

# Generation of zwitterionic trifluoromethyl *N*-allylic ylides and their use in switchable divergent annulations

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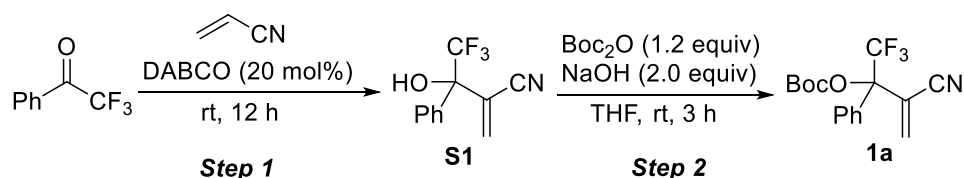
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## 1. General methods

Unless otherwise noted, all reactions were carried out under ambient atmosphere; when the reactions required heating, the heat source was oil bath.  $^1\text{H}$  NMR (400 MHz),  $^{13}\text{C}$  NMR (100 or 150 MHz) and  $^{19}\text{F}$  NMR (376 MHz) spectra were recorded on Varian INOVA-400/54, Agilent DD2-600/54 or Bruker Ascend<sup>TM</sup> 400 instruments (Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in  $\text{CDCl}_3$  solution, unless otherwise noted). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, dd = double doublet, ddd = double double doublet, dt = double triplet; td = triple doublet, m = multiplet, br = broad, and coupling constants ( $J$ ) are reported in Hertz (Hz). ESI-HRMS was recorded on a Waters SYNAPT G2, Agilent G1969-85000 or Shimadzu LCMS-IT-TOF using a time-of-flight mass spectrometer equipped with electrospray ionization (ESI) source. X-ray diffraction experiments were carried out on an Agilent Gemini or Bruker D8 VENTURE and the data obtained were deposited at the Cambridge Crystallographic Data Centre. In each case, diastereomeric ratio was determined by  $^1\text{H}$  NMR analysis and enantiomeric ratio was determined by HPLC (Agilent Technologies: 1220 Infinity II, 1200 Series, 1260 Infinity) analysis on a chiral column in comparison with authentic racemate, using a Daicel Chiralpak AD-H Column (250  $\times$  4.6 mm), Chiralpak IA Column (250  $\times$  4.6 mm), Chiralpak IB Column (250  $\times$  4.6 mm), Chiralpak ID Column (250  $\times$  4.6 mm), Chiralpak IE Column (250  $\times$  4.6 mm) or Chiralpak IG Column (250  $\times$  4.6 mm). UV detection was monitored at 254 nm. The specific optical rotation was obtained from Rudolph Research Analytical Autopol I automatic polarimeter in  $\text{CHCl}_3$  solution at 25  $^\circ\text{C}$ . The melting point was obtained from WRX-4 Mel-Temp apparatus. Column chromatography was performed on silica gel (300–400 mesh) eluting with ethyl acetate (EtOAc) and petroleum ether. TLC was performed on glass-backed silica plates. UV light,  $\text{I}_2$ , and solution of potassium permanganate were used to visualize products or starting materials. All chemicals were used without purification as commercially available unless otherwise noted. Petroleum ether (60–90  $^\circ\text{C}$ ) was redistilled. The tertiary amine catalysts **C7–C12**,<sup>1</sup> 1-azadienes<sup>2</sup> were prepared according to the literature procedures.

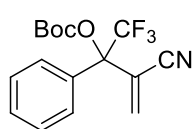
## 2. Typical procedure for the preparation of substrate 1a



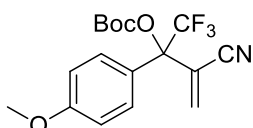
**Step 1:** To a stirred solution of 2,2,2-trifluoro-1-phenylethanone (1.4 mL, 10 mmol, 1.0 equiv) in acrylonitrile (6.5 mL, 99 mmol, 10.0 equiv) was added DABCO (22.4 mg, 0.200 mmol, 20 mol%) and stirred at room temperature for 24 h. After completion (monitored by TLC), the acrylonitrile was

removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give the compound **S1** as a colorless oil in 97% yield (2.21 g, 9.74 mmol).<sup>3</sup>

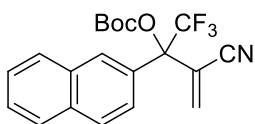
**Step 2:** To a stirred solution of allylic alcohol **S1** (1.14 g, 5.02 mmol, 1.0 equiv) in THF was added NaOH (400 mg, 10.0 mmol, 2.0 equiv) and stirred at room temperature for 20 min. Then a solution of Boc<sub>2</sub>O (1.31 g, 6.01 mmol, 1.2 equiv) in THF was added slowly, and the mixture was stirred at room temperature for 3 h. After completion (monitored by TLC), the reaction was quenched with water and extracted with EtOAc. The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether) to give compound **1a** as a colorless oil in 25% yield (412 mg, 1.26 mmol).



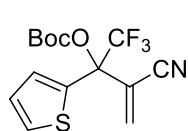
**tert-Butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate (1a):** as a colorless oil; 412 mg, yield 25%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.59–7.50 (m, 2H), 7.50–7.36 (m, 3H), 6.50 (s, 1H), 6.38 (s, 1H), 1.47 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 149.3, 136.6 (q, *J* = 1.9 Hz), 131.3, 130.0, 128.6, 127.3 (q, *J* = 1.7 Hz), 122.8 (q, *J* = 285.2 Hz), 120.6, 115.7, 84.9, 82.5 (q, *J* = 29.8 Hz), 27.5; HRMS (ESI-TOF) *m/z*: [M + Na]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>16</sub>F<sub>3</sub>NO<sub>3</sub>Na<sup>+</sup> 350.0974; Found 350.0972.



**tert-Butyl (3-cyano-1,1,1-trifluoro-2-(4-methoxyphenyl)but-3-en-2-yl) carbonate (1d):** as a colorless oil; 520 mg, yield 29%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.56–7.41 (m, 2H), 7.02–6.89 (m, 2H), 6.50 (t, *J* = 0.8 Hz, 1H), 6.40–6.30 (m, 1H), 3.83 (s, 3H), 1.47 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 160.7, 149.4, 136.3 (q, *J* = 1.7 Hz), 128.9 (q, *J* = 1.7 Hz), 123.0, 122.9 (q, *J* = 285.2 Hz), 120.8, 115.8, 113.9, 84.7, 82.6 (q, *J* = 29.9 Hz), 55.3, 27.5; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>19</sub>F<sub>3</sub>NO<sub>4</sub><sup>+</sup> 358.1261; Found 358.1259.



**tert-Butyl (3-cyano-1,1,1-trifluoro-2-(naphthalen-2-yl)but-3-en-2-yl) carbonate (1f):** as a yellow semi-solid; 587 mg, yield 31%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.11–8.03 (m, 1H), 7.97–7.80 (m, 3H), 7.6–7.45 (m, 3H), 6.57 (s, 1H), 6.44 (s, 1H), 1.48 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 149.4, 136.7, 133.5, 132.5, 128.8, 128.6, 128.5, 127.8, 127.63, 127.55, 126.9, 123.7 (q, *J* = 1.9 Hz), 122.9 (q, *J* = 285.6 Hz), 120.7, 115.7, 85.0, 82.8 (q, *J* = 29.7 Hz), 27.5; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>19</sub>F<sub>3</sub>NO<sub>3</sub><sup>+</sup> 378.1312; Found 378.1316.



**tert-Butyl (3-cyano-1,1,1-trifluoro-2-(thiophen-2-yl)but-3-en-2-yl) carbonate**

**(1g):** as a yellow oil; 568 mg, yield 34%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm)

7.58–7.51 (m, 1H), 7.48–7.42 (m, 2H), 6.52 (s, 1H), 6.39 (s, 1H), 1.47 (s, 9H); <sup>13</sup>C

NMR (150 MHz, CDCl<sub>3</sub>): δ (ppm) 149.4, 136.5, 131.3, 130.0, 128.6, 127.3, 122.8 (q, *J* = 285.3 Hz),

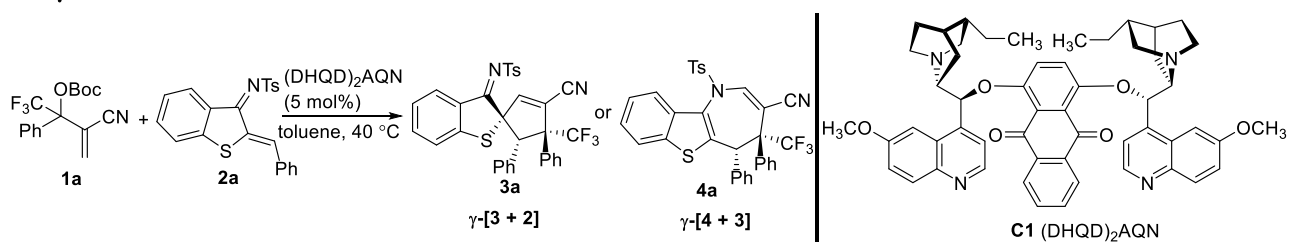
120.6, 115.7, 84.9, 82.6 (q, *J* = 29.6 Hz), 27.5; HRMS (ESI-TOF) *m/z*: [M + Na]<sup>+</sup> Calcd for

C<sub>14</sub>H<sub>14</sub>F<sub>3</sub>NO<sub>3</sub>Na<sup>+</sup> 356.0539; Found 356.0541.

### 3. More screening conditions for divergent annulations of MBH carbonate **1a** with 1-azadiene

#### **2a**

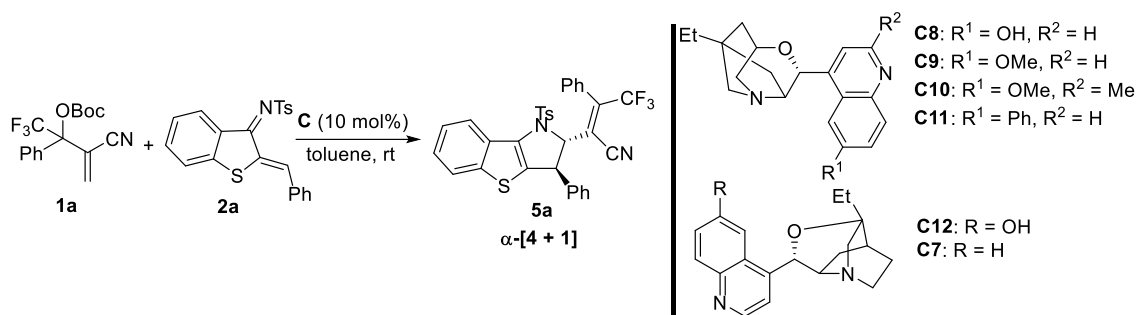
#### 3.1 $\gamma$ -[3+2] annulation of MBH carbonate **1a** with 1-azadiene **2a**<sup>a</sup>



Entry	C	Solvent	<i>T</i> (°C)	Yield (%) <sup>b</sup>	<b>3a/4a</b> <sup>c</sup>	ee (%) <sup>d</sup>
<b>[3a+4a]</b>						
1	DMAP	toluene	rt	messy	/	/
2	PPh <sub>3</sub>	toluene	rt	trace	/	/
3 <sup>e</sup>	<b>C1</b>	toluene	rt	72	6/1	96
4	<b>C1</b>	toluene	40	67	6/1	96
5	<b>C1</b>	PhCF <sub>3</sub>	40	66	4/1	89
6	<b>C1</b>	CHCl <sub>3</sub>	40	40	6/1	98
7	<b>C1</b>	THF	40	67	4/1	92
8	<b>C1</b>	CH <sub>3</sub> CN	40	bad conv.	/	/

<sup>a</sup>Unless noted otherwise, reactions were performed using **1a** (0.075 mmol, 1.5 equiv), **2a** (0.05 mmol, 1.0 equiv), **C1** (5 mol%) in toluene (0.5 mL) for 24 h. <sup>b</sup>Yield of the inseparable **3a** and **4a**. <sup>c</sup>Determined by <sup>1</sup>H NMR analysis, >19:1 dr by <sup>1</sup>H NMR analysis. <sup>d</sup>Unless noted, for product **3a**, determined by HPLC analysis using a chiral stationary phase. <sup>e</sup>**C1** (10 mol%) was used.

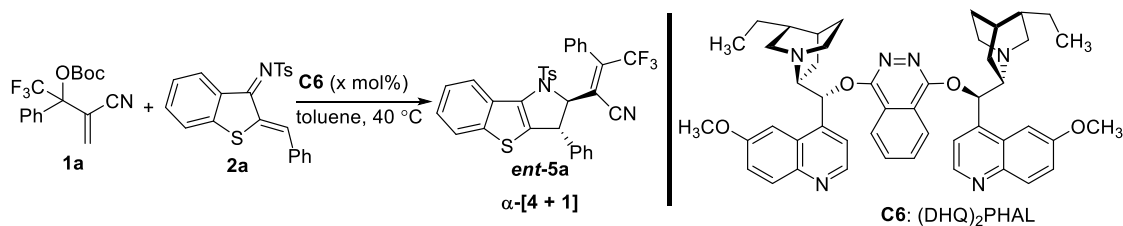
#### 3.2 Catalyst-controlled $\alpha$ -[4+1] annulation of MBH carbonate **1a** with 1-azadiene **2a**<sup>a</sup>



Entry	C	Solvent	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1 <sup>d</sup>	<b>C8</b>	toluene	80	21
2	<b>C9</b>	toluene	73	60
3	<b>C10</b>	toluene	67	55
4 <sup>e</sup>	<b>C9</b>	toluene	85	60
5 <sup>e</sup>	<b>C9</b>	PhCF <sub>3</sub>	87	55
6 <sup>e</sup>	<b>C9</b>	CHCl <sub>3</sub>	67	56
7 <sup>e</sup>	<b>C9</b>	THF	73	59
8 <sup>e</sup>	<b>C9</b>	CH <sub>3</sub> CN	73	57
9 <sup>e,f</sup>	<b>C9</b>	toluene	81	61
10 <sup>e,g</sup>	<b>C9</b>	toluene	83	63
11 <sup>e,g</sup>	<b>C11</b>	toluene	63	79
12 <sup>e,g</sup>	<b>C12</b>	toluene	75	60
13 <sup>e,g</sup>	<b>C7</b>	toluene	91	96

<sup>a</sup>Unless noted otherwise, reactions were performed using **1a** (0.0375 mmol, 1.5 equiv), **2a** (0.025 mmol, 1.0 equiv) and **C** (10 mol%) in solvent (0.25 mL) at room temperature for 12 h. <sup>b</sup>Yield of isolated product. <sup>c</sup>Determined by HPLC analysis using a chiral stationary phase; >19:1 dr by <sup>1</sup>H NMR analysis. <sup>d</sup>For 10 min. <sup>e</sup>10.0 mg 4 Å MS was used. <sup>f</sup>At 5 °C. <sup>g</sup>At -10 °C.

### 3.3 Catalyst-controlled enantiodivergent $\alpha$ -[4+1] annulation of MBH carbonate **1a** with 1-azadiene **2a**<sup>a</sup>

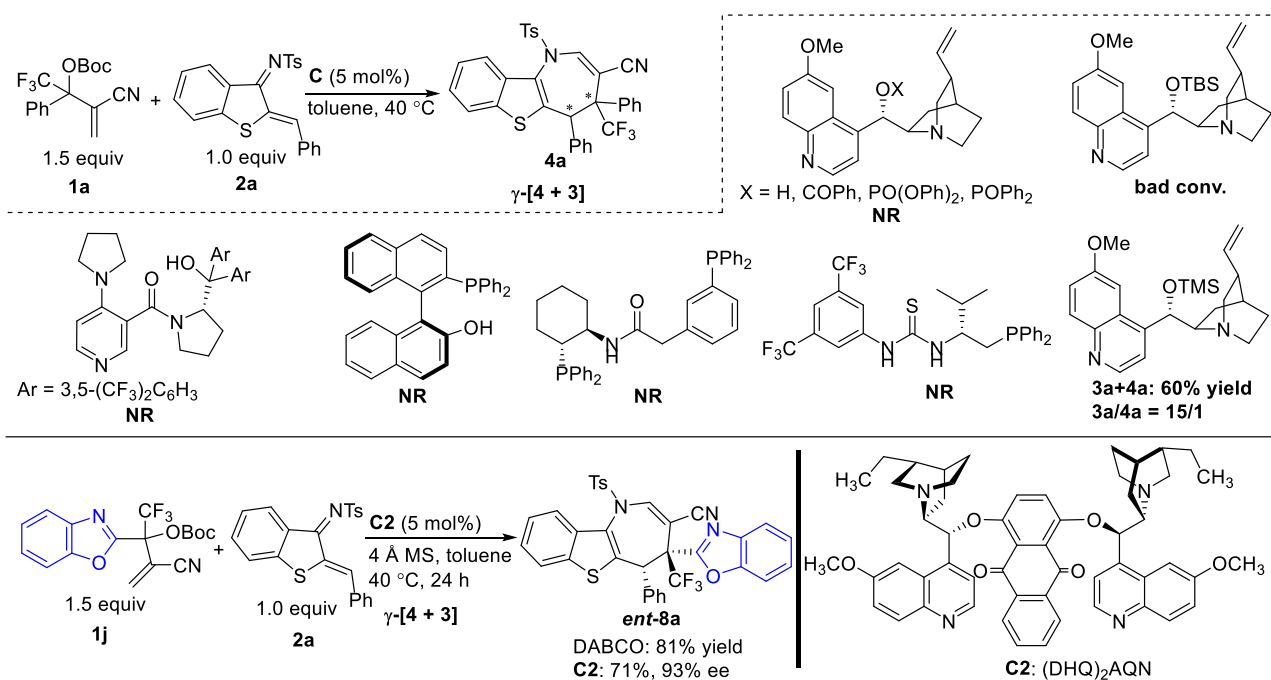


Entry	C6 (x mol%)	Solvent	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	5	toluene	33	92

2	20	toluene	53	95
3 <sup>d</sup>	20	dry toluene	[3a+4a]/5a = 1/2	/
4 <sup>e</sup>	20	toluene	Messy	/
5 <sup>f</sup>	20	toluene	45	91
6	20	PhCF <sub>3</sub>	60	96
7	20	CHCl <sub>3</sub>	46	92
8	20	THF	bad conv.	/
9	20	CH <sub>3</sub> CN	messy	/
10 <sup>g</sup>	10	PhCF <sub>3</sub>	61	98
11 <sup>g,h</sup>	10	PhCF <sub>3</sub>	65	98

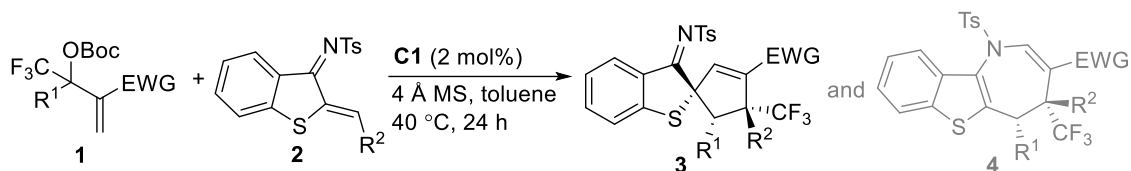
<sup>a</sup>Unless noted otherwise, reactions were performed using **1a** (0.075 mmol, 1.5 equiv), **2a** (0.05 mmol, 1.0 equiv) and **C6** (x mol%) in solvent (0.5 mL) at 40 °C for 24 h. <sup>b</sup>Yield of isolated product *ent*-**5a**. <sup>c</sup>Unless noted, for product *ent*-**5a**, determined by HPLC analysis using a chiral stationary phase; >19:1 dr by <sup>1</sup>H NMR analysis. <sup>d</sup>20.0 mg 4 Å MS was used. <sup>e</sup>*t*-BuOH/toluene = 1/10; <sup>f</sup>At 60 °C. <sup>g</sup>For 36 h. <sup>h</sup>**1a** (0.1 mmol, 2.0 equiv) was added in two portions.

### 3.4 Substrate-controlled $\gamma$ -[4+3] annulation of MBH carbonate **1a** or **1j** with 1-azadiene **2a**<sup>a</sup>



## 4. General procedure for divergent annulations of MBH carbonates with 1-azadienes

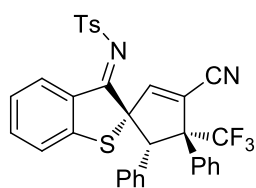
### 4.1 General procedure for asymmetric $\gamma$ -[3+2] annulations of MBH carbonates **1** with 1-azadienes **2**



**Synthesis of 3:** A mixture of MBH carbonate **1** (0.15 mmol, 1.5 equiv), 1-azadiene **2** (0.10 mmol, 1.0 equiv), **C1** (1.7 mg, 2 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at 40 °C for 24 h, and the reaction was monitored by TLC. After completion, the product **3** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether).

**Synthesis of *ent*-3:** A mixture of MBH carbonate **1** (0.15 mmol, 1.5 equiv), 1-azadiene **2** (0.10 mmol, 1.0 equiv), **C2** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at 40 °C for 24 h, and the reaction was monitored by TLC. After completion, the product *ent*-**3** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether).

**Synthesis of racemic 3:** The racemates could not be obtained under the catalysis of DABCO. So the mixture of chiral catalyst **C1** and its *pseudo*-enantiomer **C2** was used for the preparation of the samples for determining the peaks of the enantiomers.

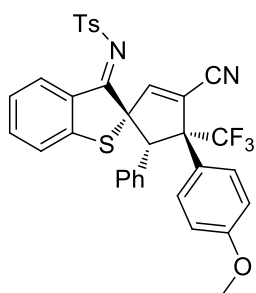


**Synthesis of 3a:** A mixture of *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenyl but-3-en-2-yl)carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv), *N*-((*Z*)-2-benzylidenebenzo[*b*]thiophen-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **2a** (39.1 mg, 0.0997 mmol, 1.0 equiv), **C1** (1.7 mg, 2 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at 40 °C for 24 h, and the reaction was

monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/10) to give a mixture of products **3a** and **4a** (**3a**:**4a** = 10:1): 53.0 mg (0.0882 mmol), as a yellow solid, 88% yield; mp = 105–107 °C;  $[\alpha]_D^{25} = +191.0$  ( $c = 0.40$  in  $\text{CHCl}_3$ ); >19:1 dr; 97% ee, determined by HPLC analysis (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 12.51$  min (major),  $t_R = 26.70$  min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.69 (d,  $J = 8.0$  Hz, 1H), 7.87 (d,  $J = 8.0$  Hz, 2H), 7.50 (t,  $J = 7.6$  Hz, 1H), 7.39 (d,  $J = 8.0$  Hz, 2H), 7.34–7.28 (m, 2H), 7.27–7.02 (m, 10H), 6.93 (s, 1H), 4.61 (s, 1H), 2.54 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 180.7, 151.9, 151.6, 143.9, 138.7, 137.0, 135.4, 132.7, 132.0, 123.0, 129.7, 129.0, 128.8, 128.5, 127.8, 126.8 (q,  $J = 2.5$  Hz), 126.7, 126.3, 125.9, 125.7 (q,  $J = 283.3$  Hz), 123.5, 118.7, 113.5, 75.2, 68.0, 66.7 (q,  $J = 25.6$  Hz), 21.7;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –61.0; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{33}\text{H}_{24}\text{F}_3\text{O}_2\text{S}_2^+$  601.1226; Found 601.1227.

**Synthesis of *ent*-3a:** A mixture of *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv), *N*-((*Z*)-2-benzylidenebenzo[*b*]thiophen-3(*2H*)-

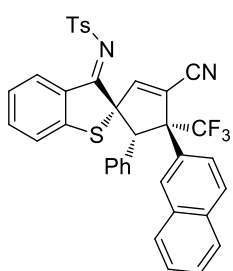
ylidene)-4-methylbenzenesulfonamide **2a** (39.1 mg, 0.0997 mmol, 1.0 equiv), **C2** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at 40 °C for 24 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/10) to give a mixture of products **ent-3a** and **ent-4a** (**ent-3a:ent-4a** = 8:1): 37.0 mg (0.0616 mmol), as a yellow solid, 62% yield;  $[\alpha]_D^{25} = -169.6$  ( $c = 0.50$  in  $\text{CHCl}_3$ ); >19:1 dr; 96% ee, determined by HPLC analysis (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 12.51$  min (minor),  $t_R = 26.51$  min (major).



**Synthesis of 3b:** A mixture of *tert*-butyl (3-cyano-1,1,1-trifluoro-2-(4-methoxyphenyl)but-3-en-2-yl)carbonate **1d** (53.6 mg, 0.150 mmol, 1.5 equiv),

*N*-((*Z*)-2-benzylidenebenzo[*b*]thiophen-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **2a** (39.1 mg, 0.0997 mmol, 1.0 equiv), **C1** (1.7 mg, 2 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at 40 °C for 24 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10)

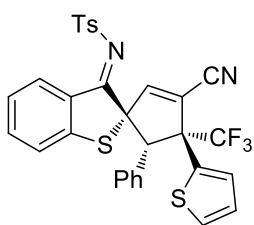
to give the product **3b**: 56.0 mg (0.0887 mmol), as a yellow solid, 89% yield; mp = 171–173 °C;  $[\alpha]_D^{25} = +218.5$  ( $c = 0.40$  in  $\text{CHCl}_3$ ); >19:1 dr; 93% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 16.35$  min (major),  $t_R = 19.64$  min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.69 (d,  $J = 8.0$  Hz, 1H), 7.93–7.84 (m, 2H), 7.52–7.45 (m, 1H), 7.40 (d,  $J = 8.0$  Hz, 2H), 7.29 (d,  $J = 8.4$  Hz, 1H), 7.24–7.16 (m, 2H), 7.15–7.04 (m, 6H), 6.89 (s, 1H), 6.73–6.59 (m, 2H), 4.59 (s, 1H), 3.80 (s, 3H), 2.54 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 180.8, 159.3, 151.7, 151.5, 143.9, 138.7, 137.0, 132.6, 132.0, 130.1, 129.7, 128.7, 128.1 (q,  $J = 2.5$  Hz), 127.8, 127.1, 126.7, 126.2, 125.3 (q,  $J = 283.4$  Hz), 125.8, 123.5, 119.0, 114.2, 113.6, 75.0, 68.1, 66.2 (q,  $J = 25.5$  Hz), 55.1, 21.6;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –61.3; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{34}\text{H}_{25}\text{F}_3\text{N}_2\text{O}_3\text{S}_2\text{Na}^+$  653.1151; Found 653.1150.



**Synthesis of 3c:** A mixture of *tert*-butyl (3-cyano-1,1,1-trifluoro-2-(naphthalen-2-yl)but-3-en-2-yl)carbonate **1f** (57.0 mg, 0.151 mmol, 1.5 equiv), *N*-((*Z*)-2-benzylidenebenzo[*b*]thiophen-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **2a** (39.1 mg, 0.0997 mmol, 1.0 equiv), **C1** (1.7 mg, 2 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at 40 °C for 24 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/10) to give the product **3c**: 60.0 mg

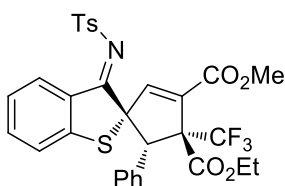


(0.0922 mmol), as a yellow solid, 92% yield; mp = 116–118 °C;  $[\alpha]_D^{25} = +106.0$  ( $c = 0.70$  in  $\text{CHCl}_3$ ); >19:1 dr; 96% ee, determined by HPLC analysis (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 16.07$  min (major),  $t_R = 28.63$  min (minor);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.72 (d,  $J = 8.0$  Hz, 1H), 7.86–7.82 (m, 2H), 7.82–7.77 (m, 1H), 7.73 (d,  $J = 2.4$  Hz, 1H), 7.66–7.62 (m, 1H), 7.57–7.47 (m, 4H), 7.31 (d,  $J = 8.0$  Hz, 1H), 7.28–7.14 (m, 5H), 7.13–7.02 (m, 4H), 6.98 (s, 1H), 4.76 (s, 1H), 2.47 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 180.5, 152.0, 151.5, 143.8, 138.6, 137.0, 132.8, 132.7, 132.6, 132.3, 132.1, 130.0, 129.7 (2C), 128.9, 128.8, 128.7, 127.9, 127.3, 127.1, 126.7 (2C), 126.6, 126.2, 125.9, 125.8 (q,  $J = 283.5$  Hz), 123.8 (d,  $J = 2.1$  Hz), 123.5, 118.6, 75.3, 67.4, 66.9 (q,  $J = 25.6$  Hz), 21.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –60.9; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{37}\text{H}_{25}\text{F}_3\text{N}_2\text{O}_2\text{S}_2\text{Na}^+$  673.1202; Found 673.1203.



**Synthesis of 3d:** A mixture of *tert*-butyl (3-cyano-1,1,1-trifluoro-2-(thiophen-2-yl)but-3-en-2-yl)carbonate **1g** (50.0 mg, 0.150 mmol, 1.5 equiv), *N*-((*Z*)-2-benzylidenebenzo[*b*]thiophen-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **2a** (39.1 mg, 0.0997 mmol, 1.0 equiv), **C1** (1.7 mg, 2 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at 40 °C for 24 h, and the reaction was

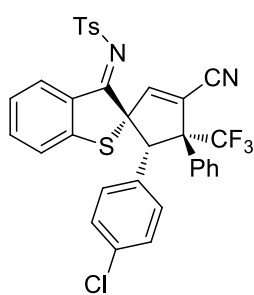
monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/10) to give the product **3d**: 41.2 mg (0.0679 mmol), as a yellow solid, 68% yield; mp = 99–101 °C;  $[\alpha]_D^{25} = +252.6$  ( $c = 0.50$  in  $\text{CHCl}_3$ ); >19:1 dr; >99% ee, determined by HPLC analysis (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 13.51$  min (major),  $t_R = 27.15$  min (minor);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.68 (d,  $J = 8.4$  Hz, 1H), 7.93–7.88 (m, 2H), 7.53–7.47 (m, 1H), 7.38 (d,  $J = 8.2$  Hz, 2H), 7.29 (dt,  $J = 8.0, 0.8$  Hz, 1H), 7.27–7.19 (m, 3H), 7.15 (d,  $J = 4.4$  Hz, 4H), 6.98–6.94 (m, 1H), 6.94–6.90 (m, 1H), 6.89 (s, 1H), 4.71 (d,  $J = 1.2$  Hz, 1H), 2.52 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 179.8, 151.7, 151.2, 143.9, 138.6, 137.4, 137.0, 132.7, 132.2 (q,  $J = 2.0$  Hz), 129.7, 129.6, 129.0, 127.9, 127.3 (q,  $J = 2.4$  Hz), 127.2, 126.9, 126.2, 126.1, 125.9, 125.1 (q,  $J = 283.5$  Hz), 123.5, 118.3, 113.3, 74.8, 67.4, 64.4 (q,  $J = 27.1$  Hz), 21.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –63.7; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{31}\text{H}_{21}\text{F}_3\text{N}_2\text{O}_2\text{S}_3\text{Na}^+$  629.0609; Found 629.0611.



**Synthesis of 3e:** A mixture of 1-ethyl 4-methyl 2-((*tert*-butoxycarbonyl)oxy)-3-methylene-2-(trifluoromethyl)succinate **1i** (53.4 mg, 0.150 mmol, 1.5 equiv), *N*-((*Z*)-2-benzylidenebenzo[*b*]thiophen-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **2a** (39.1 mg, 0.0997 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at 50 °C for 5 days, and the

reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10 to 1/5) to give the product **3e**: 47.5 mg (0.0754 mmol), as a yellow solid, 75% yield; mp = 85–87 °C;  $[\alpha]_D^{25} = -358.0$  ( $c = 0.60$  in  $\text{CHCl}_3$ ); >19:1 dr; >99% ee, determined by HPLC analysis (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 21.59$  min (minor),  $t_R = 27.12$  min (major);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.71 (d,  $J = 8.0$  Hz, 1H), 8.02–7.93 (m, 2H), 7.47–7.41 (m, 1H), 7.40 (d,  $J = 8.0$  Hz, 2H), 7.23–7.12 (m, 5H), 7.06–7.01 (m, 2H), 6.93 (s, 1H), 4.88 (s, 1H), 4.40–4.15 (m, 2H), 3.78 (s, 3H), 2.49 (s, 3H), 1.25 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 180.4, 166.3, 162.4, 151.6, 147.3, 143.8, 138.7, 136.5, 135.0, 132.6, 132.4, 130.6, 129.5, 128.6, 128.0, 126.8, 126.5, 125.5, 124.5 (q,  $J = 282.4$  Hz), 123.5, 75.9, 67.6 (q,  $J = 26.6$  Hz), 62.6, 59.3, 52.3, 21.6, 13.6;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –66.5; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{31}\text{H}_{27}\text{F}_3\text{NO}_6\text{S}_2^+$  630.1226; Found 630.1226.

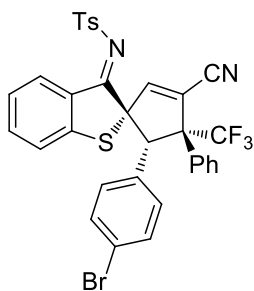
**Synthesis of *ent*-3e**: A mixture of 1-ethyl 4-methyl 2-((*tert*-butoxycarbonyl)oxy)-3-methylene-2-(trifluoromethyl)succinate **1i** (53.4 mg, 0.150 mmol, 1.5 equiv), *N*-((*Z*)-2-benzylidenebenzo[*b*]thiophen-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2a** (39.1 mg, 0.0997 mmol, 1.0 equiv), **C2** (8.6 mg, 10 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at 50 °C for 5 days, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10 to 1/5) to give the product **ent-3e**: 51.3 mg (0.0814 mmol), as a yellow solid, 81% yield;  $[\alpha]_D^{25} = +349.4$  ( $c = 0.67$  in  $\text{CHCl}_3$ ); >19:1 dr; >99% ee, determined by HPLC analysis (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 21.55$  min (major),  $t_R = 26.67$  min (minor).



**Synthesis of 3f**: A mixture of *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv), *N*-((*Z*)-2-(4-chlorobenzylidene)benzo[*b*]thiophen-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2b** (42.6 mg, 0.100 mmol, 1.0 equiv), **C1** (1.7 mg, 2 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at 40 °C for 24 h, and the reaction was monitored by TLC. After completion, the crude product was

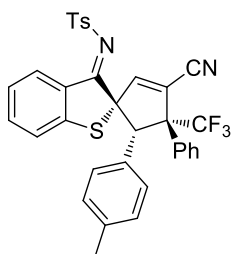
purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/10) to give a mixture of products **3f** and **4f** (**3f**:**4f** = 8:1): 58.0 mg (0.0913 mmol), as a yellow solid, 91% yield; mp = 106–107 °C;  $[\alpha]_D^{25} = +222.2$  ( $c = 0.65$  in  $\text{CHCl}_3$ ); >19:1 dr; >99% ee, determined by HPLC analysis (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 12.65$  min (major),  $t_R = 17.65$  min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.70 (d,  $J = 8.0$  Hz, 1H), 7.89–7.83 (m, 2H), 7.53 (ddd,  $J = 8.0, 6.8, 1.2$  Hz, 1H), 7.39 (d,  $J = 8.0$  Hz, 2H), 7.34–7.29 (m, 2H), 7.27–7.22 (m, 1H), 7.21–7.14 (m, 4H), 7.12–7.07 (m, 2H), 7.00 (d,  $J = 8.4$  Hz, 2H), 6.93 (s, 1H), 4.57

(s, 1H), 2.54 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 180.4, 151.7, 151.3, 144.0, 138.5, 137.2, 135.1, 135.0, 133.2, 132.7, 130.6, 129.7, 129.0, 128.7, 128.4, 128.1, 126.7 (2C), 126.1, 125.6 (q,  $J = 284.1$  Hz), 123.5, 118.7, 113.4, 74.9, 67.5, 66.6 (q,  $J = 25.7$  Hz), 21.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm)  $-60.9$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{33}\text{H}_{23}^{35}\text{ClF}_3\text{N}_2\text{O}_2\text{S}_2^+$  635.0836; Found 635.0838; Calcd for  $\text{C}_{33}\text{H}_{23}^{37}\text{ClF}_3\text{N}_2\text{O}_2\text{S}_2^+$  637.0807; Found 637.0787.



**Synthesis of 3g:** A mixture of *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv), *N*-((*Z*)-2-(4-bromobenzylidene)benzo[*b*]thiophen-3(*2H*)-ylidene)-4-methylbenzene sulfonamide **2c** (47.0 mg, 0.100 mmol, 1.0 equiv), **C1** (1.7 mg, 2 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at 40 °C for 24 h, and the reaction was monitored by TLC. After completion, the crude product was

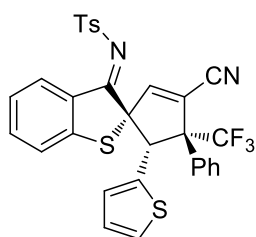
purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/10) to give a mixture of products **3g** and **4g** (**3g**:**4g** = 10:1): 60.0 mg (0.0882 mmol), as a yellow solid, 88% yield; mp = 100–101 °C;  $[\alpha]_{\text{D}}^{25} = +216.0$  ( $c = 0.60$  in  $\text{CHCl}_3$ ); >19:1 dr; 98% ee, determined by HPLC analysis (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 14.07$  min (major),  $t_{\text{R}} = 20.43$  min (minor);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.70 (d,  $J = 8.0$  Hz, 1H), 7.86 (d,  $J = 7.6$  Hz, 2H), 7.54 (t,  $J = 7.6$  Hz, 1H), 7.46–7.37 (m, 2H), 7.37–7.22 (m, 5H), 7.22–7.11 (m, 4H), 6.98–6.87 (m, 3H), 4.55 (s, 1H), 2.54 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 180.4, 151.7, 151.3, 144.0, 138.5, 137.2, 135.1, 133.5, 132.7, 131.1, 129.7, 129.00, 128.96, 128.7, 127.7, 126.73, 126.70, 126.1, 125.6 (q,  $J = 283.5$  Hz), 123.6, 123.4, 118.7, 113.4, 74.8, 67.5, 66.6 (q,  $J = 25.6$  Hz), 21.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm)  $-60.9$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd For  $\text{C}_{33}\text{H}_{23}^{79}\text{BrF}_3\text{N}_2\text{O}_2\text{S}_2^+$  679.0331; Found 679.0336; Calcd for  $\text{C}_{33}\text{H}_{23}^{81}\text{BrF}_3\text{N}_2\text{O}_2\text{S}_2^+$  681.0310; Found 681.0300.



**Synthesis of 3h:** A mixture of *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenyl but-3-en-2-yl)carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv), 4-methyl-*N*-((*Z*)-2-(4-methylbenzylidene)benzo[*b*]thiophen-3(*2H*)-ylidene)benzenesulfonamide **2d** (40.6 mg, 0.100 mmol, 1.0 equiv), **C1** (1.7 mg, 2 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at 40 °C for 24 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash

chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give a mixture of products **3h** and **4h** (**3h**:**4h** = 13:1): 59.0 mg (0.0959 mmol), as a yellow solid, 96% yield; mp = 107–109 °C;  $[\alpha]_{\text{D}}^{25} = +221.8$  ( $c = 0.65$  in  $\text{CHCl}_3$ ); >19:1 dr; 98% ee, determined by HPLC analysis (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 11.09$  min (major),  $t_{\text{R}} =$

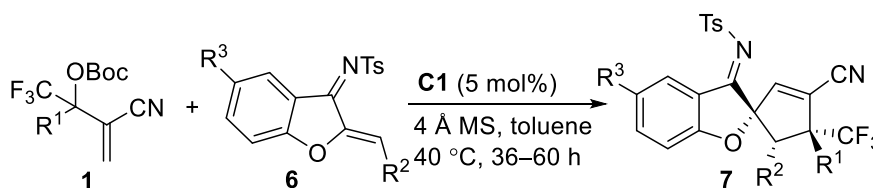
19.69 min (minor); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.70 (d, *J* = 8.0 Hz, 1H), 7.90–7.83 (m, 2H), 7.57–7.46 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.34–7.27 (m, 2H), 7.24–7.18 (m, 1H), 7.16 (d, *J* = 4.8 Hz, 4H), 6.98–6.89 (m, 5H), 4.58 (d, *J* = 1.6 Hz, 1H), 2.53 (s, 3H), 2.21 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 180.7, 152.0, 151.7, 143.9, 138.69, 138.66, 137.0, 135.5, 132.7, 131.9, 129.6, 128.8, 128.6, 128.4, 126.82, 126.78, 126.7, 126.2, 125.8, 125.7 (q, *J* = 283.7 Hz), 123.5, 118.7, 113.6, 75.2, 67.8, 66.6 (q, *J* = 25.3 Hz), 21.6, 21.0; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ (ppm) –61.0; HRMS (ESI-TOF) *m/z*: [M + Na]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>25</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>Na<sup>+</sup> 637.1202; Found 637.1199.



**Synthesis of 3i:** A mixture of *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv), 4-methyl-*N*-((*Z*)-2-(thiophen-2-ylmethylene)benzo[*b*]thiophen-3(*2H*)-ylidene)benzene sulfonamide **2e** (39.8 mg, 0.100 mmol, 1.0 equiv), **C1** (1.7 mg, 2 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at 40 °C for 24 h, and the reaction was monitored by TLC. After completion, the crude product was

purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/10) to give a mixture of products **3i** and **4i** (**3i:4i** = 10:1): 53.0 mg (0.0873 mmol), as a yellow solid, 87% yield; mp = 106–108 °C; [α]<sub>D</sub><sup>25</sup> = +147.5 (*c* = 0.32 in CHCl<sub>3</sub>); >19:1 dr; 97% ee, determined by HPLC analysis (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, *l* = 254 nm) *t*<sub>R</sub> = 15.24 min (major), *t*<sub>R</sub> = 29.16 min (minor); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.76 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.61–7.54 (m, 1H), 7.39 (d, *J* = 8.0 Hz, 3H), 7.36–7.31 (m, 1H), 7.31–7.23 (m, 1H), 7.23–7.09 (m, 5H), 6.90 (s, 1H), 6.84 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.79 (d, *J* = 3.6 Hz, 1H), 4.98 (s, 1H), 2.54 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 180.6, 152.0, 151.2, 143.9, 138.6, 137.2, 134.9, 132.8, 130.9, 130.8, 129.9, 129.7, 129.0, 128.6, 127.0 (q, *J* = 2.5 Hz), 126.8, 126.7, 126.5, 126.1, 125.4 (q, *J* = 283.3 Hz), 123.7, 118.7, 113.3, 74.9, 66.8 (q, *J* = 25.1 Hz), 63.5, 21.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ (ppm) –61.9; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>22</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>S<sub>3</sub><sup>+</sup> 607.0790; Found 607.0791.

#### 4.2 General procedure for asymmetric γ-[3+2] annulations of MBH carbonates **1** with 1-azadienes **6**

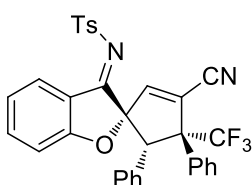


**Synthesis of 7:** To a mixture of 1-azadiene **6** (0.10 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added MBH carbonate **1** (0.15 mmol, 1.5 equiv) in two portions

(generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36–60 h, and the reaction was monitored by TLC. After completion, the product **7** was obtained after the purification by flash chromatography on silica gel (EtOAc/petroleum ether).

**Synthesis of *ent*-7:** To a mixture of 1-azadiene **6** (0.10 mmol, 1.0 equiv), **C2** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added MBH carbonate **1** (0.15 mmol, 1.5 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36–60 h, and the reaction was monitored by TLC. After completion, the product *ent*-**7** was obtained after the purification by flash chromatography on silica gel (EtOAc/petroleum ether).

**Synthesis of racemic 7:** The racemates could not be obtained under the catalysis of DABCO. So the mixture of chiral catalyst **C1** and its *pseudo*-enantiomer **C2** was used for the preparation of the samples for determining the peaks of the enantiomers.

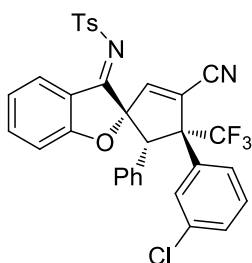


**Synthesis of 7a:** To a mixture of *N*-((*Z*)-2-benzylidenebenzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **6a** (37.5 mg, 0.100 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv) in two portions (generally at 0 h, 18 h, respectively).

The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/10) to give the product **7a**: 56.0 mg (0.0957 mmol), as a white solid, 96% yield; mp = 135–136 °C;  $[\alpha]_D^{25} = +193.3$  ( $c = 0.80$  in  $\text{CHCl}_3$ ); >19:1 dr; 98% ee, determined by HPLC analysis (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 8.12$  min (major),  $t_R = 12.93$  min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.46 (d,  $J = 8.0$  Hz, 1H), 7.87 (d,  $J = 8.4$  Hz, 2H), 7.66–7.58 (m, 1H), 7.38 (d,  $J = 8.0$  Hz, 2H), 7.31–7.22 (m, 5H), 7.20–7.13 (m, 2H), 7.13–7.07 (m, 3H), 7.07–7.01 (m, 2H), 6.92 (s, 1H), 4.18 (s, 1H), 2.51 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 179.0, 170.1, 148.0, 144.0, 140.1, 138.1, 135.0, 131.2, 131.0, 129.5, 129.1, 129.0, 128.80, 128.77, 128.2, 127.0, 126.8 (q,  $J = 2.4$  Hz), 124.9 (q,  $J = 283.5$  Hz), 124.5, 123.4, 116.7, 113.1, 112.8, 98.6, 67.9 (q,  $J = 25.7$  Hz), 67.2, 21.6;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –61.7; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{33}\text{H}_{23}\text{F}_3\text{N}_2\text{O}_3\text{SNa}^+$  607.1274; Found 607.1274.

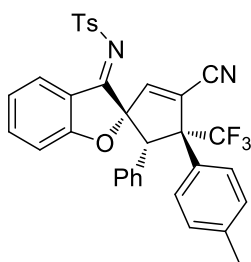
**Synthesis of *ent*-7a:** To a mixture of *N*-((*Z*)-2-benzylidenebenzofuran-3(2*H*)-ylidene)-4-methyl benzenesulfonamide **6a** (37.5 mg, 0.100 mmol, 1.0 equiv), **C2** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20

to 1/10) to give the product **ent-7a**: 52.4 mg (0.0896 mmol), as a white solid, 90% yield;  $[\alpha]_{\text{D}}^{25} = -186.4$  ( $c = 0.50$  in  $\text{CHCl}_3$ ); >19:1 dr; 96% ee, determined by HPLC analysis (Daicel Chiralpak AD-H,  $n$ -hexane/ $i$ -PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 8.14$  min (minor),  $t_{\text{R}} = 12.88$  min (major).



**Synthesis of 7b:** To a mixture of  $N$ -(( $Z$ )-2-benzylidenebenzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **6a** (37.5 mg, 0.100 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (2-(3-chlorophenyl)-3-cyano-1,1,1-trifluorobut-3-en-2-yl)carbonate **1b** (72.4 mg, 0.200 mmol, 2.0 equiv) in three portions (generally at 0 h, 18 h, 36 h, respectively). The mixture was stirred at 40 °C for 48 h, and the reaction was

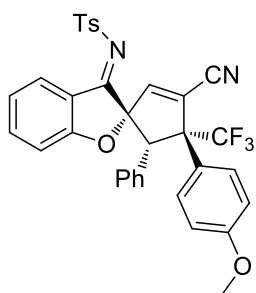
monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give the product **7b**: 55.0 mg (0.0889 mmol), as a white solid, 89% yield; mp = 79–81 °C;  $[\alpha]_{\text{D}}^{25} = +100.0$  ( $c = 0.50$  in  $\text{CHCl}_3$ ); >19:1 dr; >99% ee, determined by HPLC analysis (Daicel Chiralpak ID,  $n$ -hexane/ $i$ -PrOH = 60/40, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 7.60$  min (major),  $t_{\text{R}} = 12.29$  min (minor);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.48 (d,  $J = 8.0$  Hz, 1H), 7.87 (d,  $J = 8.0$  Hz, 2H), 7.70–7.57 (m, 1H), 7.42–7.33 (m, 3H), 7.28–7.00 (m, 10H), 6.95 (s, 1H), 4.10 (s, 1H), 2.50 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 178.6, 170.0, 148.5, 144.1, 140.1, 137.8, 136.9, 135.2, 131.2, 130.3, 129.7 (2C), 129.2, 129.0, 128.5, 128.3, 127.1 (q,  $J = 2.5$  Hz), 126.8, 125.1 (q,  $J = 2.8$  Hz), 124.7 (q,  $J = 238.6$  Hz), 123.9, 123.4, 116.6, 112.82, 112.78, 98.4, 67.5 (q,  $J = 26.1$  Hz), 67.0, 21.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –61.6; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{33}\text{H}_{22}^{35}\text{ClF}_3\text{N}_2\text{O}_3\text{SNa}^+$  641.0884; Found 641.0886; Calcd for  $\text{C}_{33}\text{H}_{22}^{37}\text{ClF}_3\text{N}_2\text{O}_3\text{SNa}^+$  643.0854; Found 643.0869.



**Synthesis of 7c:** To a mixture of  $N$ -(( $Z$ )-2-benzylidenebenzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **6a** (37.5 mg, 0.100 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-( $p$ -tolyl)but-3-en-2-yl) carbonate **1c** (51.2 mg, 0.150 mmol, 1.5 equiv) in two portions (generally at 0 h, 18 h, respectively).

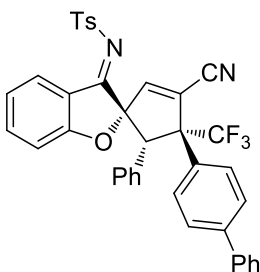
The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give the product **7c**: 58.0 mg (0.0968 mmol), as a white solid, 97% yield; mp = 77–78 °C;  $[\alpha]_{\text{D}}^{25} = +180.5$  ( $c = 0.40$  in  $\text{CHCl}_3$ ); >19:1 dr; 98% ee, determined by HPLC analysis (Daicel Chiralpak ID,  $n$ -hexane/ $i$ -PrOH = 60/40, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 7.97$  min (major),  $t_{\text{R}} = 14.69$  min (minor);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.46 (d,  $J = 8.4$  Hz,

1H), 7.88 (d,  $J = 8.0$  Hz, 2H), 7.67–7.57 (m, 1H), 7.39 (d,  $J = 8.0$  Hz, 2H), 7.19–6.97 (m, 11H), 6.89 (s, 1H), 4.16 (s, 1H), 2.52 (s, 3H), 2.36 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 179.1, 170.1, 147.7, 143.9, 140.1, 138.6, 138.0, 131.9, 131.2, 131.0, 129.8, 129.5, 129.1, 128.7, 128.2, 126.9, 126.6 (q,  $J = 2.3$  Hz), 125.0 (q,  $J = 283.6$  Hz), 124.7, 123.3, 116.7, 113.1, 112.8, 98.6, 67.6 (q,  $J = 25.7$  Hz), 67.2, 21.6, 21.0;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm)  $-61.8$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{34}\text{H}_{25}\text{F}_3\text{N}_2\text{O}_3\text{SNa}^+$  621.1430; Found 621.1430.



**Synthesis of 7d:** To a mixture of *N*-((*Z*)-2-benzylidenebenzofuran-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **6a** (37.5 mg, 0.100 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-(4-methoxyphenyl)but-3-en-2-yl) carbonate **1d** (53.6 mg, 0.150 mmol, 1.5 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion, the crude product was

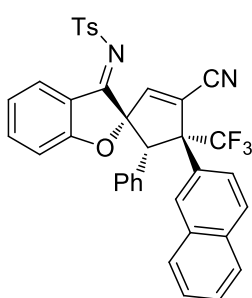
purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give the product **7d**: 57.0 mg (0.0927 mmol), as a white solid, 93% yield; mp = 167–168 °C;  $[\alpha]_{\text{D}}^{25} = +167.0$  ( $c = 0.40$  in  $\text{CHCl}_3$ ); >19:1 dr; 96% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 10.44$  min (major),  $t_{\text{R}} = 19.07$  min (minor);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.46 (d,  $J = 8.0$  Hz, 1H), 7.88 (d,  $J = 8.0$  Hz, 2H), 7.67–7.57 (m, 1H), 7.39 (d,  $J = 8.0$  Hz, 2H), 7.22–6.97 (m, 9H), 6.88 (s, 1H), 6.77 (d,  $J = 8.4$  Hz, 2H), 4.15 (s, 1H), 3.82 (s, 3H), 2.51 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 179.1, 170.1, 159.5, 147.6, 143.9, 140.1, 138.0, 131.2, 131.0, 129.5, 129.1, 128.7, 128.2, 128.1 (q,  $J = 25.0$  Hz), 126.9, 126.7, 125.0 (q,  $J = 283.5$  Hz), 124.7, 123.3, 116.7, 114.4, 113.1, 112.8, 98.6, 68.28 (q,  $J = 25.8$  Hz), 67.27, 55.2, 21.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm)  $-62.1$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{34}\text{H}_{25}\text{F}_3\text{N}_2\text{O}_4\text{SNa}^+$  637.1379; Found 637.1377.



**Synthesis of 7e:** To a mixture of *N*-((*Z*)-2-benzylidenebenzofuran-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **6a** (37.5 mg, 0.100 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added 2-([1,1'-biphenyl]-4-yl)-3-cyano-1,1,1-trifluorobut-3-en-2-yl *tert*-butyl carbonate **1e** (80.6 mg, 0.200 mmol, 2.0 equiv) in three portions (generally at 0 h, 18 h, 36 h, respectively). The mixture was stirred at 40 °C for 48 h, and

the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give the product **7e**: 64.0 mg (0.0968 mmol), as a white solid, 97% yield; mp = 119–121 °C;  $[\alpha]_{\text{D}}^{25} = +91.5$  ( $c = 0.40$  in  $\text{CHCl}_3$ ); >19:1

dr; >99% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 9.31$  min (major),  $t_R = 19.23$  min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.47 (d,  $J = 8.0$  Hz, 1H), 7.88 (d,  $J = 8.0$  Hz, 2H), 7.67–7.60 (m, 1H), 7.59 (d,  $J = 7.6$  Hz, 2H), 7.52–7.43 (m, 4H), 7.42–7.29 (m, 5H), 7.25–6.99 (m, 7H), 6.92 (s, 1H), 4.22 (s, 1H), 2.45 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 179.1, 170.1, 148.1, 143.9, 141.4, 140.1, 139.7, 138.0, 134.0, 131.3, 131.0, 129.6, 129.0, 128.9, 128.8, 128.2, 127.9, 127.6, 127.2 (q,  $J = 2.5$  Hz), 126.94, 126.92, 124.9 (q,  $J = 283.6$  Hz), 124.4, 123.4, 116.6, 113.1, 112.9, 98.6, 67.7 (q,  $J = 25.9$  Hz), 67.3, 21.6;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –61.7; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{39}\text{H}_{28}\text{F}_3\text{N}_2\text{O}_3\text{S}^+$  661.1767; Found 661.1767.



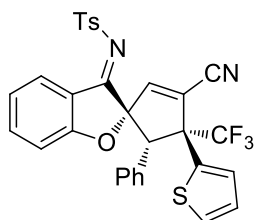
**Synthesis of 7f:** To a mixture of *N*-((*Z*)-2-benzylidenebenzofuran-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **6a** (37.5 mg, 0.100 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-(naphthalen-2-yl)but-3-en-2-yl) carbonate **1f** (57.0 mg, 0.151 mmol, 1.5 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion, the crude product was purified by

flash chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/10) to give the product **7f**: 61.0 mg (0.0961 mmol), as a white solid, 96% yield; mp = 101–103 °C;  $[\alpha]_D^{25} = +65.2$  ( $c = 0.50$  in  $\text{CHCl}_3$ ); >19:1 dr; >99% ee, determined by HPLC analysis (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 5.69$  min (major),  $t_R = 6.94$  min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.48 (d,  $J = 8.4$  Hz, 1H), 7.87 (d,  $J = 8.0$  Hz, 2H), 7.84 (d,  $J = 8.0$  Hz, 1H), 7.78 (s, 1H), 7.71–7.60 (m, 3H), 7.59–7.47 (m, 2H), 7.34 (d,  $J = 8.0$  Hz, 2H), 7.31 (dd,  $J = 8.4, 2.0$  Hz, 1H), 7.22–7.13 (m, 2H), 7.13–7.01 (m, 5H), 6.98 (s, 1H), 4.33 (s, 1H), 2.52 (s, 3H);  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 179.1, 170.1, 148.0, 143.9, 140.2, 138.0, 132.9, 132.7, 132.0, 131.2, 131.0, 129.6, 129.1, 129.0, 128.8, 128.7, 128.3, 127.4, 127.2, 126.9, 126.8, 126.7, 125.0 (q,  $J = 283.5$  Hz), 124.6, 123.7, 123.4, 116.7, 113.0, 112.9, 98.7, 68.1 (q,  $J = 26.1$  Hz), 67.1, 21.7;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –61.5; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{37}\text{H}_{25}\text{F}_3\text{N}_2\text{O}_3\text{SNa}^+$  657.1430; Found 657.1428.

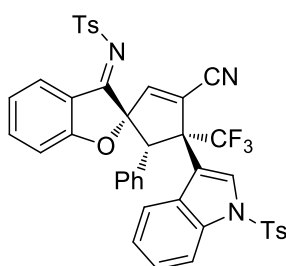
**Synthesis of *ent*-7f:** To a mixture of *N*-((*Z*)-2-benzylidenebenzofuran-3(*2H*)-ylidene)-4-methyl benzenesulfonamide **6a** (37.5 mg, 0.100 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-(naphthalen-2-yl)but-3-en-2-yl) carbonate **1f** (57.0 mg, 0.151 mmol, 1.5 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel



(EtOAc/petroleum ether = 1/20 to 1/10) to give the product **ent-7f**: 60.0 mg (0.0945 mmol), as a white solid, 94% yield;  $[\alpha]_{\text{D}}^{25} = -74.5$  ( $c = 0.55$  in  $\text{CHCl}_3$ ); >19:1 dr; 96% ee, determined by HPLC analysis (Daicel Chiralpak AD-H,  $n$ -hexane/ $i$ -PrOH = 60/40, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 5.88$  min (minor),  $t_{\text{R}} = 7.07$  min (major).

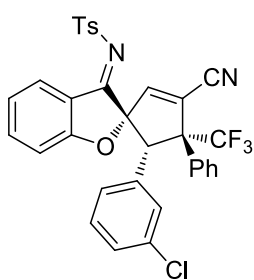


**Synthesis of 7g:** To a mixture of *N*-((*Z*)-2-benzylidenebenzofuran-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **6a** (37.5 mg, 0.100 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-(thiophen-2-yl)but-3-en-2-yl)carbonate **1g** (50.0 mg, 0.150 mmol, 1.5 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/10) to give the product **7g**: 54.0 mg (0.0914 mmol), as a white solid, 91% yield; mp = 85–86 °C;  $[\alpha]_{\text{D}}^{25} = +231.2$  ( $c = 0.50$  in  $\text{CHCl}_3$ ); >19:1 dr; 96% ee, determined by HPLC analysis (Daicel Chiralpak AD-H,  $n$ -hexane/ $i$ -PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 10.88$  min (major),  $t_{\text{R}} = 23.12$  min (minor);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.47 (d,  $J = 8.0$  Hz, 1H), 7.89 (d,  $J = 8.0$  Hz, 2H), 7.67–7.59 (m, 1H), 7.37 (d,  $J = 8.4$  Hz, 2H), 7.34 (d,  $J = 5.2$  Hz, 1H), 7.23–7.03 (m, 8H), 7.03–6.97 (m, 1H), 6.90 (s, 1H), 4.23 (s, 1H), 2.50 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 178.3, 170.0, 147.8, 144.0, 140.0, 137.9, 136.7, 131.5, 131.1, 129.5, 129.0, 128.5, 128.2, 127.5, 127.4, 127.0, 126.4, 124.5(q,  $J = 283.5$  Hz), 124.0, 123.4, 116.7, 112.9, 112.8, 98.0, 66.7, 65.5 (q,  $J = 27.0$  Hz), 21.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –64.5; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{31}\text{H}_{21}\text{F}_3\text{N}_2\text{O}_3\text{S}_2\text{Na}^+$  613.0838; Found 613.0839.



**Synthesis of 7h:** To a mixture of *N*-((*Z*)-2-benzylidenebenzofuran-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **6a** (37.5 mg, 0.100 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-(1-tosyl-1*H*-indol-3-yl)but-3-en-2-yl)carbonate **1h** (78.2 mg, 0.150 mmol, 1.5 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10 to 1/5) to give the product **7h**: 60.0 mg (0.0771 mmol), as a white solid, 77% yield; mp = 137–139 °C;  $[\alpha]_{\text{D}}^{25} = -61.2$  ( $c = 0.50$  in  $\text{CHCl}_3$ ); >19:1 dr; 97% ee, determined by HPLC analysis (Daicel Chiralpak ID,  $n$ -hexane/ $i$ -PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 15.03$  min (major),  $t_{\text{R}} = 19.38$  min (minor);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.52 (dd,  $J = 8.4, 1.2$  Hz, 1H), 7.93 (d,  $J = 8.4$  Hz, 1H), 7.83–7.77 (m,

2H), 7.68 (m, 1H), 7.64–7.59 (m, 2H), 7.57–7.52 (m, 1H), 7.44 (d,  $J = 8.0$  Hz, 1H), 7.31 (d,  $J = 8.0$  Hz, 2H), 7.24–7.09 (m, 6H), 7.05 (t,  $J = 7.6$  Hz, 2H), 7.02 (s, 1H), 6.95 (d,  $J = 7.2$  Hz, 2H), 6.26 (ddd,  $J = 8.0, 7.2, 0.8$  Hz, 1H), 4.52 (s, 1H), 2.50 (s, 3H), 2.35 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 179.5, 170.1, 147.9, 145.4, 144.1, 140.2, 137.8, 135.0, 134.5, 131.2, 130.8, 130.0, 129.7, 128.9, 128.8, 128.3, 127.1, 126.8, 126.68, 126.65, 124.9, 124.6 (q,  $J = 284.2$  Hz), 124.1, 123.6, 123.4, 119.8, 116.9, 113.9, 112.9, 112.4, 112.2, 97.9, 64.5 (q,  $J = 26.8$  Hz), 61.2, 21.61, 21.60;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –64.6; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{42}\text{H}_{30}\text{F}_3\text{N}_3\text{O}_5\text{S}_2\text{Na}^+$  778.1652; Found 778.1651.

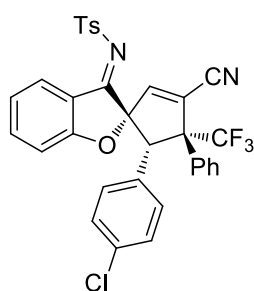


**Synthesis of **7i**:** To a mixture of *N*-((*Z*)-2-(3-chlorobenzylidene)benzofuran-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **6b** (41.0 mg, 0.100 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was

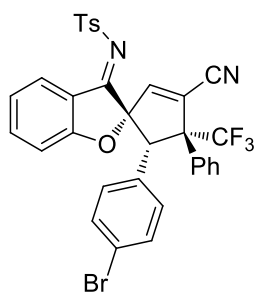
monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give the product **7i**: 60.0 mg (0.0969 mmol), as a white solid, 97% yield; mp = 259–260 °C;  $[\alpha]_{\text{D}}^{25} = +208.0$  ( $c = 0.50$  in  $\text{CHCl}_3$ ); >19:1 dr; >99% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 7.36$  min (major),  $t_{\text{R}} = 13.35$  min (minor);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.46 (s, 1H), 7.86 (d,  $J = 8.4$  Hz, 2H), 7.56 (dd,  $J = 9.2, 2.4$  Hz, 1H), 7.38 (d,  $J = 8.0$  Hz, 3H), 7.32–7.23 (m, 4H), 7.23–7.16 (m, 1H), 7.15–7.07 (m, 3H), 7.01 (d,  $J = 7.6$  Hz, 2H), 6.91 (s, 1H), 4.14 (s, 1H), 2.52 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 177.7, 168.4, 147.5, 144.3, 140.0, 137.6, 134.9, 131.2, 130.0, 129.6 (2C), 129.2, 129.0, 128.9, 128.73, 128.71, 128.3, 127.1, 126.9, 126.7 (q,  $J = 2.4$  Hz), 124.91, 124.90 (q,  $J = 283.4$  Hz), 117.7, 114.0, 112.9, 99.4, 67.8 (q,  $J = 25.5$  Hz), 67.6, 21.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –61.6; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{33}\text{H}_{22}^{35}\text{ClF}_3\text{N}_2\text{O}_3\text{SNa}^+$  641.0884; Found 641.0877; Calcd for  $\text{C}_{33}\text{H}_{22}^{37}\text{ClF}_3\text{N}_2\text{O}_3\text{SNa}^+$  643.0854; Found 643.0861.

**Synthesis of *ent*-**7i**:** To a mixture of *N*-((*Z*)-2-(3-chlorobenzylidene)benzofuran-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **6b** (41.0 mg, 0.100 mmol, 1.0 equiv), **C2** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give the product *ent*-**7i**: 60.3 mg (0.0974 mmol), as a white solid, 97% yield;  $[\alpha]_{\text{D}}^{25} = -196.0$  ( $c =$

0.75 in CHCl<sub>3</sub>); >19:1 dr; 99% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min,  $l = 254$  nm)  $t_R = 7.37$  min (minor),  $t_R = 13.12$  min (major).

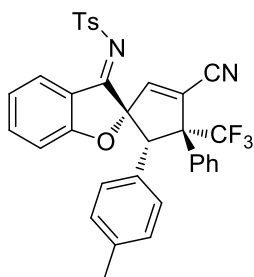


**Synthesis of 7j:** To a mixture of *N*-((*Z*)-2-(4-chlorobenzylidene)benzofuran-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **6c** (41.0 mg, 0.100 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give the product **7j**: 57.0 mg (0.0921 mmol), as a white solid, 92% yield; mp = 100–101 °C;  $[\alpha]_D^{25} = +178.0$  ( $c = 0.50$  in CHCl<sub>3</sub>); >19:1 dr; 98% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min,  $l = 254$  nm)  $t_R = 6.32$  min (major),  $t_R = 10.07$  min (minor); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.48 (d,  $J = 7.6$  Hz, 1H), 7.86 (d,  $J = 8.0$  Hz, 2H), 7.75–7.57 (m, 1H), 7.37 (d,  $J = 8.0$  Hz, 3H), 7.32–7.21 (m, 4H), 7.14 (t,  $J = 8.8$  Hz, 2H), 7.09 (d,  $J = 8.4$  Hz, 2H), 6.98 (d,  $J = 8.4$  Hz, 2H), 6.91 (s, 1H), 4.15 (s, 1H), 2.51 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 178.6, 169.9, 147.9, 144.1, 140.3, 137.9, 135.1, 134.8, 132.5, 131.1, 129.6, 129.2, 128.9, 128.5, 127.5, 126.9, 126.7 (q,  $J = 2.5$  Hz), 124.9 (q,  $J = 283.9$  Hz), 124.5, 123.6, 116.6, 112.9, 112.8, 98.3, 67.8 (q,  $J = 25.6$  Hz), 66.5, 21.6; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) –61.6; HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for C<sub>33</sub>H<sub>23</sub><sup>35</sup>ClF<sub>3</sub>N<sub>2</sub>O<sub>3</sub>S<sup>+</sup> 619.1065; Found 619.1066; Calcd for C<sub>33</sub>H<sub>23</sub><sup>37</sup>ClF<sub>3</sub>N<sub>2</sub>O<sub>3</sub>S<sup>+</sup> 621.1035; Found 621.1051.



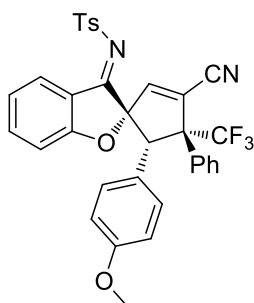
**Synthesis of 7k:** To a mixture of *N*-((*Z*)-2-(4-bromobenzylidene)benzofuran-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **6d** (45.4 mg, 0.100 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give the product **7k**: 60.0 mg (0.0904 mmol), as a white solid, 90% yield; mp = 108–110 °C;  $[\alpha]_D^{25} = +218.0$  ( $c = 0.50$  in CHCl<sub>3</sub>); >19:1 dr; 99% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min,  $l = 254$  nm)  $t_R = 6.32$  min (major),  $t_R = 10.07$  min (minor); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.49 (d,  $J = 8.4$  Hz, 1H), 7.86 (d,  $J = 7.6$  Hz, 2H), 7.73–7.60 (m, 1H), 7.38 (d,  $J = 8.0$  Hz,

3H), 7.33–7.20 (m, 6H), 7.20–7.08 (m, 2H), 6.98–6.83 (m, 3H), 4.13 (s, 1H), 2.52 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 178.6, 169.9, 147.9, 144.1, 140.3, 137.9, 134.8, 132.8, 131.5, 131.1, 129.6, 129.2, 128.9, 128.1, 126.9, 126.7 (q,  $J = 2.4$  Hz), 124.9 (q,  $J = 283.4$  Hz), 124.5, 123.6, 123.5, 116.6, 112.9, 112.8, 98.3, 67.8 (q,  $J = 25.8$  Hz), 66.6, 21.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –61.6; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{33}\text{H}_{23}^{79}\text{BrF}_3\text{N}_2\text{O}_3\text{S}^+$  663.0599; Found 663.0599; Calcd for  $\text{C}_{33}\text{H}_{23}^{81}\text{BrF}_3\text{N}_2\text{O}_3\text{S}^+$  665.0539; Found 665.0545.



**Synthesis of 7l:** To a mixture of 4-methyl-*N*-((*Z*)-2-(4-methylbenzylidene)benzofuran-3(2*H*)-ylidene)benzenesulfonamide **6e** (39.0 mg, 0.100 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was

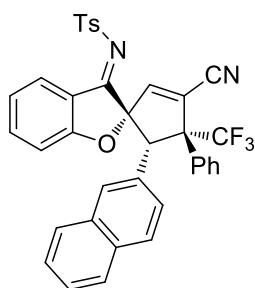
monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give the product **7l**: 57.0 mg (0.0952 mmol), as a white solid, 95% yield; mp = 79–82 °C;  $[\alpha]_{\text{D}}^{25} = +243.6$  ( $c = 0.50$  in  $\text{CHCl}_3$ ); >19:1 dr; 99% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 6.54$  min (major),  $t_{\text{R}} = 13.01$  min (minor);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.46 (d,  $J = 8.4$  Hz, 1H), 7.86 (d,  $J = 8.0$  Hz, 2H), 7.62 (ddd,  $J = 8.4, 7.2, 1.6$  Hz, 1H), 7.40–7.33 (m, 3H), 7.32–7.21 (m, 4H), 7.15 (d,  $J = 8.4$  Hz, 1H), 7.09 (t,  $J = 7.6$  Hz, 1H), 6.96–6.84 (m, 5H), 4.15 (s, 1H), 2.51 (s, 3H), 2.19 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 179.1, 170.1, 148.0, 143.9, 140.0, 138.6, 138.1, 135.1, 131.1, 131.0, 129.5, 129.1, 129.0, 128.7, 126.9, 126.8 (q,  $J = 2.4$  Hz), 125.8, 125.0 (q,  $J = 283.7$  Hz), 124.6, 123.3, 116.8, 113.1, 112.8, 98.7, 67.8 (q,  $J = 25.8$  Hz), 67.1, 21.6, 21.0;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –61.7; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{34}\text{H}_{25}\text{F}_3\text{N}_2\text{O}_3\text{SNa}^+$  621.1430; Found 621.1427.



**Synthesis of 7m:** To a mixture of *N*-((*Z*)-2-(4-methoxybenzylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **6f** (40.6 mg, 0.100 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (49.1 mg, 0.15 mmol, 1.5 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion, the crude product was purified by

flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give the product **7m**: 57.0 mg (0.0927 mmol), as a white solid, 93% yield; mp = 86–88 °C;  $[\alpha]_{\text{D}}^{25} = +189.1$  ( $c = 0.50$  in

CHCl<sub>3</sub>); >19:1 dr; >99% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm)  $t_R$  = 8.50 min (major),  $t_R$  = 17.32 min (minor); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.46 (d,  $J$  = 8.0 Hz, 1H), 7.86 (d,  $J$  = 8.4 Hz, 2H), 7.62 (ddd,  $J$  = 8.8, 7.2, 1.6 Hz, 1H), 7.41–7.34 (m, 3H), 7.31–7.23 (m, 4H), 7.14 (d,  $J$  = 8.8 Hz, 1H), 7.11–7.06 (m, 1H), 6.96 (d,  $J$  = 8.4 Hz, 2H), 6.91 (s, 1H), 6.65–6.59 (m, 2H), 4.13 (s, 1H), 3.66 (s, 3H), 2.50 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 179.2, 170.1, 159.8, 148.0, 143.9, 140.1, 138.1, 135.2, 132.5, 131.0, 129.5, 129.1, 128.7, 126.9, 126.8 (q,  $J$  = 2.4 Hz), 125.0 (q,  $J$  = 282.5 Hz), 124.6, 123.3, 120.7, 116.8, 113.6, 113.1, 112.8, 98.6, 67.6 (q,  $J$  = 25.6 Hz), 66.9, 55.0, 21.6; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) –61.7; HRMS (ESI-TOF)  $m/z$ : [M + Na]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>25</sub>F<sub>3</sub>N<sub>2</sub>O<sub>4</sub>SNa<sup>+</sup> 637.1379; Found 637.1381.

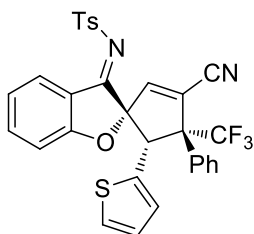


**Synthesis of 7n:** To a mixture of 4-methyl-*N*-((*Z*)-2-(naphthalen-2-ylmethylene)benzofuran-3(*2H*)-ylidene)benzenesulfonamide **6g** (42.6 mg, 0.100 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion, the crude product was

purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give the product **7n**: 56.0 mg (0.0882 mmol), as a white solid, 88% yield; mp = 117–119 °C;  $[\alpha]_D^{25}$  = +320.0 ( $c$  = 0.50 in CHCl<sub>3</sub>); >19:1 dr; >99% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm)  $t_R$  = 9.55 min (major),  $t_R$  = 19.78 min (minor); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.42 (d,  $J$  = 7.6 Hz, 1H), 7.89 (dd,  $J$  = 8.4, 1.2 Hz, 2H), 7.68 (d,  $J$  = 7.6 Hz, 1H), 7.62–7.53 (m, 3H), 7.43–7.34 (m, 6H), 7.33–7.25 (m, 4H), 7.23 (d,  $J$  = 1.2 Hz, 1H), 7.17 (d,  $J$  = 8.8 Hz, 1H), 7.02 (t,  $J$  = 7.6 Hz, 1H), 6.96 (s, 1H), 4.35 (s, 1H), 2.51 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 179.0, 170.1, 148.1, 144.0, 140.1, 138.1, 135.1, 133.1, 132.8, 131.2, 131.1, 129.6, 129.1, 128.8, 128.24, 128.22, 128.1, 127.7, 127.3, 126.9, 126.8 (q,  $J$  = 2.4 Hz), 126.6, 126.0, 125.0 (q,  $J$  = 283.5 Hz), 124.6, 123.4, 116.7, 113.1, 112.7, 98.8, 67.8 (q,  $J$  = 25.8 Hz), 67.4, 21.6; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) –61.5; HRMS (ESI-TOF)  $m/z$ : [M + Na]<sup>+</sup> Calcd for C<sub>37</sub>H<sub>25</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub>SNa<sup>+</sup> 657.1430; Found 657.1427.

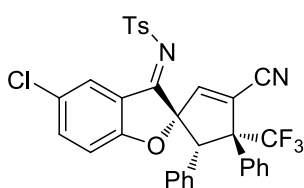
**Synthesis of *ent*-7n:** To a mixture of 4-methyl-*N*-((*Z*)-2-(naphthalen-2-ylmethylene)benzofuran-3(*2H*)-ylidene)benzenesulfonamide **6g** (42.6 mg, 0.1 mmol, 1.0 equiv), **C2** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1a** (49.1 mg, 0.15 mmol, 1.5 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion,

the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give the product **ent-7n**: 52.7 mg (0.0830 mmol), as a white solid, 83% yield;  $[\alpha]_{\text{D}}^{25} = -320.3$  ( $c = 0.70$  in  $\text{CHCl}_3$ ); >19:1 dr; 99% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 9.13$  min (minor),  $t_{\text{R}} = 18.80$  min (major).



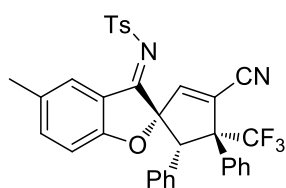
**Synthesis of 7o:** To a mixture of 4-methyl-*N*-((*Z*)-2-(thiophen-2-ylmethylene)benzofuran-3(2*H*)-ylidene)benzenesulfonamide **6h** (38.2 mg, 0.100 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv) in two potions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was

monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give the product **7o**: 52.0 mg (0.0880 mmol), as a white solid, 88% yield; mp = 99–101 °C;  $[\alpha]_{\text{D}}^{25} = +143.2$  ( $c = 0.50$  in  $\text{CHCl}_3$ ); >19:1 dr; >99% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 7.78$  min (major),  $t_{\text{R}} = 13.13$  min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.51 (d,  $J = 8.0$  Hz, 1H), 7.87 (dd,  $J = 8.4, 2.0$  Hz, 2H), 7.69 (t,  $J = 7.6$  Hz, 1H), 7.43–7.35 (m, 3H), 7.36–7.24 (m, 4H), 7.22 (d,  $J = 8.4$  Hz, 1H), 7.18–7.11 (m, 2H), 6.90 (d,  $J = 2.0$  Hz, 1H), 6.83–6.77 (m, 1H), 6.72–6.68 (m, 1H), 4.59 (s, 1H), 2.51 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 178.8, 170.3, 147.4, 144.0, 140.2, 138.0, 134.6, 131.1, 129.8, 129.5, 129.2, 128.93, 128.90, 127.5, 126.89, 126.86, 126.5, 124.8 (q,  $J = 283.4$  Hz), 124.5, 123.5, 116.7, 113.3, 112.8, 97.9, 67.7 (q,  $J = 25.3$  Hz), 62.2, 21.6;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –62.8; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{31}\text{H}_{21}\text{F}_3\text{N}_2\text{O}_3\text{S}_2\text{Na}^+$  613.0838; Found 613.0838.



**Synthesis of 7p:** To a mixture of *N*-((*Z*)-2-benzylidene-5-chlorobenzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **6i** (41.0 mg, 0.100 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv) in two potions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/10) to give the product **7b**: 58.0 mg (0.0937 mmol), as a white solid, 94% yield; mp = 263–264 °C;  $[\alpha]_{\text{D}}^{25} = +227.2$  ( $c = 0.72$  in  $\text{CHCl}_3$ ); >19:1 dr; 96% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 6.82$  min (major),  $t_{\text{R}} = 8.31$  min (minor);  $^1\text{H NMR}$

(400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.49 (d,  $J = 8.0$  Hz, 1H), 7.86 (d,  $J = 8.0$  Hz, 2H), 7.66 (ddd,  $J = 8.8, 7.2, 1.6$  Hz, 1H), 7.42–7.34 (m, 3H), 7.33–7.23 (m, 4H), 7.21–7.07 (m, 4H), 7.03 (t,  $J = 8.0$  Hz, 1H), 6.91 (s, 1H), 6.87 (d,  $J = 8.0$  Hz, 1H), 4.12 (s, 1H), 2.51 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 178.5, 169.9, 147.8, 144.1, 140.3, 137.8, 134.6, 134.0, 131.04, 131.00, 129.6, 129.42, 129.39, 129.2, 129.1, 129.0, 126.9, 126.7, 124.8 (q,  $J = 283.7$  Hz), 124.5, 123.6, 116.6, 112.8, 98.3, 67.9 (q,  $J = 25.8$  Hz), 66.5, 21.6; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) –61.6; HRMS (ESI-TOF)  $m/z$ : [M + Na]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>22</sub><sup>35</sup>ClF<sub>3</sub>N<sub>2</sub>O<sub>3</sub>SNa<sup>+</sup> 641.0884; Found 641.0880; Calcd for C<sub>33</sub>H<sub>22</sub><sup>37</sup>ClF<sub>3</sub>N<sub>2</sub>O<sub>3</sub>SNa<sup>+</sup> 643.0854; Found 643.0862.



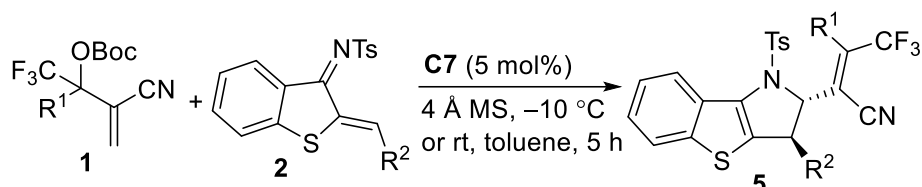
**Synthesis of 7q:** To a mixture of *N*-((*Z*)-2-benzylidene-5-methyl benzofuran-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **6j** (38.9 mg, 0.100 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenyl but-3-en-2-yl)carbonate **1a** (65.5 mg, 0.200 mmol, 2.0 equiv) in two potions

(generally at 0 h, 18 h, 36 h, respectively). The mixture was stirred at 40 °C for 60 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10 to 1/5) to give the product **7q**: 55.0 mg (0.0918 mmol), as a yellow solid, 92% yield; mp = 258–260 °C;  $[\alpha]_D^{25} = +195.2$  ( $c = 0.50$  in CHCl<sub>3</sub>); >19:1 dr; >99% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 7.17$  min (major),  $t_R = 12.46$  min (minor); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.22 (s, 1H), 7.87 (d,  $J = 8.4$  Hz, 2H), 7.45 (dd,  $J = 8.4, 2.0$  Hz, 1H), 7.41–7.34 (m, 3H), 7.31–7.23 (m, 4H), 7.21–7.14 (m, 1H), 7.14–7.01 (m, 5H), 6.90 (s, 1H), 4.18 (s, 1H), 2.52 (s, 3H), 2.31 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 179.2, 168.7, 148.2, 143.9, 141.7, 138.2, 135.1, 133.3, 131.2, 130.0, 129.5, 129.09, 129.06, 128.8, 128.7, 128.2, 126.83, 126.77 (q,  $J = 2.8$  Hz), 125.0 (q,  $J = 283.5$  Hz), 124.4, 116.6, 113.1, 112.5, 98.8, 67.9 (q,  $J = 25.7$  Hz), 67.2, 21.6, 20.8; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) –61.7; HRMS (ESI-TOF)  $m/z$ : [M + Na]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>25</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub>SNa<sup>+</sup> 621.1430; Found 621.1432.

**Synthesis of *ent*-7q:** To a mixture of *N*-((*Z*)-2-benzylidene-5-methylbenzo furan-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **6j** (38.9 mg, 0.100 mmol, 1.0 equiv), **C2** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1a** (65.5 mg, 0.200 mmol, 2.0 equiv) in two potions (generally at 0 h, 18 h, 36 h, respectively). The mixture was stirred at 40 °C for 60 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10 to 1/5) to give the product *ent*-**7q**: 48.5 mg (0.0810 mmol), as a yellow solid, 81% yield;  $[\alpha]_D^{25} = -192.0$  ( $c = 0.75$  in CHCl<sub>3</sub>); >19:1 dr; 99% ee, determined by HPLC

analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 7.84$  min (minor),  $t_R = 13.24$  min (major).

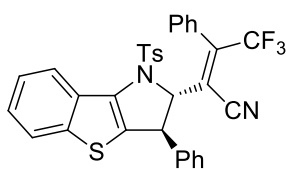
#### 4.3 General procedure for catalyst-controlled $\alpha$ -[4+1] annulations of MBH carbonates **1** with 1-azadienes **2**



**Synthesis of 5:** A mixture of MBH carbonate **1** (0.15 mmol, 1.5 equiv), 1-azadiene **2** (0.1 mmol, 1.0 equiv), **C7** (1.5 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at  $-10$  °C or rt for 5 h, and the reaction was monitored by TLC. After completion, the product **5** was obtained after the purification by flash chromatography on silica gel (EtOAc/petroleum ether).

**Synthesis of *ent*-5:** To a mixture of 1-azadiene **2** (0.1 mmol, 1.0 equiv) and **C6** (8.6 mg, 10 mol%) in PhCF<sub>3</sub> (1.0 mL) was added MBH carbonate **1** (0.20 mmol, 2.0 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36–48 h, and the reaction was monitored by TLC. After completion, the product *ent*-**5** was obtained after the purification by flash chromatography on silica gel (EtOAc/petroleum ether).

**Synthesis of racemic products 5:** The racemic products **5** were obtained under the catalysis of DABCO.



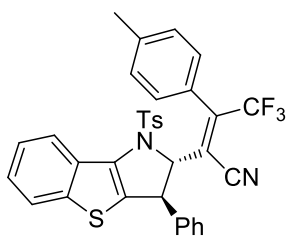
**Synthesis of 5a:** A mixture of *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv), *N*-((*Z*)-2-benzylidenebenzo[*b*]thiophen-3(2*H*)-ylidene)-4-methylbenzene sulfonamide **2a** (39.1 mg, 0.0997 mmol, 1.0 equiv), **C7** (1.5 mg, 5 mol%)

and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at  $-10$  °C for 5 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/20) to give the product **5a**: 51.4 mg (0.0855 mmol), as a white solid, 86% yield; mp = 195–197 °C;  $[\alpha]_D^{25} = +119.4$  ( $c = 0.69$  in CHCl<sub>3</sub>); >19:1 dr; 97% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 7.54$  min (minor),  $t_R = 8.69$  min (major); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.70 (d,  $J = 8.4$  Hz, 1H), 7.72–7.66 (m, 1H), 7.65–7.62 (br, 2H), 7.48 (ddd,  $J = 8.4, 7.2, 1.2$  Hz, 1H), 7.45–7.33 (m, 2H), 7.27–7.20 (m, 1H), 7.06–6.98 (m, 2H), 6.91 (d,  $J = 8.0$  Hz, 2H), 6.82 (br, 1H), 6.69–6.61 (m, 2H), 6.31 (br, 1H), 6.24–6.13 (m, 2H), 4.63 (d,  $J = 5.2$  Hz, 1H), 4.47 (d,  $J = 5.6$  Hz, 1H), 2.35 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 144.6 (q,  $J = 31.6$  Hz), 144.5, 144.2,



138.8, 138.0, 131.1, 130.6, 129.82, 129.80, 129.7, 129.0, 128.8, 128.4, 128.14 (2C), 128.11, 127.8, 125.4, 125.1, 124.2, 123.7, 121.3 (q,  $J = 274.9$  Hz), 119.5 (q,  $J = 3.0$  Hz), 112.9, 75.1, 51.7, 21.5;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm)  $-61.9$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{33}\text{H}_{23}\text{F}_3\text{N}_2\text{O}_2\text{S}_2\text{Na}^+$  623.1045; Found 623.1041.

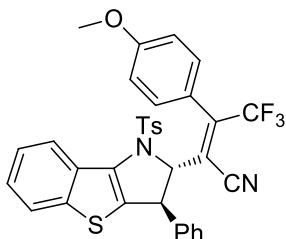
**Synthesis of *ent*-5a:** To a mixture of *N*-((*Z*)-2-benzylidenebenzo[*b*]thiophen-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **2a** (39.1 mg, 0.0997 mmol, 1.0 equiv) and **C6** (8.6 mg, 10 mol%) in  $\text{PhCF}_3$  (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (65.4 mg, 0.200 mmol, 2.0 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/20) to give the product *ent*-5a: 36.0 mg (0.0599 mmol), as a white solid, 60% yield;  $[\alpha]_{\text{D}}^{25} = -127.7$  ( $c = 0.70$  in  $\text{CHCl}_3$ ); >19:1 dr; 97% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $l = 254$  nm)  $t_{\text{R}} = 7.51$  min (major),  $t_{\text{R}} = 8.66$  min (minor).



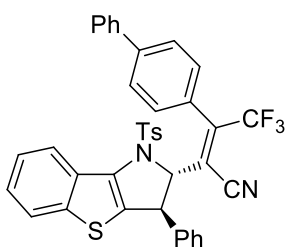
**Synthesis of 5b:** A solution of *tert*-butyl (3-cyano-1,1,1-trifluoro-2-(*p*-tolyl)but-3-en-2-yl)carbonate **1c** (51.2 mg, 0.150 mmol, 1.5 equiv), *N*-((*Z*)-2-benzylidenebenzo[*b*]thiophen-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **2a** (39.1 mg, 0.0997 mmol, 1.0 equiv), **C7** (1.5 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at  $-10$  °C for 5 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/20) to give the product **5b**: 49.6 mg (0.0807 mmol), as a white solid, 81% yield; mp = 155–156 °C;  $[\alpha]_{\text{D}}^{25} = +77.1$  ( $c = 0.68$  in  $\text{CHCl}_3$ ); >19:1 dr; 94% ee, determined by HPLC analysis (Daicel Chiralpak IA, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min,  $l = 254$  nm)  $t_{\text{R}} = 6.10$  min (minor),  $t_{\text{R}} = 16.59$  min (major);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.69 (d,  $J = 8.4$  Hz, 1H), 7.69 (d,  $J = 8.0$  Hz, 1H), 7.48 (t,  $J = 7.6$  Hz, 1H), 7.37 (t,  $J = 7.6$  Hz, 1H), 7.31–7.20 (m, 1H), 7.11 (br, 4H); 7.03 (t,  $J = 7.6$  Hz, 2H), 6.89 (d,  $J = 7.6$  Hz, 2H), 6.65 (d,  $J = 8.0$  Hz, 2H), 6.20 (d,  $J = 7.6$  Hz, 2H), 4.67 (d,  $J = 5.6$  Hz, 1H), 4.47 (d,  $J = 5.6$  Hz, 1H), 2.38 (s, 3H); 2.37 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 144.9 (q,  $J = 31.5$  Hz), 144.5, 144.2, 140.2, 138.8, 138.0, 131.1, 130.6, 129.7, 129.6, 128.7, 128.6, 128.5, 128.2, 128.1, 127.8, 126.2, 125.3, 125.1, 124.2, 123.7, 121.4 (q,  $J = 275.5$  Hz), 119.1 (q,  $J = 2.6$  Hz), 113.0, 75.1, 51.7, 21.5, 21.3;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm)  $-61.9$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{34}\text{H}_{26}\text{F}_3\text{N}_2\text{O}_2\text{S}_2^+$  637.1202; Found 637.1205.

**Synthesis of *ent*-5b:** To a mixture of *N*-((*Z*)-2-benzylidenebenzo[*b*]thiophen-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **2a** (39.1 mg, 0.0997 mmol, 1.0 equiv) and **C6** (8.6 mg, 10 mol%) in  $\text{PhCF}_3$  (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-(*p*-tolyl)but-3-en-2-yl)carbonate **1c**

(68.2 mg, 0.200 mmol, 2.0 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 48 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/20) to give the product **ent-5b**: 31.5 mg (0.0512 mmol), as a white solid, 51% yield;  $[\alpha]_D^{25} = -71.0$  ( $c = 0.20$  in  $\text{CHCl}_3$ ); >19:1 dr; 97% ee, determined by HPLC analysis (Daicel Chiralpak IA, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 6.05$  min (major),  $t_R = 16.10$  min (minor).

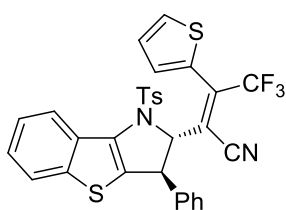


**Synthesis of 5c:** A mixture of *tert*-butyl (3-cyano-1,1,1-trifluoro-2-(4-methoxyphenyl)but-3-en-2-yl)carbonate **1d** (53.6 mg, 0.150 mmol, 1.5 equiv), *N*-((*Z*)-2-benzylidenebenzo[*b*]thiophen-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **2a** (39.1 mg, 0.0997 mmol, 1.0 equiv), **C7** (1.5 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at rt for 5 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/10) to give the product **5c**: 53.5 mg (0.0845 mmol), as a yellow solid, 85% yield; mp = 101–102 °C;  $[\alpha]_D^{25} = +46.2$  ( $c = 0.55$  in  $\text{CHCl}_3$ ); >19:1 dr; 88% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 9.52$  min (minor),  $t_R = 10.36$  min (major);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.70 (d,  $J = 8.0$  Hz, 1H), 7.68 (d,  $J = 8.0$  Hz, 1H), 7.48 (t,  $J = 7.6$  Hz, 1H), 7.36 (t,  $J = 7.6$  Hz, 1H), 7.30–7.20 (m, 1H), 7.03 (t,  $J = 7.6$  Hz, 2H), 6.92 (d,  $J = 8.0$  Hz, 2H), 6.87–6.74 (br, 2H), 6.70 (d,  $J = 8.0$  Hz, 2H), 6.66–6.37 (br, 2H), 6.21 (d,  $J = 7.6$  Hz, 2H), 4.69 (d,  $J = 5.6$  Hz, 1H), 4.47 (d,  $J = 5.6$  Hz, 1H), 3.81 (s, 3H), 2.37 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 160.9, 144.7 (q,  $J = 31.6$  Hz), 144.6, 144.2, 138.9, 137.9, 131.2, 131.1, 130.6, 129.8, 128.8, 128.4, 128.2, 128.1, 127.8, 125.3, 125.1, 124.2, 123.7, 121.4 (q,  $J = 275.1$  Hz), 121.1, 119.0, 113.4, 113.1, 75.2, 55.5, 51.7, 21.5;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –62.0; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{34}\text{H}_{26}\text{F}_3\text{N}_2\text{O}_3\text{S}_2^+$  631.1331; Found 631.1333.



**Synthesis of 5d:** A mixture of 2-([1,1'-biphenyl]-4-yl)-3-cyano-1,1,1-trifluorobut-3-en-2-yl *tert*-butyl carbonate **1e** (60.5 mg, 0.150 mmol, 1.5 equiv), *N*-((*Z*)-2-benzylidenebenzo[*b*]thiophen-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **2a** (39.1 mg, 0.0997 mmol, 1.0 equiv), **C7** (1.5 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at –10 °C for 5 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/10) to give the product **5d**: 54.6 mg (0.0806 mmol), as a yellow solid, 81% yield; mp = 188–189 °C;  $[\alpha]_D^{25} = +24.8$  ( $c = 0.58$  in  $\text{CHCl}_3$ ); >19:1 dr; 93% ee, determined by HPLC analysis (Daicel Chiralpak

IA, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, *l* = 254 nm)  $t_R$  = 9.01 min (minor),  $t_R$  = 25.08 min (major);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.71 (d,  $J$  = 8.4 Hz, 1H), 7.69 (d,  $J$  = 8.0 Hz, 1H), 7.64 (br, 1H), 7.62–7.41 (m, 9H), 7.41–7.33 (m, 1H), 7.31–7.23 (m, 1H), 7.09–7.00 (m, 2H), 6.82 (d,  $J$  = 8.0 Hz, 2H), 6.69 (d,  $J$  = 8.0 Hz, 2H), 6.29–6.17 (m, 2H), 4.67 (d,  $J$  = 5.6 Hz, 1H), 4.50 (d,  $J$  = 5.6 Hz, 1H), 2.28 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 144.55, 144.53 (q,  $J$  = 31.7 Hz), 144.3, 143.0, 139.7, 138.9, 138.0, 131.1, 130.6, 130.3, 129.8, 129.1, 128.8, 128.5, 128.23, 128.20 (2C), 127.9, 127.0, 126.60, 126.55, 125.4, 125.2, 124.2, 123.7, 121.3 (d,  $J$  = 274.8 Hz), 119.59 (d,  $J$  = 3.1 Hz), 112.9, 75.2, 51.8, 21.5;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –61.8; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{39}\text{H}_{28}\text{F}_3\text{N}_2\text{O}_2\text{S}_2^+$  677.1539; Found 677.1540.

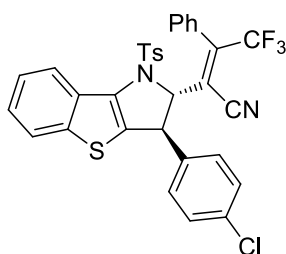


**Synthesis of 5e:** A mixture of *tert*-butyl (3-cyano-1,1,1-trifluoro-2-(thiophen-2-yl)but-3-en-2-yl)carbonate **1g** (50.0 mg, 0.150 mmol, 1.5 equiv), *N*-((*Z*)-2-benzylidenebenzo[*b*]thiophen-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2a** (39.1 mg, 0.0997 mmol, 1.0 equiv), **C7** (1.5 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at rt for 5 h,

and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/20) to give the product **5e**: 41.0 mg (0.0675 mmol), as a yellow solid, 68% yield; mp = 235–237 °C;  $[\alpha]_D^{25}$  = +104.3 ( $c$  = 1.12 in  $\text{CHCl}_3$ ); >19:1 dr; 93% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, *l* = 254 nm)  $t_R$  = 7.52 min (minor),  $t_R$  = 8.69 min (major);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.70 (d,  $J$  = 8.0 Hz, 1H), 7.69 (d,  $J$  = 8.0 Hz, 1H), 7.66–7.52 (br, 2H), 7.49 (t,  $J$  = 7.8 Hz, 1H), 7.44–7.33 (m, 2H), 7.29–7.20 (m, 1H), 7.06–7.98 (m, 2H), 6.91 (d,  $J$  = 8.0 Hz, 2H), 6.65 (d,  $J$  = 8.0 Hz, 2H), 6.19 (d,  $J$  = 7.6 Hz, 2H), 4.63 (d,  $J$  = 5.2 Hz, 1H), 4.47 (d,  $J$  = 5.6 Hz, 1H), 2.36 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 144.6 (q,  $J$  = 31.7 Hz), 144.5, 144.2, 138.8, 138.0, 131.1, 130.5, 129.82, 129.80, 129.7, 129.0, 128.8, 128.4, 128.2, 128.14, 128.12, 127.8, 125.4, 125.1, 124.2, 123.7, 121.3 (q,  $J$  = 275.0 Hz), 119.49 (q,  $J$  = 3.0 Hz), 112.9, 75.1, 51.7, 21.5;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –61.9; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{31}\text{H}_{22}\text{F}_3\text{N}_2\text{O}_2\text{S}_3^+$  607.0790; Found 607.0785.

