Supporting Information

Photochemical Difluoromethylation of Alkynes: Synthesis of CF_2H-Substituted Seven-Membered dioxodibenzothiazepines and dibenzazepines

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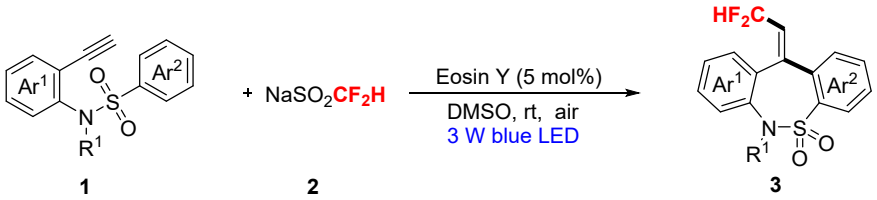
1. General Information

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 $CDCl_3$ 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 1290-6530 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). Melting points were measured with an X-4A microscopic melting point apparatus and were uncorrected. An oil bath is used as heat source for reactions that require heating. Blue LED (3 W, λ_{max} = 470 nm) was used for blue light irradiation. 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. All of alkynyl derivatives were prepared according to the method in the literature.[1]

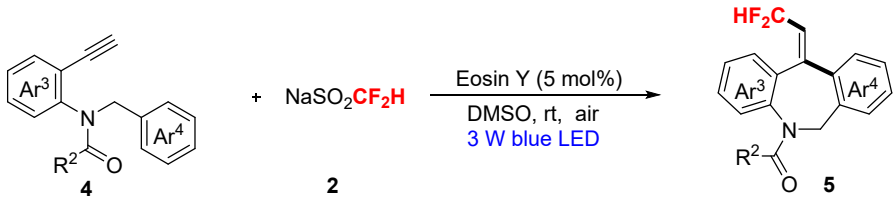
2. General procedure for the synthesis of difluoromethylated dioxodibenzothiazepines



1 2 3

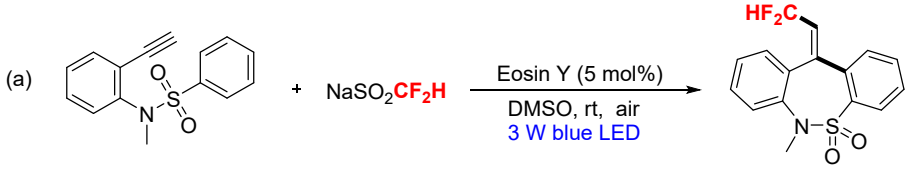
Experimental Procedure: A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with alkynes **1** (0.10 mmol, 1.0 equiv), $NaSO_2CF_2H$ **2** (0.15 mmol, 1.5 equiv), Eosin Y (3.2 mg, 0.005 mmol, 5 mol%) and DMSO (2.0 mL). The reaction mixture was then stirred and irradiation with a 3 W blue LED 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**.

3. General procedure for the synthesis of difluoromethylated dibenzazepines

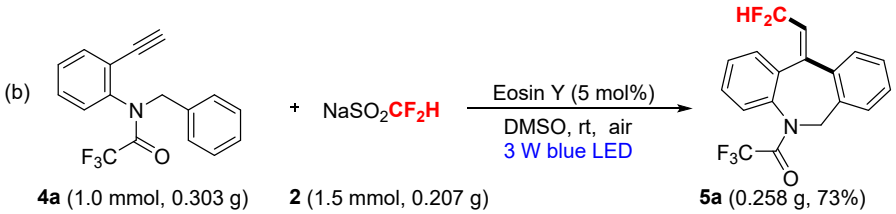


Experimental Procedure: A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with alkynes **4** (0.10 mmol, 1.0 equiv), $NaSO_2CF_2H$ **2** (0.15 mmol, 1.5 equiv), Eosin Y (3.2 mg, 0.005 mmol, 5 mol%) and DMSO (2.0 mL). The reaction mixture was then stirred and irradiation with a 3 W blue LED 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 **5**.

4. Scale-up Reaction



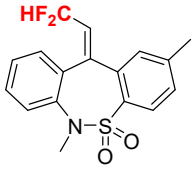
(a) A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with *N*-(2-ethynylphenyl)-*N*-methylbenzenesulfonamide **1h** (0.271 g, 1.0 mmol, 1.0 equiv), $NaSO_2CF_2H$ **2** (0.207 g, 1.5 mmol, 1.5 equiv), Eosin Y (32.4 mg, 0.05 mmol, 5 mol%) and DMSO (5.0 mL). The reaction mixture was then stirred and irradiation with a 3 W blue LED at room temperature for 24 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 = 8:1) to afford the pure product **3h** (0.215 g) in 67% yield.



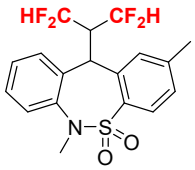
(b) A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with *N*-benzyl-*N*-(2-ethynylphenyl)-2,2,2-trifluoroacetamide **4a** (0.303 g, 1.0 mmol, 1.0 equiv), $NaSO_2CF_2H$ **2** (0.207 g, 1.5 mmol, 1.5 equiv), Eosin Y (32.4 mg, 0.05 mmol, 5 mol%) and DMSO (5.0 mL). The reaction mixture was then stirred and irradiation with a 3 W blue LED at room temperature for 24 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 = 8:1) to afford the pure product **5a** (0.258 g) in 73% yield.

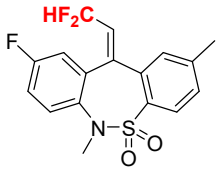
5. Characterization data of products 3



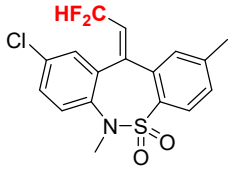
(*E*)-11-(2,2-difluoroethylidene)-2,6-dimethyl-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine (3a). White solid (24.8 mg, 74%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 161-164 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.1 Hz, 1 H), 7.54 (dd, J = 7.8 Hz, 1.2 Hz, 1 H), 7.48 (td, J = 7.5 Hz, 1.5 Hz, 1 H), 7.40 (td, J = 7.5 Hz, 1.4 Hz, 1 H), 7.33 (d, J = 8.1 Hz, 1 H), 7.28 (s, 1 H), 7.26 (dd, J = 7.5 Hz, 1.4 Hz, 1 H), 6.22 (q, H-F, $J_{H\text{-}F}$ = 7.6 Hz, 1 H), 6.00 (td, H-F, $J_{H\text{-}F}$ = 54.8 Hz, 7.6 Hz, 1 H), 3.34 (s, 3 H), 2.44 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.7 (t, C-F, $^3J_{C\text{-}F}$ = 12.8 Hz), 143.3, 137.7, 137.4, 136.3, 135.1, 131.0, 130.8, 130.3, 129.7, 129.4, 129.0, 127.9, 127.3 (t, C-F, $^2J_{C\text{-}F}$ = 27.1 Hz), 112.3 (t, C-F, $^1J_{C\text{-}F}$ = 230.3 Hz), 38.8, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -107.98 (d, F-F, $J_{F\text{-}F}$ = 323.4 Hz, 1F), -110.40 (d, F-F, $J_{F\text{-}F}$ = 319.6 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{15}F_2NNaO_2S$ 358.0684; Found 358.0698.



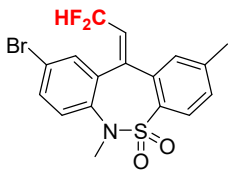
2,6-dimethyl-11-(1,1,3,3-tetrafluoropropan-2-yl)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3aa). **Melting point**: 234-236 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.90 (d, J = 8.2 Hz, 1 H), 7.65 (dd, J = 7.8 Hz, 0.8 Hz, 1 H), 7.40 (td, J = 7.6 Hz, 1.6 Hz, 1 H), 7.31 (d, J = 6.5 Hz, 1 H), 7.28 (dd, J = 6.3 Hz, 1.3 Hz, 1 H), 7.24 (dd, J = 7.5 Hz, 1.2 Hz, 1 H), 7.16 (s, 1 H), 6.00 (t, H-F, $J_{H\text{-}F}$ = 54.2 Hz, 1 H), 5.77 (t, H-F, $J_{H\text{-}F}$ = 53.8 Hz, 1 H), 4.33 (d, J = 11.5 Hz, 1 H), 3.88-3.68 (m, 1 H), 3.45 (s, 3 H), 2.39 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.3, 138.8, 137.9, 137.1, 135.7, 131.8, 130.7, 130.0, 129.8, 129.0, 128.4, 126.7, 114.7 (td, C-F, $^1J_{C\text{-}F}$ = 242.3 Hz, 8.7 Hz), 114.1 (tt, C-F, $^1J_{C\text{-}F}$ = 241.9 Hz, 5.1 Hz), 48.2 (m, C-F), 47.4 (t, C-F, $^3J_{C\text{-}F}$ = 6.5 Hz), 35.1, 21.3; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -119.91 (ddd, F-F, $J_{F\text{-}F}$ = 293.7 Hz, 6,1 Hz, 2.6 Hz, 1F), -122.30 (ddd, F-F, $J_{F\text{-}F}$ = 288.4 Hz, 5,1 Hz, 2.3 Hz, 1F), -122.74 (ddd, F-F, $J_{F\text{-}F}$ = 293.8 Hz, 11,2 Hz, 2.3 Hz, 1F), -125.51 (ddd, F-F, $J_{F\text{-}F}$ = 288.5 Hz, 12,1 Hz, 2.1 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{18}F_4NO_2S$ 388.0989; Found 388.0992.



(*E*)-11-(2,2-difluoroethylidene)-9-fluoro-2,6-dimethyl-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3b). White solid (25.1 mg, 71%). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). **Melting point**: 149-151 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.1 Hz, 1 H), 7.54 (dd, J = 8.7 Hz, 5.1 Hz, 1 H), 7.35 (dd, J = 8.1 Hz, 1.0 Hz, 1 H), 7.25 (s, 1 H), 7.16 (td, J = 8.6 Hz, 2.9 Hz, 1 H), 6.98 (dd, J = 8.0 Hz, 2.9 Hz, 1 H), 6.25 (q, H-F, $J_{H\text{-}F}$ = 7.6 Hz, 1 H), 6.05 (td, H-F_2, $J_{H\text{-}F}$ = 54.6 Hz, 7.4 Hz, 1 H), 3.32 (s, 3 H), 2.44 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.0 (d, C-F, $^1J_{C\text{-}F}$ = 250.3 Hz), 146.4 (t, C-F, $^3J_{C\text{-}F}$ = 12.6 Hz), 143.4, 138.6 (d, C-F, $^3J_{C\text{-}F}$ = 9.0 Hz), 137.4, 134.5, 133.6, 132.6 (d, C-F, $^3J_{C\text{-}F}$ = 9.2 Hz), 131.2, 129.5, 128.1, 127.8 (t, C-F, $^2J_{C\text{-}F}$ = 27.1 Hz), 117.9 (d, C-F, $^2J_{C\text{-}F}$ = 22.3 Hz), 116.5 (d, C-F, $^2J_{C\text{-}F}$ = 23.9 Hz), 111.9 (t, C-F, $^1J_{C\text{-}F}$ = 231.0 Hz), 38.8, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -108.12 (d, F-F, $J_{F\text{-}F}$ = 323.4 Hz, 1F), -110.22 (s), -110.71 (d, F-F, $J_{F\text{-}F}$ = 323.4 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{15}F_3NO_2S$ 354.0770; Found 354.0769.

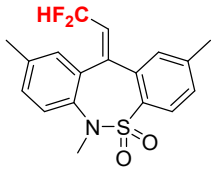


(*E*)-9-chloro-11-(2,2-difluoroethylidene)-2,6-dimethyl-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3c). White solid (25.5 mg, 69%). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). **Melting point**: 144-146 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.1 Hz, 1 H), 7.48 (d, J = 8.4 Hz, 1 H), 7.45 (dd, J = 8.5 Hz, 2.2 Hz, 1 H), 7.35 (dd, J = 8.1 Hz, 1.0 Hz, 1 H), 7.26 (d, J = 2.3 Hz, 2 H), 6.24 (q, H-F, $J_{H\text{-}F}$ = 7.8 Hz, 1 H), 6.05 (td, H-F, $J_{H\text{-}F}$ = 54.7 Hz, 7.5 Hz, 1 H), 3.32 (s, 3 H), 2.44 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.4 (t, C-F, $^3J_{C\text{-}F}$ = 12.5 Hz), 143.5, 137.8, 137.2, 136.3, 134.9, 134.5, 131.6, 131.1, 131.0, 129.5, 129.4, 128.0, 127.9 (t, C-F, $^2J_{C\text{-}F}$ = 27.2 Hz), 111.9 (t, C-F, $^1J_{C\text{-}F}$ = 230.8 Hz), 38.8, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -108.17 (d, F-F, $J_{F\text{-}F}$ = 323.4 Hz, 1F), -110.42 (d, F-F, $J_{F\text{-}F}$ = 319.6 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{14}ClF_2NNaO_2S$ 392.0294; Found 392.0289.

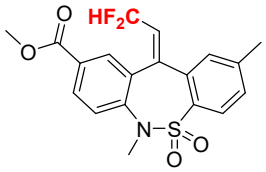


(*E*)-9-bromo-11-(2,2-difluoroethylidene)-2,6-dimethyl-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3d). White solid (29.0 mg, 70%). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). **Melting point**:

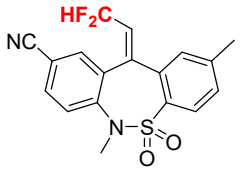
159-160 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.1 Hz, 1 H), 7.60 (dd, J = 8.4 Hz, 2.3 Hz, 1 H), 7.42 (d, J = 2.2 Hz, 1 H), 7.40 (d, J = 8.4 Hz, 1 H), 7.35 (dd, J = 8.1 Hz, 0.8 Hz, 1 H), 7.25 (s, 1 H), 6.24 (q, H-F, $J_{H\text{-}F}$ = 7.8 Hz, 1 H), 6.05 (td, H-F, $J_{H\text{-}F}$ = 54.8 Hz, 7.5 Hz, 1 H), 3.31 (s, 3 H), 2.44 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.2 (t, C-F, $^3J_{C\text{-}F}$ = 12.5 Hz), 143.5, 138.0, 137.2, 136.9, 134.6, 134.1, 132.3, 131.8, 131.1, 129.4, 128.0, 127.9 (t, C-F, $^2J_{C\text{-}F}$ = 27.3 Hz), 122.8, 111.9 (t, C-F, $^1J_{C\text{-}F}$ = 230.9 Hz), 38.7, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -108.19 (d, F-F, $J_{F\text{-}F}$ = 327.1 Hz, 1F), -110.35 (d, F-F, $J_{F\text{-}F}$ = 323.4 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{14}BrF_2NNaO_2S$ 435.9789; Found 435.9799.



(*E*)-11-(2,2-difluoroethylidene)-2,6,9-trimethyl-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3e). White solid (21.3 mg, 61%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 132-134 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.1 Hz, 1 H), 7.42 (d, J = 8.0 Hz, 1 H), 7.32 (d, J = 8.1 Hz, 1 H), 7.27 (dd, J = 7.3 Hz, 1.4 Hz, 2 H), 7.04 (s, 1 H), 6.21 (q, H-F, $J_{H\text{-}F}$ = 7.7 Hz, 1 H), 6.03 (td, H-F, $J_{H\text{-}F}$ = 55.0 Hz, 7.6 Hz, 1 H), 3.32 (s, 3 H), 2.43 (s, 3 H), 2.37 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.9 (t, C-F, $^3J_{C\text{-}F}$ = 12.5 Hz), 143.1, 139.5, 137.5, 136.4, 135.2, 134.9, 131.6, 130.8, 130.1, 130.0, 129.3, 128.1, 127.0 (t, C-F, $^2J_{C\text{-}F}$ = 27.0 Hz), 112.4 (t, C-F, $^1J_{C\text{-}F}$ = 230.1 Hz), 38.8, 21.4, 21.2; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -108.08 (d, F-F, $J_{F\text{-}F}$ = 319.6 Hz, 1F), -110.44 (d, F-F, $J_{F\text{-}F}$ = 323.4 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{17}F_2NNaO_2S$ 372.0840; Found 372.0844.

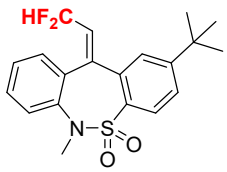


methyl (*E*)-11-(2,2-difluoroethylidene)-2,6-dimethyl-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine-9-carboxylate 5,5-dioxide (3f). White solid (20.1 mg, 51%). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). **Melting point**: 200-202 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.13 (dd, J = 8.3 Hz, 2.0 Hz, 1 H), 7.97 (d, J = 2.0 Hz, 1 H), 7.81 (d, J = 8.1 Hz, 1 H), 7.55 (d, J = 8.3 Hz, 1 H), 7.35 (d, J = 8.1 Hz, 1 H), 7.30 (s, 1 H), 6.21 (q, H-F, $J_{H\text{-}F}$ = 7.8 Hz, 1 H), 6.03 (td, H-F, $J_{H\text{-}F}$ = 54.8 Hz, 7.4 Hz, 1 H), 3.94 (s, 3 H), 3.35 (s, 3 H), 2.45 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.5, 146.7 (t, C-F, $^3J_{C\text{-}F}$ = 12.8 Hz), 143.8, 142.4, 136.6, 134.9, 134.6, 132.1, 131.2, 130.7, 130.0, 129.4, 129.2, 127.9 (t, C-F, $^2J_{C\text{-}F}$ = 27.1 Hz), 127.5, 112.0 (t, C-F, $^1J_{C\text{-}F}$ = 230.9 Hz), 62.6, 38.8, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -108.21 (d, F-F, $J_{F\text{-}F}$ = 315.8 Hz, 1F), -109.86 (d, F-F, $J_{F\text{-}F}$ = 319.6 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{17}F_2NNaO_4S$ 416.0739; Found 416.0750.



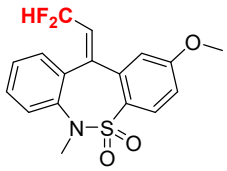
(*E*)-11-(2,2-difluoroethylidene)-2,6-dimethyl-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine-9-carbonitrile 5,5-dioxide (3g). White solid (15.1 mg, 42%). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). **Melting point**: 210-212 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.1 Hz, 1 H), 7.76 (dd, J = 8.3 Hz, 1.9 Hz, 1 H), 7.60 (d, J = 1.8 Hz, 1 H), 7.56 (d, J = 8.3 Hz, 1 H), 7.37 (dd, J = 8.0 Hz, 0.9 Hz, 1 H), 7.29 (s, 1 H), 6.21 (q, H-F, $J_{H\text{-}F}$ = 8.0 Hz, 1 H), 6.02 (td, H-F, $J_{H\text{-}F}$ = 54.6 Hz, 7.3 Hz, 1 H), 3.34 (s, 3 H), 2.46 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.9 (t, C-F, $^3J_{C\text{-}F}$ = 12.5 Hz), 144.4, 142.9, 136.1, 134.8, 134.4, 134.3, 133.7, 130.9, 129.4, 128.6 (t, C-F, $^2J_{C\text{-}F}$ = 27.6 Hz), 127.3, 117.2, 111.9, 111.6 (t, C-F, $^1J_{C\text{-}F}$ = 231.6 Hz), 38.8, 21.5; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -107.14 (d, F-F, $J_{F\text{-}F}$ = 323.4 Hz, 1F), -110.12 (d, F-F, $J_{F\text{-}F}$ = 319.6 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{14}F_2N_2NaO_2S$ 383.0636; Found 383.0639.

(*E*)-11-(2,2-difluoroethylidene)-6-methyl-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3h). White solid (24.4 mg, 76%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 172-174 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 (dd, J = 7.2 Hz, 1.9 Hz, 1 H), 7.57-7.47 (m, 5 H), 7.41 (td, J = 7.5 Hz, 1.4 Hz, 1 H), 7.28 (dd, J = 7.5 Hz, 1.4 Hz, 1 H), 6.23 (q, H-F, $J_{H\text{-}F}$ = 7.6 Hz, 1 H), 6.01 (td, H-F, $J_{H\text{-}F}$ = 54.8 Hz, 7.5 Hz, 1 H), 3.35 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.6 (t, C-F, $^3J_{C\text{-}F}$ = 12.5 Hz), 140.3, 137.6, 136.3, 135.2, 132.5, 131.1, 130.2, 130.1, 129.7, 129.1, 129.0, 127.9, 127.6 (t, C-F, $^2J_{C\text{-}F}$ = 27.1 Hz), 112.3 (t, C-F, $^1J_{C\text{-}F}$ = 230.3 Hz), 38.9; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -108.13 (d, F-F, $J_{F\text{-}F}$ = 323.4 Hz, 1F), -110.42 (d, F-F, $J_{F\text{-}F}$ = 319.6 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{14}F_2NO_2S$ 322.0708; Found 322.0720.

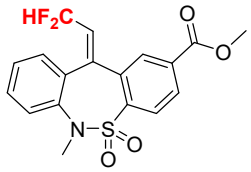


(*E*)-2-(tert-butyl)-11-(2,2-difluoroethylidene)-6-methyl-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3i). White solid (27.6 mg, 73%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 194-196 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.86 (d, J = 8.4 Hz, 1 H), 7.57-7.54 (m, 2 H), 7.48 (td, J = 7.5 Hz, 1.6 Hz, 1 H), 7.43-7.39 (m, 2 H), 7.29 (dd, J = 7.5 Hz, 1.4 Hz, 1 H), 6.22 (q, H-F, $J_{H\text{-}F}$ = 7.6 Hz, 1 H), 6.01 (td, H-F, $J_{H\text{-}F}$ = 54.8 Hz, 7.6 Hz, 1 H),

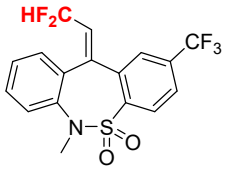
3.34 (s, 3 H), 1.36 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 156.4, 148.3 (t, C-F, $^3J_{C\text{-}F}$ = 12.6 Hz), 137.7, 137.3, 136.5, 135.0, 131.0, 130.3, 129.8, 129.0, 127.8, 127.5, 127.2 (t, C-F, $^2J_{C\text{-}F}$ = 27.0 Hz), 125.7, 112.4 (t, C-F, $^1J_{C\text{-}F}$ = 230.0 Hz), 38.8, 35.2, 31.0; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -107.91 (d, F-F, $J_{F\text{-}F}$ = 319.6 Hz, 1F), -110.34 (d, F-F, $J_{F\text{-}F}$ = 323.4 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{21}F_2NNaO_2S$ 400.1153; Found 400.1150.



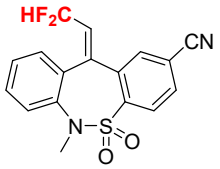
(*E*)-11-(2,2-difluoroethylidene)-2-methoxy-6-methyl-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3j). White solid (26.0 mg, 74%). Column chromatography on silica gel (Petroleum ether/EtOAc = 3:1). **Melting point**: 139-141 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.8 Hz, 1 H), 7.53 (dd, *J* = 7.8 Hz, 1.2 Hz, 1 H), 7.48 (td, *J* = 7.3 Hz, 1.5 Hz, 1 H), 7.39 (td, *J* = 7.5 Hz, 1.5 Hz, 1 H), 7.27 (dd, *J* = 7.6 Hz, 1.2 Hz, 1 H), 7.02 (dd, *J* = 8.8 Hz, 2.6 Hz, 1 H), 6.93 (d, *J* = 2.6 Hz, 1 H), 6.22 (q, H-F, $J_{H\text{-}F}$ = 7.6 Hz, 1 H), 6.01 (td, H-F, $J_{H\text{-}F}$ = 54.8 Hz, 7.6 Hz, 1 H), 3.89 (s, 3 H), 3.32 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.3, 147.7 (t, C-F, $^3J_{C\text{-}F}$ = 12.6 Hz), 137.9, 137.2, 135.8, 132.1, 131.1, 130.1, 129.9, 129.8, 128.9, 127.4 (t, C-F, $^2J_{C\text{-}F}$ = 27.3 Hz), 115.1, 114.1, 112.3 (t, C-F, $^1J_{C\text{-}F}$ = 230.4 Hz), 55.8, 38.9; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -108.08 (d, F-F, $J_{F\text{-}F}$ = 327.1 Hz, 1F), -110.43 (d, F-F, $J_{F\text{-}F}$ = 330.9 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{16}F_2NO_3S$ 352.0813; Found 352.0817.



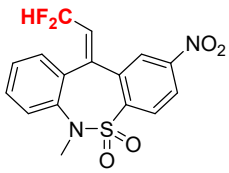
methyl(*E*)-11-(2,2-difluoroethylidene)-6-methyl-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine-2-carboxylate 5,5-dioxide (3k). White solid (24.7 mg, 65%). Column chromatography on silica gel (Petroleum ether/EtOAc = 3:1). **Melting point**: 178-180 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.15 (dd, *J* = 5.8 Hz, 1.6 Hz, 1 H), 8.01 (d, *J* = 8.7 Hz, 1 H), 7.56 (dd, *J* = 7.8 Hz, 1.3 Hz, 1 H), 7.51 (td, *J* = 7.3 Hz, 1.5 Hz, 1 H), 7.43 (td, *J* = 7.5 Hz, 1.5 Hz, 1 H), 7.30 (dd, *J* = 7.5 Hz, 1.2 Hz, 1 H), 6.31 (q, H-F, $J_{H\text{-}F}$ = 7.5 Hz, 1 H), 6.02 (td, H-F, $J_{H\text{-}F}$ = 54.8 Hz, 7.6 Hz, 1 H), 3.99 (s, 3 H), 3.36 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.2, 146.6 (t, C-F, $^3J_{C\text{-}F}$ = 12.5 Hz), 144.0, 137.3, 135.9, 135.5, 133.7, 131.3, 130.8, 130.3, 130.2, 129.8, 129.4, 128.5 (t, C-F, $^2J_{C\text{-}F}$ = 27.4 Hz), 128.4, 112.1 (t, C-F, $^1J_{C\text{-}F}$ = 230.8 Hz), 52.8, 38.9; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -108.50 (d, F-F, $J_{F\text{-}F}$ = 319.6 Hz, 1F), -110.50 (d, F-F, $J_{F\text{-}F}$ = 327.1 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{16}F_2NO_4S$ 380.0763; Found 380.0781.



(*E*)-11-(2,2-difluoroethylidene)-6-methyl-2-(trifluoromethyl)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3l). White solid (21.4 mg, 55%). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). **Melting point**: 195-196 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.2 Hz, 1 H), 7.79 (d, J = 8.3 Hz, 1 H), 7.75 (s, 1 H), 7.58-7.51 (m, 2 H), 7.45 (td, J = 7.5 Hz, 1.8 Hz, 1 H), 7.32 (dd, J = 7.4 Hz, 1.2 Hz, 1 H), 6.30 (q, H-F, $J_{H\text{-}F}$ = 7.4 Hz, 1 H), 6.02 (td, H-F, $J_{H\text{-}F}$ = 54.7 Hz, 7.4 Hz, 1 H), 3.37 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.4 (t, C-F, $^3J_{C\text{-}F}$ = 12.6 Hz), 143.7, 137.2, 135.9, 135.5, 134.4 (q, C-F, $^2J_{C\text{-}F}$ = 33.1 Hz), 131.5, 130.2, 129.9, 129.4, 128.9, 128.8 (t, C-F, $^2J_{C\text{-}F}$ = 27.4 Hz), 126.8 (q, C-F, $^3J_{C\text{-}F}$ = 3.6 Hz), 126.1 (q, C-F, $^3J_{C\text{-}F}$ = 3.6 Hz), 122.9 (q, C-F, $^1J_{C\text{-}F}$ = 271.6 Hz), 111.9 (t, C-F, $^1J_{C\text{-}F}$ = 231.1 Hz), 38.9; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -63.11 (s), -108.59 (d, F-F, $J_{F\text{-}F}$ = 327.1 Hz, 1F), -110.60 (d, F-F, $J_{F\text{-}F}$ = 319.6 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: [M + Na]$^+$ Calcd for $C_{17}H_{12}F_5NNaO_2S$ 412.0401; Found 412.0406.

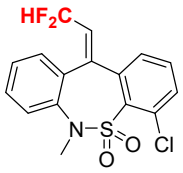


(*E*)-11-(2,2-difluoroethylidene)-6-methyl-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine-2-carbonitrile 5,5-dioxide (3m). White solid (15.9 mg, 46%). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). **Melting point**: 218-221 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.6 Hz, 1 H), 7.82-7.79 (m, 2 H), 7.58-7.52 (m, 2 H), 7.46 (m, 1 H), 7.30 (like d, J = 7.0 Hz, 1 H), 6.29 (q, H-F, $J_{H\text{-}F}$ = 7.4 Hz, 1 H), 6.01 (td, H-F, $J_{H\text{-}F}$ = 54.6 Hz, 7.4 Hz, 1 H), 3.36 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.6 (t, C-F, $^3J_{C\text{-}F}$ = 12.5 Hz), 144.4, 137.0, 136.3, 135.2, 133.1, 132.6, 131.7, 130.2, 129.9, 129.6 (t, C-F, $^2J_{C\text{-}F}$ = 26.7 Hz), 129.5, 129.0, 116.7, 116.4, 111.7 (t, C-F, $^1J_{C\text{-}F}$ = 231.7 Hz), 39.0; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -108.73 (d, F-F, $J_{F\text{-}F}$ = 327.1 Hz, 1F), -110.68 (d, F-F, $J_{F\text{-}F}$ = 327.1 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: [M + H]$^+$ Calcd for $C_{17}H_{13}F_2N_2O_2S$ 347.0660; Found 347.0664.

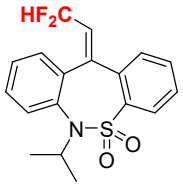


(*E*)-11-(2,2-difluoroethylidene)-6-methyl-2-nitro-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3n). White solid (12.8 mg, 35%). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). **Melting point**: 207-209 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.37-8.33 (m, 2 H), 8.13 (d, J = 8.5 Hz, 1

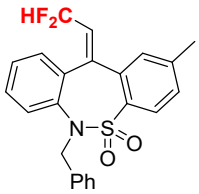
H), 7.59-7.55 (m, 2 H), 7.47 (td, J = 6.7 Hz, 2.4 Hz, 1 H), 7.33 (dd, J = 7.0 Hz, 1.1 Hz, 1 H), 6.37 (q, H-F, $J_{H\text{-}F}$ = 7.4 Hz, 1 H), 6.03 (td, H-F, $J_{H\text{-}F}$ = 54.6 Hz, 7.3 Hz, 1 H), 3.38 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.5, 145.9, 145.6 (t, C-F, $^3J_{C\text{-}F}$ = 12.6 Hz), 137.0, 136.8, 135.1, 131.8, 130.3, 129.9, 129.8, 129.7, 129.6 (t, C-F, $^2J_{C\text{-}F}$ = 27.8 Hz), 124.5, 124.1, 111.7 (t, C-F, $^1J_{C\text{-}F}$ = 231.6 Hz), 39.0; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -108.83 (d, F-F, $J_{F\text{-}F}$ = 330.9 Hz, 1F), -110.64 (d, F-F, $J_{F\text{-}F}$ = 323.4 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{13}F_2N_2O_4S$ 367.0559; Found 367.0550.



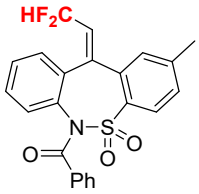
(*E*)-4-chloro-11-(2,2-difluoroethylidene)-6-methyl-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3o). White solid (12.8 mg, 36%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 182-184 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 (dd, J = 7.9 Hz, 1.1 Hz, 1 H), 7.56 (dd, J = 7.9 Hz, 1.4 Hz, 1 H), 7.51 (td, J = 7.6 Hz, 1.5 Hz, 1 H), 7.46-7.41 (m, 2 H), 7.38 (dd, J = 7.8 Hz, 1.4 Hz, 1 H), 7.24 (dd, J = 7.6 Hz, 1.3 Hz, 1 H), 6.29 (q, H-F, $J_{H\text{-}F}$ = 7.5 Hz, 1 H), 6.00 (td, H-F, $J_{H\text{-}F}$ = 54.8 Hz, 7.5 Hz, 1 H), 3.38 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.6 (t, C-F, $^3J_{C\text{-}F}$ = 12.5 Hz), 138.8, 138.1, 137.4, 136.6, 134.6, 133.4, 132.3, 131.3, 130.7, 129.8, 128.8, 128.3, 127.5 (t, C-F, $^2J_{C\text{-}F}$ = 27.3 Hz), 112.1 (t, C-F, $^1J_{C\text{-}F}$ = 230.9 Hz), 39.0; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -108.76 (d, F-F, $J_{F\text{-}F}$ = 327.1 Hz, 1F), -110.71 (d, F-F, $J_{F\text{-}F}$ = 323.4 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{12}ClF_2NNaO_2S$ 378.0138; Found 378.0138.



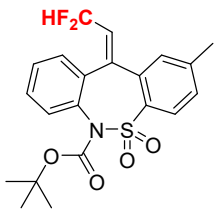
(*E*)-11-(2,2-difluoroethylidene)-6-isopropyl-2-methyl-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3p). White solid (28.7 mg, 82%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 124-126 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84 (d, J = 8.1 Hz, 1 H), 7.55 (dd, J = 7.8 Hz, 1.0 Hz, 1 H), 7.49 (td, J = 7.8 Hz, 1.5 Hz, 1 H), 7.42 (td, J = 7.5 Hz, 1.3 Hz, 1 H), 7.32 (d, J = 8.0 Hz, 1 H), 7.28-7.26 (m, 2 H), 6.22 (q, H-F, $J_{H\text{-}F}$ = 7.6 Hz, 1 H), 6.02 (td, H-F, $J_{H\text{-}F}$ = 54.9 Hz, 7.7 Hz, 1 H), 4.66-4.56 (m, 1 H), 2.43 (s, 3 H), 1.47 (like s, 3 H), 1.07 (like s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.3 (t, C-F, $^3J_{C\text{-}F}$ = 12.6 Hz), 142.8, 138.9, 138.5, 135.1, 133.5, 132.3, 130.9, 130.5, 129.9, 129.7, 129.2, 127.4, 126.4 (t, C-F, $^2J_{C\text{-}F}$ = 27.0 Hz), 112.7 (t, C-F, $^1J_{C\text{-}F}$ = 229.7 Hz), 53.7, 21.3; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -106.19 (d, F-F, $J_{F\text{-}F}$ = 323.4 Hz, 1F), -112.43 (d, F-F, $J_{F\text{-}F}$ = 323.4 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{20}F_2NO_2S$ 364.1177; Found 364.1182.



(*E*)-6-benzyl-11-(2,2-difluoroethylidene)-2-methyl-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3q). Yellow oil (14.8 mg, 36%). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.1 Hz, 1 H), 7.37-7.28 (m, 9 H), 7.23 (dd, *J* = 7.4 Hz, 1.7 Hz, 1 H), 7.09 (dd, *J* = 7.7 Hz, 1.1 Hz, 1 H), 6.29 (q, H-F, $J_{H\text{-}F}$ = 7.4 Hz, 1 H), 5.92 (td, H-F, $J_{H\text{-}F}$ = 55.0 Hz, 7.5 Hz, 1 H), 5.17 (s, 1 H), 4.45 (s, 1 H), 2.46 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.7 (t, C-F, $^{3}J_{C\text{-}F}$ = 12.7 Hz), 143.2, 137.9, 137.3, 135.9, 135.2, 135.1, 131.8, 131.0, 130.4, 129.5, 129.2, 128.9, 128.6, 128.1, 128.0, 127.1 (t, C-F, $^{2}J_{C\text{-}F}$ = 26.8 Hz), 112.4 (t, C-F, $^{1}J_{C\text{-}F}$ = 230.2 Hz), 55.1, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -107.62 (d, F-F, $J_{F\text{-}F}$ = 323.4 Hz, 1F), -110.20 (d, F-F, $J_{F\text{-}F}$ = 319.6 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{20}F_2NO_2S$ 412.1177; Found 412.1185.



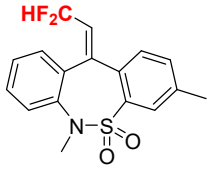
(*E*)-(11-(2,2-difluoroethylidene)-2-methyl-5,5-dioxidodibenzo[*c*,*f*][1,2]thiazepin-6(11*H*)-yl)(phenyl)methanone (3r). White solid (16.2 mg, 38%). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). **Melting point**: 97-99 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 8.3 Hz, 1 H), 7.59 (s, 1 H), 7.54-7.44 (m, 2 H), 7.37-7.31 (m, 4 H), 7.27-7.12 (m, 4 H), 6.41 (q, H-F, $J_{H\text{-}F}$ = 7.5 Hz, 1 H), 6.00 (td, H-F, $J_{H\text{-}F}$ = 55.3 Hz, 7.5 Hz, 1 H), 2.33 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.3, 146.7 (t, C-F, $^{3}J_{C\text{-}F}$ = 12.5 Hz), 139.2, 137.4, 135.8, 134.6, 131.8, 130.9, 130.7, 130.2, 129.2, 128.6, 127.7, 126.8, 124.4, 122.6 (t, C-F, $^{2}J_{C\text{-}F}$ = 26.9 Hz), 121.9, 113.3 (t, C-F, $^{1}J_{C\text{-}F}$ = 229.2 Hz), 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -107.53 (d, F-F, $J_{F\text{-}F}$ = 319.6 Hz, 1F), -108.81 (d, F-F, $J_{F\text{-}F}$ = 319.6 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + K]^+$ Calcd for $C_{23}H_{17}F_2KNO_3S$ 464.0529; Found 464.0541.



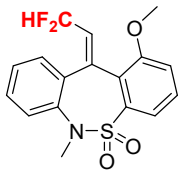
***tert*-butyl (*E*)-11-(2,2-difluoroethylidene)-2-methyldibenzo[*c*,*f*][1,2]thiazepine-6(11*H*)-carboxylate 5,5-dioxide (3s)**. White solid (26.1 mg, 62%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 172-174 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.6 Hz, 1 H), 7.57 (dd, *J* = 7.8 Hz, 1.2 Hz, 1 H), 7.52 (td, *J* = 7.5 Hz, 1.4 Hz, 1 H), 7.45 (td, *J* = 7.5 Hz, 1.5 Hz, 1 H), 7.38-

7.36 (m, 2 H), 7.30 (d, J = 7.4 Hz, 1 H), 6.22 (q, H-F, $J_{H\text{-}F}$ = 7.4 Hz, 1 H), 5.75 (td, H-F, $J_{H\text{-}F}$ = 55.0 Hz, 7.3 Hz, 1 H), 2.47 (s, 3 H), 1.37 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.1, 146.3 (t, C-F, $^3J_{C\text{-}F}$ = 12.5 Hz), 144.1, 136.9, 136.1, 134.7, 134.3, 131.1, 131.0, 130.8, 130.3, 129.8, 129.5, 129.4 (t, C-F, $^2J_{C\text{-}F}$ = 27.4 Hz), 127.4, 112.3 (t, C-F, $^1J_{C\text{-}F}$ = 230.5 Hz), 85.6, 27.7, 21.5; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -104.02 (d, F-F, $J_{F\text{-}F}$ = 319.6 Hz, 1F), -113.52 (d, F-F, $J_{F\text{-}F}$ = 315.8 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{21}F_2NO_4SNa$ 444.1052; Found 444.1051.

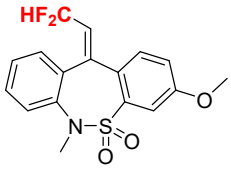
(*E*)-11-(2,2-difluoroethylidene)-1,6-dimethyl-6,11-dihydrodibenzo[*c*,f][1,2]thiazepine 5,5-dioxide (3t). White solid (12.8 mg, 38%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 172-174 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77 (d, J = 7.7 Hz, 1 H), 7.50 (d, J = 7.7 Hz, 1 H), 7.45 (td, J = 7.7 Hz, 1.6 Hz, 1 H), 7.42-7.36 (m, 2 H), 7.32-7.27 (m, 2 H), 6.11 (td, H-F, $J_{H\text{-}F}$ = 54.5 Hz, 7.6 Hz, 1 H), 5.88-5.83 (m, 1 H), 3.19 (s, 3 H), 2.47 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.2 (t, C-F, $^3J_{C\text{-}F}$ = 12.3 Hz), 140.8, 137.9, 136.0, 135.6, 134.2, 130.9, 130.8, 128.5, 128.2, 128.0 (dd, C-F, $^2J_{C\text{-}F}$ = 31.3 Hz, 22.6 Hz), 126.1, 125.9, 124.4, 112.6 (t, C-F, $^1J_{C\text{-}F}$ = 229.6 Hz), 40.2, 20.2; **^{19}F NMR** (376 MHz $CDCl_3$,): δ -106.82 (d, F-F, $J_{F\text{-}F}$ = 320.0 Hz, 1F), -110.24 (d, F-F, $J_{F\text{-}F}$ = 320.5 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{16}F_2NO_2S$ 336.0864; Found 336.0862.



(*E*)-11-(2,2-difluoroethylidene)-3,6-dimethyl-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3t′). White solid (12.1 mg, 36%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 160-162 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (s, 1 H), 7.55 (dd, J = 7.8 Hz, 1.2 Hz, 1 H), 7.48 (td, J = 7.8 Hz, 1.5 Hz, 1 H), 7.42-7.36 (m, 3 H), 7.26 (dd, J = 7.5 Hz, 1.4 Hz, 1 H), 6.20 (q, H-F, $J_{H\text{-}F}$ = 7.6 Hz, 1 H), 6.00 (td, H-F, $J_{H\text{-}F}$ = 54.8 Hz, 7.6 Hz, 1 H), 3.35 (s, 3 H), 2.41 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.5 (t, C-F, $^3J_{C\text{-}F}$ = 12.6 Hz), 140.9, 139.9, 137.5, 136.7, 133.3, 132.4, 130.9, 130.4, 129.7, 129.1, 128.9, 128.2, 127.0 (t, C-F, $^2J_{C\text{-}F}$ = 27.1 Hz), 112.4 (t, C-F, $^1J_{C\text{-}F}$ = 230.2 Hz), 38.8, 21.0; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -107.98 (d, F-F, $J_{F\text{-}F}$ = 321.1 Hz, 1F), -110.41 (d, F-F, $J_{F\text{-}F}$ = 321.4 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{16}F_2NO_2S$ 336.0864; Found 336.0867.

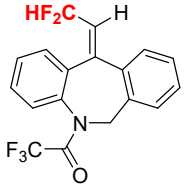


(*E*)-11-(2,2-difluoroethylidene)-1-methoxy-6-methyl-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3u). White solid (14.8 mg, 42%). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). **Melting point**: 174-176 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53 (dd, *J* = 7.9 Hz, 0.9 Hz, 1 H), 7.47-7.45 (m, 1 H), 7.43-7.40 (m, 2 H), 7.39 (dd, *J* = 7.8 Hz, 1.2 Hz, 1 H), 7.33 (td, *J* = 7.8 Hz, 1.5 Hz, 1 H), 7.14 (d, *J* = 8.2 Hz, 1 H), 6.20-6.12 (m, 1 H), 6.05 (td, H-F, $J_{H\text{-}F}$ = 54.8 Hz, 7.6 Hz, 1 H), 3.88 (s, 3 H), 3.28 (s, 3 H); **^{13}C NMR** (100 MHz $CDCl_3$,): δ 155.5, 140.5, 139.6 (t, C-F, $^3J_{C\text{-}F}$ = 13.0 Hz), 139.1, 133.4, 130.7, 130.6, 129.8, 129.3 (dd, C-F, $^2J_{C\text{-}F}$ = 29.0 Hz, 24.4 Hz), 128.1, 127.5, 123.8, 119.1, 115.4, 112.7 (t, C-F, $^1J_{C\text{-}F}$ = 229.7 Hz), 56.5, 39.6; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -108.37 (d, F-F, $J_{F\text{-}F}$ = 320.5 Hz, 1F), -110.31 (d, F-F, $J_{F\text{-}F}$ = 321.0 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: [M + Na]$^+$ Calcd for $C_{17}H_{15}F_2NNaO_3S$ 374.0633; Found 374.0635.



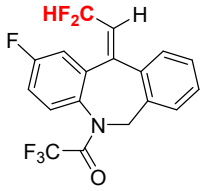
(*E*)-11-(2,2-difluoroethylidene)-3-methoxy-6-methyl-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3u′). White solid (11.2 mg, 32%). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). **Melting point**: 155-157 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (dd, *J* = 7.8 Hz, 1.2 Hz, 1 H), 7.48 (td, *J* = 7.8 Hz, 1.5 Hz, 1 H), 7.43-7.39 (m, 3 H), 7.26 (dd, *J* = 7.5 Hz, 1.5 Hz, 1 H), 7.07 (dd, *J* = 8.7 Hz, 2.6 Hz, 1 H), 6.17 (q, H-F, $J_{H\text{-}F}$ = 7.8 Hz, 1 H), 6.00 (td, H-F, $J_{H\text{-}F}$ = 55.0 Hz, 7.5 Hz, 1 H), 3.87 (s, 3 H), 3.35 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.8, 147.1 (t, C-F, $^3J_{C\text{-}F}$ = 12.8 Hz), 141.2, 137.3, 137.0, 130.9, 130.6, 130.5, 129.7, 129.2, 127.5, 126.6 (t, C-F, $^2J_{C\text{-}F}$ = 27.1 Hz), 119.6, 112.4 (t, C-F, $^1J_{C\text{-}F}$ = 230.2 Hz), 111.6, 55.9, 38.8; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -107.84 (d, F-F, $J_{F\text{-}F}$ = 313.7 Hz, 1F), -110.25 (d, F-F, $J_{F\text{-}F}$ = 318.9 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: [M + Na]$^+$ Calcd for $C_{17}H_{15}F_2NNaO_3S$ 374.0633; Found 374.0634.

6. Characterization data of products 5

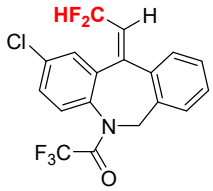


(*Z*)-1-(11-(2,2-difluoroethylidene)-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5a). White solid (30.4 mg, 86%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 154-155

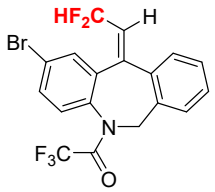
°C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51-7.40 (m, 4 H), 7.37-7.30 (m, 3 H), 7.15 (dd, J = 6.9 Hz, 0.7 Hz, 1 H), 6.22-6.16 (m, 1 H), 6.04-5.75 (m, 2 H), 4.36 (d, J = 16.9 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.1 (q, C-F, $^2J_{C\text{-}F}$ = 36.0 Hz), 147.0 (t, C-F, $^3J_{C\text{-}F}$ = 12.7 Hz), 136.7, 136.6, 134.6, 133.3, 130.2, 129.7, 129.5, 129.3, 128.0, 127.9, 127.3, 127.2, 125.3 (dd, C-F, $^2J_{C\text{-}F}$ = 31.3 Hz, 22.3 Hz), 116.2 (q, C-F, $^1J_{C\text{-}F}$ = 286.7 Hz), 112.8 (t, C-F, $^1J_{C\text{-}F}$ = 230.0 Hz), 50.8; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.14 (s, 3F), -104.63 (d, F-F, $J_{F\text{-}F}$ = 319.7 Hz, 1F), -113.18 (d, F-F, $J_{F\text{-}F}$ = 319.8 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{13}F_5NO$ 354.0912; Found 354.0908.



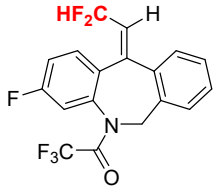
(*Z*)-1-(11-(2,2-difluoroethylidene)-2-fluoro-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5b). White solid (28.2 mg, 76%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 164-166 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43-7.39 (m, 2 H), 7.36-7.29 (m, 2 H), 7.21-7.15 (m, 2 H), 7.09 (dd, J = 7.9 Hz, 2.8 Hz, 1 H), 6.23-6.17 (m, 1 H), 6.09-5.80 (m, 2 H), 4.34 (d, J = 16.9 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.4 (d, C-F, $^1J_{C\text{-}F}$ = 251.1 Hz), 156.3 (q, C-F, $^2J_{C\text{-}F}$ = 36.3 Hz), 145.9 (t, C-F, $^3J_{C\text{-}F}$ = 12.2 Hz), 138.8 (d, C-F, $^3J_{C\text{-}F}$ = 8.5 Hz), 134.0, 133.1, 132.6, 129.8, 129.4, 129.3 (d, C-F, $^3J_{C\text{-}F}$ = 9.4 Hz), 128.1, 127.9, 125.8 (dd, C-F, $^2J_{C\text{-}F}$ = 32.1 Hz, 22.0 Hz), 117.0 (d, C-F, $^2J_{C\text{-}F}$ = 22.8 Hz), 116.5 (d, C-F, $^2J_{C\text{-}F}$ = 23.5 Hz), 116.1 (q, C-F, $^1J_{C\text{-}F}$ = 286.8 Hz), 112.4 (t, C-F, $^1J_{C\text{-}F}$ = 228.8 Hz), 50.8; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.14 (s, 3F), -104.60 (d, F-F, $J_{F\text{-}F}$ = 321.1 Hz, 1F), -109.37 (s, 1F), -113.58 (d, F-F, $J_{F\text{-}F}$ = 321.0 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{11}F_6NNaO$ 394.0637; Found 394.0637.



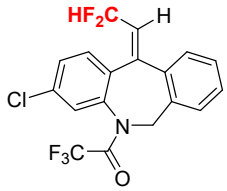
(*Z*)-1-(2-chloro-11-(2,2-difluoroethylidene)-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5c). White solid (27.1 mg, 70%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 184-186 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47 (dd, J = 8.5 Hz, 2.3 Hz, 1 H), 7.42 (dd, J = 7.5 Hz, 1.5 Hz, 1 H), 7.37-7.31 (m, 4 H), 7.15 (d, J = 7.2 Hz, 1 H), 6.23-6.17 (m, 1 H), 6.08-5.78 (m, 2 H), 4.33 (d, J = 17.0 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.1 (q, C-F, $^2J_{C\text{-}F}$ = 36.0 Hz), 145.7 (t, C-F, $^3J_{C\text{-}F}$ = 12.7 Hz), 138.2, 135.8, 135.1, 134.0, 133.0, 130.3, 129.8, 129.4, 129.2, 128.7, 128.6, 128.1, 127.9, 125.9 (dd, C-F, $^2J_{C\text{-}F}$ = 31.5 Hz, 22.8 Hz), 116.1 (q, C-F, $^1J_{C\text{-}F}$ = 286.6 Hz), 112.3 (t, C-F, $^1J_{C\text{-}F}$ = 229.9 Hz), 50.7; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.13 (s, 3F), -104.68 (d, F-F, $J_{F\text{-}F}$ = 321.3 Hz, 1F), -113.35 (d, F-F, $J_{F\text{-}F}$ = 321.1 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{11}F_5NNaO$ 410.0342; Found 410.0357.



(*Z*)-1-(2-bromo-11-(2,2-difluoroethylidene)-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5d). White solid (34.1 mg, 79%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 185-187 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 8.4 Hz, 2.2 Hz, 1 H), 7.51 (d, *J* = 2.2 Hz, 1 H), 7.42 (dd, *J* = 7.4 Hz, 1.4 Hz, 1 H), 7.36-7.28 (m, 3 H), 7.15 (d, *J* = 7.2 Hz, 1 H), 6.23-6.17 (m, 1 H), 6.08-5.78 (m, 2 H), 4.33 (d, *J* = 17.0 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.1 (q, C-F, $^2J_{C\text{-}F}$ = 36.2 Hz), 145.6 (t, C-F, $^3J_{C\text{-}F}$ = 12.6 Hz), 138.5, 135.7, 134.0, 133.3, 132.9, 132.1, 129.8, 129.4, 128.9, 128.1, 127.9, 125.9 (dd, C-F, $^2J_{C\text{-}F}$ = 31.6 Hz, 22.7 Hz), 123.7, 116.1 (q, C-F, $^1J_{C\text{-}F}$ = 286.8 Hz), 112.3 (t, C-F, $^1J_{C\text{-}F}$ = 231.4 Hz), 50.6; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.12 (s, 3F), -104.71 (d, F-F, $J_{F\text{-}F}$ = 321.3 Hz, 1F), -113.29 (d, F-F, $J_{F\text{-}F}$ = 321.1 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{11}BrF_5NNaO$ 453.9836; Found 453.9856.

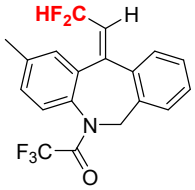


(*Z*)-1-(11-(2,2-difluoroethylidene)-3-fluoro-6,11-dihydro-5H-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5e). White solid (30.4 mg, 82%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 158-160 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 7.4 Hz, 1.4 Hz, 1 H), 7.37-7.31 (m, 3 H), 7.23-7.15 (m, 3 H), 6.21 (q, H-F, $J_{H\text{-}F}$ = 7.6 Hz, 1 H), 6.01-5.71 (m, 2 H), 4.37 (d, *J* = 16.9 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.8 (d, C-F, $^1J_{C\text{-}F}$ = 250.6 Hz), 156.0 (q, C-F, $^2J_{C\text{-}F}$ = 36.3 Hz), 146.1 (t, C-F, $^3J_{C\text{-}F}$ = 12.6 Hz), 137.9 (d, C-F, $^3J_{C\text{-}F}$ = 10.2 Hz), 134.3, 132.9, 132.7, 130.7 (d, C-F, $^3J_{C\text{-}F}$ = 9.0 Hz), 129.7, 129.3, 128.1, 127.9, 125.8 (t, C-F, $^2J_{C\text{-}F}$ = 29.0 Hz), 116.9 (d, C-F, $^2J_{C\text{-}F}$ = 21.1 Hz), 116.1 (q, C-F, $^1J_{C\text{-}F}$ = 286.6 Hz), 115.0 (d, C-F, $^2J_{C\text{-}F}$ = 24.7 Hz), 112.6 (t, C-F, $^1J_{C\text{-}F}$ = 230.1 Hz), 50.7; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.24 (s, 3F), -104.42 (d, F-F, $J_{F\text{-}F}$ = 320.4 Hz, 1F), -108.96 (s, 1F), -113.38 (d, F-F, $J_{F\text{-}F}$ = 320.4 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{11}F_6NNaO$ 394.0637; Found 394.0633.

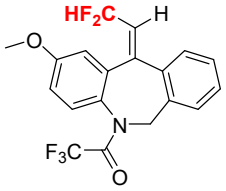


(*Z*)-1-(3-chloro-11-(2,2-difluoroethylidene)-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5f). White solid (32.6 mg, 84%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 144-146 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48 (dd, *J* = 8.1 Hz, 2.0 Hz, 1 H), 7.44-7.42 (m,

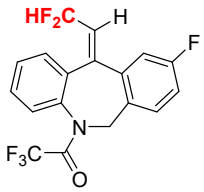
2 H), 7.36-7.30 (m, 3 H), 7.16 (d, J = 7.1 Hz, 1 H), 6.24-6.18 (m, 1 H), 6.02-5.72 (m, 2 H), 4.36 (d, J = 16.9 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.0 (q, C-F, $^2J_{C\text{-}F}$ = 36.4 Hz), 146.0 (t, C-F, $^3J_{C\text{-}F}$ = 12.8 Hz), 137.6, 135.6, 135.1, 134.1, 132.9, 130.3, 130.0, 129.7, 129.3, 128.1, 127.9, 127.7, 125.9 (dd, C-F, $^2J_{C\text{-}F}$ = 32.1 Hz, 22.0 Hz), 116.1 (q, C-F, $^1J_{C\text{-}F}$ = 286.6 Hz), 112.5 (t, C-F, $^1J_{C\text{-}F}$ = 229.5 Hz), 50.7; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.16 (s, 3F), -104.42 (d, F-F, $J_{F\text{-}F}$ = 320.7 Hz, 1F), -113.38 (d, F-F, $J_{F\text{-}F}$ = 320.8 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{11}ClF_5NNaO$ 410.0342; Found 410.0342.



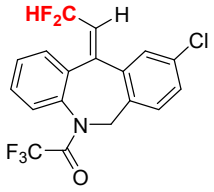
(*Z*)-1-(11-(2,2-difluoroethylidene)-2-methyl-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5g). White solid (29.8 mg, 81%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 155-157 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 (dd, J = 7.2 Hz, 1.4 Hz, 1 H), 7.35-7.28 (m, 4 H), 7.15-7.13 (m, 2 H), 6.19-6.13 (m, 1 H), 6.08-5.78 (m, 2 H), 4.34 (d, J = 16.9 Hz, 1 H), 2.41 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.4 (q, C-F, $^2J_{C\text{-}F}$ = 35.8 Hz), 147.2 (t, C-F, $^3J_{C\text{-}F}$ = 12.9 Hz), 140.1, 136.4, 134.7, 134.0, 133.3, 130.7, 129.7, 129.4, 129.3, 127.9, 127.1, 127.0, 125.0 (dd, C-F, $^2J_{C\text{-}F}$ = 31.5 Hz, 22.3 Hz), 116.3 (q, C-F, $^1J_{C\text{-}F}$ = 286.7 Hz), 112.9 (t, C-F, $^1J_{C\text{-}F}$ = 228.9 Hz), 50.9, 21.2; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.11 (s, 3F), -104.65 (d, F-F, $J_{F\text{-}F}$ = 319.4 Hz, 1F), -113.14 (d, F-F, $J_{F\text{-}F}$ = 319.7 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{15}F_5NO$ 368.1068; Found 368.1062.



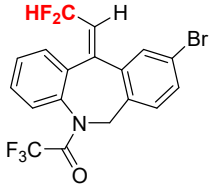
(*Z*)-1-(11-(2,2-difluoroethylidene)-2-methoxy-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5h). White solid (32.2 mg, 84%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 149-151 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 (dd, J = 7.3 Hz, 1.4 Hz, 1 H), 7.35-7.29 (m, 3 H), 7.15 (dd, J = 7.0 Hz, 0.8 Hz, 1 H), 6.96 (dd, J = 8.7 Hz, 2.9 Hz, 1 H), 6.85 (d, J = 2.8 Hz, 1 H), 6.19-6.11 (m, 1 H), 5.99-5.83 (m, 2 H), 4.34 (d, J = 16.9 Hz, 1 H), 3.83 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.0, 156.6 (q, C-F, $^2J_{C\text{-}F}$ = 35.6 Hz), 147.2 (t, C-F, $^3J_{C\text{-}F}$ = 12.7 Hz), 137.8, 134.5, 133.4, 129.5, 129.4, 129.1, 128.5, 127.9, 127.8, 125.2 (dd, C-F, $^2J_{C\text{-}F}$ = 32.1 Hz, 21.8 Hz), 116.1 (q, C-F, $^1J_{C\text{-}F}$ = 286.6 Hz), 115.1, 114.4, 112.0 (t, C-F, $^1J_{C\text{-}F}$ = 230.1 Hz), 55.7, 51.0; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.14 (s, 3F), -104.32 (d, F-F, $J_{F\text{-}F}$ = 319.1 Hz, 1F), -113.55 (d, F-F, $J_{F\text{-}F}$ = 319.8 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{15}F_5NO_2$ 384.1017; Found 384.1021.



(*Z*)-1-(11-(2,2-difluoroethylidene)-9-fluoro-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5i). White solid (30.8 mg, 83%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 148-150 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55-7.48 (m, 2 H), 7.43-7.41 (m, 1 H), 7.37-7.35 (m, 1 H), 7.19-7.11 (m, 2 H), 7.05 (td, *J* = 7.8 Hz, 2.6 Hz, 1 H), 6.23-6.17 (m, 1 H), 6.02-5.72 (m, 2 H), 4.32 (d, *J* = 16.8 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.8 (d, C-F, $^1J_{C\text{-}F}$ = 246.0 Hz), 156.2 (q, C-F, $^2J_{C\text{-}F}$ = 36.2 Hz), 145.9 (t, C-F, $^3J_{C\text{-}F}$ = 12.3 Hz), 136.5 (d, C-F, $^3J_{C\text{-}F}$ = 34.7 Hz), 136.0 (d, C-F, $^3J_{C\text{-}F}$ = 40.0 Hz), 130.5, 129.9, 129.7, 129.6, 129.4, 129.0, 127.3, 126.2 (dd, C-F, $^2J_{C\text{-}F}$ = 31.6 Hz, 22.8 Hz), 116.6 (d, C-F, $^2J_{C\text{-}F}$ = 21.4 Hz), 116.2 (q, C-F, $^1J_{C\text{-}F}$ = 286.7 Hz), 115.9 (d, C-F, $^2J_{C\text{-}F}$ = 22.6 Hz), 112.5 (t, C-F, $^1J_{C\text{-}F}$ = 229.9 Hz), 50.3; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.19 (s, 3F), -105.00 (d, F-F, $J_{F\text{-}F}$ = 321.5 Hz, 1F), -113.36 (d, F-F, $J_{F\text{-}F}$ = 321.4 Hz, 1F), -114.18 (s, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{11}F_6NNaO$ 394.0637; Found 394.0635.

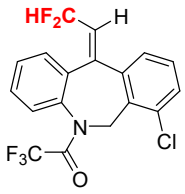


(*Z*)-1-(9-chloro-11-(2,2-difluoroethylidene)-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5j). White solid (33.0 mg, 85%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 153-155 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53-7.48 (m, 2 H), 7.45-7.41 (m, 2 H), 7.36 (dd, *J* = 6.7 Hz, 2.2 Hz, 1 H), 7.31 (dd, *J* = 8.3 Hz, 2.2 Hz, 1 H), 7.10 (d, *J* = 8.3 Hz, 1 H), 6.24-6.18 (m, 1 H), 6.02-5.73 (m, 2 H), 4.31 (d, *J* = 17.0 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.2 (q, C-F, $^2J_{C\text{-}F}$ = 36.3 Hz), 145.7 (t, C-F, $^3J_{C\text{-}F}$ = 12.7 Hz), 136.6, 136.1, 135.9, 133.6, 131.8, 130.5, 129.9, 129.5, 129.4, 129.3, 129.0, 127.4, 126.2 (dd, C-F, $^2J_{C\text{-}F}$ = 31.5 Hz, 22.7 Hz), 116.1 (q, C-F, $^1J_{C\text{-}F}$ = 286.5 Hz), 112.5 (t, C-F, $^1J_{C\text{-}F}$ = 229.5 Hz), 50.3; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.1 (s, 3F), -104.96 (d, F-F, $J_{F\text{-}F}$ = 321.6 Hz, 1F), -113.39 (d, F-F, $J_{F\text{-}F}$ = 321.9 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{11}ClF_5NNaO$ 410.0342; Found 410.0357.

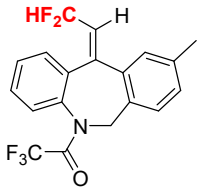


(*Z*)-1-(9-bromo-11-(2,2-difluoroethylidene)-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5k). White solid (37.6 mg, 87%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 145-147

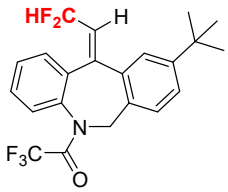
°C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 (d, J = 2.0 Hz, 1 H), 7.53-7.49 (m, 2 H), 7.47-7.41 (m, 2 H), 7.37-7.35 (m, 1 H), 7.03 (d, J = 8.3 Hz, 1 H), 6.24-6.18 (m, 1 H), 6.02-5.72 (m, 2 H), 4.29 (d, J = 17.0 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.3 (q, C-F, $^{2}J_{C\text{-}F}$ = 36.0 Hz), 145.6 (t, C-F, $^{3}J_{C\text{-}F}$ = 12.5 Hz), 136.6, 136.4, 135.9, 132.4, 132.3, 131.9, 130.5, 129.9, 129.5, 129.4, 127.4, 126.2 (dd, C-F, $^{2}J_{C\text{-}F}$ = 31.7 Hz, 23.0 Hz), 121.5, 116.1 (q, C-F, $^{1}J_{C\text{-}F}$ = 286.5 Hz), 112.4 (t, C-F, $^{1}J_{C\text{-}F}$ = 230.0 Hz), 50.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.19 (s, 3F), -104.94 (d, F-F, $J_{F\text{-}F}$ = 321.7 Hz, 1F), -113.39 (d, F-F, $J_{F\text{-}F}$ = 321.3 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{11}BrF_5NNaO$ 453.9836; Found 453.9851.



