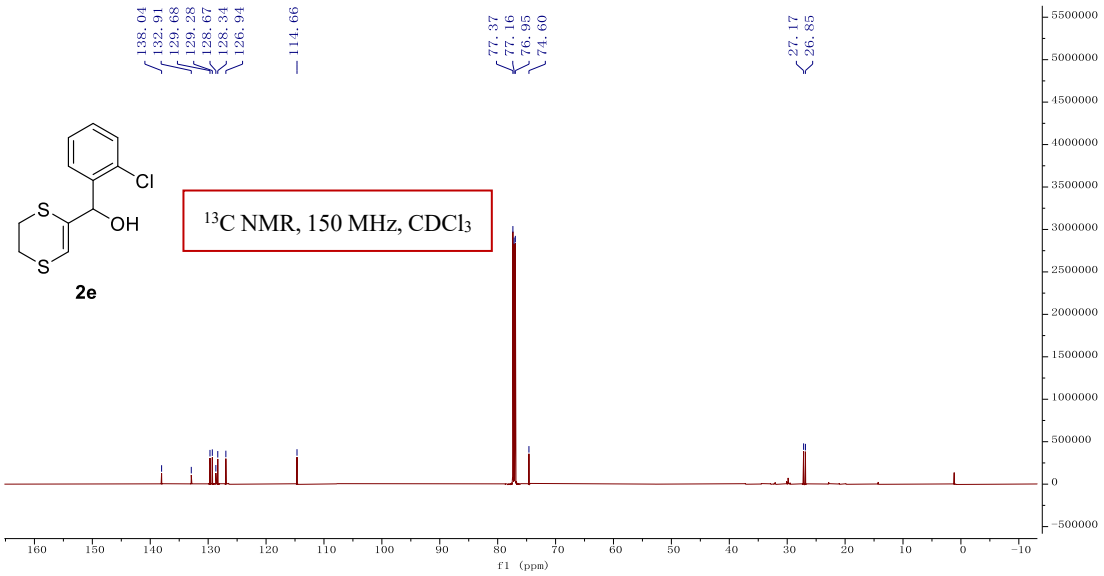

7.492
7.488
7.485
7.477
7.474
7.470
7.304
7.301
7.294
7.290
6.342
5.189
3.166
3.164
3.159
3.156
3.151
3.148
3.126
3.120
3.116
3.112
3.110
3.104
3.102
2.287
Br
S
OH
S
2c
^{1}NMR, 600 MHz, CDCl$_3$
2.00
2.08
0.97
1.02
2.13
2.13
0.92
f1 (ppm)

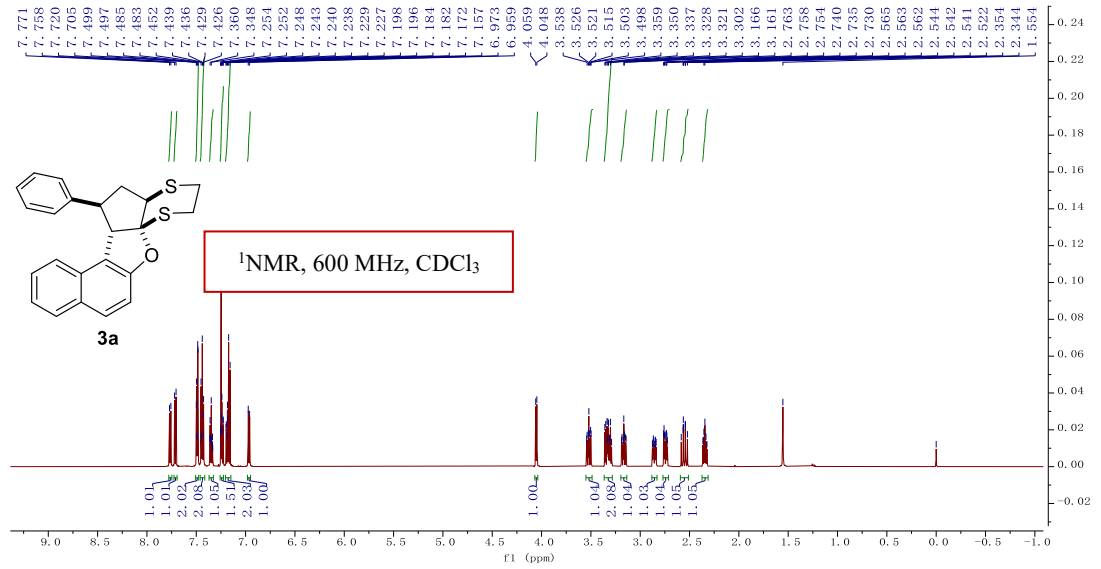

139.92
131.58
130.38
128.28
122.03
113.96
77.62
77.37
77.16
76.95
27.26
26.74
Br
S
OH
S
2c
^{13}C NMR, 150 MHz, CDCl$_3$
f1 (ppm)

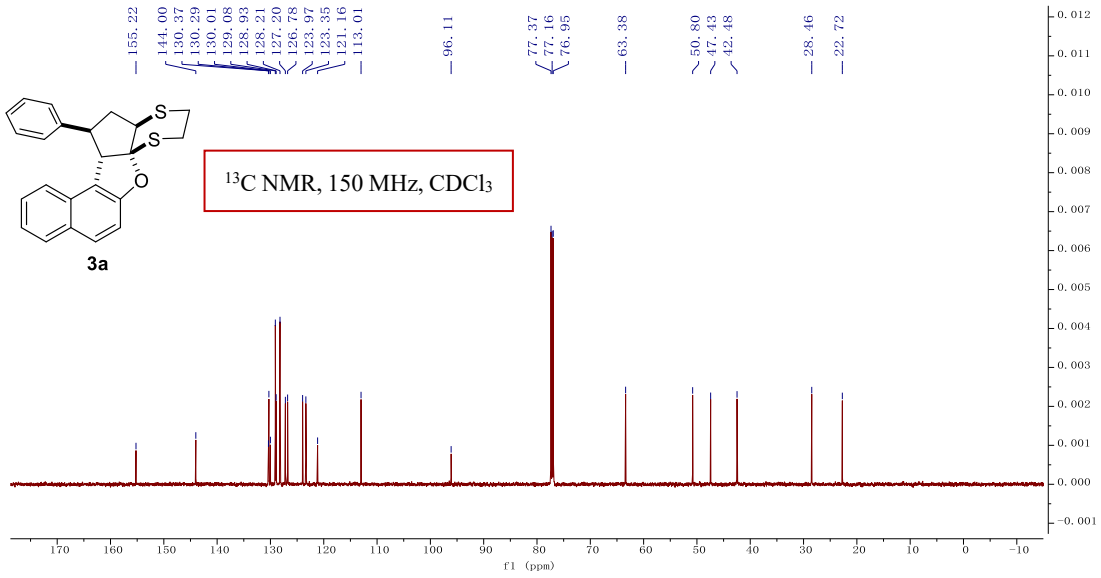

7.284
7.273
7.260
7.244
7.232
7.219
7.146
7.133
6.347
5.208
3.188
3.186
3.181
3.178
3.171
3.164
3.154
3.148
3.144
3.141
3.136
3.133
3.129
2.389
2.326
Me
S
OH
S
2d
1NMR, 600 MHz, CDCl3
1.01
2.13
1.09
1.00
1.06
2.25
2.06
3.19
1.06
f1 (ppm)

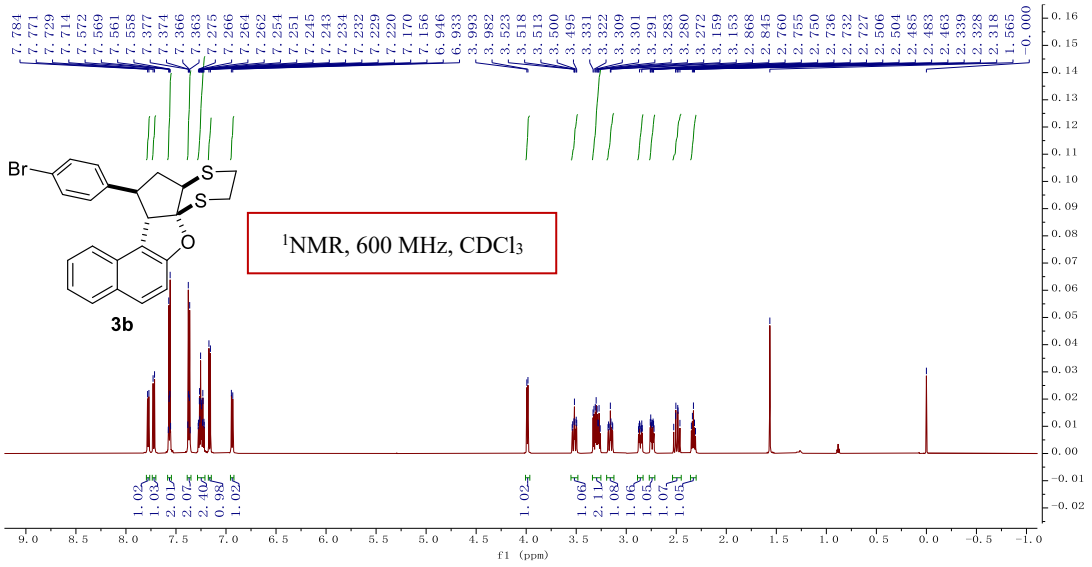

140.83
138.17
130.84
128.91
128.38
127.23
123.66
113.19
78.11
77.37
77.16
76.95
27.23
26.82
21.64
Me
S
OH
S
2d
13C NMR, 150 MHz, CDCl3
f1 (ppm)

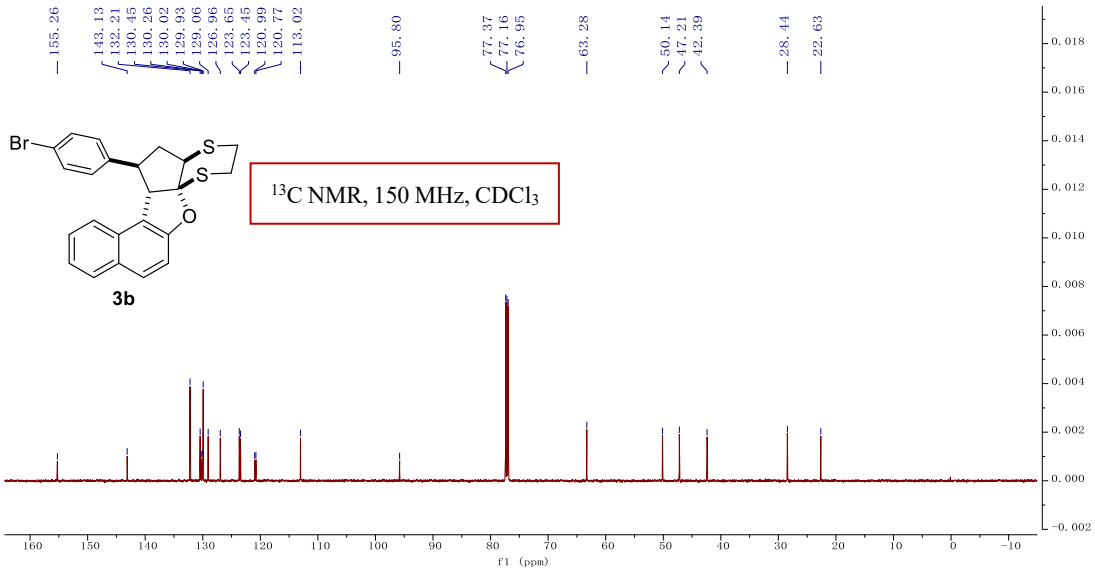

7.644
7.641
7.631
7.629
7.356
7.353
7.343
7.340
7.324
7.313
7.311
7.301
7.298
7.264
7.260
7.251
6.274
5.597
3.166
3.160
3.157
3.150
3.148
3.144
3.141
3.137
3.133
3.130
3.127
3.123
2.399
Cl
OH
S
S
2e
^{1}NMR, 600 MHz, CDCl$_3$
1.06
1.10
1.17
0.95
1.00
1.05
4.41
0.91
f1 (ppm)

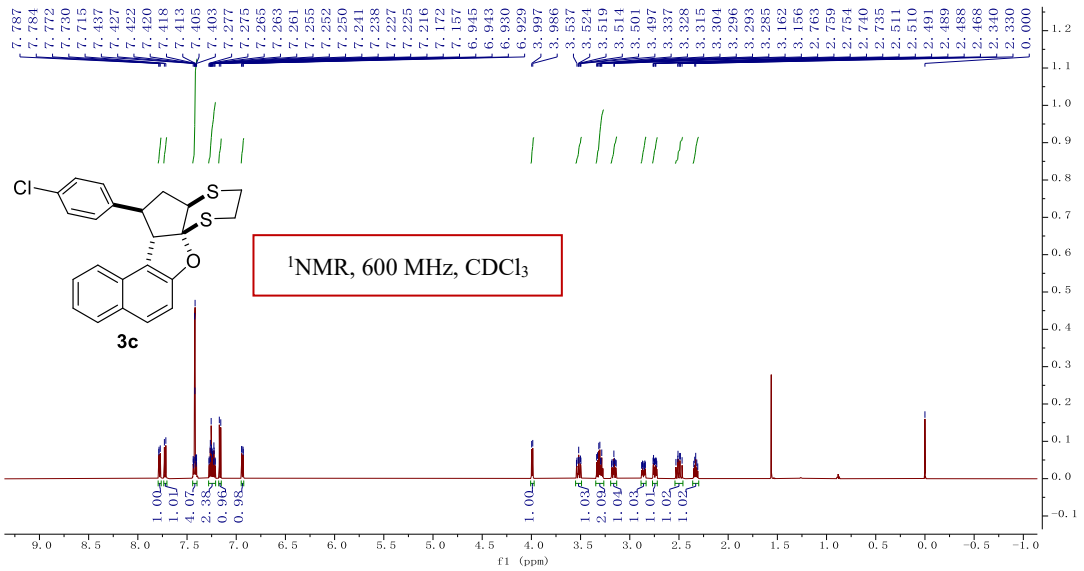

138.04
132.91
129.68
129.28
128.67
128.34
126.94
114.66
77.37
77.16
76.95
74.60
27.17
26.85
Cl
OH
S
S
2e
^{13}C NMR, 150 MHz, CDCl$_3$
f1 (ppm)

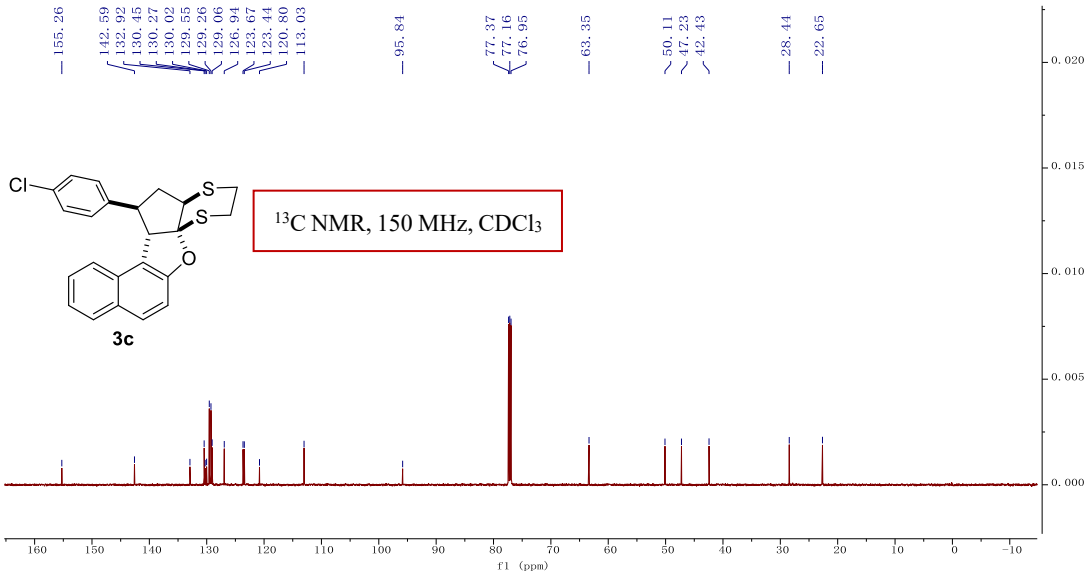

3a
^{1}NMR, 600 MHz, CDCl$_3$
f1 (ppm)

