

## Supporting Information

# Copper Catalyzed Cross-coupling of Vinyl Nitrenes and CF<sub>3</sub>-Carbenes to Synthesis of CF<sub>3</sub>-2-Azadienes

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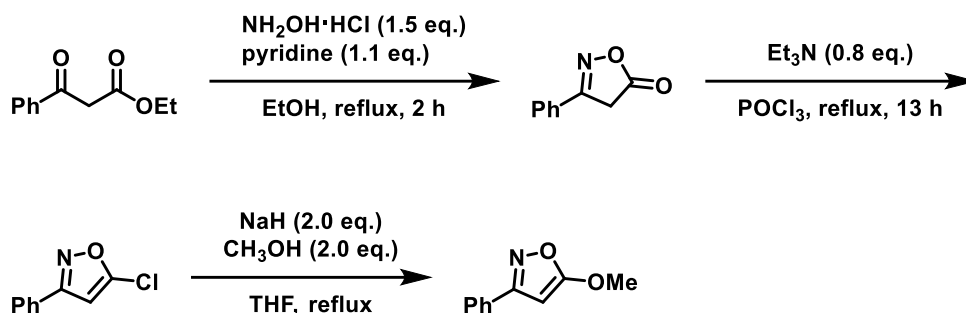
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## 1. General methods:

All reactions were carried out in flame or oven-dried glassware under argon atmosphere with freshly distilled dry solvents under anhydrous conditions unless otherwise indicated. Flash column chromatography was performed with silica gel (200 - 300 mesh). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining with base solution of potassium permanganate and molybdate. NMR spectra were recorded at room temperature on 400 MHz Bruker spectrometers and 400 MHz JEOL spectrometers. The residual solvent signals were taken as the reference (0.00 ppm for  $^1\text{H}$  NMR spectra and 77.0 ppm for  $^{13}\text{C}$  NMR spectra in  $\text{CDCl}_3$ ). Chemical shift ( $\delta$ ) is reported in ppm, coupling constants ( $J$ ) are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet. HRMS (ESI) spectra were recorded on a Waters Q-Tof premier TM mass spectrometer.

## 2. General procedure and spectral data:

### 2.1 General procedure for isoxazoles and their spectral data<sup>1</sup>:



To a 100 mL round-flask with the ethyl benzoylacetate (10 mmol, 1.0 equiv.) were added EtOH (50 mL),  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (15 mmol, 1.5 equiv.) and pyridine (11 mmol, 1.1 equiv.). Then the mixture was heated to reflux for 2 h. After cooling to room temperature, filtration with diatomite and wash with cooled MeOH gave the crude 3-phenylisoxazol-5-(4*H*)-one. The crude product was used in next step without further purification.

To a flame-dried 100 mL round-bottle flask was added isoxazol-5-(4*H*)-one (10 mmol, 1.0 equiv.) and  $\text{POCl}_3$  (9 mL) in an ice bath, then  $\text{Et}_3\text{N}$  (8.0 mmol, 0.8 equiv.) was dropwisely added, and the reaction mixture was heated to reflux until complete conversion monitored by TLC. After cooling to room temperature, the mixture was poured to cold saturated  $\text{NaHCO}_3$  aq. The solution was extracted with AcOEt and the combined organic layer was dried over  $\text{Na}_2\text{SO}_4$ . Concentration under reduced pressure after filtration gave almost pure 5-chloro-3-phenylisoxazole (1.26 g, 7.0 mmol, 70%).

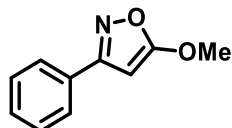
To a flame-dried 100 mL two-necked round-bottle flask were added 5-chloro-3-phenylisoxazole (7.0 mmol, 1.0 mmol) and 20 mL THF in an ice bath, NaH (14 mmol, 2.0 equiv.) in THF were added slowly, then MeOH (14 mmol, 2.0 equiv.) was dropwisely added. the reaction mixture was heated to reflux until complete conversion monitored by TLC. After cooling to room temperature, the mixture was poured to cold saturated  $\text{H}_2\text{O}$ . The solution was extracted with AcOEt and the combined organic layer was dried over  $\text{Na}_2\text{SO}_4$ . Concentration under reduced pressure and chromatograph on silica gel (PE/AcOEt = 20/1) gave 5-methoxy-3-phenylisoxazole as a white solid (0.96

<sup>1</sup>Okamoto, K.; Nanya, A.; Eguchi, A.; Ohe, K. *Angew. Chem., Int. Ed.*, **2018**, 57, 1039–1043.

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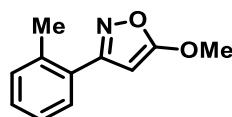
g, 5.5 mmol, 78%).

**5-Methoxy-3-phenylisoxazole (1a):**



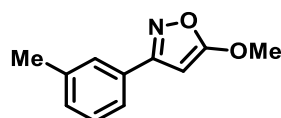
The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.6). The product was obtained as white solid in 78% yield (960 mg), Mp. 66 – 67 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 – 7.73 (m, 2H), 7.43 – 7.42 (m, 3H), 5.52 (s, 1H), 4.01 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.4, 164.1, 130.0, 129.4, 128.7, 126.3, 75.2, 58.8; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{10}\text{H}_{10}\text{NO}_2$ : 176.0706. Found: 176.0700.

**5-Methoxy-3-(*o*-tolyl)isoxazole (1b):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.5). The product was obtained as yellow liquid in 73% yield (294.0 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 – 7.46 (m, 1H), 7.35 – 7.31 (m, 1H), 7.29 – 7.24 (m, 2H), 5.39 (s, 1H), 4.04 (s, 3H), 2.48 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.8, 165.1, 136.7, 130.9, 129.4, 129.3, 129.2, 125.9, 78.1, 58.7, 20.9; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{11}\text{H}_{12}\text{NO}_2$ : 190.0863. Found: 190.0860.

**5-Methoxy-3-(*m*-tolyl)isoxazole (1c):**

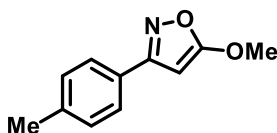


The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.5). The product was obtained as yellow liquid in 70% yield (540.0 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 – 7.59 (m, 1H), 7.54 – 7.53 (m, 1H), 7.35 – 7.31 (m, 1H),

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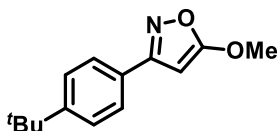
7.26 – 7.24 (m, 1H), 5.52 (s, 1H), 4.04 (s, 3H), 2.40 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.4, 164.3, 138.5, 130.8, 129.3, 128.7, 127.0, 123.6, 75.4, 58.8, 21.3; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{11}\text{H}_{12}\text{NO}_2$ : 190.0863. Found: 190.0870.

**5-Methoxy-3-(*p*-tolyl)isoxazole (1d):**



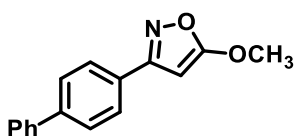
The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.5). The product was obtained as white solid in 68% yield (130.0 mg), Mp. 64 – 65 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 – 7.63 (m, 2H), 7.26 – 7.24 (m, 2H), 5.50 (s, 1H), 4.04 (s, 3H), 2.39 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 164.2, 140.2, 129.5, 126.7, 126.3, 75.3, 58.8, 21.4; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{11}\text{H}_{12}\text{NO}_2$ : 190.0863. Found: 190.0868.

**3-(4-(*Tert*-butyl)phenyl)-5-methoxyisoxazole (1e):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.5). The product was obtained as white solid in 86% yield (696.8 mg), Mp. 56 – 57 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 – 7.66 (m, 2H), 7.48 – 7.44 (m, 2H), 5.51 (s, 1H), 4.04 (s, 3H), 1.34 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 164.1, 153.3, 126.6, 126.2, 125.7, 75.2, 58.8, 34.8, 31.2; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{14}\text{H}_{18}\text{NO}_2$ : 232.1332. Found: 232.1338.

**3-([1,1'-Biphenyl]-4-yl)-5-methoxyisoxazole (1f):**

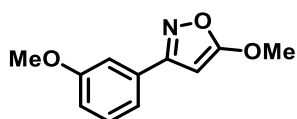


The title compound was prepared according to the general procedure (EA/PE = 1/20,

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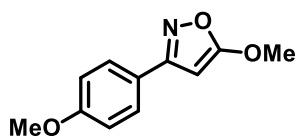
$R_f = 0.5$ ). The product was obtained as yellow solid in 76% yield (456.0 mg), Mp. 143 – 144 °C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 – 7.82 (m, 2H), 7.69 – 7.66 (m, 2H), 7.65 – 7.62 (m, 2H), 7.49 – 7.44 (m, 2H), 7.40 – 7.36 (m, 1H), 5.57 (s, 1H), 4.07 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.5, 163.9, 142.8, 140.2, 128.9, 128.4, 127.7, 127.4, 127.0, 126.8, 75.4, 58.8; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{16}\text{H}_{14}\text{NO}_2$ : 252.1019. Found: 252.1022.

**5-Methoxy-3-(3-methoxyphenyl)isoxazole (1g):**



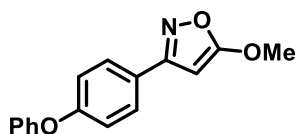
The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as yellow liquid in 72% yield (183.5 mg).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 – 7.28 (m, 3H), 7.0 – 6.97 (m, 1H), 5.52 (s, 1H), 4.04 (s, 3H), 3.85 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.4, 164.1, 159.8, 130.8, 129.8, 119.0, 116.2, 111.2, 75.5, 58.8, 55.4; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{11}\text{H}_{12}\text{NO}_3$ : 206.0812. Found: 206.0806.

**5-Methoxy-3-(4-methoxyphenyl)isoxazole (1h):**



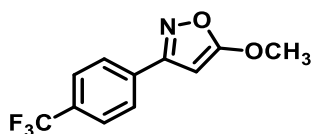
The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as white solid in 86% yield (560 mg), Mp. 83 – 84 °C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 – 7.67 (m, 2H), 6.97 – 6.94 (m, 2H), 5.47 (s, 1H), 4.03 (s, 3H), 3.85 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 163.8, 161.0, 127.8, 122.0, 114.1, 75.1, 58.8, 55.3; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{11}\text{H}_{12}\text{NO}_3$ : 206.0812. Found: 206.0809.

**5-Methoxy-3-(4-phenoxyphenyl)isoxazole (1i):**



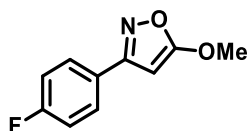
The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as white solid in 83% yield (460.5 mg), Mp. 79 – 80 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 – 7.70 (m, 2H), 7.40 – 7.35 (m, 2H), 7.18 – 7.14 (m, 1H), 7.04 – 7.03 (m, 4H), 5.49 (s, 1H), 4.04 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.4, 163.6, 159.1, 156.3, 129.9, 128.0, 124.2, 123.9, 119.5, 118.5, 75.2, 58.8; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{16}\text{H}_{14}\text{NO}_3$ : 268.0968. Found: 268.0965.

### 5-Methoxy-3-(4-(trifluoromethyl)phenyl)isoxazole (1j):



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as white solid in 64% yield (435.5 mg), Mp. 102 – 103 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 – 7.83 (m, 2H), 7.68 – 7.66 (m, 2H), 5.56 (s, 1H), 4.04 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.8, 162.9, 132.9, 131.7 (q,  $J = 32.6$  Hz), 126.7, 125.7 (q,  $J = 39.0$  Hz), 123.8 (q,  $J = 270.9$  Hz), 75.4, 58.9;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.78; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{11}\text{H}_9\text{F}_3\text{NO}_2$ : 244.0580. Found: 244.0573.

### 3-(4-Fluorophenyl)-5-methoxyisoxazole (1k):

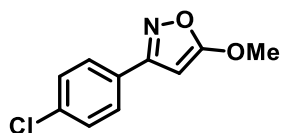


The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as white solid in 76% yield (768.8 mg), Mp. 79 – 80 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 – 7.70 (m, 2H), 7.15 – 7.09 (m, 2H), 5.49 (s, 1H), 4.04 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.5, 163.8 (d,  $J = 247.8$  Hz) 163.3, 128.3 (d,  $J = 8.5$  Hz), 125.7 (d,  $J = 3.3$  Hz), 115.9 (d,  $J = 21.6$  Hz), 75.3, 58.8;  $^{19}\text{F}$  NMR

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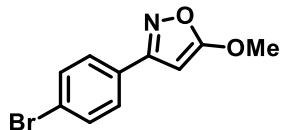
(376 MHz, CDCl<sub>3</sub>)  $\delta$  -110.41; HRMS (ESI)  $m/z$  [M+H]<sup>+</sup>: Calcd for C<sub>10</sub>H<sub>9</sub>FNO<sub>2</sub>: 194.0612. Found: 194.0605.

**3-(4-Chlorophenyl)-5-methoxyisoxazole (1l):**



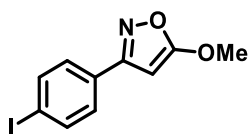
The title compound was prepared according to the general procedure (EA/PE = 1/20, R<sub>f</sub> = 0.5). The product was obtained as white solid in 68% yield (810.0 mg), Mp. 66 – 67 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.71 – 7.67 (m, 2H), 7.44 – 7.40 (m, 2H), 5.51 (s, 1H), 4.05 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  174.6, 163.2, 136.0, 129.1, 128.0, 127.7, 75.3, 58.9; HRMS (ESI)  $m/z$  [M+H]<sup>+</sup>: Calcd for C<sub>10</sub>H<sub>9</sub>ClNO<sub>2</sub>: 210.0316. Found: 210.0313.

**3-(4-Bromophenyl)-5-methoxyisoxazole (1m):**



The title compound was prepared according to the general procedure (EA/PE = 1/20, R<sub>f</sub> = 0.5). The product was obtained as white solid in 78% yield (869.6 mg), Mp. 114 – 115 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 – 7.60 (m, 2H), 7.58 – 7.55 (m, 2H), 5.50 (s, 1H), 4.05 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  174.6, 163.3, 132.0, 128.4, 127.9, 124.3, 75.3, 58.9; HRMS (ESI)  $m/z$  [M+H]<sup>+</sup>: Calcd for C<sub>10</sub>H<sub>9</sub>BrNO<sub>2</sub>: 253.9811. Found: 253.9807.

**3-(4-Iodophenyl)-5-methoxyisoxazole (1n):**



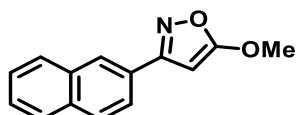
The title compound was prepared according to the general procedure (EA/PE = 1/20, R<sub>f</sub> = 0.5). The product was obtained as yellow solid in 88% yield (929.0 mg), Mp. 123



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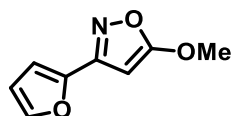
– 124 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 – 7.77 (m, 2H), 7.50 – 7.47 (m, 2H), 5.51 (s, 1H), 4.05 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.6, 163.4, 138.0, 129.0, 128.0, 96.2, 75.2, 58.9; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{10}\text{H}_9\text{INO}_2$ : 301.9672. Found: 301.9676.

**5-Methoxy-3-(naphthalen-2-yl)isoxazole (1o):**



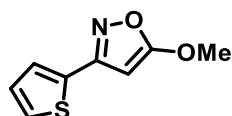
The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.5). The product was obtained as yellow liquid in 58% yield (196.8 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.44 – 8.39 (m, 1H), 7.95 – 7.89 (m, 2H), 7.69 – 7.67 (m, 1H), 7.56 – 7.51 (m, 3H), 5.55 (s, 1H), 4.07 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.9, 164.6, 133.7, 130.8, 130.1, 128.4, 127.5, 127.3, 126.9, 126.2, 125.5, 125.1, 78.8, 58.8; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{14}\text{H}_{12}\text{NO}_2$ : 226.0863. Found: 226.0867.

**3-(Furan-2-yl)-5-methoxyisoxazole (1p):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.5). The product was obtained as white solid in 50% yield (98.8 mg), Mp. 56 – 57 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 – 7.52 (m, 1H), 6.86 – 6.85 (m, 1H), 6.51 – 6.50 (m, 1H), 5.49 (s, 1H), 4.03 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.2, 156.5, 144.5, 143.7, 111.6, 109.9, 75.0, 58.9; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_8\text{H}_8\text{NO}_3$ : 166.0499. Found: 166.0495.

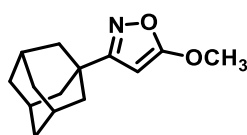
**5-Methoxy-3-(thiophen-2-yl)isoxazole (1q):**



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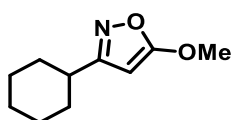
The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as yellow solid in 64% yield (260.0 mg), Mp. 57 – 58 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.39 (m, 2H), 7.11 – 7.09 (m, 1H), 5.47 (s, 1H), 4.03 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 159.4, 131.3, 127.5, 127.4, 127.2, 75.6, 58.9; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_8\text{H}_8\text{NO}_2\text{S}$ : 182.0270. Found: 180.0267.

### 3-(Adamantan-1-yl)-5-methoxyisoxazole (1r):



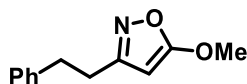
The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as white solid in 52% yield (415.5 mg), Mp. 76 – 77 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.06 (s, 1H), 3.90 (s, 3H), 2.03 – 2.00 (m, 3H), 1.88 – 1.87 (m, 6H), 1.76 – 1.68 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.1, 173.7, 74.0, 58.4, 41.0, 36.4, 34.4, 28.0; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{14}\text{H}_{20}\text{NO}_2$ : 234.1489. Found: 234.1484.

### 3-Cyclohexyl-5-methoxyisoxazole (1s):



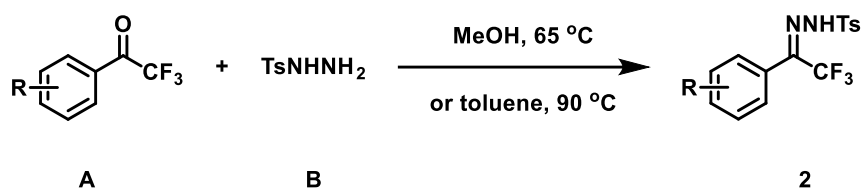
The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.6$ ). The product was obtained as yellow liquid in 64% yield (362.2 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.05 (s, 1H), 3.94 (s, 3H), 2.62 – 2.58 (m, 1H), 1.95 – 1.92 (m, 2H), 1.81 – 1.69 (m, 3H), 1.42 – 1.22 (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.8, 170.8, 75.2, 58.5, 36.7, 31.8, 25.9, 25.8; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{10}\text{H}_{16}\text{NO}_2$ : 182.1176. Found: 182.1172.

### 5-Methoxy-3-phenethylisoxazole (1t):



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.4). The product was obtained as yellow liquid in 36% yield (312.5 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 – 7.28 (m, 2H), 7.24 – 7.20 (m, 3H), 5.0 (s, 1H), 3.94 (s, 3H), 2.99 – 2.94 (m, 2H), 2.90 – 2.86 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.0, 165.7, 140.6, 128.5, 128.3, 126.3, 76.9, 34.1, 28.8; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{12}\text{H}_{14}\text{NO}_2$ : 204.1019. Found: 204.1015.

## 2.2 General procedure for hydrazones and their spectral data<sup>2</sup> :

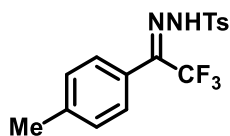


To a round bottom flask surmounted with a reflux condenser was added N-tosylhydrazide B (5.0 mmol, 1.0 equiv.) and the minimum quantity of solvent (either methanol or toluene according to individual substrates) needed to dissolve the hydrazide at reflux (approximately 1.5 M). Subsequently the reaction was cooled to room temperature and trifluoroacetophenone A (5.0 mmol, 1.0 equiv.) was added in one portion. The reaction mixture was then stirred at 65 °C (MeOH) or 90 °C (Toluene) over 4-16 h (monitor by TLC). The solution was cooled down to 0 °C, at which point the product precipitated out of solution in most cases (precipitation can be induced by addition of pentane). The precipitate was collected by vacuum filtration and washed with pentane, in which case it was used without further purification. If no precipitation occurred, the solvent was removed under reduced pressure and the residue used in the next step without further purification.

### (Z)-4-Methyl-N'-(2,2,2-trifluoro-1-(p-tolyl)ethylidene)benzenesulfonohydrazide

<sup>2</sup>Liang, X.; Guo, P.; Yang, W.; Li, M.; Jiang, C.; Sun, W.; Loh, T.-P.; Jiang, Y. *Chem. Commun.* **2020**, *56*, 2043-2046.

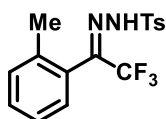
(2b):



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as white solid in 65% yield (1157.3 mg), Mp. 97-98 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (s, 1H), 7.83 – 7.79 (m, 2H), 7.36 – 7.31 (m, 4H), 7.14 – 7.12 (m, 2H), 2.46 (s, 3H), 2.41 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.9, 142.1, 141.8 (q,  $J = 35.6$  Hz), 134.6, 130.7, 129.8, 128.0, 122.1, 120.0 (q,  $J = 274.8$  Hz), 21.7, 21.5.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -68.37. HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$  : Calcd for  $\text{C}_{16}\text{H}_{16}\text{F}_3\text{N}_2\text{O}_2\text{S}$  : 357.0879. Found: 357.0874.

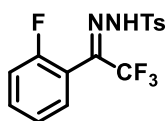
**(Z)-4-Methyl-N'-(2,2,2-trifluoro-1-(o-tolyl)ethylidene)benzenesulfonohydrazide**

(2c):



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as white solid in 52% yield (645 mg), Mp. 132 – 133 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 – 7.80 (m, 2H), 7.66 (s, 1H), 7.46 – 7.42 (m, 1H), 7.37 – 7.29 (m, 4H), 7.03 – 7.01 (m, 1H), 2.46 (s, 3H), 2.04 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.0, 137.1, 134.6, 131.6, 131.4, 129.9, 128.4, 127.9, 127.2, 124.8, 21.7, 18.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -68.88; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$  : Calcd for  $\text{C}_{16}\text{H}_{16}\text{F}_3\text{N}_2\text{O}_2\text{S}$  : 357.0879. Found: 357.0875.

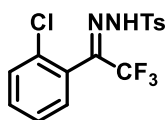
**(Z)-4-Methyl-N'-(2,2,2-trifluoro-1-(2-fluorophenyl)ethylidene)benzenesulfonohydrazide (2h):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as yellow solid in 52% yield (645 mg), Mp. 135 –

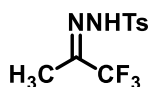
136 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92 (s, 1H), 7.83 – 7.79 (m, 2H), 7.60 – 7.54 (m, 1H), 7.37 – 7.29 (m, 3H), 7.24 – 7.20 (m, 2H), 2.46 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.1 (d, *J* = 250.8 Hz), 145.0, 134.4, 134.0 (d, *J* = 8.1 Hz), 130.0 (d, *J* = 2.6 Hz), 129.9, 128.0, 125.7 (d, *J* = 3.5 Hz), 118.4, 117.0 (d, *J* = 20.6 Hz), 113.1 (d, *J* = 17.0 Hz), 21.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ –68.38, –110.71; HRMS (ESI) *m/z* [M+H]<sup>+</sup> : Calcd for C<sub>15</sub>H<sub>13</sub>F<sub>4</sub>N<sub>2</sub>O<sub>2</sub>S : 361.0634. Found: 361.0623.

**(Z)-4-Methyl-N'-(1-(2-chlorophenyl)-2,2,2-trifluoroethylidene)benzenesulfonohydrazide (2j):**



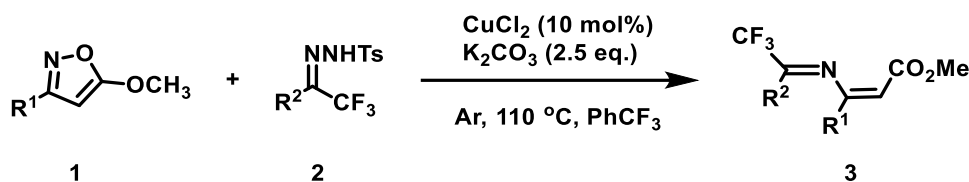
The title compound was prepared according to the general procedure (EA/PE = 1/20, R<sub>f</sub> = 0.5). The product was obtained as yellow solid in 54% yield (735 mg), Mp. 135 – 136 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.85 – 7.82 (m, 2H), 7.71 (s, 1H), 7.52 – 7.51 (m, 2H), 7.45 – 7.41 (m, 1H), 7.36 – 7.34 (m, 2H), 7.22 (d, *J* = 7.6 Hz, 1H), 2.46 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 145.0, 136.5, 134.4, 133.0, 130.6, 130.4, 129.8, 128.2, 128.0, 124.7, 21.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ –68.56; HRMS (ESI) *m/z* [M+H]<sup>+</sup> : Calcd for C<sub>15</sub>H<sub>13</sub>ClF<sub>3</sub>N<sub>2</sub>O<sub>2</sub>S : 377.0338. Found: 377.0327.

**(Z)-4-Methyl-N'-(1,1,1-trifluoropropan-2-ylidene)benzenesulfonohydrazide (2n):**



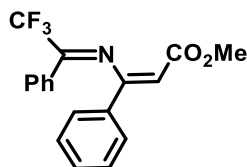
The title compound was prepared according to the general procedure (EA/PE = 1/20, R<sub>f</sub> = 0.5). The product was obtained as white solid in 45% yield (535 mg), Mp. 105 – 106 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.33 (s, 1H), 7.89 – 7.86 (m, 2H), 7.39 – 7.37 (m, 2H), 2.48 (s, 3H), 1.96 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 145.0, 134.4, 129.8, 128.1, 21.6, 10.5; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ –71.78; HRMS (ESI) *m/z* [M+H]<sup>+</sup> : Calcd for C<sub>10</sub>H<sub>12</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>S : 281.0566. Found: 281.0562.

### 2.3 General procedure for 2-azadienes and their spectral data:



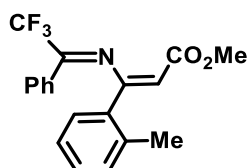
A mixture of **1** (0.2 mmol, 1.0 equiv.), **2** (0.4 mmol, 2.0 equiv.),  $\text{CuCl}_2$  (0.02 mmol, 10 mol%),  $\text{K}_2\text{CO}_3$  (0.5 mmol, 2.5 equiv.) and  $\text{PhCF}_3$  (2 mL) was sealed in a Schlenk tube under Argon protection at 110 °C and the mixture was stirred for 20 h or until **1** was consumed completely. Then the reaction mixture was filtered by diatomite and concentrated under reduced pressure and purified by column chromatography (EA/PE = 1:20) to give the desired product **3**.

#### Methyl (Z)-3-phenyl-3-(((E)-2,2,2-trifluoro-1-phenylethylidene)amino)acrylate (3aa):



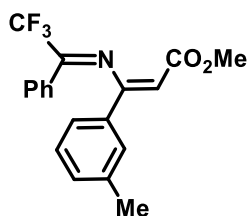
The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.5). The product was obtained as yellow solid in 82% yield (54.8 mg), Mp. 48 – 49 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.49 (m, 2H), 7.44 – 7.38 (m, 4H), 7.33 – 7.31 (m, 4H), 5.52 (s, 1H), 3.65 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 157.9, 135.6, 131.0, 130.6, 130.2, 129.0, 128.2, 127.5, 126.2, 119.2 (q,  $J$  = 279.6Hz), 96.9, 51.2;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  –68.78; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{18}\text{H}_{15}\text{F}_3\text{NO}_2$ : 334.1049. Found: 334.1043.

#### Methyl (Z)-3-(o-tolyl)-3-(((E)-2,2,2-trifluoro-1-phenylethylidene)amino)acrylate (3ba):



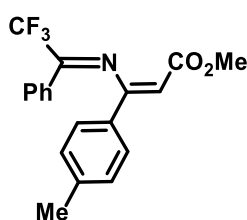
The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as yellow liquid in 65% yield (45.2 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 – 7.42 (m, 1H), 7.37 – 7.33 (m, 2H), 7.24 – 7.22 (m, 3H), 7.18 – 7.16 (m, 1H), 7.11 – 7.07 (m, 1H), 6.99 – 6.97 (m, 1H), 5.18 (s, 1H), 3.72 (s, 3H), 2.30 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 159.5, 136.8, 135.8, 131.0, 130.8, 129.3, 128.3, 127.5, 125.8, 119.2 (d,  $J = 278.7$  Hz), 101.6, 51.3, 20.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -69.67; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{19}\text{H}_{17}\text{F}_3\text{NO}_2$ : 348.1206. Found: 348.1203.

**Methyl (Z)-3-(*m*-tolyl)-3-(((*E*)-2,2,2-trifluoro-1-phenylethylidene)amino)acrylate (3ca):**



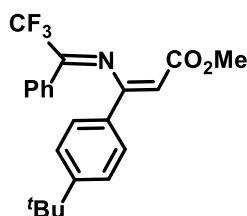
The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as yellow solid in 78% yield (54.3 mg), Mp. 66 – 67 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.40 (m, 1H), 7.33 – 7.32 (m, 5H), 7.30 – 7.29 (m, 2H), 7.27 – 7.24 (m, 1H), 5.50 (s, 1H), 3.64 (s, 3H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 158.1, 138.7, 135.6, 131.4, 131.0, 130.2, 128.9, 128.2, 127.5, 126.7, 123.4, 119.2 (d,  $J = 279.3$  Hz), 96.6, 51.2, 21.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -68.74; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{19}\text{H}_{17}\text{F}_3\text{NO}_2$ : 348.1206. Found: 348.1198.

**Methyl (Z)-3-(*p*-tolyl)-3-(((*E*)-2,2,2-trifluoro-1-phenylethylidene)amino)acrylate (3da):**



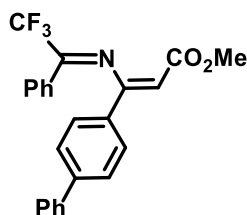
The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as yellow solid in 63% yield (43.8 mg), Mp. 73–74 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 7.38 (m, 3H), 7.34 – 7.29 (m, 4H), 7.22 – 7.18 (m, 2H), 5.49 (s, 1H), 3.65 (s, 3H), 2.39 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 157.9, 141.1, 132.7, 130.9, 130.2, 129.7, 128.2, 127.5, 126.1, 119.2 (q,  $J = 279.4$  Hz), 95.9, 51.1, 21.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  –68.79; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{19}\text{H}_{17}\text{F}_3\text{NO}_2$ : 348.1206. Found: 348.1201.

**Methyl (*Z*)-3-(4-(*tert*-butyl)phenyl)-3-(((*E*)-2,2,2-trifluoro-1-phenylethylidene)-amino)acrylate (3ea):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as yellow solid in 71% yield (55.4 mg), Mp. 97 – 98 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.40 (m, 5H), 7.36 – 7.30 (m, 4H), 5.49 (s, 1H), 3.64 (s, 3H), 1.35 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 157.9, 154.1, 132.5, 131.0, 130.2, 128.2, 127.6, 126.0, 119.2 (q,  $J = 279.6$  Hz), 95.9, 51.1, 34.8, 31.1;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  –68.63; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{22}\text{H}_{22}\text{F}_3\text{NO}_2$ : 390.1675. Found: 390.1670.

**Methyl (*Z*)-3-([1,1'-biphenyl]-4-yl)-3-(((*E*)-2,2,2-trifluoro-1-phenylethylidene)-amino)acrylate (3fa):**

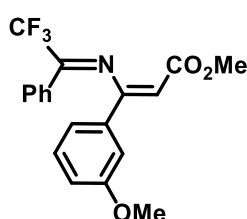


The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as yellow solid in 54% yield (49.7 mg).  $^1\text{H}$  NMR



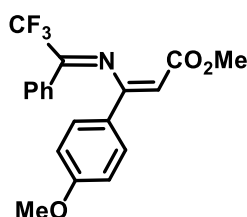
(400 MHz, CDCl<sub>3</sub>)  $\delta$  7.68 – 7.59 (m, 6H), 7.52 – 7.34 (m, 8H), 5.59 (s, 1H), 3.69 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.6, 157.5, 143.4, 139.8, 134.3, 131.0, 130.3, 128.9, 128.3, 128.0, 127.6, 127.5, 127.0, 126.6, 96.6, 51.2; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  –68.66; HRMS (ESI) m/z [M+H]<sup>+</sup>: Calcd for C<sub>24</sub>H<sub>19</sub>F<sub>3</sub>NO<sub>2</sub>: 410.1362. Found: 410.1357.

**Methyl (Z)-3-(3-methoxyphenyl)-3-(((E)-2,2,2-trifluoro-1-phenylethylidene)-amino)acrylate (3ga):**



The title compound was prepared according to the general procedure (EA/PE = 1/20, R<sub>f</sub> = 0.5). The product was obtained as yellow liquid in 79% yield (57.5 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 – 7.40 (m, 1H), 7.33 – 7.29 (m, 5H), 7.11 – 7.08 (m, 1H), 7.03 – 7.02 (m, 1H), 6.99 – 6.96 (m, 1H), 5.50 (s, 1H), 3.82 (s, 3H), 3.65 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.5, 159.8, 157.8, 137.1, 131.0, 130.2, 130.0, 128.3, 127.5, 119.2 (q, *J* = 279.0 Hz), 118.6, 116.2, 111.7, 97.1, 55.3, 51.2; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  –68.78; HRMS (ESI) m/z [M+H]<sup>+</sup>: Calcd for C<sub>19</sub>H<sub>17</sub>F<sub>3</sub>NO<sub>3</sub>: 364.1155. Found: 364.1147.

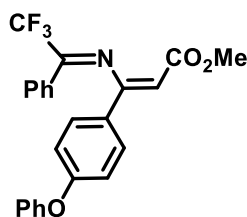
**Methyl (Z)-3-(4-methoxyphenyl)-3-(((E)-2,2,2-trifluoro-1-phenylethylidene)-amino)acrylate (3ha):**



The title compound was prepared according to the general procedure (EA/PE = 1/20, R<sub>f</sub> = 0.5). The product was obtained as yellow solid in 81% yield (58.6 mg), Mp. 68 – 69 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.47 – 7.39 (m, 3H), 7.33 – 7.29 (m, 4H), 6.93 –

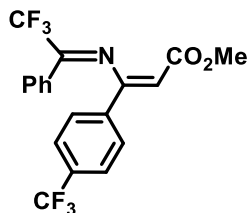
6.89 (m, 2H), 5.45 (s, 1H), 3.84 (s, 3H), 3.64 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.8, 161.5, 157.5, 130.9, 130.2, 128.2, 127.7, 127.4, 119.2 (q,  $J = 279.5$  Hz), 114.3, 95.0, 55.4, 51.1;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -68.88; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{19}\text{H}_{17}\text{F}_3\text{NO}_3$ : 364.1155. Found: 364.1152.

**Methyl (Z)-3-(4-phenoxyphenyl)-3-(((E)-2,2,2-trifluoro-1-phenylethylidene)-amino)acrylate (3ia):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as yellow liquid in 53% yield (45.2 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 – 7.37 (m, 5H), 7.34 – 7.33 (m, 4H), 7.21 – 7.17 (m, 1H), 7.08 – 7.05 (m, 2H), 7.00 – 6.97 (m, 2H), 5.45 (s, 1H), 3.64 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 159.8, 157.3, 155.7, 131.0, 130.2, 130.0, 129.7, 128.3, 127.8, 127.5, 124.3, 119.9, 118.2, 95.8, 51.2;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -68.74; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{24}\text{H}_{19}\text{F}_3\text{NO}_3$ : 426.1312. Found: 426.1308.

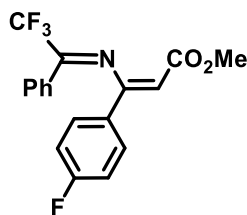
**Methyl (Z)-3-(((E)-2,2,2-trifluoro-1-phenylethylidene)amino)-3-(4-(trifluoromethyl)phenyl)acrylate (3ja):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as yellow solid in 55% yield (44.2 mg), Mp. 68 – 69 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 – 7.60 (m, 4H), 7.47 – 7.43 (m, 1H), 7.36 – 7.31 (m, 4H), 5.54 (s, 1H), 3.67 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.2, 156.4, 139.2, 132.2 (q,  $J = 32.5$  Hz), 131.3, 130.1, 128.4, 127.4, 126.6, 126.0 (q,  $J = 3.6$  Hz),

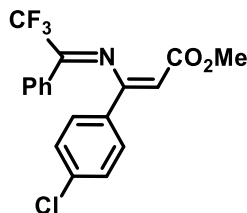
125.0, 121.4 (q,  $J = 179.5$  Hz), 117.7, 98.7, 51.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.79, -68.74; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{19}\text{H}_{14}\text{F}_6\text{NO}_2$ : 402.0923. Found: 402.0919.

**Methyl (Z)-3-(4-fluorophenyl)-3-(((E)-2,2,2-trifluoro-1-phenylethylidene)-amino)acrylate (3ka):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as yellow solid in 67% yield (47.2 mg), Mp. 100 – 101 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 – 7.41 (m, 3H), 7.35 – 7.29 (m, 4H), 7.12 – 7.06 (m, 2H), 5.45 (s, 1H), 3.65 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.5, 164.0 (d,  $J = 249.9$  Hz), 156.8, 136.5, 131.8, 130.2, 129.3, 128.3, 128.2 (d,  $J = 8.6$  Hz), 127.4, 119.2 (q,  $J = 279.2$  Hz), 116.1 (d,  $J = 21.6$  Hz), 96.9, 51.2;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -68.81, -109.03; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{18}\text{H}_{14}\text{F}_4\text{NO}_2$ : 352.0955. Found: 352.0951.

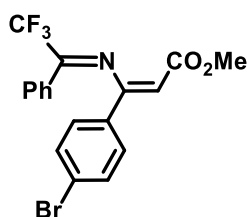
**Methyl (Z)-3-(4-chlorophenyl)-3-(((E)-2,2,2-trifluoro-1-phenylethylidene)-amino)acrylate (3la):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as yellow solid in 68% yield (50.0 mg), Mp. 87– 88 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.41 (m, 3H), 7.39 – 7.38 (m, 1H), 7.37 – 7.35 (m, 1H), 7.33 – 7.31 (m, 4H), 5.48 (s, 1H), 3.65 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3, 156.7, 136.7, 134.1, 131.1, 130.1, 129.3, 128.7, 128.3, 119.1 (q,  $J =$

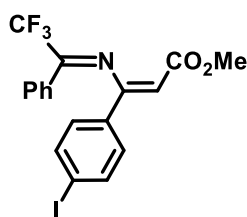
279.7 Hz), 97.3, 51.2;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -68.80; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{18}\text{H}_{14}\text{ClF}_3\text{NO}_2$ : 368.0660. Found: 368.0655.

**Methyl (Z)-3-(4-bromophenyl)-3-(((E)-2,2,2-trifluoro-1-phenylethylidene)-amino)acrylate (3ma):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.5). The product was obtained as yellow solid in 72% yield (59.3 mg), Mp. 97 – 98 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 – 7.52 (m, 2H), 7.45 – 7.41 (m, 1H), 7.38 – 7.29 (m, 6H), 5.49 (s, 1H), 3.65 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3, 156.7, 134.6, 132.2, 131.1, 130.1, 128.3, 127.6, 127.4, 125.0, 119.1 (q,  $J$  = 279.2 Hz), 97.3, 51.3;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -68.78; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{18}\text{H}_{14}\text{BrF}_3\text{NO}_2$ : 412.0155. Found: 412.0149.

**Methyl (Z)-3-(4-iodophenyl)-3-(((E)-2,2,2-trifluoro-1-phenylethylidene)-amino)acrylate (3na):**

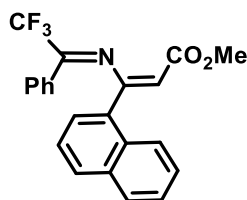


The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.5). The product was obtained as yellow solid in 54% yield (49.7 mg), Mp. 97 – 98 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 – 7.73 (m, 2H), 7.45 – 7.41 (m, 1H), 7.35 – 7.31 (m, 4H), 7.24 – 7.20 (m, 2H), 5.49 (s, 1H), 3.65 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.4, 156.9, 138.2, 135.2, 131.2, 130.1, 128.4, 127.7, 127.4, 119.1 (q,  $J$  = 279.2 Hz), 97.3, 97.1, 51.3;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -68.80; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{18}\text{H}_{14}\text{F}_3\text{INO}_2$ : 460.0016. Found: 460.0019.

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**Methyl (Z)-3-(naphthalen-2-yl)-3-(((E)-2,2,2-trifluoro-1-phenylethylidene)**

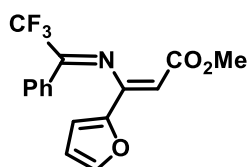
**-amino)acrylate (30a):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as yellow liquid in 73% yield (56.1 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.20 – 8.18 (m, 1H), 7.86 – 7.84 (m, 2H), 7.52 – 7.37 (m, 4H), 7.37 – 7.28 (m, 4H), 7.24 – 7.23 (m, 1H), 5.41 (s, 1H), 3.74 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 158.6, 136.5, 134.8, 133.7, 130.8, 130.6, 130.2, 129.8, 129.3, 128.4, 128.3, 127.6, 126.8, 126.3, 125.8, 124.9, 102.5, 51.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -69.57; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{22}\text{H}_{17}\text{F}_3\text{NO}_2$ : 384.1206. Found: 384.1199.

**Methyl (Z)-3-(furan-2-yl)-3-(((E)-2,2,2-trifluoro-1-phenylethylidene)**

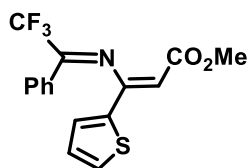
**-amino)acrylate (3pa):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as yellow solid in 75% yield (48.6 mg), Mp. 84 – 85 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 – 7.47 (m, 1H), 7.45 – 7.41 (m, 3H), 7.36 – 7.32 (m, 2H), 6.58 – 6.57 (m, 1H), 6.48 – 6.47 (m, 1H), 5.68 (s, 1H), 3.67 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.8, 147.6, 147.3, 145.0, 131.1, 130.0, 128.4, 127.5, 119.2 (q,  $J = 279.2$  Hz), 112.6, 112.2, 95.4, 51.3;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -69.72; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{16}\text{H}_{13}\text{F}_3\text{NO}_3$ : 324.0842. Found: 324.0848.

**Methyl (Z)-3-(thiophen-2-yl)-3-(((E)-2,2,2-trifluoro-1-phenylethylidene)**

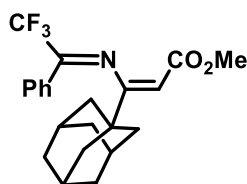
**-amino)acrylate (3qa):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.5). The product was obtained as yellow solid in 77% yield (52.4 mg), Mp. 86–87 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.39 (m, 4H), 7.36 – 7.32 (m, 2H), 7.29 – 7.27 (m, 1H), 7.08 – 7.06 (m, 1H), 5.54 (s, 1H), 3.65 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.5, 151.9, 138.0, 131.2, 130.0, 128.7, 128.3, 128.2, 127.5, 119.2 (q,  $J$  = 279.2 Hz), 95.8, 51.2;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  –68.98; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{16}\text{H}_{13}\text{F}_3\text{NO}_2\text{S}$ : 340.0614. Found: 340.0609.

**Methyl (Z)-3-(adamantan-1-yl)-3-(((E)-2,2,2-trifluoro-1-phenylethylidene)**

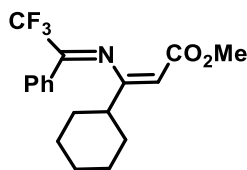
**-amino)acrylate (3ra):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.5). The product was obtained as yellow liquid in 54% yield (42.2 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 – 7.69 (m, 2H), 7.51 – 7.40 (m, 3H), 5.03 (s, 1H), 3.62 (s, 3H), 2.02 – 2.00 (m, 3H), 1.76 – 1.62 (m, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.9, 166.8, 150.2 (d,  $J$  = 32.0 Hz), 131.3, 131.2, 128.4, 128.4, 119.2 (q,  $J$  = 283.3 Hz), 92.5, 51.0, 40.7, 39.8, 36.4, 28.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  –66.07; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{22}\text{H}_{25}\text{F}_3\text{NO}_2$ : 392.1832. Found: 392.1827.

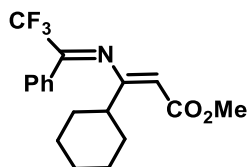
**Methyl (Z)-3-cyclohexyl-3-(((E)-2,2,2-trifluoro-1-phenylethylidene)**

**-amino)acrylate (3sa-Z):**



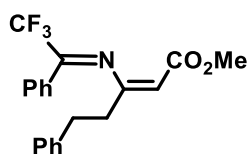
The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.6). The product was obtained as yellow liquid in 38% yield (42.2 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 – 7.53 (m, 2H), 7.50 – 7.45 (m, 1H), 7.44 – 7.39 (m, 2H), 4.99 (s, 1H), 3.64 (s, 3H), 1.98 – 1.93 (m, 1H), 1.78 – 1.74 (m, 4H), 1.67 – 1.64 (m, 1H), 1.28 – 1.16 (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.4, 166.1, 131.1, 130.9, 128.4, 127.9, 95.5, 51.0, 46.0, 31.6, 26.2, 25.8;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  –67.75; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{18}\text{H}_{21}\text{F}_3\text{NO}_2$ : 340.1519. Found: 340.1516.

**Methyl (*E*)-3-cyclohexyl-3-(((*E*)-2,2,2-trifluoro-1-phenylethylidene)-amino)acrylate (3sa-*E*):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.6). The product was obtained as yellow liquid in 24% yield (42.2 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 – 7.41 (m, 5H), 4.81 (s, 1H), 3.75 – 3.69 (m, 1H), 3.63 (s, 3H), 1.78 – 1.68 (m, 5H), 1.42 – 1.29 (m, 4H), 1.21 – 1.16 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.2, 166.6, 131.0, 129.8, 128.6, 128.3, 98.5, 51.0, 39.6, 30.8, 26.1, 25.8;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  –66.93; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{18}\text{H}_{21}\text{F}_3\text{NO}_2$ : 340.1519. Found: 340.1516.

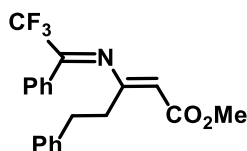
**Methyl (*Z*)-5-phenyl-3-(((*E*)-2,2,2-trifluoro-1-phenylethylidene)-amino)pent-2-enoate (3ta-*Z*):**



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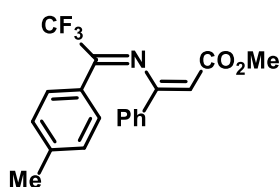
The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.5). The product was obtained as yellow liquid in 29% yield (42.2 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 – 7.47 (m, 3H), 7.43 – 7.40 (m, 2H), 7.29 – 7.25 (m, 2H), 7.22 – 7.17 (m, 1H), 7.12 – 7.10 (m, 2H), 5.06 (s, 1H), 3.66 (s, 3H), 2.84 – 2.80 (m, 2H), 2.43 – 2.38 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 160.4, 140.1, 131.1, 130.4, 128.6, 128.5, 128.2, 127.7, 126.4, 98.5, 51.2, 38.1, 33.3.;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  –68.56; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{20}\text{H}_{19}\text{F}_3\text{NO}_2$ : 362.1362. Found: 362.1365.

**Methyl (*E*)-5-phenyl-3-(((*E*)-2,2,2-trifluoro-1-phenylethylidene)-amino)pent-2-enoate (3ta-*E*):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.5). The product was obtained as yellow liquid in 41% yield (42.2 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 – 7.39 (m, 5H), 7.31 – 7.28 (m, 4H), 7.23 – 7.20 (m, 1H), 5.03 (s, 1H), 3.65 (s, 3H), 3.01 – 2.92 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.4, 164.3, 141.0, 131.2, 128.8, 128.4, 128.4, 127.9, 126.1, 51.1, 34.5, 34.2.;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  –68.82; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{20}\text{H}_{19}\text{F}_3\text{NO}_2$ : 362.1362. Found: 362.1365.

**Methyl (*Z*)-3-phenyl-3-(((*E*)-2,2,2-trifluoro-1-(*p*-tolyl)ethylidene)amino)acrylate (3ab):**

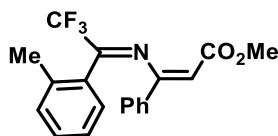


The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.6). The product was obtained as yellow solid in 76% yield (52.9 mg), Mp. 74 – 75 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 – 7.51 (m, 2H), 7.44 – 7.38 (m, 3H), 7.26 –



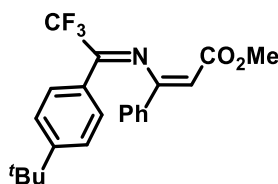
7.22 (m, 2H), 7.13 – 7.11 (m, 2H), 5.51 (s, 1H), 3.65 (s, 3H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 158.0, 141.6, 135.7, 130.6, 129.0, 129.0, 127.5, 127.3, 126.2, 96.5, 51.2, 21.5;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -68.54; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{19}\text{H}_{17}\text{F}_3\text{NO}_2$ : 348.1206. Found: 348.1202.

**Methyl (Z)-3-phenyl-3-(((E)-2,2,2-trifluoro-1-(o-tolyl)ethylidene)amino)acrylate (3ac):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.5). The product was obtained as yellow solid in 59% yield (41.1 mg), Mp. 77 – 78 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.36 (m, 1H), 7.34 – 7.27 (m, 4H), 7.25 – 7.23 (m, 1H), 7.11 – 7.06 (m, 2H), 7.03 – 7.01 (m, 1H), 5.38 (s, 1H), 3.75 (s, 3H), 1.66 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 159.0, 136.1, 135.5, 130.3, 130.3, 130.0, 130.0, 128.7, 127.5, 125.1, 119.1 (d,  $J$  = 277.0 Hz), 99.6, 51.3, 18.9;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -71.26; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{19}\text{H}_{17}\text{F}_3\text{NO}_2$ : 348.1206. Found: 348.1201.

**Methyl (Z)-3-(((E)-1-(4-(tert-butyl)phenyl)-2,2,2-trifluoroethylidene)-amino)-3-phenylacrylate (3ad):**

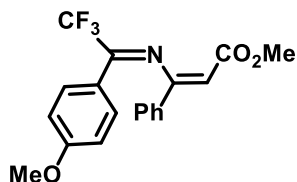


The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.6). The product was obtained as yellow solid in 74% yield (57.7 mg), Mp. 113 – 114 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 – 7.52 (m, 2H), 7.44 – 7.38 (m, 3H), 7.34 (s, 4H), 5.53 (s, 1H), 3.65 (s, 3H), 1.29 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 158.0, 154.6, 135.6, 130.5, 128.9, 127.5, 127.3, 126.2, 125.3, 119.3 (q,  $J$  = 280.3 Hz), 96.3, 51.2, 34.9, 31.0;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -67.99; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ :

Calcd for C<sub>22</sub>H<sub>23</sub>F<sub>3</sub>NO<sub>2</sub>: 390.1675. Found: 390.1671.

**Methyl (Z)-3-phenyl-3-(((E)-2,2,2-trifluoro-1-(4-methoxyphenyl)ethylidene)**

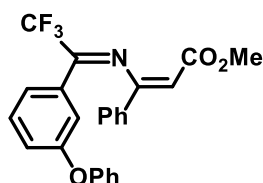
**-amino)acrylate (3ae):**



The title compound was prepared according to the general procedure (EA/PE = 1/20, R<sub>f</sub> = 0.5). The product was obtained as yellow solid in 70% yield (50.9 mg), Mp. 58 – 59 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55 – 7.52 (m, 2H), 7.45 – 7.38 (m, 5H), 6.85 – 6.81 (m, 2H), 5.53 (s, 1H), 3.81 (s, 3H), 3.64 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.7, 161.7, 158.1, 135.6, 130.6, 129.7, 129.0, 126.2, 122.4, 113.8, 96.0, 55.3, 51.2; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -67.76; HRMS (ESI) m/z [M+H]<sup>+</sup>: Calcd for C<sub>19</sub>H<sub>17</sub>F<sub>3</sub>NO<sub>3</sub>: 364.1155. Found: 364.1152.

**Methyl (Z)-3-phenyl-3-(((E)-2,2,2-trifluoro-1-(3-phenoxyphenyl)ethylidene)**

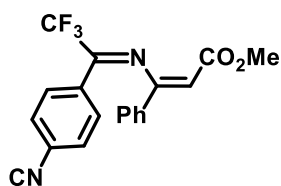
**-amino)acrylate (3af):**



The title compound was prepared according to the general procedure (EA/PE = 1/20, R<sub>f</sub> = 0.5). The product was obtained as yellow liquid in 56% yield (47.7 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42 – 7.40 (m, 3H), 7.37 – 7.28 (m, 5H), 7.15 – 7.03 (m, 3H), 6.93 – 6.88 (m, 3H), 5.50 (s, 1H), 3.62 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.6, 157.7, 157.2, 156.3, 135.3, 131.5, 130.6, 129.9, 129.8, 129.0, 126.1, 123.8, 122.1, 121.3, 119.1, 117.6, 97.1, 51.2; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -68.94; HRMS (ESI) m/z [M+H]<sup>+</sup>: Calcd for C<sub>24</sub>H<sub>19</sub>F<sub>3</sub>NO<sub>3</sub>: 426.1312. Found: 426.1315.

**Methyl (Z)-3-(((E)-1-(4-cyanophenyl)-2,2,2-trifluoroethylidene)**

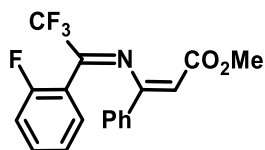
**-amino)-3-phenylacrylate (3ag):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.4). The product was obtained as yellow liquid in 31% yield (22.3 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 – 7.62 (m, 2H), 7.48 – 7.40 (m, 7H), 5.53 (s, 1H), 3.66 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.4, 157.4, 135.1, 134.5, 132.0, 131.0, 129.2, 128.3, 126.1, 117.7, 114.8, 97.1, 51.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  –68.98; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{19}\text{H}_{14}\text{F}_3\text{N}_2\text{O}_2$ : 359.1002. Found: 359.1005.

**Methyl (Z)-3-phenyl-3-(((E)-2,2,2-trifluoro-1-(2-fluorophenyl)ethylidene)**

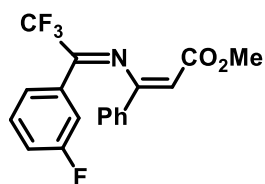
**-amino)acrylate (3ah):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.6). The product was obtained as yellow solid in 42% yield (29.6 mg), Mp. 96 – 97 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.34 (m, 6H), 7.22 – 7.18 (m, 1H), 7.11 – 7.07 (m, 1H), 6.98 – 6.94 (m, 1H), 5.52 (s, 1H), 3.71 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 157.7, 134.9, 132.7 (d,  $J$  = 8.2 Hz), 130.6, 129.4, 128.7, 126.2, 123.8, 115.8 (d,  $J$  = 20.8 Hz), 98.4, 51.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  –71.02, –110.46; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{18}\text{H}_{14}\text{F}_4\text{NO}_2$ : 352.0955. Found: 352.0959.

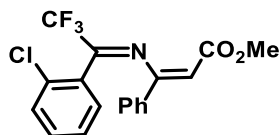
**Methyl (Z)-3-phenyl-3-(((E)-2,2,2-trifluoro-1-(3-fluorophenyl)ethylidene)**

**-amino)acrylate (3ai):**



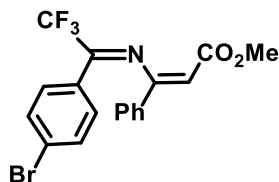
The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as yellow solid in 30% yield (21.1 mg), Mp. 98 – 99 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 – 7.47 (m, 2H), 7.45 – 7.39 (m, 3H), 7.32 – 7.28 (m, 1H), 7.15 – 7.09 (m, 3H), 5.53 (s, 1H), 3.67 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 157.8, 135.4, 130.9, 130.2 (d,  $J = 7.7$  Hz), 129.2, 128.2, 126.3, 123.5, 118.4 (d,  $J = 21.2$  Hz), 115.0 (d,  $J = 24.1$  Hz), 97.0, 51.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  –68.80, –111.13; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{18}\text{H}_{14}\text{F}_4\text{NO}_2$ : 352.0955. Found: 352.0951.

**Methyl (Z)-3-(((E)-1-(2-chlorophenyl)-2,2,2-trifluoroethylidene)-amino)-3-phenylacrylate (3aj):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as yellow solid in 67% yield (49.3 mg), Mp. 89 – 90 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.29 (m, 7H), 7.24 – 7.21 (m, 2H), 5.45 (s, 1H), 3.75 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.8, 158.4, 135.0, 131.6, 131.5, 130.5, 129.6, 129.4, 128.6, 126.6, 126.2, 99.2, 51.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  –70.86; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{18}\text{H}_{14}\text{ClF}_3\text{NO}_2$ : 368.0660. Found: 368.0665.

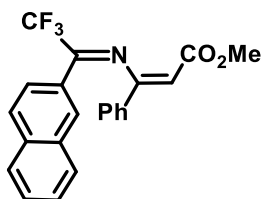
**Methyl (Z)-3-(((E)-1-(4-bromophenyl)-2,2,2-trifluoroethylidene)-amino)-3-phenylacrylate (3ak):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as yellow liquid in 32% yield (26.4 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 – 7.39 (m, 7H), 7.21 – 7.19 (m, 2H), 5.52 (s, 1H), 3.65 (s,

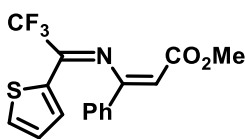
3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.5, 157.7, 135.4, 131.6, 130.8, 129.1, 126.1, 125.9, 96.8, 51.3;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -68.87; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{18}\text{H}_{14}\text{BrF}_3\text{NO}_2$ : 412.0155. Found: 412.0150.

**Methyl (Z)-3-phenyl-3-(((E)-2,2,2-trifluoro-1-(naphthalen-2-yl)ethylidene)-amino)acrylate (3al):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.5). The product was obtained as yellow liquid in 63% yield (48.4 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 – 7.74 (s, 4H), 7.58 – 7.41 (m, 8H), 5.50 (s, 1H), 3.64 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 158.2, 135.8, 134.1, 132.2, 130.7, 129.0, 128.9, 128.5, 128.1, 127.9, 127.7, 126.8, 126.3, 123.8, 119.3 (d,  $J$  = 279.4 Hz), 96.7, 51.2;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -68.19; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{22}\text{H}_{17}\text{F}_3\text{NO}_2$ : 384.1206 Found: 384.1210.

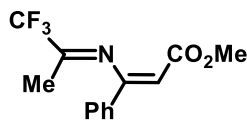
**Methyl (Z)-3-phenyl-3-(((E)-2,2,2-trifluoro-1-(thiophen-3-yl)ethylidene)-amino)acrylate (3am):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f$  = 0.5). The product was obtained as yellow solid in 53% yield (36.0 mg), Mp. 75 – 76 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (s, 1H), 7.57 – 7.54 (m, 2H), 7.46 – 7.39 (m, 3H), 7.29 – 7.27 (m, 2H), 5.63 (s, 1H), 3.64 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 157.9, 134.5, 130.8, 129.1, 127.0, 126.3, 126.2, 95.8, 51.2;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -68.45; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{16}\text{H}_{13}\text{F}_3\text{NO}_2\text{S}$ : 340.0614 Found: 340.0609.

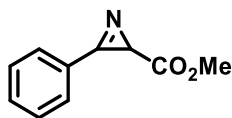
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**Methyl (*Z*)-3-phenyl-3-(((*E*)-1,1,1-trifluoropropan-2-ylidene)amino)acrylate (**3an**):**



The title compound was prepared according to the general procedure (EA/PE = 1/20,  $R_f = 0.5$ ). The product was obtained as yellow liquid in 45% yield (24.5 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 – 7.50 (m, 2H), 7.45 – 7.41 (m, 3H), 5.76 (s, 1H), 3.71 (s, 3H), 2.03 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 157.7, 134.2, 130.8, 128.9, 126.3, 97.7, 51.4, 15.5;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -74.60; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{13}\text{H}_{13}\text{F}_3\text{NO}_2$ : 272.0893. Found: 272.0890.

**Methyl 3-phenyl-2*H*-azirine-2-carboxylate(**1a'**):**



A mixture of **1a** (0.2 mmol, 1.0 equiv.),  $\text{K}_2\text{CO}_3$  (0.4 mmol, 2.0 equiv.) and  $\text{PhCF}_3$  (2 mL) was sealed in a Schlenk tube under Argon protection at 110 °C and the mixture was stirred until the **1a** was consumed completely. Then the reaction mixture was filtered by diatomite and concentrated under reduced pressure and purified by column chromatography (EA/PE = 1:20,  $R_f = 0.4$ ) to give the desired product **1a'** as white liquid (31.5 mg, 90%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 – 7.86 (m, 2H), 7.65 – 7.60 (m, 1H), 7.58 – 7.53 (m, 2H), 3.72 (s, 3H), 2.84 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.0, 158.4, 133.9, 130.4, 129.2, 122.0, 52.2, 29.3; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ : Calcd for  $\text{C}_{10}\text{H}_{10}\text{NO}_2$ : 176.0706. Found: 176.0703.

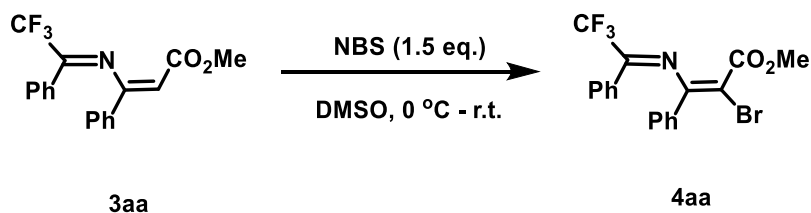
## 2.4 Applications and their spectral data

### Large-scale reaction of **3aa**:

A mixture of **1a** (10.0 mmol, 1.0 equiv.), **2a** (20.0 mmol, 2.0 equiv.),  $\text{CuCl}_2$  (1 mmol, 10 mol%),  $\text{K}_2\text{CO}_3$  (25.0 mmol, 2.5 equiv.) and  $\text{PhCF}_3$  (50 mL) was sealed in a Schlenk tube under Argon protection at 110 °C and the mixture was stirred until the **1a** was

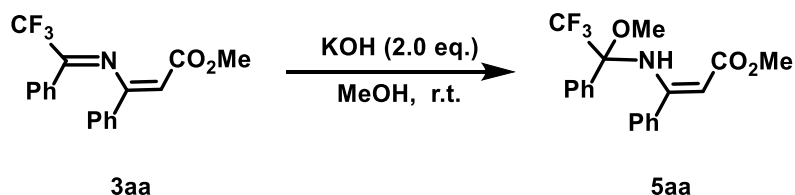
consumed completely. Then the reaction mixture was filtered by diatomite and concentrated under reduced pressure and purified by column chromatography (EA/PE = 1:20) to give the desired product **3aa** (2.03g, 61%).

**Methyl (*E*)-2-bromo-3-phenyl-3-(((*E*)-2,2,2-trifluoro-1-phenylethylidene)-amino)acrylate (**4aa**):**



2-azadiene **3aa** (0.2 mmol, 1.0 equiv.) and NBS (0.24 mmol, 1.5 equiv.) were dissolved into DMSO (4 mL) stirred at 0 °C for 12 h. After reaction, the organic phase was dried, evaporated, was purified by column chromatography to give the product was obtained as a yellow oil (55.1 mg, 67%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.51 – 7.47 (m, 1H), 7.40 – 7.36 (m, 2H), 7.34 – 7.29 (m, 3H), 7.26 – 7.22 (m, 2H), 7.06 – 7.03 (m, 2H), 3.55 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.8, 155.4, 135.8, 131.5, 130.4, 129.4, 128.6, 128.0, 127.7, 127.2, 119.1 (d, *J* = 279.1 Hz), 96.2, 52.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ –69.00; HRMS (ESI) *m/z* [M+H]<sup>+</sup>: Calcd for C<sub>18</sub>H<sub>14</sub>BrF<sub>3</sub>NO<sub>2</sub>: 412.0155. Found: 412.0151.

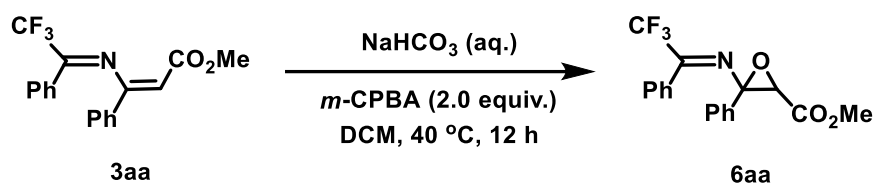
**Methyl (*Z*)-3-phenyl-3-((2,2,2-trifluoro-1-methoxy-1-phenylethyl)amino)acrylate (**5aa**):**



2-azadiene **3aa** (0.2 mmol, 1.0 equiv.) and KOH (0.4 mmol, 2.0 equiv.) were dissolved into MeOH (4 mL) stirred at room temperature until the **3aa** was consumed completely. After reaction, the organic phase was dried, evaporated, was purified by column chromatography to give the product was obtained as a colourless oil (51.1 mg,

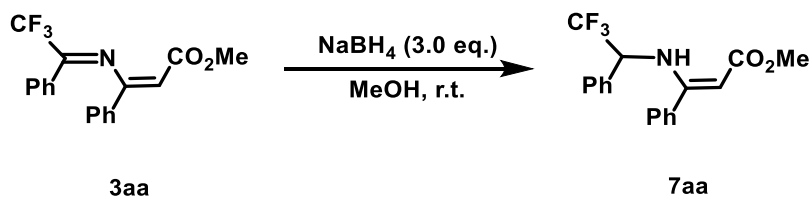
70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.99 (s, 1H), 7.32 – 7.30 (m, 2H), 7.18 – 7.05 (m, 4H), 7.0 – 6.93 (m, 2H), 6.82 – 6.80 (m, 2H), 4.84 (s, 1H), 3.79 (s, 3H), 3.69 (q, *J* = 2.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.4, 162.7, 136.0, 135.8, 128.7, 128.4, 128.1, 127.9, 127.4, 126.8, 123.4 (d, *J* = 290.8 Hz), 93.6, 51.3, 51.0; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ –76.04; HRMS (ESI) *m/z* [M+H]<sup>+</sup>: Calcd for C<sub>19</sub>H<sub>19</sub>F<sub>3</sub>NO<sub>3</sub>: 336.1312. Found: 336.1315.

**Methyl (*E*)-3-phenyl-3-((2,2,2-trifluoro-1-phenylethylidene)amino)-oxirane-2-carboxylate (6aa):**



2-azadiene **3aa** (0.2 mmol, 1.0 equiv.) in dichloromethane (4 mL) was added saturated sodium hydrogen carbonate (4 mL) followed 3-chloroperbenzoic acid (0.4 mmol) and stirred at 40 °C for 12 h. The reaction was cooled to room temperature then dichloromethane (10 mL) was added. The organic layer was washed twice with saturated sodium hydrogen carbonate, the organic phase was dried, evaporated, was purified by column chromatography to give the product was obtained as a yellow oil (54.8 mg, 52%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.99 – 7.96 (m, 2H), 7.79 – 7.77 (m, 2H), 7.56 – 7.52 (m, 1H), 7.48 – 7.39 (m, 5H), 5.79 (s, 1H), 3.79 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.0, 167.2, 135.2, 132.6, 129.6, 129.1, 128.7, 128.2, 127.3, 85.5, 53.1; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ –79.39; HRMS (ESI) *m/z* [M+H]<sup>+</sup>: Calcd for C<sub>18</sub>H<sub>15</sub>F<sub>3</sub>NO<sub>3</sub>: 350.0999. Found: 350.0993.

**Methyl 3-phenyl-3-((2,2,2-trifluoro-1-phenylethyl)amino)propanoate (7aa):**

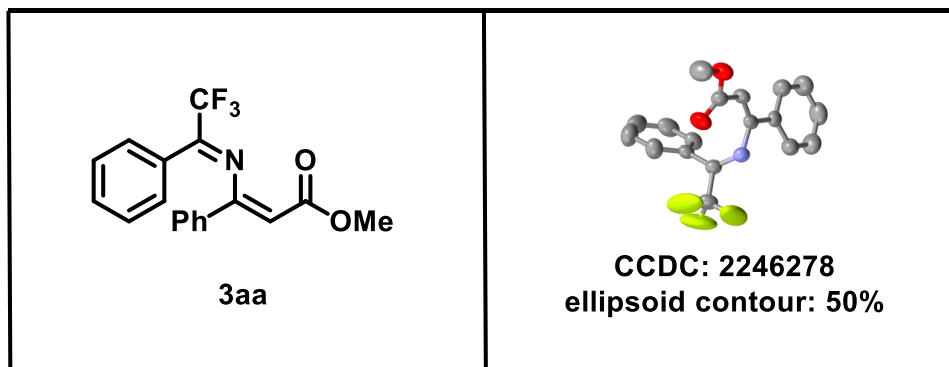




A mixture of **3aa** (0.2 mmol, 1.0 equiv.), NaBH<sub>4</sub> (0.6 mmol, 3.0 equiv.) and CH<sub>3</sub>OH (2 mL) was sealed in a Schlenk tube at room temperature and the mixture was stirred until the **3aa** was consumed completely. The reaction mixture was evaporated and purified by column chromatography to give the product was obtained as a yellow oil (57.0 mg, 85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.46 – 9.43 (d, 1H), 7.47 – 7.36 (m, 6H), 7.30 – 7.27 (m, 3H), 4.86 (s, 1H), 4.79 – 4.70 (m, 1H), 3.75 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.5, 162.9, 134.9, 133.5, 129.9, 129.1, 128.8, 128.7, 127.9, 127.7, 124.5 (q, *J* = 280.9 Hz), 90.1, 59.8 (q, *J* = 30.1 Hz), 50.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -74.25; HRMS (ESI) *m/z* [M+H]<sup>+</sup>: Calcd for C<sub>18</sub>H<sub>17</sub>F<sub>3</sub>NO<sub>2</sub>: 336.1206. Found: 336.1202.