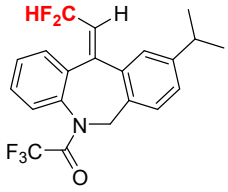
(*Z*)-1-(7-chloro-11-(2,2-difluoroethylidene)-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5l). White solid (28.3 mg, 73%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 195-197 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55-7.47 (m, 2 H), 7.45 (d, J = 7.4 Hz, 1 H), 7.40-7.33 (m, 3 H), 7.28-7.24 (m, 1 H), 6.24-6.18 (m, 1 H), 6.11-5.75 (m, 2 H), 4.23 (d, J = 17.7 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.4 (q, C-F, $^{2}J_{C\text{-}F}$ = 36.3 Hz), 146.2 (t, C-F, $^{3}J_{C\text{-}F}$ = 12.6 Hz), 137.0, 136.5, 136.2, 133.8, 130.9, 130.6, 130.4, 129.9, 128.9, 128.6, 128.2, 127.4, 125.5 (dd, C-F, $^{2}J_{C\text{-}F}$ = 32.1 Hz, 22.3 Hz), 116.1 (q, C-F, $^{1}J_{C\text{-}F}$ = 286.5 Hz), 112.5 (t, C-F, $^{1}J_{C\text{-}F}$ = 229.6 Hz), 49.5; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.17 (d, F-F, $J_{F\text{-}F}$ = 2.4 Hz, 3F), -105.00 (d, F-F, $J_{F\text{-}F}$ = 320.8 Hz, 1F), -113.55 (dd, F-F, $J_{F\text{-}F}$ = 321.1 Hz, 2.5 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{11}ClF_5NNaO$ 410.0342; Found 410.0339.



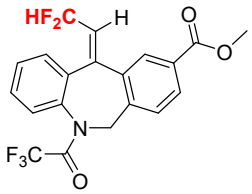
(*Z*)-1-(11-(2,2-difluoroethylidene)-9-methyl-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5m). White solid (30.1 mg, 82%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 172-174 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49-7.45 (m, 2 H), 7.40 (dd, J = 6.1 Hz, 1.0 Hz, 1 H), 7.36-7.33 (m, 1 H), 7.25 (s, 1 H), 7.15 (d, J = 7.8 Hz, 1 H), 7.03 (d, J = 7.8 Hz, 1 H), 6.21-6.16 (m, 1 H), 6.03-5.74 (m, 2 H), 4.32 (d, J = 16.8 Hz, 1 H), 2.36 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.2 (q, C-F, $^{2}J_{C\text{-}F}$ = 36.2 Hz), 147.2 (t, C-F, $^{3}J_{C\text{-}F}$ = 12.8 Hz), 137.7, 136.7, 134.3, 130.3, 130.2, 130.1, 129.7, 129.6, 129.3, 127.8, 127.3, 125.0 (dd, C-F, $^{2}J_{C\text{-}F}$ = 31.5 Hz, 22.3 Hz), 116.2 (q, C-F, $^{1}J_{C\text{-}F}$ = 286.6 Hz), 112.8 (t, C-F, $^{1}J_{C\text{-}F}$ = 229.0 Hz), 50.6, 20.9; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.14 (s, 3F), -104.51 (d, F-F, $J_{F\text{-}F}$ = 319.4 Hz, 1F), -113.15 (d, F-F, $J_{F\text{-}F}$ = 319.4 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{14}F_5NNaO$ 390.0888; Found 390.0882.



(*Z*)-1-(9-(tert-butyl)-11-(2,2-difluoroethylidene)-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5n). White solid (32.8 mg, 80%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 140-141 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49-7.47 (m, 2 H), 7.41-7.36 (m, 4 H), 7.09 (d, *J* = 8.1 Hz, 1 H), 6.22-6.16 (m, 1 H), 6.05-5.75 (m, 2 H), 4.33 (d, *J* = 16.8 Hz, 1 H), 1.34 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.2 (q, C-F, $^2J_{C\text{-}F}$ = 36.0 Hz), 151.2, 147.7 (t, C-F, $^3J_{C\text{-}F}$ = 12.7 Hz), 136.7, 134.1, 130.3, 130.1, 129.6, 129.4, 127.7, 127.3, 126.8, 125.9, 125.0 (dd, C-F, $^2J_{C\text{-}F}$ = 31.7 Hz, 22.2 Hz), 116.2 (q, C-F, $^1J_{C\text{-}F}$ = 286.7 Hz), 112.9 (t, C-F, $^1J_{C\text{-}F}$ = 228.9 Hz), 50.6, 34.6, 31.2; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.12 (s, 3F), -104.34 (d, F-F, $J_{F\text{-}F}$ = 319.3 Hz, 1F), -113.08 (d, F-F, $J_{F\text{-}F}$ = 319.6 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: [M + Na]$^+$ Calcd for $C_{22}H_{20}F_5NNaO$ 432.1357; Found 432.1370.

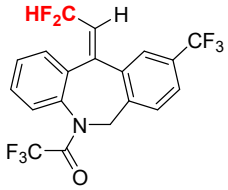


(*Z*)-1-(11-(2,2-difluoroethylidene)-9-isopropyl-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5o). White solid (34.0 mg, 86%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 110-113 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49-7.47 (m, 2 H), 7.41-7.36 (m, 2 H), 7.27 (d, *J* = 1.6 Hz, 1 H), 7.21 (dd, *J* = 8.0 Hz, 1.8 Hz, 1 H), 7.08 (d, *J* = 8.0 Hz, 1 H), 6.23-6.17 (m, 1 H), 6.04-5.75 (m, 2 H), 4.33 (d, *J* = 16.8 Hz, 1 H), 2.98-2.87 (m, 1 H), 1.27 (s, 3 H), 1.25 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.2 (q, C-F, $^2J_{C\text{-}F}$ = 35.9 Hz), 148.9, 147.2 (t, C-F, $^3J_{C\text{-}F}$ = 12.7 Hz), 136.7, 136.6, 134.4, 130.6, 130.1, 129.6, 129.3, 127.9, 127.7, 127.3, 125.0 (dd, C-F, $^2J_{C\text{-}F}$ = 31.5 Hz, 22.2 Hz), 116.2 (q, C-F, $^1J_{C\text{-}F}$ = 286.7 Hz), 112.9 (t, C-F, $^1J_{C\text{-}F}$ = 228.9 Hz), 50.7, 33.8, 23.9, 23.8; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.13 (s, 3F), -104.41 (d, F-F, $J_{F\text{-}F}$ = 319.1 Hz, 1F), -113.10 (d, F-F, $J_{F\text{-}F}$ = 319.0 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: [M + Na]$^+$ Calcd for $C_{21}H_{18}F_5NNaO$ 418.1201; Found 418.1209.

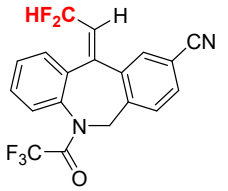


methyl(*Z*)-11-(2,2-difluoroethylidene)-5-(2,2,2-trifluoroacetyl)-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepine-9-carboxylate (5p). White solid (28.8 mg, 70%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 173-175 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 1.5 Hz, 1 H), 7.98 (dd, *J* = 8.0 Hz, 1.6

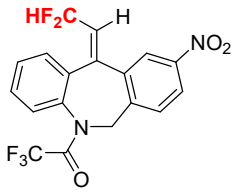
Hz, 1 H), 7.53-7.49 (m, 2 H), 7.44-7.37 (m, 2 H), 7.24 (d, J = 8.1 Hz, 1 H), 6.31-6.25 (m, 1 H), 6.05-5.75 (m, 2 H), 4.40 (d, J = 17.4 Hz, 1 H), 3.95 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.1, 156.3 (q, C-F, $^2J_{C\text{-}F}$ = 36.3 Hz), 146.0 (t, C-F, $^3J_{C\text{-}F}$ = 12.7 Hz), 138.3, 136.5, 136.2, 134.9, 130.6, 130.5, 130.2, 129.9, 129.4, 128.2, 127.4, 127.3, 126.3 (dd, C-F, $^2J_{C\text{-}F}$ = 31.9 Hz, 22.3 Hz), 116.1 (q, C-F, $^1J_{C\text{-}F}$ = 286.7 Hz), 112.5 (t, C-F, $^1J_{C\text{-}F}$ = 229.6 Hz), 52.4, 50.8; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.17 (s, 3F), -104.95 (d, F-F, $J_{F\text{-}F}$ = 321.4 Hz, 1F), -113.32 (d, F-F, $J_{F\text{-}F}$ = 321.0 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{14}F_5NNaO_3$ 434.0786; Found 434.0798.



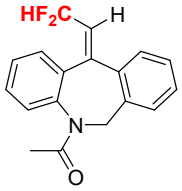
(*Z*)-1-(11-(2,2-difluoroethylidene)-9-(trifluoromethyl)-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5q). White solid (29.1 mg, 69%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 120-122 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.70 (s, 1 H), 7.59 (d, J = 8.1 Hz, 1 H), 7.57-7.51 (m, 2 H), 7.44 (d, J = 7.6 Hz, 1 H), 7.39 (dd, J = 7.4 Hz, 2.2 Hz, 1 H), 7.30 (d, J = 8.1 Hz, 1 H), 6.29-6.23 (m, 1 H), 6.04-5.75 (m, 2 H), 4.40 (d, J = 17.3 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.3 (q, C-F, $^2J_{C\text{-}F}$ = 36.3 Hz), 145.7 (t, C-F, $^3J_{C\text{-}F}$ = 12.7 Hz), 137.3, 136.5, 135.8, 135.3, 130.7, 130.0, 129.5, 128.7, 127.4, 126.7 (dd, C-F, $^2J_{C\text{-}F}$ = 32.0 Hz, 22.5 Hz), 126.3, 126.0 (q, C-F, $^3J_{C\text{-}F}$ = 3.5 Hz), 123.6 (q, C-F, $^1J_{C\text{-}F}$ = 270.7 Hz), 116.1 (q, C-F, $^1J_{C\text{-}F}$ = 286.5 Hz), 112.4 (t, C-F, $^1J_{C\text{-}F}$ = 229.3 Hz), 50.6; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -62.68 (s, 3F), -68.22 (s, 3F), -105.07 (d, F-F, $J_{F\text{-}F}$ = 322.3 Hz, 1F), -113.46 (d, F-F, $J_{F\text{-}F}$ = 322.3 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{11}F_8NNaO$ 444.0605; Found 444.0603.



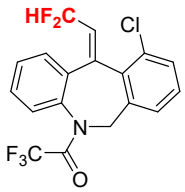
(*Z*)-11-(2,2-difluoroethylidene)-5-(2,2,2-trifluoroacetyl)-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepine-9-carbonitrile (5r). White solid (23.5 mg, 62%). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). **Melting point**: 219-220 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77 (d, J = 1.4 Hz, 1 H), 7.62 (dd, J = 8.0 Hz, 1.6 Hz, 1 H), 7.56-7.51 (m, 2 H), 7.45 (dd, J = 6.4 Hz, 0.8 Hz, 1 H), 7.39-7.37 (m, 1 H), 7.30 (d, J = 8.0 Hz, 1 H), 6.27-6.22 (m, 1 H), 6.03-5.74 (m, 2 H), 4.40 (d, J = 17.5 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.4 (q, C-F, $^2J_{C\text{-}F}$ = 36.4 Hz), 145.0 (t, C-F, $^3J_{C\text{-}F}$ = 12.6 Hz), 138.7, 136.4, 135.9, 135.5, 133.0, 132.4, 130.8, 130.2, 129.5, 129.0, 127.5, 127.2 (dd, C-F, $^2J_{C\text{-}F}$ = 31.8 Hz, 22.9 Hz), 117.7, 116.0 (q, C-F, $^1J_{C\text{-}F}$ = 286.7 Hz), 112.3, 112.2 (t, C-F, $^1J_{C\text{-}F}$ = 229.5 Hz), 50.7; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.23 (s, 3F), -105.24 (d, F-F, $J_{F\text{-}F}$ = 323.3 Hz, 1F), -113.56 (d, F-F, $J_{F\text{-}F}$ = 323.6 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{11}F_5N_2NaO$ 401.0684; Found 401.0686.



(*Z*)-1-(11-(2,2-difluoroethylidene)-9-nitro-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5s). White solid (21.1 mg, 53%). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). **Melting point**: 188-191 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 2.3 Hz, 1 H), 8.18 (dd, *J* = 8.5 Hz, 2.3 Hz, 1 H), 7.59-7.52 (m, 2 H), 7.46 (dd, *J* = 6.2 Hz, 0.8 Hz, 1 H), 7.42-7.39 (m, 1 H), 7.37 (d, *J* = 8.5 Hz, 1 H), 6.36-6.31 (m, 1 H), 6.05-5.76 (m, 2 H), 4.43 (d, *J* = 17.7 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.6 (q, C-F, $^2J_{C\text{-}F}$ = 36.8 Hz), 147.4, 144.8 (t, C-F, $^3J_{C\text{-}F}$ = 12.6 Hz), 140.5, 136.4, 136.1, 135.4, 130.9, 130.3, 129.6, 129.3, 127.6 (dd, C-F, $^2J_{C\text{-}F}$ = 31.6 Hz, 22.7 Hz), 127.5, 124.4, 123.8, 116.0 (q, C-F, $^1J_{C\text{-}F}$ = 286.5 Hz), 112.1 (t, C-F, $^1J_{C\text{-}F}$ = 229.9 Hz), 50.6; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.23 (s, 3F), -105.32 (d, F-F, $J_{F\text{-}F}$ = 323.8 Hz, 1F), -113.53 (d, F-F, $J_{F\text{-}F}$ = 323.9 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{11}F_5N_2NaO_3$ 421.0582; Found 421.0595.

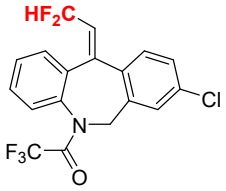


(*Z*)-1-(11-(2,2-difluoroethylidene)-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepin-5-yl)ethan-1-one (5t). White solid (18.0 mg, 60%). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). **Melting point**: 176-177 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48 (td, *J* = 7.5 Hz, 1.6 Hz, 1 H), 7.45-7.38 (m, 2 H), 7.37-7.34 (m, 2 H), 7.30 (td, *J* = 7.4 Hz, 1.4 Hz, 1 H), 7.26-7.23 (m, 1 H), 7.14 (d, *J* = 7.5 Hz, 1 H), 6.21-5.91 (m, 3 H), 4.17 (s, 1 H), 1.86 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.0, 148.9 (t, C-F, $^3J_{C\text{-}F}$ = 12.8 Hz), 140.2, 136.9, 135.6, 134.9, 130.5, 129.3, 129.1, 129.0, 128.9, 127.9, 127.5, 127.3, 124.0 (t, C-F, $^2J_{C\text{-}F}$ = 26.7 Hz), 112.8 (t, C-F, $^1J_{C\text{-}F}$ = 229.6 Hz), 48.4, 21.6; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -106.88 (d, F-F, $J_{F\text{-}F}$ = 317.0 Hz, 1F), -109.47 (d, F-F, $J_{F\text{-}F}$ = 322.4 Hz, 1F); **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{16}F_2NO$ 300.1194; Found 300.1195.

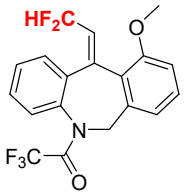


(*E*)-1-(10-chloro-11-(2,2-difluoroethylidene)-6,11-dihydro-5H-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5v). White solid (16.3 mg, 42%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 178-180 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.50-7.44 (m, 3 H), 7.42-7.40 (m, 2 H), 7.20 (t, *J* = 7.8 Hz, 1 H), 7.04 (d, *J* = 7.8 Hz, 1 H), 6.31-6.26 (m, 1 H), 6.07-5.77

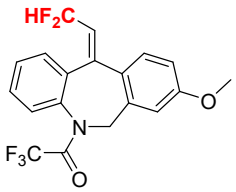
(m, 2 H), 4.32 (d, J = 17.3 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.4 (q, C-F, $^2J_{C\text{-}F}$ = 36.5 Hz), 139.4 (t, C-F, $^3J_{C\text{-}F}$ = 12.9 Hz), 137.1, 135.7, 135.0, 132.9, 132.8, 130.1, 129.9, 129.7, 129.3, 128.6, 127.2, 126.4, 116.1 (q, C-F, $^1J_{C\text{-}F}$ = 286.6 Hz), 112.4 (t, C-F, $^1J_{C\text{-}F}$ = 229.0 Hz), 50.1; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -67.79 (s, 3F), -107.57 (d, F-F, $J_{F\text{-}F}$ = 322.5 Hz, 1F), -114.23 (d, F-F, $J_{F\text{-}F}$ = 322.5 Hz, 1F); HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{18}H_{11}ClF_5KNO$ 426.0081; Found 426.0081.



(*Z*)-1-(8-chloro-11-(2,2-difluoroethylidene)-6,11-dihydro-5H-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5v′). White solid (15.5 mg, 40%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 126-127 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54-7.47 (m, 2 H), 7.43-7.38 (m, 2 H), 7.35 (dd, J = 6.8 Hz, 2.1 Hz, 1 H), 7.28 (dd, J = 8.4 Hz, 2.0 Hz, 1 H), 7.16 (s, 1 H), 6.20-6.15 (m, 1 H), 6.02-5.73 (m, 2 H), 4.32 (d, J = 17.1 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.3 (q, C-F, $^2J_{C\text{-}F}$ = 36.3 Hz), 145.9 (t, C-F, $^3J_{C\text{-}F}$ = 12.7 Hz), 136.6, 136.2, 135.4, 135.1, 133.1, 130.7, 130.5, 129.9, 129.4, 128.2, 127.8, 127.4, 125.7 (dd, C-F, $^2J_{C\text{-}F}$ = 32.0 Hz, 22.4 Hz), 116.1 (q, C-F, $^1J_{C\text{-}F}$ = 286.4 Hz), 112.6 (t, C-F, $^1J_{C\text{-}F}$ = 229.3 Hz), 50.5; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.20 (s, 3F), -104.75 (d, F-F, $J_{F\text{-}F}$ = 320.9 Hz, 1F), -113.32 (d, F-F, $J_{F\text{-}F}$ = 321.3 Hz, 1F); HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{18}H_{11}ClF_5KNO$ 426.0081; Found 426.0075.



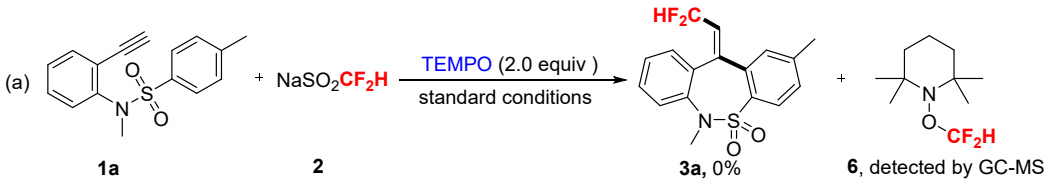
(*E*)-1-(11-(2,2-difluoroethylidene)-10-methoxy-6,11-dihydro-5H-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5w). White solid (17.3 mg, 45%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 165-166 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46-7.36 (m, 4 H), 7.22 (t, J = 8.0 Hz, 1 H), 6.85 (d, J = 8.2 Hz, 1 H), 6.73 (d, J = 7.8 Hz, 1 H), 6.32-6.27 (m, 1 H), 6.03-5.73 (m, 2 H), 4.31 (d, J = 17.2 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.5, 156.4 (q, C-F, $^2J_{C\text{-}F}$ = 35.9 Hz), 137.8, 137.7 (t, C-F, $^3J_{C\text{-}F}$ = 13.4 Hz), 136.4, 134.5, 129.8, 129.6, 129.3, 129.2, 128.6 (dd, C-F, $^2J_{C\text{-}F}$ = 29.7 Hz, 22.7 Hz), 126.9, 123.5, 119.9, 116.2 (q, C-F, $^1J_{C\text{-}F}$ = 286.6 Hz), 113.1 (t, C-F, $^1J_{C\text{-}F}$ = 230.4 Hz), 110.3, 56.1, 50.3; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -67.91 (s, 3F), -105.83 (d, F-F, $J_{F\text{-}F}$ = 319.4 Hz, 1F), -113.87 (d, F-F, $J_{F\text{-}F}$ = 319.4 Hz, 1F); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{15}F_5NO_2$ 384.1017; Found 384.1017.



(*Z*)-1-(11-(2,2-difluoroethylidene)-8-methoxy-6,11-dihydro-5H-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5w′). White solid (13.9 mg, 36%). Column chromatography on silica gel (Petroleum ether/EtOAc = 8:1). **Melting point**: 172-175 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51-7.45 (m, 2 H), 7.41-7.34 (m, 3 H), 6.84 (dd, *J* = 8.6 Hz, 2.6 Hz, 1 H), 6.65 (d, *J* = 2.5 Hz, 1 H), 6.14-6.08 (m, 1 H), 6.03-5.74 (m, 2 H), 4.32 (d, *J* = 16.9 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.4, 156.3 (q, C-F, $^2J_{C\text{-}F}$ = 35.9 Hz), 146.6 (t, C-F, $^3J_{C\text{-}F}$ = 12.4 Hz), 136.9, 136.6, 134.8, 130.8, 130.1, 129.7, 129.3, 127.2, 127.1, 124.1 (dd, C-F, $^2J_{C\text{-}F}$ = 31.8 Hz, 21.4 Hz), 116.2 (q, C-F, $^1J_{C\text{-}F}$ = 286.7 Hz), 113.8, 112.9 (t, C-F, $^1J_{C\text{-}F}$ = 229.4 Hz), 112.6, 55.4, 51.0; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.16 (s, 3F), -104.14 (d, F-F, $J_{F\text{-}F}$ = 318.3 Hz, 1F), -112.95 (d, F-F, $J_{F\text{-}F}$ = 318.4 Hz, 1F); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{15}F_5NO_2$ 384.1017; Found 384.1016.

7. Mechanistic Experiments

7.1 Radical trapping experiment



(a) A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with *N*-(2-ethynylphenyl)-*N*,4-dimethylbenzenesulfonamide **1a** (0.10 mmol, 1.0 equiv), $NaSO_2CF_2H$ **2** (0.15 mmol, 1.5 equiv), Eosin Y (3.2 mg, 0.005 mmol, 5 mol%), TEMPO (0.2 mmol, 2.0 equiv) and DMSO (2.0 mL). The reaction mixture was then stirred and irradiation with a 3 W blue LED 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. The expected adduct **6** was observed by GC-MS as following: **GC-MS** (m/z, relative intensity): 207.0 (M^+, 5%), 192.2 (100), 136.1 (10), 124.0 (65), 109.2 (86), 69.0 (62), 56.1 (58). The data for the adduct **6** were in accordance with the ones previously reported in the literature.[2]

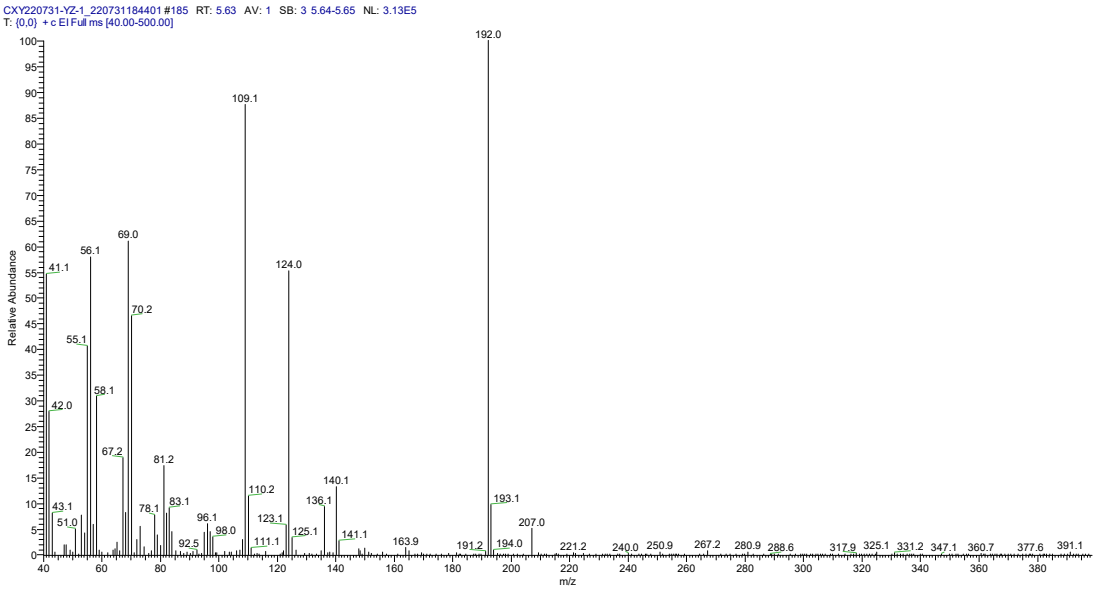
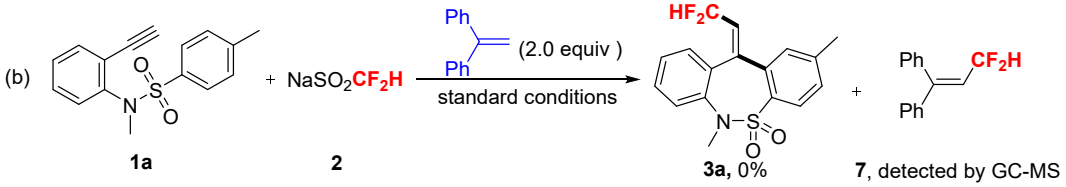


Figure S1. GC-MS (m/z) of TEMPO-CF_2H adduct **6**



(b) A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with *N*-(2-ethynylphenyl)-*N*,4-dimethylbenzenesulfonamide **1a** (0.10 mmol, 1.0 equiv), $NaSO_2CF_2H$ **2** (0.15 mmol, 1.5 equiv), Eosin Y (3.2 mg, 0.005 mmol, 5 mol%), 1, 1-diphenylethylene (0.2 mmol, 2.0 equiv) and DMSO (2.0 mL). The reaction mixture was then stirred and irradiation with a 3 W blue LED 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 **7** was observed by GC-MS as following: **GC-MS** (m/z, relative intensity): 230.1 (M^+, 100%), 209.1 (38), 178.1 (70), 165.1 (62), 152.0 (32), 133.0 (25), 94.4 (12). The data for the adduct **7** was in accordance with the ones previously reported in the literature.[3]

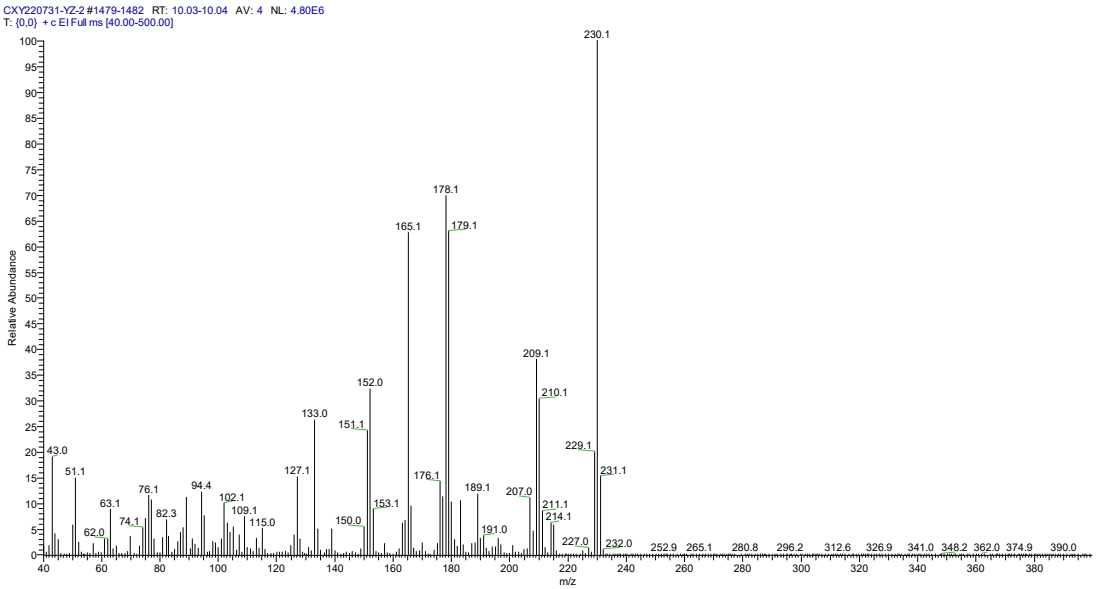


Figure S2. GC-MS (m/z) of compound **7**

7.2 UV/VIS Absorption spectra

The UV/VIS Absorption spectra were recorded in EtOH of a 0.05 mM solution in 10 mm path length quartz cuvette on a Perkin Elmer Lambda 35 Spectrometer.

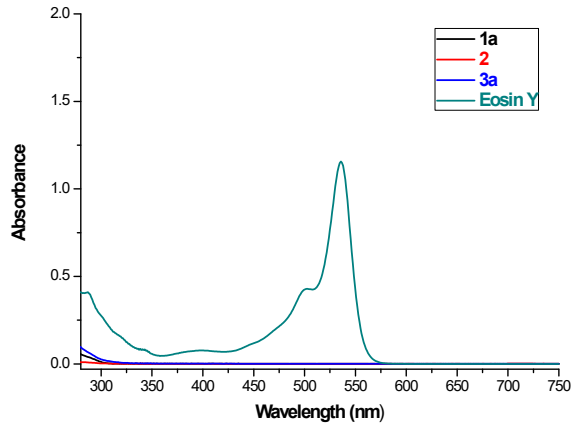


Figure S3. The UV/Vis absorption spectra of **1a**, **2**, **3a**, Eosin Y in EtOH (0.05 mM)

7.3 Fluorescence Quenching Experiments

Fluorescence quenching experiments were run with freshly prepared 0.05 Mm solution of Eosin Y in EtOH and was added the appropriate amount of a quencher in a screw-top quartz cuvette at room temperature. The solutions were irradiated at 356 nm and fluorescence was measured from 300 nm to 700 nm.

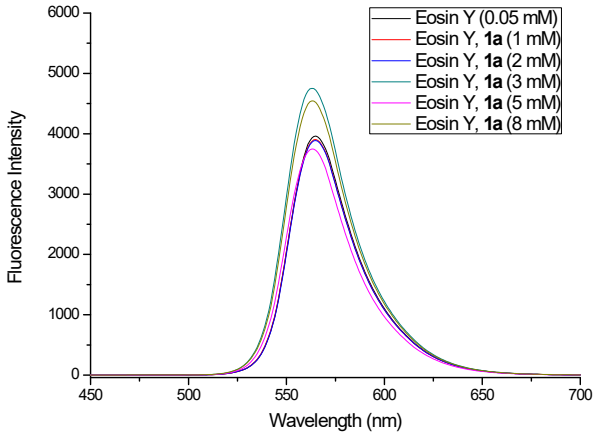


Figure S4. The emission spectra of Eosin Y with various concentrations of **1a**

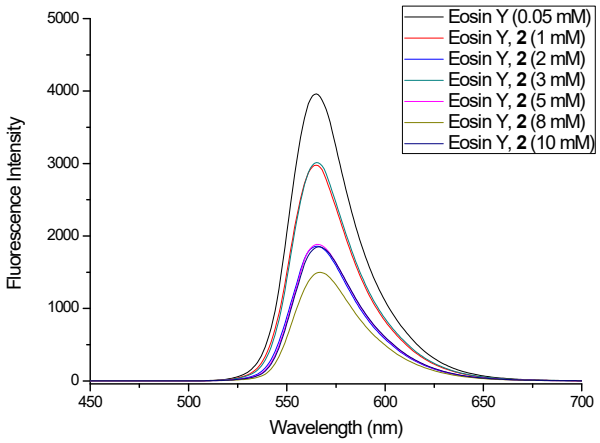


Figure S5. The emission spectra of Eosin Y with various concentrations of **2**

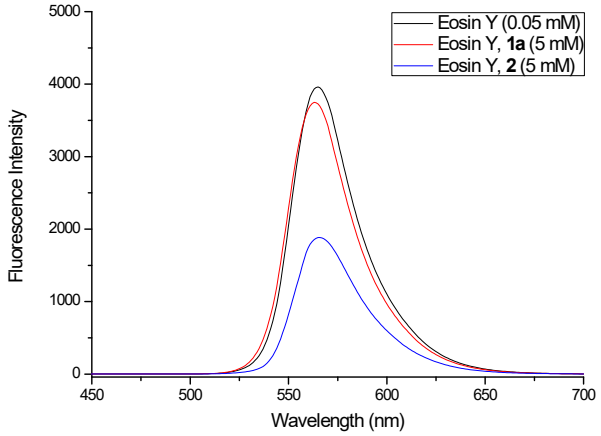


Figure S6. Luminescence quenching experiments of Eosin Y with reactants

7.4 Light/dark experiment

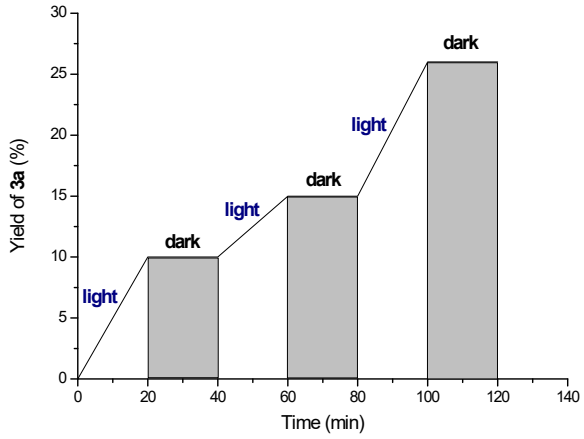


Figure S7. Light/dark experiment

Six standard reaction mixtures in Six dried 25 mL Schlenk tubes were charged with alkynes **1a** (0.10 mmol, 1.0 equiv), $NaSO_2CF_2H$ **2** (0.15 mmol, 1.5 equiv), Eosin Y (3.2 mg, 0.005 mmol, 5 mol%) and DMSO (2.0 mL). The reaction mixture was then stirred and irradiation with a 3 W blue LED at room temperature under air atmosphere. After 20 min, the Blue LED was turned off, and one vial was removed from the irradiation setup for analysis. The remaining five vials were stirred in the absence of light for an additional 20 min. Then, one vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining four reaction mixtures. After an additional 20 min of irradiation, the Blue LED was turned off, and one vial was removed for analysis. The remaining three vials were stirred in the absence of light for an additional 20 min. Then, a vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining two reaction mixtures. After 20 min, the Blue LED was turned off, and one vial was removed for analysis. The last vial was stirred in the absence of light for an additional 20 min, and then it was analyzed.

The light/dark experimental result showed that the desired product **3a** was formed only under continuous irradiation, which stresses that a photoredox process rather than a radical chain process is taking place. The yield of **3a** was determined by isolated yield.

8. X-ray crystallographic data

8.1 X-ray crystallographic data of 3a

The product **3a** was recrystallized from petroleum ether/ethyl acetate. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC**2201061**.

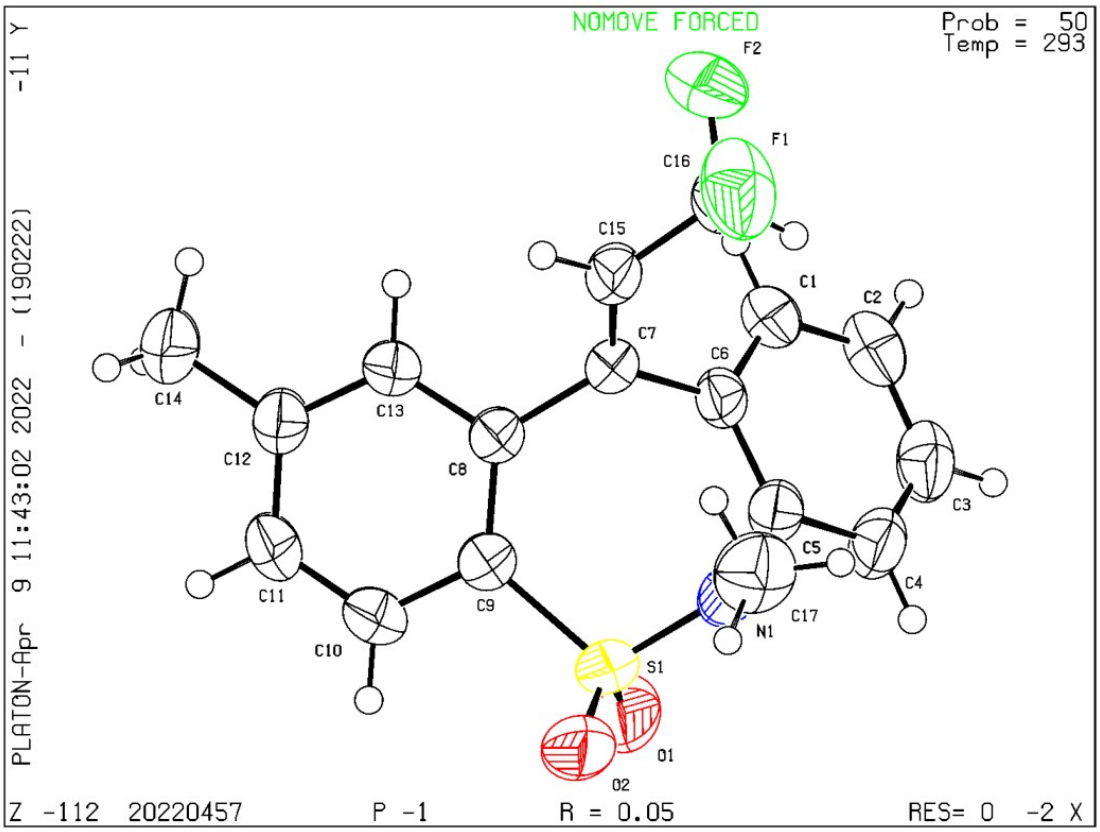


Figure S8. X-ray crystal structure of **3a** with the ellipsoid contour at 50% probability levels

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

Identification code	**3a**
Empirical formula	$C_{17}H_{15}F_2NO_2S$
Formula weight	335.36
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.2517(11)
b/Å	9.8720(12)
c/Å	10.8789(13)
α/°	110.880(11)
β/°	93.478(10)
γ/°	100.696(11)
Volume/Å^3	805.82(18)
Z	2
ρ_{calc}g/cm^3	1.382
μ/mm^{-1}	2.056
F(000)	348.0
Crystal size/mm^3	0.13×0.11×0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.784 to 134.098
Index ranges	-9≤h≤9, -10≤k≤11, -11≤l≤12

Reflections collected	5655
Independent reflections	2869 [R_{int}=0.0278, R_{sigma}=0.0421]
Data/restraints/parameters	2869/0/210
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0494, wR_2 = 0.1286
Final R indexes [all data]	R_1 = 0.0671, wR_2 = 0.1457
Largest diff. peak/hole / e $Å^{-3}$	0.19/-0.34

8.2 X-ray crystallographic data of 5a

The product **5a** was recrystallized from petroleum ether/ethyl acetate. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC**2201068**.

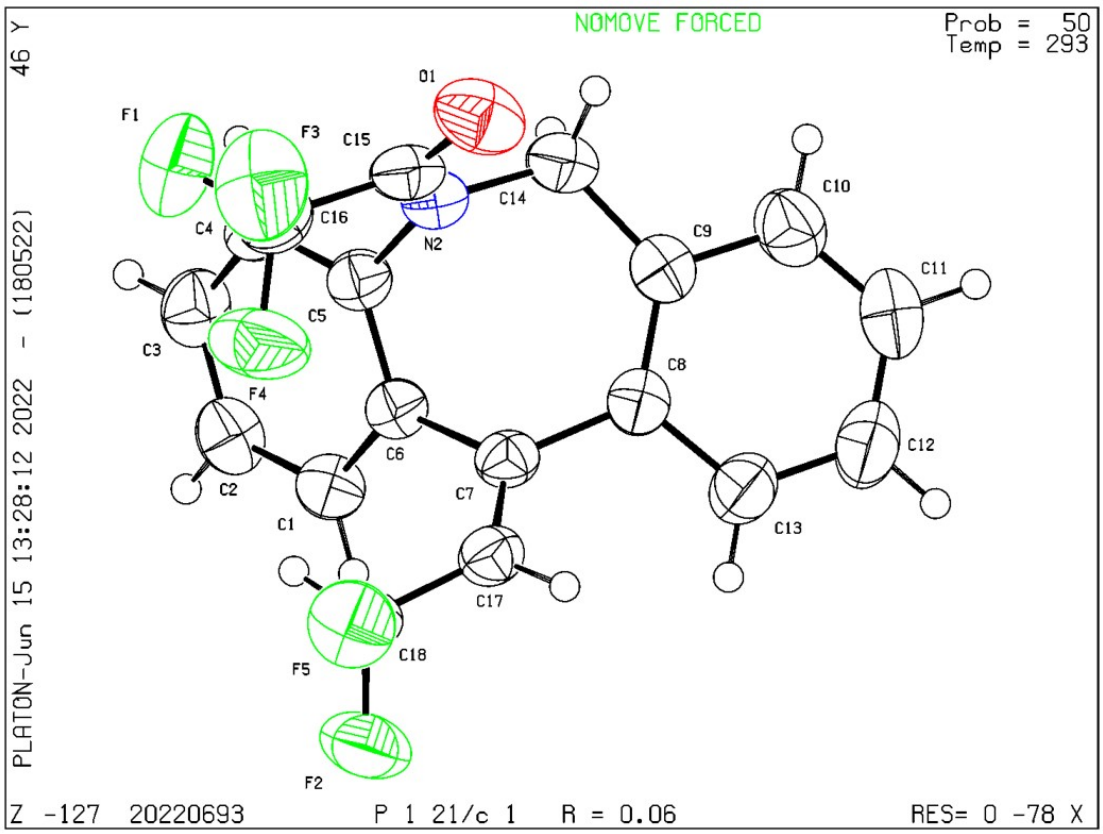


Figure S9. X-ray crystal structure of **5a** with the ellipsoid contour at 50% probability levels

Table S2. Crystal data and structure refinement for **5a**.

Identification code	**5a**
Empirical formula	$C_{18}H_{12}F_5NO$
Formula weight	353.29
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.5281(4)

b/Å	9.1272(5)
c/Å	19.9962(11)
α/°	90
β/°	90.685(5)
γ/°	90
Volume/Å^3	1556.34(15)
Z	4
ρ_{calc}g/cm^3	1.508
μ/mm^{-1}	1.180
F(000)	720.0
Crystal size/mm^3	0.14 × 0.1 × 0.08
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.654 to 134.132
Index ranges	-10≤h≤9, -10≤k≤5, -23≤l≤23
Reflections collected	5681
Independent reflections	2760 [Rint = 0.0331, Rsigma = 0.0460]
Data/restraints/parameters	2760/0/227
Goodness-of-fit on F^2	1.016
Final R indexes [I>=2σ (I)]	R1 = 0.0567, wR2 = 0.1488
Final R indexes [all data]	R1 = 0.0746, wR2 = 0.1723
Largest diff. peak/hole / e Å^{-3}	0.30/-0.24

9. References

[1] (a) Z.-Q. Zhang, Y.-H. Xu, J.-C. Dai, Y. Li, J. Sheng and X.-S. Wang, Copper-catalyzed trifluoromethylation/cyclization of alkynes for synthesis of dioxodibenzothiazepines, *Org. Lett.,* 2021, **23**, 2194-2198; (b) Q. Xiao, M. Lu, Y. Deng, J.-X. Jian, Q.-X. Tong and J.-J. Zhong, Photoinduced radical cascade cyclization: A metal-free approach to access difluoroalkylated dioxodibenzothiazepines, *Org. Lett.,* 2021, **23**, 9303-9308. (c) P. Xiong, H.-H. Xu, J. Song and H.-C. Xu, Electrochemical difluoromethylarylation of alkynes, *J. Am. Chem. Soc.,* 2018, **140***,* 2460-2464.

[2] (a) Z. Feng, B. Zhu, B. Dong, L. Cheng, Y. Li, Z. Wang and J. Wu, Visible-light-promoted synthesis of α-CF_2H-substituted ketones by radical difluoromethylation of enol acetates, *Org. Lett*. 2021, **23**, 508-513; (b) E, S. Higashi, J. L. Zhang, X. C. Cambeiro and S. Arseniyadis, Synthesis of α-difluoromethyl aryl ketones through a photoredox difluoromethylation of enol silanes, *Org. Lett.* 2021, **23**, 4239-4243.

[3] X. Chen, B. Liu, C. Pei, J. Li, D. Zou, Y. Wu and Y. Wu, Visible-light-induced radical difluoromethylation/cyclization of unactivated alkenes: access to CF_2H-substituted quinazolinones, *Org. Lett.,* 2021, **23**, 7787-7791.