**Synthesis of *ent*-5e:** To a mixture of *N*-((*Z*)-2-benzylidenebenzo[*b*]thiophen-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2a** (39.1 mg, 0.0997 mmol, 1.0 equiv) and **C6** (8.6 mg, 10 mol%) in  $\text{PhCF}_3$  (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-(thiophen-2-yl)but-3-en-2-yl)carbonate **1g** (66.6 mg, 0.200 mmol, 2.0 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/20) to give the product *ent*-**5e**: 32.0 mg (0.0527 mmol), as a yellow solid, 53% yield;  $[\alpha]_D^{25}$  =

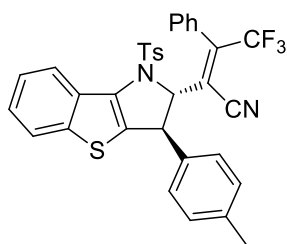
-92.4 ( $c = 0.37$  in  $\text{CHCl}_3$ ); >19:1 dr; >99% ee, determined by HPLC analysis (Daicel Chiralpak ID,  $n$ -hexane/ $i$ -PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 7.50$  min (major),  $t_{\text{R}} = 8.71$  min (minor).



**Synthesis of 5f:** A mixture of *tert*-butyl(3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv), *N*-((*Z*)-2-(4-chlorobenzylidene)benzo[*b*]thiophen-3(*2H*)-ylidene)-4-methylbenzene sulfonamide **2b** (42.6 mg, 0.100 mmol, 1.0 equiv), **C7** (1.5 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at -10 °C for 5 h, and the reaction was monitored by TLC. After completion, the crude product was

purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/20) to give the product **5f**: 50.2 mg (0.0791 mmol), as a yellow solid, 79% yield; mp = 173–174 °C;  $[\alpha]_{\text{D}}^{25} = +100.6$  ( $c = 0.65$  in  $\text{CHCl}_3$ ); >19:1 dr; 97% ee, determined by HPLC analysis (Daicel Chiralpak ID,  $n$ -hexane/ $i$ -PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 6.74$  min (minor),  $t_{\text{R}} = 7.72$  min (major);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.69 (d,  $J = 8.0$  Hz, 1H), 7.70 (d,  $J = 8.0$  Hz, 1H), 7.67–7.52 (br, 2H), 7.52–7.45 (m, 2H), 7.42–7.34 (m, 1H), 6.99 (br, 1H), 6.97–6.93 (m, 2H), 6.92 (d,  $J = 8.0$  Hz, 2H), 6.70 (d,  $J = 8.0$  Hz, 2H), 6.45 (br, 1H), 6.21–6.03 (m, 2H), 4.65 (d,  $J = 5.2$  Hz, 1H), 4.42 (d,  $J = 4.8$  Hz, 1H), 2.36 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 144.8, 144.7 (q,  $J = 31.9$  Hz), 144.3, 138.3, 137.4, 134.0, 130.9, 130.3, 130.1, 129.8, 129.6, 129.0, 128.9, 128.8, 128.4, 128.2, 128.0, 125.5, 125.4, 124.3, 123.7, 121.2 (q,  $J = 275.0$  Hz), 119.6 (q,  $J = 3.1$  Hz), 112.7, 75.0, 51.0, 21.5;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) -62.0; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{33}\text{H}_{23}^{35}\text{ClF}_3\text{N}_2\text{O}_2\text{S}_2^+$  635.0836; Found 635.0837; Calcd for  $\text{C}_{33}\text{H}_{23}^{37}\text{ClF}_3\text{N}_2\text{O}_2\text{S}_2^+$  637.0807; Found 637.0837.

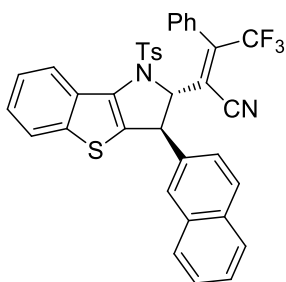
**Synthesis of ent-5f** To a mixture of *N*-((*Z*)-2-(4-chlorobenzylidene)benzo[*b*]thiophen-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **2b** (42.6 mg, 0.1 mmol, 1.0 equiv) and **C6** (8.6 mg, 10 mol%) in  $\text{PhCF}_3$  (1.0 mL) was added *tert*-butyl(3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (65.4 mg, 0.200 mmol, 2.0 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/20) to give the product **ent-5f**: 35.0 mg (0.0551 mmol), as a yellow solid, 55% yield;  $[\alpha]_{\text{D}}^{25} = -101.0$  ( $c = 0.40$  in  $\text{CHCl}_3$ ); >19:1 dr; 97% ee, determined by HPLC analysis (Daicel Chiralpak ID,  $n$ -hexane/ $i$ -PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 6.75$  min (major),  $t_{\text{R}} = 7.75$  min (minor).



**Synthesis of 5g:** A solution of *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv), 4-methyl-*N*-((*Z*)-2-(4-methylbenzylidene)benzo[*b*]thiophen-3(2*H*)-ylidene)benzenesulfonamide **2d** (40.6 mg, 0.100 mmol, 1.0 equiv), **C7** (1.5 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at  $-10\text{ }^{\circ}\text{C}$  for 5 h, and the reaction was monitored by TLC. After completion, the crude

product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) to give the product **5g**: 49.0 mg (0.0797 mmol), as a yellow solid, 80% yield; mp = 209–210  $^{\circ}\text{C}$ ;  $[\alpha]_{\text{D}}^{25} = +104.0$  ( $c = 0.40$  in  $\text{CHCl}_3$ ); >19:1 dr; 96% ee, determined by HPLC analysis (Daicel Chiralpak IA, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254\text{ nm}$ )  $t_{\text{R}} = 5.71\text{ min}$  (minor),  $t_{\text{R}} = 18.87\text{ min}$  (major);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.69 (d,  $J = 8.0\text{ Hz}$ , 1H), 7.68 (d,  $J = 8.0\text{ Hz}$ , 1H), 7.66–7.51 (br, 2H), 7.51–7.39 (m, 2H), 7.39–7.32 (m, 1H), 6.91 (d,  $J = 8.4\text{ Hz}$ , 2H), 6.85 (br, 1H), 6.83 (d,  $J = 8.0\text{ Hz}$ , 2H), 6.68–6.60 (m, 2H), 6.28 (br, 1H), 6.12–6.04 (m, 2H), 4.62 (d,  $J = 6.0\text{ Hz}$ , 1H), 4.44 (d,  $J = 5.6\text{ Hz}$ , 1H), 2.35 (s, 3H), 2.33 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 144.6 (q,  $J = 31.6\text{ Hz}$ ), 144.5, 144.2, 138.0, 137.7, 135.7, 131.4, 130.5, 129.8, 129.7, 129.4, 129.0, 128.5, 128.12, 128.11, 128.0, 127.7, 125.3, 125.1, 124.1, 123.7, 121.3 (q,  $J = 274.9\text{ Hz}$ ), 119.54 (q,  $J = 3.0\text{ Hz}$ ), 112.93 (q,  $J = 1.5\text{ Hz}$ ), 75.1, 51.4, 21.5, 21.1;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm)  $-61.9$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{34}\text{H}_{26}\text{F}_3\text{N}_2\text{O}_2\text{S}_2^+$  615.1382; Found 615.1378.

**Synthesis of *ent*-5g:** To a mixture of 4-methyl-*N*-((*Z*)-2-(4-methylbenzylidene)benzo[*b*]thiophen-3(2*H*)-ylidene)benzenesulfonamide **2d** (40.6 mg, 0.100 mmol, 1.0 equiv) and **C6** (8.6 mg, 10 mol%) in  $\text{PhCF}_3$  (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (65.4 mg, 0.200 mmol, 2.0 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at  $40\text{ }^{\circ}\text{C}$  for 48 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) to give the product *ent*-**5g**: 35.0 mg (0.0569 mmol), as a yellow solid, 57% yield;  $[\alpha]_{\text{D}}^{25} = -102.5$  ( $c = 0.24$  in  $\text{CHCl}_3$ ); >19:1 dr; >99% ee, determined by HPLC analysis (Daicel Chiralpak IA, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254\text{ nm}$ )  $t_{\text{R}} = 5.75\text{ min}$  (major),  $t_{\text{R}} = 18.39\text{ min}$  (minor).



**Synthesis of 5h:** A mixture of *tert*-butyl(3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv), 4-methyl-*N*-((*Z*)-2-(naphthalen-2-ylmethylene)benzo[*b*]thiophen-3(2*H*)-ylidene)benzenesulfonamide **2f** (44.2 mg, 0.100 mol, 1.0 equiv), **C7** (1.5 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at  $-10\text{ }^{\circ}\text{C}$  for 5 h, and the reaction was monitored by TLC. After completion, the crude product was

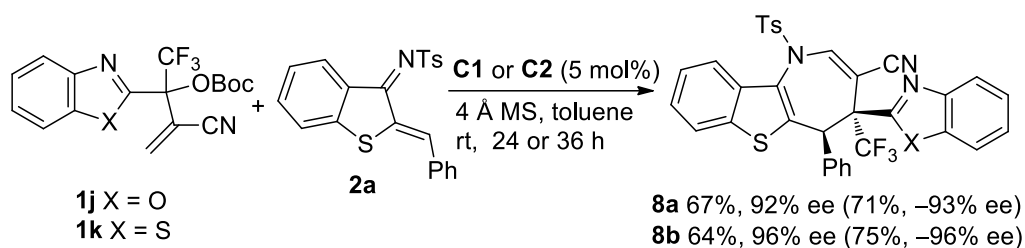
purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/20) to give the

product **5h**: 44.5 mg (0.0684 mmol), as a yellow solid, 68% yield; mp = 192–193 °C;  $[\alpha]_{\text{D}}^{25} = +83.5$  ( $c = 0.51$  in  $\text{CHCl}_3$ ); >19:1 dr; 98% ee, determined by HPLC analysis (Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 8.52$  min (major),  $t_{\text{R}} = 10.92$  min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.73 (d,  $J = 8.4$  Hz, 1H), 7.82–7.75 (m, 1H), 7.70 (d,  $J = 8.0$  Hz, 1H), 7.67–7.58 (br, 1H), 7.57–7.47 (m, 5H), 7.43–7.35 (m, 2H), 7.32–7.26 (m, 1H), 7.02 (d,  $J = 2.0$  Hz, 1H), 6.87 (d,  $J = 8.0$  Hz, 2H), 6.75–6.68 (m, 2H), 6.34 (br, 2H), 6.01 (dd,  $J = 8.4, 2.0$  Hz, 1H), 4.82 (d,  $J = 5.6$  Hz, 1H), 4.65 (d,  $J = 5.2$  Hz, 1H), 2.30 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 144.7 (q,  $J = 31.8$  Hz), 144.6, 144.3, 138.1, 135.8, 132.9, 132.7, 130.9, 129.8 (2C), 129.6, 129.04, 128.98, 128.8, 128.6, 128.1 (2C), 127.8, 127.6, 127.1, 126.7, 126.6, 125.4, 125.2, 124.7, 124.3, 123.7, 121.3 (q,  $J = 275.1$  Hz), 119.8 (q,  $J = 3.0$  Hz), 112.9, 74.9, 51.9, 21.5;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –61.9; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{37}\text{H}_{26}\text{F}_3\text{N}_2\text{O}_2\text{S}_2^+$  651.1382; Found 651.1382.

**Synthesis of ent-5h**: To a mixture of 4-methyl-*N*-((*Z*)-2-(naphthalen-2-ylmethylene)benzo[*b*]thiophen-3(*2H*)-ylidene)benzenesulfonamide **2f** (44.2 mg, 0.100 mmol, 1.0 equiv) and **C6** (8.6 mg, 10 mol%) in  $\text{PhCF}_3$  (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1a** (65.4 mg, 0.200 mmol, 2.0 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/20) to give the product **ent-5h**: 30.0 mg (0.0461 mmol), as a yellow solid, 46% yield;  $[\alpha]_{\text{D}}^{25} = -74.0$  ( $c = 0.30$  in  $\text{CHCl}_3$ ); >19:1 dr; 93% ee, determined by HPLC analysis (Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 8.61$  min (minor),  $t_{\text{R}} = 10.60$  min (major).

#### 4.4 General procedure for substrate-controlled $\gamma$ -[4+3] annulations of MBH carbonates **1** with 1-azadiene **2a**

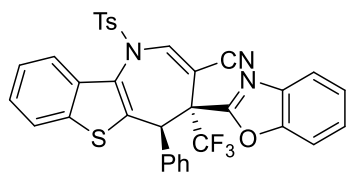
In the further exploration of the substrate scope, it was found that the  $\gamma$ -regioselective [4+3] version proceeded well by using MBH carbonate **1j** with a benzoxazole motif, and the product **8a** was isolated in 71% yield with 93% ee under the catalysis of **C1**. Interestingly, different diastereoselectivity was observed in comparison with the [3+2] product **3**, probably because of the steric and electronic effects of the heteroaryl group in both addition and cyclization step. Furthermore, the MBH carbonate **1k** having a benzothiazole motif gave the [4+3] product **8b** similarly. In addition, the corresponding enantiomers of **8a** and **8b** were obtained in good results with amine **C2**.<sup>4</sup>



**Synthesis of **8**:** A mixture of MBH carbonate **1** (0.15 mmol, 1.5 equiv), 1-azadiene **2a** (0.10 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at rt for 24 or 36 h, and the reaction was monitored by TLC. After completion, the product **8** was obtained after the purification by flash chromatography on silica gel (EtOAc/petroleum ether).

**Synthesis of *ent*-**8**:** A mixture of MBH carbonate **1** (0.15 mmol, 1.5 equiv), 1-azadiene **2a** (0.10 mmol, 1.0 equiv), **C2** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at rt for 24 or 36 h, and the reaction was monitored by TLC. After completion, the product *ent*-**8** was obtained after the purification by flash chromatography on silica gel (EtOAc/petroleum ether).

**Synthesis of racemic products **8**:** The racemic products **8** were obtained under the catalysis of DABCO.

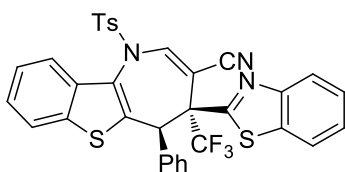


**Synthesis of **8a**:** A mixture of 2-(benzo[*d*]oxazol-2-yl)-3-cyano-1,1,1-trifluorobut-3-en-2-yl *tert*-butyl carbonate **1j** (55.2 mg, 0.150 mmol, 1.5 equiv), *N*-((*Z*)-2-benzylidenebenzo[*b*]thiophen-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **2a** (39.1 mg, 0.0997 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred

at rt for 36 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/10) to give the product **8a**: 43.2 mg (0.0673 mmol), as a white solid, 67% yield; mp = 238–240 °C;  $[\alpha]_{\text{D}}^{25} = -466.7$  ( $c = 0.30$  in  $\text{CHCl}_3$ ); >19:1 dr; 92% ee, determined by HPLC analysis (Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 10.02$  min (minor),  $t_{\text{R}} = 10.74$  min (major);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.19 (s, 1H), 8.16 (d,  $J = 8.0$  Hz, 1H), 7.78 (d,  $J = 8.0$  Hz, 2H), 7.74–7.64 (m, 1H), 7.56–7.45 (m, 4H), 7.41–7.28 (m, 4H), 7.27–7.17 (m, 3H), 7.15–6.72 (m, 1H), 6.12 (br, 1H), 4.16 (s, 1H), 2.62 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 156.7, 150.4, 146.2, 145.5, 140.0, 138.8, 137.1, 135.2, 134.9, 134.8, 130.6 (2C), 129.0, 128.7, 128.6, 127.7, 126.4, 125.5, 125.2, 125.1, 123.9, 122.9 (q,  $J = 287.6$  Hz), 122.0, 121.1, 116.7, 110.8, 99.7, 56.2 (q,  $J = 24.1$  Hz), 47.3, 21.8;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) -63.3; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{34}\text{H}_{23}\text{F}_3\text{N}_3\text{O}_3\text{S}_2^+$  642.1127; Found 642.1127.

**Synthesis of *ent*-**8a**:** A mixture of 2-(benzo[*d*]oxazol-2-yl)-3-cyano-1,1,1-trifluorobut-3-en-2-yl *tert*-butyl carbonate **1j** (55.2 mg, 0.150 mmol, 1.5 equiv), *N*-((*Z*)-2-benzylidenebenzo[*b*]thiophen-3(*2H*)-

ylidene)-4-methylbenzenesulfonamide **2a** (39.1 mg, 0.0997 mmol, 1.0 equiv), **C2** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at rt for 36 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/10) to give the product **ent-8a**: 45.5 mg (0.0709 mmol), as a white solid, 71% yield;  $[\alpha]_{\text{D}}^{25} = +465.3$  ( $c = 0.60$  in  $\text{CHCl}_3$ ); >19:1 dr; 93% ee, determined by HPLC analysis (Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 9.95$  min (major),  $t_{\text{R}} = 10.83$  min (minor).



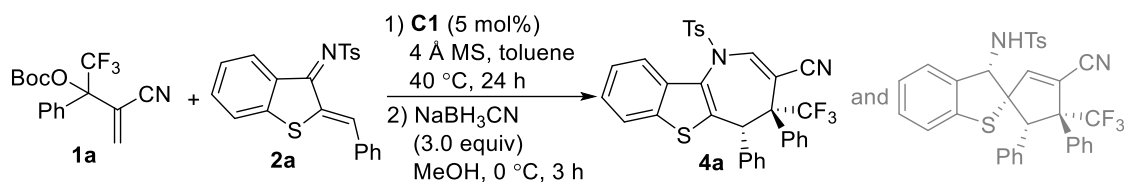
**Synthesis of 8b:** A mixture of 2-(benzo[*d*]thiazol-2-yl)-3-cyano-1,1,1-trifluorobut-3-en-2-yl *tert*-butyl carbonate **1k** (57.6 mg, 0.150 mmol, 1.5 equiv), *N*-((*Z*)-2-benzylidenebenzo[*b*]thiophen-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **2a** (39.1 mg, 0.0997 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred

at rt for 24 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/10) to give the product **8b**: 42.0 mg (0.0638 mmol), as a yellow solid, 64% yield; mp = 239–240 °C;  $[\alpha]_{\text{D}}^{25} = -462.6$  ( $c = 0.70$  in  $\text{CHCl}_3$ ); >19:1 dr; 96% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 16.80$  min (minor),  $t_{\text{R}} = 18.03$  min (major);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.18 (s, 1H), 8.17 (d,  $J = 6.8$  Hz, 1H), 7.97 (d,  $J = 8.0$  Hz, 1H), 7.81–7.74 (m, 2H), 7.71 (d,  $J = 8.0$  Hz, 1H), 7.59–7.43 (m, 5H), 7.43–7.33 (m, 2H), 7.30 (t,  $J = 7.6$  Hz, 1H), 7.24–7.15 (m, 2H), 6.99 (br, 1H), 6.07 (br, 1H), 4.15 (s, 1H), 2.62 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 161.3, 152.3, 146.2, 145.1, 139.4, 137.2, 135.72, 135.69, 134.9, 134.8, 130.7 (2C), 128.8, 128.5, 128.4, 127.7, 126.6, 126.2, 125.6, 125.1, 124.3, 123.9, 123.5 (q,  $J = 285.3$  Hz), 122.1, 121.4, 116.9, 102.0, 59.4 (q,  $J = 22.7$  Hz), 47.6, 21.8;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –62.5; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{34}\text{H}_{23}\text{F}_3\text{N}_3\text{O}_2\text{S}_3^+$  658.0899; Found 658.0898.

**Synthesis of ent-8b:** A mixture of 2-(benzo[*d*]thiazol-2-yl)-3-cyano-1,1,1-trifluorobut-3-en-2-yl *tert*-butyl carbonate **1k** (57.6 mg, 0.150 mmol, 1.5 equiv), *N*-((*Z*)-2-benzylidenebenzo[*b*]thiophen-3(*2H*)-ylidene)-4-methylbenzenesulfonamide **2a** (39.1 mg, 0.0997 mmol, 1.0 equiv), **C2** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at rt for 24 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/10) to give the product **ent-8b**: 49.5 mg (0.0752 mmol), as a yellow solid, 75% yield;  $[\alpha]_{\text{D}}^{25} = +468.4$  ( $c = 0.50$  in  $\text{CHCl}_3$ ); >19:1 dr; 96% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 16.72$  min (major),  $t_{\text{R}} = 19.16$  min (minor).



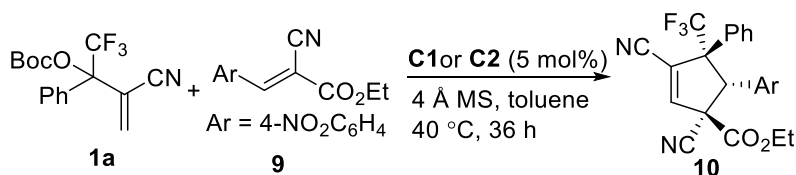
## Separation of [4+3] product **4a**:



A mixture of *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv), *N*-((*Z*)-2-benzylidenebenzo[*b*]thiophen-3(*2H*)-ylidene)-4-methylbenzene sulfonamide **2a** (39.1 mg, 0.0997 mmol, 1.0 equiv), **C1** (1.7 mg, 2 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was stirred at 40 °C for 24 h, and the reaction was monitored by TLC. After completion, the solvent was removed under reduced pressure, and the residue was dissolved in anhydrous MeOH (1.0 mL), and NaBH<sub>3</sub>CN (19.0 mg, 0.302 mmol, 3.0 equiv) was added to reduce [3+2] product **3a**. The solution was stirred at rt for 3 h. After completion, the reaction was quenched with water and extracted with DCM. The combined organic phase was concentrated and purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/10) to give the [4+3] product **4a**: 5.0 mg (0.0083 mmol), as a white solid, 8% yield; mp = 212–213 °C; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = –81.0 (*c* = 0.20 in CHCl<sub>3</sub>); >19:1 dr; 91% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, *l* = 254 nm) *t*<sub>R</sub> = 9.45 min (minor), *t*<sub>R</sub> = 15.54 min (major); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.15 (s, 1H), 8.08 (dd, *J* = 8.8, 1.2 Hz, 1H), 7.79–7.70 (m, 3H), 7.50 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.48–7.37 (m, 3H), 7.31–7.15 (br, 2H), 7.11–7.01 (m, 2H), 6.96 (t, *J* = 7.6 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.53 (br, 2H), 3.70 (d, *J* = 1.6 Hz, 1H), 2.53 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 146.1, 142.8, 138.3, 136.8, 135.2, 135.0, 134.8, 134.6, 130.6, 130.32, 130.31, 128.3, 128.1, 127.9, 127.70, 127.66, 127.5, 125.5, 125.1 (q, *J* = 284.3 Hz), 124.9, 123.8, 122.1, 117.8, 103.8, 59.2 (q, *J* = 23.8 Hz), 53.3, 21.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) –58.8; HRMS (ESI-TOF) *m/z*: [*M* + *H*]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>24</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup> 601.1226; Found 601.1227.

## 5. Asymmetric $\gamma$ -[3+2] annulation of MBH carbonate **1a** with activated alkene **9**

The activated alkene **9** also could be combined with MBH **1a**, and the  $\gamma$ -regioselective cyclopentene product **10** was obtained in a moderate yield with excellent stereoselectivity under the catalysis of amine **C1**. In addition, *ent*-**10** was delivered in similar good results by using amine **C2**.

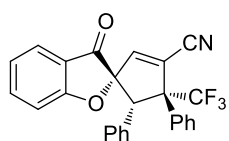
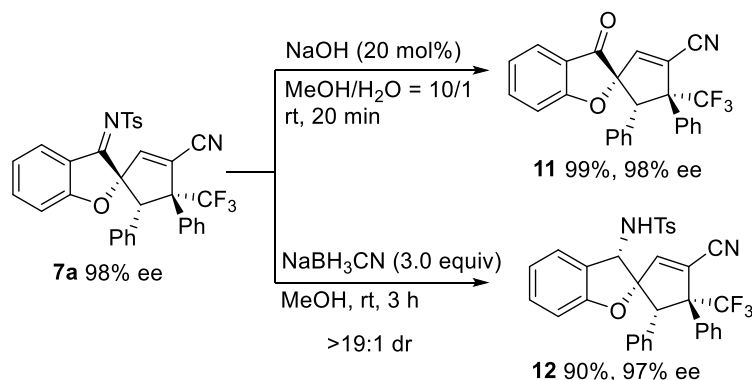


**Synthesis of 10:** To a mixture of (*E*)-ethyl 2-cyano-3-(4-nitrophenyl)acrylate **9** (24.6 mg, 0.100 mmol, 1.0 equiv), **C1** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-

cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10 to 1/5) to give the product **10**: 30.5 mg (0.0670 mmol), as a colorless oil, 67% yield;  $[\alpha]_{\text{D}}^{25} = -29.2$  ( $c = 0.50$  in  $\text{CHCl}_3$ ); >19:1 dr; 99% ee, determined by HPLC analysis (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 7.05$  min (minor),  $t_{\text{R}} = 9.51$  min (major);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.24–8.18 (m, 2H), 7.57 (d,  $J = 8.4$  Hz, 2H), 7.50–7.44 (m, 3H), 7.37–7.31 (m, 2H), 7.21 (s, 1H), 4.53 (s, 1H), 4.19 (q,  $J = 7.1$  Hz, 2H), 1.23 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 164.2, 148.6, 146.1, 137.2, 133.9, 131.7, 129.8, 129.7, 126.8 (q,  $J = 2.2$  Hz), 124.8 (q,  $J = 238.8$  Hz), 123.6, 122.2 (q,  $J = 1.7$  Hz), 113.6, 112.2, 67.6 (q,  $J = 26.3$  Hz), 65.2, 61.9, 57.2, 13.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –61.4; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{23}\text{H}_{16}\text{F}_3\text{N}_3\text{O}_4\text{Na}^+$  478.0985; Found 478.0987.

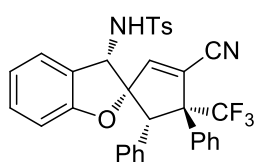
**Synthesis of *ent*-10**: To a mixture of (*E*)-ethyl 2-cyano-3-(4-nitrophenyl)acrylate **9** (24.6 mg, 0.100 mmol, 1.0 equiv), **C2** (4.3 mg, 5 mol%) and 4 Å MS (40.0 mg) in toluene (1.0 mL) was added *tert*-butyl (3-cyano-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **1a** (49.1 mg, 0.150 mmol, 1.5 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 36 h, and the reaction was monitored by TLC. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10 to 1/5) to give the product *ent*-10: 33.0 mg (0.0725 mmol), as a colorless oil, 73% yield;  $[\alpha]_{\text{D}}^{25} = +30.7$  ( $c = 0.60$  in  $\text{CHCl}_3$ ); >19:1 dr; 99% ee, determined by HPLC analysis (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 7.02$  min (major),  $t_{\text{R}} = 9.50$  min (minor).

## 6. Transformations of product **7a**



**Synthesis of **11****: A solution of compound **7a** (58.5 mg, 0.100 mmol, 1.0 equiv) and NaOH (0.8 mg, 20 mol%) in MeOH/ $\text{H}_2\text{O}$  (1.0 mL, 10/1) was stirred at rt for 20 min, and the reaction was monitored by TLC. After completion, the solvent

was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) to give the product **11**: 42.7 mg (0.0991 mmol), as a white solid, 99% yield; mp = 138–140 °C;  $[\alpha]_D^{25} = +2.7$  ( $c = 0.60$  in  $\text{CHCl}_3$ ); >19:1 dr; 98% ee, determined by HPLC analysis (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 5.25$  min (major),  $t_R = 5.76$  min (minor);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.63 (ddd,  $J = 8.8, 7.2, 1.6$  Hz, 1H), 7.55 (dd,  $J = 8.0, 1.2$  Hz, 1H), 7.45 (s, 5H), 7.23–7.09 (m, 6H), 7.04 (t,  $J = 7.6$  Hz, 1H), 6.92 (s, 1H), 4.13 (d,  $J = 1.6$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 197.9, 171.5, 147.9, 139.3, 134.6, 131.4 (q,  $J = 1.7$  Hz), 129.3 (2C), 129.0, 128.7, 128.1, 126.9 (q,  $J = 2.4$  Hz), 125.1 (q,  $J = 283.6$  Hz), 125.01, 124.98, 123.0, 119.7, 113.5, 113.3, 96.0, 67.7 (q,  $J = 25.6$  Hz), 63.0;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –61.9; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{26}\text{H}_{17}\text{F}_3\text{NO}_2^+$  432.1206; Found 432.1201.



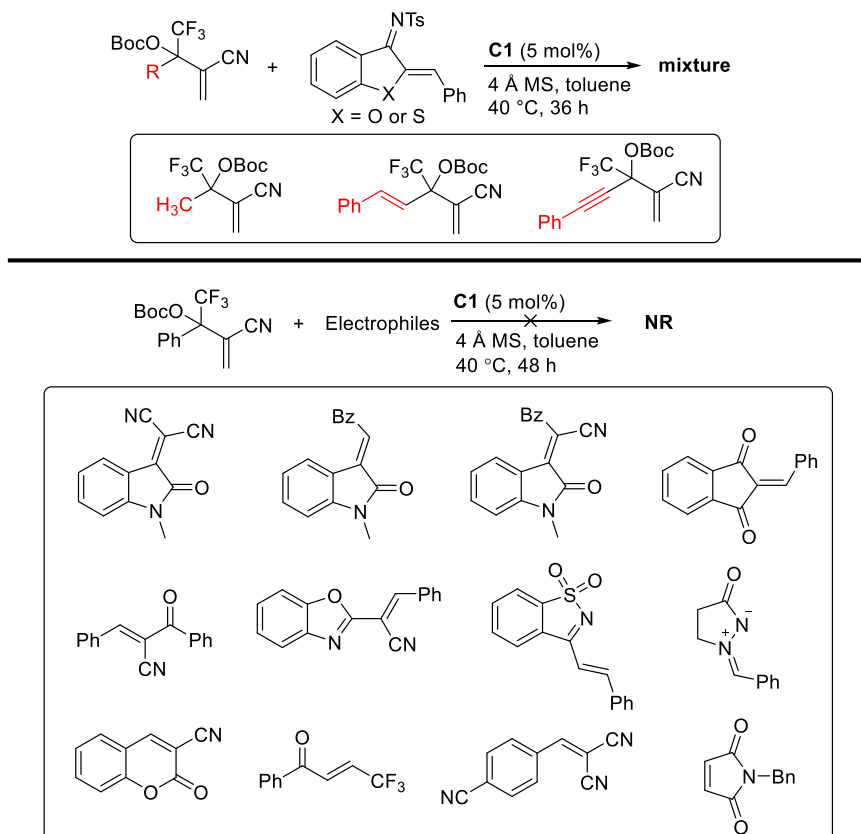
**Synthesis of 12:** A solution of compound **7a** (58.5 mg, 0.100 mmol, 1.0 equiv) and  $\text{NaBH}_3\text{CN}$  (19.0 mg, 0.302 mmol, 3.0 equiv) in MeOH (1.0 mL) was stirred at rt for 3 h,<sup>5</sup> and the reaction was monitored by TLC. After completion, the reaction was quenched with water and extracted with DCM. The

combined organic phase was concentrated and purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give the product **12**: 53.0 mg (0.0903 mmol), as a white solid, 90% yield; mp = 101–102 °C;  $[\alpha]_D^{25} = -132.0$  ( $c = 0.40$  in  $\text{CHCl}_3$ ); >19:1 dr; 97% ee, determined by HPLC analysis (Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 4.73$  min (minor),  $t_R = 9.91$  min (major);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.74–7.68 (m, 2H), 7.49–7.35 (m, 6H), 7.33 (d,  $J = 8.0$  Hz, 2H), 7.27–7.13 (m, 5H), 7.01 (s, 1H), 6.91 (d,  $J = 8.0$  Hz, 1H), 6.73 (t,  $J = 7.6$  Hz, 1H), 6.33 (d,  $J = 7.2$  Hz, 1H), 5.02 (d,  $J = 9.6$  Hz, 1H), 4.33 (d,  $J = 9.6$  Hz, 1H), 4.29 (s, 1H), 2.47 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 157.5, 150.9, 144.2, 137.5, 135.0, 132.1, 131.6, 131.3, 130.1, 129.2, 128.7, 128.2, 128.1, 126.9 (q,  $J = 2.4$  Hz), 126.9, 125.1 (q,  $J = 283.9$  Hz), 124.8, 123.9, 122.1, 121.4 (d,  $J = 2.0$  Hz), 113.7, 110.9, 97.1, 67.9 (q,  $J = 25.3$  Hz), 62.0, 60.1, 21.6;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) –61.4; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{33}\text{H}_{25}\text{F}_3\text{N}_2\text{O}_3\text{SNa}^+$  609.1430; Found 609.1433.

## 7. More substrate exploration

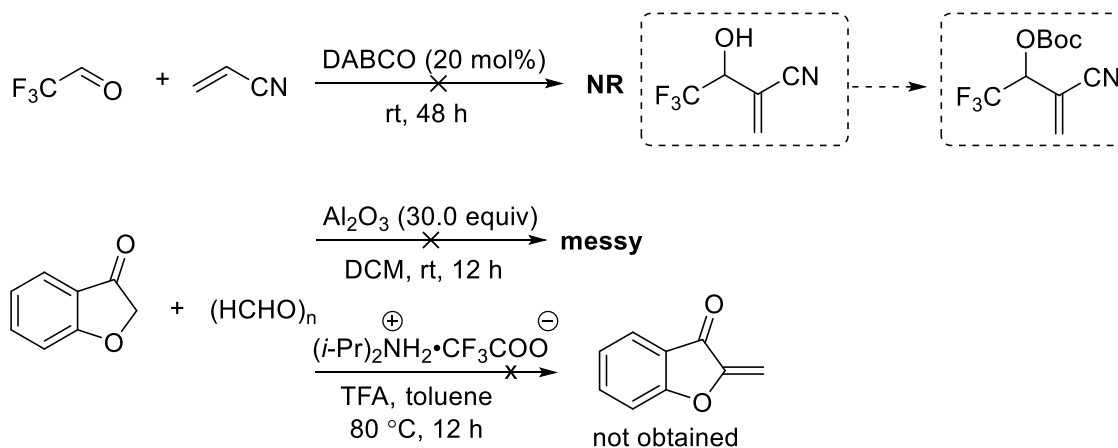
As outlined in the following scheme, the  $\text{CF}_3$ -containing MBH carbonates with an alkyl, alkenyl or alkynyl group failed to give the desired annulation products in the reactions with 1-azadienes, and a mixture was generally produced. In addition, other types of electrophiles were also explored in the reactions with MBH carbonate **1a**, but the expected annulation products were not formed.

a) More substrate exploration

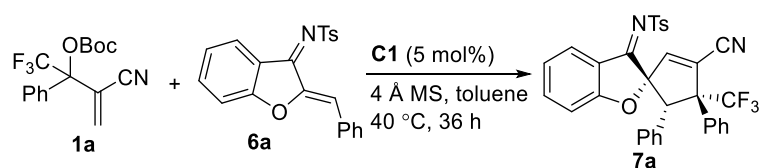


The MBH carbonate derived from 2,2,2-trifluoroacetaldehyde and the 1-azadiene with a terminal double bond are unknown compounds, and we also failed to prepare them.

b) The synthesis of more substrates



8. Asymmetric reaction on a 1.0 mmol scale

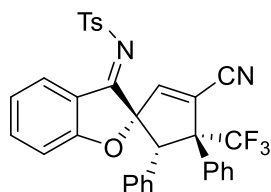
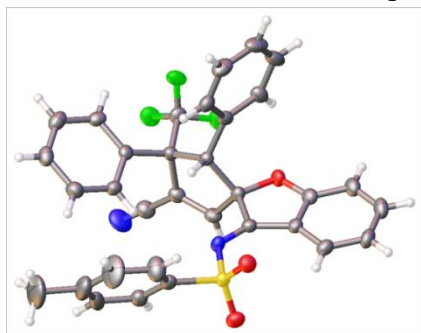


To a mixture of 1-azadiene **6a** (375.0 mg, 1.000 mmol, 1.0 equiv), **C1** (43.0 mg, 5 mol%) and 4 Å MS (400.0 mg) in toluene (10.0 mL) was added MBH carbonate **1a** (491.0 mg, 1.515 mmol, 1.5 equiv) in two portions (generally at 0 h, 18 h, respectively). The mixture was stirred at 40 °C for 48 h, and the reaction was monitored by TLC. After completion, the residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/10) to give the product **7a**: 527.0 mg (0.9009 mmol), as a white solid, 90% yield; >19:1 dr; 97% ee.

## 9. Crystal data and structural refinement

### 9.1 Crystal data and structural refinement for enantiopure **7a**

Preparation of the single crystals of enantiopure **7a**: 30.0 mg of compound **7a** (97% ee) was dissolved in Et<sub>2</sub>O (1.5 mL) in a 10 mL tube and *n*-hexane (2.0 mL) was added. The tube was sealed by a piece of weighing paper with several tiny holes, thus allowing slow evaporation of the solvents at room temperature. After 24 h, several small particles could be observed at the bottom of the tube. The crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the absolute configuration of **7a**. The data were collected by an Agilent Gemini equipped with a Cu radiation source ( $K\alpha = 1.54184 \text{ \AA}$ ) at 223(100) K. CCDC 2088342 (**7a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



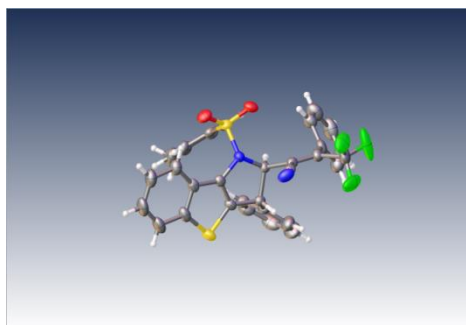
(ellipsoid contour probability 50%)

Identification code	<b>7a</b>
Empirical formula	C <sub>33</sub> H <sub>23</sub> F <sub>3</sub> N <sub>2</sub> O <sub>3</sub> S
Formula weight	584.59
Temperature/K	223(100)
Crystal system	tetragonal
Space group	P4 <sub>1</sub>
a/Å	14.8873(3)
b/Å	14.8873(3)
c/Å	13.6624(4)
$\alpha$ /°	90
$\beta$ /°	90
$\gamma$ /°	90

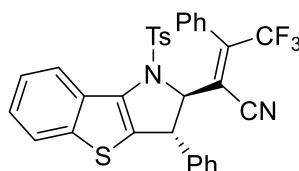
Volume/Å <sup>3</sup>	3028.01(17)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.282
μ/mm <sup>-1</sup>	1.414
F(000)	1208.0
Crystal size/mm <sup>3</sup>	0.7 × 0.5 × 0.4
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.784 to 144.996
Index ranges	-18 ≤ h ≤ 18, -11 ≤ k ≤ 17, -16 ≤ l ≤ 16
Reflections collected	10549
Independent reflections	5627 [R <sub>int</sub> = 0.0378, R <sub>sigma</sub> = 0.0430]
Data/restraints/parameters	5627/1/380
Goodness-of-fit on F <sup>2</sup>	1.055
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0789, wR <sub>2</sub> = 0.1983
Final R indexes [all data]	R <sub>1</sub> = 0.0798, wR <sub>2</sub> = 0.2009
Largest diff. peak/hole / e Å <sup>-3</sup>	0.51/-0.89
Flack parameter	-0.020(13)

## 9.2 Crystal data and structural refinement for enantiopure *ent-5a*

Preparation of the single crystals of enantiopure *ent-5a*: 30.0 mg of compound *ent-5a* (98% ee) was dissolved in *i*-PrOH (1.5 mL) in a 10 mL tube and *n*-hexane (2.0 mL) was added. The tube was sealed by a piece of weighing paper with several tiny holes, thus allowing slow evaporation of the solvents at room temperature. After 36 h, several small particles could be observed at the bottom of the tube. The crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the absolute configuration of *ent-5a*. The data were collected by an Agilent Gemini equipped with a Cu radiation source (Kα = 1.54184 Å) at 204(6) K. CCDC 2088343 (*ent-5a*) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



(ellipsoid contour probability 50%)



Identification code

***ent-5a***

Empirical formula

C<sub>33</sub>H<sub>23</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>

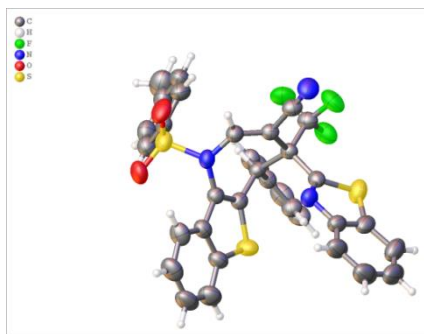
Formula weight

600.65

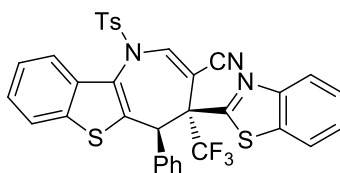
Temperature/K	204(6)
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å	11.71838(15)
b/Å	13.40753(16)
c/Å	18.3196(2)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	2878.27(6)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.386
μ/mm <sup>-1</sup>	2.136
F(000)	1240.0
Crystal size/mm <sup>3</sup>	0.45 × 0.3 × 0.3
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.172 to 145.452
Index ranges	-14 ≤ h ≤ 14, -16 ≤ k ≤ 15, -17 ≤ l ≤ 22
Reflections collected	16816
Independent reflections	5640 [R <sub>int</sub> = 0.0324, R <sub>sigma</sub> = 0.0290]
Data/restraints/parameters	5640/0/380
Goodness-of-fit on F <sup>2</sup>	1.057
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0497, wR <sub>2</sub> = 0.1267
Final R indexes [all data]	R <sub>1</sub> = 0.0512, wR <sub>2</sub> = 0.1289
Largest diff. peak/hole / e Å <sup>-3</sup>	0.32/-0.69
Flack parameter	-0.009(6)

### 9.3 Crystal data and structural refinement for enantiopure **8b**

Preparation of the single crystals of enantiopure **8b**: 30.0 mg of compound **8b** (96% ee) was dissolved in EtOAc (1.5 mL) and CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) in a 10 mL tube and *n*-hexane (3.0 mL) was added. The tube was sealed by a piece of weighing paper with several tiny holes, thus allowing slow evaporation of the solvents at room temperature. After 36 h, several small particles could be observed at the bottom of the tube. The crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the absolute configuration of **8b**. The data were collected by Bruker D8 VENTURE equipped with a Mo radiation source (Kα = 0.71073 Å) at 273.15 K. CCDC 2088344 (**8b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



(ellipsoid contour probability 50%)



Identification code	<b>8b</b>
Empirical formula	$C_{34}H_{22}F_3N_3O_2S_3$
Formula weight	657.72
Temperature/K	273.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.6266(7)
b/Å	18.4175(16)
c/Å	19.2928(17)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å <sup>3</sup>	3065.2(5)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.425
$\mu/\text{mm}^{-1}$	0.297
F(000)	1352.0
Crystal size/mm <sup>3</sup>	0.41 × 0.37 × 0.1
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\theta$ range for data collection/ $^\circ$	4.222 to 55.05
Index ranges	$-11 \leq h \leq 10, -23 \leq k \leq 23, -24 \leq l \leq 25$
Reflections collected	25772
Independent reflections	7055 [ $R_{\text{int}} = 0.1019, R_{\text{sigma}} = 0.0992$ ]
Data/restraints/parameters	7055/0/407
Goodness-of-fit on $F^2$	1.006
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0571, wR_2 = 0.1181$
Final R indexes [all data]	$R_1 = 0.1304, wR_2 = 0.1485$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.25/−0.34
Flack parameter	−0.03(6)

## References

(1) (a) Y. Iwabuchi, M. Nakatani, N. Yokoyama and S. Hatakeyama, *J. Am. Chem. Soc.*, 1999, **121**,



10219; (b) H. Waldmann, V. Khedkar, H. Dückert, M. Schürmann, I. M. Oppel and K. Kumar, *Angew. Chem., Int. Ed.*, 2008, **47**, 6869; (c) Y. Nakamoto, F. Urabe, K. Takahashi, J. Ishihara and S. Hatakeyama, *Chem. Eur. J.*, 2013, **19**, 12653.

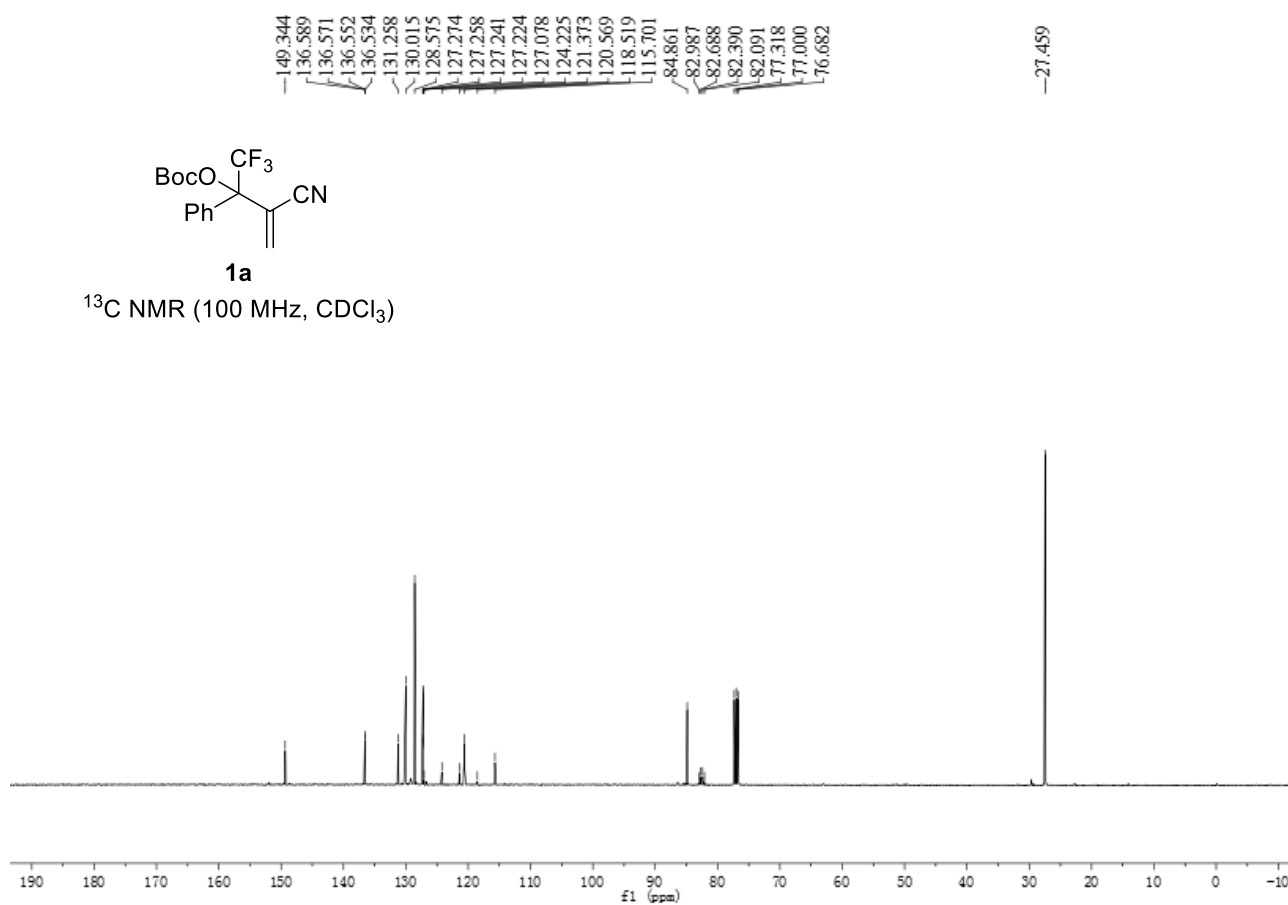
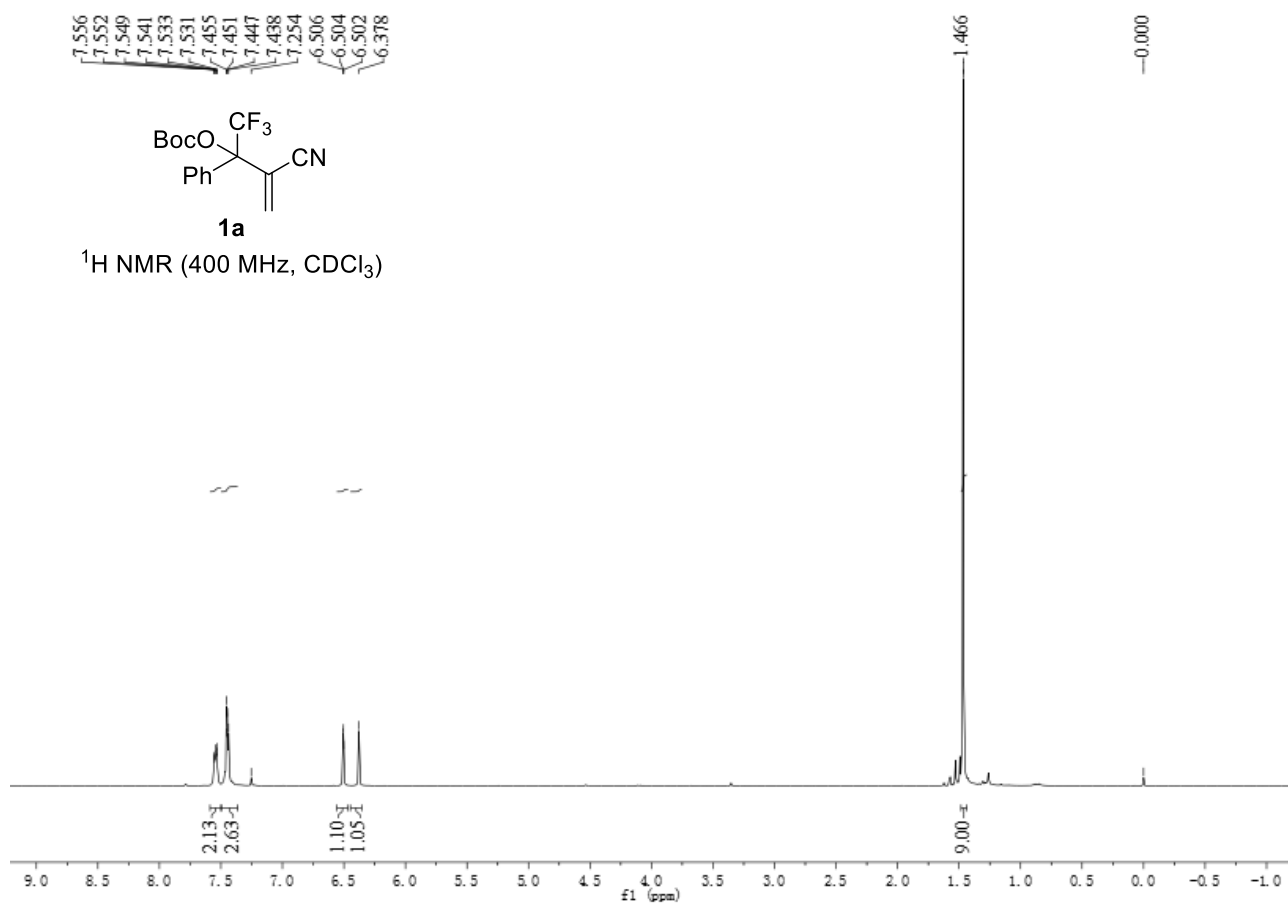
(2) (a) Z.-Q. Rong, M. Wang, C. H. E. Chow and Y. Zhao, *Chem. Eur. J.*, 2016, **22**, 9483; (b) Z. Gu, J. Zhou, G.-F. Jiang and Y.-G. Zhou, *Org. Chem. Front.*, 2018, **5**, 1148; (c) R.-J. Yan, B.-X. Liu, B.-X. Xiao, W. Du and Y.-C. Chen, *Org. Lett.*, 2020, **22**, 4240.

(3) (a) P. V. Ramachandran, M. V. Ram Reddy and M. T. Rudd, *Chem. Commun.*, 2001, 757; (b) M. V. Ram Reddy, M. T. Rudd and P. V. Ramachandran, *J. Org. Chem.*, 2002, **67**, 5382.

(4) For selected examples of substrate-controlled switchable asymmetric annulations, see: (a) Q.-H. Li, L. Wei and C.-J. Wang, *J. Am. Chem. Soc.*, 2014, **136**, 8685; (b) J.-Y. Liao, P.-L. Shao and Y. Zhao, *J. Am. Chem. Soc.*, 2015, **137**, 628; (c) D. Wang, G.-P. Wang, Y.-L. Sun, S.-F. Zhu, Y. Wei, Q.-L. Zhou and M. Shi, *Chem. Sci.*, 2015, **6**, 7319; (d) K.-K. Wang, P. Wang, Q. Ouyang, W. Du and Y.-C. Chen, *Chem. Commun.*, 2016, **52**, 11104; (e) Y. Xu, Q. Sun, T.-D. Tan, M.-Y. Yang, P. Yuan, S.-Q. Wu, X. Lu, X. Hong and L.-W. Ye, *Angew. Chem., Int. Ed.*, 2019, **58**, 16252; (f) B. M. Trost and Z. Zuo, *Angew. Chem., Int. Ed.*, 2021, **60**, 5806.

(5) T. Chen, Y. Zhang, Z. Fu and W. Huang, *Asian J. Org. Chem.*, 2019, **8**, 2175.

## 10. NMR, HRMS spectra and HPLC chromatograms

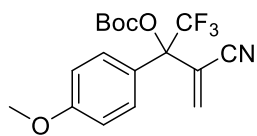


7.484  
7.482  
7.477  
7.461  
7.460  
7.260  
6.960  
6.954  
6.943  
6.937  
6.500  
6.498  
6.496  
6.355  
6.353  
6.351

-3.832

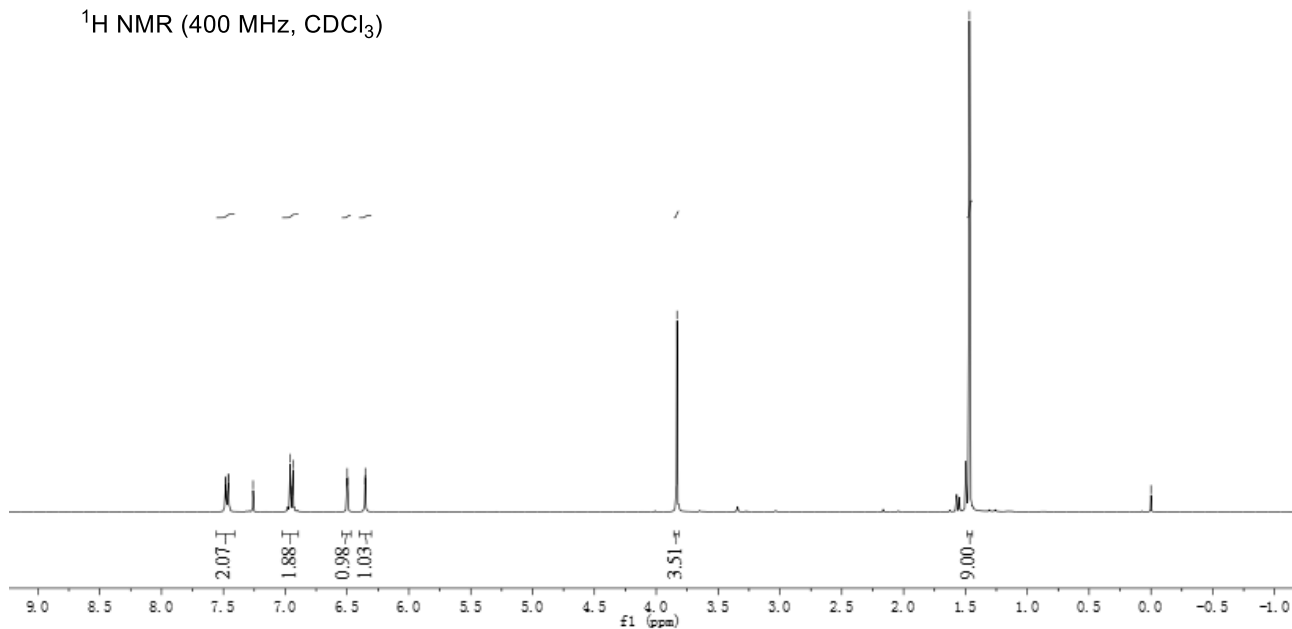
-1.468

-0.000



**1d**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



-160.656

-149.419

-136.299

-136.282

-128.955

-128.937

-128.920

-128.902

-128.149

-127.174

-124.323

-123.006

-121.471

-120.792

-118.587

-115.809

-113.934

-84.718

-83.008

-82.709

-82.410

-82.111

-77.318

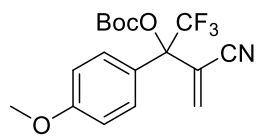
-77.000

-76.682

-55.304

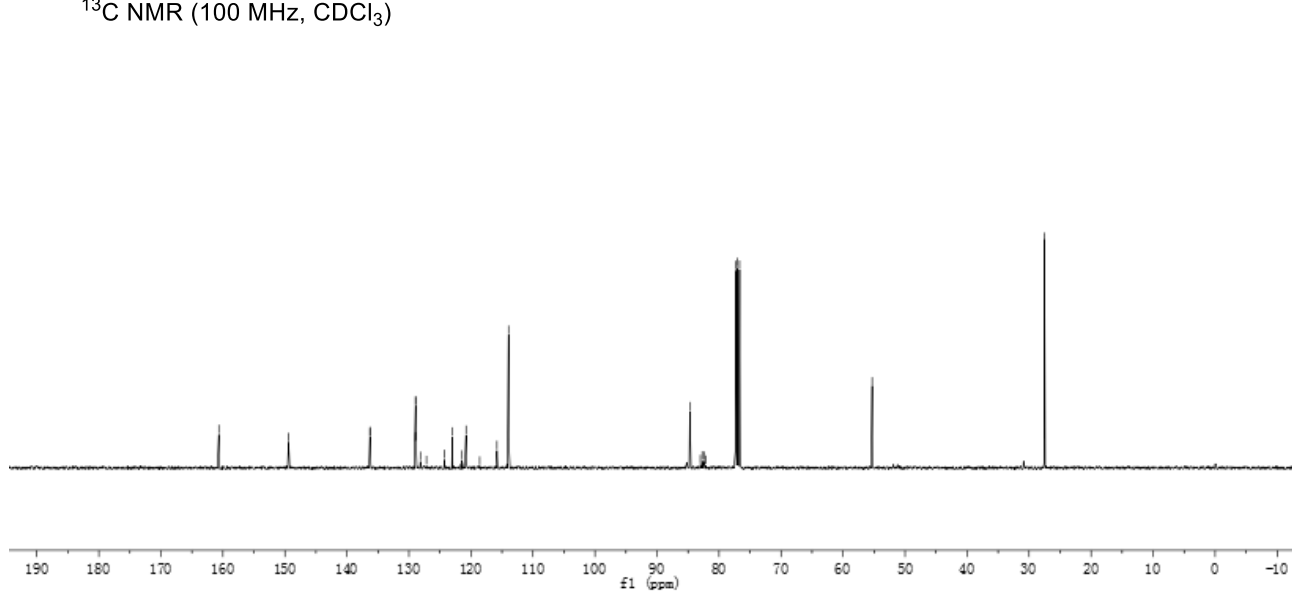
-27.521

-27.481

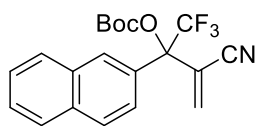


**1d**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

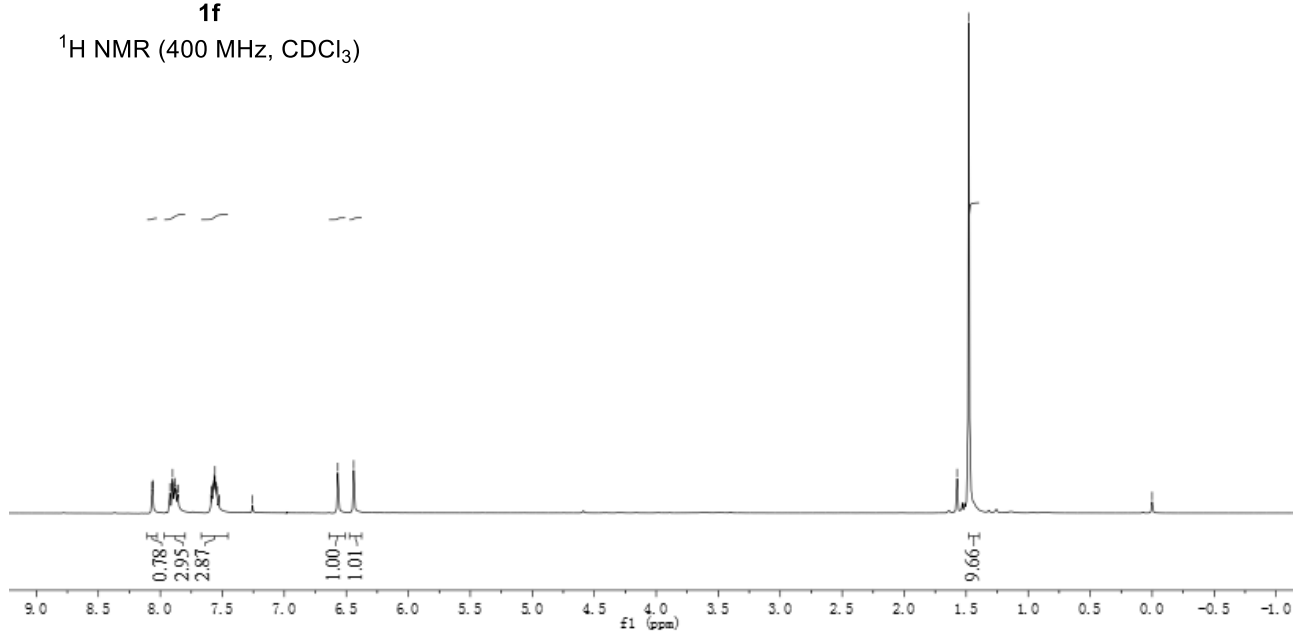


8.066  
8.063  
8.061  
7.923  
7.907  
7.901  
7.889  
7.882  
7.874  
7.865  
7.858  
7.593  
7.587  
7.582  
7.575  
7.571  
7.566  
7.559  
7.551  
7.547  
7.542  
7.529  
7.526  
7.256  
6.568  
6.440

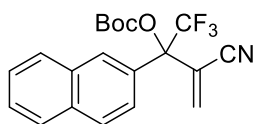


**1f**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

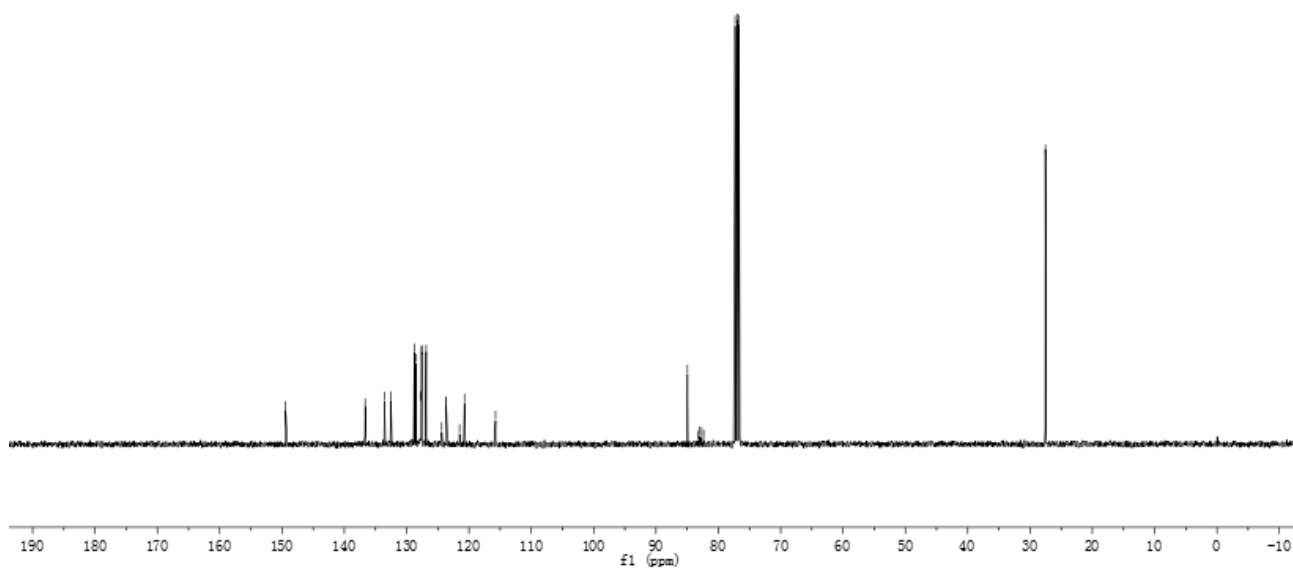


149.419  
136.659  
133.534  
132.513  
128.773  
128.581  
128.509  
127.796  
127.784  
127.632  
127.553  
126.872  
124.377  
123.664  
123.645  
121.521  
120.728  
115.747  
84.954  
83.260  
82.961  
82.664  
82.363  
77.317  
77.000  
76.681



**1f**

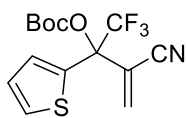
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



7.557  
7.552  
7.542  
7.532  
7.472  
7.462  
7.455  
7.445  
7.260  
6.391

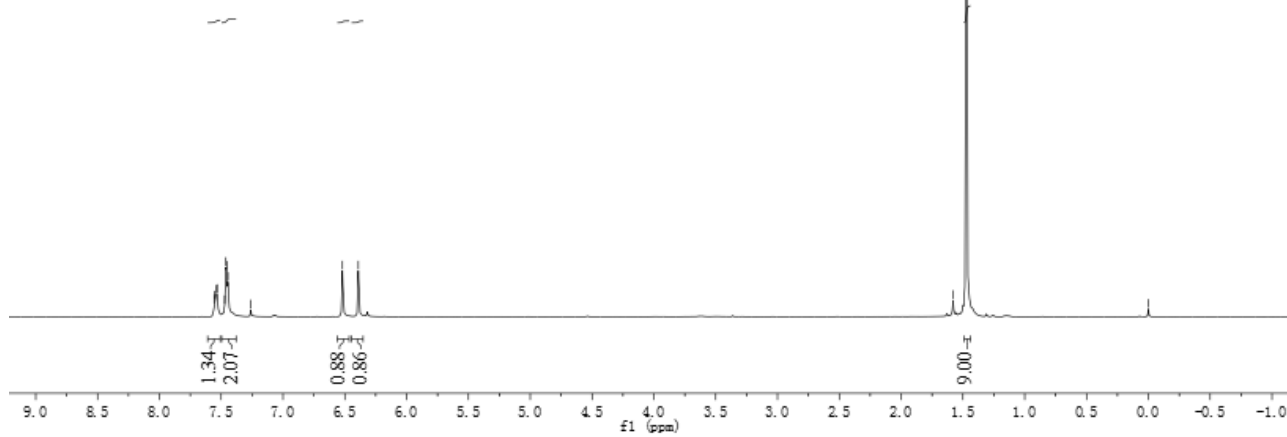
1.579  
1.471

0.000



**1g**

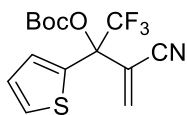
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



149.367  
136.521  
131.311  
130.033  
128.596  
127.283  
125.674  
123.771  
121.869  
120.649  
119.962  
115.713

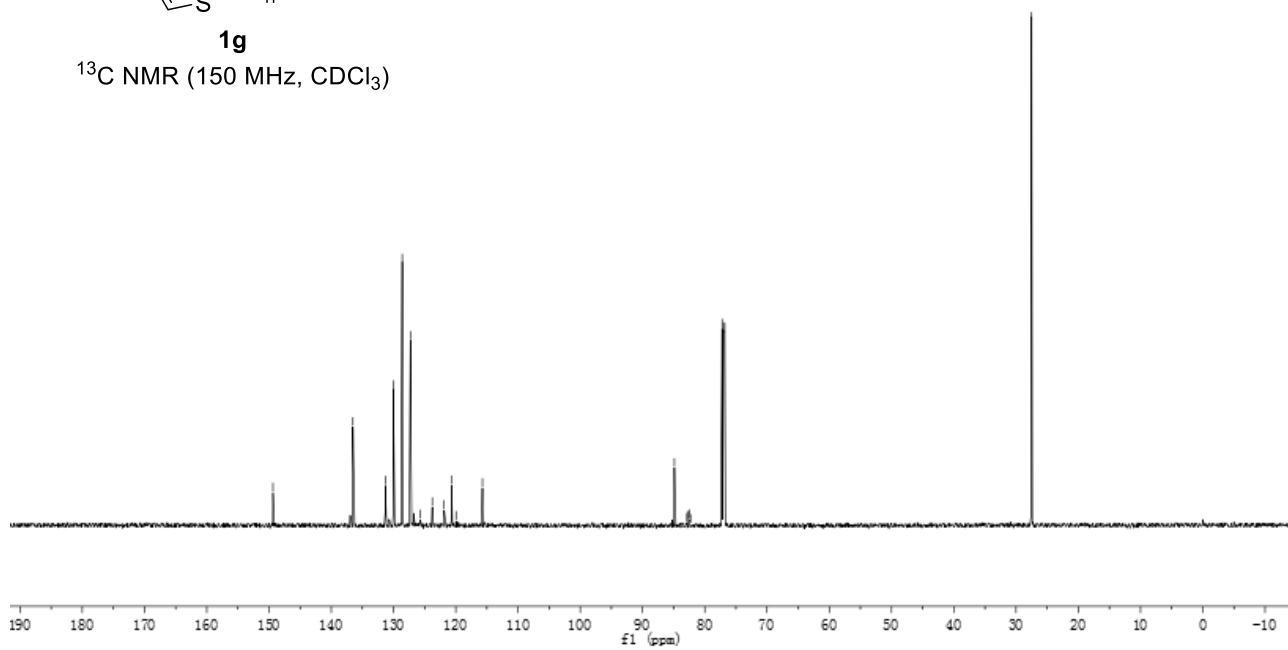
84.878  
82.877  
82.678  
82.481  
82.277  
77.213  
77.000  
76.789

27.505

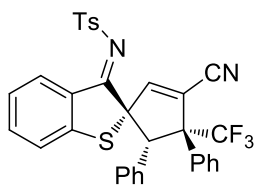


**1g**

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)



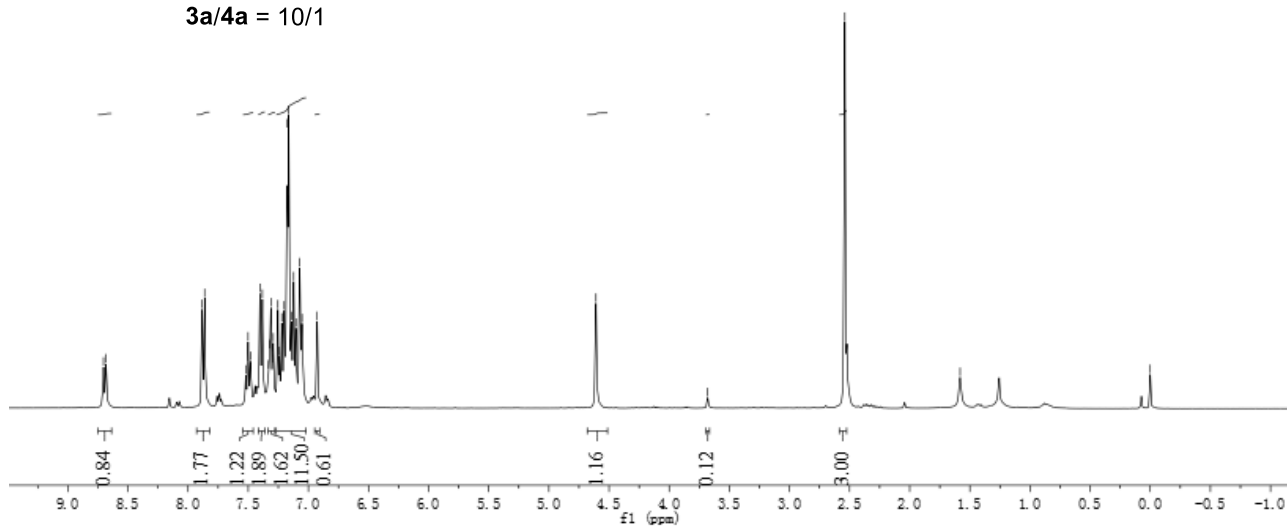
8.703  
8.683  
7.883  
7.863  
7.520  
7.501  
7.482  
7.403  
7.383  
7.331  
7.321  
7.311  
7.299  
7.292  
7.253  
7.241  
7.222  
7.201  
7.175  
7.163  
7.141  
7.122  
7.103  
7.072  
7.053  
6.927  
4.608  
-3.680  
-2.539  
-1.581  
-0.000



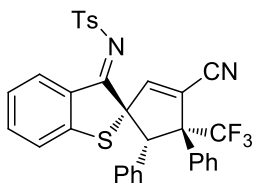
**3a**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

**3a/4a = 10/1**



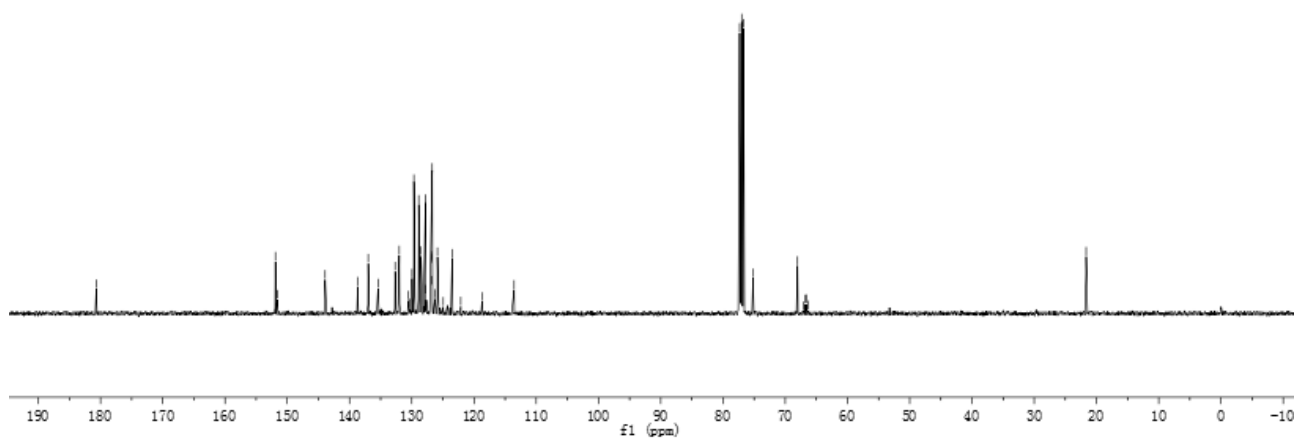
-180.690  
151.901  
151.576  
143.911  
138.679  
136.995  
135.413  
132.675  
132.002  
130.593  
130.325  
129.964  
129.660  
128.886  
128.816  
128.508  
127.847  
127.811  
126.820  
126.794  
126.771  
126.712  
126.275  
125.870  
124.932  
123.509  
122.123  
118.724  
113.547  
77.319  
77.000  
76.684  
75.179  
68.027  
67.077  
66.822  
66.566  
66.312  
-21.656



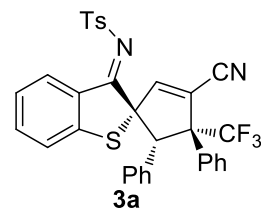
**3a**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

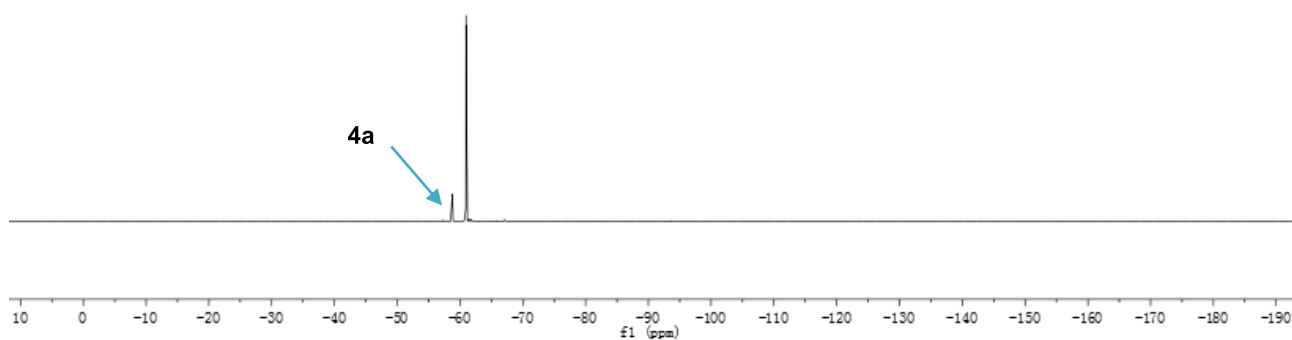
**3a/4a = 10/1**



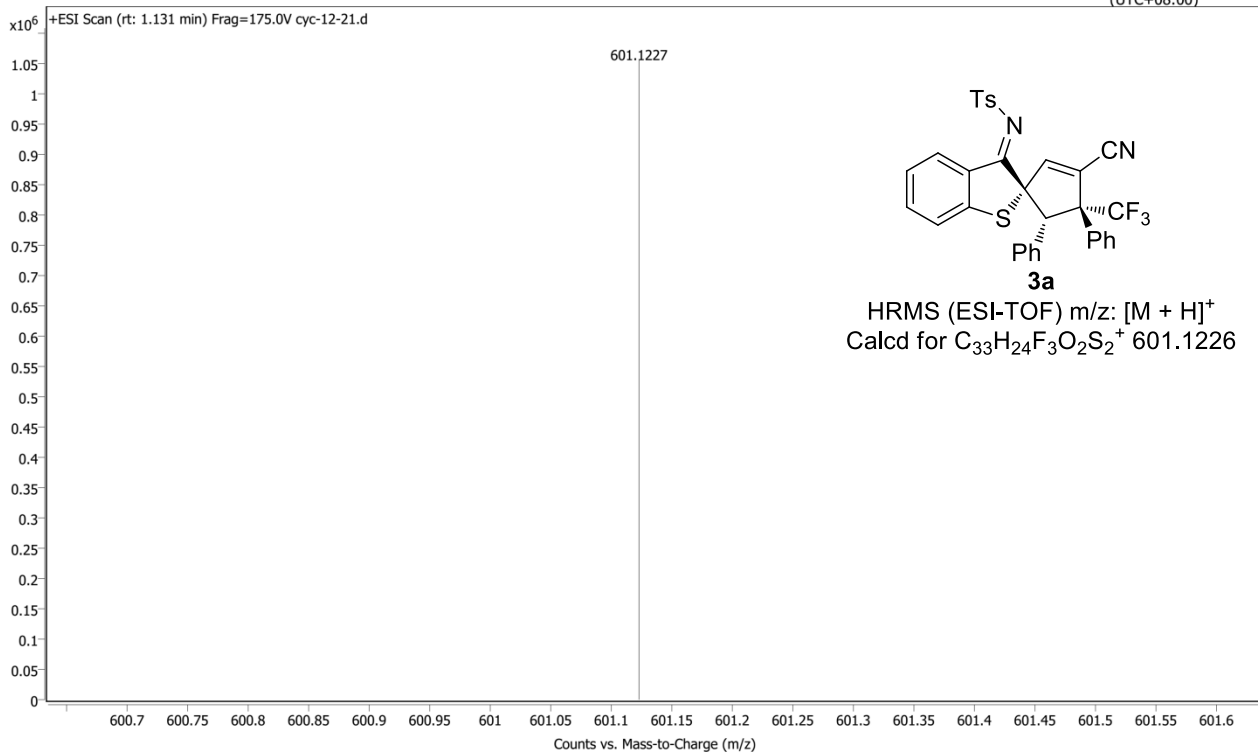
60.960

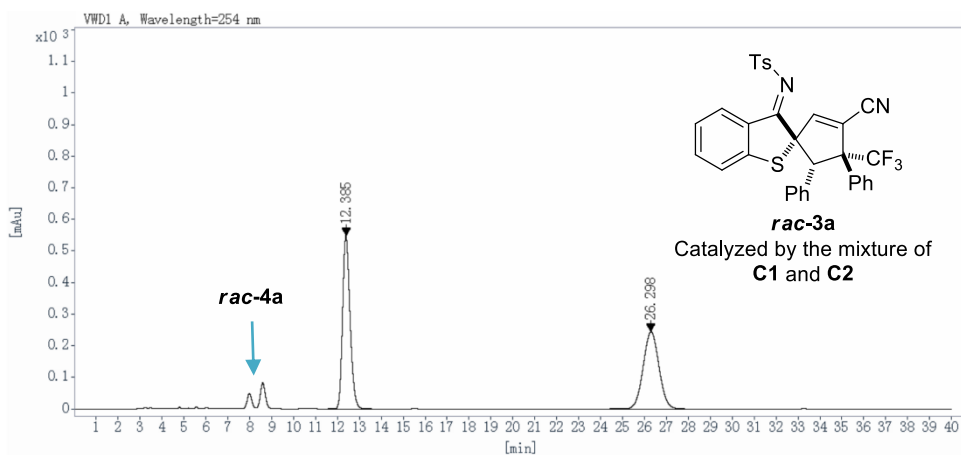


<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>)  
**3a/4a** = 10/1

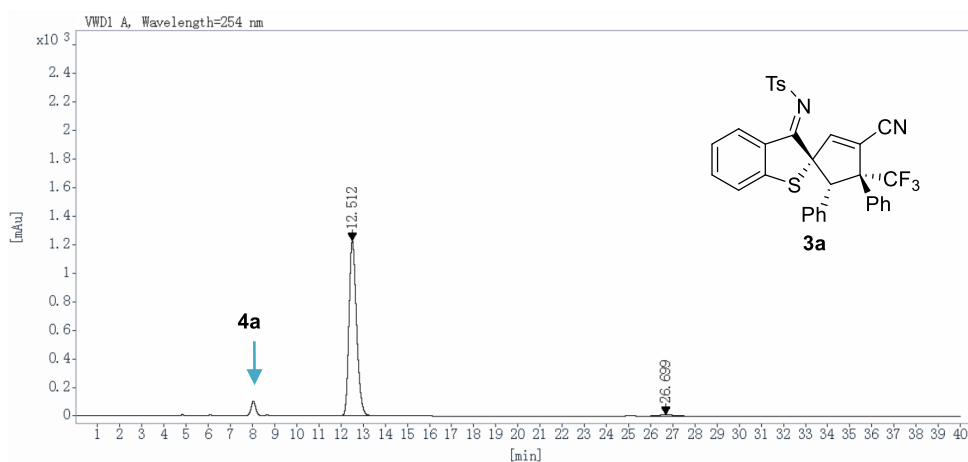


Name	cyc-12-21	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	cyc-12-21.d	Method (Acq)	TOF.m	Comment	Acq. Time (Local) 7/22/2019 6:15:35 PM (UTC+08:00)

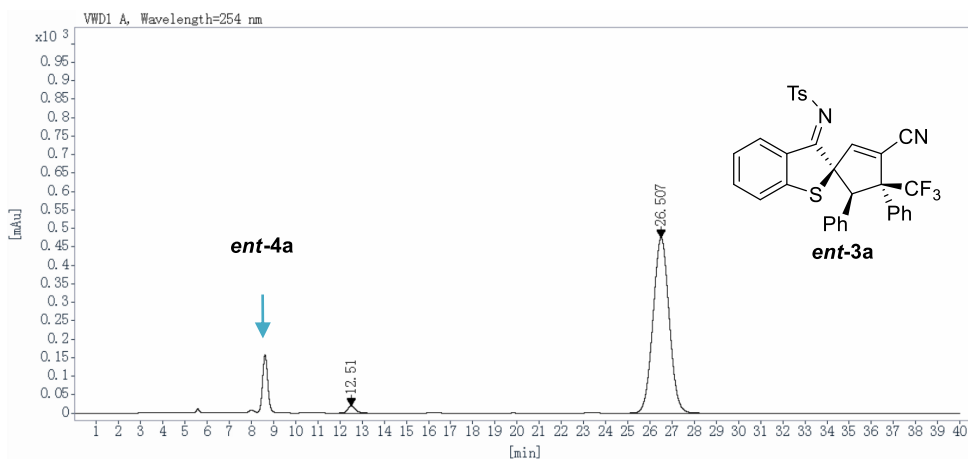




Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
12.385	BB	0.36	549.0323	12960.0703	51.4124
26.298	BB	0.78	244.1594	12247.9717	48.5876



Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
12.512	VB R	0.37	1228.4678	29231.0039	98.5573
26.699	BB	0.74	8.7647	427.8876	1.4427

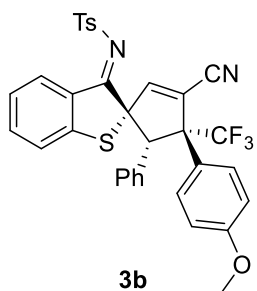


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
12.510	BB	0.38	19.4138	477.1673	1.9460
26.507	BB	0.78	475.1860	24043.4473	98.0540

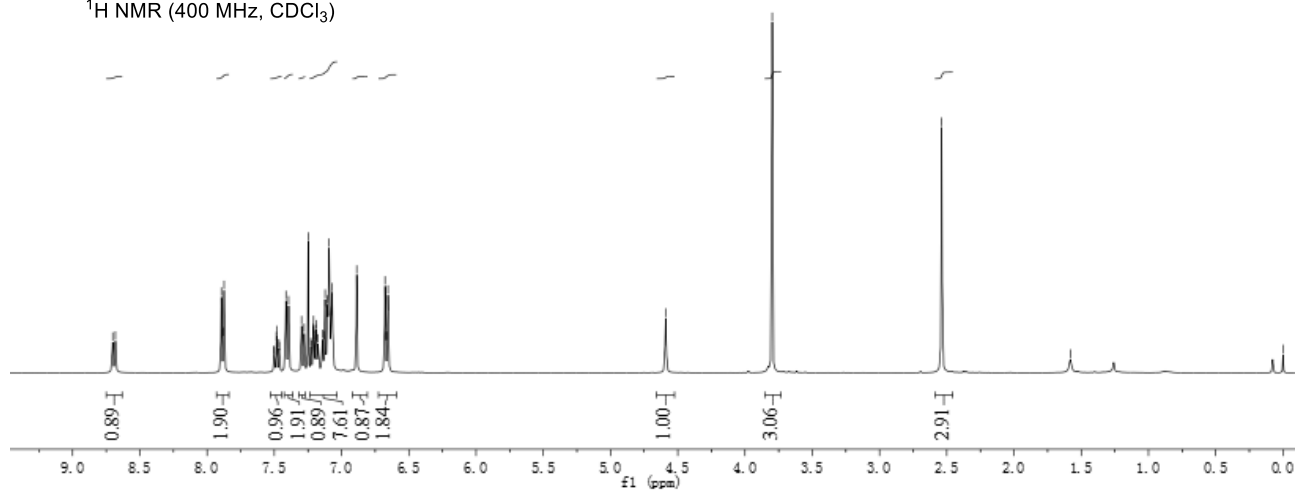


8.702  
8.682  
7.894  
7.890  
7.878  
7.873  
7.504  
7.500  
7.485  
7.482  
7.480  
7.465  
7.462  
7.414  
7.394  
7.298  
7.277  
7.249  
7.229  
7.226  
7.210  
7.208  
7.205  
7.193  
7.190  
7.187  
7.175  
7.143  
7.139  
7.128  
7.123  
7.105  
7.093  
7.075  
7.069  
6.888  
6.677  
6.671  
6.660  
6.655  
4.590  
3.798  
2.537  
-1.581

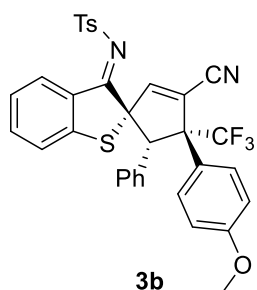
-0.000



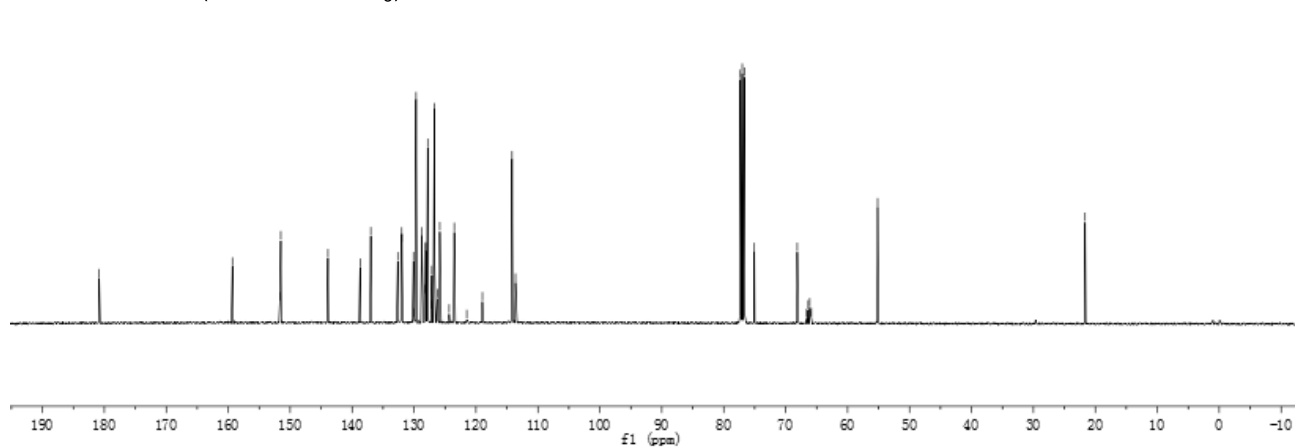
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



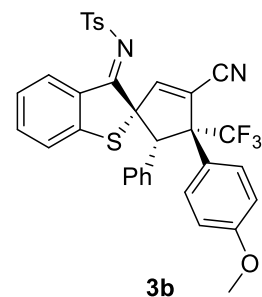
-180.821  
-159.321  
-151.663  
-151.512  
-143.891  
-138.709  
-136.980  
-132.624  
-131.979  
-131.961  
-130.088  
-129.993  
-129.664  
-128.747  
-128.156  
-128.130  
-128.105  
-128.080  
-127.790  
-127.155  
-127.121  
-126.719  
-126.243  
-125.834  
-124.321  
-123.500  
-121.484  
-118.955  
-114.169  
-113.615  
-77.319  
-77.000  
-76.682  
-75.044  
-68.123  
-66.612  
-66.359  
-66.104  
-65.849  
-55.143  
-21.645



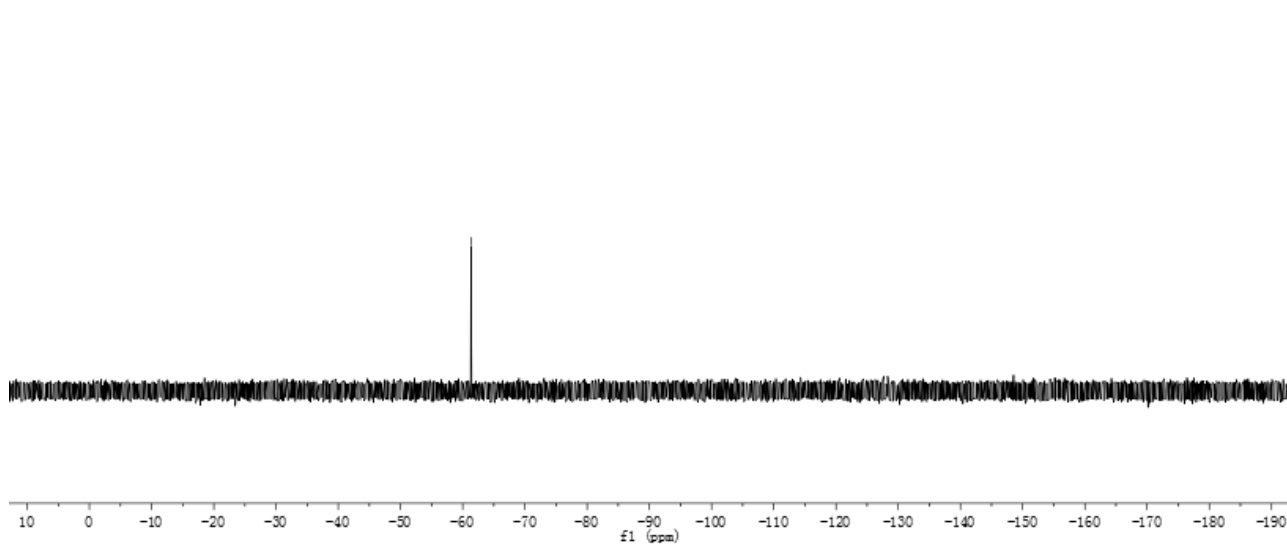
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



61.330

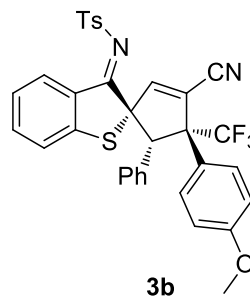
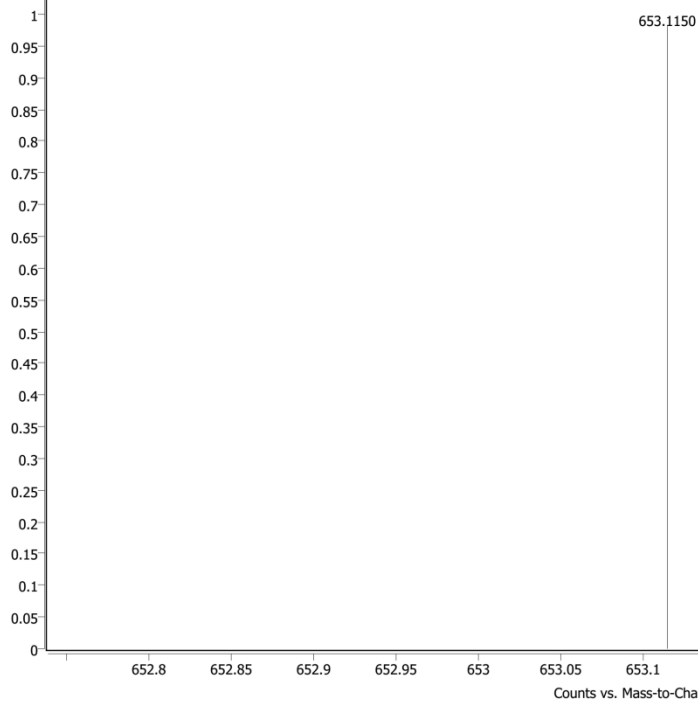


<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)

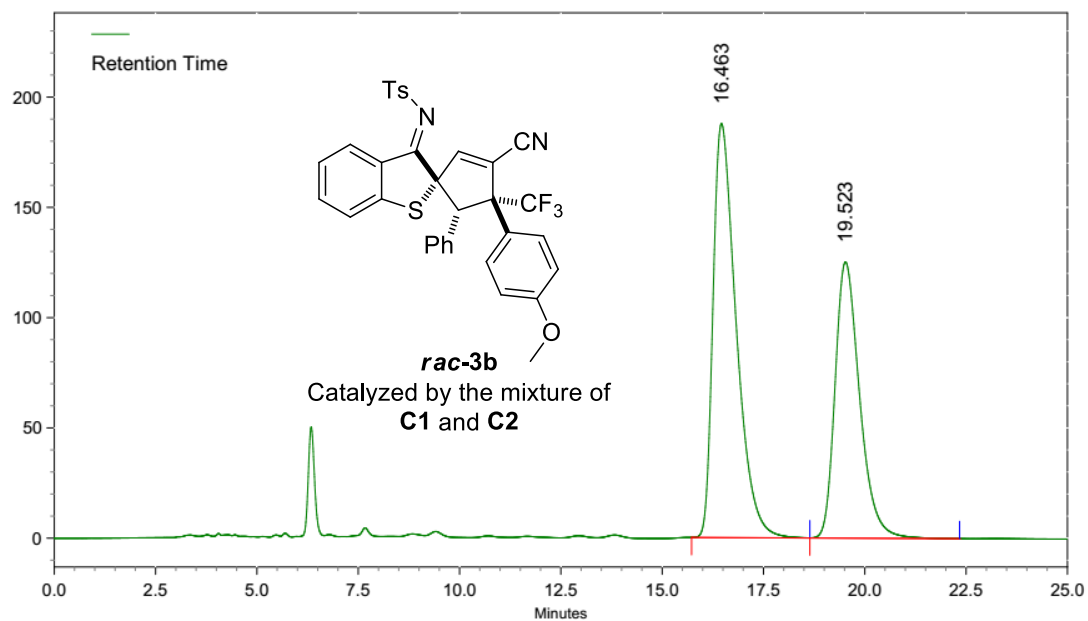


Name	cyc-190705-7	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	WorklistData-0007-r006.d	Method (Acq)	TOF.m		Acq. Time (Local) 7/9/2019 1:51:16 PM (UTC+08:00)