## 2.5 X-ray crystallography of compound **3aa**:

Good quality crystal of **3aa** (colourless block crystal) was obtained by vaporization of a petroleum ether/ethyl acetate solution of compound **3aa** (~25 mg). Single colourless plate crystals of **3aa** were used as supplied. A suitable crystal with dimensions 0.10 × 0.10 × 0.10 mm<sup>3</sup> was selected and mounted on a Bruker APEX-II CCD diffractometer. The crystal was kept at a steady T = 298 K during data collection. CCDC: 2246278 contains the supplementary crystallographic data for this paper. The ellipsoid contour % probability level is 50%. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/>.



$C_{18}H_{14}F_3NO_2$  ( $M = 333.10$  g/mol): monoclinic, space group Cc (no. 9),  $a = 9.9693(8)$  Å,  $b = 11.1128(9)$  Å,  $c = 14.6773(9)$  Å,  $\beta = 95.872(7)^\circ$ ,  $V = 1617.5(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 298.15$  K,  $\mu$  (MoK $\alpha$ ) = 1.821 mm<sup>-1</sup>,  $D_{calc} = 1.591$  g/cm<sup>3</sup>, 4169 reflections measured ( $4.942^\circ \leq 2\theta \leq 50.038^\circ$ ), 2681 unique ( $R_{int} = 0.0956$ ,  $R_{sigma} = 0.1099$ ) which were used in all calculations. The final  $R_1$  was 0.0738 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1919 (all data).

Compound	3aa
Formula	$C_{18}H_{14}F_3NO_2$
$D_{calc.}/g\ cm^{-3}$	1.591
m/mm <sup>-1</sup>	1.821
Formula Weight	333.10
Colour	colourless
Shape	block
Size/mm <sup>3</sup>	$0.43 \times 0.35 \times 0.33$
T/K	298.15
Crystal System	monoclinic
Flack Parameter	-0.03(8)
Space Group	Cc
$a/\text{Å}$	9.9693(8)
$b/\text{Å}$	11.1128(9)
$c/\text{Å}$	14.6773(9)
$\alpha/^\circ$	90
$\beta/^\circ$	95.872(7)
$\gamma/^\circ$	90
$V/\text{Å}^3$	1617.5(2)
$Z$	4
$Z'$	1
F (000)	848.0
Reflections collected/Å	4169
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
Index ranges	$-12 \leq h \leq 12$
	$-17 \leq k \leq 13$
	$-14 \leq l \leq 14$
Goodness-of-fit on $F^2$	0.974
$R_{sigma}$	0.1099
$R_{int}$	0.0956
Parameters	213
Restraints	146

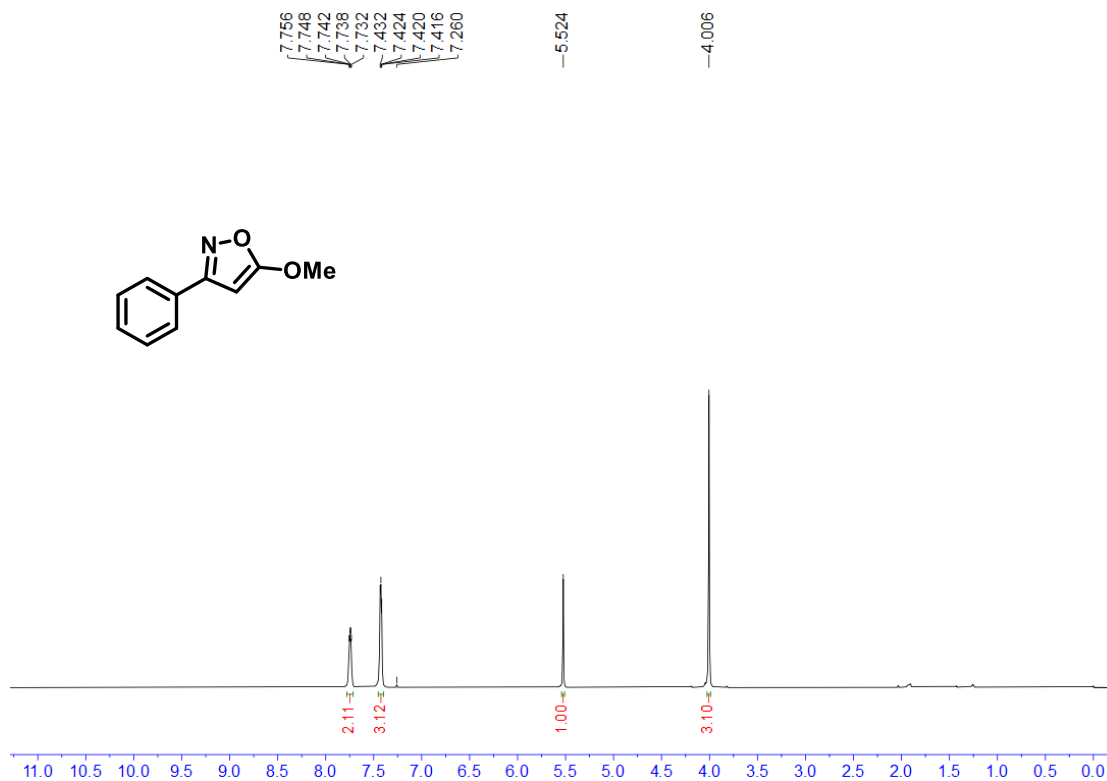
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Largest diff. Peak	0.61
Largest diff. Hole	-1.39
$wR_2$ (all data)	0.1919
$R_1$ (all data)	0.0954
$R_1$ ( $I > 2\sigma(I)$ )	0.0738
$wR_2$ ( $I > 2\sigma(I)$ )	0.1780
$2\Theta$ range for data collection/ $^\circ$	4.942 to 50.038

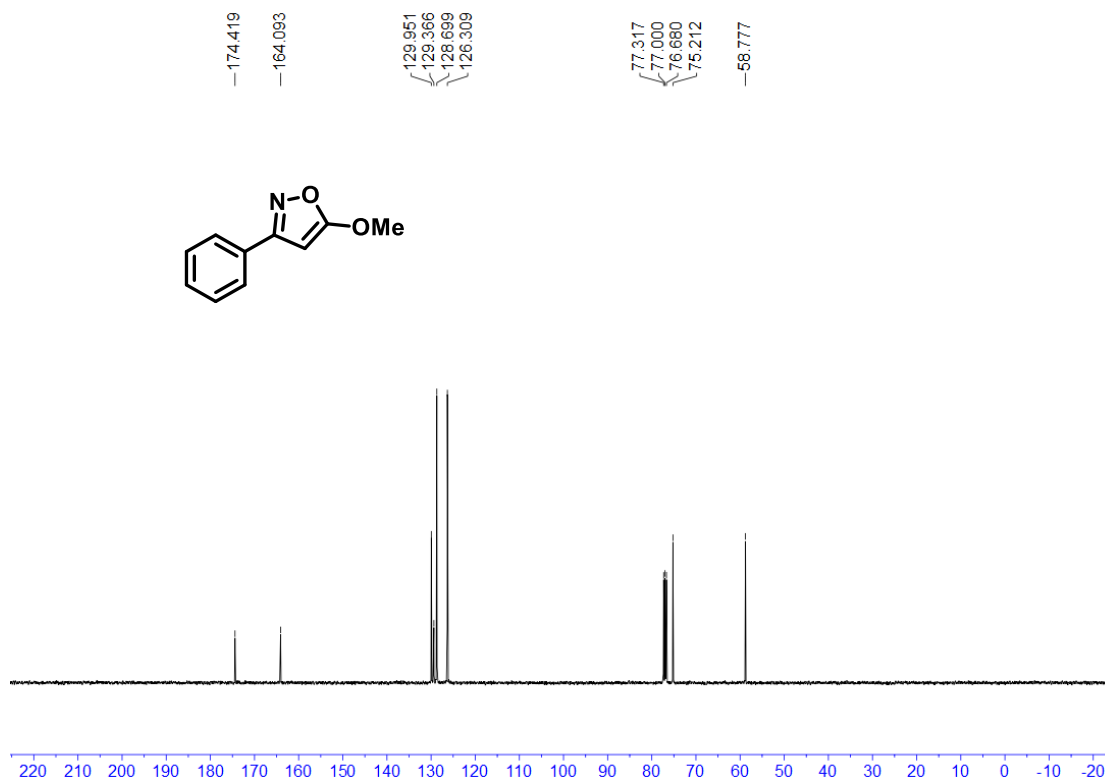
### 3. NMR spectra

#### 3.1 NMR spectra for isoxazoles

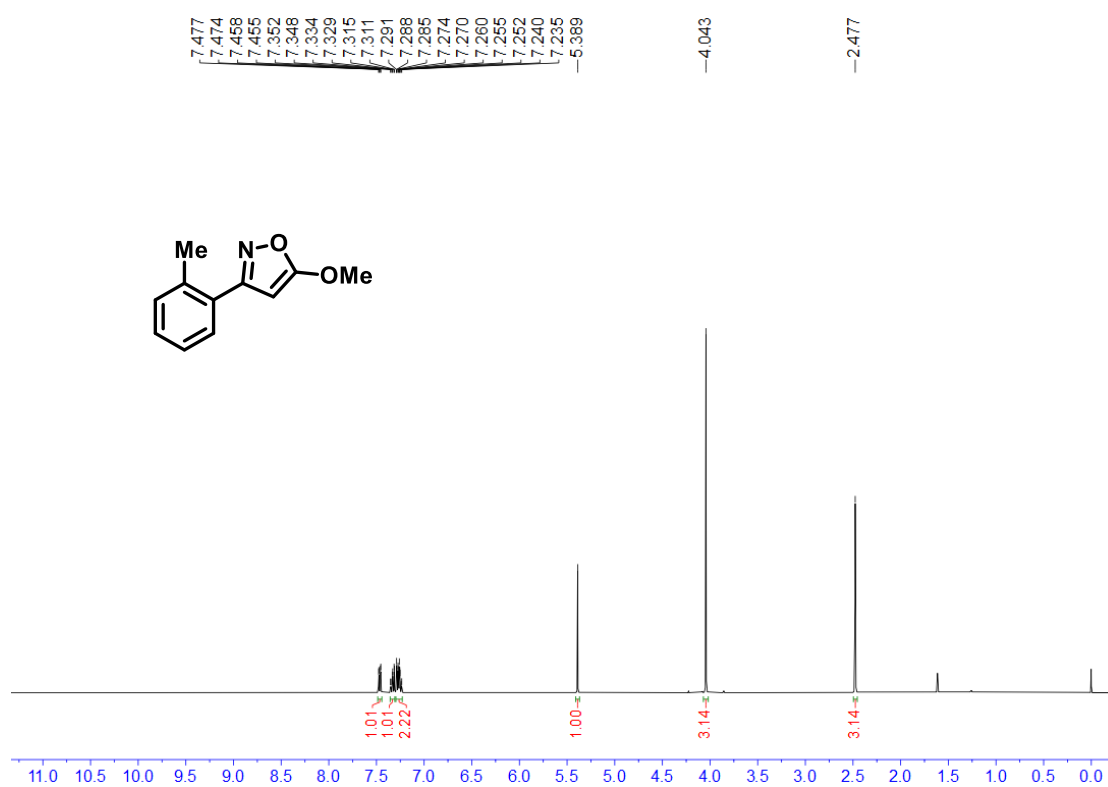
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **1a**



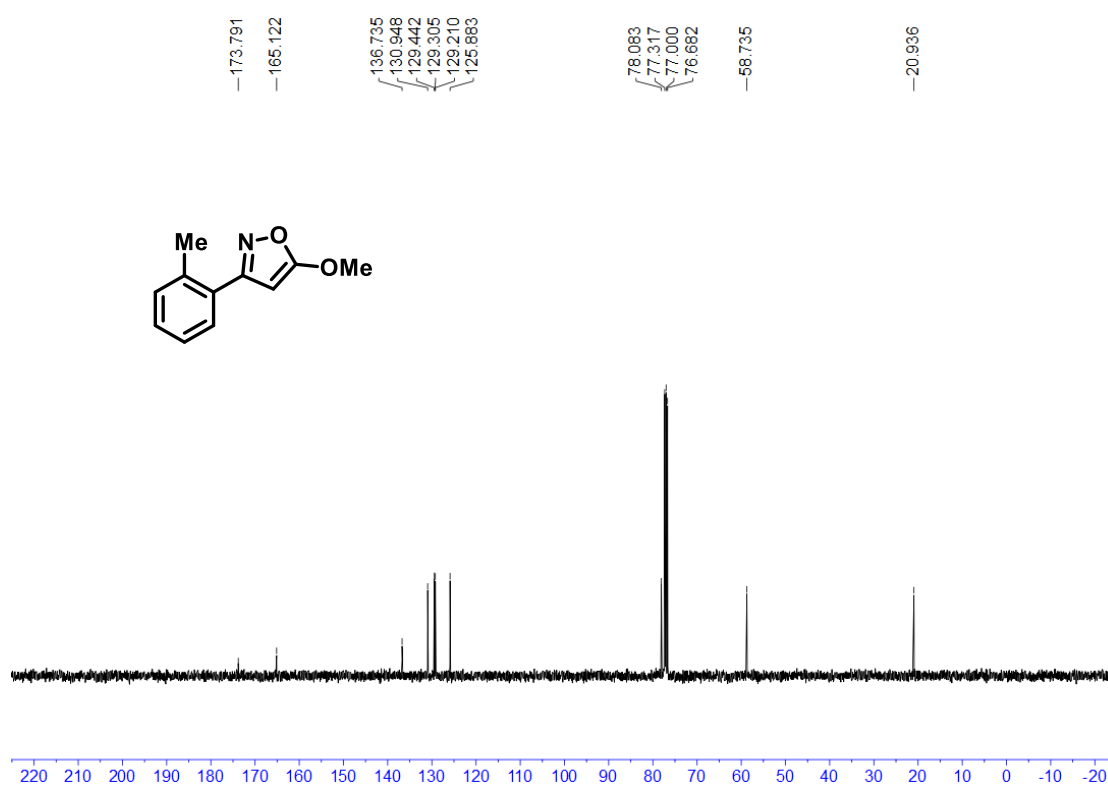
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **1a**



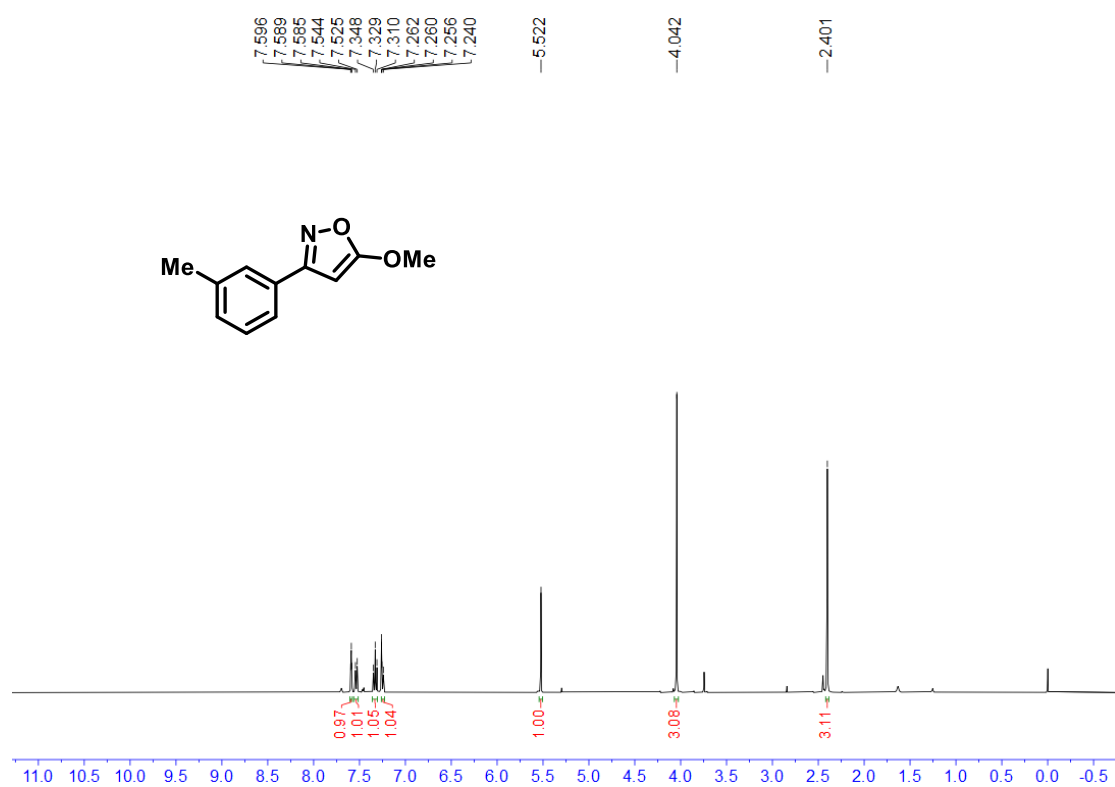
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **1b**



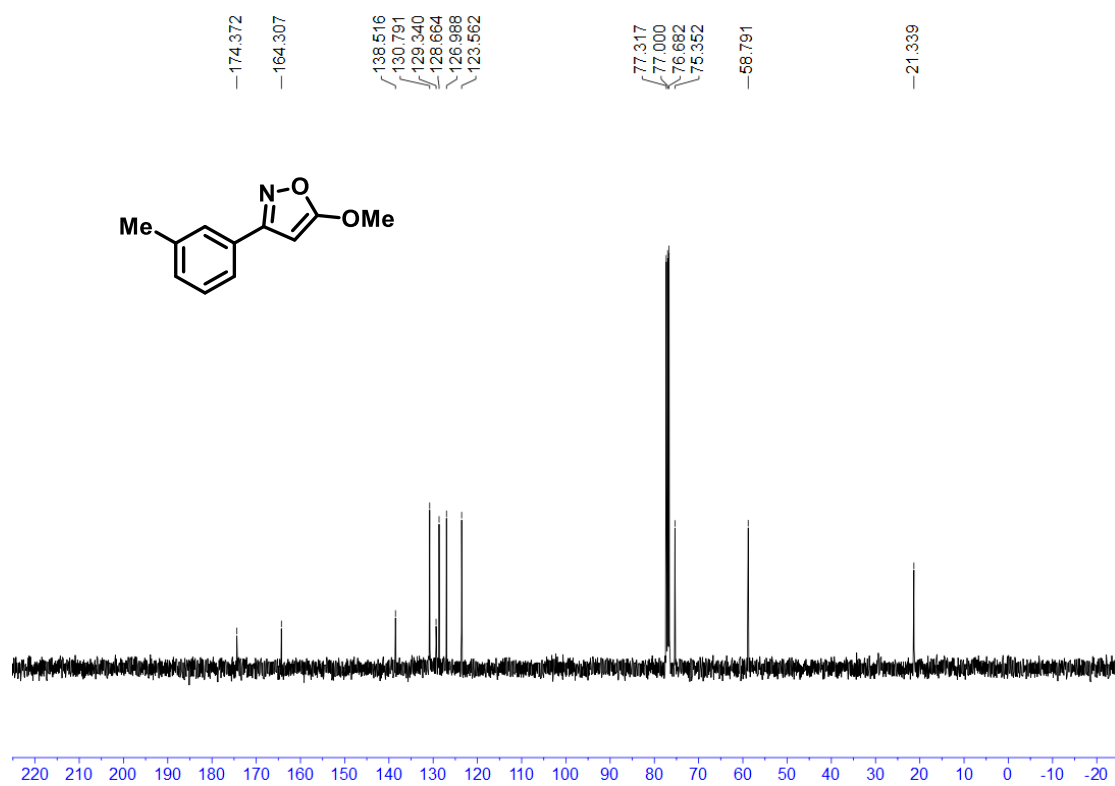
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **1b**



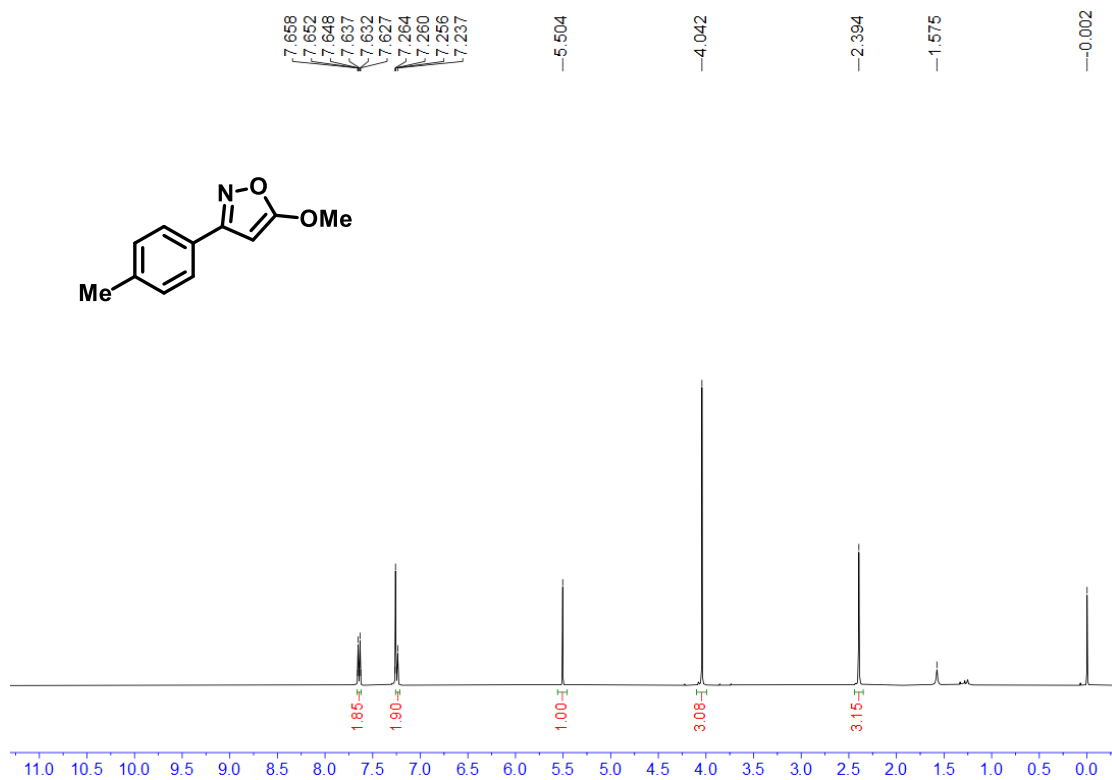
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **1c**



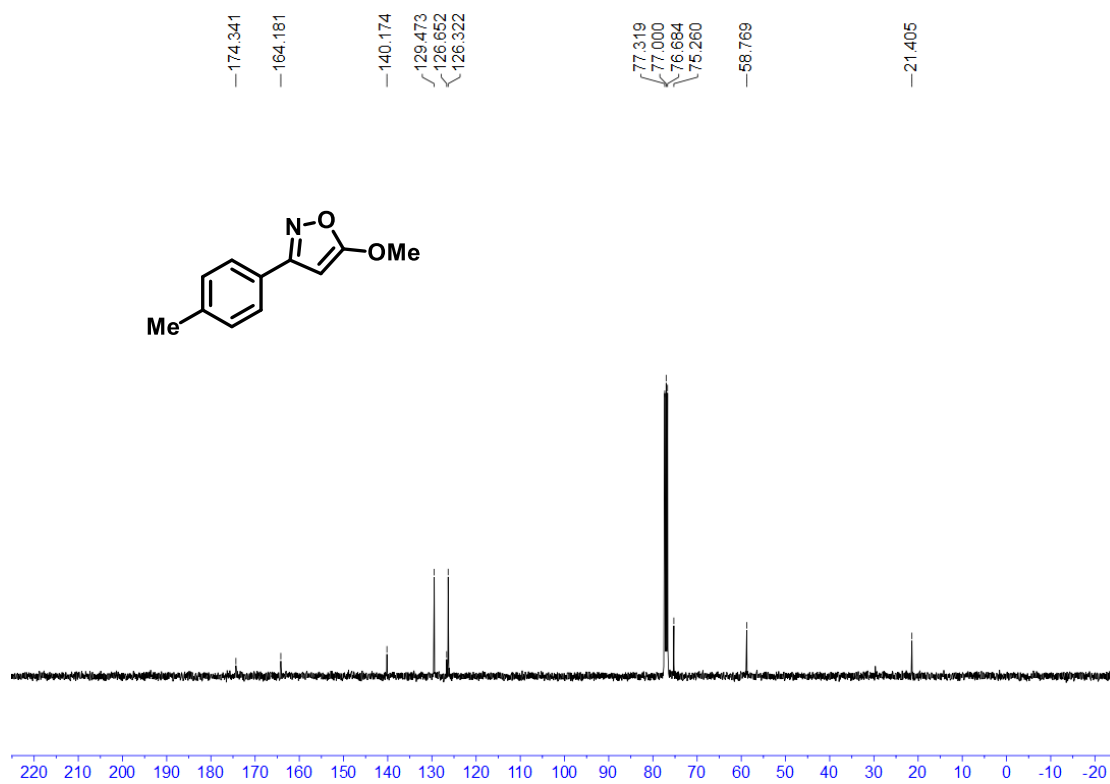
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **1c**



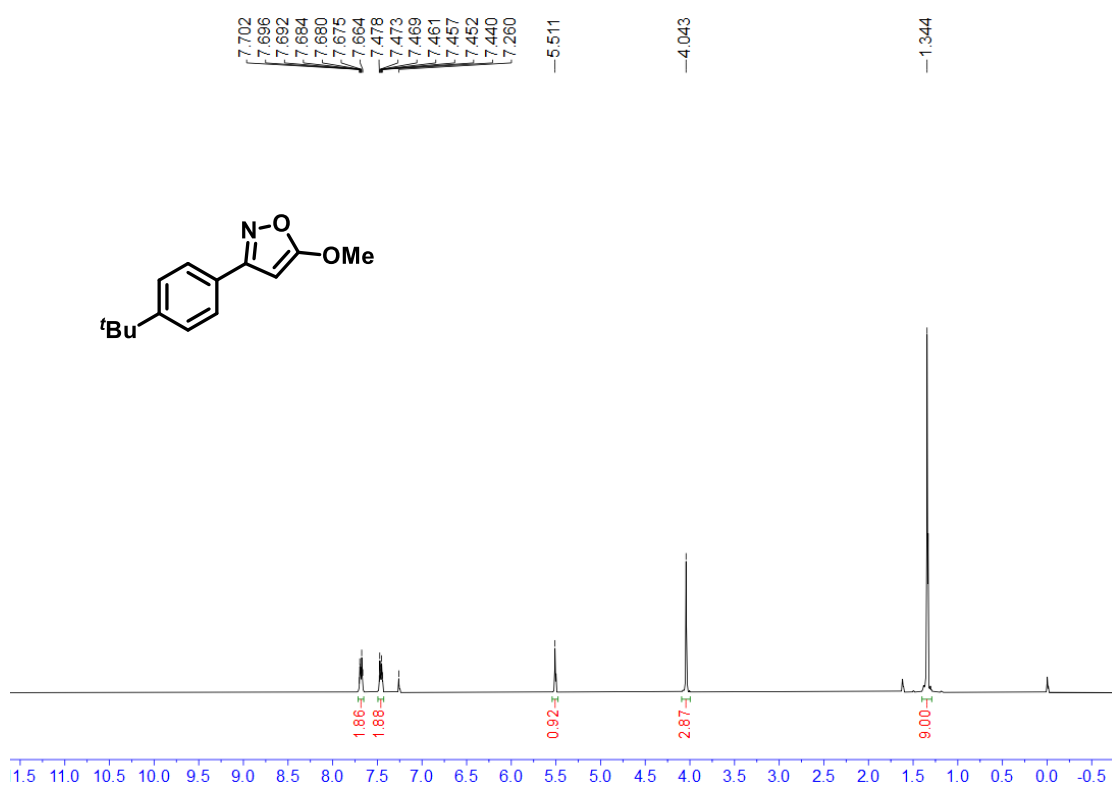
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **1d**



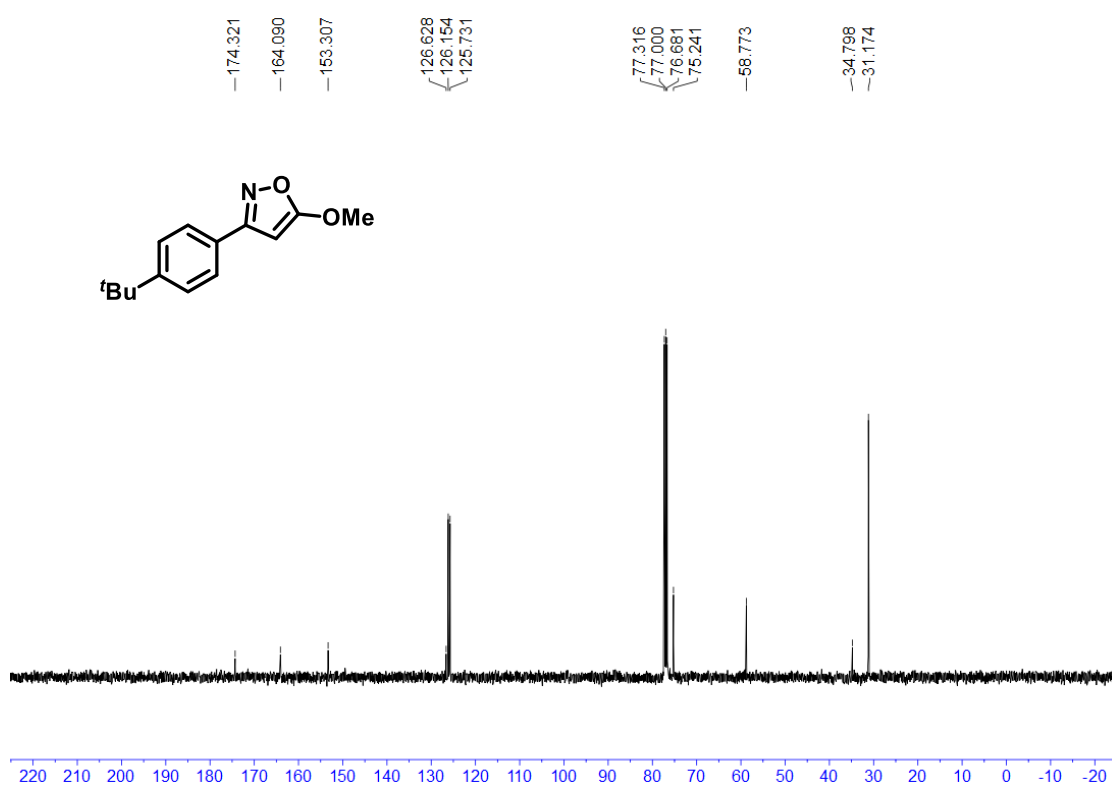
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **1d**



<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **1e**

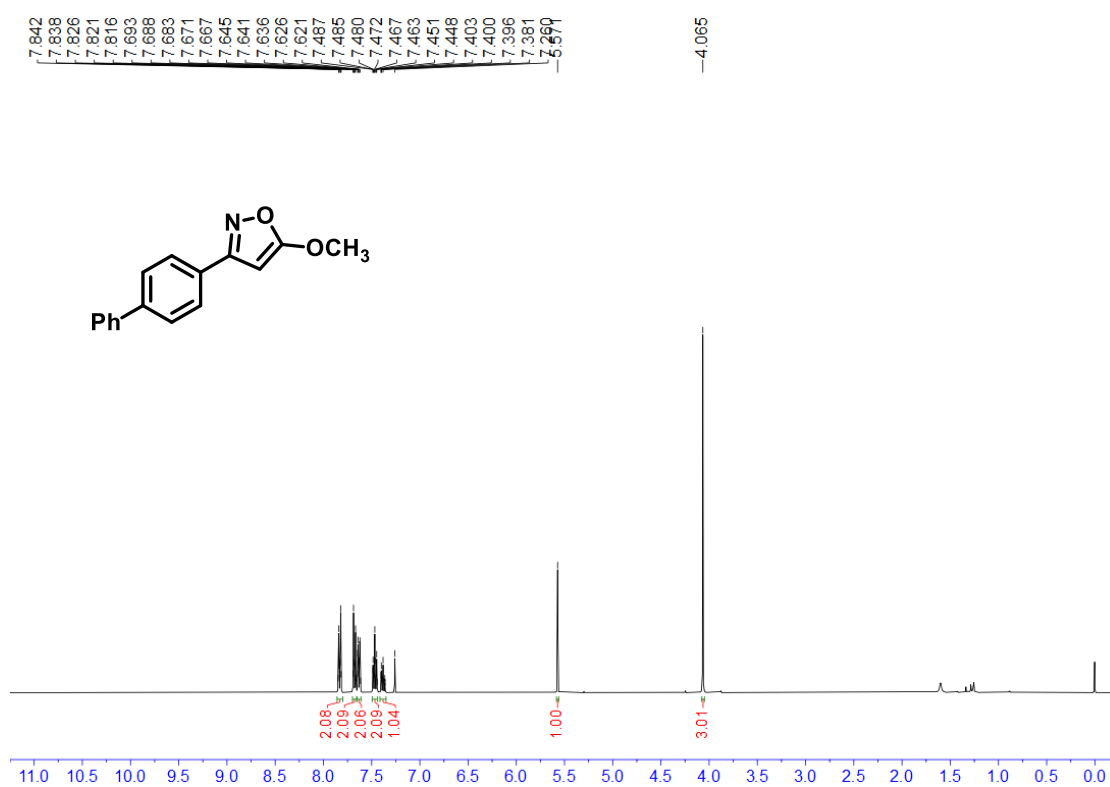


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **1e**

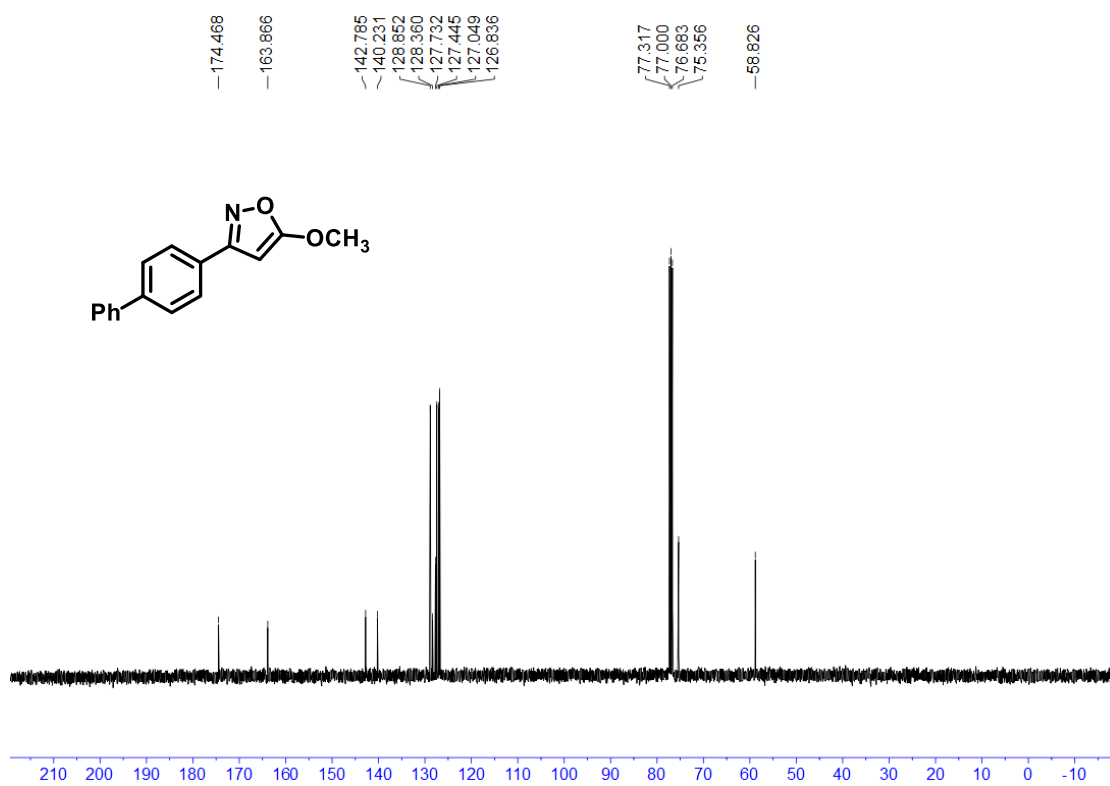




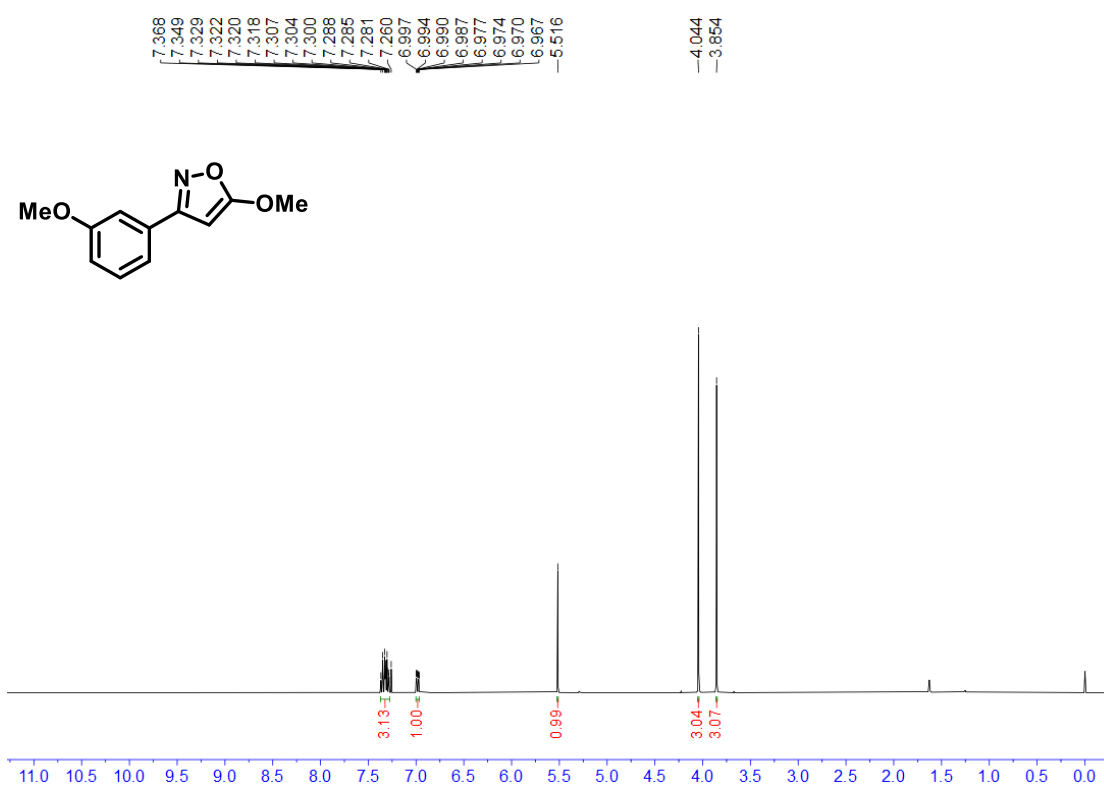
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **1f**



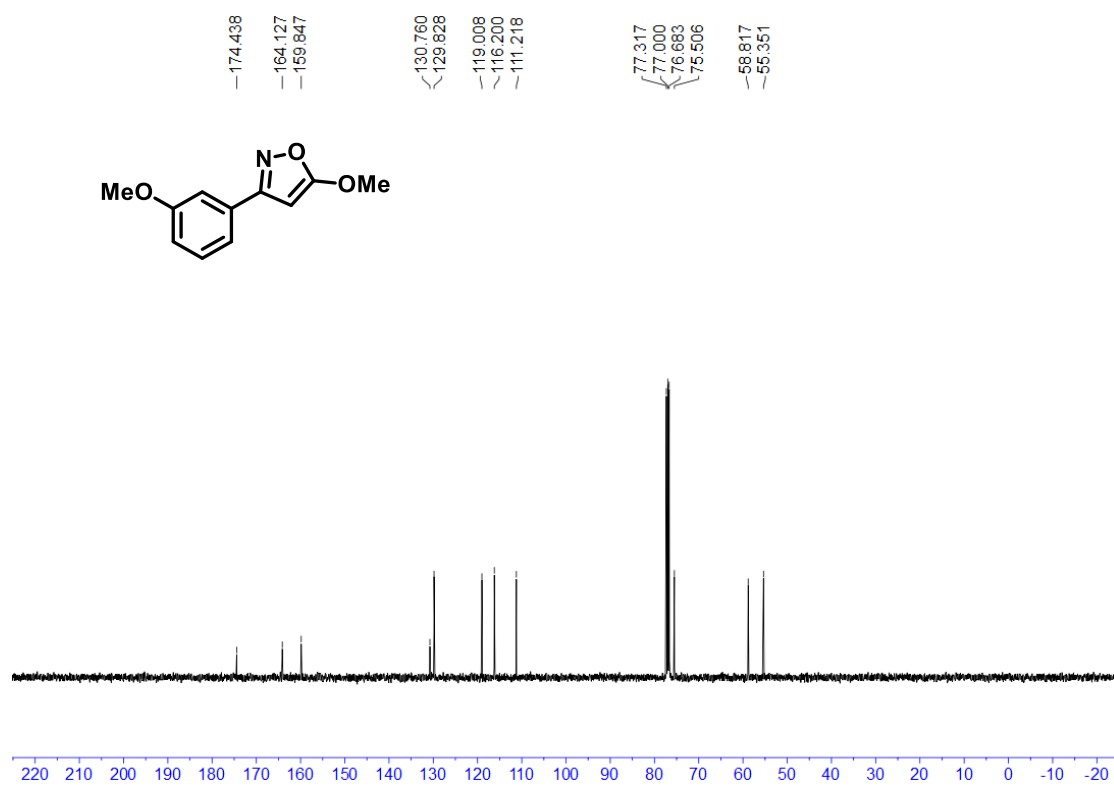
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **1f**



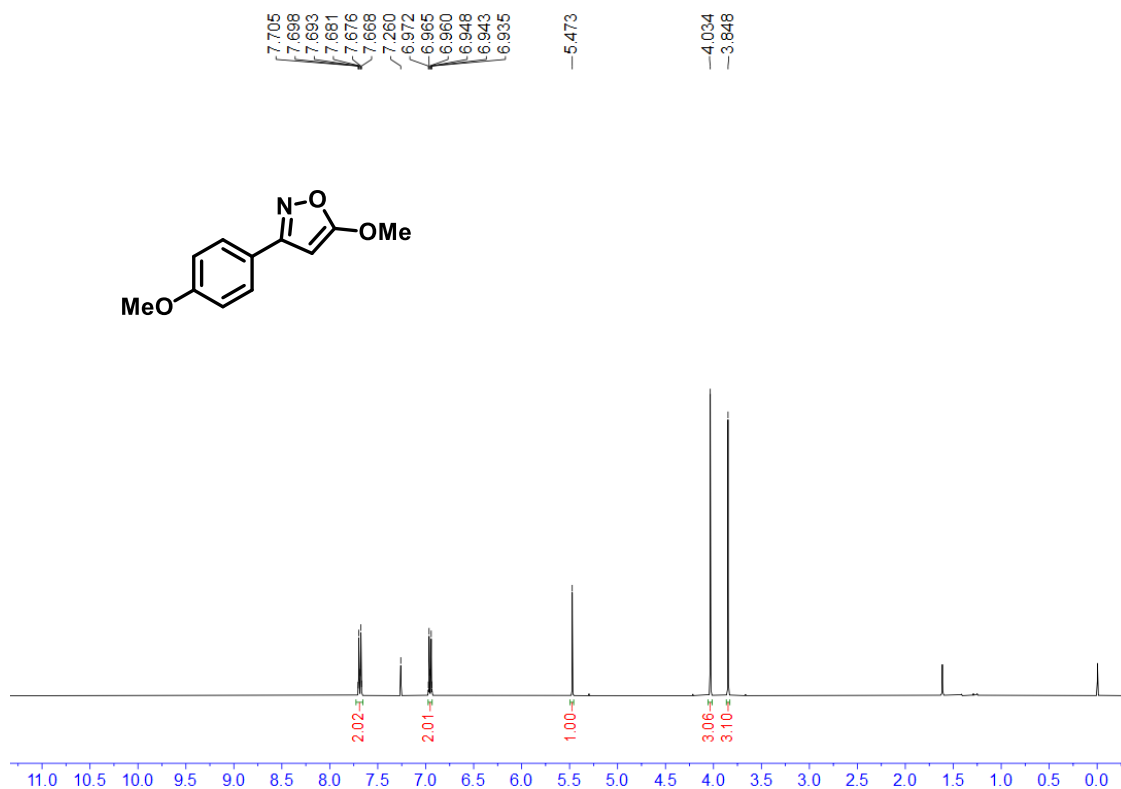
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **1g**



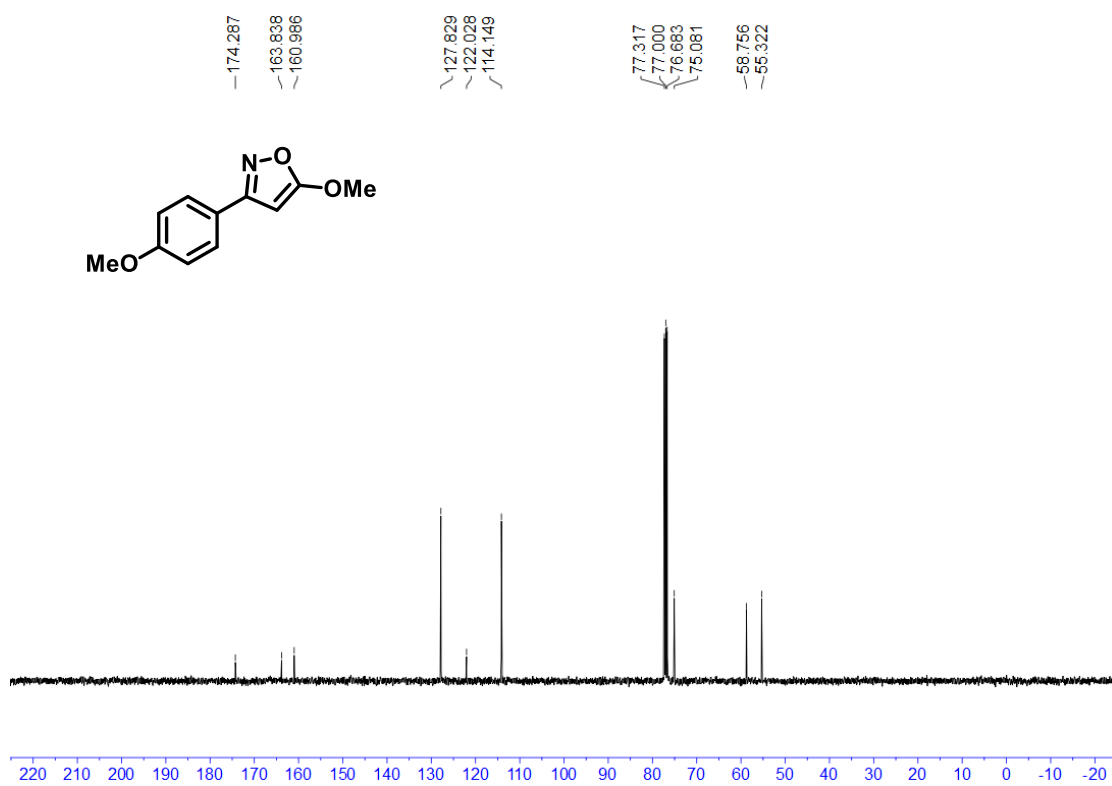
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **1g**



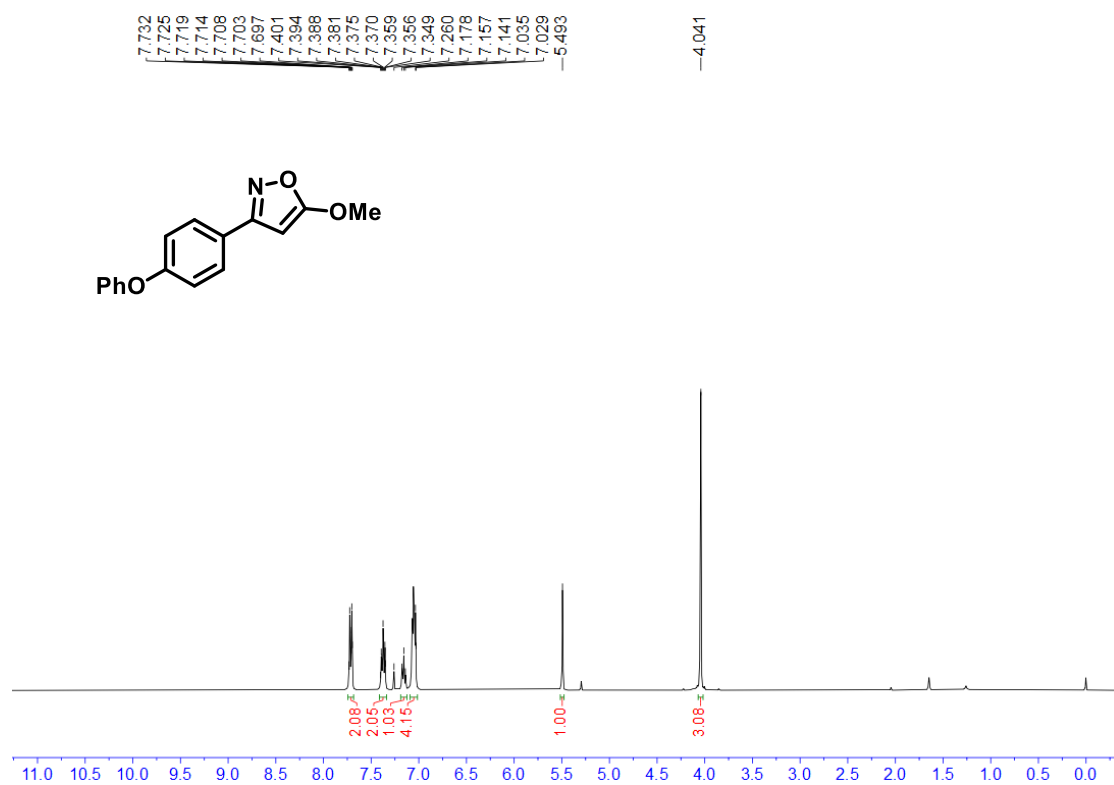
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **1h**



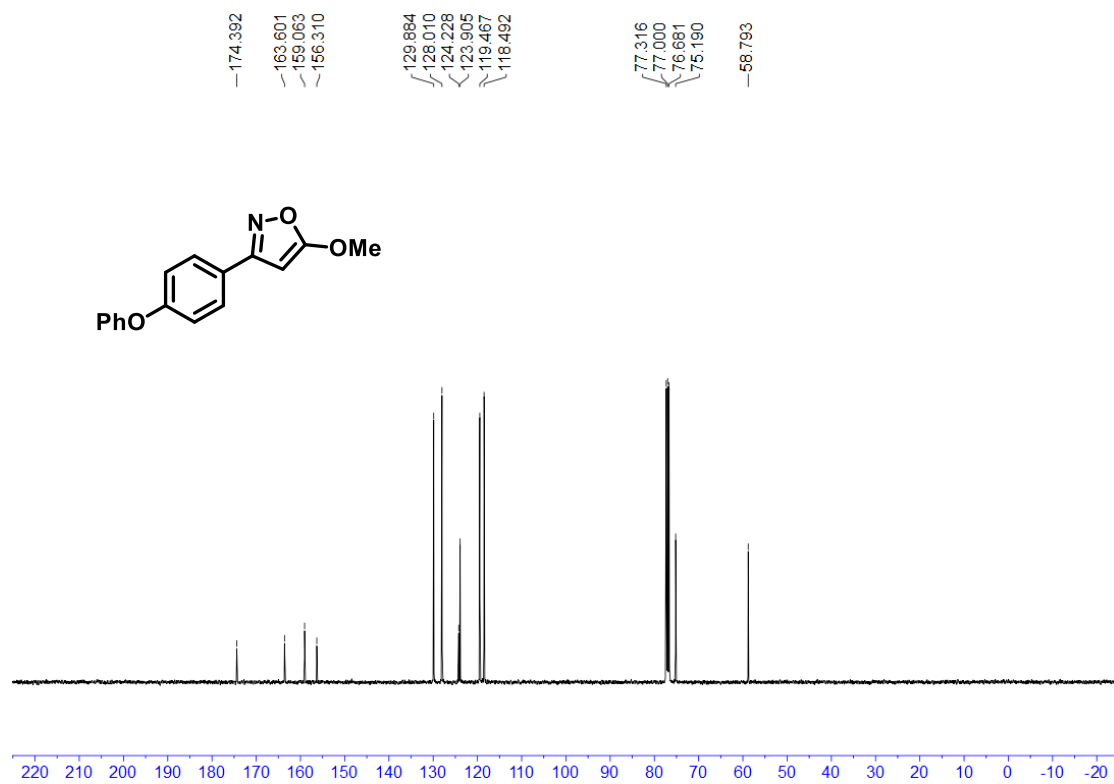
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **1h**



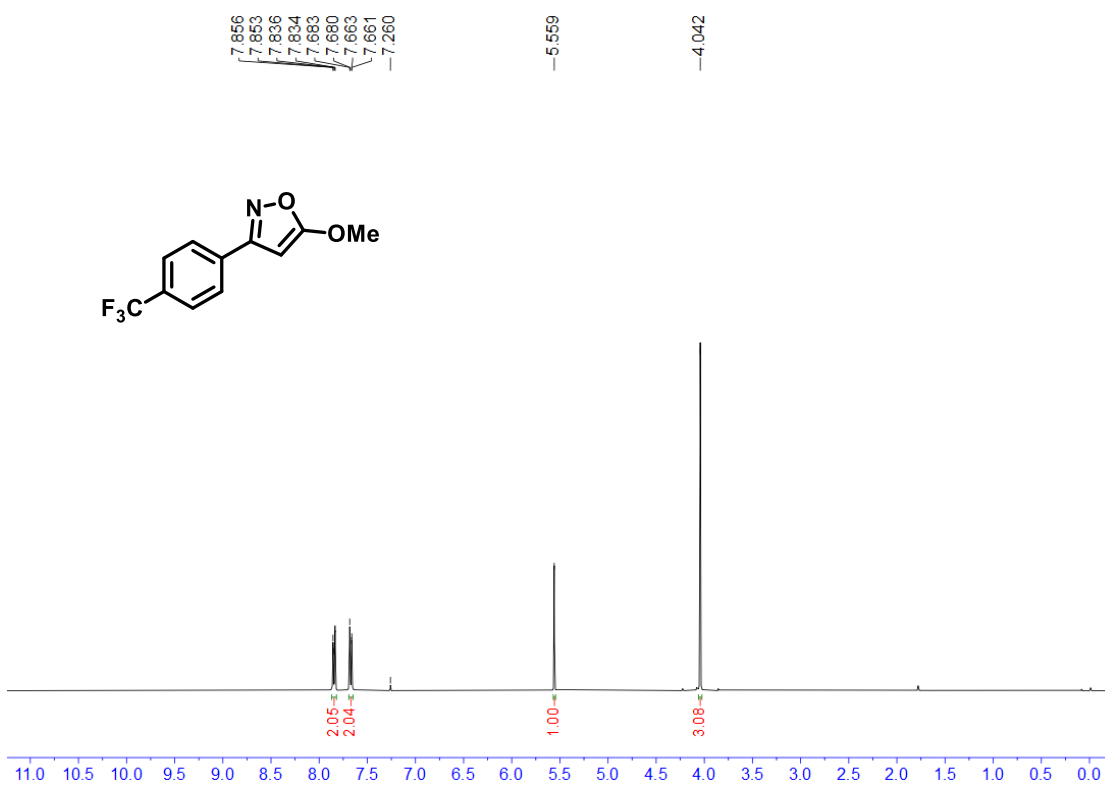
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **1i**



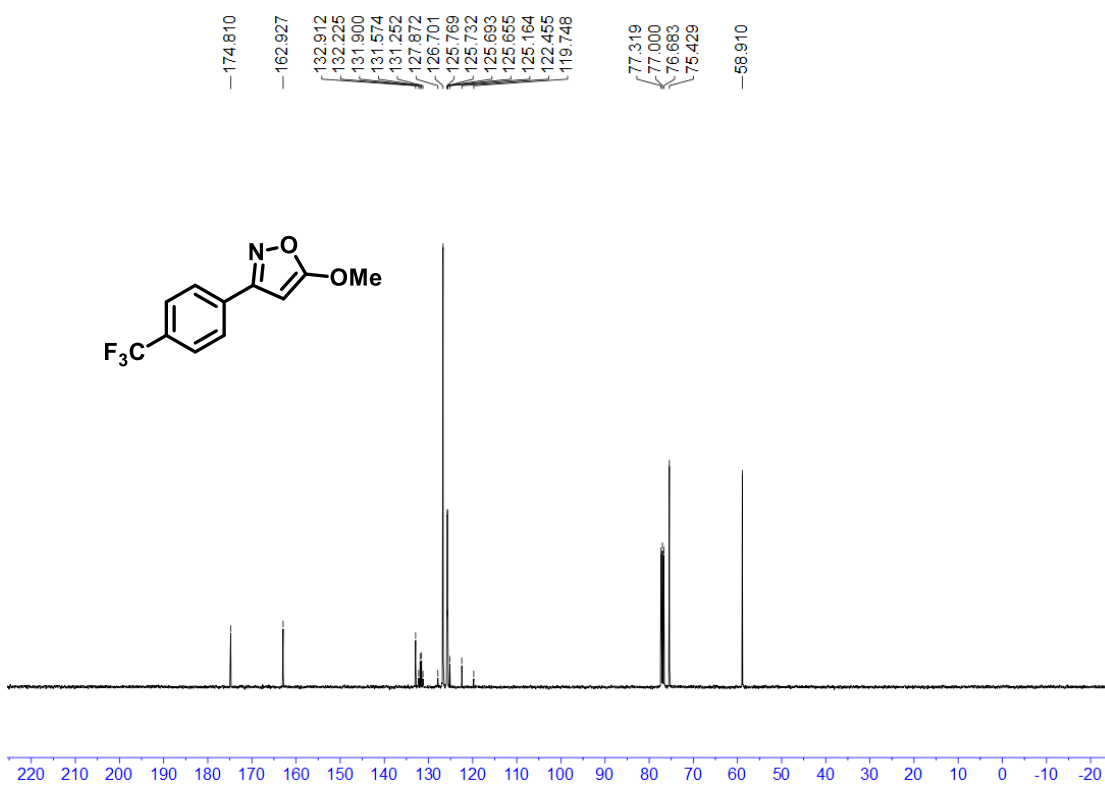
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **1i**



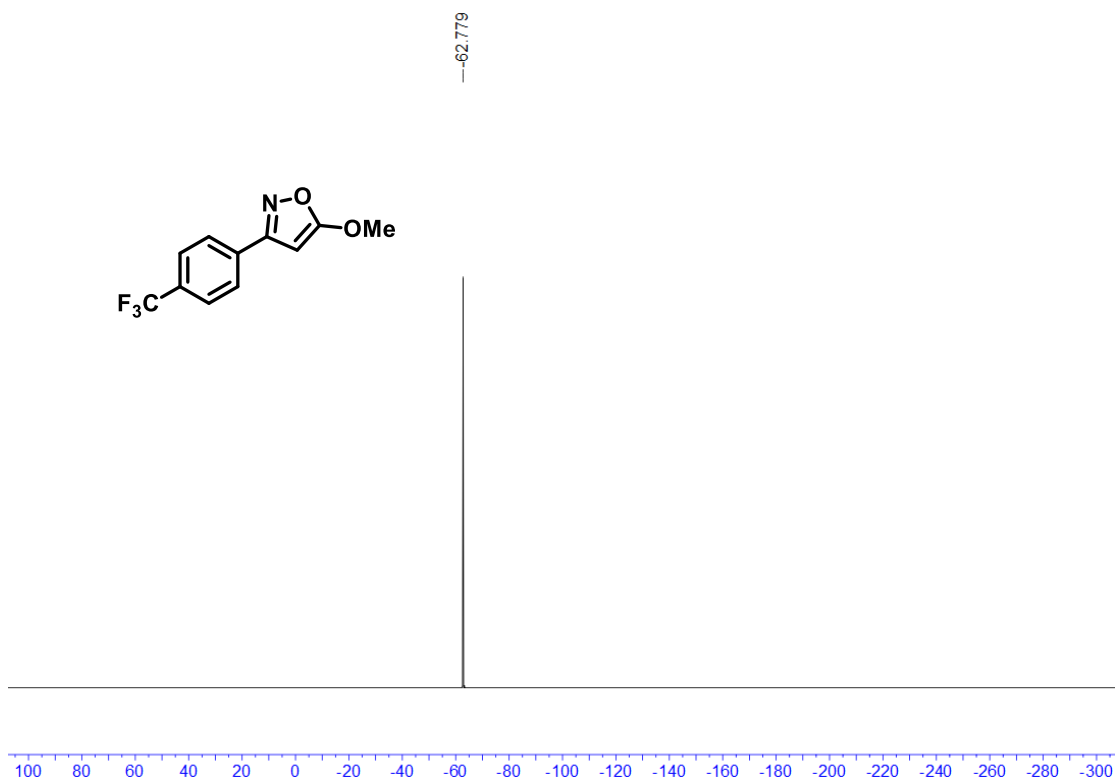
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **1j**



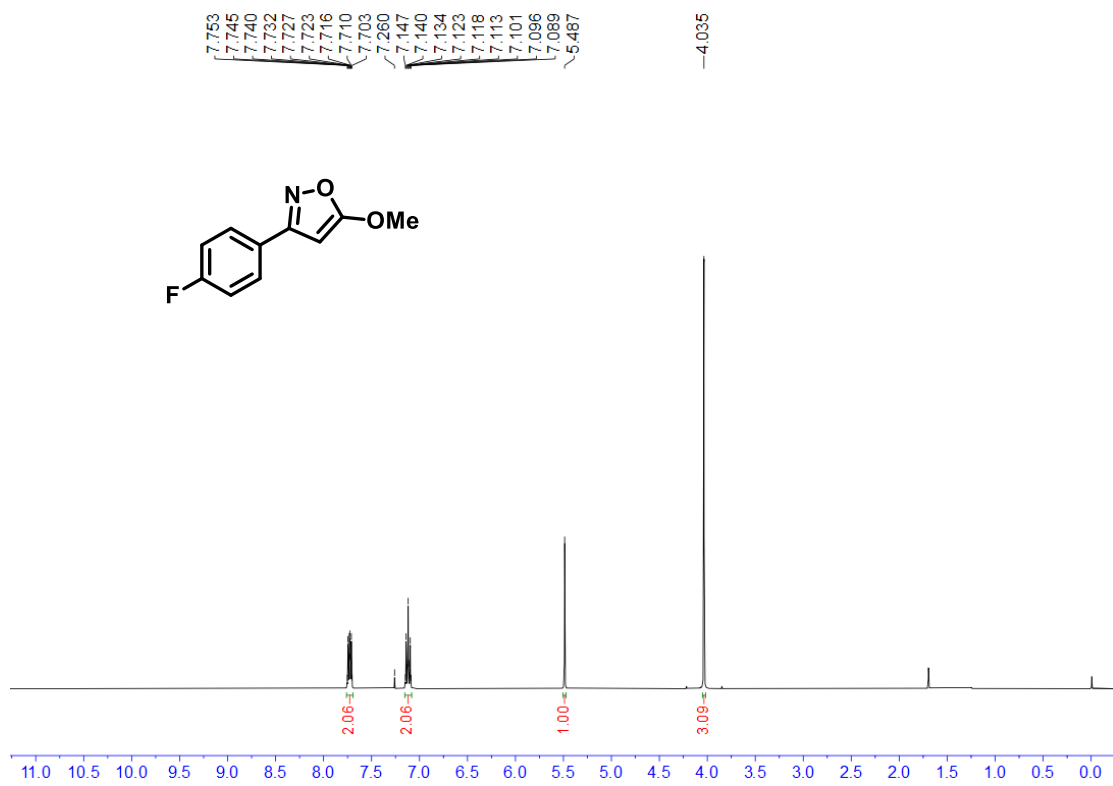
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **1j**



$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **1j**

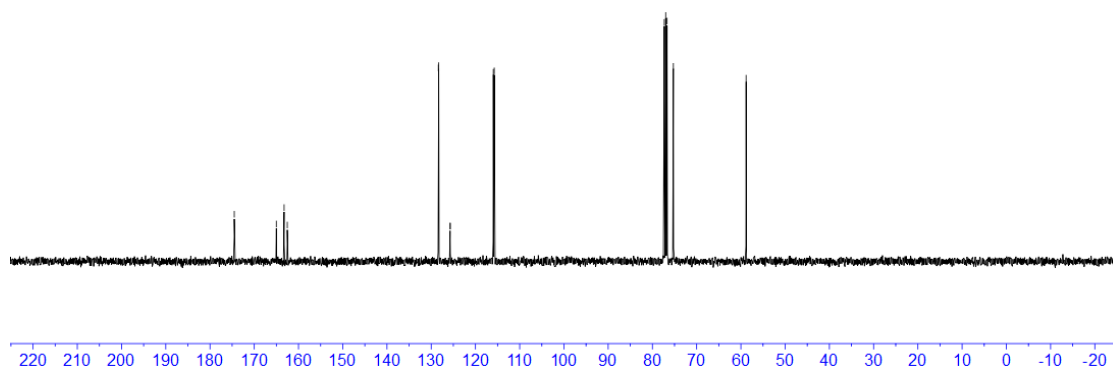
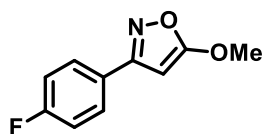


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **1k**



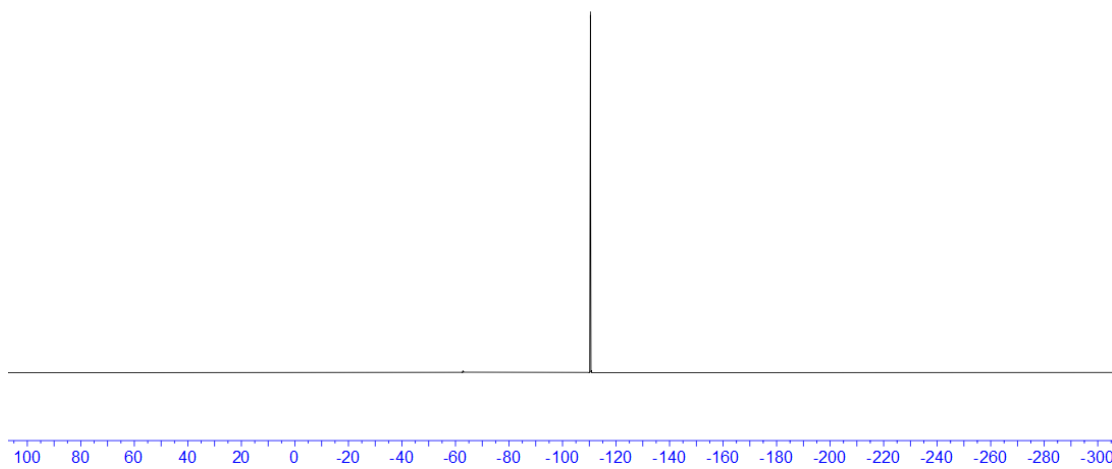
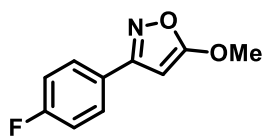
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **1k**

174.516  
165.012  
163.250  
162.534  
128.386  
128.301  
125.729  
125.696  
115.966  
115.750  
77.318  
77.000  
76.683  
75.265  
58.823

