Supporting Information

Copper-Assisted Trifluoromethylthiolation/Radical Cascade Cyclization of Alkynes to Construct SCF_3-Containing Dioxodibenzothiazepines

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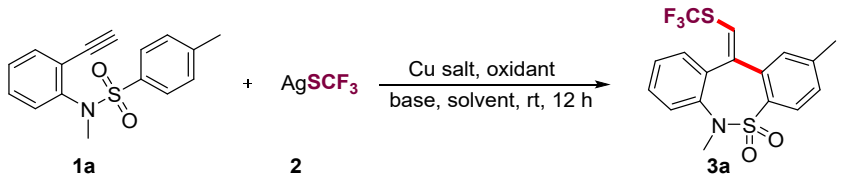
1. General Information

All manipulations were performed in dried glass reaction tube equipped with a magnetic stir bar under air atmosphere. The solvents and reagents were purchased from commercial sources without further purification unless otherwise mentioned. Products were purified by flash chromatography on silica gel (100-200 mesh). All NMR spectra were obtained on Bruker AVANCE III systems using $CDCl_3$ or DMSO-d_6 as solvent, TMS as internal standard substance, at 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR, and 376 MHz for ^{19}F NMR. The chemical shifts (δ) are reported in ppm relative to tetramethylsilane. The multiplicities of signals are designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quarter), m (multiplet), dd (doublet and doublet), td (triplet and doublet). The mass spectra were indicated by GC-MS (Thermo Fisher Scientific DSQ II). High-resolution mass spectrometry (HRMS) data were obtained on an Agilent Technologies 1290-6540 UHPLC/Accurate-Mass Quadrupole Time-of Flight (Q-TOF) LC/MS using ESI as ion source. Measured values are reported to 4 decimal places of the calculated value. X-ray analysis was performed with a single-crystal X-ray diffractometer (Gemini E). HPLC yields were determined using benzophenone as an internal standard. Melting points were measured with an XR6 microscopic melting point apparatus and were uncorrected. Magnetic hot plate stirrer (MS-H-Pro$^+$) was purchased from DLAB Scientific Co., Ltd. The material of the reaction vessel (Schlenk tubes) is borosilicate glass. *ortho*-sulfonamide phenylacetylenes **1** were prepared according to the method in the literature.[1]

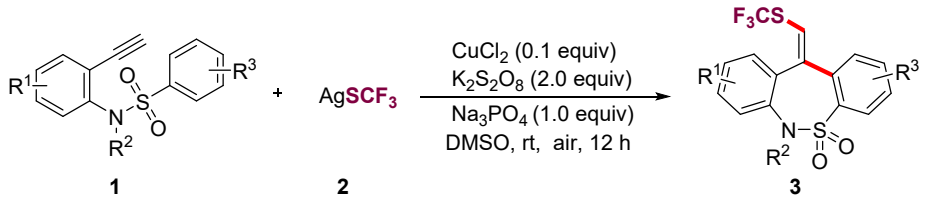
2. Optimization of the reaction conditions[a]



Entry	Cu salt	Oxidant	Base	Solvent	Yield[b] (%)
1	$CuCl_2$	$K_2S_2O_8$	Na_3PO_4	DMSO	78(73)[c]
2	$CuCl_2$	$K_2S_2O_8$	Na_3PO_4	DMSO[d]	70
3[e]	$CuCl_2$	$K_2S_2O_8$	Na_3PO_4	DMSO	35
4[f]	$CuCl_2$	$K_2S_2O_8$	Na_3PO_4	DMSO	48

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), Cu salt (0.02 mmol, 0.1 equiv), oxidant (0.4 mmol, 2.0 equiv), base (0.2 mmol, 1.0 equiv), solvent (2.0 mL), air, rt, 12 h. [b]HPLC yield using benzophenone as an internal standard. [c]Isolated yield. [d]anhydrous DMSO. [e]O_2. [f]N_2.

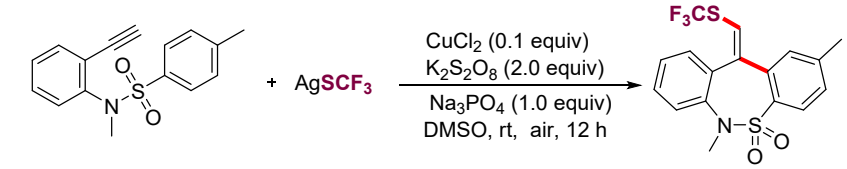
3. General procedure for the synthesis of trifluoromethylthiolated dioxodibenzothiazepines



1 2 3

Experimental Procedure: A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with *ortho*-sulfonamide phenylacetylenes **1** (0.20 mmol, 1.0 equiv), $AgSCF_3$ **2** (0.30 mmol, 1.5 equiv), $CuCl_2$ (0.02 mmol, 0.1 equiv), $K_2S_2O_8$ (0.4 mmol, 2.0 equiv), Na_3PO_4 (0.2 mmol, 1.0 equiv) and DMSO (2.0 mL). The reaction mixture was then stirred at room temperature for 12 h under air atmosphere. The reaction mixture was washed with water and extracted with ethyl acetate three times. The combined organic layer was washed with saturated NaCl solution, dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc) to afford desired products **3**.

4. Gram-scale Reaction

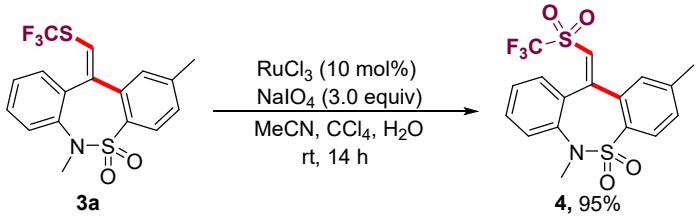


1a, 5 mmol, 1.428 g **2,** 7.5 mmol, 1.575 g **3a,** 71%, 1.368 g

A dried 100 mL Schlenk tube equipped with a magnetic stir bar was charged with *N*-(2-ethynylphenyl)-*N*,4-dimethylbenzenesulfonamide **1a** (1.428 g, 5.0 mmol, 1.0 equiv), $AgSCF_3$ **2** (1.575 g, 7.5 mmol, 1.5 equiv), $CuCl_2$ (67.3 mg, 0.5 mmol, 0.1 equiv), $K_2S_2O_8$ (2.703g, 10.0 mmol, 2.0 equiv), Na_3PO_4 (820 mg, 5.0 mmol, 1.0 equiv) and DMSO (45.0 mL). The reaction mixture was then stirred at room temperature for 12 h under air atmosphere. The reaction mixture was washed with water and extracted with ethyl acetate three times. The combined organic layer was washed with saturated NaCl solution, dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 5:1) to afford the pure product **3a** (1.368 g) in 71% yield.

5. Synthetic Applications

(1) Procedure for the oxidation of 3a

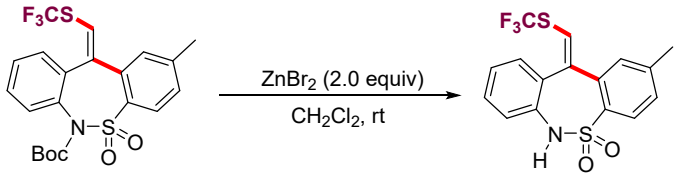


3a **4,** 95%

(*E*)-2,6-dimethyl-11-(((trifluoromethyl)sulfonyl)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (4).

A literature method of oxidation of -SCF_3 to -SO_2CF_3 was used.[2] To an intensively stirred mixture of **3a** (0.2 mmol, 1.0 equiv) in the mixed solvents of CCl_4 (1.2 mL), CH_3CN (1.2 mL) and H_2O (2.4 mL) were subsequently added $NaIO_4$ (0.6 mmol, 3.0 equiv) and $RuCl_3$ (0.02 mmol, 10 mol%) at room temperature for 14 h. The reaction mixture was washed with H_2O and extracted with DCM three times. The combined organic layer was washed with saturated NaCl solution, dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 3:1) to obtain the desired product **4**; isolated as a white solid (79.3 mg, 95% yield). M.p. = 215-216 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87 (d, J = 8.1 Hz, 1 H), 7.55-7.54 (m, 2 H), 7.44-7.36 (m, 3 H), 7.23 (like s, 1 H), 6.79 (like s, 1 H), 3.41 (s, 3 H), 2.47 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.1, 143.7, 137.7, 135.5, 135.1, 134.0, 132.5, 132.2, 129.5, 129.4, 128.7, 128.6, 128.4, 122.8, 119.4 (q, C-F, $^1J_{C\text{-}F}$ = 324.2 Hz), 38.2, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -78.36; **HRMS (ESI-TOF)** *m/z*: [M + Na]$^+$ Calcd for $C_{17}H_{14}F_3NO_4S_2Na$ 440.0209; Found 440.0210.

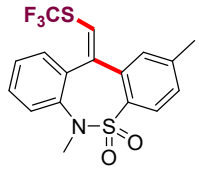
(2) Cleavage of *N*-Boc Protecting Group



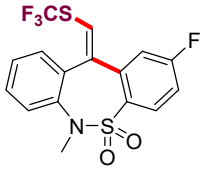
3zb **3zc**, 81%

The related literature method of cleavage of *N*-Boc protecting group was used.[3] The compound **3zb** (94.3 mg, 0.2 mmol) was added into a reaction tube. Then, $ZnBr_2$ (90.1 mg, 0.4 mmol) and DCM (3 mL) were added sequentially. The resulting mixture was stirred at room temperature for 12 hours as monitored by TLC. Upon completion, the solvent was removed under vacuum. The residue was purified directly by silica gel chromatography (Petroleum ether/EtOAc = 5:1) to obtain the desired product **3zc**; isolated as a white solid (60.2 mg, 81% yield). M.p. = 88-90 °C. **(*E*)-2-methyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3zc)**. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.0 Hz, 1 H), 7.38-7.29 (m, 3 H), 7.25-7.21 (m, 2 H), 7.09 (d, J = 8.0 Hz, 1 H), 7.03 (s, 1 H), 6.62 (s, 1 H), 2.44 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.4, 141.8, 136.5, 136.2, 133.6, 130.5, 129.9, 129.7, 129.6, 129.3 (q, C-F, $^1J_{C\text{-}F}$ = 306.7 Hz), 127.8, 125.5, 125.4, 123.8, 119.3 (q, C-F, $^3J_{C\text{-}F}$ = 3.4 Hz), 21.5; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -42.22; **HRMS (ESI-TOF)** *m/z*: [M + Na]$^+$ Calcd for $C_{16}H_{12}F_3NNaO_2S_2$ 394.0154; Found 394.0170.

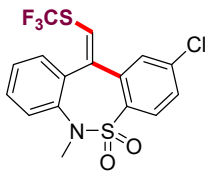
6. Characterization data of products 3



(*E*)-2,6-dimethyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3a). White solid, 73% yield (56.3 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 143-144 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.1 Hz, 1 H), 7.56 (dd, *J* = 7.8 Hz, 1.1 Hz, 1 H), 7.47 (td, *J* = 7.5 Hz, 1.5 Hz, 1 H), 7.39 (td, *J* = 7.5 Hz, 1.3 Hz, 1 H), 7.31 (d, *J* = 9.0 Hz, 1 H), 7.27 (s, 1 H), 7.23 (dd, *J* = 7.6 Hz, 1.4 Hz, 1 H), 6.81 (s, 1 H), 3.33 (s, 3 H), 2.45 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.1, 142.3, 137.6, 137.3, 137.1, 135.1, 131.0, 130.6, 130.5, 129.6, 129.4, 129.3 (q, C-F, $^{1}J_{C\text{-}F}$ = 306.6 Hz), 129.1, 128.1, 120.8 (q, C-F, $^{3}J_{C\text{-}F}$ = 3.2 Hz), 38.6, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -42.02; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{15}F_3NO_2S_2$ 386.0491; Found 386.0488.

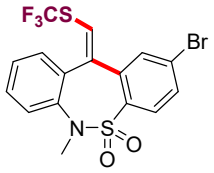


(*E*)-2-fluoro-6-methyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3b). White solid, 62% yield (48.3 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 142-143 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95 (dd, *J* = 8.3 Hz, 5.6 Hz,1 H), 7.57 (dd, *J* = 7.8 Hz, 1.2 Hz, 1 H), 7.50 (td, *J* = 7.5 Hz, 1.5 Hz, 1 H), 7.42 (td, *J* = 7.5 Hz, 1.4 Hz, 1 H), 7.25 (dd, *J* = 7.2 Hz, 1.4 Hz, 1 H), 7.24-7.17 (m, 2 H), 6.86 (s, 1 H), 3.33 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.1 (d, C-F, $^{1}J_{C\text{-}F}$ = 253.5 Hz), 140.7, 137.7 (d, C-F, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 137.3, 136.8, 136.1 (d, C-F, $^{4}J_{C\text{-}F}$ = 3.6 Hz), 131.3, 130.9 (d, C-F, $^{3}J_{C\text{-}F}$ = 9.3 Hz), 130.6, 129.7, 129.3, 129.1 (q, C-F, $^{1}J_{C\text{-}F}$ = 307.0 Hz), 122.6 (q, C-F, $^{3}J_{C\text{-}F}$ = 3.4 Hz), 116.9 (d, C-F, $^{2}J_{C\text{-}F}$ = 21.9 Hz), 115.8 (d, C-F, $^{2}J_{C\text{-}F}$ = 23.3 Hz), 38.7; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -41.93, -105.66; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{12}F_4NO_2S_2$ 390.0240; Found 390.0242.

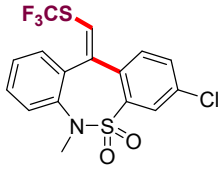


(*E*)-2-chloro-6-methyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3c). White solid, 75% yield (60.9 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 162-163 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 9.0 Hz, 1 H), 7.56 (dd, *J* = 7.8 Hz, 1.2 Hz, 1 H), 7.52-7.47 (m, 3 H), 7.42 (td, *J* = 7.5 Hz, 1.4 Hz, 1 H), 7.24 (dd, *J* = 7.6 Hz, 1.4 Hz, 1 H), 6.86 (s, 1 H), 3.33 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ

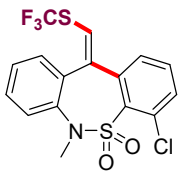
140.5, 138.5, 138.4, 137.0, 136.9, 136.6, 131.3, 130.5, 129.7, 129.7, 129.6, 129.4, 129.1 (q, C-F, $^{1}J_{C\text{-}F}$ = 307.0 Hz), 128.7, 122.5 (q, C-F, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 38.7; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -41.86; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{12}ClF_3NO_2S_2$ 405.9945; Found 405.9945.



(*E*)-2-bromo-6-methyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3d). White solid, 79% yield (71.1 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 165-166 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 9.0 Hz, 1 H), 7.65-7.62 (m, 2 H), 7.56 (dd, *J* = 7.8 Hz, 1.2 Hz, 1 H), 7.50 (td, *J* = 7.5 Hz, 1.5 Hz, 1 H), 7.42 (td, *J* = 7.5 Hz, 1.4 Hz, 1 H), 7.24 (dd, *J* = 7.5 Hz, 1.4 Hz, 1 H), 6.86 (s, 1 H), 3.33 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 140.4, 139.0, 137.0, 136.9, 136.7, 132.7, 131.5, 131.4, 130.5, 129.7, 129.6, 129.4, 129.1 (q, C-F, $^{1}J_{C\text{-}F}$ = 307.1 Hz), 126.7, 122.5 (q, C-F, $^{3}J_{C\text{-}F}$ = 3.4 Hz), 38.7; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -41.84; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{12}BrF_3NO_2S_2$ 449.9439; Found 449.9441.

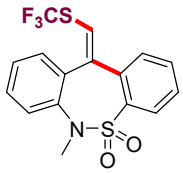


(*E*)-3-chloro-6-methyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3e). White solid, 51% yield (41.4 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 135-136 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 2.1 Hz, 1 H), 7.56 (dd, *J* = 7.8 Hz, 1.2 Hz, 1 H), 7.52-7.48 (m, 2 H), 7.44 (s, 1 H), 7.42-7.39 (m, 1 H), 7.24 (dd, *J* = 7.6 Hz, 1.4 Hz, 1 H), 6.81 (s, 1 H), 3.34 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 141.3, 140.8, 137.2, 136.9, 135.9, 133.4, 132.5, 131.3, 130.6, 130.3, 129.6, 129.4, 129.1 (q, C-F, $^{1}J_{C\text{-}F}$ = 307.0 Hz), 128.1, 121.9 (q, C-F, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 38.8; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -41.98; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{12}ClF_3NO_2S_2$ 405.9945; Found 405.9946.

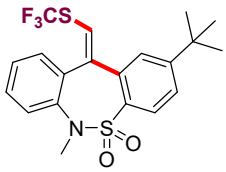


(*E*)-4-chloro-6-methyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3f). White solid, 46% yield (37.3 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 167-168 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 7.8 Hz, 1.1 Hz, 1 H), 7.54 (dd, *J* = 7.8 Hz, 1.5 Hz, 1 H), 7.50 (td, *J* = 7.6 Hz, 1.5 Hz, 1 H), 7.44-7.40 (m, 2 H),

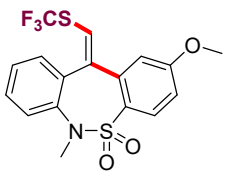
7.37 (dd, J = 7.8 Hz, 1.5 Hz, 1 H), 7.21 (dd, J = 7.5 Hz, 1.4 Hz, 1 H), 6.88 (s, 1 H), 3.39 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 141.9, 138.6, 138.3, 138.0, 136.3, 134.7, 133.0, 132.1, 131.3, 130.8, 129.7, 129.2 (q, C-F, $^1J_{C\text{-}F}$ = 306.8 Hz), 128.9, 128.3, 121.3 (q, C-F, $^3J_{C\text{-}F}$ = 3.4 Hz), 39.0; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -41.82; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{12}ClF_3NO_2S_2$ 405.9945; Found 405.9941.



(*E*)-6-methyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3g). White solid, 80% yield (59.4 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 107-108 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 (dd, J = 7.4 Hz, 1.6 Hz, 1 H), 7.58-7.51 (m, 3 H), 7.49-7.47 (m, 2 H), 7.40 (td, J = 7.5 Hz, 1.4 Hz, 1 H), 7.25 (dd, J = 7.7 Hz, 1.4 Hz, 1 H), 6.82 (s, 1 H), 3.35 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 142.0, 140.0, 137.6, 137.2, 135.1, 132.4, 131.1, 130.6, 129.8, 129.6, 129.2 (q, C-F, $^1J_{C\text{-}F}$ = 306.9 Hz), 129.1, 129.0, 128.2, 121.2 (q, C-F, $^3J_{C\text{-}F}$ = 3.5 Hz), 38.7; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -42.03; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{13}F_3NO_2S_2$ 372.0334; Found 372.0338.

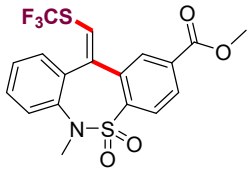


(*E*)-2-(tert-butyl)-6-methyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3h). White solid, 82% yield (70.1 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 158-159 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.86 (d, J = 8.4 Hz, 1 H), 7.56 (dd, J = 7.8 Hz, 1.1 Hz, 1 H), 7.53 (dd, J = 8.4 Hz, 2.0 Hz, 1 H), 7.47 (td, J = 7.6 Hz, 1.5 Hz, 1 H), 7.42-7.38 (m, 2 H), 7.25 (dd, J = 7.8 Hz, 1.4 Hz, 1 H), 6.77 (s, 1 H), 3.34 (s, 3 H), 1.37 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.2, 143.0, 137.8, 137.2, 137.0, 134.9, 131.0, 130.6, 129.6, 129.3 (q, C-F, $^1J_{C\text{-}F}$ = 306.7 Hz), 129.1, 128.0, 127.2, 125.7, 120.6 (q, C-F, $^3J_{C\text{-}F}$ = 3.5 Hz), 38.6, 35.2, 31.1; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -42.04; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{21}F_3NO_2S_2$ 428.0960; Found 428.0961.

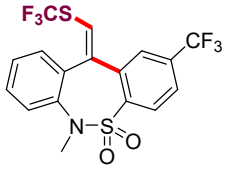


(*E*)-2-methoxy-6-methyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3i). White solid, 72% yield (57.8

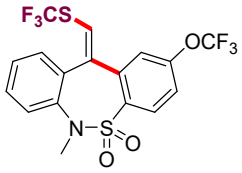
mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 130-131 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.8 Hz, 1 H), 7.56 (dd, *J* = 7.8 Hz, 1.1 Hz, 1 H), 7.47 (td, *J* = 7.5 Hz, 1.5 Hz, 1 H), 7.39 (td, *J* = 7.6 Hz, 1.5 Hz, 1 H), 7.23 (dd, *J* = 7.6 Hz, 1.4 Hz, 1 H), 7.00 (dd, *J* = 8.8 Hz, 2.6 Hz, 1 H), 6.93 (d, *J* = 2.6 Hz, 1 H), 6.82 (s, 1 H), 3.90 (s, 3 H), 3.32 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.2, 142.0, 137.4, 137.2, 137.1, 131.9, 131.1, 130.5, 130.2, 129.6, 129.2 (q, C-F, $^1J_{C\text{-}F}$ = 306.9 Hz), 129.0, 121.2 (q, C-F, $^3J_{C\text{-}F}$ = 3.4 Hz), 114.4, 55.8, 38.7; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -42.03; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{15}F_3NO_3S_2$ 402.0440; Found 402.0438.



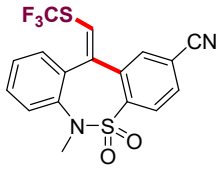
Methyl(*E*)-6-methyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine-2-carboxylate 5,5-dioxide (3j). White solid, 85% yield (73.0 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 164-165 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.15-8.12 (m, 2 H), 8.01 (d, *J* = 8.2 Hz, 1 H), 7.58 (dd, *J* = 7.8 Hz, 1.2 Hz, 1 H), 7.51 (td, *J* = 7.5 Hz, 1.5 Hz, 1 H), 7.43 (td, *J* = 7.5 Hz, 1.4 Hz, 1 H), 7.25 (dd, *J* = 7.5 Hz, 1.4 Hz, 1 H), 6.90 (s, 1 H), 3.99 (s, 3 H), 3.36 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.3, 143.8, 140.9, 137.3, 136.8, 135.4, 133.6, 131.3, 130.5, 130.3, 130.2, 129.7, 129.5, 129.1 (q, C-F, $^1J_{C\text{-}F}$ = 306.9 Hz), 128.6, 121.2 (q, C-F, $^3J_{C\text{-}F}$ = 3.4 Hz), 52.8, 38.8; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -41.85; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{15}F_3NO_4S_2$ 430.0389; Found 430.0387.



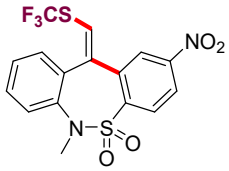
(*E*)-6-methyl-2-(trifluoromethyl)-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3k). White solid, 62% yield (54.5 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 146-147 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.2 Hz, 1 H), 7.76 (d, *J* = 8.3 Hz, 1 H), 7.73 (s, 1 H), 7.58 (dd, *J* = 7.8 Hz, 1.1 Hz, 1 H), 7.52 (td, *J* = 7.5 Hz, 1.4 Hz, 1 H), 7.44 (td, *J* = 7.5 Hz, 1.4 Hz, 1 H), 7.27 (dd, *J* = 7.5 Hz, 1.4 Hz, 1 H), 6.90 (s, 1 H), 3.36 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.4, 140.5, 136.9, 136.8, 135.8, 134.2 (q, C-F, $^2J_{C\text{-}F}$ = 33.0 Hz), 131.5, 130.5, 129.7, 129.5, 129.1, 129.0 (q, C-F, $^1J_{C\text{-}F}$ = 306.9 Hz), 126.4 (q, C-F, $^3J_{C\text{-}F}$ = 3.5 Hz), 125.9 (q, C-F, $^3J_{C\text{-}F}$ = 3.6 Hz), 123.0 (q, C-F, $^1J_{C\text{-}F}$ = 271.4 Hz), 123.1 (q, C-F, $^3J_{C\text{-}F}$ = 3.5 Hz), 38.8; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -41.81, -63.05; **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{11}F_6NNaO_2S_2$ 462.0028; Found 462.0030.



(*E*)-6-methyl-2-(trifluoromethoxy)-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3l). White solid, 45% yield (41.0 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 117-118 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.7 Hz, 1 H), 7.57 (dd, *J* = 7.8 Hz, 1.1 Hz, 1 H), 7.51 (td, *J* = 7.5 Hz, 1.4 Hz, 1 H), 7.43 (td, *J* = 7.5 Hz, 1.4 Hz, 1 H), 7.37-7.34 (m, 1 H), 7.31 (like s, 1 H), 7.26 (dd, *J* = 7.5 Hz, 1.4 Hz, 1 H), 6.86 (s, 1 H), 3.35 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.4 (q, C-F, $^3J_{C\text{-}F}$ = 1.5 Hz), 140.4, 138.4, 137.4, 137.0, 136.8, 131.4, 130.6, 130.4, 129.7, 129.4, 129.0 (q, C-F, $^1J_{C\text{-}F}$ = 306.7 Hz), 122.9 (q, C-F, $^3J_{C\text{-}F}$ = 3.5 Hz), 121.3, 120.8, 120.2 (q, C-F, $^1J_{C\text{-}F}$ = 258.1 Hz), 38.7; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -41.90, -57.60; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{12}F_6NO_3S_2$ 456.0157; Found 456.0158.

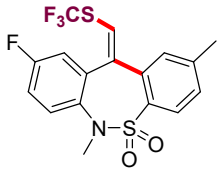


(*E*)-6-methyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine-2-carbonitrile 5,5-dioxide (3m). White solid, 57% yield (45.2 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 200-201 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.1 Hz, 1 H), 7.80-7.76 (m, 2 H), 7.58 (dd, *J* = 7.9 Hz, 1.3 Hz, 1 H), 7.53 (td, *J* = 7.8 Hz, 1.5 Hz, 1 H), 7.45 (td, *J* = 7.5 Hz, 1.5 Hz, 1 H), 7.27 (dd, *J* = 7.6 Hz, 1.4 Hz, 1 H), 6.91 (s, 1 H), 3.35 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.1, 139.4, 136.7, 136.6, 136.2, 132.6, 132.5, 131.6, 130.5, 129.8, 129.7, 129.2, 129.0 (q, C-F, $^1J_{C\text{-}F}$ = 307.1 Hz), 123.9 (q, C-F, $^3J_{C\text{-}F}$ = 3.5 Hz), 116.9, 116.3, 38.8; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -41.75; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{12}F_3N_2O_2S_2$ 397.0287; Found 397.0287.

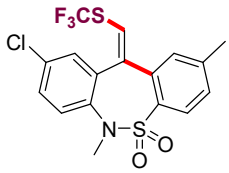


(*E*)-6-methyl-2-nitro-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3n). White solid, 39% yield (32.5 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 226-227 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 2.2 Hz, 1 H), 7.31 (dd, *J* = 8.7 Hz, 2.2 Hz, 1 H), 8.13 (d, *J* = 8.6 Hz, 1 H), 7.59 (dd, *J* = 7.9 Hz, 1.3 Hz, 1 H), 7.54 (td, *J* = 7.4 Hz, 1.5 Hz, 1 H), 7.47 (td, *J* = 7.5 Hz, 1.5 Hz, 1 H), 7.29 (dd, *J* = 7.5 Hz, 1.3 Hz, 1 H), 6.99 (s, 1 H), 3.37 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.4,

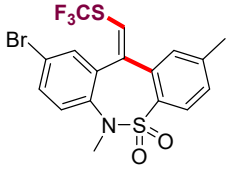
145.5, 139.4, 136.7, 136.6, 136.5, 131.7, 130.6, 130.0, 129.8, 129.7, 128.9 (q, C-F, $^{1}J_{C\text{-}F}$ = 307.4 Hz), 124.4 (q, C-F, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 124.0, 38.8; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -41.70; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{12}F_3N_2O_4S_2$ 417.0185; Found 417.0187.



(*E*)-9-fluoro-2,6-dimethyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3o). White solid, 70% yield (56.5 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 117-118 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.1 Hz, 1 H), 7.54 (dd, *J* = 8.7 Hz, 5.1 Hz, 1 H), 7.33 (dd, *J* = 8.1 Hz, 1.0 Hz, 1 H), 7.25 (s, 1 H), 7.14 (td, *J* = 8.6 Hz, 2.9 Hz, 1 H), 6.94 (dd, *J* = 8.1 Hz, 2.9 Hz, 1 H), 6.83 (s, 1 H), 3.32 (s, 3 H), 2.45 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.1 (d, C-F, $^{1}J_{C\text{-}F}$ = 250.1 Hz), 143.3, 140.9, 139.6 (d, C-F, $^{3}J_{C\text{-}F}$ = 8.7 Hz), 137.0, 134.4, 133.3 (d, C-F, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 132.7 (d, C-F, $^{3}J_{C\text{-}F}$ = 9.3 Hz), 130.7, 129.4, 129.1 (q, C-F, $^{1}J_{C\text{-}F}$ = 306.9 Hz), 128.3, 121.4 (q, C-F, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 117.8 (d, C-F, $^{2}J_{C\text{-}F}$ = 22.4 Hz), 116.5 (d, C-F, $^{2}J_{C\text{-}F}$ = 23.4 Hz), 38.7, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -41.84, -110.37; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{14}F_4NO_2S_2$ 404.0397; Found 404.0399.

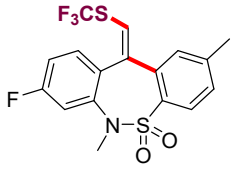


(*E*)-9-chloro-2,6-dimethyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3p). White solid, 69% yield (57.9 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 118-119 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.1 Hz, 1 H), 7.49 (d, *J* = 8.4 Hz, 1 H), 7.43 (dd, *J* = 8.4 Hz, 2.4 Hz, 1 H), 7.33 (dd, *J* = 8.1 Hz, 1.0 Hz, 1 H), 7.25 (s, 1 H), 7.22 (d, *J* = 2.3 Hz, 1 H), 6.83 (s, 1 H), 3.31 (s, 3 H), 2.45 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.4, 140.8, 139.0, 136.9, 136.0, 134.9, 134.5, 131.9, 131.0, 130.7, 129.5, 129.4, 129.1 (q, C-F, $^{1}J_{C\text{-}F}$ = 307.0 Hz), 128.2, 121.5 (q, C-F, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 38.6, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -41.82; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{14}ClF_3NO_2S_2$ 420.0101; Found 420.0100.

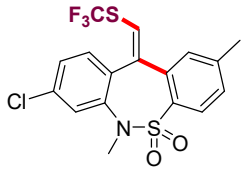


(*E*)-9-bromo-2,6-dimethyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3q). White solid, 67% yield (62.2 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. =

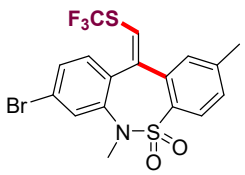
116-117 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.1 Hz, 1 H), 7.58 (dd, *J* = 8.4 Hz, 2.4 Hz, 1 H), 7.42 (d, *J* = 8.4 Hz, 1 H), 7.38 (d, *J* = 2.2 Hz, 1 H), 7.33 (dd, *J* = 8.1 Hz, 1.0 Hz, 1 H), 7.24 (s, 1 H), 6.82 (s, 1 H), 3.30 (s, 3 H), 2.45 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.4, 140.7, 139.2, 136.9, 136.5, 134.5, 134.0, 132.3, 132.1, 130.7, 129.5, 129.1 (q, C-F, $^1J_{C\text{-}F}$ = 307.0 Hz), 128.2, 122.8, 121.5 (q, C-F, $^3J_{C\text{-}F}$ = 3.5 Hz), 38.6, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -41.82; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{14}BrF_3NO_2S_2$ 463.9596; Found 463.9595.