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

10.1 Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of products 3

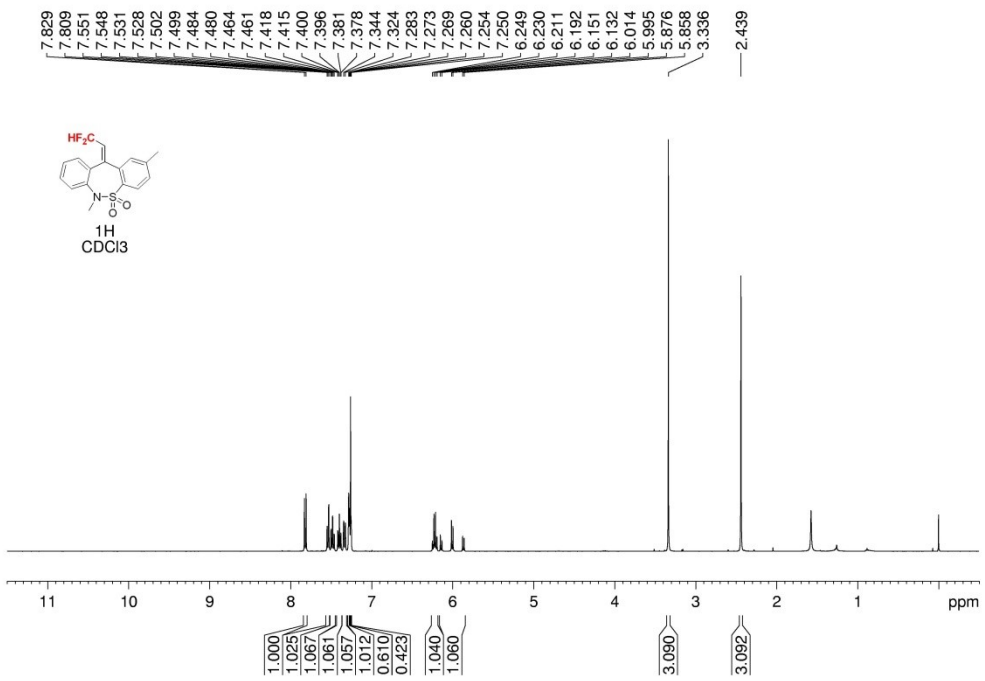


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a**

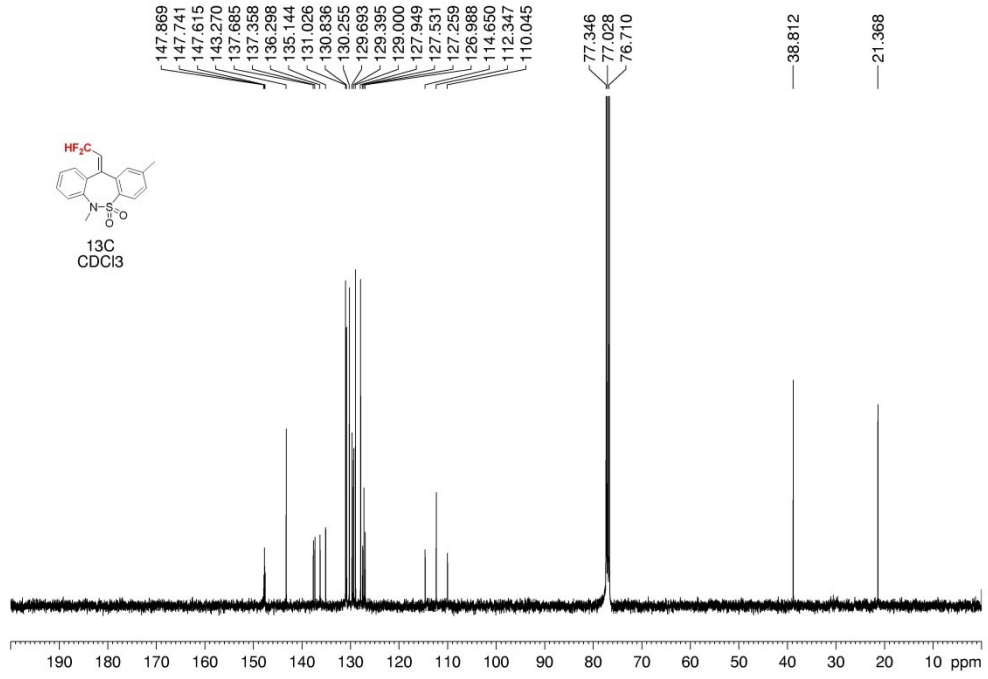


Figure S11. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3a**

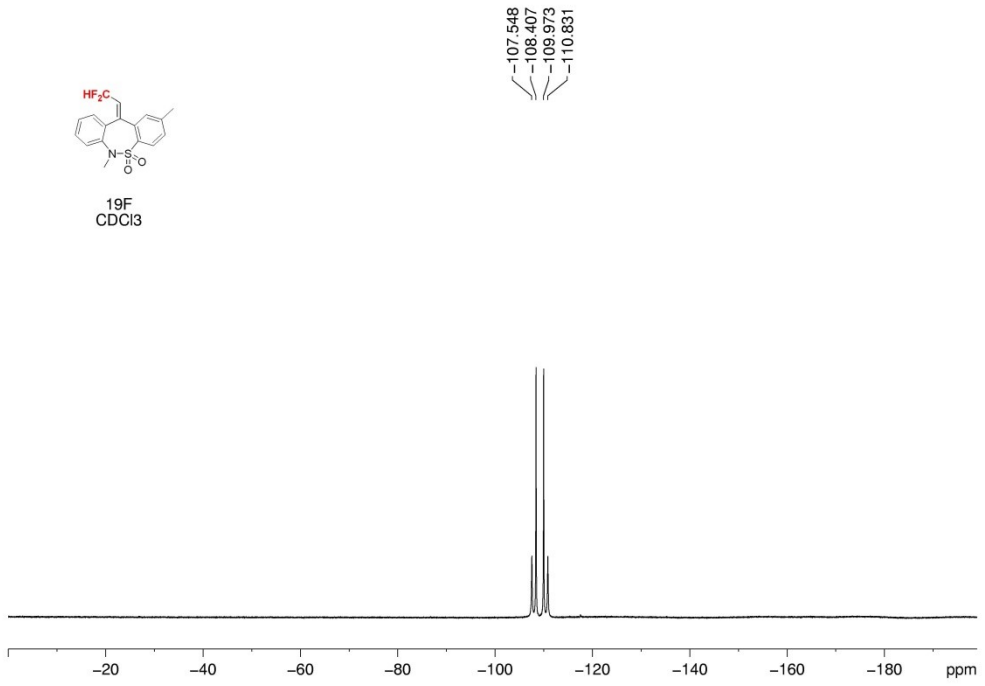


Figure S12. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3a**

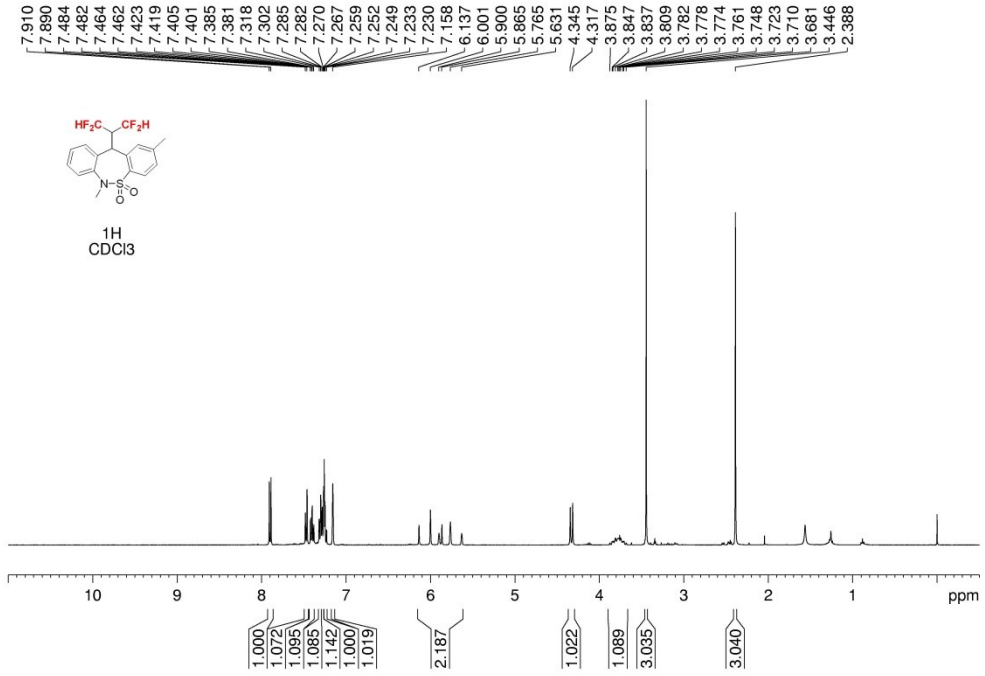


Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3aa**

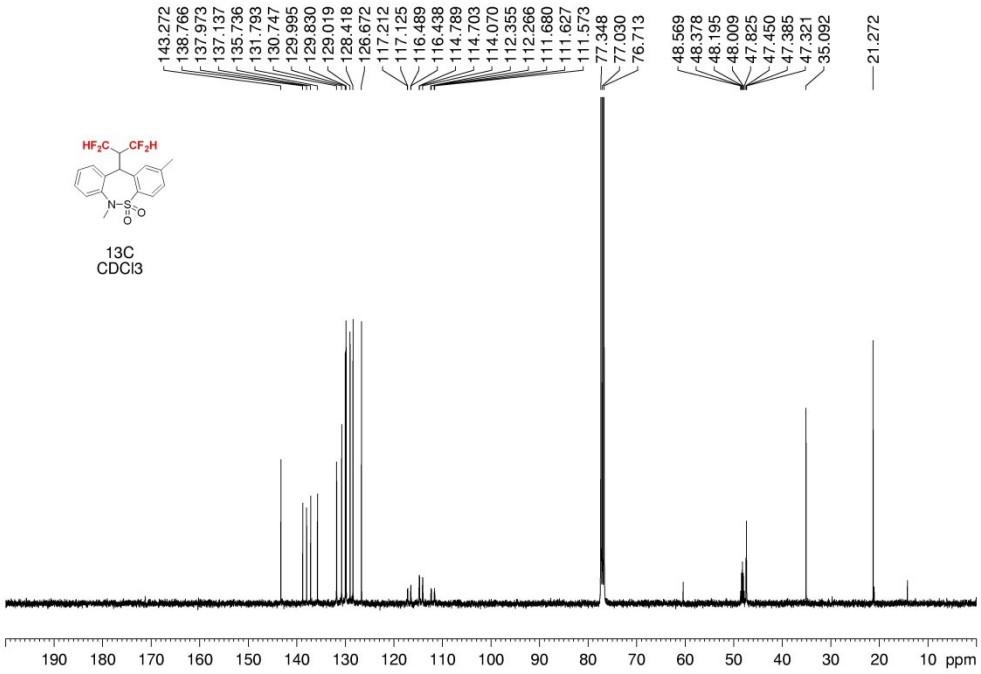


Figure S14. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3aa**

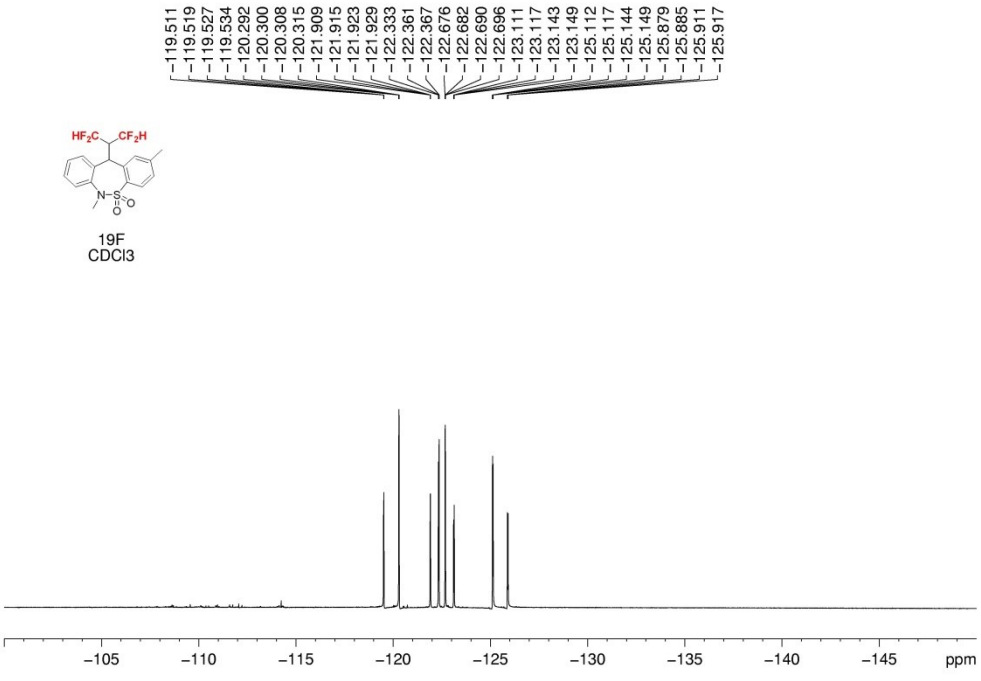


Figure S15. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3aa**

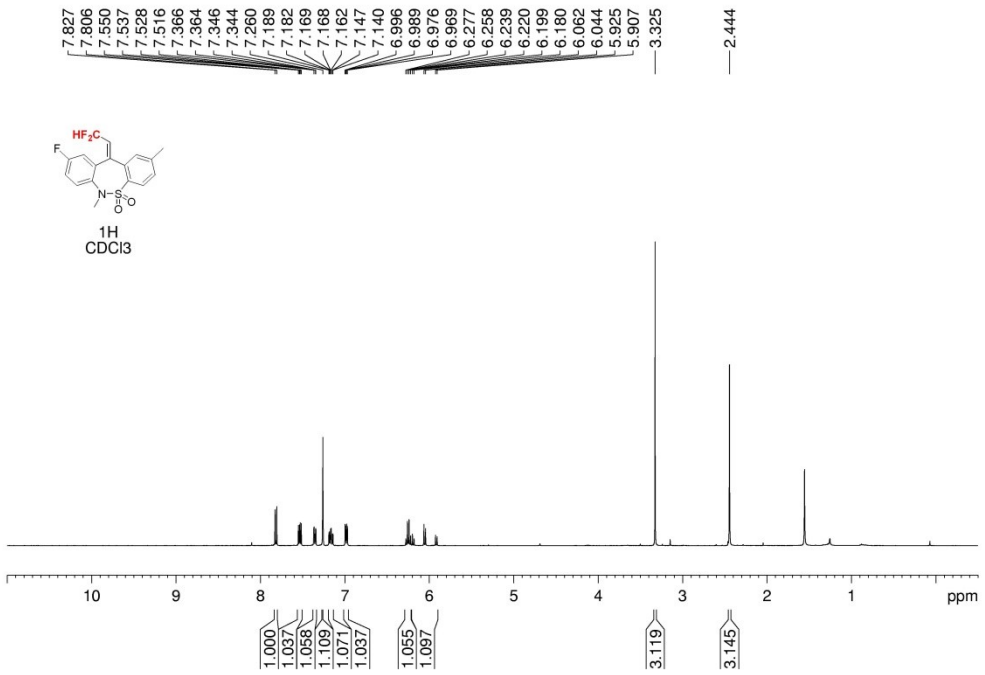


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b**

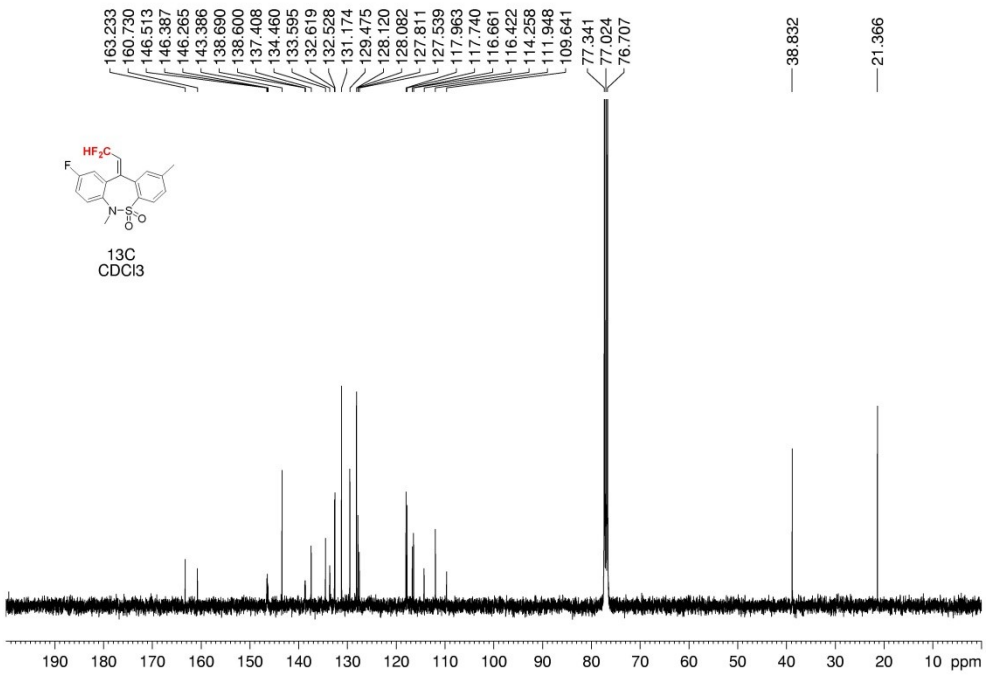


Figure S17. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3b**

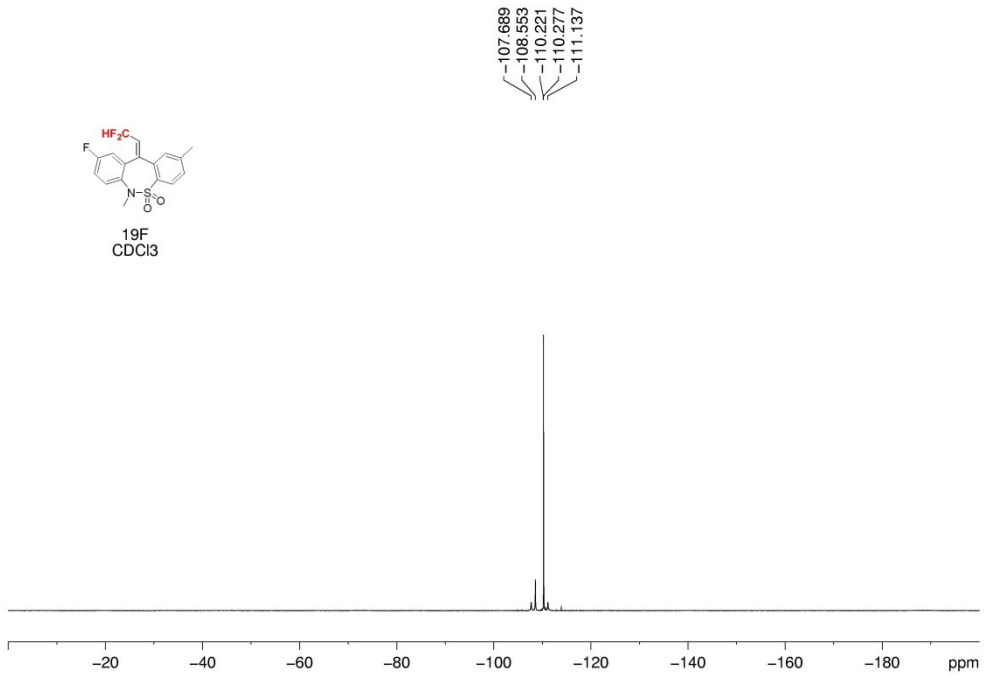


Figure S18. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3b**

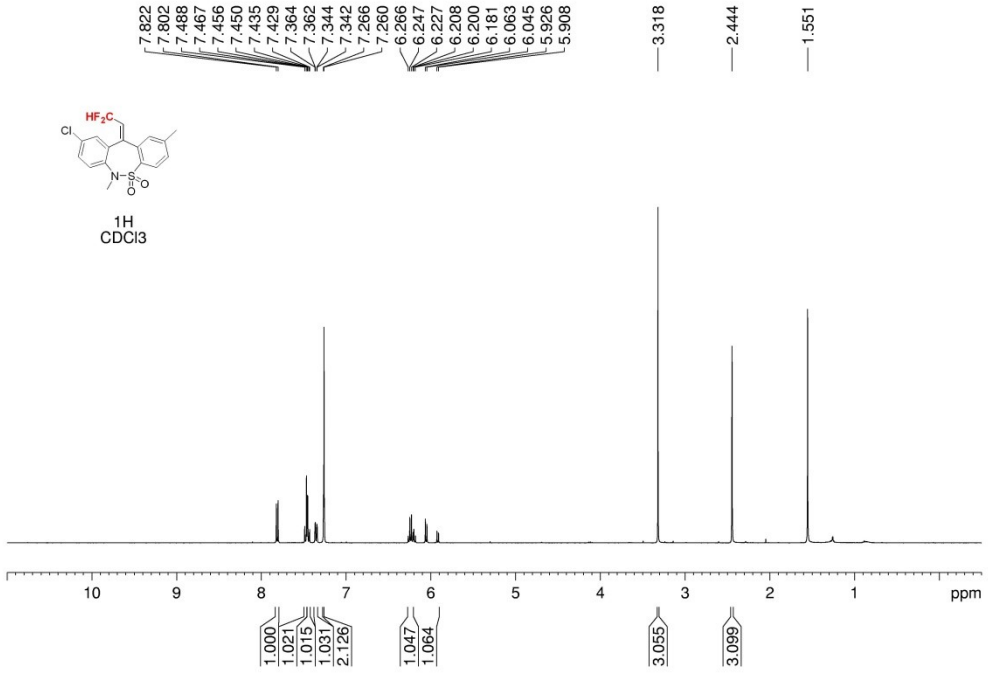


Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3c**

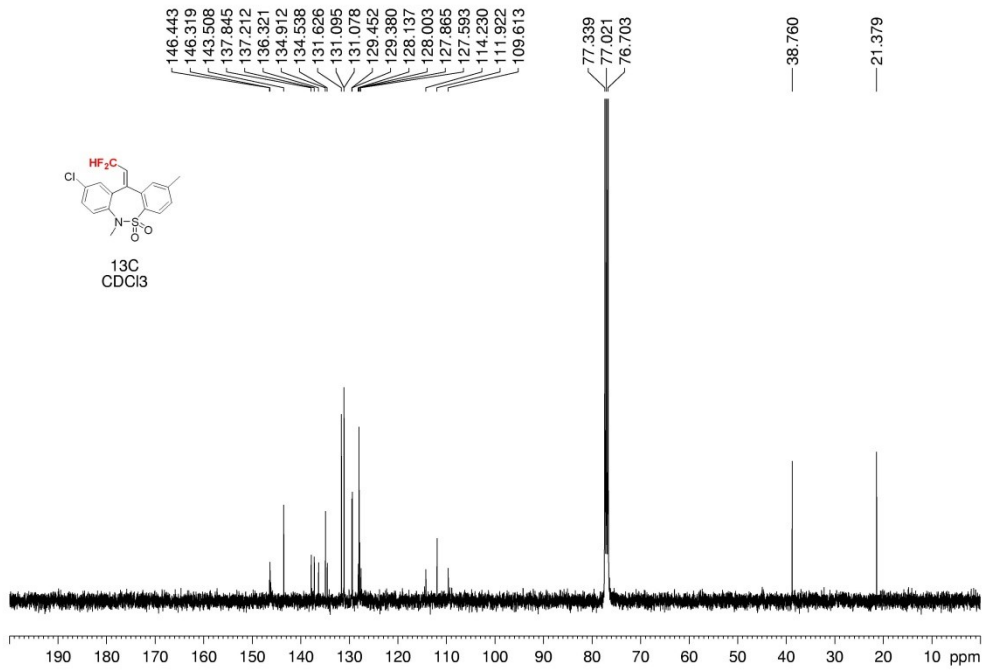


Figure S20. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3c**

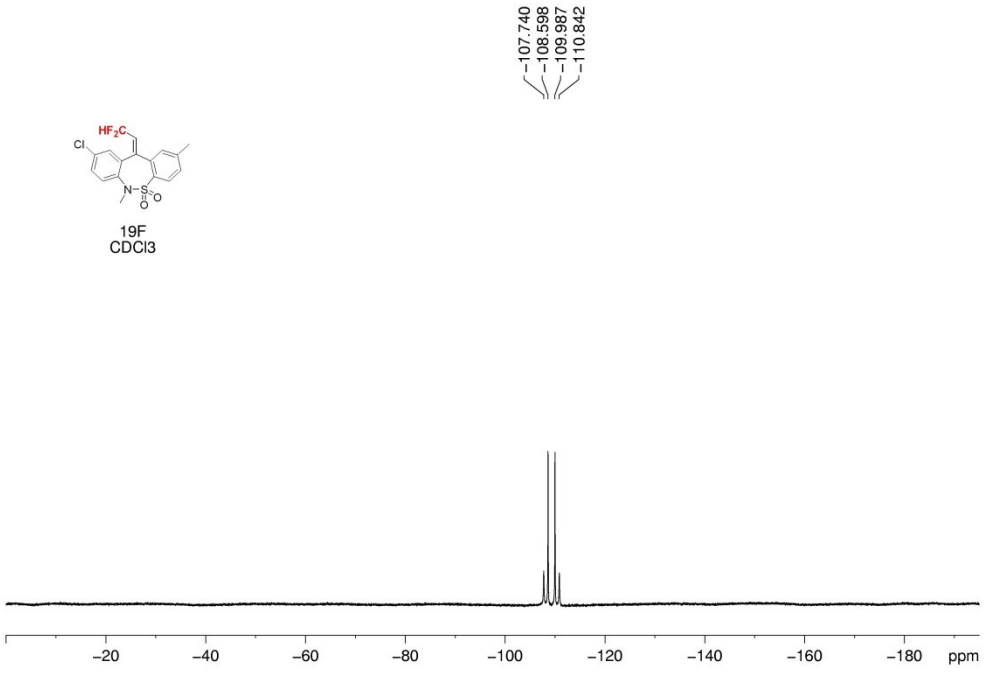


Figure S21. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3c**

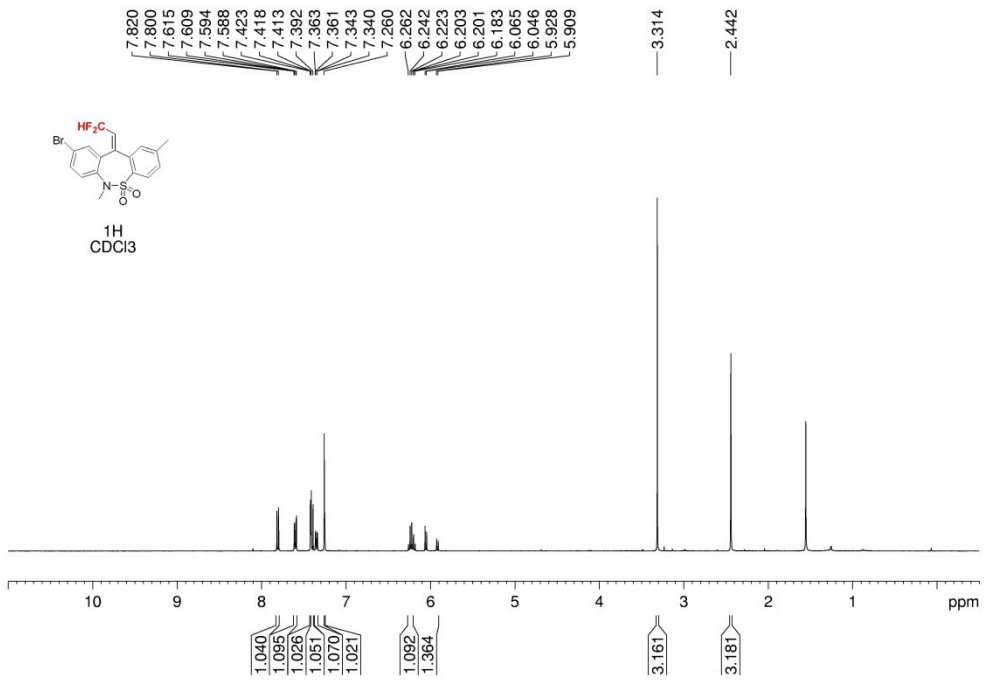


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3d**

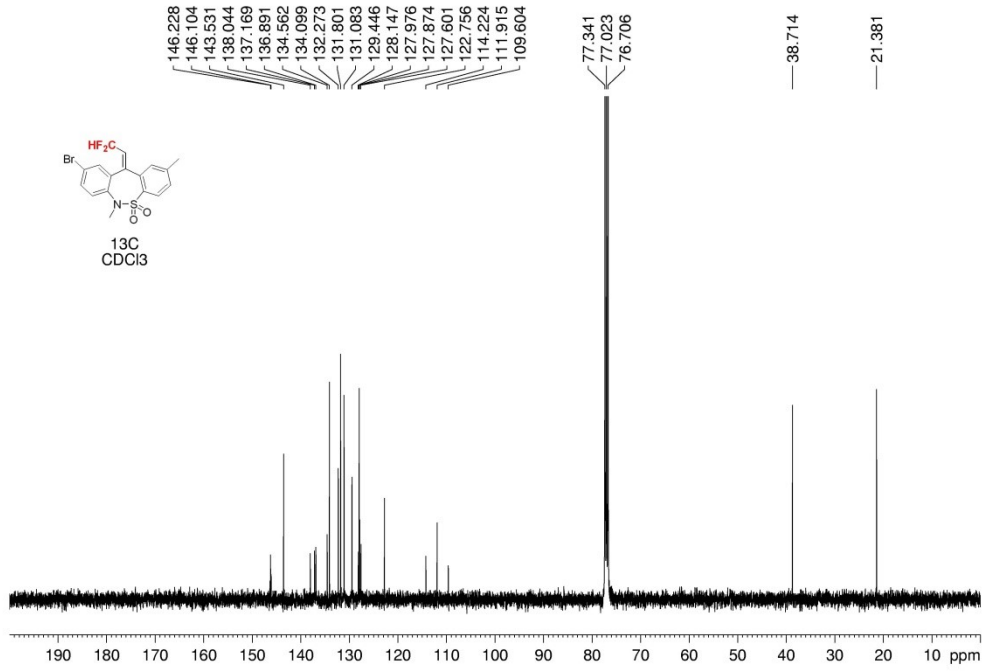


Figure S23. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3d**

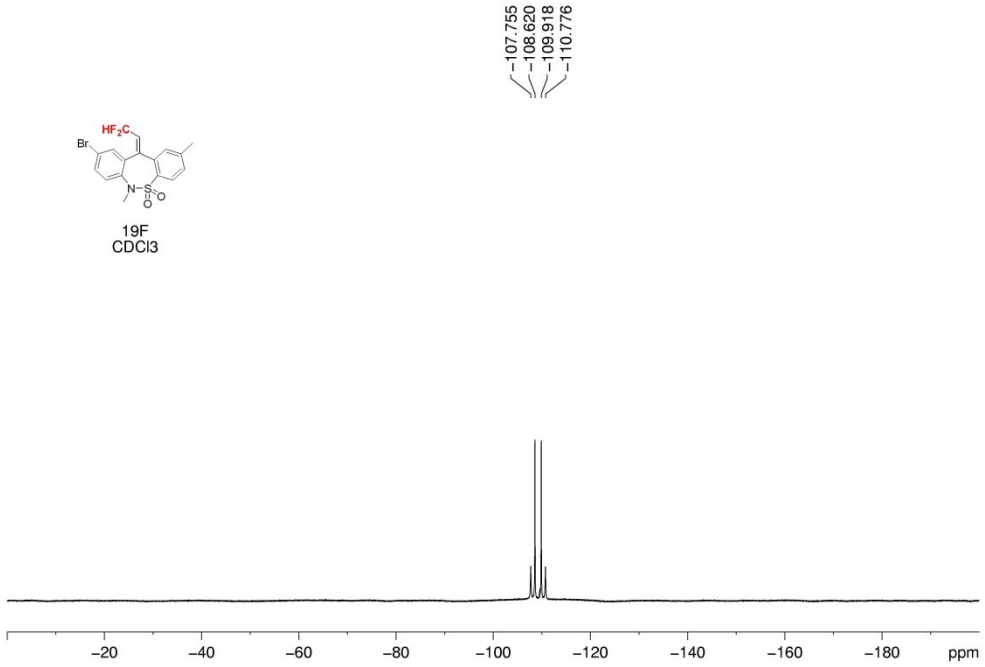


Figure S24. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3d**

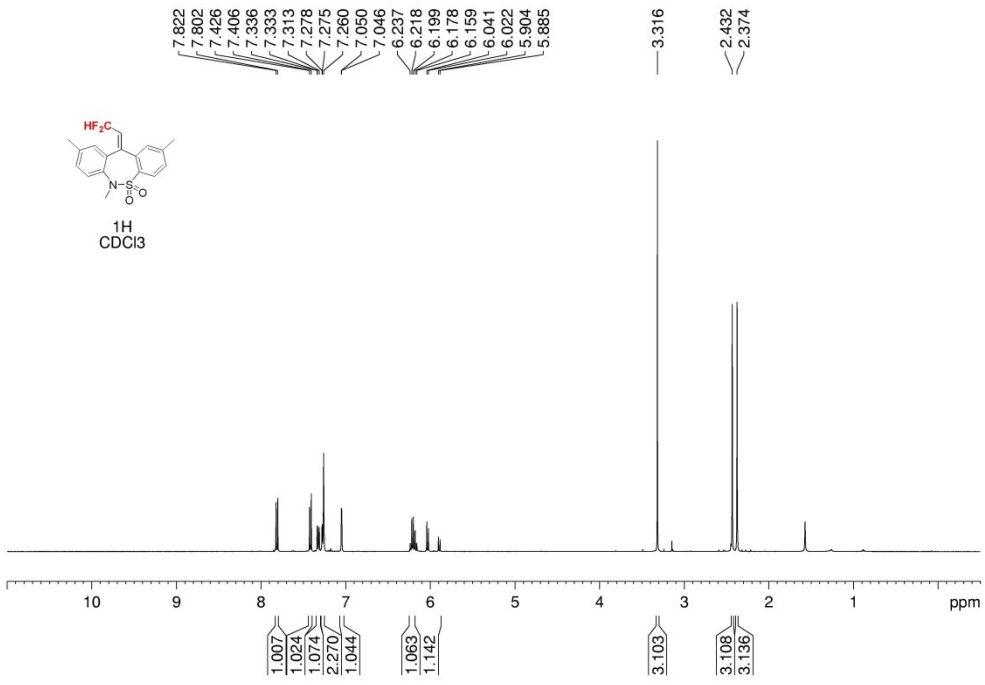


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3e**

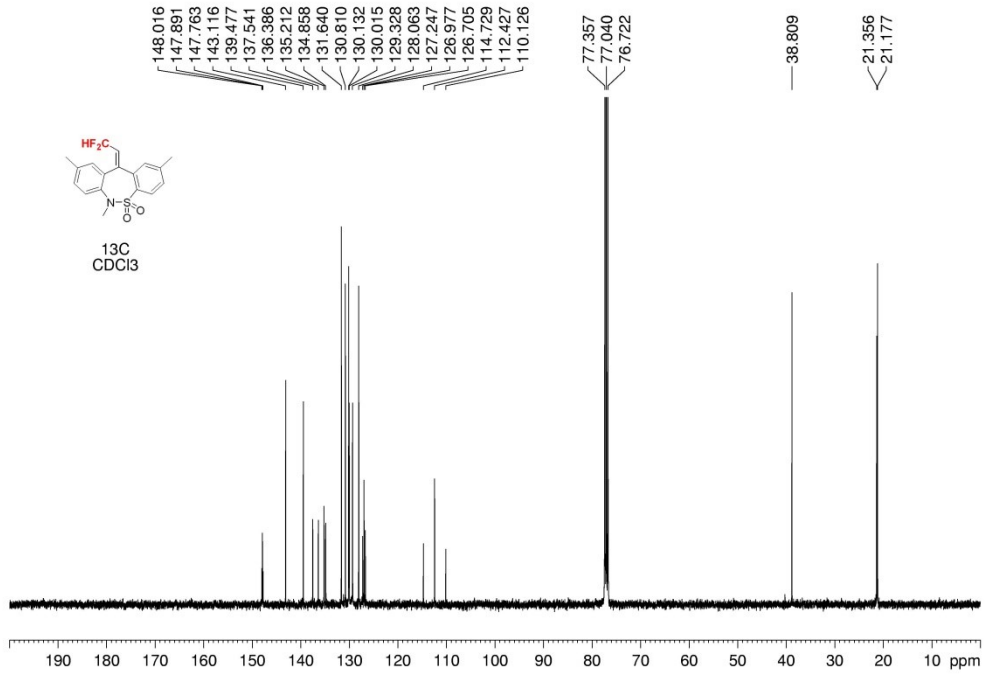


Figure S26. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3e**

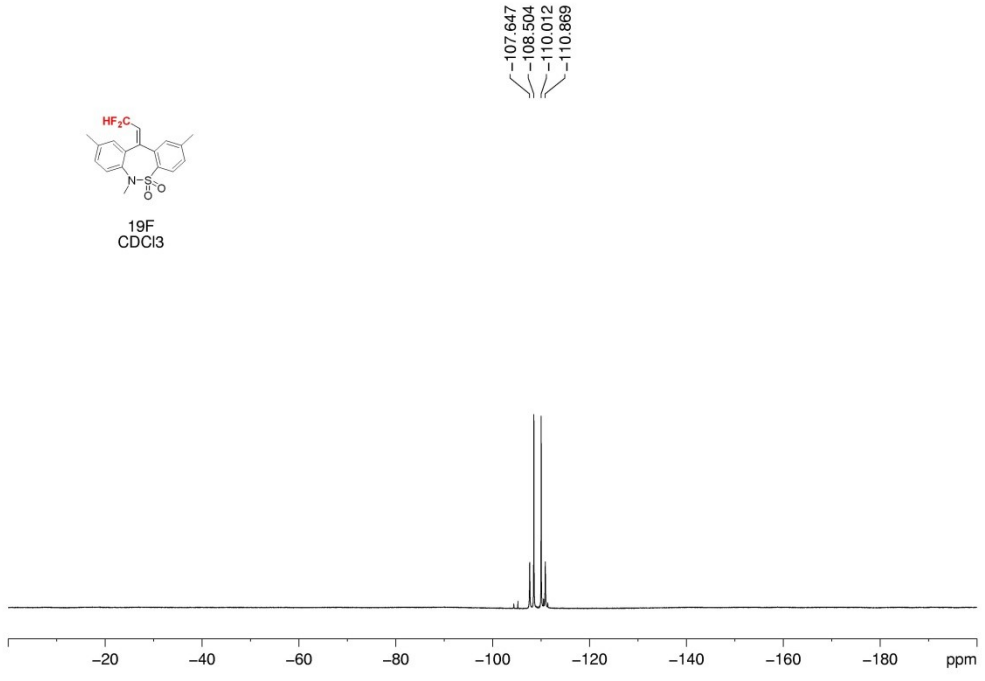


Figure S27. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3e**

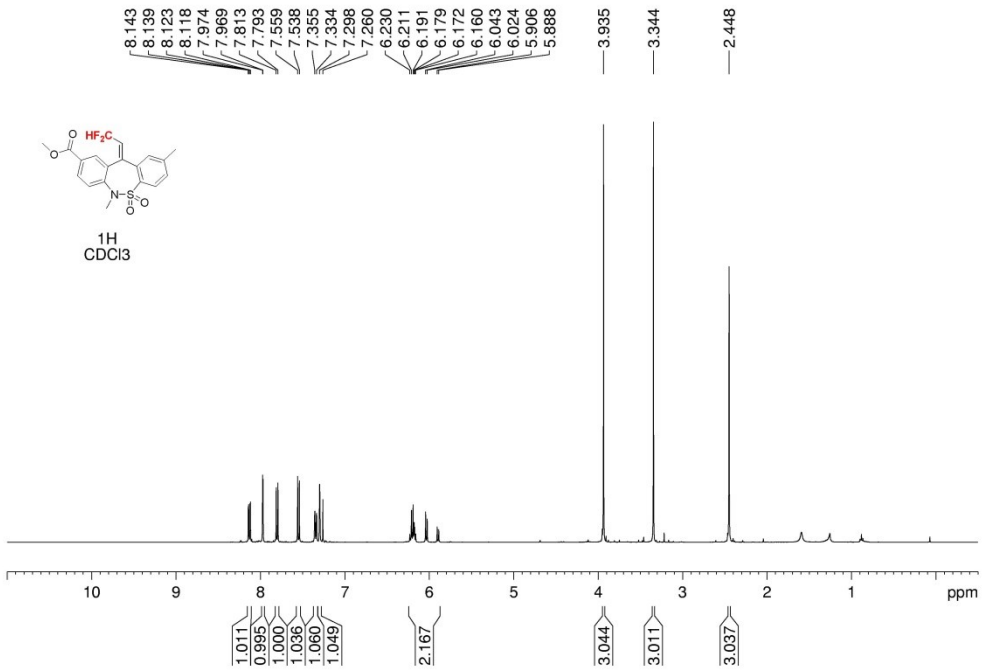


Figure S28. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3f**

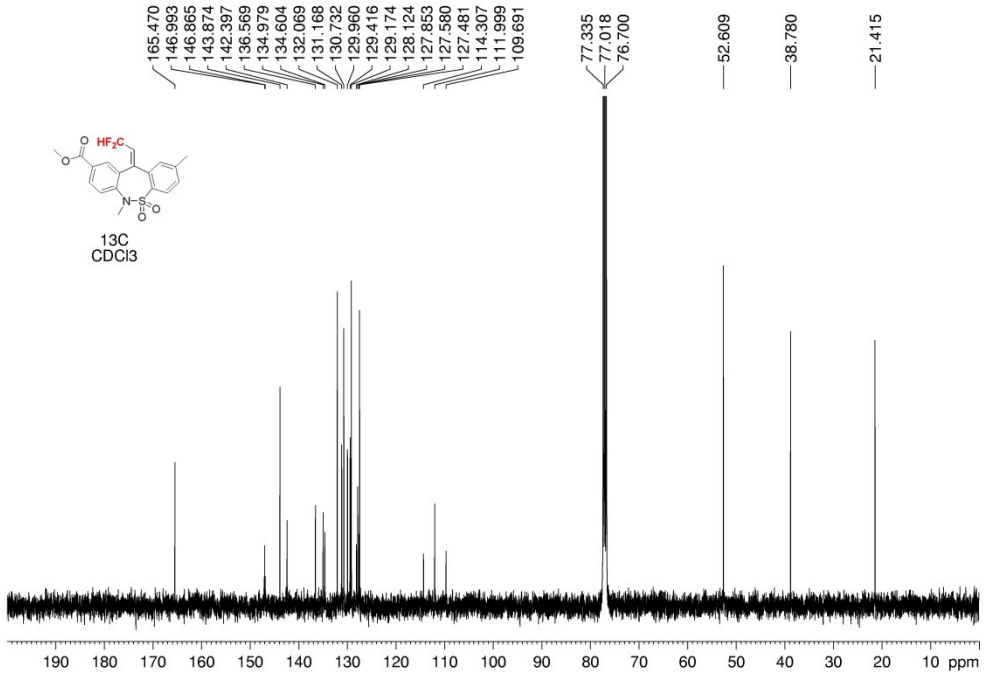


Figure S29. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3f**

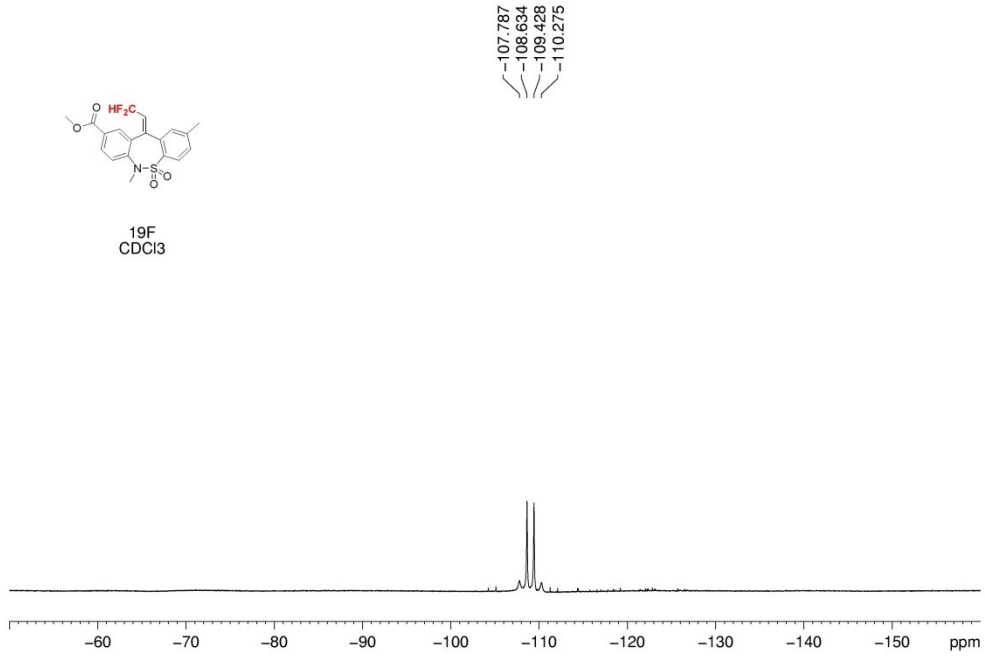


Figure S30. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3f**

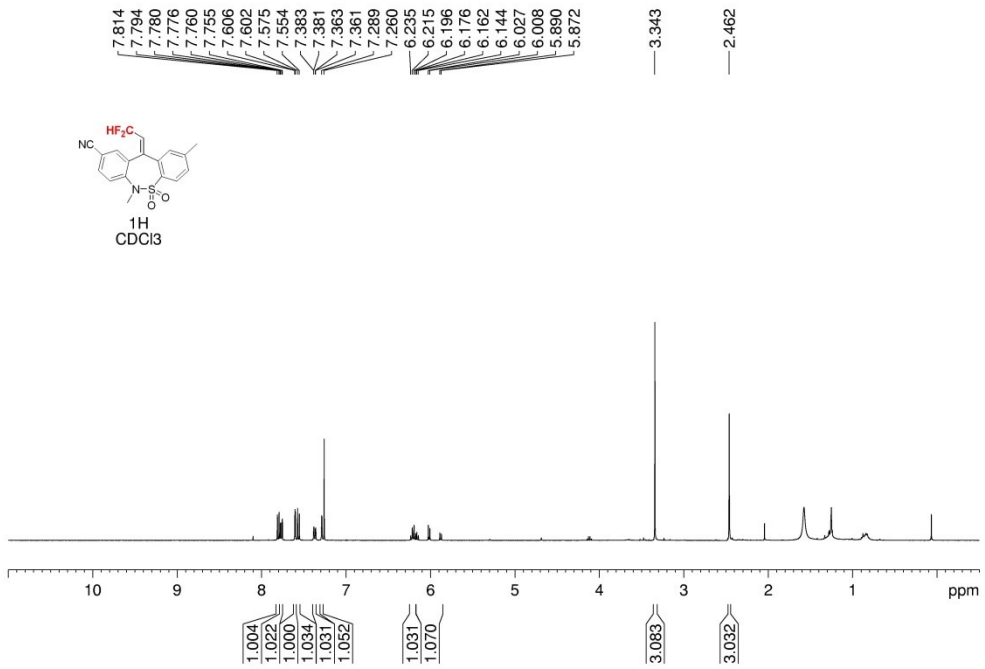


Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3g**

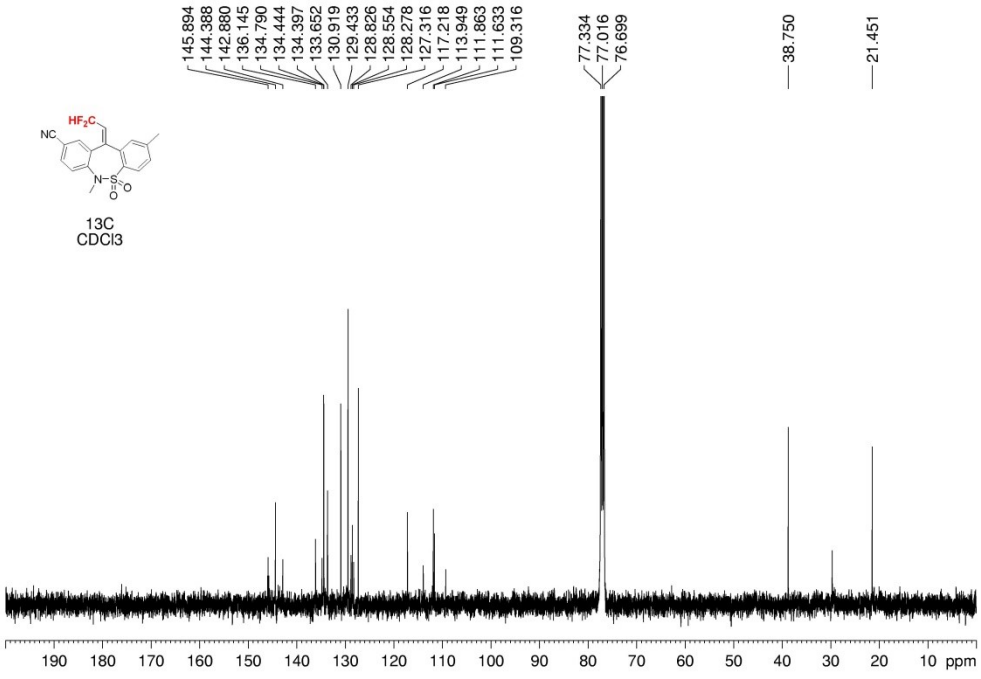


Figure S32. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3g**

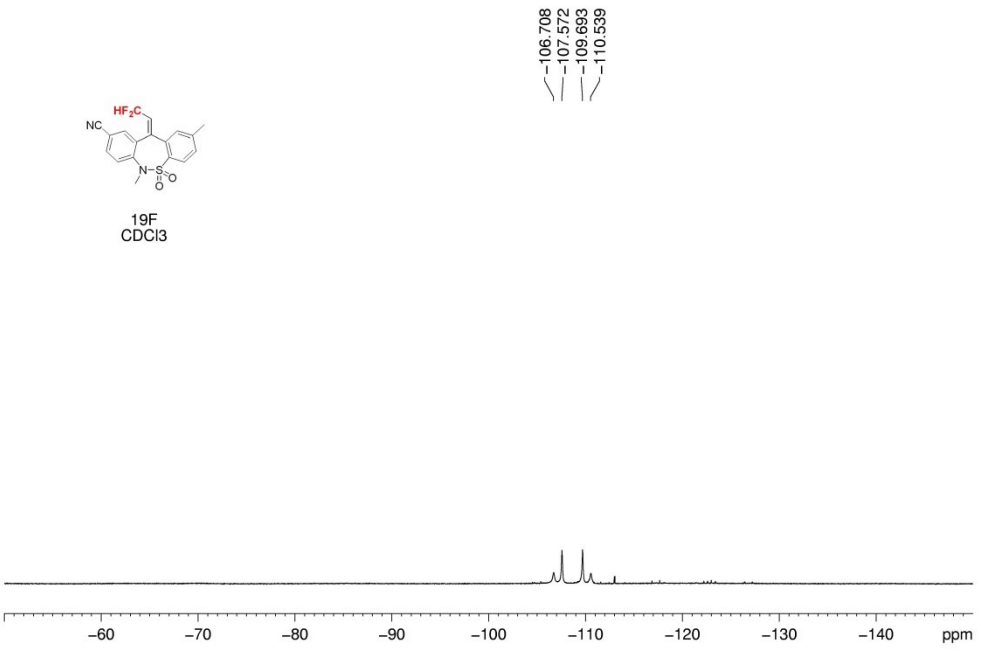


Figure S33. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3g**

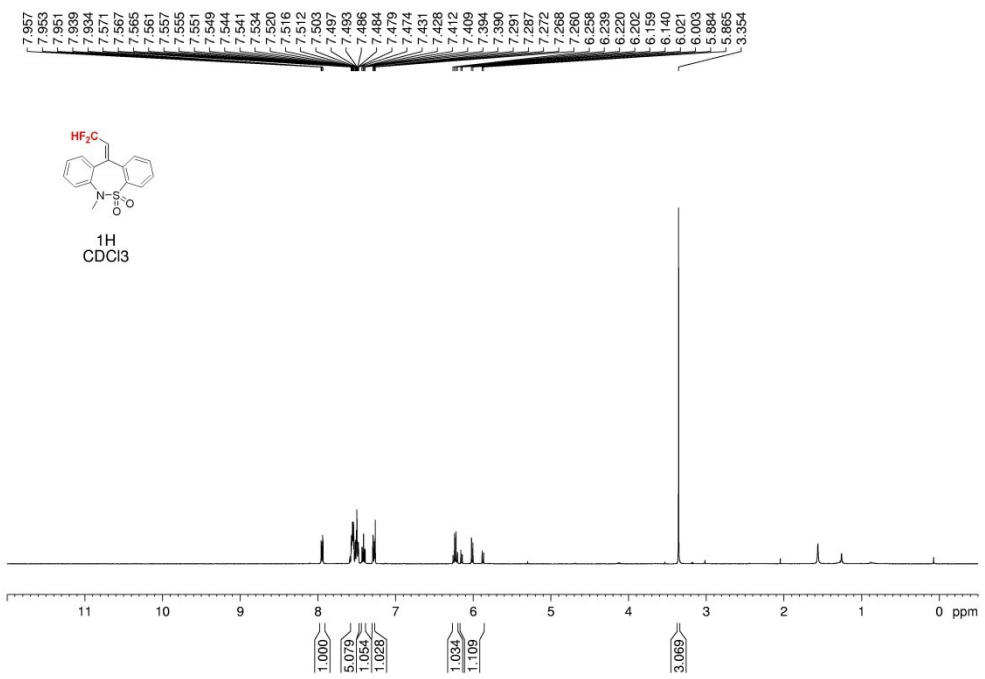


Figure S34. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3h**

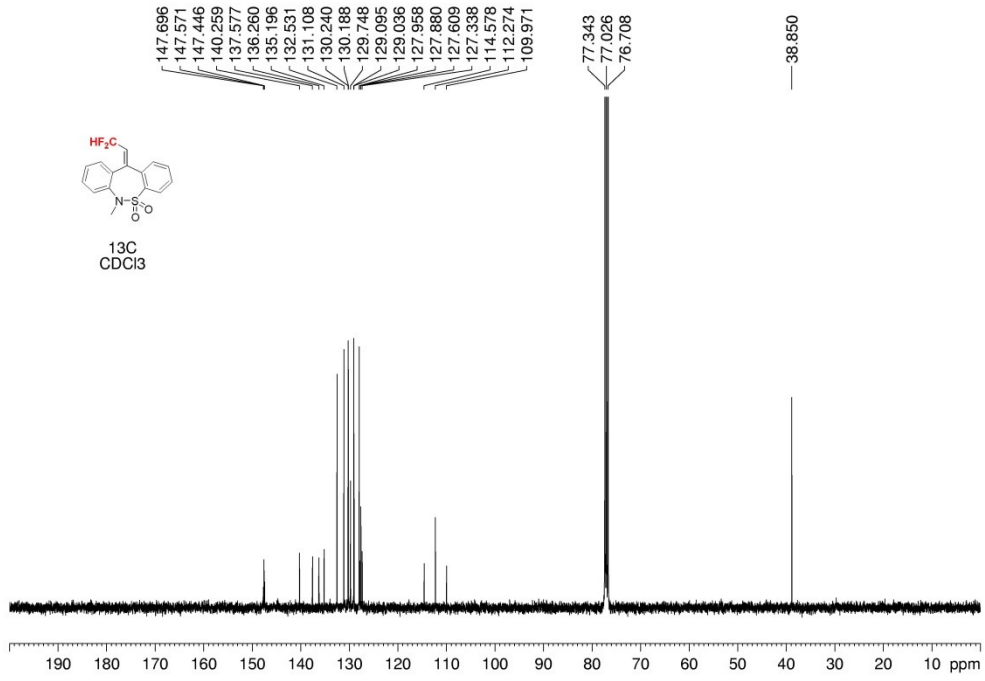


Figure S35. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3h**

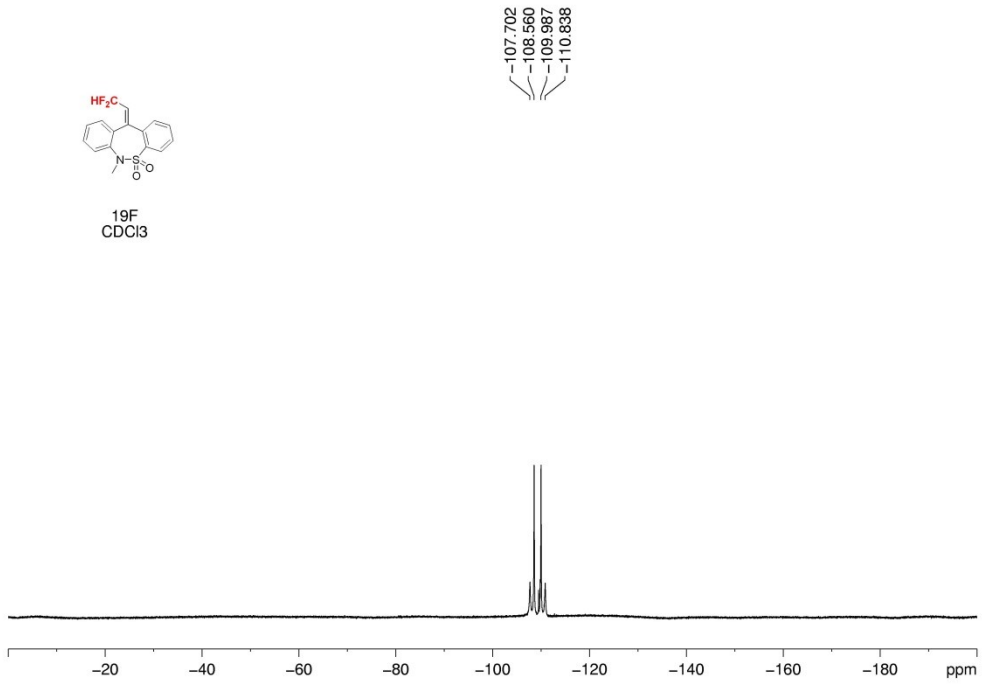


Figure S36. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3h**

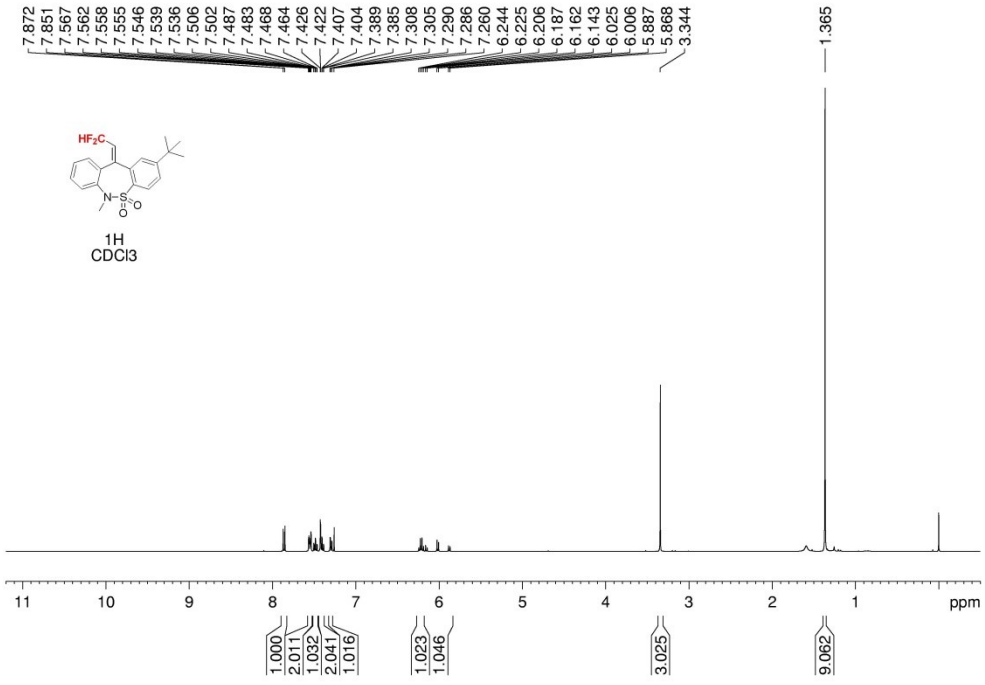


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3i**

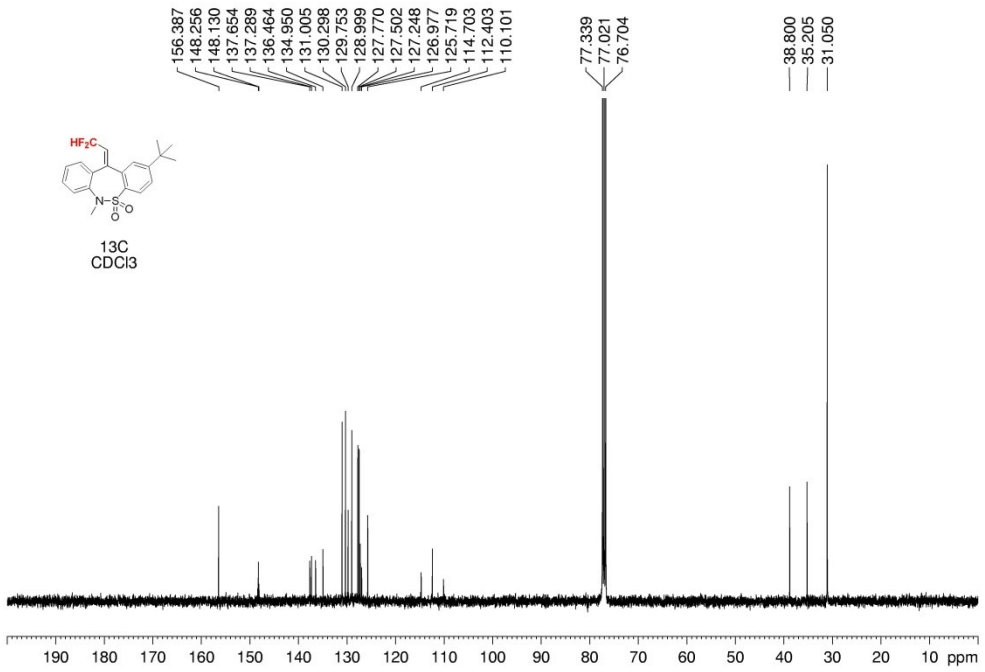


Figure S38. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3i**

