Supporting Information

Visible-Light-Induced Radical Trifluoromethylation/Cyclization of Alkynes: Synthesis of CF_3-Containing Dioxodibenzothiazepines

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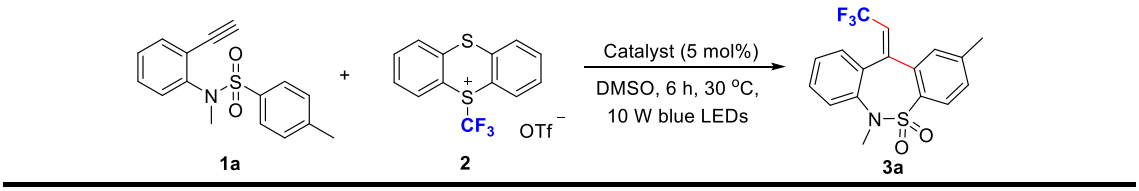
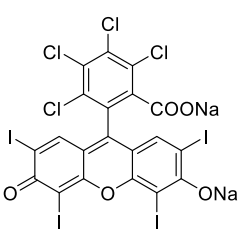
1. General Information

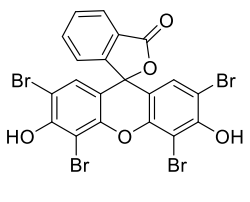
All manipulations were performed in dried glass reaction tube equipped with a magnetic stir bar under air atmosphere. The solvents and reagents were purchased from commercial sources without further purification unless otherwise mentioned. Products were purified by flash chromatography on silica gel (100-200 mesh). All NMR spectra were obtained on Bruker AVANCE III systems using $CDCl_3$ or DMSO-d_6 as solvent, TMS as internal standard substance, at 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR, and 376 MHz for ^{19}F NMR. The chemical shifts (δ) are reported in ppm relative to tetramethylsilane. The multiplicities of signals are designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quarter), m (multiplet), dd (doublet and doublet), td (triplet and doublet). The mass spectra were indicated by GC-MS (Thermo Fisher Scientific DSQ II). High-resolution mass spectrometry (HRMS) data were obtained on an Agilent Technologies 1290-6540 UHPLC/Accurate-Mass Quadrupole Time-of Flight (Q-TOF) LC/MS using ESI as ion source. Measured values are reported to 4 decimal places of the calculated value. X-ray analysis was performed with a single-crystal X-ray diffractometer (Gemini E). Melting points were measured with a SGW X-4A microscopic melting point apparatus and were uncorrected. Magnetic hot plate stirrer (MS-H-Pro$^+$) was purchased from DLAB Scientific Co., Ltd. The material of the reaction vessel (Schlenk tubes) is borosilicate glass. *ortho*-sulfonamide phenylacetylenes **1** and TT-$CF_3^+OTf^-$ **2** were prepared according to the method in the literature.[1,2]

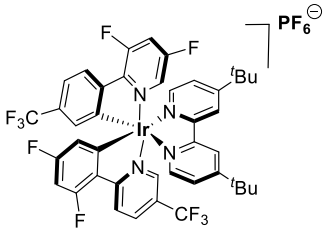
2. Optimization of the reaction conditions

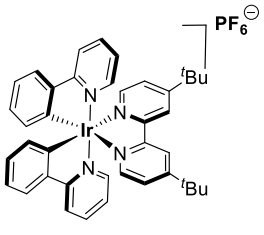
Table S1. Screening of Photocatalysts[a]

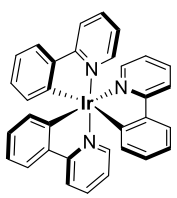


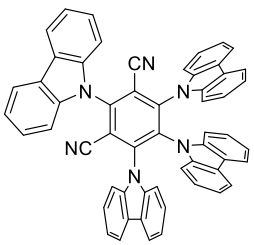

Rose Bengal

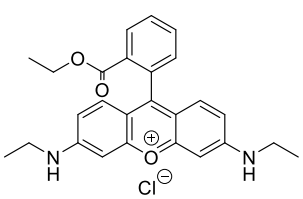

Eosin Y

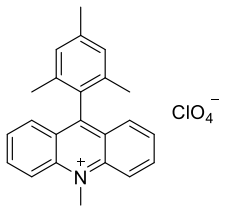

Ir[dF(CF$_3$)$_2$ppy]$_2$(dtbbpy)PF$_6$


[Ir(dtbbpy)(ppy)$_2$]PF$_6$


fac-Ir(ppy)$_3$


4CzIPN

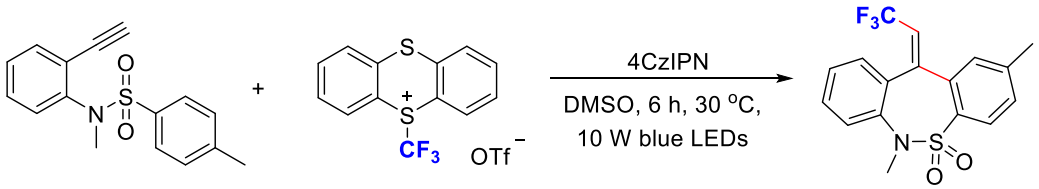

Rhodamine 6G


[Mes-Acr$^+$]ClO$_4^-$

Entry	Photocatalyst（5mol%）	Yield[b] (%)
1	-	28
2	Rose Bengal	32
3	$Ru(bpy)_3Cl_2·6H_2O$	32
4	Eosin Y	40
5	$Ir[dF(CF_3)_2ppy]_2(dtbbpy)PF_6$	44
6	$[Ir(dtbbpy)(ppy)_2]PF_6$	45
7	*fac*-$Ir(ppy)_3$	51
8	4CzIPN	60
9	Rhodaming 6G	23
10	$[Mes\text{-}Acr^+]ClO_4^-$	26

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), Photocatalyst (5 mol%), DMSO (2.0 mL), 30 °C, 6 h, air, 10 W blue LEDs. [b]Isolated yield.

Table S2. Screening of the Loading of Photocatalysts[a]

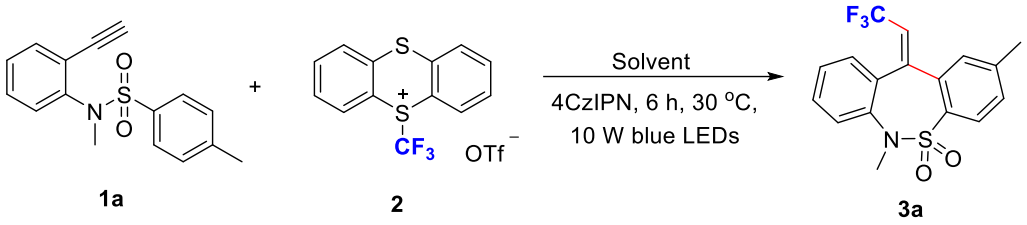


1a **2** **3a**

Entry	the volume of Catalyst	Yield[b] (%)
1	10 mol%	60
2	5 mol%	60
3	4 mol%	63
4	3 mol%	70
5	2 mol%	71
6	1 mol%	58

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), 4CzIPN, DMSO (2.0 mL), 30 °C, 6 h, air, 10 W blue LEDs. [b]Isolated yield.

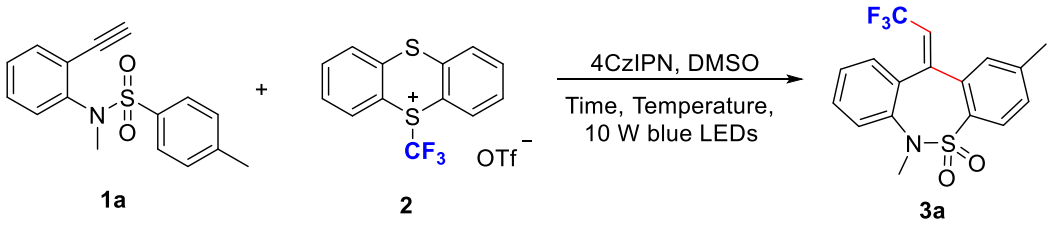
Table S3. Screening of Solvent[a]



Entry	Solvent	Yield[b] (%)
1	CH_3CN (2 mL)	trace
2	DCE (2 mL)	26
3	Dioxane (2 mL)	32
4	THF (2 mL)	41
5	MeOH (2 mL)	44
6	DMAc (2 mL)	49
7	NMP (2 mL)	50
8	DMF (2 mL)	62
9	DMSO (2 mL)	71
10	DMSO (1 mL)	57
11	DMSO (3 mL)	65

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), 4CzIPN (2 mol%), Solvent, 30 °C, 6 h, air, 10 W blue LEDs. [b]Isolated yield.

Table S4. Screening of Temperature and Time[a]

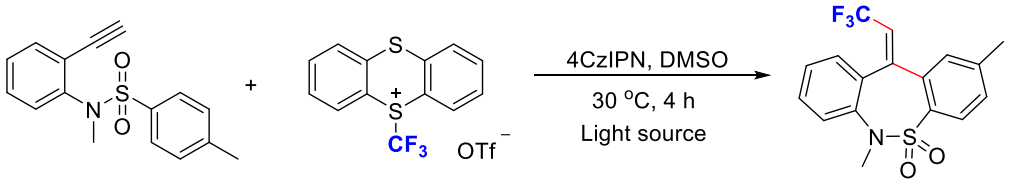


Entry	Temperature（°C）	Time(h)	Yield[b] (%)
1	30	8	71
2	30	6	71
3	30	4	71
4	30	3	60

5	20	4	40
6	30	4	71
7	40	4	65

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), 4CzIPN (2 mol%), DMSO (2.0 mL), Temperature, Time, air, 10 W blue LEDs. [b]Isolated yield.

Table S5. Screening of Light Source[a]

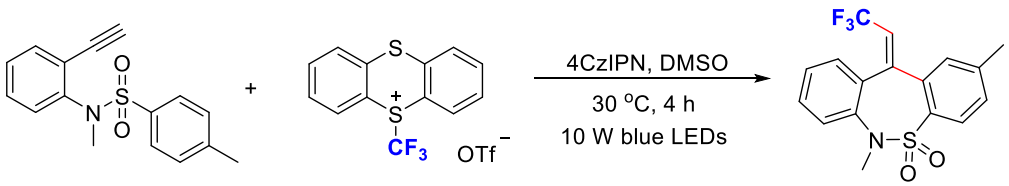


1a **2** **3a**

Entry	Light source	Yield[b] (%)
1	blue LEDs (10 W)	71
2	purple LEDs (10 W)	58
3	green LEDs (10 W)	55
4	white LEDs (10 W)	42
5	Dark	NR
6	blue LEDs (3 W)	60
7	blue LEDs (6 W)	64

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), 4CzIPN (2 mol%), DMSO (2.0 mL), 30 °C, 4 h, air, light source. [b]Isolated yield.

Table S6. Screening of atmosphere[a]



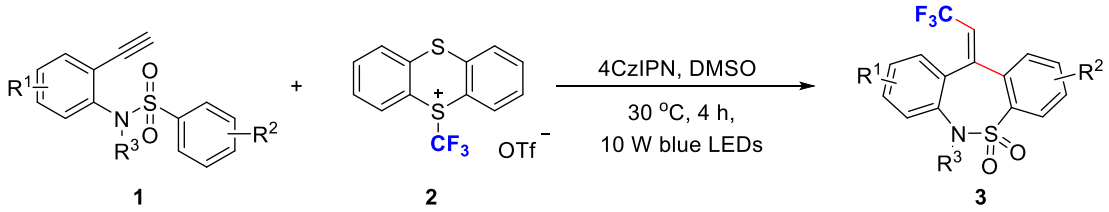
1a **2** **3a**

Entry	atmosphere	Yield[b] (%)
1	O_2	51
2	Ar	54

3	N_2	62

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), 4CzIPN (2 mol%), DMSO (2.0 mL), 30 °C, 4 h, 10 W blue LEDs, atmosphere. [b]Isolated yield.

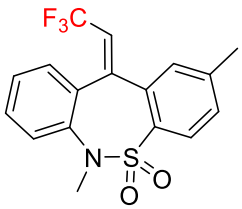
3. General procedure for the synthesis of trifluoromethylated dioxodibenzothiazepines



1 **2** **3**

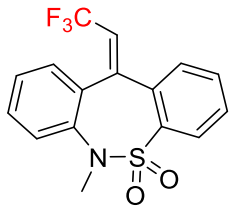
Experimental Procedure: A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with *ortho*-sulfonamide phenylacetylenes **1** (0.20 mmol, 1.0 equiv), TT-$CF_3^+OTf^-$ **2** (0.30 mmol, 1.5 equiv), 4CzIPN (2 mol%) and DMSO (2.0 mL). The reaction mixture was then stirred at room temperature for 4 h under air atmosphere. The reaction mixture was washed with water and extracted with ethyl acetate three times. The combined organic layer was washed with saturated NaCl solution, dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc) to afford desired products **3**.

4. Characterization data of products 3



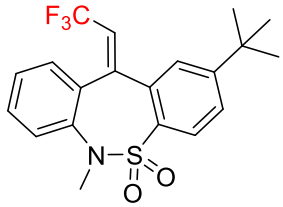
(*E*)-2,6-dimethyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3a)[3]

White solid, 71% yield (50.2 mg). M.p. = 127.6-128.9 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.81 (d, *J* = 8.1 Hz, 1 H), 7.53 (dd, *J* = 7.9 Hz, 1.3 Hz, 1 H), 7.45 (td, *J* = 7.6 Hz, 1.6 Hz, 1 H), 7.39-7.29 (m, 3 H), 7.24 (s, 1 H), 6.22 (q, *J* = 7.8 Hz, 1 H), 3.39 (s, 3H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 150.2 (q, *J* = 5.7 Hz), 143.3, 137.9, 137.5, 136.3, 135.3, 131.3, 131.0, 130.0, 129.1, 129.0, 129.0 (q, *J* = 2.3 Hz), 128.3, 122.4 (q, *J* = 34.2 Hz), 122.1 (q, *J* = 269.9 Hz), 38.5, 21.4; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.19. **MS (ESI)** m/z: 353.1.



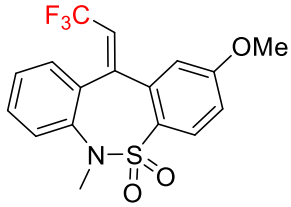
(*E*)-6-methyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3b)

White solid, 67% yield (45.5 mg). M.p. = 145.8-147.1 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.96-7.93 (m, 1 H), 7.56-7.53 (m, 3 H), 7.47-7.43 (m, 2 H), 7.38 (td, *J* = 7.5 Hz, 1.4 Hz, 1 H), 7.33-7.30 (m, 1 H), 6.22 (q, *J* = 7.8 Hz, 1 H), 3.41 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 150.1 (q, *J* = 5.7 Hz), 140.9, 137.5, 136.2, 135.4, 132.5, 131.1, 130.7, 130.0, 129.2, 129.1 (q, *J* = 2.3 Hz), 128.7, 128.4, 122.8 (q, *J* = 34.2 Hz), 122.1 (q, *J* = 269.9 Hz), 38.6; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.24. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{13}F_3NO_2S^+$ 340.0614; Found 340.0614.



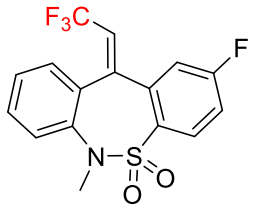
(*E*)-2-(tert-butyl)-6-methyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3c)

White solid, 78% yield (61.7 mg). M.p. = 159.0-161.5 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.86 (d, *J* = 8.4 Hz, 1 H), 7.58-7.53 (m, 2 H), 7.46 (td, *J* = 7.5 Hz, 1.8 Hz, 1 H), 7.40-7.33 (m, 3 H), 6.20 (q, *J* = 7.8 Hz, 1 H), 3.40 (s, 3 H), 1.36 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 156.4, 150.8 (q, *J* = 5.5 Hz), 137.9, 137.7, 136.3, 135.2, 131.0, 130.1, 129.1, 129.1 (q, *J* = 2.4 Hz), 128.2, 128.1, 122.5 (q, *J* = 34.1 Hz), 122.2 (q, *J* = 269.9 Hz), 38.5, 35.3, 31.2; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.07. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{21}F_3NO_2S^+$ 396.1240; Found 396.1240.



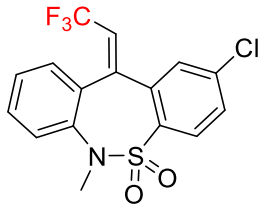
(*E*)-2-methoxy-6-methyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3d)

White solid, 45% yield 33.4 mg). M.p. = 135.5-137.5 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.87 (d, *J* = 8.8 Hz, 1 H), 7.53 (dd, *J* = 7.8 Hz, 1.3 Hz, 1 H), 7.46 (td, *J* = 7.6, 1.6 Hz, 1 H), 7.37 (td, *J* = 7.5 Hz, 1.4 Hz, 1 H), 7.30 (d, *J* = 7.8 Hz, 1 H), 7.02 (dd, *J* = 8.8Hz, 2.6 Hz, 1 H), 6.88 (d, *J* = 2.6 Hz, 1 H), 6.22 (q, *J* = 7.7 Hz, 1 H), 3.89 (s, 3 H), 3.38 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 162.2, 150.1 (q, *J* = 5.7 Hz), 137.3, 137.2, 136.4, 132.6, 131.0, 130.4, 130.0, 129.1, 129.0 (q, *J* = 2.2 Hz), 122.6 (q, *J* = 34.1 Hz), 122.1 (q, *J* = 270.0 Hz), 115.5, 114.0, 55.9, 38.5; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.27. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{15}F_3NO_2S^+$ 370.0719; Found 370.0717.



(*E*)-2-fluoro-6-methyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c,f*][1,2] thiazepine 5,5-dioxide (3e)

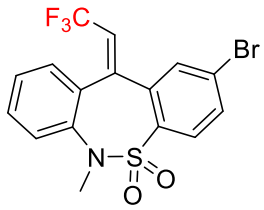
White solid, 62% yield (44.3 mg). M.p. = 134.6-136.2 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.95 (dd, *J* = 8.8 Hz, 5.4 Hz, 1 H), 7.55-7.47 (m, 2 H), 7.40 (td, *J* = 7.6 Hz, 1.6 Hz, 1 H), 7.33-7.30 (m, 1 H), 7.24-7.21 (m, 1 H), 7.16 (dd, *J* = 9.0 Hz, 2.6 Hz, 1 H), 6.24 (q, *J* = 7.7 Hz, 1 H), 3.40 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 164.1 (d, *J* = 254.3 Hz), 149.0 (q, *J* = 6.2 Hz), 138.0 (d, *J* = 7.9 Hz), 137.0 (d, *J* = 3.7 Hz), 136.7, 136.1, 131.4, 131.2, 131.1, 130.1, 129.4, 129.2 (q, *J* = 2.5 Hz), 123.6 (q, *J* = 34.3 Hz), 121.9 (q, *J* = 270.0 Hz), 117.9 (d, *J* = 21.9 Hz), 115.6 (d, *J* = 23.5 Hz),, 38.5, 35.3, 31.2; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.40, -105.36. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{12}F_4NO_2S^+$ 358.0519; Found 358.0519.



(*E*)-2-chloro-6-methyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c,f*][1,2] thiazepine 5,5-dioxide (3f)

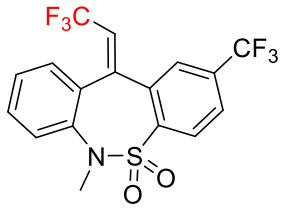
White solid, 55% yield (41.1 mg). M.p. = 120.3-122.1 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.88 (d, *J* = 8.5 Hz, 1 H), 7.55-7.47 (m, 3 H), 7.45 (d, *J* = 2.1 Hz, 1 H), 7.40 (td, *J* = 7.4 Hz, 1.5 Hz, 1 H), 7.32 (d, *J* = 7.7 Hz, 1 H), 6.25 (q, *J* = 7.6 Hz, 1 H), 3.39 (s, 3

H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 148.9 (q, *J* = 5.6 Hz), 139.3, 138.4, 136.9, 136.7, 136.0, 131.4, 130.7, 130.0, 129.9, 129.4, 129.2 (q, *J* = 2.2 Hz), 128.4, 123.6 (q, *J* = 34.4 Hz), 121.7 (q, *J* = 270.1 Hz), 38.6; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.39. **HRMS (ESI-TOF)** *m/z*: [M + H] $^+$ Calcd for $C_{16}H_{12}ClF_3NO_2S^+$ 374.0224; Found 374.0222.



(*E*)-2-bromo-6-methyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c,f*][1,2] thiazepine 5,5-dioxide (3g)

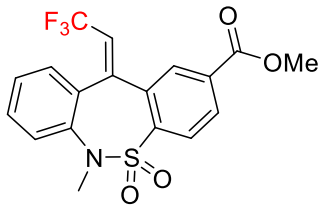
White solid, 60% yield (50.1 mg). M.p. = 155.4-156.9 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.80 (d, *J* = 8.4 Hz, 1 H), 7.67 (dd, *J* = 8.5 Hz, 2.0 Hz, 1 H), 7.61 (d, *J* = 2.0 Hz, 1 H), 7.55-7.47 (m, 2 H), 7.40 (td, *J* = 7.4 Hz, 1.5 Hz, 1 H), 7.31 (d, *J* = 7.6 Hz, 1 H), 6.25 (q, *J* = 7.6 Hz, 1 H), 3.39 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 148.7 (q, *J* = 5.5 Hz), 139.9, 136.9, 136.7, 136.0, 133.6, 131.4, 131.3,130.0, 129.9, 129.4, 1229.2 (q, *J* = 2.3 Hz), 126.7, 123.6 (q, *J* = 34.4 Hz), 121.9 (q, *J* = 270.2 Hz), 38.6; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.38. **HRMS (ESI-TOF)** *m/z*: [M + H] $^+$ Calcd for $C_{16}H_{12}BrF_3NO_2S^+$ 417.9719; Found 417.9718.



(*E*)-6-methyl-11-(2,2,2-trifluoroethylidene)-2-(trifluoromethyl)-6,11-dihydrodibe nzo[*c,f*][1,2]thiazepine 5,5-dioxide (3h)

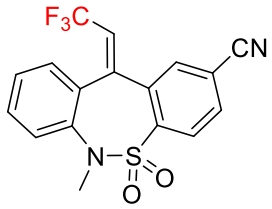
White solid, 65% yield (53.0 mg). M.p. = 161.2-162.7 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 8.08 (d, *J* = 8.3 Hz, 1 H), 7.80 (dd, *J* = 8.4 Hz, 1.1 Hz, 1 H), 7.70 (s, 1 H), 7.57-7.49 (m, 2 H), 7.42 (td, *J* = 7.4 Hz, 1.5 Hz, 1 H), 7.35 (d, *J* = 7.6, 1 H), 6.30 (q, *J* = 7.5 Hz, 1 H), 3.42 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ, 148.9 (q, *J* = 5.5 Hz), 144.3, 136.7, 136.1, 135.8, 123.4 (q, *J* = 33.3 Hz), 131.5, 130.1, 129.6, 129.4, 129.3 (q, *J* = 2.4 Hz), 127.4 (q, *J* = 3.6 Hz), 125.7 (q, *J* = 270.0 Hz), 124.1 (q, *J* = 34.5 Hz), 121.8 (q, *J* = 270.3 Hz), 121.6, 38.7; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.41, -63.11. **HRMS (ESI-TOF)** *m/z*: [M + H] $^+$ Calcd for $C_{17}H_{12}F_6NO_2S^+$ 408.0487; Found

408.0495.



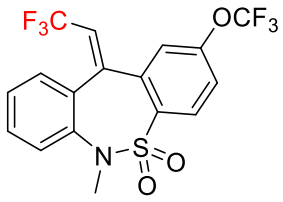
methyl (*E*)-6-methyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c,f*][1,2]thiazepine-2-carboxylate 5,5-dioxide (3i)

White solid, 57% yield (45.3 mg). M.p. = 198.7-199.6 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 8.16 (dd, *J* = 8.3, 1.7 Hz, 1 H), 8.11 (d, *J* = 1.7 Hz, 1 H), 8.02 (d, *J* = 8.2 Hz, 1 H), 7.55-7.47 (m, 2 H), 7.41 (td, *J* = 7.5 Hz, 1.4 Hz, 1 H), 7.33 (d, *J* = 7.6 Hz, 1 H), 6.30 (q, *J* = 7.6 Hz, 1 H), 3.99 (s, 3 H), 3.41 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 165.2, 149.2 (q, *J* = 5.3 Hz), 144.7, 137.0, 135.9, 135.7, 133.7, 131.4, 130.3, 130.1, 130.0, 129.5, 129.2 (q, *J* = 2.4 Hz), 128.9, 123.7 (q, *J* = 34.3 Hz), 121.9 (q, *J* = 270.3 Hz), 53.0, 38.7; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.33. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{15}F_3NO_4S^+$ 398.0668; Found 398.0668.



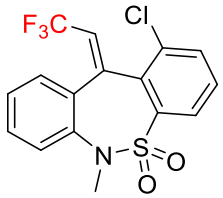
(*E*)-6-methyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c,f*][1,2]thiazepine-2-carbonitrile 5,5-dioxide (3j)

White solid, 50% yield (36.4 mg). M.p. = 207.6-208.9 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 8.05 (d, *J* = 8.2 Hz, 1 H), 7.81 (dd, *J* = 8.2 Hz, 1.6 Hz, 1 H), 7.77 (d, *J* = 1.7 Hz, 1 H), 7.56-7.50 (m, 2 H), 7.43 (td, *J* = 7.4 Hz, 1.8 Hz, 1 H), 7.34 (d, *J* = 7.7 Hz, 1 H), 6.29 (q, *J* = 7.5 Hz, 1 H), 3.41 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 148.2 (q, *J* = 5.3 Hz), 145.0, 136.4, 136.3, 135.7, 133.6, 132.3, 131.7, 130.1, 129.7, 129.5, 129.3 (q, *J* = 2.2 Hz), 124.5 (q, *J* = 34.8 Hz), 121.7 (q, *J* = 270.4 Hz), 116.7, 116.4, 38.8; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.48. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{12}F_3N_2O_2S^+$ 365.0566; Found 365.0574.



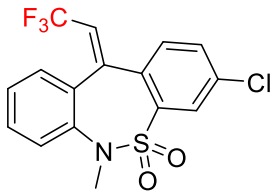
(*E*)-6-methyl-11-(2,2,2-trifluoroethylidene)-2-(trifluoromethoxy)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3k)

White solid, 55% yield (46.7 mg). M.p. = 110.7-111.9 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.99 (d, *J* = 8.7 Hz, 1 H), 7.56-7.48 (m, 2 H), 7.43-7.38 (m, 2 H), 7.35-7.29 (m, 2 H), 6.26 (q, *J* = 7.5 Hz, 1 H), 3.41 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 151.3 (d, *J* = 1.8 Hz), 148.8 (q, *J* = 5.6 Hz), 139.3, 137.6, 136.6, 136.0, 131.5, 130.7, 130.1, 129.5, 129.3 (q, *J* = 2.4 Hz), 123.9 (q, *J* = 34.4 Hz), 122.3, 121.8 (q, *J* = 270.0 Hz), 120.5, 120.3 (q, *J* = 258.4 Hz), 38.7; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.43, -57.71. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{17}H_{12}F_6NO_3S^{+}$ 424.0437; Found 424.0440.



(*E*)-1-chloro-6-methyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3l)

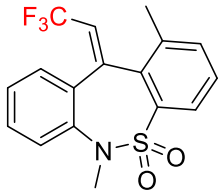
White solid, 27% yield (20.2 mg). M.p. = 146.6-147.9 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.92 (d, *J* = 2.1 Hz, 1 H), 7.54-7.46 (m, 3 H), 7.42-7.38 (m, 2 H), 7.31 (d, *J* = 7.6 Hz, 1 H), 6.21 (q, *J* = 7.7 Hz, 1 H), 3.40 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 149.0 (q, *J* = 5.4 Hz), 142.2, 137.0, 136.9, 135.8, 133.6, 132.6, 131.3, 130.1, 130.0, 129.4, 129.1 (q, *J* = 2.1 Hz), 128.4, 123.2 (q, *J* = 34.3 Hz), 121.9 (q, *J* = 270.0 Hz), 38.7; **^{19}F NMR** (376 MHz, ClC D_3, ppm) δ -56.33. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{16}H_{12}ClF_3NO_2S^{+}$ 374.0224; Found 374.0222.



(*E*)-3-chloro-6-methyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3l')

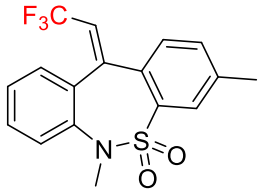
White solid, 27% yield (20.2 mg). M.p. = 162.7-164.3 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.85 (dd, *J* = 7.9 Hz, *J* = 1.0 Hz, 1 H), 7.66 (dd, *J* = 8.0 Hz, *J* = 1.1 Hz, 1 H), 7.48-7.41 (m, 4 H), 7.38-7.34 (m, 1 H), 6.16 (q, *J* = 7.8 Hz, 1 H), 3.35 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 143.3 (q, *J* = 5.8 Hz), 141.9, 137.2, 136.9, 134.1, 133.0, 132.2, 131.1, 130.3, 129.4 (q, *J* = 2.6 Hz), 128.2, 127.9, 126.3, 125.5 (q, *J* = 33.9 Hz), 122.0 (q, *J* = 270.3 Hz), 39.3; **^{19}F NMR** (376 MHz, ClC D_3, ppm) δ -57.40. **HRMS**

(ESI-TOF) *m/z*: [M + H] $^{+}$ Calcd for $C_{16}H_{12}ClF_3NO_2S^{+}$ 374.0224; Found 374.0222.



