Supplementary Information

Divergent Access to Polycyclic Spiro- and Fused-*N*,*O*-Ketals through $Bi(OTf)_3$-Catalyzed [4+2]-Annulation of Cyclic *N*-Sulfonyl Ketimines and Alkynols

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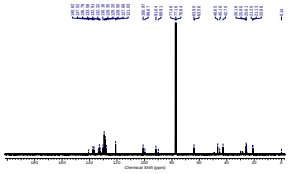
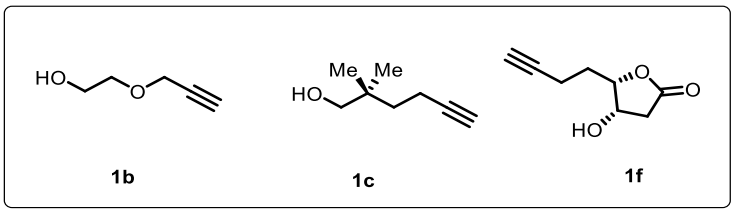
1. General Information: All reactions were performed under argon atmosphere with oven (80 ºC) or flame-dried glassware with a septum seal. Tetrahydrofuran (THF) was distilled from sodium-benzophenone under the argon atmosphere immediately before use. Anhydrous dichloromethane, dichloroethane, methanol, and fluorobenzene were purchased from commercial sources and used without any further treatment. Reaction temperatures are reported as the temperature of the bath surrounding the reaction vessel, and 30 °C corresponds to the room temperature (35 ^{o}C)(rt) of the laboratory when the experiments were carried out. Analytical thin-layer chromatography (TLC) was performed on TLC Silica gel 60 F_{254}. Visualization was accomplished with short-wave UV light, anisaldehyde, or $KMnO_4$ staining solutions followed by heating. Chromatography was performed on silica gel (100-200 mesh) by standard techniques eluting with solvents as indicated. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 200, 400, and 500 in solvents as indicated. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ H = 7.27 ppm, δ C = 77.00 ppm), the following abbreviations were used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublet; td, triplet doublet; and br, broad. Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments. HRMS data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump, FT-IR instrument (Bruker Alpha Model) at normal temperature with a NaCl pellet (IR grade). Experimental procedures for all new compounds and known compounds without published experimental procedures are described below. Compounds that are not presented in the main text (manuscript) are numbered starting from **S1**.

2. Synthesis of 5-hexyn-1-ols (1):



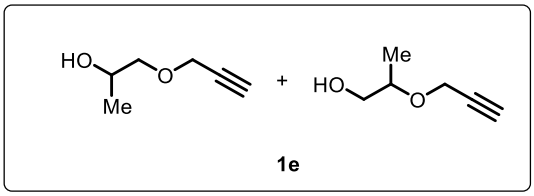
Alkynol **1a** was purchased from commercial sources.

2-(Prop-2-yn-1-yloxy)ethan-1-ol (1b), 2,2-dimethylhex-5-yn-1-ol (1c), and 5-(But-3-yn-1-yl)-4-hydroxydihydrofuran-2(3*H*)-one (1f):



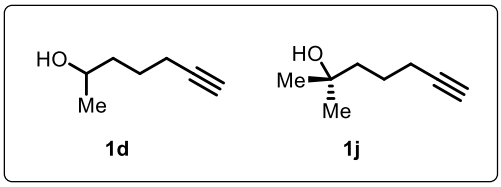
2-(Prop-2-yn-1-yloxy)ethan-1-ol (**1b**), 2,2-dimethylhex-5-yn-1-ol (**1c**), and 5-(but-3-yn-1-yl)-4-hydroxydihydrofuran-2(3*H*)-one (**1f**) were prepared using reported procedures.[1]

1-(Prop-2-yn-1-yloxy)propan-2-ol and 2-(prop-2-yn-1-yloxy)propan-1-ol (1e):



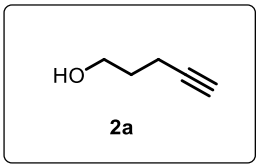
1-(Prop-2-yn-1-yloxy)propan-2-ol and 2-(prop-2-yn-1-yloxy)propan-1-ol (**1e**) was prepared using reported procedure**.**[2]

Hept-6-yn-2-ol(1d) and 2-methylhept-6-yn-2-ol(1j):

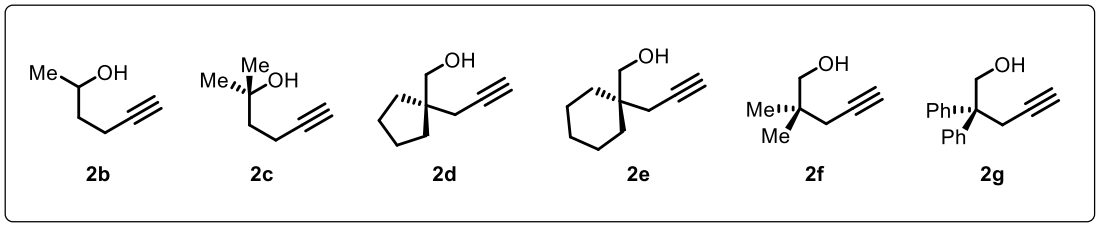


Hept-6-yn-2-ol(**1d**), 2-methylhept-6-yn-2-ol**(1j)** was prepared using reported procedure.[3]

3. Synthesis of 4-pentyn-1-ols (2):



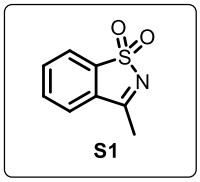
Alkynol **2a** was purchased from commercial sources.



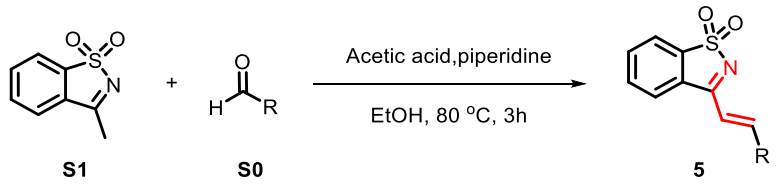
Compound **2b**-**2g** were prepared using known literature procedures.[4]

1 (a) Nakate, A. K.; Thorat, S. S.; Jain, S.; Gamidi, R. K.; Kumar, V.; Kontham, R. *Org. Chem. Front*, **2022**, 9, 802–809. (b) Ashwini K. N.; Madhukar S. P.; Ravindar K. *Org. Biomol. Chem.*, **2018**, *16*, 3229-3240.
2 Harada, T.; Muramatsu, K.; Mizunashi, K.; Kitano, C.; Imaoka, D.; Fujiwara, T.; Kataoka, H. *J. Org. Chem.*, **2008**, *73*, 249–258.
3 Thorat, S. S.; Kataria, P.; Kontham, R. *Org. Lett.* **2018**, 20, 872−875.

4. Synthesis of methylbenzo[*d*]isothiazole 1,1-dioxide (S1): Following the literature procedure[22] saccharin (10 g, 54.5 mmol, 1.0 eq.) was dissolved in anhydrous THF (100 mL) and cooled to 0 ^{o}C under argon atmosphere. Then, methyl magnesium bromide (0.3 M in Et_2O, 36 mL, 109 mmol, 2.0 eq.) was added over 10 minutes. The reaction mixture was moved to room temperature (35 ^{o}C) for 17 h. After completion of the reaction, it was quenched through the slow addition of sat. aq. solution of NH_4Cl (50 mL) at 0 ^{o}C, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3x50 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated to dryness under reduced pressure to give **S1** as an off-white solid (5.34 g, 29.5 mmol, 54%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.99-7.87 (m, 1H), 7.80-7.70 (m, 3H), 2.67 (s, 3H).

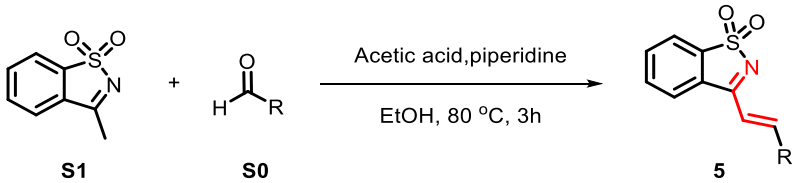


5. General Procedure for the synthesis of cyclic *N*-sulfonyl ketimines (5):

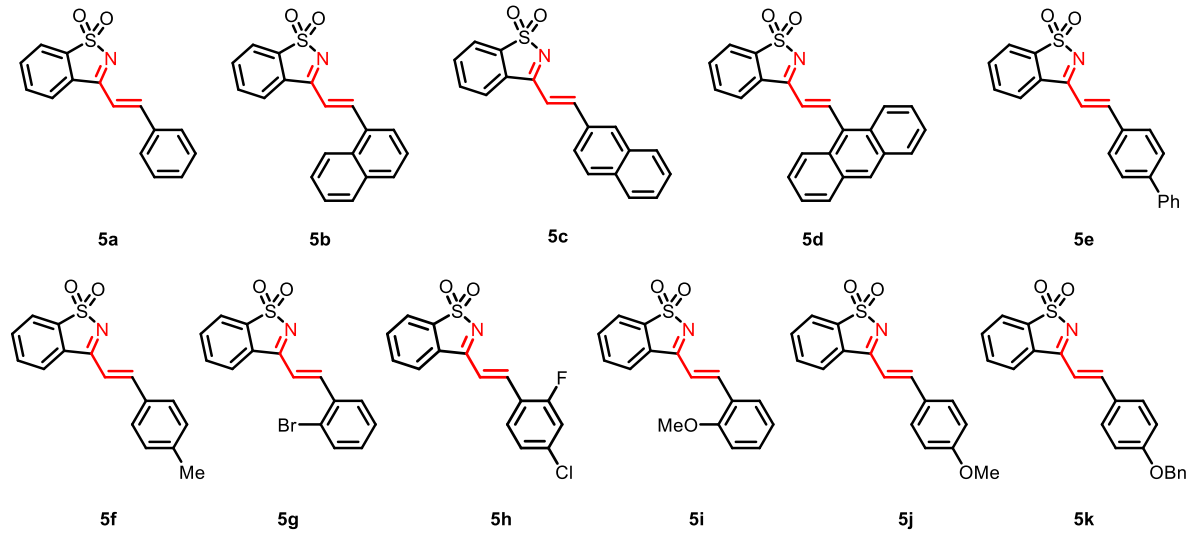


Following the known literature procedure, compound **S1** (1 eq) and aldehyde derivatives **S0** (1 eq) were dissolved in ethanol (10 mL). Then, added acetic acid (0.1 eq) followed by piperidine (0.1 eq), and the resulting mixture was stirred at 80 ^{o}C for 3 h, then cooled to 0 ^{o}C and filtered. The obtained cake was washed with cold ethanol and subjected to the next step without further purification **5**. (Please see Supporting Information for chemical structures of **5a**-**5k**).

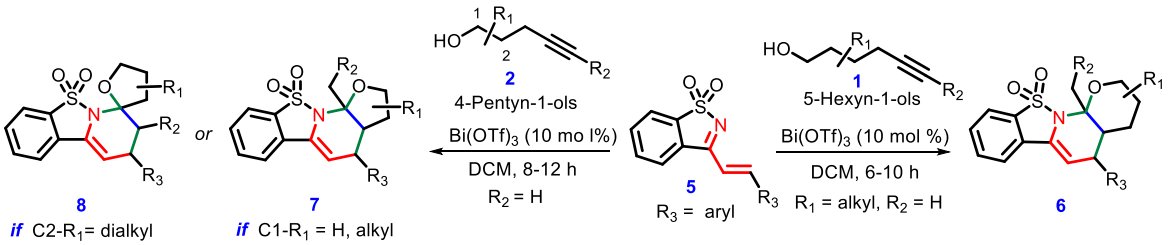
6. Chemical structures of cyclic *N*-sulfonyl ketimines (5):



[4] (a) Kambale, D. A.; Thorat, S. S.; Pratapure, M. S.; Gonnade, R. G.; Kontham, R. *Chem. Commun.*, **2017**, *53*, 6641−6644. (b) Kambale, D. A.; Borade, B. R.; Kontham, R. *Org. Bio. Chem.* **2021**, *19*, 6618–6622.



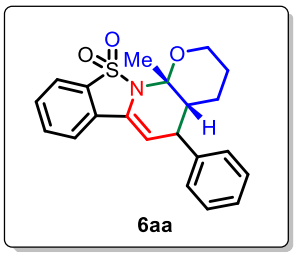
7. General Procedure for the synthesis of spiro- and fused-*N*,*O*-ketals (6, 7 and 8) from cyclic *N*-sulfonyl ketimines (5) and alkynols (1 and 2):



To a single neck 10 mL round bottom flask equipped with positive argon flow, alkynol **1** or **2** (1.01 mmol) and *α,β*-unsaturated ketimines 5 (1.01 mmol) in 2 mL of anhydrous CH_2Cl_2 were taken under argon atmosphere, then $Bi(OTf)_3$ (0.101 mmol) was added to the reaction mixture at room temperature (35 ^oC). The resulting reaction mixture was stirred at rt for 8 h. After completion of the reaction (monitored by TLC, visualized using UV, anisaldehyde, and $KMnO_4$ staining solutions), the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution, the aqueous layer was extracted with CH_2Cl_2 (2x5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified using silica-gel column chromatography (100-200 mesh) to afford the corresponding spiro- and fused-*N*,*O*-ketals **6**, **7** and **8**.

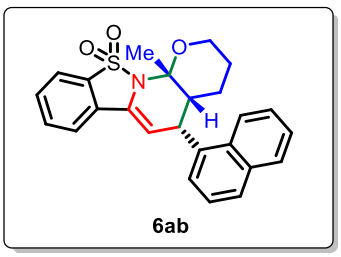
8. Synthesis and characterization of fused-*N*,*O*-ketals (6) from 5-hexyn-1-ols (1) and cyclic *N*-sulfonyl ketimines (5):

*12a-Methyl-5-phenyl-3,4,4a,12a-tetrahydro-2H,5H-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (**6aa**)*: Following the General Procedure, to the mixture of 5-hexyn-1-ol (**1a**) (0.1 g, 1.01 mmol) and (*E*)-3-styrylbenzo[*d*]isothiazole 1,1-dioxide (**5a**) (0.272 g, 1.01 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.066 g, 0.101 mmol) was added under argon atmosphere at room temperature (35 ^oC)and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 12a-methyl-5-phenyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-*a*]pyrano[3,2-*e*]pyridine 11,11-dioxide **(6aa)** (0.308 g, 82%) with dr (1:0.2) as an off-white solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.74-7.01 (m, 1H), 7.66-7.01 (m, 1H), 7.59-7.51 (m, 1H), 7.41-7.35 (m, 2H), 7.32-7.27 (m, 1H), 7.25-7.22 (m, 2H), 5.79 (dd, *J* = 4.25, 0.63 Hz, 0.1H), 5.67 (dd, *J* = 2.3, 1.0 Hz, 1H), 4.39-4.29 (m, 1H), 4.21 (dd, *J* = 5.88, 2.38 Hz, 1H), 3.92-3.83 (m, 1H), 1.95-1.87 (m, 4H), 1.60-1.51 (m, 2H), 1.37-1.25 (m, 1H), 1.04-0.92 (m, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 143.7, 140.6, 133.5, 132.9, 132.4, 130.2, 129.1, 128.7, 128.6, 127.8, 127.1, 126.8, 121.0, 121.0, 100.6, 99.4, 91.6, 89.8, 63.8, 63.5, 49.2, 46.6, 45.5, 43.1, 26.1, 25.9, 25.5, 25.5, 20.9; IR (KBr, cm^{-1}): υ 3153, 3072, 2934, 1717, 1461, 1305, 1177, 1071, 1010, 758, 699; MP: 200-204.5 ^oC; HRMS (ESI) *m/z* calcd for $C_{21}H_{21}O_3NS$ $[M+H]^+$ 368.1315, found 368.1306.



6aa

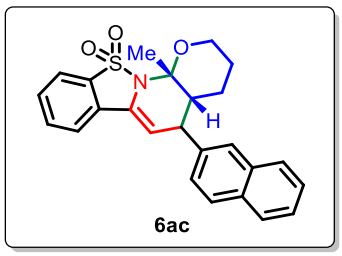
*12a-Methyl-5-(naphthalen-1-yl)-3,4,4a,12a-tetrahydro-2H,5H-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (**6ab**)*: Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**1a**) (0.1 g, 1.01 mmol) and (*E*)-3-(2-(naphthalen-1-yl)vinyl)benzo[*d*]isothiazole 1,1-dioxide (**5b**) (0.322 g, 1.01 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.066 g, 0.101 mmol) was added under argon atmosphere at room temperature (35 ^oC)and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 12a-methyl-5-(naphthalen-1-yl)-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-*a*]pyrano[3,2-*e*]pyridine 11,11-dioxide (**6ab**) (0.330 g, 79%) as a white crystal. TLC: R_f = 0.50 (SiO_2, 15% EtOAc/hexanes); **6ab** was confirmed by ^1H NMR,



6ab

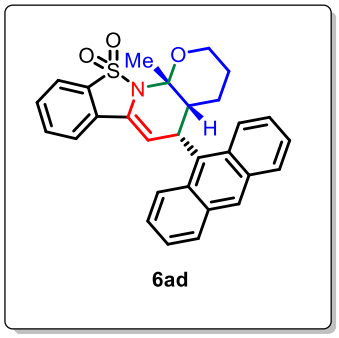
^{13}C NMR, DEPT, HRMS and XRD analysis;[20] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (d, *J* = 8.38 Hz, 1H), 7.92 (dd, *J* = 7.88, 1.13 Hz, 1H), 7.86-7.74 (m, 3H), 7.68-7.63 (m, 1H), 7.61-7.52 (m, 3H), 7.50-7.45 (m, 1H), 7.40 (dd, *J* = 7.07, 1.06 Hz, 1H), 5.76 (d, *J* = 1.25 Hz, 1H), 5.02 (dd, *J* = 5.63, 2.25 Hz, 1H), 4.35 (td, *J* = 11.76, 3.63 Hz, 1H), 3.86 (td, *J* = 11.76, 2.63 Hz, 1H), 2.33-2.20 (m, 1H), 2.08 (s, 3H) 1.51-1.29 (m, 3H), 0.80-0.71 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 136.2, 134.1, 133.6, 133, 132.5, 131.4, 130.2, 129.4, 129.2, 127.9, 126.7, 126.4, 126.1, 125.3, 122.5, 121.1, 101.6, 91.6, 63.8, 44.5, 25.8, 25.5, 21.5; IR (KBr, cm^{-1}): υ 3142, 3064, 2930, 1705, 1459, 1311, 1177, 1069, 1027, 794, 698; HRMS (ESI) *m/z* calcd for $C_{25}H_{23}O_3NS$ $[M+H]^+$ 418.1471, found 418.1466.

12a-Methyl-5-(naphthalen-2-yl)-3,4,4a,12a-tetrahydro-2H,5H-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (***6ac***): Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**1a**) (0.1 g, 1.01 mmol) and (*E*)-3-(2-(naphthalen-2-yl)vinyl)benzo[*d*]isothiazole 1,1-dioxide (**5c**) (0.322 g, 1.01 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.066 g, 0.101 mmol) was added under argon atmosphere at room temperature (35 °C)and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 12a-methyl-5-(naphthalen-2-yl)-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-*a*]pyrano[3,2-*e*]pyridine 11,11-dioxide (**6ac**) (0.299 g, 71%) as an off-white solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87-7.82 (m, 4H), 7.79 (d, *J* = 7.93 Hz, 1H), 7.69 (s, 1H), 7.66 (t, *J* = 7.63 Hz, 1H), 7.61-7.56 (m, 1H), 7.54-7.46 (m, 2H), 7.36 (dd, *J* = 1.53, 8.24 Hz, 1H), 5.85-5.74 (m, 1H), 4.38 (dd, *J* = 2.44, 5.49 Hz, 1H), 4.35 (dd, *J* = 3.97, 6.41 Hz, 1H), 3.88 (d, *J* = 12.21 Hz, 1H), 2.34-2.28 (m, 1H), 2.02 (td, *J* = 5.49, 10.38 Hz, 1H), 1.96 (s, 3H), 1.55-1.49 (m, 2H), 1.40-1.34 (m, 1H), 1.00-0.95 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 138.2, 133.7, 133.5, 133, 132.6, 132.6, 130.3, 129.2, 128.4, 127.8, 127.8, 127, 126.9, 126.5, 126, 121.1, 121.1, 100.5, 91.6, 63.9, 46.6, 43.2, 25.9, 25.5, 21.1; IR (KBr, cm^{-1}): υ 3143, 3004, 2929, 1702, 1599, 1464, 1308, 1178, 1069, 1011, 746; MP: 176-179.2 °C; HRMS (ESI) *m/z* calcd for $C_{25}H_{23}O_3NS$ $[M+H]^+$ 418.1471, found 418.1464.



6ac

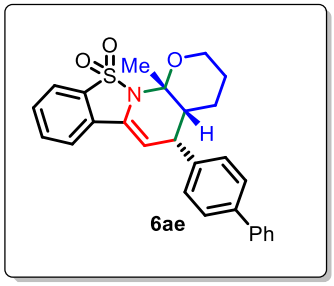
5-(Anthracen-9-yl)-12a-methyl-3,4,4a,12a-tetrahydro-2H,5H-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (***6ad***): Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**1a**) (0.1 g, 1.01 mmol) and (*E*)-3-(2-(anthracen-9-



6ad

yl)vinyl)benzo[*d*]isothiazole 1,1-dioxide (**5d**) (0.376 g, 1.01 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.066 g, 0.101 mmol) was added under argon atmosphere at room temperature (35 ^oC)and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 5-(anthracen-9-yl)-12a-methyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo [2,3-*a*]pyrano[3,2-*e*]pyridine 11,11-dioxide (**6ad**) (0.325 g, 68%) as an off-white solid. TLC: R_f = 0.50 (SiO_2, 15% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 9.01 Hz, 1H), 8.46 (s, 1H), 8.28 (d, *J* = 9.01 Hz, 1H), 8.08 (d, *J* = 8.25 Hz, 1H), 8.03 (d, *J* = 8.26 Hz, 1H), 7.89 (d, *J* = 7.50 Hz, 1H), 7.73-7.58 (m, 4H), 7.58-7.50 (m, 1H), 7.50-7.34 (m, 2H), 6.09 (m, 1H), 5.69-5.66 (m, 1H), 4.46 (dt, *J* = 3.63, 11.88 Hz, 1H), 3.96-3.90 (m, 1H), 2.53-2.45 (m, 1H), 2.18 (s, 3H), 2.12-1.82 (m, 2H), 1.60 (br. s., 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 133.6, 133.1, 132.1, 131.7, 131.6, 131.3, 130.7, 130.1, 130.0, 129.7, 129.6, 129.5, 128.4, 127.0, 126.7, 125.2, 125.1, 124.8, 122.9, 121.2, 120.9, 105.3, 91.4, 64.3, 46.9, 39.5, 26.0, 26.0, 22.8; HRMS (ESI): *m/z* calcd for $C_{29}H_{26}O_3NS$ $[M+H]^+$ 468.1628, found 468.1622.

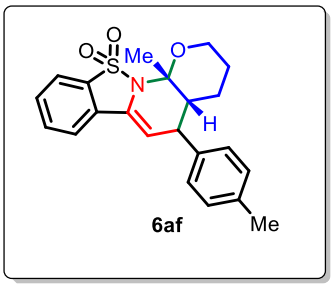
*5-([1,1'-Biphenyl]-4-yl)-12a-methyl-3,4,4a,12a-tetrahydro-2H,5H-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (**6ae**)*: Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**1a**) (0.1 g, 1.01 mmol) and (*E*)-3-(2-([1,1'-biphenyl]-4-yl)vinyl)benzo[*d*]isothiazole 1,1-dioxide (**5e**) (0.348 g, 1.01 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.066 g, 0.101 mmol) was added under argon atmosphere at room temperature (35 ^oC)and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 5-([1,1'-biphenyl]-4-yl)-12a-methyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-*a*]pyrano[3,2-*e*]pyridine 11,11-dioxide (**6ae**) (0.294 g, 65%) as an off-white solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.80 (m, 1H), 7.74 (d, *J* = 7.75 Hz, 1H), 7.67-7.53 (m, 6H), 7.48-7.43 (m, 2H), 7.37 (td, *J* = 1.13, 7.25 Hz, 1H), 7.31(d, *J* = 8.13 Hz, 2H), 5.70 (dd, *J* = 1.13, 2.50 Hz, 1H), 4.40-4.29 (m, 1H), 4.25 (dd, *J* = 2.38, 5.88 Hz, 1H), 3.95-3.84 (m, 1H), 1.99-1.94 (m, 1H), 1.93 (s, 3H), 1.65-1.55 (m, 4H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.7, 140.1, 139.7, 133.6, 133.0, 132.5, 130.2, 129.1, 129.0, 129.0,



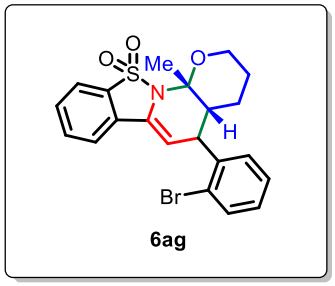
6ae

127.5, 127.3, 127.1, 121.0, 121.0, 100.5, 91.6, 63.9, 46.6, 42.8, 25.9, 25.6, 21.0; HRMS (ESI): *m/z* calcd for $C_{27}H_{26}O_3NS$ $[M+H]^+$ 444.1628, found 444.1621.

12a-Methyl-5-(p-tolyl)-3,4,4a,12a-tetrahydro-2H,5H-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (***6af***): Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**1a**) (0.1 g, 1.01 mmol) and (*E*)-3-(4-methylstyryl)benzo[d]isothiazole 1,1-dioxide (**5f**) (0.286 g, 1.01 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.066 g, 0.101 mmol) was added under argon atmosphere at room temperature (35 ^oC) and the reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 12a-methyl-5-(p-tolyl)-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-*a*]pyrano[3,2-*e*]pyridine 11,11-dioxide **(6af)** (0.246 g, 64%) with dr (1:0.1) as an off-white solid.. TLC: R_f = 0.70 (SiO_2, 15% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.79 (d, *J* = 7.88 Hz, 1H), 7.72 (d, *J* = 7.75 Hz, 1H), 7.66-7.60 (m, 1H), 7.55 (t, *J* = 7.38 Hz 1H), 7.18 (d, *J* = 7.88 Hz, 2H), 7.12 (d, *J* = 8.13 Hz, 2H), 5.68-5.63 (m, 1H), 4.39-4.29 (m, 1H), 4.17 (dd, *J* = 2.25, 5.75 Hz, 1H), 3.91-3.83 (m, 1H), 2.37 (s, 3H), 1.90 (s, 3H), 1.89-1.84 (m, 1H), 1.59-1.50 (m, 2H), 1.39-1.20 (m, 2H), 1.07-0.96 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 137.5, 136.8, 133.6, 132.9, 132.3, 130.1, 129.3, 129.2, 128.5, 121, 101, 91.6, 63.9, 46.6, 42.7, 25.6, 25.6, 21.2, 20.9; IR (KBr, cm^{-1}): υ 3133, 3071, 2940, 1667, 1511, 1463, 1308, 1176, 1069, 1008, 932, 748; MP: 216-219 ^oC; HRMS (ESI) *m/z* calcd for $C_{22}H_{23}O_3NS$ $[M+H]^+$ 382.1471, found 382.1469.

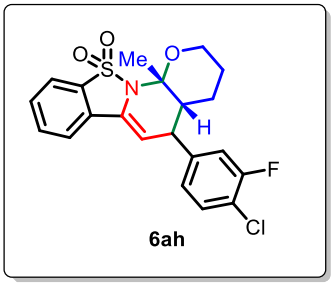


5-(2-Bromophenyl)-12a-methyl-3,4,4a,12a-tetrahydro-2H,5H-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (***6ag***): Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**1a**) (0.1 g, 1.01 mmol) and (*E*)-3-(2-bromostyryl)benzo[d]isothiazole 1,1-dioxide (**5g**) (0.351 g, 1.01 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.066 g, 0.101 mmol) was added under argon atmosphere at room temperature (35 ^oC) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 5-(2-bromophenyl)-12a-methyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-*a*]pyrano[3,2-*e*]pyridine 11,11-dioxide (**6ag**) (0.380 g, 83%) in dr (1:0.3) as a white solid. TLC: R_f = 0.70 (SiO_2, 15% EtOAc/hexanes); ^1H NMR



($CDCl_3$, 400 MHz): δ 7.86 - 7.80 (m, 1H), 7.78 - 7.69 (m, 1H), 7.68-7.55 (m, 4H), 7.36-7.29 (m, 1H), 7.25-7.09 (m, 2H), 5.65 (dd, *J* = 4.88, 1.0 Hz, 0.34H),), 5.61-5.55 (m, 1H), 4.62 (dd, *J* = 2.4, 5.6 Hz, 1H), 4.40-4.23 (m, 1H), 3.95-3.82 (m, 1H), 2.34-2.20 (m, 1H), 1.95 (s, 3H), 1.60-1.56 (m, 2H), 139-1.25 (m, 1H), 0.96-0.86 (m 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 140.6, 137.5, 136.8, 133.6, 133.0, 132.9, 132.3, 130.2, 129.4, 129.2, 128.5, 127.7, 121.0, 101.0, 99.7, 91.6, 89.9, 63.9, 63.6, 46.6, 45.2, 42.7, 26.2, 25.9, 25.6, 21.2, 21; IR (KBr, cm^{-1}): υ 3191, 3144, 3069, 2928, 2859, 1699, 1666, 1462, 1391, 1311, 1184, 1012, 933, 750, 693; MP: 197-199.4 ^{o}C; HRMS (ESI) *m/z* calcd for $C_{21}H_{20}O_3NBrS$ $[M+H]^+$ 446.0420, found 446.0411.

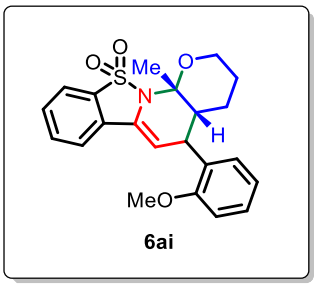
*5-(4-Chloro-2-fluorophenyl)-12a-methyl-3,4,4a,12a-tetrahydro-2H,5H-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (**6ah**)*: Following the



6ah

General Procedure, to the mixture of 5-hexyn-1-ol (**1a**) (0.1 g, 1.01 mmol) and (*E*)-3-(4-chloro-2-fluorostyryl)benzo[d]isothiazole 1,1-dioxide (**5h**) (0.321 g, 1.01 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.066 g, 0.101 mmol) was added under argon atmosphere at room temperature (35 ^{o}C) and the reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 5-(4-chloro-2-fluorophenyl)-12a-methyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (**6ah**) (0.169 g, 39%) with dr (1:0.5) as an off-white solid. TLC: R_f = 0.70 (SiO_2, 15% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.79 (m, 2H), 7.76-7.69 (m, 2H), 7.65 (d, *J* = 7.63 Hz, 1H), 7.58 (d, *J* = 7.38 Hz, 1H), 7.19 (d, *J* = 8.00 Hz, 1H), 7.16-7.13 (m, 2H), 7.12-7.09 (m, 1H), 5.60 (d, *J* = 4.38 Hz, 1H), 5.54-5.51 (m, 1H), 4.47 (dd, *J* = 2.25, 5.63 Hz, 1H), 4.37-4.29 (m, 1H), 4.25 (dt, *J* = 2.75, 11.76 Hz, 1H), 3.91-3.86 (m, 2H), 3.72 (d, *J* = 4.63 Hz, 1H), 2.13-2.00 (m, 2H), 1.89 (s, 3H), 1.76-1.70 (m, 1H), 1.61-1.55 (m, 3H), 1.36-1.28 (m, 1H), 1.00-0.93 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.8, 159.3, 133.8, 133.7, 133.6, 133.5, 133.1, 133.0, 133.0, 132.9, 131.0, 130.9, 130.5, 130.4, 130.3, 130.2, 128.8, 128.8, 126.5, 126.4, 124.5, 124.5, 124.4, 124.3, 121.1, 121.0, 116.6, 116.3, 98.7, 97.0, 91.4, 89.9, 63.8, 43.9, 36.3, 36.3, 25.7, 25.6, 25.4, 21.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.37, -115.91; HRMS (ESI): *m/z* calcd for $C_{21}H_{20}O_3NClFS$ $[M+H]^+$ 420.0831, found 420.0825.

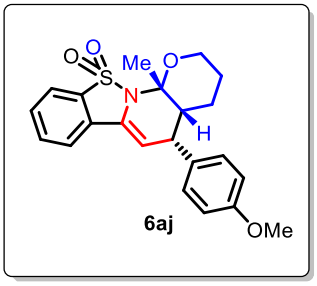
5-(2-Methoxyphenyl)-12a-methyl-3,4,4a,12a-tetrahydro-2H,5H-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide ***(6ai)***: Following the *General Procedure*, to the



6ai

mixture of 5-hexyn-1-ol (**1a**) (0.1 g, 1.01 mmol) and (*E*)-3-(2-methoxystyryl)benzo[*d*]isothiazole 1,1-dioxide (**5i**) (0.302 g, 1.01 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.066 g, 0.101 mmol) was added under argon atmosphere at room temperature (35 ^oC) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 5-(2-methoxyphenyl)-12a-methyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-*a*]pyrano[3,2-*e*]pyridine 11,11-dioxide (**6ai**) (0.325 g, 80%) with dr. 1:0.2 as a white solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.83-7.79 (m, 1H), 7.76-7.70 (m, 1H), 7.62 (td, *J* = 7.25, 1.06 Hz, 1H), 7.58-7.52 (m, 1H), 7.30-7.27(m, 1H), 7.23-7.16 (m, 1H), 6.98-6.85 (m, 2.46H), 5.68 (dd, *J* = 4.88, 1.08 hz, 0.23H), 5.63 (dd, *J* = 2.56, 1.08 hz, 1H), 4.59 (dd, *J* = 5.63, 2.50 Hz, 1H), 4.40-4.23 (m, 1H), 3.90-3.88 (m, 1H), 3.86 (m, 3H), 2.22-2.12 (m, 1H), 1.92 (s, 3H), 1.60-1.53(m, 2H), 1.35-1.22 (m, 1H), 0.99-0.88(m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 157.1, 133.5, 132.9, 132.9, 132.2, 130.1, 130, 129.5, 129.3, 128.8, 128.2, 128, 121.1, 120.9, 120.3, 120.3, 110.4, 101.7, 99.9, 91.8, 90.6, 63.8,, 63.6, 55.5, 55.5, 47.2, 43, 41.1, 36.8, 26.6, 256, 25.7, 25.7, 21.4; HRMS (ESI) *m/z* calcd for $C_{22}H_{23}O_4NS$ $[M+H]^+$ 398.1421, found 398.1413.

5-(4-Methoxyphenyl)-12a-methyl-3,4,4a,12a-tetrahydro-2H,5H-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide ***(6aj)***: Following the *General Procedure*, to the

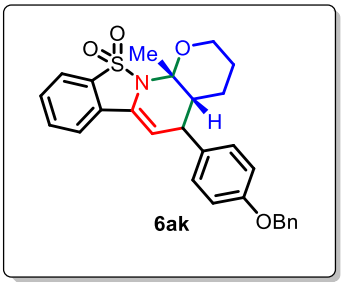


6aj

mixture of 5-hexyn-1-ol (**1a**) (0.1 g, 1.01 mmol) and (*E*)-3-(4-methoxystyryl)benzo[*d*]isothiazole 1,1-dioxide (**5j**) (0.302 g, 1.01 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.066 g, 0.101 mmol) was added under argon atmosphere at room temperature (35 ^oC) and the reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 5-(4-methoxyphenyl)-12a-methyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-*a*]pyrano[3,2-*e*]pyridine 11,11-dioxide (**6aj**) (0.332 g, 82%) as an white solid, **6aj** was confirmed by ^1H NMR, ^{13}C NMR, DEPT, HRMS and 2D analysis;[20] TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.81 (d, *J* = 7.78 Hz, 1H), 7.70 (d, *J* = 7.78 Hz, 1H), 7.65-7.60 (m, 1H), 7.58-7.53 (m, 1H), 7.16-7.12 (m, 2H), 6.93-6.88 (m, 2H), 5.63 (dd, *J* = 2.40 Hz, 1.03 1H), 4.39-4.28 (m, 1H),

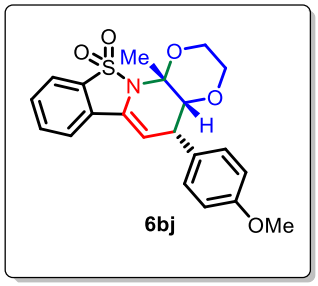
4.16 (dd, *J* = 5.72, 2.29 Hz, 1H), 3.87 (dt, *J* = 11.27, 1.92 Hz, 1H), 3.82 (s, 3H), 1.92-1.83 (m, 4H), 1.57-1.54 (m, 2H), 1.34-1.27 (m, 1H), 1.07-0.97 (m, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 158.8, 133.6, 132.9, 132.5, 132.3, 130.2, 129.6, 129.2, 121.1, 114.1, 101.1, 91.7, 63.9, 55.5, 46.7, 42.3, 25.9, 25.6, 20.6; HRMS (ESI) *m/z* calcd for $C_{22}H_{23}O_4NS$ $[M+H]^+$ 398.1421, found 398.1416.

5-(4-(Benzyloxy)phenyl)-12a-methyl-3,4,4a,12a-tetrahydro-2H,5H-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide ***(6ak)***: Following the



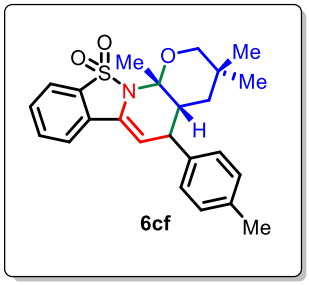
General Procedure, to the mixture of 5-hexyn-1-ol (**1a**) (0.1 g, 1.01 mmol) and (*E*)-3-(4-(benzyloxy)styryl)benzo[*d*]isothiazole 1,1-dioxide (**5k**) (0.380 g, 1.01 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.066 g, 0.101 mmol) was added under argon atmosphere at room temperature (35 ^{o}C) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 5-(4-(benzyloxy)phenyl)-12a-methyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5] isothiazolo[2,3-*a*]pyrano[3,2-*e*]pyridine 11,11-dioxide (**6ak**) (0.313 g, 65%) as a white solid. TLC: R_f = 0.70 (SiO_2, 15% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81 (d, *J* = 7.75 Hz, 1H), 7.72-7.67 (m, 1H), 7.65-7.59 (m, 1H), 7.59-7.52 (m, 1H), 7.48-7.32 (m, 5H), 7.14 (d, *J* = 8.63 Hz, 2H), 6.98 (d, *J* = 8.63 Hz, 2H), 5.68-5.59 (m, 1H), 5.08 (s, 2H), 4.39-4.28 (m, 1H), 4.22 (t, *J* = 5.75 Hz, 1H), 4.16 (dd, *J* = 2.38, 5.75 Hz, 1H), 3.92-3.82 (m, 1H), 1.90 (s, 3H), 1.86 (dd, *J* = 3.13, 8.13 Hz, 1H), 1.48-1.38 (m, 1H), 1.36-1.29 (m, 2H), 1.07-0.98 (m, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz): δ 158. 137.1, 133.6, 132.9, 132.8, 132.3, 130.2, 129.6, 129.2, 128.8, 128.2, 127.6, 121, 121, 115, 101.1, 91.6, 70.3, 63.9, 46.7, 42.3, 25.9, 25.6, 21; IR (KBr, cm^{-1}): υ 3747, 3401, 3363, 3293, 2934, 1510, 1452, 1307, 1244, 1179, 1057, 934, 815, 697; HRMS (ESI) *m/z* calcd for $C_{28}H_{27}O_4NS$ $[M+H]^+$ 474.1734, found 474.1731.

5-(4-Methoxyphenyl)-12a-methyl-2,3,4a,12a-tetrahydro-5H-benzo[4,5]isothiazolo[2,3-a][1,4]dioxino[2,3-e]pyridine 11,11-dioxide ***(6bj)***: Following the *General Procedure*, to the mixture of 2-(prop-2-yn-1-yloxy)ethan-1-ol (**1b**) (0.1 g, 1.01 mmol) and (*E*)-3-(4-methoxystyryl)benzo[*d*]isothiazole 1,1-dioxide (**5j**) (0.299 g, 1.01 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.066 g, 0.101 mmol) was added under argon atmosphere at room temperature (35 ^{o}C) and the reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 5-(4-

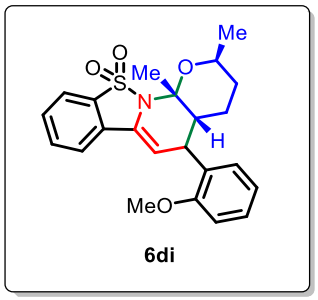


methoxyphenyl)-12a-methyl-2,3,4a,12a-tetrahydro-5H-benzo[4,5]isothiazolo[2,3-*a*][1,4] dioxino[2,3-*e*]pyridine 11,11-dioxide (**6bj**) (0.230 g, 58%) as a white solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.82 (d, *J* = 7.93 Hz, 1H), 7.69 (d, *J* = 7.63 Hz, 1H), 7.62 (td, *J* = 7.32, 1.22 Hz, 1H), 7.59-7.55 (m, 1H), 7.25-7.23 (m, 2H), 6.95-6.88(m, 2H), 5.57 (dd, *J* = 2.44, 1.22 Hz, 1H), 4.61 (d, *J* = 3.36 Hz, 1H), 4.03-3.97 (m, 1H), 3.82 (s, 3H), 3.81-3.78 (m, 1H), 3.69-3.62 (m, 2H), 3.54 (dd, *J* = 4.27, 1.22 Hz, 1H), 1.80 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 133.5, 133, 131.6, 131.1, 130.4, 130.2, 129, 121.2, 121, 113.8, 100.2, 88.2, 79.4, 67.5,61.9, 55.4, 42.9, 23.5; HRMS (ESI) *m/z* calcd for $C_{21}H_{21}NO_5S$ $[M+H]^+$ 400.1213, found 400.1205.

3,3,12a-Trimethyl-5-(p-tolyl)-3,4,4a,12a-tetrahydro-2H,5H-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (***6cf***): Following the *General Procedure*, to the mixture of 3,3-dimethylhex-5-yn-1-ol (**1c**) (0.1 g, 0.792 mmol) and (*E*)-3-(4-methylstyryl)benzo[*d*]isothiazole 1,1-dioxide (**5f**) (0.223 g, 0.792 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.051 g, 0.079 mmol) was added under argon atmosphere at room temperature (35 ^{o}C) and the reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 3,3,12a-trimethyl-5-(*p*-tolyl)-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-*a*]pyrano[3,2-*e*]pyridine 11,11-dioxide (**6cf**) dr. 1:0.1 (0.195 g, 60%) as an off-white solid. TLC: R_f = 0.70 (SiO_2, 15% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81 (d, *J* = 7.75 Hz, 1H), 7.71(d, *J* = 7.88 Hz, 1H), 7.63 (td, *J* = 7.25, 1.13 Hz, 1H), 7.58-7.53 (m, 1H), 7.19-7.16 (m, 2H), 7.13-7.08 (m, 2H), 5.65 (dd, *J* = 2.38, 1.00 Hz, 1H), 4.18 (dd, *J* = 5.88, 2.38 Hz, 1H), 4.06 (d, *J* = 11.88 Hz, 1H), 3.36 (dd, *J* = 11.63, 2.63 Hz, 1H), 2.37 (s, 3H), 2.18-2.08 (m, 1H), 1.94 (s, 3H), 1.14 (d, *J* = 13.3 Hz, 1H), 0.91 (s, 3H), 0.73 (s, 3H), 0.68-0.64 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 137.4, 136.7, 133.6, 132.9, 132.3, 130.1, 129.4, 129.2, 128.4, 121, 101, 91.1, 73.1, 42.7, 42.2, 34.2, 30.5, 27.4, 25.7, 23.7, 21.2; HRMS (ESI) *m/z* calcd for $C_{24}H_{27}O_3NS$ $[M+H]^+$ 410.1784, found 410.1779.



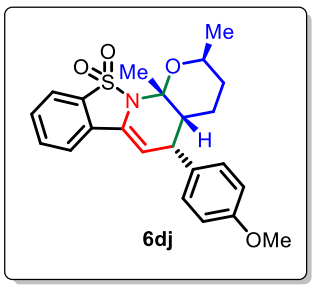
5-(2-Methoxyphenyl)-2,12a-dimethyl-3,4,4a,12a-tetrahydro-2H,5H-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide ***(6di)***: Following the



6di

General Procedure, to the mixture of hept-6-yn-2-ol (**1d**) (0.1 g, 0.892 mmol) and (*E*)-3-(2-methoxystyryl)benzo[*d*]isothiazole 1,1-dioxide (**5i**) (0.266 g, 0.892 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.058 g, 0.089 mmol) was added under argon atmosphere at room temperature (35 ^oC) and the reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 5-(2-methoxyphenyl)-2,12a-dimethyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-*a*]pyrano[3,2-*e*]pyridine 11,11-dioxide (**6di**) (0.290 g, 79%) with dr. 2:1 as a white solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.79-7.69 (m, 3H), 7.66-7.58 (m, 1.43H), 7.53 (q, *J* = 7.84 Hz, 1.46H), 7.31-7.26 (m, 1H), 7.24-7.16 (m, 2H), 6.99-6.83 (m, 3H), 5.66 (d, *J* = 4.48 Hz, 0.5H); 5.61 (s, 1H), 4.63-4.55 (m, 1H), 4.47-4.31 (m, 1H), 3.89 (s, 1H), 3.86 (s, 3H), 2.17-2.05 (m, 2H), 1.92 (s, 3H), 1.72 (d, *J* = 11.13, Hz, 1H), 1.60-1.54 (m, 1H), 1.32 (dd, *J* = 12.88, 2.63 Hz, 1H),1.25-1.21 (m, 4H), 0.91 (dd, *J* = 13.13, 3.25 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 157.1, 156.9, 133.6, 133.4, 132.8, 132.7, 132.1, 131.5, 130, 129.9, 129.4, 129.1, 128.9, 128.7, 128, 127.9, 121, 120.9, 120.7, 120.2, 120.1, 110.2, 101.4, 99.5, 91.8, 90.7, 69.1, 68.9, 55.4, 55.4, 46.8, 42.5, 40.9, 36.5, 33.3, 32.8, 28.9, 27, 25.9, 22, 21.4, 21.3; IR (KBr, cm^{-1}): υ 3175, 3145, 3077, 2933, 1705, 1661, 1593, 1532, 1458, 1307, 1241, 1169, 1075, 1023, 916, 833, 752, 647; M. P:197.4 ^oC ; HRMS (ESI) *m/z* calcd for $C_{23}H_{25}O_4NS$ $[M+H]^+$ 412.1577, found 412.1571.

5-(4-Methoxyphenyl)-2,12a-dimethyl-3,4,4a,12a-tetrahydro-2H,5H-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide ***(6dj)***: Following the

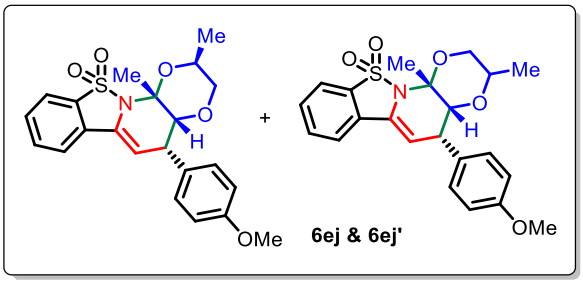


6dj

General Procedure, to the mixture of hept-6-yn-2-ol (**1d**) (0.1 g, 0.892 mmol) and (*E*)-3-(4-methoxystyryl)benzo[*d*]isothiazole 1,1-dioxide (**5j**) (0.266 g, 0.892 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.058 g, 0.089 mmol) was added under argon atmosphere at room temperature (35 ^oC) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 5-(4-methoxyphenyl)-2,12a-dimethyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-*a*]pyrano[3,2-*e*]pyridine 11,11-dioxide (**6dj**) (0.299 g, 81%) as an white crystal. **6dj** was confirmed by ^1H NMR, ^{13}C NMR,

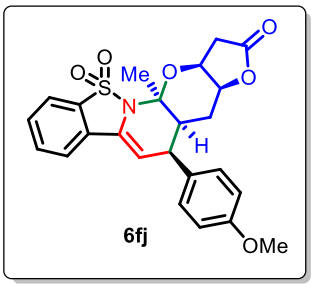
DEPT, and XRD analysis;[20] TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.82 - 7.52 (m, 6H), 7.23 - 7.11 (m, 3H),6.95-6.81 (m, 3H), 5.62 (dd, *J* = 2.38, 1.13 Hz, 1 H), 4.49-4.36 (m, 1H), 4.16 (dd, *J* = 5.82, 2.31 Hz, 1 H), 3.85-3.81 (m, 3H), 3.79 (s, 3H), 1.90 (s, 4H), 1.86-1.80 (m, 2H), 1.65-1.53 (m, 3H), 1.26-1.21 (m, 4H), 1.04-0.94 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 158.7, 133.6, 132.8, 132.8, 132.2, 130.1, 129.5, 129.1, 121.0, 120.9, 114.0, 113.9, 100.9, 99.1, 91.8, 90.3, 69.3, 55.4, 49.4, 46.4, 45.0, 42.1, 32.8, 27.1, 26.1, 21.6, 21.4; IR (KBr, cm^{-1}): υ 3146, 3074, 2952, 1722, 1603, 1458, 1373, 1260, 1174, 1127, 1038, 978, 831, 698; HRMS (ESI) *m/z* calcd for $C_{23}H_{25}O_4NS$ $[M+H]^+$ 412.1577, found 412.1574.

5-(4-Methoxyphenyl)-2,12a-dimethyl-2,3,4a,12a-tetrahydro-5H-benzo[4,5]isothiazolo [2,3-a][1,4]dioxino[2,3-e]pyridine 11,11-dioxide and 5-(4-methoxyphenyl)-3,12a-dimethyl -2,3,4a,12a-tetrahydro-5H-benzo[4,5]isothiazolo[2,3-a][1,4]dioxino[2,3-e]pyridine 11,11-dioxide (***6ej** & **6ej'***): Following the *General Procedure*, to the mixture of 1-(prop-2-yn-1-yloxy)propan-2-ol (**1e**) (0.1 g, 0.876 mmol) and (*E*)-3-(2-methoxystyryl)benzo[*d*]isothiazole 1,1-dioxide (**5j**) (0.262 g, 0.876 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.057 g, 0.087 mmol) was added under argon atmosphere at room temperature (35 ^{o}C) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 5-(2-methoxyphenyl)-2,12a-dimethyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-*a*]pyrano[3,2-*e*]pyridine 11,11-dioxide and 5-(4-methoxyphenyl)-3,12a-dimethyl -2,3,4a,12a-tetrahydro-5*H*-benzo[4,5]isothiazolo[2,3-a][1,4]dioxino[2,3-e]pyridine 11,11-dioxide (**6ej** and **6ej'**) (0.219 g, 60%) as a 1:0.6 mixture as an off-white solid. TLC: R_f = 0.80 (SiO_2, 15% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.83-7.77 (m, 1.56H), 7.73-7.67 (m, 1.65H), 7.61(t, *J* = 7.44 Hz, 1.58H), 7.57-7.52 (m, 1.55H), 7.32-7.27 (m, 3H), 7.00-6.94 (m, 1H), 6.94-6.90 (m, 1.6H), 5.58 (dd, *J* = 2.29, 1.14 Hz, 1H), 5.56-5.54 (m, 0.5H), 4.65 (ddd, *J* = 10.68, 6.48, 3.05, Hz, 1H), 4.60-4.54 (m, 1.54H), 4.18-4.12 (m, 1H), 3.91-3.86 (m, 5H), 3.72-3.69 (m, 2H), 3.66-3.61 (m, 1H), 3.20 (t, *J* = 11.44 Hz, 1H), 1.86-1.77 (m, 5H), 1.13 (d, *J* = 6.10 Hz, 3H); 0.94 (d, *J* = 6.10 Hz, 1.69H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 156.8, 133.4, 132.9, 131.9, 131.4, 130.8, 130, 129.9, 129.1, 128.4, 128.1, 127.3, 121.1, 120.9, 120.5, 120.3, 110.1, 110, 100.9, 100.1, 88.6, 87.4, 76.4, 73,



72.2, 67.3, 66.7, 55.6, 36.5, 36.3, 23.5, 23.1, 16.7, 16.3; HRMS (ESI) *m/z* calcd for $C_{22}H_{23}O_5NS$ $[M+H]^+$ 414.1370, found 414.1367.

5-(4-Methoxyphenyl)-12a-methyl-1,3a,4,4a,12a,13a-hexahydro-2H,5H-benzo[4,5]isothiazolo[2,3-a]furo[2',3':5,6]pyrano[3,2-e]pyridin-2-one 11,11-dioxide ***(6fj)***:

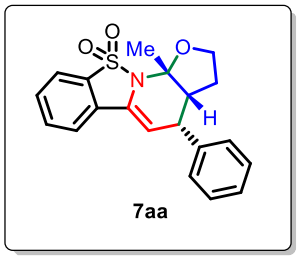


6fj

Following the *General Procedure*, to the mixture of (4*R*,5*S*)-5-(but-3-yn-1-yl)-4-hydroxydihydrofuran-2(3*H*)-one (**1f**) (0.1 g, 0.648 mmol) and (*E*)-3-(4-methoxystyryl)benzo[*d*]isothiazole 1,1-dioxide (**5**j) (0.073 g, 0.648 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.042 g, 0.064 mmol) was added under argon atmosphere at room temperature (35 ^oC) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 5-(4-methoxyphenyl)-12a-methyl-1,3a,4,4a,12a,13a-hexahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-*a*]furo[2',3':5,6]pyrano[3,2-*e*]pyridin-2-one 11,11-dioxide (**6fj**) (0.173 g, 59%) as an white solid. TLC: R_f = 0.40 (SiO_2, 15% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.82 (d, *J* = 7.63 Hz, 1H), 7.76-7.72 (m, 1H), 7.67 (td, *J* = 7.57, 1.25 Hz, 1H), 7.62-7.57 (m, 1H), 7.18-7.09 (m, 2H), 6.95-6.87 (m, 2H), 5.72 (d, *J* = 2.44, 1.19 Hz, 1H), 5.17 (q, *J* = 2.50, Hz, 1H), 4.42 (q, *J* = 3.00, Hz, 1H), 4.22 (dd, *J* = 5.75, 2.38 Hz, 1H), 3.83 (s, 3H), 2.74 (d, *J* = 2.50 Hz, 2H), 2.27-2.16 (m, 1H), 1.87 (s, 3H), 1.59-1.57 (m, 1H), 1.55-1.51 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 176.1, 159, 133.3, 132.4, 131.1, 130.5, 129.4, 129, 121.2, 121.1, 114.3, 101.4, 90.3, 77.5, 69.9, 55.5, 41.3, 39, 38.7, 25.1, 22.6; IR (KBr, cm^{-1}): υ 3144, 3037, 2924, 1781, 1702, 1653, 1510, 1464, 1307, 1248, 1180, 1105, 1047, 935, 832, 698; HRMS (ESI) *m/z* calcd for $C_{24}H_{23}O_6NS$ $[M+H]^+$ 454.1319, found 454.1314.

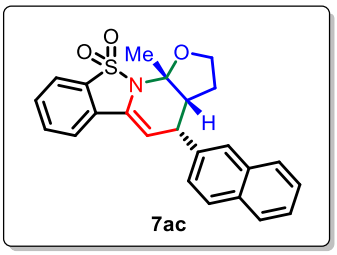
9. Synthesis and characterization of fused-*N*,*O*-ketals (7) from 4-pentyn-1-ols (2) and cyclic *N*-sulfonyl ketimines (5):

11a-Methyl-4-phenyl-2,3,3a,11a-tetrahydro-4H-benzo[4,5]isothiazolo[2,3-a]furo[3,2-e]pyridine 10,10-dioxide ***(7aa)***: Following the *General Procedure*, to the mixture of 4-pentyn-1-ol (**2a**) (0.1 g, 1.18 mmol) and (*E*)-3-styrylbenzo[*d*]isothiazole 1,1-dioxide (**5a**) (0.317 g, 1.18 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.077 g, 0.118 mmol) was added under argon atmosphere at room temperature (35 ^oC) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30%

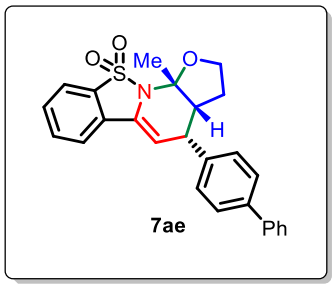


EtOAc/hexanes) afforded 4-([1,1'-biphenyl]-4-yl)-11a-methyl-2,3,3a,11a-tetrahydro-4*H*-benzo[4,5]isothiazolo[2,3-*a*]furo[3,2-*e*]pyridine 10,10-dioxide **(7aa)** (0.299 g, 71%) as an off-white solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.81 (d, *J* = 7.63 Hz, 1H), 7.70 (d, *J* = 7.63 Hz, 1H), 7.63 - 7.59 (m, 1H), 7.58-7.54 (m, 1H), 7.38-7.34 (m, 2H), 7.31-7.27 (m, 3H), 5.61 (d, *J* = 1.53 Hz, 1H), 4.39-4.31 (m, 1H), 4.15 (dd, *J* = 6.10, 2.29 Hz, 1H), 3.95 (q, *J* = 8.52 Hz, 1H), 2.49-2.40 (m, 1H), 2.01-1.93 (m, 1H), 1.92 (s, 3H), 1.45-1.38 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 141.7, 134.1, 132.7, 130.7, 130.2, 128.9, 128.7, 127.9, 127.3, 121.1, 120.9, 98.5, 95.2, 67.3, 52, 40.3, 26.6, 22.9; HRMS (ESI) *m/z* calcd for $C_{20}H_{19}O_3NS$ $[M+H]^+$ 354.1158 found 354.1155.