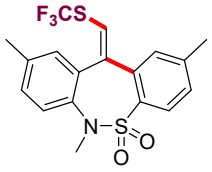
(*E*)-8-fluoro-2,6-dimethyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3r). White solid, 84% yield (67.8 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 186-187 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.1 Hz, 1 H), 7.32 (dd, *J* = 8.1 Hz, 1.0 Hz, 1 H), 7.28-7.25 (m, 1 H), 7.21 (dd, *J* = 8.5 Hz, 5.8 Hz, 1 H), 7.10 (td, *J* = 8.1 Hz, 2.6 Hz, 1 H), 6.80 (s, 1 H), 3.32 (s, 3 H), 2.45 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.3 (d, C-F, $^1J_{C\text{-}F}$ = 250.9 Hz), 143.4, 141.3, 139.3 (d, C-F, $^3J_{C\text{-}F}$ = 10.6 Hz), 136.7, 134.9, 133.2 (d, C-F, $^4J_{C\text{-}F}$ = 3.6 Hz), 131.0 (d, C-F, $^3J_{C\text{-}F}$ = 9.1 Hz), 130.5, 129.4, 129.2 (q, C-F, $^1J_{C\text{-}F}$ = 306.8 Hz), 128.0, 121.2 (q, C-F, $^3J_{C\text{-}F}$ = 3.2 Hz), 117.7 (d, C-F, $^2J_{C\text{-}F}$ = 22.4 Hz), 116.2 (d, C-F, $^2J_{C\text{-}F}$ = 21.5 Hz), 38.5, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -41.93, -108.51; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{14}F_4NO_2S_2$ 404.0397; Found 404.0397.



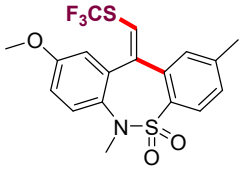
(*E*)-8-chloro-2,6-dimethyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3s). White solid, 76% yield (63.8 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 151-152 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.1 Hz, 1 H), 7.55 (d, *J* = 2.1 Hz, 1 H), 7.37 (dd, *J* = 8.2 Hz, 2.1 Hz, 1 H), 7.33 (dd, *J* = 8.1 Hz, 1.0 Hz, 1 H), 7.26 (s, 1 H), 7.17 (d, *J* = 8.2 Hz, 1 H), 6.80 (s, 1 H), 3.31 (s, 3 H), 2.45 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.4, 141.2, 138.7, 136.8, 136.2, 135.6, 134.7, 130.6, 130.5, 129.4, 129.2, 129.1 (q, C-F, $^1J_{C\text{-}F}$ = 307.0 Hz), 128.1, 121.3 (q, C-F, $^3J_{C\text{-}F}$ = 3.5 Hz), 38.6, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -41.89; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{14}ClF_3NO_2S_2$ 420.0101; Found 420.0100.



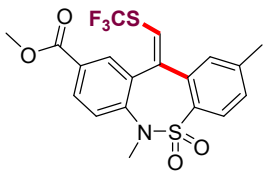
(*E*)-8-bromo-2,6-dimethyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3t). White solid, 72% yield (66.9 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 131-132 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.1 Hz, 1 H), 7.70 (d, *J* = 1.9 Hz, 1 H), 7.52 (dd, *J* = 8.2 Hz, 2.0 Hz, 1 H), 7.32 (d, *J* = 8.1 Hz, 1 H), 7.25 (s, 1 H), 7.11 (d, *J* = 8.2 Hz, 1 H), 6.80 (s, 1 H), 3.31 (s, 3 H), 2.45 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.4, 141.2, 138.8, 136.8, 136.1, 134.7, 133.5, 132.2, 130.8, 130.6, 129.4, 129.3 (q, C-F, $^1J_{C\text{-}F}$ = 307.0 Hz), 128.1, 124.0, 121.3 (q, C-F, $^3J_{C\text{-}F}$ = 3.4 Hz), 38.6, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -41.89; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{14}BrF_3NO_2S_2$ 463.9596; Found 463.9600.



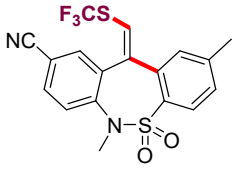
(*E*)-2,6,9-trimethyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3u). White solid, 67% yield (53.5 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 160-161 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.1 Hz, 1 H), 7.43 (d, *J* = 8.0 Hz, 1 H), 7.30 (d, *J* = 8.2 Hz, 1 H), 7.27-7.25 (m, 2 H), 7.01 (s, 1 H), 6.78 (s, 1 H), 3.31 (s, 3 H), 2.44 (s, 3 H), 2.37 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.0, 142.3, 139.5, 137.5, 137.2, 135.1, 134.5, 131.6, 130.4, 130.3, 129.9, 129.3, 129.3 (q, C-F, $^1J_{C\text{-}F}$ = 306.7 Hz), 128.2, 120.5 (q, C-F, $^3J_{C\text{-}F}$ = 3.4 Hz), 38.6, 21.4, 21.1; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -42.05; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{17}F_3NO_2S_2$ 400.0647; Found 400.0648.



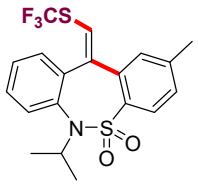
(*E*)-9-methoxy-2,6-dimethyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3v). White solid, 68% yield (56.5 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 154-155 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.1 Hz, 1 H), 7.47 (d, *J* = 8.7 Hz, 1 H), 7.31 (d, *J* = 8.1 Hz, 1 H), 7.25 (s, 1 H), 6.94 (dd, *J* = 8.7 Hz, 2.8 Hz, 1 H), 6.80 (s, 1 H), 6.70 (d, *J* = 2.8 Hz, 1 H), 3.81 (s, 3 H), 3.31 (s, 3 H), 2.44 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.7, 143.0, 142.0, 139.0, 137.3, 134.8, 132.0, 130.5, 129.5, 129.3, 129.3 (q, C-F, $^1J_{C\text{-}F}$ = 306.9 Hz), 128.3, 120.7 (q, C-F, $^3J_{C\text{-}F}$ = 3.5 Hz), 115.7, 114.7, 55.7, 38.8, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -42.03; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{17}F_3NO_3S_2$ 416.0596; Found 416.0598.



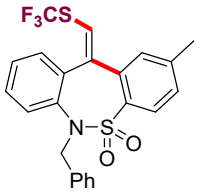
methyl(*E*)-2,6-dimethyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine-9-carboxylate 5,5-dioxide (3w). White solid, 67% yield (59.4 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 128-129 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.12 (dd, *J* = 8.2 Hz, 2.0 Hz, 1 H), 7.94 (d, *J* = 1.9 Hz, 1 H), 7.81 (d, *J* = 8.0 Hz, 1 H), 7.58 (d, *J* = 8.2 Hz, 1 H), 7.33 (dd, *J* = 8.1 Hz, 1.0 Hz, 1 H), 7.28 (s, 1 H), 6.80 (s, 1 H), 3.94 (s, 3 H), 3.33 (s, 3 H), 2.46 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.5, 143.7, 141.9, 141.4, 136.5, 136.3, 134.9, 132.0, 131.1, 130.4, 130.2, 129.8, 129.5, 129.1 (q, C-F, $^1J_{C\text{-}F}$ = 307.0 Hz), 127.8, 121.4 (q, C-F, $^3J_{C\text{-}F}$ = 3.3 Hz), 52.6, 38.6, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -41.94; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{17}F_3NO_4S_2$ 444.0546; Found 444.0547.



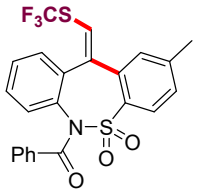
(*E*)-2,6-dimethyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine-9-carbonitrile 5,5-dioxide (3x). White solid, 58% yield (47.6 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 183-184 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.1 Hz, 1 H), 7.75 (dd, *J* = 8.2 Hz, 1.9 Hz, 1 H), 7.60 (d, *J* = 8.3 Hz, 1 H), 7.58 (d, *J* = 1.8 Hz, 1 H), 7.36 (dd, *J* = 8.1 Hz, 0.9 Hz, 1 H), 7.28 (s, 1 H), 6.82 (s, 1 H), 3.33 (s, 3 H), 2.47 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.1, 142.4, 140.3, 136.6, 136.2, 134.4, 134.3, 133.4, 130.7, 130.3, 129.6, 129.0 (q, C-F, $^1J_{C\text{-}F}$ = 307.1 Hz), 127.6, 122.1 (q, C-F, $^3J_{C\text{-}F}$ = 3.5 Hz), 117.3, 112.2, 38.6, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -41.71; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{14}F_3N_2O_2S_2$ 411.0443; Found 411.0441.



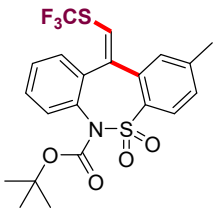
(*E*)-6-isopropyl-2-methyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3y). White solid, 86% yield (71.1 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 138-139 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.0 Hz, 1 H), 7.53 (dd, *J* = 7.9 Hz, 1.2 Hz, 1 H), 7.47 (td, *J* = 7.8 Hz, 1.6 Hz, 1 H), 7.40 (td, *J* = 7.5 Hz, 1.5 Hz, 1 H), 7.30-7.25 (m, 3 H), 6.79 (s, 1 H), 4.62-4.52 (m, 1 H), 2.43 (s, 3 H), 1.27 (like s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 142.7, 142.1, 139.6, 138.2, 135.0, 133.2, 132.5, 130.5, 130.3, 129.5, 129.2, 129.3 (q, C-F, $^1J_{C\text{-}F}$ = 306.8 Hz), 127.4, 120.6 (q, C-F, $^3J_{C\text{-}F}$ = 3.4 Hz), 53.8, 21.3; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -42.09; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{19}F_3NO_2S_2$ 414.0804; Found 414.0804.



(*E*)-6-benzyl-2-methyl-11-(((trifluoromethyl)thio)methylene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3z). White solid, 56% yield (51.7 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 161-163 °C. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 7.79 (d, J = 8.1 Hz, 1 H), 7.57 (s, 1 H), 7.46 (dd, J = 7.7 Hz, 1.0 Hz, 1 H), 7.43 (dd, J = 7.5 Hz, 1.2 Hz, 1 H), 7.39-7.31 (m, 6 H), 7.25 (d, J = 8.2 Hz, 2 H), 7.04 (dd, J = 7.6 Hz, 1.1 Hz, 1 H), 5.09 (s, 1 H), 4.31 (s, 1 H), 2.44 (s, 3 H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ 143.2, 141.6, 137.8, 136.5, 135.9, 134.6, 134.0, 131.3, 130.6, 130.5, 130.4, 129.8, 129.4, 128.6, 128.3, 127.9, 129.1 (q, C-F, $^{1}J_{C\text{-}F}$ = 306.9 Hz), 127.3, 120.6 (q, C-F, $^{3}J_{C\text{-}F}$ = 3.4 Hz), 54.3, 20.7; **^{19}F NMR** (376 MHz, DMSO-d_6): δ -40.69; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{19}F_3NO_2S_2$ 462.0804; Found 462.0809.

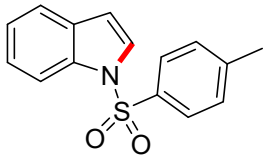


(*E*)-(2-methyl-5,5-dioxido-11-(((trifluoromethyl)thio)methylene)dibenzo[*c*,*f*][1,2]thiazepin-6(11*H*)-yl)(phenyl)methanone (3za). White solid, 71% yield (67.5 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 190-191 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.1 Hz, 1 H), 7.83 (d, J = 7.9 Hz, 1 H), 7.67 (d, J = 7.4 Hz, 2 H), 7.49 (td, J = 7.7 Hz, 1.2 Hz, 1 H), 7.42 (t, J = 7.3 Hz, 1 H), 7.38-7.28 (m, 5 H), 7.21 (d, J = 7.6 Hz, 1 H), 6.90 (s, 1 H), 2.47 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 169.5, 144.0, 138.3, 138.0, 136.1, 134.4, 134.3, 133.1, 132.7, 132.2, 130.9, 130.6, 130.3, 130.2, 130.0, 129.4, 129.2 (q, C-F, $^{1}J_{C\text{-}F}$ = 306.9 Hz), 128.0, 127.5, 123.3 (q, C-F, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 21.5; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -41.76; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{17}F_3NO_3S_2$ 476.0596; Found 476.0597.



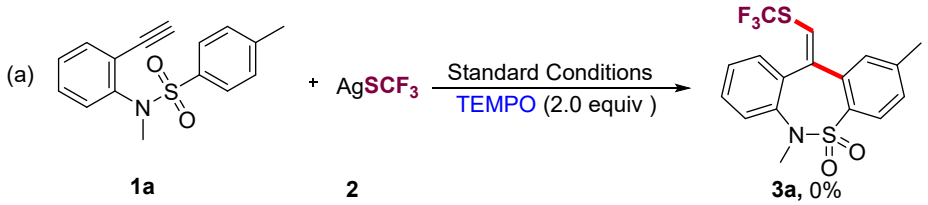
tert-butyl(*E*)-2-methyl-11-(((trifluoromethyl)thio)methylene)dibenzo[*c*,*f*][1,2]thiazepine-6(11*H*)-carboxylate 5,5-dioxide (3zb). White solid, 81% yield (76.4 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 4:1). M.p. = 160-161 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.0 Hz, 1 H), 7.58 (dd, J = 7.8 Hz, 1.1 Hz, 1 H), 7.50 (td, J =

7.5 Hz, 1.5 Hz, 1 H), 7.44 (td, J = 7.6 Hz, 1.4 Hz, 1 H), 7.37-7.33 (m, 3 H), 6.84 (s, 1 H), 2.48 (s, 3 H), 1.38 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.9, 144.0, 138.7, 136.6, 135.9, 134.7, 134.6, 131.3, 130.6, 130.4, 130.1, 129.6, 129.2, 129.4 (q, C-F, $^1J_{C\text{-}F}$ = 306.7 Hz), 127.4, 123.6 (q, C-F, $^3J_{C\text{-}F}$ = 3.4 Hz), 85.2, 27.6, 21.5; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -41.67; **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{20}F_3NO_4S_2Na$ 494.0678; Found 494.0674.

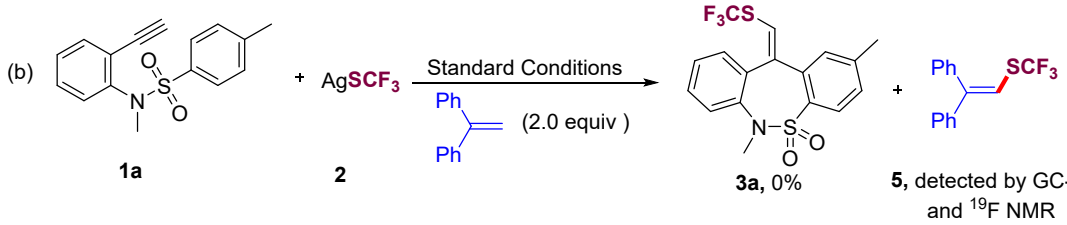


1-tosyl-1*H*-indole (3zc').[4] White solid, 72% yield (39.1 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 78-80 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.00 (dd, J = 8.3 Hz, 0.8 Hz, 1 H), 7.77 (d, J = 8.4 Hz, 2 H), 7.57 (d, J = 3.6 Hz, 1 H), 7.53 (d, J = 7.7 Hz, 1 H), 7.33-7.29 (m, 1 H), 7.24-7.20 (m, 3 H), 6.65 (dd, J = 3.7 Hz, 0.7 Hz, 1 H), 2.33 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.9, 135.3, 134.8, 130.8, 129.9, 126.8, 126.3, 124.5, 123.3, 121.4, 113.5, 109.0, 21.6; **GC−MS (EI, m/z)**: $[M]^+$ 271, 206, 178, 155, 139, 116, 91, 77, 65.

7. Mechanistic Experiments



(a) A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with *N*-(2-ethynylphenyl)-*N*,4-dimethylbenzenesulfonamide **1a** (0.20 mmol, 1.0 equiv), $AgSCF_3$ **2** (0.30 mmol, 1.5 equiv), $CuCl_2$ (0.02 mmol, 0.1 equiv), $K_2S_2O_8$ (0.4 mmol, 2.0 equiv), Na_3PO_4 (0.2 mmol, 1.0 equiv), TEMPO (0.4 mmol, 2.0 equiv) and DMSO (2.0 mL). The reaction mixture was then stirred at room temperature for 12 h under air atmosphere. The reaction mixture was washed with water and extracted with ethyl acetate three times. The combined organic layer was washed with saturated NaCl solution, dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The analysis of crude mixture showed that the yield of **3a** was completely inhibited.



(b) A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with *N*-(2-ethynylphenyl)-*N*,4-dimethylbenzenesulfonamide **1a** (0.20 mmol, 1.0 equiv), $AgSCF_3$ **2** (0.30 mmol, 1.5 equiv), $CuCl_2$ (0.02 mmol, 0.1 equiv), $K_2S_2O_8$ (0.4 mmol, 2.0 equiv), Na_3PO_4 (0.2 mmol, 1.0 equiv), 1, 1-diphenylethylene (0.4 mmol, 2.0 equiv)

and DMSO (2.0 mL). The reaction mixture was then stirred at room temperature for 12 h under air atmosphere. The reaction mixture was washed with water and extracted with ethyl acetate three times. The combined organic layer was washed with saturated NaCl solution, dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The analysis of crude mixture showed that the yield of **3a** was totally suppressed. The expected adduct **5** was observed by ^{19}F NMR and GC-MS as following: **^{19}F NMR** (376 MHz, $CDCl_3$, ppm): δ -42.48 (s); **GC-MS** (m/z, relative intensity): 280 (M^+, 94), 211 (100), 178 (74), 165 (35), 152 (20), 105 (12). The data for the adduct **5** were in accordance with the ones previously reported in the literature.[5]

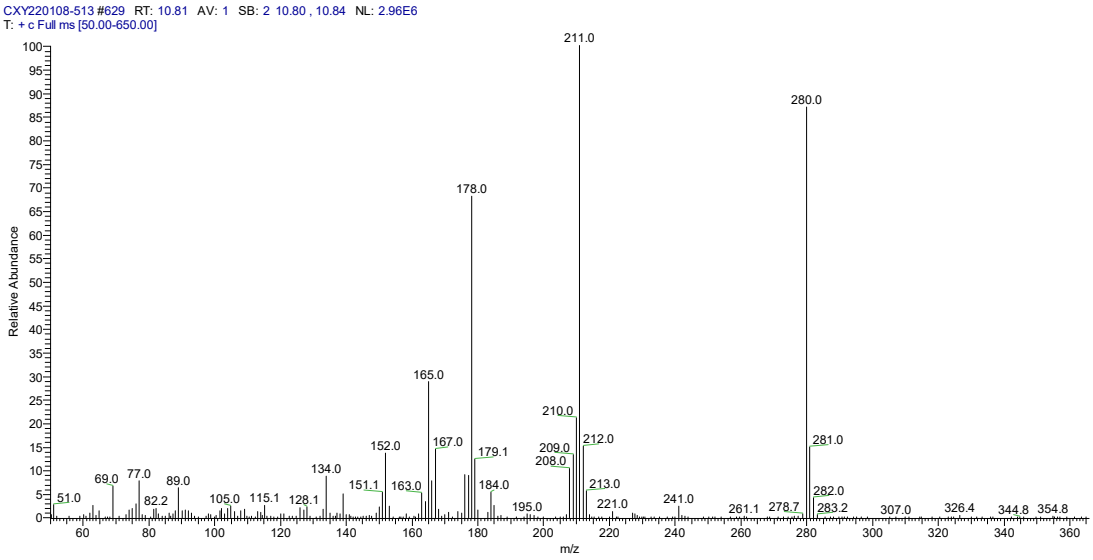


Figure S1. GC-MS (m/z) of adduct **5**

8. X-ray crystallographic data of 3a

The product **3a** was recrystallized from petroleum ether/EtOAc. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC**2153893**.

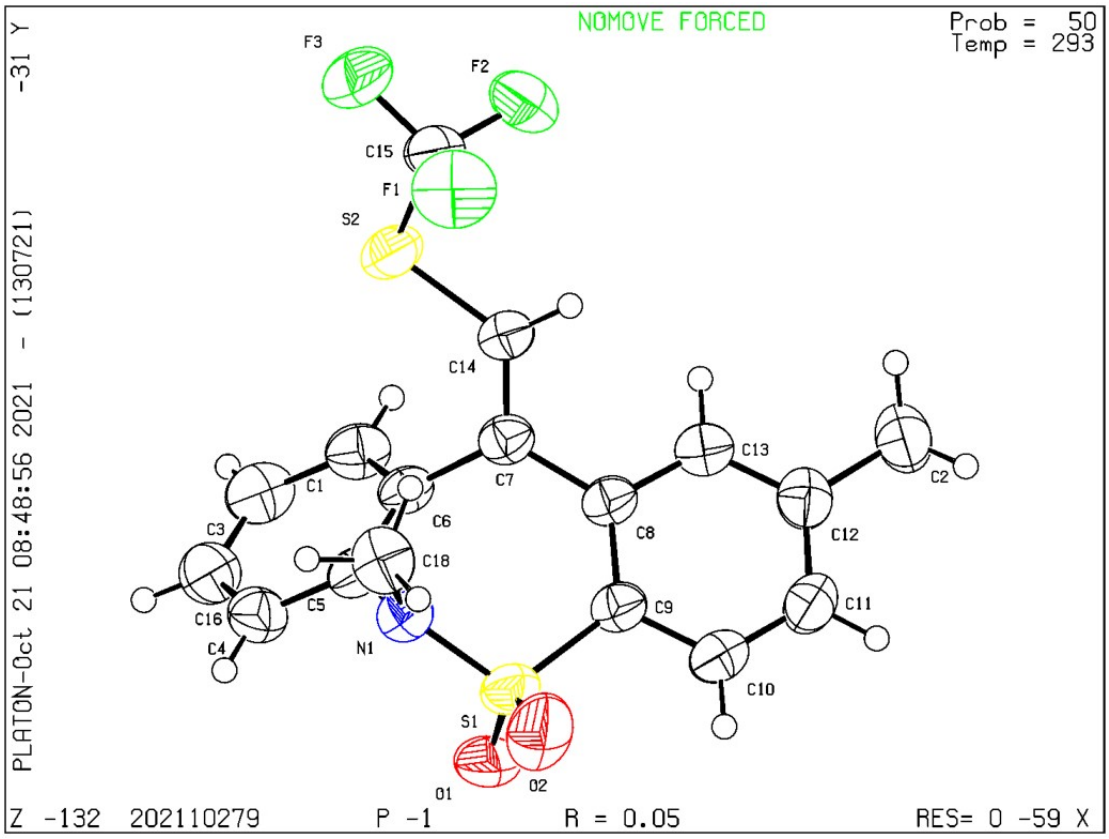


Figure S2. X-ray crystal structure of **3a** with the ellipsoid contour at 50% probability levels

Table S1. Crystal data and structure refinement for **3a**.

Identification code	**3a**
Empirical formula	$C_{17}H_{14}F_3NO_2S_2$
Formula weight	385.41
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.4571(9)
b/Å	9.5073(8)
c/Å	9.5073(8)
α/°	82.722(7)
β/°	74.531(8)
γ/°	73.505(8)
Volume/Å^3	855.27(14)
Z	2
ρ_{calc}g/cm^3	1.497
μ/mm^{-1}	3.216
F(000)	396.0
Crystal size/mm^3	0.17×0.14×0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.914 to 134.134
Index ranges	-8≤h≤11, -11≤k≤10, -10≤l≤12

Reflections collected	6069
Independent reflections	3063 [R_{int}=0.0241, R_{sigma}=0.0415]
Data/restraints/parameters	3063/0/228
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0479, wR_2 = 0.1224
Final R indexes [all data]	R_1 = 0.0669, wR_2 = 0.1418
Largest diff. peak/hole / e Å^{-3}	0.29/-0.30

9. References

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[5] (a) H. Li, S. Liu, Y. Huang, X.-H. Hu and F.-L. Qing, *Chem. Commun.,* 2017, **53**, 10136; (b) R. Honeker, R. A. Garza-Sanchez, M. N. Hopkinson and F. Glorius, *Chem. Eur. J.,* 2016, **22**, 4395; (c) M. Li, J. L. Petersen and J. M. Hoover, *Org. Lett.,* 2017, **19**, 638.

10. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

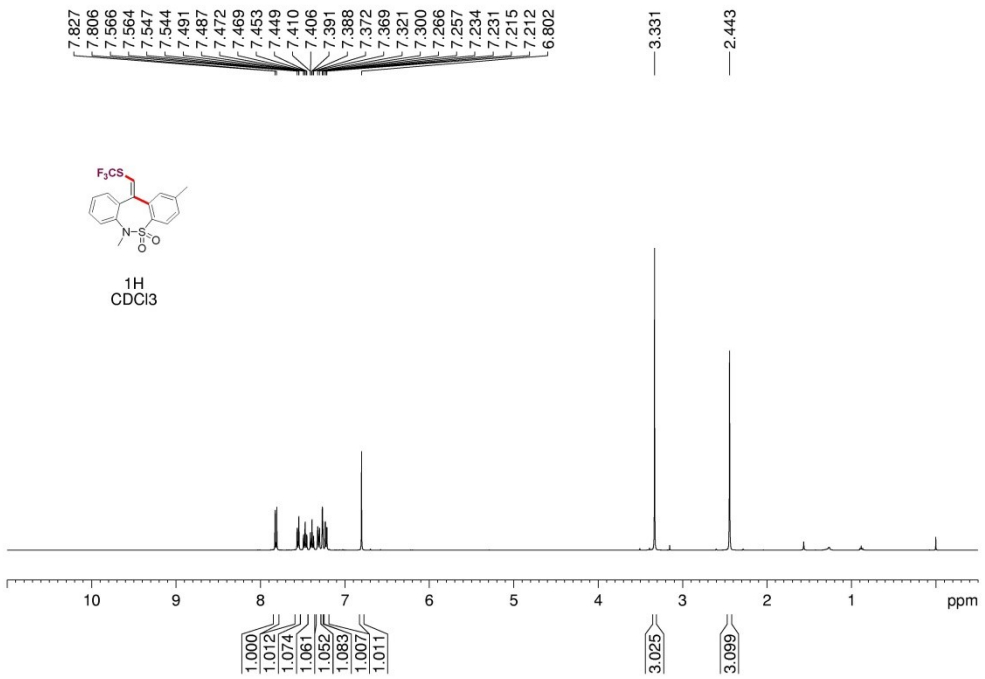

Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a**

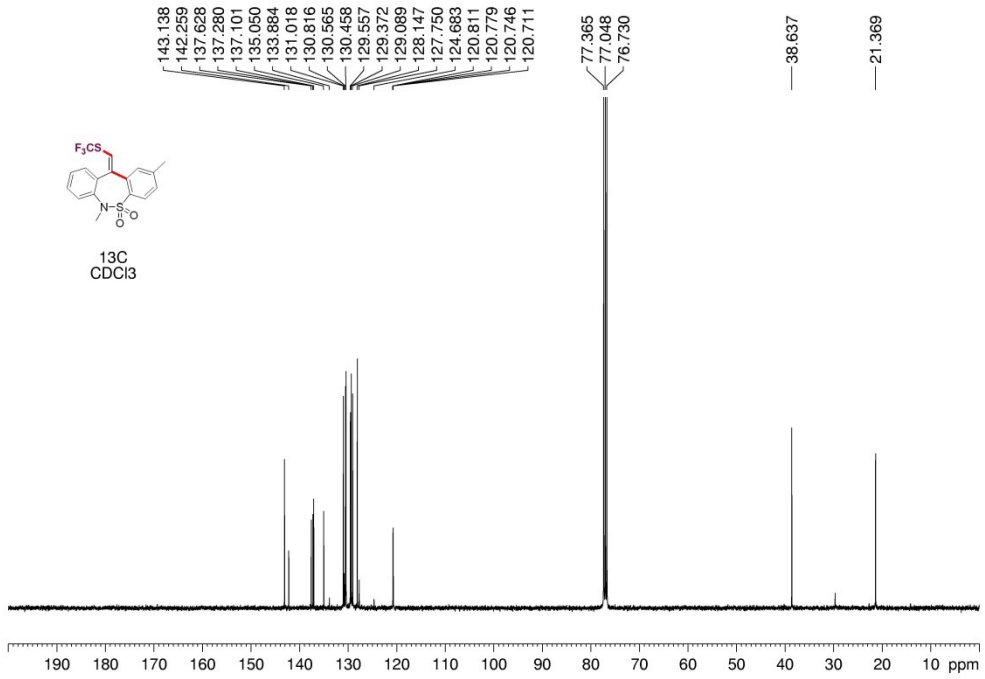

Figure S4. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3a**

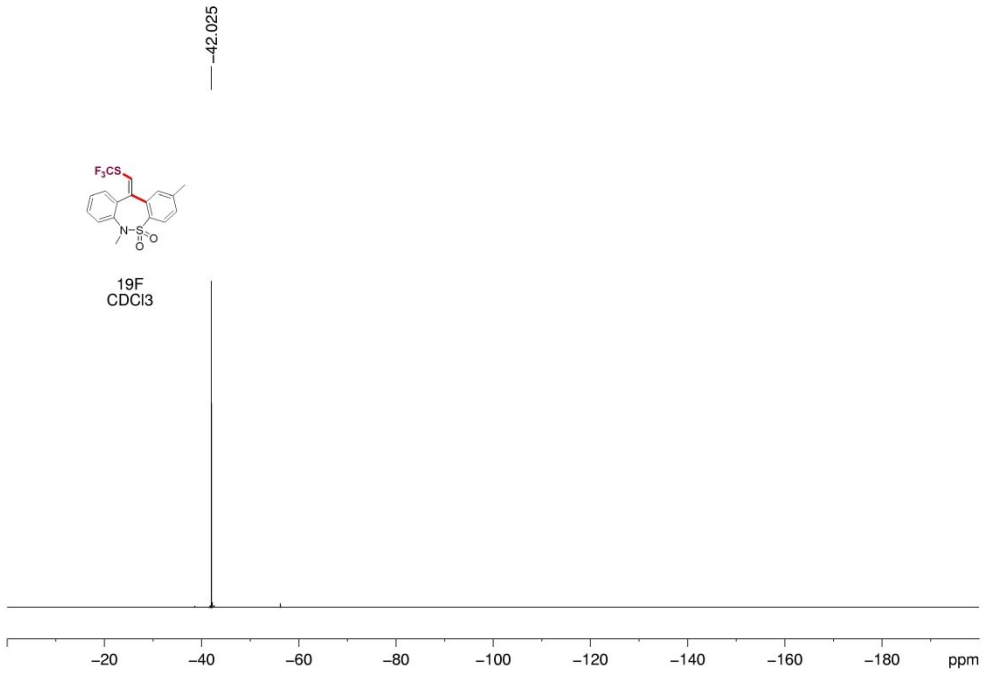

Figure S5. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3a**

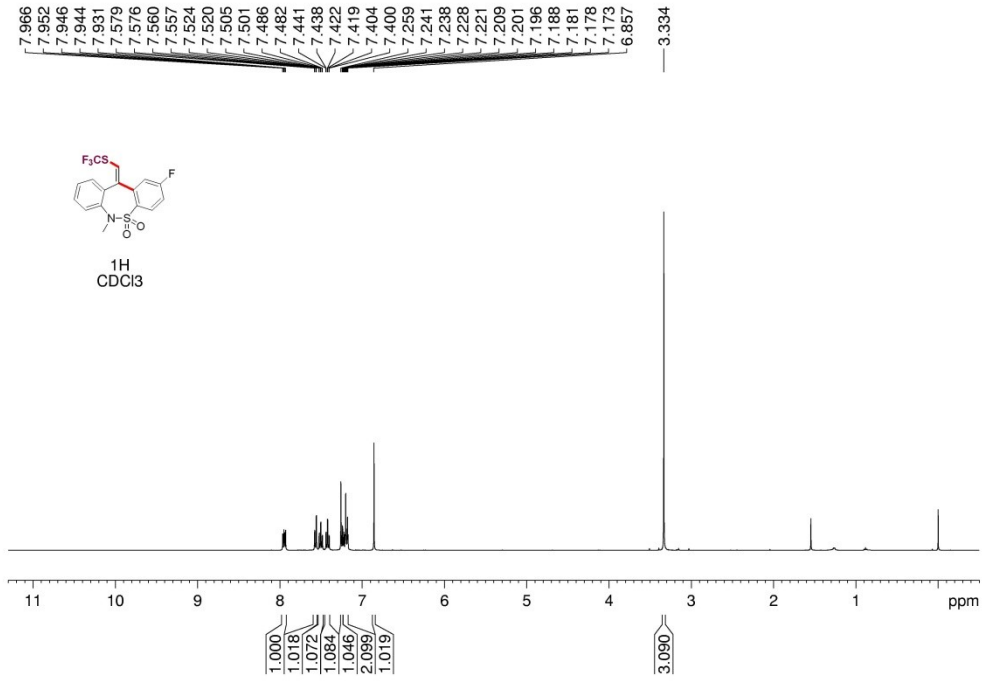

Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b**

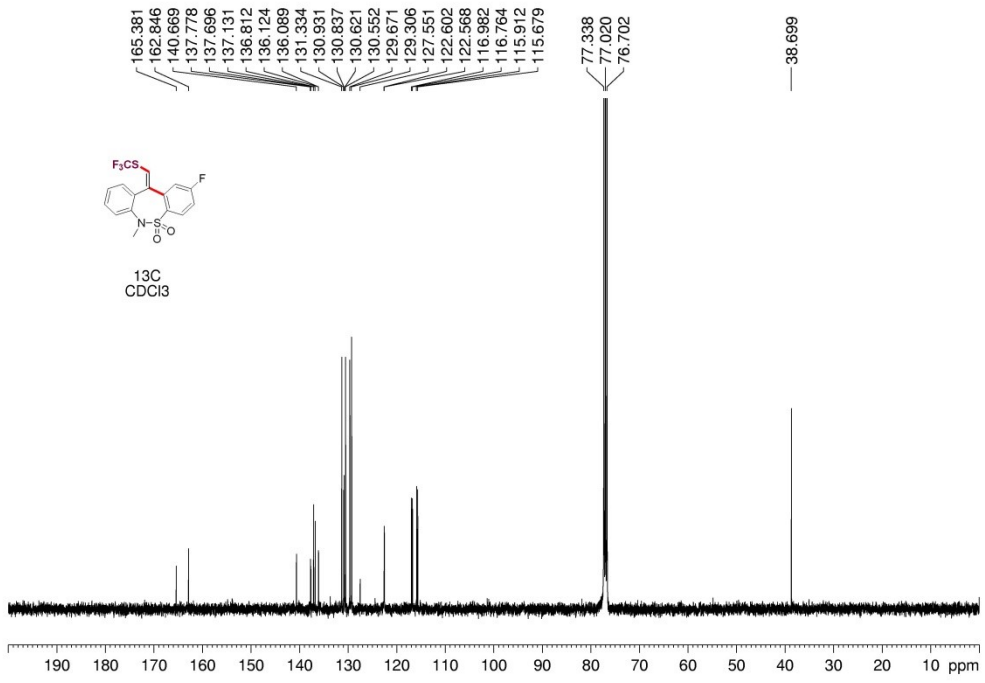

Figure S7. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3b**

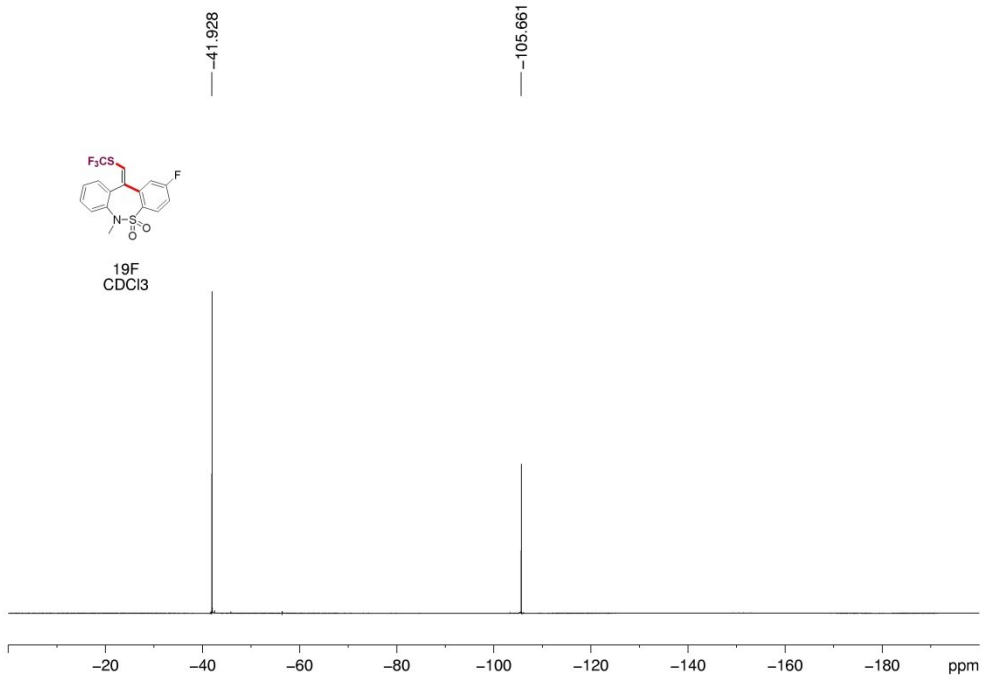

Figure S8. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3b**

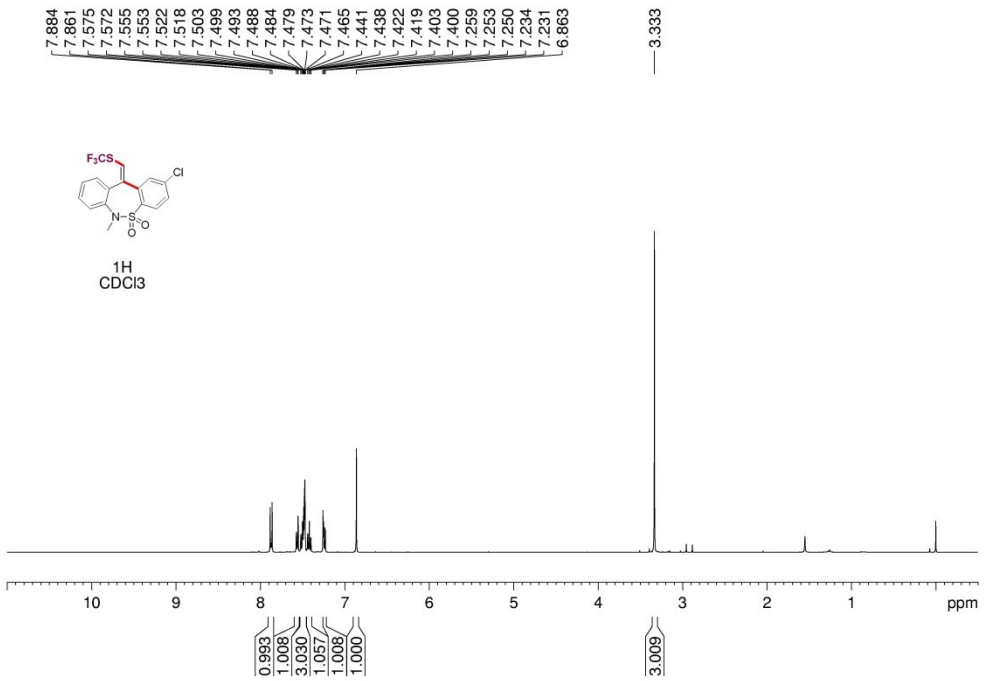

Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3c**

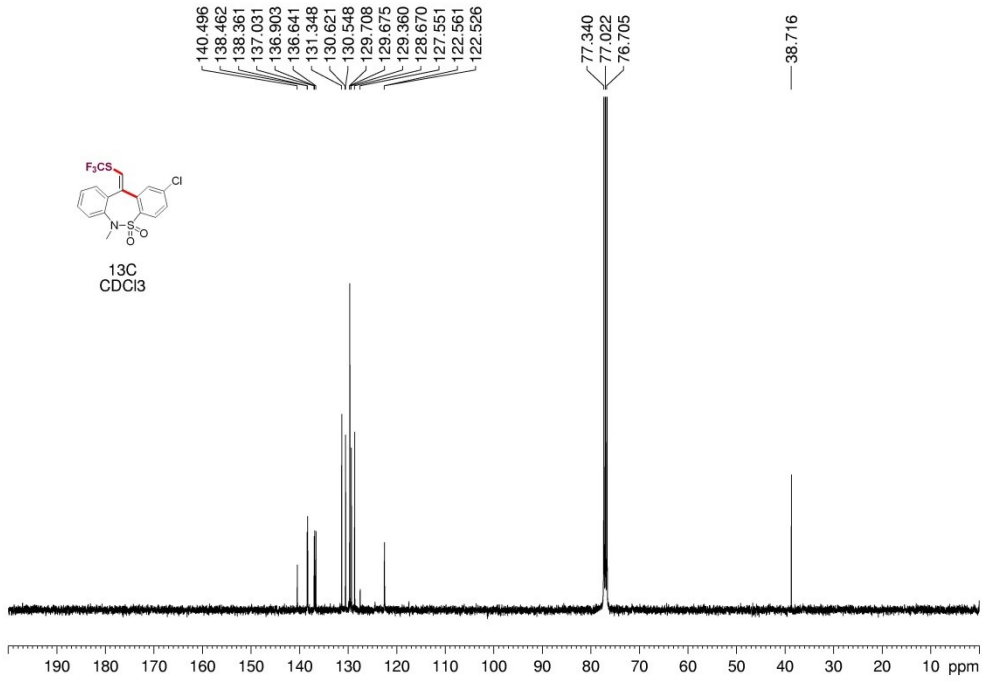

Figure S10. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3c**

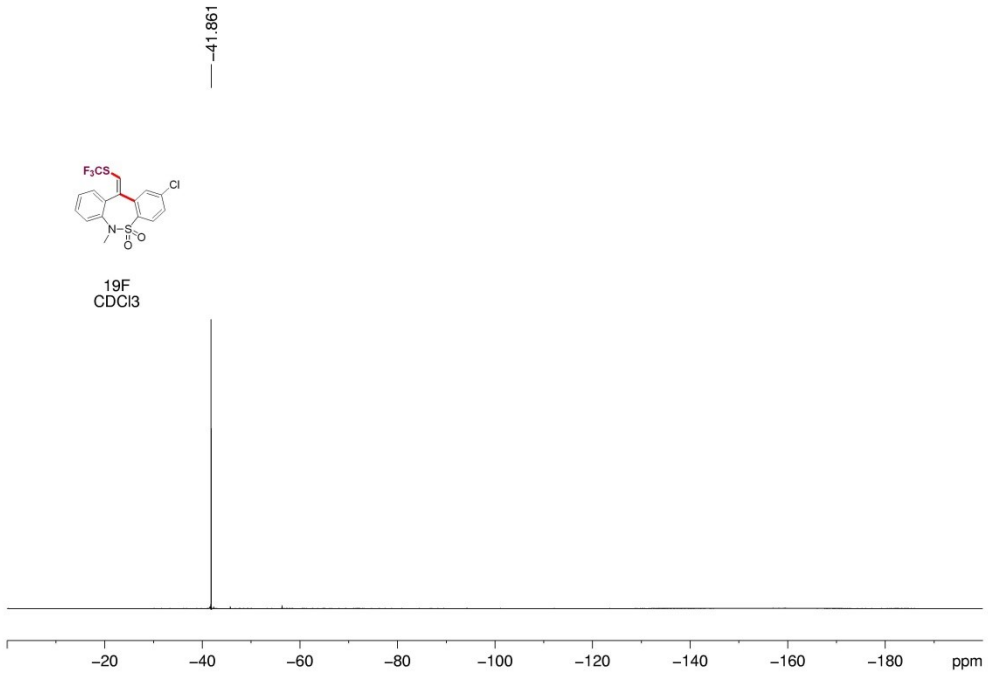

Figure S11. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3c**

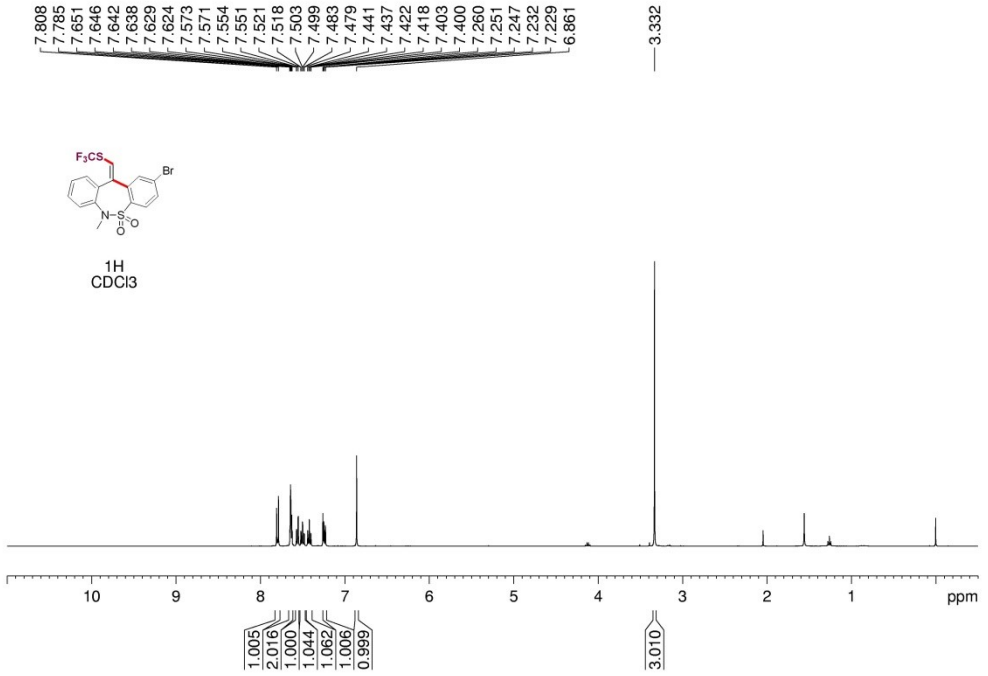

Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3d**

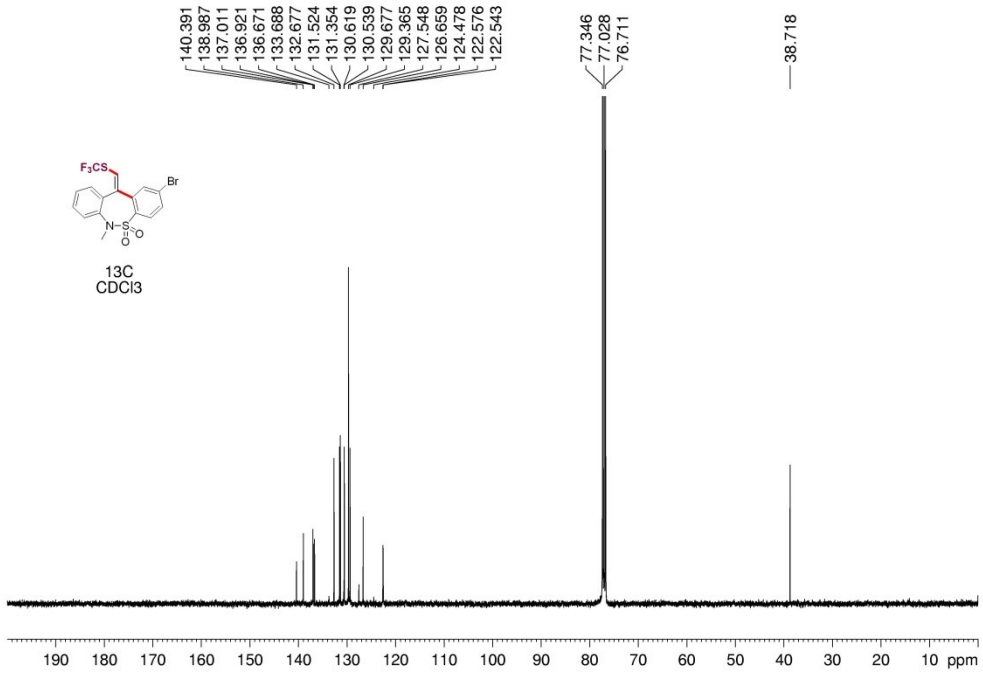

Figure S13. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3d**

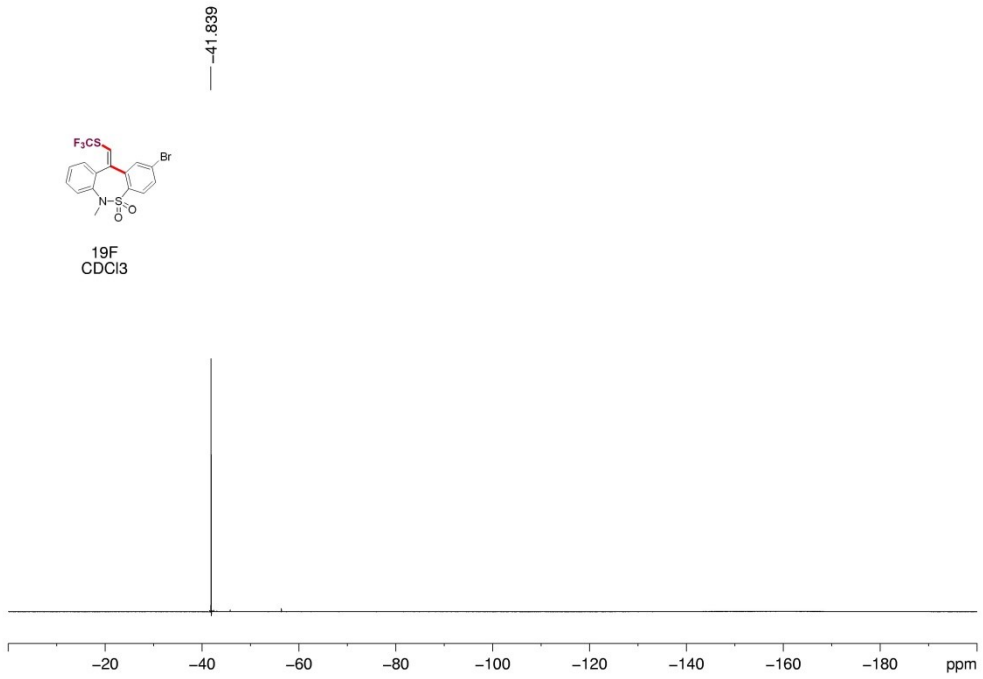

Figure S14. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3d**

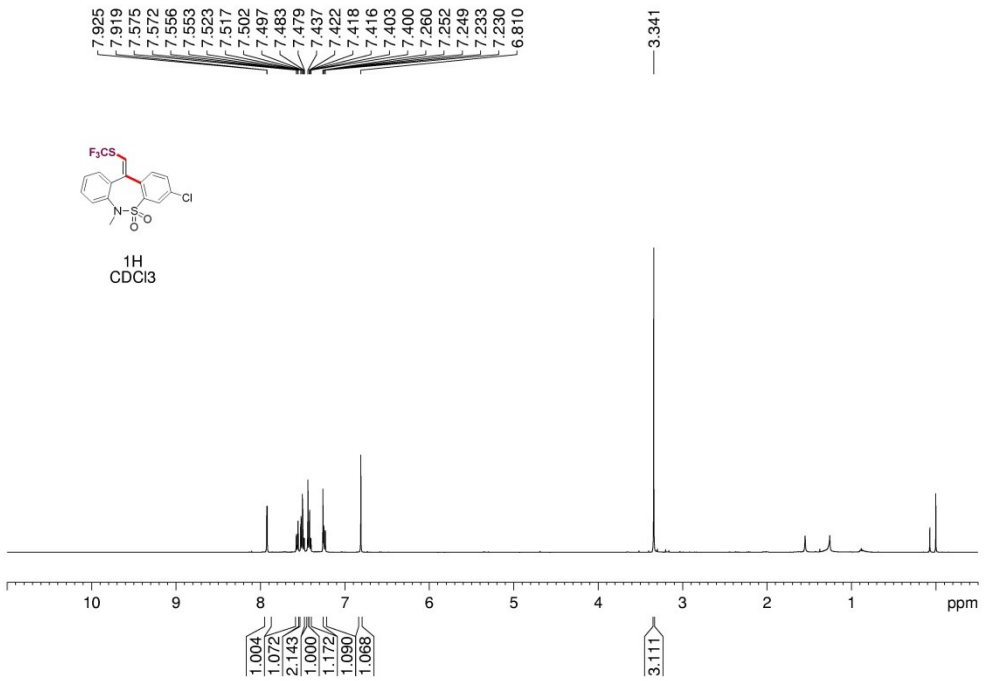

Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3e**

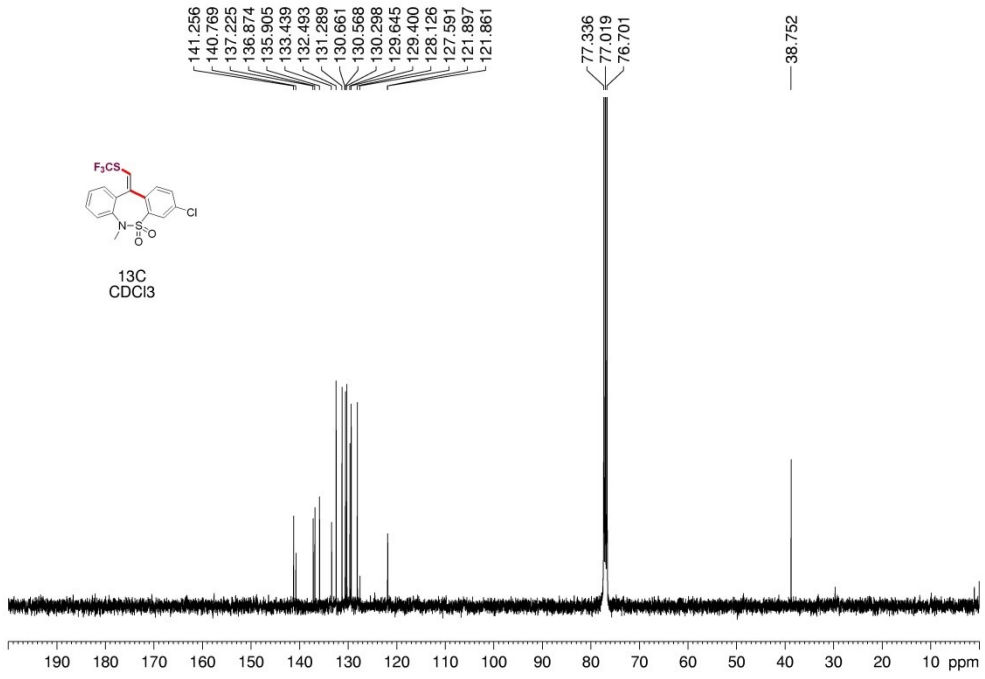

Figure S16. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3e**

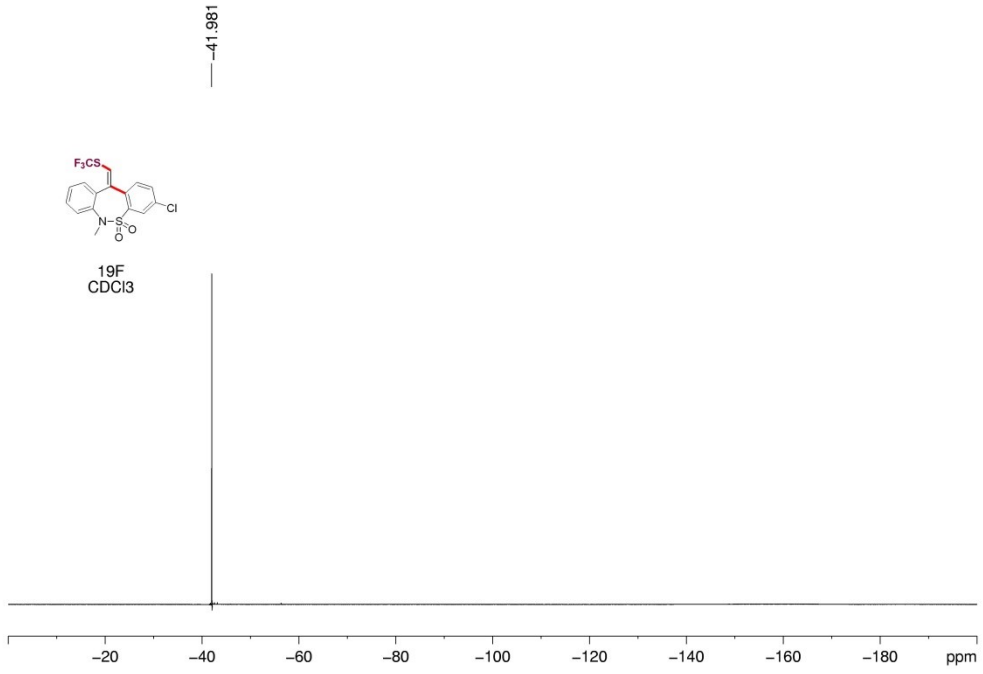

Figure S17. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3e**

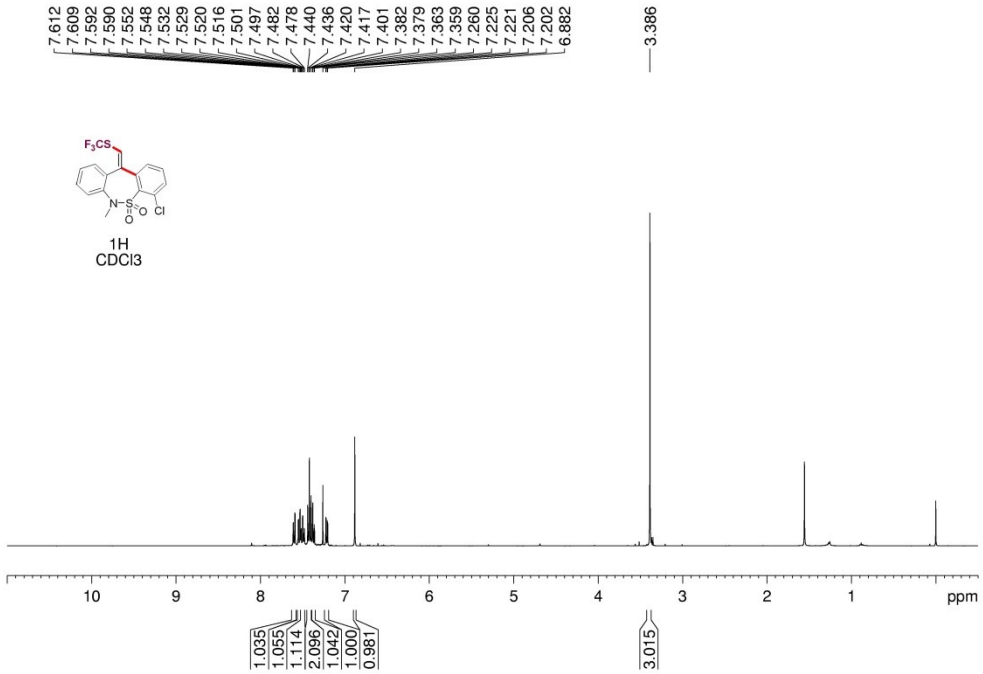

Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3f**

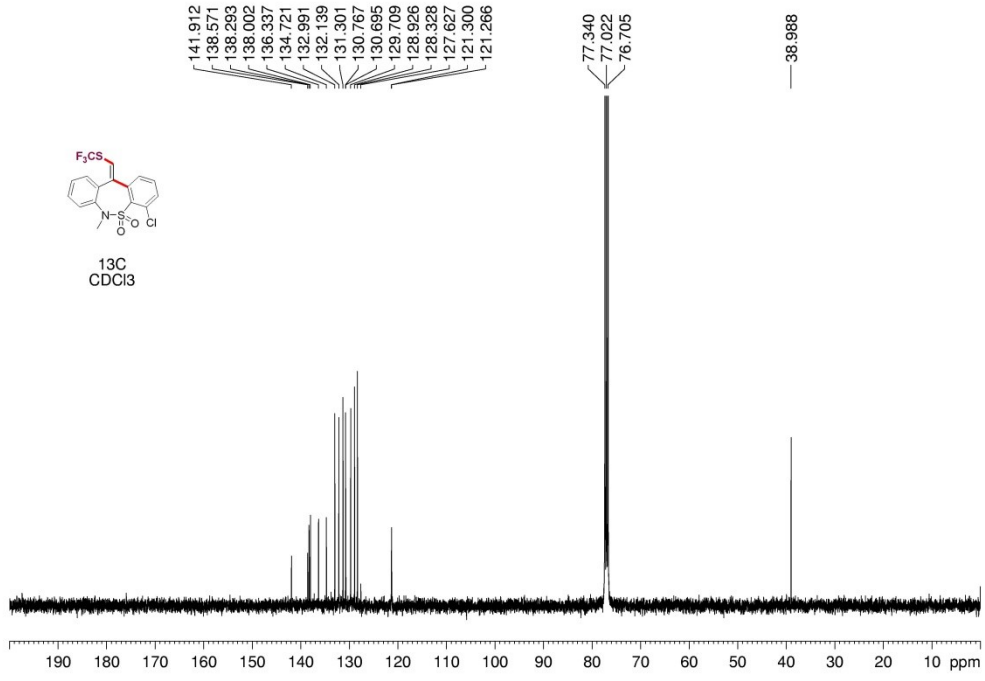

Figure S19. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3f**

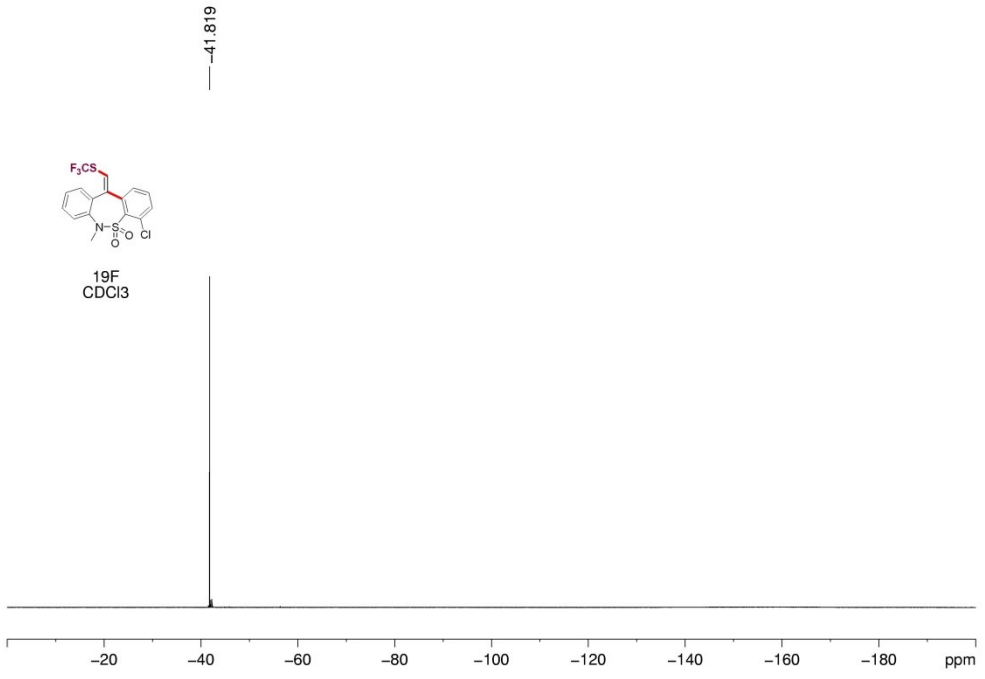

Figure S20. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3f**

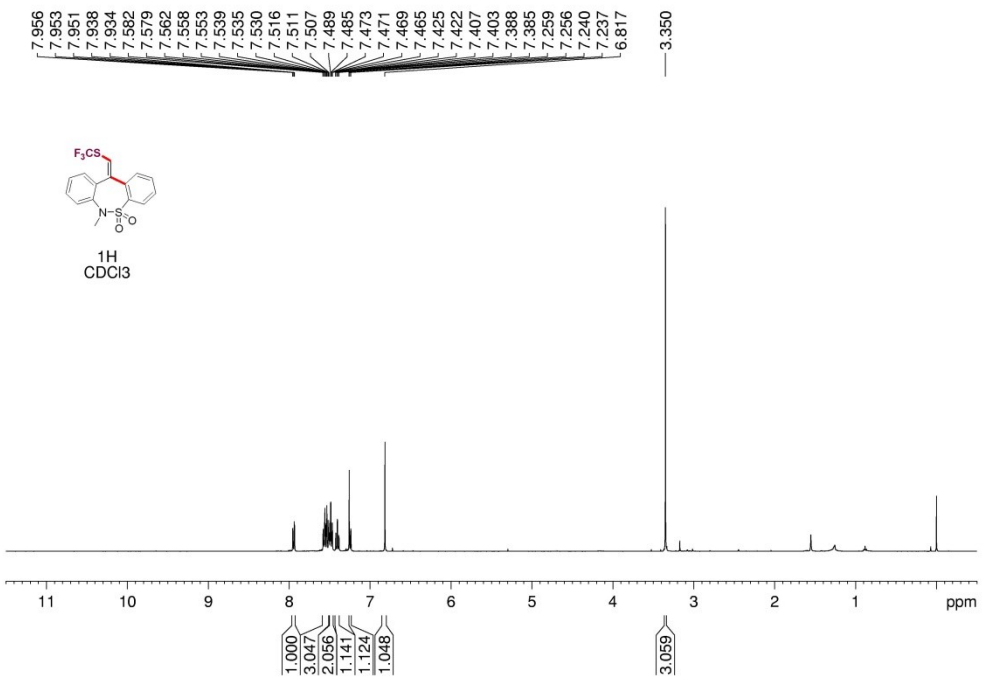

Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3g**

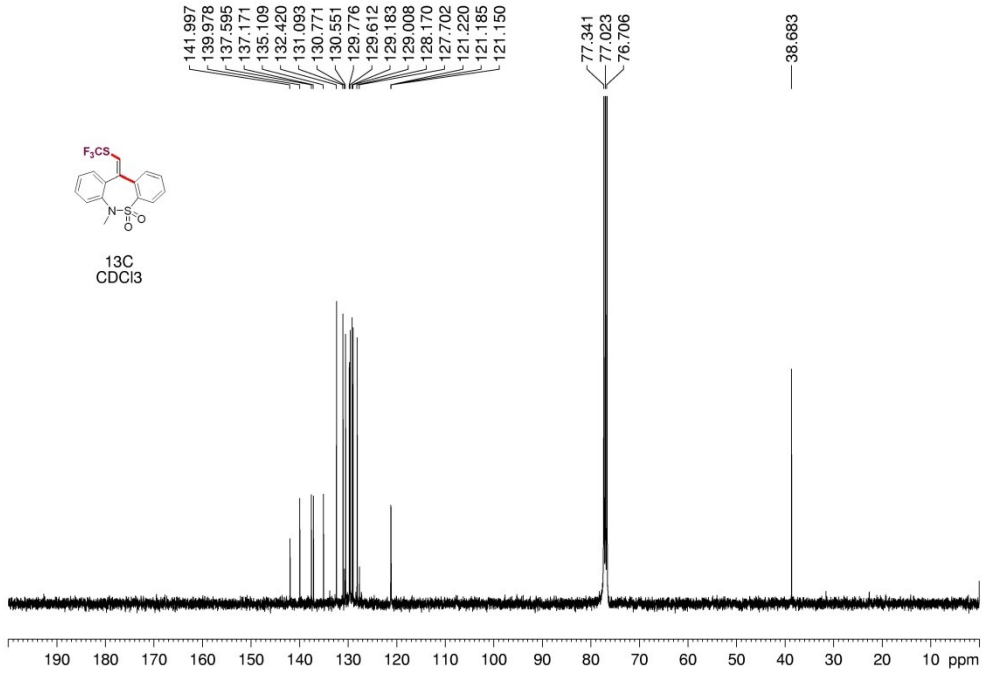

Figure S22. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3g**

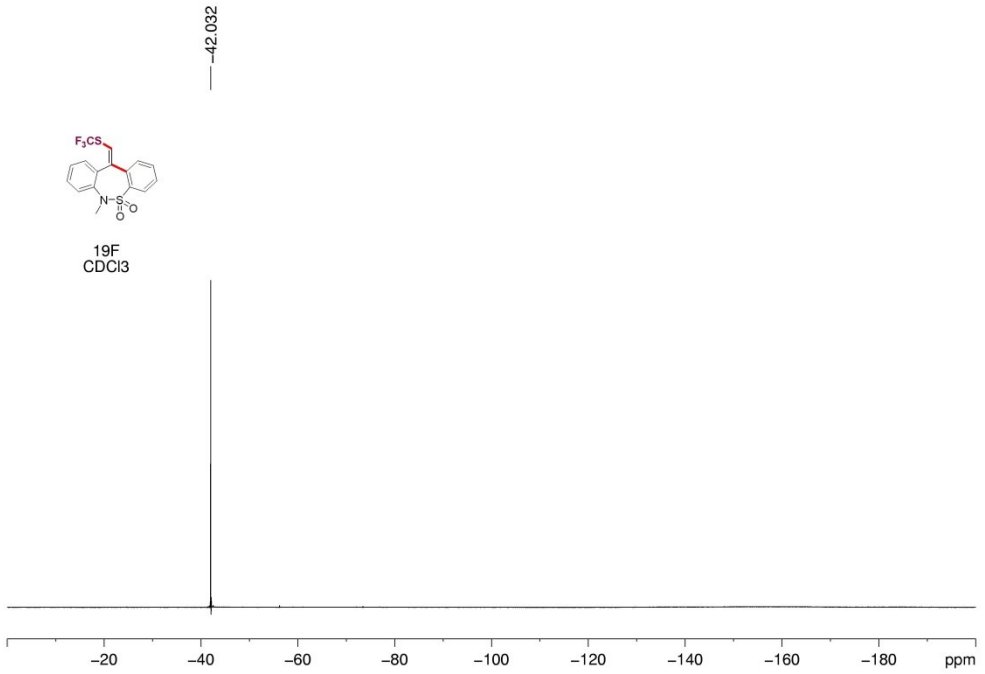

Figure S23. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3g**

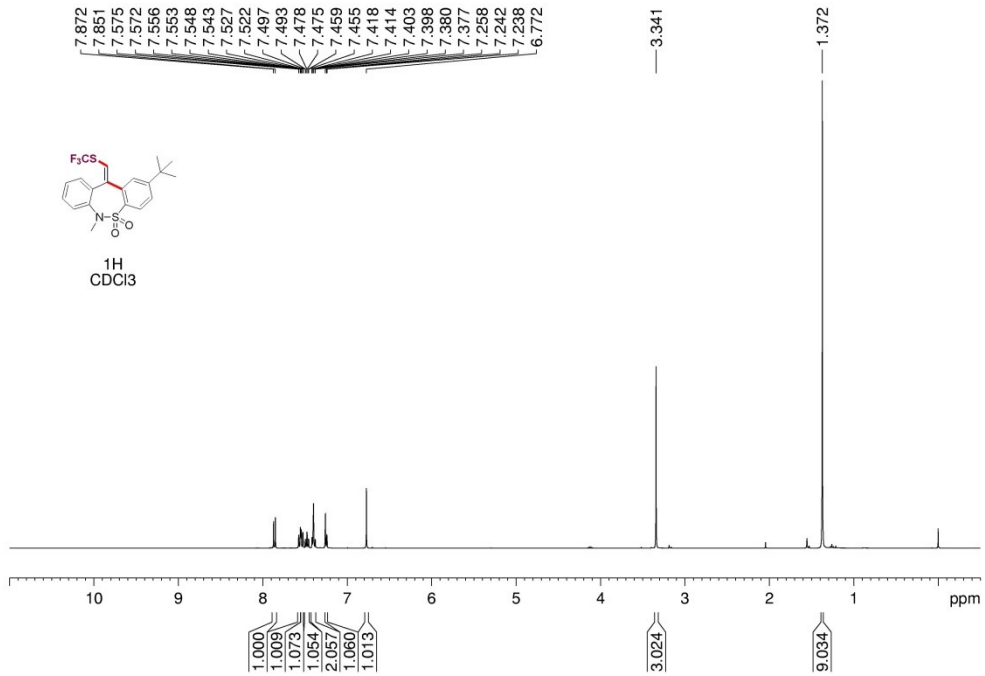

Figure S24. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3h**

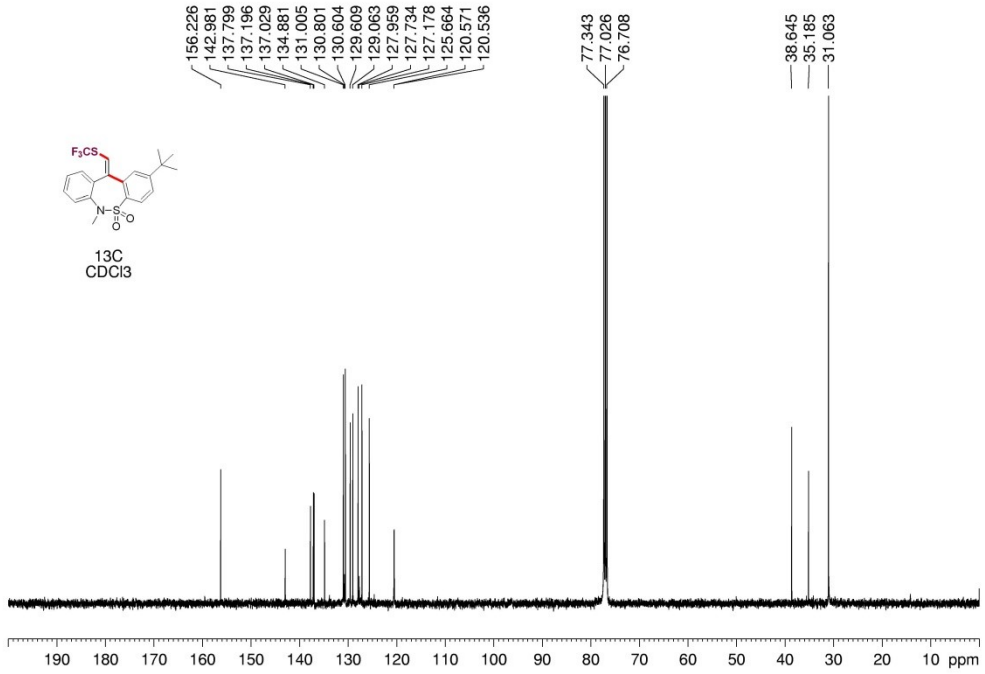

Figure S25. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3h**

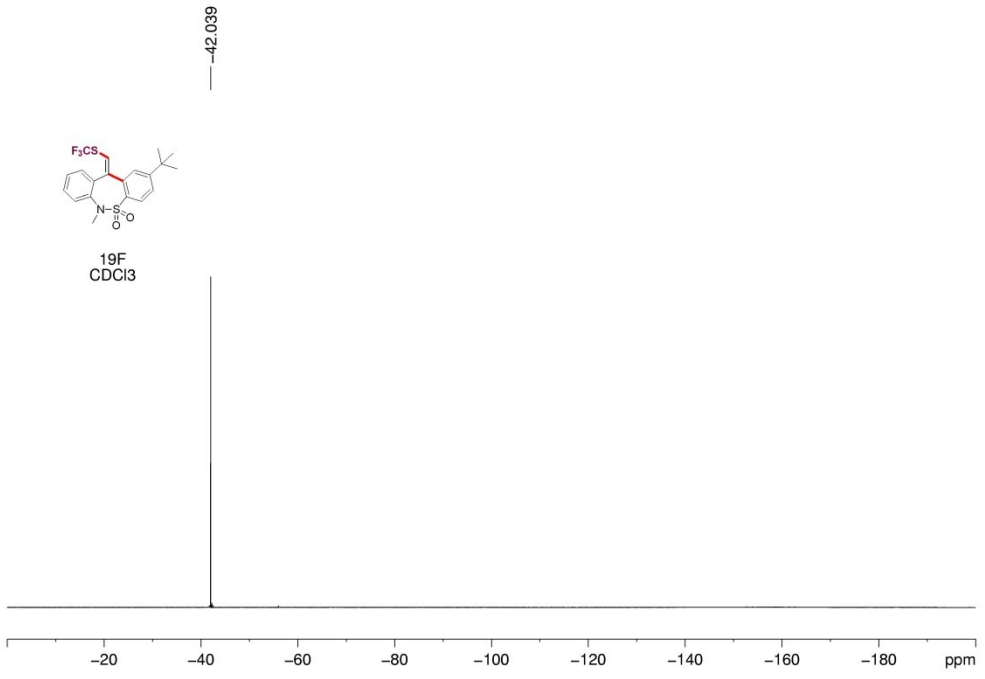

Figure S26. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3h**

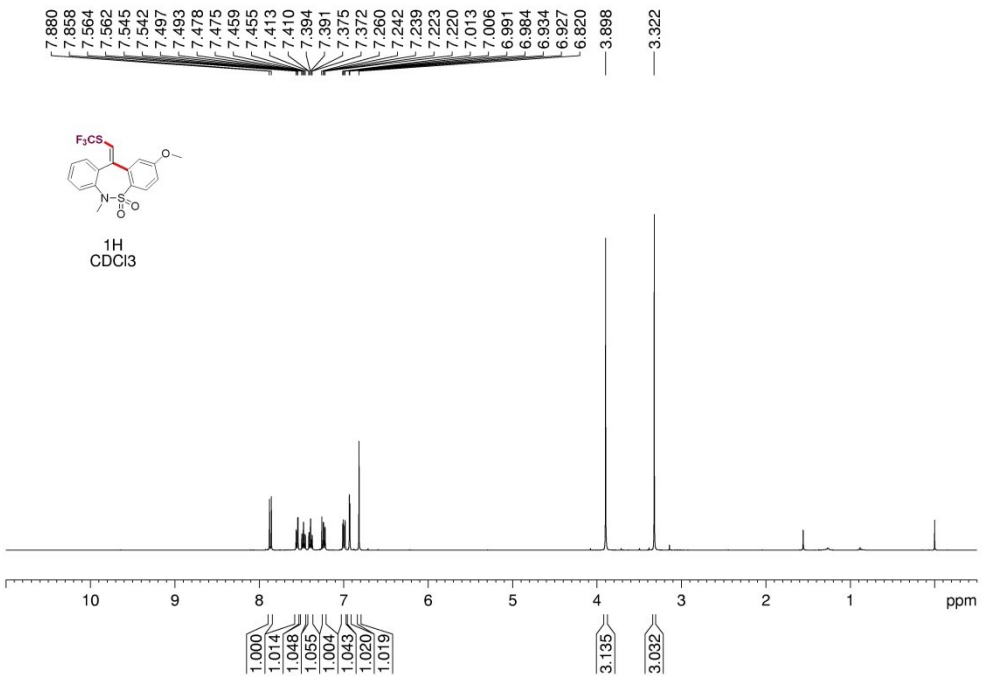

Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3i**

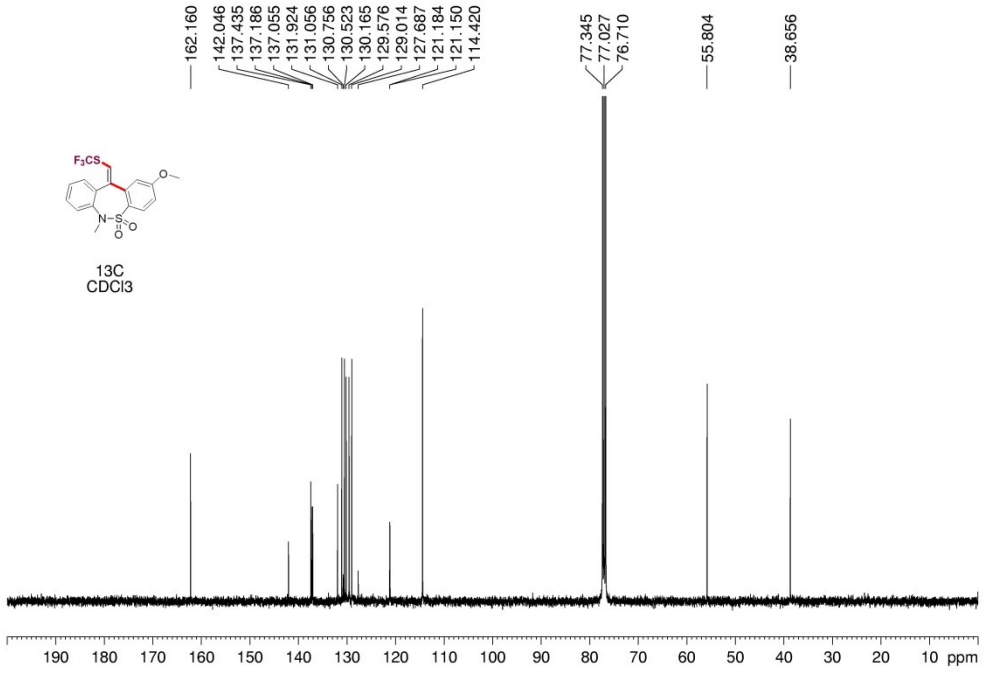

Figure S28. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3i**

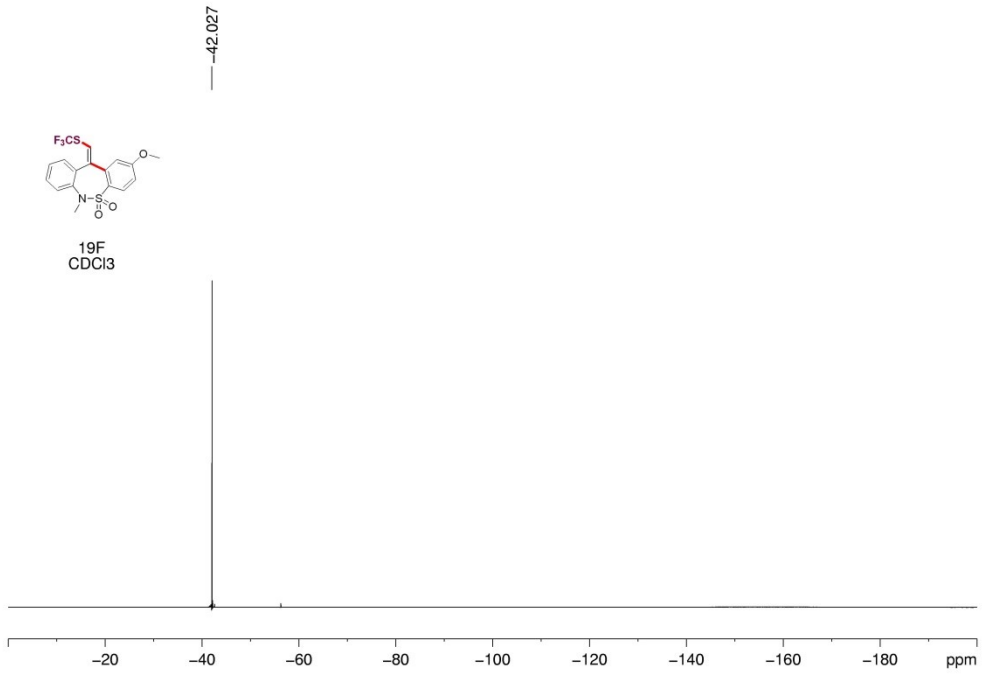

Figure S29. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3i**

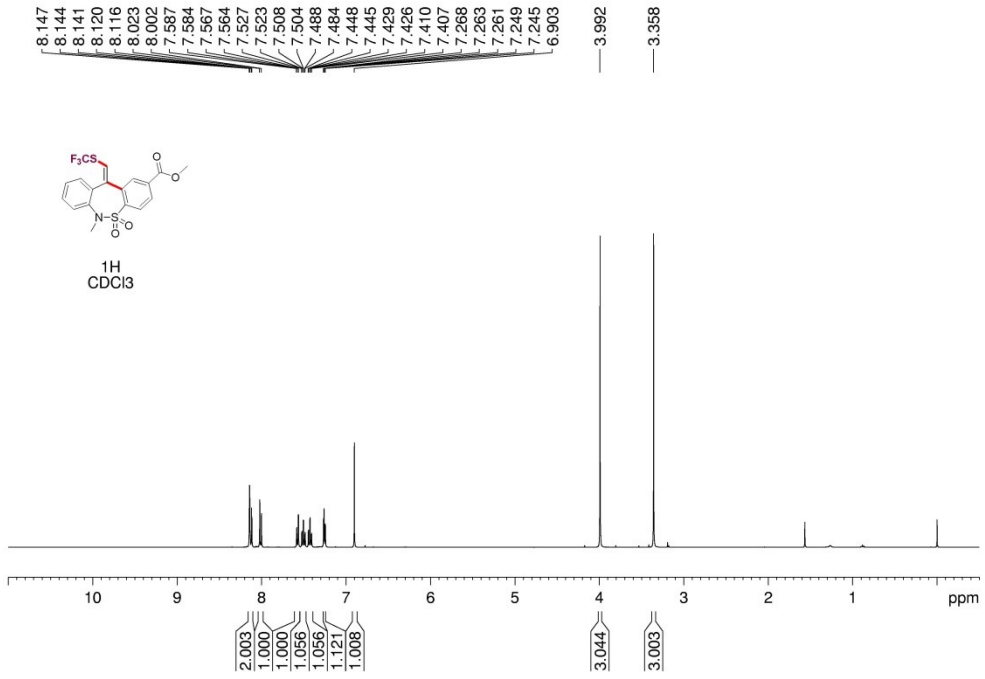

Figure S30. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3j**

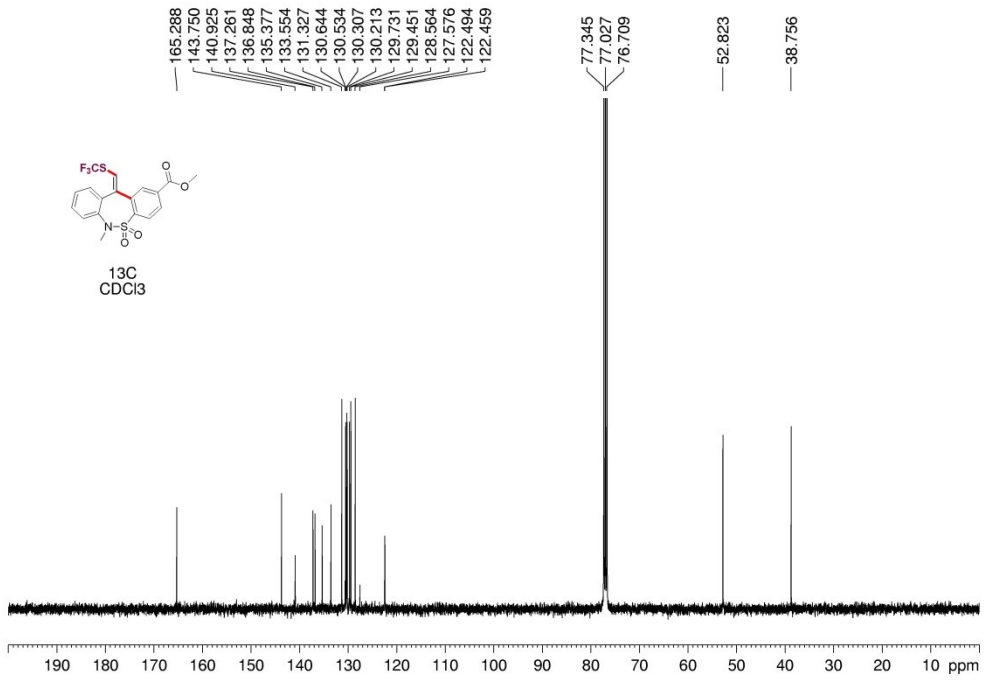

Figure S31. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3j**

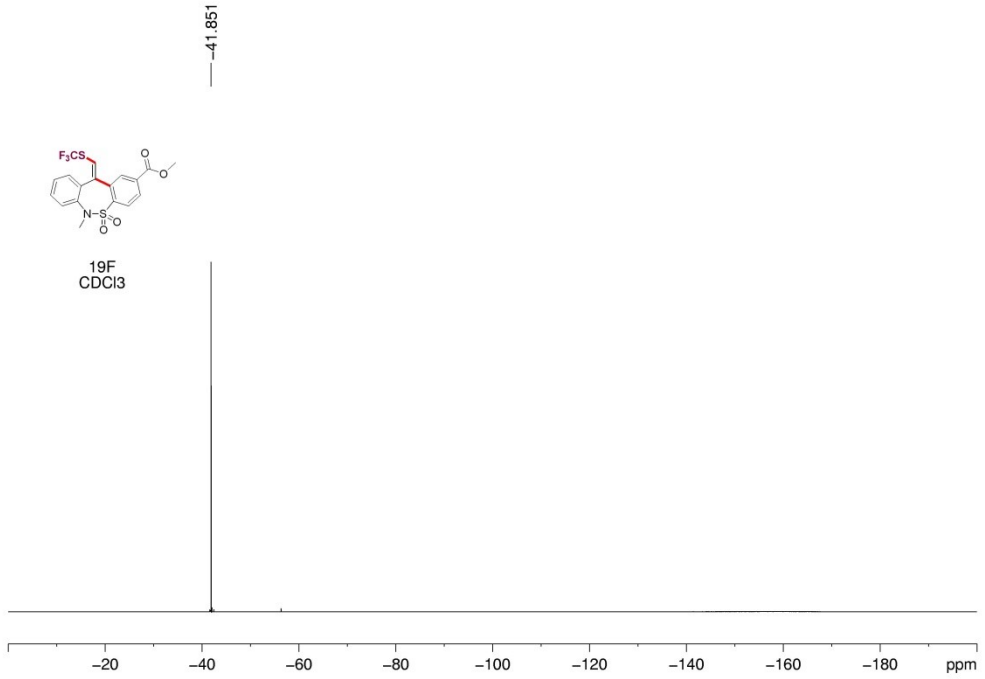

Figure S32. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3j**

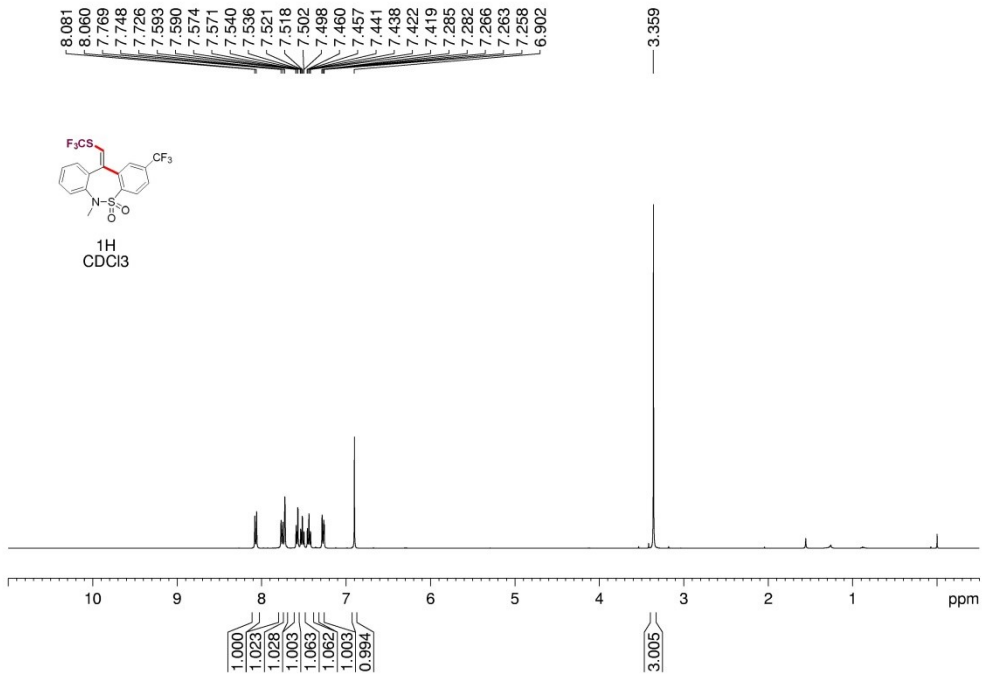

Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3k**