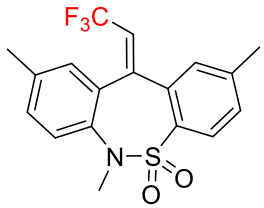
(E)-1,6-dimethyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[c,f][1,2]thiazepine 5,5-dioxide (3m)

White solid, 28% yield (19.8 mg). M.p. = 181.6-183.1 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.78 (d, *J* = 7.8 Hz, 1 H), 7.48-7.36 (m, 5 H), 7.32-7.28 (m, 1 H), 5.91 (q, *J* = 8.0 Hz, 1 H), 3.30 (s, 3 H), 2.51 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 146.7 (q, *J* = 5.8 Hz), 142.2, 139.4, 138.3, 135.3, 134.1, 132.7, 130.8, 129.2 (q, *J* = 2.7 Hz), 128.9, 127.1, 127.0, 125.1, 123.1 (q, *J* = 33.8 Hz), 122.2 (q, *J* = 270.0 Hz), 39.4, 20.7; **^{19}F NMR** (376 MHz, ClC D_3, ppm) δ -57.02. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{17}H_{15}F_3NO_2S^{+}$ 354.0770; Found 354.0768.



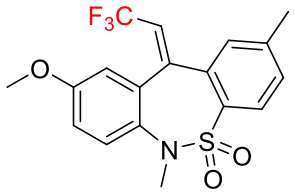
(*E*)-3,6-dimethyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3m')

White solid, 28% yield (19.8 mg). M.p. = 196.1-197.9 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.75 (s, 1 H), 7.53 (dd, *J* = 7.8 Hz, *J* = 1.0 Hz, 1 H), 7.47-7.43 (m, 1 H), 7.39-7.29 (m, 4 H), 6.19 (q, *J* = 7.8 Hz, 1 H), 3.40 (s, 3 H), 2.39 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 150.0 (q, *J* = 5.5 Hz), 141.4, 140.5, 137.7, 136.1, 133.3, 132.6, 130.9, 130.1, 129.2, 129.0 (q, *J* = 2.5 Hz), 128.6, 128.5, 127.9, 126.3, 122.3 (q, *J* = 34.0 Hz), 122.1 (q, *J* = 269.8 Hz), 38.6, 21.1; **^{19}F NMR** (376 MHz, ClC D_3, ppm) δ -56.16. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{17}H_{15}F_3NO_2S^{+}$ 354.0770; Found 354.0768.



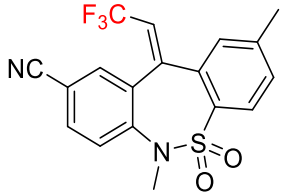
(*E*)-2,6,9-trimethyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3o)

White solid, 59% yield (43.5 mg). M.p. = 123.6-125.3 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.81 (d, *J* = 8.1 Hz, 1 H), 7.40 (d, *J* = 8.0 Hz, 1 H), 7.33 (dd, *J* = 8.0 Hz, 0.8 Hz, 1 H), 7.25-7.21 (m, 1 H), 7.21 (d, *J* = 1.8 Hz, 1 H), 7.09 (s, 1 H), 6.19 (q, *J* = 7.8 Hz, 1 H), 3.37 (s, 3 H), 2.43 (s, 3 H), 2.35 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 150.4 (q, *J* = 5.7 Hz), 143.2, 139.4, 138.0, 137.4, 135.5, 133.5, 131.6, 131.3, 129.8, 129.4 (q, *J* = 2.2 Hz), 129.0, 128.5, 122.2 (q, *J* = 34.1 Hz), 122.2 (q, *J* = 269.9 Hz), 38.6, 21.5, 21.3; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.21. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{17}F_3NO_2S^+$ 368.0927; Found 368.0926.



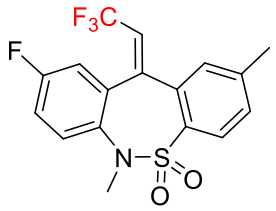
(*E*)-9-methoxy-2,6-dimethyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c*, *f*][1,2]thiazepine 5,5-dioxide (3p)

White solid, 53% yield (40.9 mg). M.p. = 139.7-141.2 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.80 (d, *J* = 8.1 Hz, 1 H), 7.43 (d, *J* = 2.2 Hz, 1 H), 7.34 (dd, *J* = 8.1 Hz, 0.8 Hz, 1 H), 8.23 (s, 1 H), 6.93 (dd, *J* = 8.7 Hz, 2.9 Hz, 1 H), 6.79 (d, *J* = 2.1 Hz, 1 H), 6.21 (q, *J* = 7.8 Hz, 1 H), 3.78 (s, 3 H), 3.36 (s, 3 H), 2.43 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 159.7, 150.1 (q, *J* = 5.3 Hz), 143.1, 138.8, 138.1, 135.1, 131.4, 129.1, 128.5, 122.1 (q, *J* = 270.0 Hz), 122.4 (q, *J* = 34.2 Hz), 116.0, 114.1 (q, *J* = 2.5 Hz), 55.7, 38.7, 21.4; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.13. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{17}F_3NO_3S^+$ 384.0876; Found 384.0879.



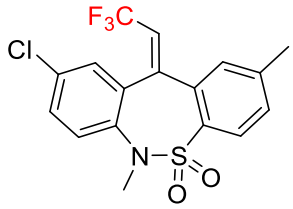
(*E*)-2,6-dimethyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine-9-carbonitrile 5,5-dioxide (3q)

White solid, 73% yield (55.5 mg). M.p. = 168.4-170.1 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.82-7.74 (m, 2 H), 7.63-7.60 (m, 2 H), 7.39 (d, *J* = 8.0 Hz, 1 H), 6.25 (q, *J* = 7.6 Hz, 1 H), 3.39 (s, 3 H), 2.46 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 147.9 (q, *J* = 5.4 Hz), 144.1, 141.1, 137.5, 137.1, 134.6, 134.5, 134.2, 132.9 (q, *J* = 2.7 Hz), 131.7, 130.3, 129.2, 128.0, 123.7 (q, *J* = 34.5 Hz), 121.8 (q, *J* = 270.0 Hz), 117.4, 112.8, 38.3, 21.5; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.22. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{14}F_3N_2O_2S^+$ 379.0723; Found 379.0727



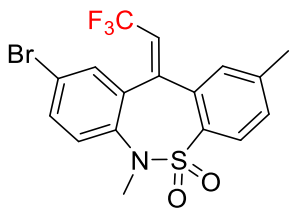
(*E*)-9-fluoro-2,6-dimethyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3r)

White solid, 70% yield (52.0 mg). M.p. = 150.8-152.2 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.81 (d, *J* = 8.1 Hz, 1 H), 7.51 (dd, *J* = 8.7 Hz, 5.0 Hz, 1 H), 7.36 (dd, *J* = 8.0 Hz, 0.9 Hz, 1 H), 7.22 (s, 1 H), 7.14 (td, *J* = 8.2 Hz, 2.9 Hz, 1 H), 7.01 (dd, *J* = 7.9 Hz, 2.4 Hz, 1 H), 6.23 (q, *J* = 7.8 Hz, 1 H), 3.37 (s, 3 H), 2.44 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 162.2 (d, *J* = 249.7 Hz), 148.8 (q, *J* = 4.1 Hz), 143.5, 139.6 (d, *J* = 9.0 Hz), 137.9, 134.6, 132.3, 132.2, 131.7, 129.2, 128.5, 123.0 (d, *J* = 34.3 Hz), 121.9 (q, *J* = 270.2 Hz), 117.9 (d, *J* = 22.6 Hz), 116.1 (dd, *J* = 24.3 Hz, 2.5 Hz), 38.6, 21.5; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.29, -110.68. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{14}F_4NO_2S^+$ 372.0676; Found 372.0674.



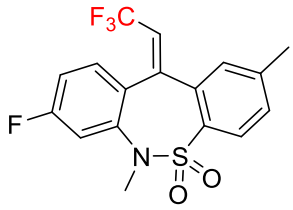
(*E*)-9-chloro-2,6-dimethyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3s)

White solid, 69% yield (53.4 mg). M.p. = 147.0-148.5 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.81 (d, *J* = 8.1 Hz, 1 H), 7.47-7.40 (m, 2 H), 7.36 (dd, *J* = 8.1 Hz, 0.9 Hz, 1 H), 7.30 (d, *J* = 0.9 Hz, 1 H), 7.22 (s, 1 H), 6.23 (q, *J* = 7.7 Hz, 1 H), 3.37 (s, 3 H), 2.44 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 148.7 (q, *J* = 5.7 Hz), 143.5, 139.0, 137.8, 135.0, 134.9, 134.7, 131.6, 131.4, 131.1, 129.1, 128.9 (q, *J* = 2.3 Hz), 128.4, 123.1 (q, *J* = 32.3 Hz), 122.0 (q, *J* = 270.0 Hz), 38.5, 21.5; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.27. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{14}ClF_3NO_2S^+$ 388.0380; Found 388.0382.



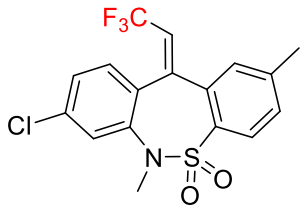
(*E*)-9-bromo-2,6-dimethyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3t)

White solid, 62% yield (53.5 mg). M.p. = 163.2-164.8 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.81 (d, *J* = 8.1 Hz, 1 H), 7.58 (dd, *J* = 8.4 Hz, 2.3 Hz, 1 H), 7.45 (d, *J* = 1.0 Hz, 1 H), 7.39 (d, *J* = 8.4 Hz, 1 H), 7.36 (dd, *J* = 8.1 Hz, 0.9 Hz, 1 H), 7.22 (s, 1 H), 6.23 (q, *J* = 7.7 Hz, 1 H), 3.37 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 148.7 (q, *J* = 5.7 Hz), 143.6, 139.2, 137.8, 135.5, 134.7, 134.1, 131.8 (q, *J* = 2.6 Hz), 131.63, 131.62, 129.1, 128.4, 123.0 (q, *J* = 34.2 Hz), 122.9, 122.0 (q, *J* = 270.2 Hz), 38.4, 21.5; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.26. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{17}H_{14}BrF_3NO_2S^{+}$ 431.9875; Found 431.9872.



(*E*)-8-fluoro-2,6-dimethyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3u)

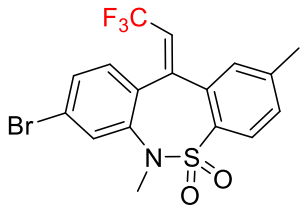
White solid, 71% yield (52.8 mg). M.p. = 134.8-136.3 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.81 (d, *J* = 8.1 Hz, 1 H), 7.36 (d, *J* = 8.1 Hz, 1 H), 7.28 (dd, *J* = 8.3 Hz, 6.6 Hz, 1 H), 7.25-7.23 (m, 2 H), 7.08 (td, *J* = 8.3 Hz, 2.5 Hz, 1 H), 6.21 (q, *J* = 7.8 Hz, 1 H), 3.37 (s, 3 H), 2.44 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 163.5 (d, *J* = 250.6 Hz), 149.3 (q, *J* = 5.4 Hz), 143.6, 138.2 (d, *J* = 10.2 Hz), 137.6, 135.2, 133.2 (d, *J* = 3.4 Hz), 131.5 130.5 (dd, *J* = 9.2 Hz, 2.5 Hz), 129.1, 128.3, 123.0 (q, *J* = 34.0 Hz), 122.1 (q, *J* = 270.0 Hz), 117.2 (d, *J* = 22.5 Hz), 116.4 (d, *J* = 21.6 Hz), 38.4, 21.5; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.24, -108.90. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{17}H_{14}F_4NO_2S^{+}$ 372.0676; Found 372.0678.



(*E*)-8-chloro-2,6-dimethyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3v)

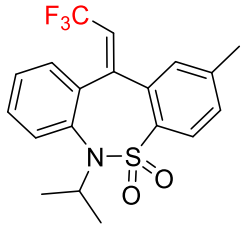
White solid, 69% yield (53.5 mg). M.p. = 176.1-177.7 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.81 (d, *J* = 8.1 Hz, 1 H), 7.52 (d, *J* = 2.0 Hz, 1 H), 7.37-7.34 (m, 2 H), 7.25-

7.23 (m, 2 H), 6.22 (q, J = 7.8 Hz, 1 H), 3.37 (s, 3 H), 2.44 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 149.2 (q, J = 5.6 Hz), 143.6, 137.7, 136.3, 135.7, 131.5, 130.2, 130.0 (q, J = 2.6 Hz), 129.4, 129.1, 128.3, 123.0 (q, J = 34.2 Hz), 122.0 (q, J = 270.0 Hz), 38.5, 21.5; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.20. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{14}ClF_3NO_2S^+$ 388.0380; Found 388.0382.



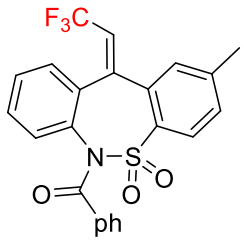
(*E*)-8-bromo-2,6-dimethyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3w)

White solid, 73% yield (63.0 mg). M.p. = 186.0-187.3 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.81 (d, J = 8.1 Hz, 1 H), 7.68 (d, J = 1.9 Hz, 1 H), 7.50 (dd, J = 8.2 Hz, 1.9 Hz, 1 H), 7.36 (dd, J = 8.1 Hz, 0.9 Hz, 1 H), 7.22 (s, 1 H), 7.18 (d, J = 8.2 Hz, 1 H), 6.22 (q, J = 7.7 Hz, 1 H), 3.37 (s, 3 H), 2.44 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 149.2 (q, J = 5.3 Hz), 143.6, 137.7, 137.6, 136.2, 134.8, 133.1, 132.3, 131.5, 130.2 (q, J = 2.3 Hz), 129.1, 128.3, 124.1, 123.0 (q, J = 34.2 Hz), 122.0 (q, J = 269.9 Hz), 38.5, 21.5; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.18. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{14}BrF_3NO_2S^+$ 431.9875; Found 431.9874.



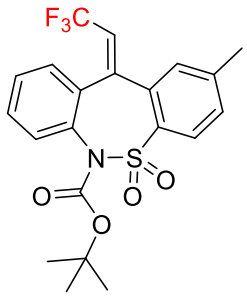
(*E*)-6-isopropyl-2-methyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide (3x)[3]

White solid, 79% yield (60.2 mg). M.p. = 145.1-146.9 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.84 (d, J = 8.1 Hz, 1 H), 7.53 (dd, J = 7.9 Hz, 1.3 Hz, 1H), 7.46 (td, J = 7.6 Hz, 1.7 Hz, 1 H), 7.38 (td, J = 7.5, Hz 1.3 Hz, 1 H), 7.34-7.30 (m, 2 H), 7.24 (s, 1 H), 6.17 (q, J = 8.0 Hz, 1H), 4.64-4.57 (m, 1 H), 2.42 (s, 3 H), 1.49 (like s, 3 H), 1.19 (like s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 150.2 (q, J = 5.5 Hz), 142.9, 139.3, 138.9, 135.4, 132.9, 131.9, 131.3, 130.4, 129.5, 129.1, 129.1 (q, J = 4.9 Hz), 127.8, 122.2 (q, J = 269.7 Hz), 121.3 (q, J = 34.3 Hz), 54.2, 24.2, 21.6, 21.4; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.34. **MS (ESI)** m/z: 381.1.



(*E*)-(2-methyl-5,5-dioxido-11-(2,2,2-trifluoroethylidene)dibenzo[*c,f*][1,2]thiazepin-6(11H)-yl)(phenyl)methanone (3y)[3]

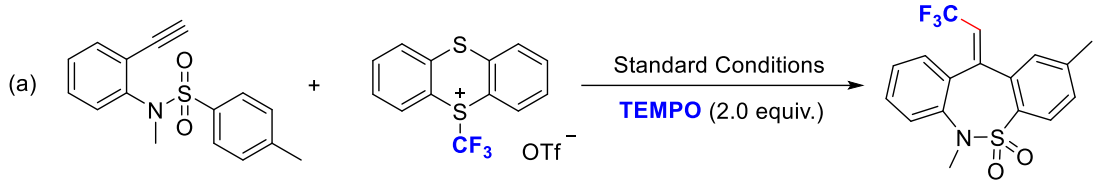
White solid, 70% yield (62.1 mg). M.p. = 179.5-181.0 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.89 (d, *J* = 8.1 Hz, 1H), 7.82 (dd, *J* = 8.0 Hz, 1.2 Hz, 1 H), 7.75-7.73 (m, 2 H), 7.52-7.38 (m, 4 H), 7.36-7.31 (m, 4 H), 7.23 (d, *J* = 7.7 Hz, 1 H), 6.26 (q, *J* = 7.7 Hz, 1 H), 2.47 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 169.4, 147.9 (q, *J* = 5.4 Hz), 144.2, 137.5, 137.3, 134.6, 133.1, 132.9, 132.8, 132.6, 131.9, 130.7, 130.4, 130.1, 130.0, 129.0 (q, *J* = 2.3 Hz), 128.2, 127.7, 123.9 (q, *J* = 34.2 Hz), 121.6 (q, *J* = 270.2 Hz), 21.6; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.56. **MS (ESI)** m/z: $[M + H]^+$ 444.1.



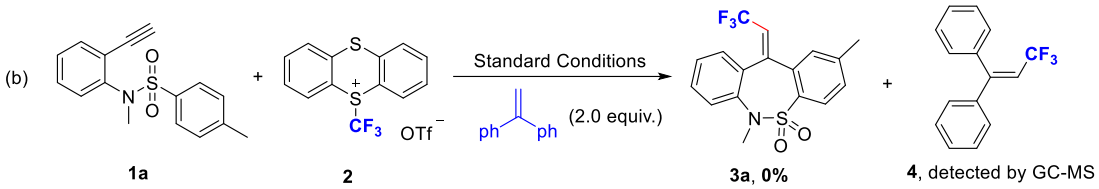
tert-butyl (*E*)-2-methyl-11-(2,2,2-trifluoroethylidene)dibenzo[*c,f*][1,2]thiazepine-6(11H)-carboxylate 5,5-dioxide (3z)[3]

White solid, 70% yield (61.5 mg). M.p. = 125.8-127.3 °C. **^{1}H NMR** (400 MHz, $ClCD_3$, ppm) δ 7.89 (d, *J* = 8.1 Hz, 1 H), 7.55 (dd, *J* = 7.9 Hz, 1.4 Hz, 1 H), 7.49 (td, *J* = 7.6 Hz, 1.6 Hz, 1 H), 7.43-7.38 (m, 2 H), 7.34-7.33 (m, 2 H), 6.21 (q, *J* = 7.7 Hz, 1 H), 2.46 (s, 3 H), 1.39 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 149.5, 148.4 (q, *J* = 5.7 Hz), 144.1, 137.2, 136.1, 134.6, 133.2, 131.6, 131.1, 130.7, 130.3, 129.6, 128.8 (q, *J* = 2.6 Hz), 127.6, 124.1 (q, *J* = 34.3 Hz), 121.8 (q, *J* = 270.2 Hz), 85.4, 27.6, 21.5; **^{19}F NMR** (376 MHz, $ClCD_3$, ppm) δ -56.08. **MS (ESI)** m/z: $[M + H]^+$ 440.1.

5. Mechanistic Experiments



(a) A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with *N*-(2-ethynylphenyl)-*N*,4-dimethylbenzenesulfonamide **1a** (0.20 mmol, 1.0 equiv), TT-$CF_3^+OTf^-$ **2** (0.30 mmol, 1.5 equiv), 4CzIPN (2 mol%), TEMPO (0.4 mmol, 2.0 equiv) and DMSO (2.0 mL). The reaction mixture was then stirred at room temperature for 4 h under air atmosphere. The reaction mixture was washed with water and extracted with ethyl acetate three times. The combined organic layer was washed with saturated NaCl solution, dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The analysis of crude mixture showed that the yield of **3a** was completely inhibited.



(b) A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with *N*-(2-ethynylphenyl)-*N*,4-dimethylbenzenesulfonamide **1a** (0.20 mmol, 1.0 equiv), TT-$CF_3^+OTf^-$ **2** (0.30 mmol, 1.5 equiv), 4CzIPN (2 mol%), 1, 1-diphenylethylene (0.4 mmol, 2.0 equiv) and DMSO (2.0 mL). The reaction mixture was then stirred at room temperature for 4 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 **4** was observed by GC-MS as following: **GC-MS** (m/z, relative intensity): 248 (M^+, 90), 178 (100), 165 (100), 151 (30), 89 (43), 76 (37). The data for the adduct **4** were in accordance with the ones previously reported in the literature.[4]

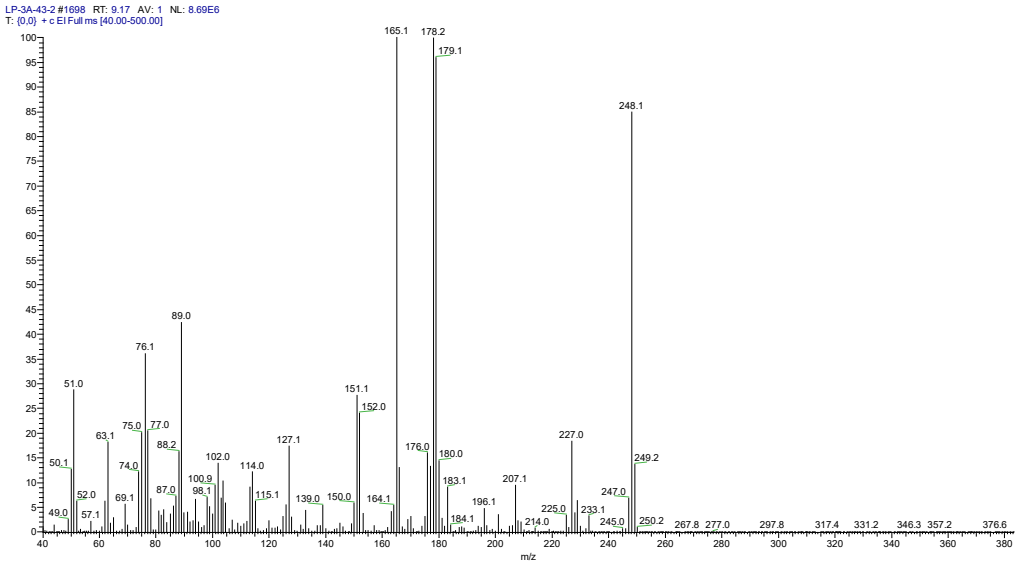


Figure S1. GC-MS (m/z) of adduct **4**

6. X-ray crystallographic data of 3a

The product **3a** was recrystallized from petroleum ether/EtOAc. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC **2425399**.

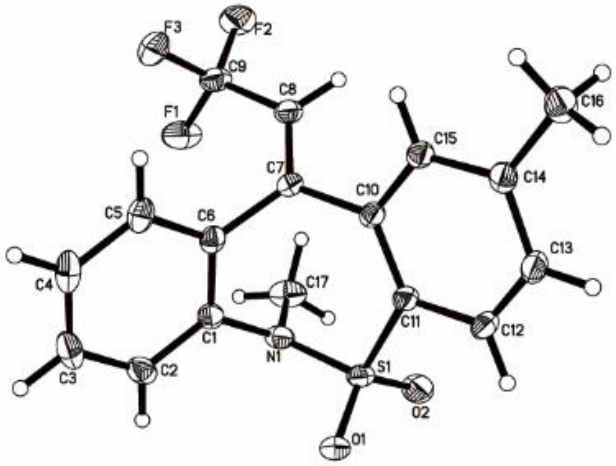


Figure S2. X-ray crystal structure of **3a** （CDCC：2425399）

Table S7. Crystal data and structure refinement for **3a**.	
Identification code	**3a**
Empirical formula	$C_{17}H_{14}F_3NO_2S$
Formula weight	353.35
Temperature/K	150

Crystal system	triclinic
Space group	P-1
a/Å	7.8410 (4)
b/Å	9.9763 (5)
c/Å	10.8160 (6)
α/°	90.279 (6)
β/°	101.789 (5)
γ/°	106.790 (5)
Volume/Å$_3$	791.07 (8)
Z	2
ρcalcg/cm^3	1.483
μ/mm^{-1}	0.247
F(000)	364.0
Crystal size/mm^3	0.16 × 0.11 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.556 to 52.742

7. References

[1] (a) Xiao Q, Lu M J, Deng Y L, et al. Photoinduced Radical Cascade Cyclization: A Metal-Free Approach to Access Difluoroalkylated Dioxodibenzothiazepines. *Org. Lett.* **2021**, *23*, 9303-9308. (b) Zheng X Y, Shen Q T, Yin C L, et al. Photoinduced Three-Component Difluoroamidosulfonylation/Bicyclization: Regioselectivity Synthesis of Seven-Membered Dibenzosultams. *Adv. Synth. Catal.* **2022**, *364*, 1750-1756. (c) Chen X Y, Geng Y, Liu B, et al. Photochemical difluoromethylation of alkynes: synthesis of CF_2H-substituted seven-membered dioxodibenzothiazepines and dibenzazepines. *Org. Chem. Front.,* **2023**, *10*, 1968-1974. (d) Guo C Y, Li L J, Yan Q Q, et al. Photoinduced Tandem Cyanomethylation/Cyclization of Unsaturated Compounds: Access to Cyanomethylated 7- or 5-Membered N-Heterocycles. *J. Org. Chem.* **2023**, *88*, 12141-12149. (e) Tian Y F, Zheng L P, Guo D Y, et al. Photo~Induced Difluoroethylation or Monofluoromethyl Sulfonylation of 2-Amino Aryl Ethynes to Access Diverse Seven-Membered N-Heterocycles. *Eur. J. Org. Chem.* **2024**, *27*, 1-4.

[2] Jia H, Häring A P, Berger F, et al. Trifluoromethyl Thianthrenium Triflate: A Readily Available Trifluoromethylating Reagent with Formal CF_3^+, $CF_3^\bullet$, and CF_3^- Reactivity. *J. Am. Chem. Soc.,* **2021**, *143*, 7623-7628.

[3] Zhang, Z.-Q.; Xu, Y.-H.; Dai, J.-C.; Li, Y.; Sheng, J.; Wang, X.-S. Copper-Catalyzed Trifluoromethylation/Cyclization of Alkynes for Synthesis of Dioxodibenzothiazepines. *Org. Lett*. **2021**, *23*, 2194-2198.

[4] (a) Xu, C., Huang, W., Zhang, R., Gao, C., Li, Y., Wang, M. Trifluoromethylations of Alkenes Using $PhICF_3Cl$ as Bifunctional Reagent. *J. Org. Chem.* **2019**, *84*, 14209-14216. (b) Ma, J. J., Yi, W. B., Lu, G. P., Cai, C. Decarboxylative and Denitrative Trifluoromethylation for the Synthesis of Cvinyl-CF_3 Compounds with Togni (II) Reagent. *Adv. Synth. Catal.*, **2015**, *357*, 3447-3452.