*11a-Methyl-4-(naphthalen-2-yl)-2,3,3a,11a-tetrahydro-4H benzo[4,5]isothiazolo[2,3-a]furo[3,2-e]pyridine 10,10-dioxide (**7ac**)*: Following the *General Procedure*, to the mixture of 4-pentyn-1-ol (**2a**) (0.1 g, 1.18 mmol) and (*E*)-3-(2-(naphthalen-2-yl)vinyl)benzo[*d*]isothiazole 1,1-dioxide (**5c**) (0.379 g, 1.18 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.077 g, 0.118 mmol) was added under argon atmosphere at room temperature (35 ^{o}C) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 11a-methyl-4-(naphthalen-2-yl)-2,3,3a,11a-tetrahydro-4*H*-benzo[4,5]isothiazolo[2,3-*a*]furo[3,2-*e*]pyridine 10,10-dioxide (**7ac**) (0.360 g, 75%) as an off-white solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.80 (m, 4H), 7.76 (d, *J* = 7.75 Hz, 1H), 7.73 (s, 1H), 7.64 (dt, *J* = 1.13, 7.50 Hz, 1H), 7.60-7.54 (m, 1H), 7.51-7.47 (m, 2H), 7.41 (dd, *J* = 1.75, 8.50 Hz, 1H), 5.73 (dd, *J* = 1.00, 2.50 Hz, 1H), 4.42-4.28 (m, 2H), 3.94 (q, *J* = 8.38 Hz, 1H), 2.60-2.51 (m, 1H), 2.08-1.98 (m, 1H), 1.96 (s, 3H), 1.62 (s, 2H), 1.44-1.34(m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.2, 134.1, 133.6, 132.8, 132.7, 130.9, 130.3, 128.7, 128.6, 127.8, 127.8, 126.5, 126.3, 126.2, 126.0, 121.2, 120.9, 98.5, 95.3, 67.3, 51.9, 40.4, 26.7, 22.9; HRMS (ESI): *m/z* calcd for $C_{24}H_{22}O_3NS$ $[M+H]^+$ 404.1315, found 404.1313.

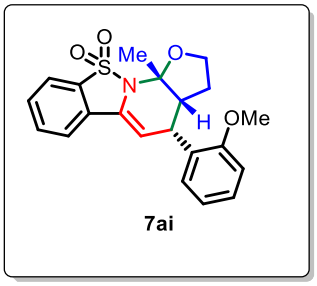


*4-([1,1'-Biphenyl]-4-yl)-11a-methyl-2,3,3a,11a-tetrahydro-4H-benzo[4,5]isothiazolo[2,3-a]furo[3,2-e]pyridine 10,10-dioxide (**7ae**)*: Following the *General Procedure*, to the mixture of 4-pentyn-1-ol (**2a**) (0.1 g, 1.18 mmol) and (*E*)-3-(2-([1,1'-biphenyl]-4-



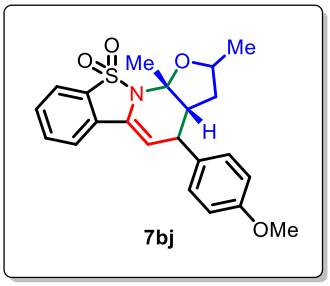
yl)vinyl)benzo[*d*]isothiazole 1,1-dioxide (**5e**) (0.450 g, 1.18 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.077 g, 0.118 mmol) was added under argon atmosphere at room temperature (35 ^oC) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 4-([1,1'-biphenyl]-4-yl)-11a-methyl-2,3,3a,11a-tetrahydro-4*H*-benzo[4,5]isothiazolo[2,3-*a*]furo[3,2-*e*]pyridine 10,10-dioxide (**7ae**) (0.331 g, 65%) as an off-white solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.82 (d, *J* = 7.63 Hz, 1H), 7.72 (d, *J* = 7.63 Hz, 1H), 7.65 - 7.55 (m, 6H), 7.49-7.42 (m, 2H), 7.39-7.33 (m, 3H), 5.64 (d, *J* = 1.75 Hz, 1H), 4.44-4.34 (m, 1H), 4.20 (dd, *J* = 6.19, 2.31 Hz, 1H), 3.98 (q, *J* = 8.46 Hz, 1H), 2.55-2.47 (m, 1H), 2.06-1.94 (m, 1H), 1.94 (s, 3H), 0.88-0.84 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 140.8, 140.7, 140.3, 134.1, 132.7, 130.8, 130.3, 129, 128.7, 128.3, 127.6, 127.2, 121.2, 120.9, 98.5, 95.3, 67.4, 51.9, 40.1, 26.6, 22.9; HRMS (ESI) *m/z* calcd for $C_{26}H_{23}O_3NS$ $[M+H]^+$ 430.1471, found 430.1470.

*4-(2-Methoxyphenyl)-11a-methyl-2,3,3a,11a-tetrahydro-4H-benzo[4,5]isothiazolo[2,3-a]furo[3,2-e]pyridine 10,10-dioxide (**7ai**)*: Following the *General Procedure*, to the mixture of 4-pentyn-1-ol (**2a**) (0.1 g, 1.18 mmol) and (*E*)-3-(2-methoxystyryl)benzo[*d*]isothiazole 1,1-dioxide (**5i**) (0.355 g, 1.18 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.077 g, 0.118 mmol) was added under argon atmosphere at room temperature (35 ^oC) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) 4-(2-methoxyphenyl)-11a-methyl-2,3,3a,11a-tetrahydro-4*H*-benzo[4,5]isothiazolo[2,3-*a*]furo[3,2-*e*]pyridine 10,10-dioxide **(7ai)** (0.354 g, 78%) as an off-white solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes) **7ai** was confirmed by ^1H NMR, ^{13}C NMR, DEPT, and 2D analysis;[20] ^1H NMR ($CDCl_3$, 400 MHz): δ 7.81 (d, *J* = 7.75 Hz, 1H), 7.70 (d, *J* = 7.75 Hz, 1H), 7.65 - 7.52 (m, 2H), 7.29 (s, 1H), 7.21 (d, *J* = 7.50 Hz, 1H), 6.97-6.88 (m, 2H), 5.57 (d, *J* = 2.25 Hz, 1H), 4.55 (dd, *J* = 6.13, 2.50 Hz, 1H), 4.37-4.30 (m, 1H), 3.95 (q, *J* = 8.59 Hz, 1H), 3.88 (s, 3H), 2.78-2.66 (m, 1H), 1.92 (s, 3H), 0.87-0.84 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 156.9, 134 132.6, 130.5, 130.3, 128.3, 128.3, 121.1, 120.9, 120.7, 110.3, 99.5, 95.3, 67.4, 55.6, 48.5, 26.9, 22.8; IR (KBr, cm^{-1}): υ 3200, 3143,

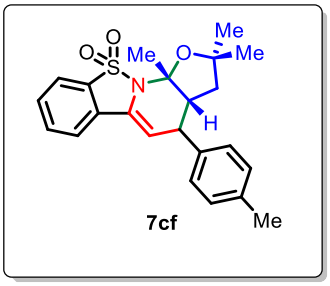


2927, 1705, 1651, 1605, 1465, 1304, 1242, 1174, 1025, 962, 896, 752, 695; HRMS (ESI) *m/z* calcd for $C_{21}H_{21}O_4NS$ $[M+H]^+$ 384.1264, found 384.1257.

*4-(4-Methoxyphenyl)-2,11a-dimethyl-2,3,3a,11a-tetrahydro-4H-benzo[4,5]isothiazolo[2,3-a]furo[3,2-e]pyridine 10,10-dioxide (**7bj**)*: Following the *General Procedure*, to the mixture of hex-5-yn-2-ol (**2b**) (0.1 g, 1.01 mmol) and (*E*)-3-(4-methoxystyryl)benzo[*d*]isothiazole 1,1-dioxide (**5j**) (0.304 g, 1.01 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.066 g, 0.101 mmol) was added under argon atmosphere at room temperature (35 ^oC) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 4-(4-methoxyphenyl)-2,11a-dimethyl-2,3,3a,11a-tetrahydro-4*H*-benzo[4,5]isothiazolo[2,3-*a*]furo[3,2-*e*]pyridine 10,10-dioxide (**7bj**) (0.285 g, 70%) with dr (1:0.3) as an off-white solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.83-7.51 (m, 6H), 7.23-7.12 (m, 3H), 6.93-6.86 (m, 3H), 5.70-5.63 (m, 0.3H), 5.56 (d, *J* = 1.63 Hz, 1H), 4.71-4.63 (m,1H), 4.08 (dd, *J* = 6.13, 2.38 Hz, 1H), 3.82 (s, 3H), 2.54-2.44 (m, 1H), 2.14-1.97 (m, 1H), 1.91-1.87 (m, 3H), 1.19(d, *J* = 6.38 Hz, 4H), 1.10-1.00(m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 158.8, 134.1, 133.8, 132.7, 132.7, 130.8, 130.2, 130.2, 129.2, 129.1, 128.9, 128.9, 128.8, 121.1, 120.9, 114.3, 114.2, 114.1, 98.9, 95.8, 74.6, 55.5, 50.9, 39.4, 33.3, 23.3, 22.6; IR (KBr, cm^{-1}): υ 3267, 3194, 3143, 3076, 2931, 1728, 1655, 1607, 1513, 1460, 1305, 1246, 1175, 1115, 1031, 957, 896, 753; HRMS (ESI) *m/z* calcd for $C_{22}H_{23}O_4NS$ $[M+H]^+$ 398.1421, found 398.1417.



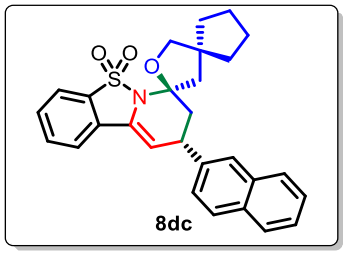
*4-(4-Methoxyphenyl)-2,2,11a-trimethyl-2,3,3a,11a-tetrahydro-4H-benzo[4,5]isothiazolo[2,3-a]furo[3,2-e]pyridine 10,10-dioxide (**7cf**)*: Following the *General Procedure*, to the mixture of 2-methylhex-5-yn-2-ol (**2c**) (0.1 g, 0.892 mmol) and (*E*)-3-(4-methylstyryl)benzo[*d*]isothiazole 1,1-dioxide (**5f**) (0.252 g, 0.892 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.058 g, 0.089 mmol) was added under argon atmosphere at room temperature (35 ^oC) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 4-(4-methoxyphenyl)-2,2,11a-trimethyl-2,3,3a,11a-tetrahydro-4*H*-benzo[4,5]isothiazolo[2,3-*a*]furo[3,2-*e*]pyridine 10,10-dioxide (**7cf**) (0.253 g, 71%) with dr. 1:0.3 as an off-white solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^1H NMR ($CDCl_3$,



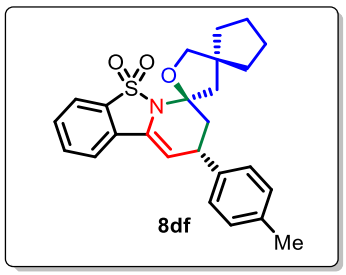
400 MHz): δ 7.83 - 7.78 (m, 1H), 7.70 - 7.66 (m, 1H), 7.64-7.51 (m, 3H), 7.20-7.12 (m 5H), 5.61 (d, *J* = 2.25 Hz, 1H), 5.70 (d, *J* = 4.63 Hz, 0.3H), 4.10 (dd, *J* = 6.63, 2.63 Hz, 1H), 2.70-2.59 (m, 1H), 2.39-2.32 (m, 4H), 2.17-210 (m, 1H), 1.94-1.90 (m, 3H), 1.25 (s, 6H), 1.19 (s, 4H), 0.92-0.79 (m, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz): δ 138.8, 136.9, 134.1, 132.8, 132.7, 130.9, 130.2, 129.5, 128.8, 127.9, 121.1, 120.9, 99.6, 95.6, 83.5, 51.7, 39.9, 39.8, 29.7, 29.4, 24.7, 21.2; HRMS (ESI) *m/z* calcd for $C_{23}H_{25}NO_3S$ $[M+H]^+$ 398.1628, found 398.1619.

10. Synthesis and characterization of spiro-*N,O*-ketals (8) from 4-pentyn-1-ols (2) and cyclic *N*-sulfonyl ketimines (5):

*9-(Naphthalen-2-yl)-8,9-dihydro-3'H,5'H-dispiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan-4',1''-cyclopentane] 5,5-dioxide (**8dc**)*: Following the *General Procedure*, to the mixture of (1-(prop-2-yn-1-yl)cyclopentyl)methanol (**2d**) (0.1 g, 0.724 mmol) and (*E*)-3-(2-(naphthalen-2-yl)vinyl)benzo[*d*]isothiazole 1,1-dioxide (**5c**) (0.230 g, 0.724 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.047 g, 0.072 mmol) was added under argon atmosphere at room temperature (35 ^{o}C) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 9-(naphthalen-2-yl)-8,9-dihydro-3'*H*,5'*H*-dispiro[benzo[4,5]isothiazolo[2,3-*a*]pyridine-7,2'-furan-4',1''-cyclopentane] 5,5-dioxide (**8dc**) (0.264 g, 80%) as an yellow semi-solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87-7.79 (m, 4H), 7.77 (s, 1H), 7.70 - 7.66 (m, 1H), 7.64-7.53 (m, 2H), 7.51-7.41 (m, 3H), 5.87 (m, 1H), 4.27-4.16 (m, 2H), 3.92 (d, *J* = 8.50, Hz, 1H), 3.45 (d, *J* = 6.38 Hz, 1H), 3.25 (d, *J* = 14.76 Hz, 1H), 2.31 (d, *J* = 12.51 Hz, 1H), 2.14 (d, *J* = 14.88 Hz, 1H), 1.80-1.67 (m, 4H), 1.57-1.50 (m, 4H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz): δ 140.9, 133.6, 132.9, 132.6, 132.4, 131.5, 130, 129.2, 128.6, 127.7, 127.6, 126.3, 126.2, 126.1, 125.8, 120.9, 104.9, 94.1, 68.8, 46.7, 44.1, 37.4, 36.8, 35. 25.9, 25.8, 24.4, 23.1; IR (KBr, cm^{-1}): υ 3065, 2924, 1699, 1632, 1536, 1455, 1455, 1301, 1238, 1170, 1020, 748; HRMS (ESI) *m/z* calcd for $C_{28}H_{27}O_3NS$ $[M+H]^+$ 458.1784, found 458.1770.

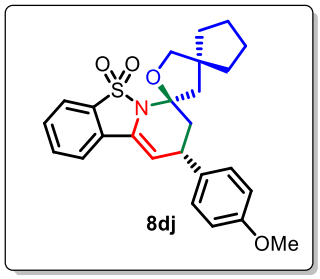


*9-(p-Tolyl)-8,9-dihydro-3'H,5'H-dispiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan-4',1''-cyclopentane] 5,5-dioxide (**8df**)*: Following the *General Procedure*, to the mixture of (1-(prop-2-yn-1-yl)cyclopentyl)methanol (**2d**) (0.1 g, 0.724 mmol) and (*E*)-3-(4-



methylstyryl)benzo[*d*]isothiazole 1,1-dioxide (**5f**) (0.194 g, 0.724 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.047 g, 0.072 mmol) was added under argon atmosphere at room temperature (35 ^oC) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 9-(*p*-tolyl)-8,9-dihydro-3'*H*,5'*H*-dispiro[benzo[4,5]isothiazolo[2,3-*a*]pyridine-7,2'-furan-4',1''-cyclopentane] 5,5-dioxide (**8df**) (0.240 g, 78%) as a yellow semi-solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.77 (d, *J* = 7.63, Hz, 1H), 7.67-7.49 (m, 3H), 7.22-7.13 (m, 4H), 5.76 (m, 1H), 4.16 (d, *J* = 8.50, Hz, 1H), 4.00 (ddd, *J* = 12.35, 5.66, 2.25 Hz, 1H), 3.87 (d, *J* = 8.50, Hz, 1H), 3.21 (d, *J* = 14.76, Hz, 1H), 2.35 (s, 3H), 2.31-2.23 (m, 1H) 2.20-2.07 (m, 2H), 1.69-1.60 (m, 2H), 1.54-1.42 (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 140.6, 136.8, 133, 132.5, 131.4, 130, 129.6, 129.4, 127.7, 121, 120.9, 105.5, 94.3, 78.3, 46.9, 44.2, 37, 36.8, 35.1, 26.1, 24.5, 23.2, 21.2; IR (KBr, cm^{-1}): υ 3065, 2924, 1699, 1632, 1536, 1455, 1455, 1301, 1238, 1170, 1020, 748; HRMS (ESI) *m/z* calcd for $C_{25}H_{27}O_3NS$ $[M+H]^+$ 422.1784, found 422.1778.

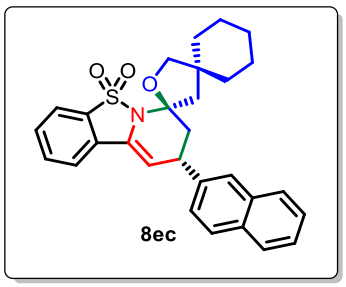
*9-(4-Methoxyphenyl)-8,9-dihydro-3'H,5'H-dispiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan-4',1''-cyclopentane] 5,5-dioxide (**8dj**)*: Following the *General Procedure*, to the mixture



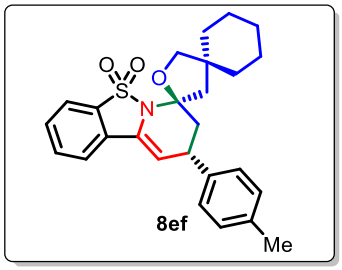
of (1-(prop-2-yn-1-yl)cyclopentyl)methanol (**2d**) (0.1 g, 0.724 mmol) and (*E*)-3-(4-methoxystyryl)benzo[*d*]isothiazole 1,1-dioxide (**5j**) (0.215 g, 0.724 mmol) in anhydrous CH_2Cl_2 (2 mL) $Bi(OTf)_3$ (0.047 g, 0.072 mmol) was added under argon atmosphere at room temperature (35 ^oC) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 9-(4-methoxyphenyl)-8,9-dihydro-3'*H*,5'*H*-dispiro[benzo[4,5]isothiazolo[2,3-*a*]pyridine-7,2'-furan-4',1''-cyclopentane] 5,5-dioxide (**8dj**) (0.260 g, 82%) with dr 1:3 as an yellow solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.77 (td, *J* = 1.0, 7.7 Hz, 2H), 7.65-7.45 (m, 5H), 7.24-7.18 (m, 3H), 6.92-6.83 (m, 3H), 5.80-5.73 (m, 2H), 4.26-4.13 (m, 2H), 3.99 (ddd, *J* = 2.5, 5.7, 12.3 Hz, 2H), 3.87 (d, *J* = 8.5 Hz, 1H), 3.83-3.80 (m, 5H), 3.80-3.73 (m, 2H), 3.49 (d, *J* = 14.4 Hz, 1H), 3.21 (d, *J* = 14.8 Hz, 0.5H), 2.37-2.23 (m, 2H), 2.17-2.07 (m, 3H), 1.90-1.61 (m, 11H), 1.59-1.42 (m, 7H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 158.6, 135.5, 135.5, 132.8, 132.8, 132.3, 131.2, 129.8, 129.2, 129.2, 128.6, 120.8, 120.8, 120.7,

114.1, 105.5, 105.4, 94.2, 94.1, 78.8, 55.3, 50.8, 46.8, 46.1, 45.9, 44.0, 39.5, 36.6, 36.4, 36.2, 34.9, 34.8, 29.5, 25.8, 25.8, 24.8, 24.3, 24.2, 23.0; IR (KBr, cm^{-1}): υ 3068, 2935, 1725, 1653, 1603, 1511, 1456, 1456, 1303, 1245, 1171, 1029, 832, 746; HRMS (ESI) *m/z* calcd for $C_{25}H_{27}O_4NS$ $[M+H]^+$ 438.1734, found 438.1719.

*9-(Naphthalen-2-yl)-8,9-dihydro-3'H,5'H-dispiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan-4',1''-cyclohexane] 5,5-dioxide (**8ec**)*: Following the *General Procedure*, to the mixture of (1-(prop-2-yn-1-yl)cyclohexyl)methanol (**2e**) (0.1 g, 0.657 mmol) and (*E*)-3-(2-(naphthalen-2-yl)vinyl)benzo[*d*]isothiazole 1,1-dioxide (**5c**) (0.207 g, 0.657 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.042 g, 0.065 mmol) was added under argon atmosphere at room temperature (35 °C) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 9-(naphthalen-2-yl)-8,9-dihydro-3'*H*,5'*H*-dispiro[benzo[4,5]isothiazolo[2,3-*a*]pyridine-7,2'-furan-4',1''-cyclopentane] 5,5-dioxide (**8ec**) (0.242 g, 78%) as an yellow solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87-7.79 (m, 4H), 7.76 (s, 1H), 7.71 - 7.65 (m, 1H), 7.64-7.58 (m, 1H), 7.58-7.51 (m, 1H), 7.50-7.46 (m, 2H), 7.42 (dd, *J* = 8.50, 1.63 Hz, 1H), 5.87 (s, 1H), 4.29-4.18 (m, 2H), 3.80 (d, *J* = 8.13, Hz, 1H), 3.52 (d, *J* = 14.51 Hz, 1H), 2.46-2.37 (m, 1H), 2.31-2.21 (m, 1H), 2.13 (d, *J* = 14.51 Hz, 1H), 1.76-1.60 (m, 8H), 1.57-1.48 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 141.1, 133.7, 133.1, 132.7, 132.5, 131.7, 130.1, 129.4, 128.7, 127.8, 127.7, 126.4, 126.3, 126.2, 125.9, 121.1, 121, 105.2, 94.3, 79.1, 51, 46.3, 45.9, 39.7, 37.4, 35, 25, 24.4; IR (KBr, cm^{-1}): υ 3066, 2942, 2867, 1697, 1665, 1599, 1464, 1305, 1243, 1172, 1005, 815, 746 ; HRMS (ESI) *m/z* calcd for $C_{29}H_{29}O_3NS$ $[M+H]^+$ 472.1941, found 472.1928.

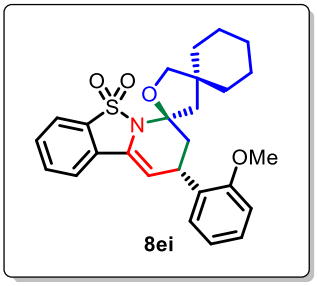


*9-(p-Tolyl)-8,9-dihydro-3'H,5'H-dispiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan-4',1''-cyclohexane] 5,5-dioxide (**8ef**)*: Following the *General Procedure*, to the mixture of (1-(prop-2-yn-1-yl)cyclohexyl)methanol (**2e**) (0.1 g, 0.657 mmol) and (*E*)-3-(4-methylstyryl)benzo[*d*]isothiazole 1,1-dioxide (**5f**) (0.186 g, 0.657 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.042 g, 0.065 mmol) was added under argon atmosphere at room temperature (35 °C) and reaction mixture was stirred for 8



h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 9-(*p*-tolyl)-8,9-dihydro-3'*H*,5'*H*-dispiro[benzo[4,5]isothiazolo[2,3-*a*]pyridine-7,2'-furan-4',1''-cyclohexane] 5,5-dioxide (**8ef**) (0.220 g, 79%) as a yellow semi-solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77 (d, *J* = 7.6 Hz, 1 H), 7.65-7.50 (m, 3 H), 7.22-7.14 (m, 4 H), 5.76 (s, 1 H), 4.16 (d, *J* = 8.5 Hz, 1 H), 4.00 (ddd, *J* = 2.1, 5.6, 12.3 Hz, 1 H), 3.87 (d, *J* = 8.4 Hz, 1 H), 3.21 (d, *J* = 14.8 Hz, 1 H), 2.35 (s, 3 H), 2.32-2.24 (m, 1 H), 1.79-1.59 (m, 3 H), 1.55-140 (m.,7 H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 140.7, 136.9, 133.0, 132.5, 131.4, 130.0, 129.7, 129.4, 127.8, 121.0, 121.0, 105.5, 94.3, 77.5, 76.9, 46.9, 44.2, 37.0, 36.9, 35.1, 26.1, 24.5, 23.3, 21.2; HRMS (ESI) *m/z* calcd for $C_{26}H_{29}NO_3S$ $[M+H]^+$ 436.1941, found 436.1934.

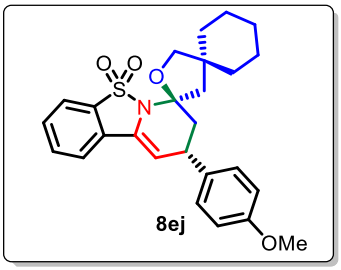
*9-(2-Methoxyphenyl)-8,9-dihydro-3'H,5'H-dispiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan-4',1''-cyclohexane] 5,5-dioxide (**8ei**)*: Following the *General Procedure*, to the mixture



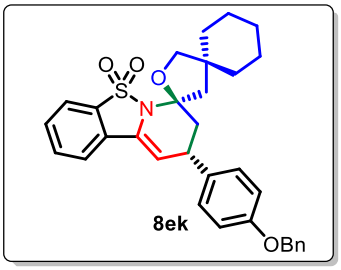
8ei

of (1-(prop-2-yn-1-yl)cyclohexyl)methanol (**2e**) (0.1 g, 0.657 mmol) and (*E*)-3-(2-methoxystyryl)benzo[*d*]isothiazole 1,1-dioxide (**5i**) (0.194 g, 0.657 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.042 g, 0.065 mmol) was added under argon atmosphere at room temperature (35 ^{o}C) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromaography (SiO_2, 30% EtOAc/hexanes) afforded 9-(2-methoxyphenyl)-8,9-dihydro-3'*H*,5'*H*-dispiro[benzo[4,5]isothiazolo[2,3-*a*]pyridine-7,2'-furan-4',1''-cyclohexane] 5,5-dioxide (**8ei**) (0.220 g, 75%) as a yellow solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, *J* = 7.75 Hz, 1H), 7.62-7.57 (m, 1H), 7.57-7.50 (m, 1H), 7.44 (d, *J* = 7.75 Hz, 1H), 7.22-7.16 (m, 1H), 7.11 (dd, *J* = 1.38, 7.63 Hz, 1H), 6.92-6.83 (m, 2H), 4.71 (s, 1H), 4.33 (d, *J* = 8.63 Hz, 1H), 4.03 (d, *J* = 9.01 Hz, 1H), 3.85 (s, 3H), 3.73 (s, 1H), 3.65-3.54 (m, 1H), 2.53 (dd, *J* = 4.75, 17.13 Hz, 1H), 2.39 (dd, *J* = 11.76, 16.88 Hz, 1H), 2.23-2.13 (m, 2H), 1.71 (dd, *J* = 3.75, 12.88 Hz, 1H), 1.61 (d, *J* = 11.01 Hz, 2H), 1.46 (d, *J* = 12.13 Hz, 1H), 1.36 (d, *J* = 13.01 Hz, 1H), 1.19 (d, *J* = 12.63 Hz, 1H), 1.01-0.82 (m, 3H), 0.73-0.59 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 159.7, 157.2, 143.6, 135.8, 132.6, 131.3, 129.6, 127.9, 126.4, 125.8, 121.5, 120.7, 112.6, 110.7, 79.3, 65.3, 55.5, 49.1, 47.4, 36.8, 35.6, 31.9, 29.8, 24.9, 23.7, 23.2; IR (KBr, cm^{-1}): υ 3011, 2944, 2355, 1673, 1600, 1454, 1345, 1289, 1241, 1163, 1036, 938, 750; HRMS (ESI) *m/z* calcd for $C_{26}H_{29}O_4NS$ $[M+H]^+$ 452.1890, found 452.1874.

*9-(4-Methoxyphenyl)-8,9-dihydro-3'H,5'H-dispiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan-4',1''-cyclohexane] 5,5-dioxide (**8ej**)*: Following the *General Procedure*, to the mixture of (1-(prop-2-yn-1-yl)cyclohexyl)methanol (**2e**) (0.1 g, 0.657 mmol) and (*E*)-3-(4-methoxystyryl)benzo[*d*]isothiazole 1,1-dioxide (**5j**) (0.194 g, 0.657 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.042 g, 0.065 mmol) was added under argon atmosphere at room temperature (35 ^oC) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 9-(4-methoxyphenyl)-8,9-dihydro-3'*H*,5'*H*-dispiro[benzo[4,5]isothiazolo[2,3-*a*]pyridine-7,2'-furan-4',1''-cyclohexane] 5,5-dioxide (**8ej**) (0.246 g, 82%) with dr 1:3 as an yellow solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.77 (d, *J* = 7.5 Hz, 2 H), 7.67 - 7.48 (m, 5 H), 7.24 - 7.14 (m, 4 H), 6.93 - 6.86 (m, 3 H), 5.75 (br. s., 1.5 H), 4.22 (d, *J* = 8.1 Hz, 1 H), 4.16 (d, *J* = 8.4 Hz, 1 H), 4.03-3.94 (m, 2 H), 3.87 (d, *J* = 8.5 Hz, 1 H), 3.81 (s, 5 H), 3.79 - 3.74 (m, 1 H), 3.52 - 3.42 (m, 1 H), 3.21 (d, *J* = 14.9 Hz, 1 H), 2.35 - 2.23 (m, 2 H), 2.20 - 2.07 (m, 4 H), 1.87 - 1.57 (m, 9 H), 1.57 - 1.42 (m, 10 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 158.6, 135.5, 135.5, 132.8, 132.8, 132.3, 131.2, 131.2, 129.9, 129.2, 129.2, 128.6, 120.8, 120.8, 120.8, 114.2, 105.5, 105.4, 94.2, 94.1, 78.9, 68.8, 55.3, 50.8, 46.8, 46.1, 45.9, 44.0, 40.5, 39.5, 36.7, 36.4, 36.2, 34.9, 34.8, 26.6, 25.9, 25.8, 24.8, 24.3, 24.2, 23.1; IR (KBr, cm^{-1}): υ 3019, 2938, 1706, 1664, 1607, 1514, 1449, 1305, 1242, 1172, 1023, 833, 743; HRMS (ESI) *m/z* calcd for $C_{26}H_{29}O_4NS$ $[M+H]^+$ 452.1890, found 452.1876.

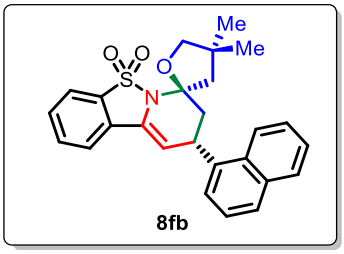


*9-(4-(Benzyloxy)phenyl)-8,9-dihydro-3'H,5'H-dispiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan-4',1''-cyclohexane] 5,5-dioxide (**8ek**)*: Following the *General Procedure*, to the mixture of (1-(prop-2-yn-1-yl)cyclohexyl)methanol (**2e**) (0.1 g, 0.657 mmol) and (*E*)-3-(4-(benzyloxy)styryl)benzo[*d*]isothiazole 1,1-dioxide (**5k**) (0.244 g, 0.657 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.042 g, 0.065 mmol) was added under argon atmosphere at room temperature (35 ^oC) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 9-(4-(benzyloxy)phenyl)-8,9-dihydro-3'*H*,5'*H*-dispiro[benzo[4,5]isothiazolo[2,3-*a*]pyridine-7,2'-furan-4',1''-cyclohexane] 5,5-dioxide (**8ek**) (0.208 g, 60%) as an off-white solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, *J* = 7.75, Hz, 1H), 7.65-7.50 (m,

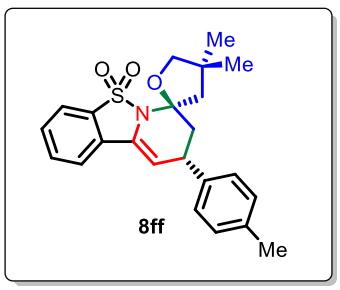


3H), 7.46-7.33 (m, 5H), 7.21(d, *J* = 8.50, Hz, 2H), 6.96 (d, *J* = 8.63, Hz, 2H), 5.76 (s, 2H), 4.21 (d, *J* = 8.38, Hz, 1H), 3.99 (d, *J* = 12.88, Hz, 1H), 3.76 (d, *J* = 8.25, Hz, 1H), 3.48 (d, *J* = 14.38, Hz, 1H), 2.37-2.31 (m, 1H), 2.16-2.08 (m, 2H), 1.70-1.64 (m, 4H), 1.49 (d, *J* = 6.38, Hz, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz): δ 158, 136.0, 133.0, 130.1, 128.9, 128.8, 128.1, 127.6, 121.1, 120.9, 115.3, 105.7, 94.4, 79.1, 70.3, 51.0, 46.1, 39.7, 36.4, 35, 25, 24.4.

4',4'-Dimethyl-9-(naphthalen-1-yl)-4',5',8,9-tetrahydro-3'H-spiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan] 5,5-dioxidedioxide (***8fb***): Following the *General Procedure*, to the mixture of 2,2-dimethylpent-4-yn-1-ol (**2f**) (0.1 g, 0.891 mmol) and (*E*)-3-(2-(naphthalen-1-yl)vinyl)benzo[*d*]isothiazole 1,1-dioxide (**5b**) (0.284 g, 0.891 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.038 g, 0.89 mmol) was added under argon atmosphere at (35 ^{o}C) and the reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 4',4'-dimethyl-9-(naphthalen-1-yl)-4',5',8,9-tetrahydro-3'*H*-spiro[benzo[4,5]isothiazolo[2,3-*a*]pyridine-7,2'-furan] 5,5-dioxidedioxide (**8fb**) (0.284 g, 74%) as a yellow semi-solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes) 8fb was confirmed by ^{1}H NMR, ^{13}C NMR, DEPT, HRMS and 2D NMR analysis;[20] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.22 (d, *J* = 8.38 Hz, 1 H), 7.95-7.89 (m, 1 H), 7.83 - 7.76 (m, 2 H), 7.70-7.63 (m, 1 H), 7.62-7.50 (m, 4 H), 7.48-7.43 (m, 2 H), 5.96 (s, 1 H), 4.94 (s, 1 H), 4.31 (d, *J* = 8.25, Hz, 1 H), 3.77 (d, *J* = 8.13, Hz, 1 H), 3.37 (d, *J* = 14.76 Hz, 1 H), 2.57 (dd, *J* = 12.69, 4.57 Hz, 1 H), 2.36-2.20 (m, 1 H), 2.01 (d, *J* = 14.63 Hz, 1 H), 1.31 (s, 3 H), 1.24 (s, 3 H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 139.4, 134.2, 133.1, 132.5, 131.5, 131.1, 130.1, 129.4, 129.3, 129, 127.7, 126.6, 125.9, 125.9, 123, 121.1, 121, 105.5, 95, 80.4, 61.8, 47.8, 45.3, 40.1, 28.9, 25; HRMS (ESI) *m/z* calcd for $C_{26}H_{25}NO_3S$ $[M+H]^+$ 432.1628, found 432.1628.

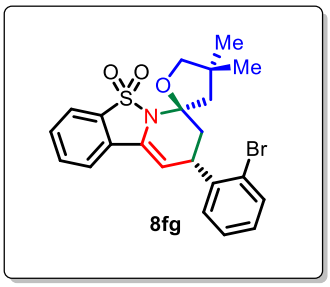


4',4'-Dimethyl-9-(p-tolyl)-4',5',8,9-tetrahydro-3'H-spiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan] 5,5-dioxide (***8ff***): Following the *General Procedure*, to the mixture of 2,2-dimethylpent-4-yn-1-ol (**2f**) (0.1 g, 0.891 mmol) and (*E*)-3-(4-methylstyryl)benzo[*d*]isothiazole 1,1-dioxide (**5f**) (0.252 g, 0.891 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.058 g, 0.089 mmol) was added under argon atmosphere at room temperature (35 ^{o}C) and the reaction mixture was stirred for 8 h



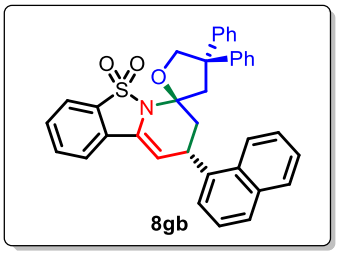
at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 4',4'-dimethyl-9-(*p*-tolyl)-4',5',8,9-tetrahydro-3'*H*-spiro[benzo[4,5]isothiazolo[2,3-*a*]pyridine-7,2'-furan] 5,5-dioxide (**8ff**) (0.234 g, 66%) as an off-white solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80-7.76 (m, 1H), 7.65-7.56 (m, 2H), 7.55-7.50 (m, 1H),7.22-7.14 (m, 4H), 5.80-5.74 (m, 1H), 4.22 (d, *J* = 8.25 Hz, 1H), 4.02 (ddd, *J* = 12.48, 5.72, 2.44 Hz, 1H), 3.67 (d, *J* = 8.25 Hz, 1H), 3.32 (d, *J* = 14.76 Hz, 1H), 2.40-2.29 (m, 4H), 2.22-2.12 (m, 1H), 2.07-1.95(m, 1H), 1.28 (s, 3H), 1.22 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 140.6, 136.9, 133, 132.5, 131.4, 130, 129.6, 127.7, 121, 120.9, 105.5, 94.9, 80.4, 47.8, 46.6, 40.1, 37, 29, 25, 21.2; HRMS (ESI) *m/z* calcd for $C_{23}H_{25}NO_3S$ $[M+H]^+$ 398.1628, found 398.1619.

*9-(2-Bromophenyl)-4',4'-dimethyl-4',5',8,9-tetrahydro-3'H-spiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan] 5,5-dioxide (**8fg**)*: Following the *General Procedure*, to the mixture of



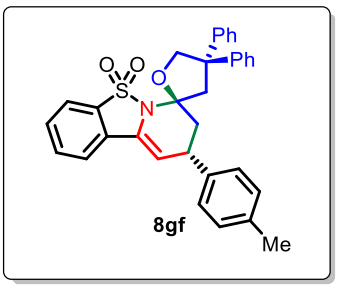
2,2-dimethylpent-4-yn-1-ol (**2f**) (0.1 g, 0.891 mmol) and (*E*)-3-(2-bromostyryl)benzo[*d*]isothiazole 1,1-dioxide (**5g**) (0.310 g, 0.891 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.058 g, 0.089 mmol) was added under argon atmosphere at room temperature (35 ^{o}C) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 9-(2-bromophenyl)-4',4'-dimethyl-4',5',8,9-tetrahydro-3'*H*-spiro[benzo[4,5]isothiazolo[2,3-*a*]pyridine-7,2'-furan] 5,5-dioxide (**8fg**) (0.340 g, 83%) as an off-white solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes, **8fg** was confirmed by ^{1}H NMR, ^{13}C NMR, DEPT, and 2D NMR analysis;[20] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79 (d, *J* = 7.75 Hz, 1H), 7.71-7.66 (m, 1H), 7.64-7.51 (m, 3H), 7.31 (d, *J* = 7.75 Hz, 2H), 7.17-7.10 (m, 1H), 5.78 (s, 1H), 4.58 (ddd, *J* = 12.29, 5.41, 2.31 Hz, 1H), 4.20 (d, *J* = 8.25 , Hz, 1H), 3.70 (d, *J* = 8.13 , Hz, 1H), 3.30 (d, *J* = 14.63, Hz, 1H), 2.54 (dd, *J* = 12.95, 4.57 Hz, 1H), 2.04-1.94 (m, 2H), 1.25 (s, 3H), 1.28 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 142.6, 133.2, 133.1, 132.5, 132.3, 130.2, 129.3, 128.9, 128.6, 128.2, 124.5, 121.1, 120.9, 104.1, 94.7, 80.4, 47.8, 44.2, 40.1, 36.8, 28.8, 25.1; HRMS (ESI) *m/z* calcd for $C_{22}H_{22}BrNO_3S$ $[M+H]^+$ 460.0577, found 460.0571.

*9-(Naphthalen-1-yl)-4',4'-diphenyl-4',5',8,9-tetrahydro-3'H-spiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan] 5,5-dioxide (**8gb**)*: Following the *General Procedure*, to the mixture of 2,2-diphenylpent-4-yn-1-ol (**2g**) (0.1 g, 0.423 mmol) and (*E*)-3-(2-(naphthalen-1-



yl)vinyl)benzo[*d*]isothiazole 1,1-dioxide (**5b**) (0.135 g, 0.423 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.027 g, 0.042 mmol) was added under argon atmosphere at room temperature (35 ^oC) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 9-(naphthalen-1-yl)-4',4'-diphenyl-4',5',8,9-tetrahydro-3'*H*-spiro[benzo[4,5]isothiazolo[2,3-*a*]pyridine-7,2'-furan] 5,5-dioxide (**8gb**) (0.203 g, 86%) as an off-white crystal, **8gb** was confirmed by ^1H NMR, ^{13}C NMR, DEPT, and XRD analysis;[20] TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.91-7.80 (m, 3H), 7.73 (t, *J* = 7.00 Hz, 2H), 7.64 (td, *J* = 7.60, 1.19 Hz, 1H), 7.59-7.43 (m, 5H), 7.42-7.28 (m 8H), 7.24-7.20 (m 1H), 7.11-7.06 (m, 1H), 6.01-5.94 (m, 1H), 5.11-5.03 (m, 1H), 4.83-4.71(m, 2H), 4.44 (d, *J* = 14.13 Hz, 1H), 2.86 (dd, *J* = 14.20, 1.31 Hz, 1H), 2.09-1.96 (m, 1H), 1.88(d, *J* = 12.26 Hz, 1H): $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 145.9, 143.9, 139.5, 133.9, 133.2, 132.3, 131.3, 130.2, 129.4, 129, 128.8, 128.7, 127.6, 128.5, 127.6, 127.4, 127.3, 126.8, 126.7, 126.4, 125.9, 123.1, 121.1, 121.1, 105.6, 94.9, 76.2, 56.1, 46.1, 43.8; IR (KBr, cm^{-1}): υ 3067, 3031, 2926, 1595, 1539, 1492, 1451, 1306, 1249, 1174, 1039, 813, 751, 696; HRMS (ESI) *m/z* calcd for $C_{36}H_{29}O_3NS$ $[M+H]^+$ 556.1941, found 556.1931.

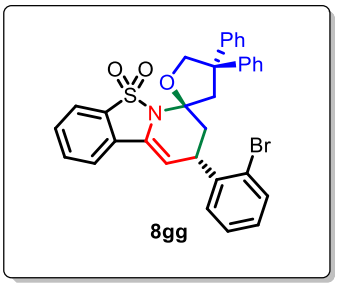
*4',4'-Diphenyl-9-(p-tolyl)-4',5',8,9-tetrahydro-3'H-spiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan] 5,5-dioxide (**8gf**)*: Following the *General Procedure*, to the mixture of



2,2-diphenylpent-4-yn-1-ol (**2g**) (0.1 g, 0.423 mmol) and (*E*)-3-(4-methylstyryl)benzo[*d*]isothiazole 1,1-dioxide (**5f**) (0.119 g, 0.423 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.027 g, 0.042 mmol) was added under argon atmosphere at room temperature (35 ^oC) and the reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 4',4'-diphenyl-9-(*p*-tolyl)-4',5',8,9-tetrahydro-3'*H*-spiro[benzo[4,5]isothiazolo[2,3-*a*]pyridine-7,2'-furan] 5,5-dioxide (**8gf**) (0.152 g, 69%) as an off-white solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, *J* = 7.88 Hz, 1H), 7.67-7.58 (m, 2H), 7.56-7.51 (m, 1H), 7.42 (d, *J* = 7.75 Hz, 2H), 7.33-7.29 (m, 5H), 7.25-7.16 (m, 3H), 7.10 (d, *J* = 8.00 Hz, 2H), 7.03 (m, *J* = 7.88 Hz, 2H) 5.79 (s, 1H), 4.97 (d, *J* = 9.38 Hz, 1H), 4.67 (d, *J* = 9.26 Hz, 1H), 4.42 (d, *J* = 14.01 Hz, 1H), 3.95-3.83 (m, 1H), 2.85 (d, *J* = 14.13 Hz, 1H), 2.31 (s, 3H), 1.87-1.76 (m, 1H), 1.74-1.65 (m, 1H): $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 146.1, 144.1, 140.5, 136.6,

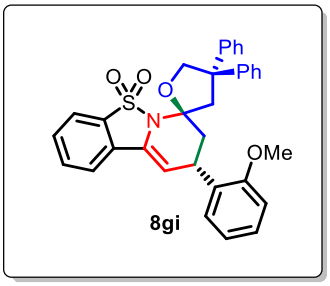
133.1, 130.1, 129.5, 129.4, 128.7, 128.6, 127.5, 127.5, 127.3, 126.8, 126.7, 121.1, 120.9, 105.7, 94.8, 76.3, 56, 46.1, 44.9. 36.2, 21.1; IR (KBr, cm^{-1}): υ 3062, 3014, 2927, 1659, 1596, 1491, 1449, 1304, 1174, 1037, 751, 695; HRMS (ESI) *m/z* calcd for $C_{33}H_{29}O_3NS$ $[M+H]^+$ 520.1941, found 520.1927.

*9-(2-Bromophenyl)-4',4'-diphenyl-4',5',8,9-tetrahydro-3'H-spiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan] 5,5-dioxide (**8gg**)*: Following the *General Procedure*, to the mixture of



2,2-diphenylpent-4-yn-1-ol (**2g**) (0.1 g, 0.423 mmol) and (*E*)-3-(2-bromostyryl)benzo[*d*]isothiazole 1,1-dioxide (**5g**) (0.147 g, 0.423 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.027 g, 0.042 mmol) was added under argon atmosphere at room temperature (35 ^oC) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 9-(2-bromophenyl)-4',4'-diphenyl-4',5',8,9-tetrahydro-3'*H*-spiro[benzo[4,5]isothiazolo[2,3-*a*]pyridine-7,2'-furan] 5,5-dioxide (**8gg**) (0.205 g, 83%) as an off-white solid. TLC: R_f = 0. (SiO_2, 15% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.79 (d, *J* = 7.63 Hz, 1H), 7.71-7.67 (m, 1H), 7.66-7.60 (m, 1H), 7.56 (d, *J* = 7.75 Hz, 1H), 7.49 (d, *J* = 7.75 Hz, 1H), 7.42 (d, *J* = 7.38 Hz, 2H), 7.35-7.29 (m, 6H), 7.25-7.20 (m, 4H), 7.09-7.04 (m, 1H), 5.77 (s, 1H), 4.99 (d, *J* = 9.51 Hz, 1H), 4.67 (d, *J* = 9.26 Hz, 1H), 4.52-4.40 (m, 2H), 2.82 (d, *J* = 14.01 Hz, 1H), 2.00-1.90 (m, 1H), 1.65(t, *J* = 12.44 Hz, 1H): $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ146.2, 144.2, 142.6, 133.2, 133.1, 132.4, 130.3, 129.2, 129, 128.9, 128.7, 128.5, 128.5, 128.1, 128, 127.6, 127.4, 126.8, 126.6, 124.5, 121.2, 121, 104.5, 94.9, 76.5, 56.1, 46.1, 43, 36.4; IR (KBr, cm^{-1}): υ 3745, 3073, 3040, 2997, 2924, 2336, 1699, 1656, 1590, 1468, 1306, 1245, 1174, 1024, 868, 755, 697; HRMS (ESI) *m/z* calcd for $C_{32}H_{26}BrNO_3S$ $[M+H]^+$ 584.0890 found, 584.0884.

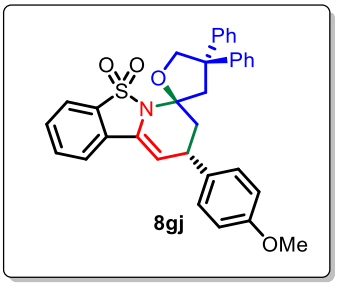
*9-(2-Methoxyphenyl)-4',4'-diphenyl-4',5',8,9-tetrahydro-3'H-spiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan] 5,5-dioxide (**8gi**)*: Following the *General Procedure*, to the mixture of



2,2-diphenylpent-4-yn-1-ol (**2g**) (0.1 g, 0.423 mmol) and (*E*)-3-(2-methoxystyryl)benzo[*d*]isothiazole 1,1-dioxide (**5i**) (0.126 g, 0.423 mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.027 g, 0.042 mmol) was added under argon atmosphere at room temperature (35 ^oC) and reaction mixture was stirred for 8 h at rt.

Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 9-(2-methoxyphenyl)-4',4'-diphenyl-4',5',8,9-tetrahydro-3'*H*-spiro[benzo[4,5] isothiazolo[2,3-*a*]pyridine-7,2'-furan] 5,5-dioxide (**8gi**) (0.181 g, 80%) as an off-white solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, *J* = 7.50 Hz, 1H), 7.71-7.66 (m, 1H), 7.60 (td, *J* = 7.25, 1.13 Hz, 1H), 7.56- 7.5 (m, 1H), 7.44-7.37 (m, 2H), 7.31-7.27 (m, 5H), 7.23-7.16 (m, 4H), 7.12 (dd, *J* = 7.63, 1.75 Hz, 1H), 6.88 (td, *J* = 7.50, 1.13 Hz, 1H), 6.81 (dd, *J* = 8.25, 0.88 Hz, 1H), 5.80 (dd, *J* = 2.25, 1.25 Hz, 1H), 4.97 (dd, *J* = 8.00, 1.25 Hz, 1H), 4.68 (d, *J* = 9.26 Hz, 1H), 4.43-4.32 (m, 2H), 3.76 (s, 3H), 2.84 (dd, *J* = 14.13, 1.38 Hz, 1H), 1.86 (qd, *J* = 12.88, 5.75, 1.38 Hz, 1H), 1.72 (t, *J* = 11.66 Hz, 1H): ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 157.1, 146.3, 133.1, 132.3, 131.9, 131.6, 129.9, 129.6, 128.7, 128.5, 128, 127.9, 127.6, 127.4, 126.8, 126.4, 121.1, 120.9, 120.8, 110.5, 105.7, 95.1, 76.4, 56.1, 55.4, 46.2, 42.6, 30.1; IR (KBr, cm^{-1}): υ 3062, 3008, 2886, 1702, 1665, 1598, 1491, 1443, 1378, 1292, 1221, 1044, 747, 696.

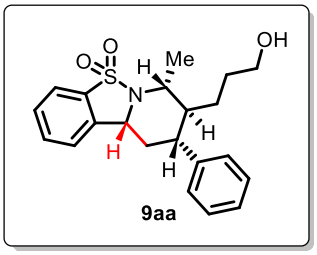
*9-(4-Methoxyphenyl)-4',4'-diphenyl-4',5',8,9-tetrahydro-3'H-spiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan] 5,5-dioxide (**8gj**)*: Following the *General Procedure*, to the mixture of



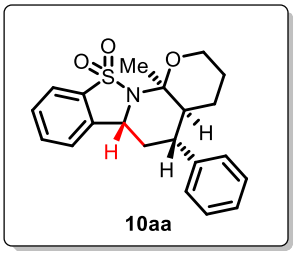
2,2-diphenylpent-4-yn-1-ol (**2g**) (0.1 g, 0.423 mmol) and (*E*)-3-(4-methoxystyryl)benzo[*d*]isothiazole 1,1-dioxide (**5j**) (0.126 g, 0.423mmol) in anhydrous CH_2Cl_2 (2 mL), $Bi(OTf)_3$ (0.027 g, 0.042 mmol) was added under argon atmosphere at room temperature (35 ^{o}C) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 9-(4-methoxyphenyl)-4',4'-diphenyl-4',5',8,9-tetrahydro-3'*H*-spiro[benzo[4,5]isothiazolo[2,3-*a*]pyridine-7,2'-furan] 5,5-dioxide (**8gj**) (0.189 g, 83%) as an off-white solid. TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83-7.76 (m, 1H), 7.69-7.49 (m, 3H), 7.47-7.38 (m, 2H), 7.34-7.27 (m, 6H), 7.25-7.15 (m, 2H), 7.08-7.01 (m, 2H), 6.85-6.80 (m, 2H), 5.78 (dd, *J* = 2.38, 1.50 Hz, 1H), 5.01-4.94 (m, 1H), 4.68 (d, *J* = 9.26 Hz, 1H), 4.42 (d, *J* = 14.13 Hz, 1H), 3.89 (ddd, *J* = 12.10, 5.63, 2.38 Hz, 1H), 3.81-3.73 (m, 3H), 2.85 (dd, *J* = 14.07, 1.3 Hz, 1H), 1.81 (t, *J* = 12.57 Hz, H), 1.64-1.72 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 158.6, 146.1, 144.1, 135.5, 133.1, 132.3, 131.5, 130.1, 129.4, 128.7, 128.6, 128.6, 127.5, 127.3, 126.8, 126.7, 121.1, 120.9, 114.3, 105.8, 94.8, 76.3, 56, 55.4, 46.1, 45, 35.8; IR (KBr, cm^{-1}): υ 3064, 3011, 2886, 1745, 1703, 1664, 1604, 1508, 1459, 1305, 1243, 1170, 1028, 831, 746; HRMS (ESI) *m/z* calcd for $C_{33}H_{29}O4NS$ $[M+H]^+$ 536.1890, found 536.1882.

11. Synthetic utility:

*8-(3-Hydroxypropyl)-7-methyl-9-phenyl-8,9,10,10a-tetrahydro-7H-benzo[4,5]isothiazolo[2,3-a]pyridine 5,5-dioxide (**9aa**)*: To a solution of 12a-methyl-5-phenyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo [4,5]isothiazolo[2,3-*a*]pyrano[3,2-*e*] pyridine 11,11-dioxide **(6aa)** (0.1 g, 0.27 mmol), in anhydrous CH_2Cl_2 (2 mL) was added Et_3SiH (0.062 g, 0.54 mmol) and $BF_3.Et_2O$ (0.042 g, 0.54 mmol) dropwise under argon atmosphere at room temperature (35 ^oC) and the reaction mixture was stirred for 2 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 8-(3-hydroxypropyl)-7-methyl-9-phenyl-8,9,10,10a-tetrahydro-7*H*-benzo[4,5]isothiazolo[2,3-a]pyridine 5,5-dioxide (**9aa**) (0.088 g, 88%) as an off-white solid. The **9aa** was confirmed by ^1H NMR, ^{13}C NMR, DEPT, and 2D NMR analysis;[20] TLC: R_f = 0.80 (SiO_2, 15% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.58-7.49 (m, 2H), 7.35-7.32 (m, 2H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.24-7.21 (m, 2H), 4.30 (dd, *J* = 2.4, 11.9 Hz, 1H), 3.52-3.33 (m, 3H), 2.78 (dt, *J* = 3.5, 11.8 Hz, 1H), 2.44 (td, *J* = 3.2, 12.9 Hz, 1H), 1.93-1.86 (m, 1H), 1.80 (d, *J* = 6.4 Hz, 3H), 1.54-1.46 (m, 2H), 1.38-1.32 (m, 1H), 0.90-0.84 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 143.5, 137.4, 136.2, 132.8, 129.3, 129.0, 127.7, 127.2, 122.6, 121.3, 63.0, 60.7, 56.5, 47.0, 46.3, 38.4, 28.2, 24.3, 16.3.