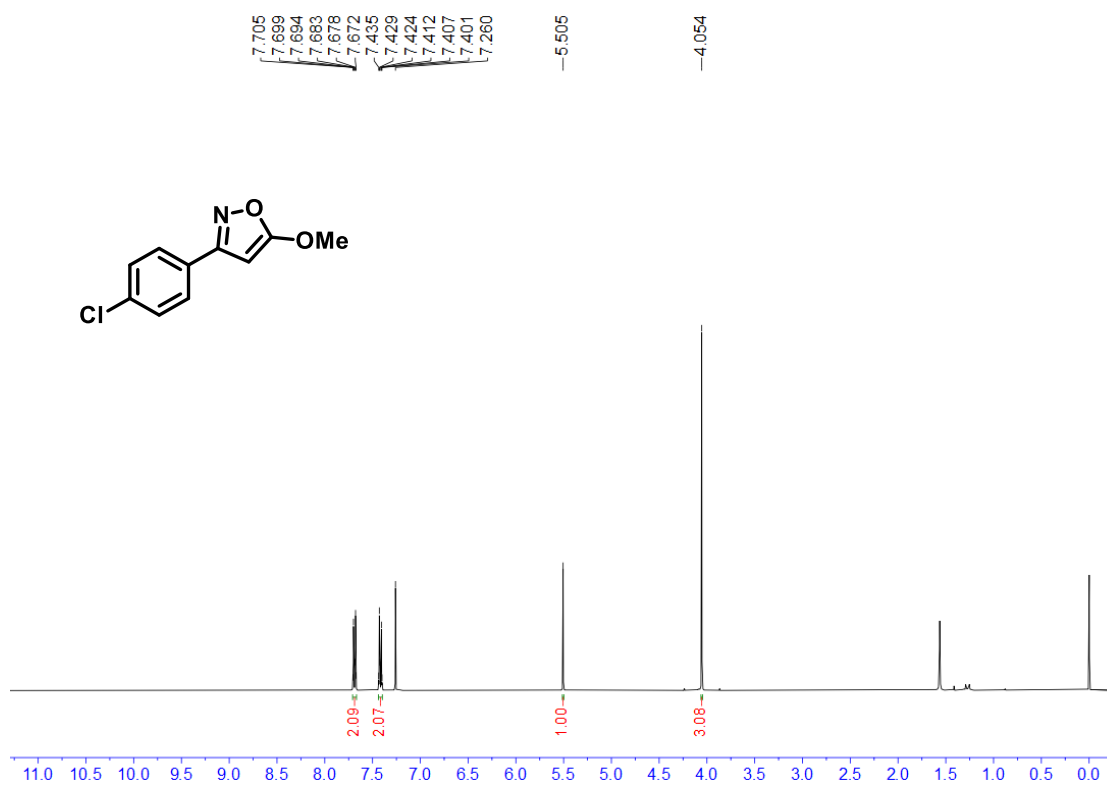


$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **1k**

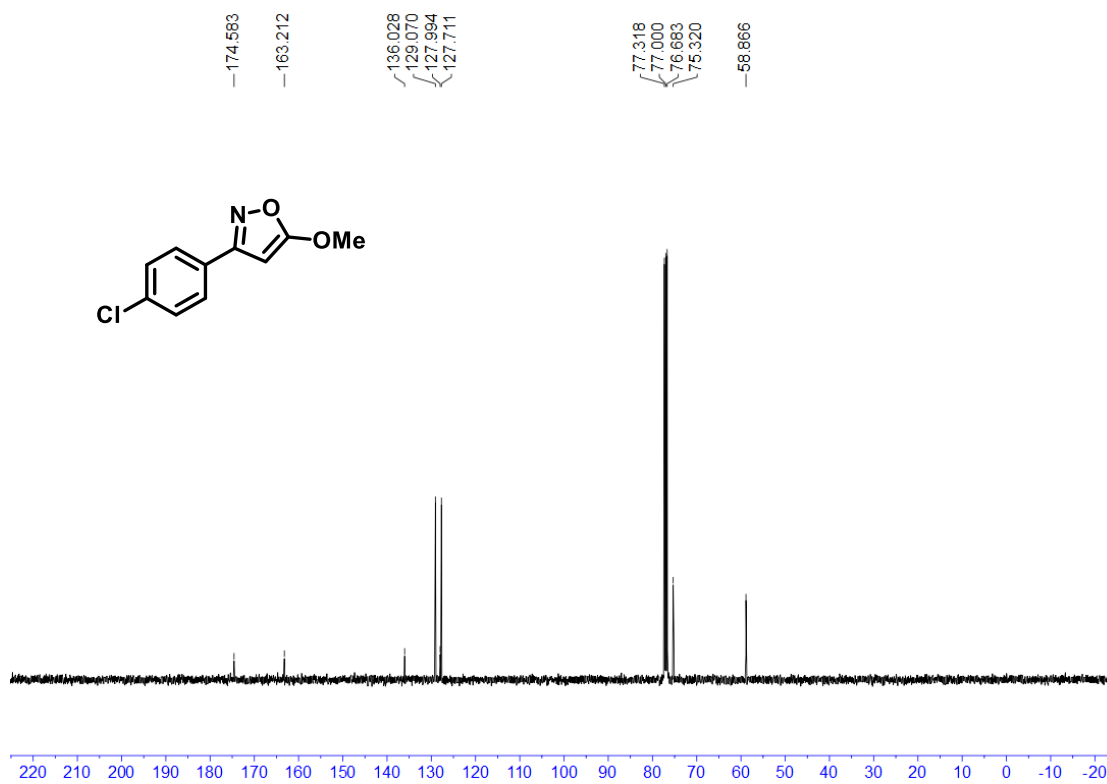
-110.413



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **11**

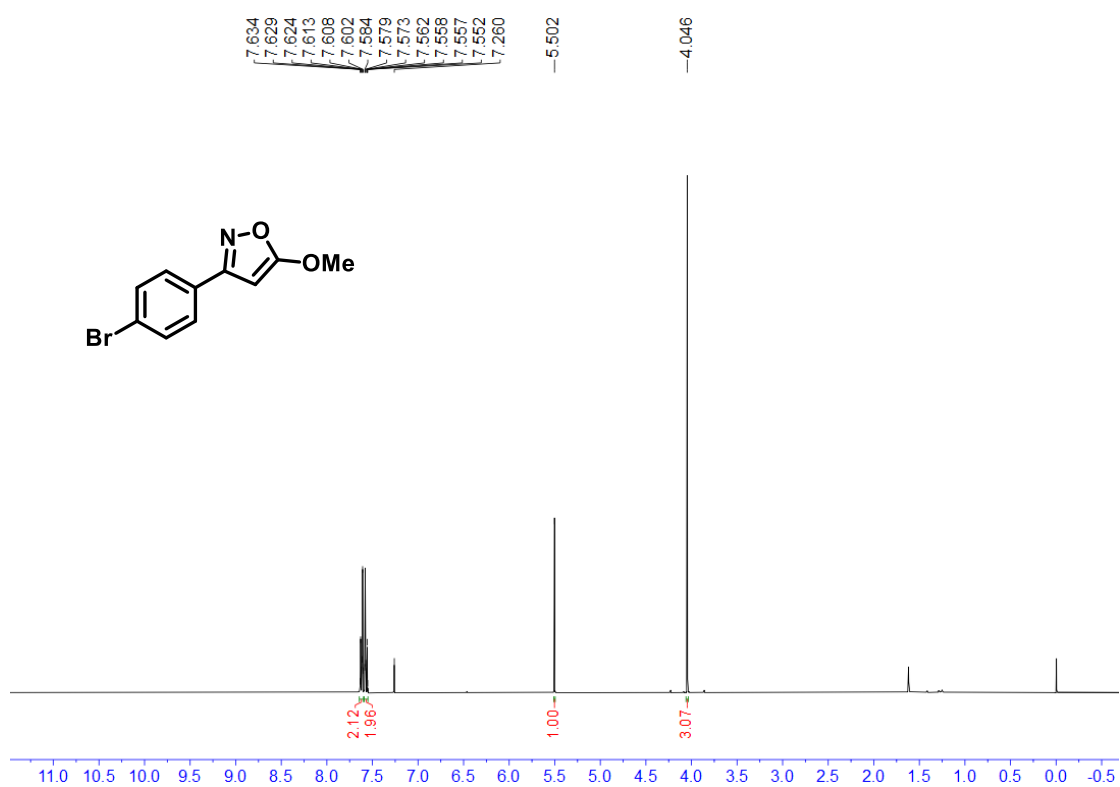


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **11**

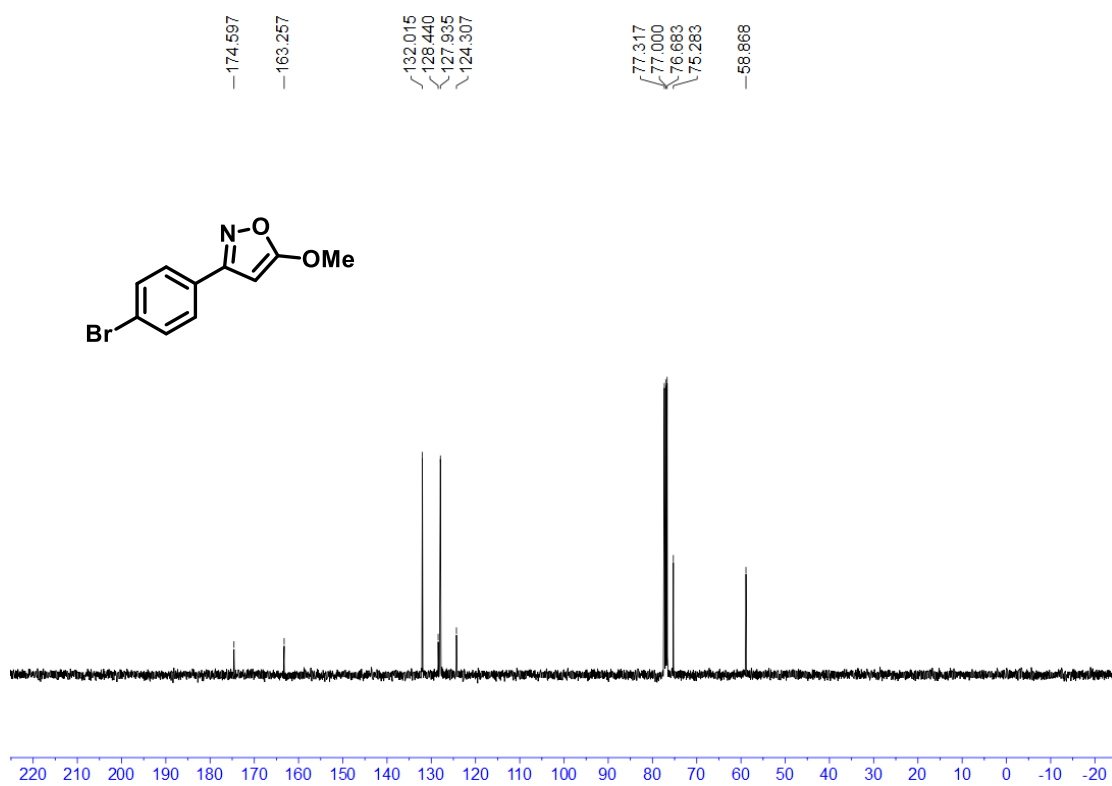




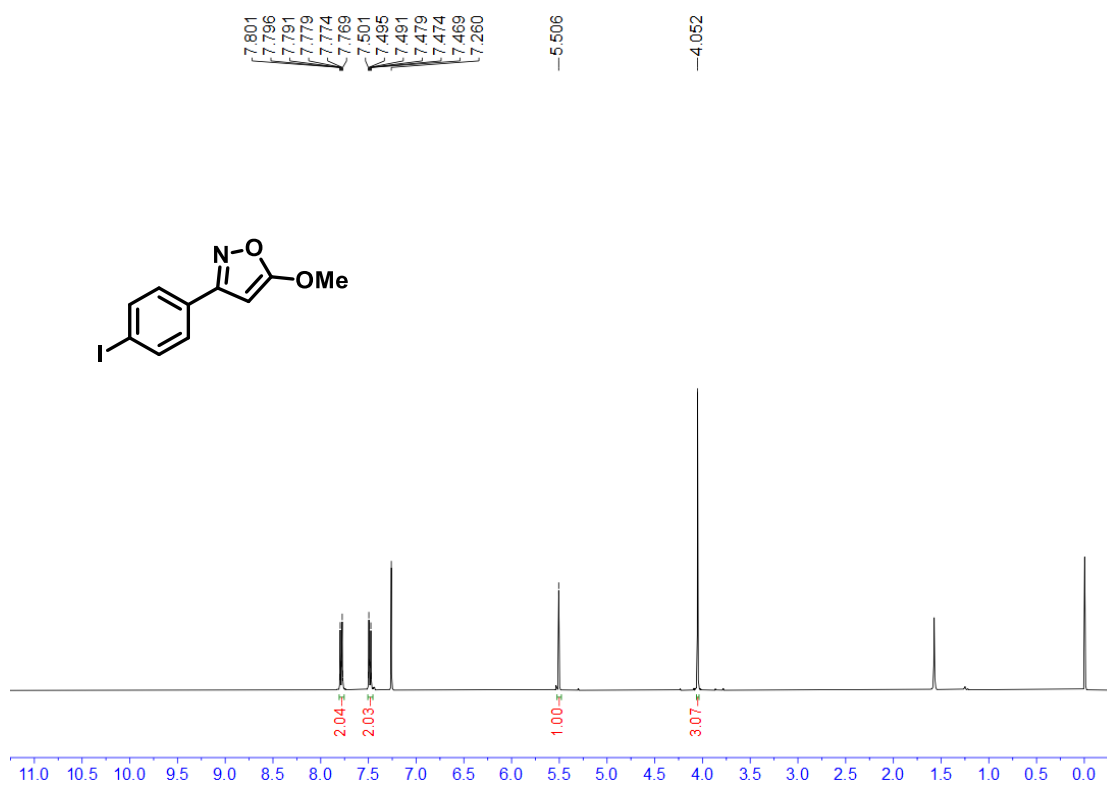
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **1m**



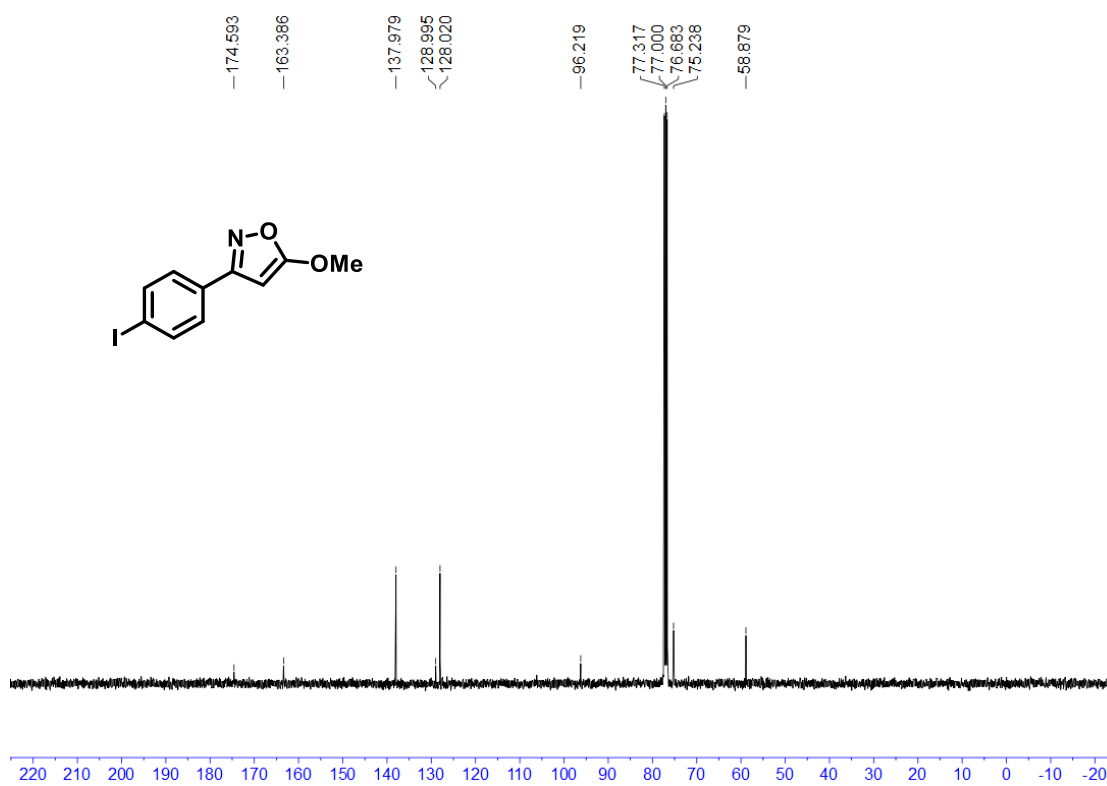
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **1m**



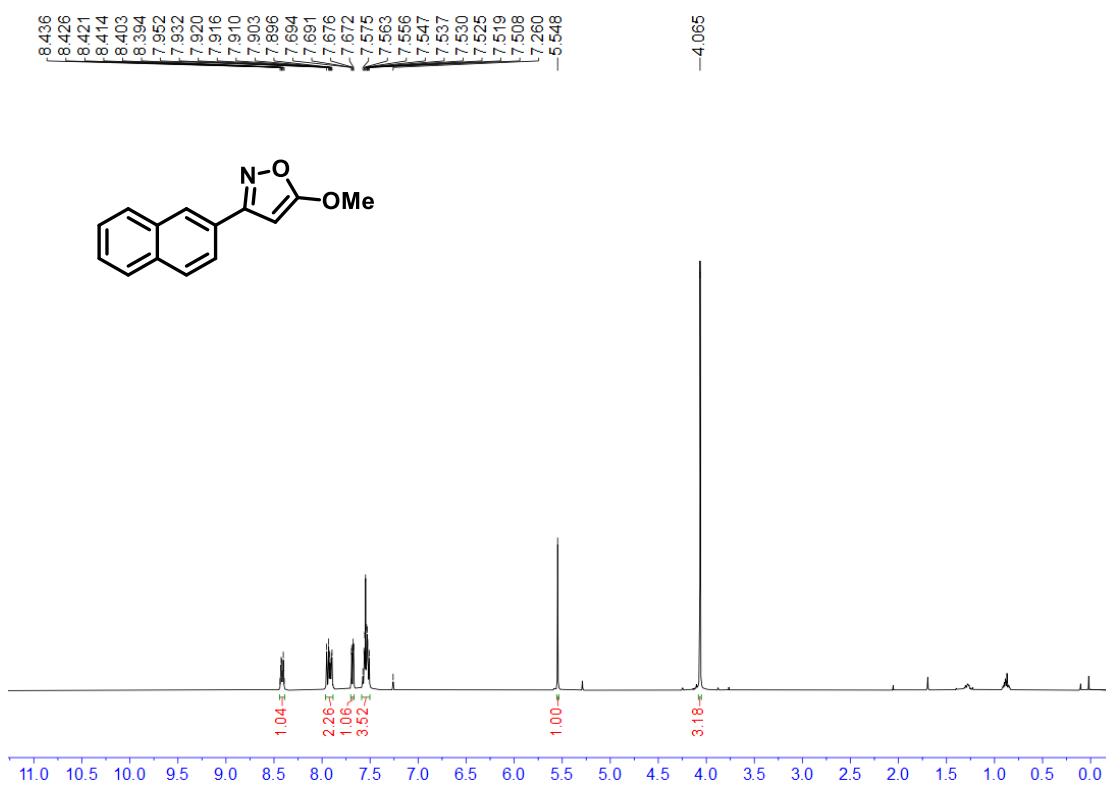
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **1n**



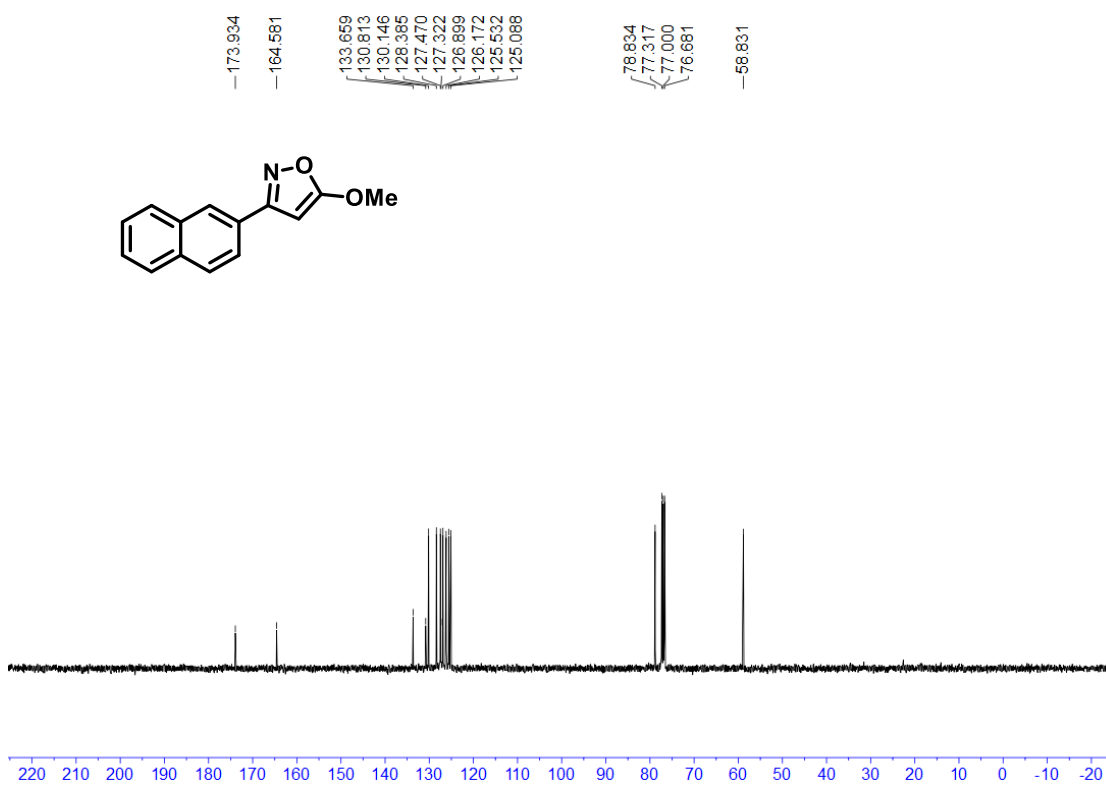
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **1n**



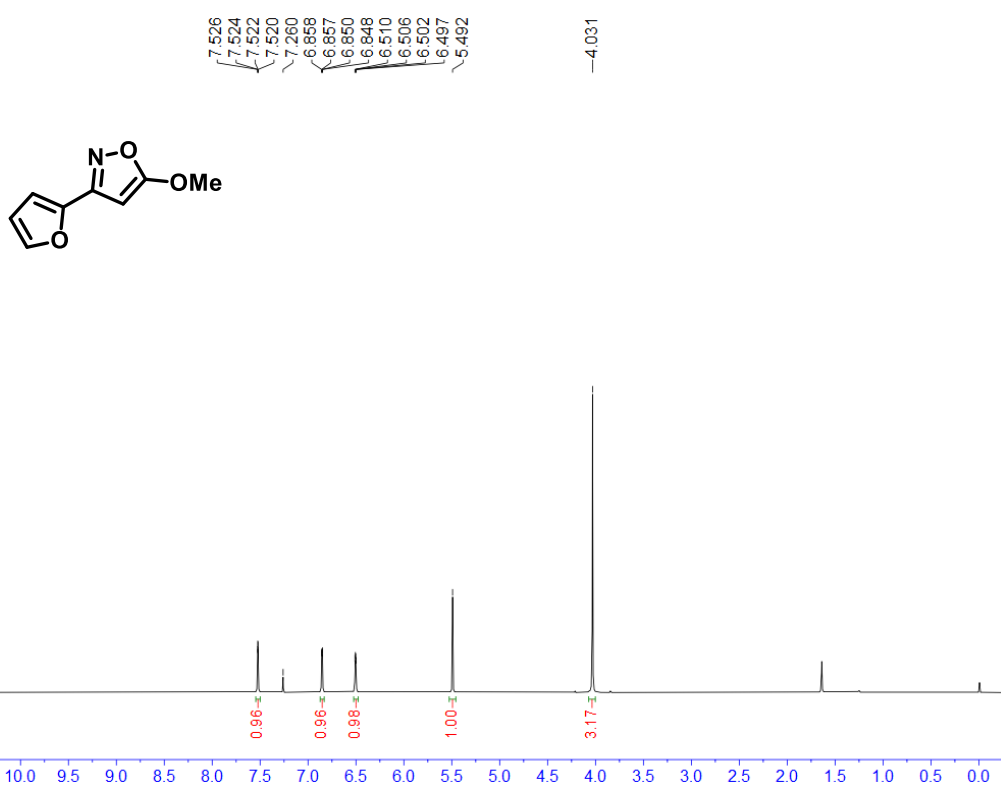
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **1o**



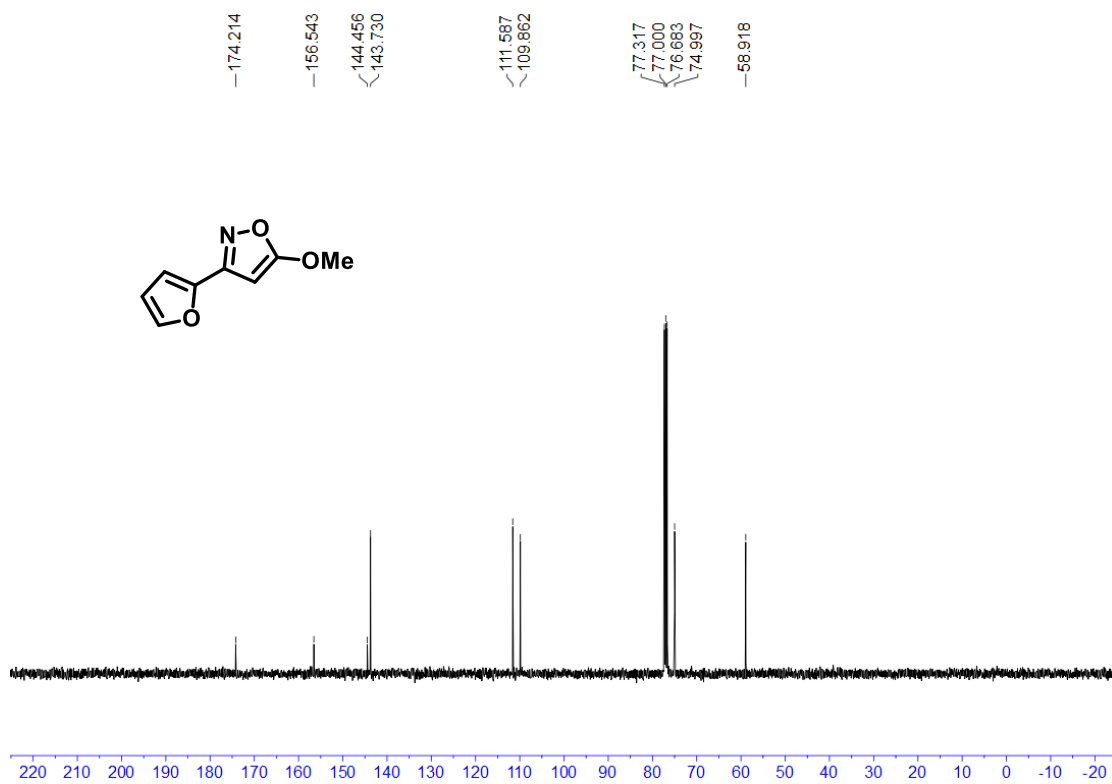
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **1o**



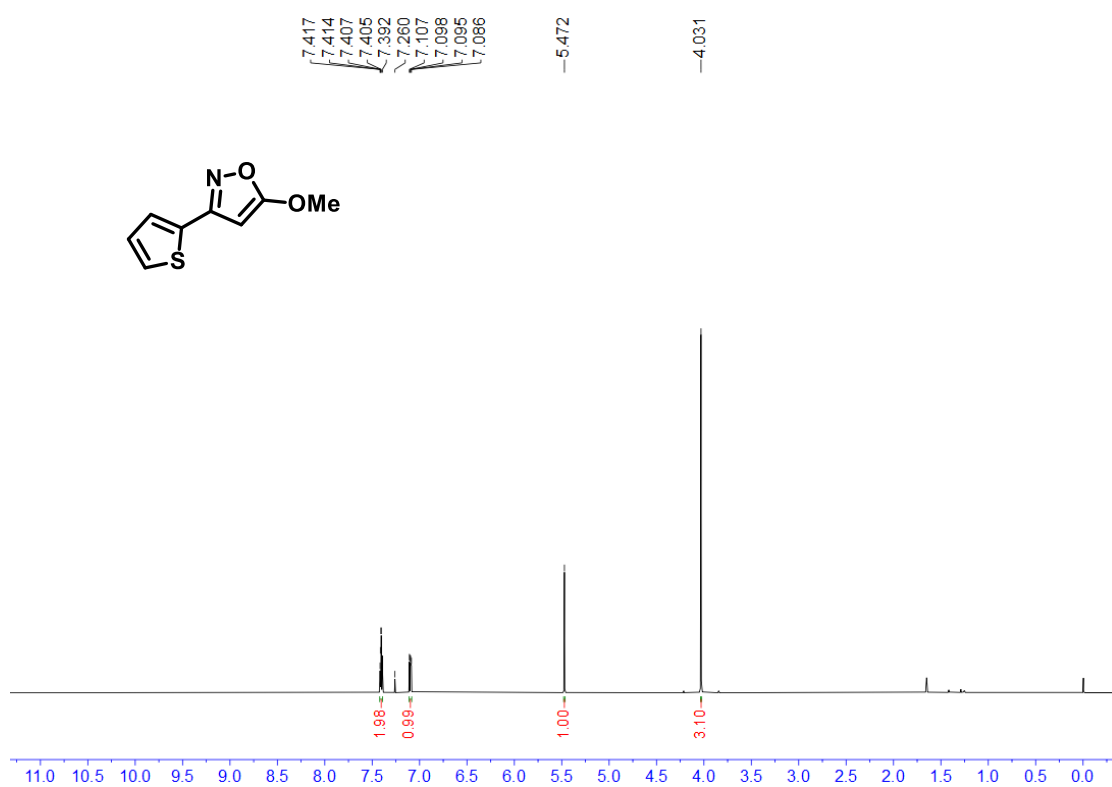
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **1p**



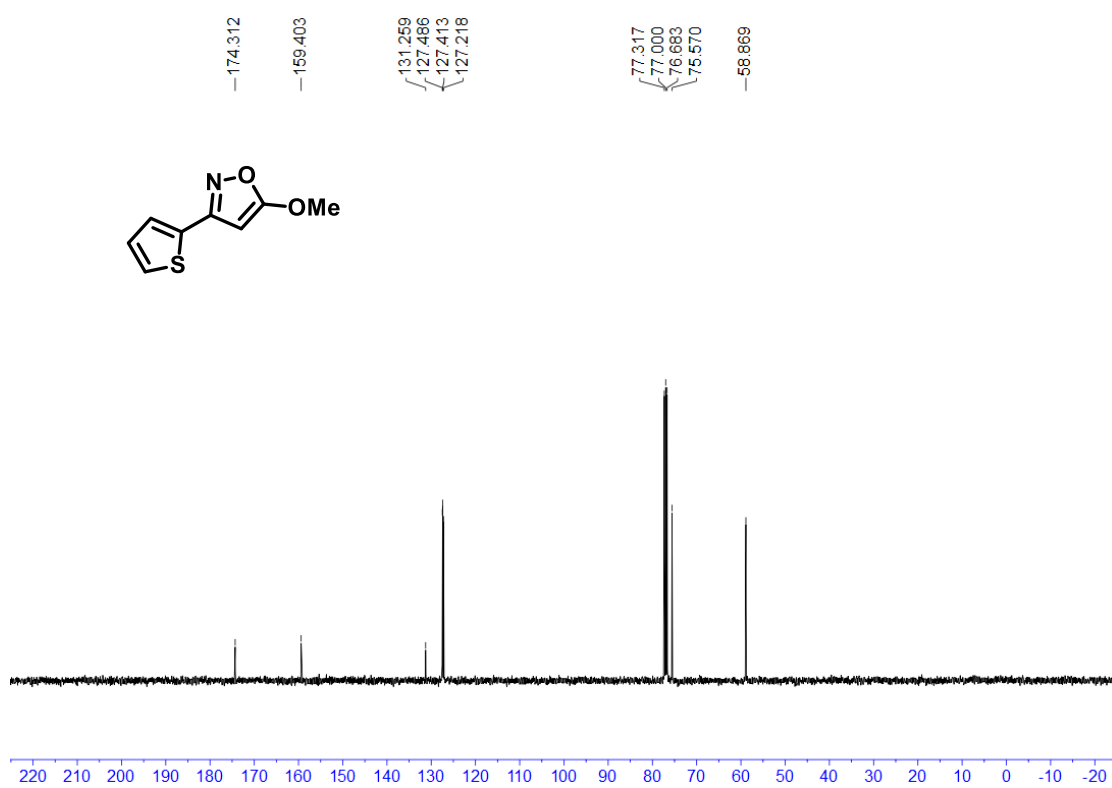
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **1p**



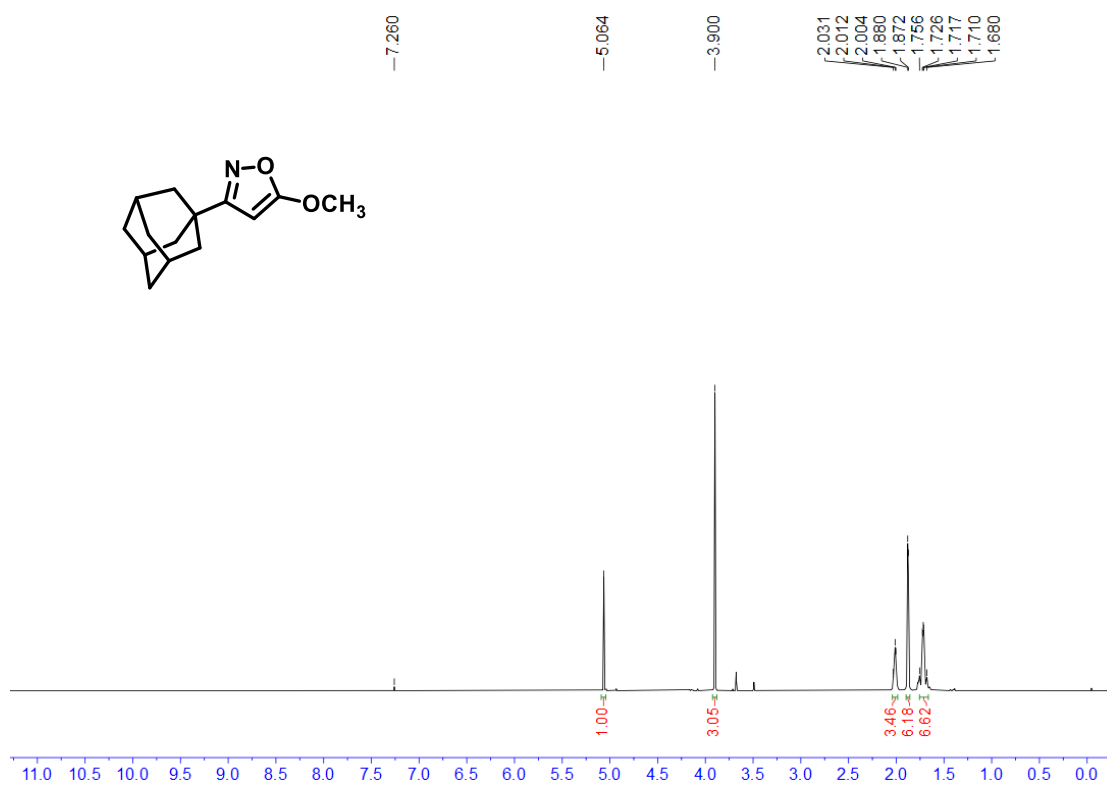
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **1q**



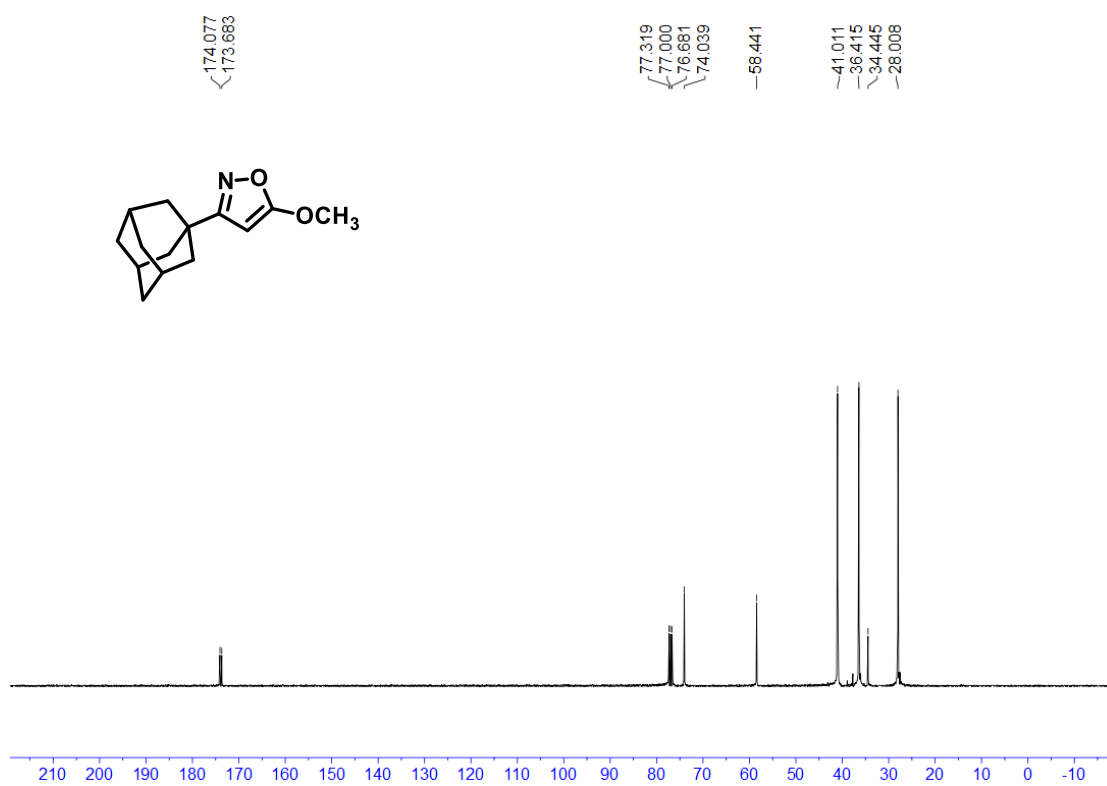
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **1q**



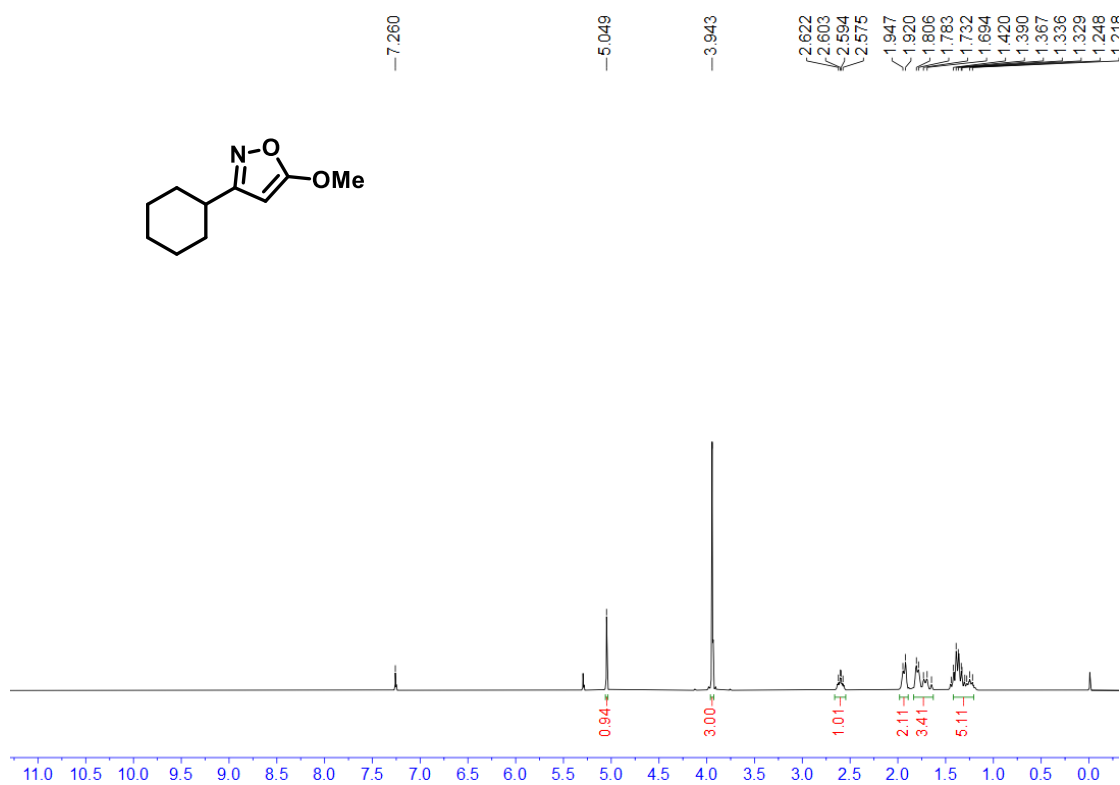
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **1r**



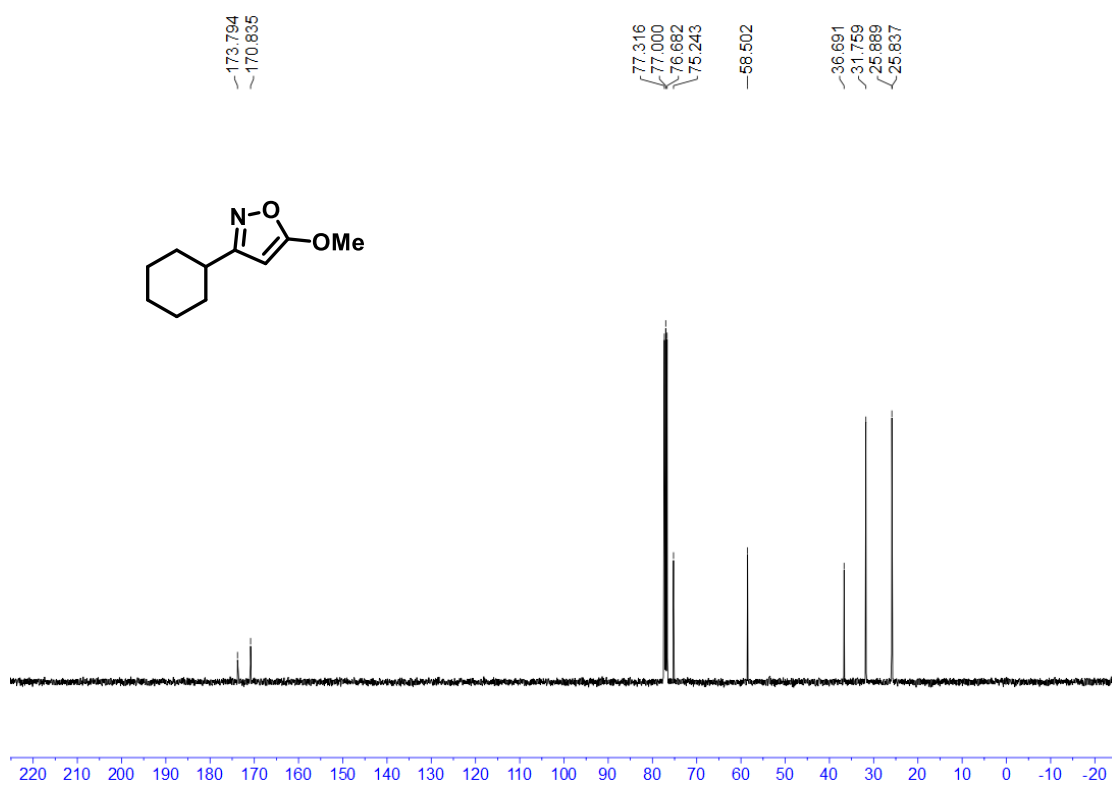
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **1r**



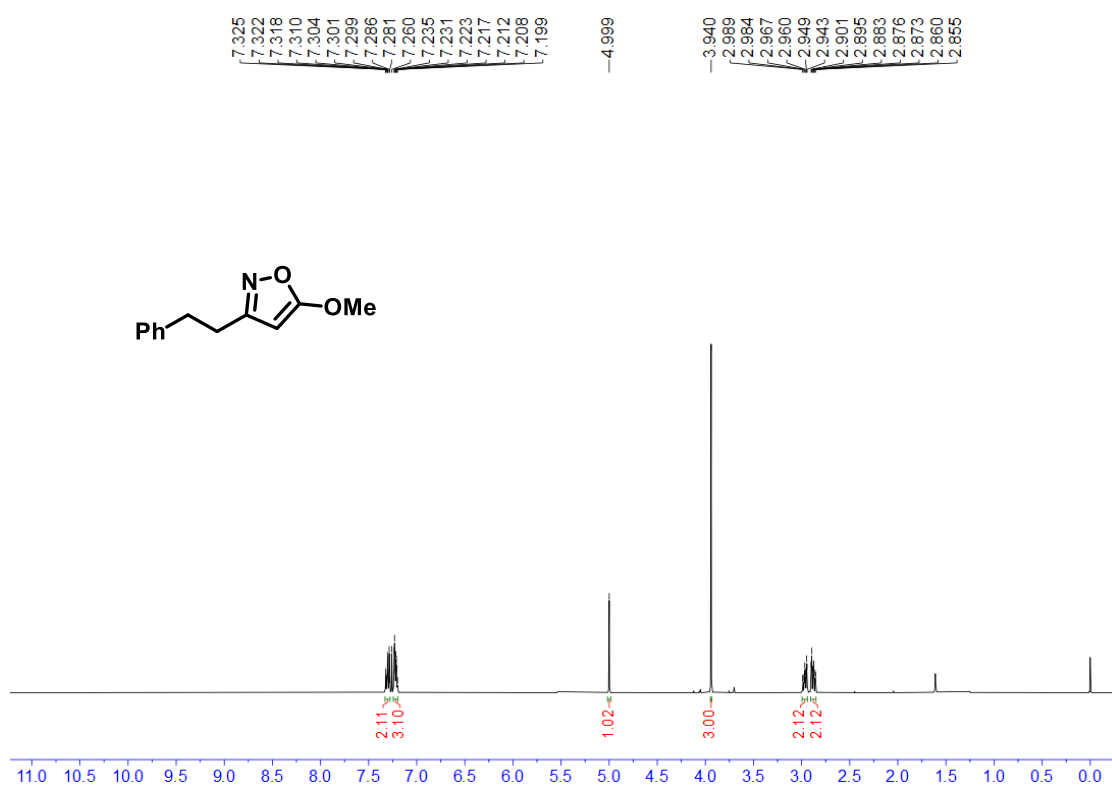
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **1s**



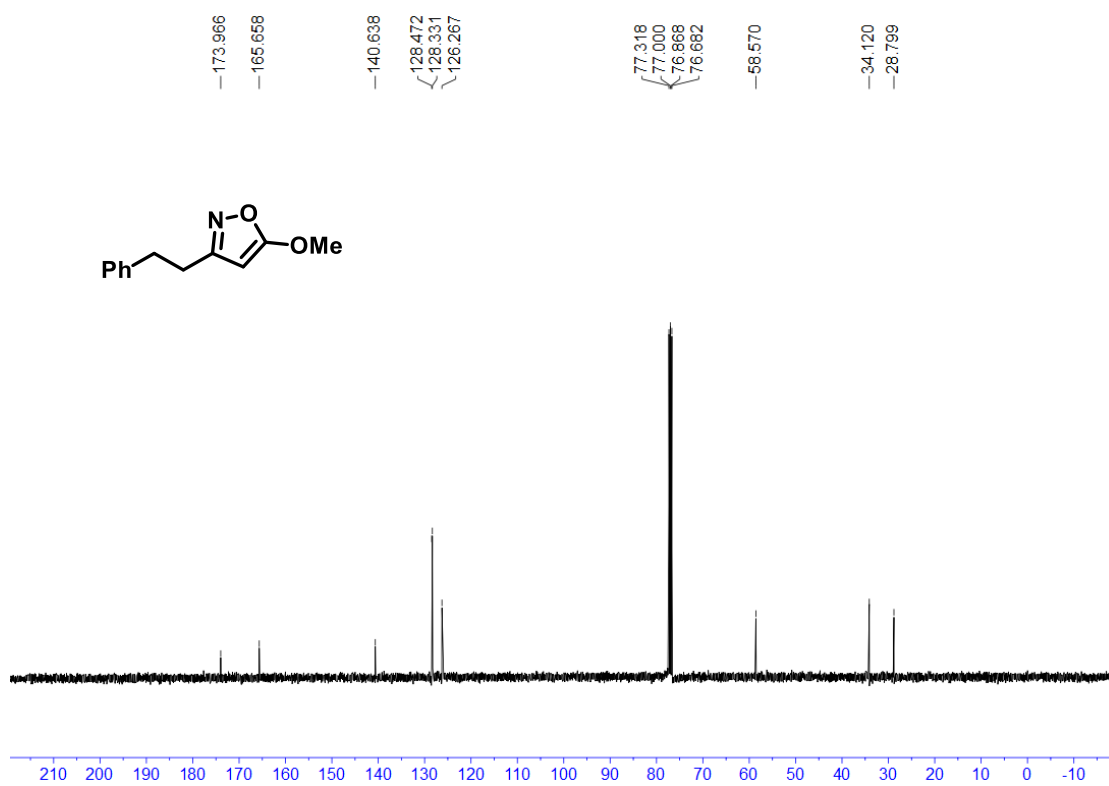
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **1s**



<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **1t**



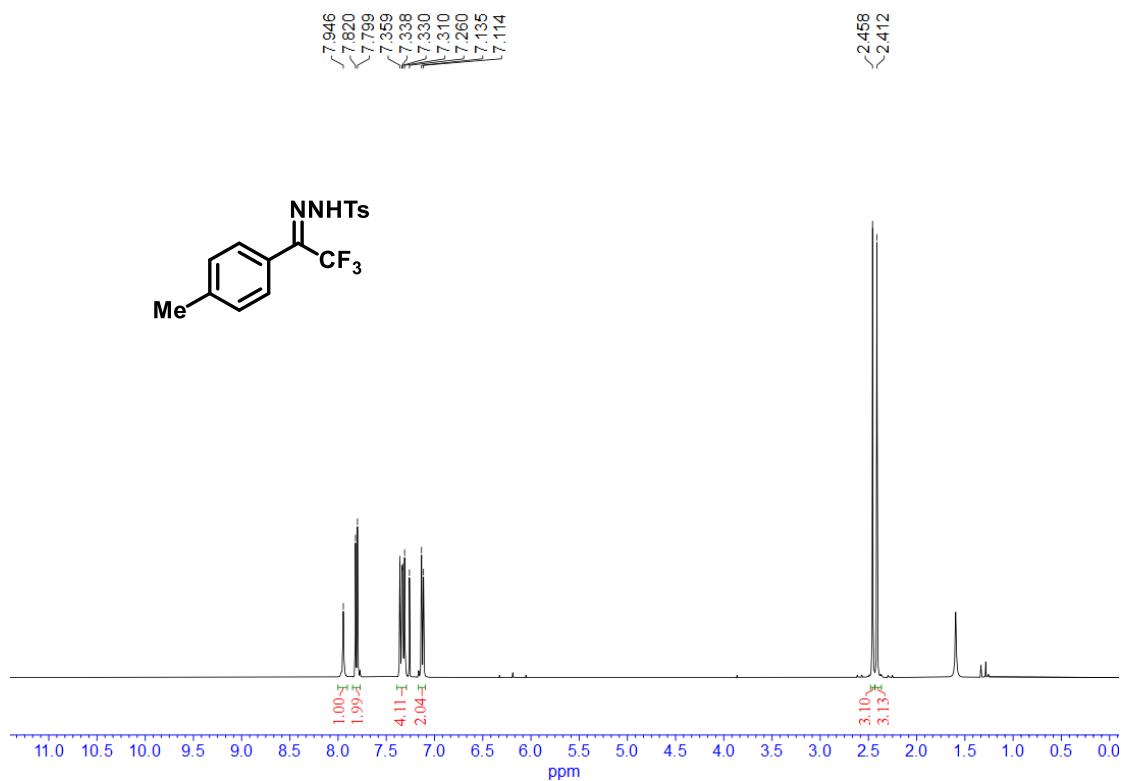
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **1t**



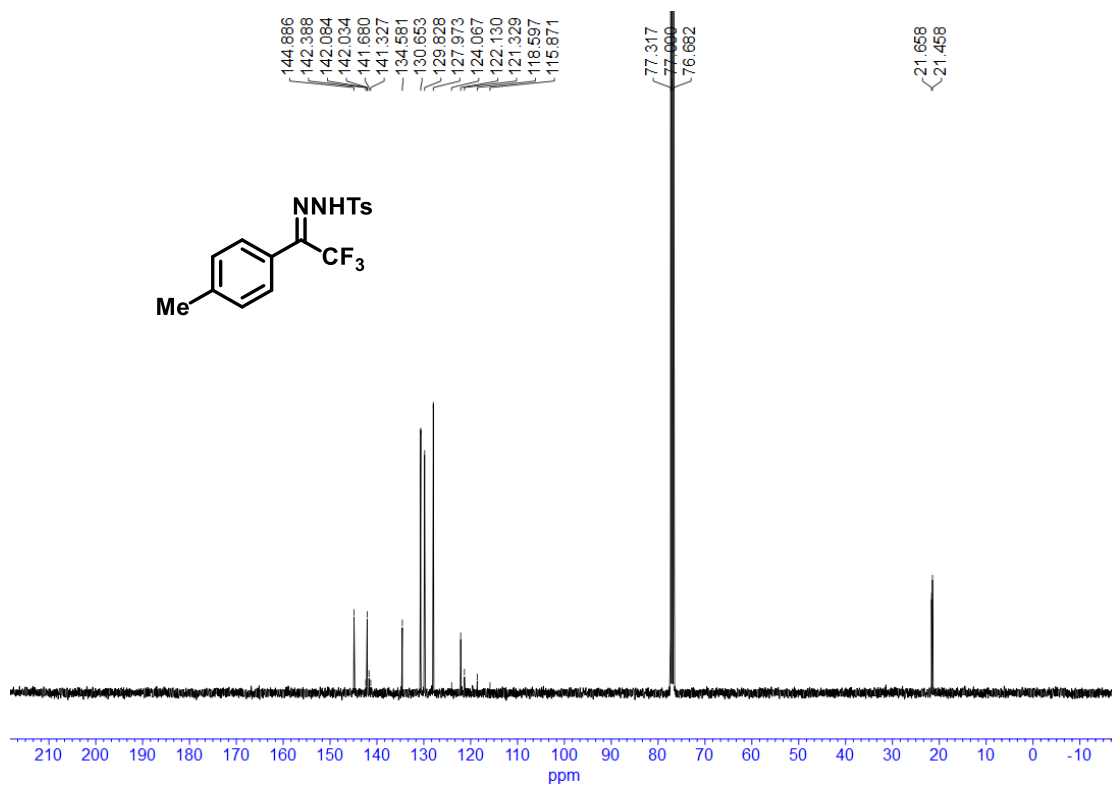


### 3.2 NMR spectra for hydrazones

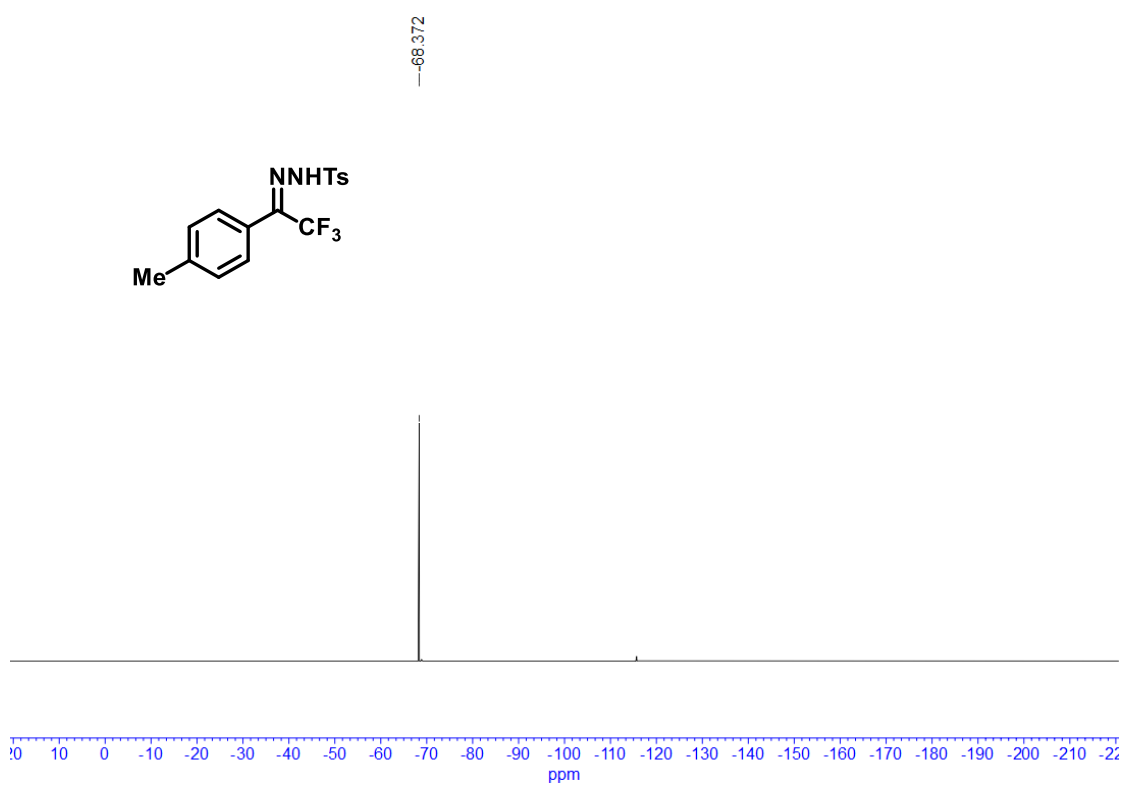
$^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **2b**



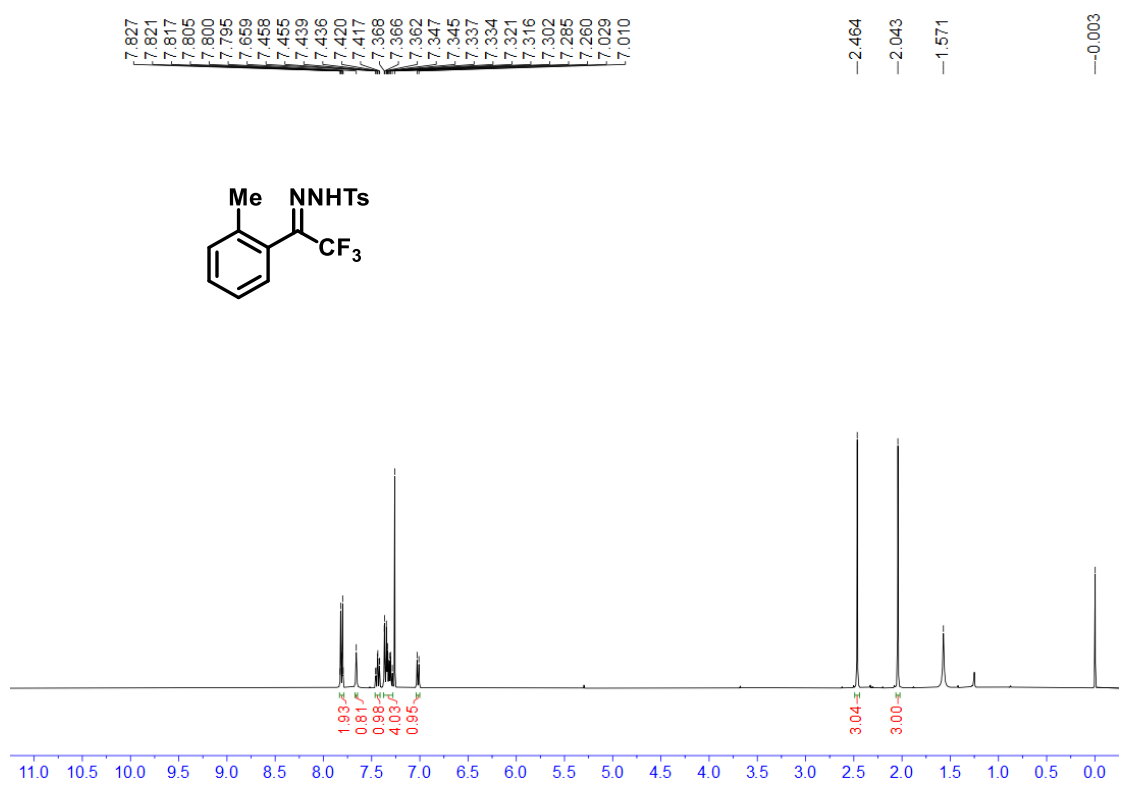
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **2b**



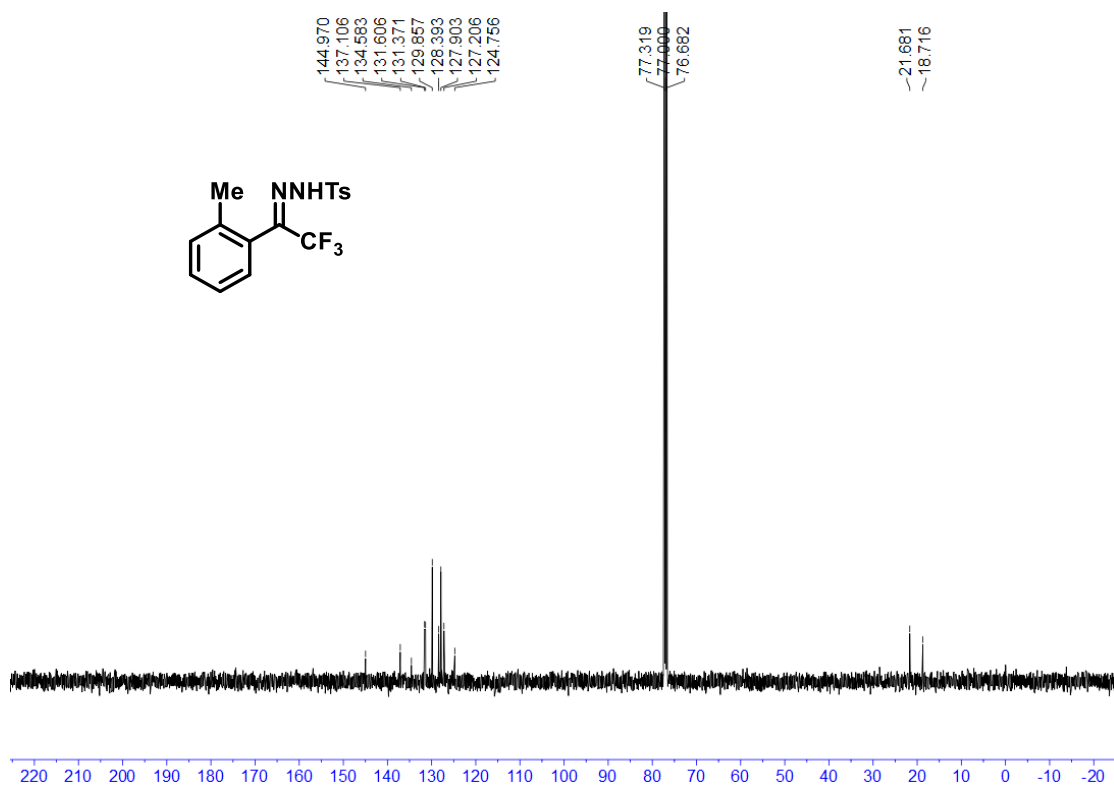
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **2b**



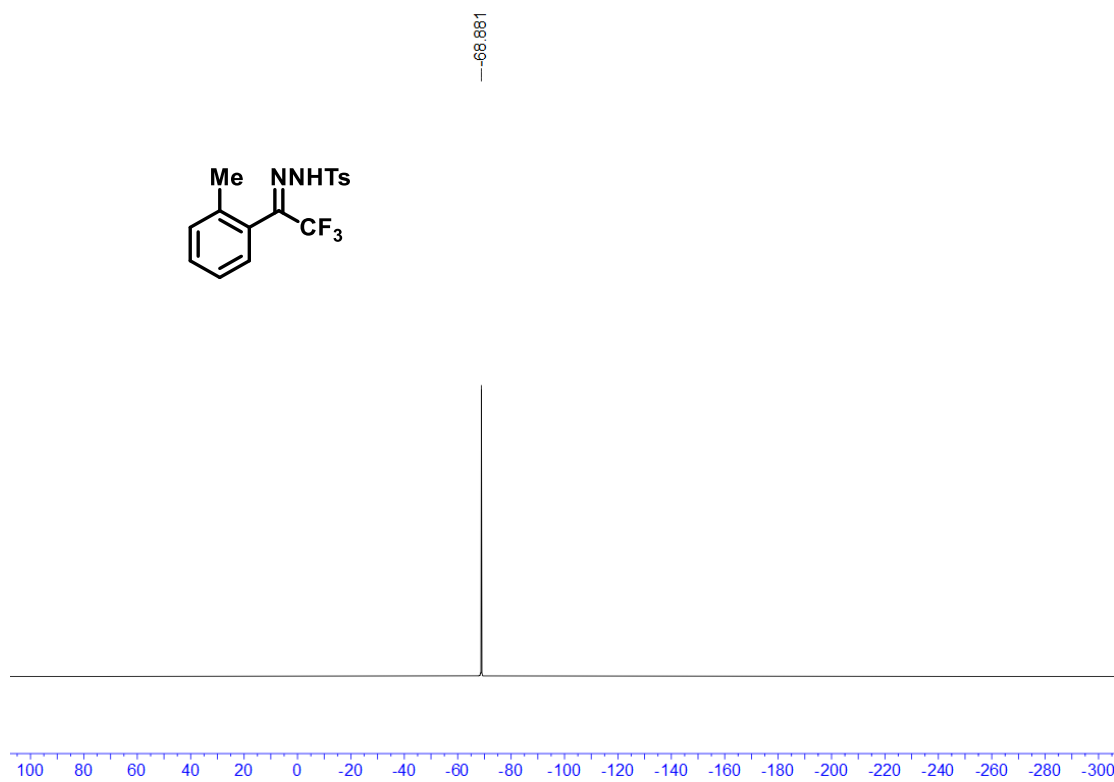
$^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **2c**



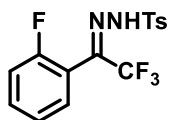
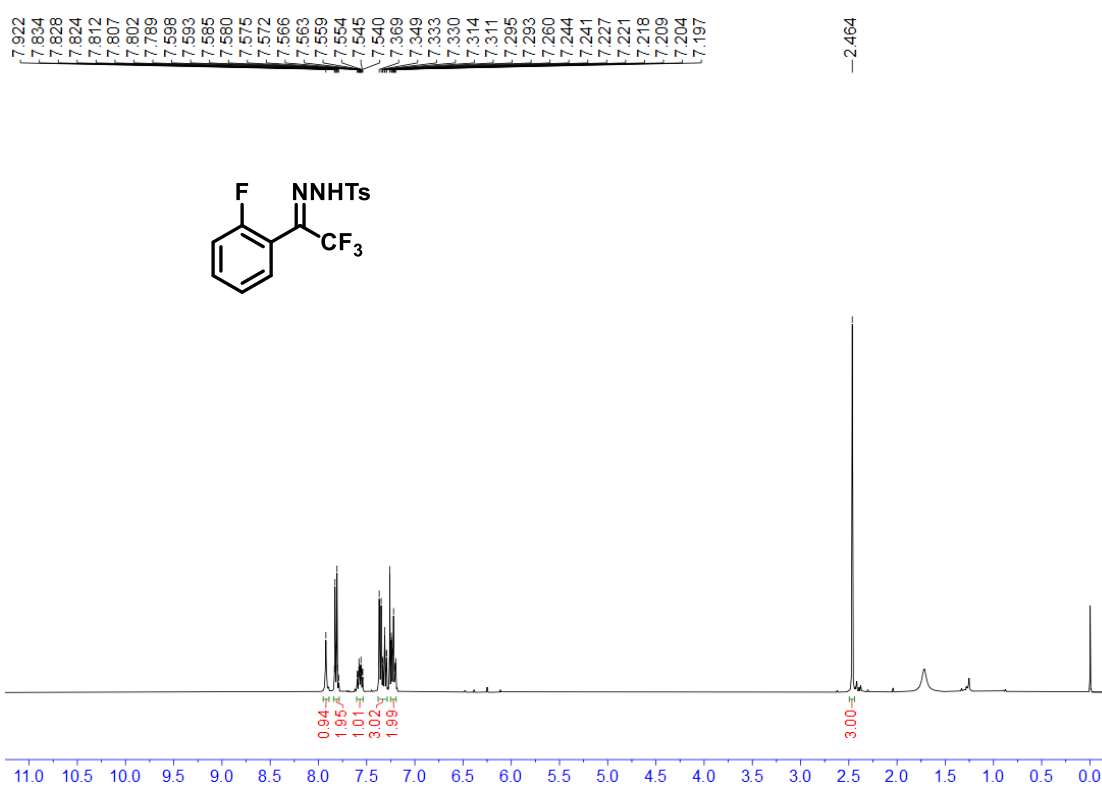
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **2c**



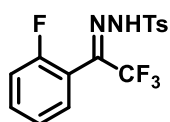
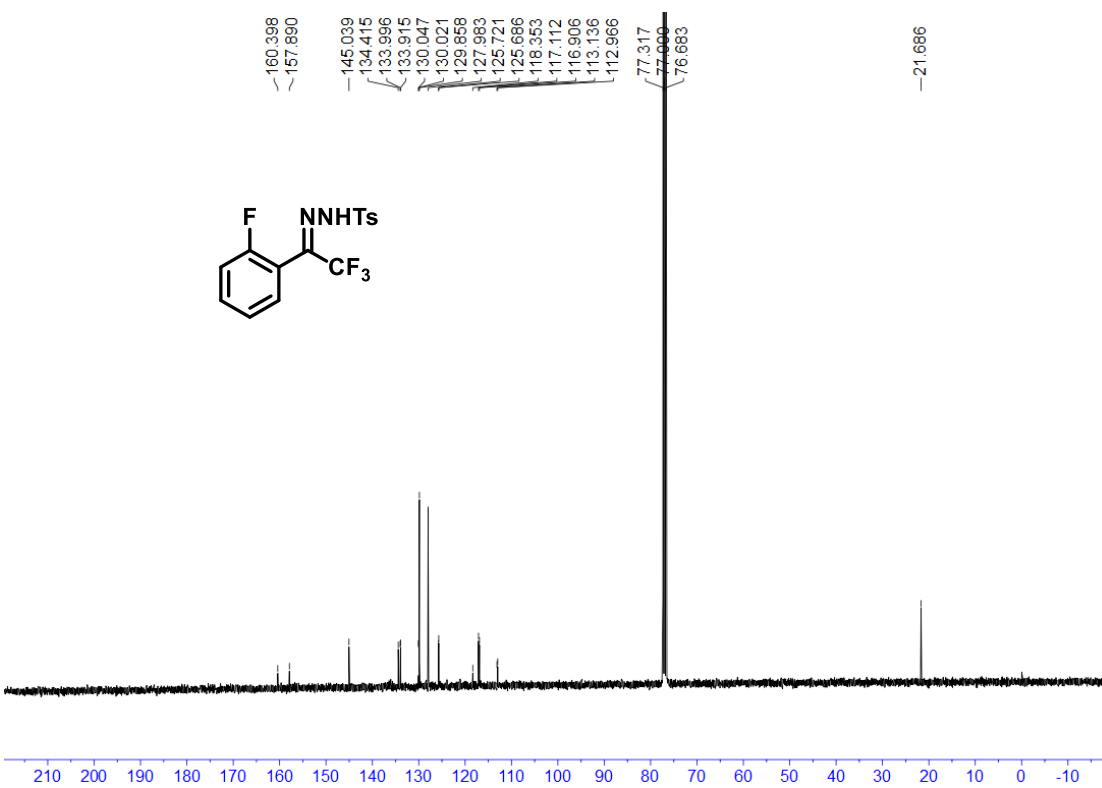
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **2c**