+ESI Scan (rt: 1.225 min) Frag=175.0V WorklistData-0007-r006.d

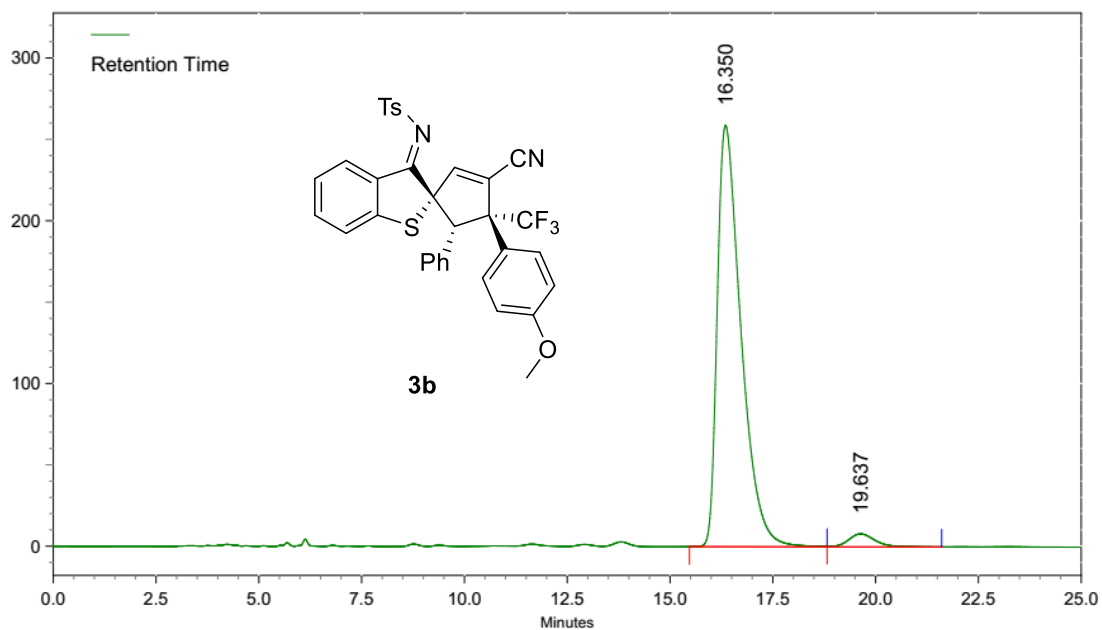


HRMS (ESI-TOF) m/z: [M + Na]<sup>+</sup>  
Calcd for C<sub>34</sub>H<sub>25</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub>S<sub>2</sub>Na<sup>+</sup> 653.1151



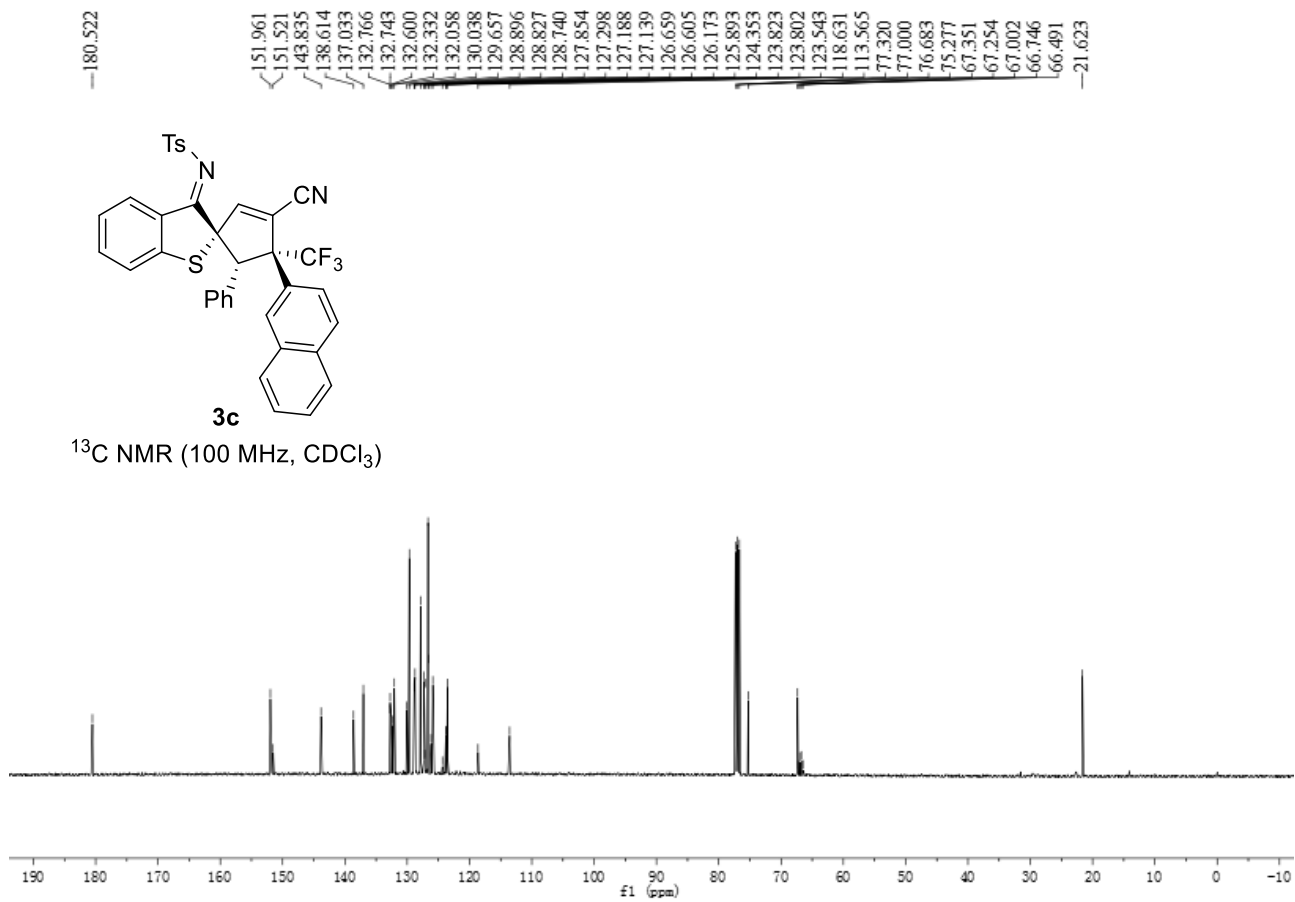
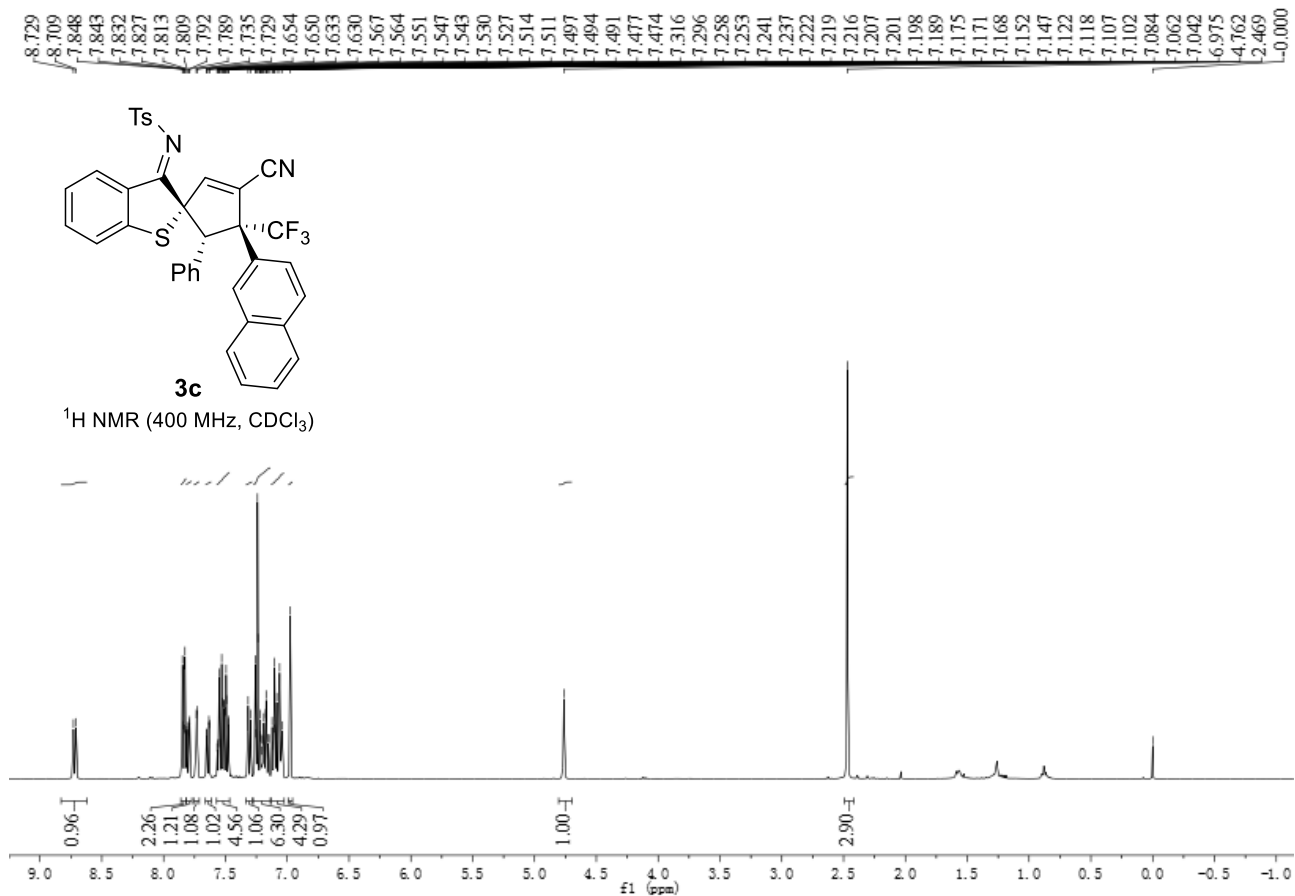
### AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	16.463	2.917	3149501	125093428	58.5725
2	19.523	3.697	2101460	88476781	41.4275

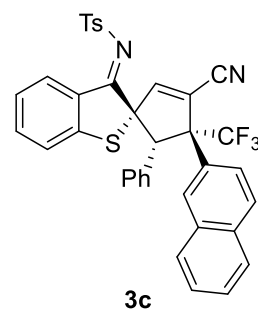


### AREA PERCENT REPORT

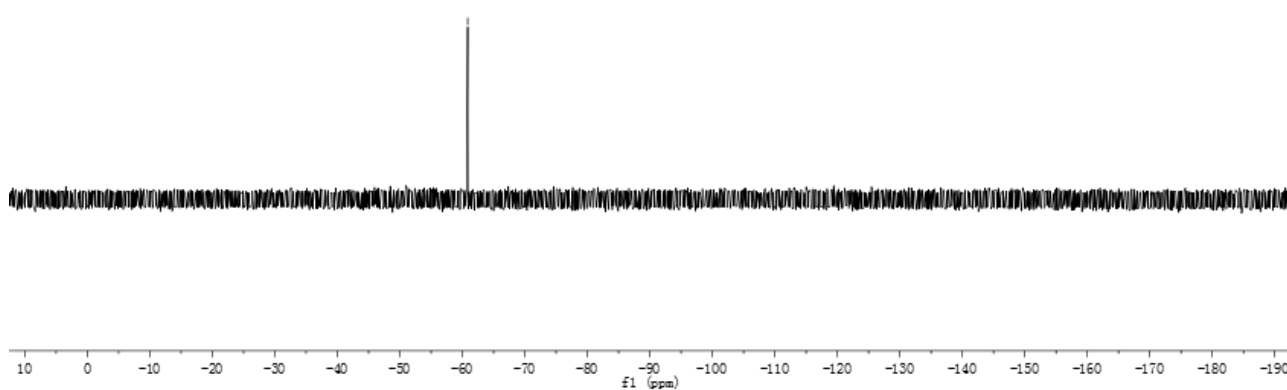
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	16.350	3.347	4343503	174296716	96.6773
2	19.637	2.787	134167	5990328	3.3227



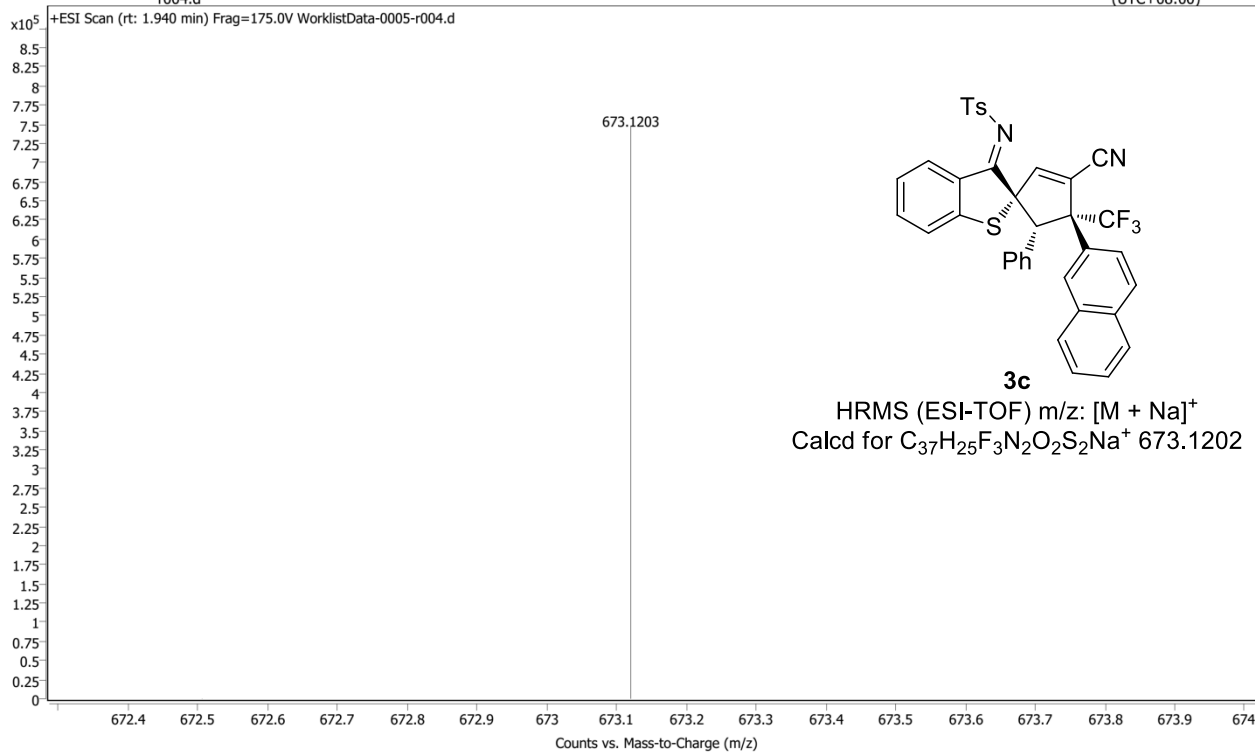
—60.853

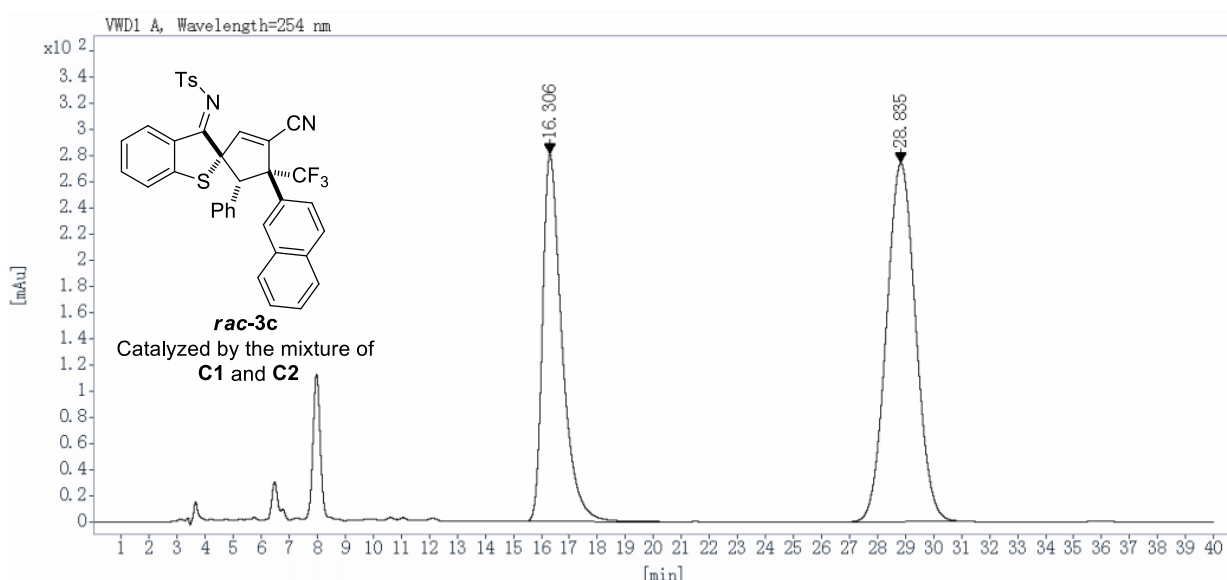


**3c**  
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)

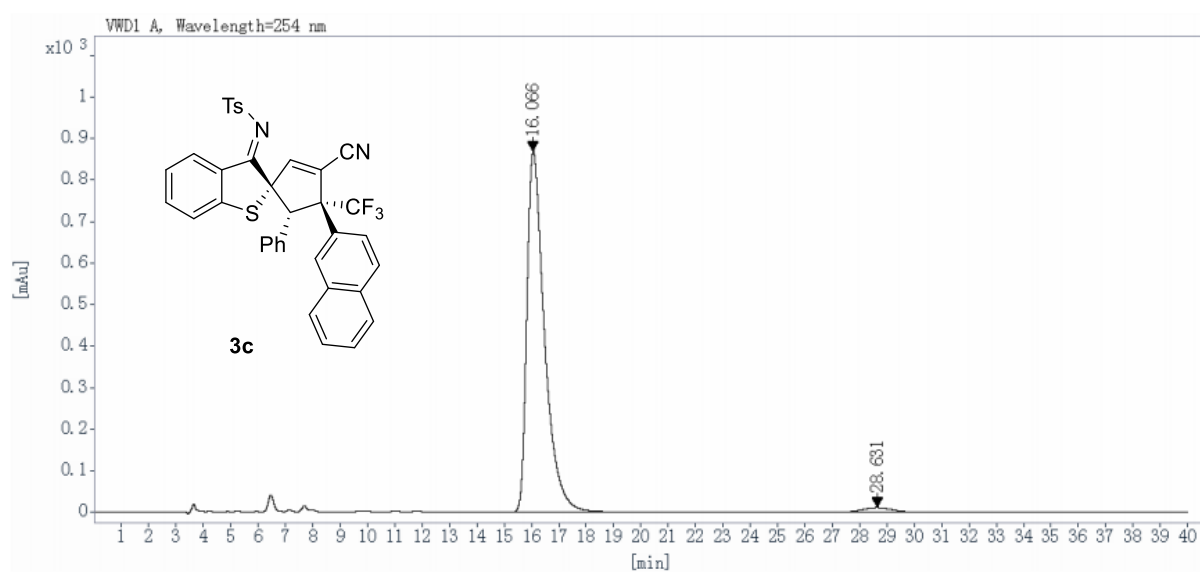


Name	cyc-190705-5	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	WorklistData-0005-r004.d	Method (Acq)	TOF.m		Acq. Time (Local)
					7/9/2019 1:45:39 PM (UTC+08:00)



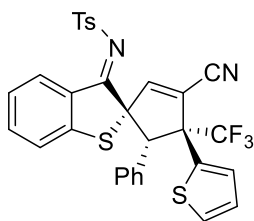


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
16.306	BB	0.72	280.7423	13499.8076	40.4833
28.835	BB S	1.13	273.8016	19846.8223	59.5167



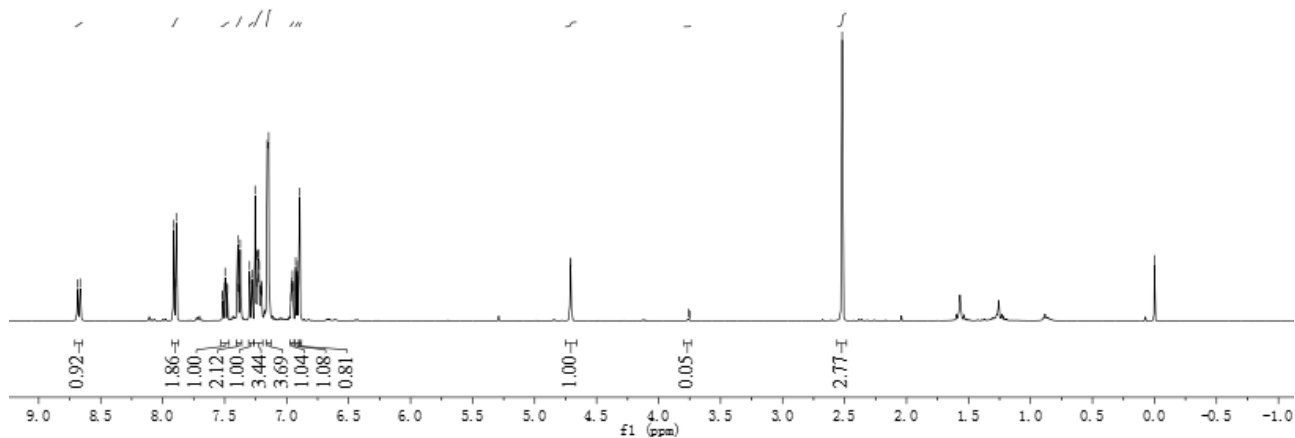
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
16.066	BB	0.67	868.6877	38880.5273	98.0496
28.631	BB S	1.11	10.7477	773.4229	1.9504

8.686  
8.665  
7.911  
7.906  
7.895  
7.890  
7.517  
7.514  
7.499  
7.497  
7.479  
7.476  
7.394  
7.389  
7.379  
7.374  
7.301  
7.299  
7.297  
7.281  
7.279  
7.277  
7.255  
7.249  
7.246  
7.242  
7.236  
7.233  
7.227  
7.223  
7.221  
7.211  
7.209  
7.206  
7.203  
7.200  
7.156  
7.145  
6.966  
6.963  
6.960  
6.957  
6.954  
6.951  
6.927  
6.918  
6.915  
6.905  
6.894  
4.711  
4.708  
4.708  
3.760  
3.744  
2.519  
-0.000

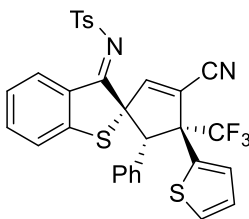


**3d**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

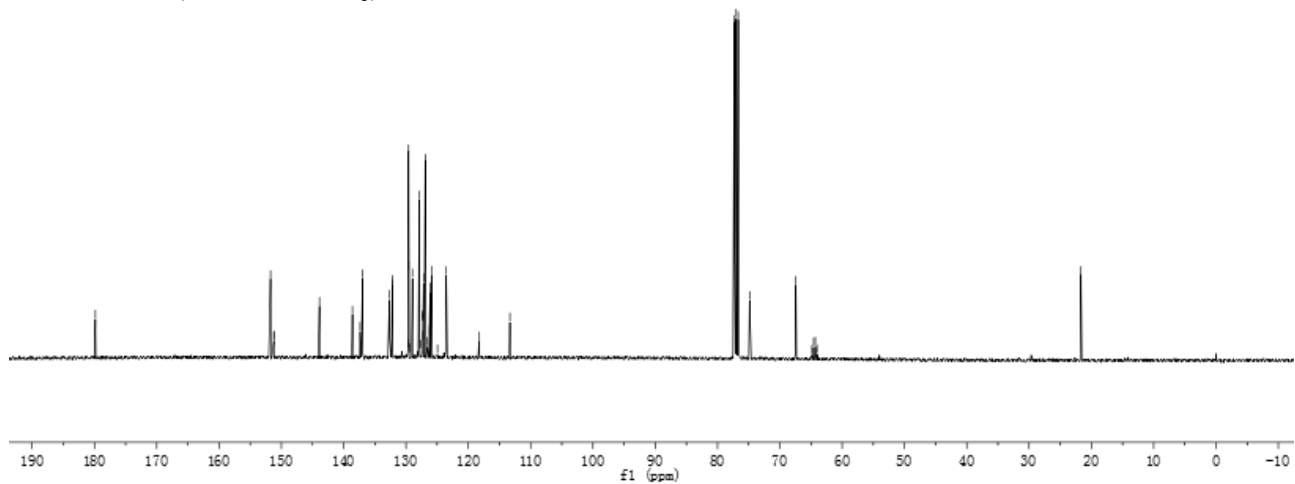


179.848  
151.739  
151.214  
151.197  
143.887  
138.590  
137.370  
136.977  
132.668  
132.204  
132.184  
129.660  
129.582  
129.567  
129.392  
128.969  
127.878  
127.662  
127.310  
127.289  
127.265  
127.175  
126.916  
126.558  
126.212  
126.138  
125.898  
124.940  
123.532  
118.269  
113.325  
77.317  
77.000  
76.683  
74.849  
67.420  
64.849  
64.578  
64.307  
64.034  
21.669

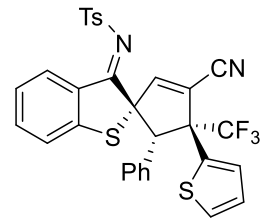


**3d**

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

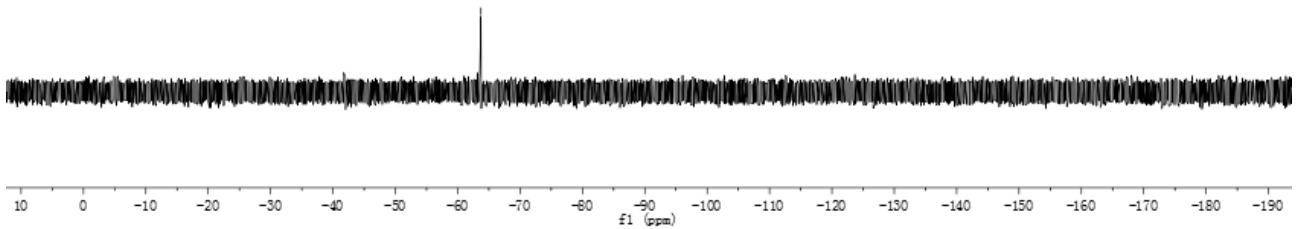


—63.729



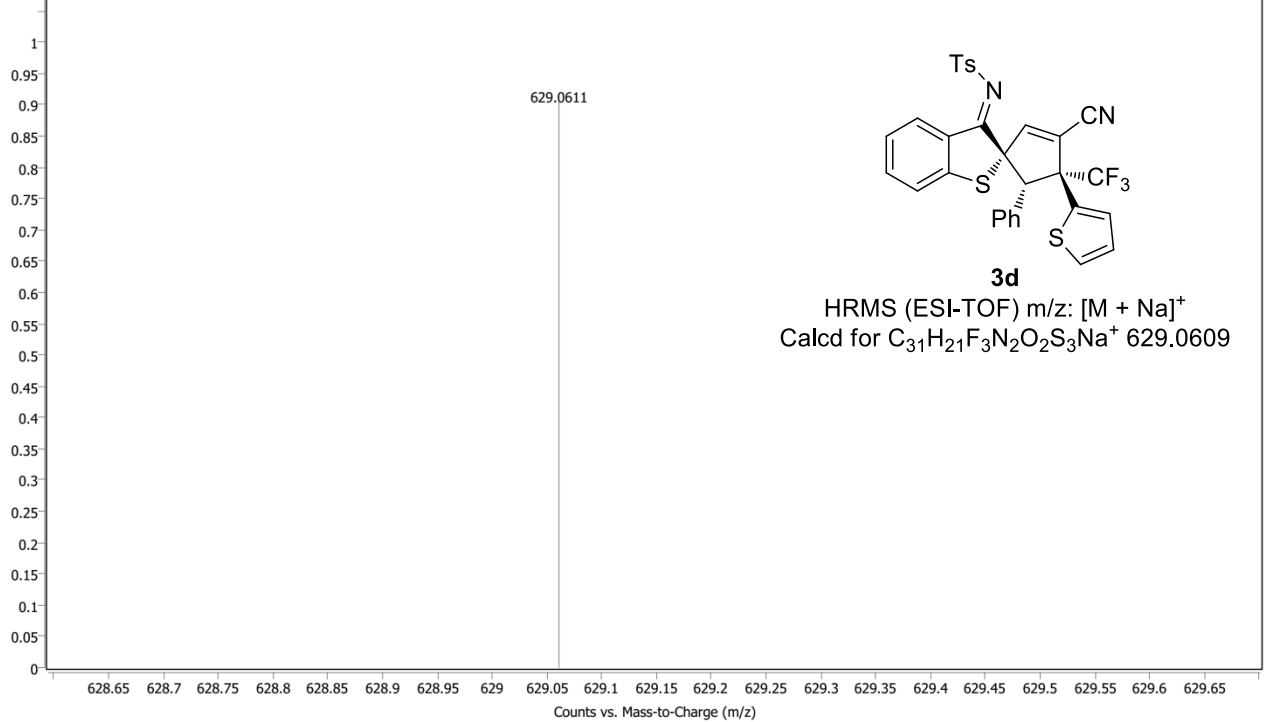
**3d**

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)

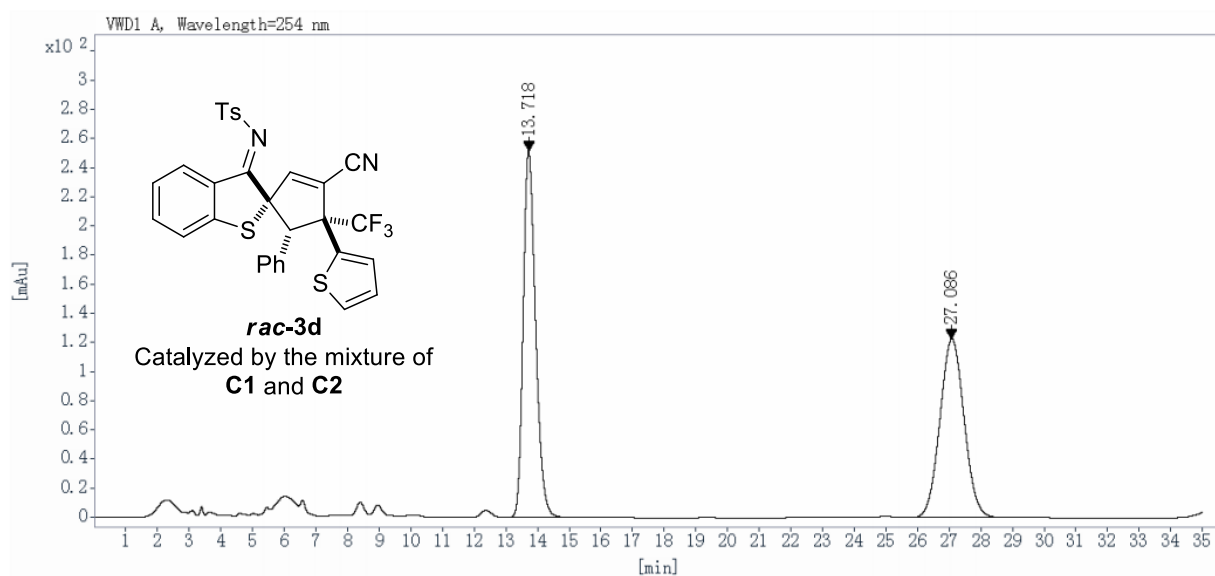


Name	cyc-190705-6	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	10	Plate Pos.		IRM Status	Success		
Data File	WorklistData-0006-r005.d	Method (Acq)	TOF.m	Comment		Acq. Time (Local)	7/9/2019 1:48:27 PM (UTC+08:00)

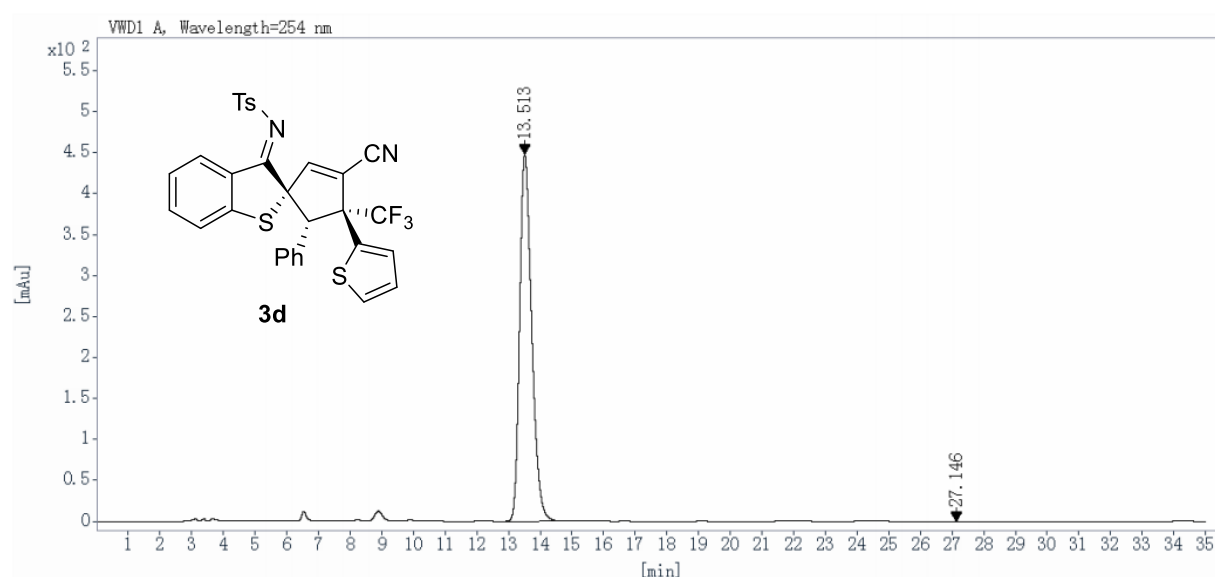
+ESI Scan (rt: 1.025 min) Frag=175.0V WorklistData-0006-r005.d



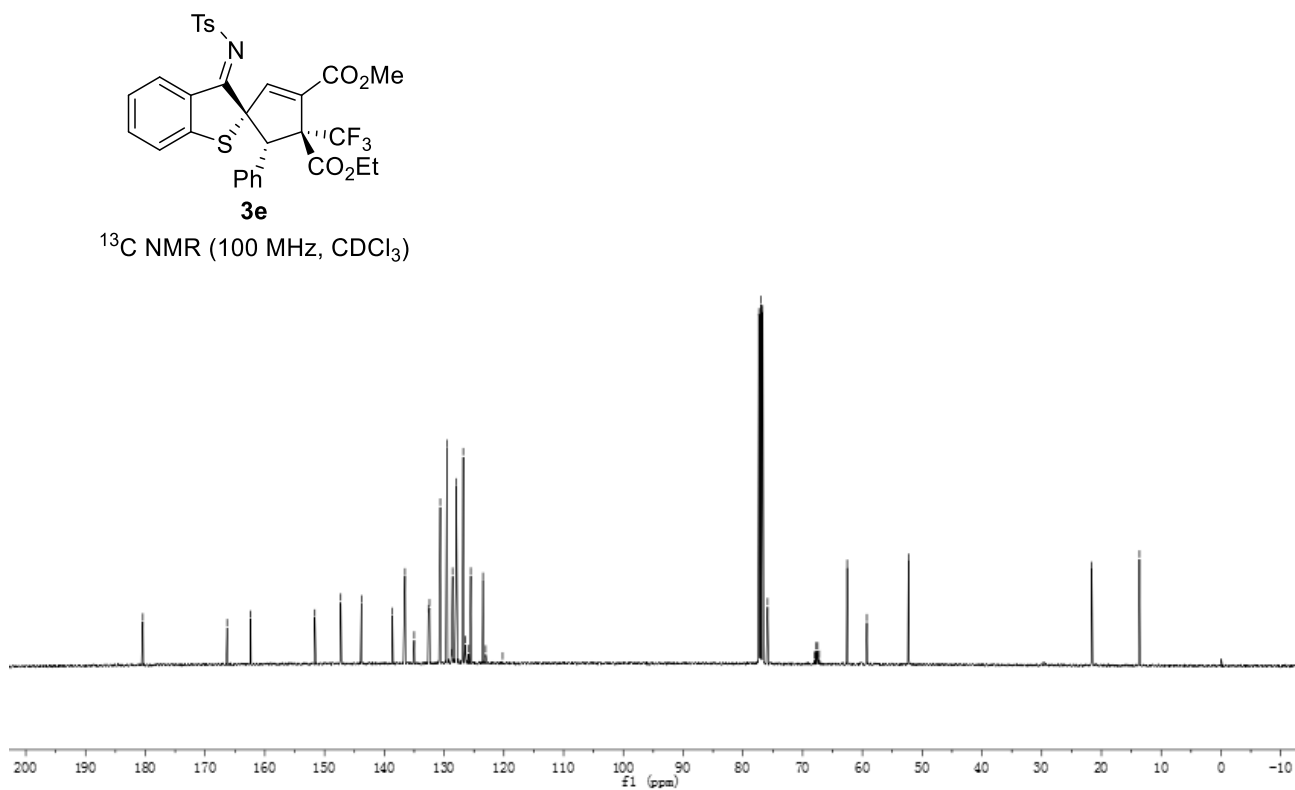
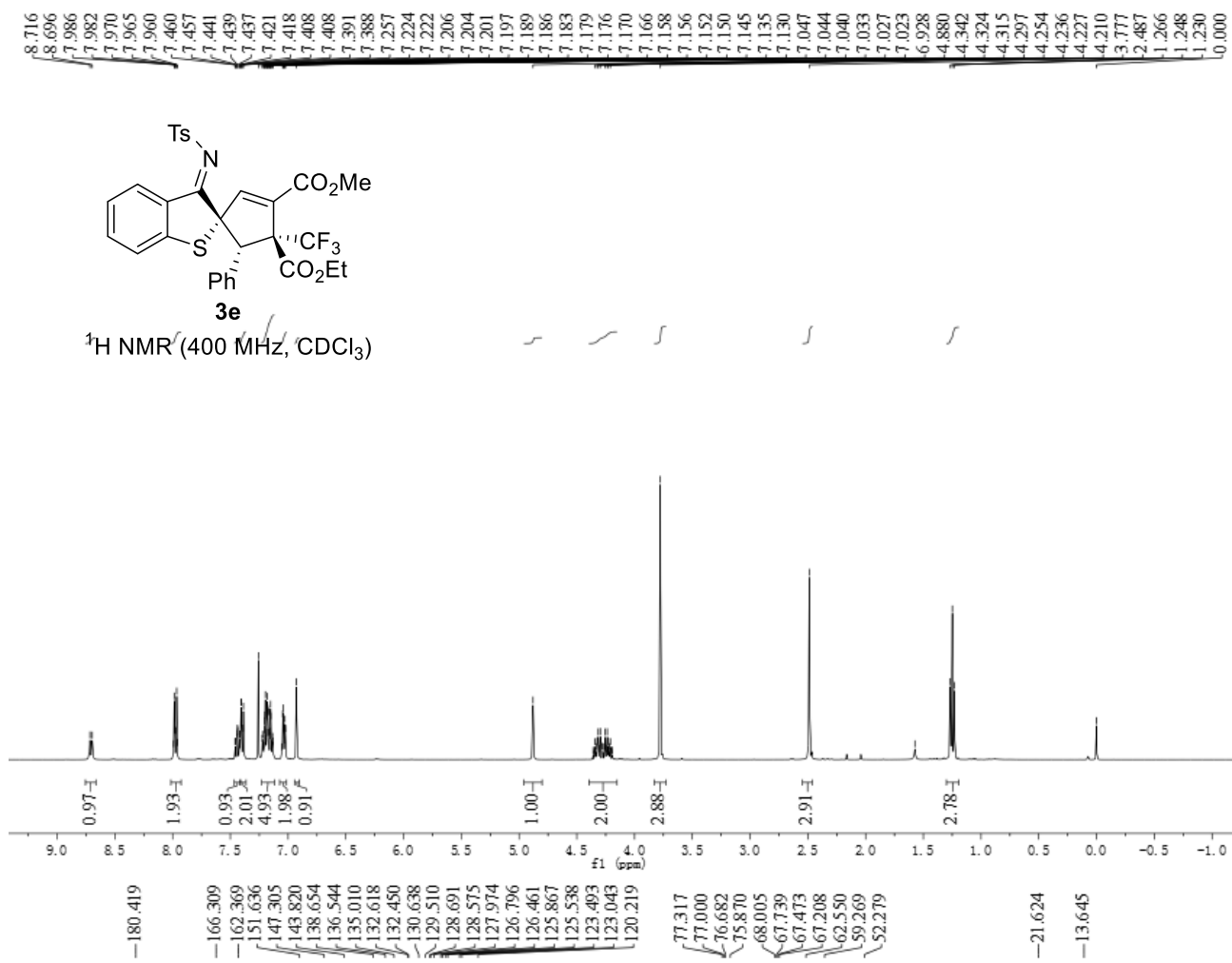




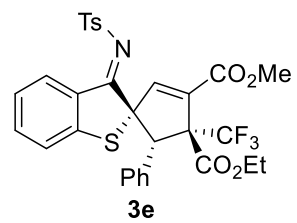
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
13.718	BB	0.42	251.2882	6821.3608	51.1078
27.086	BB	0.83	122.7864	6525.6533	48.8922



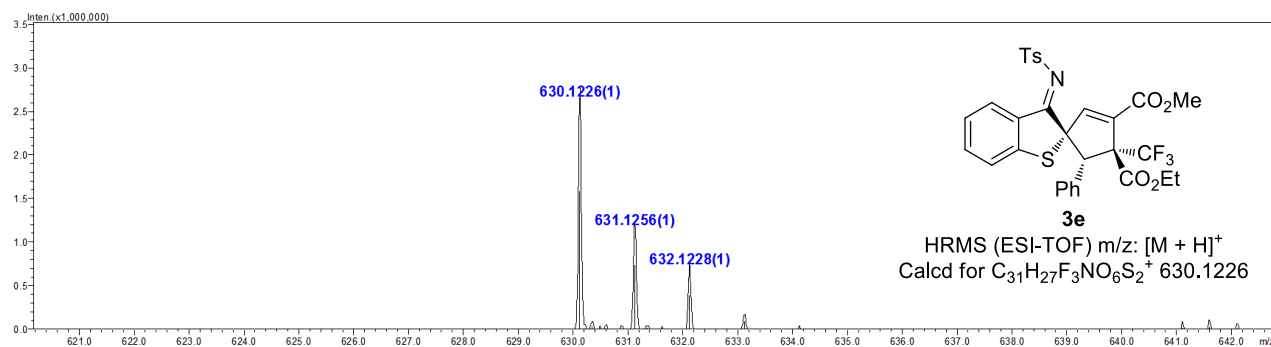
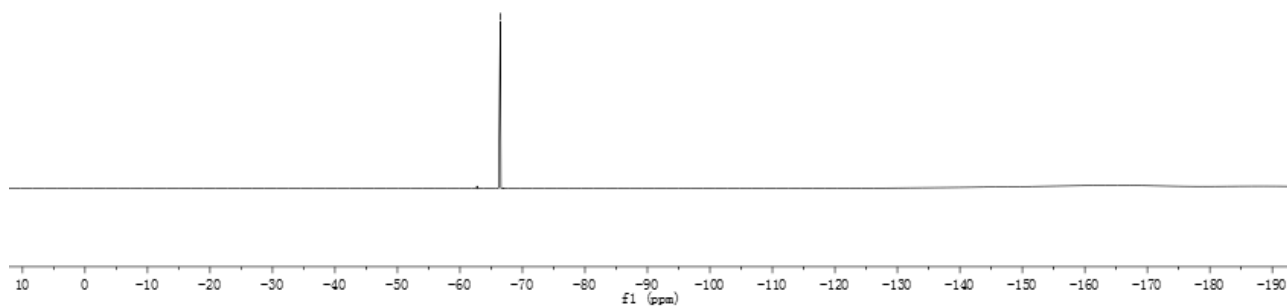
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
13.513	BBA	0.41	447.4220	11809.3057	99.9999
27.146	BB	0.03	0.0032	0.0070	0.0001

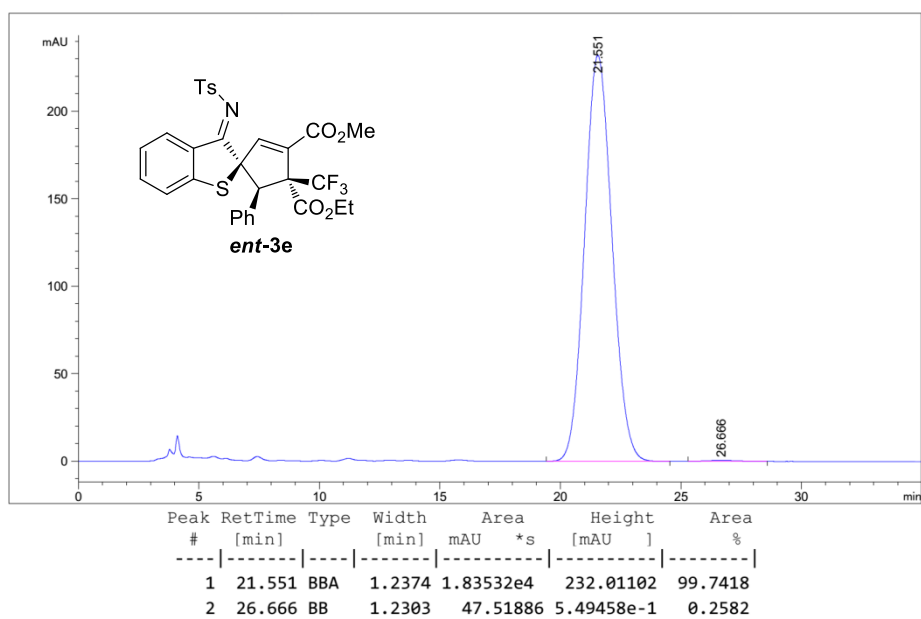
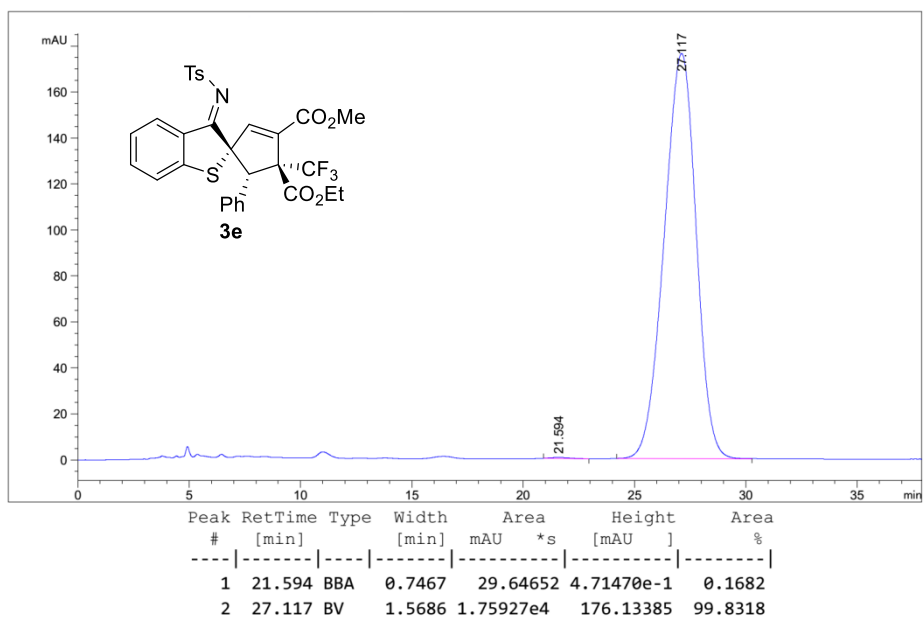
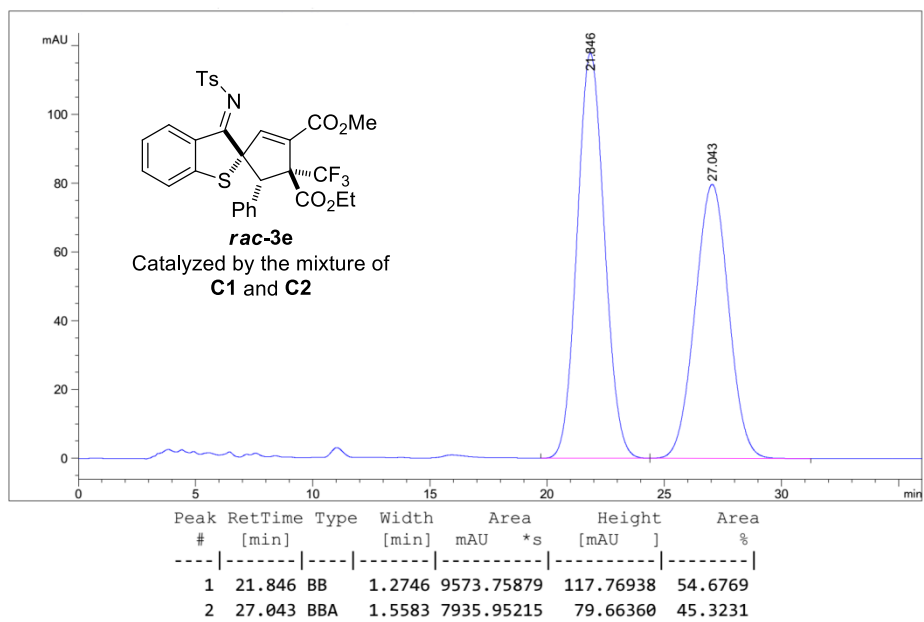


—66.456

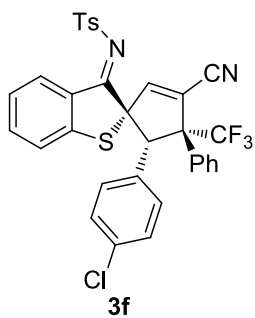


<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



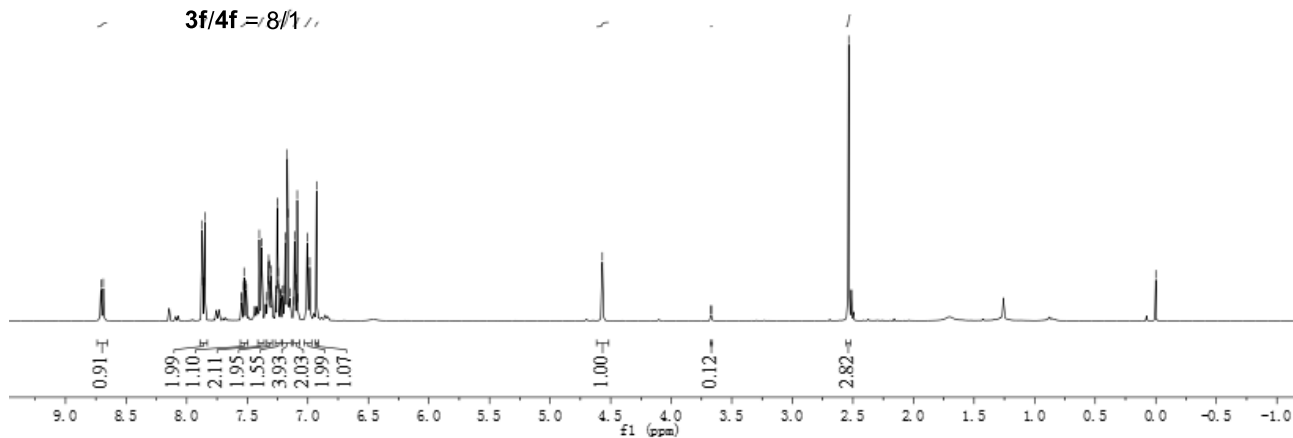


8.708  
8.688  
7.871  
7.867  
7.855  
7.851  
7.547  
7.544  
7.530  
7.527  
7.524  
7.509  
7.506  
7.400  
7.380  
7.336  
7.331  
7.323  
7.320  
7.314  
7.310  
7.302  
7.265  
7.263  
7.253  
7.247  
7.245  
7.242  
7.227  
7.224  
7.208  
7.192  
7.187  
7.170  
7.165  
7.148  
7.116  
7.109  
7.104  
7.093  
7.087  
7.081  
7.006  
6.985  
6.928  
4.569  
3.672  
3.668  
2.535  
0.000

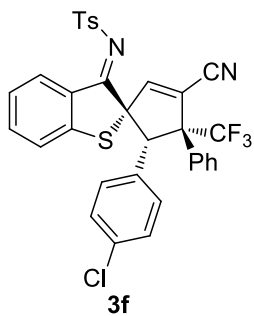


$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )

$3\text{f}/4\text{f} = 8/1$

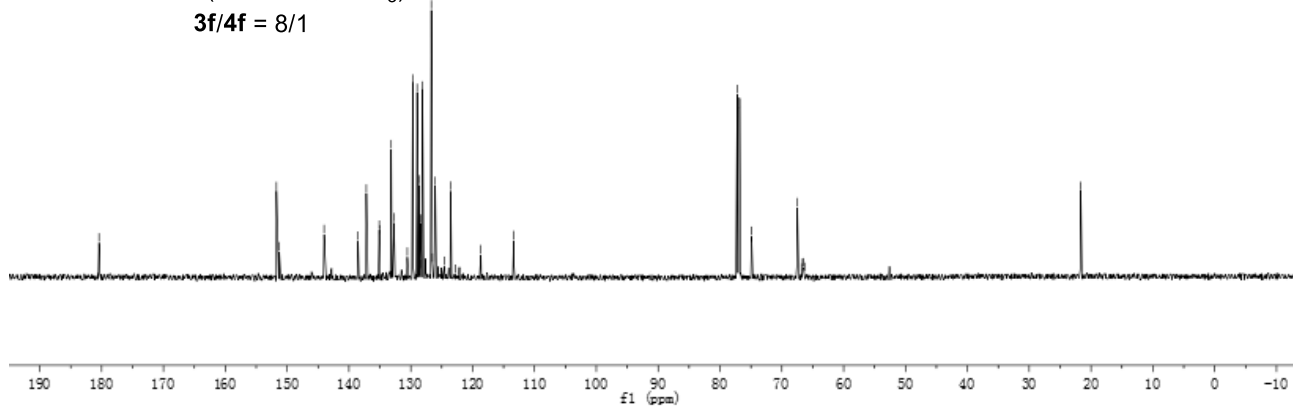


180.425  
151.729  
151.272  
144.023  
138.528  
137.193  
135.101  
135.037  
133.166  
132.711  
130.564  
129.683  
128.984  
128.663  
128.474  
128.418  
128.108  
126.686  
126.513  
126.051  
124.619  
123.544  
122.734  
118.662  
113.364  
77.212  
77.000  
76.788  
74.899  
67.491  
66.830  
66.659  
66.488  
66.319  
-21.654

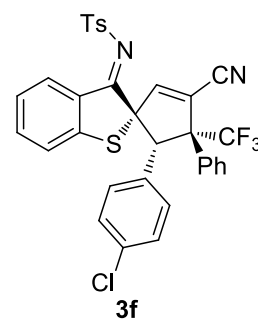


$^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )

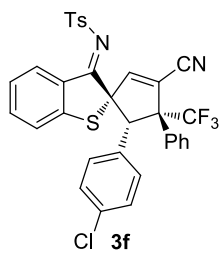
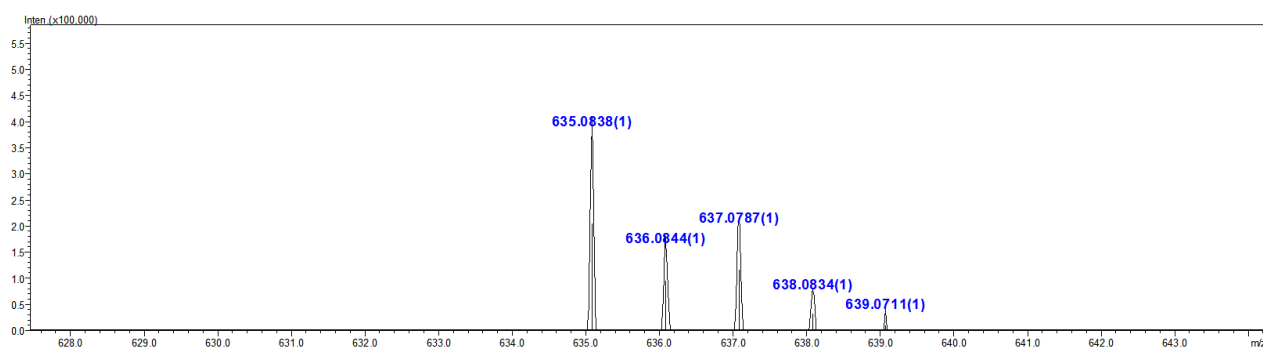
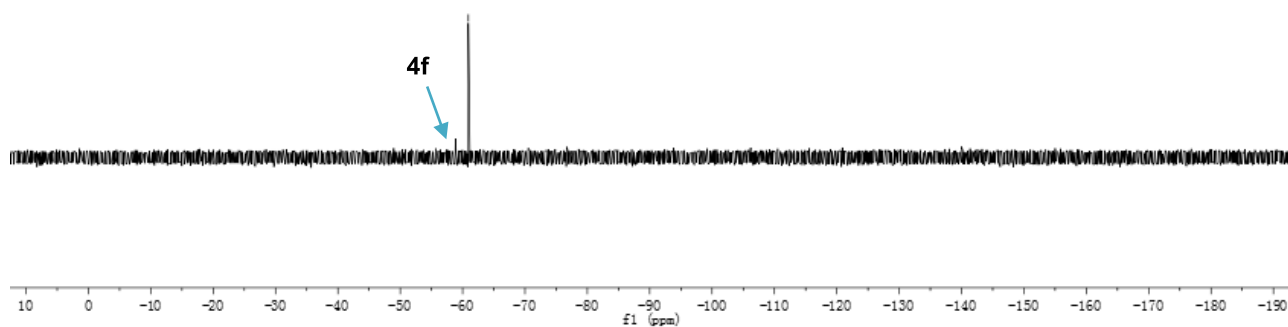
$3\text{f}/4\text{f} = 8/1$



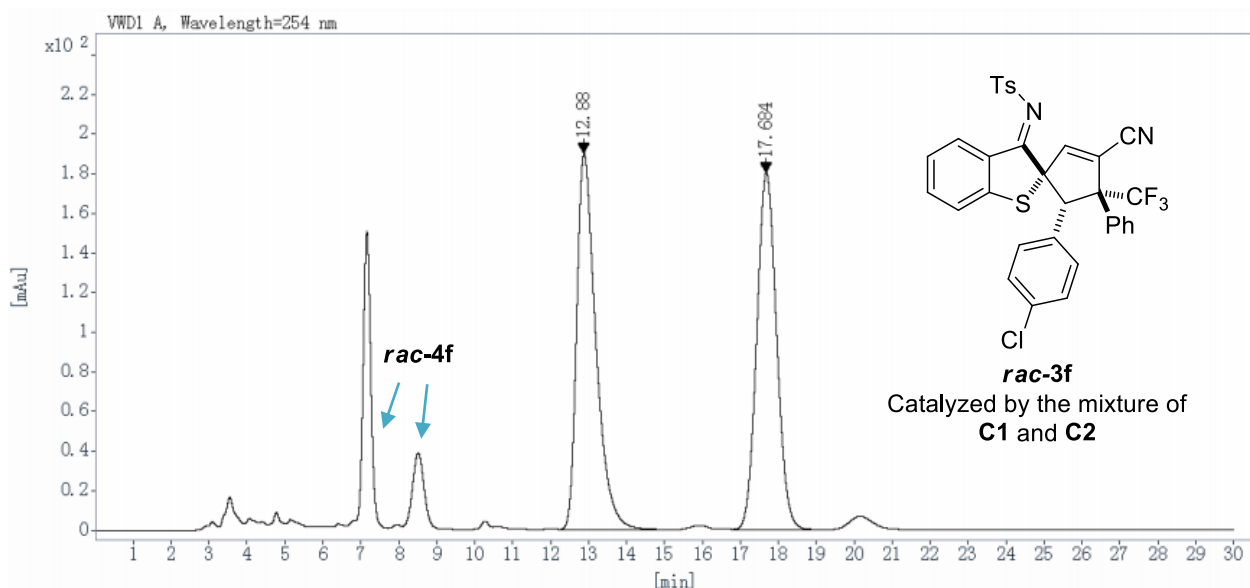
—60.915



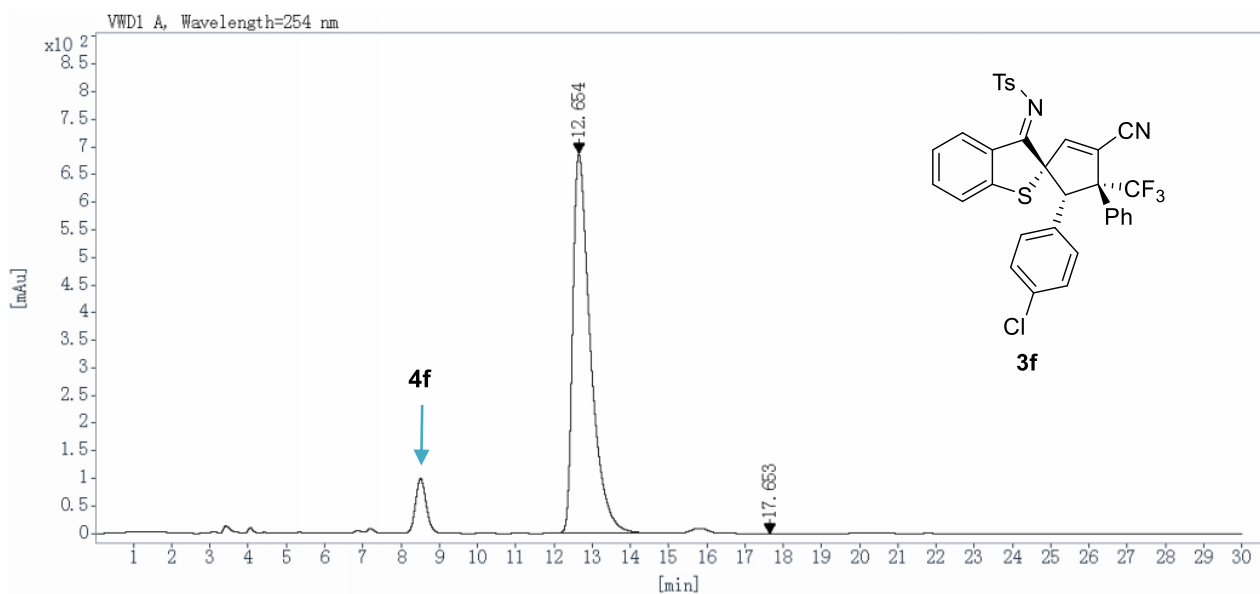
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  
 $3\text{f}/4\text{f} = 8/1$



HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$   
Calcd for  $\text{C}_{33}\text{H}_{23}^{35}\text{ClF}_3\text{N}_2\text{O}_2\text{S}_2^+$  635.0836  
Calcd for  $\text{C}_{33}\text{H}_{23}^{37}\text{ClF}_3\text{N}_2\text{O}_2\text{S}_2^+$  637.0807

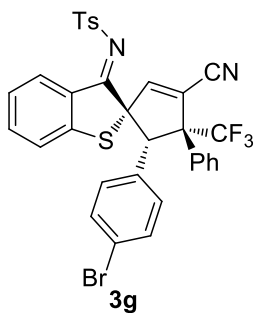


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
12.880	BBA	0.53	189.6992	6645.6851	50.4622
17.684	BB	0.56	180.2429	6523.9380	49.5378

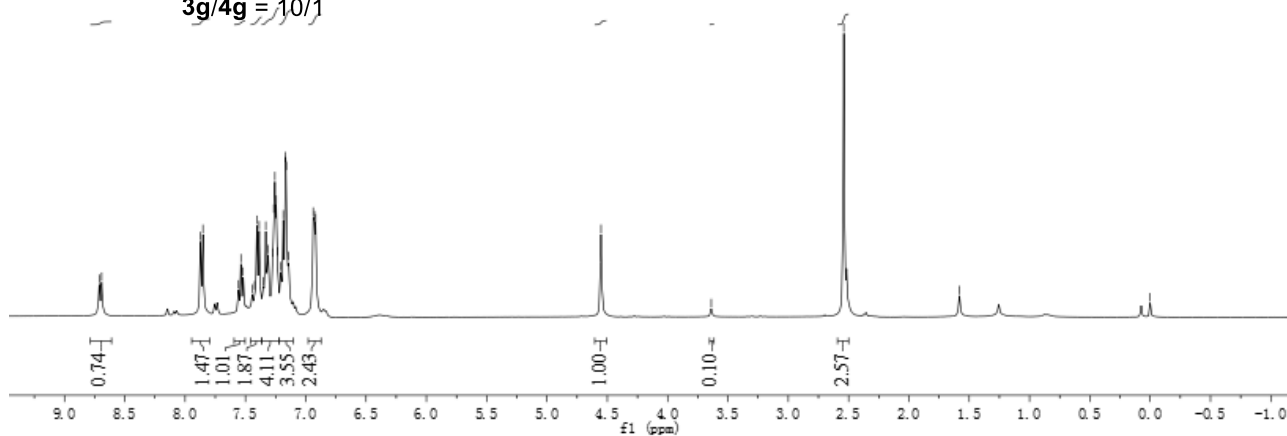


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
12.654	BB	0.48	686.8723	22067.1250	99.9999
17.653	BB	0.05	0.0038	0.0148	0.0001
Totals:				22067.1398	100.0000

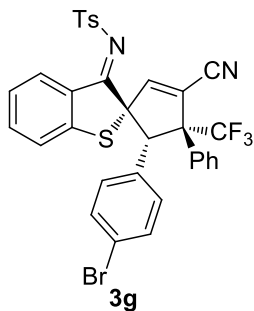
8.712, 8.692, 7.872, 7.853, 7.557, 7.538, 7.519, 7.443, 7.424, 7.406, 7.386, 7.352, 7.332, 7.311, 7.275, 7.265, 7.256, 7.244, 7.235, 7.207, 7.187, 7.168, 7.161, 7.142, 6.938, 6.927, 6.918, 4.552, -3.638, -2.540, -1.582, -0.000



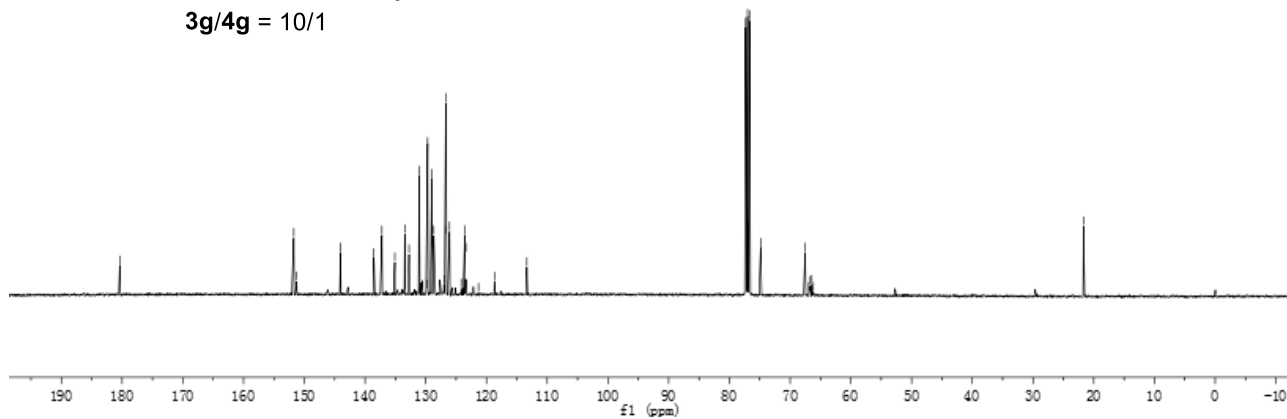
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  
 $3\text{g}/4\text{g} = 10/1$



180.392, 151.734, 151.268, 144.037, 138.541, 137.219, 135.098, 133.461, 132.749, 131.091, 129.826, 129.694, 129.000, 128.961, 128.679, 126.988, 126.726, 126.698, 126.085, 124.153, 123.561, 123.410, 121.314, 118.674, 113.355, 77.318, 77.000, 76.682, 74.843, 67.530, 66.939, 66.687, 66.431, 66.176, -21.669

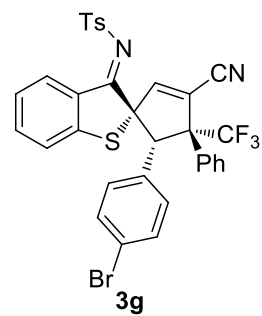


$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  
 $3\text{g}/4\text{g} = 10/1$

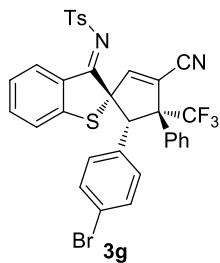
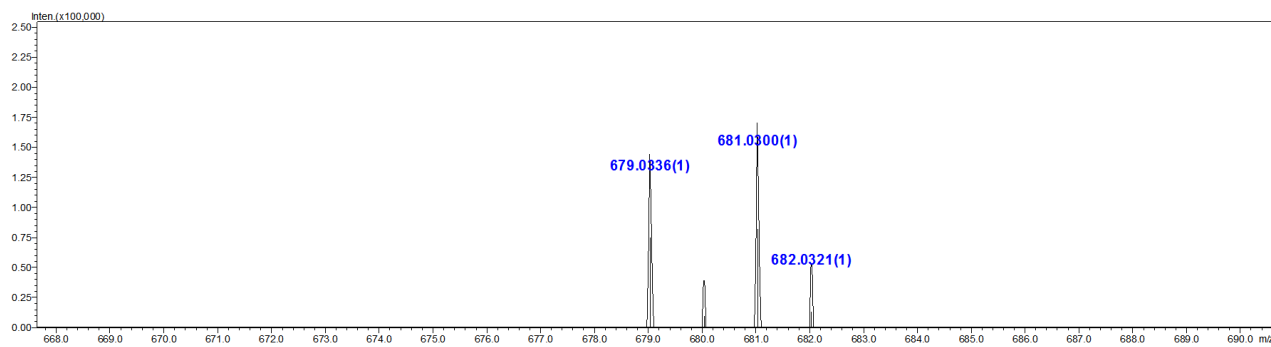
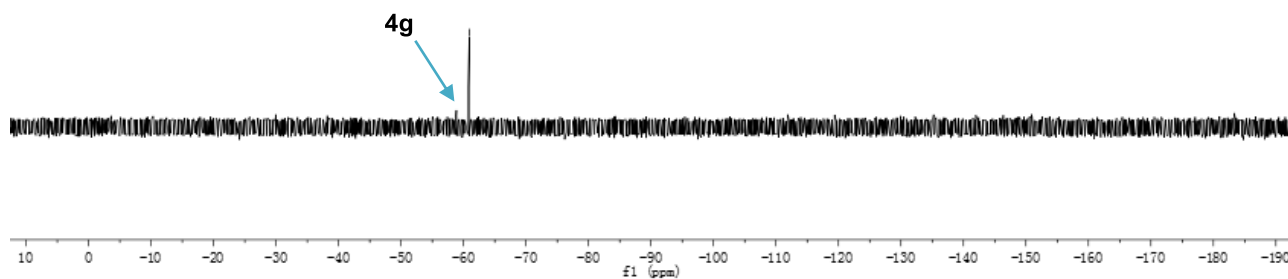




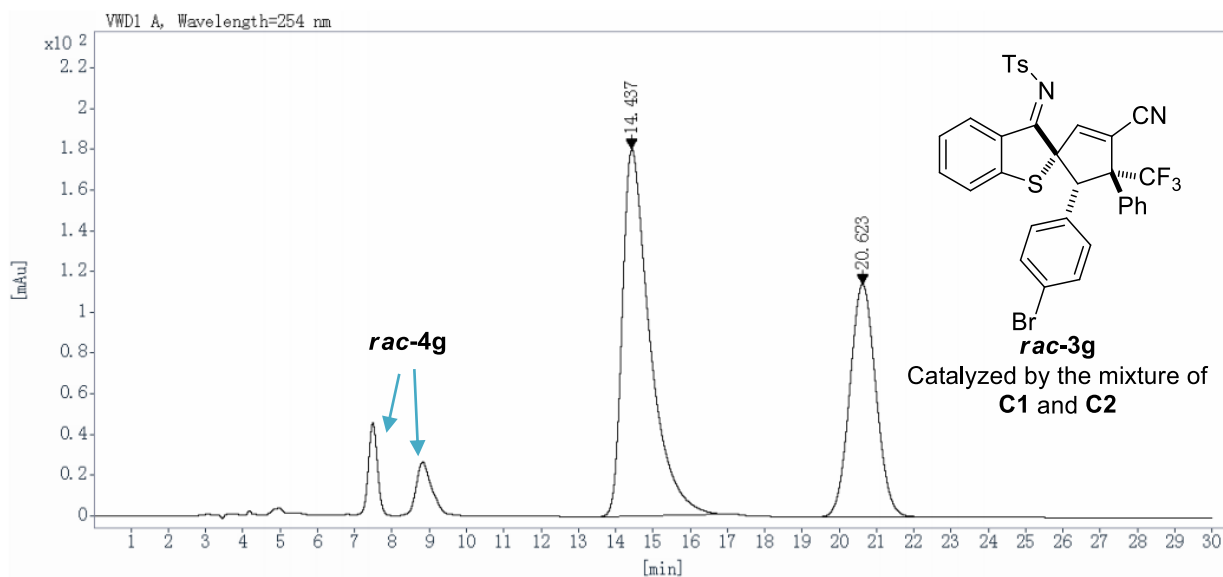
--60.912



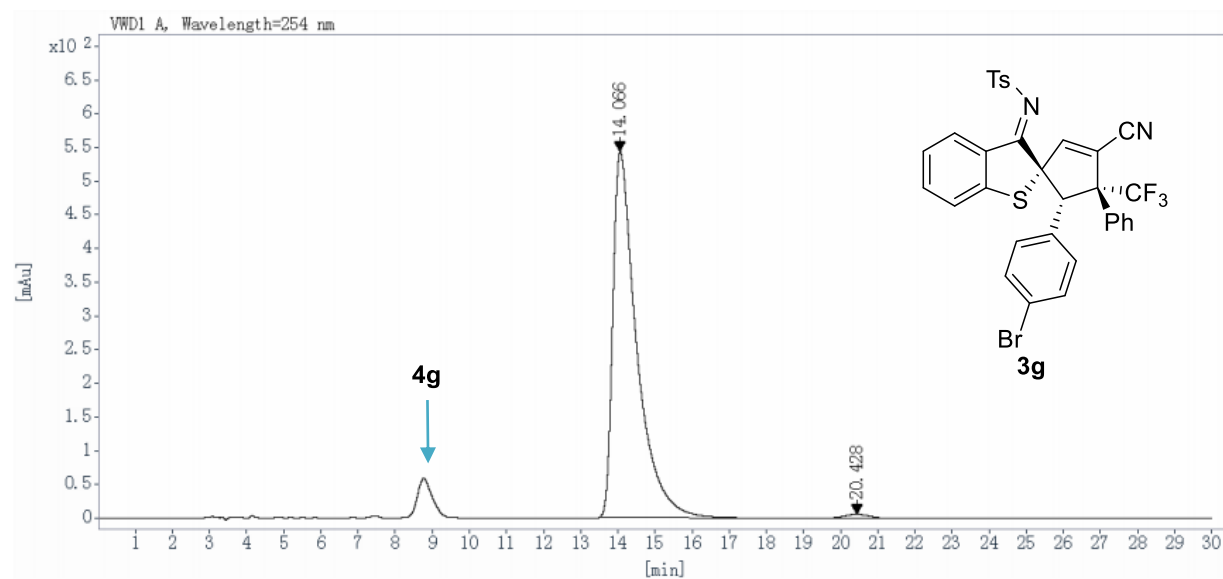
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  
**3g/4g = 10/1**



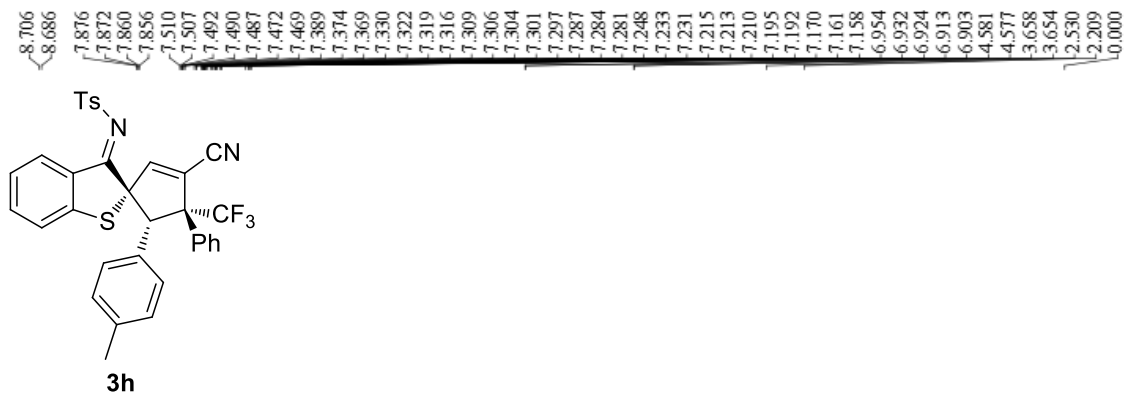
HRMS (ESI-TOF) m/z: [M + H]<sup>+</sup>  
Calcd for C<sub>33</sub>H<sub>23</sub><sup>79</sup>BrF<sub>3</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup> 679.0331  
Calcd for C<sub>33</sub>H<sub>23</sub><sup>81</sup>BrF<sub>3</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup> 681.0310



Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
14.437	BB	0.76	180.2025	9231.7256	62.3710
20.623	BB	0.76	114.4708	5569.5894	37.6290

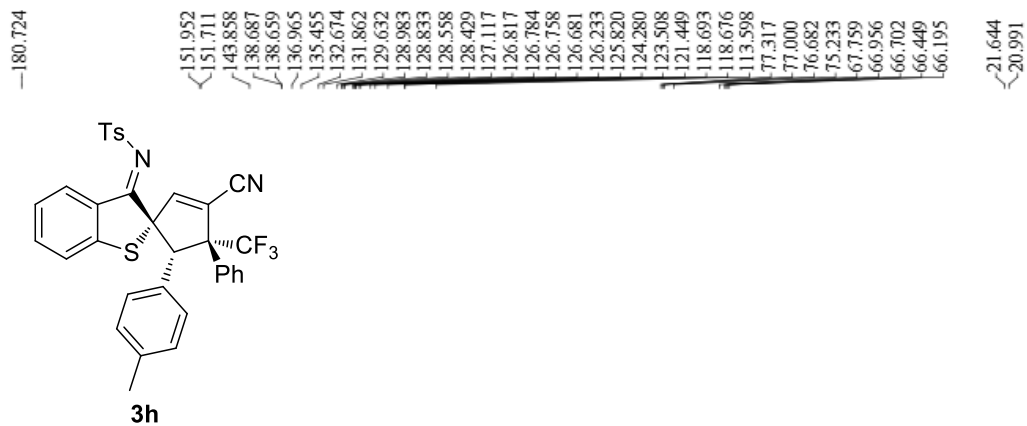
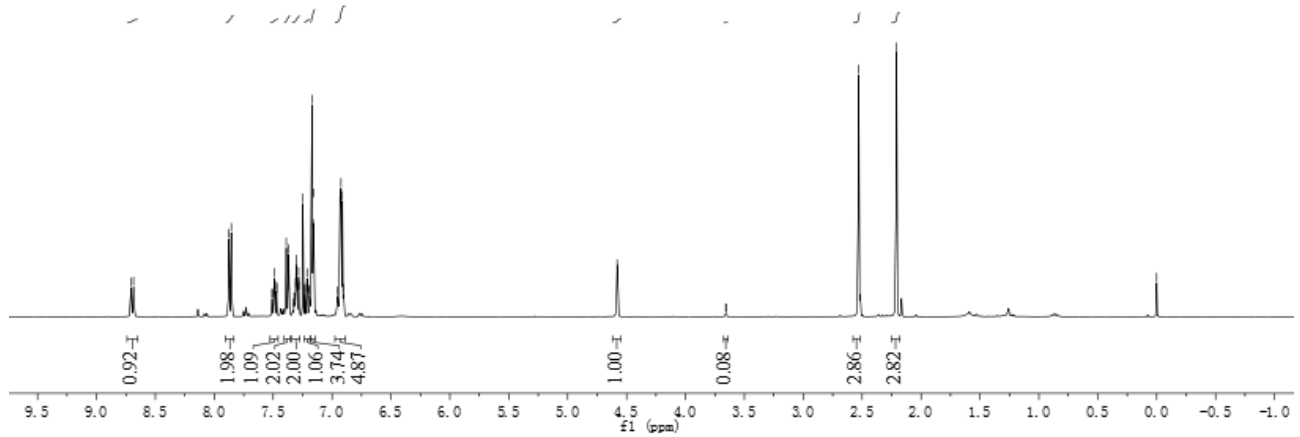


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
14.066	BB	0.65	542.4650	24281.6563	98.8182
20.428	BB	0.72	6.0932	290.4020	1.1818



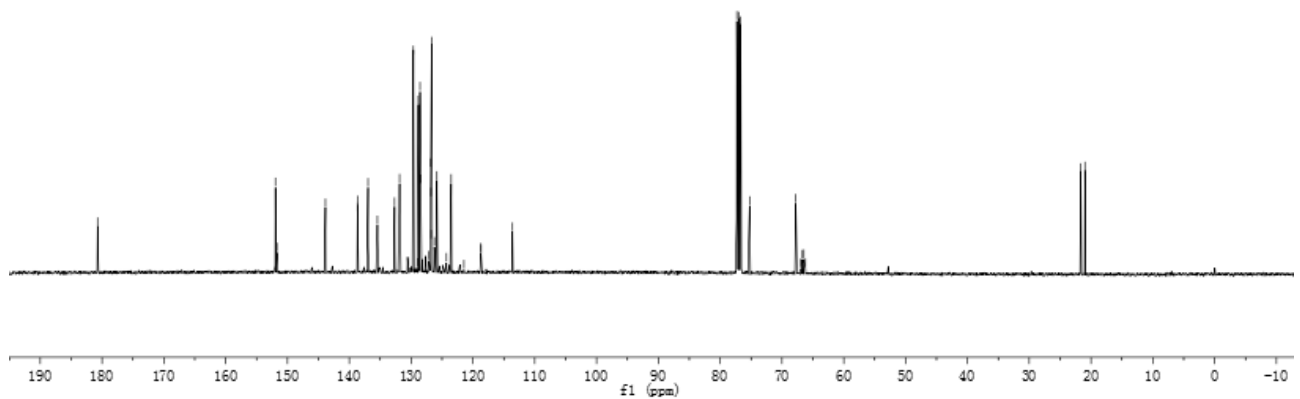
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )

**3h/4h** = 13/1

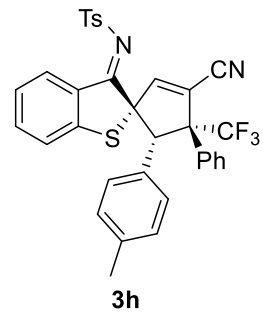


$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

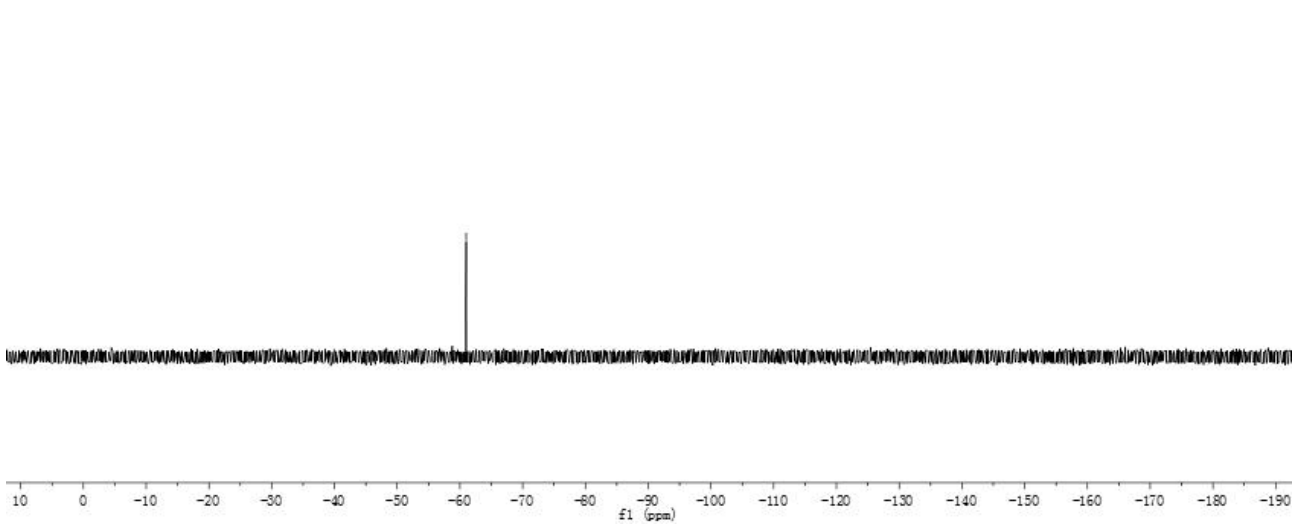
**3h/4h** = 13/1



---60.999

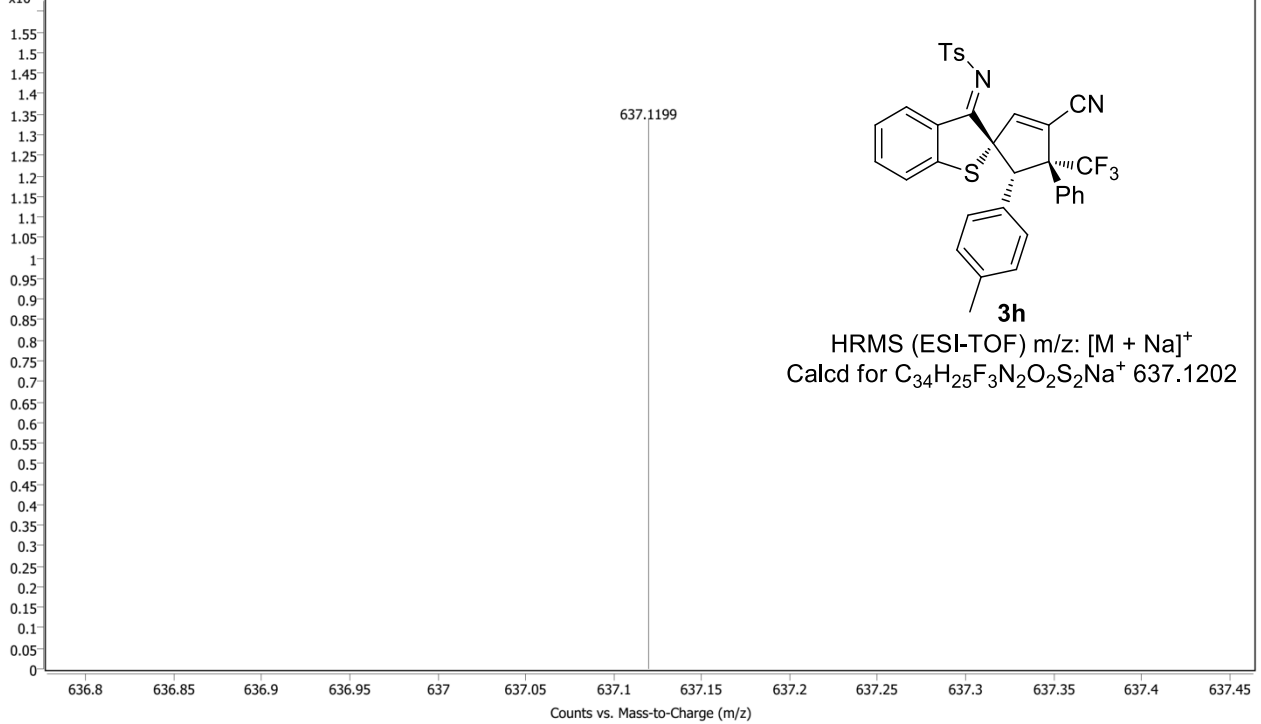


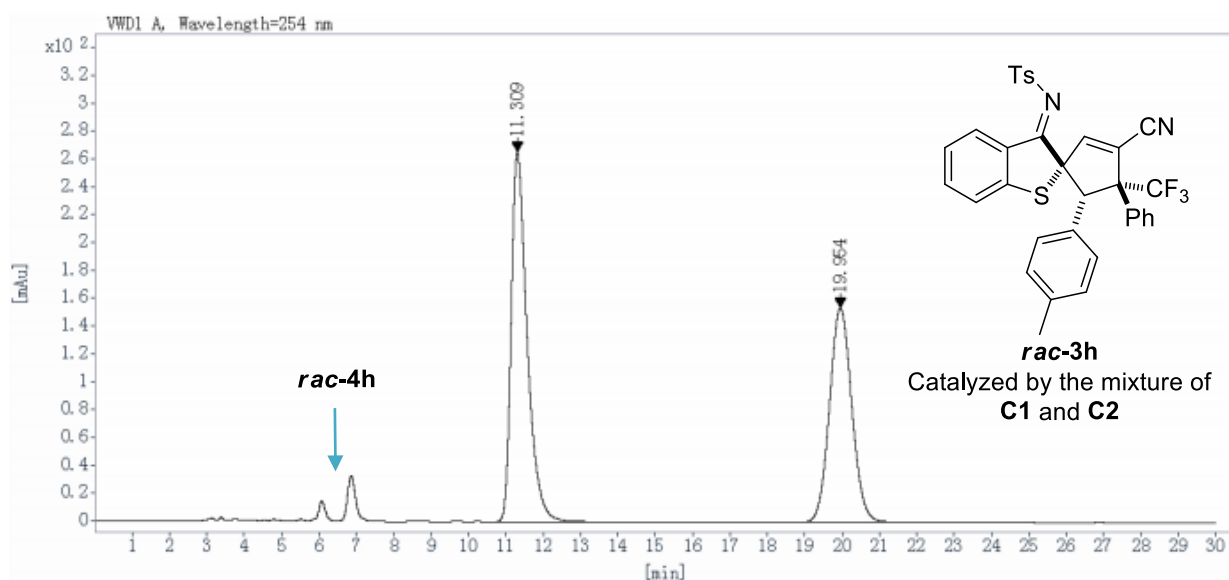
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



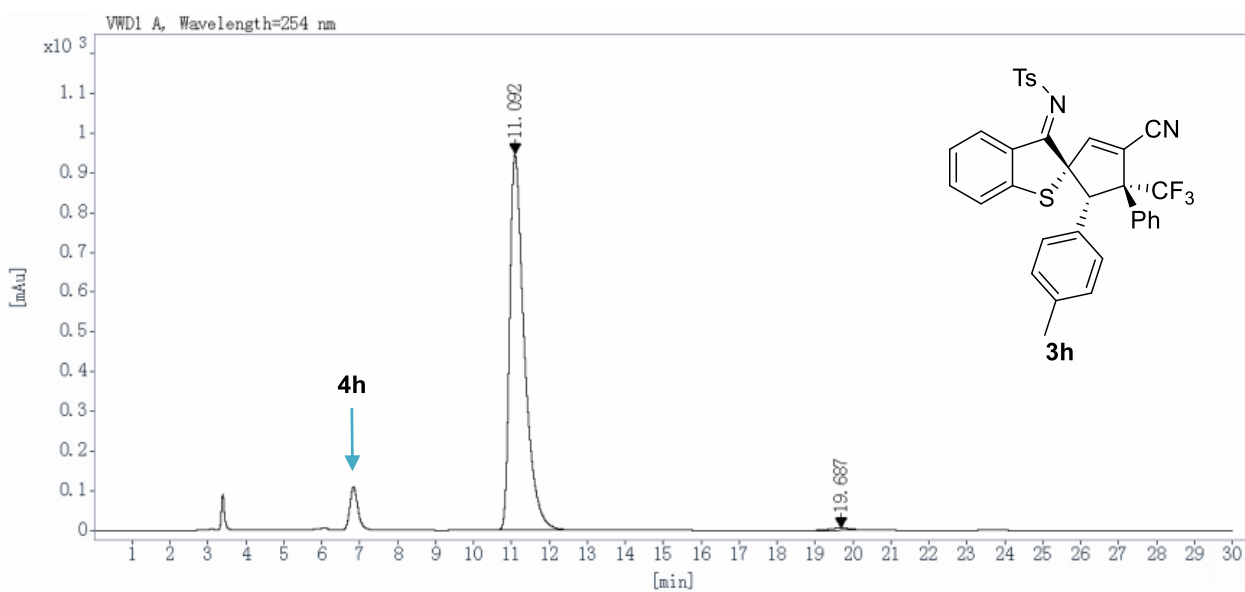
Name	cyc-190705-3	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	WorklistData-0003-r002.d	Method (Acq)	TOF.m	Comment	Acq. Time (Local) 7/9/2019 1:40:00 PM (UTC+08:00)

+ESI Scan (rt: 1.858 min) Frag=175.0V WorklistData-0003-r002.d



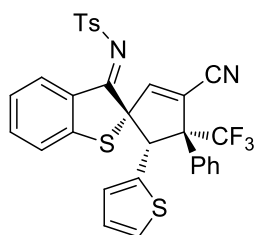


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
11.309	BB	0.44	265.2004	7819.3813	55.1875
19.954	BB	0.64	153.4943	6349.3857	44.8125



Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
11.092	BB	0.40	947.5350	25425.9707	99.1525
19.687	BB	0.57	5.9174	217.3207	0.8475

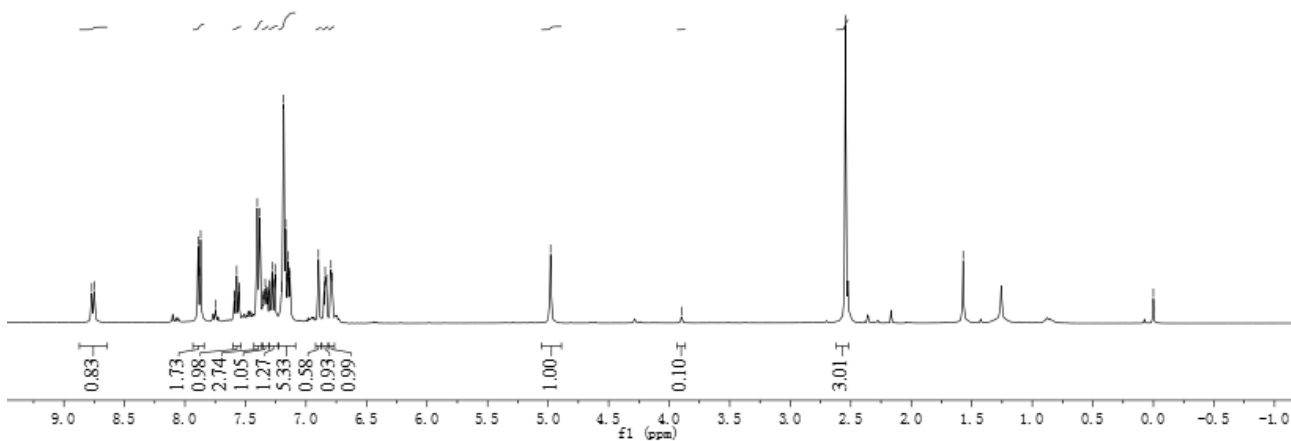
8.770  
8.749  
7.891  
7.875  
7.870  
7.747  
7.593  
7.590  
7.573  
7.555  
7.552  
7.402  
7.382  
7.357  
7.352  
7.344  
7.336  
7.330  
7.326  
7.320  
7.315  
7.301  
7.298  
7.281  
7.262  
7.256  
7.203  
7.185  
7.168  
7.161  
7.146  
7.134  
7.131  
6.897  
6.851  
6.842  
6.838  
6.829  
6.793  
6.784  
4.980  
3.898  
2.544  
-1.571  
-0.000



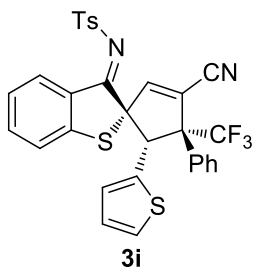
**3i**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

**3i/4i = 10/1**



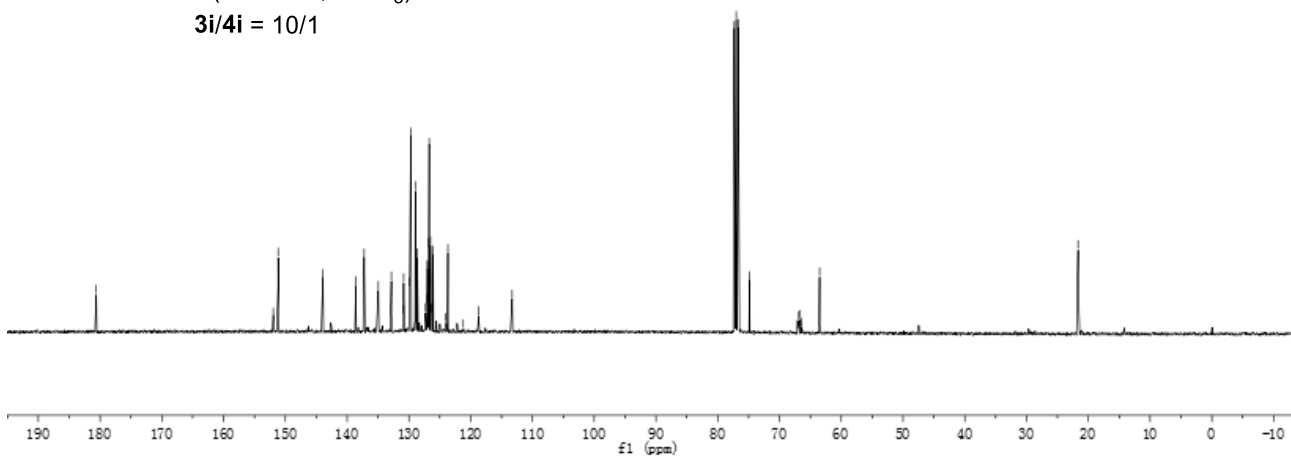
-180.615  
151.956  
151.171  
143.911  
138.595  
137.236  
134.945  
132.836  
130.932  
130.842  
129.881  
129.680  
128.964  
128.636  
127.306  
127.018  
126.995  
126.971  
126.945  
126.851  
126.807  
126.710  
126.509  
126.325  
126.078  
124.018  
123.679  
121.188  
118.704  
113.273  
77.317  
77.000  
76.682  
74.850  
67.133  
66.883  
66.632  
66.382  
63.499  
21.660



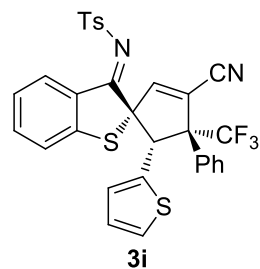
**3i**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

