Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


*Supporting Information of*

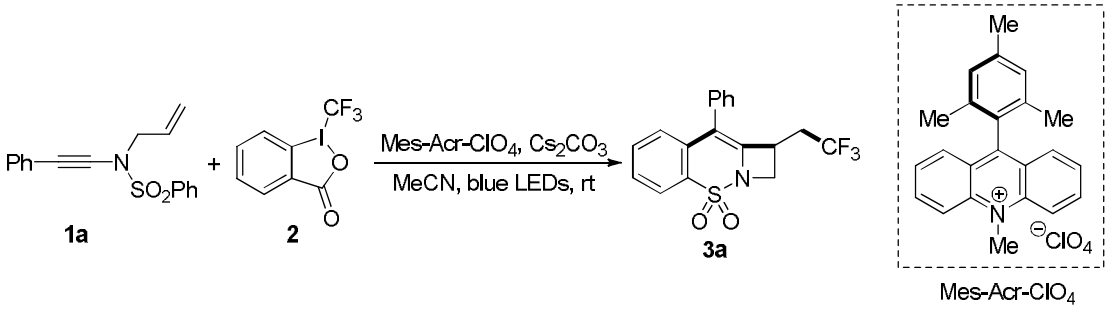
# Synthesis of polysubstituted azetidines via cascade trifluoromethylation/cyclization of *N*-allyl ynamides

*Genlai Zhou,[a] Jingwen Su,[a] Tianbo Shang,[a] Xiaojuan Wang,[a] Yihui Bai,[a]* Zheliang Yuan,[a]* and Gangguo Zhu[a]**

Contents

**General.** Unless otherwise noted, materials obtained from commercial suppliers were used directly without further purification. $^{1}H$, $^{13}C$, and $^{19}F$ NMR spectra were measured on a 600 MHz or 400 MHz NMR spectrometer using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The proton-decoupled $^{19}F$ NMR spectroscopy was used to determine the $^{19}F$ NMR data. Chemical shifts ($\delta$) are given in parts per million relative to TMS, and the coupling constants are given in hertz. High-resolution mass spectrometry (HRMS) analysis were carried out using a TOF MS instrument with an ESI source. Melting points reported here were measured by a melting point instrument and were uncorrected. The starting materials **1** were prepared via the Cu-catalyzed coupling of allyl amides with bromoalkynes reported in the literature.[1]

**General procedure A for the synthesis of polysubstituted azetidines via a cascade trifluoromethylation/cyclization of *N*-allyl ynamides**

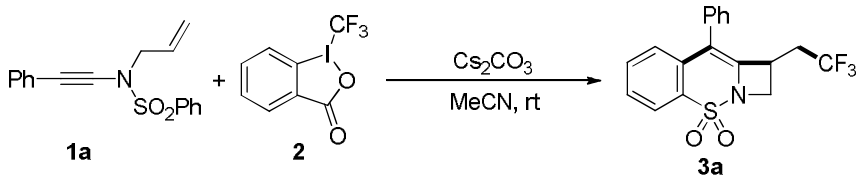



To a mixture of **1a** (60.0 mg, 0.2 mmol), **2** (126.4 mg, 0.4 mmol), and $Cs_2CO_3$ (141.1 mg, 0.4 mmol) in 3 mL of dry MeCN was added Mes-Acr-$ClO_4$ (3.3 mg, 0.008 mmol) under a nitrogen atmosphere. After 36 h of irradiation at a distance of ~5 cm from 15 W blue LEDs (BESTLLON® lamps, 450 nm, 100% light intensity) at 25 °C, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous $Na_2SO_4$, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 20:1) gave 51 mg (70% yield) of **3a** as a light yellow solid; mp 156-158 $^{o}$C; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; $^{1}H$ NMR (600 MHz, $CDCl_3$) $\delta$ 8.06 (d, $J$ = 7.9 Hz, 1H), 7.53–7.51 (m, 1H), 7.49–7.43 (m, 4H), 7.32–7.30 (m, 2H), 7.15 (d, $J$ = 8.0 Hz, 1H), 4.44–4.42 (m, 1H), 4.39–4.37 (m,

[1] W.-B. Shen, X.-T. Tang, T.-T. Zhang, D.-C. Lv, D. Zhao, T.-F. Su and L. Meng, Copper(I)-catalyzed enyne oxidation/cyclopropanation: divergent and enantioselective synthesis of cyclopropanes, *Org. Lett.*, 2021, **23**, 1285.

1H), 3.97–3.93 (m, 1H), 2.38–2.28 (m, 1H), 2.06–1.98 (m, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 144.3, 134.9, 132.7, 131.8, 131.3, 129.6, 129.3, 128.6, 127.4, 125.8, 125.7 (q, $J$ = 277.3 Hz), 123.7, 115.7, 49.9, 34.4 (q, $J$ = 3.2 Hz), 33.8 (q, $J$ = 29.0 Hz); $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -65.6; HRMS (ESI) calcd for $C_{18}H_{15}F_3NO_2S$ $[M + H]^+$ 366.0770, found 366.0774.

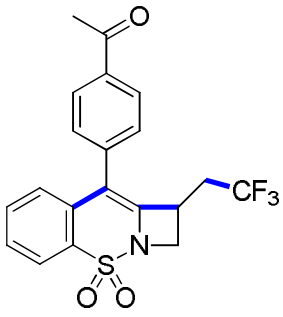
**General procedure B for the synthesis of polysubstituted azetidines via a cascade trifluoromethylation/cyclization of *N*-allyl ynamides**




To a mixture of **1a** (60.0 mg, 0.2 mmol) and **2** (126.4 mg, 0.4 mmol) in 3 mL of dry MeCN was added $Cs_2CO_3$ (141.1 mg, 0.4 mmol) under a nitrogen atmosphere. After stirring at 25 °C for 36 h, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous $Na_2SO_4$, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 20:1) gave 47 mg (64% yield) of **3a** as a light yellow solid.

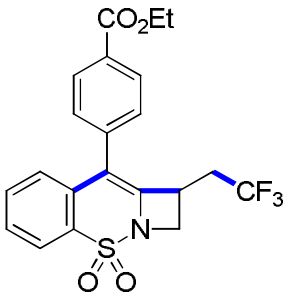
**Scale-up synthesis of 3a**

To a mixture of **1a** (297 mg, 1.0 mmol) and **2** (632 mg, 2.0 mmol) in 15 mL of dry MeCN was added $Cs_2CO_3$ (750 mg, 2.0 mmol) under a nitrogen atmosphere. After stirring at 25 °C for 36 h, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous $Na_2SO_4$, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 20:1) gave 248 mg (68% yield) of **3a** as a light yellow solid.



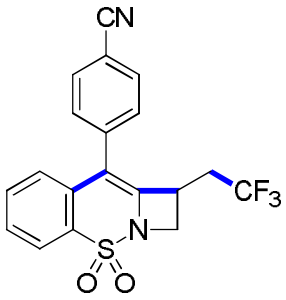

**3b**

*Compound* ***3b***: 58 mg, 71% yield (general procedure A), light yellow solid, mp 154-156 $^{o}$C; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.07 (d, $J$ = 8.2 Hz, 3H), 7.54 (t, $J$ = 7.7 Hz, 1H), 7.48 (t, $J$ = 7.6 Hz, 1H), 7.44 (d, $J$ = 8.2 Hz, 2H), 7.11 (d, $J$ = 7.9 Hz, 1H), 4.46–4.39 (m, 2H), 4.05–3.93 (m, 1H), 2.67 (s, 3H), 2.40–2.32 (m, 1H), 2.05–2.00 (m, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 197.2, 145.2, 137.0, 137.0, 134.2, 132.9, 131.3, 129.8, 129.2, 127.7, 125.6, 125.6 (q, $J$= 277.4 Hz), 123.9, 114.8, 50.0, 34.5 (q, $J$ = 3.0 Hz), 33.8 (q, $J$ = 29.1 Hz), 26.7; $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -65.5; HRMS (ESI) calcd for $C_{20}H_{17}F_3NO_2S$ $[M + H]^+$ 408.0876, found, 408.0873. 49 mg (60% yield) of the title compound could be obtained using the general procedure B as a light yellow solid.



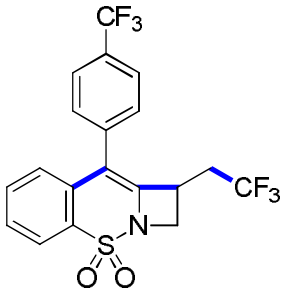

**3c**

*Compound* ***3c***: 69 mg, 79% yield (general procedure A), gray solid, mp 158-160 $^{o}$C; Flash column chromatography conditions: petroleum ethers/EtOAc = 15:1; $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.15 (d, $J$ = 8.2 Hz, 2H), 8.07 (d, $J$ = 7.7 Hz, 1H), 7.53 (t, $J$ = 7.3 Hz, 1H), 7.48 (t, $J$ = 7.5 Hz, 1H), 7.48 (t, $J$ = 7.5 Hz, 1H), 7.41 (d, $J$ = 8.2 Hz, 2H), 7.11 (d, $J$ = 7.9 Hz, 1H), 4.46–4.38 (m, 4H), 4.05–3.96 (m, 1H), 2.47–2.17 (m, 1H), 2.11–1.94 (m, 1H), 1.43 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 165.9, 145.1, 136.7, 134.3, 132.9, 131.3, 130.7, 130.5, 129.6, 127.6, 125.6, 125.6 (q, $J$ = 277.4 Hz), 123.9, 114.9, 61.3, 50.0, 34.5 (q, $J$ = 3.1 Hz), 33.4 (q, $J$ = 29.0 Hz), 14.3; $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -65.5; HRMS (ESI) calcd for $C_{21}H_{19}F_3NO_4S$ $[M + H]^+$ 438.0981, found 438.0968. 71 mg (81% yield) of the title compound could be obtained using the general procedure B as a gray solid.




**3d**

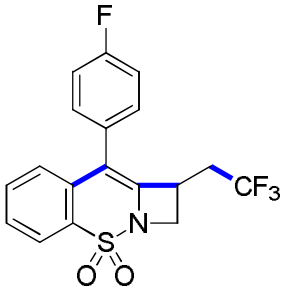
*Compound **3d***: 59 mg, 75% yield (general procedure A), gray solid, mp 179-181 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 15:1; $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.08 (d, $J$ = 7.9 Hz, 1H), 7.79 (d, $J$ = 8.2 Hz, 2H), 7.56 (t, $J$ = 7.7 Hz, 1H), 7.50 (t, $J$ = 7.6 Hz, 1H), 7.47 (d, $J$ = 8.2 Hz, 2H), 7.07 (d, $J$ = 7.9 Hz, 1H), 4.46–4.43 (m, 1H), 4.43–4.41 (m, 1H), 3.97–3.95 (m, 1H), 2.40–2.32 (m, 1H), 2.00–1.96 (m, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 145.7, 137.1, 133.8, 133.1, 133.0, 131.4, 130.4, 127.9, 125.4 (q, $J$ = 277.4 Hz), 125.4, 124.0, 118.1, 114.2, 112.6, 50.1, 34.4 (q, $J$ = 3.1 Hz), 33.9 (q, $J$ = 29.2 Hz); $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -65.5; HRMS (ESI) calcd for $C_{19}H_{14}F_3N_2O_2S$ $[M + H]^+$ 391.0723, found 391.0723. 56 mg (72% yield) of the title compound could be obtained using the general procedure B as a gray solid.




**3e**

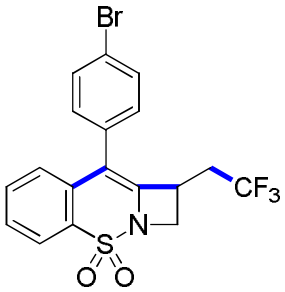
*Compound **3e***: 55 mg, 63% yield (general procedure A), light yellow solid, mp 179-181 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.08 (d, $J$ = 7.1 Hz, 1H), 7.75 (d, $J$ = 8.1 Hz, 2H), 7.55 (t, $J$ = 7.2 Hz, 1H), 7.49 (d, $J$ = 7.4 Hz, 1H), 7.47 (d, $J$ = 8.3 Hz, 2H), 7.08 (d, $J$ = 7.9 Hz, 1H), 4.46–4.40 (m, 2H), 3.99–3.96 (m, 1H), 2.40–2.34 (m, 1H), 2.04–1.96 (m, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 145.3, 136.0, 134.2, 133.0, 131.3, 130.9 (q, $J$ = 30.0 Hz), 130.1, 127.7, 126.3 (q, $J$ = 3.6 Hz), 125.6 (q, $J$ = 277.5 Hz), 125.5, 123.9, 123.9 (q, $J$ = 272.3 Hz), 114.5, 50.0, 34.4 (q, $J$ = 3.1 Hz), 34.0 (q, $J$ = 29.1 Hz); $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -62.7, -65.5; HRMS (ESI) calcd for $C_{19}H_{13}F_6NO_2S$ $[M + H]^+$ 434.0644,

found 434.0646. 56 mg (65% yield) of the title compound could be obtained using the general procedure B as a light yellow solid.




**3f**

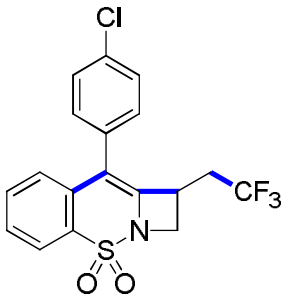
Compound ***3f***: 49 mg, 64% yield (general procedure A), light yellow solid, mp 185-187 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.06 (d, $J$ = 7.9 Hz, 1H), 7.53 (t, $J$ = 7.7 Hz, 1H), 7.46 (t, $J$ = 7.6 Hz, 1H), 7.32–7.28 (m, 2H), 7.18 (t, $J$ = 8.5 Hz, 2H), 7.10 (d, $J$ = 8.0 Hz, 1H), 4.43–4.37(m, 2H), 3.95–3.91 (m, 1H), 2.38–2.32 (m, 1H), 2.10–1.95 (m, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 162.7 (d, $J$ = 249.1 Hz), 144.5, 134.8, 132.8, 131.4 (d, $J$ = 8.2 Hz), 131.3, 127.8 (d, $J$ = 3.4 Hz), 127.5, 125.6 (q, $J$ = 277.4 Hz), 125.6, 123.8, 116.5 (d, $J$ = 21.6 Hz), 114.7, 49.9, 34.3 (q, $J$ = 3.2 Hz), 33.9 (q, $J$ = 28.9 Hz); $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -65.6, -112.2; HRMS (ESI) calcd for $C_{18}H_{14}F_4NO_2S$ $[M + H]^+$ 384.0676, found 384.0675. 48 mg (63% yield) of the title compound could be obtained using the general procedure B as a light yellow solid.




**3g**

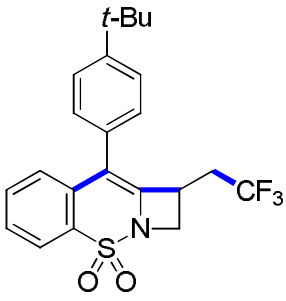
*Compound **3g***: 60 mg, 68% yield (general procedure A), light yellow solid, mp 135-137 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.06 (d, $J$ = 7.9 Hz, 1H), 7.62 (d, $J$ = 8.3 Hz, 2H), 7.53 (t, $J$ = 7.7 Hz, 1H), 7.47 (t, $J$ = 7.6 Hz, 1H), 7.20 (d, $J$ = 8.3 Hz, 2H), 7.10 (d, $J$ = 8.0 Hz, 1H), 4.44–4.38 (m, 2H), 3.96–3.92 (m, 1H),

2.43–2.29 (m, 1H), 2.15–2.00 (m, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) δ 144.7, 134.4, 132.8, 132.6, 131.3, 131.2, 130.9, 127.6, 125.6 (q, $J$ = 277.4 Hz), 125.6, 123.8, 122.9, 114.6, 49.9, 34.4 (q, $J$ = 3.1 Hz), 33.9 (q, $J$ = 29.0 Hz); $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -65.5; HRMS (ESI) calcd for $C_{18}H_{14}BrF_3NO_2S$ $[M + H]^+$ 443.9875, found 443.9875. 58 mg (66% yield) of the title compound could be obtained using the general procedure B as a light yellow solid.




**3h**

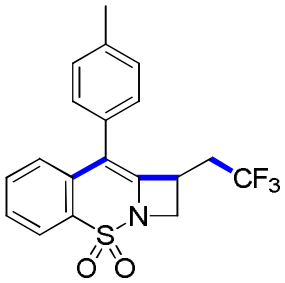
*Compound* ***3h***: 52 mg, 65% yield (general procedure A), light yellow solid, mp 155-157 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.06 (d, $J$ = 7.9 Hz, 1H), 7.53 (t, $J$ = 7.7 Hz, 1H), 7.48–7.45 (m, 3H), 7.26 (d, $J$ = 8.4 Hz, 2H), 7.10 (d, $J$ = 7.9 Hz, 1H), 4.44–4.38 (m, 2H), 4.00–3.89 (m, 1H), 2.45–2.28 (m, 1H), 2.11–1.98 (m, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 144.7, 134.7, 134.5, 132.8, 131.3, 131.0, 130.4, 129.6, 127.6, 125.6 (q, $J$ = 277.4 Hz), 125.6, 123.8, 114.6, 49.9, 34.4 (q, $J$ = 3.1 Hz), 33.9 (q, $J$ = 29.0 Hz); $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -65.5; HRMS (ESI) calcd for $C_{18}H_{14}ClF_3NO_2S$ $[M + H]^+$ 400.0380, found 400.0382. 53 mg (67% yield) of the title compound could be obtained using the general procedure B as a light yellow solid.




**3i**

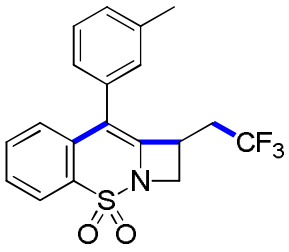
*Compound* ***3i***: 50 mg, 60% yield (general procedure A), light yellow solid, mp 163-165 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; $^1$H NMR (600 MHz, $CDCl_3$)

$\delta$ 8.06 (d, $J$ = 7.8 Hz, 1H), 7.52 (t, $J$ = 7.6 Hz, 1H), 7.47 (d, $J$ = 8.2 Hz, 2H), 7.44 (t, $J$ = 7.6 Hz, 1H), 7.22 (d, $J$ = 8.2 Hz, 2H), 7.18 (d, $J$ = 8.0 Hz, 1H), 4.42–4.37 (m, 2H), 3.97–3.93 (m, 1H), 2.35–2.33 (m, 1H), 2.08–2.05 (m, 1H), 1.37 (s, 9H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 151.7, 144.0, 135.1, 132.7, 131.3, 129.2, 128.7,, 127.3, 126.1, 126.0, 125.8 (q, $J$ = 277.4 Hz), 123.7, 115.7, 49.8, 34.7, 34.5 (q, $J$ = 3.1 Hz), 33.9 (q, $J$ = 28.8 Hz), 31.3; $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -62.7; HRMS (ESI) calcd for $C_{19}H_{17}ClF_3NO_2S$ $[M + H]^+$ 422.1396, found 422.1400. 47 mg (56% yield) of the title compound could be obtained using the general procedure B as a light yellow solid.



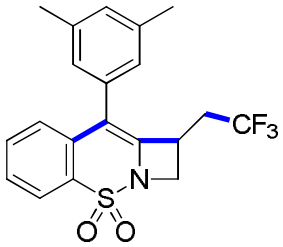

**3j**

*Compound* ***3j***: 55 mg, 72% yield (general procedure A), light yellow solid, mp 153-155 $^{o}$C; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.06 (d, $J$ = 7.9 Hz, 1H), 7.51 (t, $J$ = 7.7 Hz, 1H), 7.45 (t, $J$ = 7.6 Hz, 1H), 7.27 (d, $J$ = 7.8 Hz, 2H), 7.19 (d, $J$ = 8.0 Hz, 2H), 7.16 (d, $J$ = 8.0 Hz, 1H), 4.43–4.36 (m, 2H), 3.95–3.93 (m, 1H), 2.42 (s, 3H), 2.39–2.28 (m, 1H), 2.14–1.99 (m, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 144.0, 138.6, 135.1, 132.7, 131.4, 130.0, 129.5, 128.7, 127.3, 125.9, 125.8 (q, $J$ = 277.2 Hz), 123.7, 115.7, 49.8, 34.5 (q, $J$ = 3.3 Hz), 33.9 (q, $J$ = 28.9 Hz), 21.3; $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -65.6; HRMS (ESI) calcd for $C_{19}H_{17}ClF_3NO_2S$ $[M + H]^+$ 380.0927, found 380.0925. 50 mg (66% yield) of the title compound could be obtained using the general procedure B as a light yellow solid.



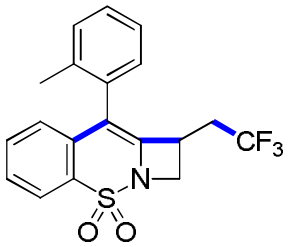

**3k**

*Compound* ***3k***: 55 mg, 73% yield (general procedure A), light yellow solid, mp 103-105 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.06 (d, $J$ = 7.9 Hz, 1H), 7.52 (t, $J$ = 7.7 Hz, 1H), 7.45 (t, $J$ = 7.6 Hz, 1H), 7.35 (t, $J$ = 7.6 Hz, 1H), 7.24 (d, $J$ = 7.6 Hz, 1H), 7.17 (d, $J$ = 7.5 Hz, 1H), 7.12 (s, 1H), 7.10 (d, $J$ = 7.6 Hz, 1H), 4.43–4.36 (m, 2H), 3.97–3.92 (m, 1H), 2.40 (s, 3H), 2.37–2.28 (m, 1H), 2.10–1.97 (m, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 144.1, 139.0, 135.0, 132.7, 131.7, 131.3, 130.2, 129.4, 129.1, 127.3, 126.6, 125.9, 125.8 (q, $J$ = 277.3 Hz), 123.7, 115.8, 49.9, 34.4 (q, $J$ = 3.2 Hz), 33.9 (q, $J$ = 28.9 Hz), 21.4; $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -65.6; HRMS (ESI) calcd for $C_{19}H_{17}F_3NO_2S$ $[M + H]^+$ 380.0927, found 380.0910. 53mg (70% yield) of the title compound could be obtained using the general procedure B as a light yellow solid.



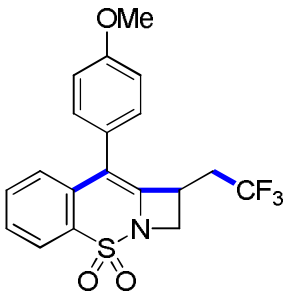

**3l**

*Compound* ***3l***: 40 mg, 51% yield (general procedure A), light yellow solid, mp 143-145 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.05 (d, $J$ = 7.9 Hz, 1H), 7.52 (t, $J$ = 7.6, 1H), 7.44 (t, $J$ = 7.6 Hz, 1H), 7.18 (d, $J$ = 8.0, 1H), 7.05 (s, 1H), 6.91 (s, 2H), 4.42–4.35 (m, 2H), 3.96–3.94 (m, 1H), 2.35 (s, 6H), 2.34–2.21 (m, 1H), 2.10–2.03 (m, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 143.9, 138.9, 135.1, 132.7, 131.6, 131.4, 130.2, 127.3, 127.2, 126.0, 125.8 (q, $J$= 277.4 Hz), 123.6, 116.0, 49.9, 34.5 (q, $J$ = 3.2 Hz), 33.9 (q, $J$= 29.0 Hz), 21.3; $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -65.7; HRMS (ESI) calcd for $C_{20}H_{19}F_3NO_2S$ $[M + H]^+$ 394.1083, found 394.1089. 35 mg (44% yield) of the title compound could be obtained using the general procedure B as a light yellow solid.