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

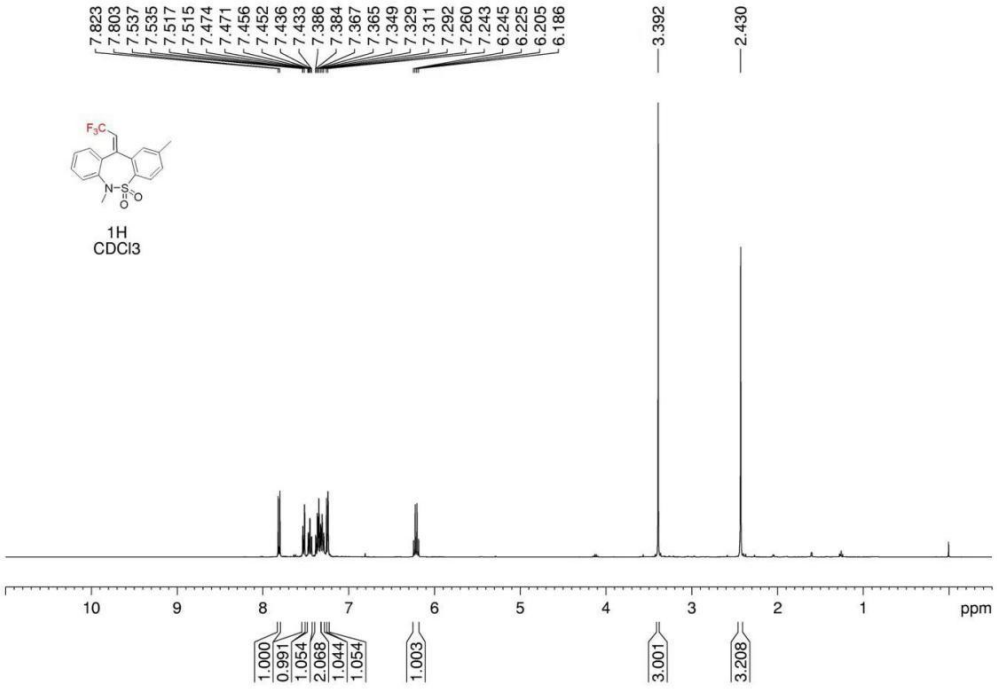


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a**

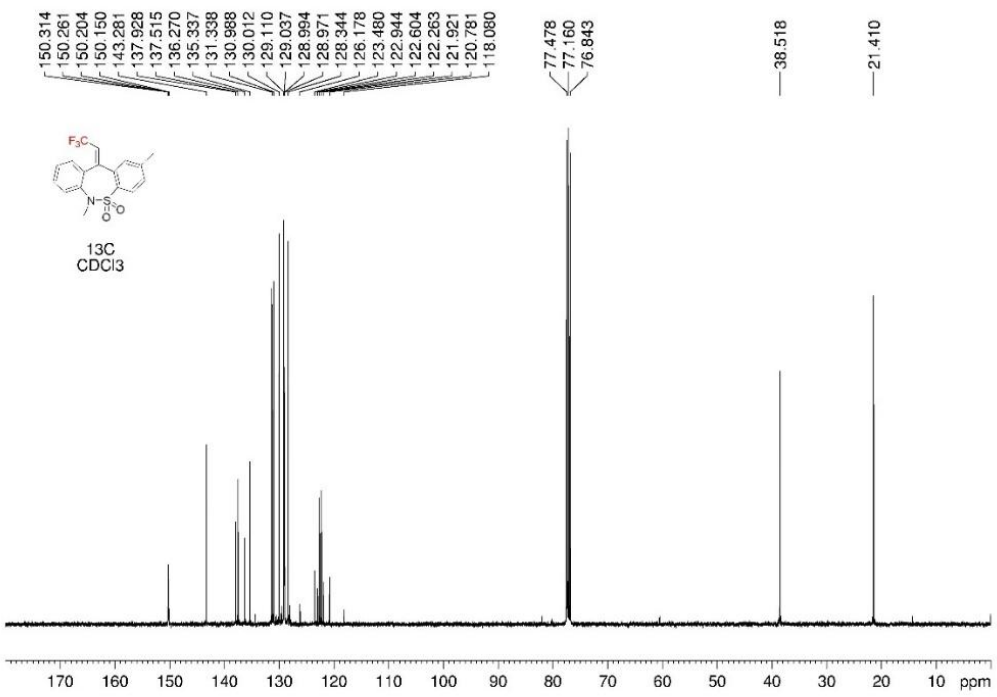


Figure S4. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3a**

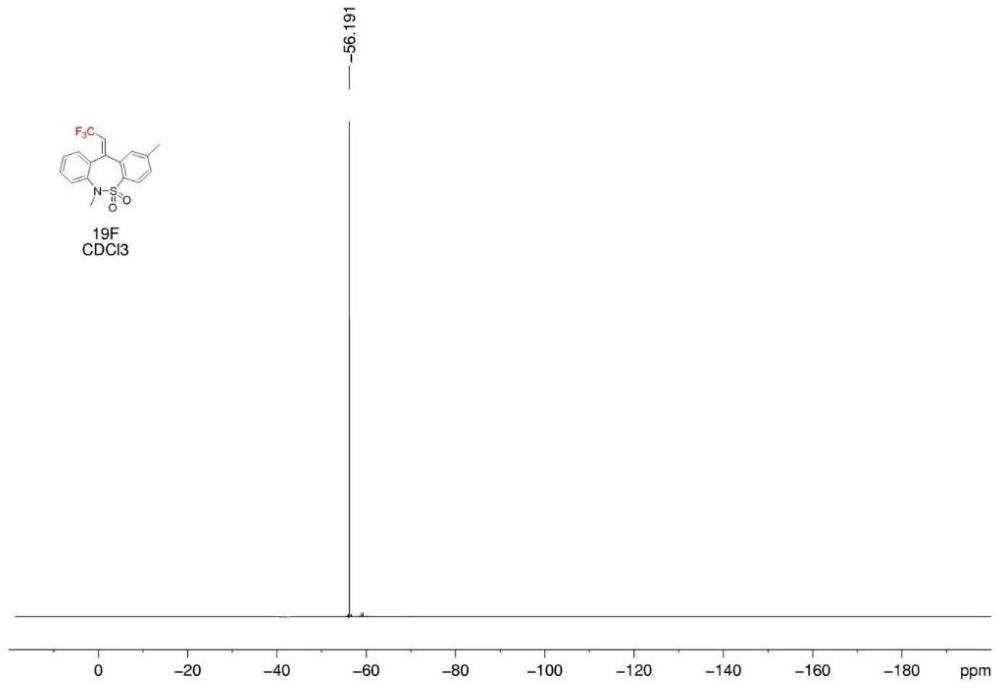


Figure S5. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3a**

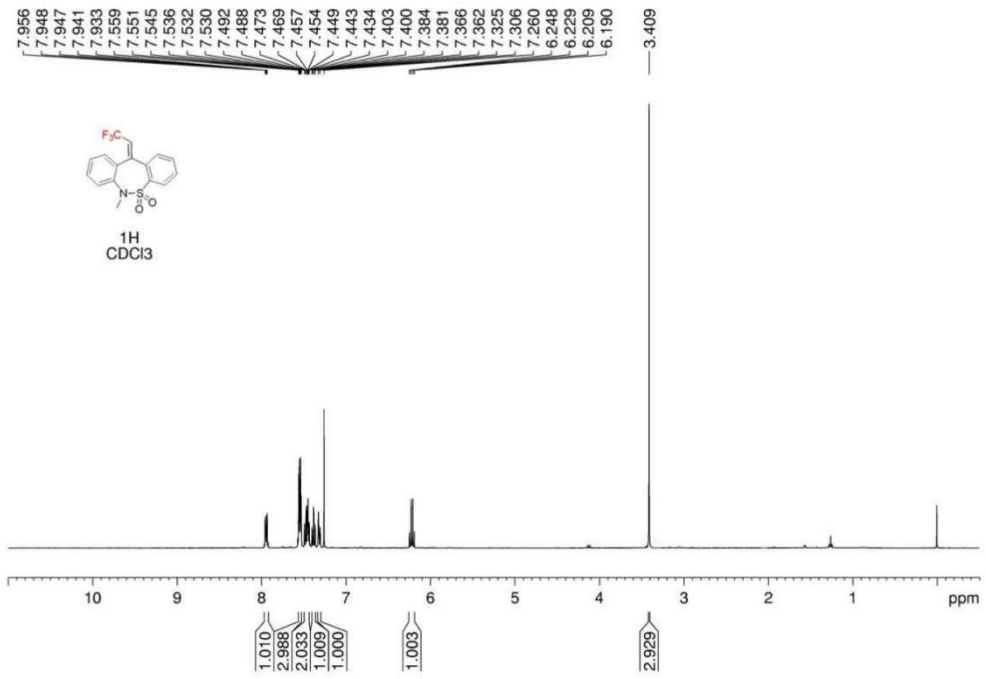


Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b**

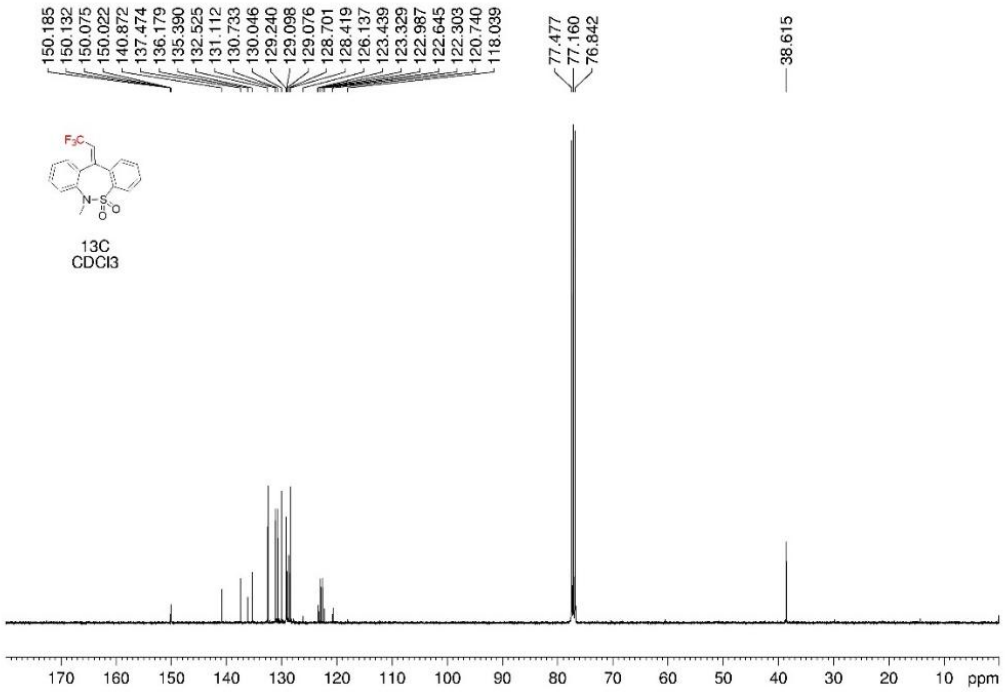


Figure S7. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3b**

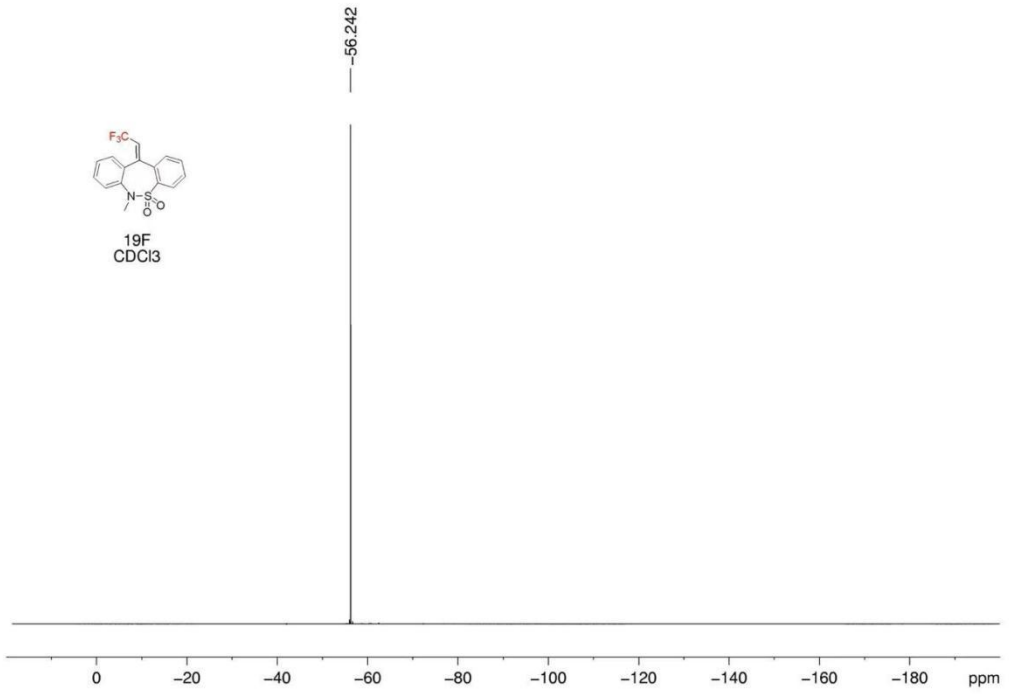


Figure S8. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3b**

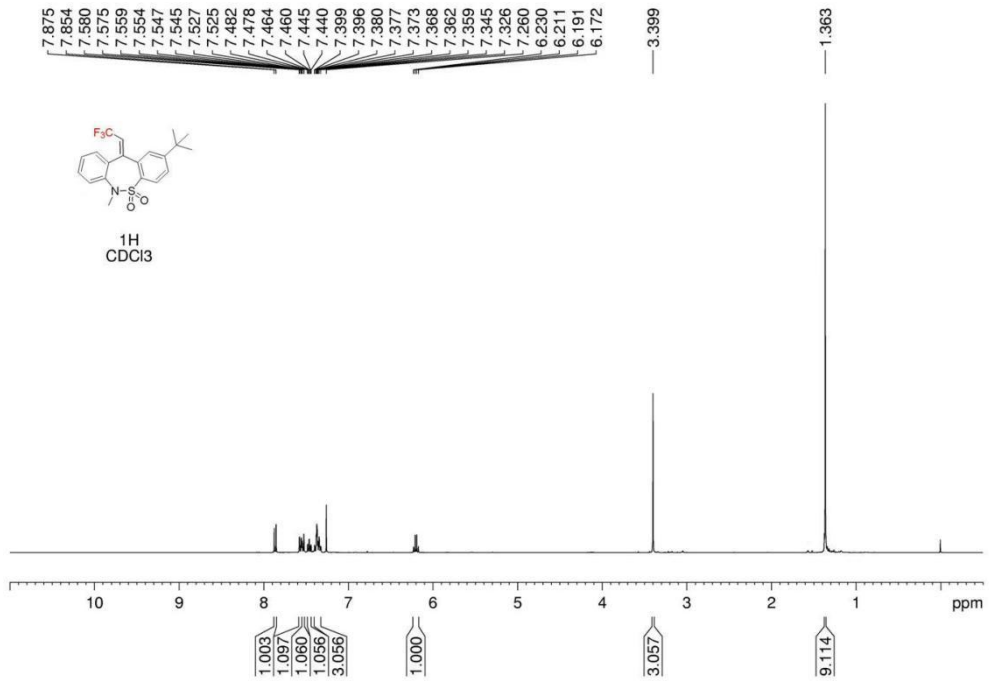


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3c**

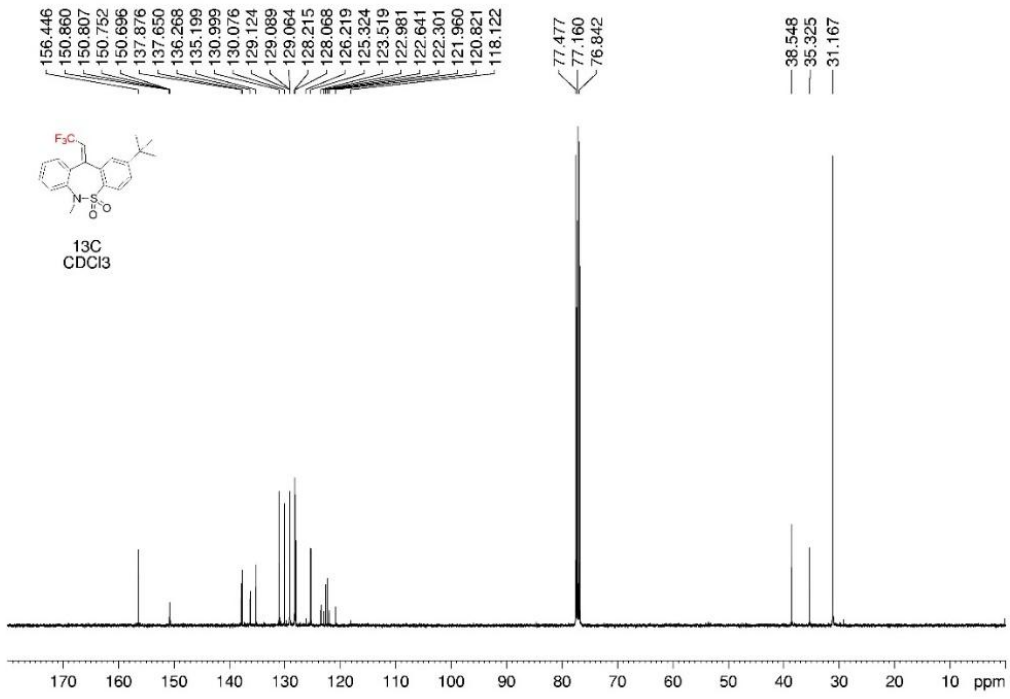


Figure S10. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3c**

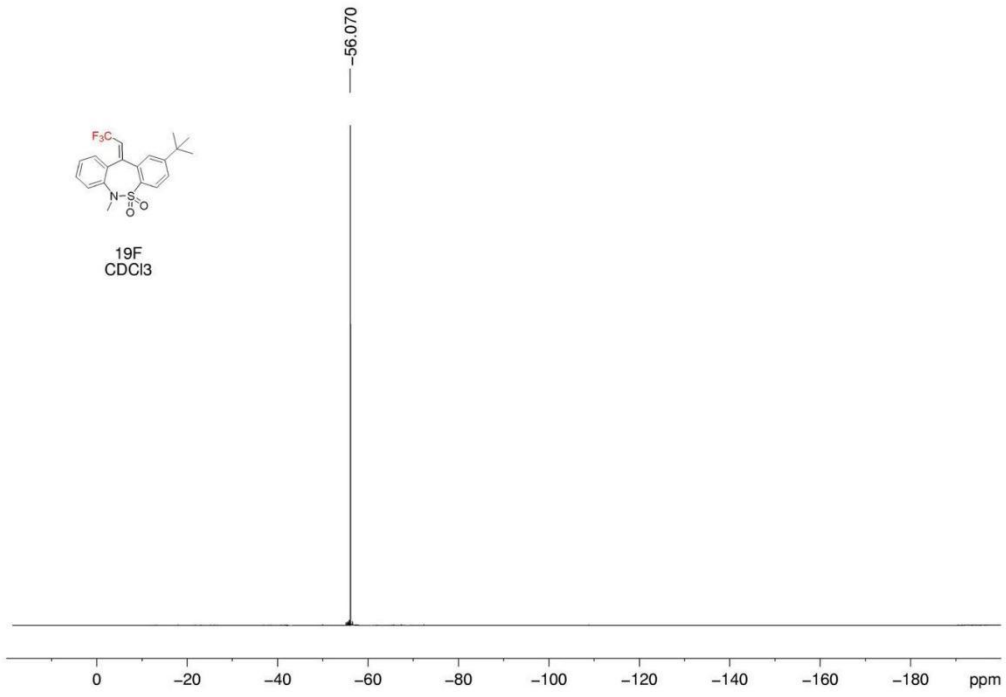


Figure S11. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3c**

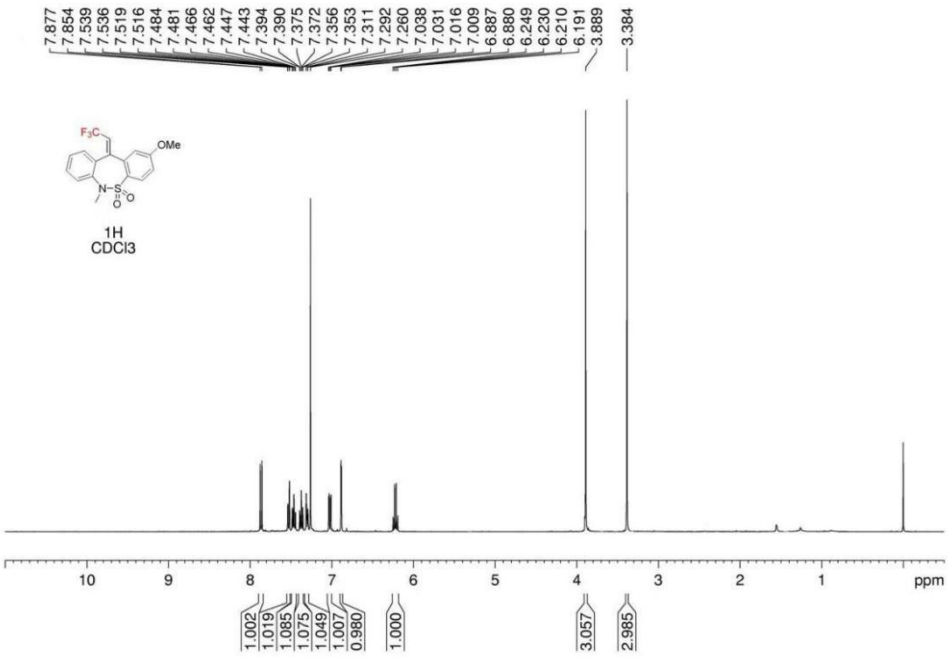


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3d**

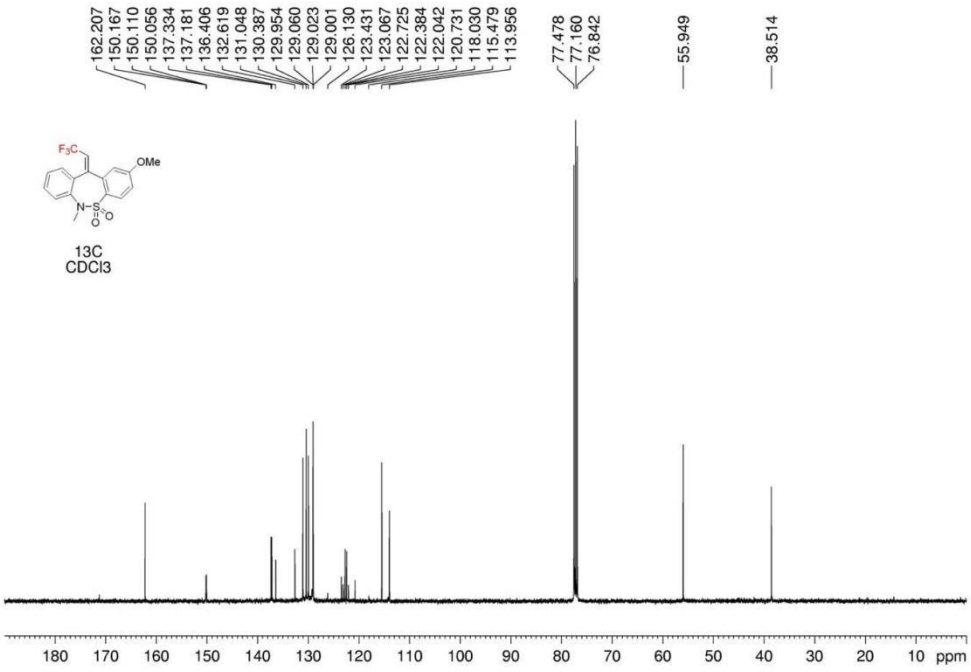


Figure S13. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3d**

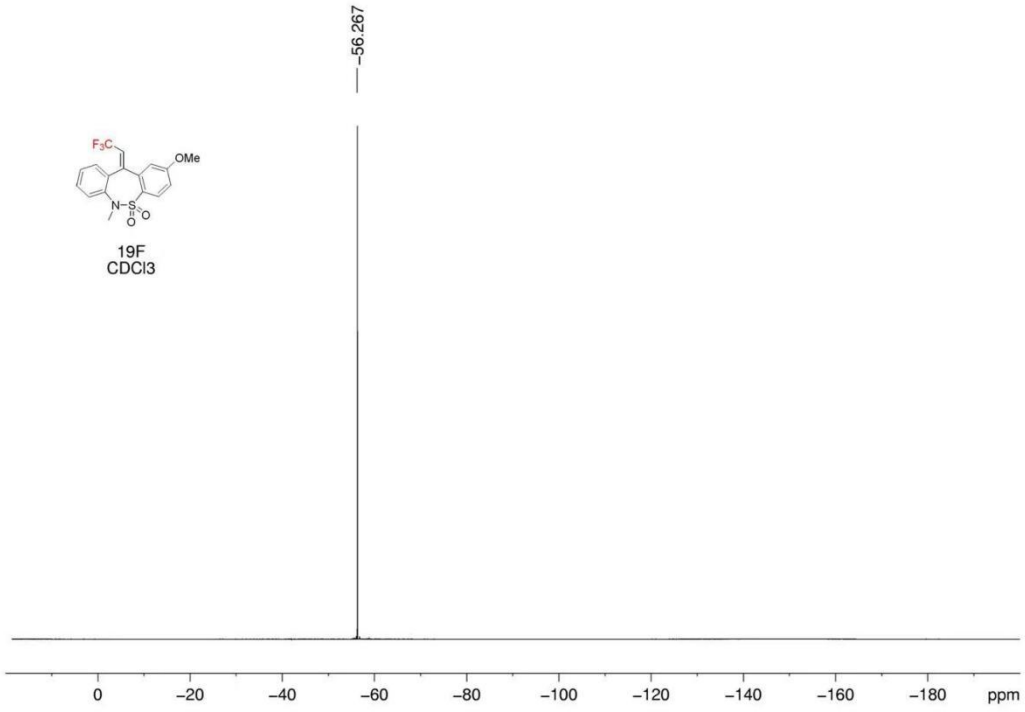


Figure S14. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3d**

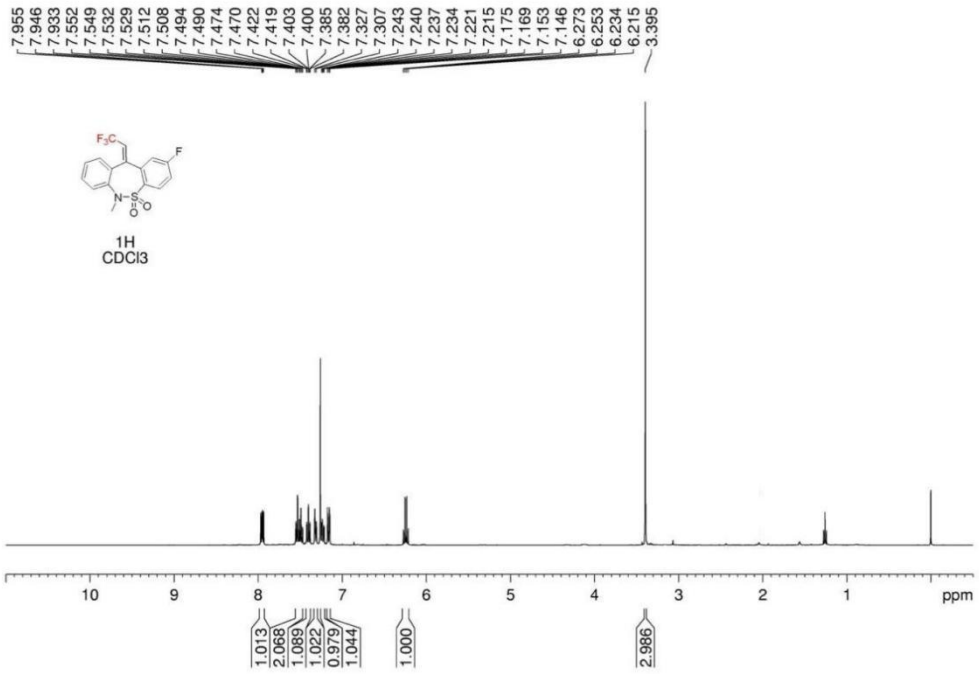


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3e**

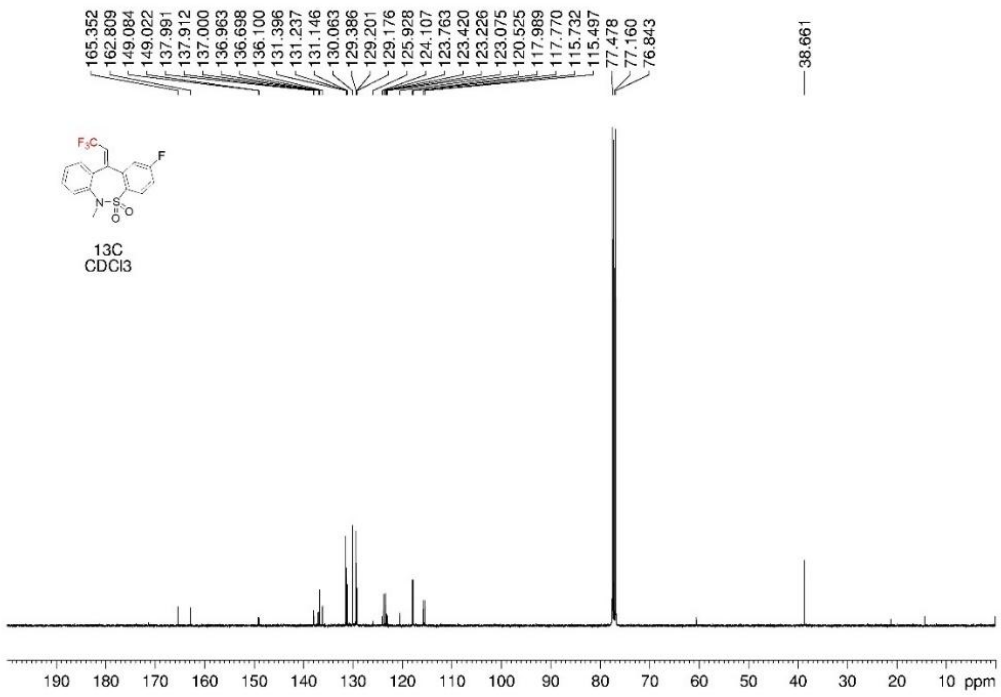