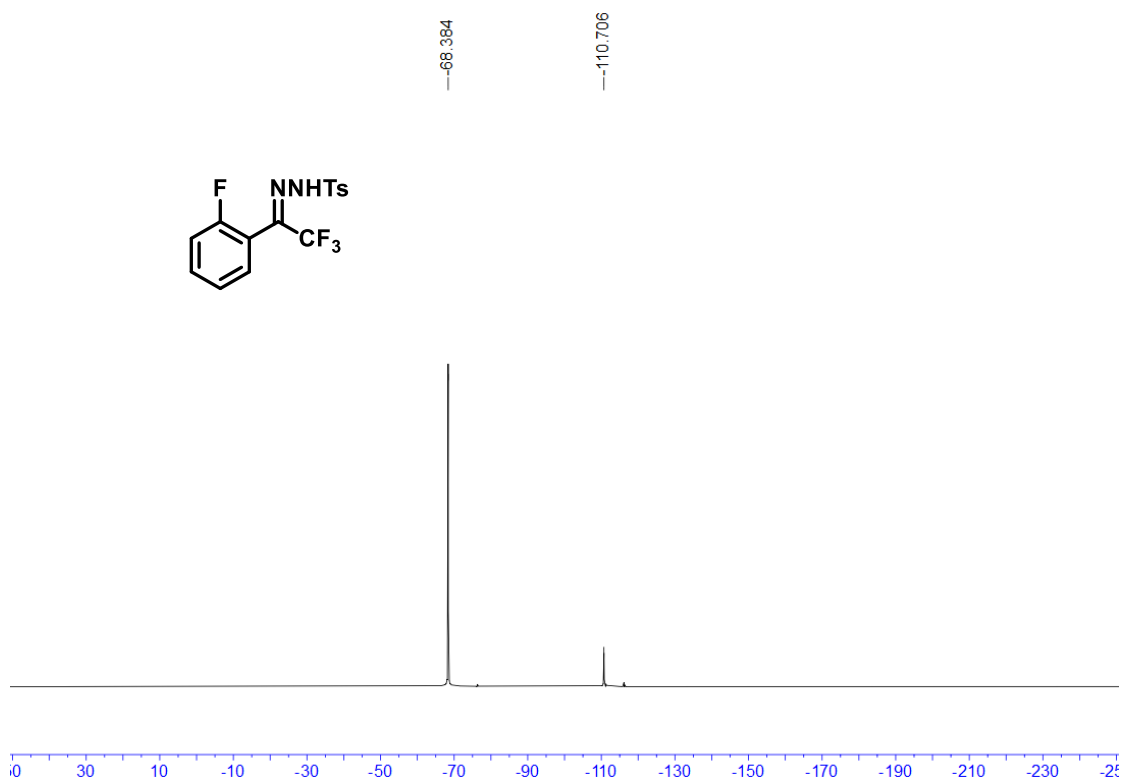
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **2h**



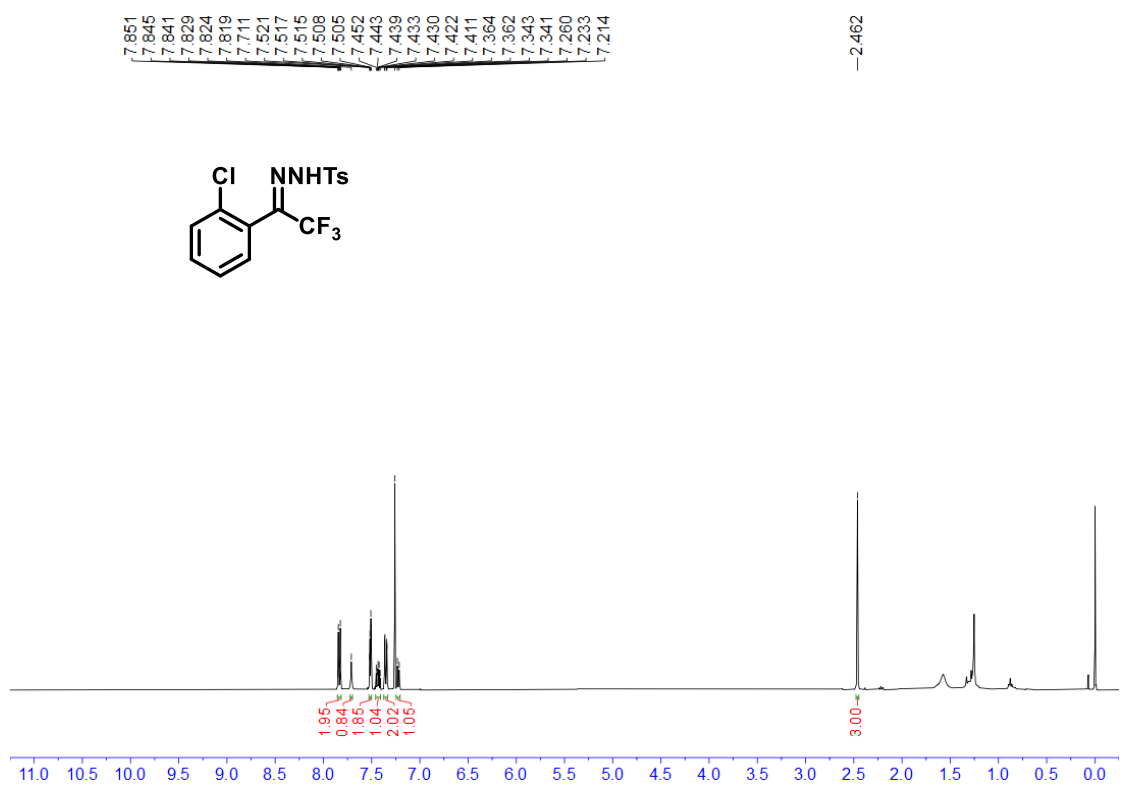
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **2h**



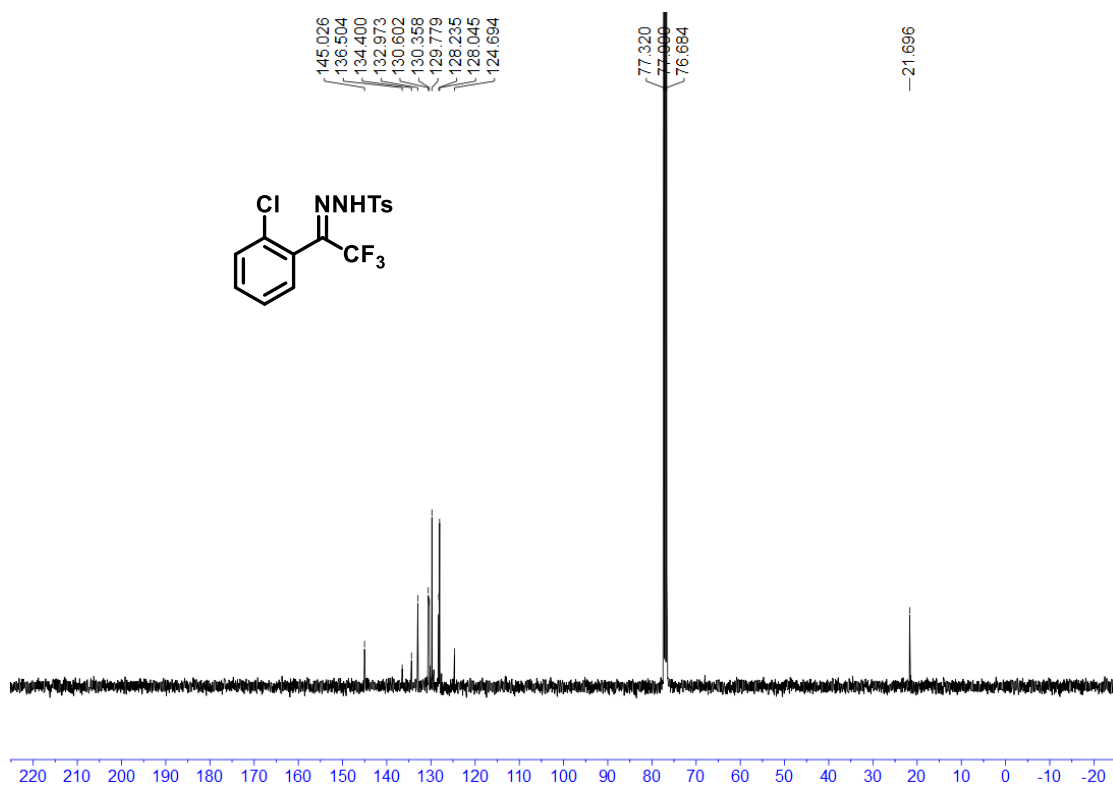
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **2h**



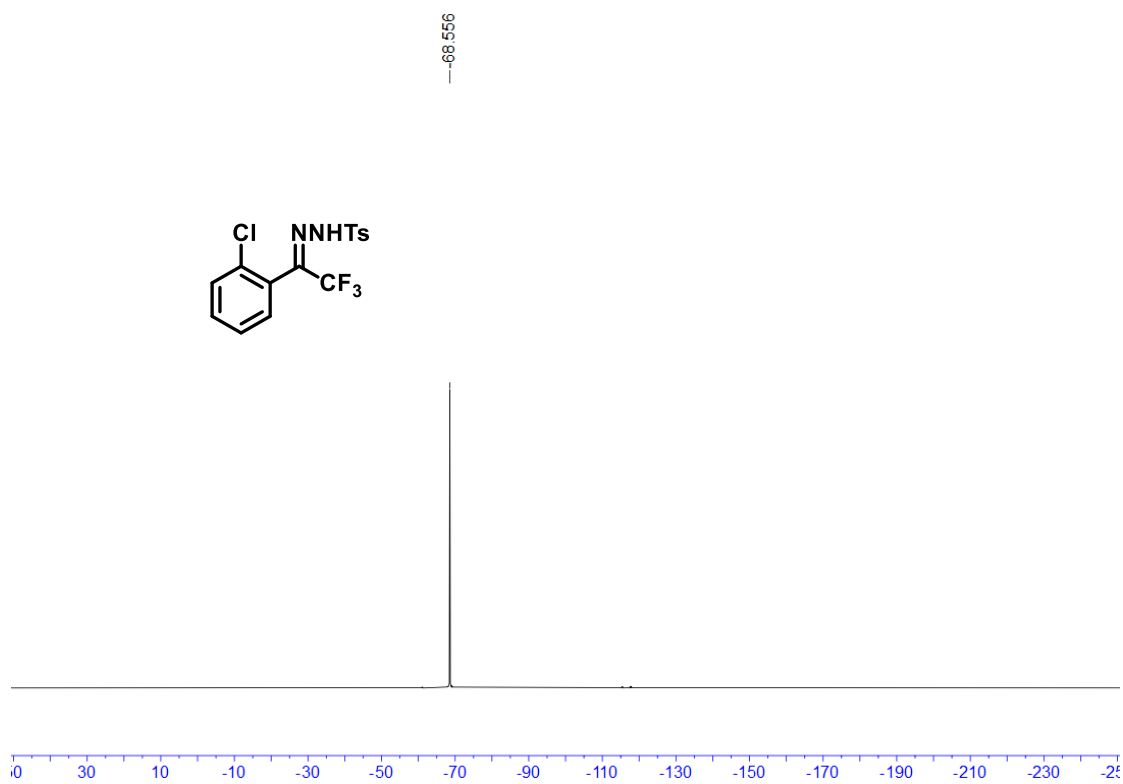
$^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **2j**



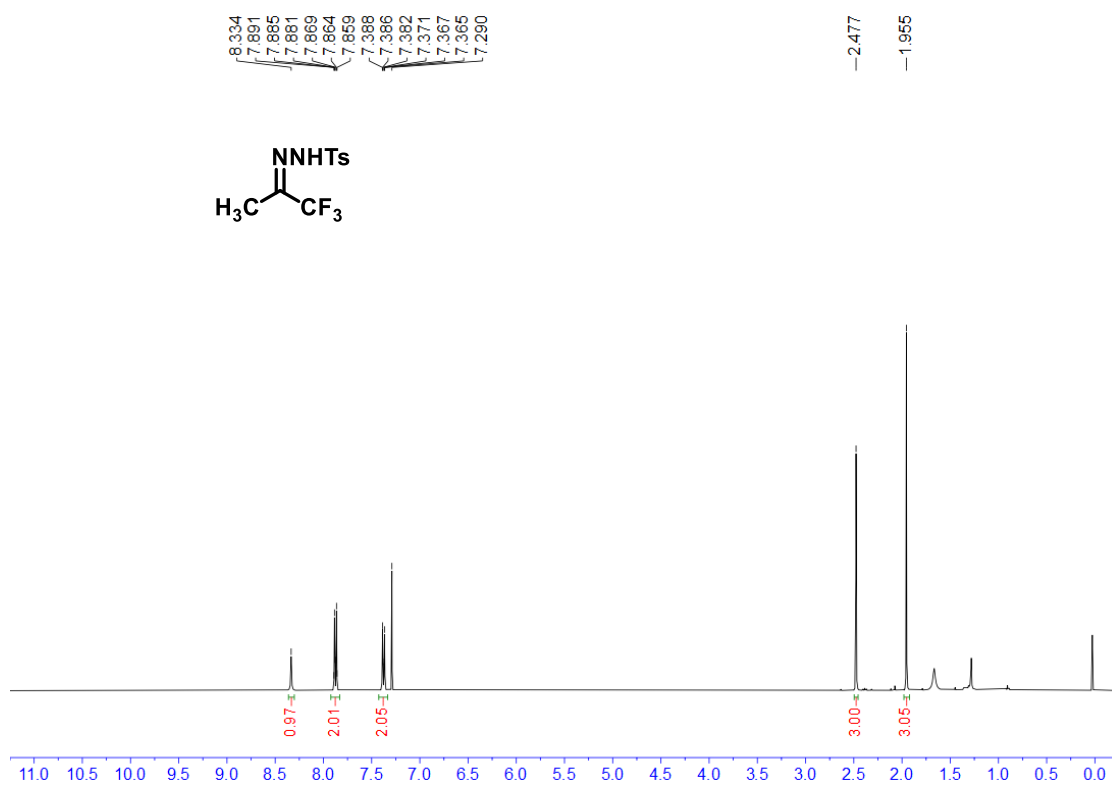
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **2j**



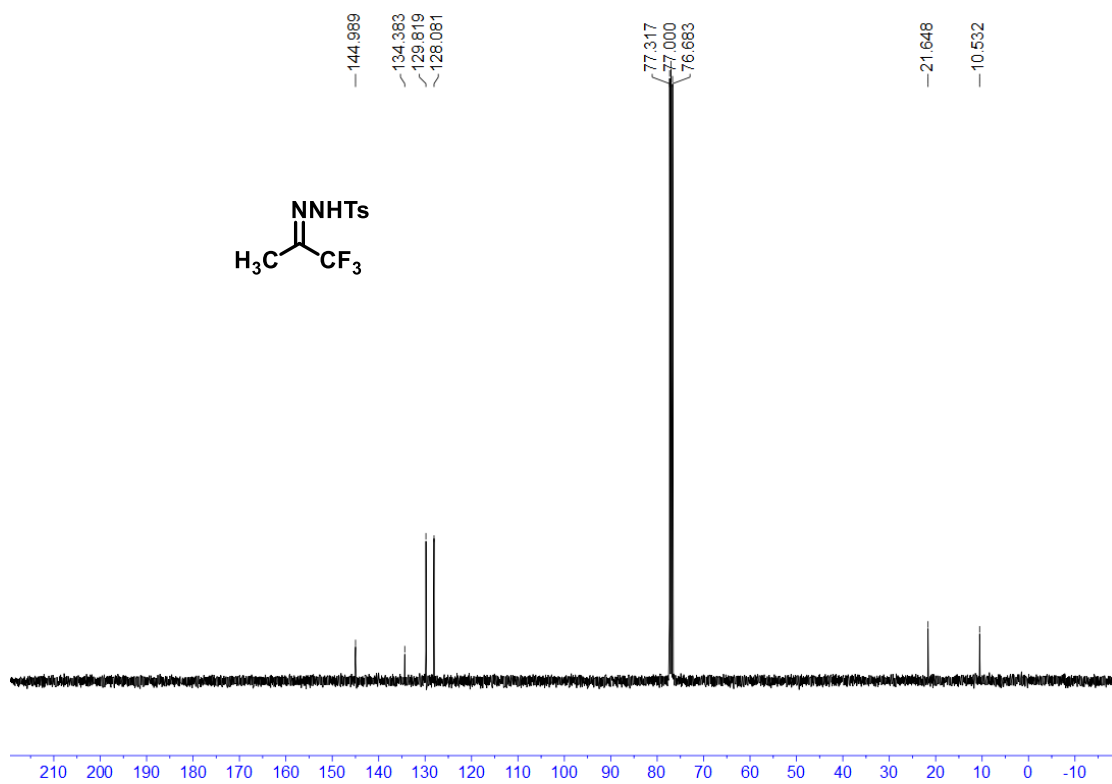
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **2j**



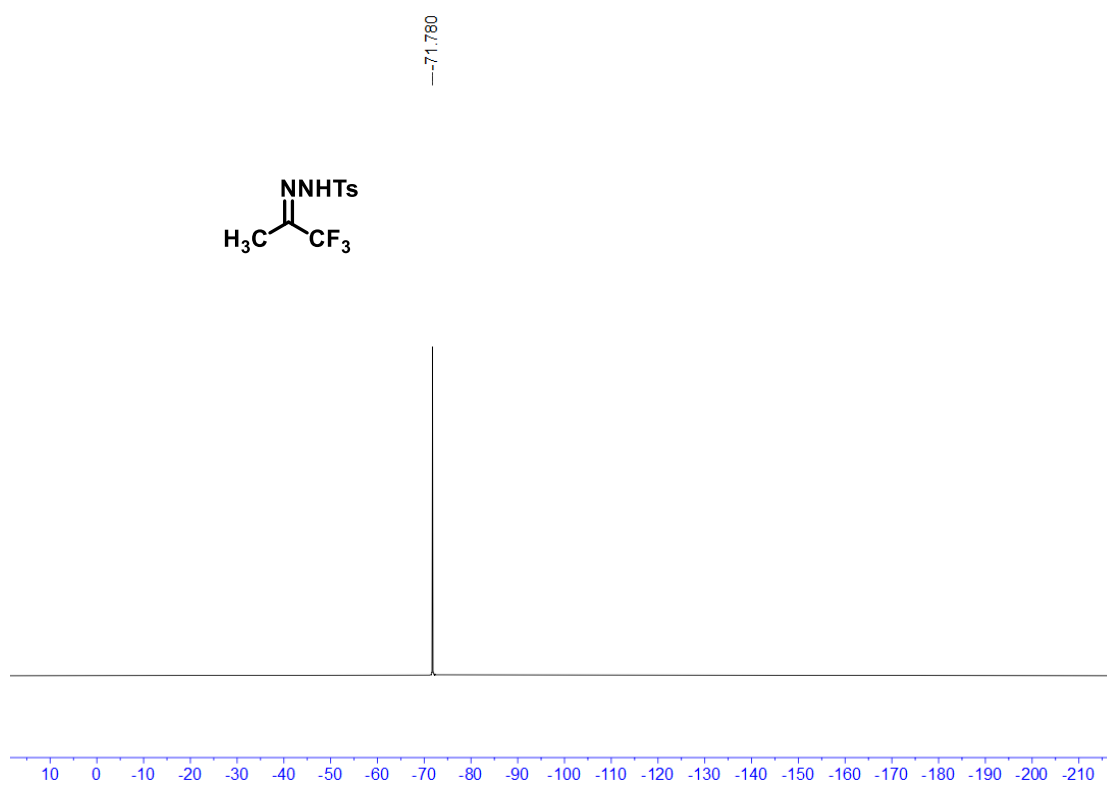
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **2n**



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **2n**

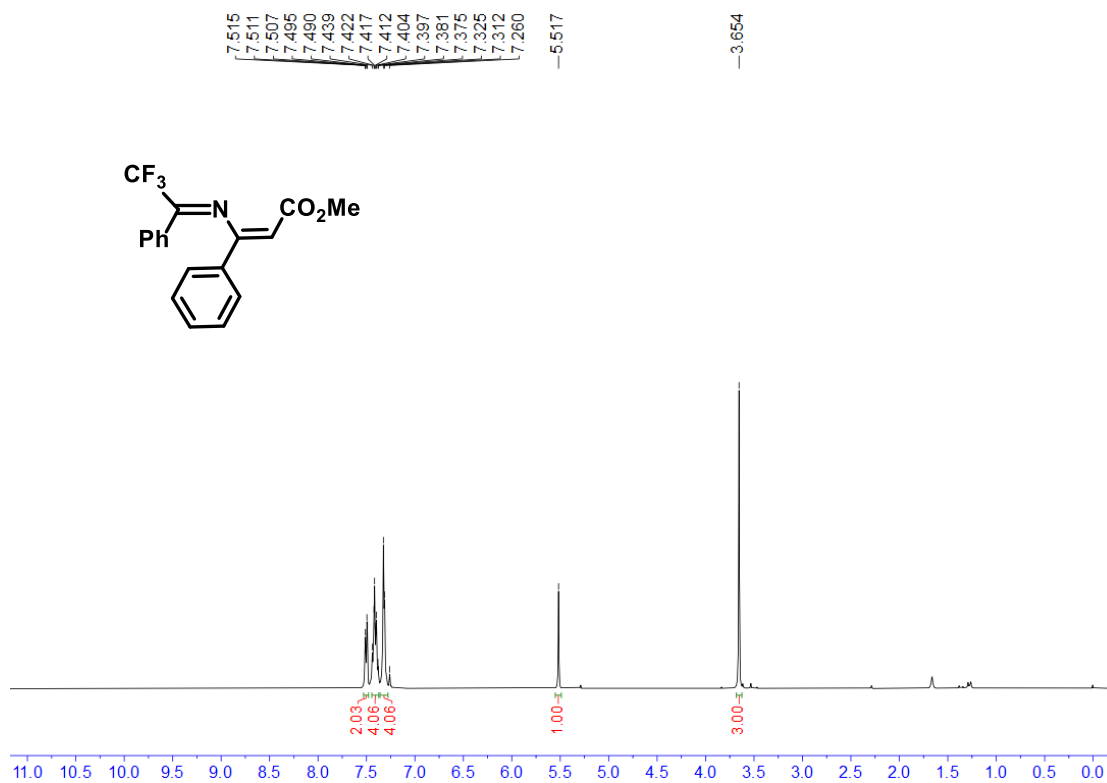


$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **2n**



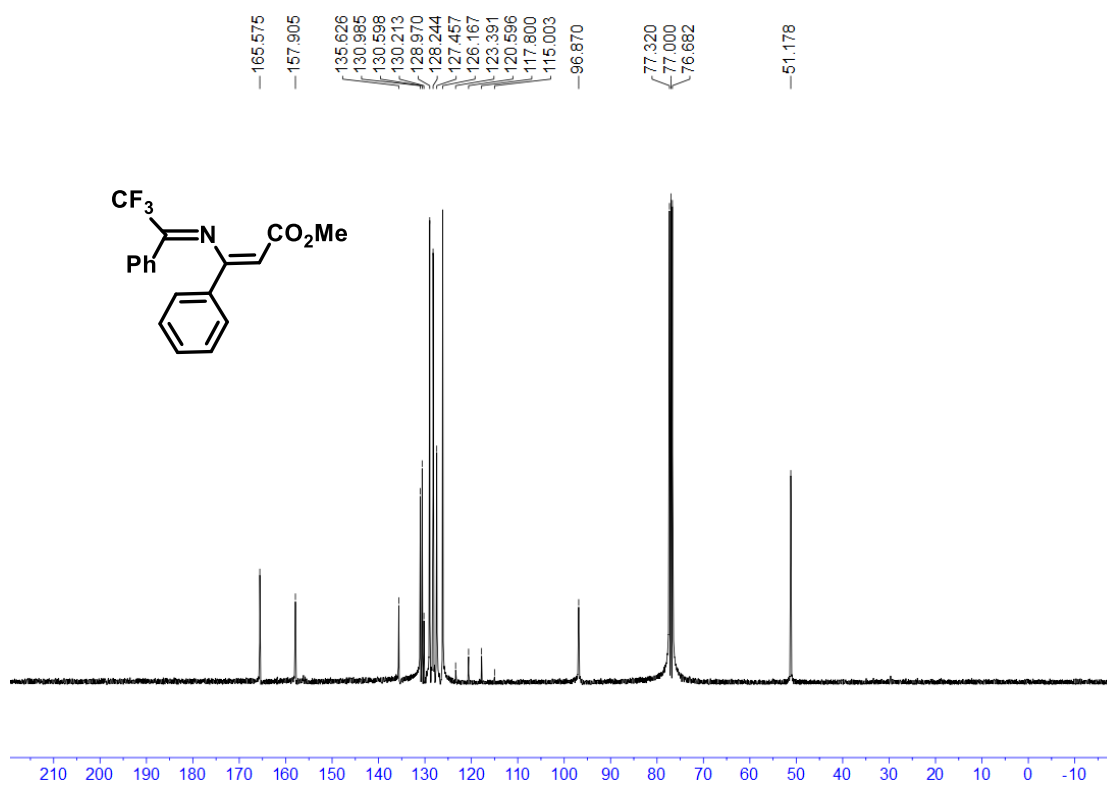
### 3.3 NMR spectra for 2-azadienes

$^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3aa**

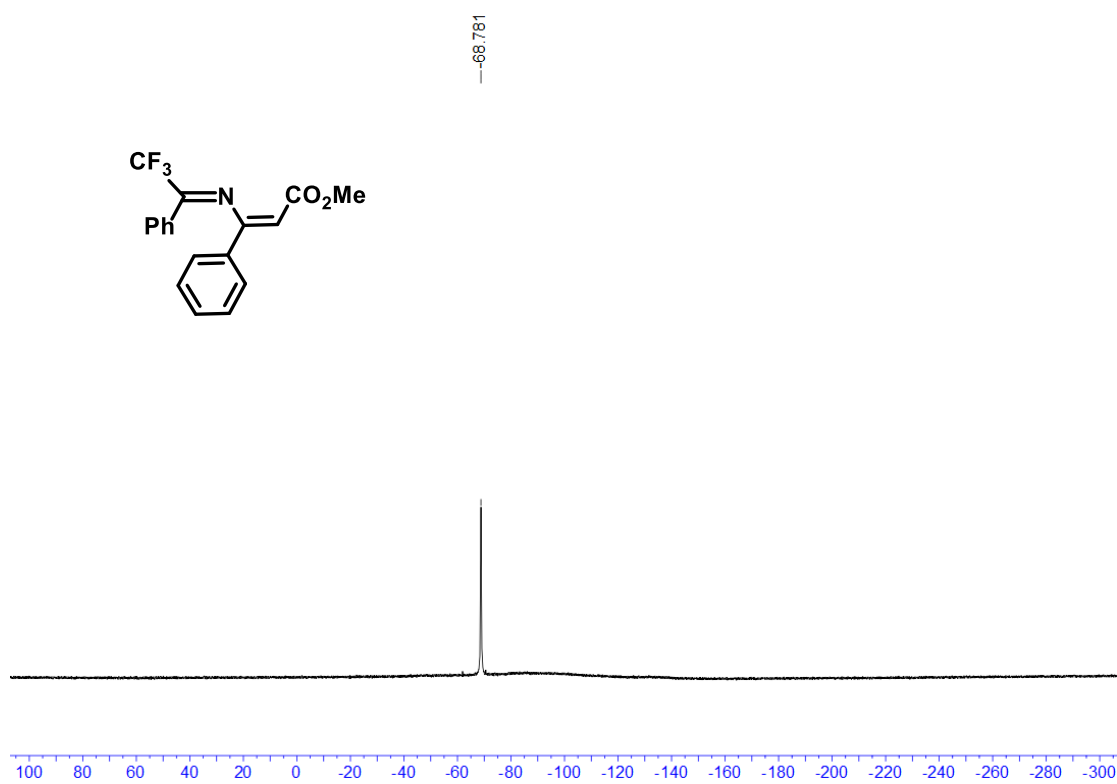




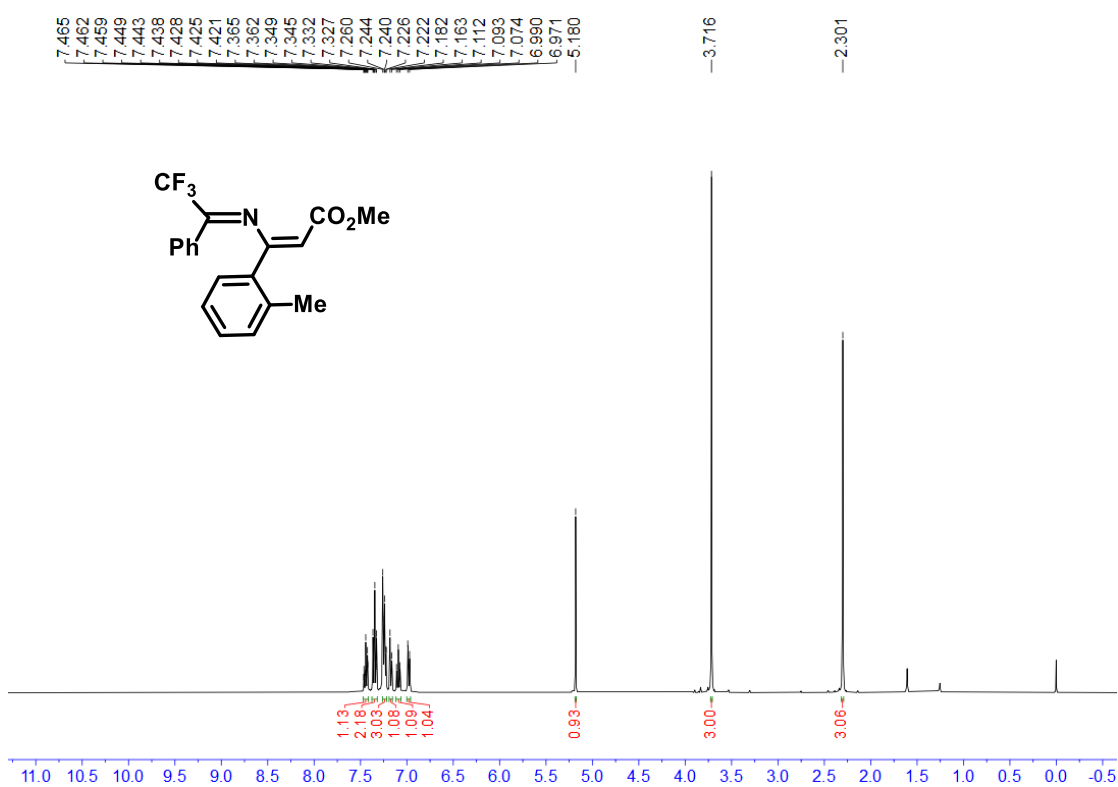
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3aa**



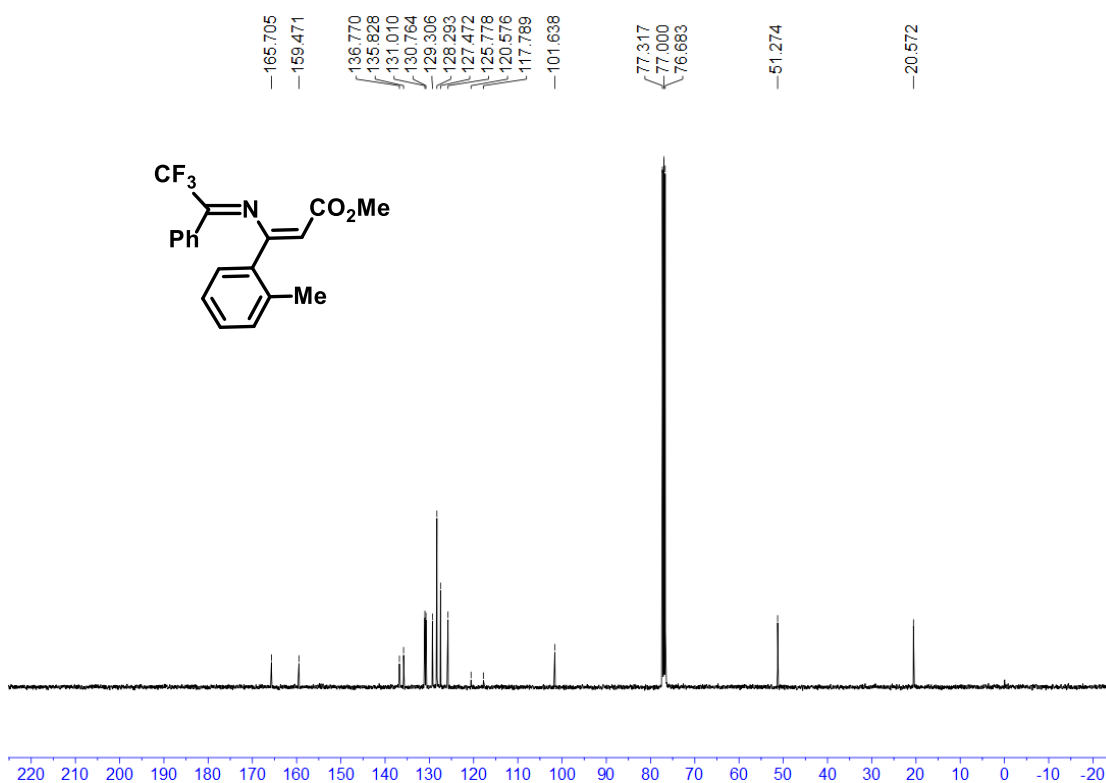
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **3aa**



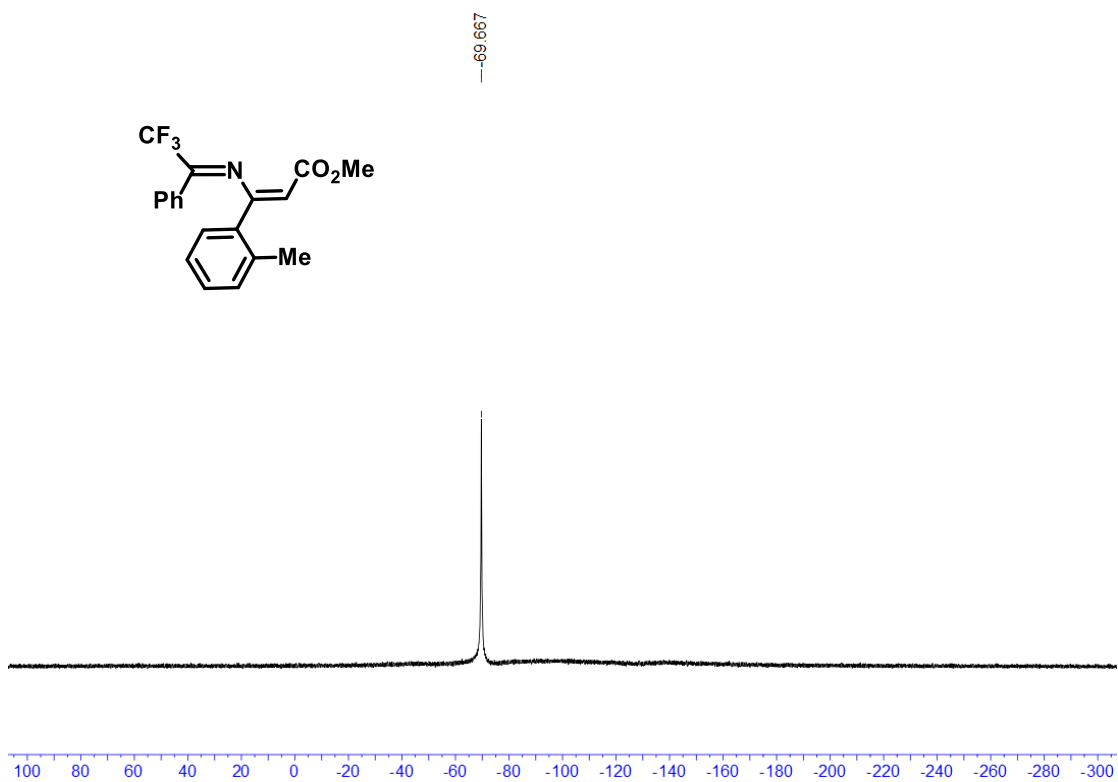
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3ba**



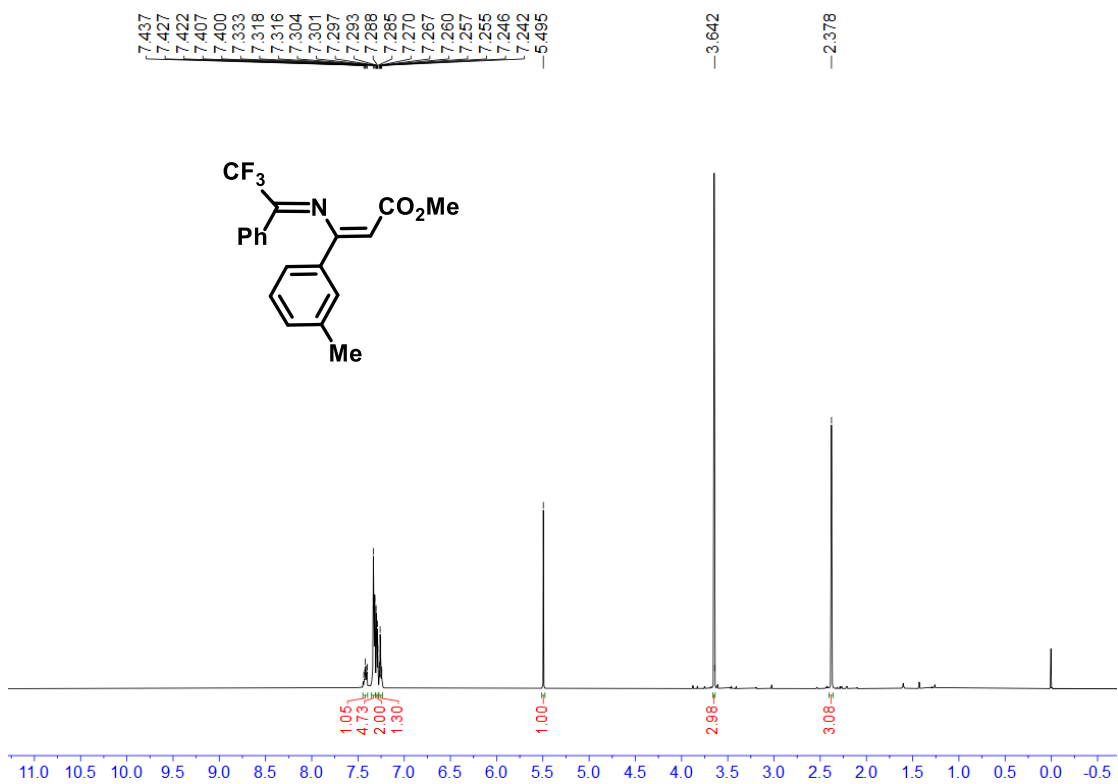
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3ba**



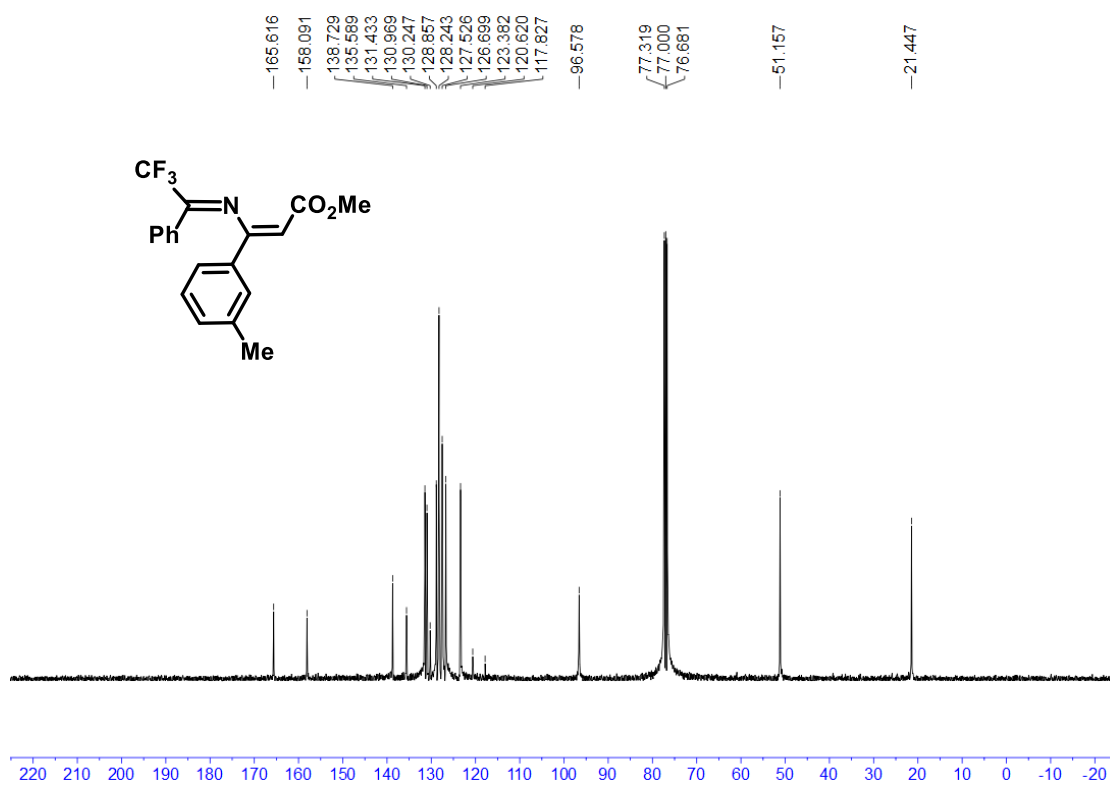
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3ba**



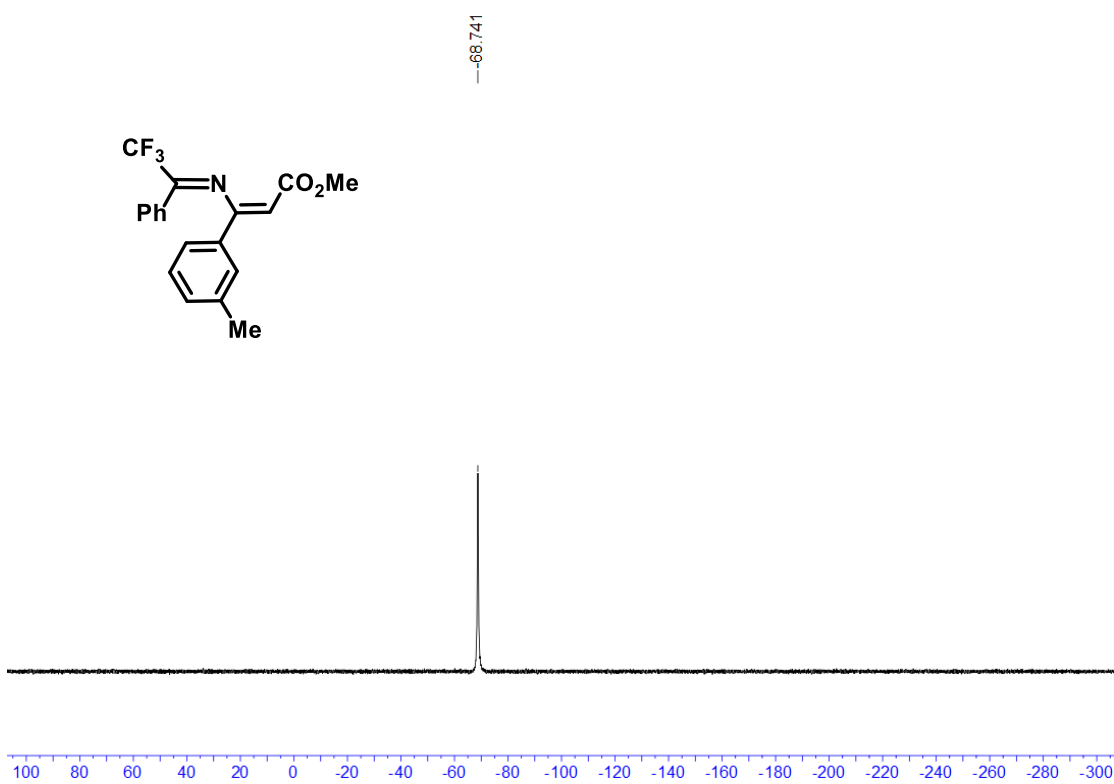
$^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ca**



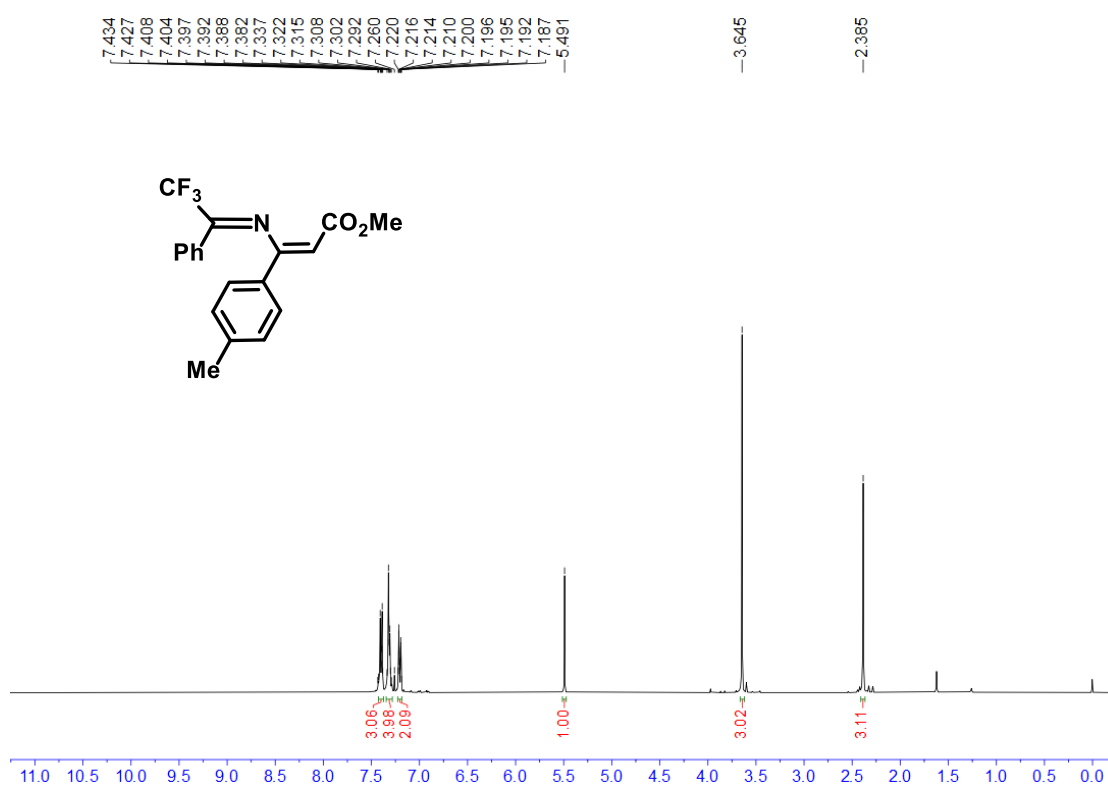
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3ca**



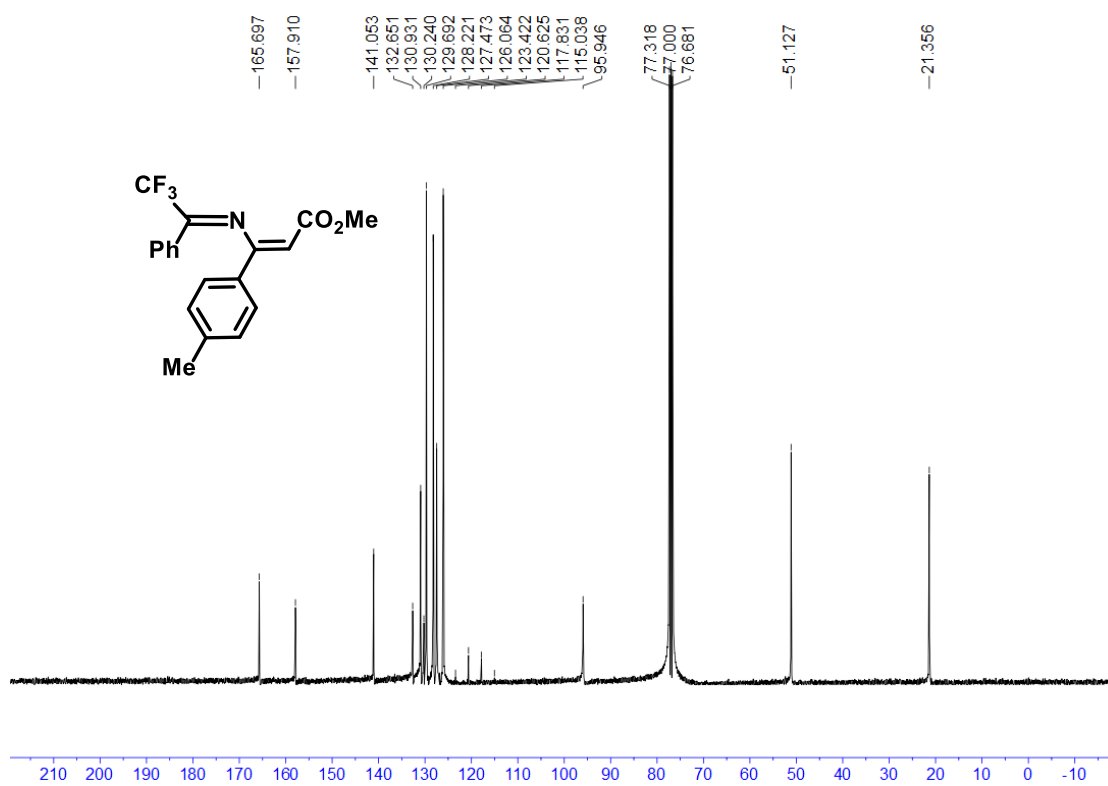
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **3ca**



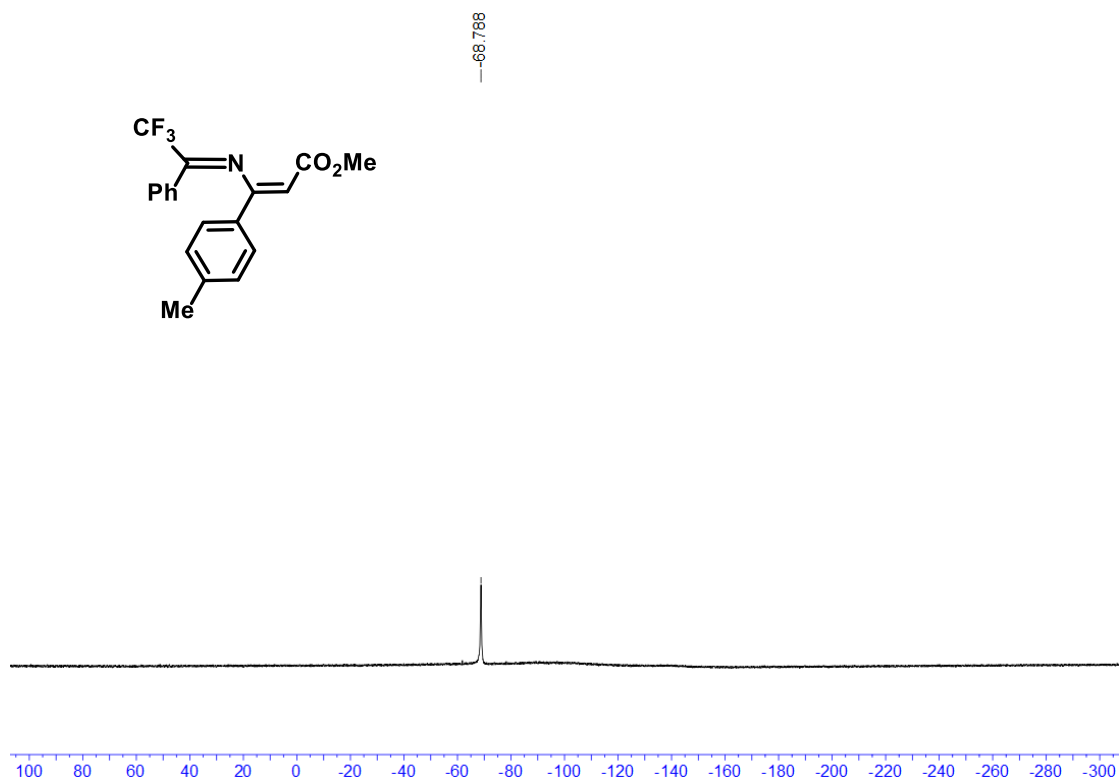
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3da**



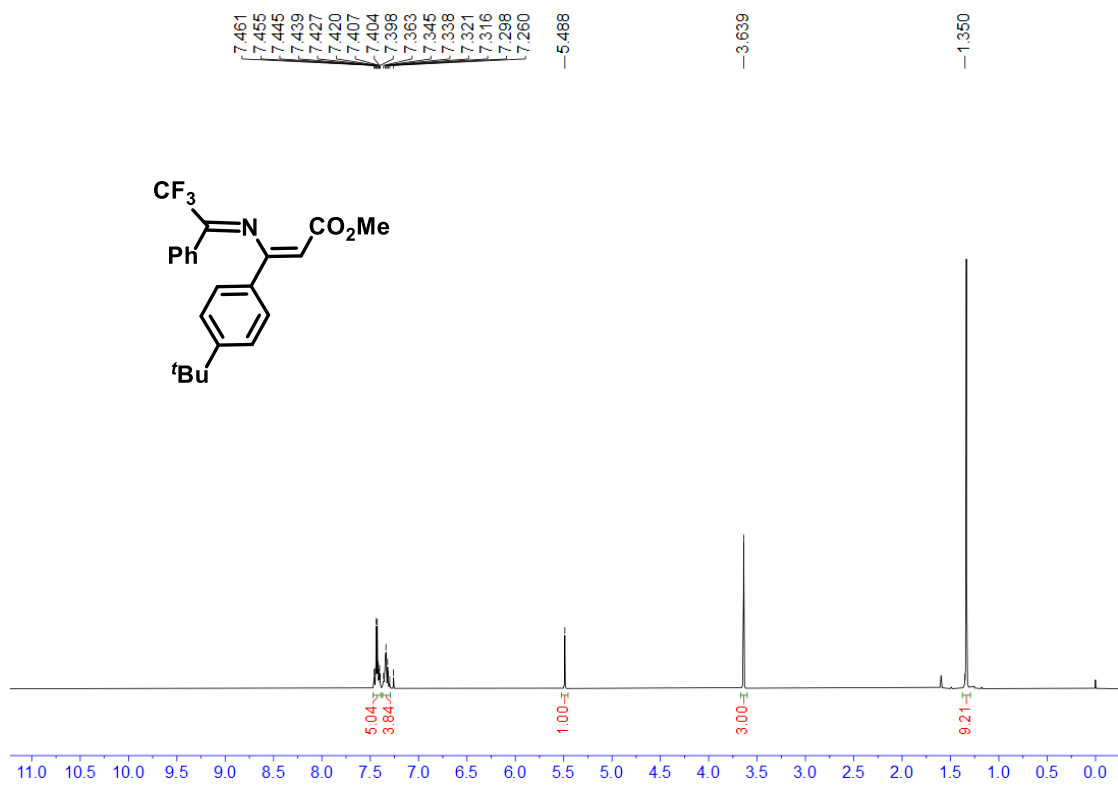
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3da**



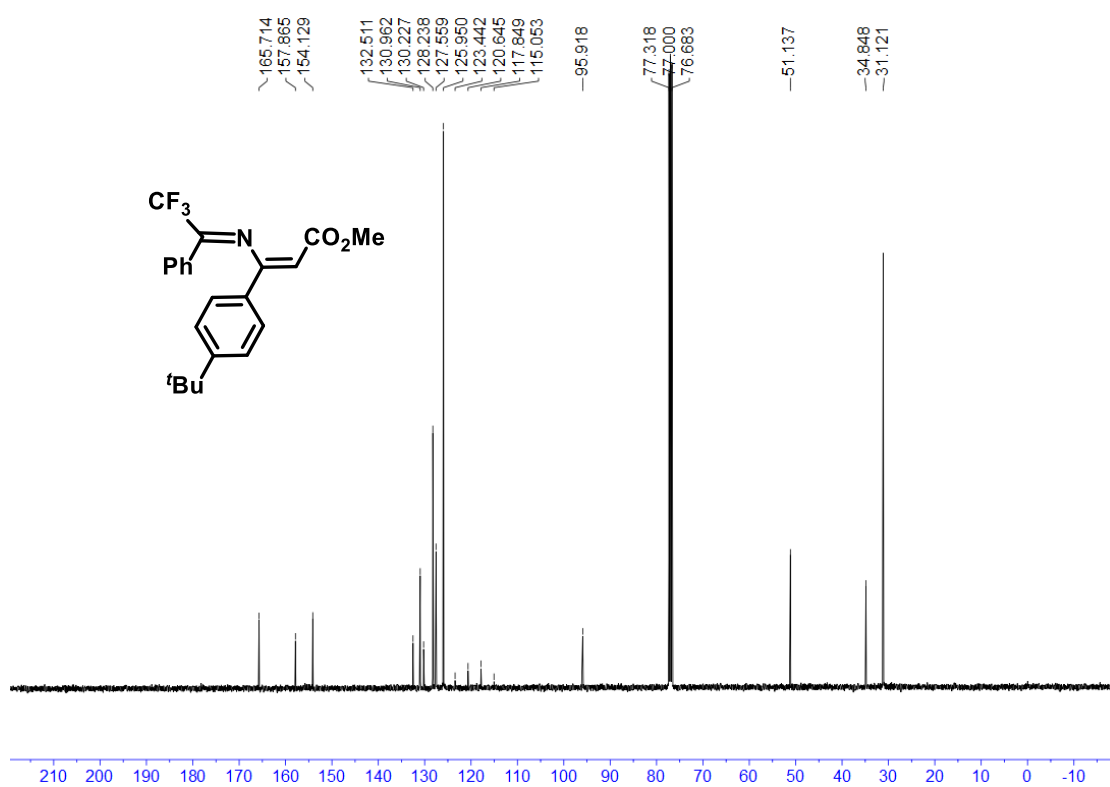
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3da**



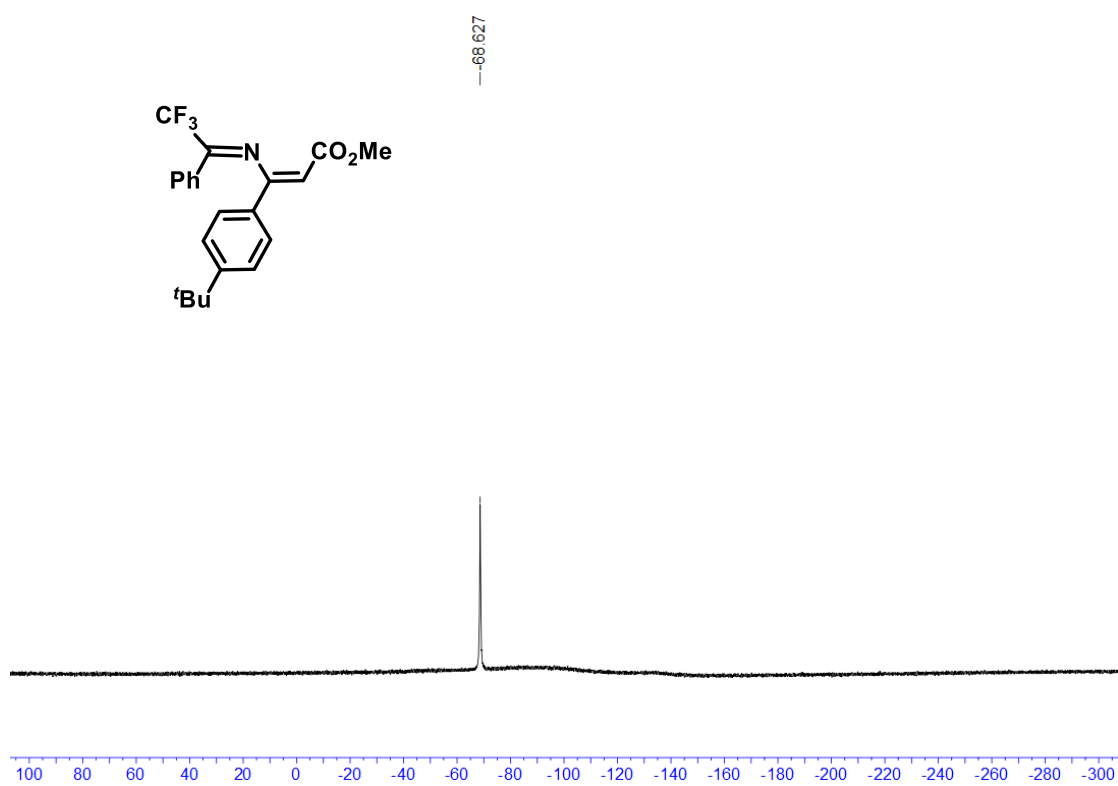
$^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ea**



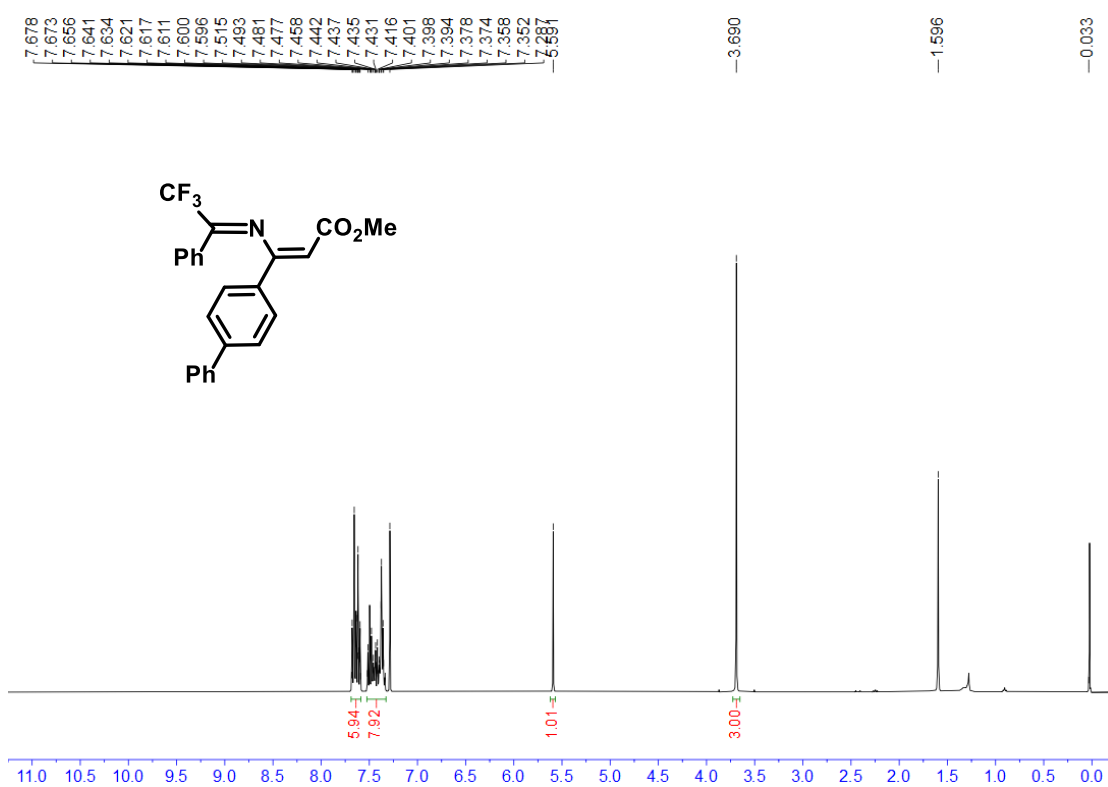
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3ea**



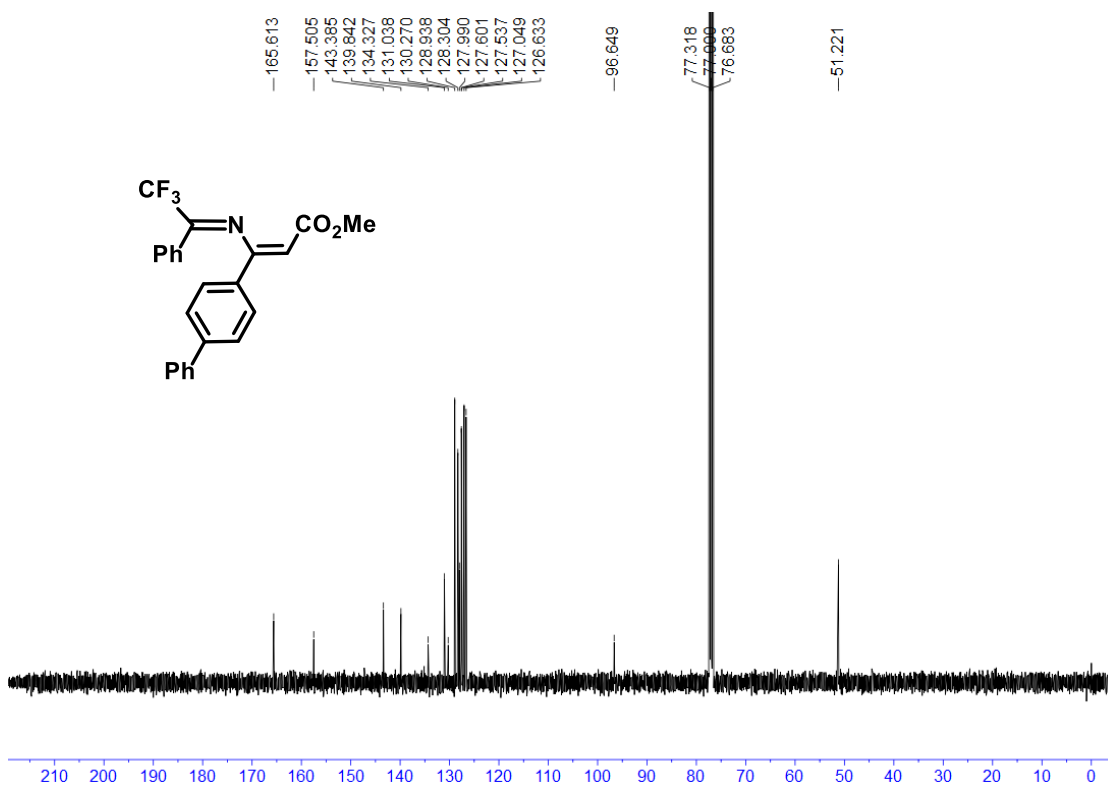
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **3ea**



