# A general approach to nitrile- and sulfonyl fluoride-substituted cyclopropanes

Zai-Wei Zhang, K. P. Rakesh, Jing Liu, Hua-Li Qin* and Haolin Tang*

School of Chemistry, Chemical Engineering and Life Science; and State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

*Email*: qinhuali@whut.edu.cn; thln@whut.edu.cn

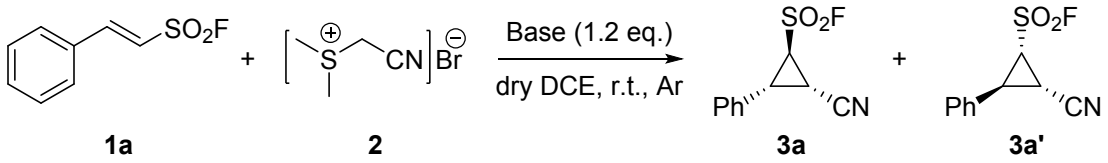
## Table of contents

## 1. General Information.

All reactions were carried out under air atmosphere, unless otherwise specified. NMR spectra were recorded in $CDCl_3$ on a 500 MHz (for $^1H$), 471 MHz (for $^{19}F$), and 126 MHz (for $^{13}C$) spectrometer. All chemical shifts were reported in ppm relative to TMS ($^1H$ NMR, 0 ppm) as internal standards. Melting points of the products were measured on a micro melting point apparatus (SGW X-4) and uncorrected. HRMS experiments were performed on a TOF-Q ESI instrument. Dioxane, Benzene, Toluene, $CHCl_3$ and DCE were dried according to literature prior to use.[1] Other reagents used in the reactions were all purchased from commercial sources and used without further purification. The coupling constants were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

## 2. Optimization of the reaction conditions.

**Table S1. Screening of the base[a].**




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

| Entry | Base | Time[b]/ h | Yield (**3a**)[c]/% | Yield (**3a'**)[c]/% |
|---|---|---|---|---|
| 1[d] | $Na_2CO_3$ | 36 | / | / |
| **2** | **$K_2CO_3$** | **36** | **60** | **34** |
| 3 | $Cs_2CO_3$ | 12 | 44 | 28 |
| 4 | $K_3PO_4$ | 18 | 51 | 29 |
| 5[e] | $K_3PO_4$ | 18 | 52 | 25 |
| 6[f] | $K_3PO_4$ | 18 | 42 | 26 |
| 5[g] | DIEPA | 12 | / | / |
| 6[g] | $Et_3N$ | 12 | / | / |
| 7[g] | DBU | 12 | / | / |

[a] A mixture of (*E*)-2-phenylethene-1-sulfonyl fluoride (**1a**, 1.0 mmol), acetonitrile sulfide salt (**2**, 2.0 eq.) and base (1.2 eq.) in dry DCE (3 mL) was stirred at room temperature for the corresponding time under argon atmosphere.

[b] The time was determined *via* the full consumption of (*E*)-2-phenylethene-1-sulfonyl fluoride (**1a**) monitored by TLC.

[c] Isolated yield.

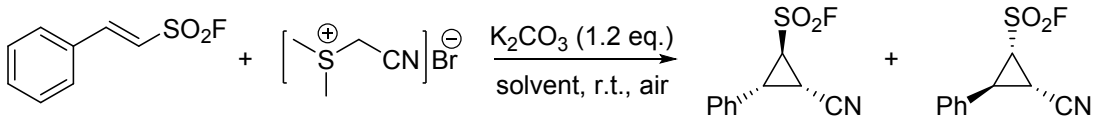
[d] Very little consumption of (*E*)-2-phenylethene-1-sulfonyl fluoride (**1a**).

[e] Under air atmosphere.

[f] Regular undried DCE was used.

[g] A mass of mixture was detected by TLC.

**Table S2. Screening of the solvent[a].**




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

| Entry | Solvent | Time[b]/h | Yield (**3a**)[c]/% | Yield (**3a'**)[c]/% |
|---|---|---|---|---|
| **1** | **DCE (dry)** | **36** | **60** | **34** |
| 2 | Dioxane (dry) | 24 | 42 | 31 |
| 3 | Benzene (dry) | 30 | 33 | 20 |
| 4 | Toluene (dry) | 36 | 36 | 17 |
| 5 | $CHCl_3$ (dry) | 18 | 27 | 13 |
| 6 | DCM (dry) | 24 | 53 | 22 |
| 7[d] | DMF (dry) | 24 | / | / |
| 8[d] | THF (dry) | 24 | / | / |
| 9[d] | Acetonitrile (dry) | 24 | / | / |
| 10[d] | Ethyl acetate | 24 | / | / |

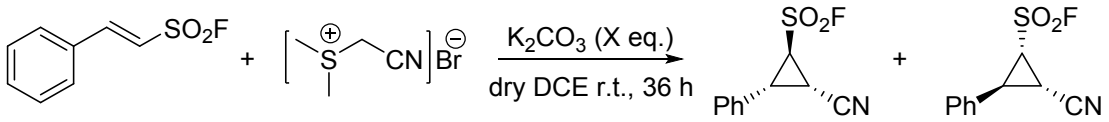
[a] A mixture of (*E*)-2-phenylethene-1-sulfonyl fluoride (**1a**, 1.0 mmol), acetonitrile sulfide salt (**2**, 2.0 eq.) and $K_2CO_3$ (1.2 eq.) in dry solvent (3 mL) was stirred at room temperature for the corresponding time under air atmosphere.

[b] The time was determined *via* the full consumption of (*E*)-2-phenylethene-1-sulfonyl fluoride (**1a**) monitored by TLC.

[c] Isolated yield.

[d] A mass of mixture was detected by TLC.

**Table S3. Screening of the base loading[a].**



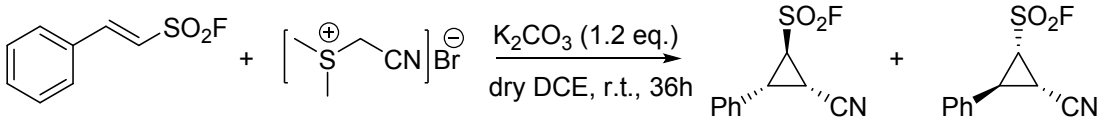

**1a** **2** **3a** **3a'**

| Entry | $K_2CO_3$ (X eq.) | Yield (**3a**)[b]/% | Yield (**3a'**)[b]/% |
|---|---|---|---|
| 1 | 1.0 | 52 | 26 |
| **2** | **1.2** | **60** | **34** |
| 3 | 1.5 | 52 | 23 |
| 4 | 2.0 | 35 | 17 |

[a] A mixture of (E)-2-phenylethene-1-sulfonyl fluoride (**1a**, 1.0 mmol), acetonitrile sulfide salt (**2**, 2.0 eq.) and $K_2CO_3$ (X eq.) in dry DCE (3 mL) was stirred at room temperature for 36 h under air atmosphere.

[b] Isolated yield.

**Table S4. Screening of the cyanomethyl sulfonium salt loading[a].**




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

| Entry | **2** (X eq.) | Yield (**3a**)[b]/% | Yield (**3a'**)[b]/% |
|---|---|---|---|
| 1 | 1.1 | 62 | 29 |
| **2** | **1.2** | **64** | **31** |
| 3 | 2.0 | 60 | 34 |
| 4 | 5.0 | 56 | 25 |

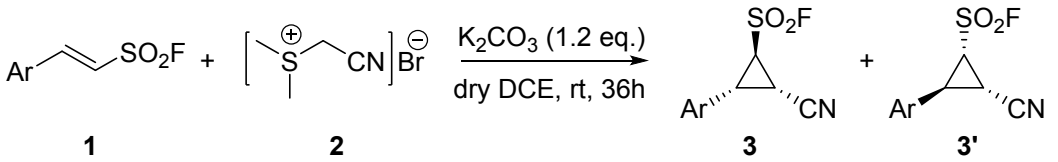
[a] A mixture of (E)-2-phenylethene-1-sulfonyl fluoride (**1a**, 1.0 mmol), acetonitrile sulfide salt (**2**, X eq.) and $K_2CO_3$ (1.2 eq.) in dry DCE (3 mL) was stirred at room temperature for 36 h under air atmosphere.

[b] Isolated yield.

## 3. Raw material preparation.

All of the 2-(hetero)arylethenesulfonyl fluorides (**1)** were prepared according to literature[2]. Acetonitrile sulfide salt (**2**) was prepared according to literature[3].

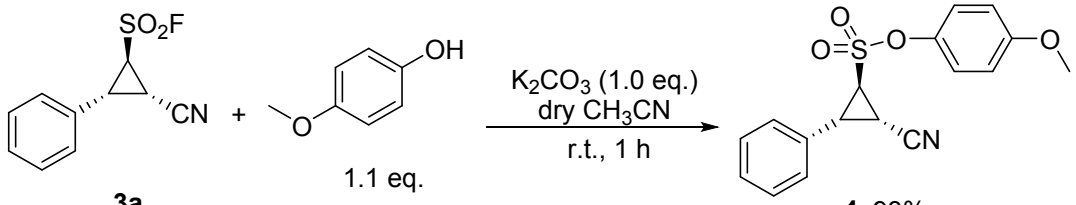
## 4. General procedure for synthesis of 3.




**1** **2** **3** **3'**

A mixture of 2-(hetero)arylethenesulfonyl fluorides (**1**, 1.0 mmol, 1.0 eq.), acetonitrile sulfide salt (**2**, 1.2 mmol, 1.2 eq.), $K_2CO_3$ (1.2 mmol, 1.2 eq.) and dry DCE (3.0 mL) was stirred at room temperature for 36 h. The reaction was monitored by TLC until the disappearance of 2-(hetero)arylethenesulfonyl fluorides (**1**). The solvent was evaporated under vacuum and the residue was purified through flash silica gel chromatography to get the desired product **3** or **3'**.

## 5. General procedure for synthesis of 4.

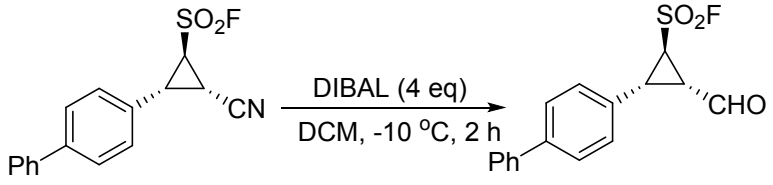



**3a**
0.2 mmol

**4,** 93%

A mixture of (1R,2S,3R)-2-cyano-3-phenylcyclopropane-1-sulfonyl fluoride (**3a**, 0.2 mmol, 1.0 eq.), 4-methoxyphenol (0.22 mmol, 1.1 eq.), $K_2CO_3$ (0.2 mmol, 1.0 eq.) and dry $CH_3CN$ (2.0 mL) was stirred at room temperature for 1 h. The reaction was monitored by TLC. The solvent was evaporated under vacuum and the residue was purified through flash silica gel chromatography to get the desired product **4**.

## 6. General procedure for synthesis of 5.



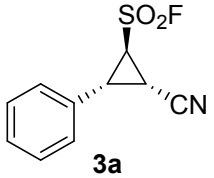

**3b**
0.4 mmol

**5**, 78%

To a solution of (1R,2R,3S)-2-([1,1'-biphenyl]-4-yl)-3-cyanocyclopropane-1-sulfonyl fluoride (**3b**, 0.4 mmol, 1.0 eq.) dissolved in DCM (3.0 mL) was added DIBAL (1.6 mmol, 4.0 eq.) dropwise at -10 °C. After the addition was over, the mixture was

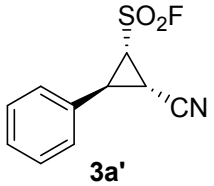
stirred at -10 °C for 2 h. The solvent was evaporated under vacuum and the residue was purified through flash silica gel chromatography to get the desired product **5**.

## 7. Characterization



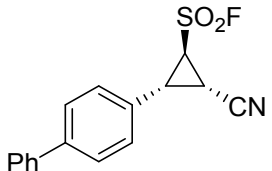

**3a**

**(1R,2S,3R)-2-cyano-3-phenylcyclopropane-1-sulfonyl fluoride (3a).** white solid, 144 mg, 64% yield. Mp: 53-55 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.47-7.43 (m, 3H), 7.34-7.32 (m, 2H), 3.65 (q, $J$ = 5.1 Hz, 1H), 3.39 (dd, $J_1$ = 9.7 Hz, $J_2$ = 6.1 Hz, 1H), 2.81 (dd, $J_1$ = 9.8 Hz, $J_2$ = 4.9 Hz, 1H). $^{19}$F{$^{1}$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 58.4. $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ 129.7, 129.5, 128.2, 113.9, 38.9 (d, $J$ = 31.8 Hz), 29.3, 13.8. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{10}H_9FNO_2S$: 226.0333; found: 226.0336.



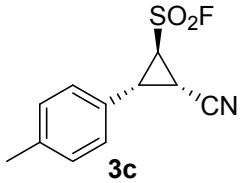

**3a'**

**(1S,2S,3S)-2-cyano-3-phenylcyclopropane-1-sulfonyl fluoride (3a')**. White solid, 70 mg, 31% yield. Mp: 78-80 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.43-7.39 (m, 3H), 7.20-7.18 (m, 2H), 3.55 (t, $J$ = 6.3 Hz, 1H), 3.41-3.37 (m, 1H), 2.54 (t, $J$ = 7.9 Hz, 1H). $^{19}$F{$^{1}$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 61.8. $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ131.7, 129.6, 129.5, 126.9, 113.9, 39.7 (d, $J$ = 29.9 Hz), 31.2, 13.2. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{10}H_9FNO_2S$: 226.0333; found: 226.0337.



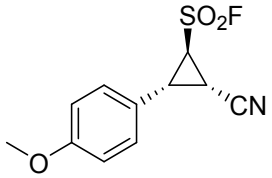

**3b**

**(1R,2R,3S)-2-([1,1'-biphenyl]-4-yl)-3-cyanocyclopropane-1-sulfonyl fluoride** (**3b**). White solid, 166 mg, 55% yield. Mp: 124-126 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.68-7.66 (m, 2H), 7.60-7.59 (m, 2H), 7.49-7.46 (m, 2H), 7.41-7.38 (m, 3H), 3.69-3.66 (m, 1H), 3.43 (dd, $J_1$ = 9.6 Hz, $J_2$ = 6.0 Hz, 1H), 2.84 (dd, $J_1$ = 9.8 Hz, $J_2$ = 5.1 Hz, 1H). $^{19}$F{$^{1}$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 58.4 (d). $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ142.7, 140.0, 129.1, 128.6, 128.3, 128.1, 128.1, 127.3, 114.0, 39.0 (d, $J$ = 31.8 Hz), 29.1, 13.9. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{16}H_{13}FNO_2S$: 302.0646; found: 302.0650.



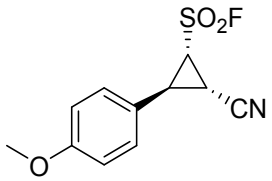

**3c**

**(1R,2S,3R)-2-cyano-3-(p-tolyl)cyclopropane-1-sulfonyl fluoride (3c)**. White solid, 148 mg, 62% yield. Mp: 75-77 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, $J$ = 8.0 Hz, 2H), 7.20 (d, $J$ = 8.1 Hz, 2H), 3.62 (q, $J$ = 5.1 Hz, 1H), 3.35 (dd, $J_1$ = 9.6 Hz, $J_2$ = 6.1 Hz, 1H), 2.78 (dd, $J_1$ = 9.7 Hz, $J_2$ = 4.8 Hz, 1H), 2.38 (s, 3H). $^{19}$F{$^{1}$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 58.3. $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ 138.7, 129.1, 127.0, 125.4, 113.1, 37.9 (d, $J$ = 30.9 Hz), 28.1, 20.3, 12.8. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{11}H_{11}FNO_2S$: 240.0489; found: 240.0486.



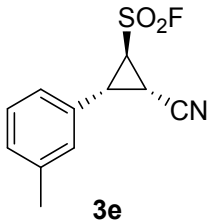

**3d**

**(1R,2S,3R)-2-cyano-3-(4-methoxyphenyl)cyclopropane-1-sulfonyl fluoride (3d)**. Colorless oil, 163 mg, 64% yield. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, $J$ = 8.7 Hz, 2H), 6.95 (d, $J$ = 8.7 Hz, 2H), 3.83 (s, 3H), 3.58 (q, $J$ = 5.1 Hz, 1H), 3.34 (dd, $J_1$ = 9.7 Hz, $J_2$ = 6.0 Hz, 1H), 2.76 (dd, $J_1$ = 9.6 Hz, $J_2$ = 4.8 Hz, 1H). $^{19}$F{$^{1}$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 58.3. $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ 160.6, 129.4, 121.4, 114.9, 114.1, 55.5, 39.1 (d, $J$ = 30.9 Hz), 28.9, 13.8. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{11}H_{11}FNO_3S$: 256.0438; found: 256.0443.



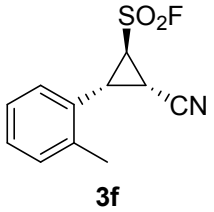

**3d'**

**(1S,2S,3S)-2-cyano-3-(4-methoxyphenyl)cyclopropane-1-sulfonyl fluoride** (**3d'**). White solid, 74 mg, 29% yield. Mp: 85-87 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.11-7.09 (m, 2H), 6.92-6.90 (m, 2H), 3.81 (s, 3H), 3.50 (t, $J$ = 6.4 Hz, 1H), 3.34-3.31 (m, 1H), 2.48 (t, $J$ = 7.6 Hz, 1H). $^{19}$F{$^{1}$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 61.8. $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ160.4, 128.2, 123.5, 114.9, 114.0 (d, $J$ = 2.7 Hz), 55.6, 39.7 (d, $J$ = 30.0 Hz), 30.9, 13.2. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{11}H_{11}FNO_3S$: 256.0438; found: 256.0443.



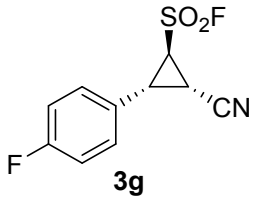

**3e**

**(1R,2S,3R)-2-cyano-3-(m-tolyl)cyclopropane-1-sulfonyl fluoride (3e)**. White solid, 86 mg, 36% yield. Mp: 54-56 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, $J$ = 7.4 Hz, 1H), 7.23 (d, $J$ = 7.4 Hz, 1H), 7.12-7.11 (m, 2H), 3.64 (q, $J$ = 4.8 Hz, 1H), 3.35 (dd, $J_1$ = 9.6 Hz, $J_2$ = 6.1 Hz, 1H), 2.79 (dd, $J_1$ = 9.7 Hz, $J_2$ = 4.9 Hz, 1H), 2.40 (s, 3H). $^{19}$F{$^{1}$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 58.3. $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ 139.4, 130.4, 129.4, 129.3, 128.8, 125.1, 114.0, 38.8 (d, $J$ = 30.9 Hz), 29.3, 21.5, 13.8. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{11}H_{11}FNO_2S$: 240.0489; found: 240.0493.



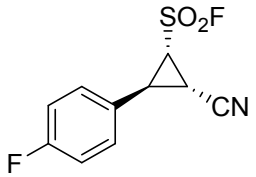

**3f**

**(1R,2S,3R)-2-cyano-3-(o-tolyl)cyclopropane-1-sulfonyl fluoride** (**3f**). White solid, 105 mg, 44% yield. Mp: 100-102 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.36-7.25 (m, 3H), 7.20 (d, $J$ = 7.4 Hz, 1H), 3.67 (q, $J$ = 5.2 Hz, 1H), 3.34 (dd, $J_1$ = 9.5 Hz, $J_2$ = 6.4 Hz, 1H), 2.85 (dd, $J_1$ = 9.6 Hz, $J_2$ = 4.7 Hz, 1H), 2.45 (s, 3H). $^{19}$F{$^{1}$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 58.7 (d) $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ 138.2, 131.2, 129.8, 128.0, 127.7, 126.8, 114.0, 38.8 (d, $J$ = 30.9 Hz), 28.4, 19.6, 13.3. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{11}H_{11}FNO_2S$: 240.0489; found: 240.0486.



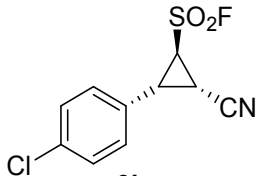

**3g**

**(1R,2S,3R)-2-cyano-3-(4-fluorophenyl)cyclopropane-1-sulfonyl fluoride** (**3g**). White solid, 148 mg, 61% yield. Mp: 48-50 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.33-7.31 (m, 2H), 7.16-7.13 (m, 2H), 3.63-3.60 (m, 1H), 3.37 (dd, $J_1$ = 9.6 Hz, $J_2$ = 6.1 Hz, 1H), 2.81 (dd, $J_1$ = 9.6 Hz, $J_2$ = 4.9 Hz, 1H). $^{19}$F{$^{1}$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 58.4, -110.9 (m). $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ163.4 (d, $J$ = 249.8 Hz), 130.1 (d, $J$ = 9.0 Hz), 125.4 (d, $J$ = 3.6 Hz), 116.7 (d, $J$ = 22.7 Hz), 113.8, 39.1 (d, $J$ = 31.8 Hz), 28.6, 13.8. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{10}H_8F_2NO_2S$: 244.0238; found: 244.0241.



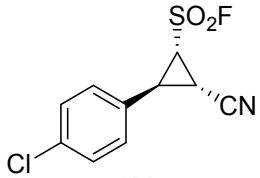

**3g'**

**(1S,2S,3S)-2-cyano-3-(4-fluorophenyl)cyclopropane-1-sulfonyl fluoride** (**3g'**). White solid, 73 mg, 30% yield. Mp: 104-106 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.21-7.18 (m, 2H), 7.12-7.09 (m, 2H), 3.54 (t, *J* = 6.4 Hz, 1H), 3.38-3.35 (m, 1H), 2.52 (t, *J* = 7.5 Hz, 1H). $^{19}$F{$^{1}$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 61.9, -111.0 (m). $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ163.2 (d, *J* = 250.7 Hz), 129.0 (d, *J* = 8.1 Hz), 127.5 (d, *J* = 2.7 Hz), 116.7 (d, *J* = 21.8 Hz), 113.8, 39.7 (d, *J* = 30.0 Hz), 30.6, 13.2. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{10}H_8F_2NO_2S$: 244.0238; found: 244.0242.



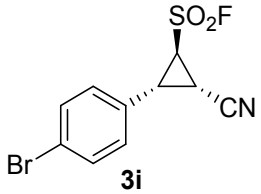

**3h**

**(1R,2R,3S)-2-(4-chlorophenyl)-3-cyanocyclopropane-1-sulfonyl fluoride** (**3h**). White solid, 127 mg, 49% yield. Mp: 69-71 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.27(d, *J* = 8.3 Hz, 2H), 3.62 (q, *J* = 5.0 Hz, 1H), 3.35 (dd, $J_1$ = 9.7 Hz, $J_2$ = 6.2 Hz, 1H), 2.82 (dd, $J_1$ = 9.6 Hz, $J_2$ = 4.9 Hz, 1H). $^{19}$F{$^{1}$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 58.4. $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ 135.9, 129.8, 129.6, 128.1, 113.7, 39.0 (d, *J* = 31.8 Hz), 28.7, 13.8. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{10}H_8ClFNO_2S$: 259.9943; found: 259.9946.



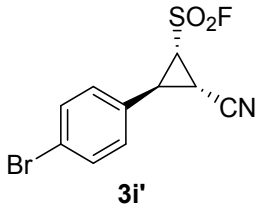

**3h'**

**(1S,2S,3S)-2-(4-chlorophenyl)-3-cyanocyclopropane-1-sulfonyl fluoride** (**3h'**). White solid, 70 mg, 27% yield. Mp: 86-88 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.40-7.37 (m, 2H), 7.15-7.13 (m, 2H), 3.53 (t, *J* = 6.4 Hz, 1H), 3.40-3.36 (m, 1H), 2.54-2.51 (m, 1H). $^{19}$F{$^{1}$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 62.0. $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ135.7 (d, *J* = 5.4 Hz), 130.2, 129.8 (d, *J* = 1.8 Hz), 128.4 (d, *J* = 1.8 Hz), 113.7 (d, *J* = 13.6 Hz), 39.6 (d, *J* = 30.9 Hz), 30.6, 13.2. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{10}H_8ClFNO_2S$: 259.9943; found: 259.9946.