Figure S16. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3e**

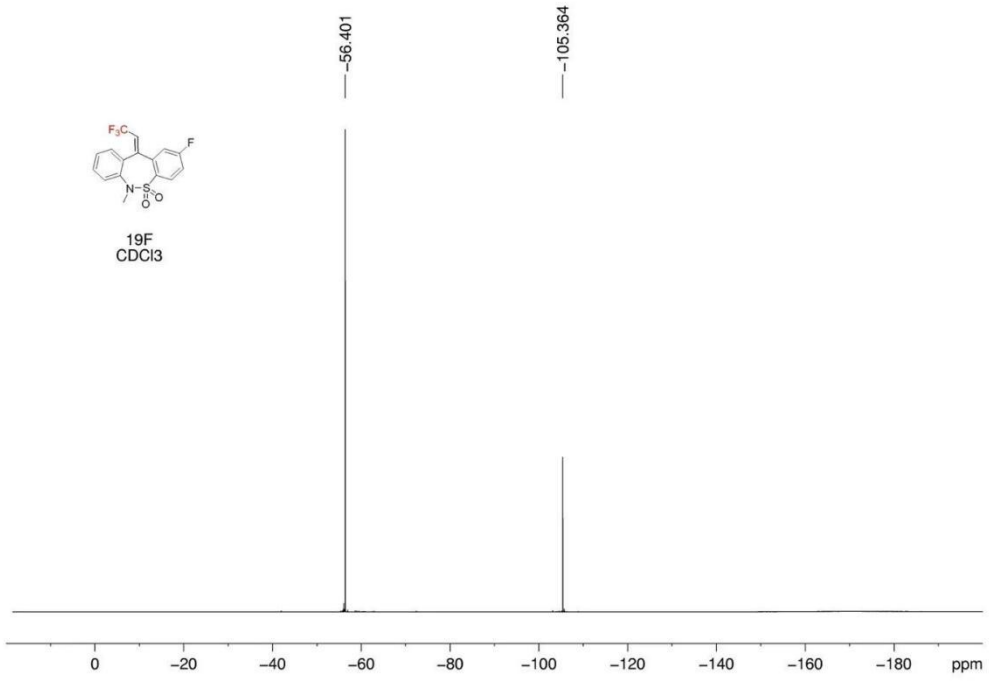


Figure S17. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3e**

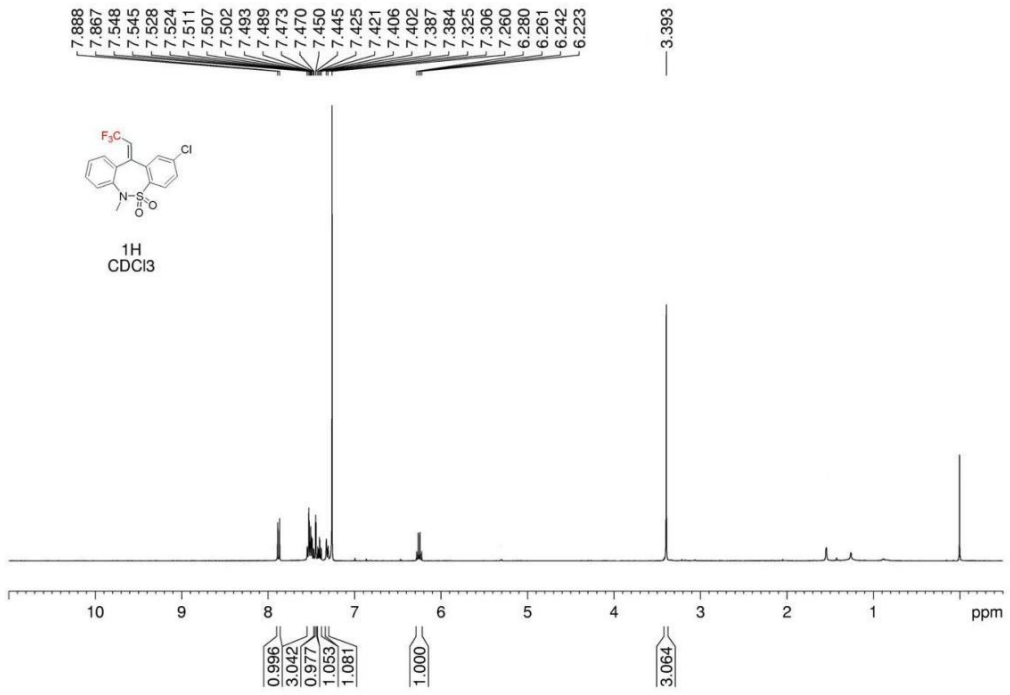


Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3f**

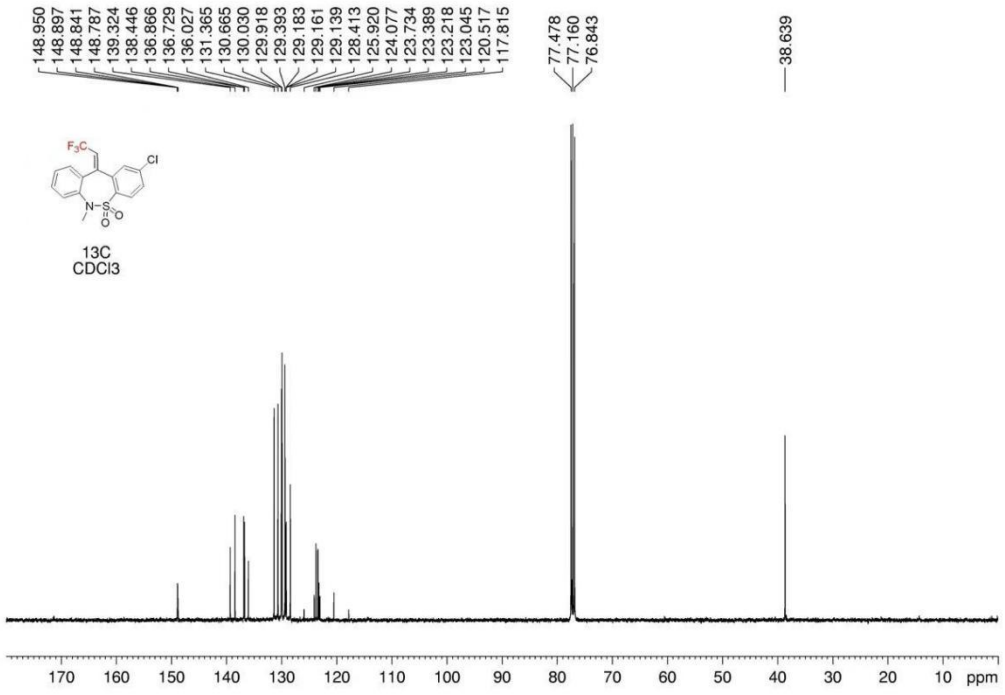


Figure S19. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3f**

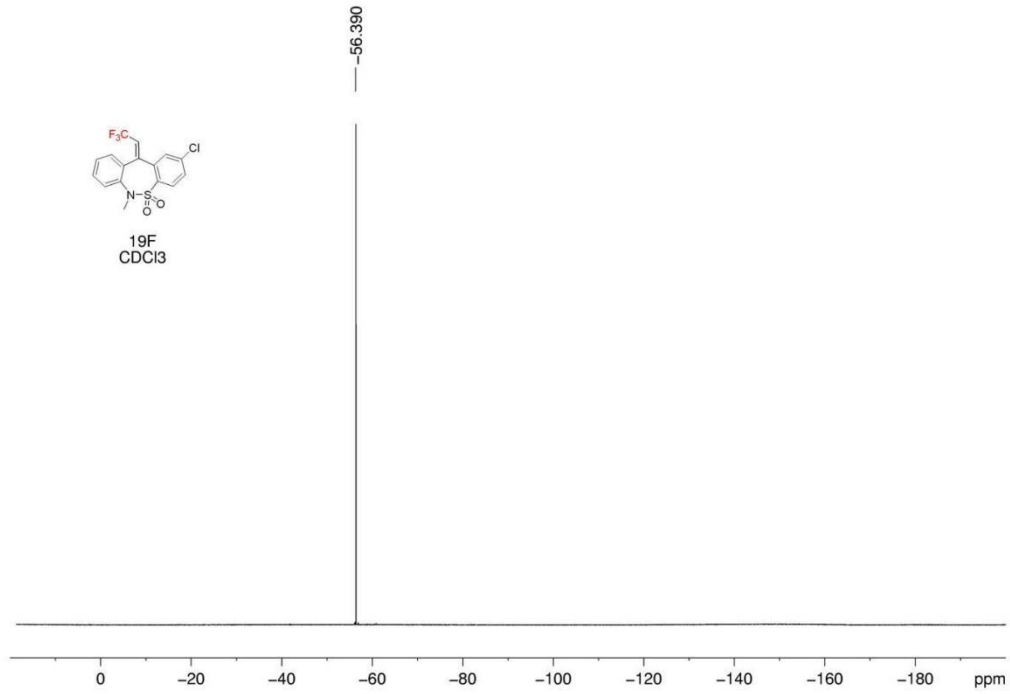


Figure S20. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3f**

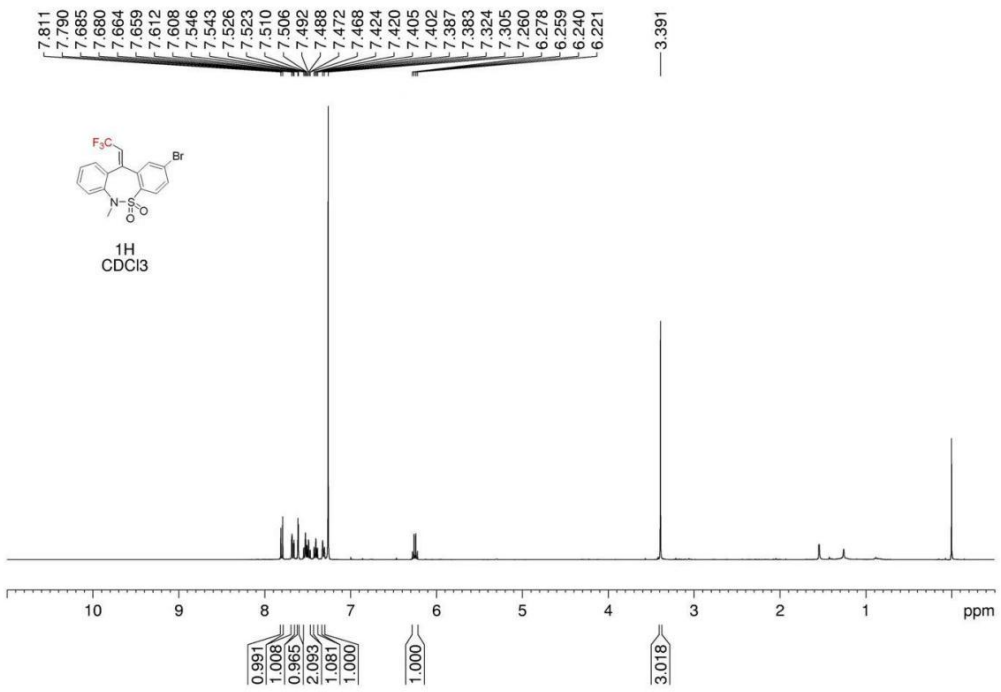


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3g**

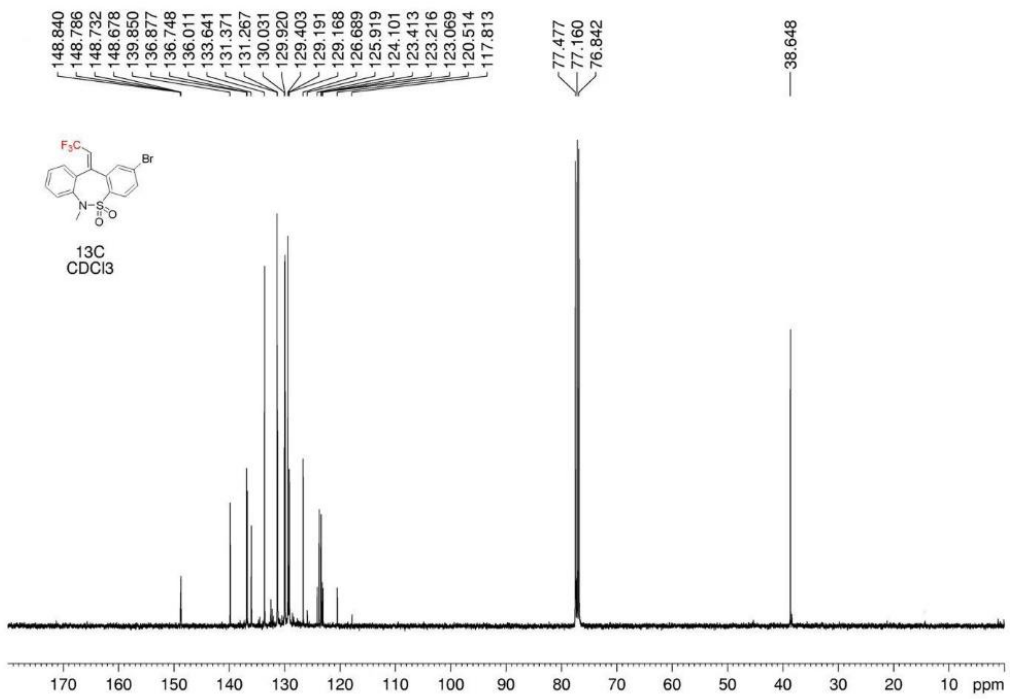


Figure S22. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3g**

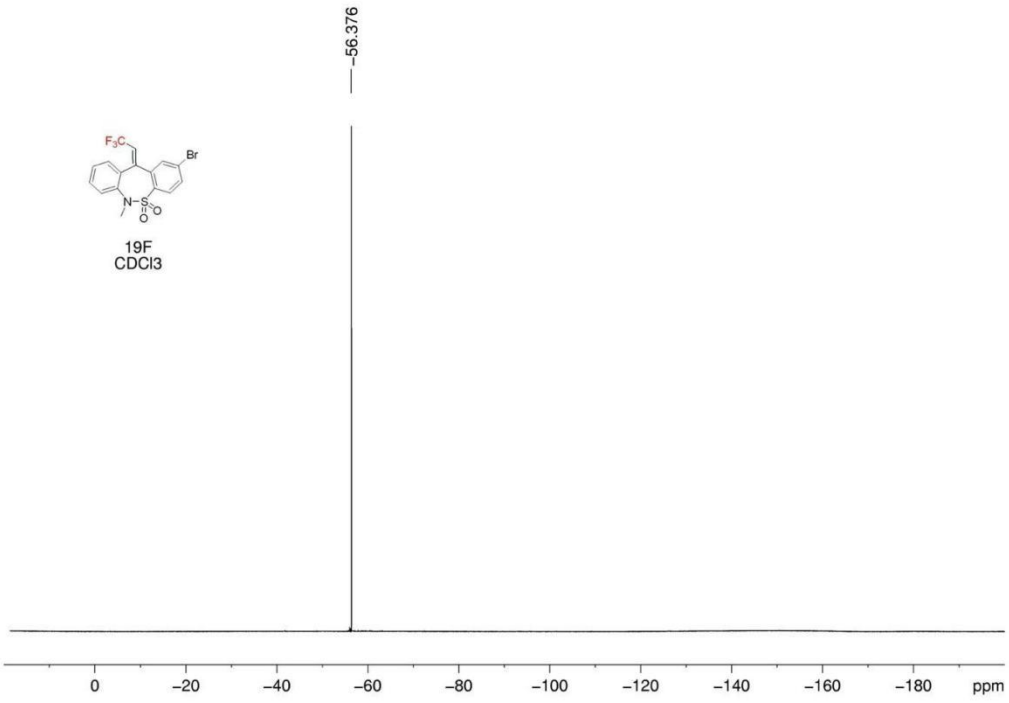


Figure S23. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3g**

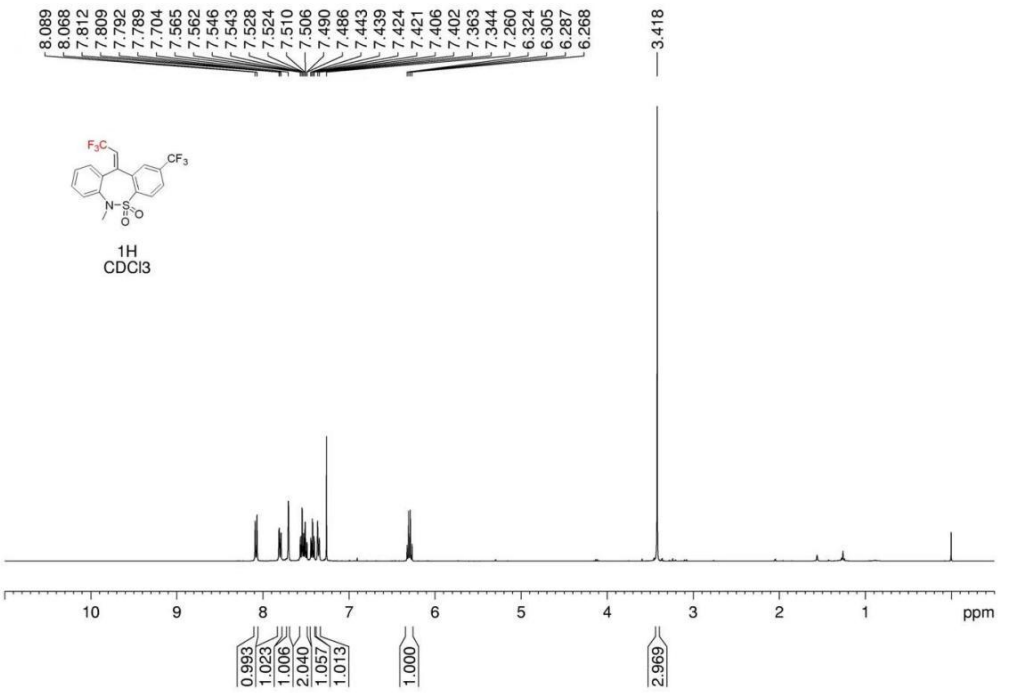


Figure S24. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3h**

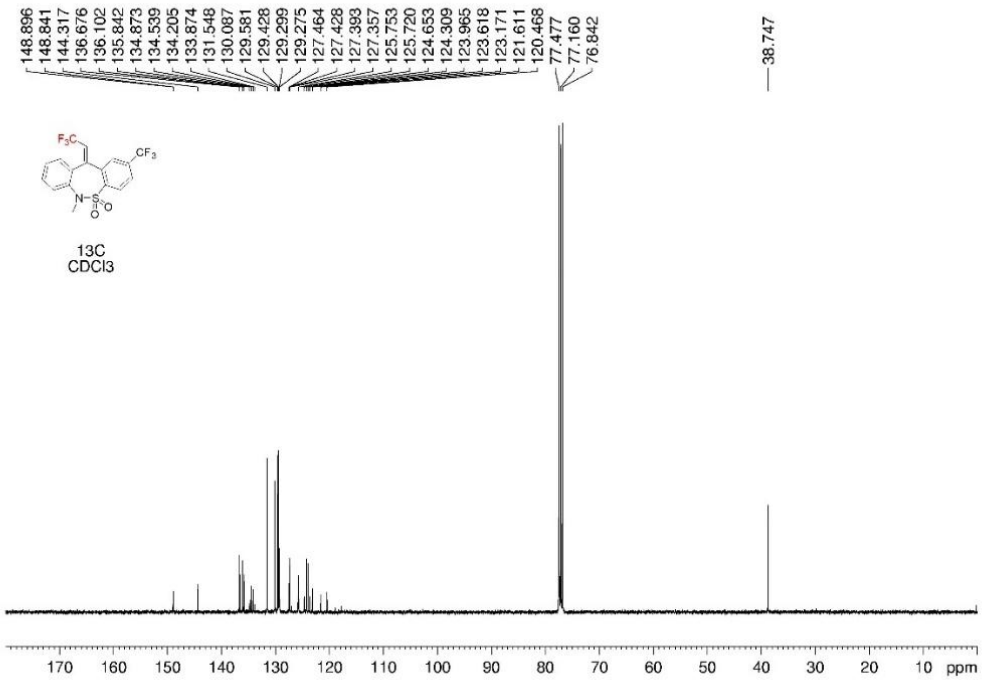


Figure S25. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3h**

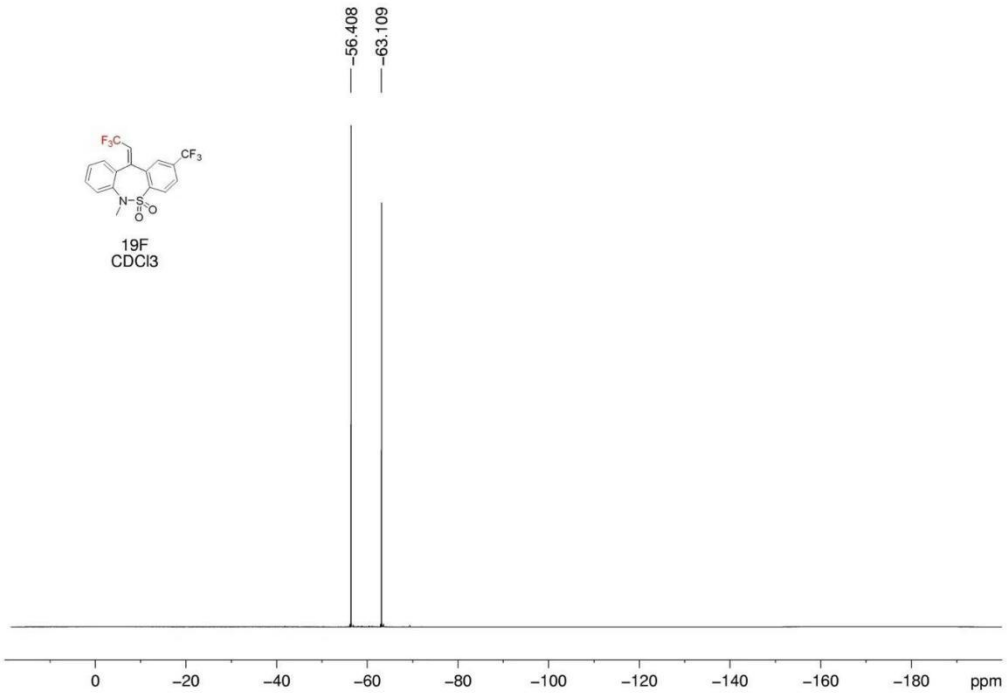


Figure S26. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3h**

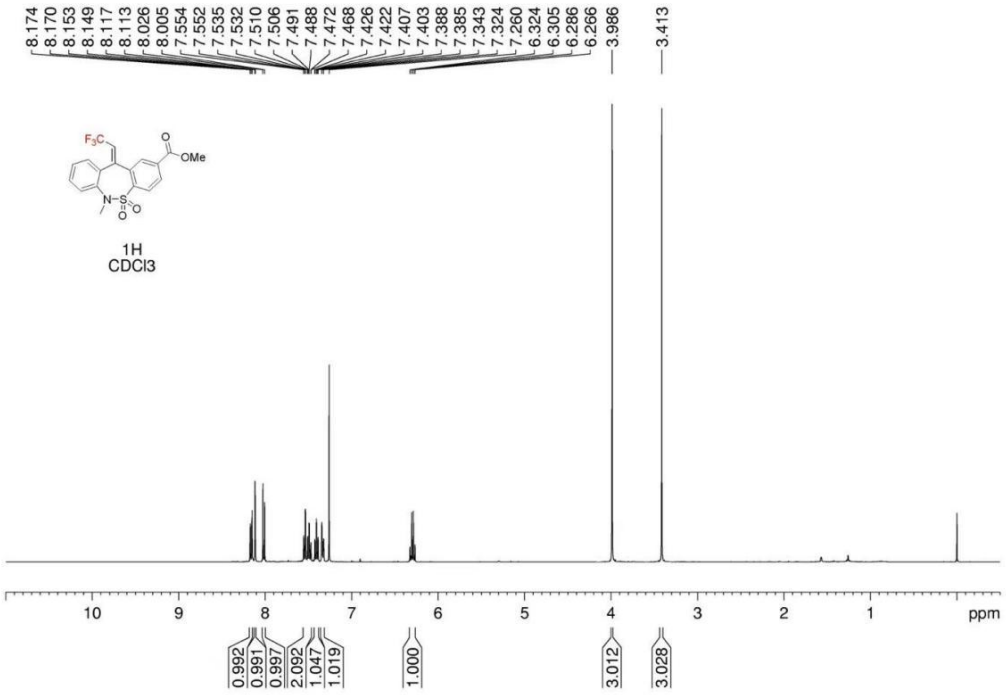


Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3i**

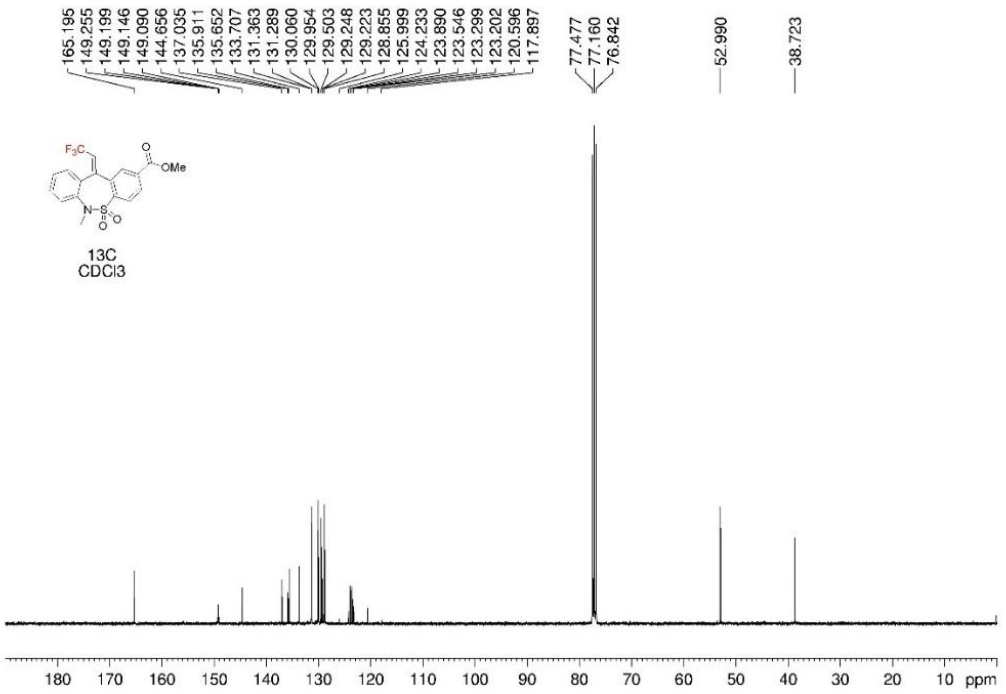


Figure S28. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3i**

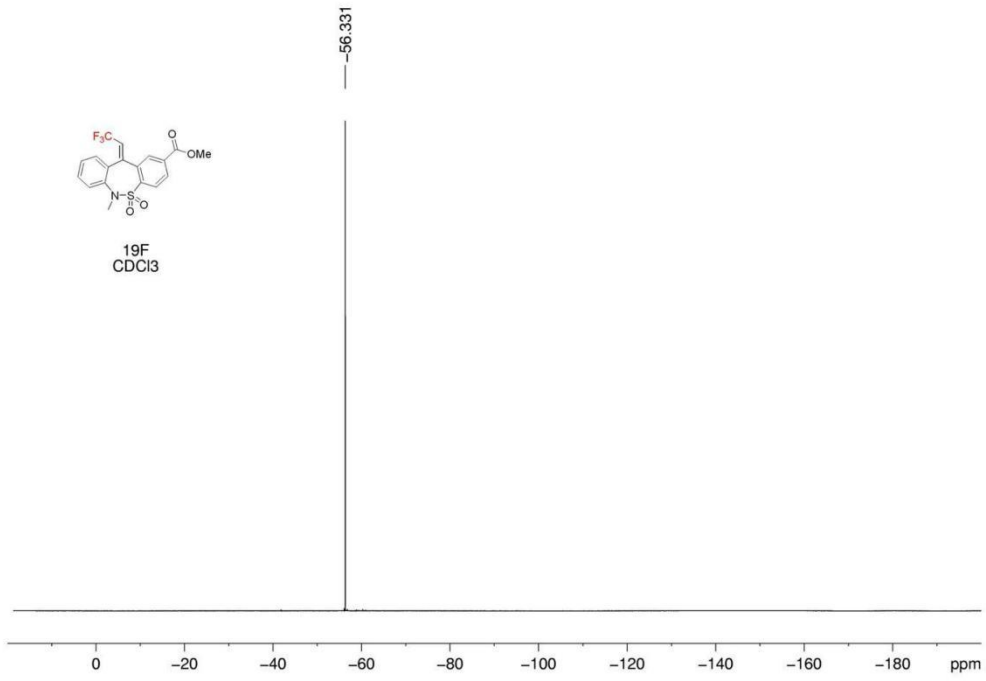


Figure S29. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3i**