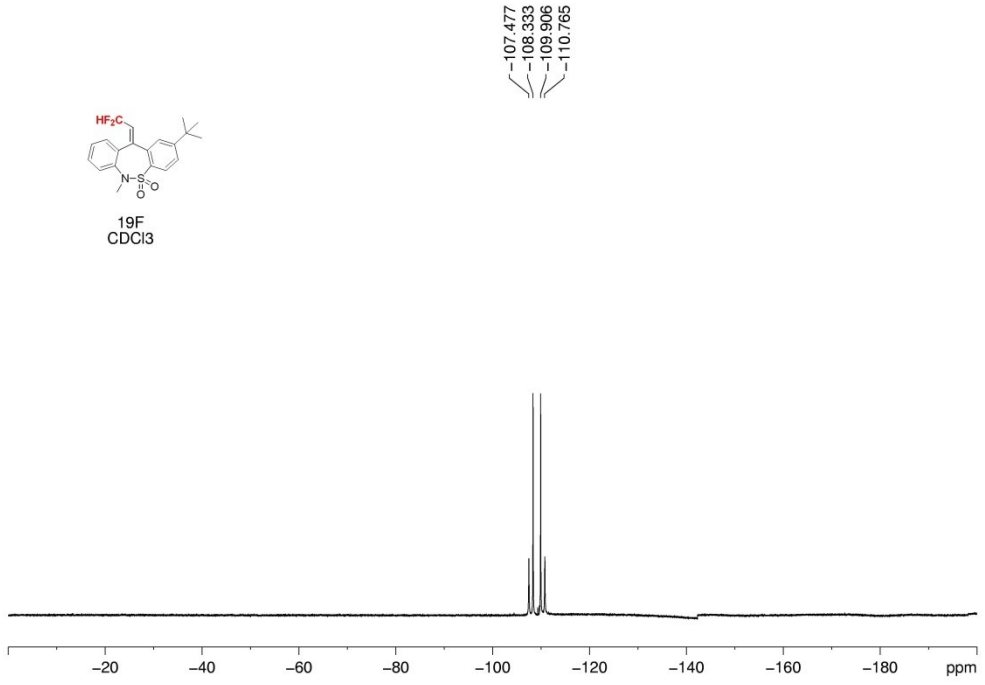


Figure S39. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3i**

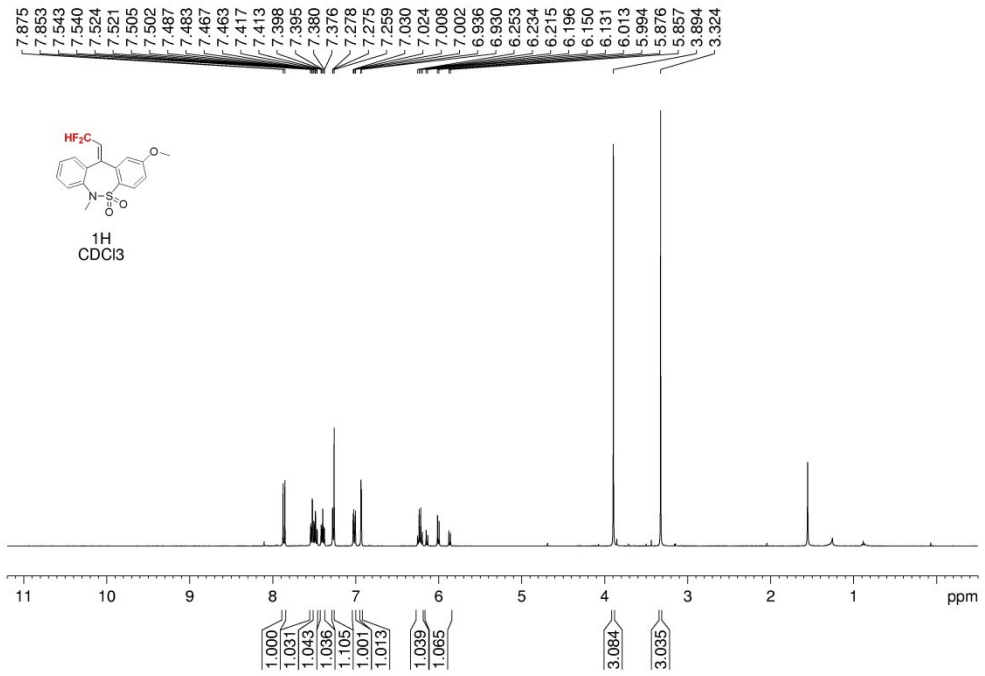


Figure S40. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3j**

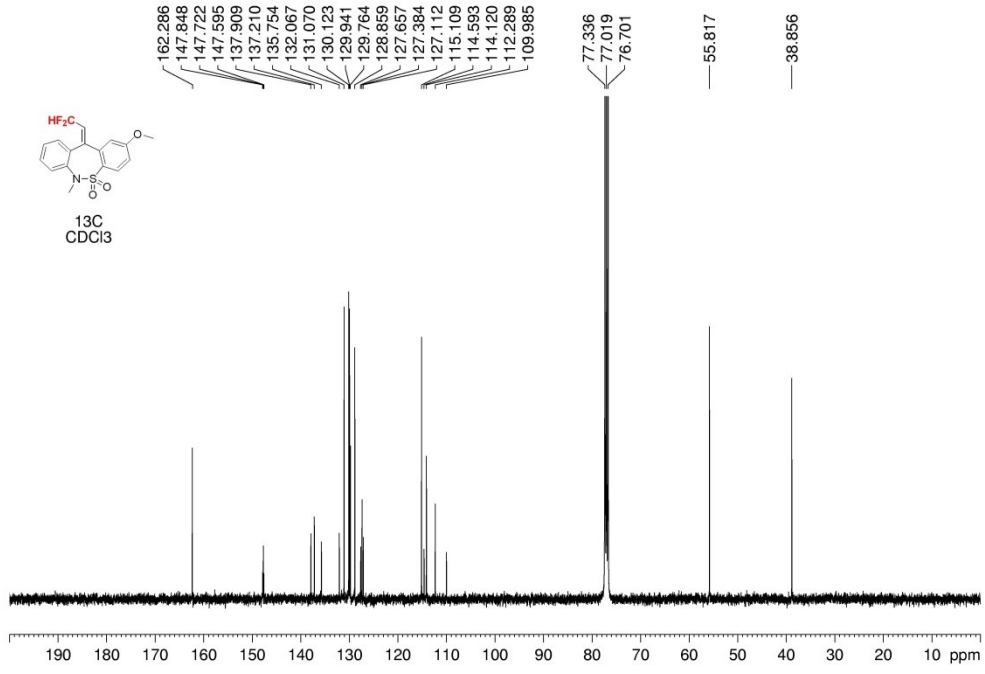


Figure S41. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3j**

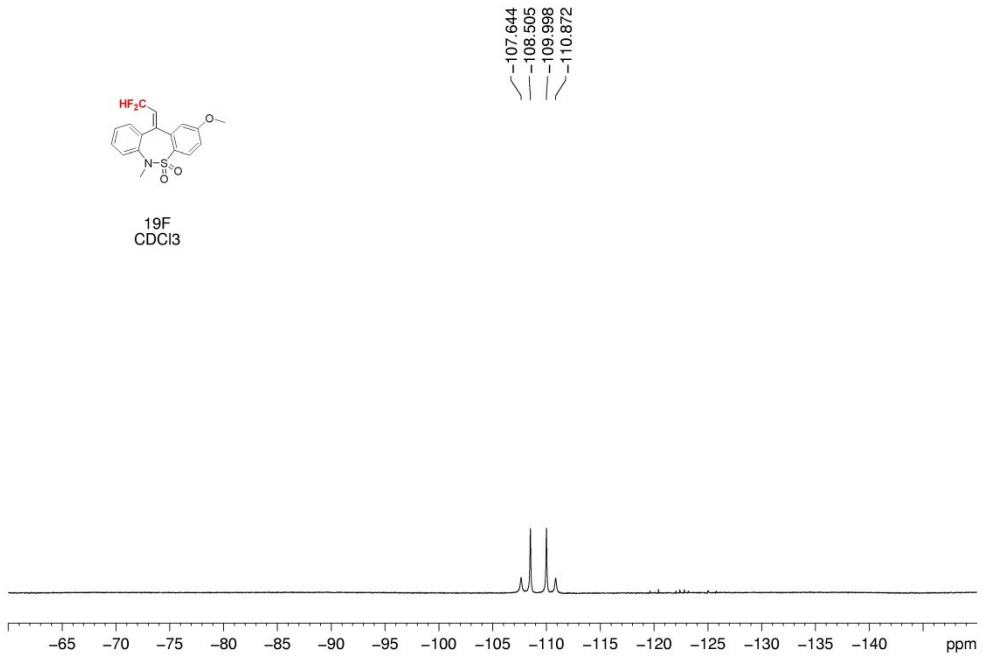


Figure S42. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3j**

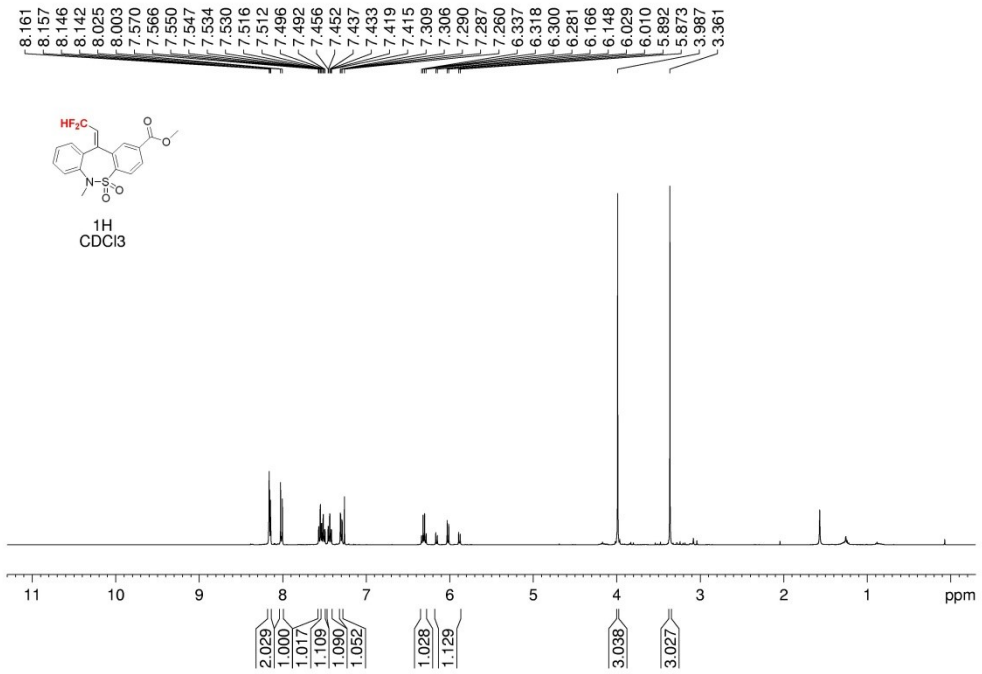


Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3k**

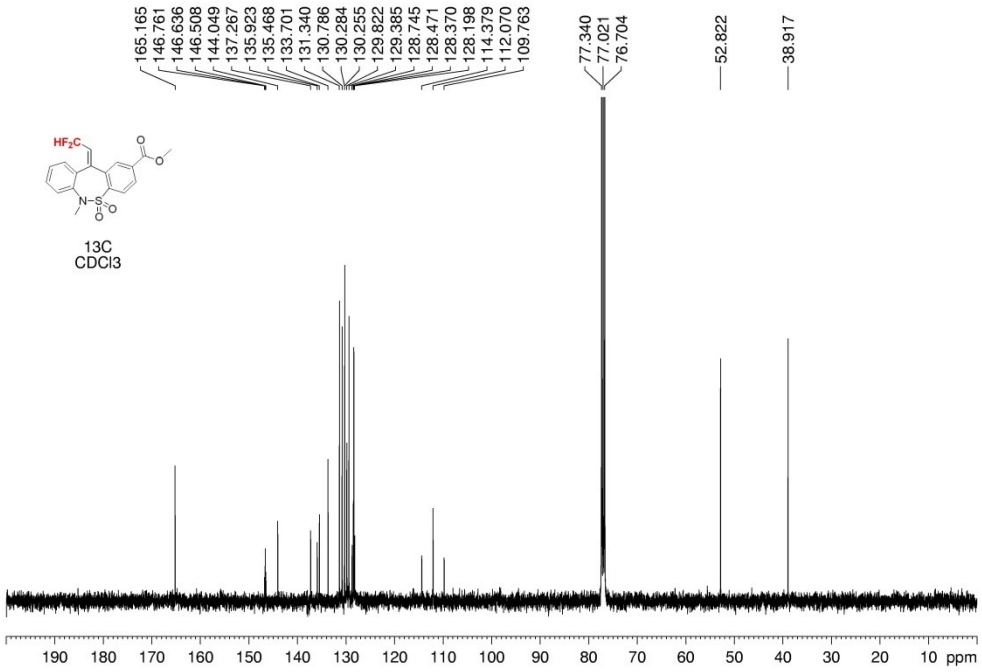


Figure S44. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3k**

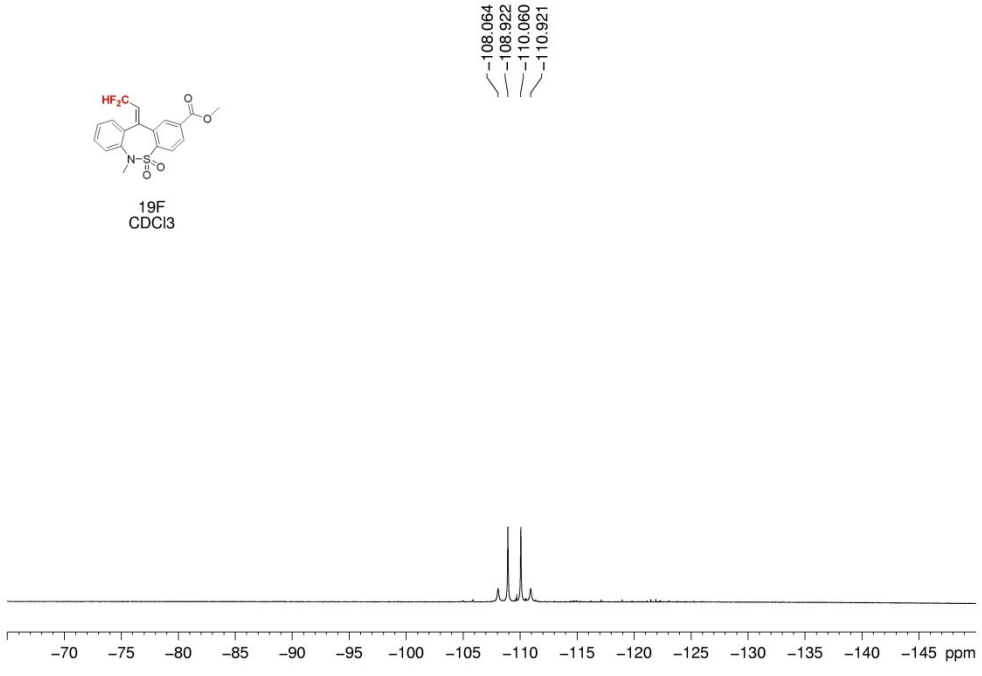


Figure S45. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3k**

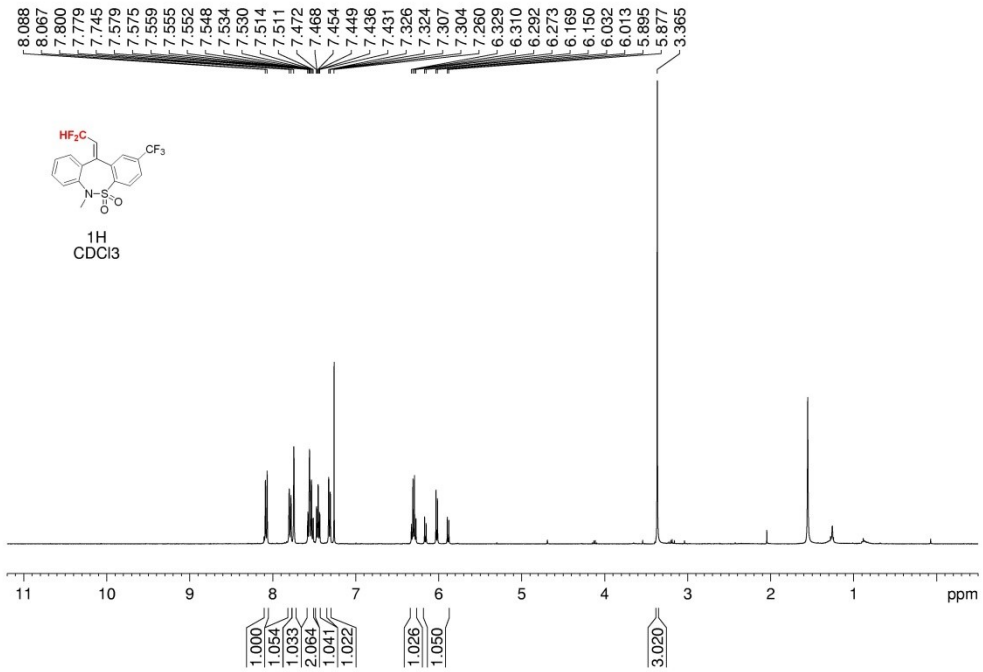


Figure S46. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3l**

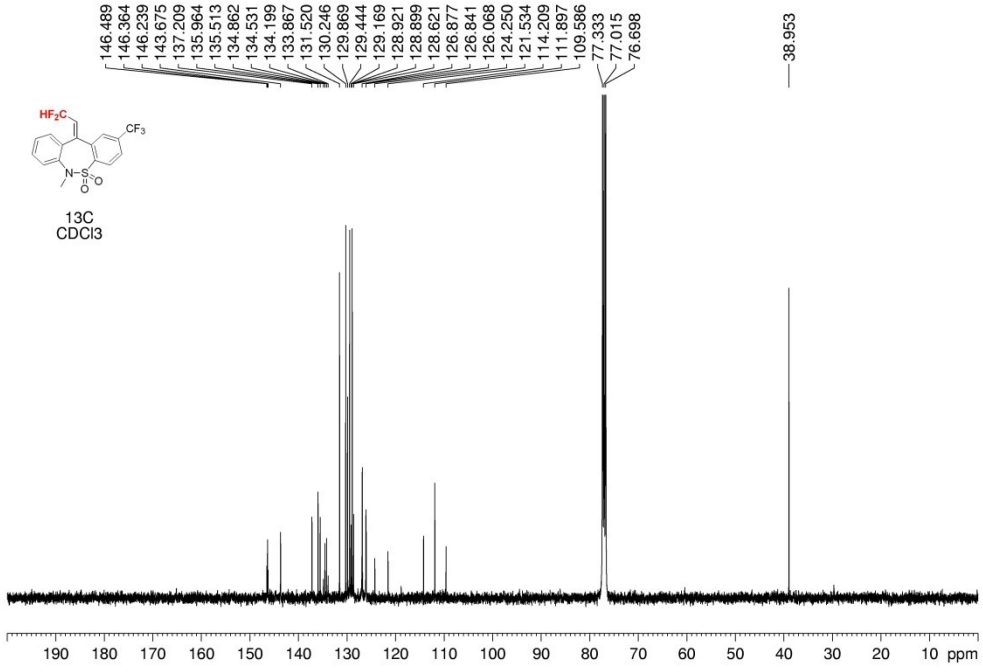


Figure S47. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3l**

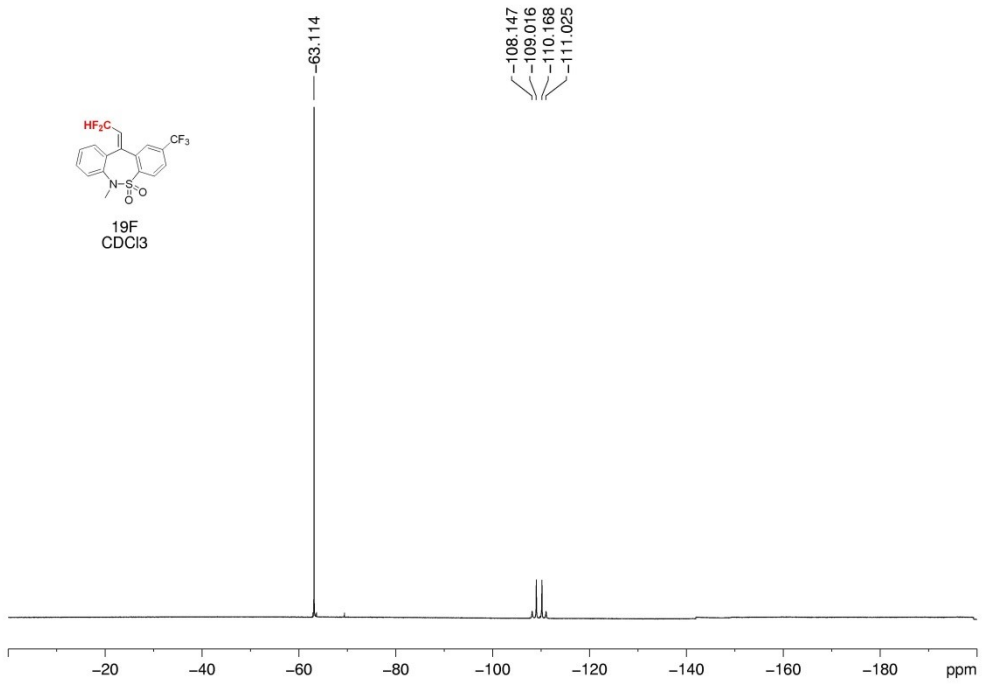


Figure S48. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3l**

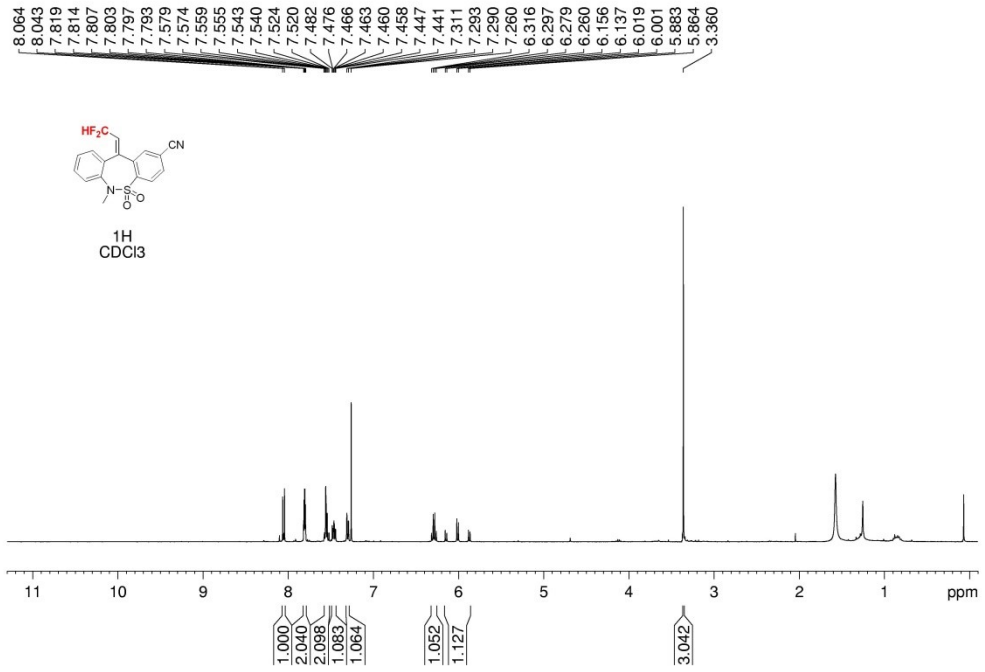


Figure S49. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3m**

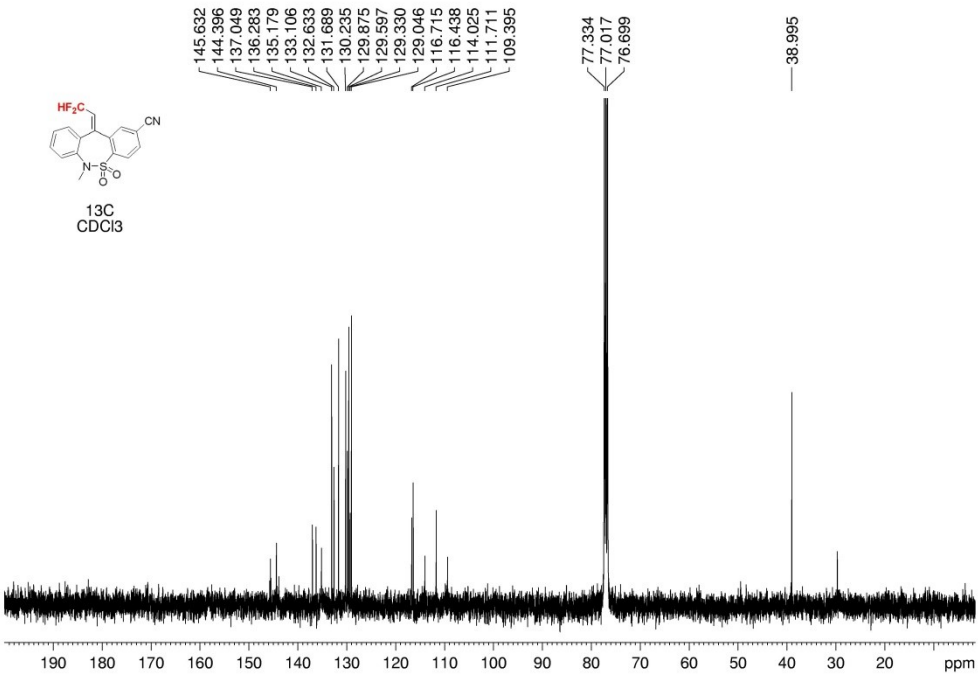


Figure S50. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3m**

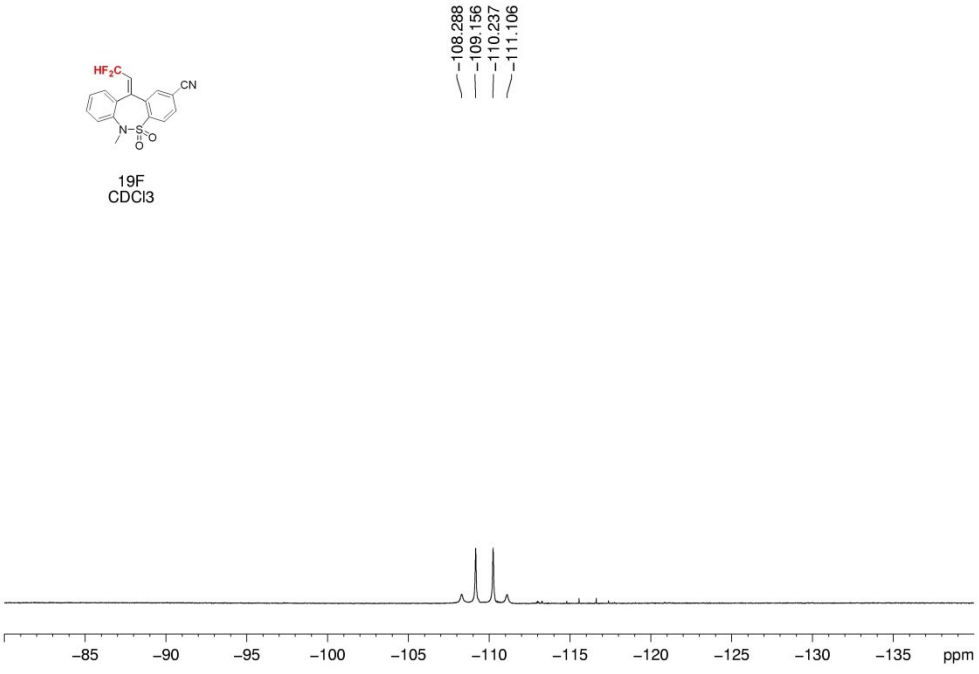


Figure S51. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3m**

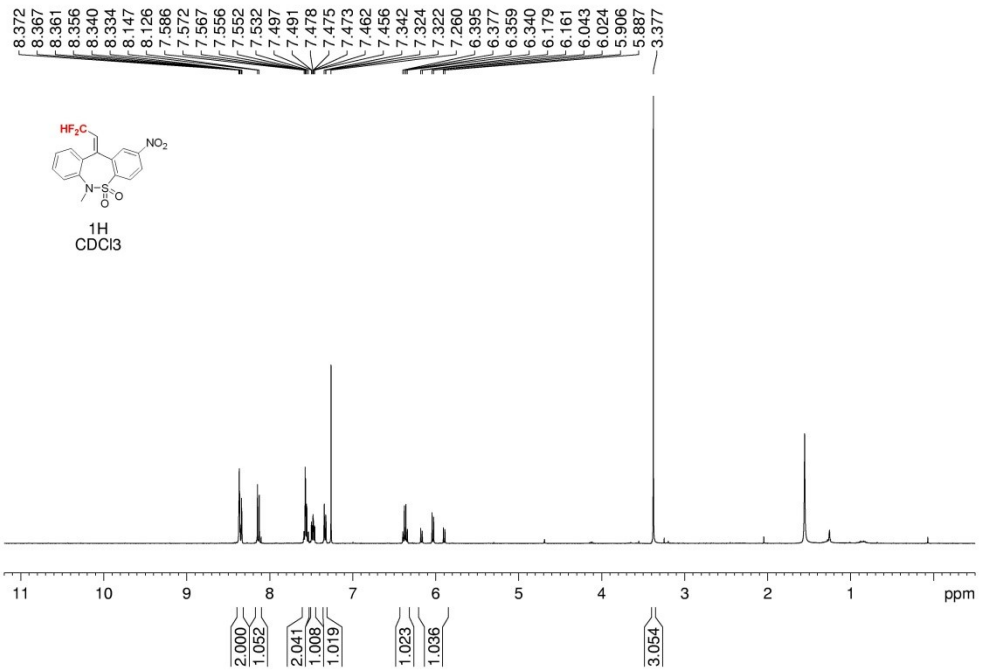


Figure S52. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3n**

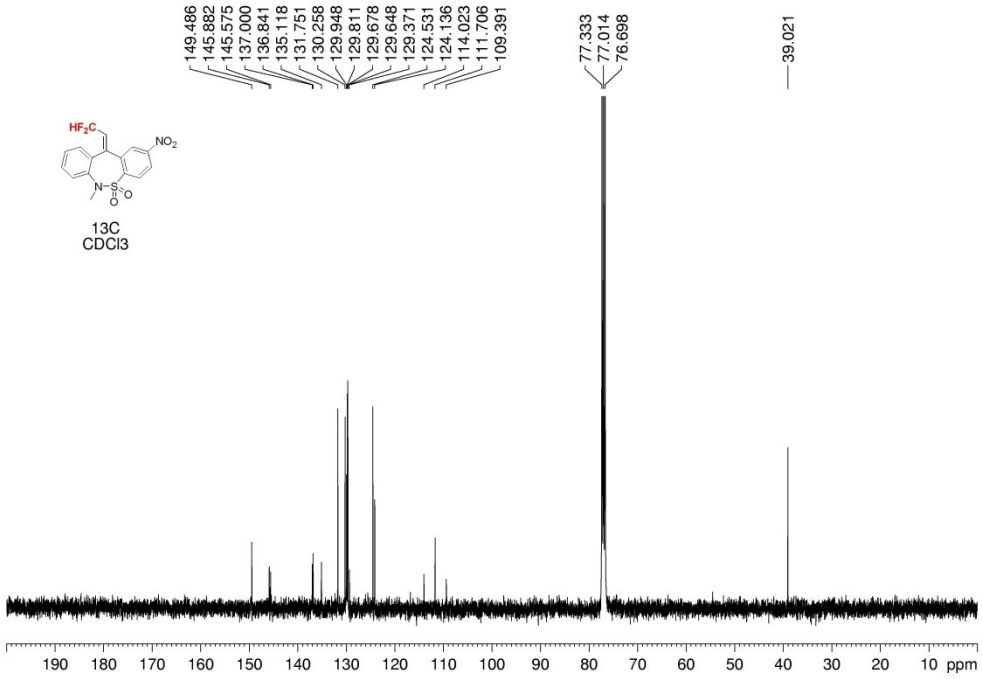


Figure S53. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3n**

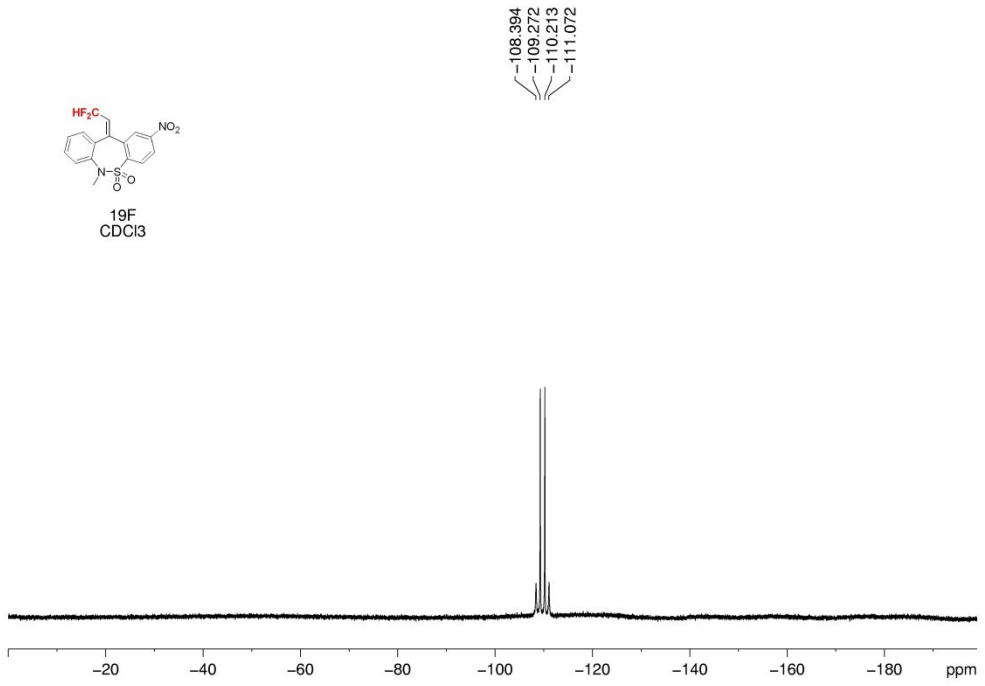


Figure S54. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3n**

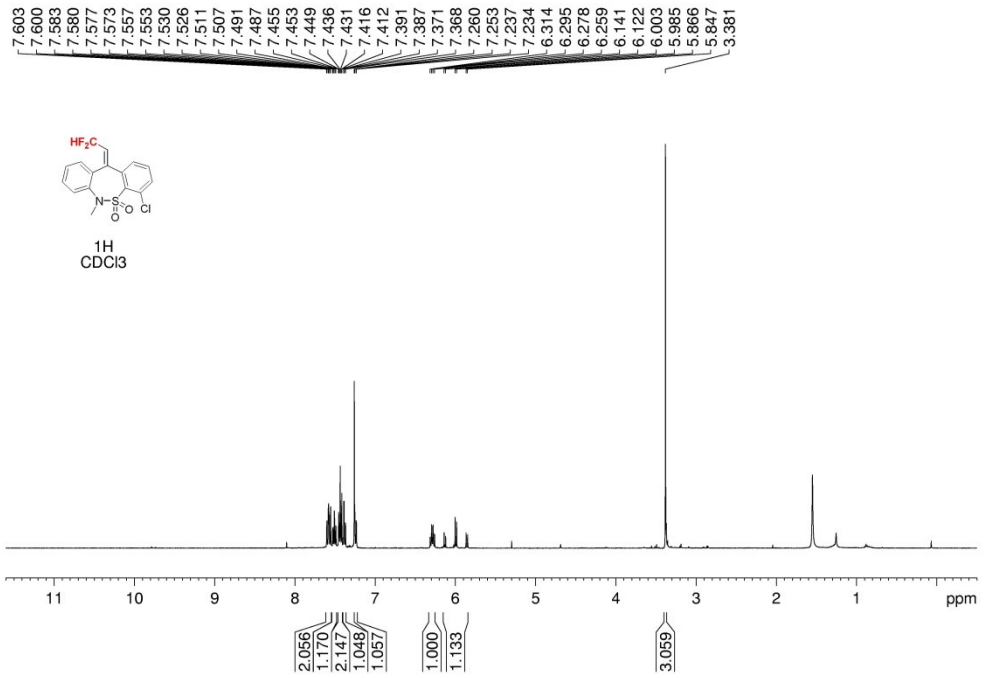


Figure S55. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3o**

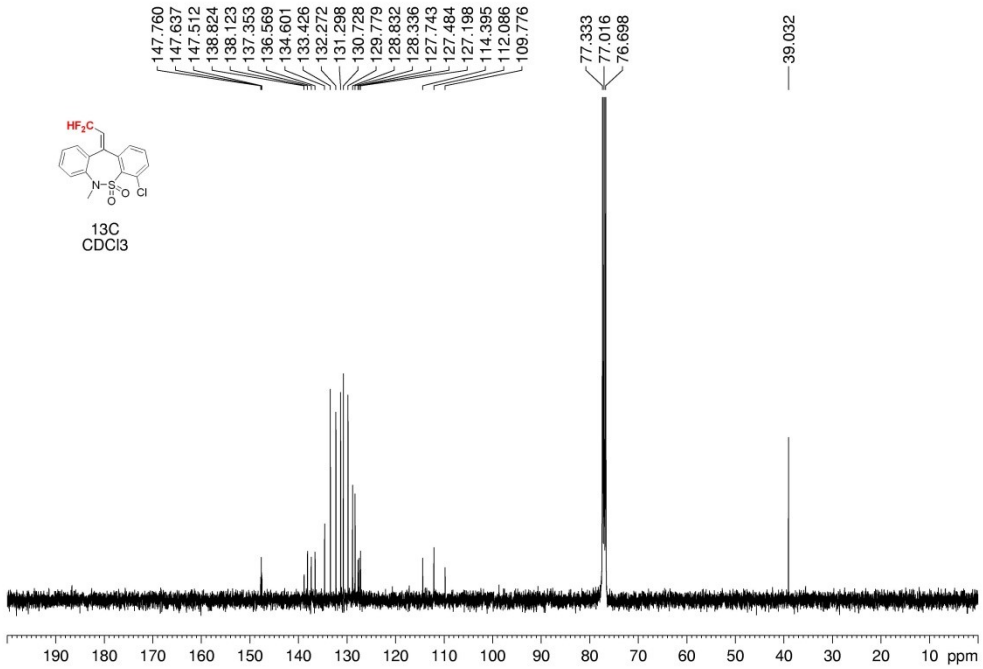


Figure S56. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3o**

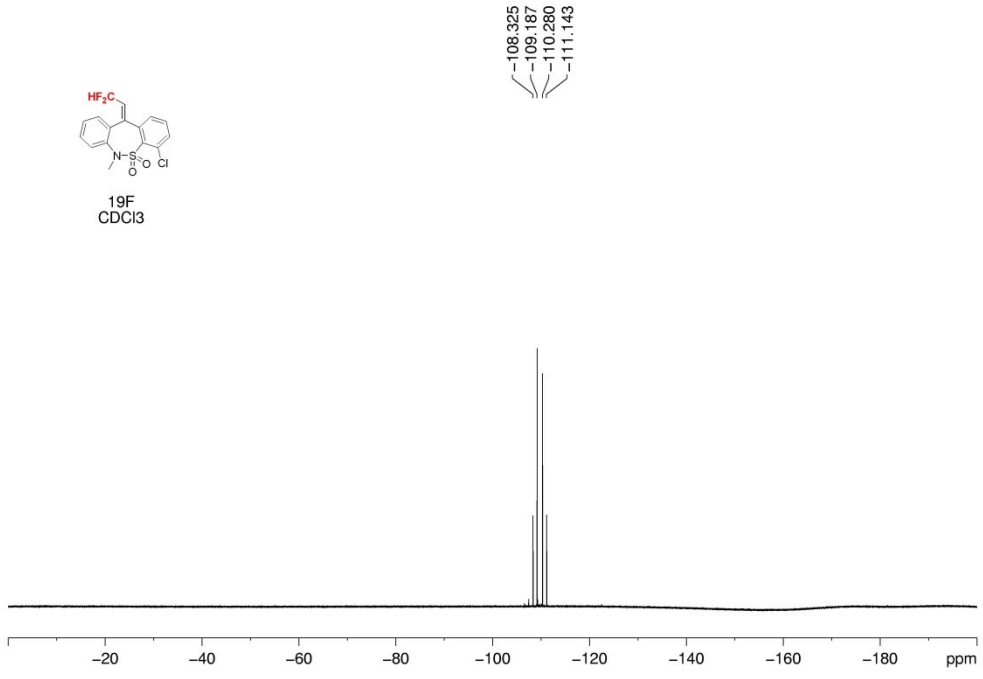


Figure S57. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3o**

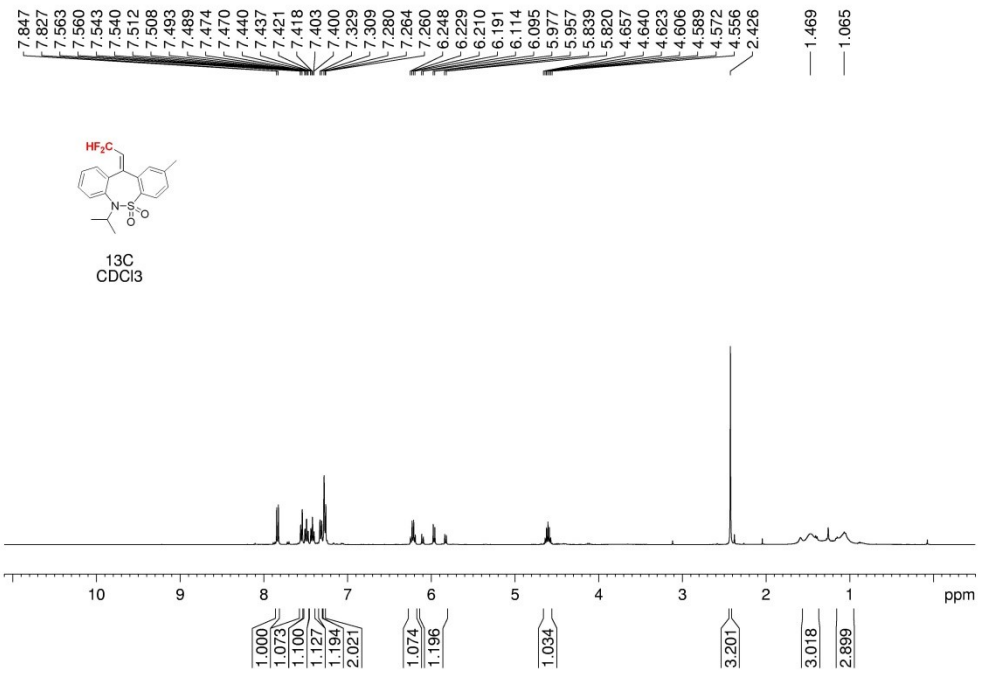


Figure S58. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3p**

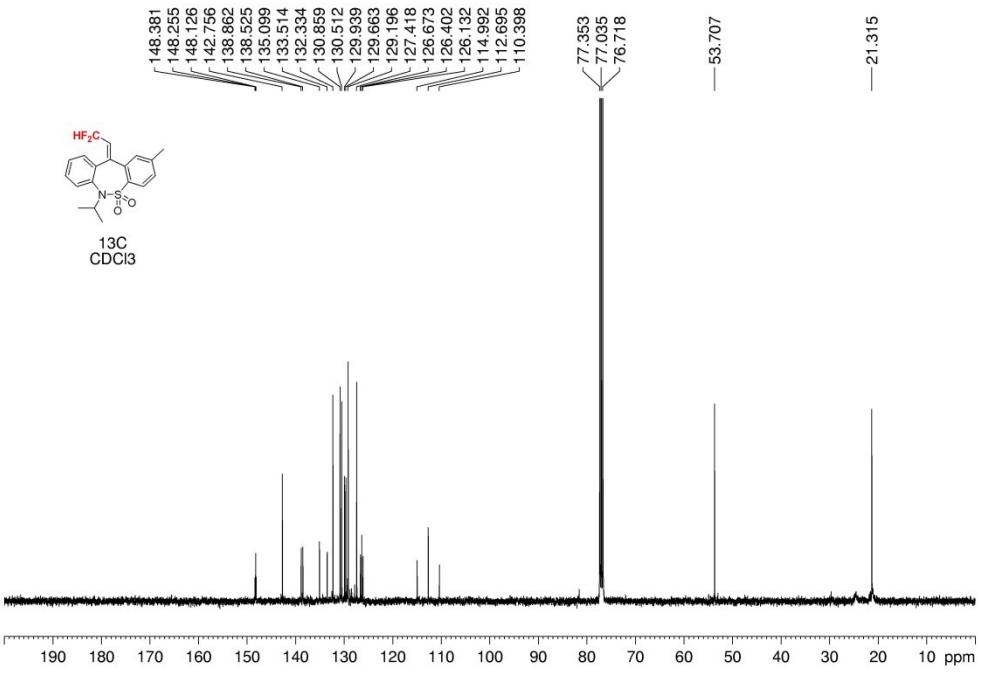


Figure S59. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3p**

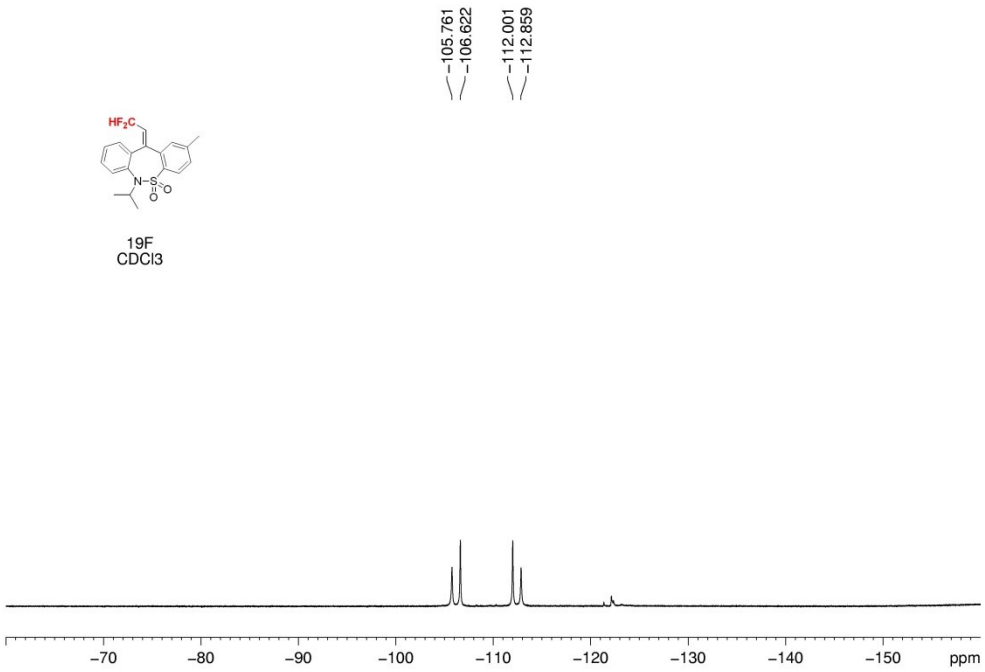


Figure S60. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3p**

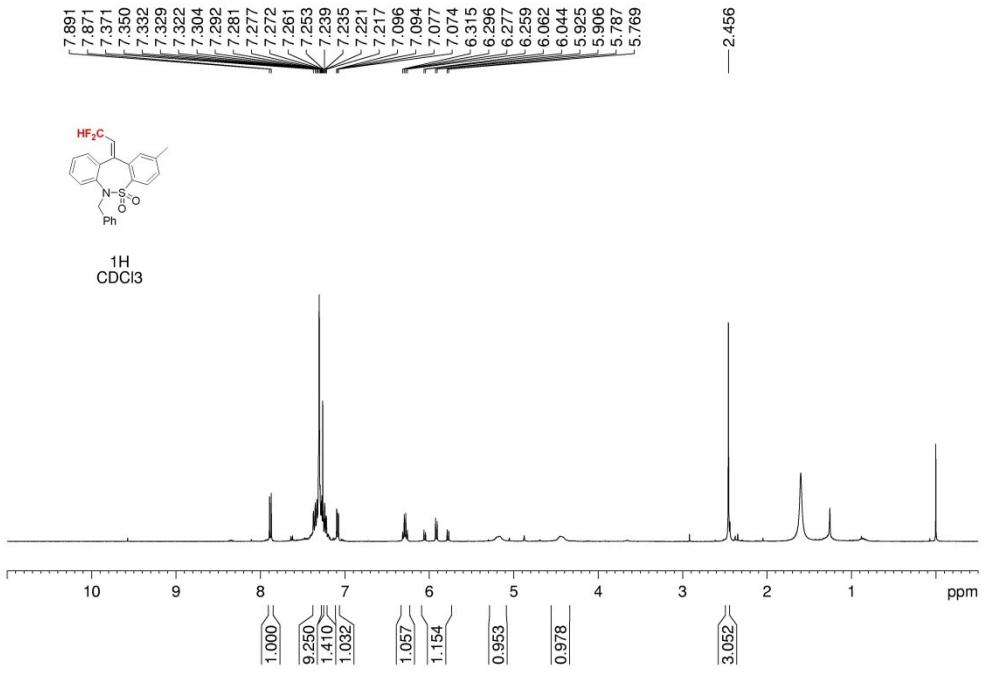


Figure S61. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3q**

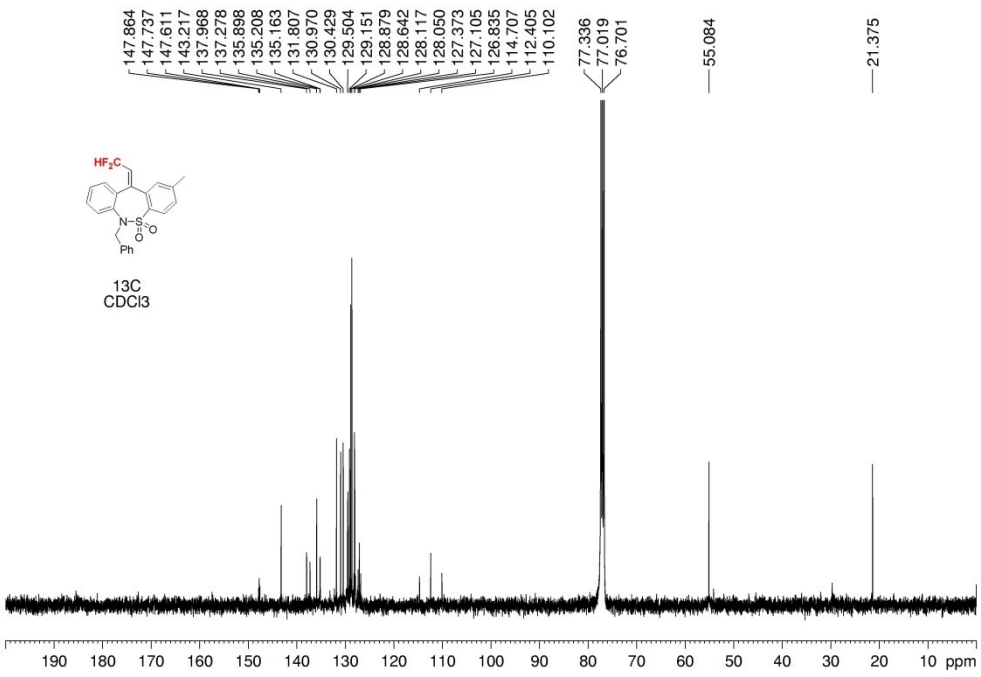


Figure S62. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3q**

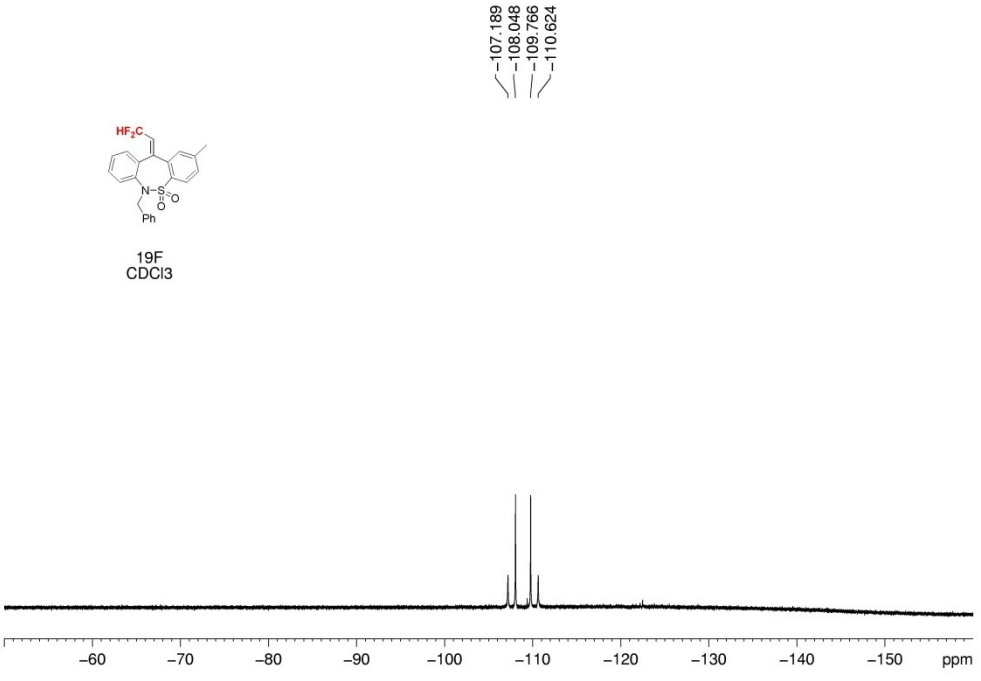


Figure S63. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3q**

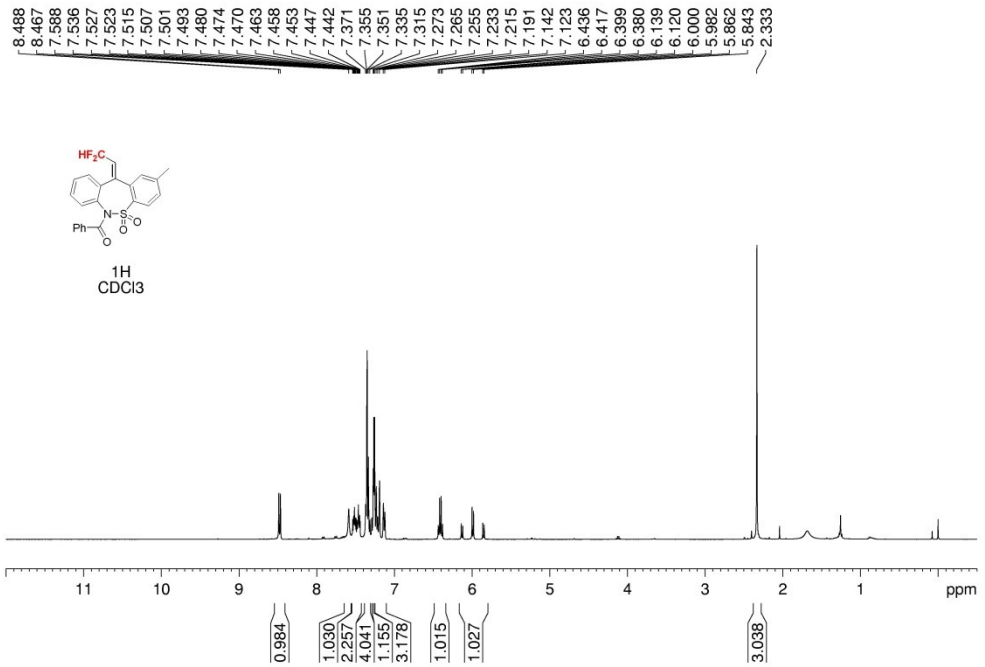


Figure S64. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3r**

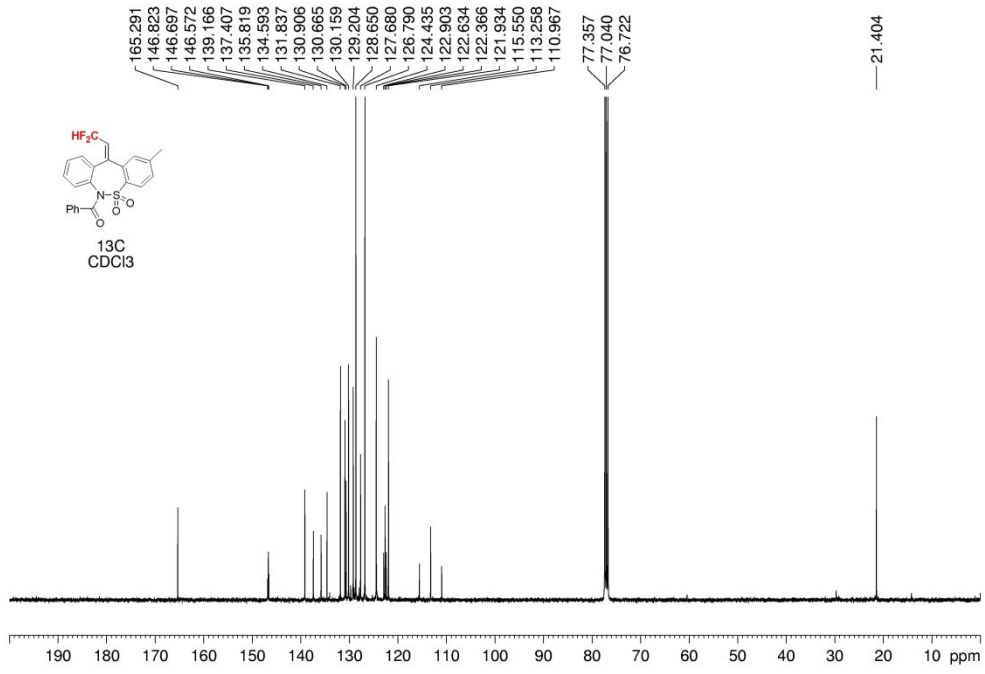


Figure S65. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3r**

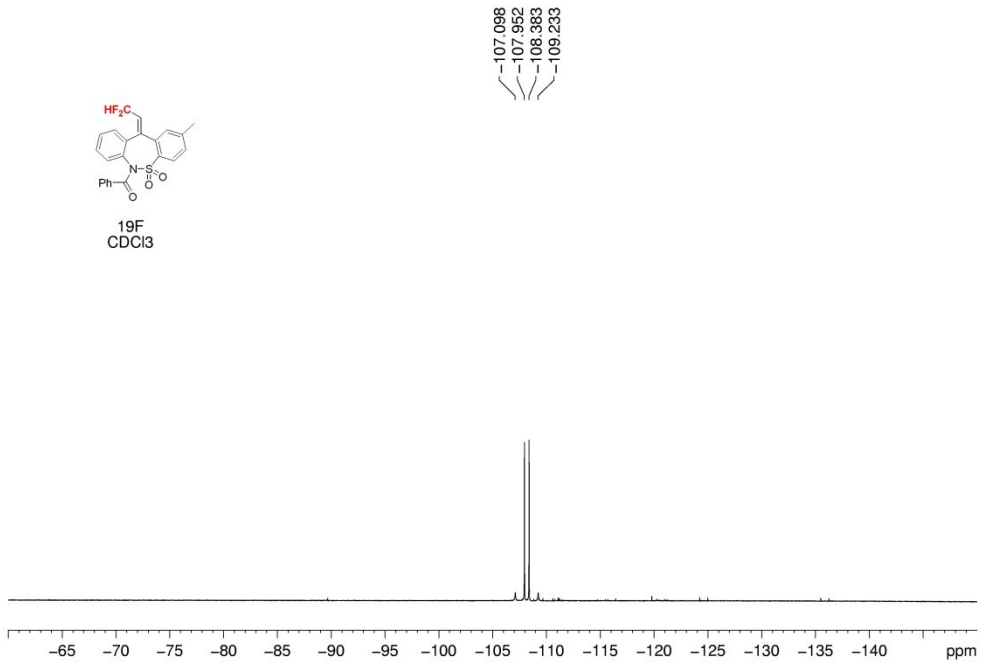


Figure S66. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3r**

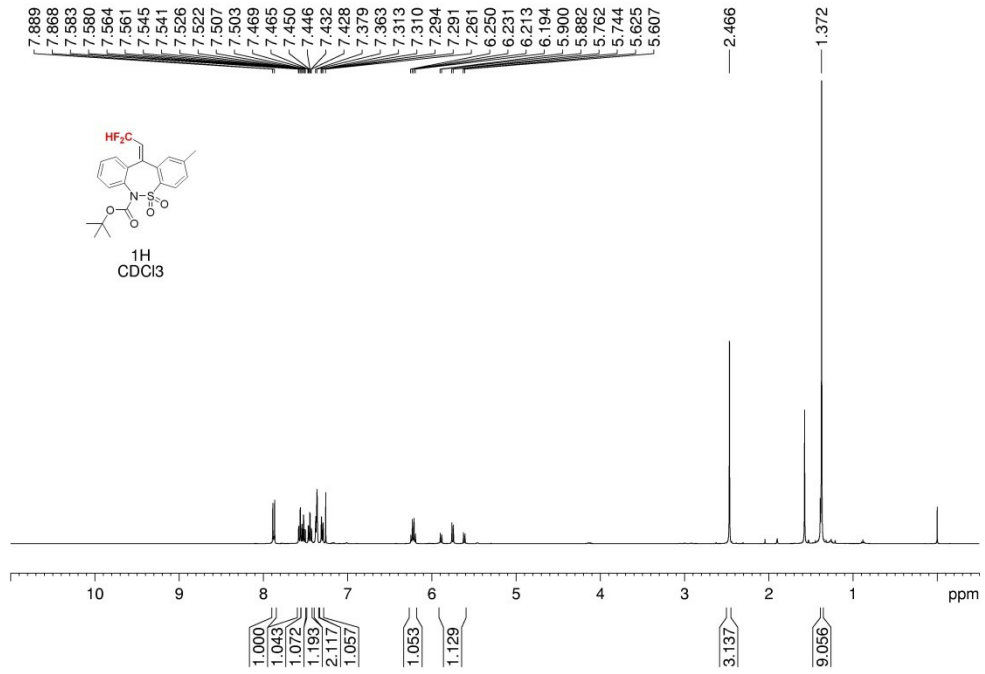


Figure S67. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3s**

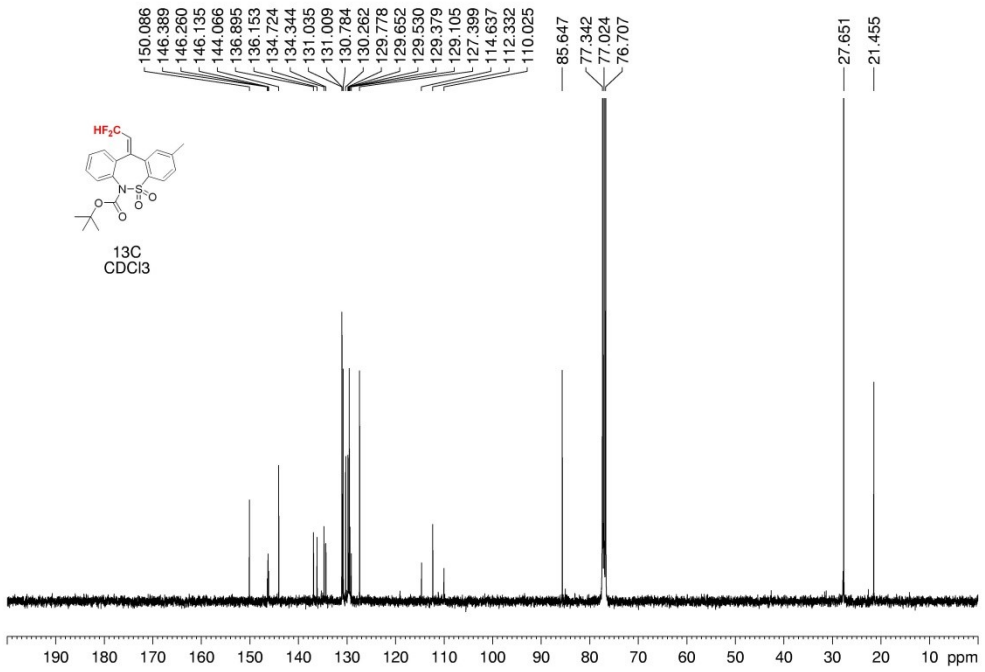