**3m**

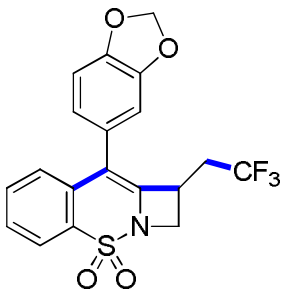
*Compound* ***3m***: 42 mg, 55% yield (general procedure A), light yellow oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; dr = 1.5:1; The two rotamers can't be separated after flash column chromatography. Data of the major rotamer: $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.06 (d, $J$ = 7.9 Hz, 1H), 7.51–7.46 (m, 1H), 7.44 (t, $J$ = 7.6 Hz, 1H), 7.40–7.34 (m, 1H), 7.35–7.27 (m, 2H), 7.21 (d, $J$ = 7.6 Hz, 1H), 6.84 (d, $J$ = 7.9 Hz, 1H), 4.48–4.42 (m, 1H), 4.33 (dd, $J$ = 7.4, 7.4 Hz, 1H), 3.91–3.80 (m, 1H), 2.34–2.22 (m, 1H), 2.09 (s, 3H), 1.85–1.73 (m, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 144.5, 137.8, 134.8, 132.9, 131.1, 130.9, 130.8, 130.4, 129.2, 127.3, 126.7, 125.6 (q, $J$ = 277.4 Hz), 125.3, 123.8, 115.2, 49.7, 34.1 (q, $J$ = 3.3 Hz), 33.1 (q, $J$ = 28.9 Hz), 19.9; $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -65.4. Data of the Minor rotamer: $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.06 (d, $J$ = 7.9 Hz, 1H), 7.52–7.47 (m, 1H), 7.44 (t, $J$ = 7.6, 1H), 7.41–7.33 (m, 1H), 7.33–7.27 (m, 2H), 7.16 (d, $J$ = 7.6 Hz, 1H), 6.82 (d, $J$ = 7.9 Hz, 1H), 4.56 (dd, $J$ = 7.4, 7.4 Hz, 1H), 4.29 (dd, $J$ = 7.8, 4.7 Hz, 1H), 3.67–3.55 (m, 1H), 2.55–2.42 (m, 1H), 2.19 (s, 3H), 2.18–2.00 (m, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 144.4, 138.0, 135.2, 132.8, 131.2, 131.0, 130.8, 130.7, 129.1, 127.3, 126.3, 125.6 (q, $J$ = 277.9 Hz), 125.5, 123.6, 114.6, 49.9, 35.3 (q, $J$ = 28.8 Hz), 34.6 (9, $J$ = 3.3 Hz), 19.5; $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -65.6; HRMS (ESI) Calcd for $C_{19}H_{17}F_3NO_2S$ $[M + H]^+$ 380.0927, found 380.0927. 43 mg (57% yield) of the title compound could be obtained using the general procedure B as a light yellow oil.




**3n**

*Compound* ***3n***: 59 mg, 75% yield (general procedure A), light yellow solid, mp 124-126 $^{o}$C; Flash

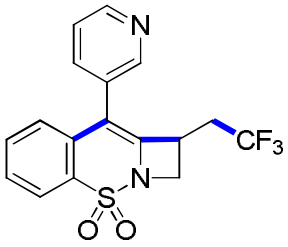
column chromatography conditions: petroleum ethers/EtOAc = 20:1; $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.05 (d, $J$ = 7.9 Hz, 1H), 7.52 (t, $J$ = 7.9 Hz, 1H), 7.44 (t, $J$ = 7.8 Hz, 1H), 7.22 (d, $J$ = 8.7 Hz, 1H), 7.16 (d, $J$ = 8.0 Hz, 1H), 6.99 (d, $J$ = 8.7 Hz, 1H), 4.43–4.35 (m, 2H), 3.94–3.87 (m, 1H), 3.87 (s, 3H), 2.36–2.32 (m, 1H), 2.09–2.04 (m, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 159.7, 143.8, 135.2, 132.7, 131.4, 130.8, 127.3, 125.8, 125.8 (q, $J$= 277.4 Hz), 123.7, 123.7, 115.4, 114.7, 55.3, 49.8, 34.4 (q, $J$ = 3.2 Hz), 33.9 (q, $J$ = 28.8 Hz); $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -65.5; HRMS (ESI) calcd for $C_{19}H_{17}F_3NO_3S$ $[M + H]^+$ 396.0876, found 396.0864. 49 mg (62% yield) of the title compound could be obtained using the general procedure B as a light yellow solid.




**3o**

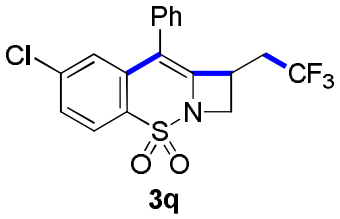
*Compound* ***3o***: 56 mg, 68% yield (general procedure A), light yellow solid, mp 130-132 $^{o}$C; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.05 (d, $J$ = 7.9 Hz, 1H), 7.53 (t, $J$ = 7.7 Hz, 1H), 7.45 (t, $J$ = 7.7 Hz, 1H), 7.17 (d, $J$ = 8.0 Hz, 1H), 6.90 (d, $J$ = 8.3 Hz, 1H), 6.76 (td, $J$ = 4.1, 1.7 Hz, 2H), 6.06 (d, $J$ = 2.7 Hz, 1H), 4.43–4.35 (m, 2H), 3.93–3.91 (m, 1H), 2.44–2.29 (m, 1H), 2.24–2.07 (m, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 148.4, 147.9, 144.2, 135.0, 132.7, 131.3, 127.4, 125.8 (q, $J$ = 277.5 Hz), 125.8, 125.2, 123.7, 123.2, 115.4, 109.8, 109.0, 101.5, 49.8, 34.4 (q, $J$ = 3.2 Hz), 34.0 (q, $J$ = 28.2 Hz); $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -65.5; HRMS (ESI) calcd for $C_{19}H_{15}F_3NO_4S$ $[M + H]^+$ 410.0668, found 410.0667.

56 mg (68% yield) of the title compound could be obtained using the general procedure B as a light yellow solid.



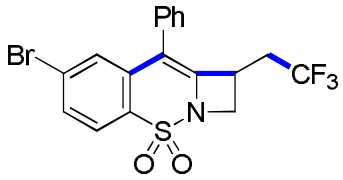
**3p**

*Compound **3p***: 47 mg, 64% yield (general procedure A), light yellow solid, mp 148-150 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 1:1; $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.71 (d, $J$ = 3.6 Hz, 1H), 8.60 (d, $J$ = 1.4 Hz, 1H), 8.08 (dd, $J$ = 7.9, 0.9 Hz, 1H), 7.67 (dt, $J$ = 7.8, 1.9 Hz, 1H), 7.55 (td, $J$ = 7.9, 1.3 Hz, 1H), 7.49 (t, $J$ = 7.6 Hz, 1H), 7.44 (dd, $J$ = 7.7, 4.9 Hz, 1H), 7.06 (d, $J$ = 7.8 Hz, 1H), 4.44 (d, $J$ = 6.0 Hz, 2H), 4.00–3.94 (m, 1H), 2.42–2.36 (m, 1H), 2.05–2.00 (m, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 150.3, 150.0, 145.7, 137.2, 134.2, 133.0, 131.3, 128.2, 127.8, 125.5 (q, $J$ = 277.5 Hz), 125.3, 124.0, 124.0, 112.1, 50.0, 34.4 (q, $J$ = 3.1 Hz), 34.2 (q, $J$ = 29.1 Hz); $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -65.4; HRMS (ESI) calcd for $C_{19}H_{17}F_3NO_2S$ $[M + H]^+$ 367.0723, found 367.0722. 40 mg (55% yield) of the title compound could be obtained using the general procedure B as a light yellow solid.



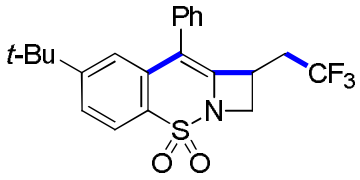
**3q**

*Compound **3q***: 50 mg, 60% yield (general procedure A), light yellow solid, mp 168-170 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.99 (d, $J$ = 8.5 Hz, 1H), 7.53–7.45 (m, 3H), 7.41 (d, $J$ = 8.5 Hz, 1H), 7.29 (d, $J$ = 6.9 Hz, 2H), 7.10 (d, $J$ = 1.7 Hz, 1H), 4.46–4.37 (m, 2H), 4.01–3.88 (m, 1H), 2.43–2.24 (m, 1H), 2.02–1.98 (m, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 145.8, 139.5, 136.7, 131.1, 129.6, 129.5, 129.0, 128.3, 127.4, 125.6, 125.6 (q, $J$ = 277.3 Hz), 125.4, 115.0, 50.1, 34.5 (q, $J$ = 3.1 Hz), 33.8 (q, $J$ = 29.0 Hz); $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -65.6; HRMS (ESI) calcd for $C_{18}H_{13}ClF_3NO_2SNa$ $[M + Na]^+$ 422.0200, found 422.0180. 44 mg (52% yield) of the title compound could be obtained using the general procedure B as a light yellow solid.



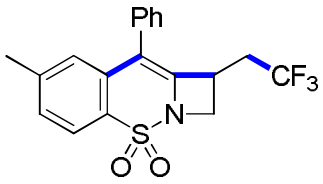

**3r**

*Compound* ***3r***: 40 mg, 45% yield (general procedure A), white solid, mp 182-184 $^{o}$C; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1 $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.96–7.78 (m, 1H), 7.76–7.56 (m, 1H), 7.54–7.45 (m, 3H), 7.34–7.28 (m, 2H), 7.26 (d, $J$ = 2.4 Hz, 1H), 4.46–4.36 (m, 2H), 4.00–3.88 (m, 1H), 2.37–2.26 (m, 1H), 2.07–1.92 (m, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 145.8, 136.7, 136.3, 134.5, 131.1, 130.4, 129.5, 129.0, 128.5, 125.62 (q, $J$ = 277.5 Hz), 125.4, 125.1, 114.9, 50.1, 34.5 (q, $J$ = 3.2 Hz), 33.8 (q, $J$ = 28.9 Hz); $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -65.6; HRMS (ESI) calcd for $C_{18}H_{15}F_3NO_2S$ $[M + H]^+$ 443.9865, found 443.9875. 35 mg (40% yield) of the title compound could be obtained using the general procedure B as a white solid.



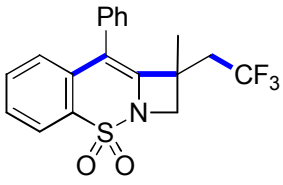

**3s**

*Compound* ***3s***: 55 mg, 65% yield (general procedure A), light yellow solid, mp 193-195 $^{o}$C; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.99 (d, $J$ = 8.4 Hz, 1H), 7.52–7.46 (m, 3H), 7.44 (d, $J$ = 7.4 Hz, 1H), 7.32 (d, $J$ = 6.9 Hz, 2H), 7.16 (d, $J$ = 1.8 Hz, 1H), 4.42–4.34 (m, 2H), 3.97–3.93 (m, 1H), 2.35–2.26 (m, 1H), 2.05–1.97 (m, 1H), 1.22 (s, 9H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 156.6, 144.1, 134.5, 132.0, 129.5, 129.2, 128.6, 128.6, 125.8 (q, $J$ = 277.4 Hz), 124.7, 123.6, 122.8, 116.0, 49.8, 35.2, 34.4 (q, $J$ = 3.1 Hz), 33.8 (q, $J$ = 28.9 Hz), 30.9; $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -65.6; HRMS (ESI) calcd for $C_{18}H_{15}F_3NO_2S$ $[M + H]^+$ 422.1396, found 422.1377. 43 mg (51% yield) of the title compound could be obtained using the general procedure B as a light yellow solid.



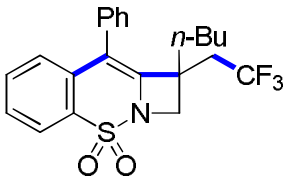

**3t**

*Compound* ***3t***: 56 mg, 74% yield (general procedure A), light yellow solid, mp 167-169 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.95 (d, $J$ = 8.1 Hz, 1H), 7.48 (t, $J$ = 7.2 Hz, 2H), 7.45 (d, $J$ = 7.1 Hz, 1H), 7.32–7.28 (m, 2H), 7.28–7.22 (m, 1H), 6.92 (s, 1H), 4.41–4.34 (m, 2H), 3.94–3.91 (m, 1H), 2.33 (s, 3H), 2.31–2.24 (m, 1H), 2.00–1.96 (m, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 144.3, 143.6, 134.8, 132.0, 129.6, 129.3, 128.7, 128.6, 128.2, 126.1, 125.7 (q, $J$= 277.3 Hz), 123.8, 115.6, 49.8, 34.4 (q, $J$= 3.3 Hz), 33.9 (q, $J$ = 29.0 Hz), 21.7; $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -65.6; HRMS (ESI) calcd for $C_{18}H_{15}F_3NO_2S$ $[M + H]^+$ 380.0927, found 380.0915. 50 mg (66% yield) of the title compound could be obtained using the general procedure B as a light yellow solid.



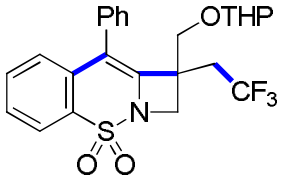

**3v**

*Compound* ***3v***: 58 mg, 76% yield (general procedure A), light yellow solid, mp 124-126 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.06 (d, $J$ = 7.8 Hz, 1H), 7.54–7.40 (m, 5H), 7.34–7.24 (m, 2H), 6.94 (d, $J$ = 7.9 Hz, 1H), 4.51 (d, $J$ = 7.6 Hz, 1H), 4.08 (d, $J$ = 7.6 Hz, 1H), 2.63–2.48 (m, 1H), 2.11–1.84 (m, 1H), 1.52 (s, 3H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 149.6, 135.8, 132.7, 132.3, 130.8, 130.3, 129.1, 128.7, 127.2, 126.1, 125.7 (q, $J$ = 278.6 Hz), 123.5, 114.5, 55.3, 42.6 (q, $J$ = 2.1 Hz), 39.6 (q, $J$ = 27.7 Hz), 23.1; $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -61.2; HRMS (ESI) calcd for $C_{19}H_{17}F_3NO_2S$ $[M + H]^+$ 380.0927, found 380.0929. 55 mg (73% yield) of the title compound could be obtained using the general procedure B as a light yellow solid.




**3w**

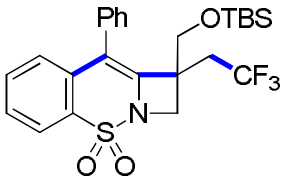
*Compound* ***3w***: 53 mg, 63% yield (general procedure A), light yellow solid, mp 123-125 $^{o}$C; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.05 (dd, $J$ = 7.8, 1.0 Hz, 1H), 7.54–7.39 (m, 5H), 7.31–7.27 (m, 1H), 7.26–7.22 (m, 1H), 6.95 (d, $J$ = 7.9 Hz, 1H), 4.47 (d, $J$ = 7.8 Hz, 1H), 4.17 (d, $J$ = 7.8 Hz, 1H), 2.59–2.54 (m, 1H), 2.07–2.03 (m, 1H), 1.82–1.64 (m, 1H), 1.56–1.49 (m, 2H), 1.46 (dd, $J$ = 11.9, 4.8 Hz, 1H), 1.34 (tt, $J$ = 13.9, 6.9 Hz, 2H), 0.91 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 148.0, 135.7, 132.6, 132.5, 130.8, 130.3, 129.1, 128.7, 127.2, 126.0, 125.8 (q, $J$ = 278.8 Hz), 123.5, 114.9, 52.1, 46.8, 39.6 (q, $J$ = 27.6 Hz), 34.9, 26.7, 22.8, 13.8; $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -60.6; HRMS (ESI) Calcd for $C_{22}H_{23}F_3NO_2S$ $[M + H]^+$ 422.1396, found 422.1401. 38 mg (45% yield) of the title compound could be obtained using the general procedure B as a light yellow solid.




**3x**

*Compound* ***3x***: 67 mg, 70% yield (general procedure A), light yellow oil; dr = 1.6:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; The two isomers can't be separated after flash column chromatography. Data of the major isomer: $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.06 (d, $J$ = 7.8 Hz, 1H), 7.51–7.37 (m, 5H), 7.36–7.27 (m, 2H), 6.94 (d, $J$ = 7.8 Hz, 1H), 4.57 (t, $J$ = 3.6 Hz, 1H), 4.49 (d, $J$ = 7.6 Hz, 1H), 4.40 (d, $J$ = 7.6 Hz, 1H), 3.86 (d, $J$ = 10.3 Hz, 1H), 3.81–3.73 (m, 1H), 3.55–3.48 (m, 1H), 3.42 (d, $J$ = 10.3 Hz, 1H), 2.54–2.39 (m, 1H), 2.39–2.25 (m, 1H), 1.86–1.77 (m, 1H), 1.76–1.47 (m, 5H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 146.4, 135.8, 132.5, 132.4, 131.0, 130.2, 128.9, 128.6, 127.2, 126.1, 125.6 (d, $J$ = 278.4 Hz), 123.4, 115.3, 99.3, 68.8, 62.5, 51.3, 46.9, 36.4 (q, $J$ = 28.7 Hz), 30.3, 25.2, 19.2; $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -60.9. Data of the minor isomer: $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.05 (d, $J$ = 7.8 Hz, 1H), 7.51–7.36 (m, 5H), 7.34–7.27 (m, 2H), 6.94 (d, $J$ = 7.8 Hz, 1H), 4.59 (t, $J$ = 3.5 Hz, 1H), 4.53 (d, $J$ = 7.8 Hz, 1H),

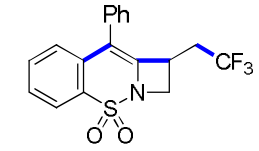
4.33 (d, $J$ = 7.8 Hz, 1H), 3.96 (d, $J$ = 10.3 Hz, 1H), 3.81–3.72 (m, 1H), 3.55–3.49 (m, 1H), 3.46 (d, $J$ = 10.3 Hz, 1H), 2.53– 2.39 (m, 1H), 2.39–2.24 (m, 1H), 1.76–1.46 (m, 6H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 146.4, 135.8, 132.5, 132.5, 131.0, 130.7, 128.9, 128.6, 127.2, 126.2, 125.7 (d, $J$ = 278.2 Hz), 123.4, 115.4, 99.4, 69.7, 62.3, 51.3, 46.8, 36.3 (q, $J$ = 28.4 Hz), 30.1, 25.2, 19.2; $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -61.0; HRMS (ESI) Calcd for $C_{24}H_{25}F_3NO_4S$ $[M + H]^+$ 480.1451, found 480.1502. 71 mg (74% yield) of the title compound could be obtained using the general procedure B as a light yellow oil.




**3y**

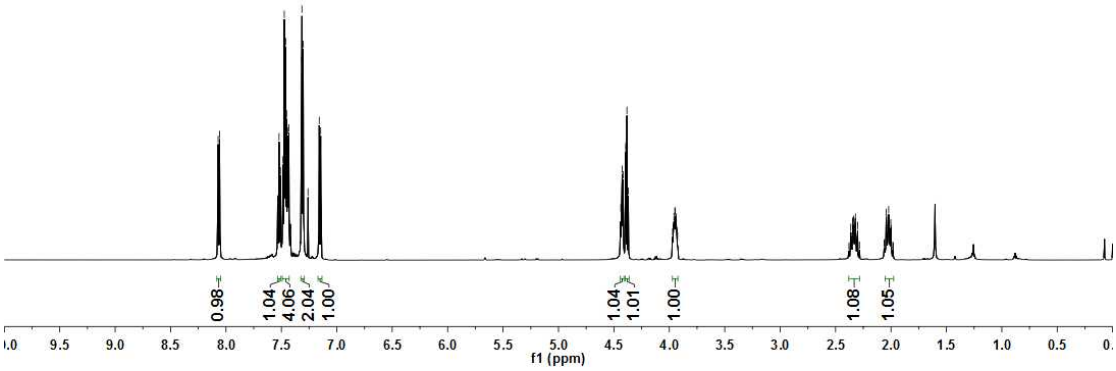
*Compound* ***3y***: 75 mg, 74% yield (general procedure A), white solid, mp 104-106 $^{o}$C; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.05 (d, $J$ = 7.8 Hz, 1H), 7.50–7.39 (m, 5H), 7.31 (m, 2H), 6.93 (d, $J$ = 7.1 Hz, 1H), 4.49 (d, $J$ = 7.7 Hz, 1H), 4.29 (d, $J$ = 7.7 Hz, 1H), 3.75 (d, $J$ = 10.4 Hz, 1H), 3.61 (d, $J$ = 10.4 Hz, 1H), 2.39–2.25 (m, 2H), 0.86 (s, 9H), 0.05 (d, $J$ = 8.9 Hz, 6H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 146.3, 135.7, 132.5, 130.9, 130.5, 130.2, 128.9, 128.6, 127.2, 126.0, 125.7 (q, $J$= 278.2 Hz), 123.4, 115.2, 65.4, 51.1, 48.4, 35.9 (q, $J$ = 28.7 Hz), 25.7, 18.2, -5.6 (d, $J$ = 12.3 Hz); $^{19}$F NMR (565 MHz, $CDCl_3$) $\delta$ -60.9; HRMS (ESI) Calcd for $C_{25}H_{31}F_3NO_3SSi$ $[M + H]^+$ 510.1741, found 510.1743. 66 mg (65% yield) of the title compound could be obtained using the general procedure B as a white solid.

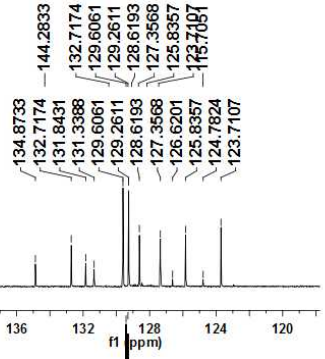
## NMR spectra

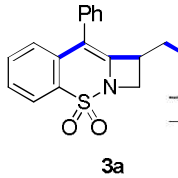




**3a**

$^1$H NMR (600 MHz, $CDCl_3$)

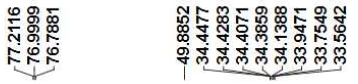


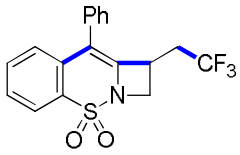




**3a**

$^{13}$C NMR (151 MHz, $CDCl_3$)

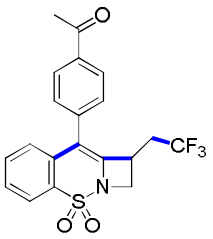





**3a**

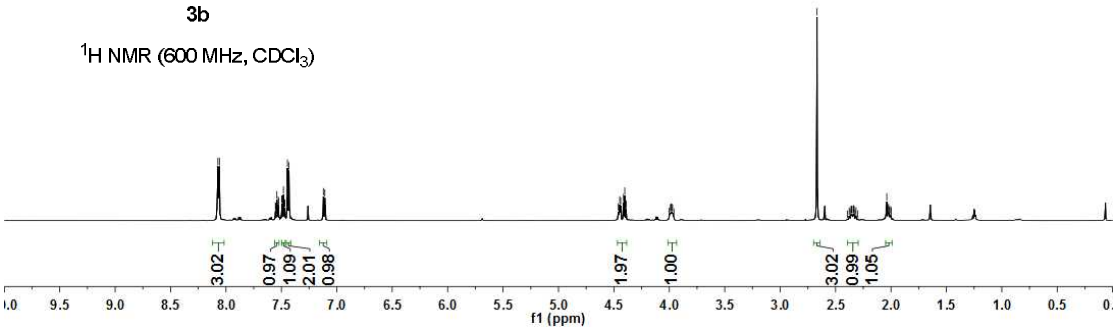
$^{19}$F NMR (565 MHz, $CDCl_3$)