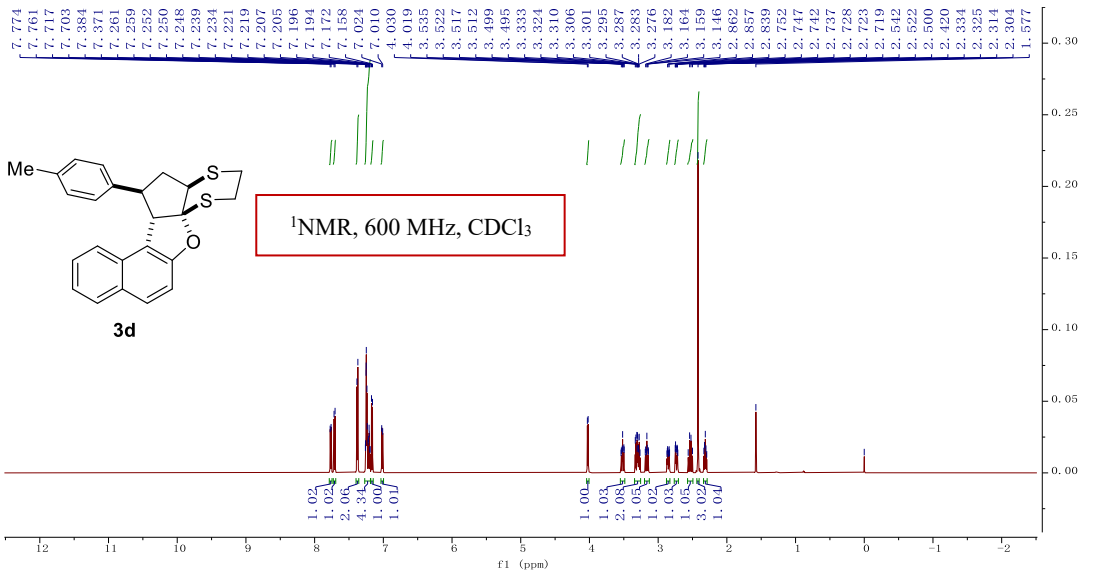

3a
^{13}C NMR, 150 MHz, CDCl$_3$
f1 (ppm)

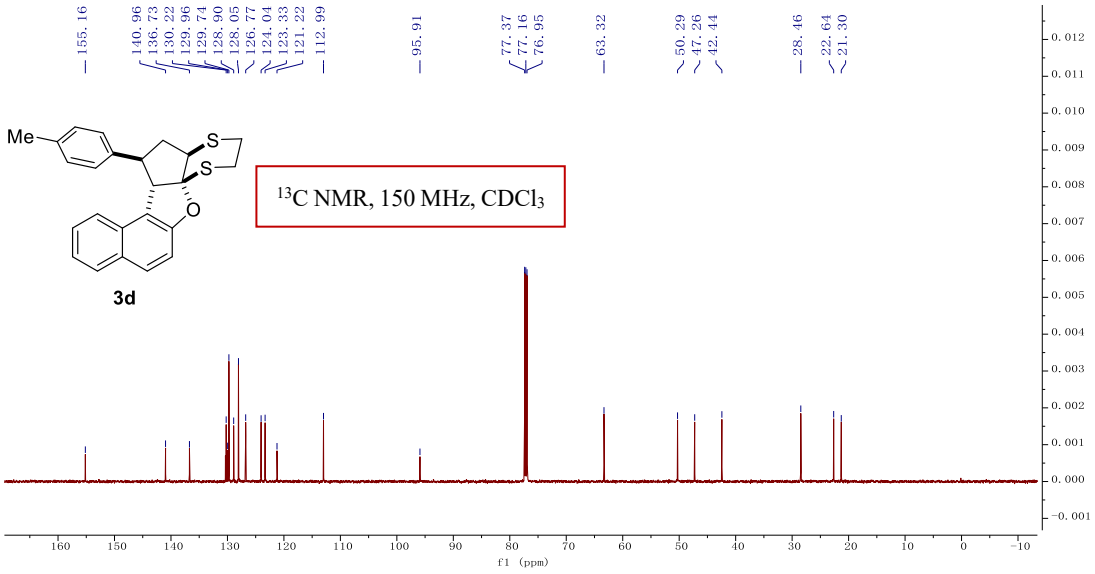

Br
S
S
O
3b
1NMR, 600 MHz, CDCl3
f1 (ppm)

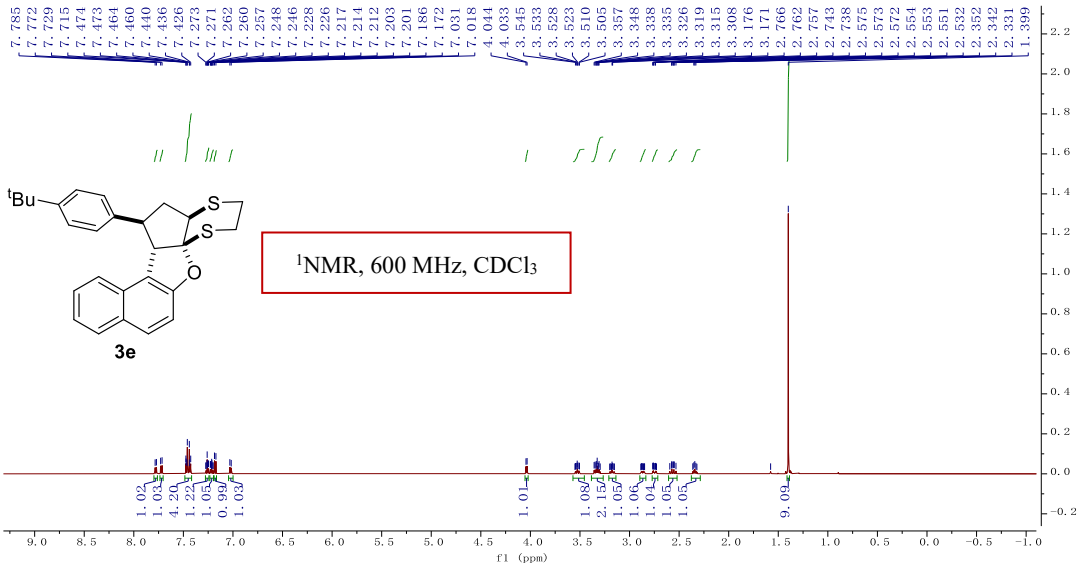

Br
S
S
O
3b
13C NMR, 150 MHz, CDCl3
f1 (ppm)

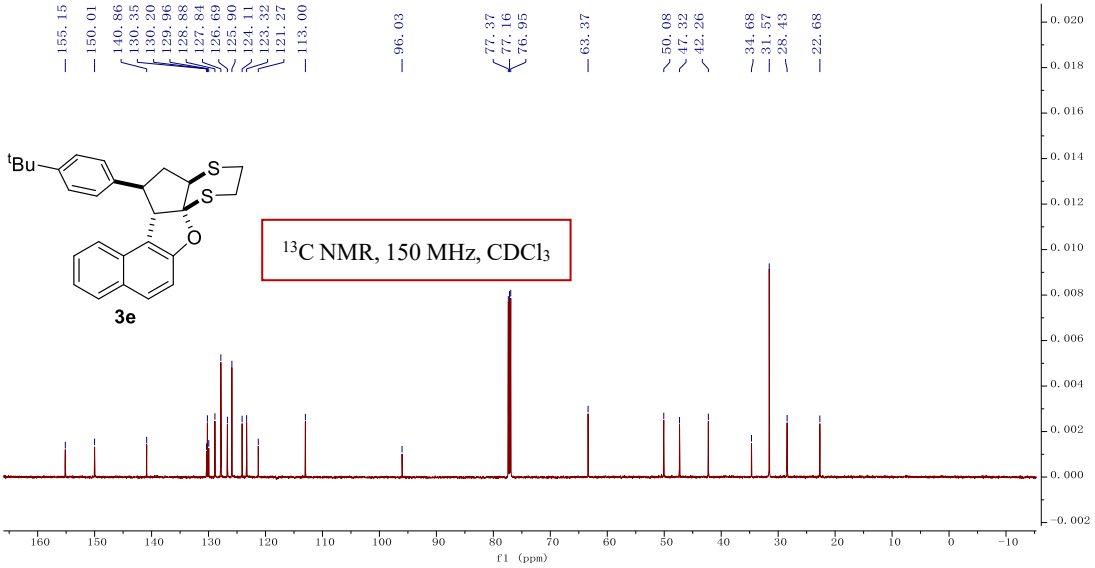

Cl
S
S
O
3c
^{1}NMR, 600 MHz, CDCl$_3$
f1 (ppm)

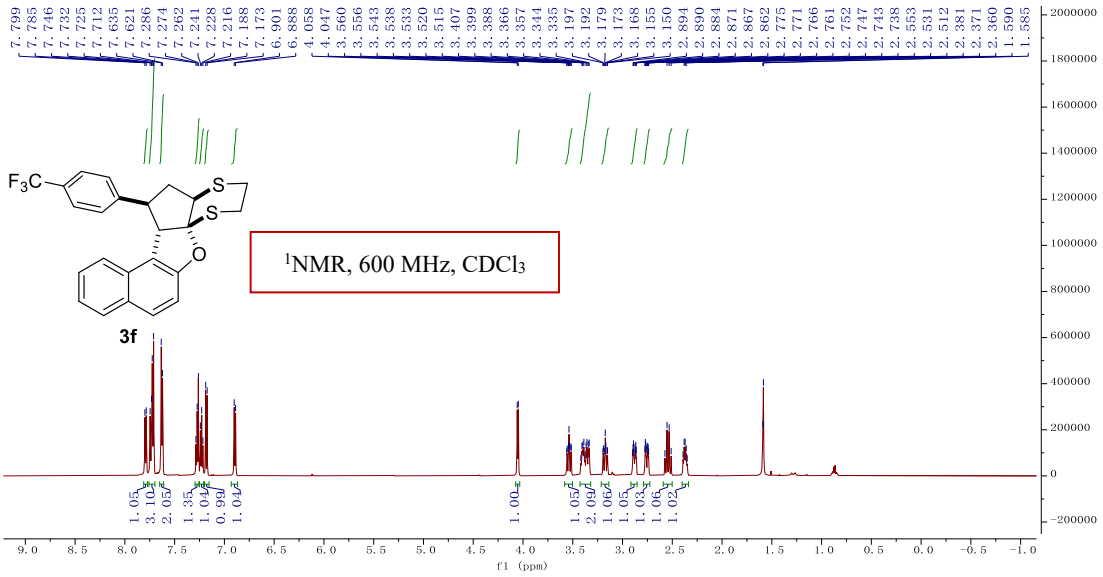

Cl
S
S
O
3c
^{13}C NMR, 150 MHz, CDCl$_3$
f1 (ppm)

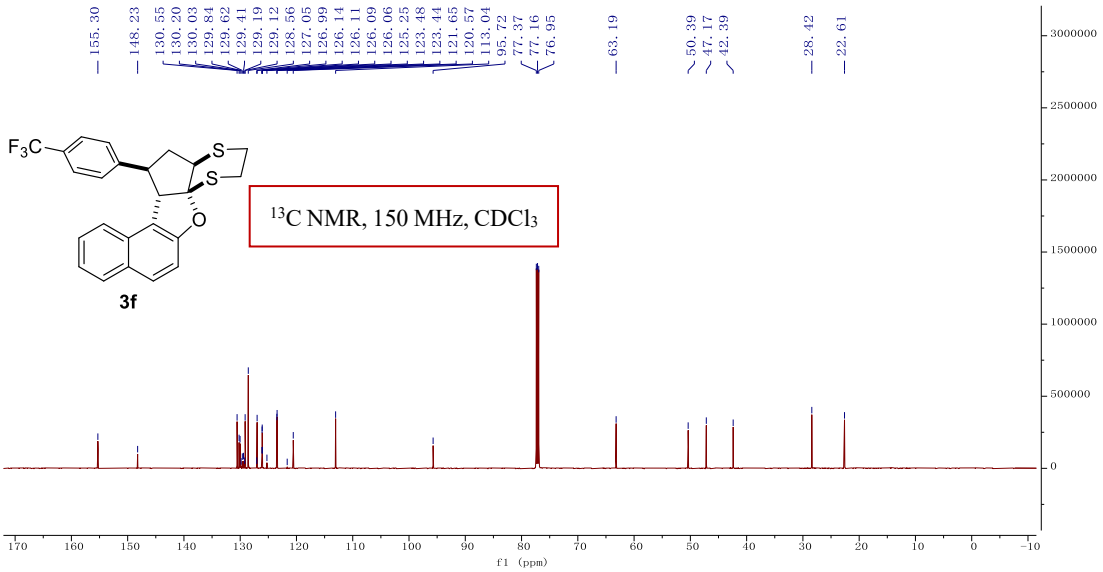

Me
S
S
O
3d
^{1}NMR, 600 MHz, CDCl$_3$
f1 (ppm)

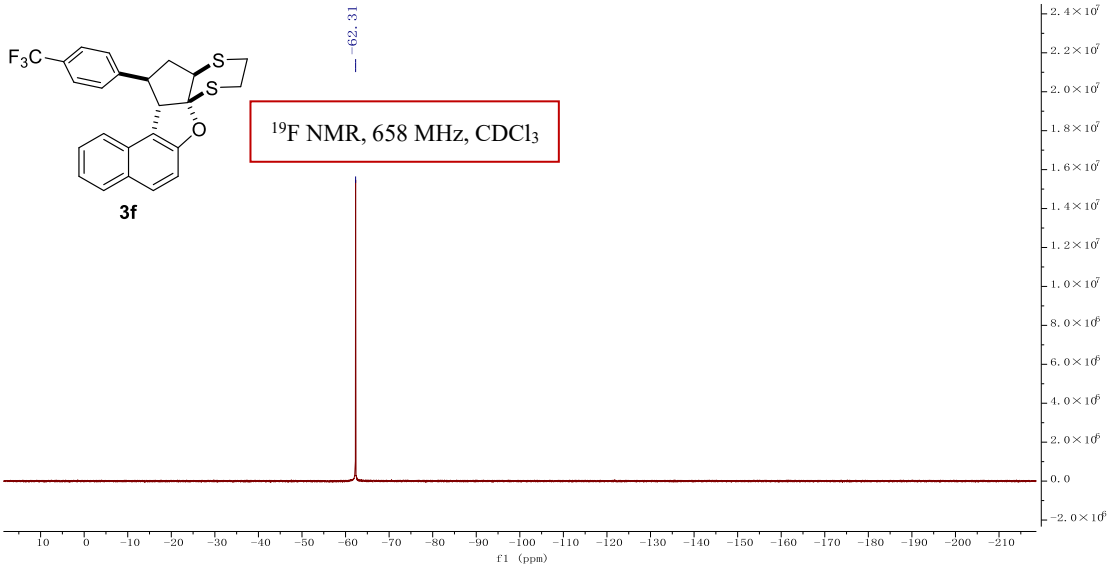

Me
S
S
O
3d
^{13}C NMR, 150 MHz, CDCl$_3$
f1 (ppm)