Figure S68. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3s**

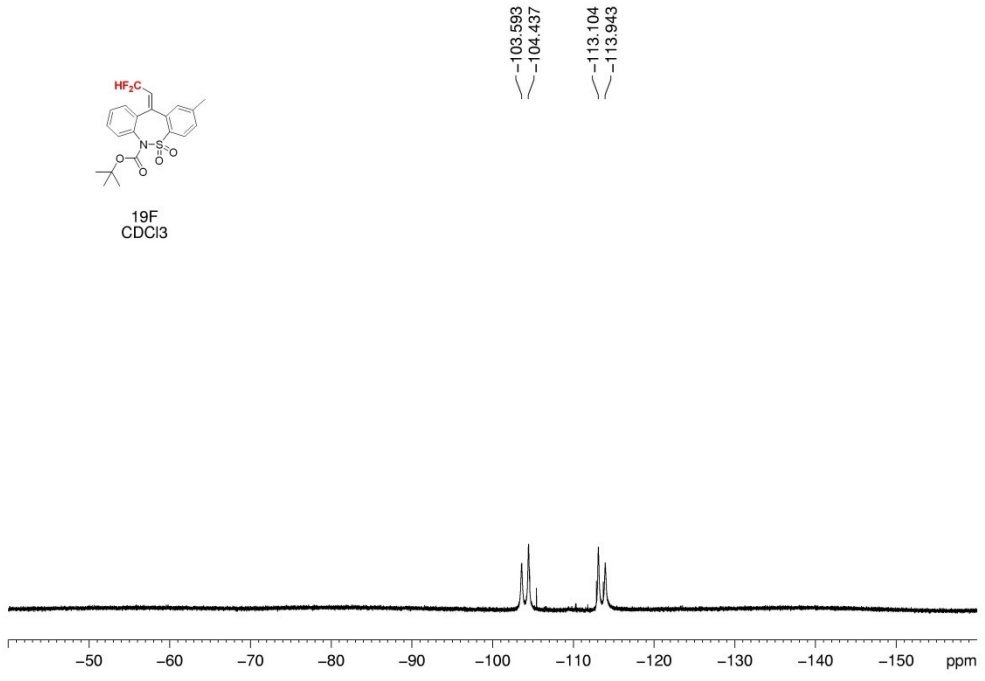


Figure S69. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3s**

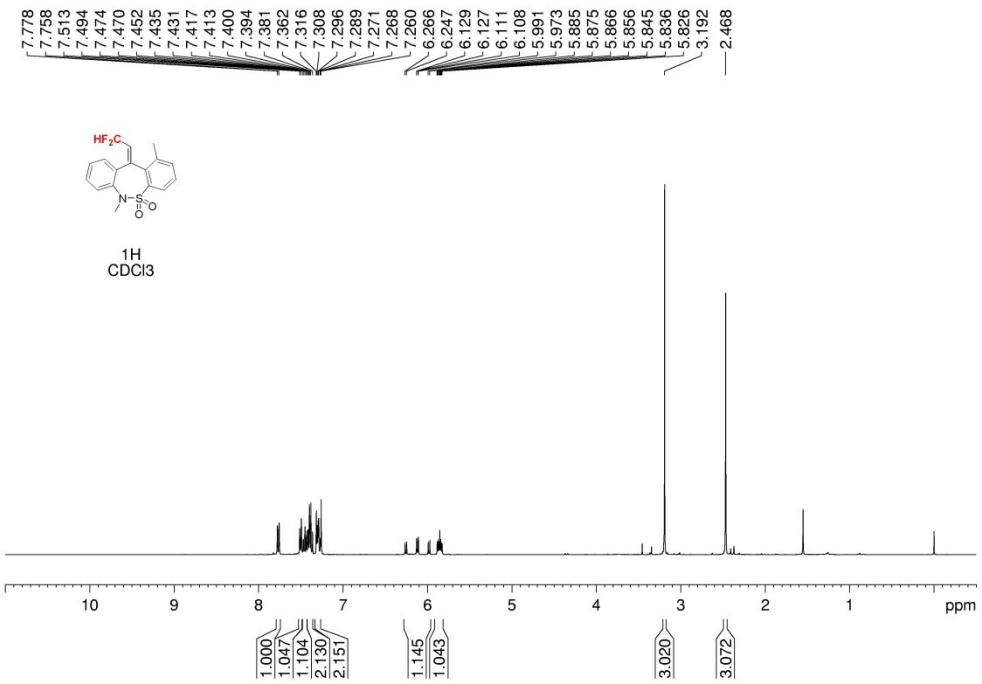


Figure S70. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3t**

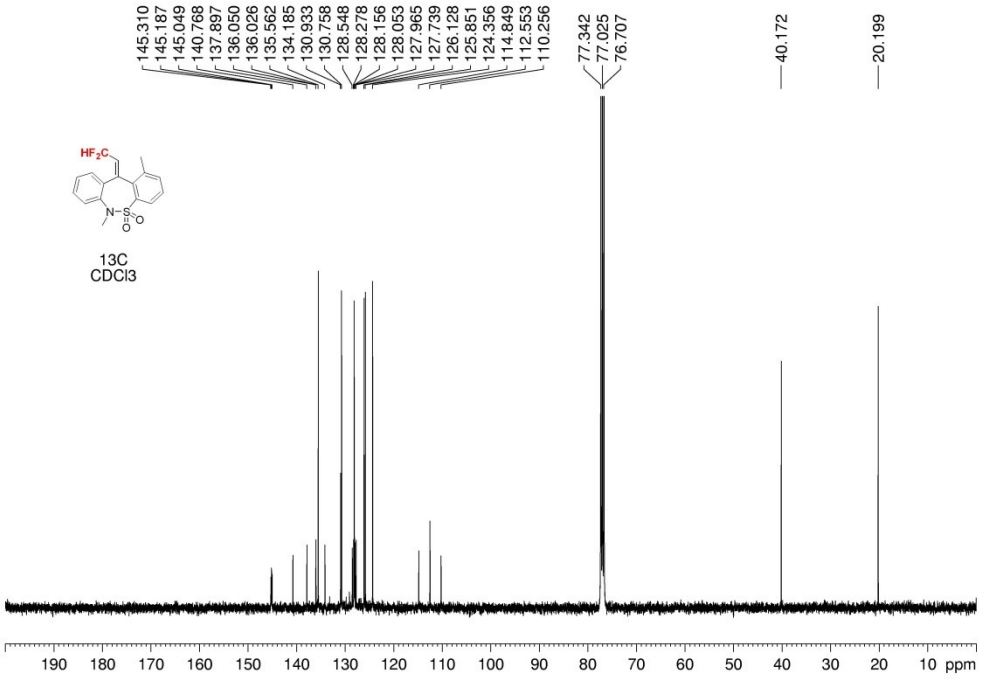


Figure S71. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3t**

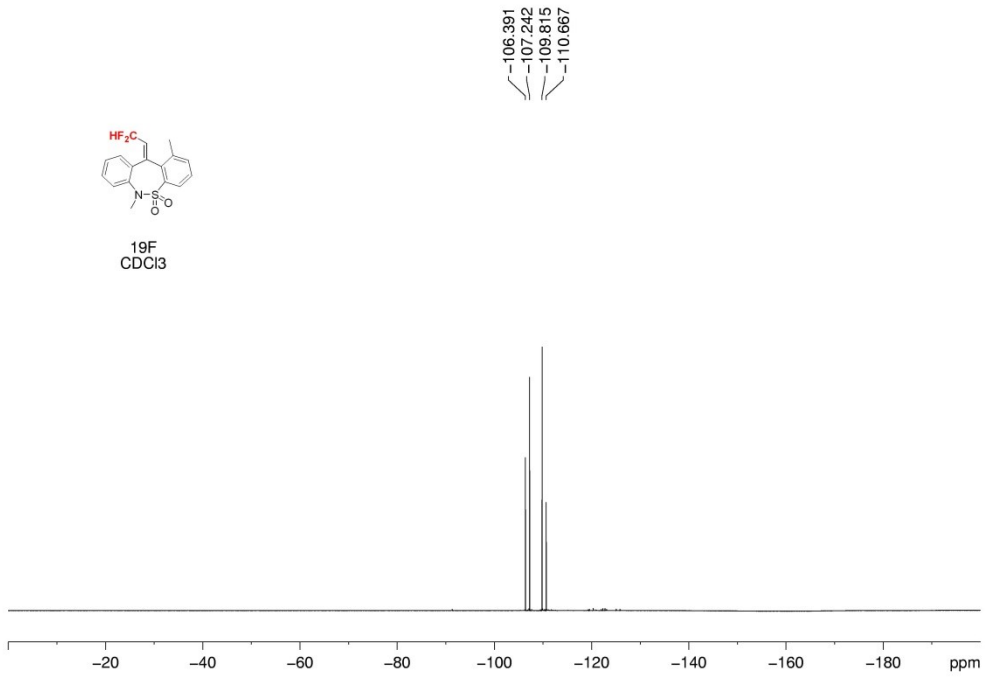


Figure S72. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3t**

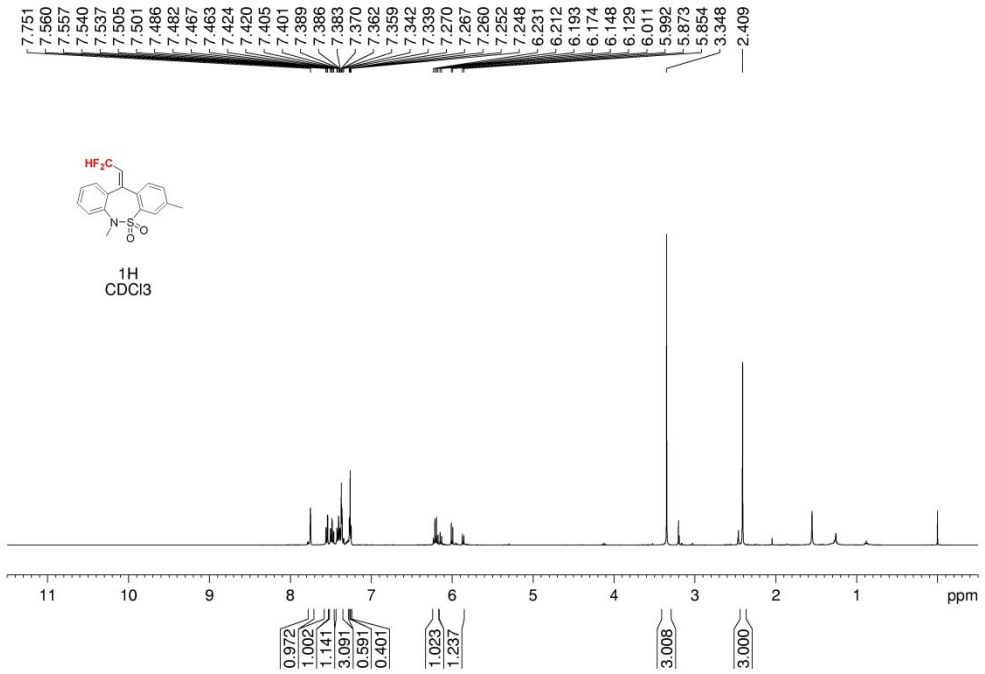


Figure S73. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3t′**

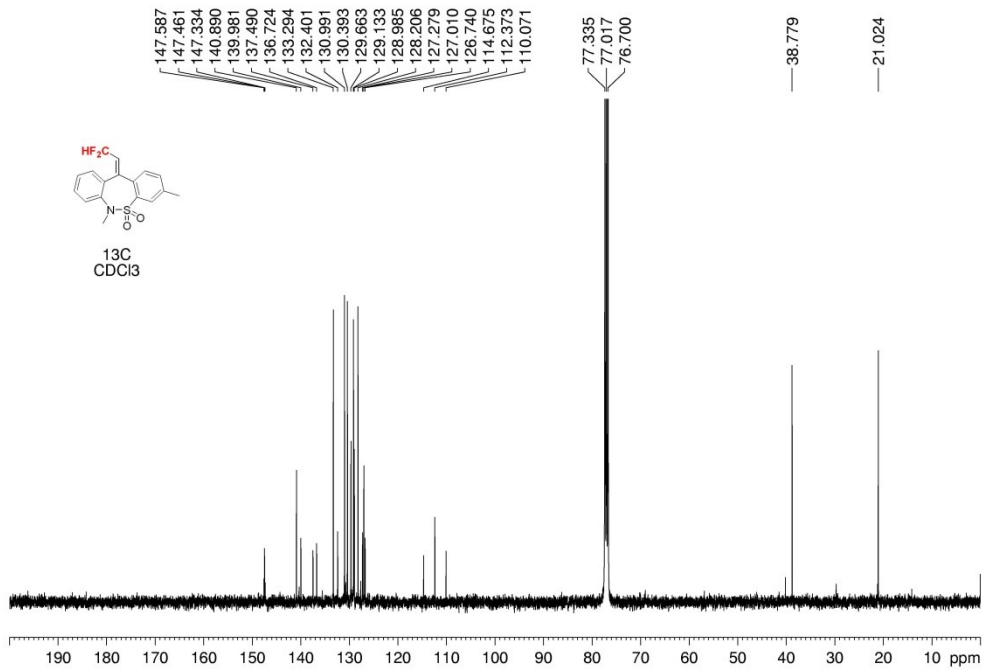


Figure S74. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3t′**

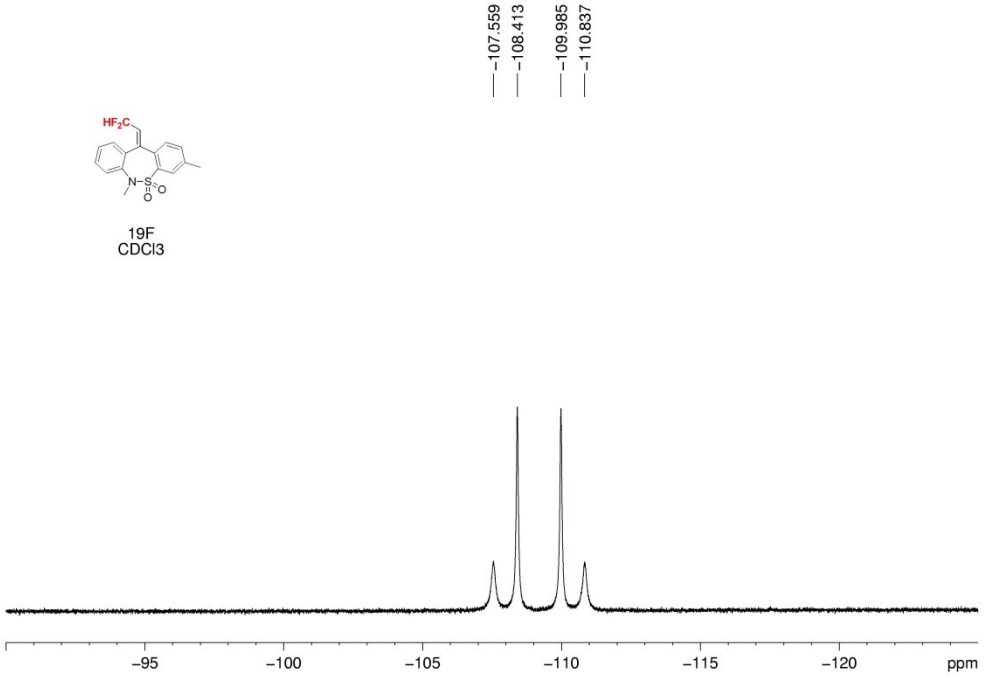


Figure S75. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3t′**

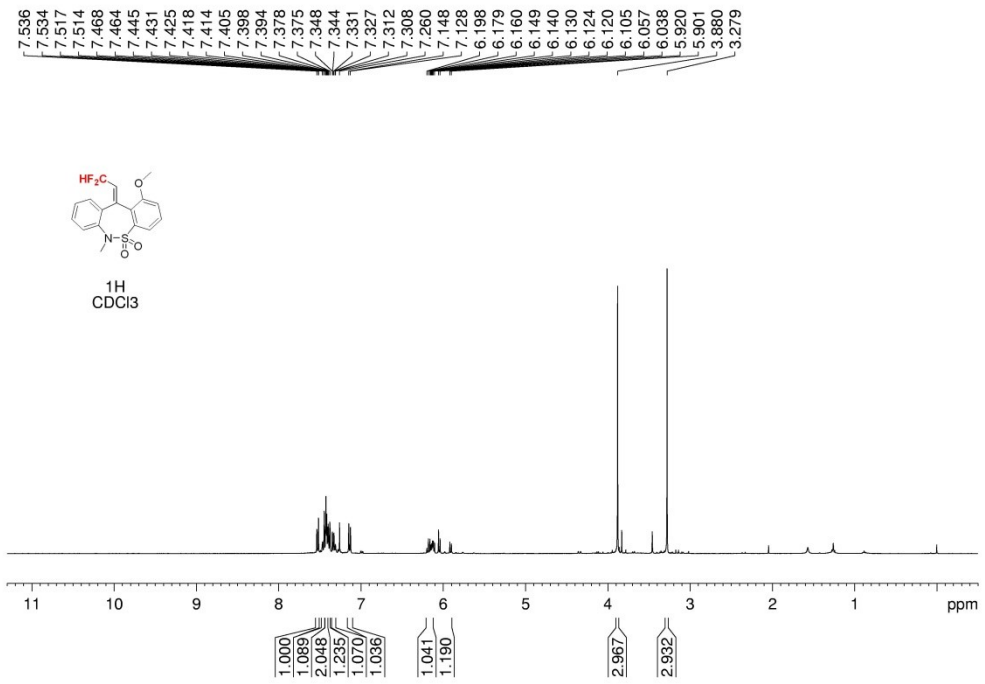


Figure S76. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3u**

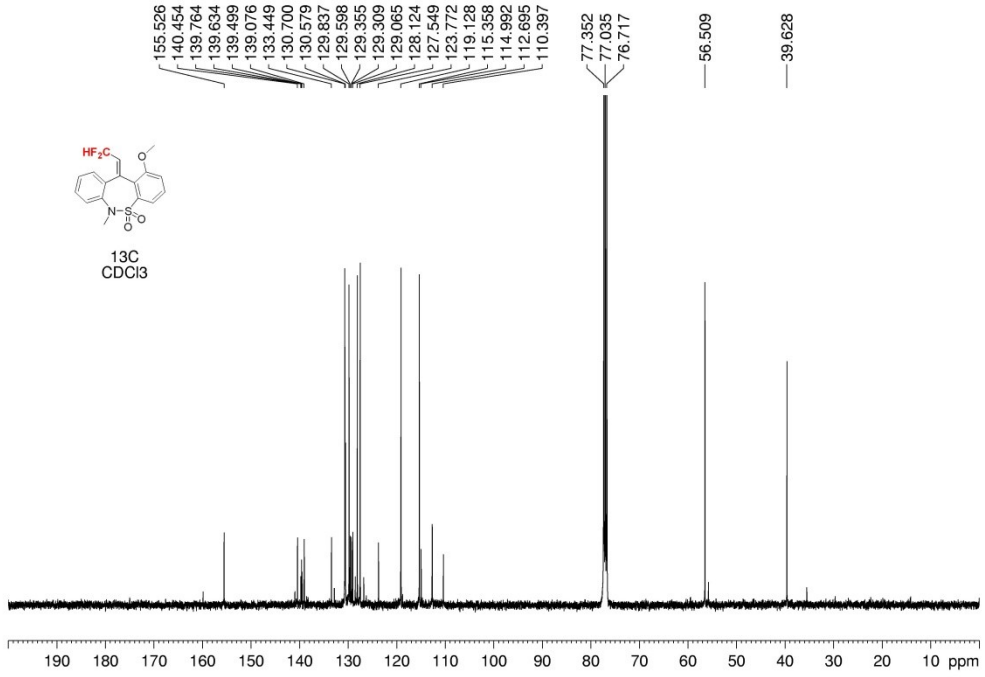


Figure S77. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3u**

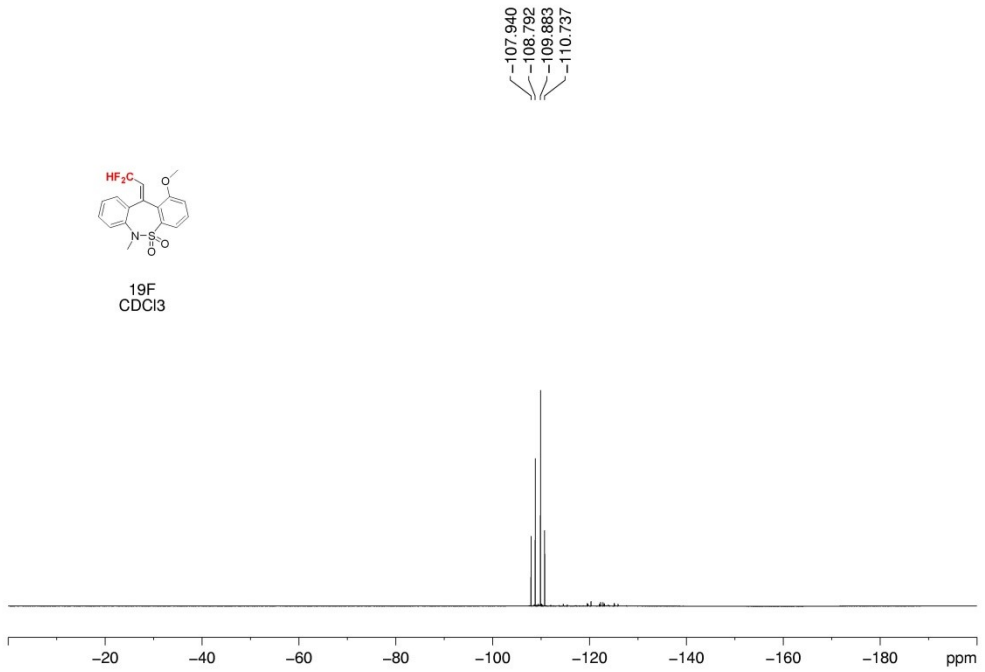


Figure S78. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3u**

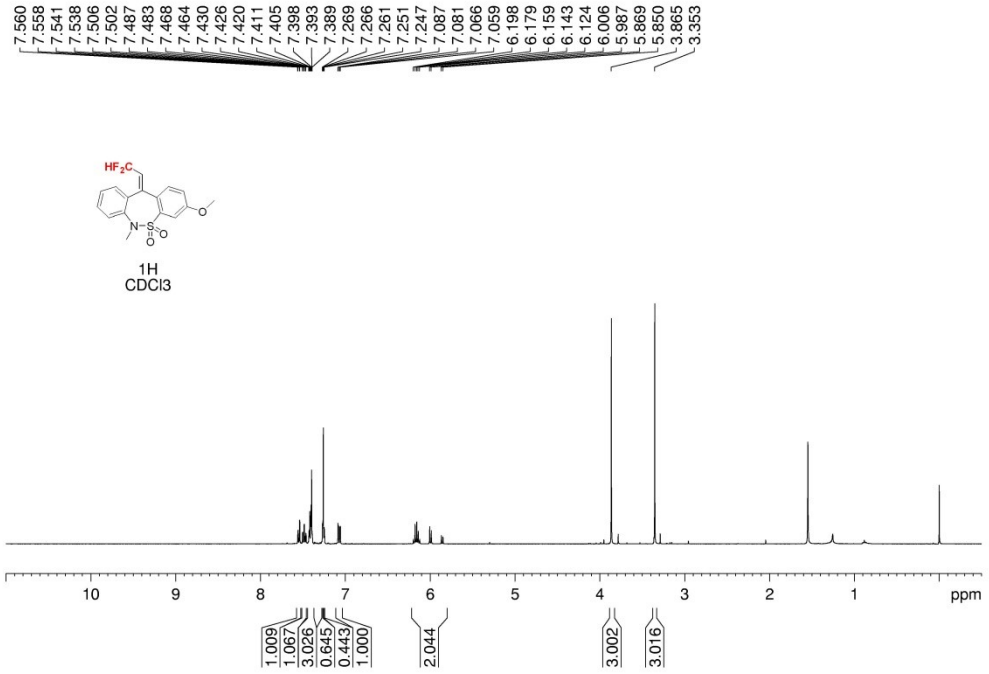


Figure S79. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3u′**

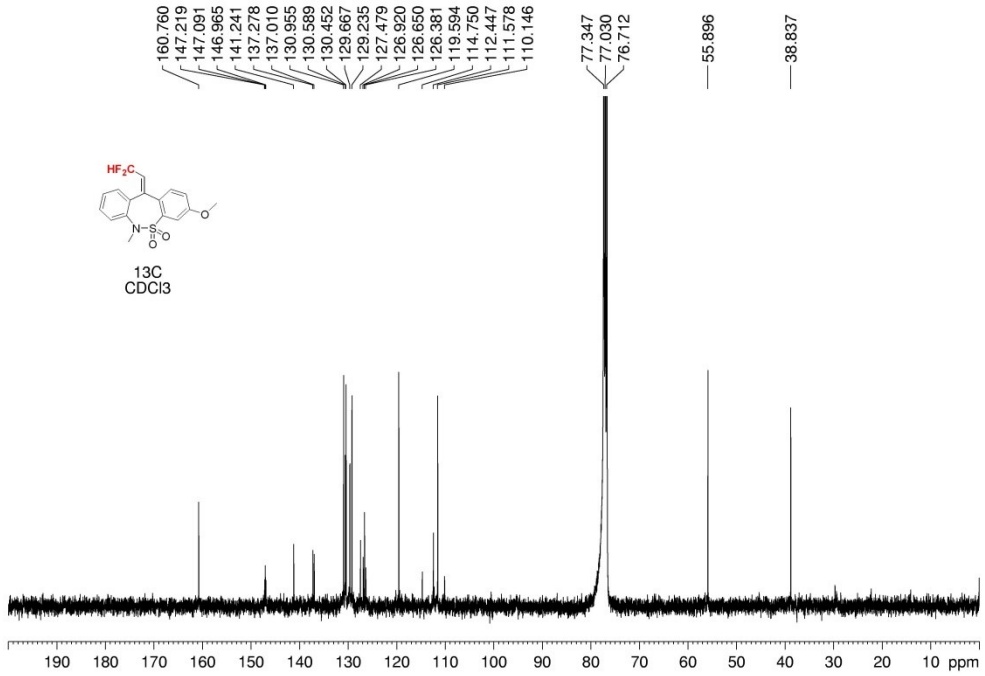


Figure S80. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3u′**

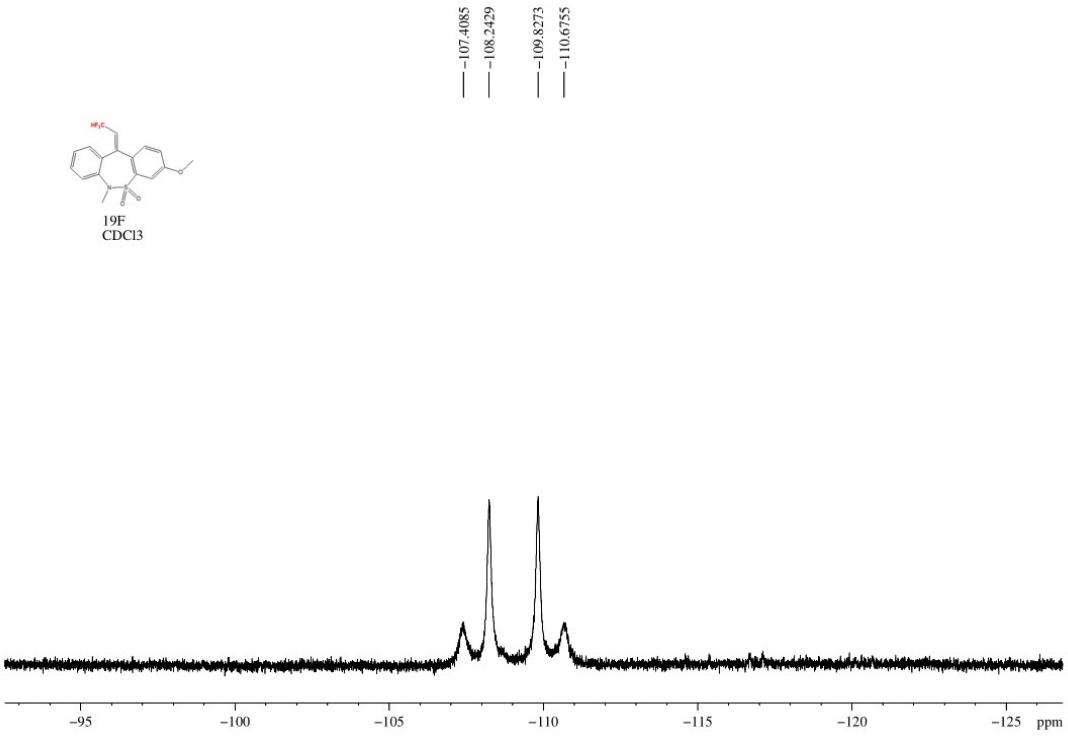


Figure S81. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3u′**

10.2 Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of products 5

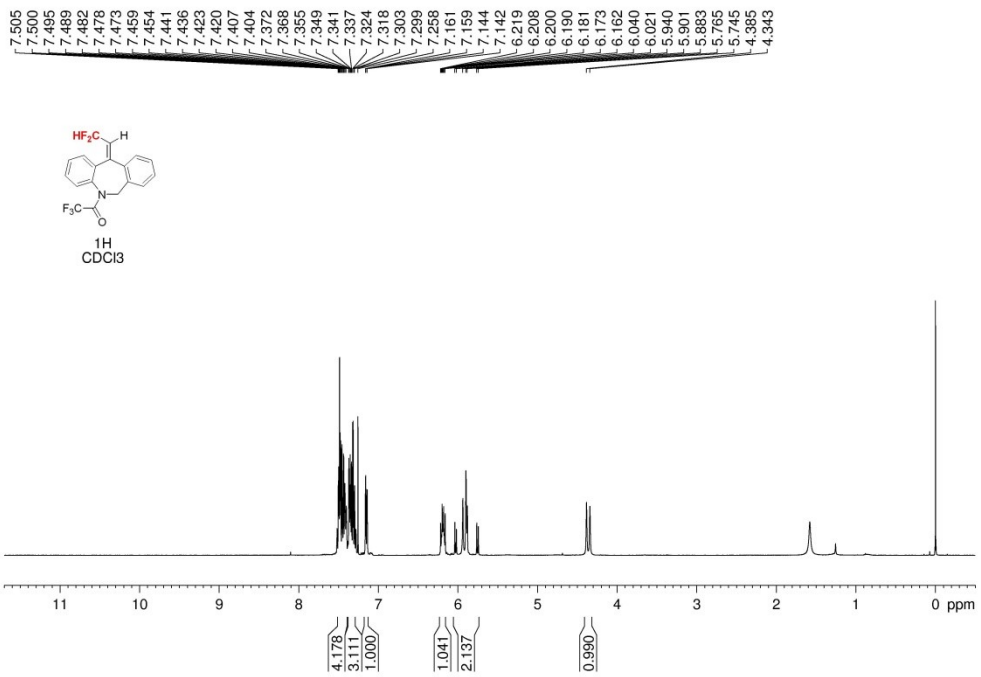


Figure S82. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5a**

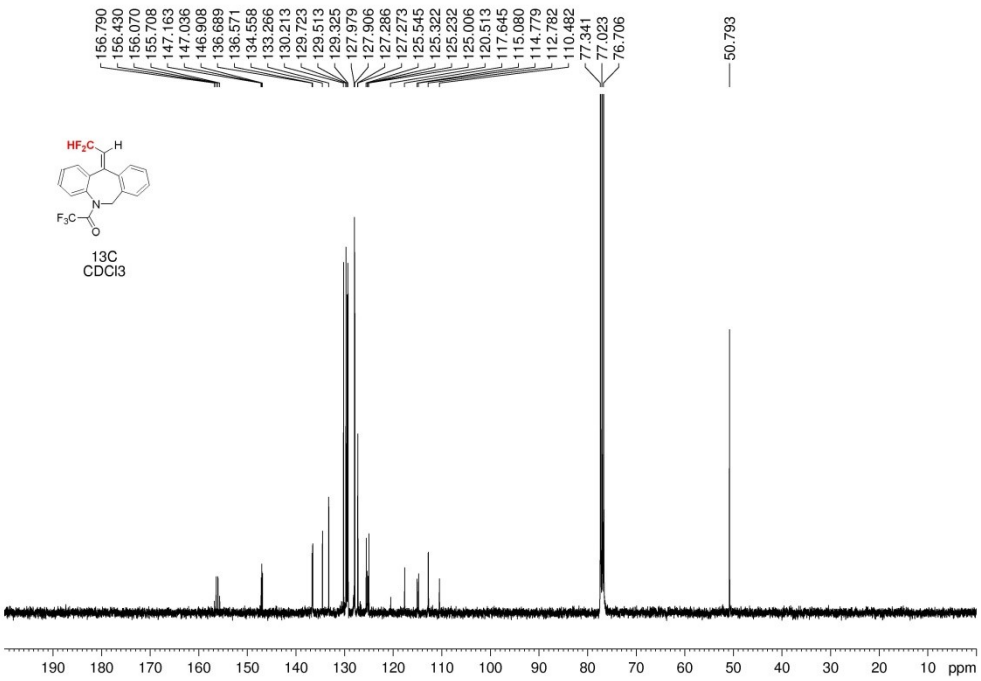


Figure S83. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5a**

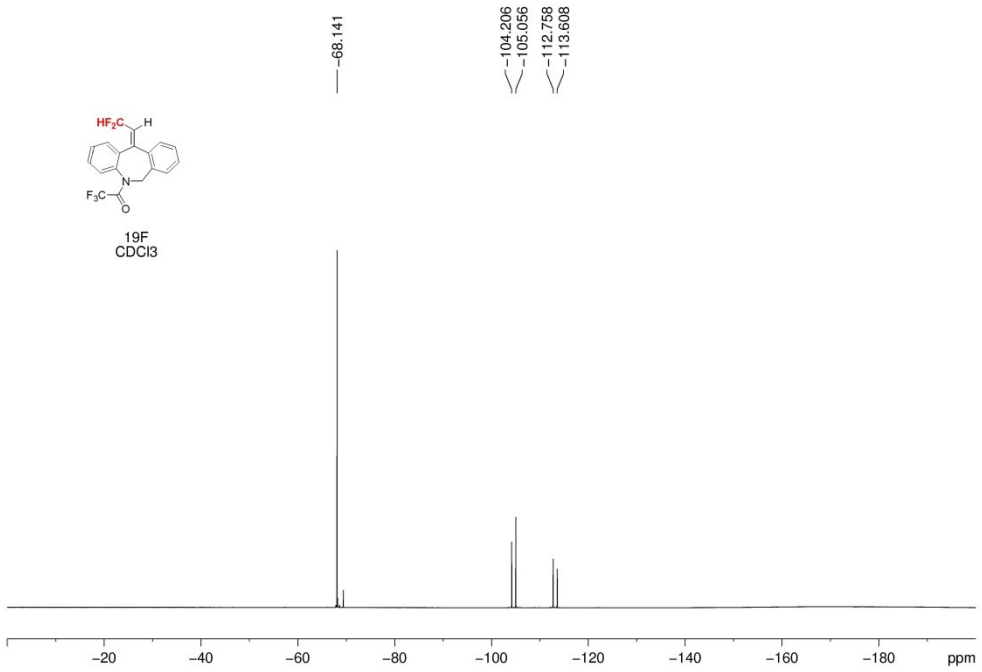


Figure S84. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5a**

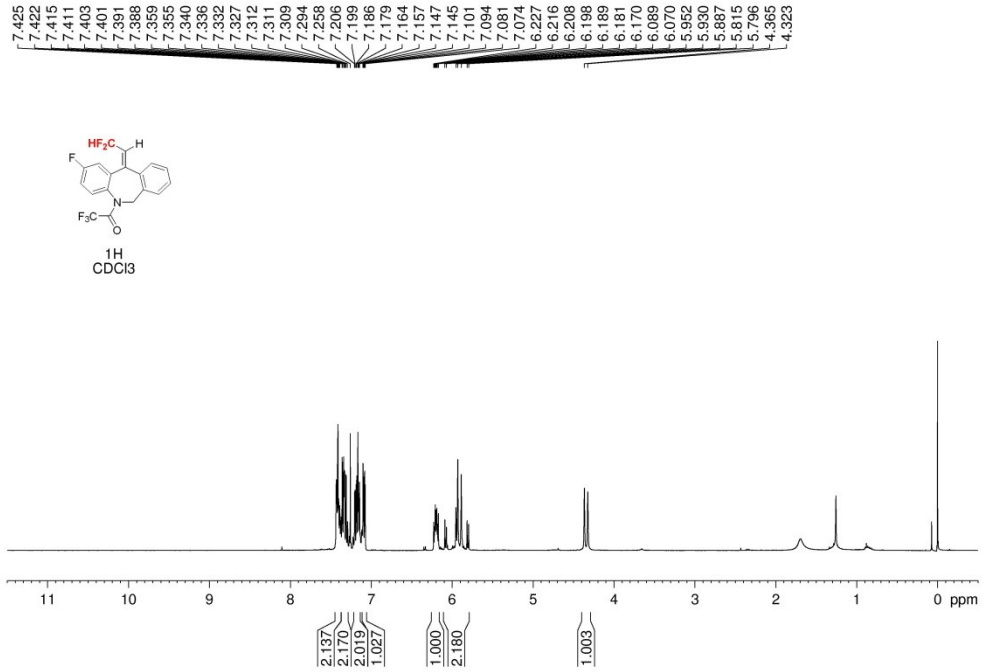


Figure S85. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5b**

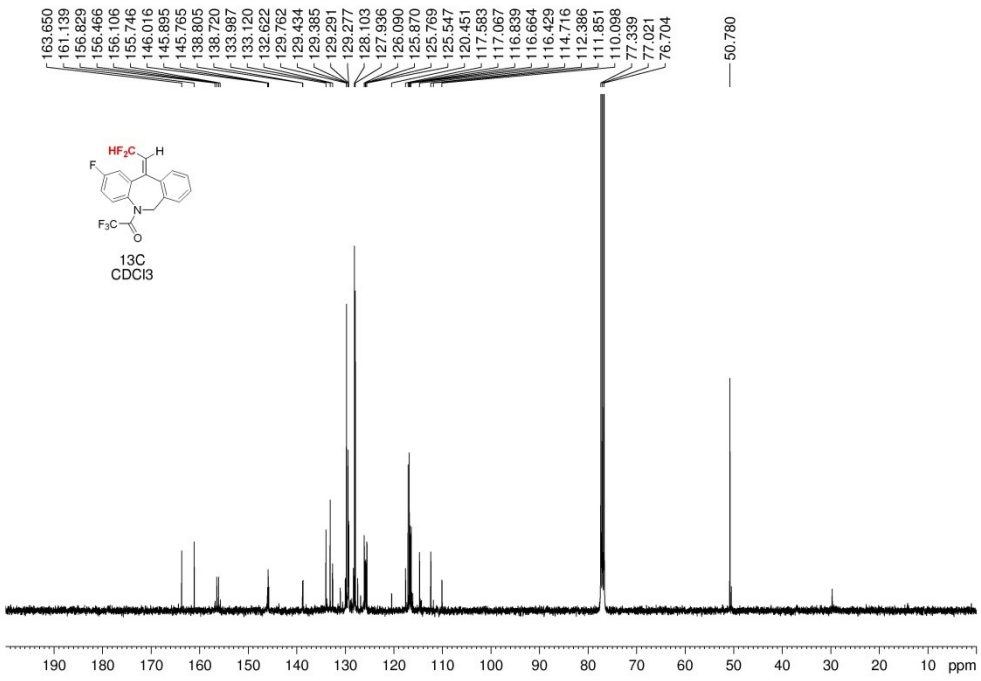


Figure S86. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5b**

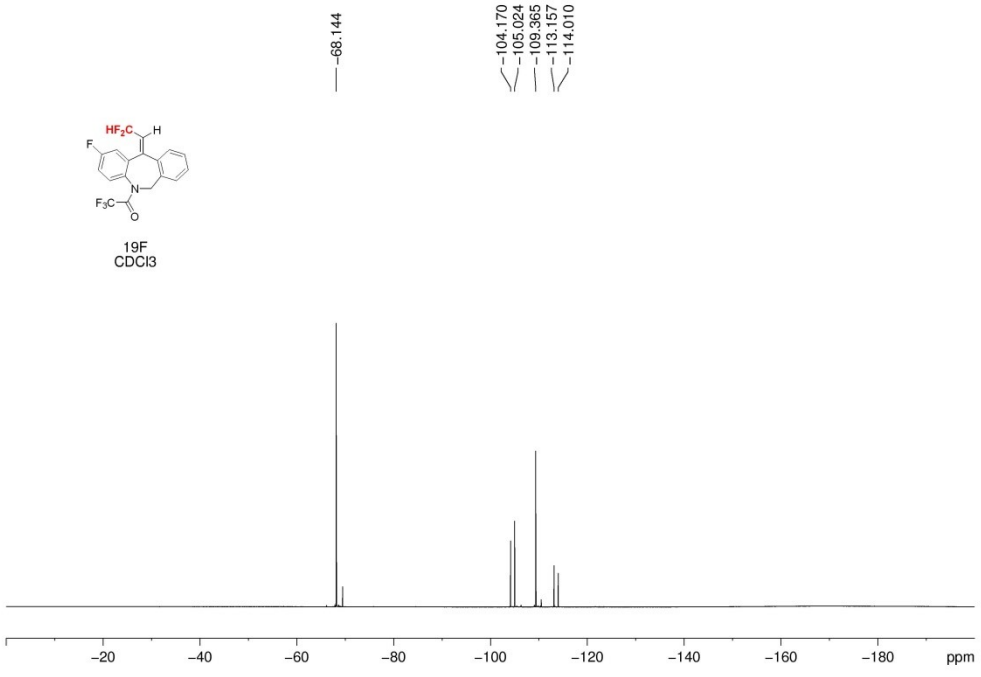


Figure S87. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5b**

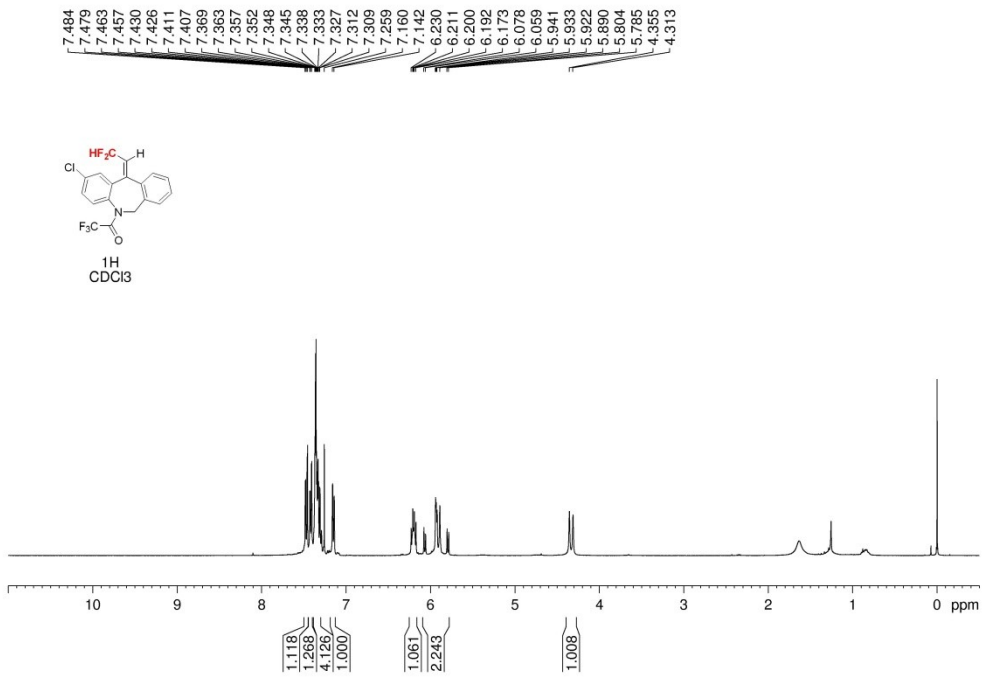


Figure S88. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5c**

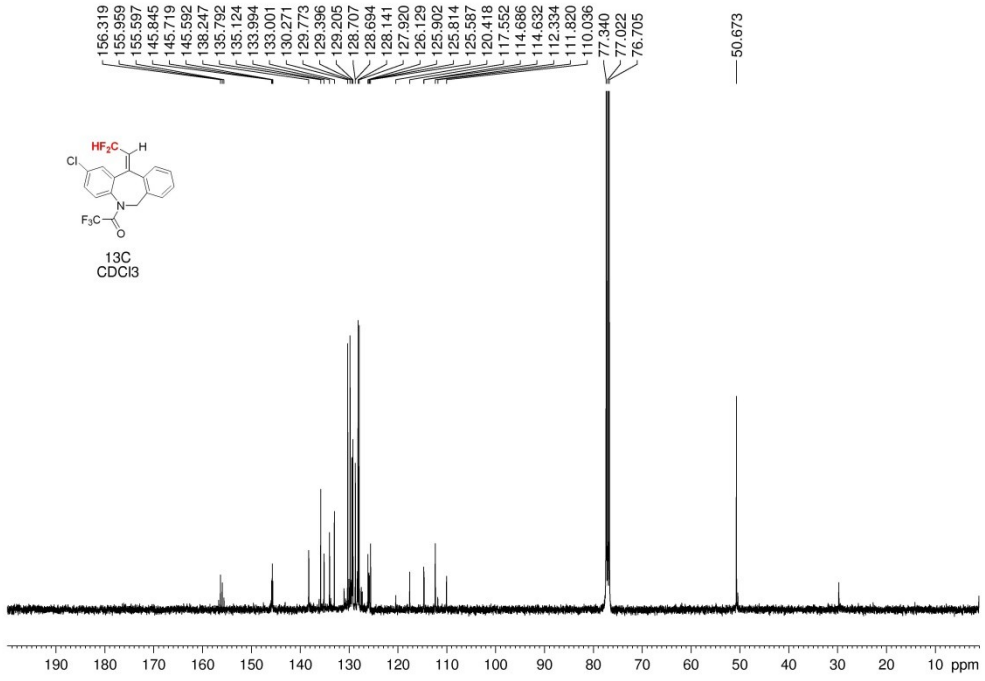


Figure S89. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5c**

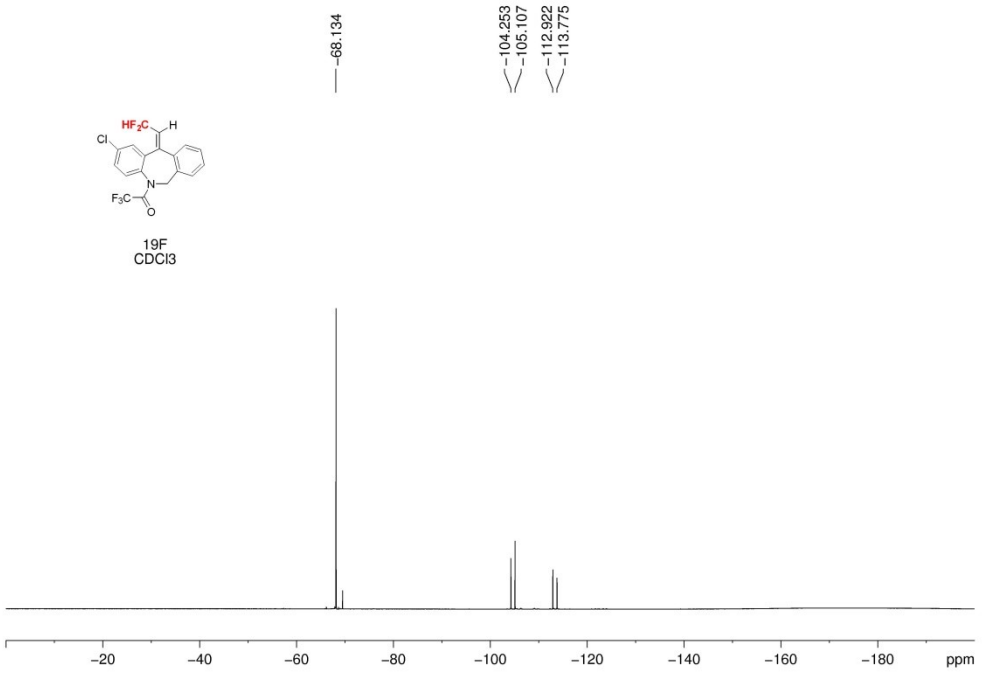


Figure S90. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5c**

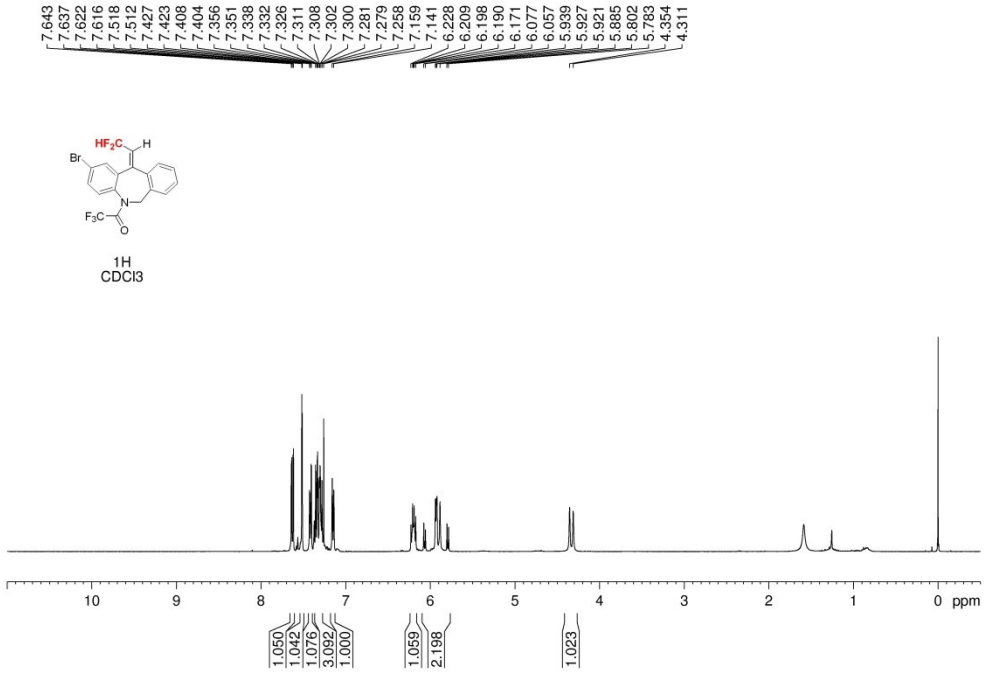


Figure S91. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5d**

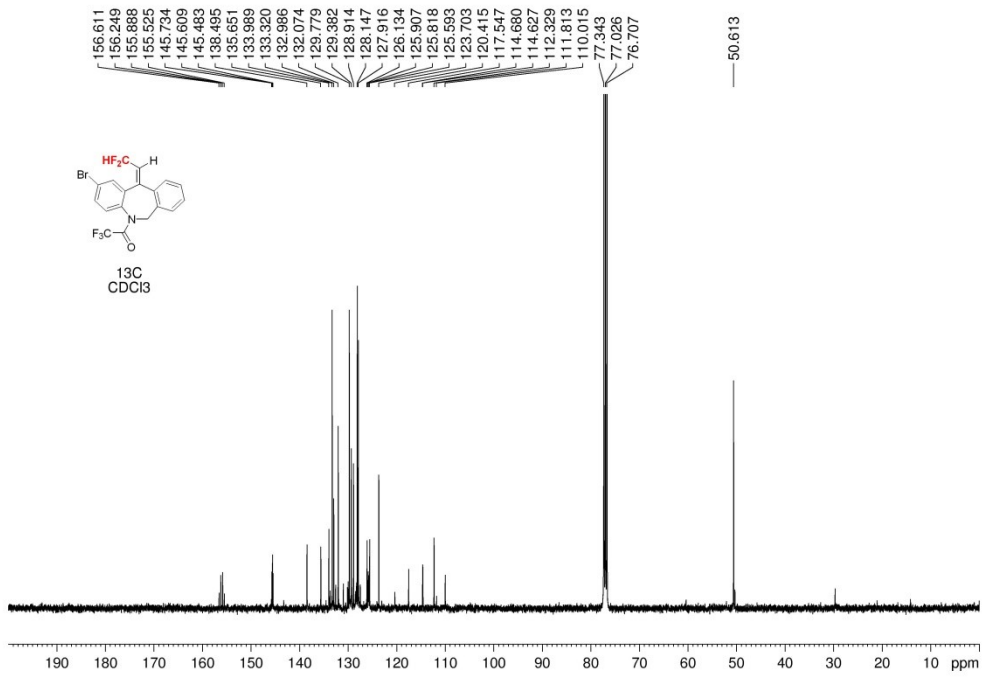


Figure S92. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5d**

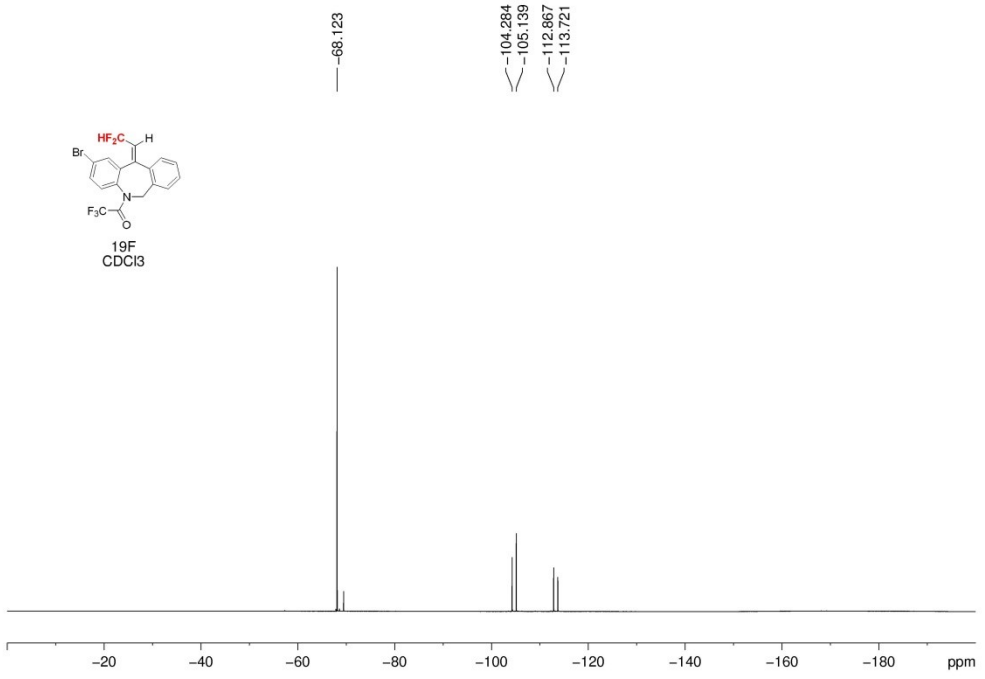


Figure S93. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5d**

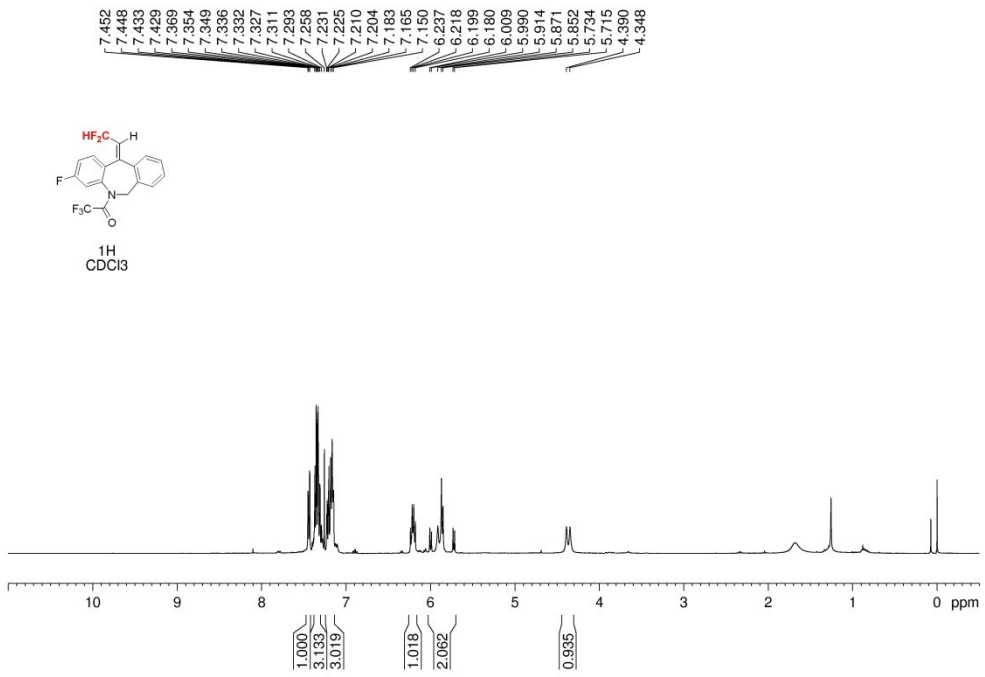


Figure S94. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5e**

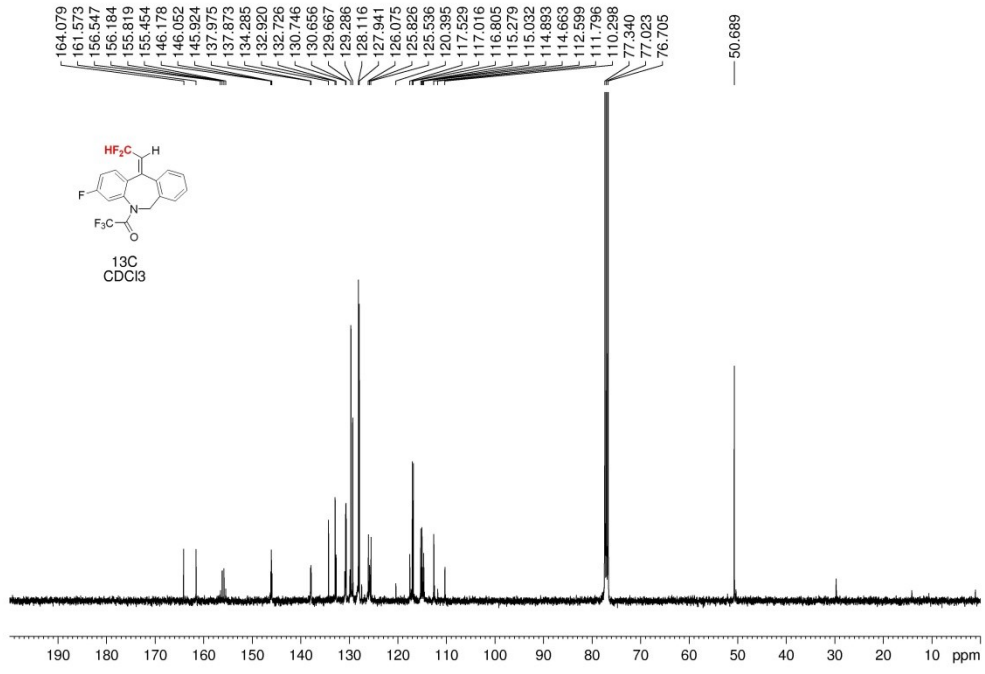


Figure S95. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5e**

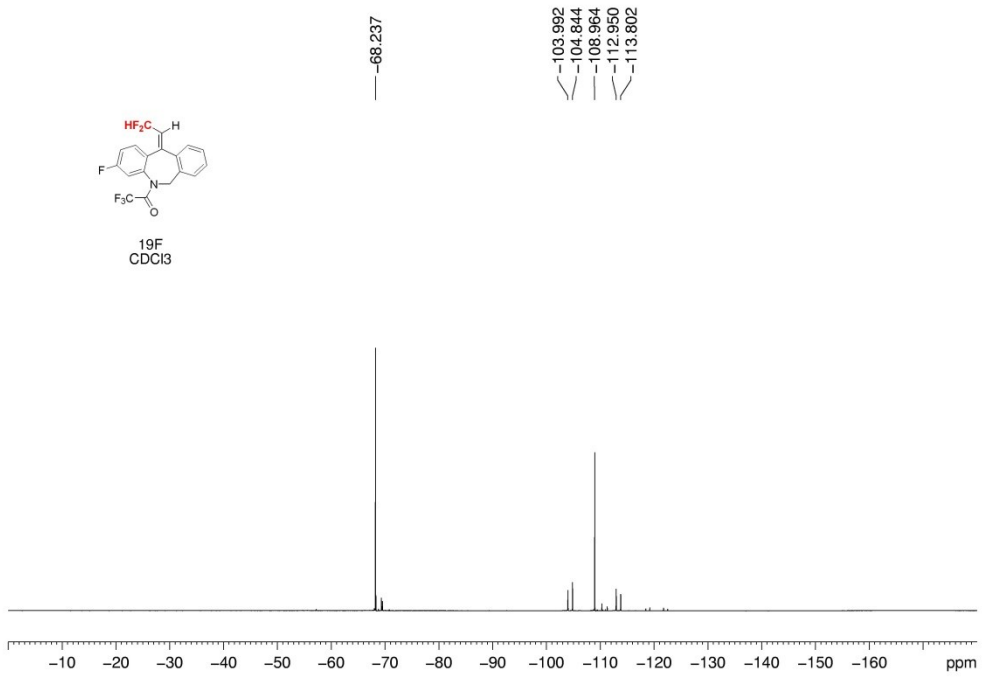


Figure S96. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5e**