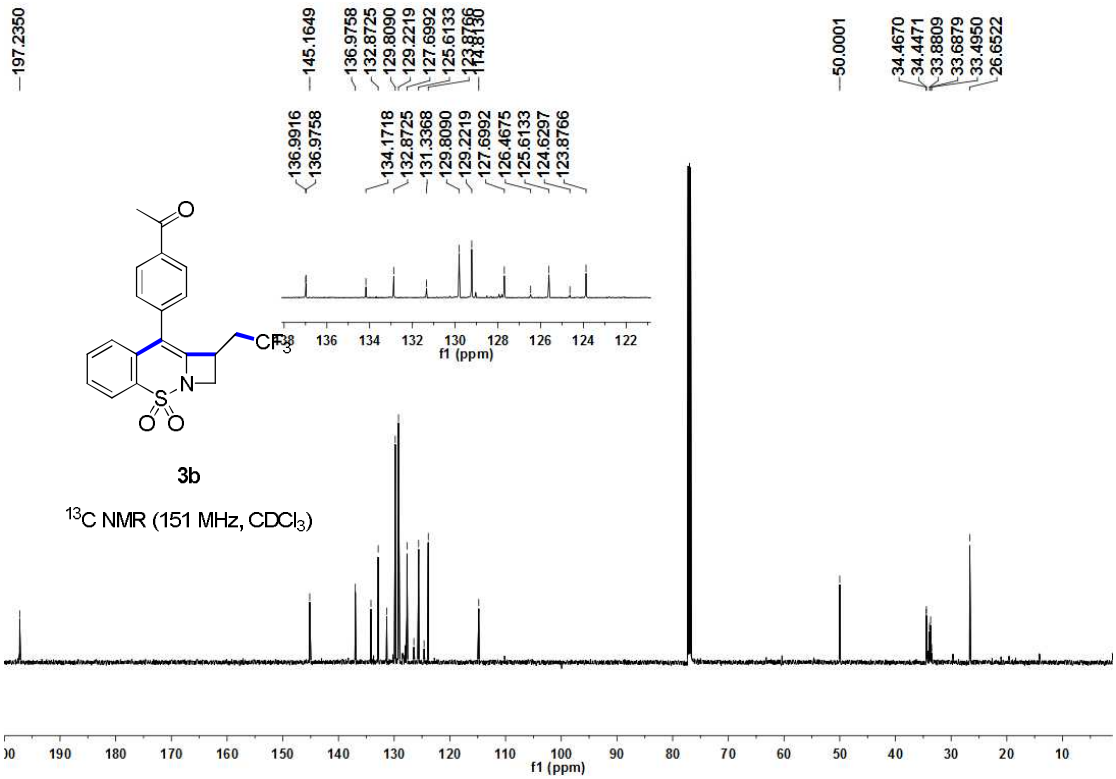



**3b**

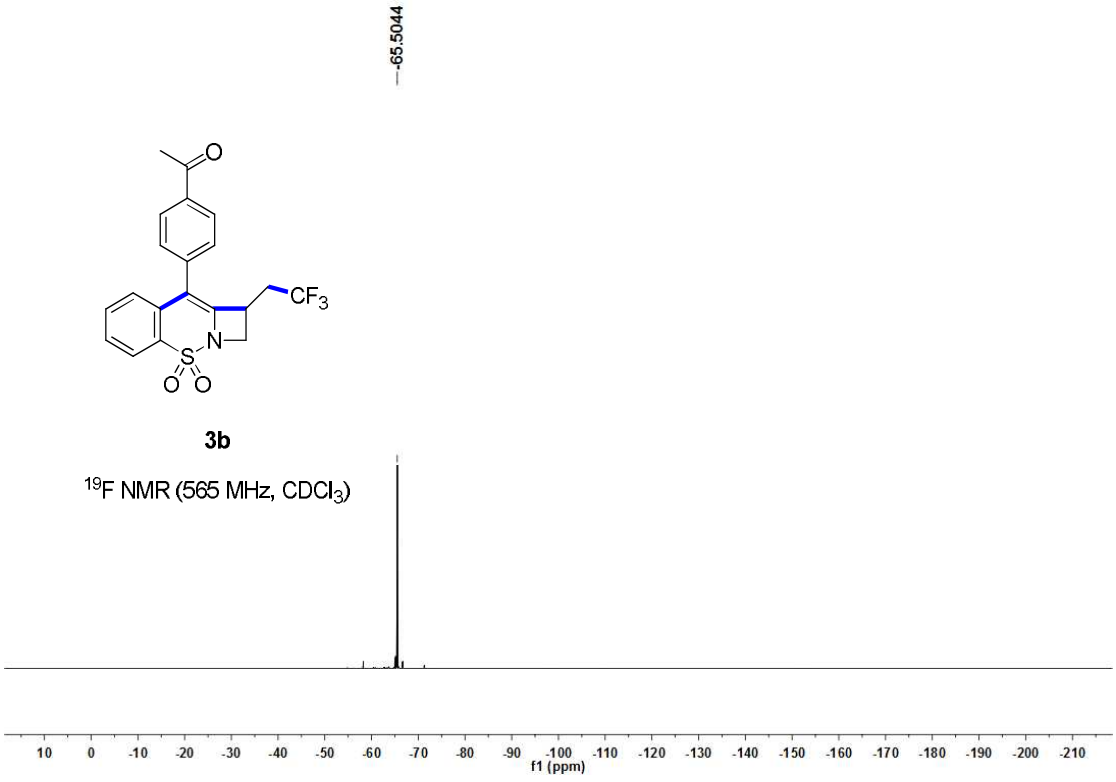
$^{1}$H NMR (600 MHz, $CDCl_3$)





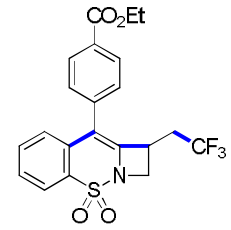

**3b**

$^{13}$C NMR (151 MHz, $CDCl_3$)



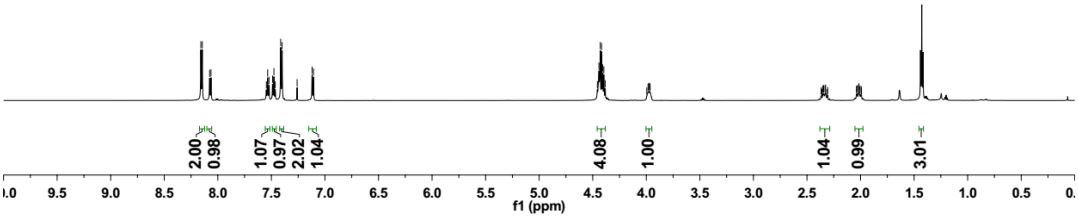

**3b**

$^{19}$F NMR (565 MHz, $CDCl_3$)

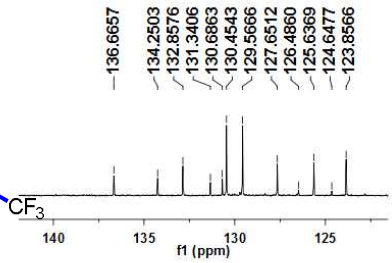



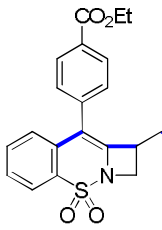

**3c**

$^{1}$H NMR (600 MHz, $CDCl_3$)



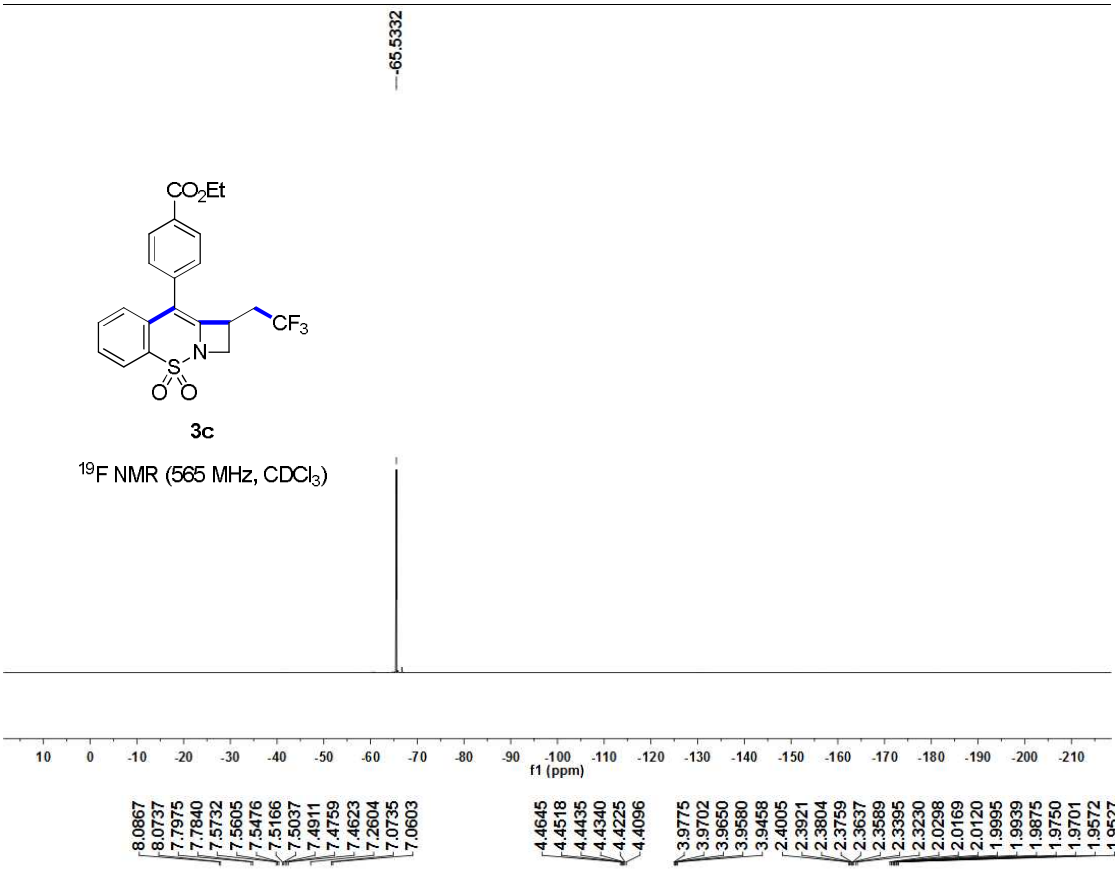




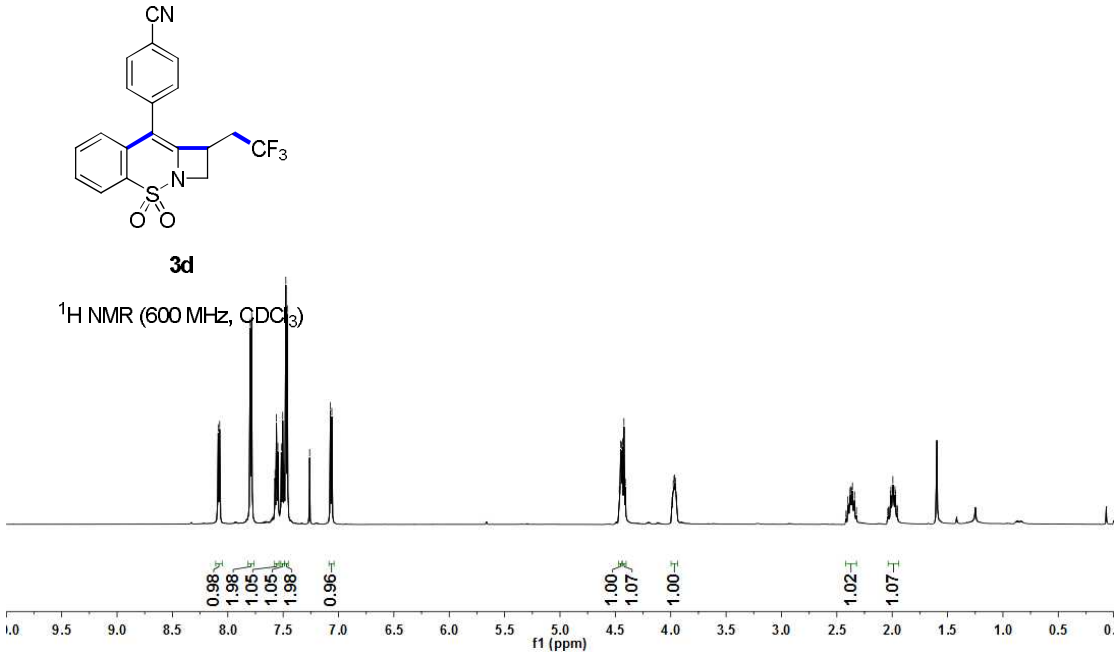

**3c**

$^{13}$C NMR (151 MHz, $CDCl_3$)



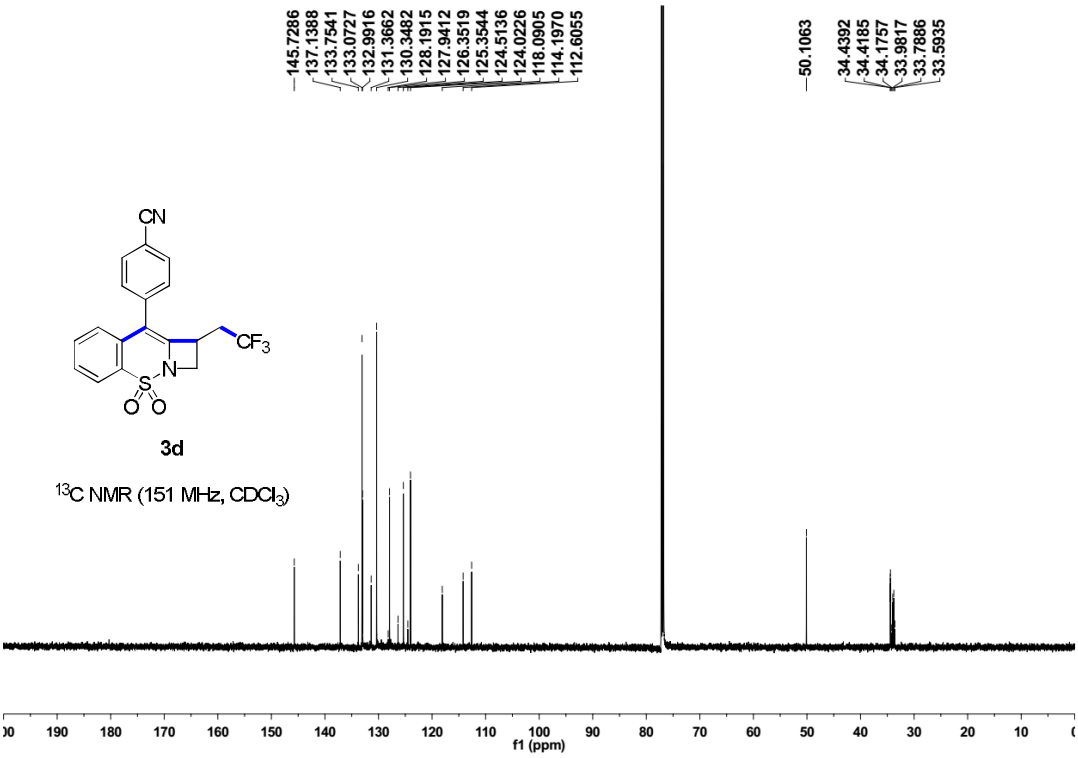

**3c**

$^{19}$F NMR (565 MHz, $CDCl_3$)



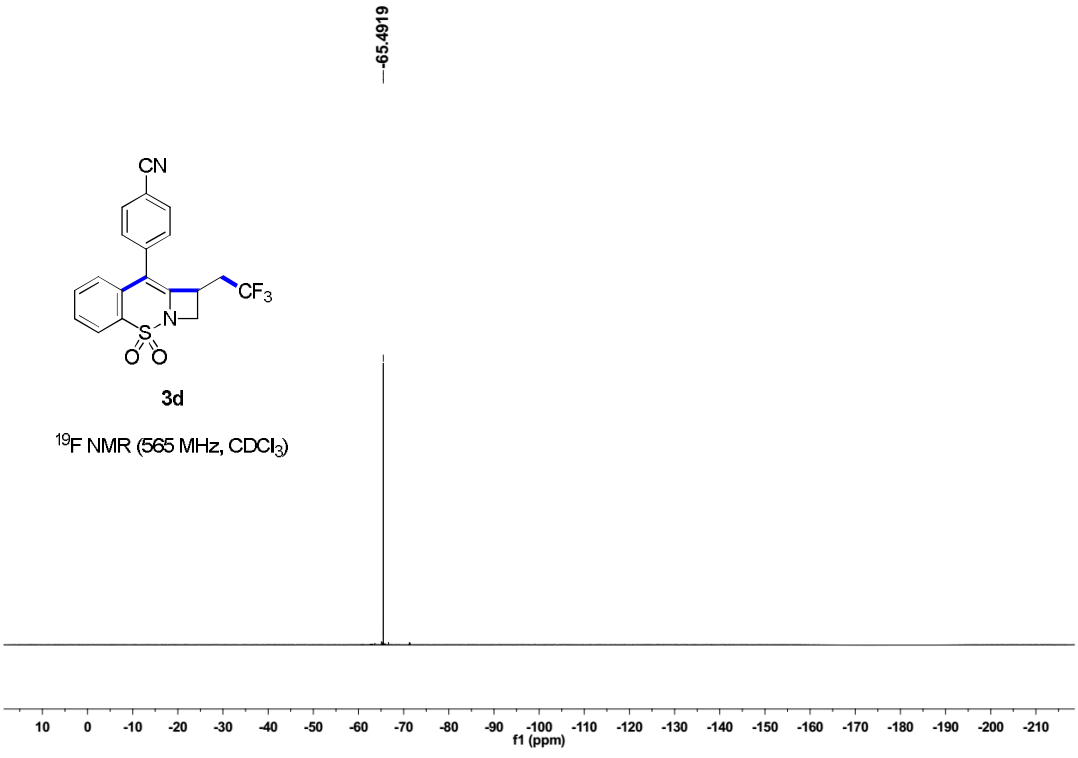

**3d**

$^{1}$H NMR (600 MHz, $CDCl_3$)



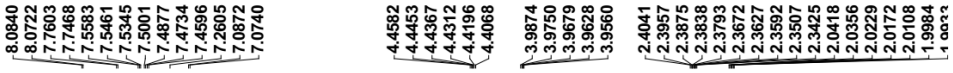

**3d**

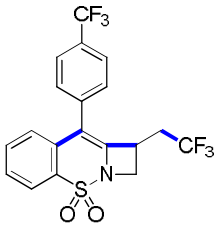
$^{13}$C NMR (151 MHz, $CDCl_3$)




**3d**

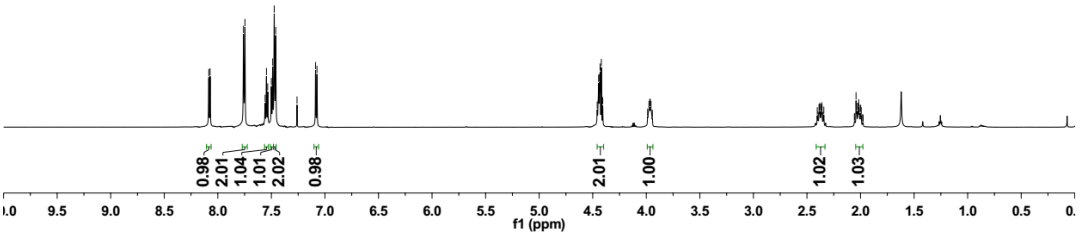
$^{19}$F NMR (565 MHz, $CDCl_3$)



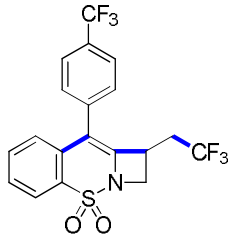




**3e**

$^{1}$H NMR (600 MHz, $CDCl_3$)

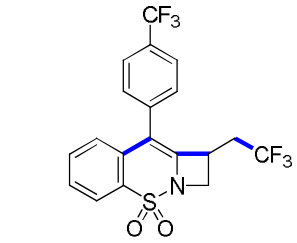







**3e**

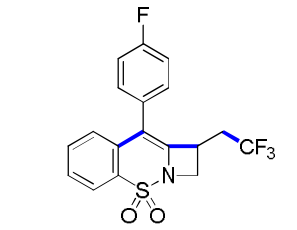
$^{13}$C NMR (151 MHz, $CDCl_3$)



**3e**

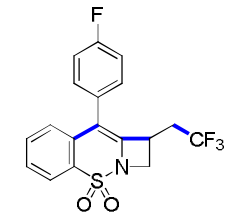
$^{19}$F NMR (565 MHz, $CDCl_3$)



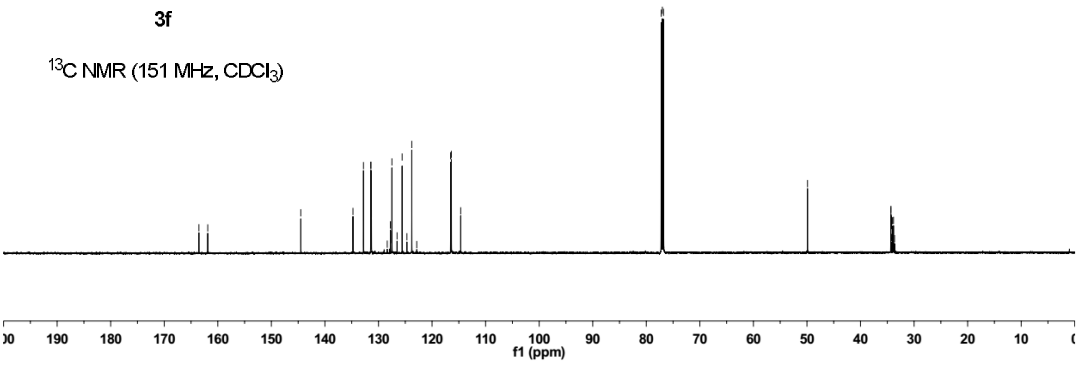
**3f**

$^{1}$H NMR (600 MHz, $CDCl_3$)

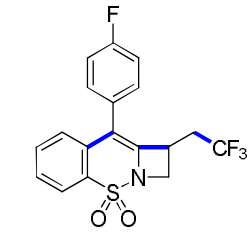




**3f**

$^{13}$C NMR (151 MHz, $CDCl_3$)

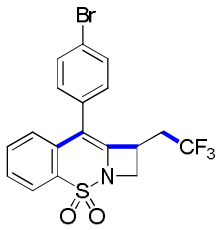






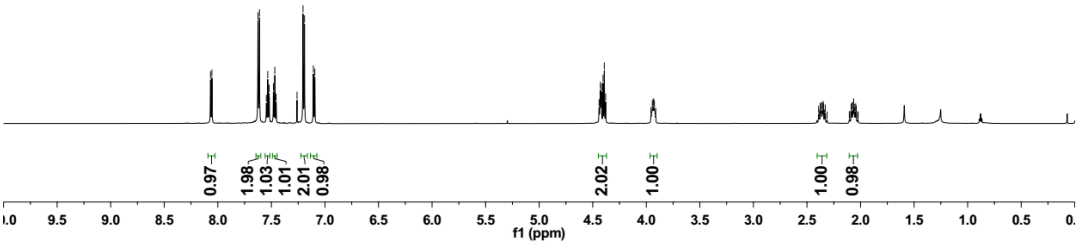

**3f**

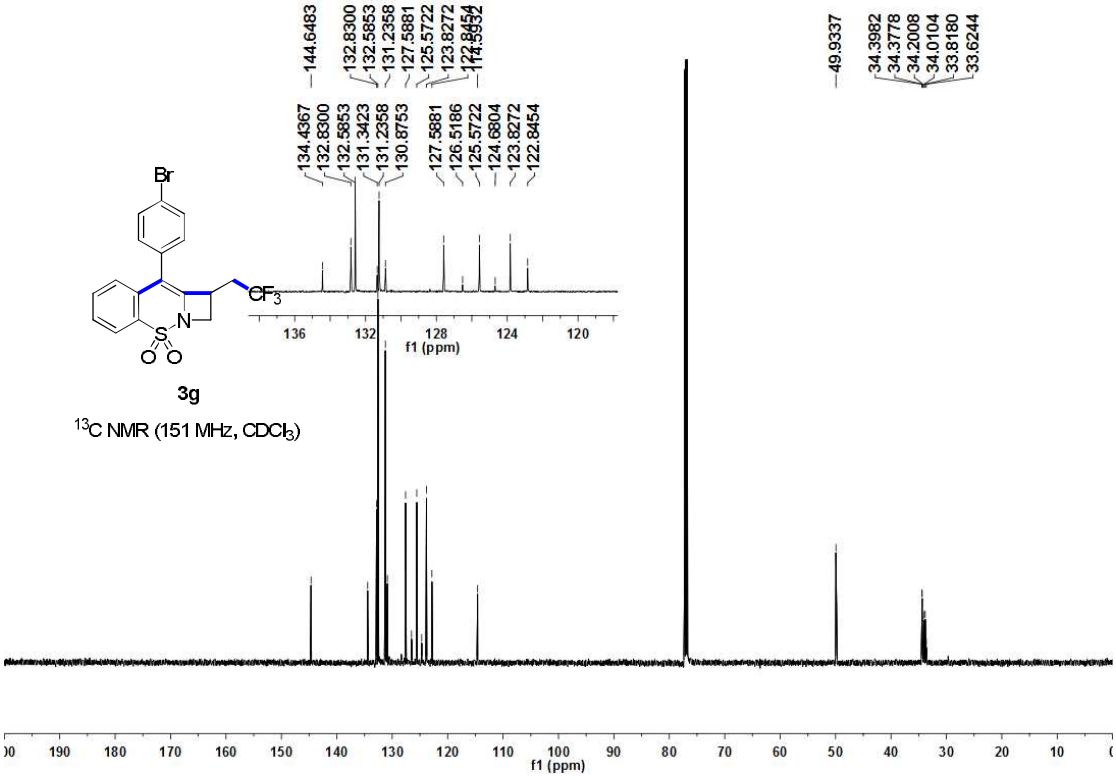
$^{19}$F NMR (565 MHz, $CDCl_3$)


**3g**

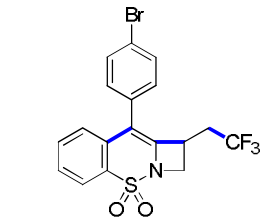
$^{1}$H NMR (600 MHz, $CDCl_3$)




