

Supporting Information

Rhodium-Catalyzed Asymmetric Arylation/Defluorination of 1-(Trifluoromethyl)alkenes Forming Enantioenriched 1,1-Difluoroalkenes

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1. General information

All air-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or argon. Solvents were degassed prior to use when necessary. NMR spectra were recorded on Bruker ACF-300 spectrometer (300 MHz for ^1H , 75 MHz for ^{13}C , and 282 MHz for ^{19}F), ACF-400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C , and 377 MHz for ^{19}F) and ACF-500 spectrometer (500 MHz for ^1H , 125 MHz for ^{13}C). Chemical shifts are reported in δ (ppm) referenced to an internal SiMe_4 standard ($\delta = 0$ ppm) for ^1H NMR, chloroform- d ($\delta = 77.0$ ppm) for ^{13}C NMR. The following abbreviations were used; s: singlet, d: doublet, t: triplet, q: quartet, quint: quintet, m: multiplet, br: broad. Optical rotations were measured on an Anton Paar MCP 200 polarimeter. HRMS(ESI) were recorded on a time-of-flight (TOF) LC/MS instrument. Flash column chromatography was performed with Silica gel 60 (Merck) or Al_2O_3 (activated 200) (Merck). The products were further purified by GPC (Gel Permeation Chromatography) if necessary. Enantiomeric excesses (ee) were determined by HPLC analysis on Shimadzu HPLC with Daicel chiral columns.

2. Materials

All chemicals and solvents were purchased from commercial company and used as received. Solvents were degassed before use if necessary.

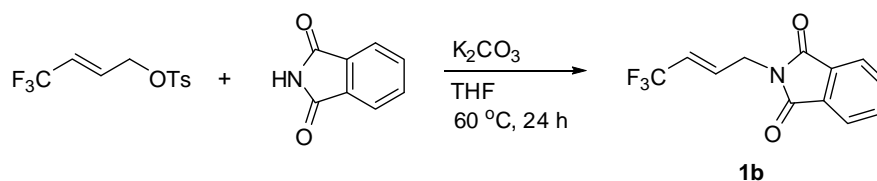
Rhodium complexes, $[\text{RhCl}(\text{cod})]_2$,¹ $[\text{RhCl}(\text{coe})_2]_2$,² $[\text{RhCl}((R,R)\text{-Fc-tfb*})]_2$,³ $[\text{RhCl}((R,R)\text{-Ph-tfb*})]_2$,³ $[\text{RhCl}((R,R)\text{-Ph-bod*})]_2$,⁴ $[\text{RhCl}((R,R)\text{-Fc-bod*})]_2$,⁵ and $[\text{RhCl}(R)\text{-diene*}]_2$,⁶ were prepared according to the reported procedures. $[\text{RhCl}(R)\text{-segphos}]_2$ and $[\text{RhCl}(R)\text{-binap}]_2$ were generated in situ from $[\text{RhCl}(\text{coe})_2]_2$ with $(R)\text{-segphos}$ and $(R)\text{-binap}$, respectively.

Boroxines were prepared according to the following general procedure:⁷ A solution of arylboronic acid (10 mmol) in toluene (30 mL) was refluxed for 2 h with a Dean–Stark trap. The resulting solution was filtered and concentrated under vacuum. The solid thus obtained was washed with pentane and dried under vacuum to give the corresponding arylboroxine as a colorless solid (90–99% yield).

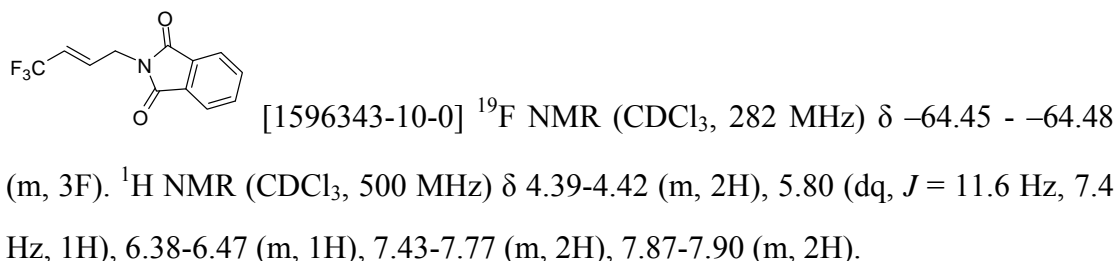
3. Preparation of substrates

1a [610272-47-4],⁸ **1c** [1683527-00-5],⁹ **1d** [1821070-58-9],⁹ **1i** [78622-55-6],¹⁰ and **1j** [1373497-86-9]¹⁰ were prepared according to reported procedures. **1h** was purchased from TCI (Tokyo Chemical Industry Co., Ltd.) and used as received.

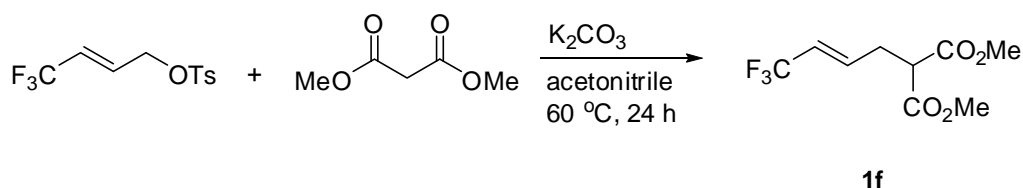
(1) **1b** [1596343-10-0]¹¹ was prepared by the following procedure:



To a solution of (*E*)-4,4,4-trifluorobut-2-en-1-yl 4-methylbenzenesulfonate⁹ (2.00 g, 7.14 mmol, 1.0 equiv) and phthalimide (1.26 g, 8.57 mmol, 1.2 equiv) in THF (20 mL) was added K₂CO₃ (1.18 g, 8.57 mmol, 1.2 equiv). After stirring at 60 °C for 24 h, water (10 mL) was added and the mixture was extracted with Et₂O (20 mL x 3). The organic layers were combined, washed with brine and water, and dried over anhydrous Na₂SO₄. After removal of solvent, the residue was purified by flash chromatography on silica gel (ethyl acetate/hexane = 1/7) to give **1b** (1.60 g, 88% yield) as a white solid.

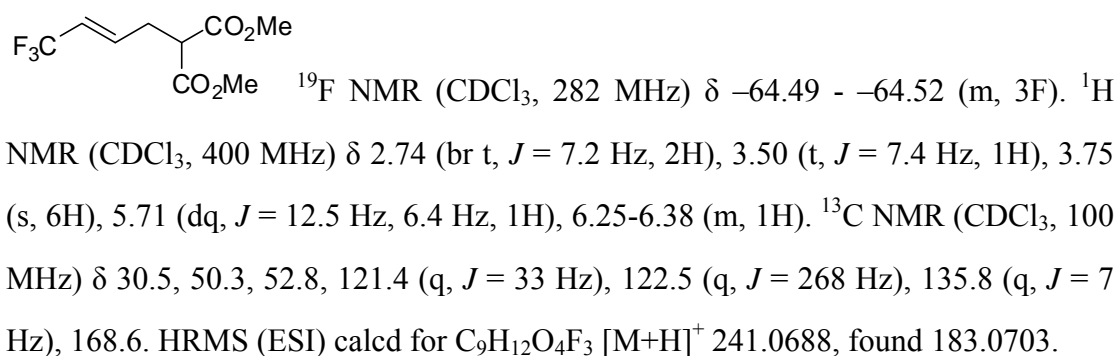


(2) **1f** was prepared by the reported procedure with slight modifications:⁹

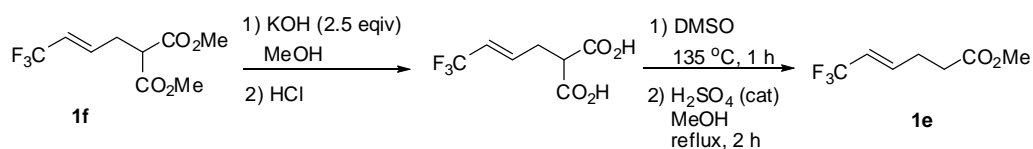


To a solution of (*E*)-4,4,4-trifluorobut-2-en-1-yl 4-methylbenzenesulfonate⁹ (2.00 g,

7.14 mmol, 1.0 equiv) and dimethyl malonate (9.42 g, 71.4 mmol, 10 equiv) in acetonitrile (20 mL) was added K₂CO₃ (1.18 g, 8.57 mmol, 1.2 equiv). After stirring at 60 °C for 24 h, water (10 mL) was added and the mixture was extracted with Et₂O (20 mL x 3). The organic layers were combined, washed with brine and water, and dried over anhydrous Na₂SO₄. After removal of solvent, the residue was fractionally distilled to give **1f** (1.53 g, 89% yield) as a colorless liquid. (It was further purified by flash chromatography on silica gel with ethyl acetate/hexane = 1/10 if it contains dimethyl malonate)



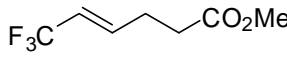
(3) **1e** was prepared by the following procedure:



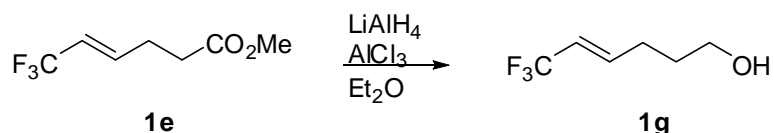
To a solution of KOH (1.75 g, 31.3 mmol, 2.5 equiv) in MeOH (10 mL) was added compound **1f** (3.00 g, 12.5 mmol). After the mixture was stirred at room temperature for 10 h, the solvent was removed thoroughly under reduced pressure. An aqueous HCl (2%) was added to acidify the mixture (pH2) and it was extracted with Et₂O (30 mL x 3). The organic layers were combined, washed with brine and water, and dried over anhydrous Na₂SO₄. Filtration and removal of solvent gave a crude malonic acid which was used directly for the next step.

The crude malonic acid obtained above was dissolved in DMSO (10 mL) and the solution was heated at 135 °C for 2 h. The mixture was poured into water and extracted with Et₂O (30 mL x 3). The organic layers were combined, washed with

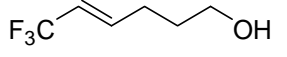
brine and water, and dried over anhydrous Na₂SO₄. After filtration and removal of solvent, the residue was dissolved in MeOH (20 mL) and a drop of H₂SO₄ was added. The mixture was heated to reflux and kept stirring for 2 h. After removal of solvent, the residue was purified by flash chromatography on silica gel (ethyl acetate/hexane = 1/10) to give **1e** (2.00 g, 88% yield based on **1f**) as a colorless oil.

 ¹⁹F NMR (CDCl₃, 282 MHz) δ -64.20 - -64.23 (m, 3F). ¹H NMR (CDCl₃, 500 MHz) δ 2.47-2.49 (m, 4H), 3.69 (s, 3H), 5.67 (dq, *J* = 12.6 Hz, 6.6 Hz, 1H), 6.36-6.41 (m, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 26.6, 32.2, 51.8, 119.6 (q, *J* = 33 Hz), 122.8 (q, *J* = 267 Hz), 138.4 (q, *J* = 7 Hz), 172.5. HRMS (ESI) calcd for C₇H₁₀O₂F₃ [M+H]⁺ 183.0633, found 183.0637.

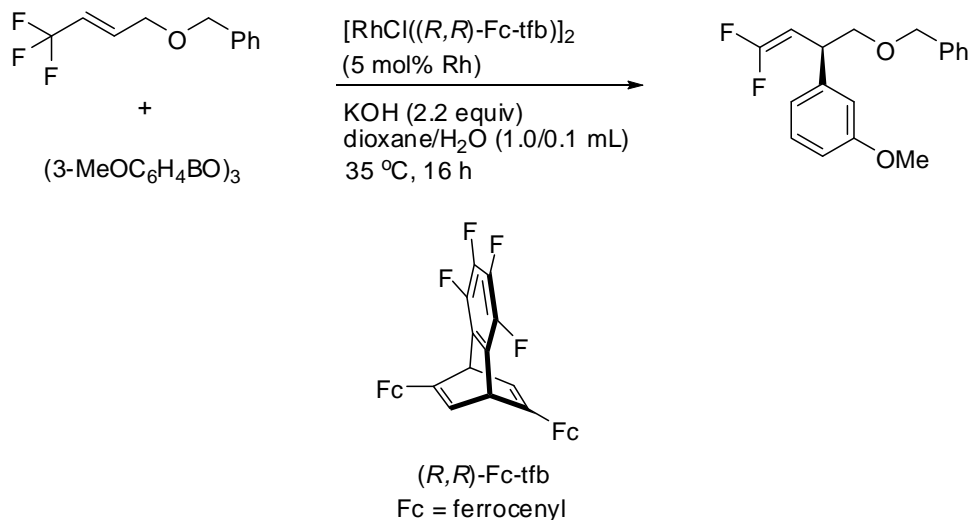
(4) **1g** was prepared by the following procedure:



To a suspension of LiAlH₄ (0.42 g, 11.0 mmol) and AlCl₃ (0.51 g, 3.8 mmol) in Et₂O (20 mL) was added a solution of **1e** (1.00 g, 5.49 mmol) in Et₂O (5 mL) at 0 °C. After the mixture was stirred at 0 °C for 4 h, 10% aqueous HCl (10 mL) was carefully added to decompose excess LiAlH₄. It was extracted with Et₂O (3 x 20 mL), and the combined extracts were dried over Na₂SO₄. After filtration and removal of solvent, the residue was purified by flash chromatography on silica gel (ethyl acetate/hexane = 1/10) to give **1g** (0.61 g, 72%) (somewhat volatile).

 ¹⁹F NMR (CDCl₃, 377 MHz) δ -63.99 - -64.03 (m, 3F). ¹H NMR (CDCl₃, 500 MHz) δ 1.68-1.75 (m, 2H), 1.78 (br s, 1H), 2.24-2.30 (m, 2H), 3.67 (t, *J* = 6.3 Hz, 2H), 5.65 (dq, *J* = 13.9 Hz, 7.1 Hz, 1H), 6.37-6.44 (m, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 27.8, 30.8, 61.8, 118.9 (q, *J* = 33 Hz), 123.0 (q, *J* = 267 Hz), 139.9 (q, *J* = 7 Hz). HRMS (ESI) calcd for C₆H₁₀OF₃ [M+H]⁺ 155.0684, found 155.0683.

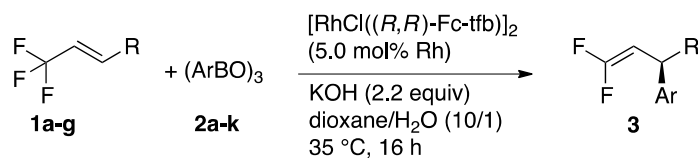
4. A typical procedure for Table 1 (entry 10)



[RhCl((*R,R*)-Fc-tfb*)]₂ (4.4 mg, 0.0060 mmol of Rh), (3-MeOC₆H₄BO)₃ (**2a**) (48.2 mg, 0.120 mmol, 0.360 mmol of B), trifluoromethylalkenes **1a** (25.9 mg, 0.12 mmol), and KOH (14.8 mg, 0.264 mmol) were placed in a Schlenk tube under nitrogen. 1,4-Dioxane (1.0 mL) and water (0.1 mL) were added, and the mixture was stirred at 35 °C for 16 h. The reaction mixture was passed through a short column of silica-gel with EtOAc as eluent. The solvent was removed on a rotary evaporator and the residue was subjected to silica-gel chromatography with EtOAc/hexane (5/95) to give **3aa** (32.5 mg, 0.108 mmol, 90% yield) as a colorless oil.

In entries 15 and 16, [RhCl(*R*)-binap)]₂ and [RhCl(*R*)-segphos)]₂ were generated in situ from [RhCl(coe)₂]₂ (2.15 mg, 0.0060 mmol of Rh) with (*R*)-binap (4.11 mg, 0.0066 mmol) and (*R*)-segphos (4.03 mg, 0.0066 mmol), respectively.

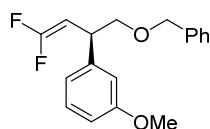
5. A general procedure for Table 2



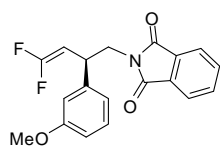
[RhCl((*R,R*)-Fc-tfb*)]₂ (4.4 mg, 0.0060 mmol of Rh), arylboronoxine **2** (0.120 mmol, 0.360 mmol of B), trifluoromethylalkene **1** (0.12 mmol), and KOH (14.8 mg, 0.264 mmol) were placed in a Schlenk tube under nitrogen. 1,4-Dioxane (1.0 mL) and water

(0.1 mL) were added, and the mixture was stirred at 35 °C for 16 h. The reaction mixture was passed through a short column of silica-gel with EtOAc as eluent. The solvent was removed on a rotary evaporator and the residue was subjected to silica-gel chromatography to give **3**.

6. Characterization of the products

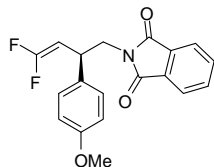


Compound (R)-3aa. The ee was measured by HPLC (Daicel Chiralpak IA column), CH₂Cl₂/hexane = 5/95, flow 0.8 mL/min, 280 nm, t_1 = 10.5 min (major), t_2 = 11.9 min (minor). $[\alpha]_D^{25}$ -34.6 (c 1.11, CHCl₃) for 99% ee (*R*). ¹⁹F NMR (CDCl₃, 282 MHz) δ -88.5 (dd, J = 42.6 Hz, 25.0 Hz, 1F), -87.4 (d, J = 42.6 Hz, 1F). ¹H NMR (CDCl₃, 500 MHz) δ 3.61 (dd, J = 9.4 Hz, 7.5 Hz, 1H), 3.67 (dd, J = 9.4 Hz, 5.9 Hz, 1H), 3.77-3.82 (m, 1H), 3.80 (s, 3H), 4.52 (ddd, J = 25.0 Hz, 9.8 Hz, 2.7 Hz, 1H), 4.53 (s, 2H), 6.79 (s, 1H), 6.80 (d, J = 7.8 Hz, 1H), 6.83 (d, J = 7.6 Hz, 1H), 7.24 (t, J = 8.5 Hz, 1H), 7.27-7.35 (m, 5H). ¹³C NMR (CDCl₃, 125 MHz) δ 40.1 (d, J = 5 Hz), 55.2, 73.0, 73.7 (t, J = 2 Hz), 79.7 (dd, J = 23 Hz, 19 Hz), 112.1, 113.6, 119.8, 127.5, 127.6, 128.3, 129.5, 138.1, 142.5, 156.4 (t, J = 286 Hz), 159.8. HRMS (ESI) calcd for C₁₈H₁₉O₂F₂ [M+H]⁺ 305.1353, found 305.1352.

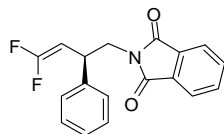


Compound (R)-3ba. The ee was measured by HPLC (Daicel Chiralpak IA column), 2-propanol/hexane = 3/97, flow 2.0 mL/min, 280 nm, t_1 = 6.1 min (major), t_2 = 8.0 min (minor). $[\alpha]_D^{25}$ -20.7 (c 1.16, CHCl₃) for 99% ee (*R*). ¹⁹F NMR (CDCl₃, 282 MHz) δ -88.3 (dd, J = 40 Hz, 24 Hz, 1F), -85.9 (d, J = 40 Hz, 1F). ¹H NMR (CDCl₃, 400 MHz) δ 3.79 (s, 3H), 3.91 (d, J = 8.7 Hz, 2H), 4.07 (br q, J = 8.6 Hz, 1H), 4.52 (ddd, J = 24.2 Hz, 10.2 Hz, 2.1 Hz, 1H), 6.79 (dd, J = 7.8 Hz, 2.1 Hz, 1H), 6.83 (t, J = 2.1 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H), 7.24 (t, J = 7.8 Hz, 1H), 7.68-7.74 (m, 2H), 7.82-7.86 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 38.8 (d, J = 5

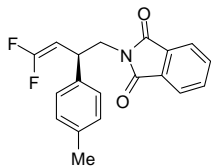
Hz), 43.0, 55.2, 79.4 (dd, $J = 23$ Hz, 19 Hz), 112.8, 113.1, 119.6, 123.4, 129.9, 131.8, 134.0, 141.6, 156.7 (t, $J = 287$ Hz), 159.9, 168.1. HRMS (ESI) calcd for $C_{19}H_{16}NO_3F_2$ $[M+H]^+$ 344.1098, found 344.1099.



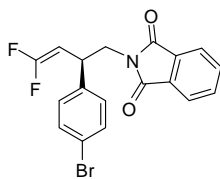
Compound (R)-3bb. The ee was measured by HPLC (Daicel Chiralpak IA column), 2-propanol/hexane = 3/97, flow 2.0 mL/min, 280 nm, $t_1 = 7.7$ min (major), $t_2 = 9.1$ min (minor). $[\alpha]_D^{25} -17.5$ (c 1.27, $CHCl_3$) for 99% ee (*R*). ^{19}F NMR ($CDCl_3$, 282 MHz) δ -88.5 (dd, $J = 41$ Hz, 24 Hz, 1F), -86.3 (d, $J = 41$ Hz, 1F). 1H NMR ($CDCl_3$, 400 MHz) δ 3.78 (s, 3H), 3.87 (d, $J = 8.7$ Hz, 2H), 4.05 (br q, $J = 8.9$ Hz, 1H), 4.50 (ddd, $J = 24.4$ Hz, 10.2 Hz, 2.2 Hz, 1H), 6.85 (d, $J = 8.6$ Hz, 2H), 7.21 (d, $J = 8.6$ Hz, 2H), 7.68-7.74 (m, 2H), 7.82-7.86 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 38.0 (d, $J = 5$ Hz), 43.1, 55.2, 79.6 (dd, $J = 22$ Hz, 19 Hz), 114.2, 123.3, 128.3, 131.8, 132.1, 134.0, 156.6 (t, $J = 287$ Hz), 158.8, 168.1. HRMS (ESI) calcd for $C_{19}H_{16}NO_3F_2$ $[M+H]^+$ 344.1098, found 344.1105.



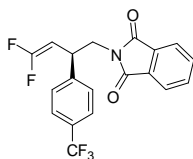
Compound (R)-3bc. The ee was measured by HPLC (Daicel Chiralpak IA column), 2-propanol/hexane = 3/97, flow 2.0 mL/min, 280 nm, $t_1 = 10.3$ min (major), $t_2 = 12.8$ min (minor). $[\alpha]_D^{25} -24.5$ (c 1.10, $CHCl_3$) for 98% ee (*R*). ^{19}F NMR ($CDCl_3$, 377 MHz) δ -88.3 (dd, $J = 41$ Hz, 24 Hz, 1F), -85.9 (d, $J = 41$ Hz, 1F). 1H NMR ($CDCl_3$, 400 MHz) δ 3.90-3.93 (m, 2H), 4.10 (br q, $J = 8.8$ Hz, 1H), 4.51 (ddd, $J = 24.3$ Hz, 10.3 Hz, 2.2 Hz, 1H), 7.23-7.36 (m, 5H), 7.68-7.74 (m, 2H), 7.82-7.86 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 38.8 (d, $J = 5$ Hz), 43.1, 79.4 (dd, $J = 23$ Hz, 19 Hz), 123.3, 127.3, 127.4, 128.8, 131.8, 134.0, 140.0, 156.7 (t, $J = 287$ Hz), 168.1. HRMS (ESI) calcd for $C_{18}H_{14}NO_2F_2$ $[M+H]^+$ 314.0993, found 314.0992.



Compound (R)-3bd. The ee was measured by HPLC (Daicel Chiralpak IA column), IPA/hexane = 1/99, flow 2.0 mL/min, 280 nm, t_1 = 8.0 min (major), t_2 = 9.0 min (minor). $[\alpha]_D^{25}$ -28.6 (c 1.26, CHCl₃) for 99% ee (*R*). ¹⁹F NMR (CDCl₃, 282 MHz) δ -88.6 (dd, J = 41 Hz, 24 Hz, 1F), -86.2 (d, J = 41 Hz, 1F). ¹H NMR (CDCl₃, 300 MHz) δ 2.32 (s, 3H), 3.87-3.91 (m, 2H), 4.07 (br q, J = 8.7 Hz, 1H), 4.52 (ddd, J = 24.3 Hz, 10.2 Hz, 2.2 Hz, 1H), 7.13 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 7.68-7.74 (m, 2H), 7.82-7.86 (m, 2H). ¹³C NMR (CDCl₃, 75 MHz) δ 21.0, 38.4 (d, J = 5 Hz), 43.1, 79.6 (dd, J = 22 Hz, 19 Hz), 123.3, 127.2, 129.5, 131.8, 134.0, 137.0, 137.1, 156.7 (t, J = 287 Hz), 168.1. HRMS (ESI) calcd for C₁₉H₁₆NO₂F₂ [M+H]⁺ 328.1149, found 328.1140.

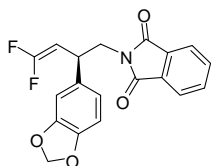


Compound (R)-3be. The ee was measured by HPLC (Daicel Chiralpak IA column), IPA/hexane = 1/99, flow 2.0 mL/min, 280 nm, t_1 = 12.3 min (major), t_2 = 13.4 min (minor). $[\alpha]_D^{25}$ -9.7 (c 2.59, CHCl₃) for 99% ee (*R*). ¹⁹F NMR (CDCl₃, 377 MHz) δ -87.4 (dd, J = 39 Hz, 24 Hz, 1F), -85.4 (d, J = 39 Hz, 1F). ¹H NMR (CDCl₃, 400 MHz) δ 3.88 (d, J = 8.1 Hz, 2H), 4.07 (br q, J = 8.7 Hz, 1H), 4.49 (ddd, J = 24.2 Hz, 10.1 Hz, 2.1 Hz, 1H), 7.17 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.70-7.75 (m, 2H), 7.81-7.85 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 38.3 (d, J = 5 Hz), 42.8, 79.1 (dd, J = 23 Hz, 19 Hz), 121.3, 123.4, 129.1, 131.7, 132.0, 134.1, 139.0, 156.7 (t, J = 288 Hz), 168.0. HRMS (ESI) calcd for C₁₈H₁₃NO₂F₂Br [M+H]⁺ 392.0098, found 392.0107.



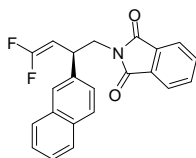
Compound (R)-3bf. The ee was measured by HPLC (Daicel Chiralpak IA column), 2-propanol/hexane = 1/99, flow 2.0 mL/min, 280 nm, t_1 = 11.1

min (major), $t_2 = 14.2$ min (minor). $[\alpha]_D^{25} -14.5$ (c 1.21, CHCl_3) for 99% ee (*R*). ^{19}F NMR (CDCl_3 , 377 MHz) δ -87.1 (dd, $J = 38$ Hz, 24 Hz, 1F), -85.0 (d, $J = 38$ Hz, 1F), -62.6 (s, 3F). ^1H NMR (CDCl_3 , 400 MHz) δ 3.93 (d, $J = 8.1$ Hz, 2H), 4.18 (br q, $J = 8.8$ Hz, 1H), 4.54 (ddd, $J = 24.0$ Hz, 10.2 Hz, 2.0 Hz, 1H), 7.43 (d, $J = 8.1$ Hz, 2H), 7.59 (d, $J = 8.1$ Hz, 2H), 7.70-7.76 (m, 2H), 7.81-7.87 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 38.7 (d, $J = 5$ Hz), 42.7, 78.9 (dd, $J = 24$ Hz, 19 Hz), 121.5, 124.0 (q, $J = 270$ Hz), 125.8 (q, $J = 4$ Hz), 127.8, 129.8 (q, $J = 32$ Hz), 131.7, 134.2, 144.1, 156.9 (t, $J = 288$ Hz), 168.0. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{13}\text{NO}_2\text{F}_5$ $[\text{M}+\text{H}]^+$ 382.0866, found 382.0866.



Compound (*R*)-3bg. The ee was measured by HPLC (Daicel

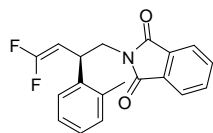
Chiralpak IA column), 2-propanol/hexane = 3/97, flow 2.0 mL/min, 280 nm, $t_1 = 8.9$ min (major), $t_2 = 10.4$ min (minor). $[\alpha]_D^{25} -9.1$ (c 1.21, CHCl_3) for 99% ee (*R*). ^{19}F NMR (CDCl_3 , 282 MHz) δ -88.1 (dd, $J = 40$ Hz, 24 Hz, 1F), -86.0 (d, $J = 40$ Hz, 1F). ^1H NMR (CDCl_3 , 300 MHz) δ 3.86 (d, $J = 8.0$ Hz, 2H), 4.01 (br q, $J = 8.7$ Hz, 1H), 4.47 (ddd, $J = 24.3$ Hz, 10.1 Hz, 2.2 Hz, 1H), 5.92 (d, $J = 1.3$ Hz, 1H), 5.93 (d, $J = 1.3$ Hz, 1H), 6.72-6.77 (m, 2H), 6.79 (s, 1H), 7.70-7.76 (m, 2H), 7.81-7.87 (m, 2H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 38.5 (d, $J = 5$ Hz), 43.1, 79.5 (dd, $J = 23$ Hz, 19 Hz), 101.1, 107.7, 108.5, 120.5, 123.4, 131.8, 133.9, 134.0, 146.8, 148.0, 156.6 (t, $J = 288$ Hz), 168.1. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{14}\text{NO}_4\text{F}_2$ $[\text{M}+\text{H}]^+$ 358.0891, found 358.0903.



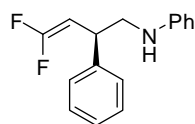
Compound (*R*)-3bh. The ee was measured by HPLC (Daicel

Chiralpak IA column), 2-propanol/hexane = 1/99, flow 2.0 mL/min, 280 nm, $t_1 = 11.3$ min (major), $t_2 = 15.9$ min (minor). $[\alpha]_D^{25} -26.7$ (c 1.48, CHCl_3) for 99% ee (*R*). ^{19}F NMR (CDCl_3 , 377 MHz) δ -88.0 (dd, $J = 40$ Hz, 24 Hz, 1F), -85.6 (d, $J = 40$ Hz, 1F). ^1H NMR (CDCl_3 , 500 MHz) δ 4.02 (d, $J = 8.6$ Hz, 2H), 4.32 (br q, $J = 7.1$ Hz, 1H), 4.64 (ddd, $J = 24.3$ Hz, 10.3 Hz, 2.0 Hz, 1H), 7.46-7.53 (m, 3H), 7.71-7.88 (m, 8H).

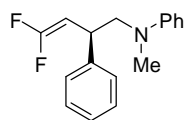
^{13}C NMR (CDCl_3 , 100 MHz) δ 39.0 (d, $J = 5$ Hz), 43.0, 79.5 (dd, $J = 23$ Hz, 19 Hz), 123.4, 125.3, 126.0, 126.1, 126.3, 127.7, 127.8, 128.7, 131.8, 132.7, 133.5, 134.1, 137.4, 156.8 (t, $J = 288$ Hz), 168.2. HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{16}\text{NO}_2\text{F}_2$ $[\text{M}+\text{H}]^+$ 364.1149, found 364.1136.



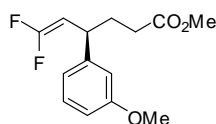
Compound (R)-3bi. The ee was measured by HPLC (Daicel Chiralpak IA column), 2-propanol/hexane = 1/99, flow 2.0 mL/min, 280 nm, $t_1 = 6.2$ min (major), $t_2 = 6.9$ min (minor). $[\alpha]_{\text{D}}^{25} -61$ (c 0.80, CHCl_3) for 99% ee (*R*). ^{19}F NMR (CDCl_3 , 282 MHz) δ -88.4 (dd, $J = 41$ Hz, 24 Hz, 1F), -86.4 (dd, $J = 41$ Hz, 2 Hz, 1F). ^1H NMR (CDCl_3 , 300 MHz) δ 2.47 (s, 3H), 3.80 (dd, $J = 13.6$ Hz, 5.4 Hz, 1H), 3.94 (dd, $J = 13.6$ Hz, 10.2 Hz, 1H), 4.30-4.40 (m, 1H), 4.55 (ddd, $J = 24.3$ Hz, 10.3 Hz, 2.2 Hz, 1H), 7.13-7.31 (m, 4H), 7.70-7.76 (m, 2H), 7.83-7.88 (m, 2H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 19.3, 34.6 (d, $J = 5$ Hz), 42.4, 79.5 (dd, $J = 22$ Hz, 19 Hz), 123.4, 126.2, 126.5, 127.2, 130.9, 131.8, 134.1, 136.0, 138.4, 156.7 (t, $J = 287$ Hz), 168.2. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{16}\text{NO}_2\text{F}_2$ $[\text{M}+\text{H}]^+$ 328.1149, found 328.1141.



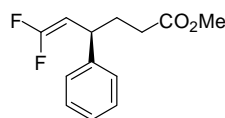
Compound (R)-3cc. The ee was measured by HPLC (Daicel Chiralpak IB column), 2-propanol/hexane = 1/99, flow 0.7 mL/min, 220 nm, $t_1 = 9.1$ min (minor), $t_2 = 10.3$ min (major). $[\alpha]_{\text{D}}^{25} +21.8$ (c 1.04, CHCl_3) for 97% ee (*R*). ^{19}F NMR (CDCl_3 , 377 MHz) δ -87.9 (dd, $J = 42$ Hz, 25 Hz, 1F), -86.7 (d, $J = 42$ Hz, 1F). ^1H NMR (CDCl_3 , 400 MHz) δ 3.40 (d, $J = 7.3$ Hz, 1H), 3.64 (s, br, 1H), 3.83 (br q, $J = 8.3$ Hz, 1H), 4.52 (ddd, $J = 24.6$ Hz, 10.0 Hz, 1.8 Hz, 1H), 6.60 (d, $J = 8.2$ Hz, 2H), 6.74 (t, $J = 7.2$ Hz, 1H), 7.19 (t, $J = 7.6$ Hz, 2H), 7.23-7.30 (m, 3H), 7.36 (t, $J = 7.5$ Hz, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 39.3 (d, $J = 4$ Hz), 49.5, 80.2 (dd, $J = 22$ Hz, 20 Hz), 113.2, 117.9, 127.2, 127.4, 128.9, 129.3, 141.1, 147.5, 156.6 (t, $J = 287$ Hz). HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{16}\text{NF}_2$ $[\text{M}+\text{H}]^+$ 260.1251, found 260.1252.



Compound (R)-3dc. The ee was measured by HPLC (Daicel Chiralpak IB column), 2-propanol/hexane = 1/99, flow 1.0 mL/min, 220 nm, t_1 = 5.5 min (minor), t_2 = 6.3 min (major). $[\alpha]_D^{25}$ +53 (c 0.98, CHCl_3) for 98% ee (*R*). ^{19}F NMR (CDCl_3 , 377 MHz) δ -88.4 (dd, J = 43 Hz, 25 Hz, 1F), -87.0 (d, J = 43 Hz, 1F). ^1H NMR (CDCl_3 , 400 MHz) δ 2.74 (s, 3H), 3.50 (dd, J = 14.6 Hz, 7.3 Hz, 1H), 3.66 (dd, J = 14.6 Hz, 7.6 Hz, 1H), 3.93 (br q, J = 8.4 Hz, 1H), 4.53 (ddd, J = 24.5 Hz, 10.1 Hz, 2.5 Hz, 1H), 6.68 (d, J = 8.1 Hz, 2H), 6.72 (t, J = 7.3 Hz, 1H), 7.20-7.27 (m, 5H), 7.33 (t, J = 7.3 Hz, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 38.4 (d, J = 4 Hz), 39.3, 59.4, 80.0 (dd, J = 22 Hz, 20 Hz), 112.0, 116.4, 127.0, 127.4, 128.8, 129.2, 141.7, 148.7, 156.3 (t, J = 287 Hz). HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{18}\text{NF}_2$ $[\text{M}+\text{H}]^+$ 274.1407, found 274.1404.

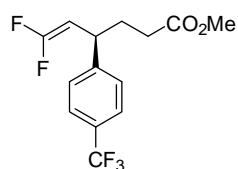


Compound (R)-3ea. The ee was measured by HPLC (Daicel Chiralpak IB column), 2-propanol/hexane = 1/99, flow 1.0 mL/min, 220 nm, t_1 = 7.7 min (minor), t_2 = 8.3 min (major). $[\alpha]_D^{25}$ -40.6 (c 1.78, CHCl_3) for 95% ee (*R*). ^{19}F NMR (CDCl_3 , 377 MHz) δ -89.3 (dd, J = 44 Hz, 25 Hz, 1F), -88.1 (d, J = 44 Hz, 1F). ^1H NMR (CDCl_3 , 400 MHz) δ 1.93-2.11 (m, 2H), 2.23-2.37 (m, 2H), 3.45 (br q, J = 8.6 Hz, 1H), 3.66 (s, 3H), 3.80 (s, 3H), 4.36 (ddd, J = 24.5 Hz, 10.3 Hz, 2.5 Hz, 1H), 6.73-6.80 (m, 3H), 7.24 (t, J = 7.9 Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 31.6, 31.9, 39.1 (d, J = 5 Hz), 51.6, 55.2, 81.8 (dd, J = 21 Hz, 19 Hz), 111.9, 113.1, 119.3, 129.8, 144.6, 156.2 (t, J = 286 Hz), 159.9, 173.5. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{17}\text{O}_3\text{F}_2$ $[\text{M}+\text{H}]^+$ 271.1146, found 271.1147.

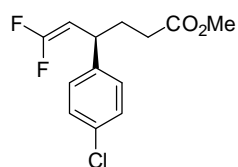


Compound (R)-3ec. The ee was measured by HPLC (Daicel Chiralpak IB column), 2-propanol/hexane = 1/99, flow 1.0 mL/min, 220 nm, t_1 = 5.6 min (minor), t_2 = 6.3 min (major). $[\alpha]_D^{25}$ -47.0 (c 1.08, CHCl_3) for 96% ee (*R*). ^{19}F NMR (CDCl_3 , 377 MHz) δ -89.4 (dd, J = 45 Hz, 25 Hz, 1F), -88.1 (d, J = 45 Hz, 1F).

^1H NMR (CDCl_3 , 400 MHz) δ 1.94-2.12 (m, 2H), 2.23-2.37 (m, 2H), 3.48 (br q, J = 8.6 Hz, 1H), 3.66 (s, 3H), 4.38 (ddd, J = 24.5 Hz, 10.3 Hz, 2.5 Hz, 1H), 7.18-7.25 (m, 3H), 7.32 (t, J = 7.8 Hz, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 31.6, 31.9, 39.0 (d, J = 5 Hz), 51.6, 81.7 (dd, J = 21 Hz, 20 Hz), 126.8, 127.0, 128.8, 142.9, 156.2 (t, J = 286 Hz), 173.5. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{O}_2\text{F}_2$ $[\text{M}+\text{H}]^+$ 241.1040, found 241.1038.