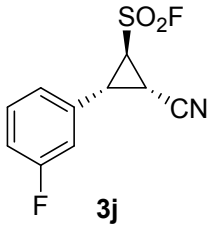

**3i**

**(1R,2R,3S)-2-(4-bromophenyl)-3-cyanocyclopropane-1-sulfonyl fluoride** (**3i**). White solid, 170 mg, 56% yield. Mp: 74-76 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, $J$ = 8.4 Hz, 2H), 7.20 (d, $J$ = 8.4 Hz, 2H), 3.62 (q, $J$ = 5.1 Hz, 1H), 3.33 (dd, $J_1$ = 9.6 Hz, $J_2$ = 6.1 Hz, 1H), 2.82 (dd, $J_1$ = 9.8 Hz, $J_2$ = 4.9 Hz, 1H). $^{19}$F{$^{1}$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 58.5. $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ 132.8, 129.8, 128.6, 124.0, 113.7, 38.9 (d, $J$ = 31.8 Hz), 28.7, 13.7. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{10}H_8BrFNO_2S$: 303.9438; found: 303.9435.



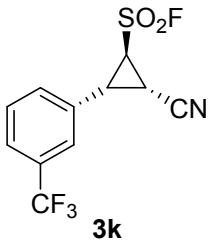

**3i'**

**(1S,2S,3S)-2-(4-bromophenyl)-3-cyanocyclopropane-1-sulfonyl fluoride** (**3i'**). White solid, 109 mg, 36% yield. Mp: 99-101 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, $J$ = 8.4 Hz, 2H), 7.08 (d, $J$ = 8.2 Hz, 2H), 3.51 (t, $J$ = 6.4 Hz, 1H), 3.40-3.36 (m, 1H), 2.53 (t, $J$ = 7.9 Hz, 1H). $^{19}$F{$^{1}$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 61.9. $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ132.8, 130.7, 128.6, 123.7, 113.6, 39.6 (d, $J$ = 29.9 Hz), 30.7, 13.2. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{10}H_8BrFNO_2S$: 303.9438; found: 303.9434.



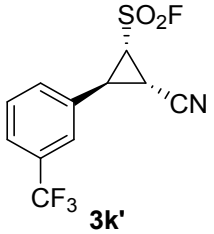

**3j**

**(1R,2S,3R)-2-cyano-3-(3-fluorophenyl)cyclopropane-1-sulfonyl fluoride** (**3j**). Colorless oil, 102 mg, 42% yield. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.33-7.31 (m, 2H), 7.15 (t, $J$ = 8.4 Hz, 2H), 3.61 (q, $J$ = 5.1 Hz, 1H), 3.37 (dd, $J_1$ = 9.6 Hz, $J_2$ = 6.1 Hz, 1H), 2.81 (dd, $J_1$ = 9.6 Hz, $J_2$ = 4.9 Hz, 1H). $^{19}$F{$^{1}$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 58.4 (d), -110.9 (m). $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ 163.4 (d, $J$ = 250.7 Hz), 130.1 (d, $J$ = 9.1 Hz), 125.4 (d, $J$ = 3.7 Hz), 116.7 (d, $J$ = 22.7 Hz), 113.8, 39.1 (d, $J$ = 31.8 Hz), 28.6, 13.8. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{10}H_8F_2NO_2S$: 244.0238; found: 244.0235.



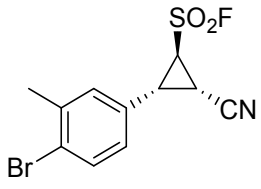

**3k**

**(1R,2S,3R)-2-cyano-3-(3-(trifluoromethyl)phenyl)cyclopropane-1-sulfonyl fluoride** (**3k**). Colorless oil, 126 mg, 43% yield. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, $J$ = 8.1 Hz, 1H), 7.61 (t, $J$ = 7.6 Hz, 2H), 7.52 (d, $J$ = 8.2 Hz, 1H), 3.73 (q, $J$ = 5.2 Hz, 1H), 3.44 (dd, $J_1$ = 9.6 Hz, $J_2$ = 5.9 Hz, 1H), 2.88 (dd, $J_1$ = 9.8 Hz, $J_2$ = 4.9 Hz, 1H). $^{19}$F{$^{1}$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 58.5, -62.9. $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ 132.1 (q, $J$ = 32.7 Hz), 131.3, 130.7, 130.2, 126.6 (q, $J$ = 3.6 Hz), 125.5 (q, $J$ = 3.7 Hz), 123.6 (q, $J$ = 272.5 Hz), 38.8 (d, $J$ = 31.8 Hz), 28.7, 13.8. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{11}H_8F_4NO_2S$: 294.0206; found: 294.0201.




**3k'**

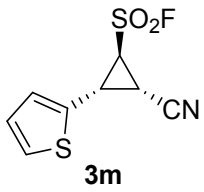
**(1S,2S,3S)-2-cyano-3-(3-(trifluoromethyl)phenyl)cyclopropane-1-sulfonyl fluoride** (**3k'**). White solid, 64 mg, 22% yield. Mp: 91-93 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, $J$ = 7.8 Hz, 1H), 7.57 (t, $J$ = 7.7 Hz, 1H), 7.43 (d, $J$ = 8.4 Hz, 2H), 3.61 (t, $J$ = 6.4 Hz, 1H), 3.49-3.45 (m, 1H), 2.62-2.59 (m, 1H). $^{19}$F{$^{1}$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 62.0, -62.9. $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ132.8, 132.2 (q, $J$ = 32.7 Hz), 130.7, 130.3, 126.4 (q, $J$ = 3.6 Hz), 123.8 (q, $J$ = 3.7 Hz), 123.6 (q, $J$ = 272.4 Hz), 113.5, 39.6 (d, $J$ = 30.9 Hz), 30.7, 13.3. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{11}H_8F_4NO_2S$: 294.0206; found: 294.0201.




**3l**

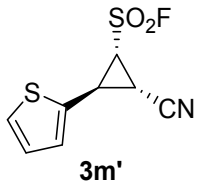
**(1R,2R,3S)-2-(4-bromo-3-methylphenyl)-3-cyanocyclopropane-1-sulfonyl fluoride (3l)**. White solid, 120 mg, 38% yield. Mp: 84-86 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, $J$ = 8.3 Hz, 1H), 7.18 (d, $J$ = 1.5 Hz, 1H), 7.00 (dd, $J_1$ = 8.3 Hz, $J_2$ = 2.0 Hz, 1H), 3.62 (q, $J$ = 5.1 Hz, 1H), 3.31 (dd, $J_1$ = 9.7 Hz, $J_2$ = 6.1 Hz, 1H), 2.80 (dd, $J_1$ = 9.8 Hz, $J_2$ = 4.9 Hz, 1H), 2.43 (s, 3H). $^{19}$F{$^{1}$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 58.4. $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ 139.5, 133.5, 130.5, 128.7, 126.8, 126.4, 113.8, 38.8 (d, $J$ = 30.9 Hz), 28.7, 23.1, 13.7. HRMS ESI (m/z): $[M+H]^+$ calcd for

$C_{11}H_{10}BrFNO_2S$: 317.9594; found: 317.9598.



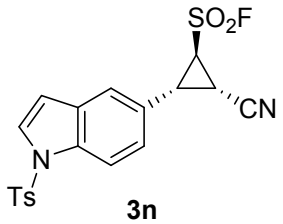

**3m**

**(1S,2S,3S)-2-cyano-3-(thiophen-2-yl)cyclopropane-1-sulfonyl fluoride (3m)**. Yellow oil, 141 mg, 61% yield. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 5.0 Hz, 1H), 7.12 (d, *J* = 3.3 Hz, 1H), 7.06 (t, *J* = 4.6 Hz, 1H), 3.64 (q, *J* = 5.0 Hz, 1H), 3.50 (dd, $J_1$ = 9.1 Hz, $J_2$ = 5.8 Hz, 1H), 2.82 (dd, $J_1$ = 9.3 Hz, $J_2$ = 5.0 Hz, 1H) . $^{19}$F{$^1$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 58.5 (d). $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) δ 131.8, 127.8, 127.3, 113.7, 40.3 (d, *J* = 31.8 Hz), 24.9, 14.8. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_8H_7FNO_2S_2$: 231.9897; found: 231.9893.



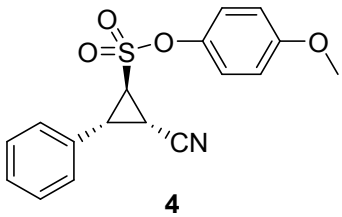

**3m'**

**(1R,2S,3R)-2-cyano-3-(thiophen-2-yl)cyclopropane-1-sulfonyl fluoride (3m')**. White solid, 65 mg, 28% yield. Mp: 107-109 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, $J_1$ = 4.1 Hz, $J_2$ = 1.9 Hz, 1H), 7.01-7.00 (m, 2H), 3.70 (t, *J* = 6.3 Hz, 1H), 3.43-3.39 (m, 1H), 2.57 (t, *J* = 7.4 Hz, 1H). $^{19}$F{$^1$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 62.1. $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) δ134.4, 127.9, 127.3, 126.7, 113.4, 40.7 (d, *J* = 30.9 Hz), 26.9, 14.5. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_8H_7FNO_2S_2$: 231.9897; found: 231.9893.



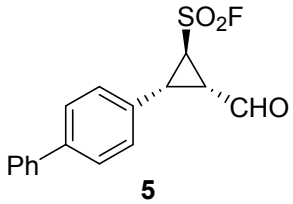

**3n**

**(1R,2S,3R)-2-cyano-3-(1-tosyl-1H-indol-5-yl)cyclopropane-1-sulfonyl fluoride (3n)**. White solid, 171 mg, 41% yield. Mp: 125-127 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 3.6 Hz, 1H), 7.49 (s, 1H), 7.25 (d, *J* = 8.1 Hz, 3H), 6.66 (d, *J* = 3.7 Hz, 1H), 3.65 (q, *J* = 5.1 Hz, 1H), 3.45 (dd, $J_1$ = 9.6 Hz, $J_2$ = 6.1 Hz, 1H), 2.82 (dd, $J_1$ = 9.8 Hz, $J_2$ = 4.9 Hz, 1H), 2.35 (s, 3H). $^{19}$F{$^1$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 58.4. $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) δ 145.5, 135.2, 135.1, 131.4, 130.2, 127.9, 127.0, 124.5, 124.5, 121.1, 114.5, 114.0, 108.7, 39.2 (d, *J* = 30.9 Hz), 29.4, 21.7, 13.9. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{19}H_{16}FN_2O_4S_2$: 419.0530; found: 419.0533.




**4**

**4-methoxyphenyl (1R,2S,3R)-2-cyano-3-phenylcyclopropane-1-sulfonate (4)**. White solid, 0.2 mmol scale, 61 mg, 93% yield. Mp: 102-104 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.42-7.40 (m, 3H), 7.26-7.25 (m, 2H), 7.22-7.20 (m, 2H), 6.92-6.90 (m, 2H), 3.82 (s, 3H), 3.47 (t, $J$ = 5.8 Hz, 1H), 3.21 (dd, $J_1$ = 9.5 Hz, $J_2$ = 6.1 Hz, 1H), 2.57 (dd, $J_1$ = 9.4 Hz, $J_2$ = 5.0 Hz, 1H). $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ 159.1, 142.7, 130.5, 129.3, 129.3, 128.1, 123.2, 115.3, 114.9, 55.9, 39.0, 28.7, 13.5. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{17}H_{16}NO_4S$: 330.0795; found: 330.0790.




**5**

**(1R,2R,3S)-2-([1,1'-biphenyl]-4-yl)-3-formylcyclopropane-1-sulfonyl fluoride (5)**. White solid, 0.4 mmol scale, 95 mg, 78% yield. Mp: 94-96 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.38 (d, $J$ = 2.6 Hz, 1H), 7.57 (t, $J$ = 8.1 Hz, 4H), 7.45 (t, $J$ = 7.4 Hz, 2H), 7.38 (t, $J$ = 7.2 Hz, 1H),7.32 (d, $J$ = 8.1 Hz, 2H), 4.02 (q, $J$ = 5.1 Hz, 1H), 3.65 (dd, $J_1$ = 10.4 Hz, $J_2$ = 6.3 Hz, 1H), 3.25-3.22 (m, 1H). $^{19}$F{$^{1}$H, $^{13}$C} NMR (471 MHz, $CDCl_3$) δ 58.2 (d) $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ 192.6, 141.9, 140.1, 129.4, 129.0, 128.8, 127.9, 127.8, 127.2, 37.9 (d, $J$ = 30.9 Hz), 34.6, 32.6. HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{16}H_{14}FO_3S$: 305.0642; found: 305.0639.

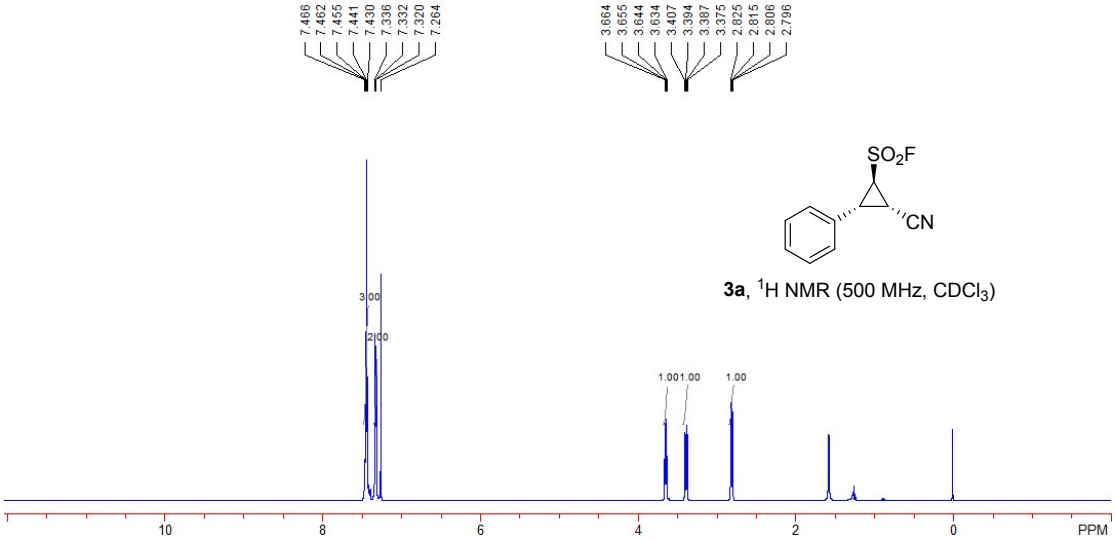
## 8. References.

[1] Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth Heinemann: Oxford, **2003**.

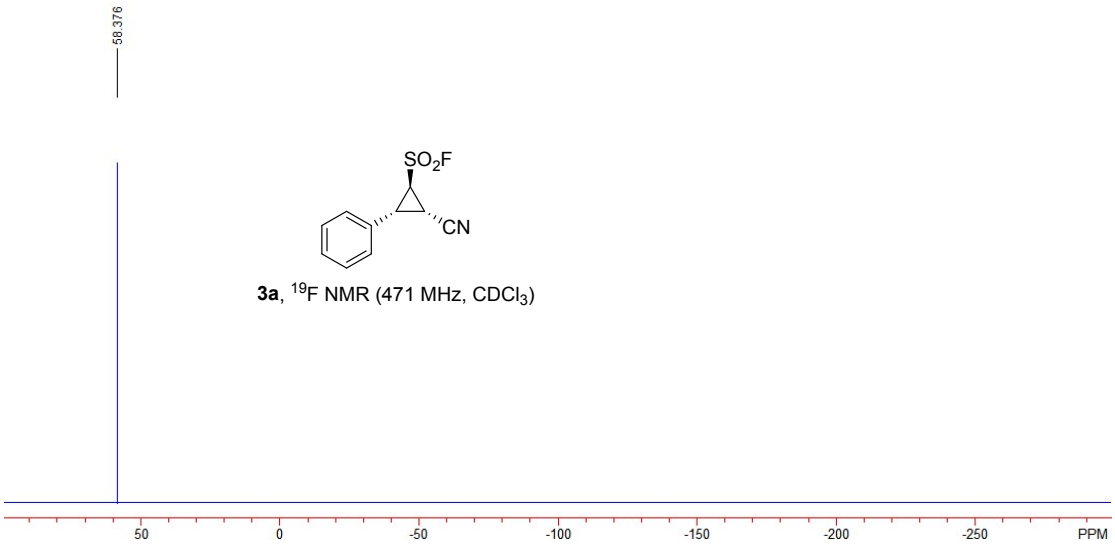
[2] G.-F. Zha, Q. Zheng, J. Leng, P. Wu, H.-L. Qin and K. B. Sharpless, *Angew. Chem., Int. Ed.,* 2017, **56**, 4849.

[3] R. Hommelsheim, K. J. Hock, C. Schumacher, M. A. Hussein, T. V. Nguyen and R. M. Koenigs, *Chem. Commun.*, 2018, **54**, 11439.

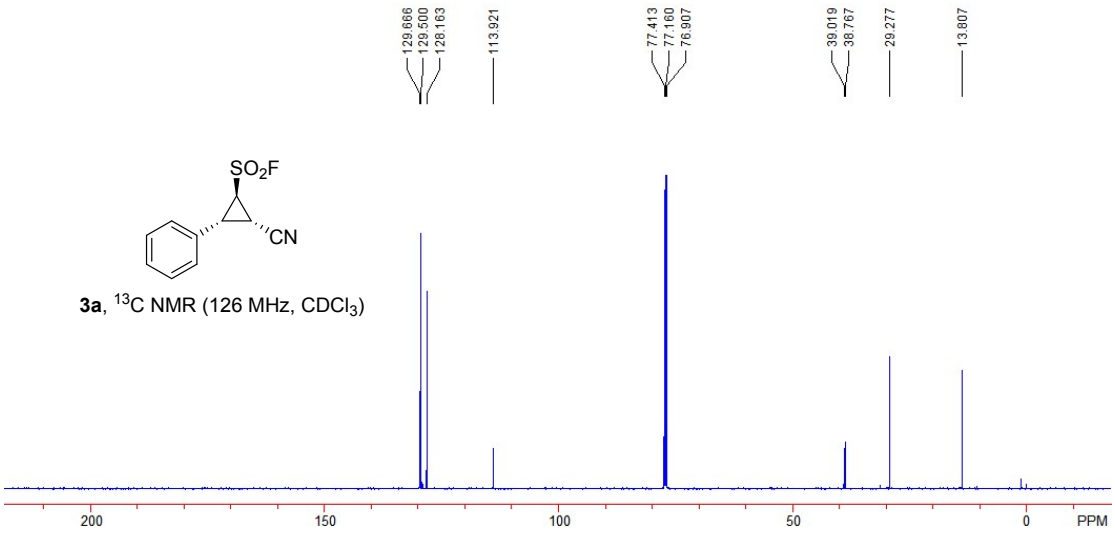
## 9. NMR spectra.