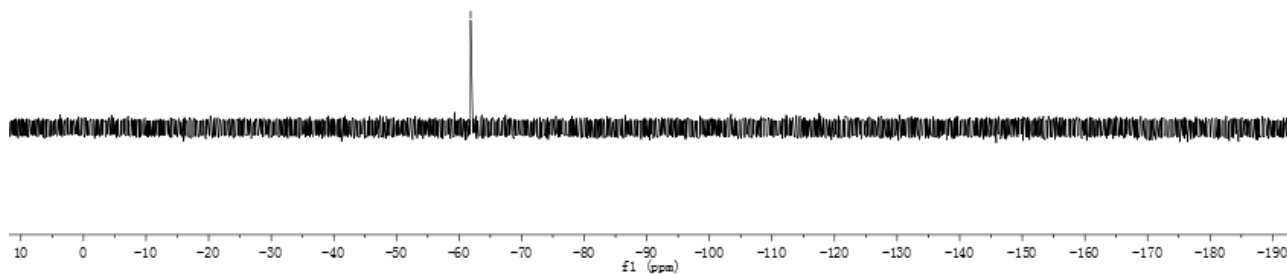
**3i/4i = 10/1**



-61.853

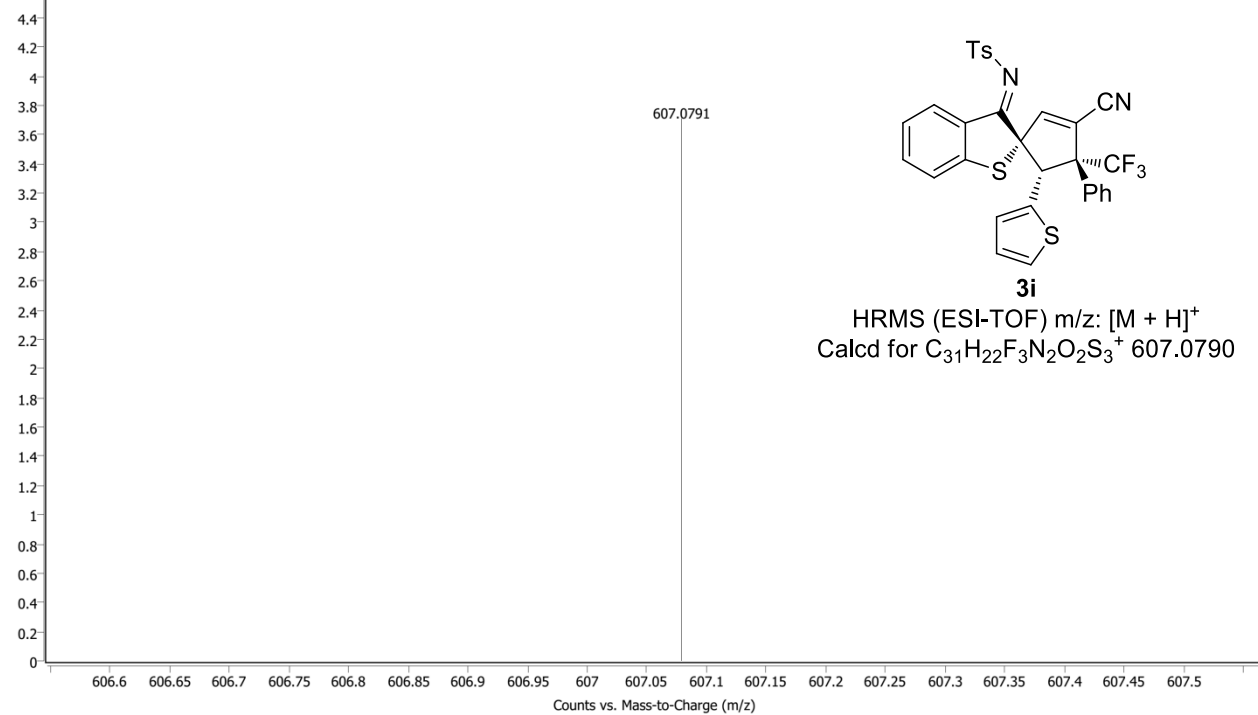


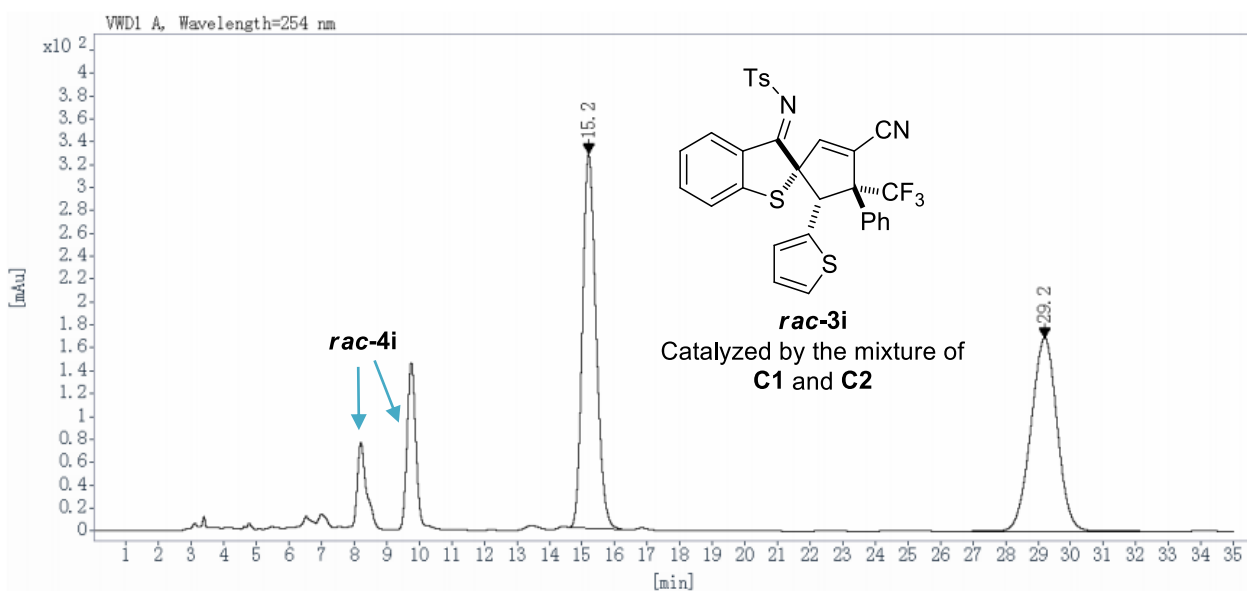
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  
**3i/4i** = 10/1



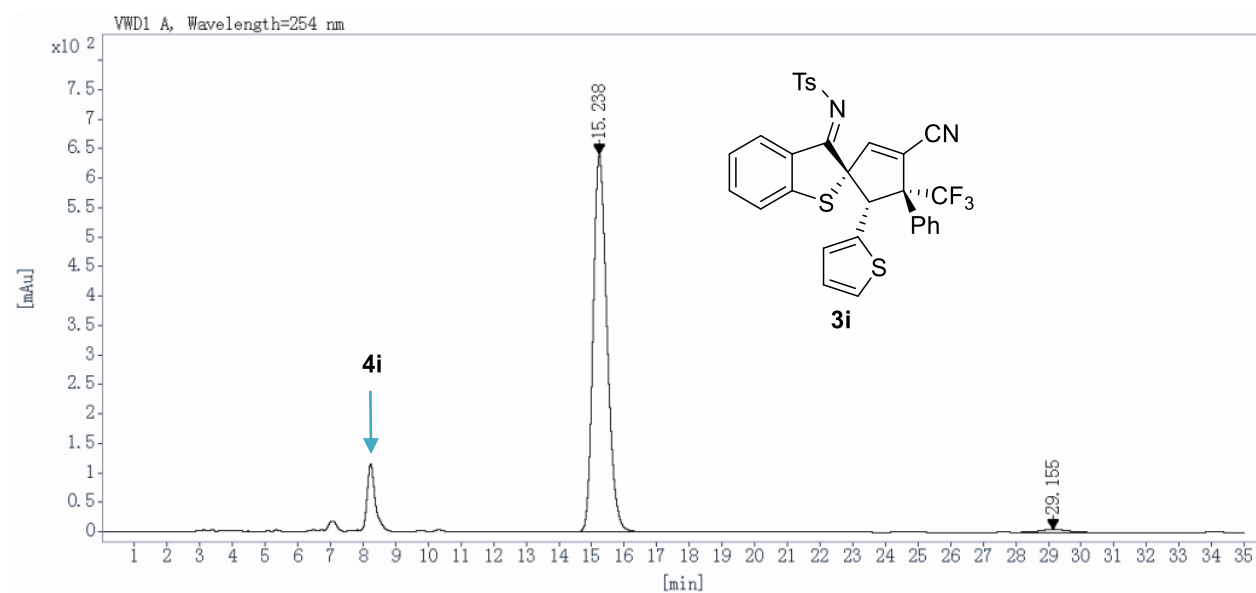
Name	cyc-12-16	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	cyc-12-16.d	Method (Acq)	TOF.m	Comment	Acq. Time (Local) 7/22/2019 6:01:30 PM (UTC+08:00)

x10<sup>5</sup> +ESI Scan (rt: 1.040 min) Frag=175.0V cyc-12-16.d





Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
15.200	BBA	0.45	326.4763	9453.3213	50.0033
29.200	BB	0.87	168.8473	9452.0586	49.9967



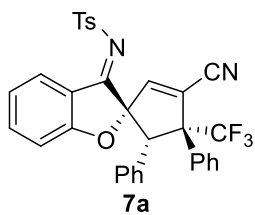
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
15.238	BB	0.46	639.6916	18913.2598	98.6540
29.155	BB	0.80	4.7092	258.0514	1.3460



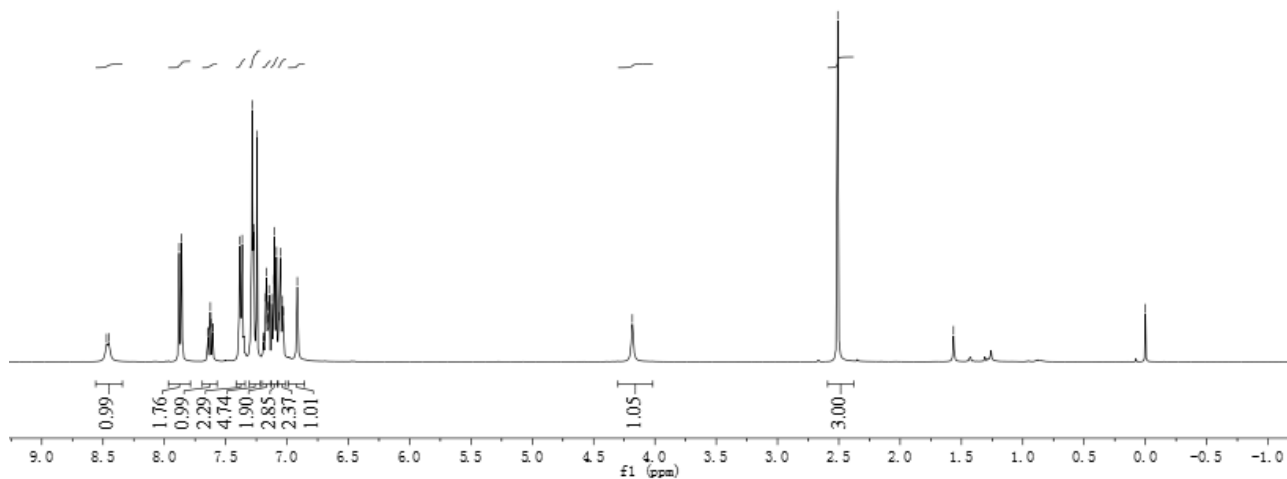
8.472  
8.452  
7.880  
7.859  
7.646  
7.643  
7.629  
7.625  
7.622  
7.607  
7.604  
7.386  
7.366  
7.285  
7.276  
7.272  
7.246  
7.193  
7.189  
7.181  
7.175  
7.168  
7.160  
7.157  
7.153  
7.147  
7.122  
7.108  
7.103  
7.086  
7.068  
7.055  
7.036  
7.032  
6.916  
4.184  
2.509

-1.565

-0.000

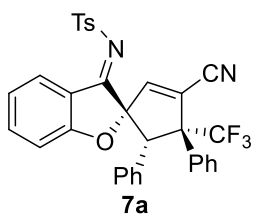


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

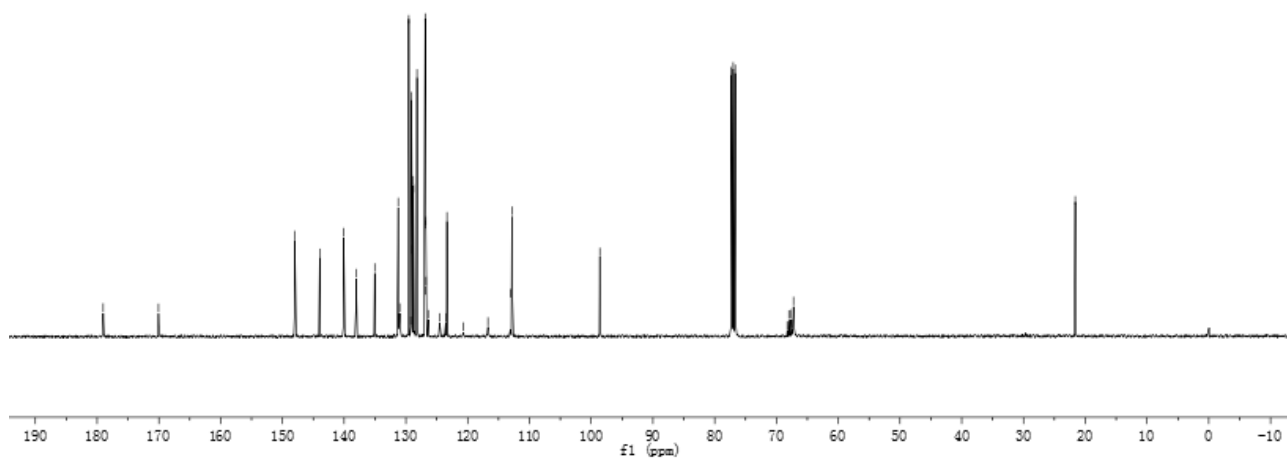


179.009  
170.063  
147.989  
143.950  
140.071  
138.061  
135.048  
131.243  
131.003  
129.531  
129.227  
129.097  
128.996  
128.800  
128.772  
128.207  
126.884  
126.817  
126.789  
126.765  
126.740  
126.391  
124.538  
123.556  
123.357  
120.721  
116.722  
113.052  
112.836  
98.601  
77.318  
77.000  
76.682  
68.254  
67.994  
67.737  
67.477  
67.242

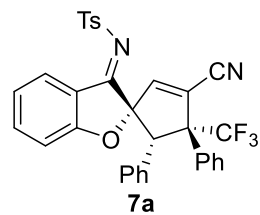
-21.621



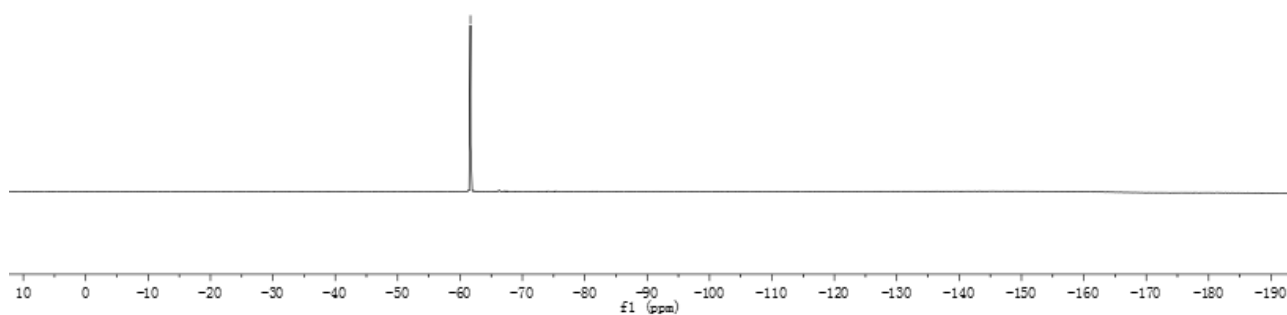
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



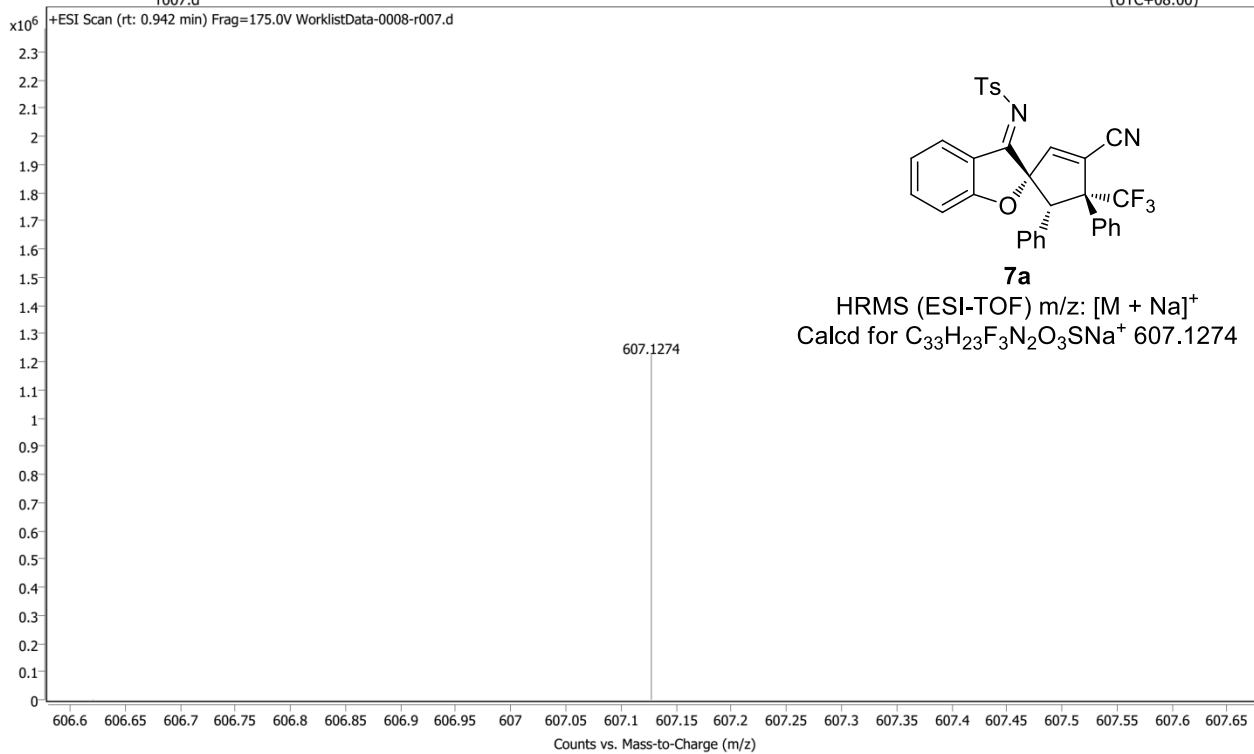
61.672

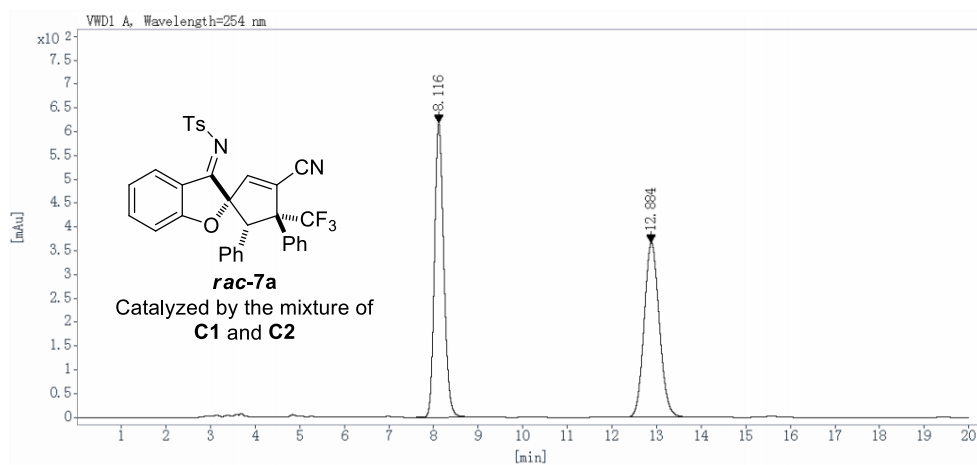


<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)

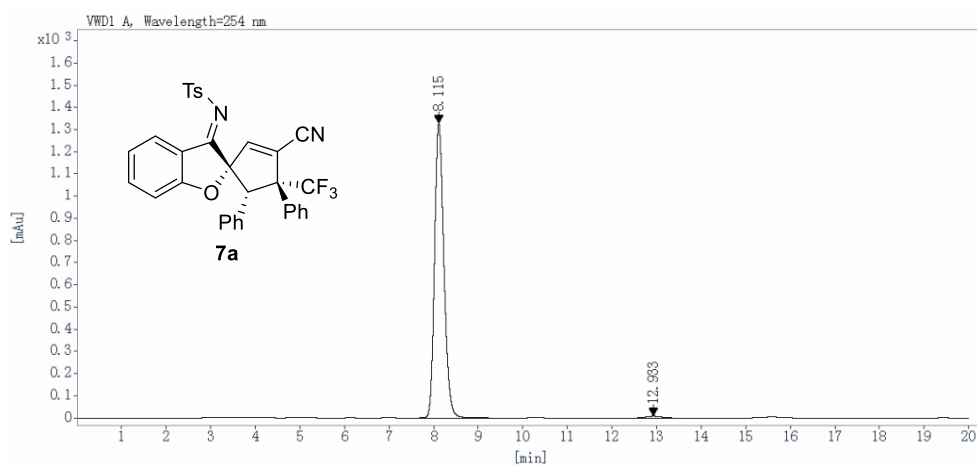


Name	cyc-190705-8	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	WorklistData-0008-r007.d	Method (Acq)	TOF.m	Comment	Acq. Time (Local) 7/9/2019 1:54:05 PM (UTC+08:00)

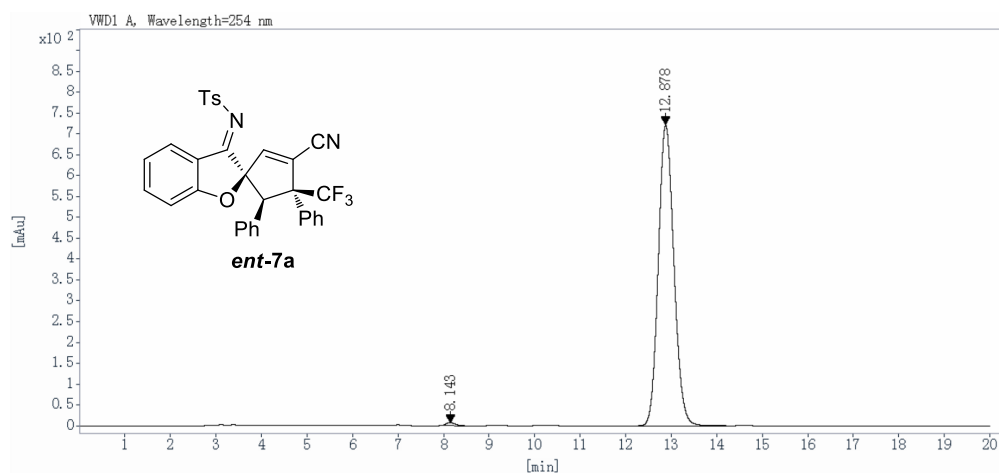




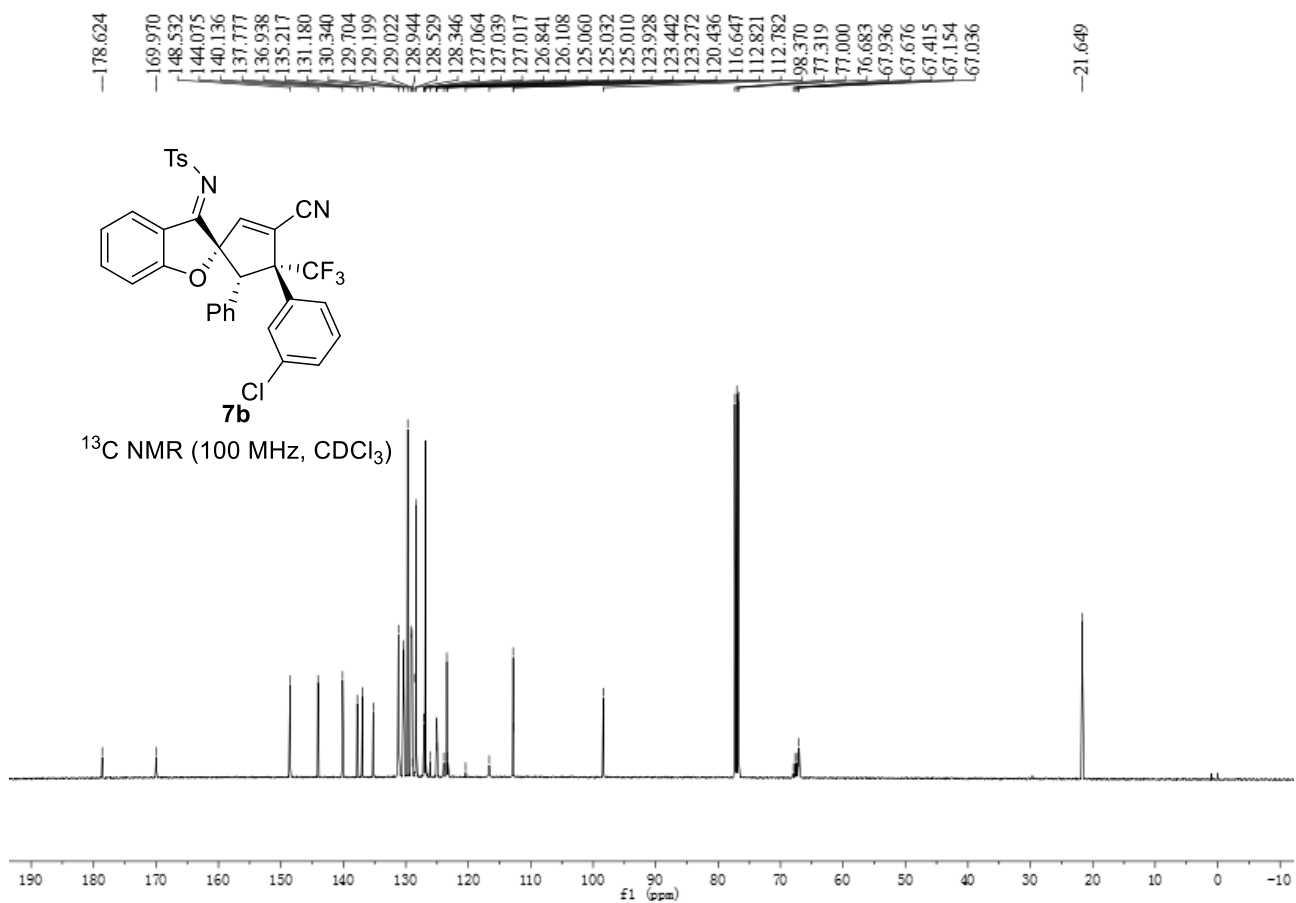
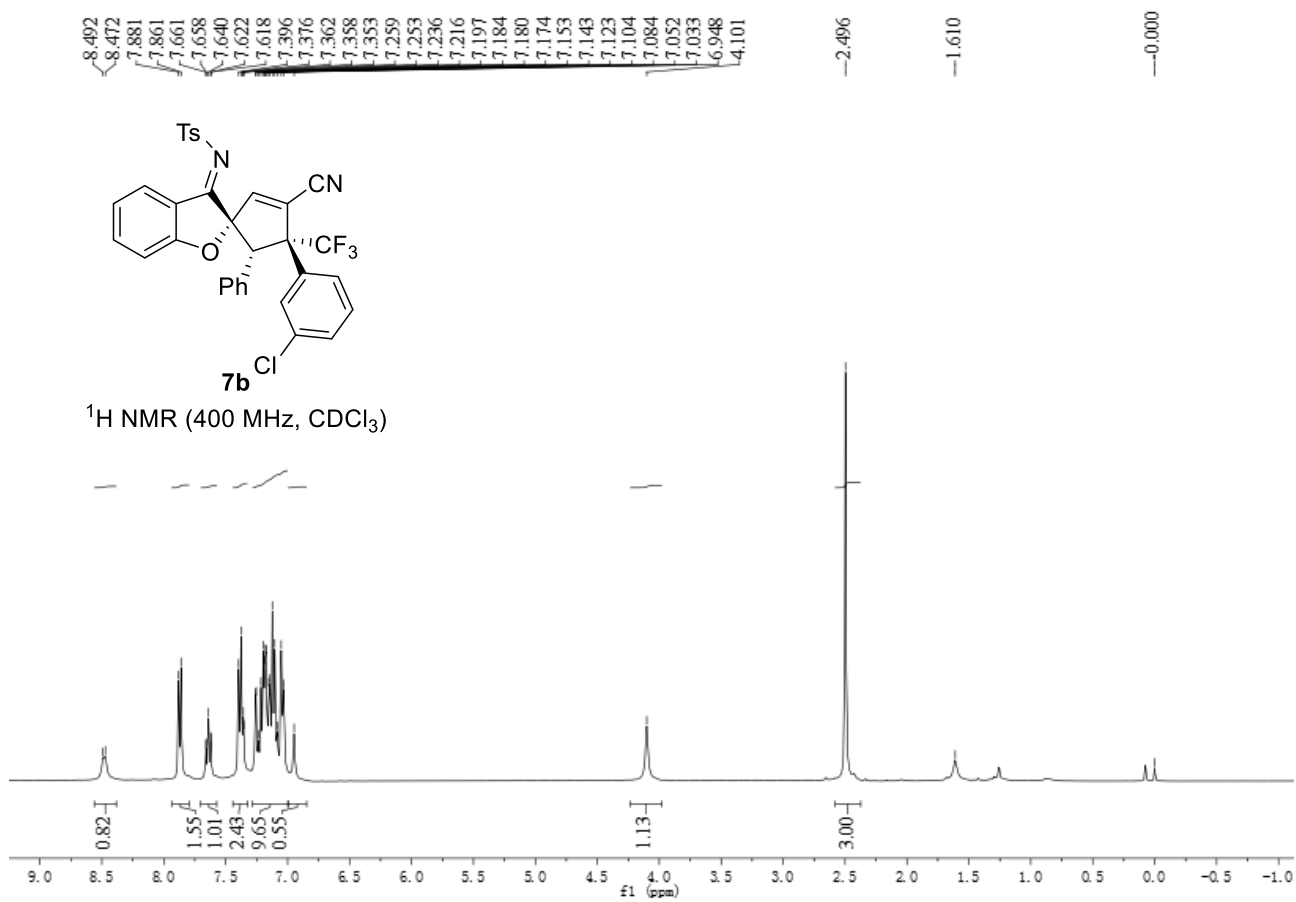
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
8.116	BB	0.22	617.3583	8912.1582	50.6220
12.884	BB	0.37	366.8416	8693.1621	49.3780



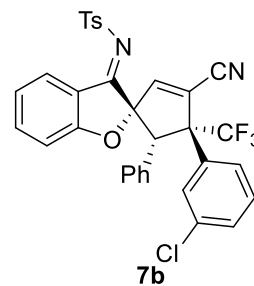
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
8.115	BB	0.22	1327.4924	19318.6309	99.0214
12.933	BB	0.38	7.8879	190.9203	0.9786



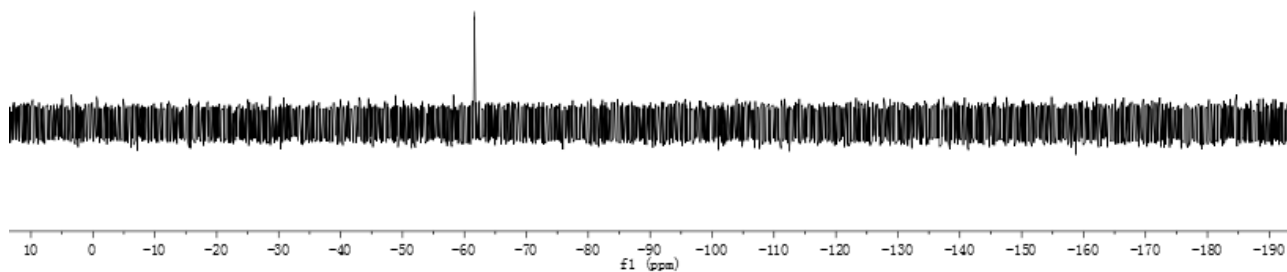
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
8.143	BB	0.22	7.6189	107.0719	0.6228
12.878	BB	0.37	721.1548	17084.2031	99.3772



-61.623

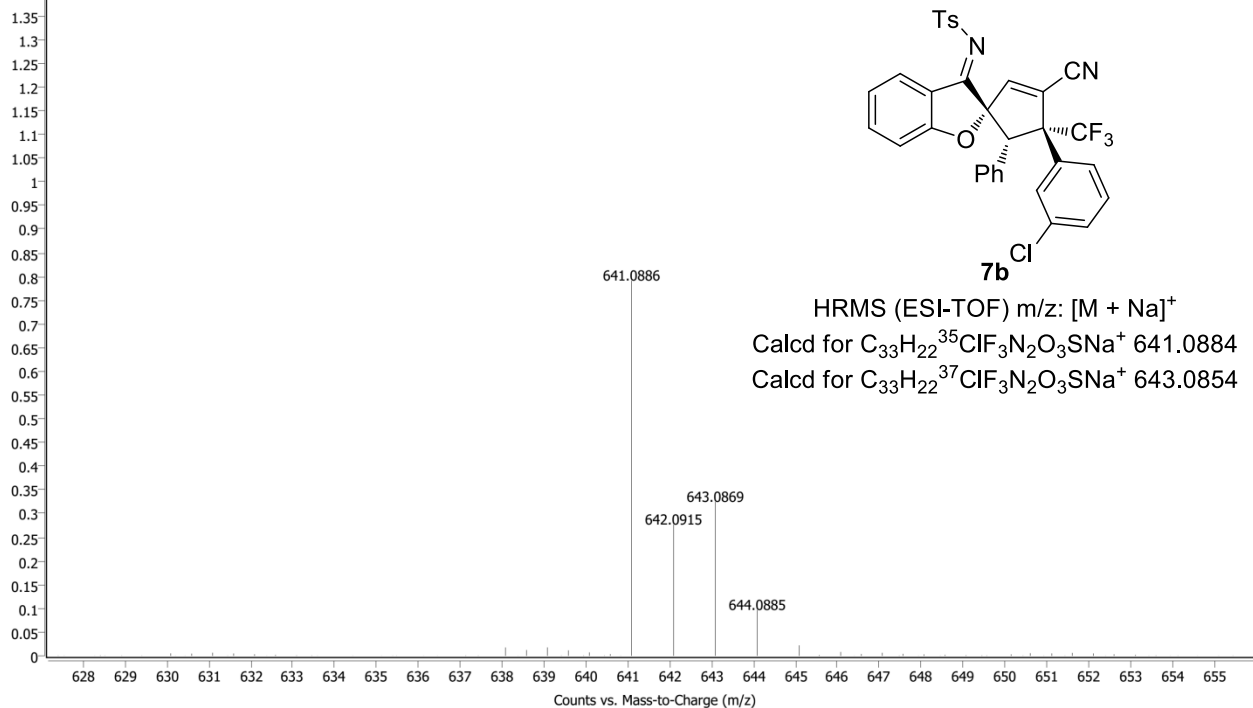


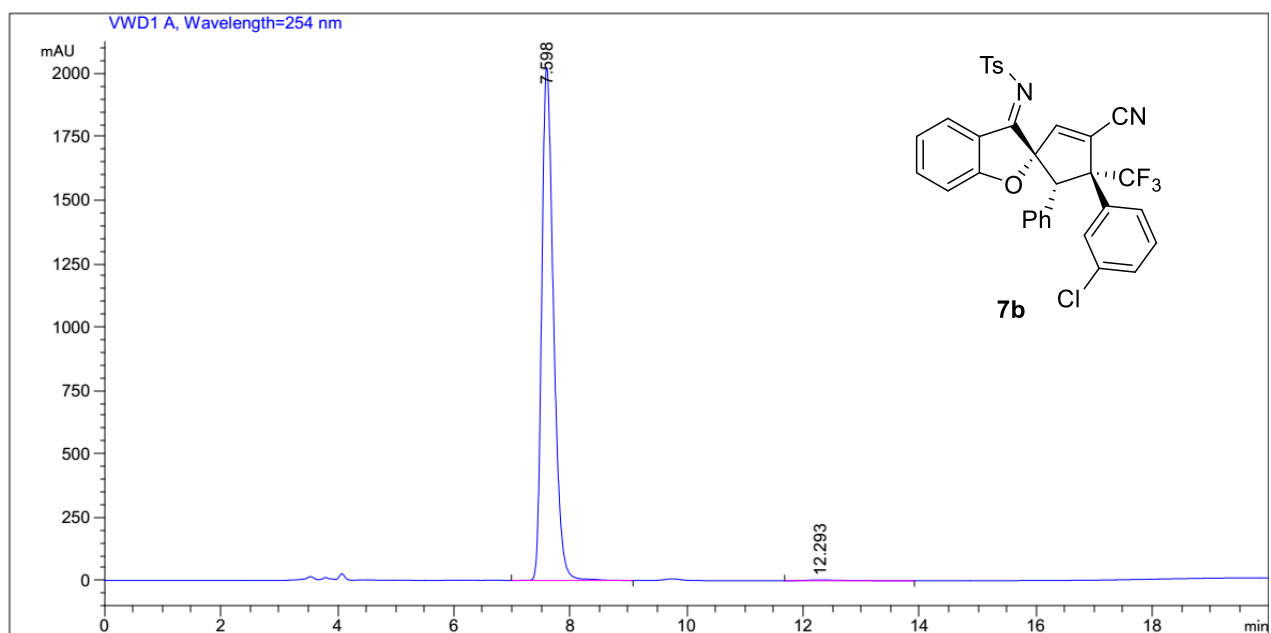
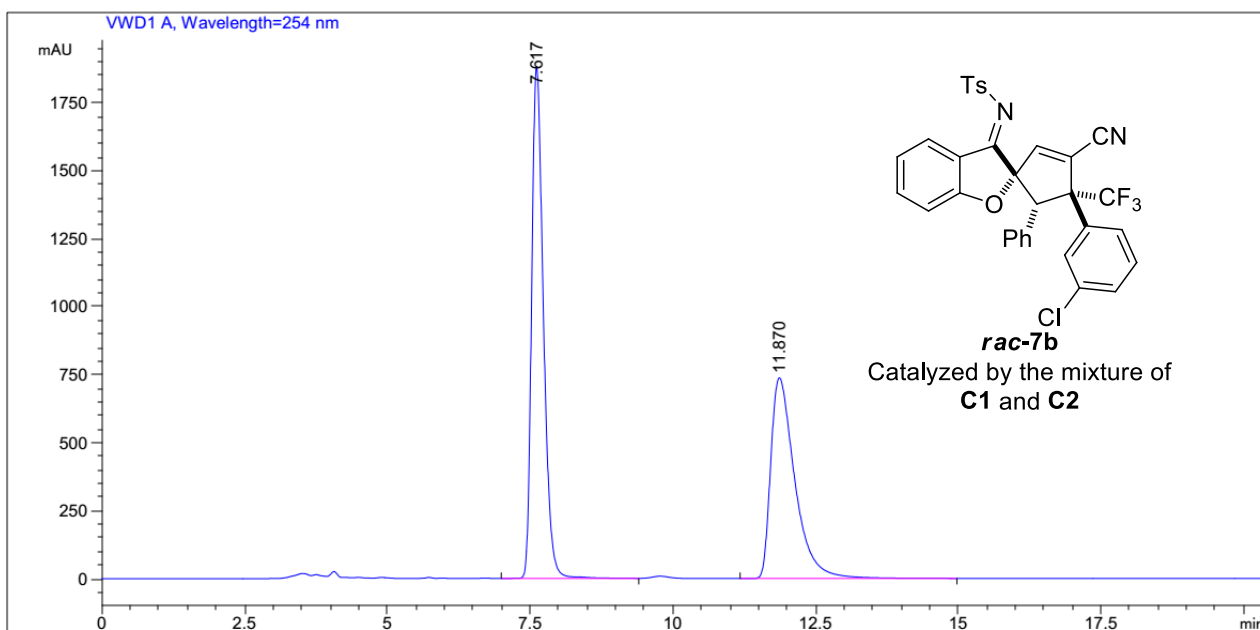
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



Name	cyc-190705-23	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	WorklistData-0023-r012.d	Method (Acq)	TOF.m		Acq. Time (Local) 7/9/2019 2:36:19 PM (UTC+08:00)

+ESI Scan (rt: 1.416 min) Frag=175.0V WorklistData-0023-r012.d





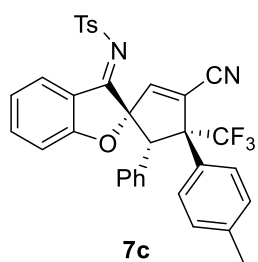
8.468  
8.447  
7.888  
7.868  
7.646  
7.626  
7.607  
7.396  
7.376  
7.248  
7.191  
7.166  
7.145  
7.124  
7.105  
7.087  
7.066  
7.046  
6.892

-4.162

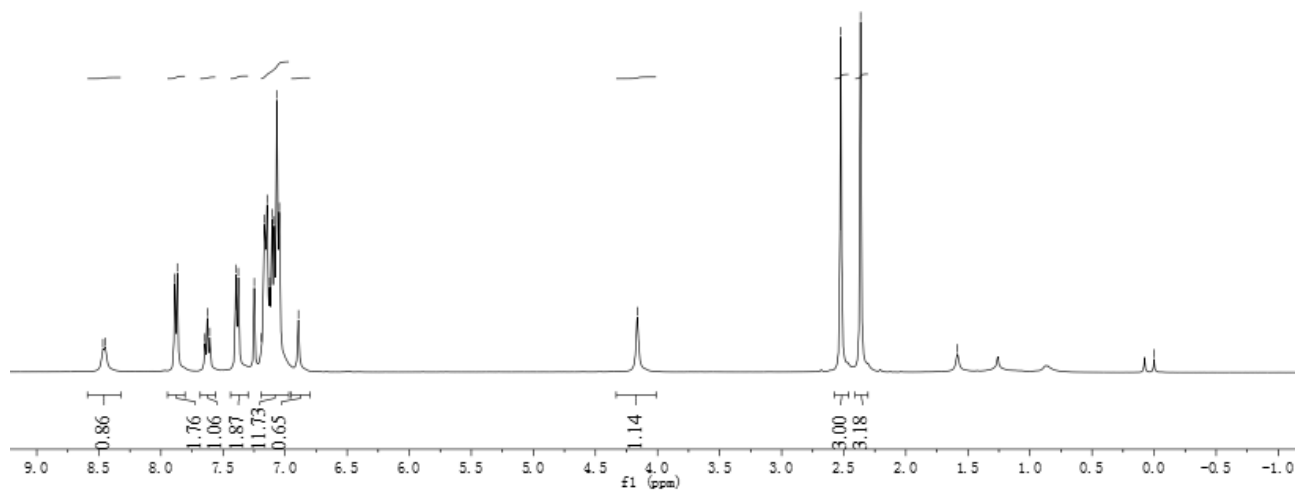
-2.524  
-2.364

-1.584

-0.000

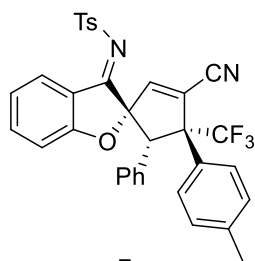


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

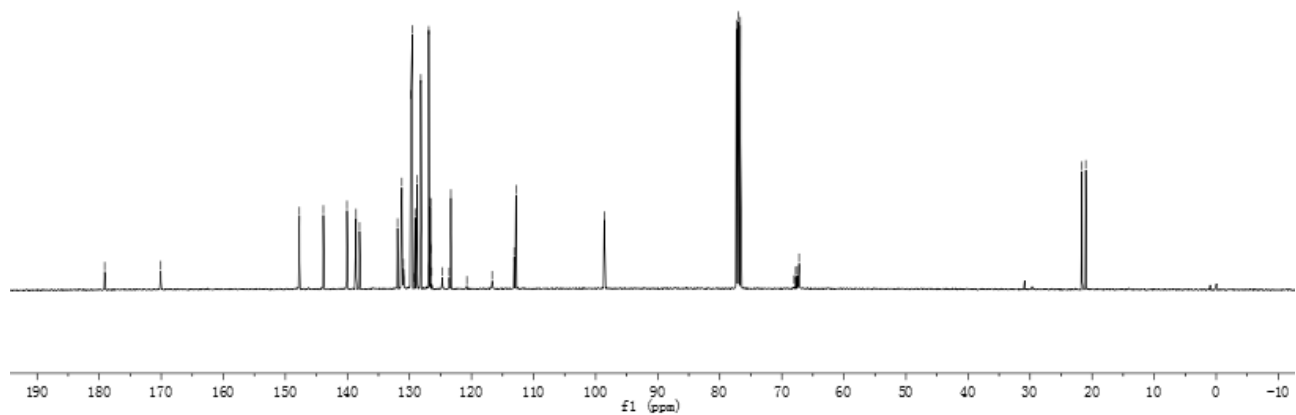


179.121  
170.078  
147.740  
143.879  
140.072  
138.602  
138.049  
131.928  
131.233  
130.973  
129.780  
129.538  
129.261  
129.103  
128.729  
128.172  
126.895  
126.662  
126.616  
126.592  
126.423  
124.711  
123.587  
123.332  
120.754  
116.687  
113.127  
112.844  
98.627  
77.318  
77.000  
76.682  
68.029  
67.771  
67.515  
67.223

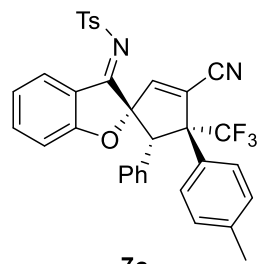
21.637  
21.028



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

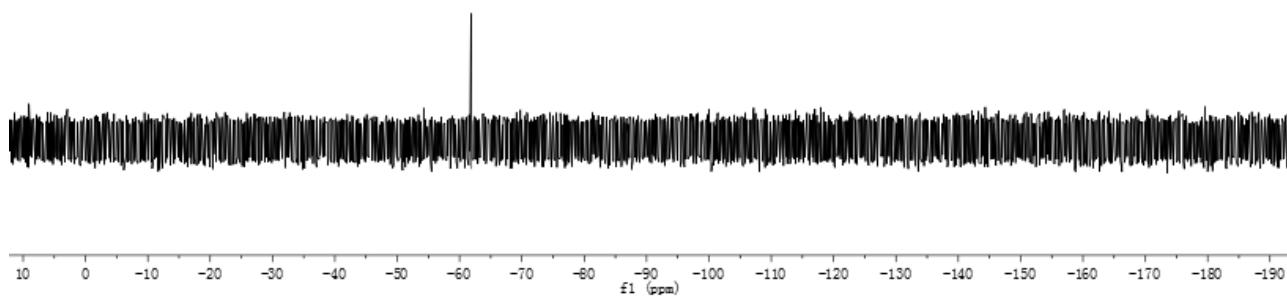


61.821



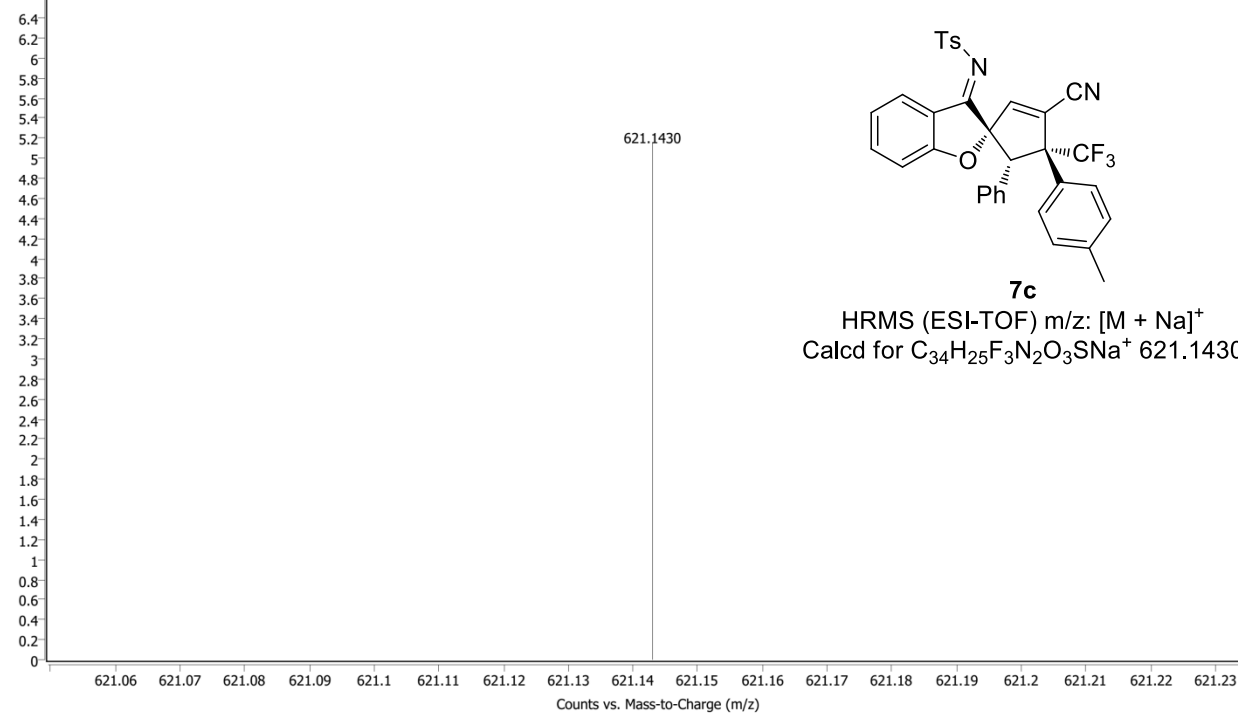
7c

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)

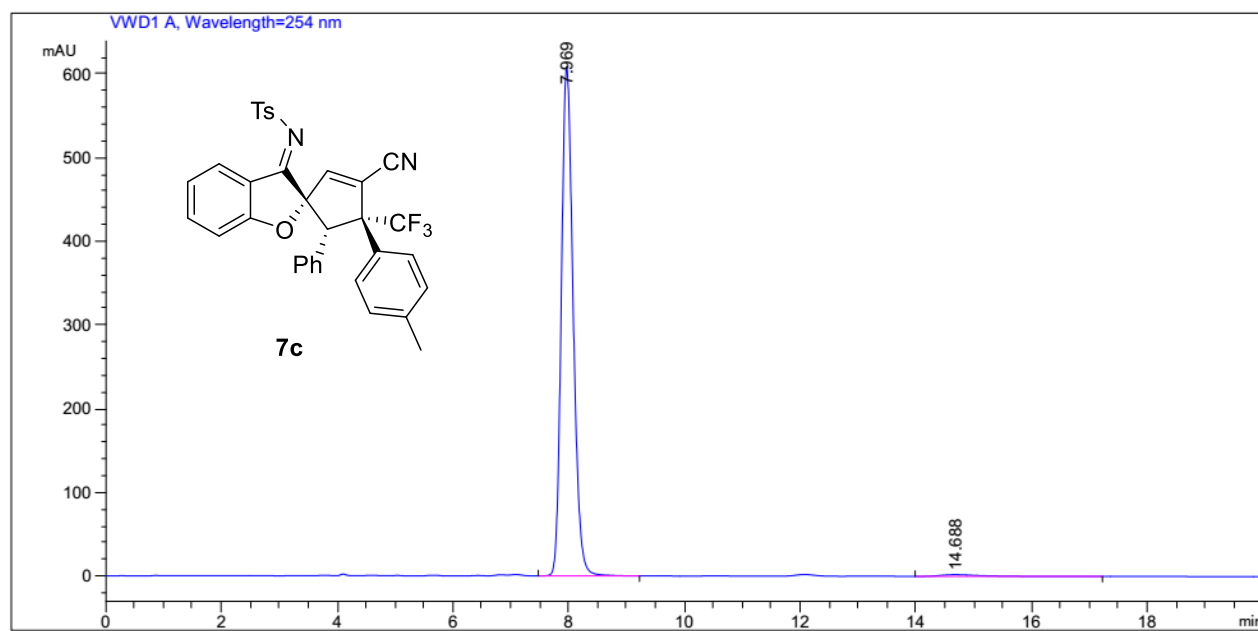
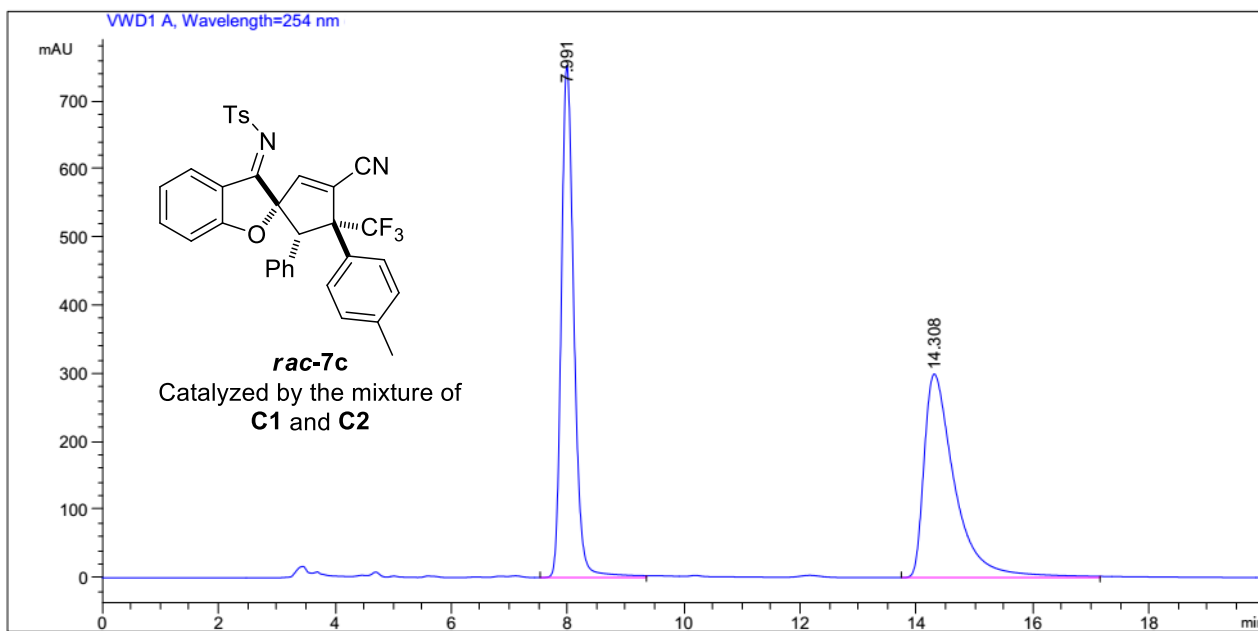


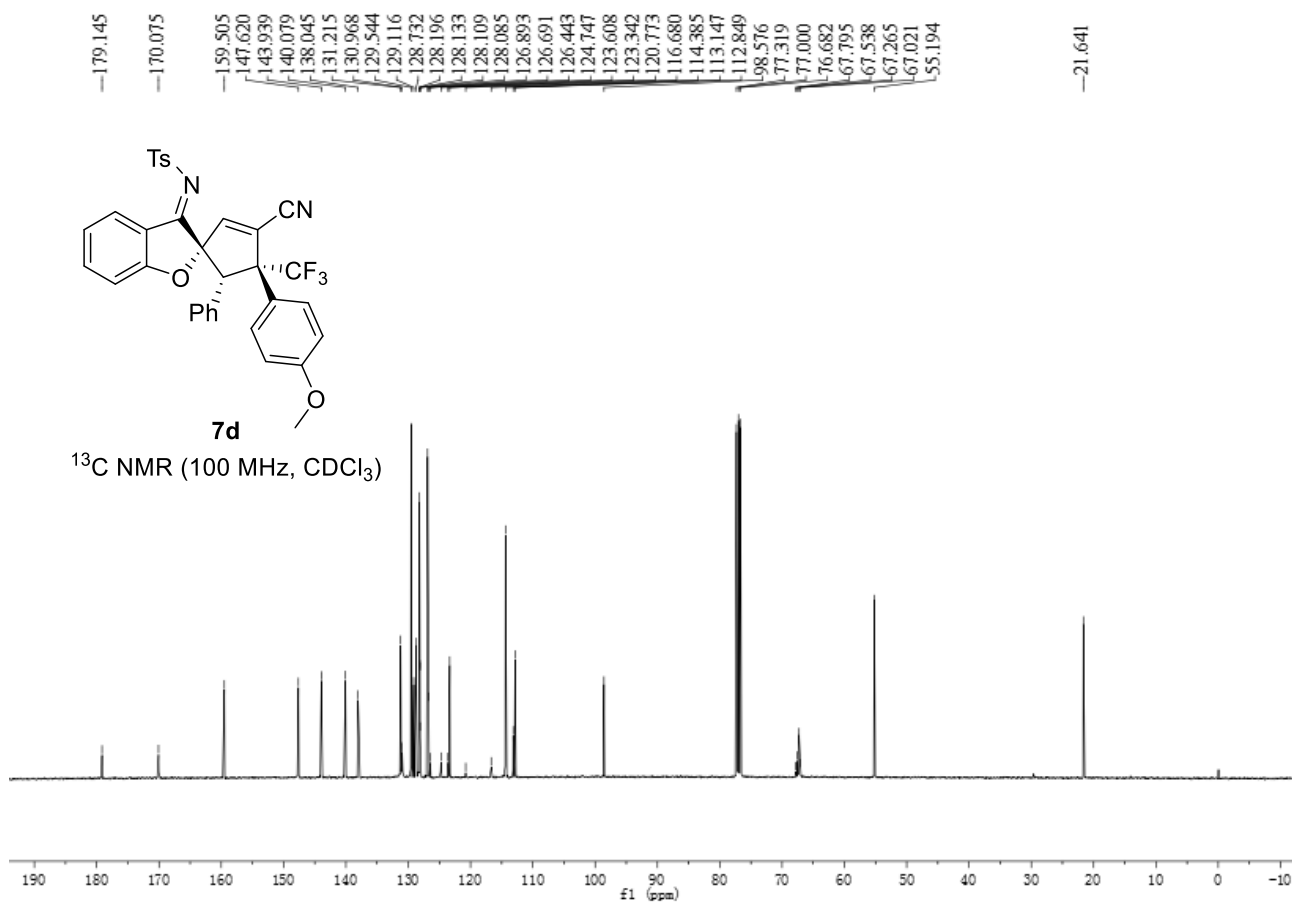
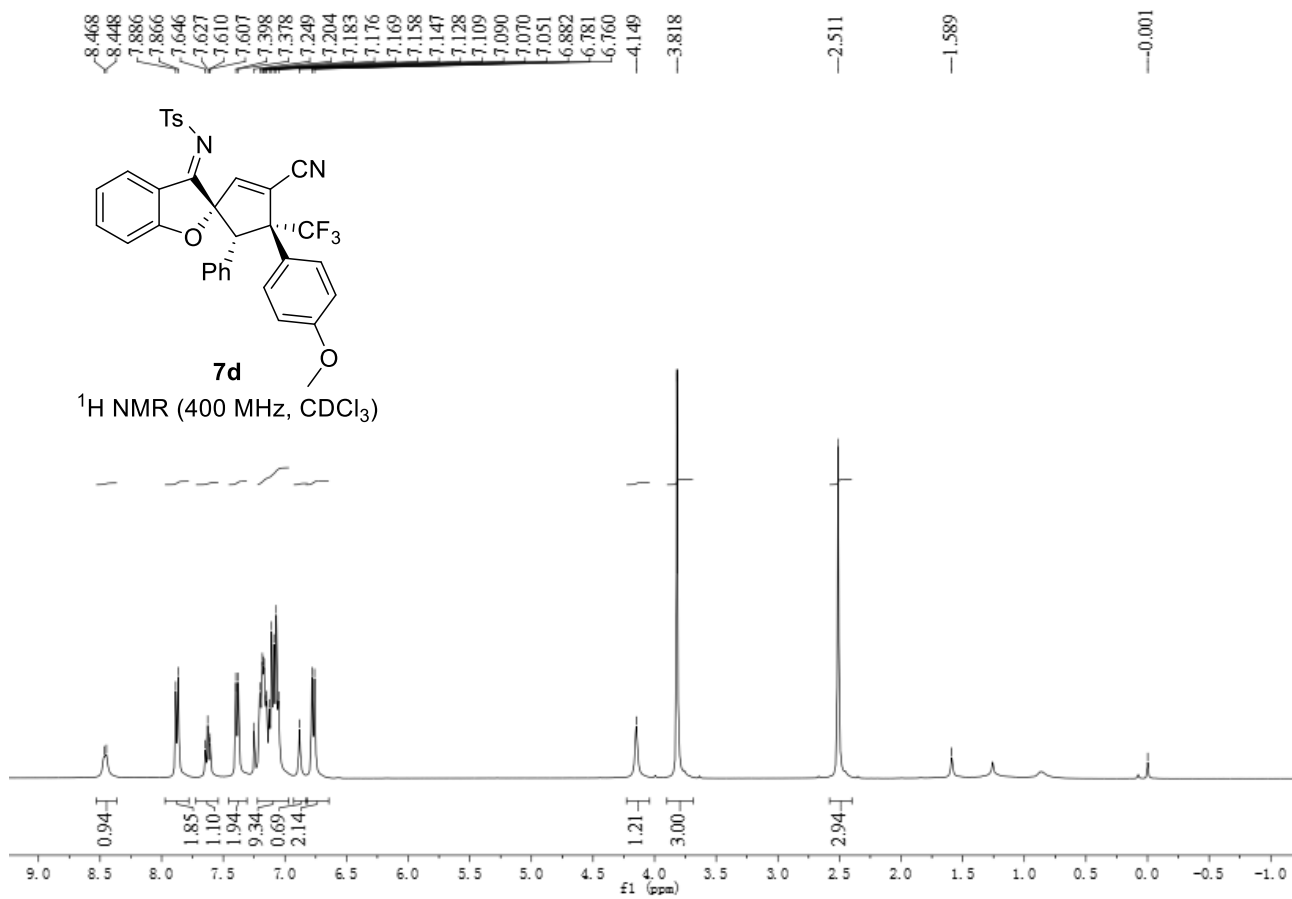
Name	cyc-190705-21	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	WorklistData-0021-r010.d	Method (Acq)	TOF.m		Acq. Time (Local)
					7/9/2019 2:30:41 PM (UTC+08:00)

+ESI Scan (rt: 1.412 min) Frag=175.0V WorklistData-0021-r010.d

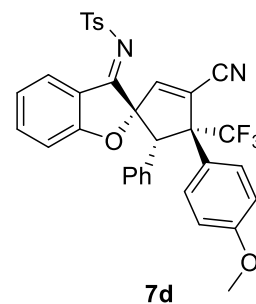




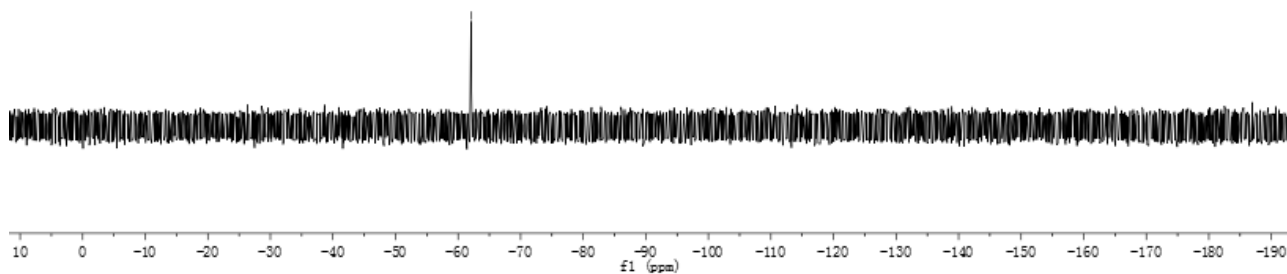




62.062

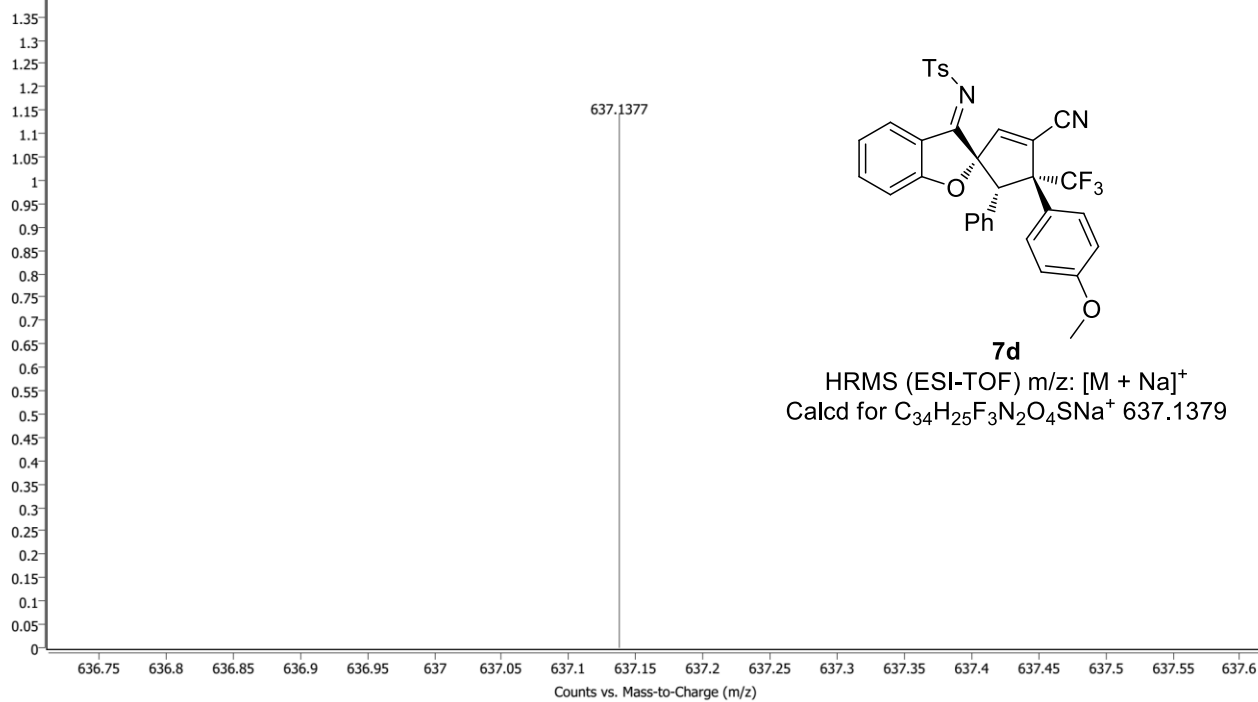


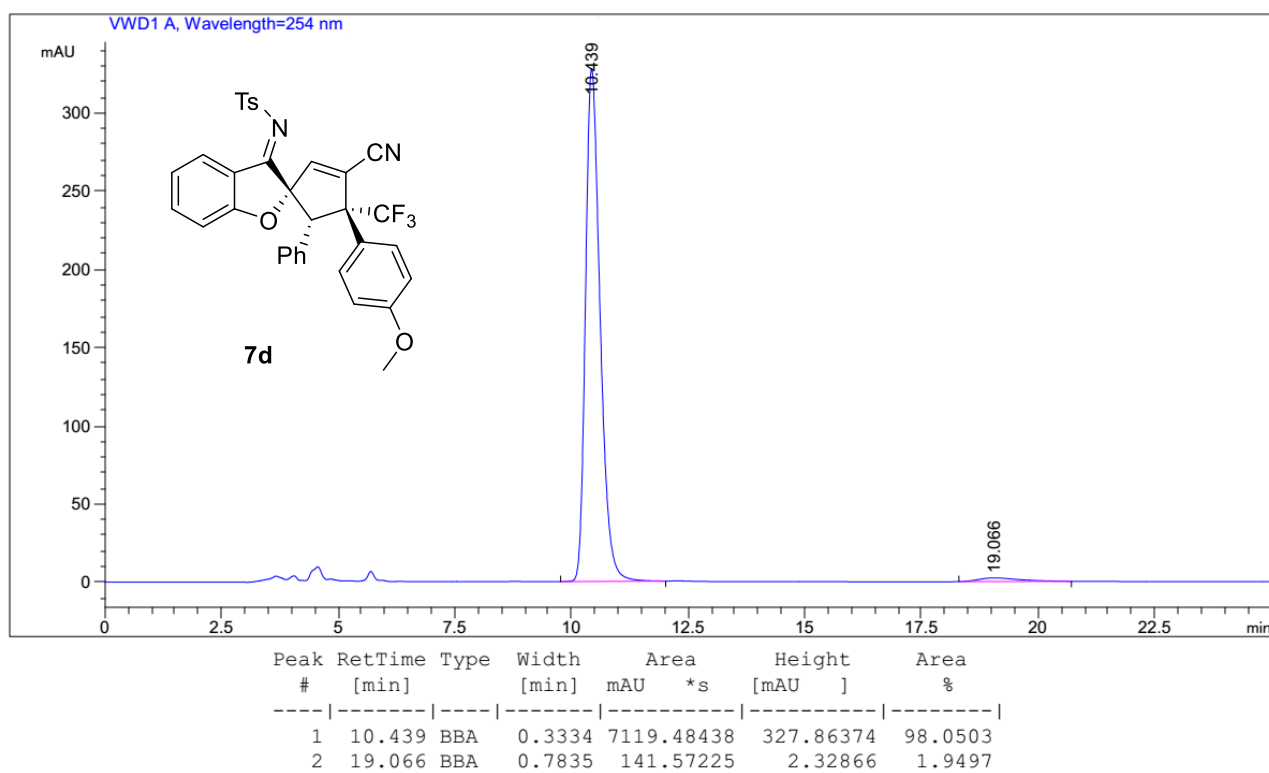
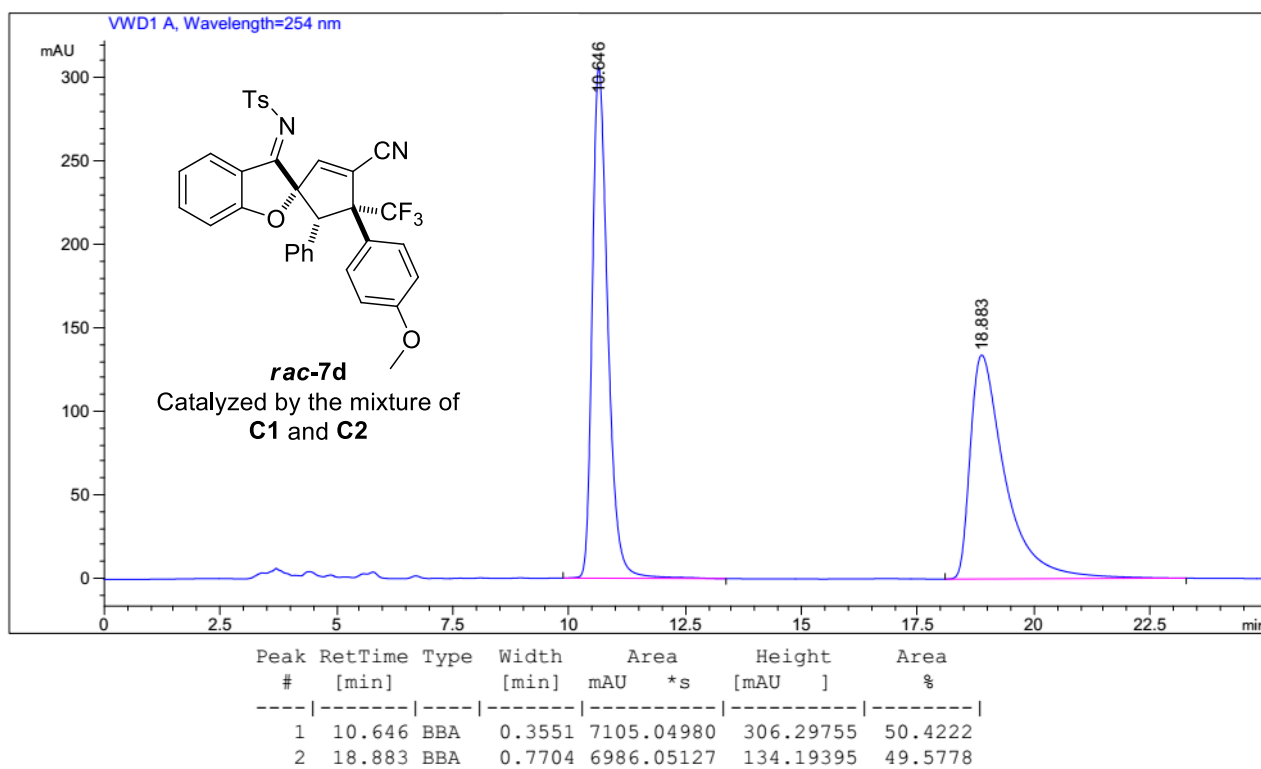
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



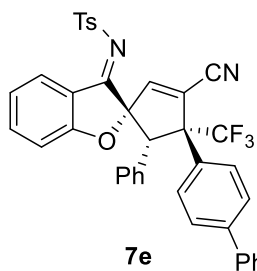
Name	cyc-190705-20	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	WorklistData-0020-r009.d	Method (Acq)	TOF.m	Comment	Acq. Time (Local) 7/9/2019 2:27:52 PM (UTC+08:00)

+ESI Scan (rt: 1.137 min) Frag=175.0V WorklistData-0020-r009.d

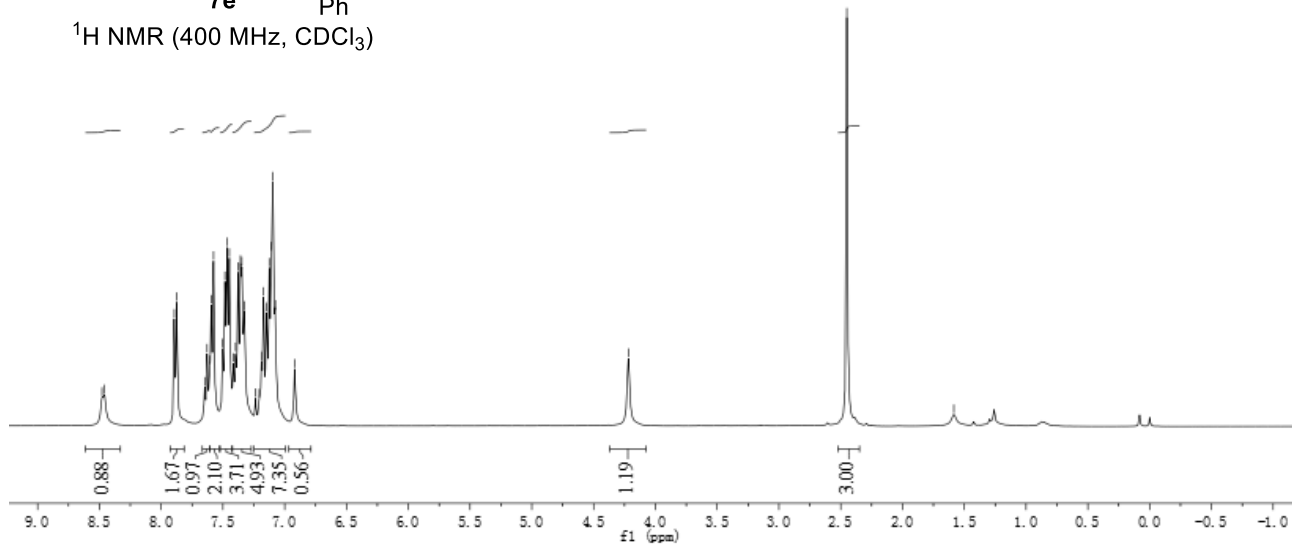




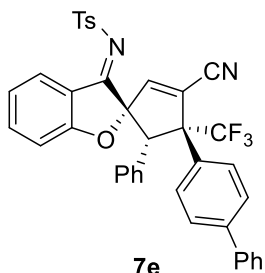
8.479  
8.459  
7.894  
7.874  
7.648  
7.628  
7.609  
7.595  
7.576  
7.503  
7.484  
7.467  
7.448  
7.415  
7.397  
7.378  
7.359  
7.347  
7.326  
7.237  
7.206  
7.189  
7.171  
7.148  
7.125  
7.108  
7.096  
7.076  
6.919  
4.218



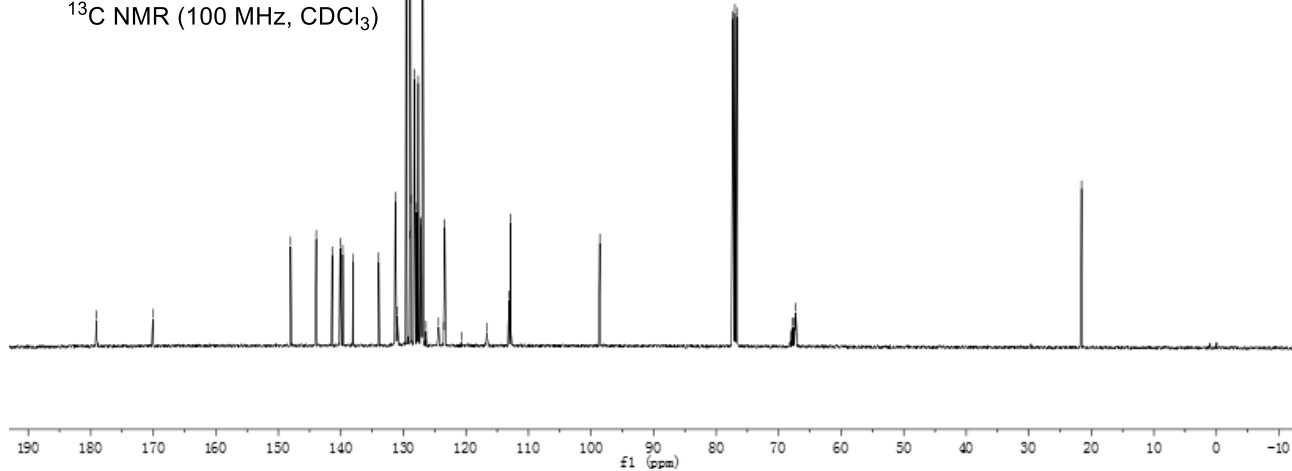
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )



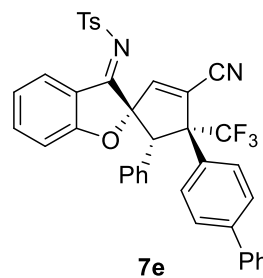
179.081  
170.072  
148.054  
143.940  
141.392  
140.124  
139.704  
138.043  
133.960  
131.298  
130.983  
129.572  
129.003  
128.916  
128.827  
128.246  
127.881  
127.624  
127.199  
127.175  
127.152  
126.939  
126.922  
126.385  
124.382  
123.549  
123.396  
120.716  
116.641  
113.098  
112.858  
98.603  
77.318  
77.000  
76.684  
68.111  
67.855  
67.596  
67.333  
67.265



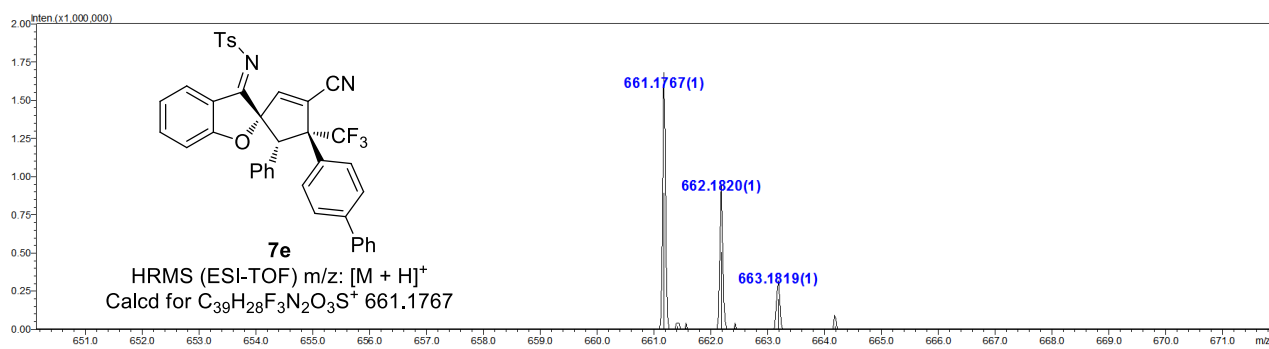
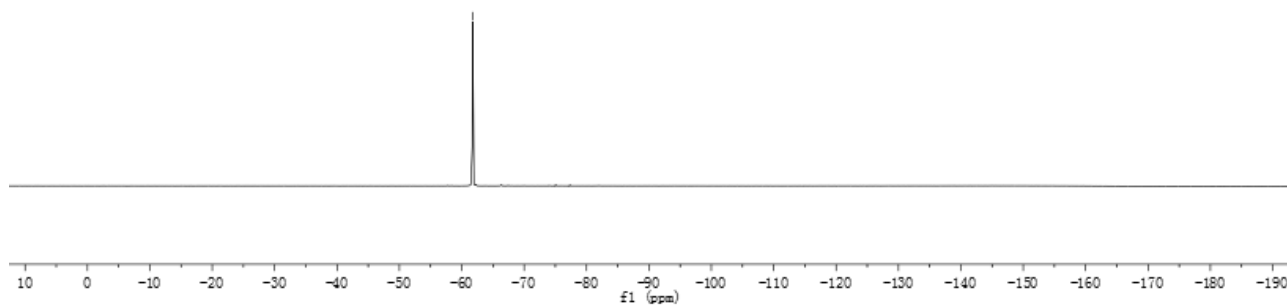
$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

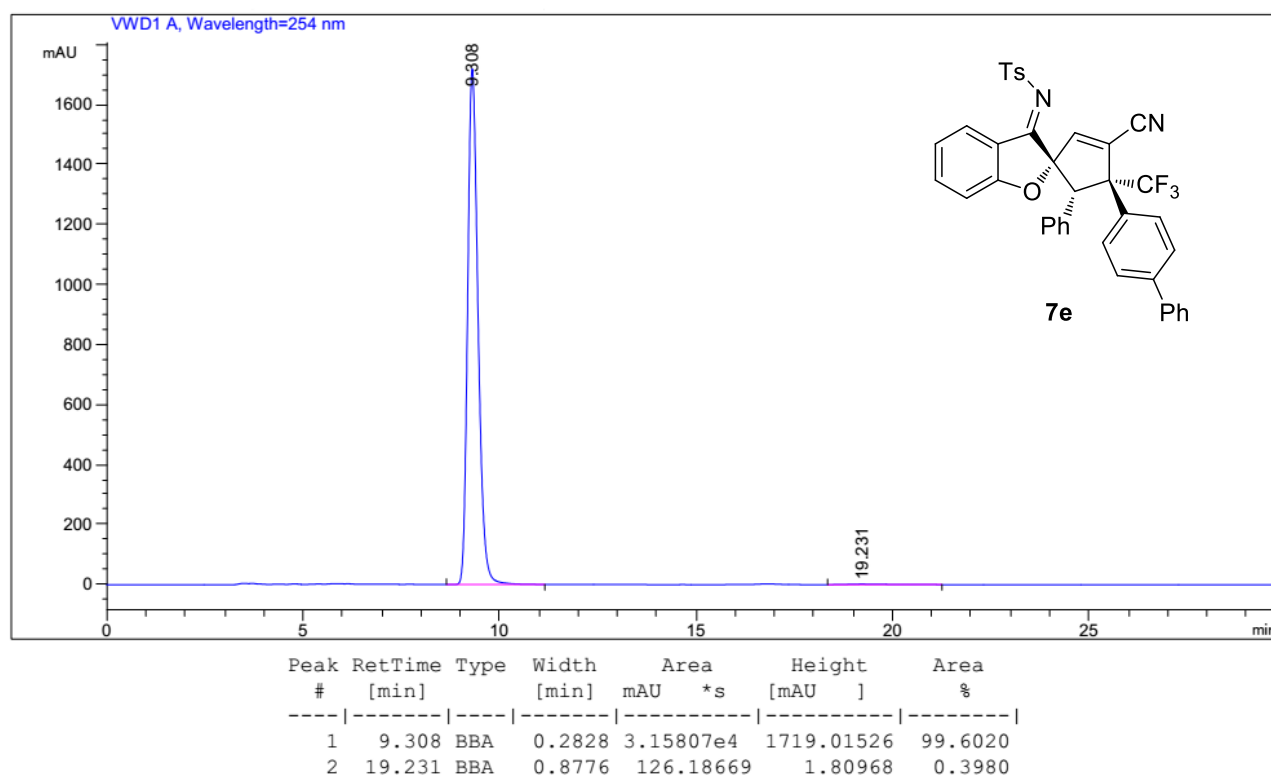
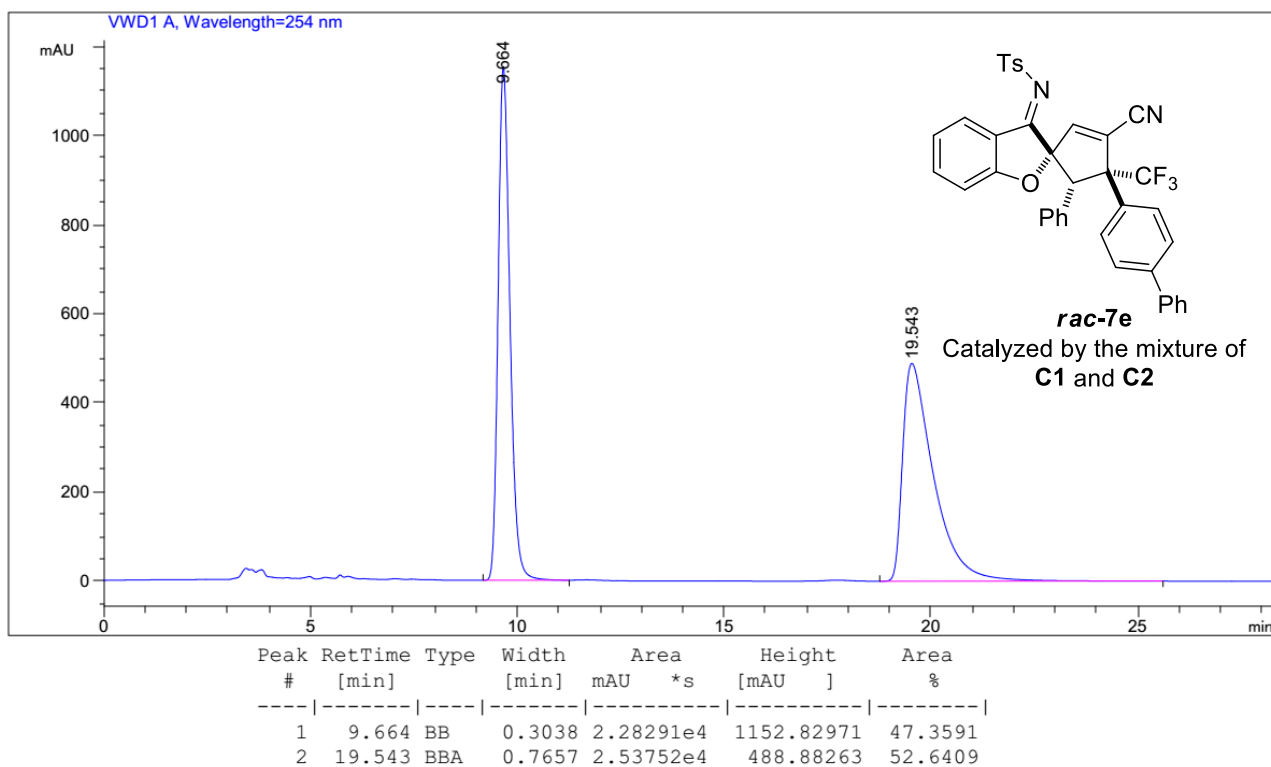


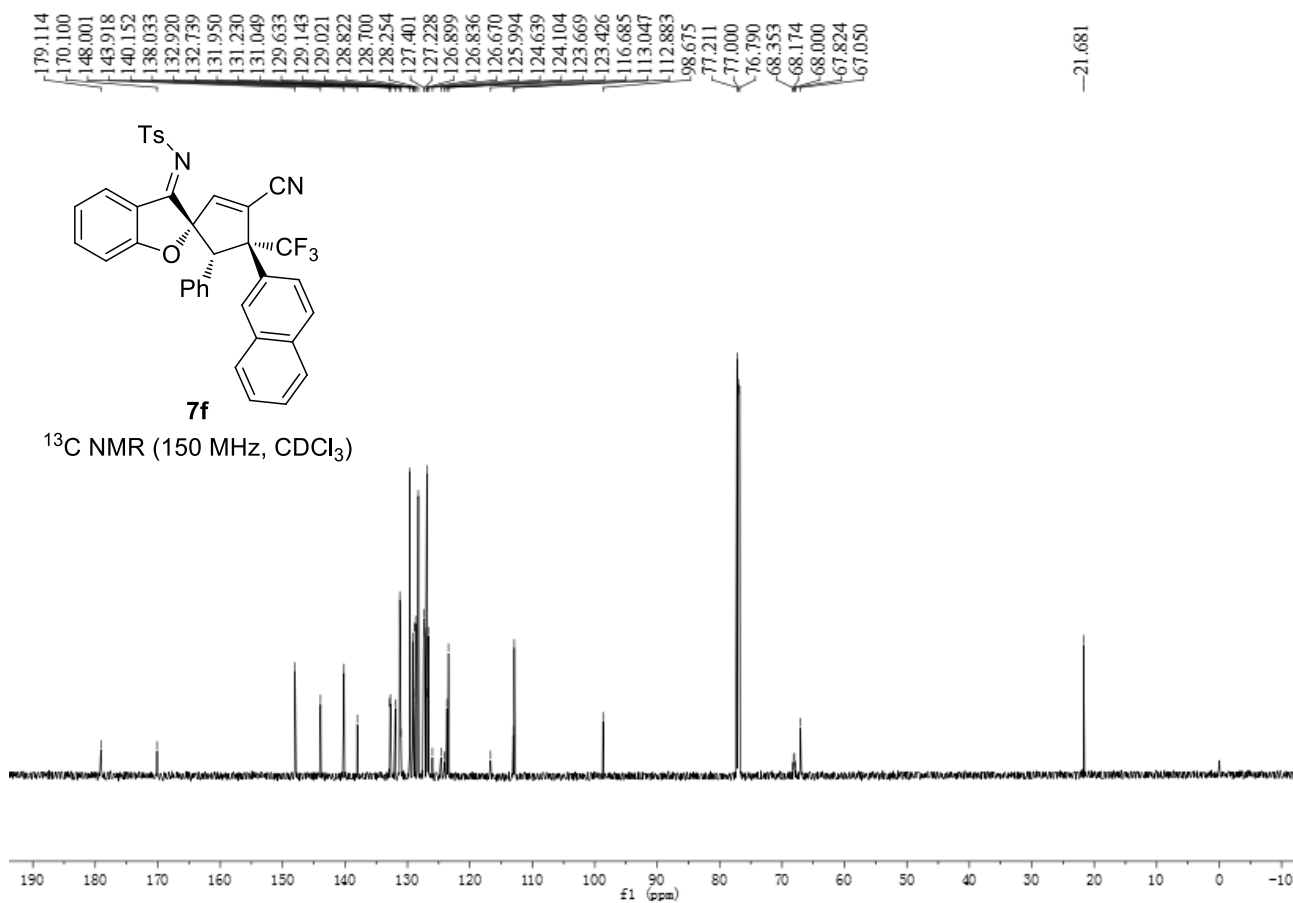
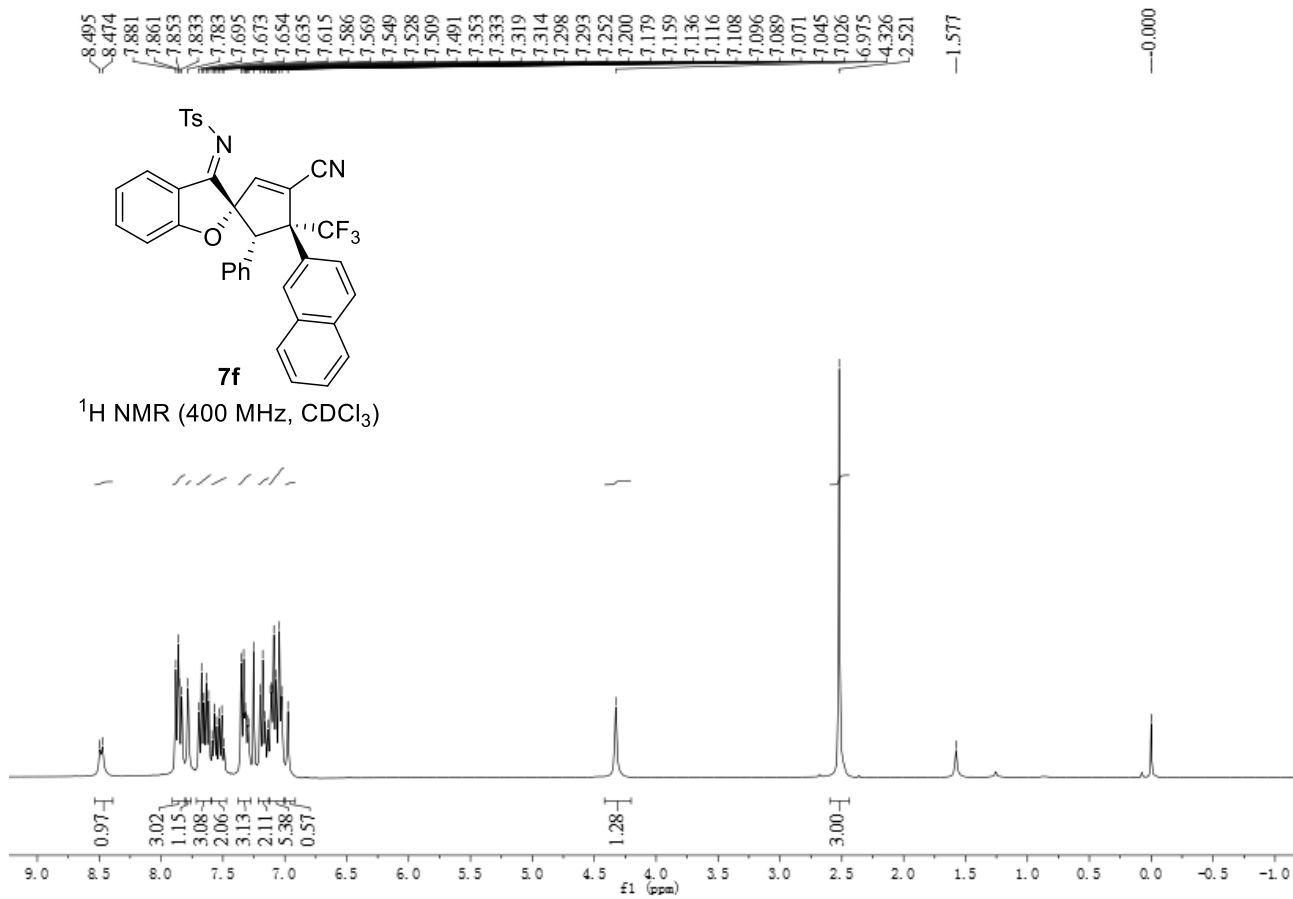
-61.732



<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)