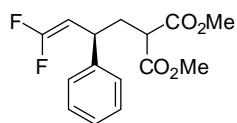


Compound (R)-3ef. The ee was measured by HPLC (Daicel Chiralpak IB column), 2-propanol/hexane = 1/99, flow 0.6 mL/min, 220 nm, t_1 = 9.7 min (minor), t_2 = 10.1 min (major). $[\alpha]_{\text{D}}^{25}$ -38 (c 0.92, CHCl_3) for 98% ee (*R*). ^{19}F NMR (CDCl_3 , 377 MHz) δ -88.3 (dd, J = 42 Hz, 24 Hz, 1F), -87.1 (d, J = 42 Hz, 1F), -62.5 (s, 3F). ^1H NMR (CDCl_3 , 400 MHz) δ 1.95-2.13 (m, 2H), 2.24-2.38 (m, 2H), 3.57 (br q, J = 8.6 Hz, 1H), 3.66 (s, 3H), 4.37 (ddd, J = 24.2 Hz, 10.2 Hz, 2.4 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 31.4, 31.7, 38.9 (d, J = 5 Hz), 51.7, 81.1 (dd, J = 22 Hz, 20 Hz), 124.0 (q, J = 270 Hz), 125.7 (q, J = 4 Hz), 127.4, 129.3 (q, J = 32 Hz), 147.0, 156.4 (t, J = 288 Hz), 173.2. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{14}\text{NO}_2\text{F}_5$ $[\text{M}+\text{H}]^+$ 309.0914, found 309.0911.

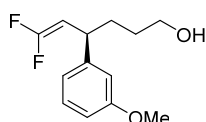


Compound (R)-3ej. The ee was measured by HPLC (Daicel Chiralpak IA column), CH_2Cl_2 /hexane = 5/95, flow 1.0 mL/min, 230 nm, t_1 = 13.4 min (major), t_2 = 15.2 min (minor). $[\alpha]_{\text{D}}^{25}$ -55 (c 0.92, CHCl_3) for 96% ee (*R*). ^{19}F NMR (CDCl_3 , 282 MHz) δ -88.8 (dd, J = 43 Hz, 24 Hz, 1F), -87.6 (d, J = 43 Hz, 1F). ^1H NMR (CDCl_3 , 300 MHz) δ 1.92-2.08 (m, 2H), 2.20-2.32 (m, 2H), 3.47 (br q, J = 8.5 Hz, 1H), 3.66 (s, 3H), 4.32 (ddd, J = 24.3 Hz, 10.2 Hz, 2.5 Hz, 1H), 7.12 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 31.5, 31.8, 38.4 (d, J = 5 Hz), 51.6, 81.5 (dd, J = 21 Hz, 20 Hz), 128.4, 128.9, 132.6, 141.4, 156.3 (t, J = 287 Hz), 173.3. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{14}\text{O}_2\text{F}_2\text{Cl}$ $[\text{M}+\text{H}]^+$ 275.0659, found

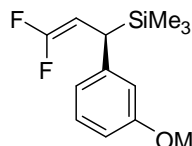
275.0650.



Compound (R)-3fc. The ee was measured by HPLC (Daicel Chiralpak IA column), IPA/hexane = 1/99, flow 2.0 mL/min, 280 nm, t_1 = 4.2 min (major), t_2 = 5.4 min (minor). $[\alpha]_D^{25}$ -30 (c 0.98, CHCl_3) for 96% ee (*R*). ^{19}F NMR (CDCl_3 , 282 MHz) δ -88.7 (dd, J = 43 Hz, 24 Hz, 1F), -87.3 (d, J = 43 Hz, 1F). ^1H NMR (CDCl_3 , 300 MHz) δ 2.20-2.42 (m, 2H), 3.35 (t, J = 7.4 Hz, 1H), 3.50 (br q, J = 8.5 Hz, 1H), 3.71 (s, 3H), 3.75 (s, 3H), 4.38 (ddd, J = 24.2 Hz, 10.4 Hz, 2.5 Hz, 1H), 7.18-7.30 (m, 5H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 35.5, 37.7 (d, J = 5 Hz), 49.8, 52.59, 52.63, 81.4 (dd, J = 22 Hz, 19 Hz), 127.0, 127.1, 128.8, 142.2, 156.3 (t, J = 288 Hz), 169.3, 169.5. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{17}\text{O}_4\text{F}_2$ $[\text{M}+\text{H}]^+$ 299.1095, found 299.1095.

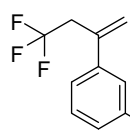


Compound (R)-3ga. The ee was measured by HPLC (Daicel Chiralpak IC column), 2-propanol/hexane = 3/97, flow 1.0 mL/min, 280 nm, t_1 = 13.0 min (minor), t_2 = 16.4 min (major). $[\alpha]_D^{25}$ -60.9 (c 1.40, CHCl_3) for 98% ee (*R*). ^{19}F NMR (CDCl_3 , 377 MHz) δ -90.0 (dd, J = 46 Hz, 25 Hz, 1F), -88.8 (d, J = 46 Hz, 1F). ^1H NMR (CDCl_3 , 400 MHz) δ 1.31 (br s, 1H), 1.46-1.86 (m, 4H), 3.43 (br q, J = 8.4 Hz, 1H), 3.64 (t, J = 6.5 Hz, 2H), 3.80 (s, 3H), 4.37 (ddd, J = 24.7 Hz, 10.2 Hz, 2.6 Hz, 1H), 6.74-6.80 (m, 3H), 7.23 (t, J = 7.8 Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 30.6, 32.9, 39.5 (d, J = 5 Hz), 55.2, 62.6, 82.4 (t, J = 20 Hz), 111.6, 113.1, 119.3, 129.6, 145.5, 156.0 (t, J = 286 Hz), 159.8. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{17}\text{O}_2\text{F}_2$ $[\text{M}+\text{H}]^+$ 243.1197, found 243.1188.



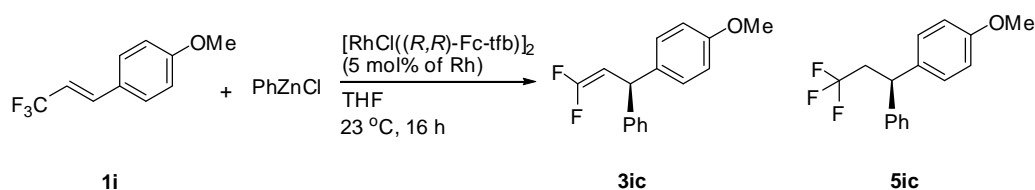
Compound (R)-3ha (It was purified by GPC. It would decompose in silica-gel column). The ee was measured by HPLC (Daicel Chiralpak IB column), pure hexane, flow 0.8 mL/min, 280 nm, t_1 = 9.5 min (minor), t_2 = 16.4 min (major).

$[\alpha]_D^{25}$ -33.4 (c 1.73, CHCl_3) for 96% ee (*R*). ^{19}F NMR (CDCl_3 , 282 MHz) δ -90.6 (dd, $J = 49$ Hz, 23 Hz, 1F), -90.3 (ddd, $J = 49$ Hz, 4 Hz, 2 Hz, 1F). ^1H NMR (CDCl_3 , 300 MHz) δ 0.00 (s, 9H), 2.95 (dd, $J = 11.7$ Hz, 2.1 Hz, 1H), 3.79 (s, 3H), 4.57 (ddd, $J = 22.6$ Hz, 11.7 Hz, 4.0 Hz, 1H), 6.58-6.70 (m, 3H), 7.18 (t, $J = 7.9$ Hz, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ -3.2 , 31.5 (d, $J = 2$ Hz), 55.1, 78.3 (t, $J = 22$ Hz), 110.0, 113.0, 119.4, 129.3, 143.2, 155.3 (t, $J = 284$ Hz), 159.6. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{19}\text{OF}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 257.1173, found 257.1170.

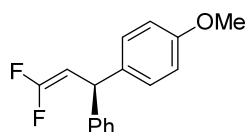


Compound 4 [1402156-80-2]¹². ^{19}F NMR (CDCl_3 , 377 MHz) δ -64.5 (t, $J = 10$ Hz, 3F). ^1H NMR (CDCl_3 , 400 MHz) δ 3.27 (q, $J = 10.7$ Hz, 2H), 3.84 (s, 3H), 5.38 (s, 1H), 5.61 (s, 1H), 6.87 (dd, $J = 8.2$ Hz, 2.6 Hz, 1H), 6.91 (t, $J = 1.9$ Hz, 1H), 6.99 (dd, $J = 8.2$ Hz, 1.6 Hz, 1H), 7.28 (t, $J = 8.2$ Hz, 1H);

7. A typical procedure for scheme 3.

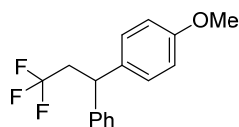


$[\text{RhCl}((R,R)\text{-Fc-tfb}^*)_2]$ (4.4 mg, 0.0060 mmol of Rh) and trifluoromethylalkene **1i** (24.3 mg, 0.12 mmol) were placed in a Schlenk tube under nitrogen. PhZnCl (0.48 mmol, 4.0 equiv, prepared from ZnCl_2 and PhMgBr) was added, and the mixture was stirred at room temperature (23°C) for 16 h. NH_4Cl (aq) was added at 0°C and it was extracted with ethyl acetate. The organic layer was combined, dried over Na_2SO_4 , and evaporated under vacuum. The crude product was purified by silica-gel column chromatography with ethyl EtOAc/hexane (5/95) to give **3ic** (26.5 mg, 85%) as slight yellow liquid.

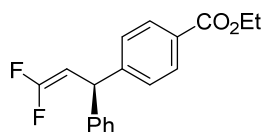


Compound (R)-3ic. The ee was measured by HPLC (Daicel

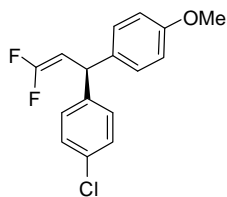
Chiralpak IA x 2 columns) (Two IA columns are connected), pure hexane, flow 0.6 mL/min, 280 nm, t_1 = 28.9 min (minor), t_2 = 30.0 min (major). $[\alpha]_D^{25}$ +16.8 (c 1.30, CHCl₃) for 99% ee (*R*). ¹⁹F NMR (CDCl₃, 377 MHz) δ -90.1 (dd, J = 44 Hz, 25 Hz, 1F), -88.5 (d, J = 44 Hz, 1F). ¹H NMR (CDCl₃, 400 MHz) δ 3.80 (s, 3H), 4.75 (ddd, J = 23.6 Hz, 10.6 Hz, 2.2 Hz, 1H), 4.86 (d, J = 11.0 Hz, 1H), 6.86 (d, J = 8.7 Hz, 2H), 7.11 (d, J = 8.7 Hz, 2H), 7.19 (d, J = 7.4 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 7.32 (t, J = 7.3 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 43.7 (d, J = 5 Hz), 55.3, 82.2 (dd, J = 19 Hz, 22 Hz), 114.0, 126.6, 127.9, 128.6, 128.9, 135.3, 143.5, 155.9 (t, J = 286 Hz), 158.4. HRMS (ESI) calcd for C₁₆H₁₅OF₂ [M+H]⁺ 261.1091, found 201.1095



Compound 5ic [1618086-15-9]¹³. ¹⁹F NMR (CDCl₃, 377 MHz) δ -63.7 (t, J = 10 Hz, 3F). ¹H NMR (CDCl₃, 400 MHz) δ 2.88 (qd, J = 10.4 Hz, 7.4 Hz, 2H), 3.78 (s, 3H), 4.29 (t, J = 7.4 Hz, 1H), 6.84 (d, J = 8.7 Hz, 2H), 7.17 (d, J = 8.7 Hz, 2H), 7.21-7.26 (m, 3H), 7.31 (t, J = 7.4 Hz, 2H).



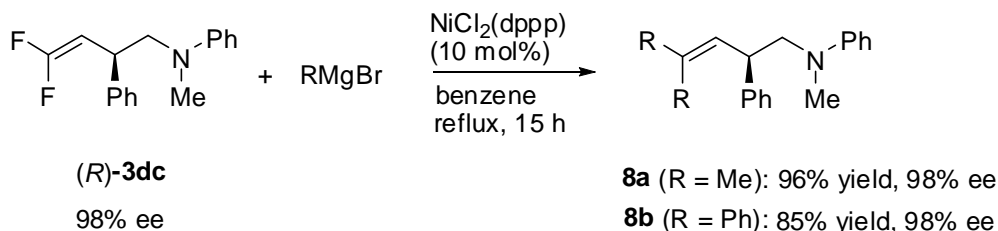
Compound (*R*)-3jc. The ee was measured by HPLC (Daicel Chiralpak IF column), 2-propanol/hexane = 1/99, flow 1.0 mL/min, 254 nm, t_1 = 7.3 min (minor), t_2 = 7.9 min (major). $[\alpha]_D^{25}$ -2.76 (c 1.05, CHCl₃) for 99% ee (*R*). ¹⁹F NMR (CDCl₃, 282 MHz) δ -89.1 (dd, J = 41 Hz, 24 Hz, 1F), -87.4 (d, J = 41 Hz, 1F). ¹H NMR (CDCl₃, 400 MHz) δ 1.38 (t, J = 7.1 Hz, 3H), 4.37 (q, J = 7.1 Hz, 3H), 4.75 (ddd, J = 23.7 Hz, 10.4 Hz, 2.1 Hz, 1H), 4.93 (d, J = 10.5 Hz, 1H), 7.16 (d, J = 7.2 Hz, 2H), 7.23-7.27 (m, 3H), 7.32 (t, J = 7.3 Hz, 2H), 7.99 (d, J = 8.3 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 14.3, 44.5 (d, J = 5 Hz), 60.9, 81.5 (dd, J = 23 Hz, 19 Hz), 127.0, 127.86, 127.92, 128.8, 129.1, 129.9, 142.4, 148.1, 156.1 (t, J = 287 Hz), 166.4. HRMS (ESI) calcd for C₁₈H₁₇O₂F₂ [M+H]⁺ 303.1197, found 303.1194.



Compound (S)-3ij. The ee was measured by HPLC (Daicel Chiralpak IA x 2 columns) (Two IA columns are connected), pure hexane, flow 0.6 mL/min, 280 nm, t_1 = 38.8 min (major), t_2 = 43.6 min (minor). $[\alpha]_D^{25}$ -26 (c 0.75, CHCl_3) for 99% ee (*S*). ^{19}F NMR (CDCl_3 , 377 MHz) δ -89.6 (dd, J = 42 Hz, 23 Hz, 1F), -87.9 (d, J = 42 Hz, 1F). ^1H NMR (CDCl_3 , 400 MHz) δ 3.80 (s, 3H), 4.69 (ddd, J = 23.6 Hz, 10.4 Hz, 2.2 Hz, 1H), 4.81 (d, J = 10.4 Hz, 1H), 6.85 (d, J = 8.7 Hz, 2H), 7.07 (d, J = 8.7 Hz, 2H), 7.10 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 43.2 (d, J = 5 Hz), 55.3, 81.9 (dd, J = 22 Hz, 19 Hz), 114.1, 128.7, 128.8, 129.2, 132.5, 134.7, 142.0, 156.0 (t, J = 287 Hz), 158.5. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{14}\text{OF}_2\text{Cl}$ $[\text{M}+\text{H}]^+$ 295.0701, found 295.0705.

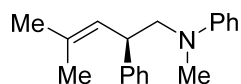
8. Derivatization of the Arylation/Defluorination Products

(1) Transformation of 3dc to 8a and 8b

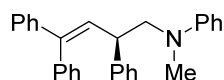


To a solution of **3dc** (41.0 mg, 0.15 mmol) and $\text{NiCl}_2(\text{dppp})$ (8.1 mg, 0.01 mmol) in benzene (1.0 mL), MeMgBr (1.4 M in THF/toluene (1/3), 1.07 mL, 1.50 mmol) was added dropwise at 0 °C. The mixture was heated to reflux for 15 h. NH_4Cl (aq) was added at 0 °C and it was extracted with ethyl acetate. The organic layer was combined, dried over Na_2SO_4 , and evaporated under vacuum. The crude product was purified by silica gel column chromatography with ethyl EtOAc/hexane (5/95) to give **8a** (38.2 mg, 96% yield) as a slight yellow liquid.

8b was prepared according to the above procedure using PhMgBr (3.0 M in diethyl ether, 5.0 mL, 1.5 mmol) instead of MeMgBr in 85% yield.

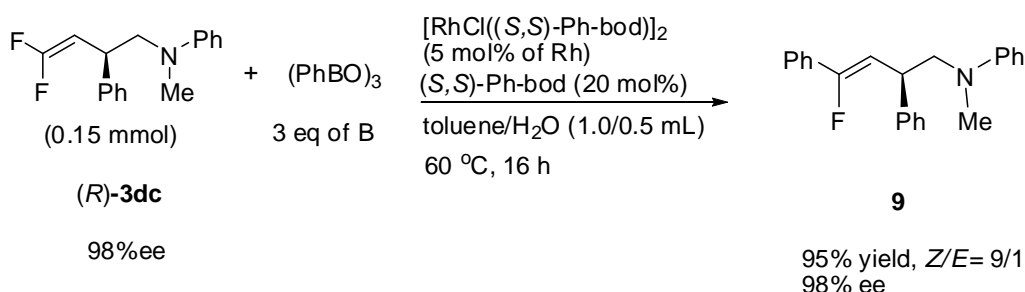


Compound (R)-8a. The ee was measured by HPLC (Daicel Chiralpak IB column), pure hexane, flow 0.7 mL/min, 280 nm, t_1 = 13.1 min (minor), t_2 = 13.9 min (major). $[\alpha]_D^{25}$ +12.4 (c 1.32, CHCl_3) for 98% ee (*R*). ^1H NMR (CDCl_3 , 400 MHz) δ 1.58 (s, 3H), 1.75 (s, 3H), 2.77 (s, 3H), 3.57 (dd, J = 11.2 Hz, 4.1 Hz, 1H), 3.62 (dd, J = 11.2 Hz, 4.3 Hz, 1H), 3.99 (br q, J = 8.4 Hz, 1H), 5.48 (d, J = 9.6 Hz, 1H), 6.71 (d, J = 8.2 Hz, 2H), 6.72 (t, J = 7.8 Hz, 1H), 7.22-7.30 (m, 5H), 7.34 (t, J = 7.5 Hz, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 18.2, 26.1, 39.6, 42.8, 59.8, 111.8, 115.7, 125.7, 126.3, 127.7, 128.6, 129.1, 133.5, 144.0, 148.9. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{24}\text{N}$ $[\text{M}+\text{H}]^+$ 266.1909, found 266.1910.



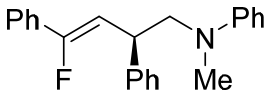
Compound (R)-8b. The ee was measured by HPLC (Daicel Chiralpak IF column), CH_2Cl_2 /hexane = 1/99, flow 1.0 mL/min, 280 nm, t_1 = 13.1 min (major), t_2 = 14.3 min (minor). $[\alpha]_D^{25}$ -94.7 (c 1.55, CHCl_3) for 98% ee (*R*). ^1H NMR (CDCl_3 , 400 MHz) δ 2.67 (s, 3H), 3.54 (dd, J = 14.5 Hz, 6.8 Hz, 1H), 3.81 (dd, J = 14.5 Hz, 8.0 Hz, 1H), 3.94 (dt, J = 10.6 Hz, 7.5 Hz, 1H), 6.39 (d, J = 10.5 Hz, 1H), 6.55 (d, J = 8.3 Hz, 2H), 6.71 (t, J = 7.2 Hz, 1H), 7.07-7.38 (m, 17H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 39.1, 44.2, 59.5, 68.7, 111.9, 115.8, 126.5, 127.09, 127.10, 127.3, 127.7, 128.0, 128.1, 128.7, 128.8, 129.1, 129.7, 139.7, 142.3, 142.94, 142.96, 148.8. HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{28}\text{N}$ $[\text{M}+\text{H}]^+$ 390.2222, found 390.2219.

(2) Transformation of 3dc to 9

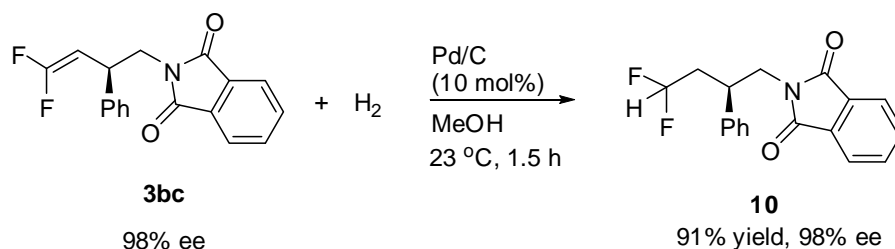


$[\text{RhCl}((S,S)\text{-Ph-bod}^*)]_2$ (2.9 mg, 0.0075 mmol of Rh), (*S,S*)-Ph-bod (7.8 mg, 0.03 mmol), phenylboroxine (**2c**) (46.8 mg, 0.150 mmol, 0.450 mmol of B), **3dc** (41.0 mg,

0.15 mmol), and KOH (18.5 mg, 0.330 mmol) were placed in a Schlenk tube under nitrogen. Toluene (1.0 mL) and water (0.5 mL) were added, and the mixture was stirred at 60 °C for 16 h. The reaction mixture was passed through a short column of silica-gel with EtOAc as eluent. The solvent was removed on a rotary evaporator. The crude ^{19}F NMR of the mixture revealed *Z/E* isomers were formed in a ratio of 9/1. The residue was further purified by silica-gel chromatography.

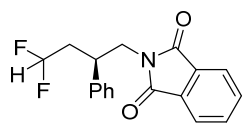
 **Compound (R)-9**. The ee was measured by HPLC (Daicel Chiralpak IC column), $\text{CH}_2\text{Cl}_2/\text{hexane} = 1/99$, flow 1.0 mL/min, 254 nm, $t_1 = 34.4$ min (minor), $t_2 = 39.9$ min (major). $[\alpha]_{\text{D}}^{25} -16.1$ (c 1.77, CHCl_3) for 98% ee (*R*) (mixture of *Z/E* isomers in a ratio of 9:1). ^{19}F NMR (CDCl_3 , 282 MHz) $\delta -117.2$ (d, $J = 36$ Hz, 1F, for *Z*-isomer), $(-95.7$ (d, $J = 22$ Hz, 1F, for *E*-isomer)). ^1H NMR (CDCl_3 , 400 MHz) δ 2.73 (s, 3H), 3.60 (dd, $J = 14.6$ Hz, 7.6 Hz, 1H), 3.86 (dd, $J = 14.6$ Hz, 7.2 Hz, 1H), 4.45 (br q, $J = 8.1$ Hz, 1H), 5.70 (dd, $J = 36.3$ Hz, 9.6 Hz, 1H), 6.71 (t, $J = 8.0$ Hz, 1H), 6.75 (d, $J = 7.9$ Hz, 2H), 7.23-7.36 (m, 10H), 7.46 (d, $J = 7.9$ Hz, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 39.2, 40.0 (d, $J = 3$ Hz), 59.4 (d, $J = 1$ Hz), 106.9 (d, $J = 17$ Hz), 112.1, 116.1, 124.2 (d, $J = 7$ Hz), 126.7, 127.7, 128.4 (d, $J = 2$ Hz), 128.7, 129.2, 132.3 (d, $J = 29$ Hz), 142.4, 148.9, 157.3 (d, $J = 248$ Hz). HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{23}\text{NF}$ $[\text{M}+\text{H}]^+$ 332.1815, found 332.1818.

(3) Transformation of **3bc** to **10**



To a 25 mL flask equipped with a stir bar were added (*R*)-**3bc** (47.0 mg, 0.15 mmol), which was obtained in entry 4 in Table 2, in 2 mL of MeOH and 10% Pd/C (16.5 mg, 0.015 mmol). The mixture was allowed to stir under H_2 atmosphere (using H_2 balloon) at room temperature (23 °C) for 1.5 h. The reaction mixture was passed through a short column of silica-gel with EtOAc as eluent. The filtrate was

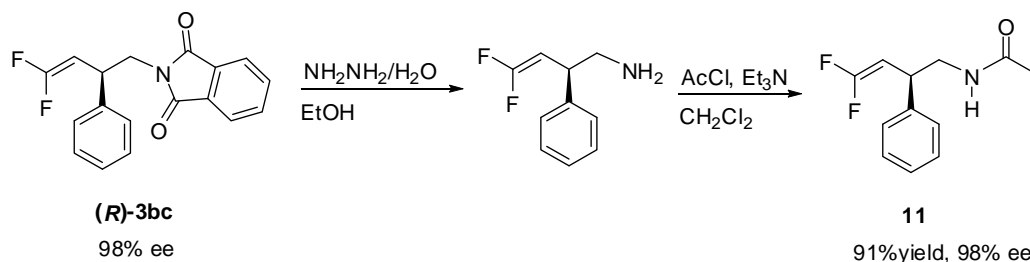
concentrated under reduce pressure and the residue was subjected to silica-gel chromatography with EtOAc/hexane (1/8) to give **10** (43.0 mg, 91%) as a white solid.



Compound (R)-10. The ee was measured by HPLC (Daicel

Chiralpak IA column), 2-propanol/hexane = 3/97, flow 2.0 mL/min, 280 nm, t_1 = 9.8 min (major), t_2 = 11.1 min (minor). $[\alpha]_D^{25}$ +92 (c 0.85, CHCl_3) for 98% ee (*R*). ^{19}F NMR (CDCl_3 , 282 MHz) δ -117.6 (dddd, J = 284 Hz, 57 Hz, 25 Hz, 17 Hz, 1F), -114.9 (ddt, J = 284 Hz, 56 Hz, 11 Hz, 1F). ^1H NMR (CDCl_3 , 400 MHz) δ 2.20-2.33 (m, 2H), 3.46 (quint, J = 9.0 Hz, 1H), 3.87-3.97 (m, 2H), 5.56 (tdd, J = 56.5 Hz, 6.7 Hz, 3.0 Hz, 1H), 7.23-7.34 (m, 5H), 7.70-7.74 (m, 2H), 7.80-7.83 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 37.8 (t, J = 21 Hz), 39.1 (dd, J = 8 Hz, 3 Hz), 43.2, 116.1 (t, J = 238 Hz), 123.3, 127.6, 127.7, 128.9, 131.7, 134.0, 139.3, 168.1. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{16}\text{NO}_2\text{F}_2$ $[\text{M}+\text{H}]^+$ 316.1149, found 316.1149.

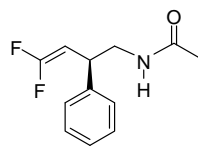
(4) Transformation of **3bc** to **11**



To a solution of (*R*)-**3bc** (98% ee, 62.7 mg, 0.20 mmol), which was obtained in entry 4 in Table 2, in EtOH (2 mL) was added NH_2NH_2 (80% in H_2O , 61 μL , 1.0 mmol). After stirring at 80 $^\circ\text{C}$ for 3 h, the mixture was diluted with Et_2O (2 mL). The precipitated solid was filtered off and the filter cake was washed with Et_2O . The filtrate was concentrated on a rotary evaporator. To a solution of the residue in THF (2 mL) was added $\text{LiOH}\cdot\text{H}_2\text{O}$ (12.6 mg, 0.30 mmol) in H_2O (2 mL), and the mixture was stirred at room temperature for 2 h. The reaction mixture was extracted with dichloromethane (20 mL x 3). The organic layers were combined, washed with brine and water, and dried over anhydrous Na_2SO_4 . Filtration and removal of solvent gave

the crude primary amine.

The crude primary amine obtained above was dissolved in 10 mL dichloromethane and the solution was cooled to 0 °C. AcCl (17.3 mg, 0.22 mmol) and Et₃N (40.4 mg, 0.4 mmol) were added dropwise sequently. After addition, the reaction mixture was warmed to room temperature and kept stirring for 10 h. After removal of solvent, the residue was purified by flash chromatography on silica gel (ethyl acetate/hexane = 1/3) to give **11** (41.0 mg, 91% yield based on (*R*)-**3bc**) as a slight yellow oil.



Compound (*R*)-11. The ee was measured by HPLC (Daicel Chiralpak IC column), 2-propanol/hexane = 5/95, flow 2.0 mL/min, 254 nm, *t*₁ = 10.8 min (major), *t*₂ = 12.9 min (minor). [α]_D²⁵ –21.5 (*c* 1.18, CHCl₃) for 98% ee (*R*). ¹⁹F NMR (CDCl₃, 377 MHz) δ –88.0 (dd, *J* = 42 Hz, 25 Hz, 1F), –86.7 (d, *J* = 42 Hz, 1F). ¹H NMR (CDCl₃, 400 MHz) δ 1.96 (s, 3H), 3.49–3.58 (m, 2H), 3.72 (br q, *J* = 8.4 Hz, 1H), 4.46 (ddd, *J* = 24.6 Hz, 10.0 Hz, 2.3 Hz, 1H), 5.63 (br s, 1H), 7.23 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 23.2, 39.8 (d, *J* = 5 Hz), 44.6, 79.8 (dd, *J* = 22 Hz, 19 Hz), 127.26, 127.29, 128.9, 140.7, 156.6 (t, *J* = 287 Hz), 170.2. HRMS (ESI) calcd for C₁₂H₁₄NOF₂ [M+H]⁺ 226.1043, found 226.1040.

9. Reference

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10. Data for X-ray crystal structure of (R)-3be

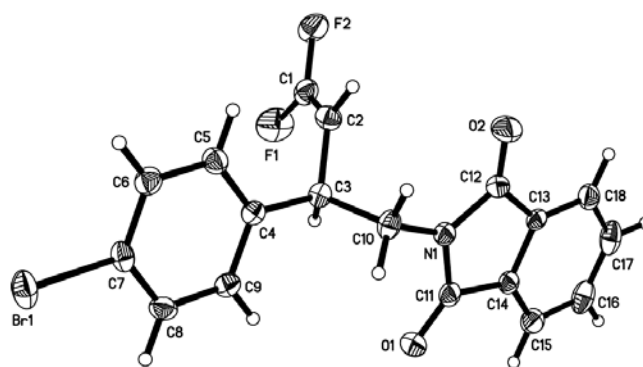
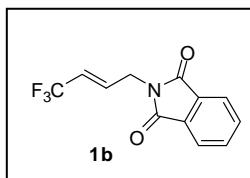
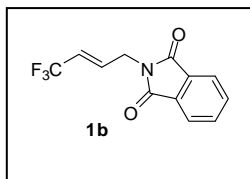


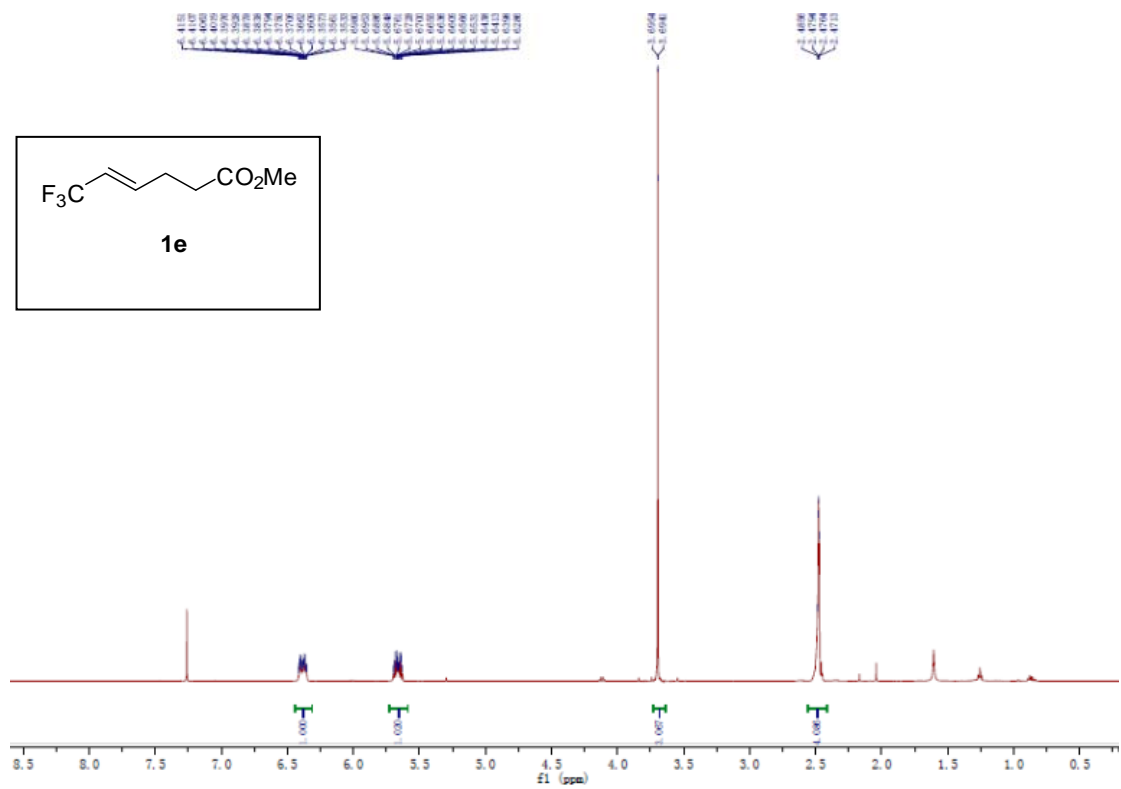
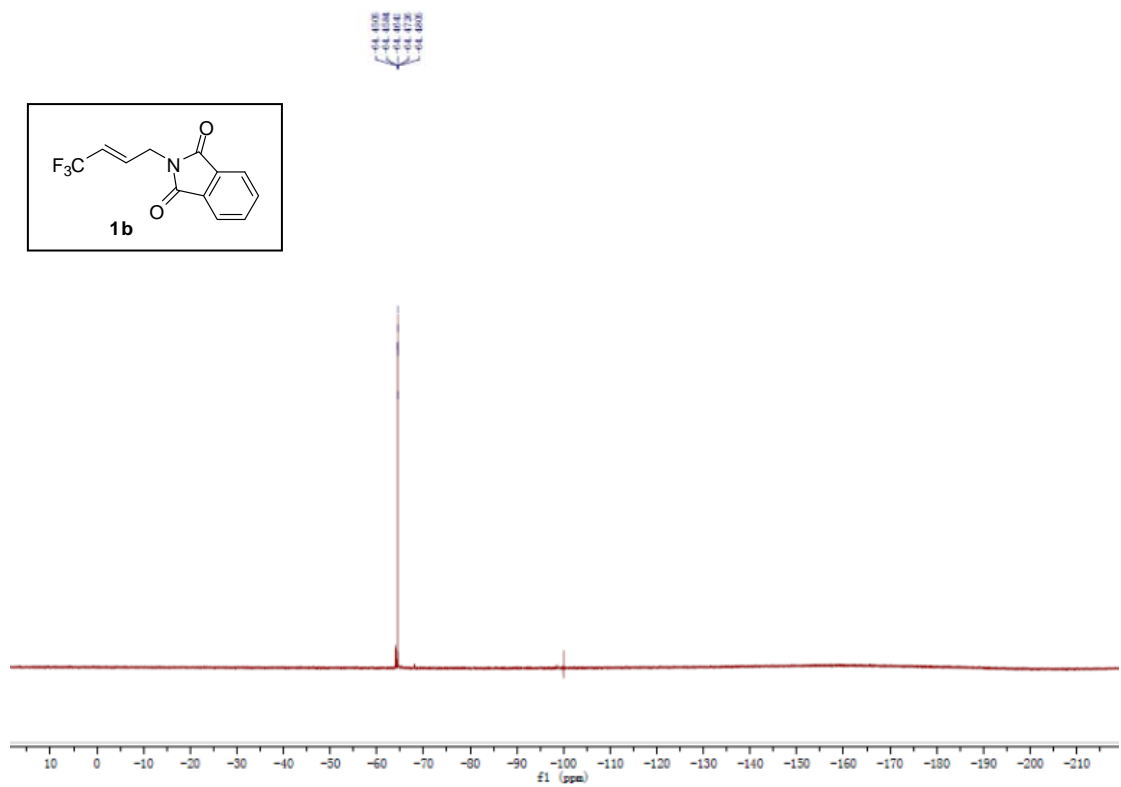
Figure S1. ORTEP illustration of (R)-**3be** with thermal ellipsoids drawn at 50% probability level.