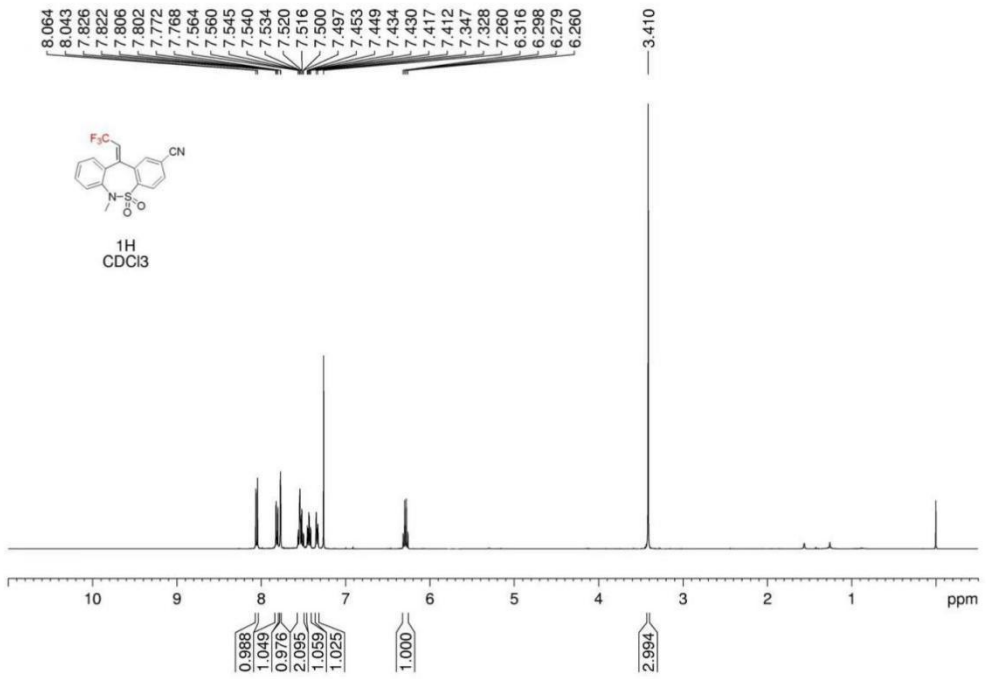


Figure S30. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3j**

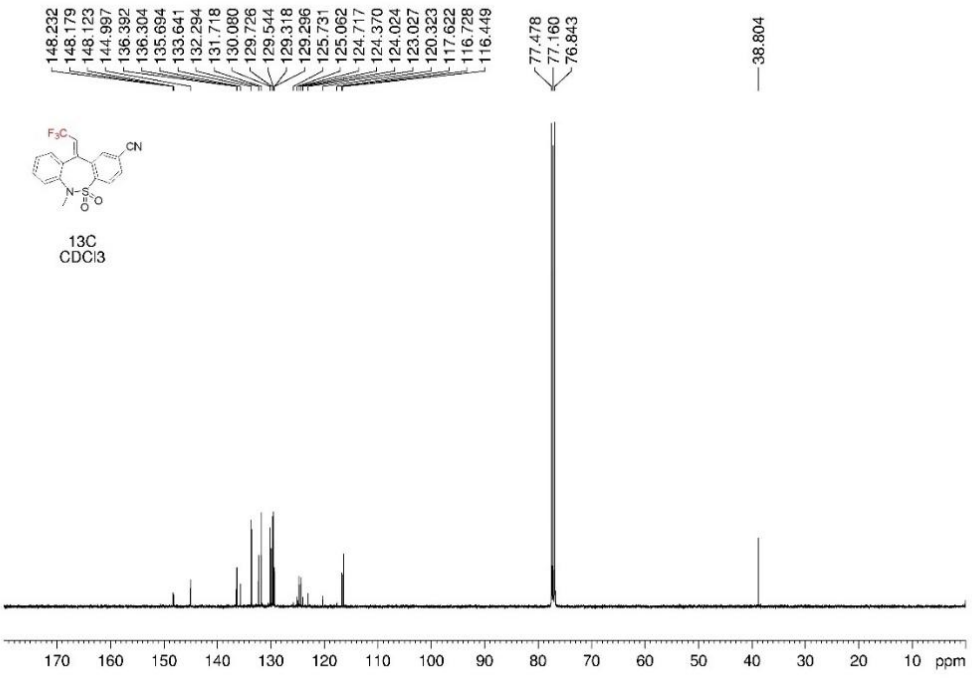


Figure S31. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3j**

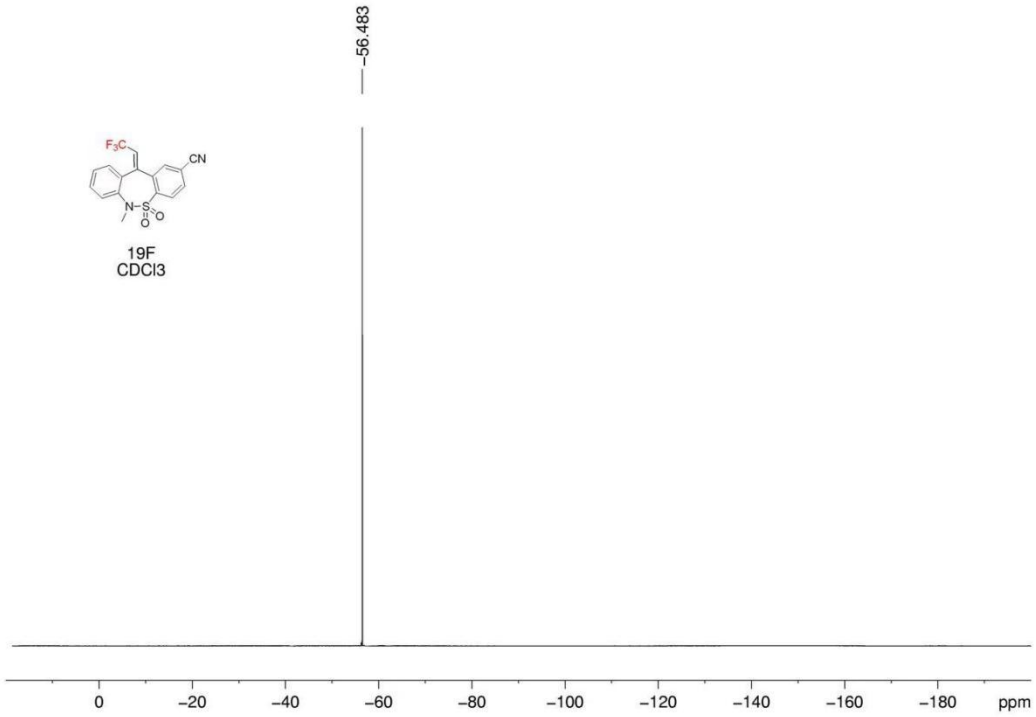


Figure S32. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3j**

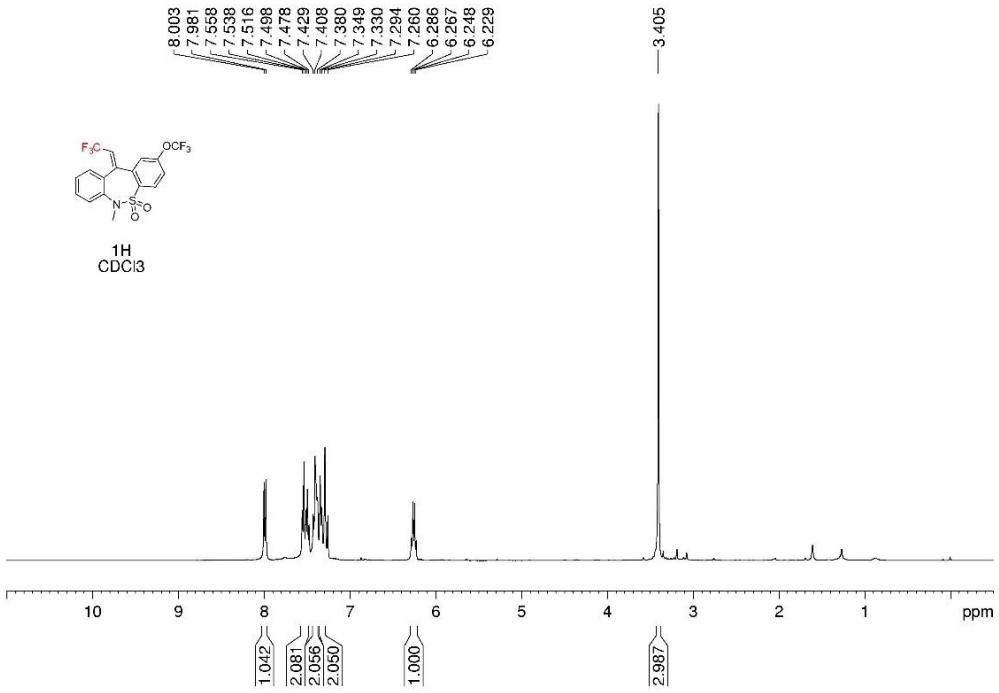


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3k**

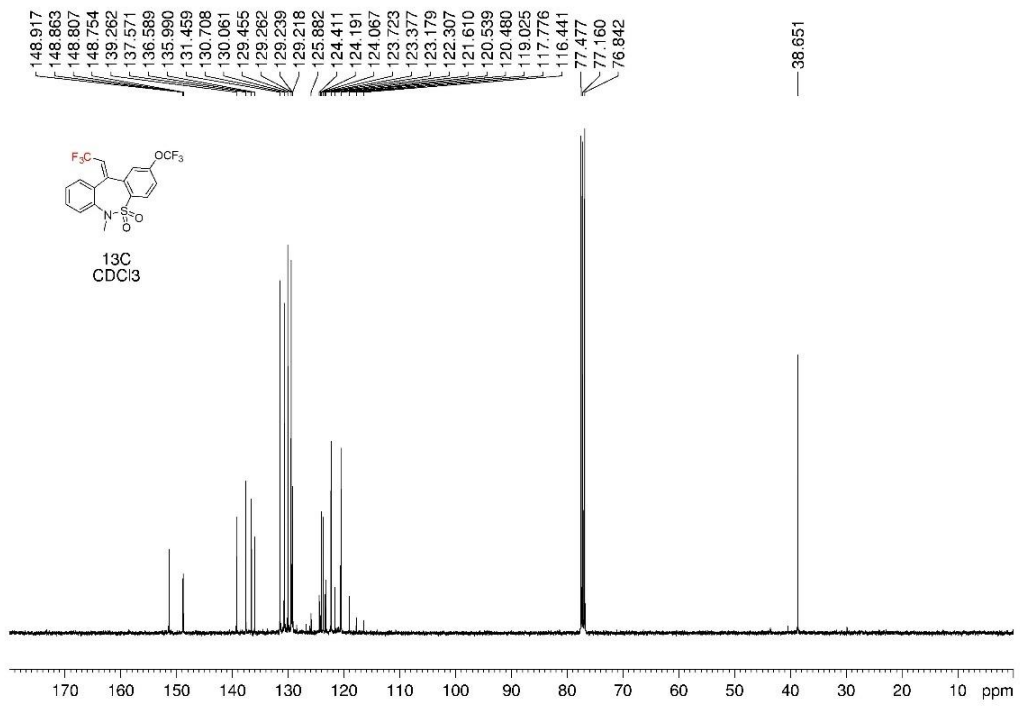


Figure S34. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3k**

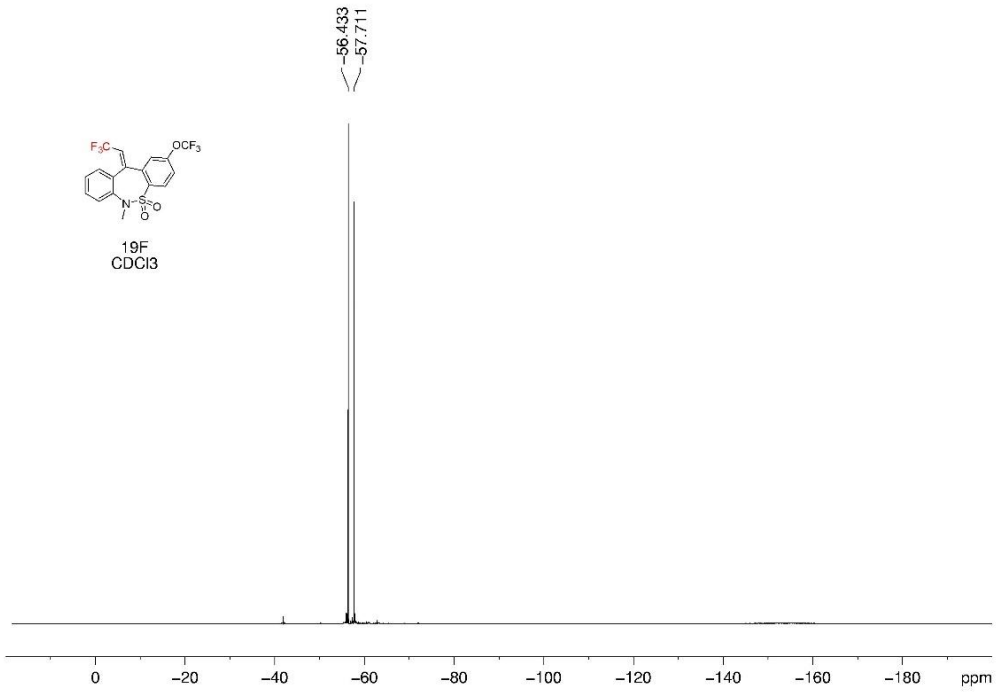


Figure S35. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3k**

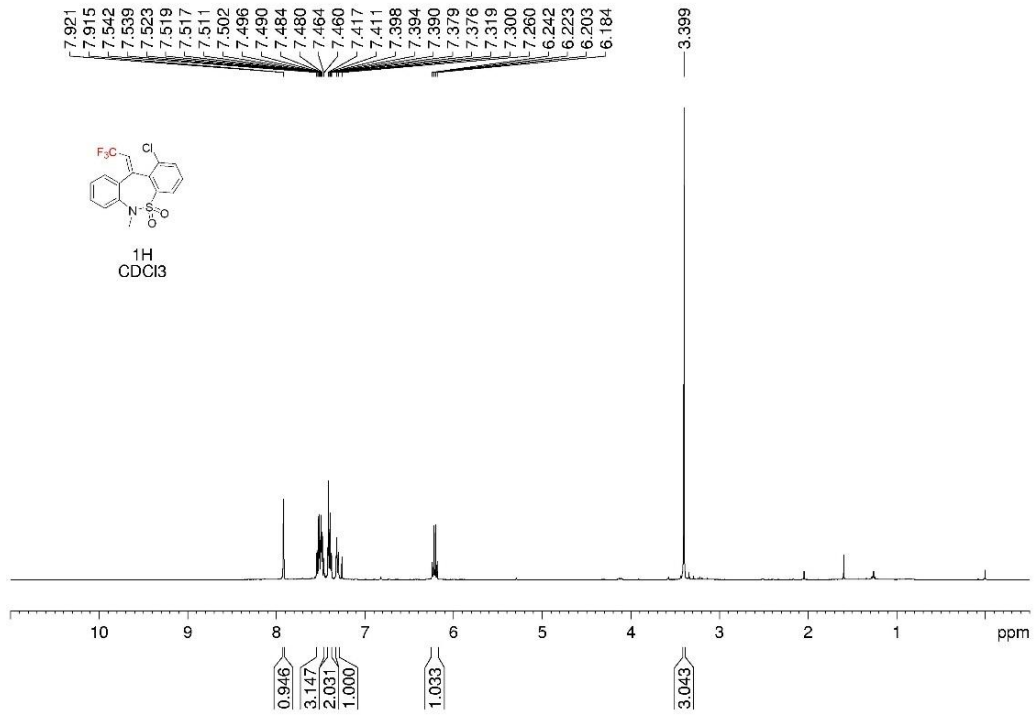


Figure S36. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3l**

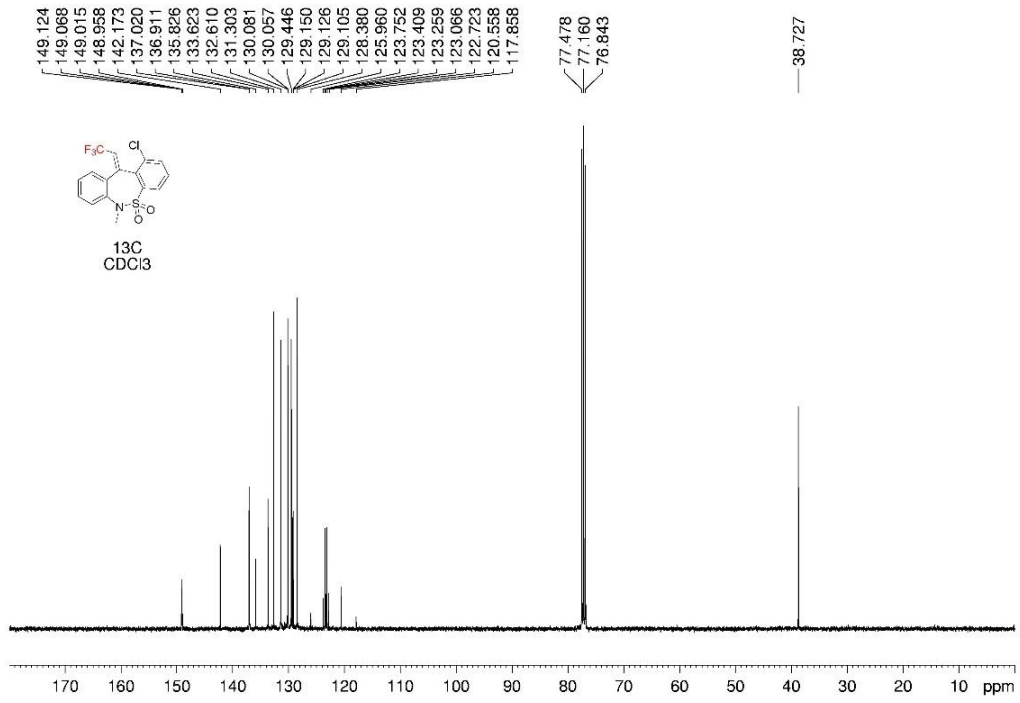


Figure S37. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3l**

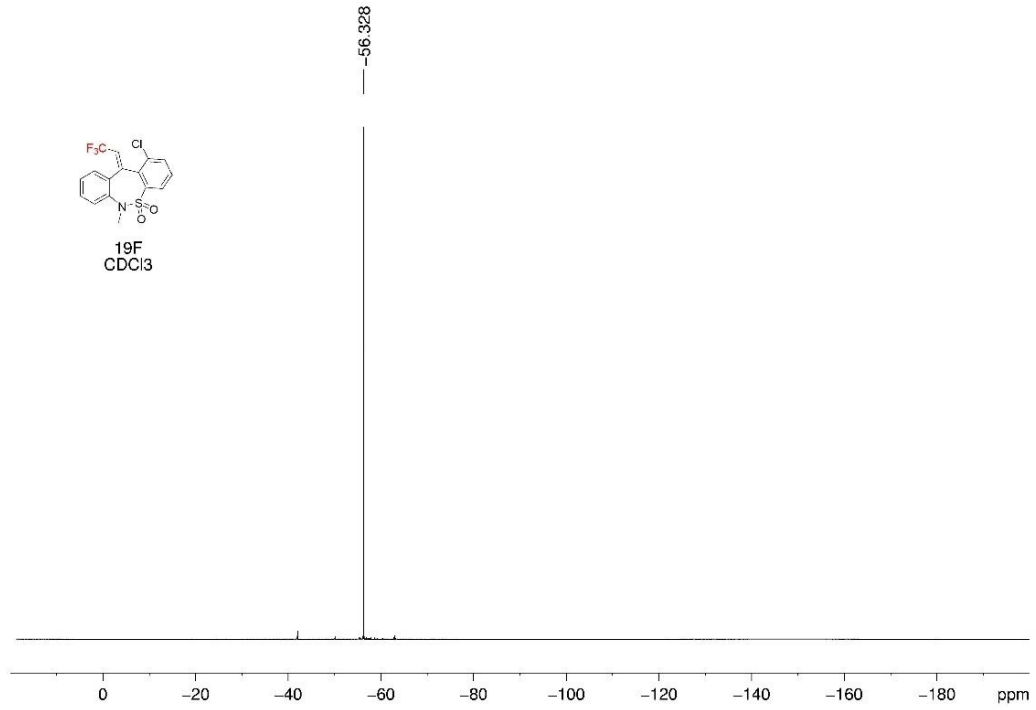


Figure S38. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3l**

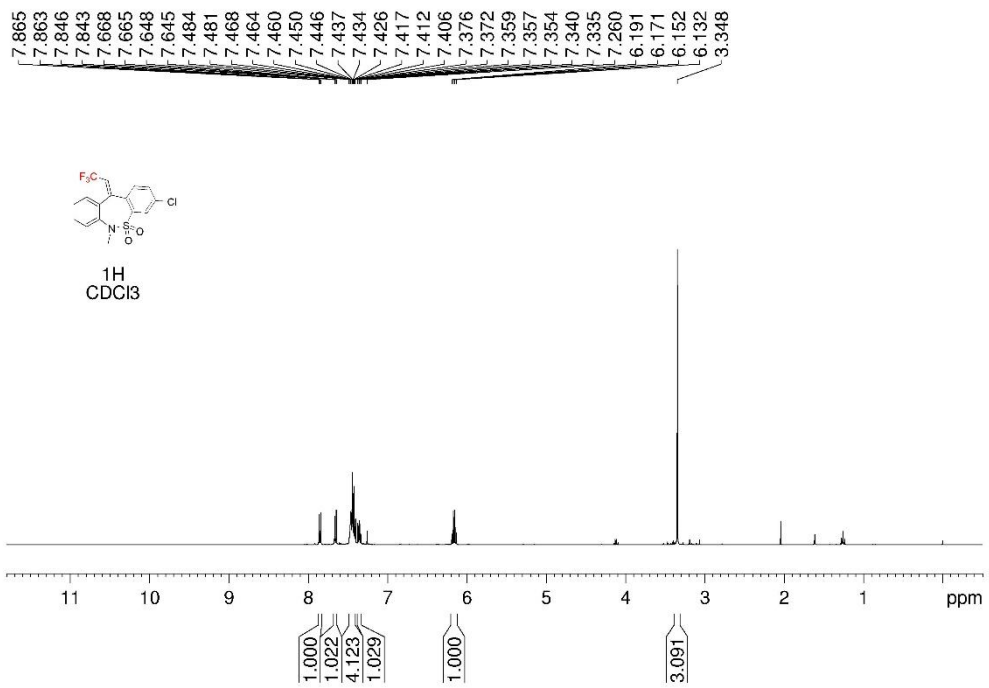


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3l'**

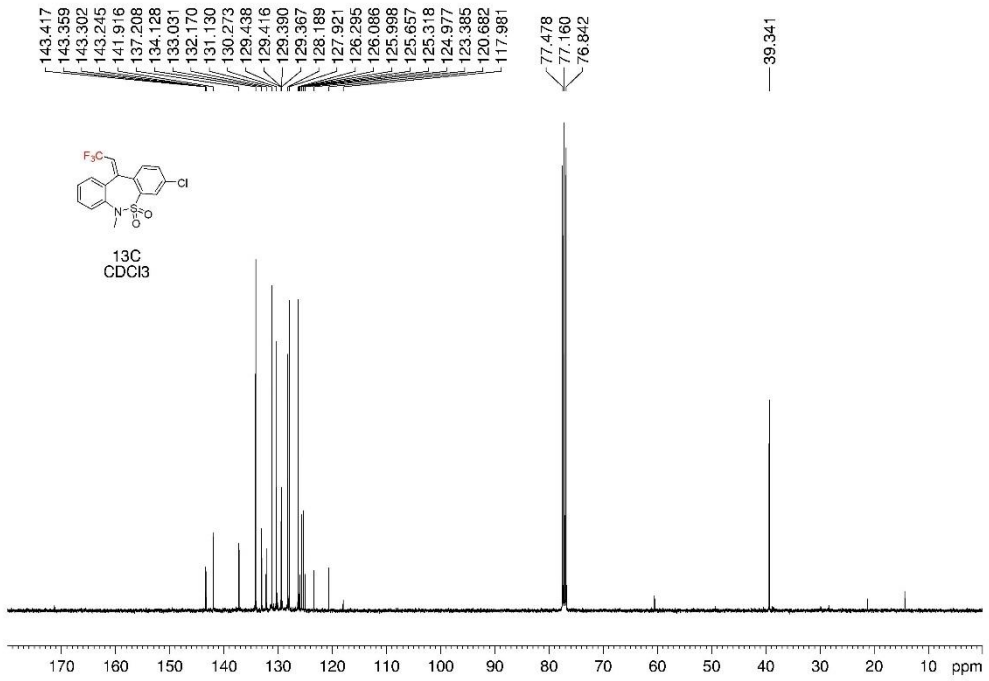


Figure S40. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3l'**

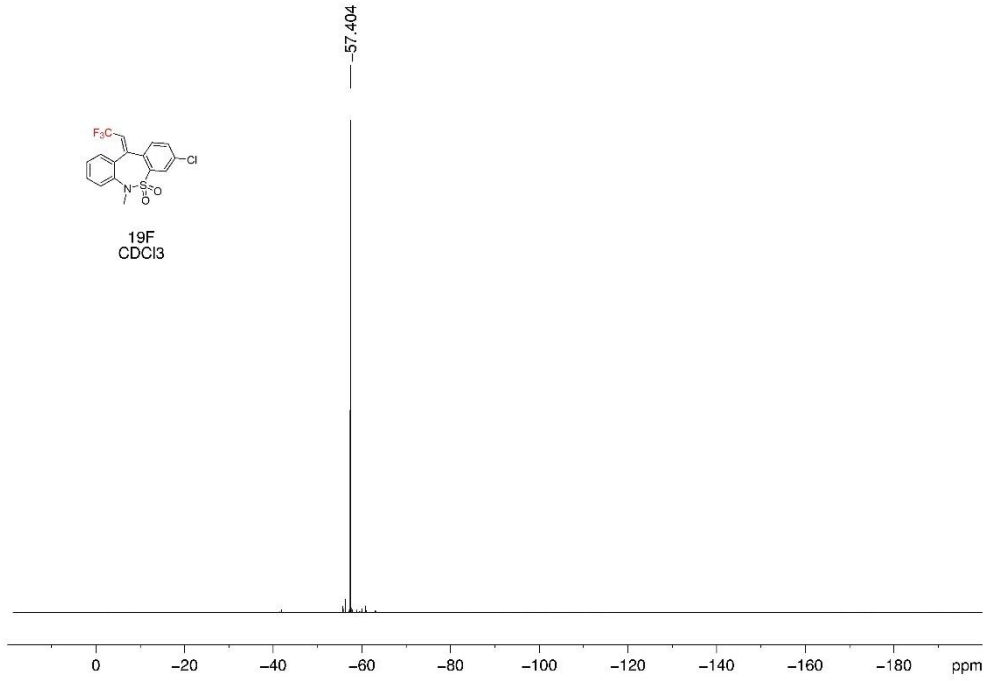


Figure S41. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3l'**

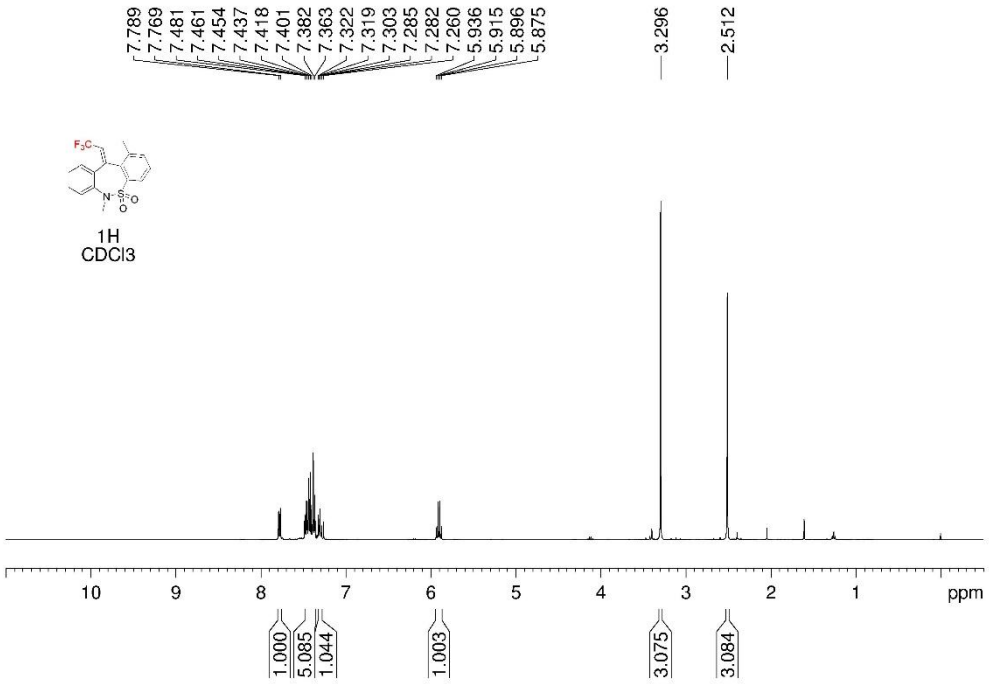


Figure S42. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3m**

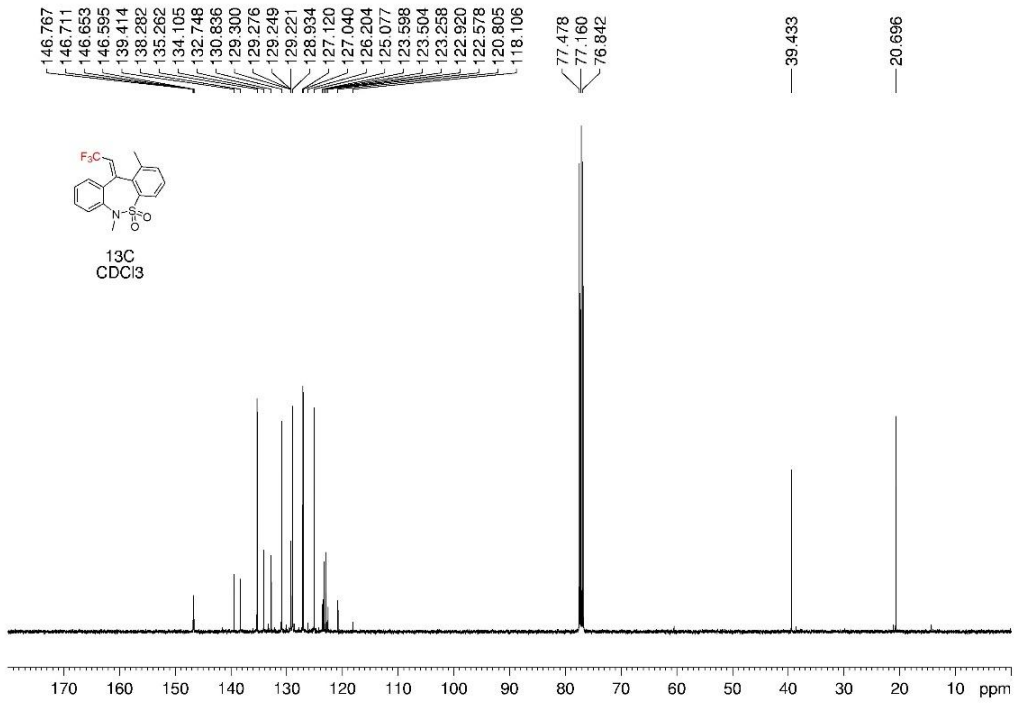