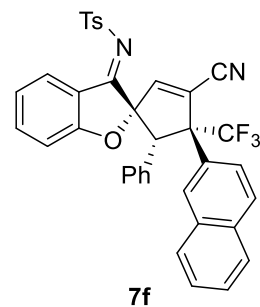




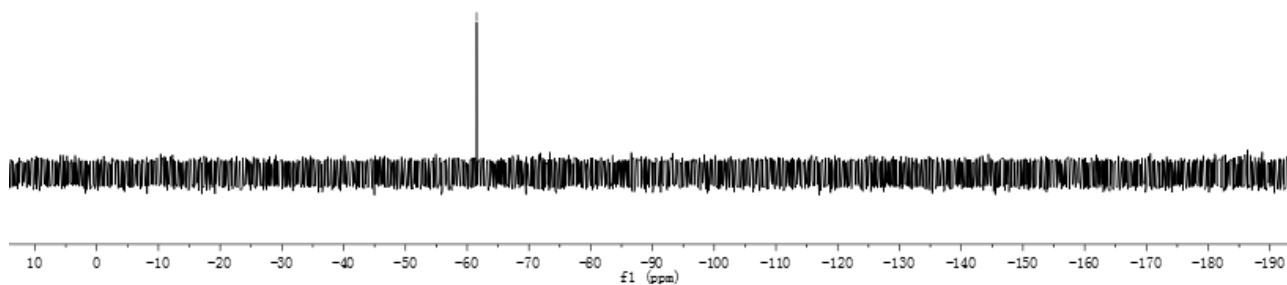




-61.531

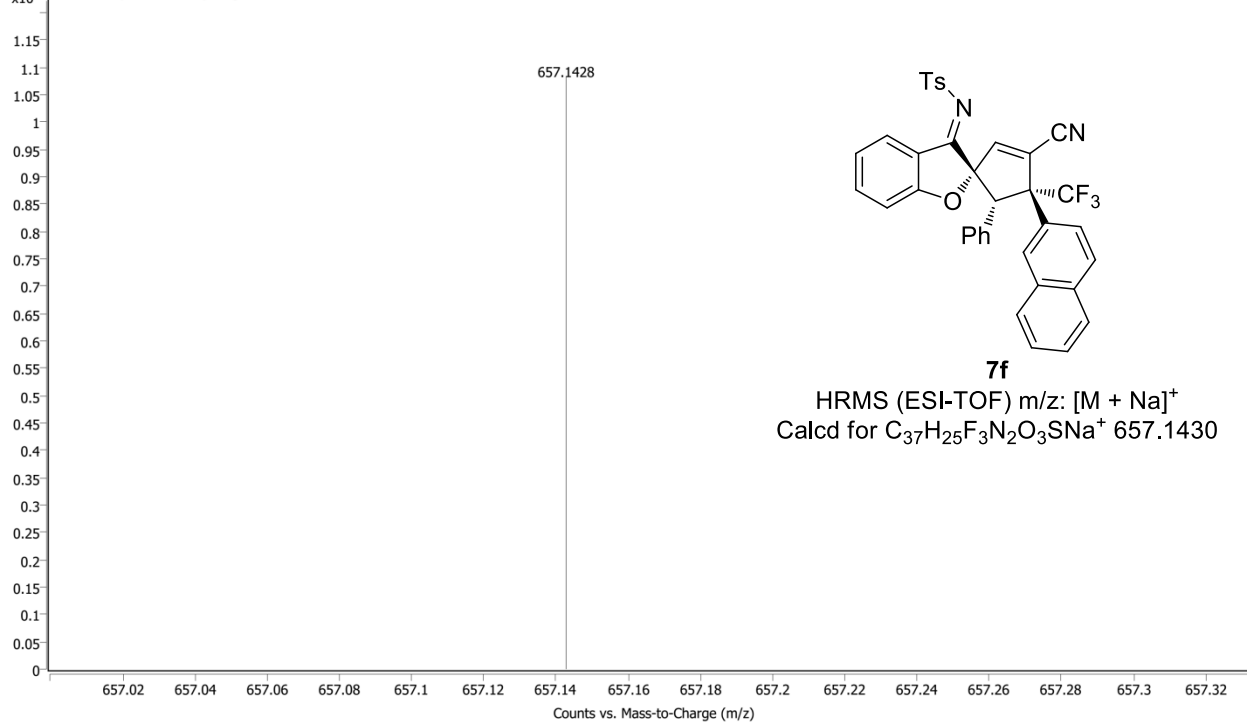


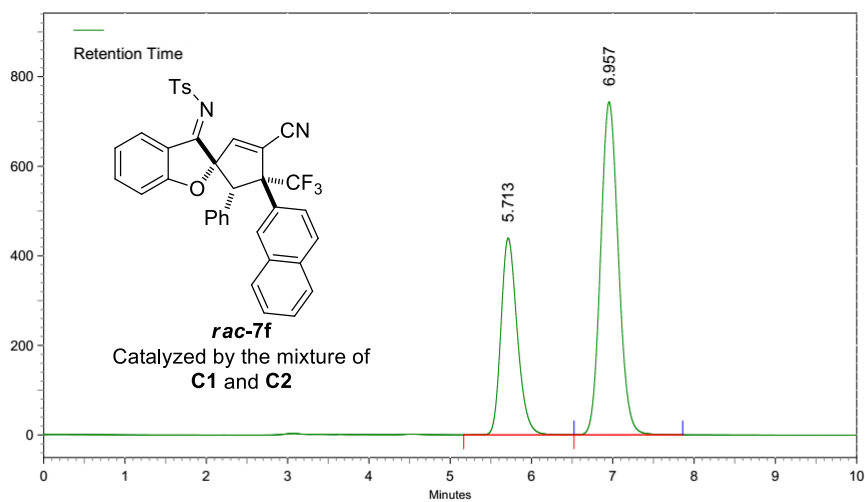
**7f**  
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



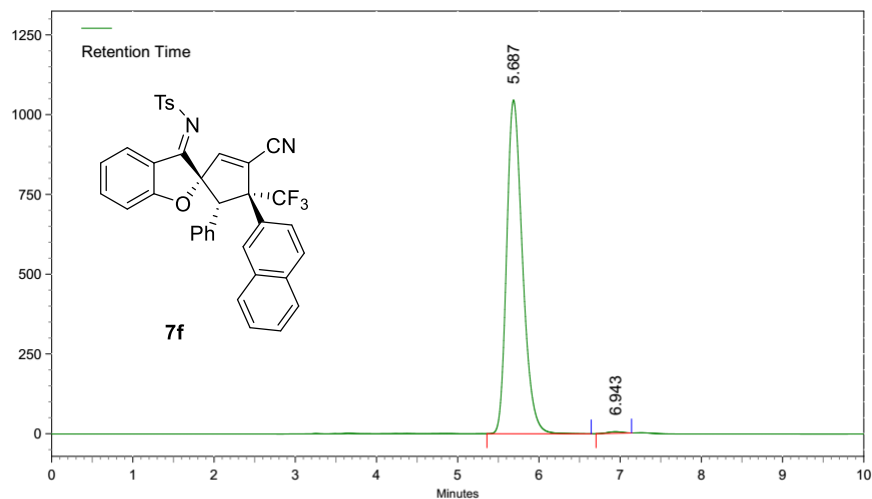
Name	cyc-190705-18	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	WorklistData-0018-r007.d	Method (Acq)	TOF.m	Comment	Acq. Time (Local) 7/9/2019 2:22:14 PM (UTC+08:00)

+ESI Scan (rt: 1.490 min) Frag=175.0V WorklistData-0018-r007.d

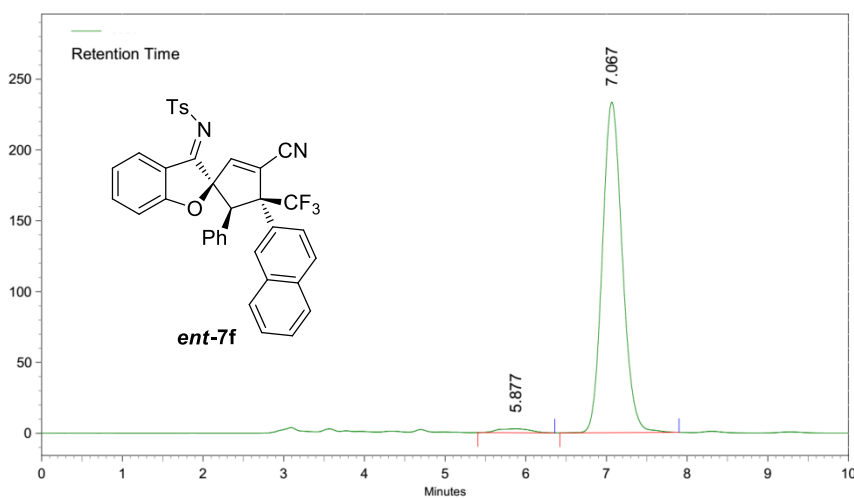




Peak No.	Ret Time	Width	Height	Area	Area [%]
1	5.713	1.357	7374777	102662623	35.1546
2	6.957	1.337	12475230	189369362	64.8454



Peak No.	Ret Time	Width	Height	Area	Area [%]
1	5.687	1.283	17545565	237785242	99.5769
2	6.943	0.437	82737	1010423	0.4231

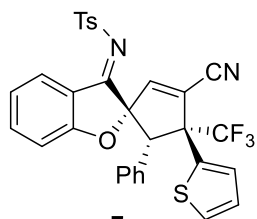


Peak No.	Ret Time	Width	Height	Area	Area [%]
1	5.877	0.953	48139	1343416	1.9605
2	7.067	1.477	3914576	67181128	98.0395

8.477  
8.457  
7.901  
7.881  
7.654  
7.633  
7.613  
7.378  
7.357  
7.350  
7.337  
7.257  
7.224  
7.217  
7.207  
7.200  
7.186  
7.166  
7.158  
7.142  
7.122  
7.114  
7.094  
7.076  
7.013  
7.004  
7.000  
6.991  
6.899  
4.233

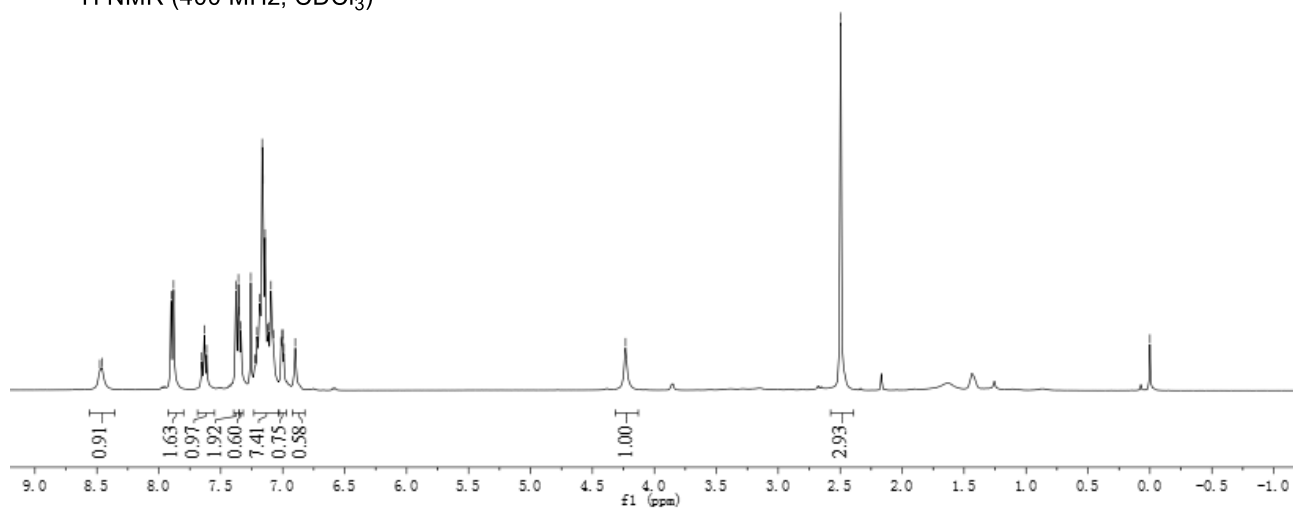
-2.496

-0.000



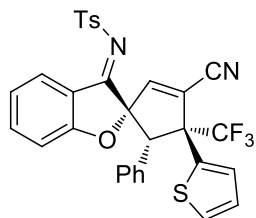
**7g**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



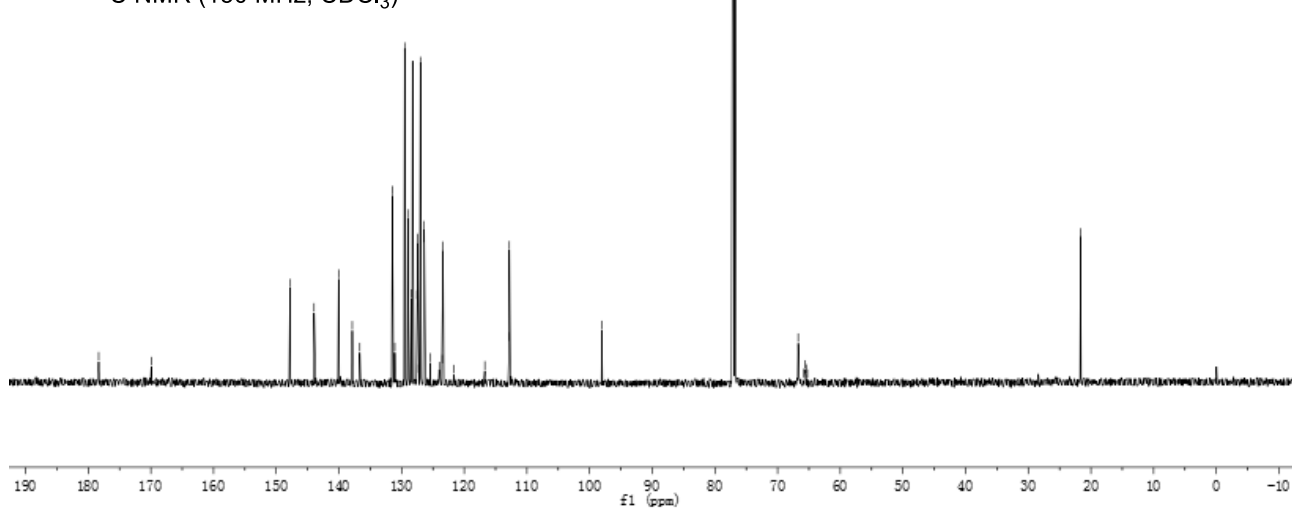
178.327  
169.951  
147.802  
143.953  
140.042  
137.868  
136.666  
131.463  
131.085  
129.503  
129.002  
128.479  
127.535  
127.395  
127.284  
126.988  
126.380  
125.395  
123.977  
123.505  
123.371  
121.612  
116.719  
112.914  
112.801  
98.040  
77.211  
77.000  
76.789  
66.716  
65.802  
65.621  
65.441  
65.250

-21.654

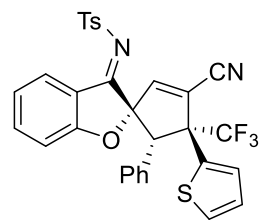


**7g**

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)

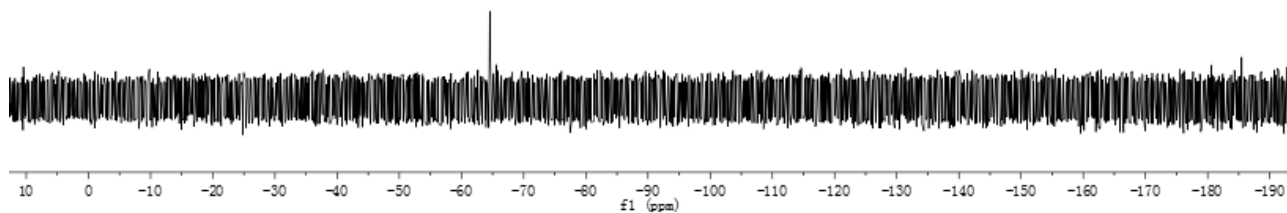


—64.547



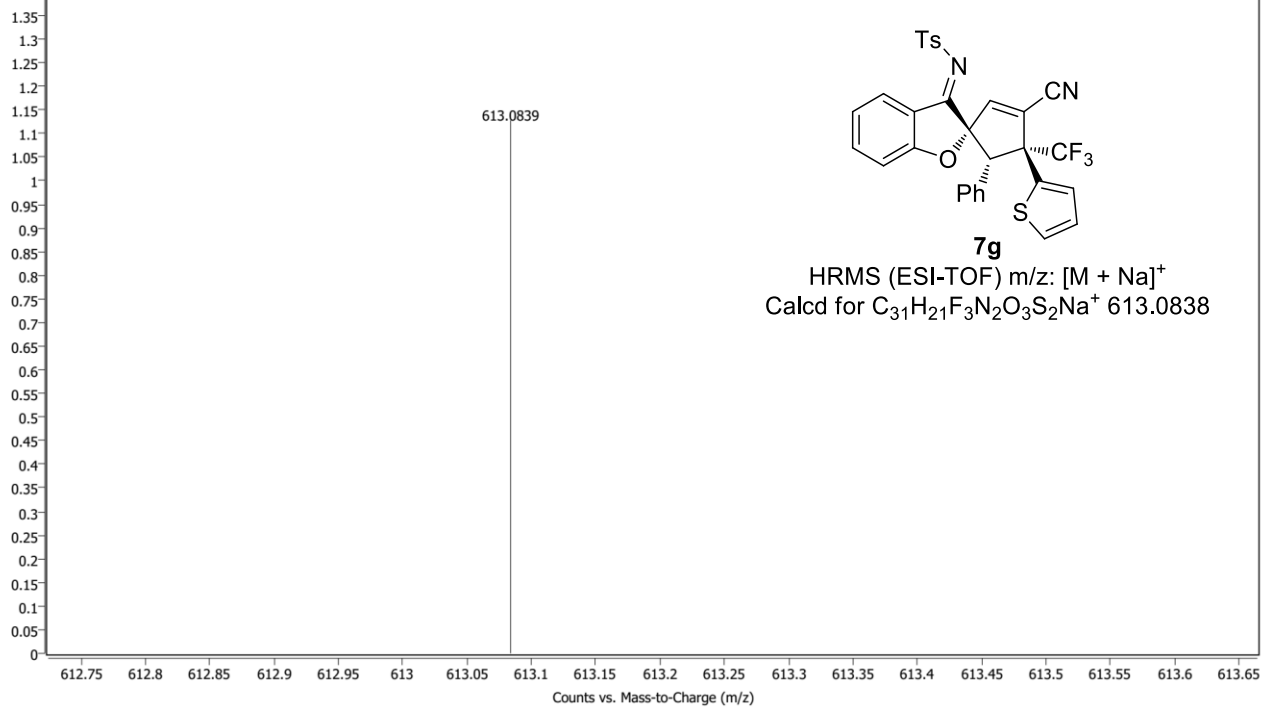
**7g**

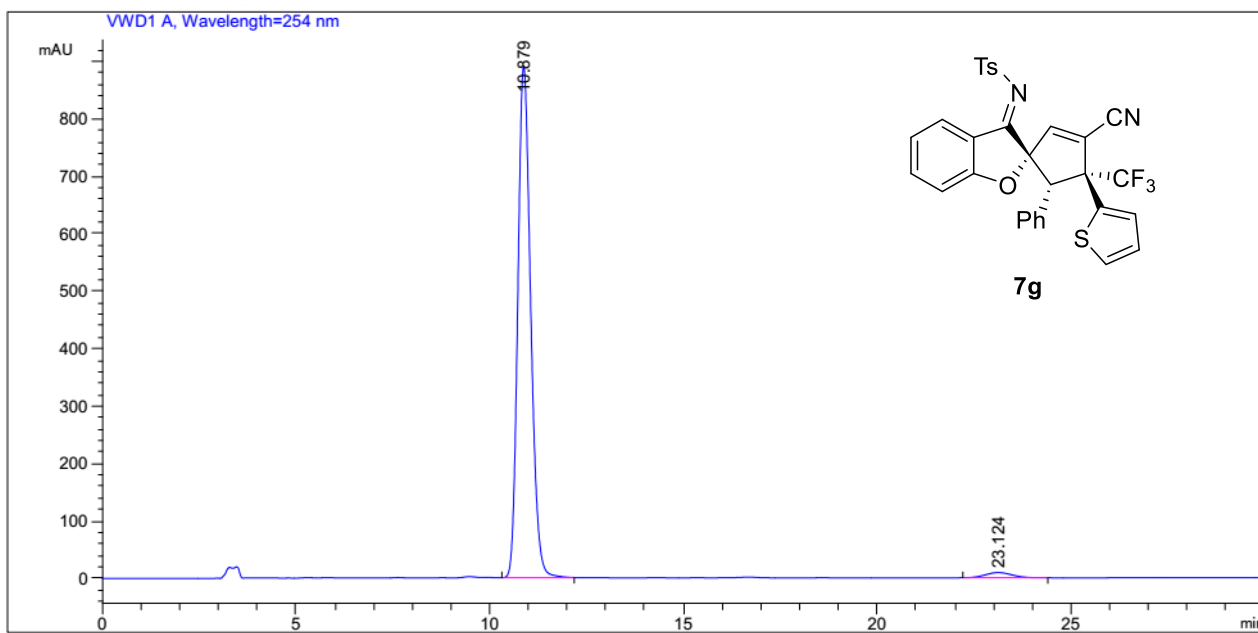
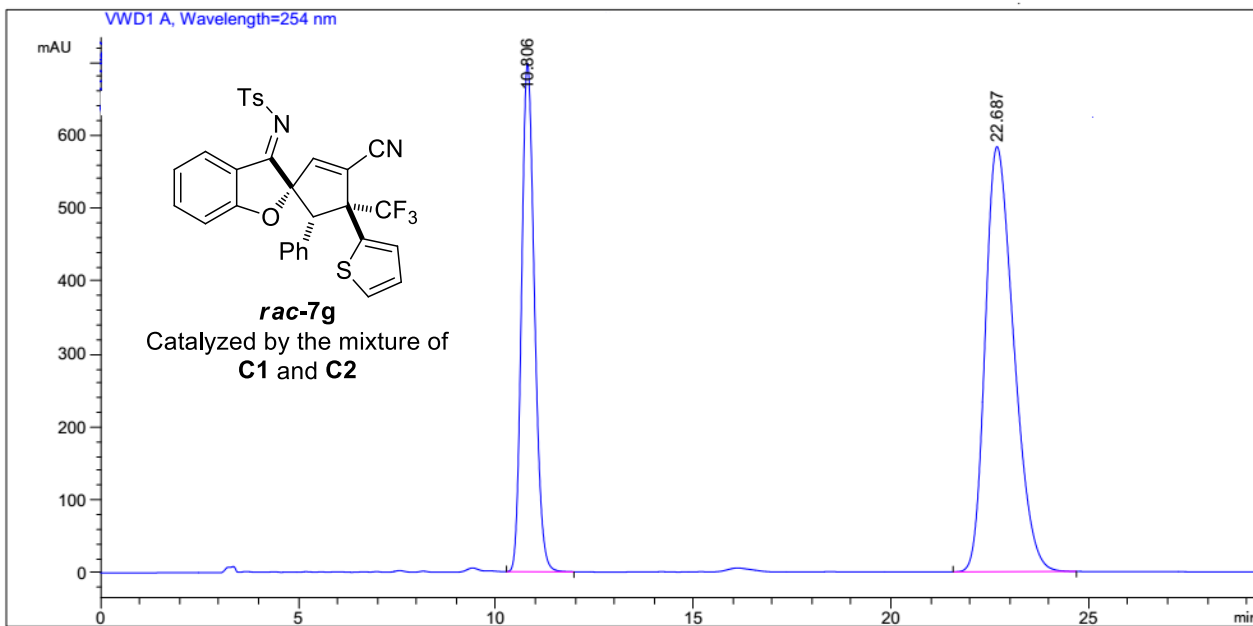
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



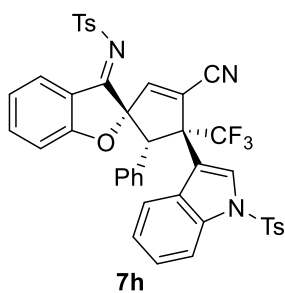
Name	cyc-190705-19	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	WorklistData-0019-r008.d	Method (Acq)	TOF.m		Acq. Time (Local) 7/9/2019 2:25:03 PM (UTC+08:00)

+ESI Scan (rt: 0.985 min) Frag=175.0V WorklistData-0019-r008.d

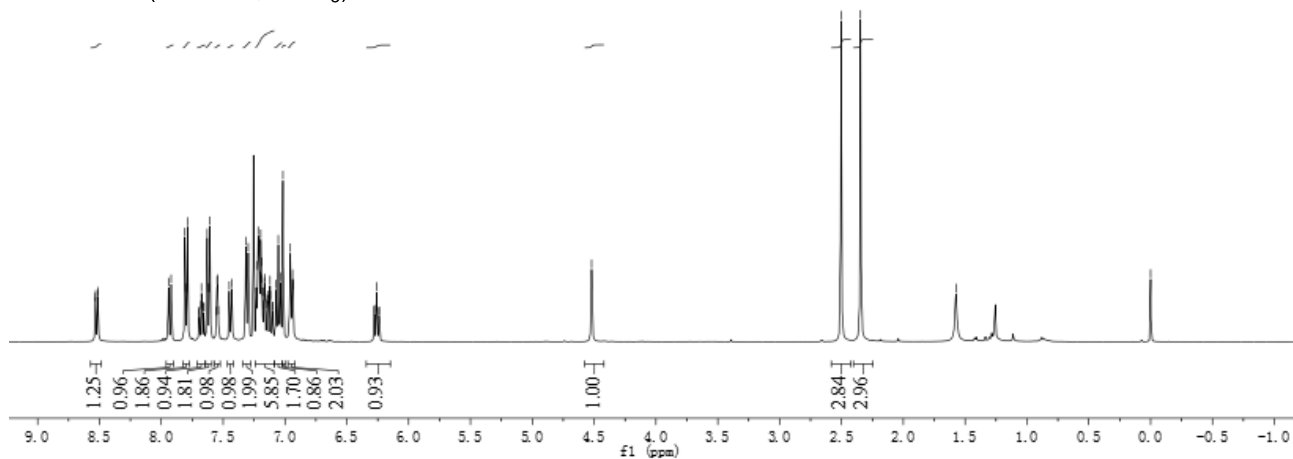




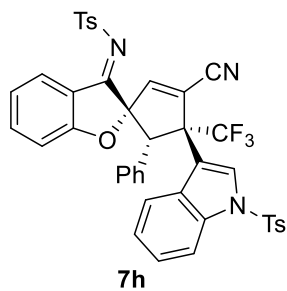
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8.531  
8.513  
8.510  
7.941  
7.920  
7.809  
7.805  
7.793  
7.788  
7.679  
7.676  
7.672  
7.628  
7.624  
7.612  
7.607  
7.549  
7.544  
7.450  
7.430  
7.317  
7.297  
7.229  
7.217  
7.208  
7.196  
7.189  
7.185  
7.183  
7.174  
7.171  
7.167  
7.164  
7.161  
7.146  
7.143  
7.140  
7.138  
7.123  
7.120  
7.118  
7.102  
7.100  
7.073  
7.054  
7.035  
7.016  
6.957  
6.939  
6.935  
6.261  
6.258  
6.256  
4.520  
2.503  
2.346  
1.574  
0.000



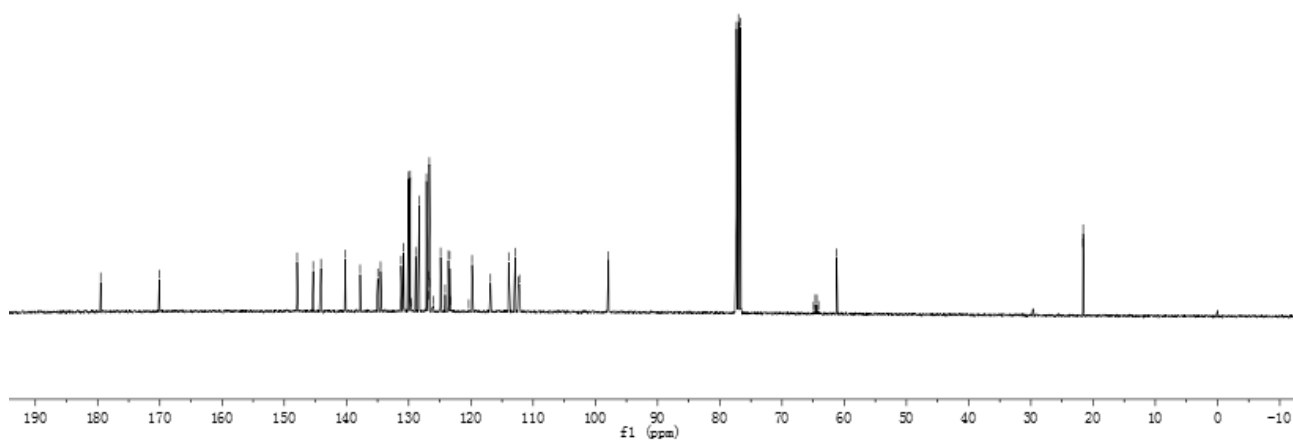
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )



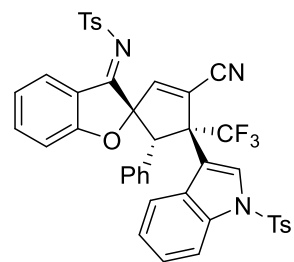
179.510  
170.082  
147.928  
145.356  
144.096  
140.195  
137.801  
134.959  
134.521  
131.232  
130.794  
130.009  
129.747  
129.642  
128.887  
128.836  
128.301  
127.149  
126.781  
126.739  
126.683  
126.650  
126.035  
124.868  
124.141  
123.618  
123.402  
123.191  
120.353  
119.817  
116.858  
113.940  
112.873  
112.395  
112.204  
97.884  
77.318  
77.000  
76.683  
64.935  
64.664  
64.396  
64.122  
61.216  
21.613  
21.599



$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

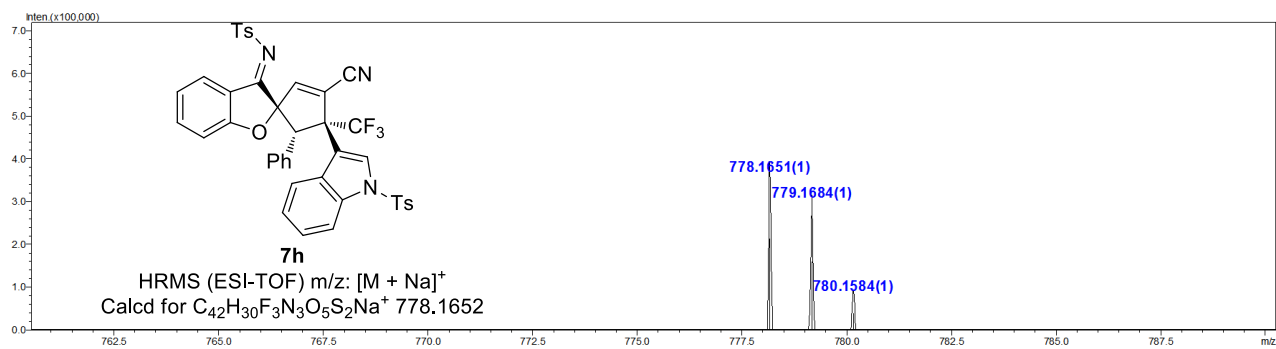
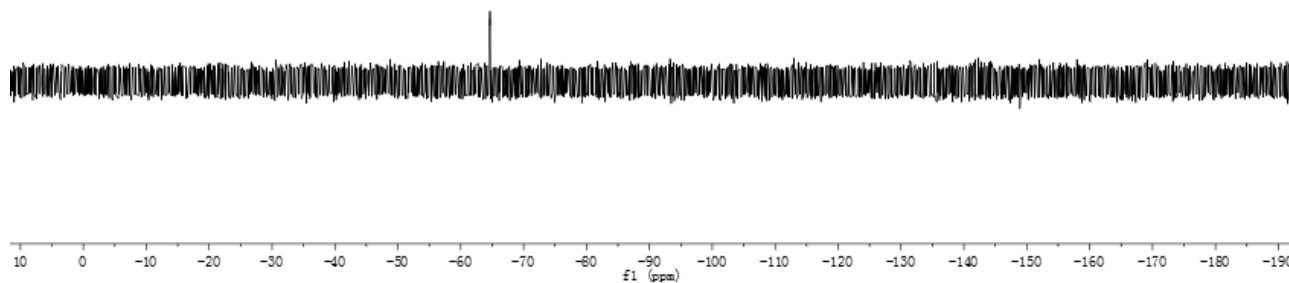


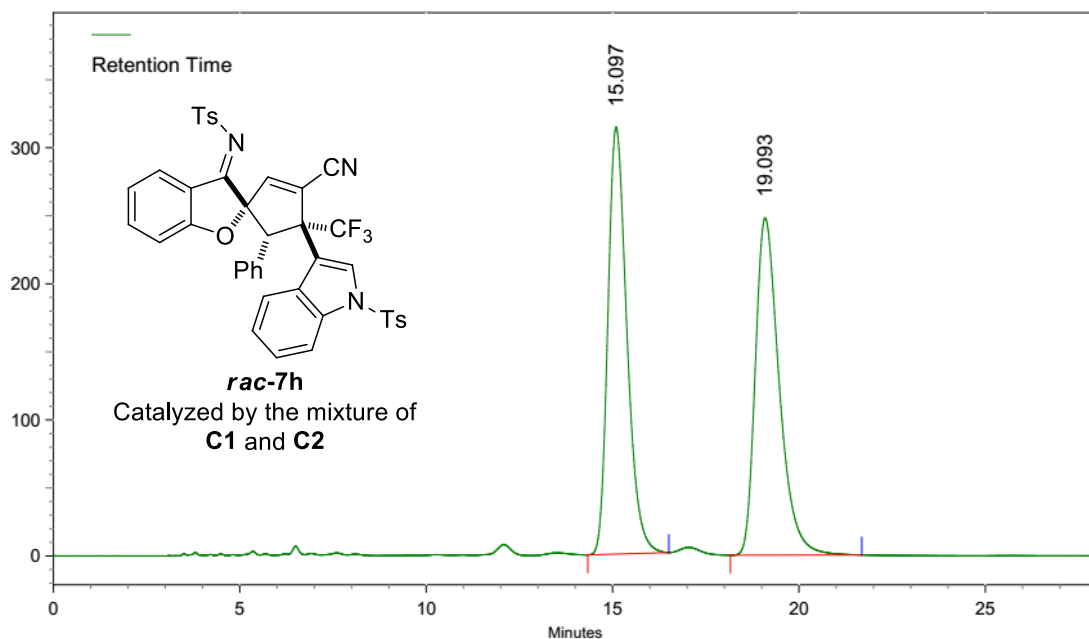
-64.635



**7h**

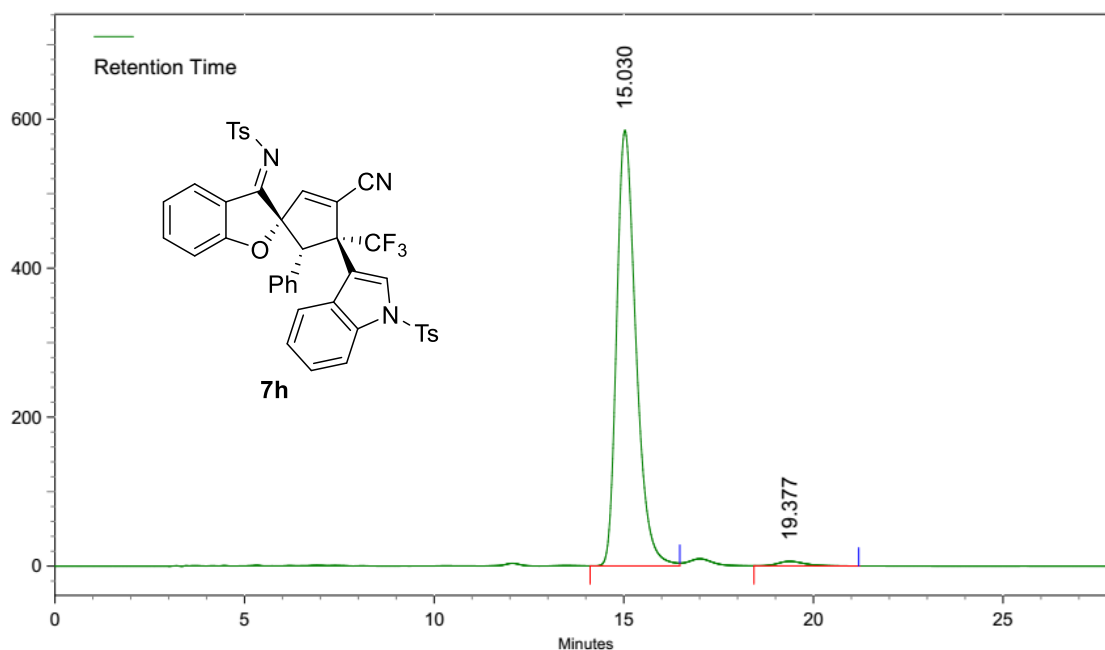
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)





### AREA PERCENT REPORT

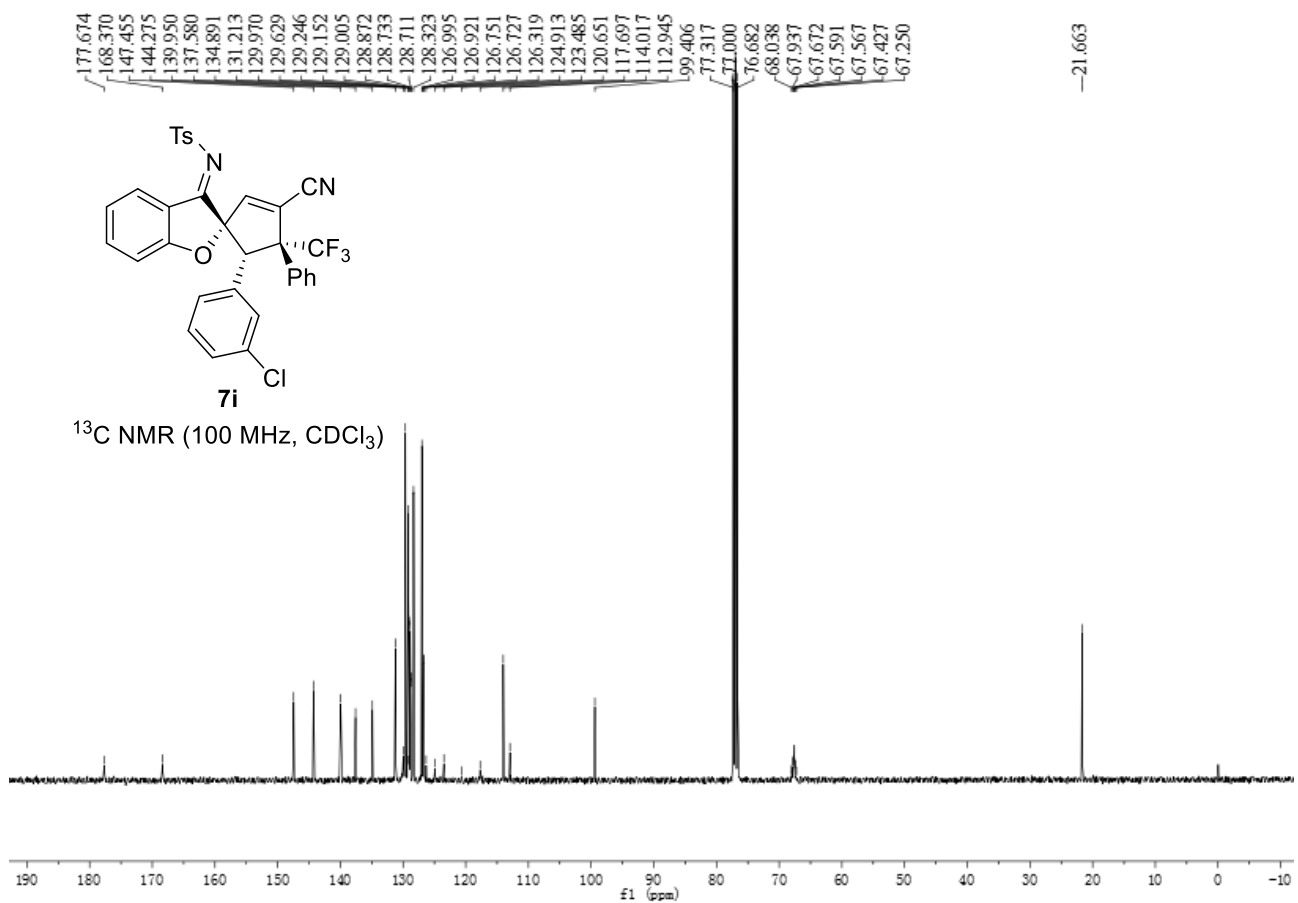
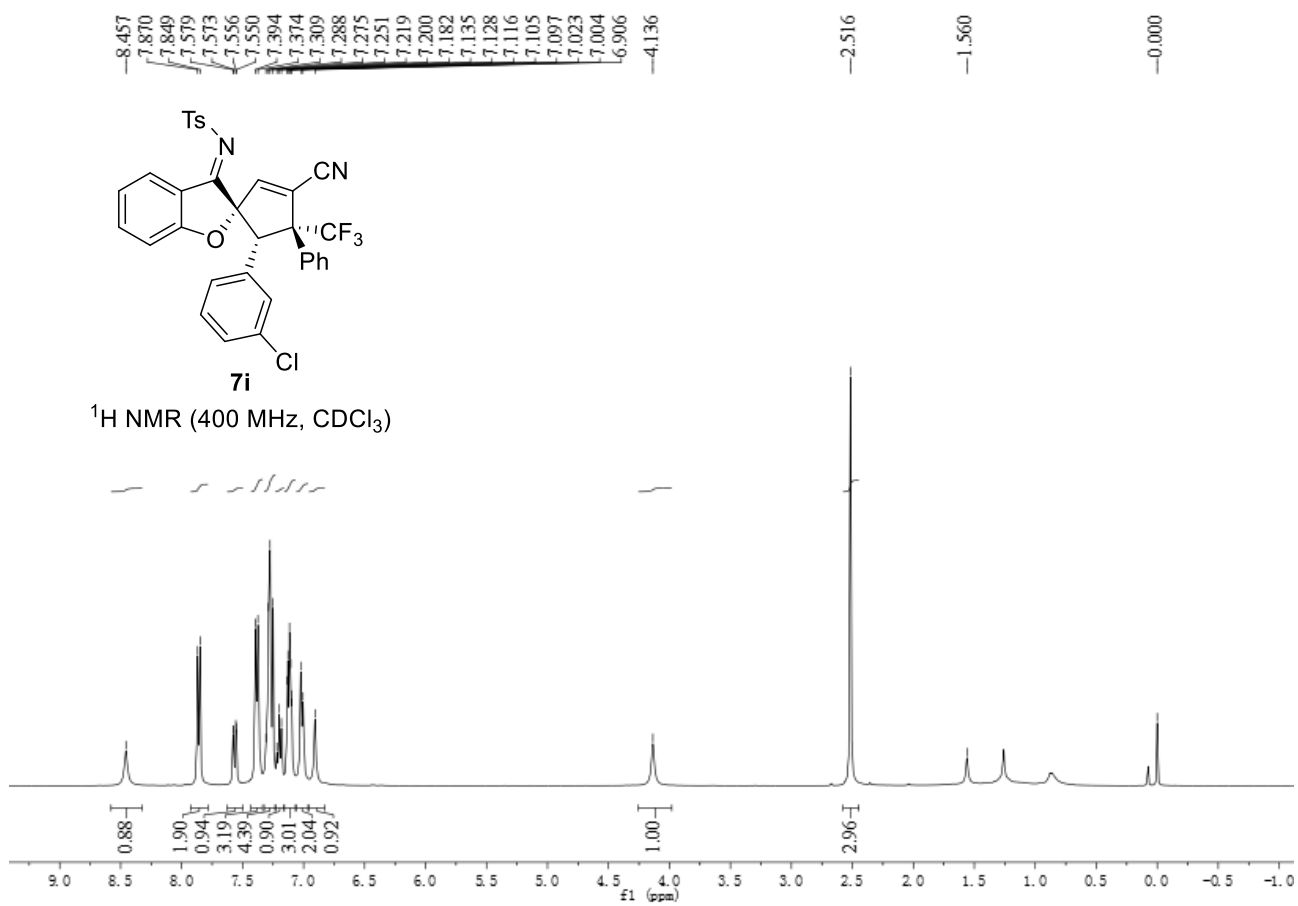
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	15.097	2.173	5264992	186312187	50.1659
2	19.093	3.523	4158783	185079805	49.8341



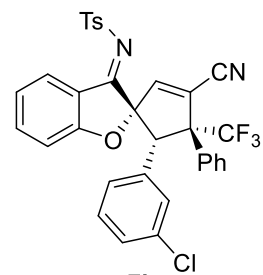
### AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
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2	19.377	2.763	102399	5033864	1.4318

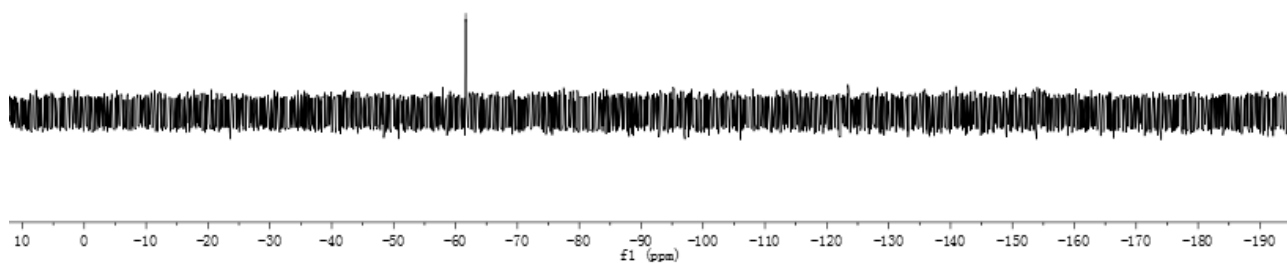




61.649

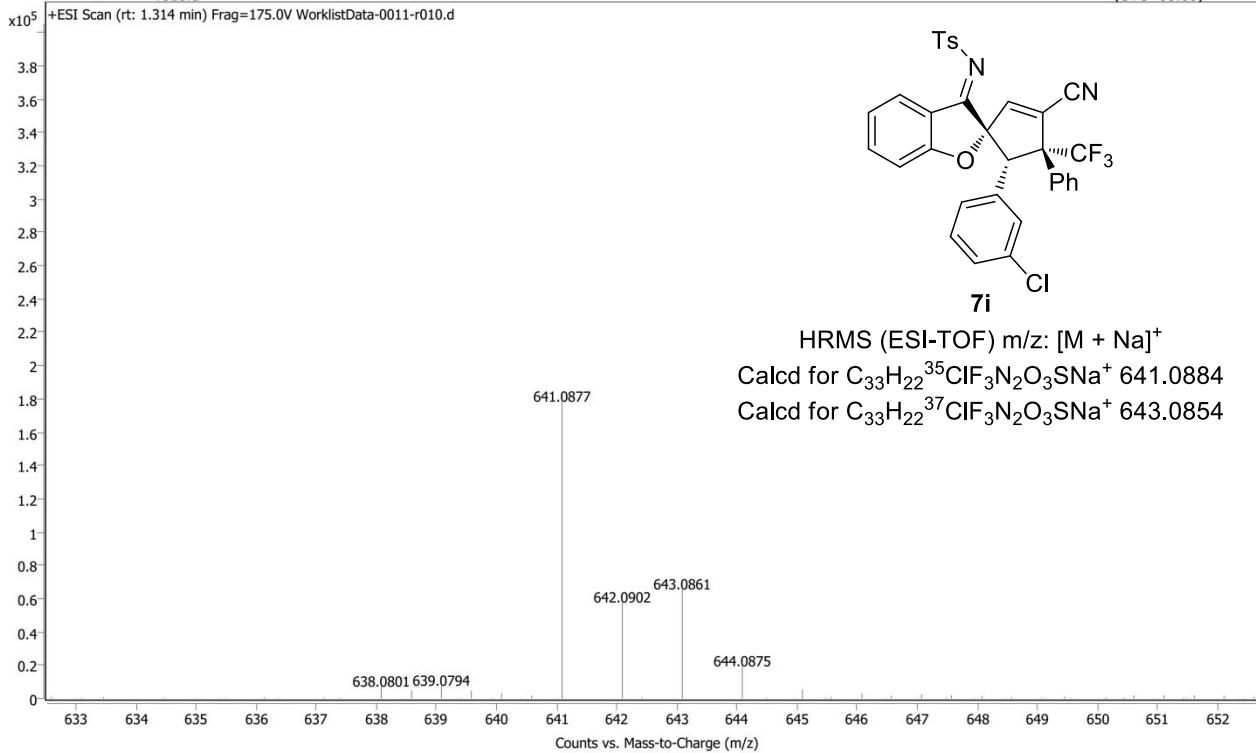


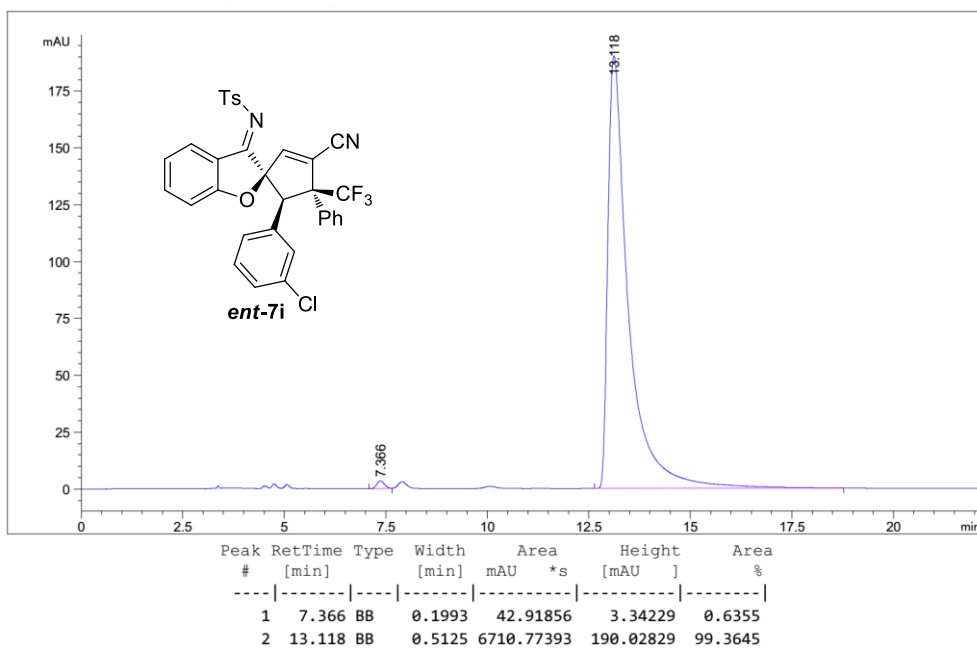
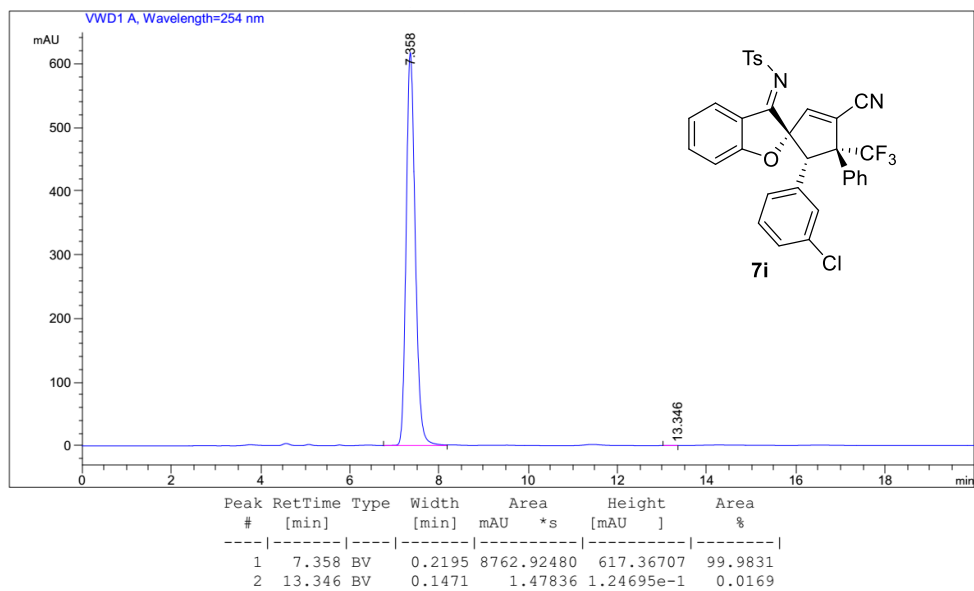
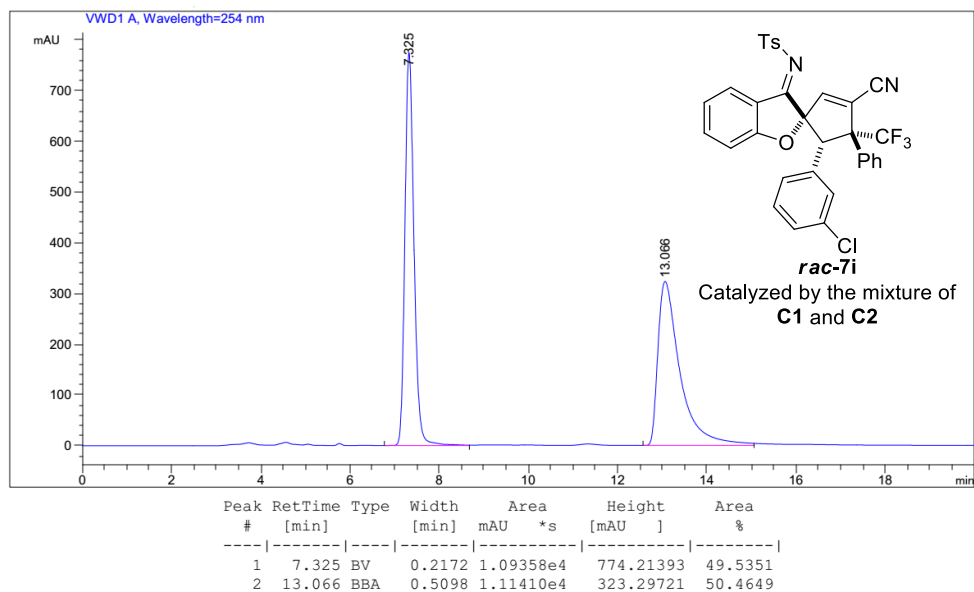
**7i**  
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



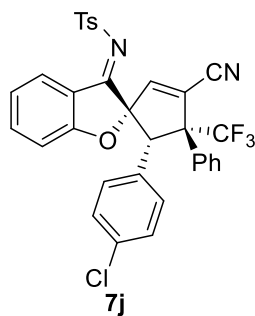
Name	cyc-190705-11	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	WorklistData-0011-r010.d	Method (Acq)	TOF.m		Acq. Time (Local) 7/9/2019 2:02:32 PM (UTC+08:00)

+ESI Scan (rt: 1.314 min) Frag=175.0V WorklistData-0011-r010.d

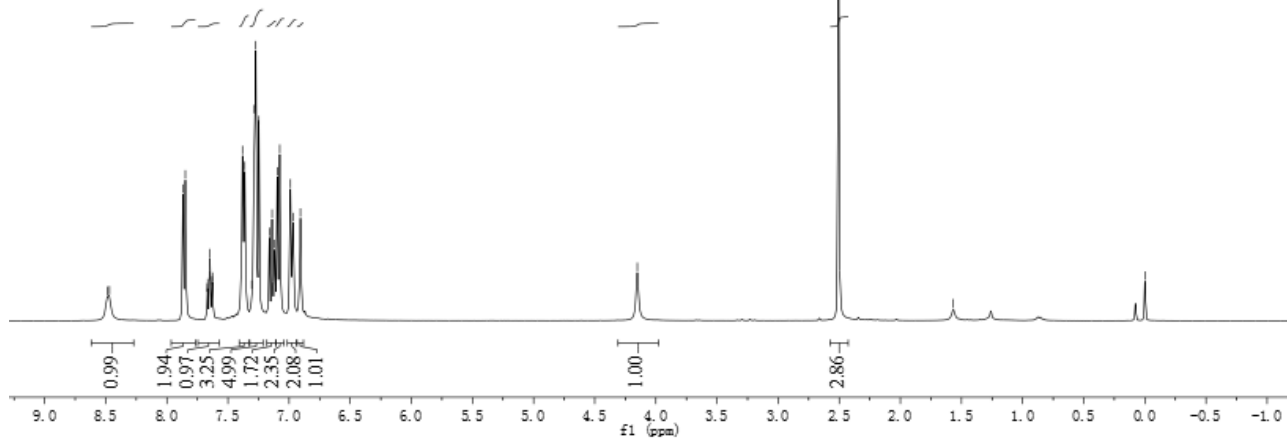




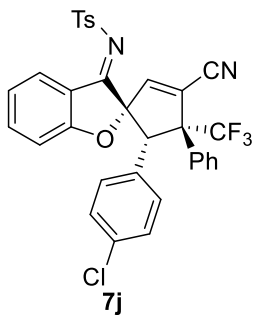
8.488  
8.469  
7.869  
7.849  
7.669  
7.666  
7.652  
7.647  
7.630  
7.627  
7.382  
7.362  
7.306  
7.284  
7.273  
7.247  
7.162  
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7.118  
7.097  
7.076  
6.989  
6.968  
6.907  
-4.151



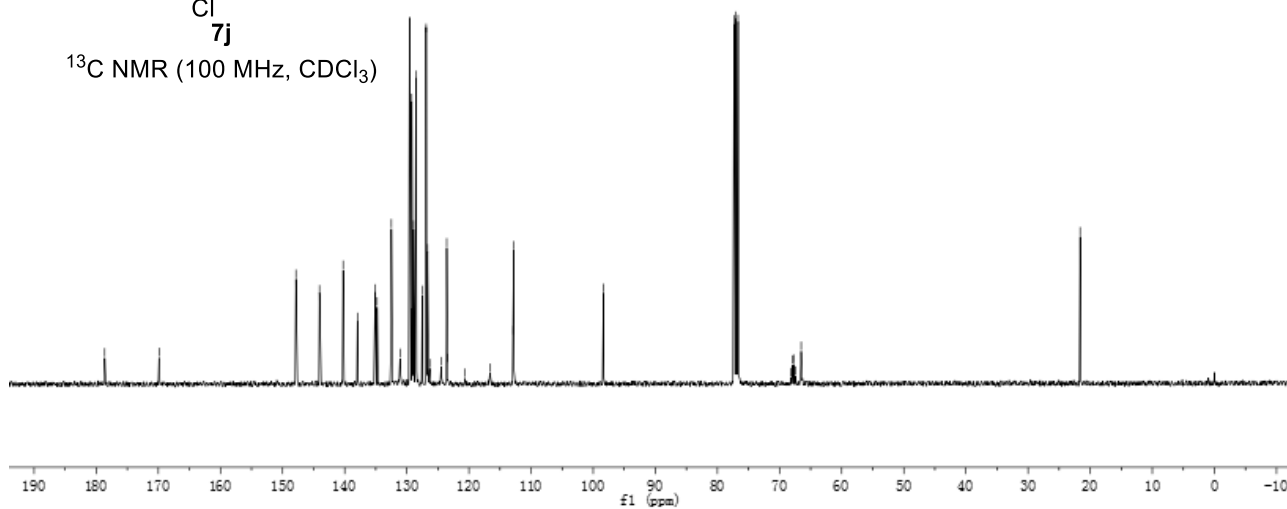
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



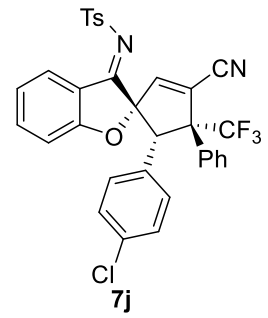
178.631  
169.885  
147.852  
144.057  
140.251  
137.940  
135.097  
134.774  
132.483  
131.096  
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129.206  
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128.929  
128.538  
127.527  
126.890  
126.693  
126.668  
126.311  
124.469  
123.574  
123.472  
120.639  
116.625  
112.883  
112.789  
98.349  
77.318  
77.000  
76.682  
68.179  
67.920  
67.664  
67.405  
66.520  
-21.622



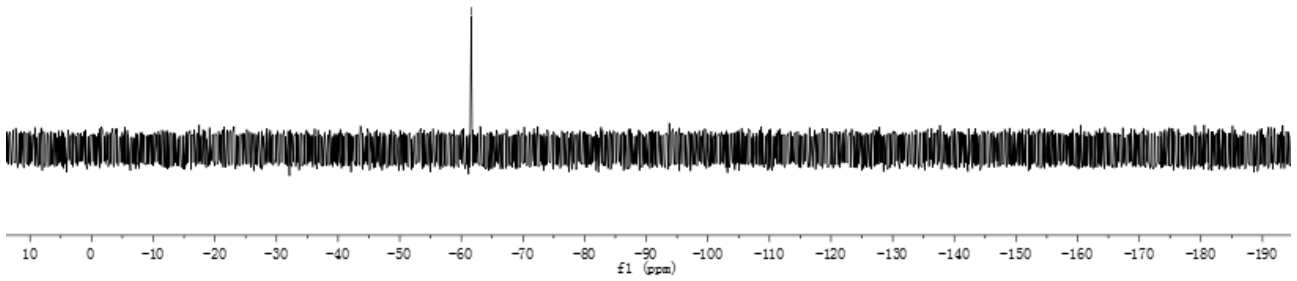
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



61.596

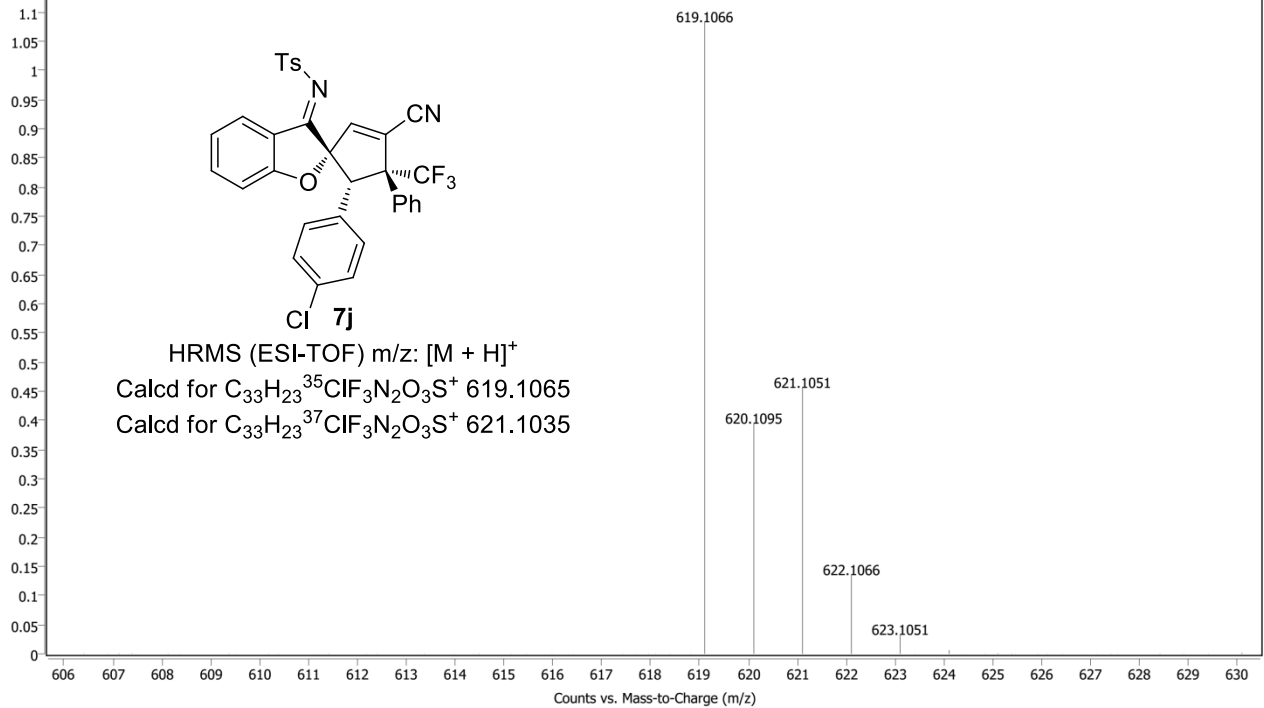


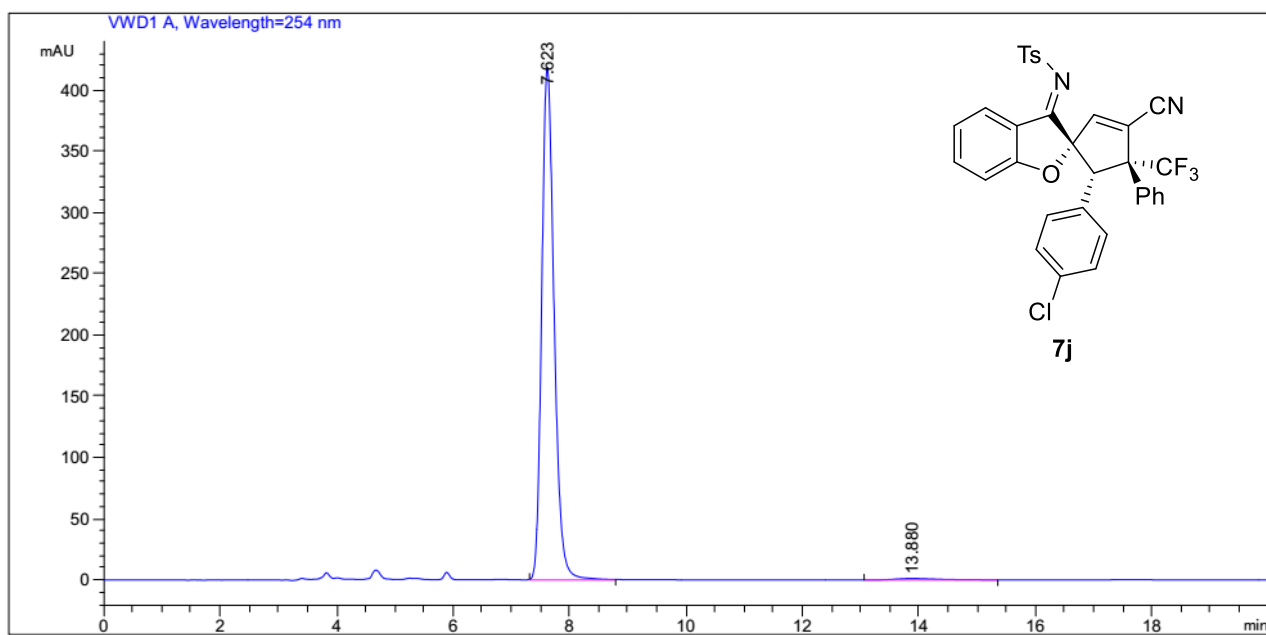
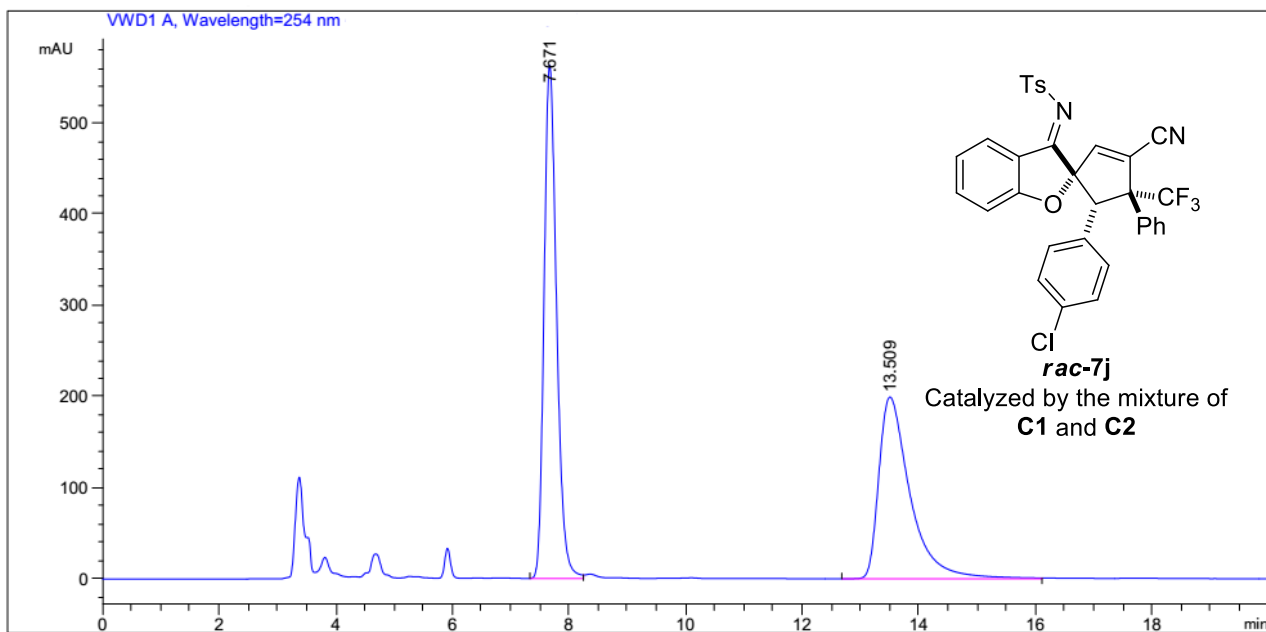
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)

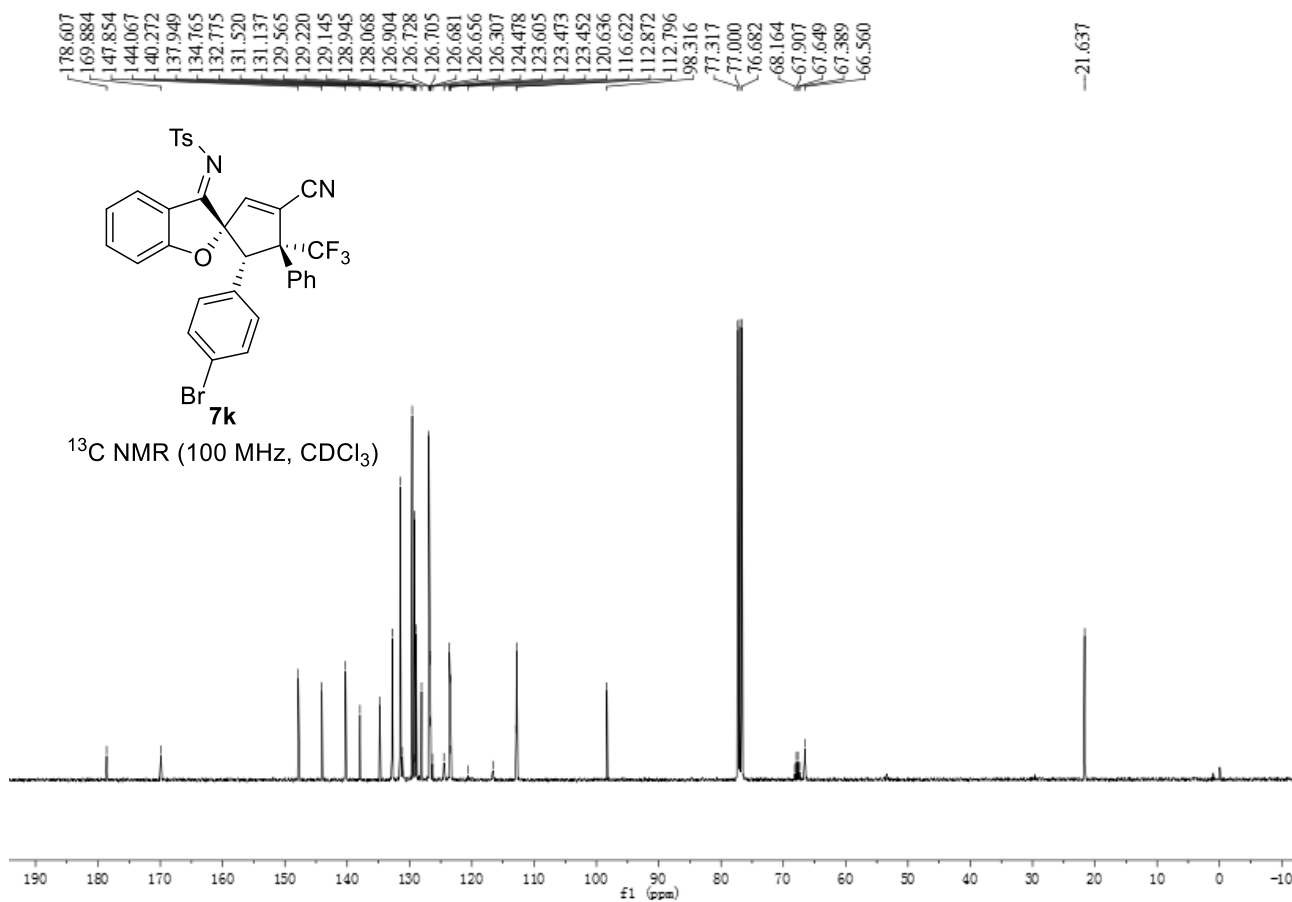
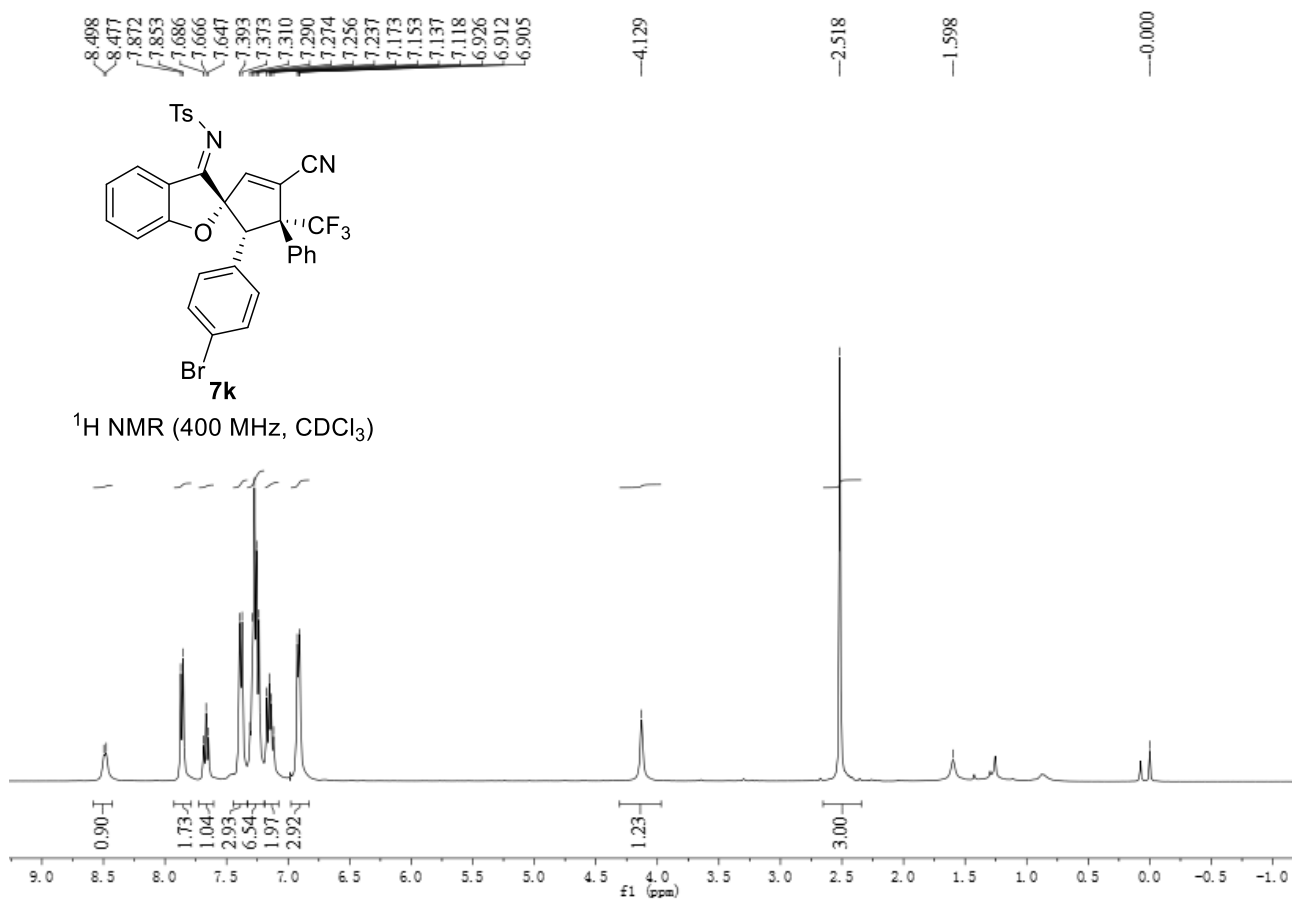


Name	cyc-190705-10	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	WorklistData-0010-r009.d	Method (Acq)	TOF.m		Acq. Time (Local)
					7/9/2019 1:59:43 PM (UTC+08:00)

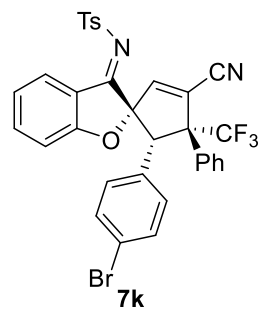
+ESI Scan (rt: 1.549 min) Frag=175.0V WorklistData-0010-r009.d



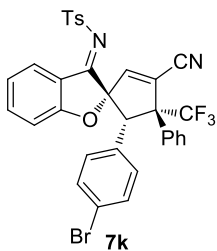
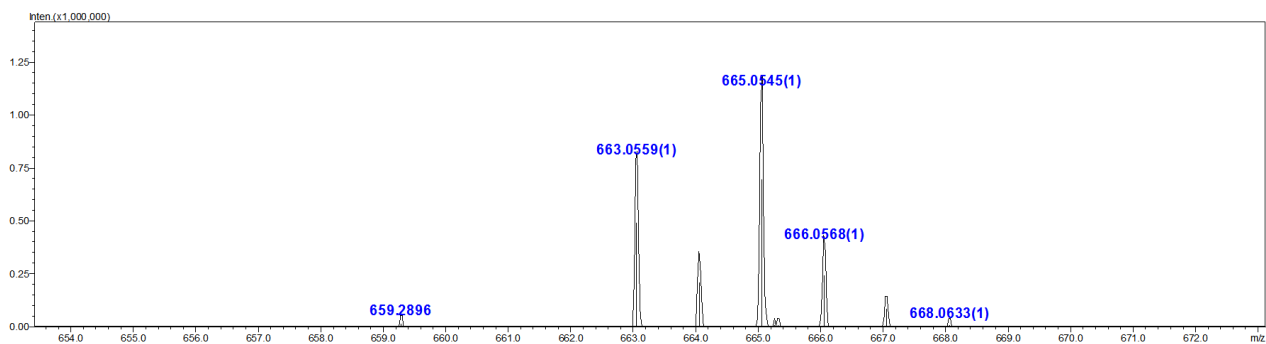
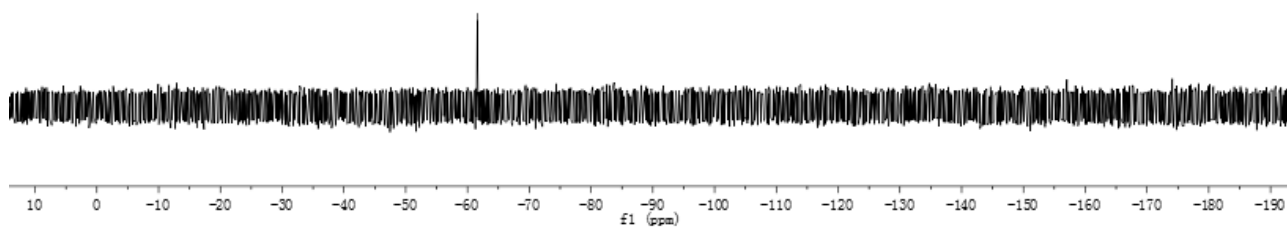




—61.579

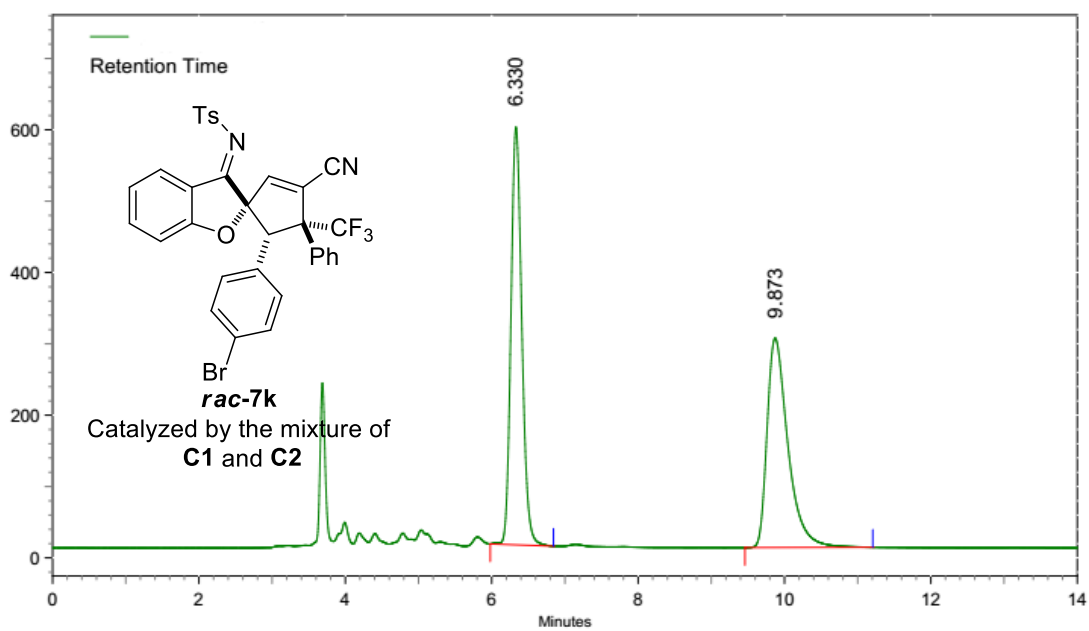


$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



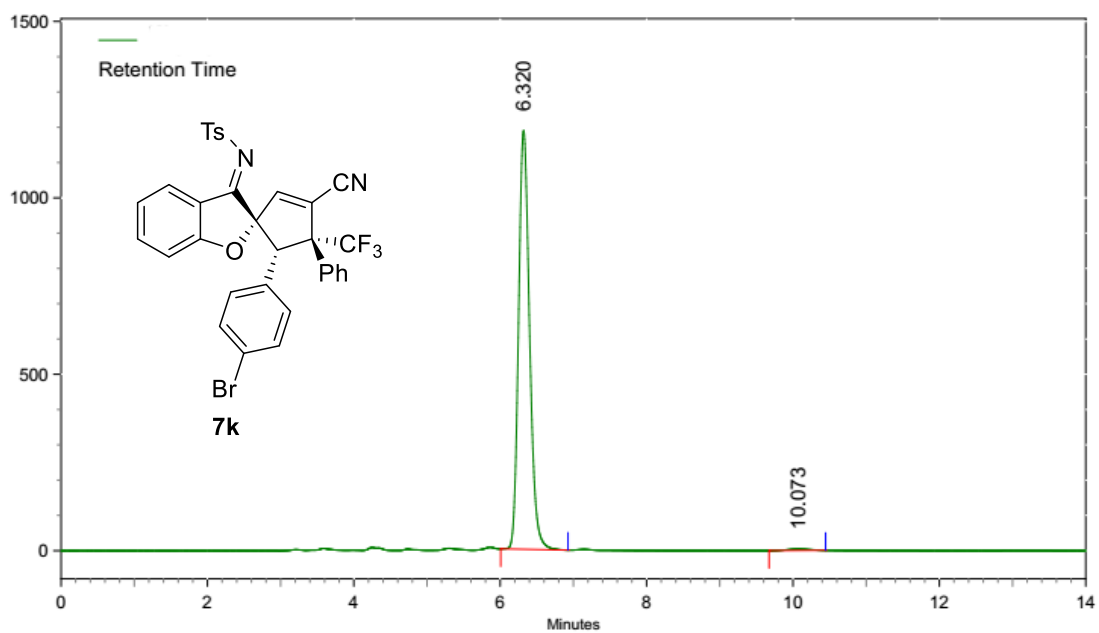
HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$   
Calcd for  $\text{C}_{33}\text{H}_{23}^{79}\text{BrF}_3\text{N}_2\text{O}_3\text{S}^+$  663.0599  
Calcd for  $\text{C}_{33}\text{H}_{23}^{81}\text{BrF}_3\text{N}_2\text{O}_3\text{S}^+$  665.0539





### AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	6.330	0.863	9821948	101260128	50.9952
2	9.873	1.747	4922941	97307656	49.0048

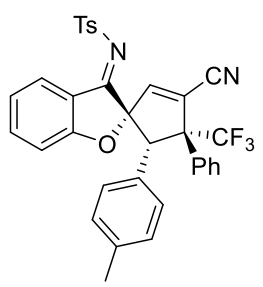


### AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	6.320	0.920	19905448	206909255	99.3638
2	10.073	0.773	62124	1324836	0.6362

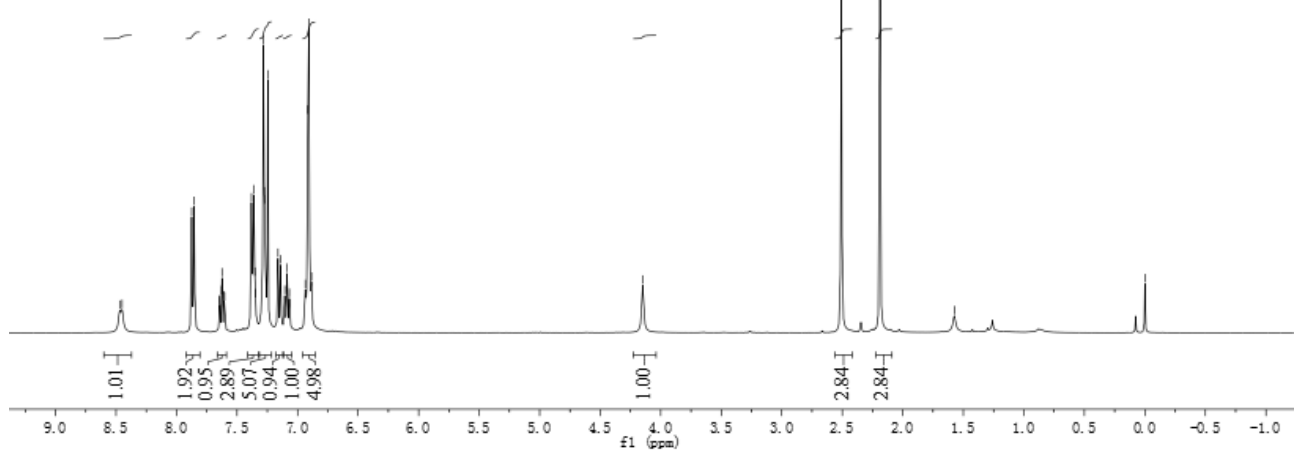
8.470  
8.449  
7.875  
7.855  
7.646  
7.643  
7.628  
7.625  
7.621  
7.607  
7.603  
7.381  
7.361  
7.353  
7.346  
7.282  
7.275  
7.268  
7.247  
7.161  
7.140  
7.106  
7.087  
7.068  
6.936  
6.915  
6.907  
6.885  
4.148

-2.508  
-2.189  
-1.574  
-0.000



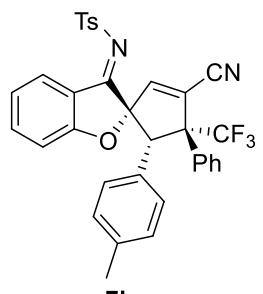
71

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



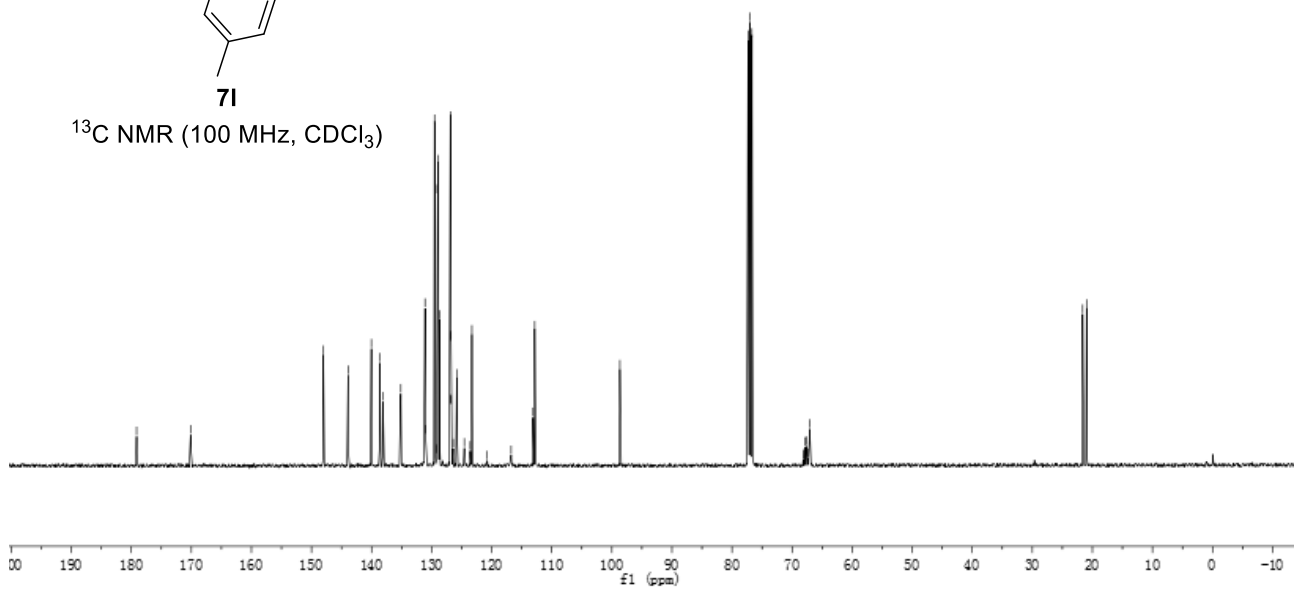
179.122  
170.128  
148.031  
143.911  
140.037  
138.639  
138.111  
135.136  
131.107  
131.008  
129.518  
129.254  
129.061  
128.966  
128.713  
126.883  
126.821  
126.798  
126.774  
126.751  
126.421  
125.814  
124.561  
123.584  
123.299  
120.750  
116.764  
113.113  
112.840  
98.663  
77.318  
77.000  
76.682  
68.151  
67.893  
67.635  
67.380  
67.062

21.621  
20.969

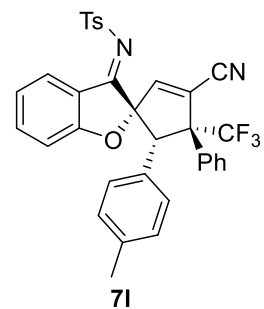


71

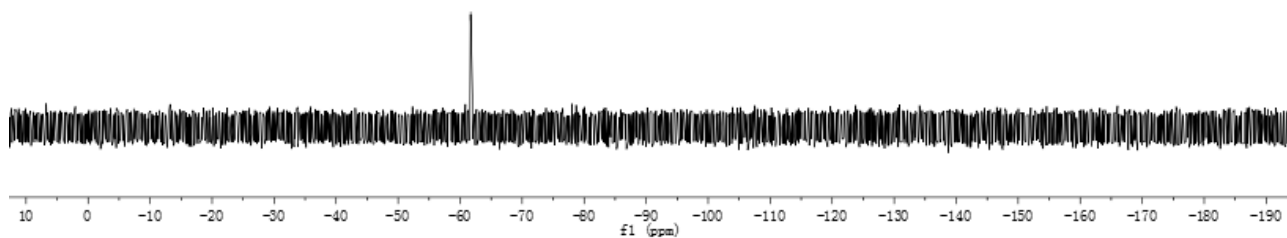
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



61.696

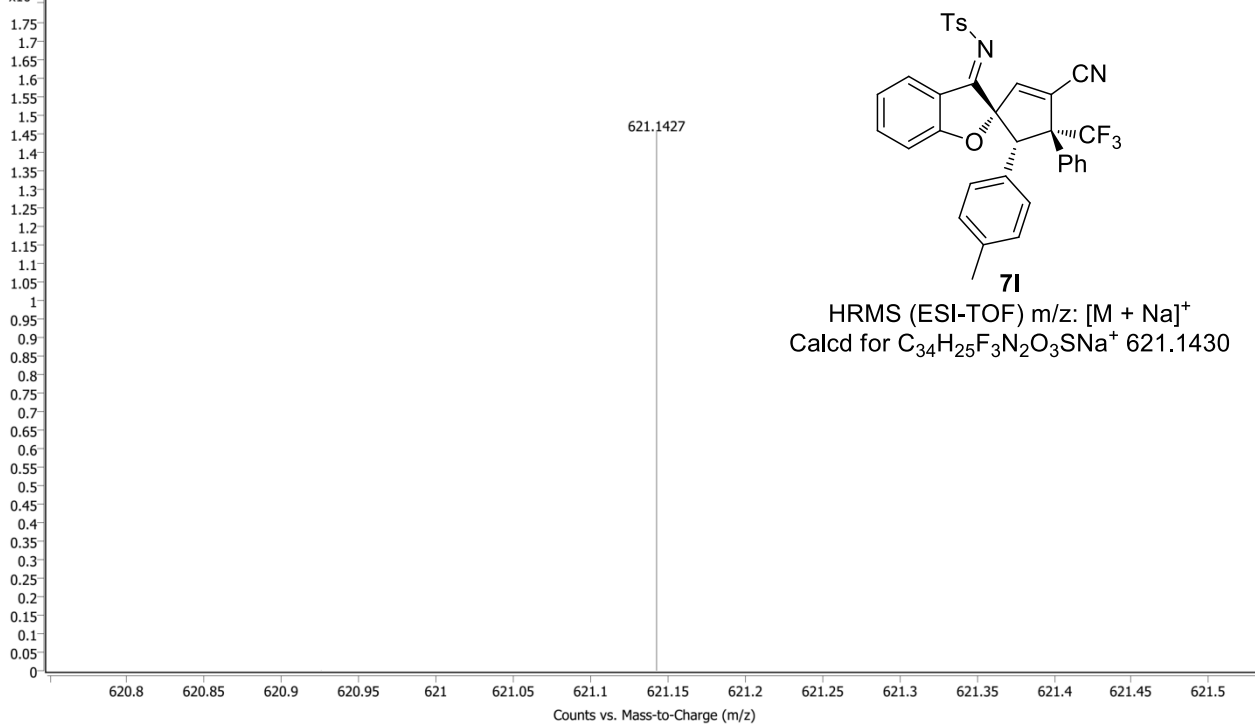


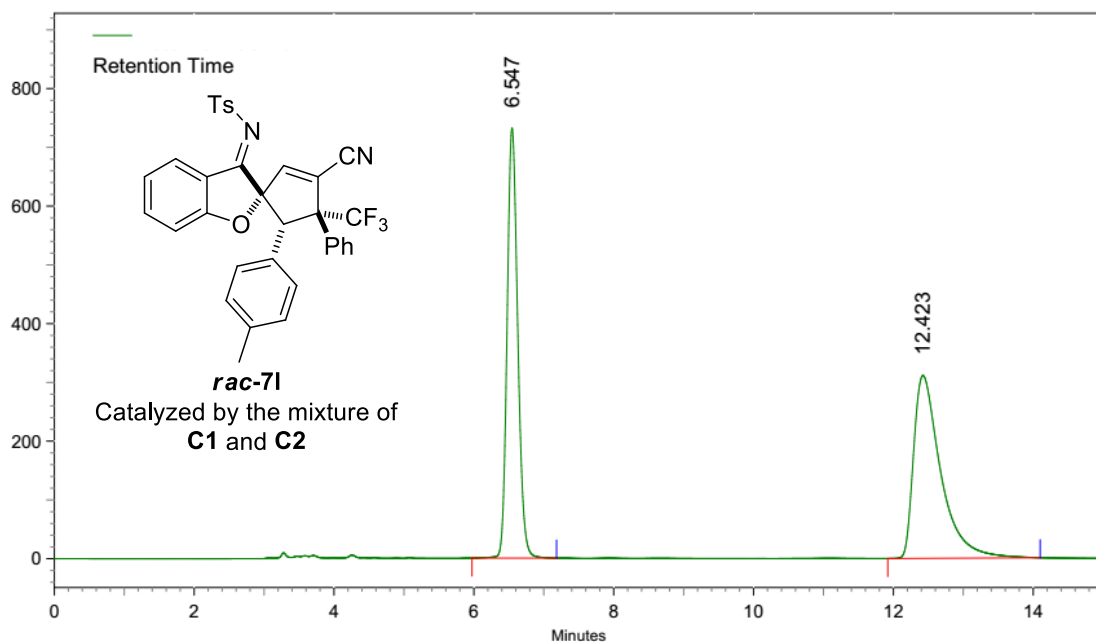
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



Name	cyc-190705-13	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	WorklistData-0013-r002.d	Method (Acq)	TOF.m	Comment	Acq. Time (Local) 7/9/2019 2:08:10 PM (UTC+08:00)

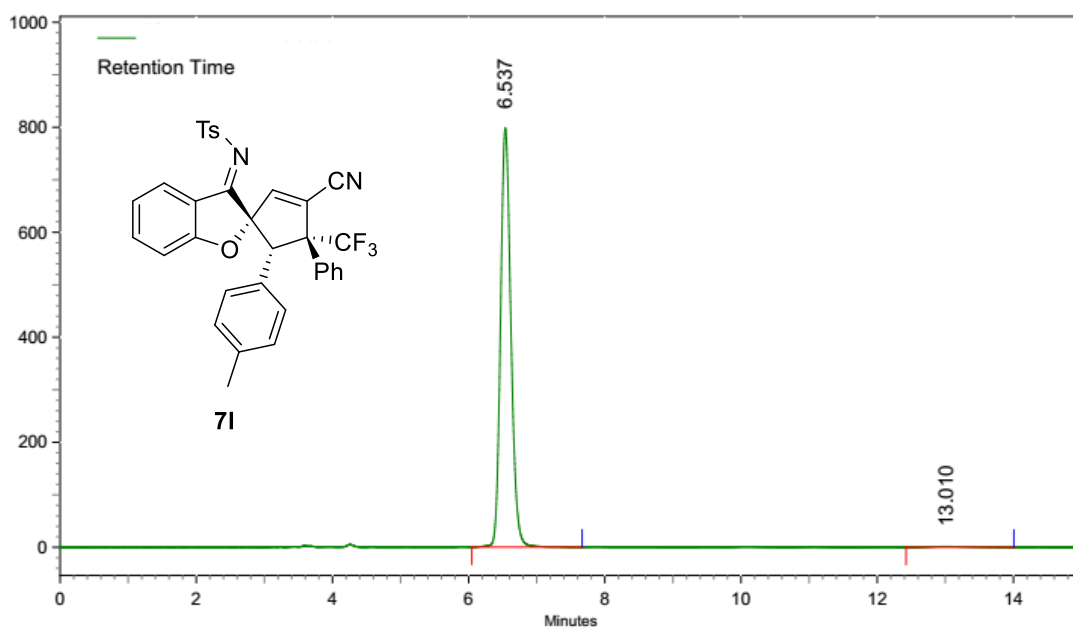
+ESI Scan (rt: 1.243 min) Frag=175.0V WorklistData-0013-r002.d