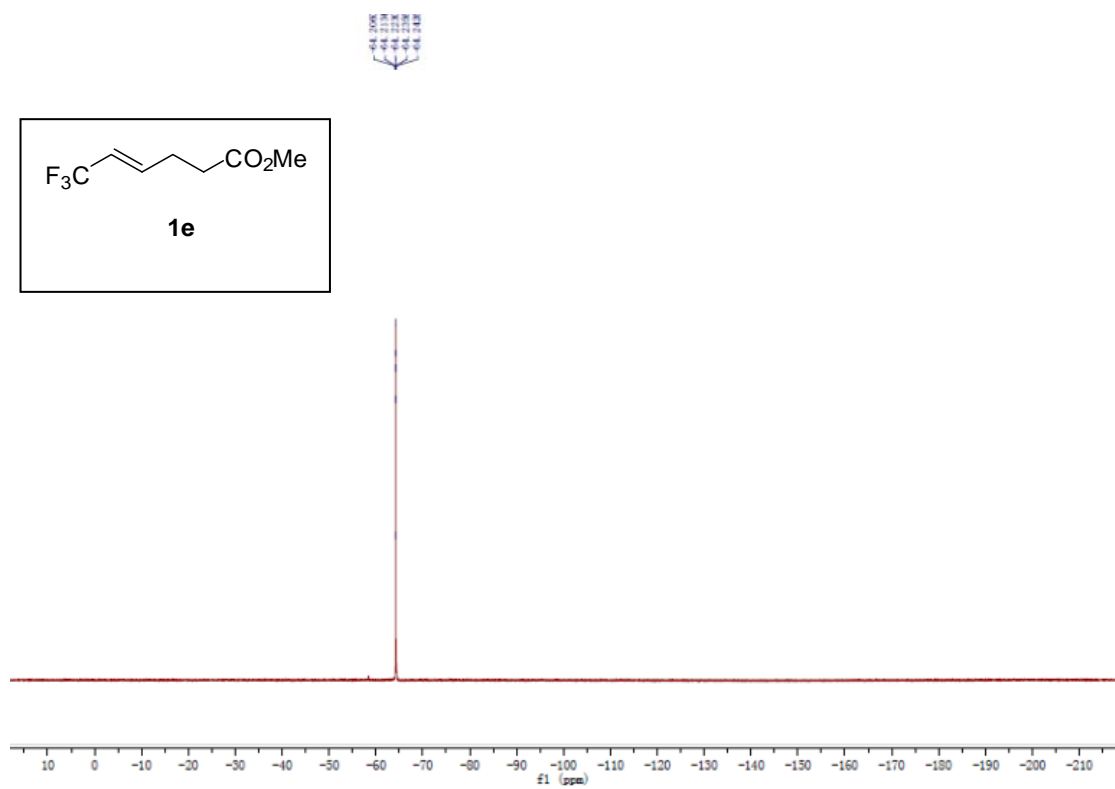
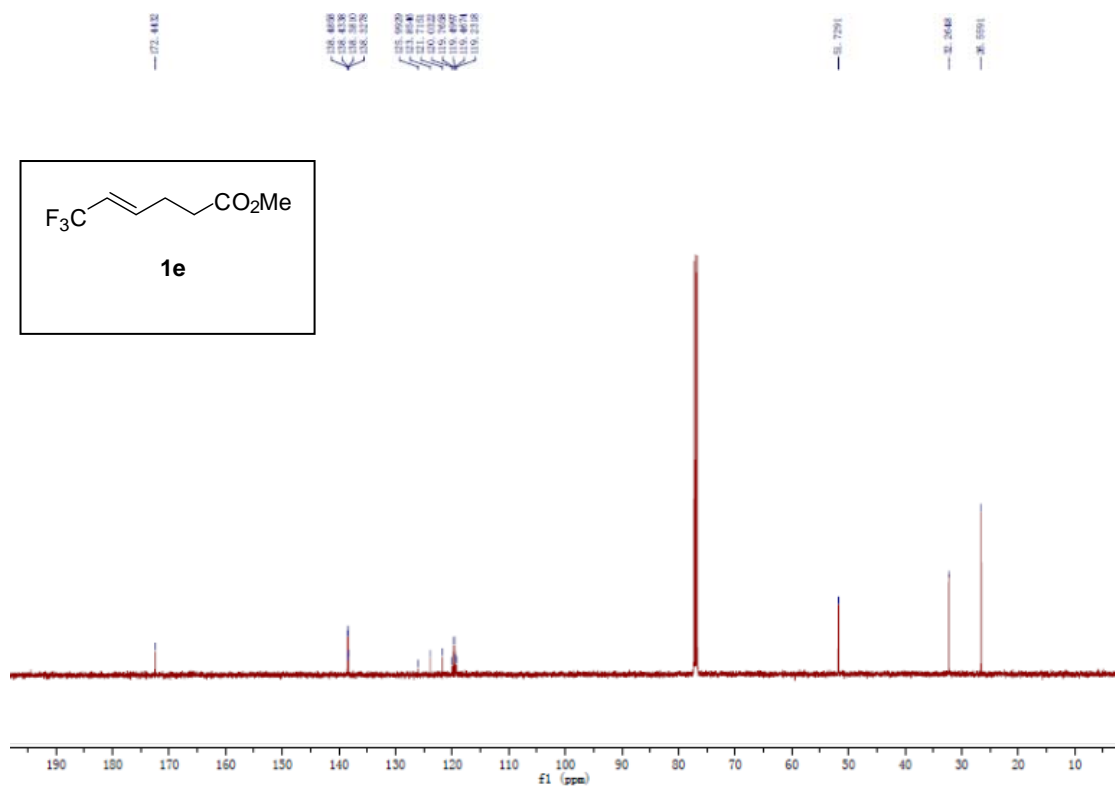
Table 1. Sample and crystal data for (R)-3be.

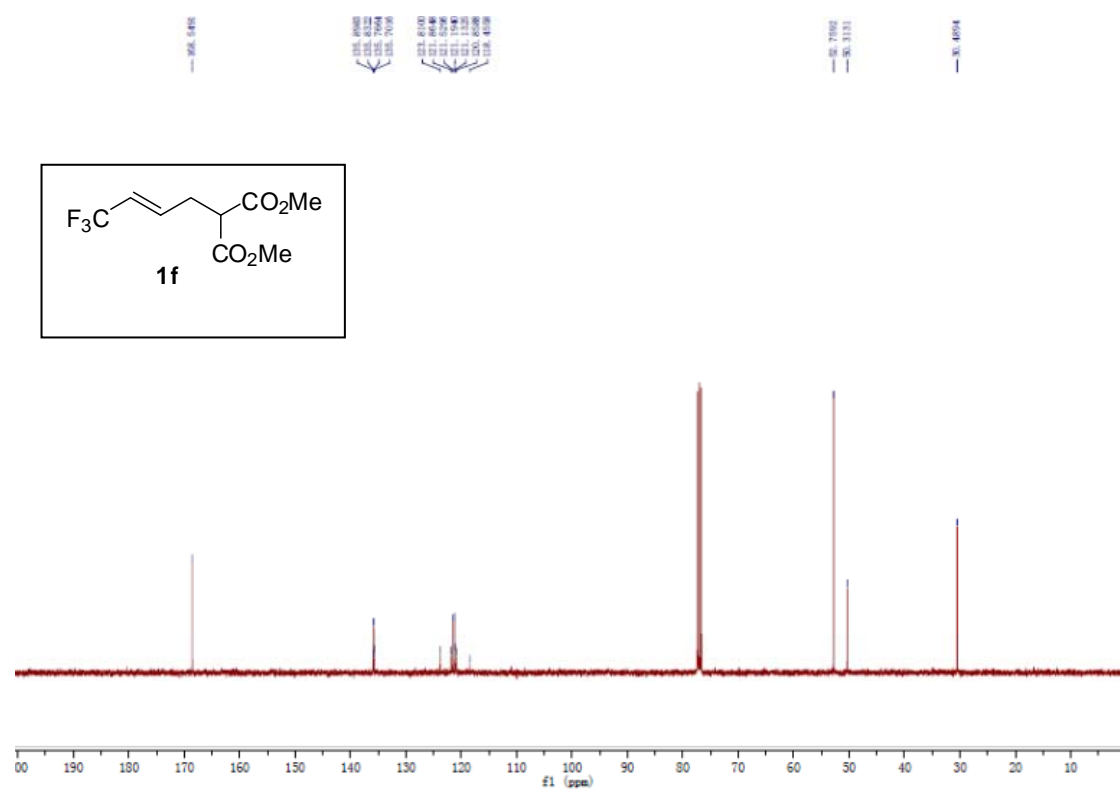
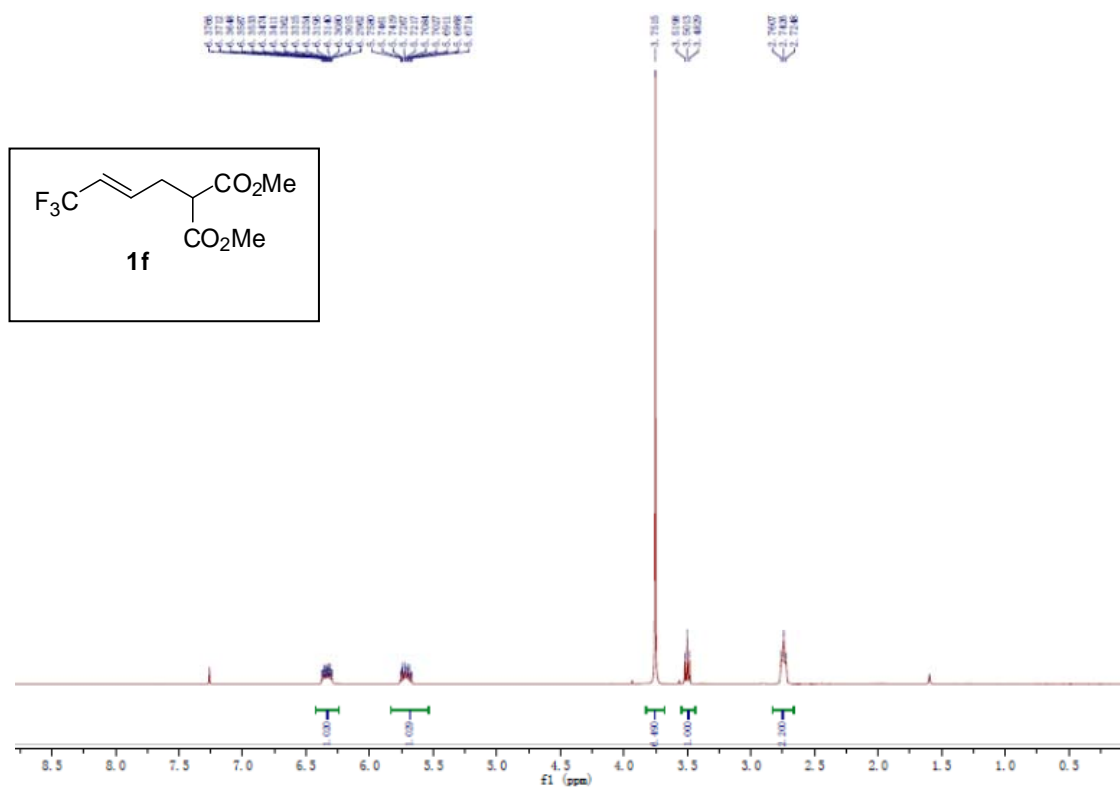
Chemical formula	C ₁₈ H ₁₂ BrF ₂ NO ₂
Formula weight	392.20 g/mol

Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.120 x 0.160 x 0.380 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 7.2467(3) Å	$\alpha = 90^\circ$
	b = 12.0275(4) Å	$\beta = 109.1021(19)^\circ$
	c = 9.5303(4) Å	$\gamma = 90^\circ$
Volume	784.92(5) Å ³	
Z	2	
Density (calculated)	1.659 g/cm ³	
Absorption coefficient	2.650 mm ⁻¹	
F(000)	392	
Theta range for data collection	2.83 to 31.20°	
Index ranges	-10 ≤ h ≤ 10, -17 ≤ k ≤ 17, -13 ≤ l ≤ 13	
Reflections collected	17205	
Independent reflections	5034 [R(int) = 0.0531]	
Coverage of independent reflections	98.8%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.7420 and 0.4320	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2014/4	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5034 / 1 / 217	
Goodness-of-fit on F²	0.905	
Final R indices	3917 data; I > 2σ(I)	R1 = 0.0353, wR2 = 0.0633
	all data	R1 = 0.0576, wR2 = 0.0701
Weighting scheme	w = 1/[σ ² (F _o ²)] where P = (F _o ² + 2F _c ²)/3	
Absolute structure parameter	-0.0(0)	
Largest diff. peak and hole	0.414 and -0.345 eÅ ⁻³	
R.M.S. deviation from mean	0.073 eÅ ⁻³	

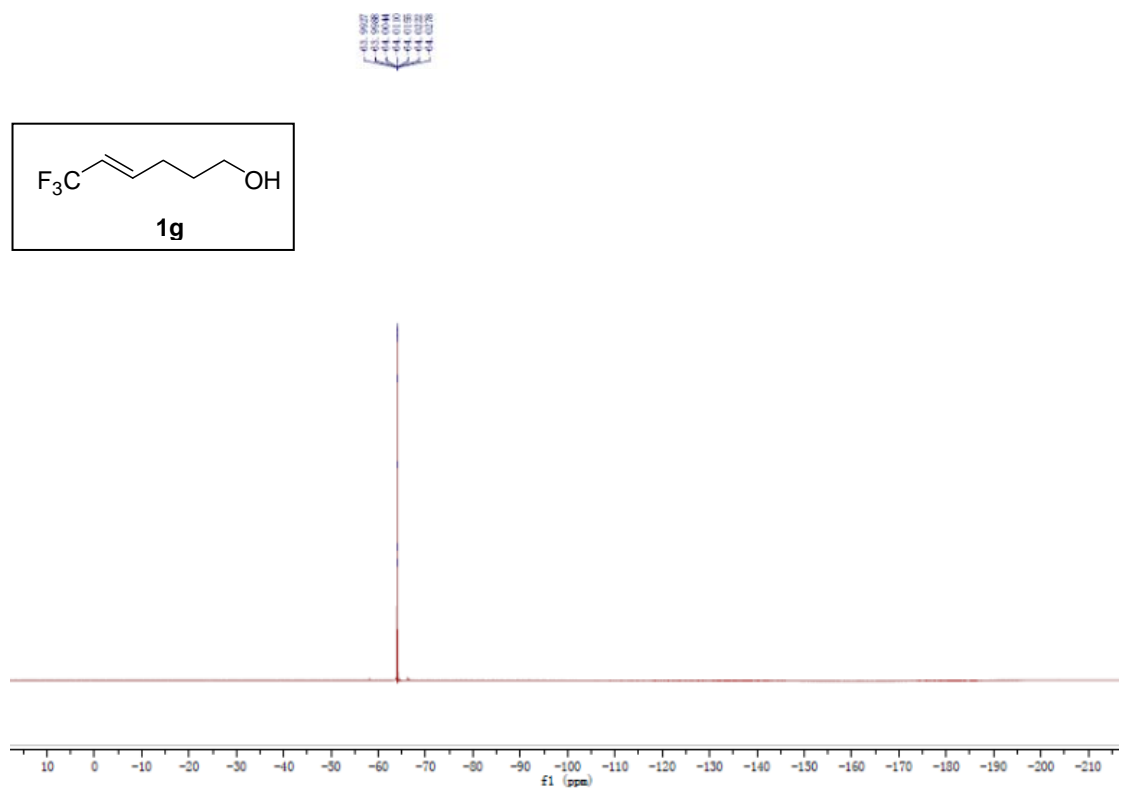
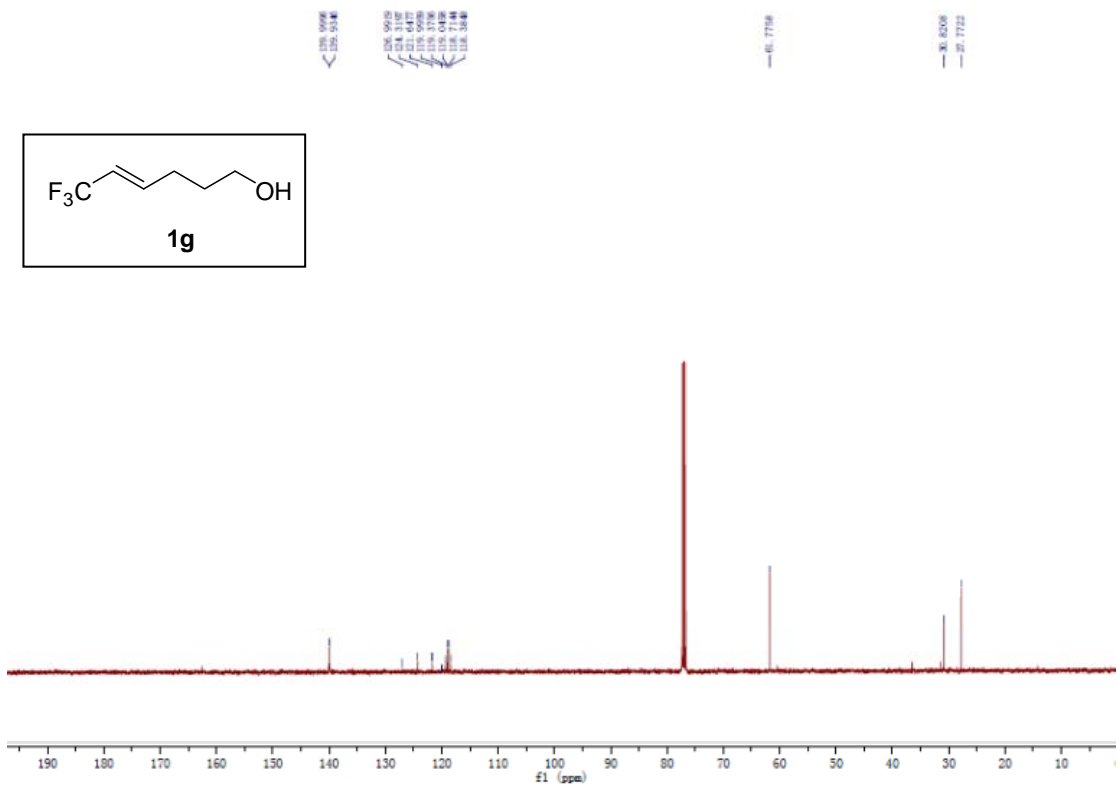


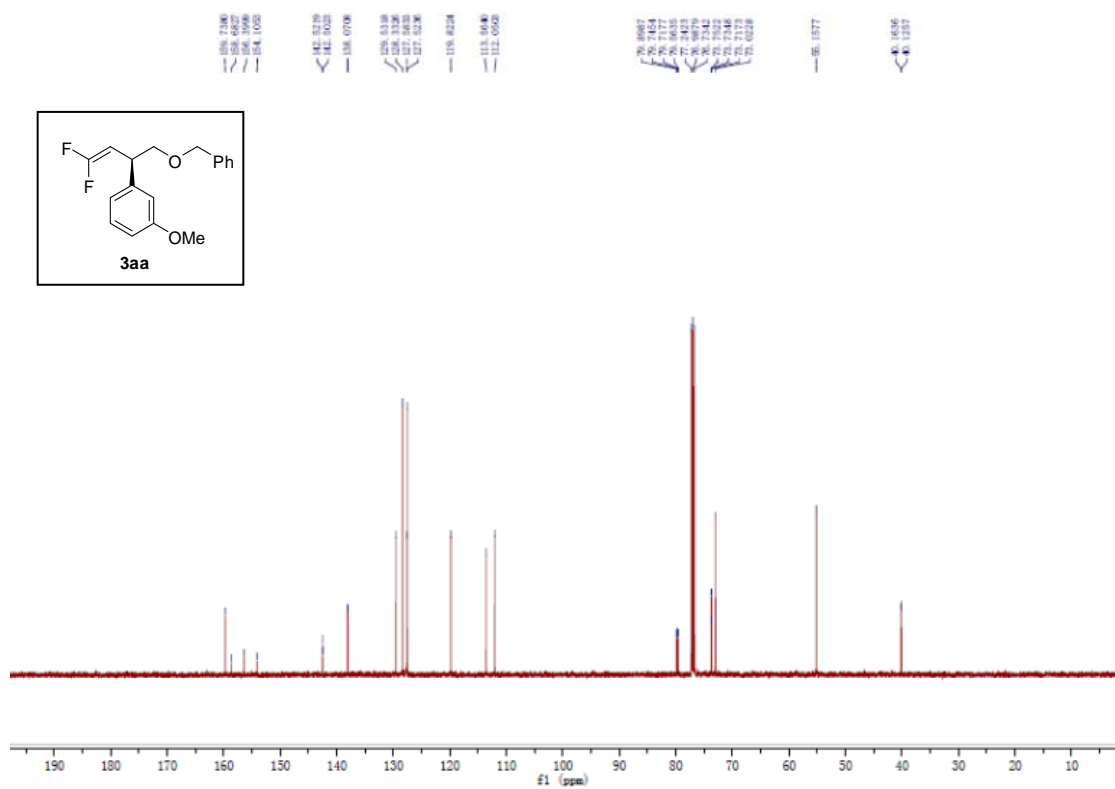
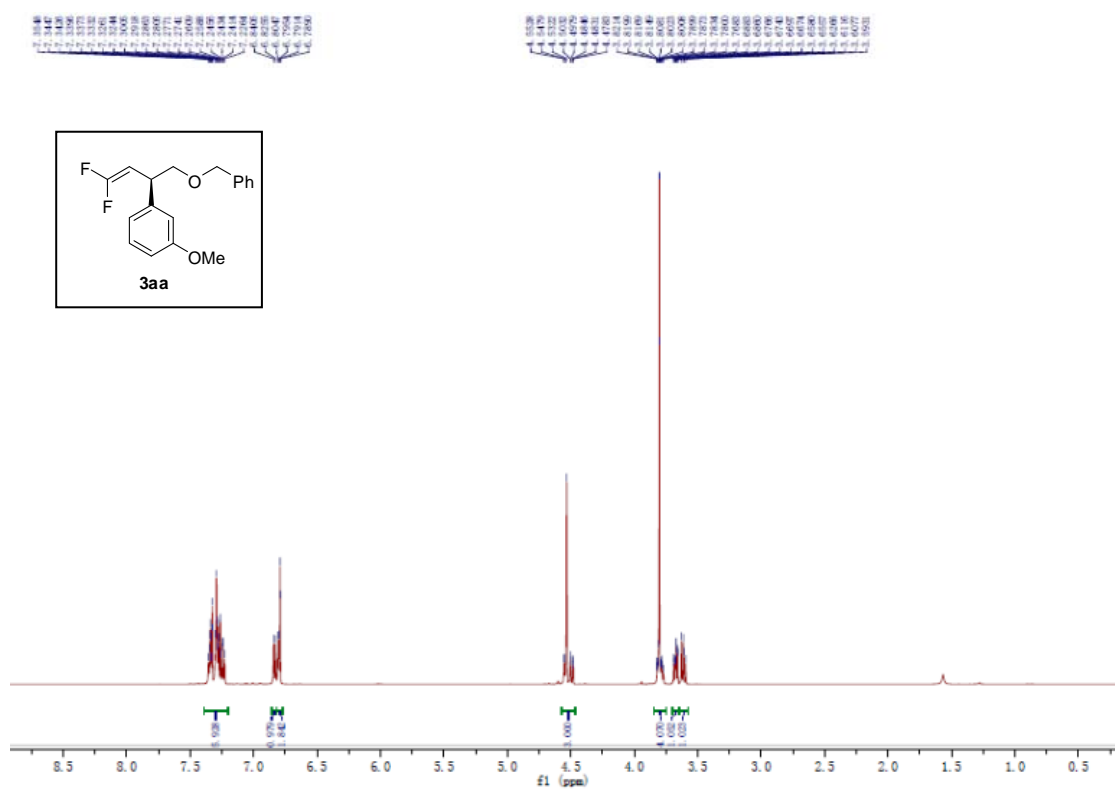


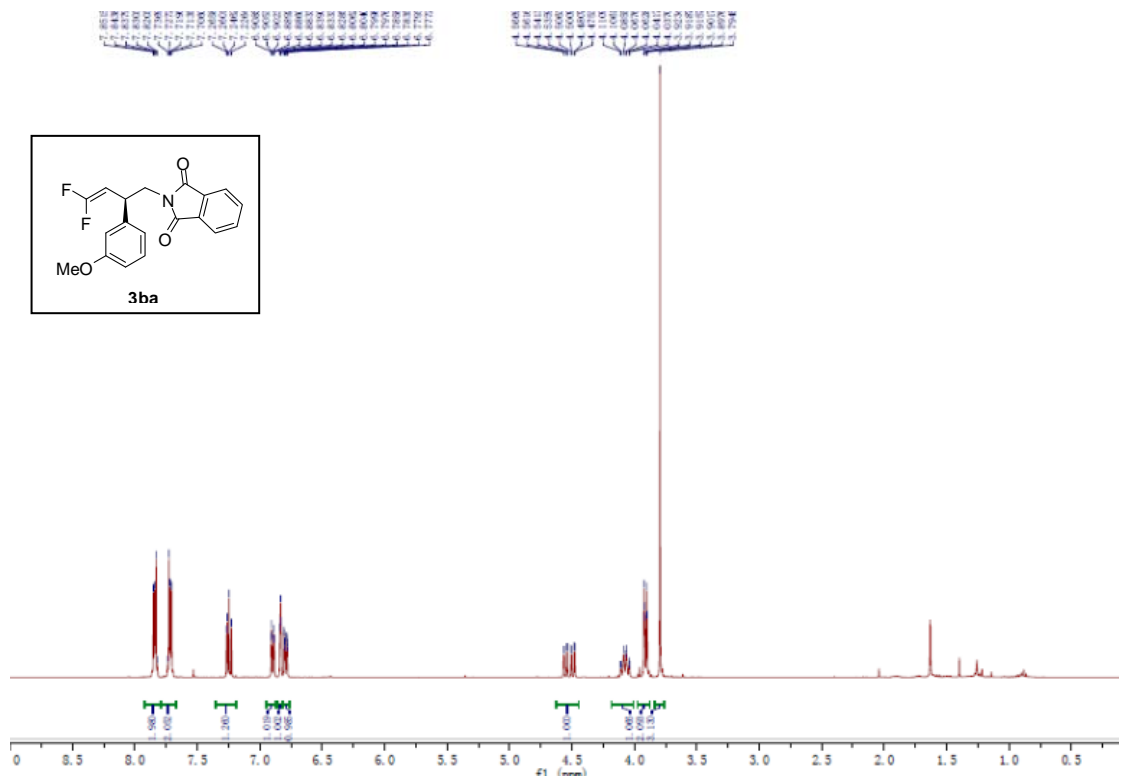
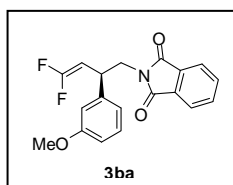
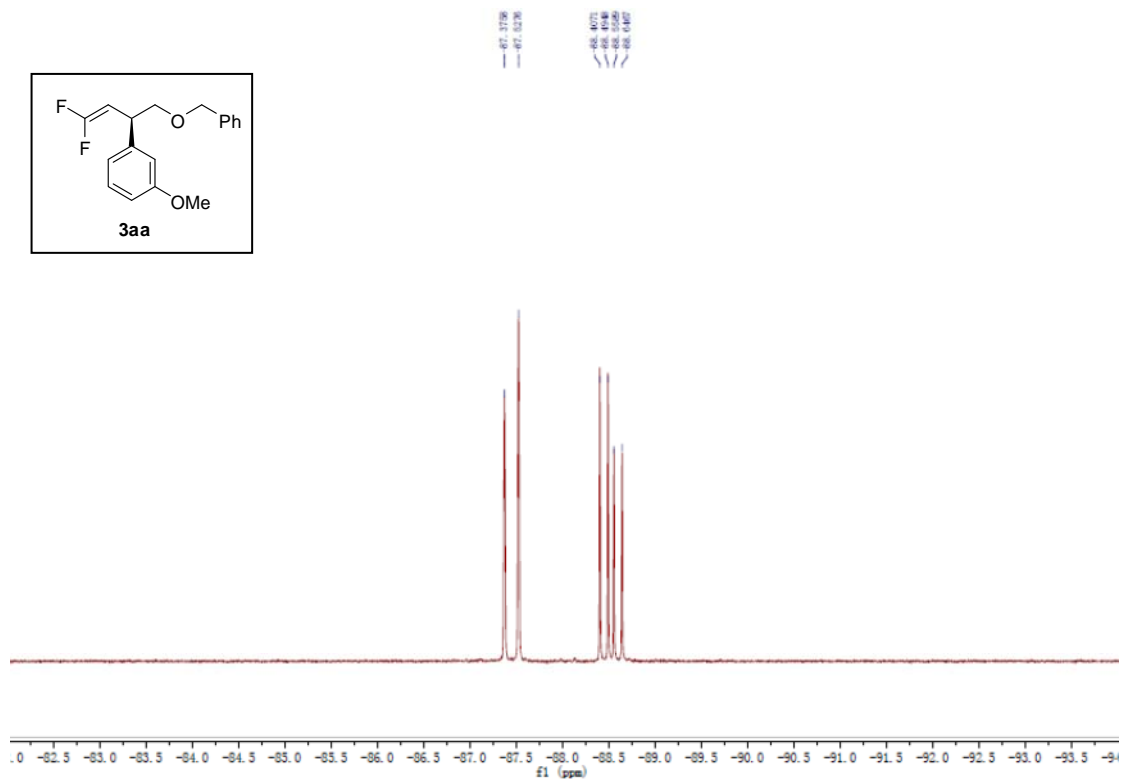
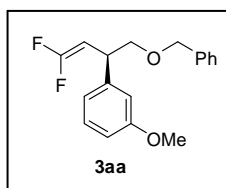


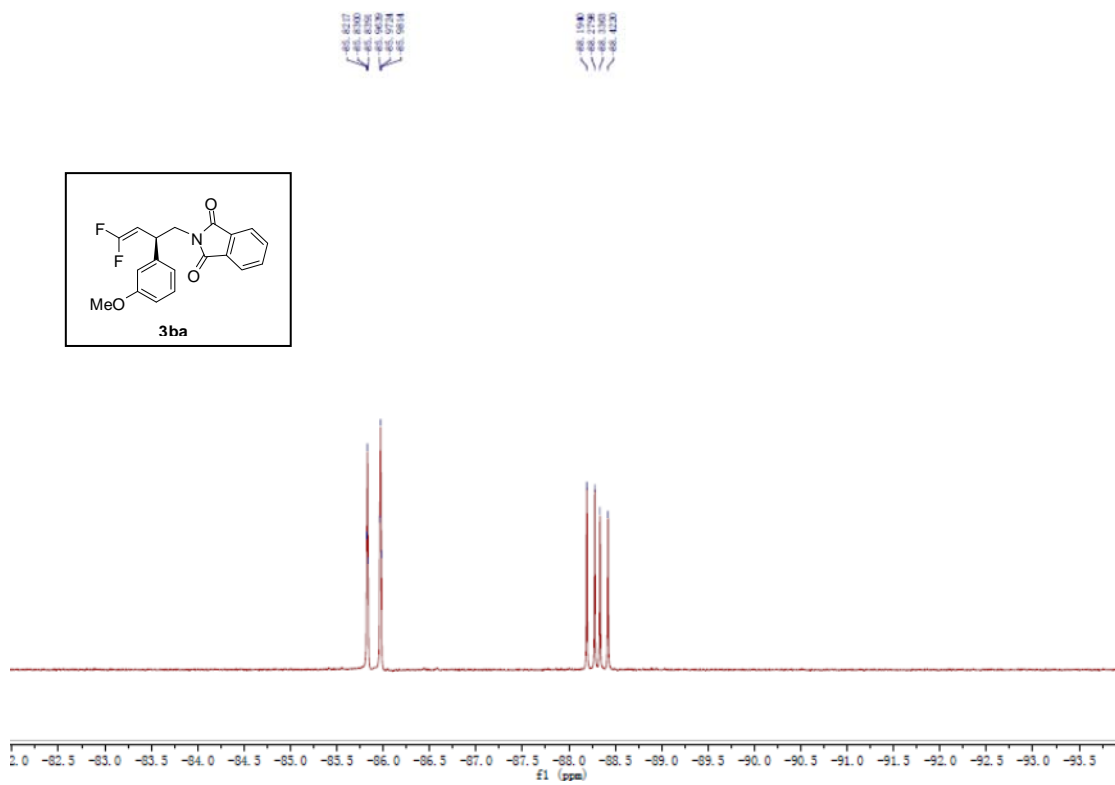
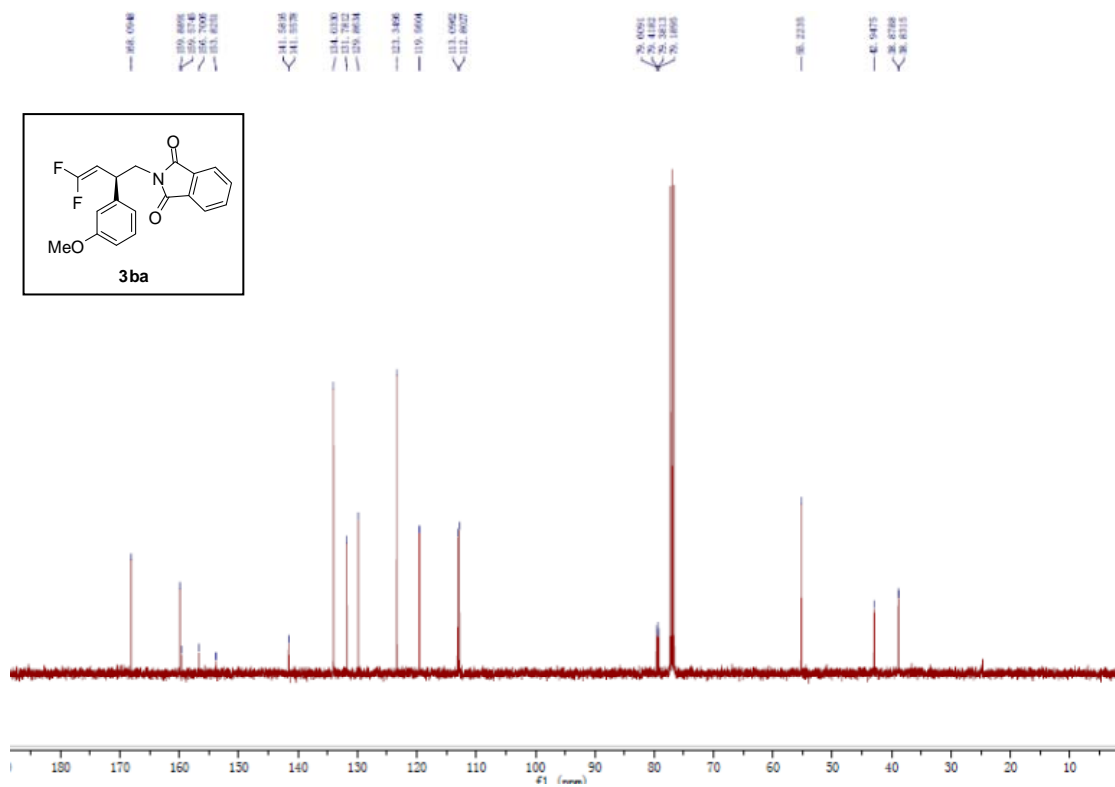


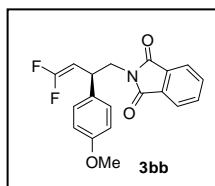
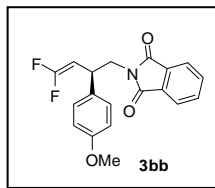


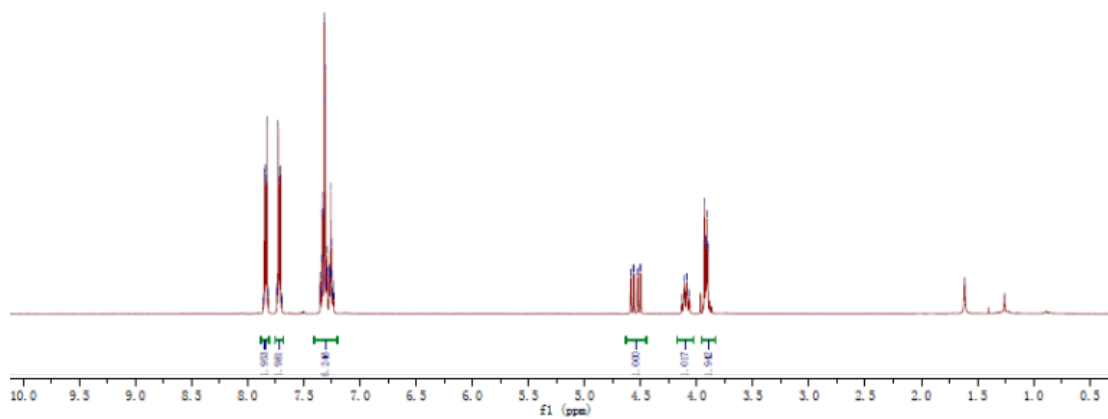
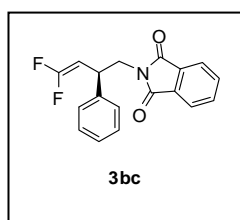
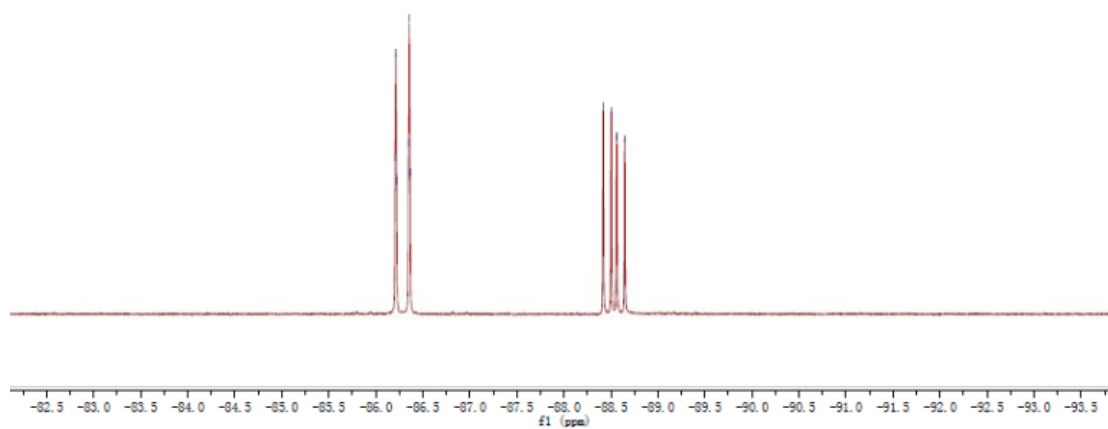