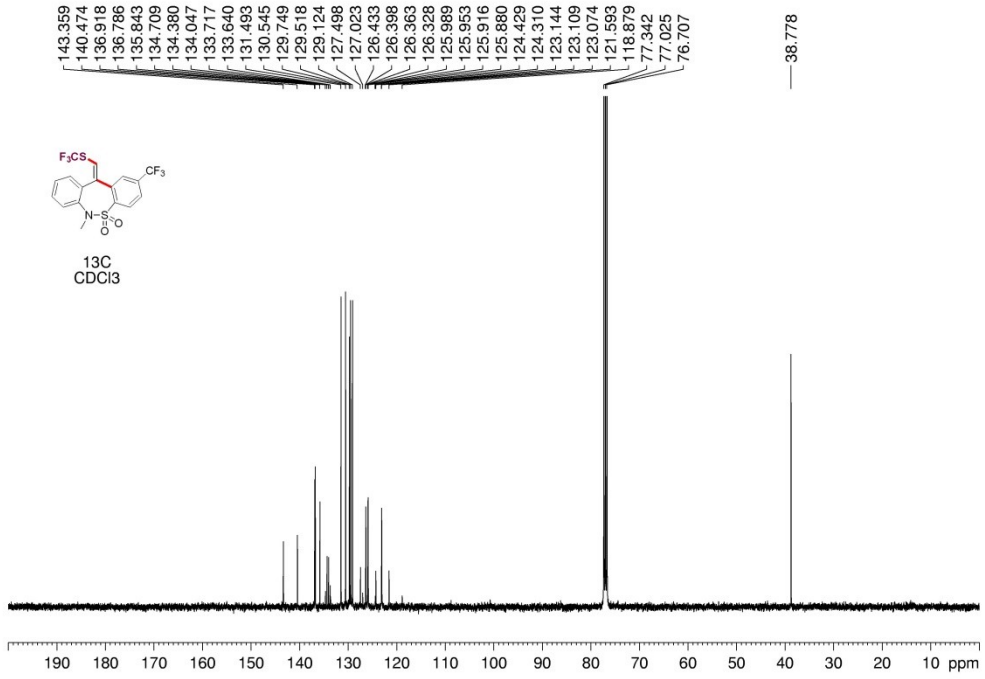

Figure S34. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3k**

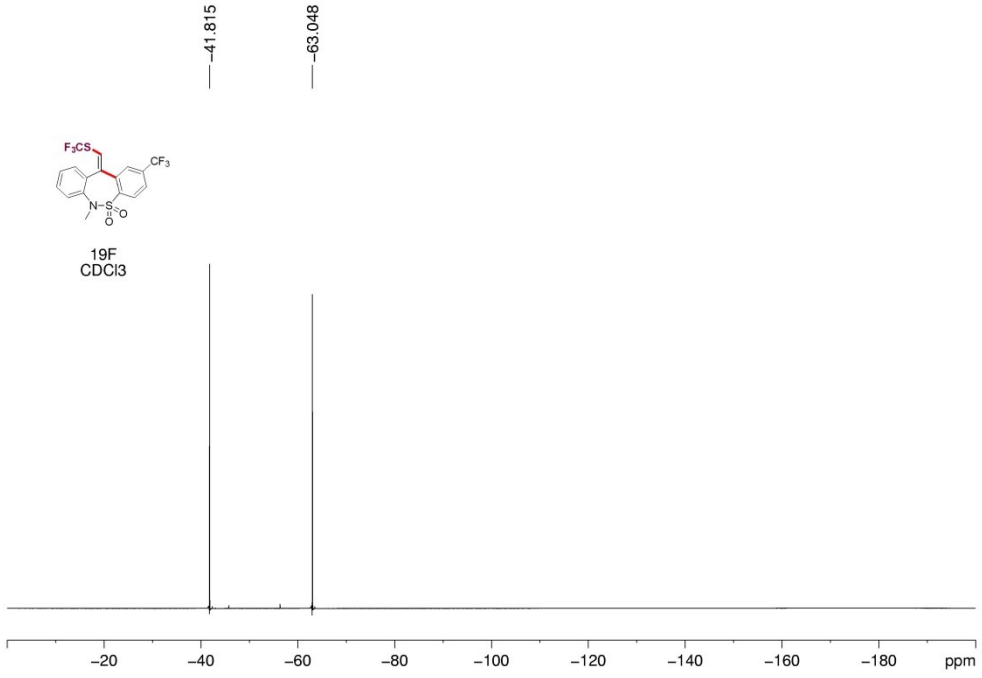

Figure S35. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3k**

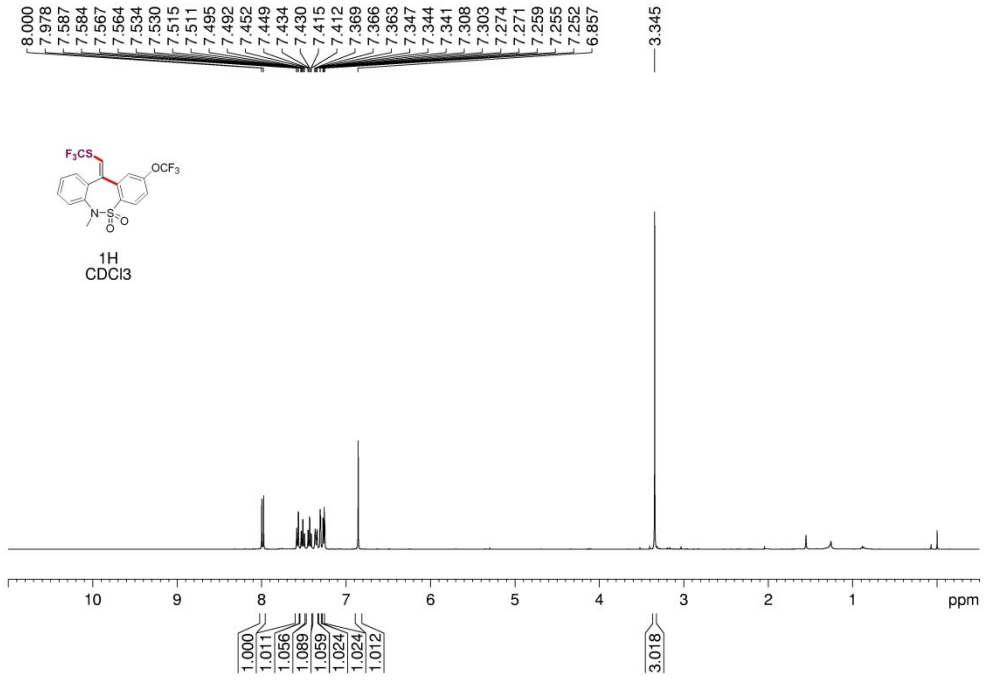

Figure S36. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3l**

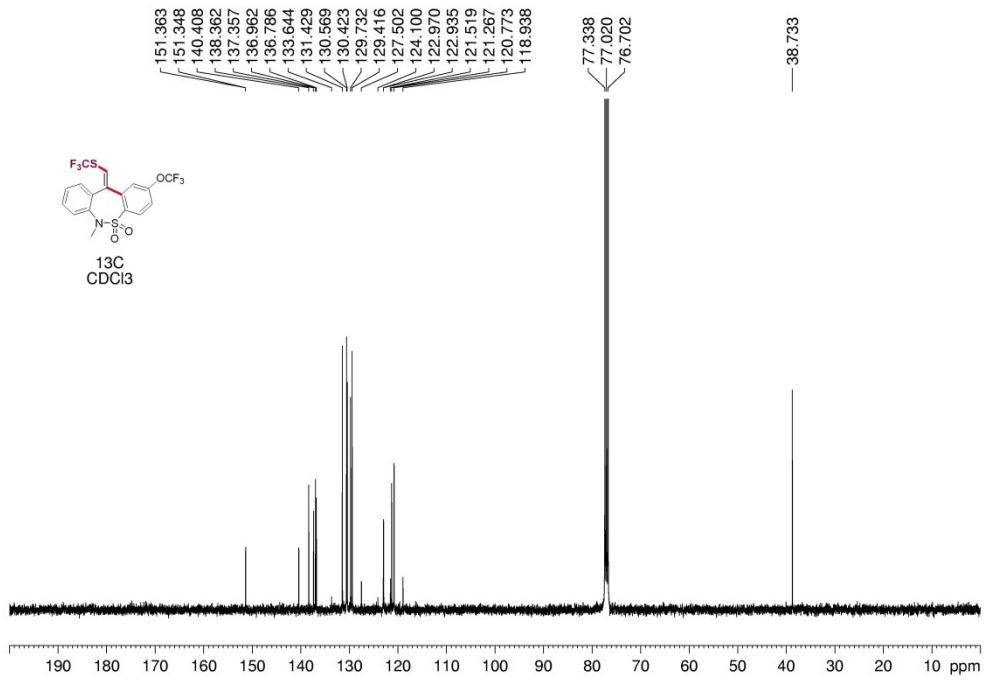

Figure S37. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3l**

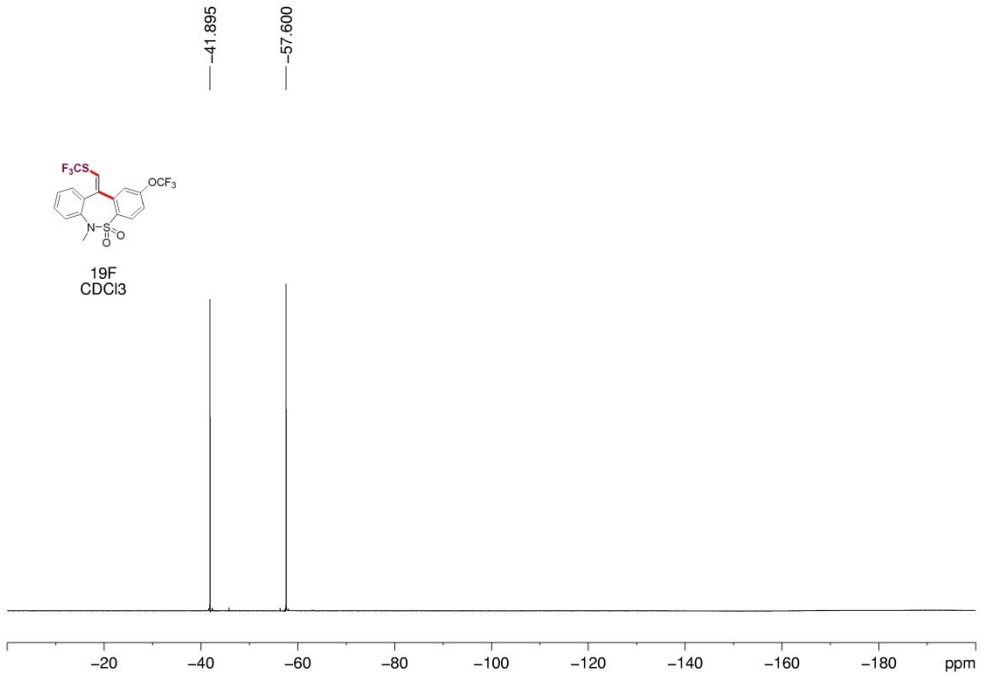

Figure S38. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3l**

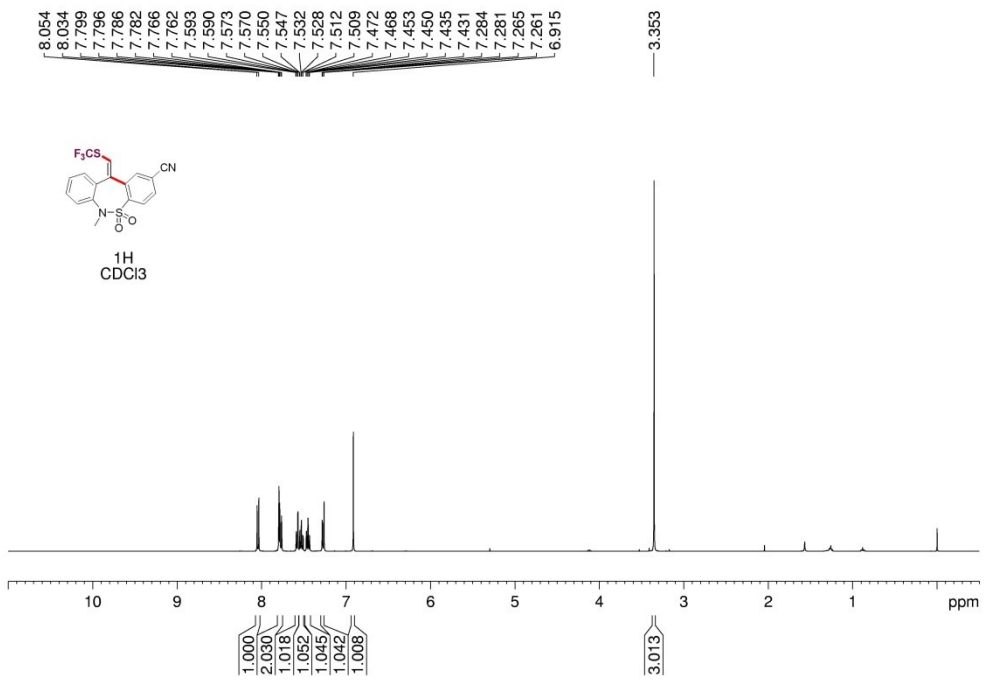

Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3m**

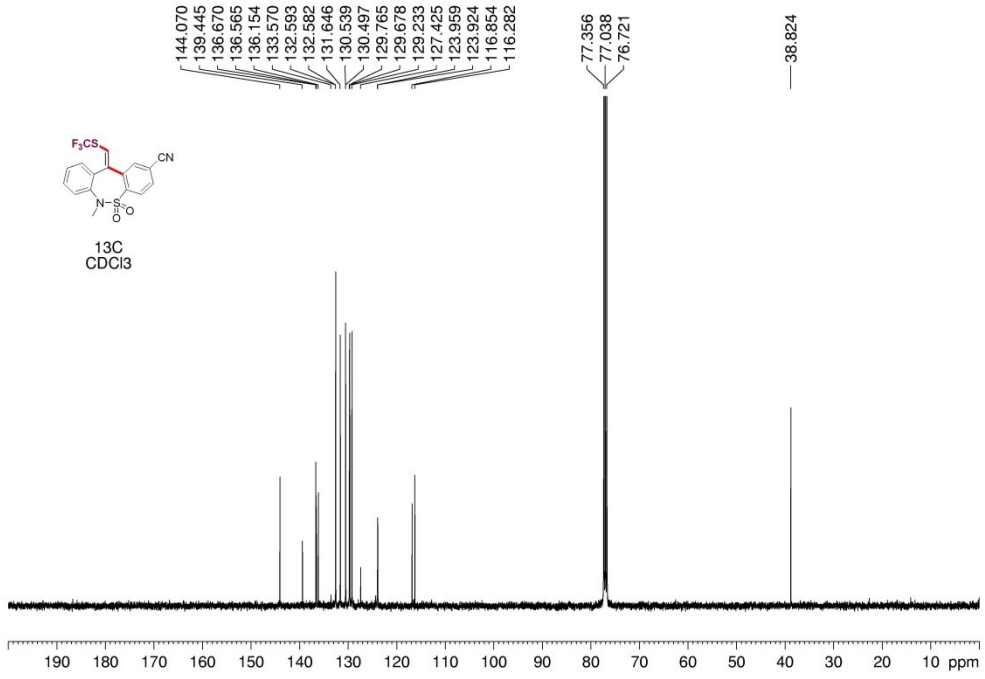

Figure S40. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3m**

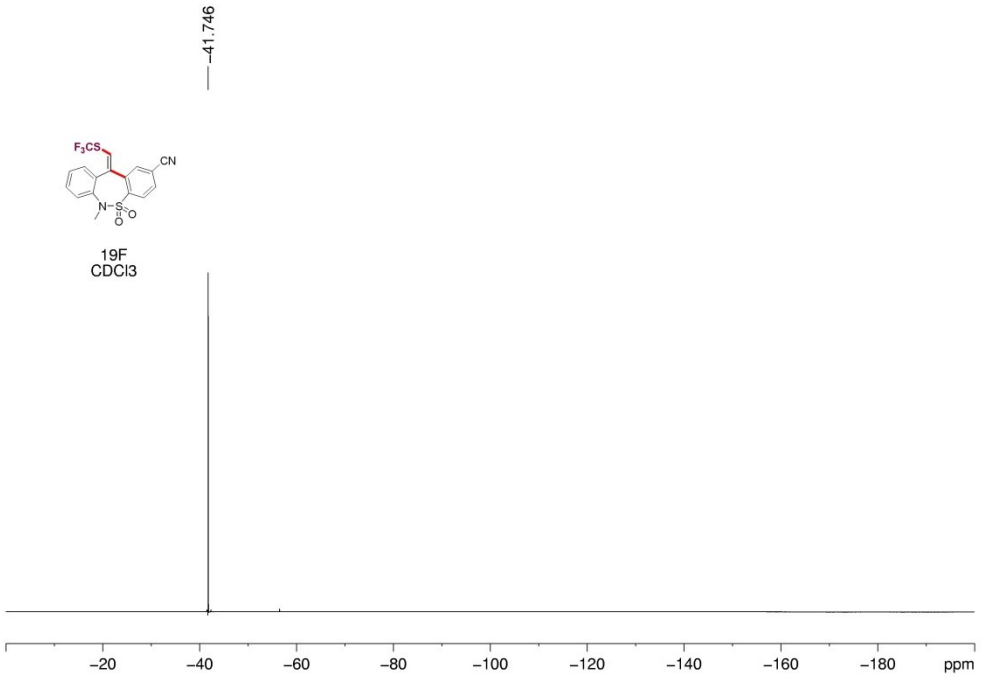

Figure S41. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3m**

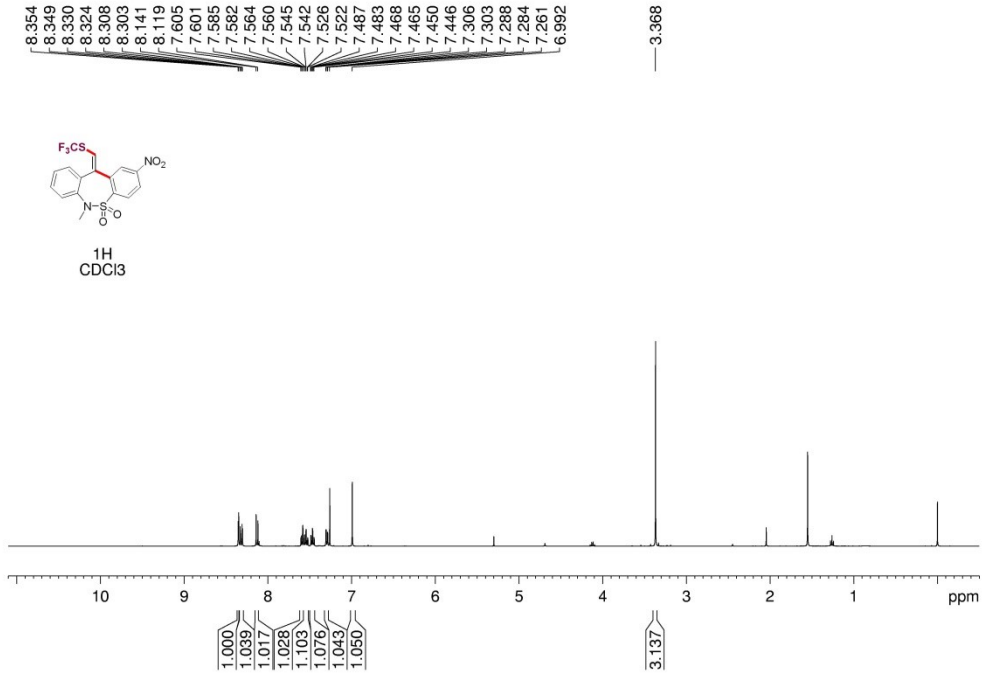

Figure S42. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3n**

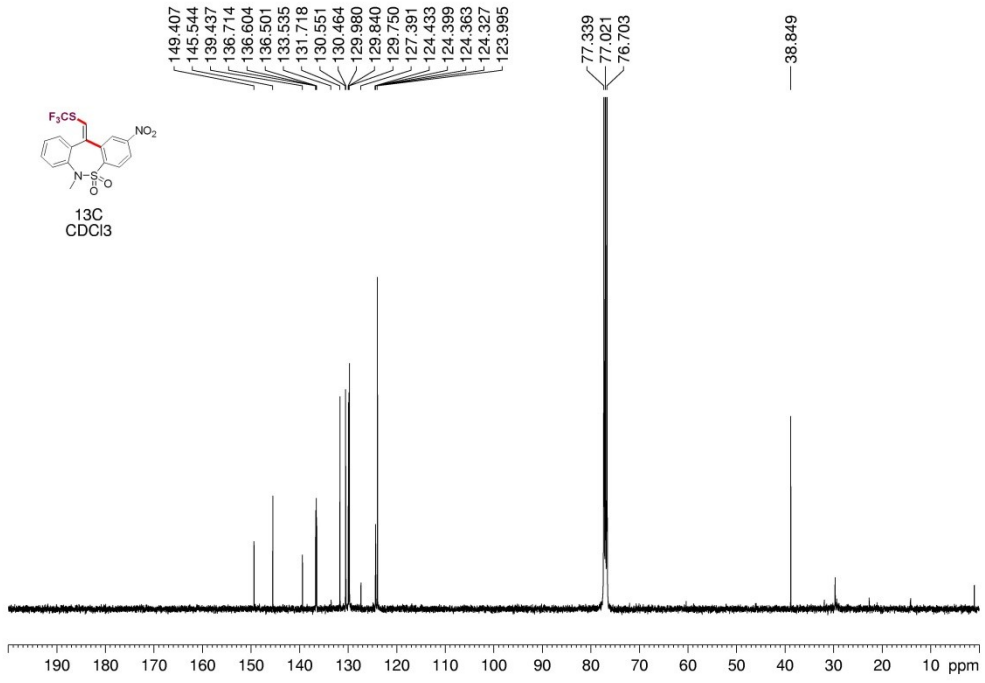

Figure S43. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3n**

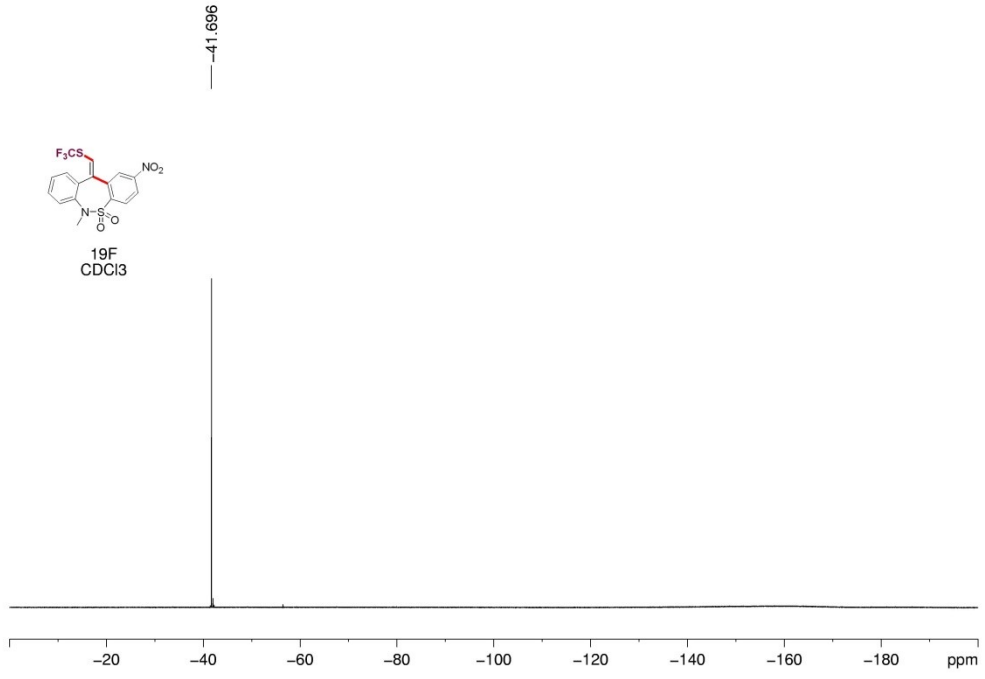

Figure S44. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3n**

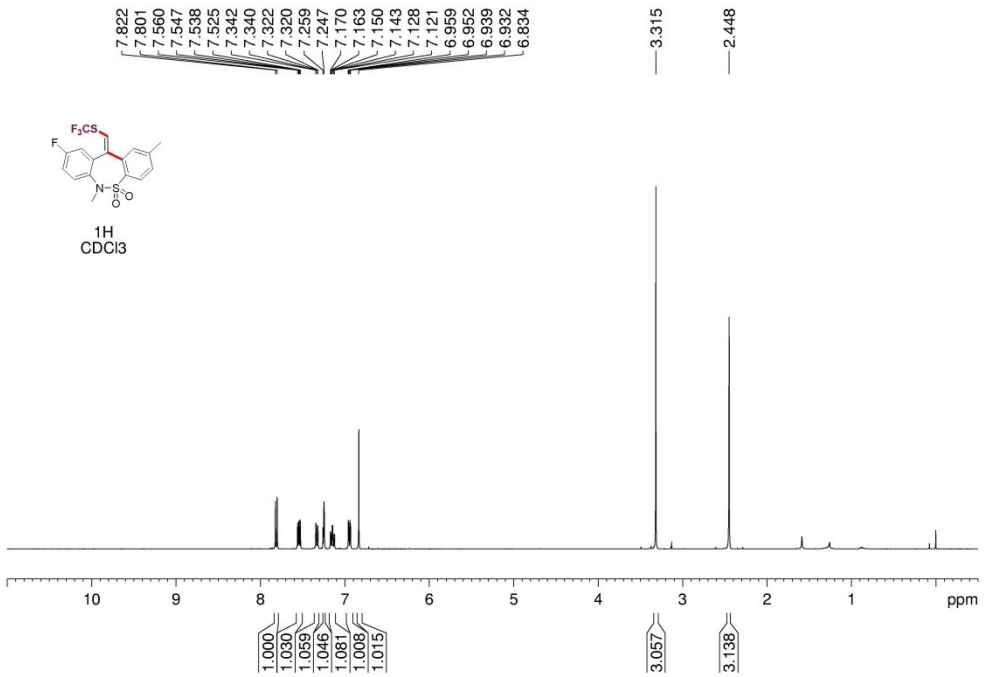

Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3o**

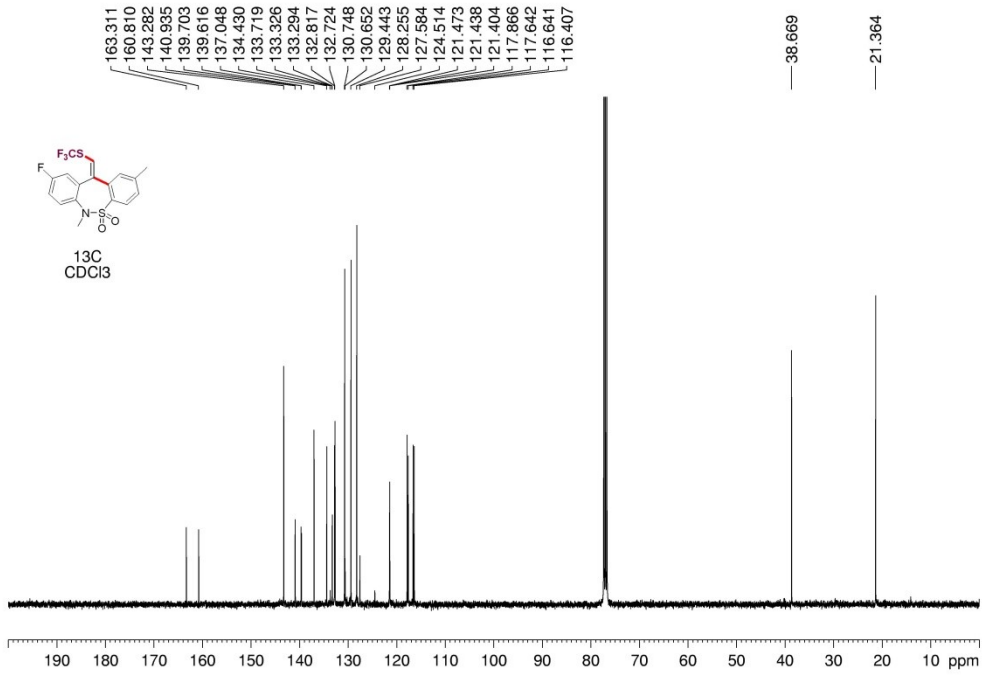

Figure S46. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3o**

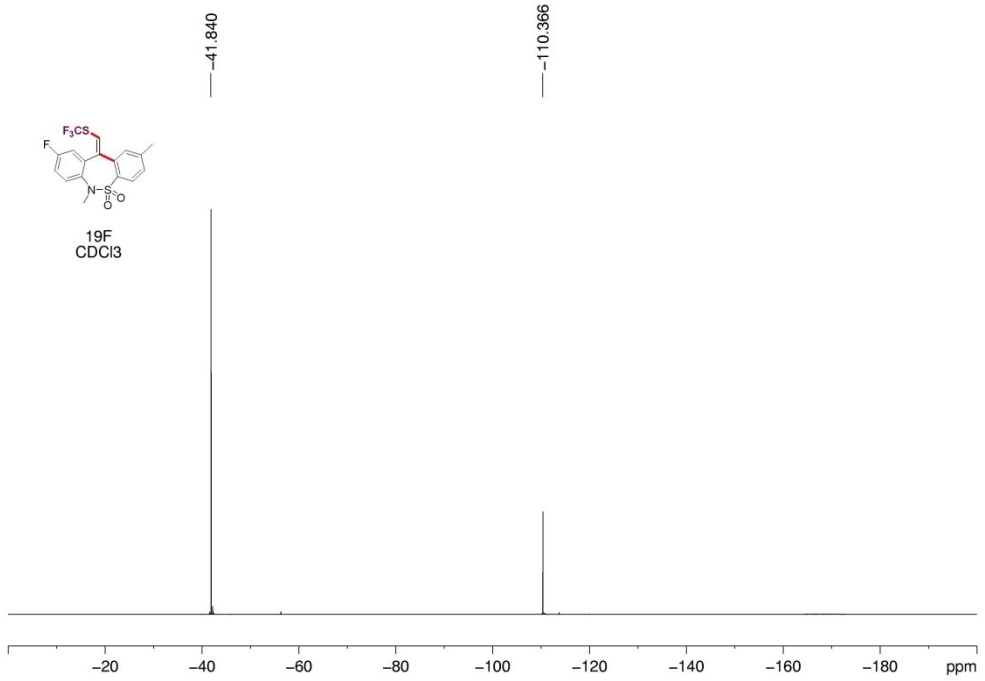

Figure S47. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3o**

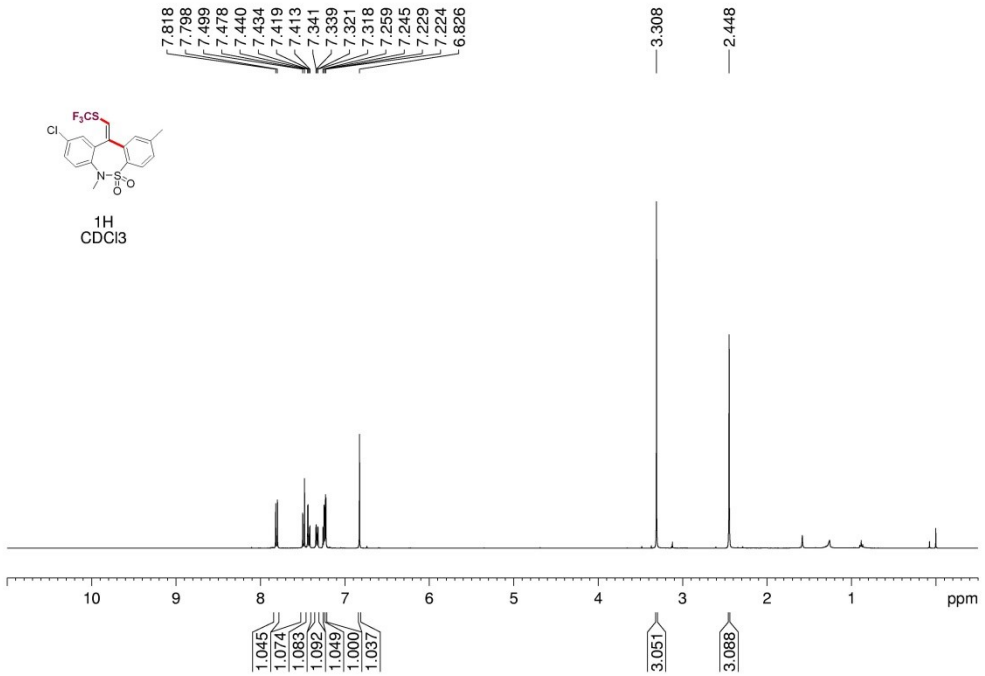

Figure S48. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3p**

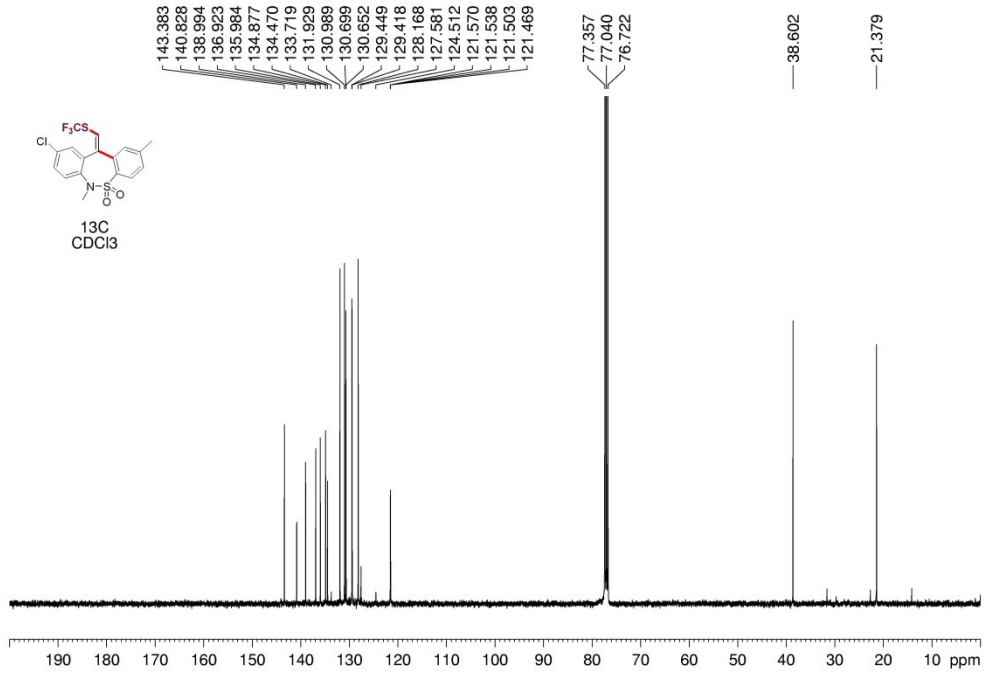