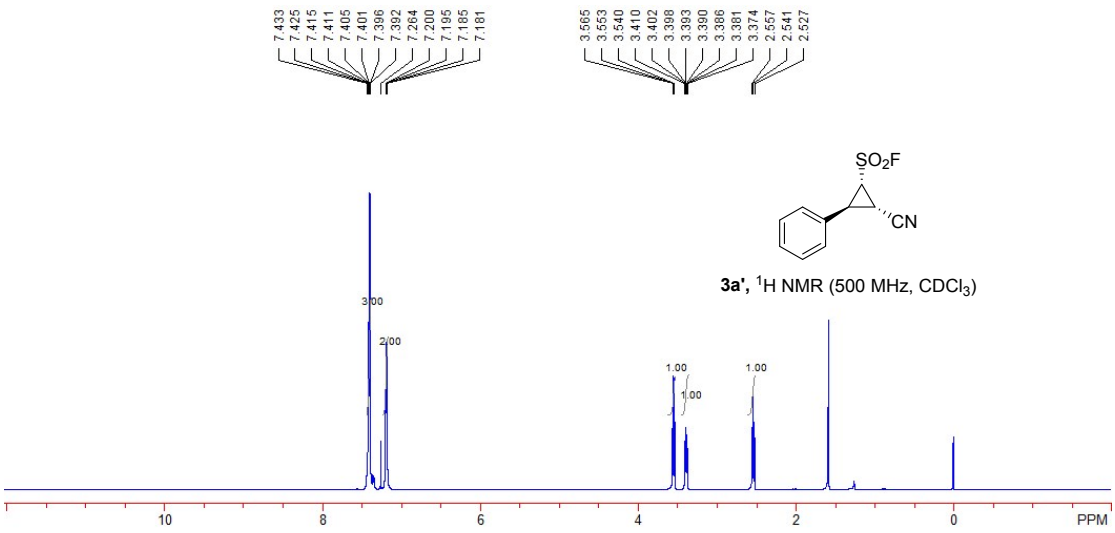

**3a**, $^{1}$H NMR (500 MHz, $CDCl_3$)



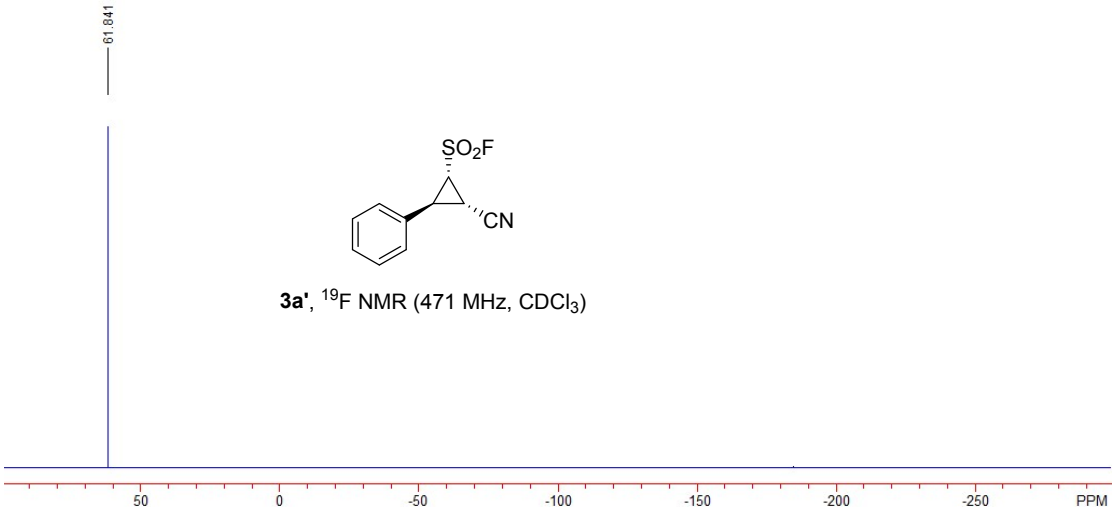

**3a**, $^{19}$F NMR (471 MHz, $CDCl_3$)



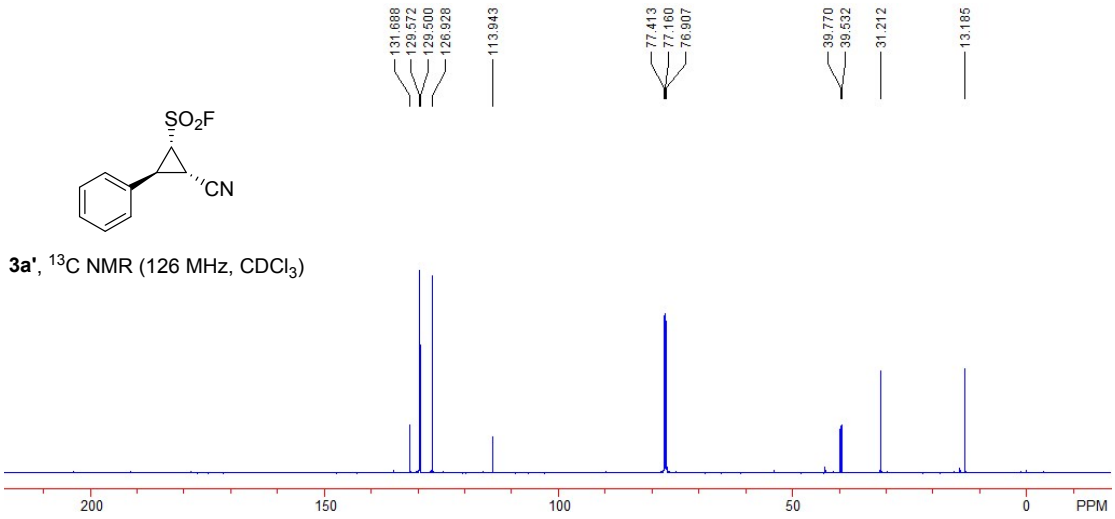

**3a**, $^{13}$C NMR (126 MHz, $CDCl_3$)



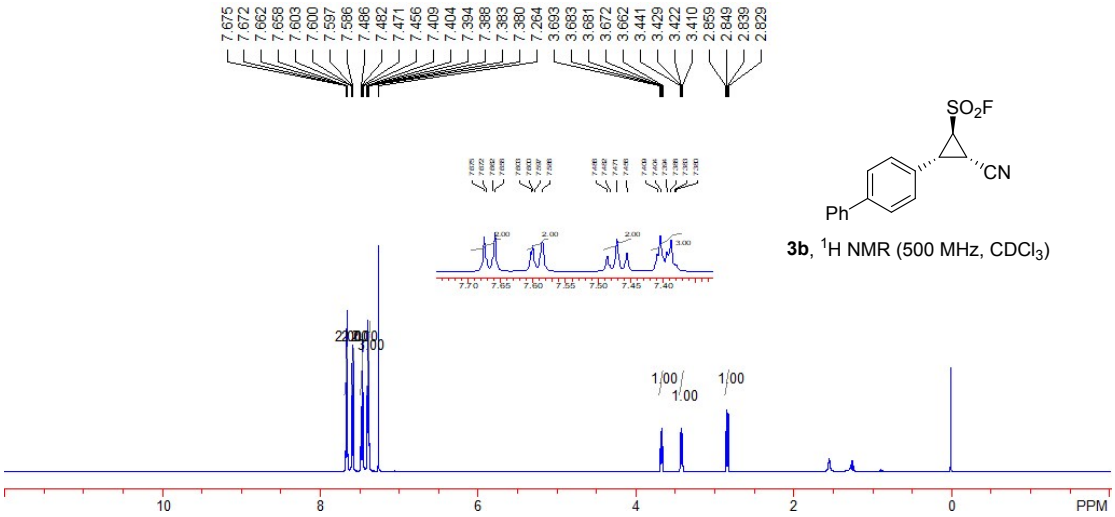

**3a',** $^{1}$H NMR (500 MHz, $CDCl_3$)



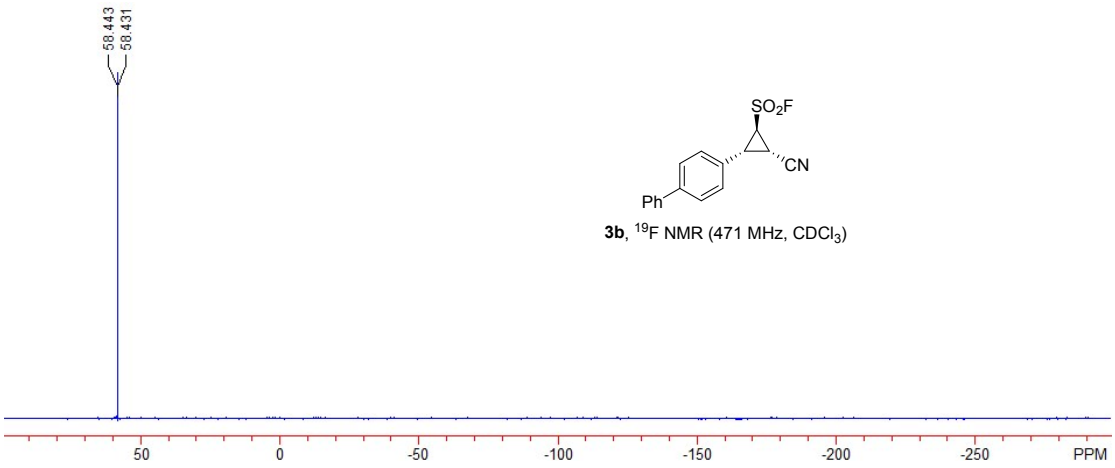

**3a'**, $^{19}$F NMR (471 MHz, $CDCl_3$)



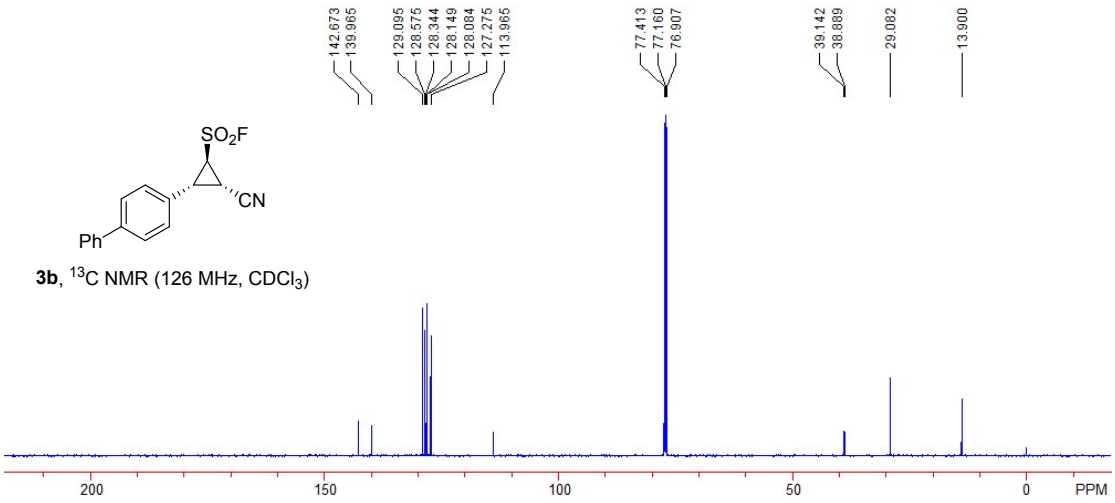

**3a'**, $^{13}$C NMR (126 MHz, $CDCl_3$)



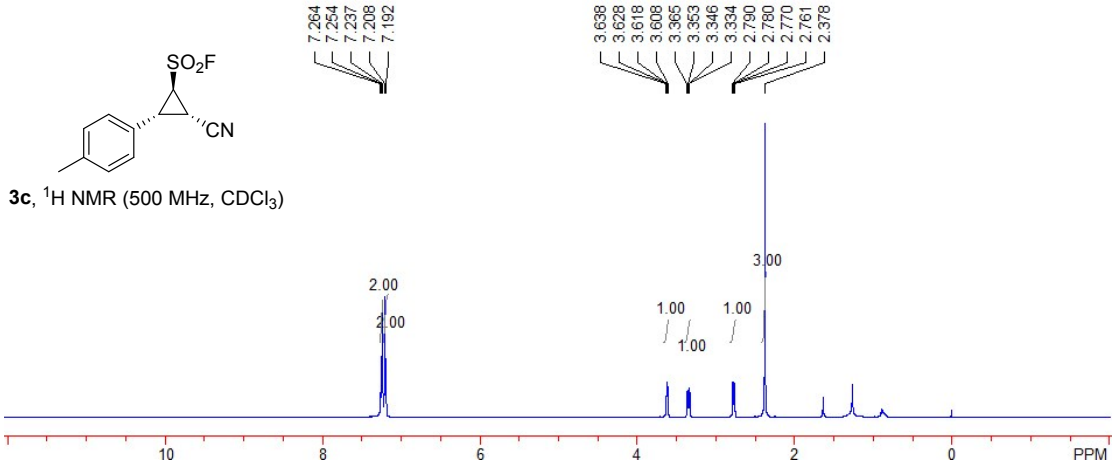

**3b**, $^{1}$H NMR (500 MHz, $CDCl_3$)



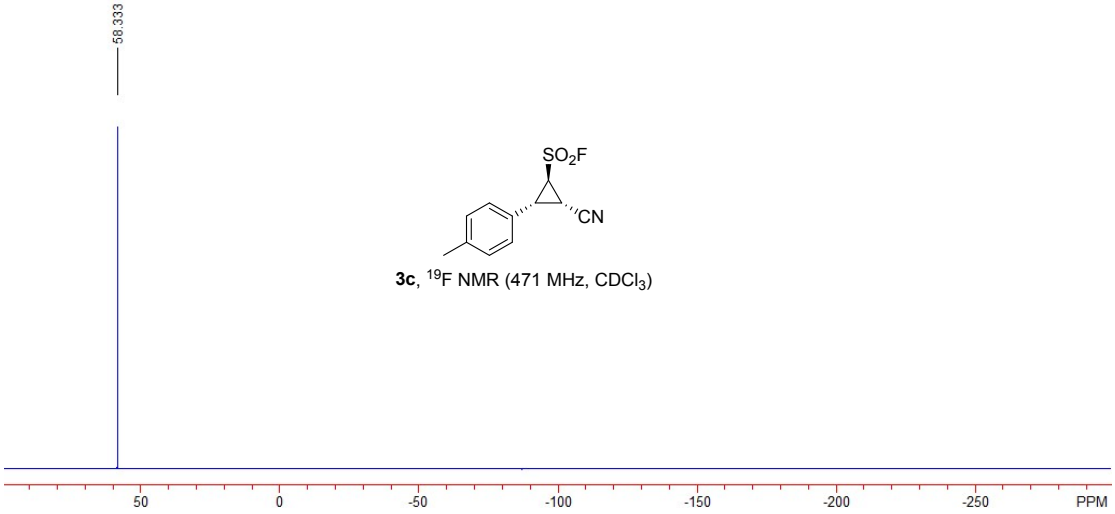

**3b**, $^{19}$F NMR (471 MHz, $CDCl_3$)



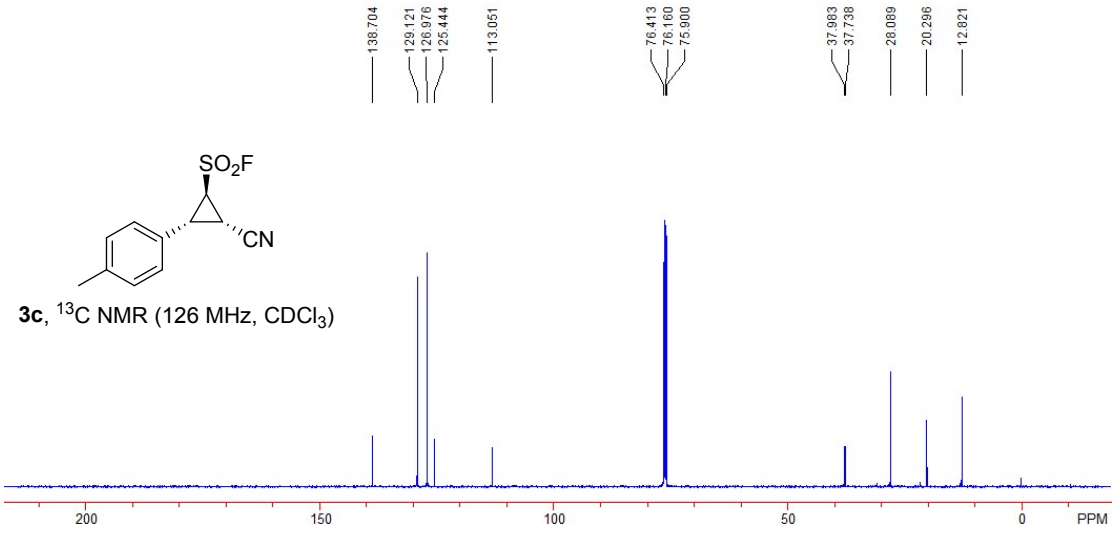

**3b**, $^{13}$C NMR (126 MHz, $CDCl_3$)



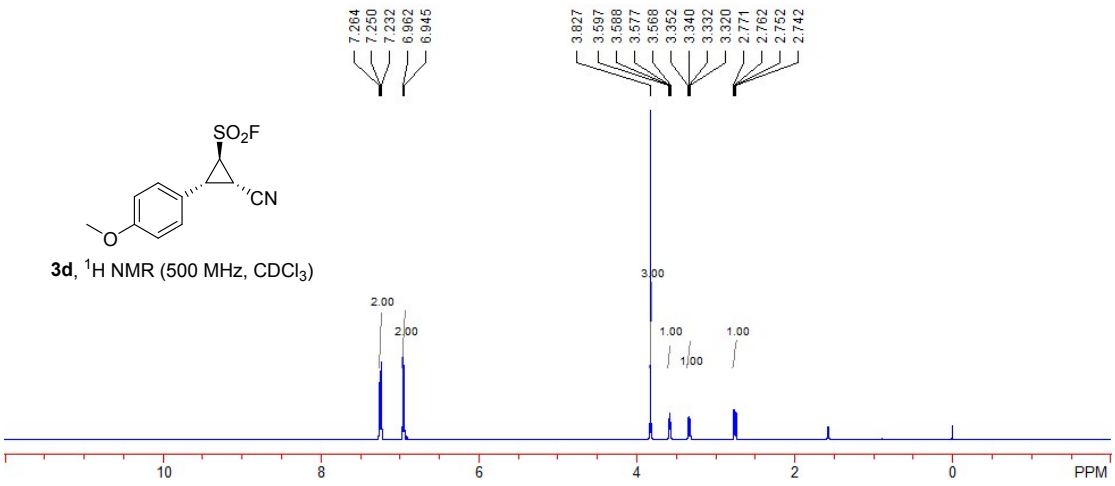

**3c**, $^{1}$H NMR (500 MHz, $CDCl_3$)



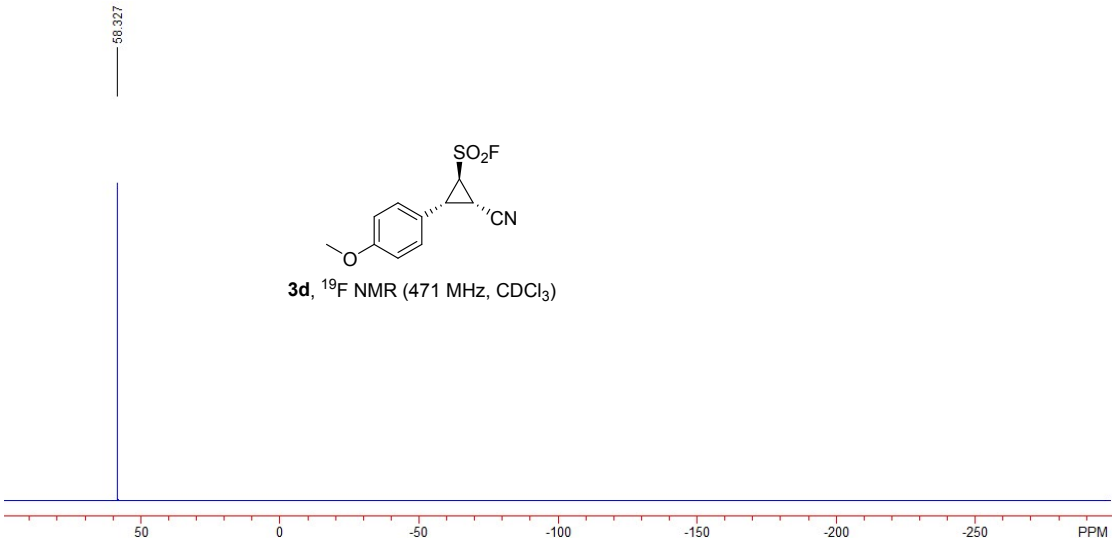

**3c**, $^{19}$F NMR (471 MHz, $CDCl_3$)



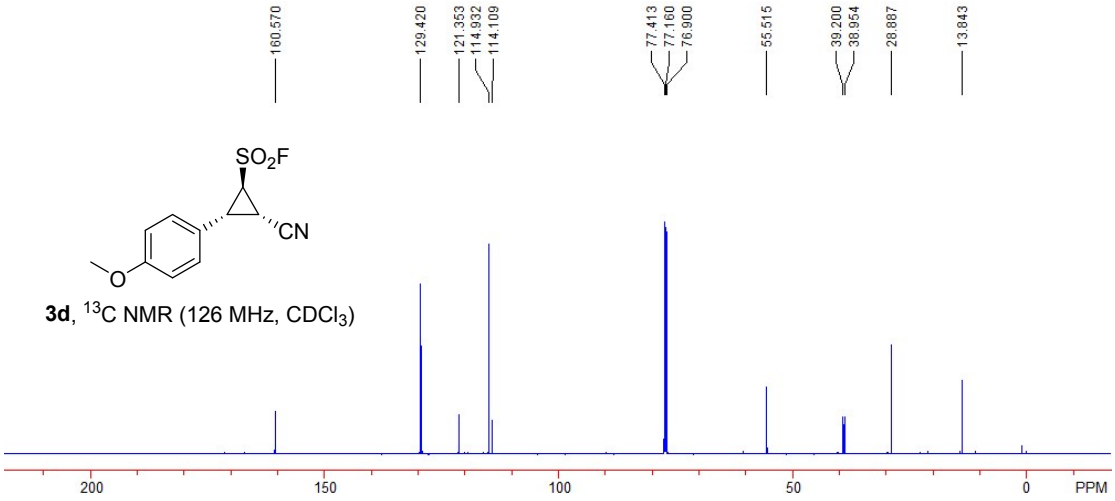

**3c**, $^{13}$C NMR (126 MHz, $CDCl_3$)



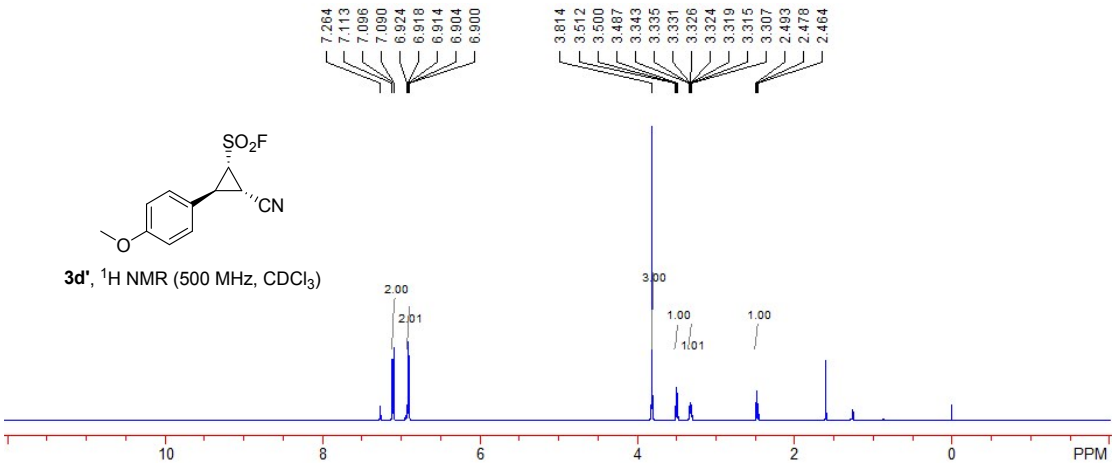

**3d**, $^{1}$H NMR (500 MHz, $CDCl_3$)



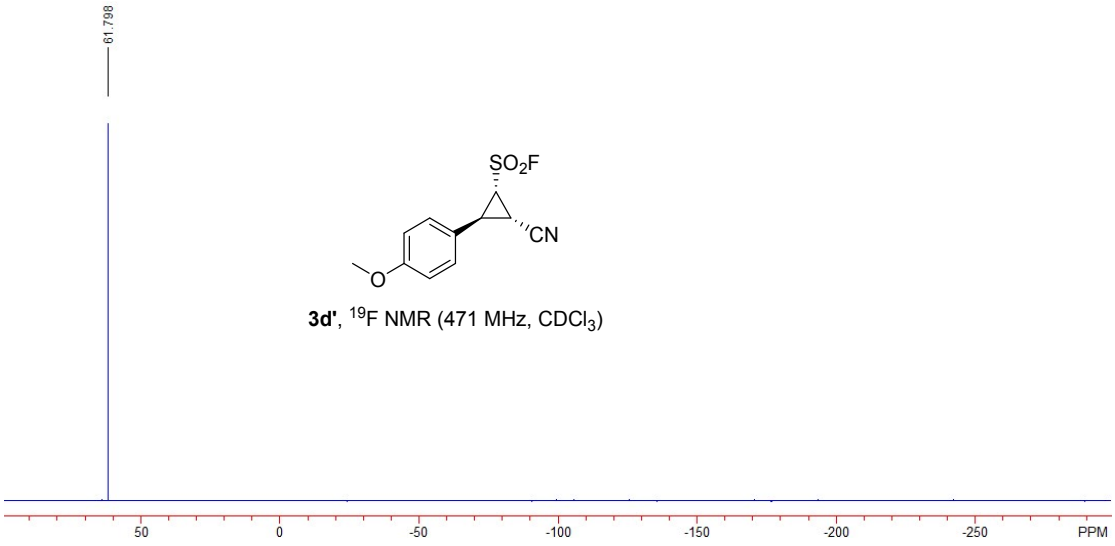

**3d**, $^{19}$F NMR (471 MHz, $CDCl_3$)



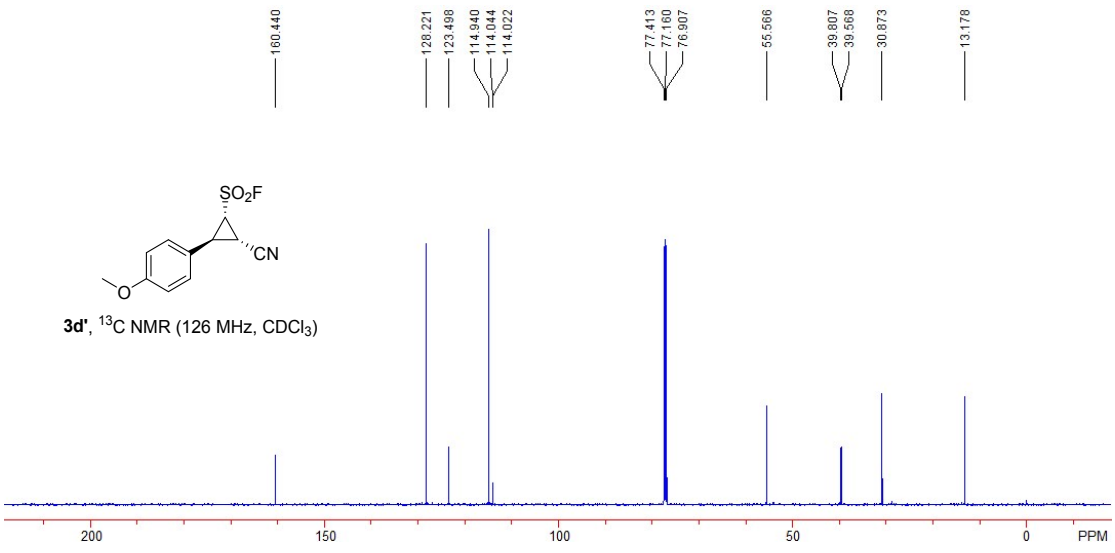

**3d**, $^{13}$C NMR (126 MHz, $CDCl_3$)



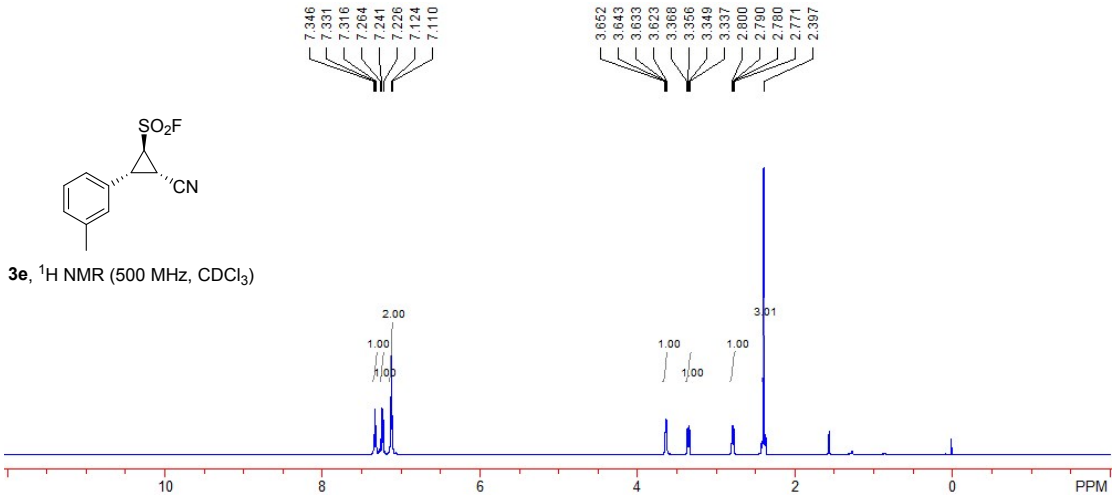

**3d'**, $^{1}$H NMR (500 MHz, $CDCl_3$)



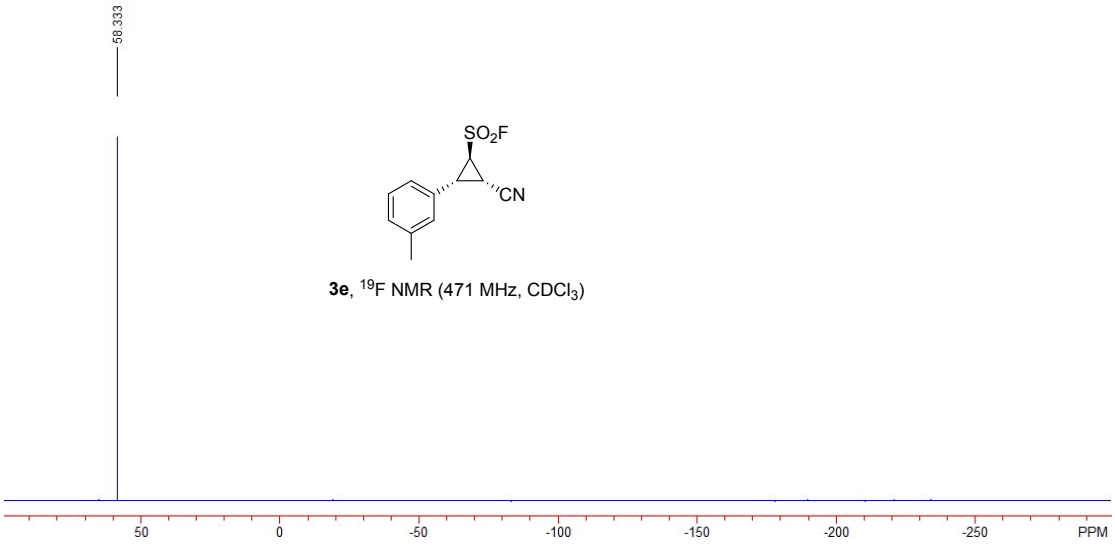

**3d'**, $^{19}$F NMR (471 MHz, $CDCl_3$)



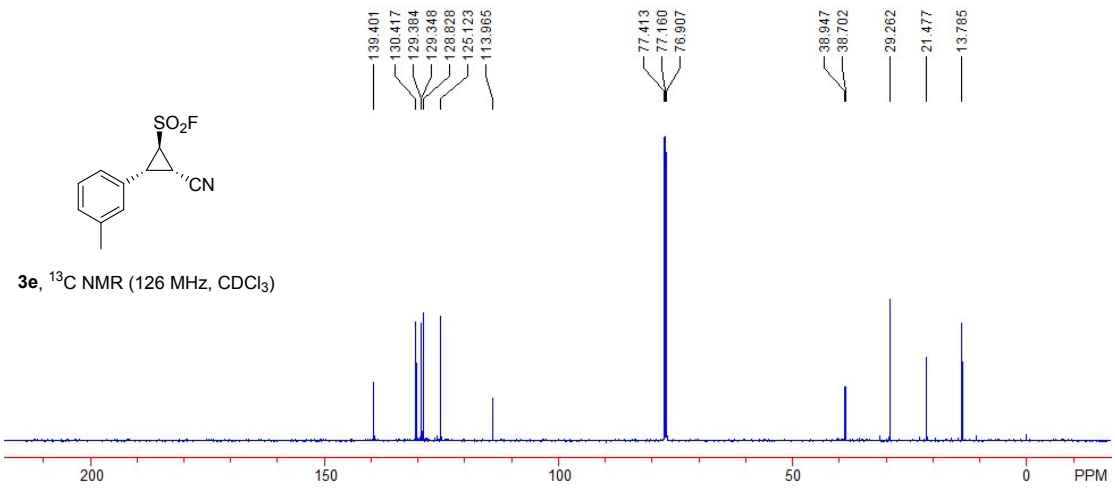

**3d'**, $^{13}$C NMR (126 MHz, $CDCl_3$)



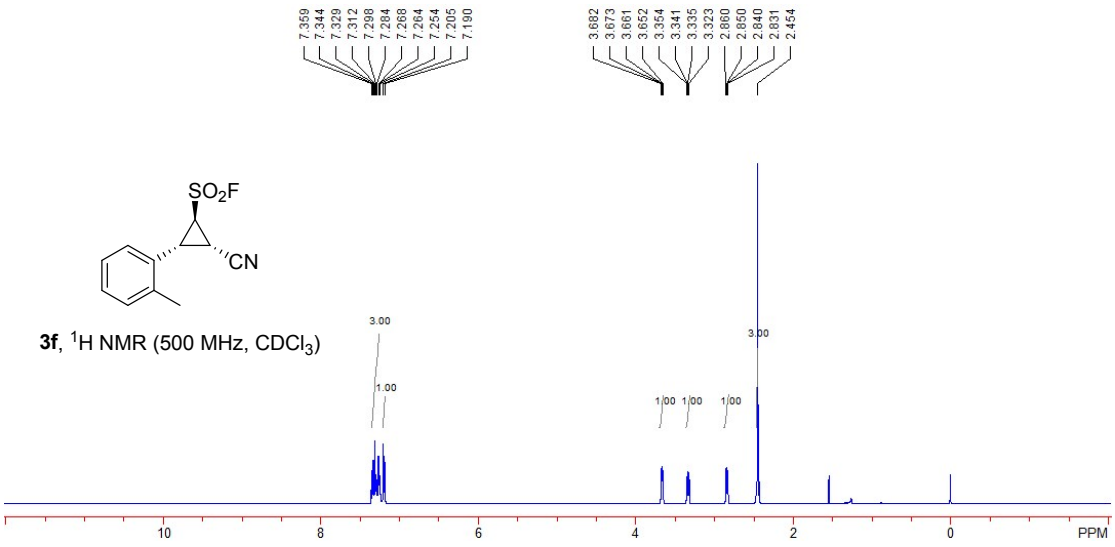