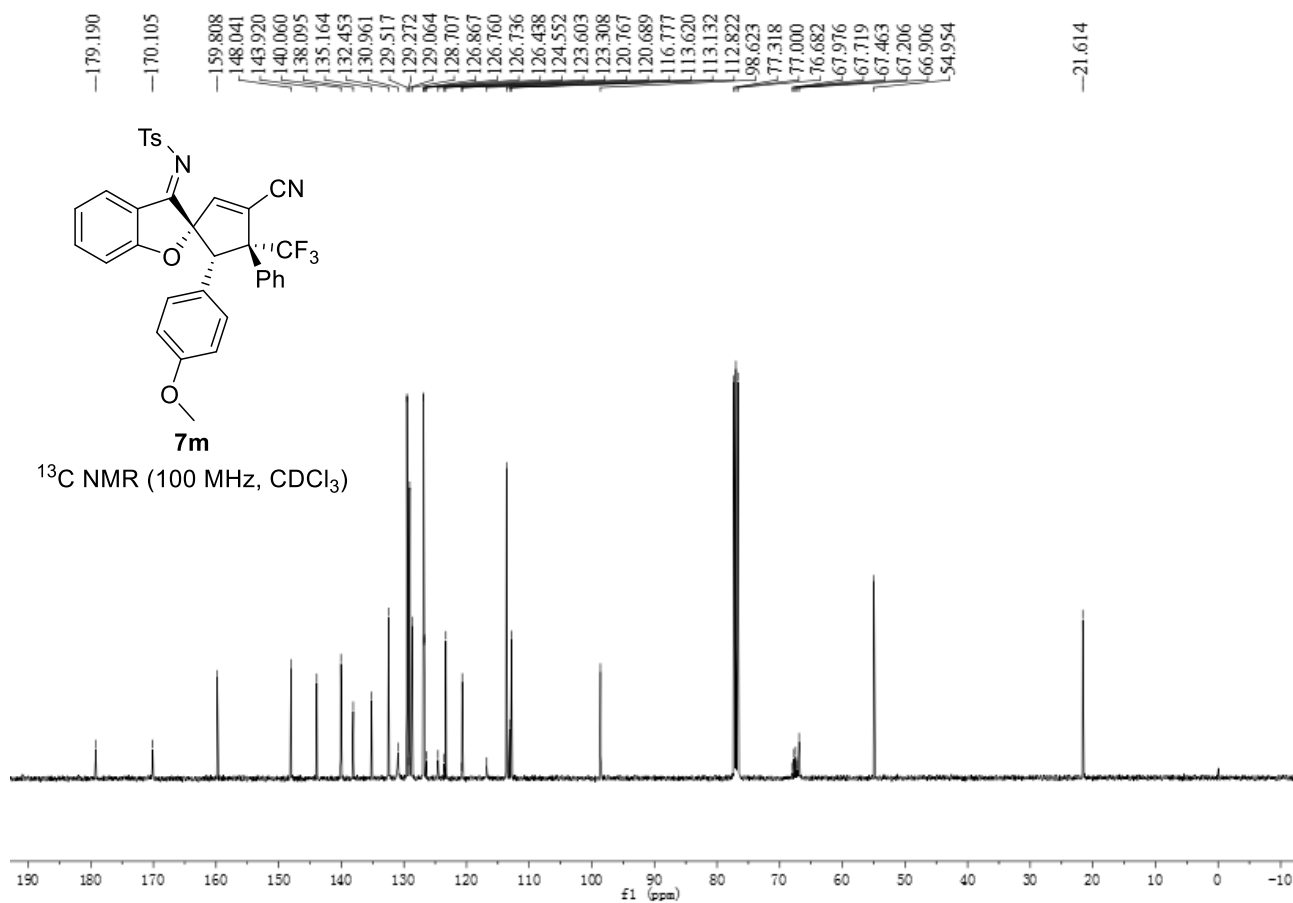
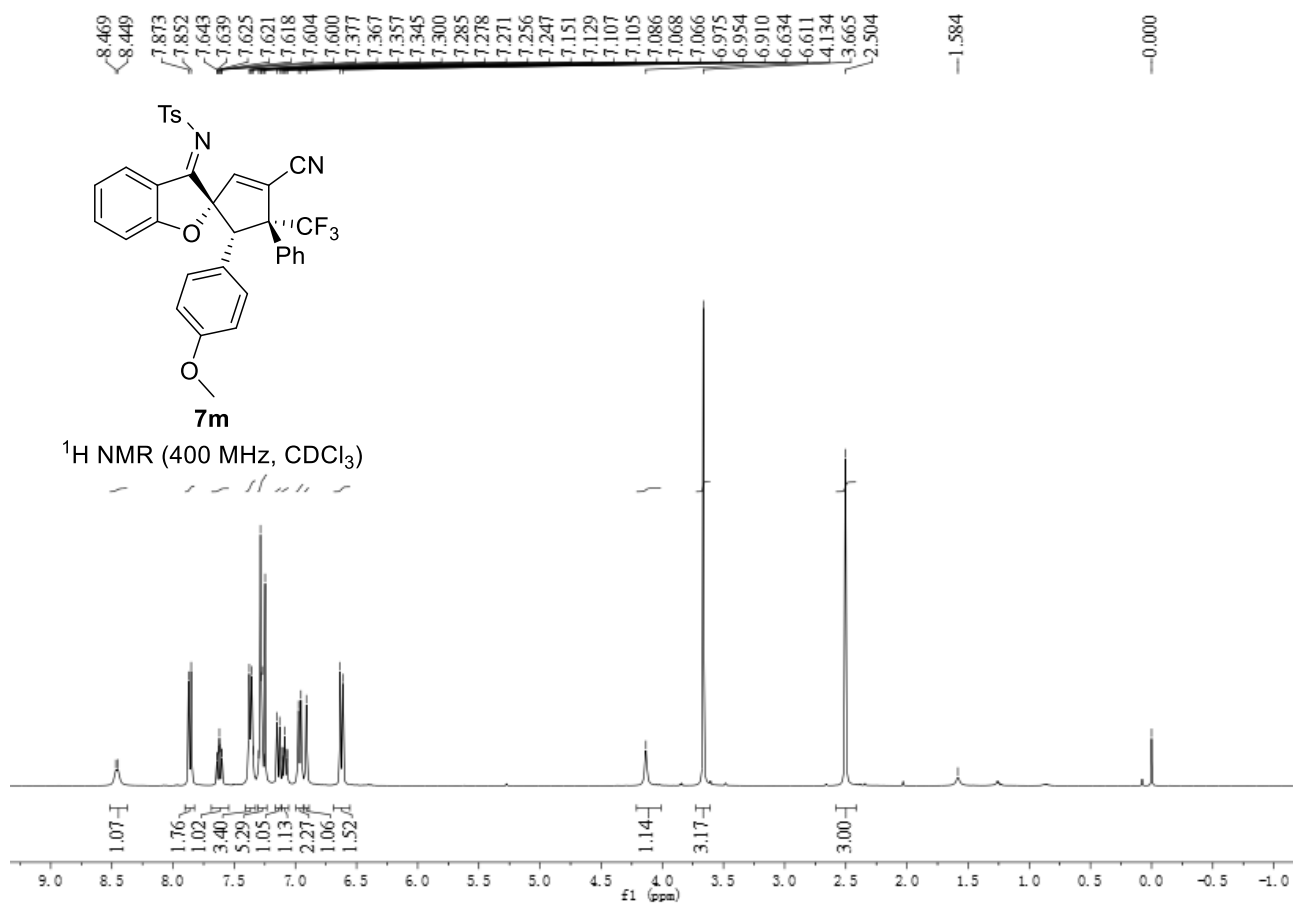
### AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	6.547	1.210	12277066	129390601	47.9444
2	12.423	2.180	5221233	140485622	52.0556

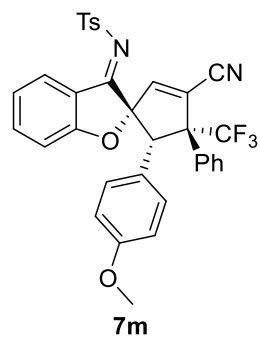


### AREA PERCENT REPORT

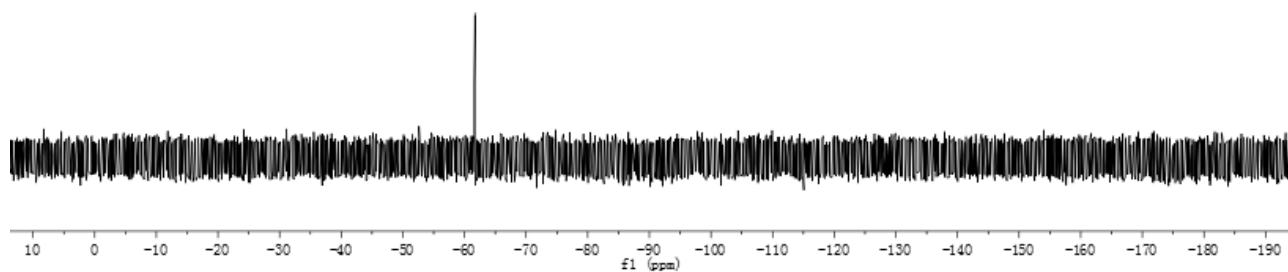
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	6.537	1.620	13386437	141472227	99.3977
2	13.010	1.583	19998	857194	0.6023



61.700

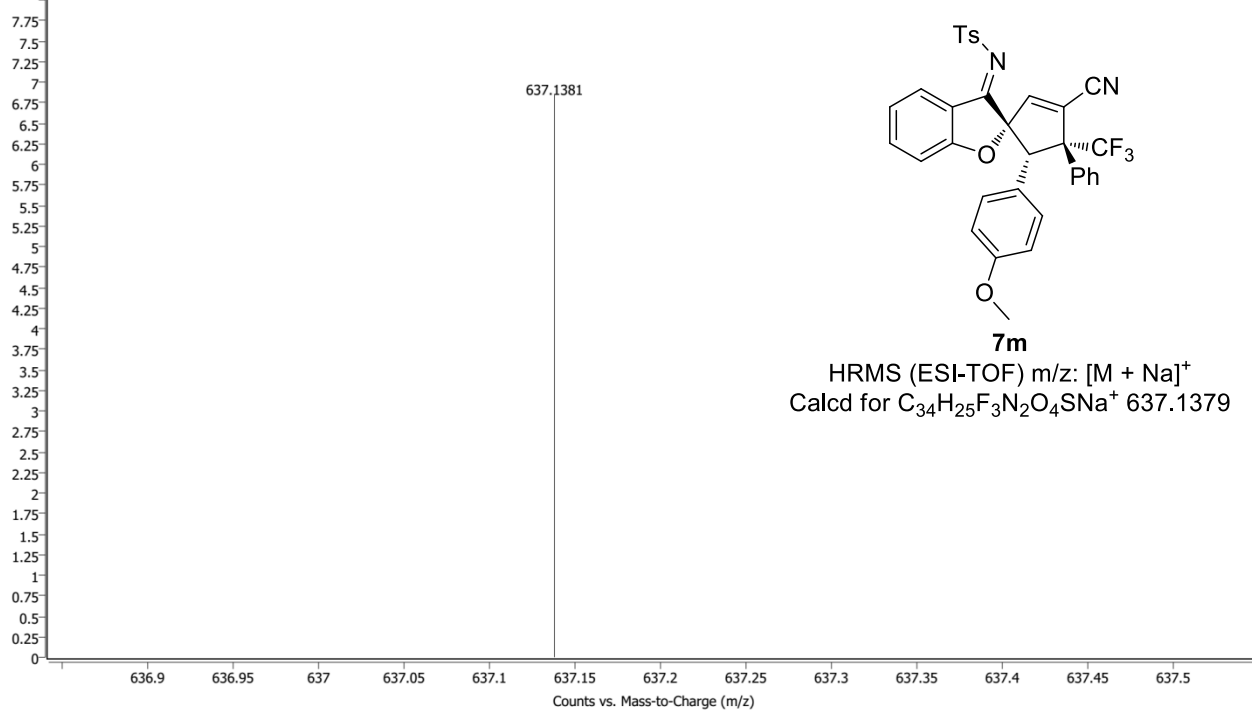


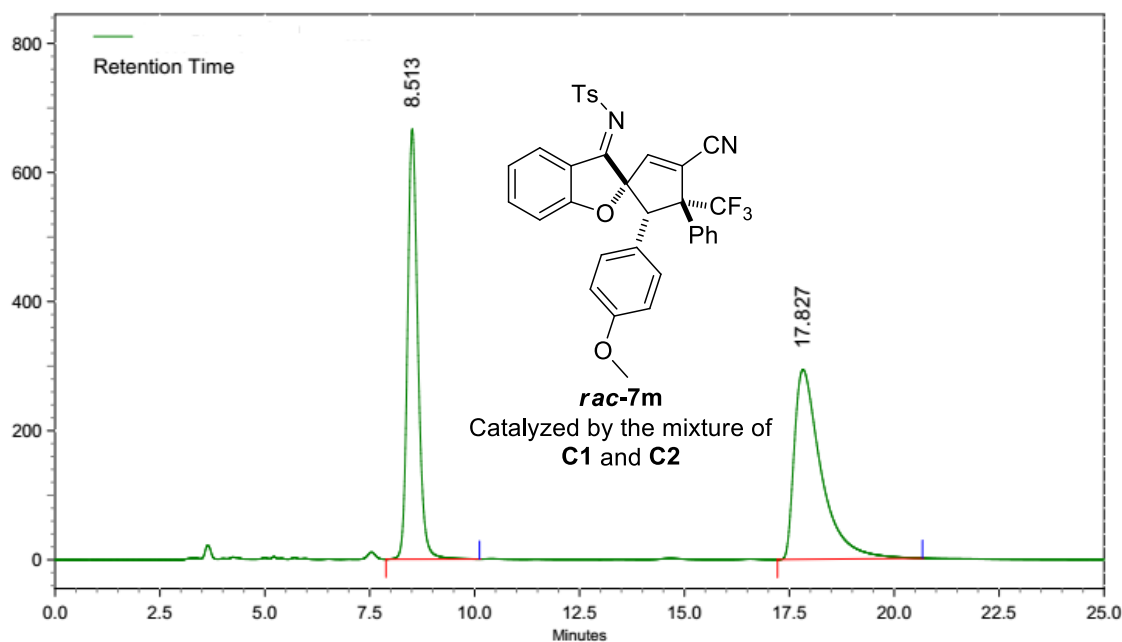
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



Name	cyc-190705-12	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	WorklistData-0012-r001.d	Method (Acq)	TOF.m		Acq. Time (Local)
					7/9/2019 2:05:21 PM (UTC+08:00)

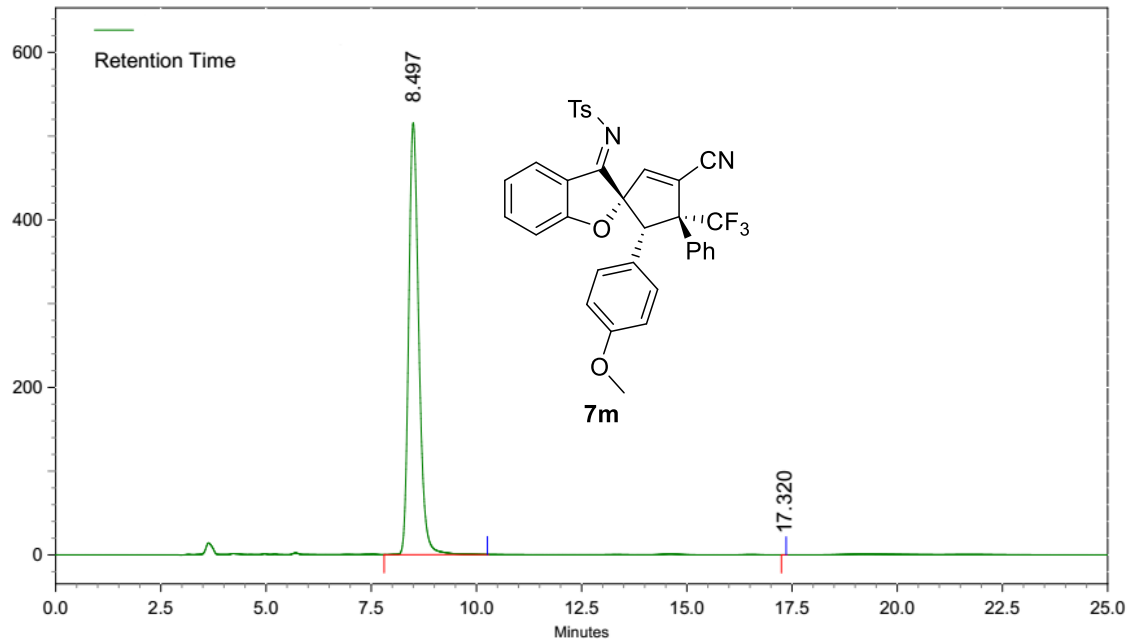
+ESI Scan (rt: 0.899 min) Frag=175.0V WorklistData-0012-r001.d





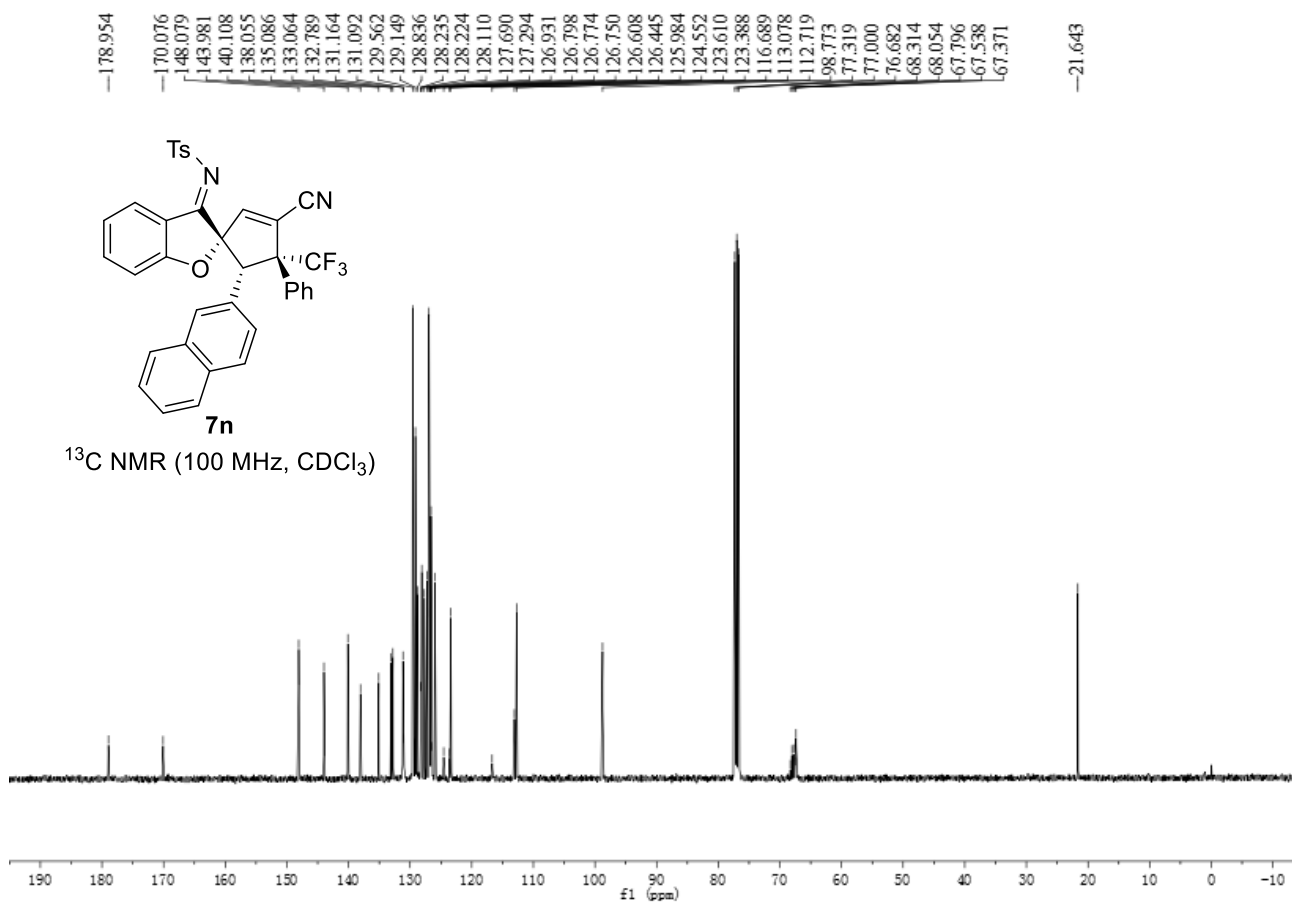
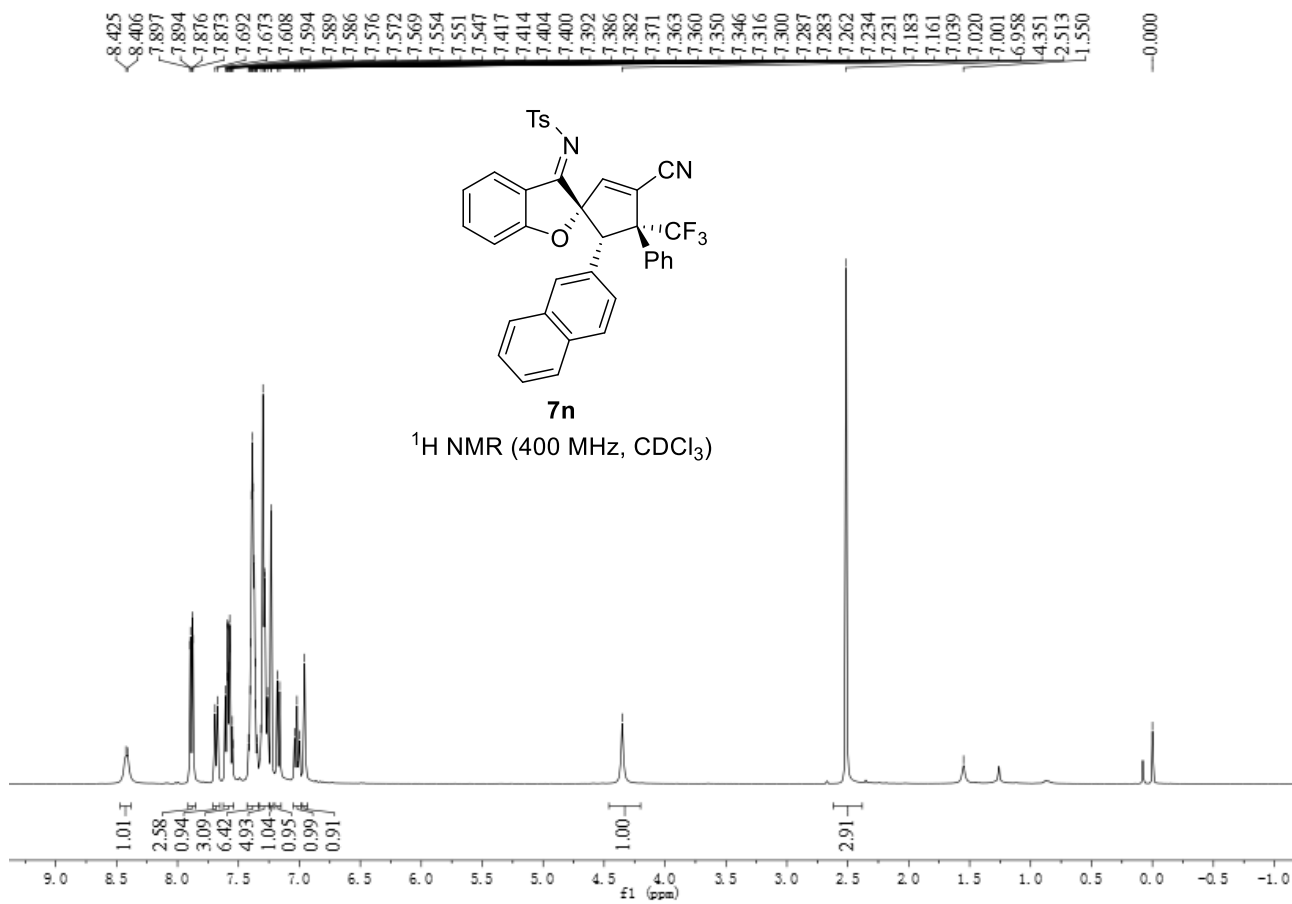
### AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	8.513	2.230	11177890	191624840	46.5664
2	17.827	3.453	4934045	219883882	53.4336



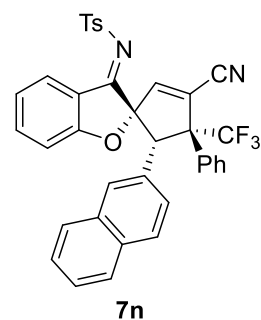
### AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	8.497	2.453	8646894	144720037	99.9999
2	17.320	0.113	51	159	0.0001

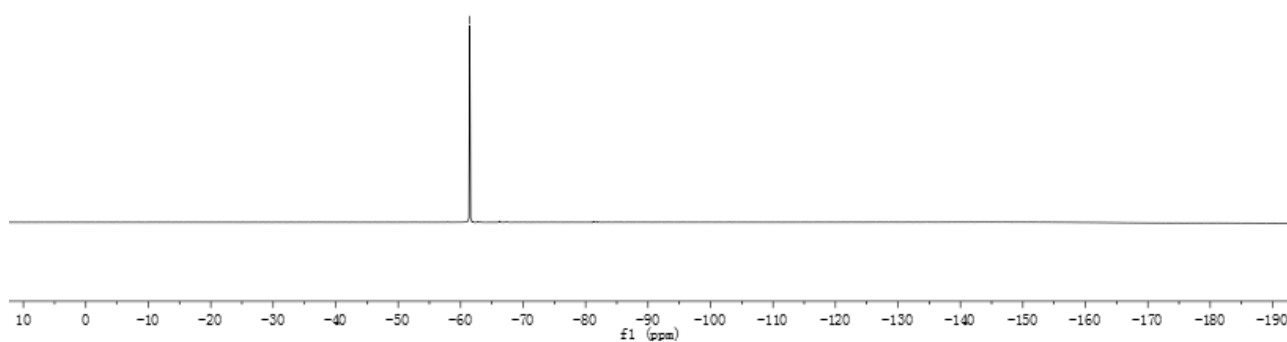




-61.457

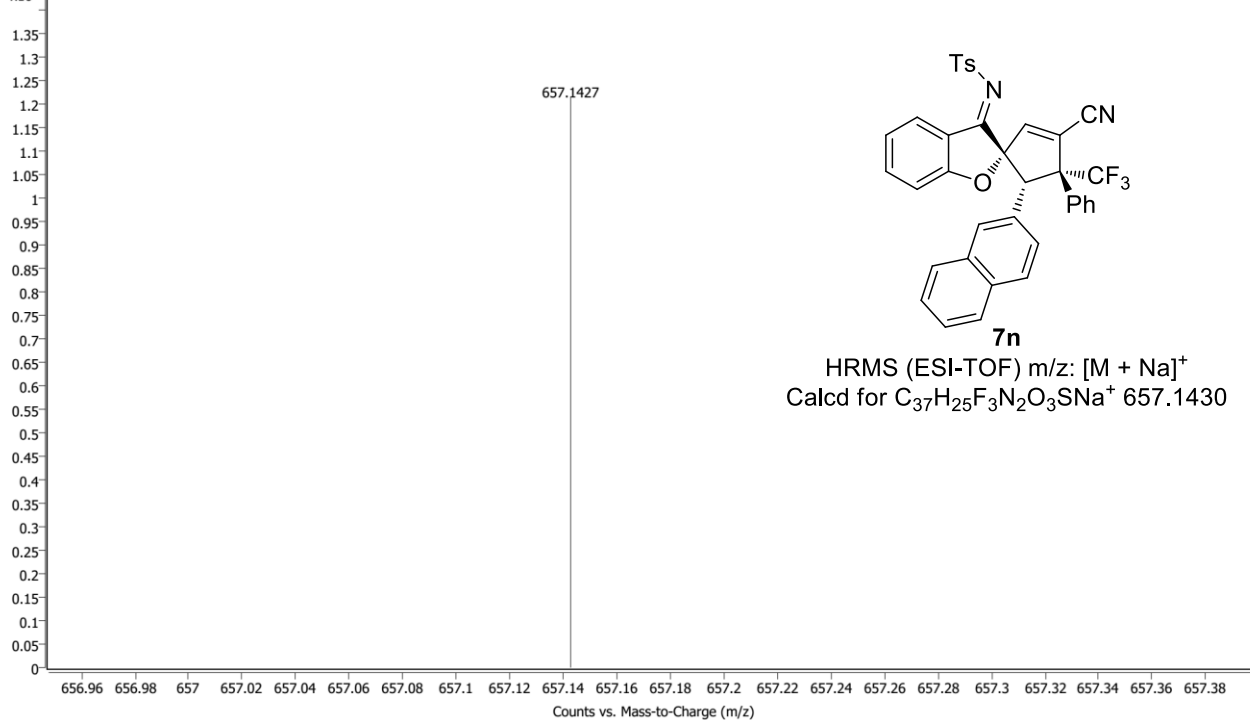


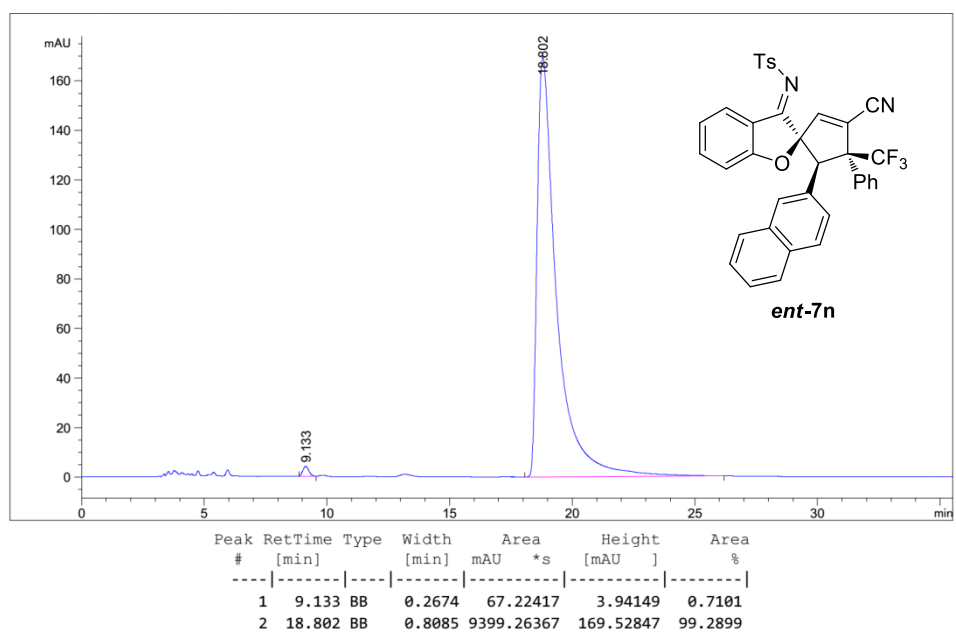
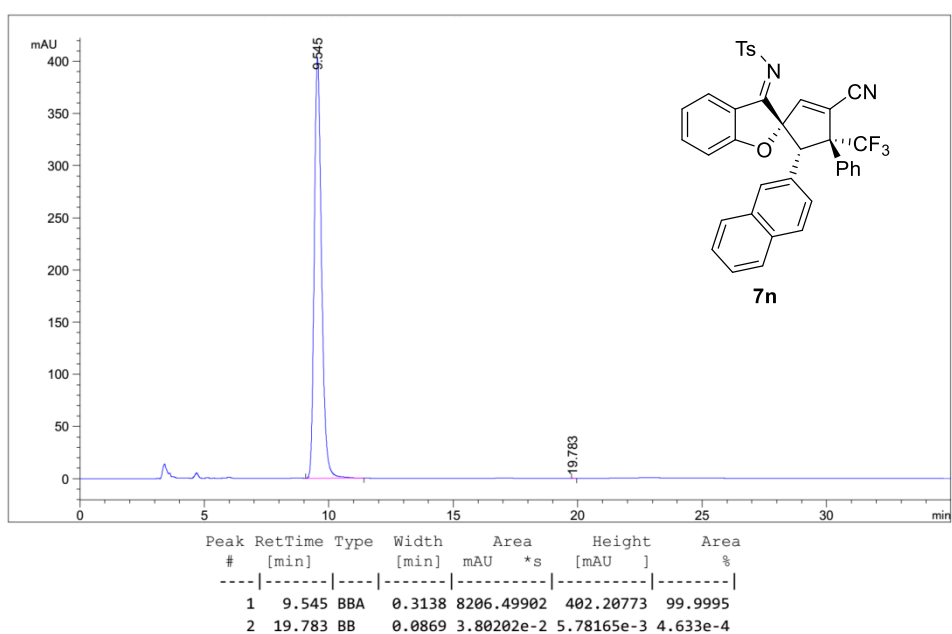
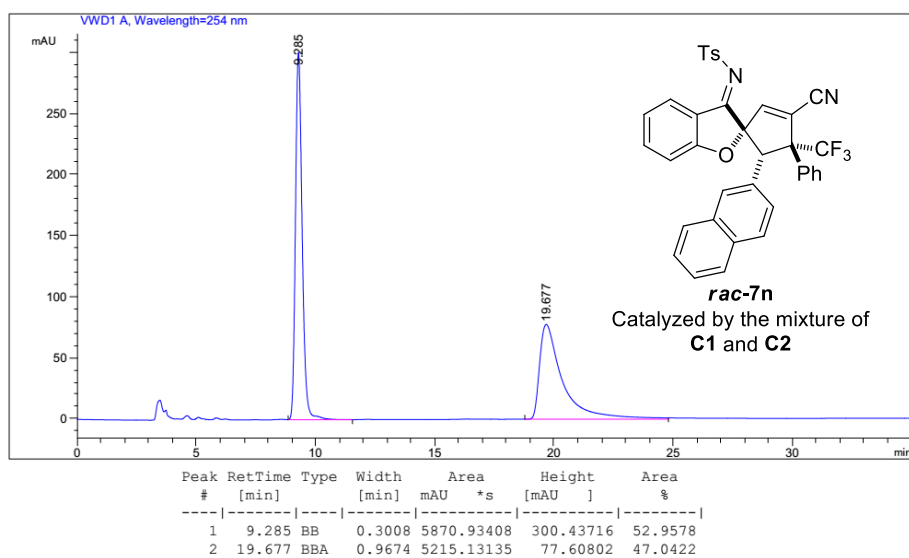
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



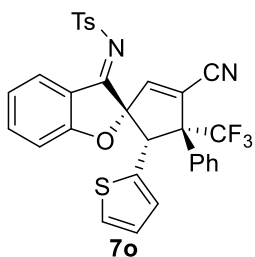
Name	cyc-190705-14	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	WorklistData-0014-r003.d	Method (Acq)	TOF.m	Comment	Acq. Time (Local) 7/9/2019 2:10:59 PM (UTC+08:00)

+ESI Scan (rt: 1.509 min) Frag=175.0V WorklistData-0014-r003.d

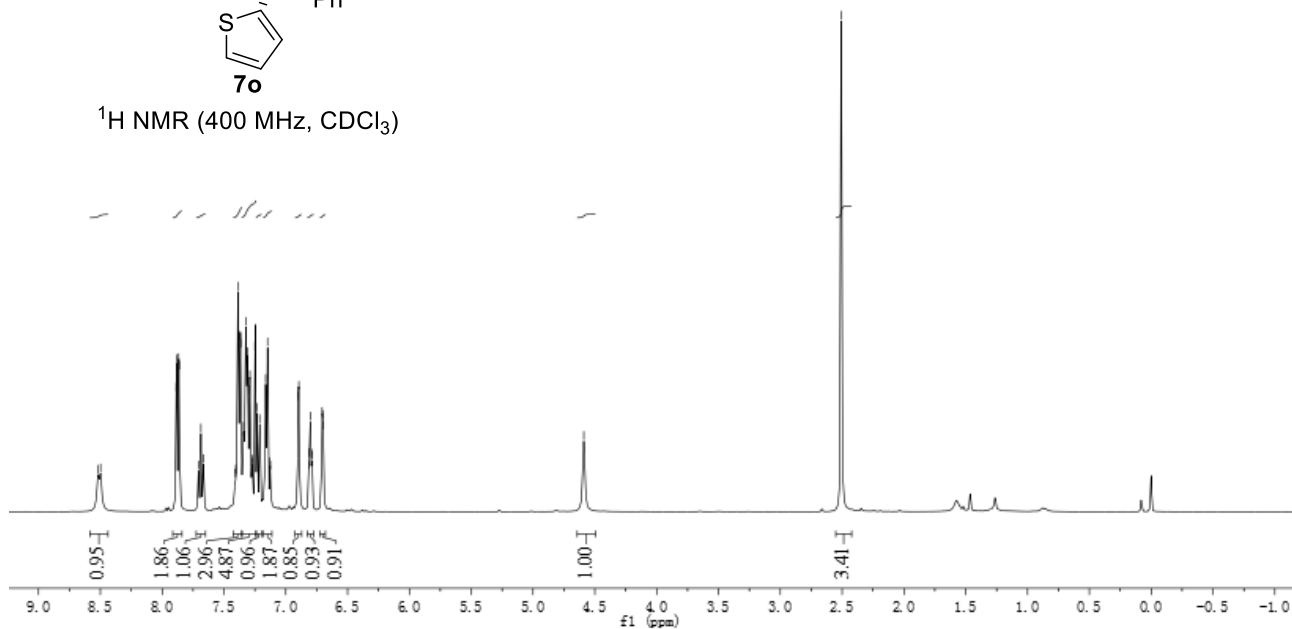




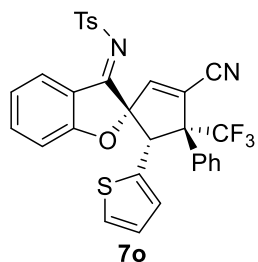
8.518  
8.498  
7.887  
7.882  
7.866  
7.861  
7.705  
7.686  
7.667  
7.410  
7.405  
7.387  
7.369  
7.365  
7.343  
7.323  
7.311  
7.307  
7.294  
7.290  
7.273  
7.269  
7.250  
7.246  
7.232  
7.211  
7.163  
7.147  
7.128  
7.124  
6.899  
6.894  
6.814  
6.810  
6.801  
6.792  
6.788  
6.706  
6.701  
6.696  
4.589  
2.507



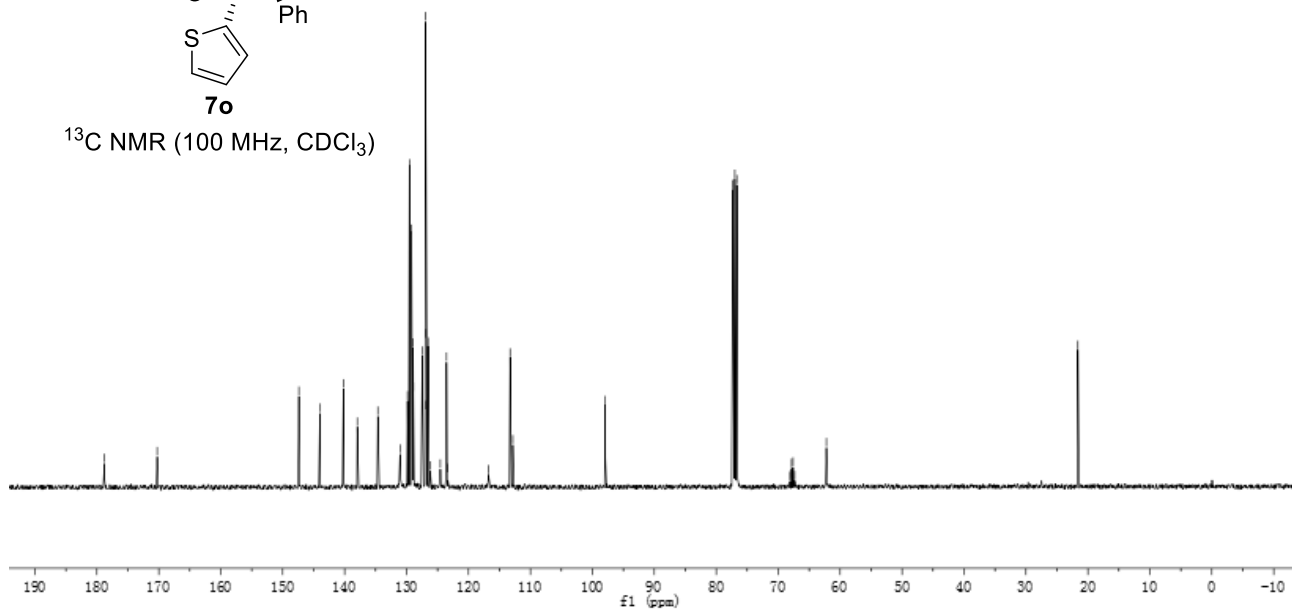
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )



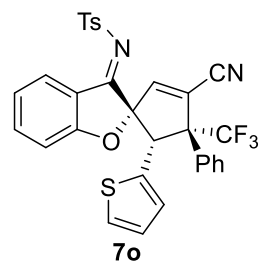
178.783  
170.264  
147.381  
143.994  
140.194  
137.952  
134.640  
131.056  
129.841  
129.534  
129.192  
128.930  
128.899  
127.469  
126.889  
126.864  
126.847  
126.521  
126.181  
124.548  
123.548  
123.347  
116.740  
113.284  
112.844  
97.917  
77.317  
77.000  
76.684  
68.102  
67.849  
67.596  
67.345  
62.217  
-21.616



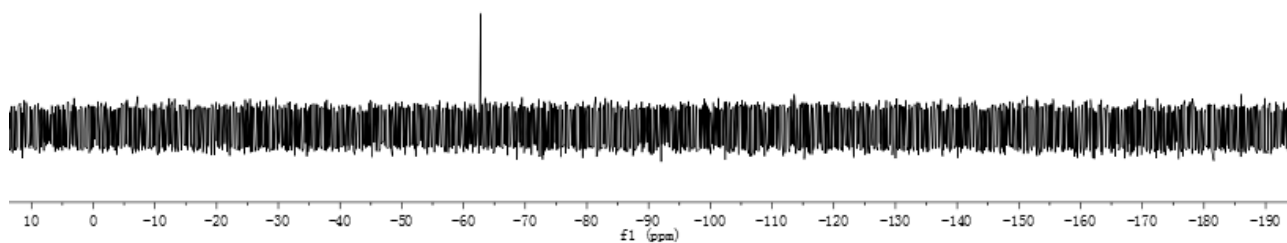
$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )



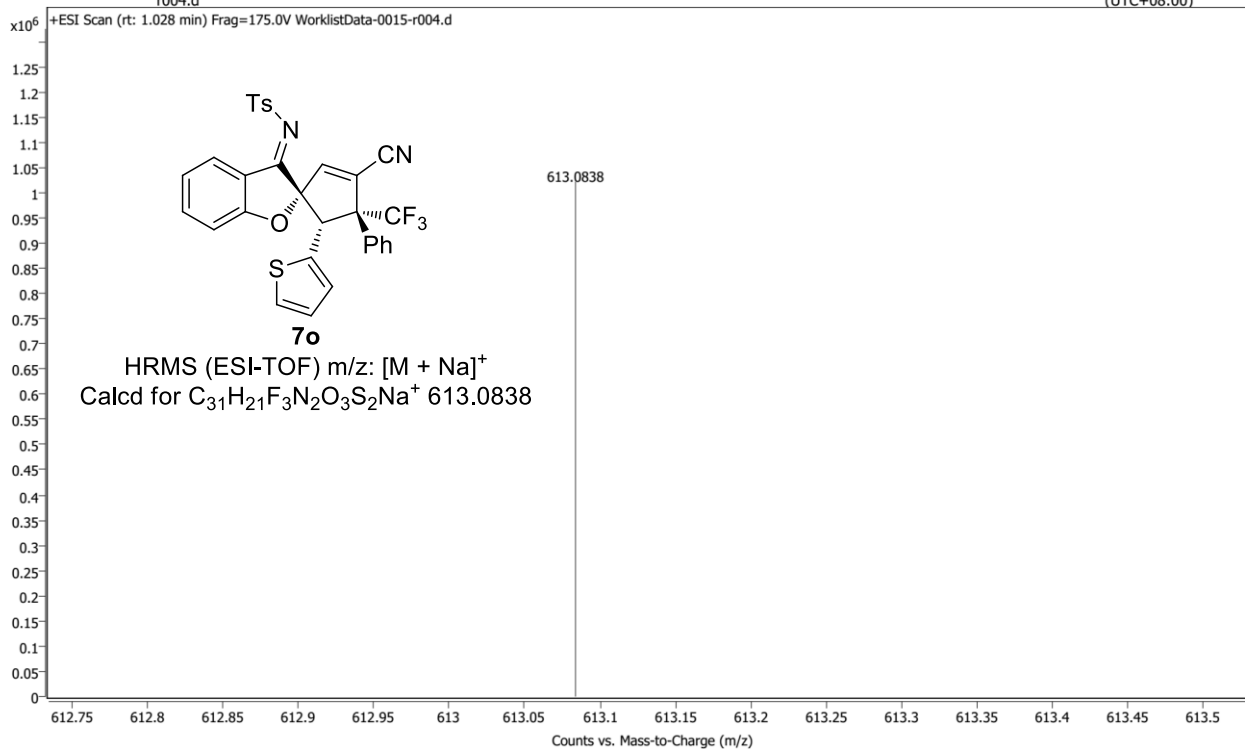
—62.754

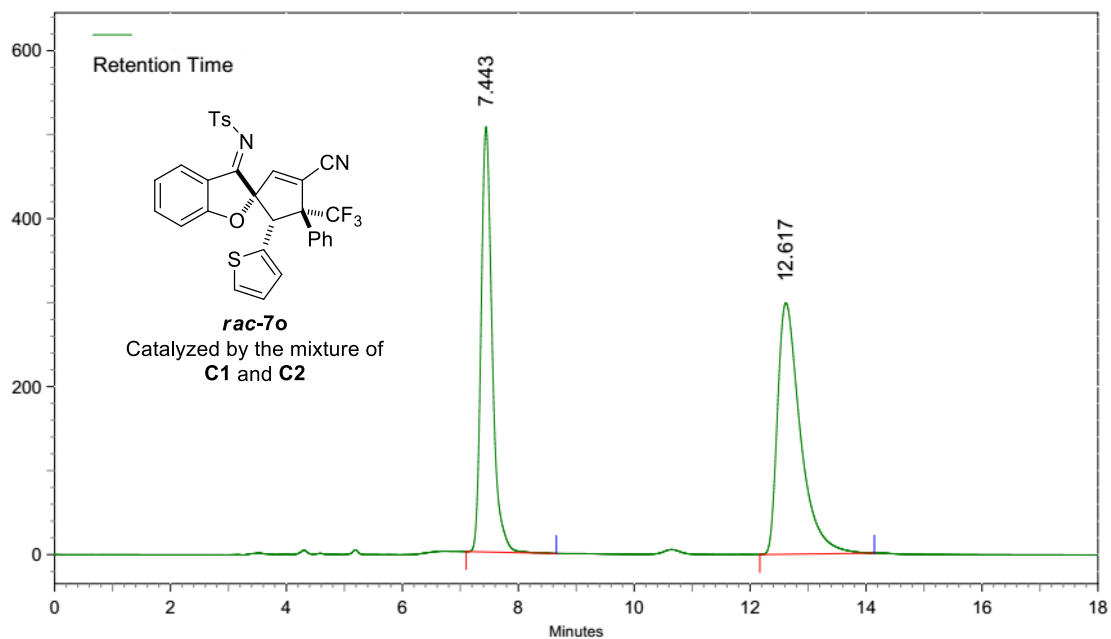


<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



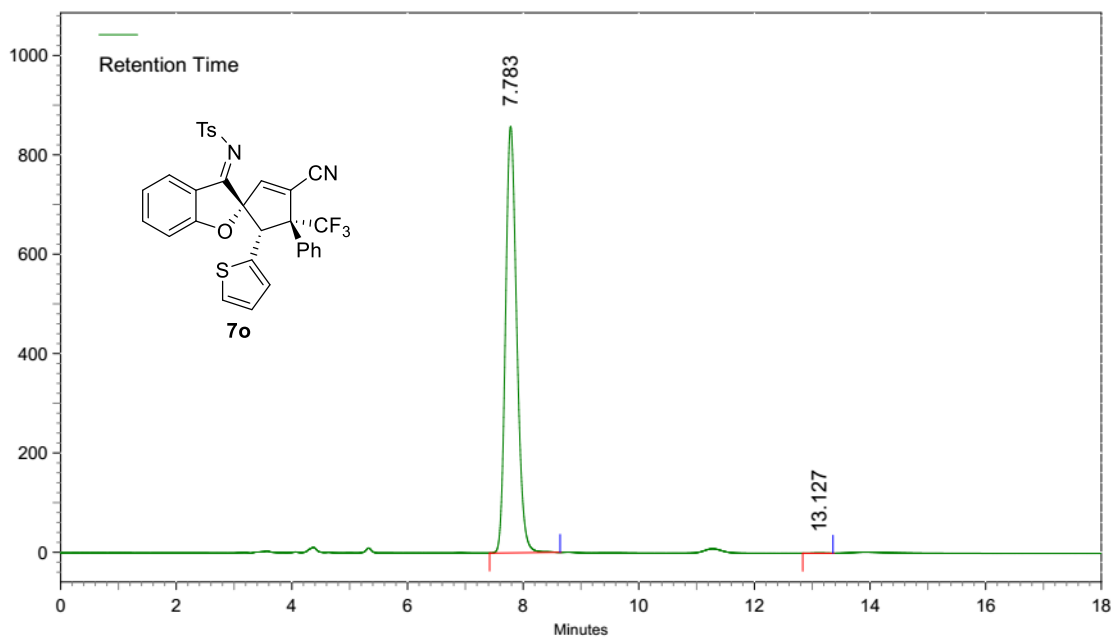
Name	cyc-190705-15	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	WorklistData-0015-r004.d	Method (Acq)	TOF.m	Comment	Acq. Time (Local) 7/9/2019 2:13:48 PM (UTC+08:00)





### AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	7.443	1.557	8490766	112900540	45.1747
2	12.617	1.977	5024095	137019262	54.8253

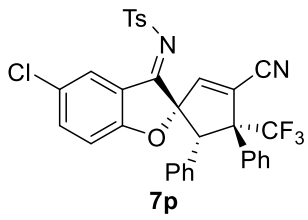


### AREA PERCENT REPORT

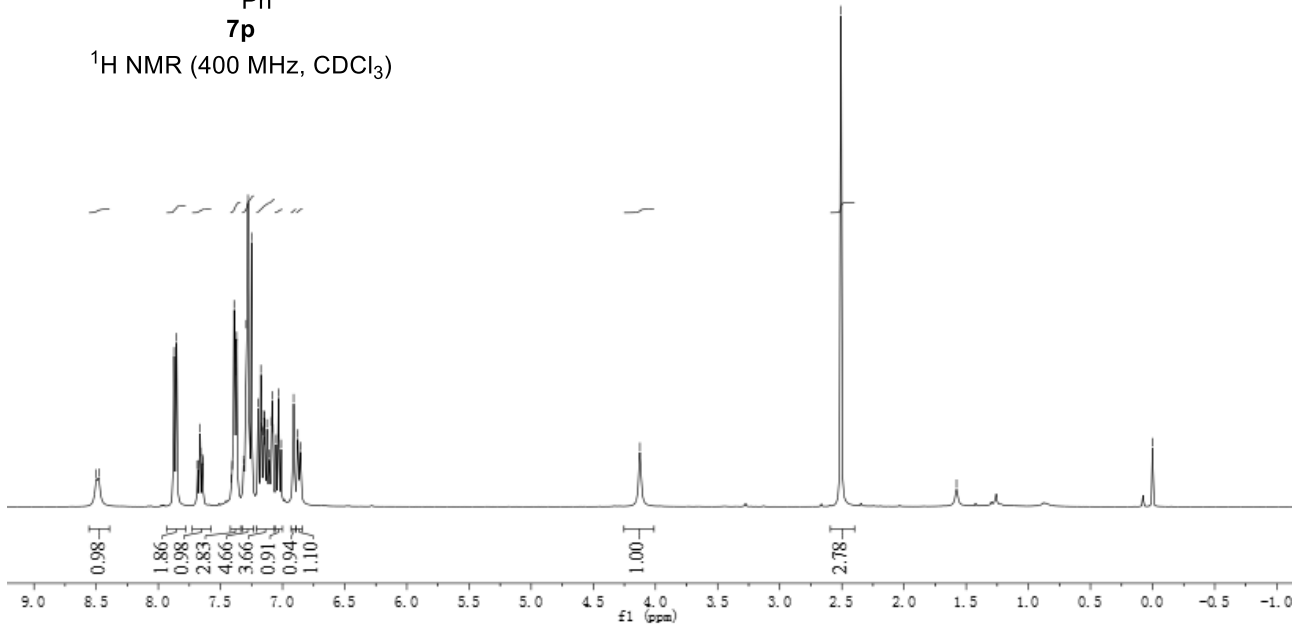
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	7.783	1.220	14397166	193782578	99.9590
2	13.127	0.523	5458	79446	0.0410

8.499  
8.479  
7.873  
7.853  
7.685  
7.681  
7.667  
7.663  
7.660  
7.646  
7.642  
7.411  
7.405  
7.390  
7.374  
7.369  
7.314  
7.309  
7.293  
7.279  
7.262  
7.250  
7.197  
7.175  
7.170  
7.155  
7.151  
7.147  
7.144  
7.126  
7.107  
7.088  
7.084  
7.079  
7.052  
7.032  
7.012  
6.911  
6.877  
6.857  
4.125  
2.508  
1.577

-0.000

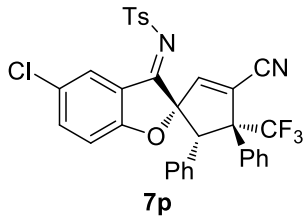


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

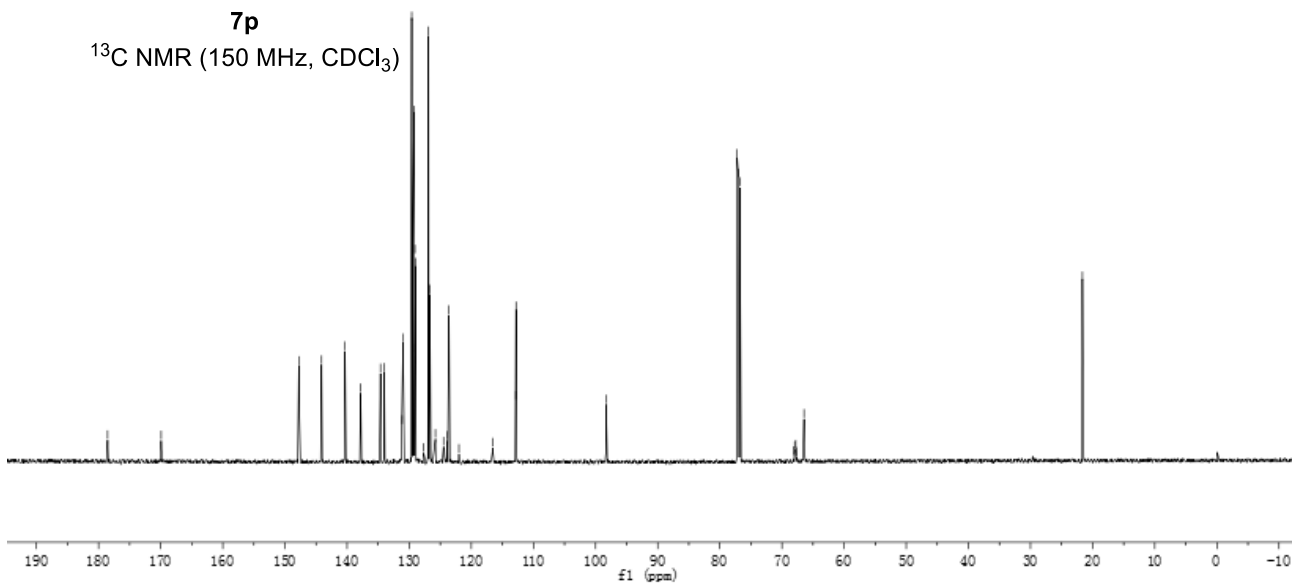


178.547  
169.922  
147.765  
144.108  
140.326  
137.814  
134.625  
134.009  
131.136  
131.039  
130.997  
129.593  
129.424  
129.395  
129.232  
129.079  
128.981  
127.670  
126.891  
126.686  
125.778  
124.472  
123.887  
123.597  
121.992  
116.566  
112.835  
112.808  
98.312  
77.211  
77.000  
76.788  
68.125  
67.957  
67.785  
67.614  
66.452

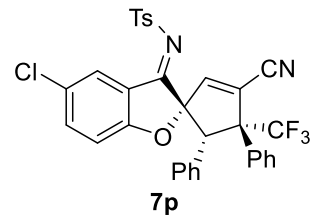
-21.643



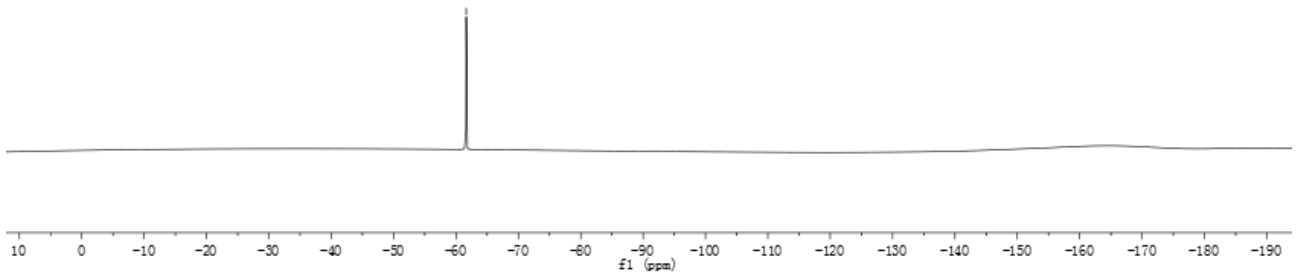
<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)



-61.642

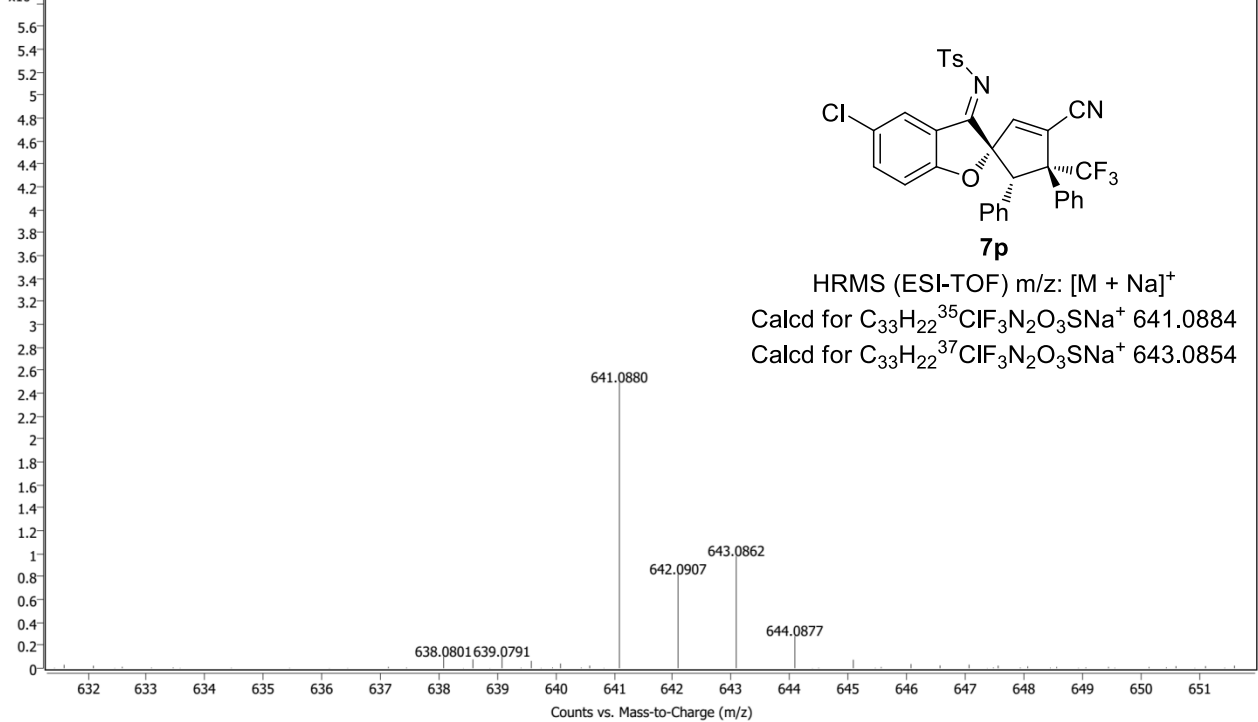


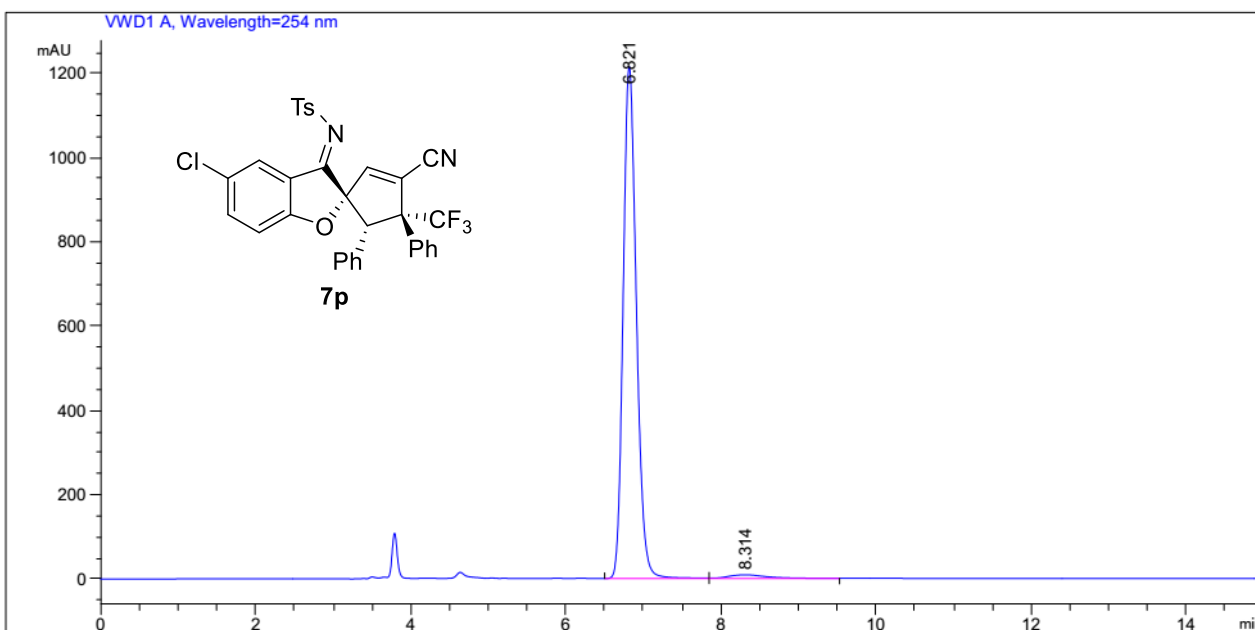
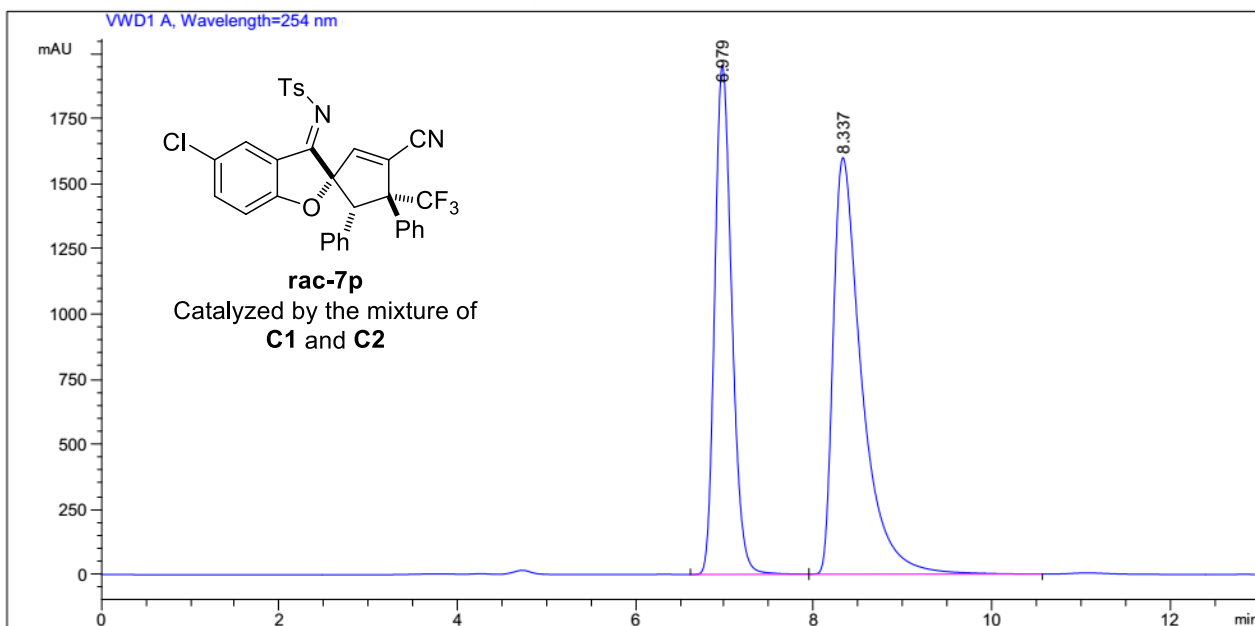
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



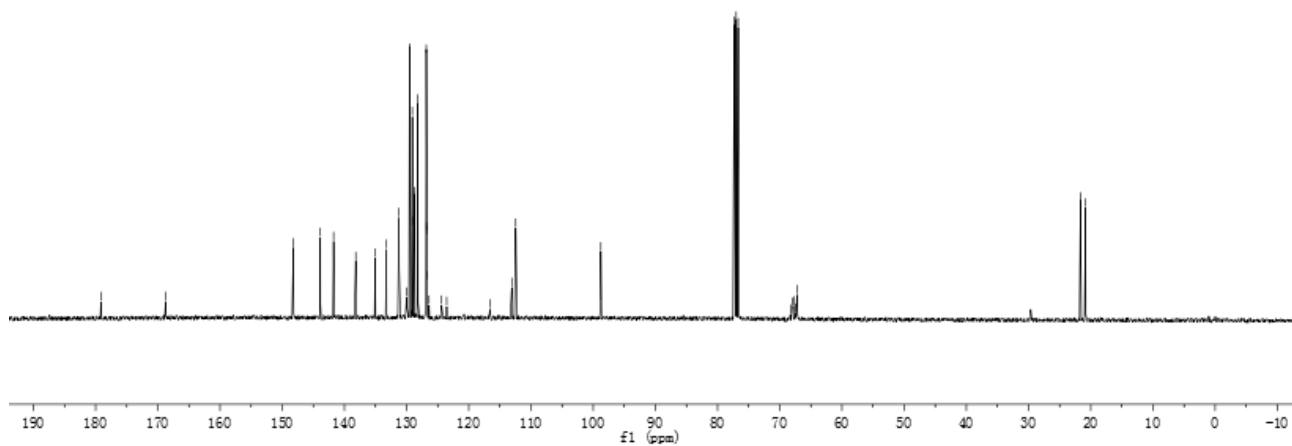
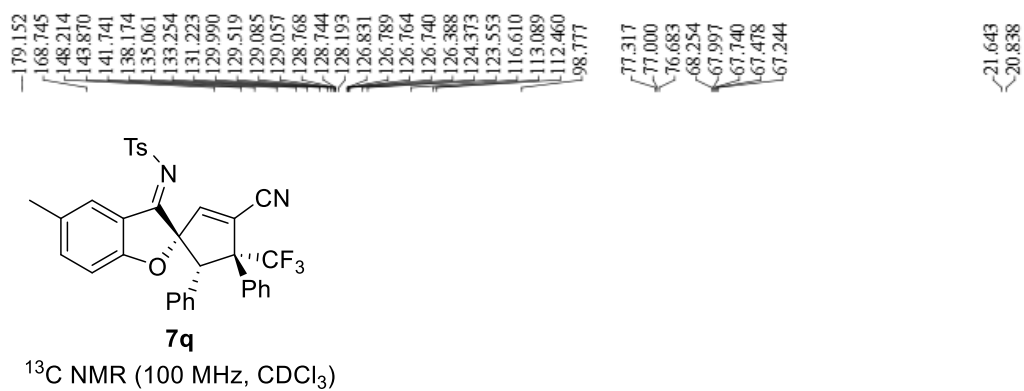
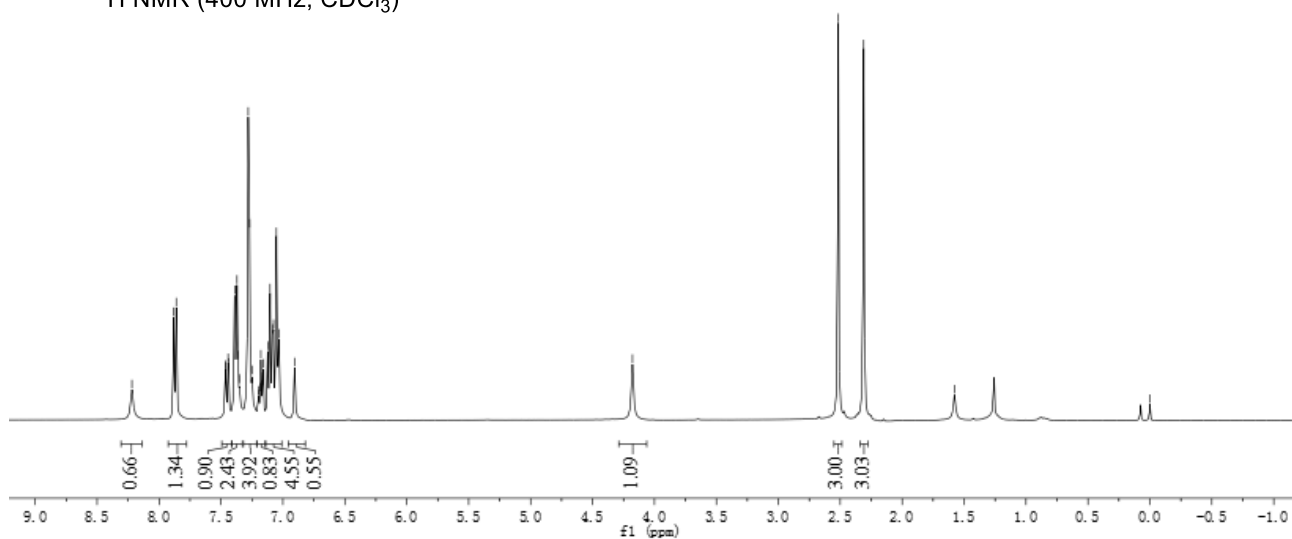
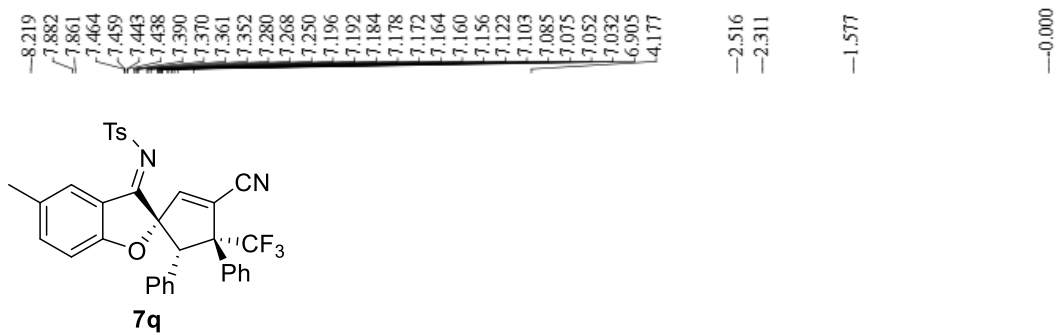
Name	cyc-190705-17	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	WorklistData-0017-r006.d	Method (Acq)	TOF.m		Acq. Time (Local) 7/9/2019 2:19:25 PM (UTC+08:00)

+ESI Scan (rt: 1.238 min) Frag=175.0V WorklistData-0017-r006.d

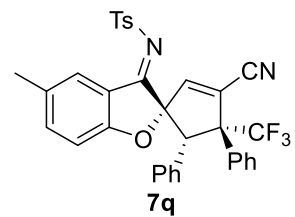




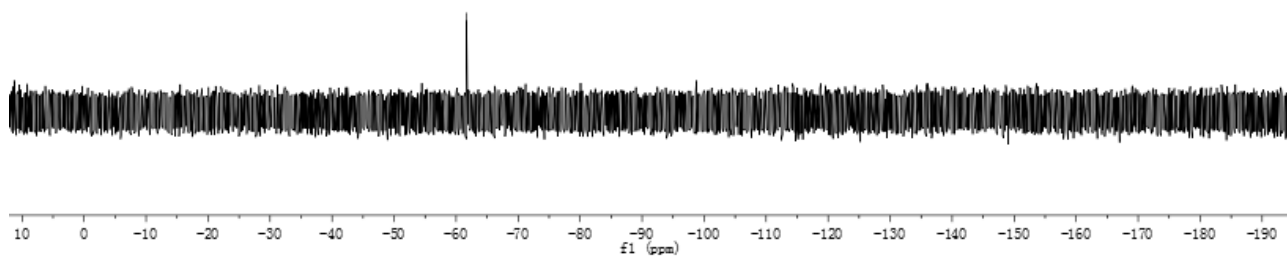




61.690

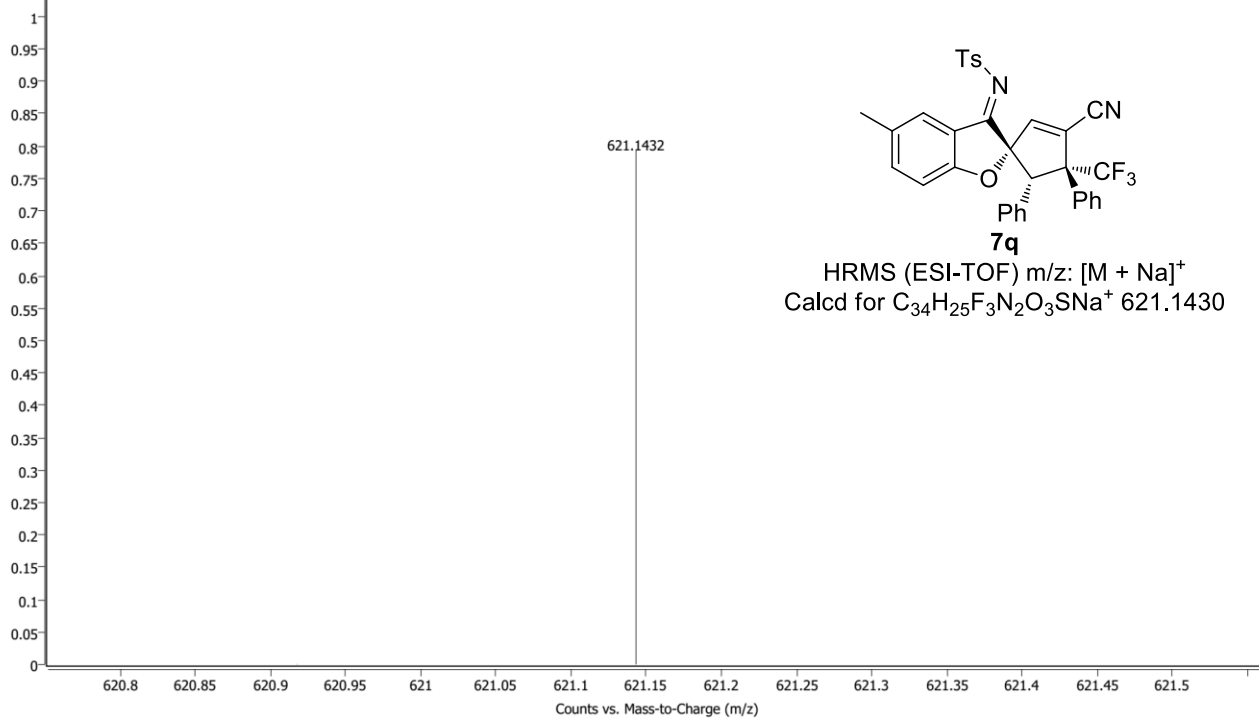


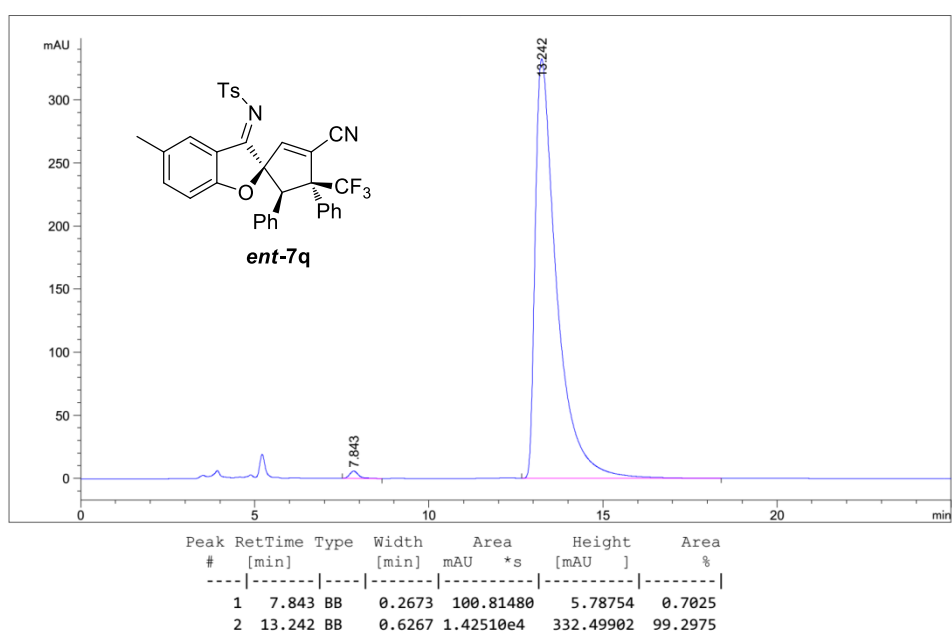
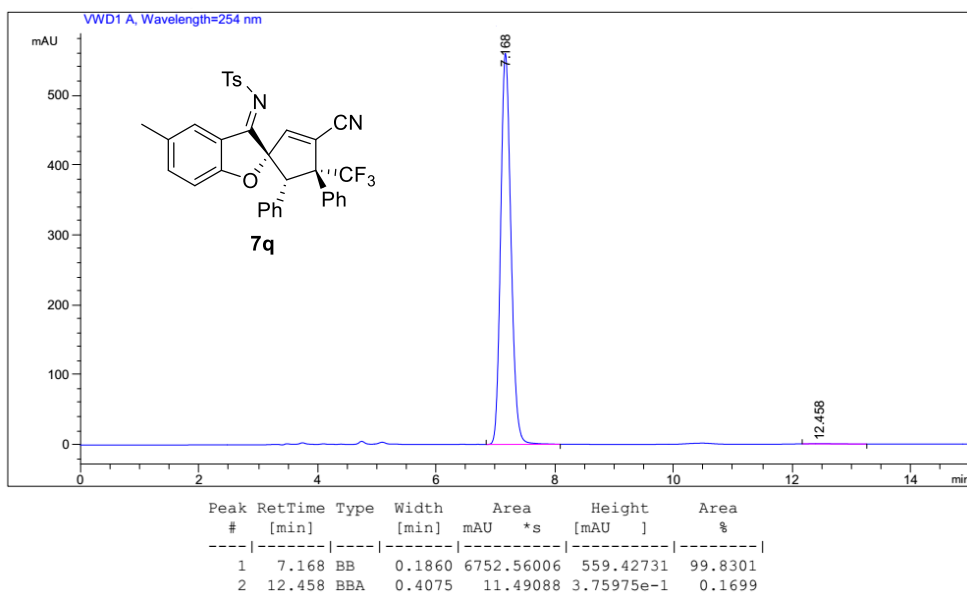
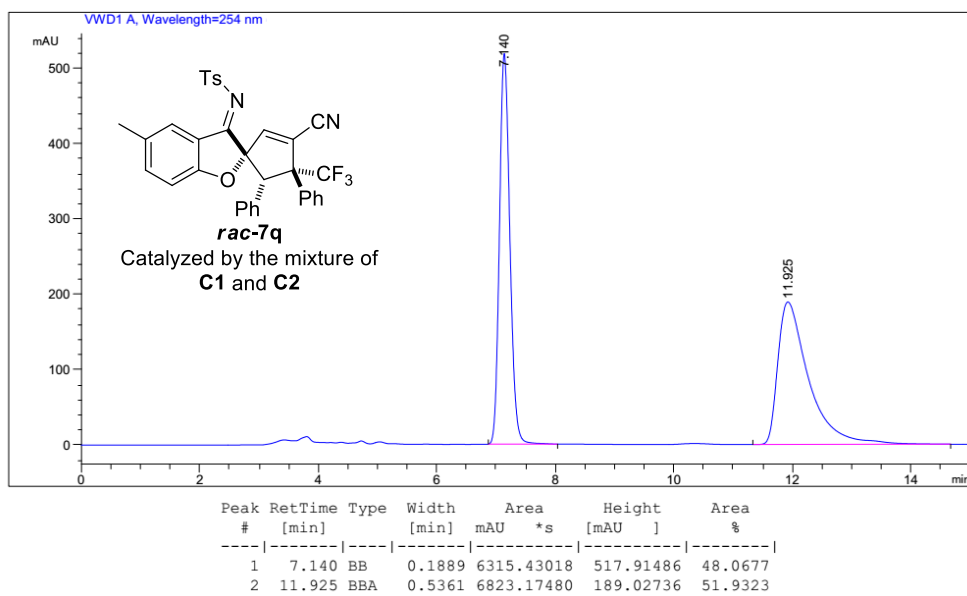
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



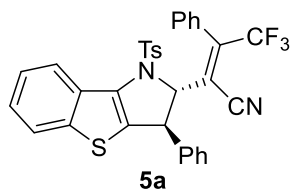
Name	cyc-190705-16	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	WorklistData-0016-r005.d	Method (Acq)	TOF.m	Comment	Acq. Time (Local) 7/9/2019 2:16:37 PM (UTC+08:00)

+ESI Scan (rt: 1.163 min) Frag=175.0V WorklistData-0016-r005.d

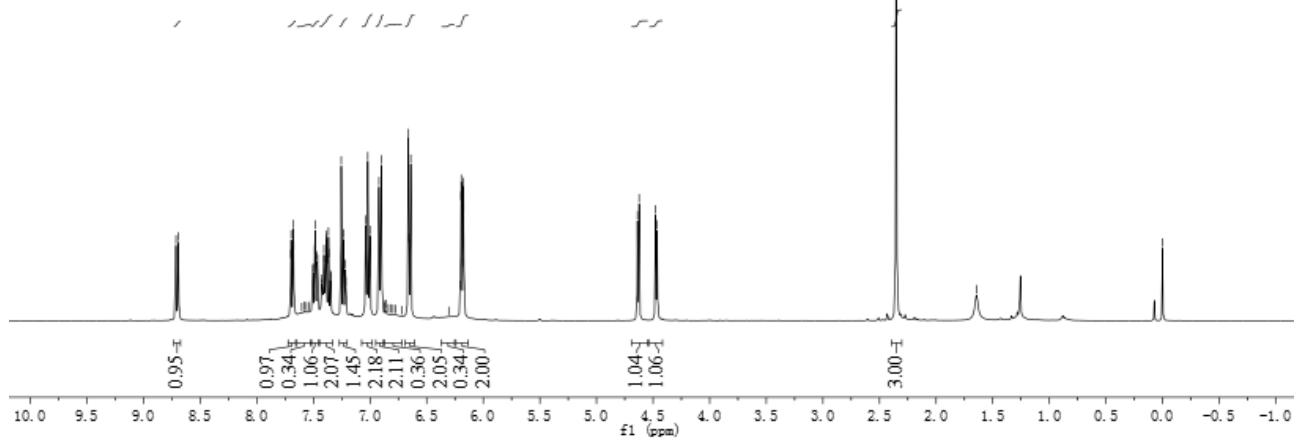




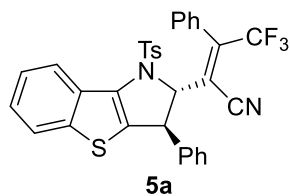
8.714  
8.693  
7.699  
7.697  
7.695  
7.677  
7.675  
7.583  
7.540  
7.506  
7.503  
7.488  
7.485  
7.482  
7.467  
7.464  
7.428  
7.425  
7.407  
7.388  
7.385  
7.370  
7.367  
7.364  
7.349  
7.346  
7.254  
7.239  
7.236  
7.232  
7.220  
7.217  
7.214  
7.039  
7.035  
7.020  
7.005  
7.000  
6.921  
6.901  
6.864  
6.864  
6.662  
6.657  
6.645  
6.641  
6.202  
6.197  
6.194  
6.181  
6.177  
6.173  
4.637  
4.624  
4.478  
4.464  
2.353  
1.644  
-0.000



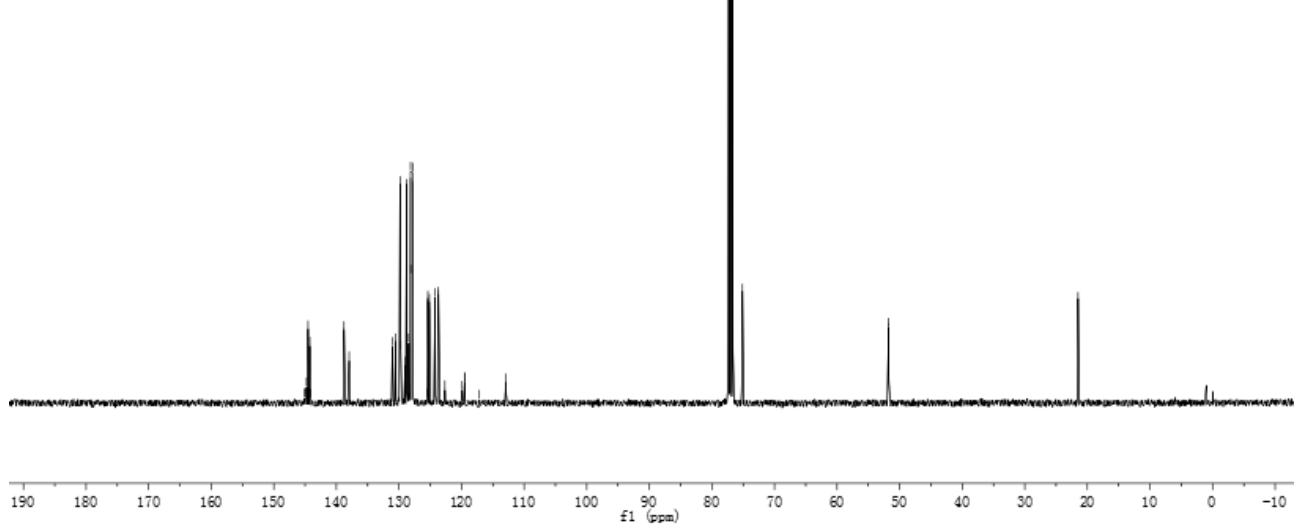
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



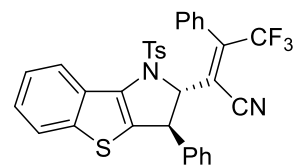
145.091  
144.774  
144.521  
144.458  
144.249  
144.141  
141.141  
138.775  
137.953  
131.050  
130.560  
129.825  
129.797  
129.723  
129.014  
128.764  
128.439  
128.143  
128.113  
127.800  
125.431  
125.382  
125.145  
124.225  
123.693  
122.657  
119.908  
119.534  
119.506  
119.476  
119.447  
117.160  
112.894  
77.317  
77.000  
76.682  
75.115  
51.746  
-21.490



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

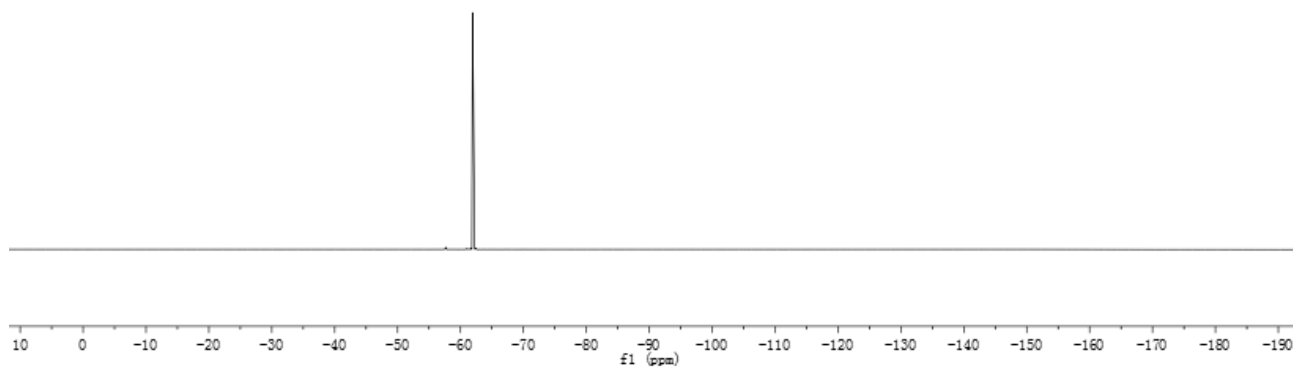


-61.923



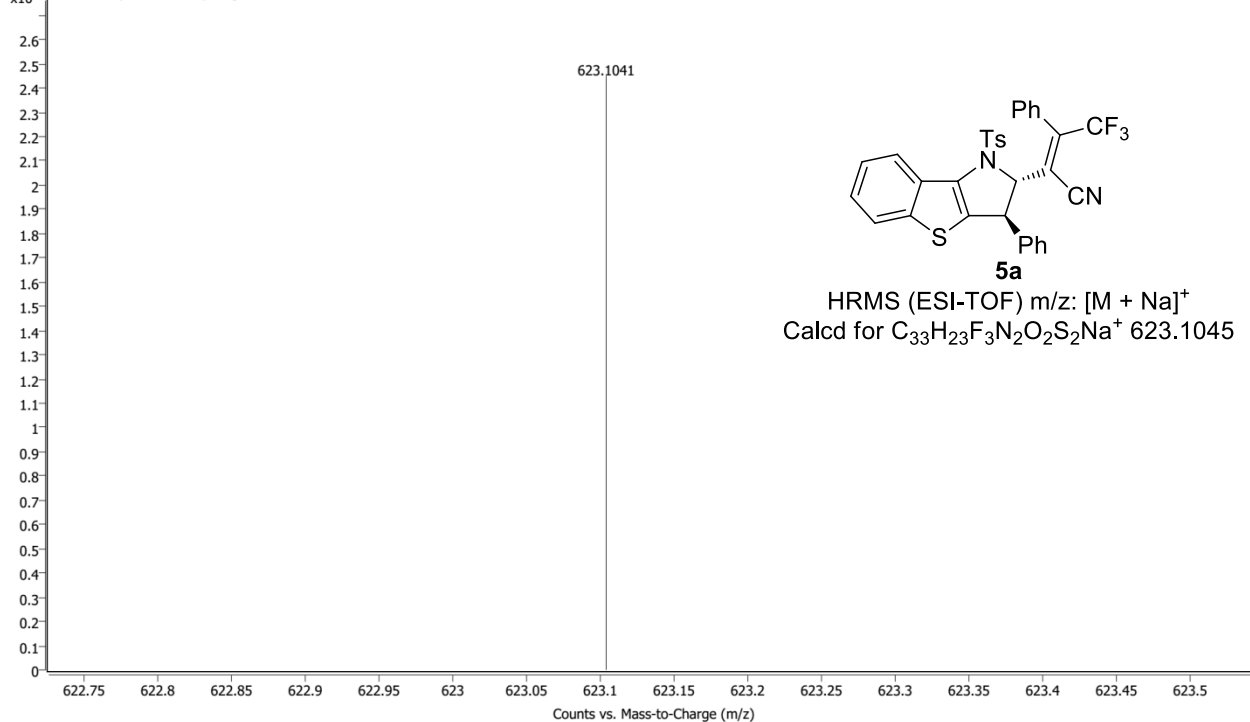
**5a**

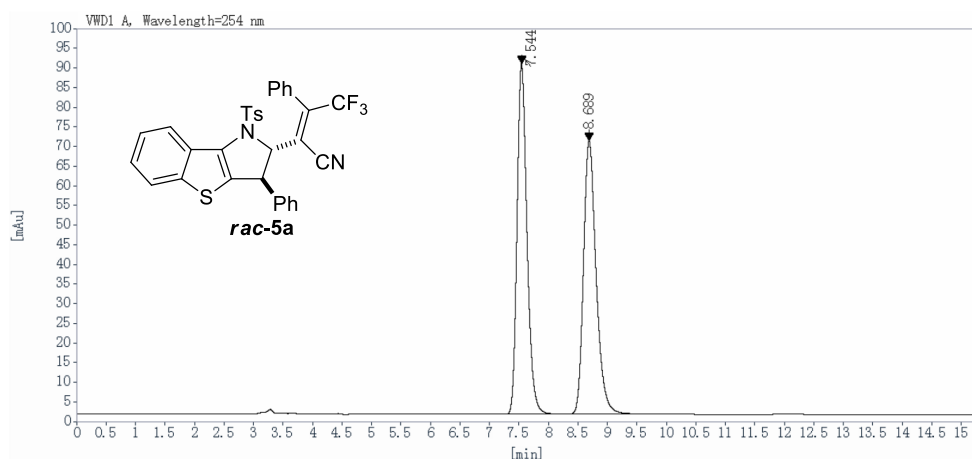
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



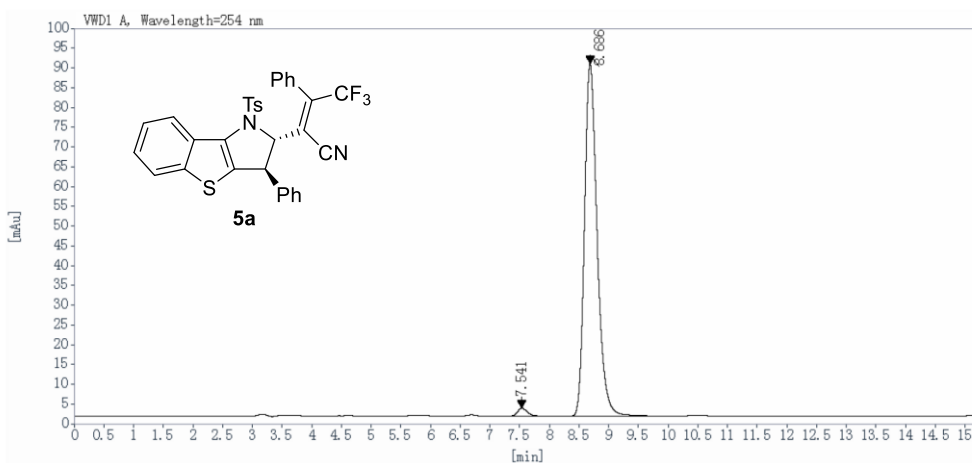
Name	cyc-190705-24	Rack Pos.		Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.		IRM Status	Success	
Data File	WorklistData-0024-r013.d	Method (Acq)	TOF.m	Comment		Acq. Time (Local) 7/9/2019 2:39:08 PM (UTC+08:00)

+ESI Scan (rt: 1.842 min) Frag=175.0V WorklistData-0024-r013.d

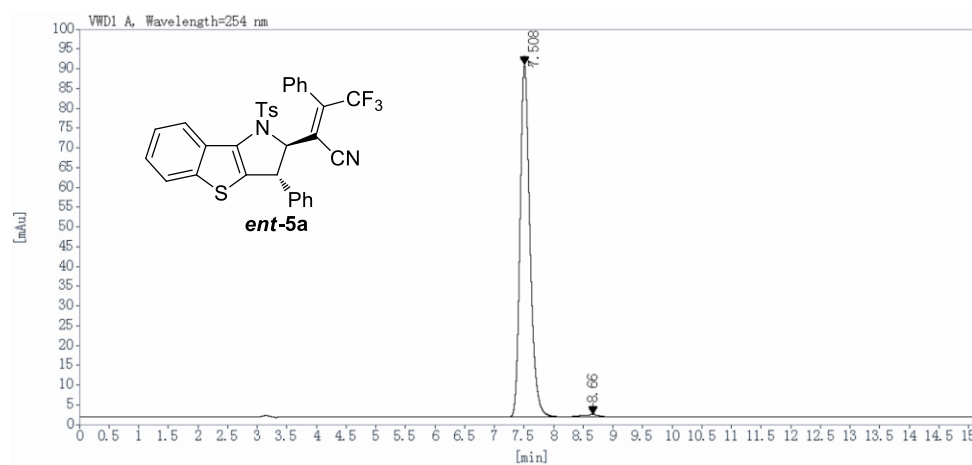




Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
7.544	BB	0.18	489.6311	5697.7524	50.1373
8.689	BB	0.23	381.1694	5666.5435	49.8627



Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
7.541	BB	0.18	10.5657	122.0278	1.7216
8.686	BB	0.23	471.0184	6965.9683	98.2784



Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
7.508	BV R	0.18	633.3124	7313.7432	98.4874
8.660	VB E	0.35	4.3093	112.3303	1.5126

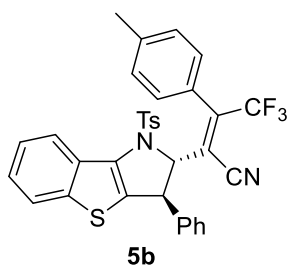
8.704  
8.683  
7.699  
7.679  
7.503  
7.484  
7.465  
7.386  
7.367  
7.348  
7.269  
7.255  
7.250  
7.232  
7.112  
7.050  
7.031  
7.012  
6.903  
6.884  
6.661  
6.641  
6.210  
6.191