**3g**

$^{13}$C NMR (151 MHz, $CDCl_3$)

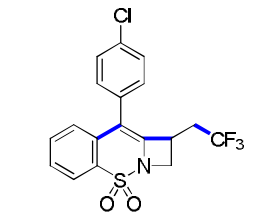



**3g**

$^{19}$F NMR (565 MHz, $CDCl_3$)

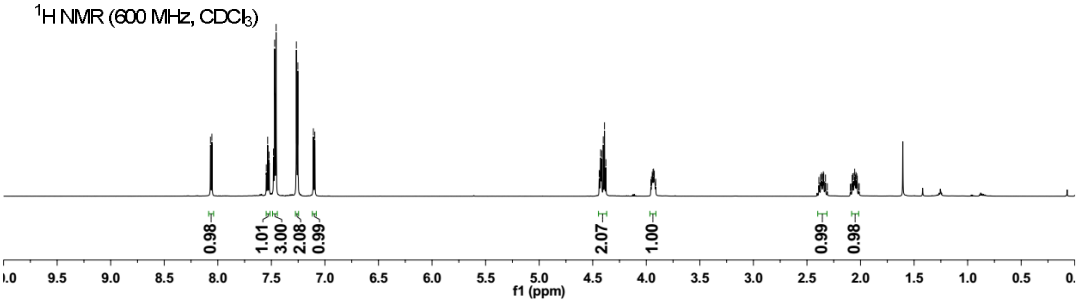


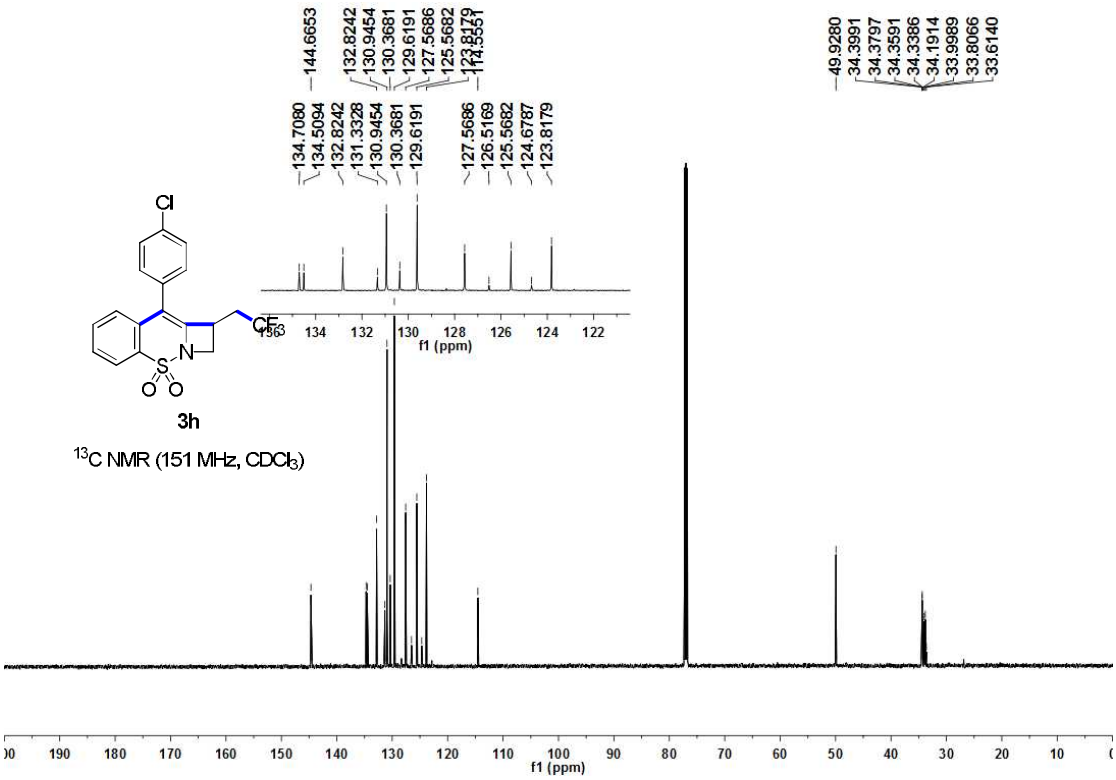





**3h**

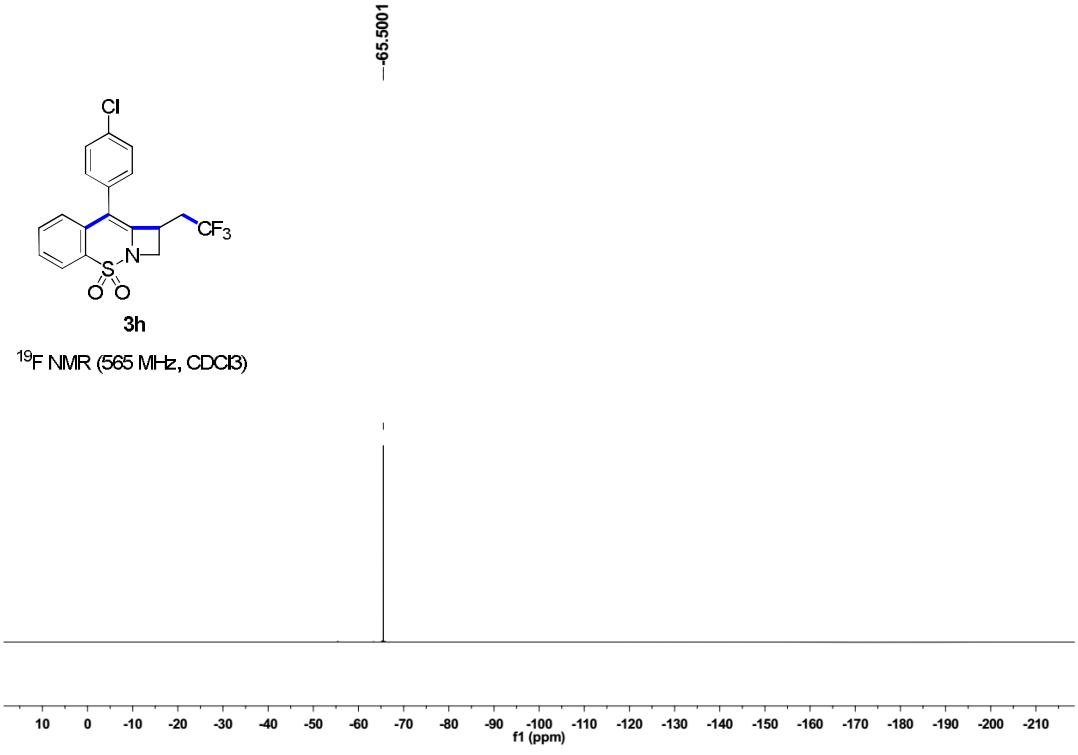
$^{1}$H NMR (600 MHz, $CDCl_3$)





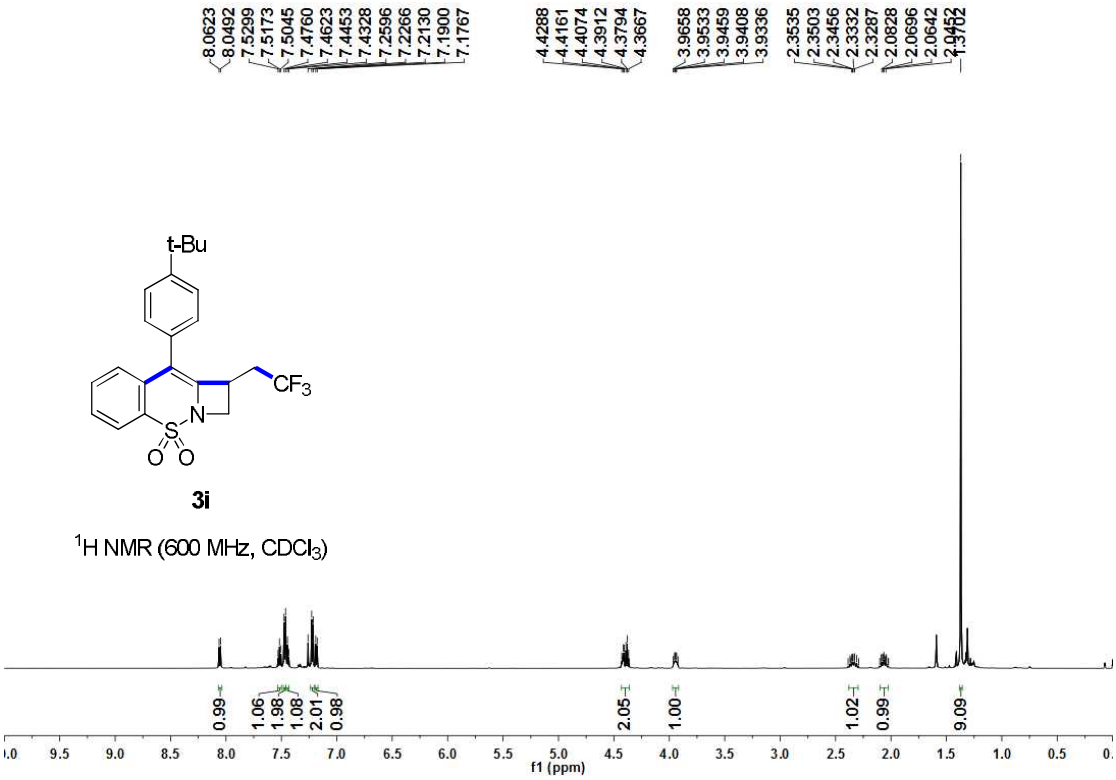

3h

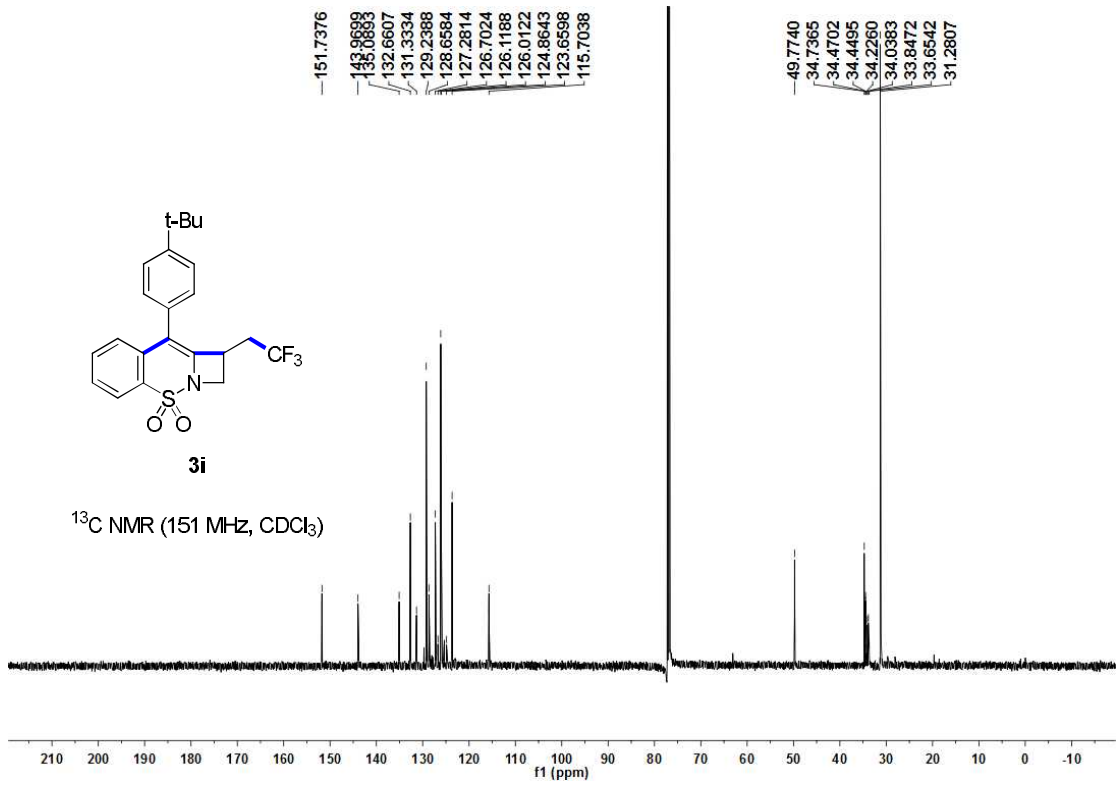
$^{13}$C NMR (151 MHz, $CDCl_3$)

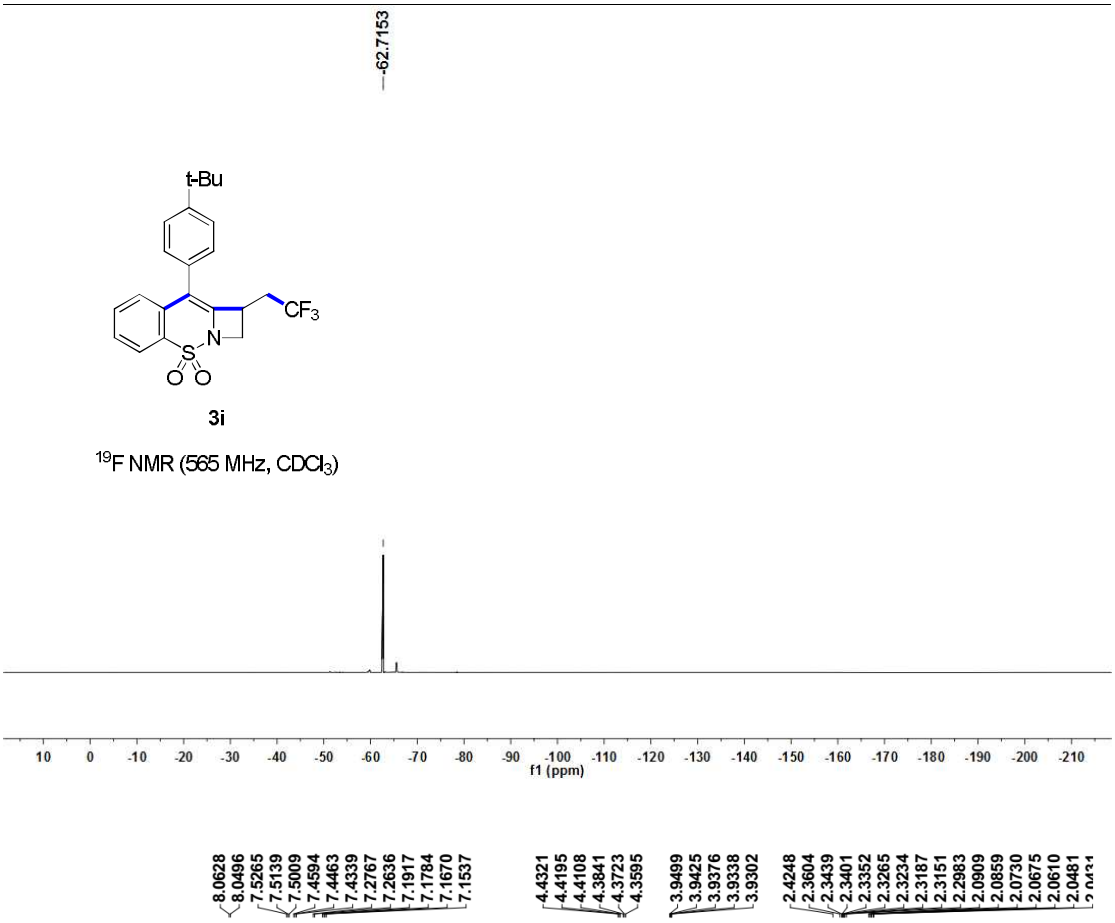



3h

$^{19}$F NMR (565 MHz, CDCl3)


8.0623
8.0492
7.5299
7.5173
7.5045
7.4760
7.4623
7.4453
7.4328
7.2596
7.2266
7.2130
7.1900
7.1767
4.4288
4.4161
4.4074
4.3912
4.3794
4.3667
3.9658
3.9533
3.9459
3.9408
3.9336
2.3535
2.3503
2.3456
2.3332
2.3287
2.0828
2.0696
2.0642
2.0452
1.3702
t-Bu
CF3
N
S
O
O
3i
1H NMR (600 MHz, CDCl3)
0.99
1.06
1.98
1.08
2.01
0.98
2.05
1.00
1.02
0.99
9.09
f1 (ppm)

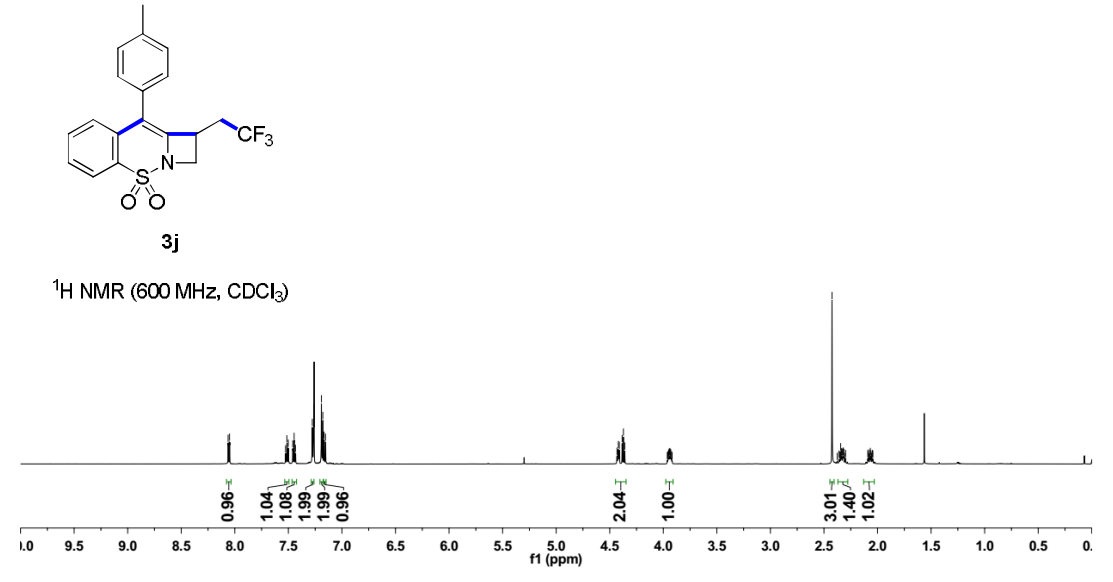

151.7376
143.9699
135.0893
132.6607
131.3334
129.2388
128.6584
127.2814
126.7024
126.1188
126.0122
124.8643
123.6598
115.7038
49.7740
34.7365
34.4702
34.4495
34.2260
34.0383
33.8472
33.6542
31.2807
t-Bu
CF3
N
S
O
O
3i
13C NMR (151 MHz, CDCl3)
f1 (ppm)




**3i**

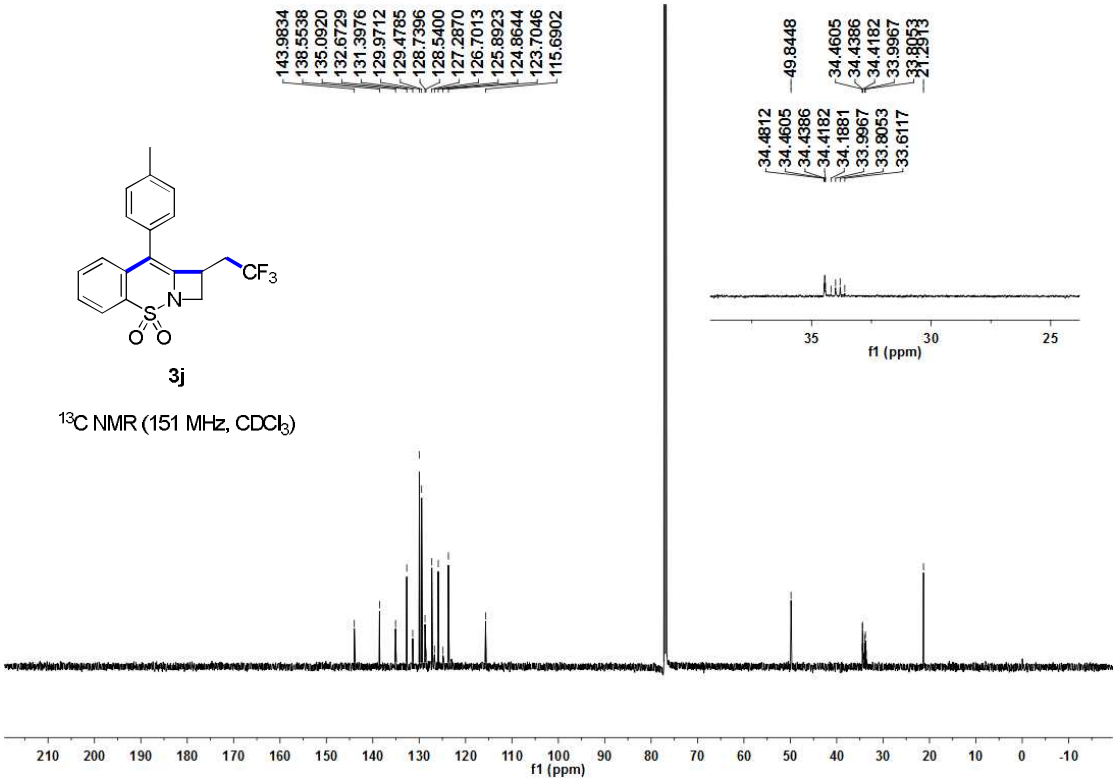
$^{19}$F NMR (565 MHz, $CDCl_3$)





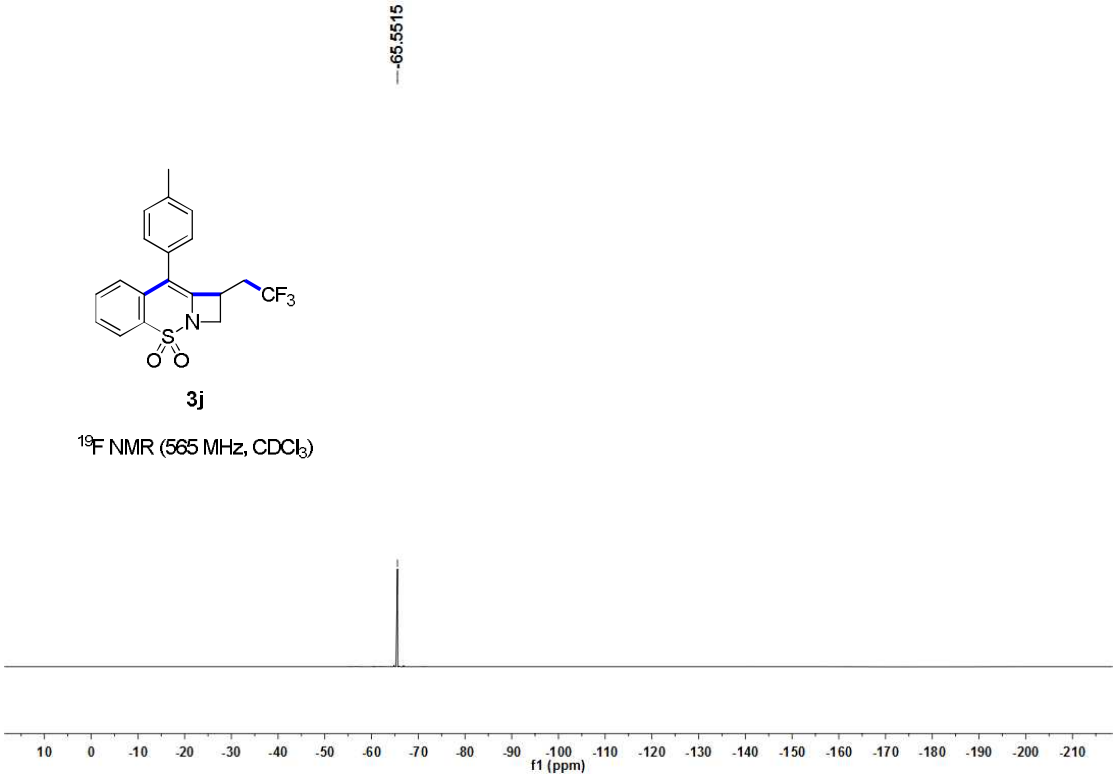

**3j**

$^{1}$H NMR (600 MHz, $CDCl_3$)



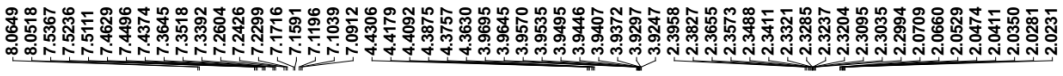

**3j**

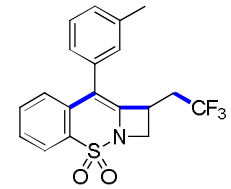
$^{13}C$ NMR (151 MHz, $CDCl_3$)