<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3fa**

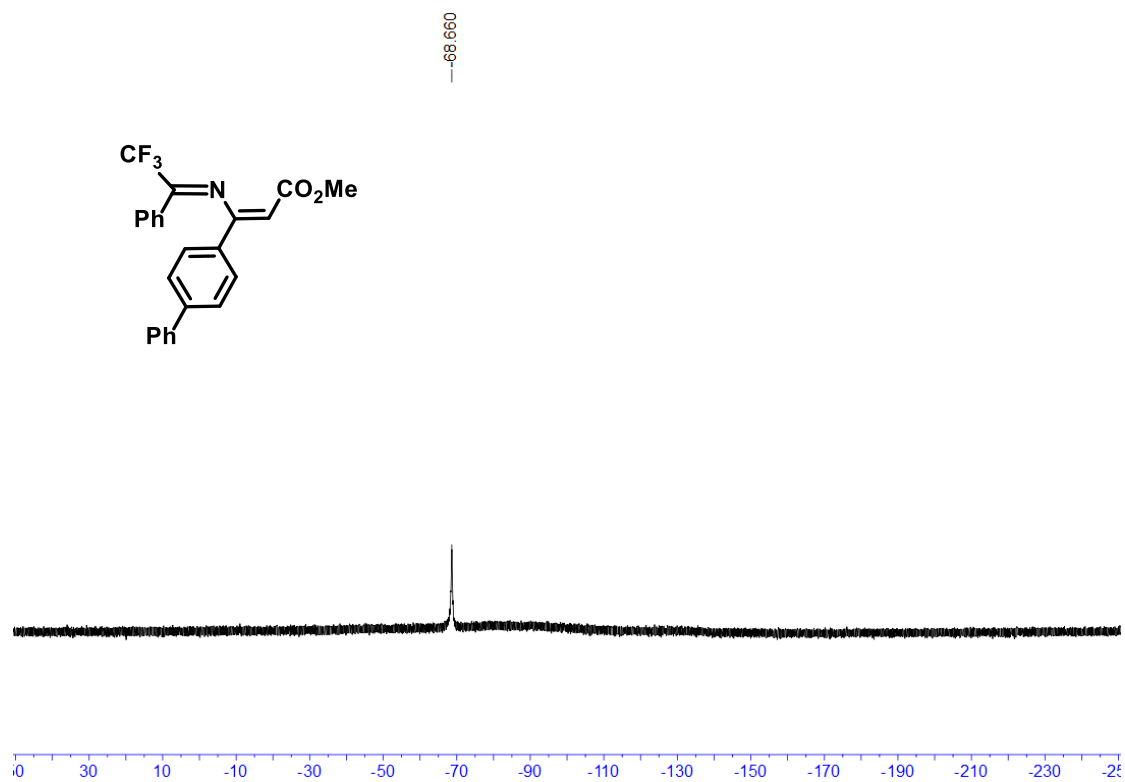


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3fa**

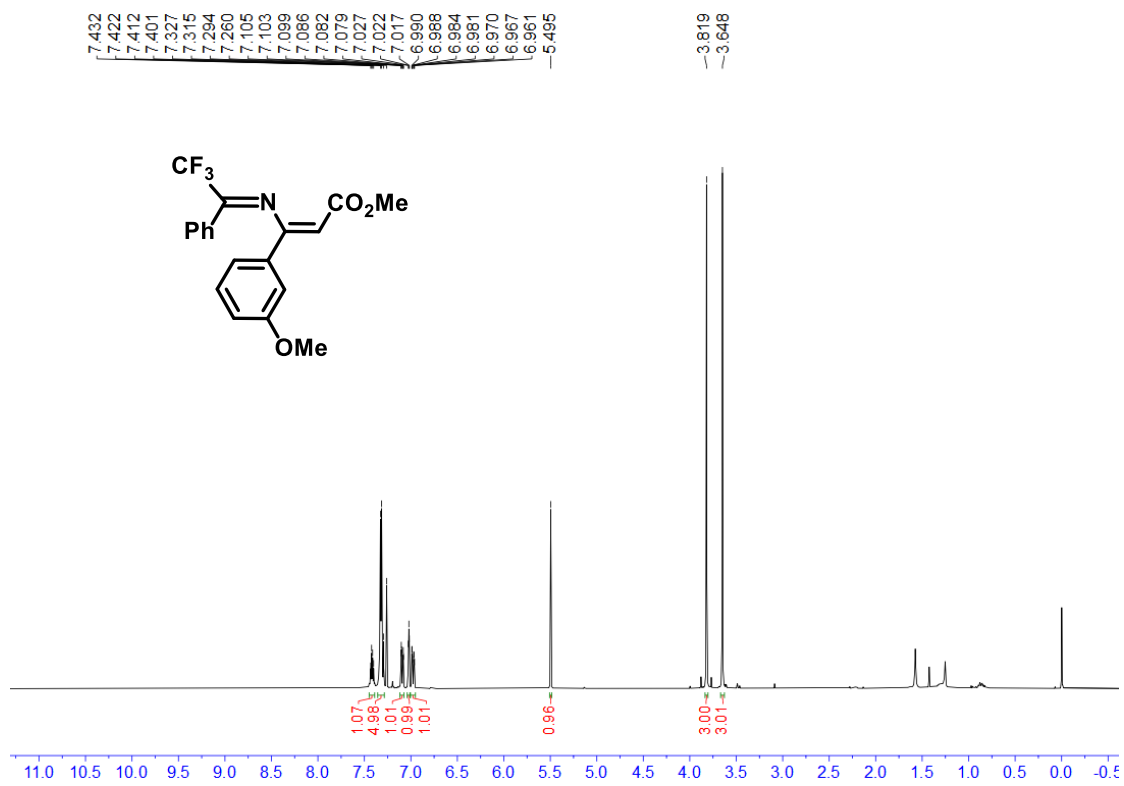




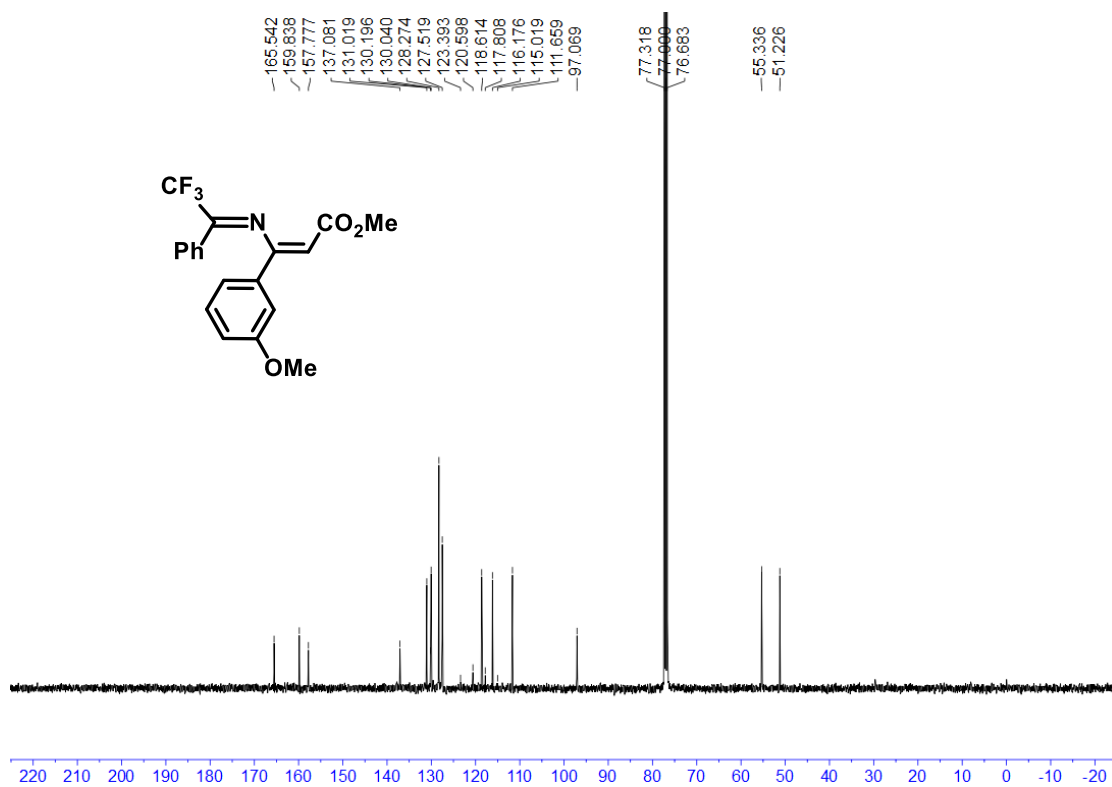
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3fa**



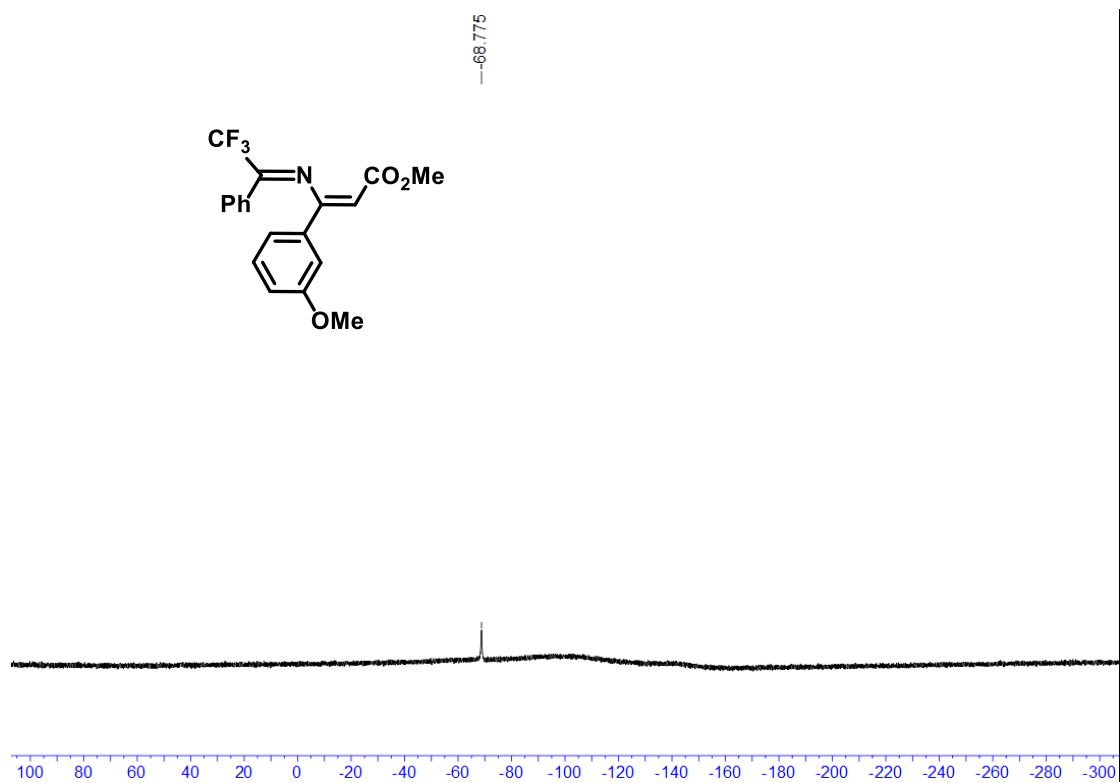
$^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ga**



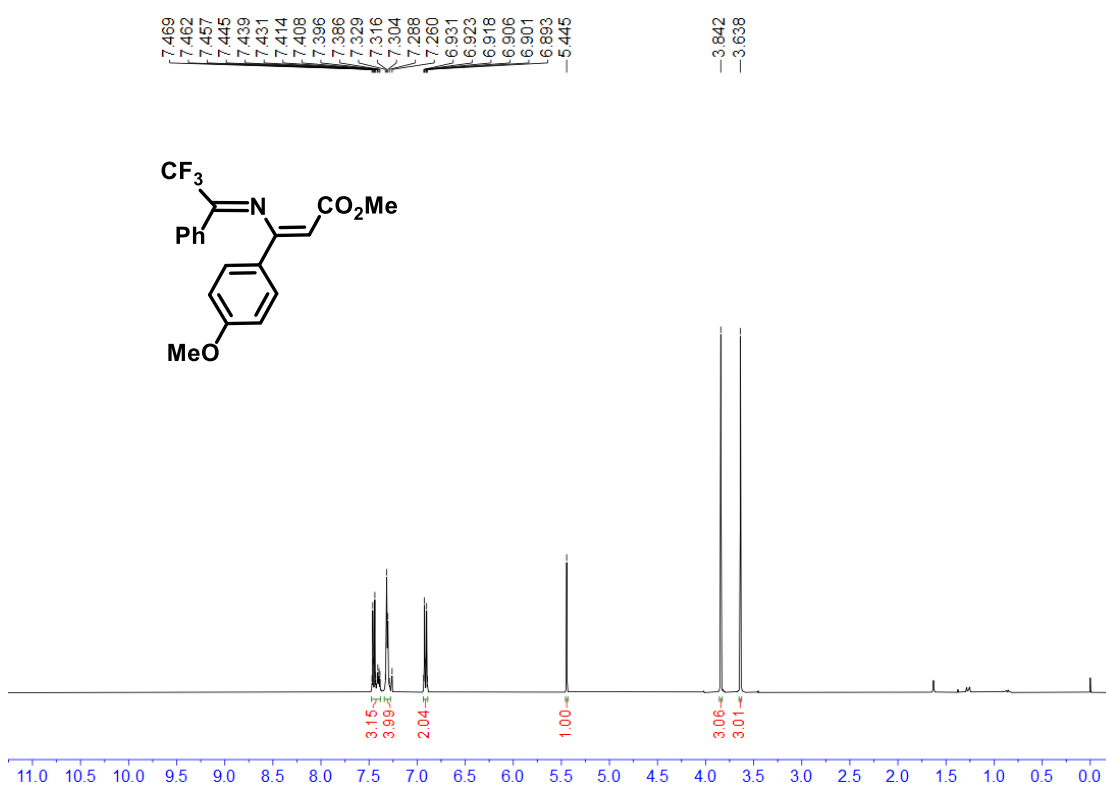
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3ga**



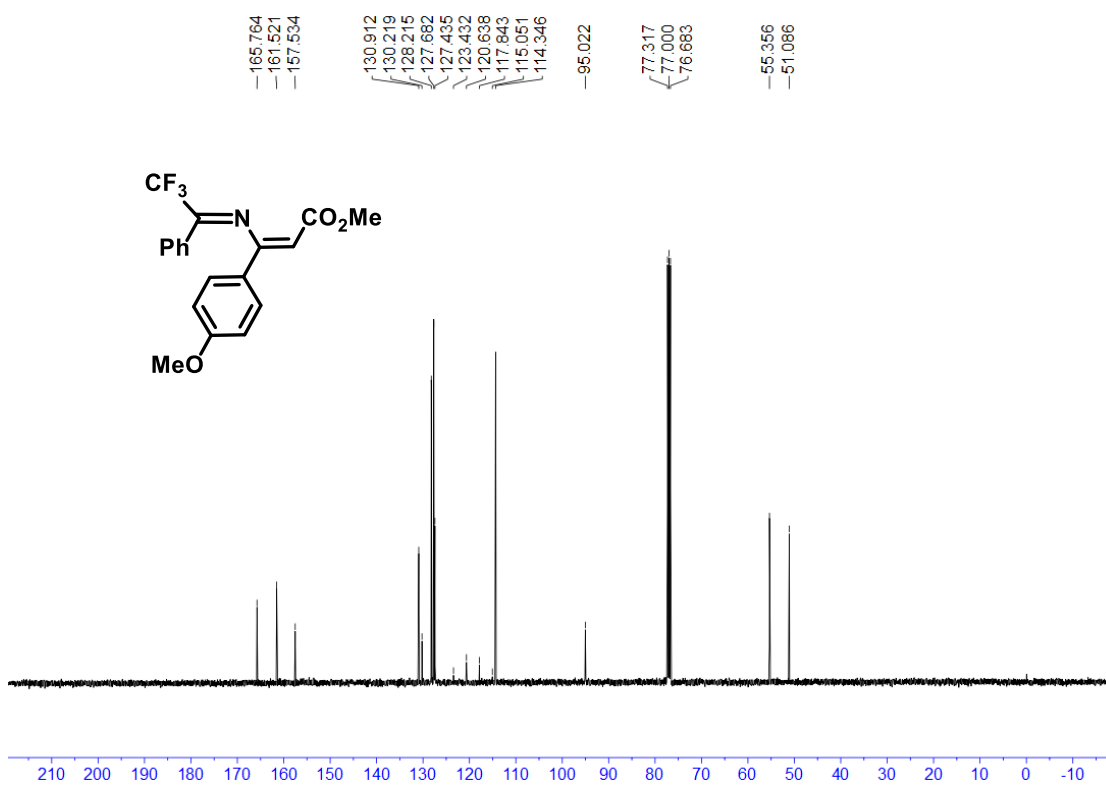
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **3ga**



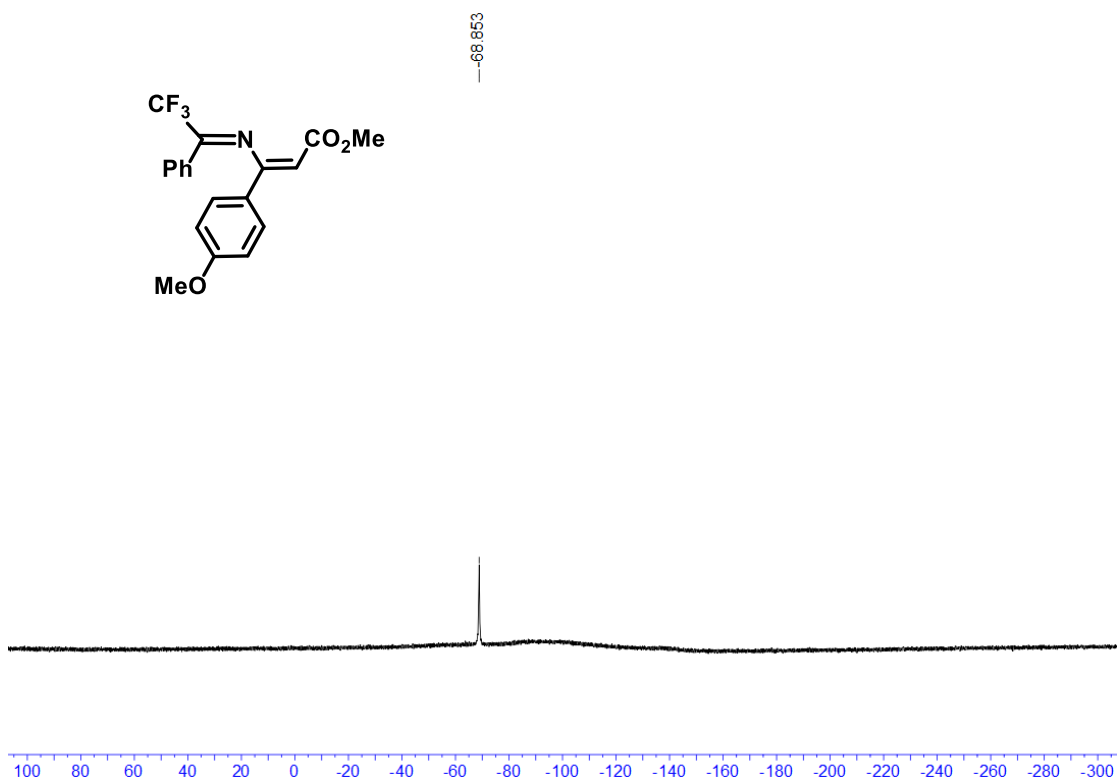
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3ha**



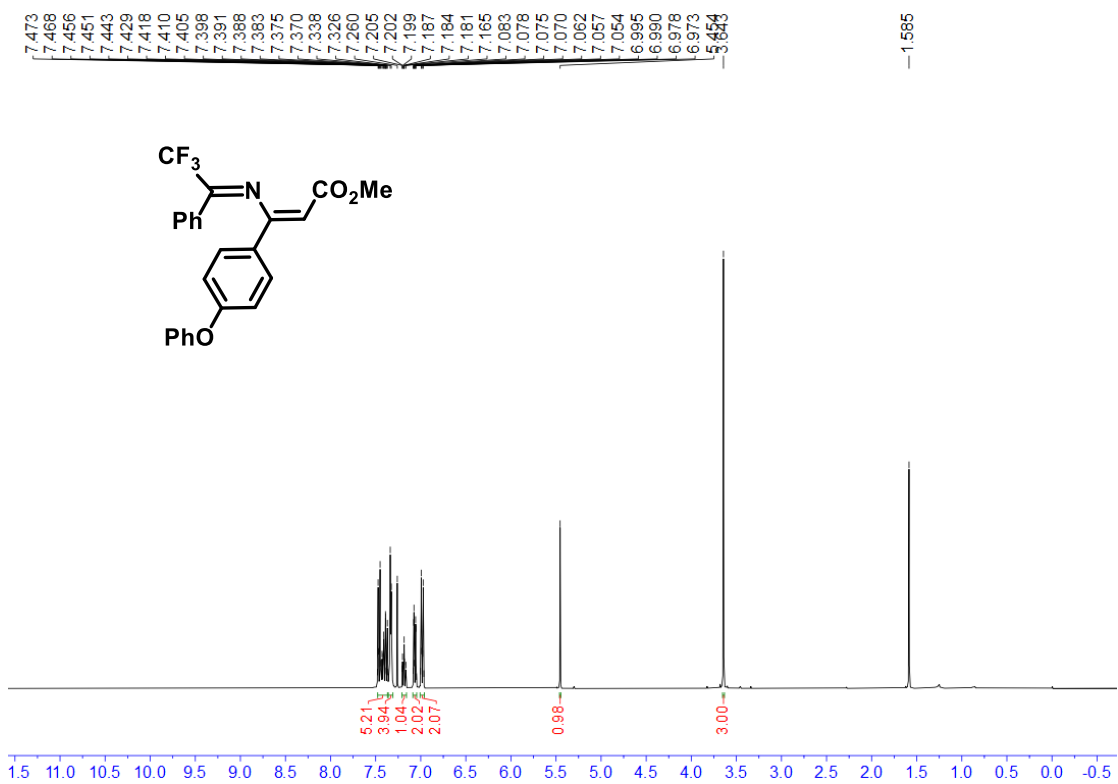
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3ha**



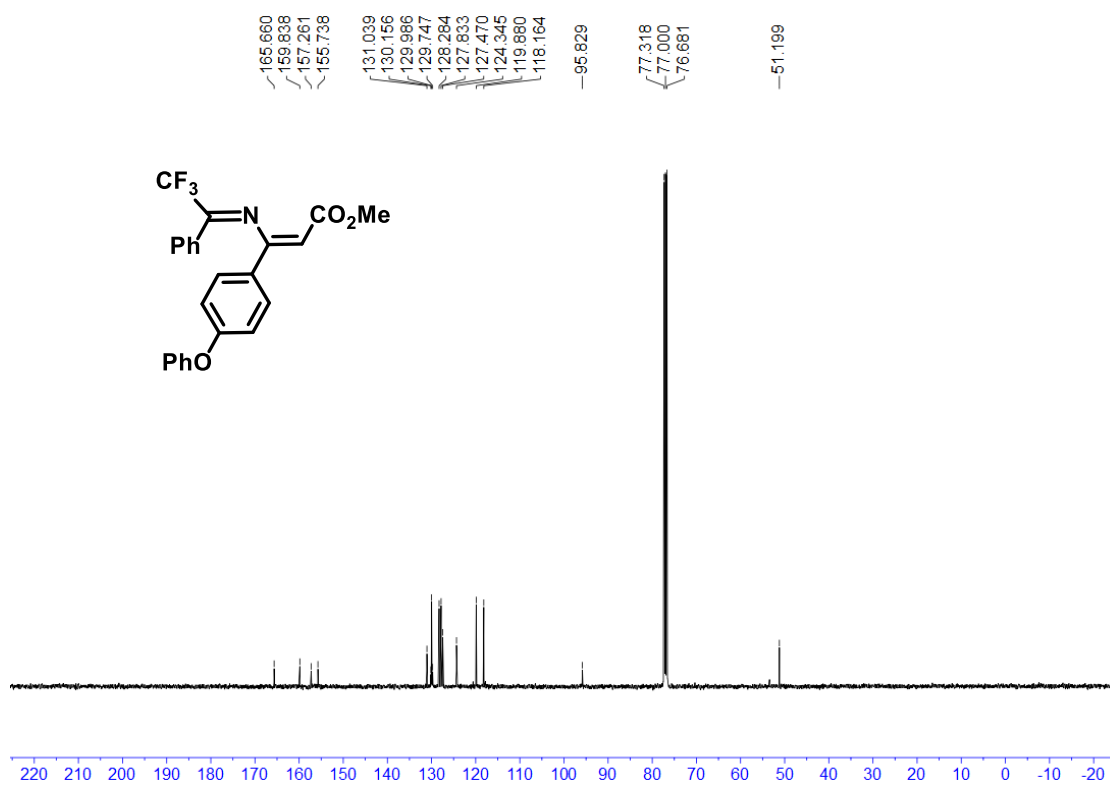
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3ha**



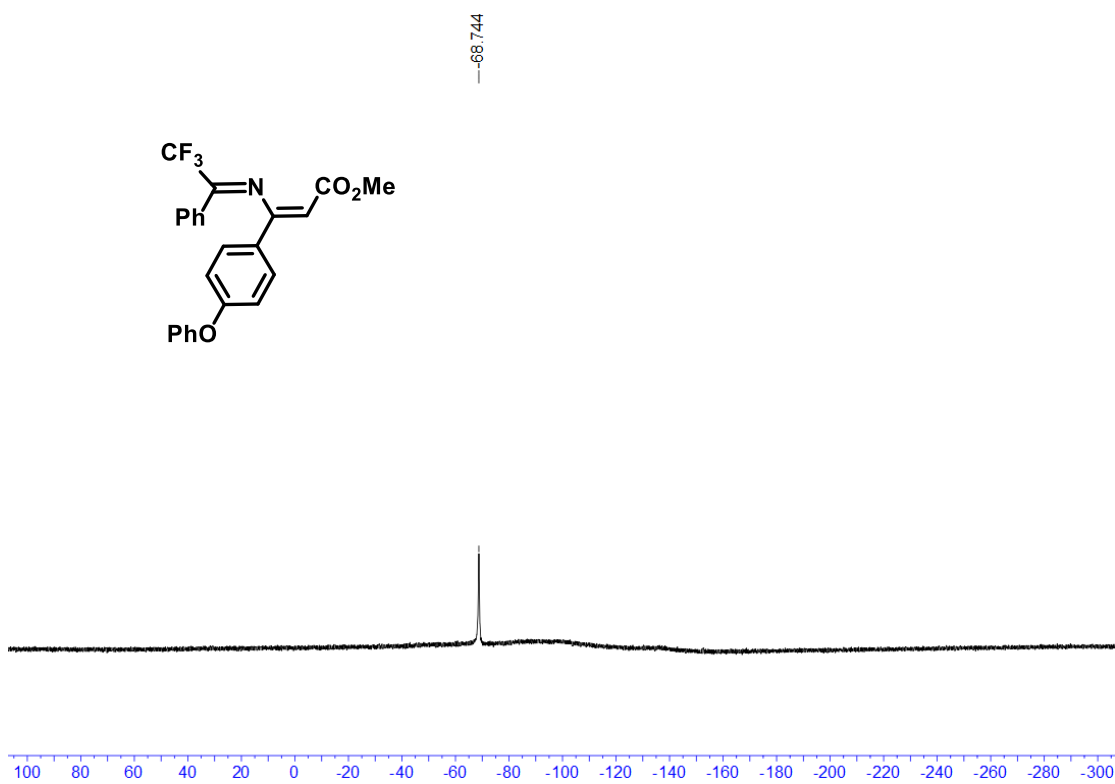
$^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ia**



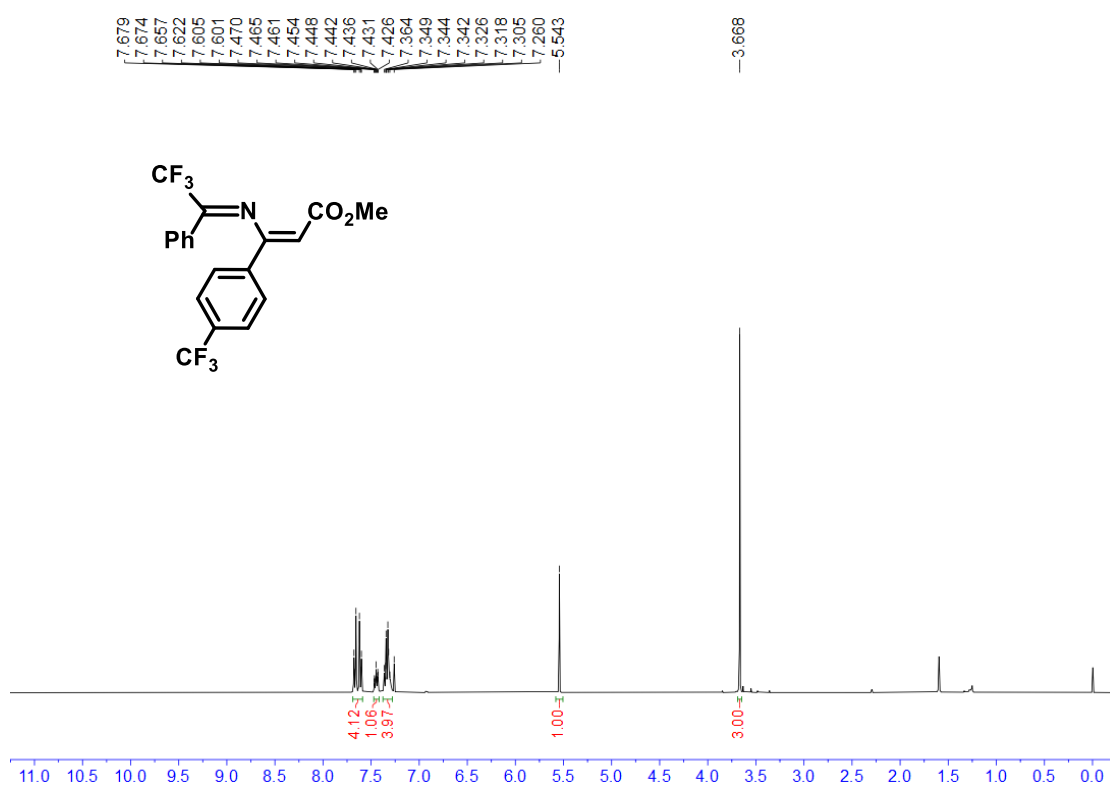
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3ia**



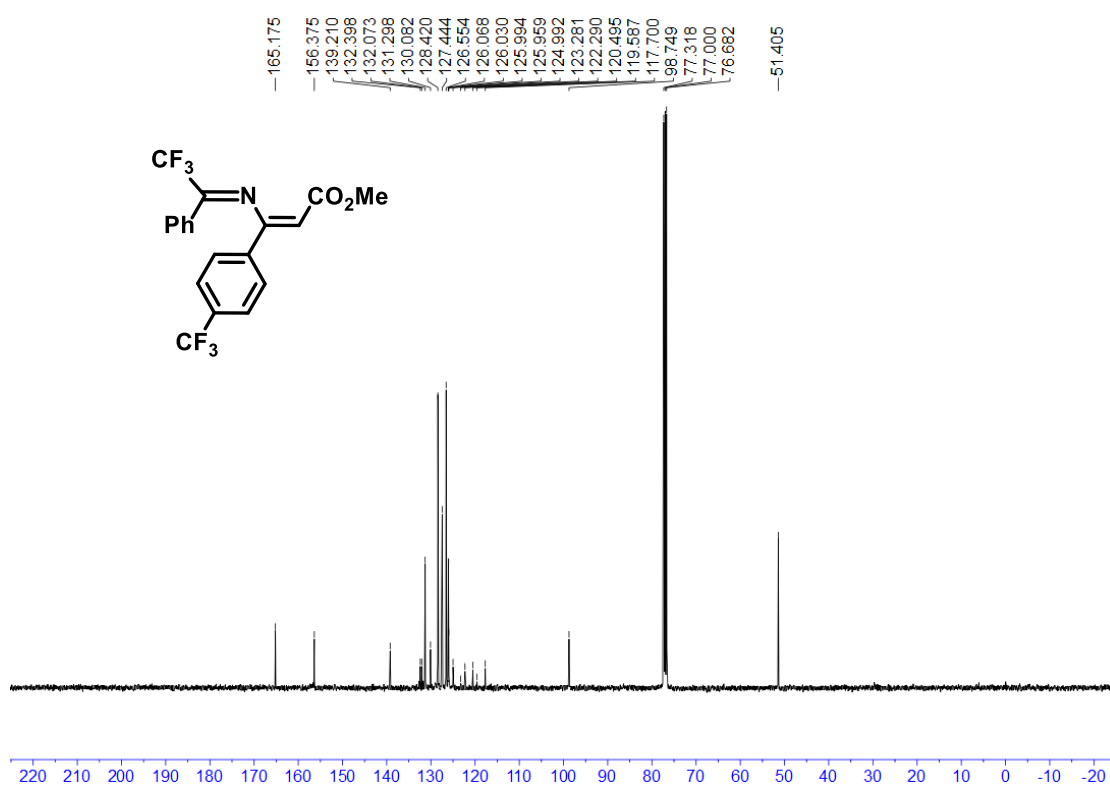
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **3ia**



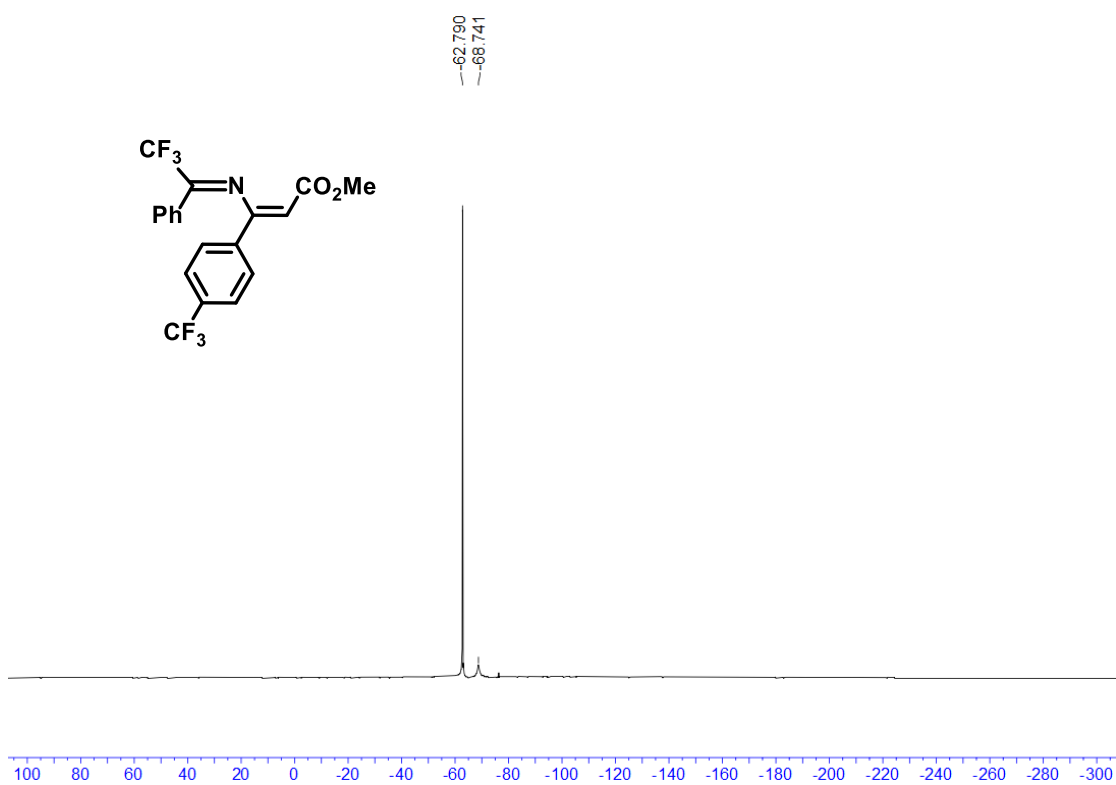
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3ja**



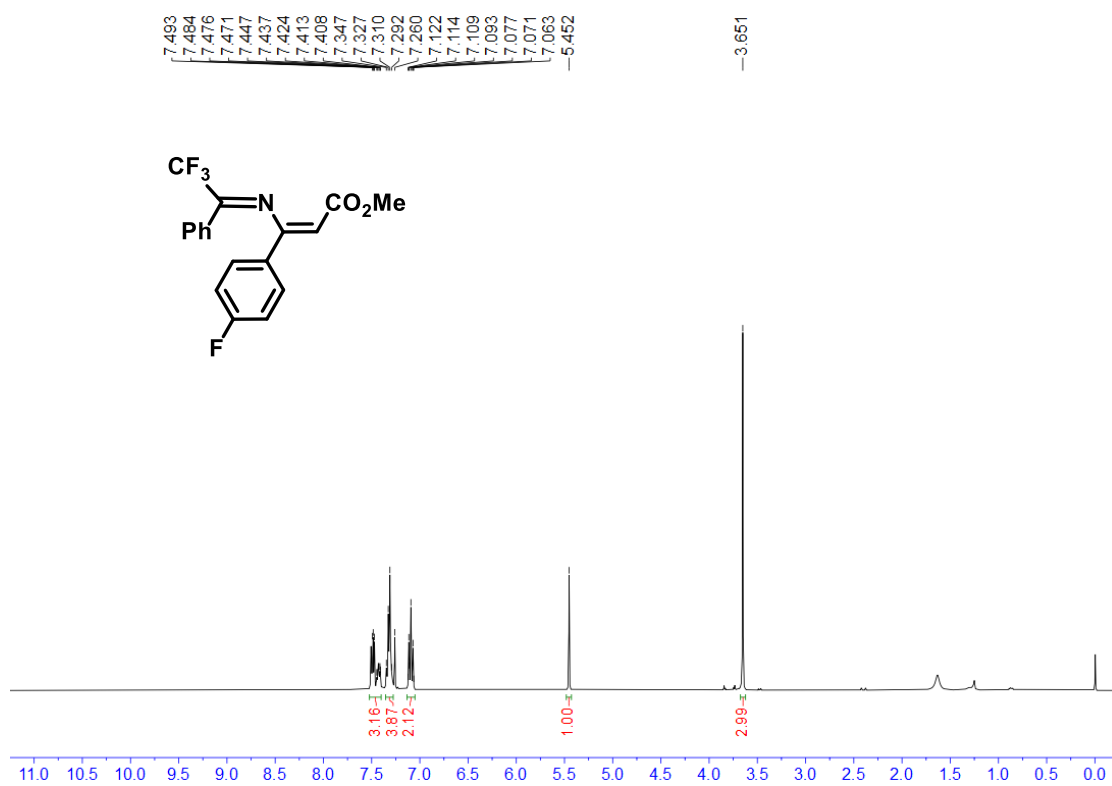
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3ja**



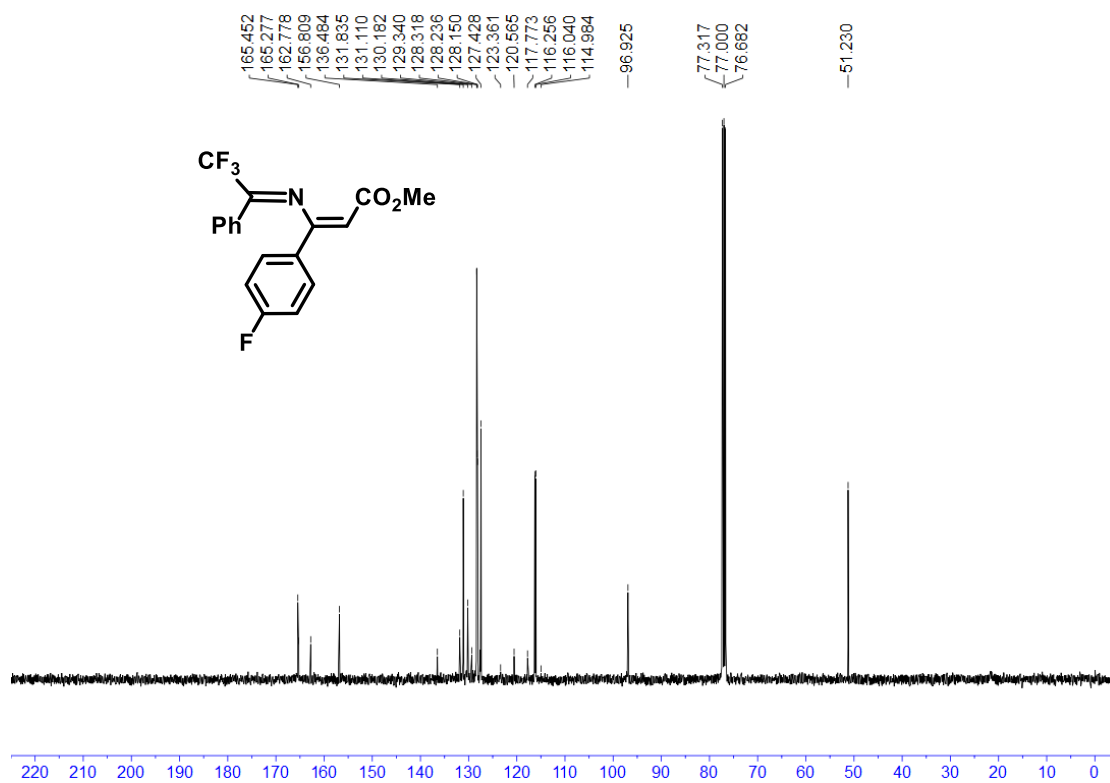
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3ja**



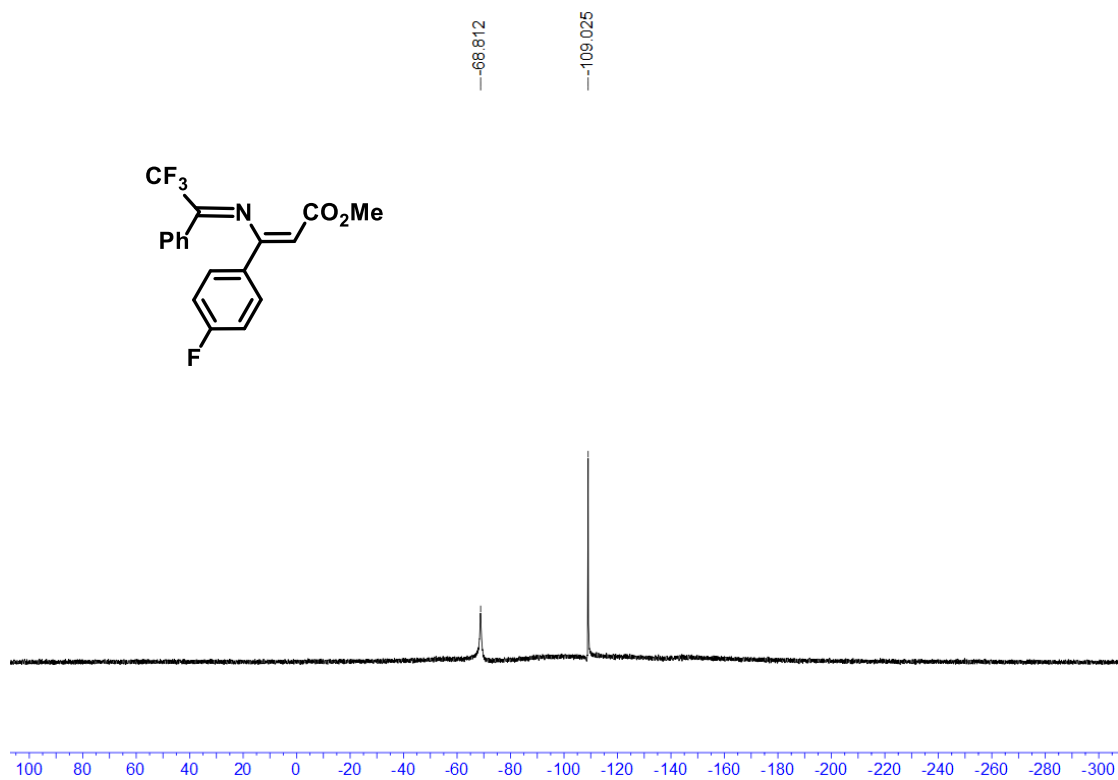
$^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ka**



$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ka**

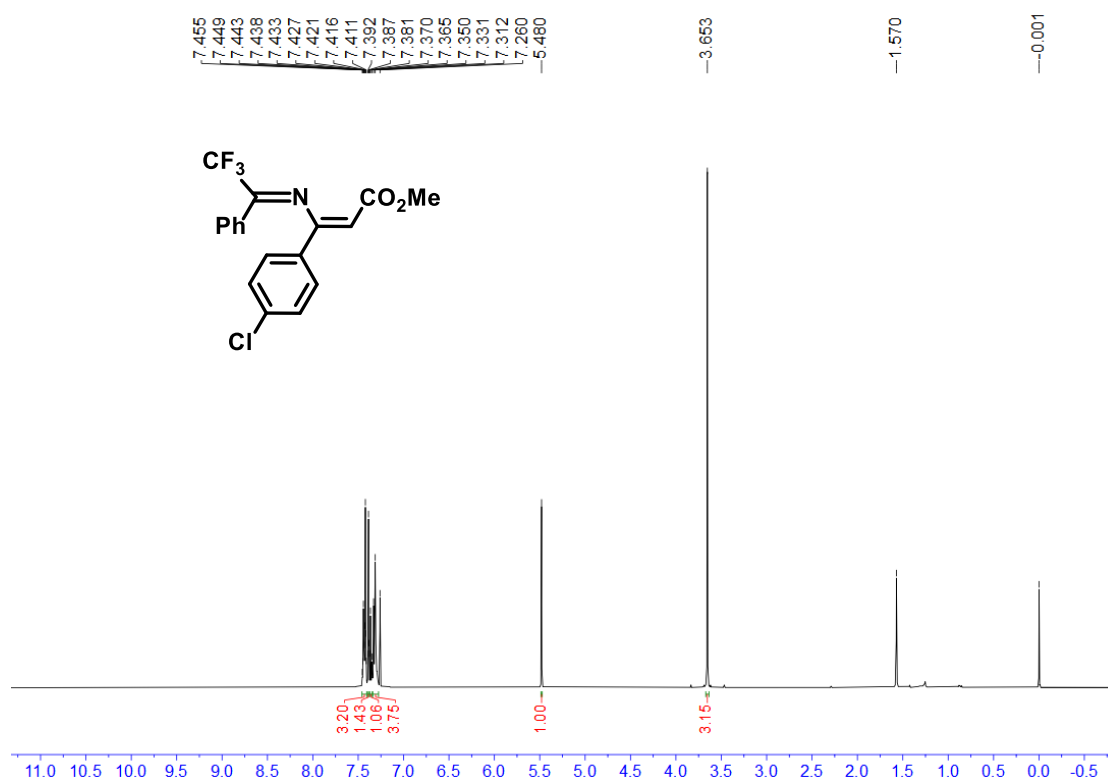


$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3ka**

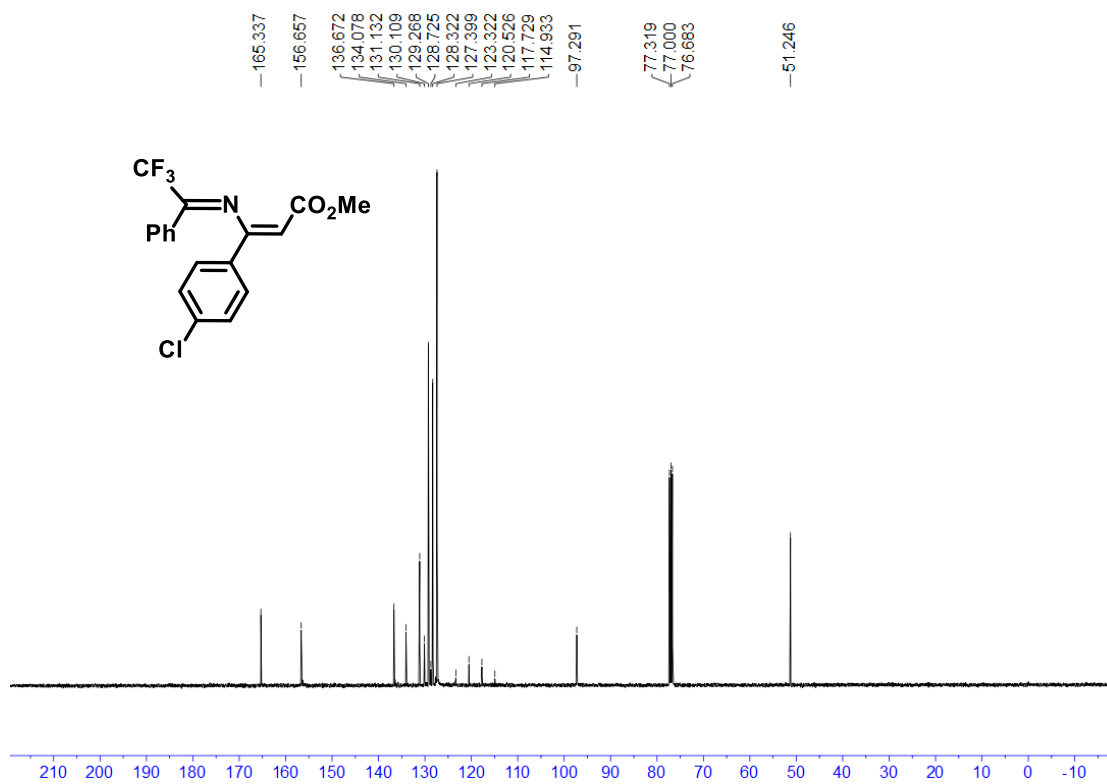




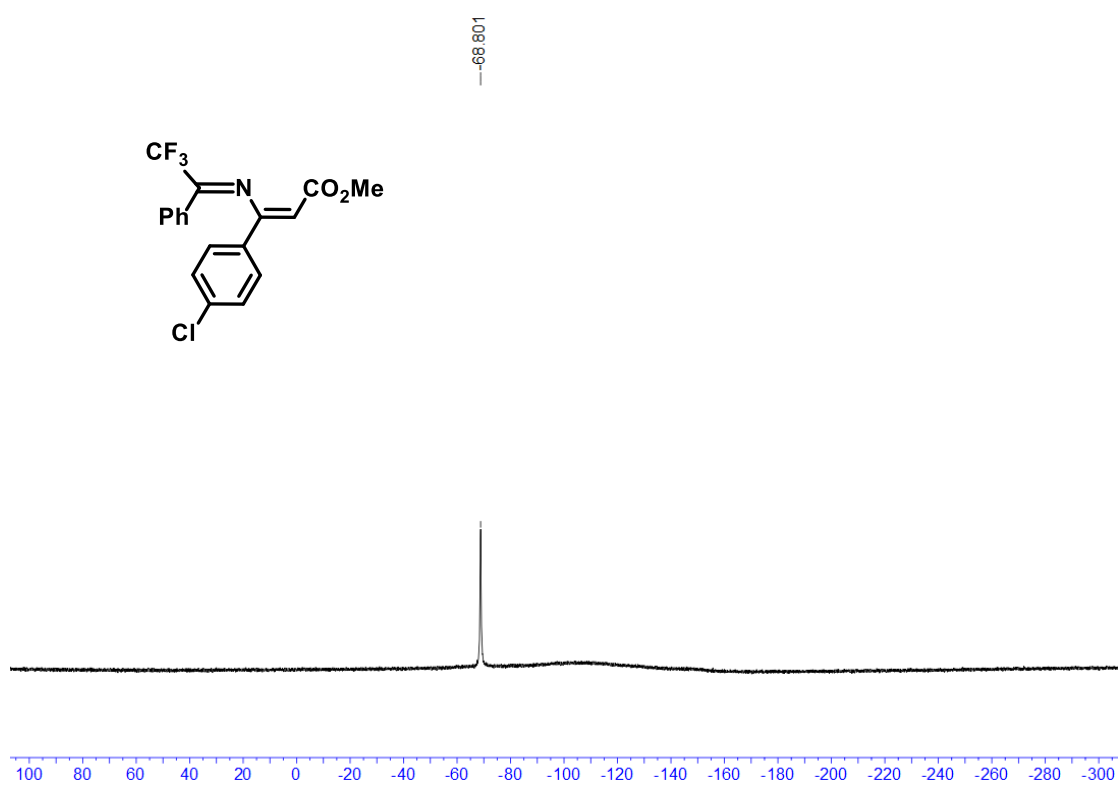
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3la**



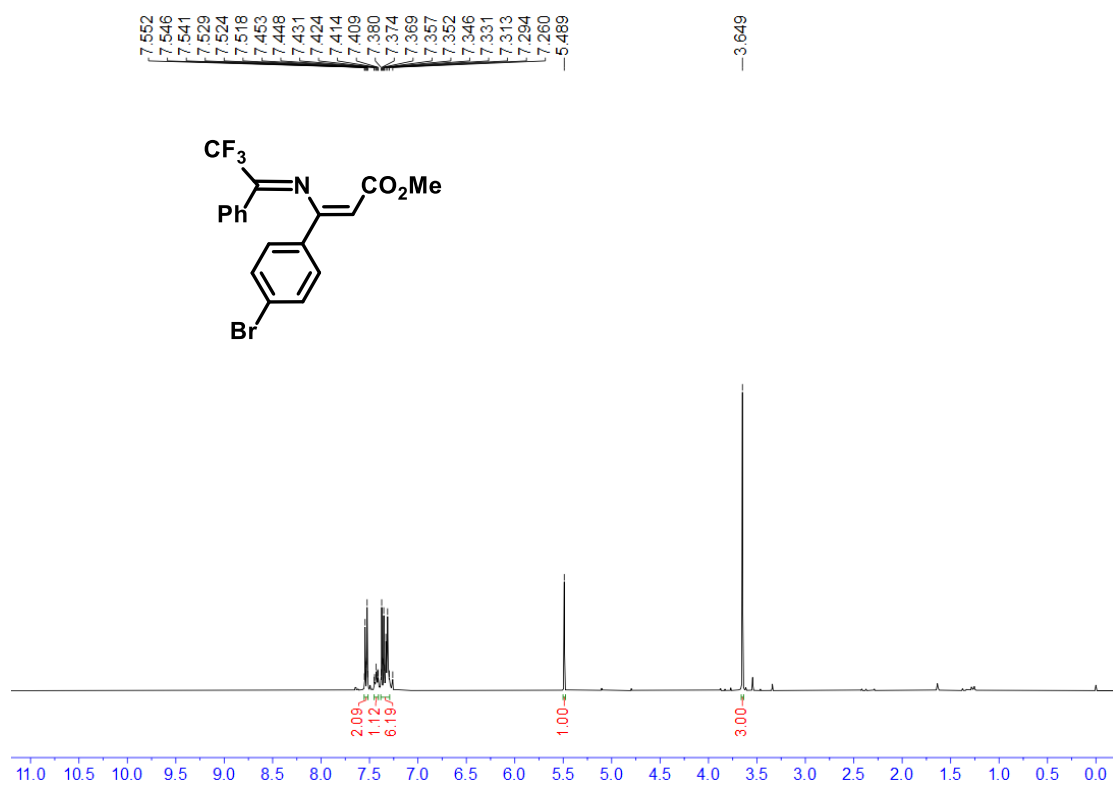
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3la**



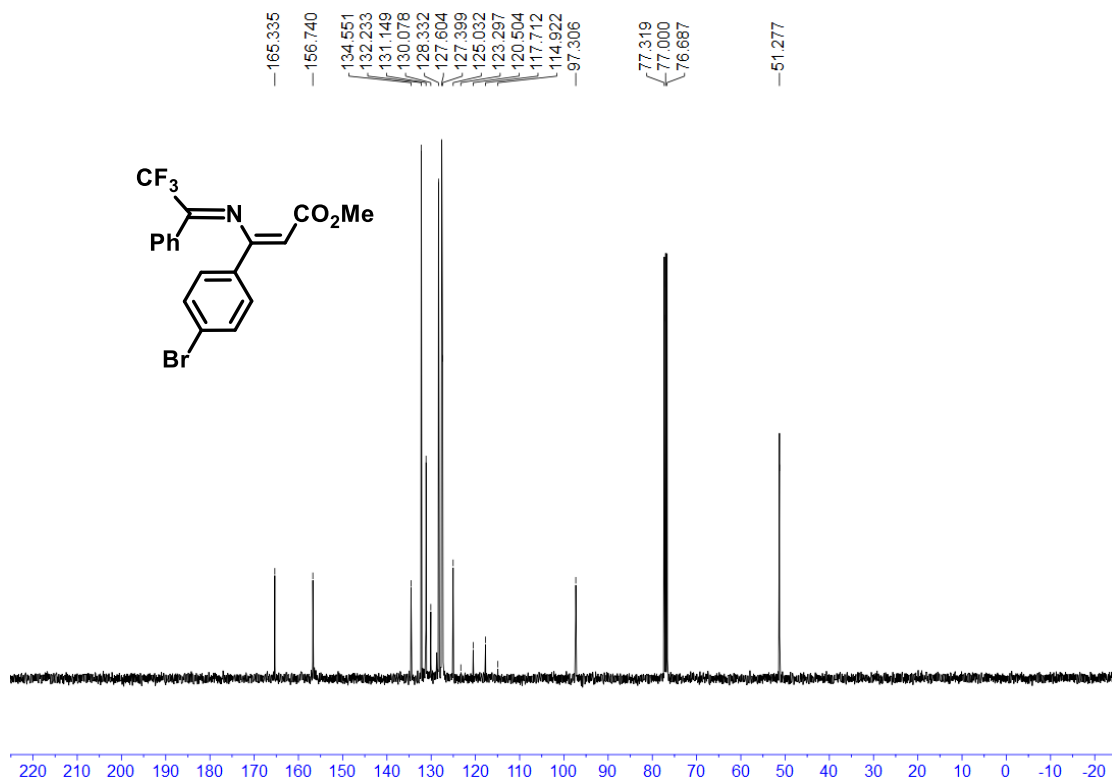
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3la**



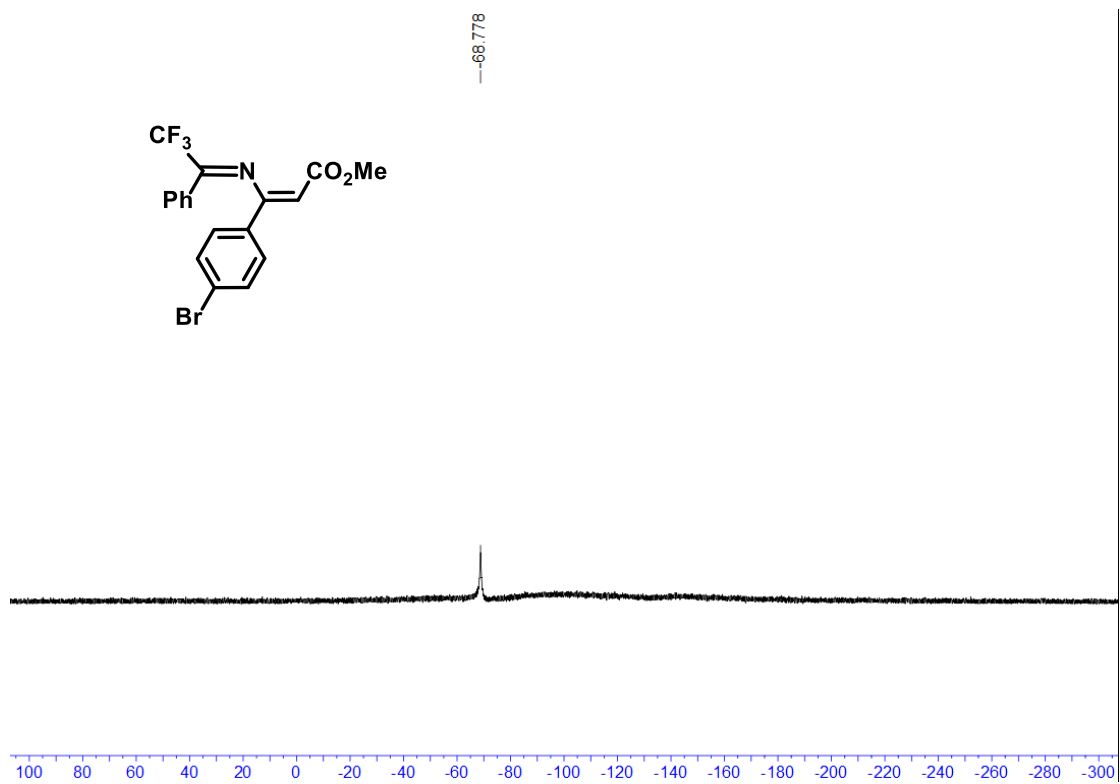
$^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ma**



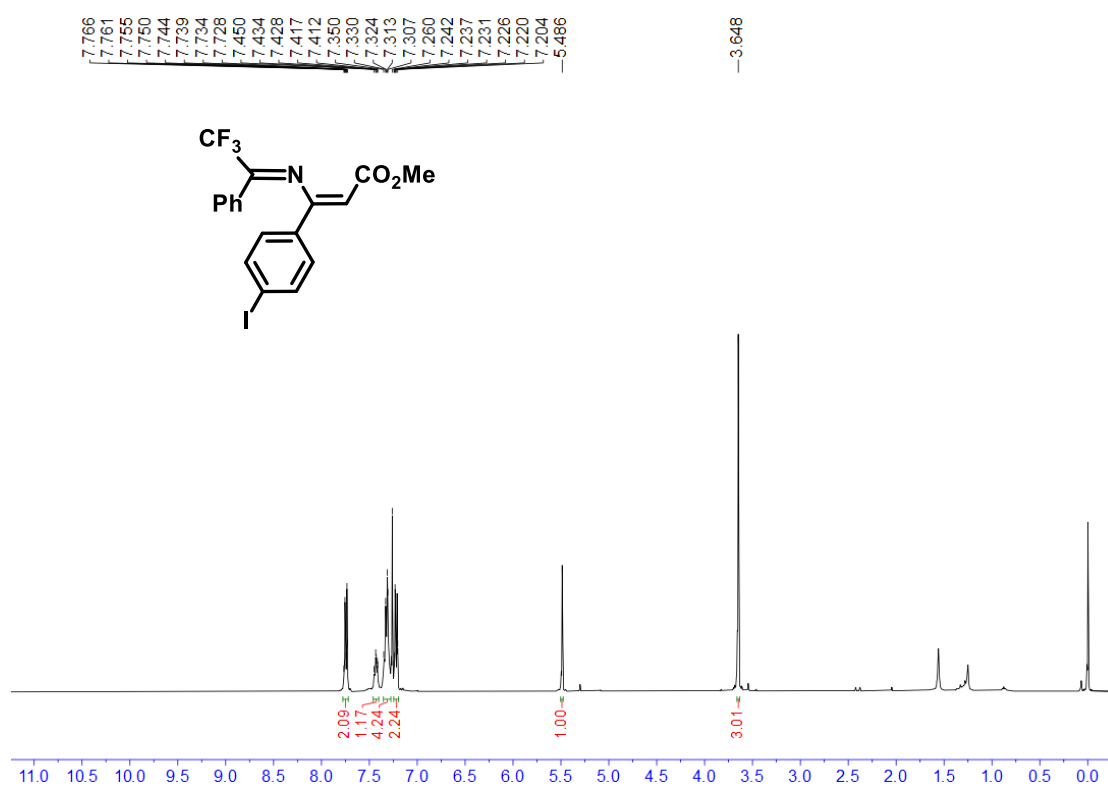
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3ma**



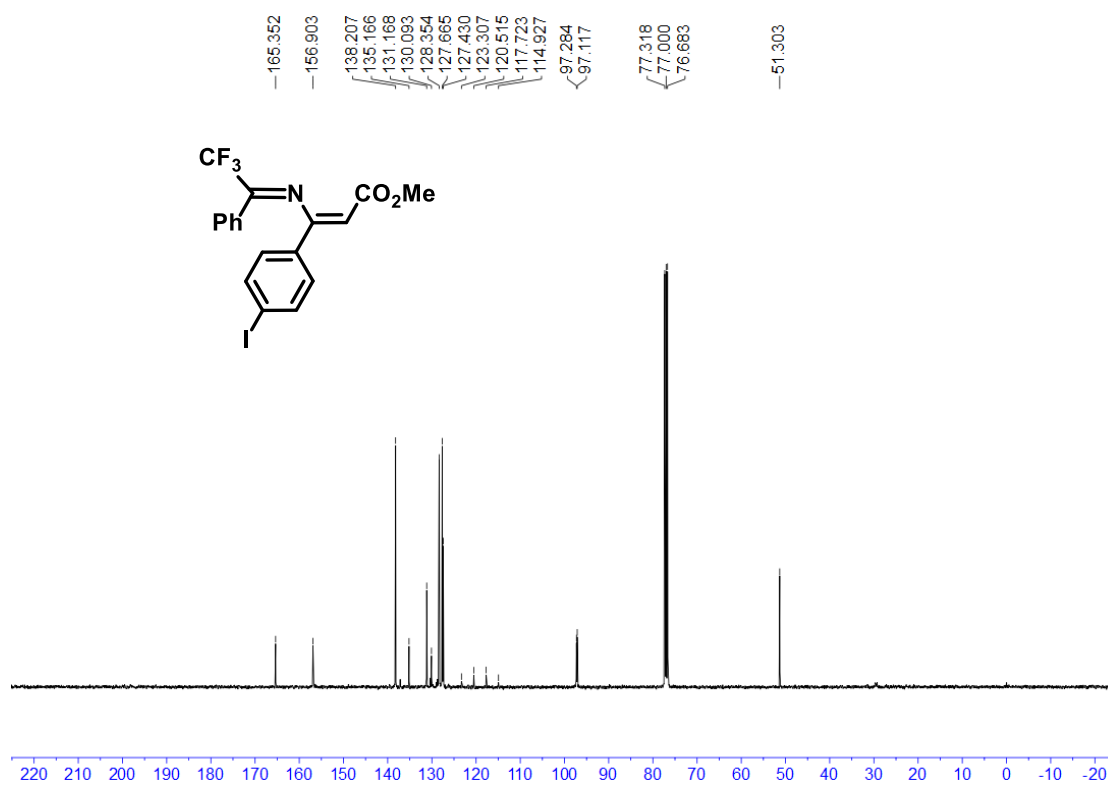
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **3ma**



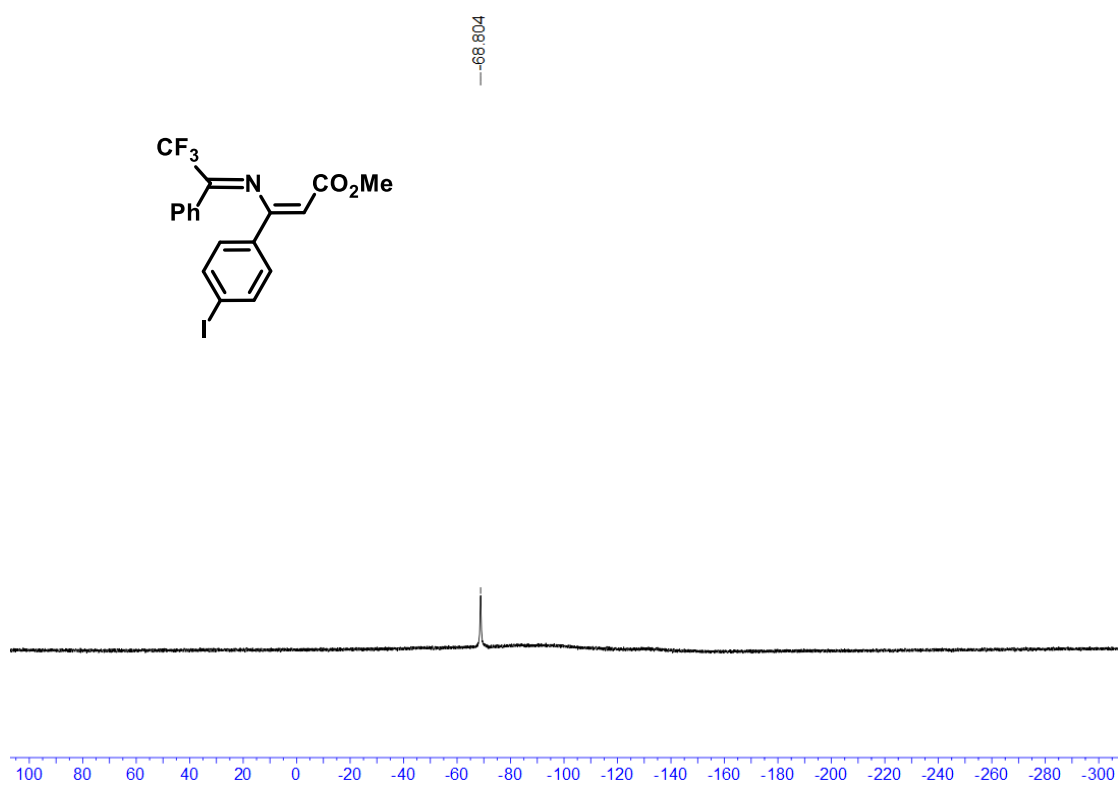
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3na**



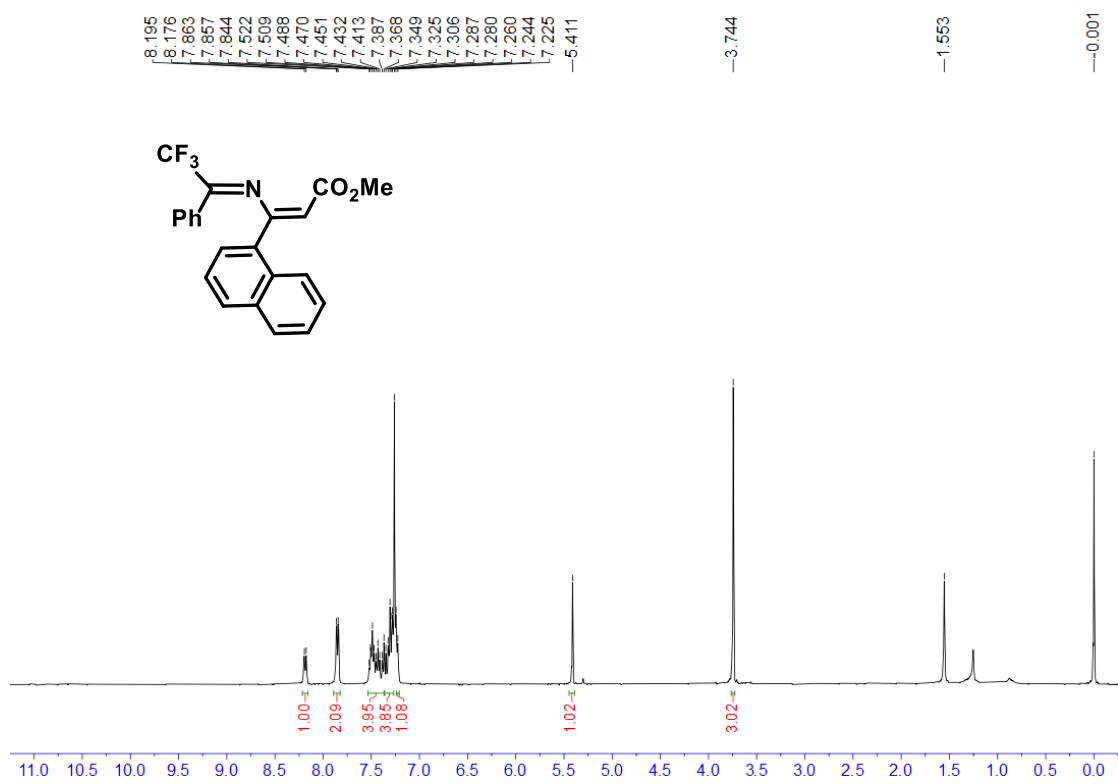
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3na**