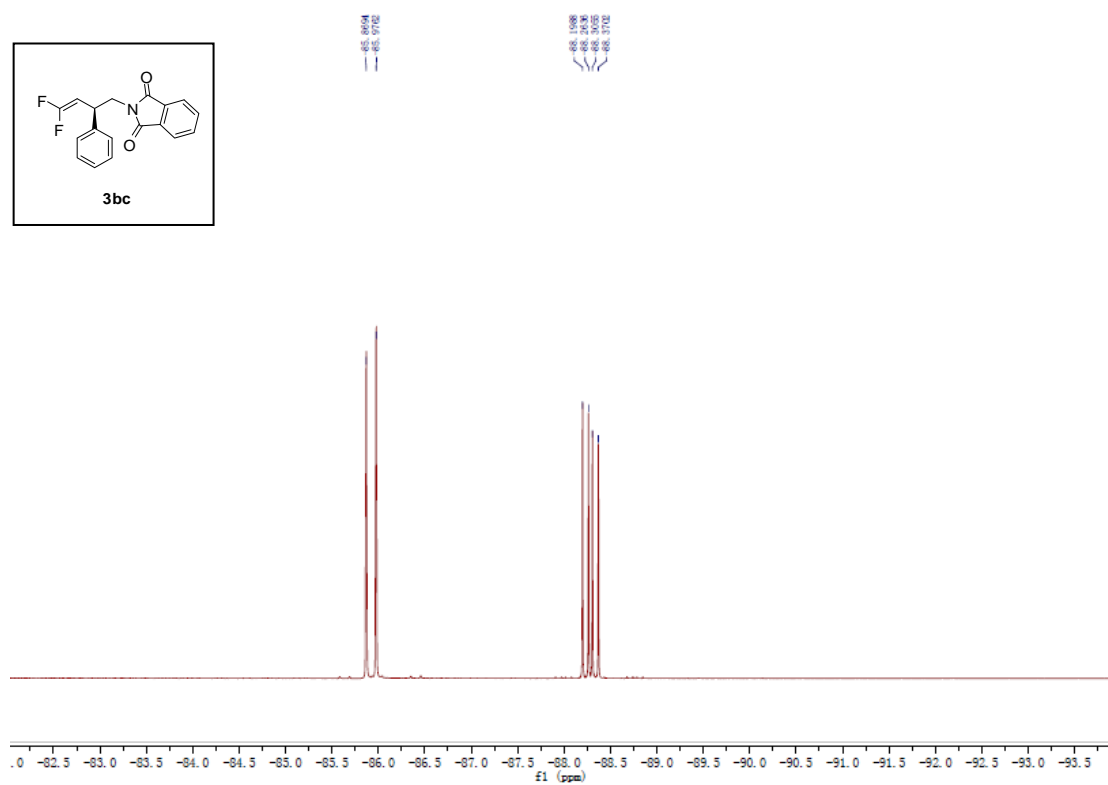
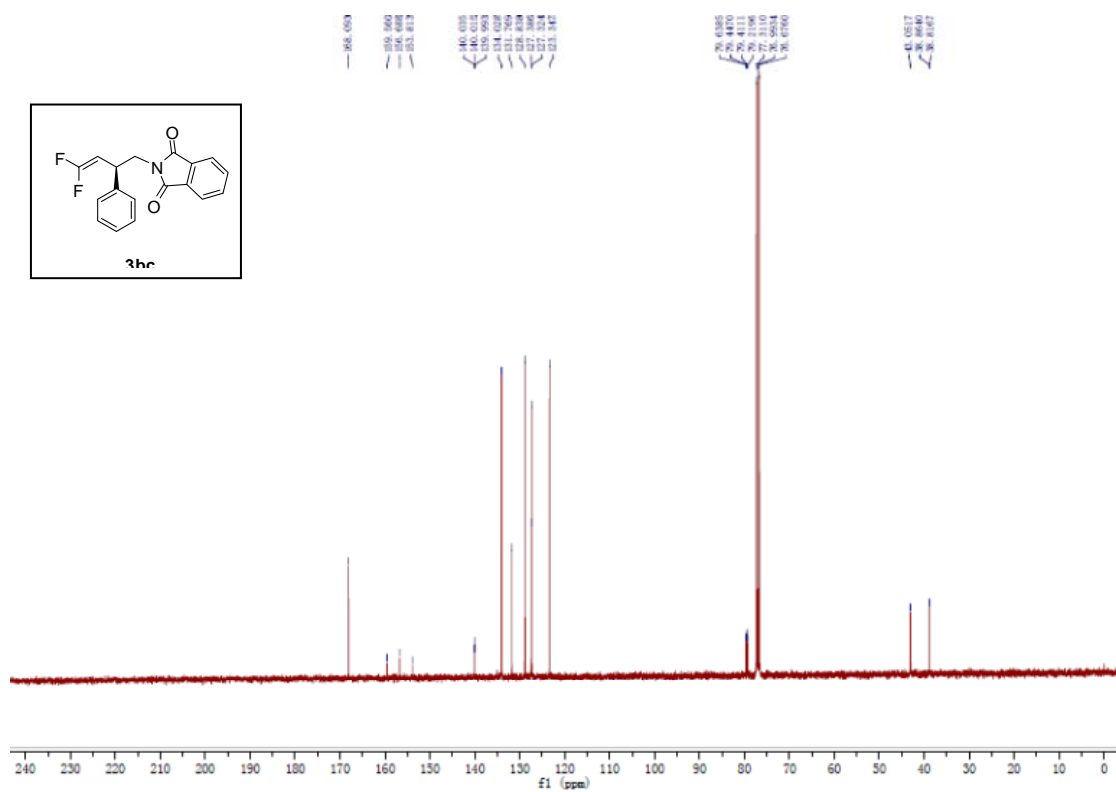


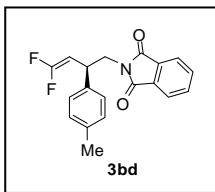
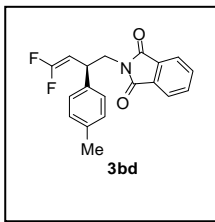


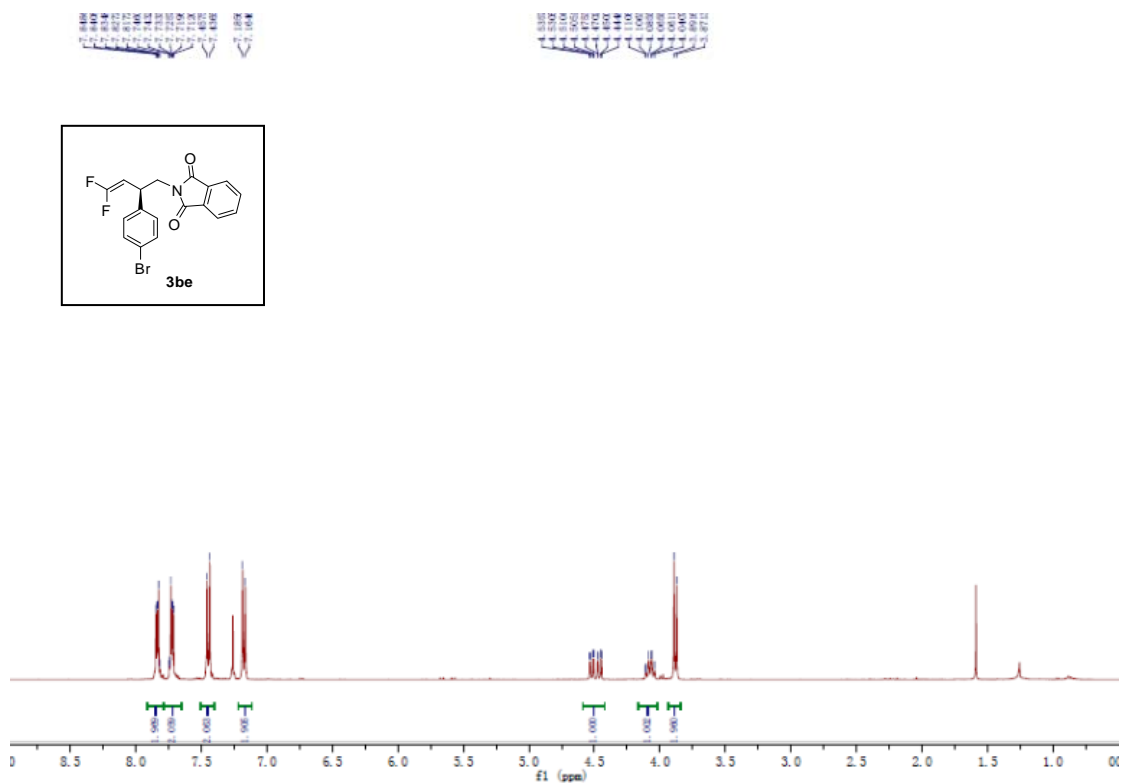
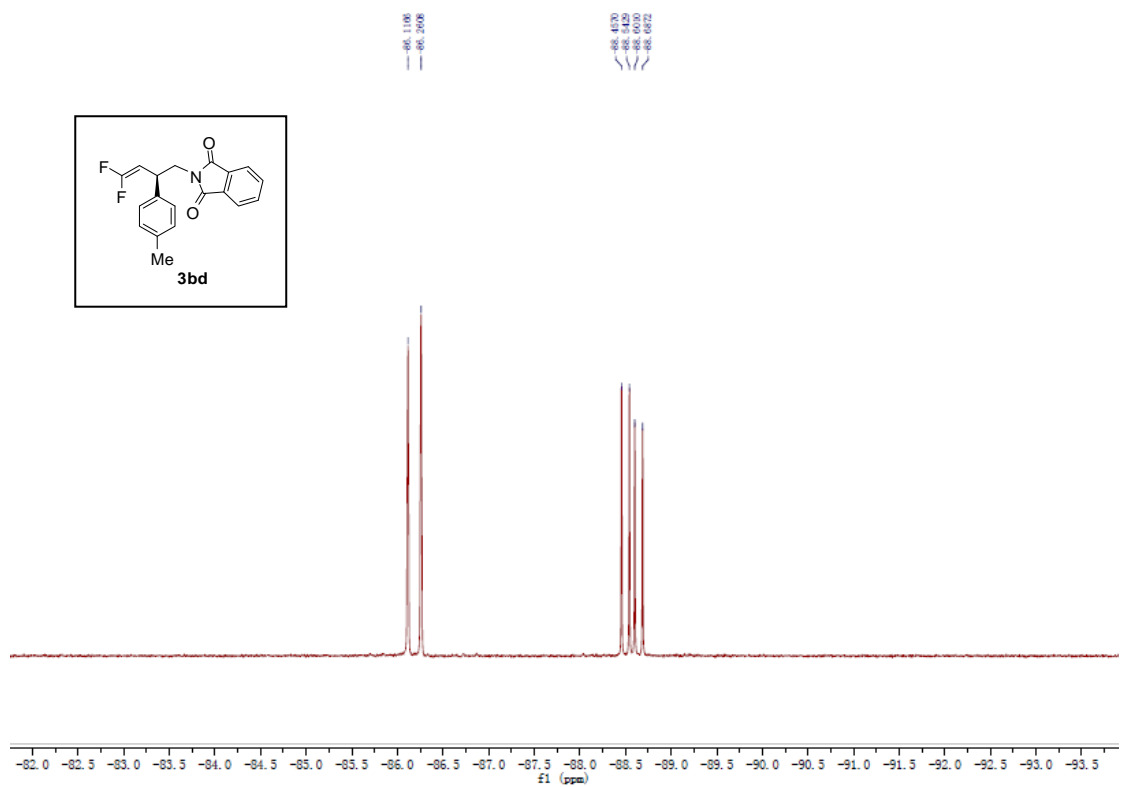


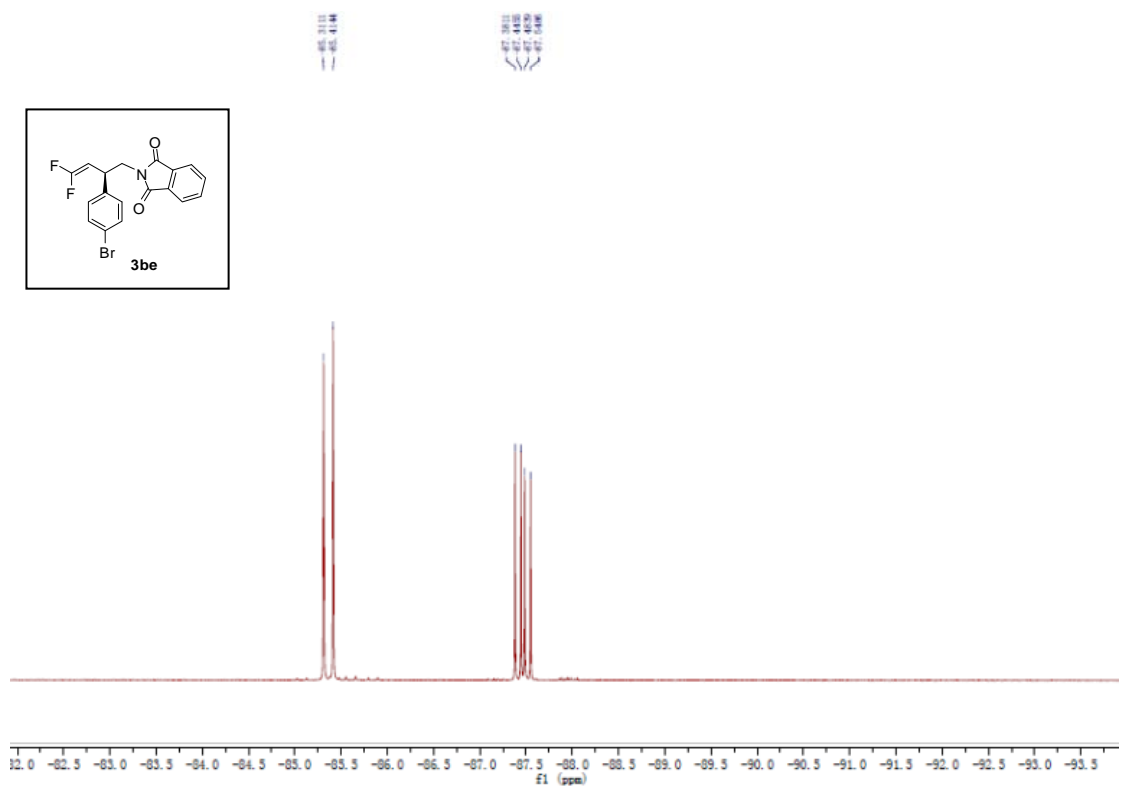
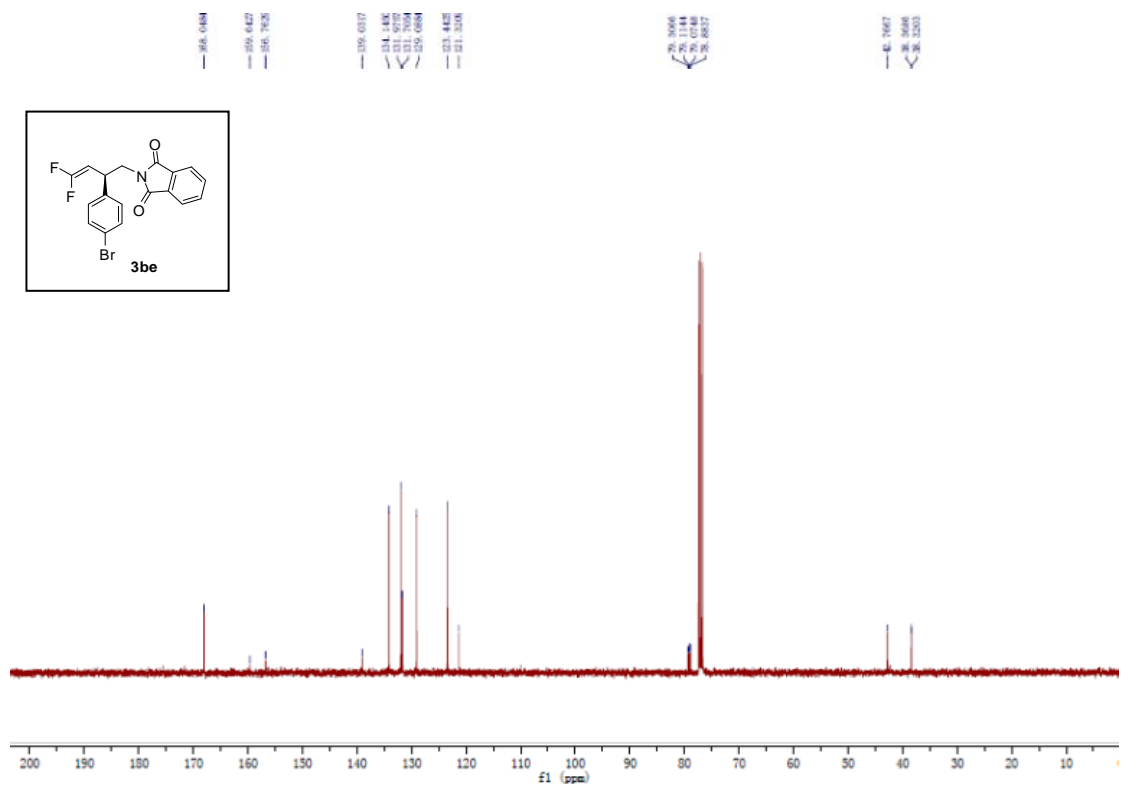


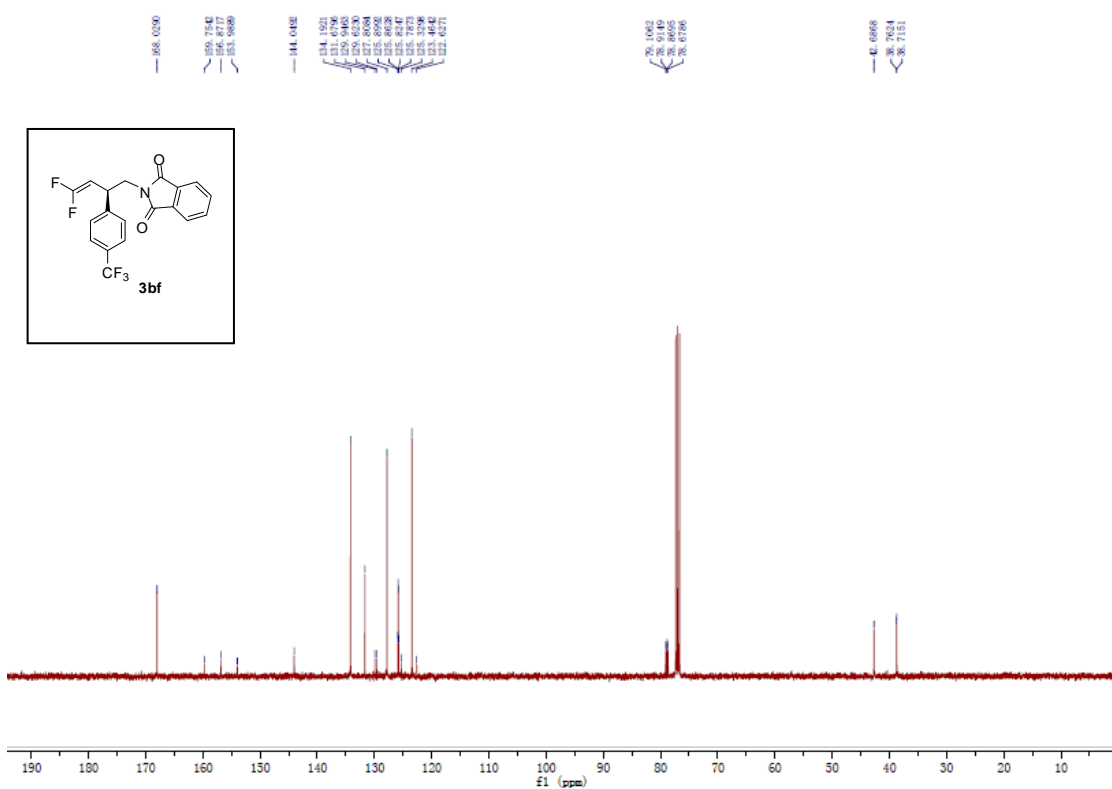


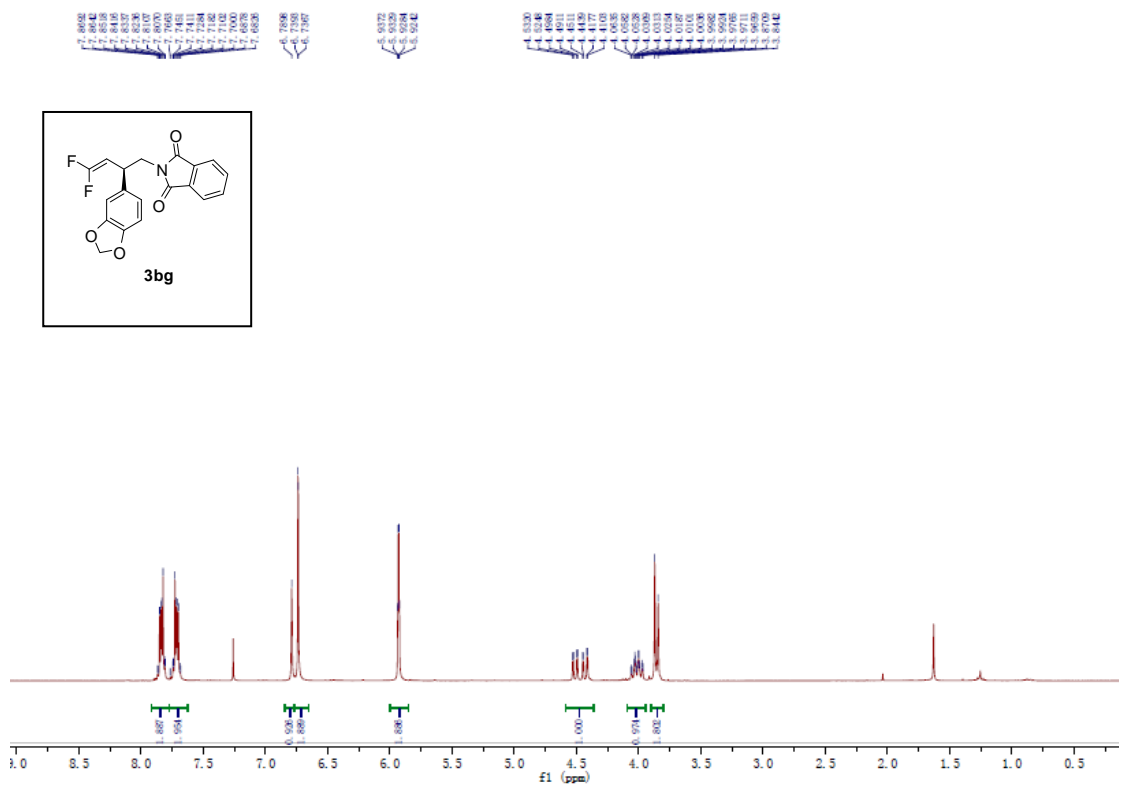
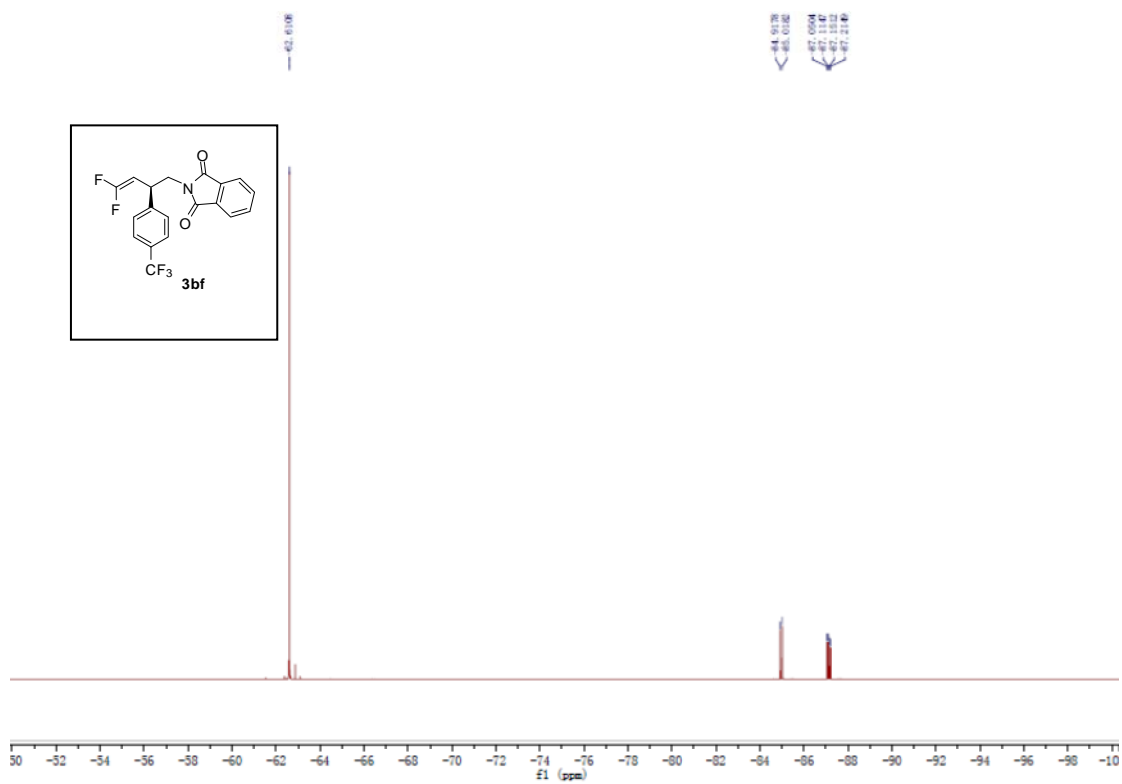


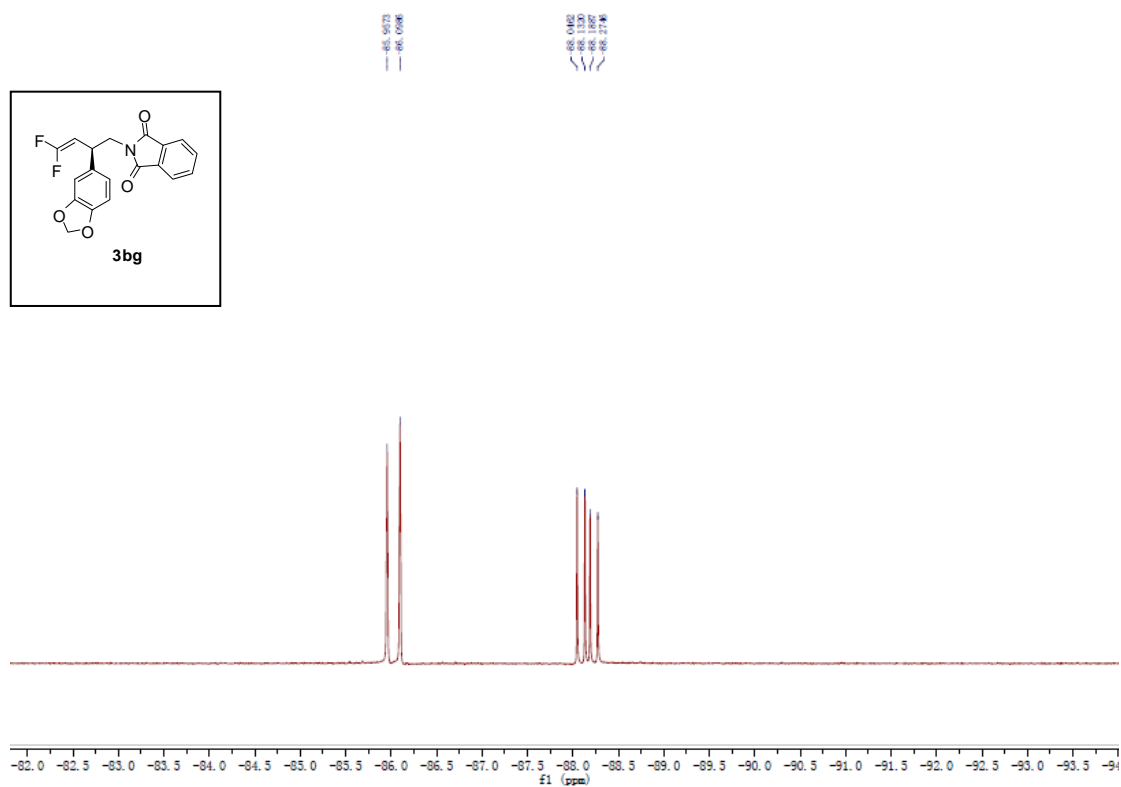
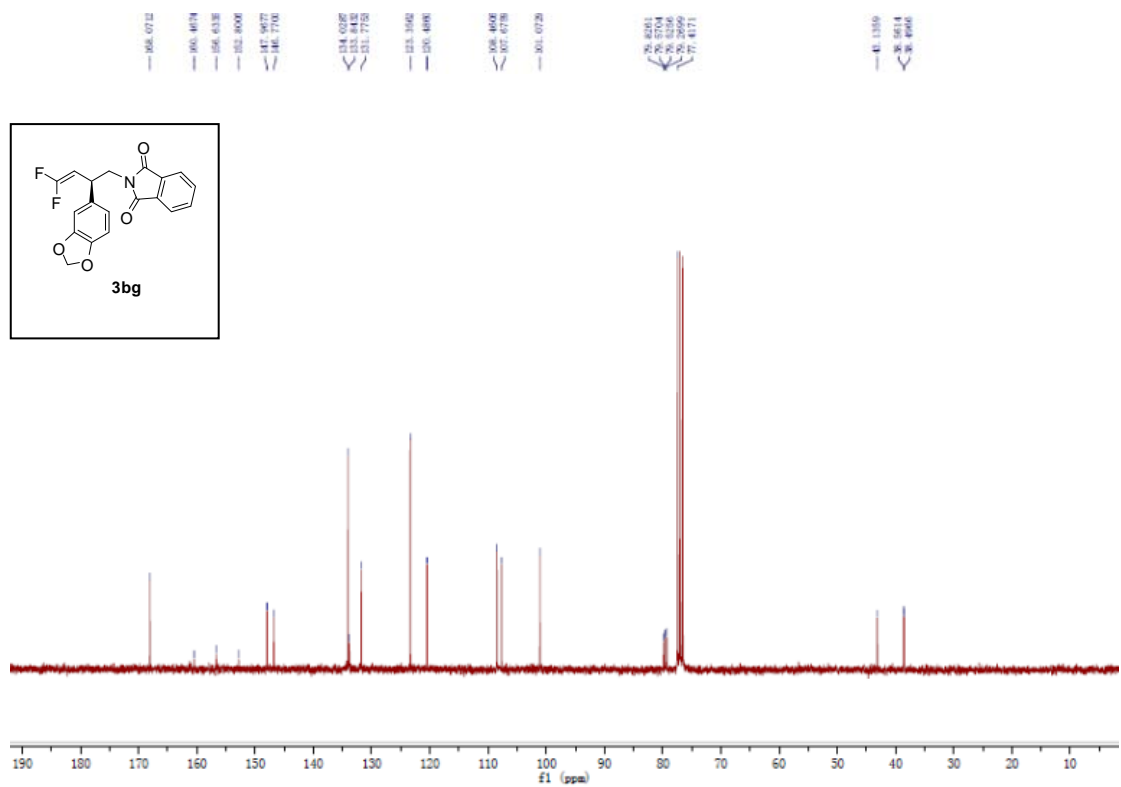


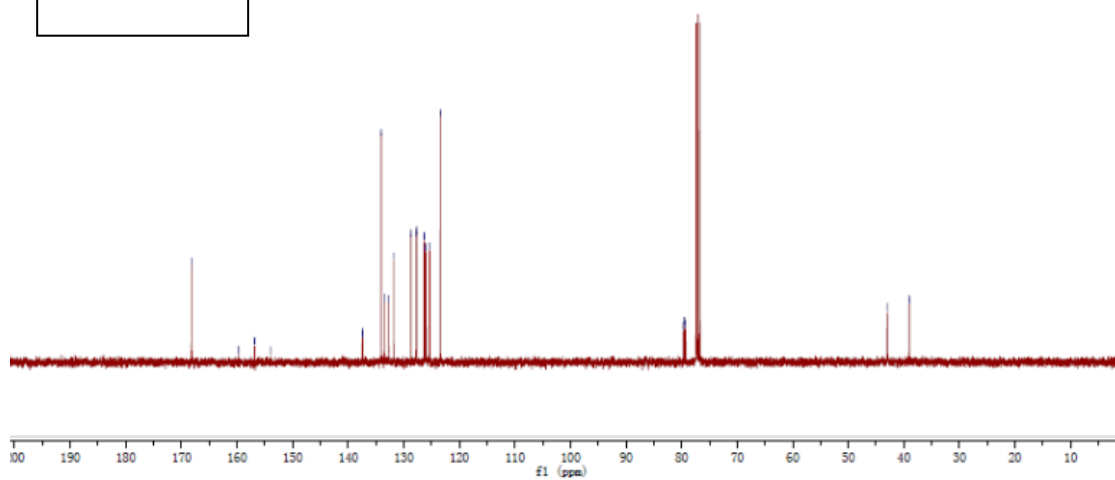
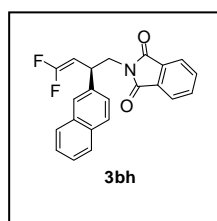
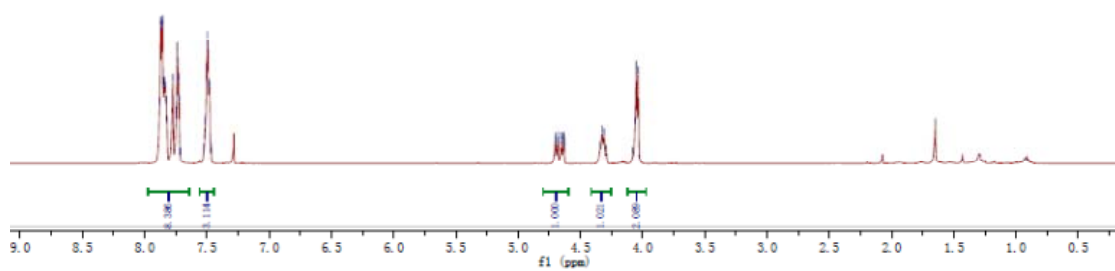


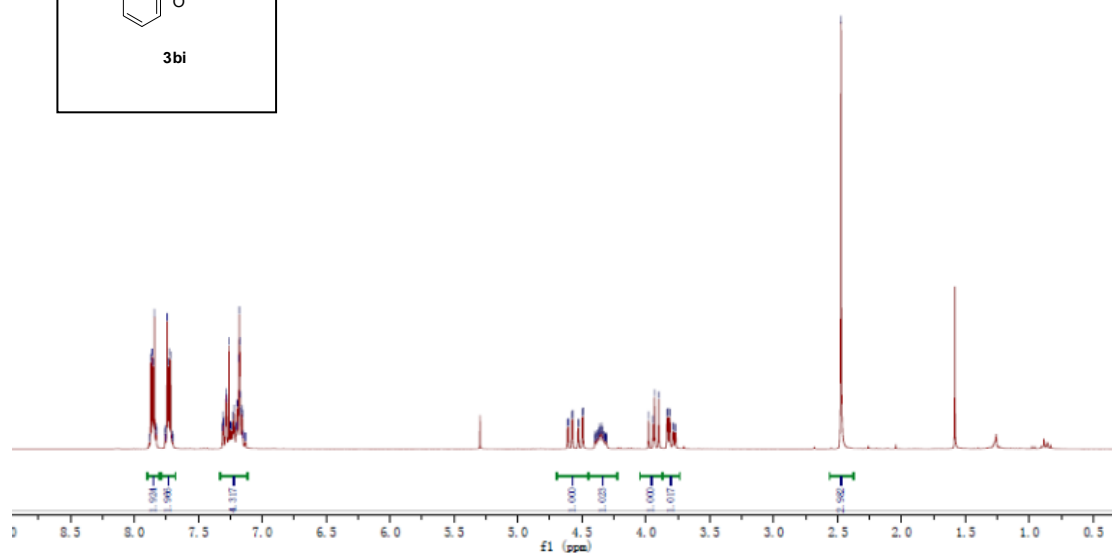
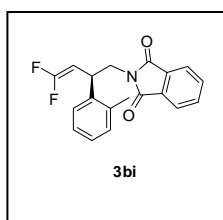
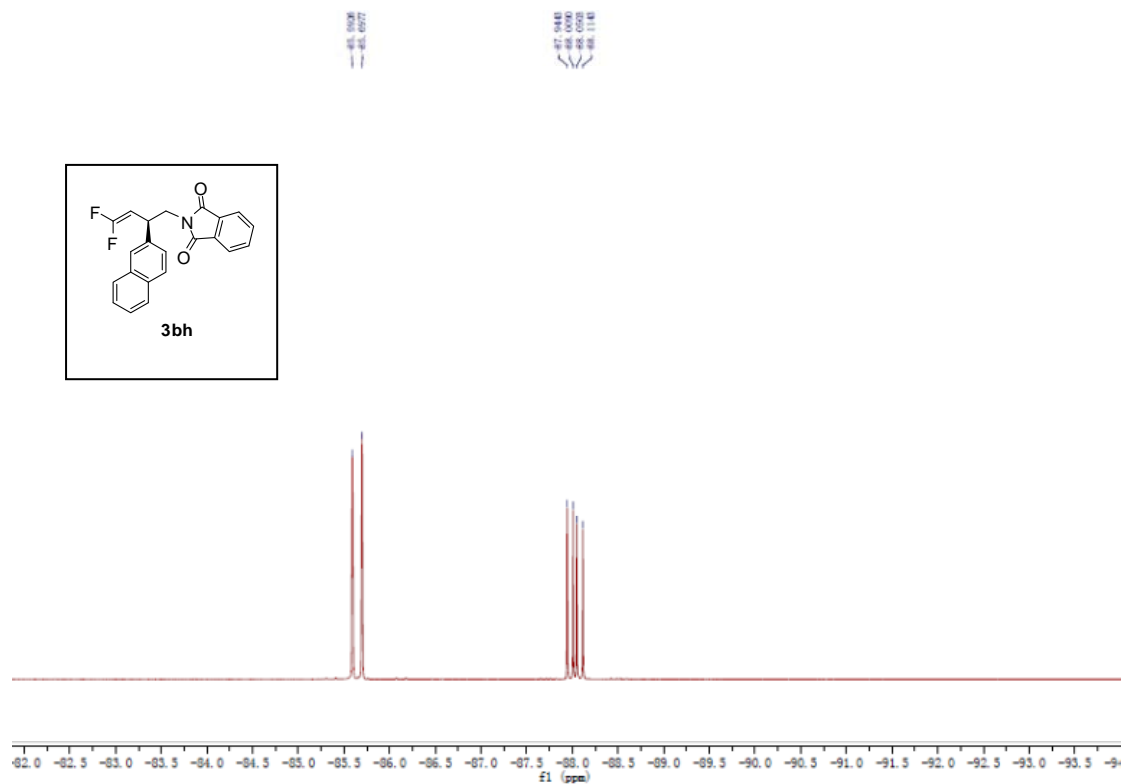
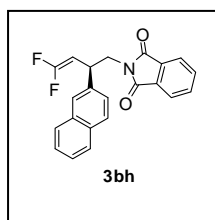