**3j**

$^{19}F$ NMR (565 MHz, $CDCl_3$)



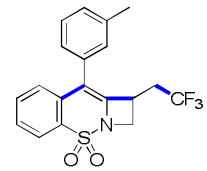




**3k**

$^{1}$H NMR (600 MHz, $CDCl_3$)

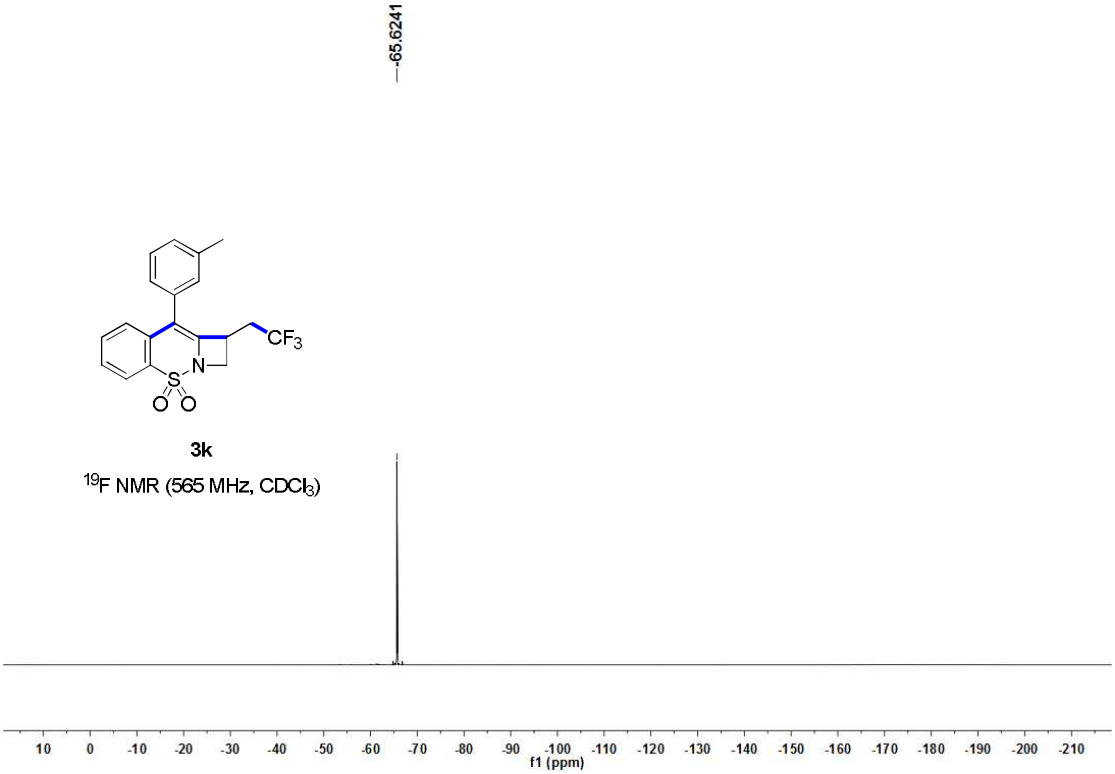




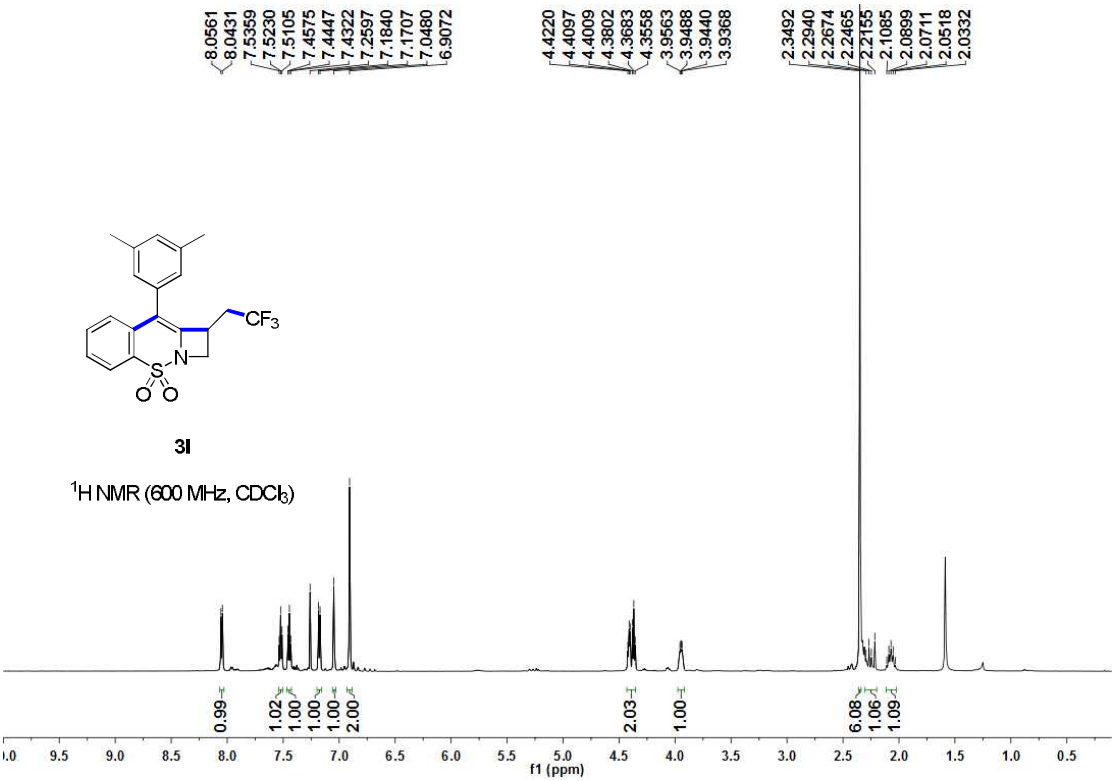

**3k**

$^{13}$C NMR (151 MHz, $CDCl_3$)



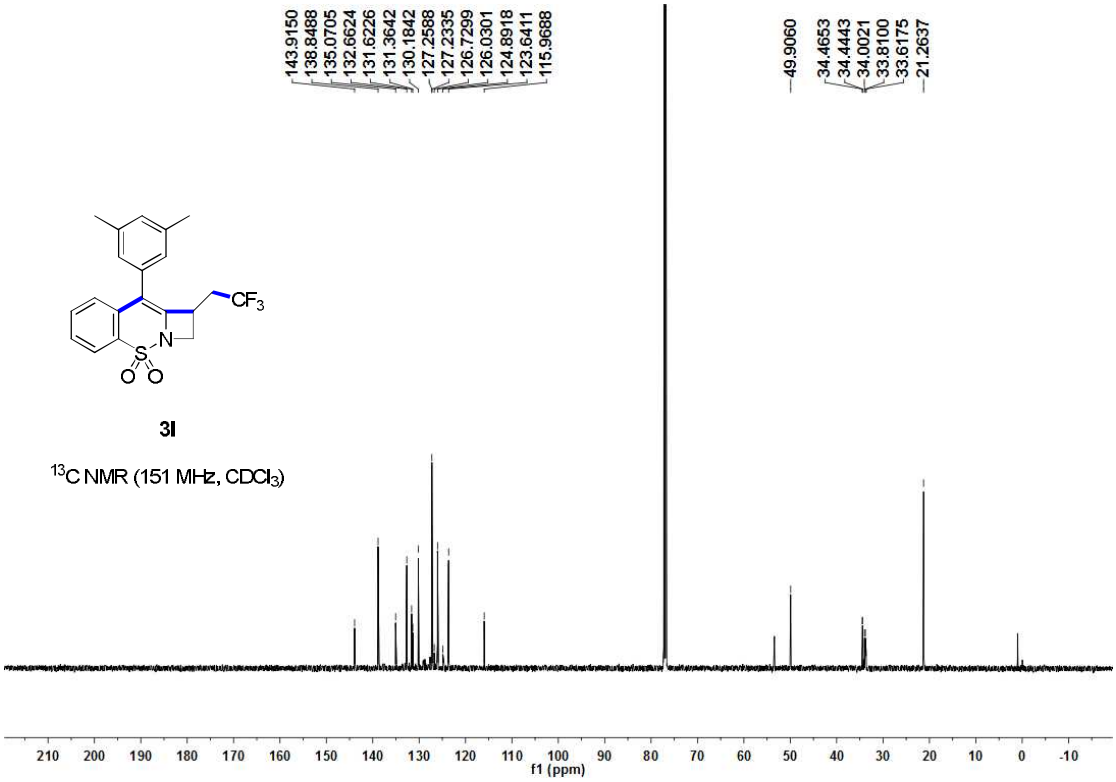

**3k**

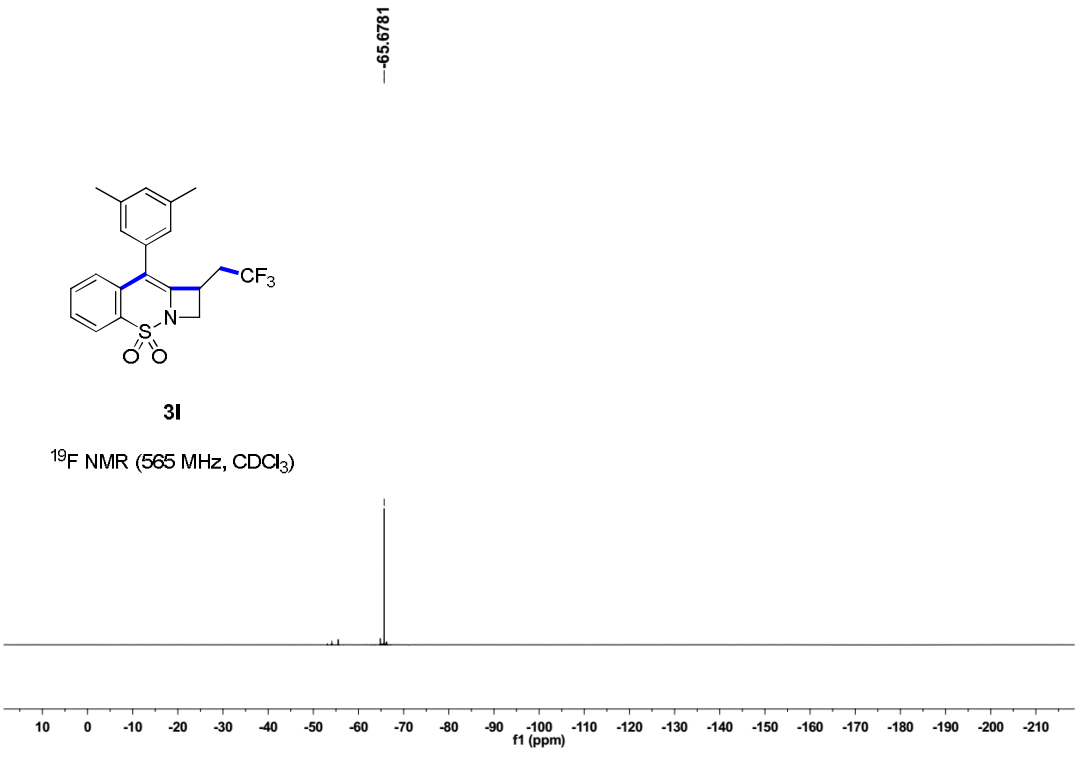
$^{19}$F NMR (565 MHz, $CDCl_3$)

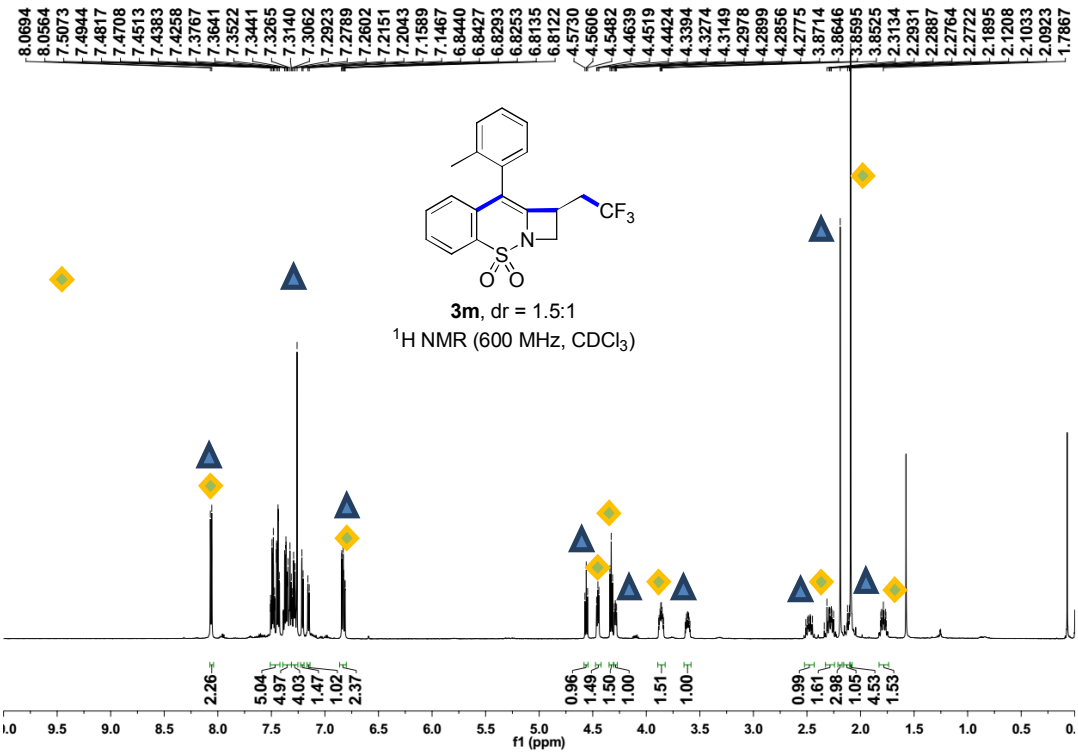


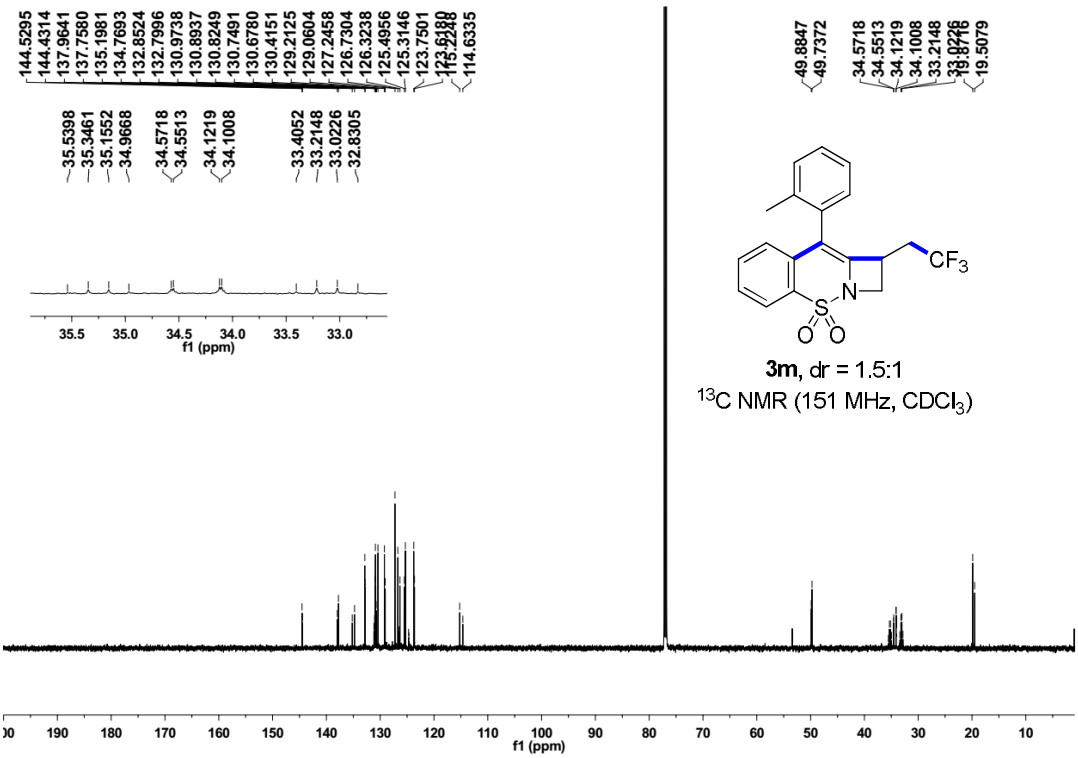

**3l**

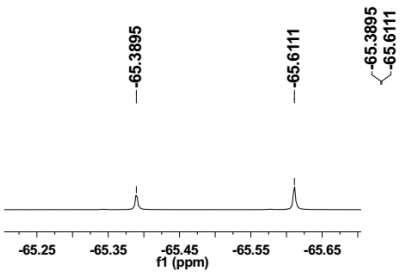
$^{1}$H NMR (600 MHz, $CDCl_3$)

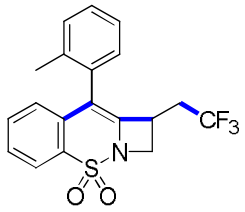

143.9150
138.8488
135.0705
132.6624
131.6226
131.3642
130.1842
127.2588
127.2335
126.7299
126.0301
124.8918
123.6411
115.9688
49.9060
34.4653
34.4443
34.0021
33.8100
33.6175
21.2637
CF3
N
S
O
O
3l
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-65.6781
CF3
N
S
O
O
3l
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


CF3
N
S
O
O
3m, dr = 1.5:1
1H NMR (600 MHz, CDCl3)
f1 (ppm)

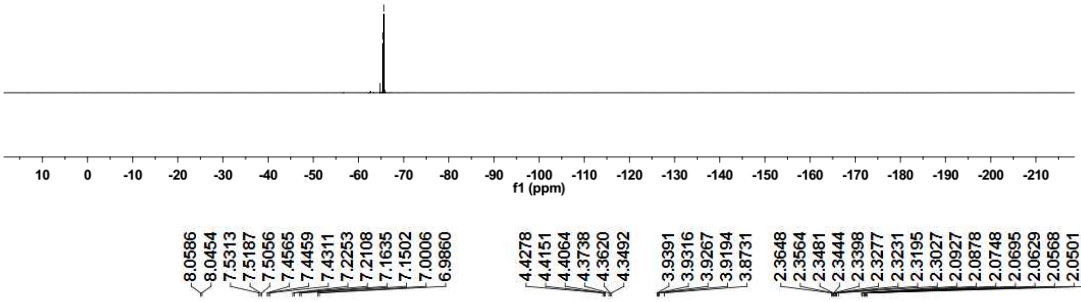

CF3
N
S
O
O
3m, dr = 1.5:1
13C NMR (151 MHz, CDCl3)
f1 (ppm)



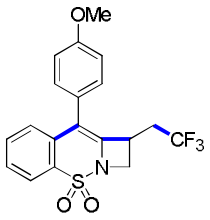

**3m**, dr = 1.5:1

$^{19}$F NMR (565 MHz, $CDCl_3$)



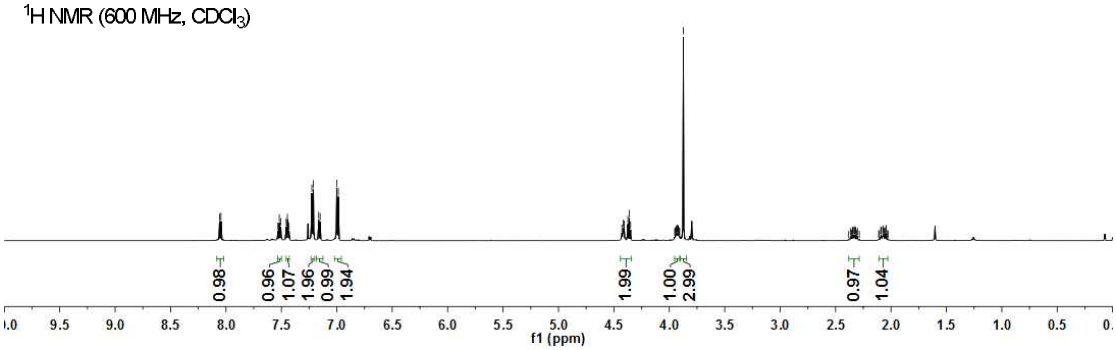






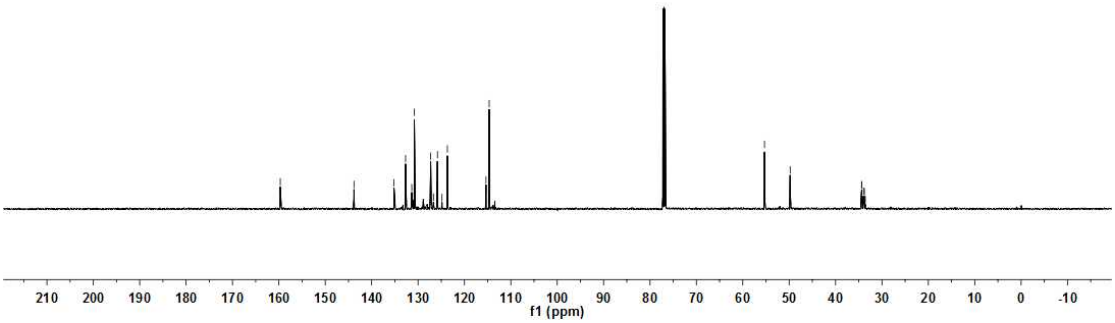

**3n**

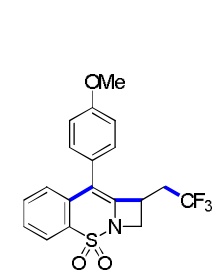
$^{1}$H NMR (600 MHz, $CDCl_3$)




**3n**

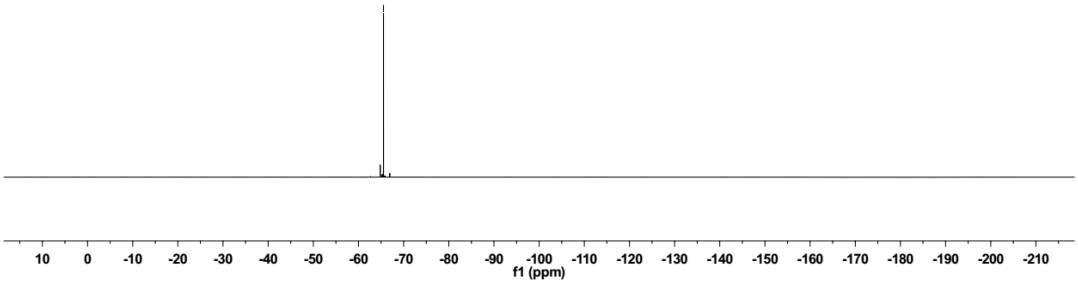
$^{13}C$ NMR (151 MHz, $CDCl_3$)

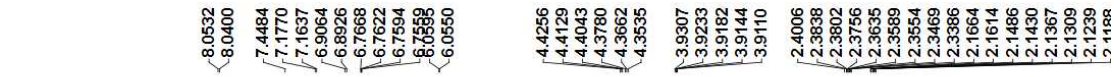


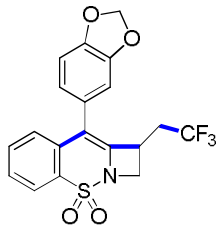




**3n**

$^{19}F$ NMR (565 MHz, $CDCl_3$)

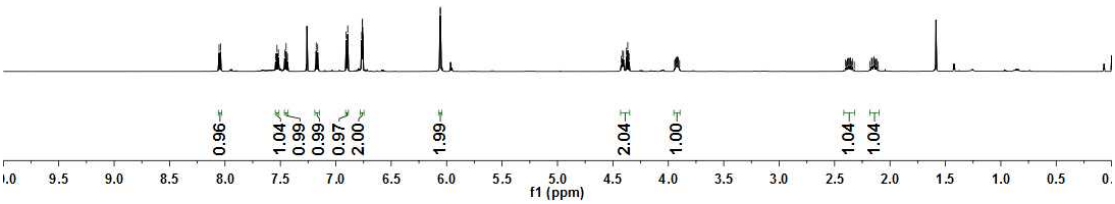


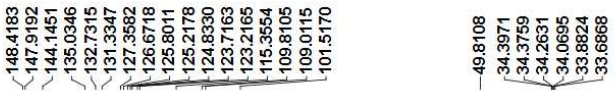


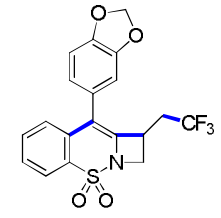




**3o**

$^{1}$H NMR (600 MHz, $CDCl_3$)