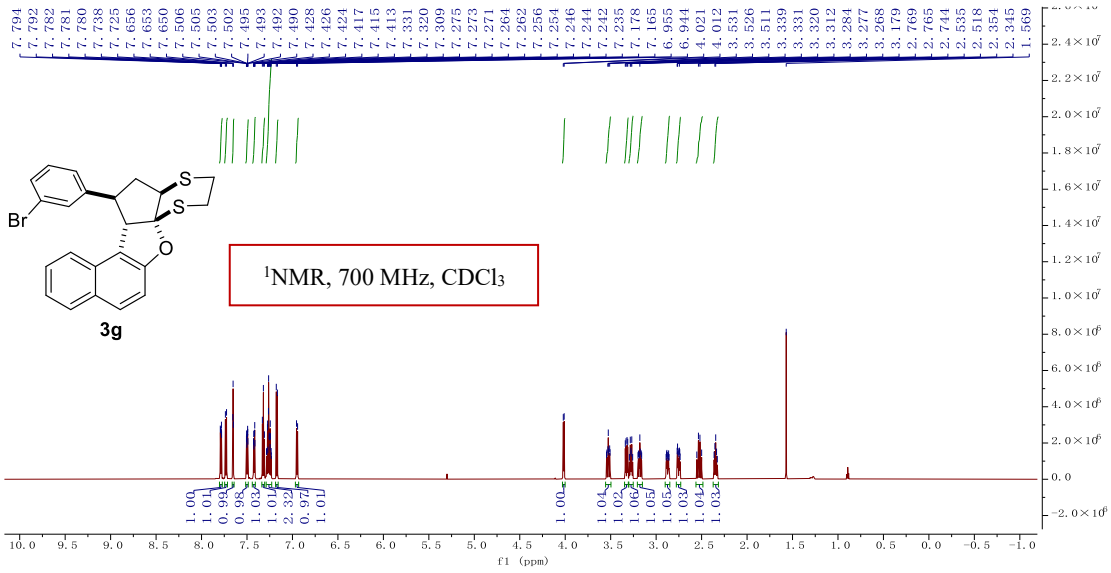

tBu
S
S
O
3e
1NMR, 600 MHz, CDCl3

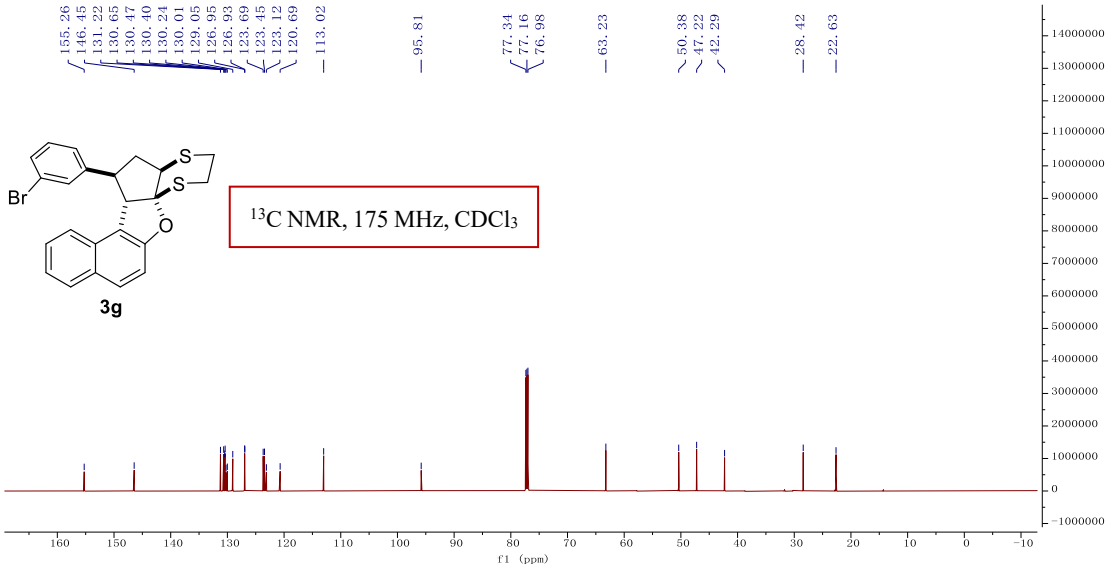

tBu
S
S
O
3e
13C NMR, 150 MHz, CDCl3

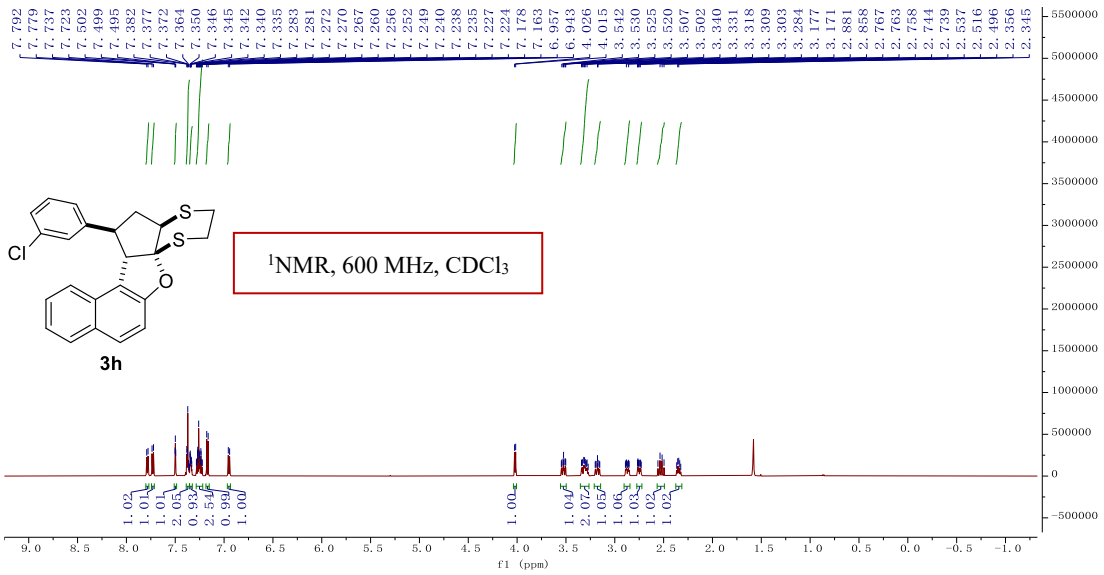

F3C
S
S
O
3f
1NMR, 600 MHz, CDCl3

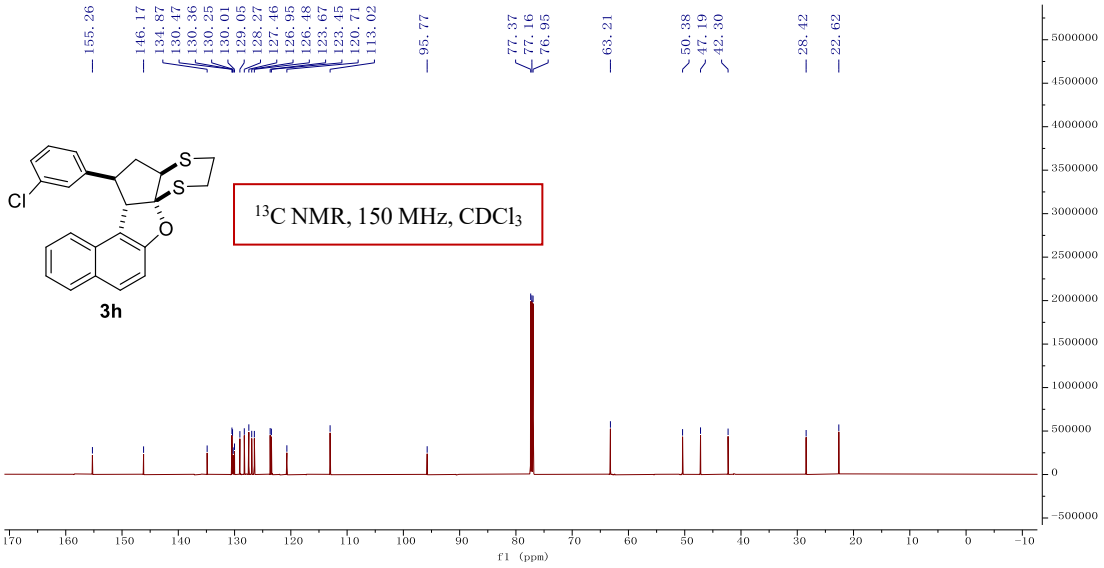

F3C
S
S
O
3f
13C NMR, 150 MHz, CDCl3

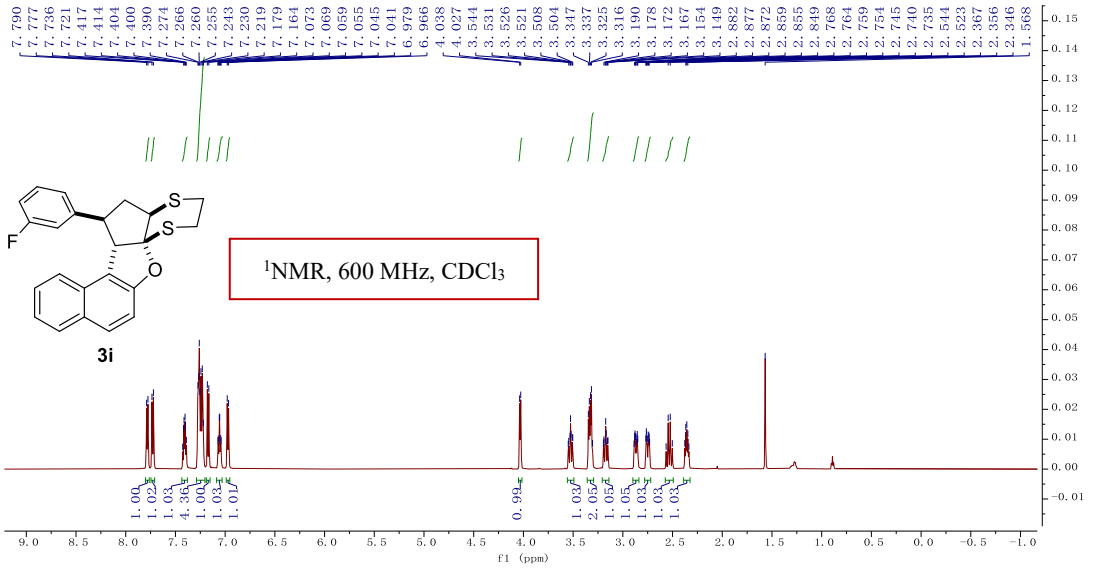

F3C
S
S
O
3f
19F NMR, 658 MHz, CDCl3

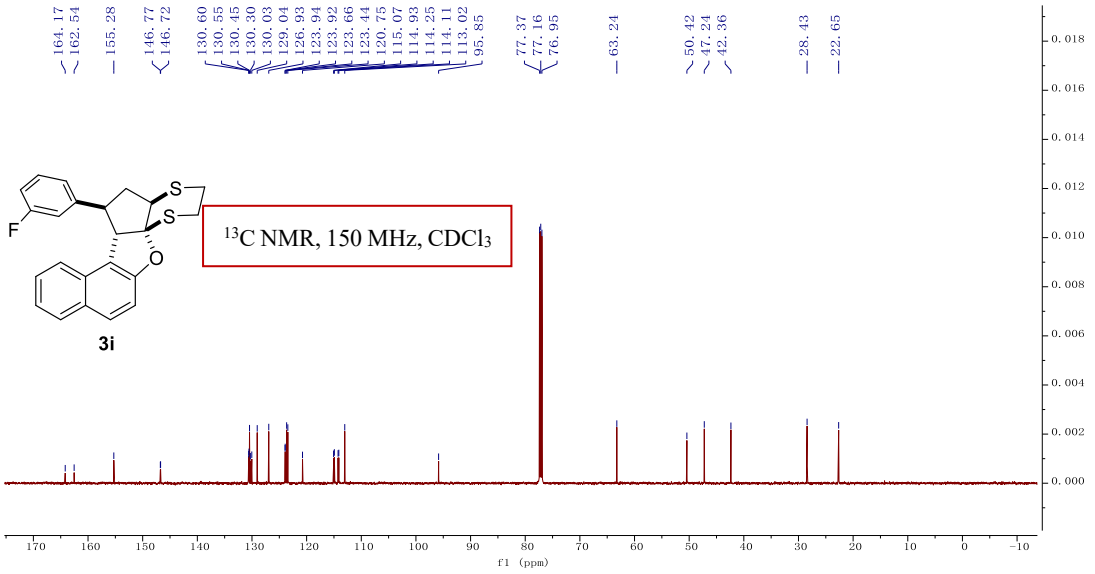

Br
S
S
O
3g
1NMR, 700 MHz, CDCl3
f1 (ppm)

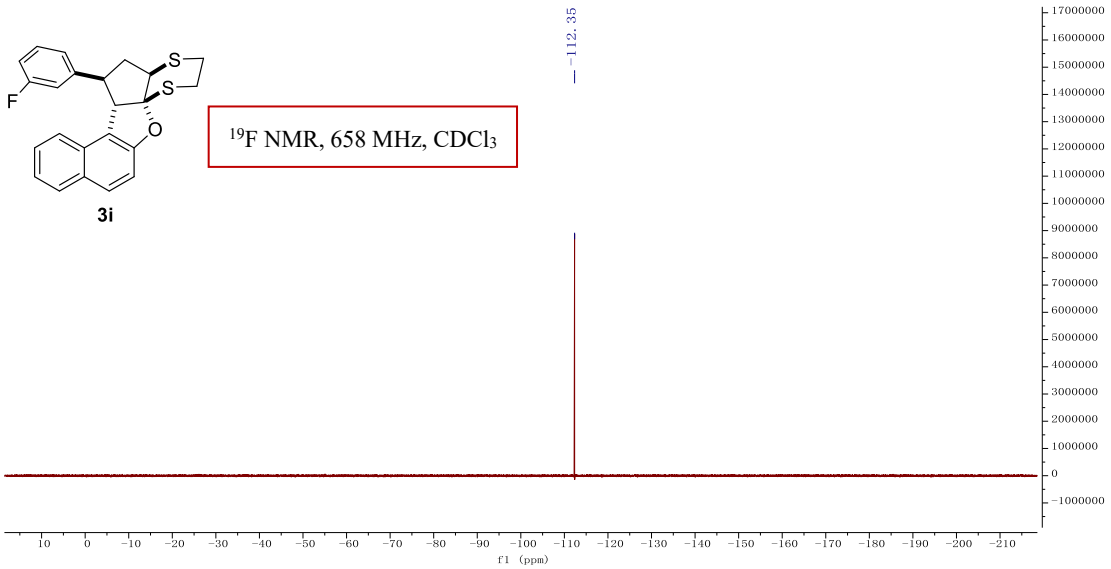

Br
S
S
O
3g
13C NMR, 175 MHz, CDCl3
f1 (ppm)

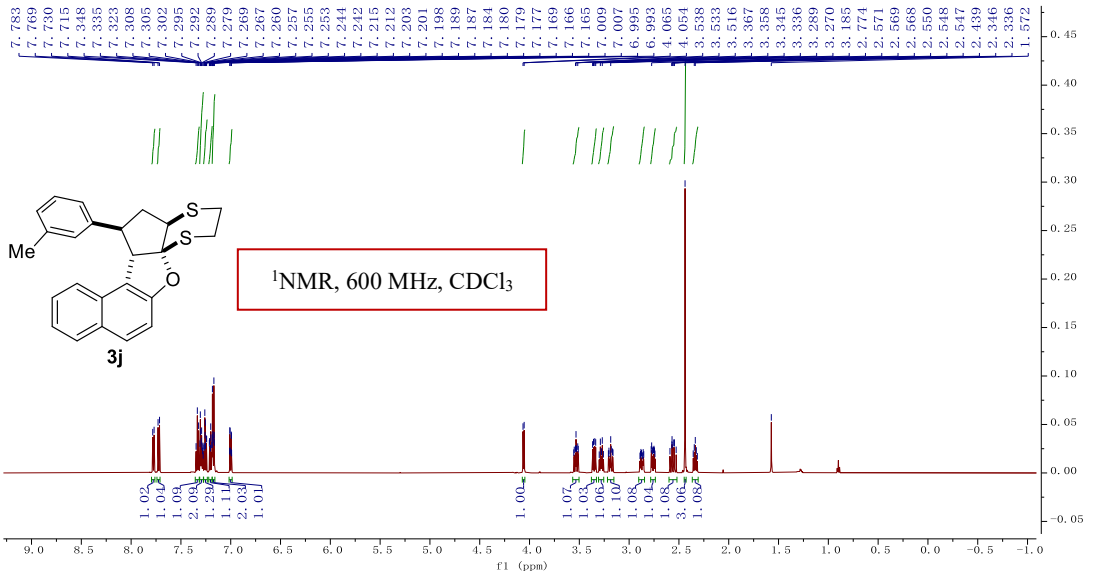

7.792 7.779 7.737 7.723 7.502 7.499 7.495 7.382 7.377 7.372 7.364 7.350 7.346 7.345 7.342 7.340 7.335 7.283 7.281 7.272 7.270 7.267 7.260 7.256 7.252 7.249 7.240 7.238 7.235 7.227 7.224 7.178 7.163 6.957 6.943 4.026 4.015 3.542 3.530 3.525 3.520 3.507 3.502 3.340 3.331 3.318 3.309 3.303 3.284 3.177 3.171 2.881 2.858 2.767 2.763 2.758 2.744 2.739 2.537 2.516 2.496 2.356 2.345
Cl
S
S
O
3h
[1]NMR, 600 MHz, CDCl3
1.02 1.01 1.01 2.05 0.93 2.54 0.99 1.00 1.00 1.04 2.07 1.05 1.06 1.03 1.02 1.02
f1 (ppm)