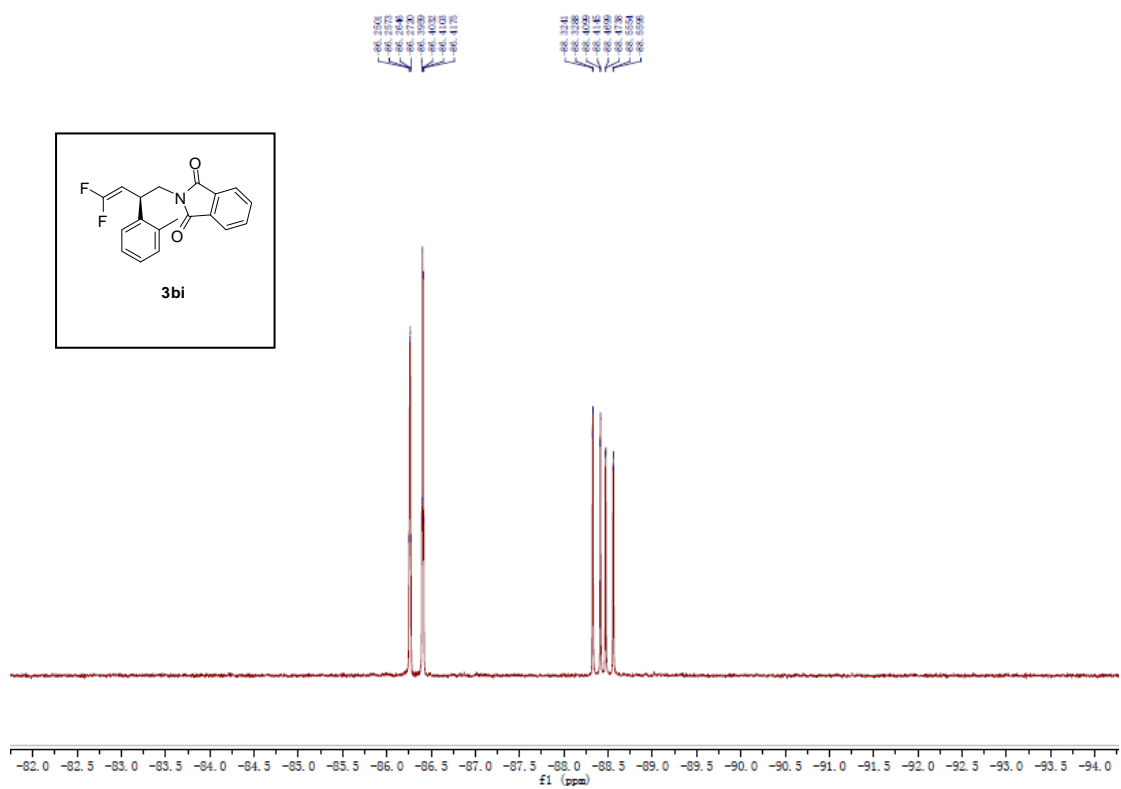
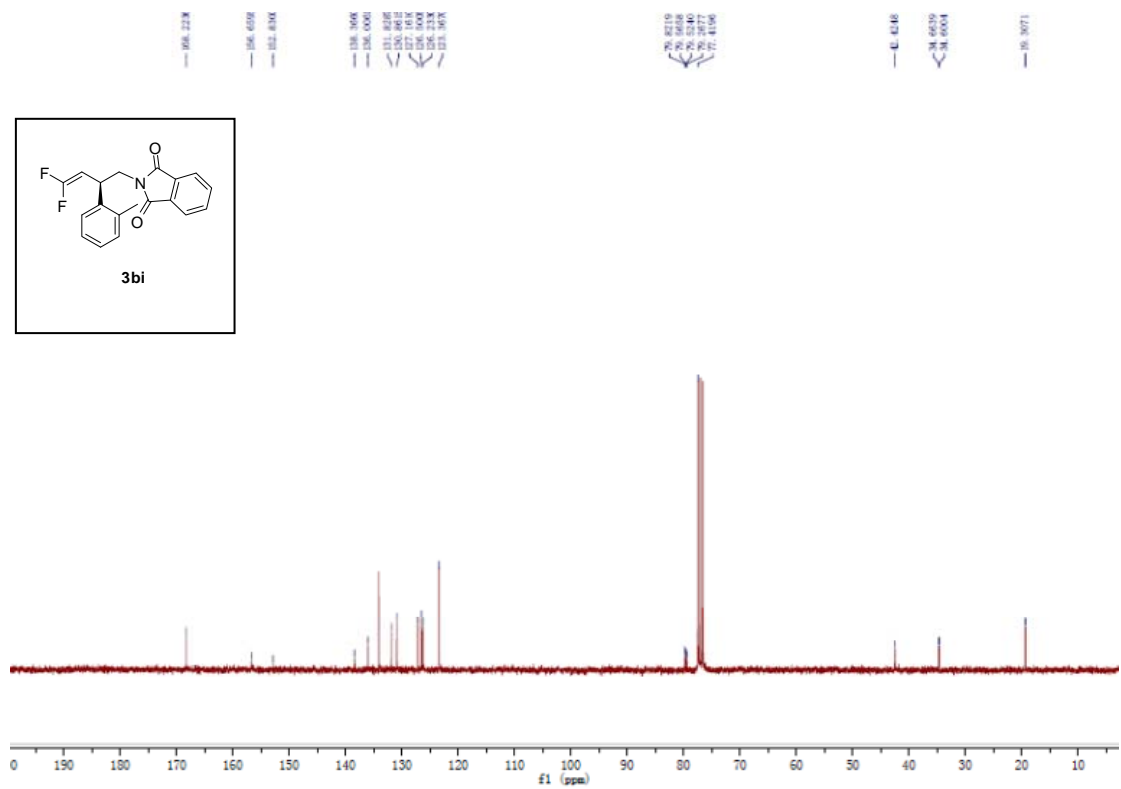


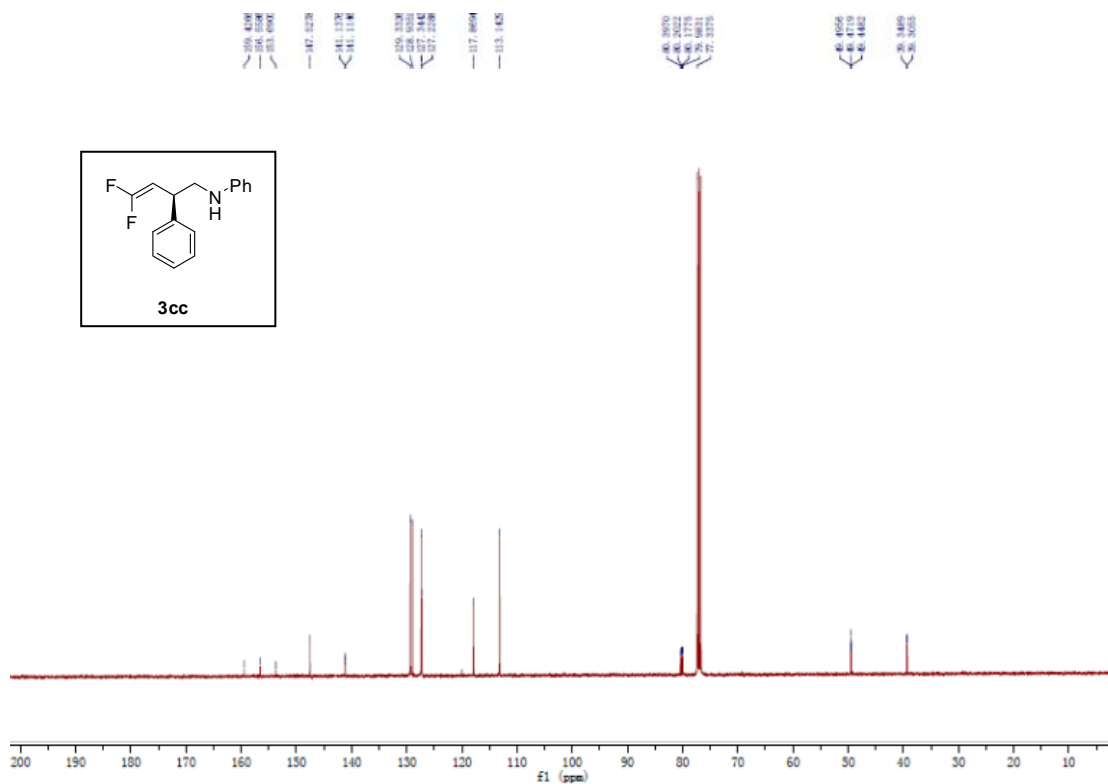
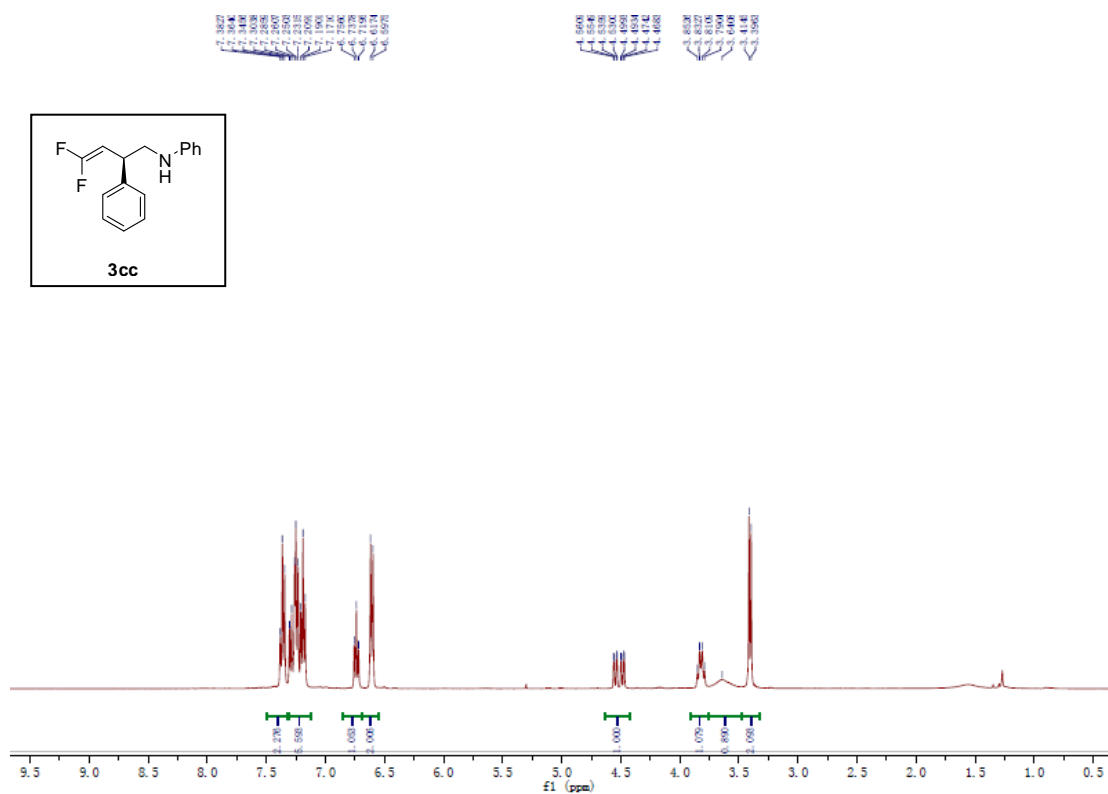
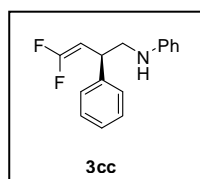


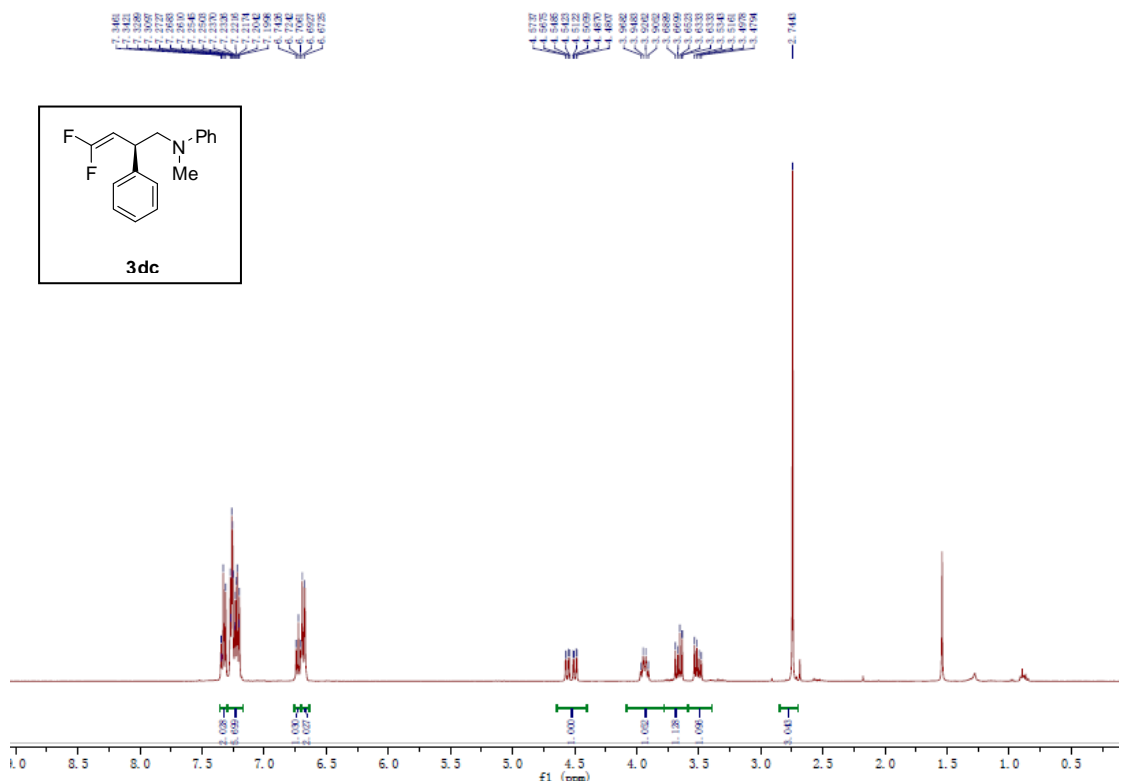


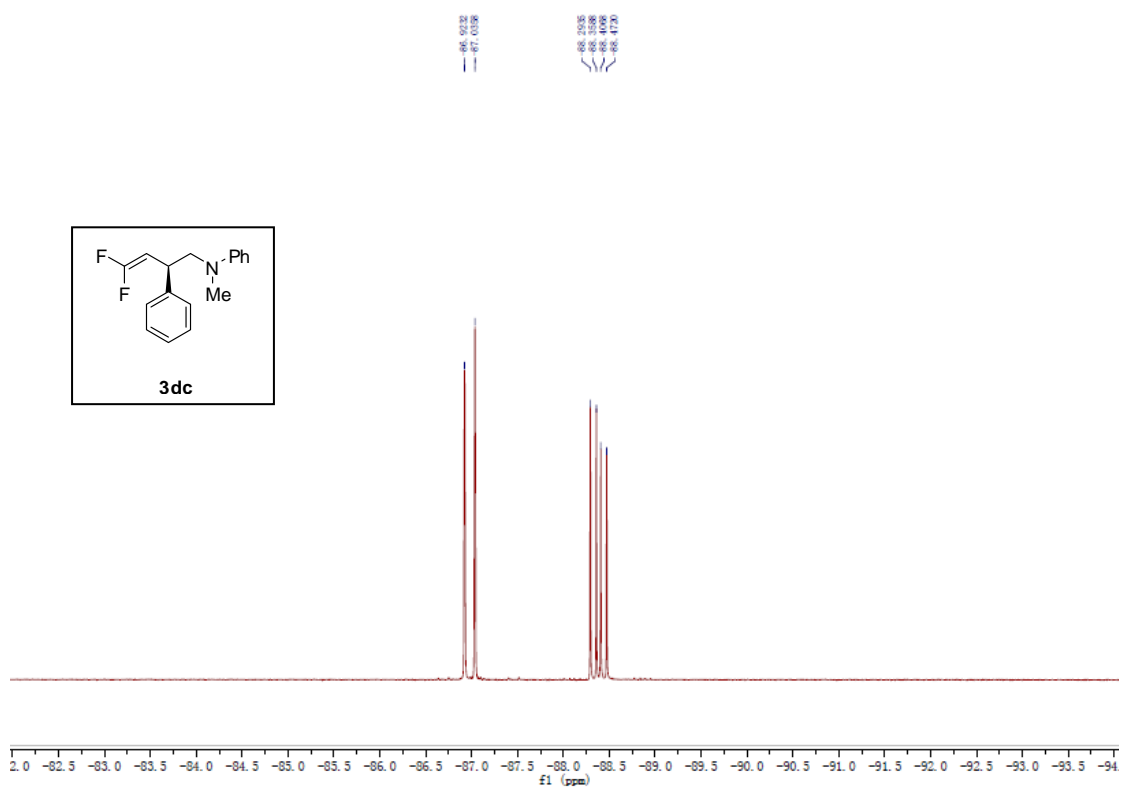
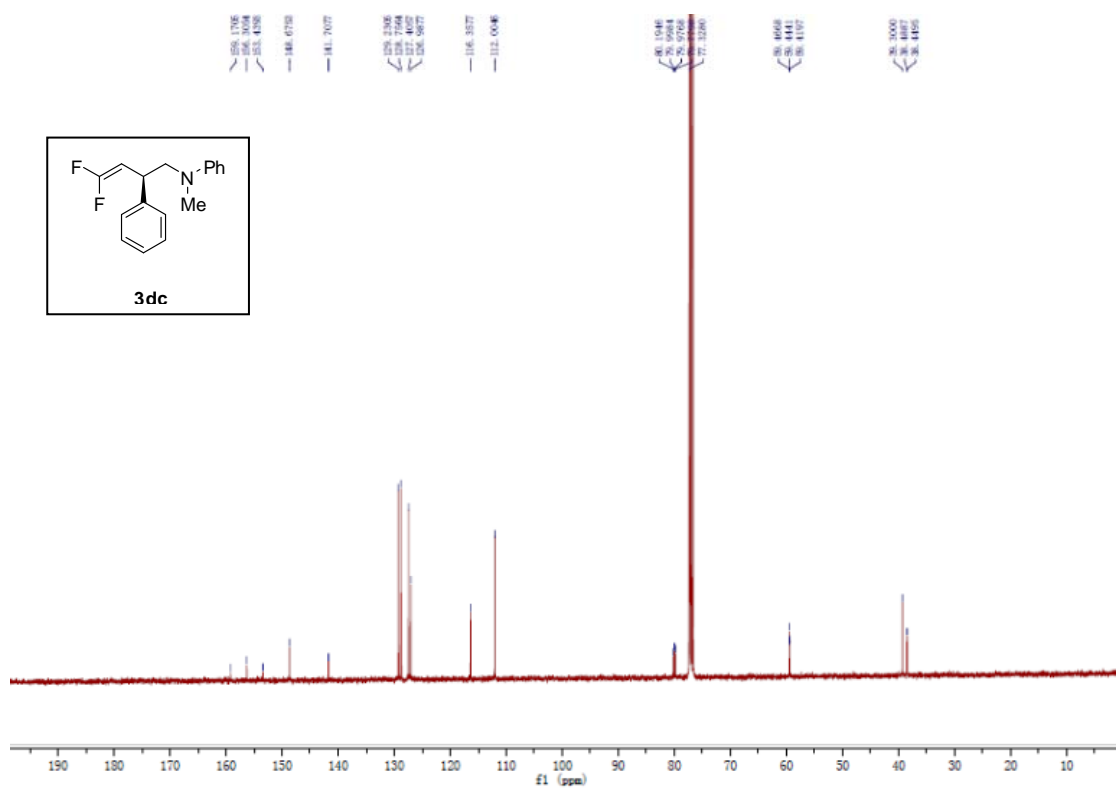


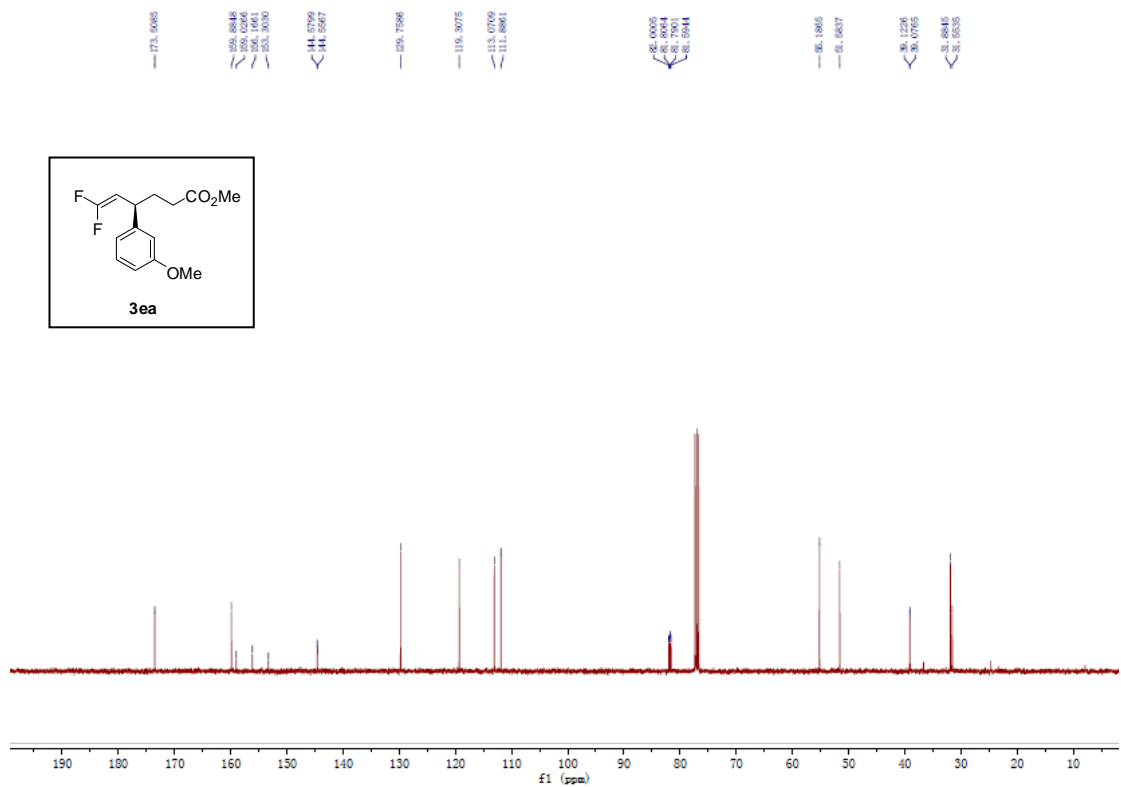
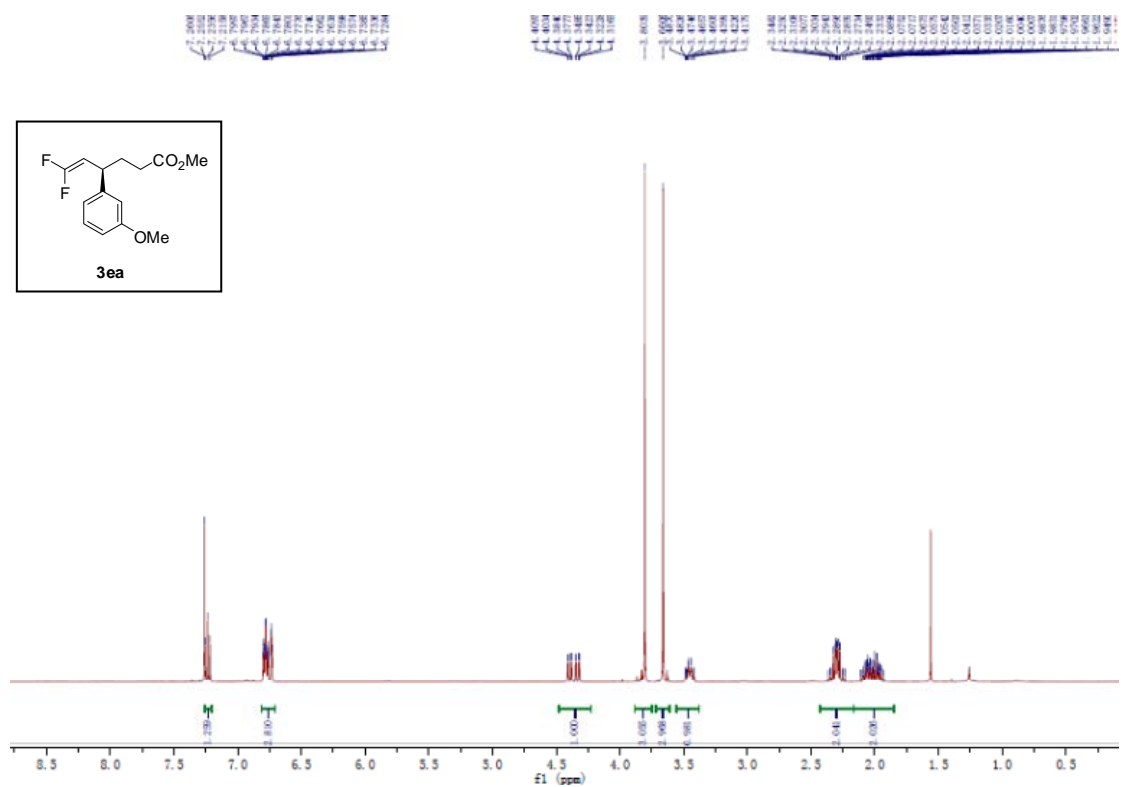


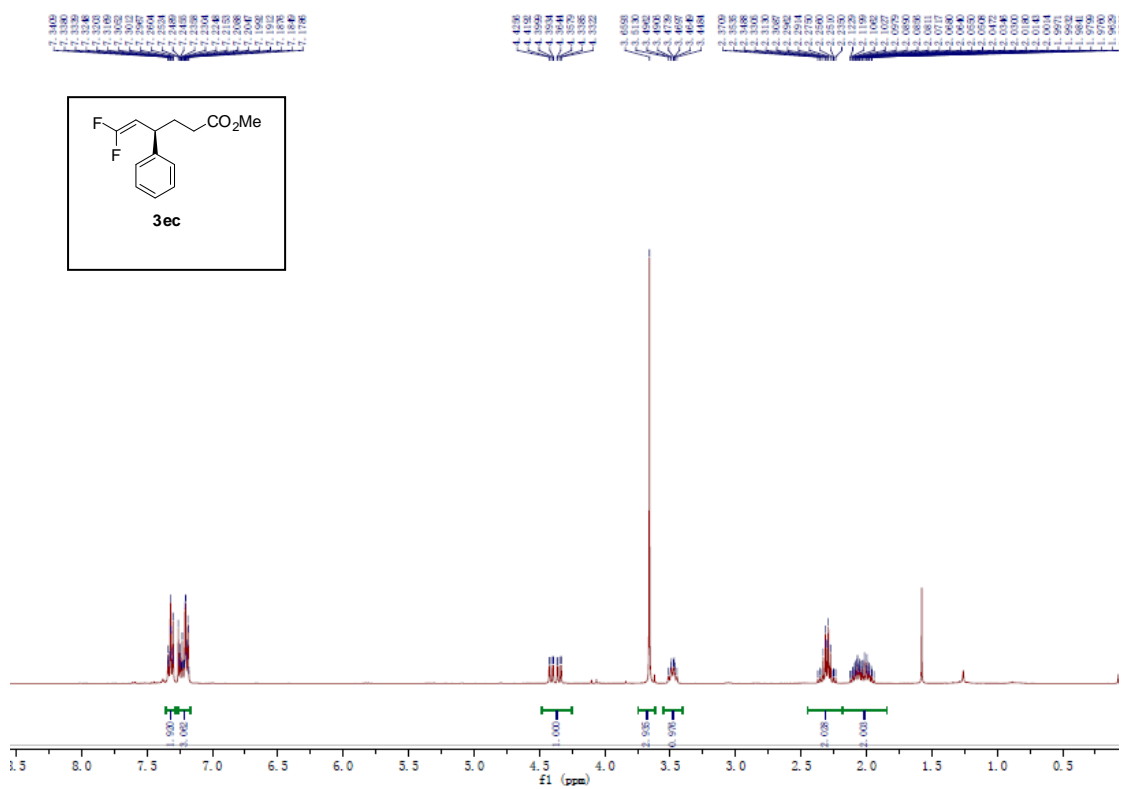
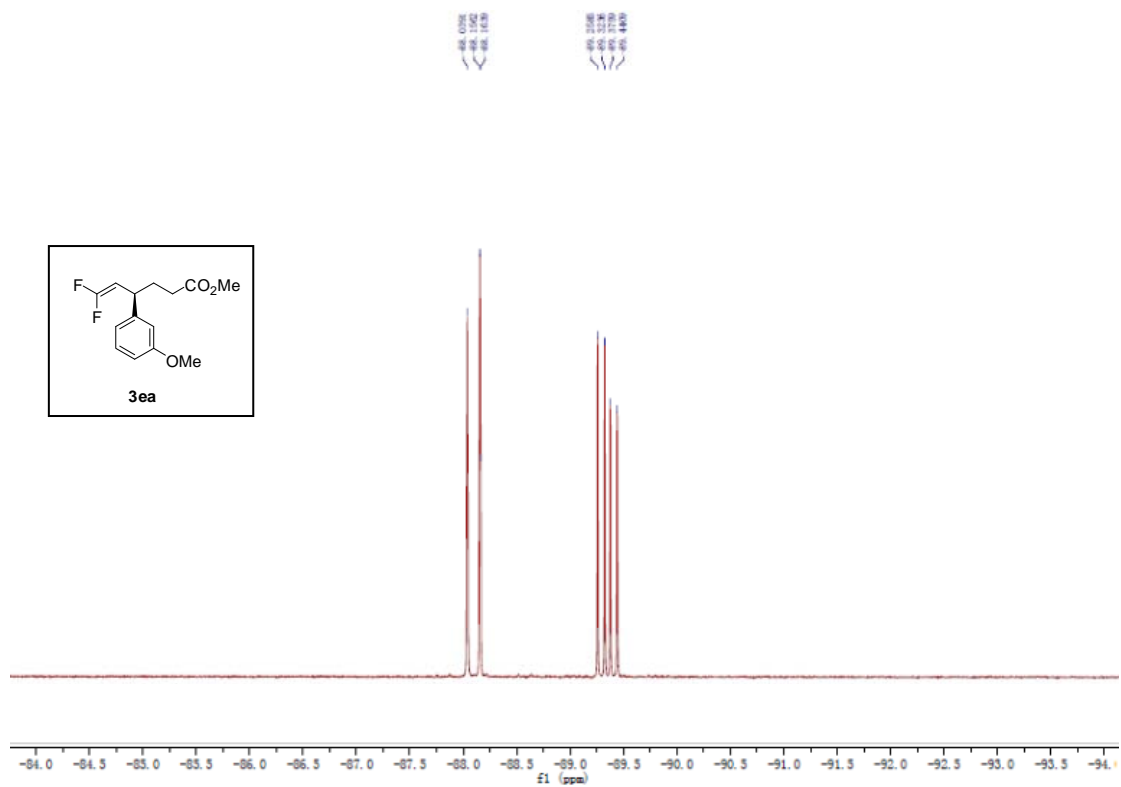


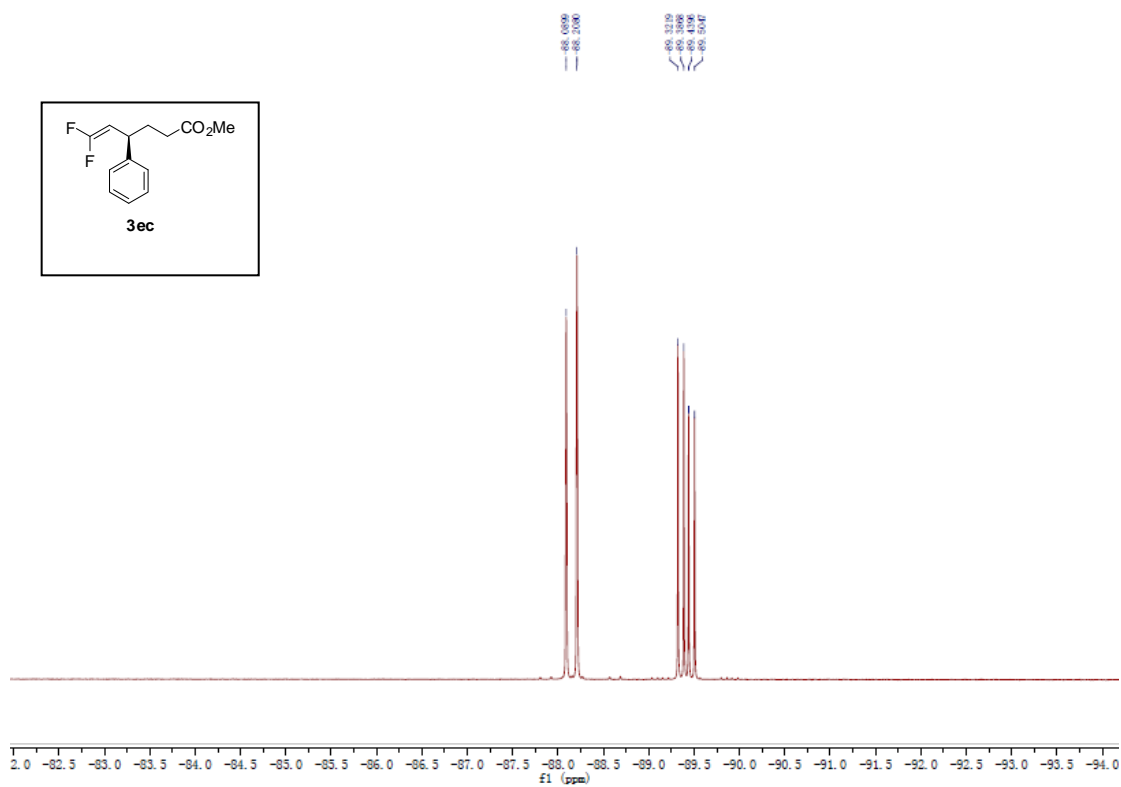
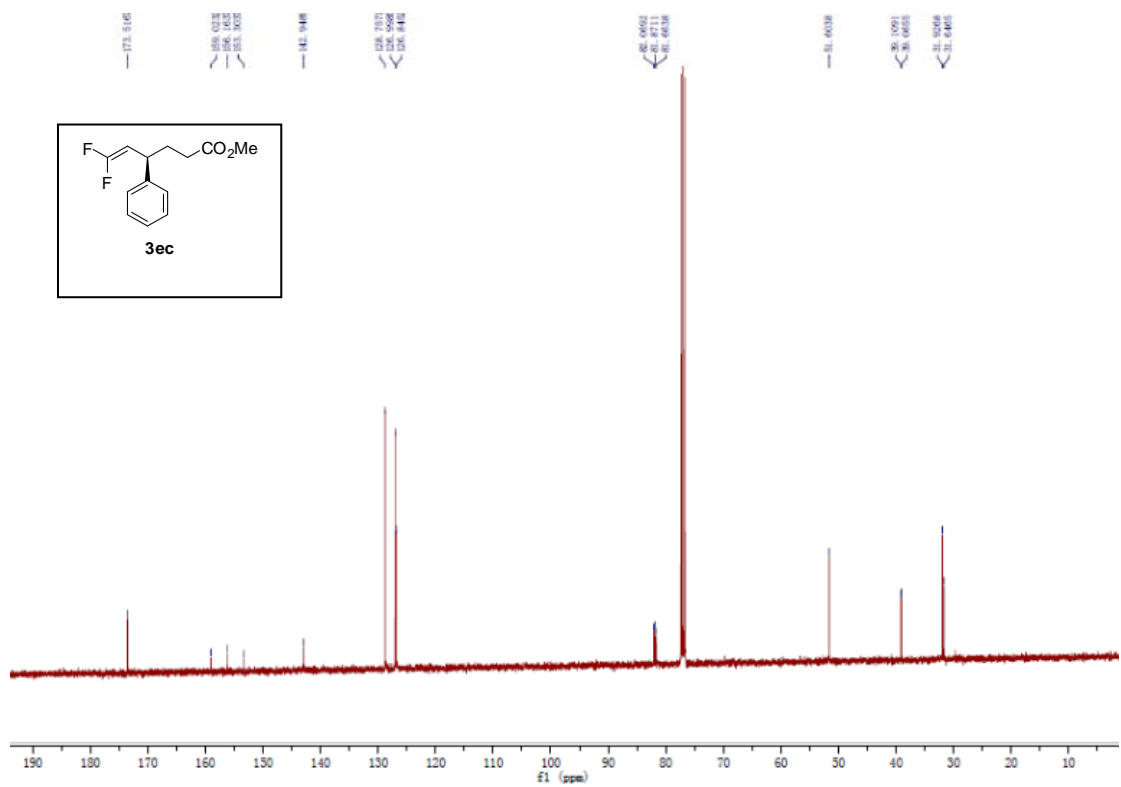


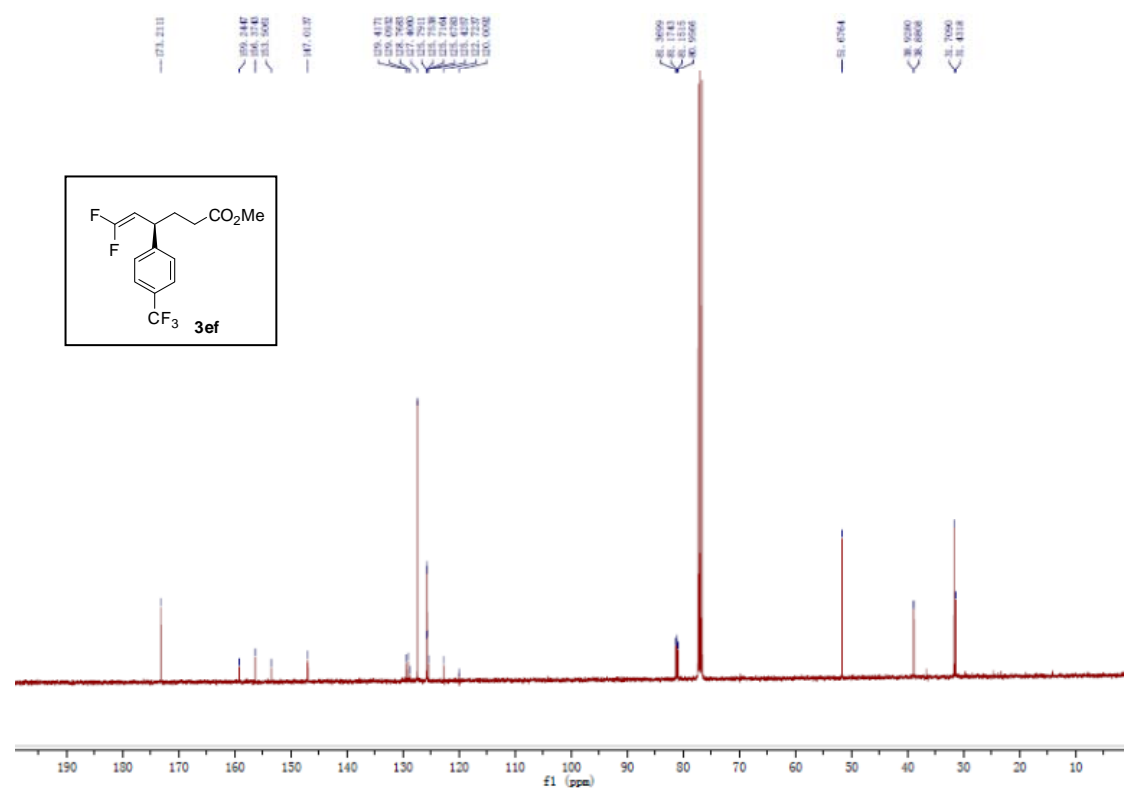


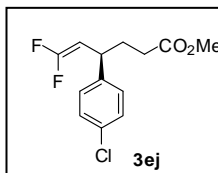
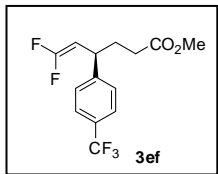