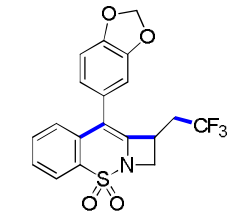



**3o**

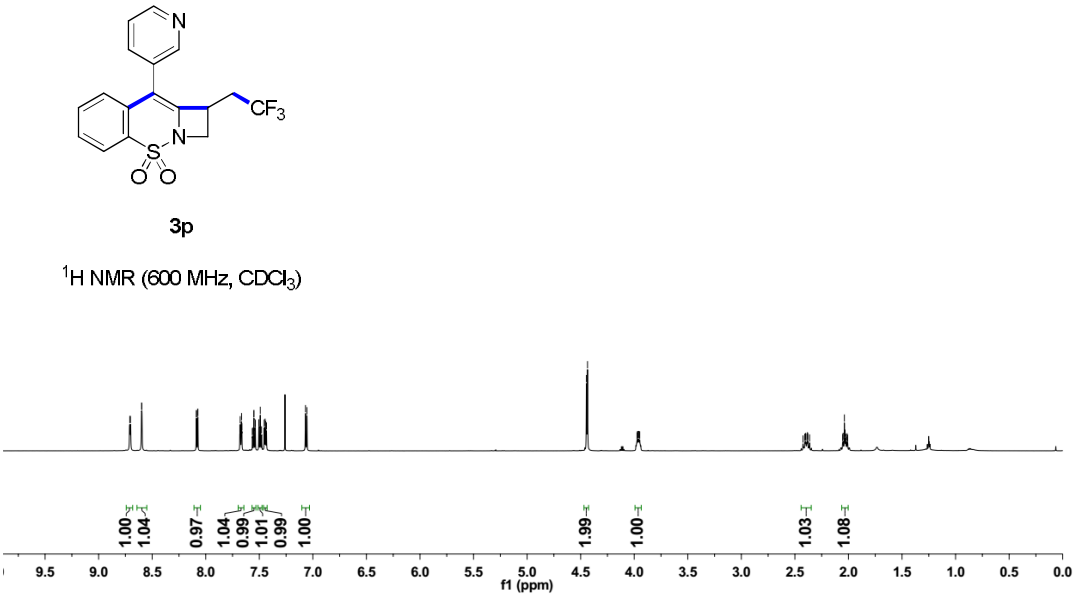
$^{13}$C NMR (151 MHz, $CDCl_3$)



3o

$^{19}$F NMR (565 MHz, $CDCl_3$)

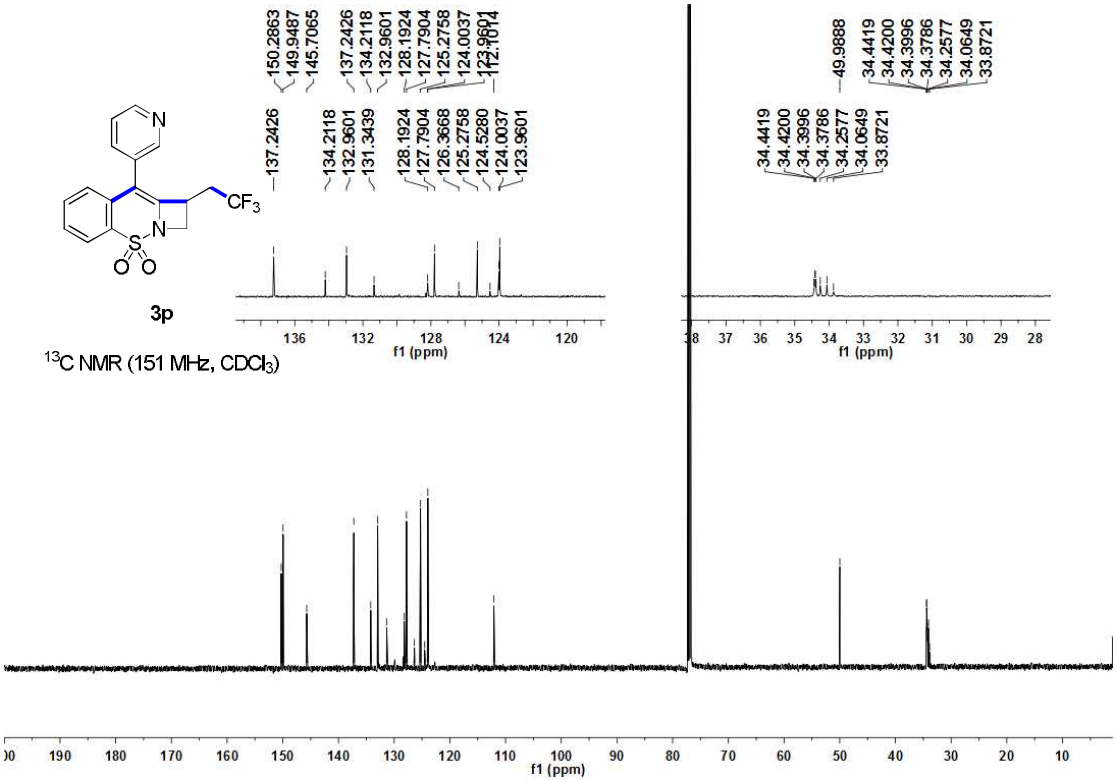


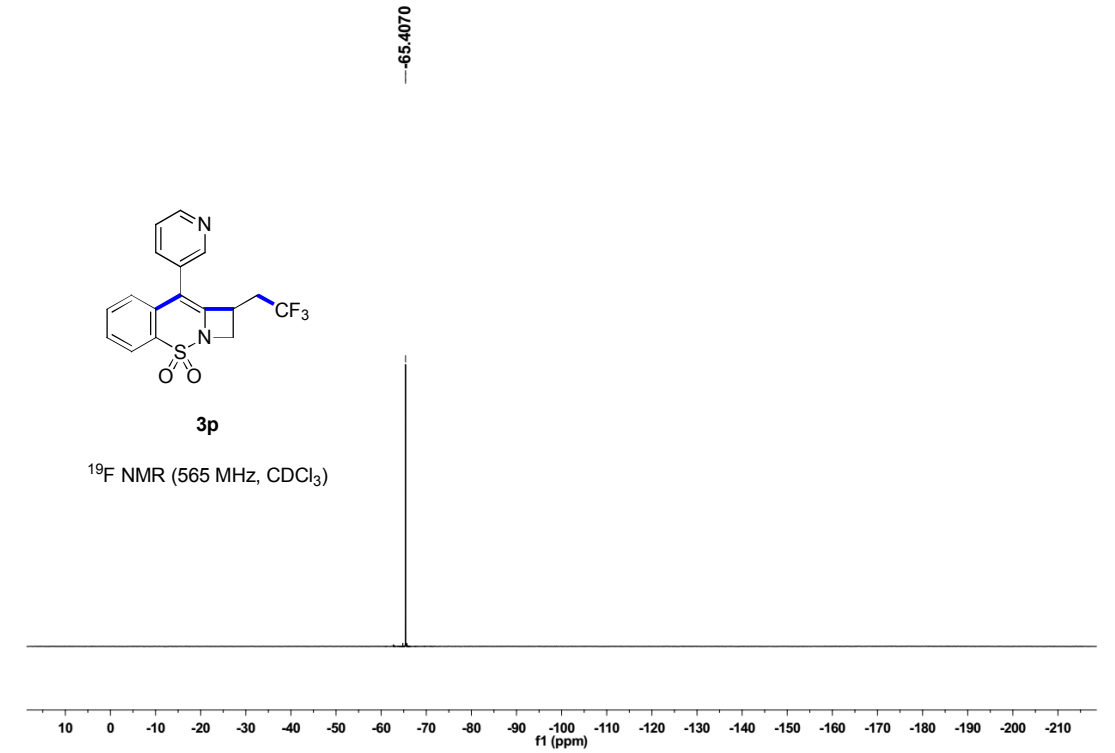



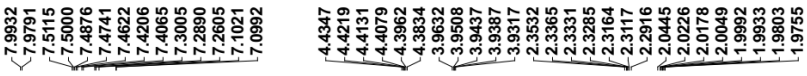


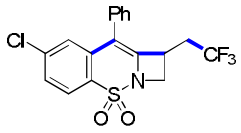

3p

$^{1}$H NMR (600 MHz, $CDCl_3$)


150.2863
149.9487
145.7065
137.2426
134.2118
132.9601
128.1924
127.7904
125.2758
124.0037
123.9601
112.1014
49.9888
34.4419
34.4200
34.3996
34.3786
34.2577
34.0649
33.8721
CF3
N
S
O
O
3p
13C NMR (151 MHz, CDCl3)
f1 (ppm)

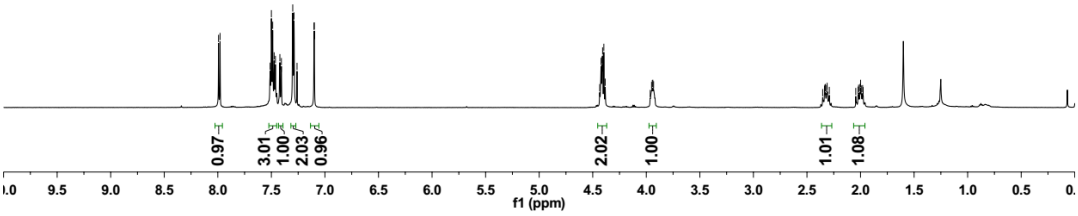

-65.4070
CF3
N
S
O
O
3p
19F NMR (565 MHz, CDCl3)
f1 (ppm)



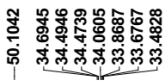



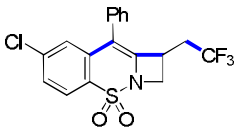

3q

$^{1}$H NMR (600 MHz, $CDCl_3$)



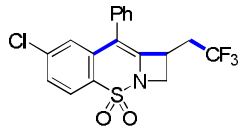





3q

$^{13}$C NMR (151 MHz, $CDCl_3$)

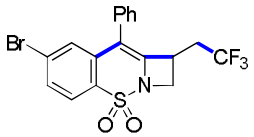



**3q**

$^{19}$F NMR (565 MHz, $CDCl_3$)

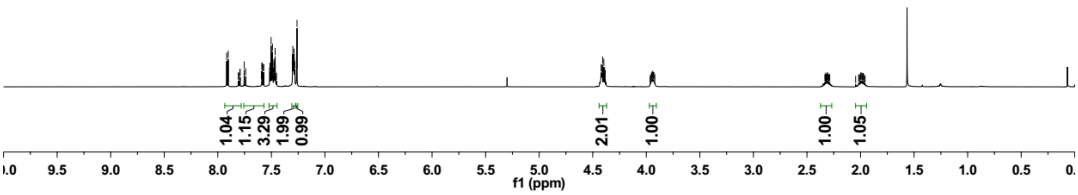


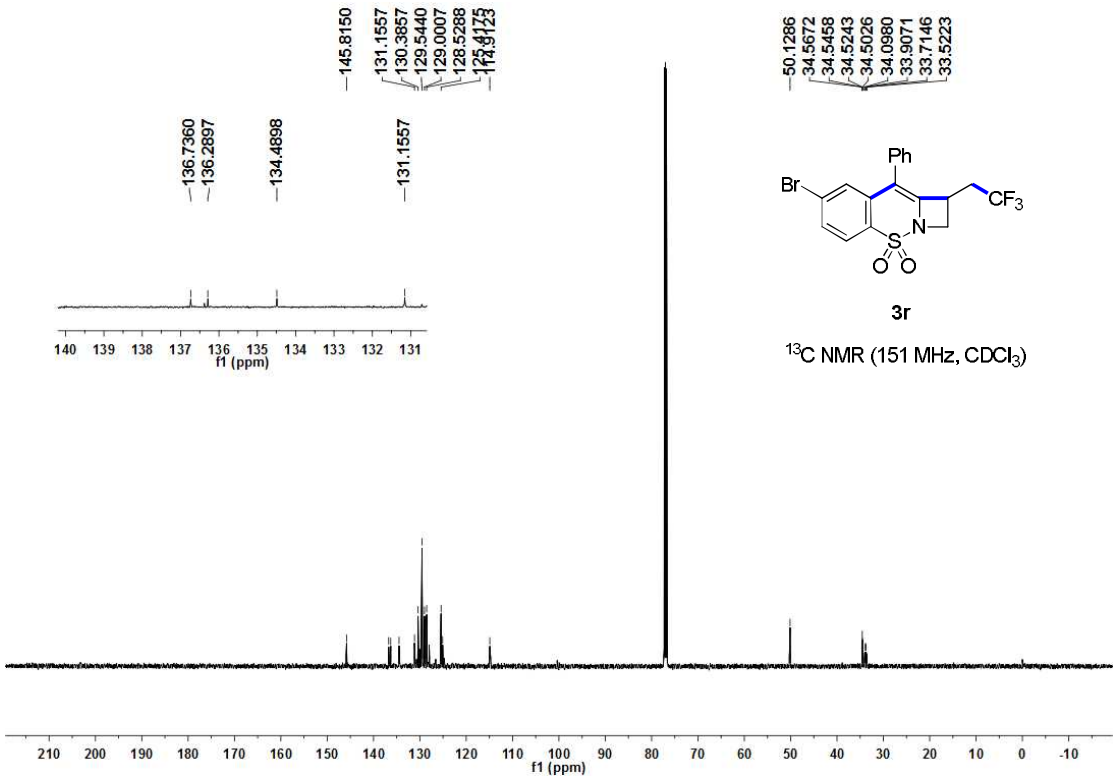





**3r**

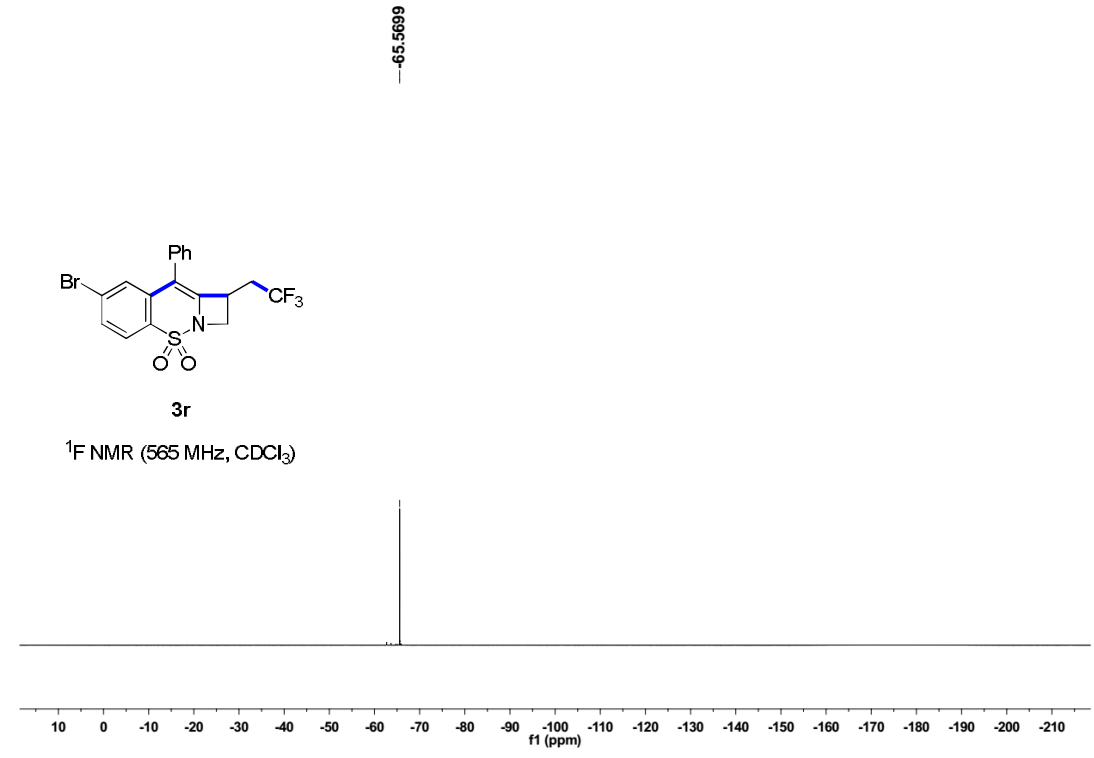
$^{1}$H NMR (600 MHz, $CDCl_3$)





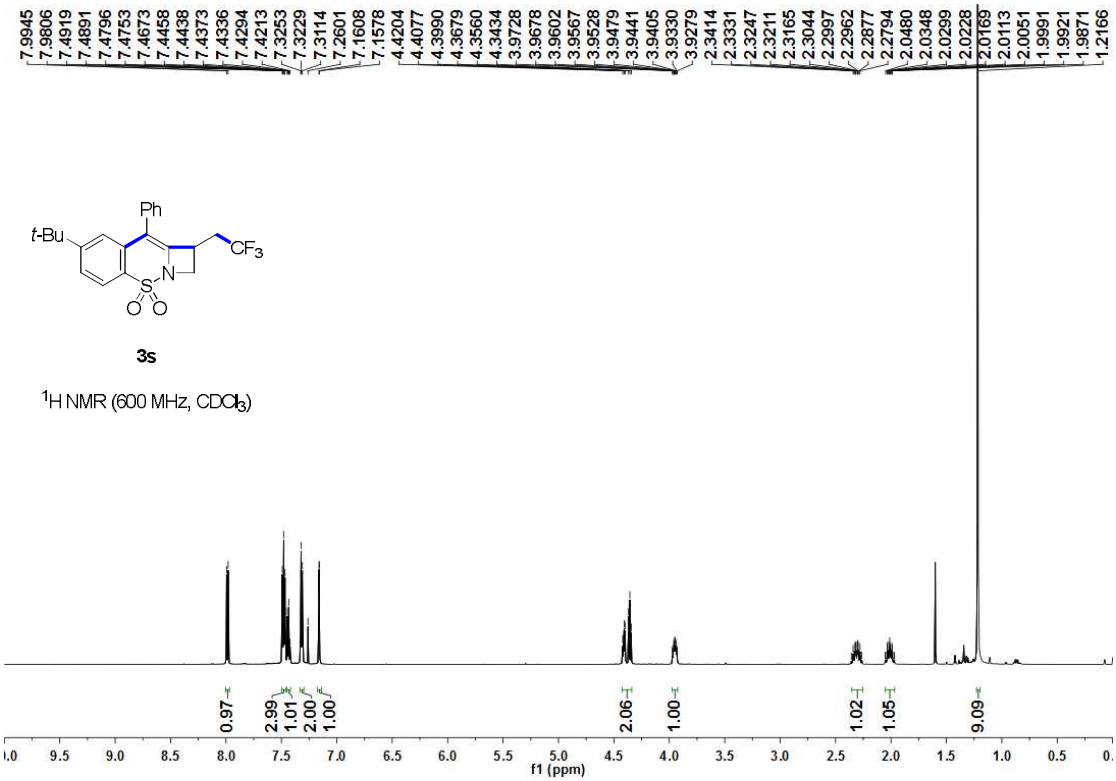

**3r**

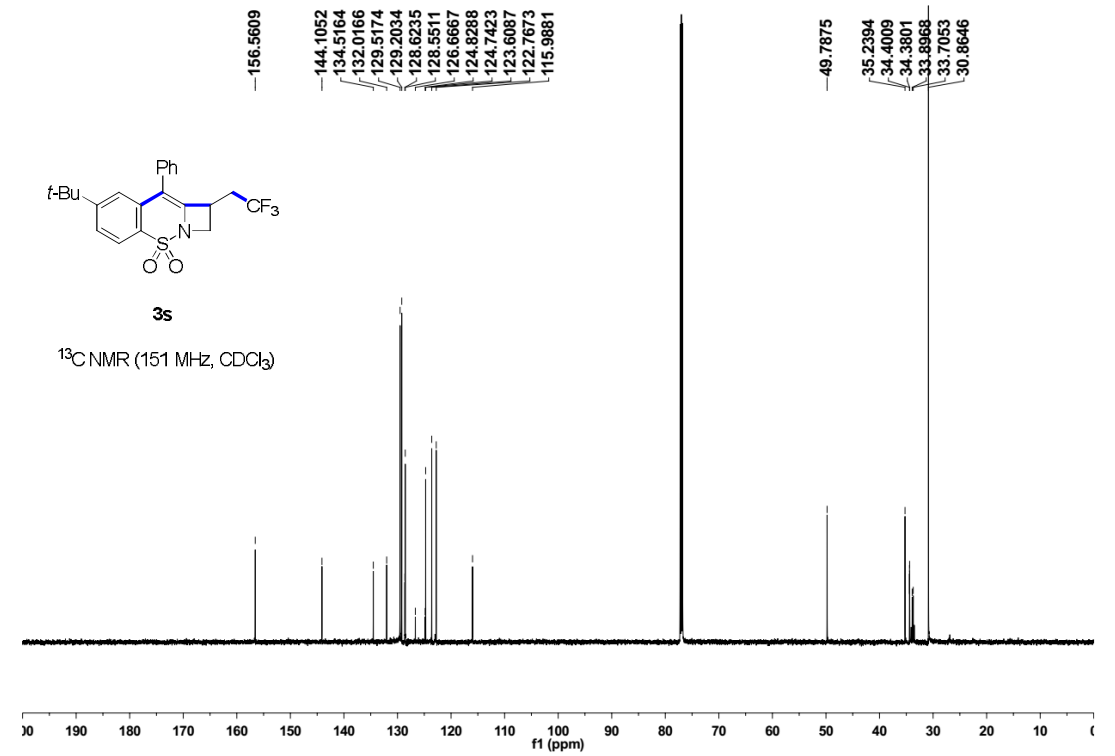
$^{13}C$ NMR (151 MHz, $CDCl_3$)

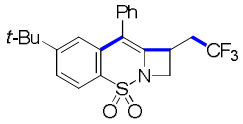



**3r**

$^{1}F$ NMR (565 MHz, $CDCl_3$)


7.9945
7.9806
7.4919
7.4891
7.4796
7.4753
7.4673
7.4458
7.4438
7.4373
7.4336
7.4294
7.4213
7.3253
7.3229
7.3114
7.2601
7.1608
7.1578
4.4204
4.4077
4.3990
4.3679
4.3560
4.3434
3.9728
3.9678
3.9602
3.9567
3.9528
3.9479
3.9441
3.9405
3.9330
3.9279
2.3414
2.3331
2.3247
2.3211
2.3165
2.3044
2.2997
2.2962
2.2877
2.2794
2.0480
2.0348
2.0299
2.0228
2.0169
2.0113
2.0051
1.9991
1.9921
1.9871
1.2166
Ph
t-Bu
CF3
N
S
O
O
3s
1H NMR (600 MHz, CDCl3)
0.97
2.99
1.01
2.00
1.00
2.06
1.00
1.02
1.05
9.09
f1 (ppm)


156.5609
144.1052
134.5164
132.0166
129.5174
129.2034
128.6235
128.5511
126.6667
124.8288
124.7423
123.6087
122.7673
115.9881
49.7875
35.2394
34.4009
34.3801
33.8968
33.7053
30.8646
Ph
t-Bu
CF3
N
S
O
O
3s
13C NMR (151 MHz, CDCl3)
f1 (ppm)



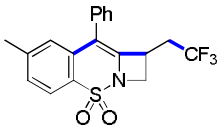

**3s**

$^{19}$F NMR (565 MHz, $CDCl_3$)