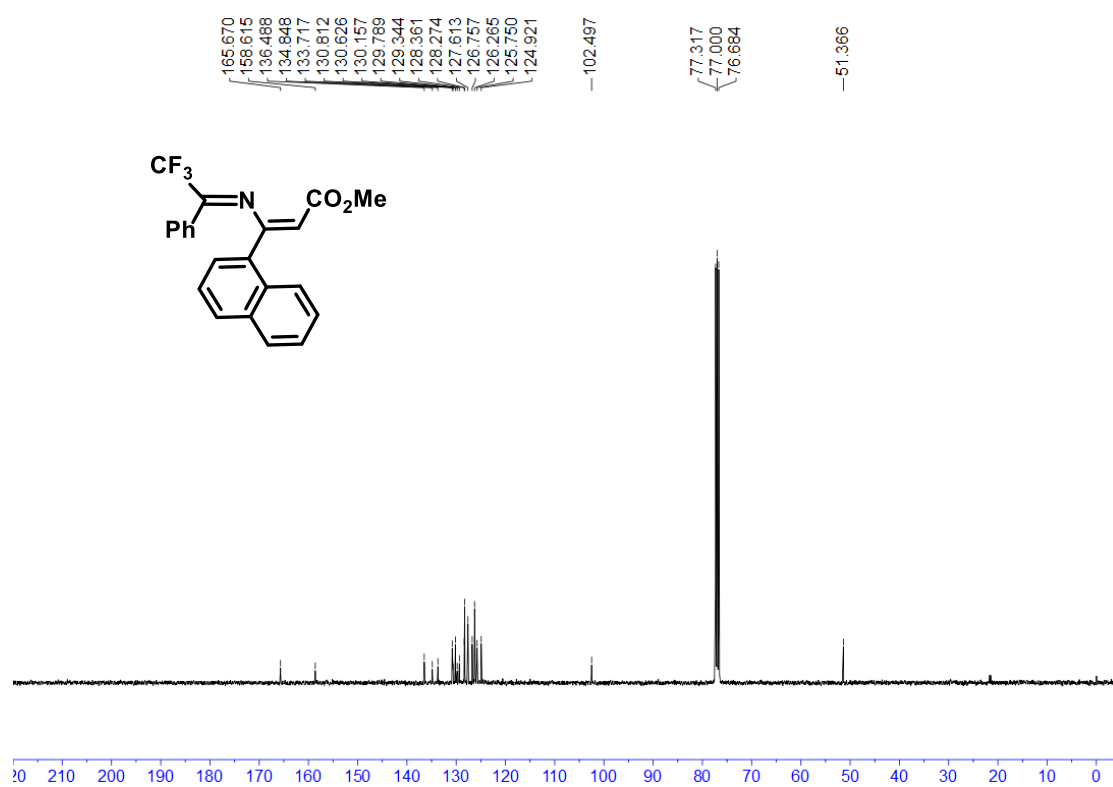
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3na**



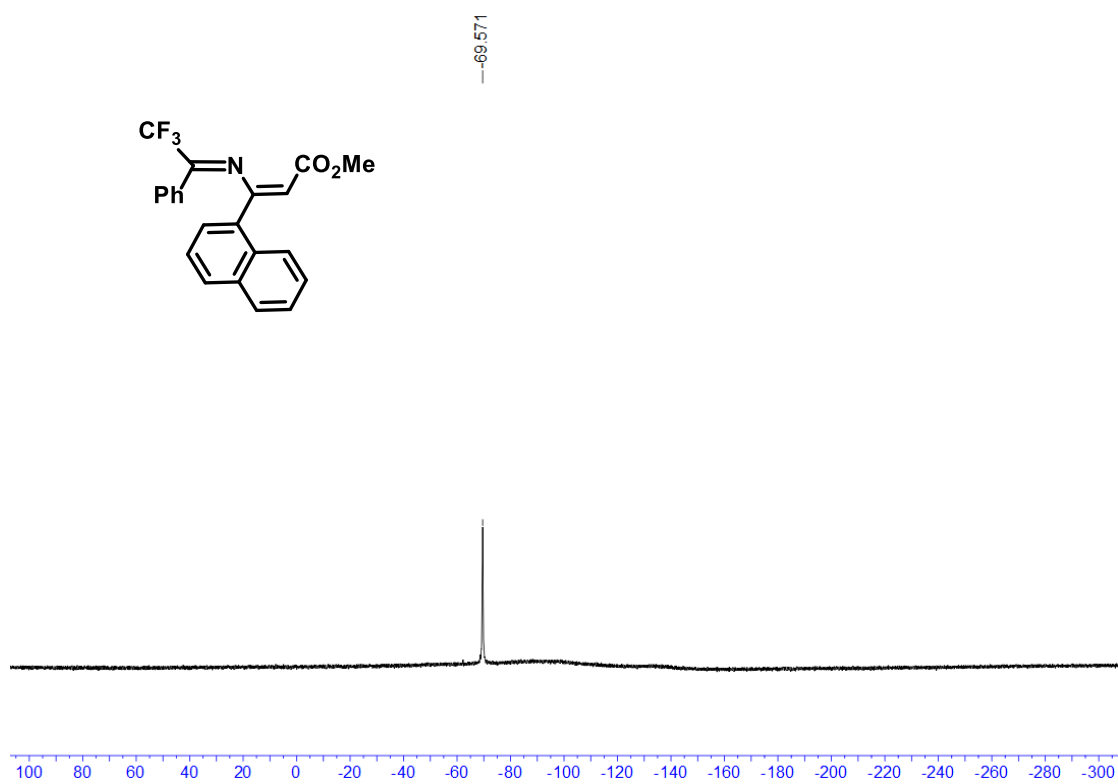
$^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3oa**



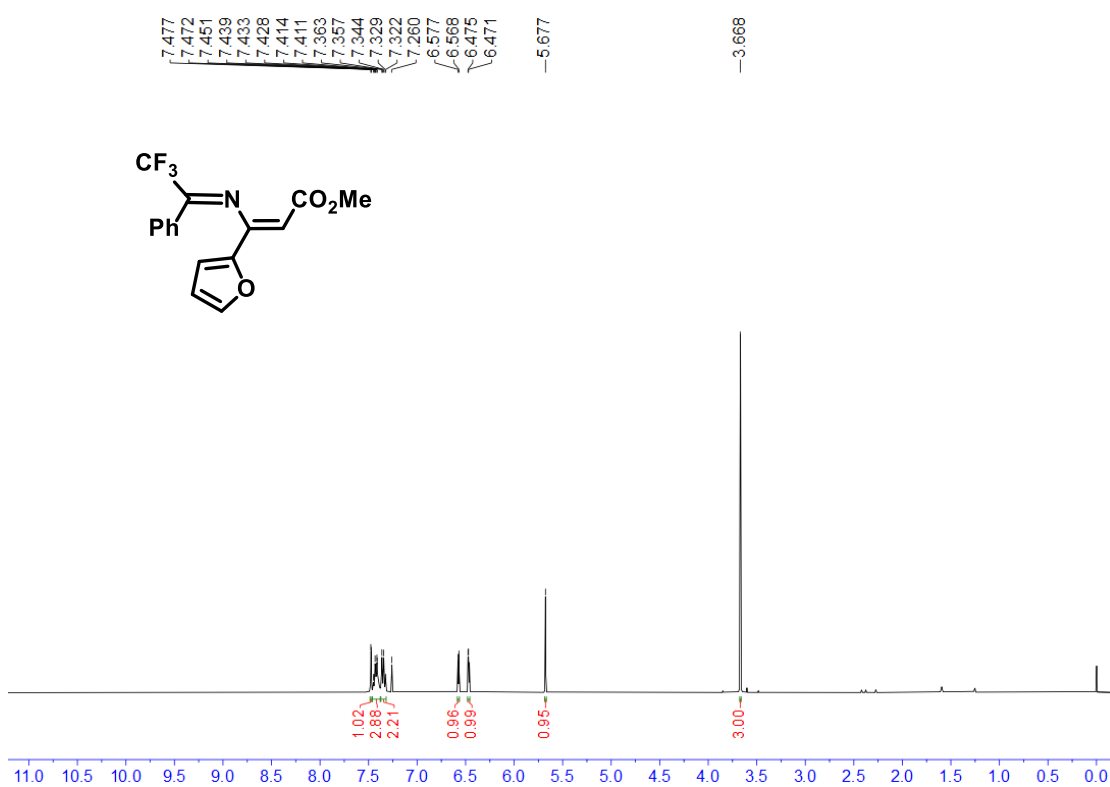
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3oa**



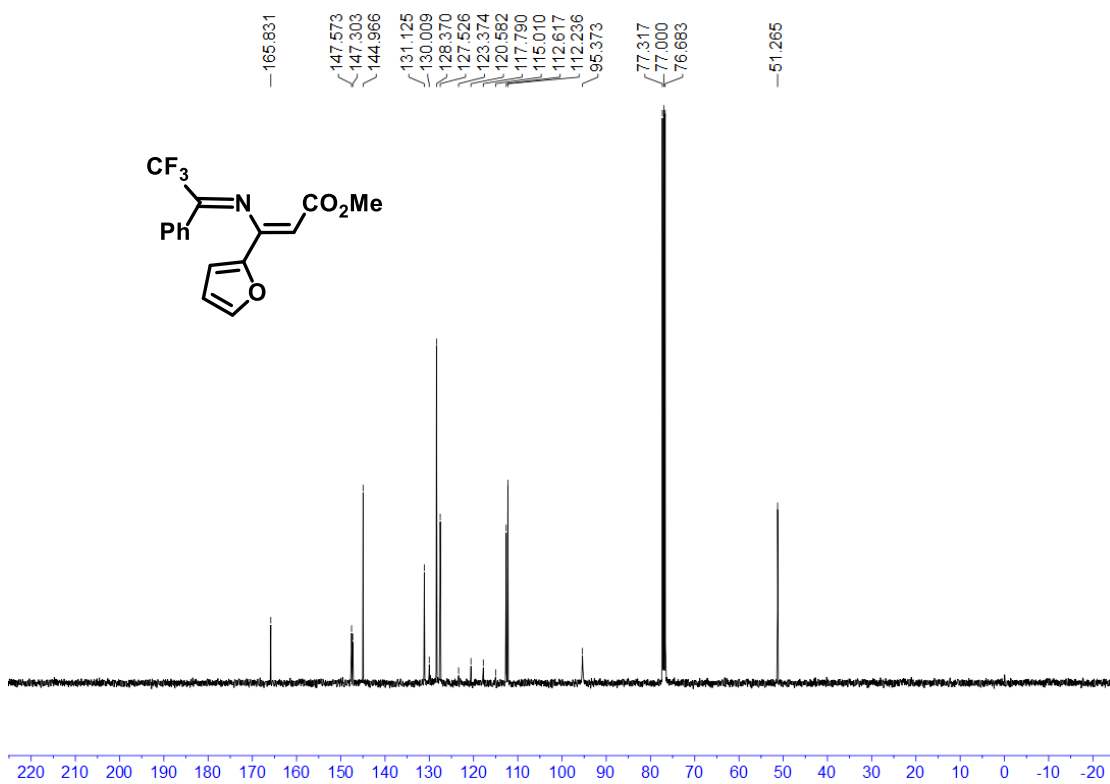
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **3oa**



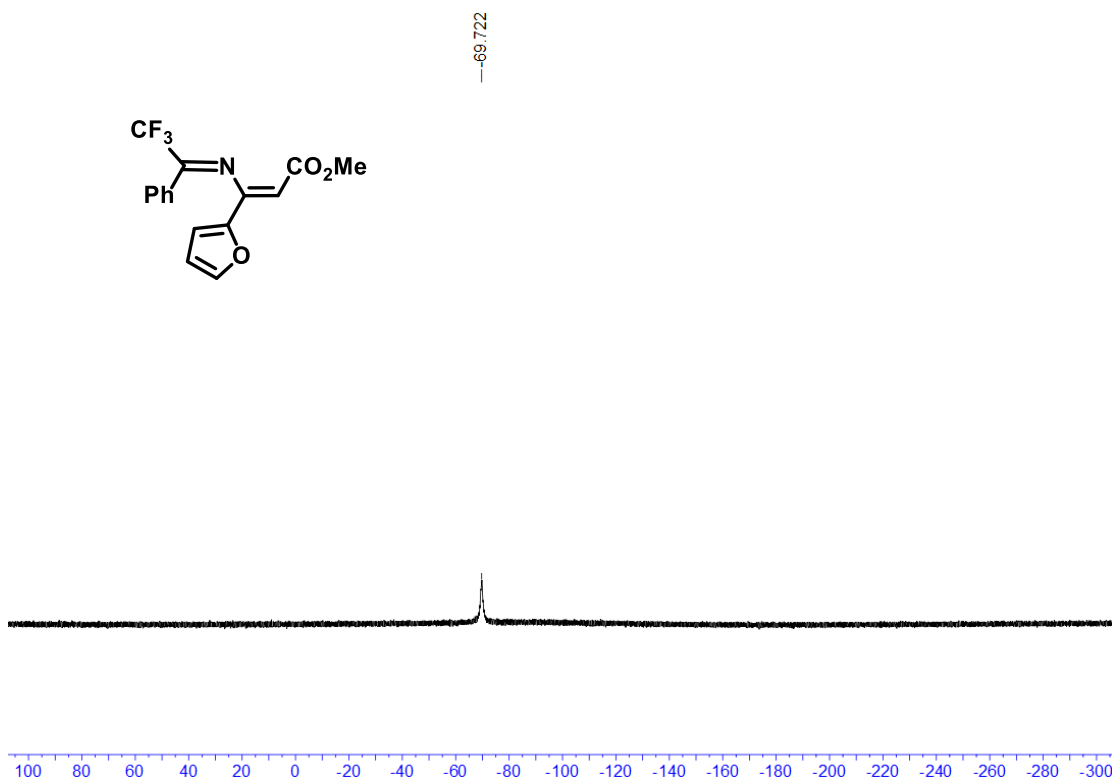
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3pa**



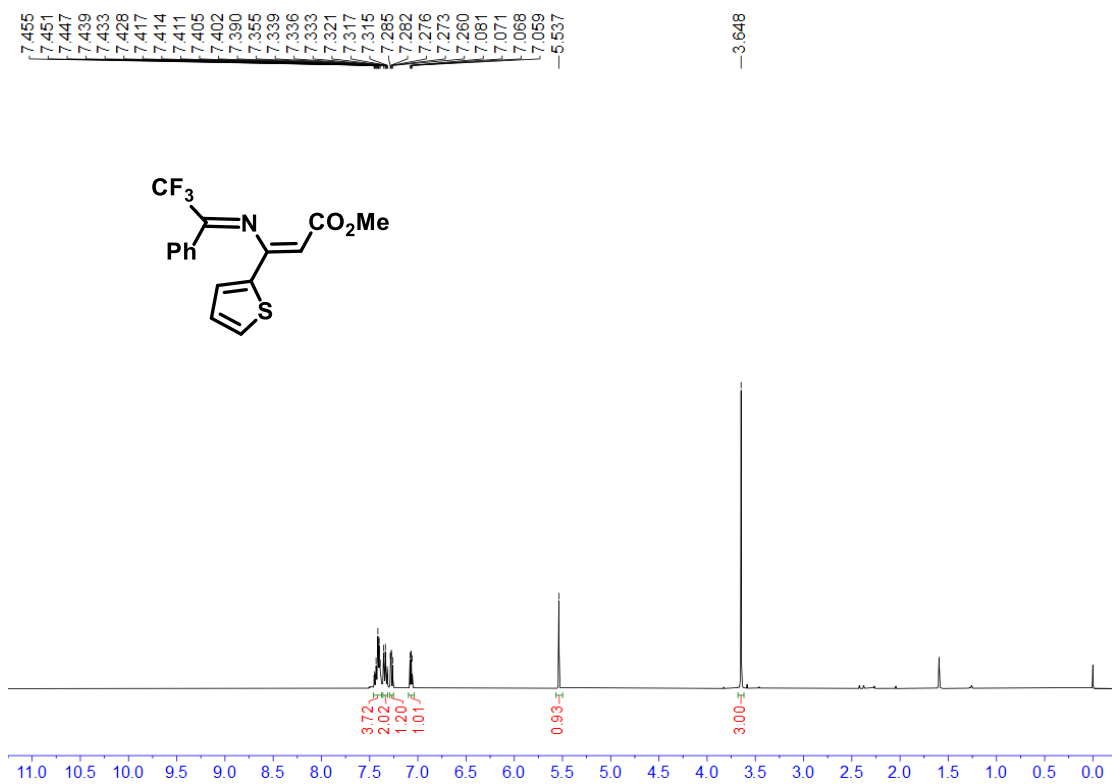
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3pa**



$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3pa**

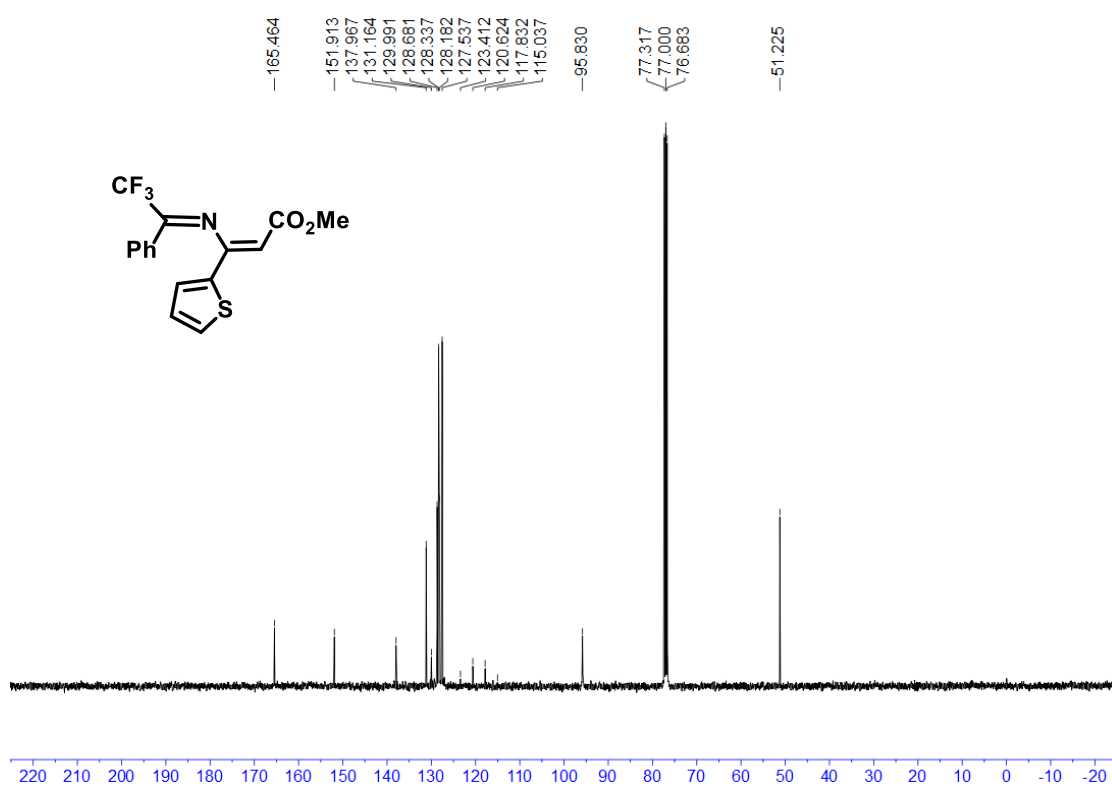


$^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3qa**

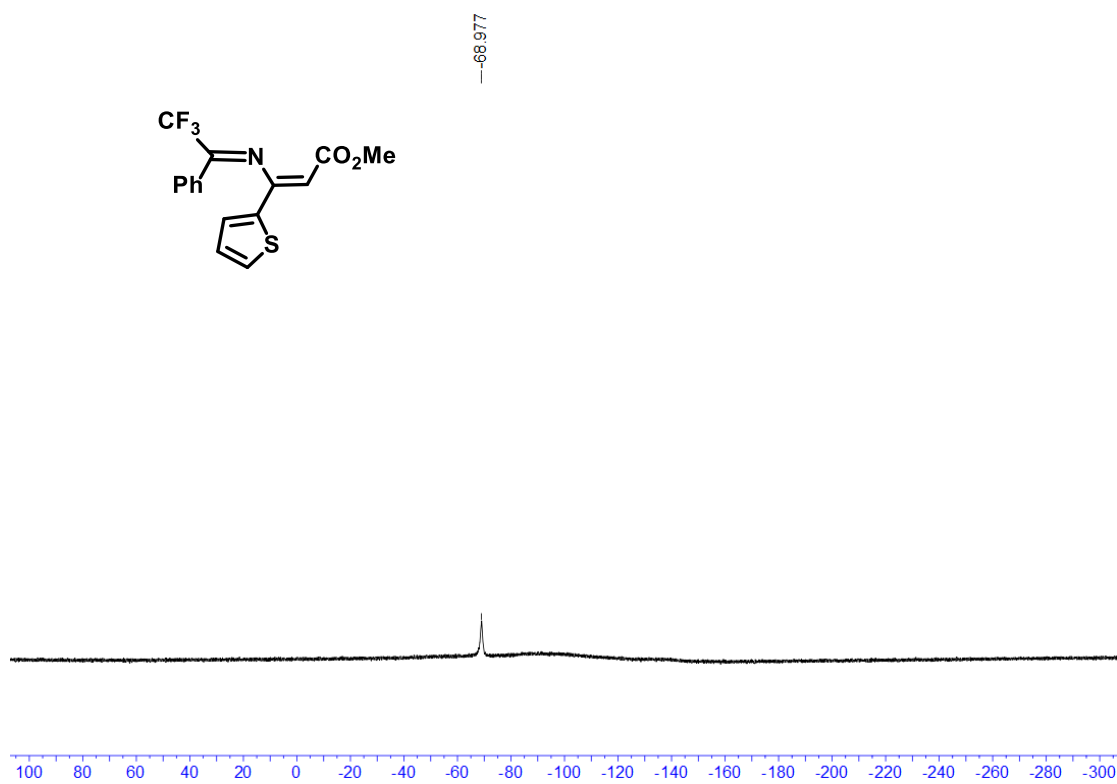




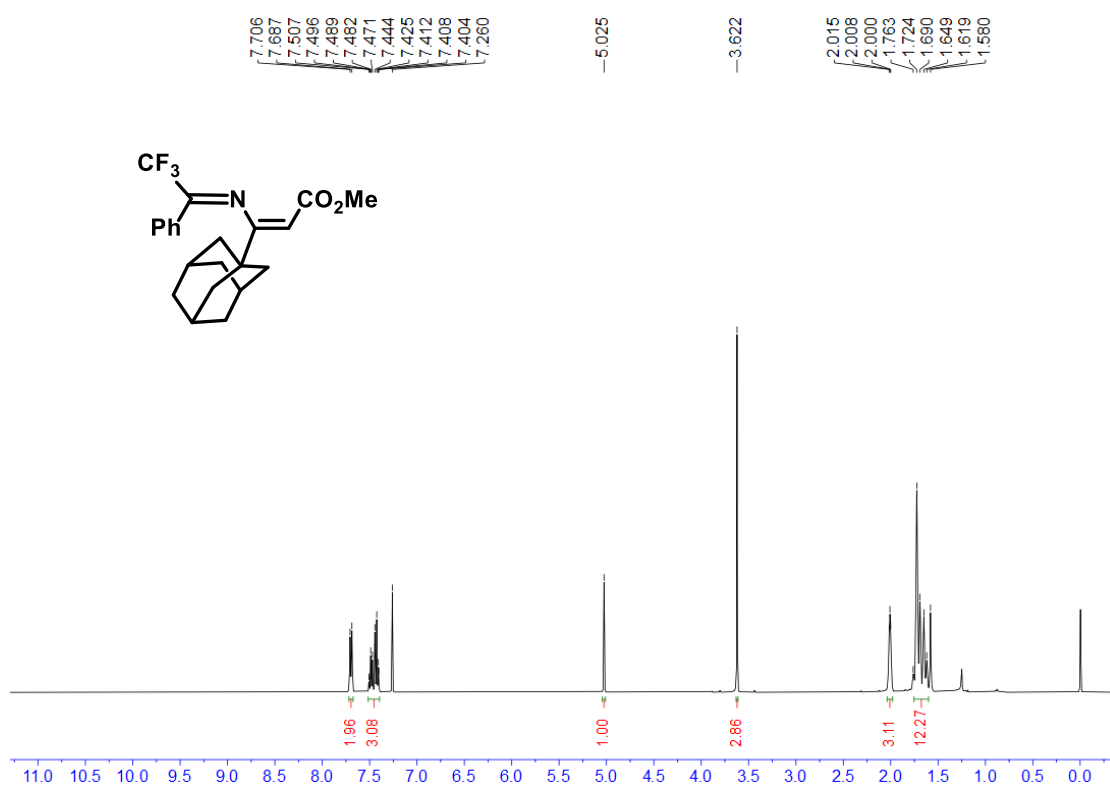
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3qa**



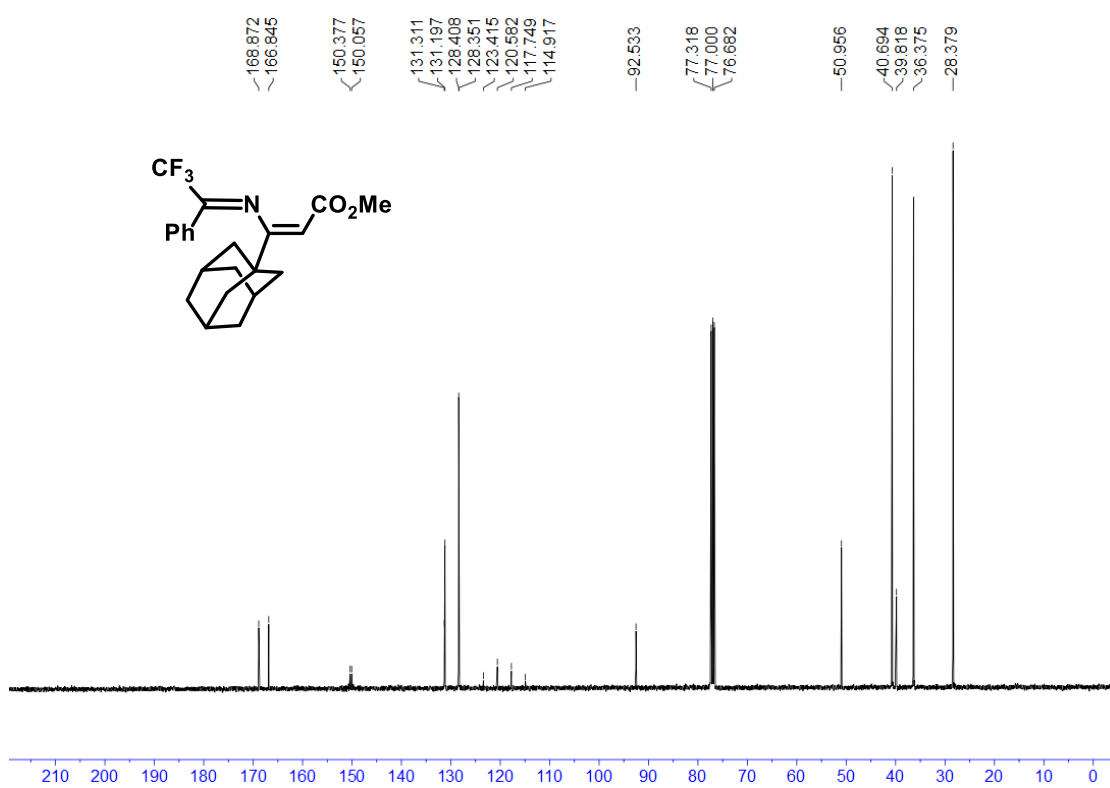
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **3qa**



<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3ra**

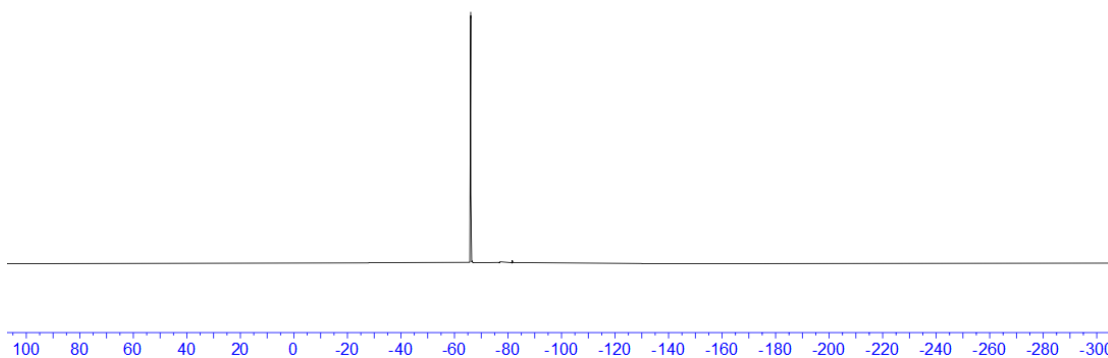
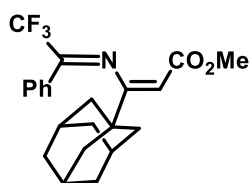


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3ra**

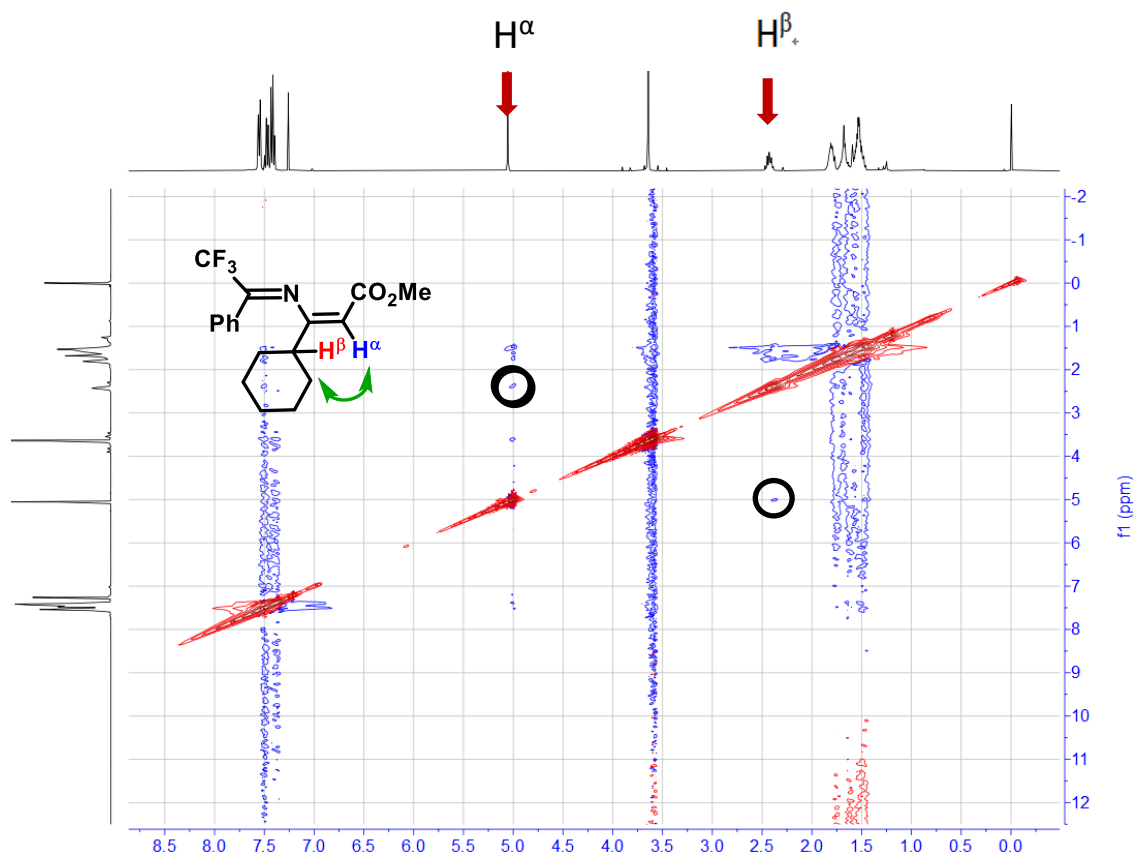


$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3ra**

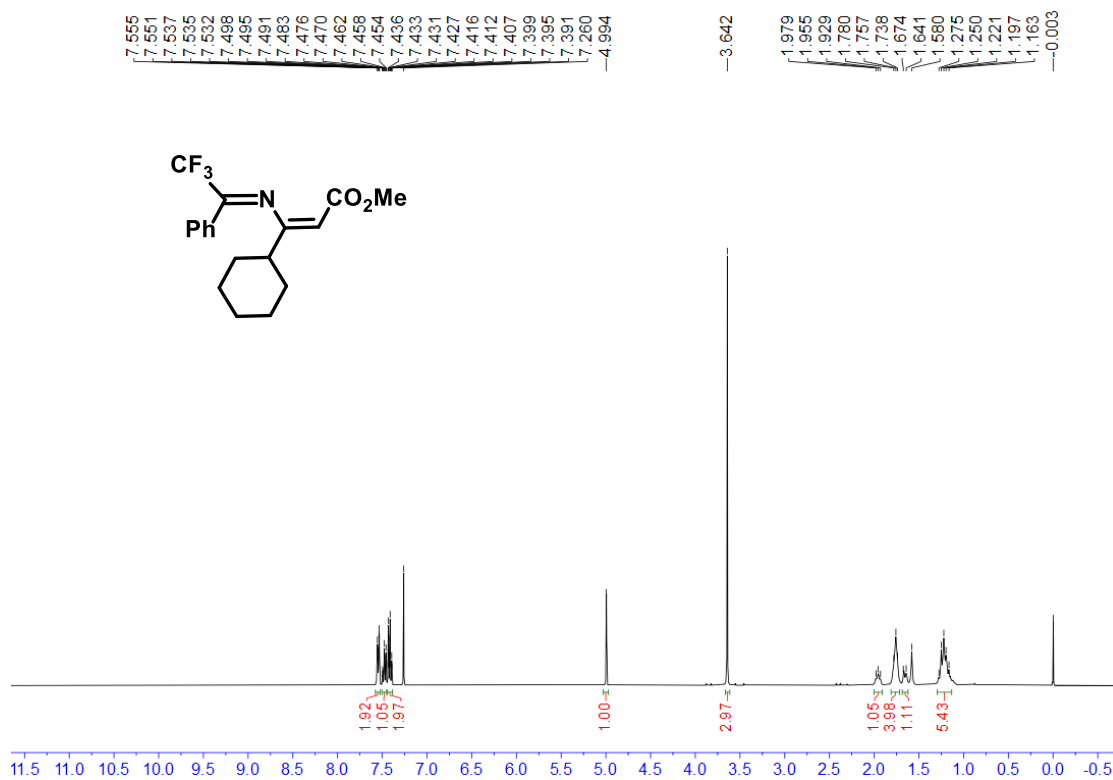
-66.073



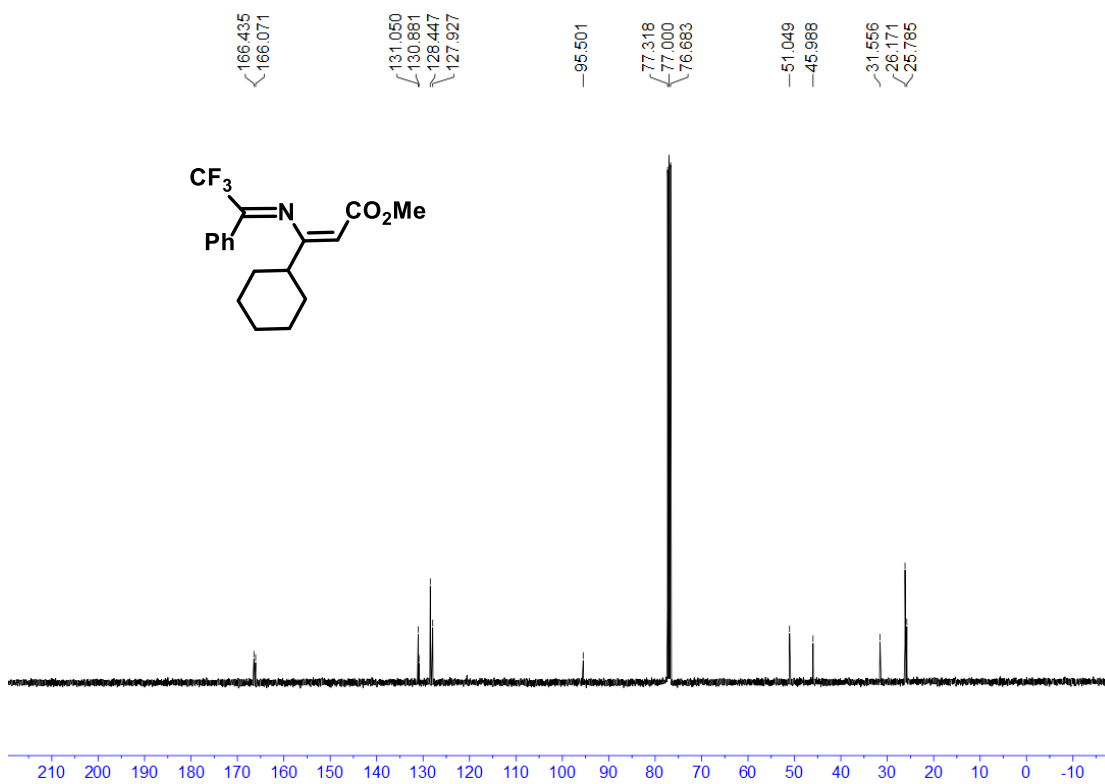
An NOE was observed between  $\text{H}^\alpha$  and  $\text{H}^\beta$



<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3sa-Z**

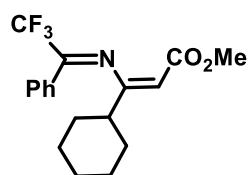


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3ra-Z**

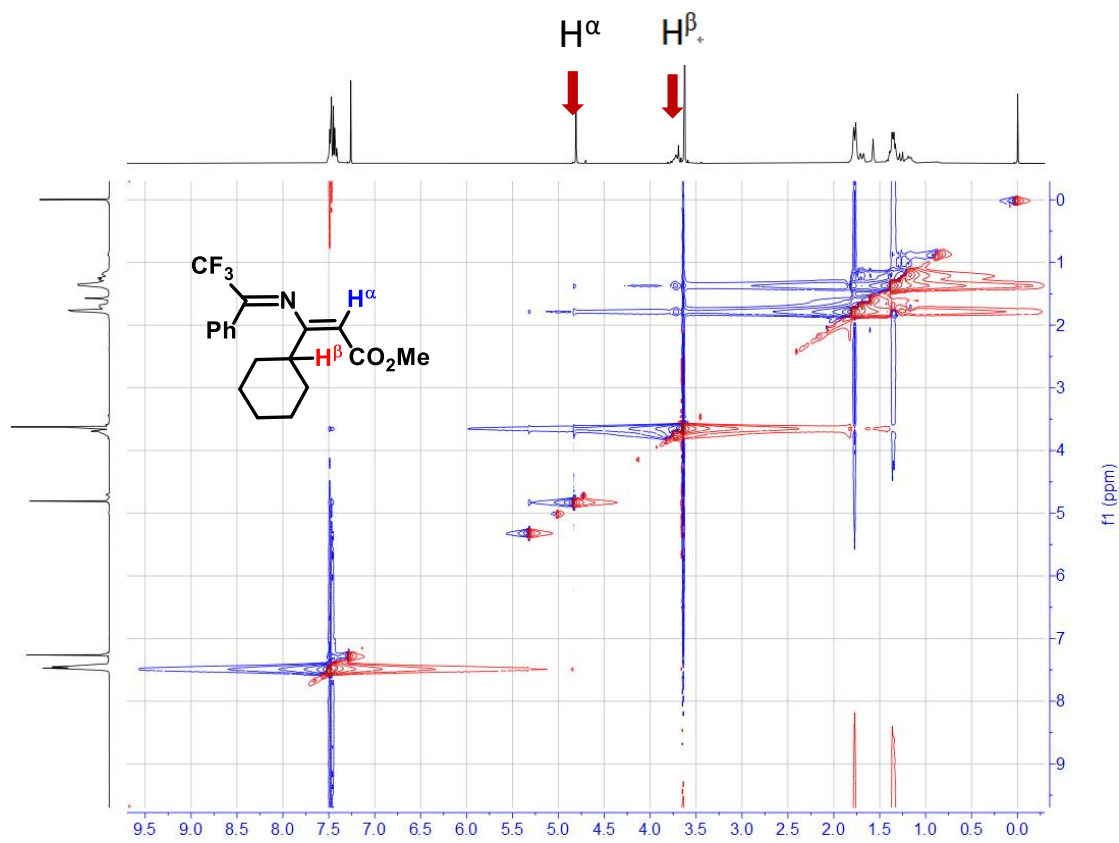


$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3sa-Z**

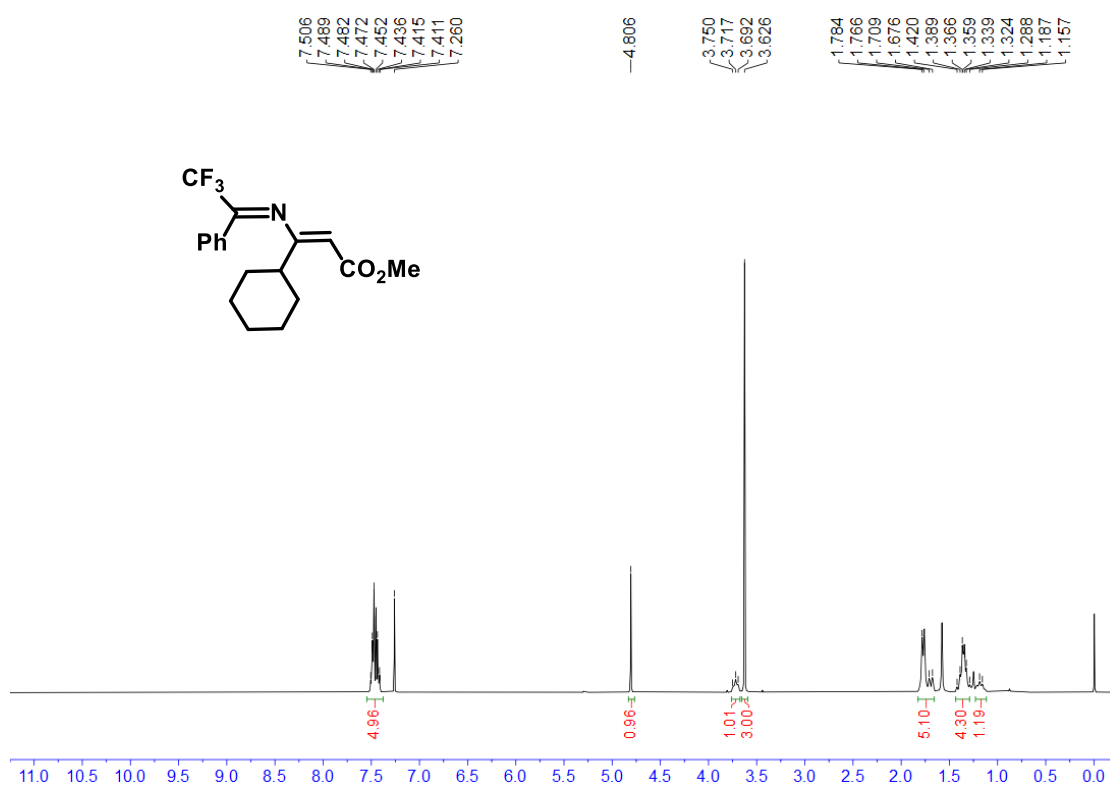
—67.750



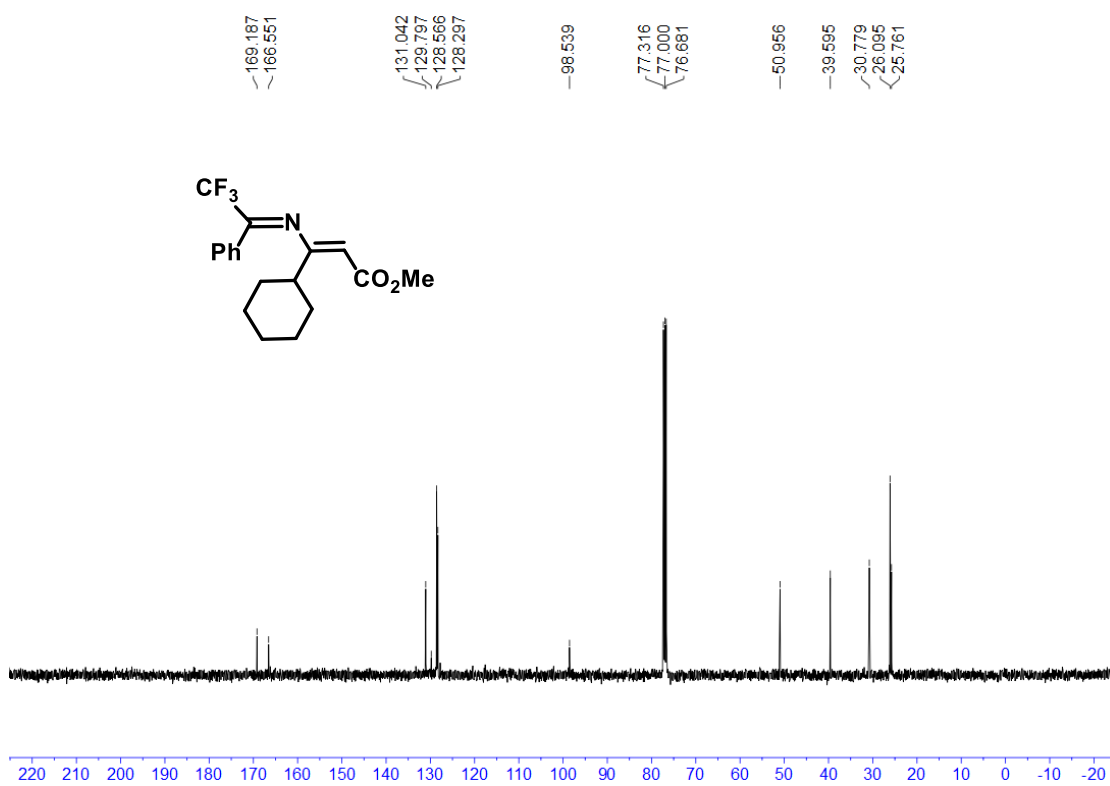
No NOE was observed between  $\text{H}^\alpha$  and  $\text{H}^\beta$



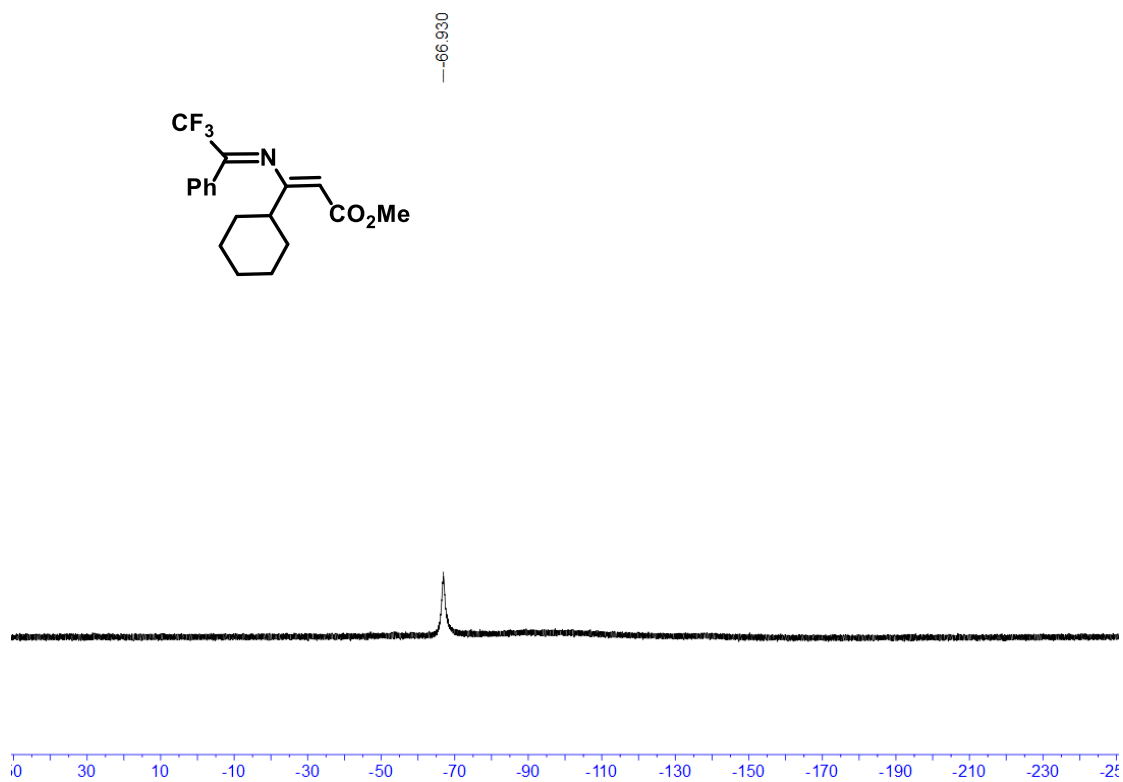
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3sa-E**



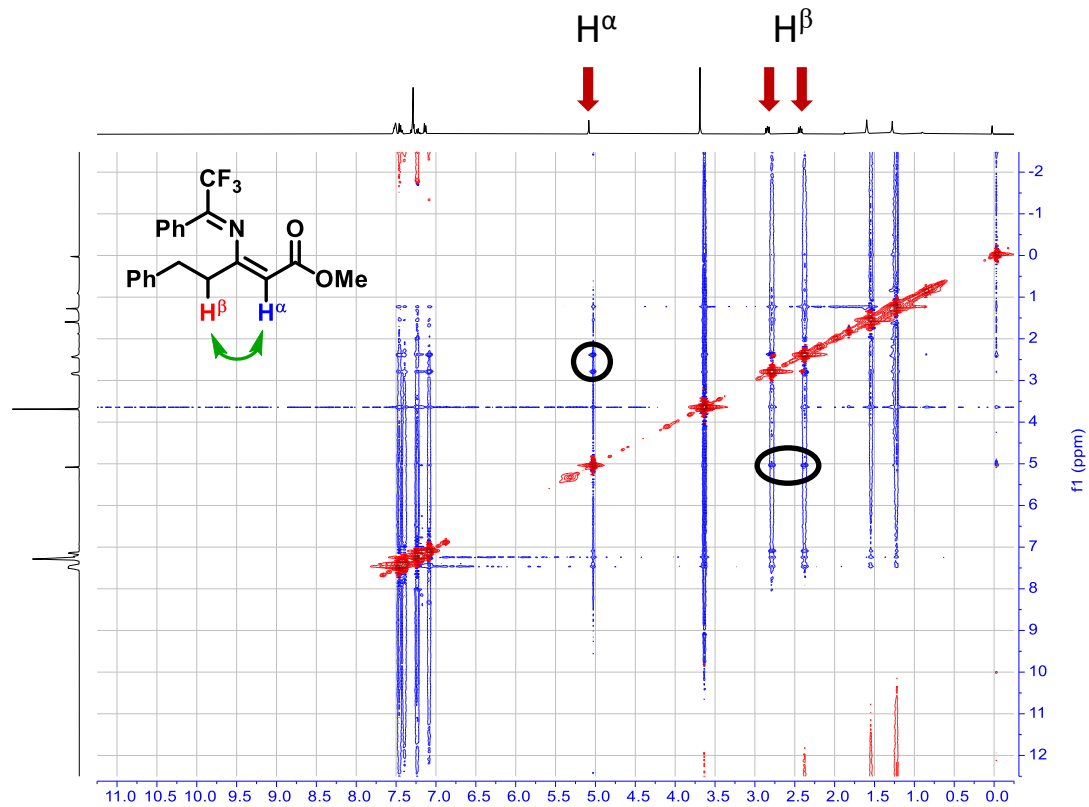
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3sa-E**



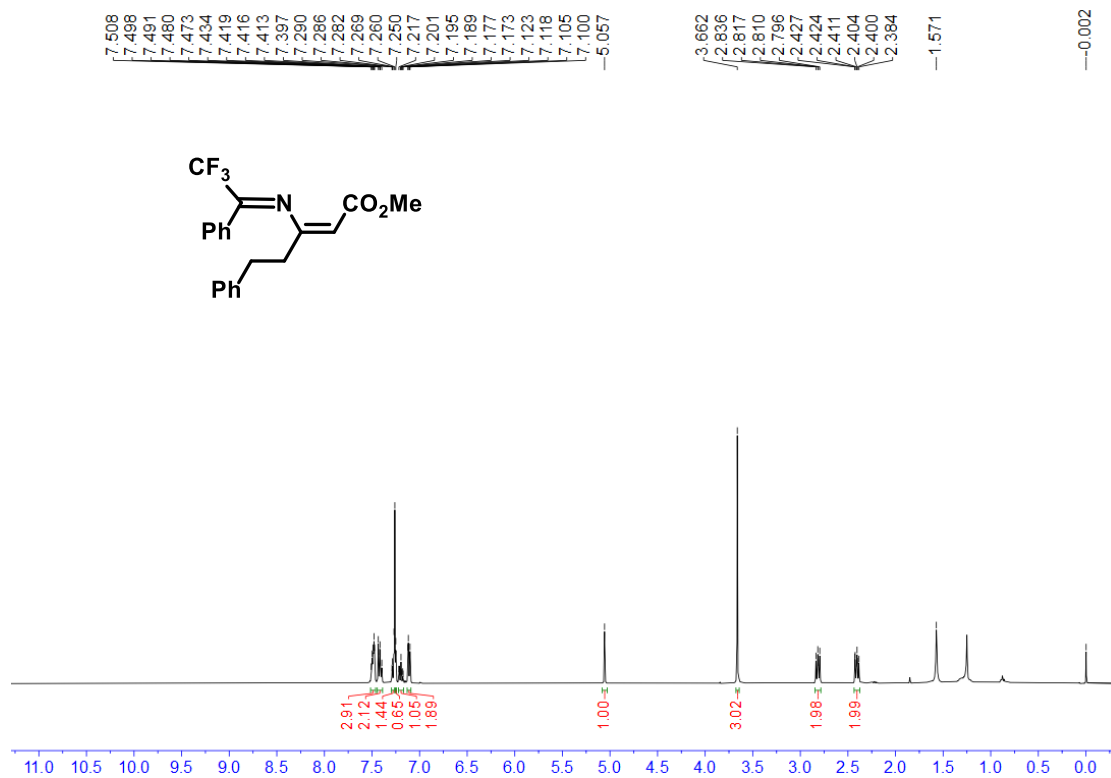
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3sa-E**



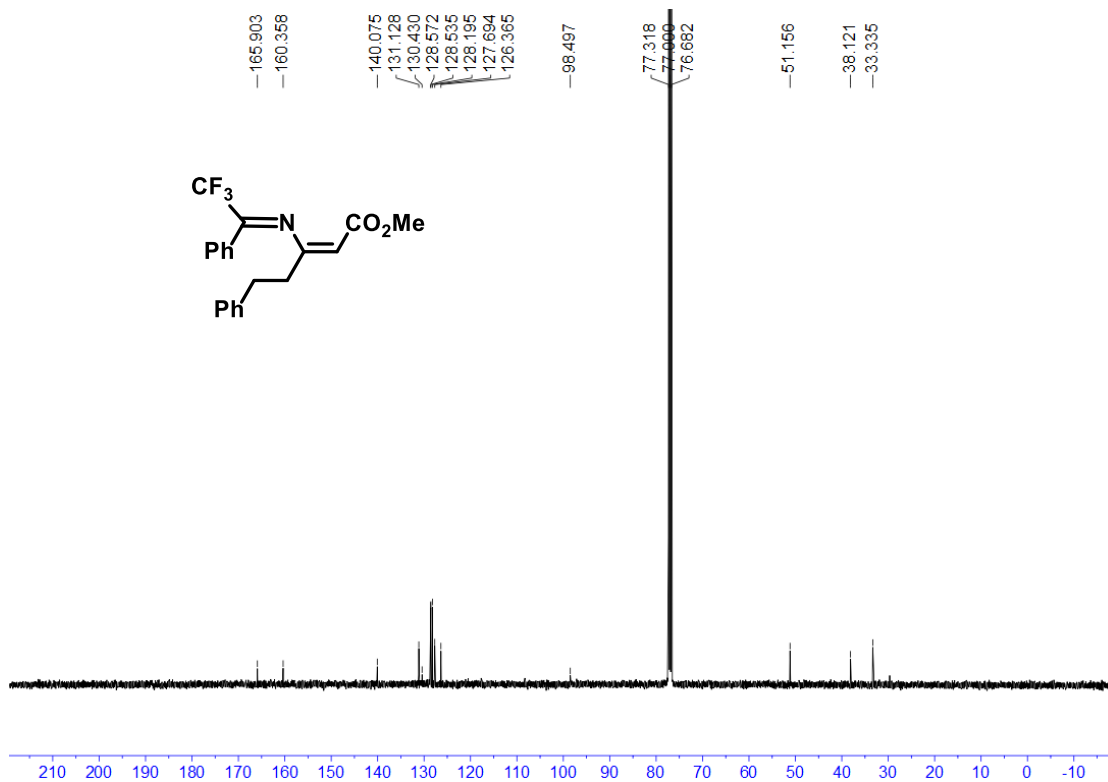
An NOE was observed between  $\text{H}^\alpha$  and  $\text{H}^\beta$



$^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ta-Z**



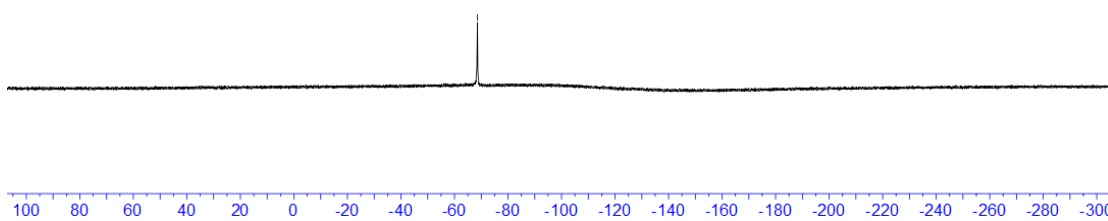
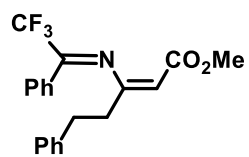
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3ta-Z**



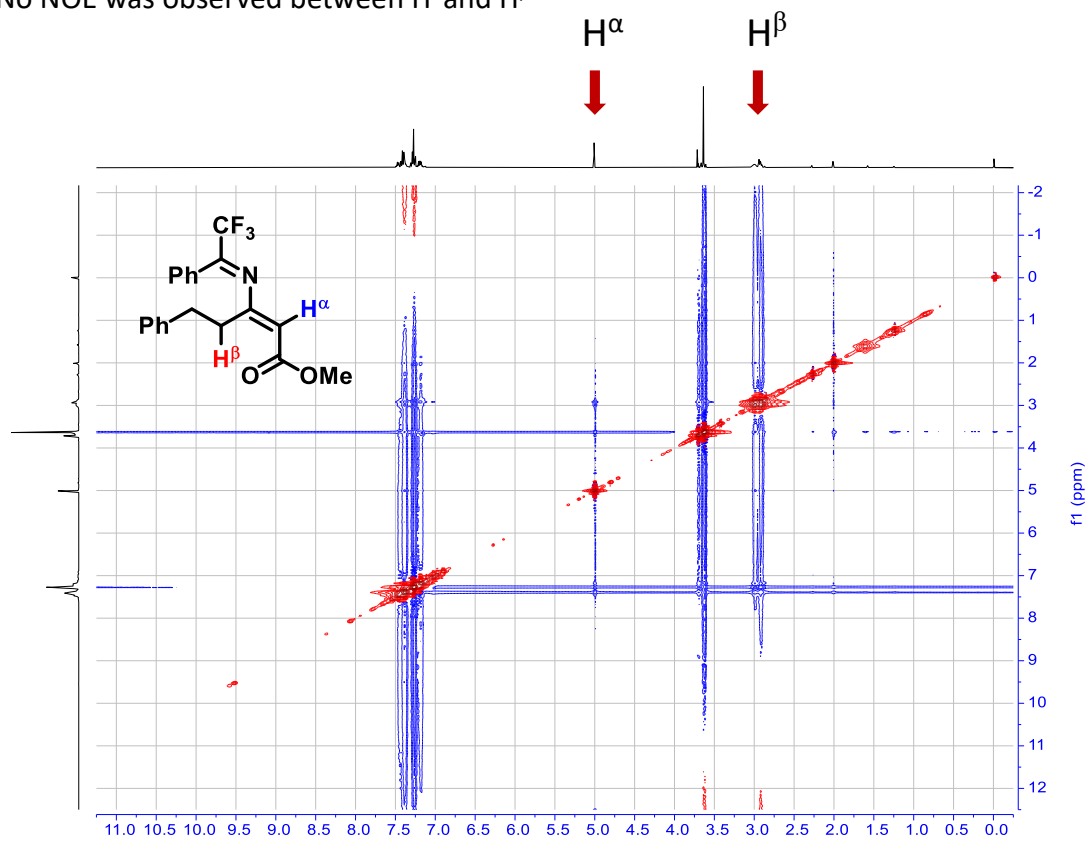
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **3ta-Z**



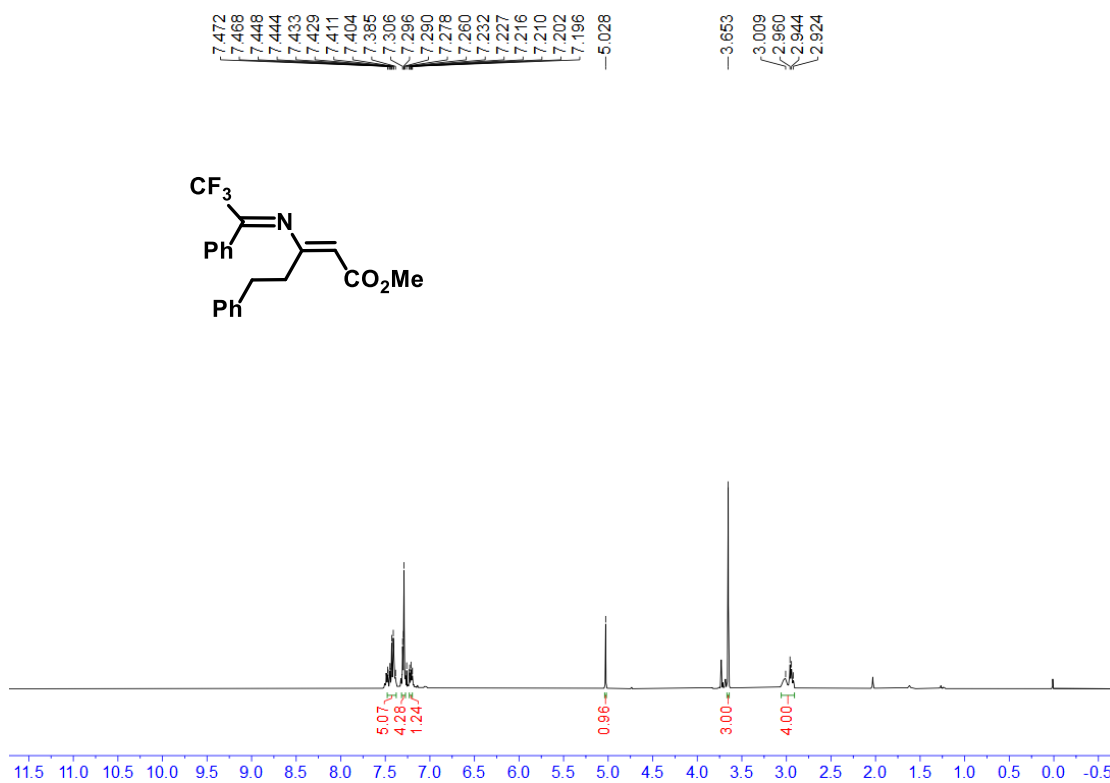
—68.556



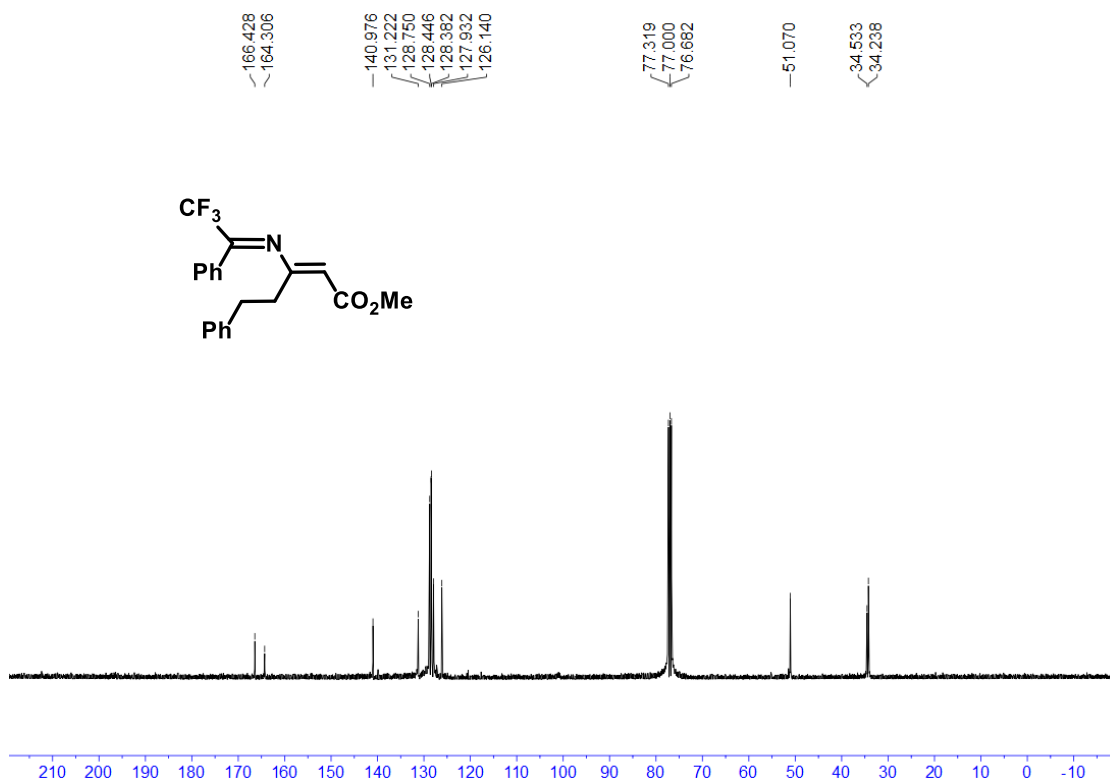
No NOE was observed between  $H^\alpha$  and  $H^\beta$



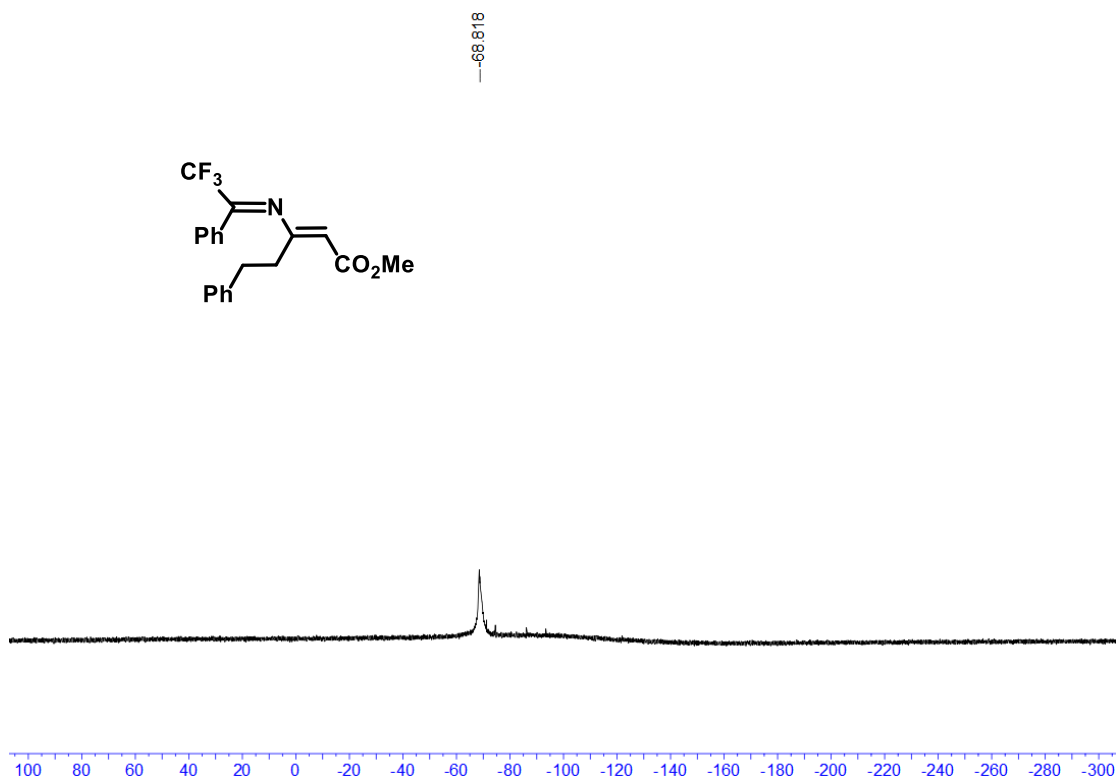
$^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ta-E**