Figure S43. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3m**

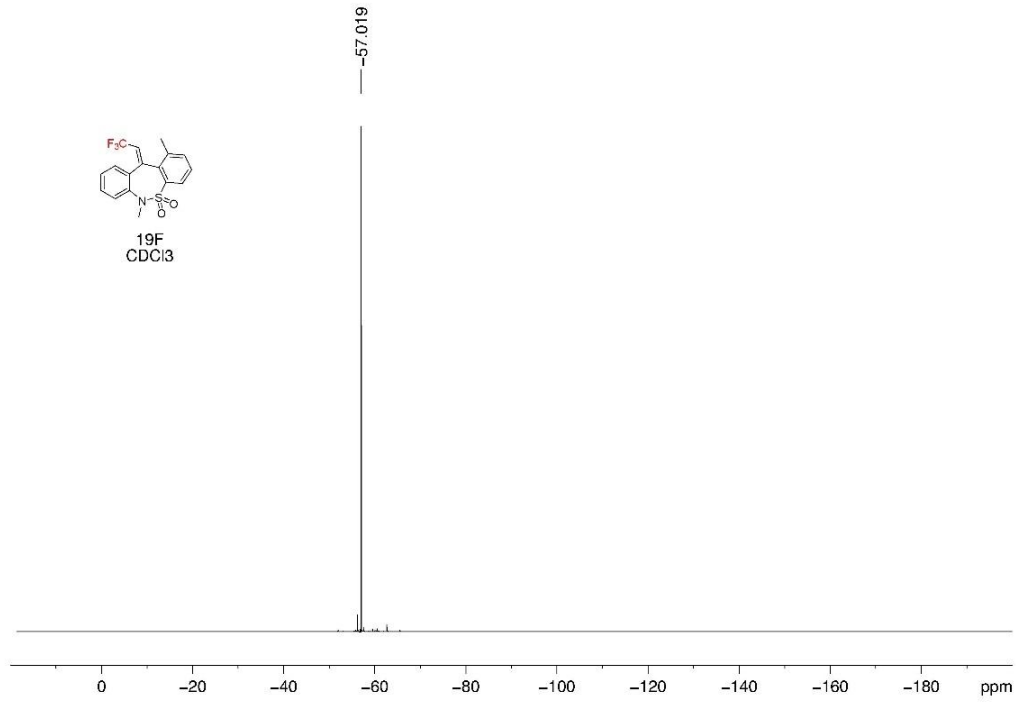


Figure S44. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3m**

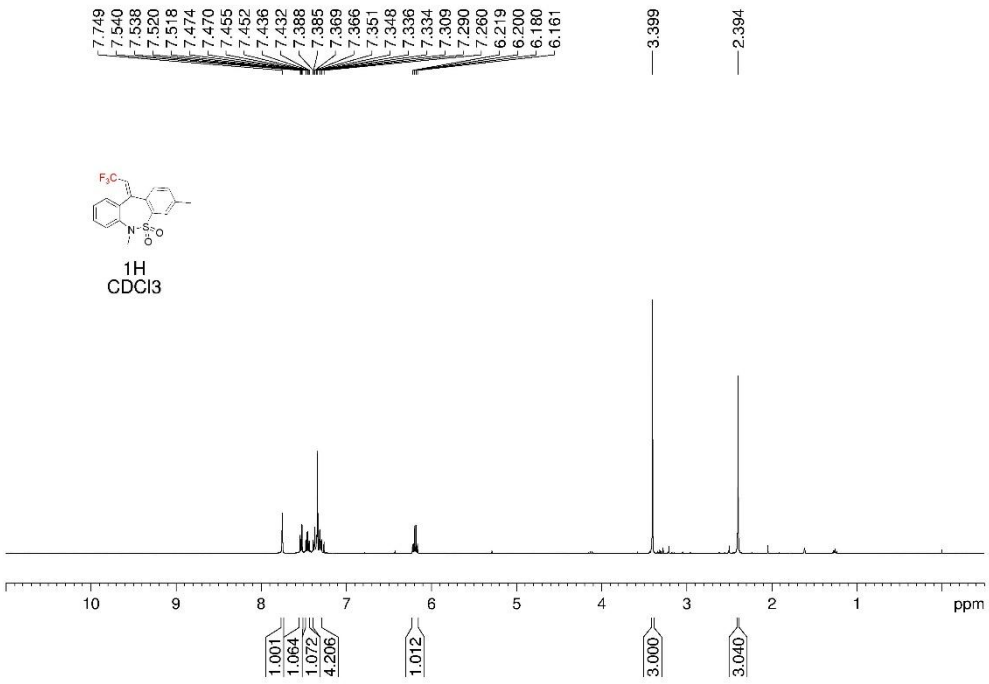


Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3m'**

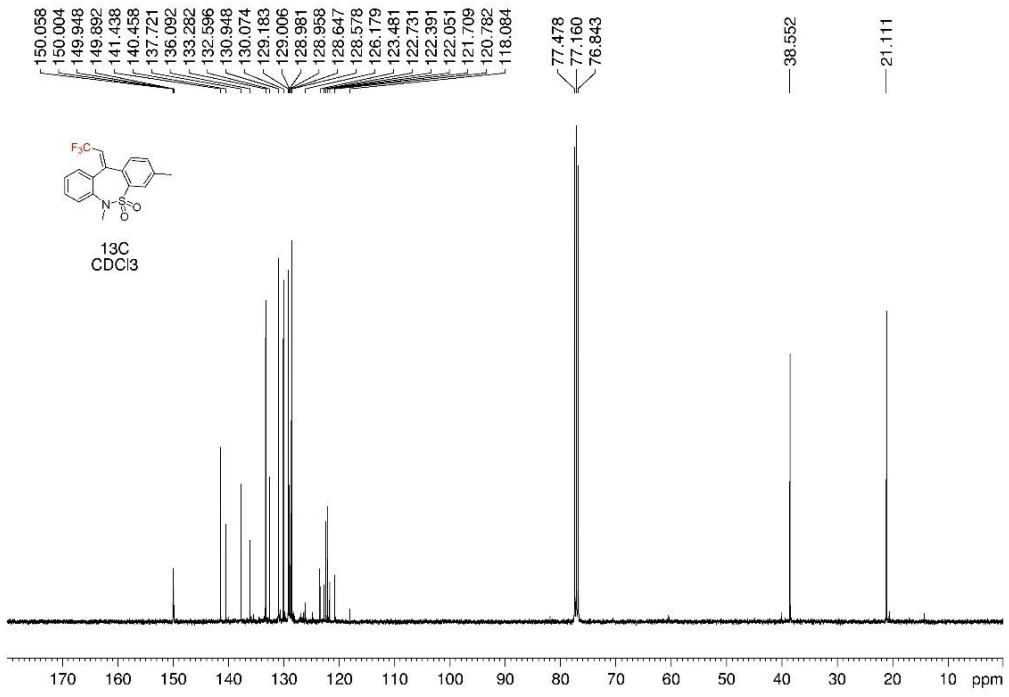


Figure S46. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3m'**

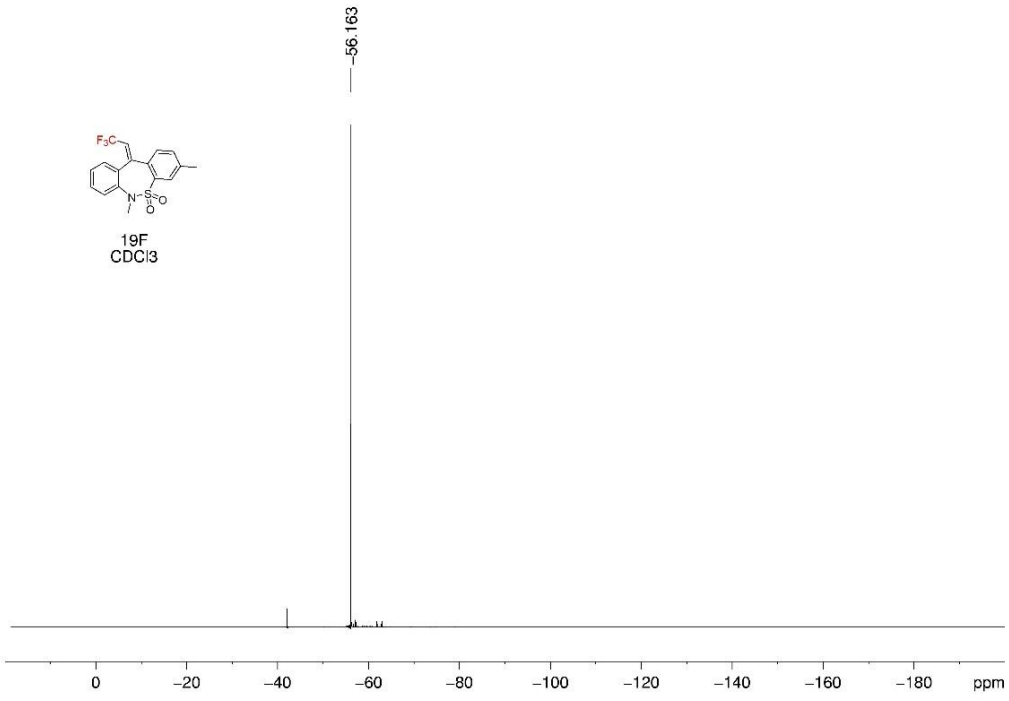


Figure S47. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3m'**

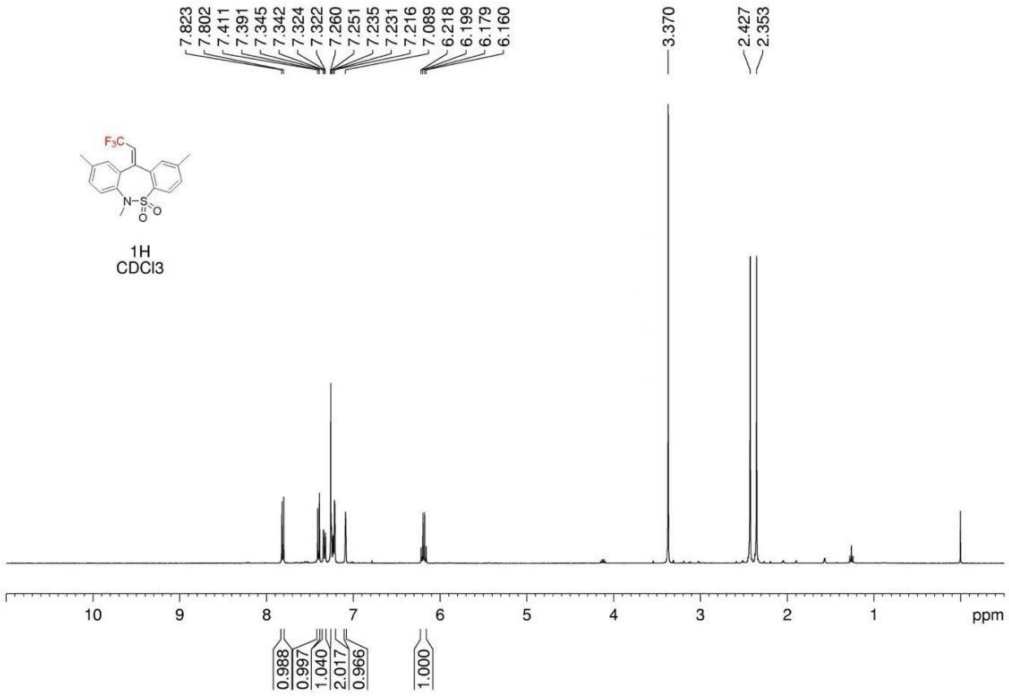


Figure S48. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3o**

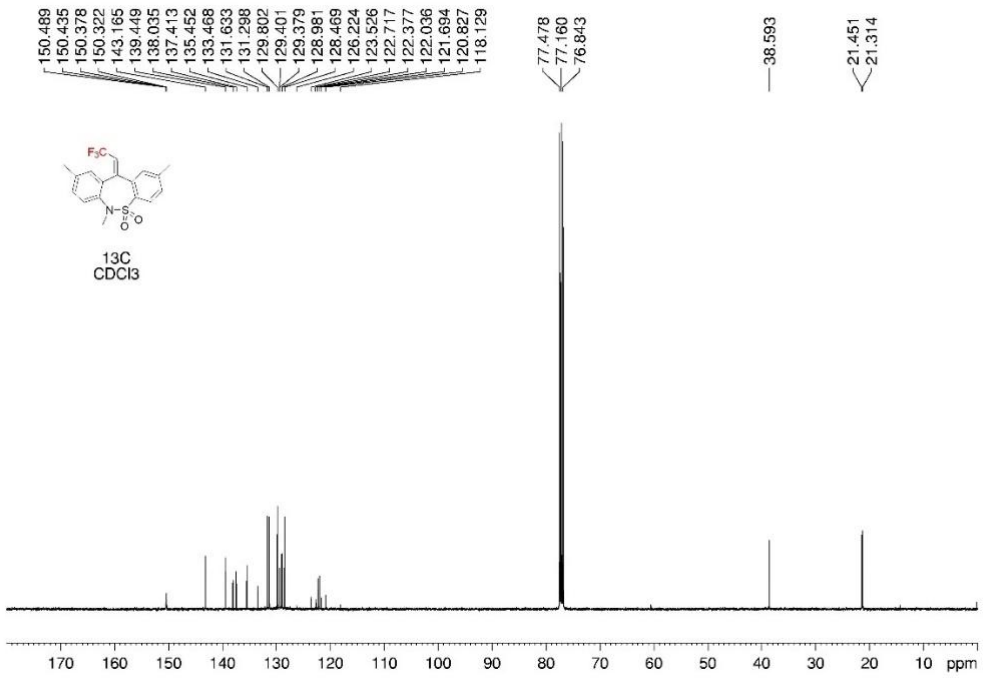


Figure S49. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3o**

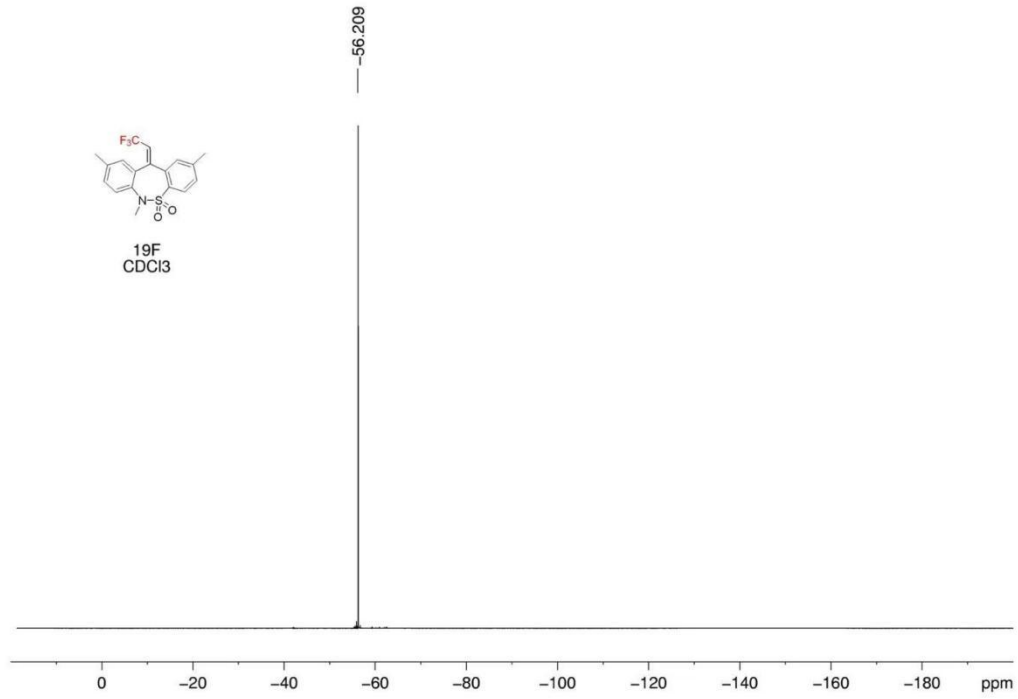


Figure S50. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3o**

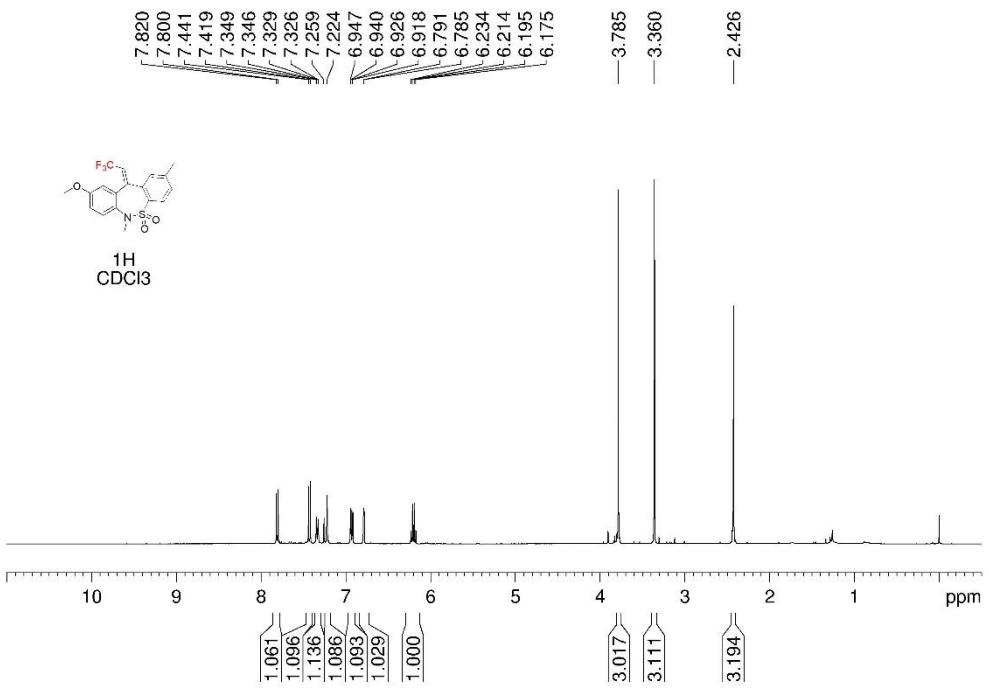


Figure S51. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3p**

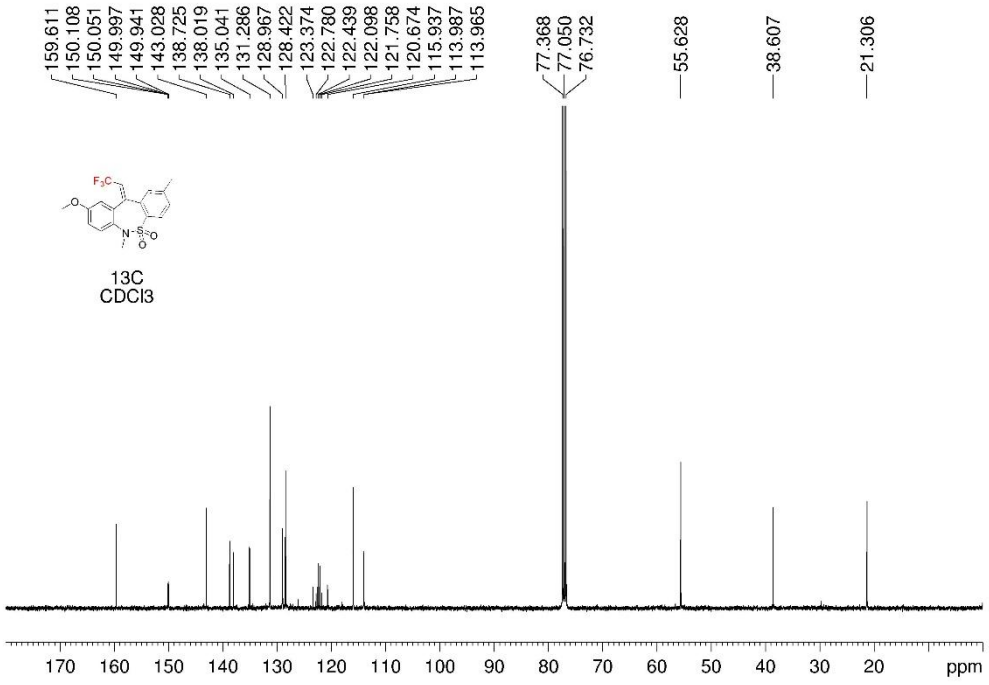


Figure S52. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3p**

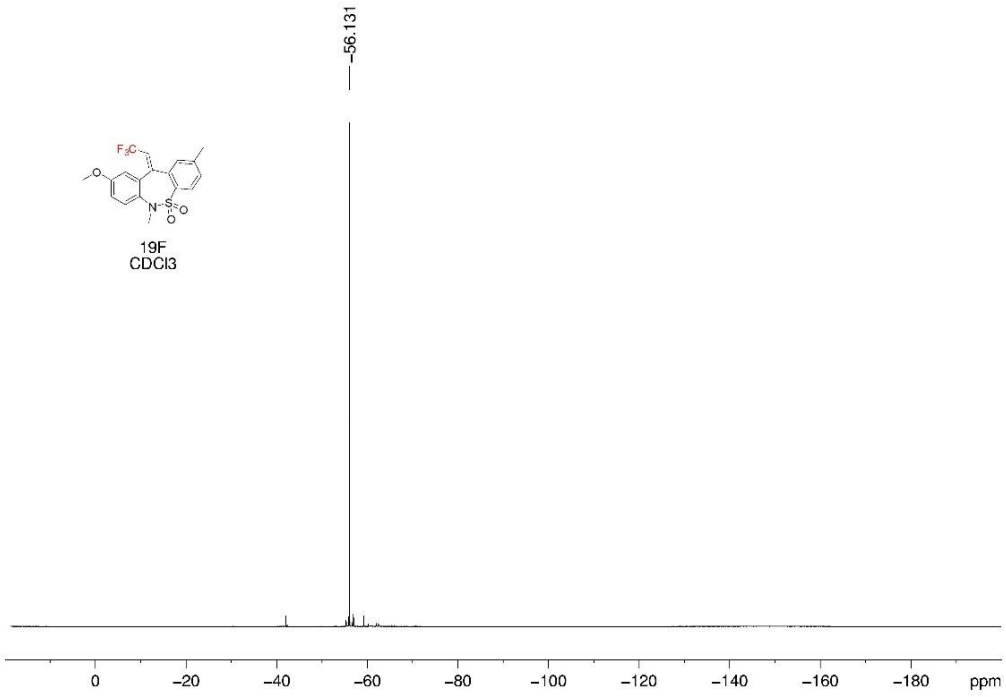


Figure S53. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3p**

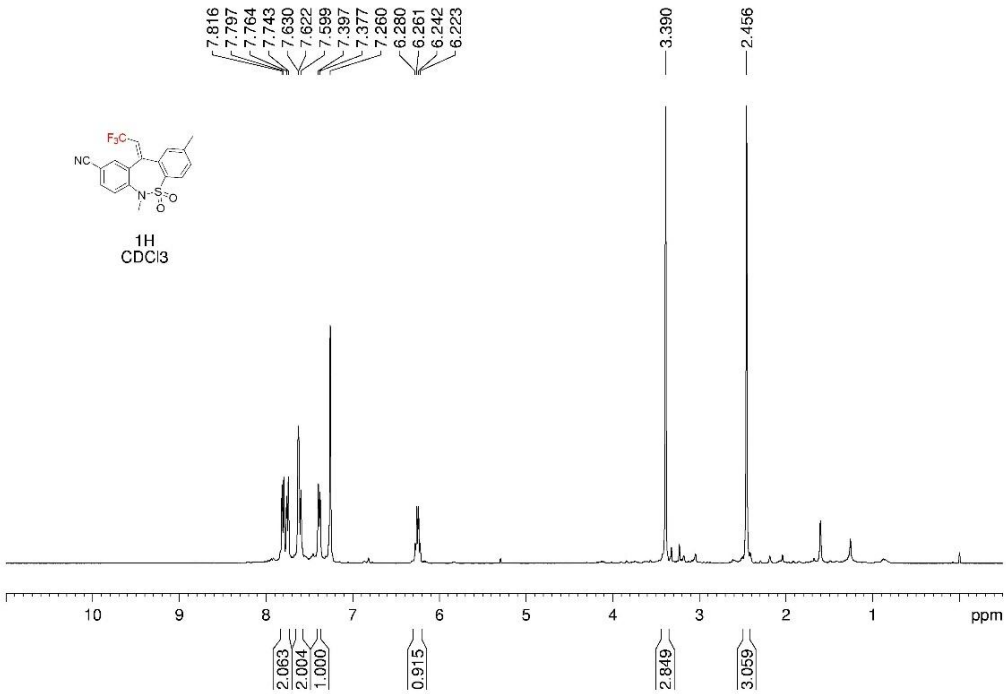


Figure S54. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3q**

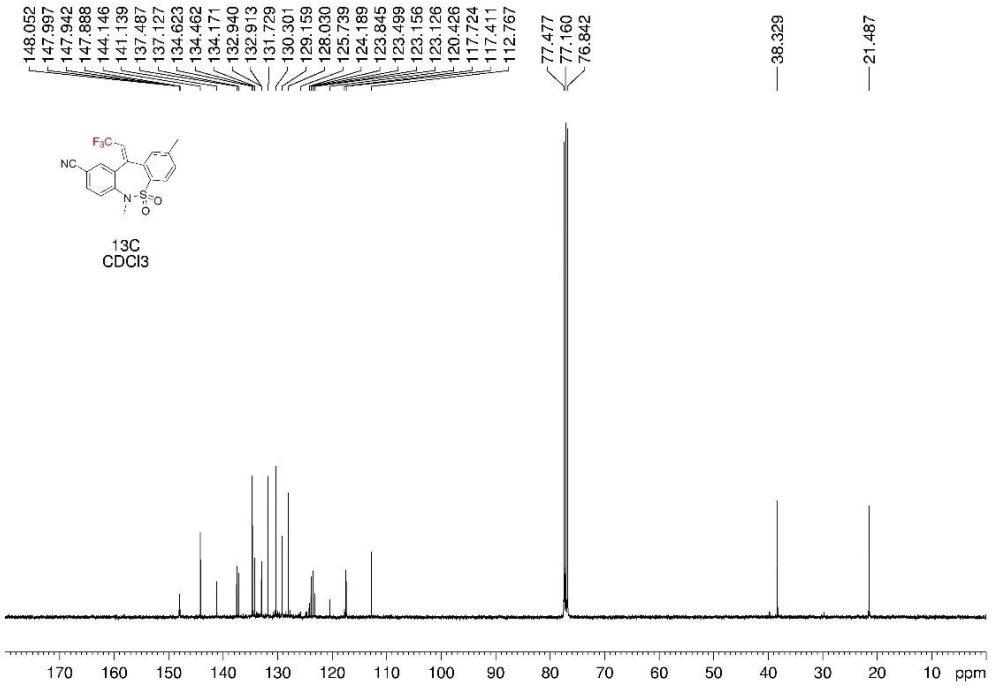


Figure S55. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3q**

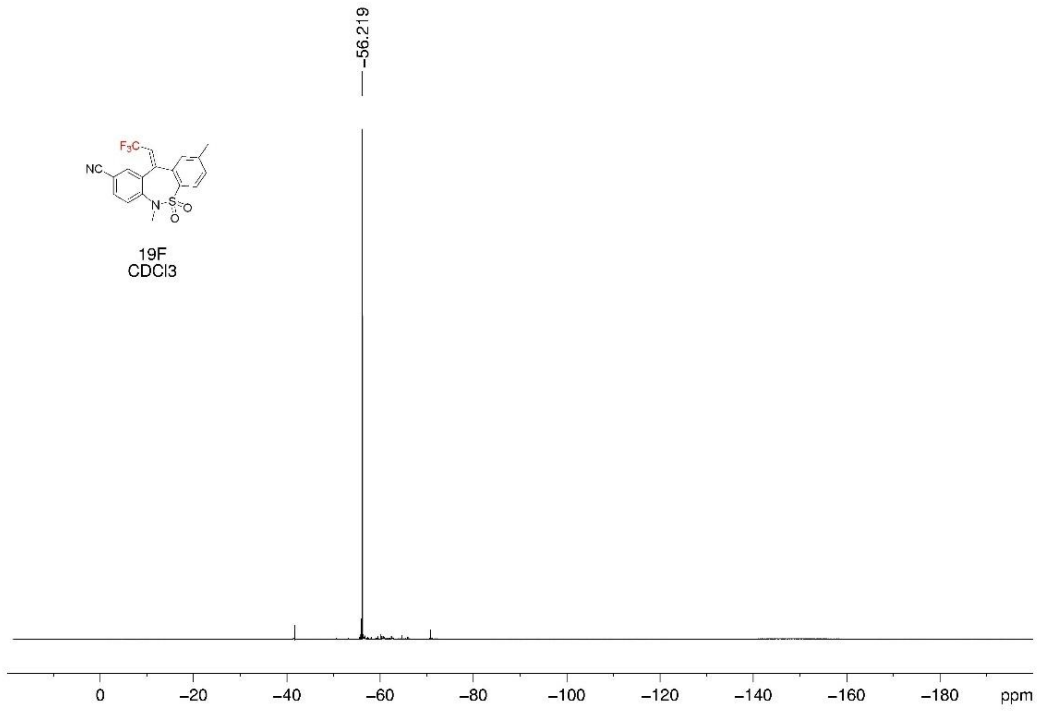


Figure S56. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3q**