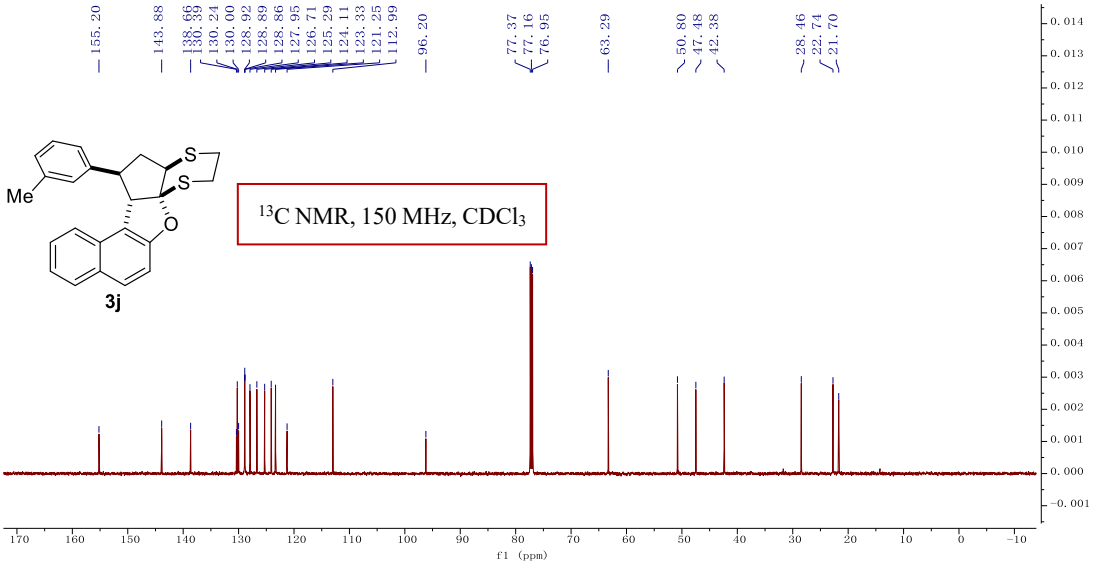

155.26 146.17 134.87 130.47 130.36 130.25 130.01 129.05 128.27 127.46 126.95 126.48 123.67 123.45 120.71 113.02 95.77 77.37 77.16 76.95 63.21 50.38 47.19 42.30 28.42 22.62
Cl
S
S
O
3h
[13]C NMR, 150 MHz, CDCl3
f1 (ppm)

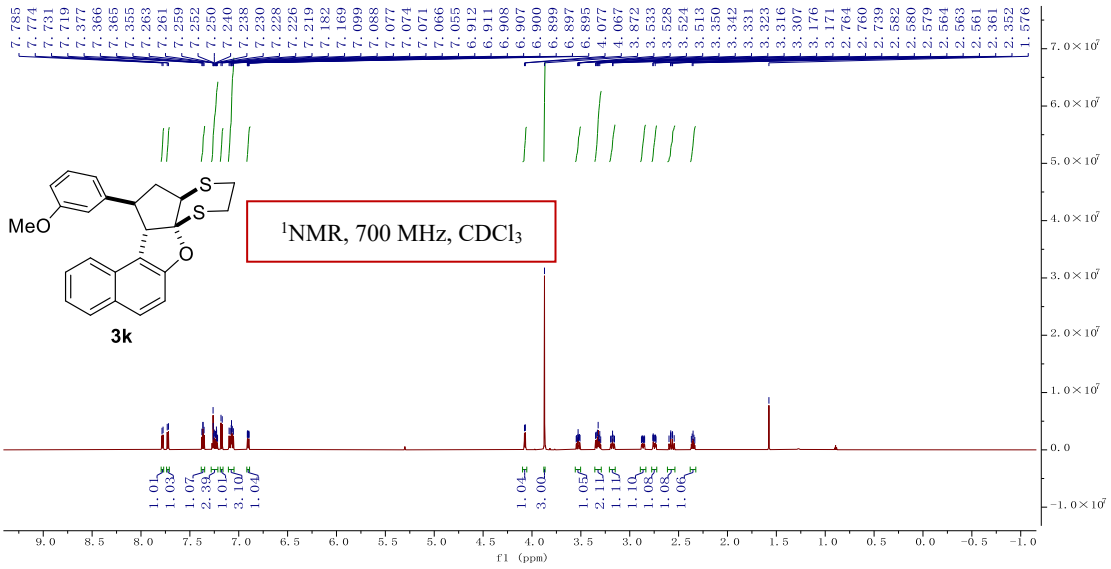

7.790 7.777 7.736 7.721 7.417 7.414 7.404 7.400 7.390 7.274 7.266 7.260 7.255 7.243 7.230 7.219 7.179 7.164 7.073 7.069 7.059 7.055 7.045 7.041 6.979 6.966
4.038 4.027 3.544 3.531 3.526 3.521 3.508 3.504 3.347 3.337 3.325 3.316 3.190 3.178 3.172 3.167 3.154 3.149 2.882 2.877 2.872 2.859 2.855 2.849 2.768 2.764 2.759 2.754 2.745 2.740 2.735 2.544 2.523 2.367 2.356 2.346 1.568
S
S
F
O
3i
^{1}NMR, 600 MHz, CDCl$_3$
1.00 1.02 1.03 4.38 1.00 1.03 1.01 0.99 1.03 2.05 1.05 1.03 1.03 1.03
f1 (ppm)

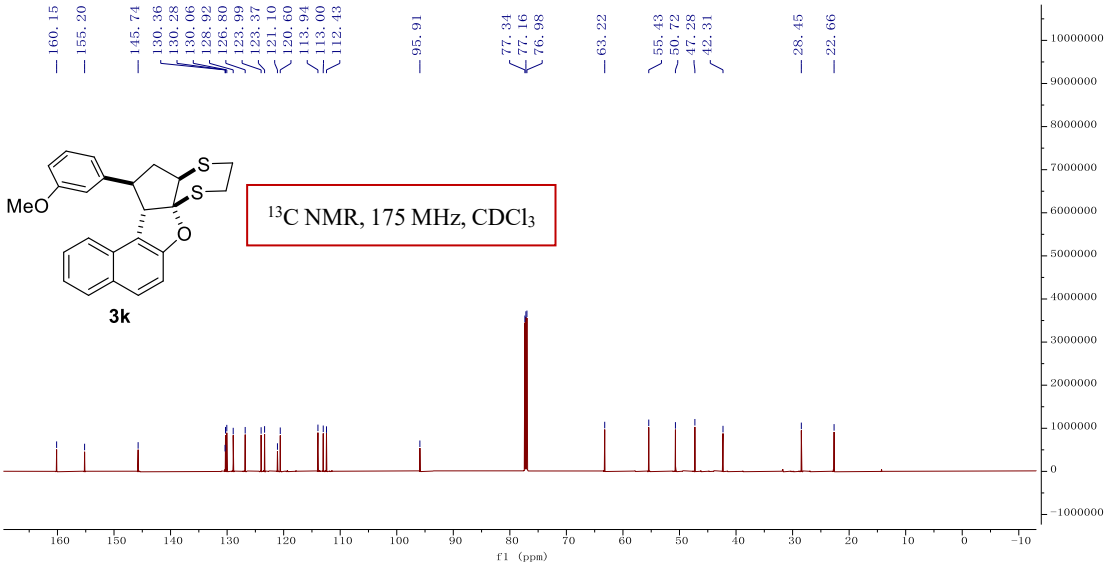

164.17 162.54 155.28 146.77 146.72 130.60 130.55 130.45 130.30 130.03 129.04 126.93 123.94 123.92 123.66 123.44 120.75 115.07 114.93 114.25 114.11 113.02 95.85
77.37 77.16 76.95 63.24 50.42 47.24 42.36 28.43 22.65
S
S
F
O
3i
^{13}C NMR, 150 MHz, CDCl$_3$
f1 (ppm)

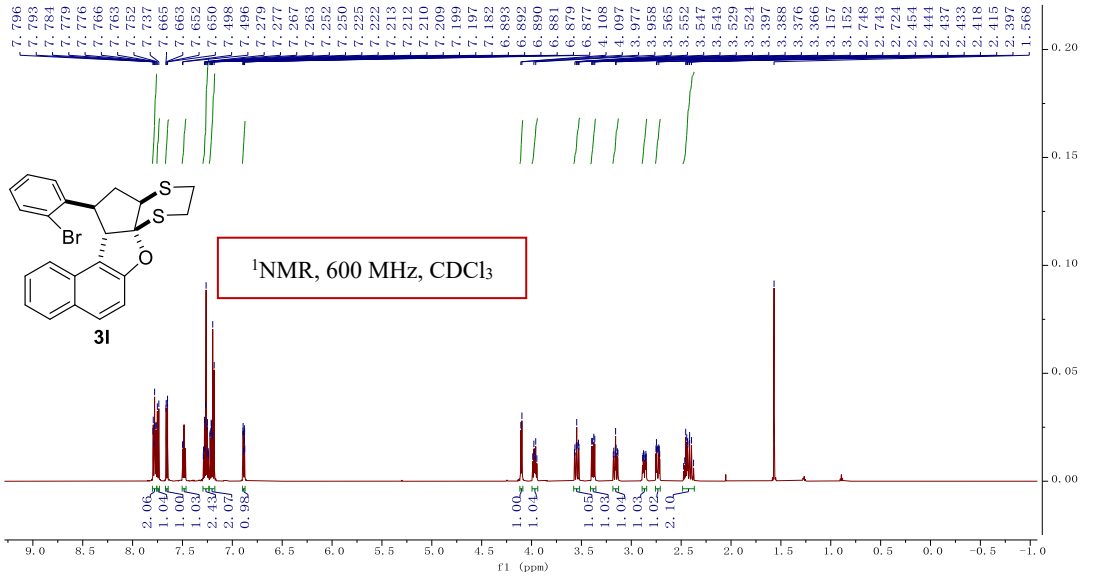

-112.35
S
S
F
O
3i
^{19}F NMR, 658 MHz, CDCl$_3$
f1 (ppm)

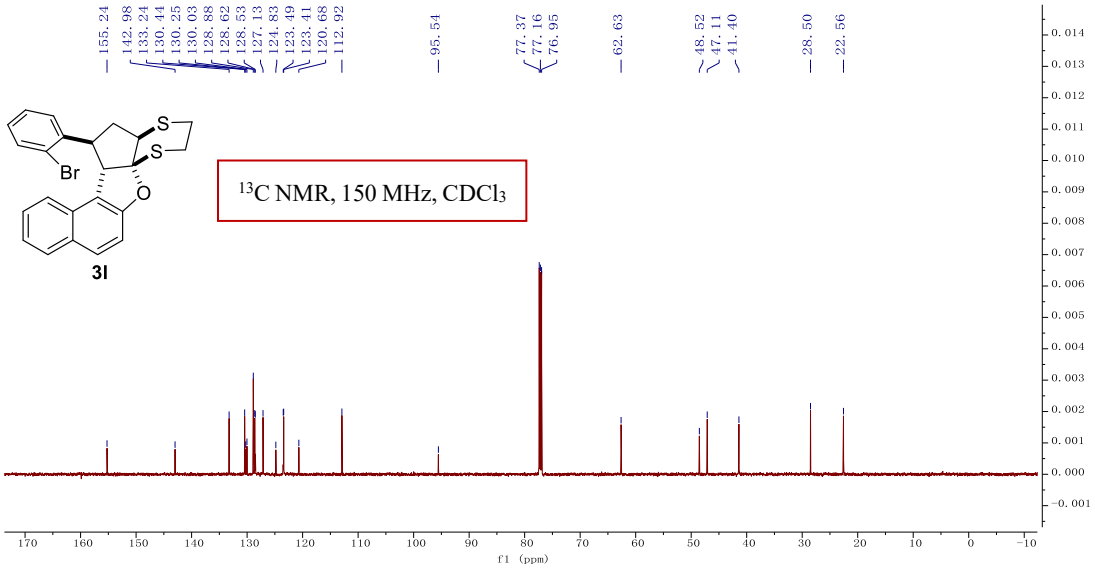

Me
S
S
O
3j
^{1}NMR, 600 MHz, $CDCl_3$
f1 (ppm)

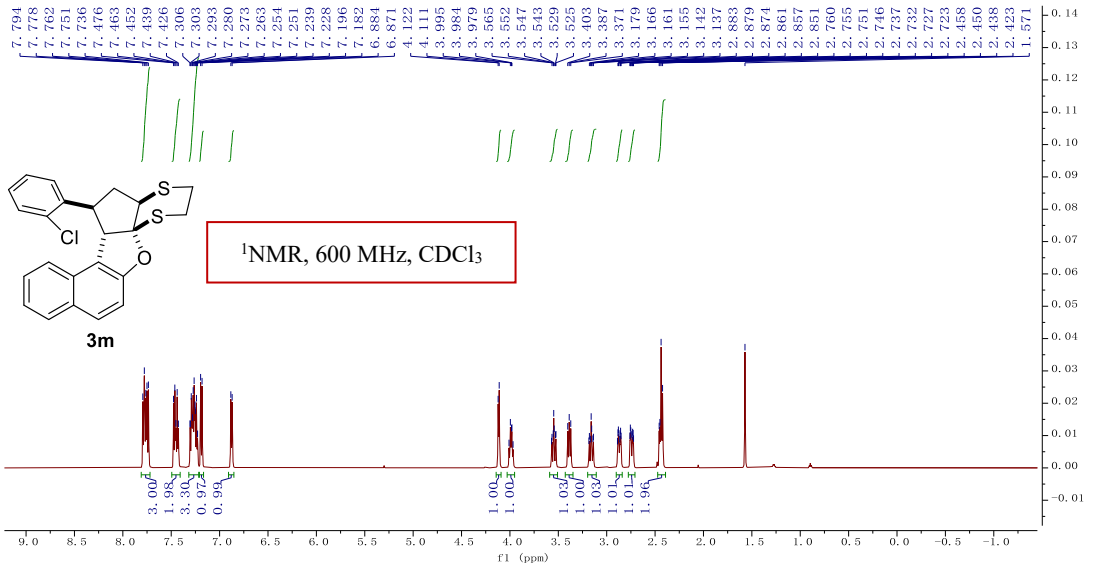

Me
S
S
O
3j
^{13}C NMR, 150 MHz, $CDCl_3$
f1 (ppm)