**3e**, $^{1}$H NMR (500 MHz, $CDCl_3$)



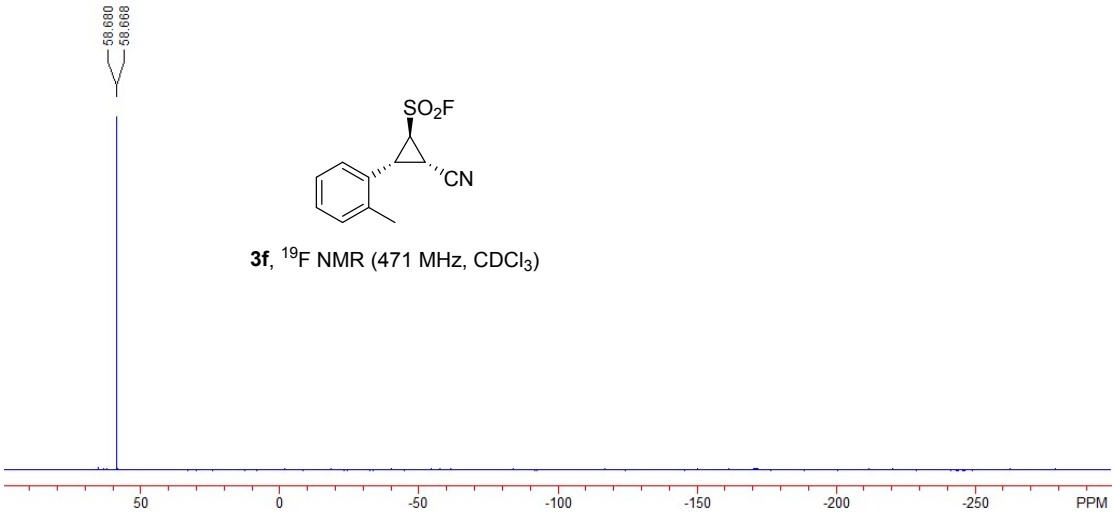

**3e**, $^{19}$F NMR (471 MHz, $CDCl_3$)



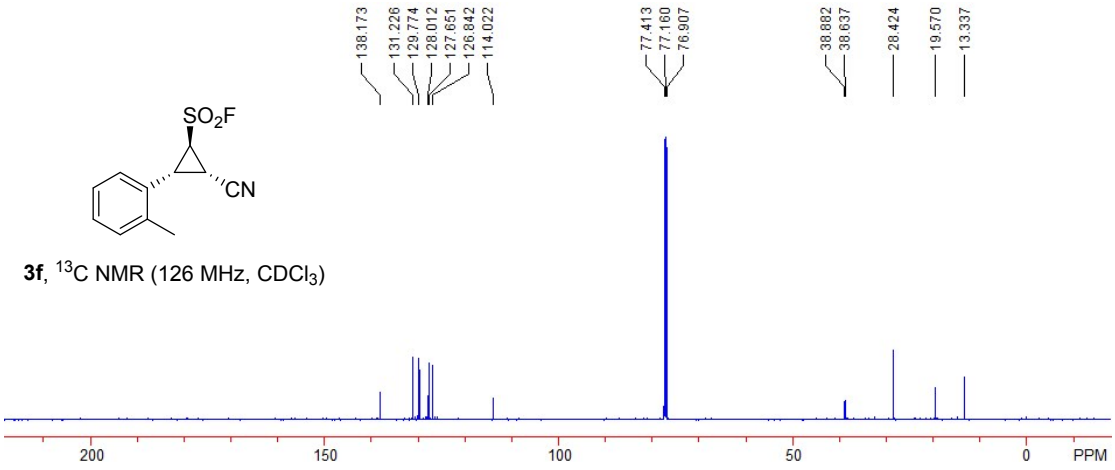

**3e**, $^{13}$C NMR (126 MHz, $CDCl_3$)



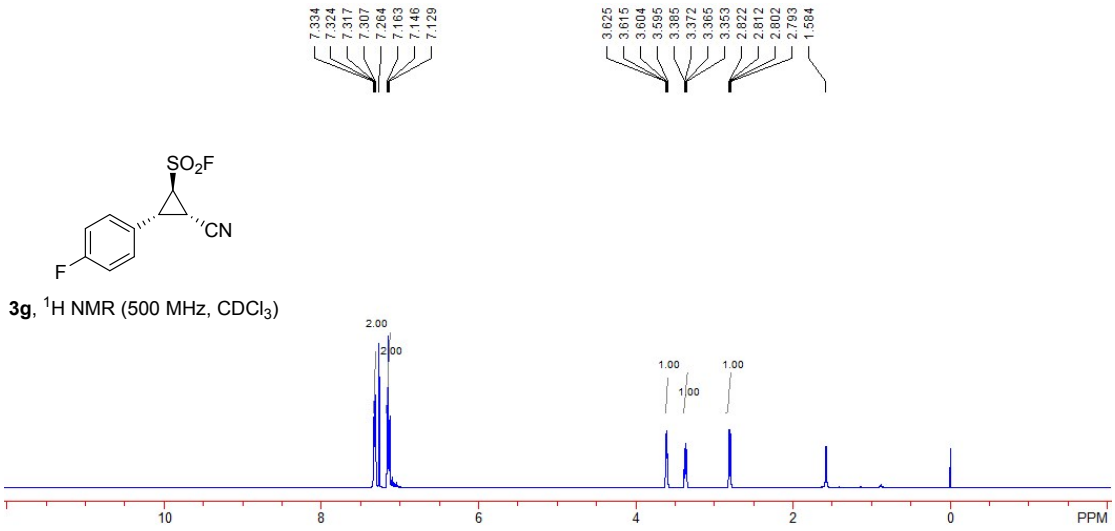

**3f**, $^{1}$H NMR (500 MHz, $CDCl_3$)



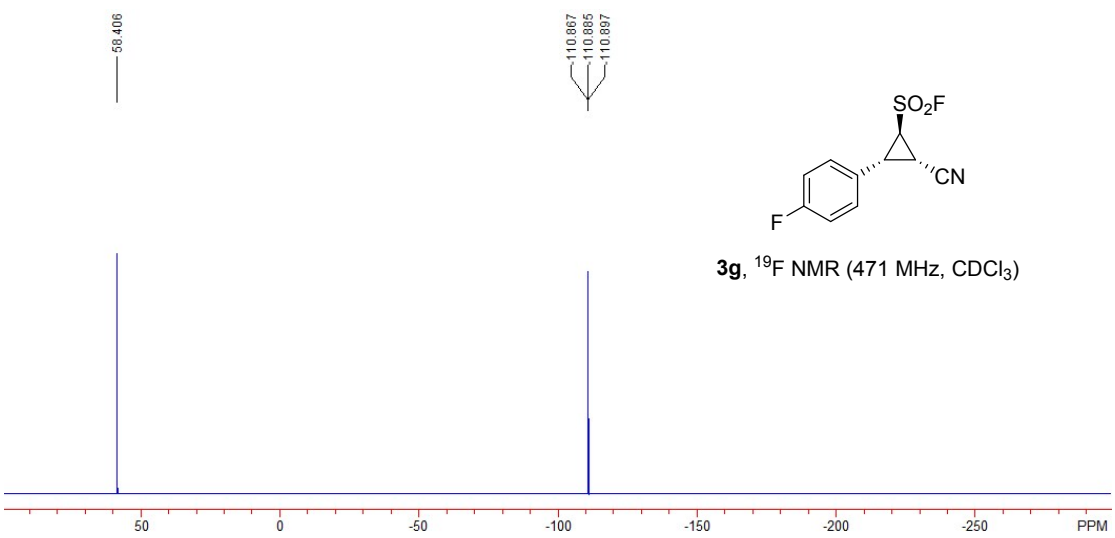

**3f**, $^{19}$F NMR (471 MHz, $CDCl_3$)



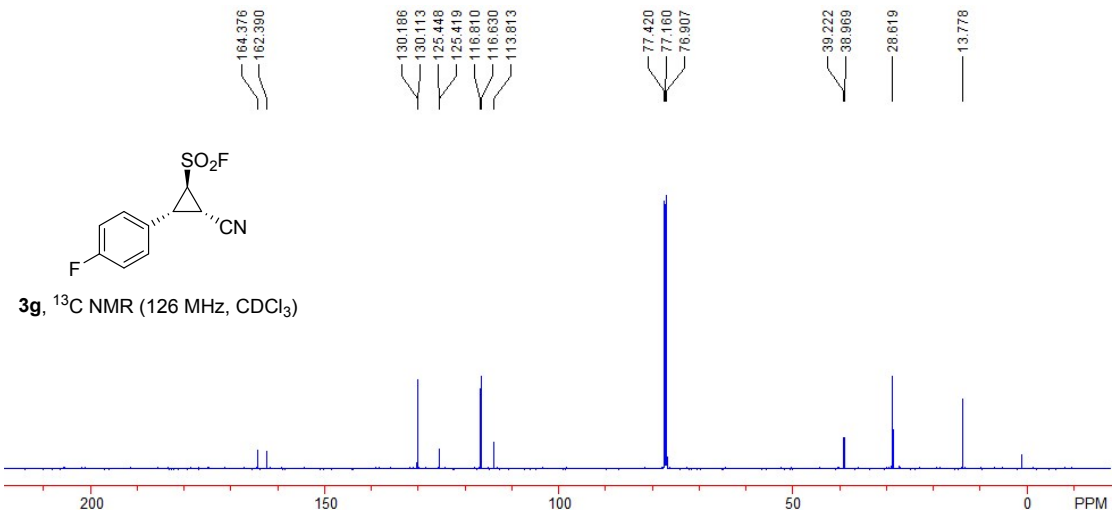

**3f**, $^{13}$C NMR (126 MHz, $CDCl_3$)



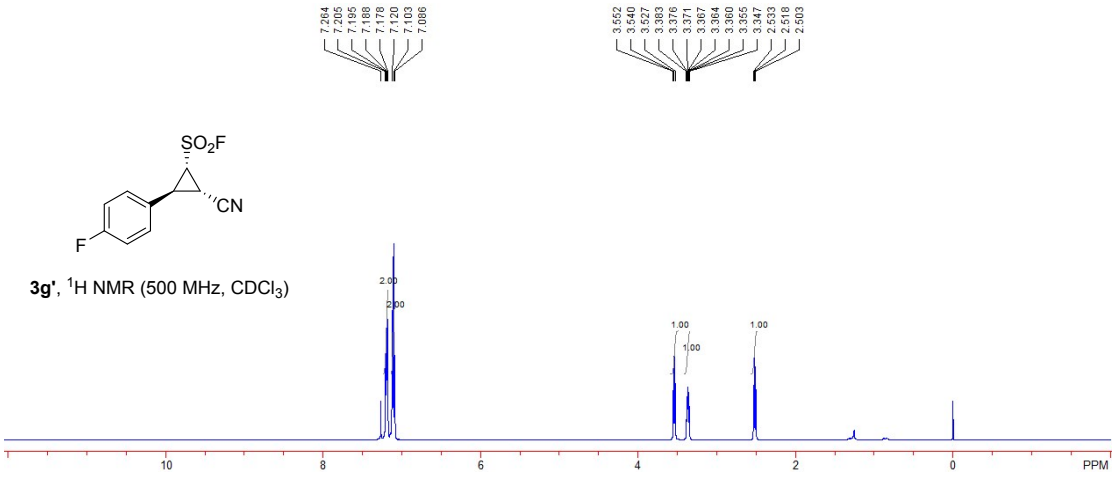

**3g**, $^{1}$H NMR (500 MHz, $CDCl_3$)



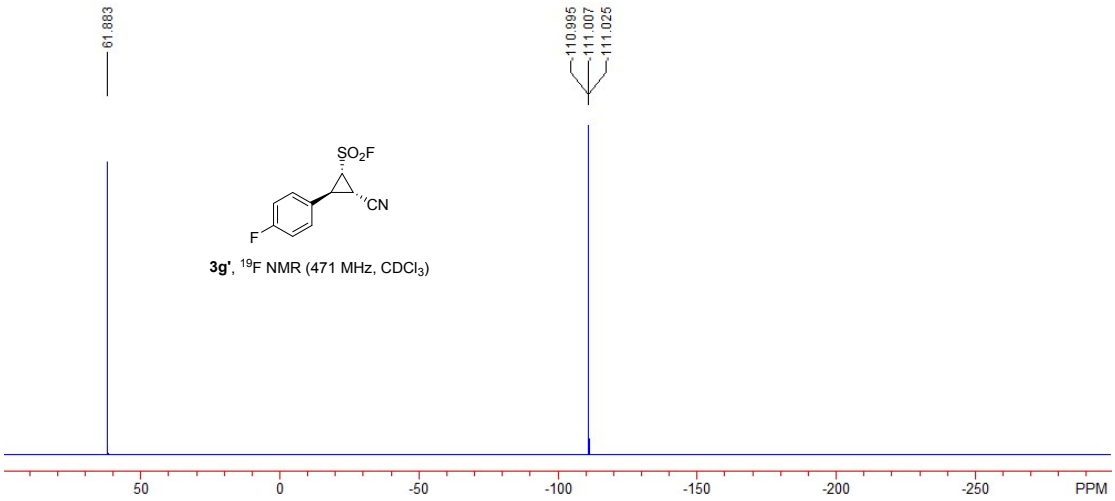

**3g**, $^{19}$F NMR (471 MHz, $CDCl_3$)



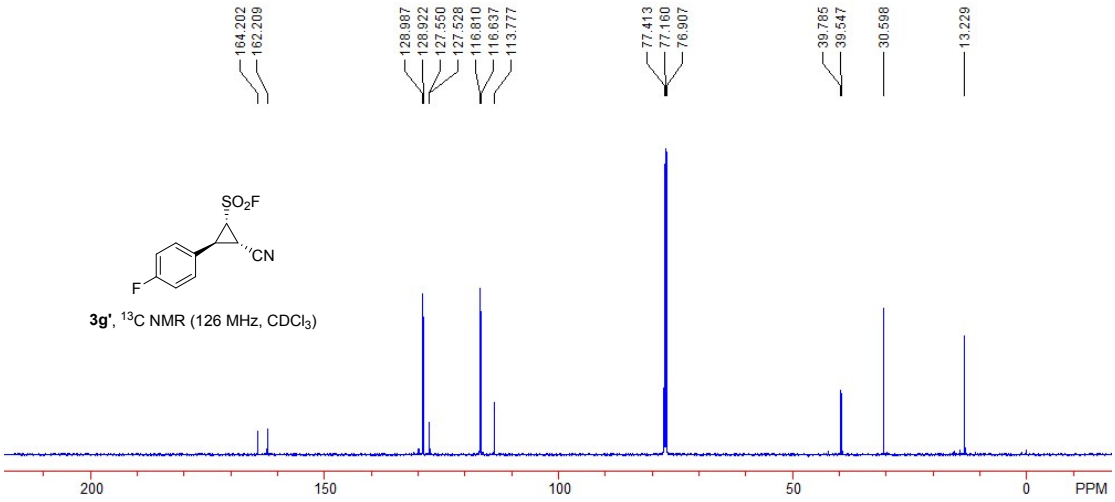

**3g**, $^{13}$C NMR (126 MHz, $CDCl_3$)



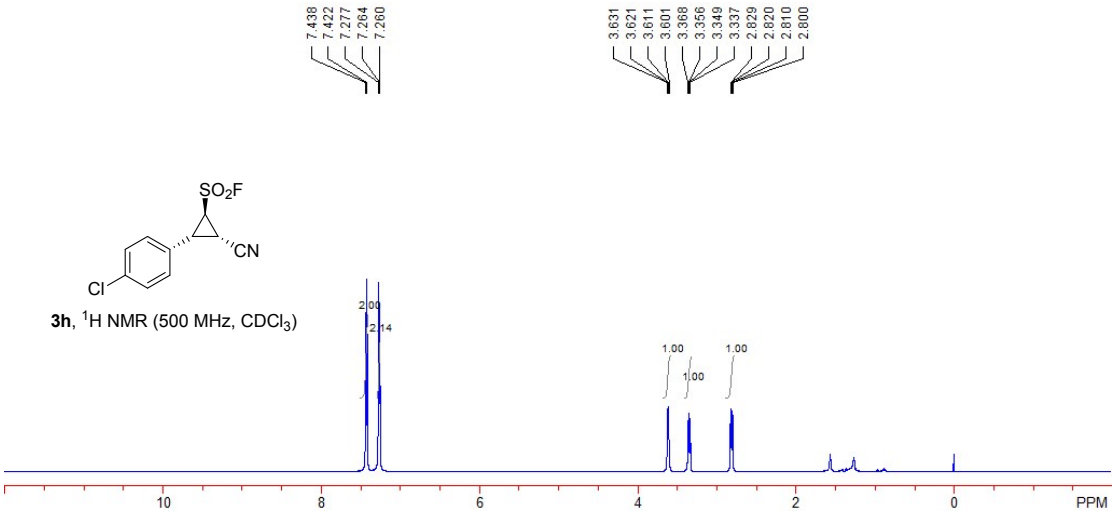

**3g'**, $^{1}$H NMR (500 MHz, $CDCl_3$)



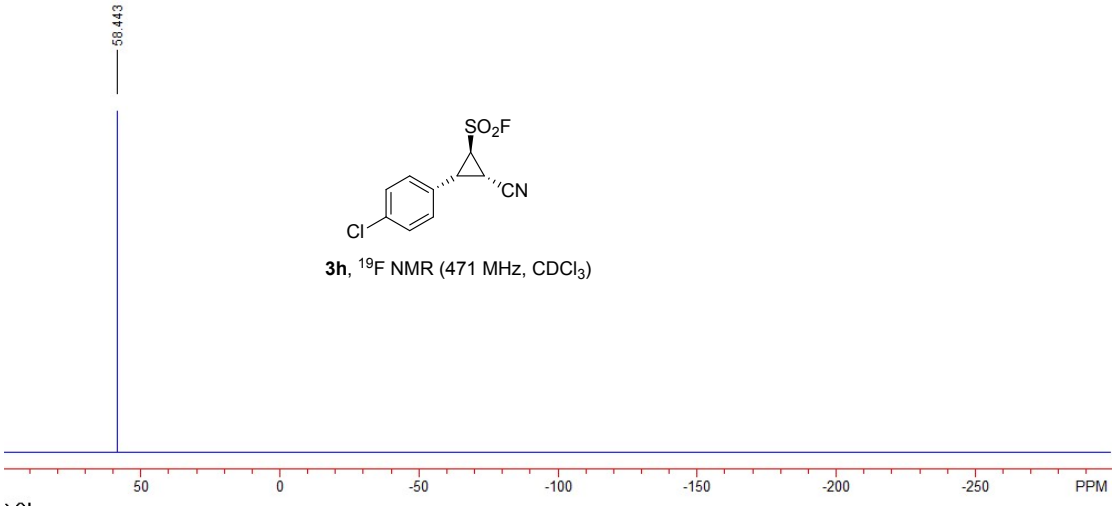

**3g'**, $^{19}$F NMR (471 MHz, $CDCl_3$)



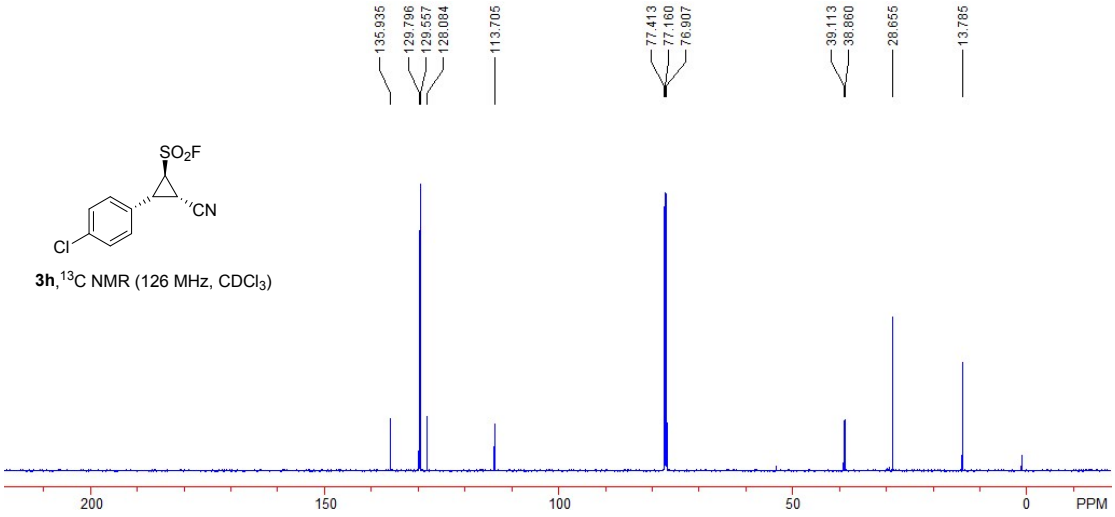

**3g'**, $^{13}$C NMR (126 MHz, $CDCl_3$)



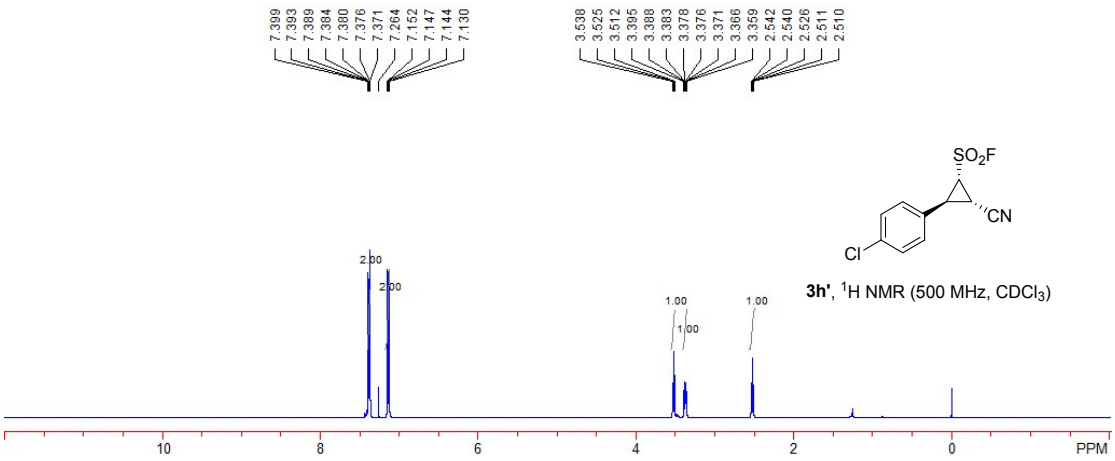

**3h**, $^{1}$H NMR (500 MHz, $CDCl_3$)



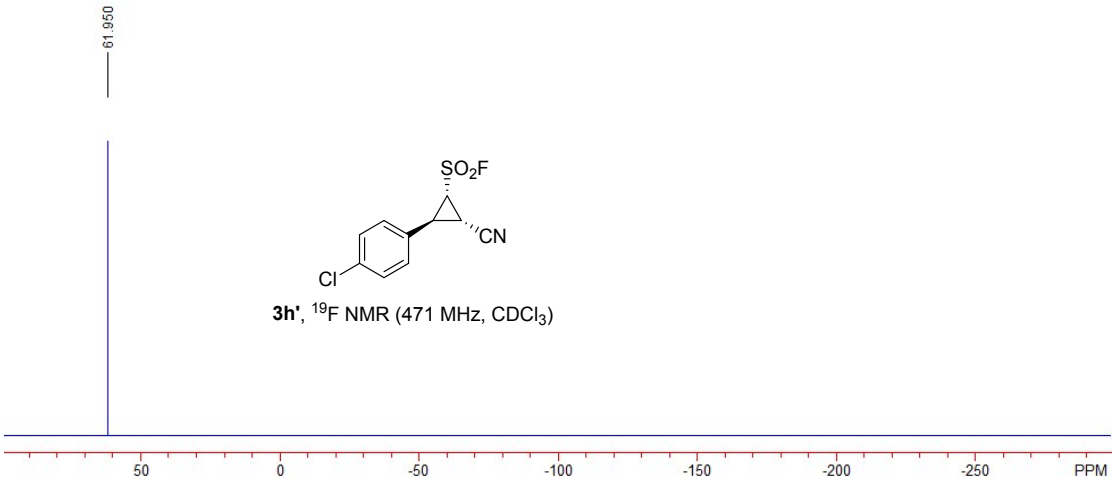

**3h**, $^{19}$F NMR (471 MHz, $CDCl_3$)



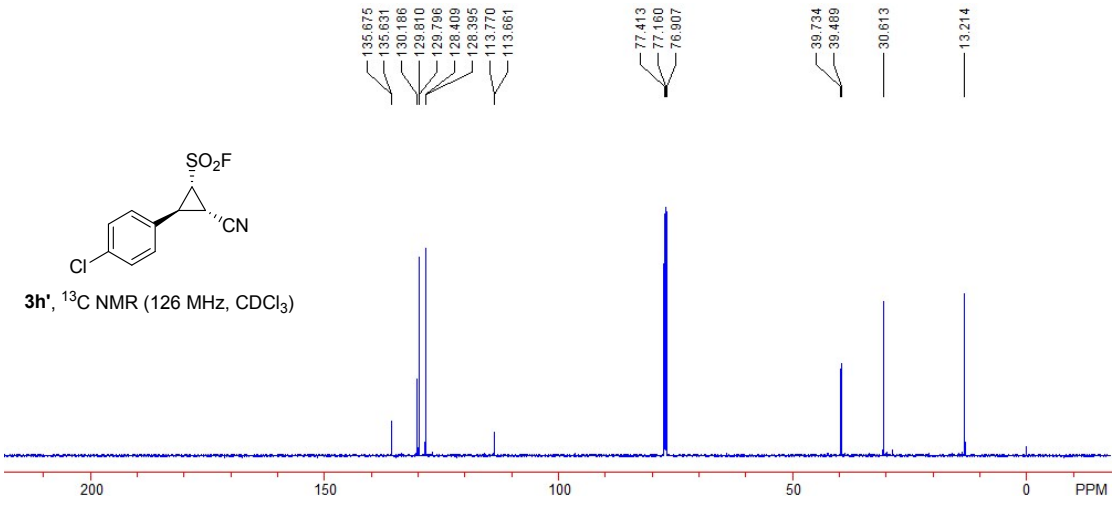

**3h**,$^{13}$C NMR (126 MHz, $CDCl_3$)



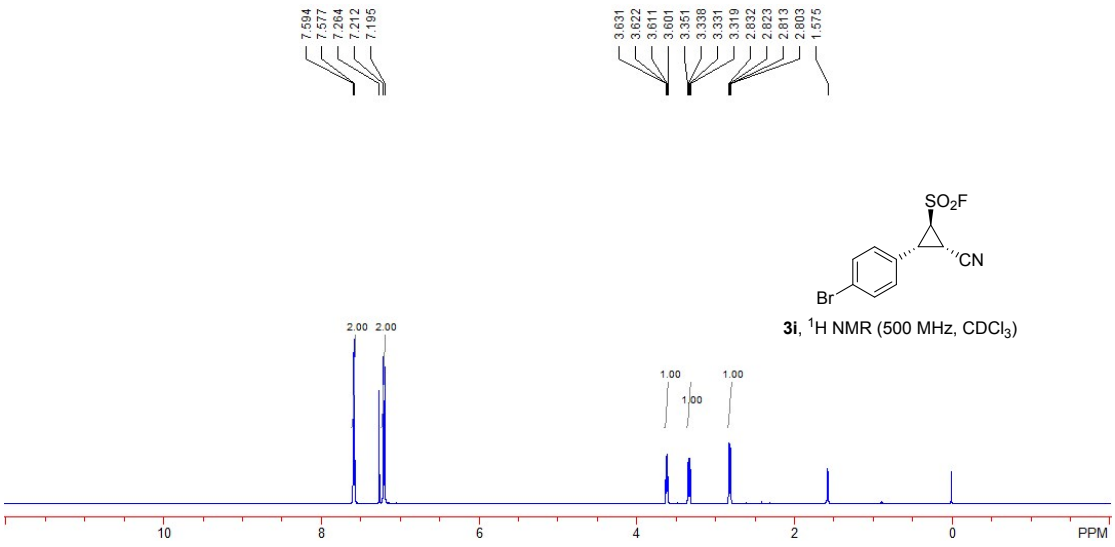

**3h'**, $^{1}$H NMR (500 MHz, $CDCl_3$)



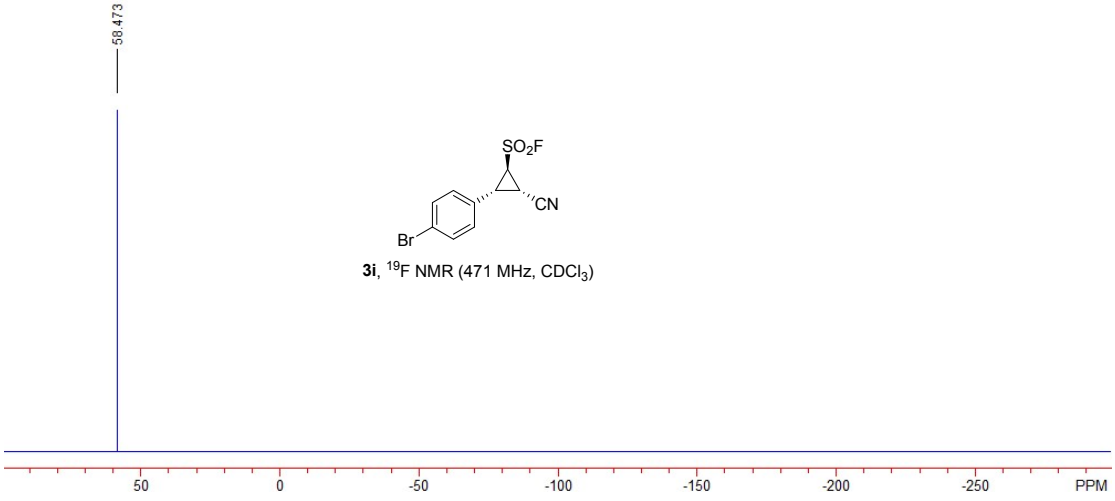

**3h'**, $^{19}$F NMR (471 MHz, $CDCl_3$)



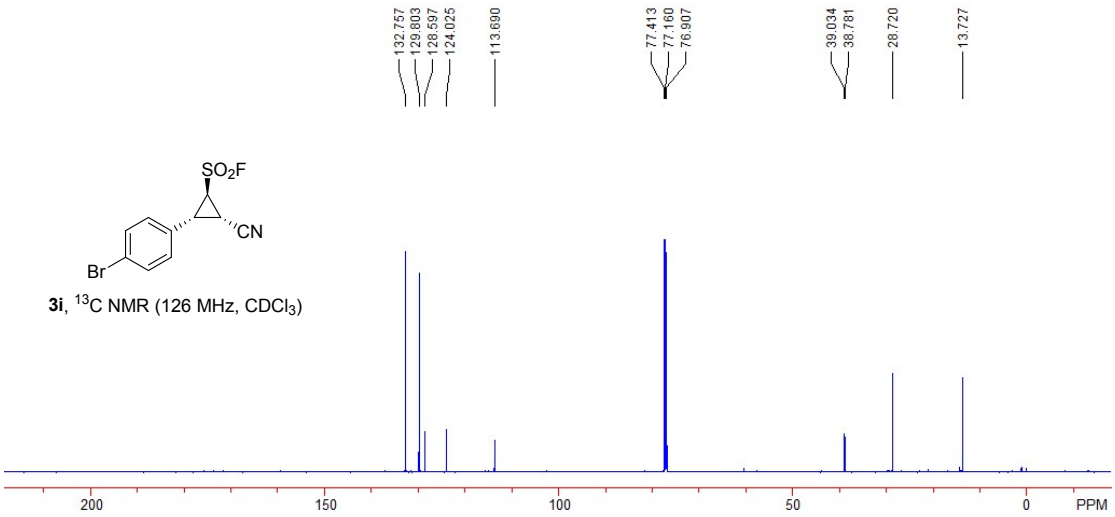

**3h'**, $^{13}$C NMR (126 MHz, $CDCl_3$)



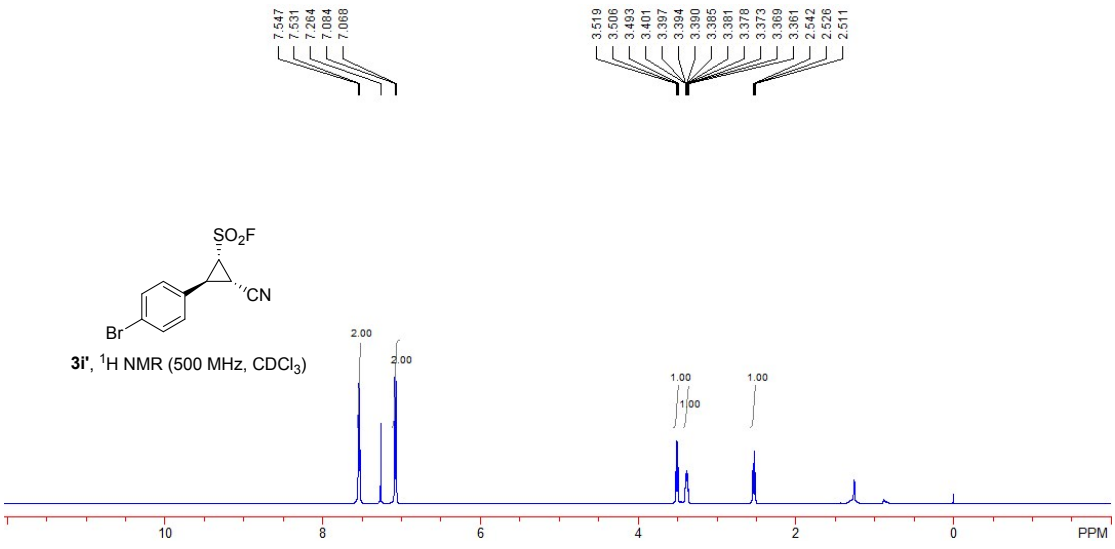