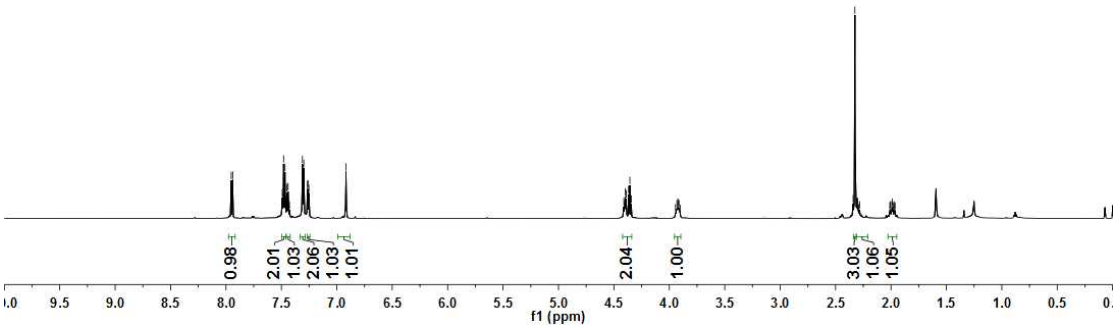


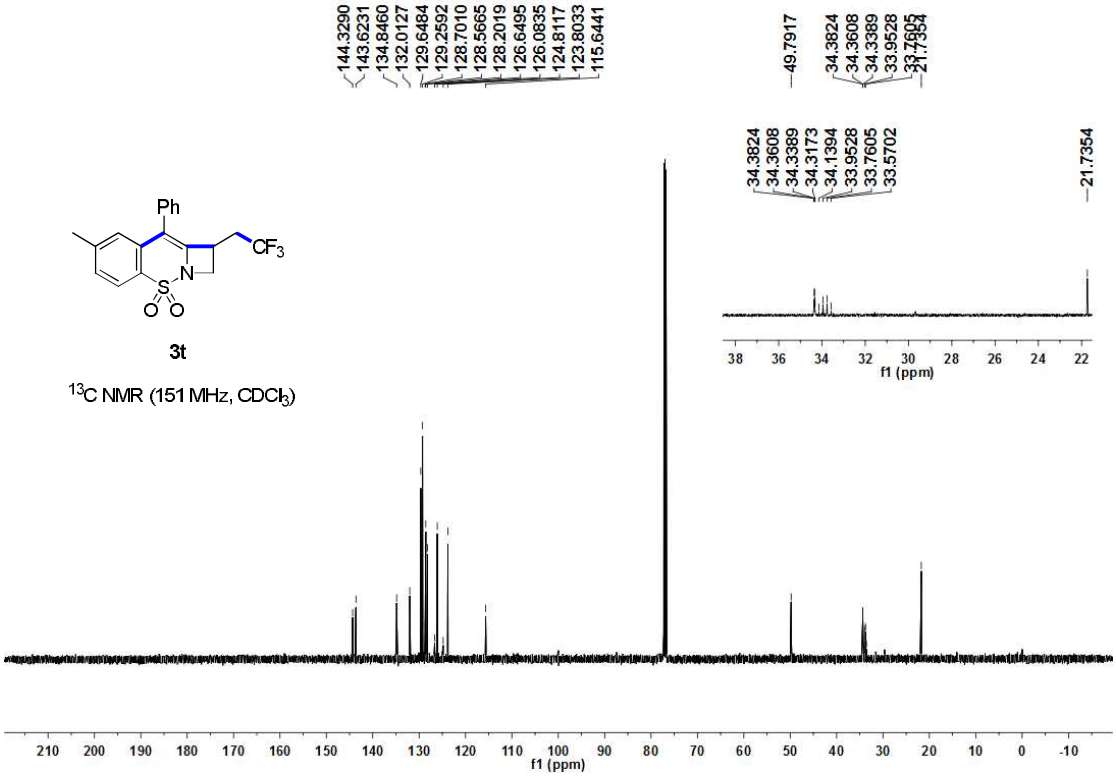


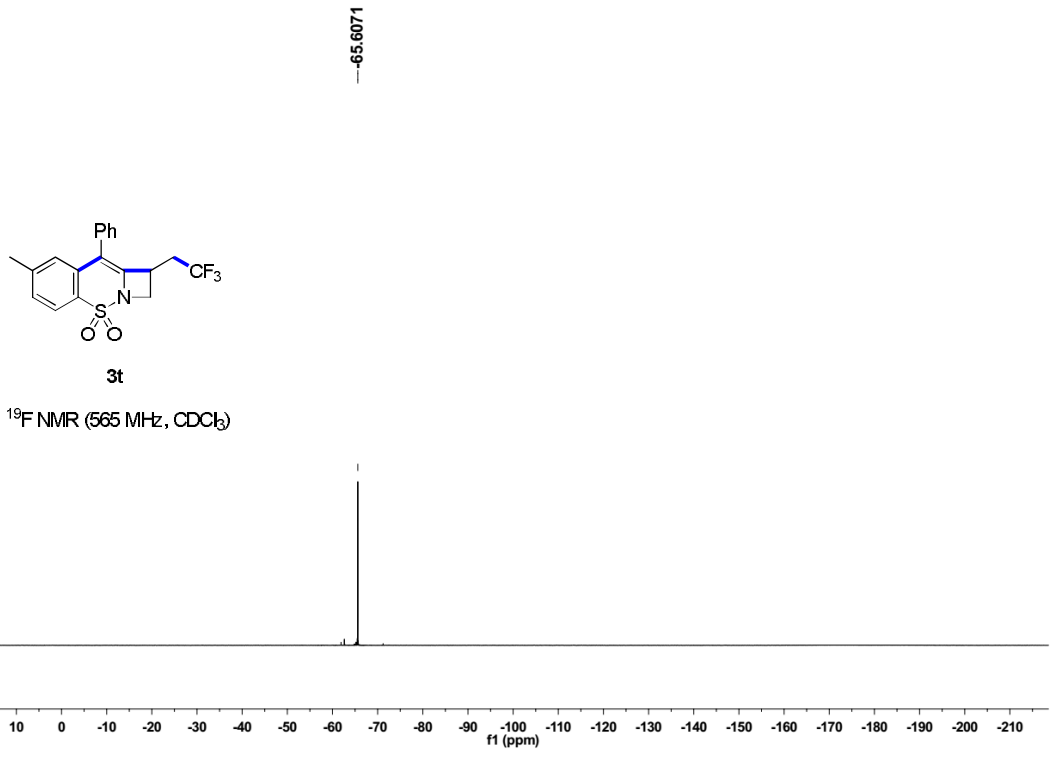


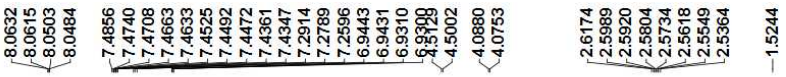

**3t**

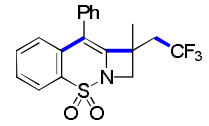
$^{1}$H NMR (600 MHz, $CDCl_3$)




144.3290
143.6231
134.8460
132.0127
129.6484
129.2592
128.7010
128.5665
128.2019
126.6495
126.0835
124.8117
123.8033
115.6441
49.7917
34.3824
34.3608
34.3389
33.9528
33.7605
21.7354
Ph
CF3
N
S
O
O
3t
13C NMR (151 MHz, CDCl3)
f1 (ppm)

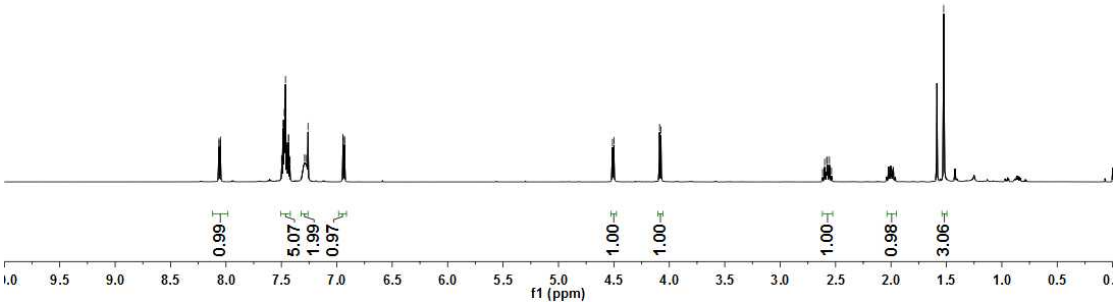

-65.6071
Ph
CF3
N
S
O
O
3t
19F NMR (565 MHz, CDCl3)
f1 (ppm)

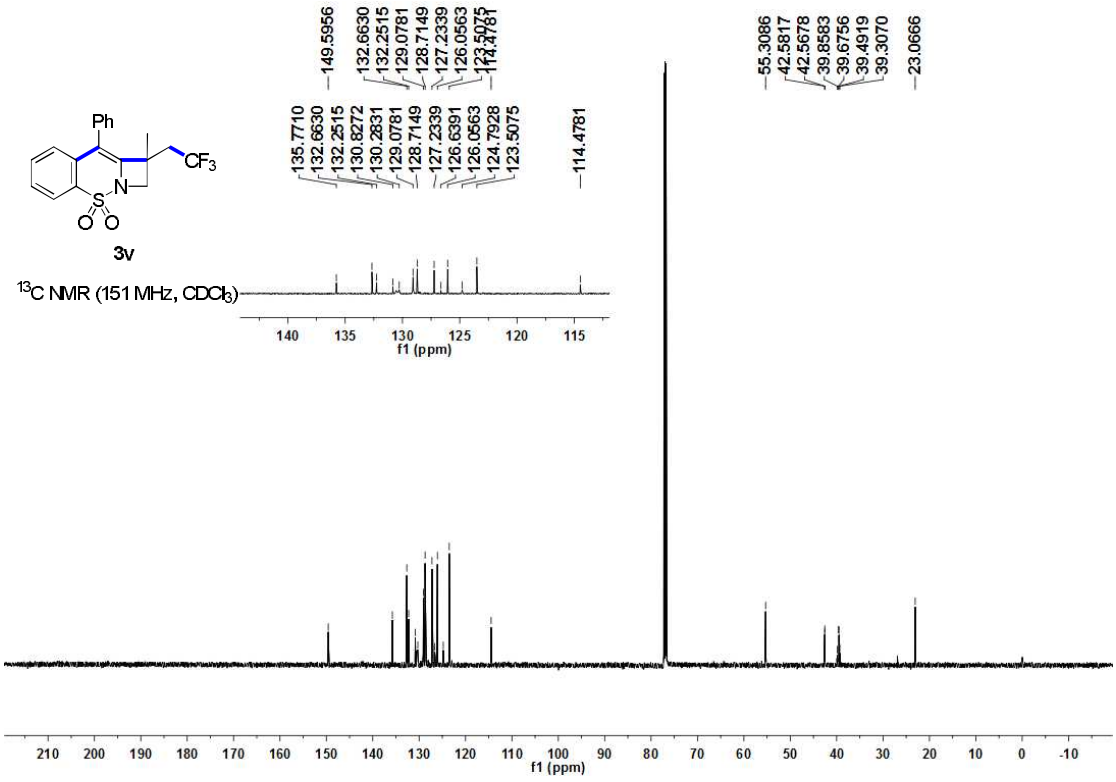



**3v**

$^{1}$H NMR (600 MHz, $CDCl_3$)



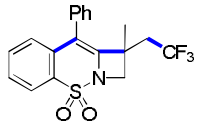







**3v**

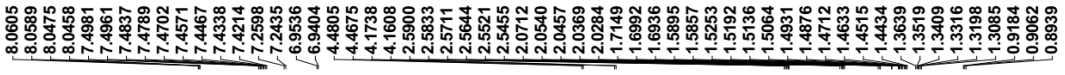
$^{13}$C NMR (151 MHz, $CDCl_3$)

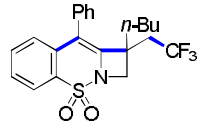


**3v**

$^{19}$F NMR (565 MHz, $CDCl_3$)

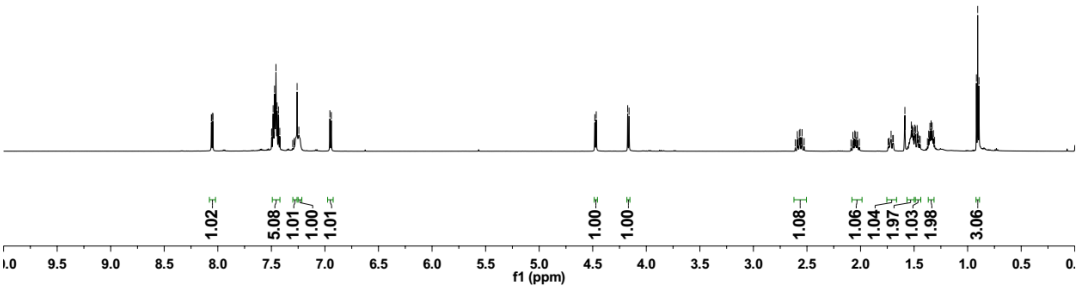


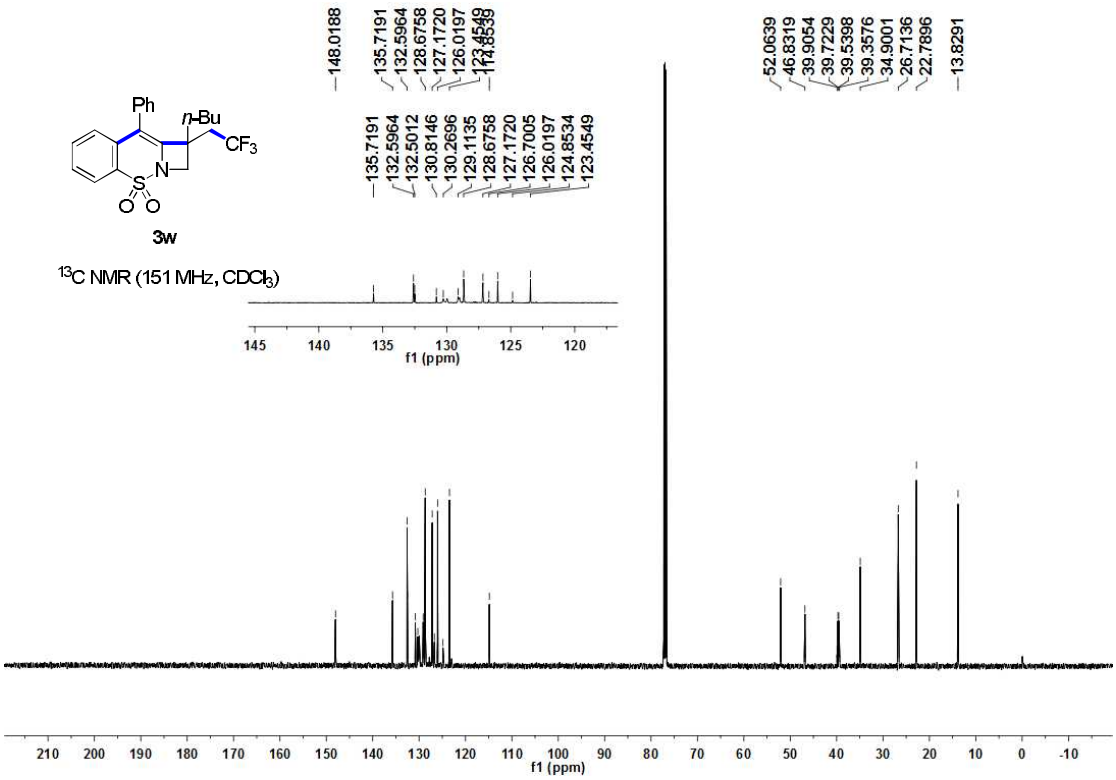



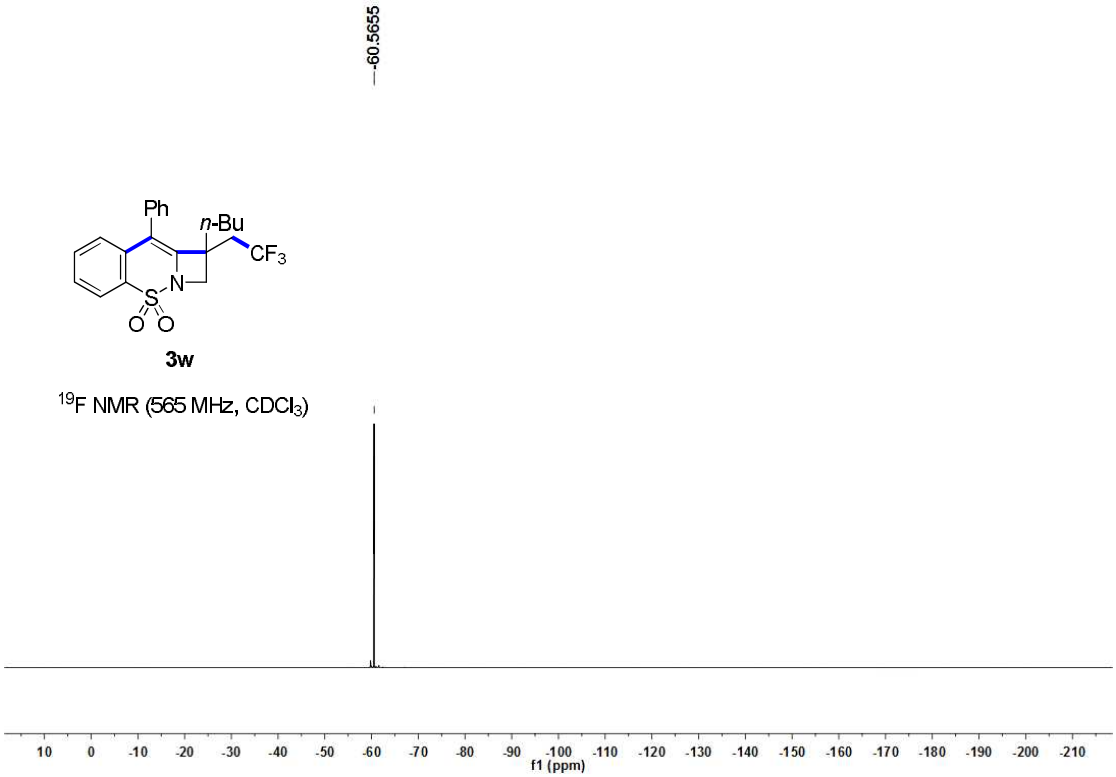



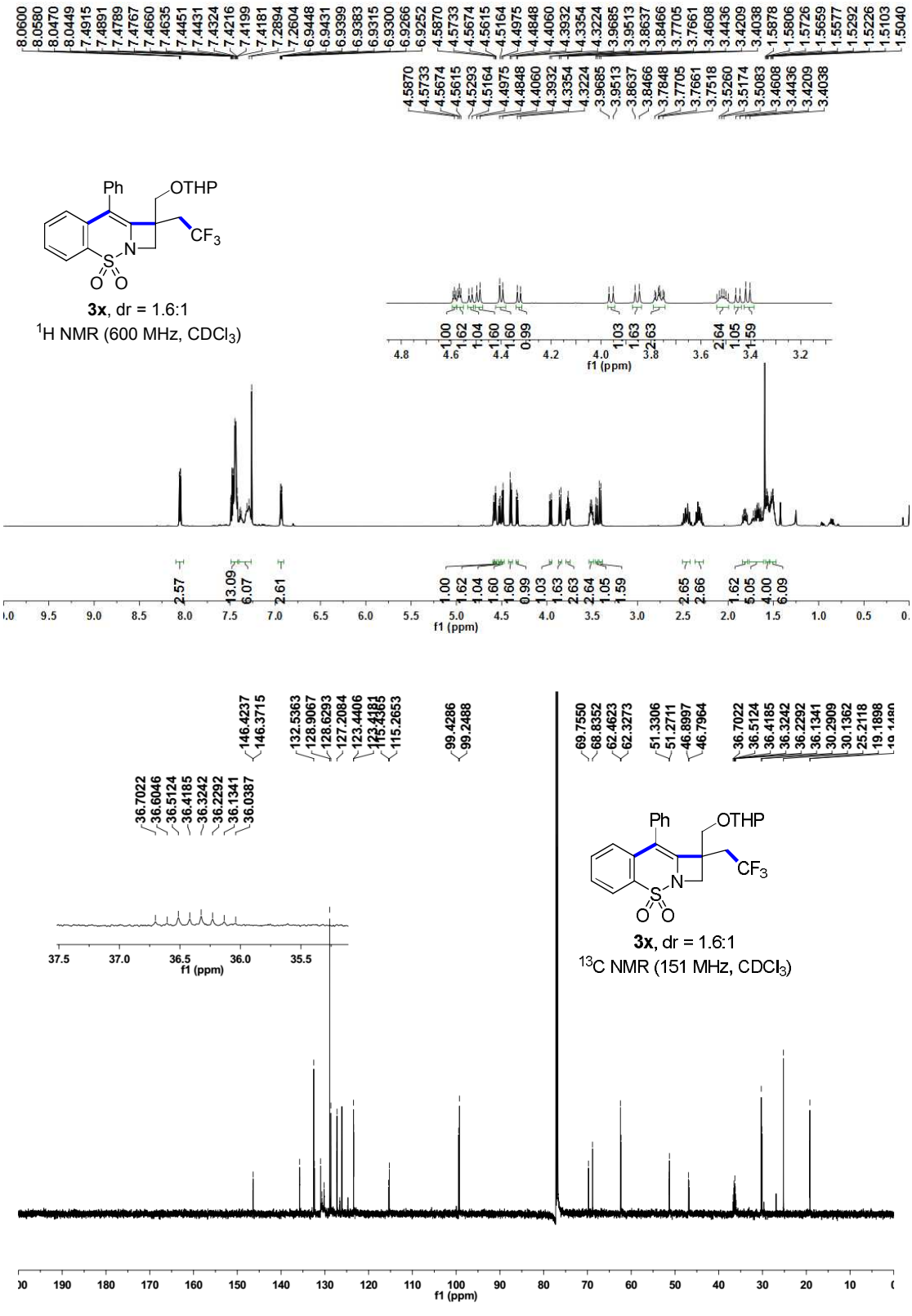
**3w**

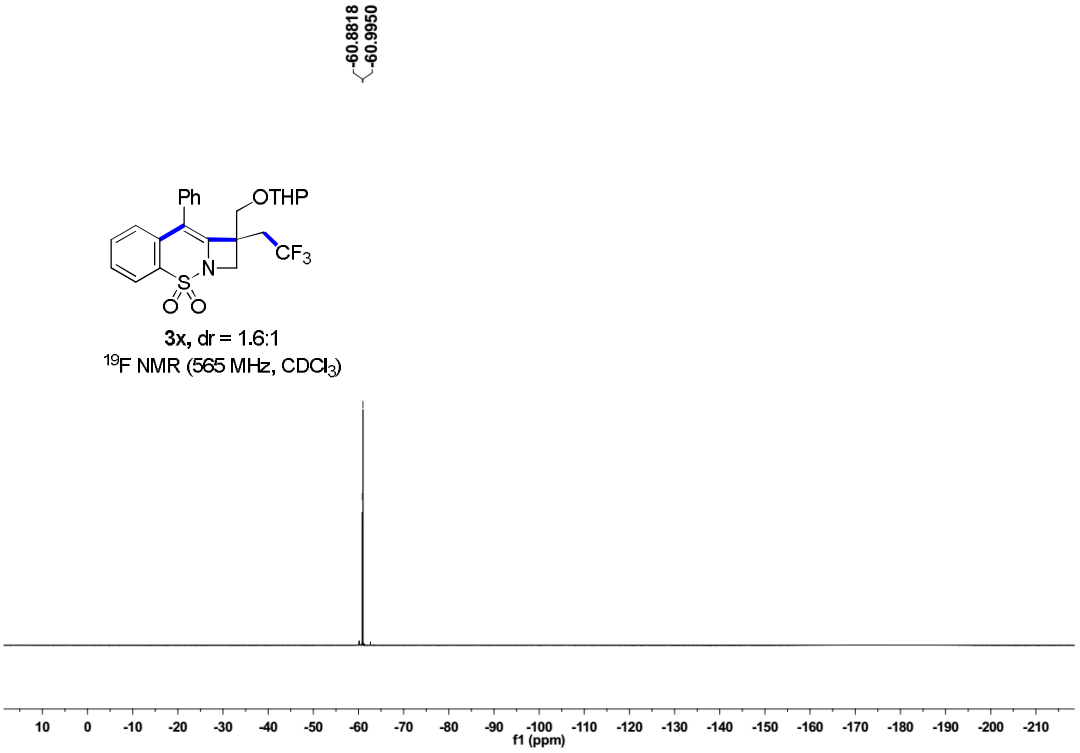
$^{1}$H NMR (600 MHz, $CDCl_3$)




148.0188
135.7191
132.5964
128.6758
127.1720
126.0197
52.0639
46.8319
39.9054
39.7229
39.5398
39.3576
34.9001
26.7136
22.7896
13.8291
Ph
n-Bu
CF3
N
S
O
O
3w
13C NMR (151 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