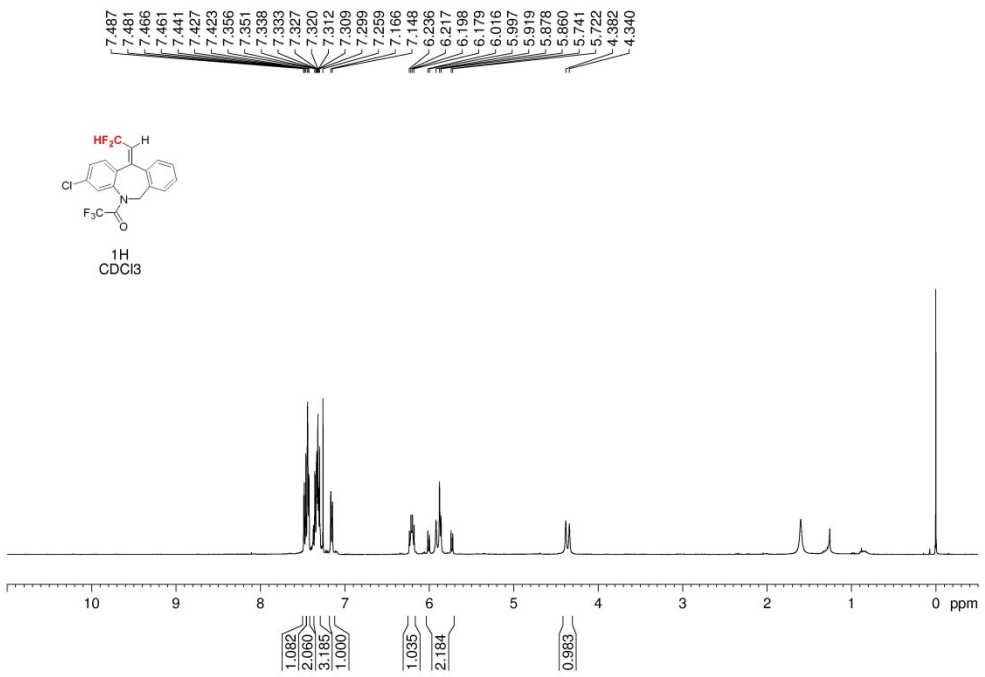


Figure S97. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5f**

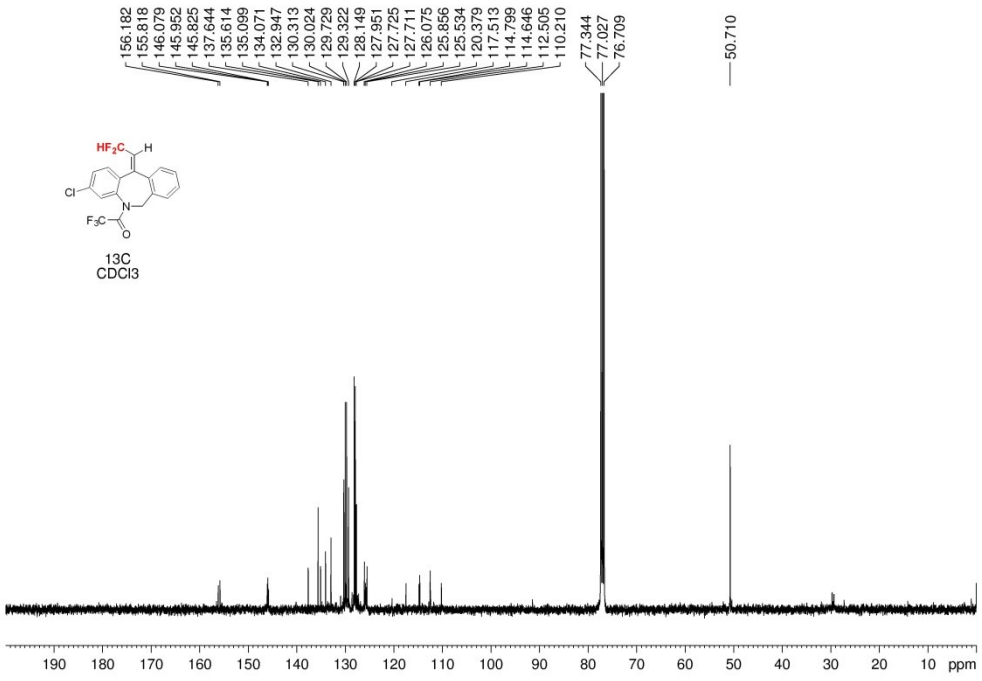


Figure S98. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5f**

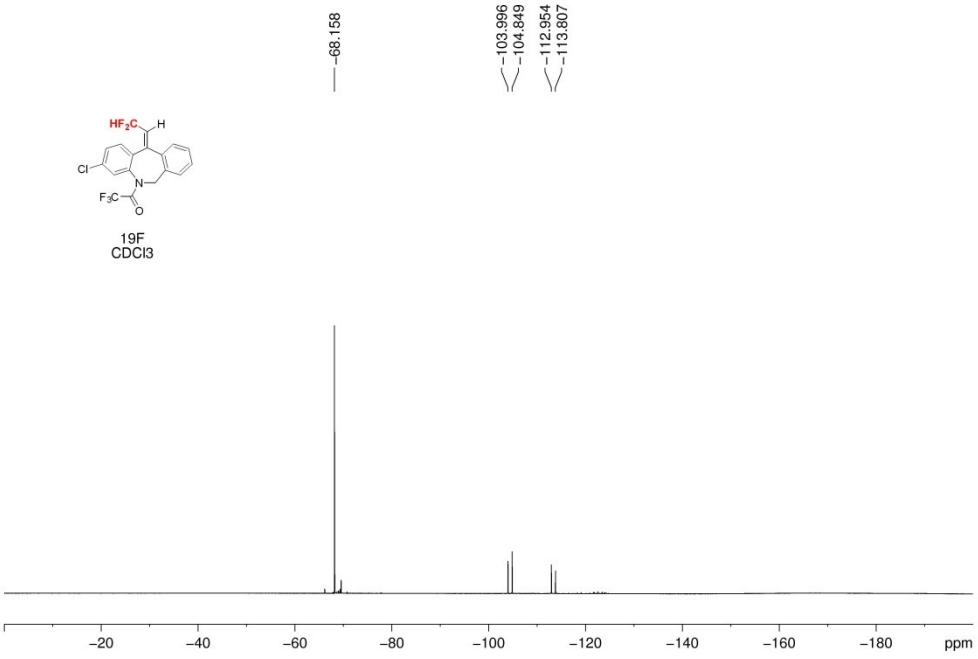


Figure S99. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5f**

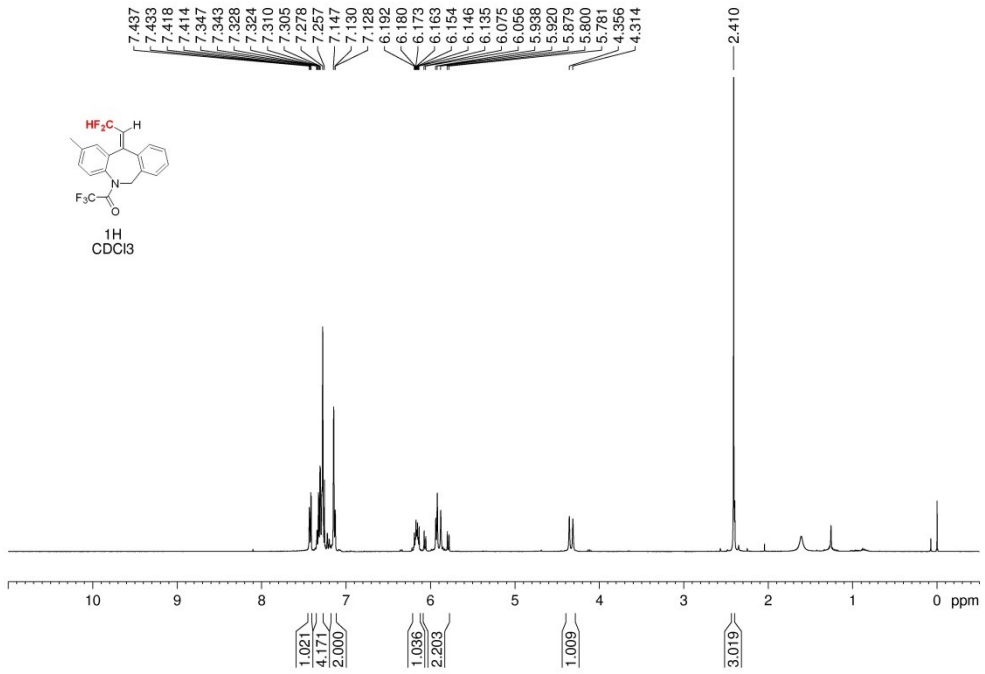


Figure S100. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5g**

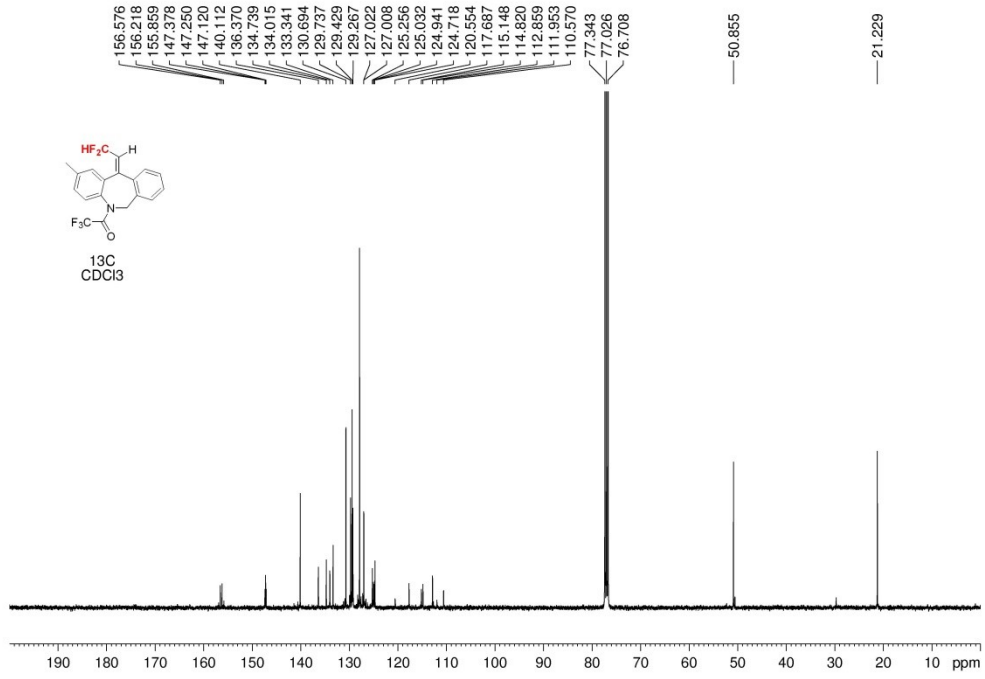


Figure S101. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5g**

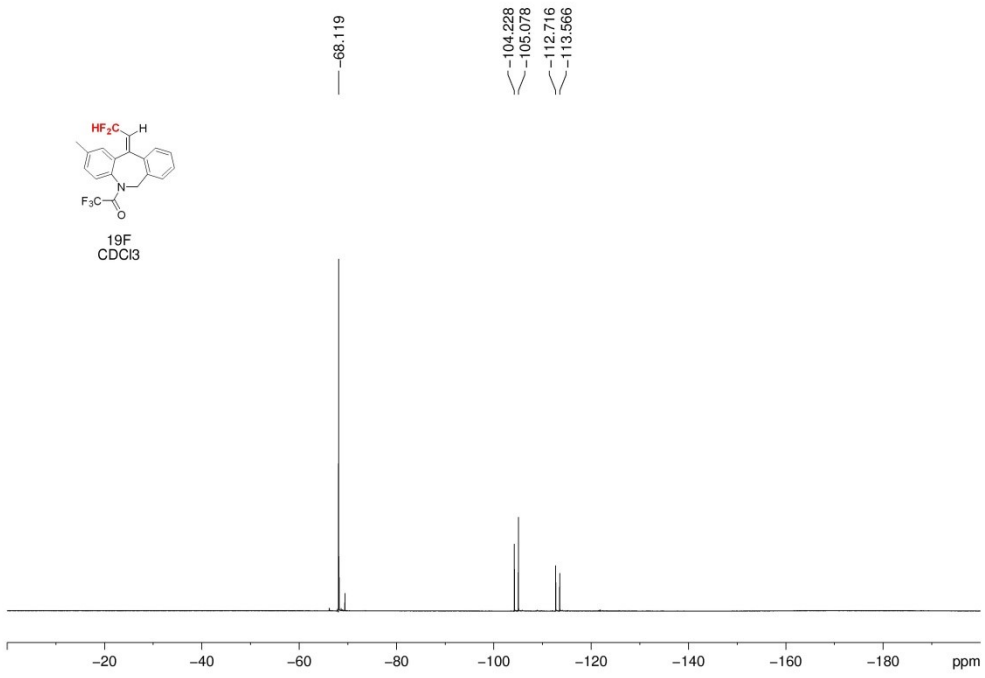


Figure S102. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5g**

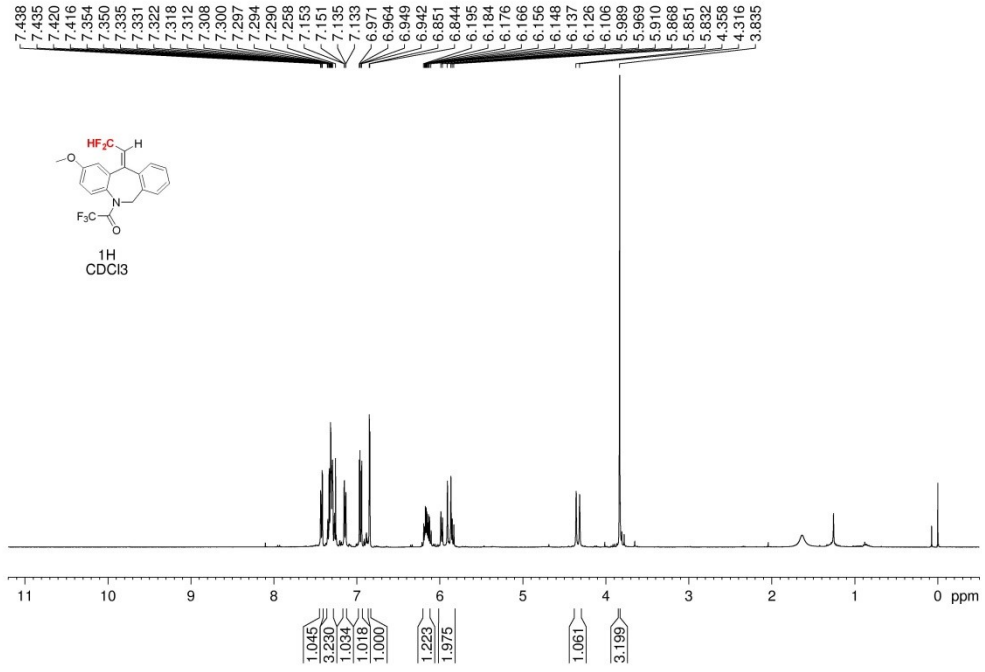


Figure S103. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5h**

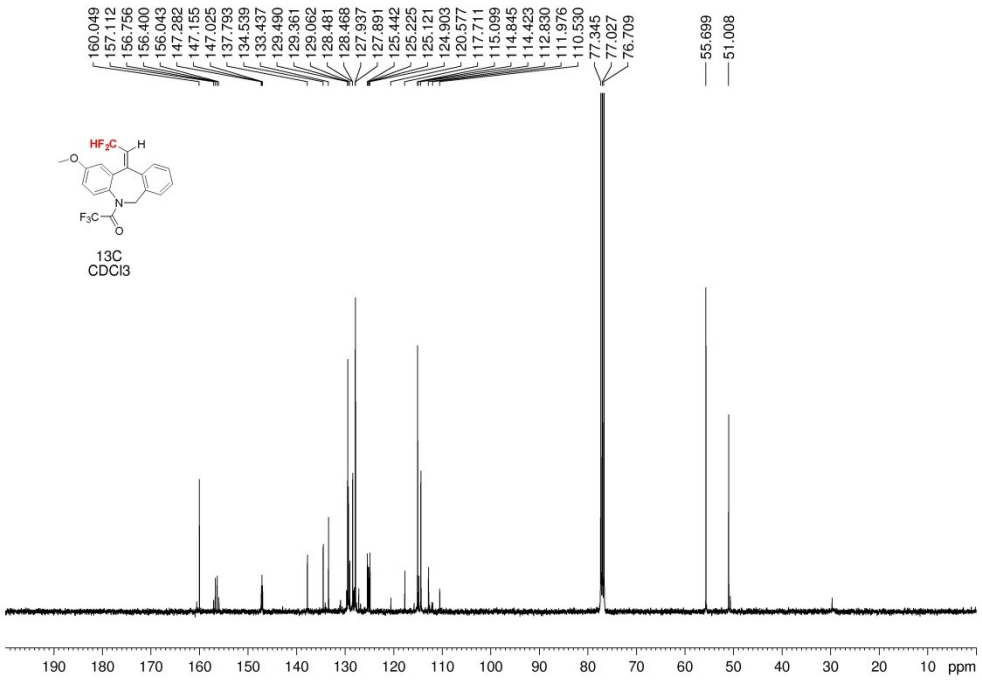


Figure S104. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5h**

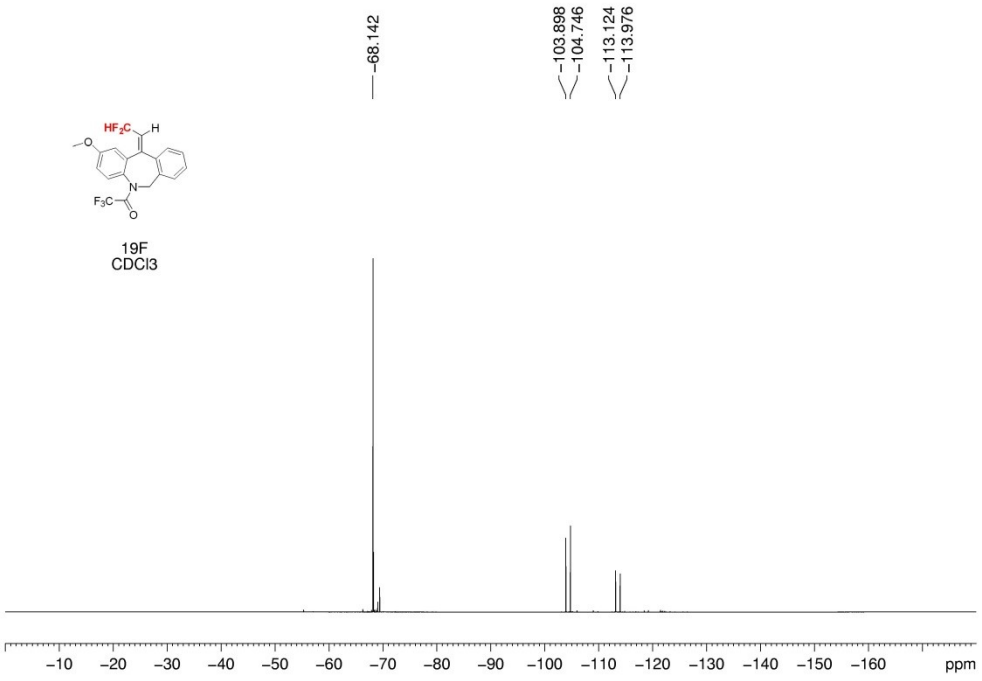


Figure S105. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5h**

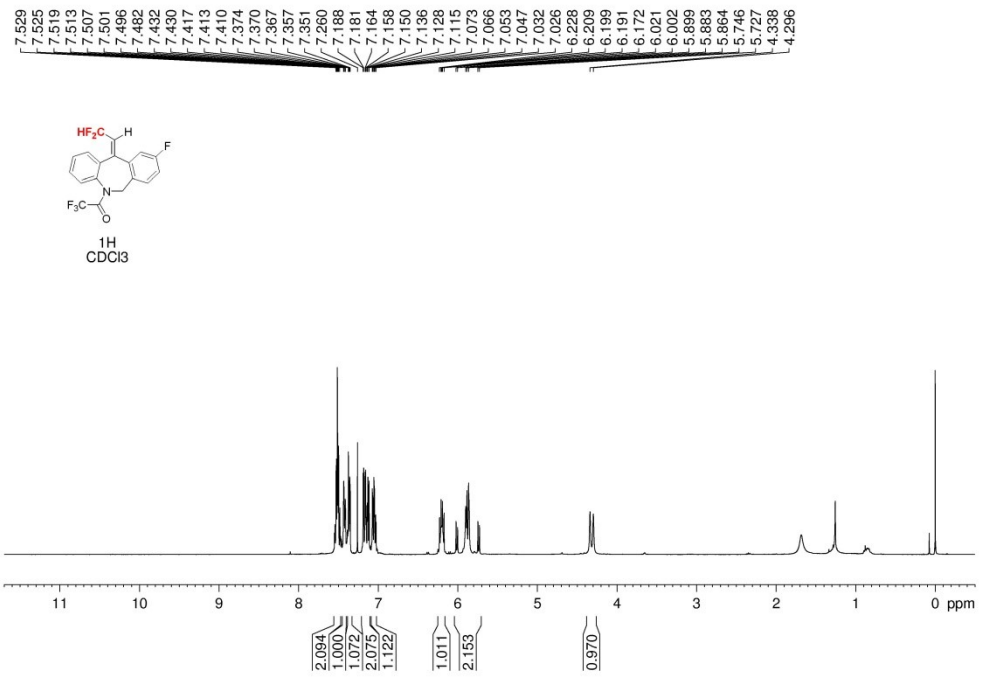


Figure S106. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5i**

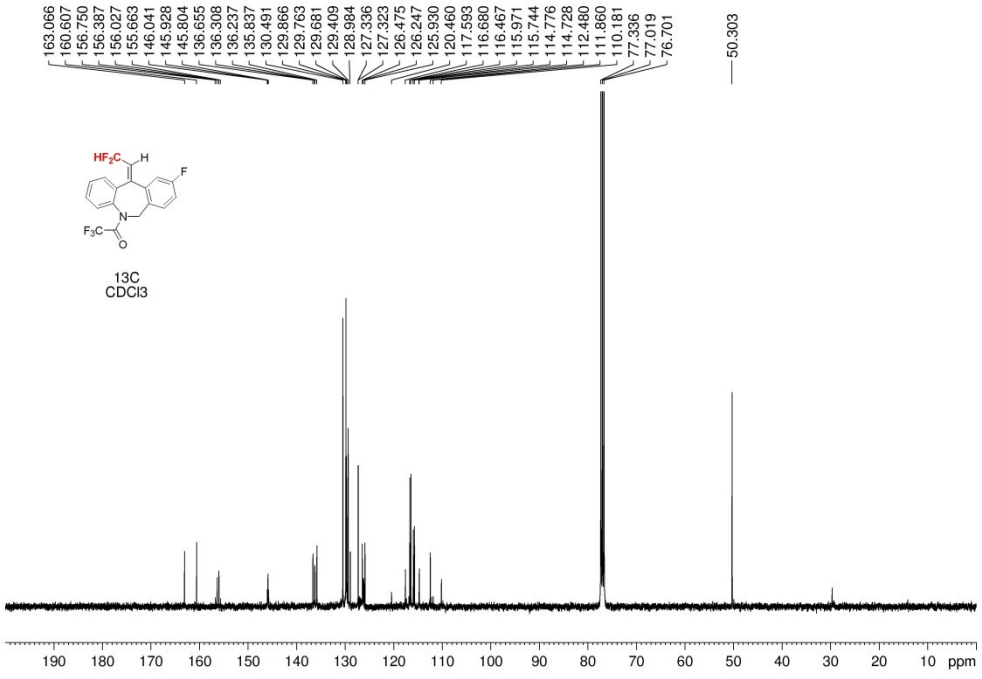


Figure S107. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5i**

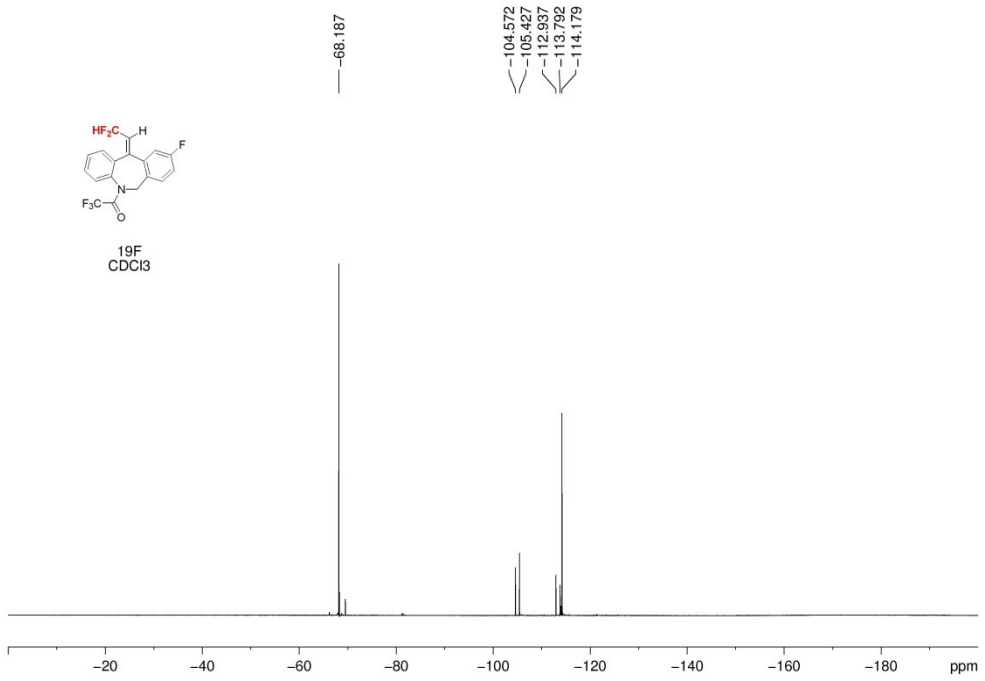


Figure S108. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5i**

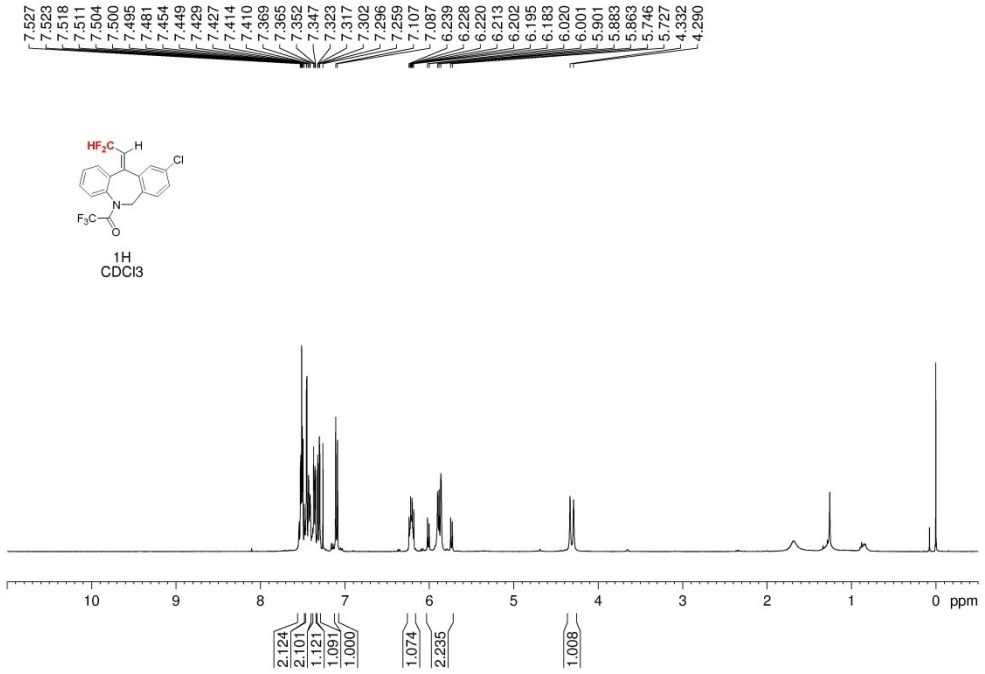


Figure S109. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5j**

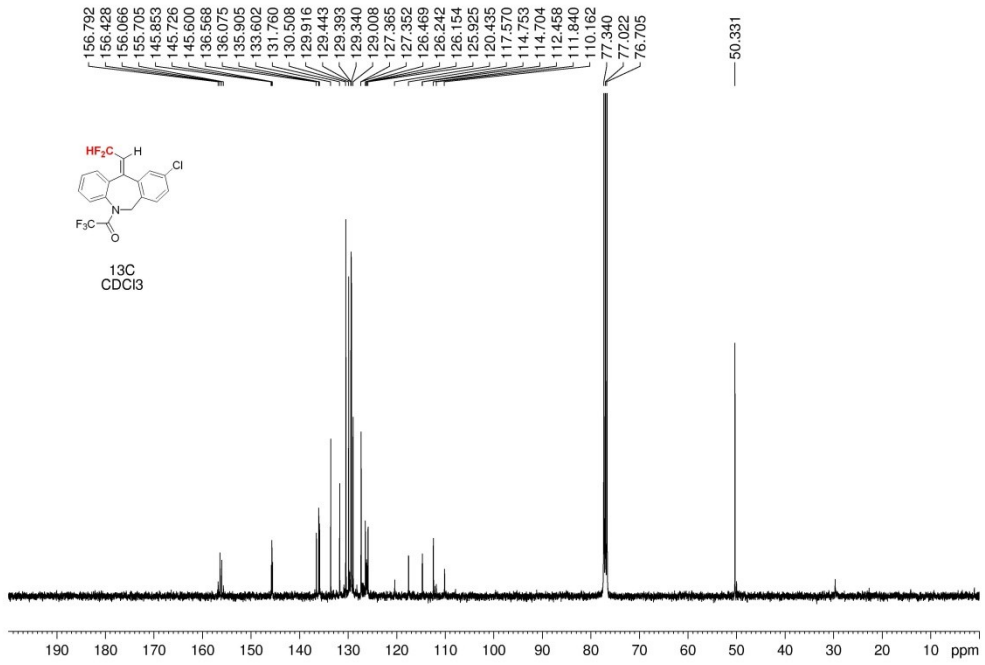


Figure S110. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5j**

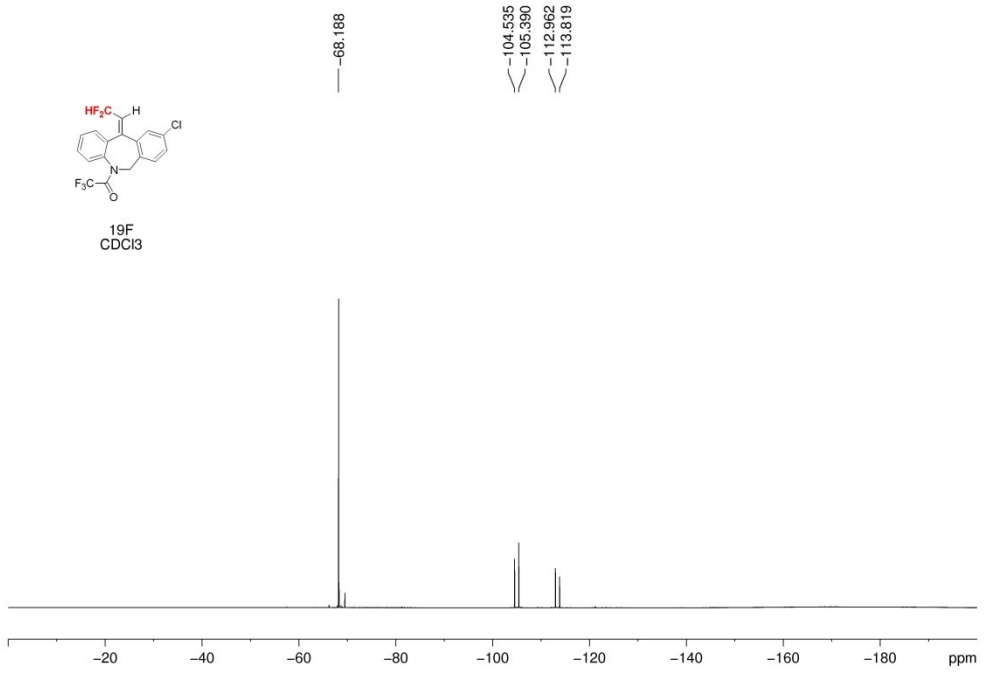


Figure S111. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5j**

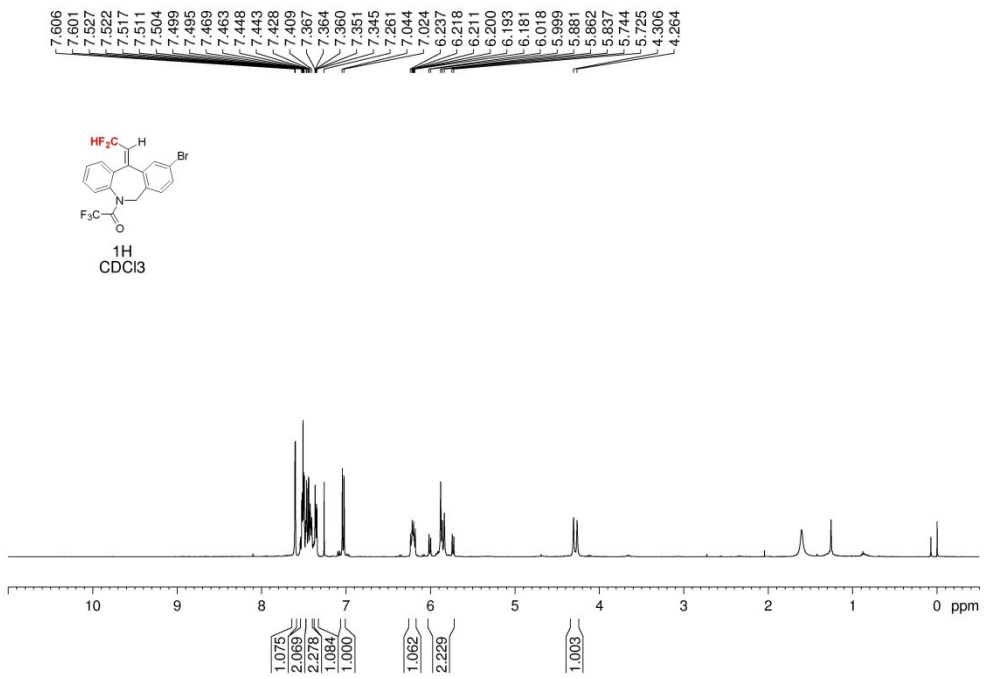


Figure S112. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5k**

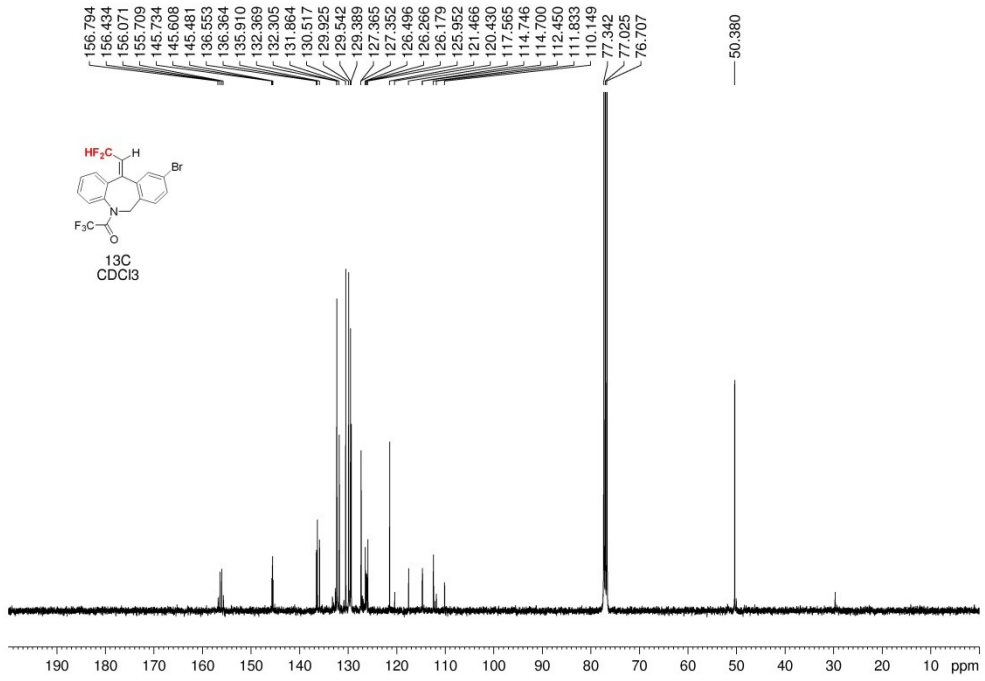


Figure S113. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5k**

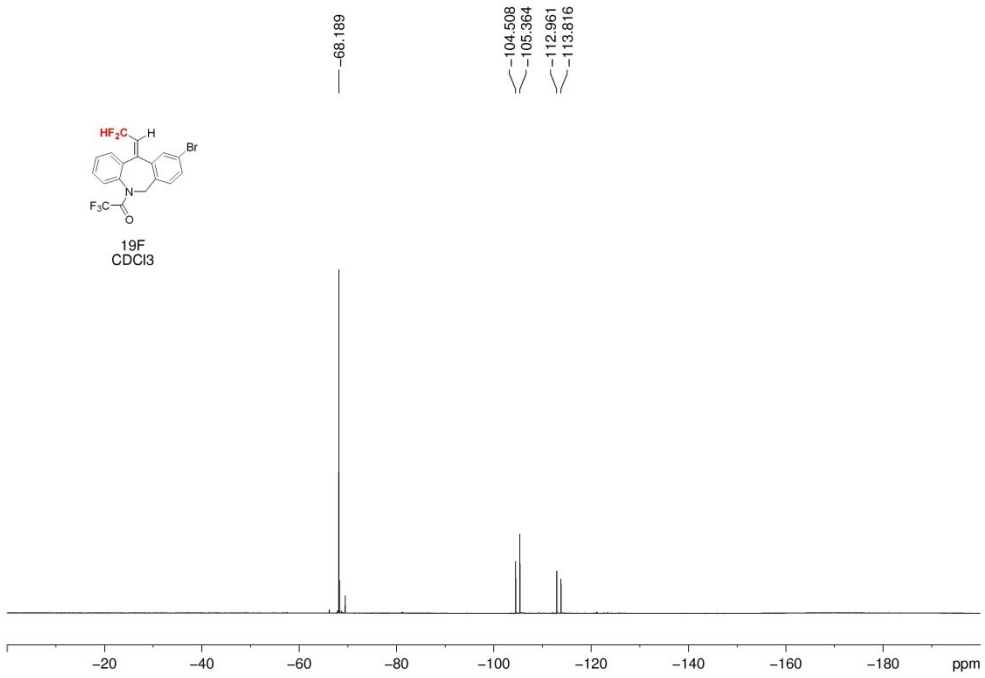


Figure S114. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5k**

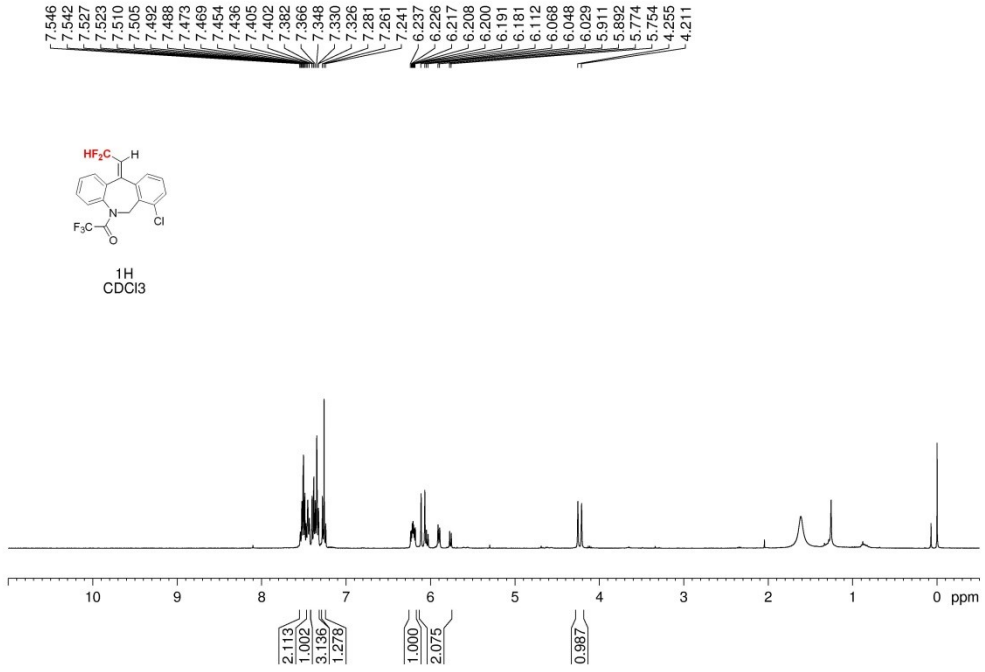


Figure S115. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5l**

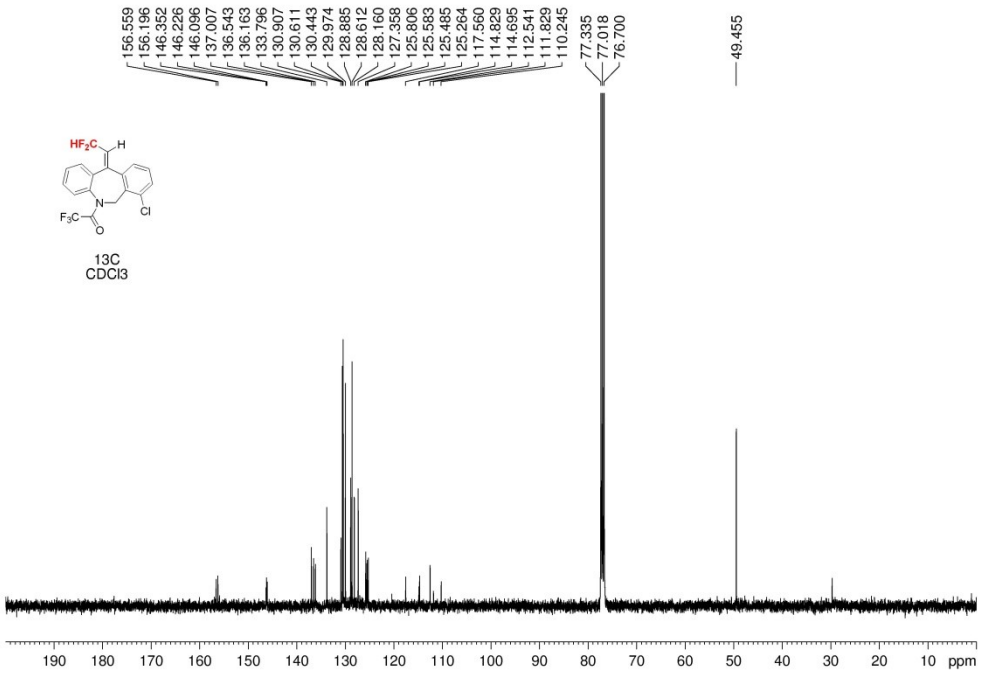


Figure S116. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5l**

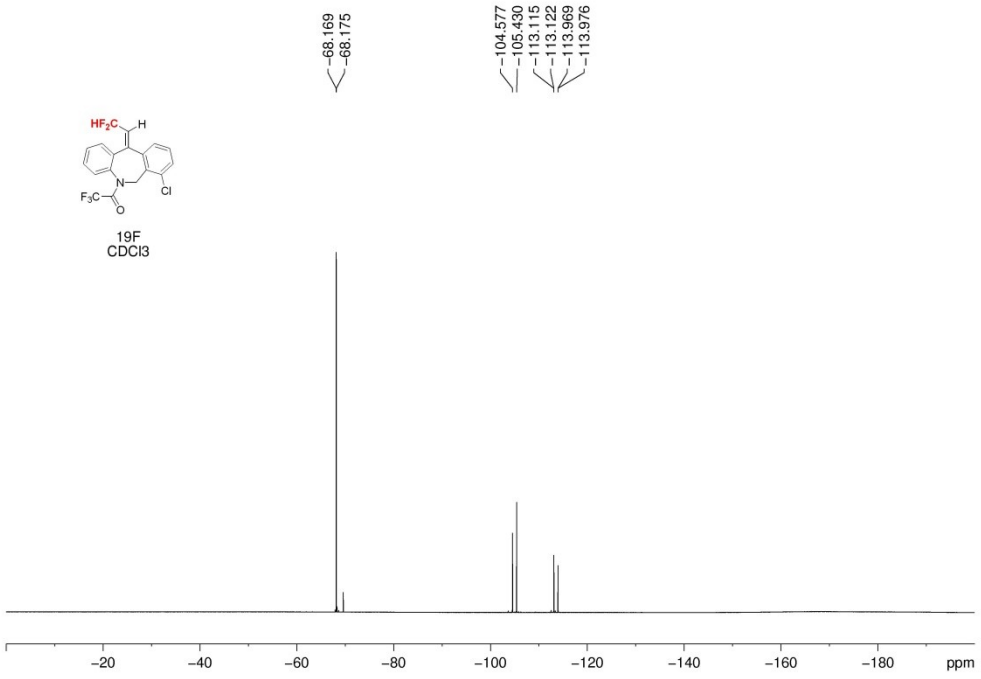


Figure S117. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5l**

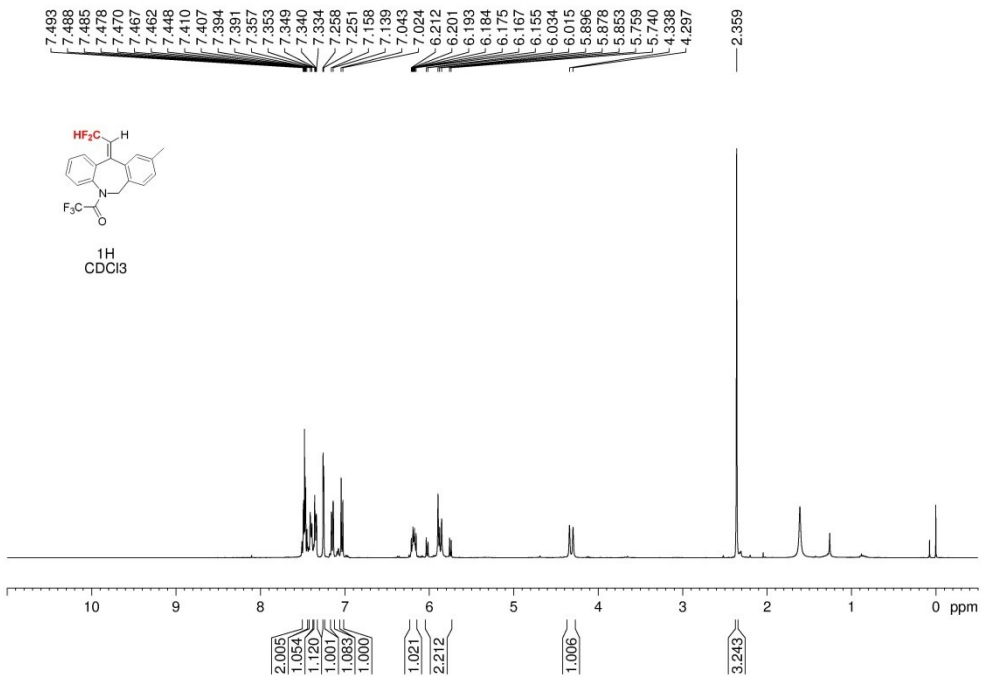


Figure S118. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5m**

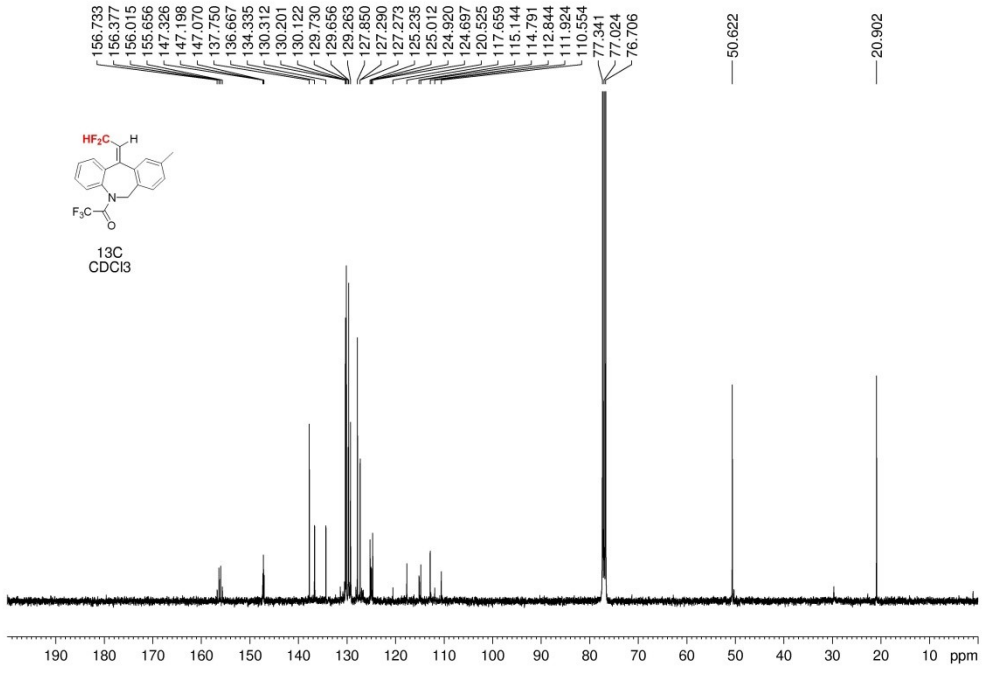


Figure S119. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5m**

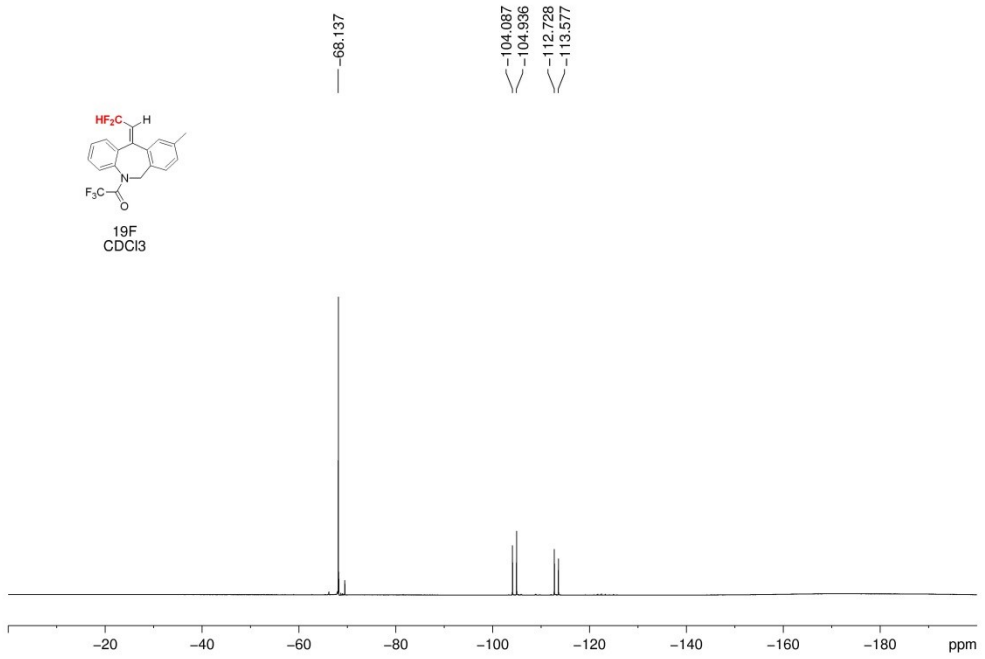


Figure S120. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5m**

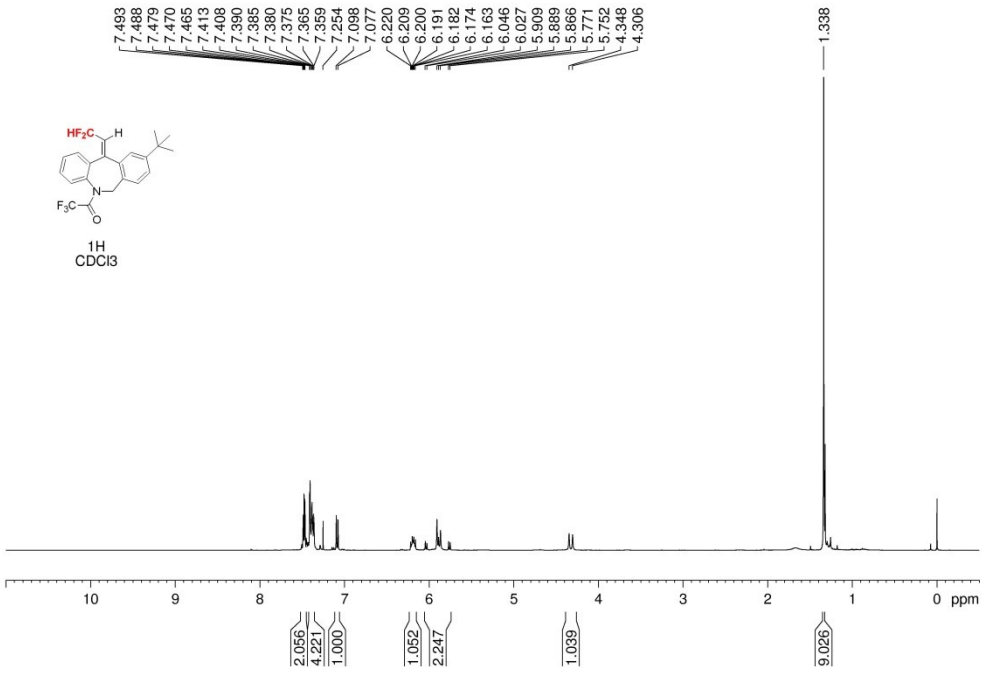


Figure S121. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5n**

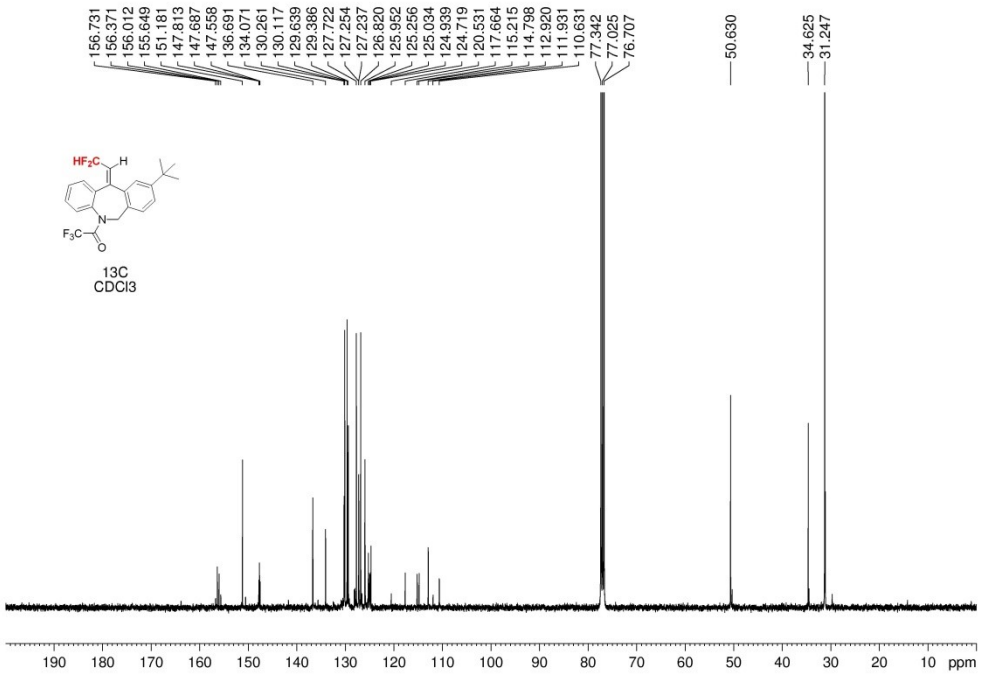


Figure S122. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5n**

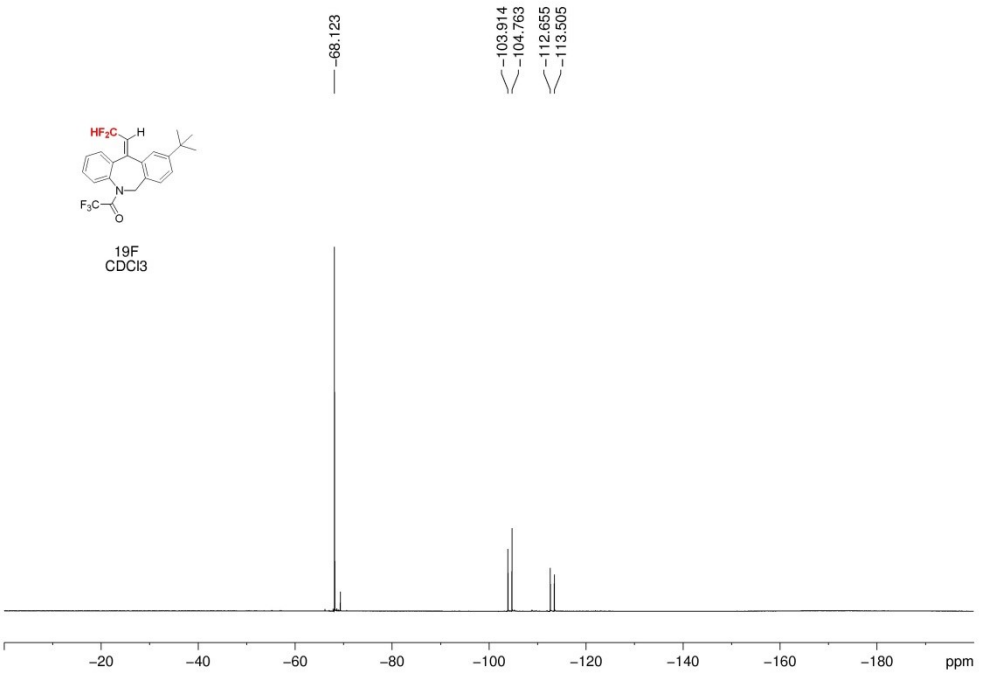


Figure S123. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5n**

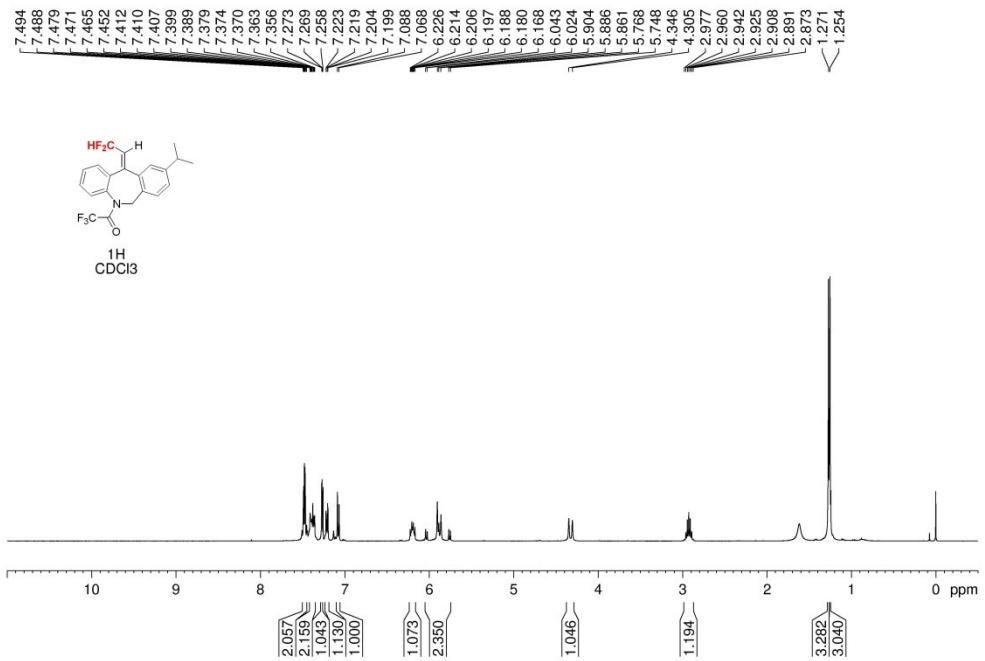


Figure S124. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5o**

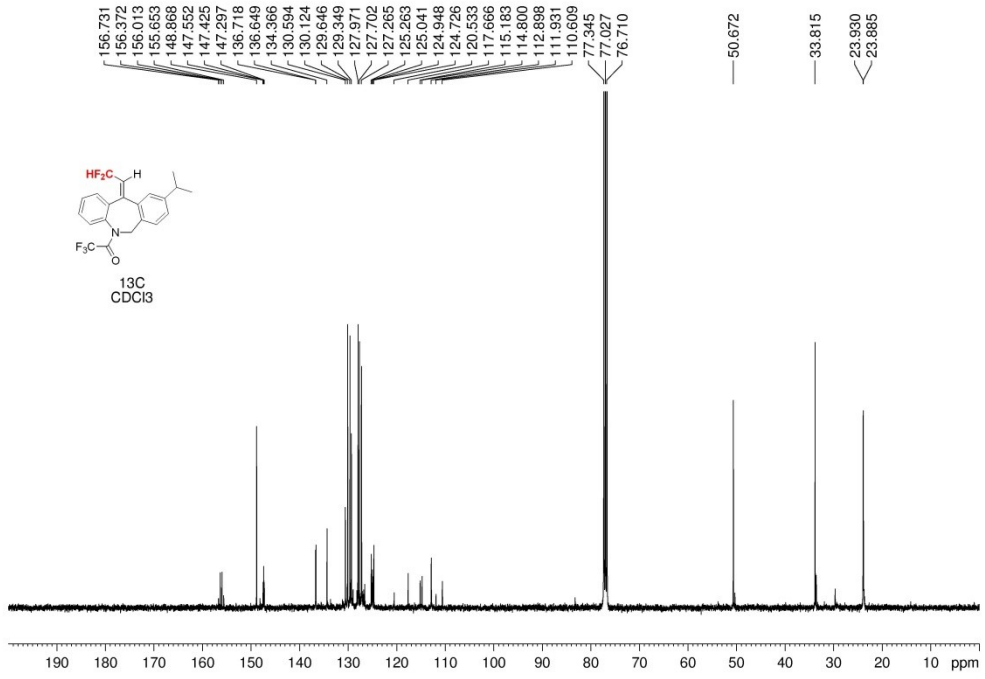


Figure S125. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5o**