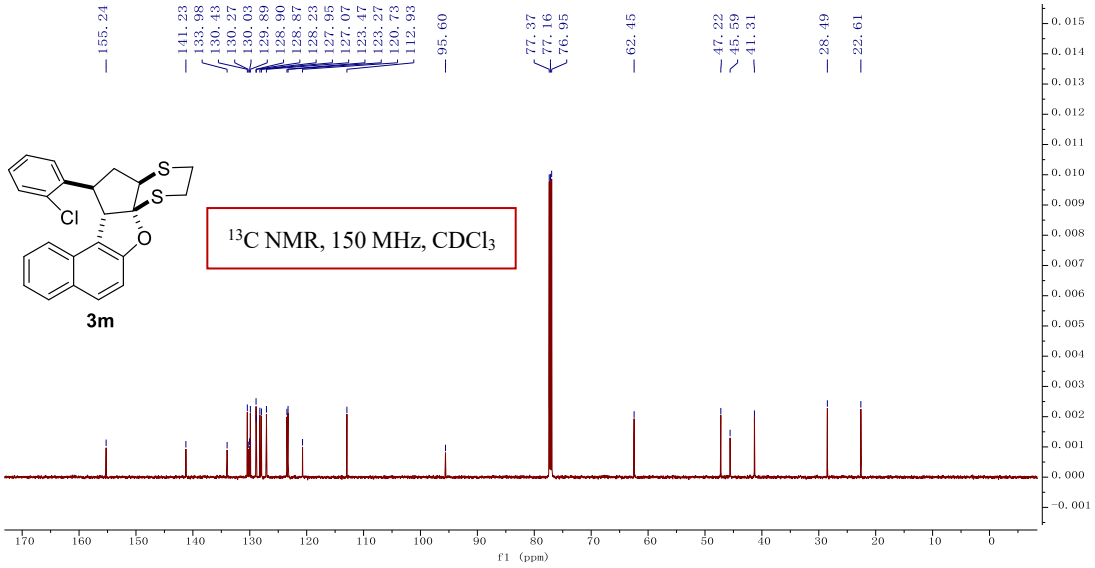

MeO
S
S
O
3k
^{1}NMR, 700 MHz, $CDCl_3$
f1 (ppm)

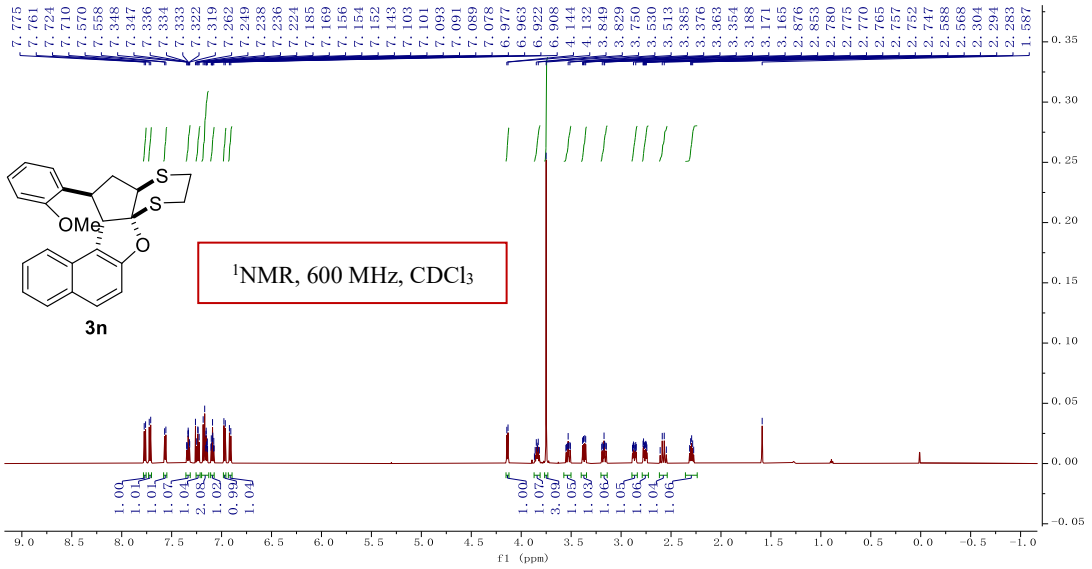

MeO
S
S
O
3k
^{13}C NMR, 175 MHz, $CDCl_3$
f1 (ppm)

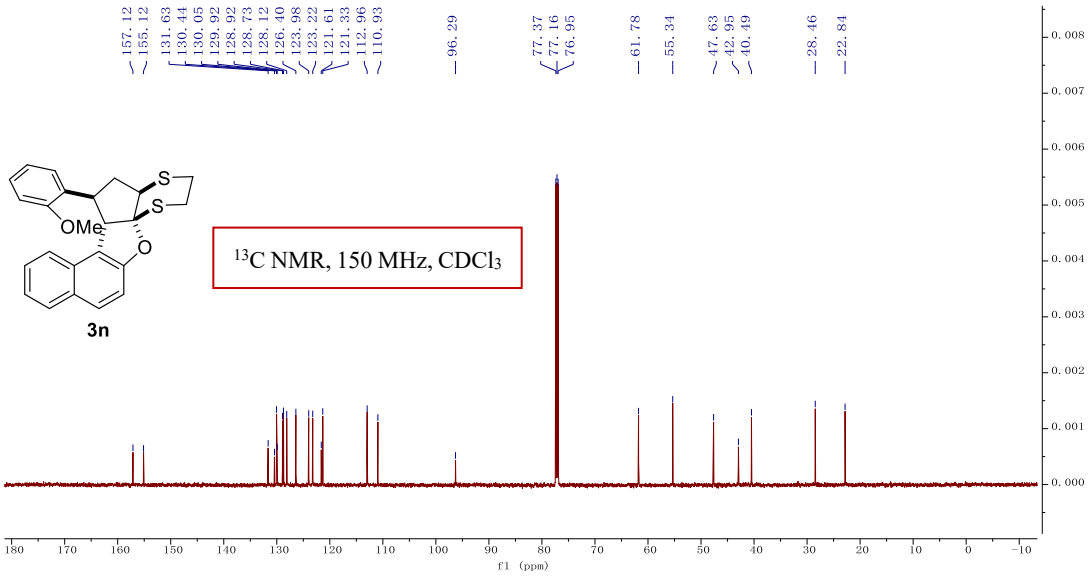

Br
S
S
O
3l
^{1}NMR, 600 MHz, CDCl$_3$

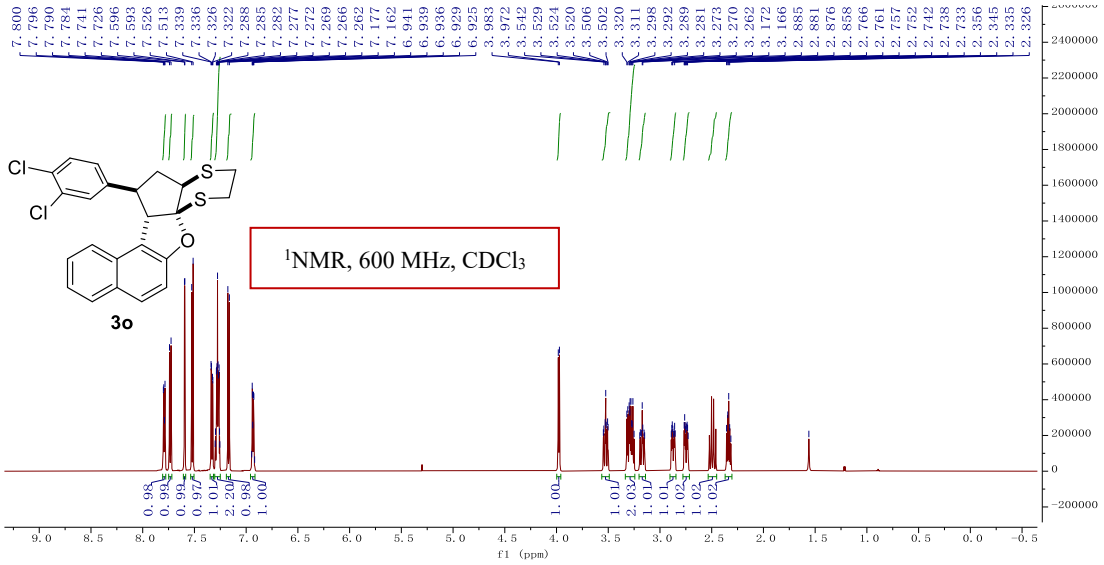

Br
S
S
O
3l
^{13}C NMR, 150 MHz, CDCl$_3$

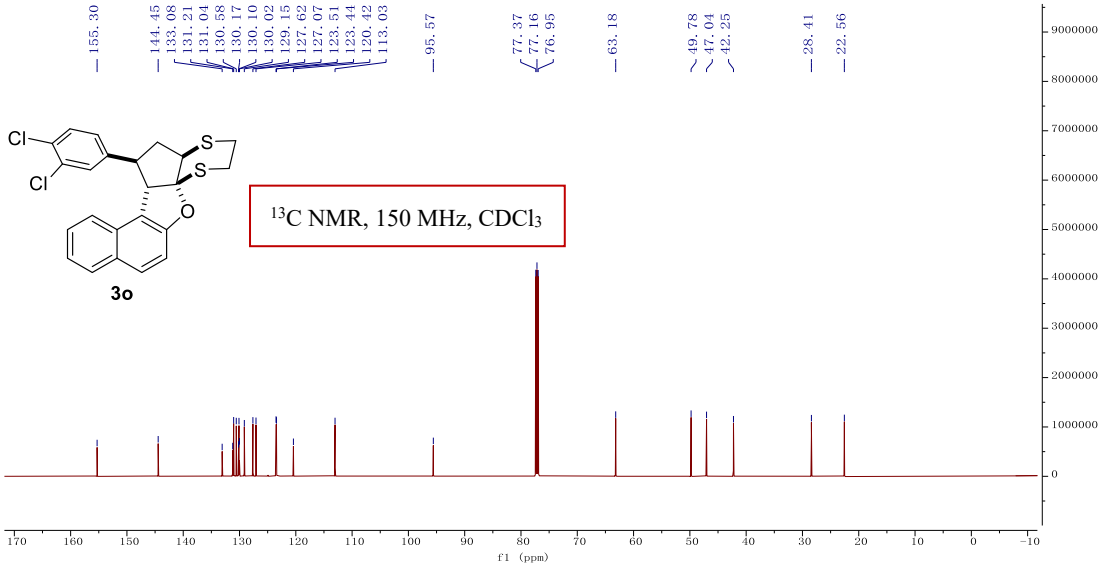

Cl
S
S
O
3m
^{1}NMR, 600 MHz, $CDCl_3$

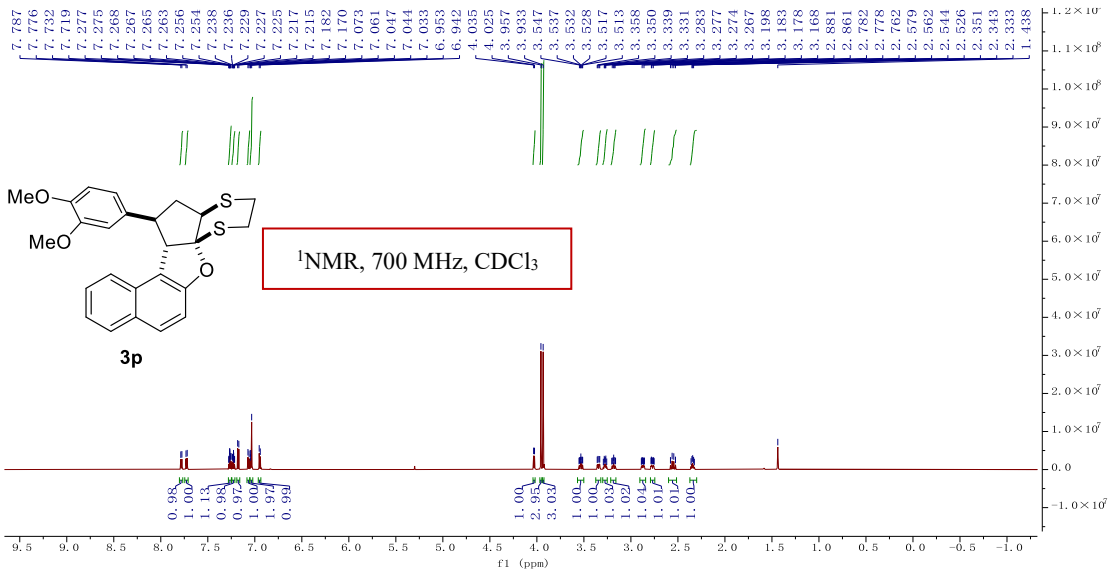

Cl
S
S
O
3m
^{13}C NMR, 150 MHz, $CDCl_3$

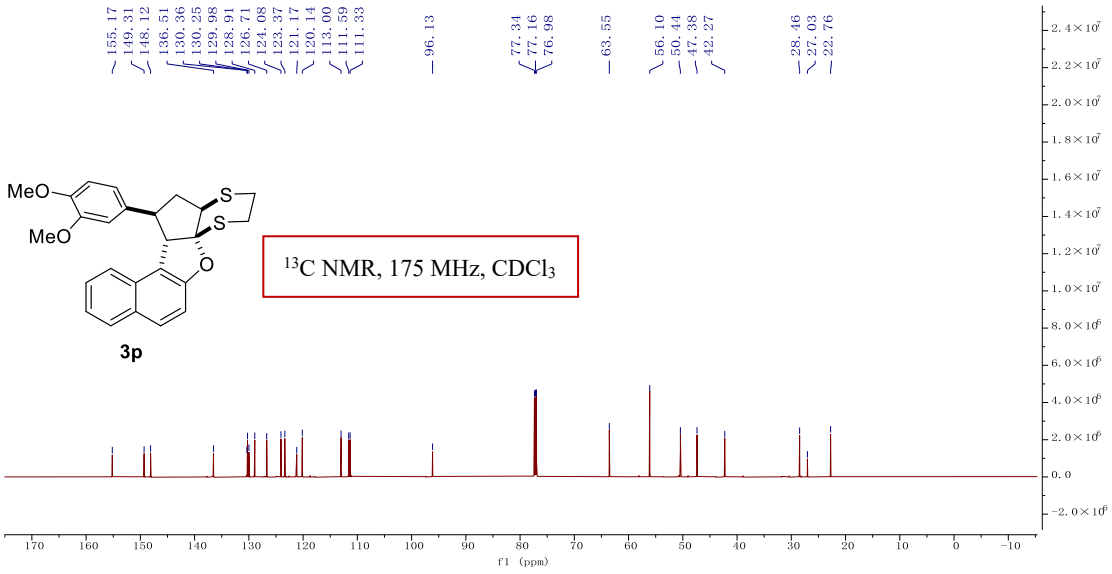

7.775 7.761 7.724 7.710 7.570 7.558 7.348 7.347 7.336 7.334 7.333 7.322 7.319 7.262 7.249 7.238 7.236 7.224 7.185 7.169 7.156 7.154 7.152 7.143 7.103 7.101 7.093 7.091 7.089 7.078 6.977 6.963 6.922 6.908 4.144 4.132 3.849 3.829 3.750 3.530 3.513 3.385 3.376 3.363 3.354 3.188 3.171 3.165 2.876 2.853 2.780 2.775 2.770 2.765 2.757 2.752 2.747 2.588 2.568 2.304 2.294 2.283 1.587
S
S
OMe
O
3n
1NMR, 600 MHz, CDCl3
1.00 1.01 1.01 1.07 1.04 2.02 1.02 0.99 1.04
1.00 1.07 3.09 1.05 1.03 1.02 1.05 1.06 1.04 1.06
f1 (ppm)