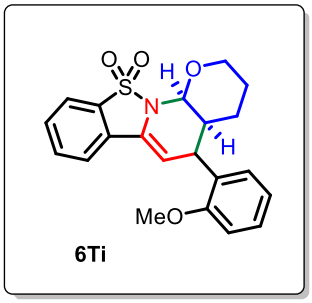
*12a-Methyl-5-phenyl-3,4,4a,6,6a,12a-hexahydro-2H,5H-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (**10aa**)*: Synthesis of **10**: The 10 mL round bottom flask charged with 12a-methyl-5-phenyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo [4,5] isothiazolo [2,3-*a*]pyrano[3,2-*e*]pyridine 11,11-dioxide (**6aa**) (0.1 g, 0.27 mmol), in anhydrous MeOH (2 mL), then 10% Pd/C (5.7 mg, 0.054 mmol) was added under an argon atmosphere. The resulting suspension was hydrogenated for 12 h at room temperature (35 ^oC) under the H_2 balloon pressure (1 atm). Then the mixture was filtered through a celite pad, and the filtrate was concentrated to give the crude product, which was purified by silica-gel chromatography (SiO_2, 20% EtOAc/hexanes) to afford 12a-methyl-5-phenyl-3,4,4a,6,6a,12a-hexahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (**10aa**) as a white solid (0.067 g, 67%). TLC: R_f = 0.40 (SiO_2, 30% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.79 (d, *J* = 7.5 Hz, 1H), 7.64-7.59 (m, 1H),



7.57-7.52 (m, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.38-7.34 (m, 2H), 7.29 (s, 1H), 7.18 (d, *J* = 7.4 Hz, 2H), 4.63 (dd, *J* = 2.6, 11.8 Hz, 1H), 4.35-4.24 (m, 1H), 3.91-3.77 (m, 1H), 3.56-3.42 (m, 1H), 2.46-2.34 (m, 1H), 2.24-2.09 (m, 1H), 2.00 (s, 3H), 1.91-1.83 (m, 1H), 1.53 (br. s., 3H), 1.11-1.02 (m, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz): δ 141.4, 137.2, 136.8, 132.6, 129.4, 128.7, 127.6, 126.9, 122.4, 121.0, 90.8, 63.9, 58.3, 48.1, 42.6, 28.0, 25.3, 23.9, 19.2.

12. Control experiment:

*5-(2-Methoxyphenyl)-3,4,4a,12a-tetrahydro-2H,5H-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (**6Ti**)*: Following the *General Procedure*, to the mixture of 3,4-dihydro-2*H*-pyran (**T**) (0.1 g, 1.18 mmol) and (*E*)-3-(2-methoxystyryl)benzo[*d*]isothiazole 1,1-dioxide (**5i**) (0.355 g, 1.18 mmol) in anhydrous CH_2Cl_2 (2 mL) was add $Bi(OTf)_3$ (0.077 g, 0.118 mmol) under argon atmosphere at room temperature (35 ^{o}C) and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 30% EtOAc/hexanes) afforded 5-(2-methoxyphenyl)-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-*a*]pyrano[3,2-*e*]pyridine 11,11-dioxide **(6Ti)** (0.310 g, 68%) as an off-white solid.



6Ti

TLC: R_f = 0.60 (SiO_2, 15% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, *J* = 7.63 Hz, 1H), 7.67-7.60 (m, 2H), 7.58-7.53 (m, 1H), 7.26-7.22 (m, 1H), 7.25-7.21 (m, 1H), 6.96-6.90 (m, 2H), 5.61(d, *J* = 3.50 Hz, 1H), 5.40 (d, *J* = 3.00 Hz, 1H), 4.33-4.17 (m, 2H), 3.87 (s, 3H), 3.84-3.76 (m, 1H), 2.16-2.09 (m, 1H), 2.0-1.90 (m, 1H), 1.78-1.68 (m, 2H), 0.93-0.82 (m, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz): δ 157.2, 133.1, 132.8, 131.4, 130, 129.6, 129.1, 128.2, 121.4, 121.2, 120.9 110.7, 103.8, 79.3, 55.6, 39.6, 28.8, 25.5; IR (KBr, cm^{-1}): υ 3200, 3144, 3065, 3030, 2929, 2853, 1737, 1661, 1594, 1527, 1457, 1311, 1244, 1166, 1094, 1025, 847, 753, 696; HRMS (ESI) *m/z* calcd for $C_{21}H_{21}O_4NS$ $[M+H]^+$ 384.1264, found 384.1261.

13. Single crystal X-ray analyses:

SC-XRD: The single crystal X-ray diffraction measurements were performed to determine the crystal structure of compounds **6ab**, **6dj**, **8gb** and **10aa** at 100 K using APEX3 (Bruker, 2016; Bruker D8 VENTURE Kappa Duo PHOTON II CPAD) diffractometer having graphite-monochromatized (**6ab**, **6dj** and **8gb** collected with MoKα = 0.71073 Å, while **10aa** using with CuKα source (1.5417 Å)). The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of unit cell parameters and an orientation matrix were calculated from 36 frames, and the cell refinement was performed by SAINT-Plus (Bruker, 2016). An optimized strategy used for data collection consisted of different sets of φ and ω scans with 0.5θ steps φ/ω. The data were collected with a time frame of 10 sec for both thecomponents by setting the sample to a detector distance fixed at 40 cm. All the data points were corrected for Lorentzian, polarization, and absorption effects using SAINT-Plus and SADABS programs (Bruker, 2016). The structure was refined by full-matrix least-squares refinement on F^2 with anisotropic displacement parameters for non-H atoms using SHELXL-2013,[1 2] constrained and fixed isotropic thermal parameters for aliphatic C−H hydrogen atoms following the riding model, localization of N−H hydrogen atoms from the difference Fourier map and free refinement of their positions with fixed isotropic thermal parameters.[1, 2] The molecular graphics of ORTEP diagrams were performed by Mercury software.The crystal symmetry of the components was cross-checked by running the cif files through PLATON (Spek, 2020) software and notified that no additional symmetry was observed. The Encifer software was used to correct the cif files. The compound **6ab** was crystallized by a slow evaporation method using a solvent system of 30% EtOAc/hexanes. The compound **6dj** was crystallized by a slow evaporation method using a solvent system of 30% EtOAc/hexanes. The compound **8gb** was crystallized by a slow evaporation method using a solvent system of 40% EtOAc/hexanes. The compound **10aa** was crystallized by a slow evaporation method using a solvent system of 50% EtOAc/hexanes.

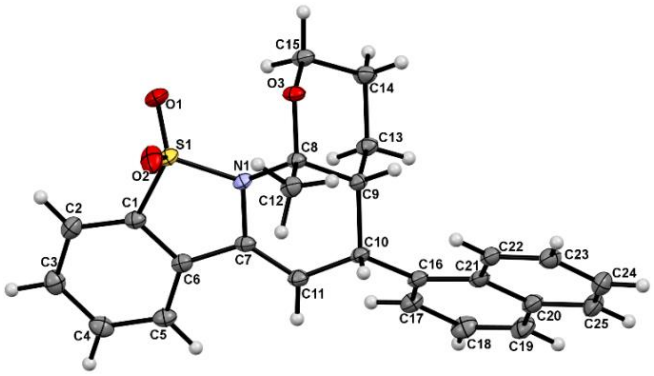


Figure 1. ORTEP diagram of compound **6ab**, the asymmetric unit contains a single molecule. Herein, the ellipsoids are drawn with a 50% probability.

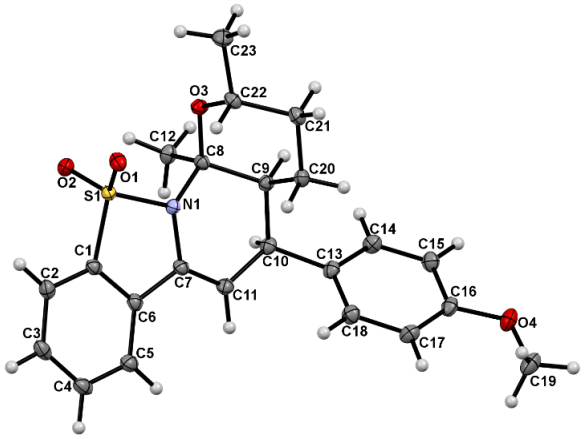


Figure 2. ORTEP diagram of compound 6dj, the asymmetric unit contains a single molecule. Herein, the ellipsoids are drawn with a 50% probability.

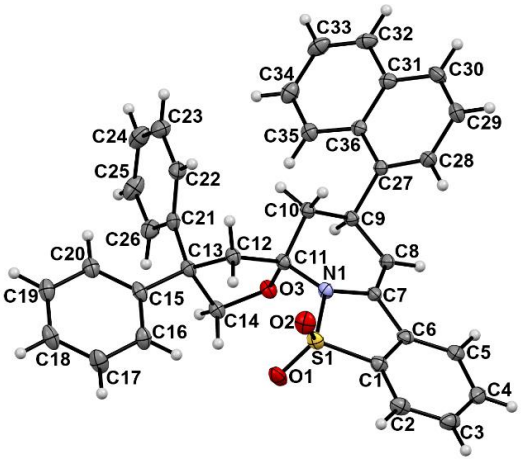


Figure 3. ORTEP diagram of compound 8gb, the asymmetric unit contains a single molecule. Herein, the ellipsoids are drawn with a 50% probability.

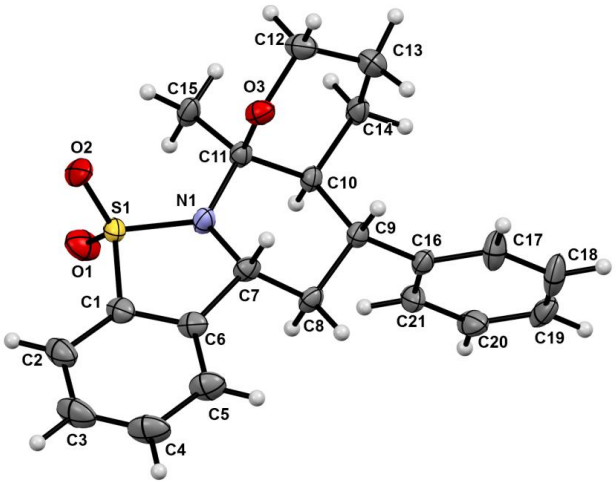


Figure 4. ORTEP diagram of compound **10aa**, the asymmetric unit contains a single molecule. Herein, the ellipsoids are drawn with a 50% probability.

Table 1. Crystallographic information details of compounds **6ab**, **6dj, 8gb** and **10aa**.

Crystal data	**6ab**	**6dj**	**8gb**	**10aa**
Chemical formula	$C_{25}H_{23}NO_3S$	$C_{23}H_{25}NO_4S$	$C_{36}H_{29}NO_3S$	$C_{21}H_{23}NO_3S$
Formula weight (M_r)	417.50	411.50	555.66	369.46
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_12_12_1$
Temperature T (K)	100	100	100	100
a (Å)	10.9271 (10)	10.2361 (15)	18.5043 (18)	10.2093 (5)
b (Å)	16.5749 (17)	18.336 (3)	8.0564 (8)	12.4520 (6)
c (Å)	10.9904 (10)	10.7234 (18)	18.6190 (19)	14.4031 (6)
α (°)	90	90	90	90
β (°)	93.352 (3)	98.878 (7)	103.185 (4)	90
γ (°)	90	90	90	90
Z	4	4	4	4
Volume (Å^3)	1987.1 (3)	1988.6 (6)	2702.5 (5)	1831.01 (15)
Source of radiation	MoKα	MoKα	MoKα	CuKα
D_{calc} (Mg m^{-3})	1.396	1.375	1.366	1.340
Crystal size (mm)	0.16×0.12×0.1	0.16×0.09×0.08	0.23×0.12×0.09	0.23×0.12×0.09
μ (mm^{-1})	0.19	0.19	0.16	1.74
Data collection				
Diffractometer	Bruker D8 VENTURE Kappa Duo PHOTON II CPAD	Bruker D8 VENTURE Kappa Duo PHOTON II CPAD	Bruker D8 VENTURE Kappa Duo PHOTON II CPAD	Bruker D8 VENTURE Kappa Duo PHOTON II CPAD
Absorption correction	Multi-scan (SADABS; Bruker, 2016)	Multi-scan (SADABS; Bruker, 2016)	Multi-scan (SADABS; Bruker, 2016)	Multi-scan (SADABS; Bruker, 2016)
T_{min}, T_{max}	0.711, 0.746	0.705, 0.746	0.694, 0.739	0.5105, 0.7543
No. of measured, independent and observed [I > 2σ(I)] reflections	95965, 4321, 4113	107127, 4308, 4173	132550, 5900, 5062	71574, 3884, 3878

Theta range (°)	2.46−27.49	2.30-27.49	2.26-28.49	7.11-79.76
R_{int}	0.055	0.043	0.097	0.053
Refinement				
R[F^2> 2σ (F^2)], wR(F^2)	0.046, 0.130	0.034, 0.109	0.043, 0.105	0.034, 0.087
GOF on F^2	1.18	1.19	1.06	1.07
No. of independent reflections	4321	4308	5900	3884
No. of parameters	273	266	371	237
F_000	880	872	1168	784
No. of restraints	0	0	0	0
H-atom treatment	Constr	Constr	Constr	Constr
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $A^{\circ -3}$)	0.63, −0.57	0.51, −0.39	0.49, −0.40	0.47, −0.38
CCDC number	2184885	2184884	2184883	2269306

Table 2. Hydrogen-bond geometry (A˚, °) of **6ab**, **6dj**, **8gb** and **10aa** components are given below.

Name of the compound	*D*–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
6ab	C5−H5···O3	0.9500	2.5400	3.252(2)	132
	C11−H11···O1	0.9500	2.4500	3.382(2)	168
	C12−H12C···O2	0.9800	2.4900	3.061(2)	117
	C15−H15B···O1	0.9900	2.4700	3.202(2)	131
6dj	C10−H10····O2	1.0000	2.4800	3.3882(17)	151
	C12−H12A···O2	0.9800	2.4400	3.1143(17)	125
	C12−H12C···O1	0.9800	2.4900	3.3736(17)	150
	C22−H22···O1	1.0000	2.3800	3.1239(16)	130
	C23−H23B···O2	0.9800	2.5700	3.4433(18)	149
8gb	C2−H2···O1	0.9500	2.3500	3.210(2)	150
	C12−H12B···O2	0.9900	2.5800	3.341(2)	134
	C14−H14A···O1	0.9900	2.4500	3.184(2)	130
10aa	C4−H4···O2	0.950	2.590	3.2266(2)	124
	C7−H7··O3	1.000	2.520	2.8634(1)	100
	C9−H9···O1	1.000	2.530	3.3424(2)	138

	C15−H15A···O2	0.980	2.570	3.1892(2)	121
	C15−H15B···O1	0.980	2.570	3.0999(2)	114
	C18−H18···O2	0.950	2.570	3.3661(2)	142
	C20−H20···O2	0.950	2.590	3.1930(2)	121

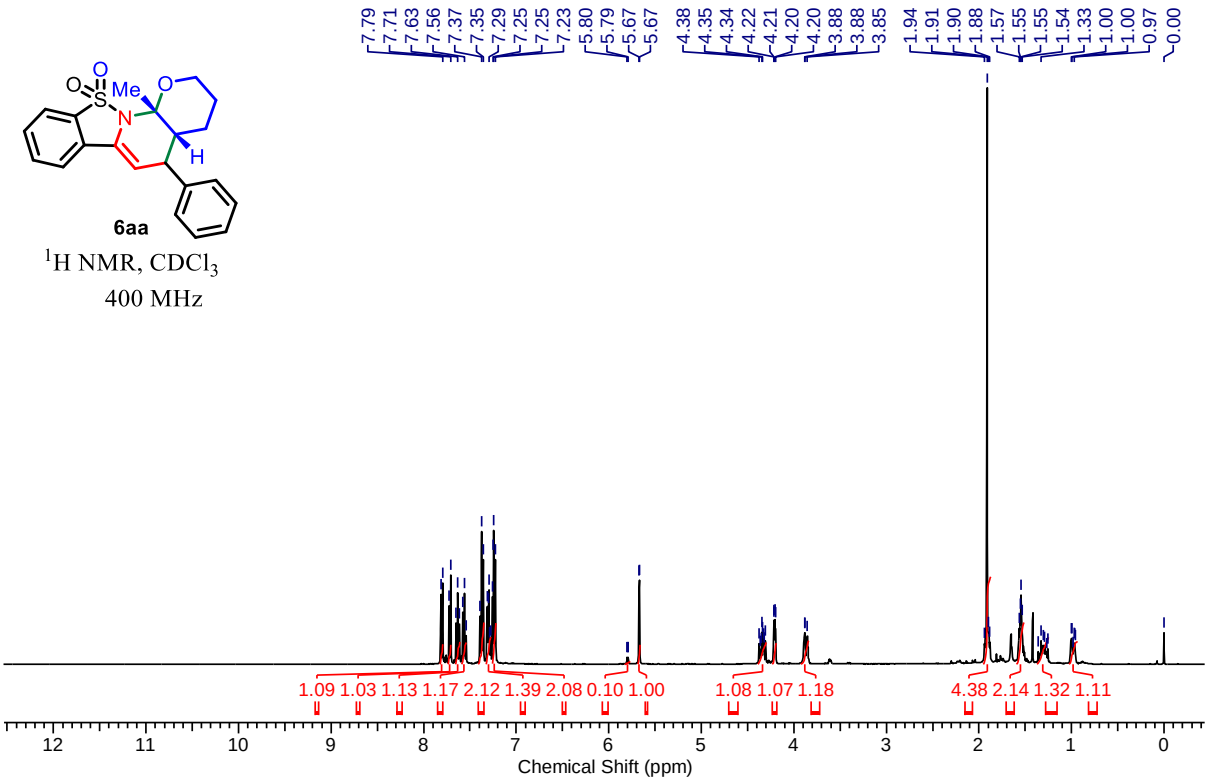
References

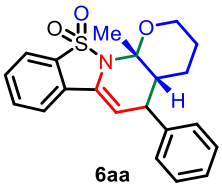
1. G. M. Sheldrick, Crystal structure refinement with SHELXL, Acta Cryst. (2015). C71, 3–8.

2. G. M. Sheldrick, SHELXT - Integrated space-group and crystal-structure determination, Acta Cryst. (2015). A71, 3–8

14. ^{1}H, ^{13}C and 2D NMR Spectra

12a-Methyl-5-phenyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (6aa):





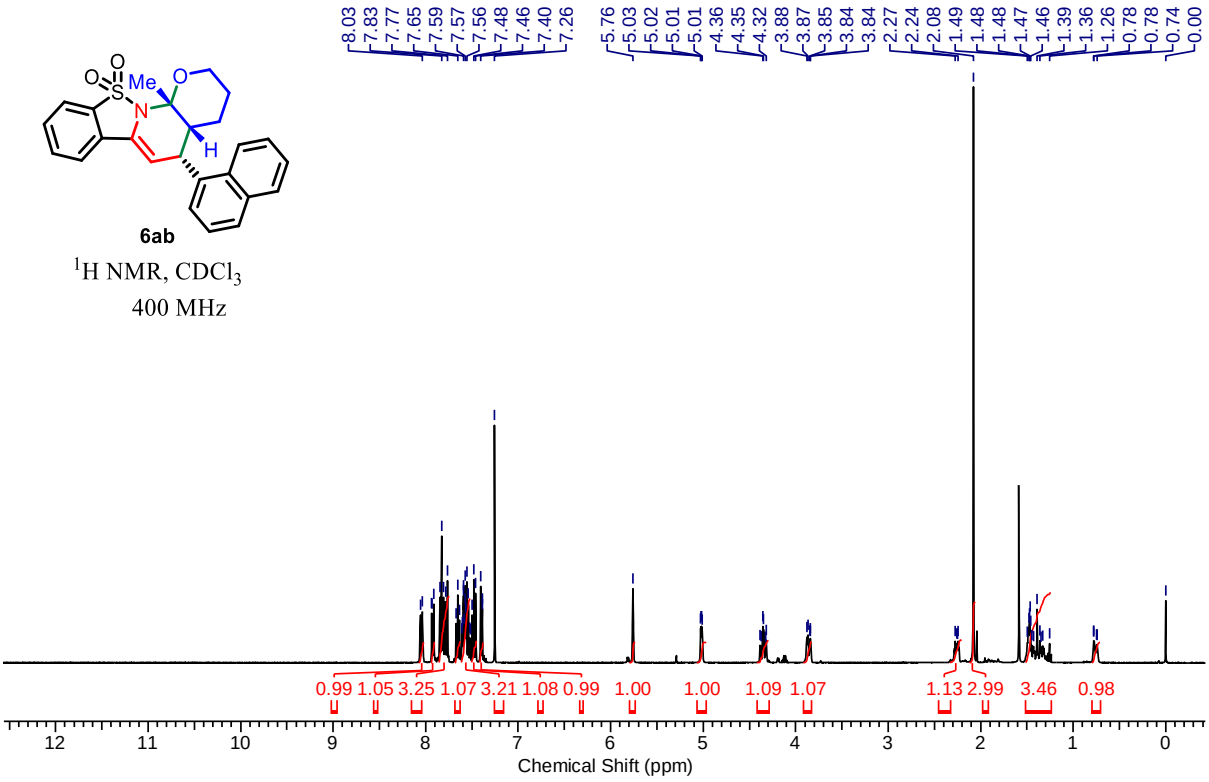
6aa

^{1}H NMR, $CDCl_3$
400 MHz

6aa

^{13}C NMR, $CDCl_3$
101 MHz

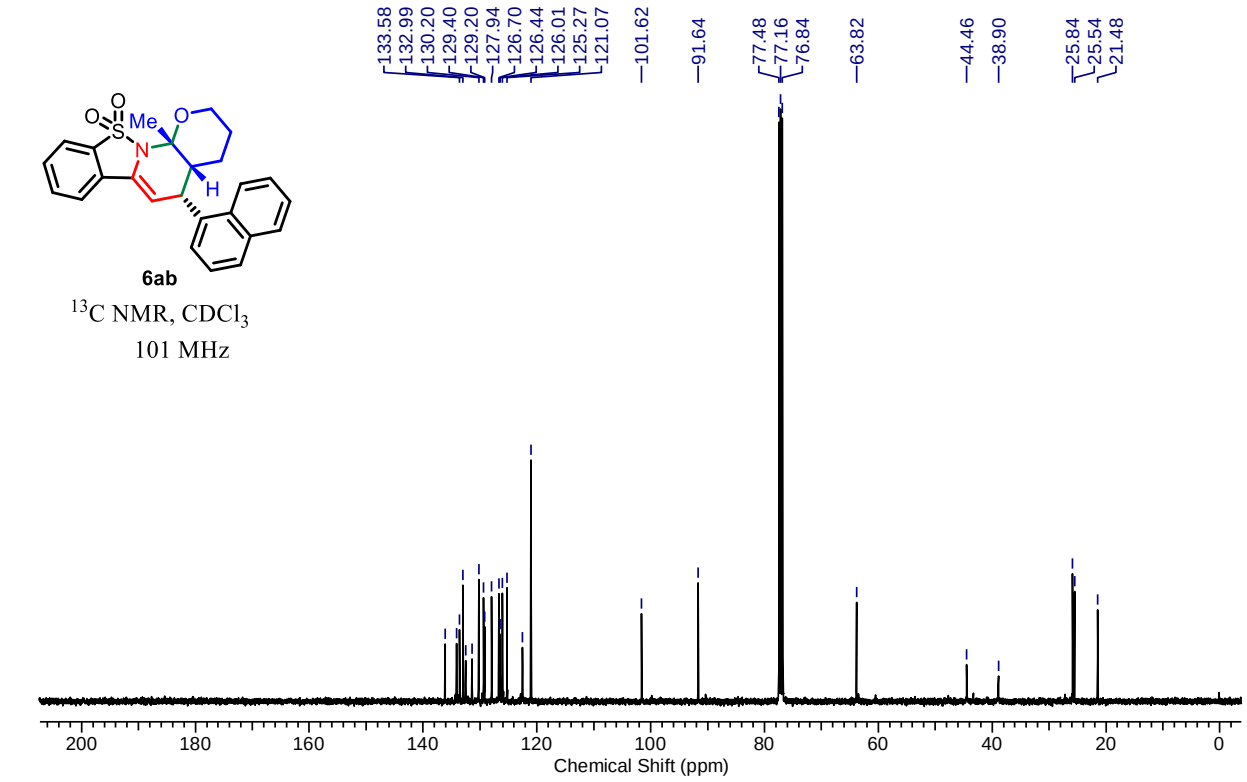
12a-Methyl-5-(naphthalen-1-yl)-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (6ab):



6ab

^{1}H NMR, $CDCl_3$

400 MHz

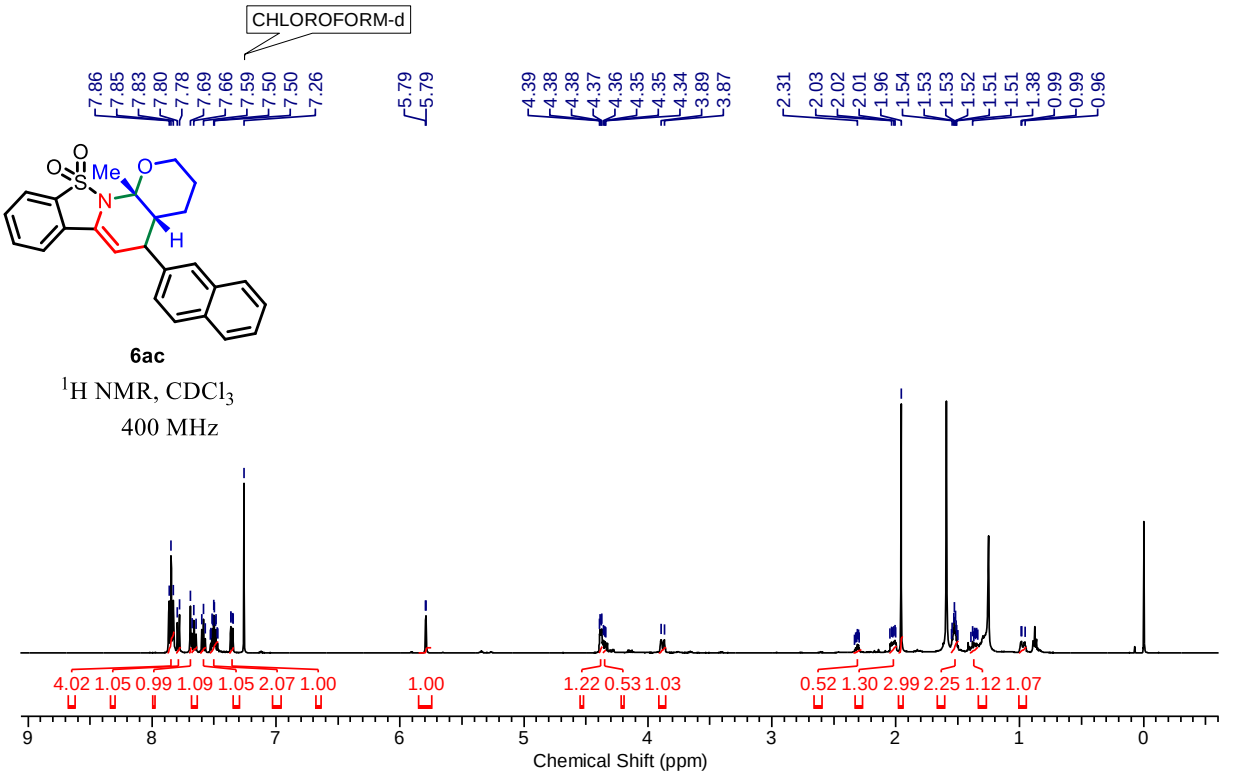


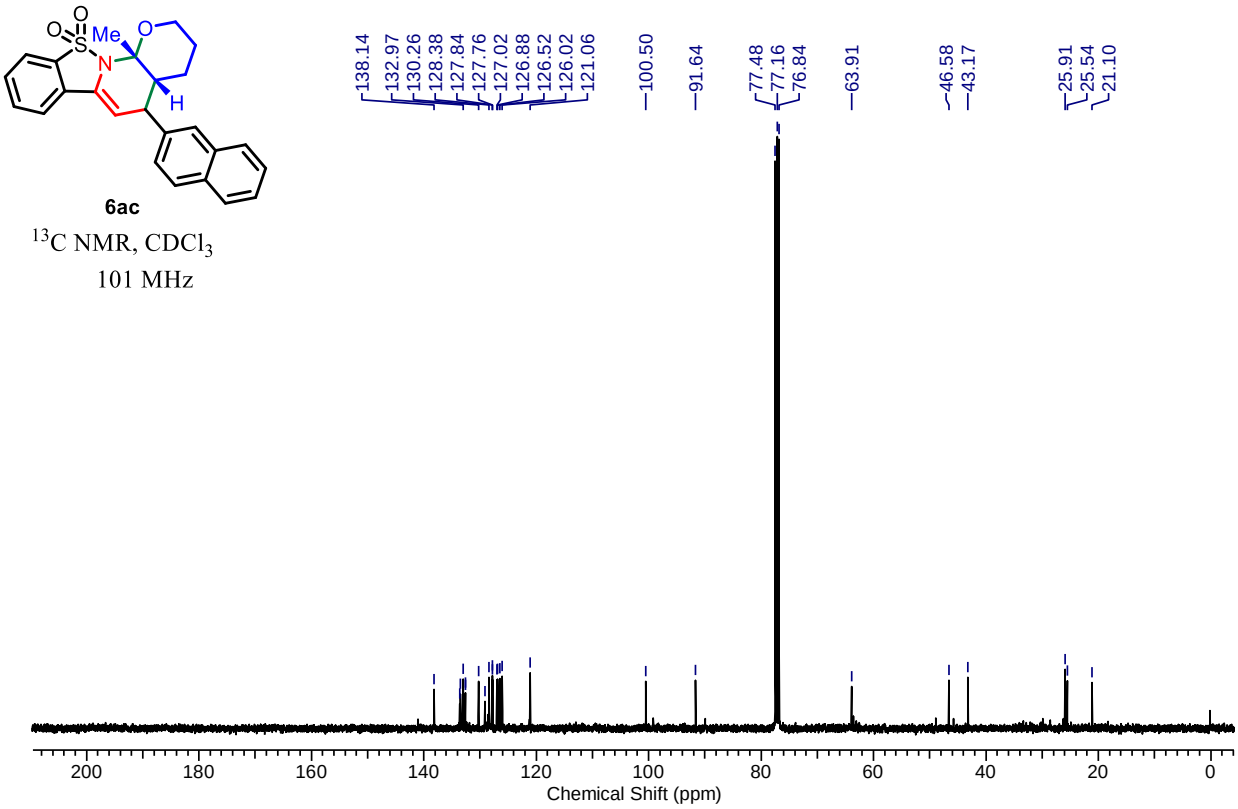
6ab

^{13}C NMR, $CDCl_3$

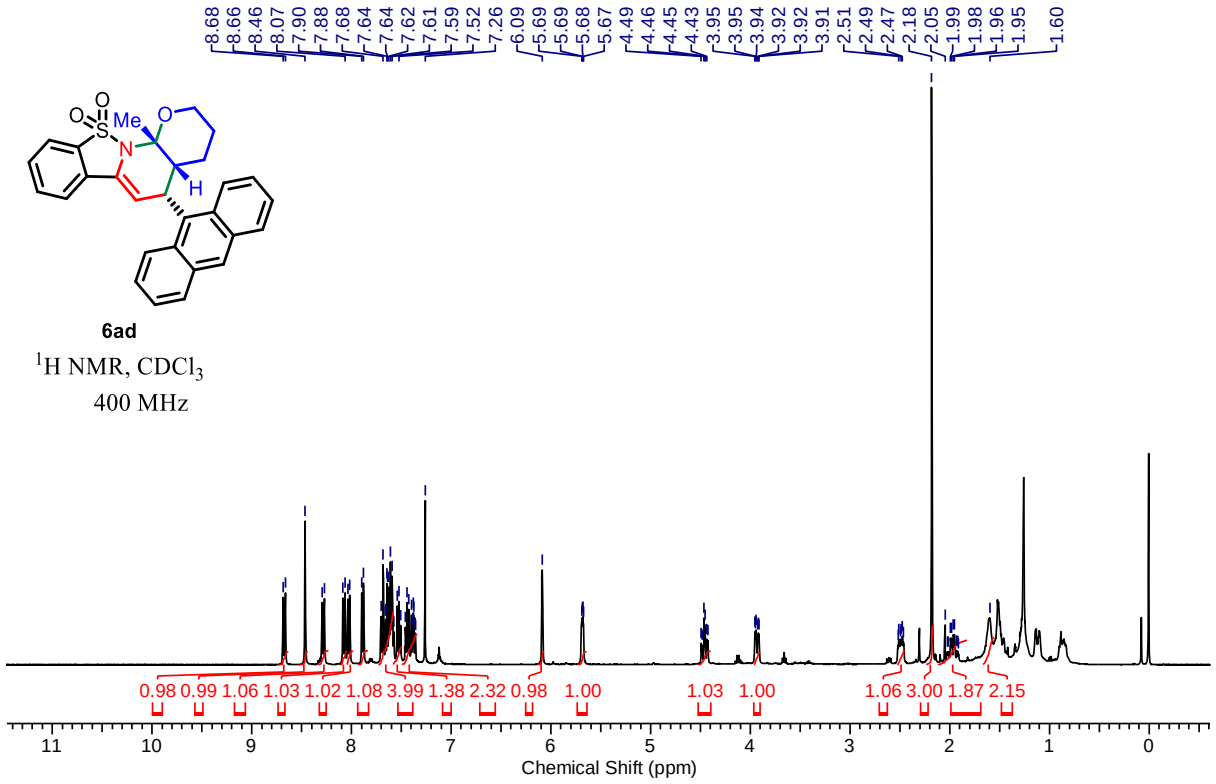
101 MHz

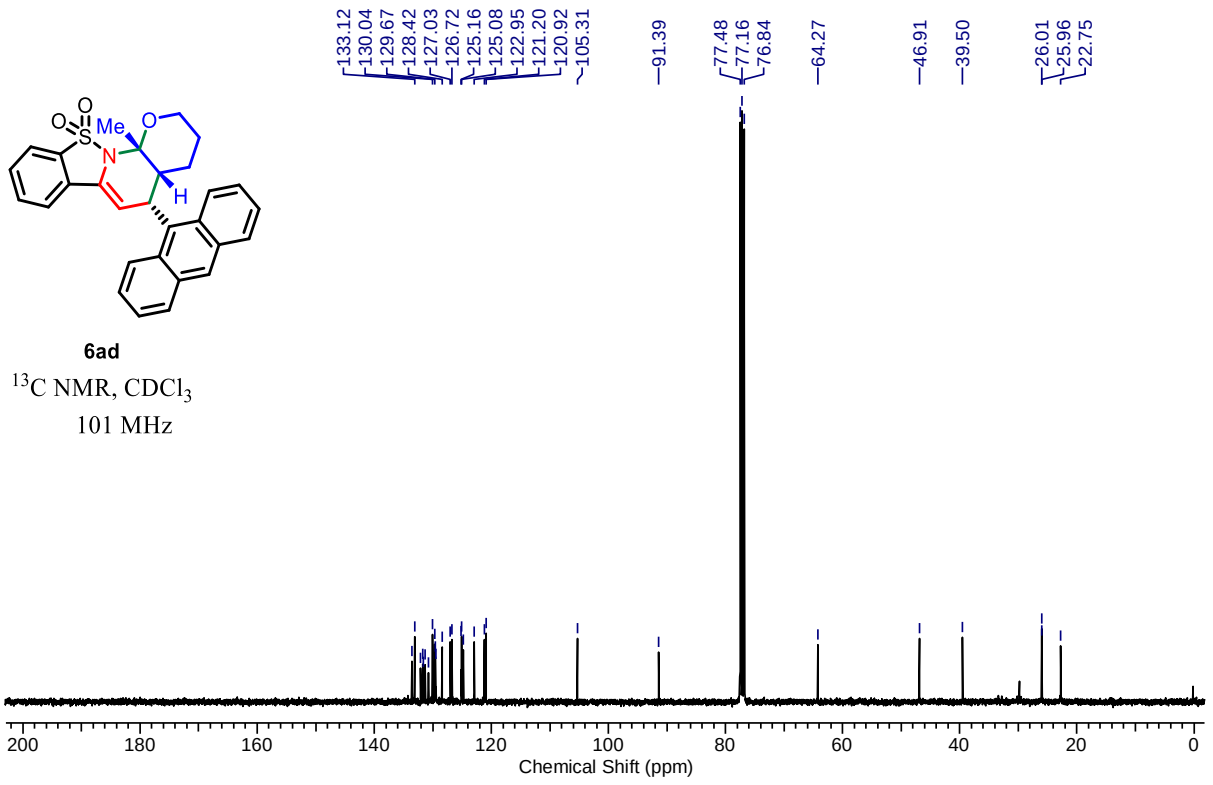
12a-Methyl-5-(naphthalen-2-yl)-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (6ac):



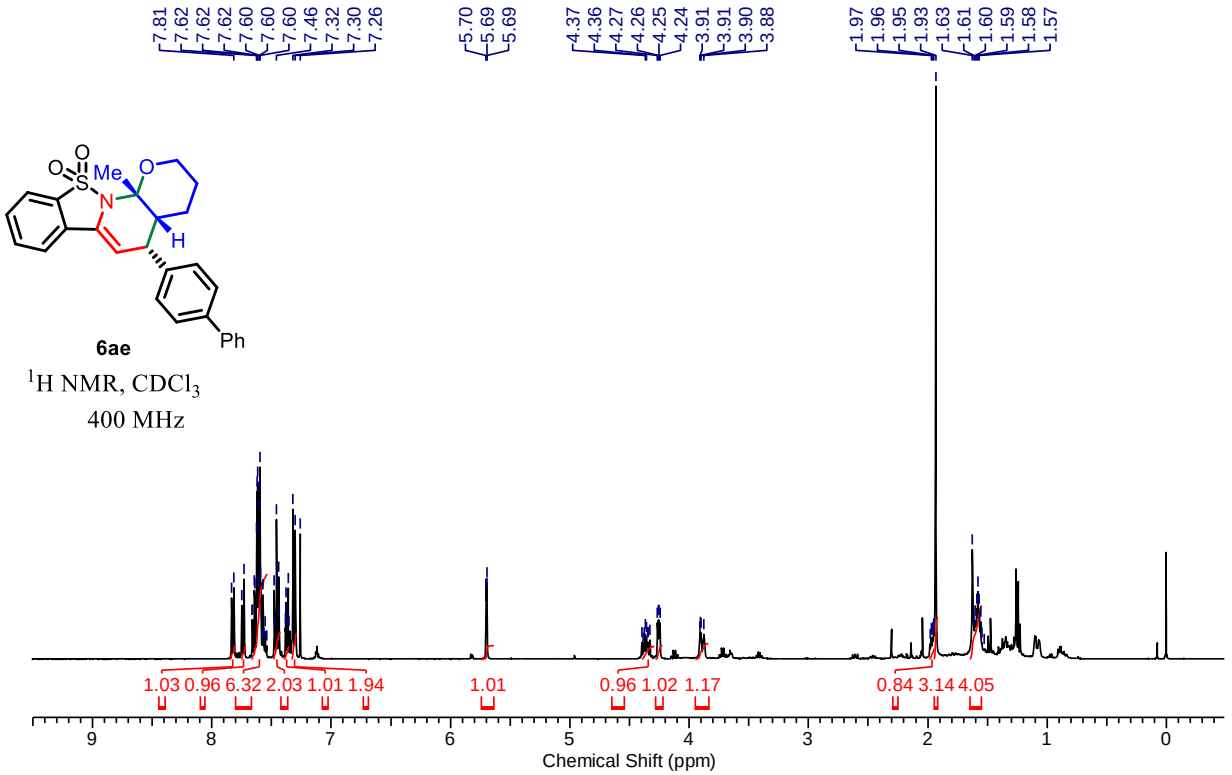


5-(Anthracen-9-yl)-12a-methyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (6ad):





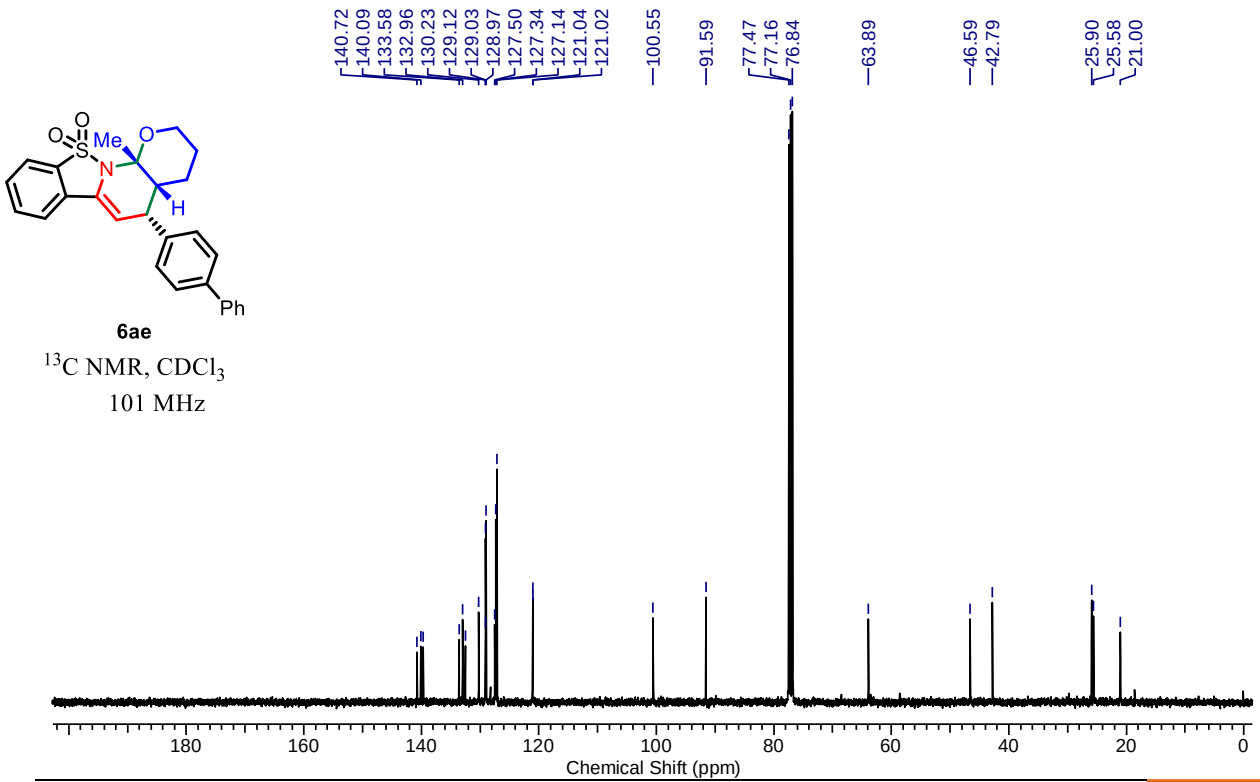
5-([1,1'-Biphenyl]-4-yl)-12a-methyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (6ae):



6ae

^{1}H NMR, $CDCl_3$

400 MHz

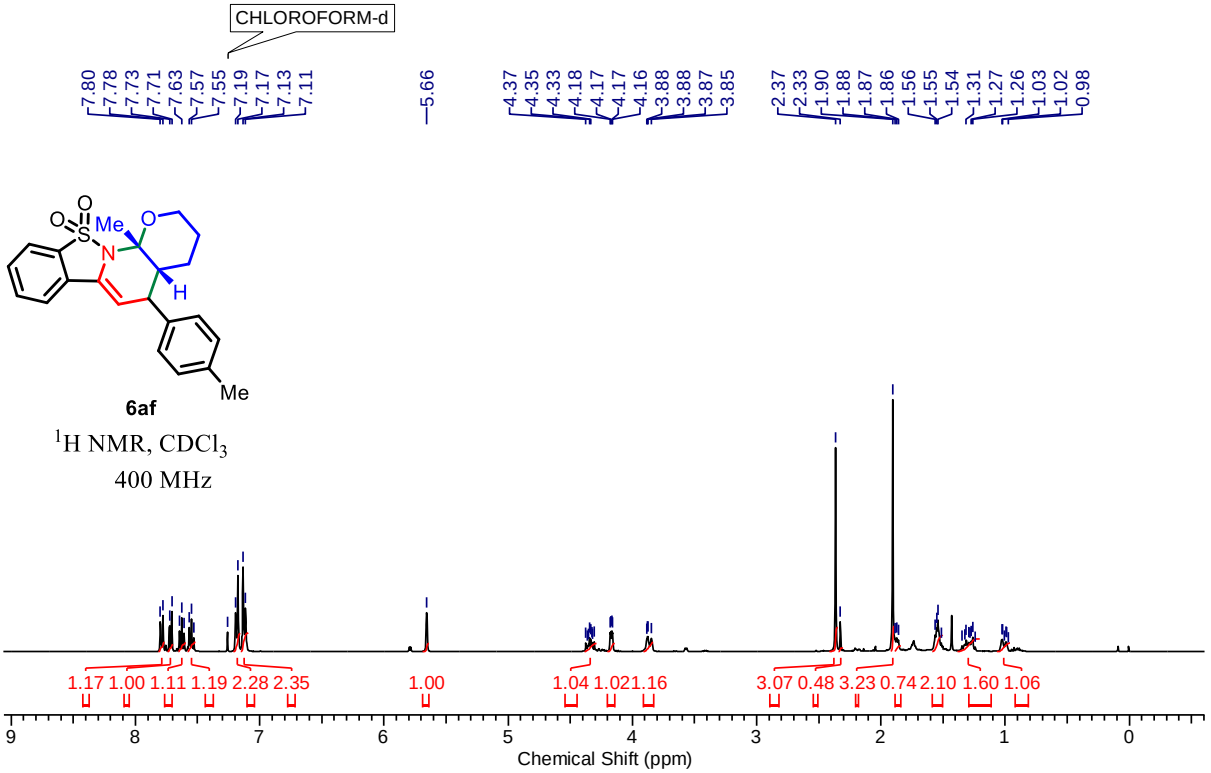


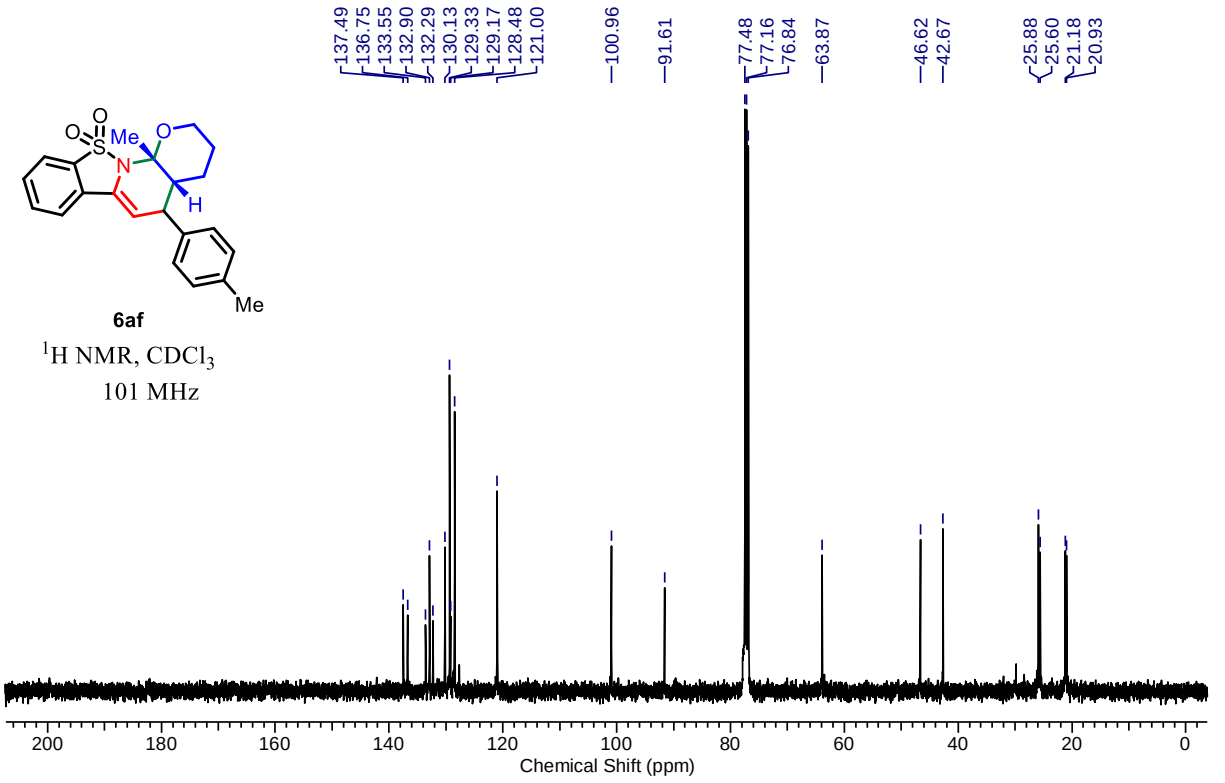
6ae

^{13}C NMR, $CDCl_3$

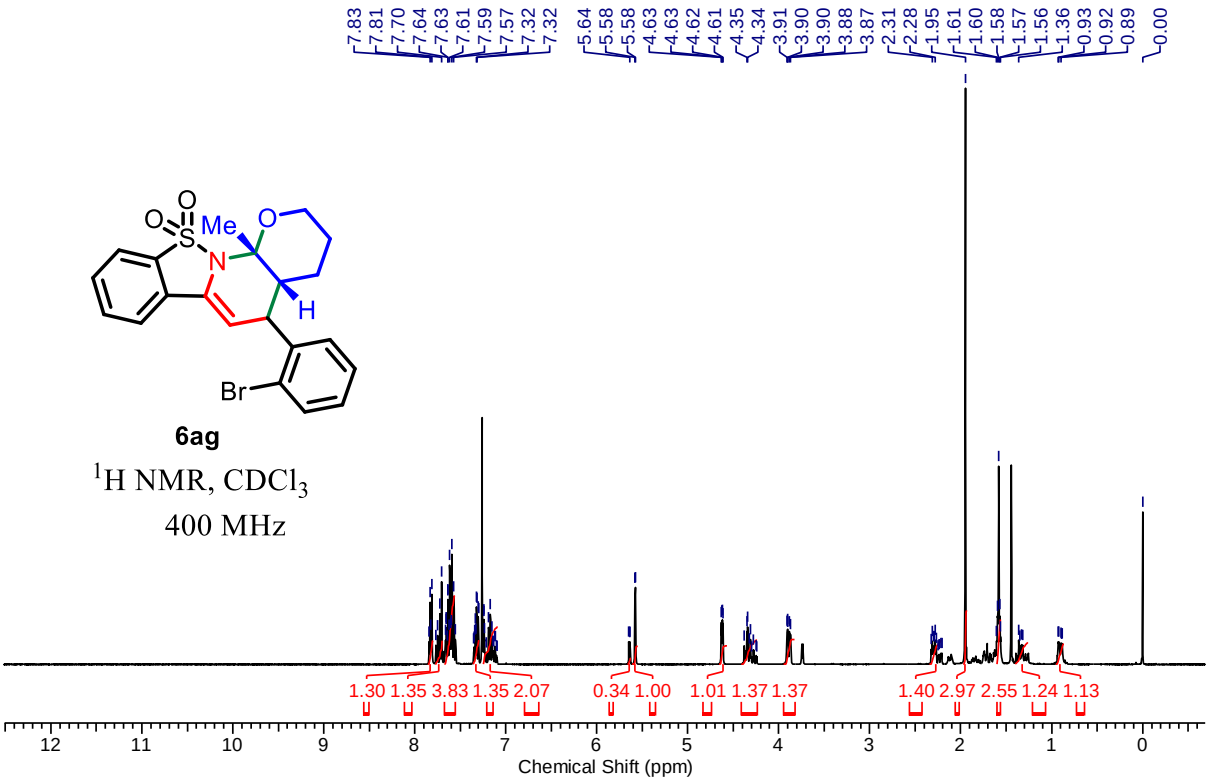
101 MHz

12a-Methyl-5-(p-tolyl)-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (6af):





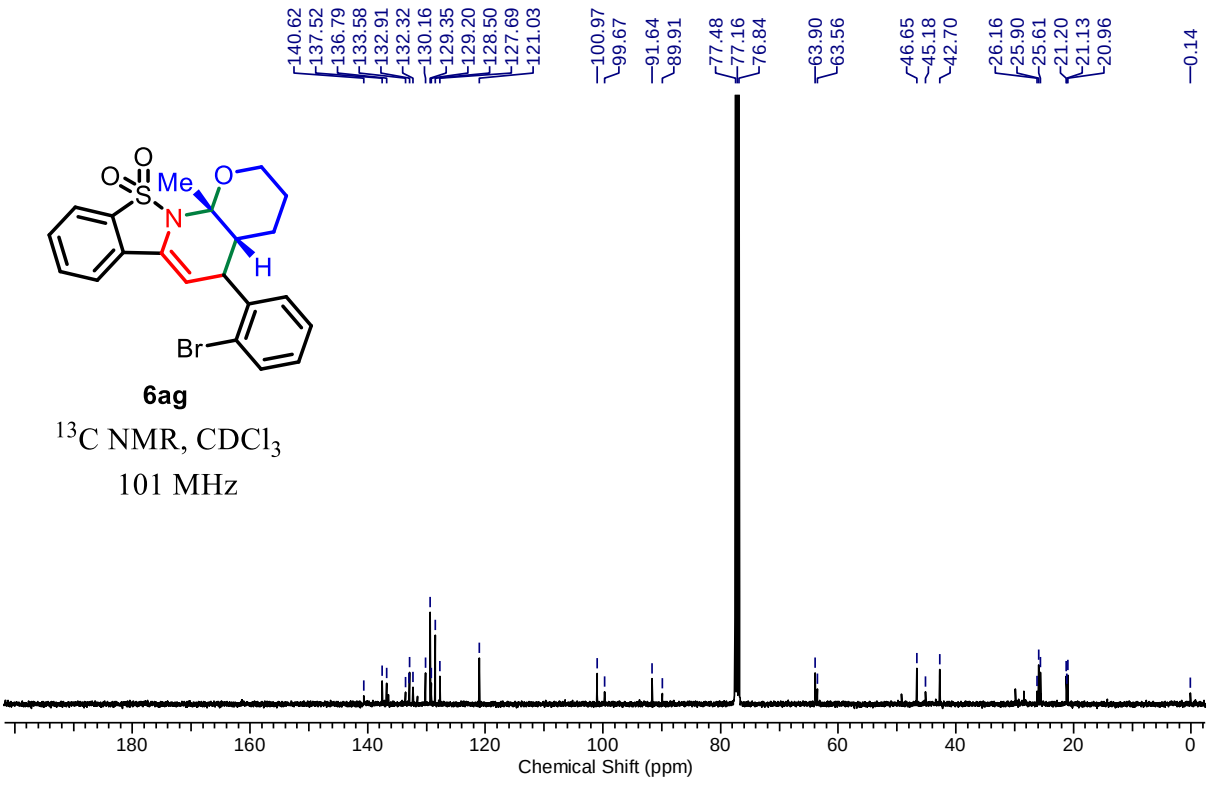
5-(2-Bromophenyl)-12a-methyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (6ag):