Figure S49. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3p**

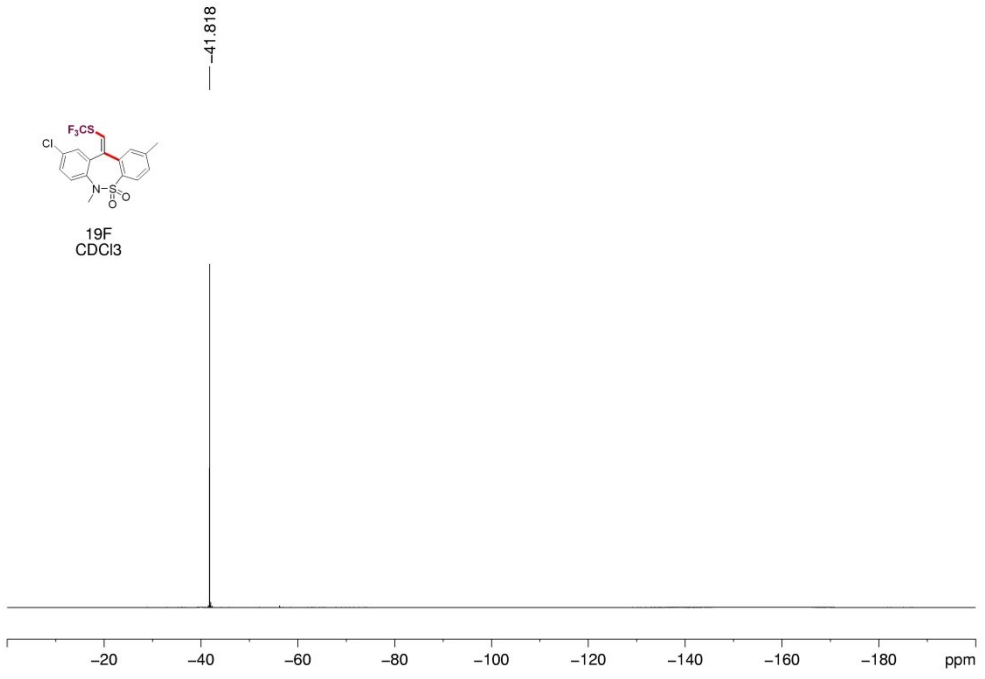

Figure S50. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3p**

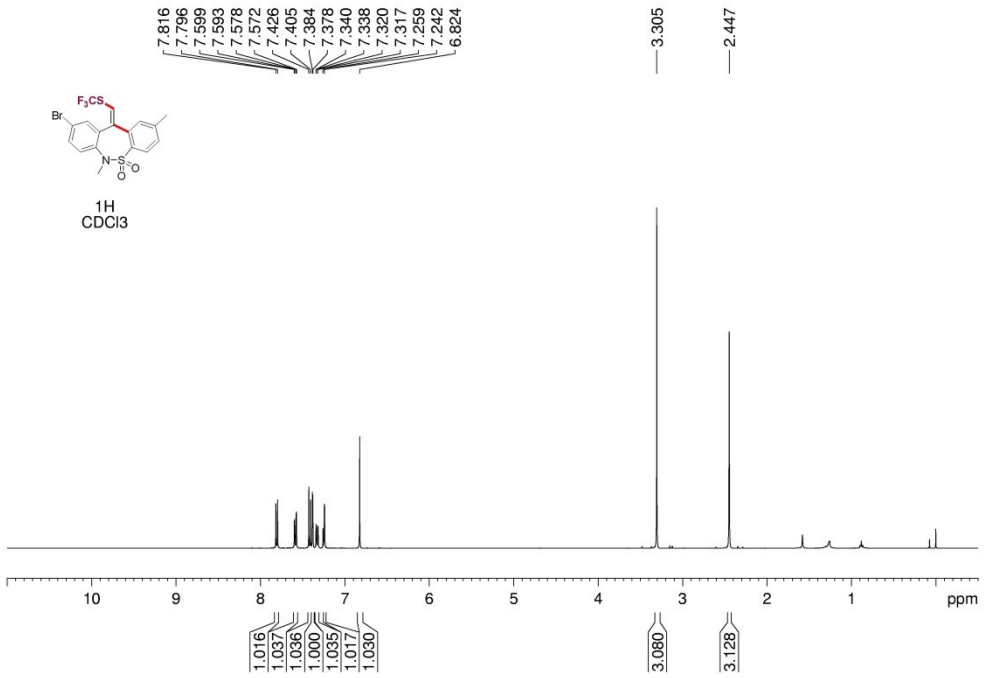

Figure S51. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3q**

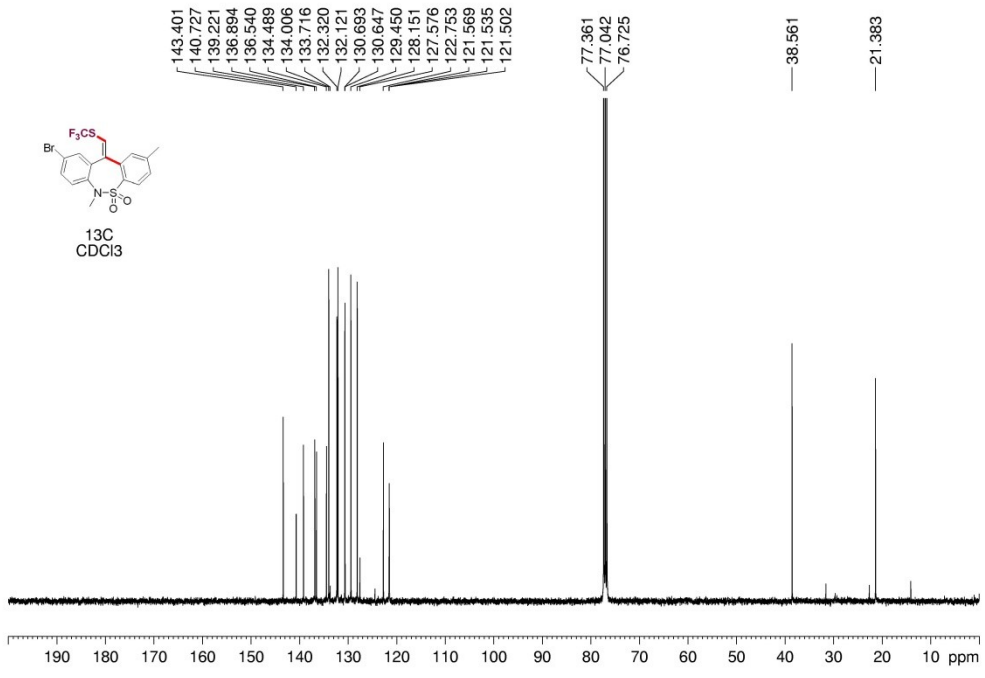

Figure S52. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3q**

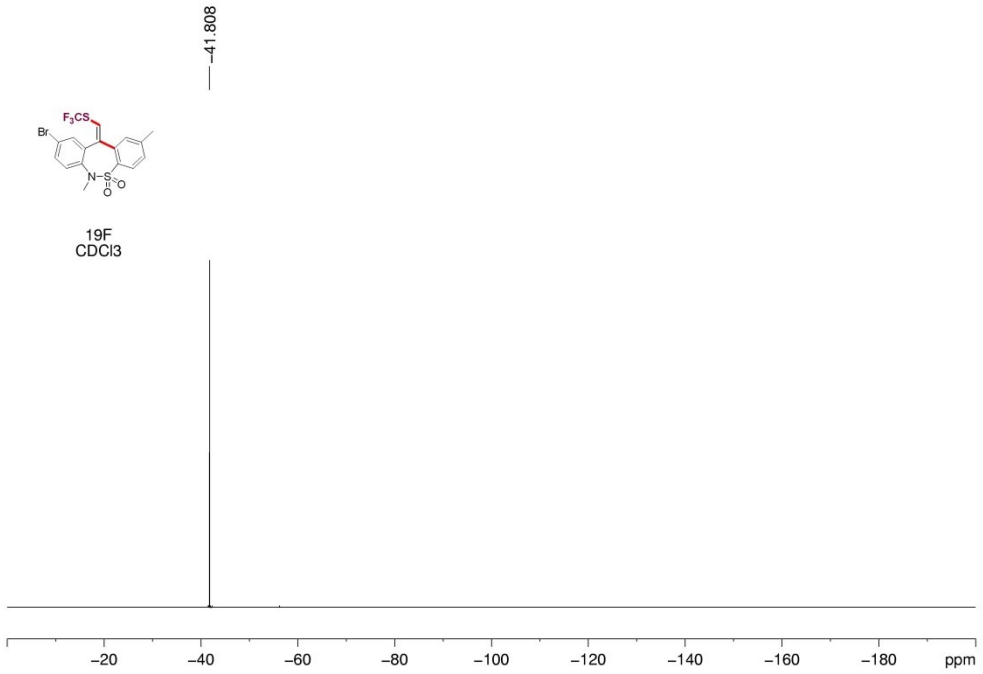

Figure S53. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3q**

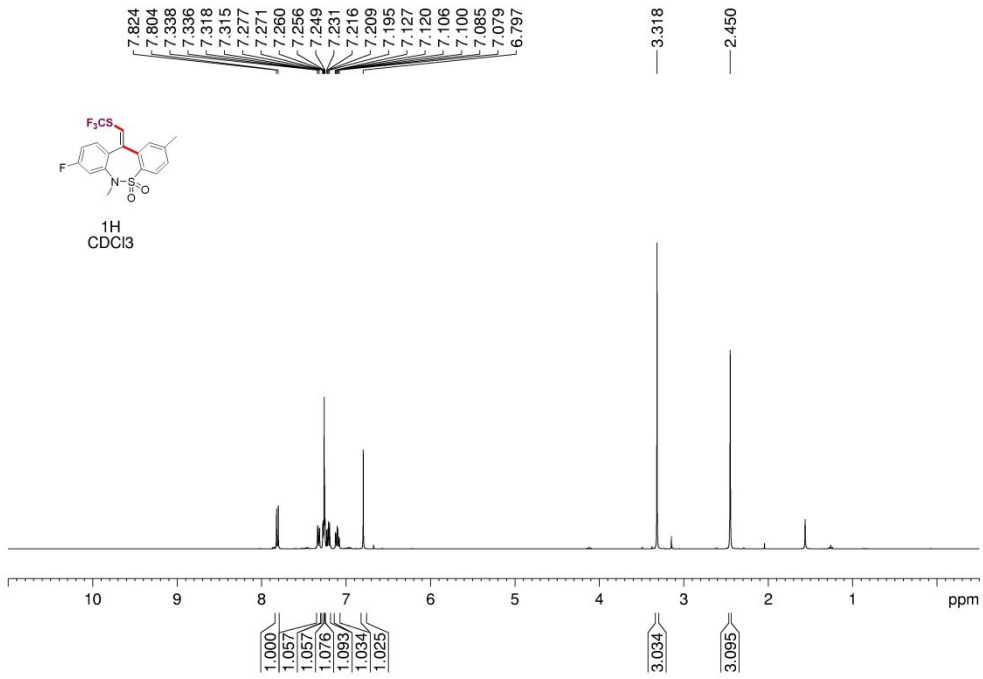

Figure S54. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3r**

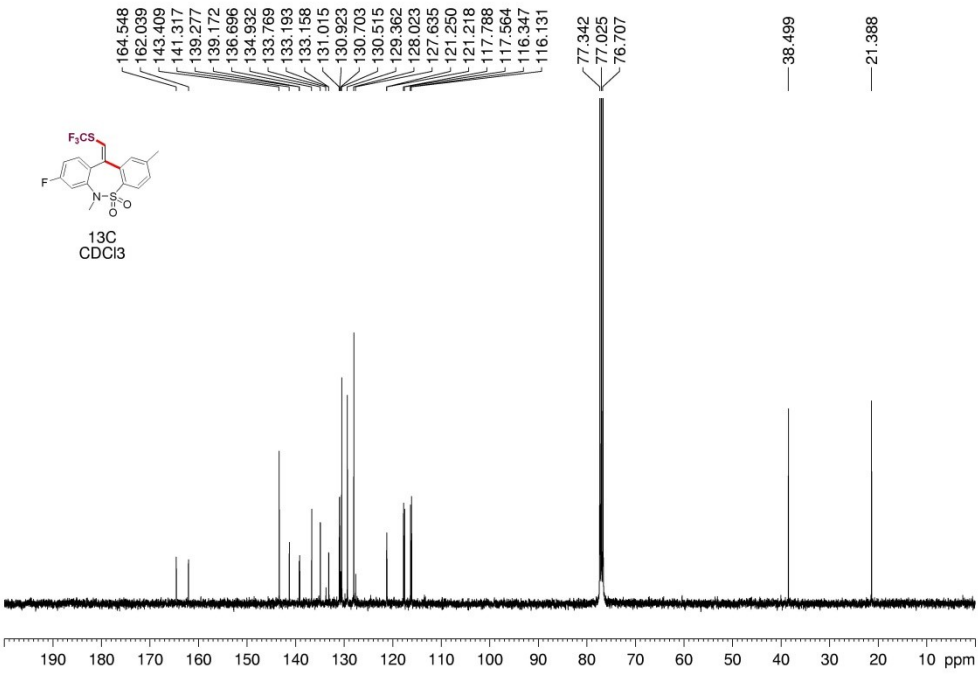

Figure S55. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3r**

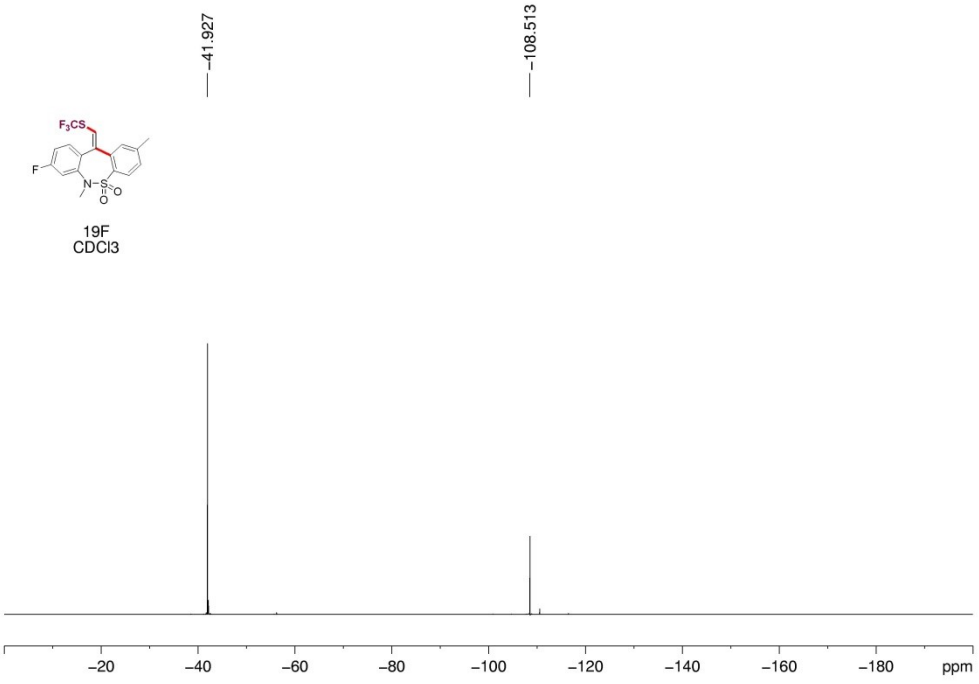

Figure S56. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3r**

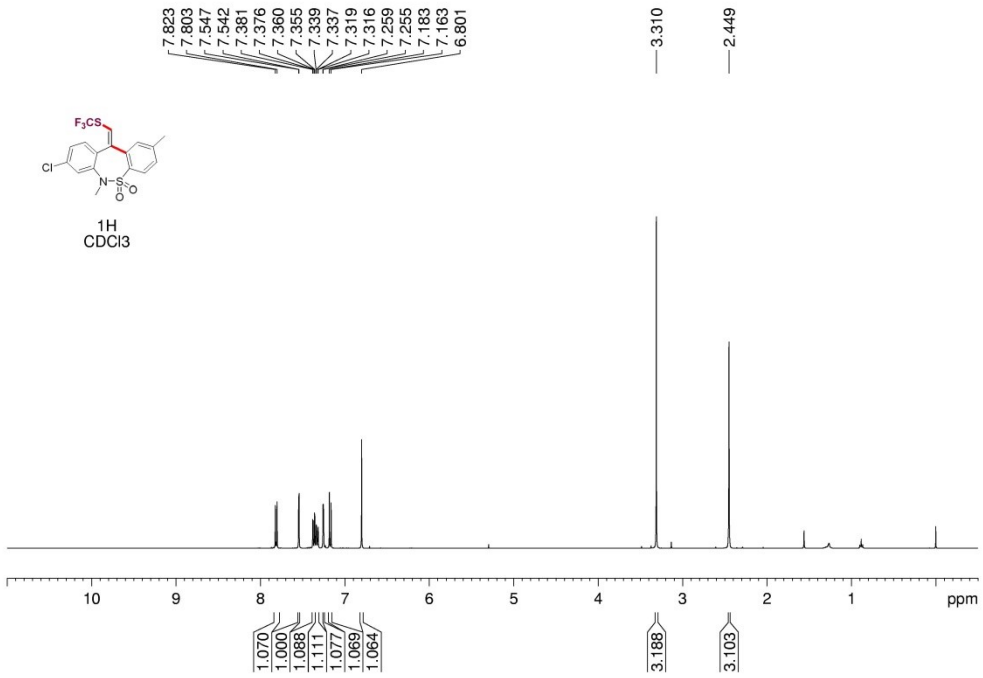

Figure S57. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3s**

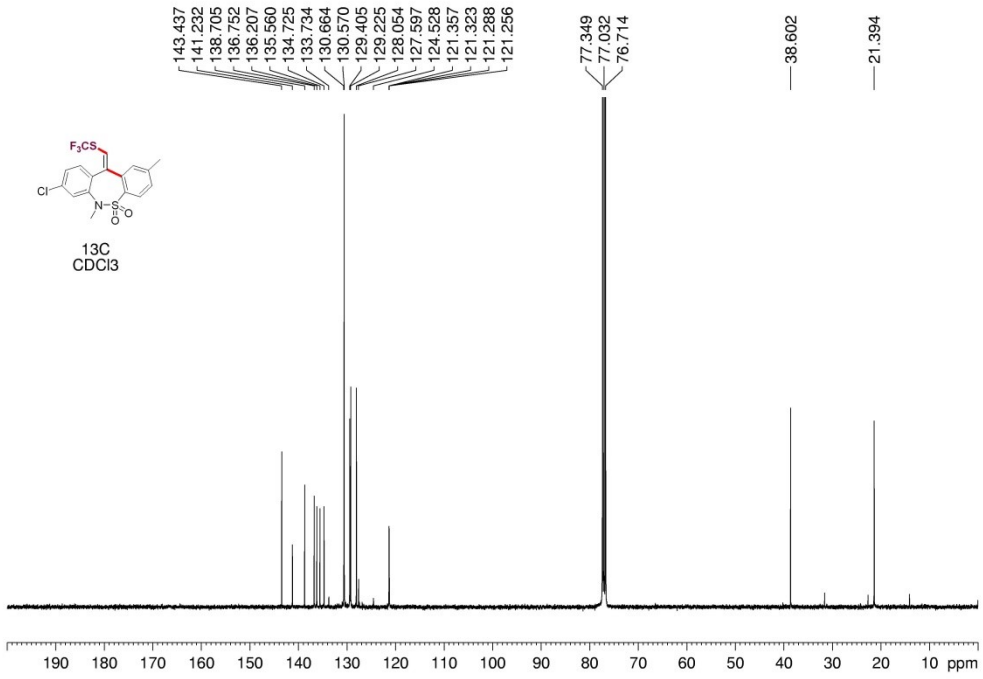

Figure S58. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3s**

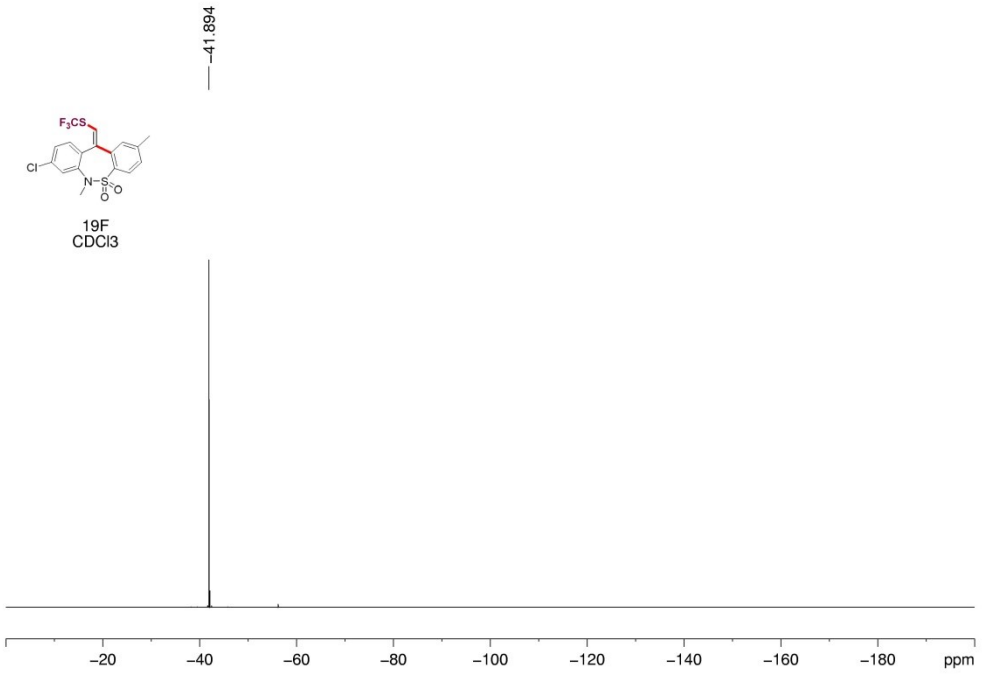

Figure S59. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3s**

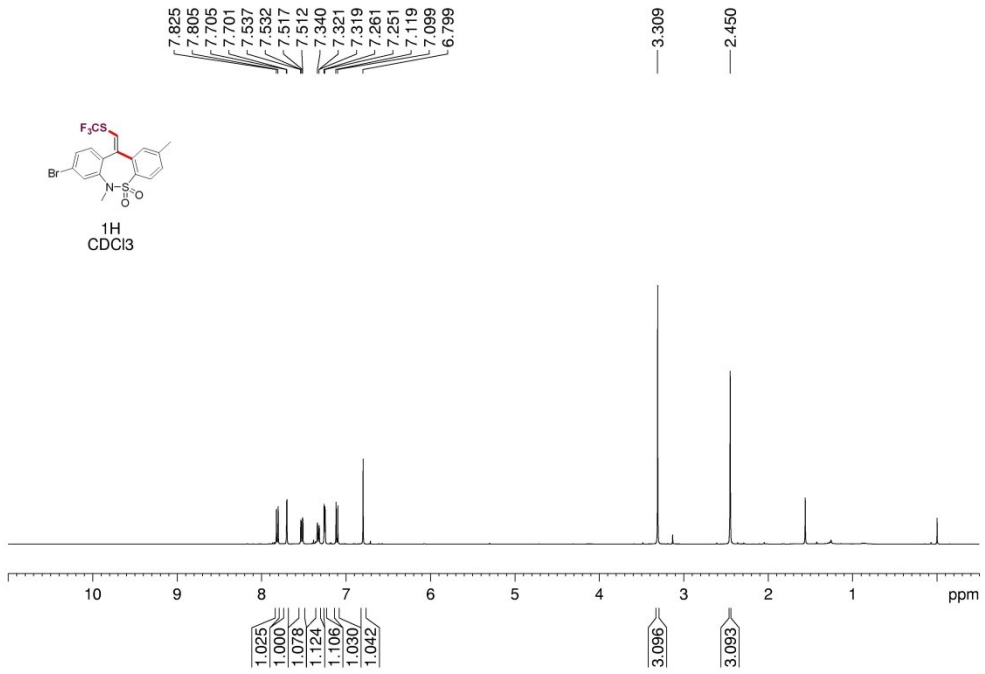

Figure S60. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3t**

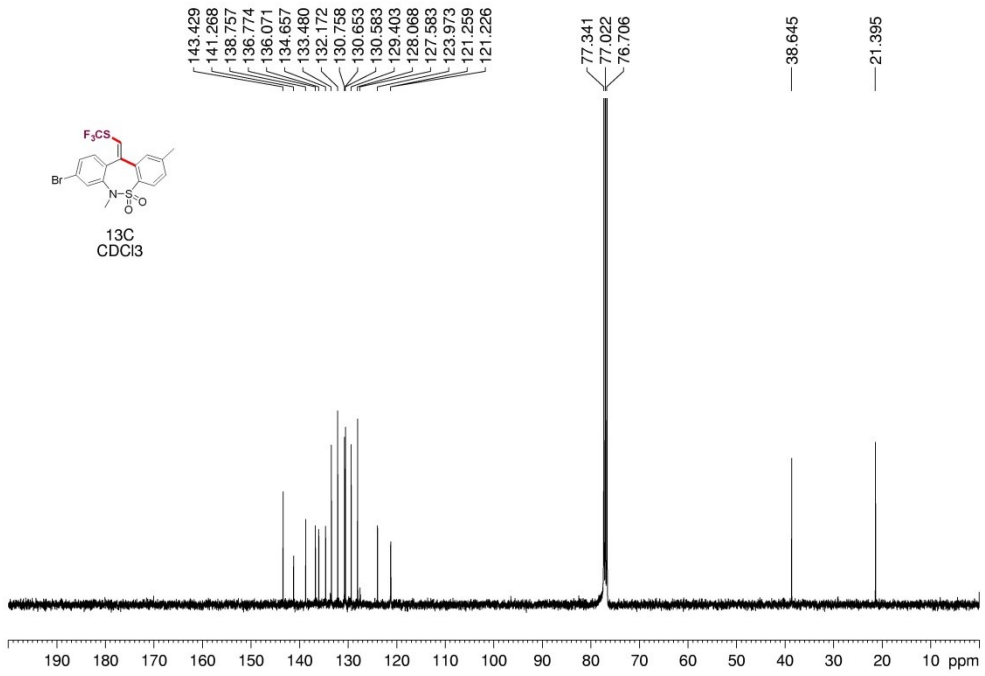

Figure S61. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3t**

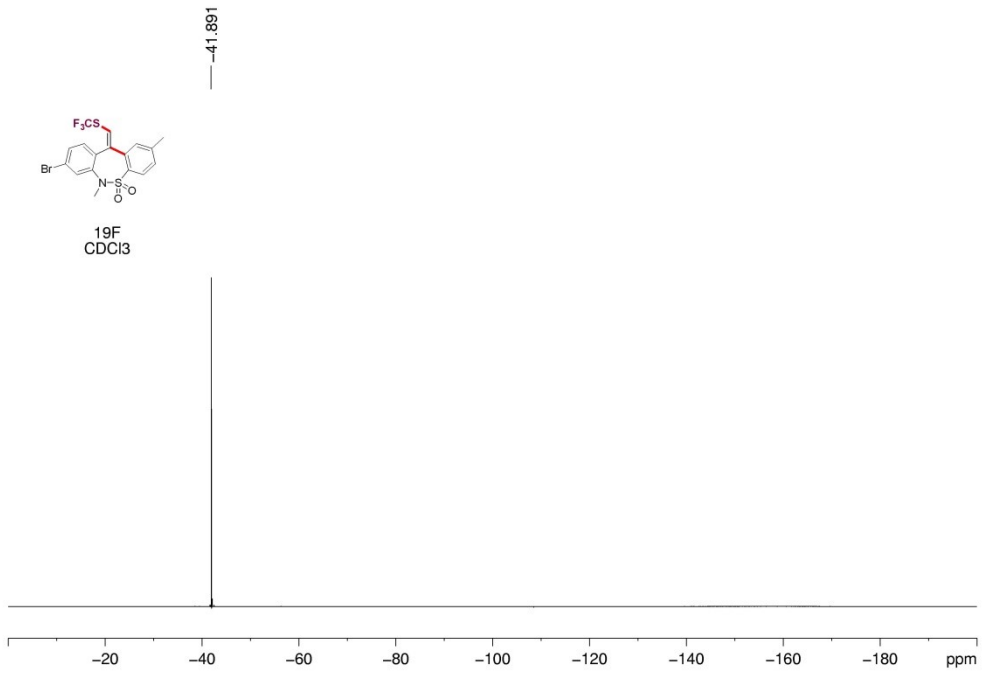

Figure S62. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3t**

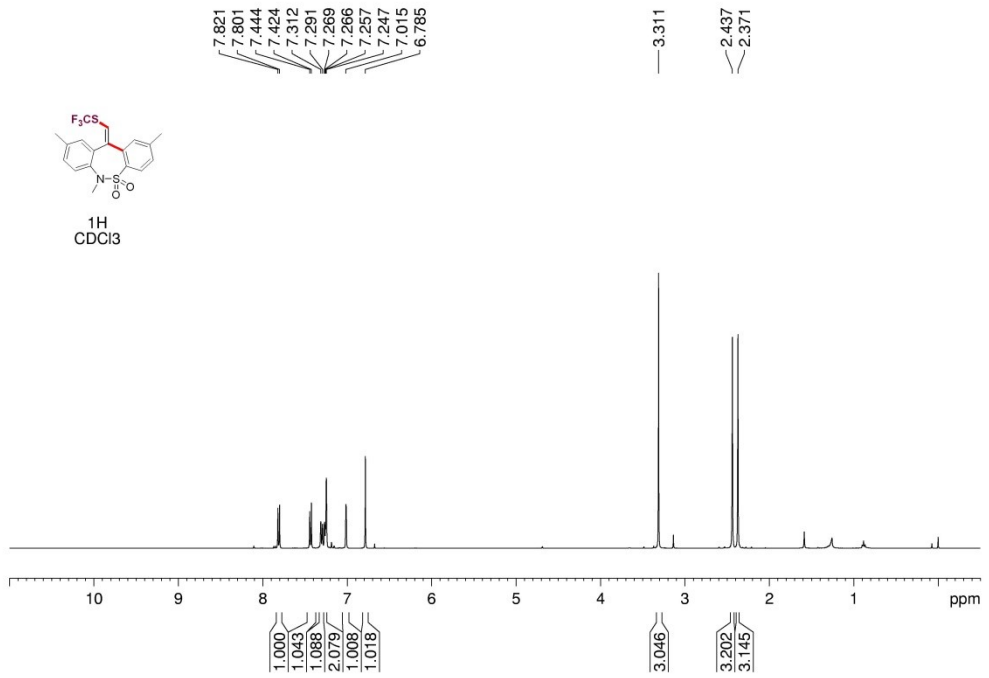

Figure S63. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3u**

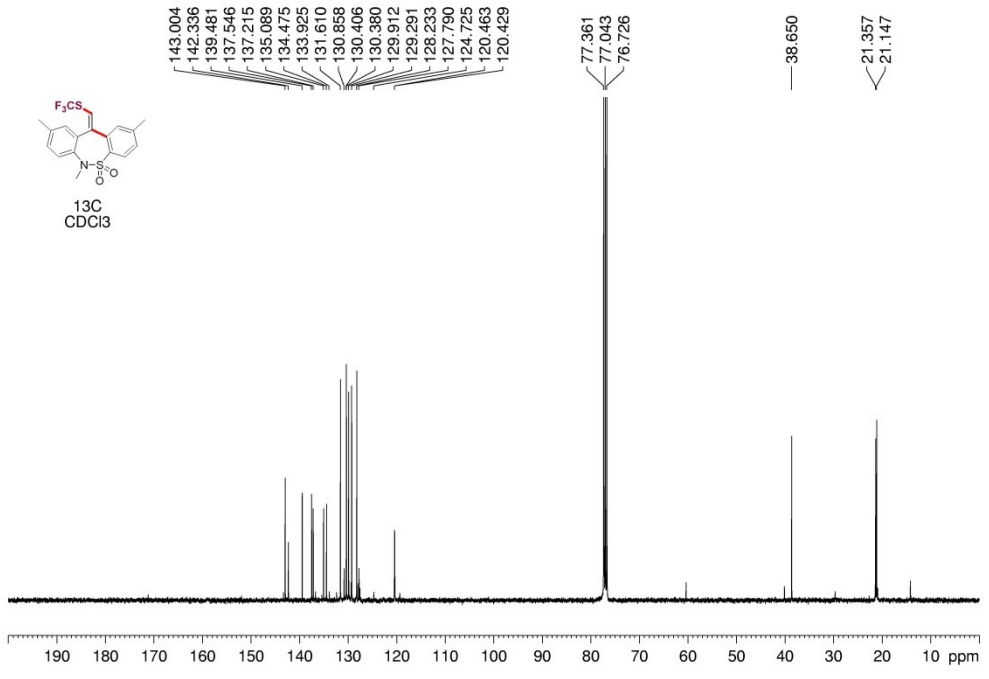