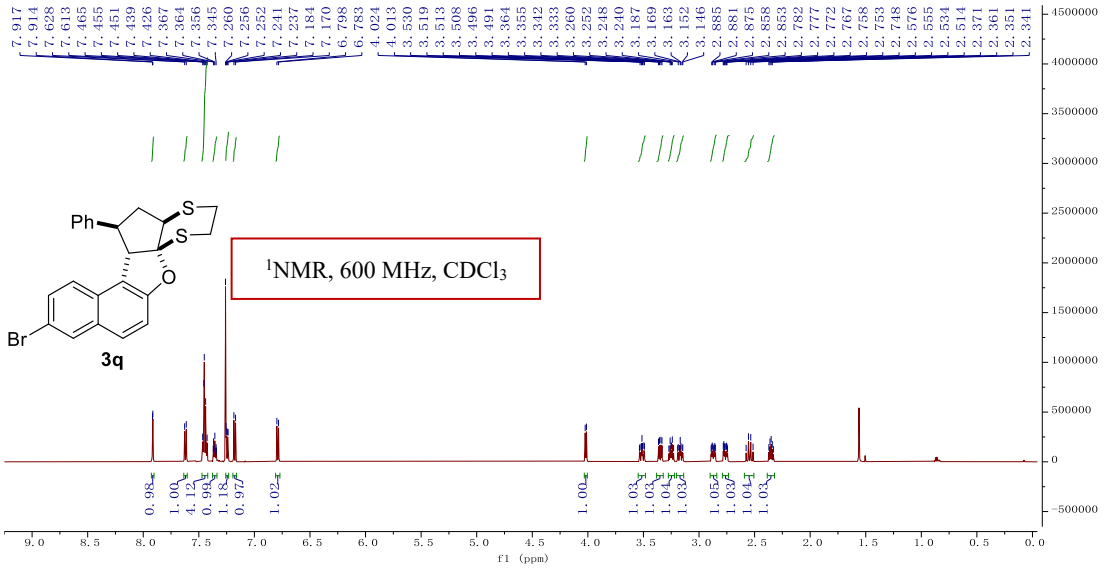

157.12 155.12 131.63 130.44 130.05 129.92 128.92 128.73 128.12 126.40 123.98 123.22 121.61 121.33 112.96 110.93 96.29 77.37 77.16 76.95 61.78 55.34 47.63 42.95 40.49 28.46 22.84
S
S
OMe
O
3n
13C NMR, 150 MHz, CDCl3
f1 (ppm)

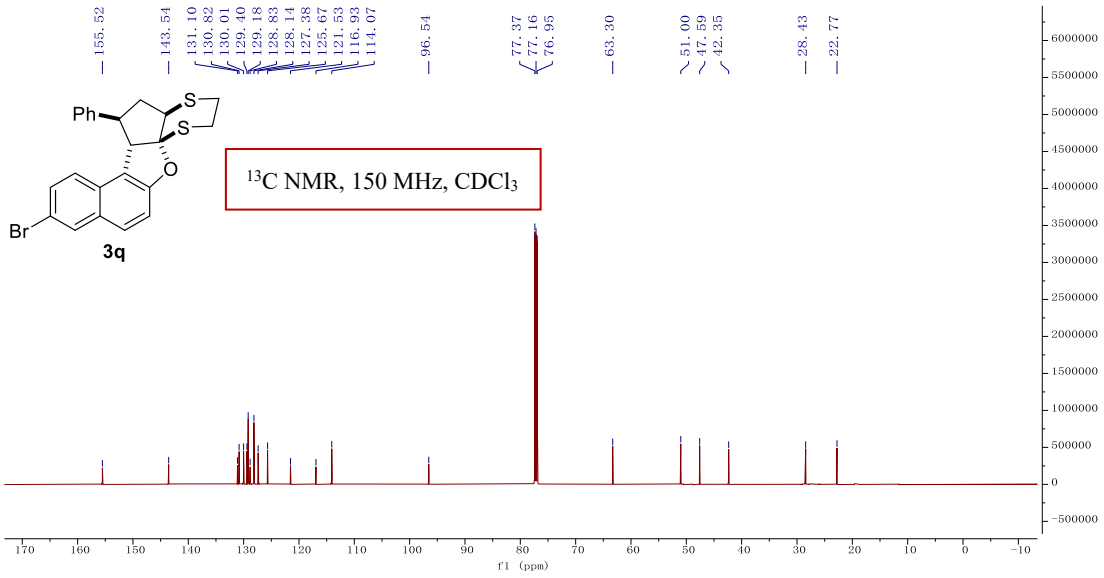

Cl
Cl
S
S
O
3o
^{1}NMR, 600 MHz, CDCl$_3$
f1 (ppm)

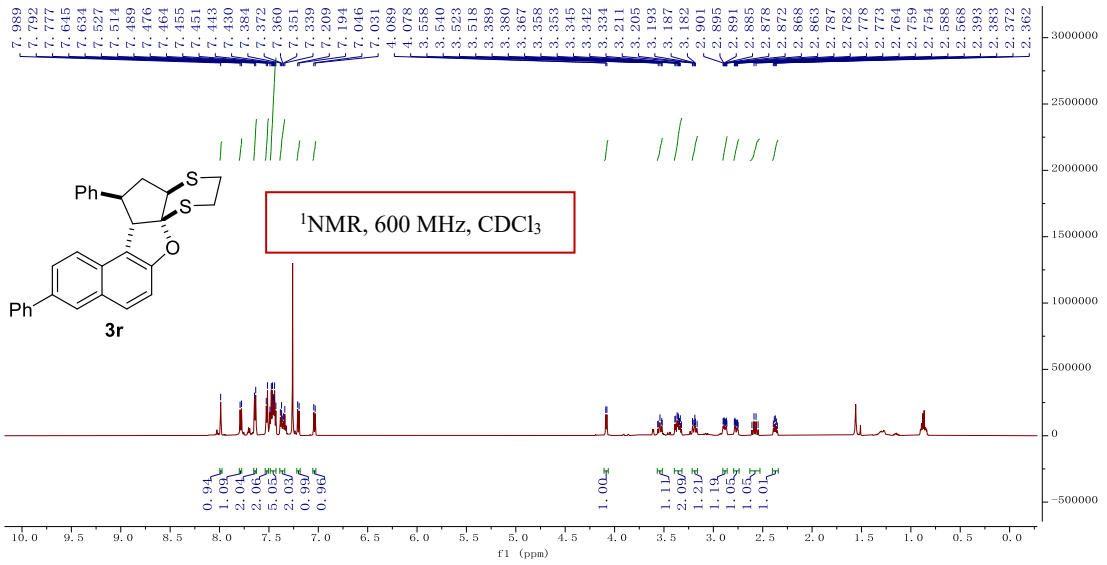

Cl
Cl
S
S
O
3o
^{13}C NMR, 150 MHz, CDCl$_3$
f1 (ppm)

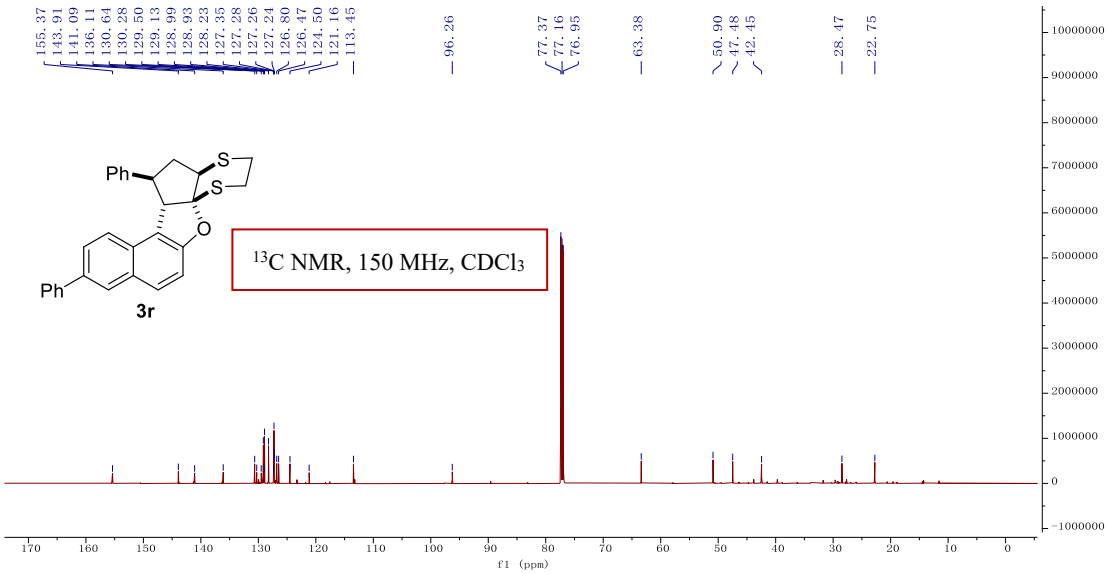

MeO
MeO
S
S
O
3p
^{1}NMR, 700 MHz, CDCl$_3$
f1 (ppm)

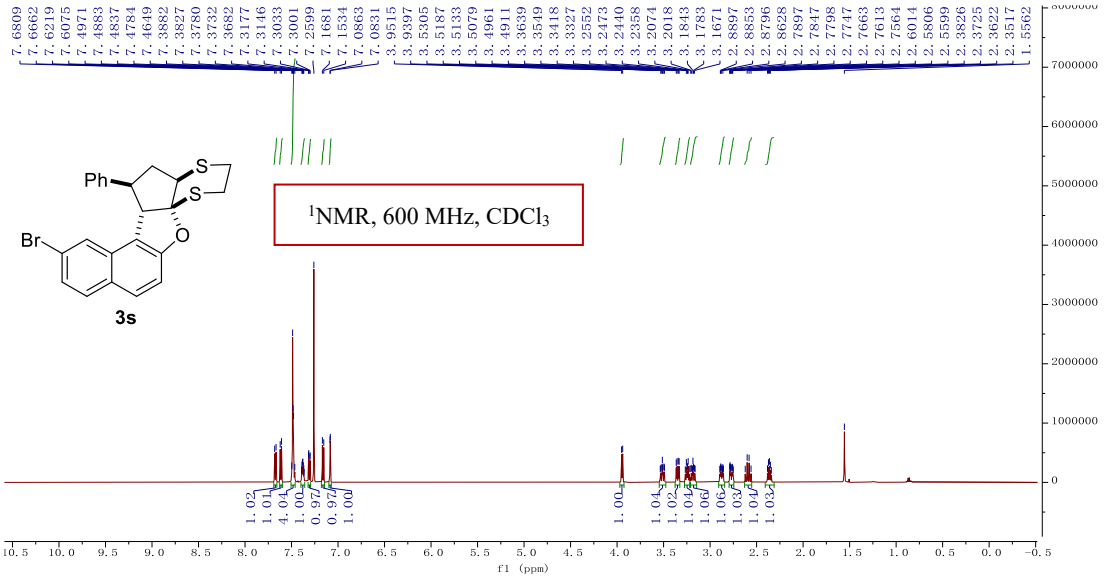

MeO
MeO
S
S
O
3p
^{13}C NMR, 175 MHz, CDCl$_3$
f1 (ppm)

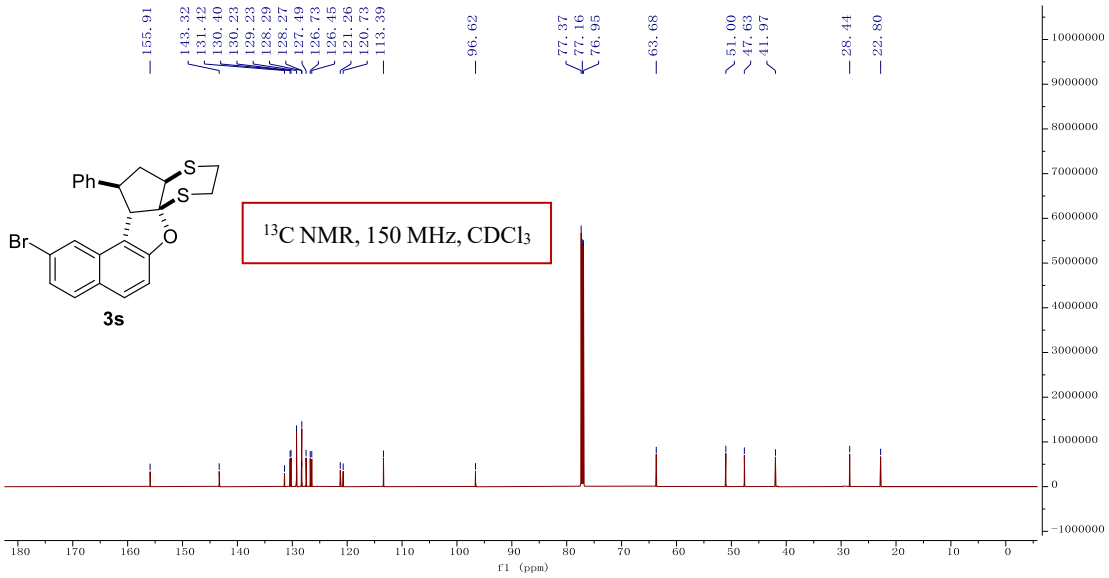

Ph
S
S
O
Br
3q
^{1}NMR, 600 MHz, CDCl$_3$
f1 (ppm)

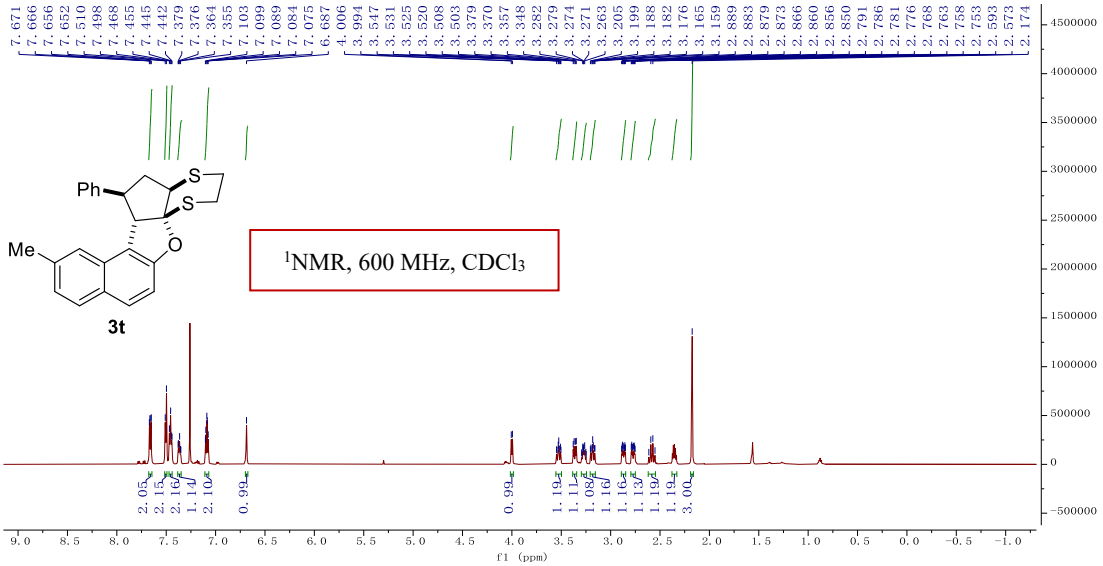

Ph
S
S
O
Br
3q
^{13}C NMR, 150 MHz, CDCl$_3$
f1 (ppm)