**3i**, $^{1}$H NMR (500 MHz, $CDCl_3$)



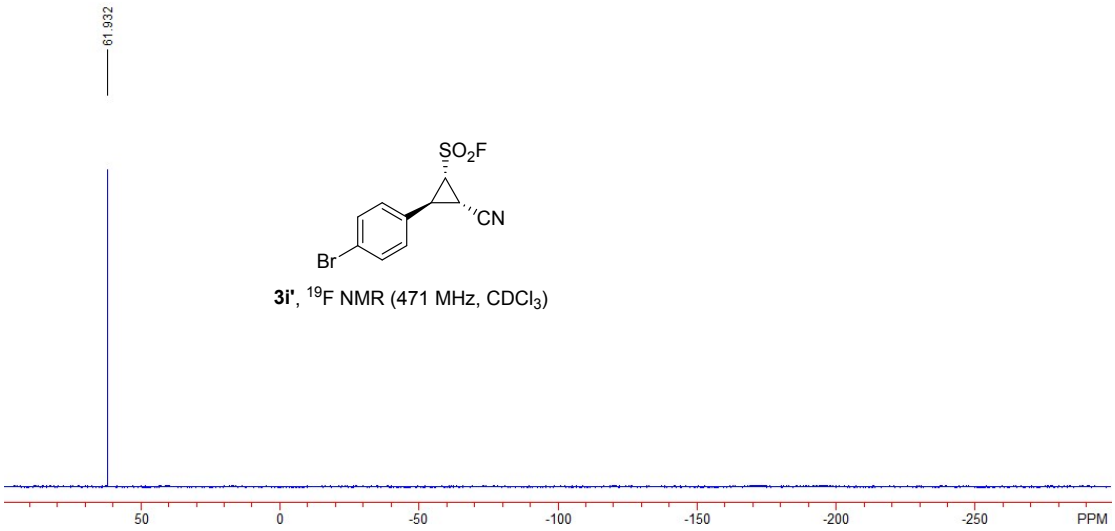

**3i**, $^{19}$F NMR (471 MHz, $CDCl_3$)



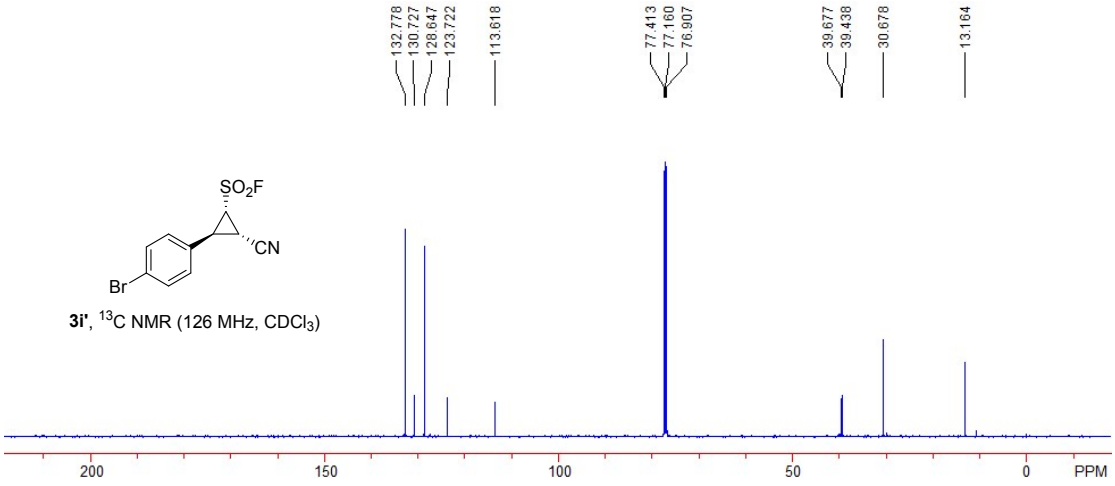

**3i**, $^{13}$C NMR (126 MHz, $CDCl_3$)



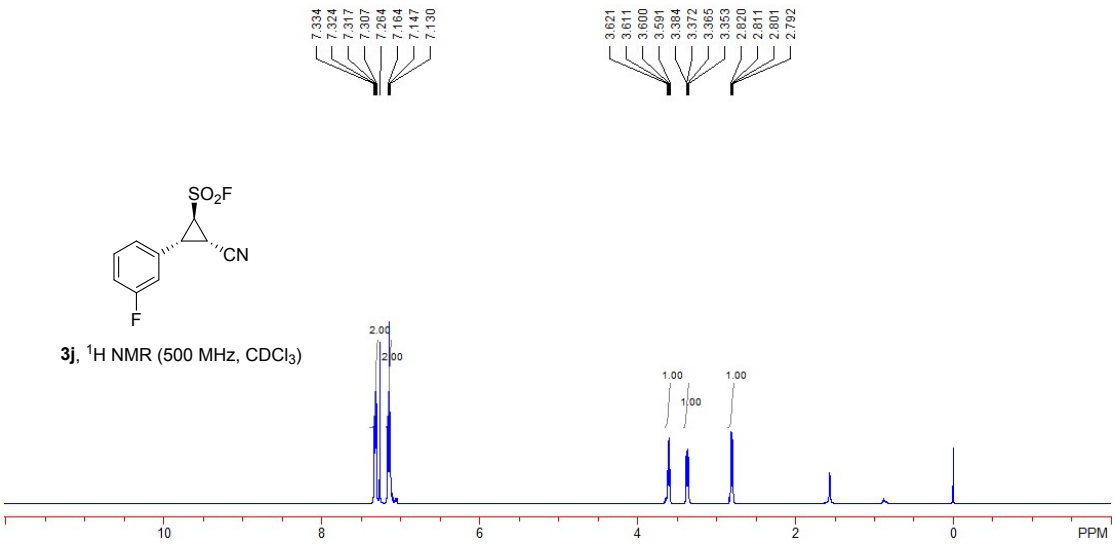

**3i'**, $^{1}$H NMR (500 MHz, $CDCl_3$)



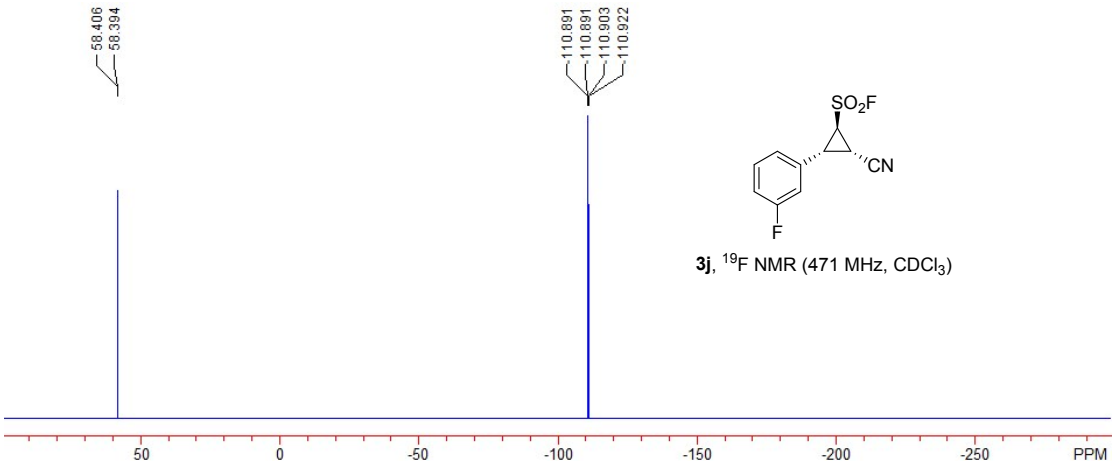

**3i'**, $^{19}$F NMR (471 MHz, $CDCl_3$)



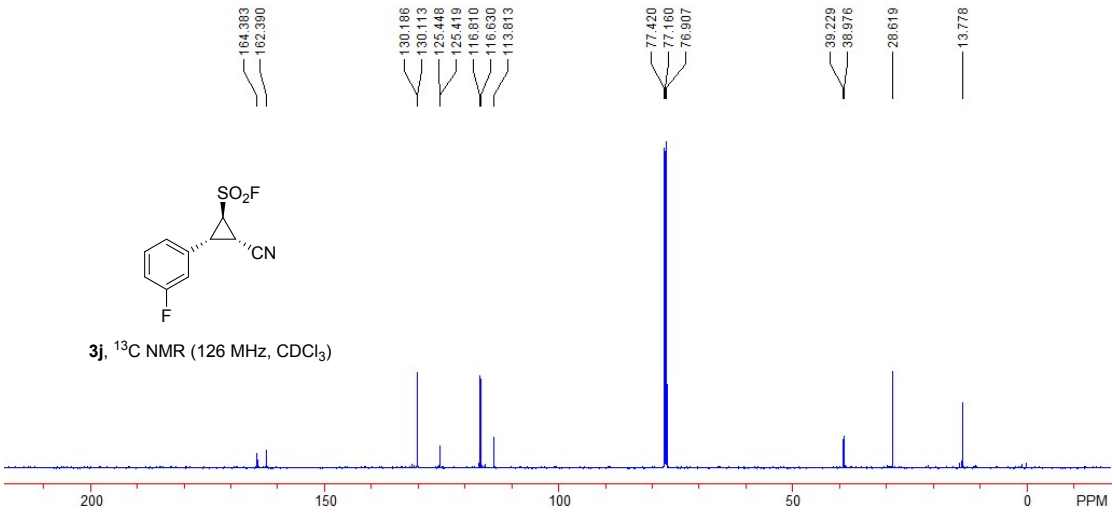

**3i'**, $^{13}$C NMR (126 MHz, $CDCl_3$)



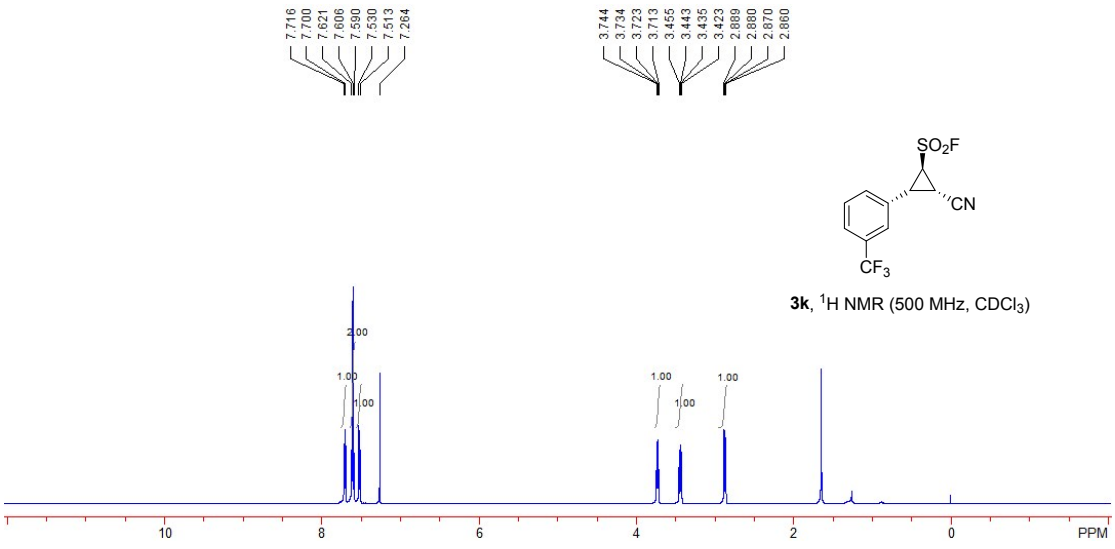

**3j**, $^{1}$H NMR (500 MHz, $CDCl_3$)



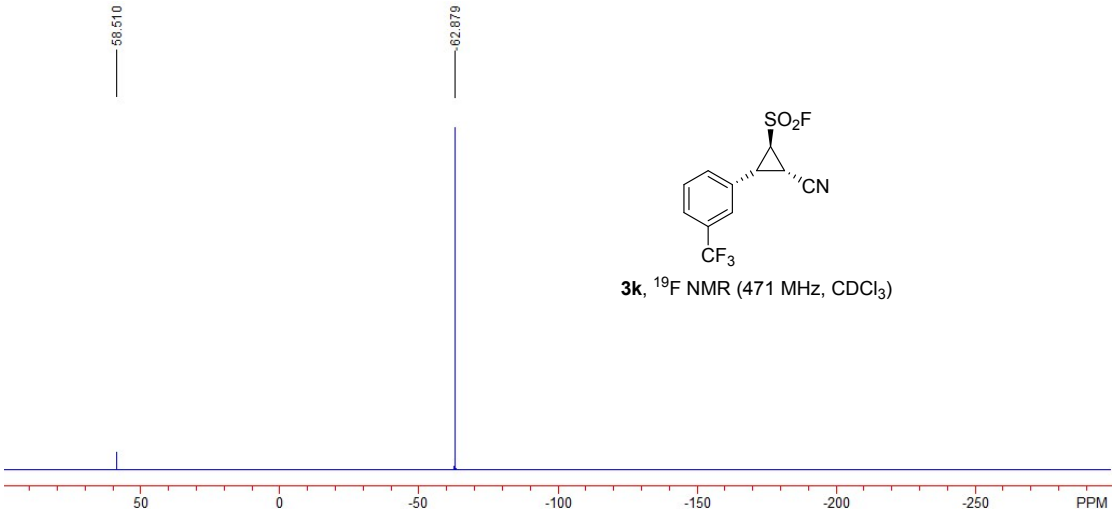

**3j**, $^{19}$F NMR (471 MHz, $CDCl_3$)



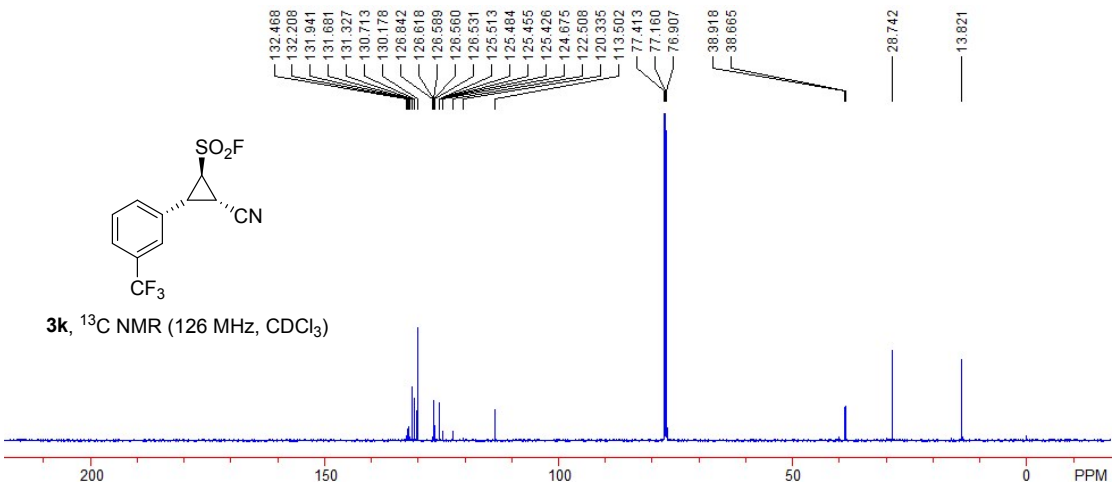

**3j**, $^{13}$C NMR (126 MHz, $CDCl_3$)



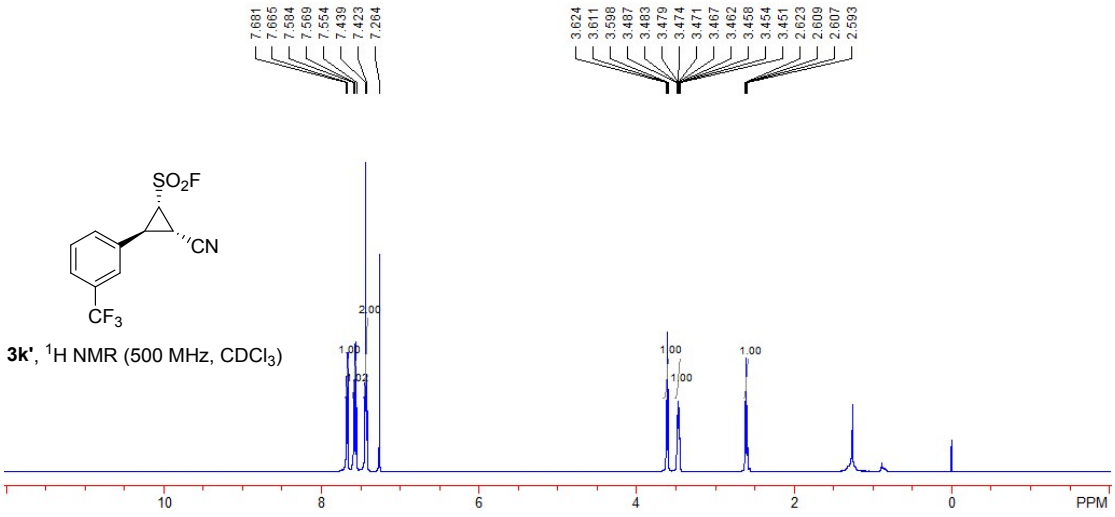

**3k**, $^{1}$H NMR (500 MHz, $CDCl_3$)



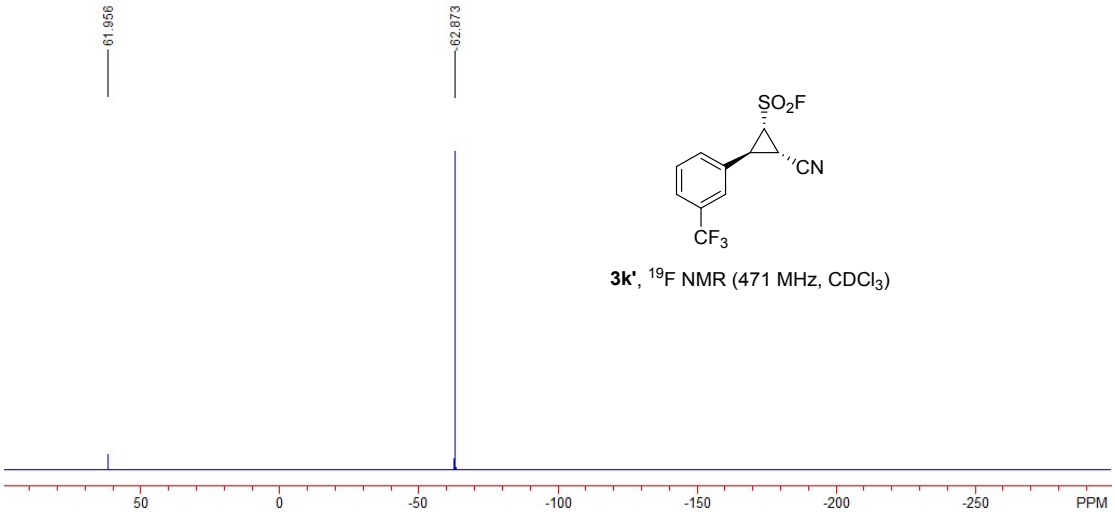

**3k**, $^{19}$F NMR (471 MHz, $CDCl_3$)



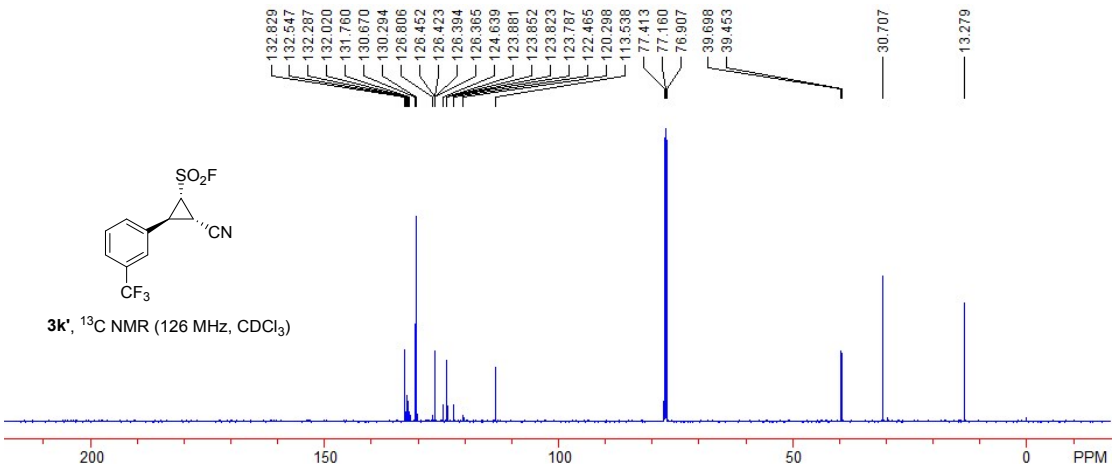

**3k**, $^{13}$C NMR (126 MHz, $CDCl_3$)



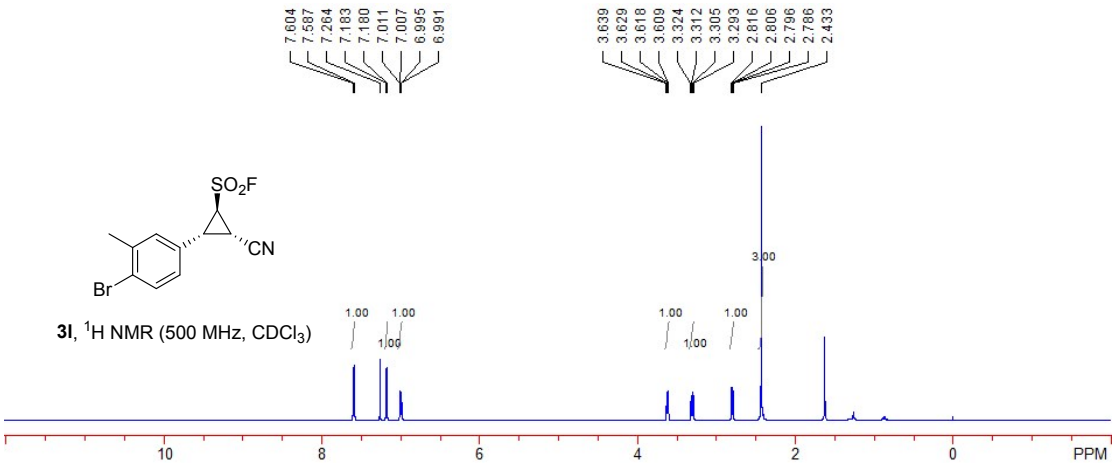

**3k'**, $^{1}$H NMR (500 MHz, $CDCl_3$)



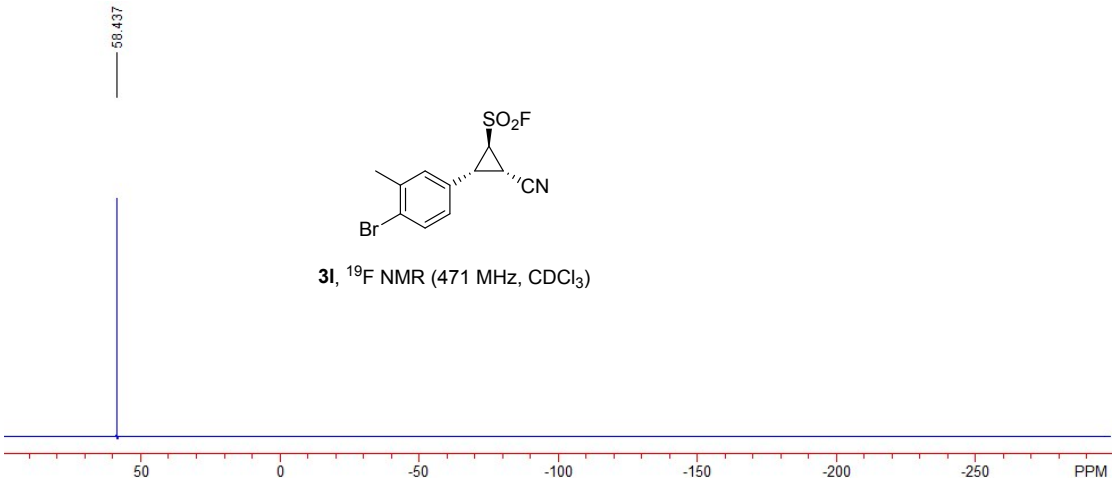

**3k'**, $^{19}$F NMR (471 MHz, $CDCl_3$)



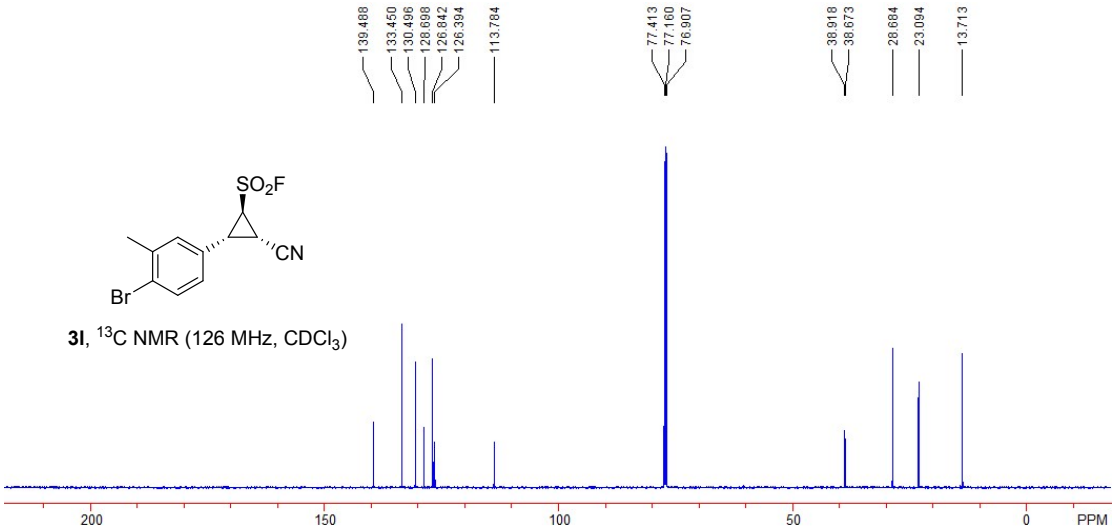

**3k'**, $^{13}$C NMR (126 MHz, $CDCl_3$)



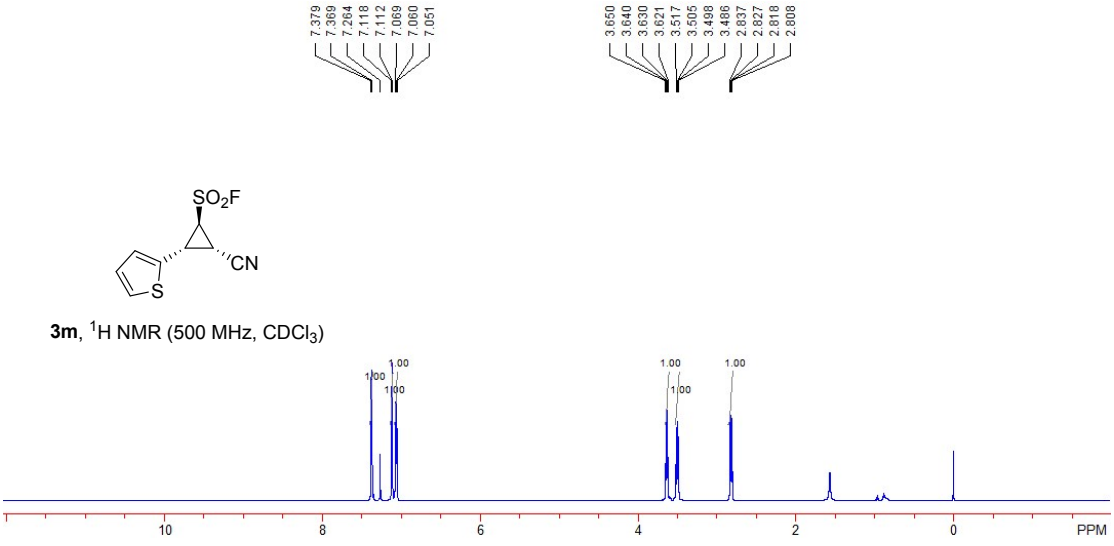

**3l**, $^{1}$H NMR (500 MHz, $CDCl_3$)



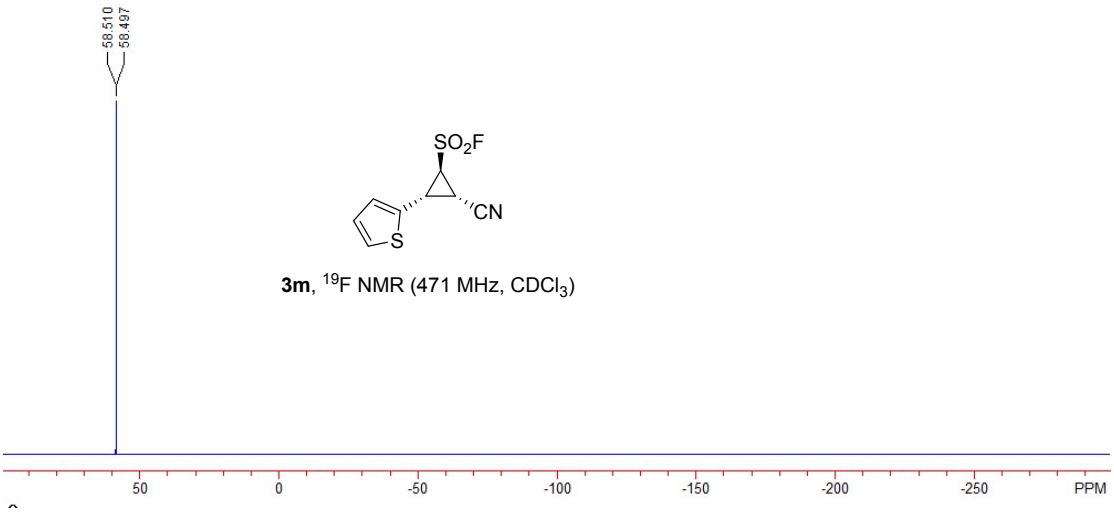

**3l**, $^{19}$F NMR (471 MHz, $CDCl_3$)



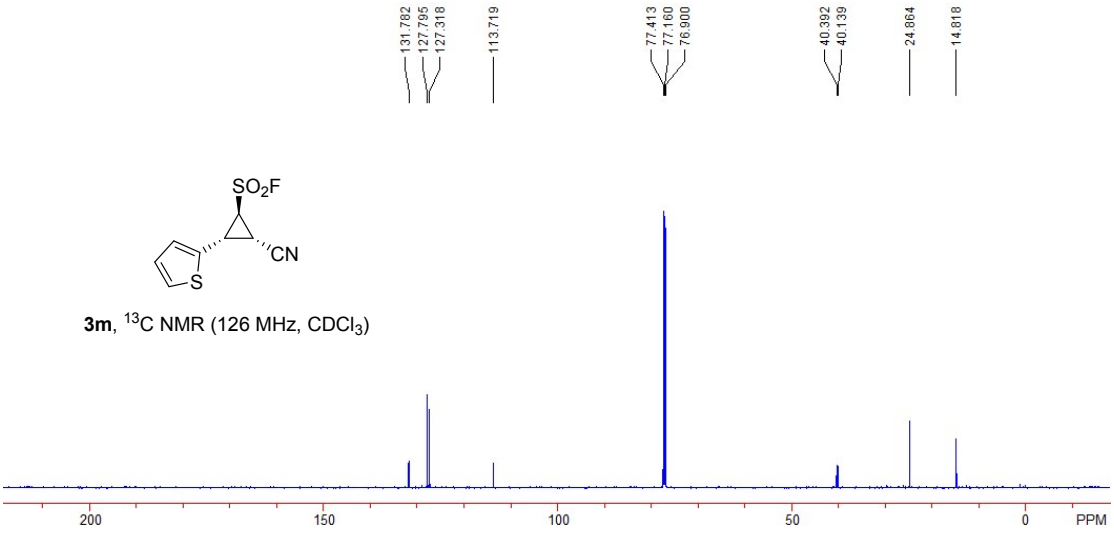

**3l**, $^{13}$C NMR (126 MHz, $CDCl_3$)



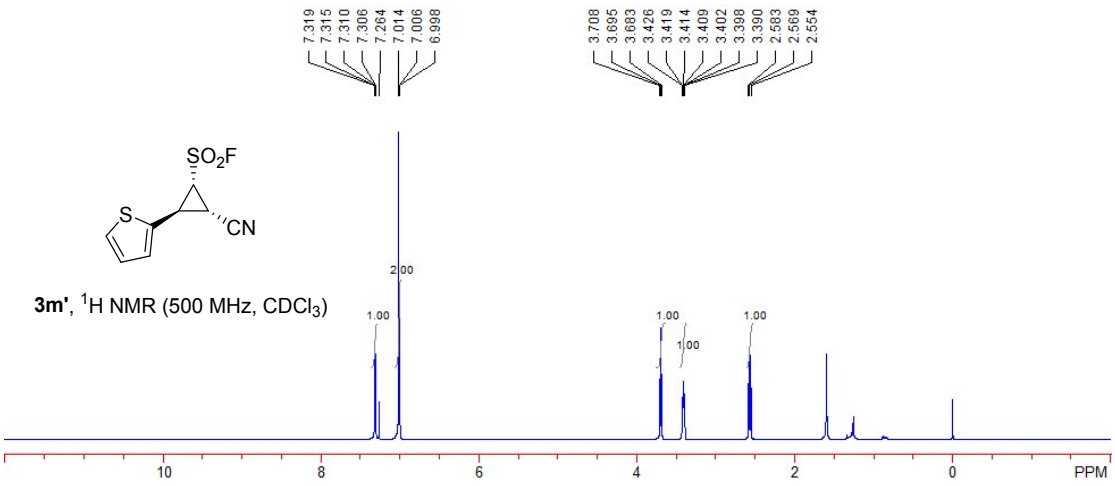

**3m**, $^{1}$H NMR (500 MHz, $CDCl_3$)



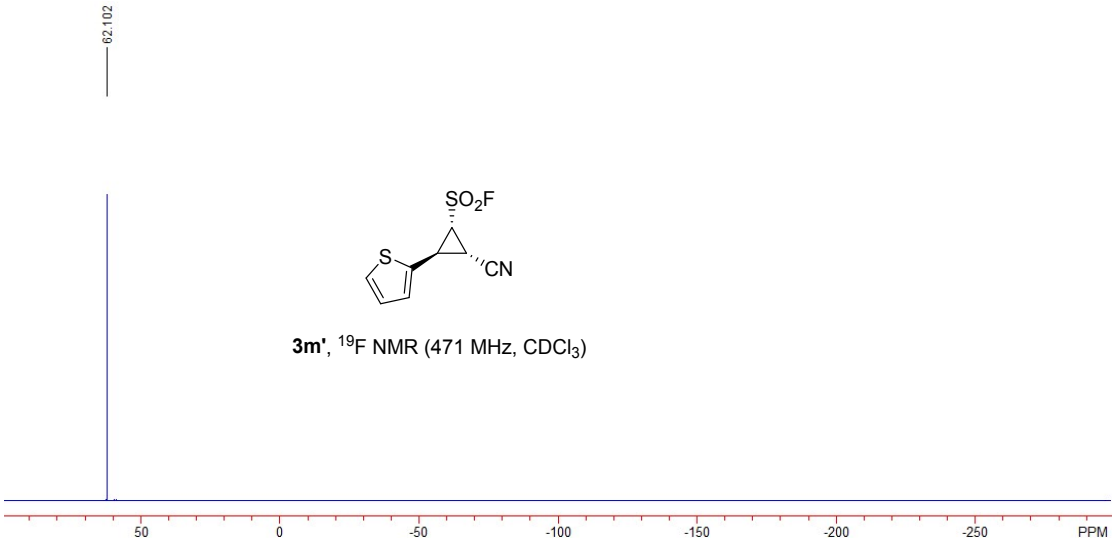