4.680  
4.666  
4.476  
4.462

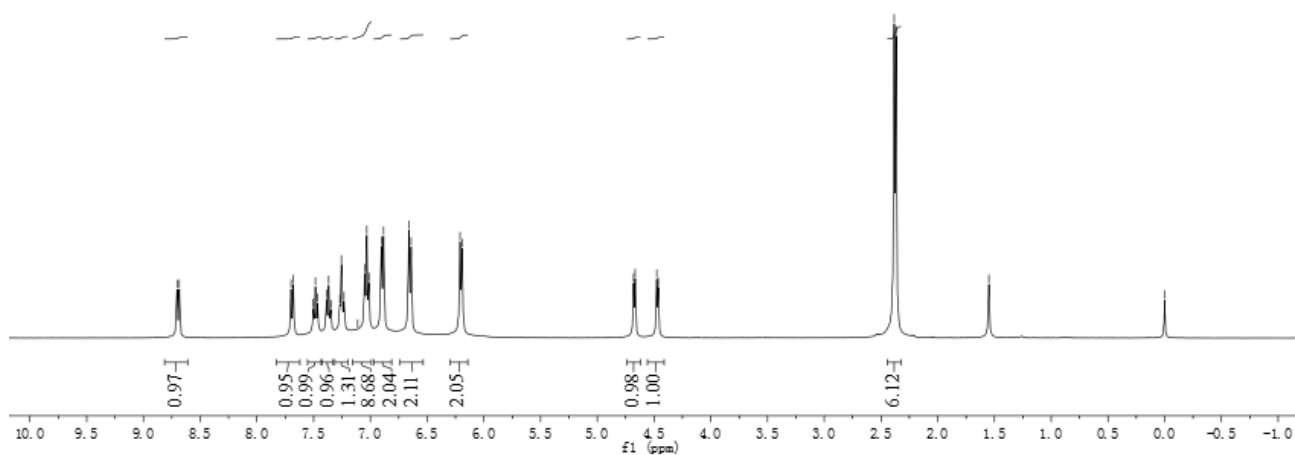
2.384  
2.367

-1.550

-0.000

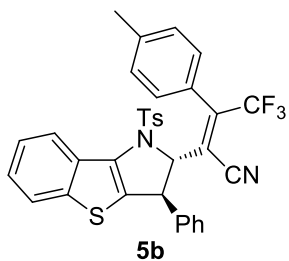


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

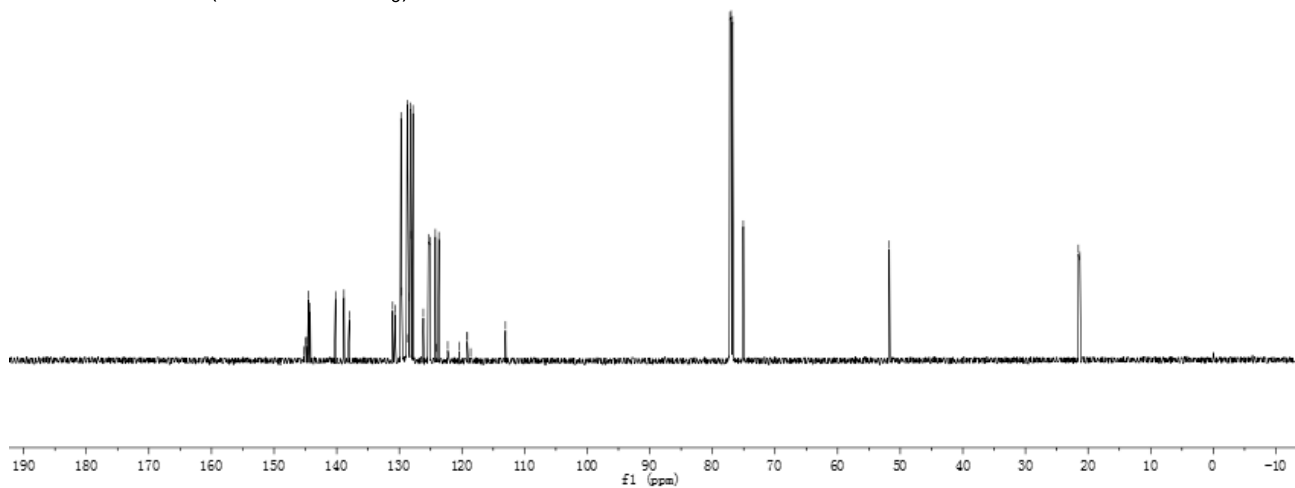


145.246  
145.036  
144.827  
144.613  
144.494  
144.247  
140.193  
138.844  
137.987  
131.060  
130.635  
129.738  
129.618  
128.741  
128.611  
128.471  
128.248  
128.092  
127.823  
126.164  
125.348  
125.113  
124.236  
124.106  
123.679  
122.267  
120.435  
119.155  
119.138  
118.596  
113.047  
77.212  
77.000  
76.788  
75.064  
51.747

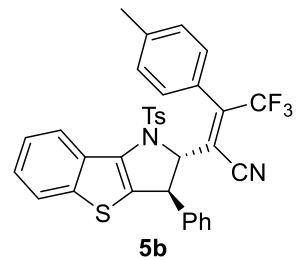
21.545  
21.308



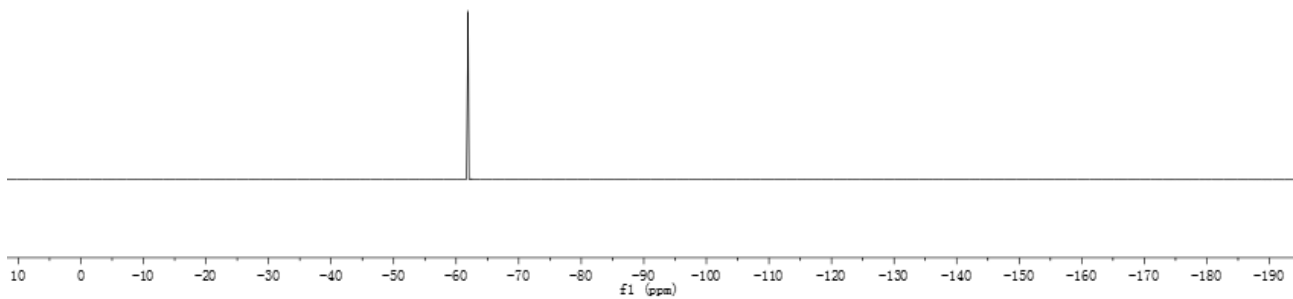
<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)



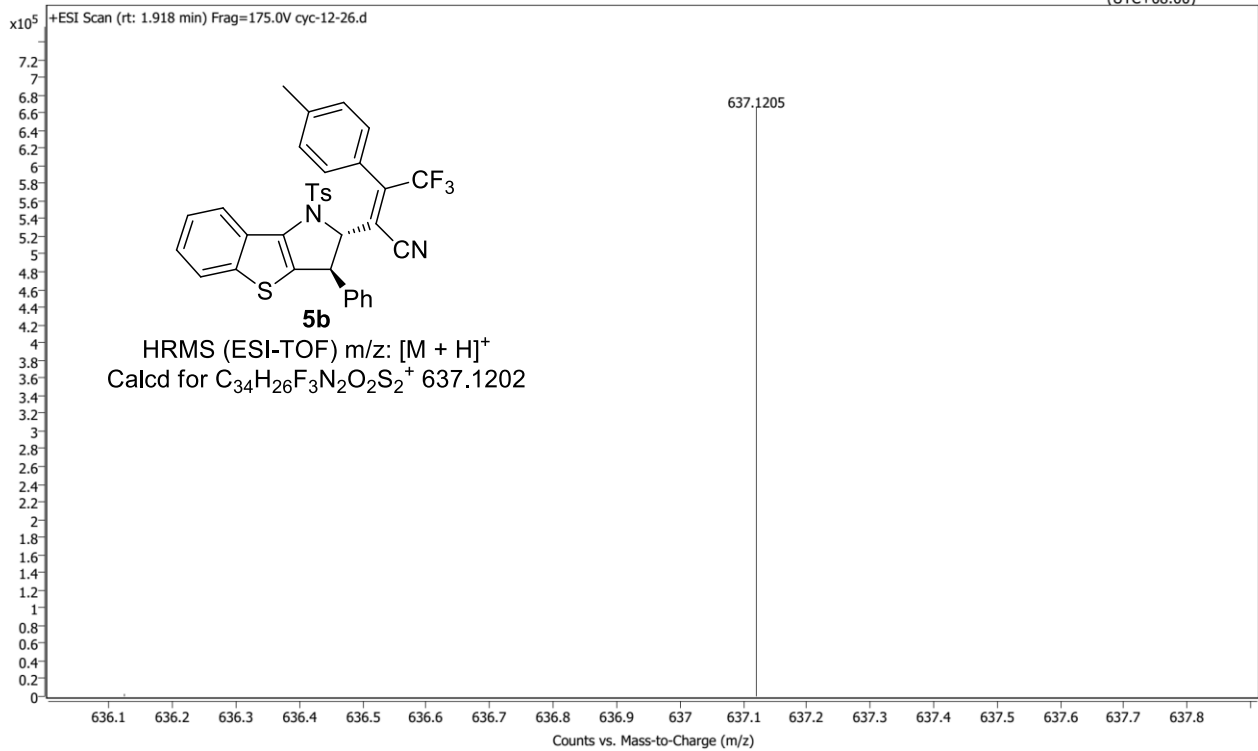
-61.906



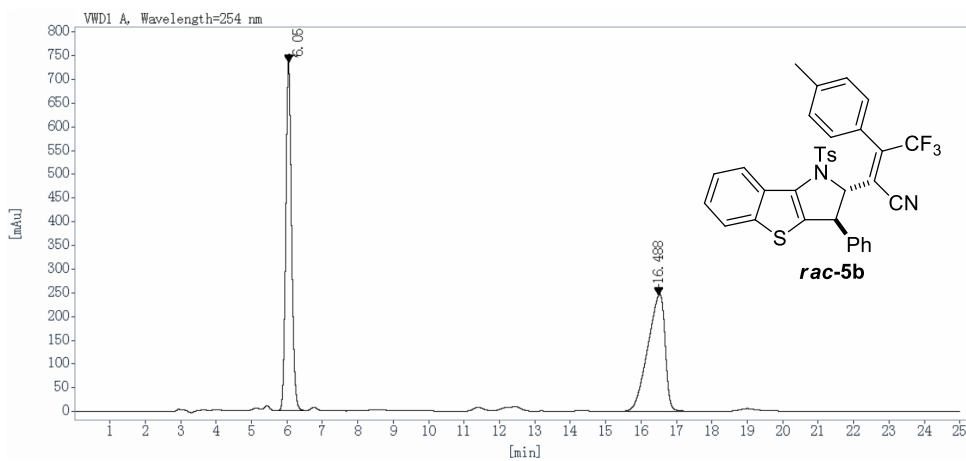
**5b**  
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



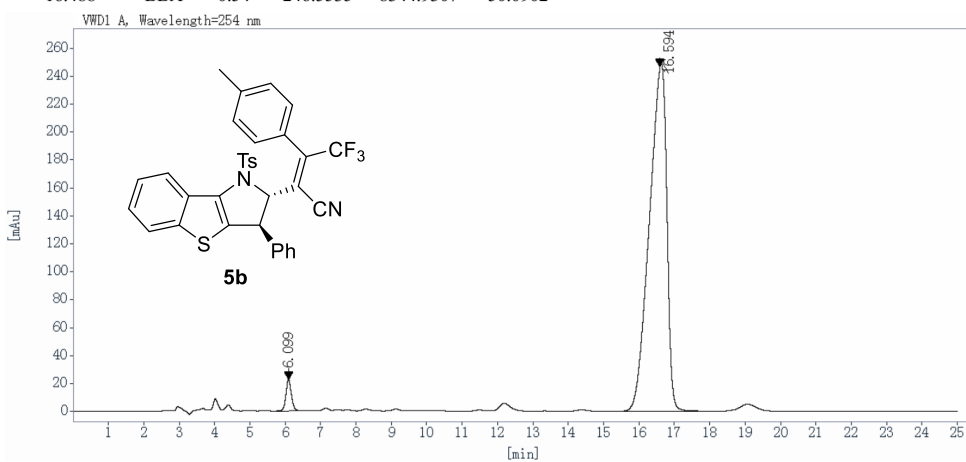
Name	cyc-12-26	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	cyc-12-26.d	Method (Acq)	TOF.m		Acq. Time (Local) 7/22/2019 6:29:39 PM (UTC+08:00)



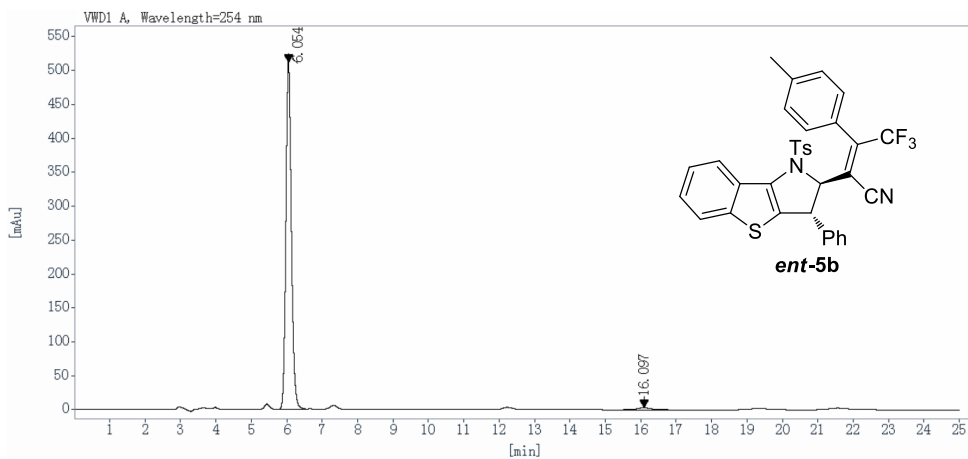




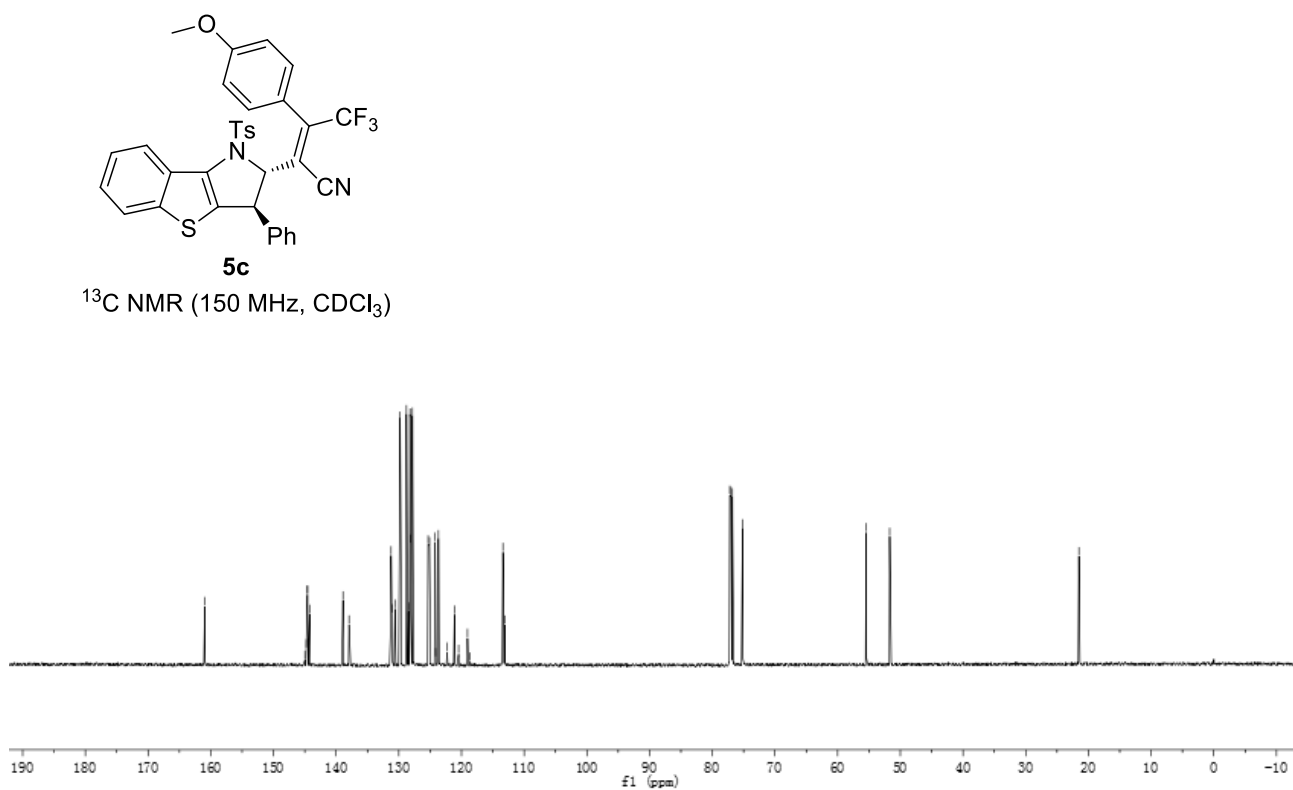
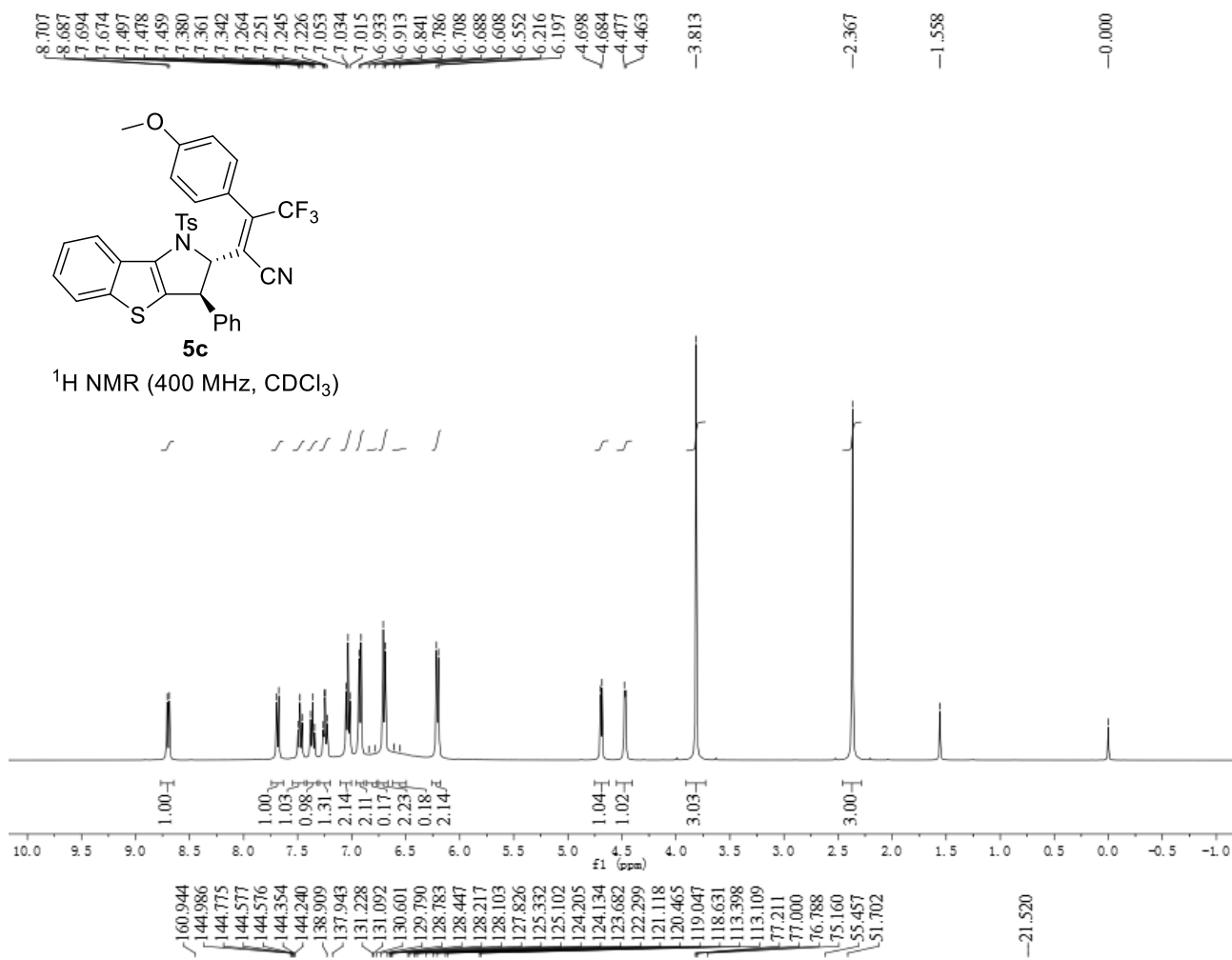
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
6.050	BBA	0.22	714.4682	8314.8623	49.9098
16.488	BBA	0.54	246.5535	8344.9307	50.0902



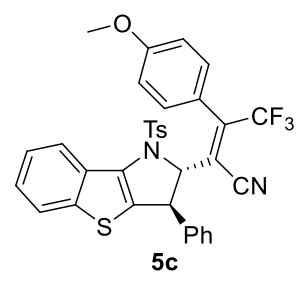
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
6.099	BBA	0.21	21.5910	240.6503	2.7529
16.594	BBA	0.54	249.0474	8500.9795	97.2471



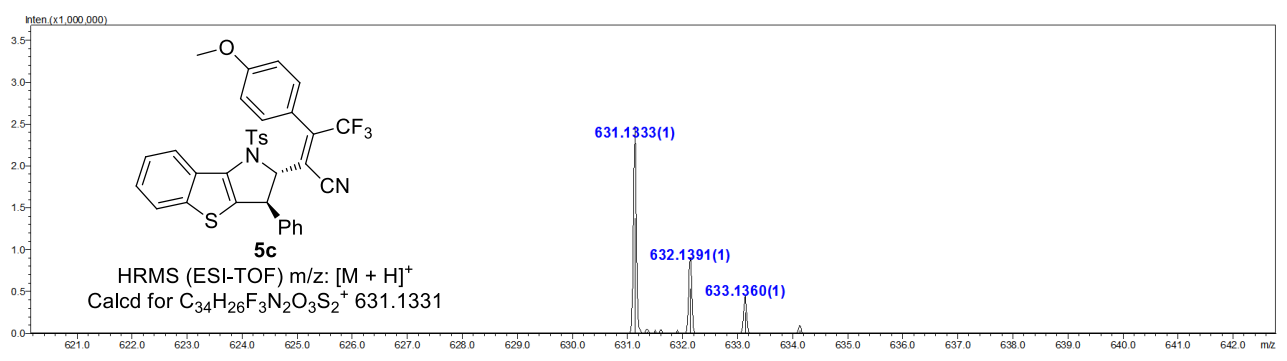
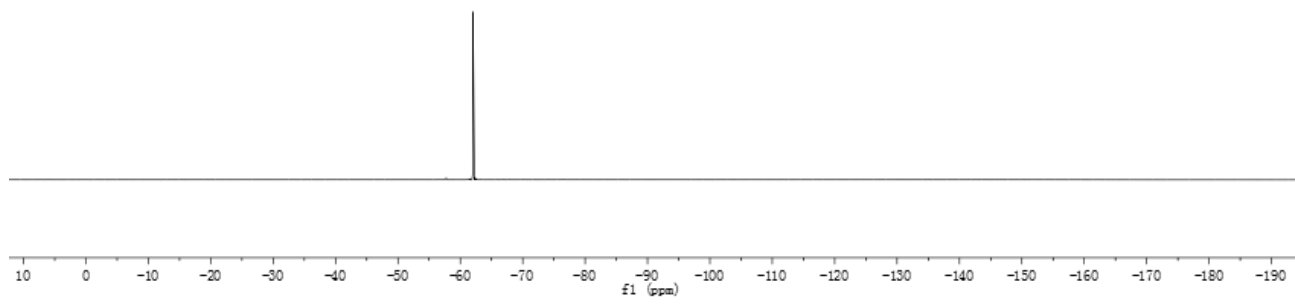
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
6.054	BBA	0.21	497.7755	5495.4058	98.6394
16.097	BBA	0.42	2.8285	75.8026	1.3606

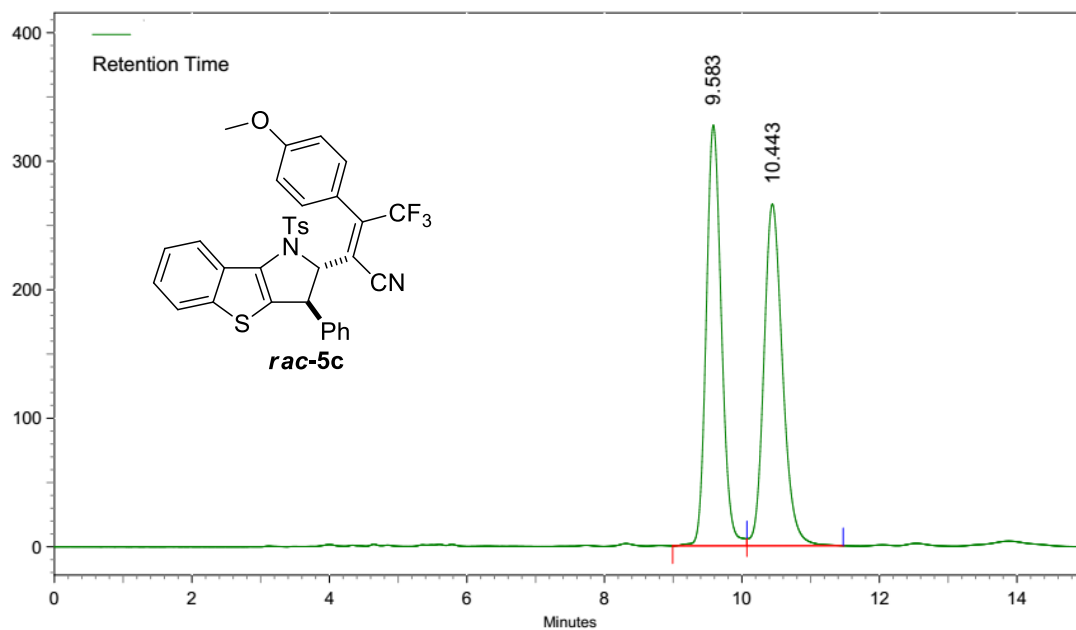


62.028



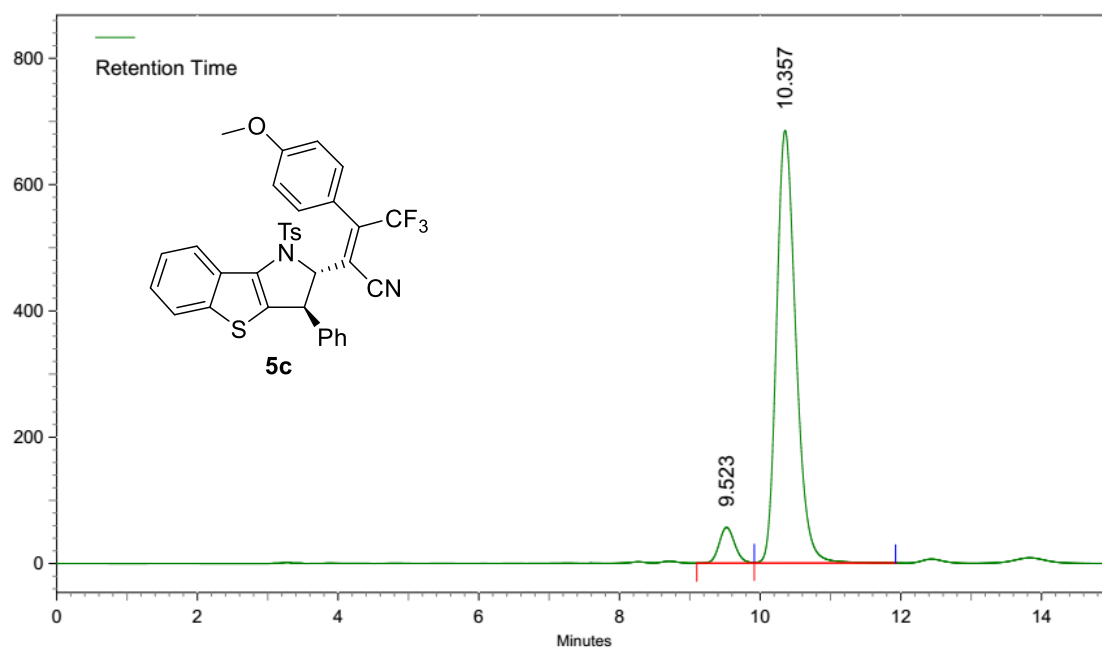
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)





### AREA PERCENT REPORT

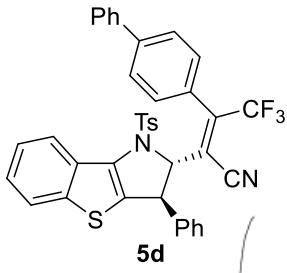
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	9.583	1.080	5489729	84226553	49.9785
2	10.443	1.400	4458657	84299093	50.0215



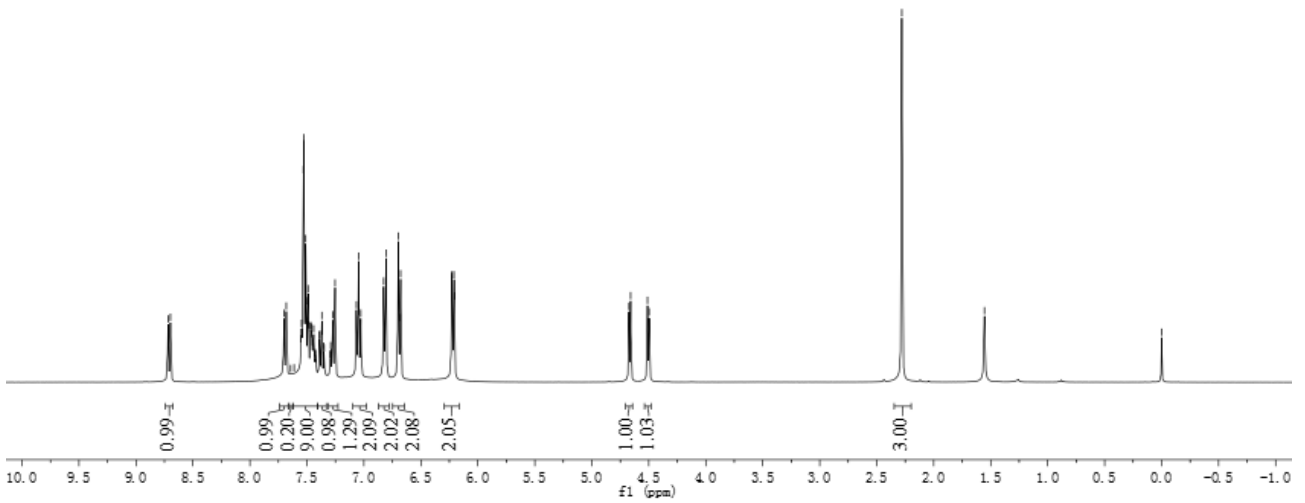
### AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	9.523	0.817	949280	14567522	6.2427
2	10.357	2.010	11488194	218787242	93.7573

8.718  
8.697  
7.701  
7.681  
7.643  
7.612  
7.552  
7.547  
7.531  
7.527  
7.511  
7.505  
7.494  
7.490  
7.487  
7.484  
7.469  
7.466  
7.462  
7.457  
7.451  
7.447  
7.440  
7.433  
7.428  
7.424  
7.419  
7.390  
7.387  
7.369  
7.351  
7.348  
7.294  
7.291  
7.288  
7.273  
7.253  
7.066  
7.047  
7.032  
7.027  
6.826  
6.806  
6.698  
6.682  
6.678  
6.229  
6.226  
6.209  
6.206  
4.674  
4.660  
4.511  
4.497  
2.280  
1.555  
0.000

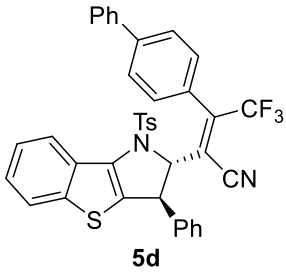


$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )

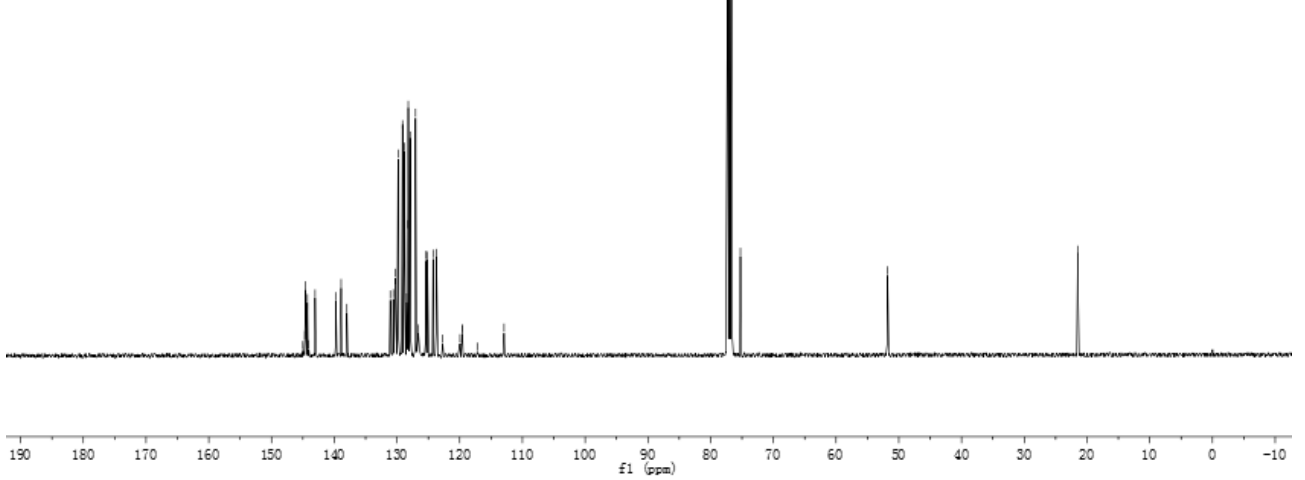


145.008  
144.689  
144.548  
144.372  
144.272  
144.056  
143.045  
139.738  
138.897  
137.979  
131.066  
130.589  
130.272  
129.822  
129.116  
128.814  
128.458  
128.234  
128.195  
127.898  
127.033  
126.587  
125.447  
125.393  
125.154  
124.249  
123.702  
122.700  
119.950  
119.601  
119.570  
117.204  
112.922  
77.318  
77.000  
76.682  
76.682  
75.245  
51.792

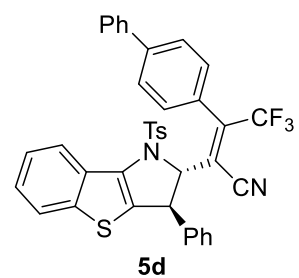
-21.462



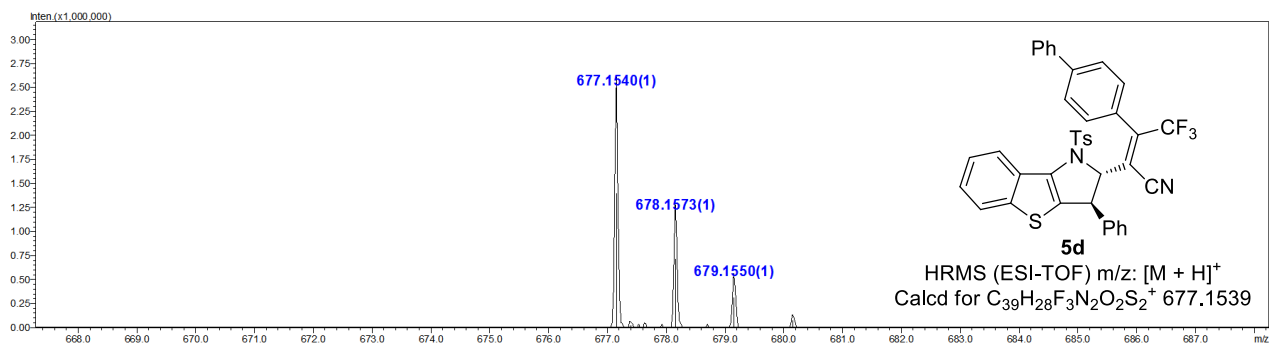
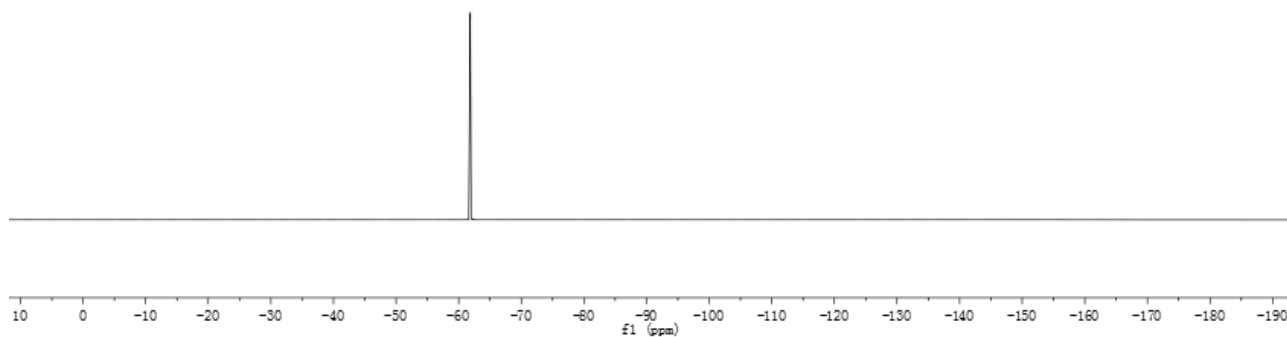
$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

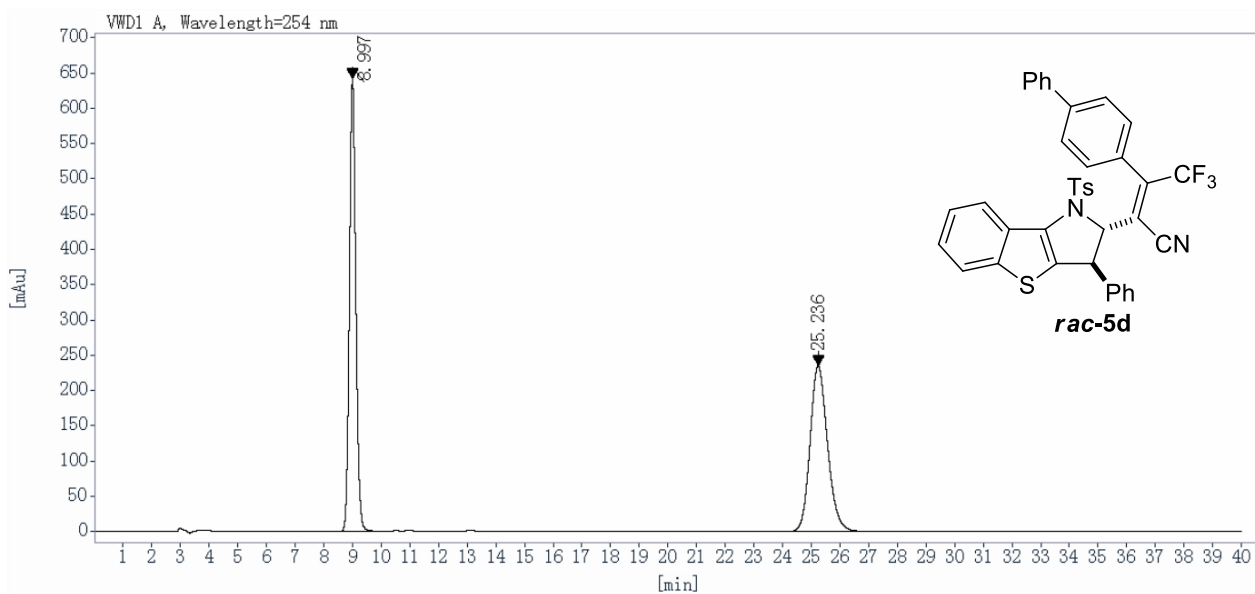


---61.849

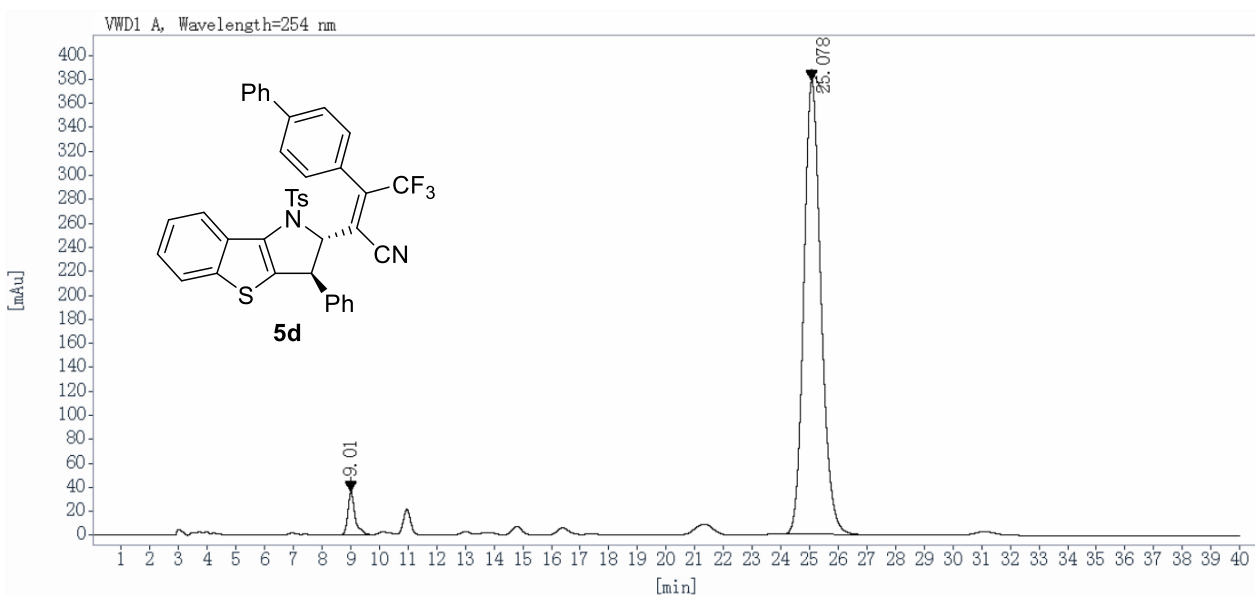


**5d**  
 $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )

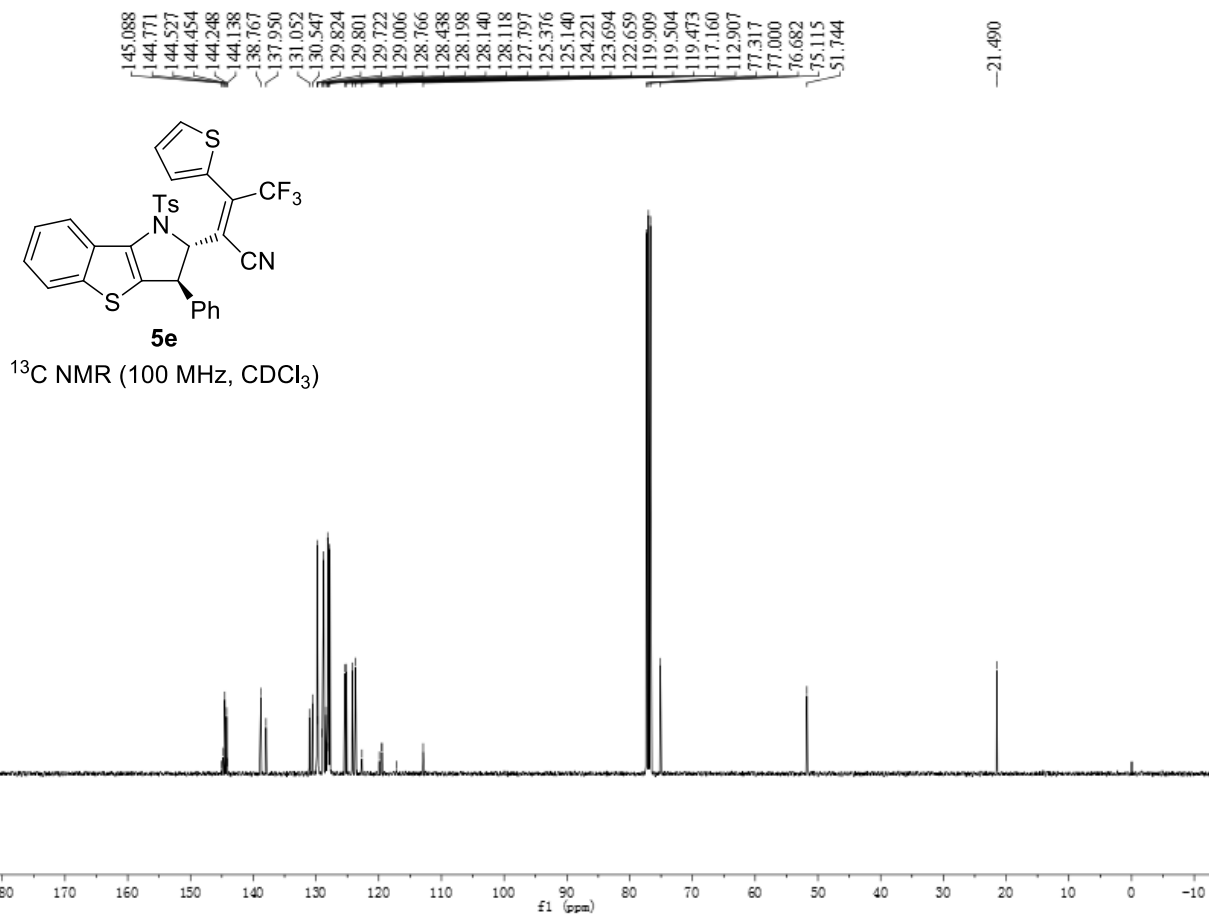
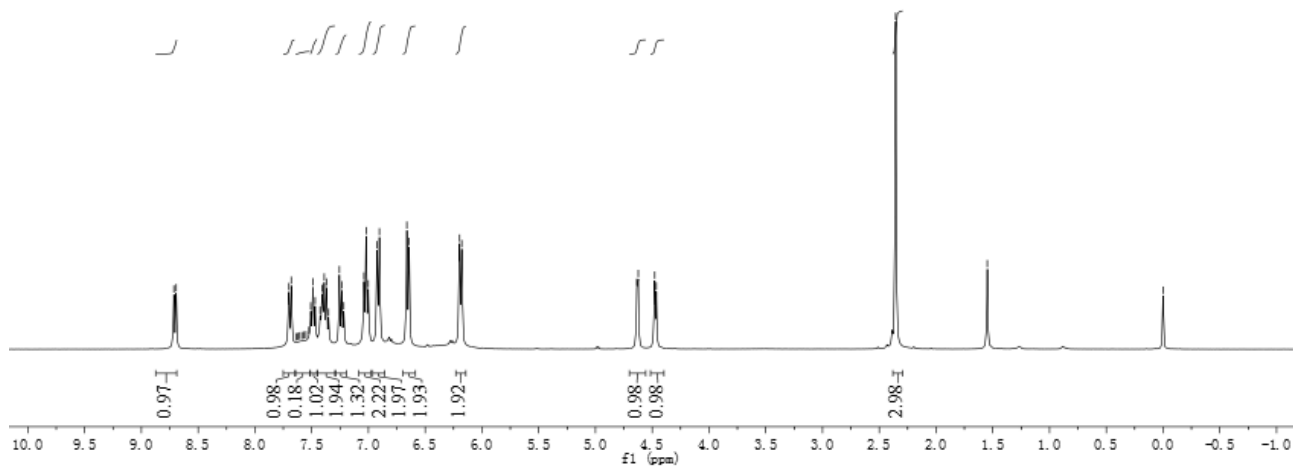
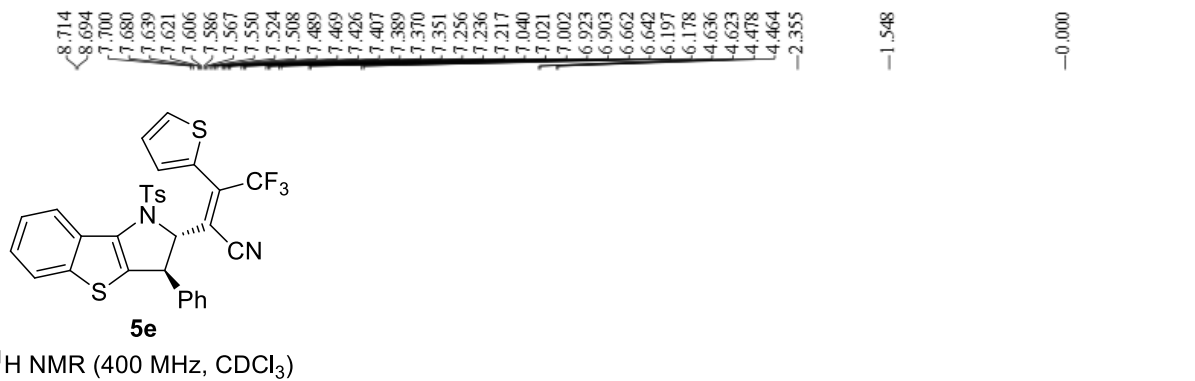




Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
8.997	VB R	0.24	642.7047	9982.0693	50.0856
25.236	BB	0.65	235.5494	9947.9336	49.9144

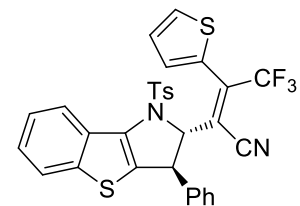


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
9.010	BBA	0.26	35.8341	611.5853	3.7369
25.078	BB	0.64	378.5762	15754.4648	96.2631



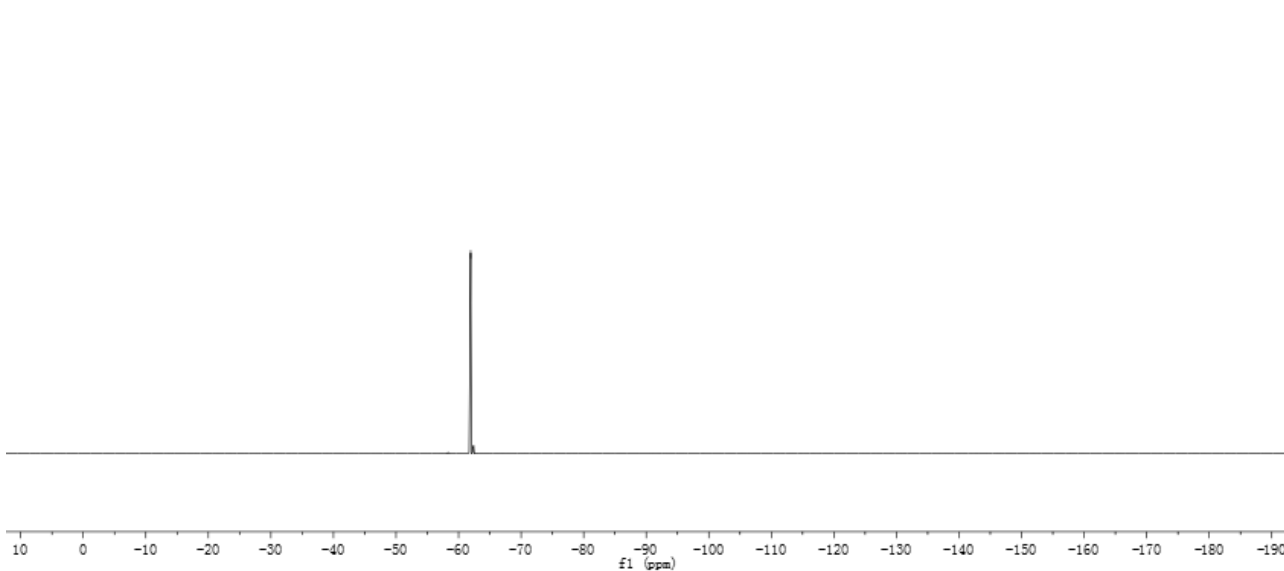


---61.929

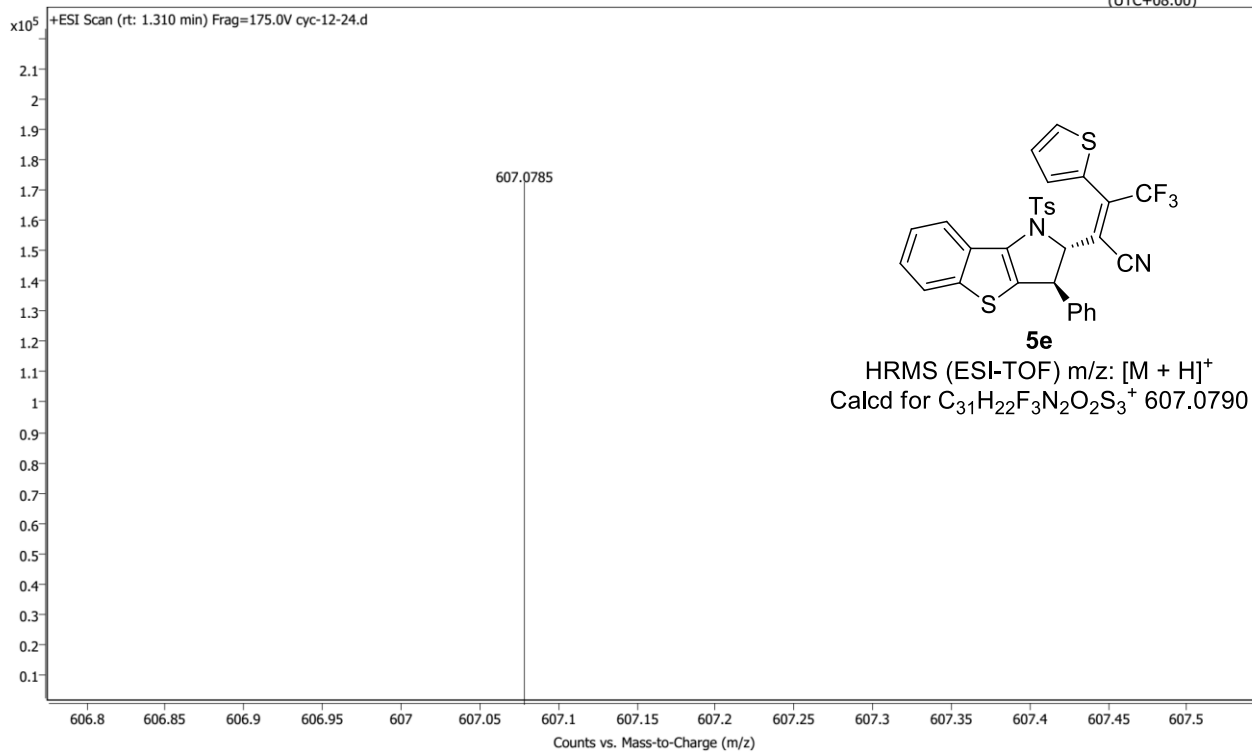


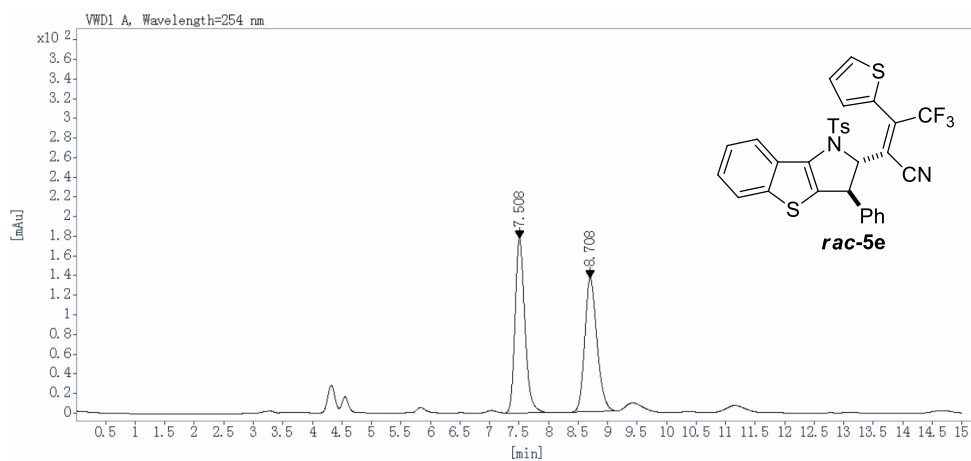
**5e**

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )

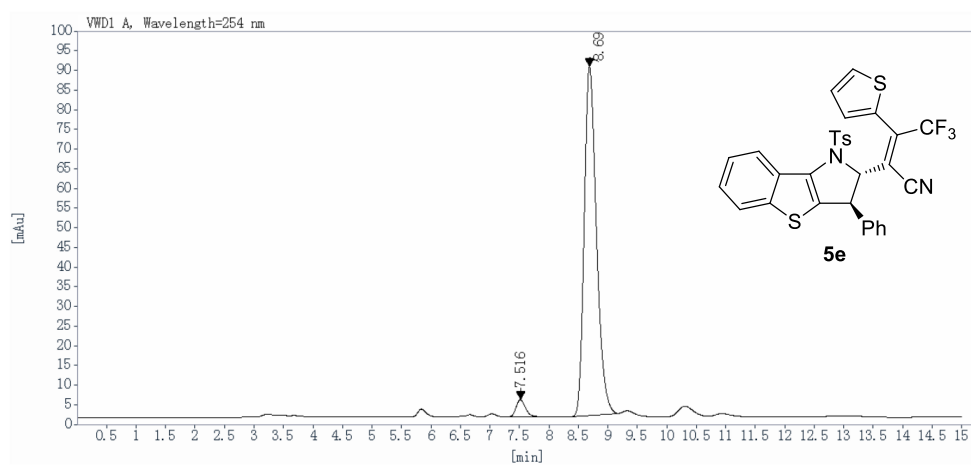


Name	cyc-12-24	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	cyc-12-24.d	Method (Acq)	TOF.m	Comment	Acq. Time (Local) 7/22/2019 6:24:01 PM (UTC+08:00)

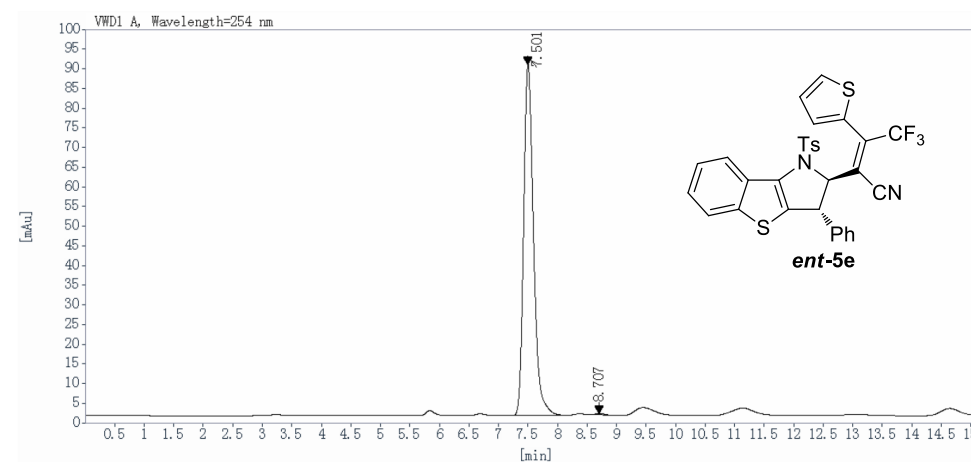




Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
7.508	BB	0.18	177.6230	2043.6824	50.8187
8.708	BB	0.22	135.8996	1977.8372	49.1813

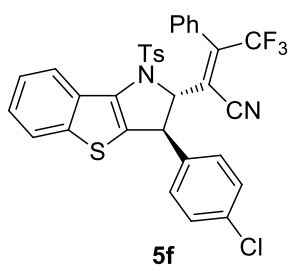


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
7.516	BB	0.17	35.1886	400.0902	3.7571
8.690	BB	0.22	706.3945	10248.8447	96.2429

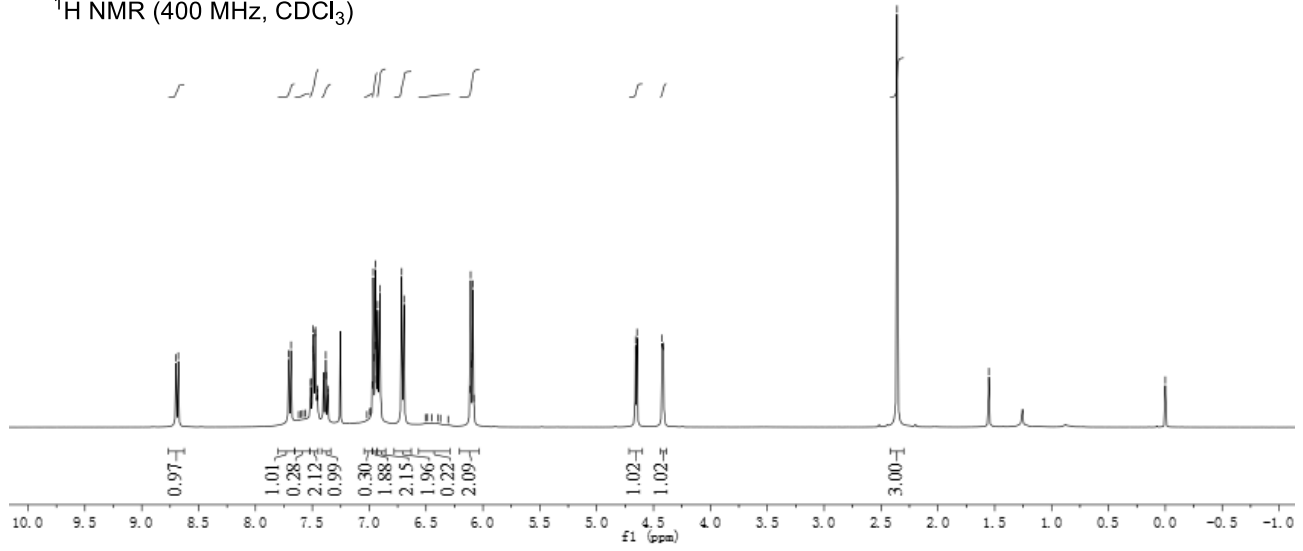


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
7.501	BBA	0.18	894.1706	10336.3262	99.5651
8.707	BB	0.19	3.7510	45.1508	0.4349

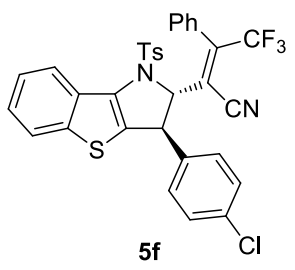
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7.494  
7.490  
7.476  
7.473  
7.456  
7.453  
7.403  
7.400  
7.382  
7.379  
7.364  
7.361  
7.020  
6.993  
6.990  
6.972  
6.965  
6.960  
6.949  
6.944  
6.937  
6.926  
6.906  
6.714  
6.694  
6.506  
6.487  
6.449  
6.394  
6.373  
6.306  
6.115  
6.108  
6.103  
6.092  
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4.645  
4.424  
4.412  
2.359  
1.552  
-0.000



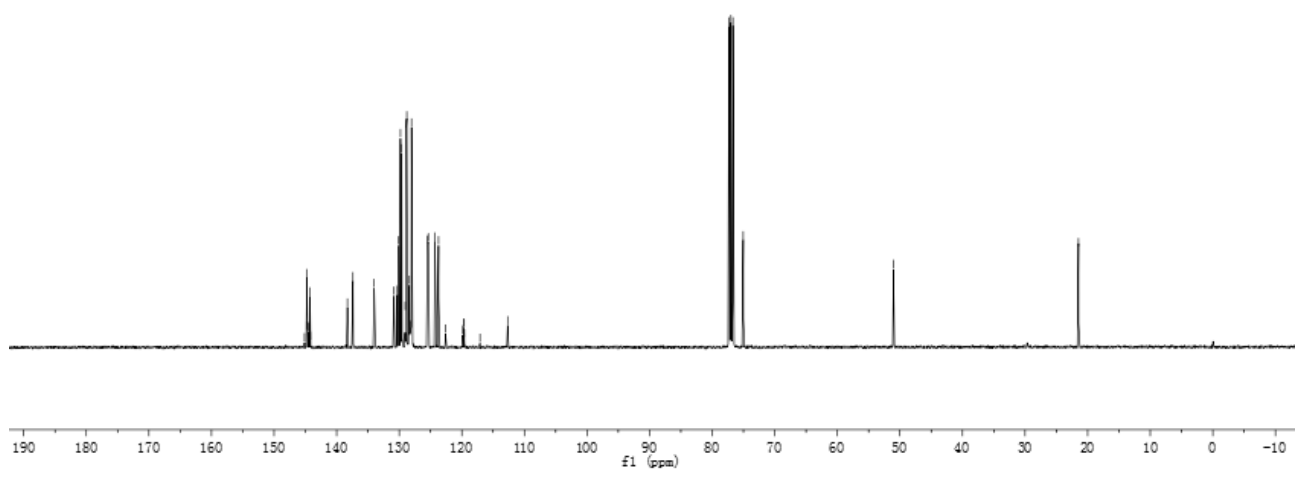
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



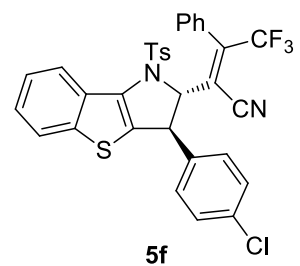
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130.314  
130.094  
129.802  
129.607  
129.048  
128.901  
128.798  
128.380  
128.238  
128.044  
125.497  
125.350  
124.293  
123.719  
122.598  
119.848  
119.648  
119.617  
119.589  
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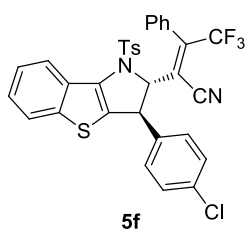
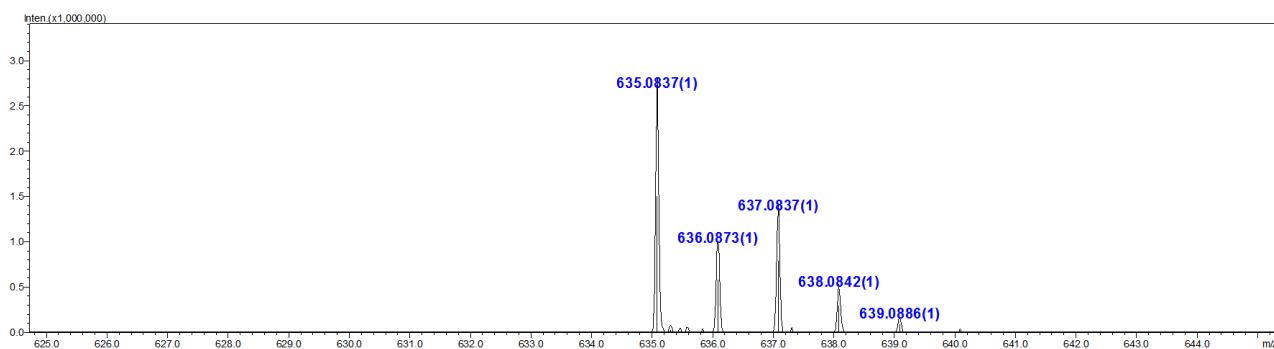
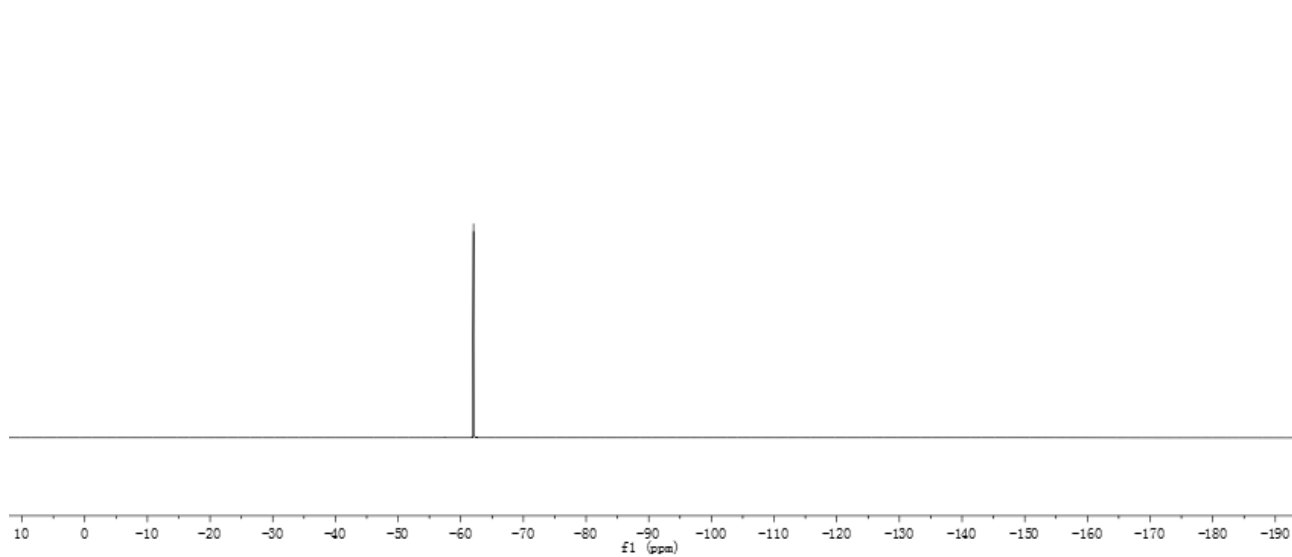
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



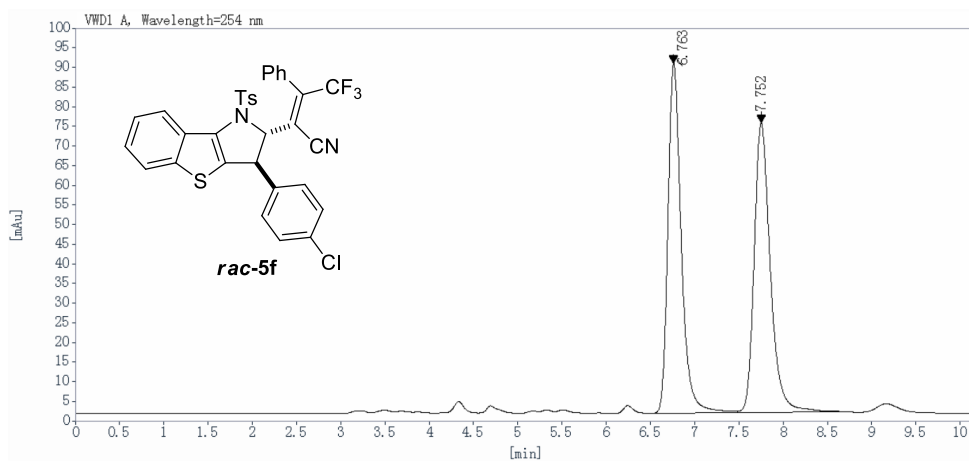
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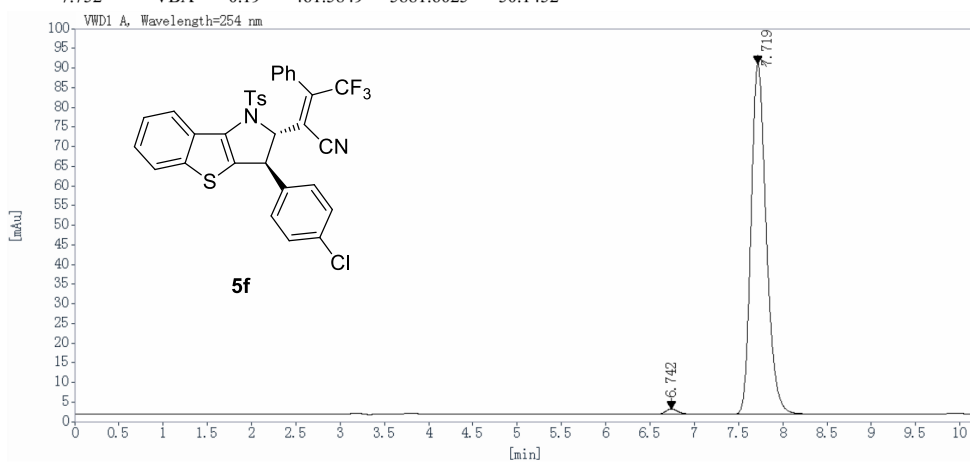
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



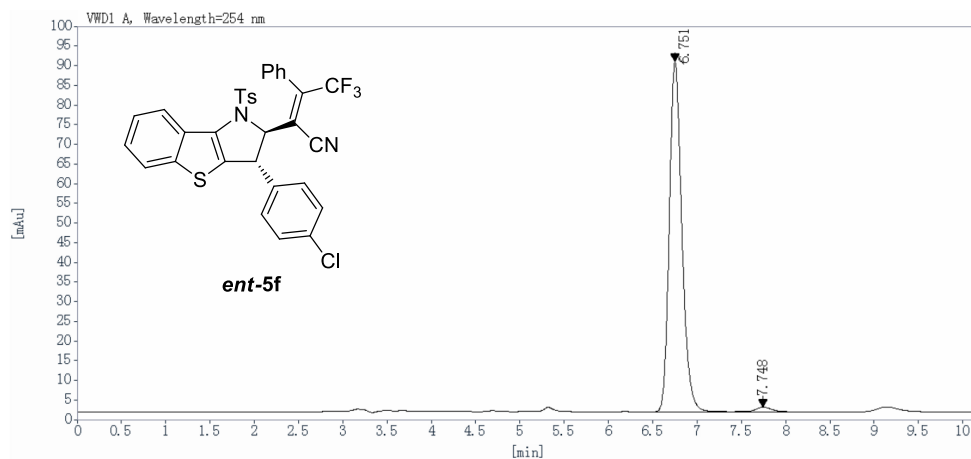
HRMS (ESI-TOF) m/z: [M + H]<sup>+</sup>  
Calcd for C<sub>33</sub>H<sub>23</sub><sup>35</sup>ClF<sub>3</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup> 635.0836  
Calcd for C<sub>33</sub>H<sub>23</sub><sup>37</sup>ClF<sub>3</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup> 637.0807



Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
6.763	BV	0.16	558.4097	5847.5410	49.8548
7.752	VBA	0.19	461.5849	5881.6025	50.1452

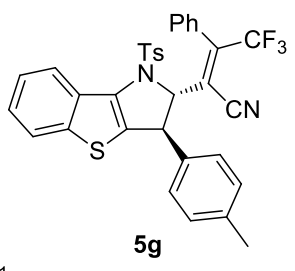


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
6.742	BB	0.15	10.5012	104.5874	1.2658
7.719	BBA	0.18	681.9732	8158.2510	98.7342

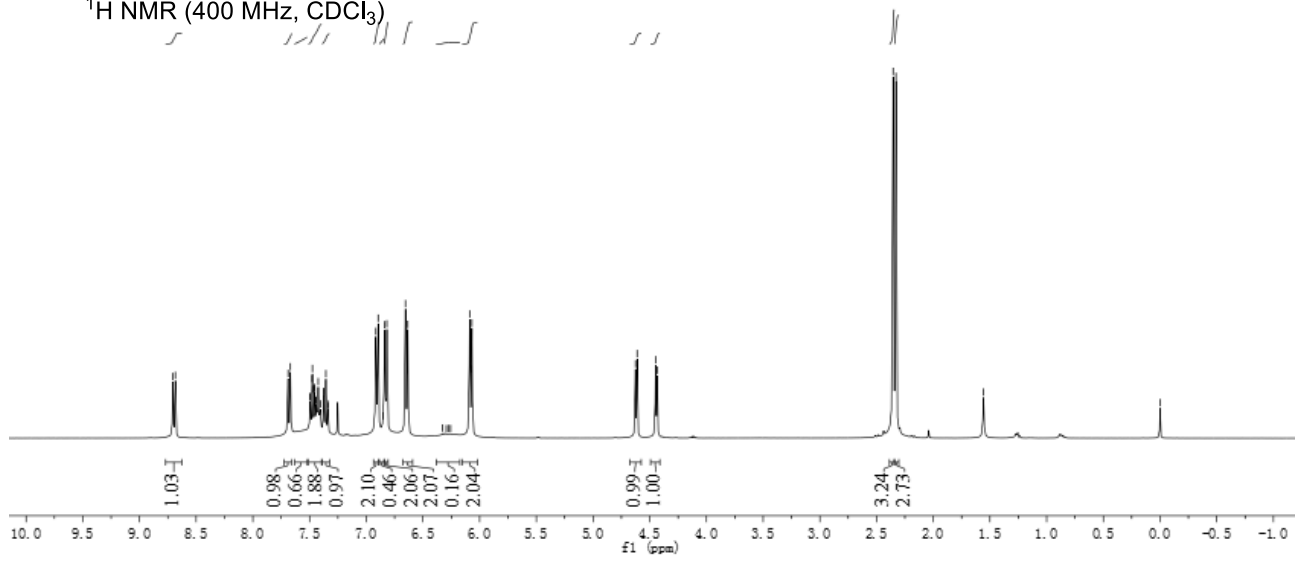


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
6.751	BB	0.15	243.3822	2394.7207	98.4297
7.748	BB	0.19	3.1336	38.2045	1.5703

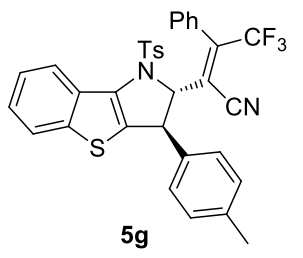
8.704 8.684 8.689 7.669 7.496 7.493 7.478 7.475 7.472 7.457 7.454 7.444 7.440 7.423 7.405 7.377 7.374 7.356 7.339 7.336 6.916 6.895 6.852 6.838 6.818 6.654 6.638 6.634 6.328 6.294 6.277 6.256 6.088 6.073 6.068 4.626 4.611 4.448 4.434 4.354 2.329 -1.557 -0.000



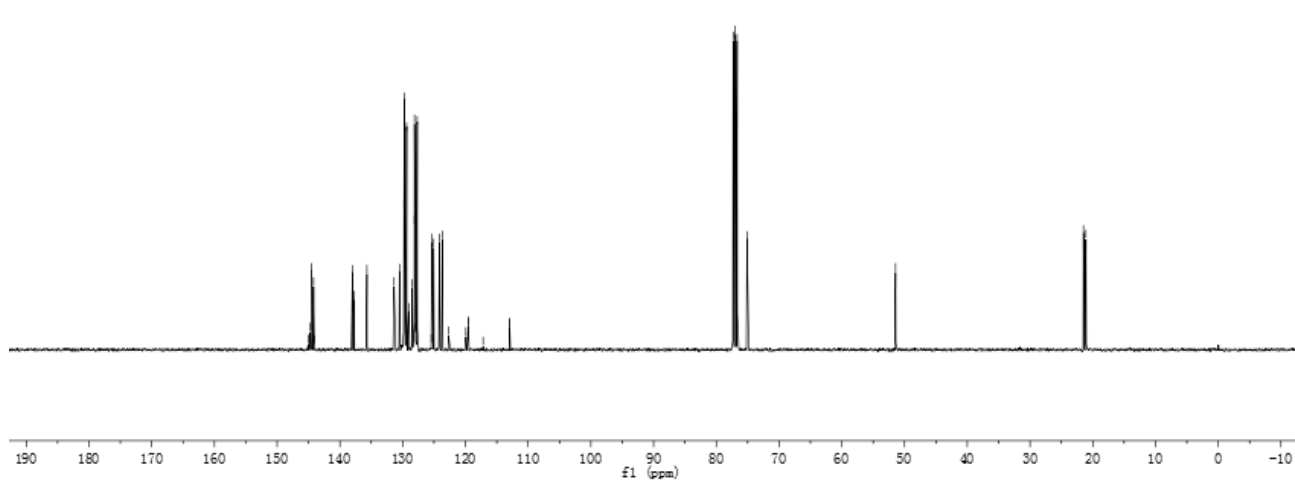
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



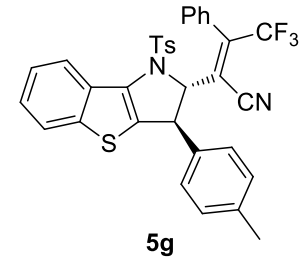
145.030 144.715 144.493 144.397 144.197 144.081 137.994 137.734 135.689 131.361 130.502 129.786 129.743 129.371 129.044 128.477 128.116 128.108 127.988 127.676 125.423 125.315 125.051 124.148 123.679 122.673 119.924 119.589 119.560 119.530 119.499 112.935 112.920 112.318 77.000 76.683 75.113 -51.431 21.483 21.088



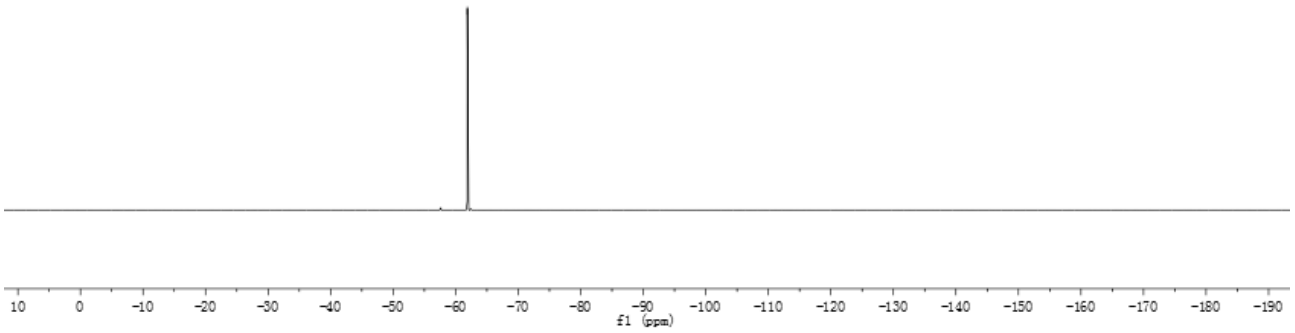
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



61.876

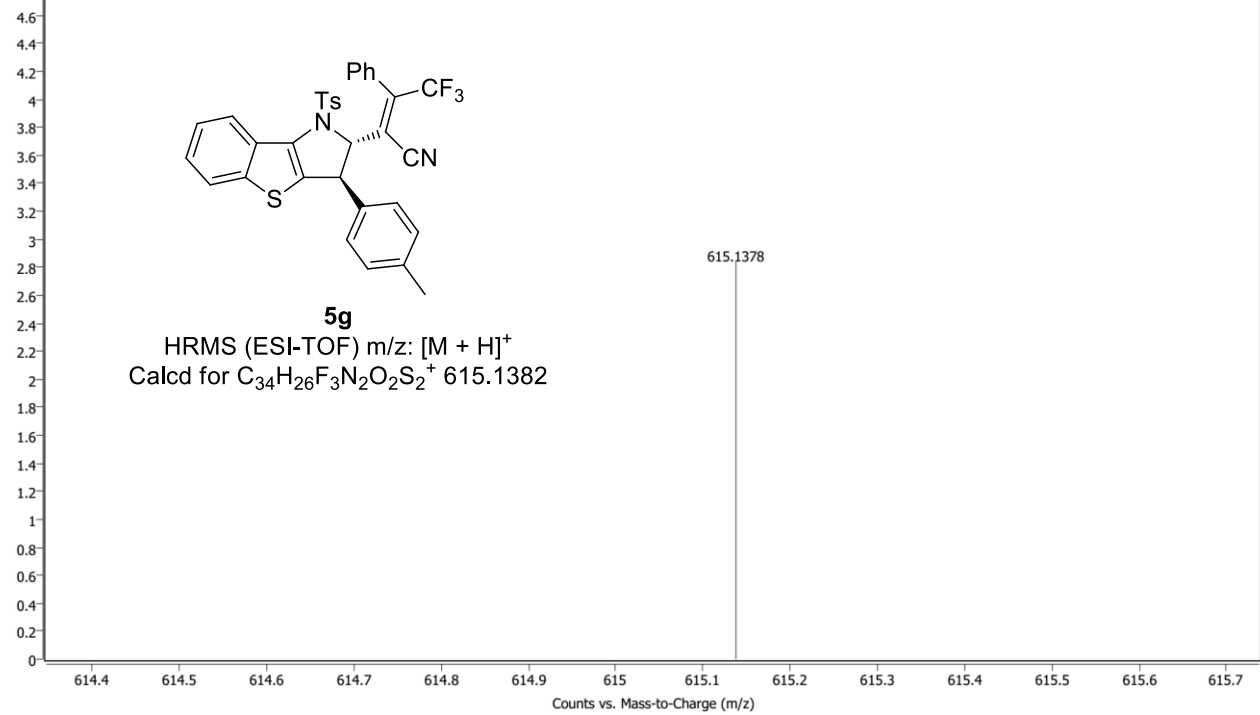


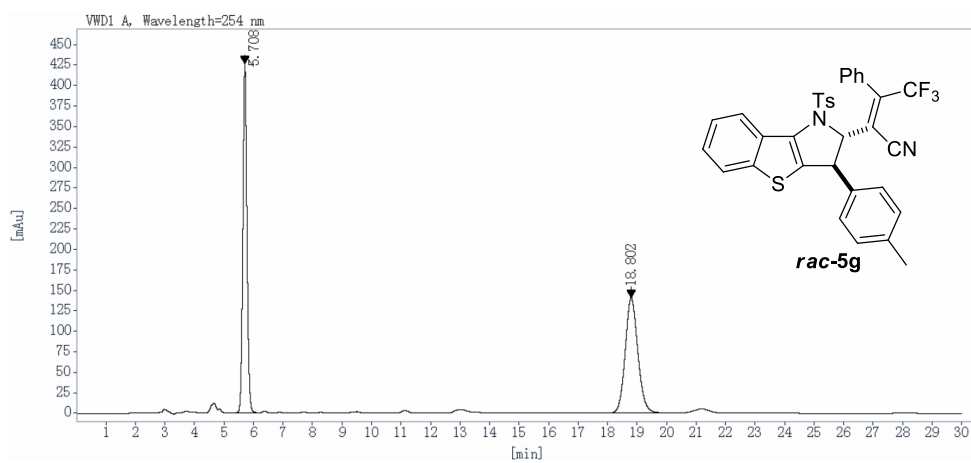
**5g**  
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



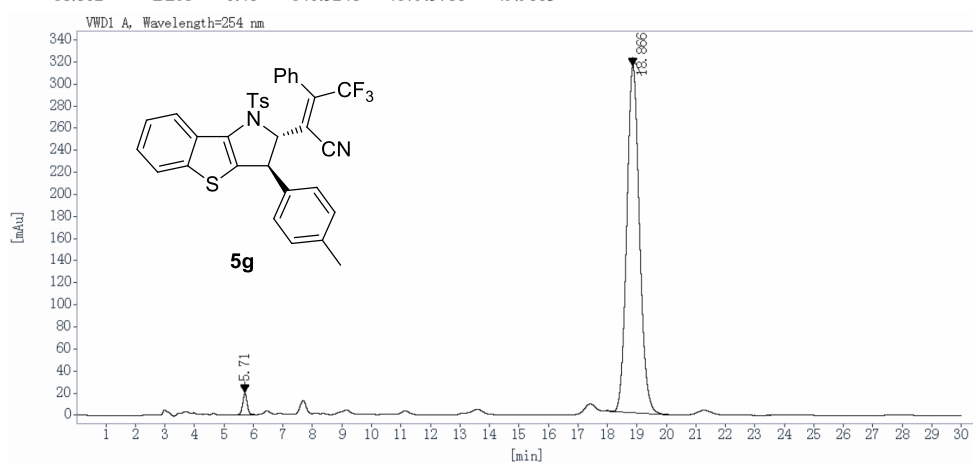
Name	cyc-12-22	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	cyc-12-22.d	Method (Acq)	TOF.m		Acq. Time (Local)
					7/22/2019 6:18:23 PM (UTC+08:00)

+ESI Scan (rt: 1.994 min) Frag=175.0V cyc-12-22.d

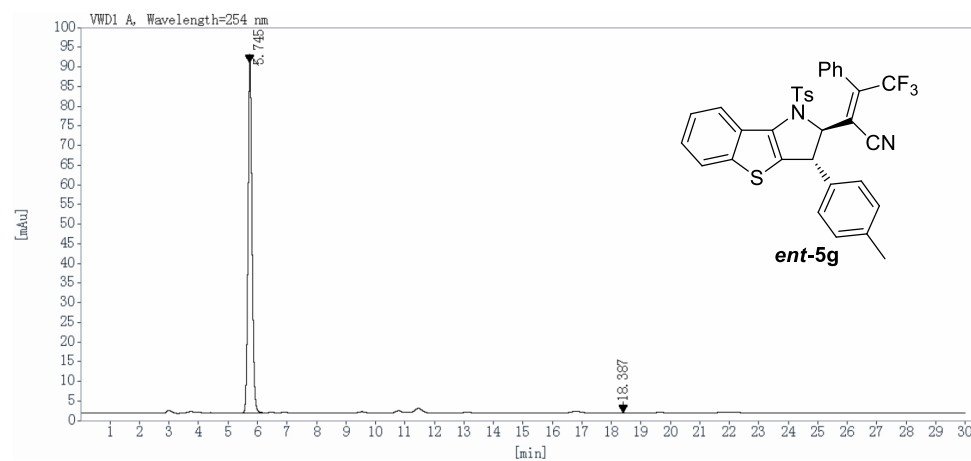




Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
5.708	BB	0.15	426.3466	4185.2217	50.0337
18.802	BBA	0.46	140.5248	4179.5786	49.9663

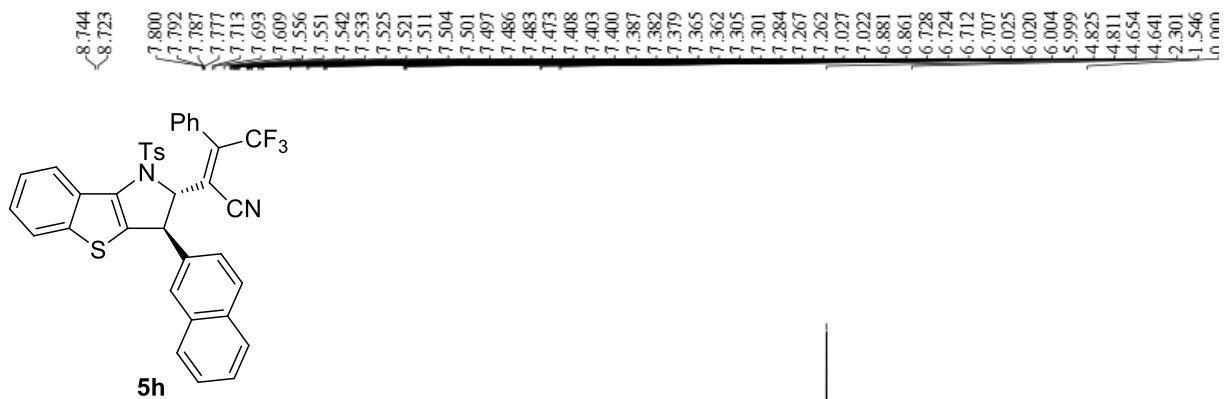


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
5.710	BB	0.16	19.5260	202.7465	2.1155
18.866	VBAR	0.46	314.1886	9381.0361	97.8845

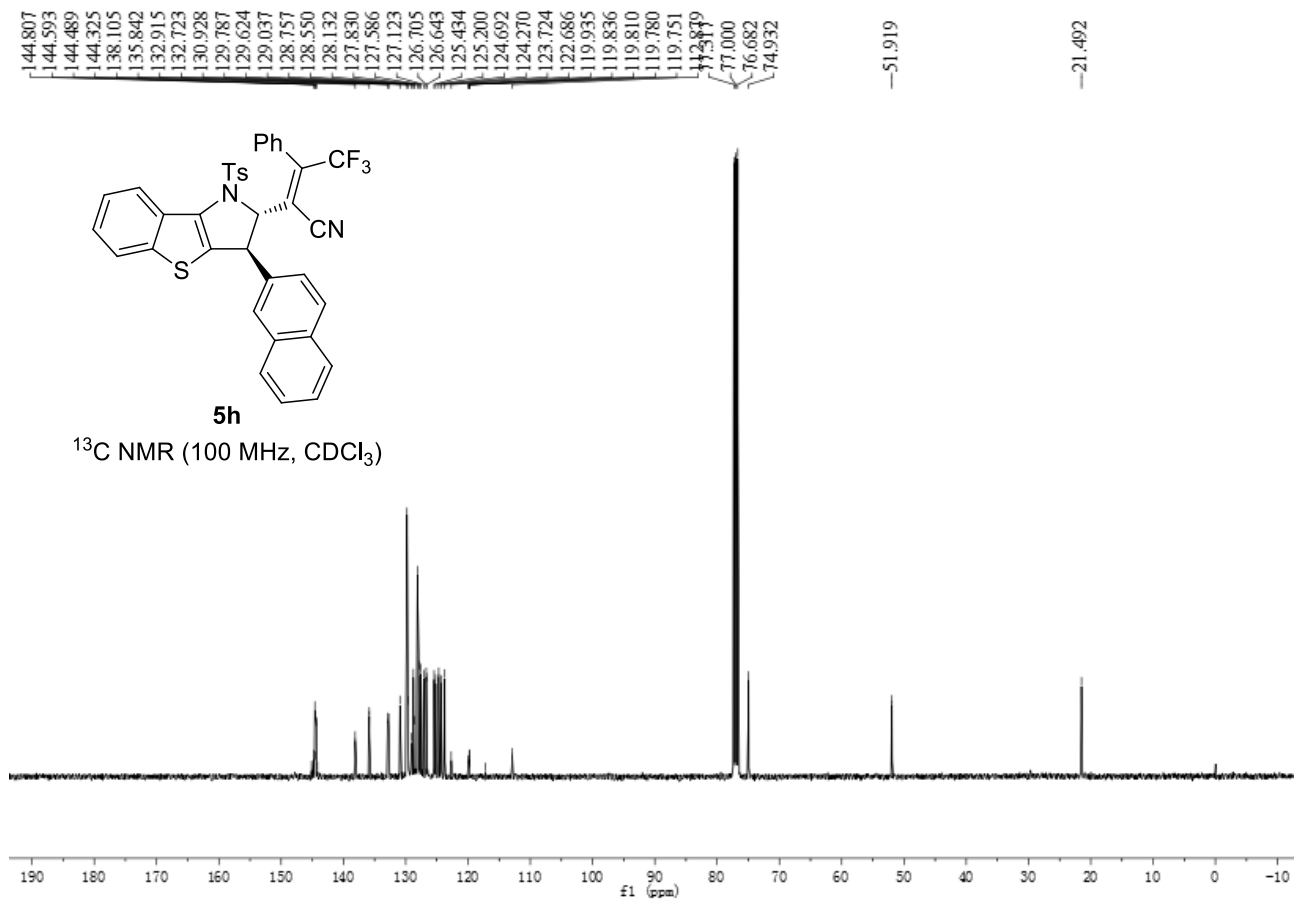
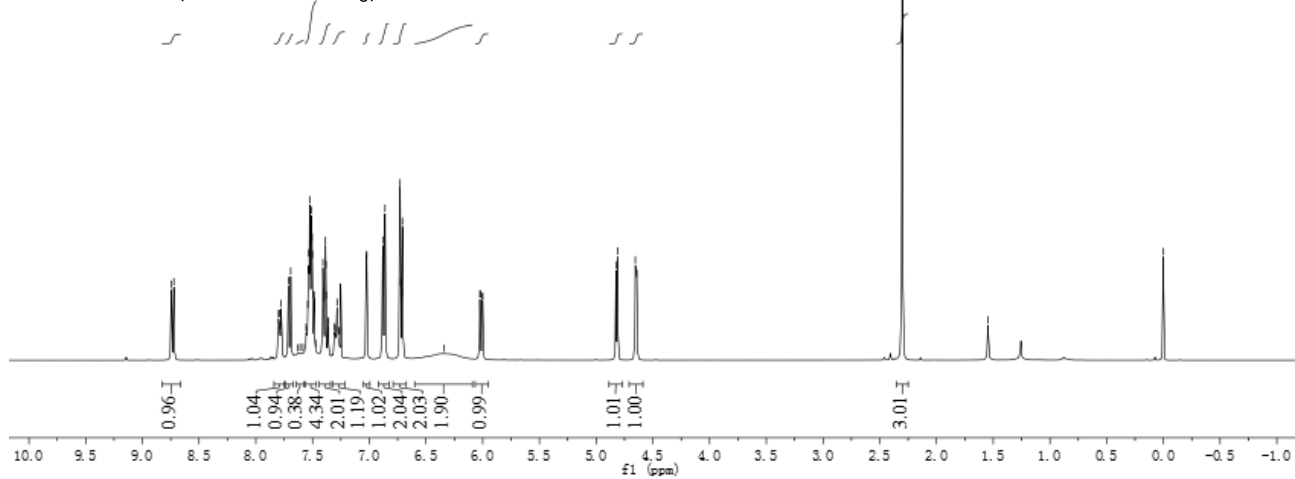


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
5.745	BBA	0.15	612.7847	5862.0049	99.9496
18.387	VV R	0.33	0.1067	2.9549	0.0504