6ag

^{1}H NMR, $CDCl_3$

400 MHz

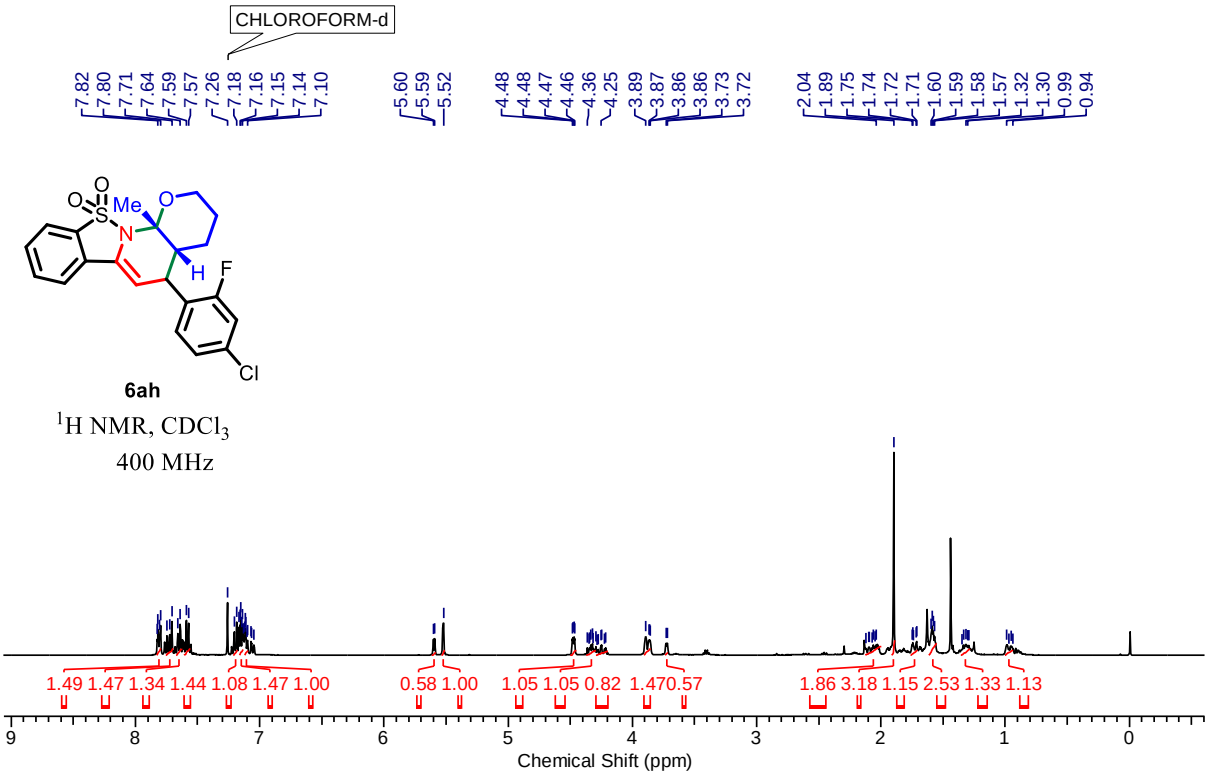


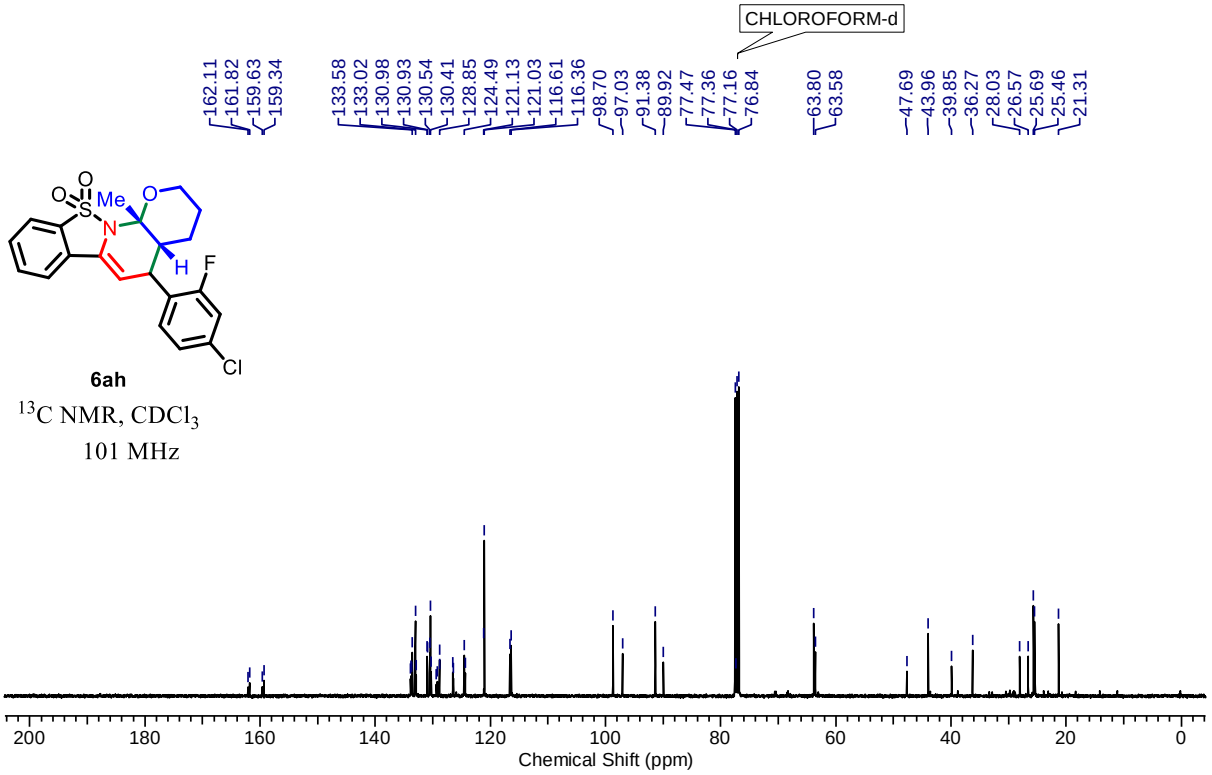
6ag

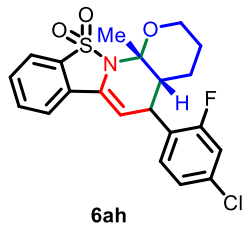
^{13}C NMR, $CDCl_3$

101 MHz

5-(4-Chloro-2-fluorophenyl)-12a-methyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (6ah):





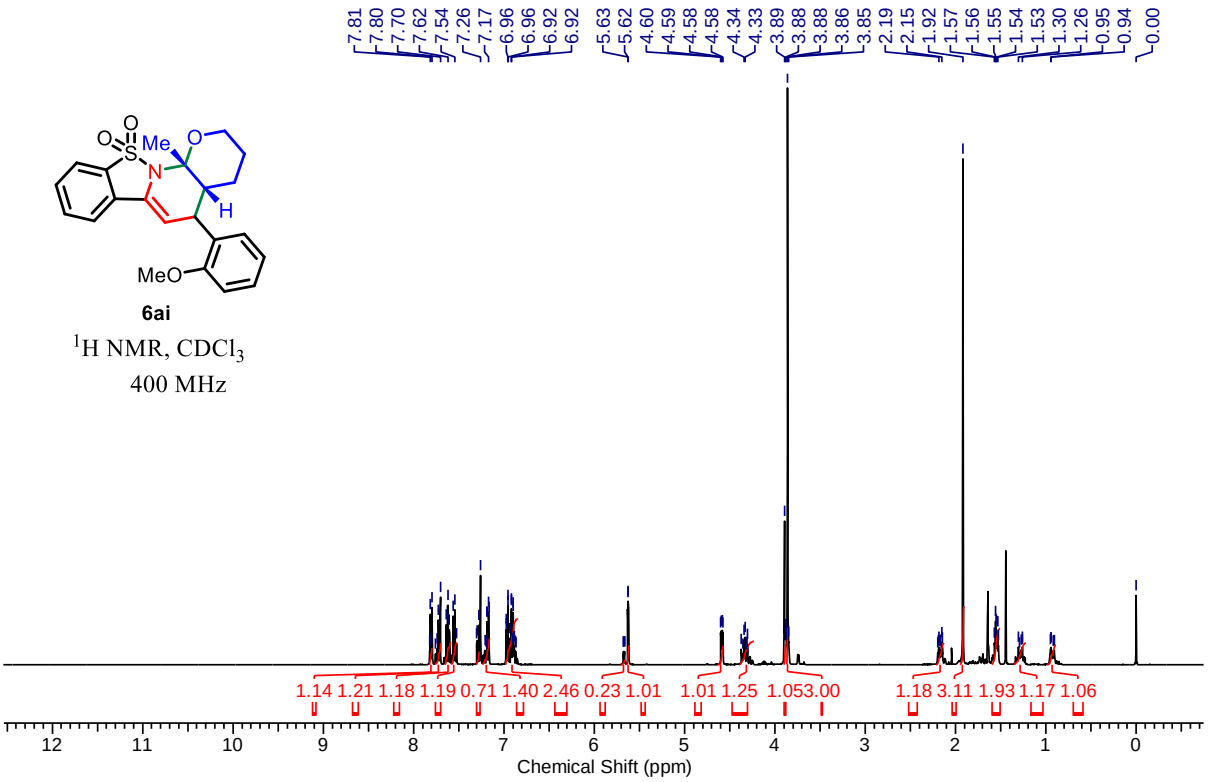


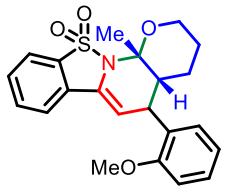
6ah

^{19}F NMR, $CDCl_3$

376 MHz

5-(2-Methoxyphenyl)-12a-methyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (6ai):





6ai

^{1}H NMR, $CDCl_3$

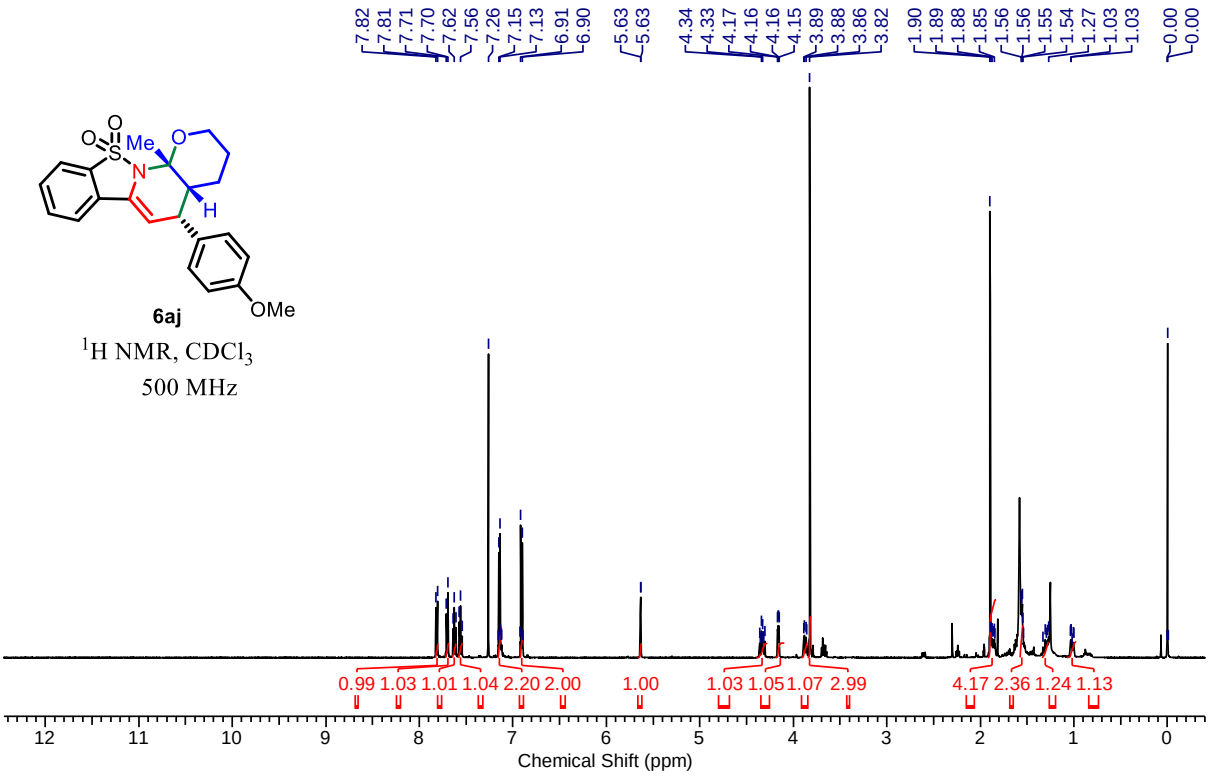
400 MHz

6ai

^{13}C NMR, $CDCl_3$

101 MHz

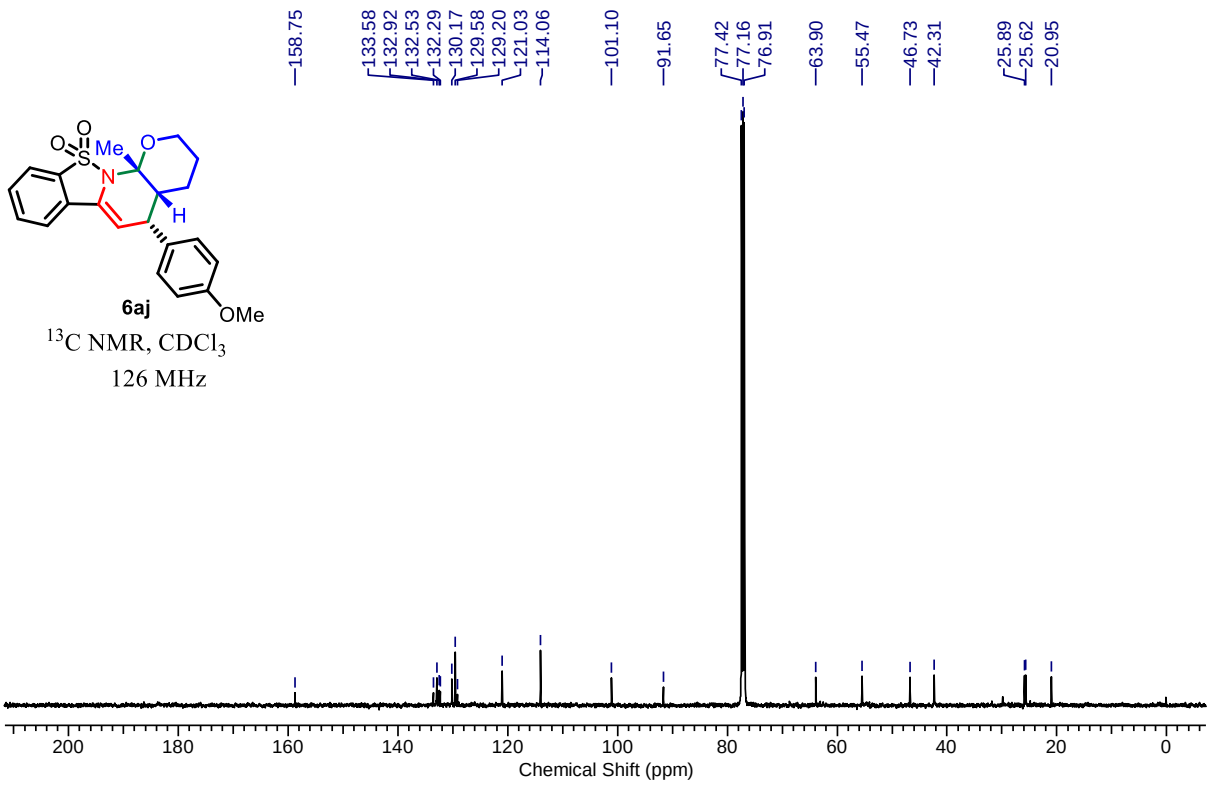
5-(4-Methoxyphenyl)-12a-methyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (6aj):



6aj

^{1}H NMR, $CDCl_3$

500 MHz

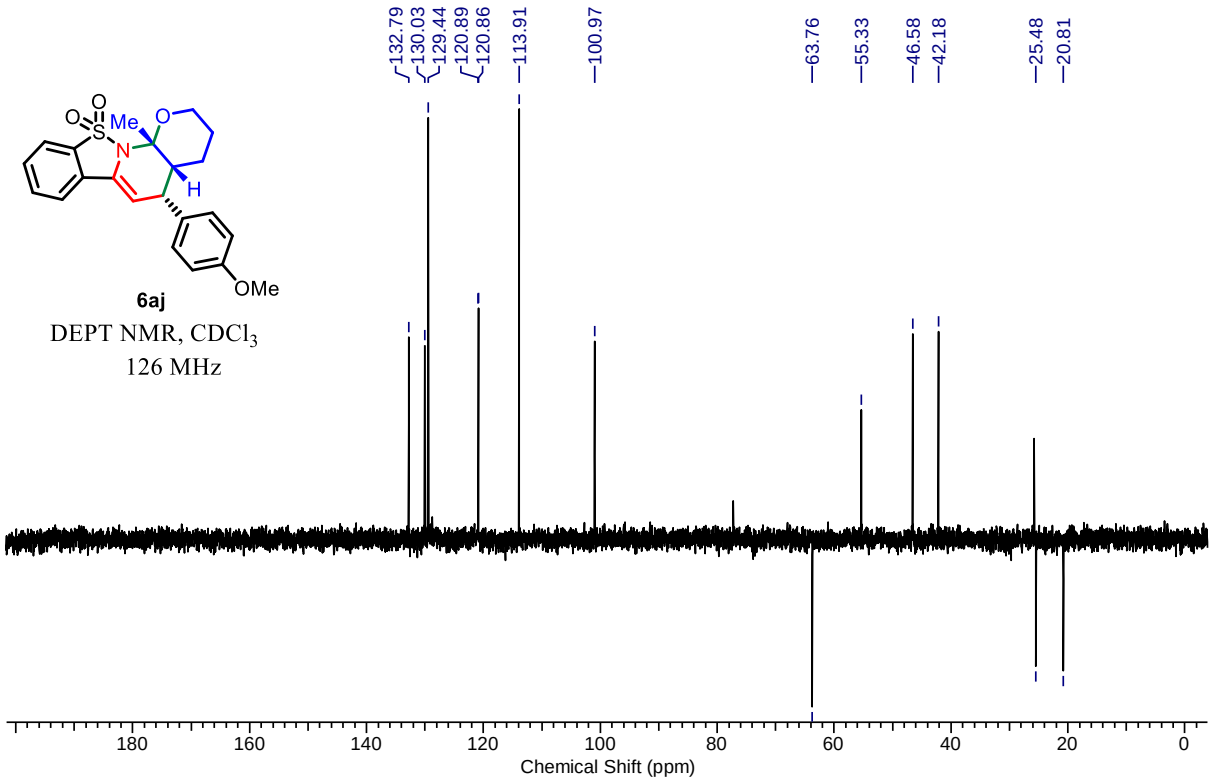


6aj

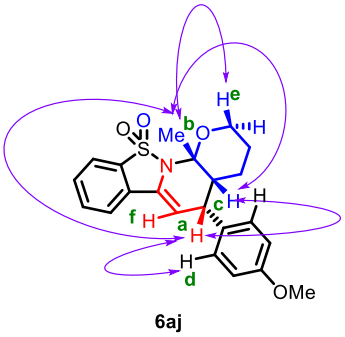
^{13}C NMR, $CDCl_3$

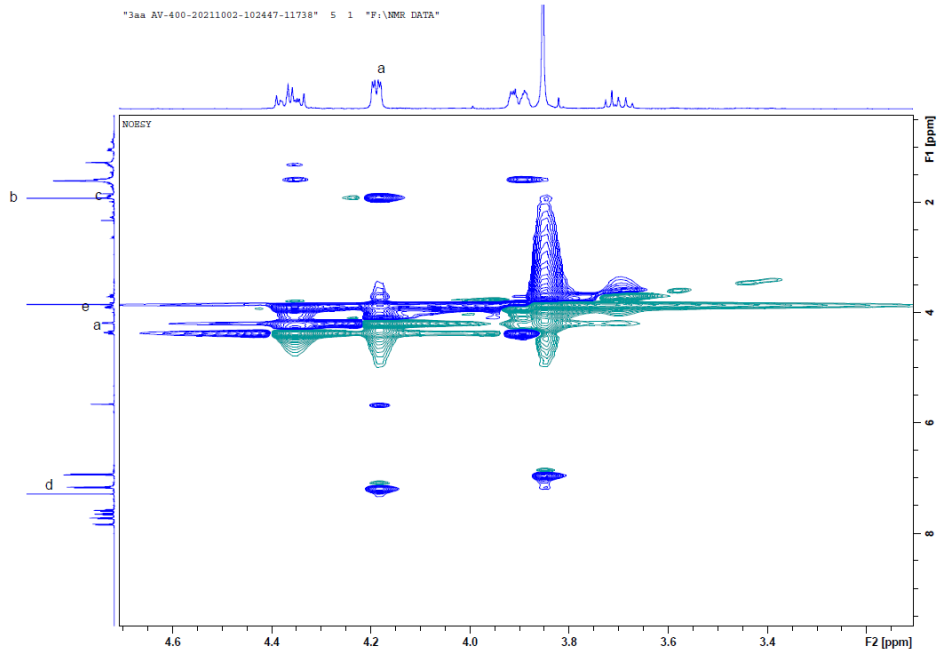
126 MHz

5-(4-Methoxyphenyl)-12a-methyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (6aj):

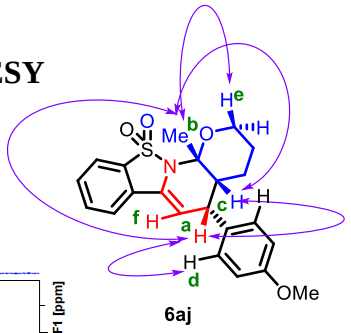


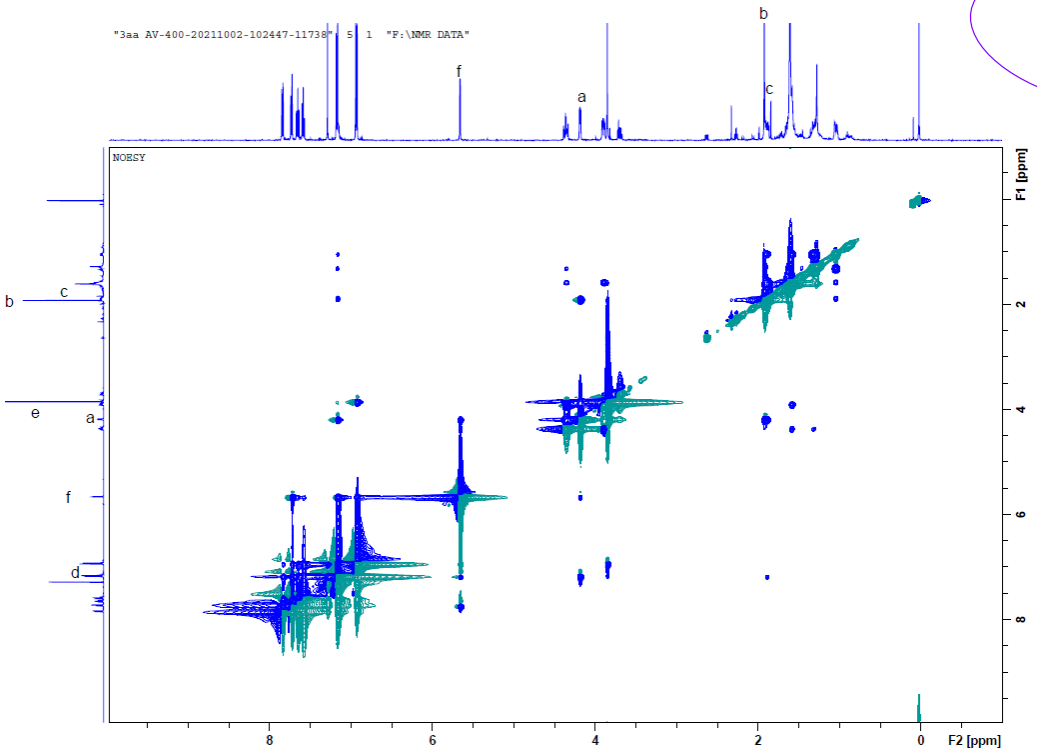
NOESY:





5-(4-Methoxyphenyl)-12a-methyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (6aj): NOESY





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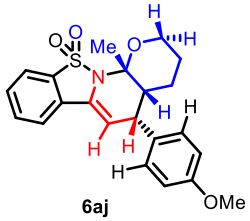
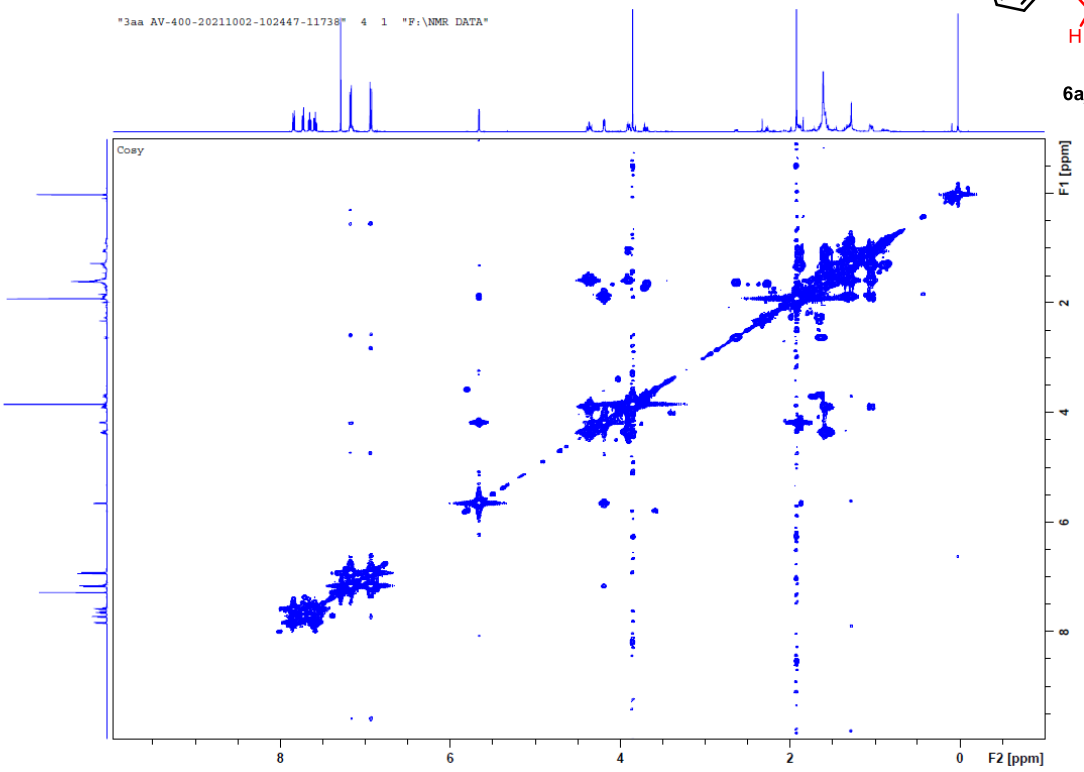
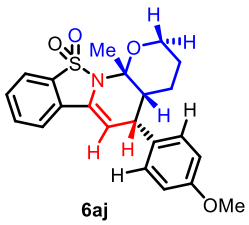
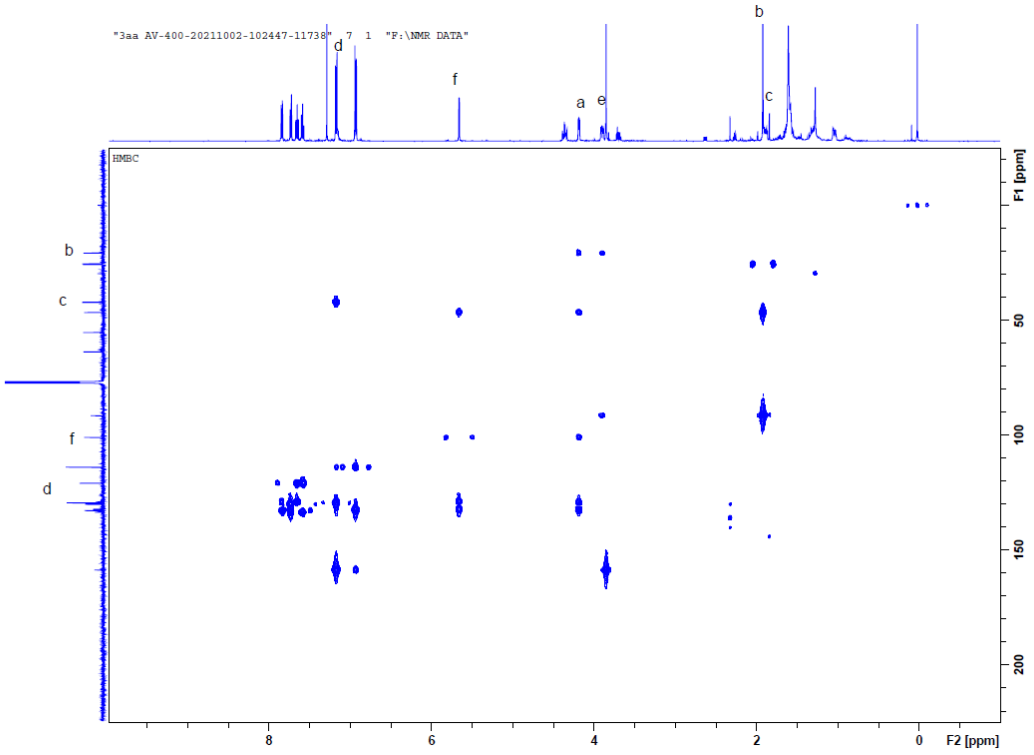




5-(4-Methoxyphenyl)-12a-methyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (6aj):



HMBC:



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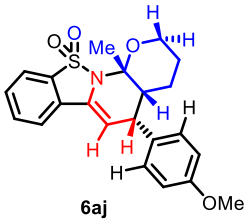
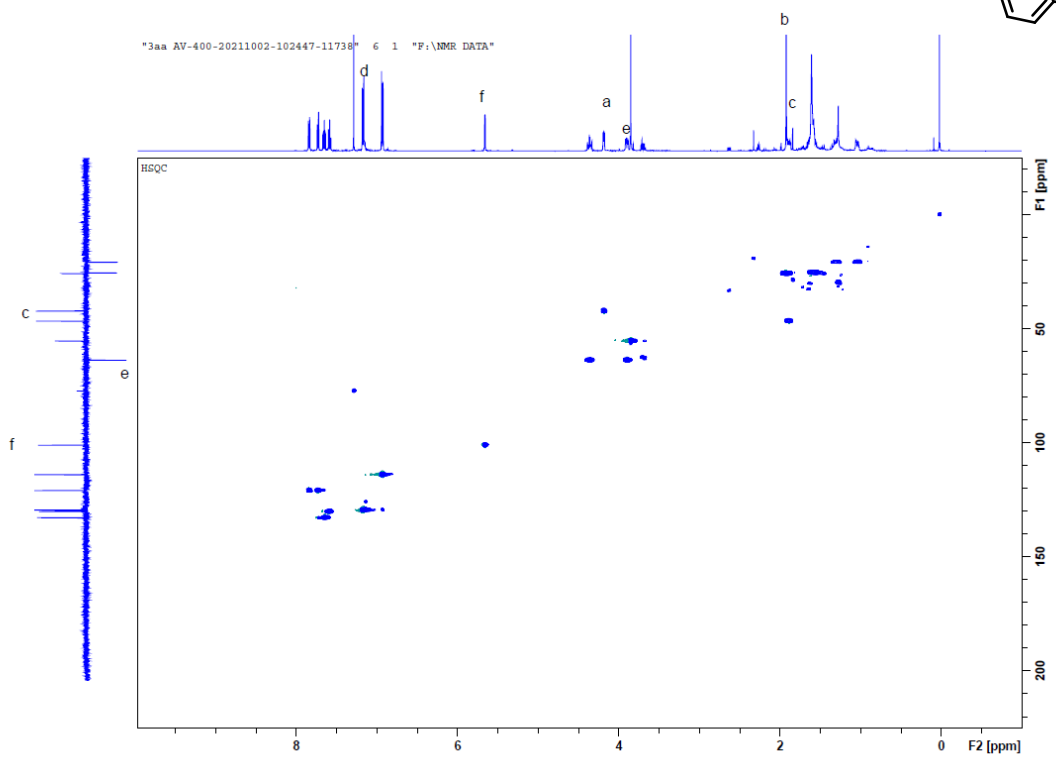
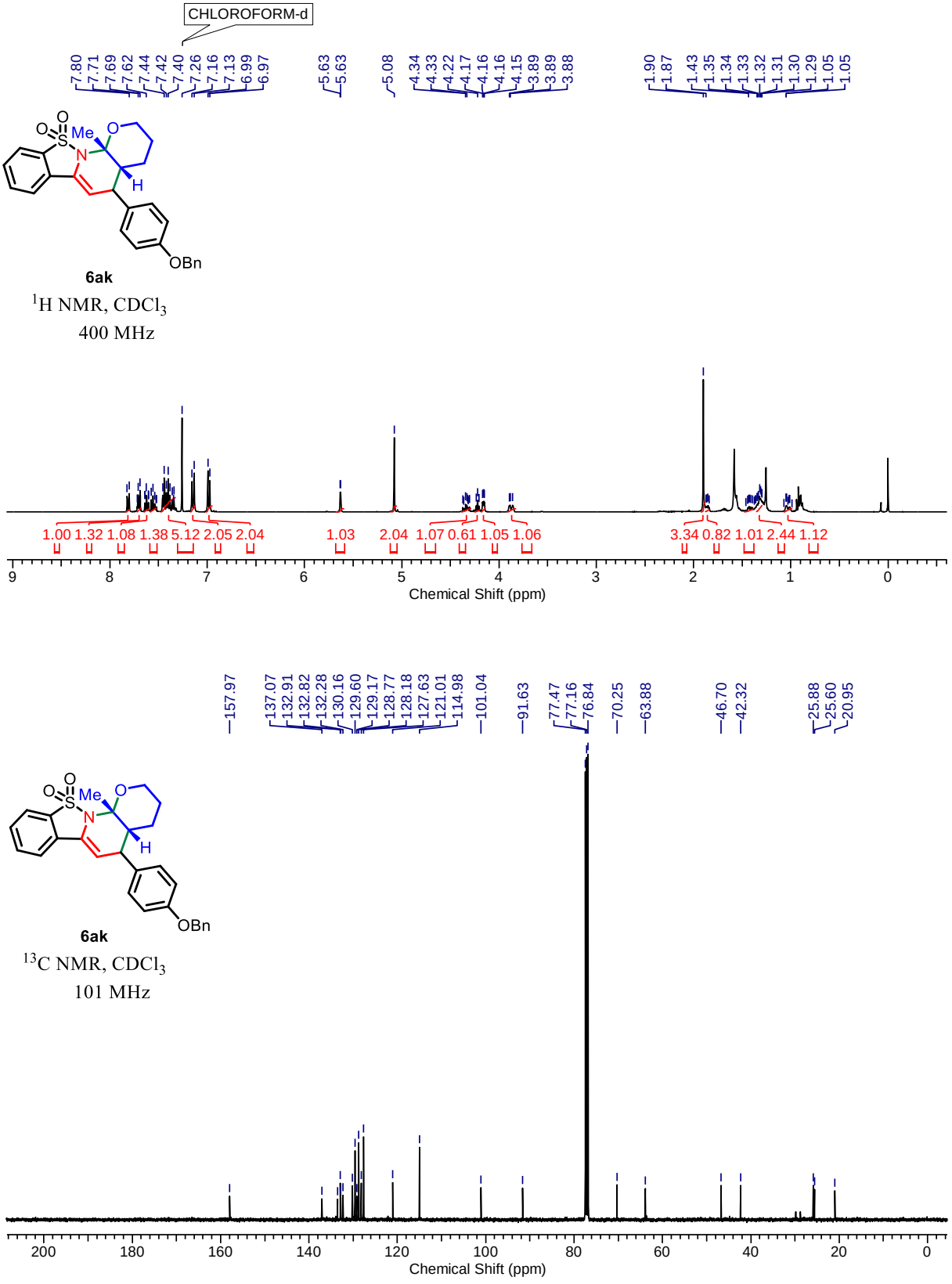
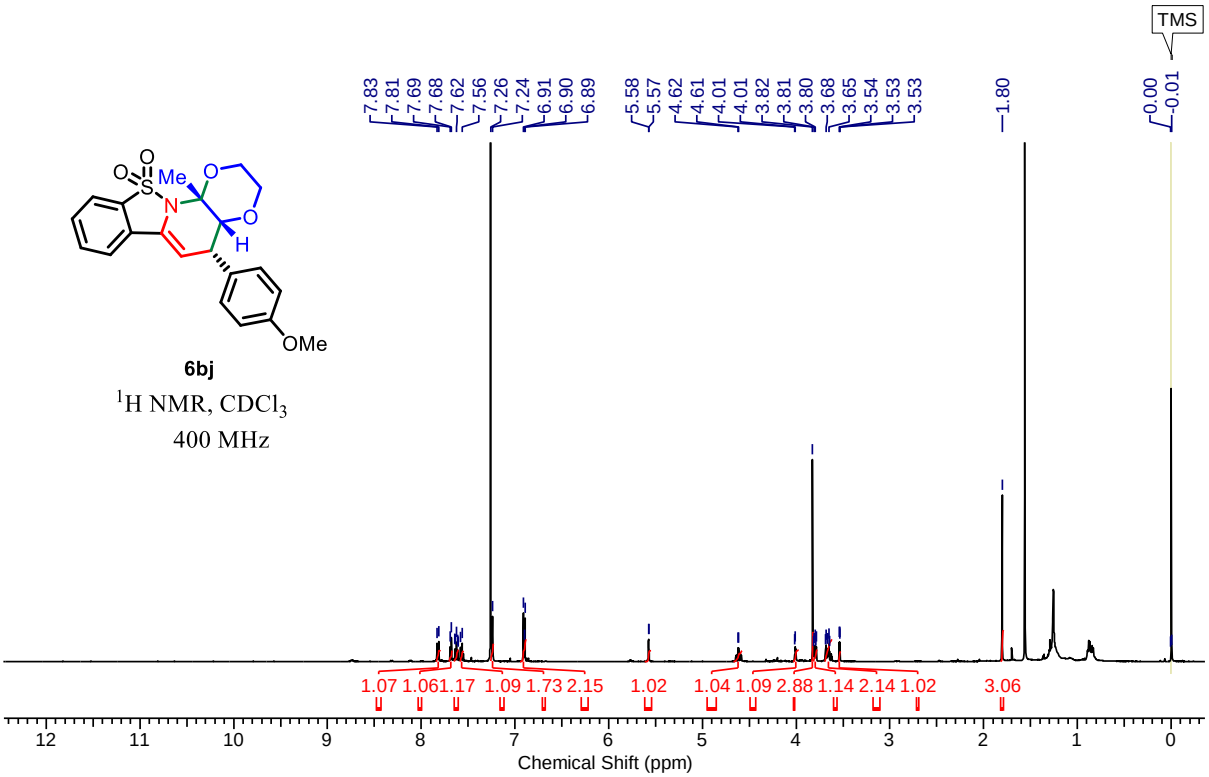




5-(4-(Benzyloxy)phenyl)-12a-methyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (6ak):



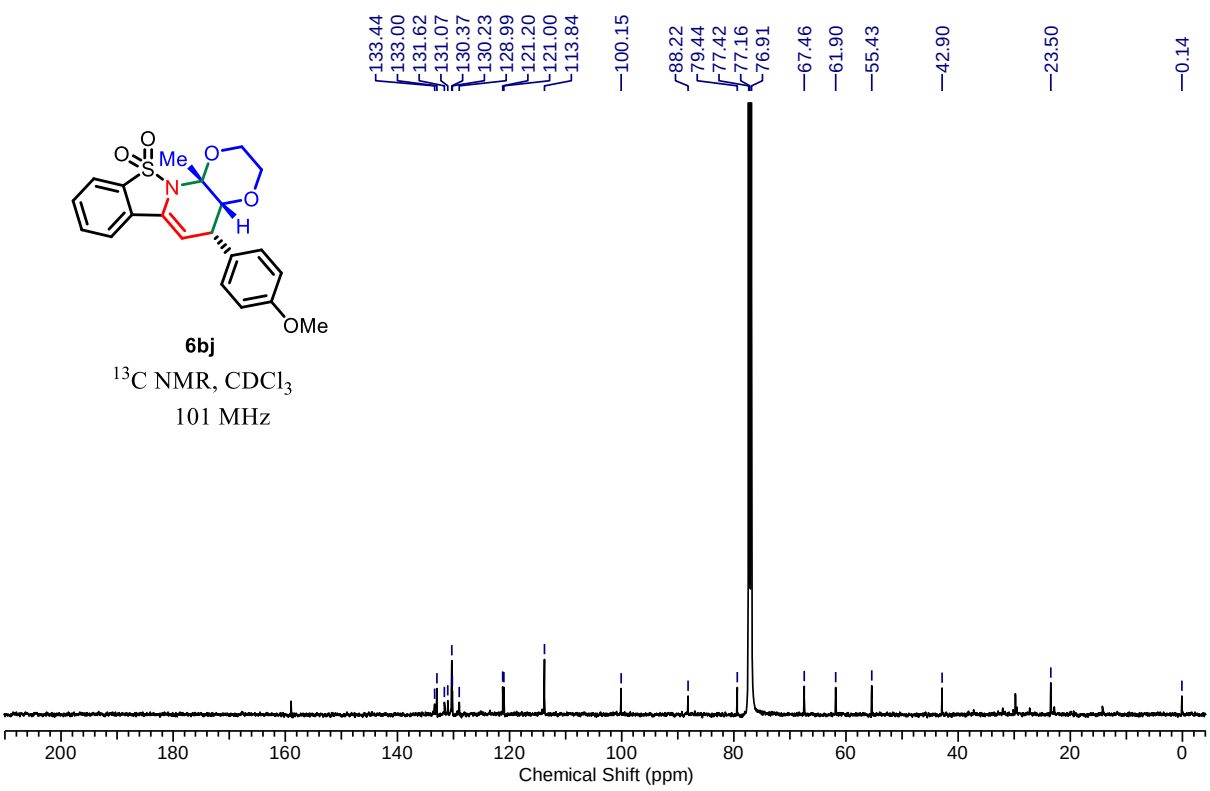
5-(4-Methoxyphenyl)-12a-methyl-2,3,4a,12a-tetrahydro-5*H*-benzo[4,5]isothiazolo[2,3-a][1,4]dioxino[2,3-e]pyridine 11,11-dioxide (6bj):



6bj

^{1}H NMR, $CDCl_3$

400 MHz

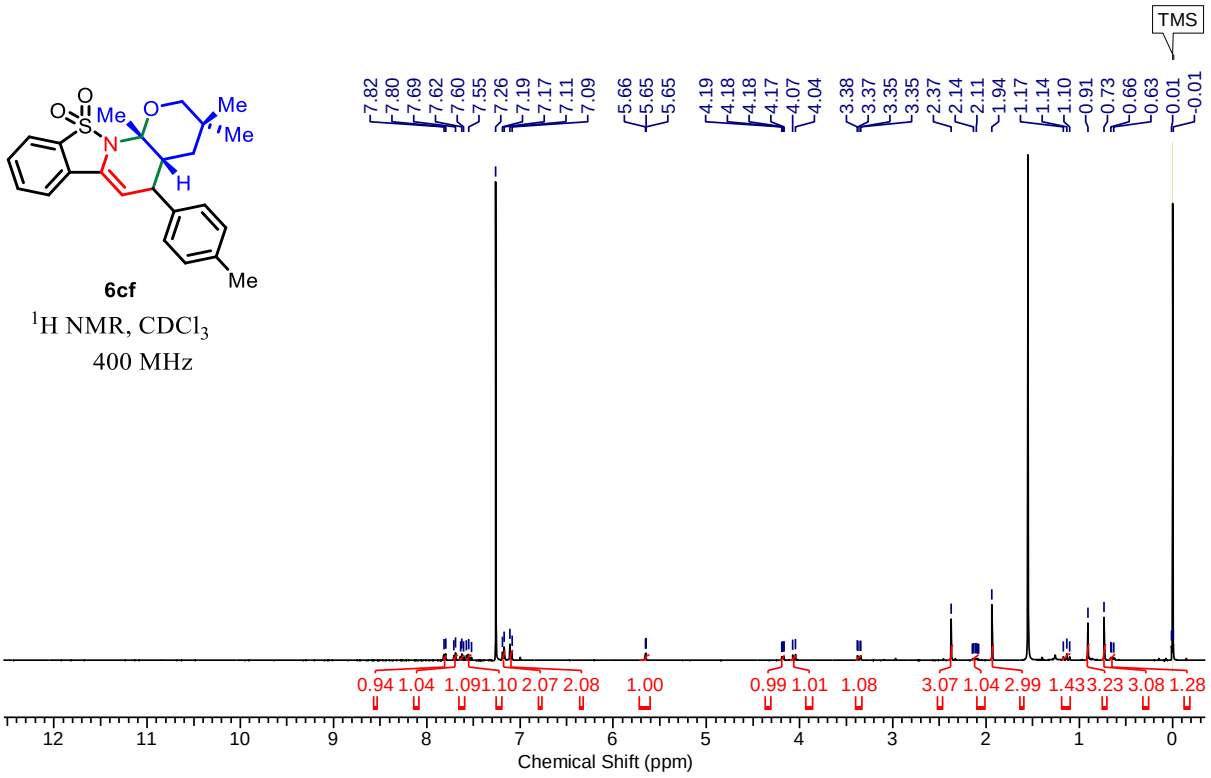


6bj

^{13}C NMR, $CDCl_3$

101 MHz

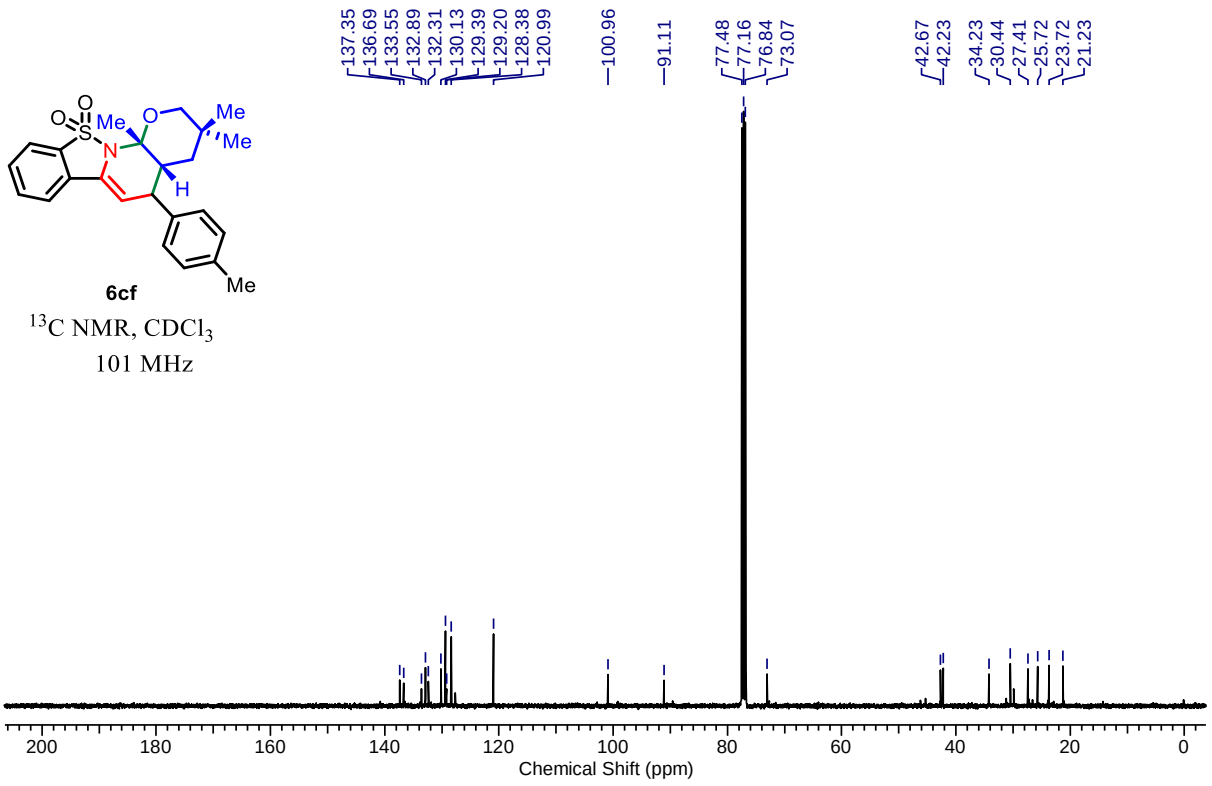
3,3,12a-Trimethyl-5-(p-tolyl)-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (6cf):



6cf

^{1}H NMR, $CDCl_3$

400 MHz

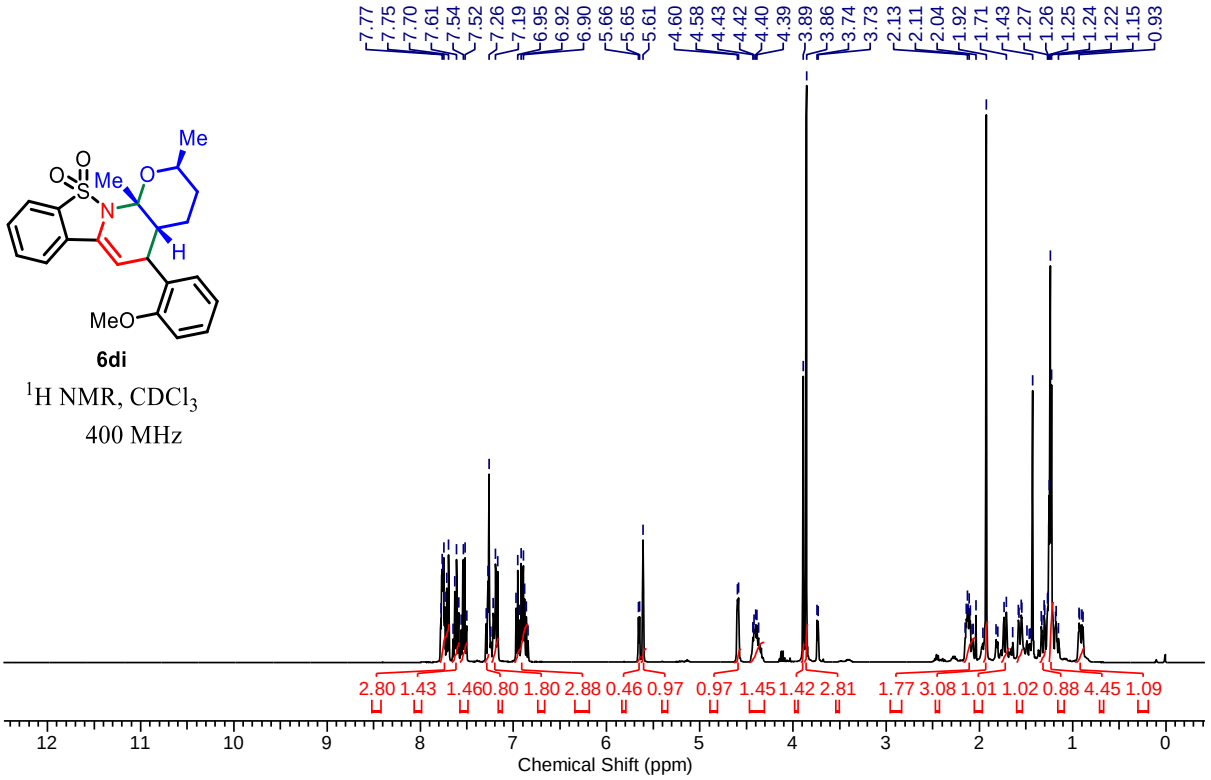


6cf

^{13}C NMR, $CDCl_3$

101 MHz

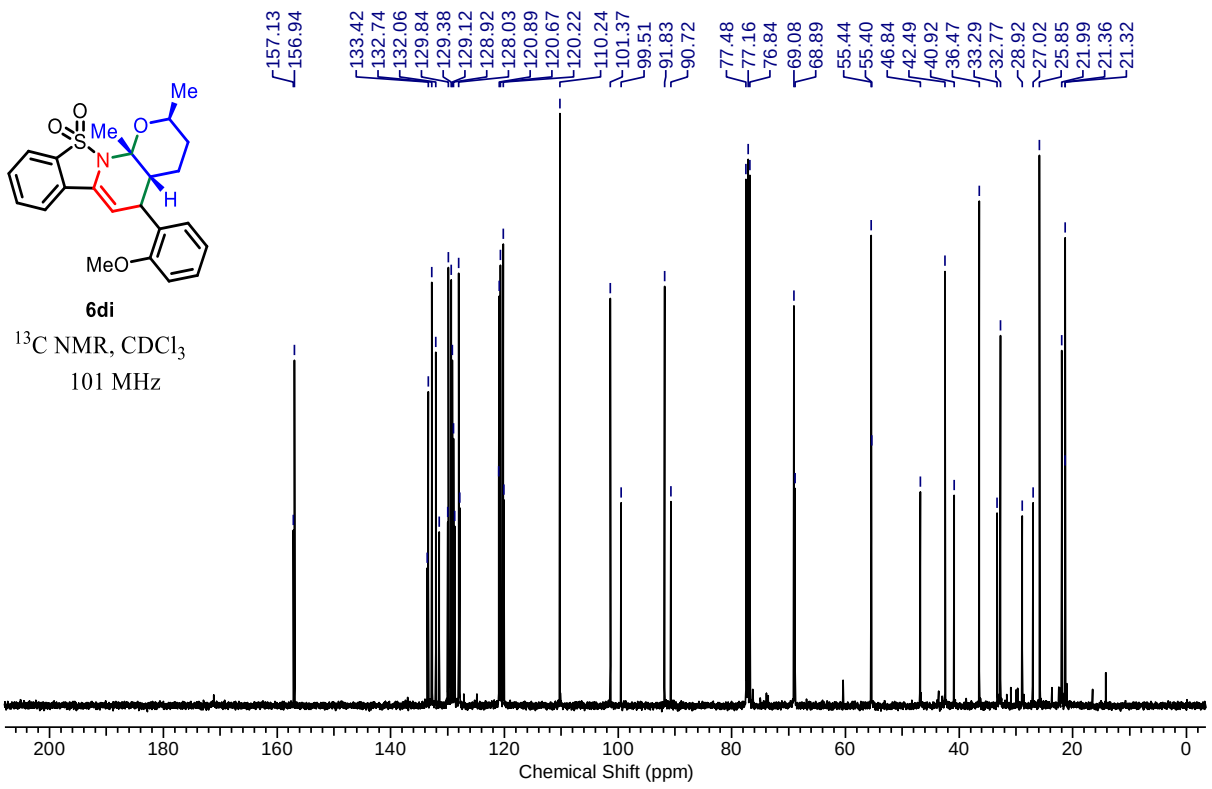
5-(2-Methoxyphenyl)-2,12a-dimethyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (6di):



6di

^{1}H NMR, $CDCl_3$

400 MHz

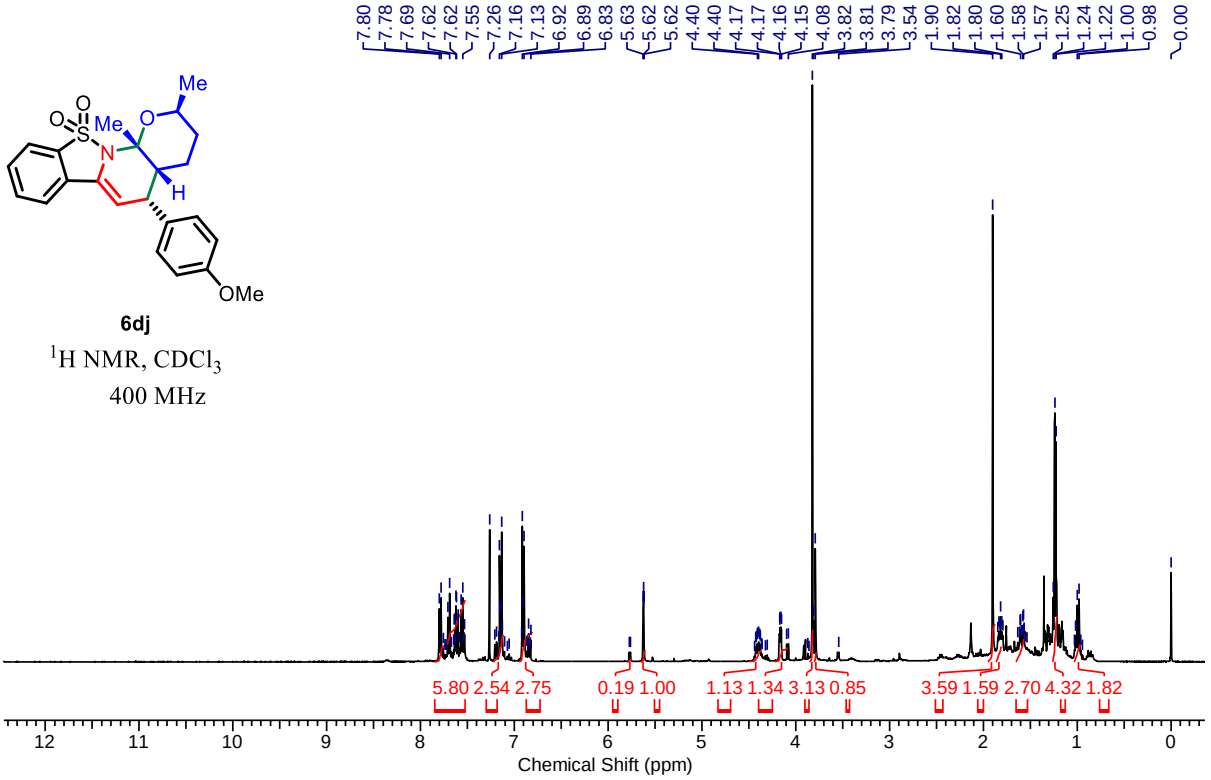


6di

^{13}C NMR, $CDCl_3$

101 MHz

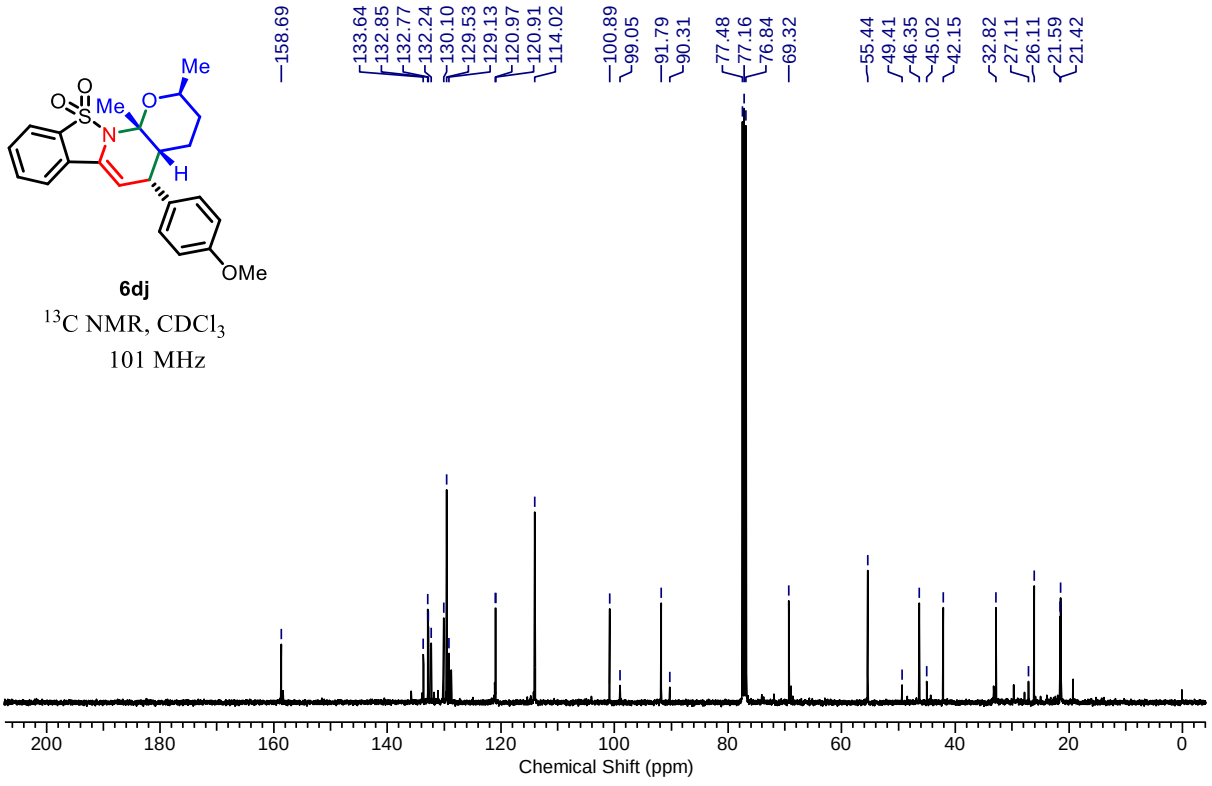
5-(2-Methoxyphenyl)-2,12a-dimethyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (6dj):