**3m**, $^{19}$F NMR (471 MHz, $CDCl_3$)



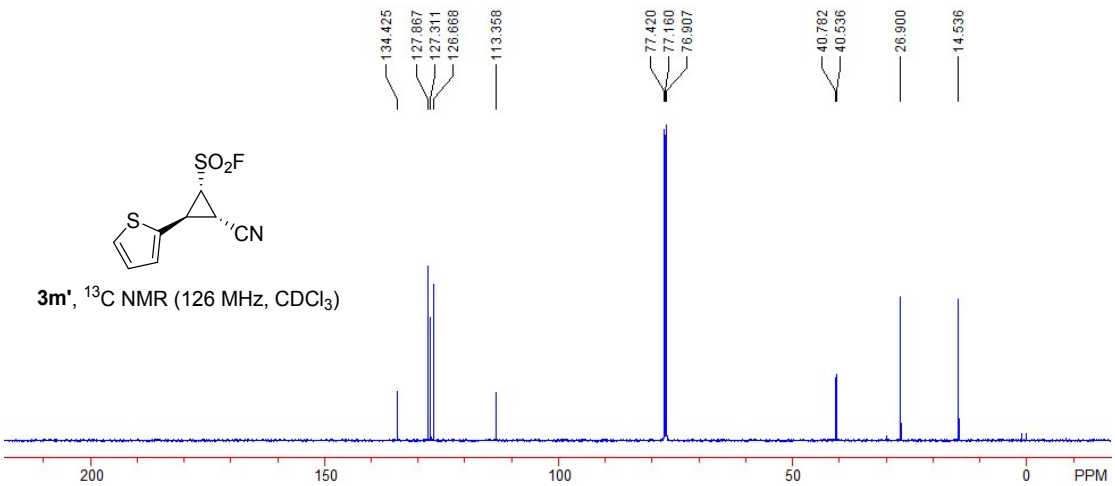

**3m**, $^{13}$C NMR (126 MHz, $CDCl_3$)



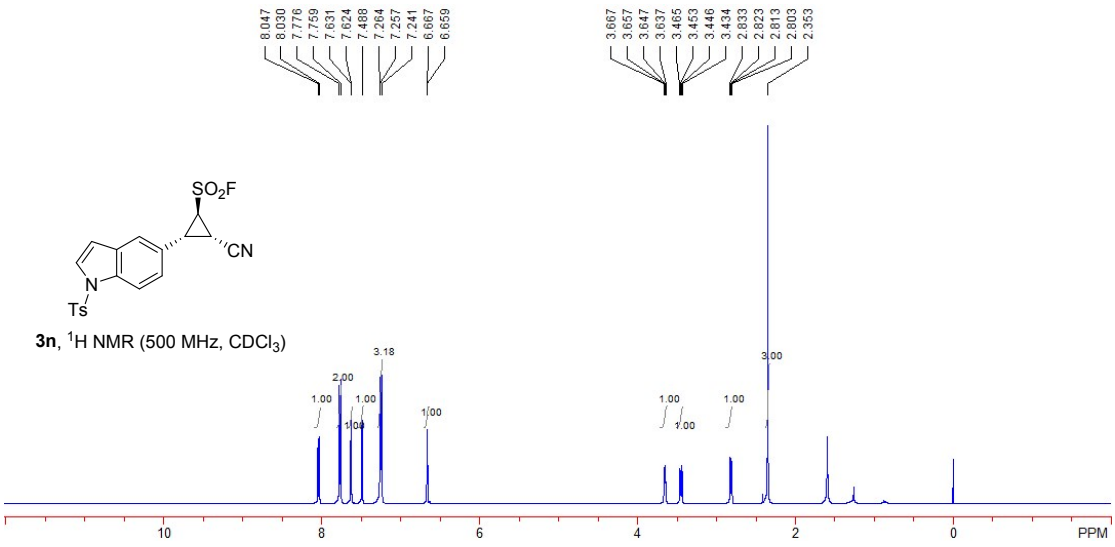

**3m'**, $^{1}$H NMR (500 MHz, $CDCl_3$)



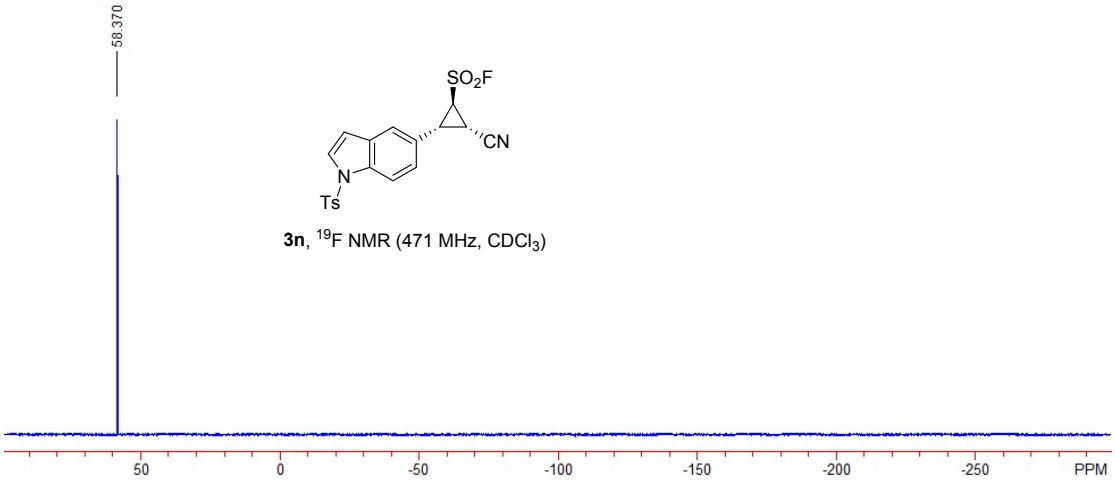

**3m'**, $^{19}$F NMR (471 MHz, $CDCl_3$)



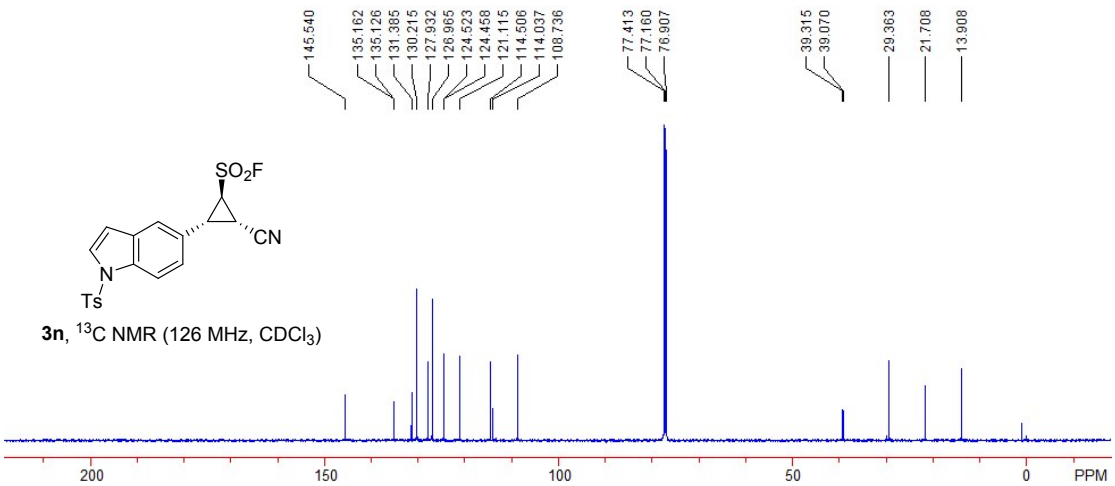

**3m'**, $^{13}$C NMR (126 MHz, $CDCl_3$)



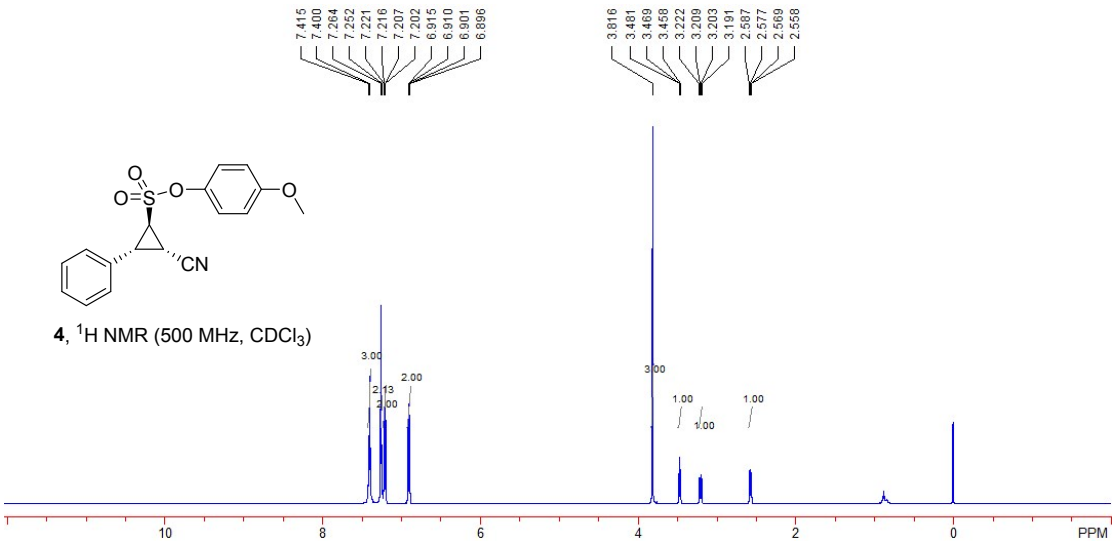

**3n**, $^{1}$H NMR (500 MHz, $CDCl_3$)



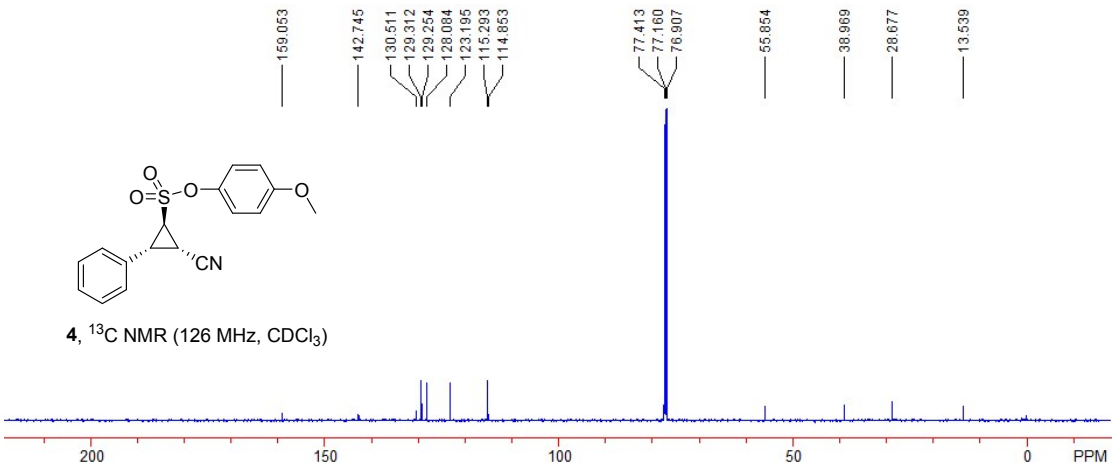

**3n**, $^{19}$F NMR (471 MHz, $CDCl_3$)



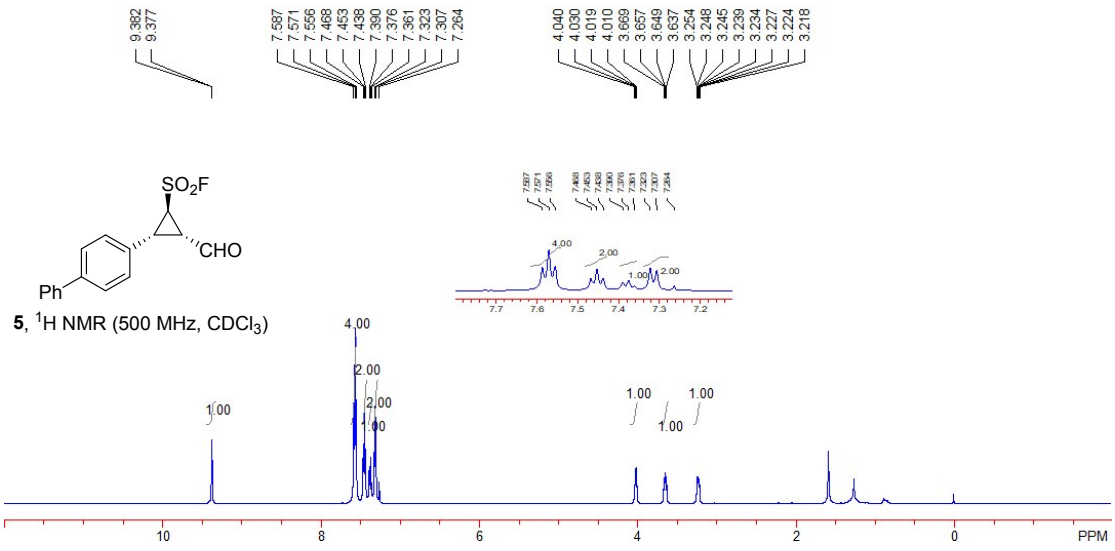

**3n**, $^{13}$C NMR (126 MHz, $CDCl_3$)



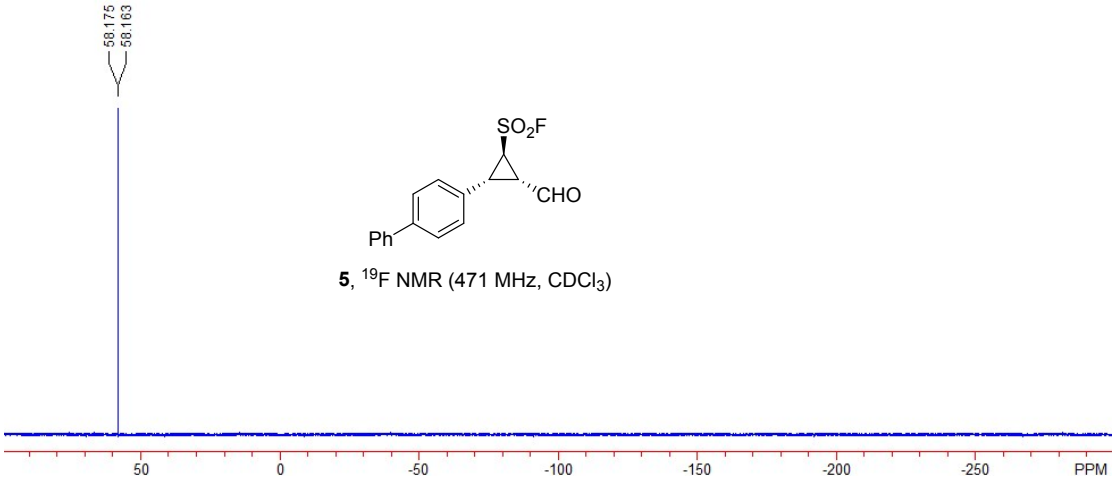

**4**, $^{1}$H NMR (500 MHz, $CDCl_3$)



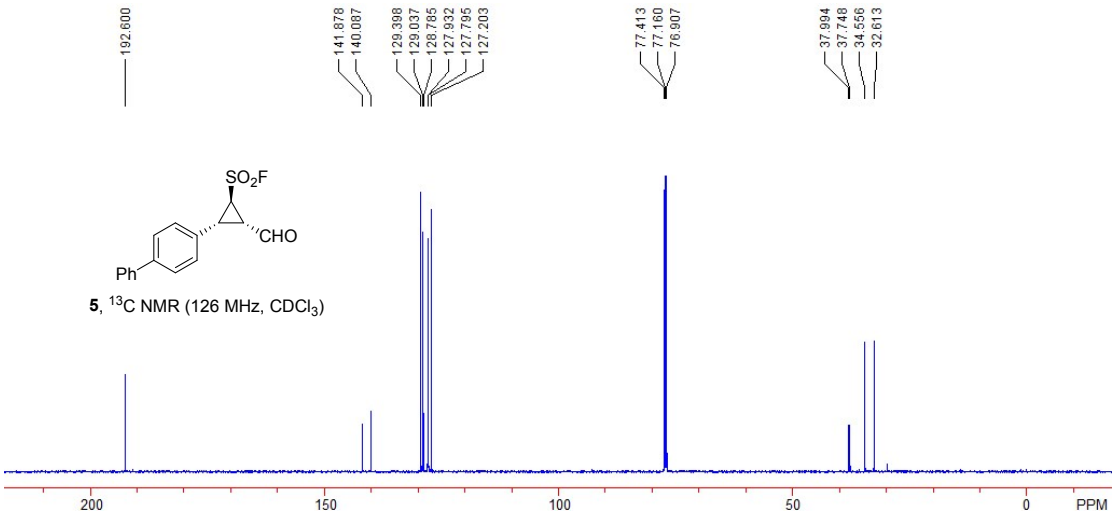

**4**, $^{13}$C NMR (126 MHz, $CDCl_3$)




**5**, $^{1}$H NMR (500 MHz, $CDCl_3$)




**5**, $^{19}$F NMR (471 MHz, $CDCl_3$)




**5**, $^{13}$C NMR (126 MHz, $CDCl_3$)

## 10. X-ray crystallographic data of 3a' and 3b.

X-ray crystallographic data of **3a'**

**Table S5**. Crystal data and structure refinement for 210114f.

| | |
|---|---|
| Identification code | 210114f |
| Empirical formula | C10 H8 F N O2 S |
| Formula weight | 225.23 |
| Temperature | 298(2) K |
| Wavelength | 0.71073 A |
| Crystal system, space group | Monoclinic, P2(1)/c |
| Unit cell dimensions | a = 7.7520(6) A alpha = 90 deg.<br>b = 23.8360(19) A beta = 97.925(2) deg.<br>c = 5.6189(5) A gamma = 90 deg. |
| Volume | 1028.33(15) A^3 |
| Z, Calculated density | 4, 1.455 Mg/m^3 |