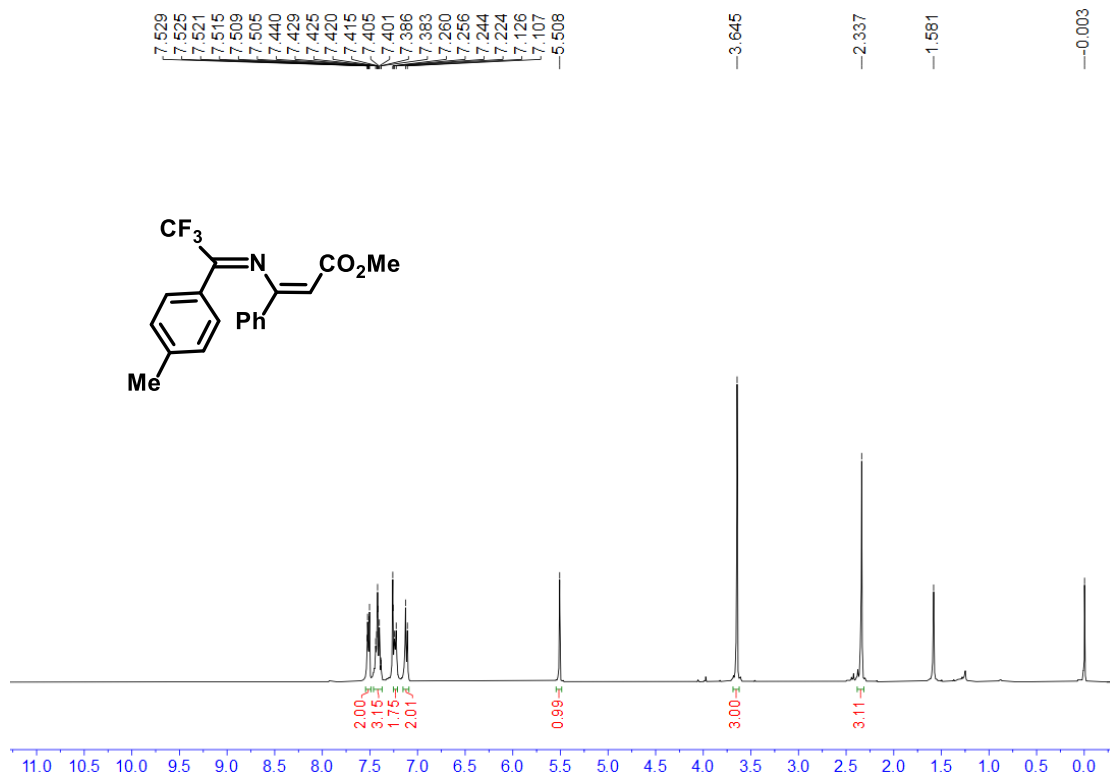
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ta-E**



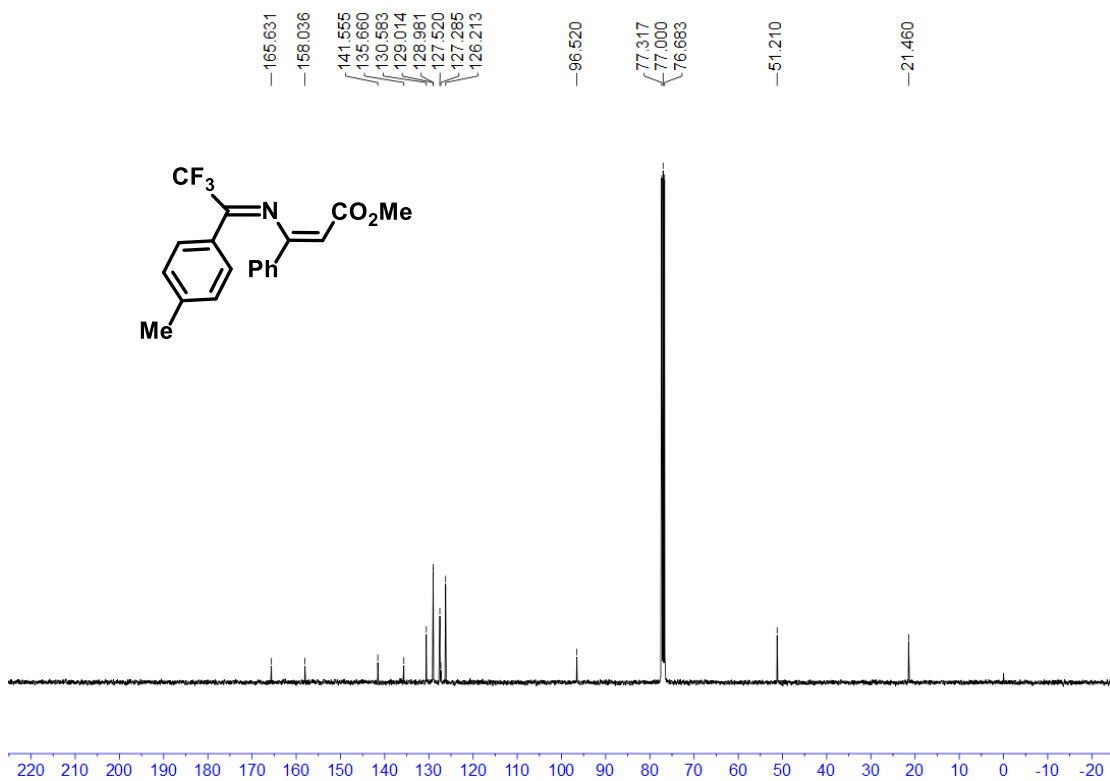
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3ta-E**



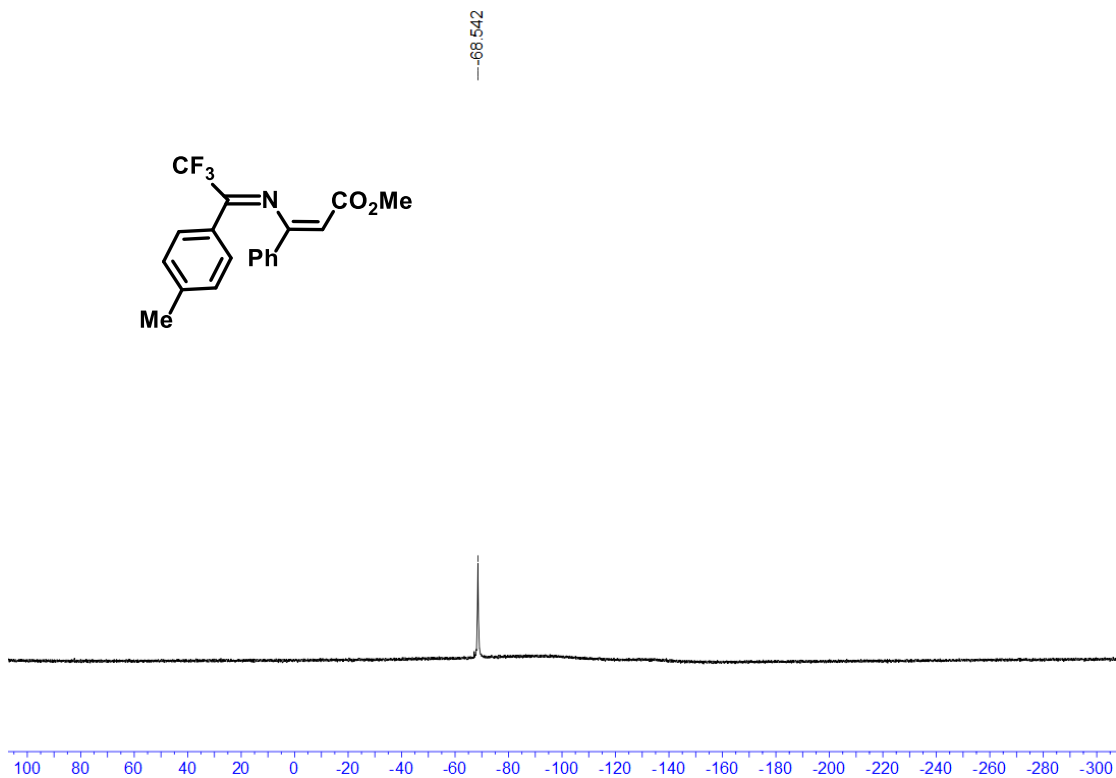
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3ab**



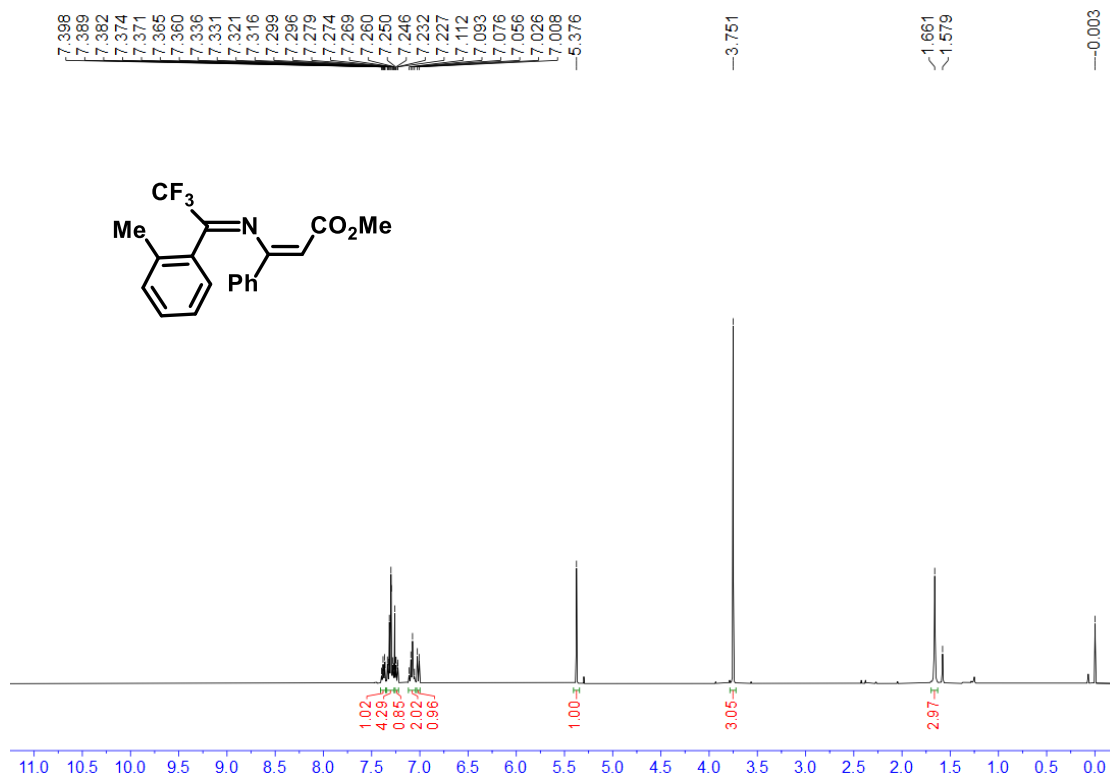
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3ab**



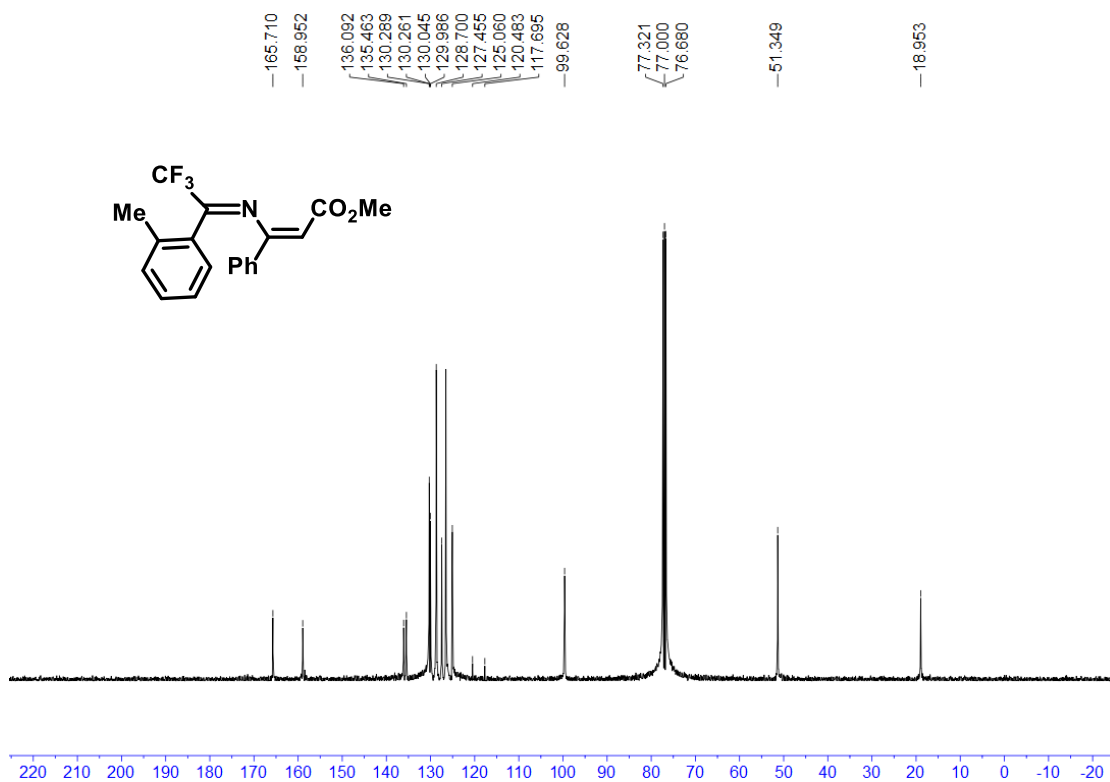
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **3ab**



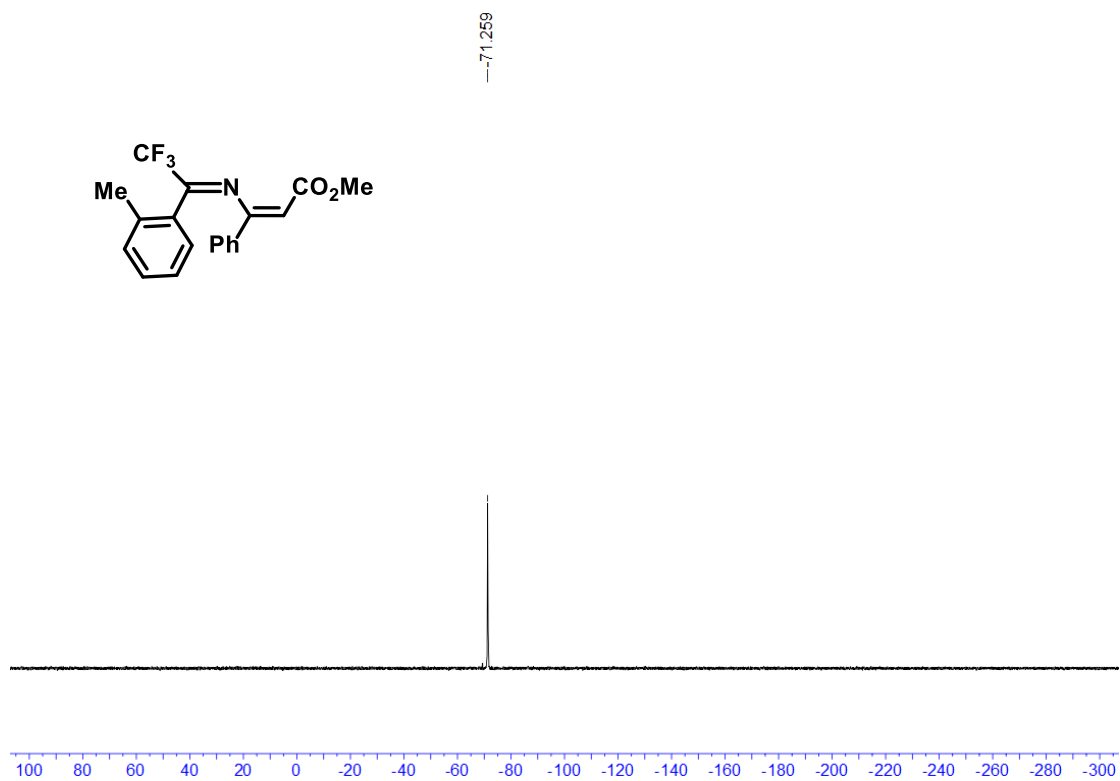
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3ac**



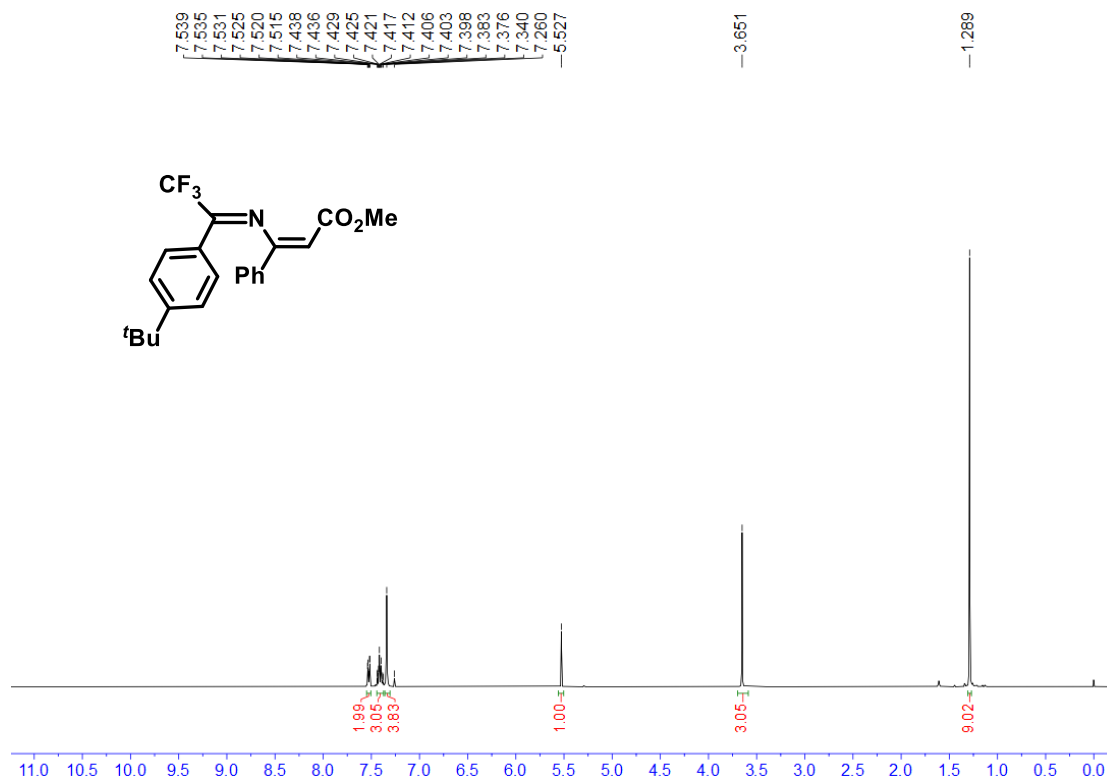
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3ac**



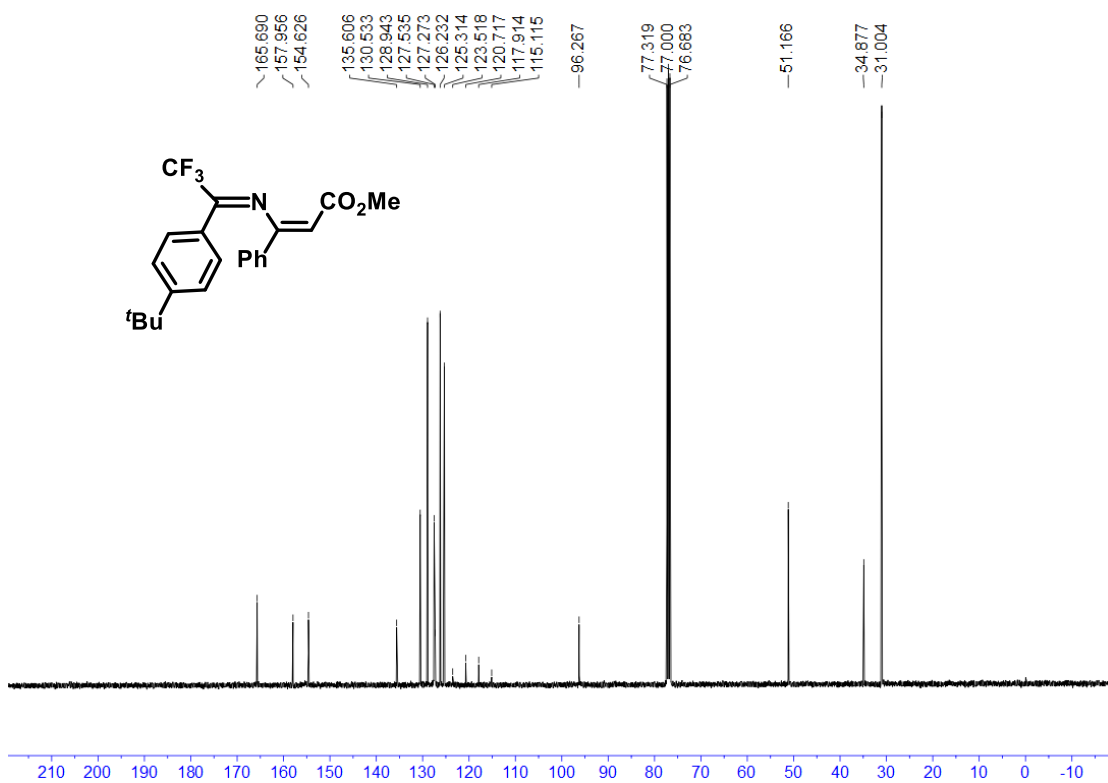
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **3ac**



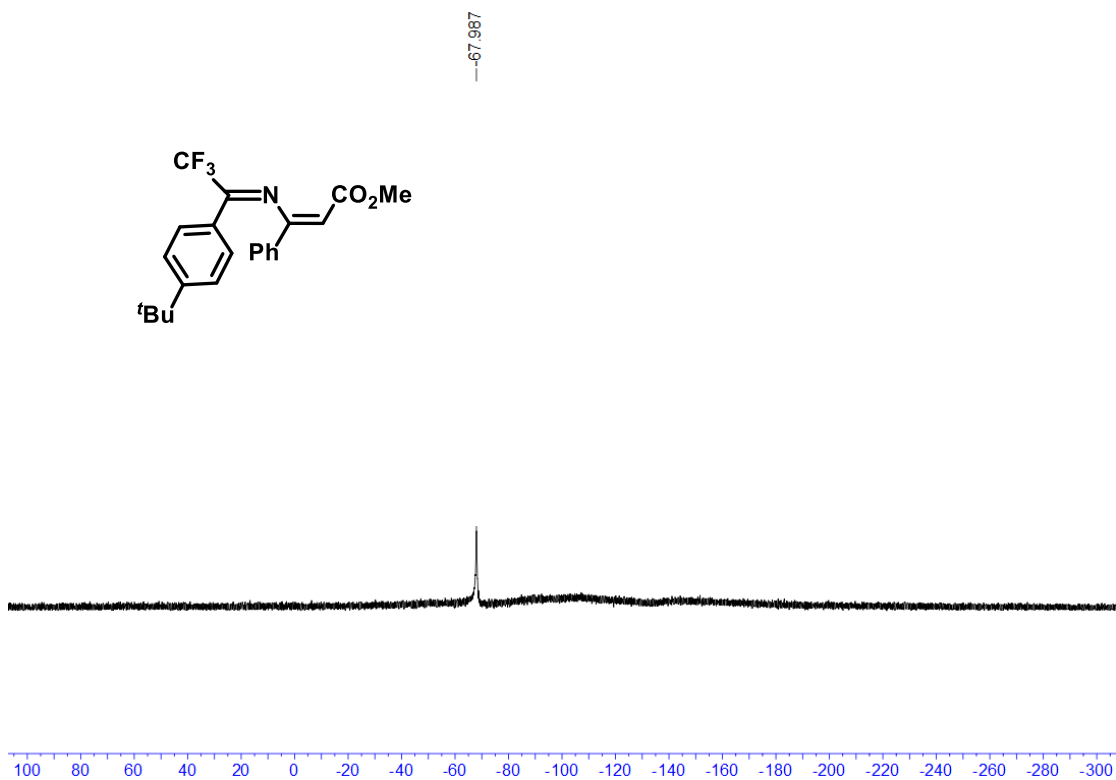
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3ad**



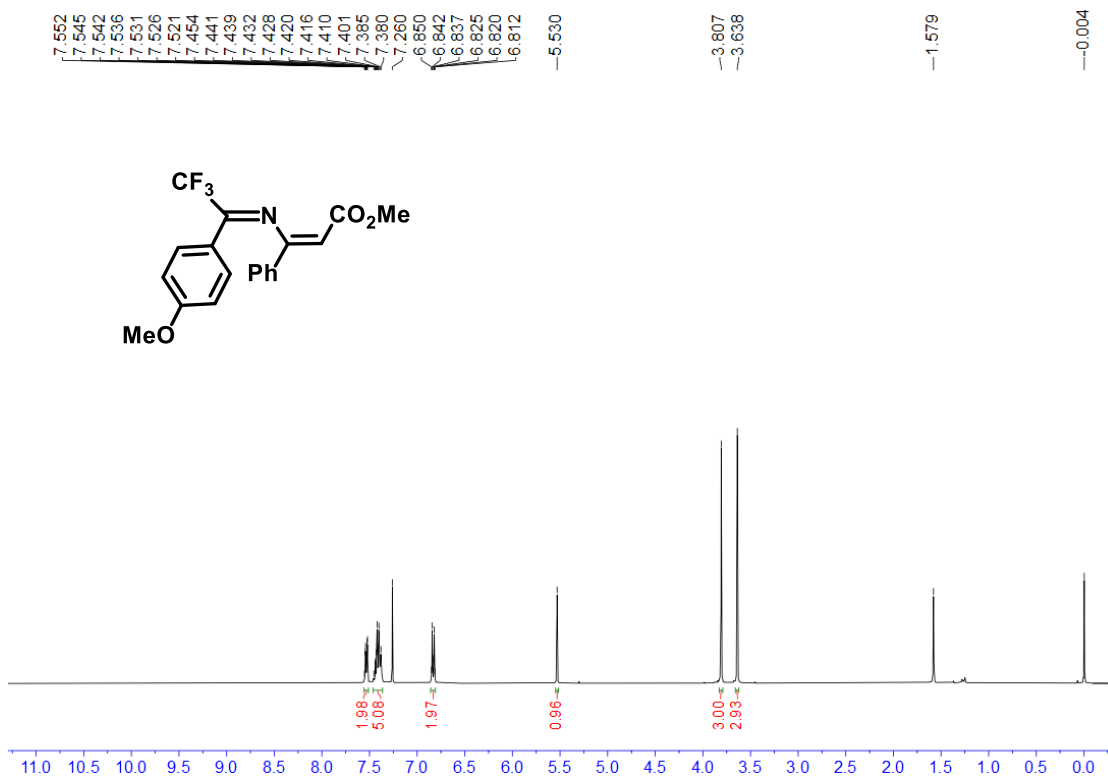
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3ad**



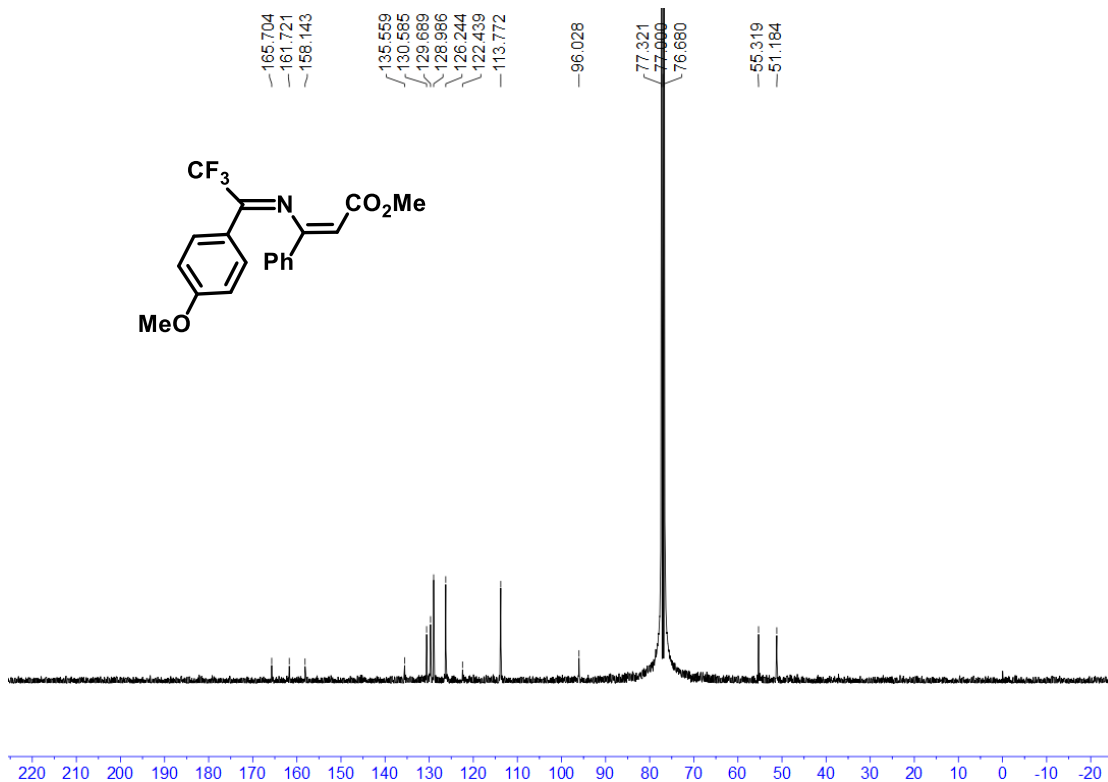
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **3ad**



<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3ae**

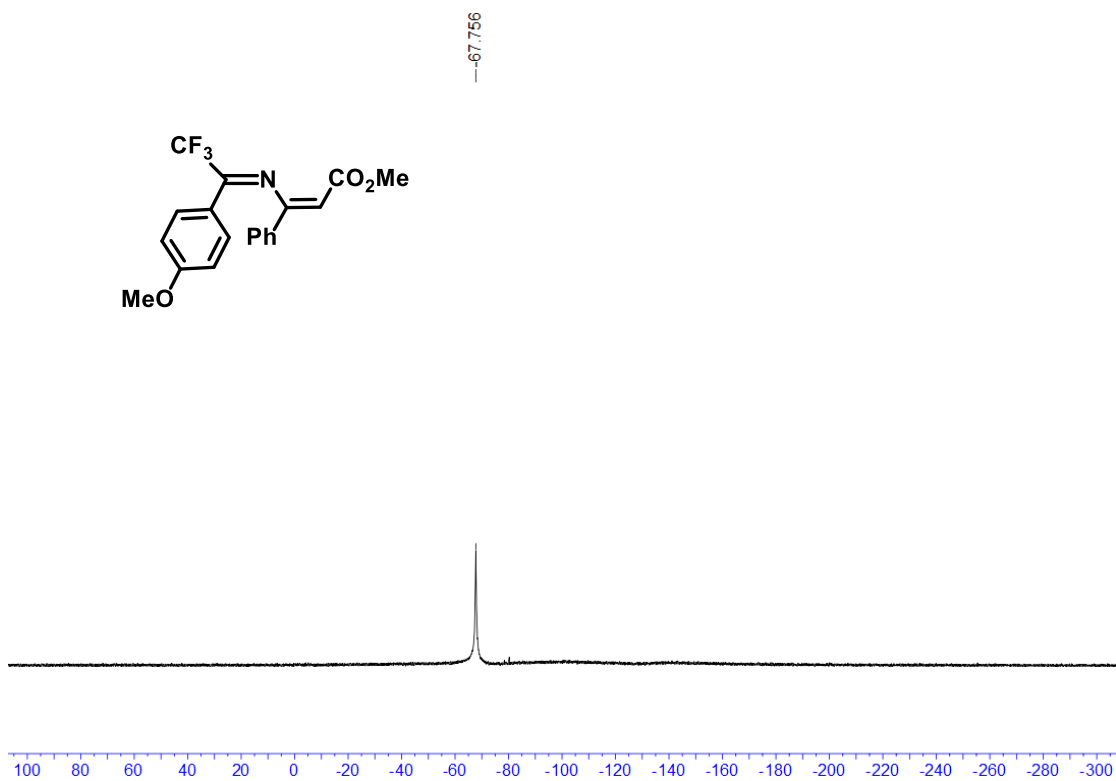
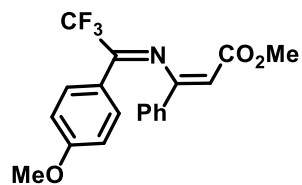


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3ae**

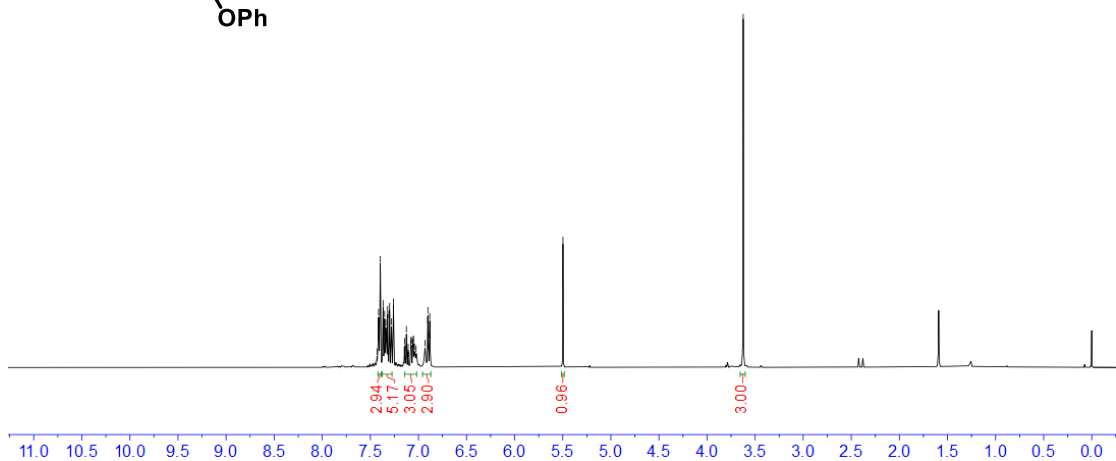
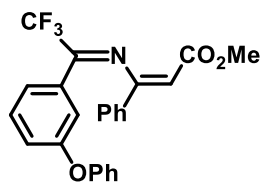
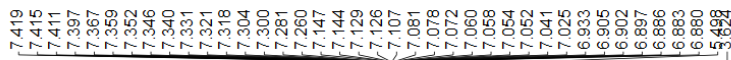


<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **3ae**

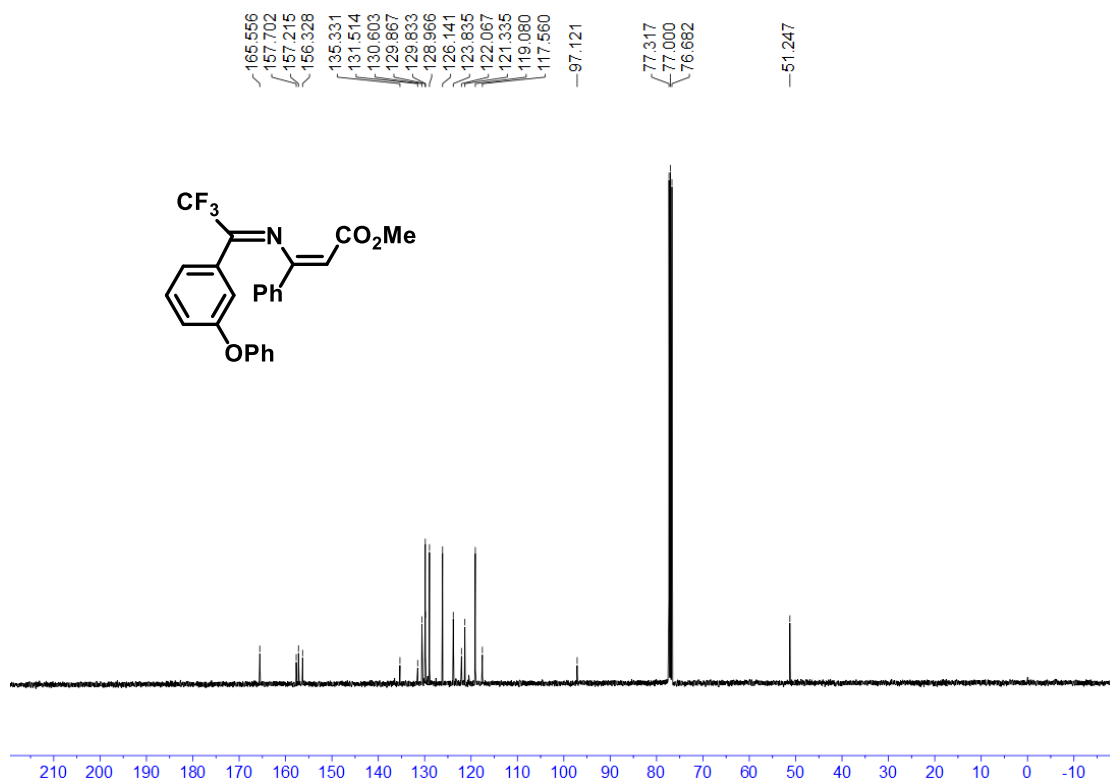




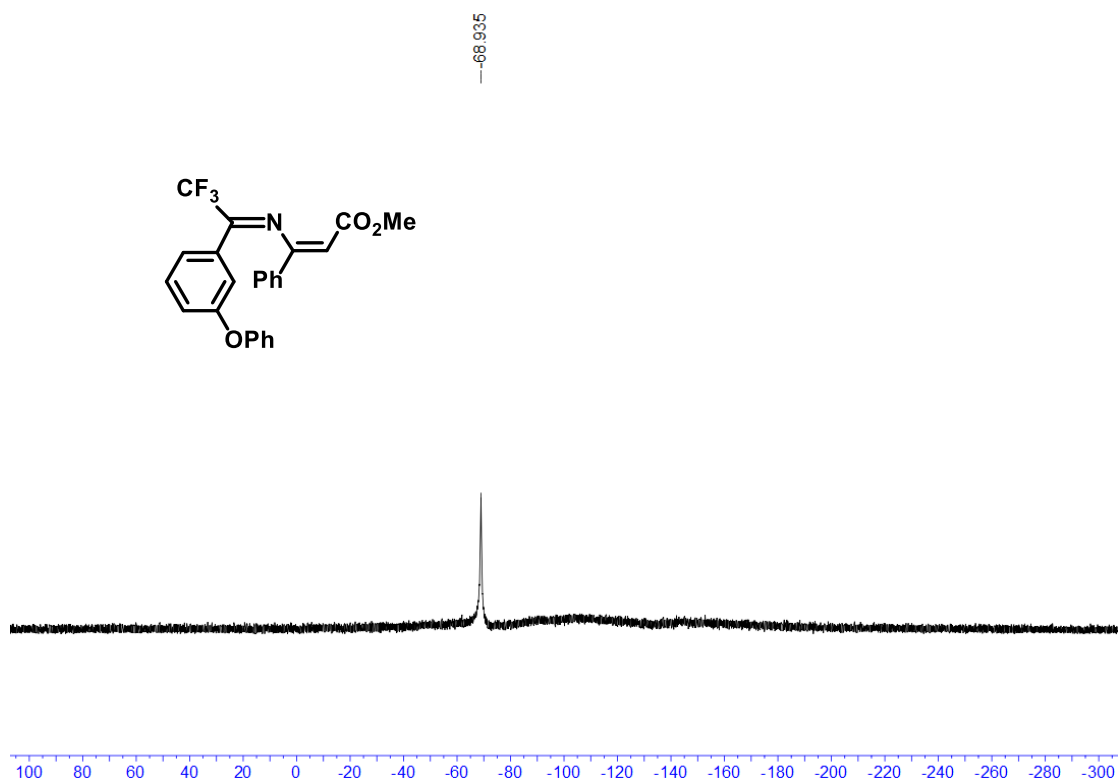
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3af**



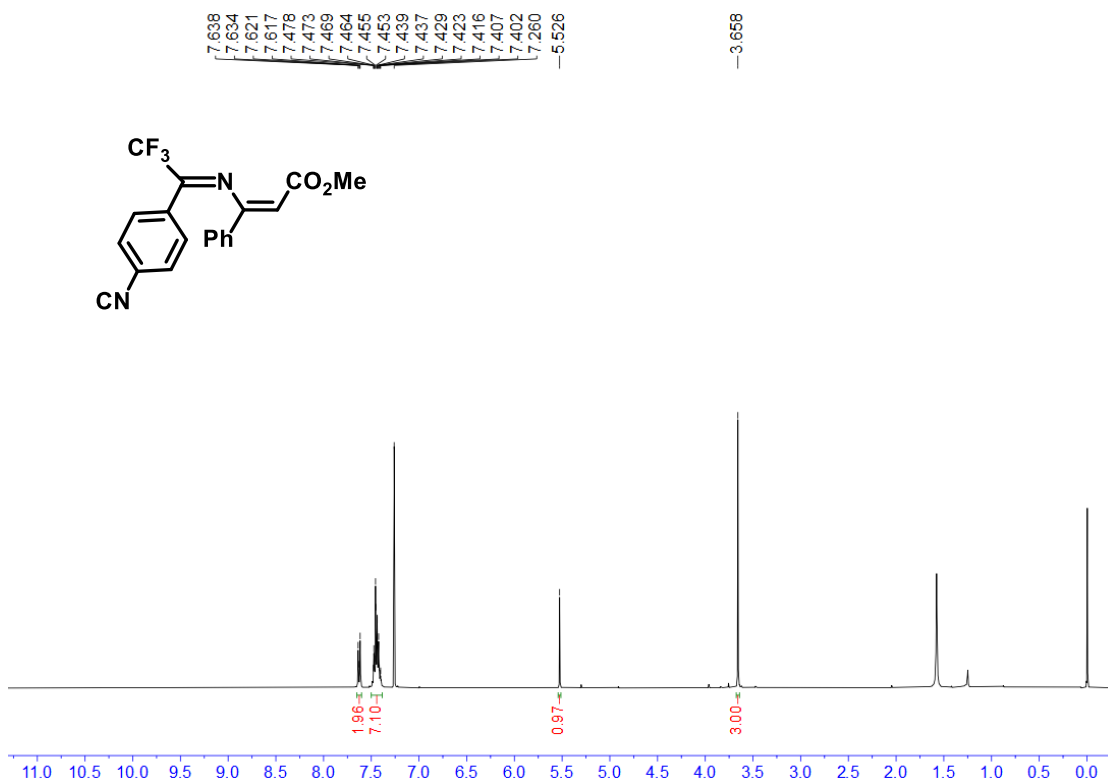
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3af**



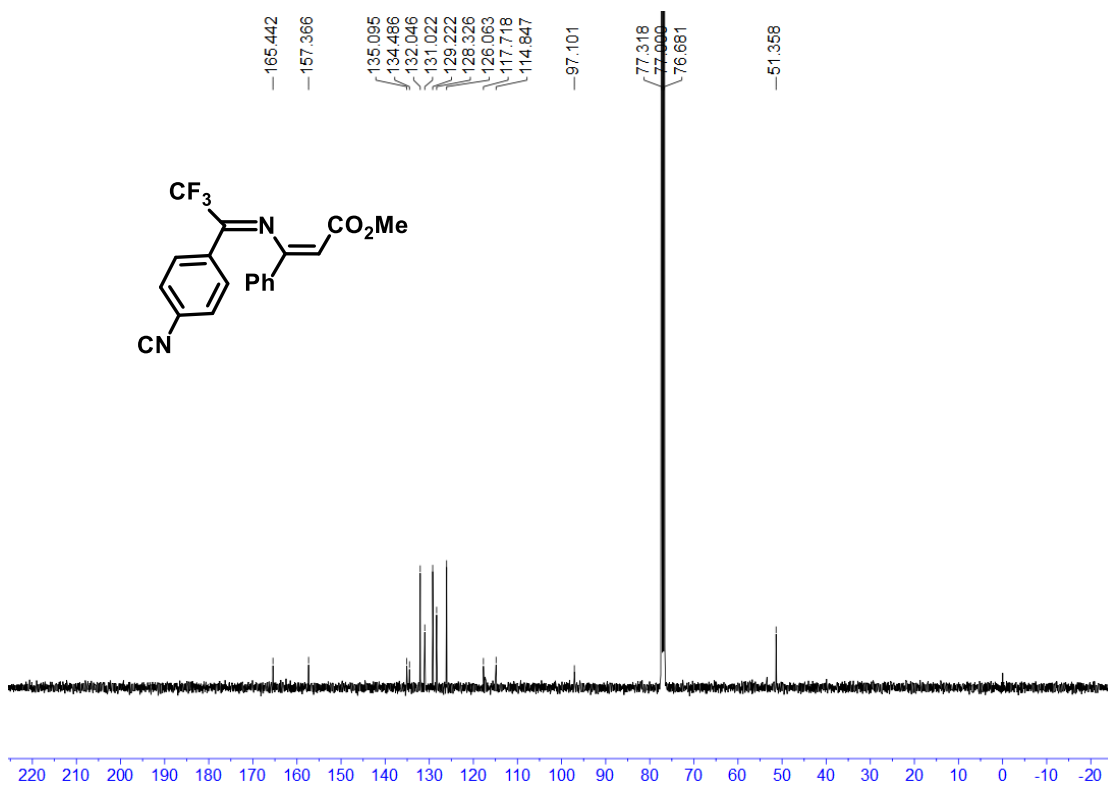
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3af**



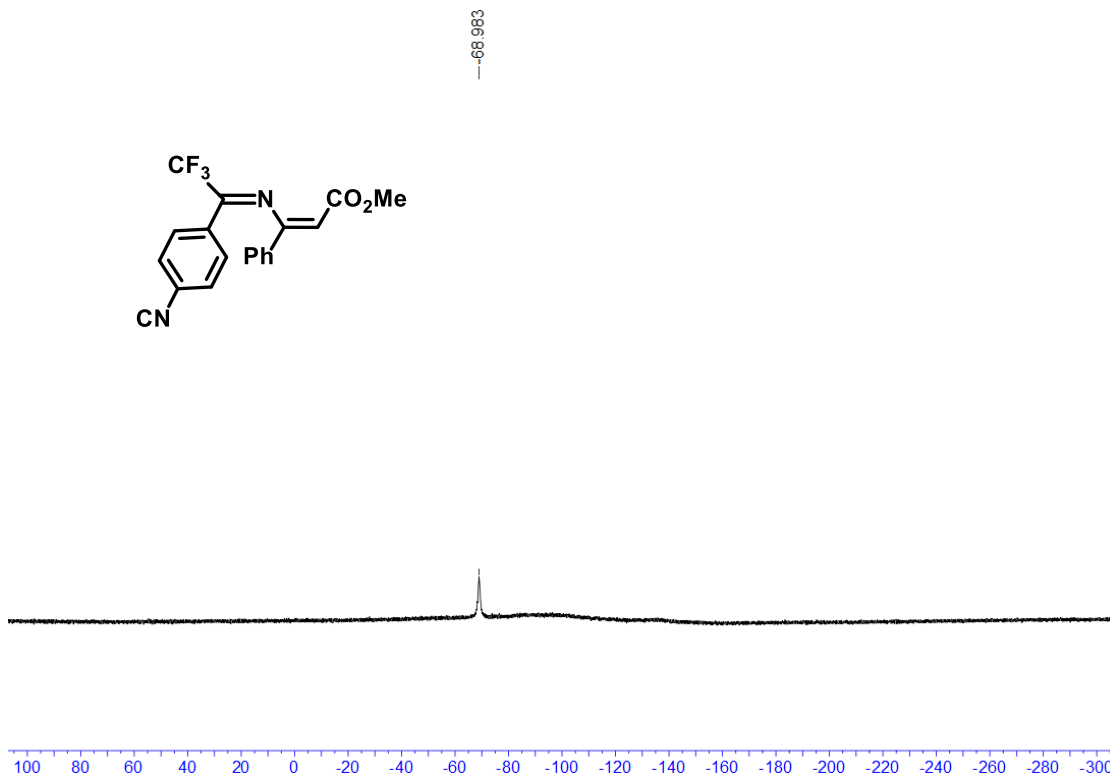
$^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ag**



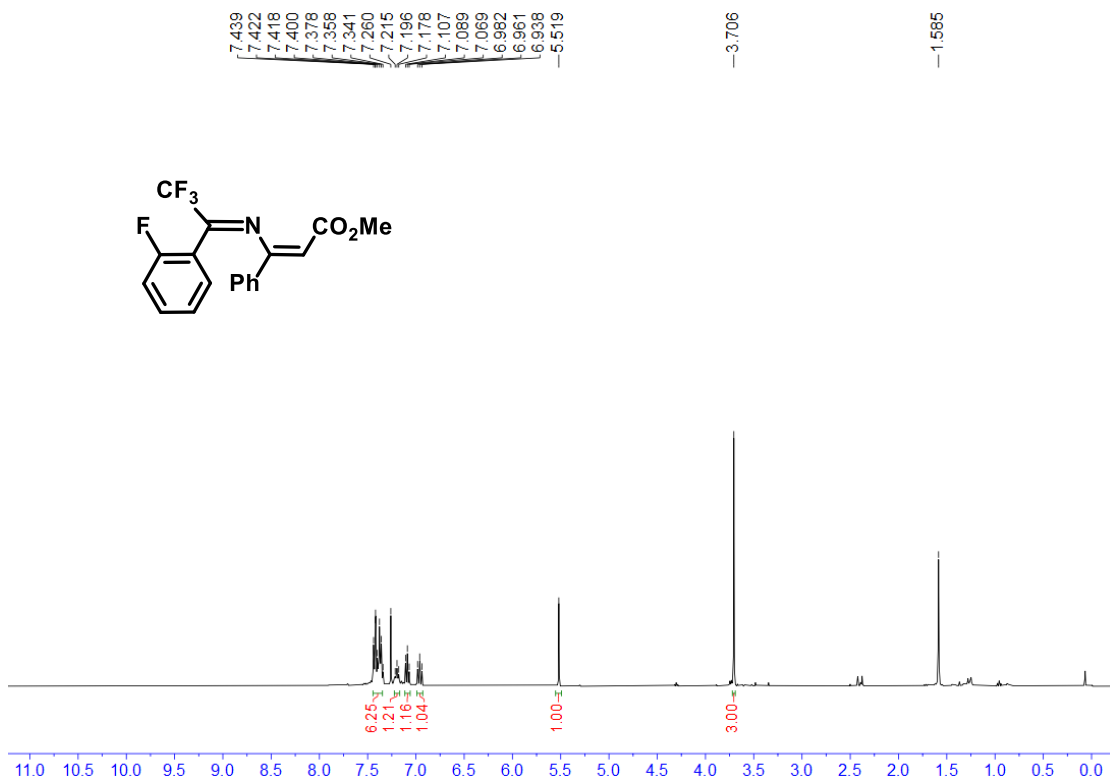
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3ag**



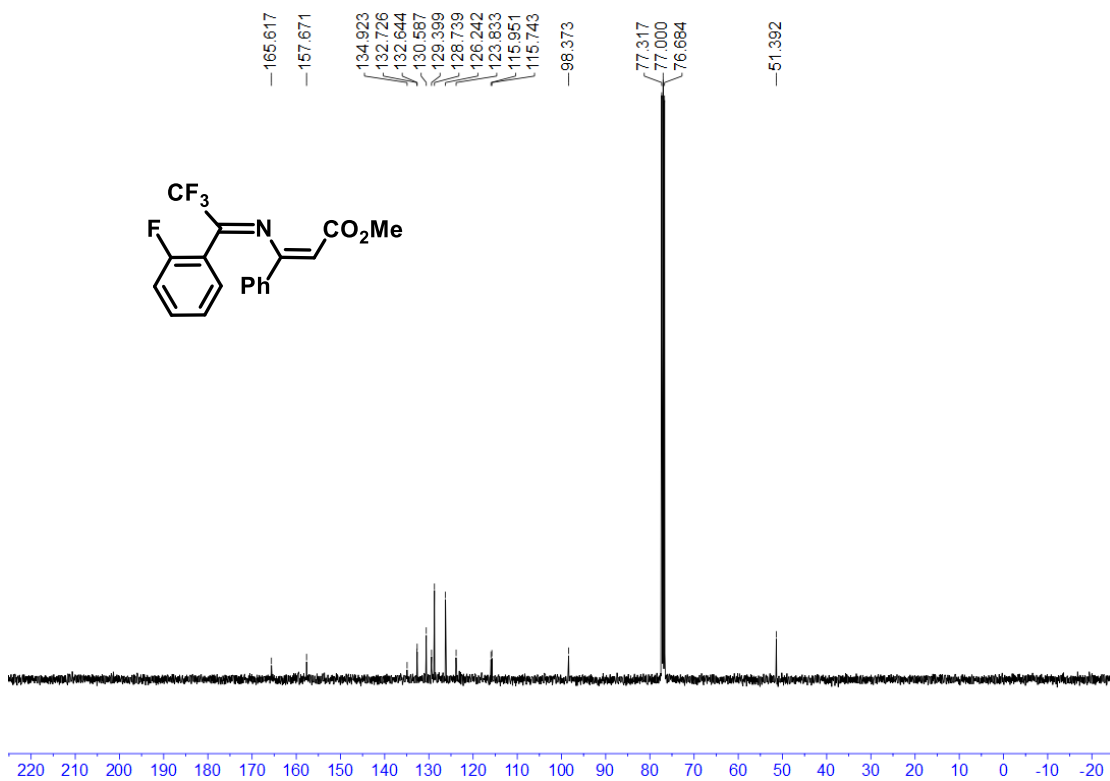
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **3ag**



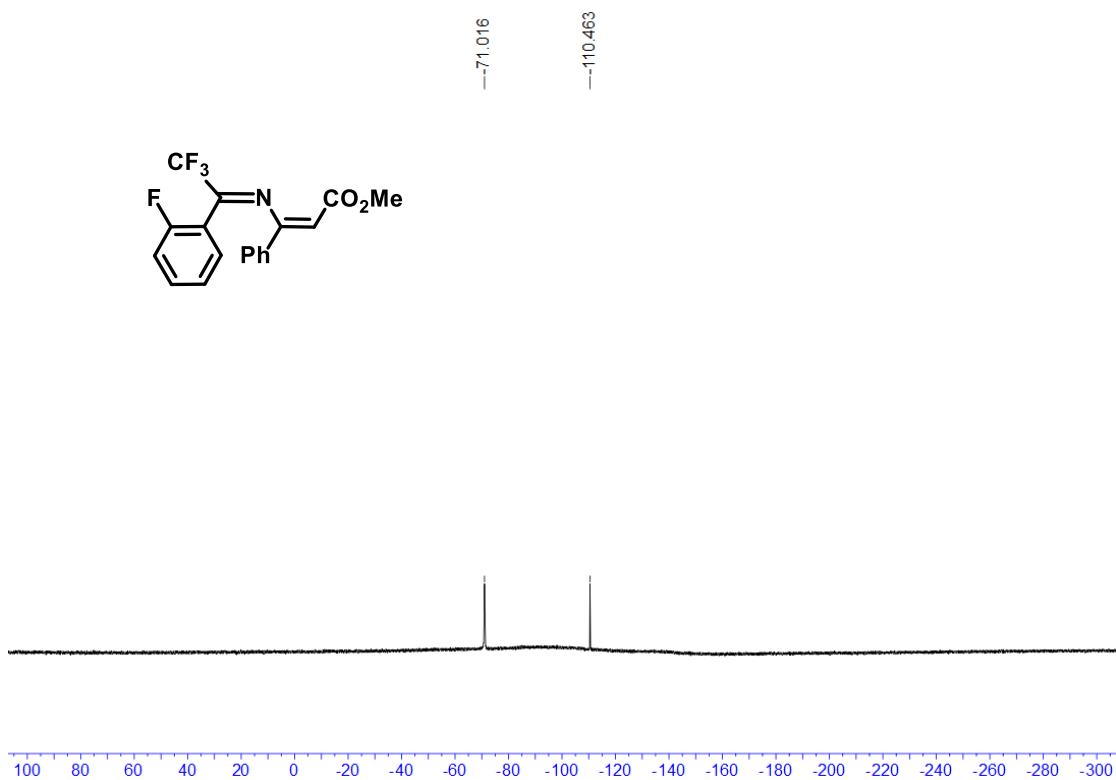
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3ah**



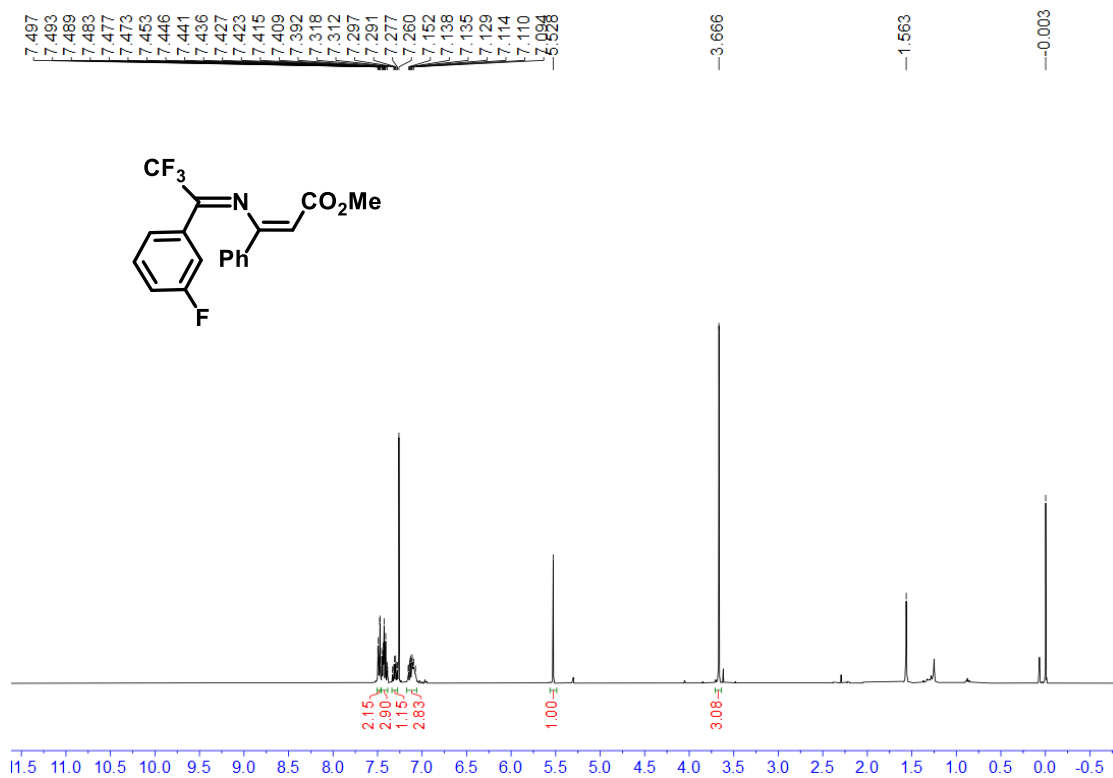
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3ah**



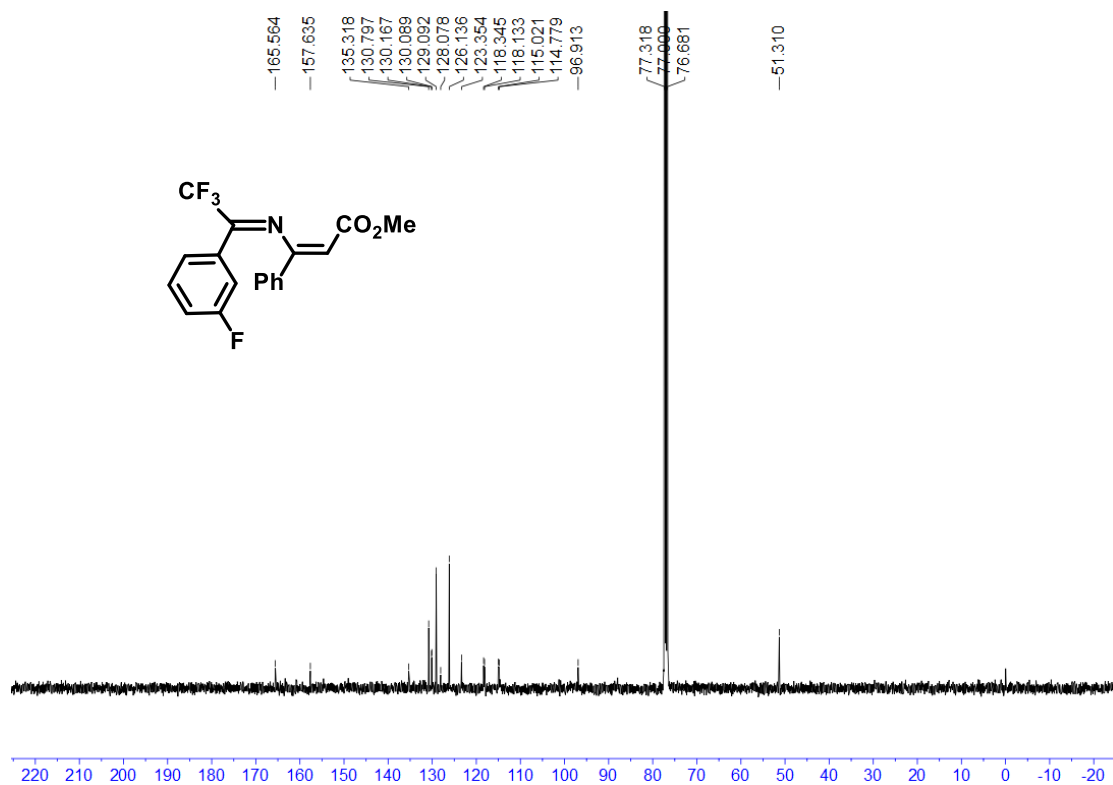
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **3ah**



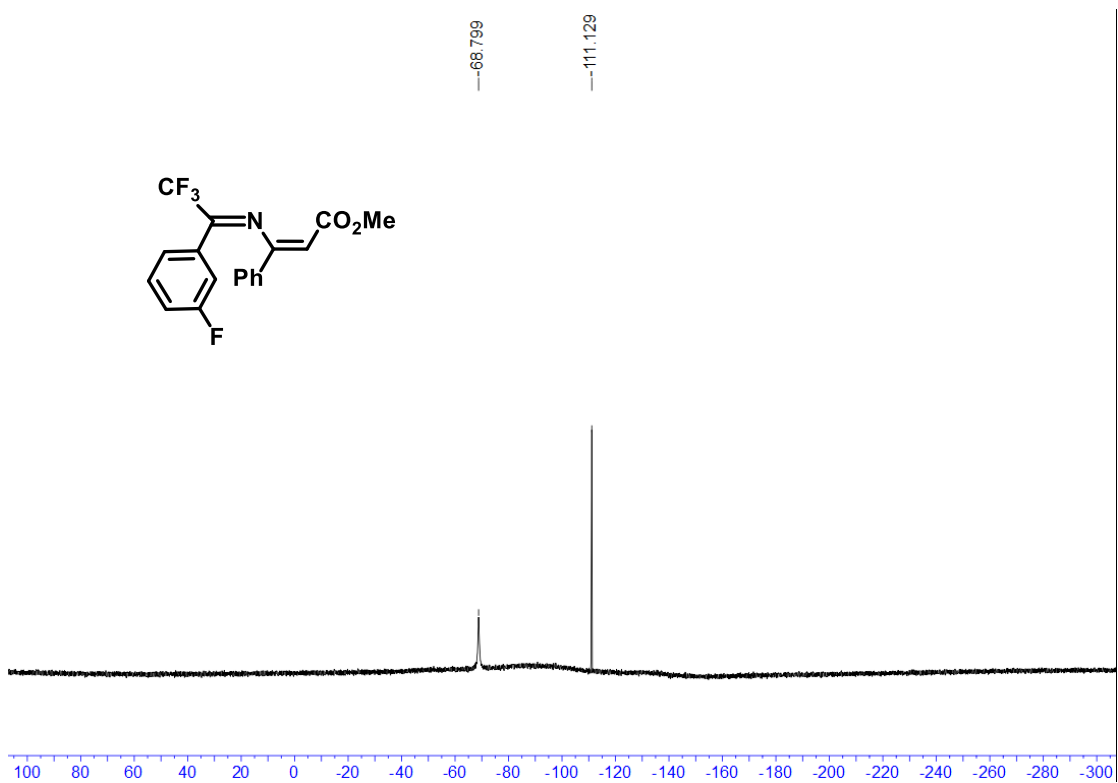
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3ai**



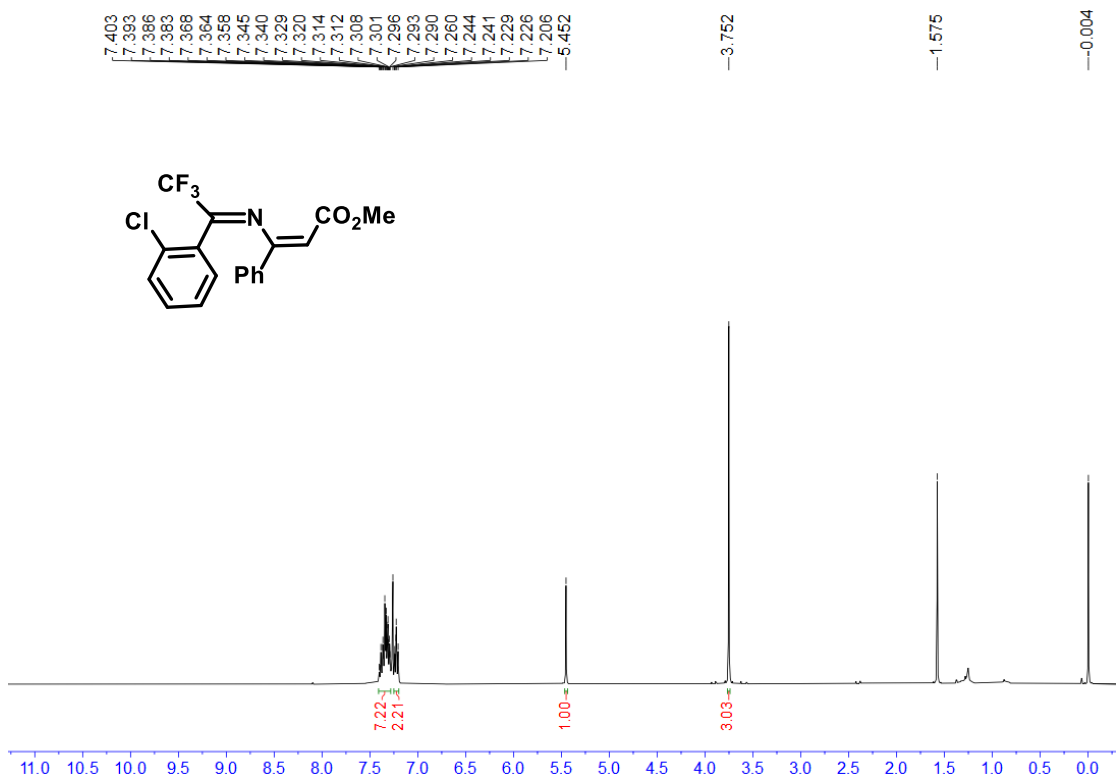
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3ai**



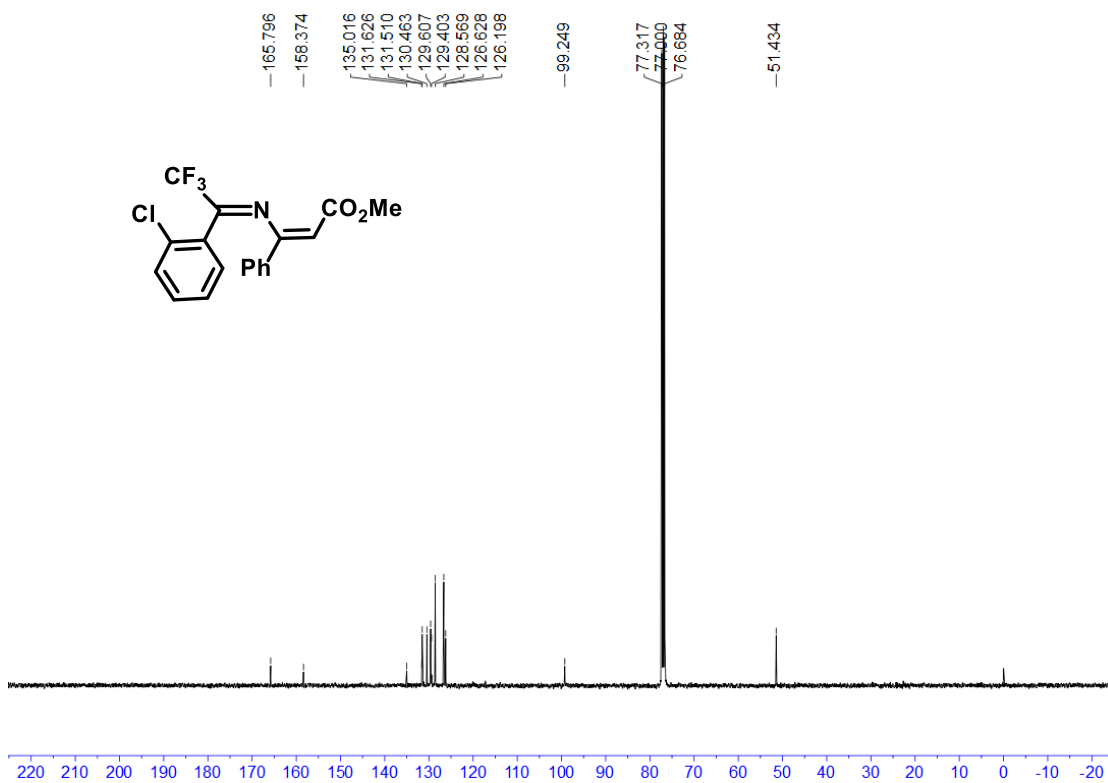
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **3ai**