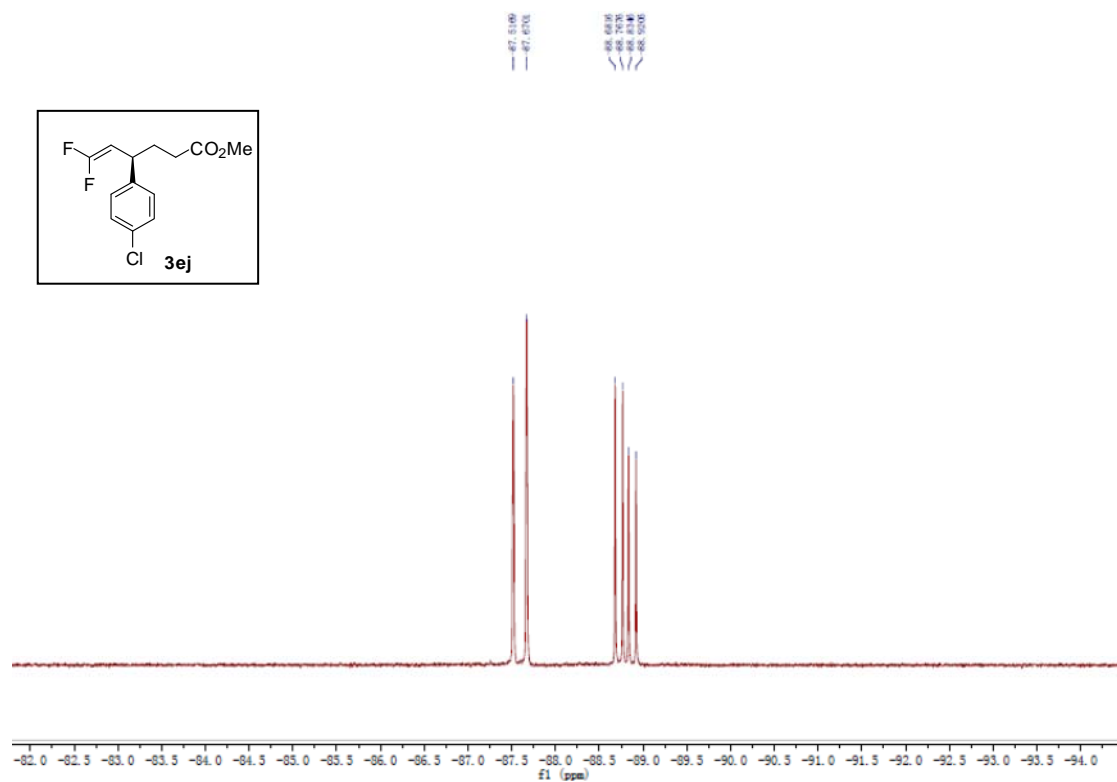
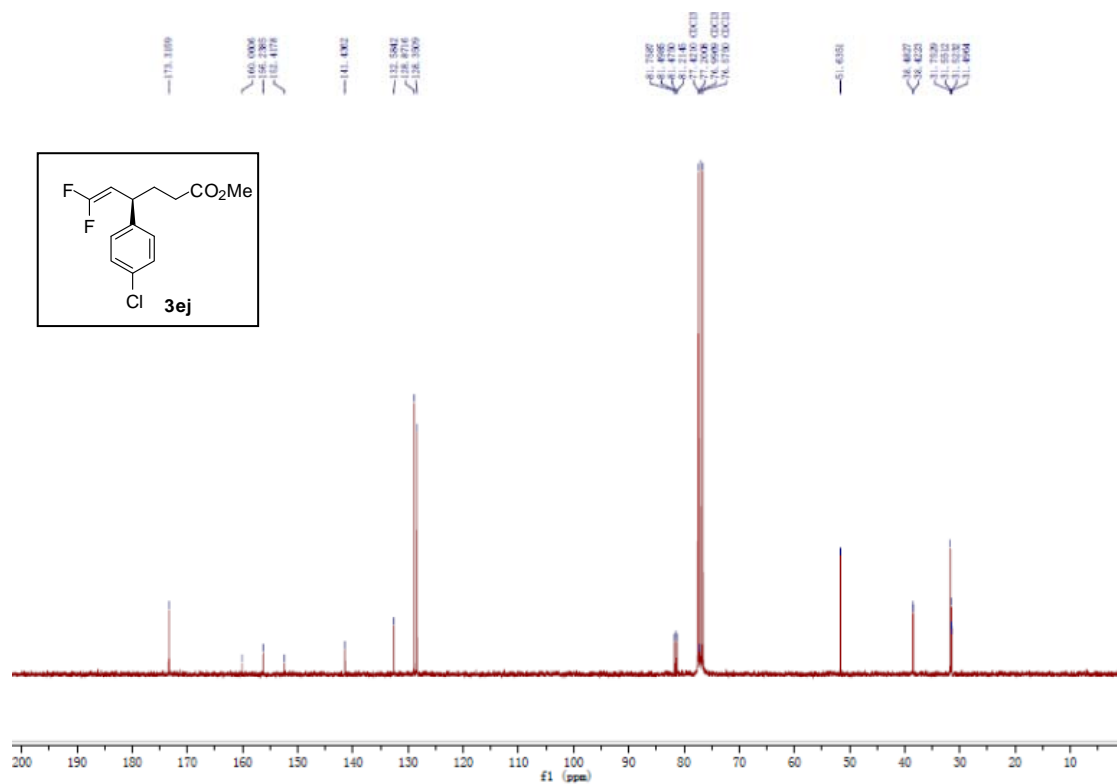


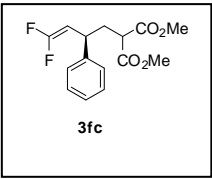
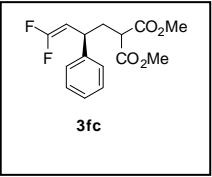


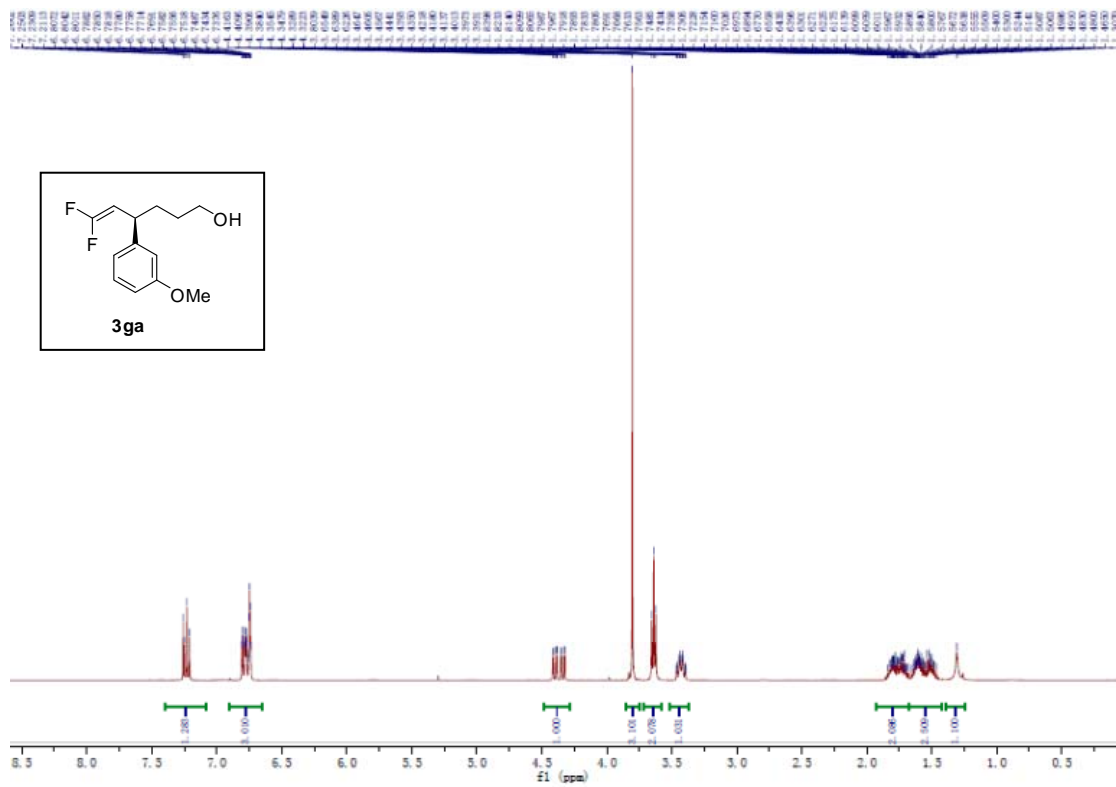
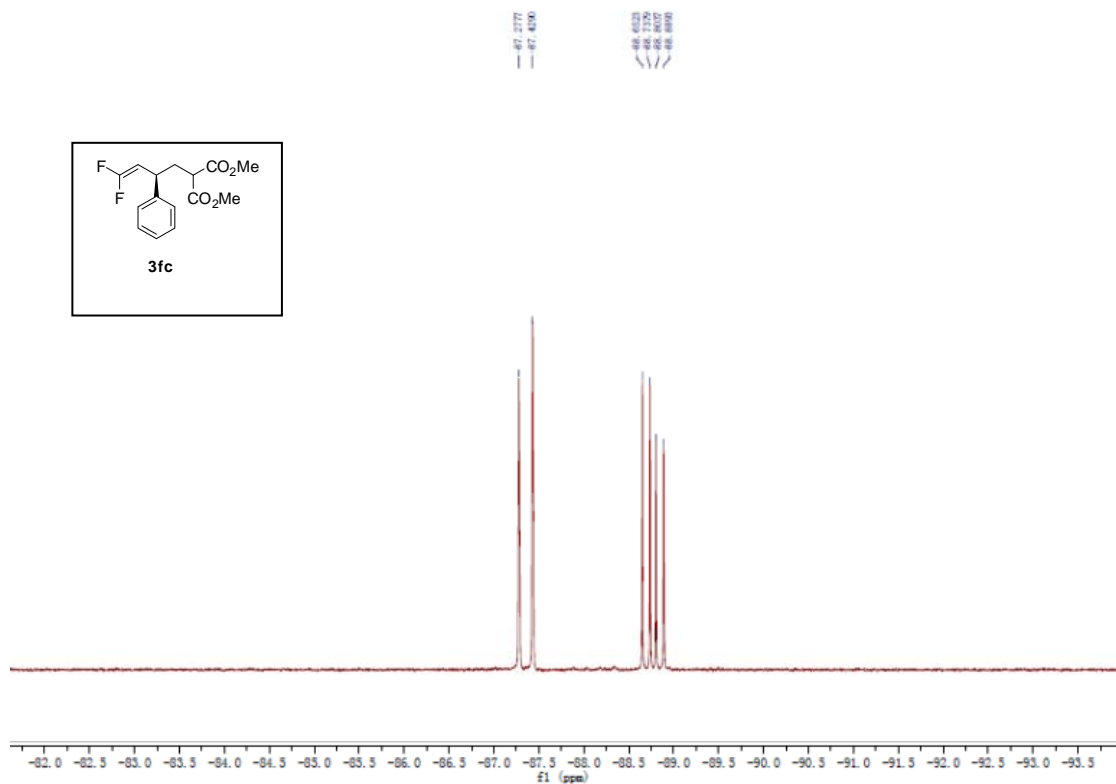


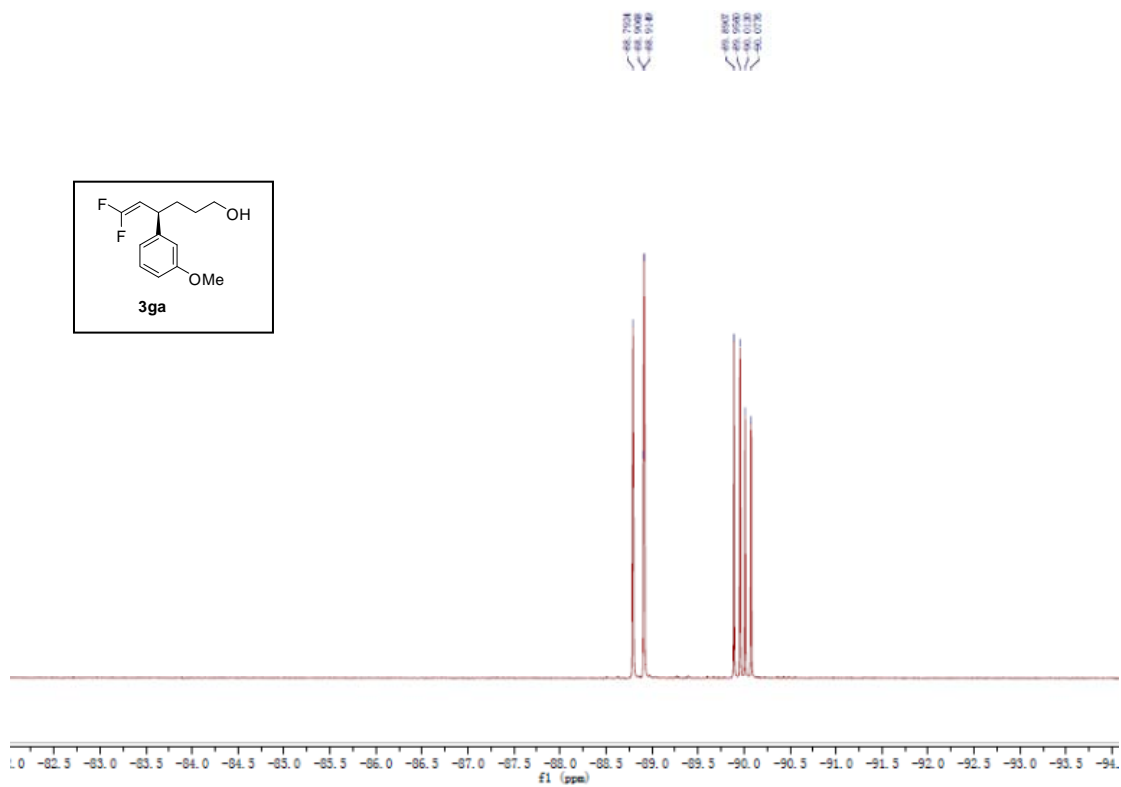
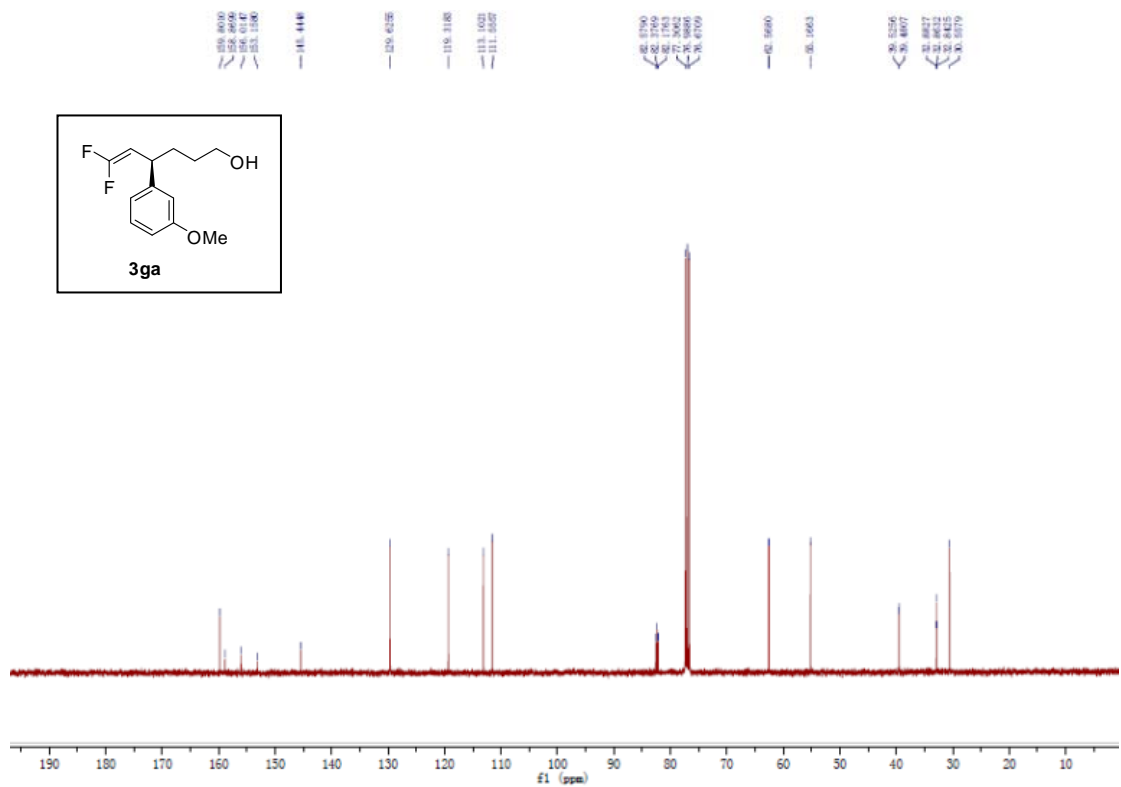


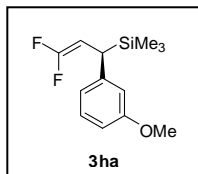
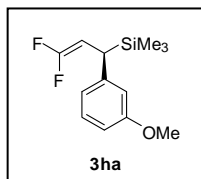


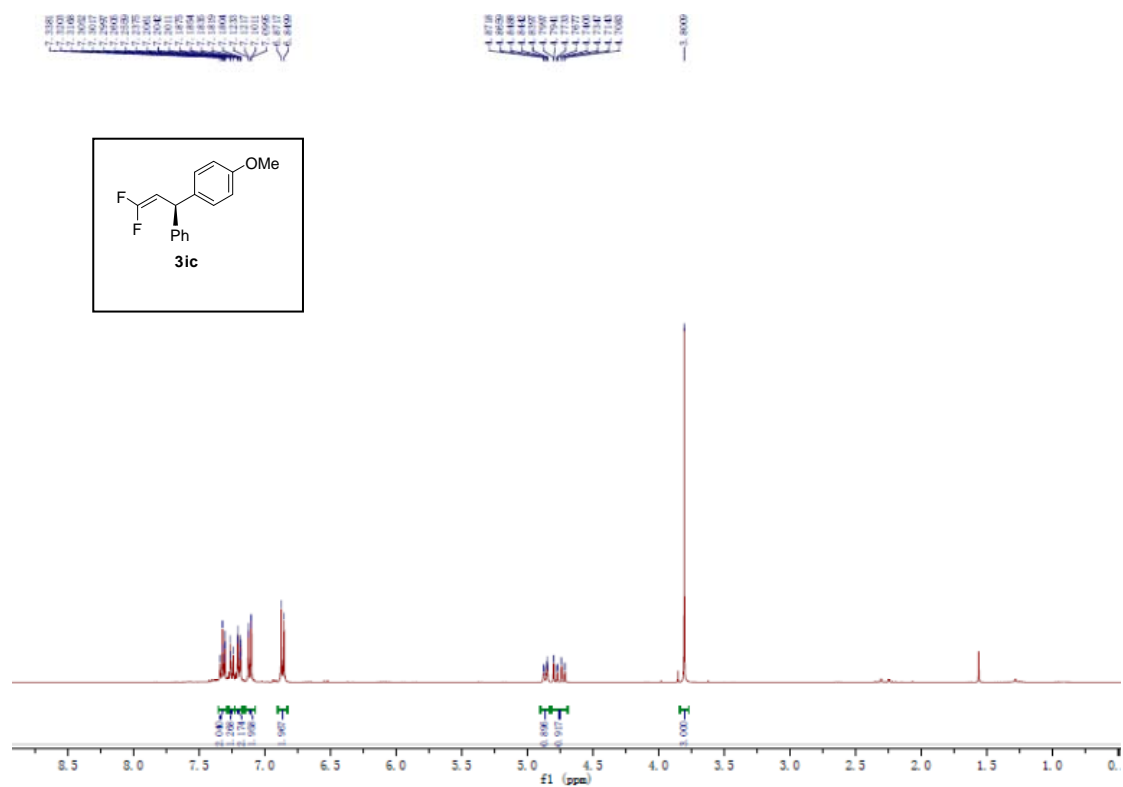
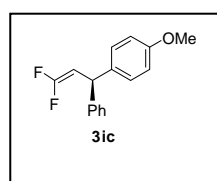
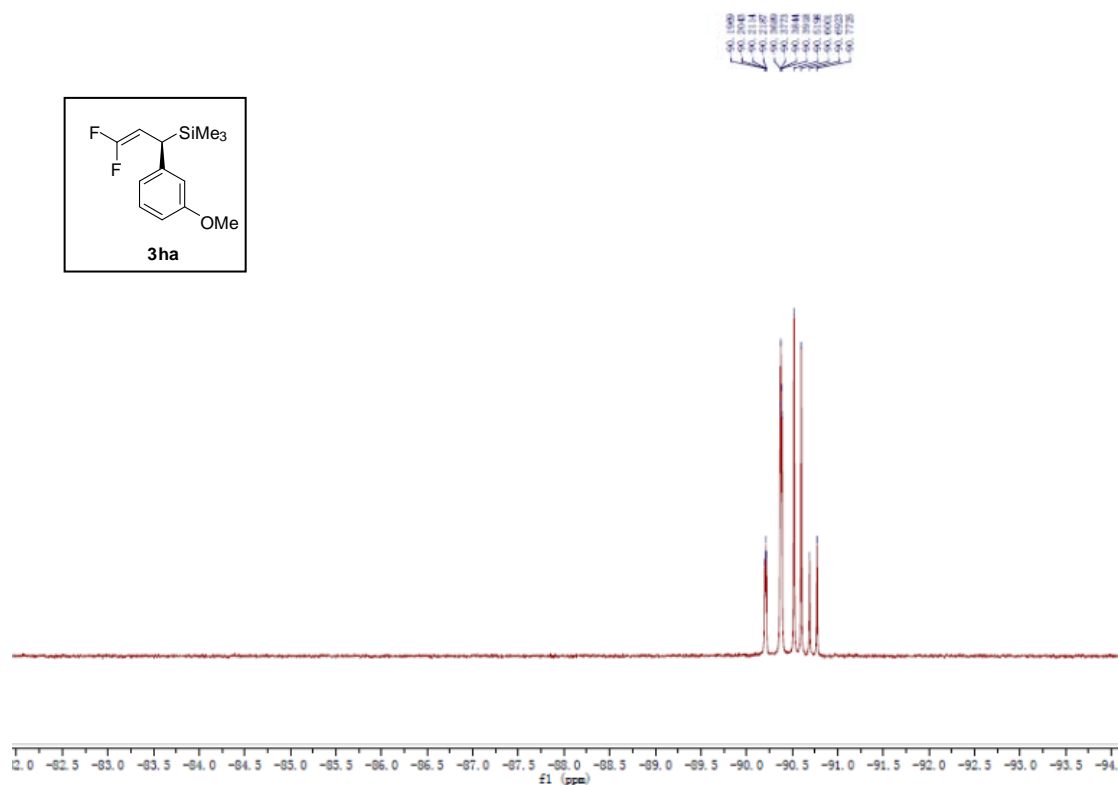
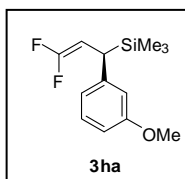


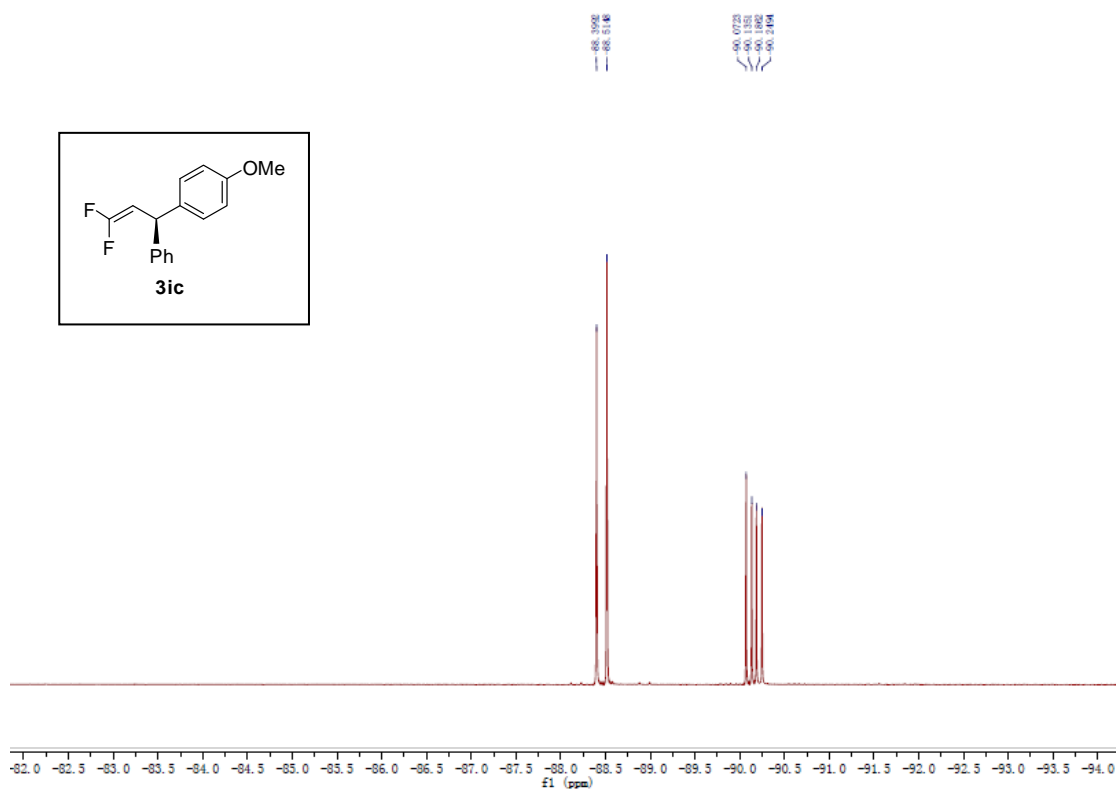
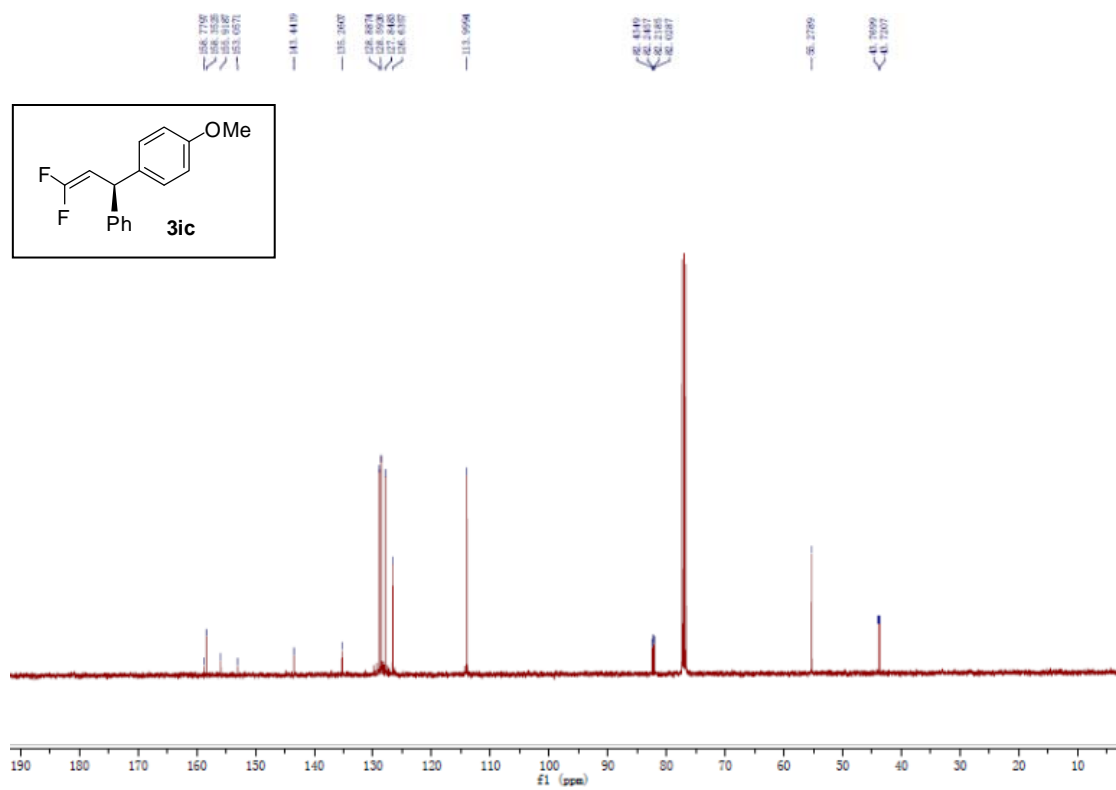


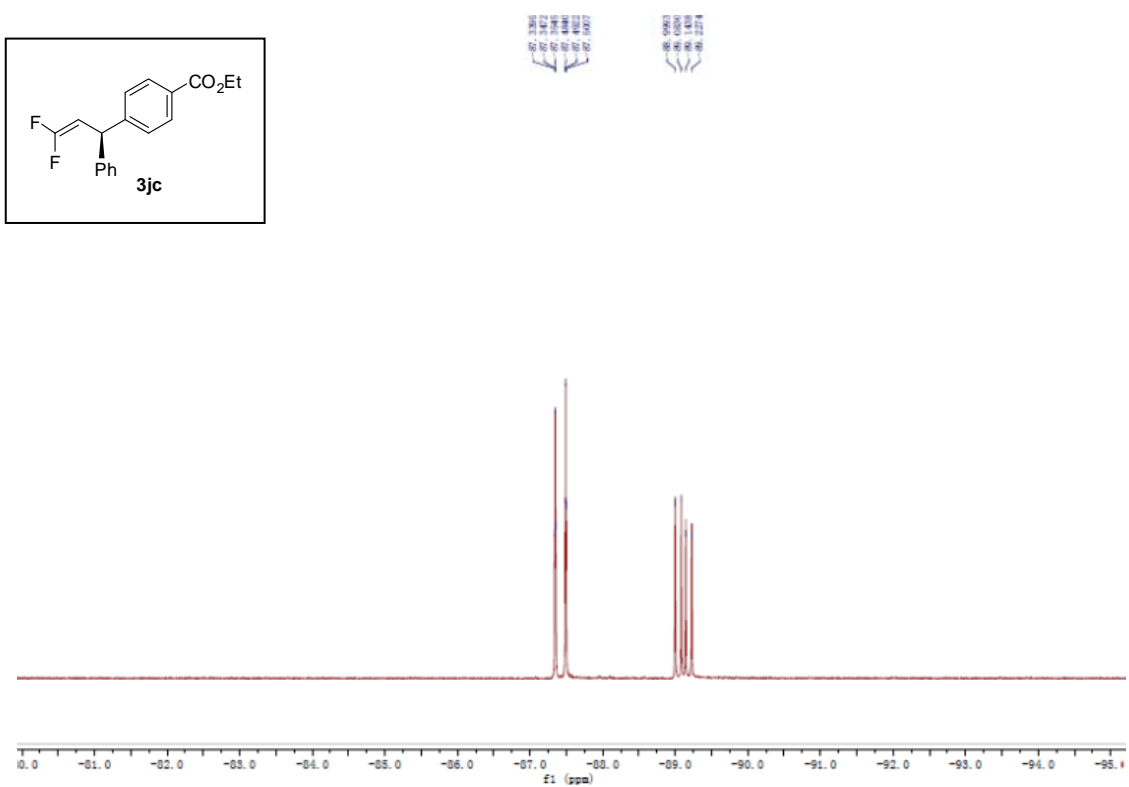


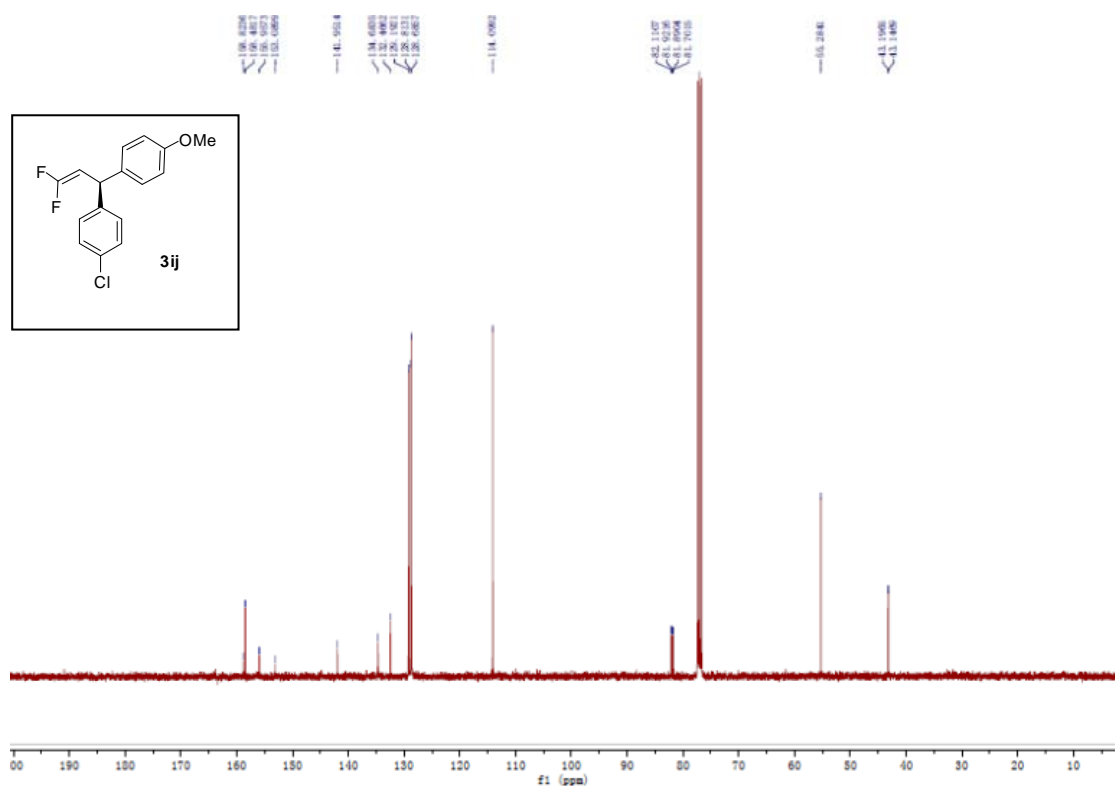
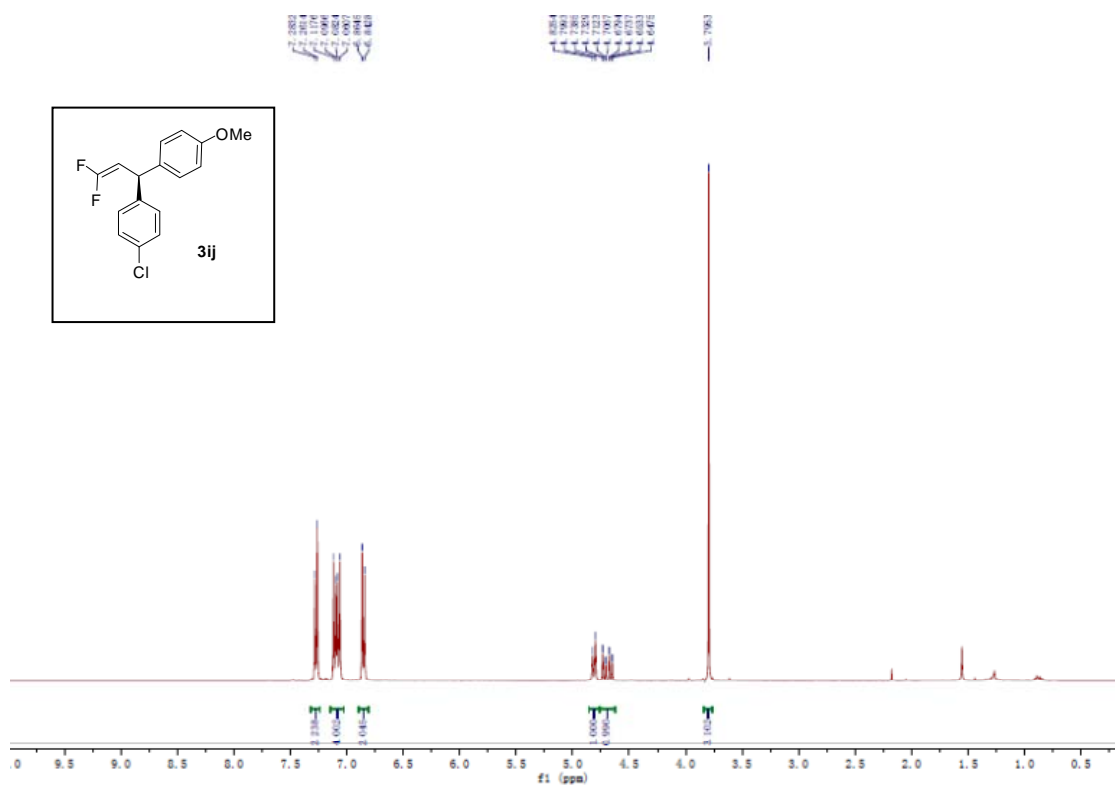