6dj

^{1}H NMR, $CDCl_3$

400 MHz

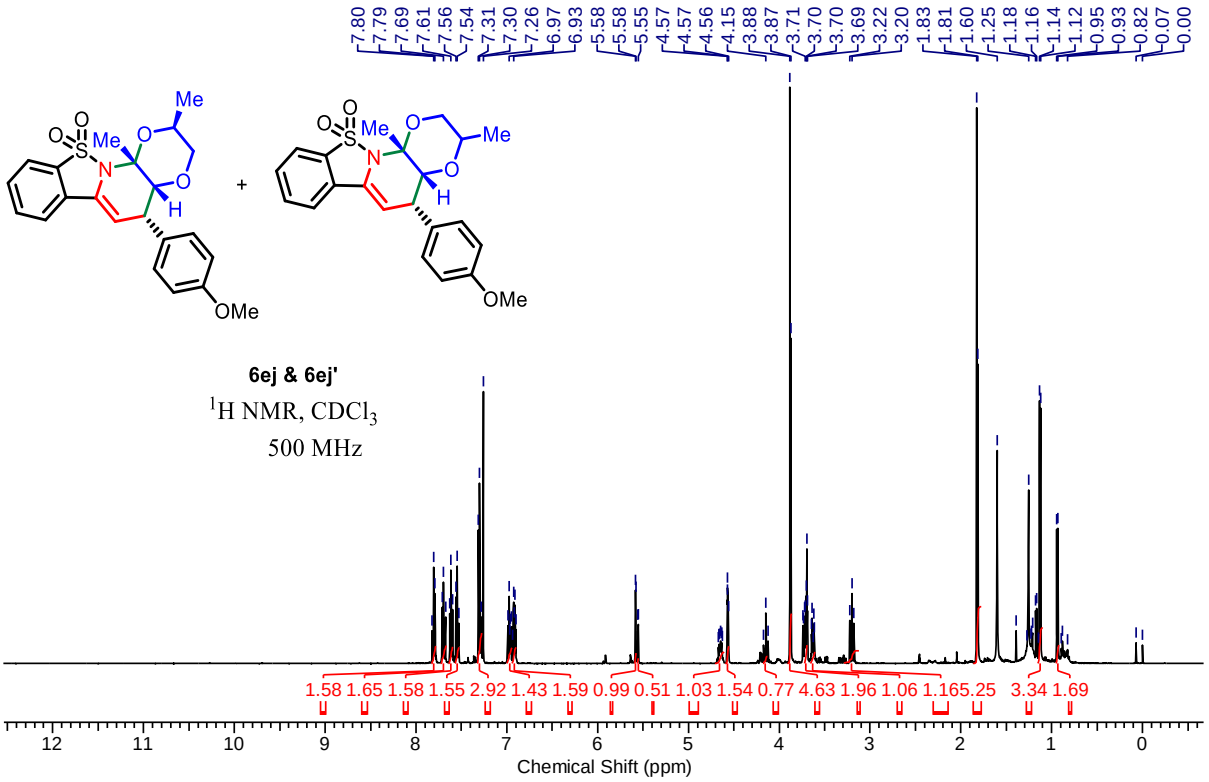


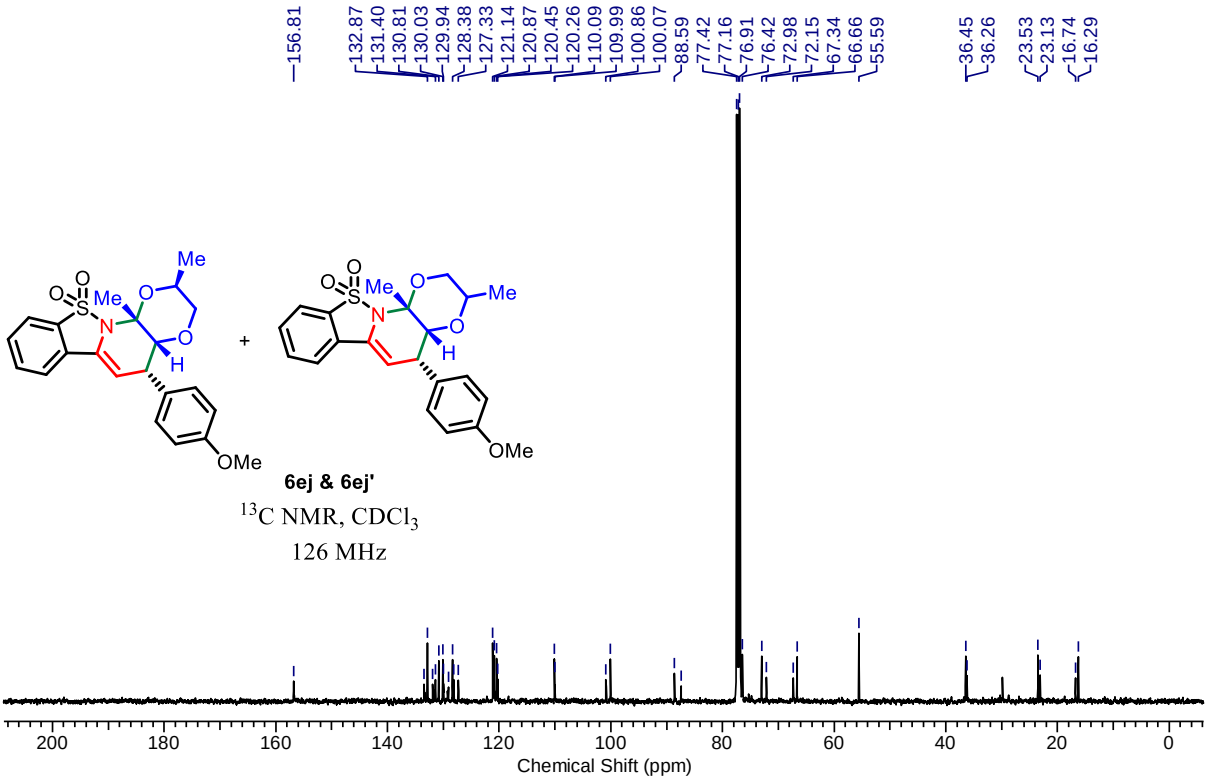
6dj

^{13}C NMR, $CDCl_3$

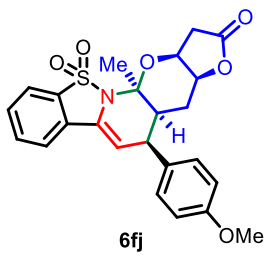
101 MHz

5-(4-Methoxyphenyl)-2,12a-dimethyl-2,3,4a,12a-tetrahydro-5*H*-benzo[4,5]isothiazolo [2,3-a][1,4]dioxino[2,3-e]pyridine 11,11-dioxide and 5-(4-methoxyphenyl)-3,12a-dimethyl -2,3,4a,12a-tetrahydro-5*H*-benzo[4,5]isothiazolo[2,3-a][1,4]dioxino[2,3-e]pyridine 11,11-dioxide (6ej & 6ej')



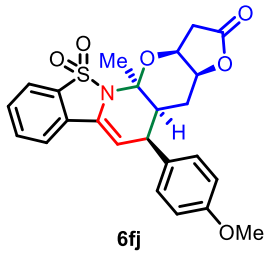


5-(4-Methoxyphenyl)-12a-methyl-1,3a,4,4a,12a,13a-hexahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-*a*]furo[2',3':5,6]pyrano[3,2-*e*]pyridin-2-one 11,11-dioxide (6fj):



6fj

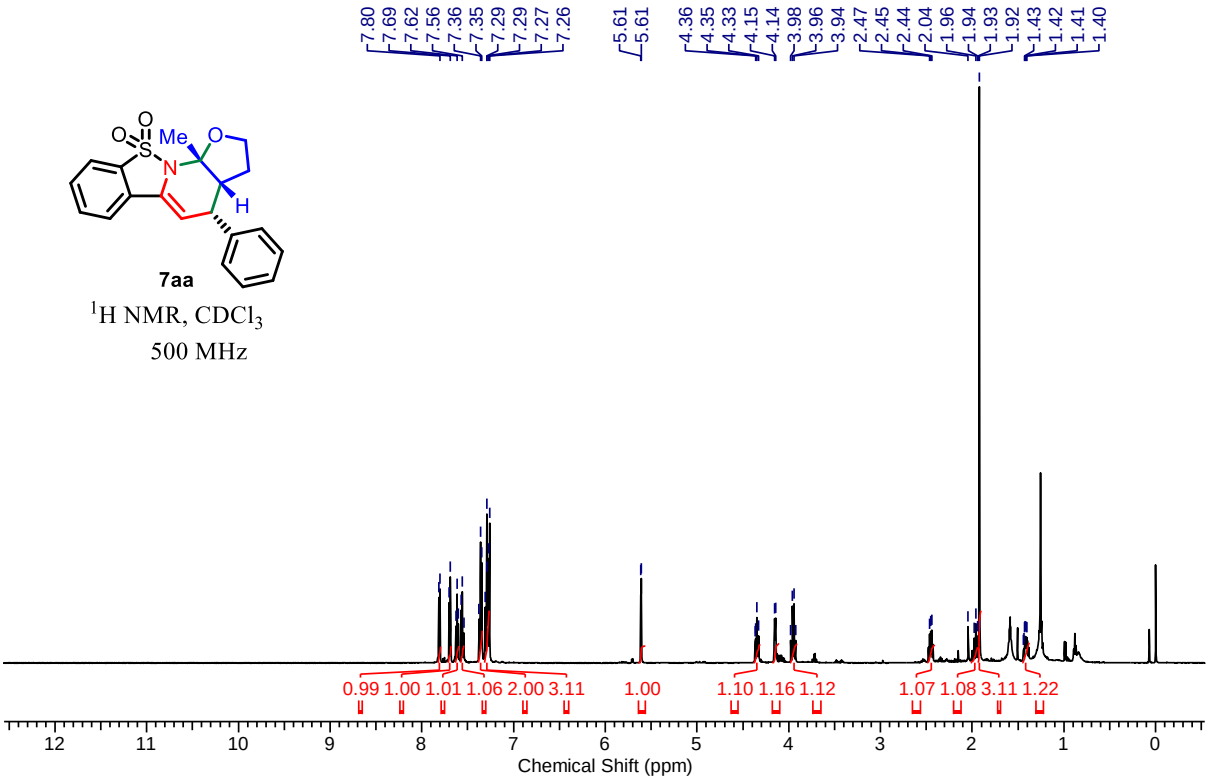
^{1}H NMR, $CDCl_3$
400 MHz



6fj

^{13}C NMR, $CDCl_3$
101 MHz

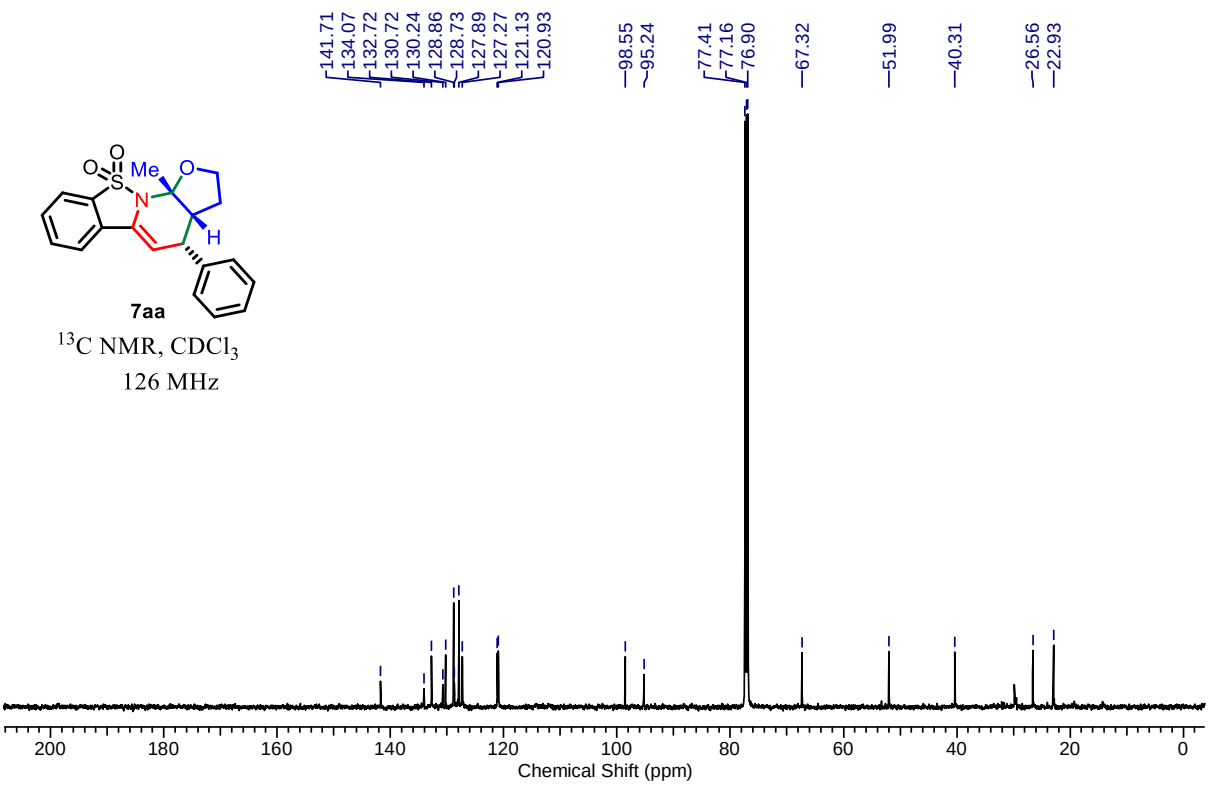
1a-Methyl-4-phenyl-2,3,3a,11a-tetrahydro-4*H*-benzo[4,5]isothiazolo[2,3-a]furo[3,2-e]pyridine 10,10-dioxide (7aa)



7aa

^{1}H NMR, $CDCl_3$

500 MHz

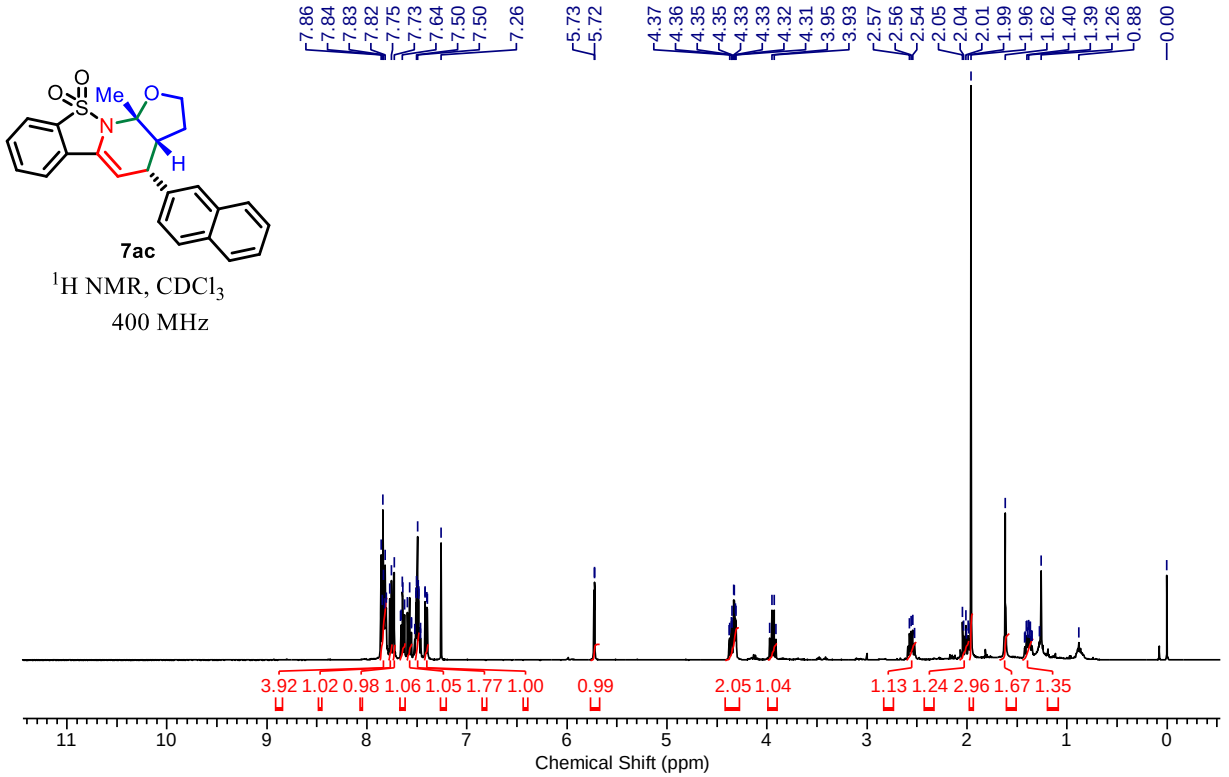


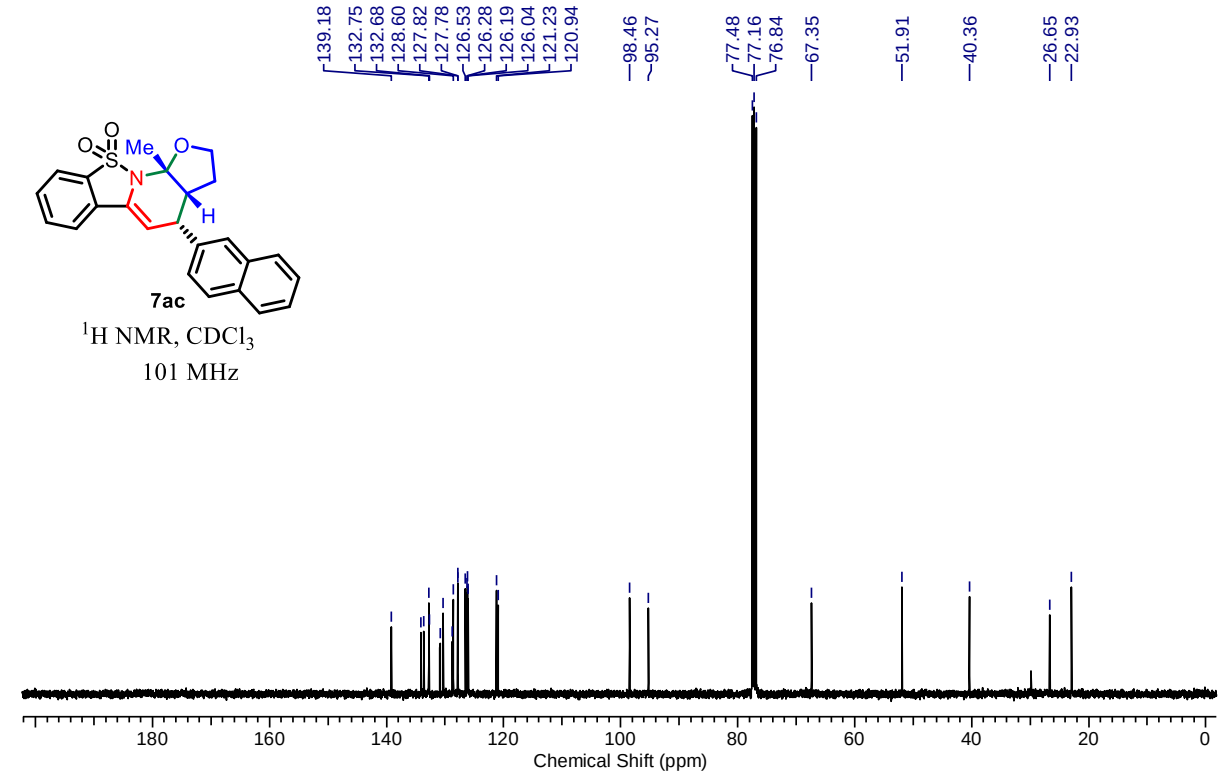
7aa

^{13}C NMR, $CDCl_3$

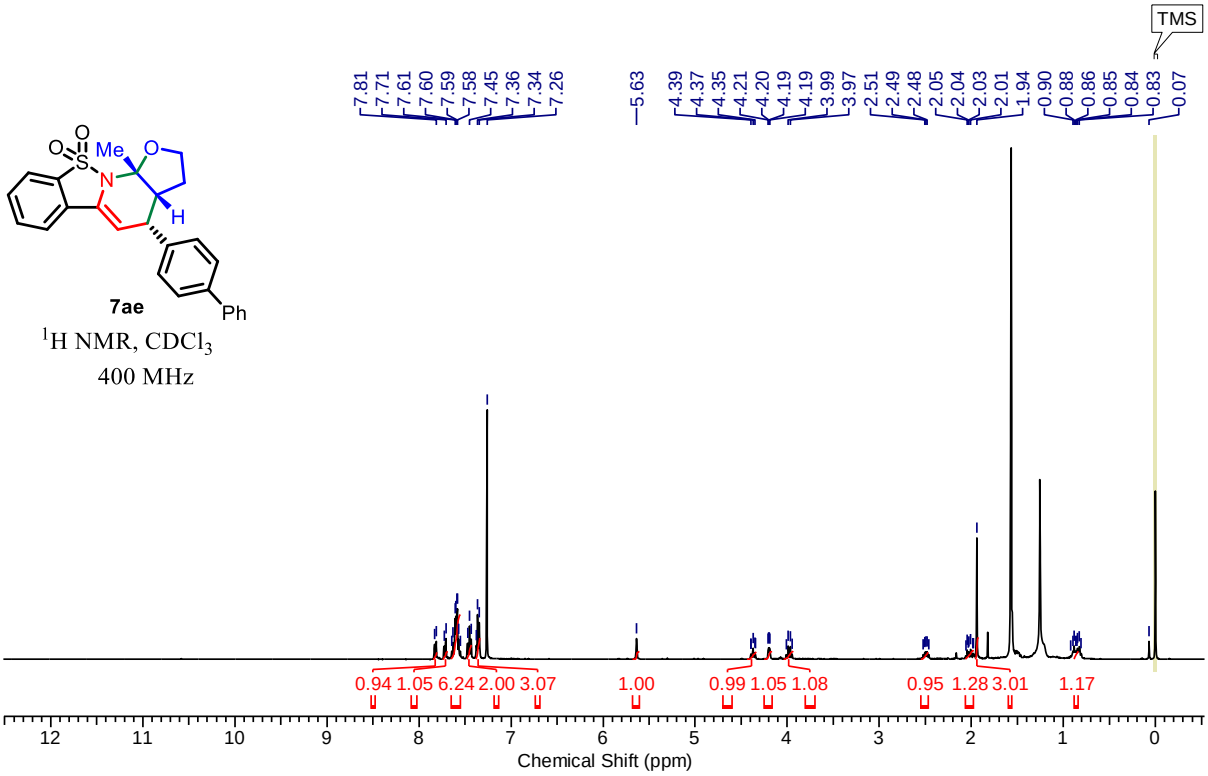
126 MHz

11a-Methyl-4-(naphthalen-2-yl)-2,3,3a,11a-tetrahydro-4*H*-benzo[4,5]isothiazolo[2,3-a]furo[3,2-e]pyridine 10,10-dioxide (7ac)





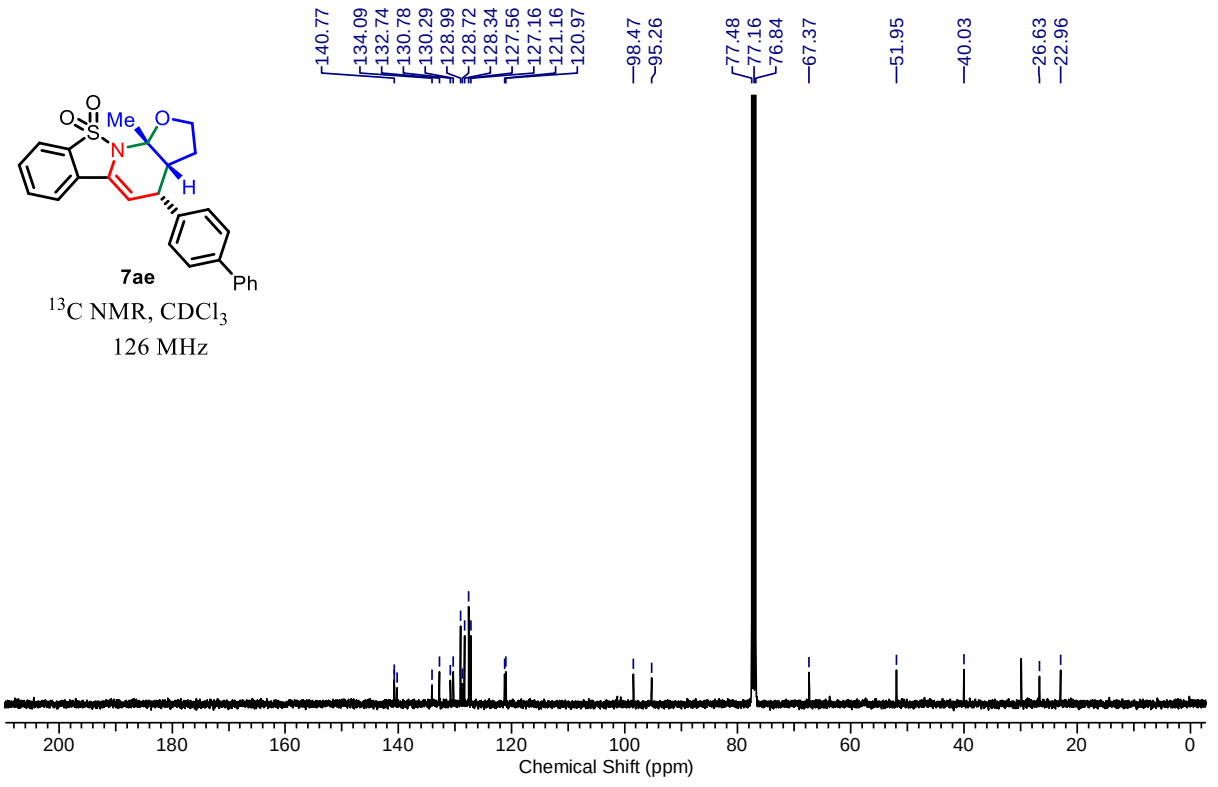
4-([1,1'-Biphenyl]-4-yl)-11a-methyl-2,3,3a,11a-tetrahydro-4*H*-benzo[4,5]isothiazolo[2,3-a]furo[3,2-e]pyridine 10,10-dioxide (7ae)



7ae

^{1}H NMR, $CDCl_3$

400 MHz

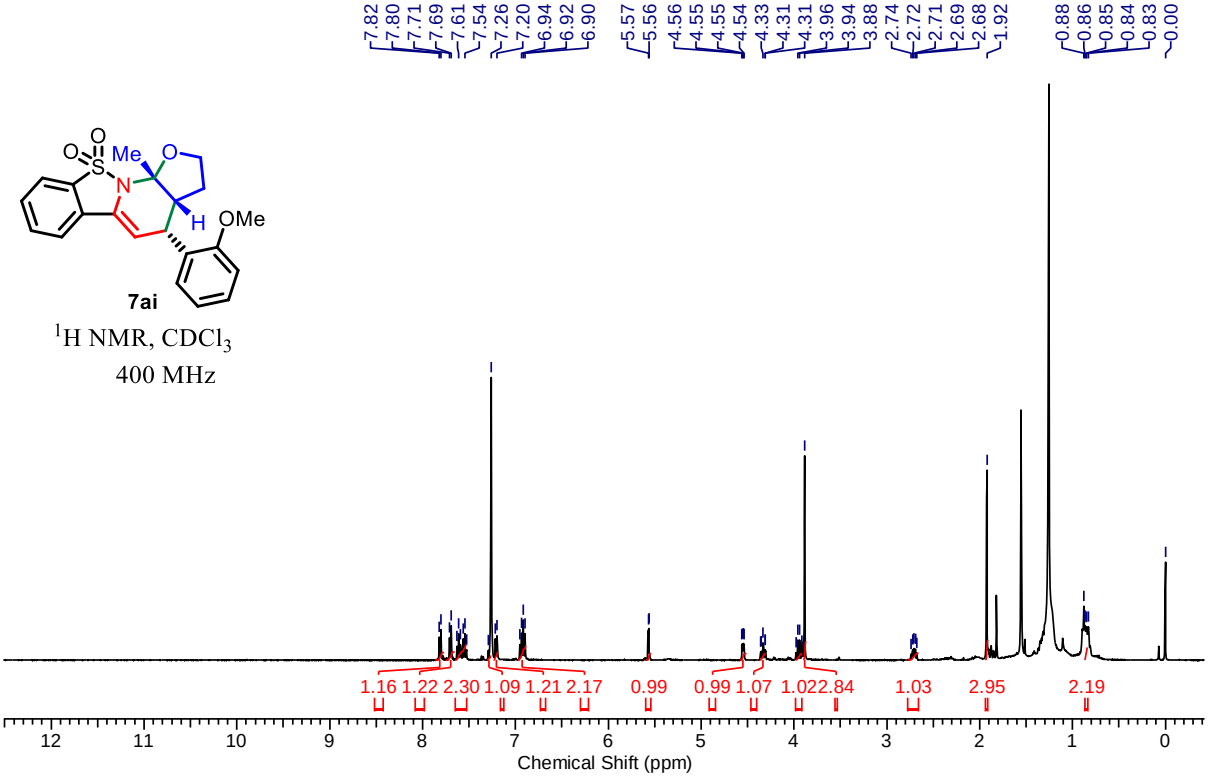


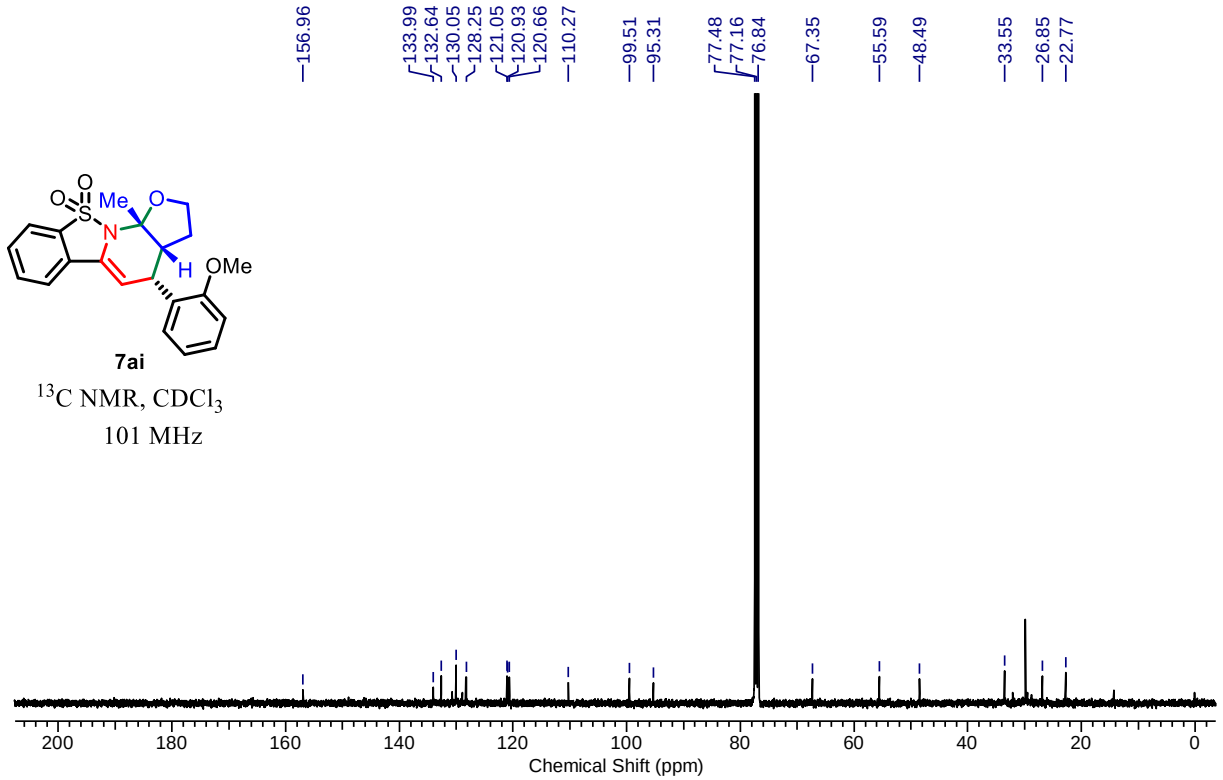
7ae

^{13}C NMR, $CDCl_3$

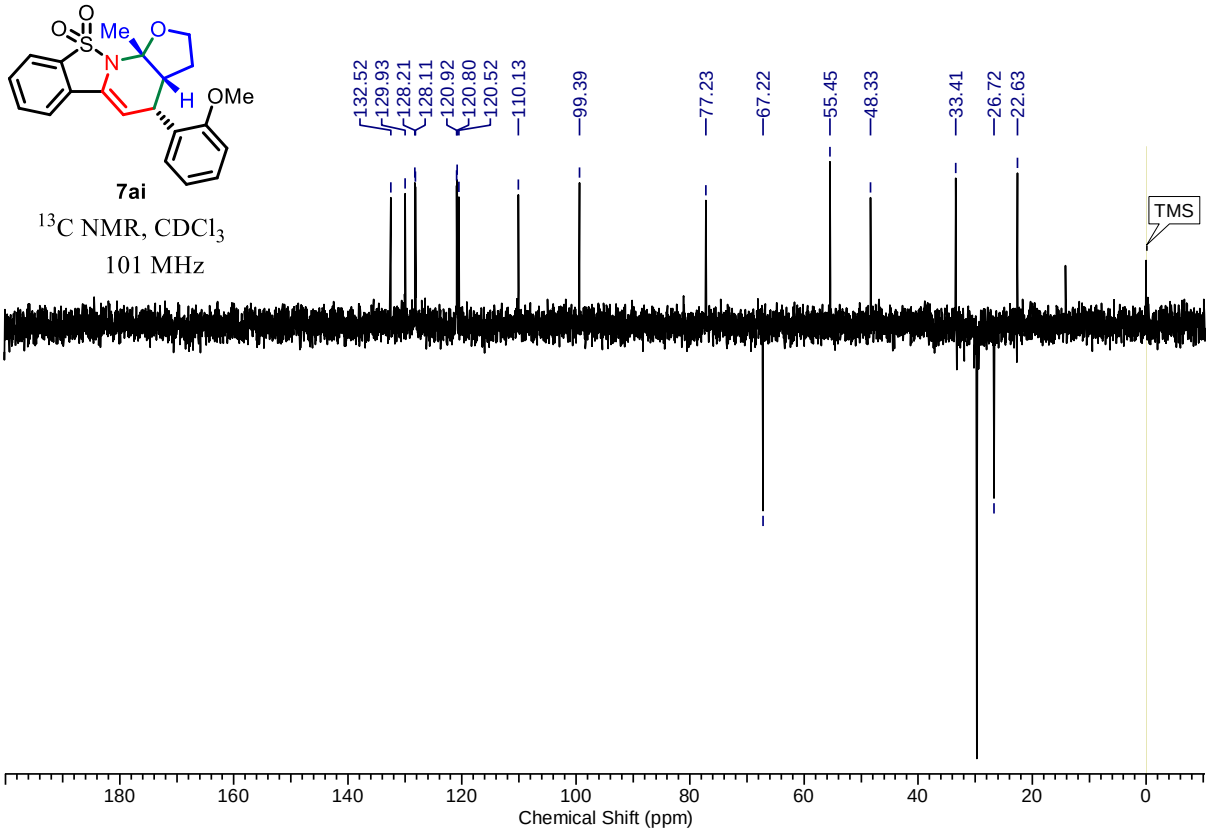
126 MHz

4-(2-Methoxyphenyl)-11a-methyl-2,3,3a,11a-tetrahydro-4*H*-benzo[4,5]isothiazolo[2,3-a]furo[3,2-e]pyridine 10,10-dioxide (7ai)

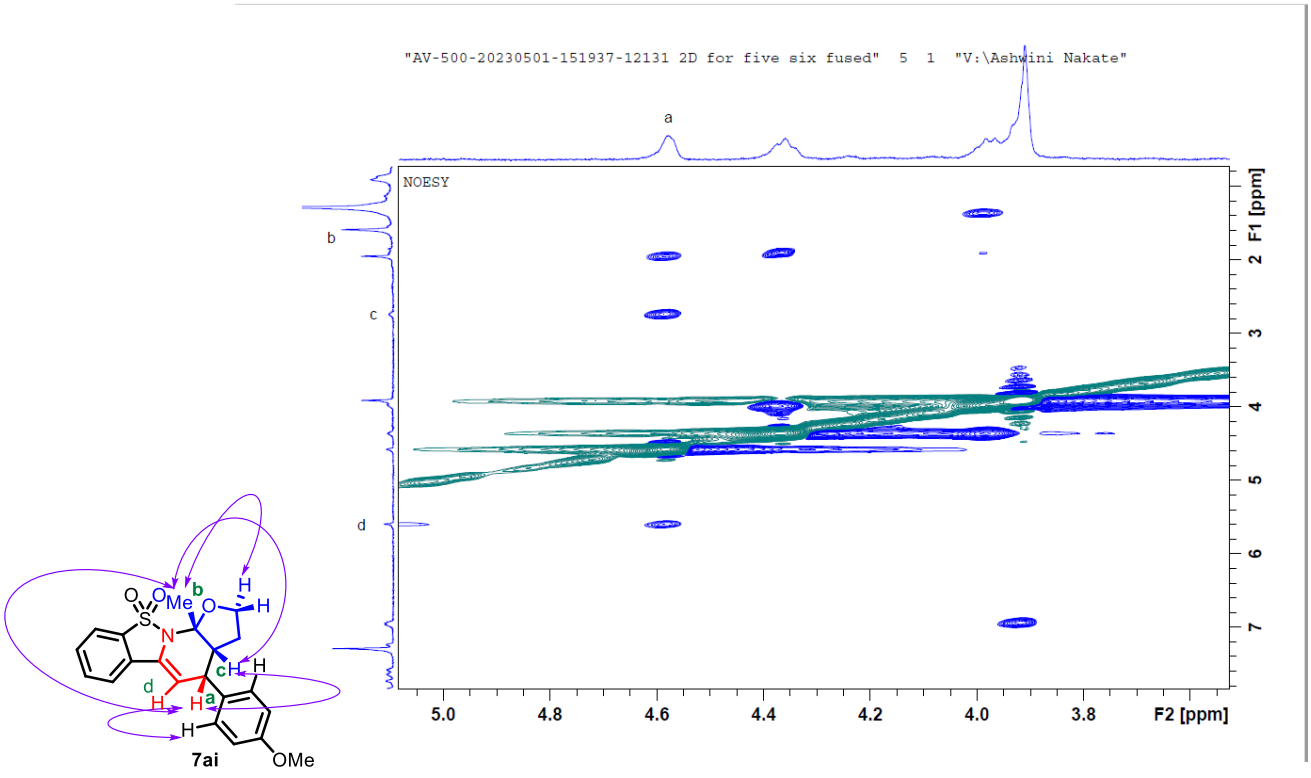




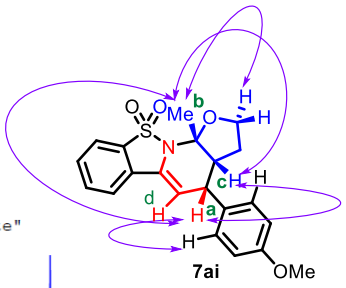
4-(2-Methoxyphenyl)-11a-methyl-2,3,3a,11a-tetrahydro-4*H*-benzo[4,5]isothiazolo[2,3-a]furo[3,2-e]pyridine 10,10-dioxide (7ai)

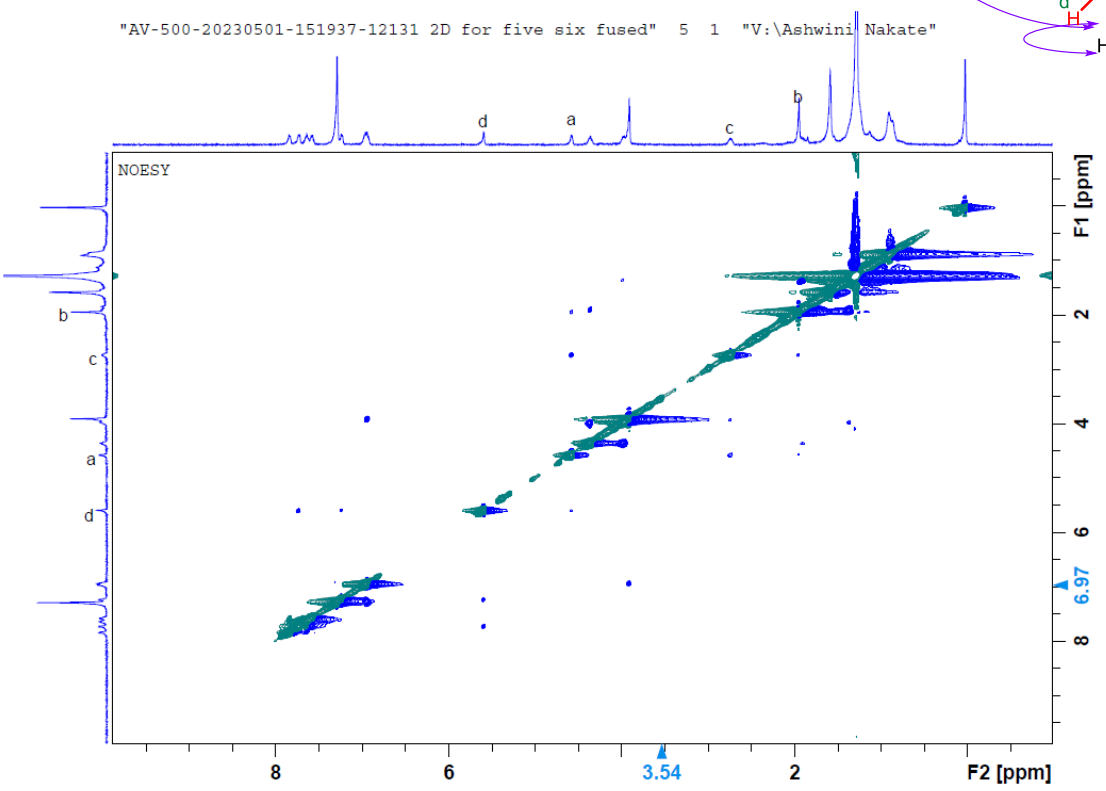


NOESY zoomed

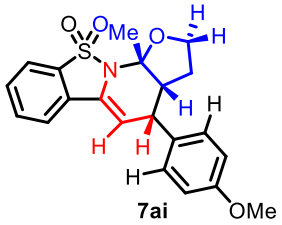


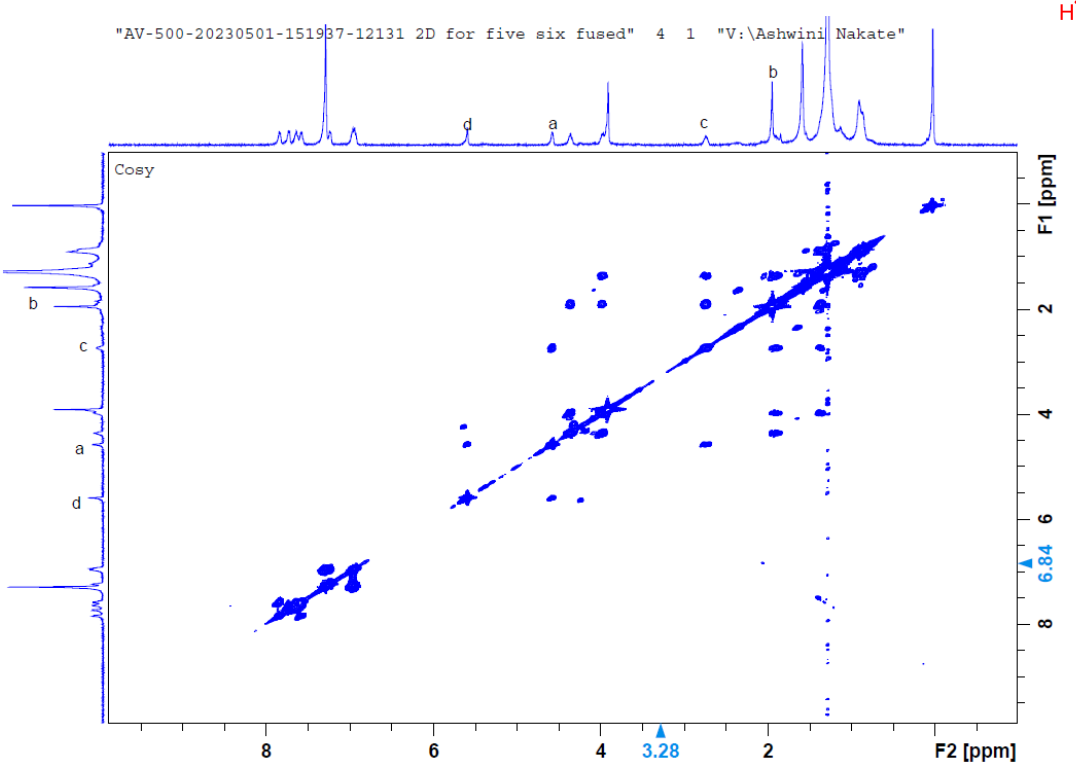
7ai: NOESY



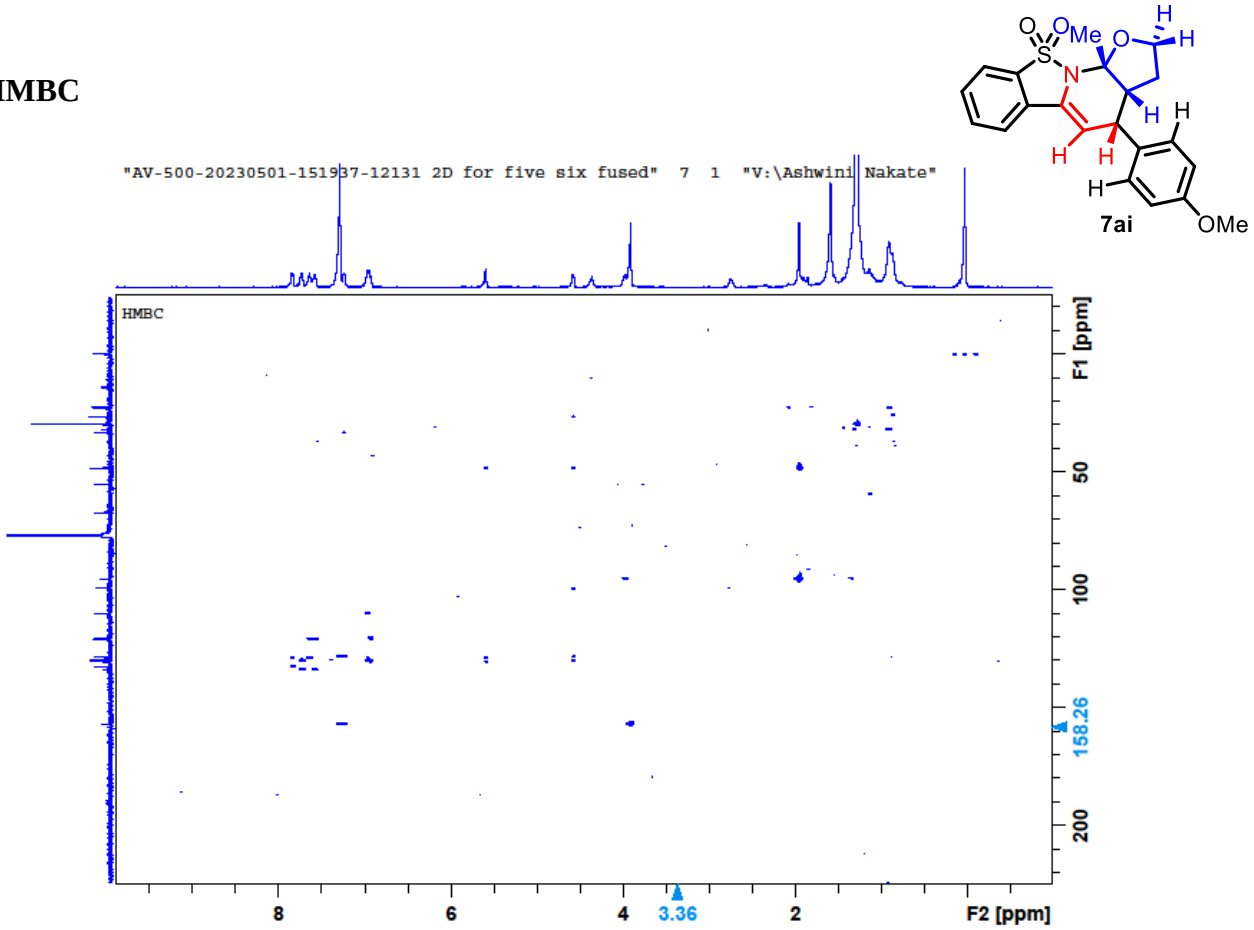


7ai: COSY

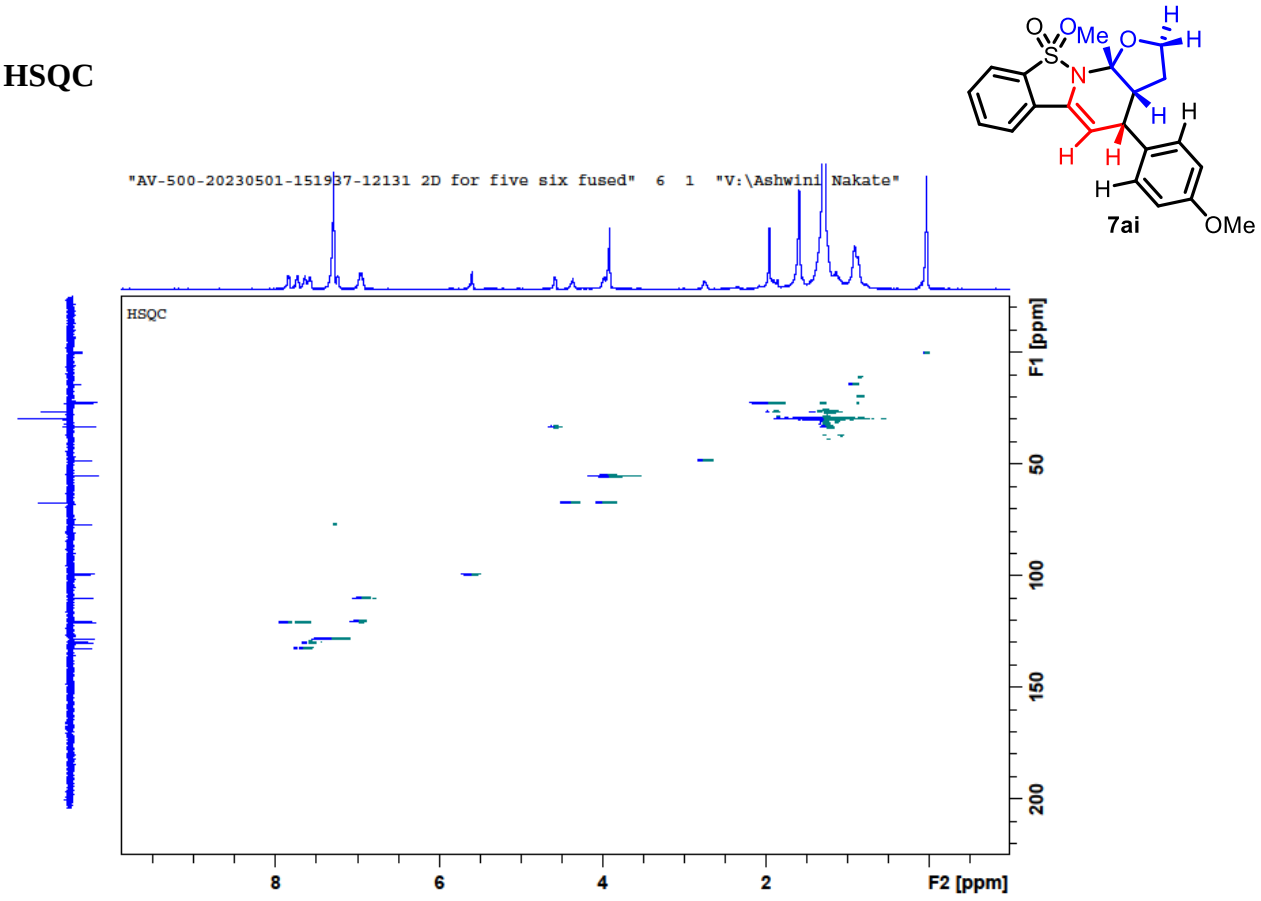




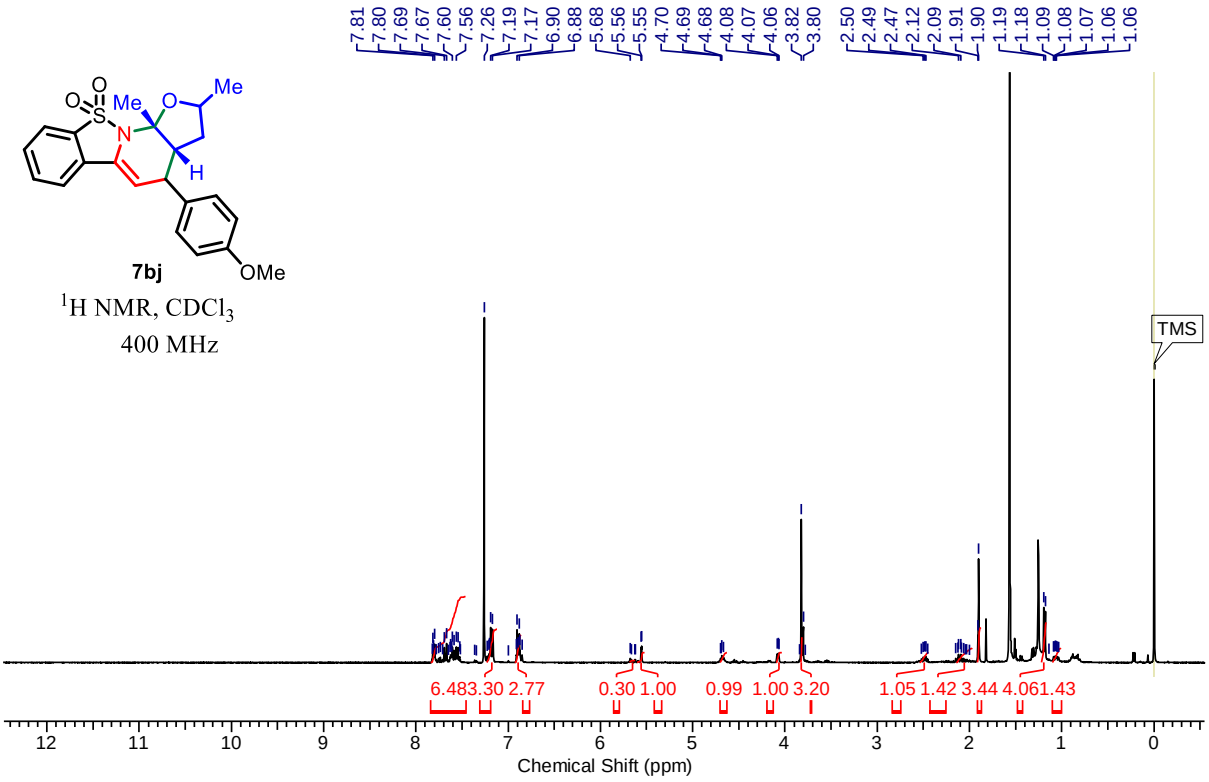
7ai:HMBC

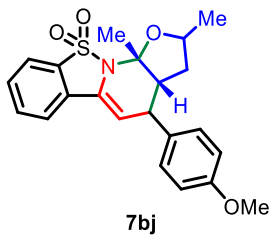


7ai: HSQC



4-(4-Methoxyphenyl)-2,11a-dimethyl-2,3,3a,11a-tetrahydro-4*H*-benzo[4,5]isothiazolo[2,3-a]furo[3,2-e]pyridine 10,10-dioxide (7bj):