| Absorption coefficient | 0.307 mm^-1 |
| F(000) | 464 |
| Crystal size | 0.35 x 0.15 x 0.11 mm |
| Theta range for data collection | 2.79 to 25.02 deg. |
| Limiting indices | -8<=h<=9, -22<=k<=28, -6<=l<=6 |
| Reflections collected / unique | 4917 / 1818 [R(int) = 0.0522] |
| Completeness to theta = 25.02 | 99.8 % |
| Absorption correction | Semi-empirical from equivalents |

| | |
|---|---|
| Max. and min. transmission | 0.9671 and 0.9003 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 1818 / 0 / 136 |
| Goodness-of-fit on F^2 | 1.146 |
| Final R indices [I>2sigma(I)] | R1 = 0.0776, wR2 = 0.1600 |
| R indices (all data) | R1 = 0.0974, wR2 = 0.1669 |
| Largest diff. peak and hole | 0.334 and -0.407 e.A^-3 |

**Table S6**. Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 210114f.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| F(1) | 13985(4) | 4241(2) | 5191(6) | 81(1) |
| N(1) | 11615(7) | 3000(2) | 1642(9) | 72(2) |
| O(1) | 12092(6) | 4964(2) | 5933(7) | 75(1) |
| O(2) | 11533(5) | 4387(2) | 2387(6) | 56(1) |
| S(1) | 12104(2) | 4444(1) | 4835(2) | 45(1) |
| C(1) | 11306(7) | 3173(2) | 3382(9) | 45(1) |
| C(2) | 10849(6) | 3365(2) | 5654(8) | 41(1) |
| C(3) | 11166(6) | 3954(2) | 6525(8) | 37(1) |
| C(4) | 9368(6) | 3765(2) | 5655(8) | 36(1) |
| C(5) | 8044(6) | 3685(2) | 7295(8) | 37(1) |
| C(6) | 7690(6) | 4093(2) | 8871(8) | 45(1) |
| C(7) | 6403(7) | 4017(3) | 10286(9) | 61(2) |
| C(8) | 5467(7) | 3534(3) | 10144(11) | 64(2) |
| C(9) | 5805(7) | 3128(3) | 8593(12) | 68(2) |
| C(10) | 7104(7) | 3201(2) | 7177(11) | 59(2) |