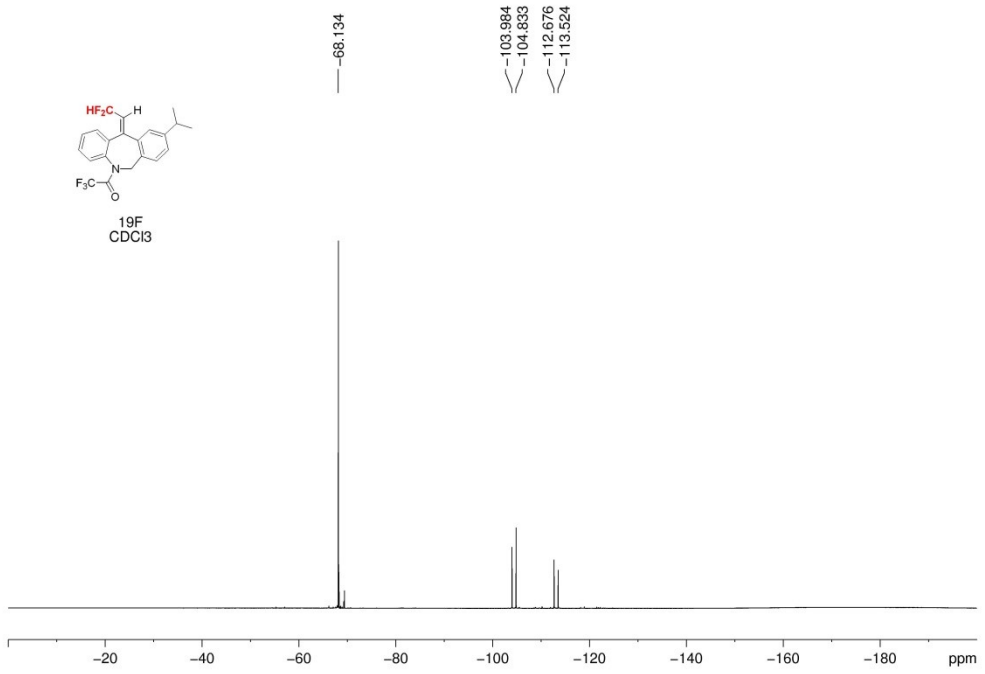


Figure S126. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5o**

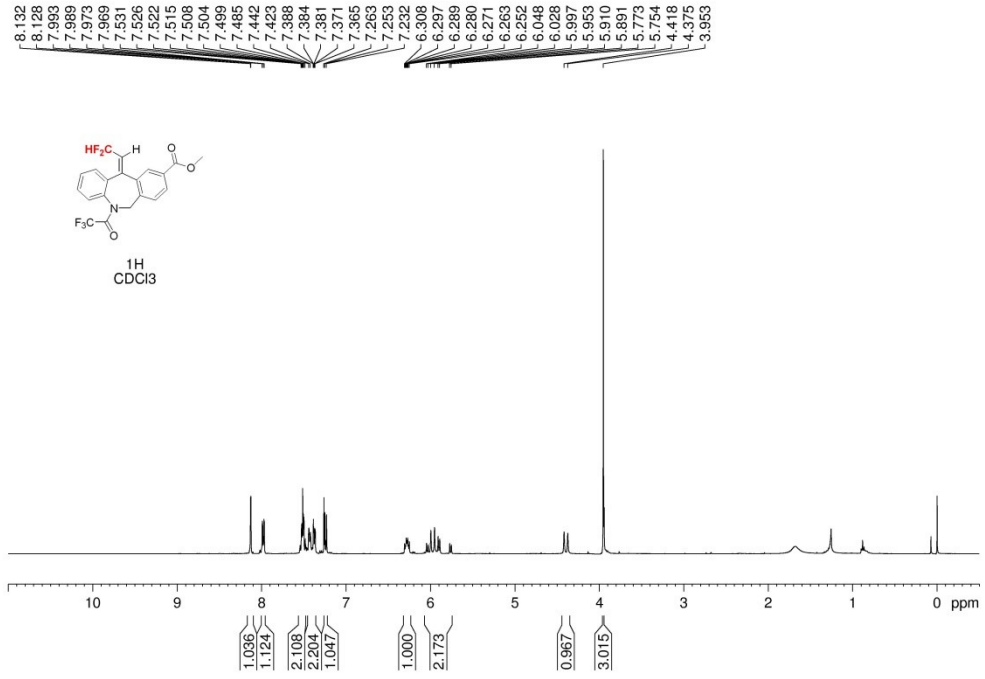


Figure S127. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5p**

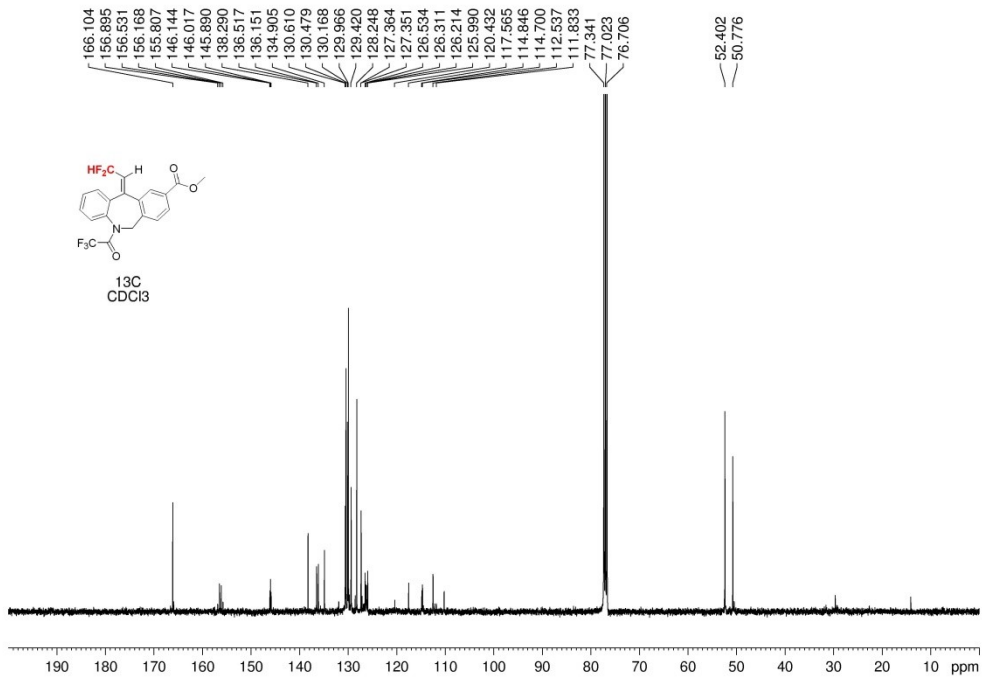


Figure S128. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5p**

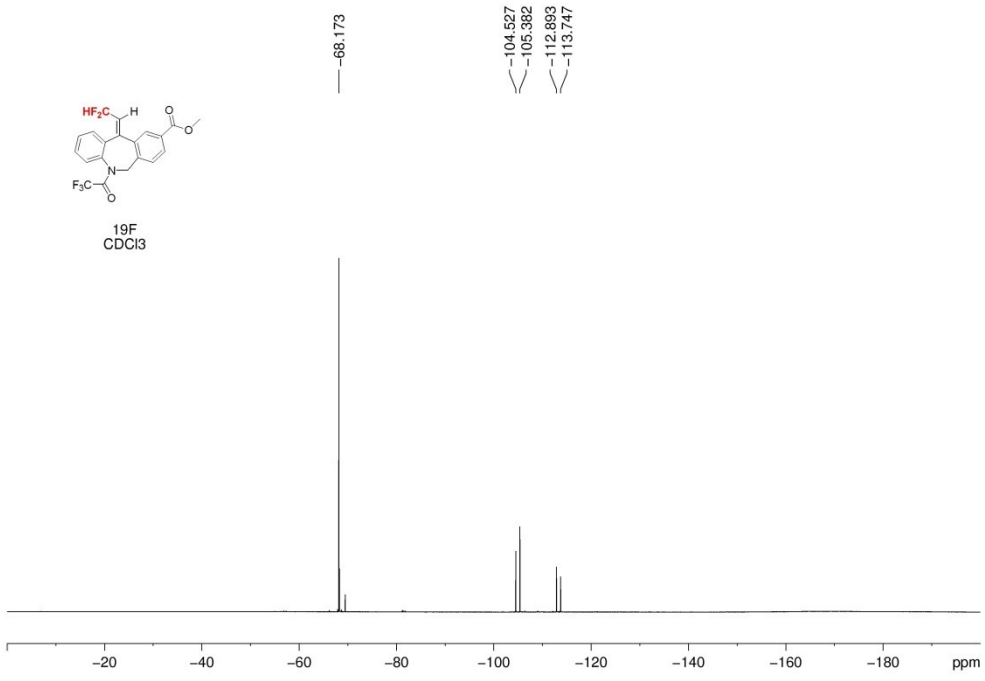


Figure S129. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5p**

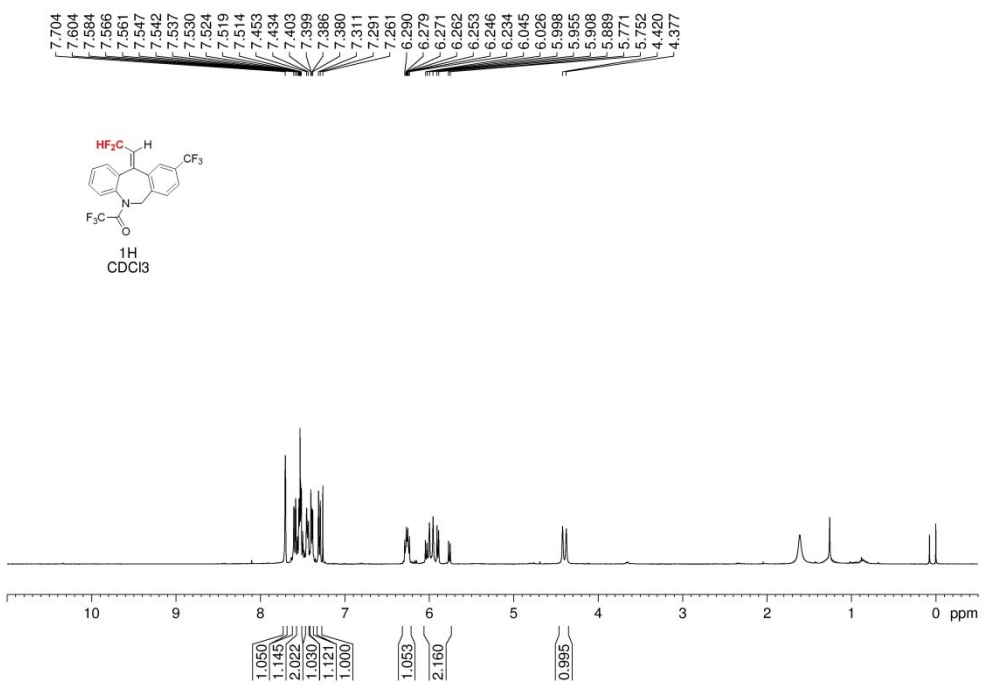


Figure S130. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5q**

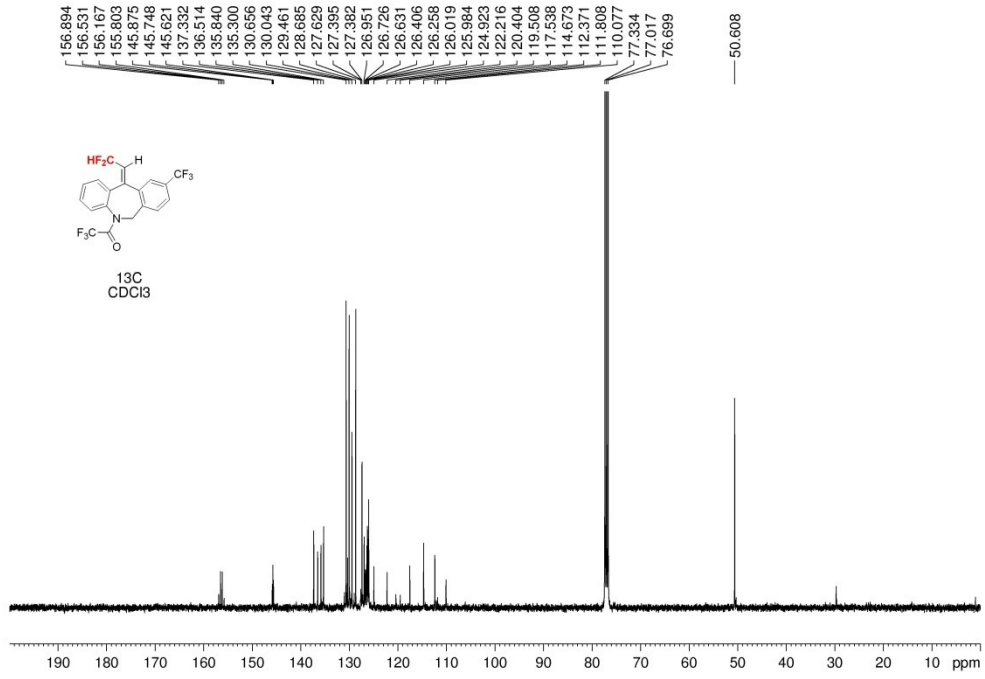


Figure S131. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5q**

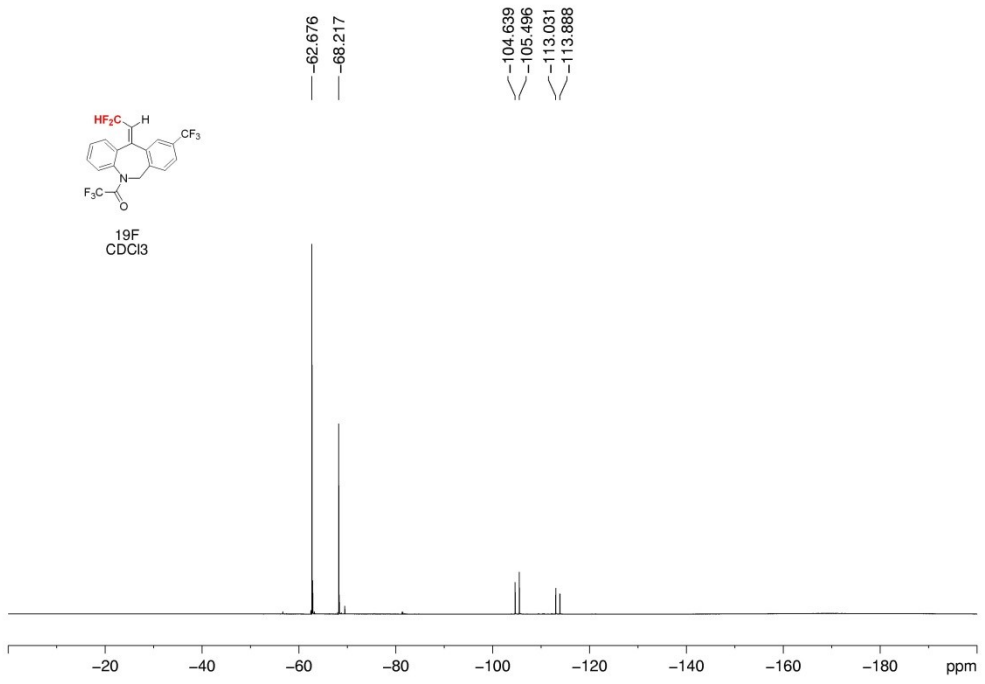


Figure S132. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5q**

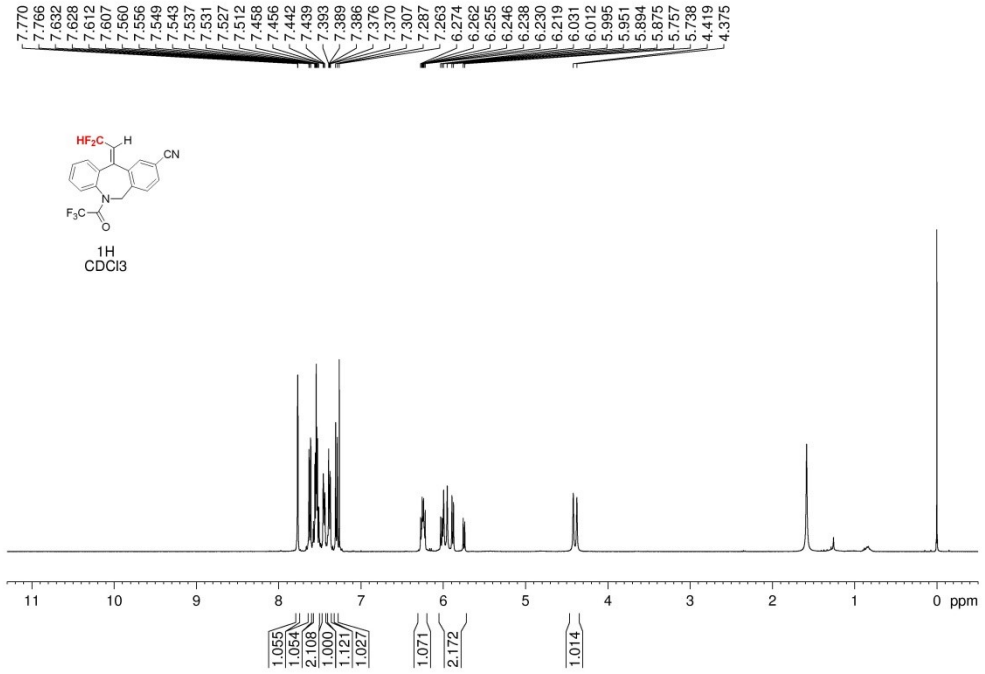


Figure S133. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5r**

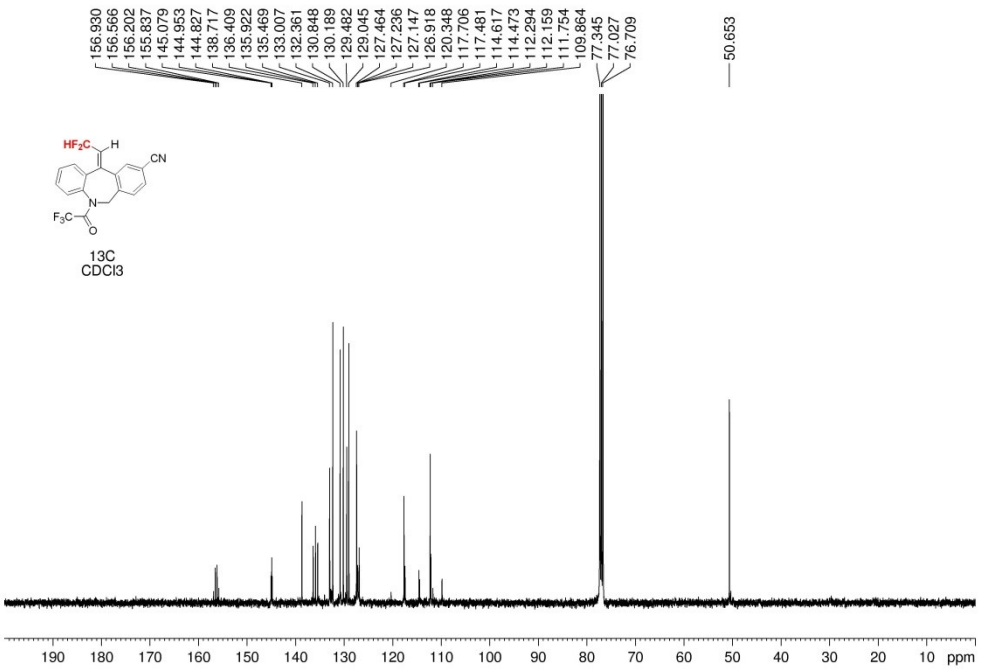


Figure S134. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5r**

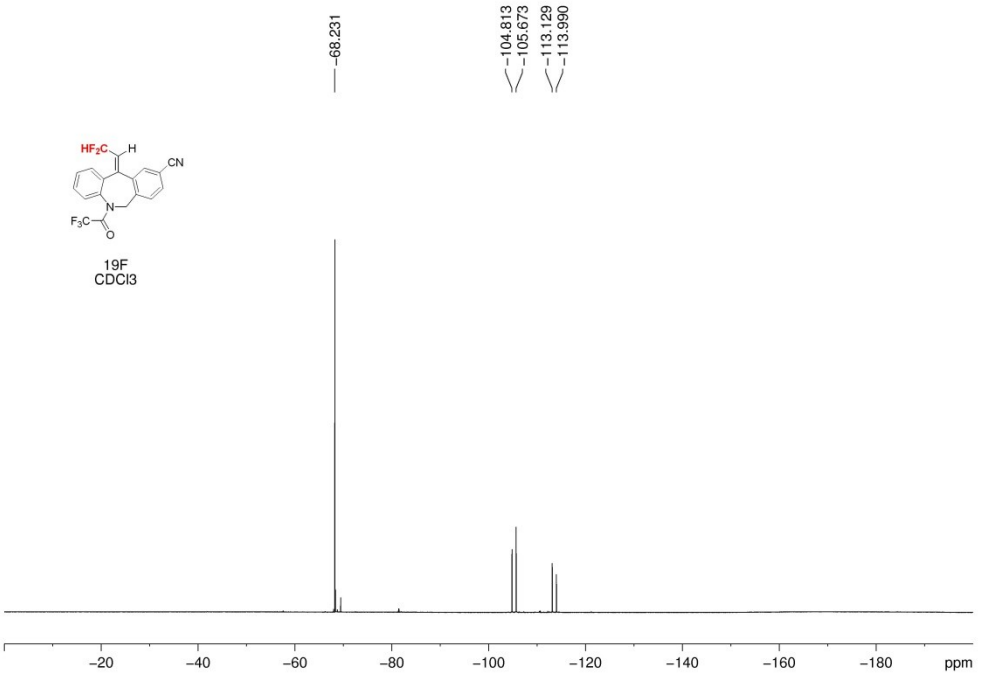


Figure S135. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5r**

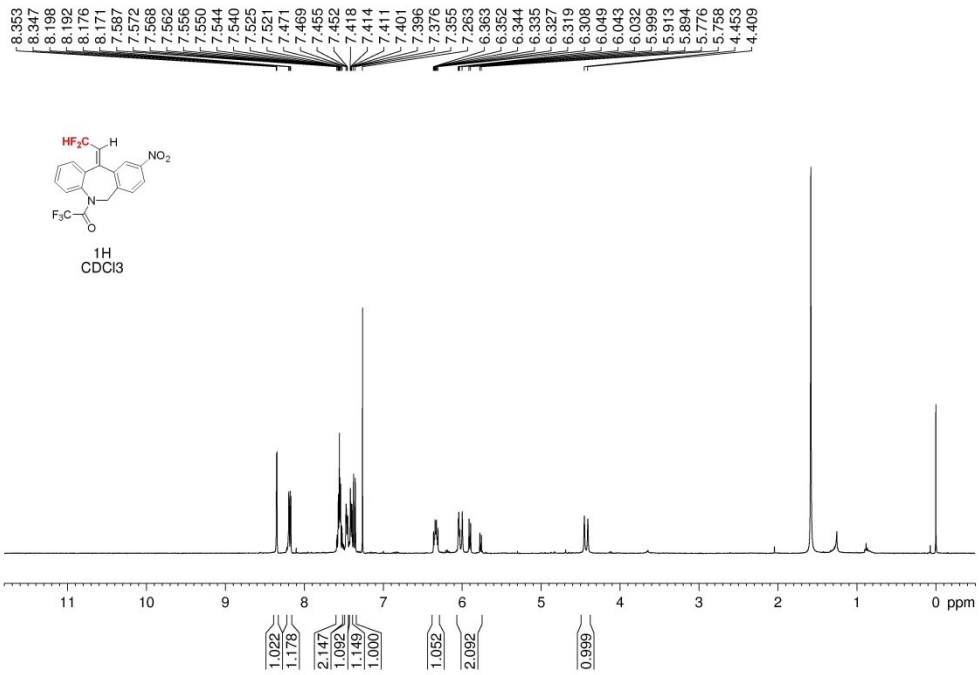


Figure S136. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5s**

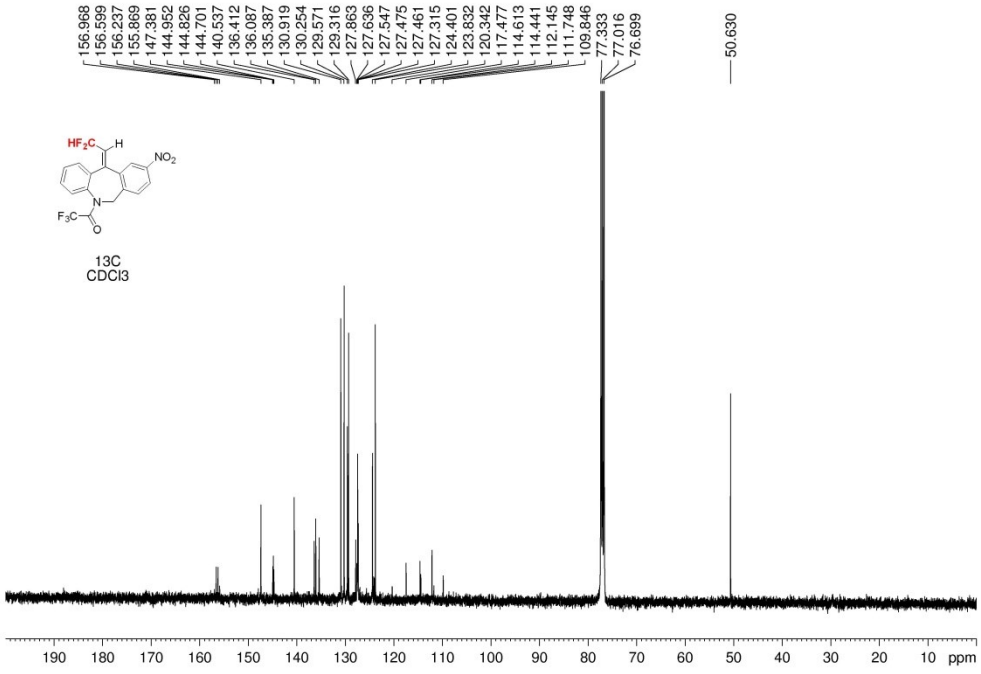


Figure S137. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5s**

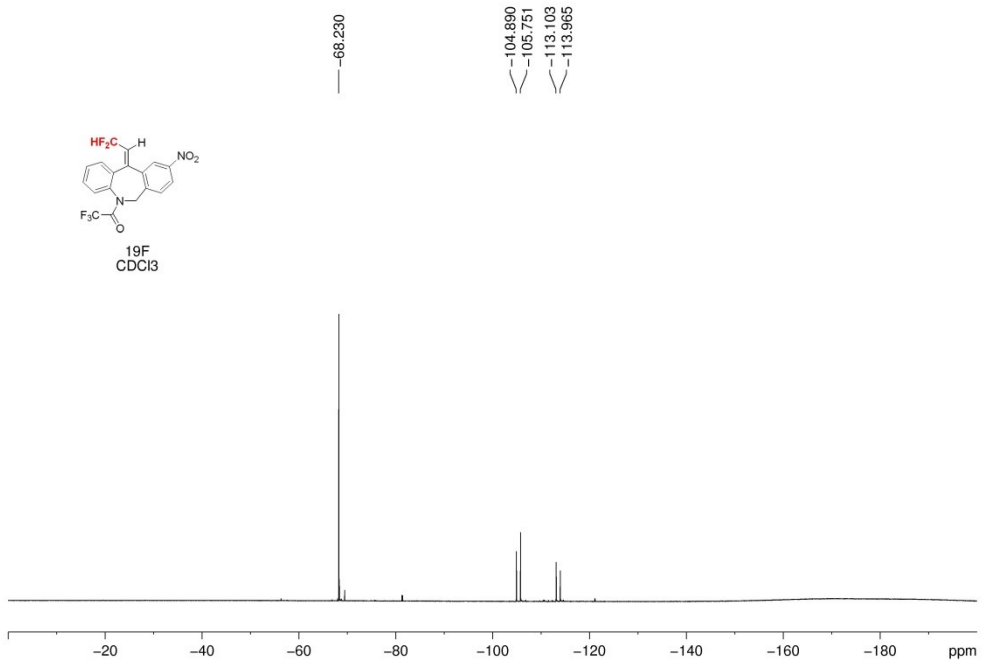


Figure S138. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5s**

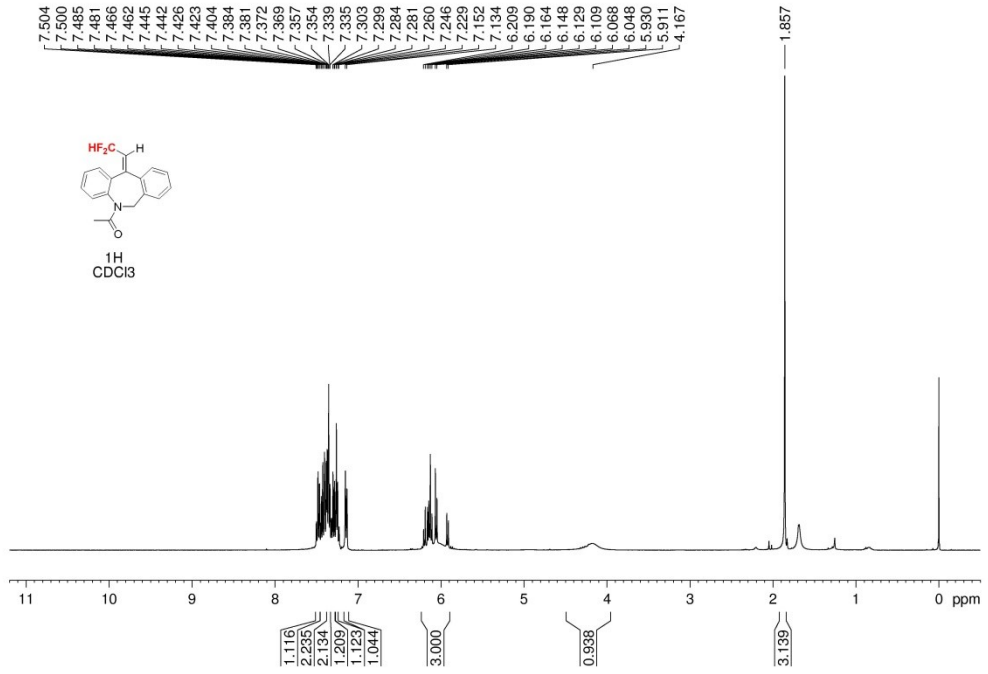


Figure S139. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5t**

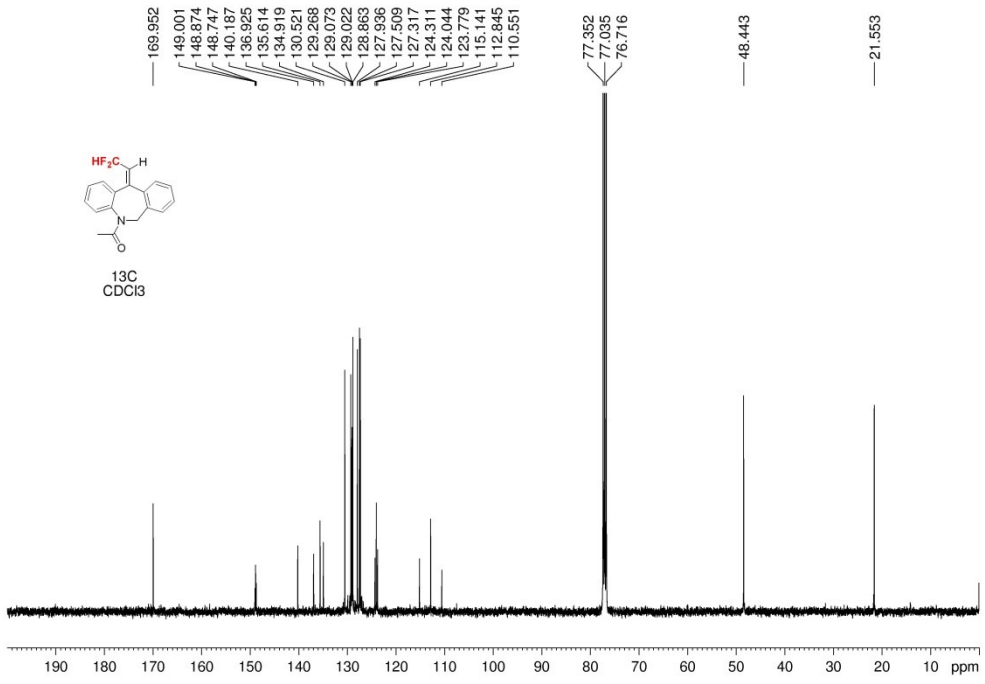


Figure S140. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5t**

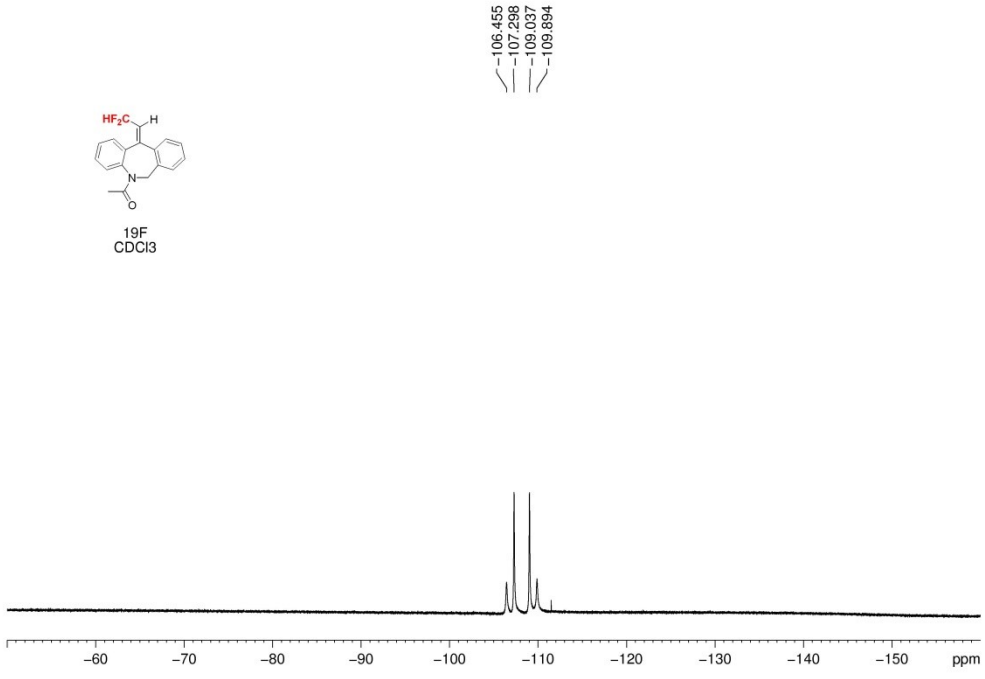


Figure S141. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5t**

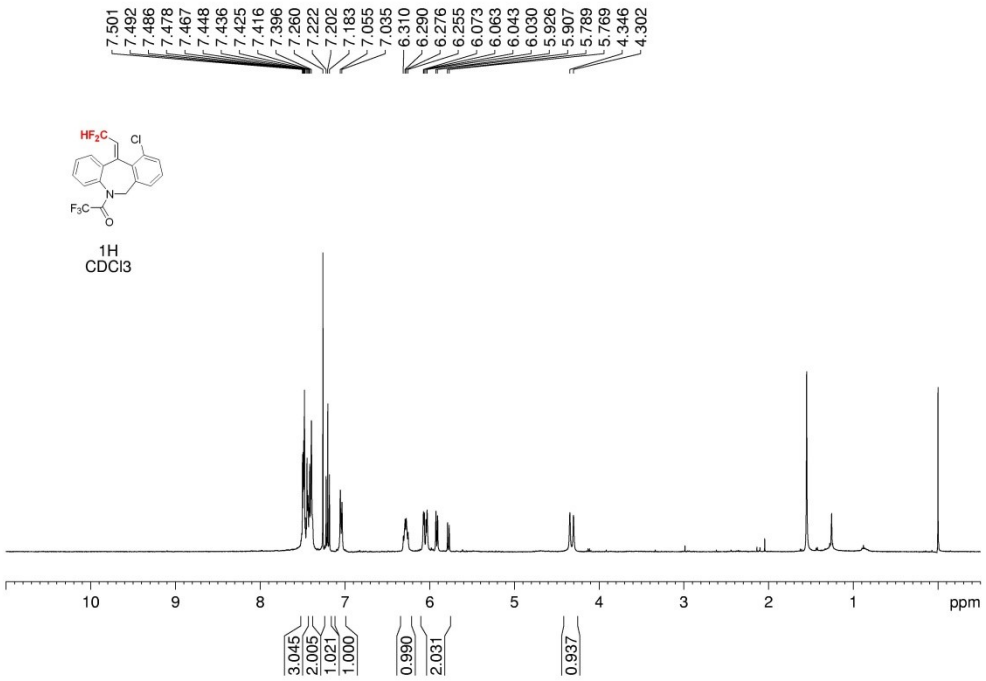


Figure S142. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5v**

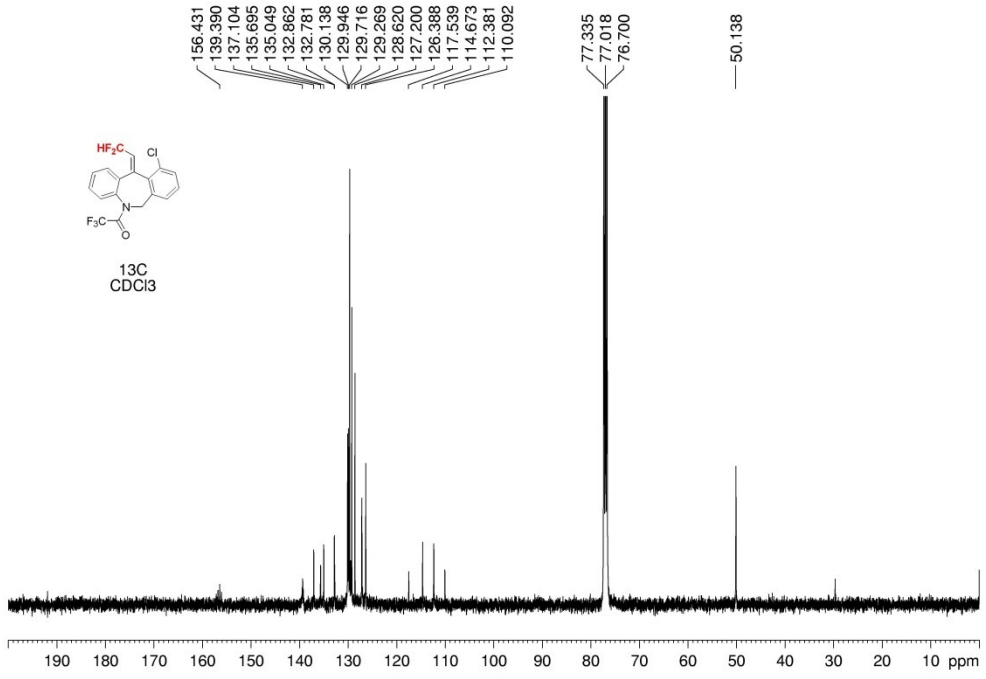


Figure S143. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5v**

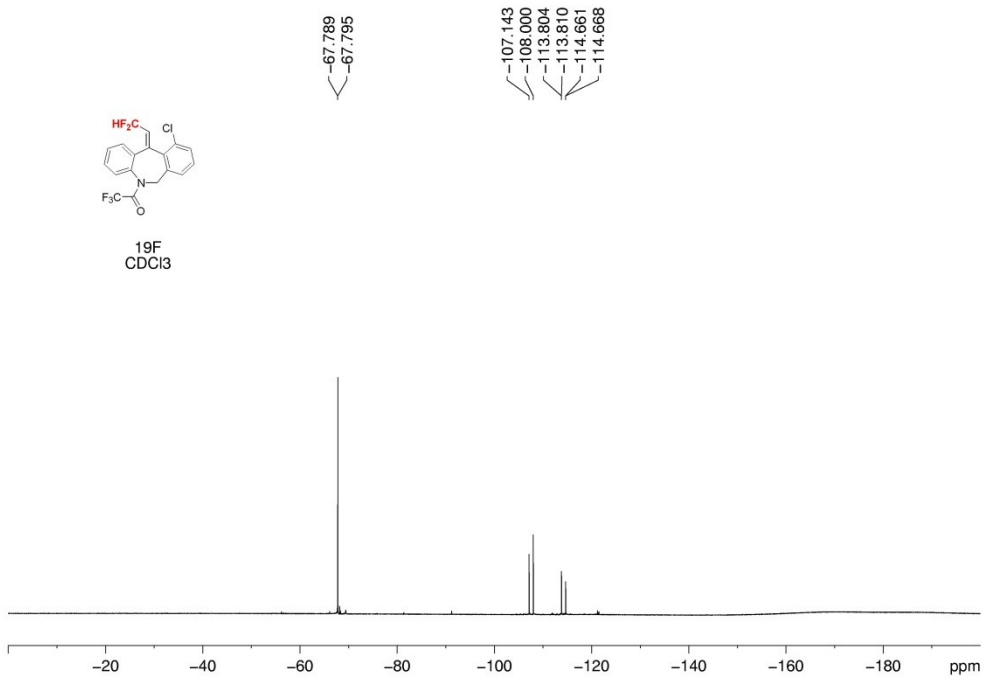


Figure S144. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5v**

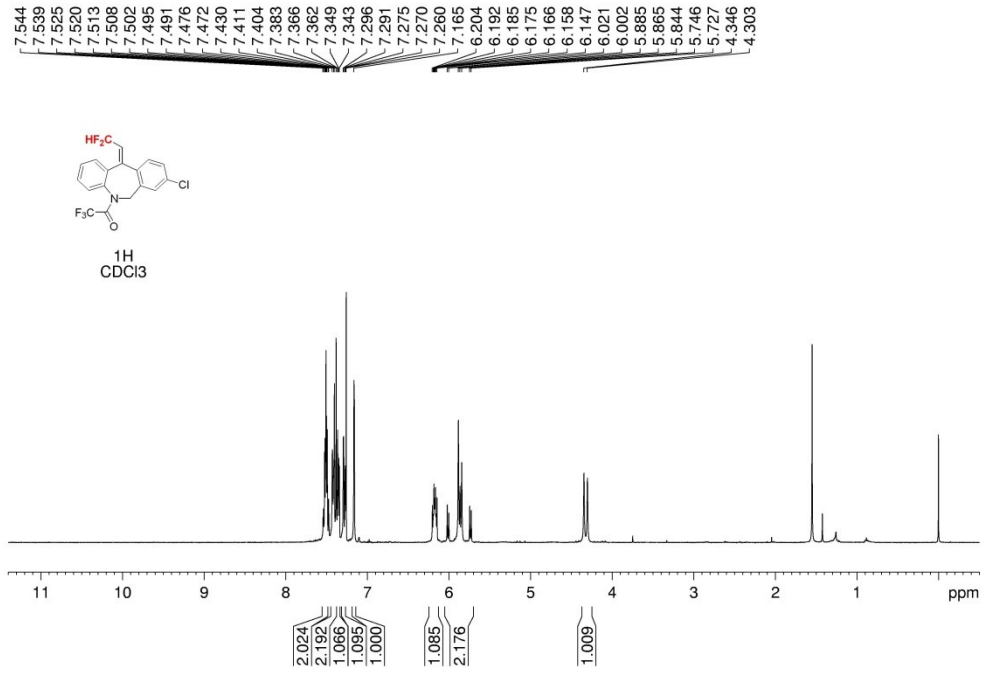


Figure S145. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5v′**

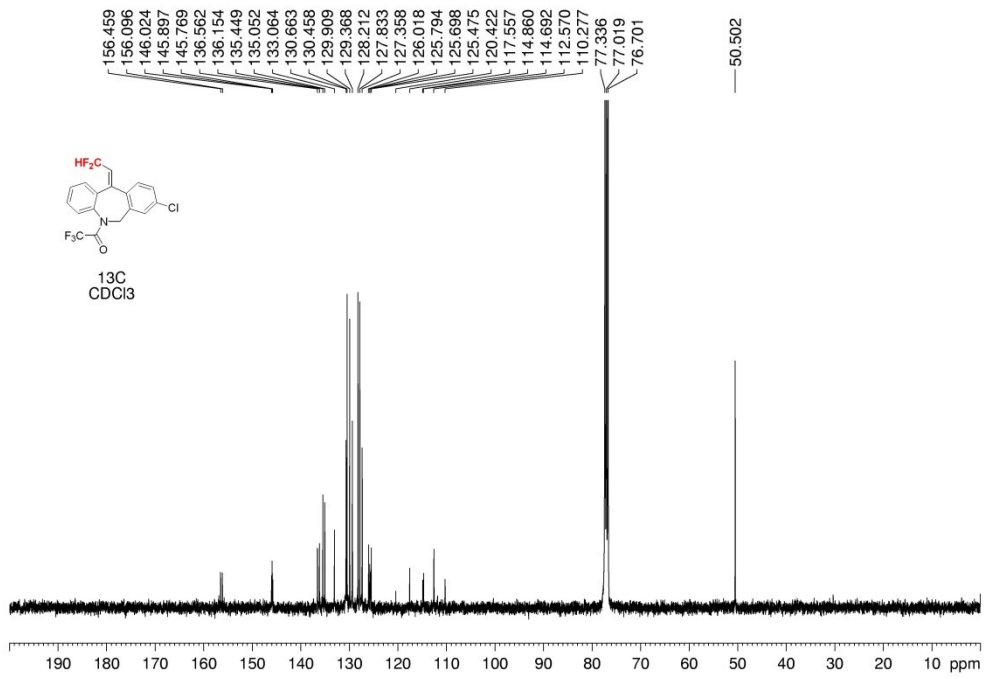


Figure S146. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5v′**

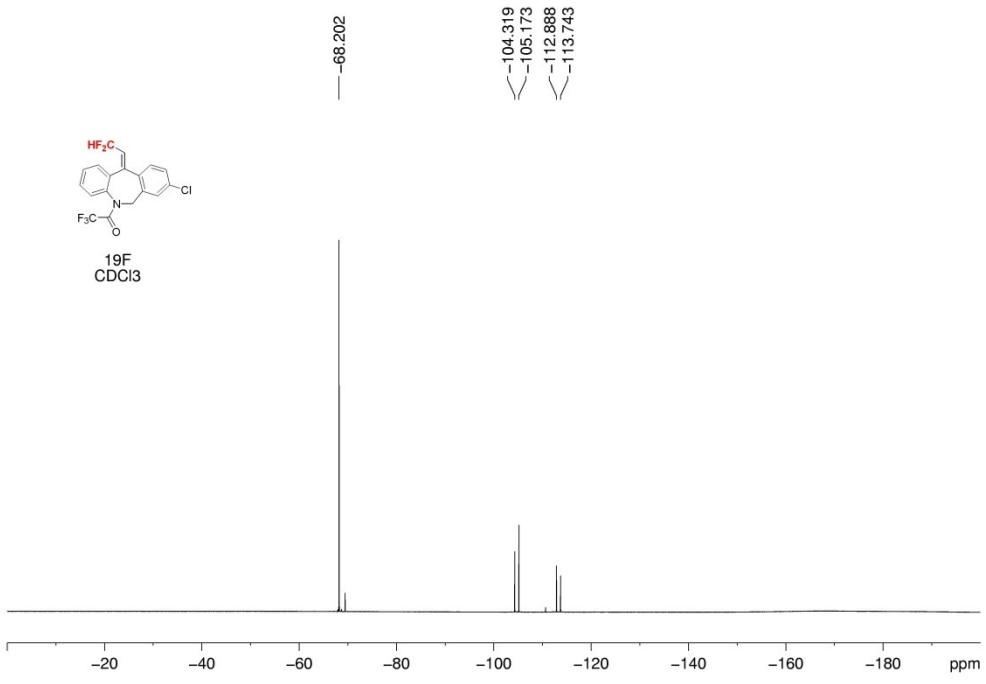


Figure S147. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5v′**

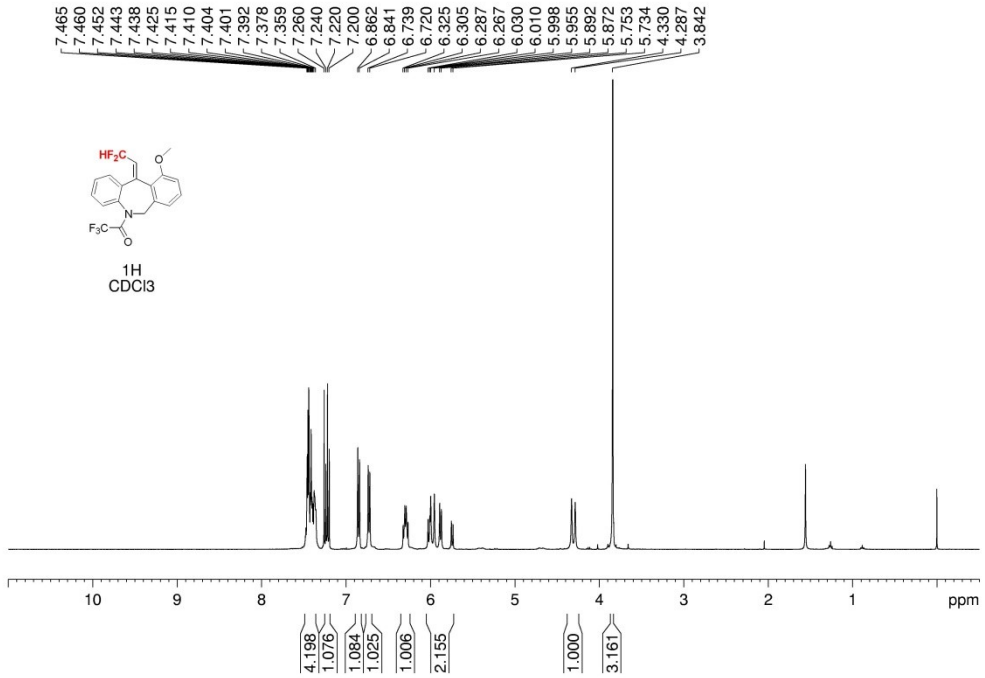


Figure S148. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5w**

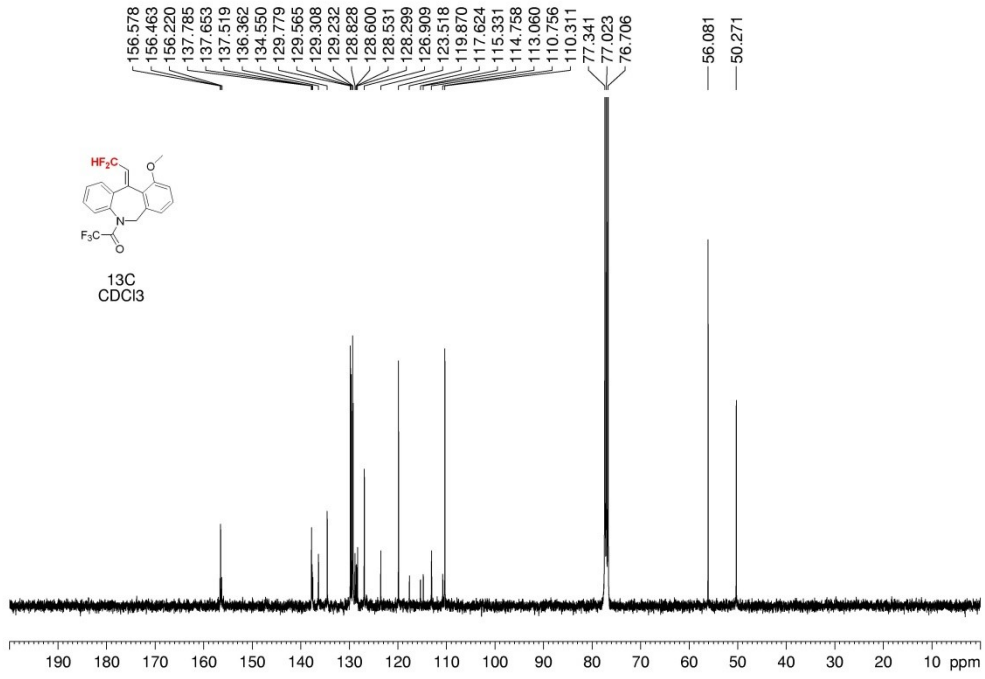


Figure S149. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5w**

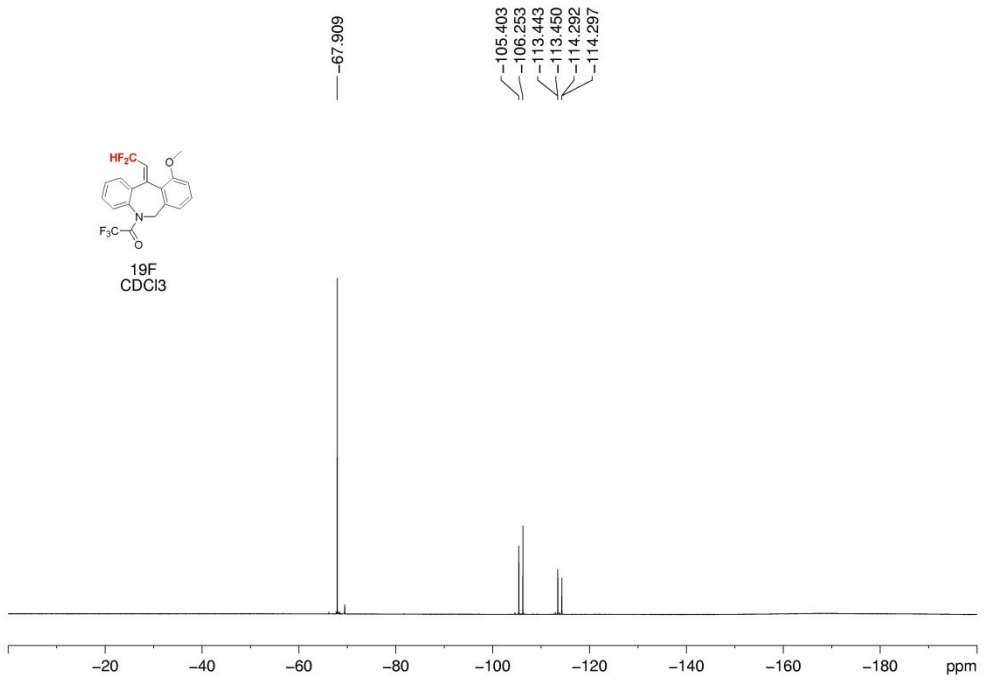


Figure S150. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5w**

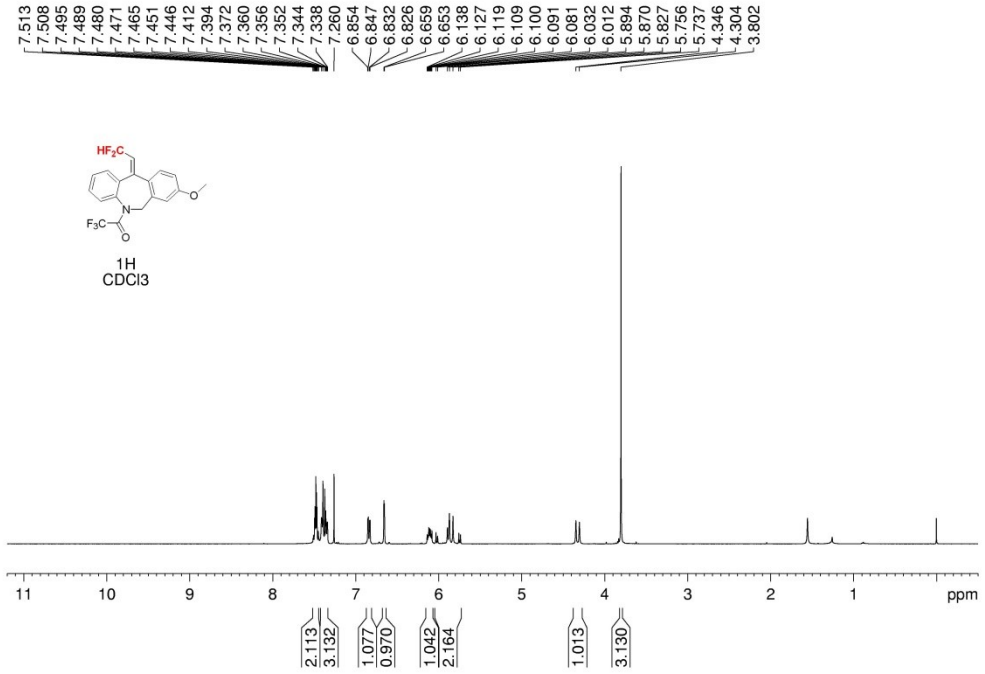


Figure S151. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5w′**

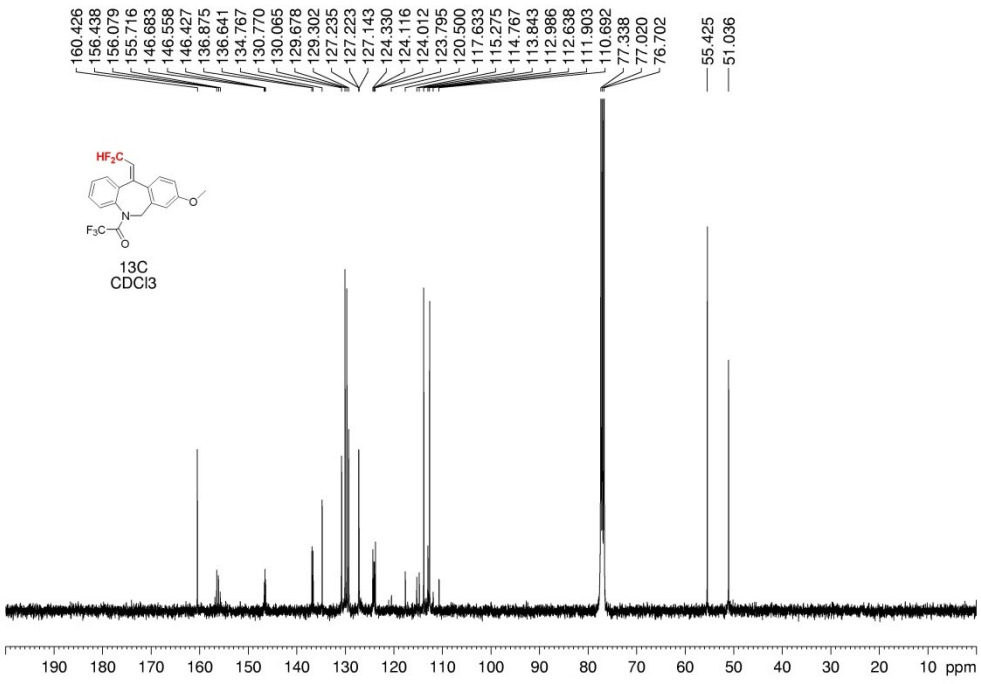


Figure S152. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5w′**

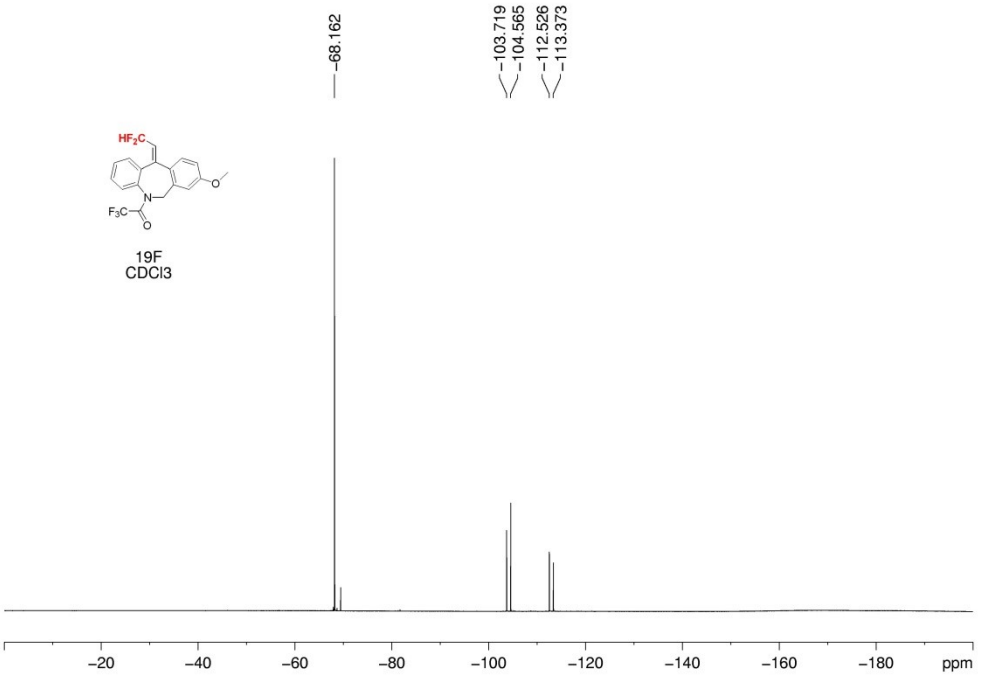


Figure S153. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **5w′**

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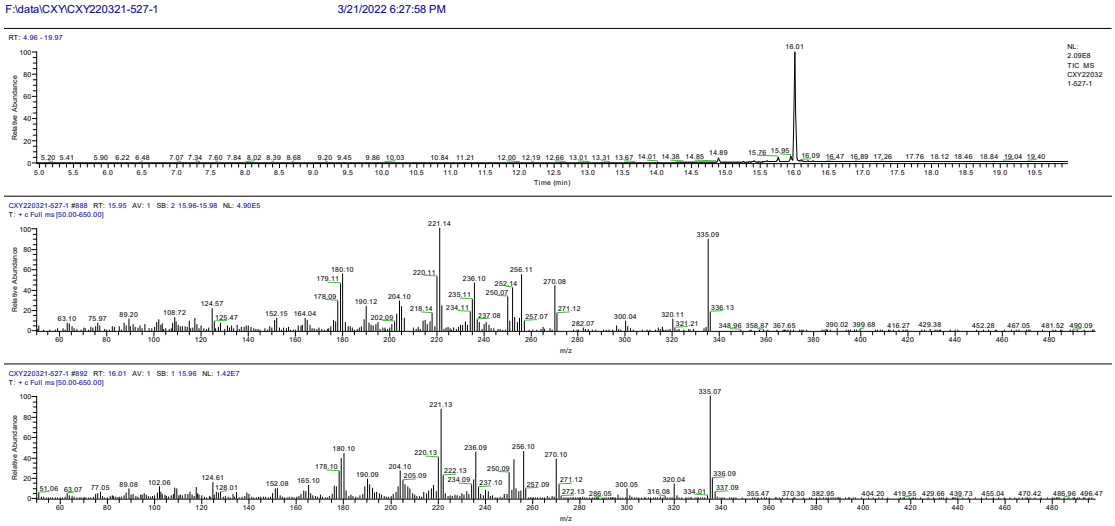