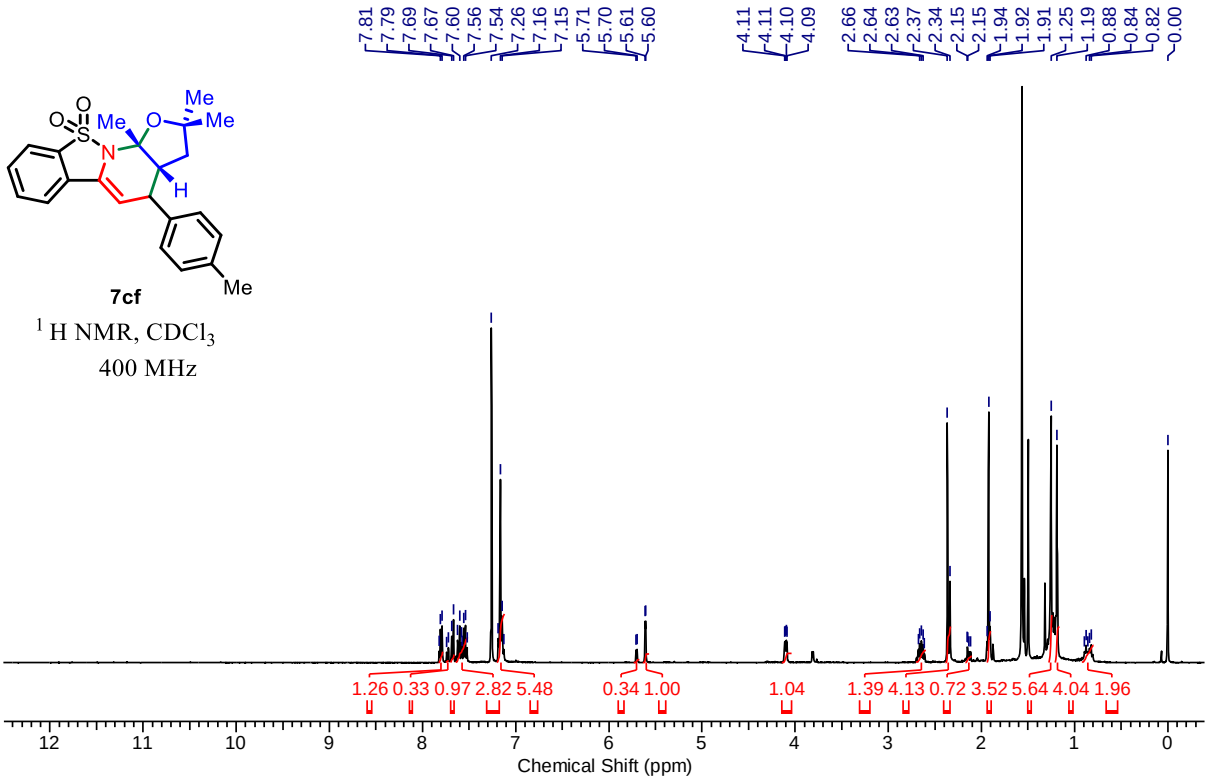
7bj

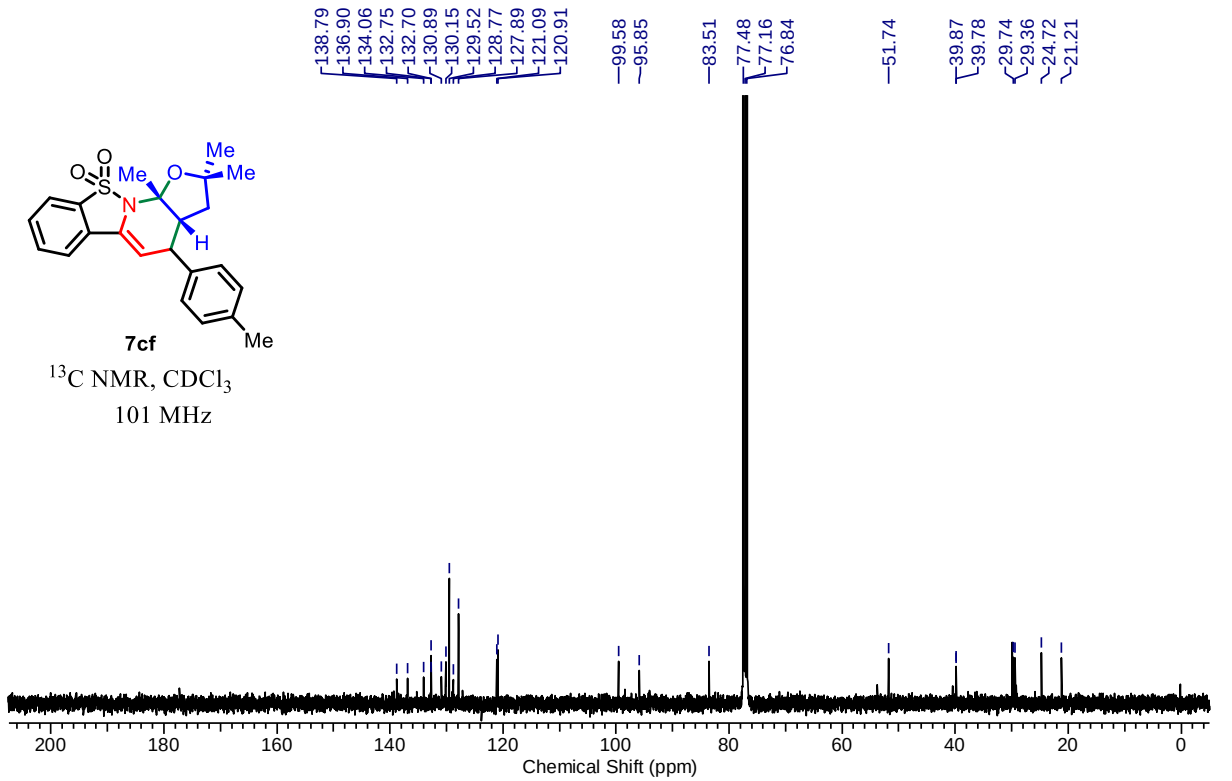
^{1}H NMR, $CDCl_3$
400 MHz

7bj

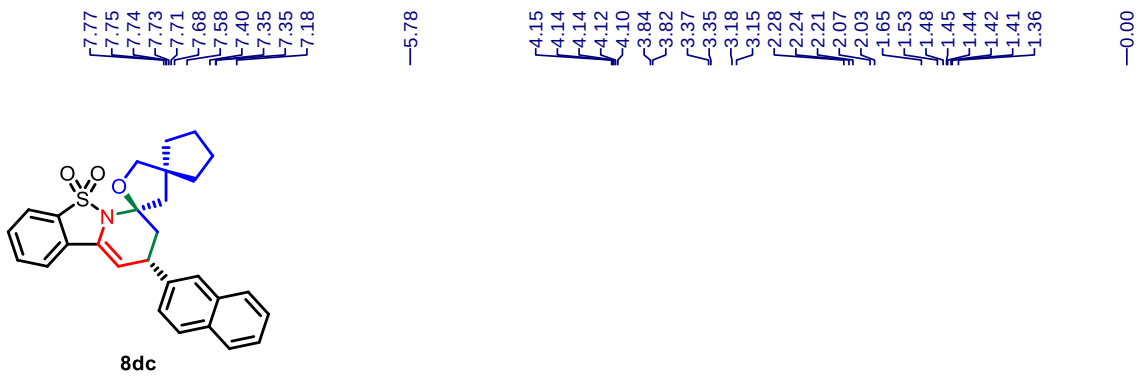
^{13}C NMR, $CDCl_3$
101 MHz

4-(4-Methoxyphenyl)-2,2,11a-trimethyl-2,3,3a,11a-tetrahydro-4*H*-benzo[4,5]isothiazolo[2,3-a]furo[3,2-e]pyridine 10,10-dioxide (7cf):





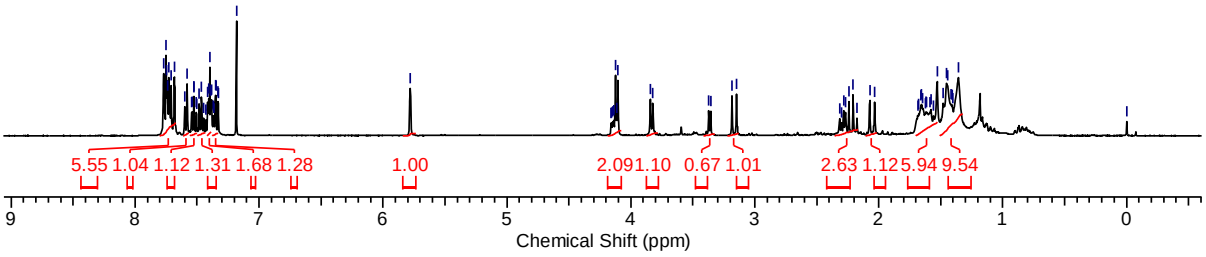
9-(Naphthalen-2-yl)-8,9-dihydro-3'*H*,5'*H*-dispiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan-4',1''-cyclopentane] 5,5-dioxide (8dc)

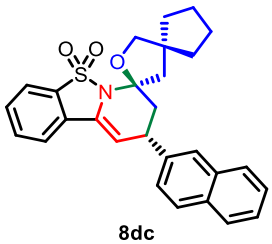


8dc

^{1}H NMR, $CDCl_3$

400 MHz

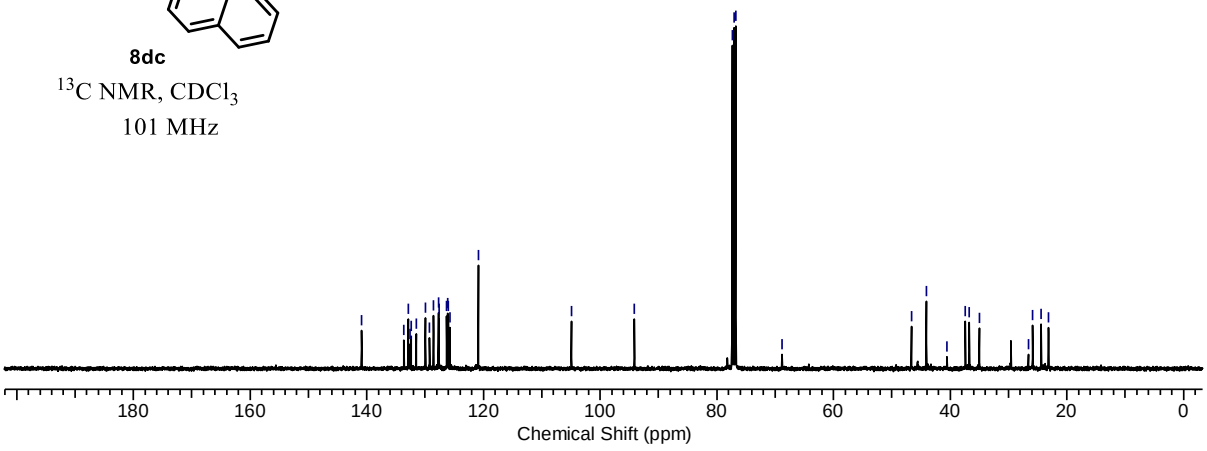




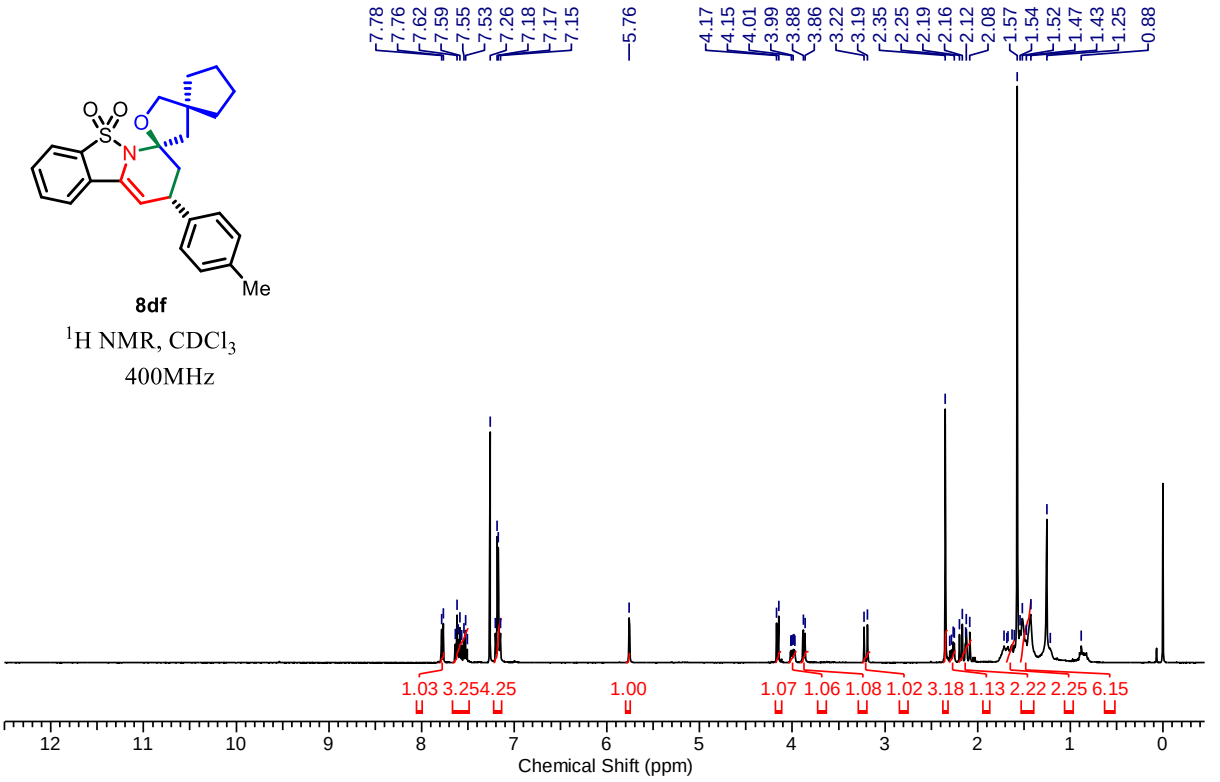
8dc

^{13}C NMR, $CDCl_3$

101 MHz



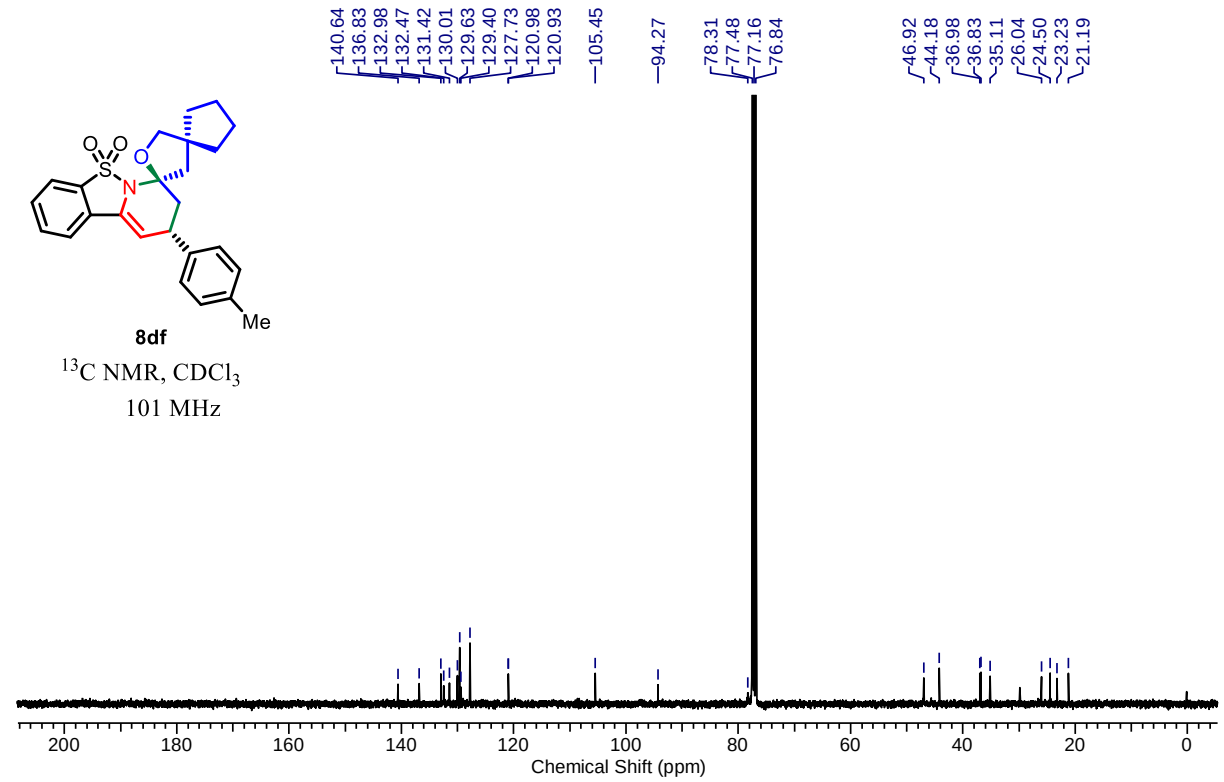
9-(*p*-Tolyl)-8,9-dihydro-3'*H*,5'*H*-dispiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan-4',1''-cyclopentane] 5,5-dioxide (8df):



8df

^{1}H NMR, $CDCl_3$

400MHz

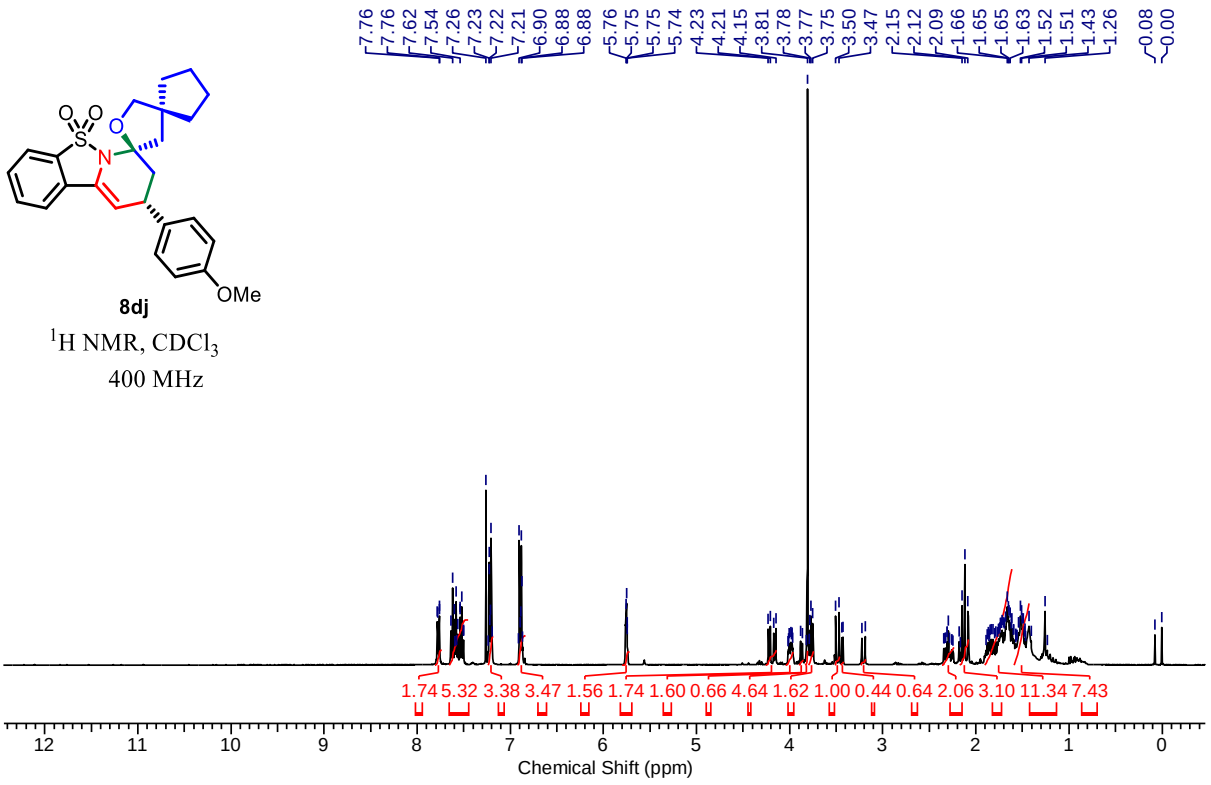


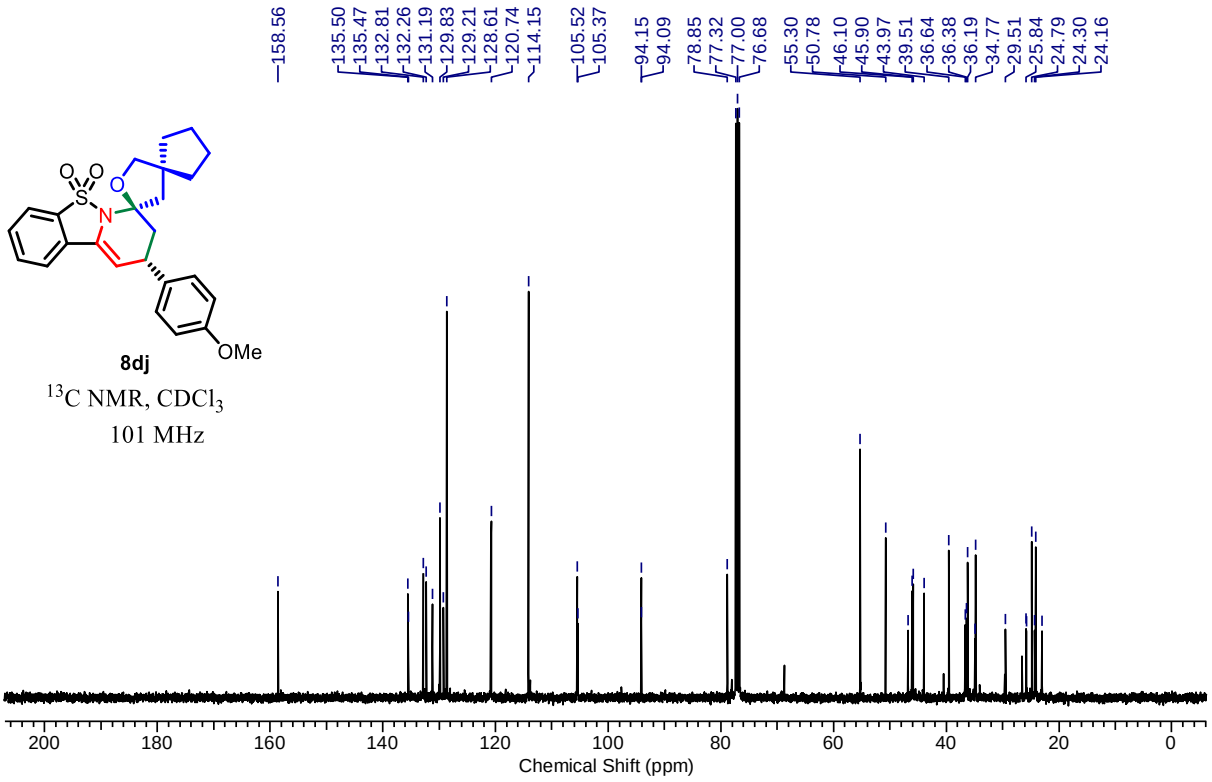
8df

^{13}C NMR, $CDCl_3$

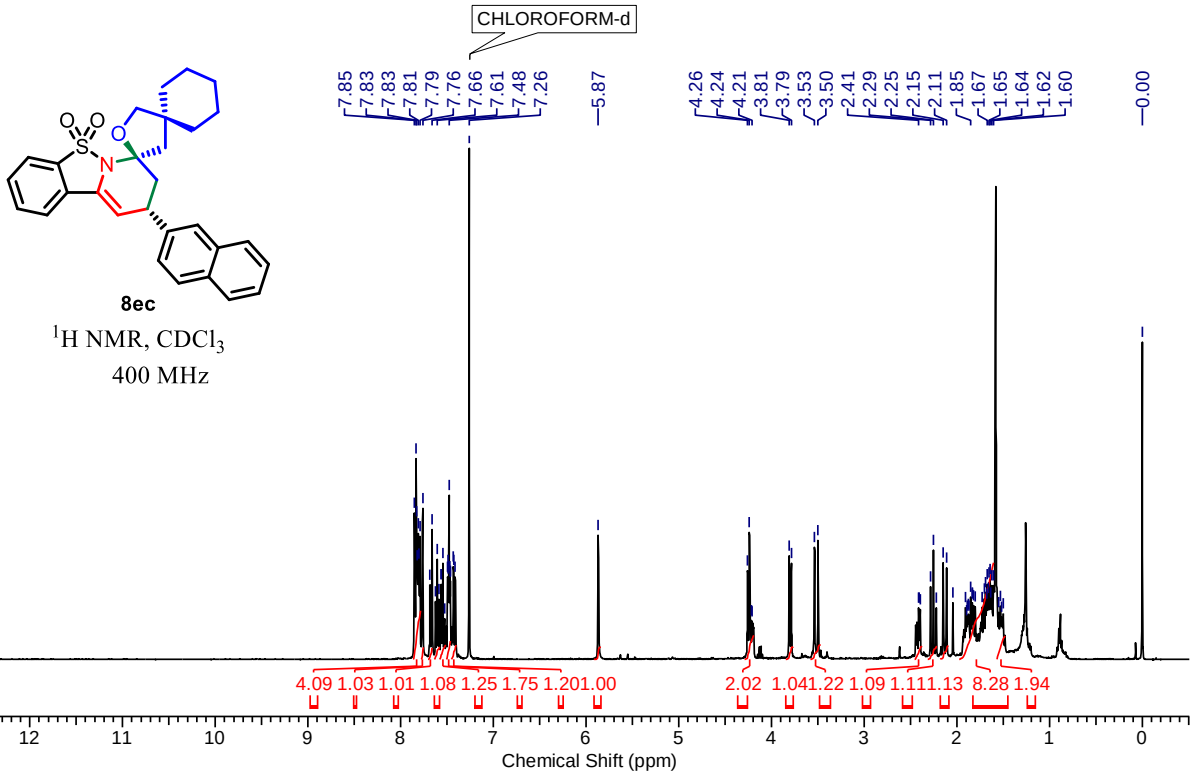
101 MHz

9-(4-Methoxyphenyl)-8,9-dihydro-3'*H*,5'*H*-dispiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan-4',1''-cyclopentane] 5,5-dioxide (8dj):





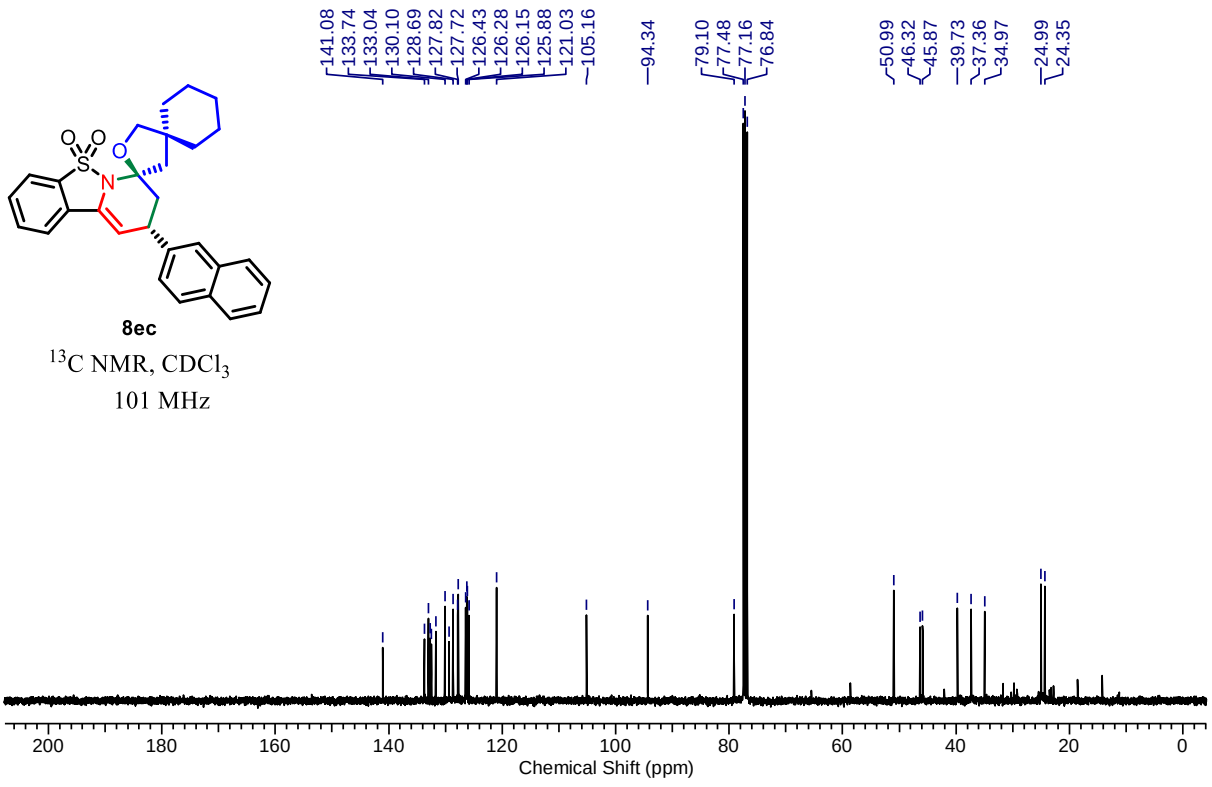
9-(Naphthalen-2-yl)-8,9-dihydro-3'*H*,5'*H*-dispiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan-4',1''-cyclohexane] 5,5-dioxide (8ec):



8ec

^{1}H NMR, $CDCl_3$

400 MHz

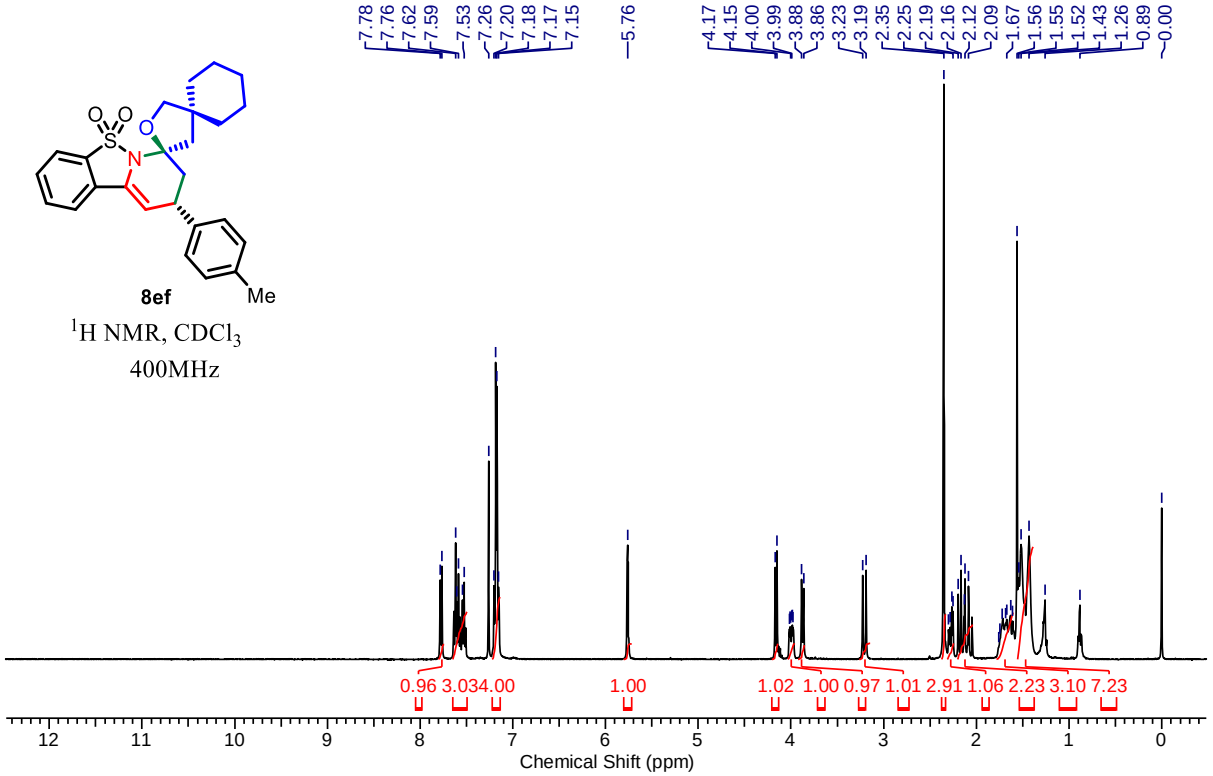


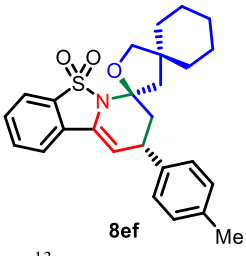
8ec

^{13}C NMR, $CDCl_3$

101 MHz

9-(*p*-Tolyl)-8,9-dihydro-3'*H*,5'*H*-dispiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan-4',1''-cyclohexane] 5,5-dioxide (8ef):

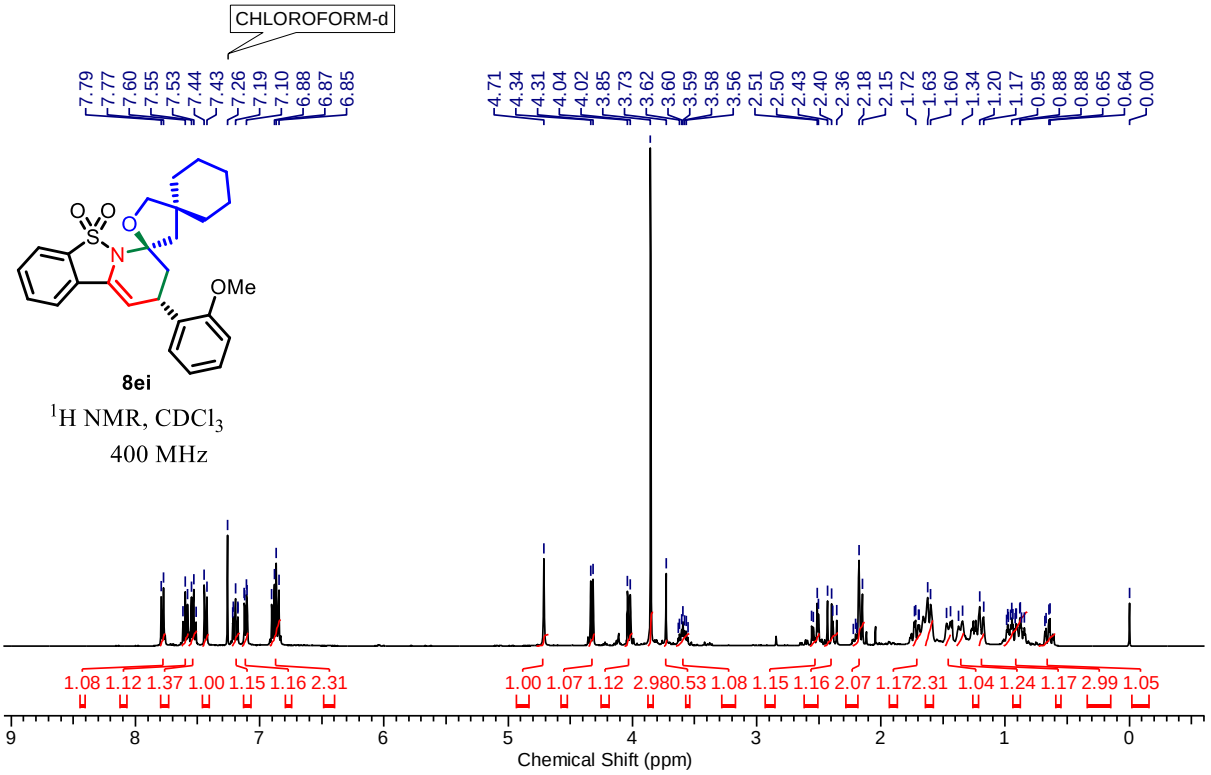


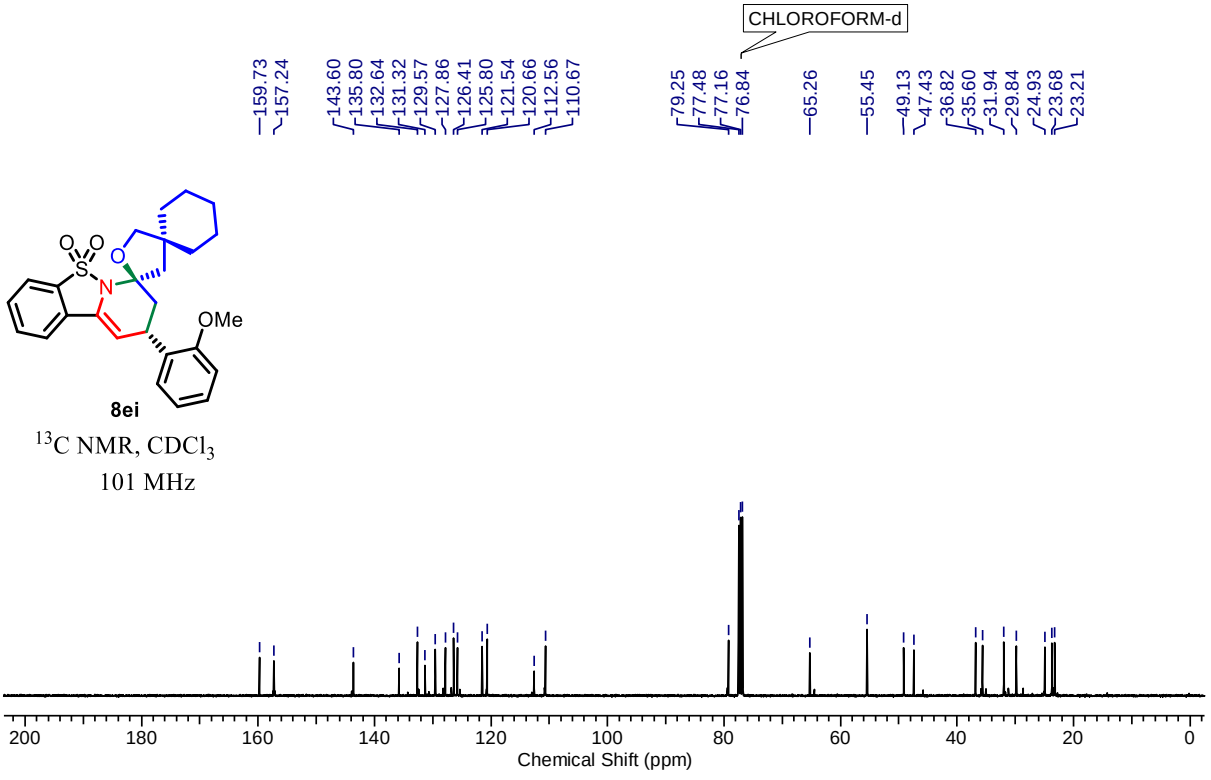


^{1}H NMR, $CDCl_3$
400MHz

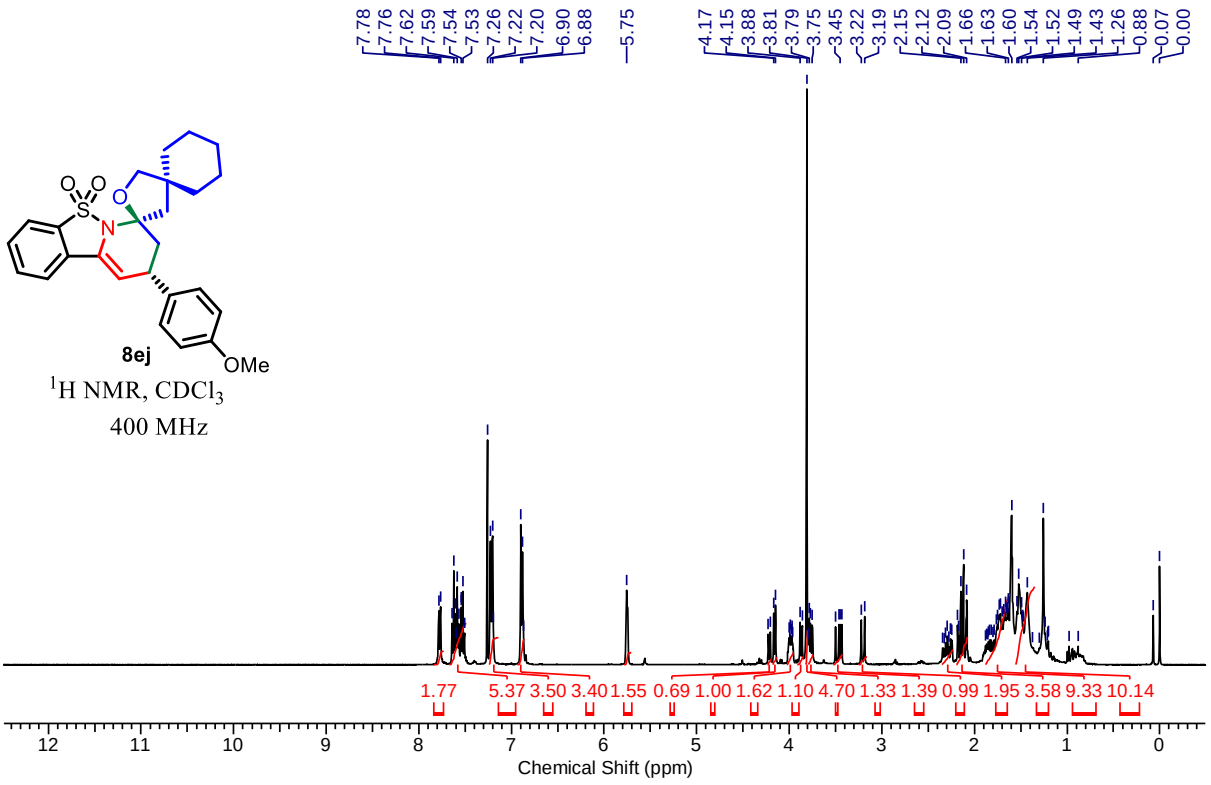
^{13}C NMR, $CDCl_3$
101MHz

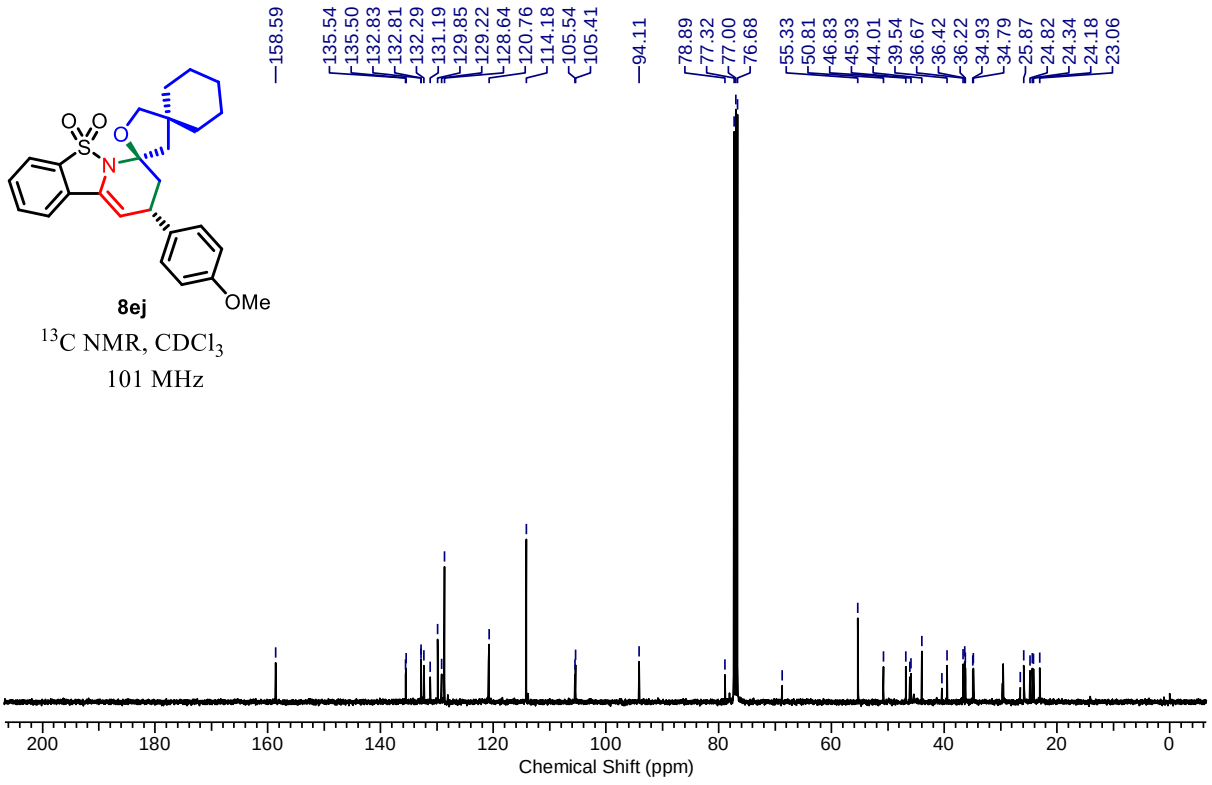
9-(2-Methoxyphenyl)-8,9-dihydro-3'*H*,5'*H*-dispiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan-4',1''-cyclohexane] 5,5-dioxide (8ei):



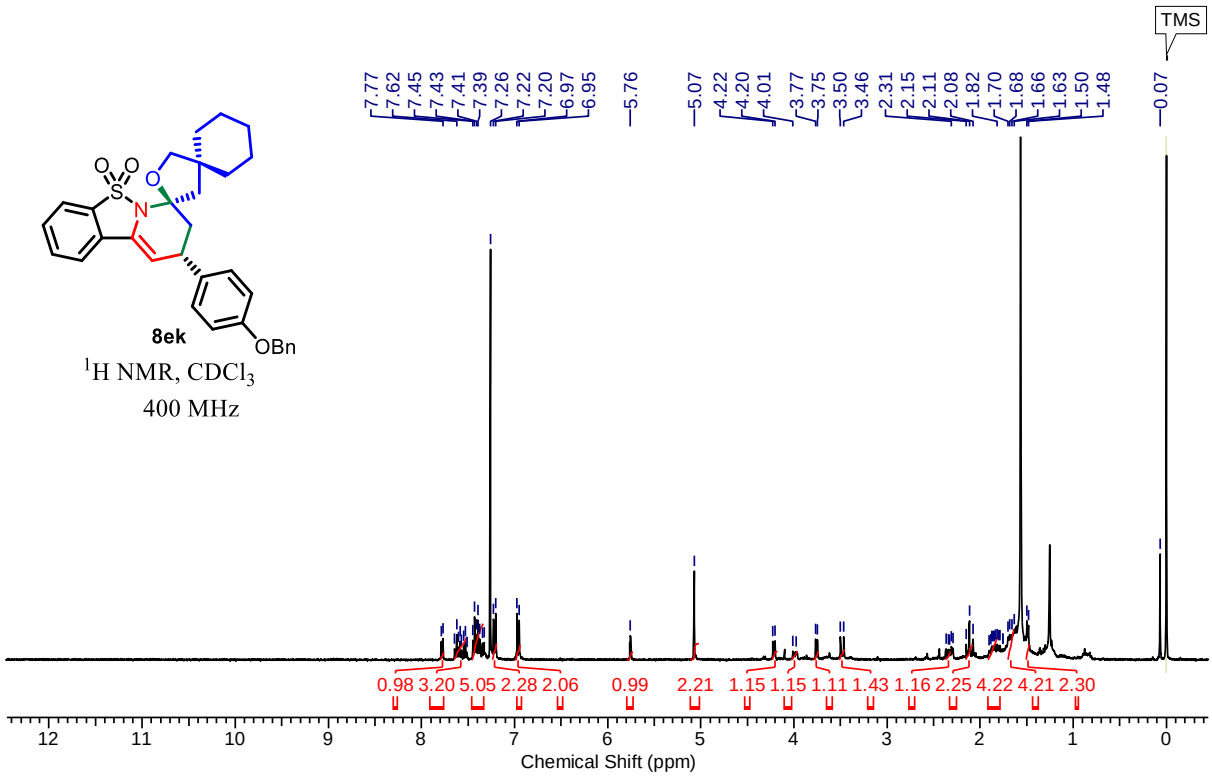


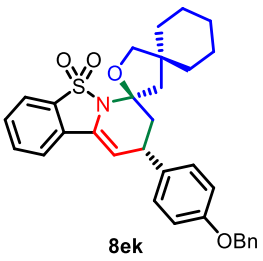
9-(4-Methoxyphenyl)-8,9-dihydro-3'*H*,5'*H*-dispiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan-4',1''-cyclohexane] 5,5-dioxide (8ej):





9-(4-(Benzyloxy)phenyl)-8,9-dihydro-3'*H*,5'*H*-dispiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan-4',1''-cyclohexane] 5,5-dioxide (8ek):

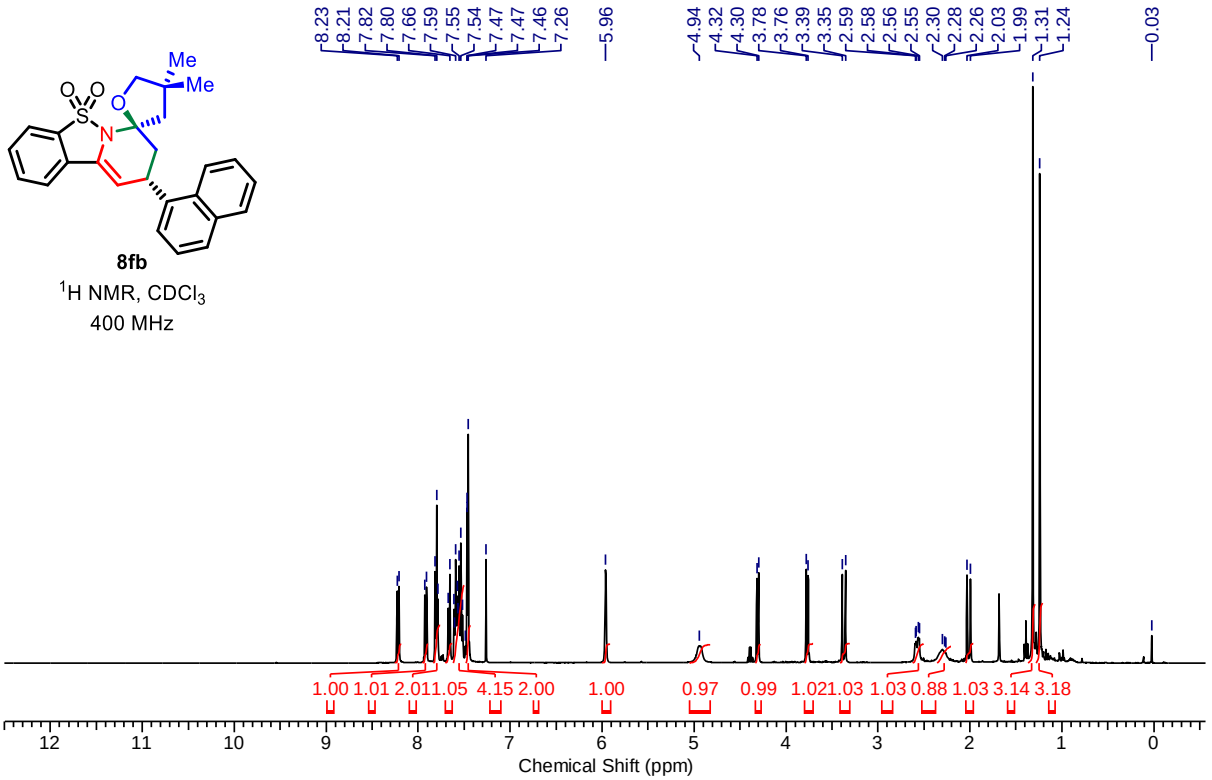


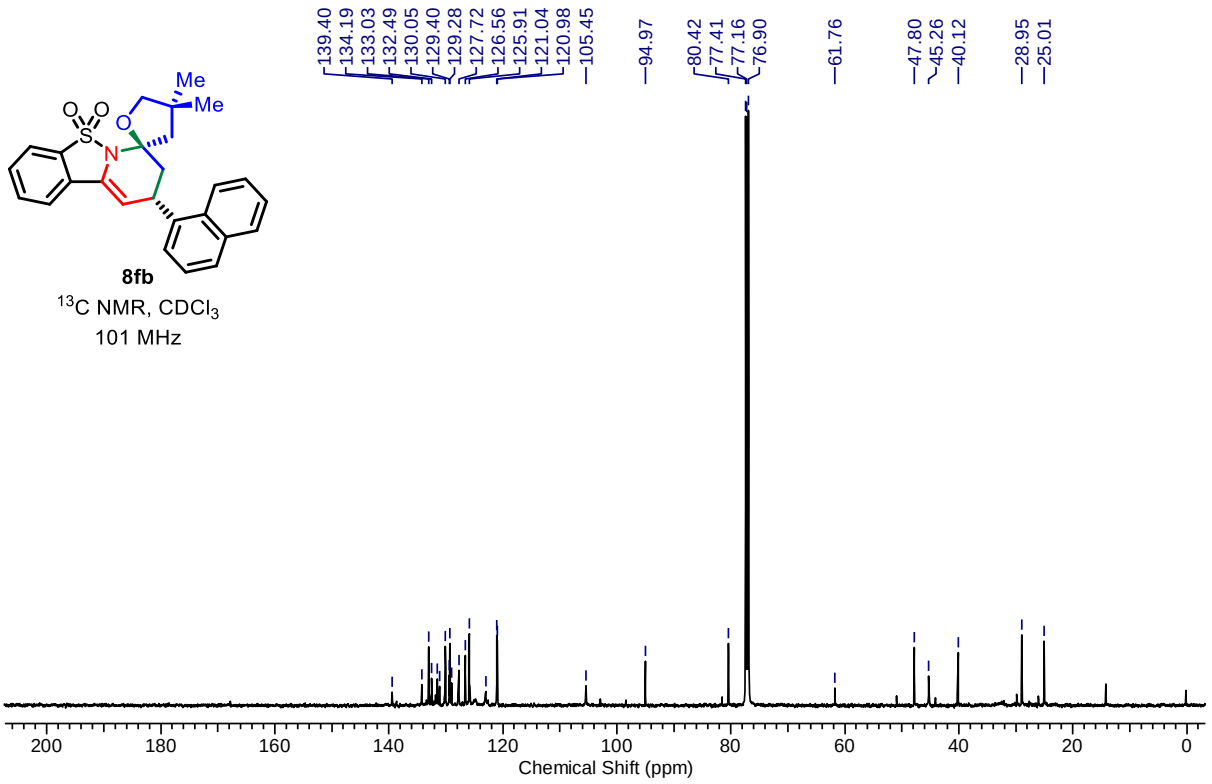


^{1}H NMR, $CDCl_3$
400 MHz

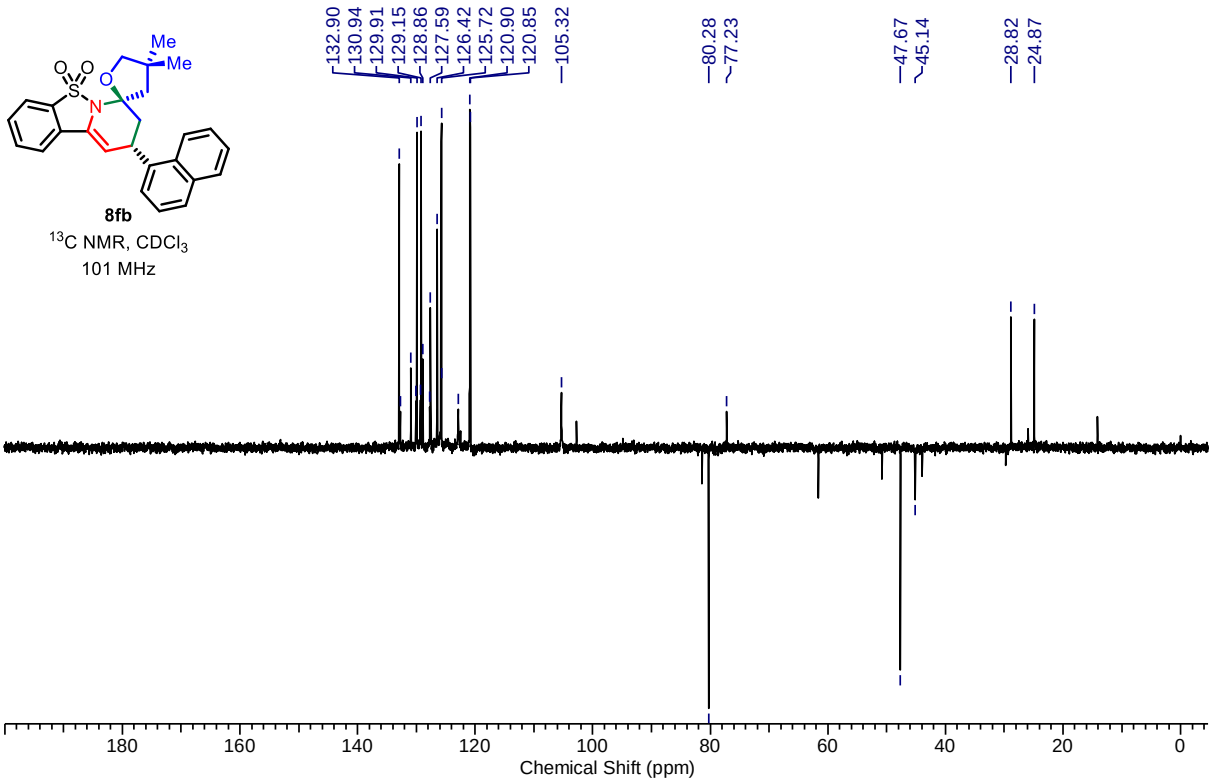
^{13}C NMR, $CDCl_3$
101 MHz

4',4'-Dimethyl-9-(naphthalen-1-yl)-4',5',8,9-tetrahydro-3'*H*-spiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan] 5,5-dioxidedioxide (8fb):