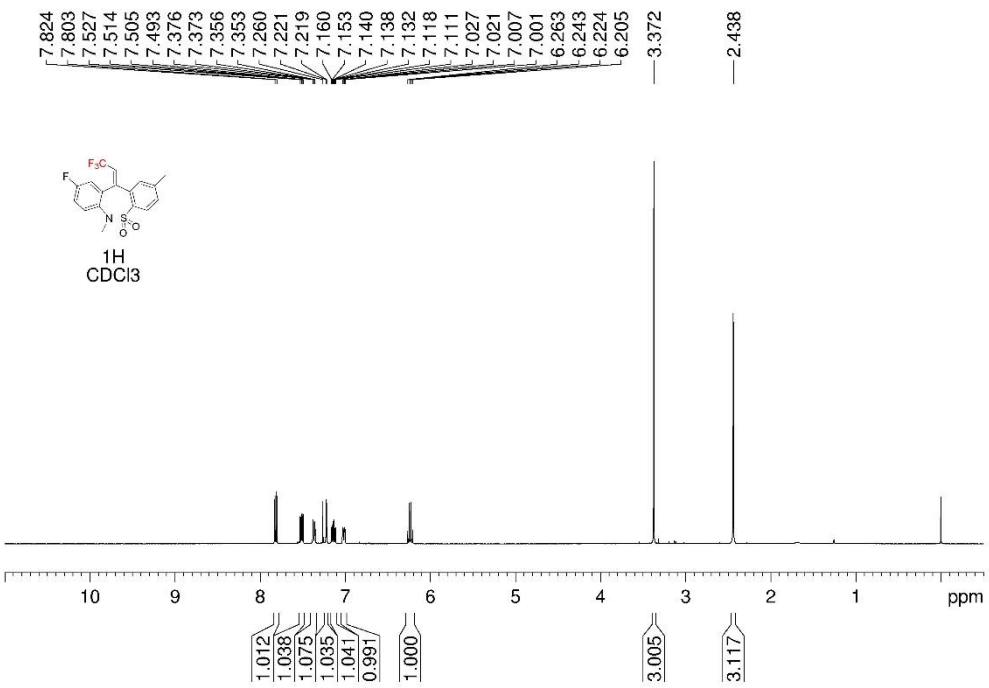


Figure S57. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3r**

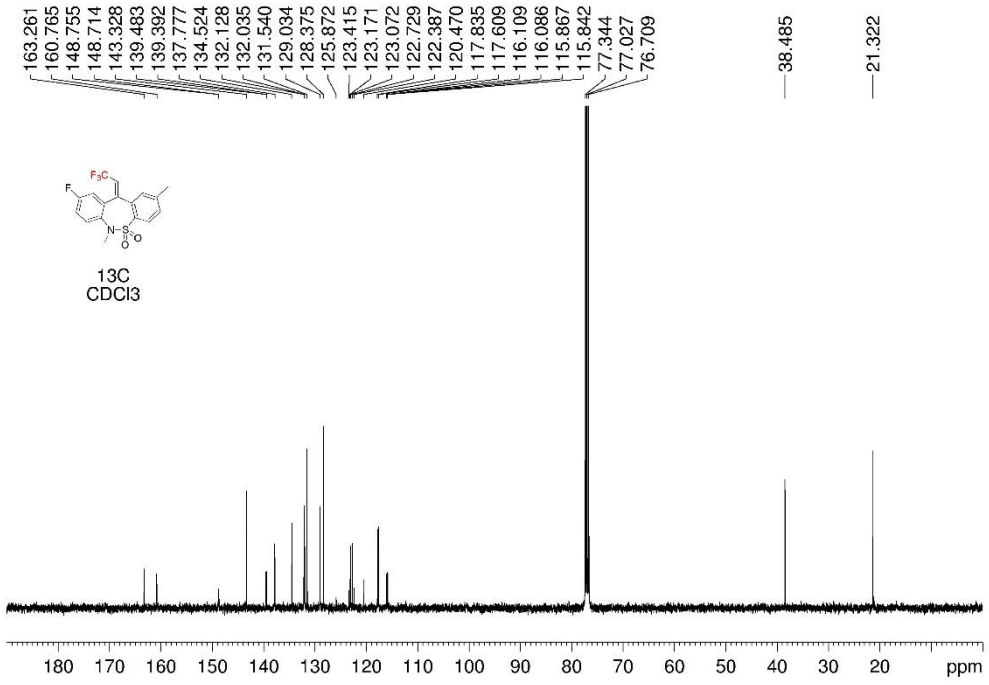


Figure S58. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3r**

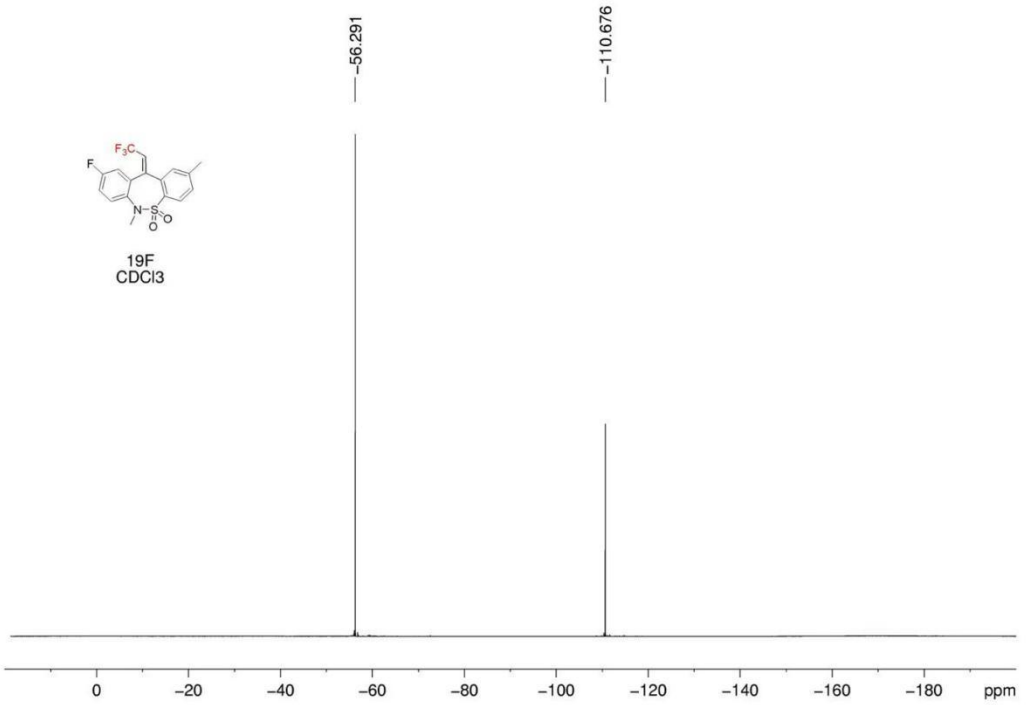


Figure S59. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3r**

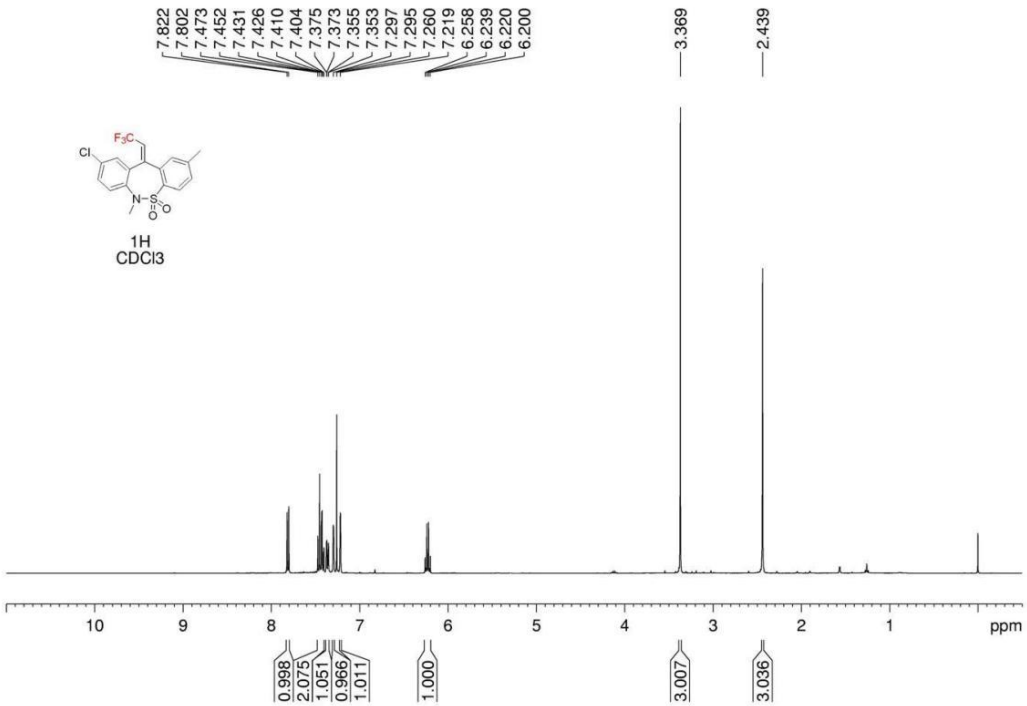


Figure S60. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3s**

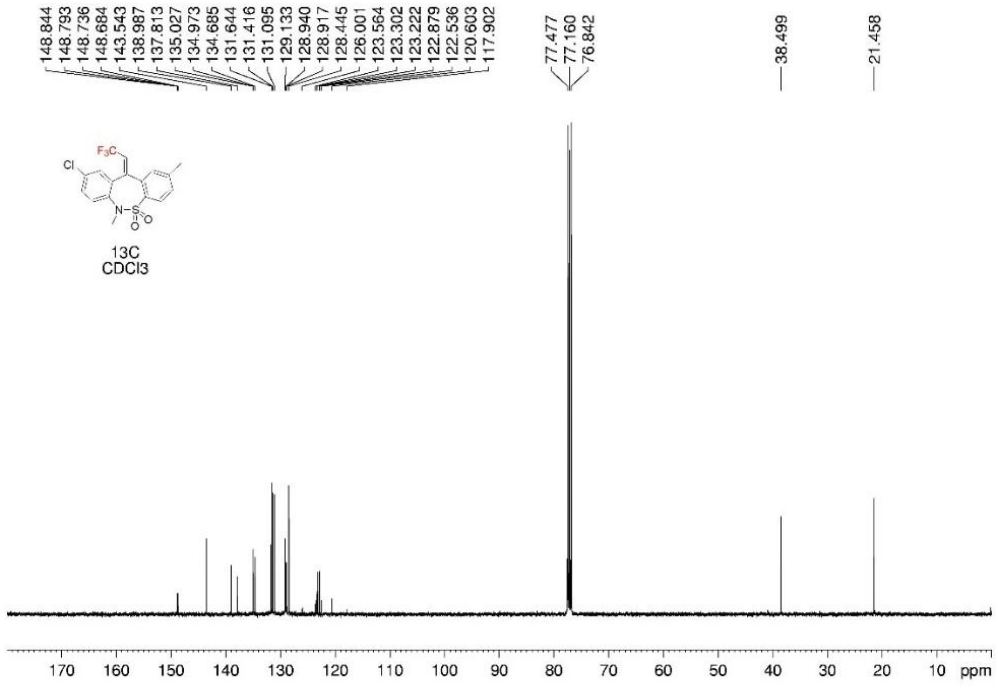


Figure S61. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3s**

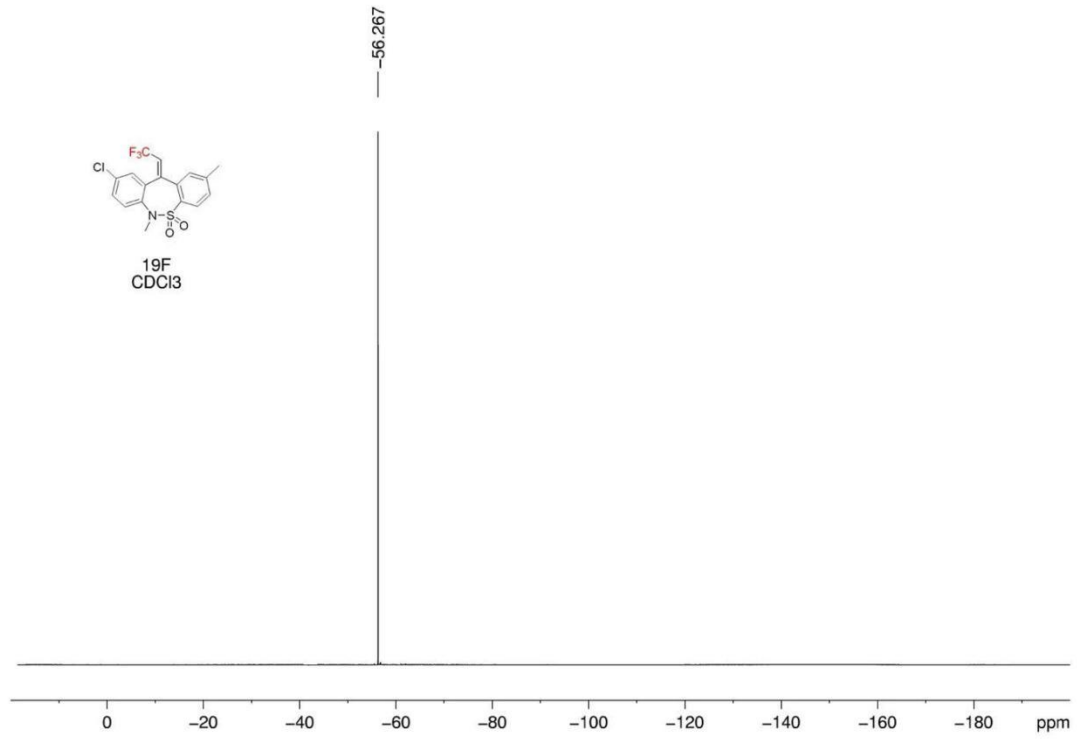


Figure S62. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3s**

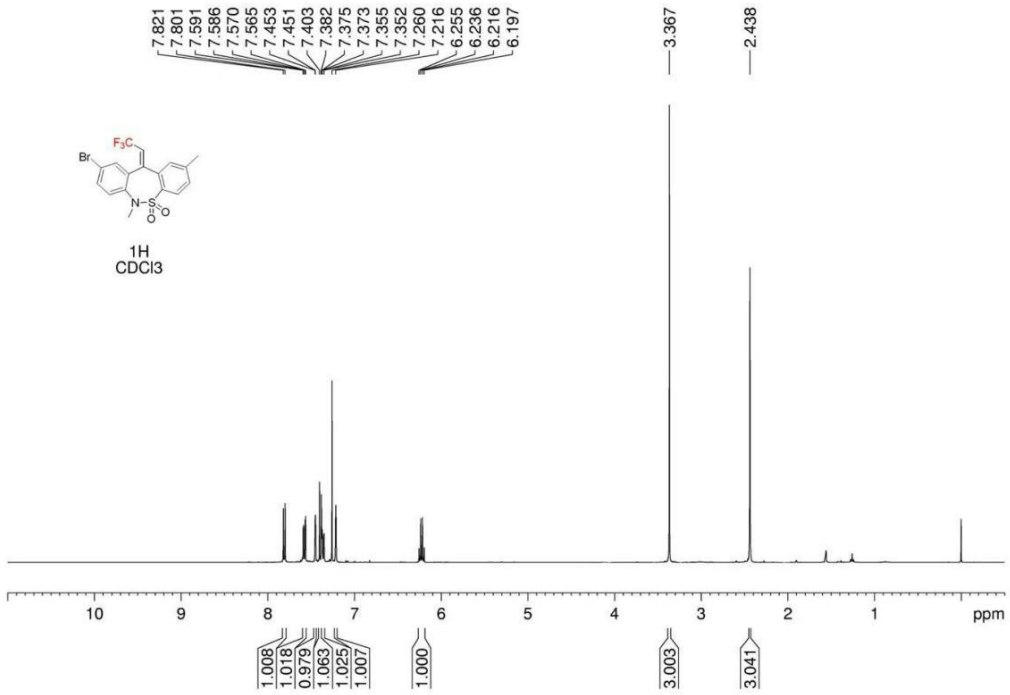


Figure S63. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3t**

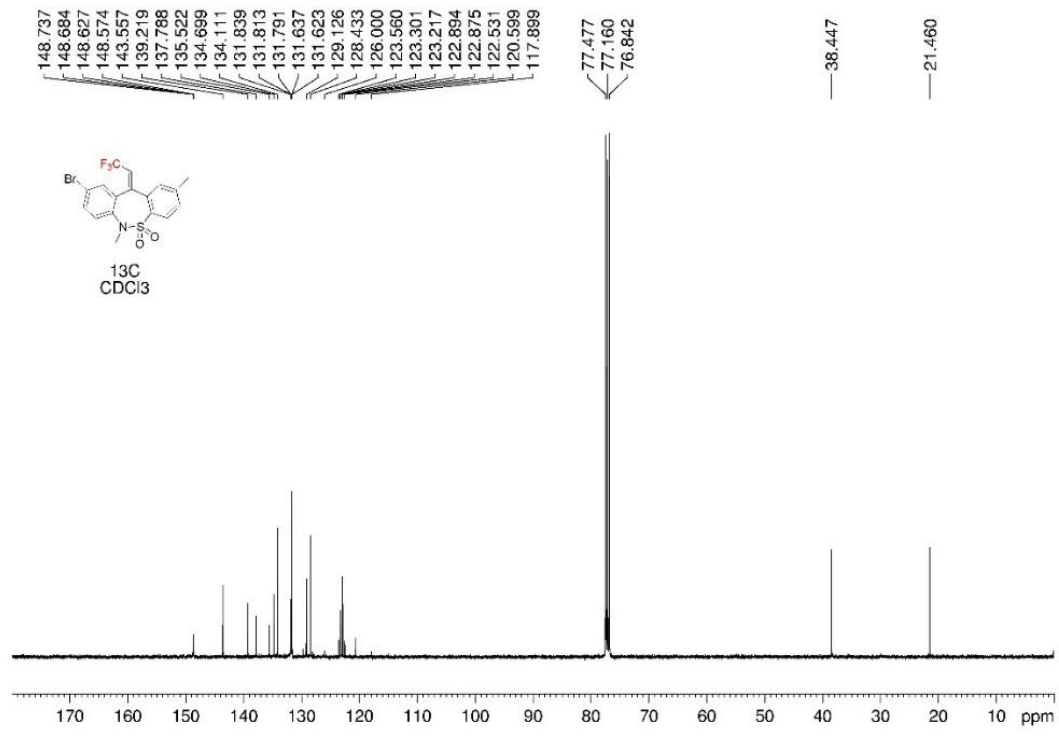


Figure S64. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3t**

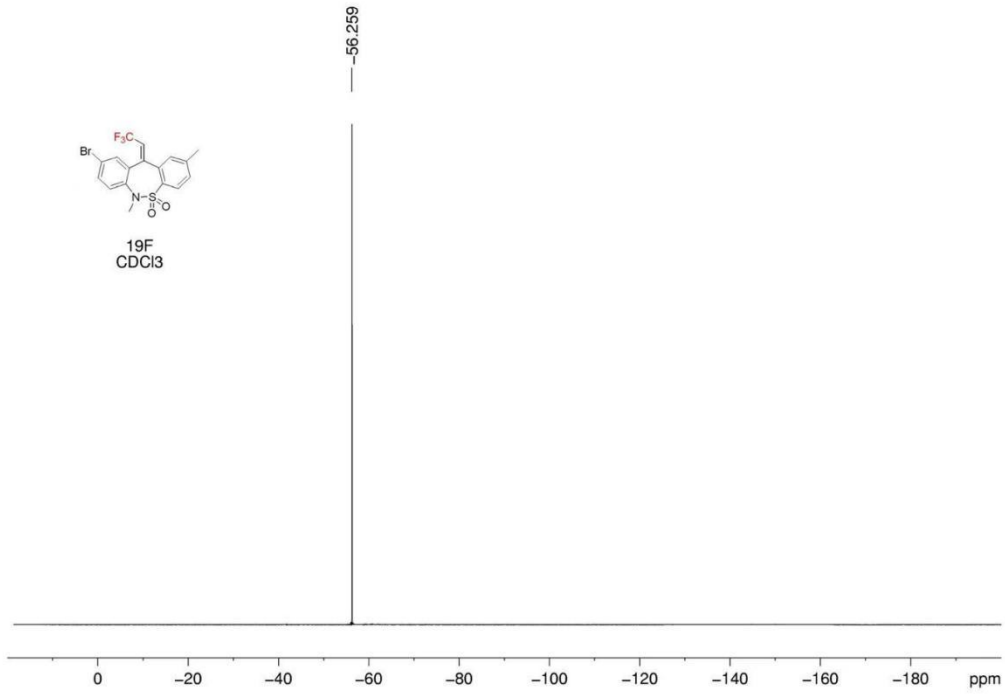


Figure S65. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3t**

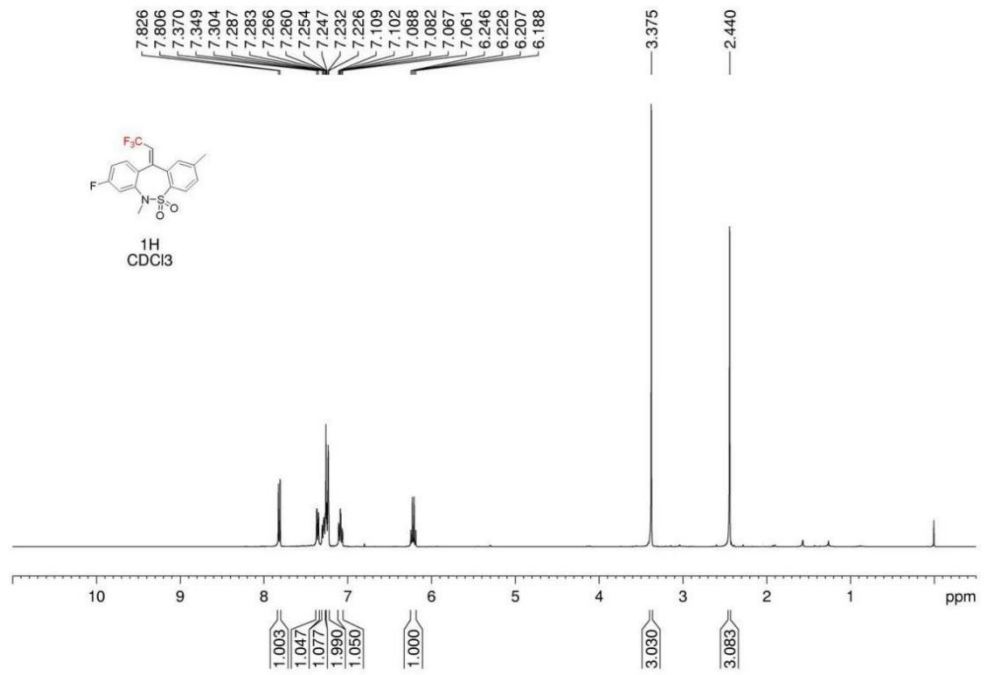


Figure S66. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3u**

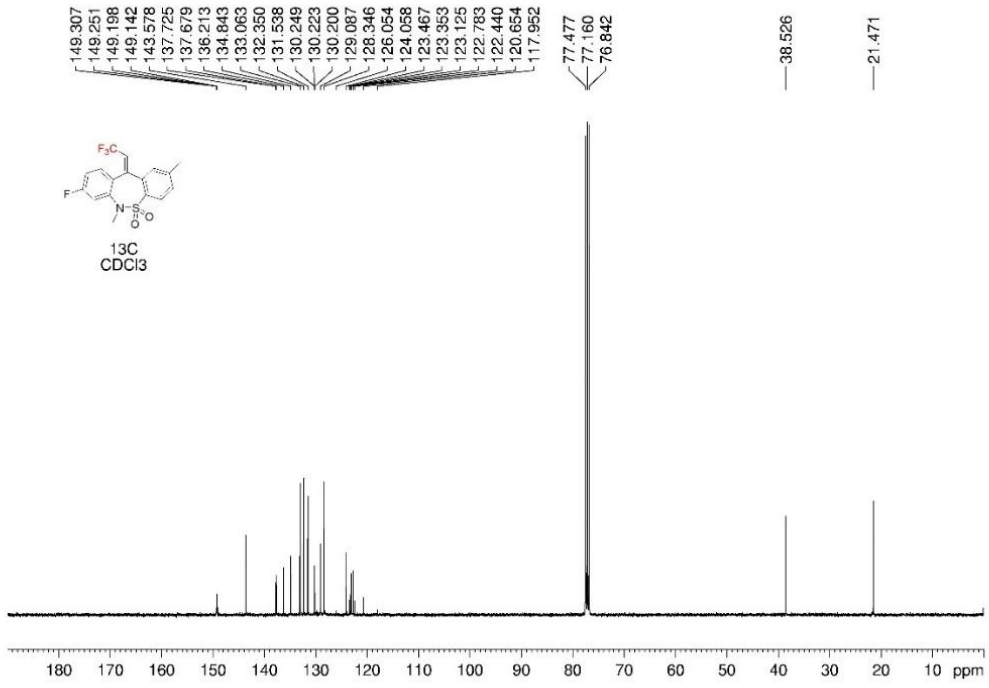


Figure S67. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3u**

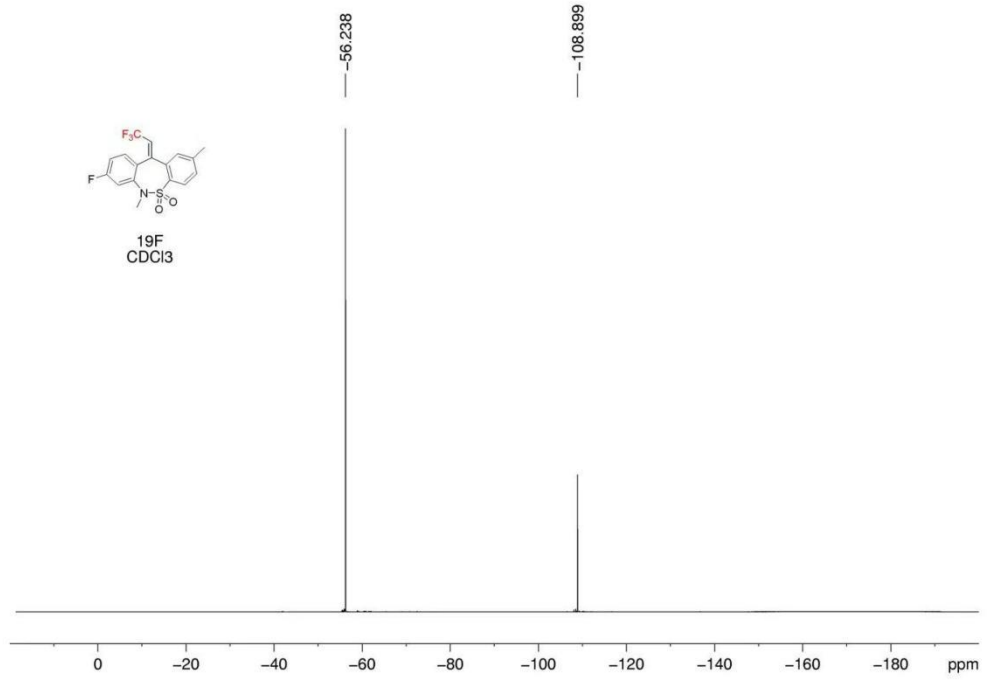


Figure S68. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3u**

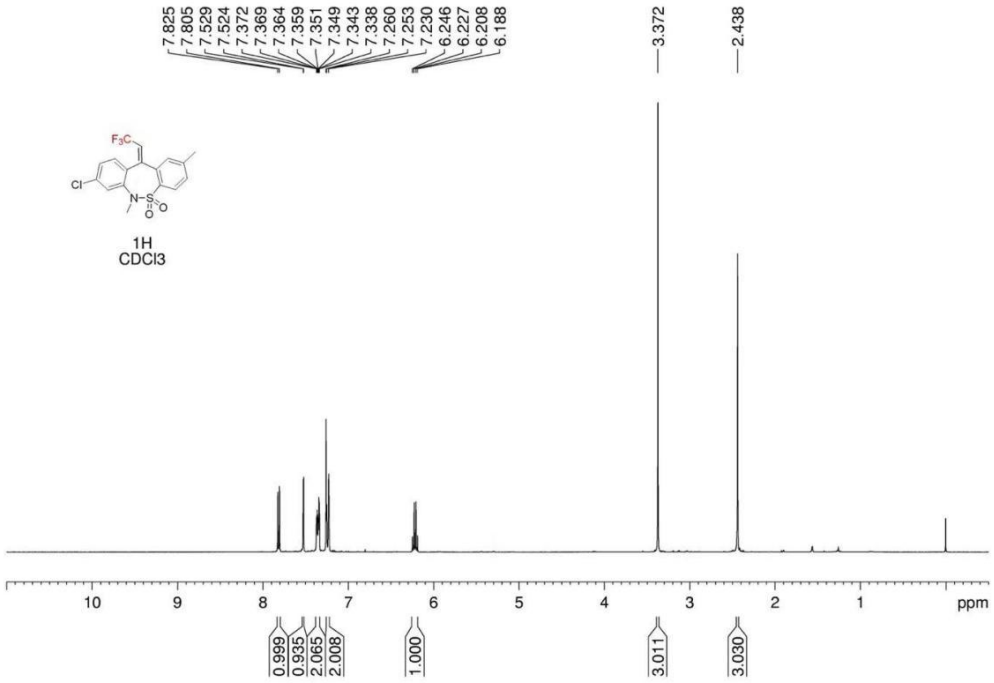


Figure S69. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3v**

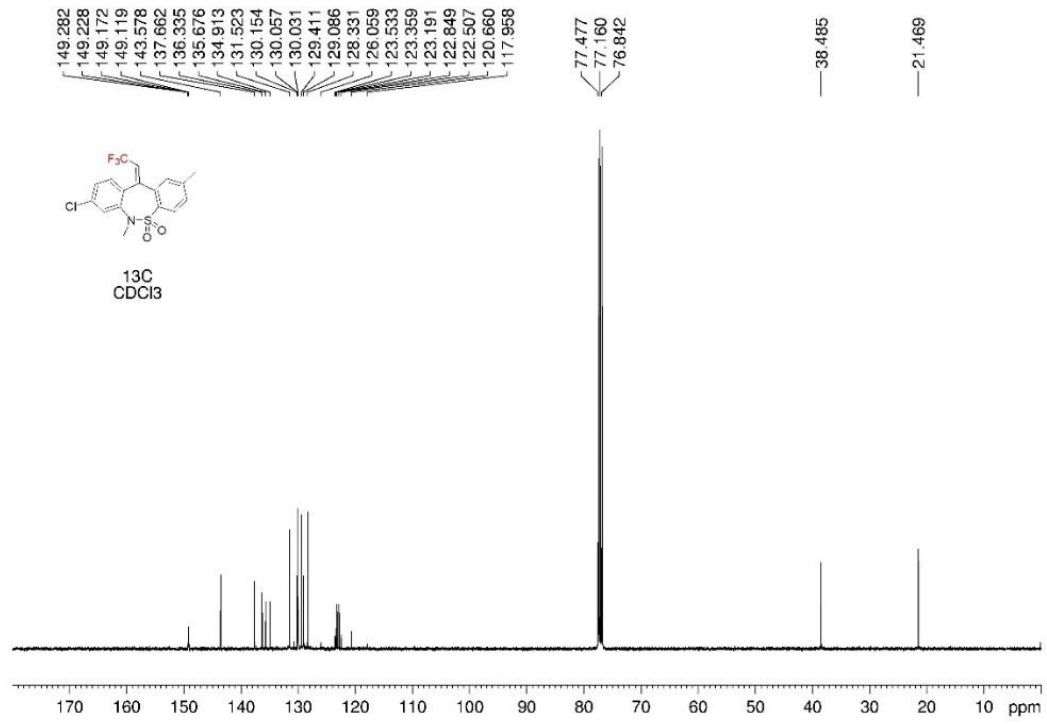