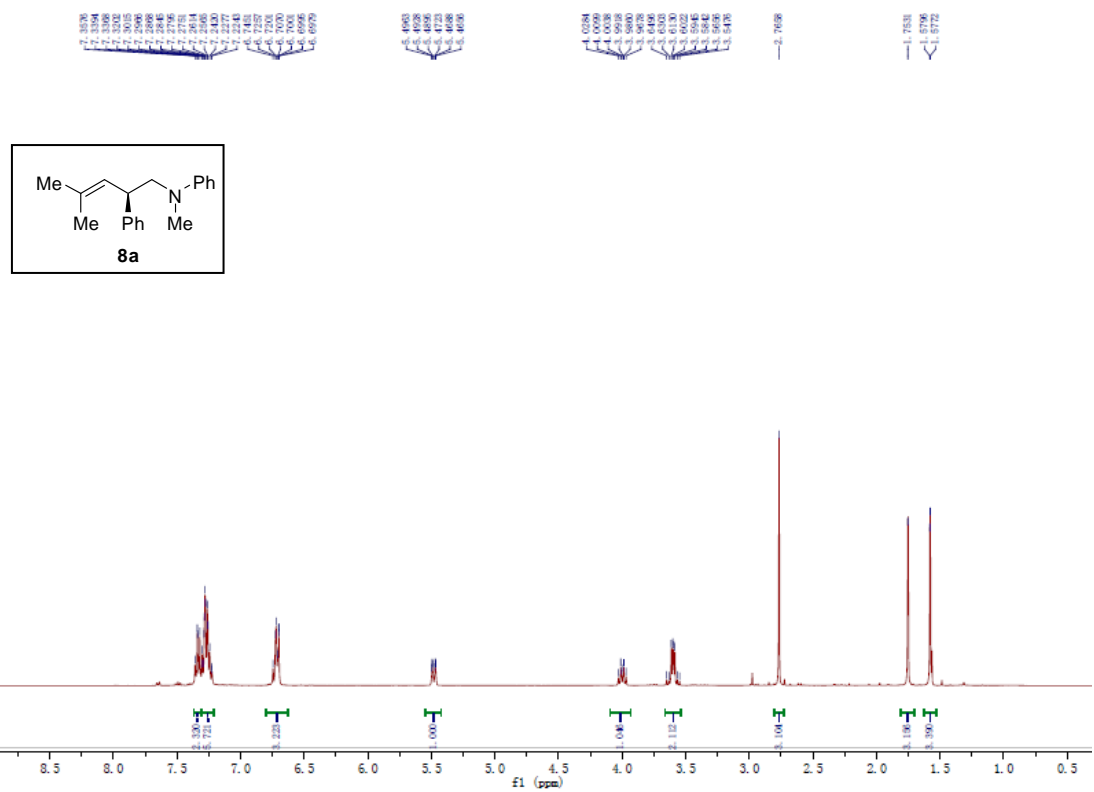
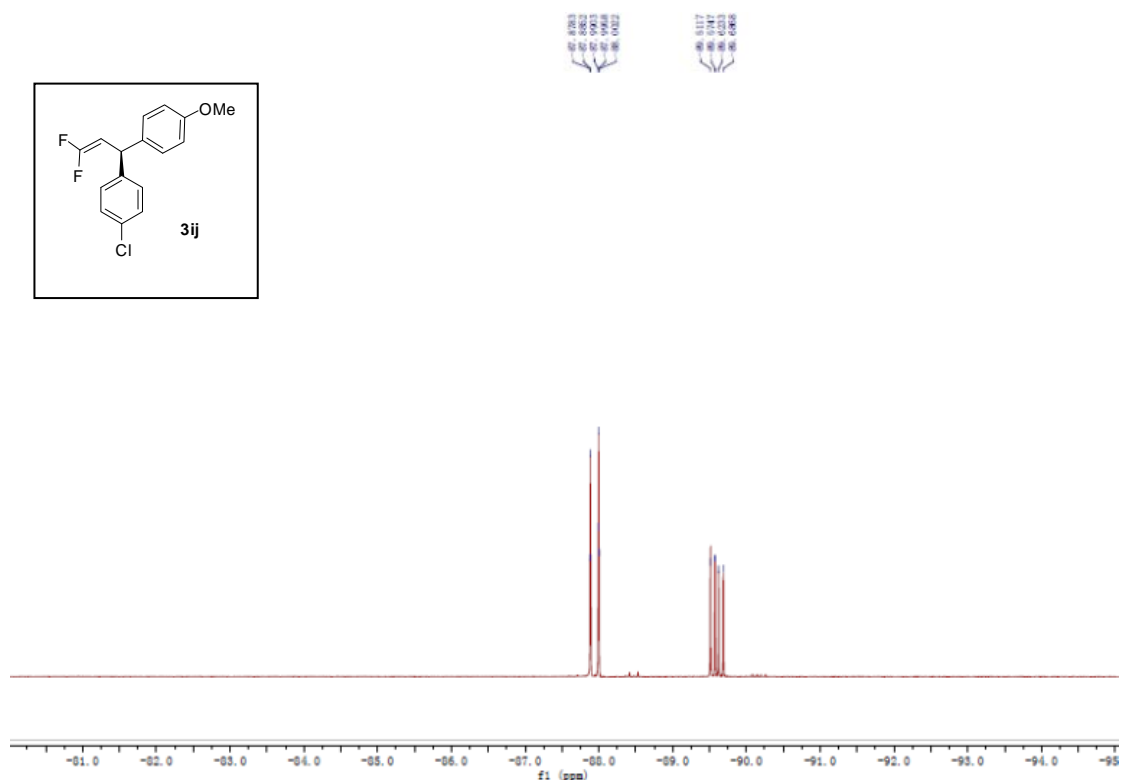


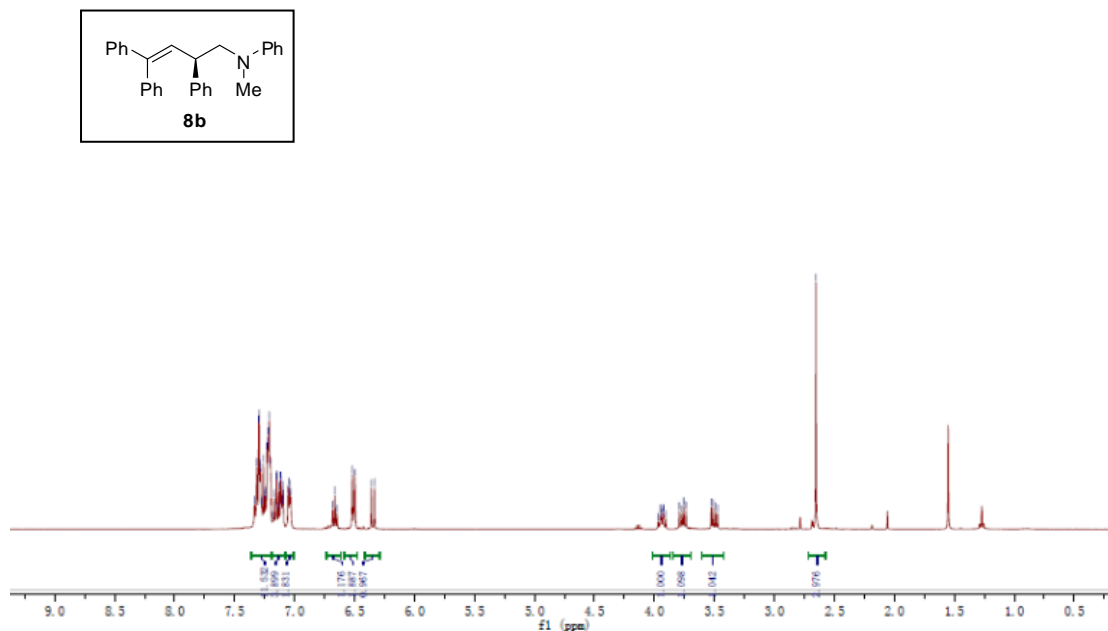
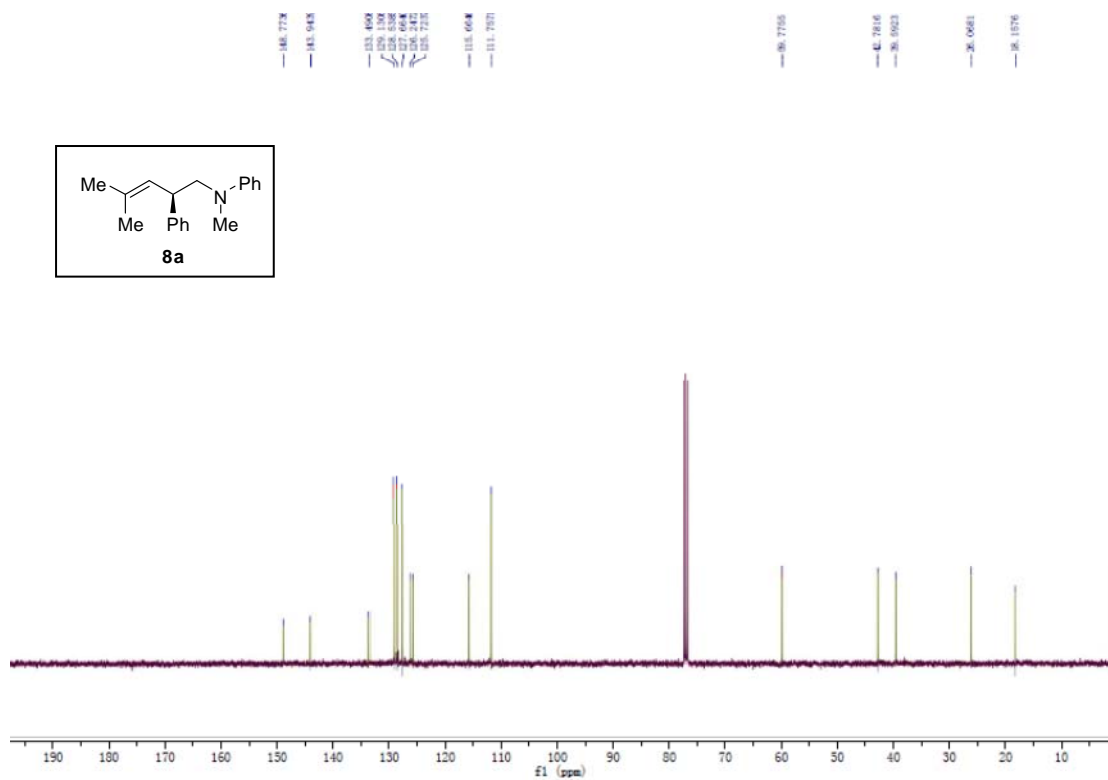


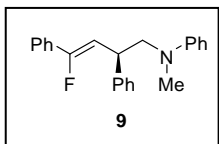
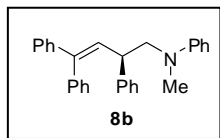


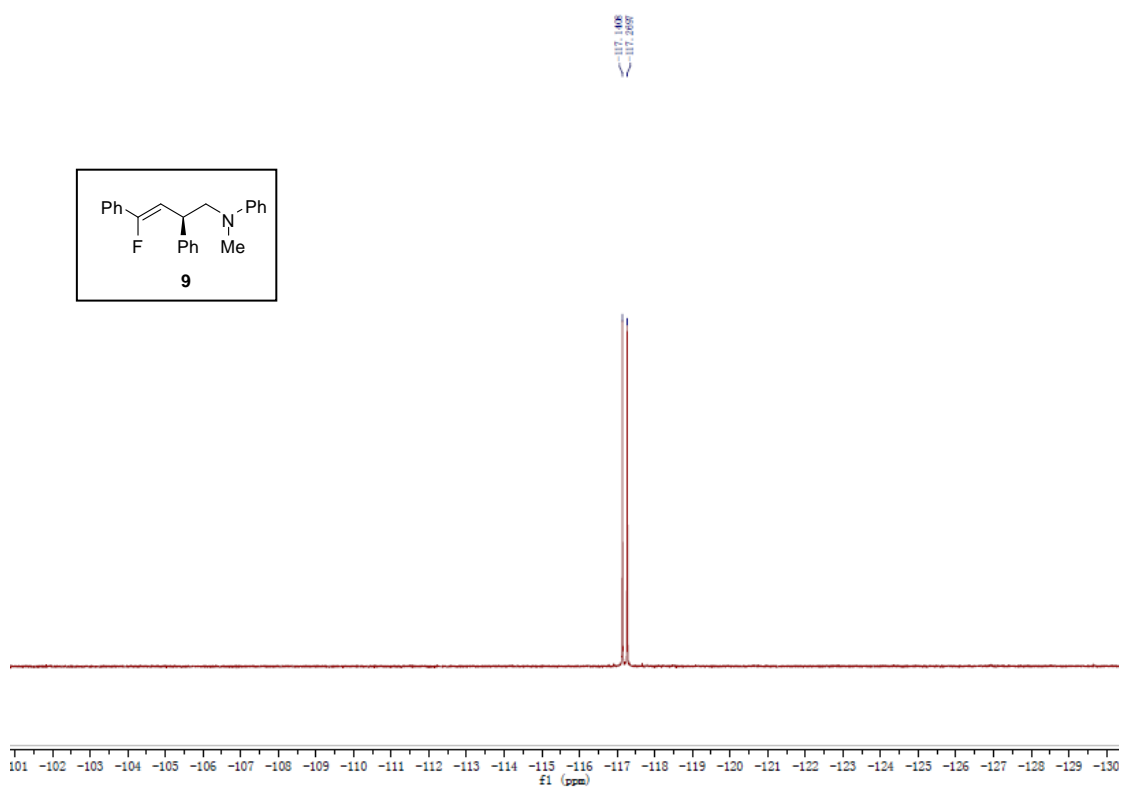
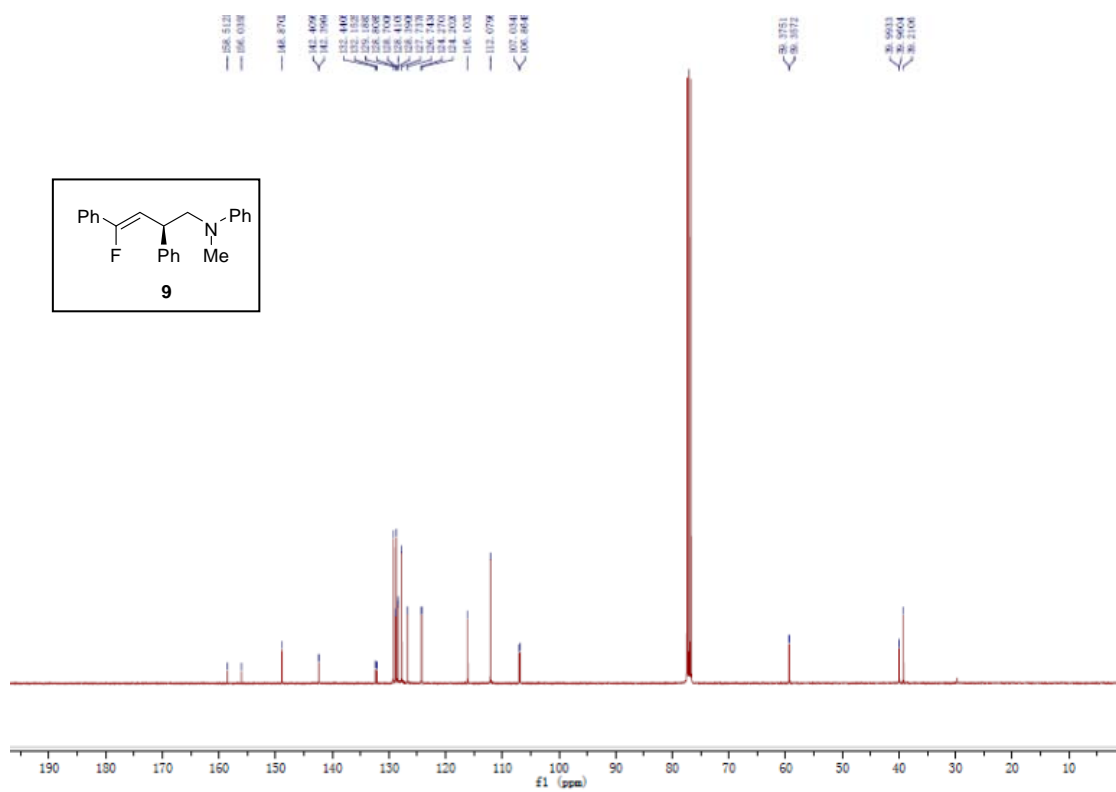


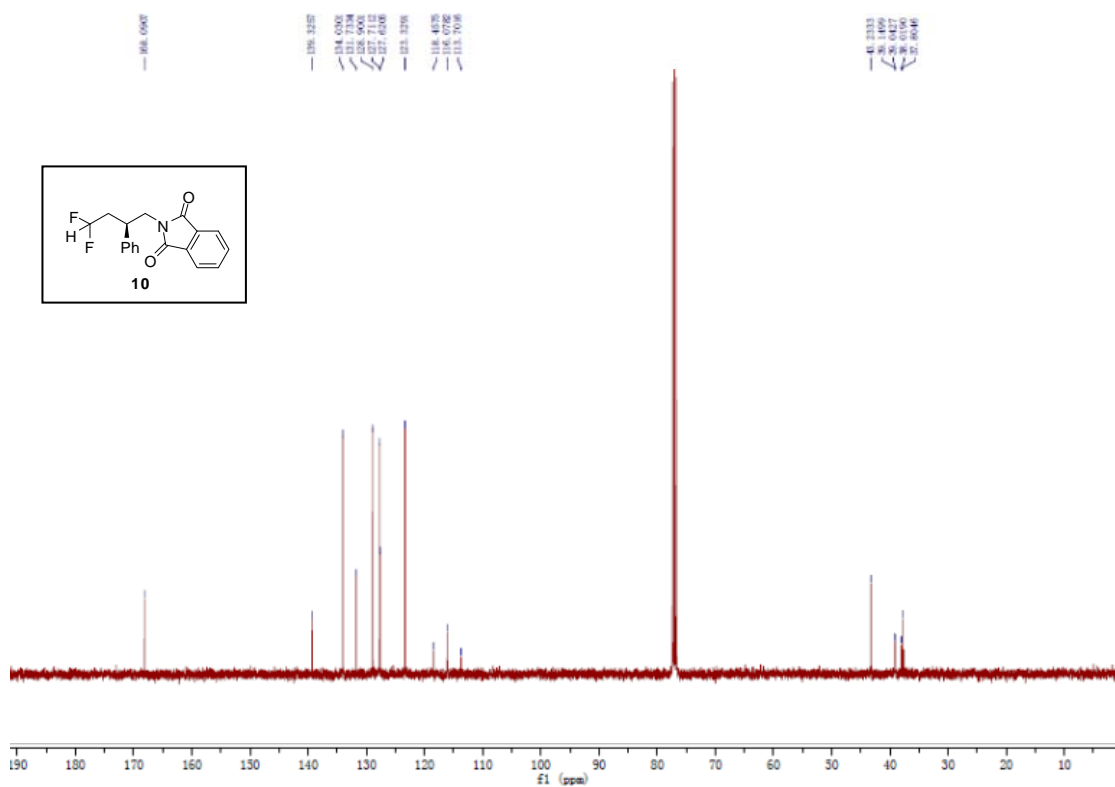
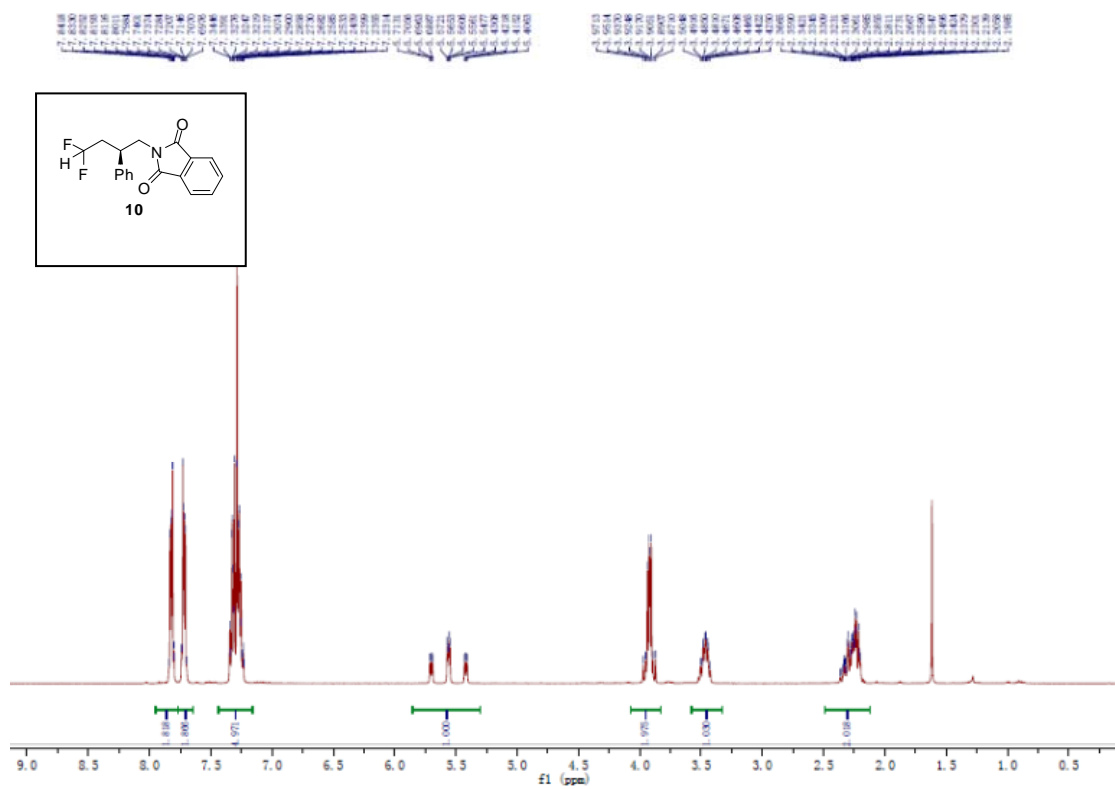


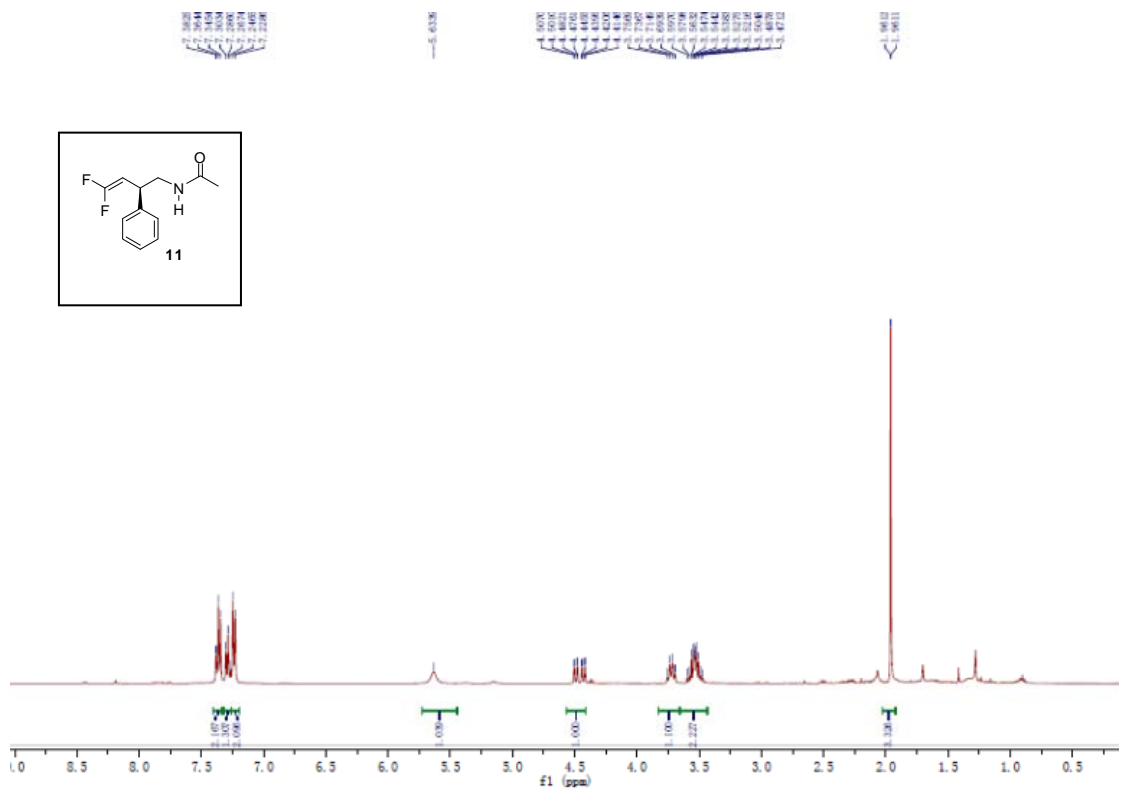
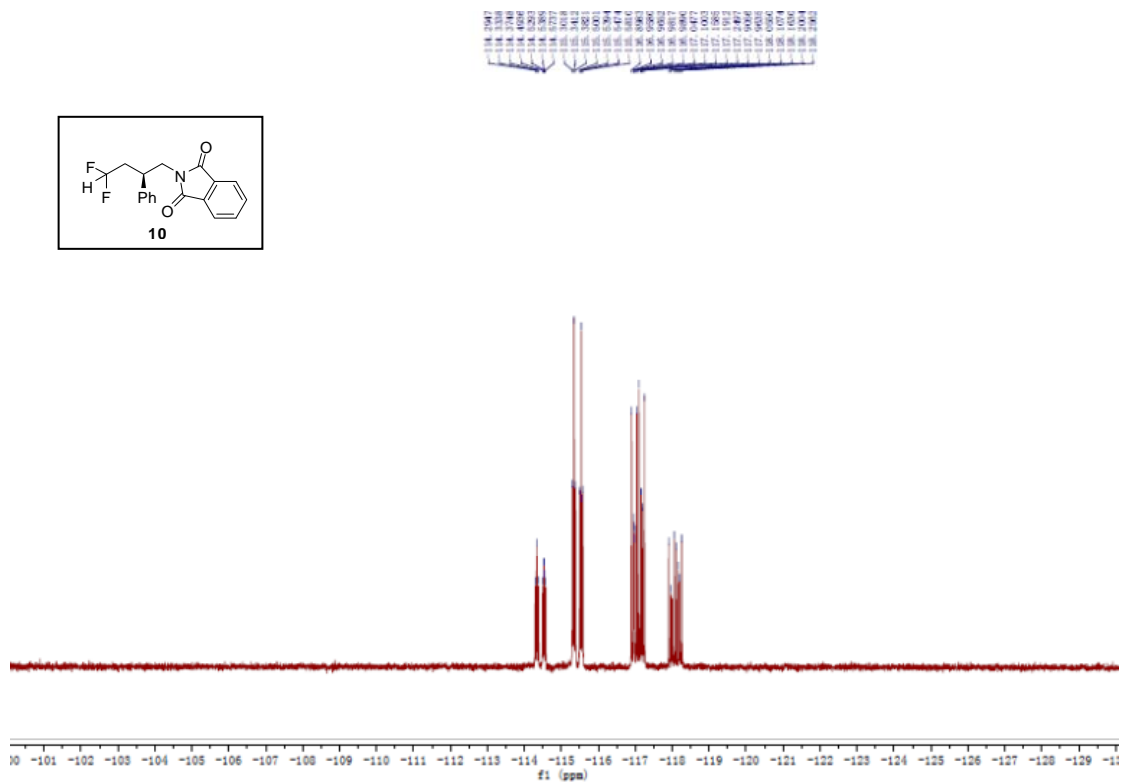


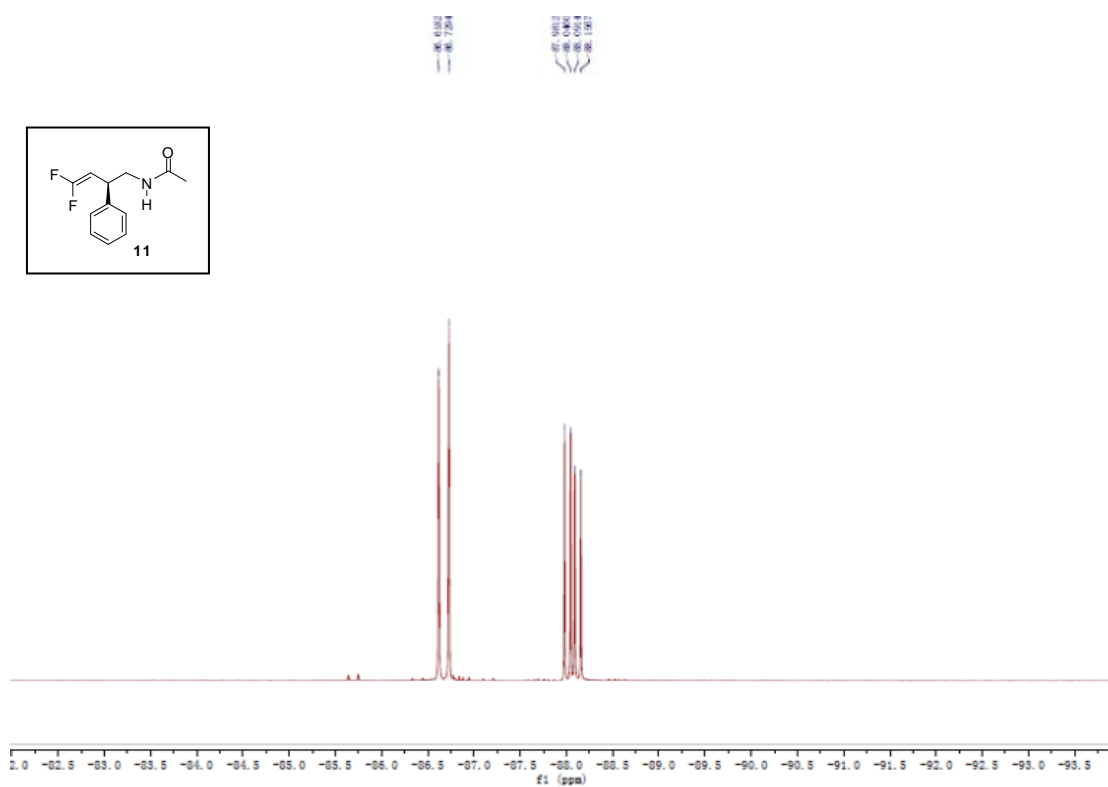
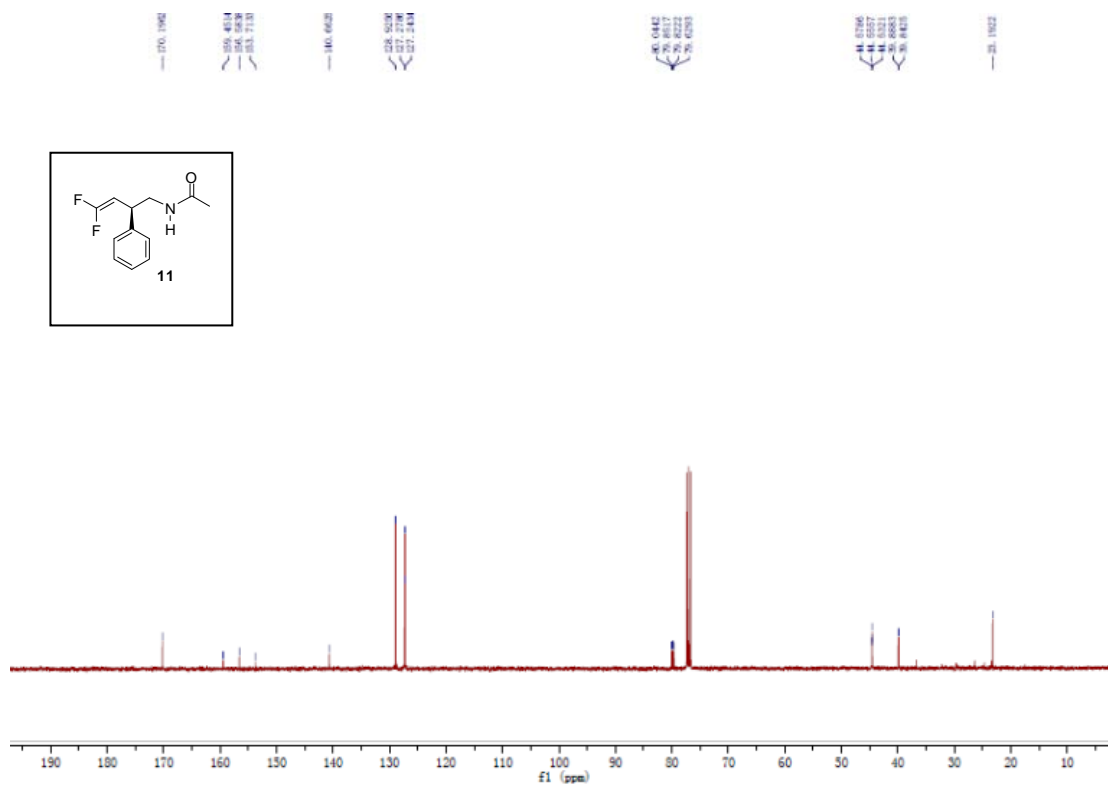


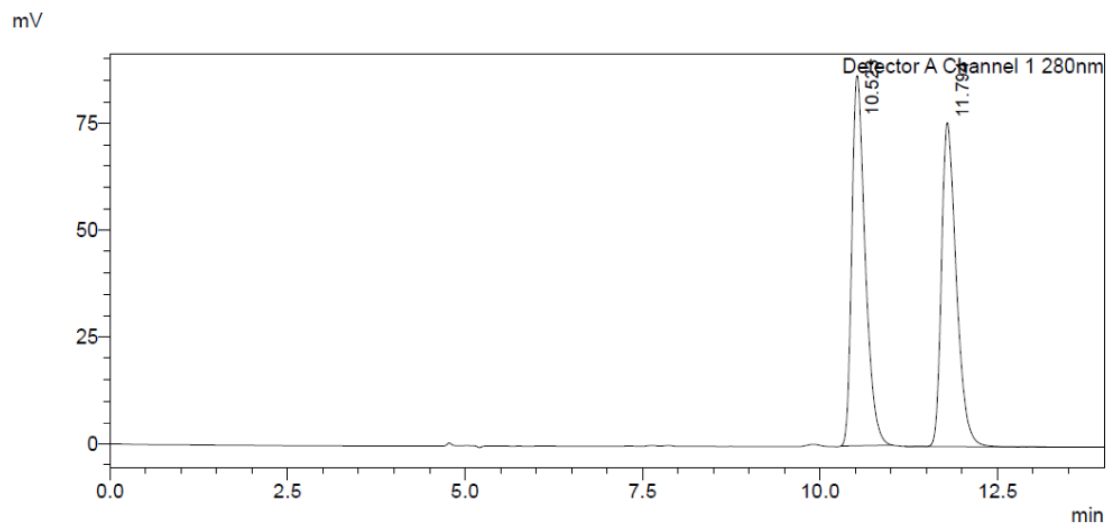
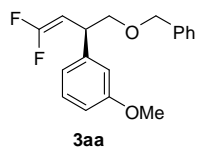








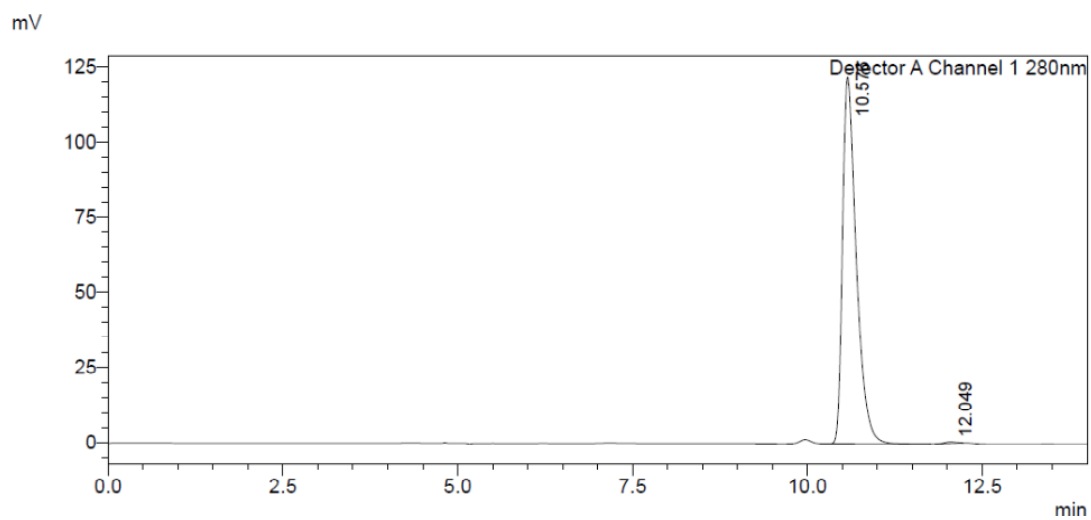




<Peak Table>

Detector A Channel 1 280nm

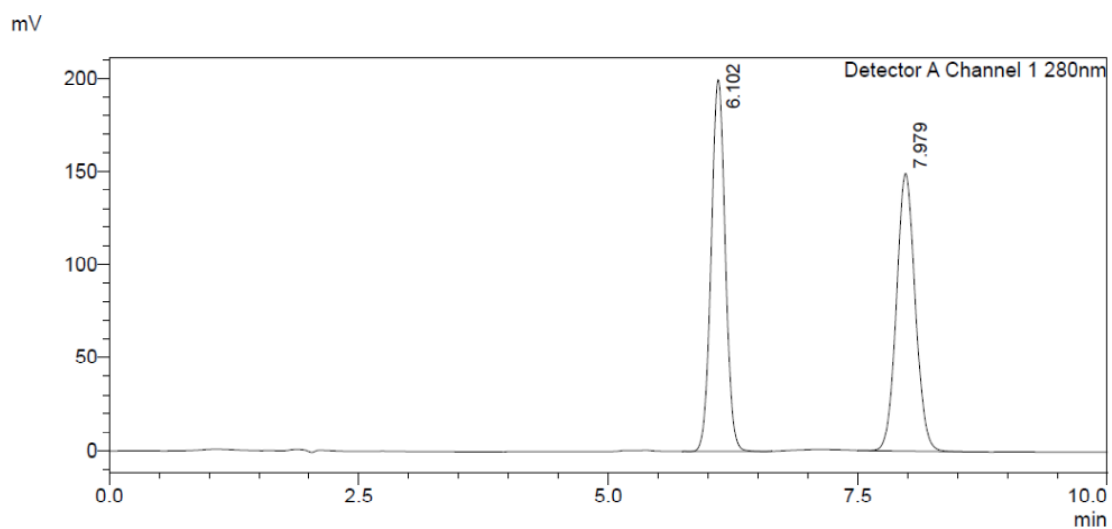
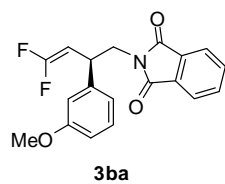
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.523	1133093	86637	50.661		M	
2	11.794	1103524	75760	49.339		M	
Total		2236616	162397				



<Peak Table>

Detector A Channel 1 280nm

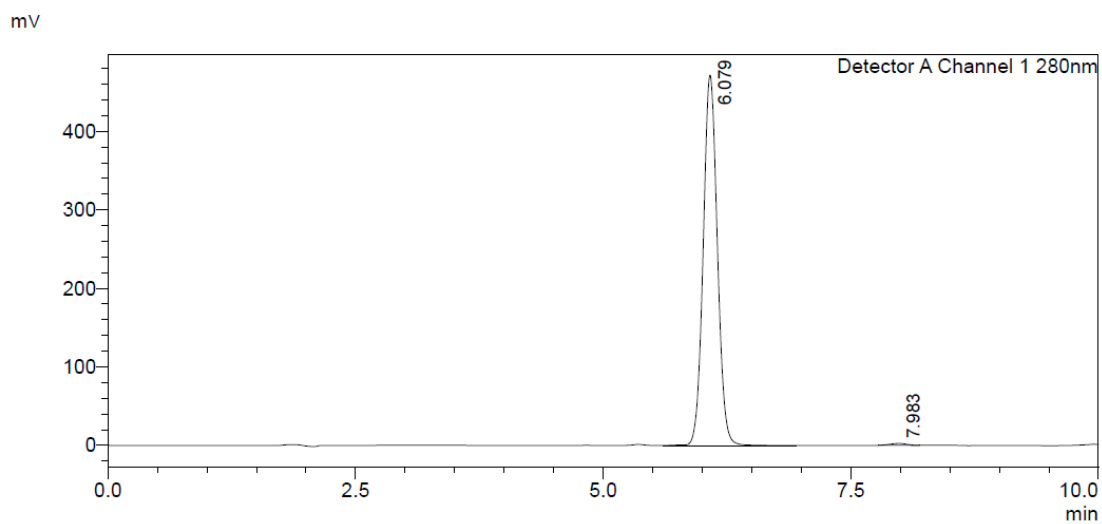
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.576	1663713	121891	99.679		M	
2	12.049	5364	495	0.321		M	
Total		1669077	122386				