Figure S64. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3u**

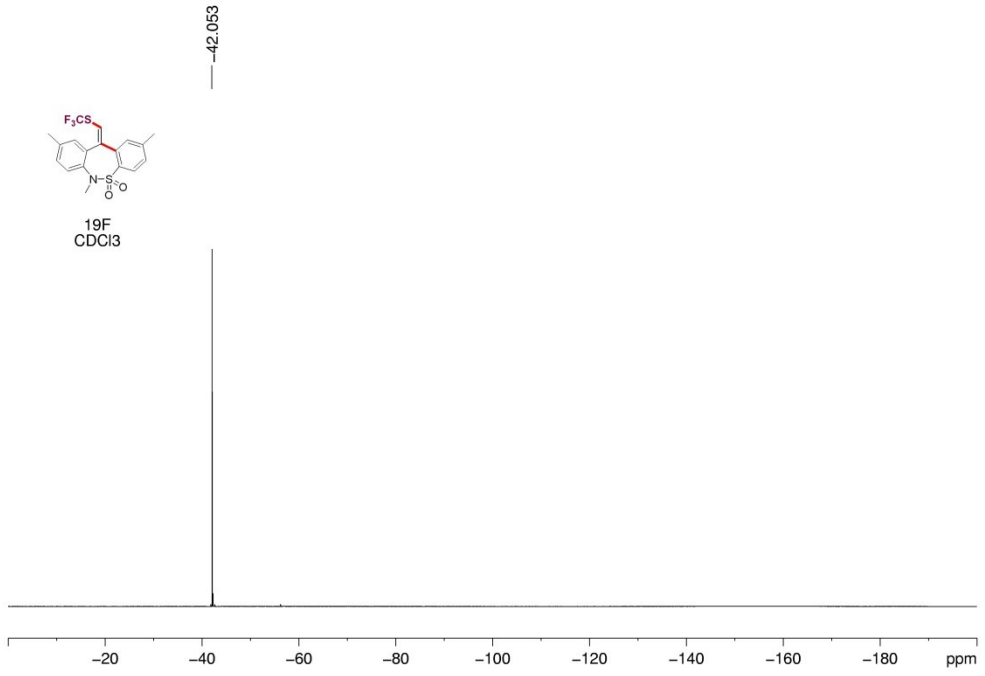

Figure S65. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3u**

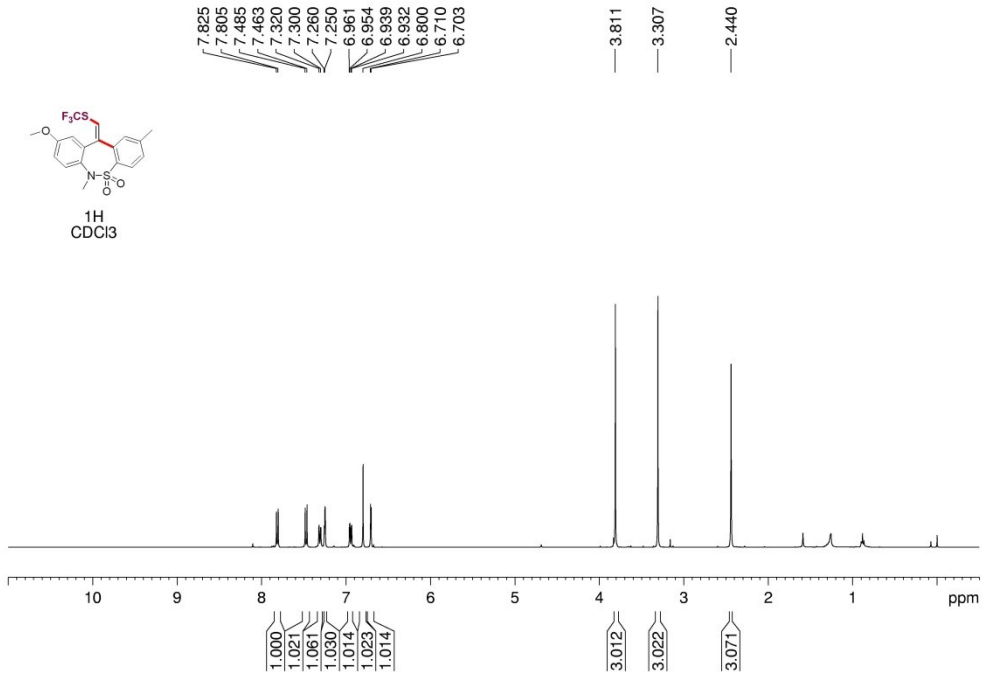

Figure S66. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3v**

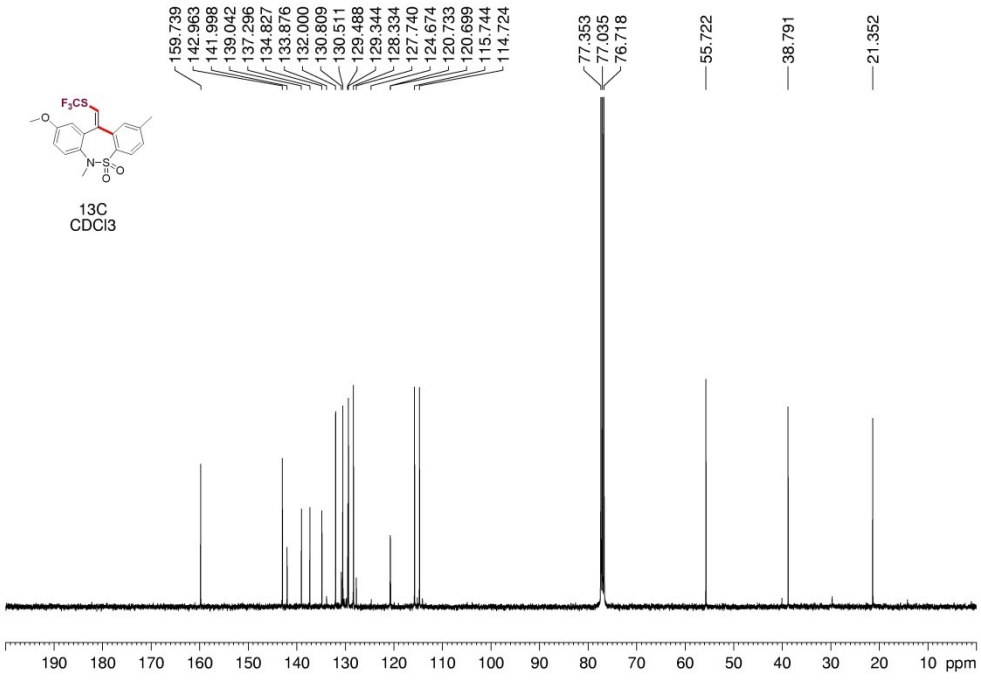

Figure S67. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3v**

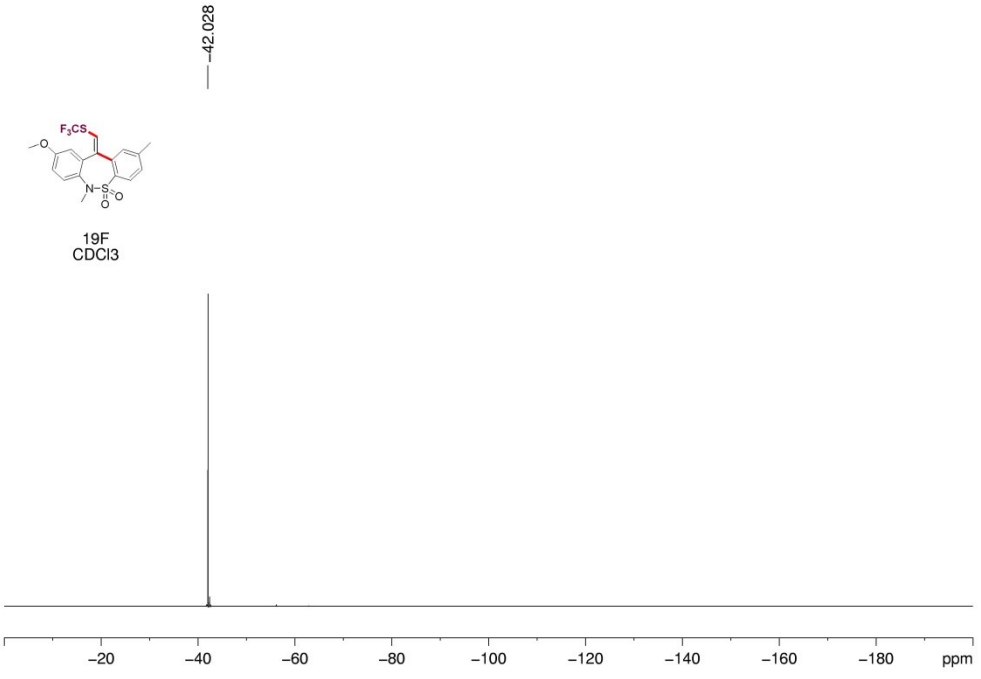

Figure S68. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3v**

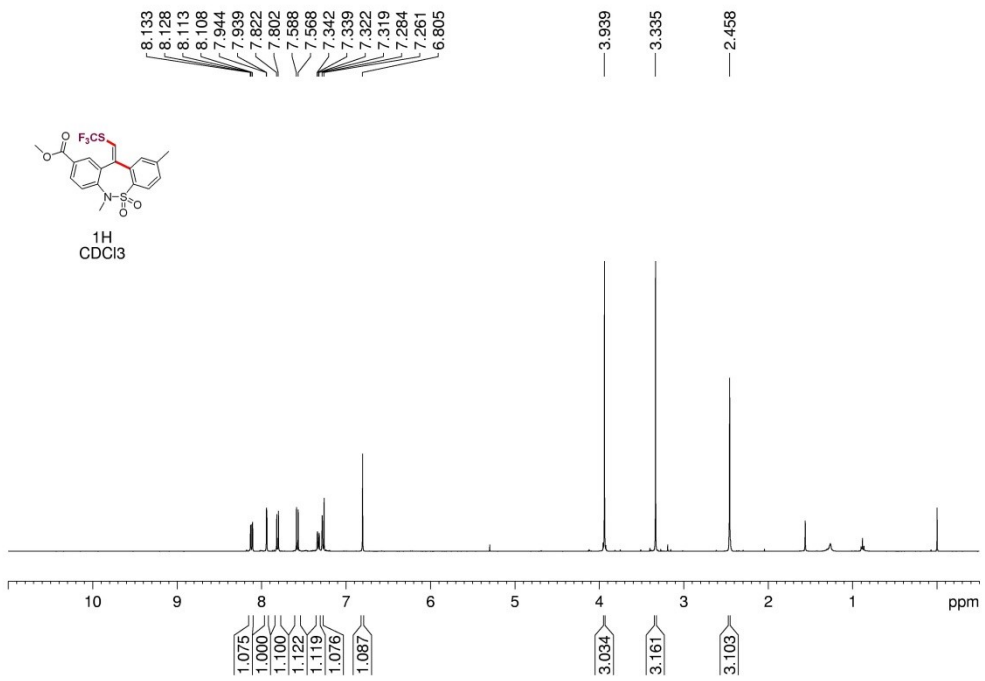

Figure S69. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3w**

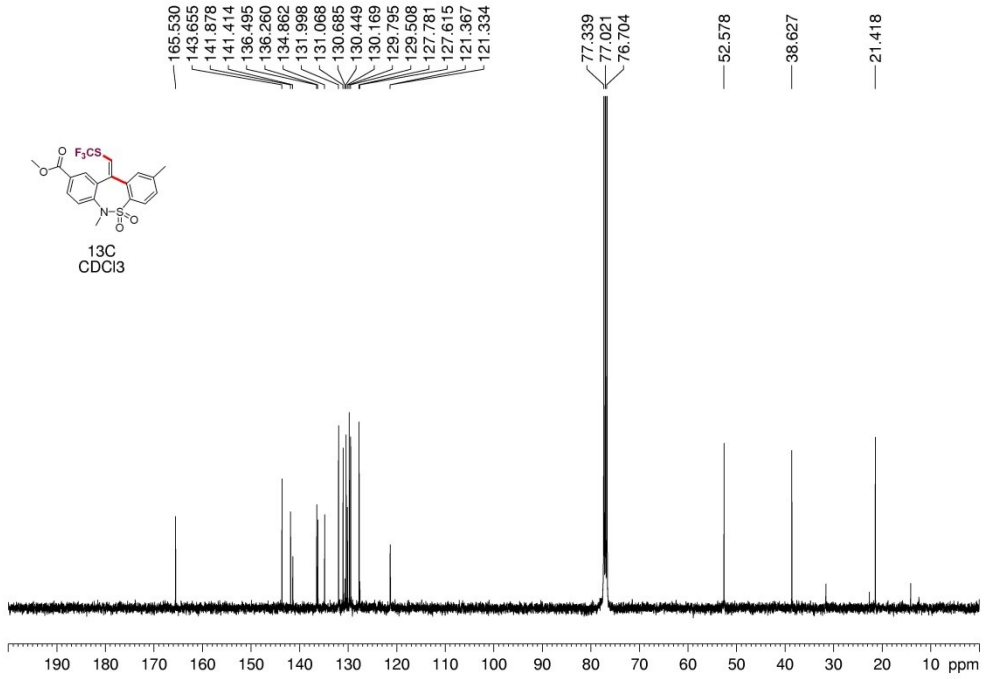

Figure S70. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3w**

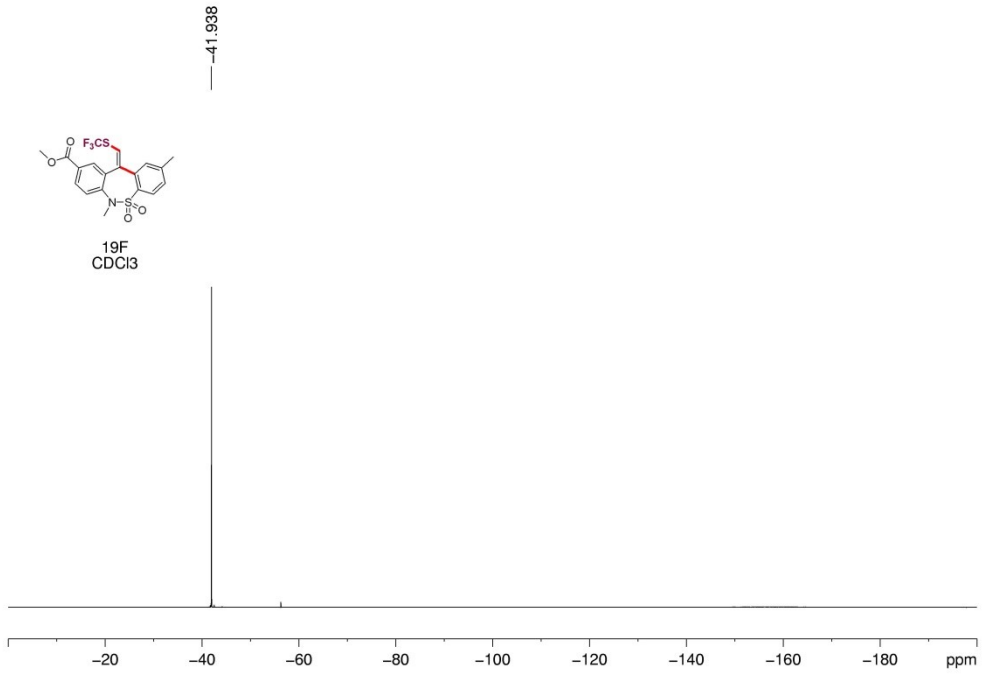

Figure S71. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3w**

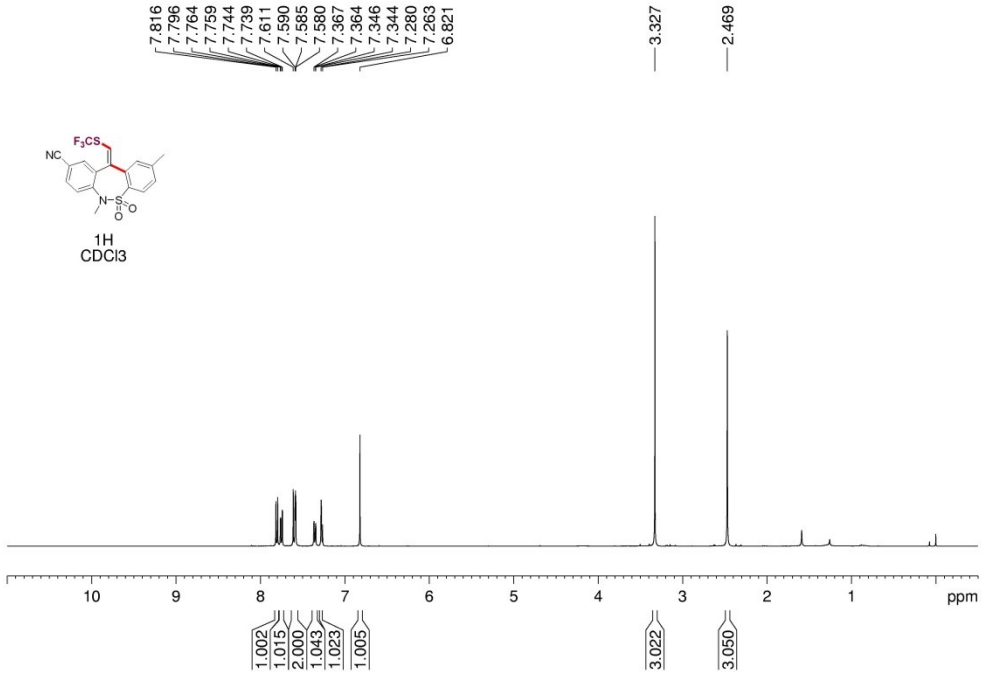

Figure S72. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3x**

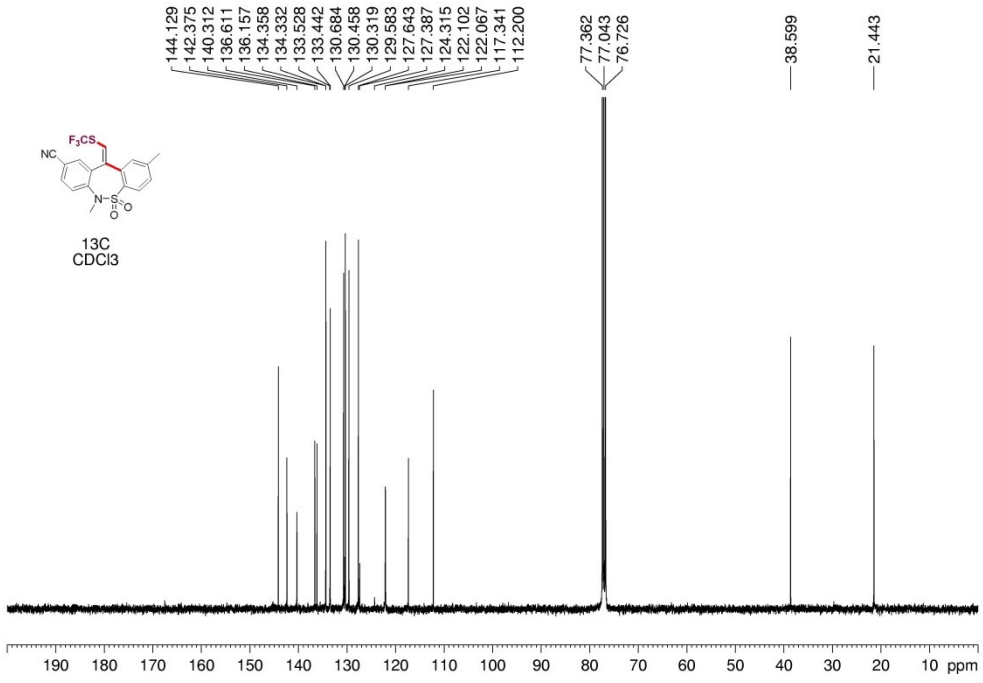

Figure S73. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3x**

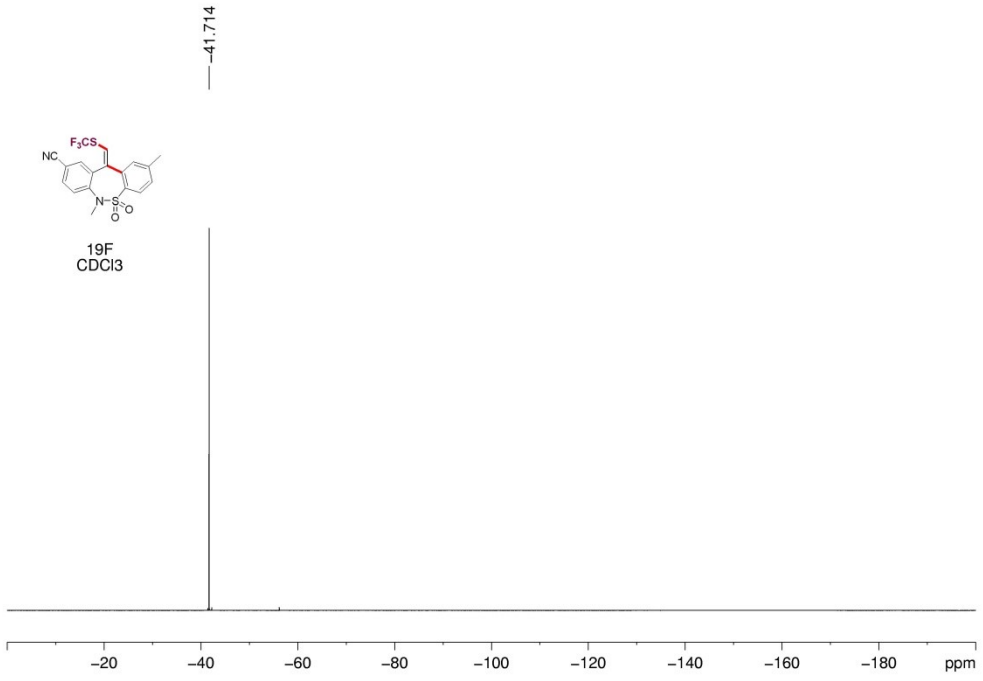

Figure S74. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3x**

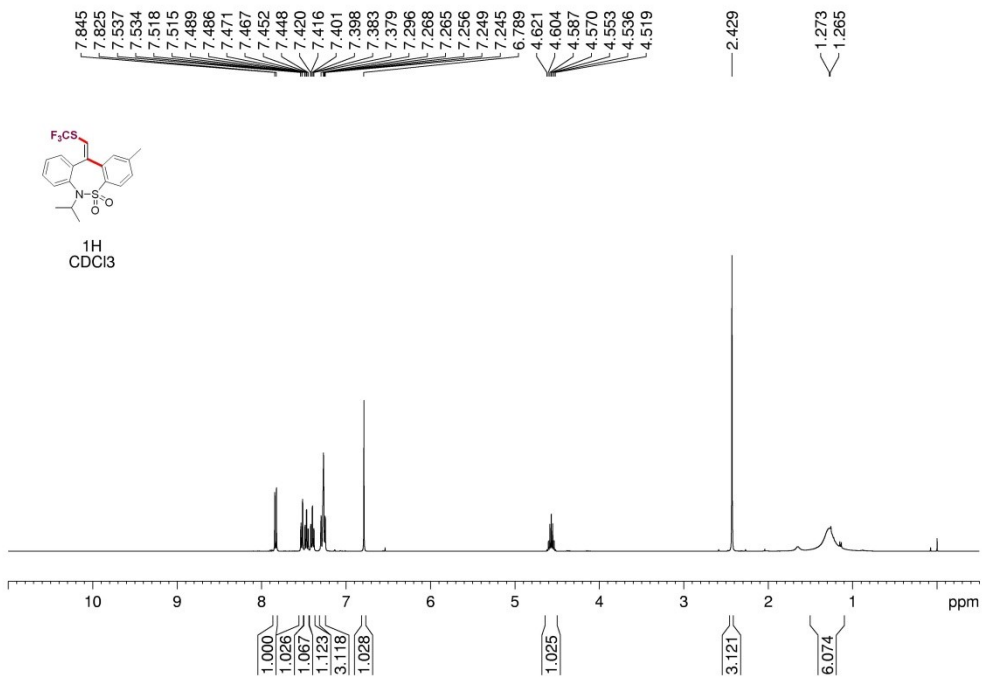

Figure S75. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3y**

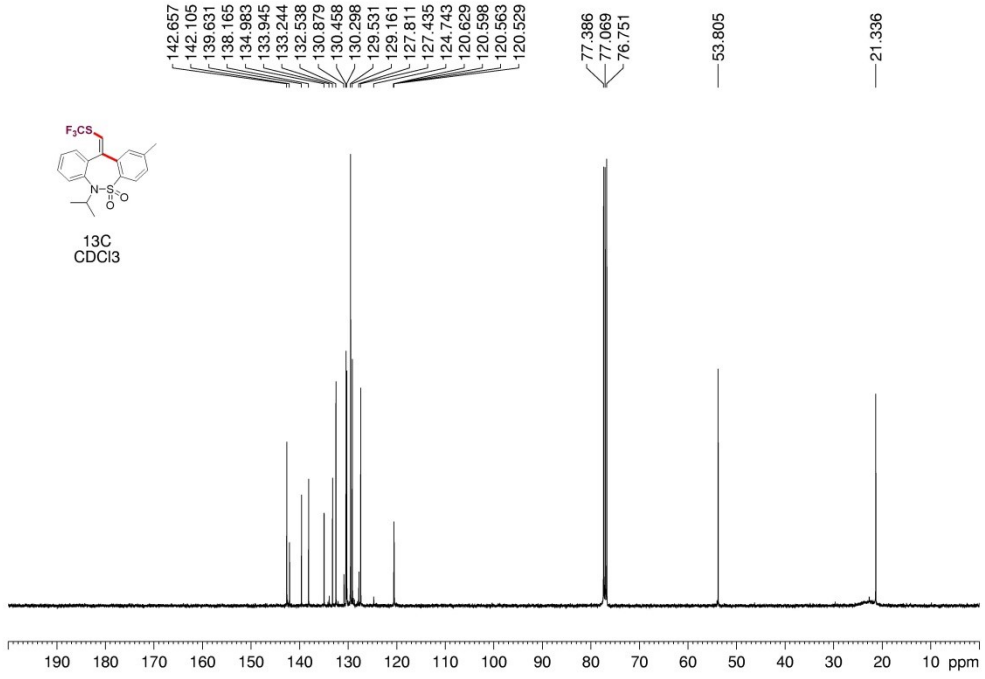

Figure S76. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3y**

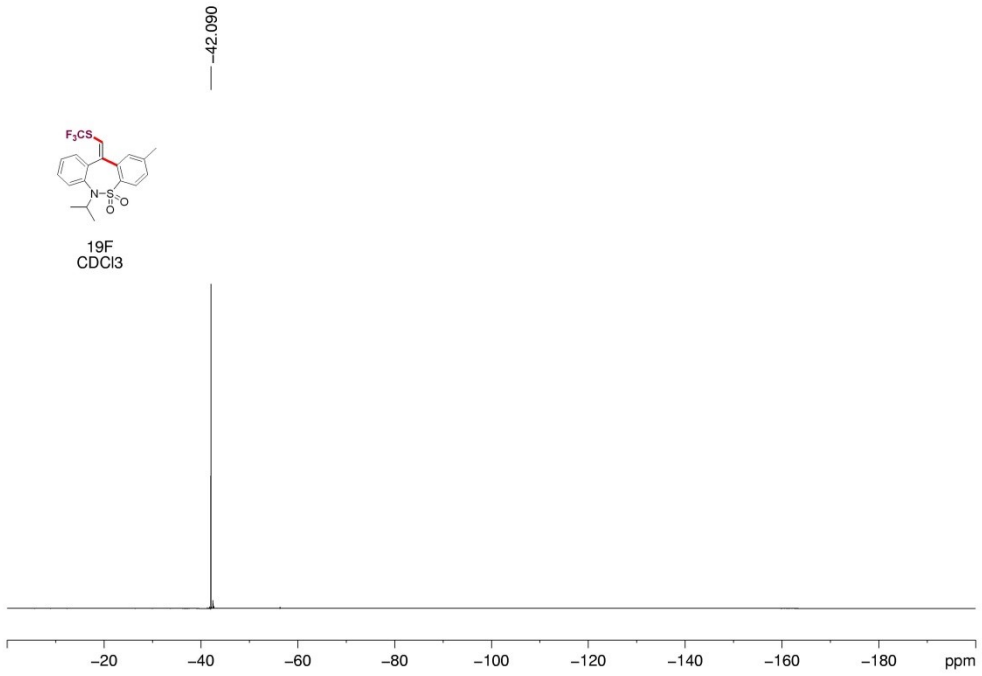

Figure S77. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3y**

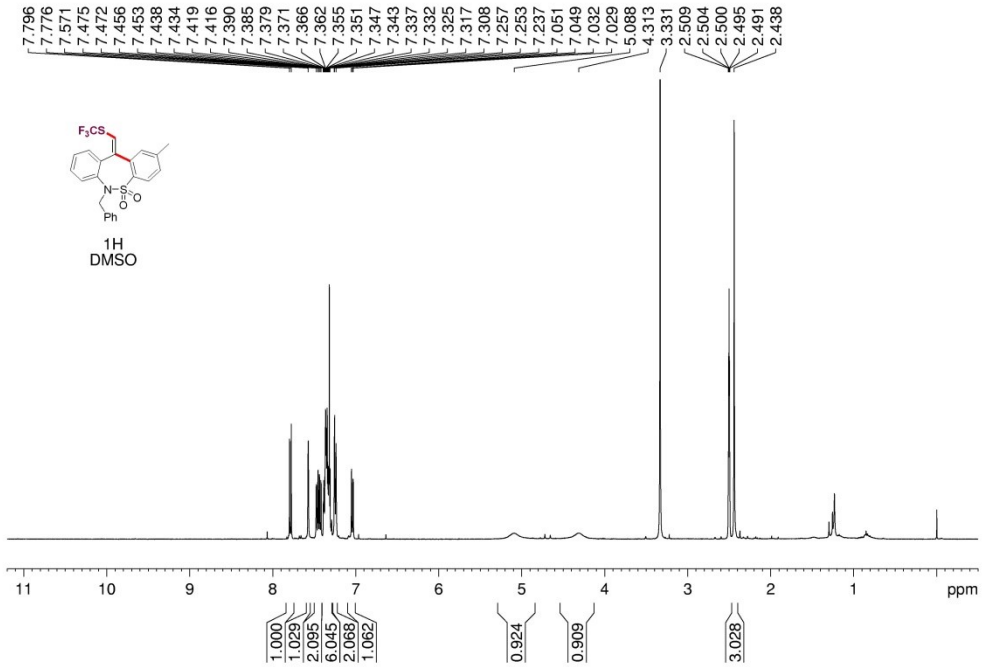

Figure S78. ^{1}H NMR (400 MHz, DMSO-d_6) of compound **3z**

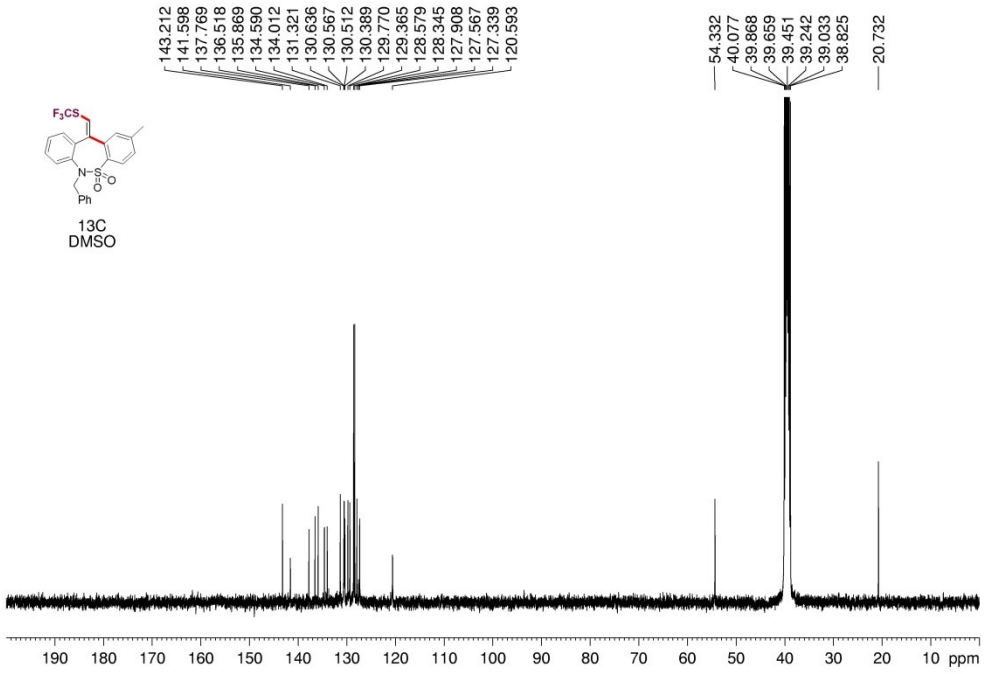

Figure S79. ^{13}C NMR (100 MHz, DMSO-d_6) of compound **3z**