Figure S154. GC–MS spectra of compound **3a**

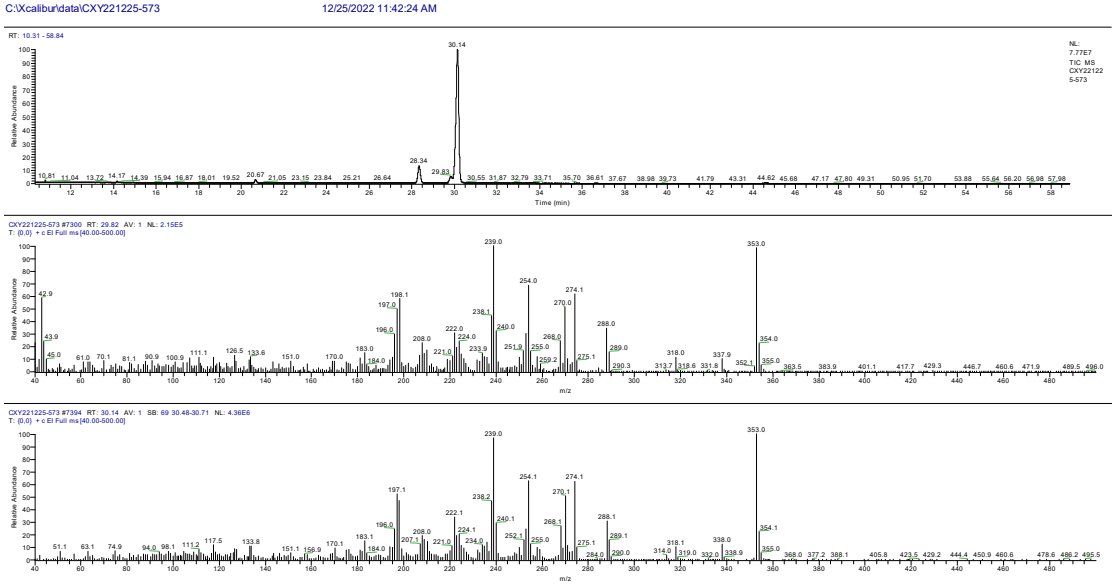

Figure S155. GC–MS spectra of compound **3b**

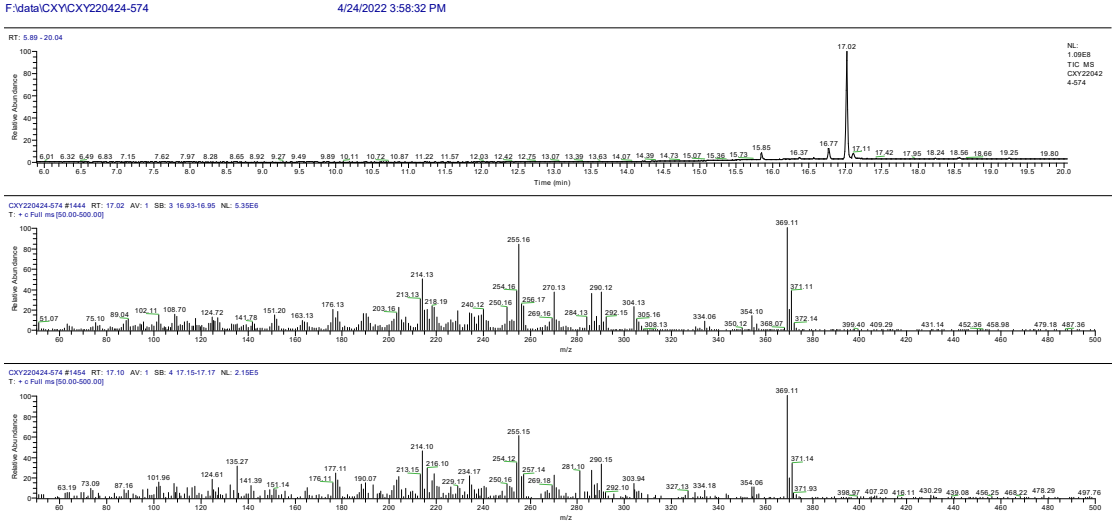

Figure S156. GC–MS spectra of compound **3c**

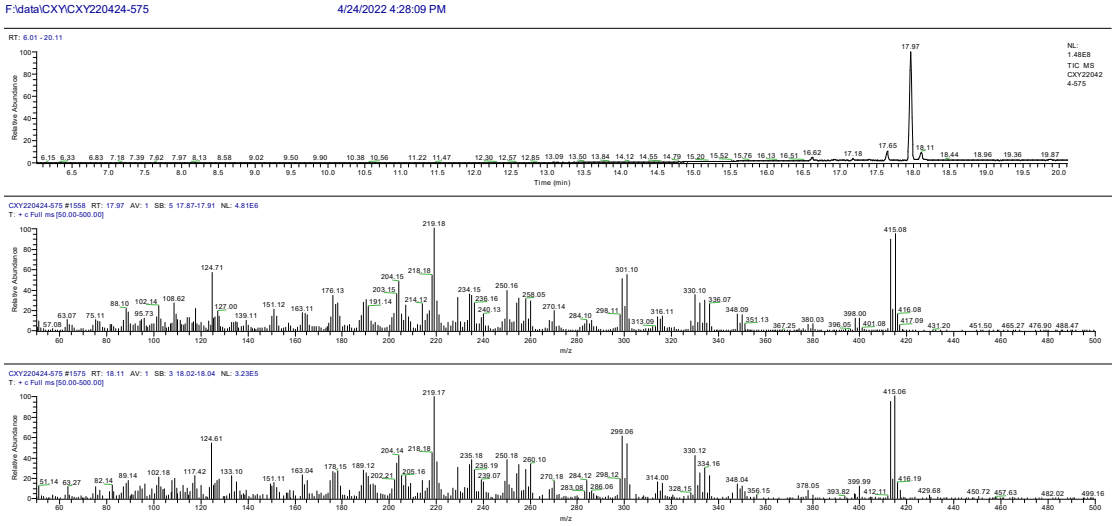

Figure S157. GC–MS spectra of compound **3d**

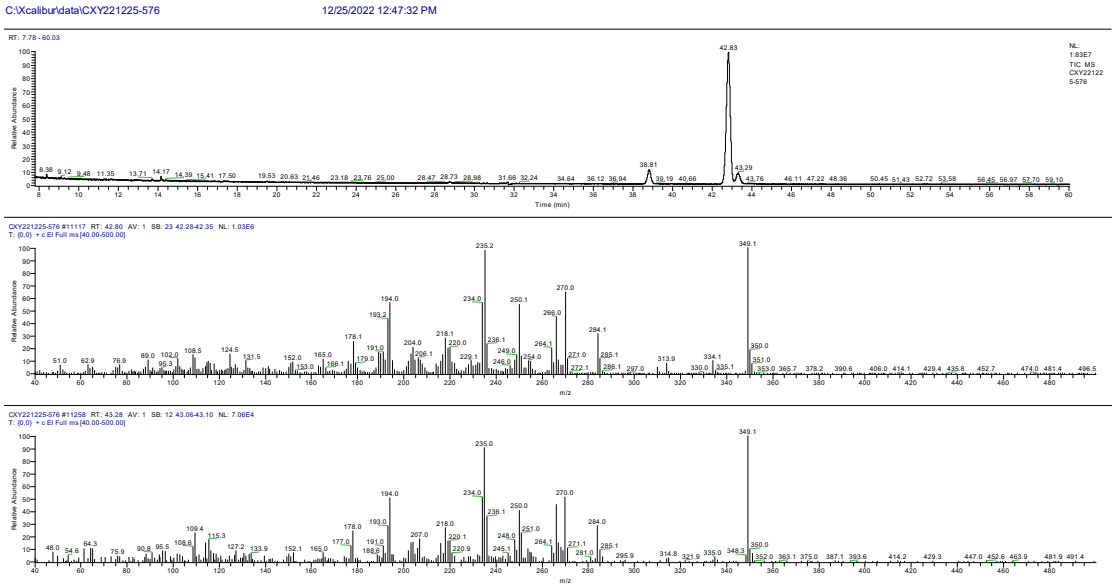

Figure S158. GC–MS spectra of compound **3e**

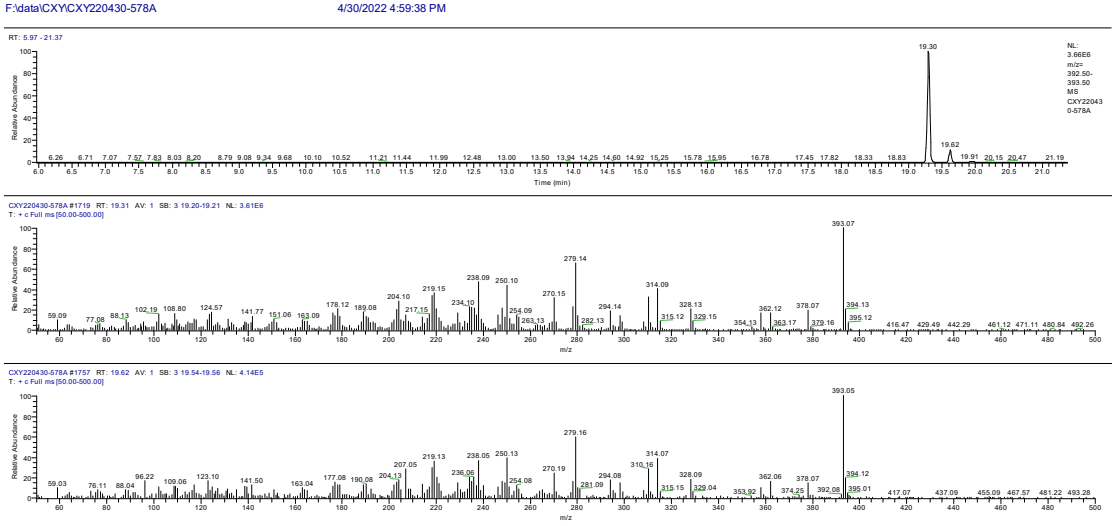

Figure S159. GC–MS spectra of compound **3f**

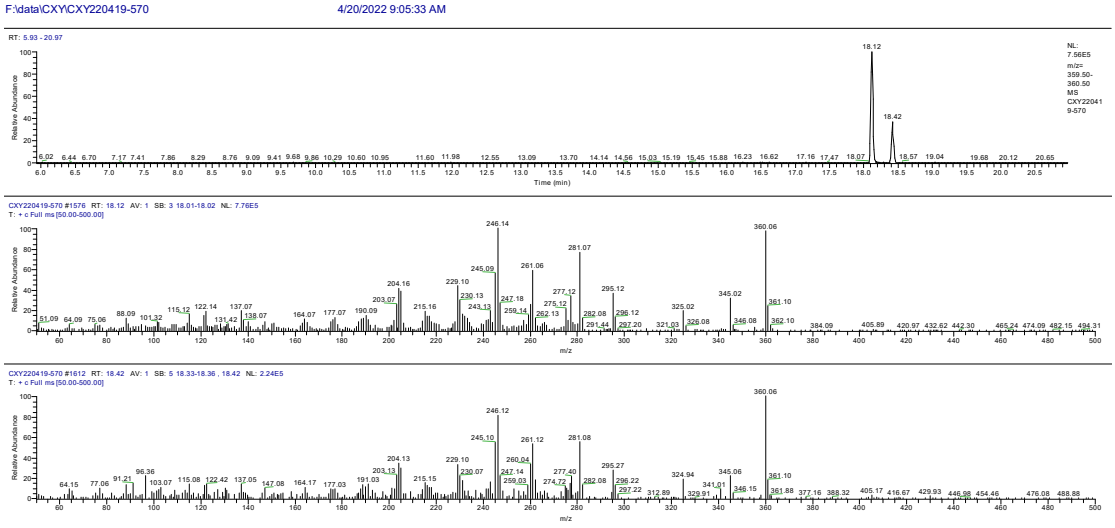

Figure S160. GC–MS spectra of compound **3g**

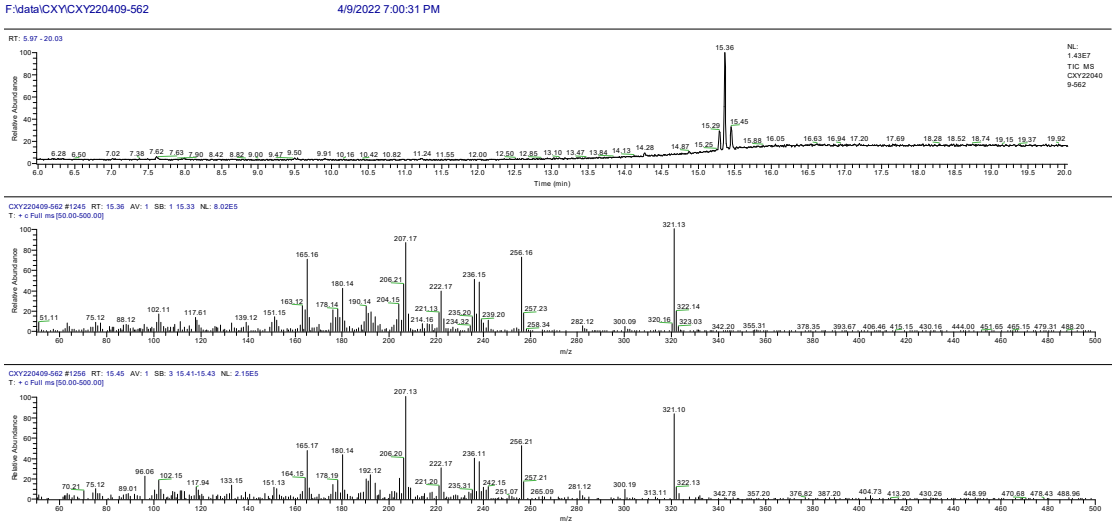

Figure S161. GC–MS spectra of compound **3h**

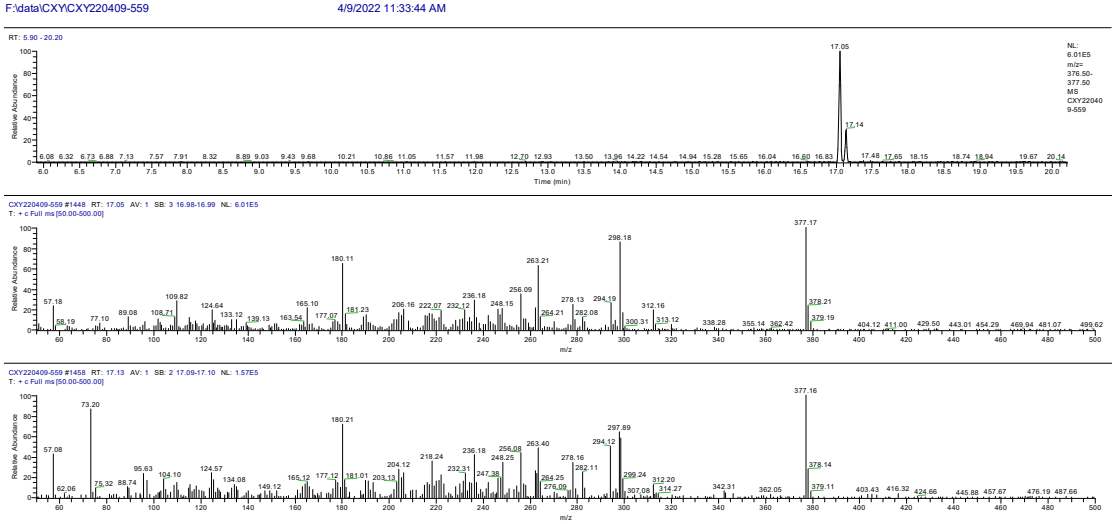

Figure S162. GC–MS spectra of compound **3i**

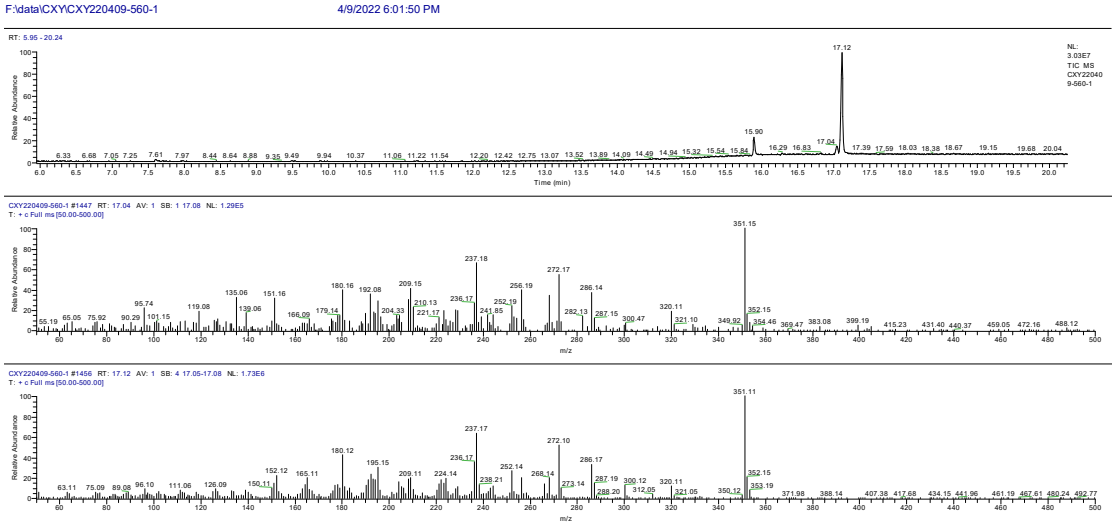

Figure S163. GC–MS spectra of compound **3j**

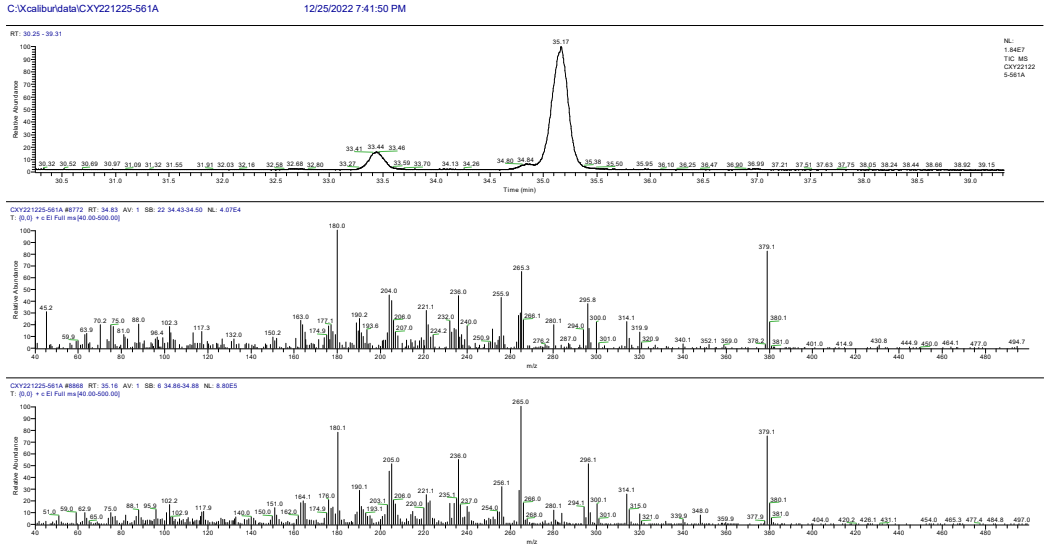

Figure S164. GC–MS spectra of compound **3k**

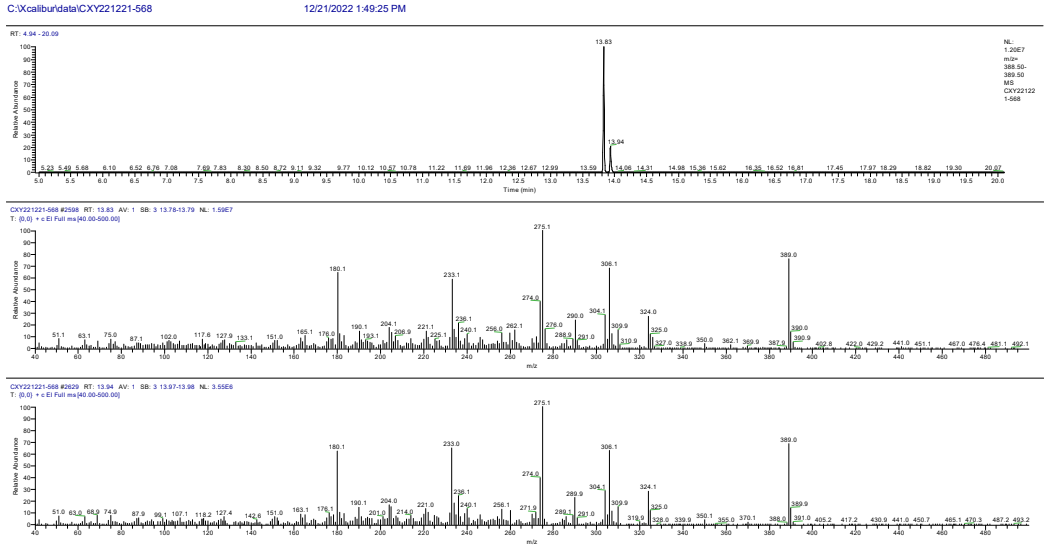

Figure S165. GC–MS spectra of compound **3l**

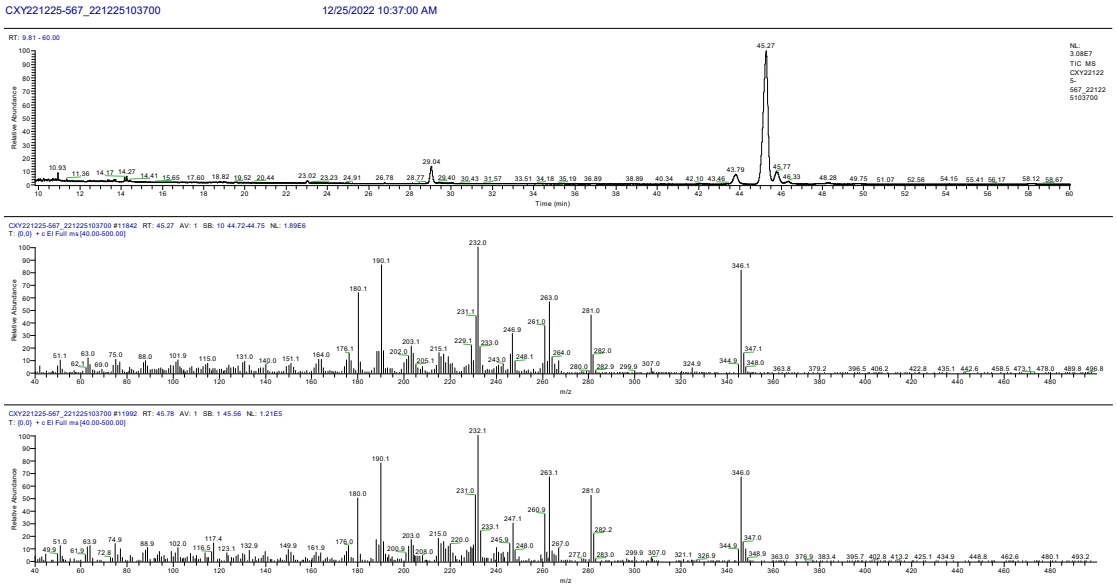

Figure S166. GC–MS spectra of compound **3m**

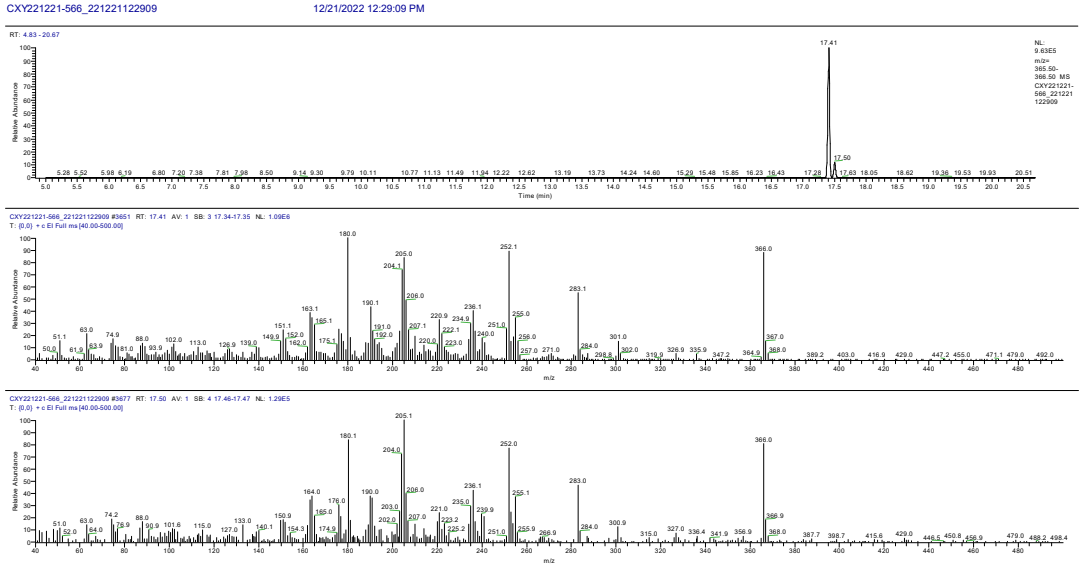

Figure S167. GC–MS spectra of compound **3n**

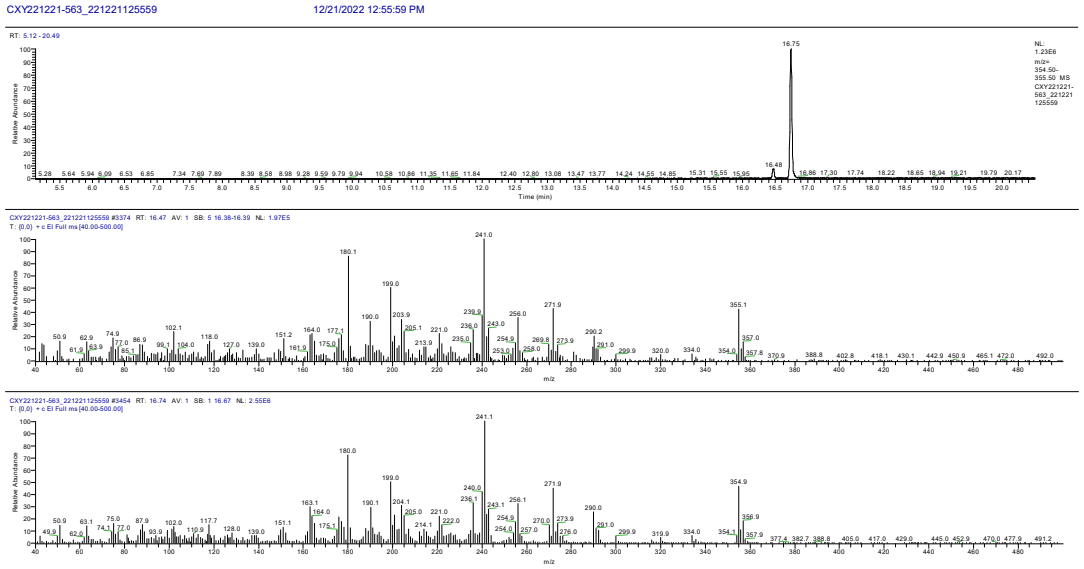

Figure S168. GC–MS spectra of compound **3o**

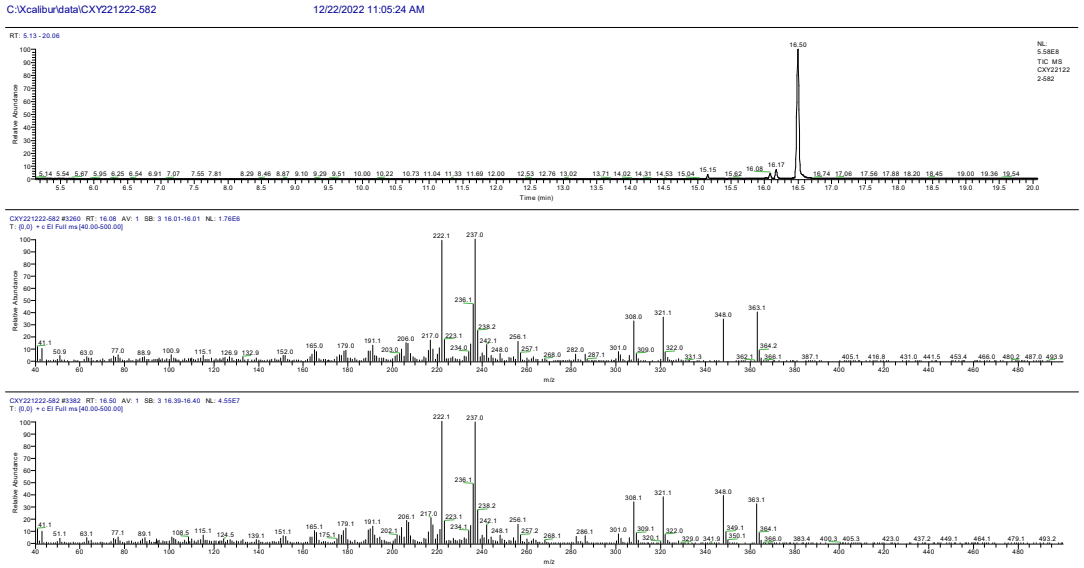

Figure S169. GC–MS spectra of compound **3p**

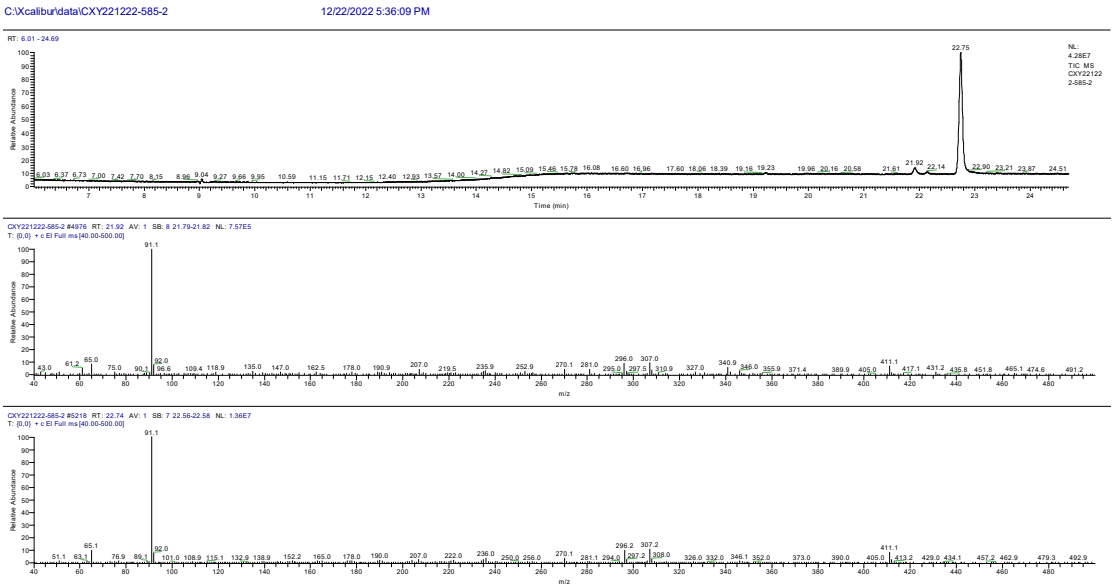

Figure S170. GC–MS spectra of compound **3q**

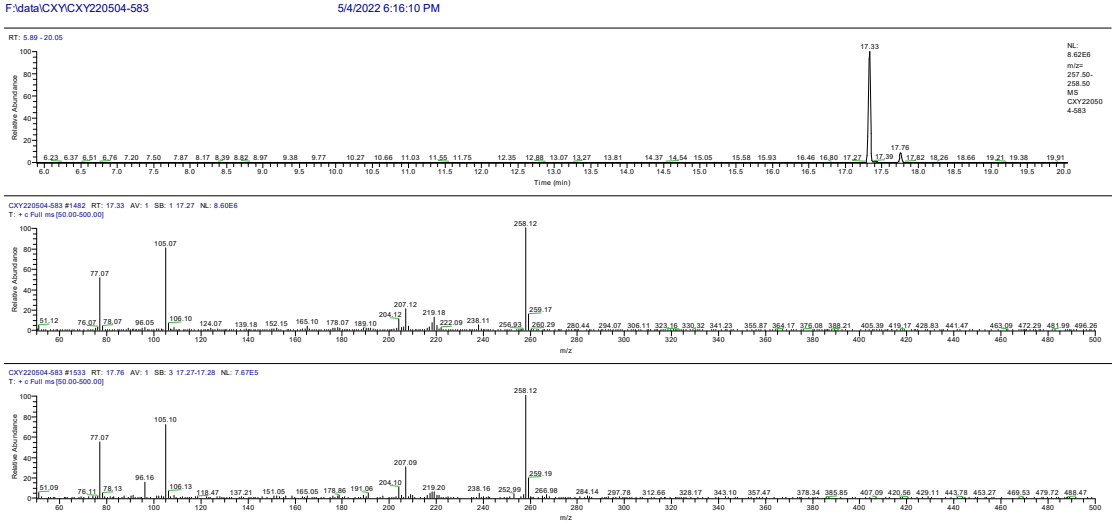

Figure S171. GC–MS spectra of compound **3r**

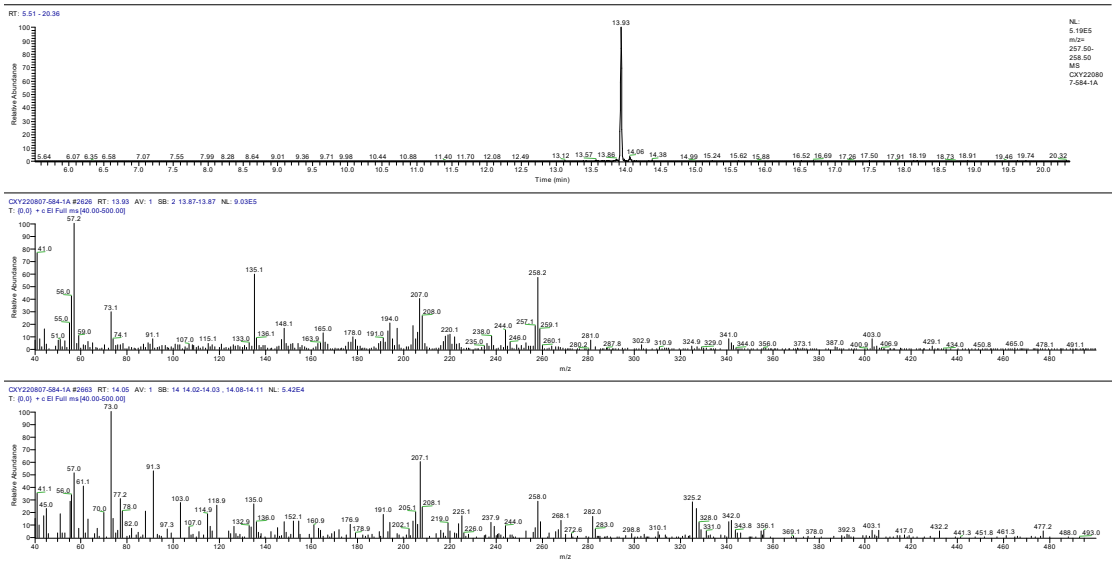

Figure S172. GC–MS spectra of compound **3s**

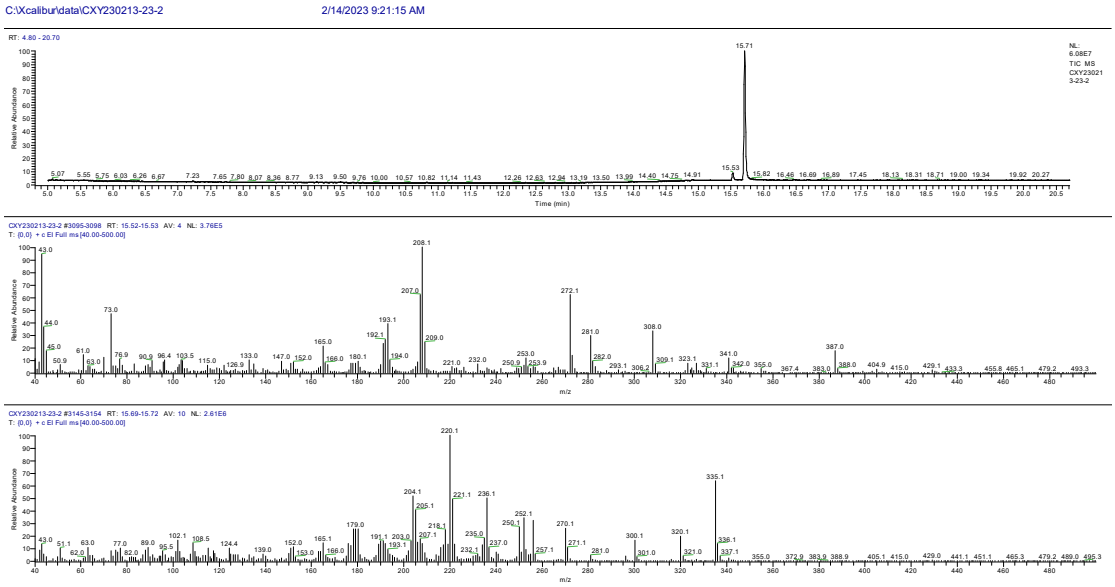

Figure S173. GC–MS spectra of compound **3t**

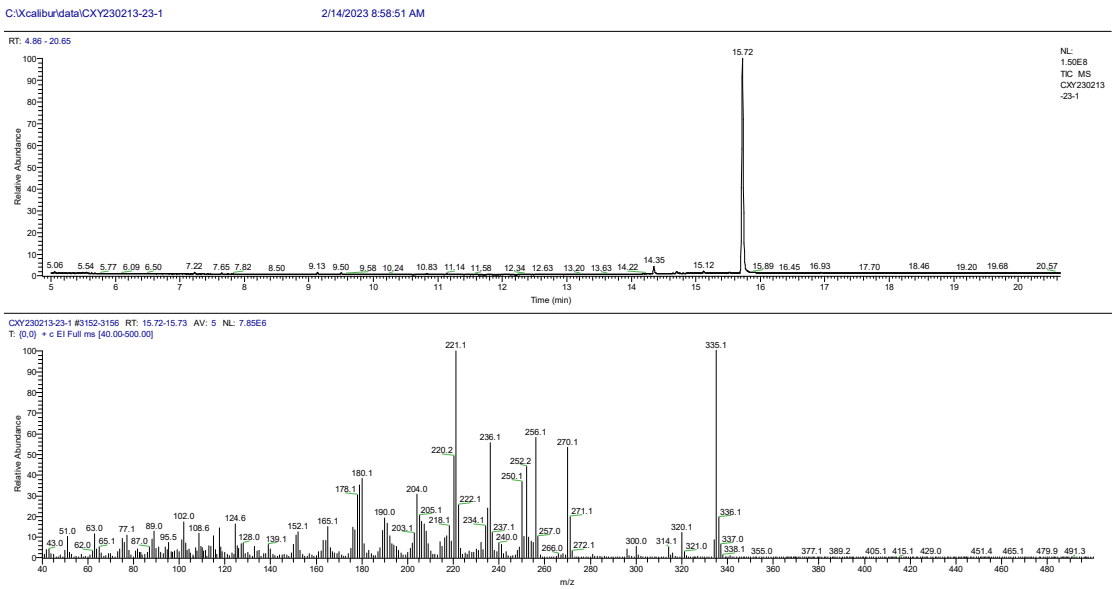

Figure S174. GC–MS spectra of compound **3t′**

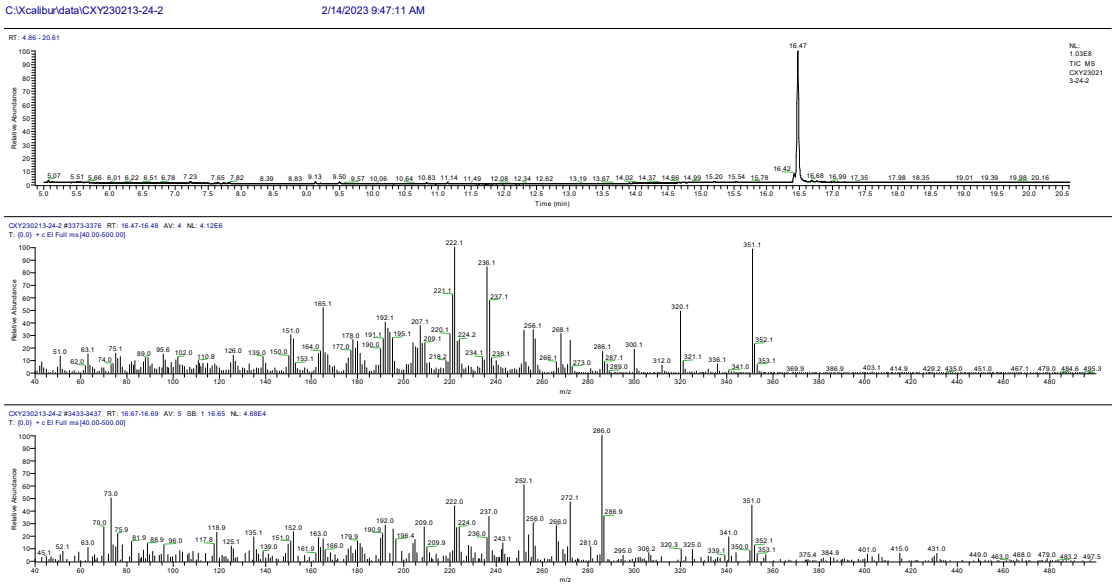

Figure S175. GC–MS spectra of compound **3u**

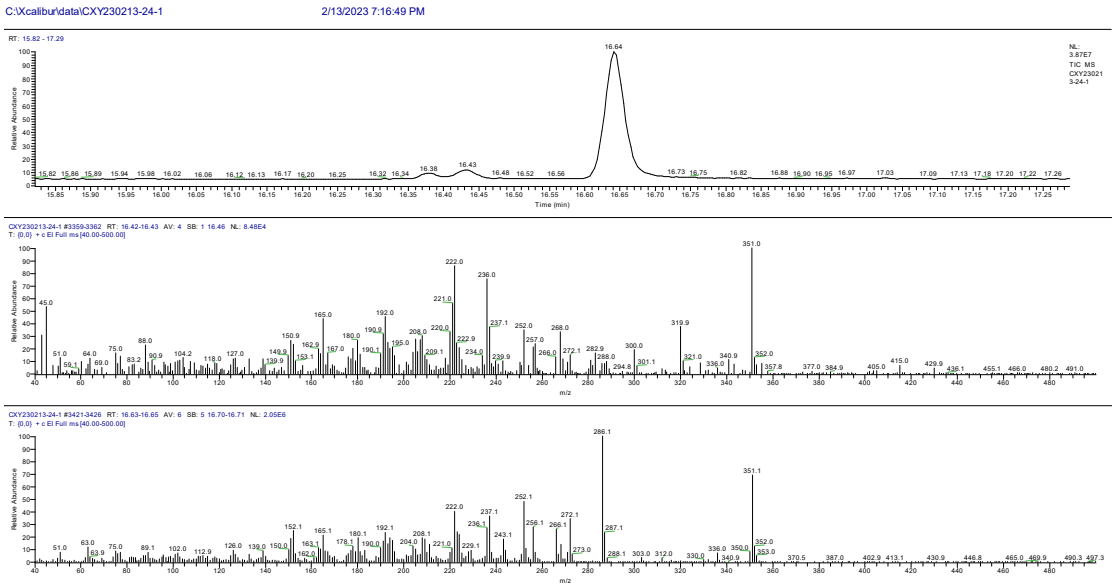

Figure S176. GC–MS spectra of compound **3u′**

12. GC–MS spectra for compounds 5

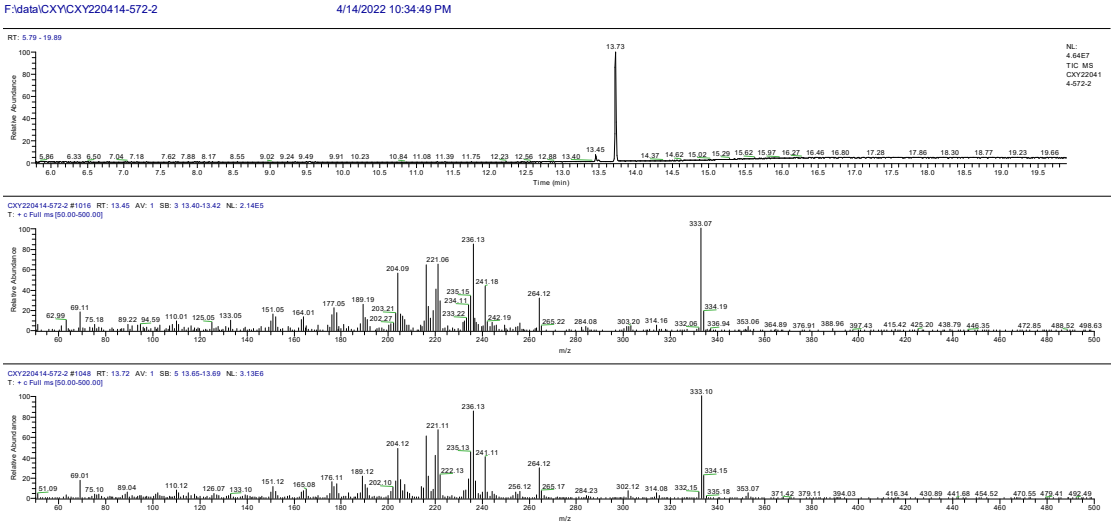

Figure S177. GC–MS spectra of compound **5a**

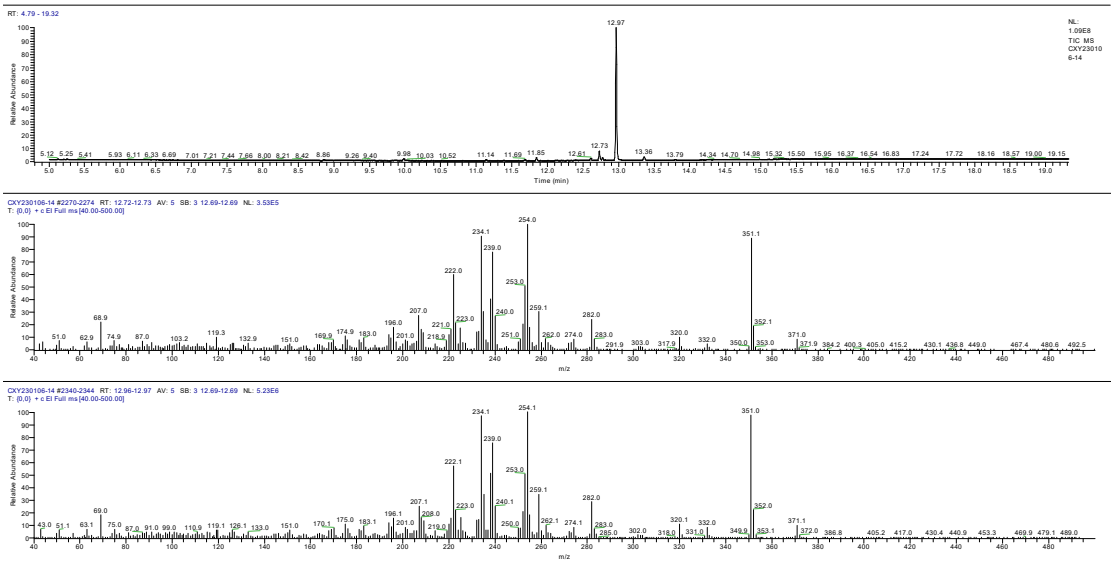

Figure S178. GC–MS spectra of compound **5b**

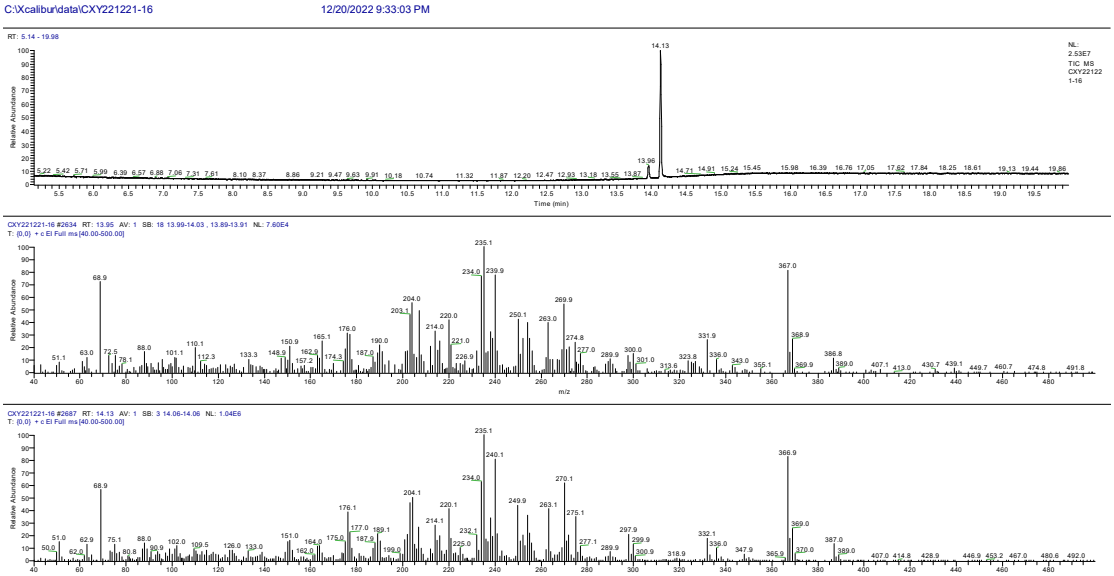

Figure S179. GC–MS spectra of compound **5c**

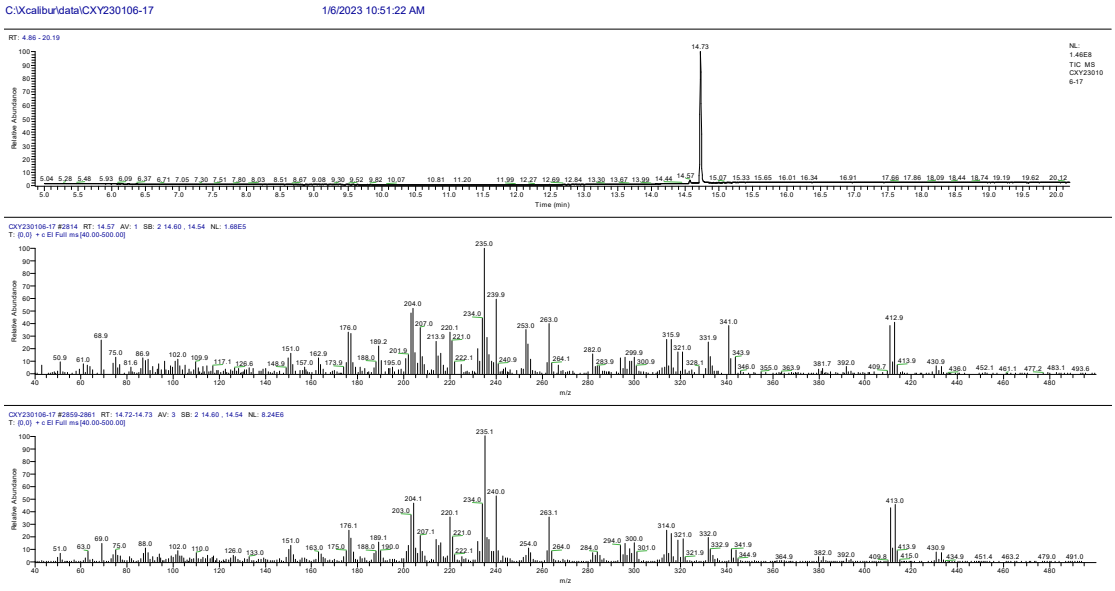

Figure S180. GC–MS spectra of compound **5d**

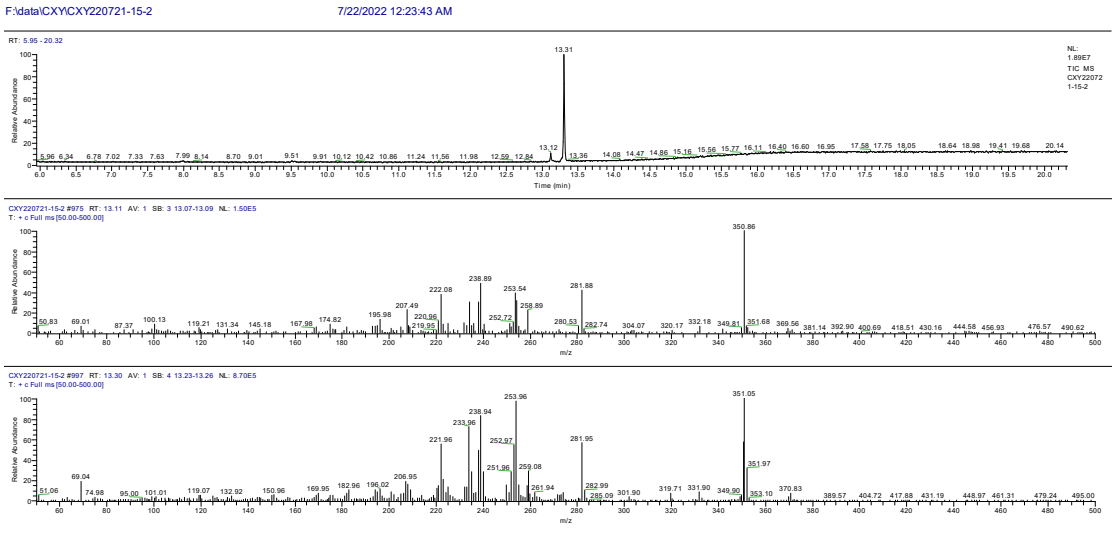

Figure S181. GC–MS spectra of compound **5e**

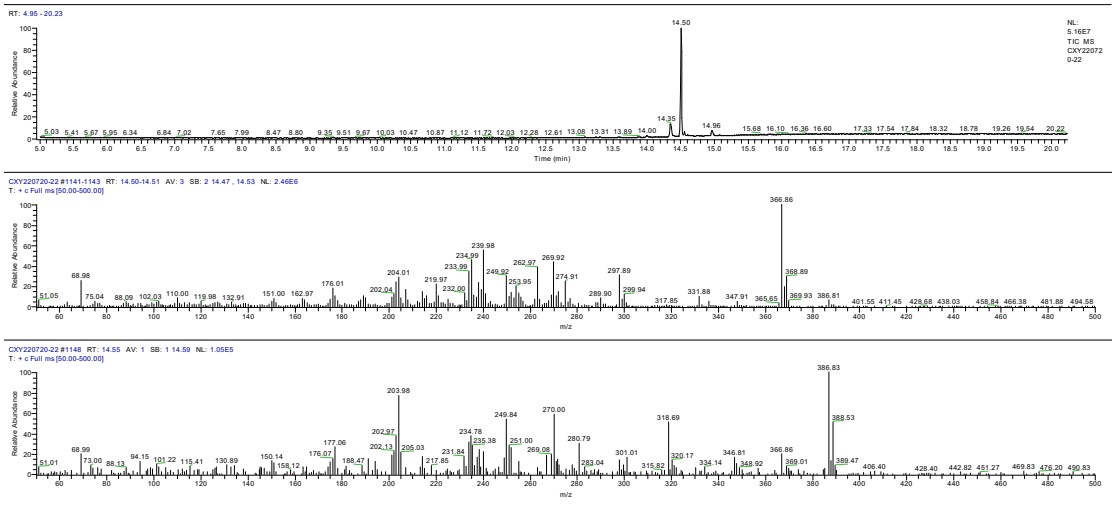

Figure S182. GC–MS spectra of compound **5f**

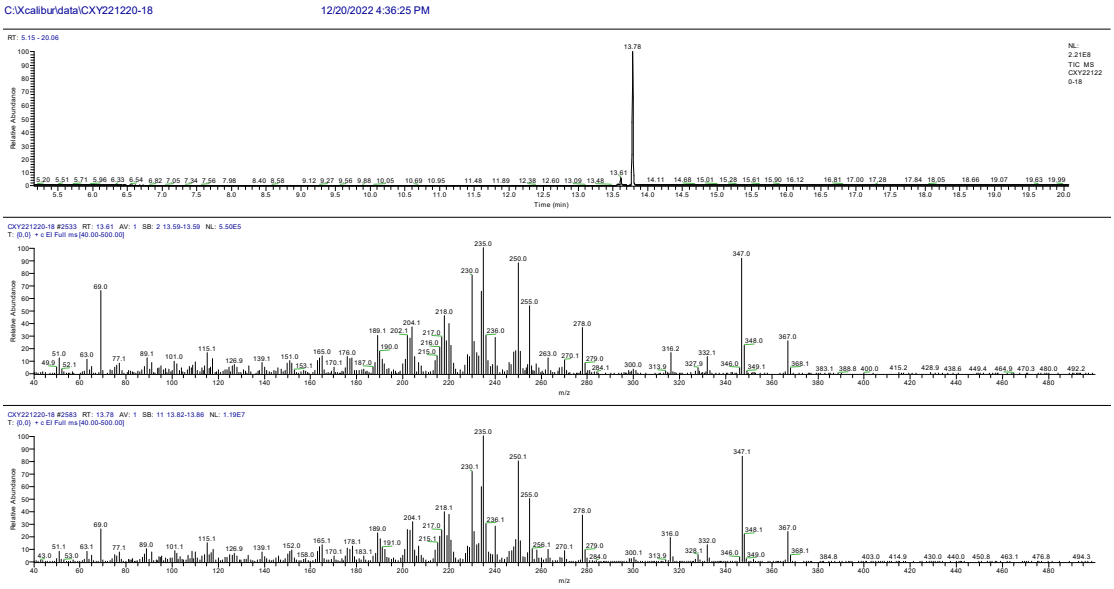

Figure S183. GC–MS spectra of compound **5g**

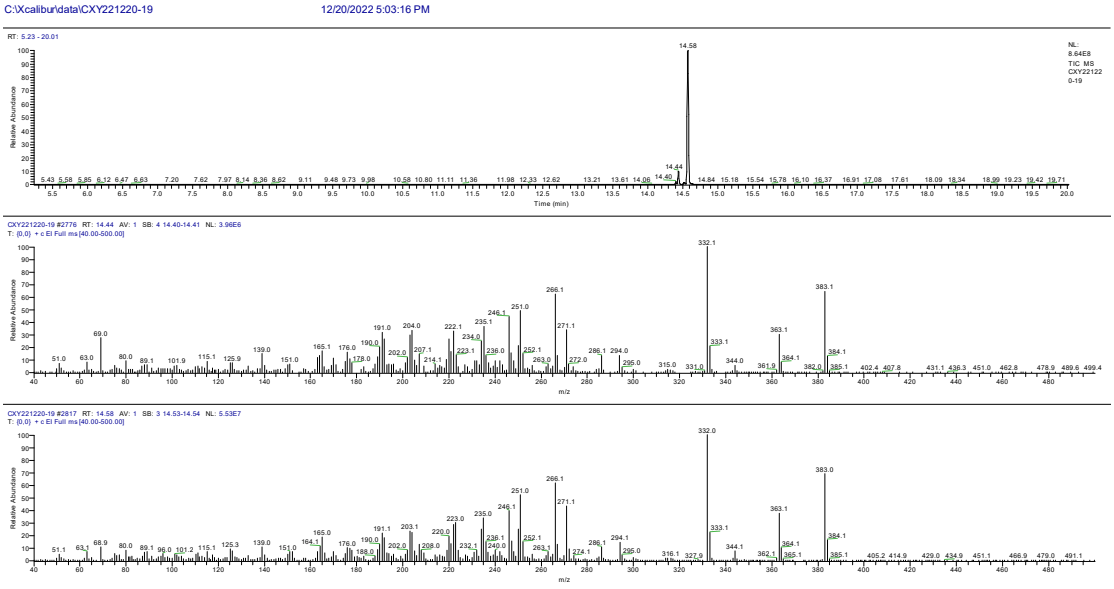

Figure S184. GC–MS spectra of compound **5h**

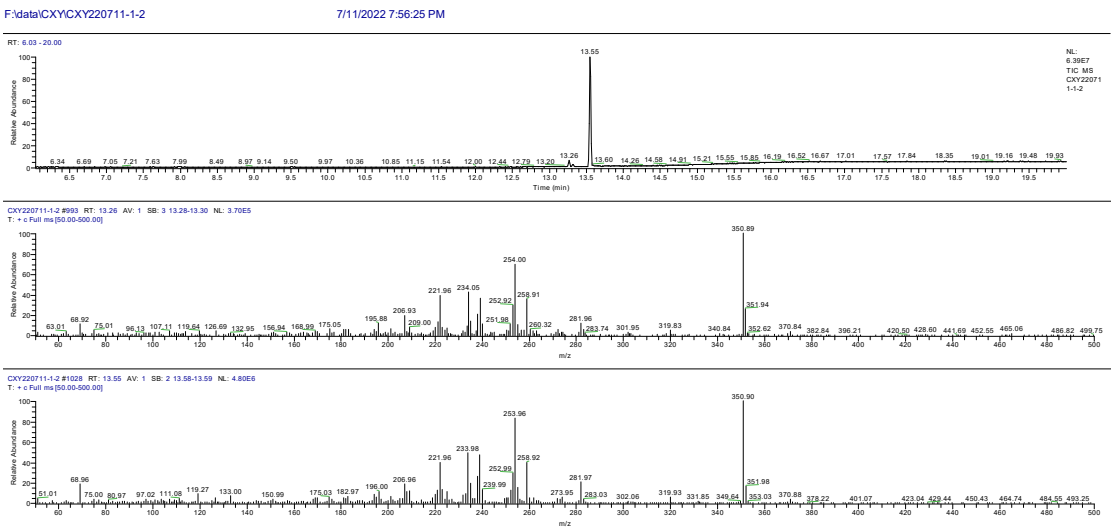

Figure S185. GC–MS spectra of compound **5i**

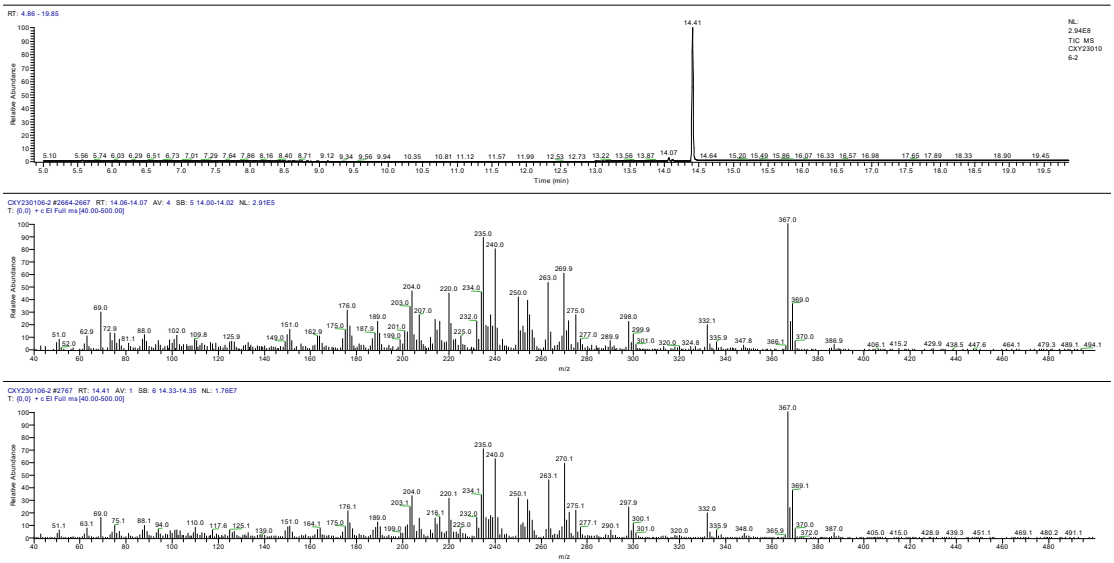

Figure S186. GC–MS spectra of compound **5j**

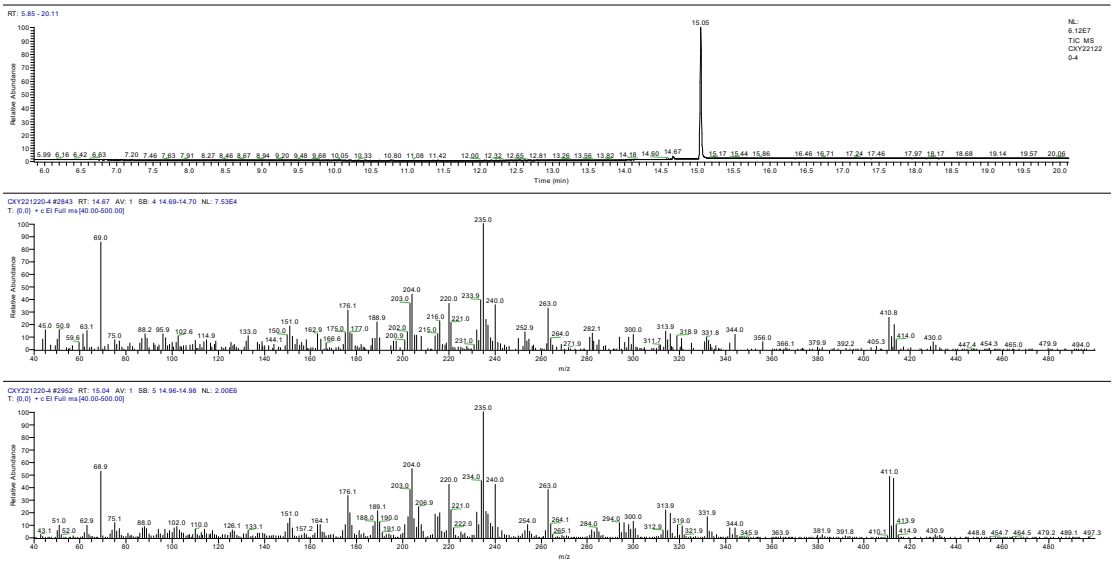

Figure S187. GC–MS spectra of compound **5k**

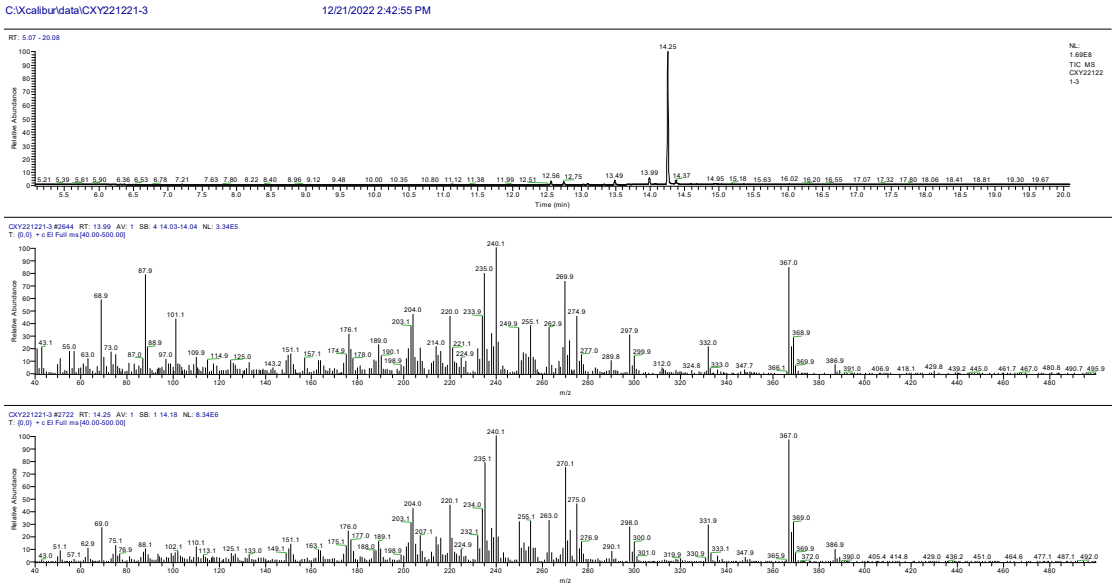

Figure S188. GC–MS spectra of compound **5l**

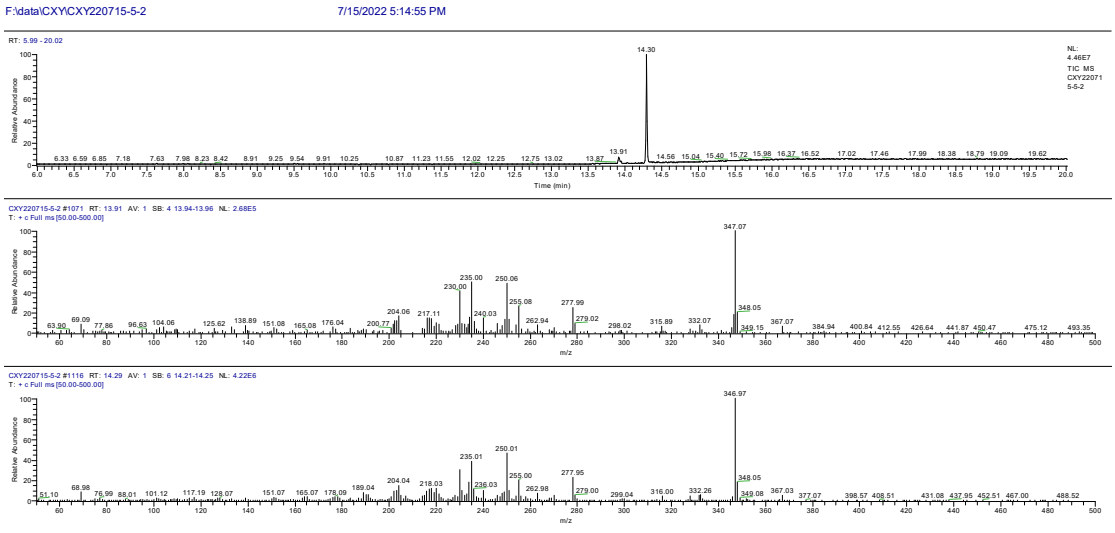

Figure S189. GC–MS spectra of compound **5m**

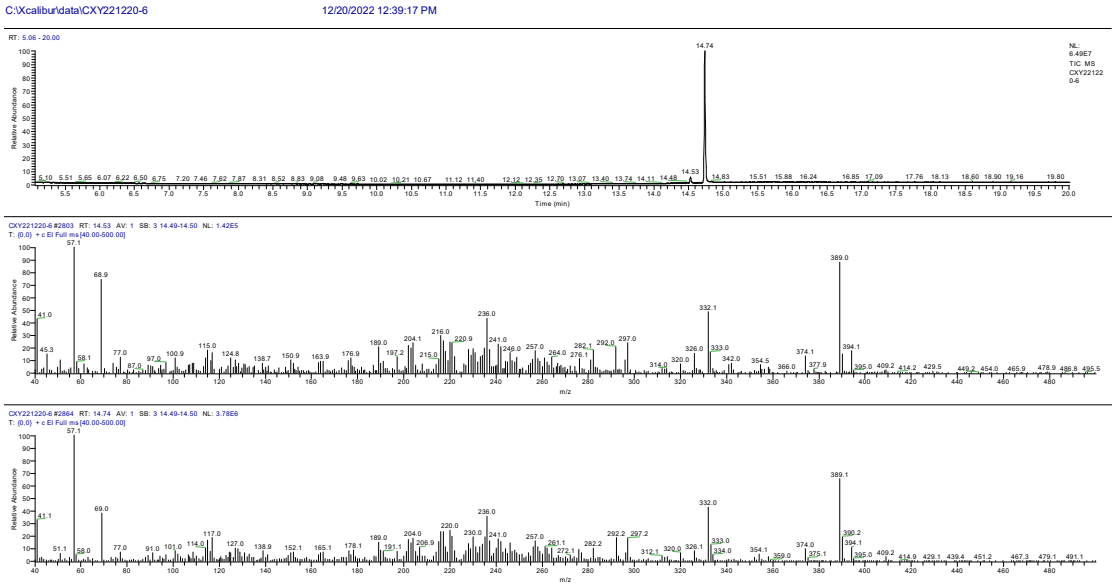

Figure S190. GC–MS spectra of compound **5n**

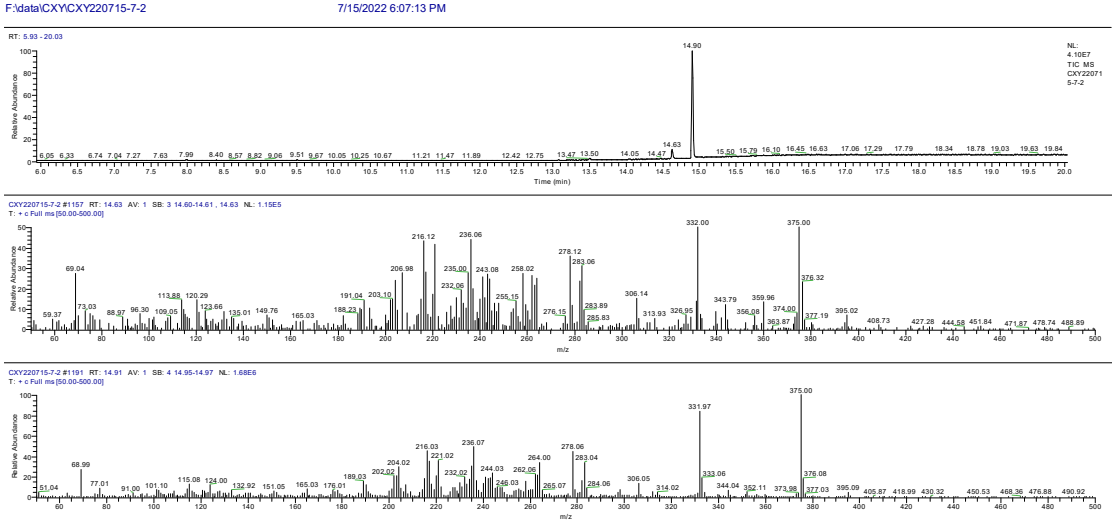

Figure S191. GC–MS spectra of compound **5o**

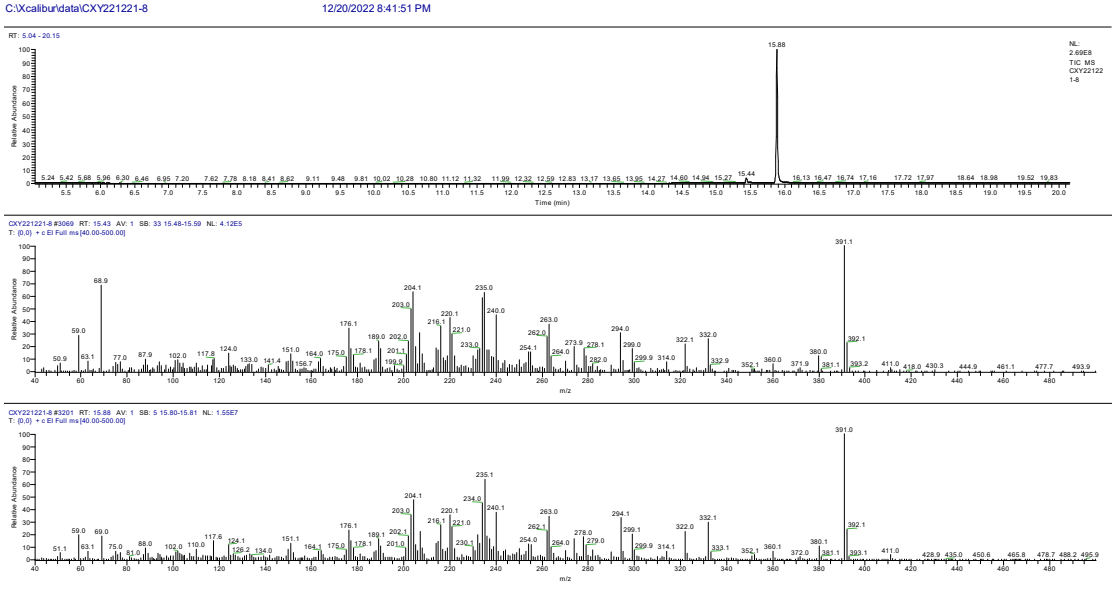

Figure S192. GC–MS spectra of compound **5p**

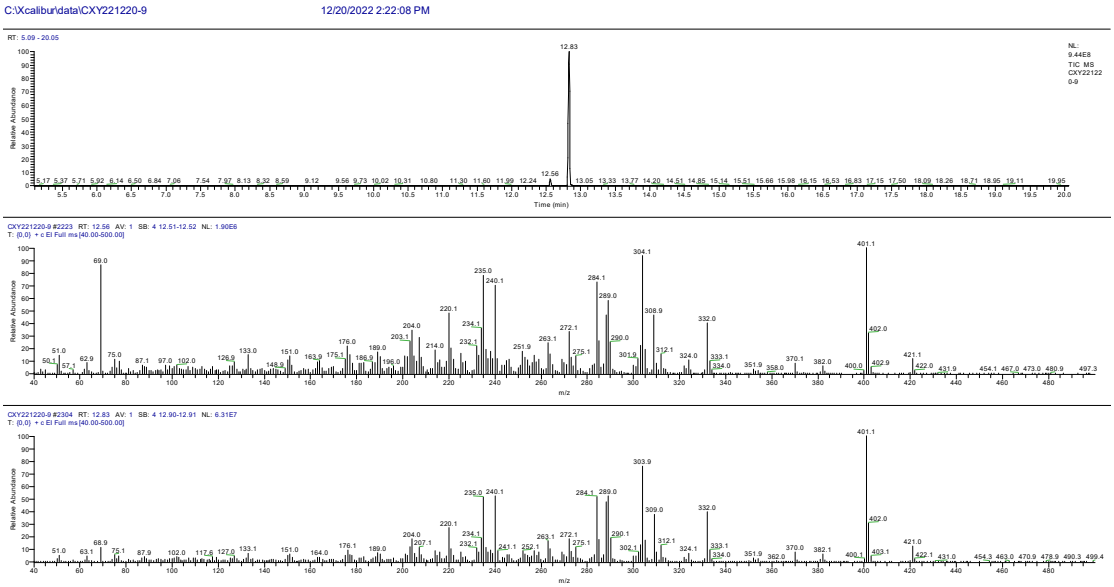

Figure S193. GC–MS spectra of compound **5q**

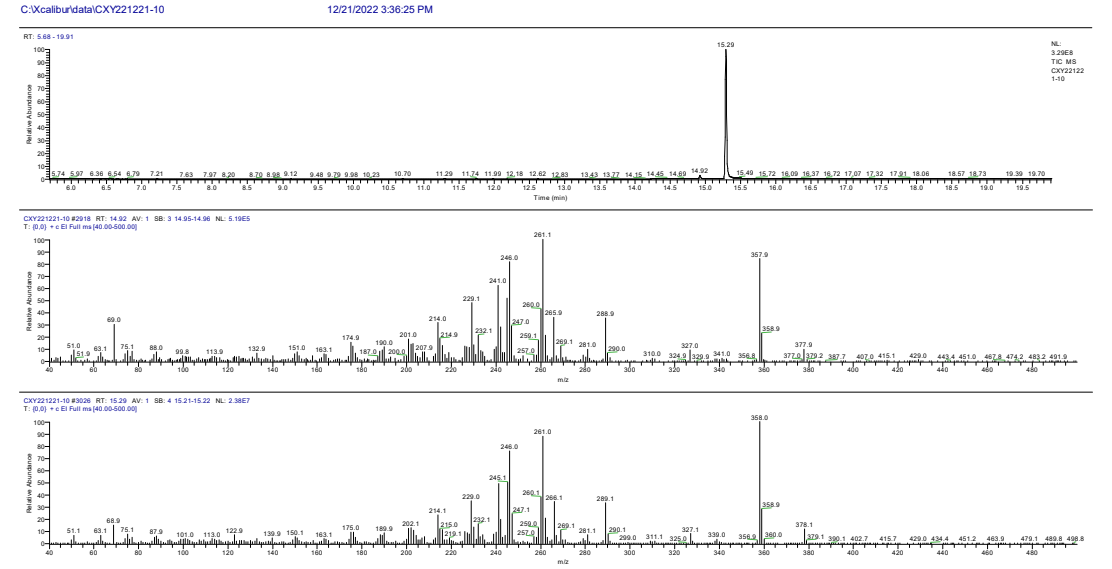

Figure S194. GC–MS spectra of compound **5r**

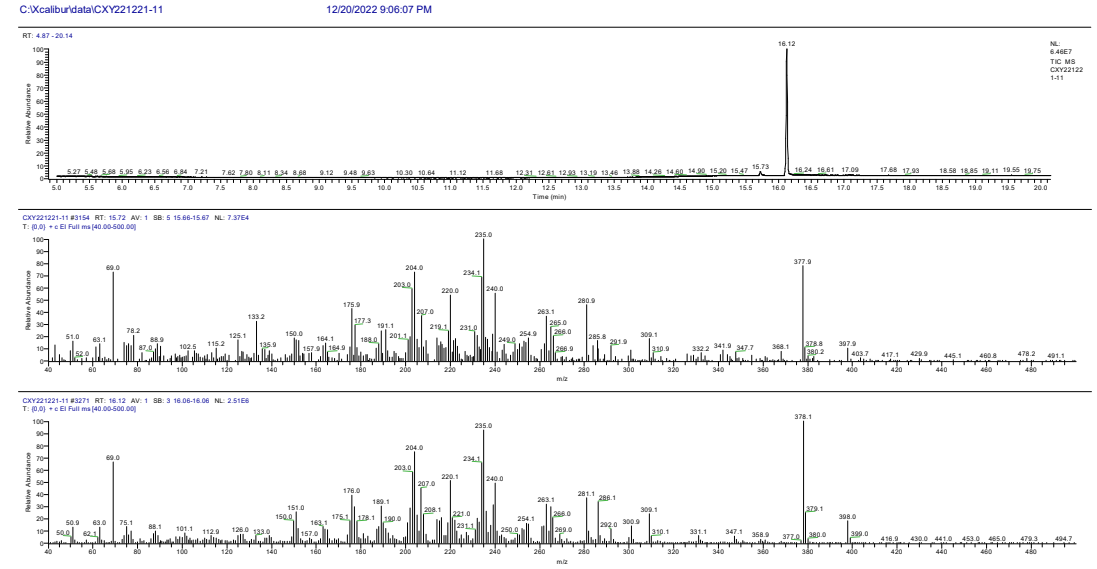

Figure S195. GC–MS spectra of compound **5s**

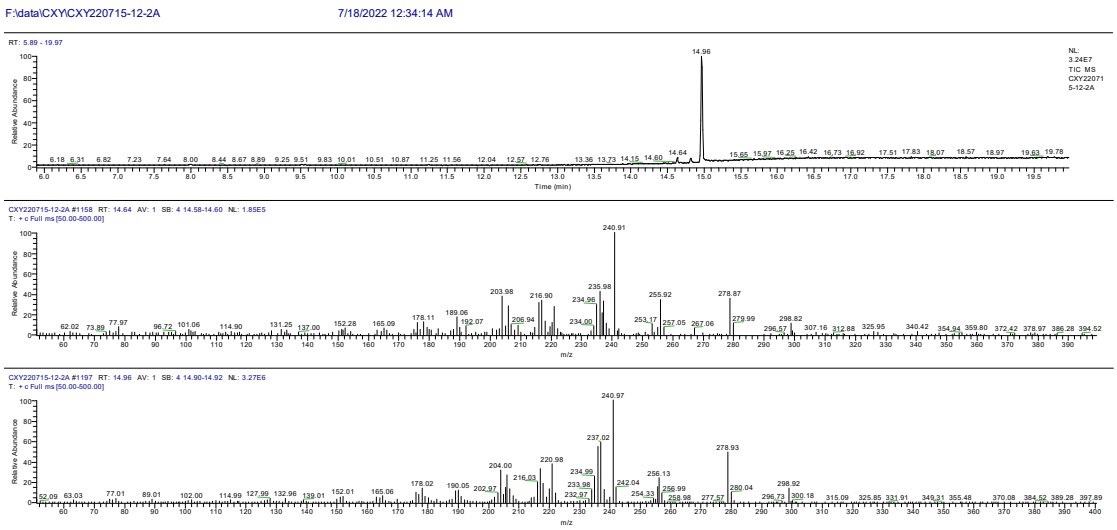

Figure S196. GC–MS spectra of compound **5t**

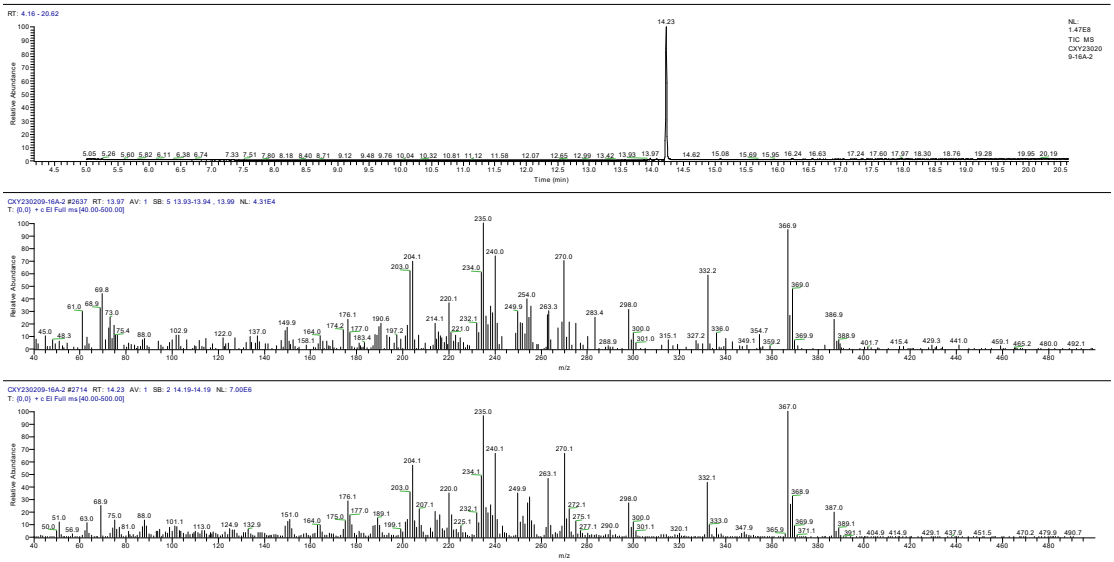

Figure S197. GC–MS spectra of compound **5v**

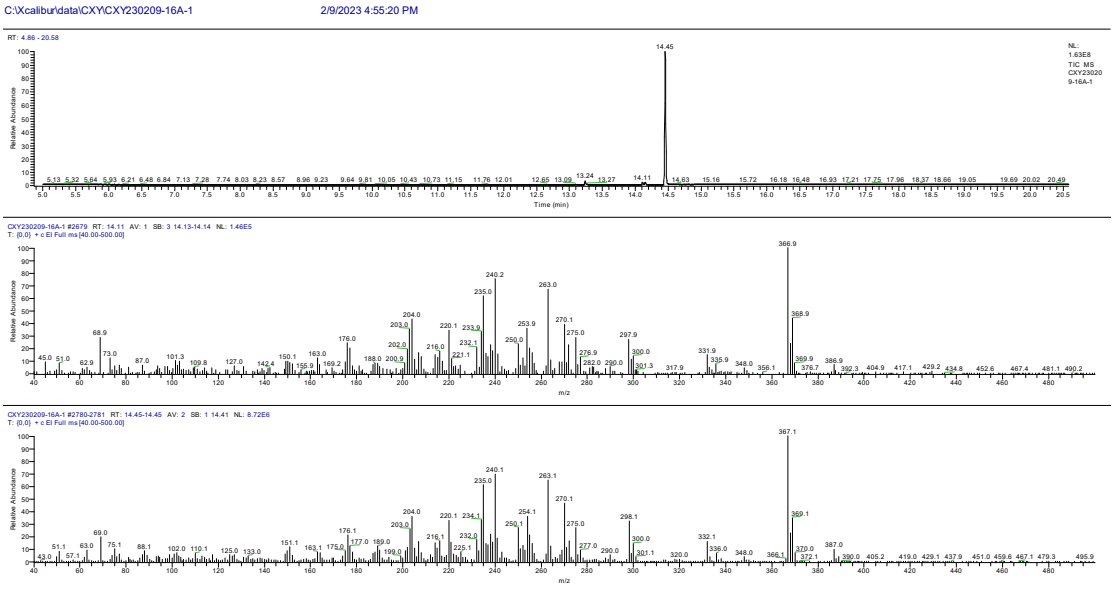

Figure S198. GC–MS spectra of compound **5v′**

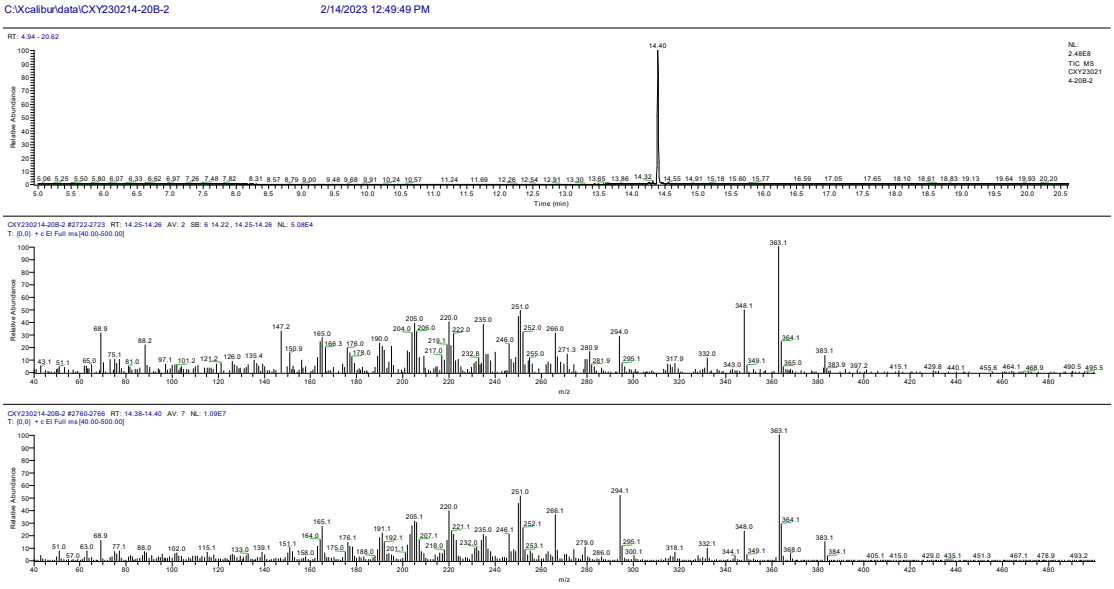

Figure S199. GC–MS spectra of compound **5w**

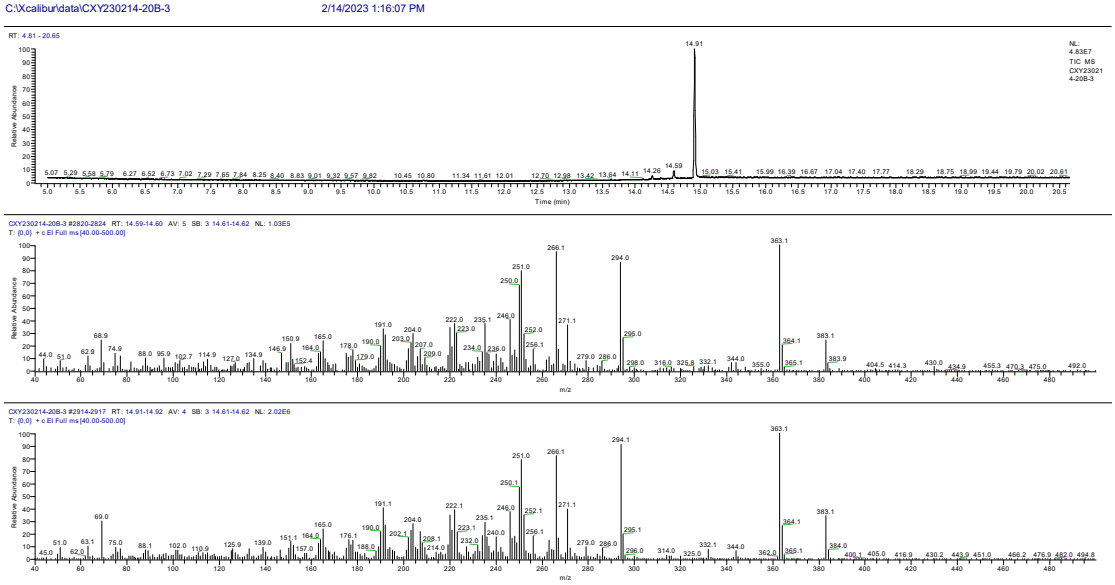

Figure S200. GC–MS spectra of compound **5w′**