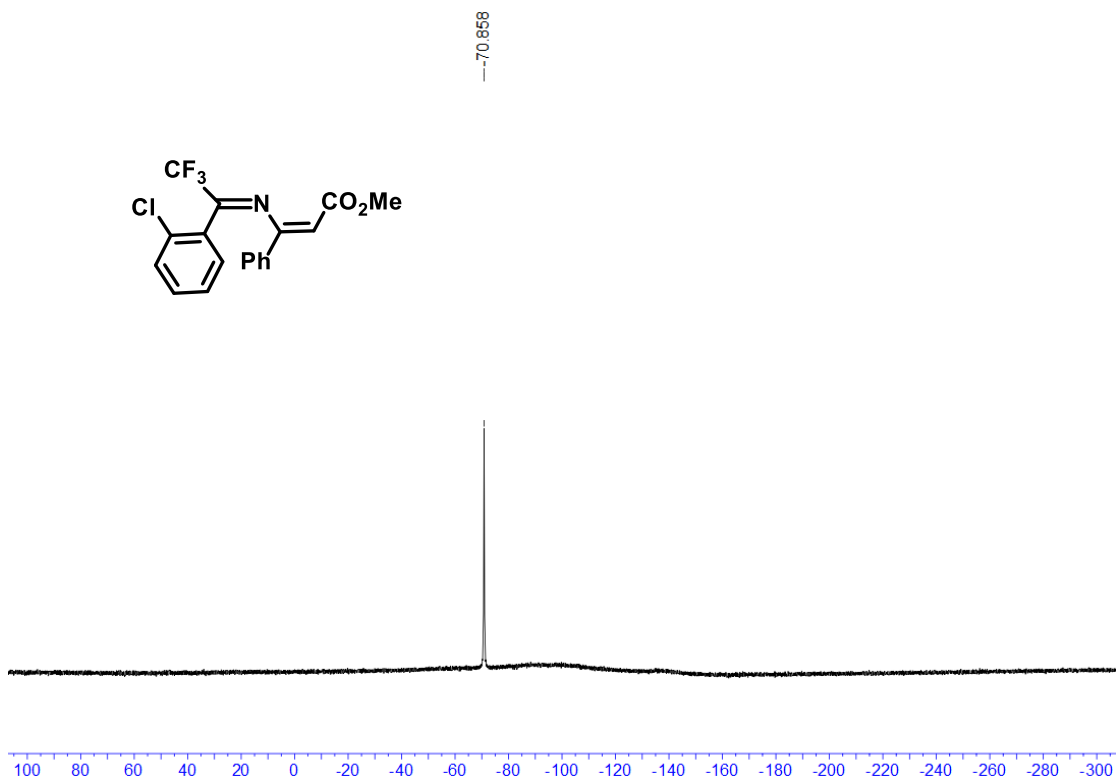
$^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3aj**



$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3aj**

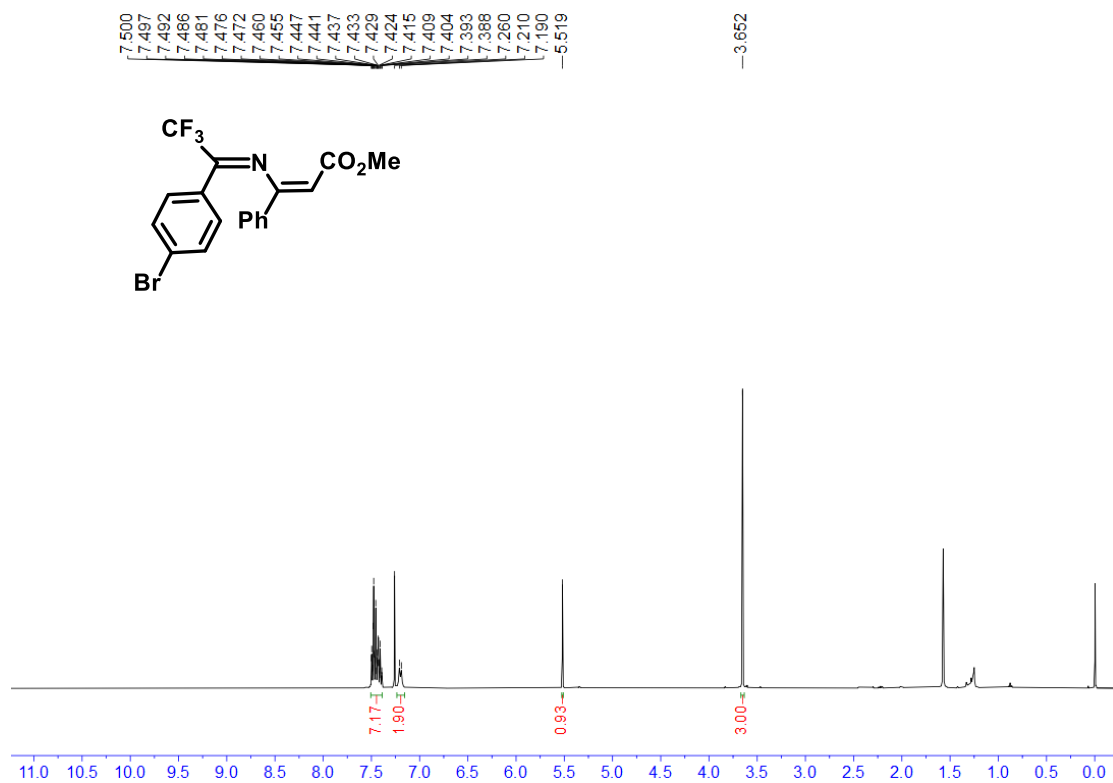


<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **3aj**

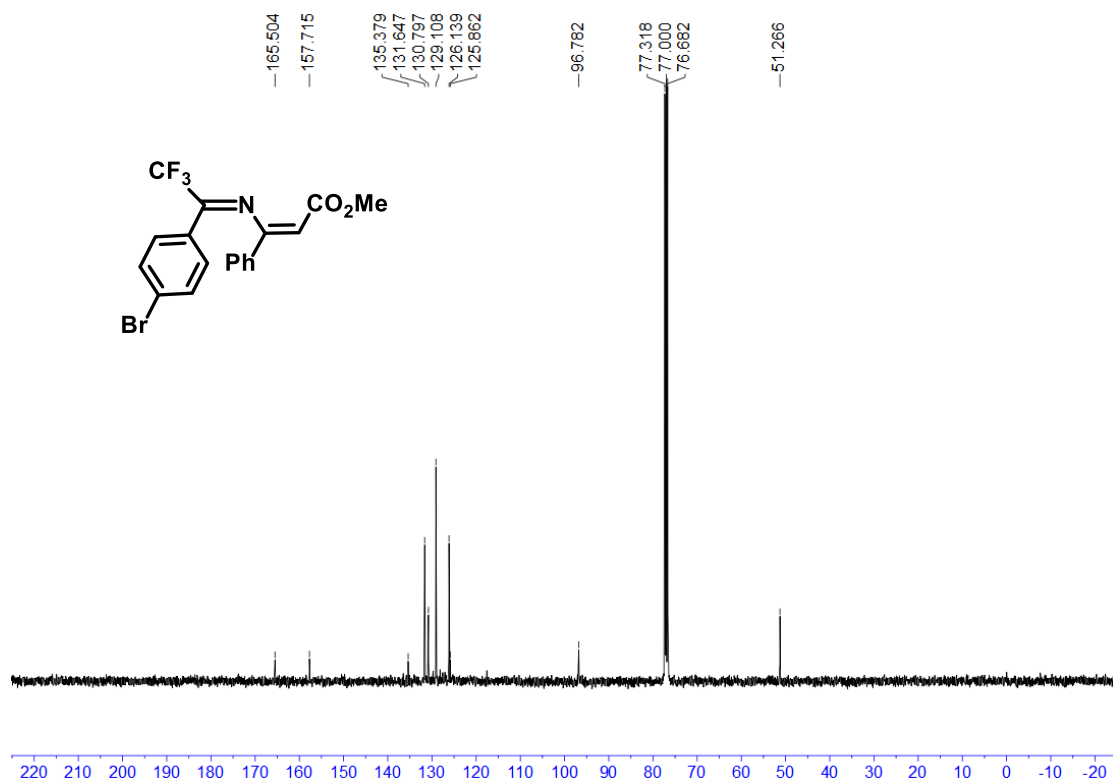


<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3ak**

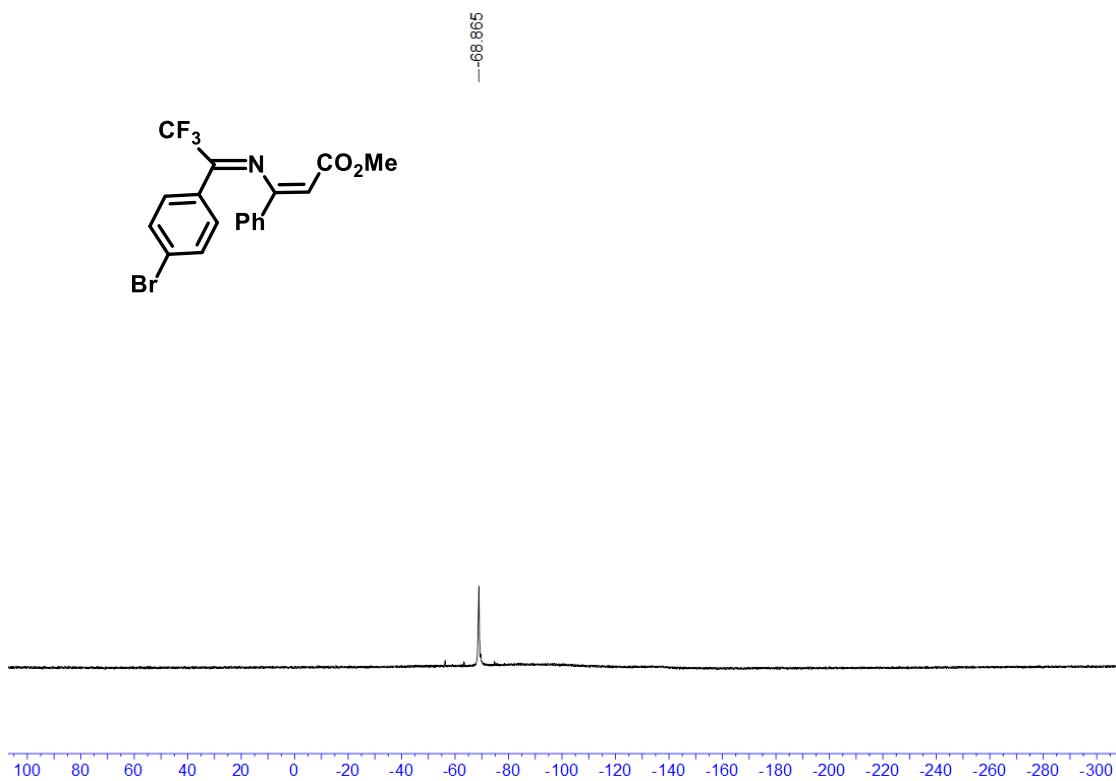




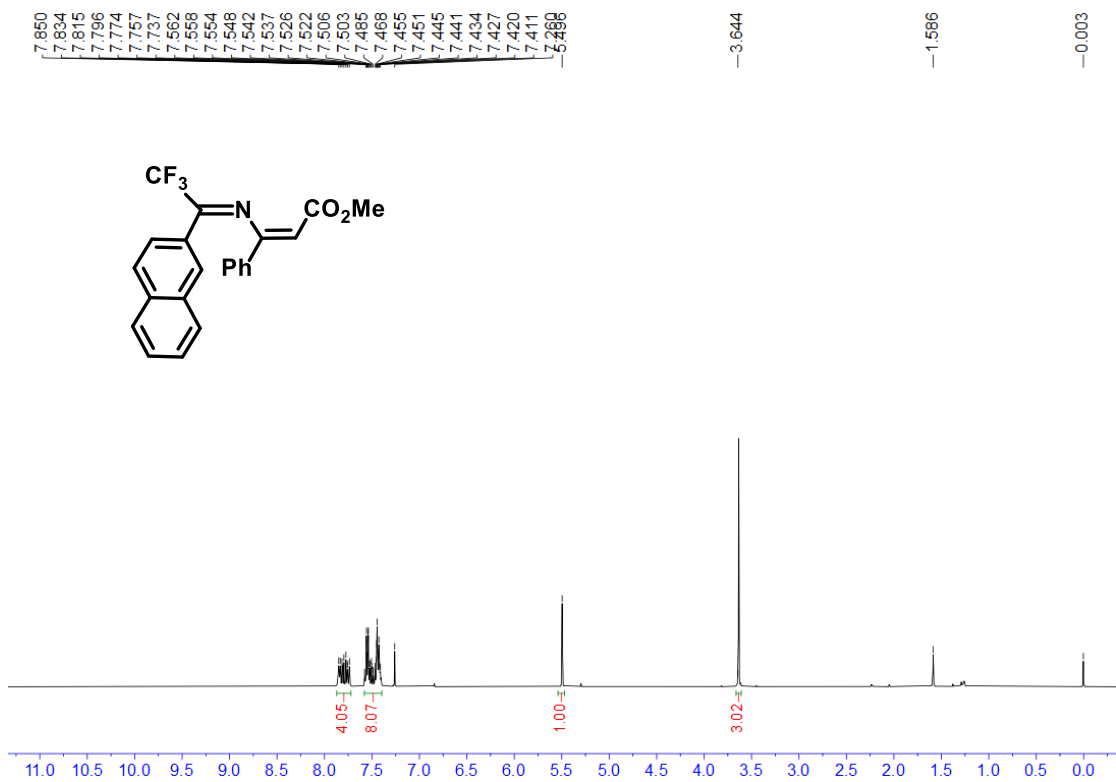
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3ak**



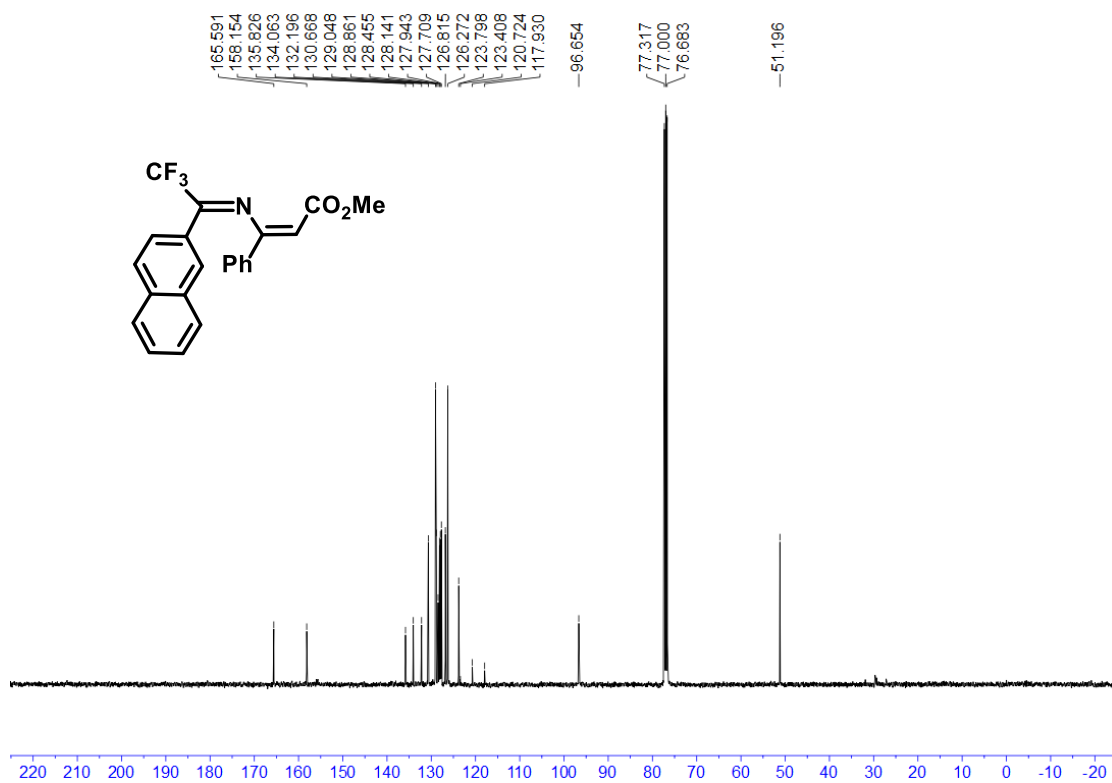
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **3ak**



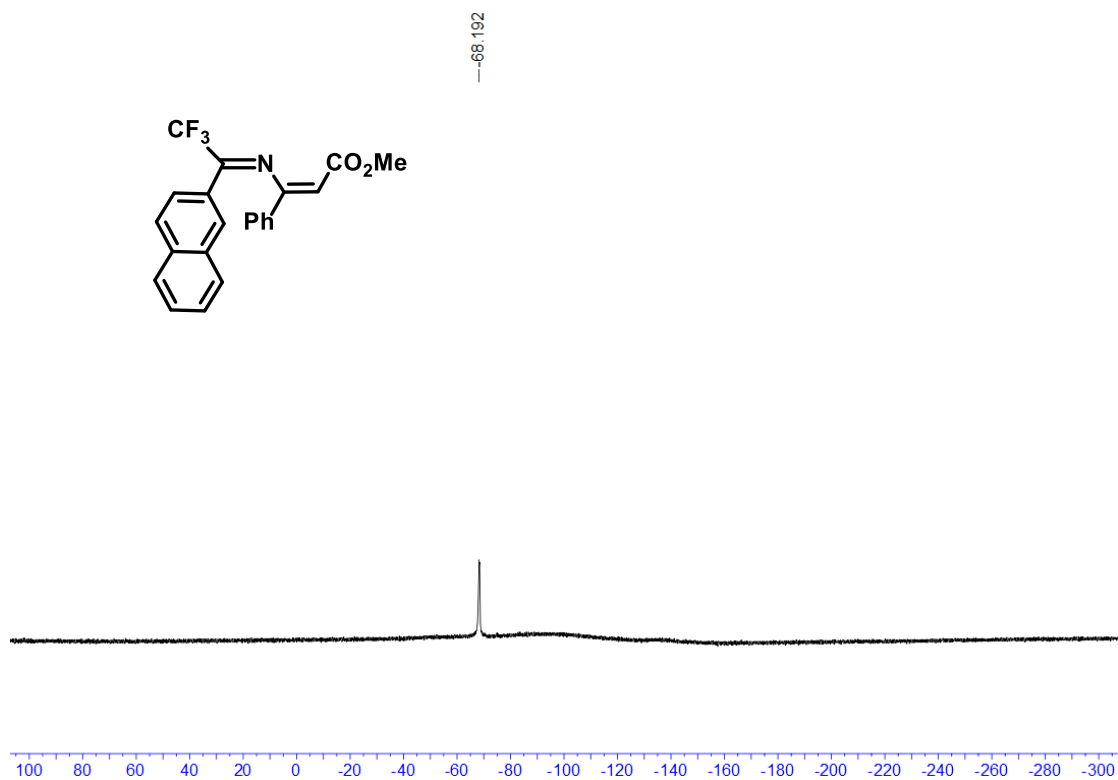
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3al**



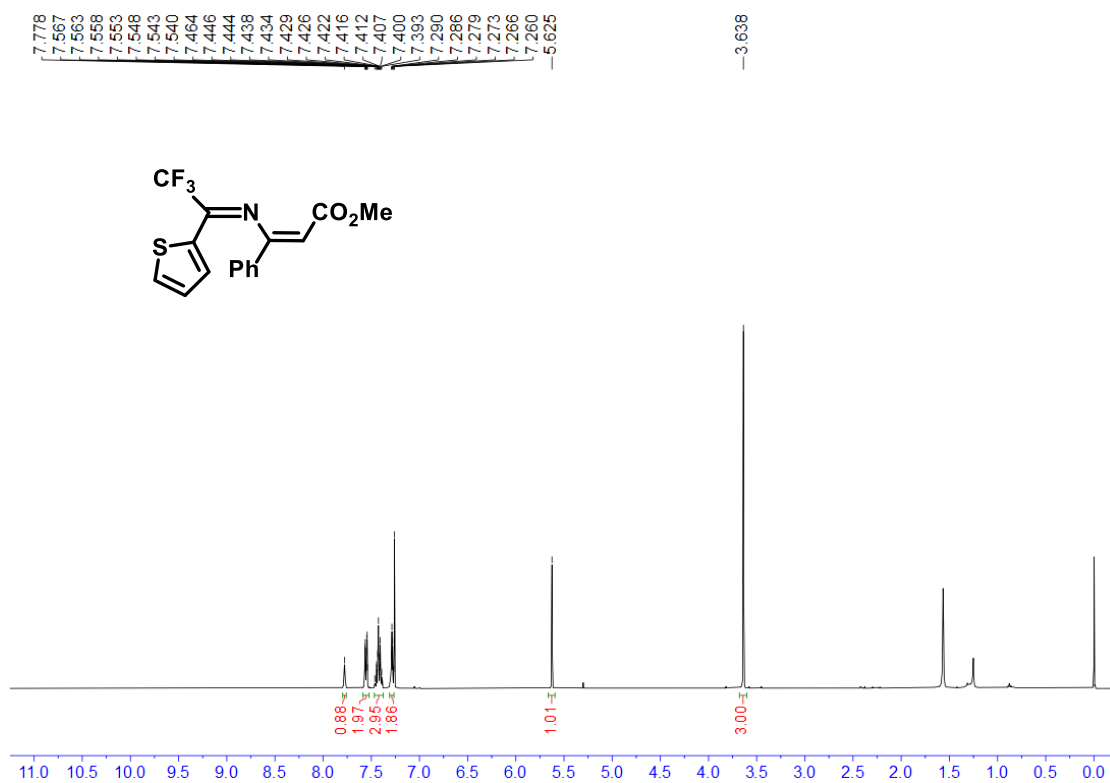
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3al**



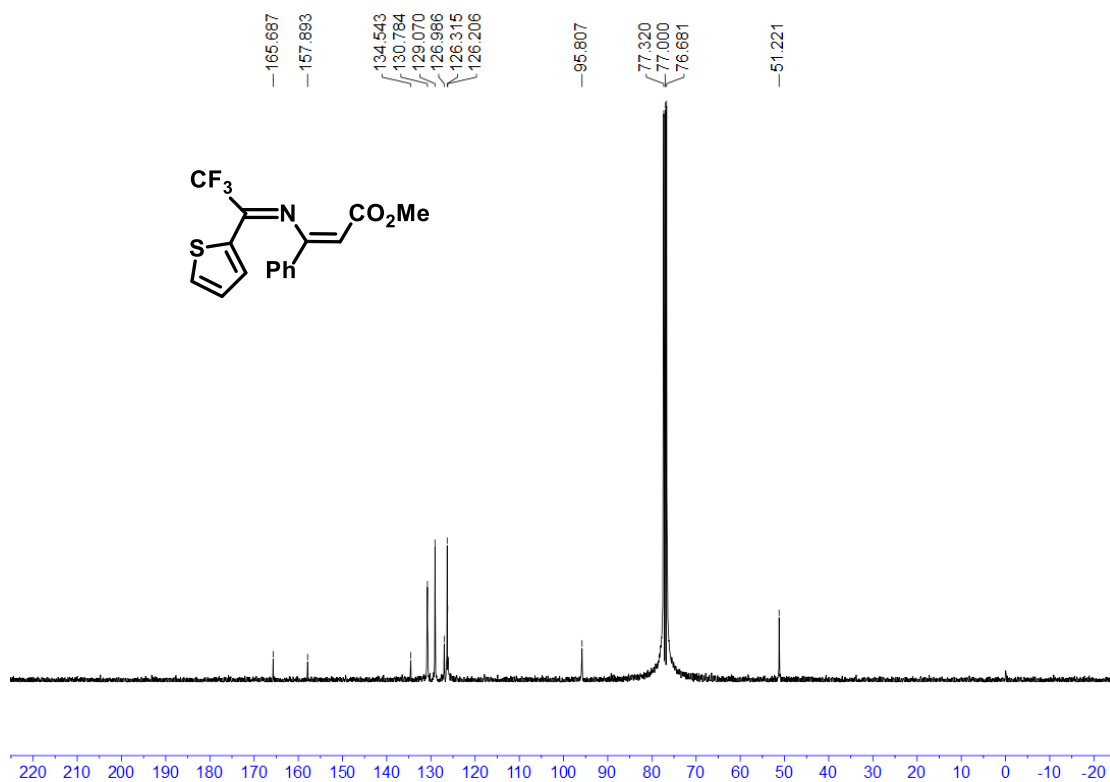
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **3aI**



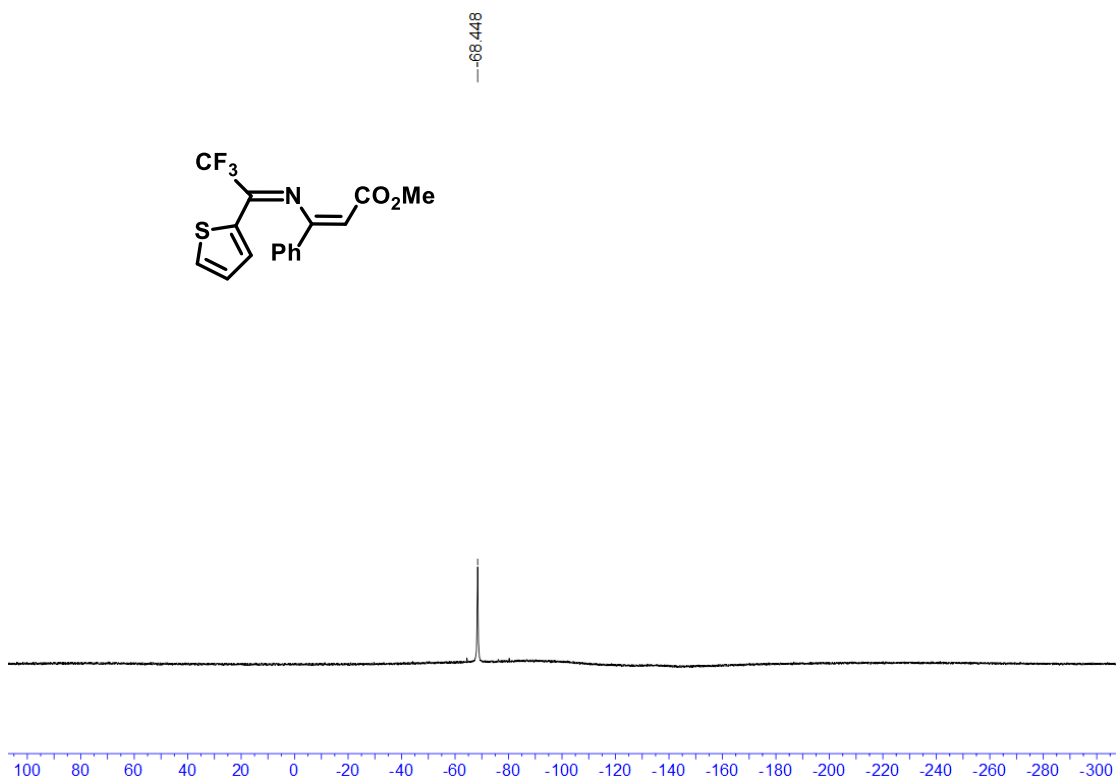
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **3aI**



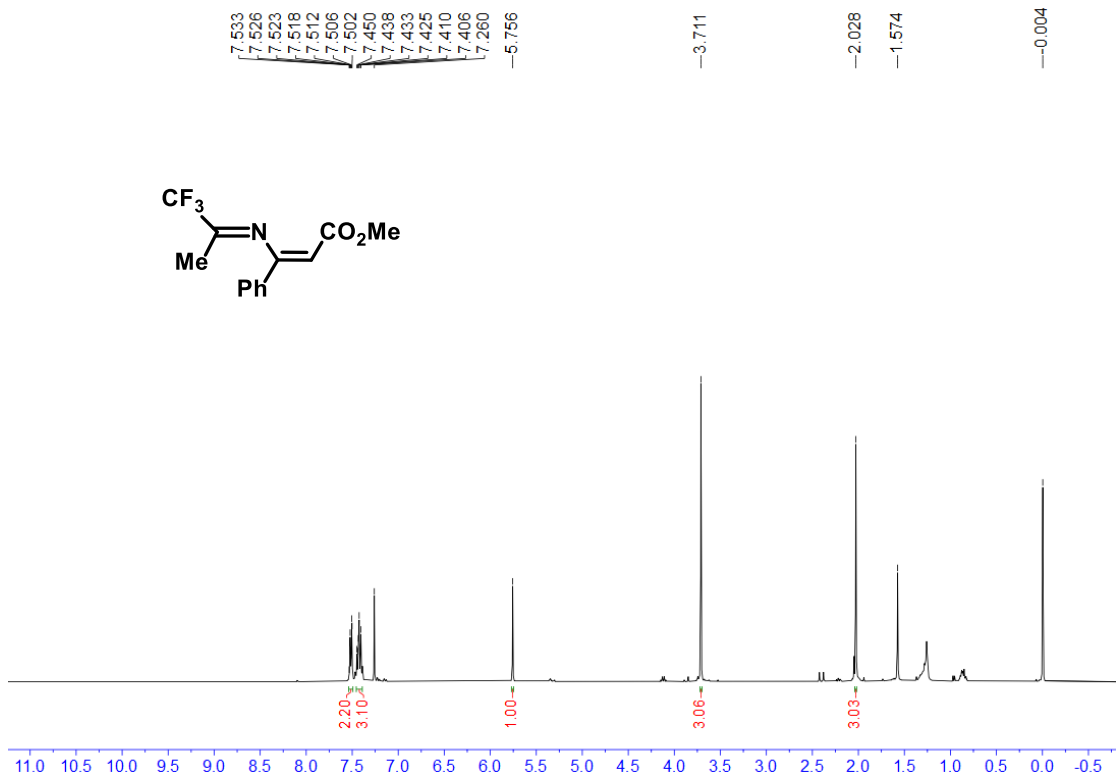
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3am**



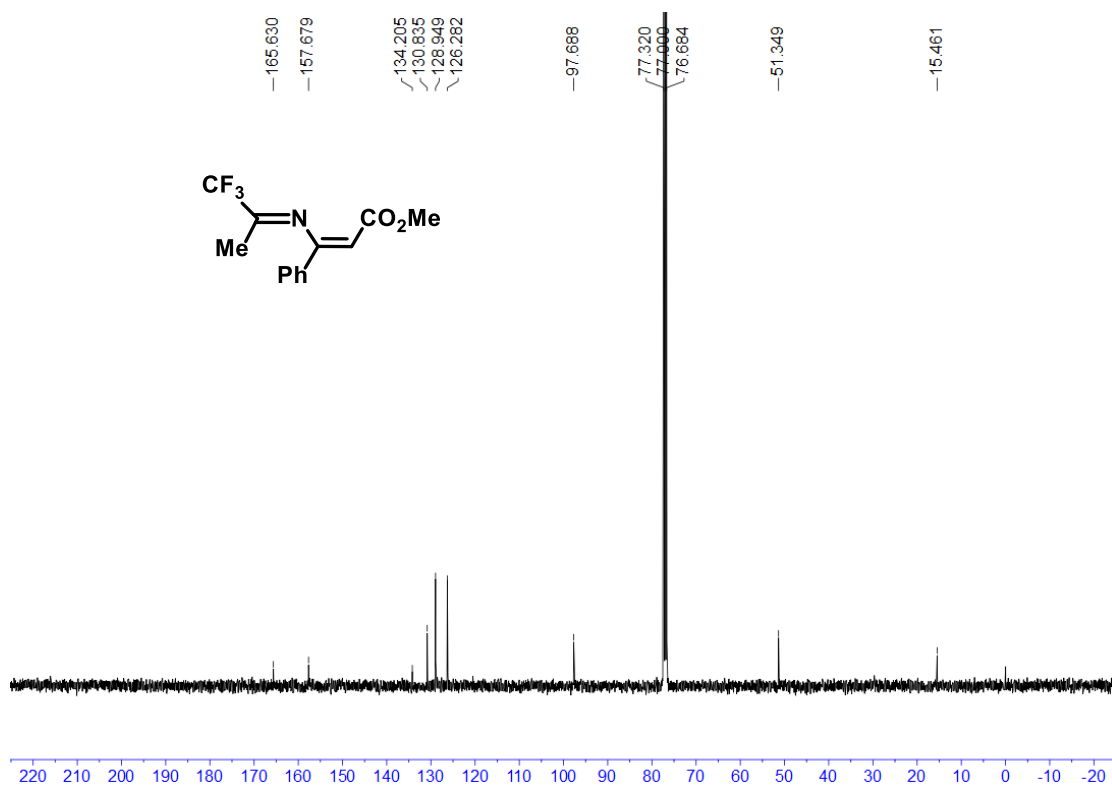
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **3am**



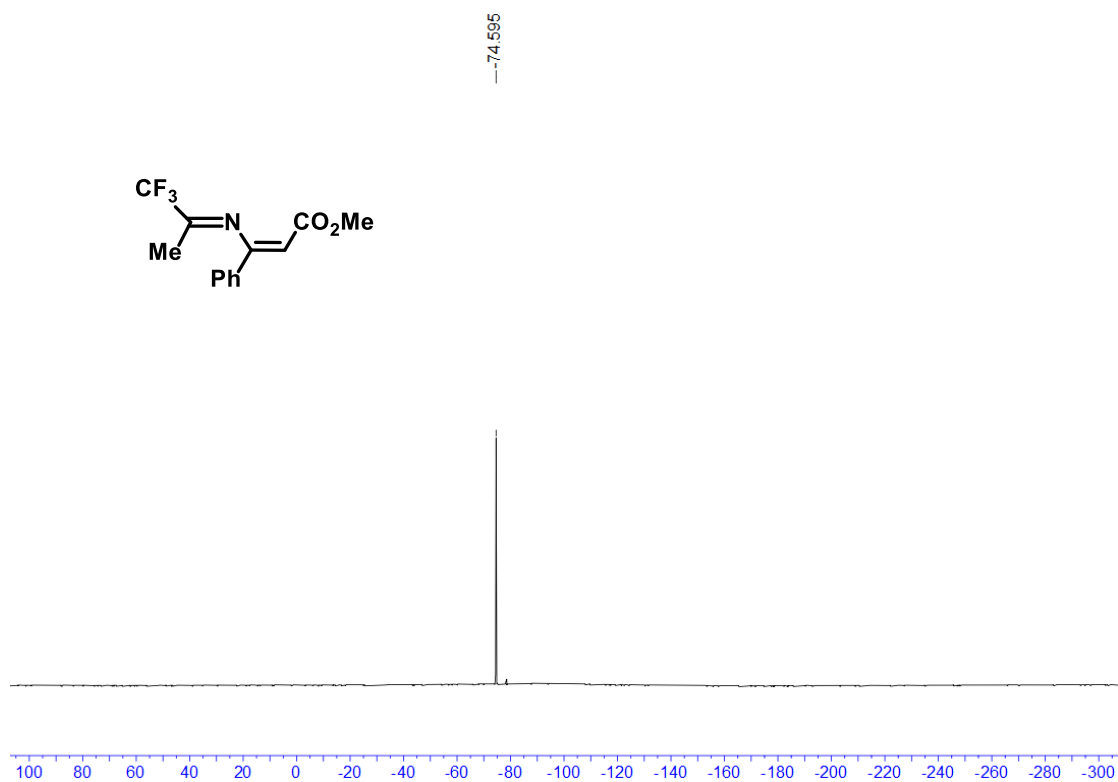
$^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3an**



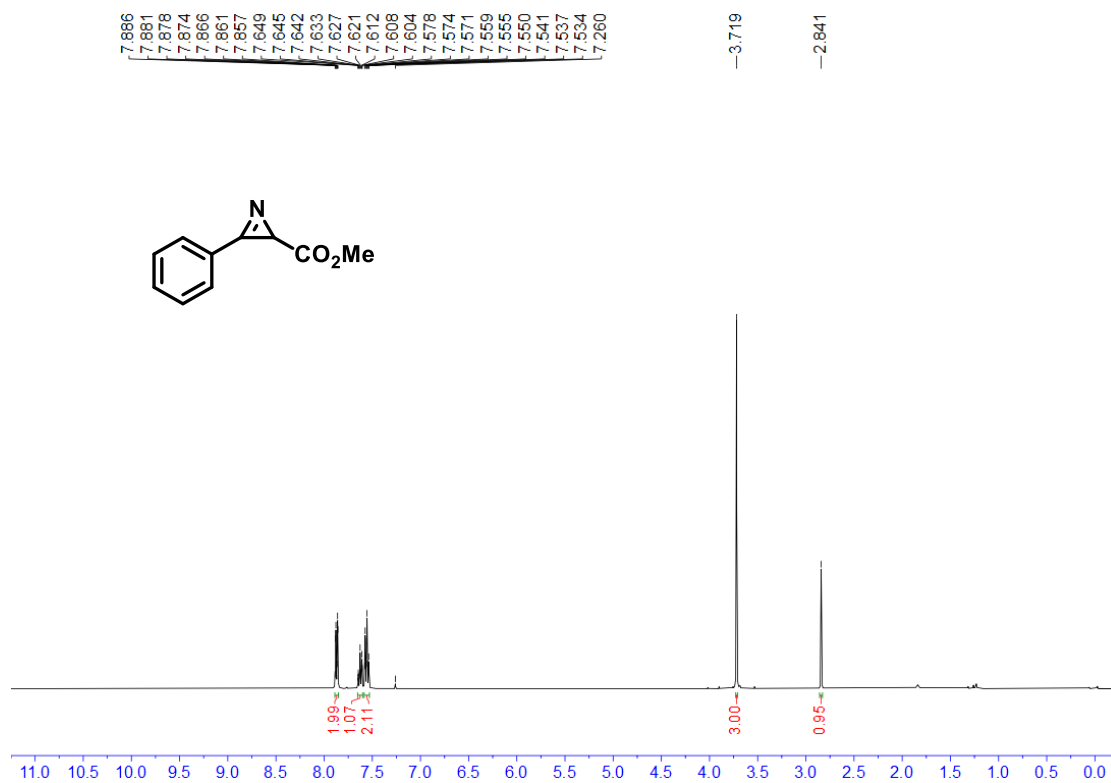
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3an**



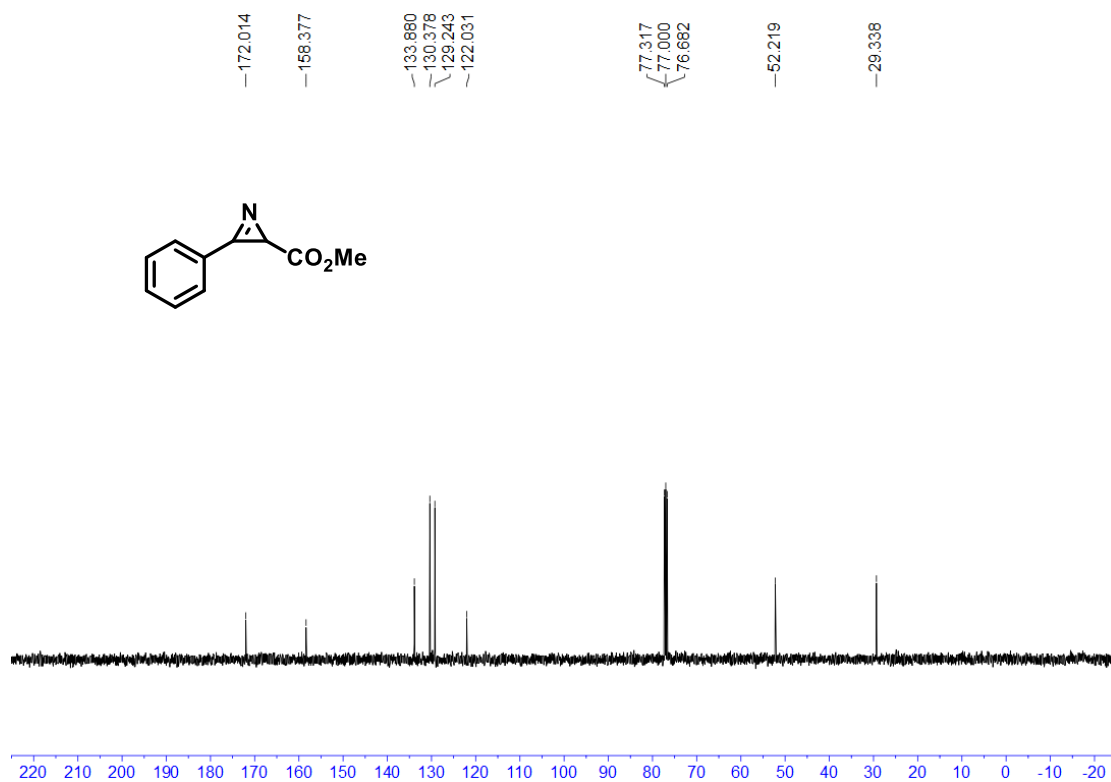
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3an**



$^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **1a'**

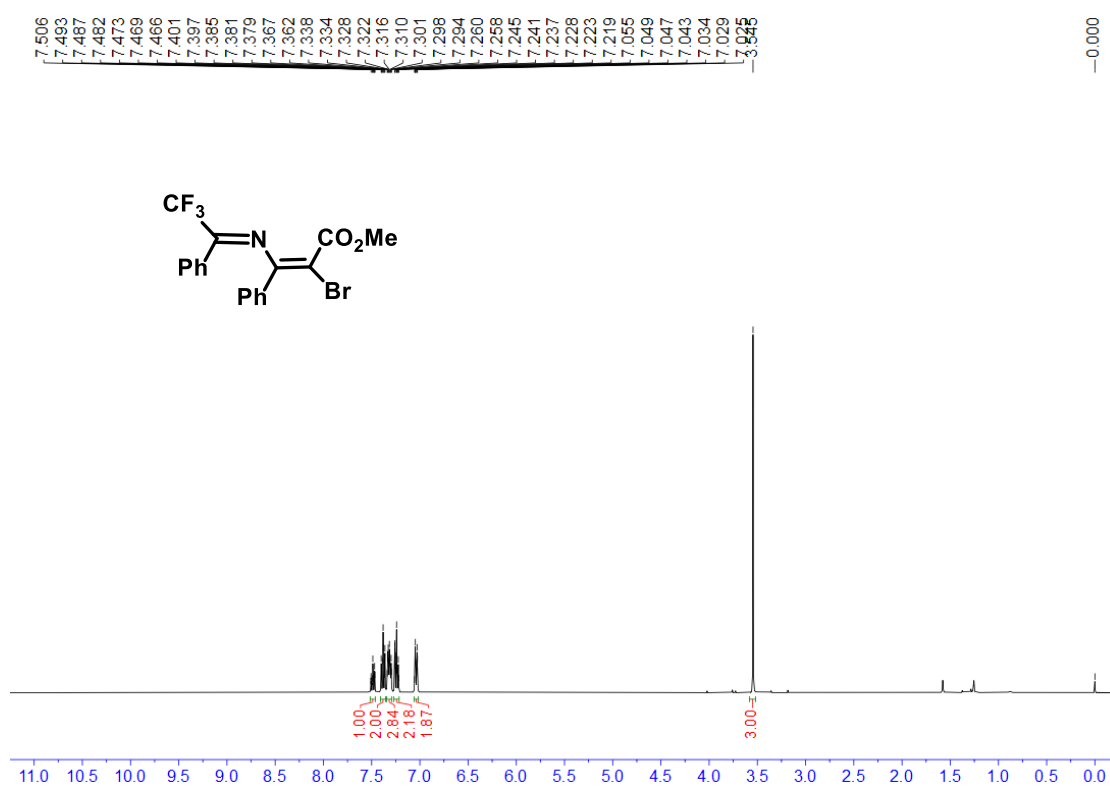


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **1a'**

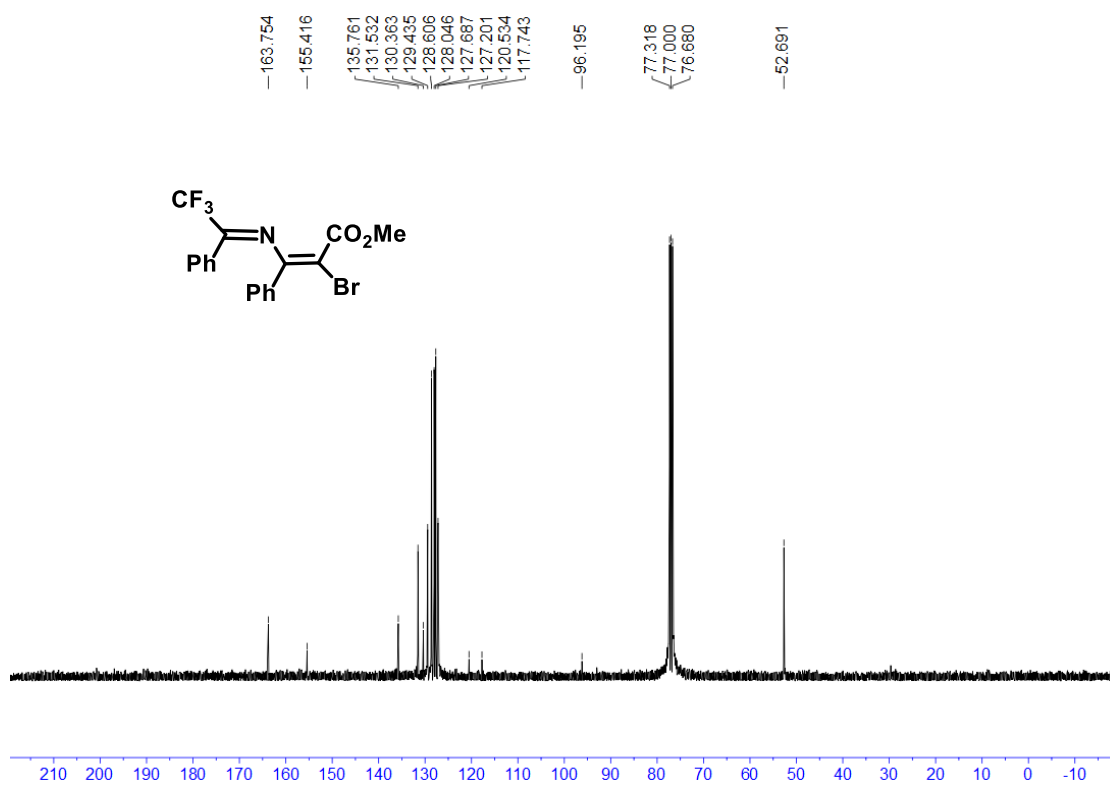


### 3.4 NMR spectra for applications

<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **4aa**

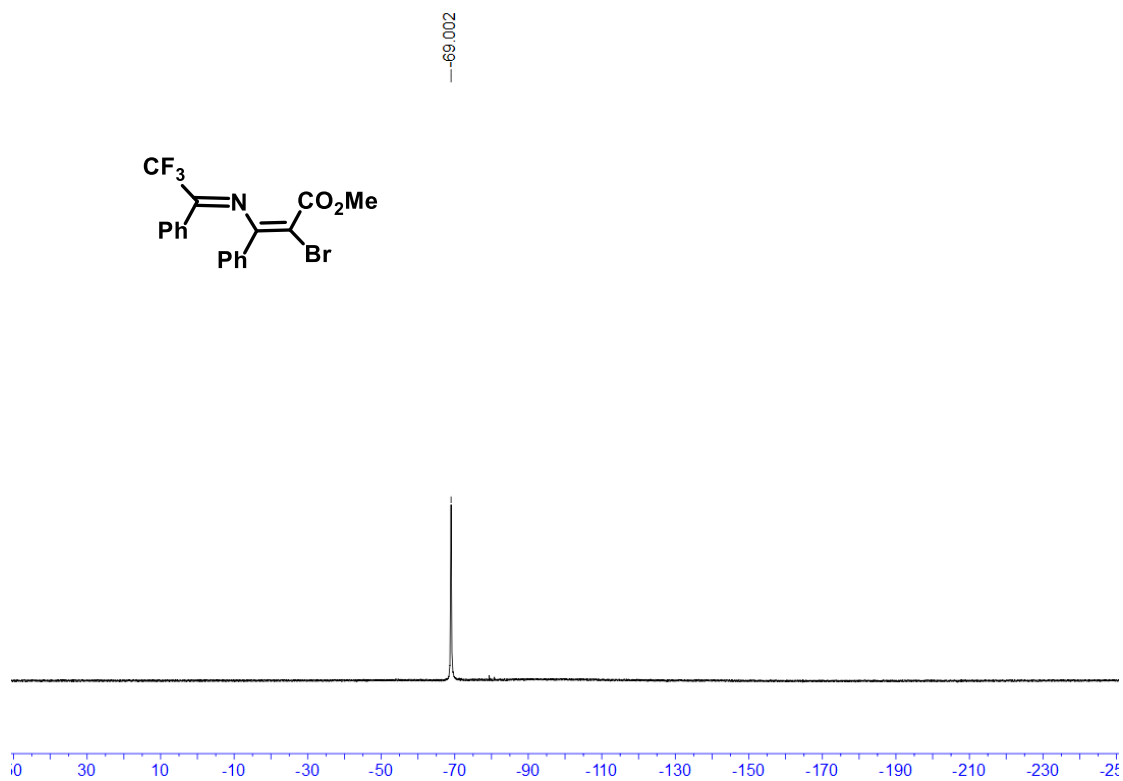


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **4aa**

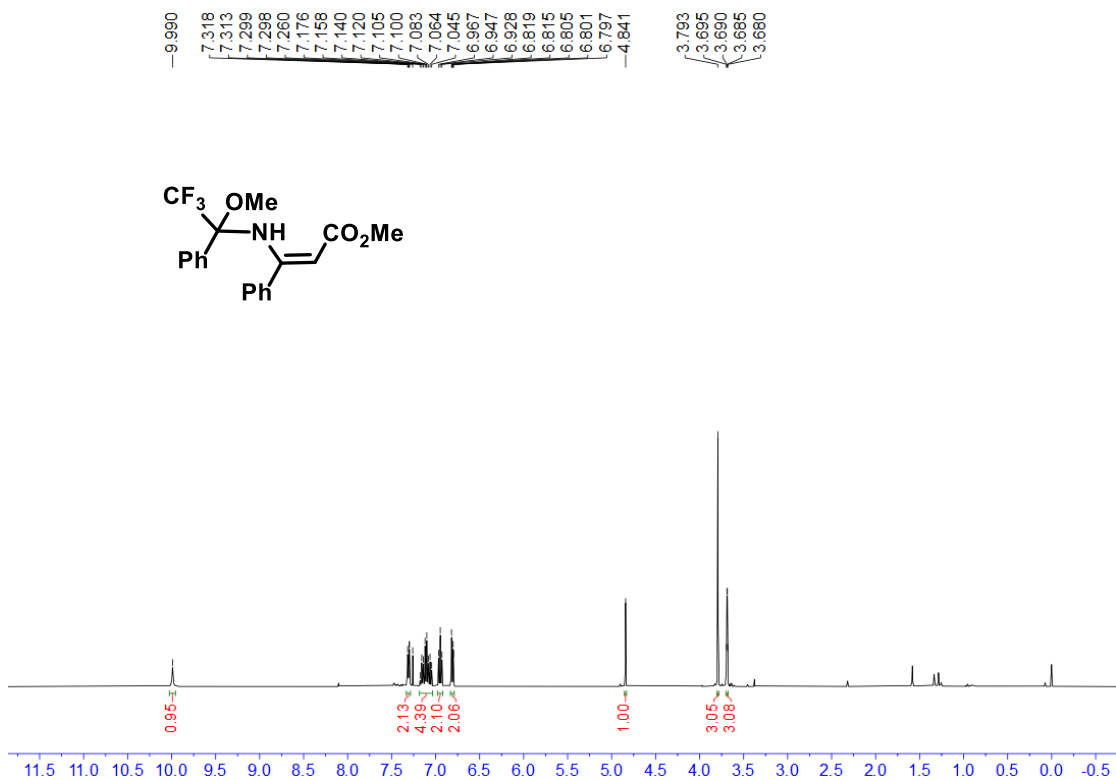


<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **4aa**

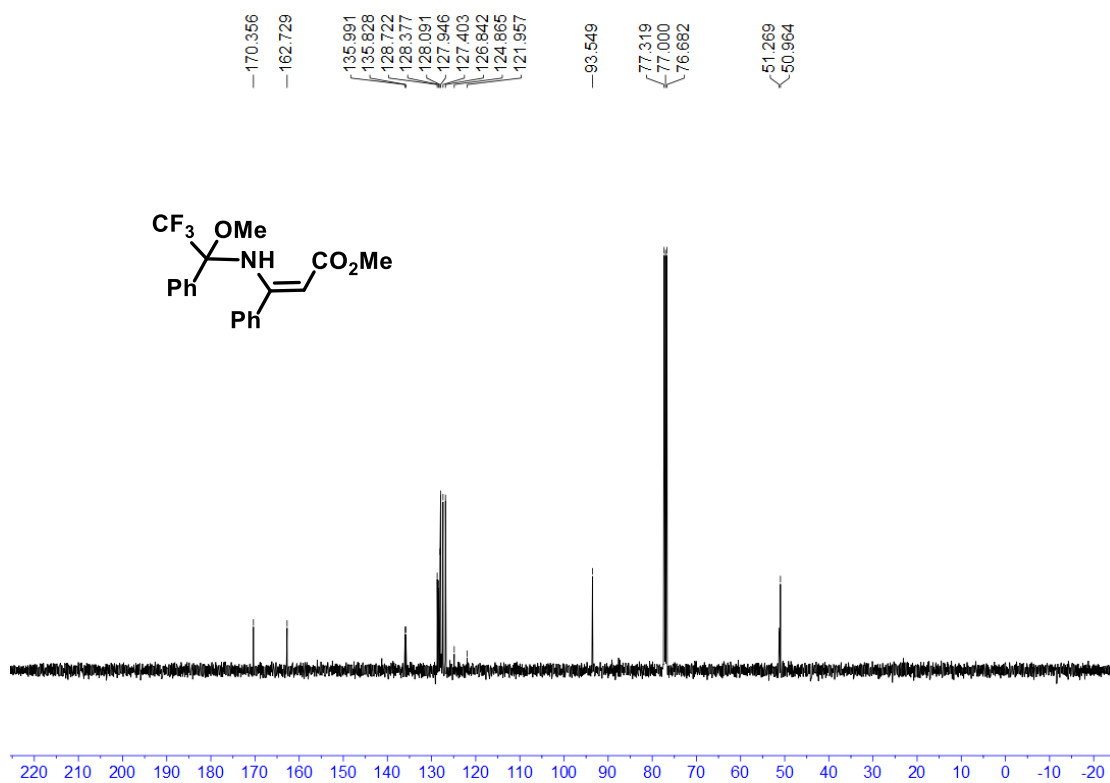




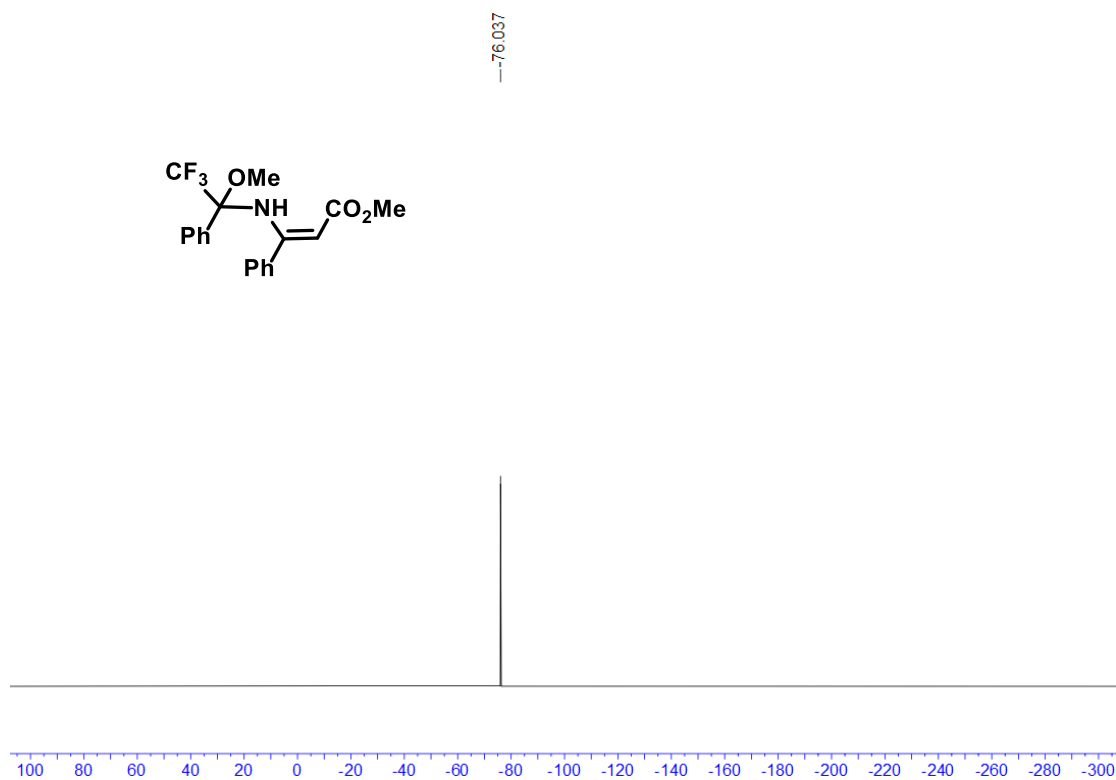
$^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **5aa**



$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **5aa**

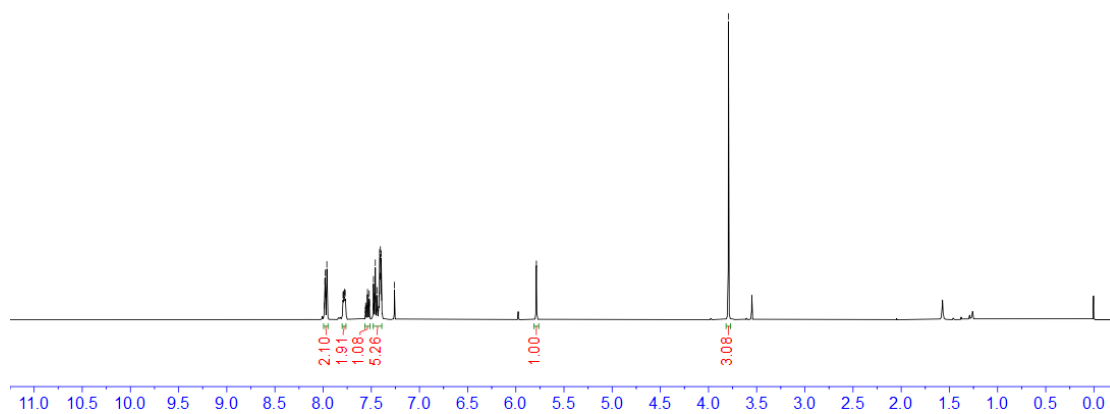
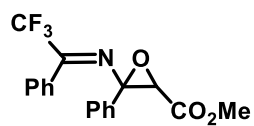


<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of **5aa**

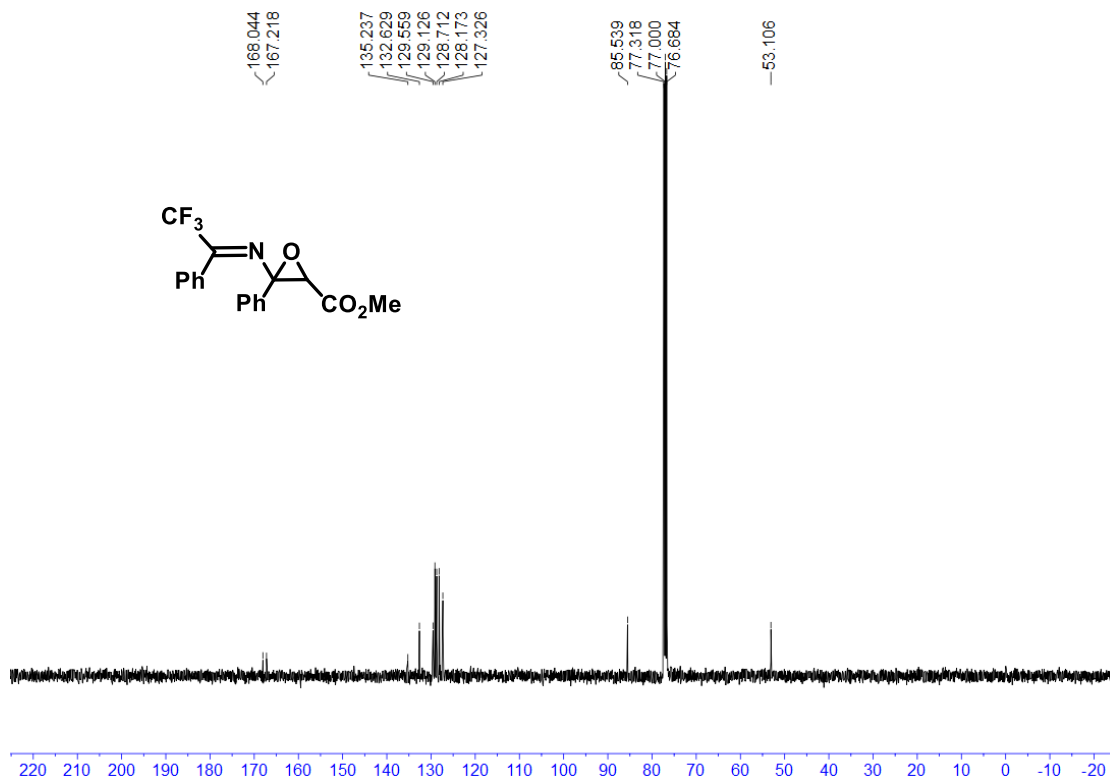


<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **6aa**

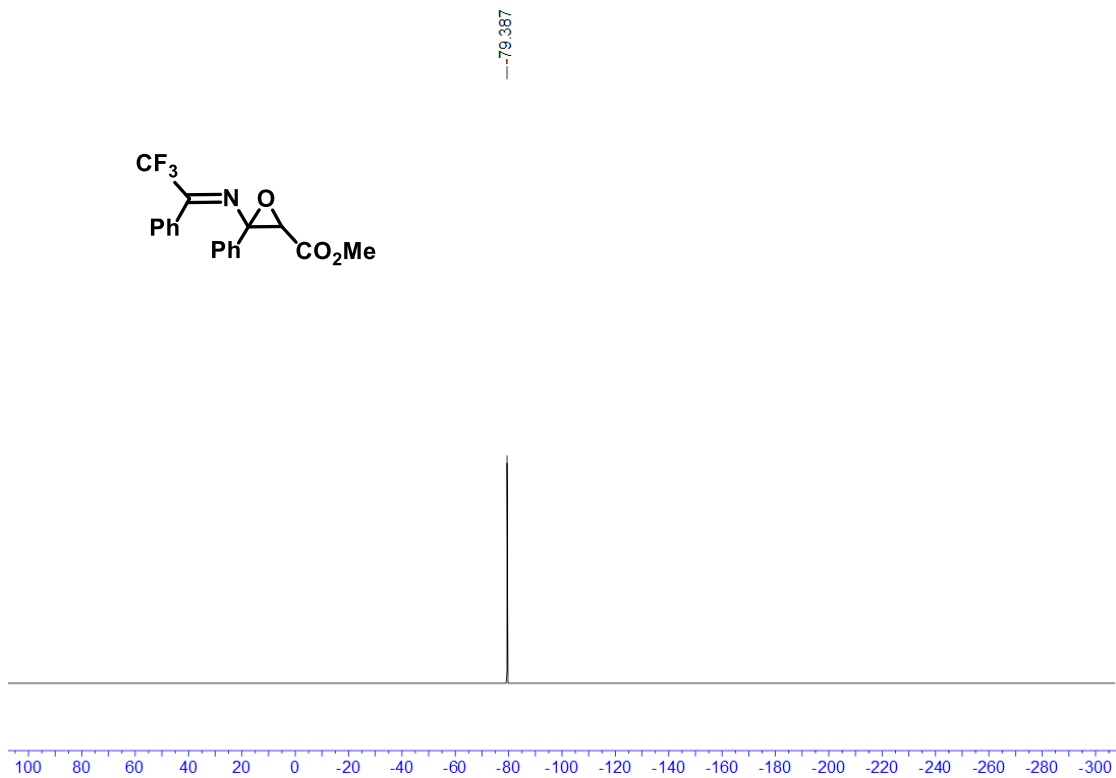
7.987  
7.982  
7.979  
7.975  
7.967  
7.961  
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7.788  
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7.777  
7.771  
7.558  
7.546  
7.539  
7.535  
7.525  
7.521  
7.518  
7.482  
7.477  
7.474  
7.462  
7.458  
7.454  
7.444  
7.440  
7.437  
7.437  
7.418  
7.414  
7.409  
7.406  
7.403  
7.397  
7.393  
7.260  
5.789



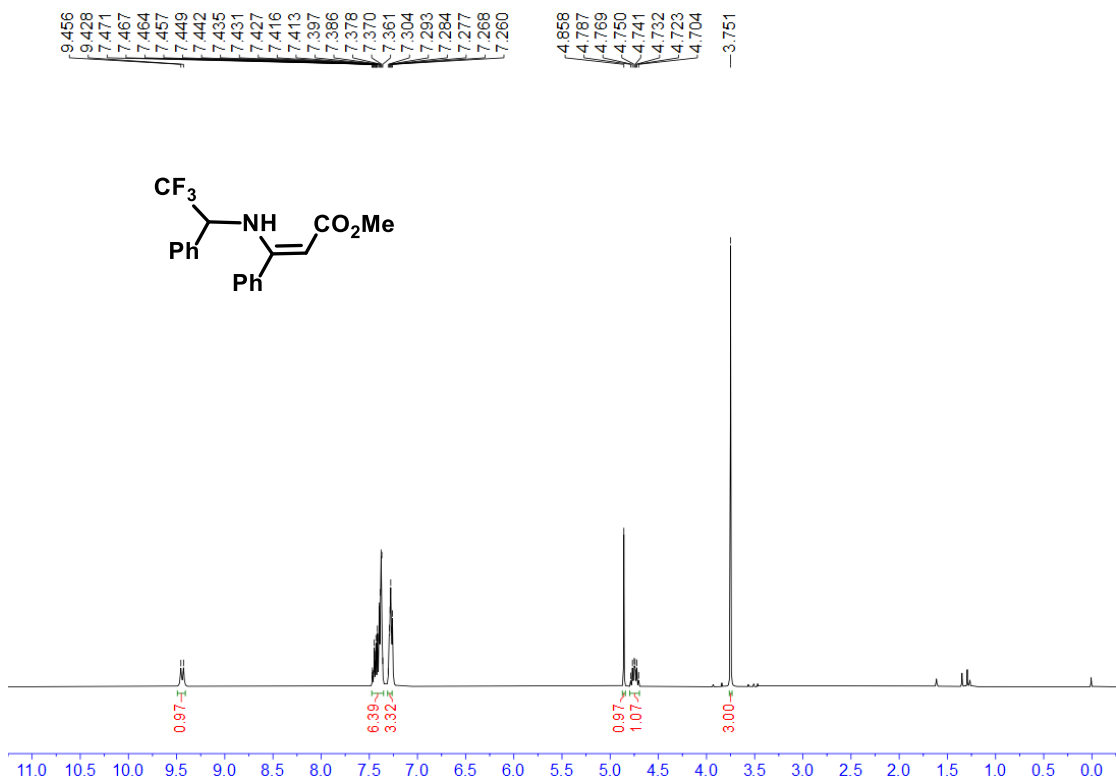
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **6aa**



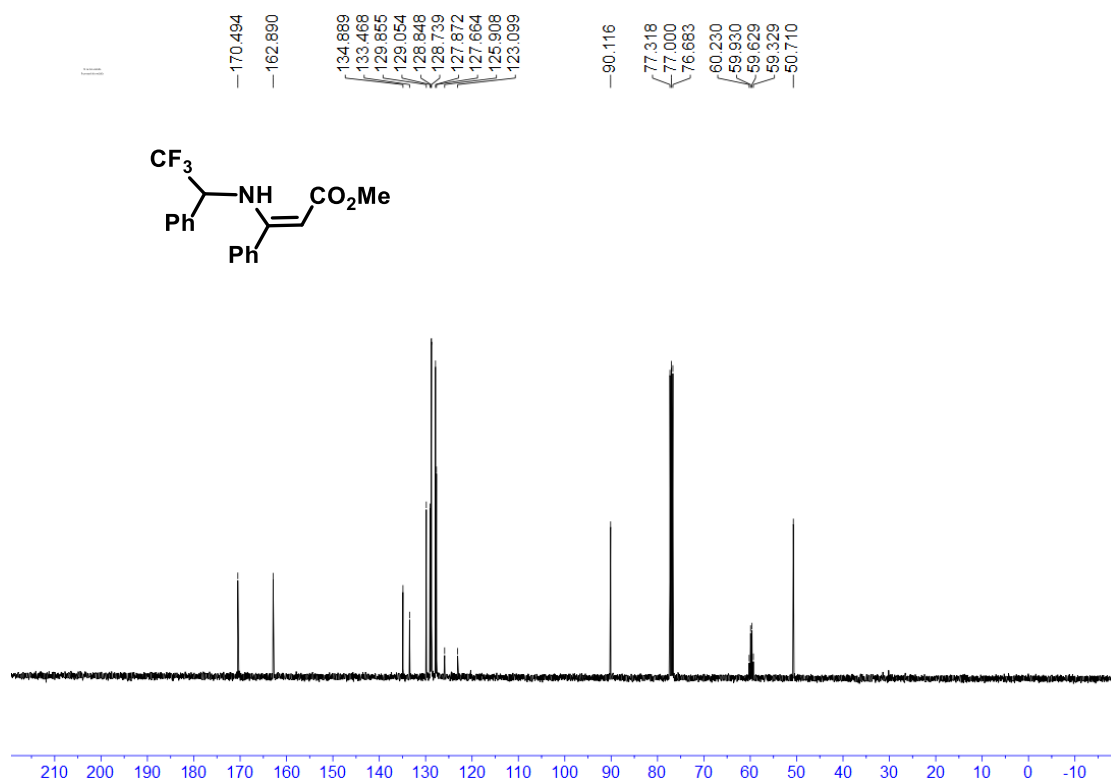
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **6aa**



<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) of **7aa**



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **7aa**



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