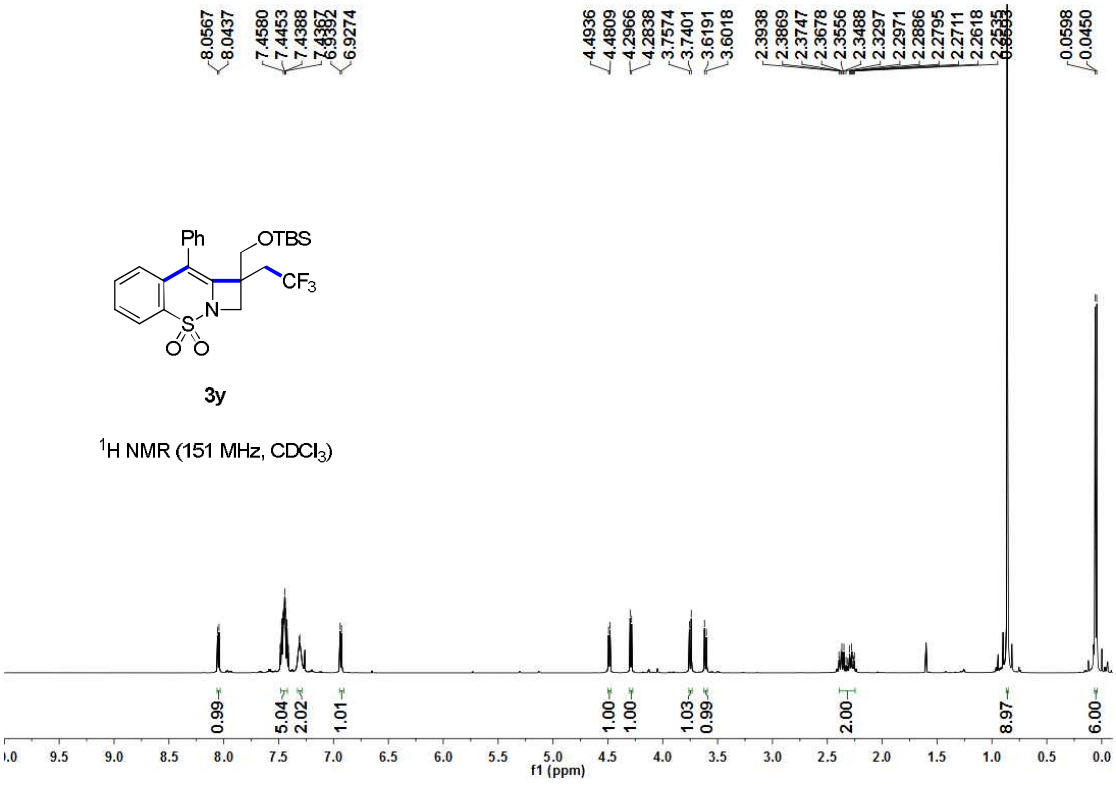

-60.5655
Ph
n-Bu
CF3
N
S
O
O
3w
19F NMR (565 MHz, CDCl3)
f1 (ppm)


Ph
OTHP
CF3
N
S
O O
3x, dr = 1.6:1
1H NMR (600 MHz, CDCl3)
f1 (ppm)
3x, dr = 1.6:1
13C NMR (151 MHz, CDCl3)
f1 (ppm)



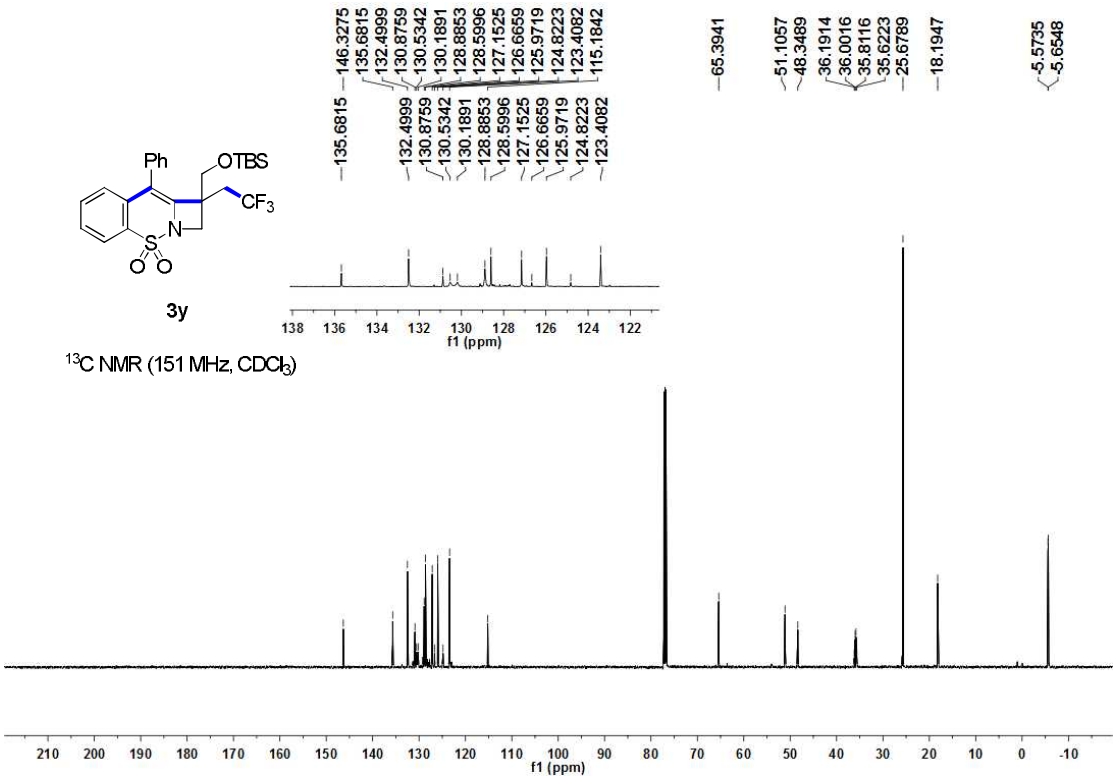

**3x**, dr = 1.6:1

$^{19}$F NMR (565 MHz, $CDCl_3$)

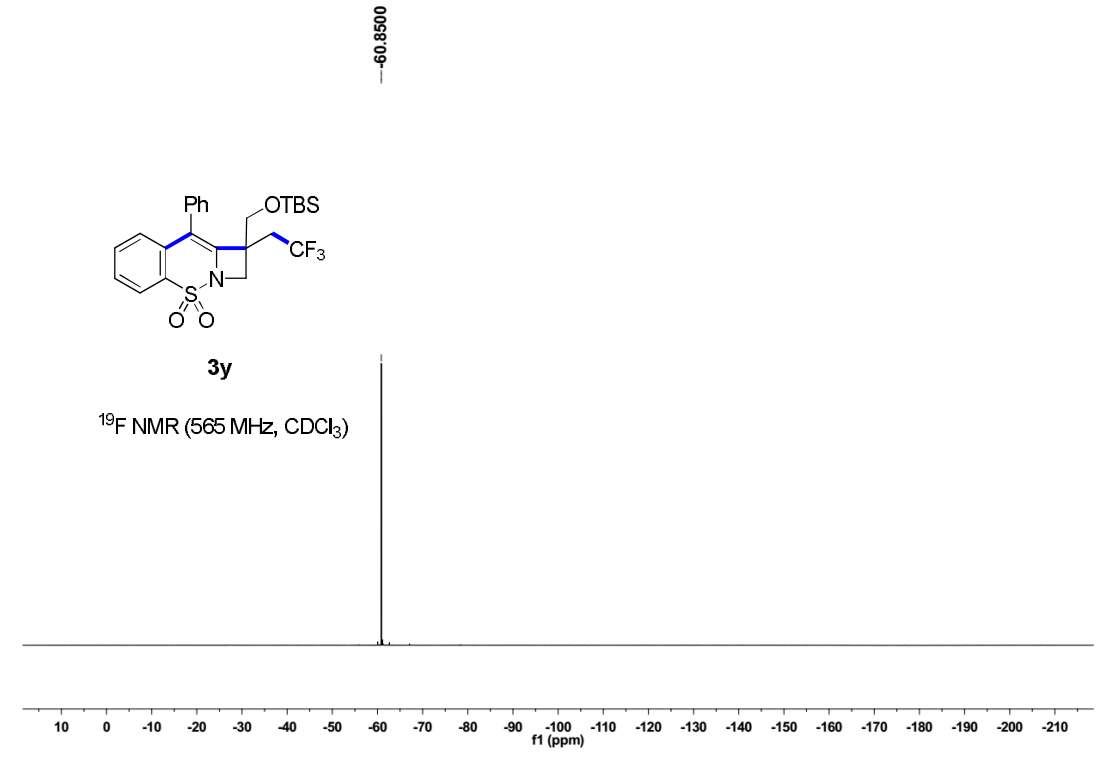



**3y**

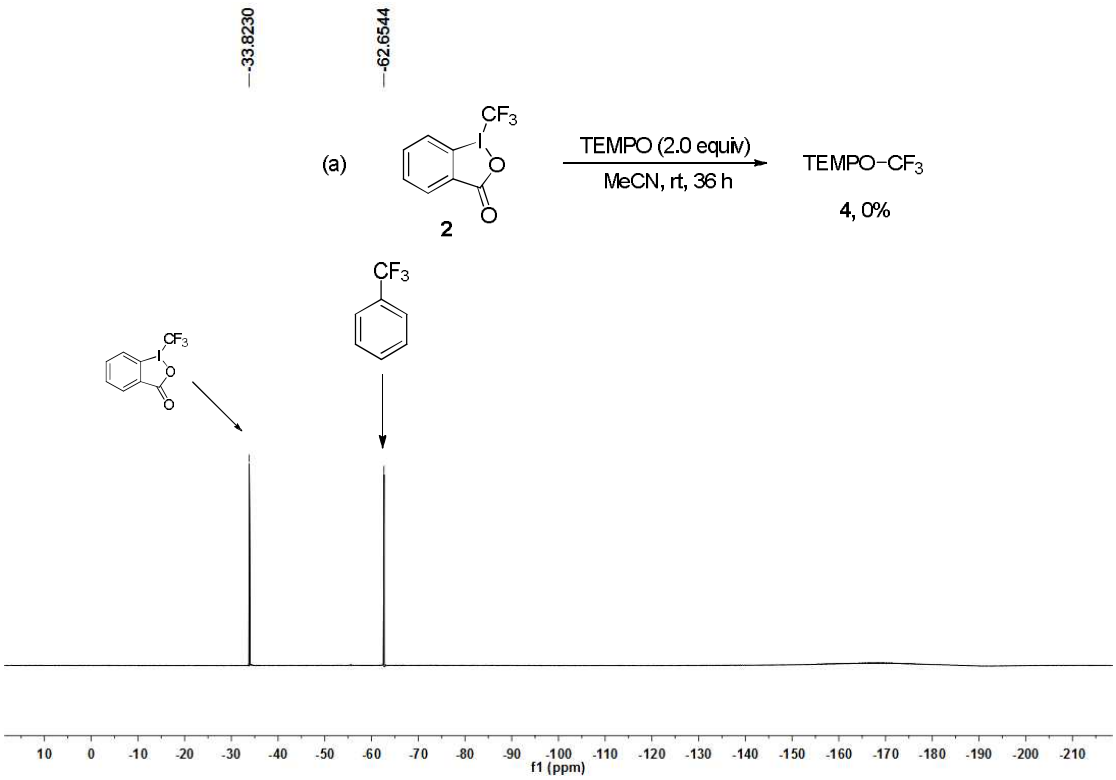
$^{1}$H NMR (151 MHz, $CDCl_3$)

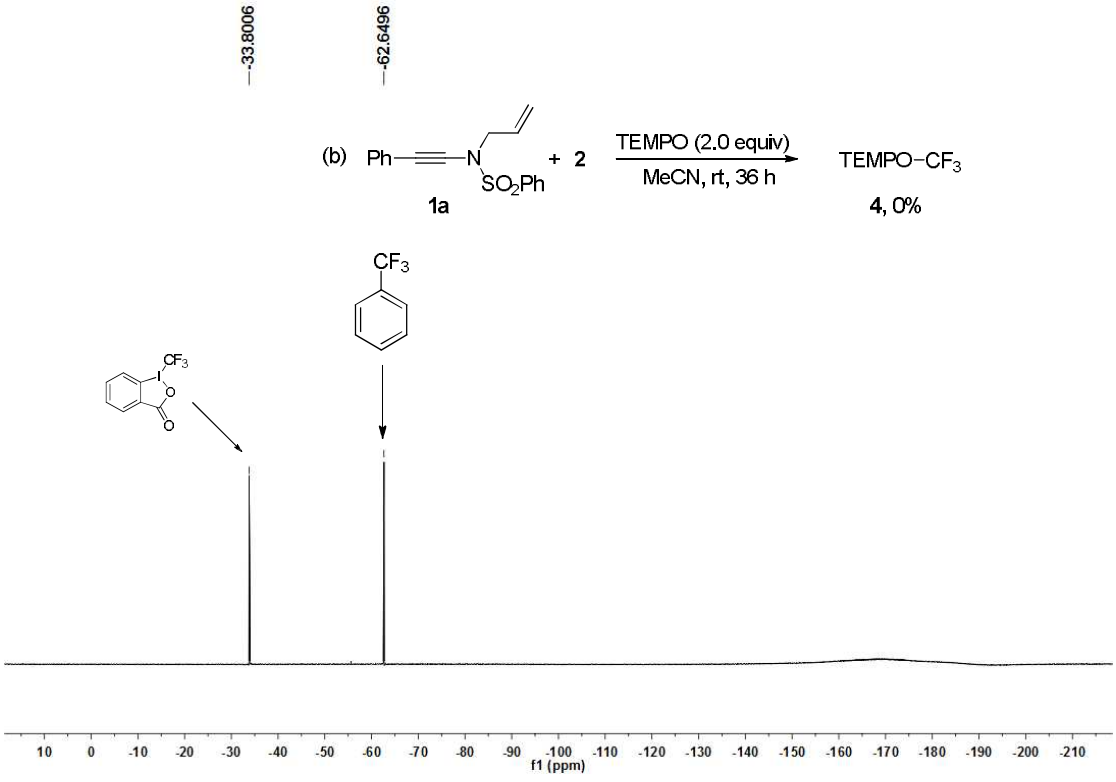


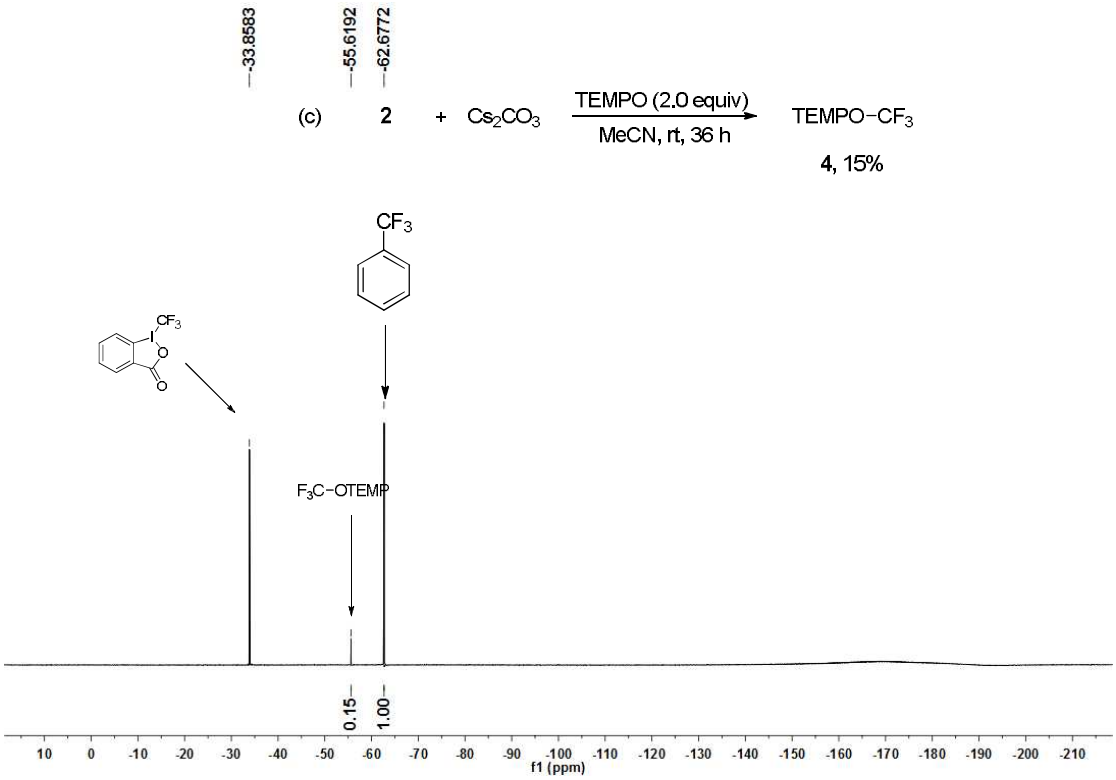

$^{13}$C NMR (151 MHz, $CDCl_3$)

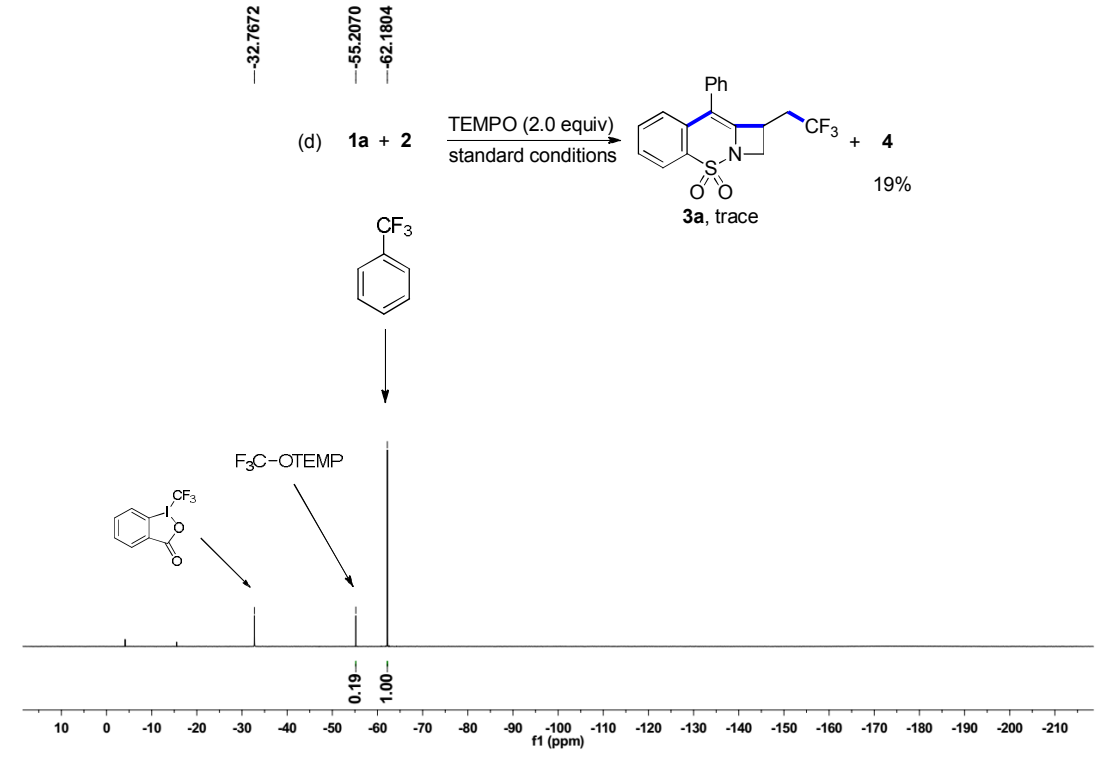



$^{19}$F NMR (565 MHz, $CDCl_3$)

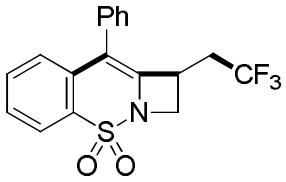

-33.8230
-62.6544
(a)
CF3
I
O
O
2
TEMPO (2.0 equiv)
MeCN, rt, 36 h
TEMPO−CF3
4, 0%
CF3
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


-33.8006
-62.6496
(b)
Ph
N
SO2Ph
1a
+ 2
TEMPO (2.0 equiv)
MeCN, rt, 36 h
TEMPO−CF3
4, 0%
CF3
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


-33.8583
-55.6192
-62.6772
(c) 2 + Cs2CO3
TEMPO (2.0 equiv)
MeCN, rt, 36 h
TEMPO-CF3
4, 15%
CF3
F3C-OTEMP
0.15
1.00
f1 (ppm)


-32.7672
-55.2070
-62.1804
(d) 1a + 2
TEMPO (2.0 equiv)
standard conditions
Ph
CF3
+ 4
19%
3a, trace
F3C-OTEMP
0.19
1.00
f1 (ppm)

**X-Ray crystallographic data**




**3a**

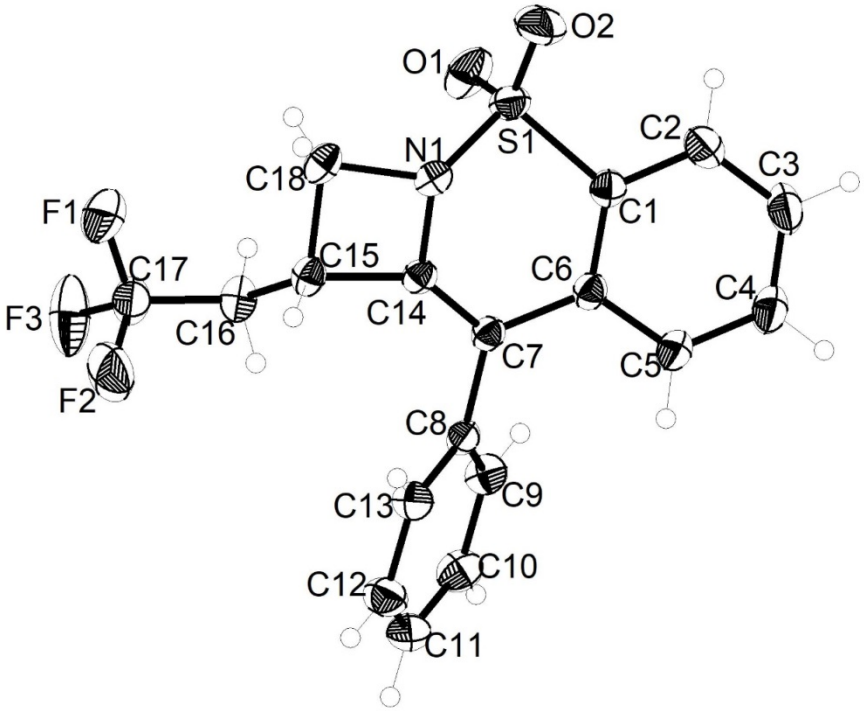



**Figure S1 ORTEP drawing of 3a showing the atom-labeling scheme and displacement ellipsoids drawn at the 50% probability level.**

# checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

## Datablock: 1

Bond precision: C-C = 0.0033 A Wavelength=0.71073

Cell: a=10.8837(3) b=16.9833(5) c=9.3334(3)
alpha=90 beta=103.008(2) gamma=90
Temperature: 296 K

| | Calculated | Reported |
|---|---|---|
| Volume | 1680.93(9) | 1680.93(9) |
| Space group | P 21/c | P 1 21/c 1 |
| Hall group | -P 2ybc | -P 2ybc |
| Moiety formula | C18 H14 F3 N O2 S | C18 H14 F3 N O2 S |
| Sum formula | C18 H14 F3 N O2 S | C18 H14 F3 N O2 S |
| Mr | 365.36 | 365.36 |
| Dx,g cm-3 | 1.444 | 1.444 |
| Z | 4 | 4 |
| Mu (mm-1) | 0.235 | 0.235 |
| F000 | 752.0 | 752.0 |
| F000' | 752.95 | |
| h,k,lmax | 14,22,12 | 14,21,12 |
| Nref | 3828 | 3818 |
| Tmin,Tmax | | |
| Tmin' | | |

Correction method= Not given

Data completeness= 0.997 Theta(max)= 27.434

R(reflections)= 0.0471( 3048) wR2(reflections)= 0.1287( 3818)

S = 1.048 Npar= 227

The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

**Alert level C**

```
PLAT053_ALERT_1_C Minimum Crystal Dimension Missing (or Error) ...     Please Check
PLAT054_ALERT_1_C Medium  Crystal Dimension Missing (or Error) ...     Please Check
PLAT055_ALERT_1_C Maximum Crystal Dimension Missing (or Error) ...     Please Check
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd.  #          1 Note
              C18 H14 F3 N O2 S
```

**Alert level G**

```
PLAT012_ALERT_1_G No       _shelx_res_checksum Found in CIF ......     Please Check
PLAT242_ALERT_2_G Low    'MainMol' Ueq as Compared to Neighbors of        C17 Check
PLAT434_ALERT_2_G Short Inter HL..HL Contact F3       ..F3              2.65 Ang.
                                                 3-x,-y,-z  =      3_855 Check
PLAT793_ALERT_4_G Model has Chirality at C15         (Centro SPGR)          R Verify
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   4 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   4 ALERT level G = General information/check it is not something unexpected

   4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   0 ALERT type 3 Indicator that the structure quality may be low
   2 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

**Publication of your CIF in IUCr journals**

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

**Publication of your CIF in other journals**

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

**PLATON version of 22/03/2021; check.def file version of 19/03/2021**

**Datablock 1** - ellipsoid plot