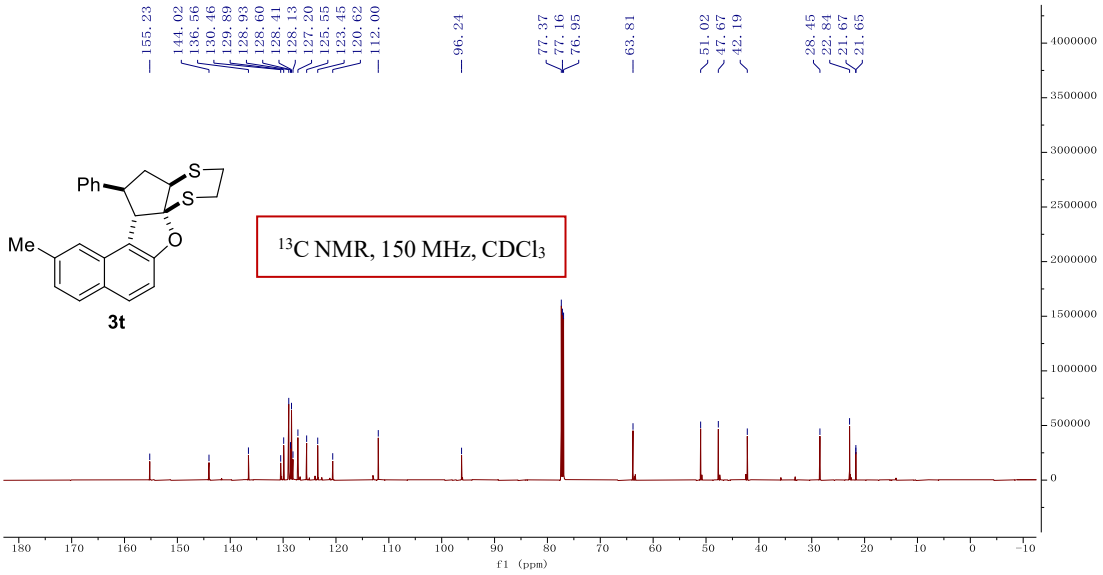

Ph
S
S
O
Ph
3r
^{1}NMR, 600 MHz, CDCl$_3$
f1 (ppm)

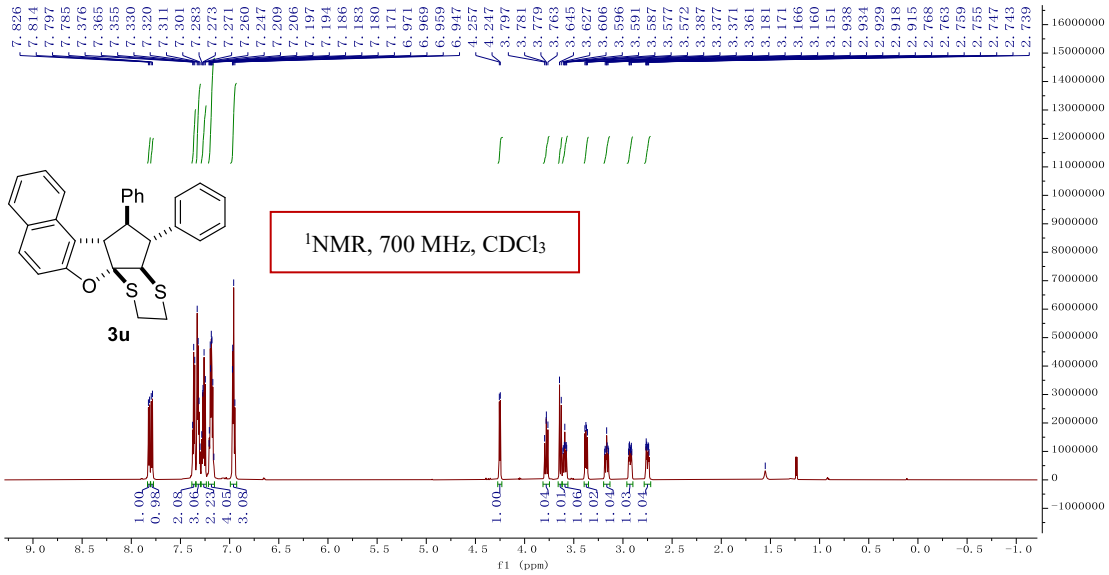

Ph
S
S
O
Ph
3r
^{13}C NMR, 150 MHz, CDCl$_3$
f1 (ppm)

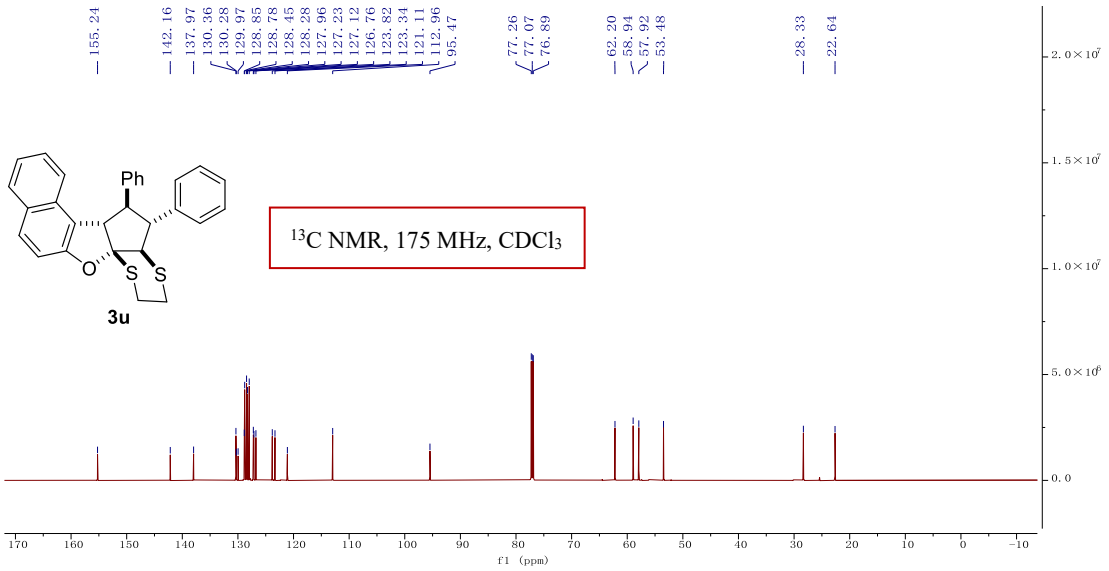

Ph
S
S
O
Br
3s
^{1}NMR, 600 MHz, CDCl$_3$
f1 (ppm)

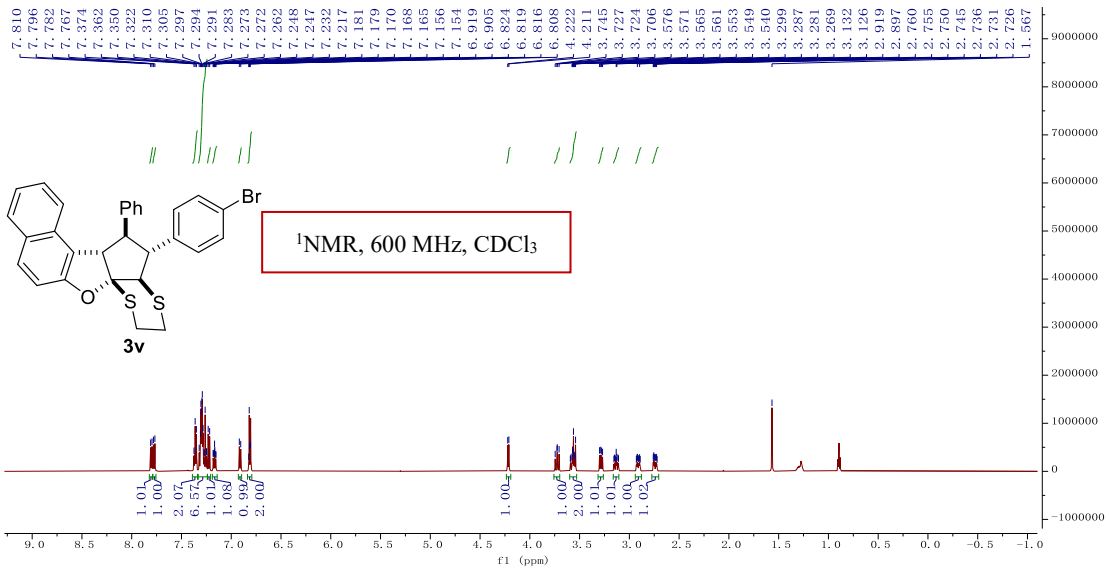

Ph
S
S
O
Br
3s
^{13}C NMR, 150 MHz, CDCl$_3$
f1 (ppm)