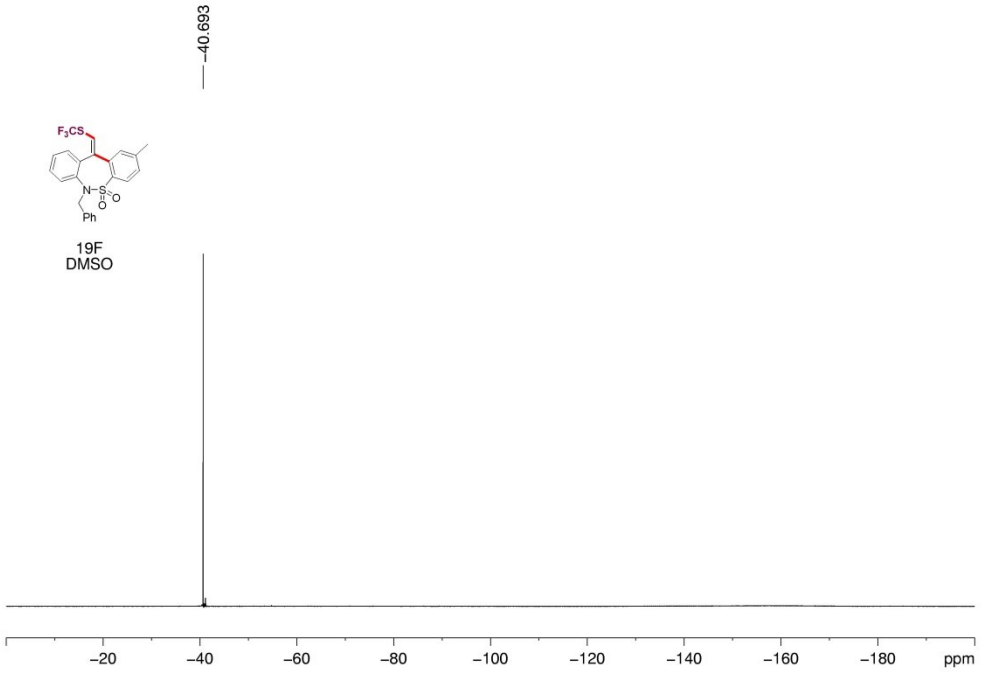

Figure S80. ^{19}F NMR (376 MHz, DMSO-d_6) of compound **3z**

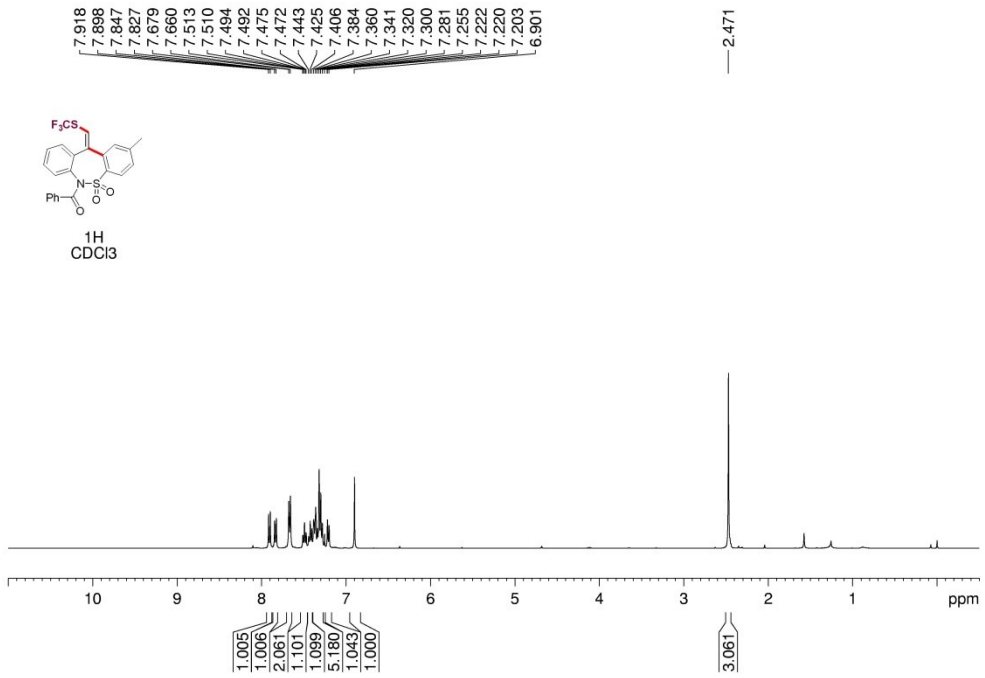

Figure S81. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3za**

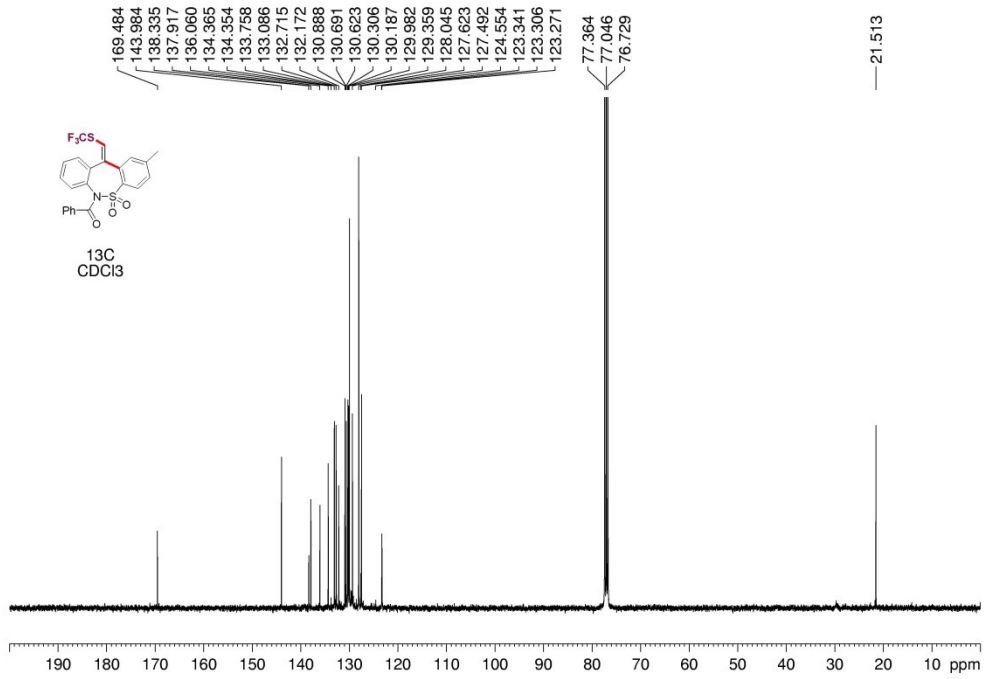

Figure S82. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3za**

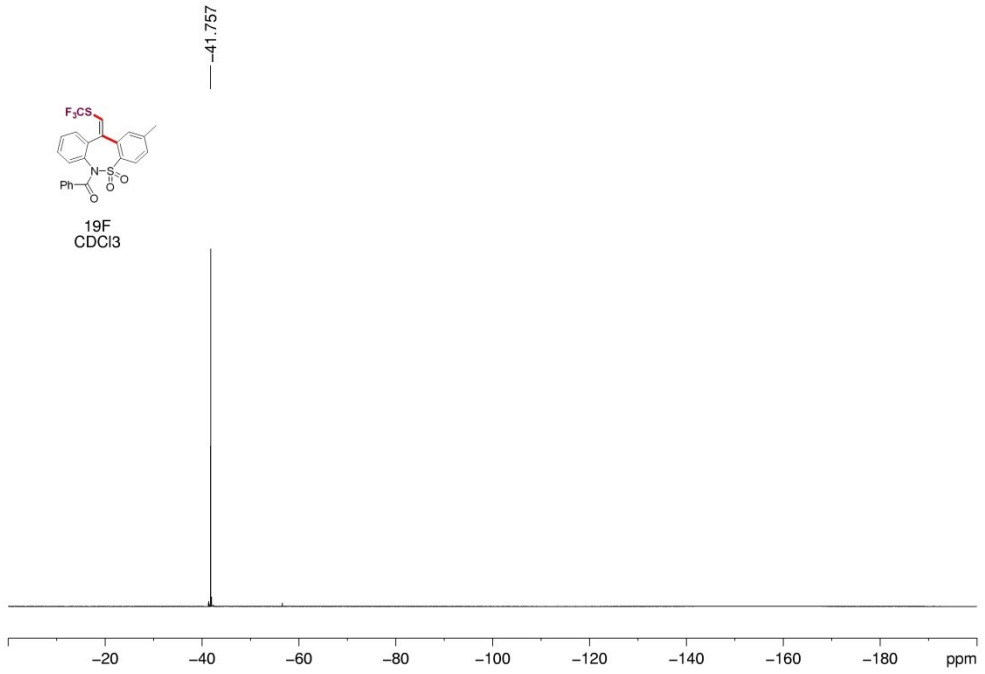

Figure S83. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3za**

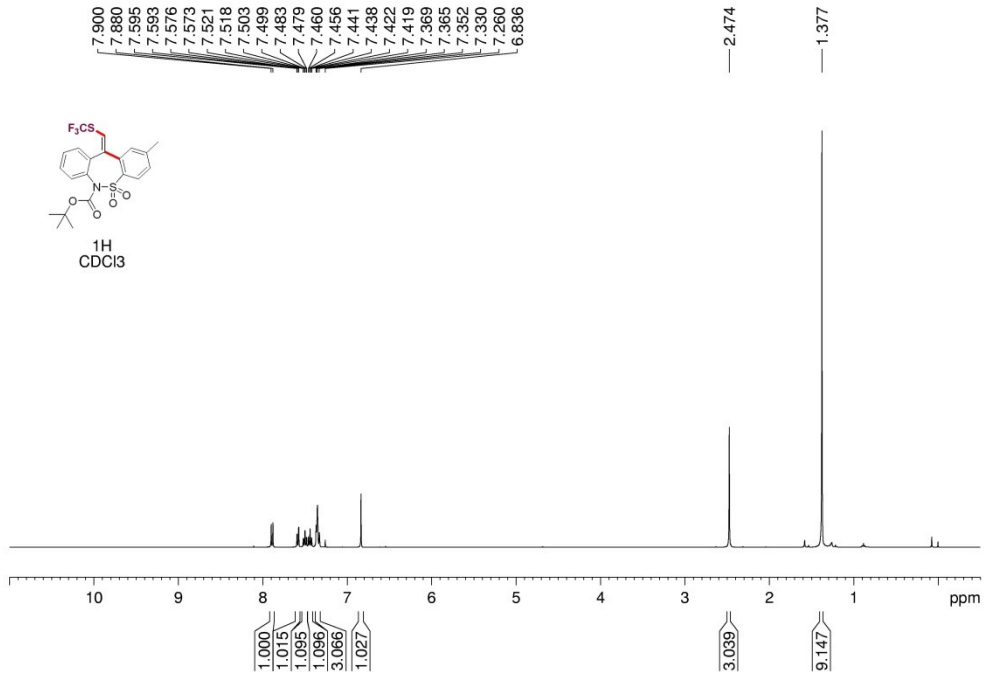

Figure S84. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3zb**

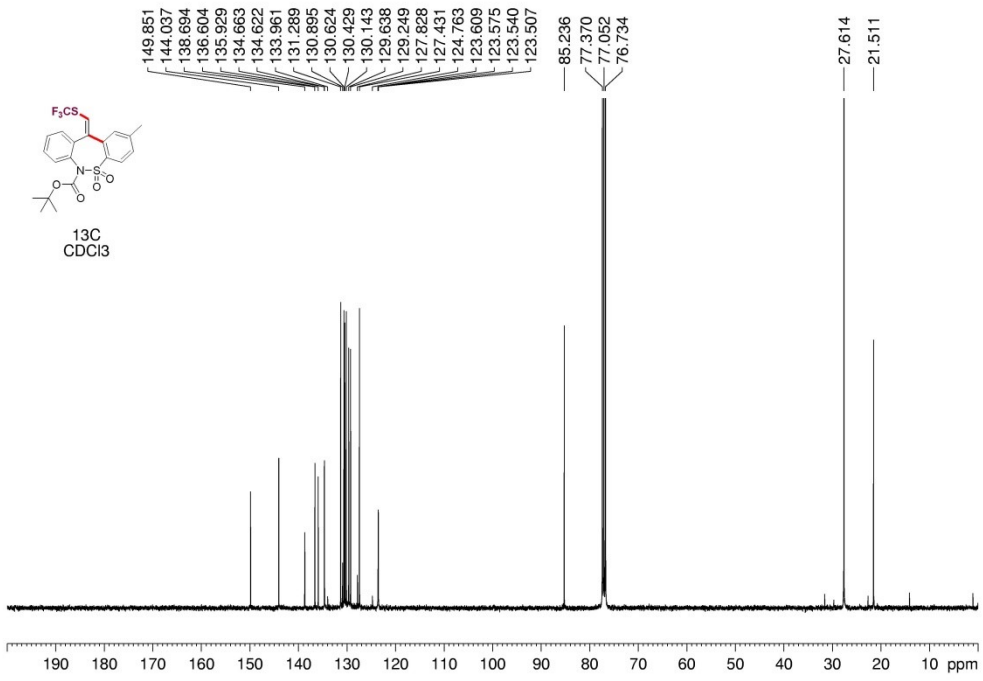

Figure S85. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3zb**

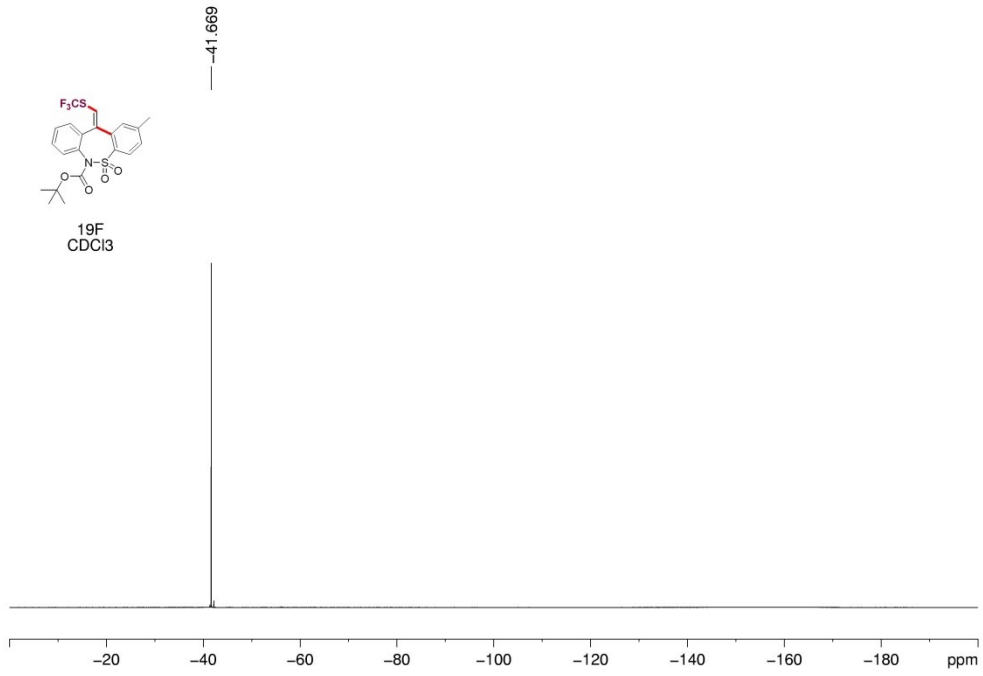

Figure S86. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3zb**

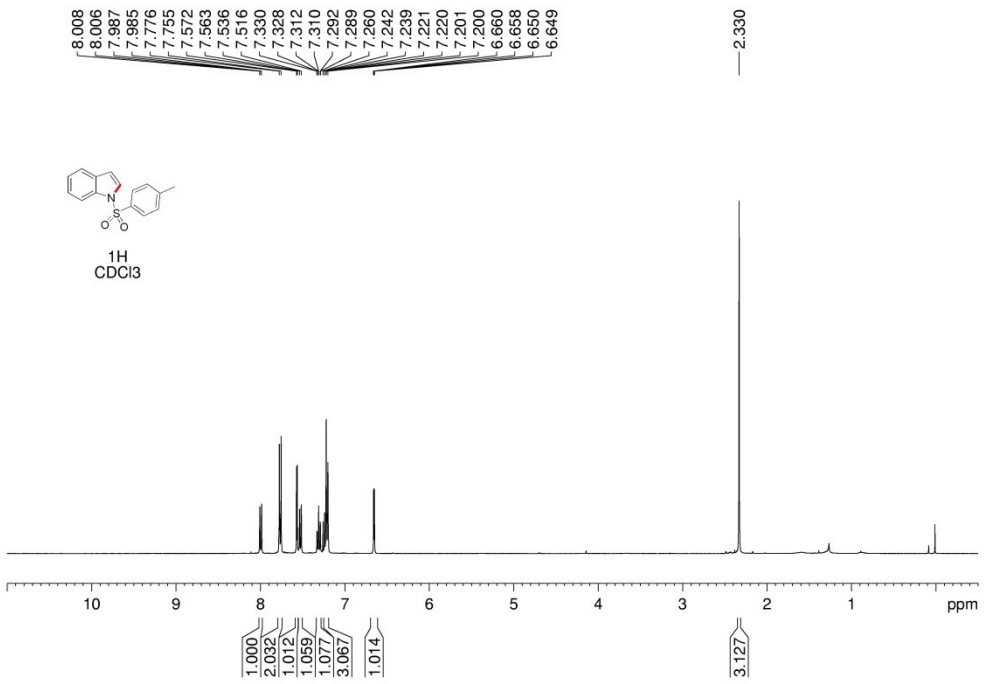

Figure S87. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3zc'**

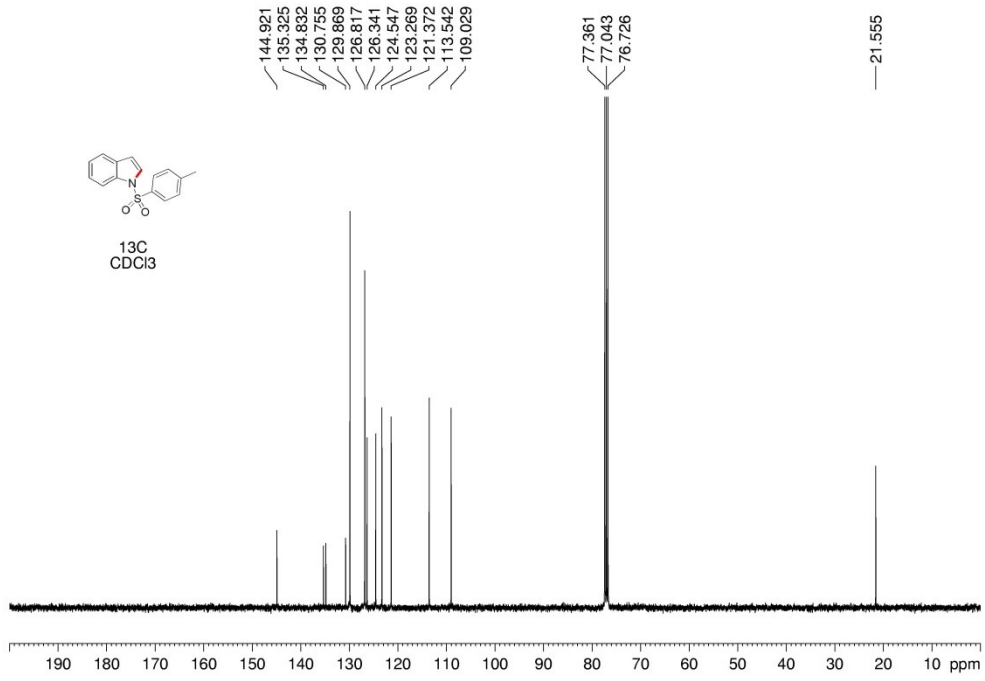

Figure S88. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3zc'**

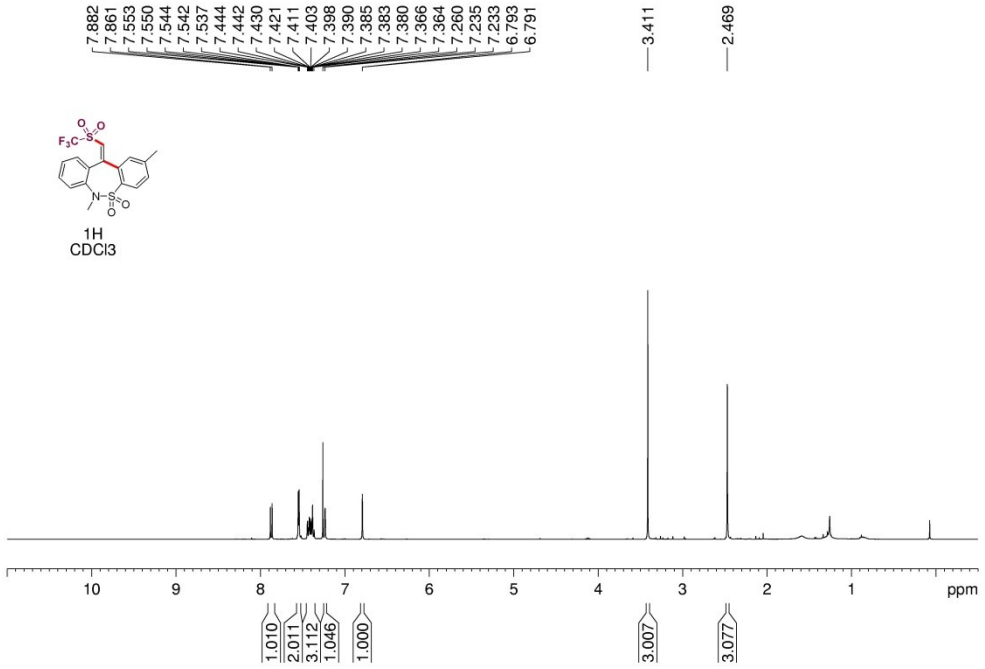

Figure S89. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4**

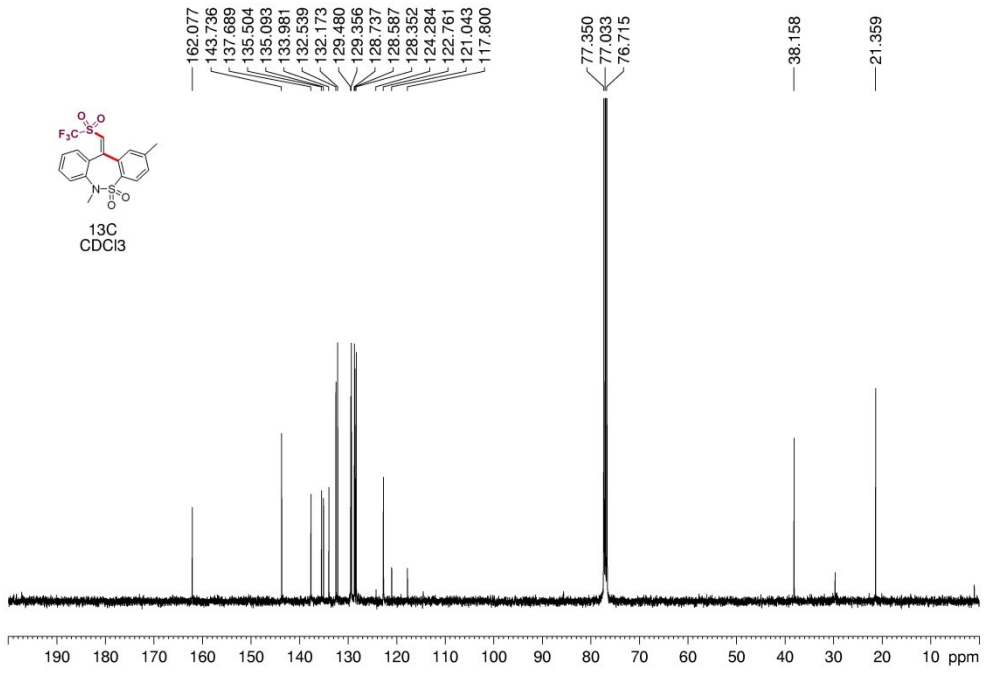

Figure S90. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4**

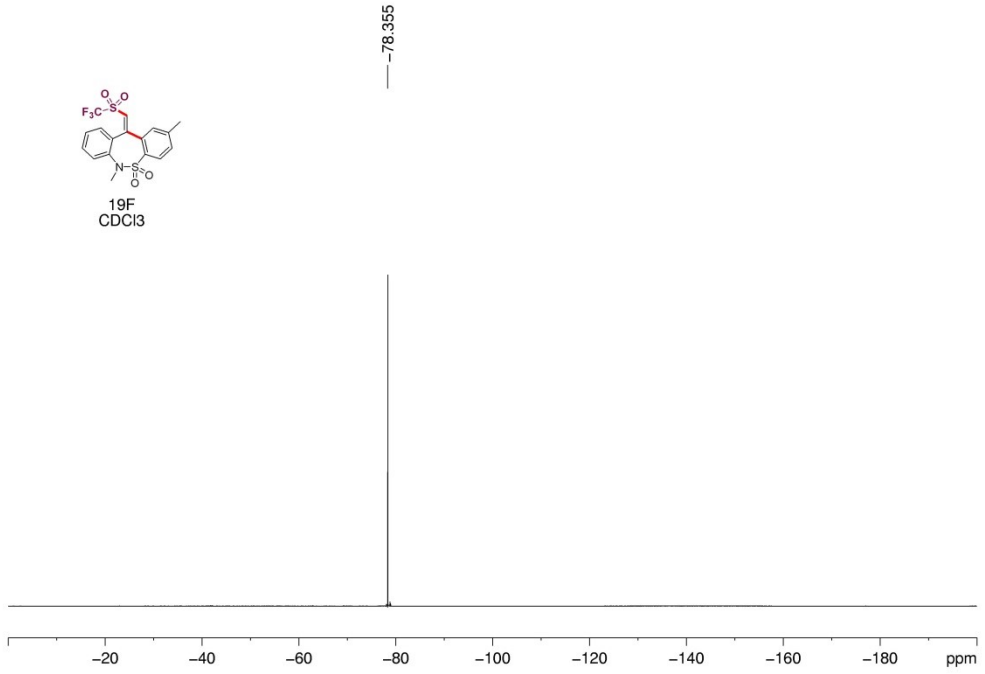

Figure S91. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **4**

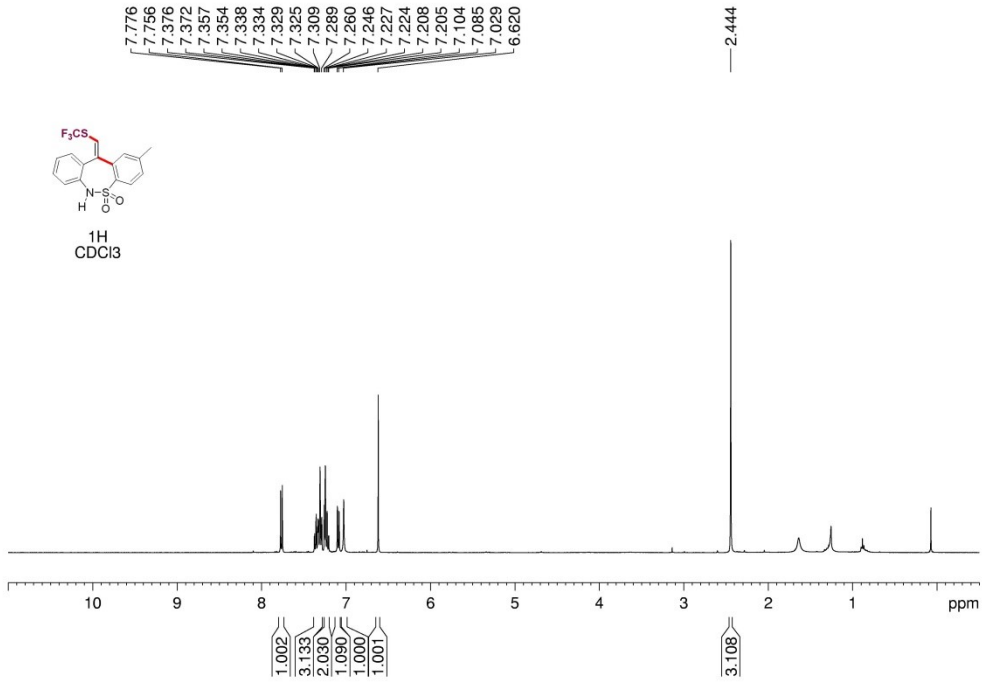

Figure S92. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3zc**

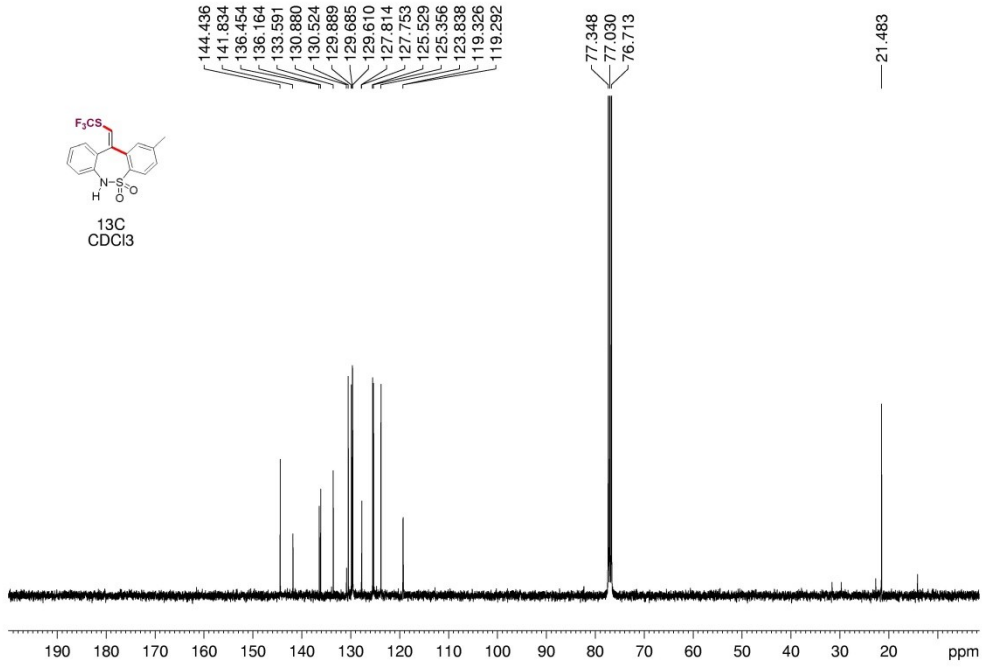

Figure S93. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3zc**

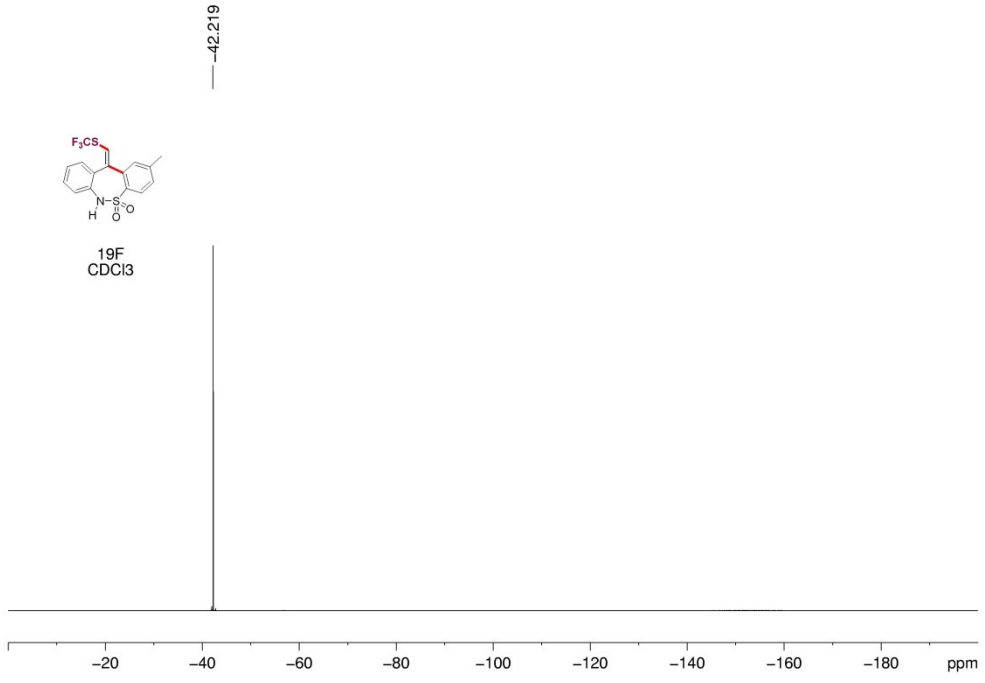

Figure S94. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3zc**