**Table S7**. Bond lengths [A] and angles [deg] for 210114f.

| | |
|---|---|
| F(1)-S(1) | 1.523(3) |
| N(1)-C(1) | 1.118(6) |
| O(1)-S(1) | 1.385(4) |
| O(2)-S(1) | 1.392(3) |
| S(1)-C(3) | 1.728(4) |
| C(1)-C(2) | 1.445(6) |
| C(2)-C(4) | 1.492(6) |
| C(2)-C(3) | 1.496(6) |
| C(2)-H(2) | 0.9800 |
| C(3)-C(4) | 1.482(6) |
| C(3)-H(3) | 0.9800 |
| C(4)-C(5) | 1.483(6) |
| C(4)-H(4) | 0.9800 |
| C(5)-C(10) | 1.362(7) |
| C(5)-C(6) | 1.368(6) |
| C(6)-C(7) | 1.371(7) |
| C(6)-H(6) | 0.9300 |
| C(7)-C(8) | 1.356(8) |
| C(7)-H(7) | 0.9300 |
| C(8)-C(9) | 1.353(8) |
| C(8)-H(8) | 0.9300 |
| C(9)-C(10) | 1.378(7) |
| C(9)-H(9) | 0.9300 |
| C(10)-H(10) | 0.9300 |
| | |
| O(1)-S(1)-O(2) | 120.5(3) |
| O(1)-S(1)-F(1) | 106.9(3) |
| O(2)-S(1)-F(1) | 105.5(2) |
| O(1)-S(1)-C(3) | 109.3(2) |
| O(2)-S(1)-C(3) | 112.1(2) |
| F(1)-S(1)-C(3) | 100.4(2) |
| N(1)-C(1)-C(2) | 176.4(5) |
| C(1)-C(2)-C(4) | 119.0(4) |
| C(1)-C(2)-C(3) | 122.5(4) |
| C(4)-C(2)-C(3) | 59.5(3) |
| C(1)-C(2)-H(2) | 114.9 |
| C(4)-C(2)-H(2) | 114.9 |
| C(3)-C(2)-H(2) | 114.9 |
| C(4)-C(3)-C(2) | 60.2(3) |

| | |
|---|---|
| C(4)-C(3)-S(1) | 118.2(3) |
| C(2)-C(3)-S(1) | 121.1(3) |
| C(4)-C(3)-H(3) | 115.4 |
| C(2)-C(3)-H(3) | 115.4 |
| S(1)-C(3)-H(3) | 115.4 |
| C(3)-C(4)-C(5) | 122.3(4) |
| C(3)-C(4)-C(2) | 60.4(3) |
| C(5)-C(4)-C(2) | 121.1(4) |
| C(3)-C(4)-H(4) | 114.2 |
| C(5)-C(4)-H(4) | 114.2 |
| C(2)-C(4)-H(4) | 114.2 |
| C(10)-C(5)-C(6) | 118.7(5) |
| C(10)-C(5)-C(4) | 119.3(4) |
| C(6)-C(5)-C(4) | 121.9(4) |
| C(5)-C(6)-C(7) | 120.5(5) |
| C(5)-C(6)-H(6) | 119.8 |
| C(7)-C(6)-H(6) | 119.8 |
| C(8)-C(7)-C(6) | 120.3(5) |
| C(8)-C(7)-H(7) | 119.8 |
| C(6)-C(7)-H(7) | 119.8 |
| C(9)-C(8)-C(7) | 119.7(5) |
| C(9)-C(8)-H(8) | 120.2 |
| C(7)-C(8)-H(8) | 120.2 |
| C(8)-C(9)-C(10) | 120.2(5) |
| C(8)-C(9)-H(9) | 119.9 |
| C(10)-C(9)-H(9) | 119.9 |
| C(5)-C(10)-C(9) | 120.5(5) |
| C(5)-C(10)-H(10) | 119.7 |
| C(9)-C(10)-H(10) | 119.7 |

---

Symmetry transformations used to generate equivalent atoms:

**Table S8**. Anisotropic displacement parameters (A^2 x 10^3) for 210114f. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| F(1) | 47(2) | 108(3) | 89(3) | 29(2) | 15(2) | 9(2) |
| N(1) | 109(4) | 46(3) | 70(3) | -13(3) | 45(3) | -14(3) |
| O(1) | 105(3) | 44(2) | 78(3) | -16(2) | 21(2) | -21(2) |
| O(2) | 73(2) | 60(2) | 37(2) | 10(2) | 9(2) | -10(2) |
| S(1) | 48(1) | 41(1) | 45(1) | 1(1) | 9(1) | -7(1) |
| C(1) | 63(3) | 33(3) | 44(3) | -3(2) | 24(2) | -1(2) |
| C(2) | 56(3) | 31(2) | 40(3) | 3(2) | 18(2) | 0(2) |
| C(3) | 42(3) | 42(3) | 29(2) | -1(2) | 7(2) | -1(2) |
| C(4) | 42(3) | 36(2) | 30(2) | 0(2) | 5(2) | -4(2) |
| C(5) | 36(2) | 41(3) | 34(2) | 2(2) | 2(2) | -2(2) |
| C(6) | 38(3) | 58(3) | 39(3) | -4(2) | 3(2) | -7(2) |
| C(7) | 47(3) | 92(5) | 42(3) | -10(3) | 6(2) | 2(3) |
| C(8) | 39(3) | 95(5) | 62(4) | 15(3) | 18(3) | 4(3) |
| C(9) | 57(4) | 56(4) | 95(5) | 16(3) | 21(3) | -18(3) |
| C(10) | 59(3) | 41(3) | 80(4) | -3(3) | 24(3) | -7(3) |

**Table S9**. Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 210114f.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 10940 | 3080 | 6922 | 50 |
| H(3) | 11443 | 3997 | 8271 | 45 |
| H(4) | 8898 | 3907 | 4061 | 43 |
| H(6) | 8328 | 4425 | 8983 | 54 |
| H(7) | 6170 | 4297 | 11348 | 73 |
| H(8) | 4596 | 3483 | 11109 | 77 |
| H(9) | 5159 | 2798 | 8482 | 82 |
| H(10) | 7341 | 2917 | 6132 | 70 |

**Table S10**. Torsion angles [deg] for 210114f.

| | |
|---|---|
| N(1)-C(1)-C(2)-C(4) | -101(10) |
| N(1)-C(1)-C(2)-C(3) | -171(10) |
| C(1)-C(2)-C(3)-C(4) | 107.0(5) |
| C(1)-C(2)-C(3)-S(1) | 0.2(7) |
| C(4)-C(2)-C(3)-S(1) | -106.8(4) |
| O(1)-S(1)-C(3)-C(4) | 103.9(4) |
| O(2)-S(1)-C(3)-C(4) | -32.4(4) |
| F(1)-S(1)-C(3)-C(4) | -144.0(3) |
| O(1)-S(1)-C(3)-C(2) | 174.2(4) |
| O(2)-S(1)-C(3)-C(2) | 37.9(4) |
| F(1)-S(1)-C(3)-C(2) | -73.6(4) |
| C(2)-C(3)-C(4)-C(5) | 110.2(5) |
| S(1)-C(3)-C(4)-C(5) | -138.2(4) |
| S(1)-C(3)-C(4)-C(2) | 111.6(4) |
| C(1)-C(2)-C(4)-C(3) | -112.7(5) |
| C(1)-C(2)-C(4)-C(5) | 135.3(4) |
| C(3)-C(2)-C(4)-C(5) | -112.0(5) |
| C(3)-C(4)-C(5)-C(10) | -131.1(5) |
| C(2)-C(4)-C(5)-C(10) | -58.7(6) |
| C(3)-C(4)-C(5)-C(6) | 51.3(6) |
| C(2)-C(4)-C(5)-C(6) | 123.7(5) |
| C(10)-C(5)-C(6)-C(7) | -0.6(7) |
| C(4)-C(5)-C(6)-C(7) | 177.0(5) |
| C(5)-C(6)-C(7)-C(8) | 0.2(8) |
| C(6)-C(7)-C(8)-C(9) | -0.2(9) |
| C(7)-C(8)-C(9)-C(10) | 0.5(9) |
| C(6)-C(5)-C(10)-C(9) | 1.0(8) |
| C(4)-C(5)-C(10)-C(9) | -176.7(5) |
| C(8)-C(9)-C(10)-C(5) | -0.9(9) |

Symmetry transformations used to generate equivalent atoms:

**Table S11**. Hydrogen bonds for 210114f [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|

X-ray crystallographic data of **3b**

**Table S12**. Crystal data and structure refinement for 181206b.

| | |
|---|---|
| Identification code | 181206b |
| Empirical formula | C16 H12 F N O2 S |
| Formula weight | 301.33 |
| Temperature | 298(2) K |
| Wavelength | 0.71073 A |
| Crystal system, space group | Triclinic, P-1 |
| Unit cell dimensions | a = 6.4301(5) A alpha = 95.348(2) deg.<br>b = 7.7504(6) A beta = 100.866(3) deg.<br>c = 14.9740(12) A gamma = 105.796(3) deg. |
| Volume | 696.89(9) A^3 |
| Z, Calculated density | 2, 1.436 Mg/m^3 |
| Absorption coefficient | 0.247 mm^-1 |
| F(000) | 312 |
| Crystal size | 0.45 x 0.27 x 0.18 mm |
| Theta range for data collection | 2.76 to 25.02 deg. |
| Limiting indices | -7<=h<=7, -7<=k<=9, -14<=l<=17 |
| Reflections collected / unique | 3439 / 2396 [R(int) = 0.0425] |
| Completeness to theta = 25.02 | 97.2 % |
| Absorption correction | Semi-empirical from equivalents |

| | |
|---|---|
| Max. and min. transmission | 0.9569 and 0.8971 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 2396 / 0 / 190 |
| Goodness-of-fit on F^2 | 1.009 |
| Final R indices [I>2sigma(I)] | R1 = 0.0836, wR2 = 0.2110 |
| R indices (all data) | R1 = 0.1269, wR2 = 0.2441 |
| Largest diff. peak and hole | 0.914 and -0.413 e.A^-3 |

**Table S13**. Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 181206b.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| F(1) | -4880(5) | 3883(5) | 1216(2) | 68(1) |
| N(1) | 1313(9) | -709(8) | 1255(3) | 76(2) |
| O(1) | -2395(6) | 4635(5) | 232(3) | 69(1) |
| O(2) | -5384(6) | 1829(5) | -119(2) | 58(1) |
| S(1) | -3708(2) | 3175(2) | 529(1) | 46(1) |
| C(1) | 743(8) | 539(8) | 1164(3) | 49(1) |
| C(2) | 94(7) | 2146(7) | 1038(3) | 41(1) |
| C(3) | -2075(7) | 2199(6) | 1261(3) | 37(1) |
| C(4) | 29(7) | 3389(6) | 1862(3) | 39(1) |
| C(5) | 749(7) | 3058(6) | 2823(3) | 38(1) |
| C(6) | -752(8) | 2516(7) | 3366(4) | 48(1) |
| C(7) | -49(8) | 2298(7) | 4270(4) | 48(1) |
| C(8) | 2168(7) | 2579(6) | 4658(3) | 39(1) |
| C(9) | 3654(8) | 3122(7) | 4092(3) | 47(1) |
| C(10) | 2957(7) | 3347(7) | 3210(3) | 45(1) |
| C(11) | 2924(8) | 2382(6) | 5628(3) | 40(1) |
| C(12) | 1815(9) | 2735(7) | 6304(4) | 52(1) |
| C(13) | 2544(10) | 2577(8) | 7209(4) | 59(2) |
| C(14) | 4416(10) | 2070(8) | 7462(4) | 61(2) |
| C(15) | 5563(9) | 1711(8) | 6817(4) | 58(2) |
| C(16) | 4830(8) | 1853(7) | 5911(4) | 49(1) |

**Table S14**. Bond lengths [A] and angles [deg] for 181206b.

| | |
|---|---|
| F(1)-S(1) | 1.529(3) |
| N(1)-C(1) | 1.135(7) |
| O(1)-S(1) | 1.380(4) |
| O(2)-S(1) | 1.413(4) |
| S(1)-C(3) | 1.741(4) |
| C(1)-C(2) | 1.435(7) |
| C(2)-C(3) | 1.504(6) |
| C(2)-C(4) | 1.508(7) |
| C(2)-H(2) | 0.9800 |
| C(3)-C(4) | 1.483(6) |
| C(3)-H(3) | 0.9800 |
| C(4)-C(5) | 1.494(6) |
| C(4)-H(4) | 0.9800 |
| C(5)-C(10) | 1.376(6) |
| C(5)-C(6) | 1.381(6) |
| C(6)-C(7) | 1.385(7) |
| C(6)-H(6) | 0.9300 |
| C(7)-C(8) | 1.383(6) |
| C(7)-H(7) | 0.9300 |
| C(8)-C(9) | 1.401(7) |
| C(8)-C(11) | 1.479(7) |
| C(9)-C(10) | 1.356(7) |
| C(9)-H(9) | 0.9300 |
| C(10)-H(10) | 0.9300 |
| C(11)-C(12) | 1.391(7) |
| C(11)-C(16) | 1.399(7) |
| C(12)-C(13) | 1.376(7) |
| C(12)-H(12) | 0.9300 |
| C(13)-C(14) | 1.364(8) |
| C(13)-H(13) | 0.9300 |
| C(14)-C(15) | 1.373(8) |
| C(14)-H(14) | 0.9300 |
| C(15)-C(16) | 1.375(7) |
| C(15)-H(15) | 0.9300 |
| C(16)-H(16) | 0.9300 |
| | |
| O(1)-S(1)-O(2) | 119.6(3) |
| O(1)-S(1)-F(1) | 108.8(3) |
| O(2)-S(1)-F(1) | 105.8(2) |

| | |
|---|---|
| O(1)-S(1)-C(3) | 110.5(2) |
| O(2)-S(1)-C(3) | 110.9(2) |
| F(1)-S(1)-C(3) | 99.1(2) |
| N(1)-C(1)-C(2) | 177.9(6) |
| C(1)-C(2)-C(3) | 117.1(4) |
| C(1)-C(2)-C(4) | 119.8(4) |
| C(3)-C(2)-C(4) | 59.0(3) |
| C(1)-C(2)-H(2) | 116.2 |
| C(3)-C(2)-H(2) | 116.2 |
| C(4)-C(2)-H(2) | 116.2 |
| C(4)-C(3)-C(2) | 60.7(3) |
| C(4)-C(3)-S(1) | 118.6(3) |
| C(2)-C(3)-S(1) | 116.9(3) |
| C(4)-C(3)-H(3) | 116.4 |
| C(2)-C(3)-H(3) | 116.4 |
| S(1)-C(3)-H(3) | 116.4 |
| C(3)-C(4)-C(5) | 120.2(4) |
| C(3)-C(4)-C(2) | 60.4(3) |
| C(5)-C(4)-C(2) | 121.9(4) |
| C(3)-C(4)-H(4) | 114.6 |
| C(5)-C(4)-H(4) | 114.6 |
| C(2)-C(4)-H(4) | 114.6 |
| C(10)-C(5)-C(6) | 117.5(4) |
| C(10)-C(5)-C(4) | 120.8(4) |
| C(6)-C(5)-C(4) | 121.7(4) |
| C(5)-C(6)-C(7) | 121.0(4) |
| C(5)-C(6)-H(6) | 119.5 |
| C(7)-C(6)-H(6) | 119.5 |
| C(8)-C(7)-C(6) | 121.6(4) |
| C(8)-C(7)-H(7) | 119.2 |
| C(6)-C(7)-H(7) | 119.2 |
| C(7)-C(8)-C(9) | 116.3(4) |
| C(7)-C(8)-C(11) | 121.6(4) |
| C(9)-C(8)-C(11) | 122.1(4) |
| C(10)-C(9)-C(8) | 121.9(4) |
| C(10)-C(9)-H(9) | 119.1 |
| C(8)-C(9)-H(9) | 119.1 |
| C(9)-C(10)-C(5) | 121.7(5) |
| C(9)-C(10)-H(10) | 119.1 |
| C(5)-C(10)-H(10) | 119.1 |
| C(12)-C(11)-C(16) | 116.8(5) |
| C(12)-C(11)-C(8) | 122.2(5) |
| C(16)-C(11)-C(8) | 121.0(4) |
| C(13)-C(12)-C(11) | 122.0(5) |

| | |
|---|---|
| C(13)-C(12)-H(12) | 119.0 |
| C(11)-C(12)-H(12) | 119.0 |
| C(14)-C(13)-C(12) | 119.7(5) |
| C(14)-C(13)-H(13) | 120.2 |
| C(12)-C(13)-H(13) | 120.2 |
| C(13)-C(14)-C(15) | 120.2(5) |
| C(13)-C(14)-H(14) | 119.9 |
| C(15)-C(14)-H(14) | 119.9 |
| C(14)-C(15)-C(16) | 120.3(5) |
| C(14)-C(15)-H(15) | 119.9 |
| C(16)-C(15)-H(15) | 119.9 |
| C(15)-C(16)-C(11) | 121.0(5) |
| C(15)-C(16)-H(16) | 119.5 |
| C(11)-C(16)-H(16) | 119.5 |

---

Symmetry transformations used to generate equivalent atoms:

**Table S15**. Anisotropic displacement parameters (A^2 x 10^3) for 181206b. The anisotropic displacement factor exponent takes the form:
-2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| F(1) | 61(2) | 84(2) | 69(2) | 3(2) | 11(2) | 43(2) |
| N(1) | 98(4) | 92(4) | 61(3) | 15(3) | 12(3) | 68(4) |
| O(1) | 47(2) | 67(3) | 105(3) | 53(2) | 18(2) | 21(2) |
| O(2) | 52(2) | 54(2) | 56(2) | -2(2) | -13(2) | 15(2) |
| S(1) | 37(1) | 48(1) | 58(1) | 20(1) | 8(1) | 19(1) |
| C(1) | 46(3) | 69(4) | 36(3) | 10(3) | 4(2) | 27(3) |
| C(2) | 36(2) | 50(3) | 41(3) | 11(2) | 7(2) | 17(2) |
| C(3) | 32(2) | 35(3) | 45(3) | 16(2) | 8(2) | 10(2) |
| C(4) | 36(2) | 35(3) | 44(3) | 10(2) | 8(2) | 6(2) |
| C(5) | 35(2) | 35(3) | 41(3) | 3(2) | 5(2) | 7(2) |
| C(6) | 28(2) | 59(3) | 53(3) | 8(3) | 3(2) | 8(2) |
| C(7) | 36(3) | 62(3) | 48(3) | 10(3) | 15(2) | 13(2) |
| C(8) | 39(3) | 40(3) | 34(3) | -4(2) | 5(2) | 9(2) |
| C(9) | 33(2) | 57(3) | 43(3) | 8(2) | 3(2) | 7(2) |
| C(10) | 36(3) | 58(3) | 40(3) | 11(2) | 10(2) | 12(2) |
| C(11) | 42(3) | 32(3) | 41(3) | 4(2) | 11(2) | 5(2) |
| C(12) | 51(3) | 57(3) | 45(3) | 6(3) | 13(3) | 10(3) |
| C(13) | 70(4) | 56(4) | 45(3) | 2(3) | 23(3) | 4(3) |
| C(14) | 78(4) | 62(4) | 36(3) | 15(3) | 9(3) | 12(3) |
| C(15) | 57(3) | 56(4) | 55(4) | 15(3) | 5(3) | 13(3) |
| C(16) | 46(3) | 53(3) | 47(3) | 8(2) | 9(2) | 14(2) |

**Table S16**. Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 181206b.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 473 | 2725 | 511 | 50 |
| H(3) | -2866 | 1153 | 1512 | 44 |
| H(4) | 358 | 4673 | 1789 | 47 |
| H(6) | -2258 | 2293 | 3121 | 58 |
| H(7) | -1092 | 1953 | 4624 | 57 |
| H(9) | 5162 | 3334 | 4328 | 56 |
| H(10) | 3998 | 3706 | 2856 | 54 |
| H(12) | 541 | 3089 | 6139 | 62 |
| H(13) | 1764 | 2815 | 7646 | 71 |
| H(14) | 4917 | 1967 | 8073 | 73 |
| H(15) | 6842 | 1371 | 6993 | 69 |
| H(16) | 5611 | 1593 | 5479 | 59 |

**Table S17**. Torsion angles [deg] for 181206b.

| | |
|---|---|
| N(1)-C(1)-C(2)-C(3) | 179(100) |
| N(1)-C(1)-C(2)-C(4) | -113(17) |
| C(1)-C(2)-C(3)-C(4) | 110.1(5) |
| C(1)-C(2)-C(3)-S(1) | -140.6(4) |
| C(4)-C(2)-C(3)-S(1) | 109.3(4) |
| O(1)-S(1)-C(3)-C(4) | 32.9(5) |
| O(2)-S(1)-C(3)-C(4) | 167.9(3) |
| F(1)-S(1)-C(3)-C(4) | -81.2(4) |
| O(1)-S(1)-C(3)-C(2) | -36.6(5) |
| O(2)-S(1)-C(3)-C(2) | 98.4(4) |
| F(1)-S(1)-C(3)-C(2) | -150.7(4) |
| C(2)-C(3)-C(4)-C(5) | -111.8(5) |
| S(1)-C(3)-C(4)-C(5) | 141.6(4) |
| S(1)-C(3)-C(4)-C(2) | -106.5(4) |
| C(1)-C(2)-C(4)-C(3) | -105.6(5) |
| C(1)-C(2)-C(4)-C(5) | 3.6(7) |
| C(3)-C(2)-C(4)-C(5) | 109.2(5) |
| C(3)-C(4)-C(5)-C(10) | 144.1(5) |
| C(2)-C(4)-C(5)-C(10) | 72.2(6) |
| C(3)-C(4)-C(5)-C(6) | -38.2(7) |
| C(2)-C(4)-C(5)-C(6) | -110.1(6) |
| C(10)-C(5)-C(6)-C(7) | 0.9(8) |
| C(4)-C(5)-C(6)-C(7) | -176.9(5) |
| C(5)-C(6)-C(7)-C(8) | -1.2(8) |
| C(6)-C(7)-C(8)-C(9) | 0.9(8) |
| C(6)-C(7)-C(8)-C(11) | 178.8(5) |
| C(7)-C(8)-C(9)-C(10) | -0.4(8) |
| C(11)-C(8)-C(9)-C(10) | -178.2(5) |
| C(8)-C(9)-C(10)-C(5) | 0.2(8) |
| C(6)-C(5)-C(10)-C(9) | -0.4(8) |
| C(4)-C(5)-C(10)-C(9) | 177.4(5) |
| C(7)-C(8)-C(11)-C(12) | -30.3(7) |
| C(9)-C(8)-C(11)-C(12) | 147.4(5) |
| C(7)-C(8)-C(11)-C(16) | 150.7(5) |
| C(9)-C(8)-C(11)-C(16) | -31.6(7) |
| C(16)-C(11)-C(12)-C(13) | 0.1(7) |
| C(8)-C(11)-C(12)-C(13) | -179.0(5) |
| C(11)-C(12)-C(13)-C(14) | 0.4(8) |
| C(12)-C(13)-C(14)-C(15) | -0.3(9) |

| | |
|---|---|
| C(13)-C(14)-C(15)-C(16) | -0.3(9) |
| C(14)-C(15)-C(16)-C(11) | 0.7(8) |
| C(12)-C(11)-C(16)-C(15) | -0.6(7) |
| C(8)-C(11)-C(16)-C(15) | 178.4(4) |

---

Symmetry transformations used to generate equivalent atoms:

**Table S18**. Hydrogen bonds for 181206b [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|