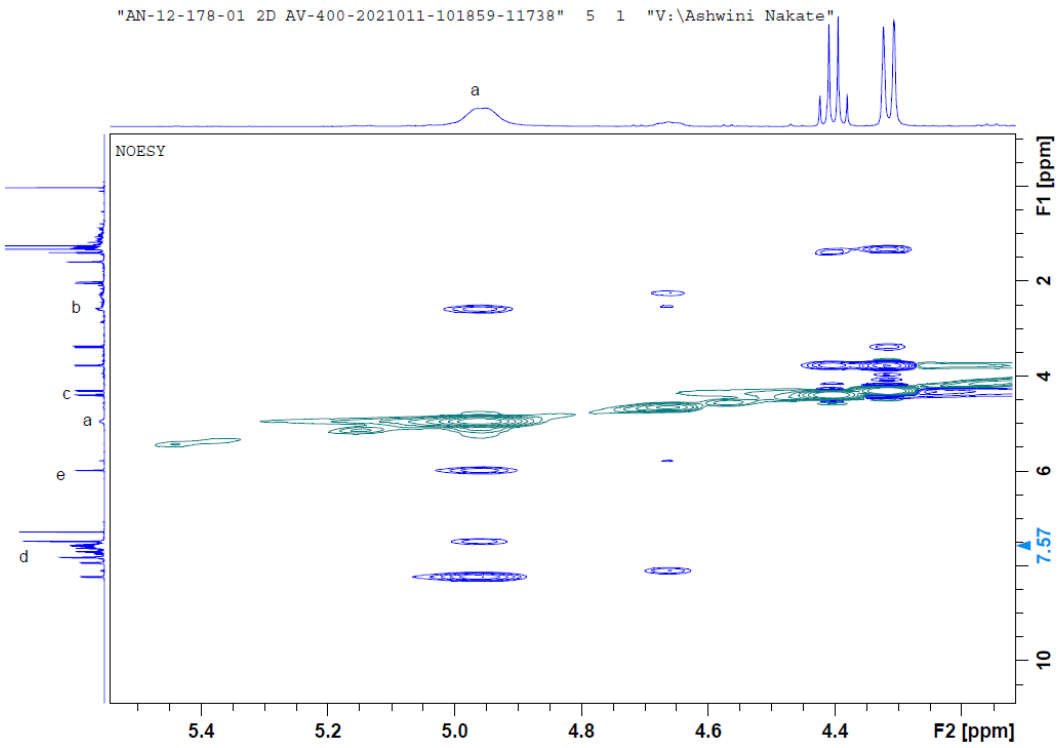


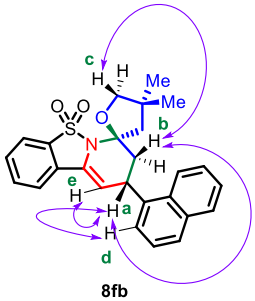


4',4'-Dimethyl-9-(naphthalen-1-yl)-4',5',8,9-tetrahydro-3'*H*-spiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan] 5,5-dioxidedioxide (8fb):

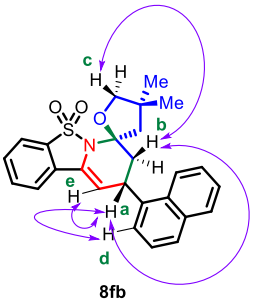


Zoomed NOESY

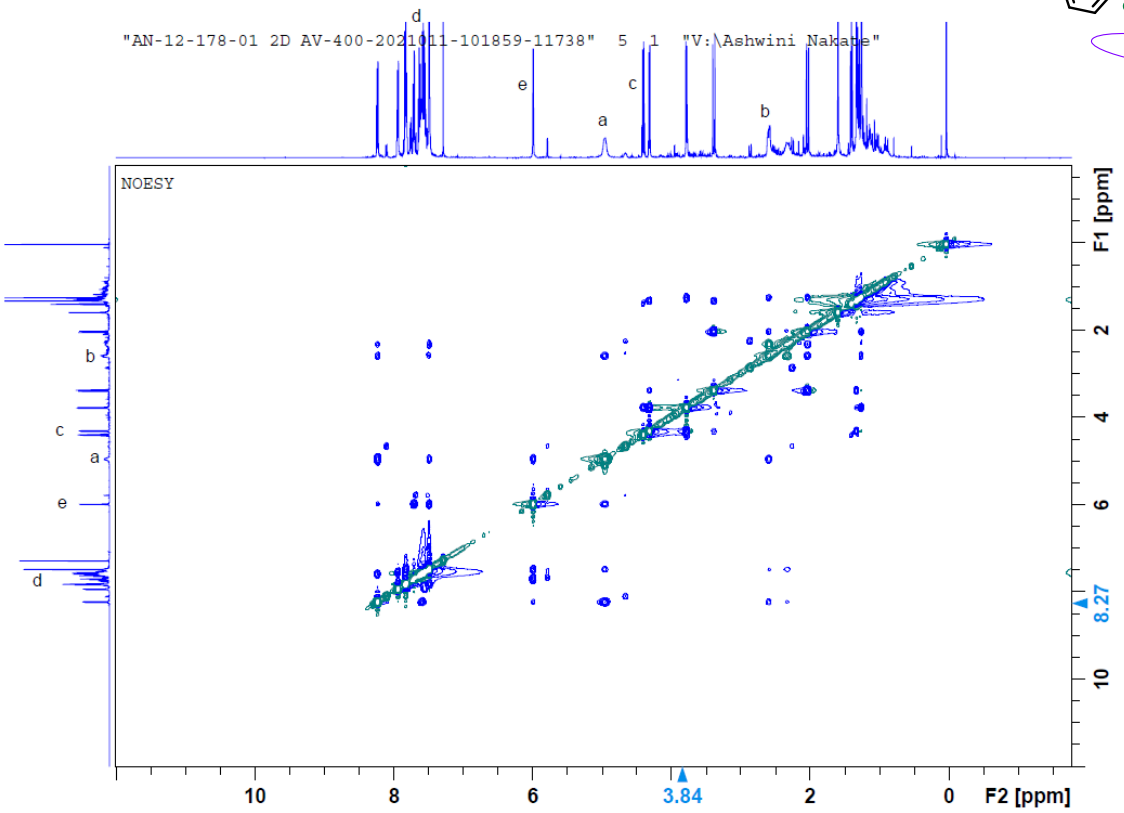




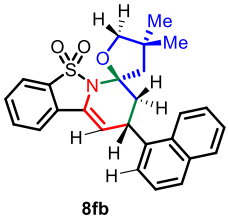
NOESY:



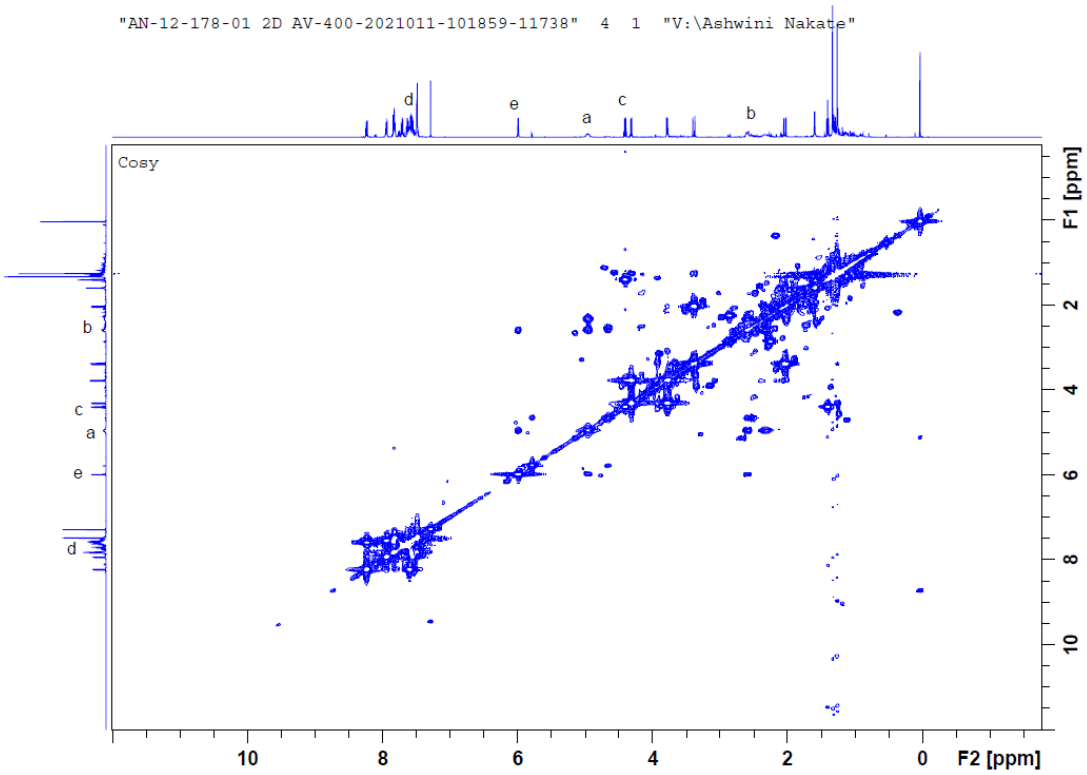
8fb



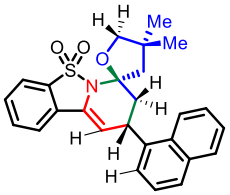
COSY:



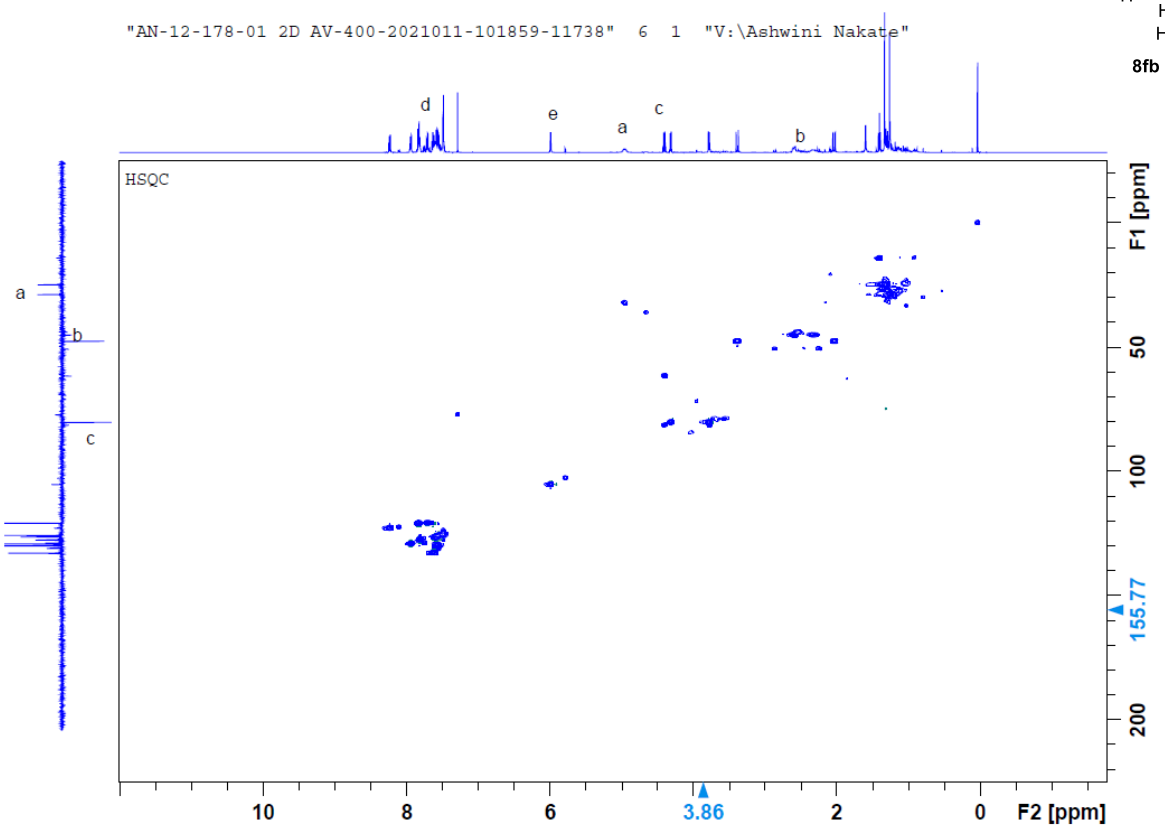
8fb



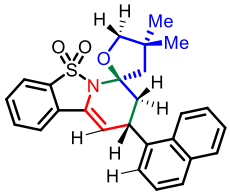
HSQC:



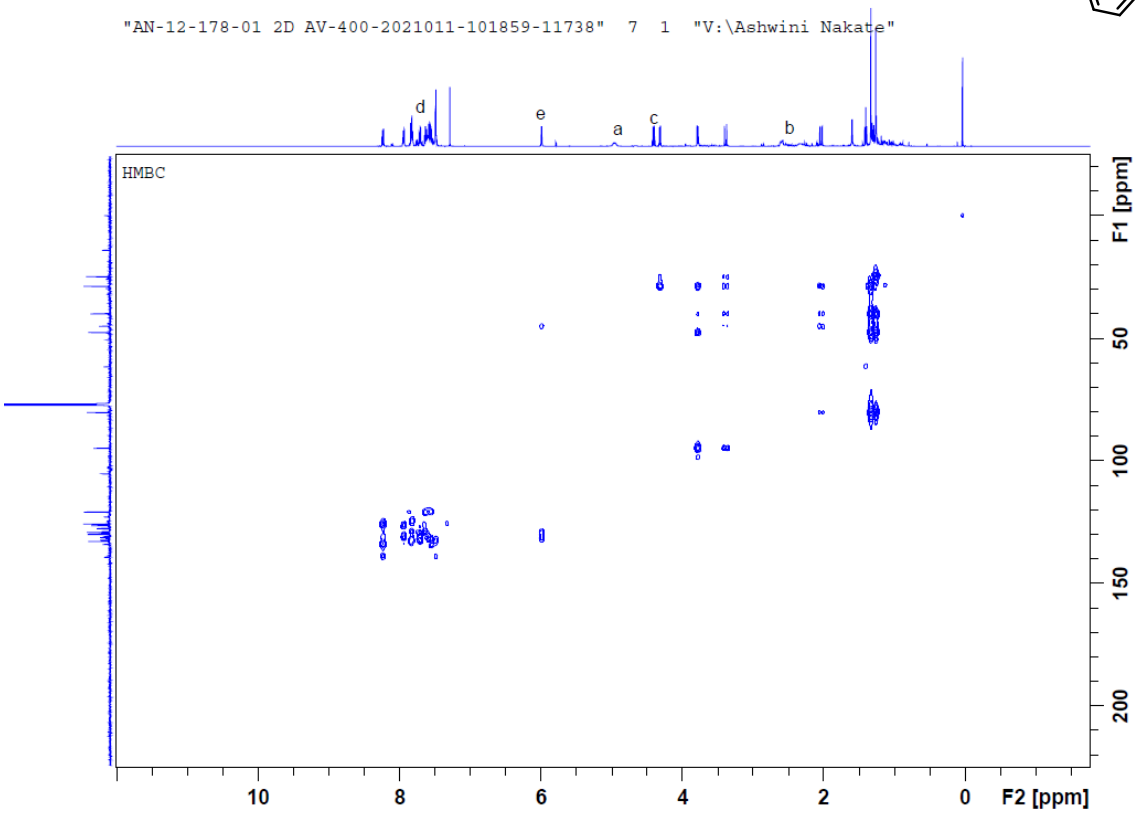
8fb



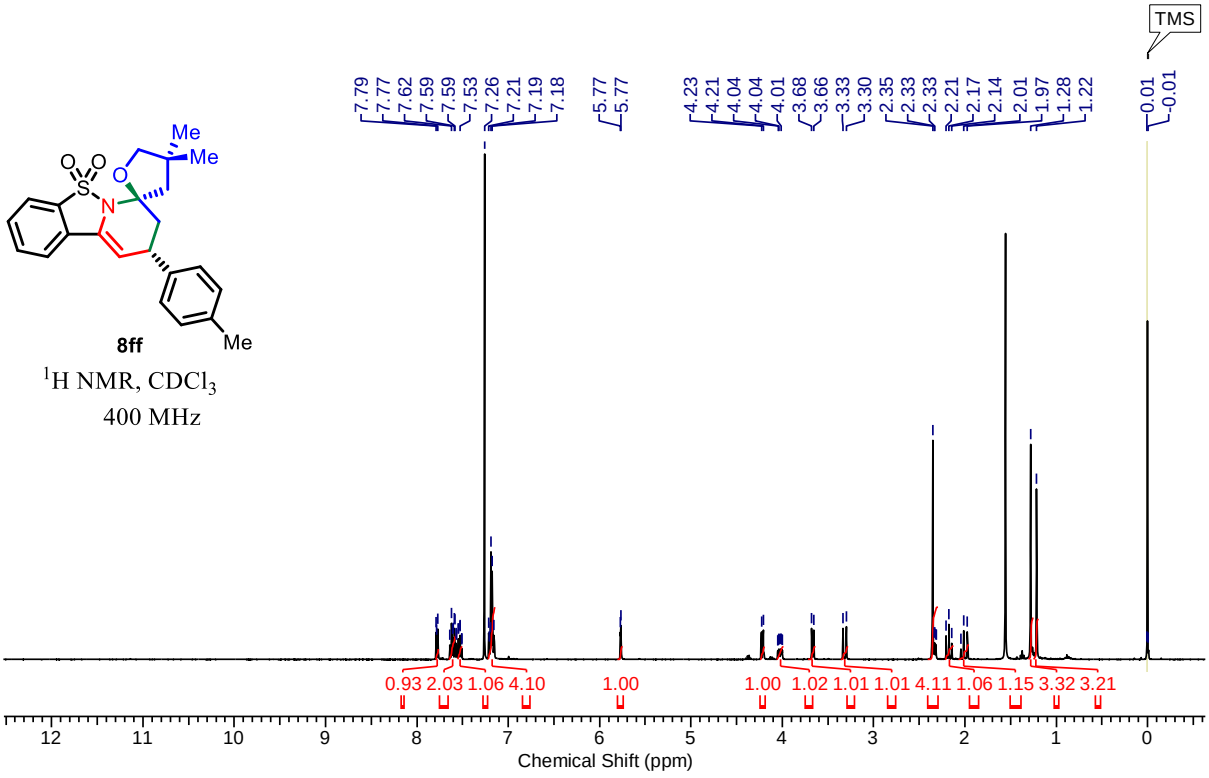
HMBC:

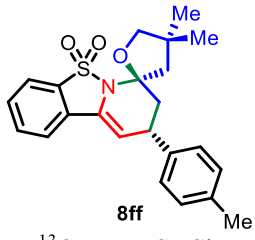


8fb



4',4'-Dimethyl-9-(p-tolyl)-4',5',8,9-tetrahydro-3'*H*-spiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan] 5,5-dioxide (8ff):

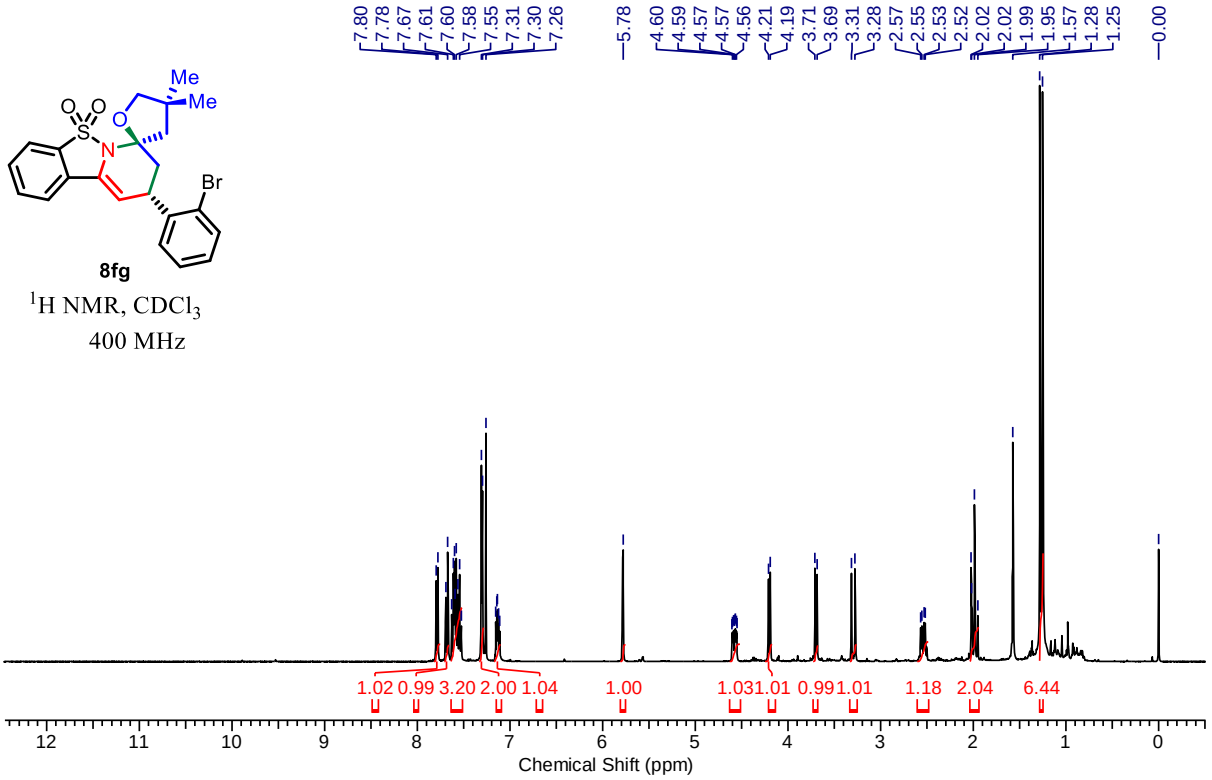


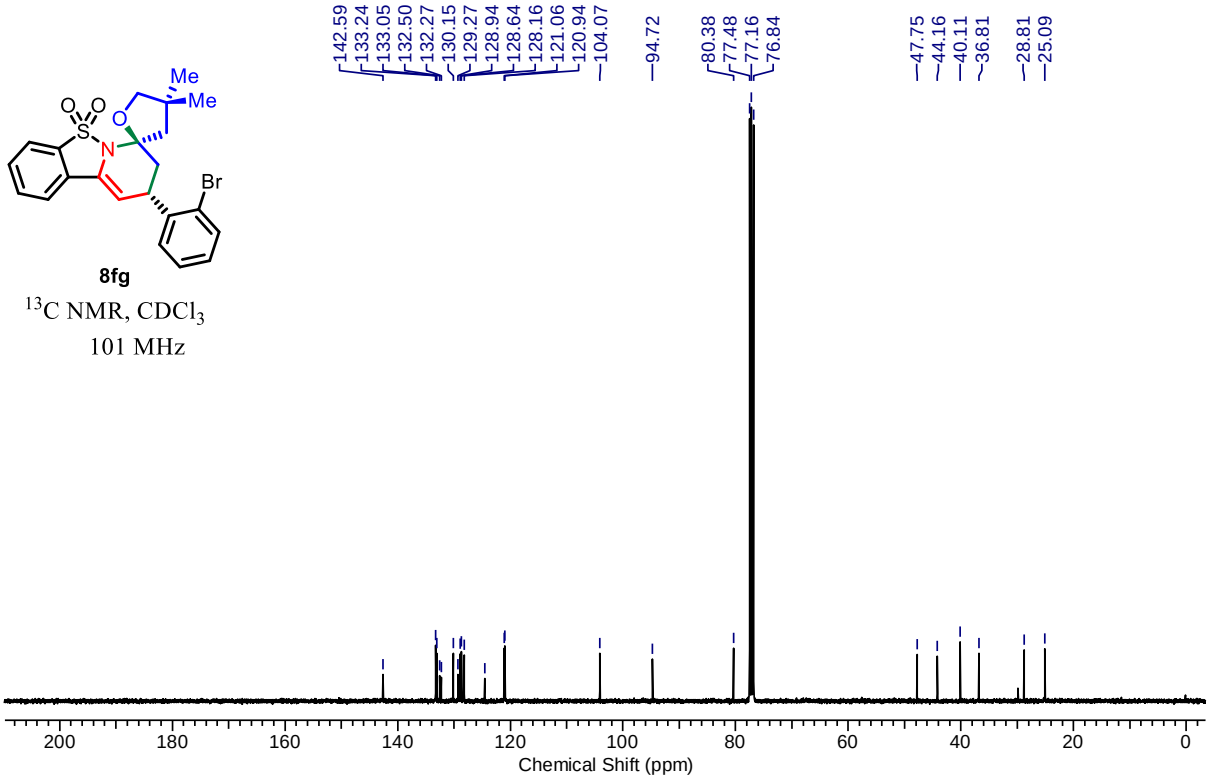


^{1}H NMR, $CDCl_3$
400 MHz

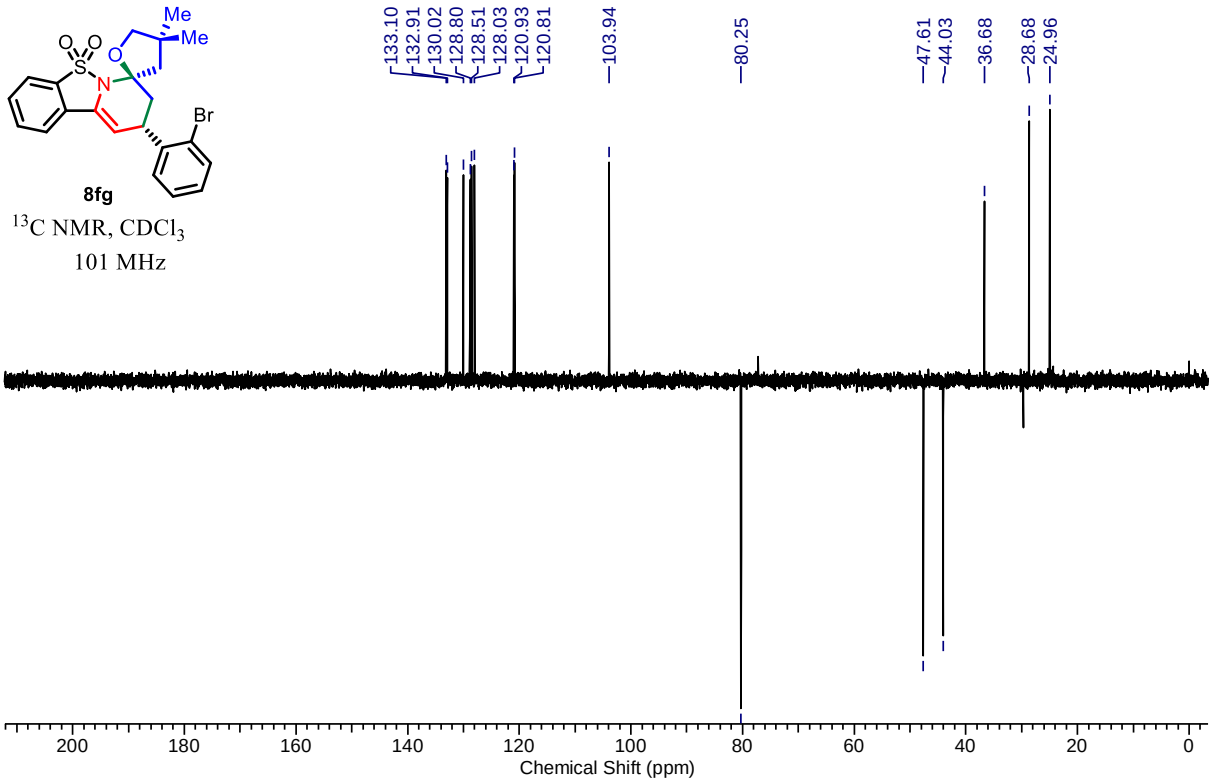
^{13}C NMR, $CDCl_3$
101 MHz

9-(2-Bromophenyl)-4',4'-dimethyl-4',5',8,9-tetrahydro-3'*H*-spiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan] 5,5-dioxide (8fg):

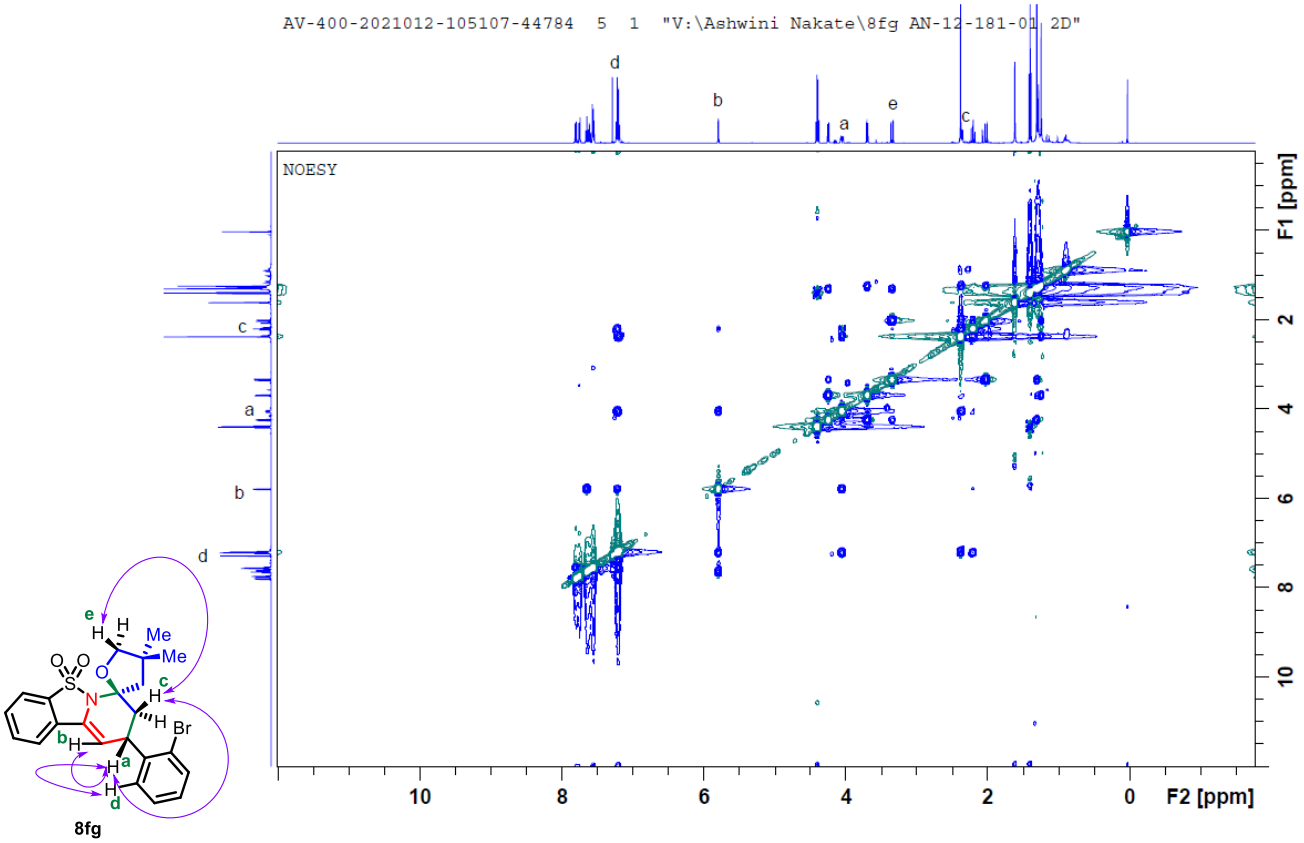




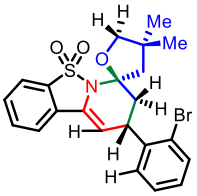
9-(2-Bromophenyl)-4',4'-dimethyl-4',5',8,9-tetrahydro-3'H-spiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan] 5,5-dioxide (8fg):



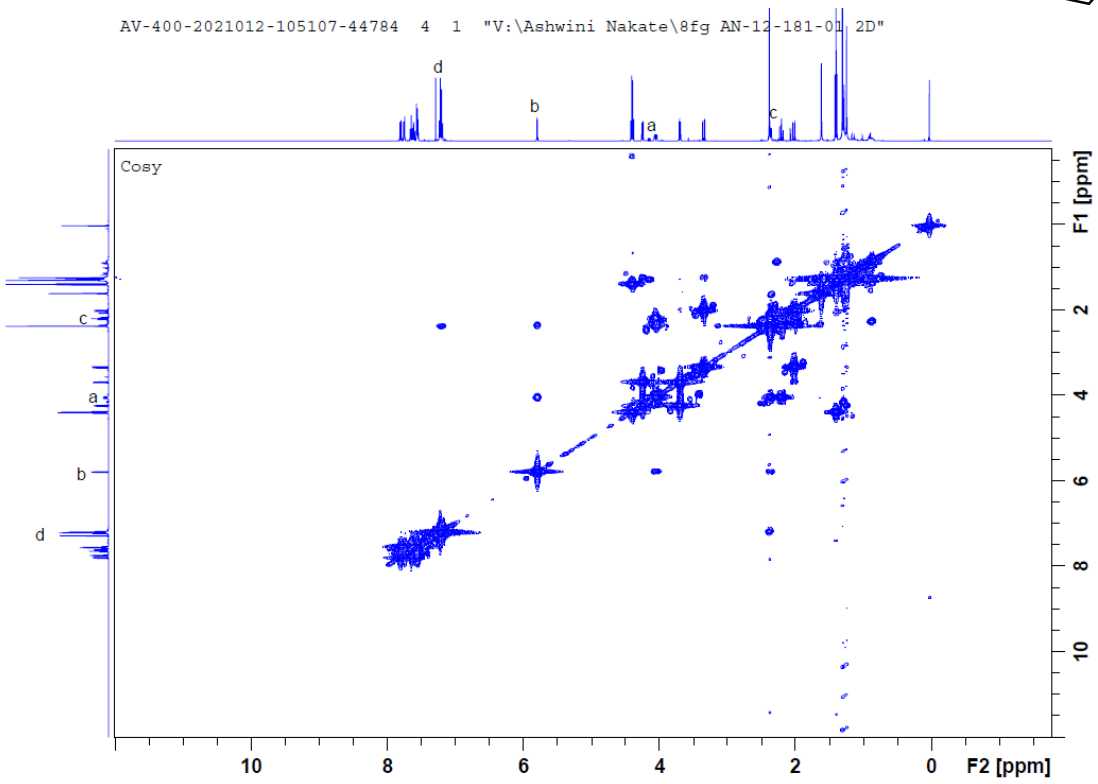
NOESY:



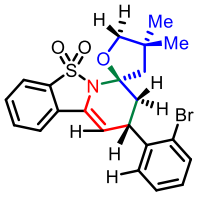
COSY:



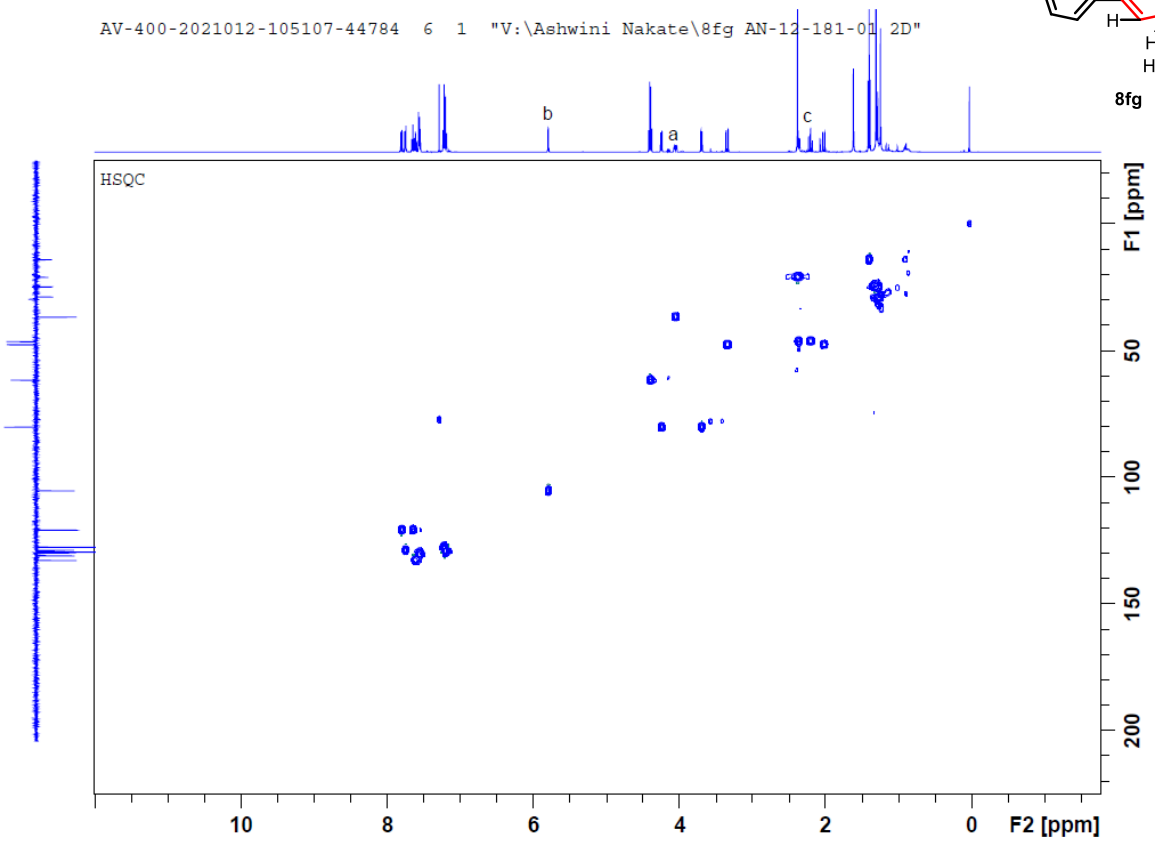
8fg



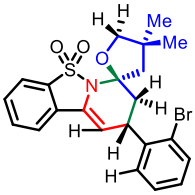
HSQC:



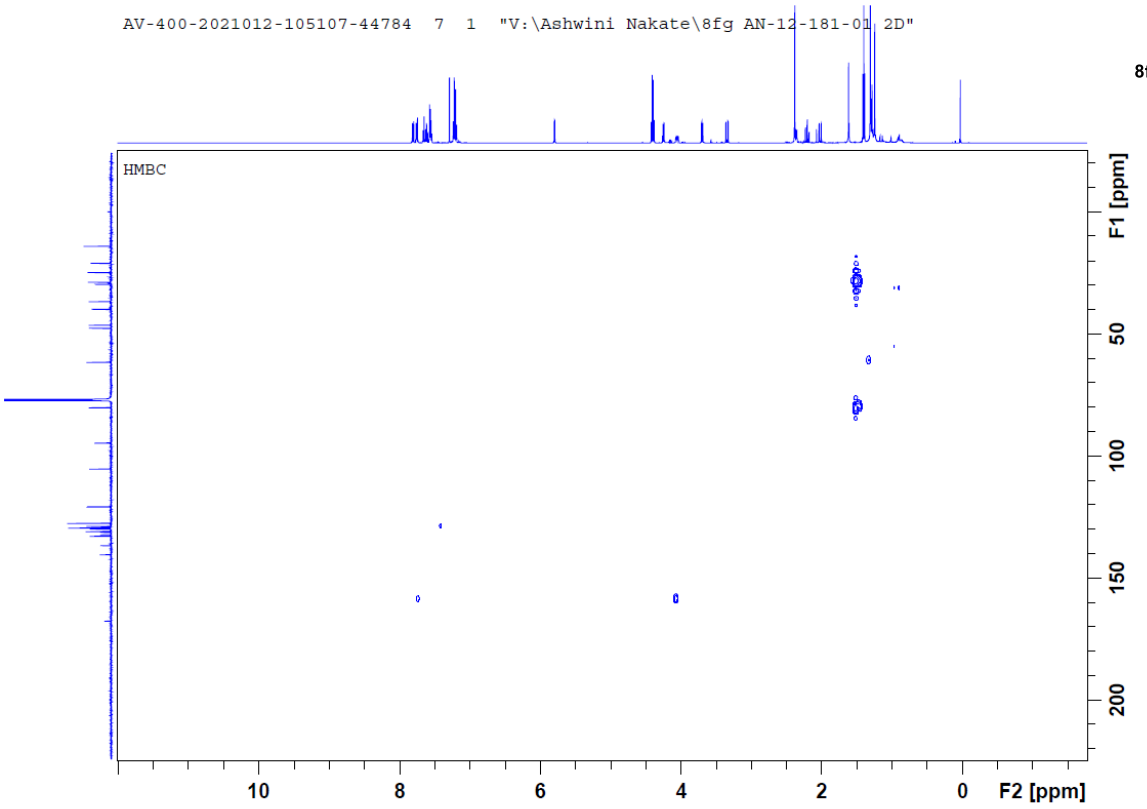
8fg



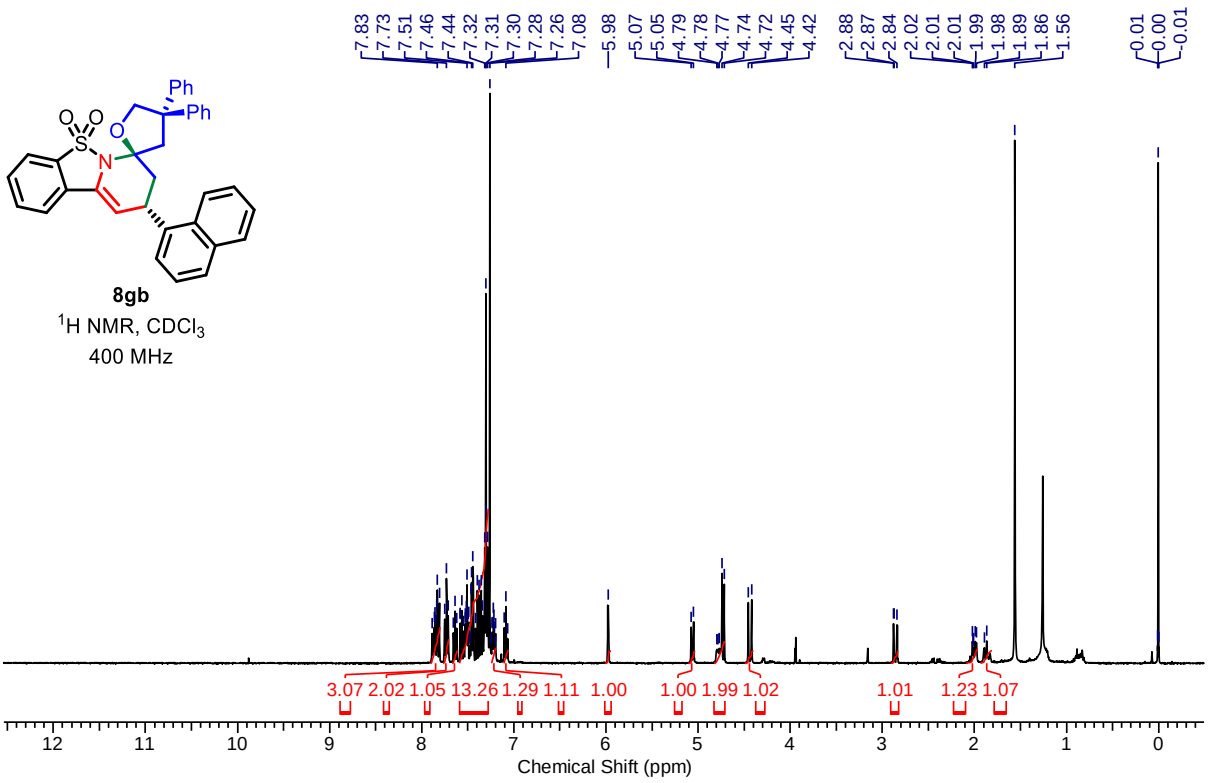
HMBC:

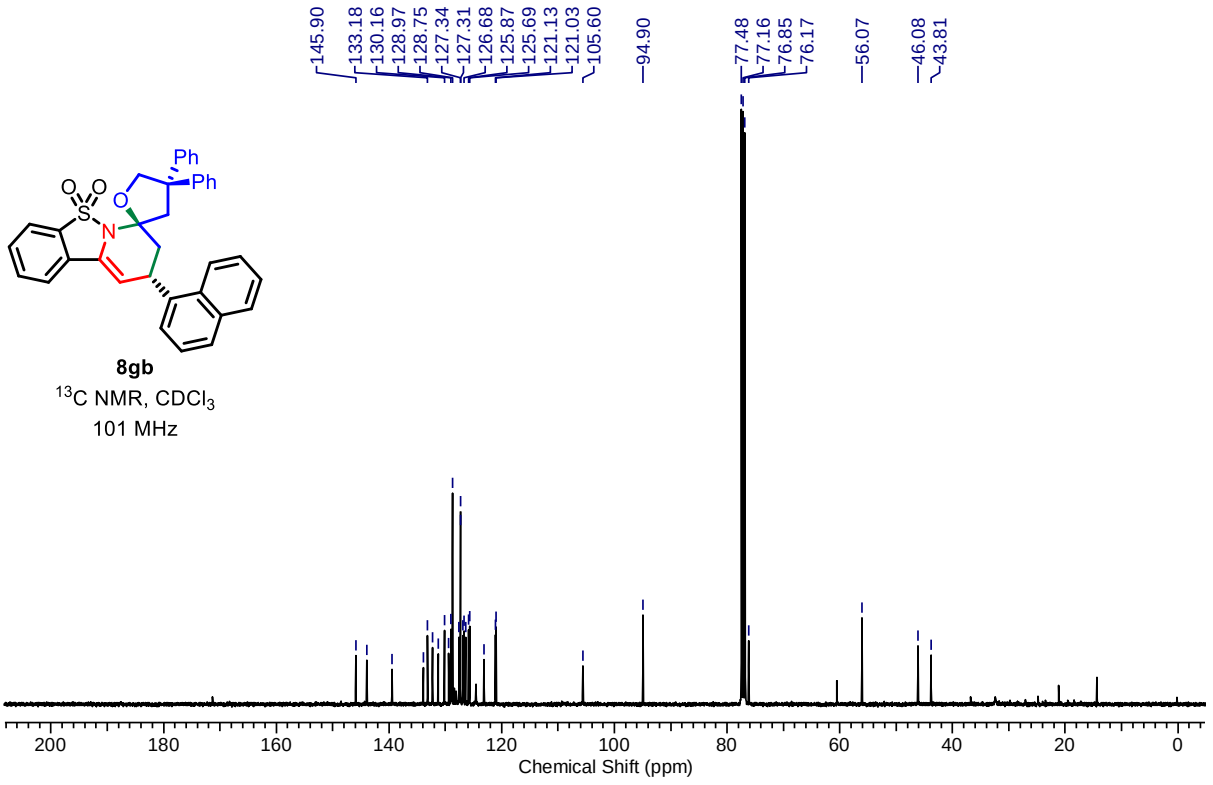

H
H
Me
Me
O
O
S
O
N
H
H
Br
H
H

8fg

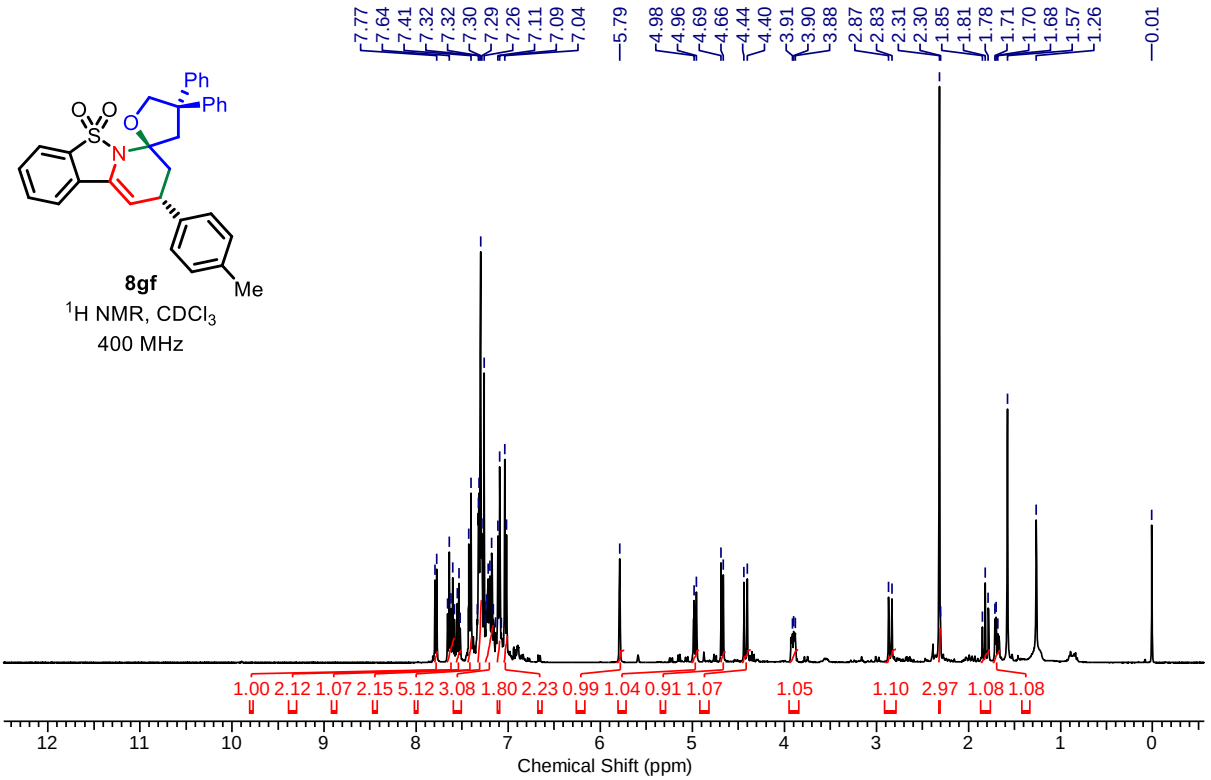

AV-400-2021012-105107-44784 7 1 "V:\Ashwini Nakate\8fg AN-12-181-01 2D"
HMBC
F1 [ppm]
50
100
150
200
10
8
6
4
2
0
F2 [ppm]

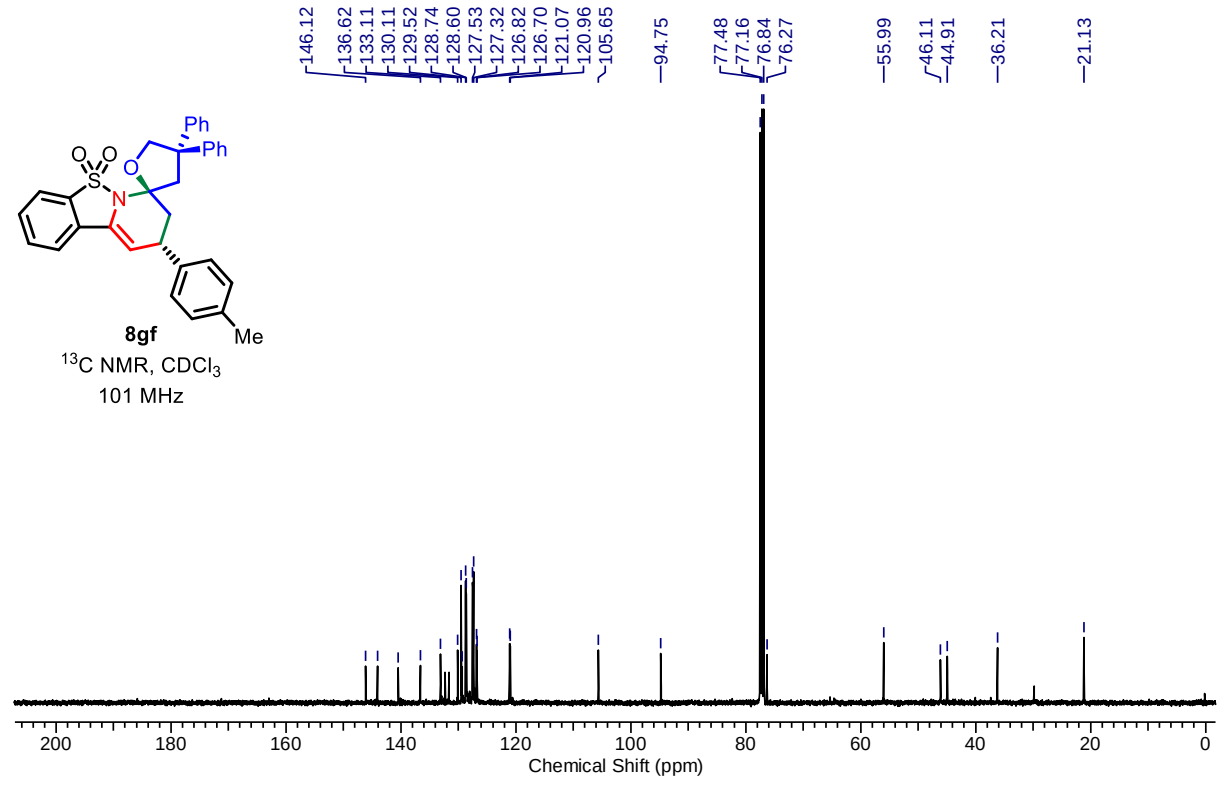
9-(Naphthalen-1-yl)-4',4'-diphenyl-4',5',8,9-tetrahydro-3'*H*-spiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan] 5,5-dioxide (8gb):