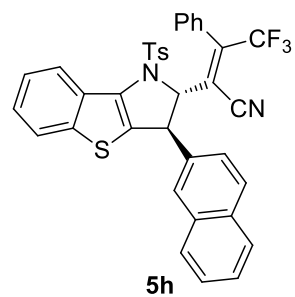




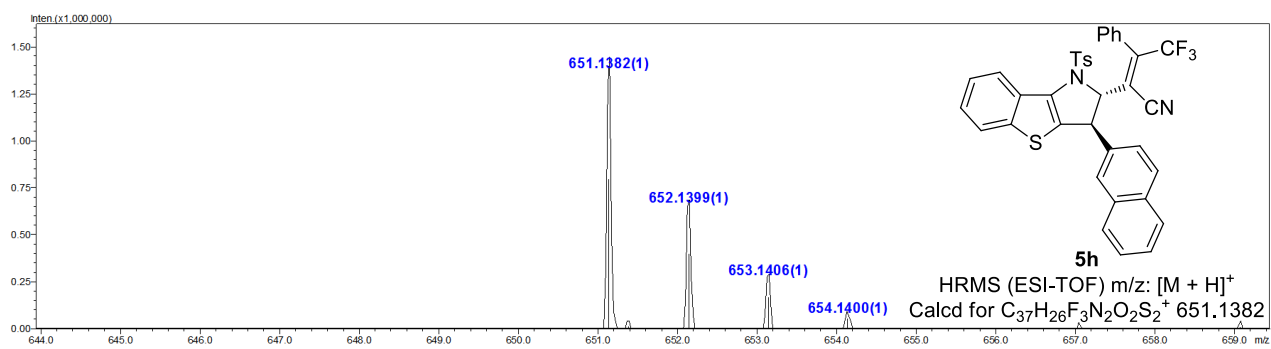
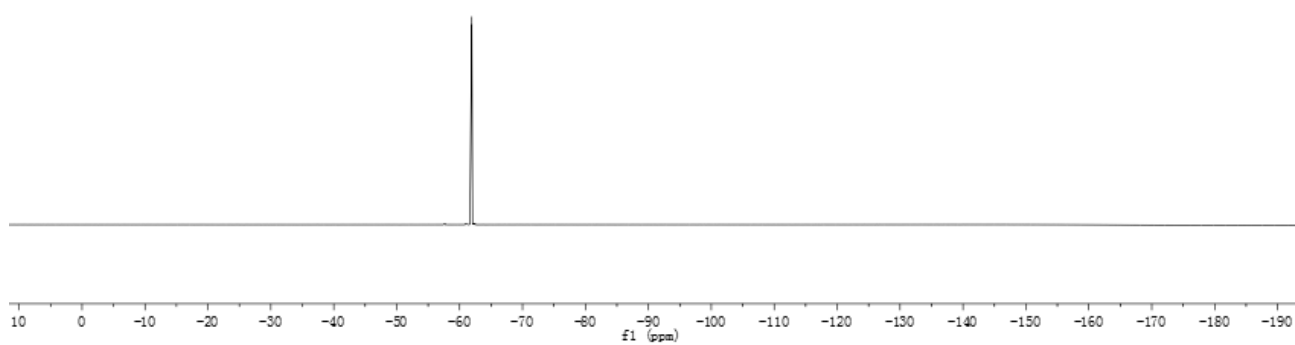
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )

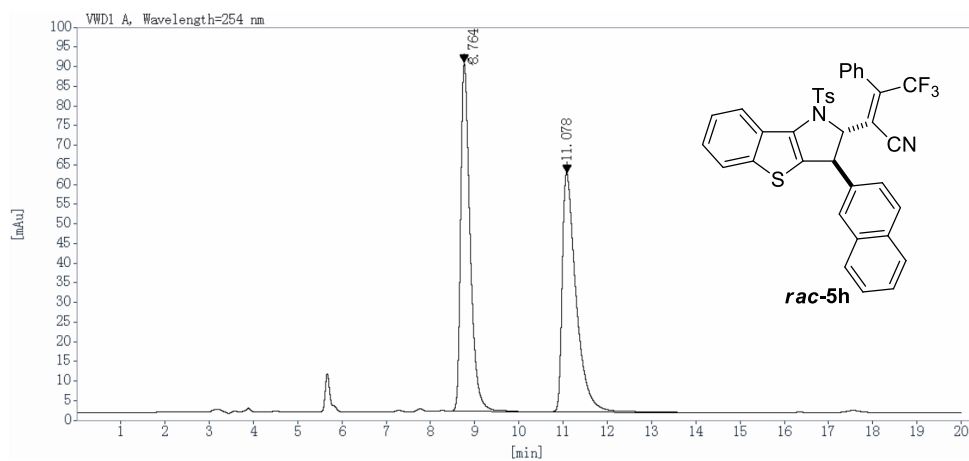


-61.936

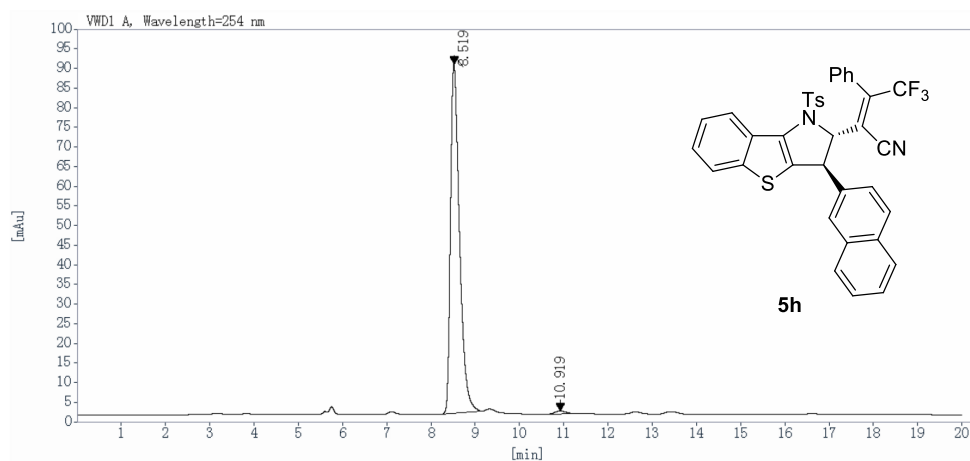


<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)

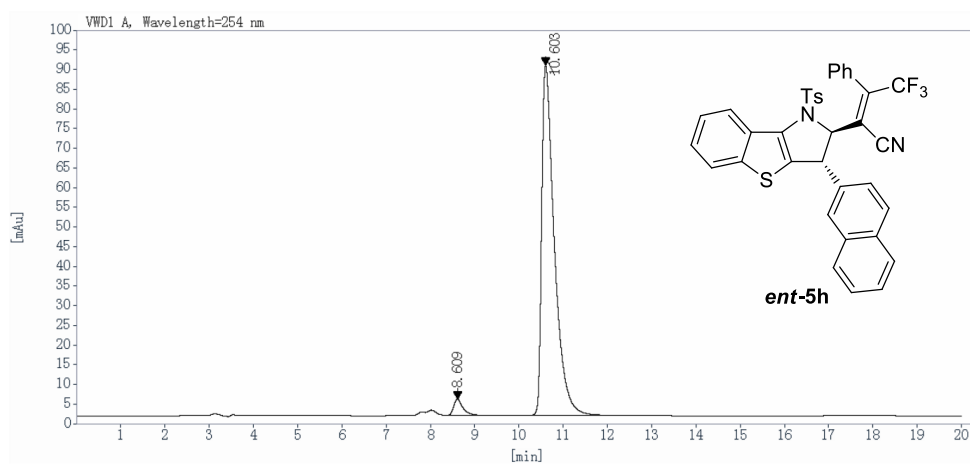




Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
8.764	BB	0.22	598.3477	8913.8438	49.9995
11.078	BV R	0.32	409.5488	8914.0156	50.0005

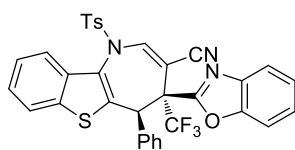


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
8.519	BB	0.21	1136.4475	16064.9111	98.8600
10.919	BBA	0.29	10.0890	185.2544	1.1400



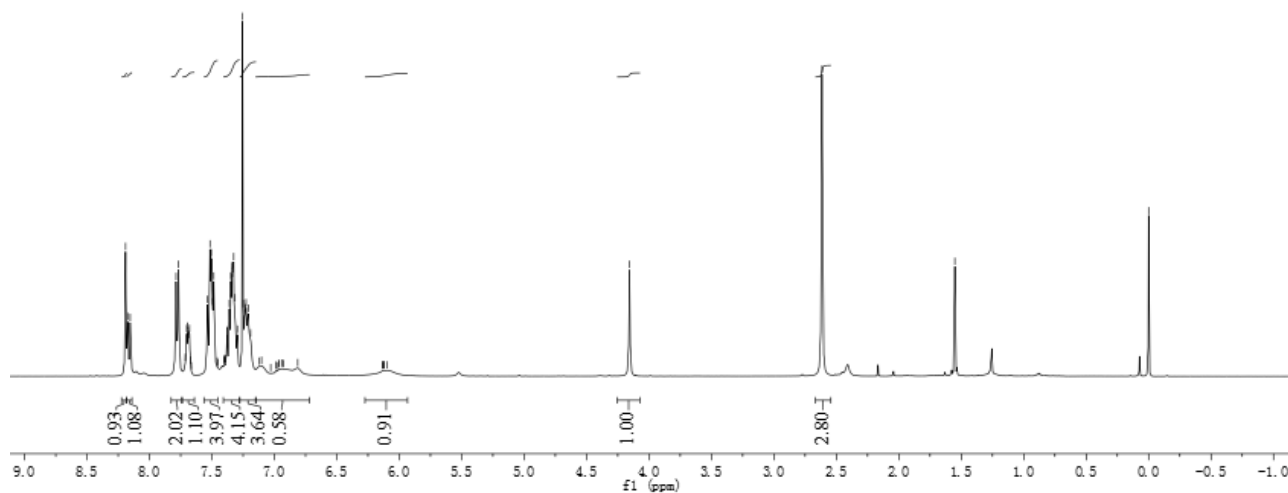
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
8.609	BV R	0.22	38.3580	577.8461	3.3698
10.603	BB	0.30	831.7119	16570.0703	96.6302

8.191  
8.174  
8.154  
7.787  
7.767  
7.713  
7.702  
7.694  
7.690  
7.684  
7.679  
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7.485  
7.458  
7.450  
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7.399  
7.397  
7.391  
7.380  
7.377  
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7.349  
7.343  
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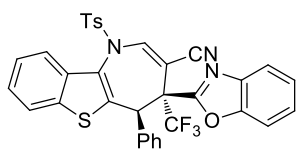


**8a**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

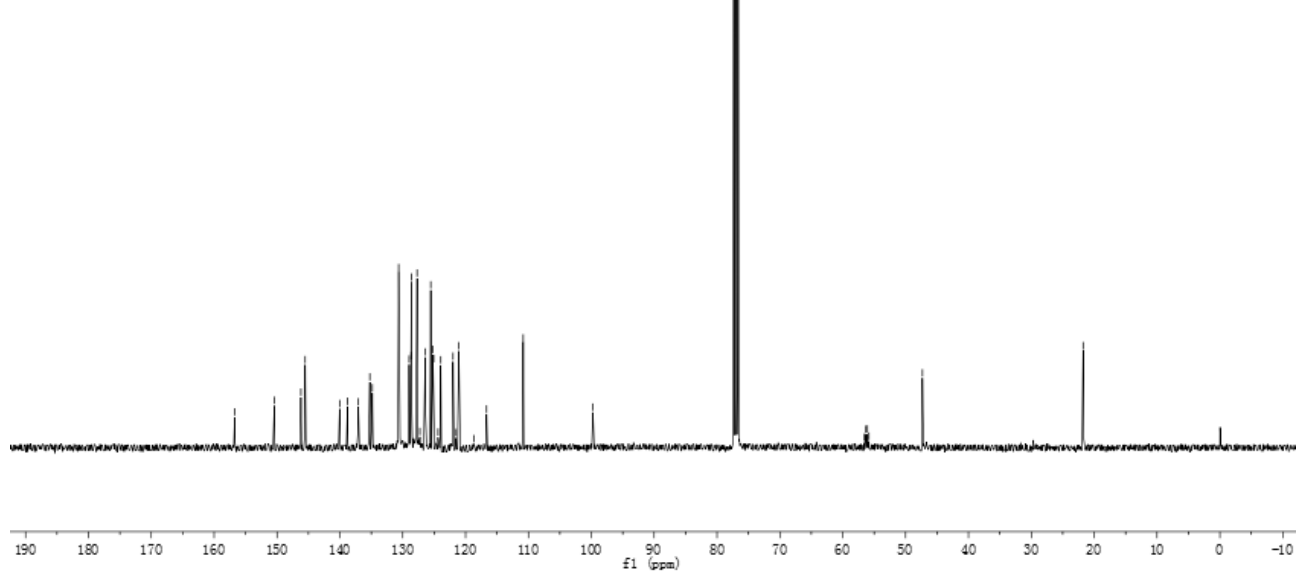


156.727  
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146.194  
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140.031  
138.791  
137.061  
135.236  
134.881  
134.838  
130.645  
128.978  
128.672  
128.618  
127.721  
127.264  
126.424  
125.543  
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124.385  
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121.993  
121.509  
121.073  
116.667  
99.989  
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77.000  
76.682  
56.555  
56.317  
56.073  
55.832  
47.321  
-21.759

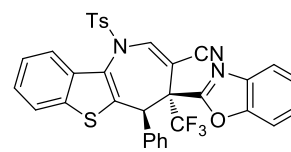


**8a**

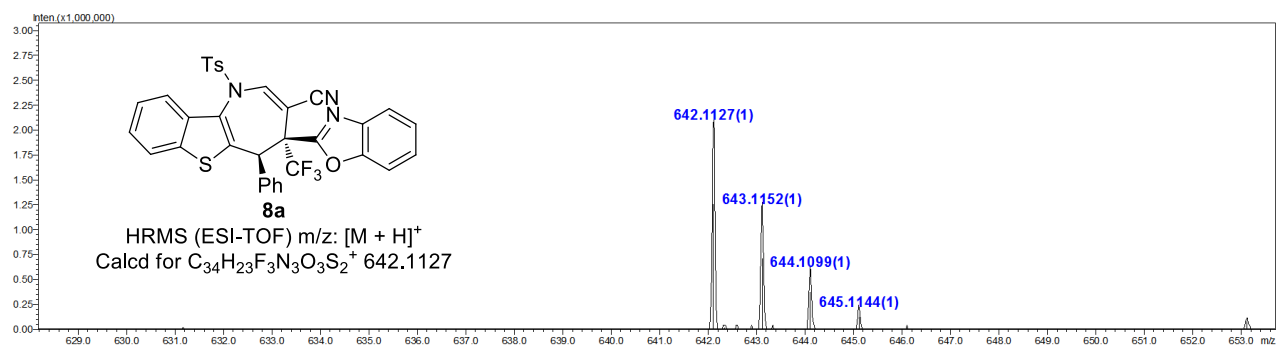
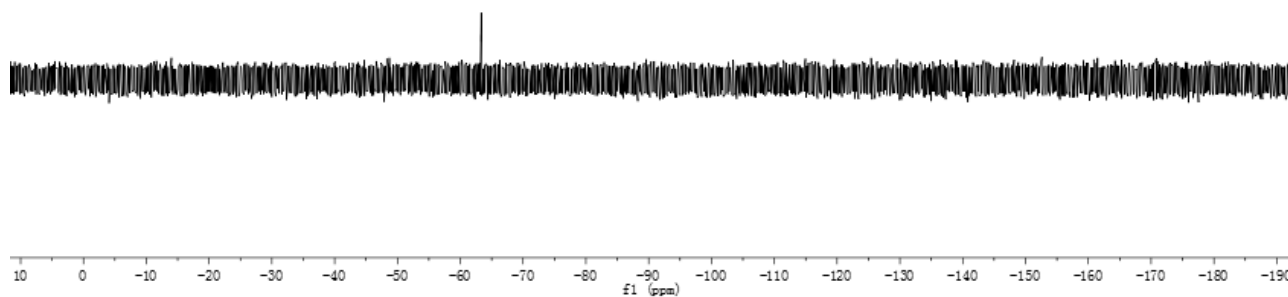
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

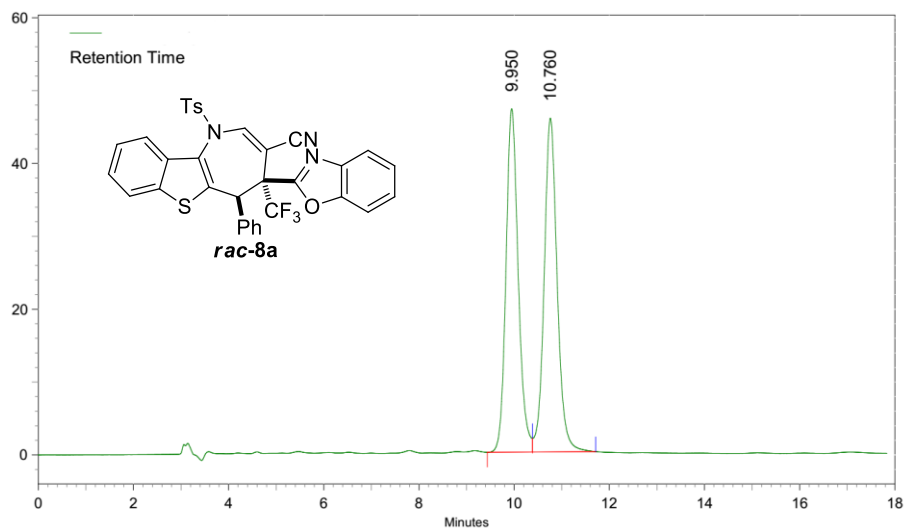


---63.317

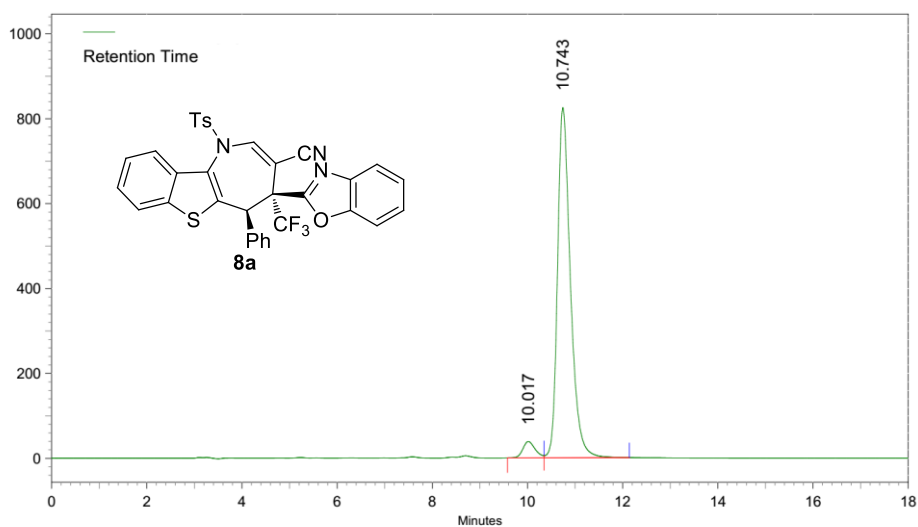


**8a**  
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)

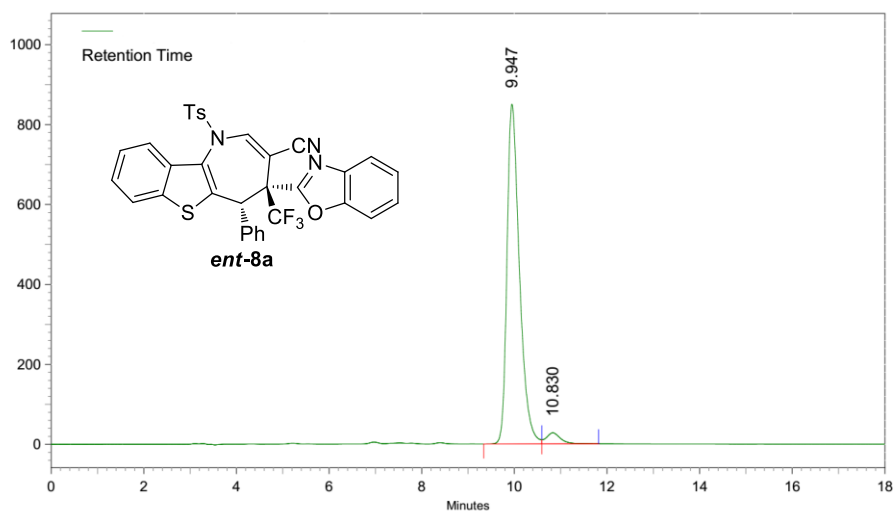




Peak No.	Ret Time	Width	Height	Area	Area [%]
1	9.950	0.950	790496	14143412	49.1923
2	10.760	1.327	768381	14607867	50.8077

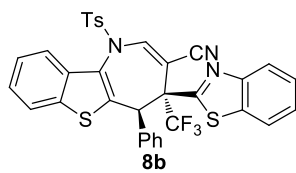


Peak No.	Ret Time	Width	Height	Area	Area [%]
1	10.017	0.767	643979	11457281	4.2153
2	10.743	1.793	13835890	260342198	95.7847

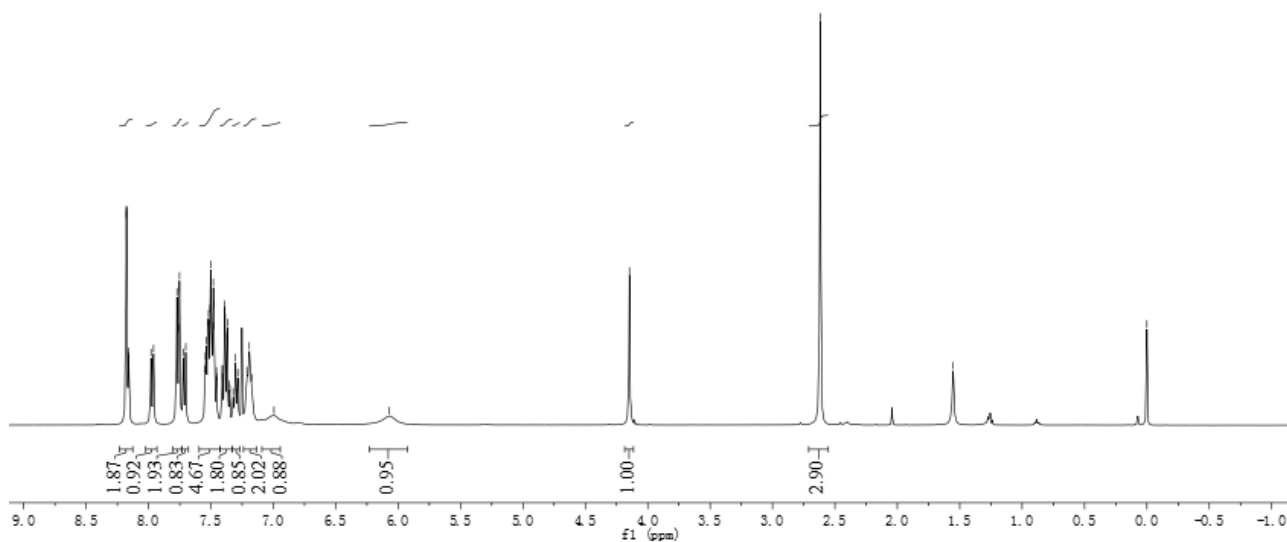


Peak No.	Ret Time	Width	Height	Area	Area [%]
1	9.947	1.253	14254977	266335839	96.4027
2	10.830	1.227	463407	9938404	3.5973

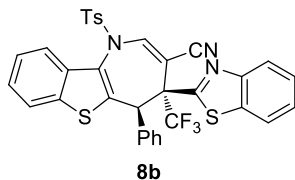
8.177  
8.160  
8.157  
8.157  
8.157  
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7.960  
7.772  
7.756  
7.752  
7.722  
7.702  
7.546  
7.543  
7.538  
7.526  
7.519  
7.516  
7.507  
7.502  
7.491  
7.481  
7.477  
7.474  
7.456  
7.453  
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7.406  
7.389  
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7.303  
7.284  
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6.070  
4.146  
2.618  
-1.553  
-0.000



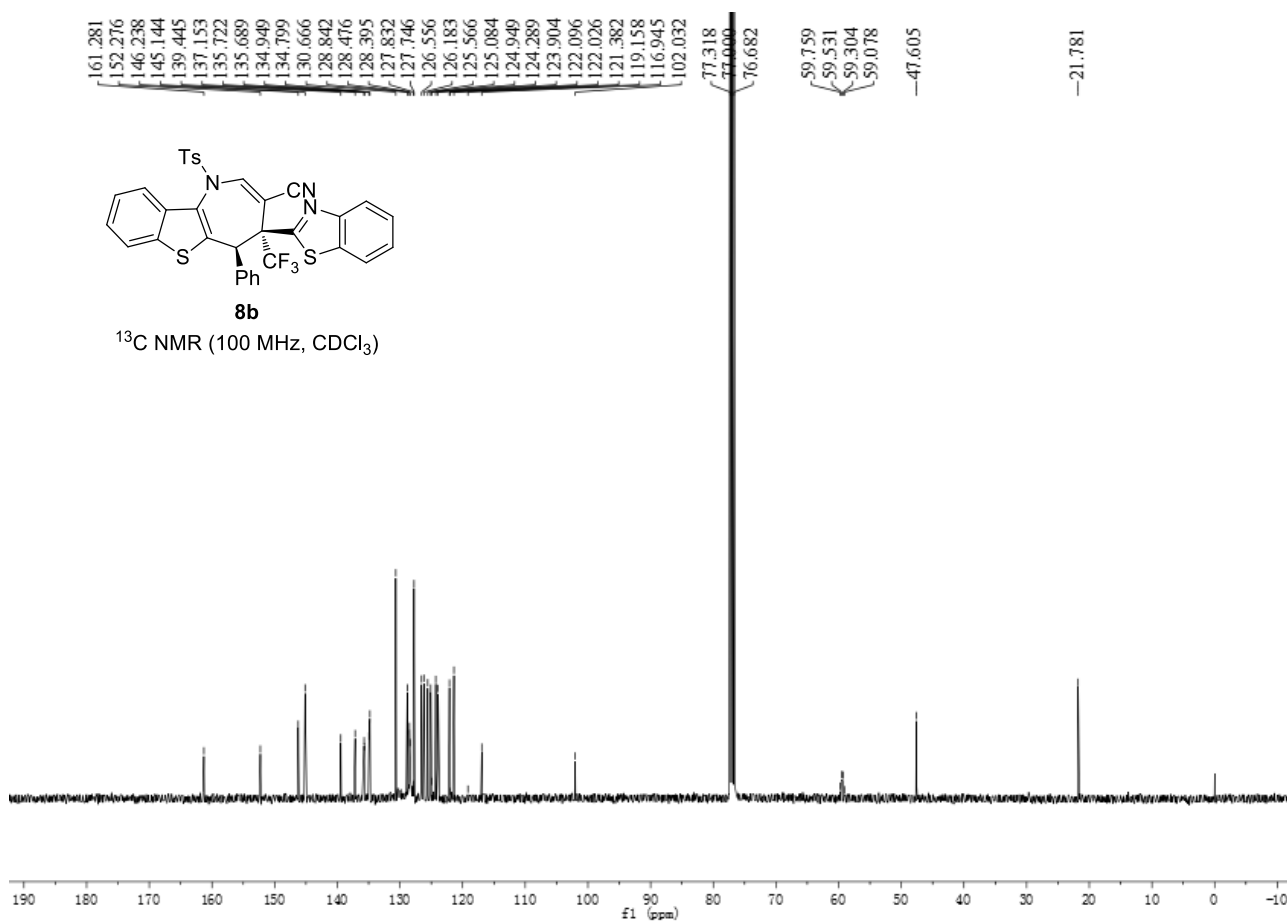
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )



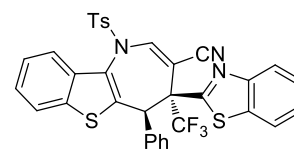
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134.949  
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130.666  
128.842  
128.476  
128.395  
127.832  
127.746  
126.556  
126.183  
125.566  
125.084  
124.949  
124.289  
123.904  
122.096  
122.026  
121.382  
119.158  
116.945  
102.032  
77.318  
77.000  
76.682  
59.759  
59.531  
59.304  
59.078  
-47.605  
-21.781



$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

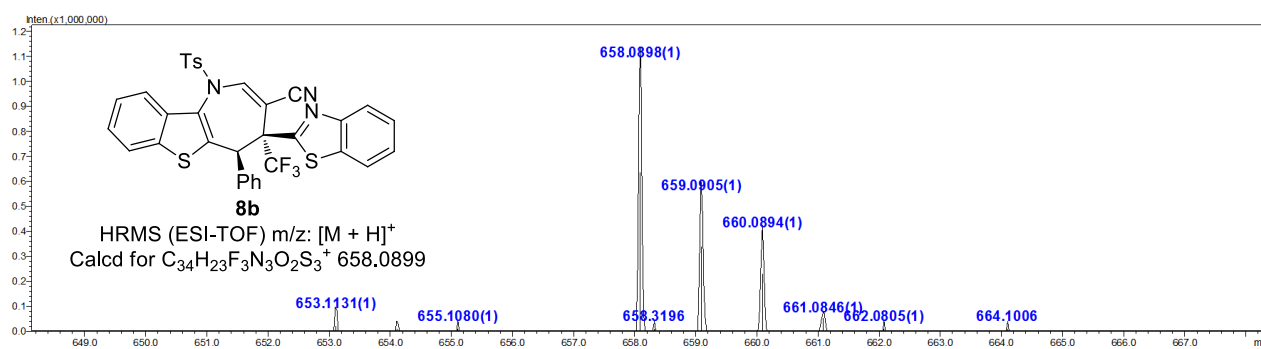
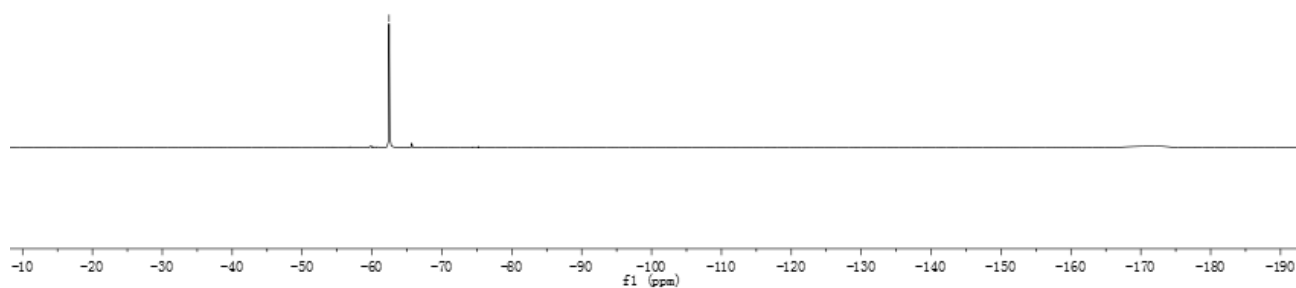


-62.450

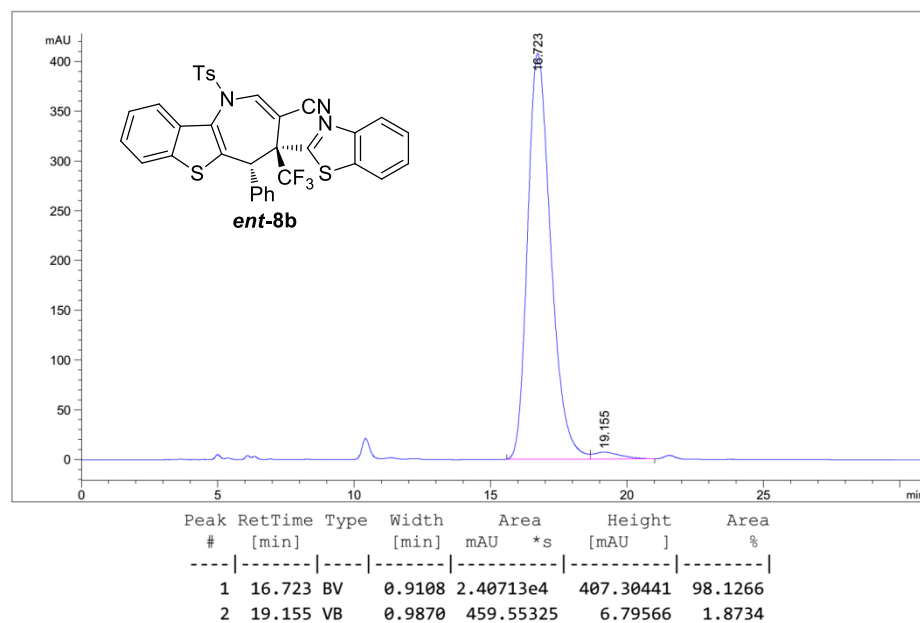
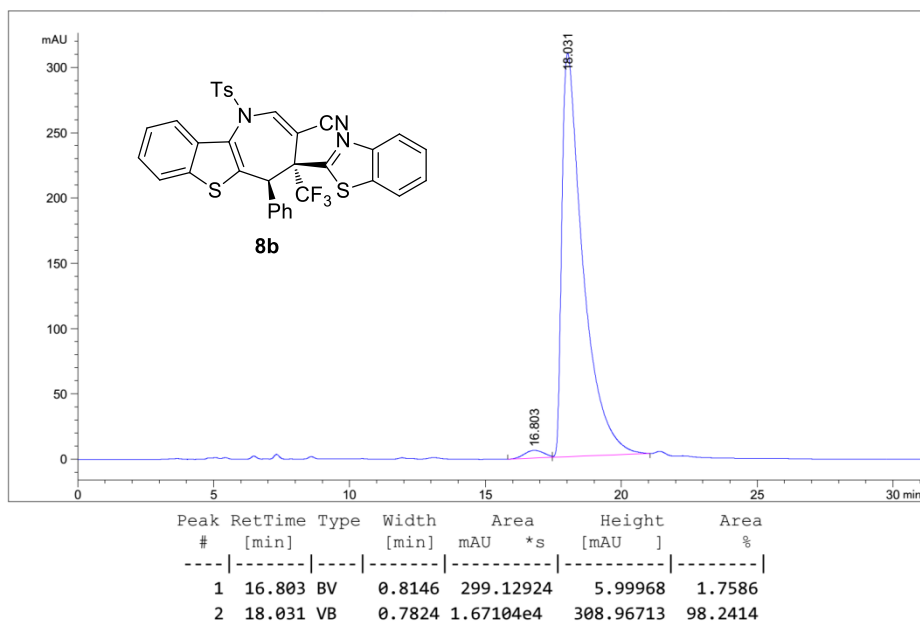
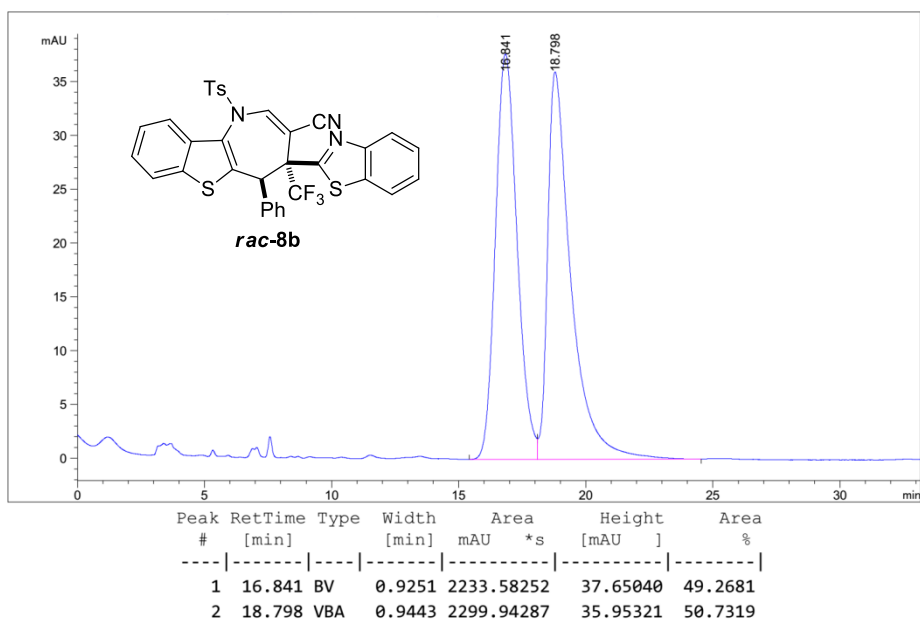


**8b**

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)

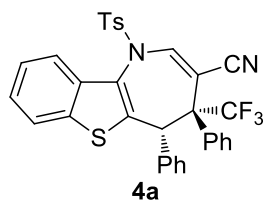




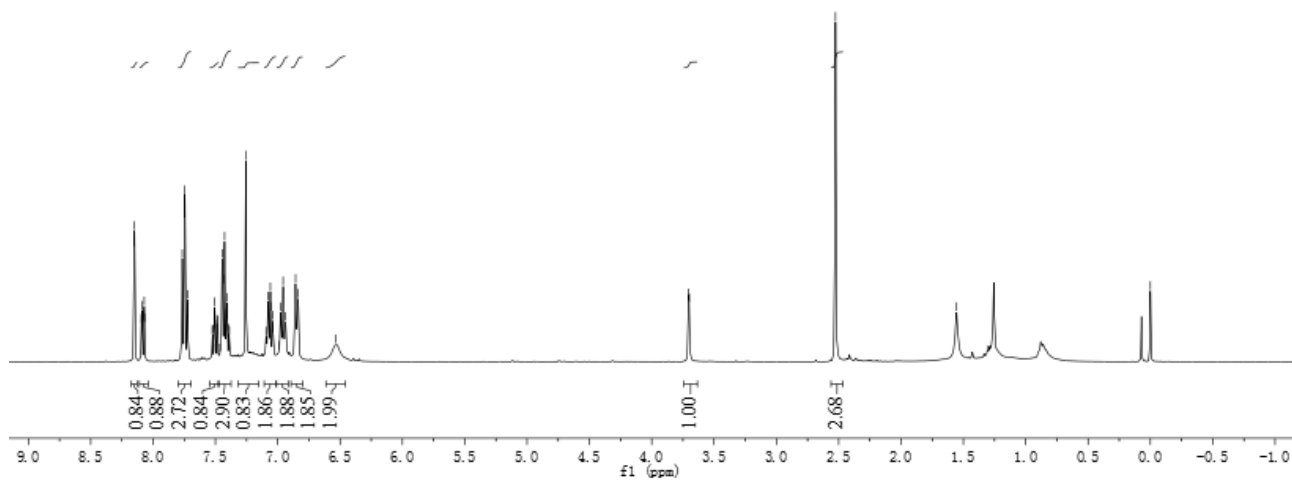


8.149  
8.093  
8.091  
8.073  
8.070  
8.068  
7.766  
7.761  
7.745  
7.724  
7.525  
7.522  
7.515  
7.507  
7.504  
7.502  
7.487  
7.484  
7.465  
7.446  
7.430  
7.426  
7.412  
7.409  
7.406  
7.392  
7.389  
7.256  
7.094  
7.076  
7.059  
7.056  
7.044  
7.037  
6.992  
6.976  
6.957  
6.938  
6.857  
6.837  
6.532  
6.3703  
3.699  
2.526  
1.555

-0.000



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

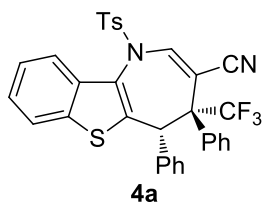


146.084  
142.836  
138.266  
136.767  
135.187  
134.969  
134.839  
134.634  
130.604  
130.324  
130.313  
130.306  
128.268  
128.139  
127.863  
127.701  
127.657  
127.467  
126.497  
125.487  
124.938  
123.841  
123.645  
122.134  
117.834  
117.834

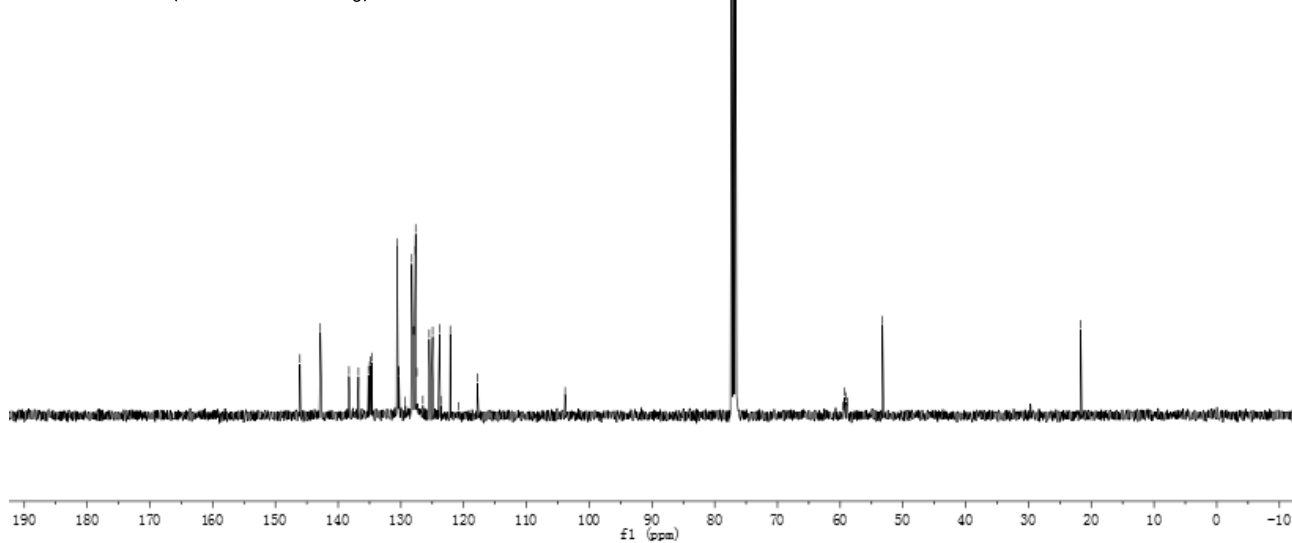
77.318  
77.000  
76.683

59.534  
59.292  
59.054  
58.817  
53.264

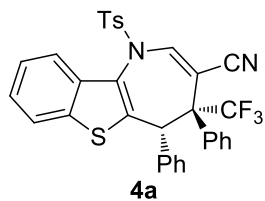
-21.662



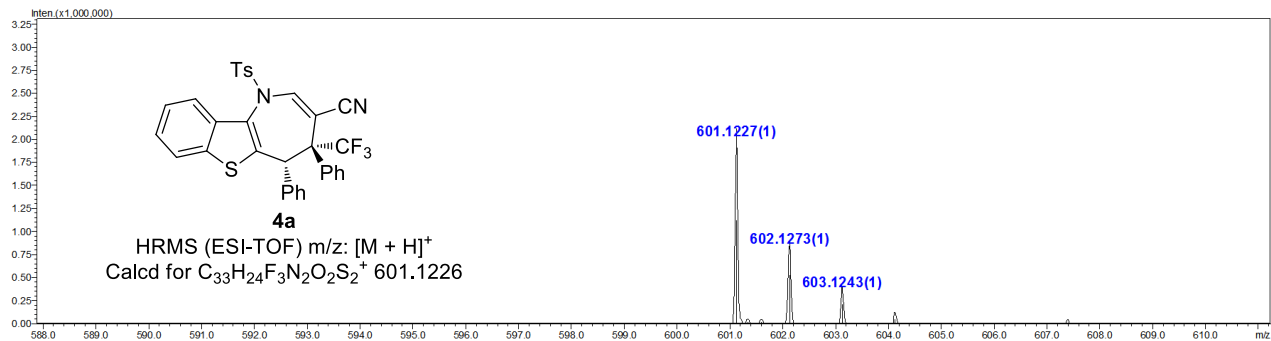
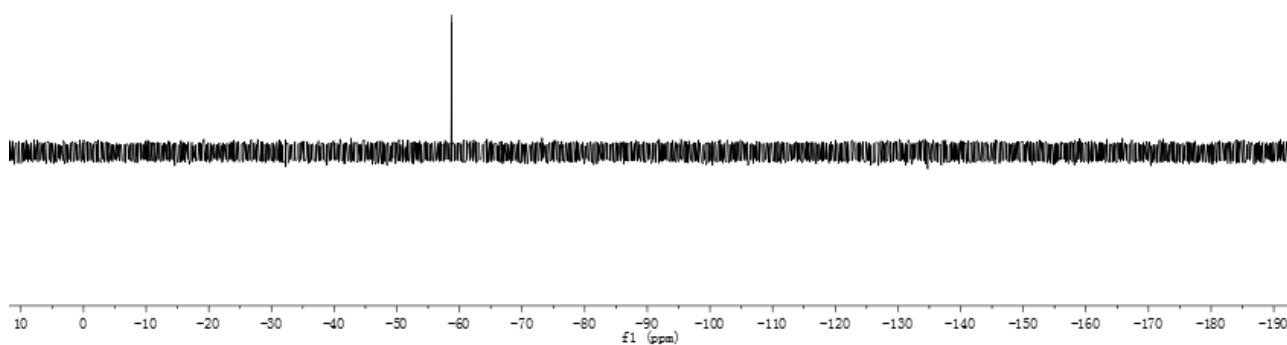
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

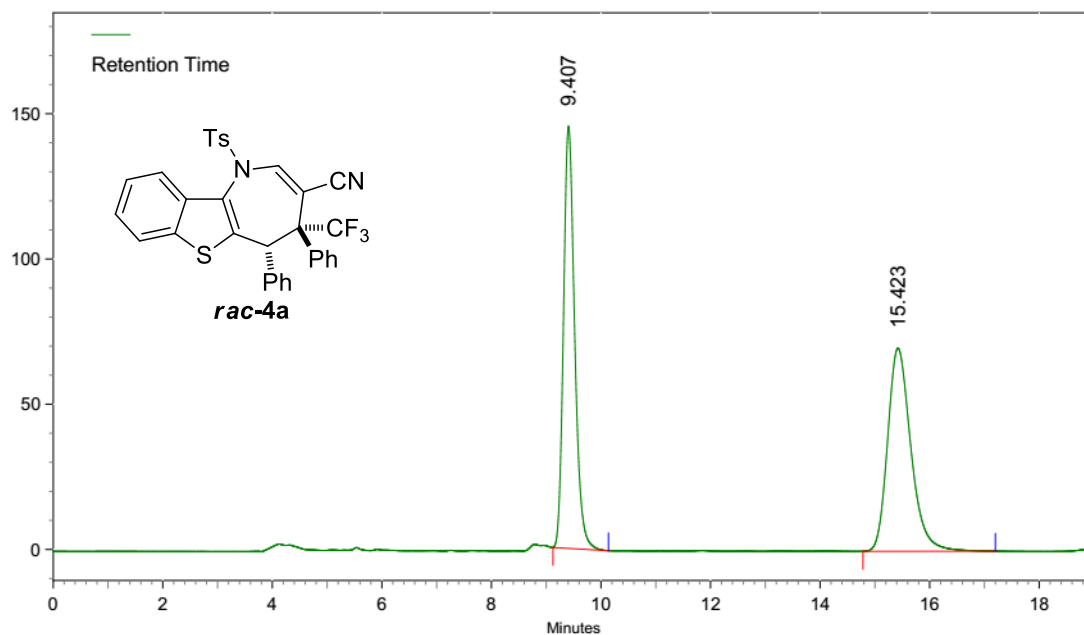


—58.788



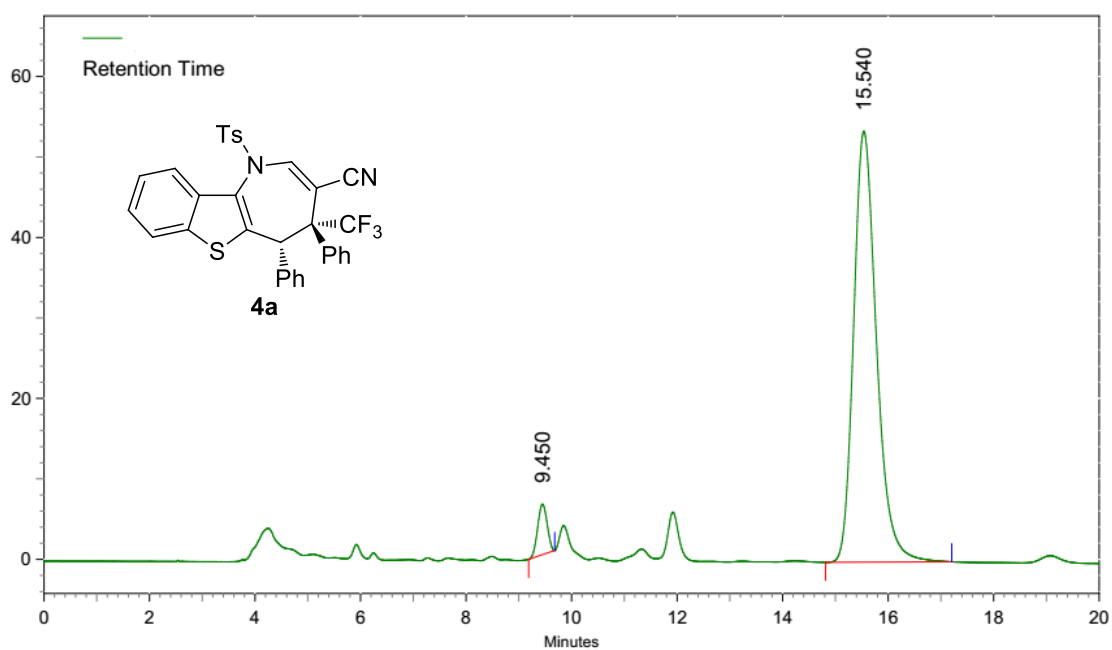
**4a**  
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)





### AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	9.407	1.013	2437883	34350154	49.7978
2	15.423	2.417	1173213	34629049	50.2022



### AREA PERCENT REPORT

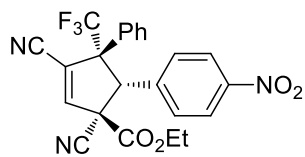
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	9.450	0.493	105223	1313808	4.6425
2	15.540	2.393	898095	26985489	95.3575

8.229  
8.222  
8.217  
8.205  
8.200  
8.193  
8.187  
7.582  
7.561  
7.502  
7.488  
7.478  
7.471  
7.462  
7.455  
7.451  
7.365  
7.354  
7.347  
7.338  
7.330  
7.214

4.532  
4.220  
4.203  
4.185  
4.167

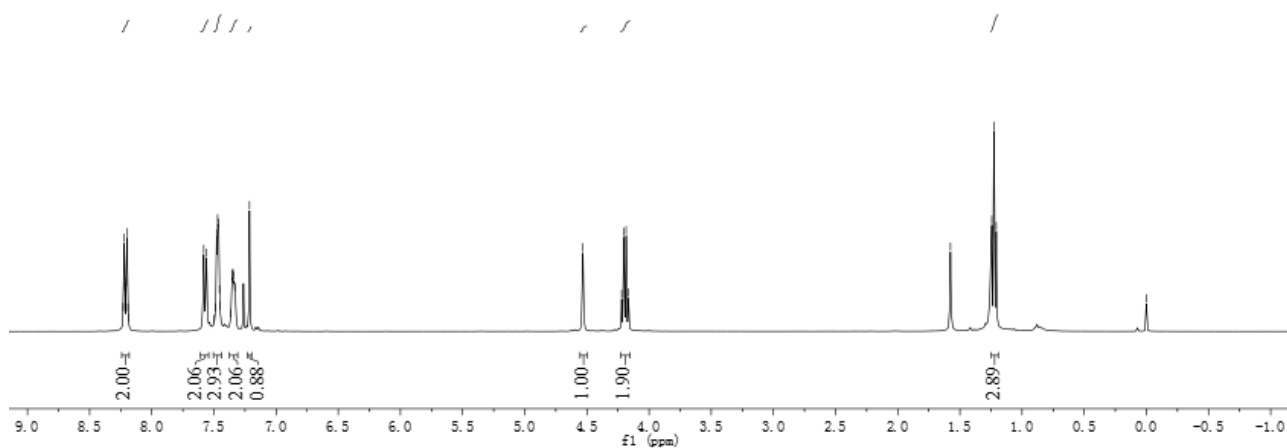
1.576  
1.243  
1.226  
1.208

-0.000

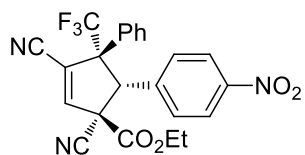


**10**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

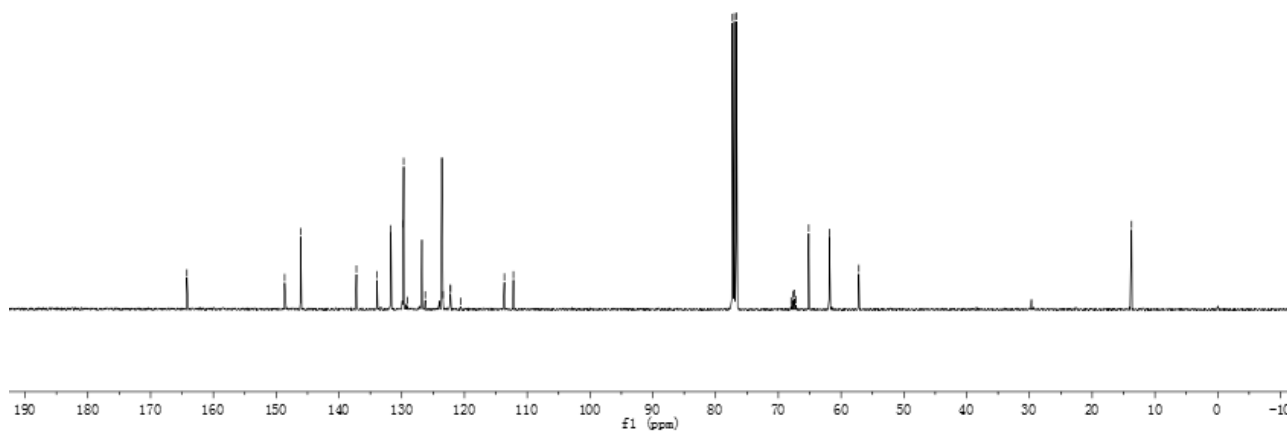


164.220  
148.649  
146.094  
137.209  
133.929  
131.724  
129.790  
129.686  
129.087  
126.250  
123.412  
122.237  
122.220  
120.574  
113.640  
112.199  
77.318  
77.000  
76.682  
67.970  
67.708  
67.445  
67.185  
65.158  
61.877  
57.172  
-13.728

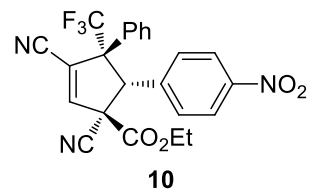


**10**

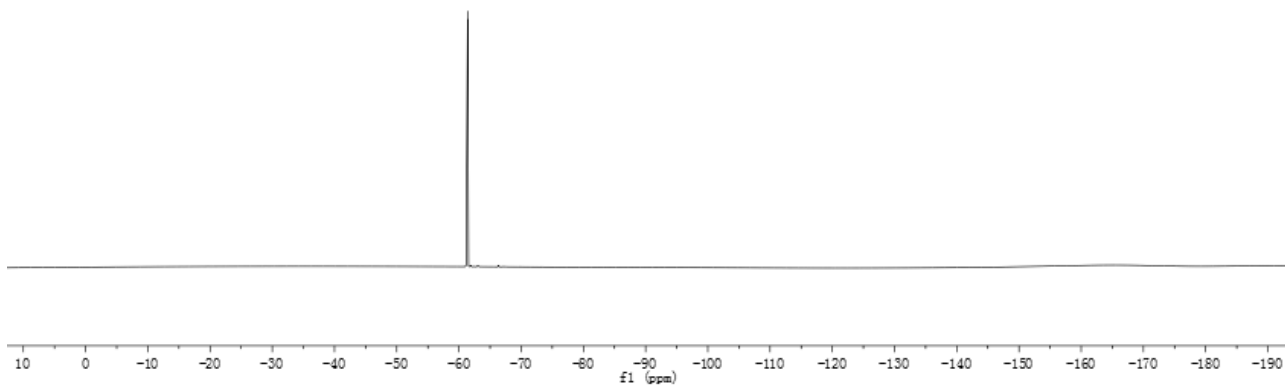
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



---61.397

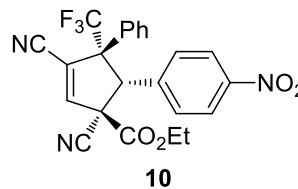
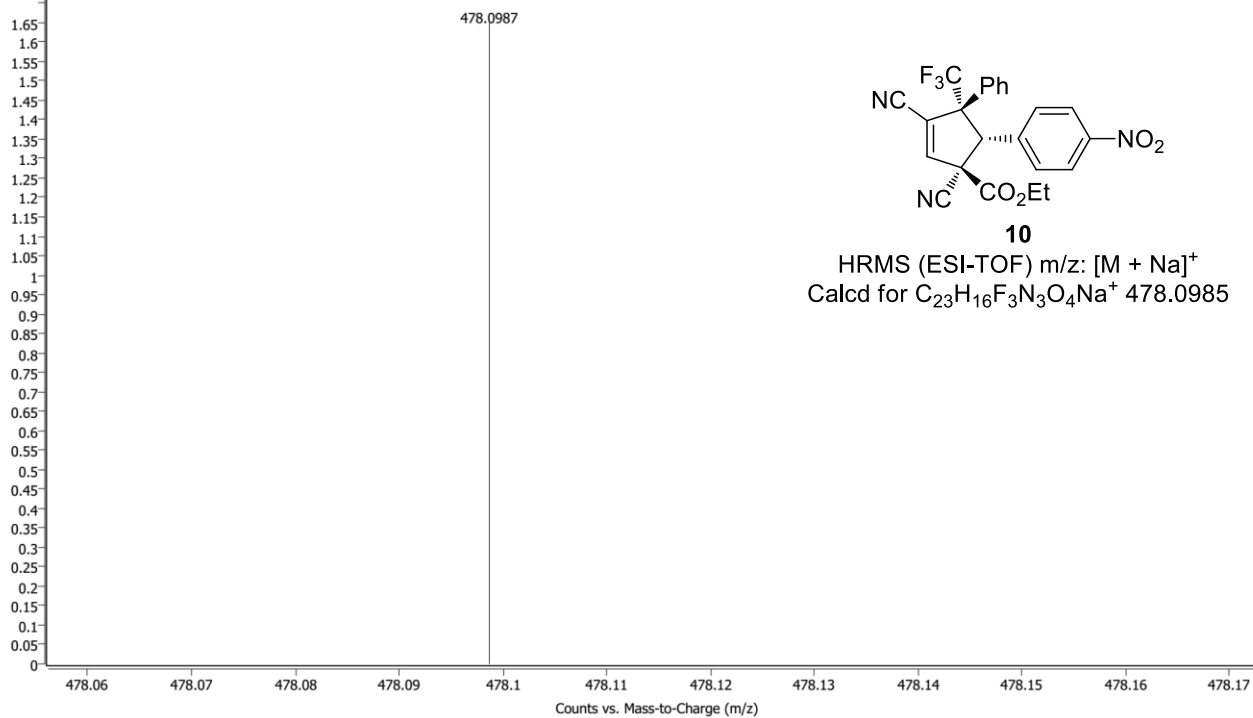


<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)

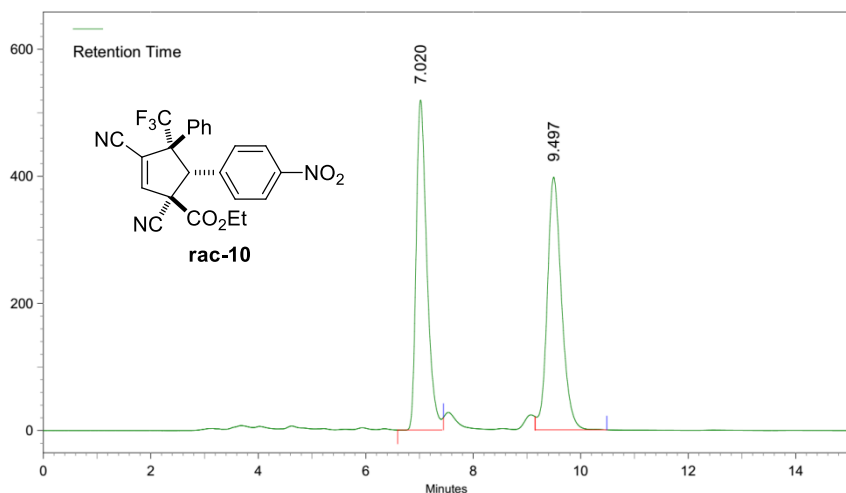


Name	CYC-20210412-10	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	8	Plate Pos.	IRM Status	Success	
Data File	CYC-20210412-10.d	Method (Acq)	ZYJ-20201106.m	Comment	Acq. Time (Local) 4/16/2021 11:26:55 AM (UTC+08:00)

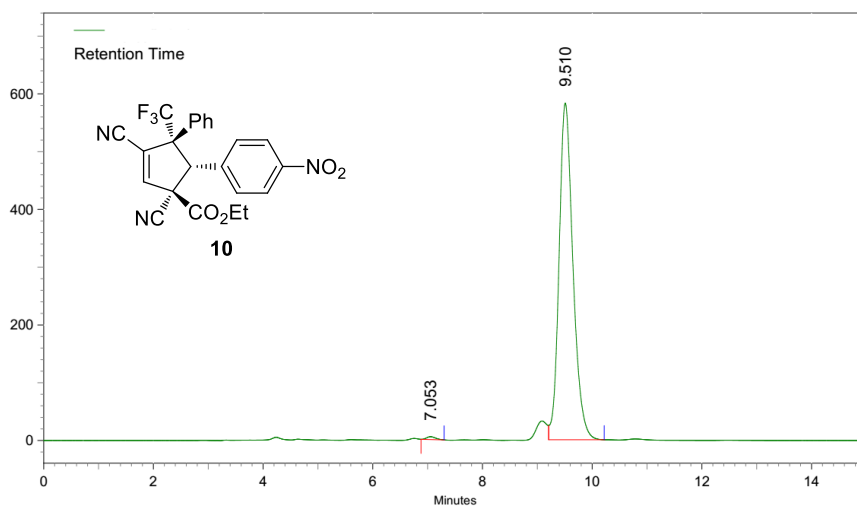
+ESI Scan (rt: 0.179 min) Frag=175.0V CYC-20210412-10.d



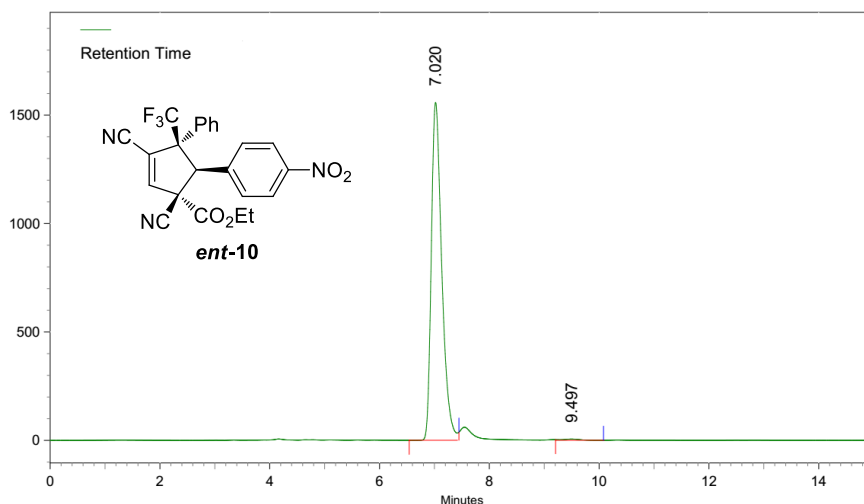
HRMS (ESI-TOF) m/z: [M + Na]<sup>+</sup>  
Calcd for C<sub>23</sub>H<sub>16</sub>F<sub>3</sub>N<sub>3</sub>O<sub>4</sub>Na<sup>+</sup> 478.0985



Peak No.	Ret Time	Width	Height	Area	Area [%]
1	7.020	0.853	8713593	120567367	49.4623
2	9.497	1.333	6673030	123188781	50.5377



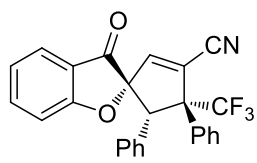
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	7.053	0.420	82671	930976	0.5383
2	9.510	1.013	9780714	172027680	99.4617



Peak No.	Ret Time	Width	Height	Area	Area [%]
1	7.020	0.907	26142820	346316296	99.4003
2	9.497	0.873	96103	2089359	0.5997

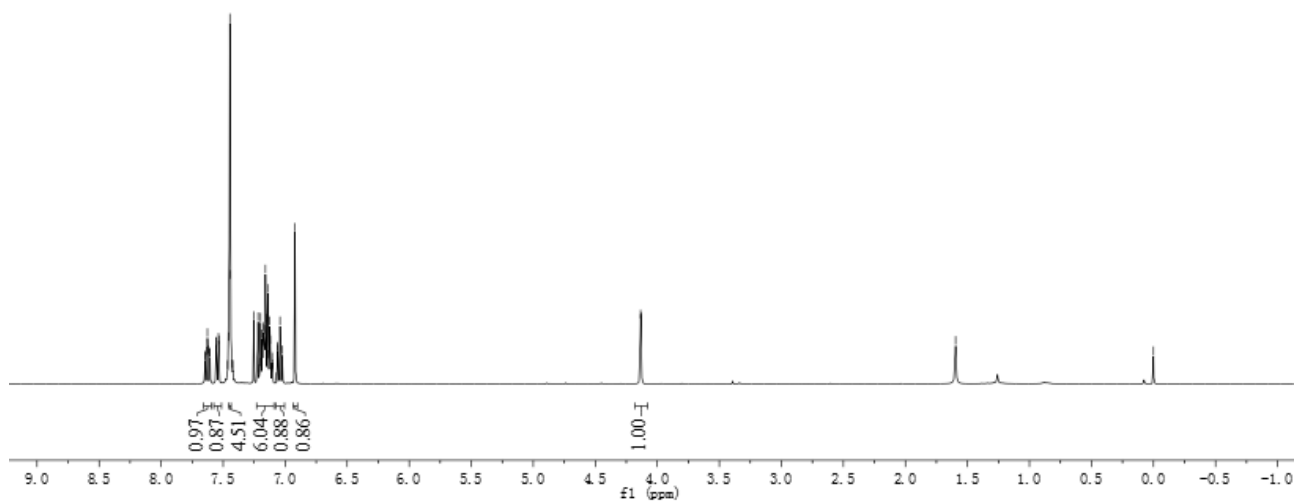
7.648  
7.644  
7.630  
7.627  
7.623  
7.609  
7.605  
7.557  
7.554  
7.538  
7.534  
7.464  
7.457  
7.446  
7.440  
7.427  
7.422  
7.253  
7.219  
7.209  
7.205  
7.198  
7.188  
7.181  
7.176  
7.168  
7.159  
7.154  
7.142  
7.134  
7.127  
7.123  
7.120  
7.109  
7.105  
7.102  
7.071  
7.061  
7.059  
7.042  
7.023  
6.920  
4.135  
4.131  
1.596

0.000



**11**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



197.914

171.470

147.884

139.330

134.627

131.410

131.393

131.378

129.311

128.951

128.665

128.075

126.954

126.931

126.907

126.883

126.469

125.011

124.981

123.633

122.954

120.796

119.686

113.525

113.282

95.997

77.318

77.000

76.682

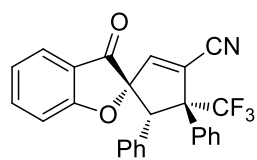
68.051

67.794

67.538

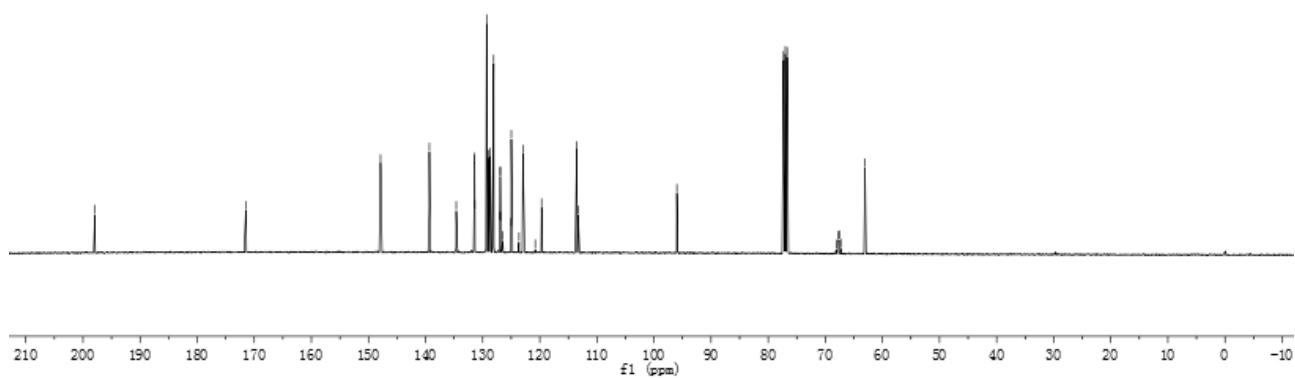
67.281

63.038

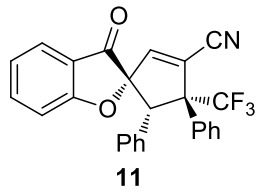


**11**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

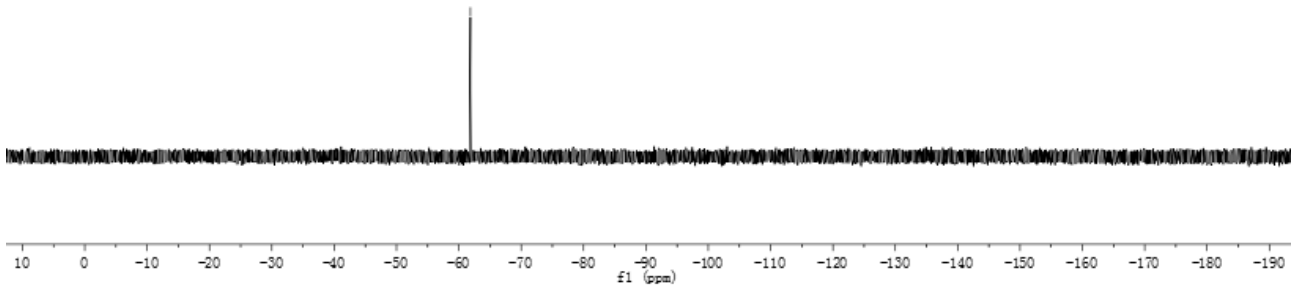




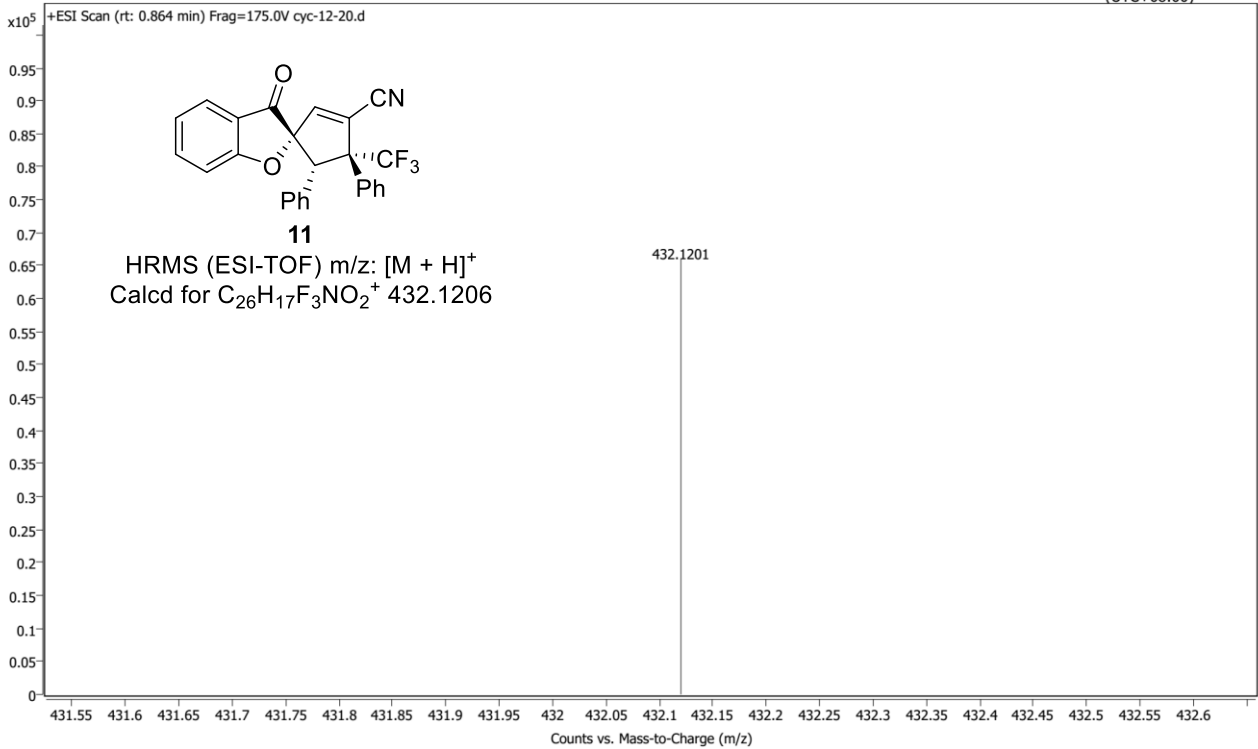


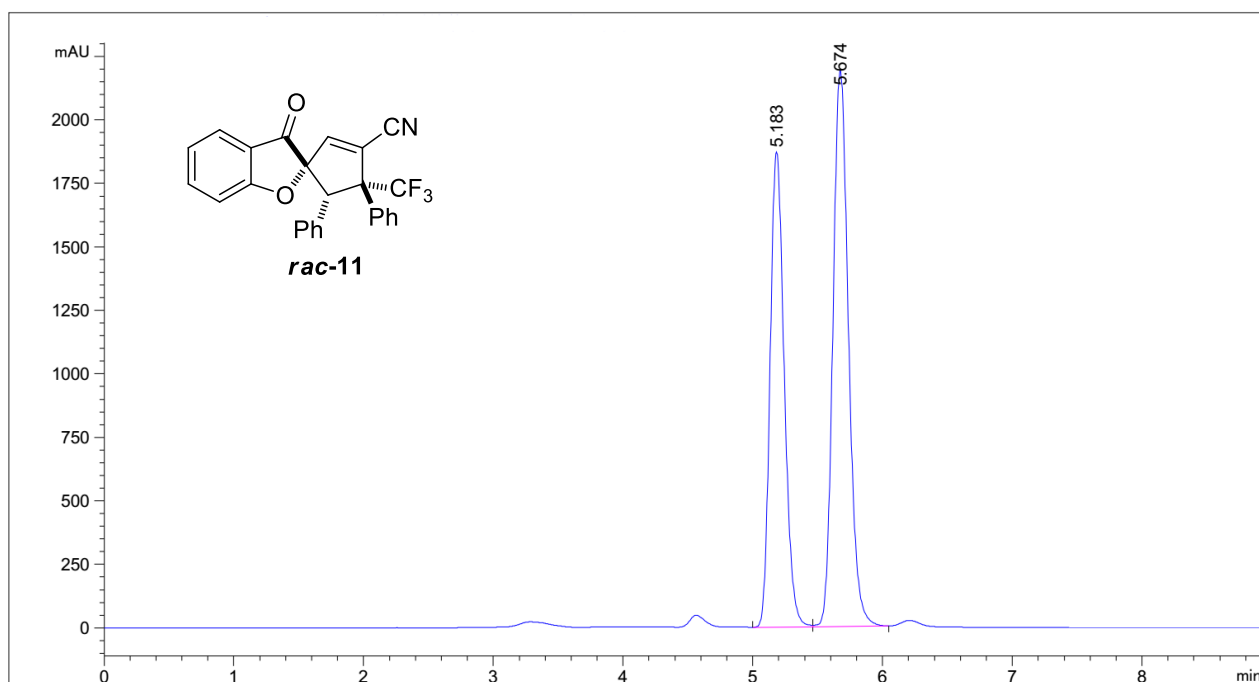
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )

→ -61.855

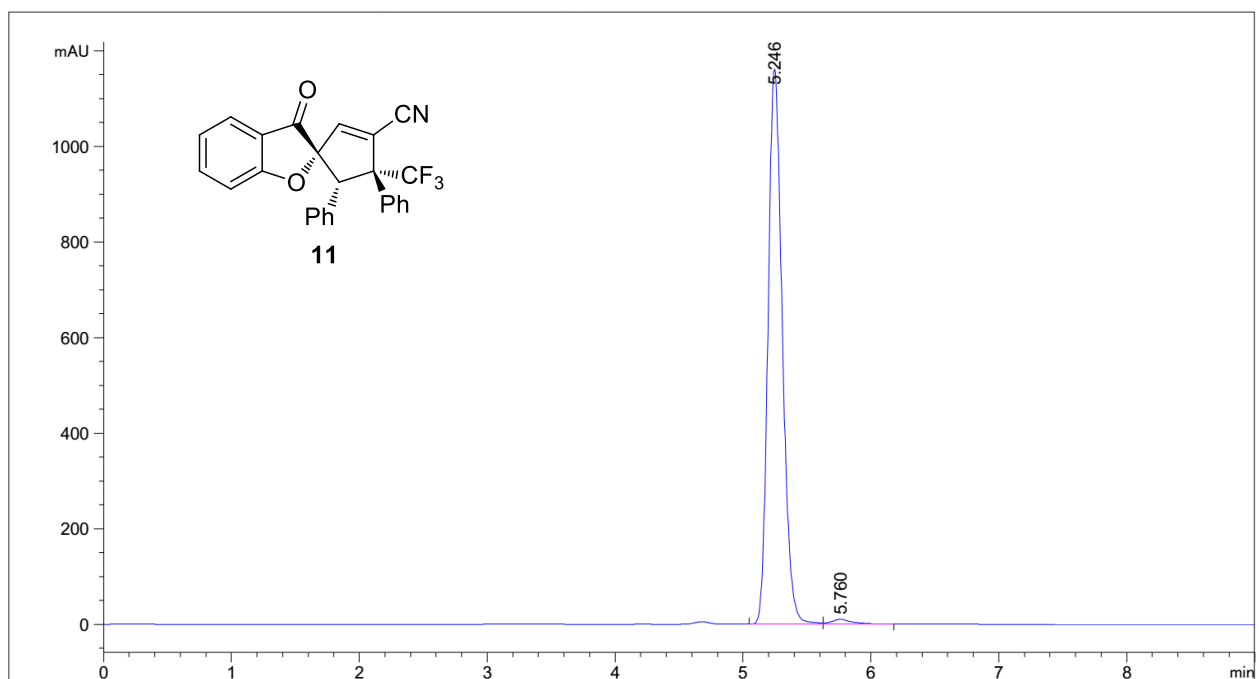


Name	cyc-12-20	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	cyc-12-20.d	Method (Acq)	TOF.m		Acq. Time (Local) 7/22/2019 6:12:46 PM (UTC+08:00)





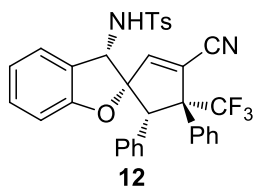
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.183	BV	0.1189	1.41634e4	1871.40063	43.7620
2	5.674	VB	0.1290	1.82012e4	2189.55176	56.2380



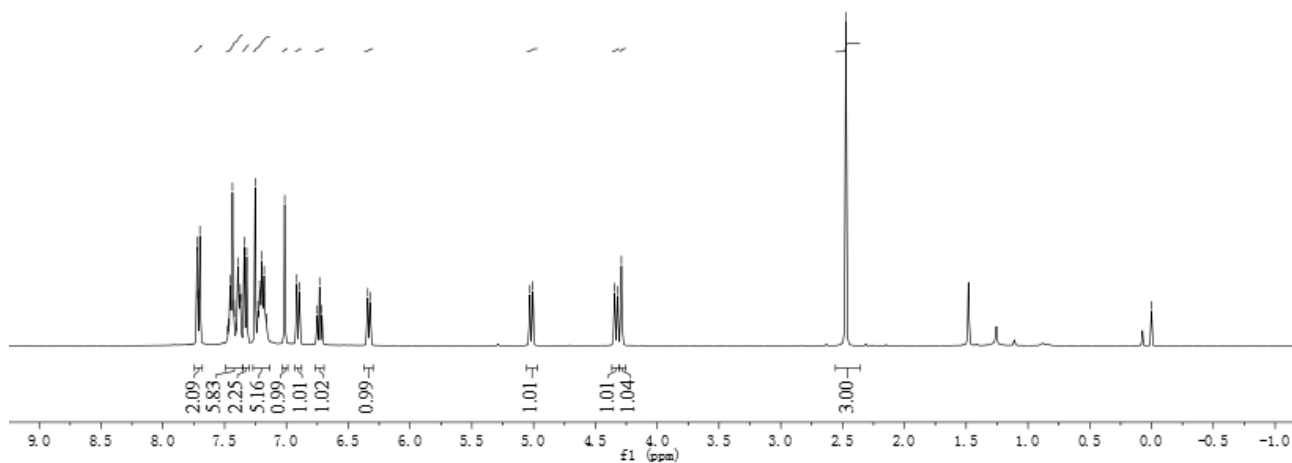
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.246	BV	0.1207	8970.96387	1160.74243	98.7608
2	5.760	VBA	0.1605	112.56356	9.99910	1.2392

7.721  
7.717  
7.706  
7.701  
7.477  
7.469  
7.464  
7.454  
7.437  
7.424  
7.421  
7.409  
7.394  
7.388  
7.374  
7.370  
7.342  
7.322  
7.253  
7.231  
7.217  
7.211  
7.199  
7.180  
7.163  
7.014  
6.916  
6.896  
6.751  
6.732  
6.713  
6.342  
6.324  
5.030  
5.006  
4.344  
4.320  
4.289  
-2.473

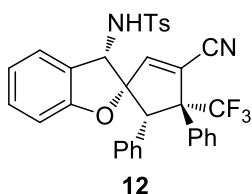
-0.000



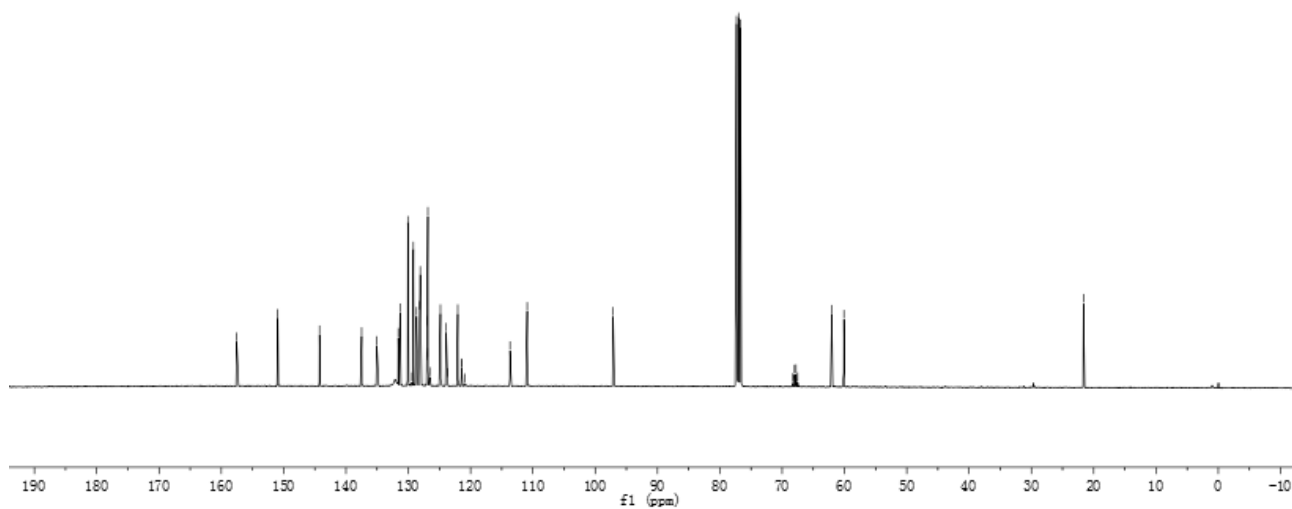
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

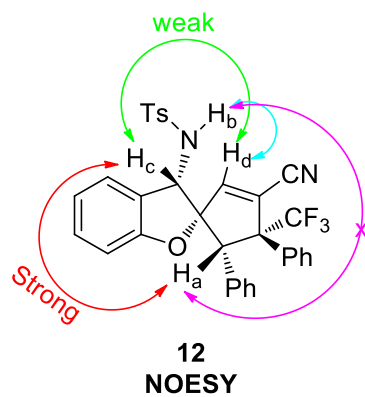
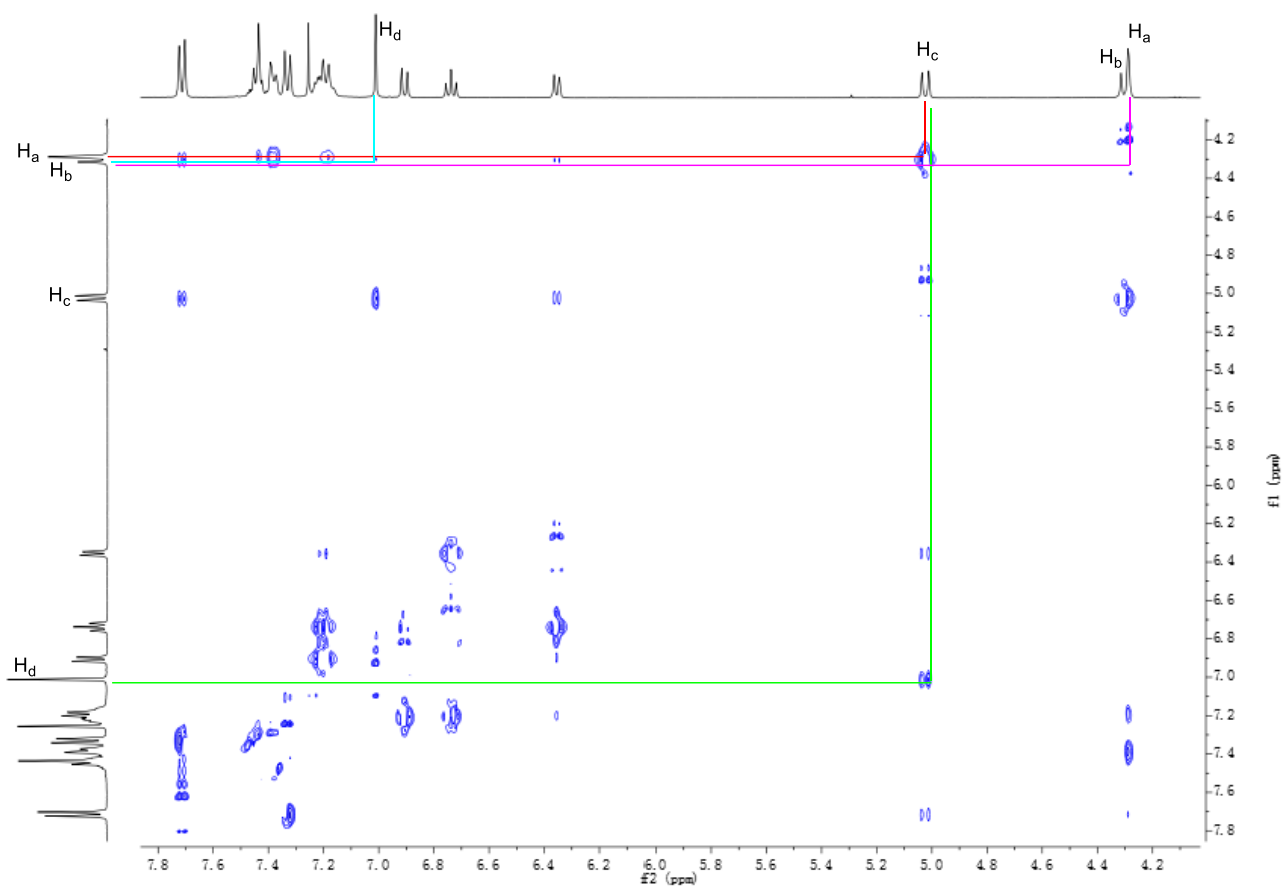


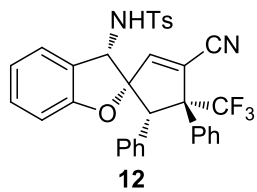
157.536  
150.935  
144.245  
137.480  
135.042  
131.607  
131.331  
130.070  
129.176  
128.674  
128.166  
128.077  
126.986  
126.960  
126.936  
126.909  
126.853  
124.836  
123.910  
122.056  
121.420  
119.402  
119.315  
-97.119  
77.317  
77.000  
76.682  
68.270  
68.017  
67.764  
67.510  
62.026  
60.092  
-21.635



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

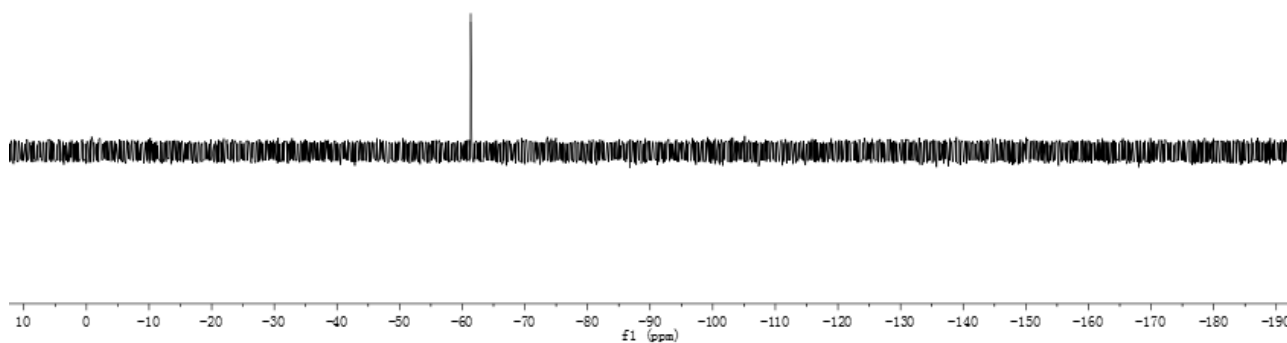




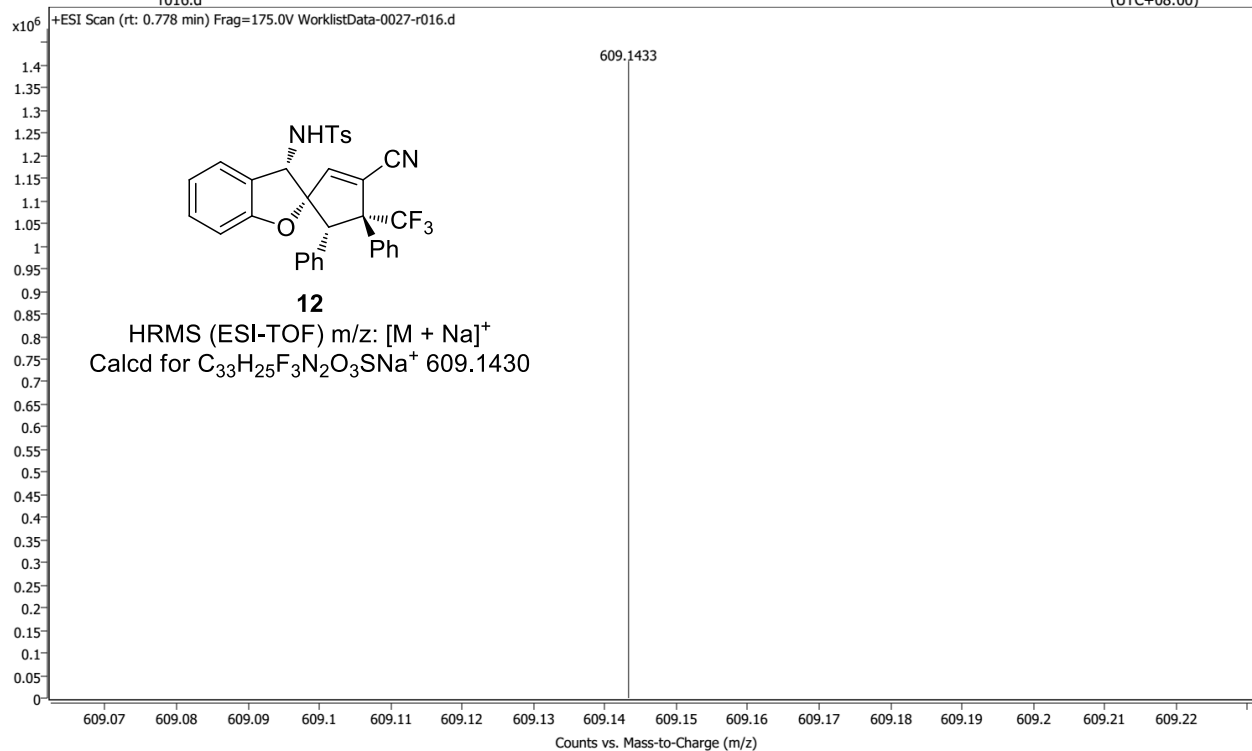


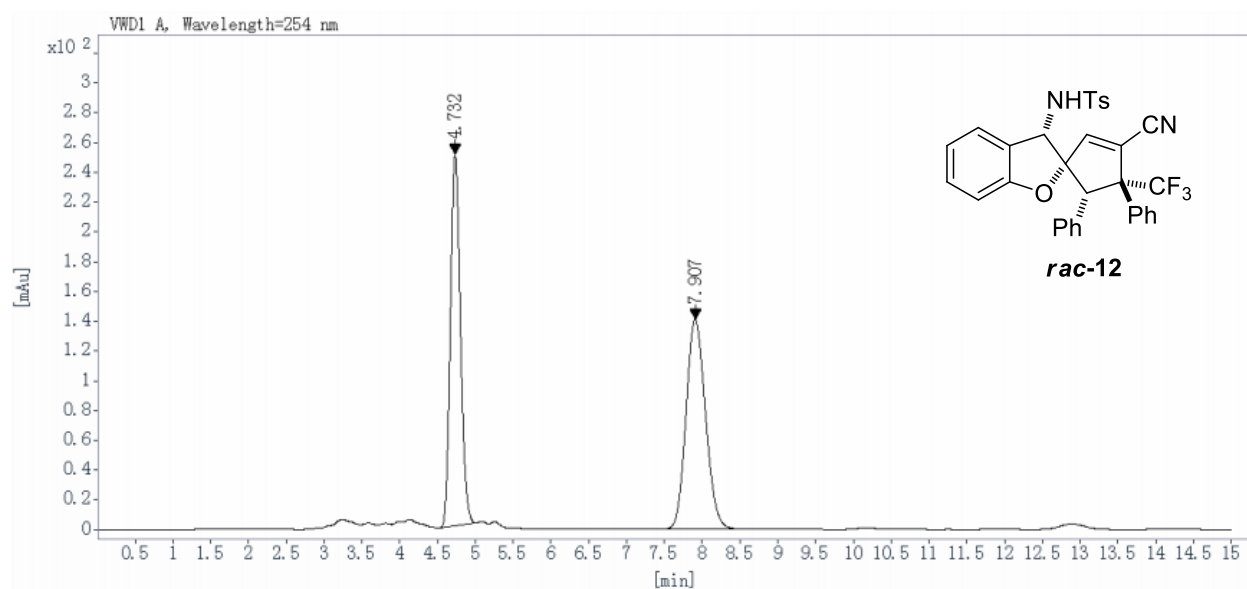
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )

---61.352

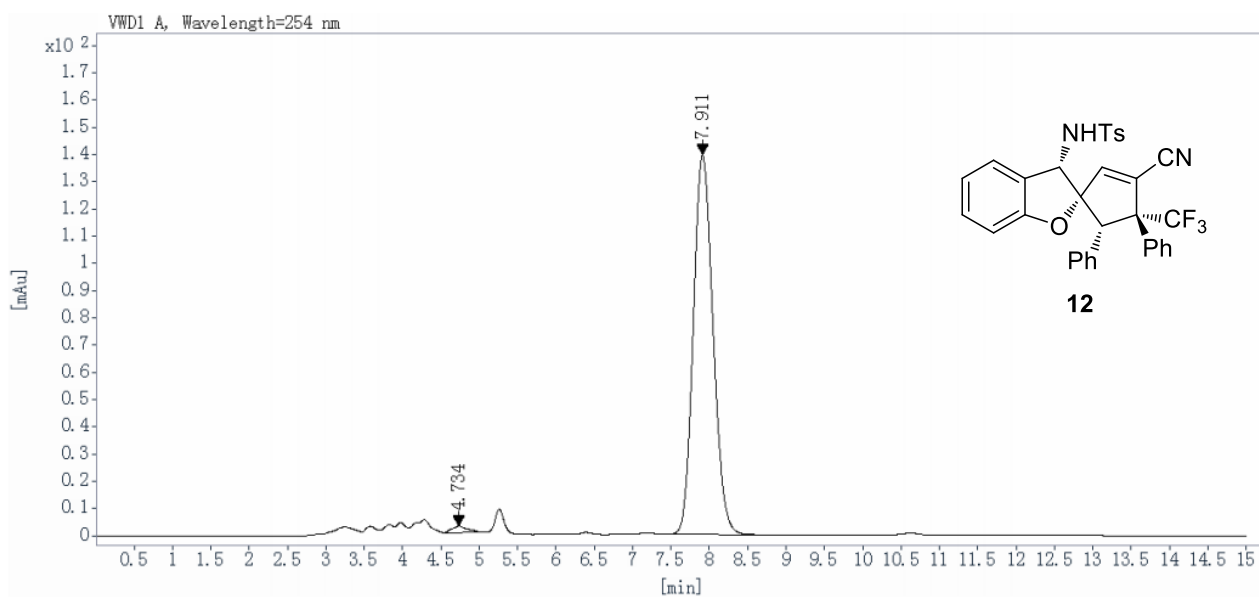


Name	cyc-190705-27	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	10	Plate Pos.	IRM Status	Success	
Data File	WorklistData-0027-r016.d	Method (Acq)	TOF.m		Acq. Time (Local)
					7/9/2019 2:47:35 PM (UTC+08:00)





Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
4.732	BB	0.14	249.4912	2289.0042	47.5280
7.907	BB	0.28	141.1504	2527.1145	52.4720



Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
4.734	BBA	0.19	2.3648	32.6403	1.2952
7.911	BB	0.28	139.5174	2487.4663	98.7048