Figure S70. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3v**

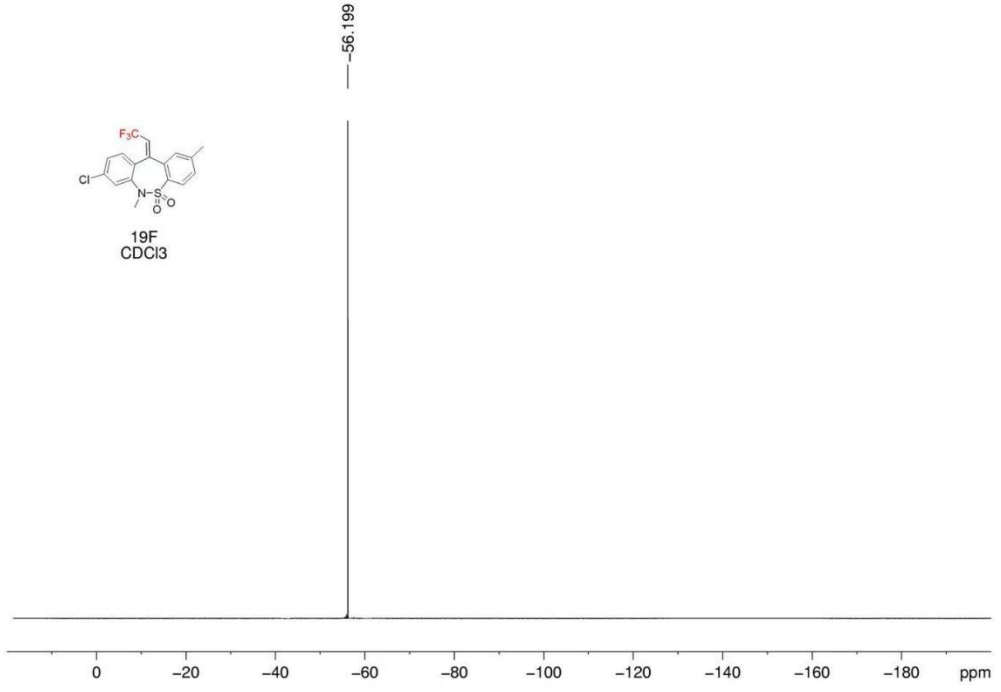


Figure S71. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3v**

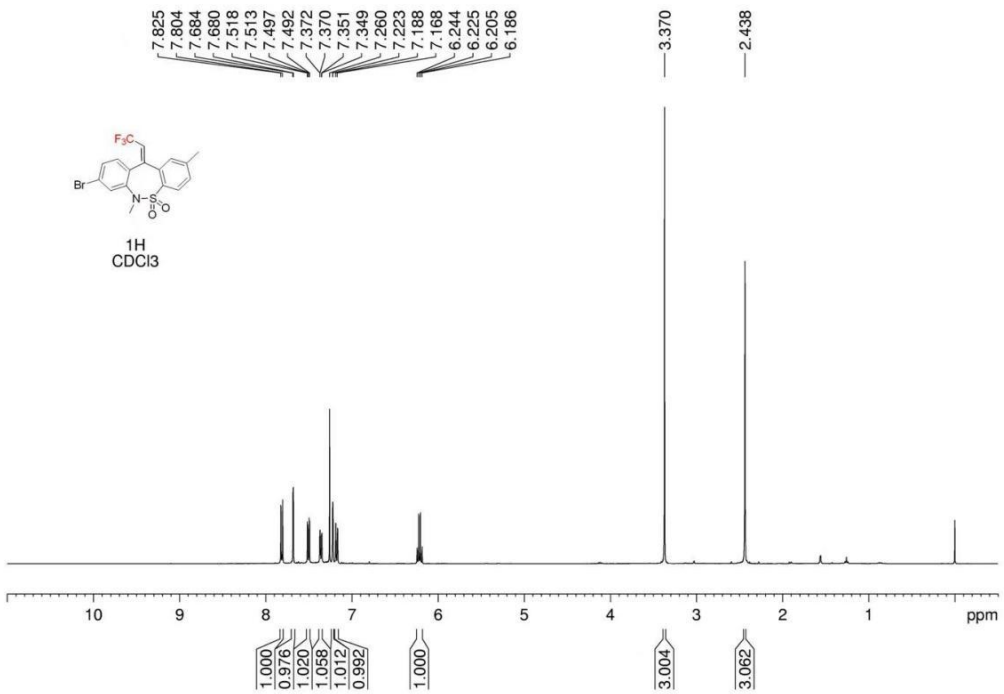


Figure S72. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3w**

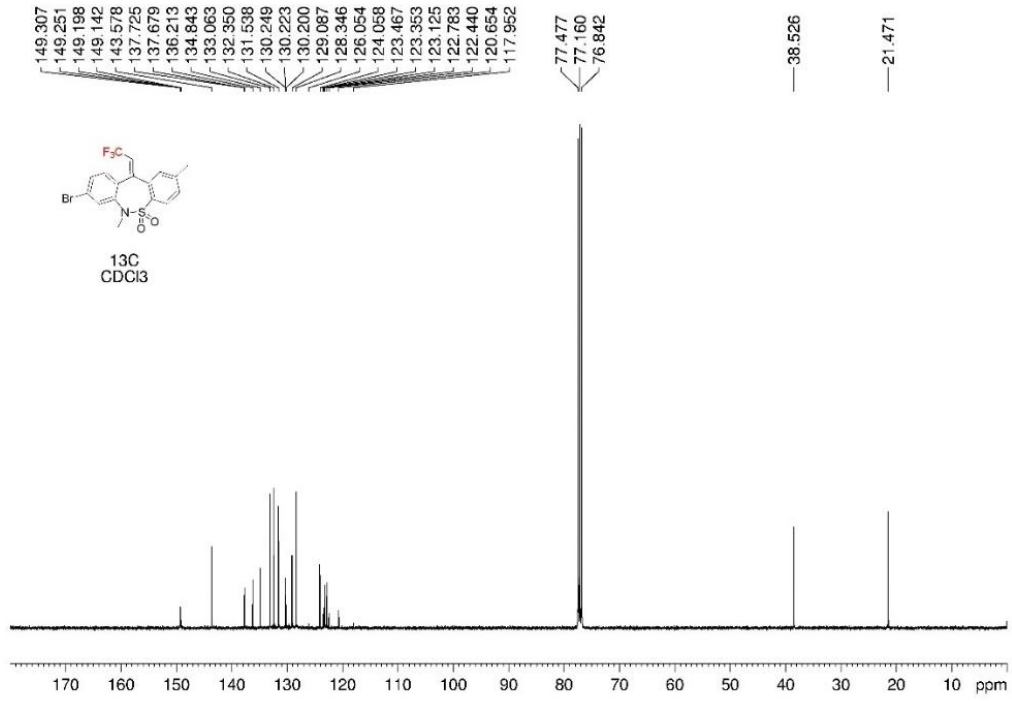


Figure S73. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3w**

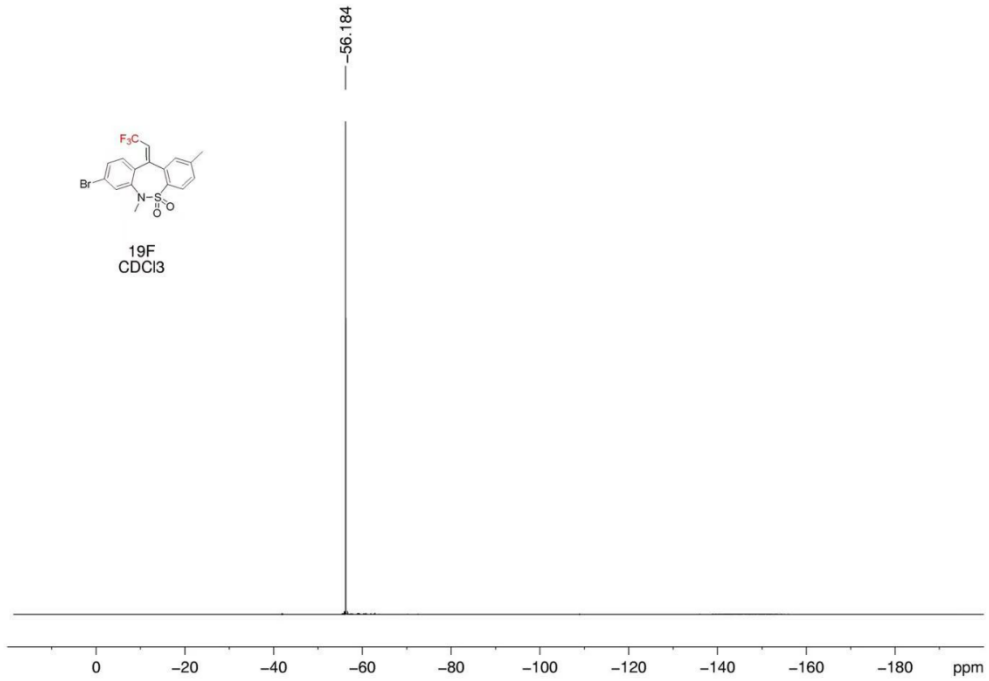


Figure S74. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3w**

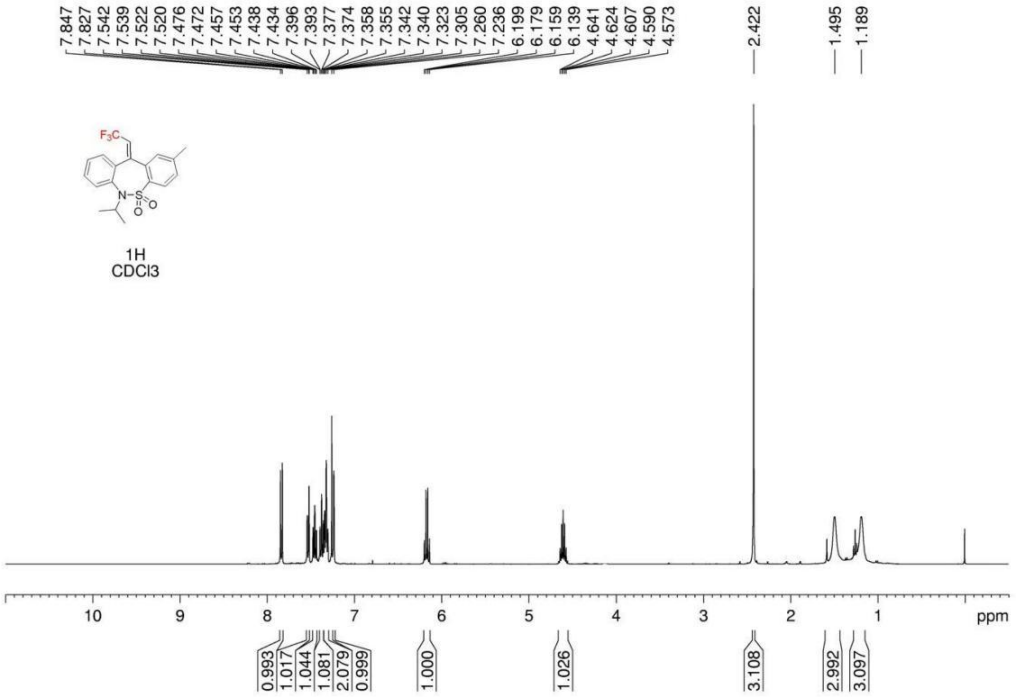


Figure S75. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3x**

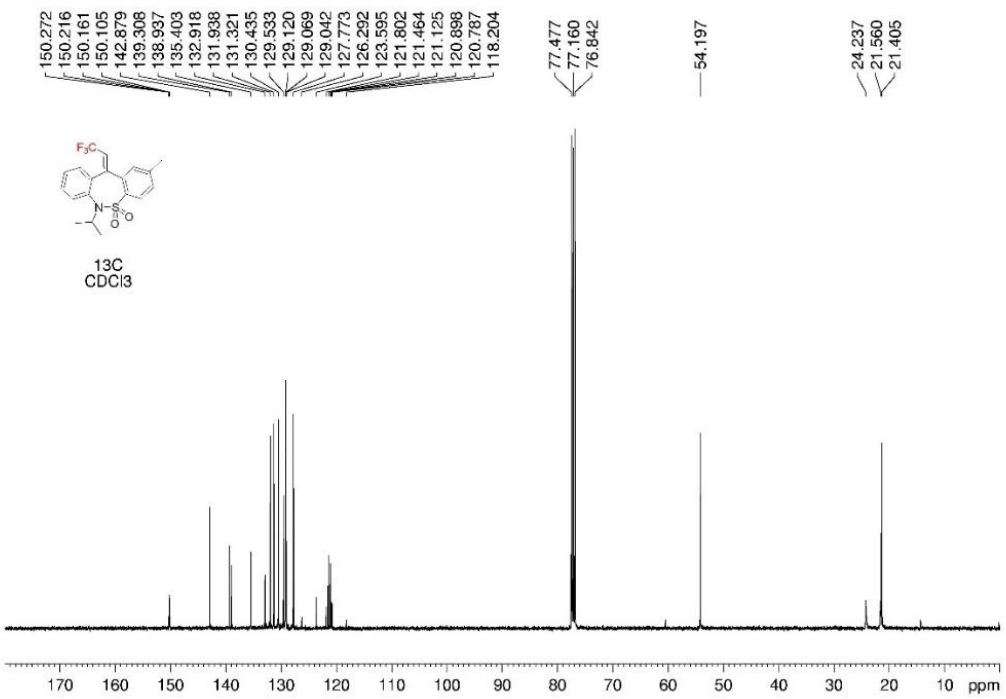


Figure S76. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3x**

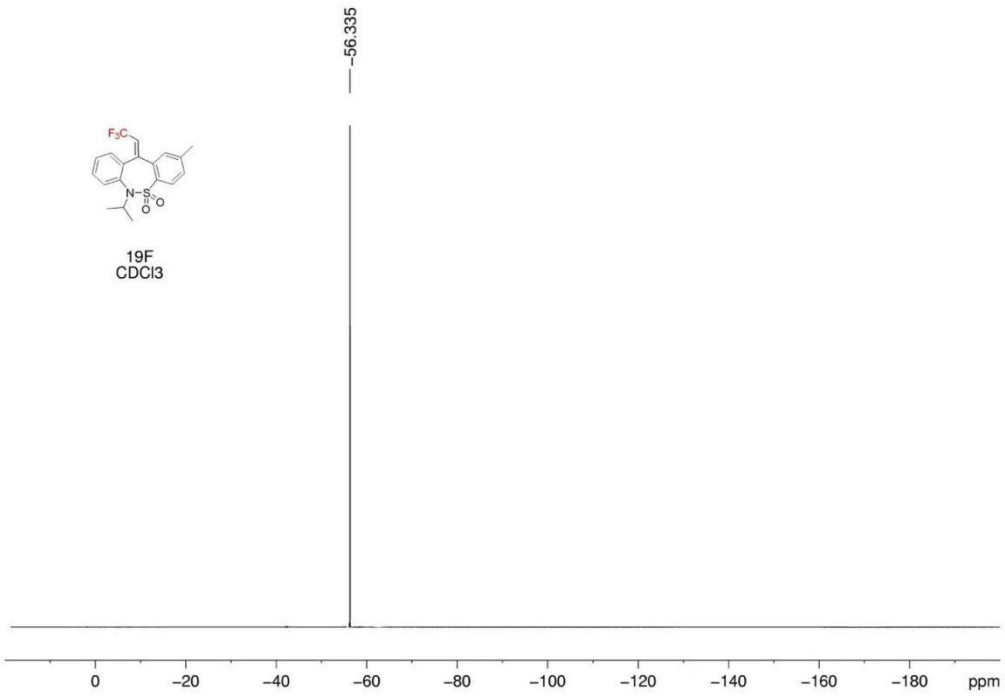


Figure S77. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3x**

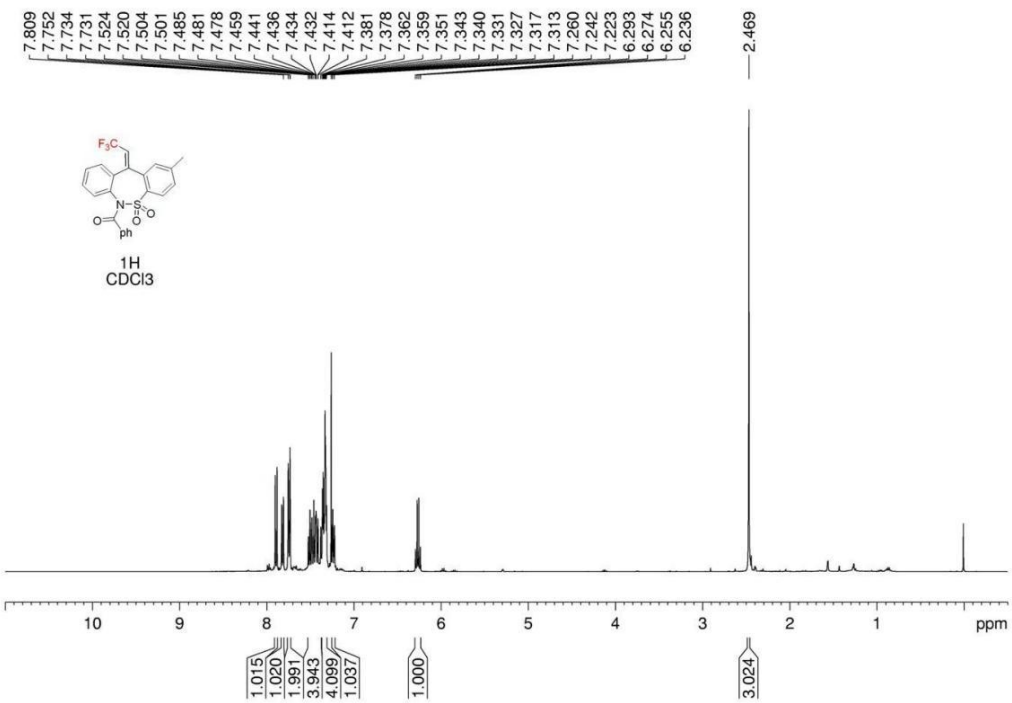


Figure S78. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3y**

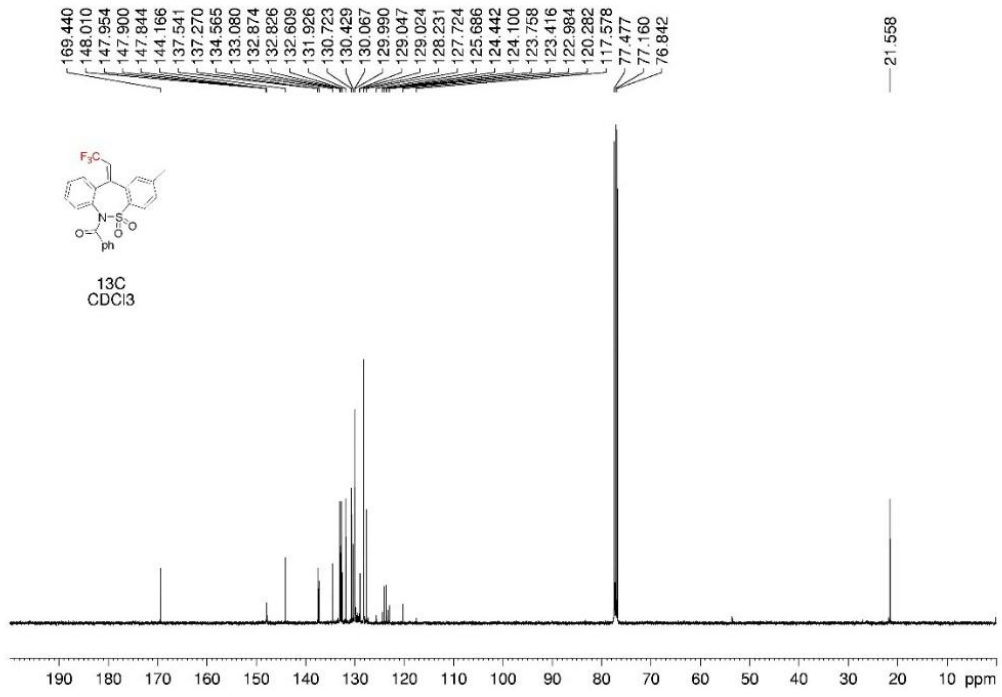


Figure S79. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3y**

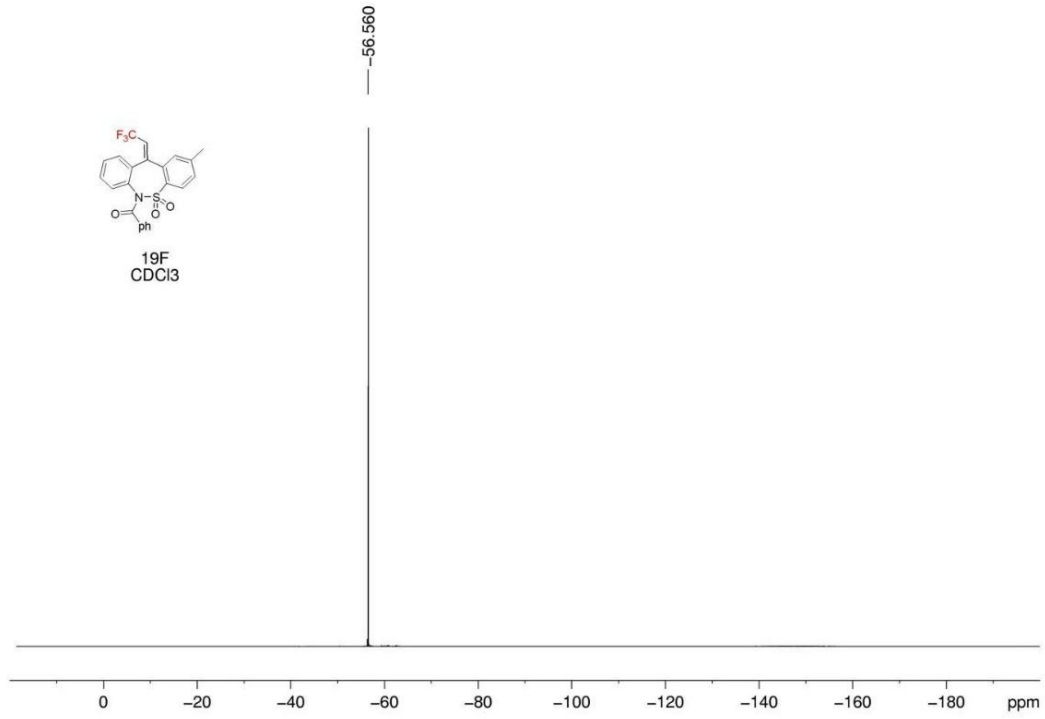


Figure S80. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3y**

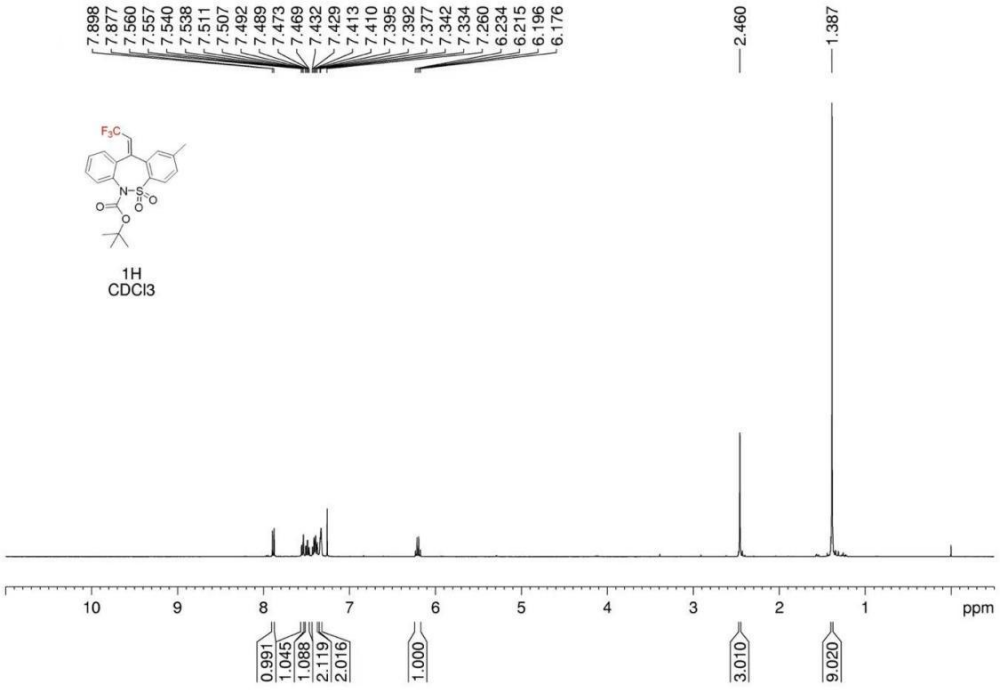


Figure S81. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3z**

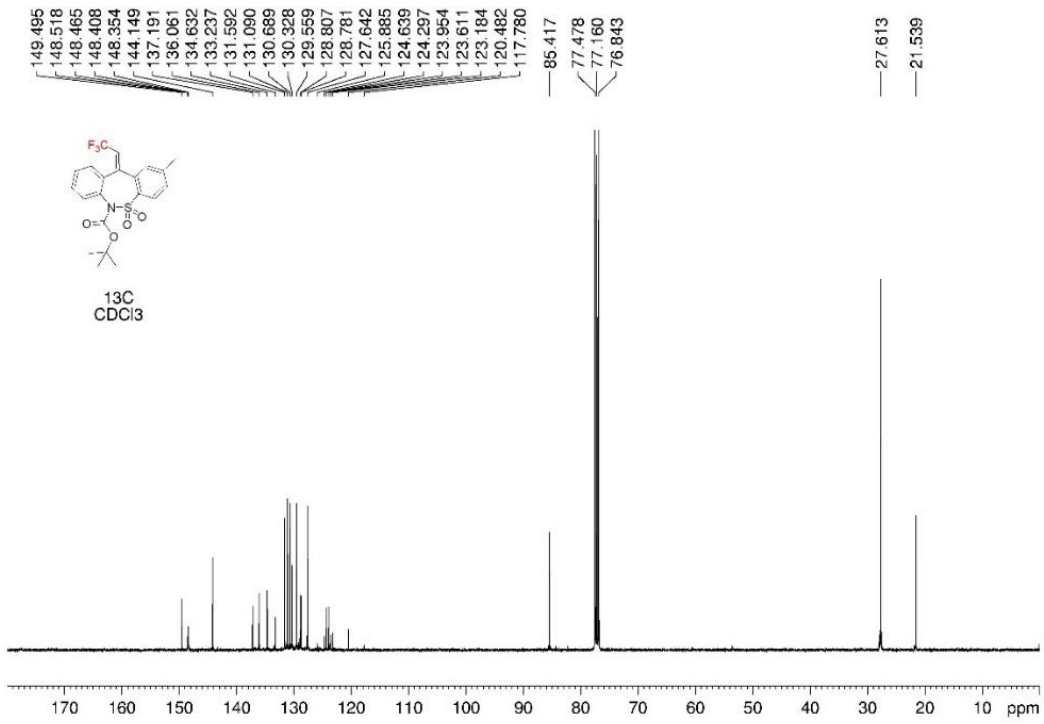


Figure S82. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3z**

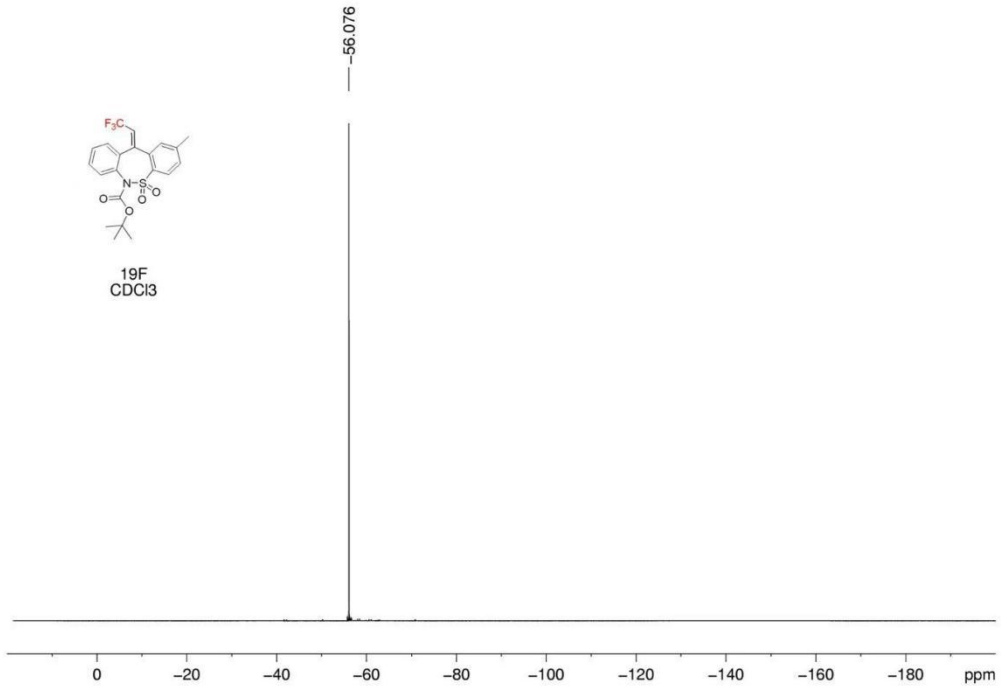


Figure S83. ^{19}F NMR (376 MHz, $CDCl_3$) of compound **3z**