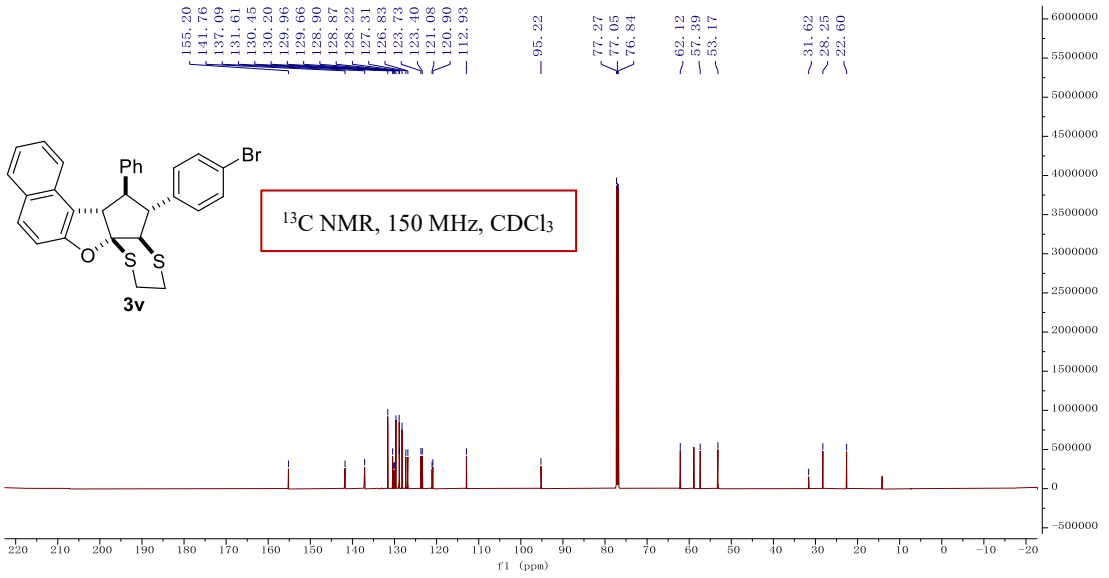

Ph
S
S
O
Me
3t
^{1}NMR, 600 MHz, CDCl$_3$

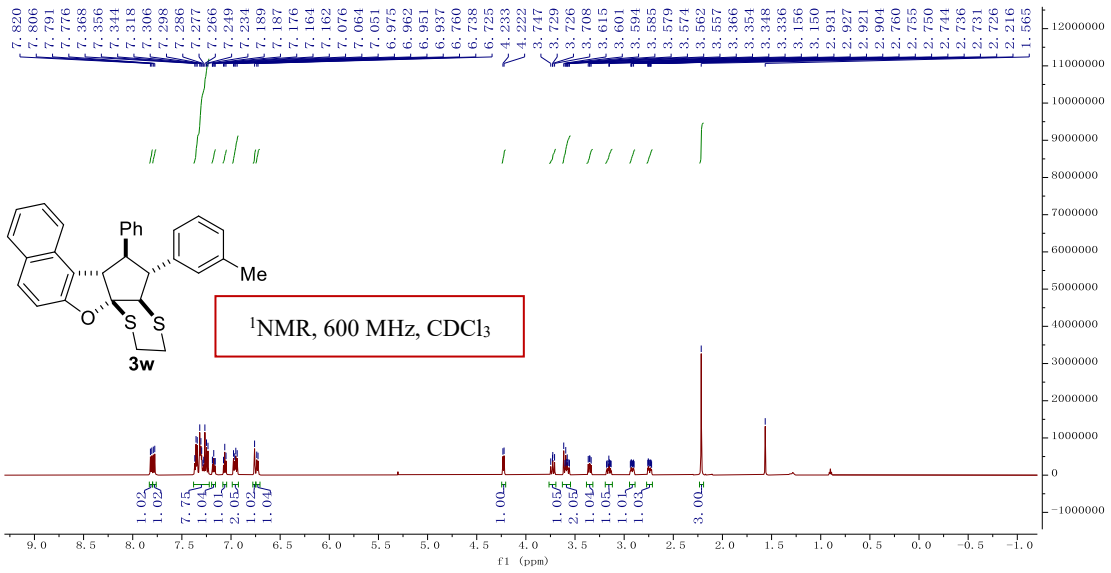

Ph
S
S
O
Me
3t
^{13}C NMR, 150 MHz, CDCl$_3$

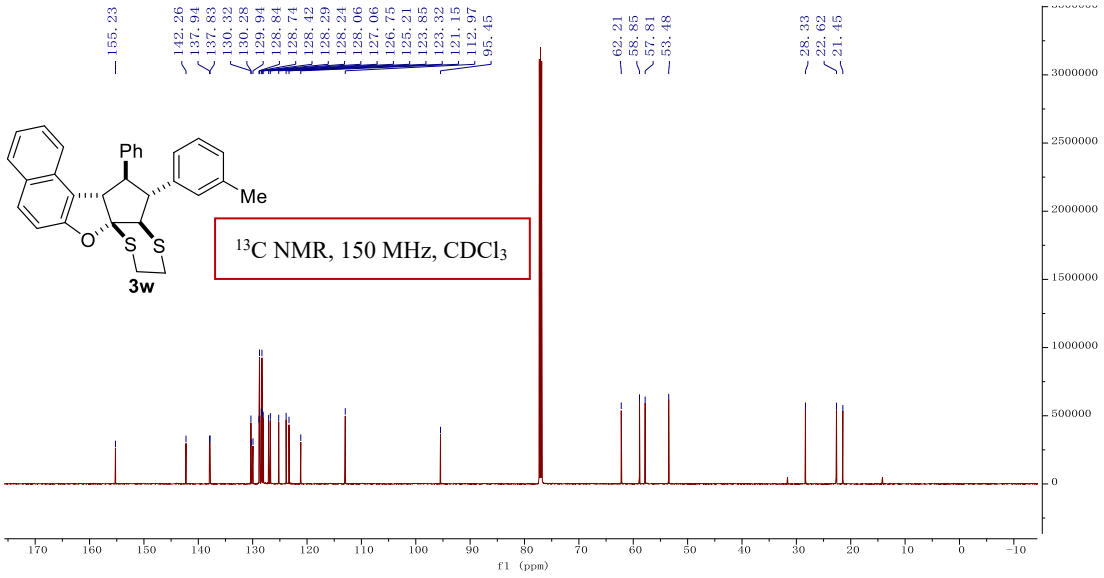

Ph
O
S
S
3u
^{1}NMR, 700 MHz, CDCl$_3$

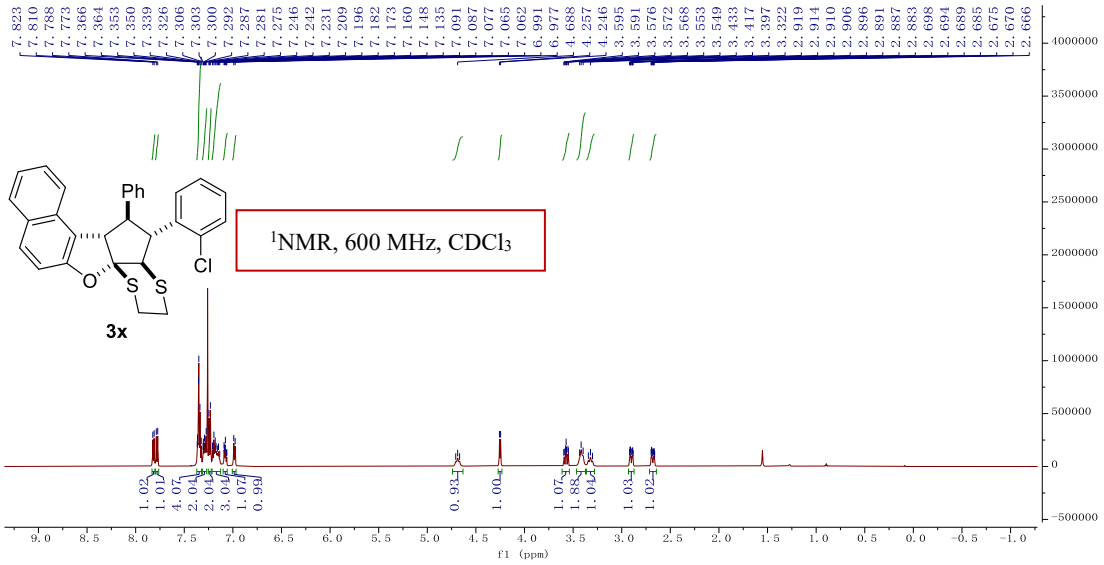

Ph
O
S
S
3u
^{13}C NMR, 175 MHz, CDCl$_3$

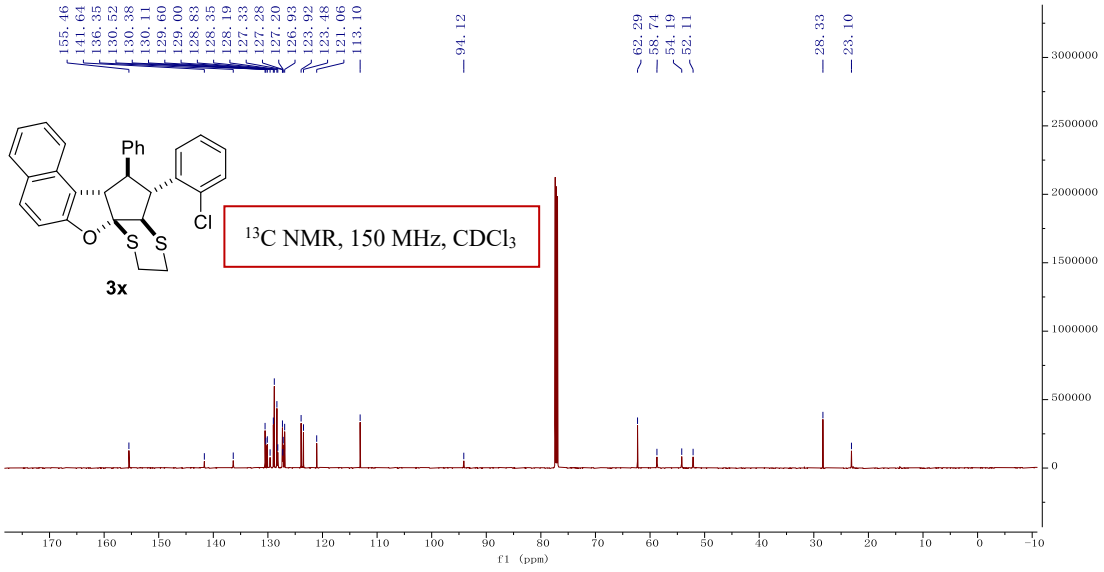

Ph
Br
O
S
S
3v
^{1}NMR, 600 MHz, CDCl$_3$
f1 (ppm)

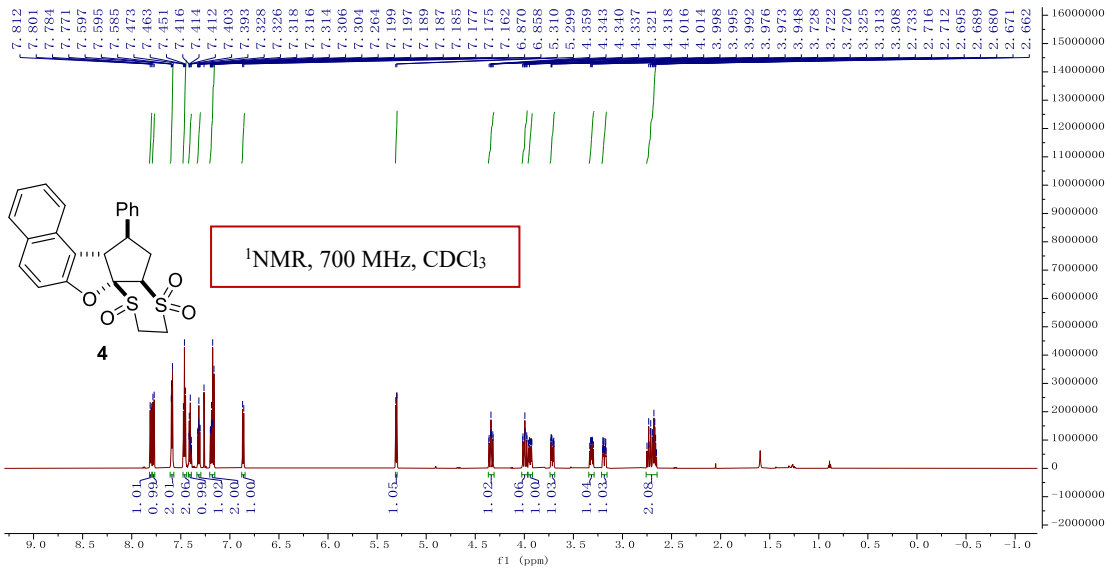

Ph
Br
O
S
S
3v
^{13}C NMR, 150 MHz, CDCl$_3$
f1 (ppm)

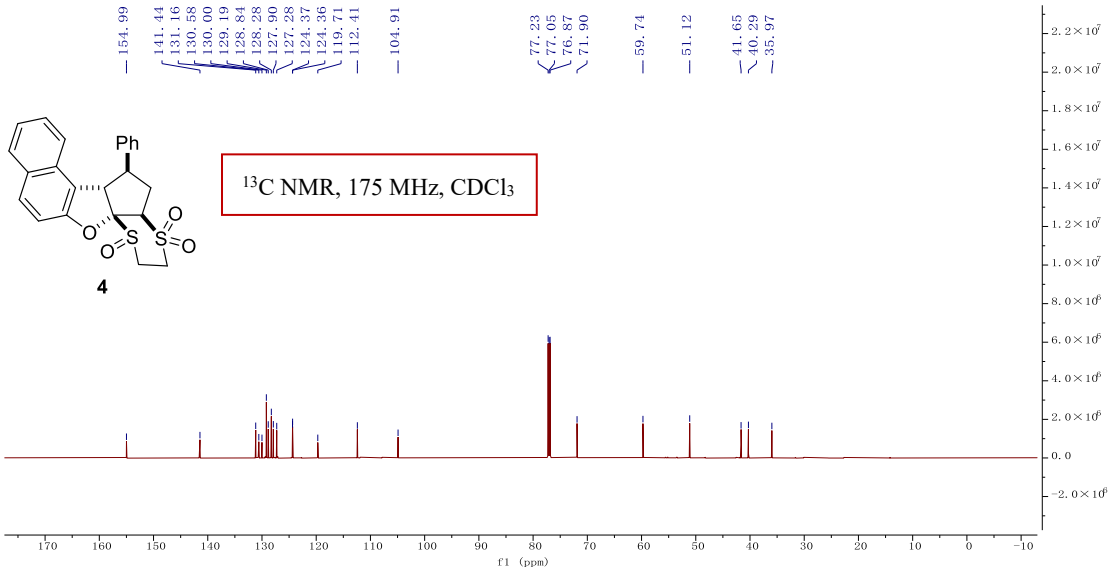

Ph
Me
O
S
S
3w
^{1}NMR, 600 MHz, CDCl$_3$

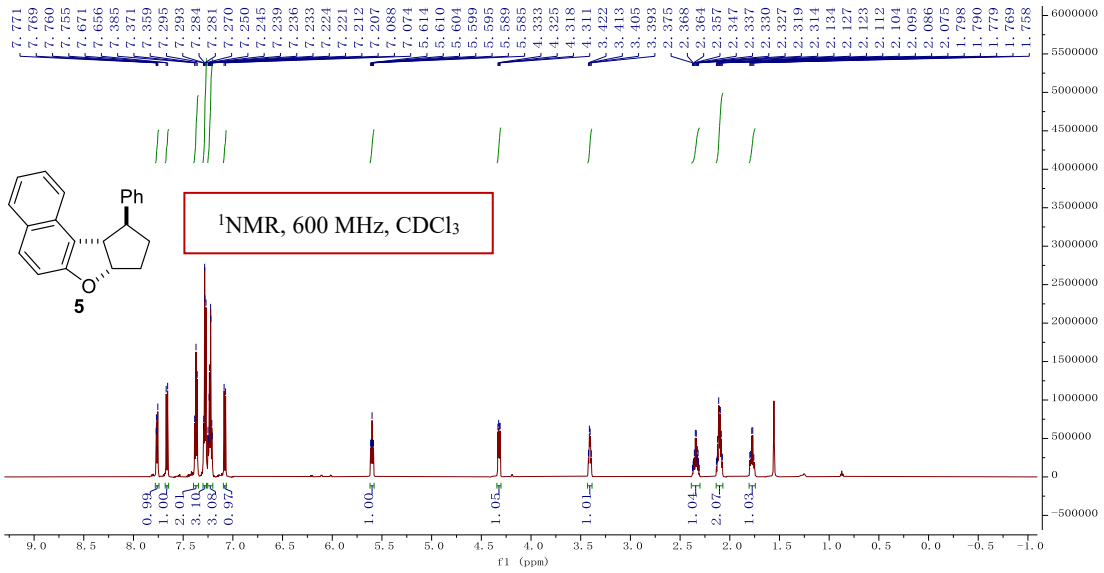

Ph
Me
O
S
S
3w
^{13}C NMR, 150 MHz, CDCl$_3$

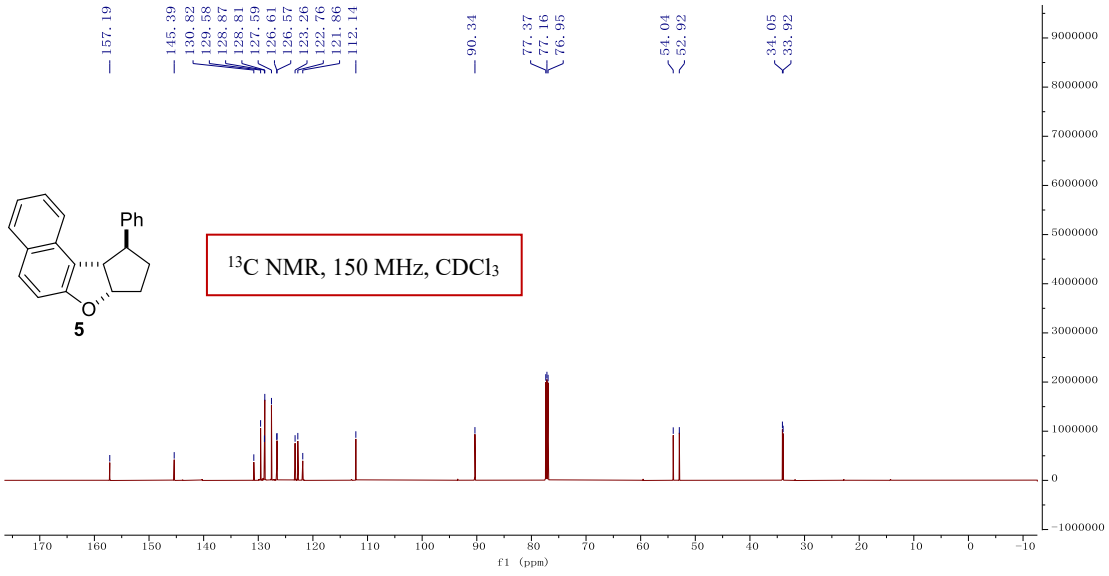

Ph
Cl
O
S
S
3x
^{1}NMR, 600 MHz, CDCl$_3$

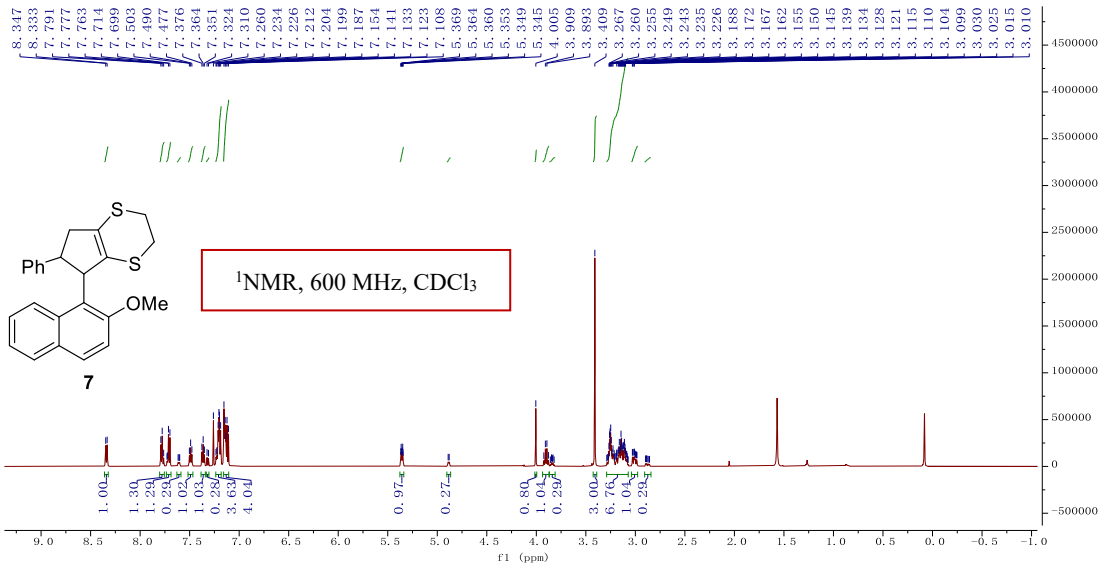

Ph
Cl
O
S
S
3x
^{13}C NMR, 150 MHz, CDCl$_3$

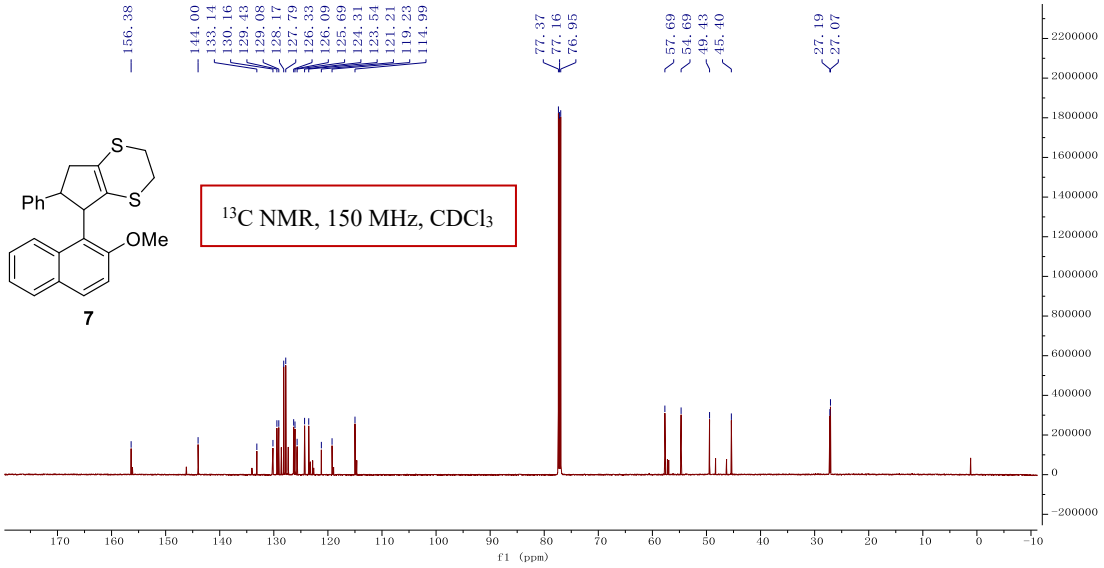

Ph
O
S
S
O
O
O
O
4
^{1}NMR, 700 MHz, CDCl$_3$
f1 (ppm)


Ph
O
S
S
O
O
O
O
4
^{13}C NMR, 175 MHz, CDCl$_3$
f1 (ppm)


Ph
O
5
^{1}NMR, 600 MHz, CDCl$_3$


Ph
O
5
^{13}C NMR, 150 MHz, CDCl$_3$


Ph
S
S
OMe
7
^{1}NMR, 600 MHz, CDCl$_3$


Ph
S
S
OMe
7
^{13}C NMR, 150 MHz, CDCl$_3$