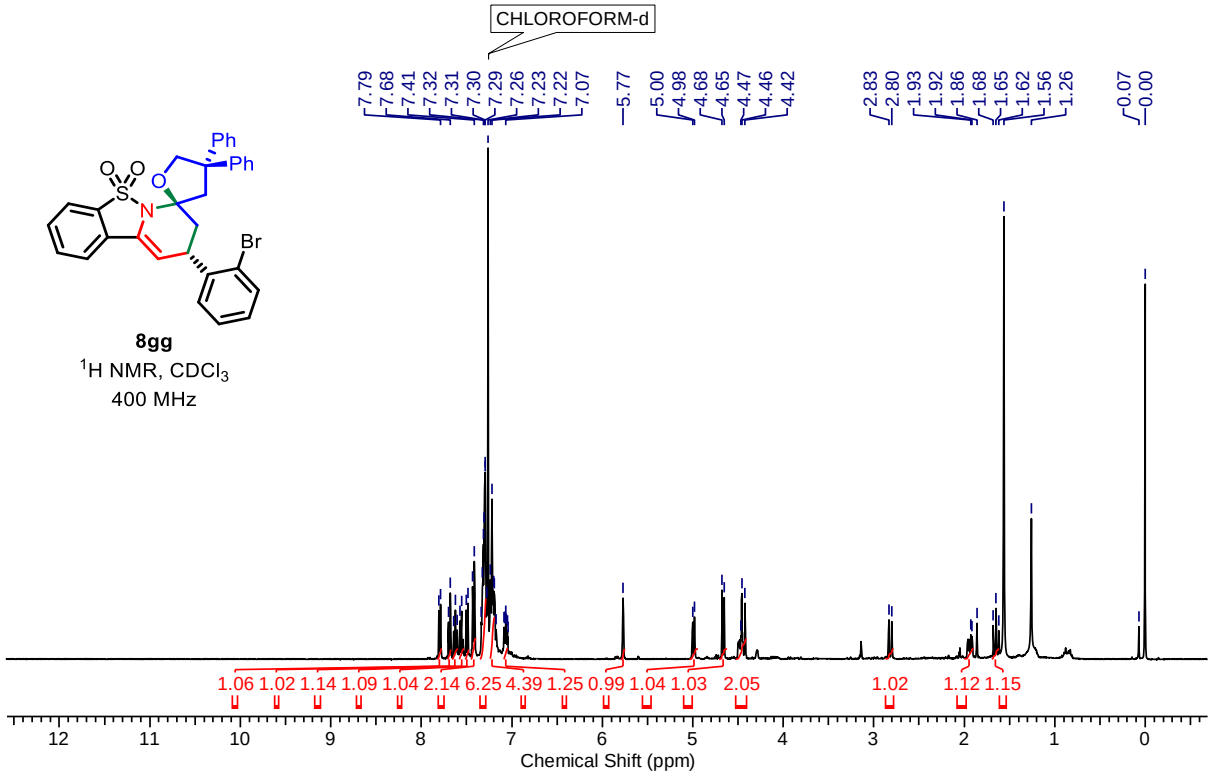


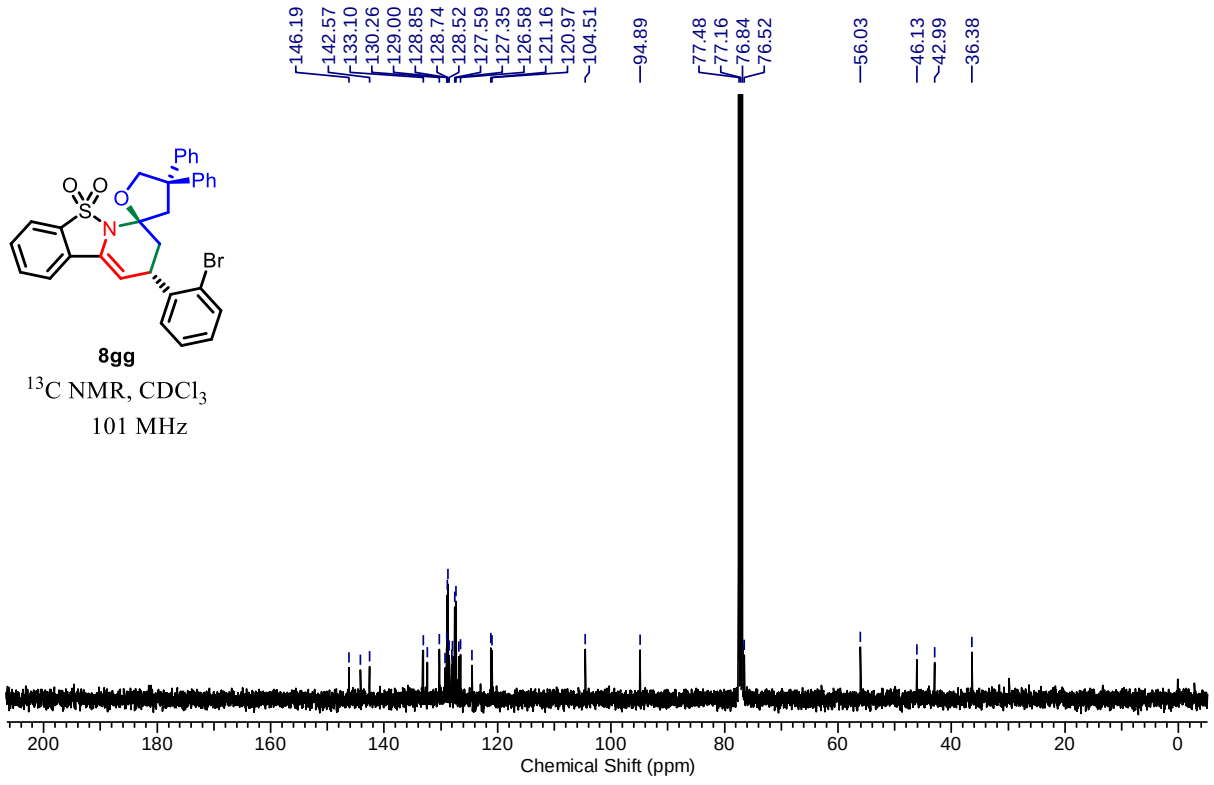
4',4'-Diphenyl-9-(p-tolyl)-4',5',8,9-tetrahydro-3'*H*-spiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan] 5,5-dioxide (8gf):



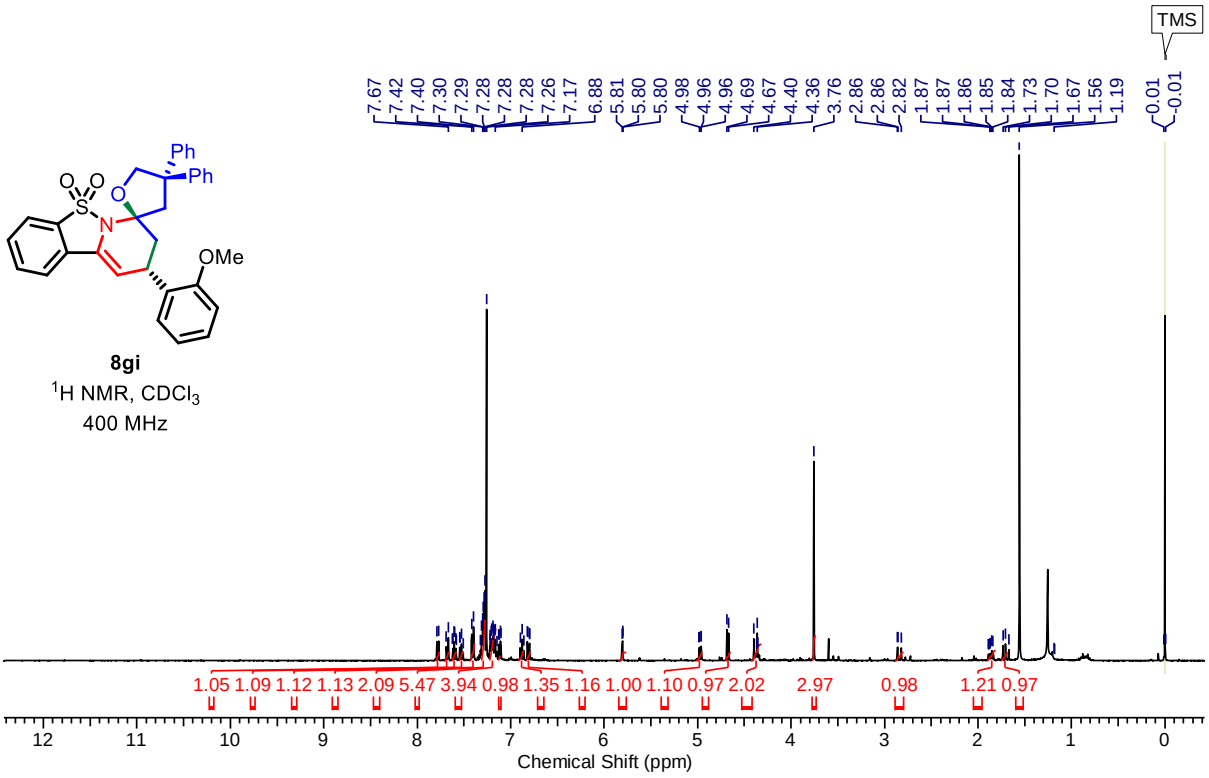


9-(2-Bromophenyl)-4',4'-diphenyl-4',5',8,9-tetrahydro-3'*H*-spiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan] 5,5-dioxide (8gg):





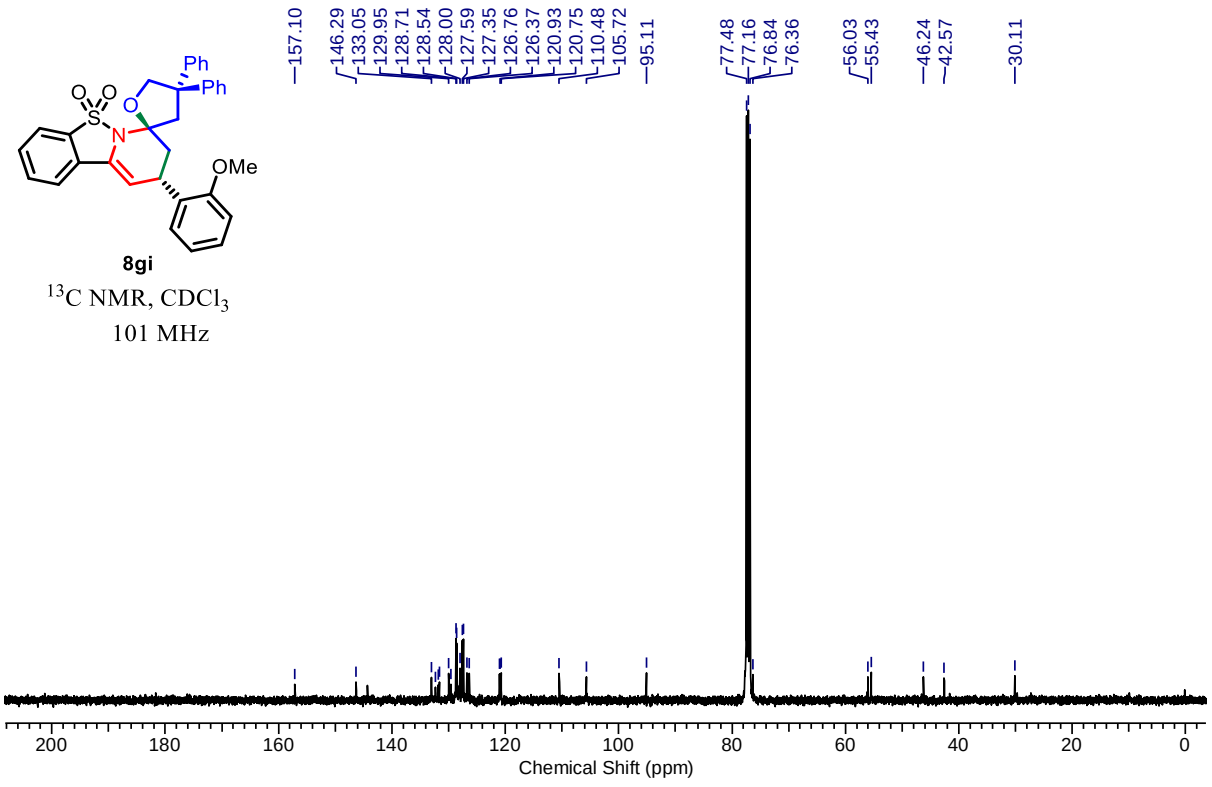
9-(2-Methoxyphenyl)-4',4'-diphenyl-4',5',8,9-tetrahydro-3'*H*-spiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan] 5,5-dioxide (8gi):



8gi

^{1}H NMR, $CDCl_3$

400 MHz

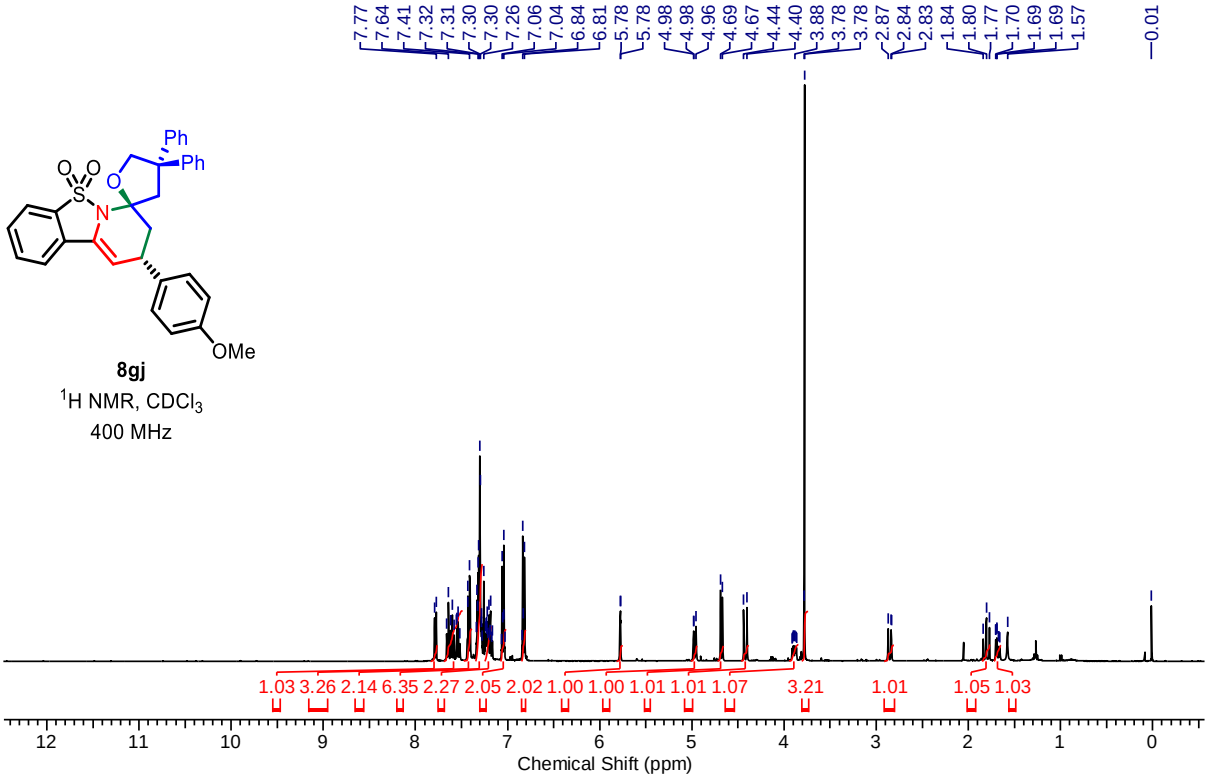


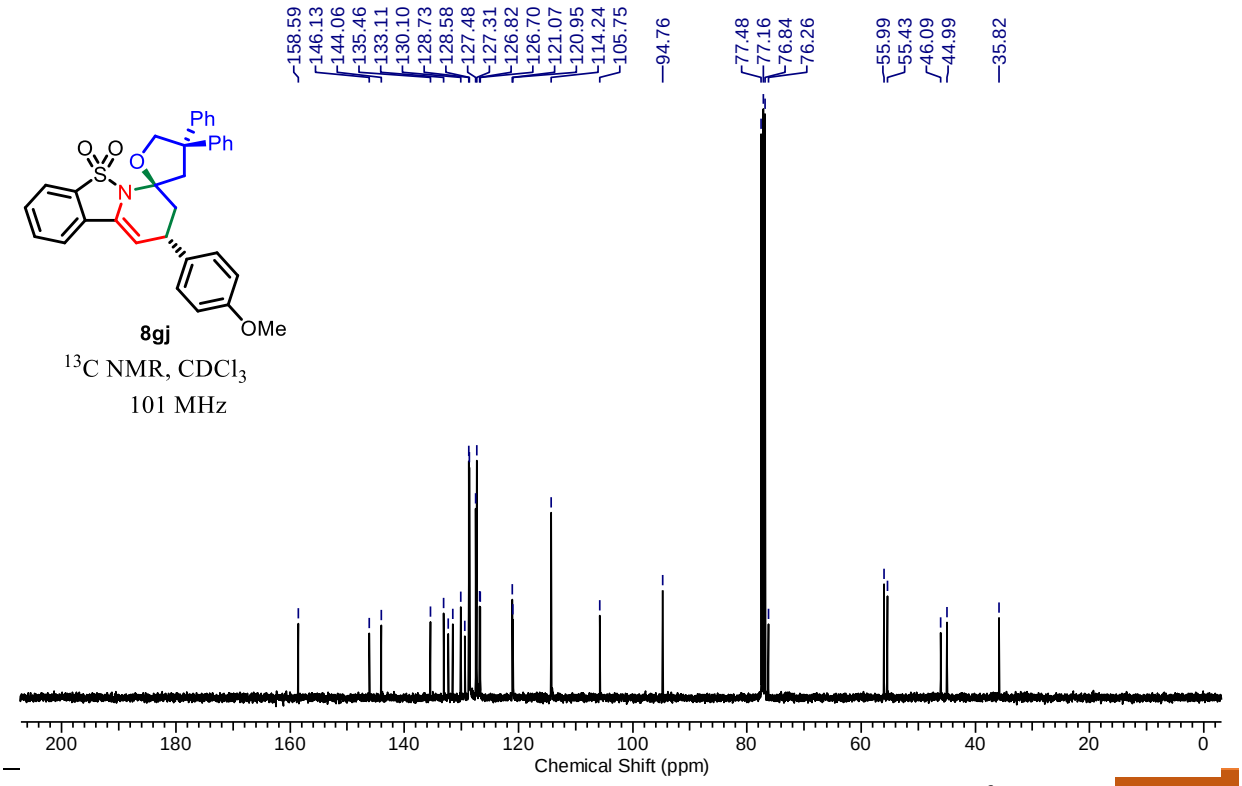
8gi

^{13}C NMR, $CDCl_3$

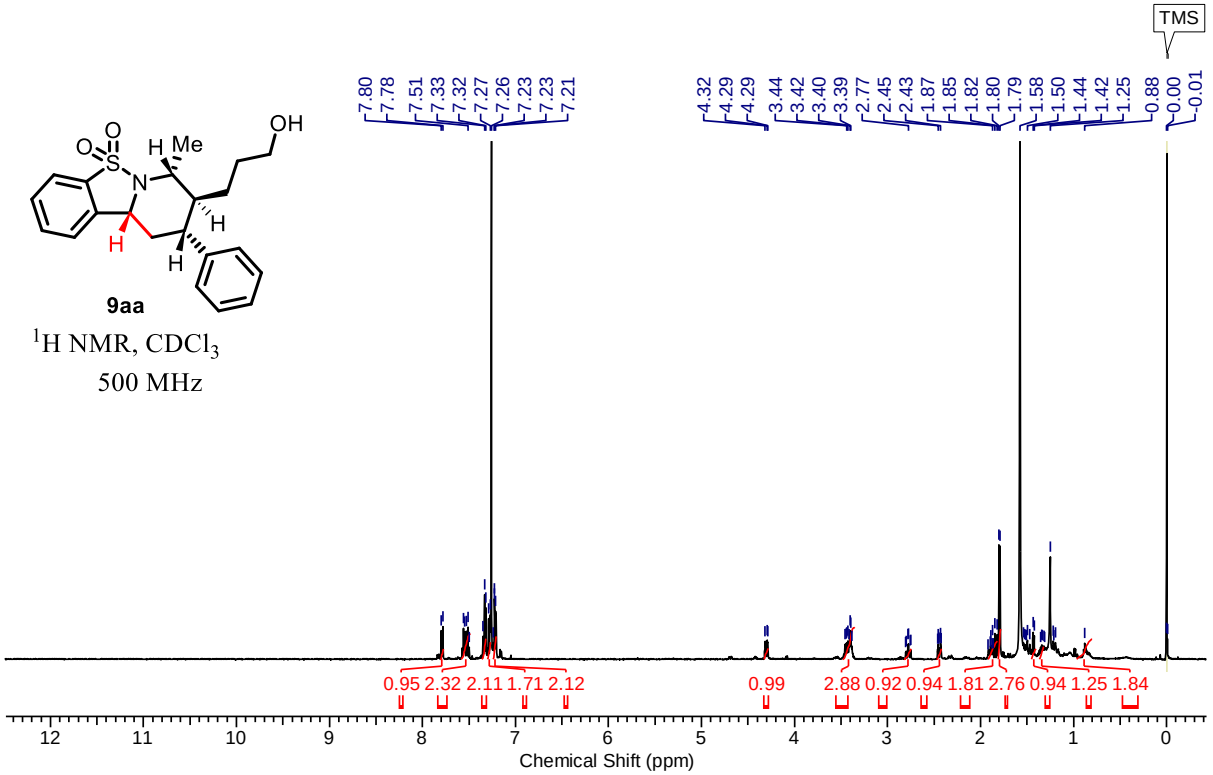
101 MHz

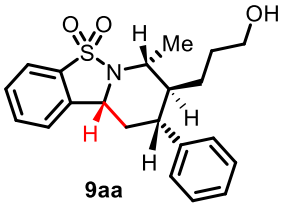
9-(4-Methoxyphenyl)-4',4'-diphenyl-4',5',8,9-tetrahydro-3'*H*-spiro[benzo[4,5]isothiazolo[2,3-a]pyridine-7,2'-furan] 5,5-dioxide (8gj):





8-(3-Hydroxypropyl)-7-methyl-9-phenyl-8,9,10,10a-tetrahydro-7*H*-benzo[4,5]isothiazolo[2,3-a]pyridine 5,5-dioxide (9aa):





9aa

^{1}H NMR, $CDCl_3$

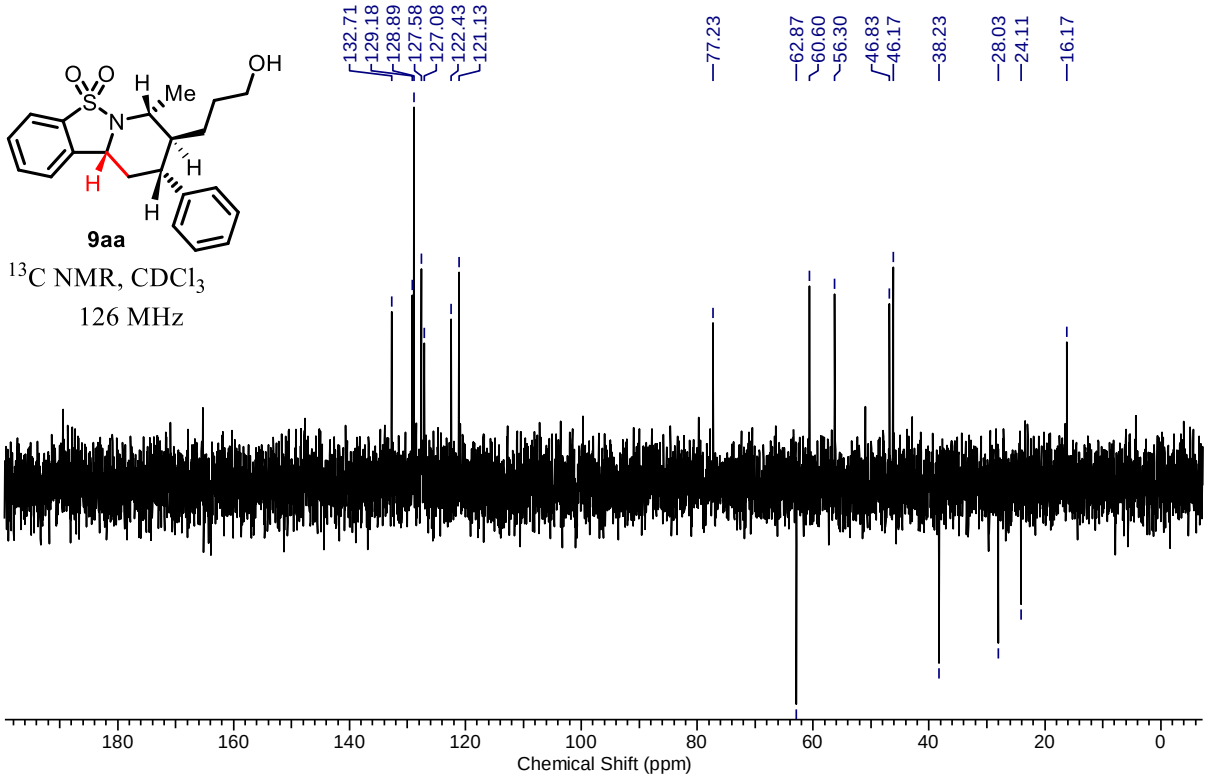
500 MHz

9aa

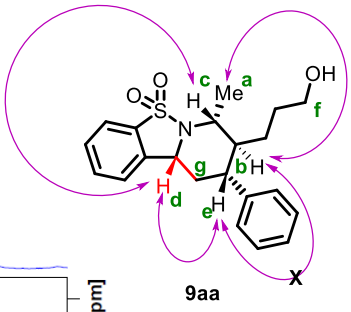
^{13}C NMR, $CDCl_3$

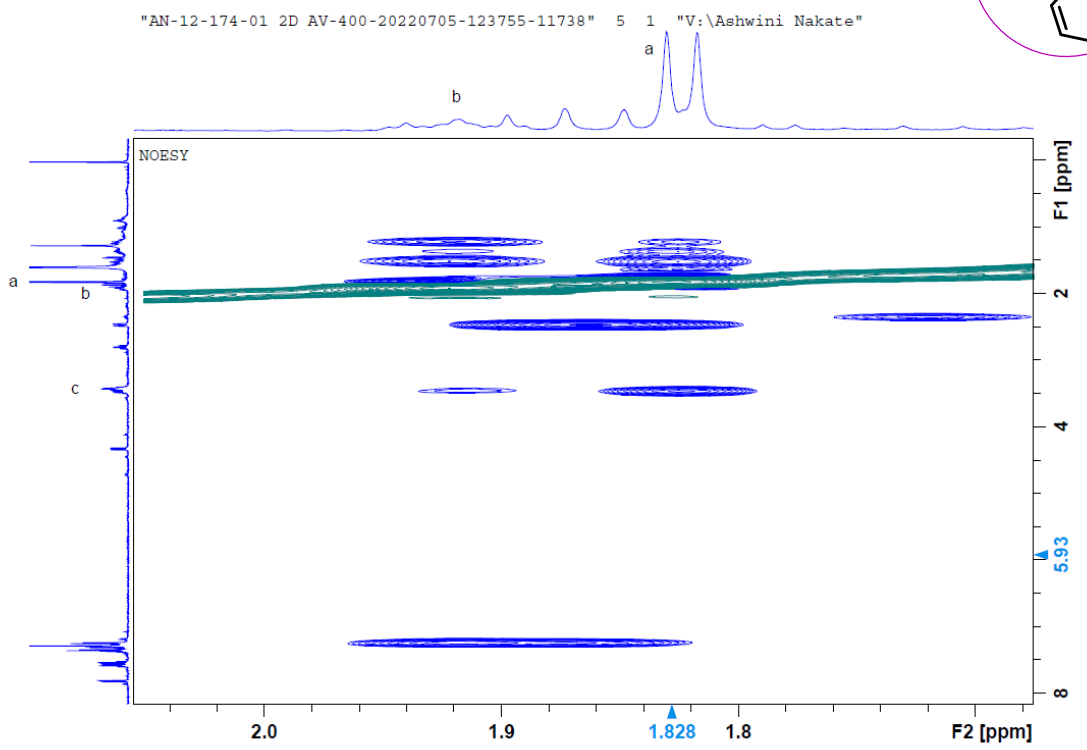
126 MHz

8-(3-Hydroxypropyl)-7-methyl-9-phenyl-8,9,10,10a-tetrahydro-7*H*-benzo[4,5]isothiazolo[2,3-a]pyridine 5,5-dioxide (9aa):

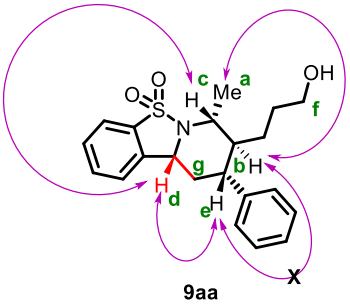


NOESY correlation of Me-H^{a}:

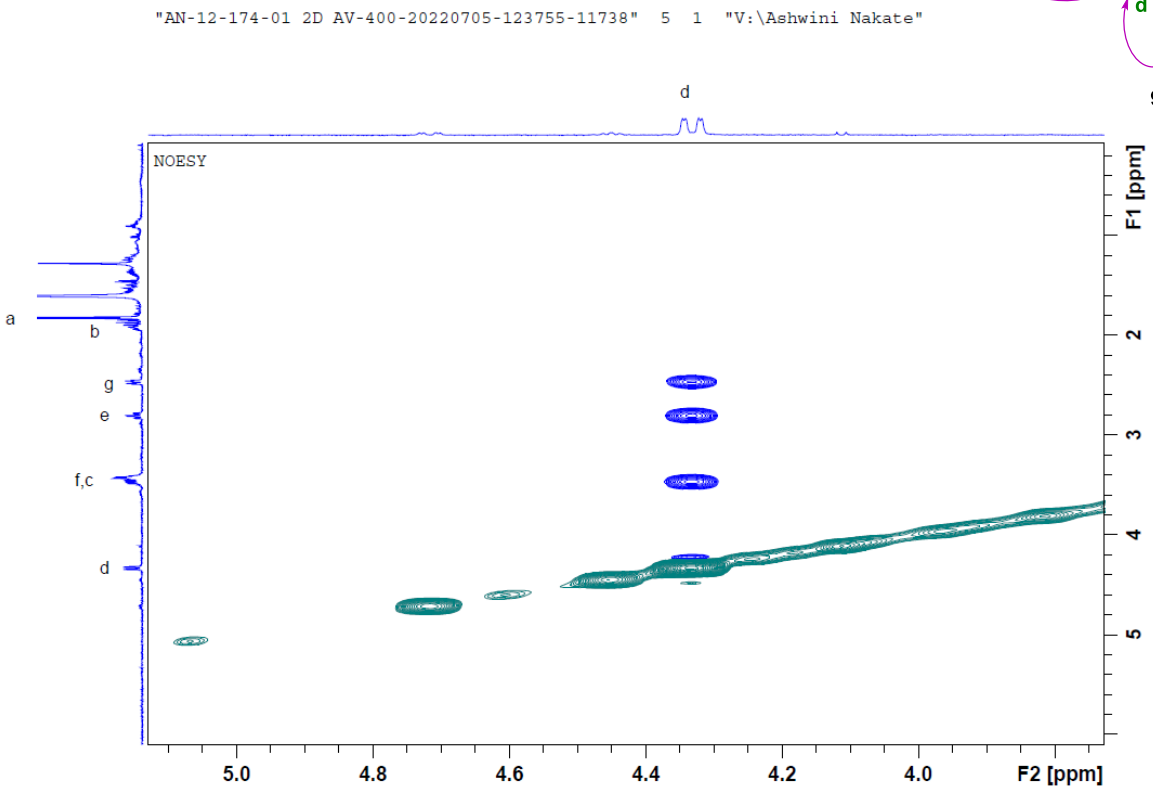




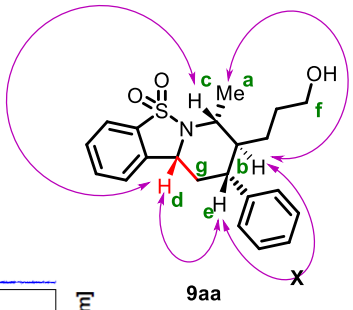
NOESY correlation of N-C-H^{d}:



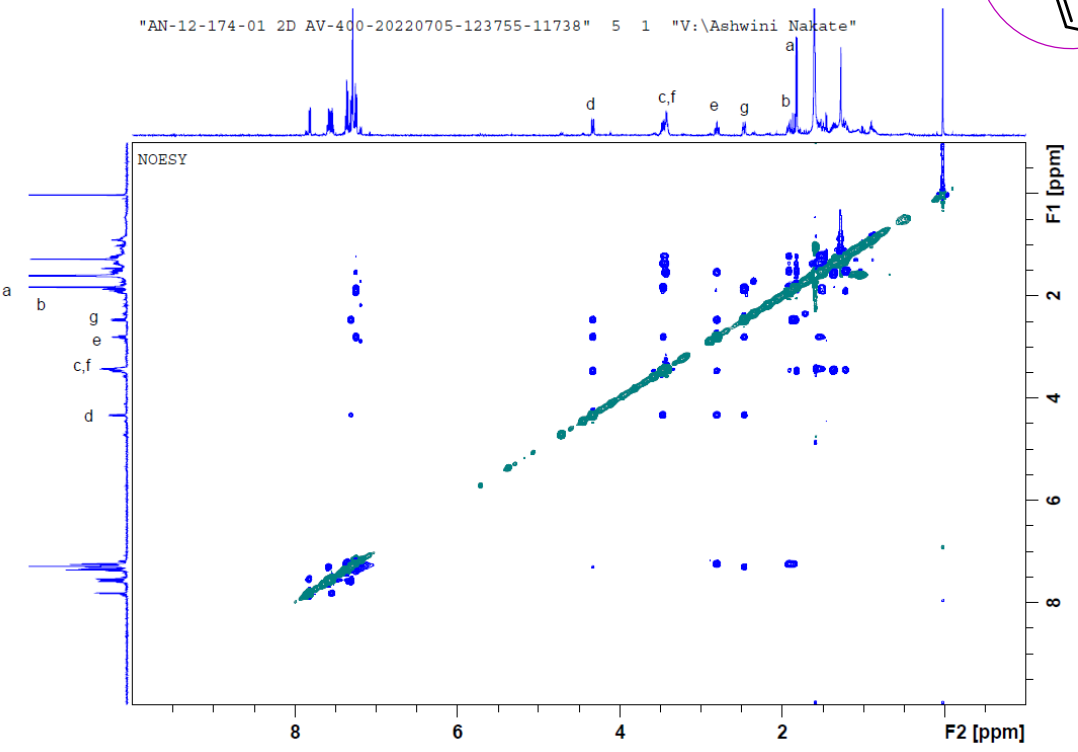
9aa



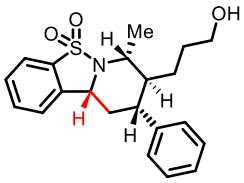
NOESY:



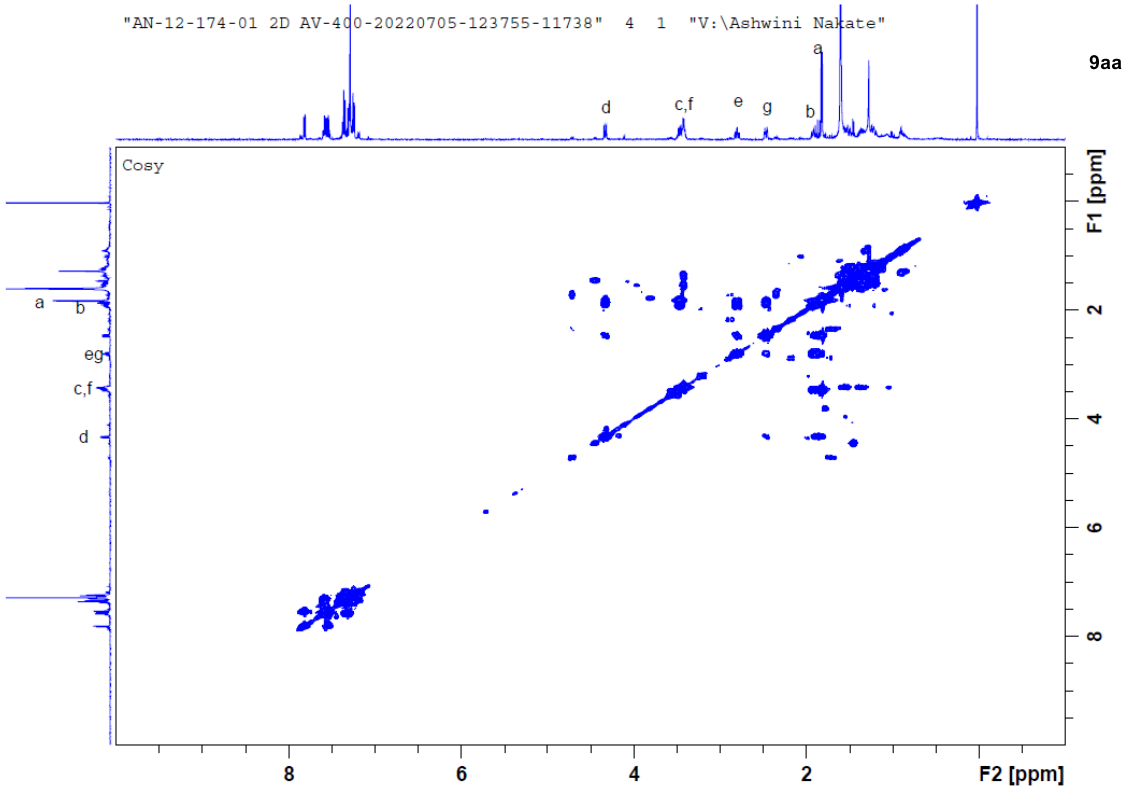
9aa



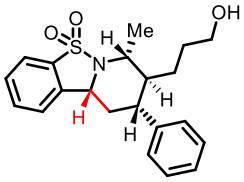
COSY:



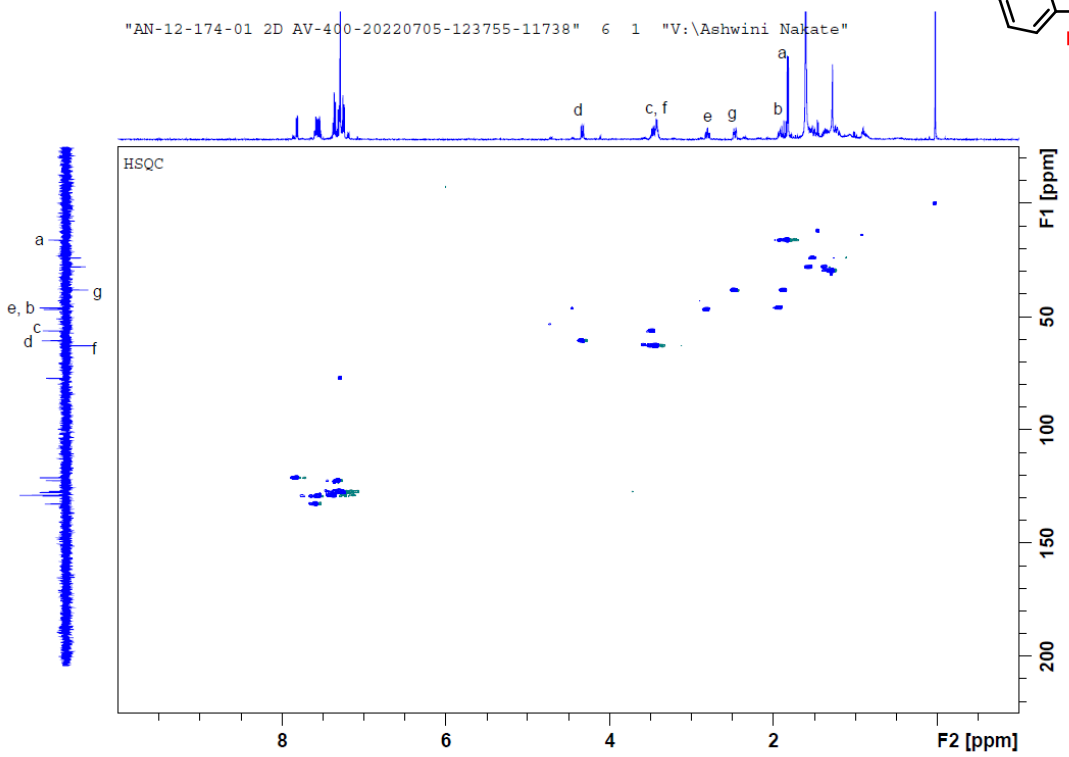
9aa



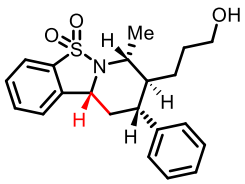
HSQC:



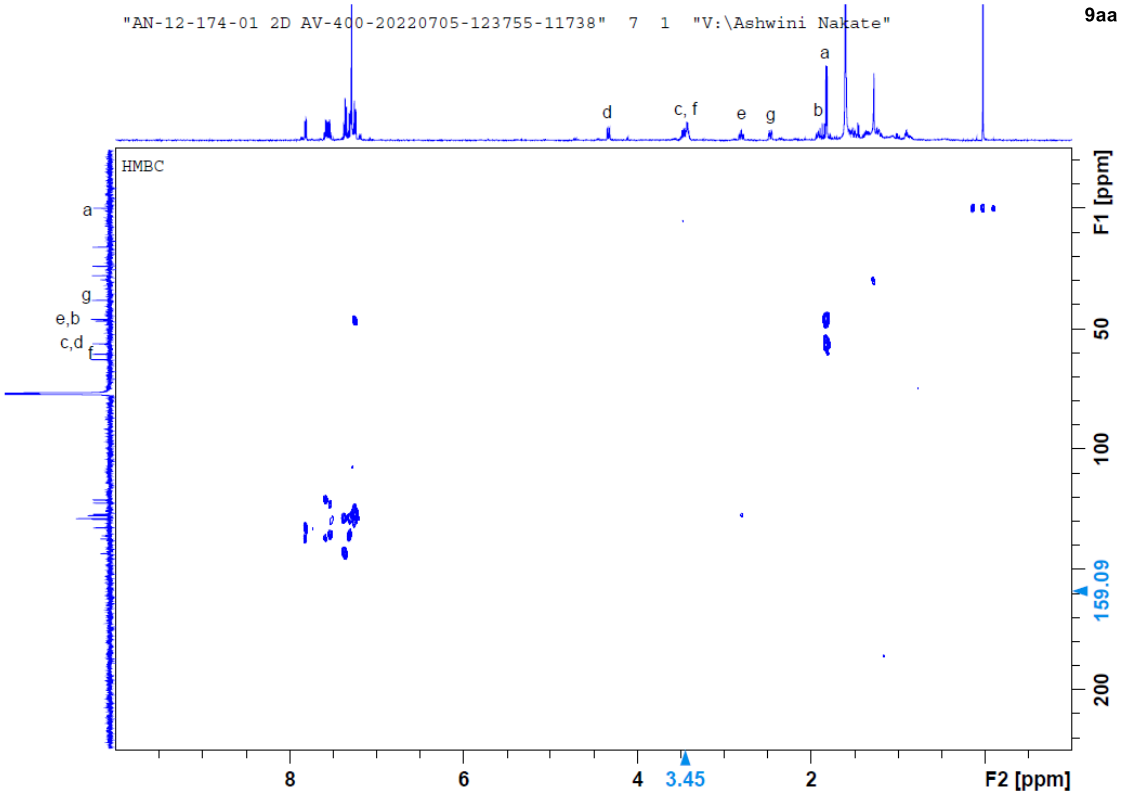
9aa



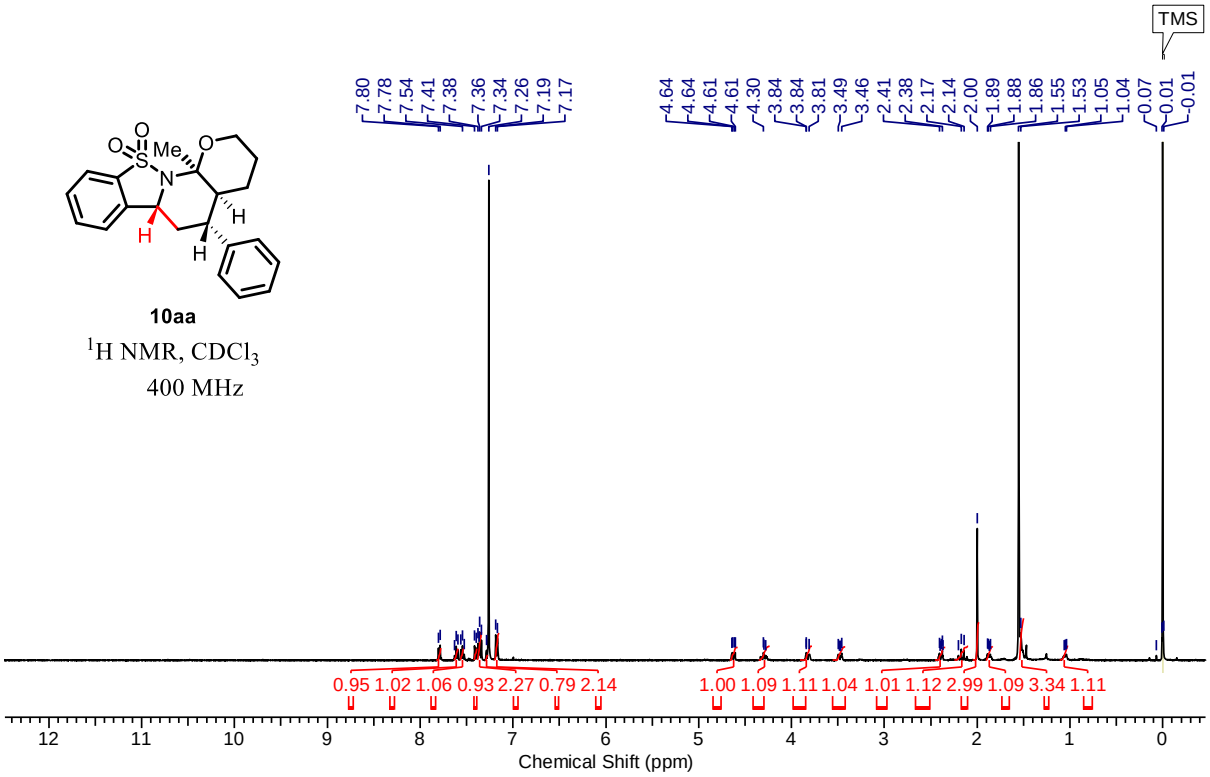
HMBC:


O
O
S
N
H
Me
OH
H
H
H

9aa


"AN-12-174-01 2D AV-400-20220705-123755-11738" 7 1 "V:\Ashwini Nakate"
HMBC
a
d
c, f
e
g
b
a
g
e,b
c,d
f
F1 [ppm]
50
100
159.09
200
8
6
4
3.45
2
F2 [ppm]

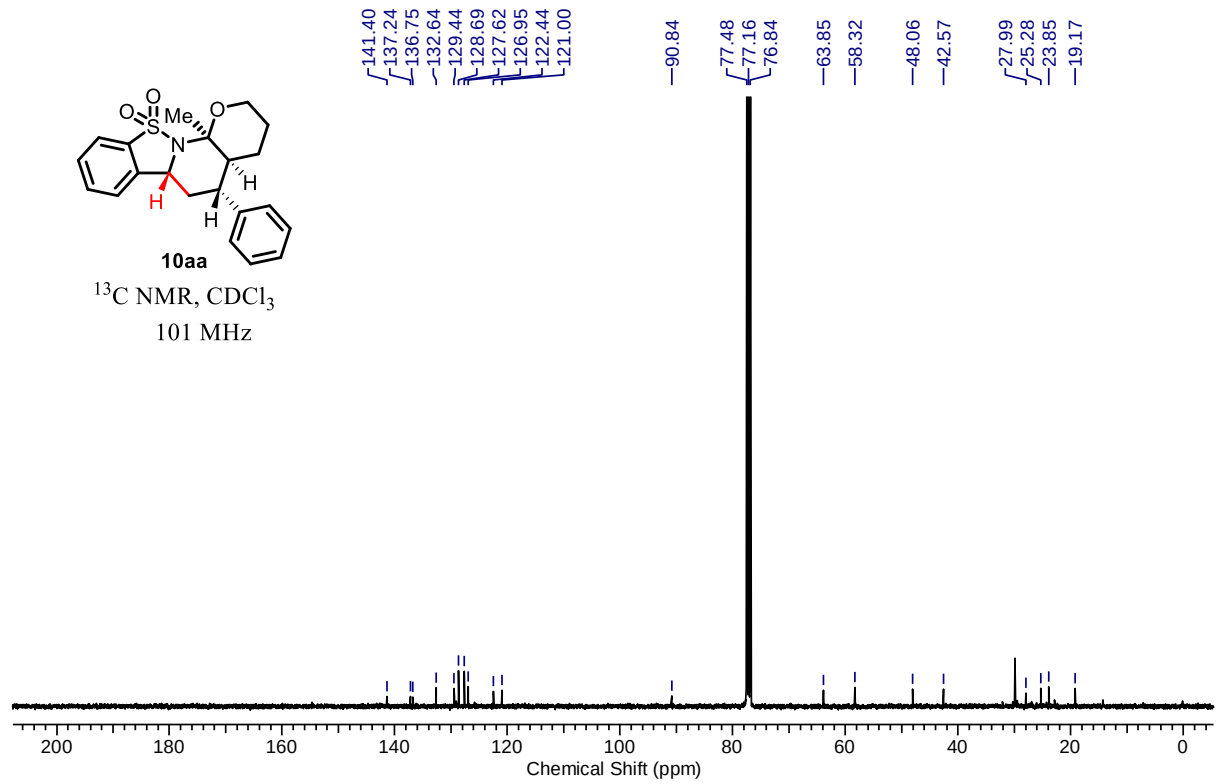
12a-Methyl-5-phenyl-3,4,4a,6,6a,12a-hexahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (10aa):



10aa

^{1}H NMR, $CDCl_3$

400 MHz

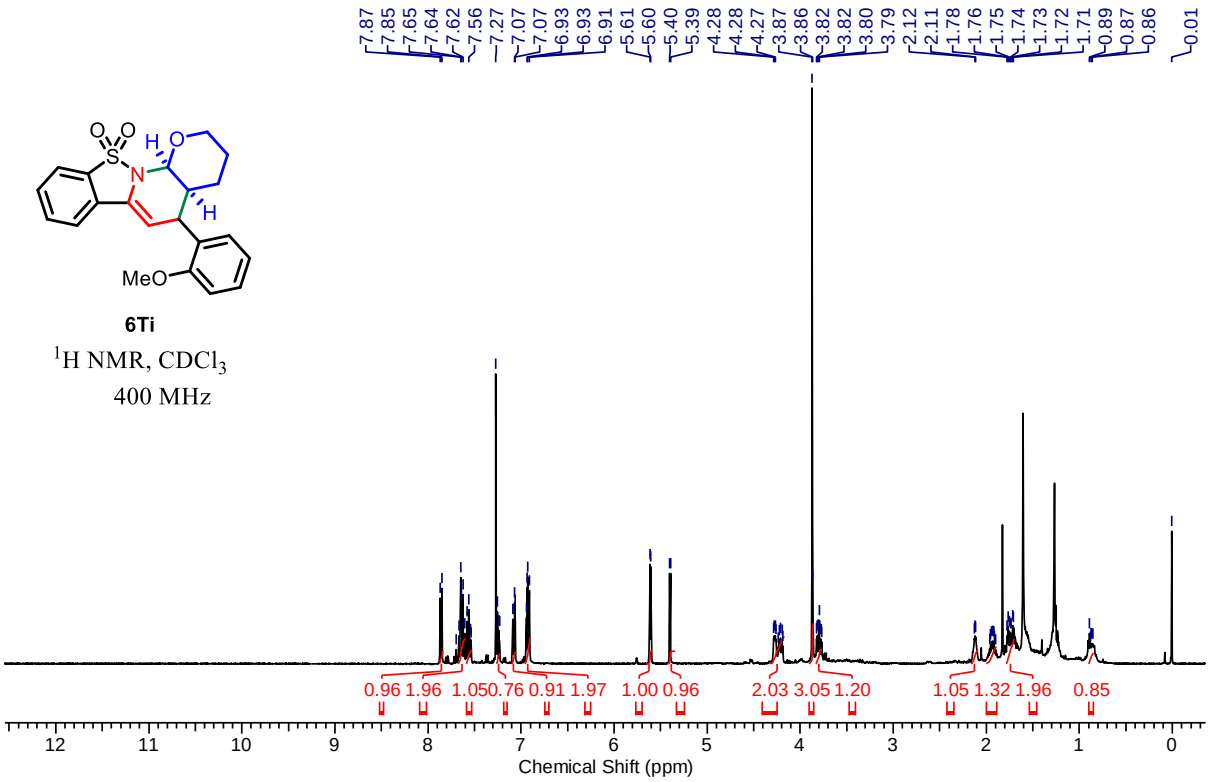


10aa

^{13}C NMR, $CDCl_3$

101 MHz

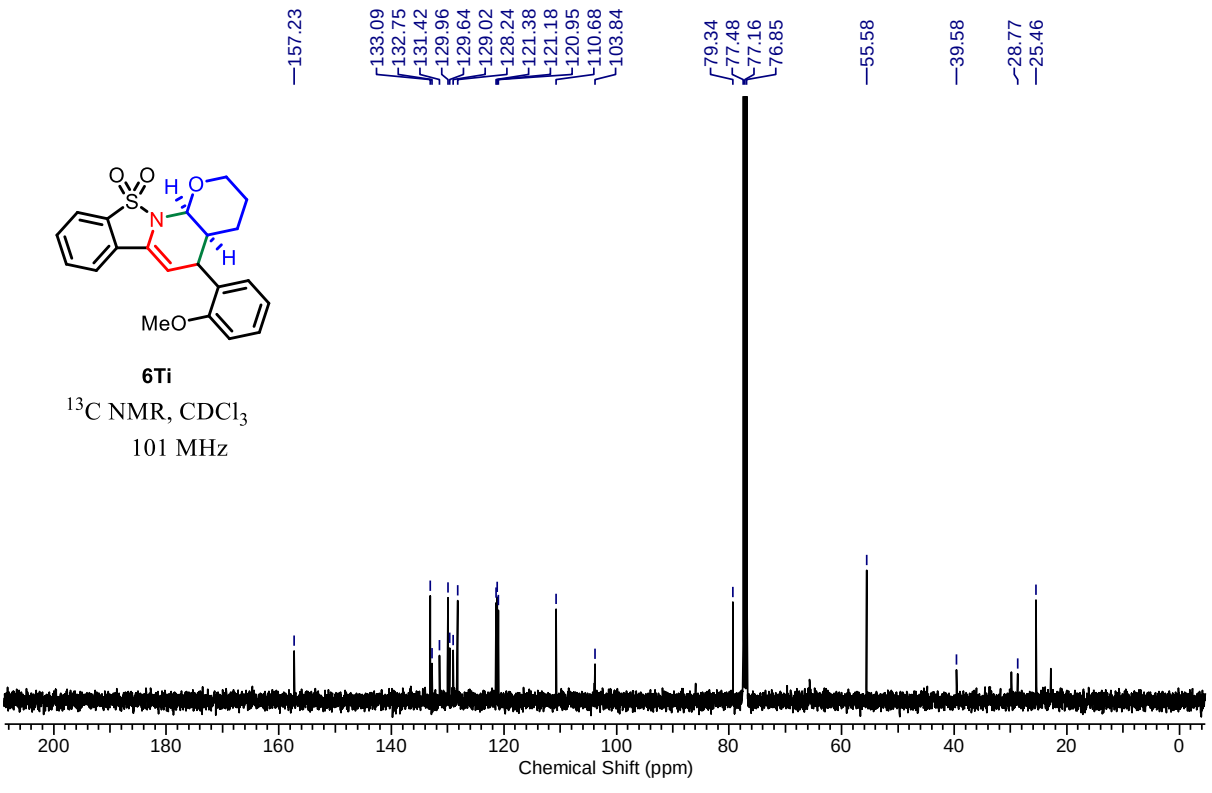
5-(2-Methoxyphenyl)-3,4,4a,12a-tetrahydro-2*H*,5*H*-benzo[4,5]isothiazolo[2,3-a]pyrano[3,2-e]pyridine 11,11-dioxide (6Ti):



6Ti

^{1}H NMR, $CDCl_3$

400 MHz



6Ti

^{13}C NMR, $CDCl_3$

101 MHz

THE END