<Peak Table>

Detector A Channel 1 280nm

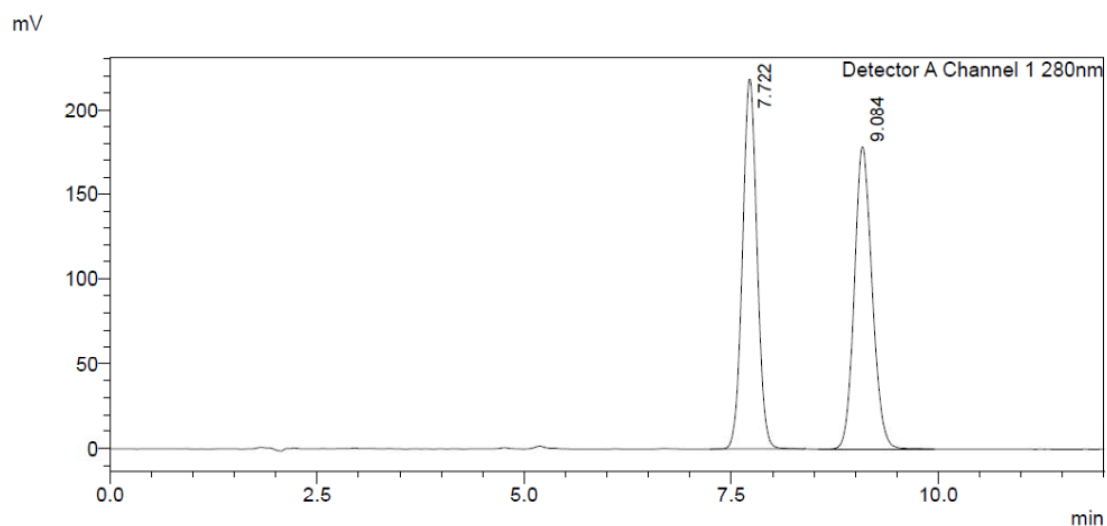
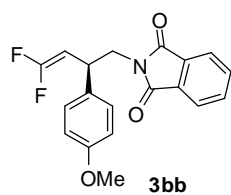
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.102	1951222	199869	50.025		M	
2	7.979	1949285	148856	49.975		M	
Total		3900507	348725				



<Peak Table>

Detector A Channel 1 280nm

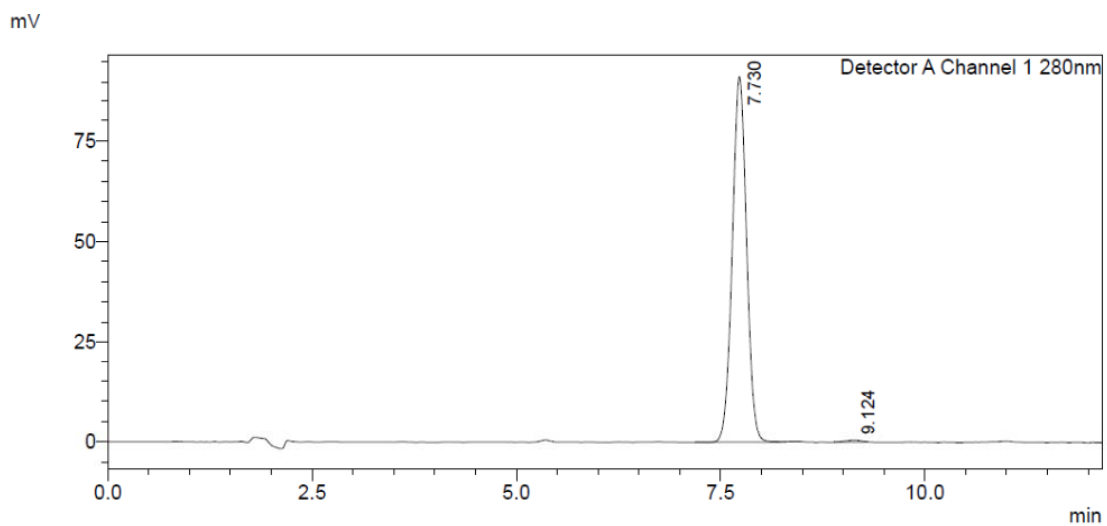
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.079	4679532	471659	99.384		M	
2	7.983	29016	2430	0.616		M	
Total		4708549	474089				



<Peak Table>

Detector A Channel 1 280nm

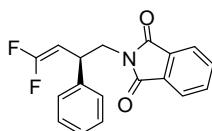
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.722	2658734	218661	49.999		M	
2	9.084	2658854	178417	50.001		M	
Total		5317588	397079				



<Peak Table>

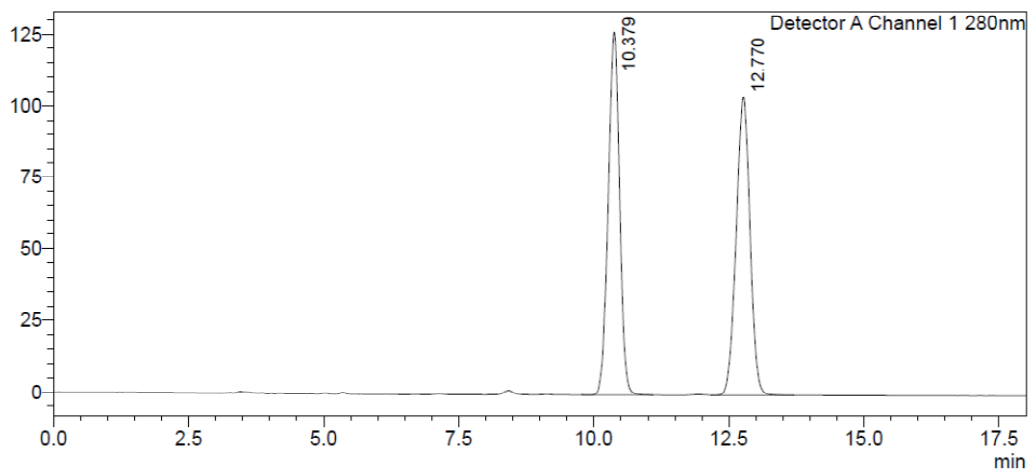
Detector A Channel 1 280nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.730	1110403	91372	99.499		M	
2	9.124	5595	452	0.501		M	
Total		1115998	91824				



3bc

mV

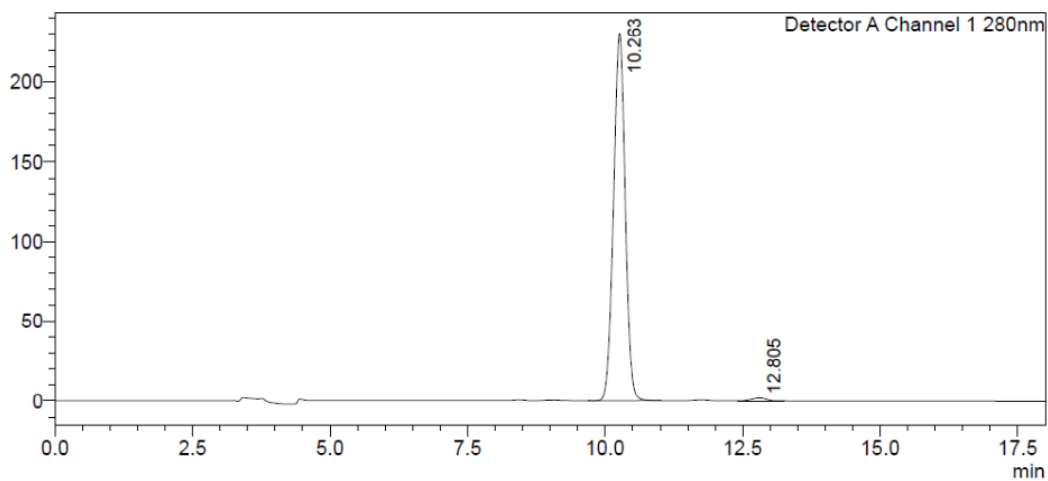


<Peak Table>

Detector A Channel 1 280nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.379	1861502	126752	49.971		M	
2	12.770	1863651	104242	50.029		M	
Total		3725153	230994				

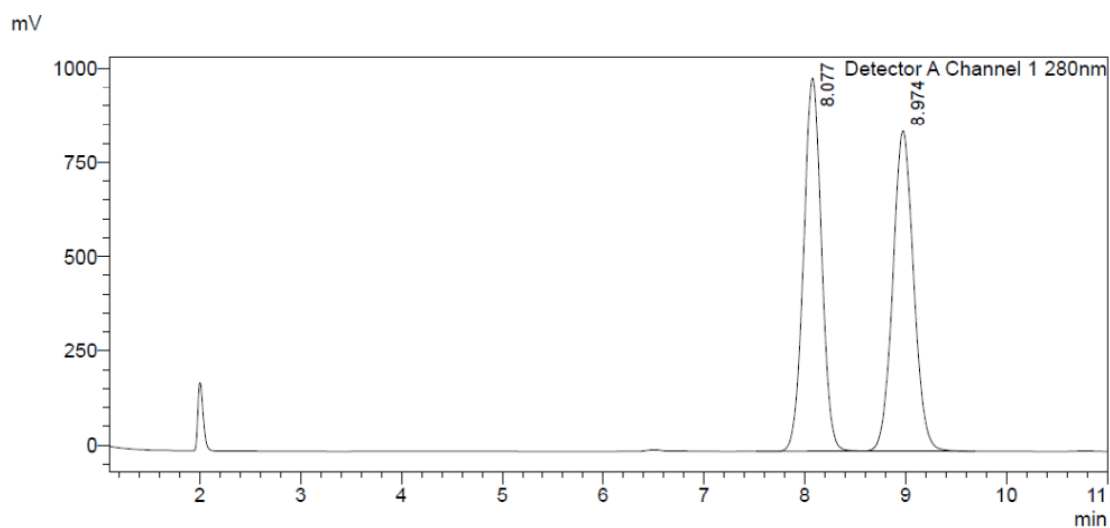
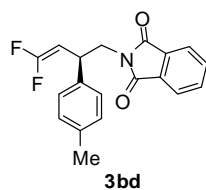
mV



<Peak Table>

Detector A Channel 1 280nm

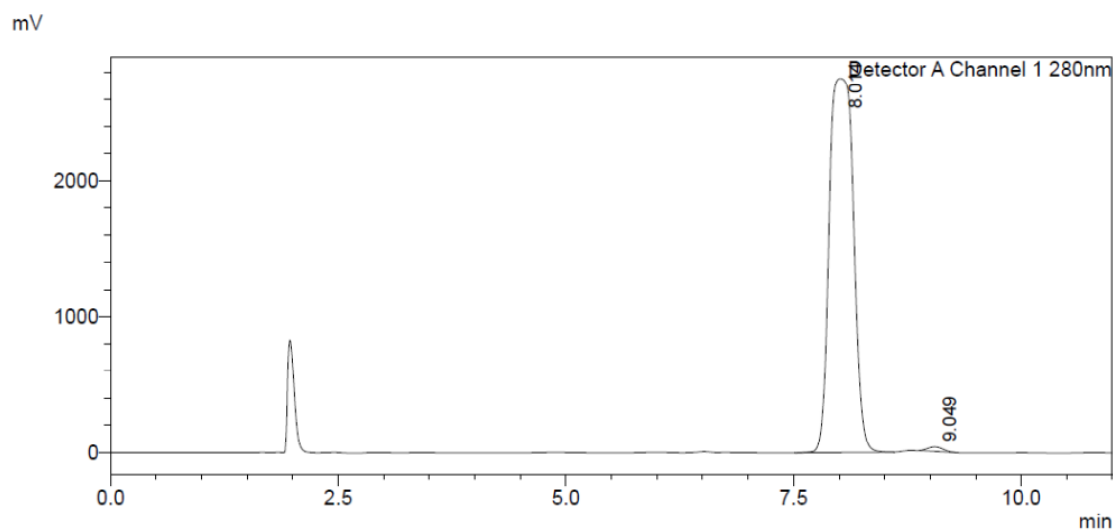
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.263	3409204	230457	99.075		M	
2	12.805	31814	1785	0.925		M	
Total		3441018	232242				



<Peak Table>

Detector A Channel 1 280nm

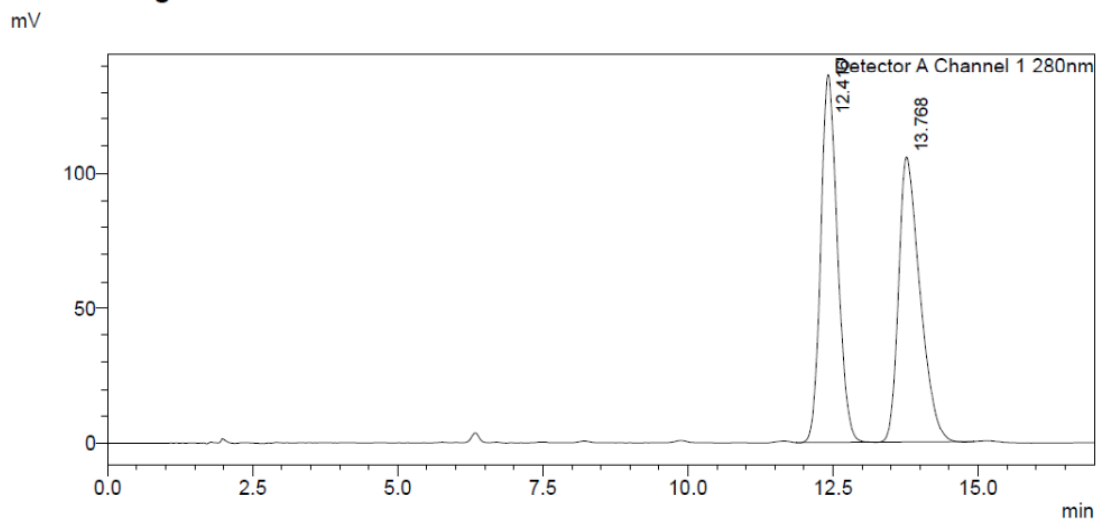
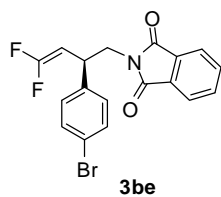
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.077	12180725	989764	49.992		M	
2	8.974	12184485	847279	50.008		M	
Total		24365210	1837042				



<Peak Table>

Detector A Channel 1 280nm

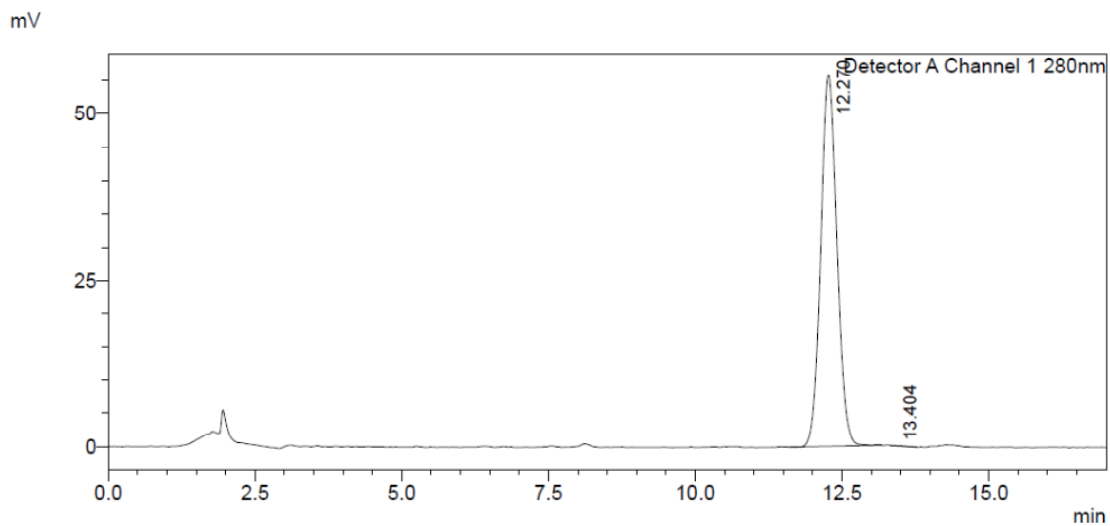
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.014	50863427	2753754	99.254		M	
2	9.049	382059	33145	0.746		M	
Total		51245485	2786899				



<Peak Table>

Detector A Channel 1 280nm

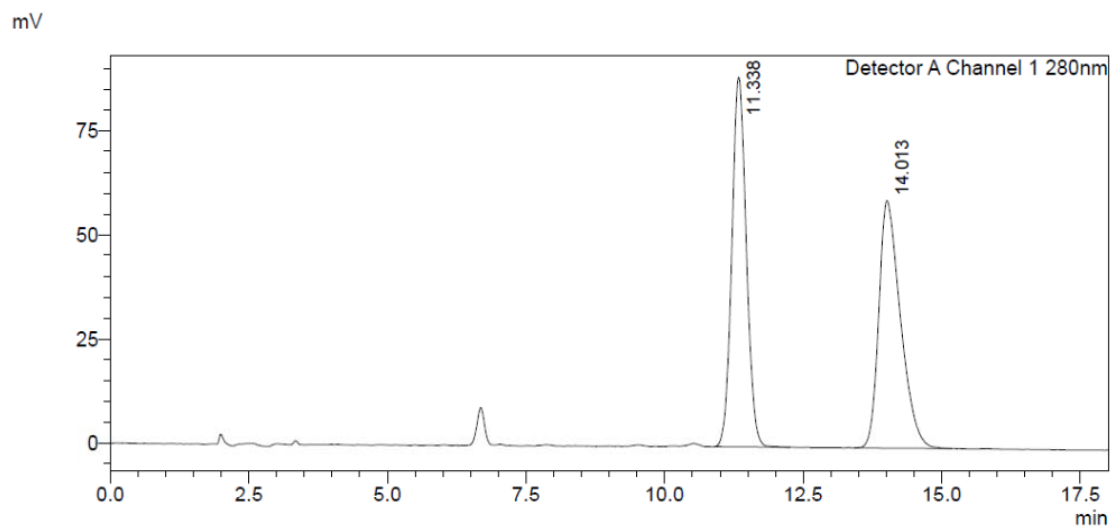
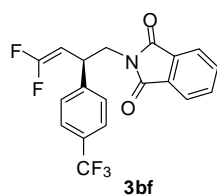
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.416	2723738	136353	50.101		M	
2	13.768	2712784	105549	49.899		M	
Total		5436522	241902				



<Peak Table>

Detector A Channel 1 280nm

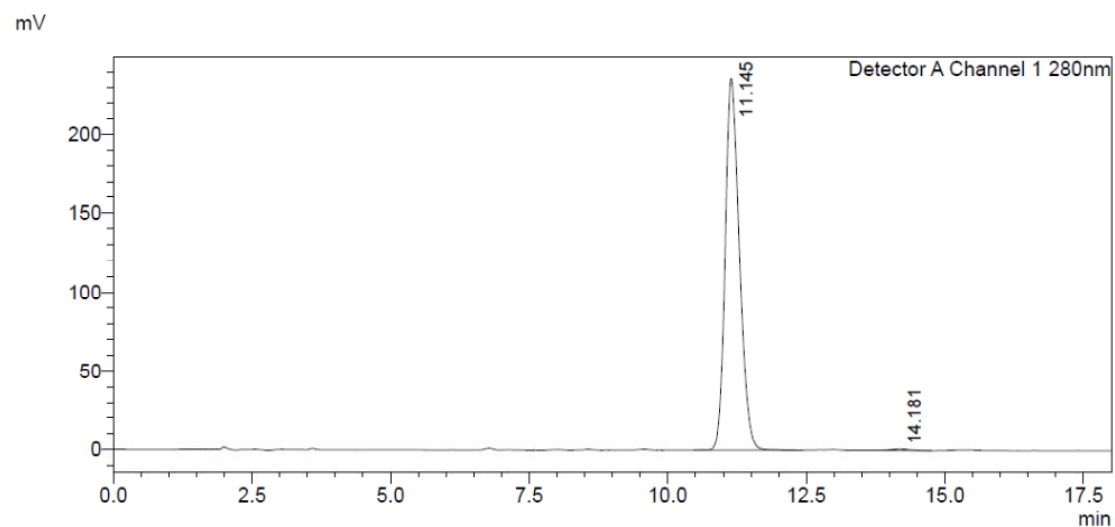
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.270	1072265	55843	99.975		M	
2	13.404	266	37	0.025		M	
Total		1072532	55880				



<Peak Table>

Detector A Channel 1 280nm

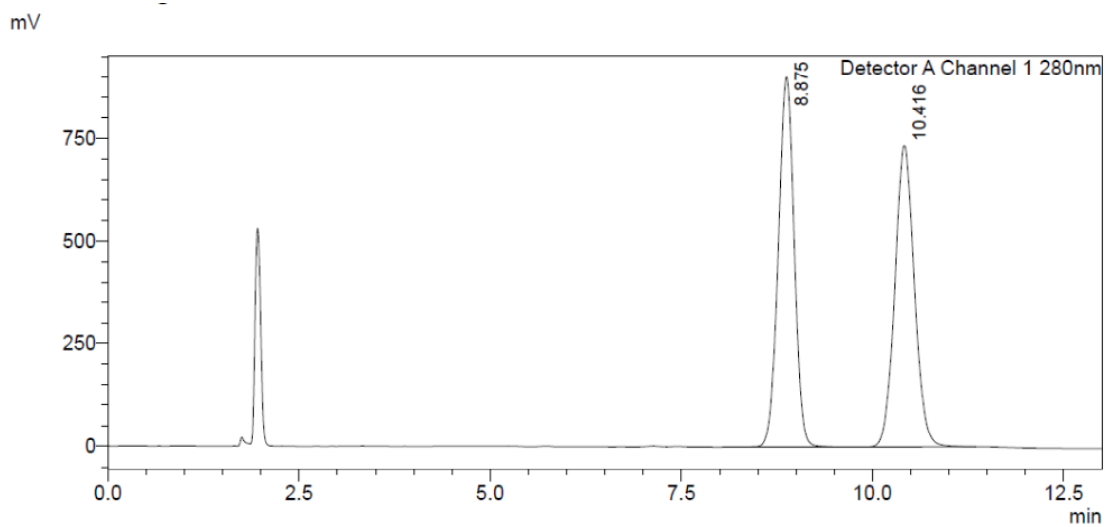
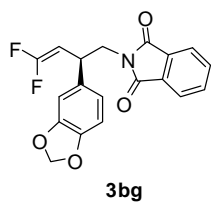
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.338	1610393	88934	49.932		M	
2	14.013	1614748	59478	50.068		M	
Total		3225141	148413				



<Peak Table>

Detector A Channel 1 280nm

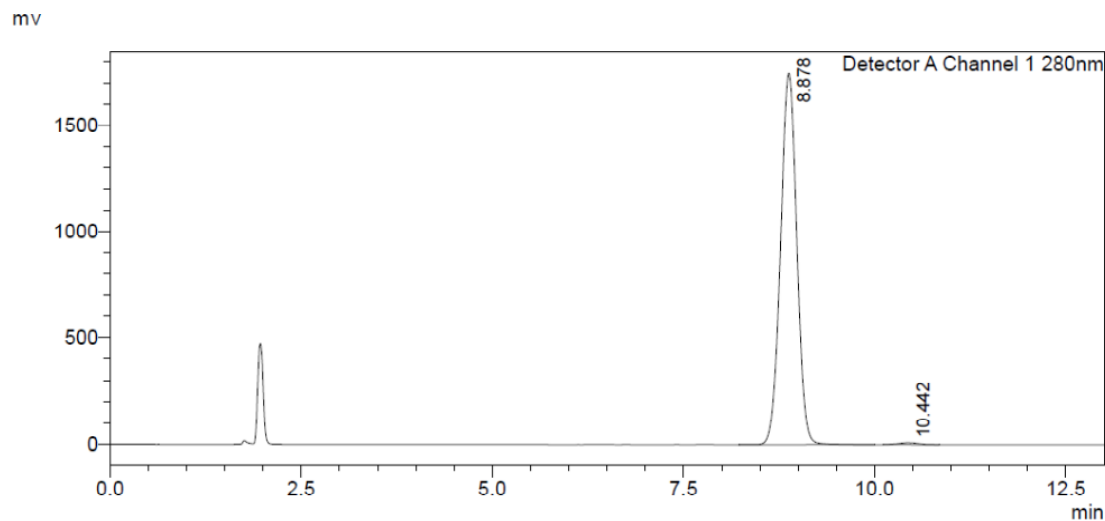
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.145	4223211	236475	99.506		M	
2	14.181	20981	938	0.494		M	
Total		4244192	237413				



<Peak Table>

Detector A Channel 1 280nm

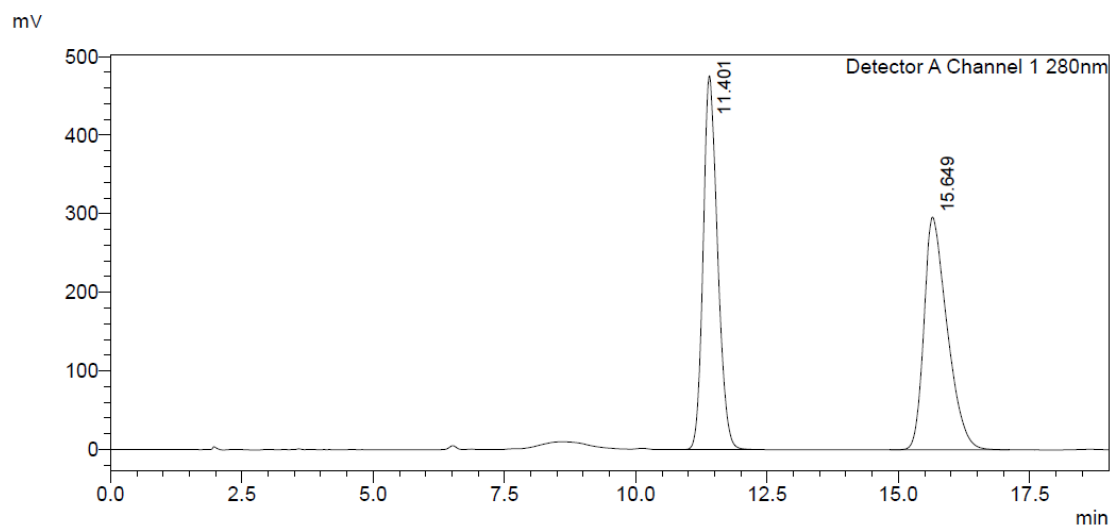
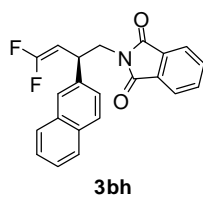
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.875	13039089	902707	49.919		M	
2	10.416	13081154	734479	50.081		M	
Total		26120243	1637186				



<Peak Table>

Detector A Channel 1 280nm

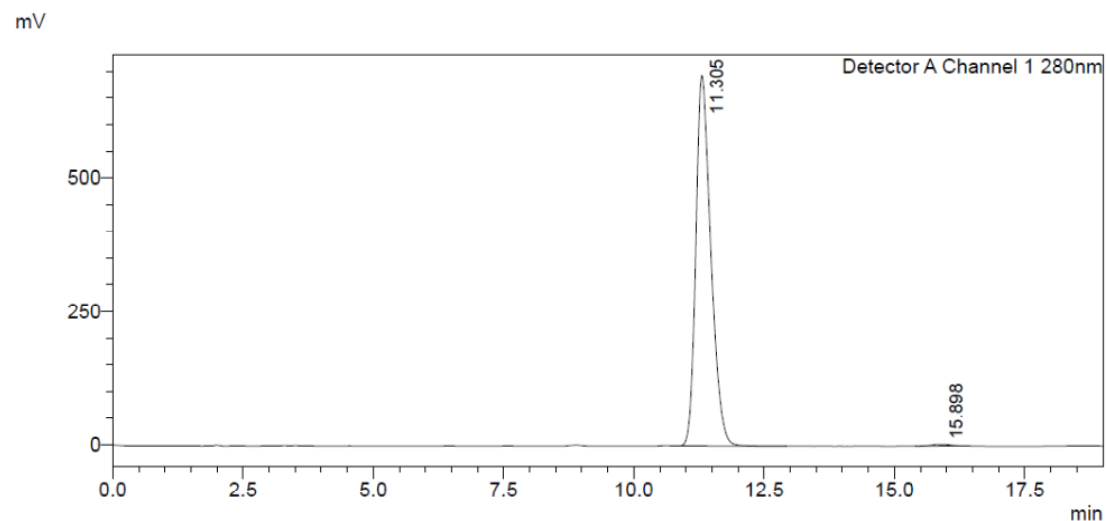
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.878	25781118	1746772	99.405		M	
2	10.442	154251	8769	0.595		M	
Total		25935369	1755541				



<Peak Table>

Detector A Channel 1 280nm

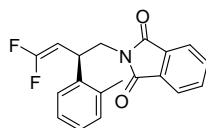
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.401	9085482	475459	49.961		M	
2	15.649	9099843	296032	50.039		M	
Total		18185325	771491				



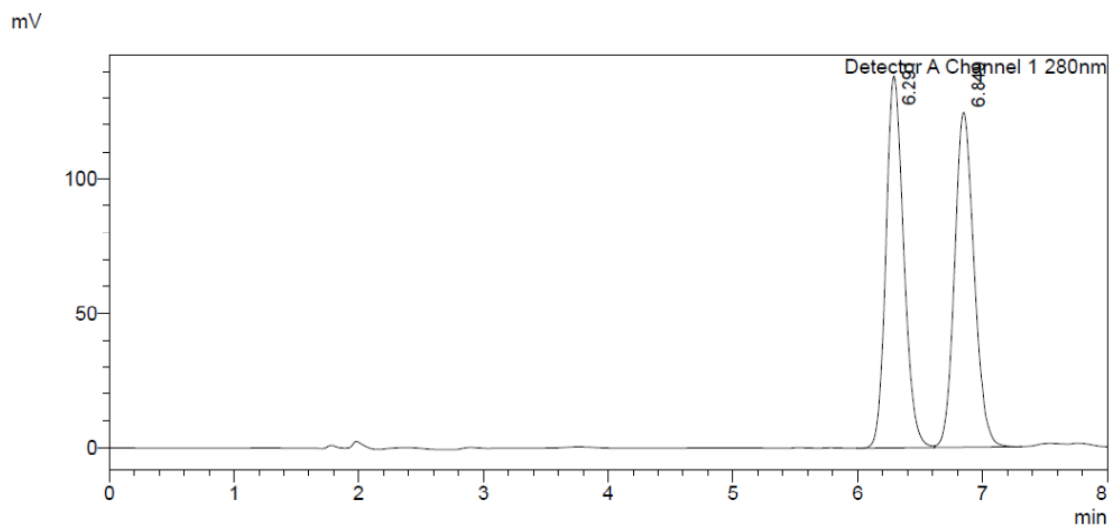
<Peak Table>

Detector A Channel 1 280nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.305	13932685	694867	99.428		M	
2	15.898	80132	3153	0.572		M	
Total		14012817	698020				



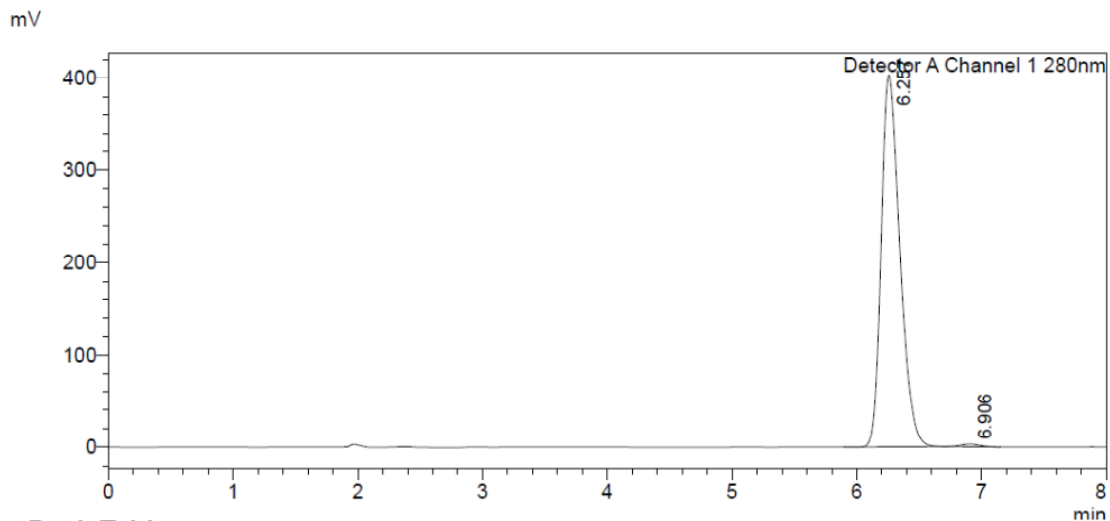
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<Peak Table>

Detector A Channel 1 280nm

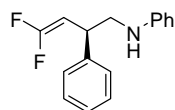
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.291	1367153	138507	50.211		M	
2	6.849	1355665	124651	49.789		V M	
Total		2722819	263158				



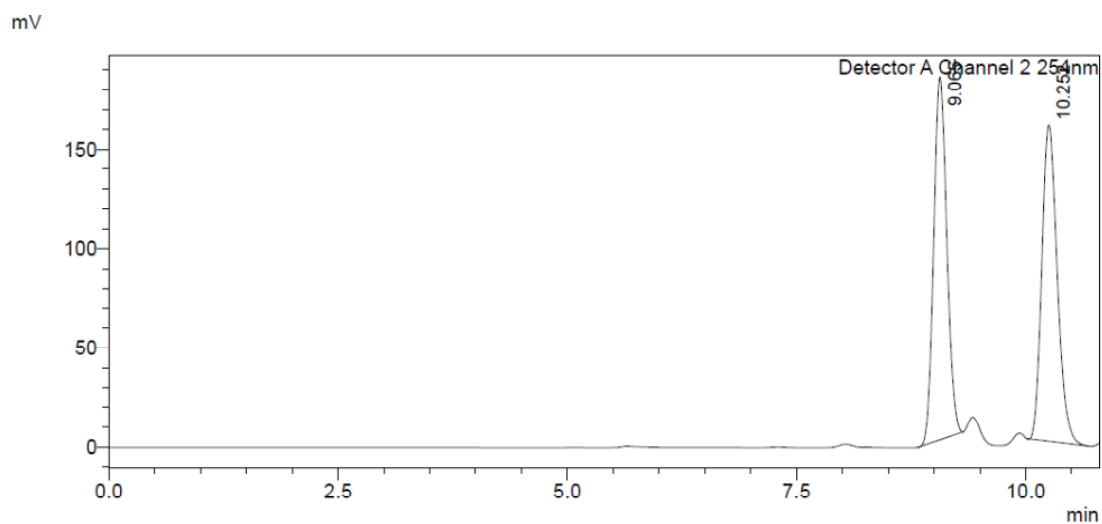
<Peak Table>

Detector A Channel 1 280nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.257	4192521	403505	99.279		M	
2	6.906	30459	2879	0.721		M	
Total		4222980	406384				



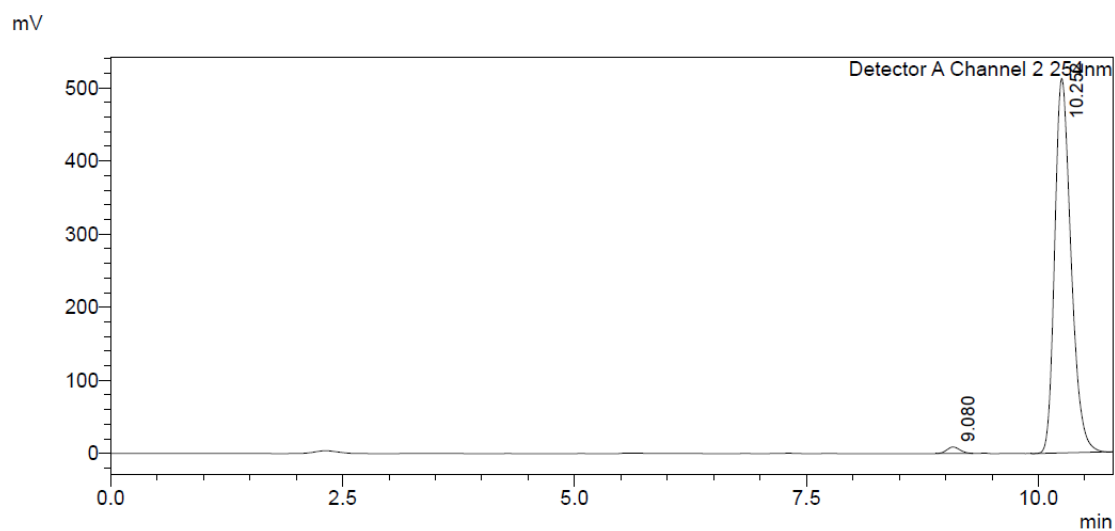
3cc



<Peak Table>

Detector A Channel 2 254nm

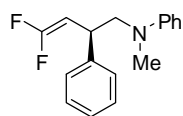
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.065	1815523	182867	49.420		M	
2	10.252	1858100	159557	50.580		M	
Total		3673623	342424				



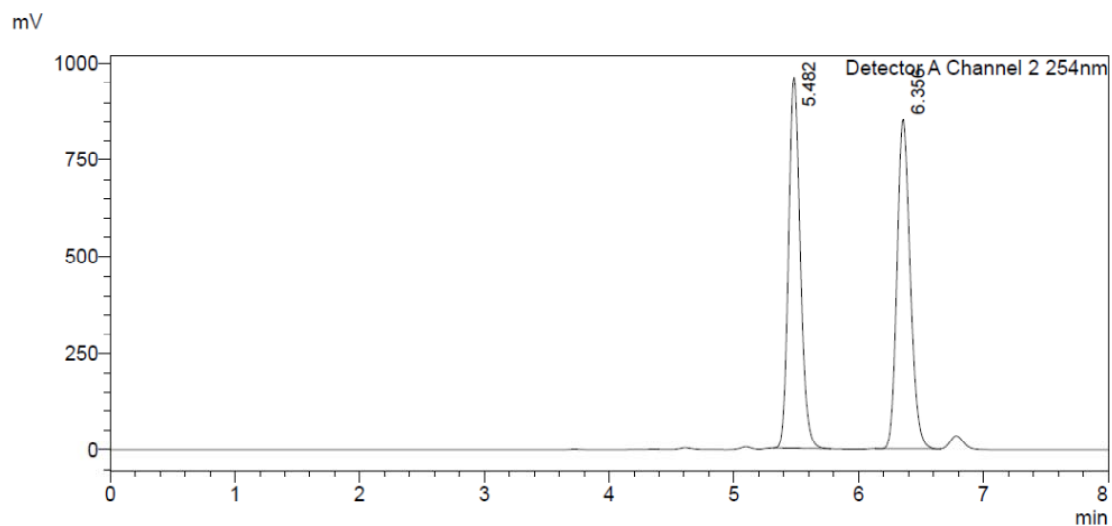
<Peak Table>

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.080	85668	8762	1.348		M	
2	10.252	6271650	512357	98.652		M	
Total		6357318	521118				



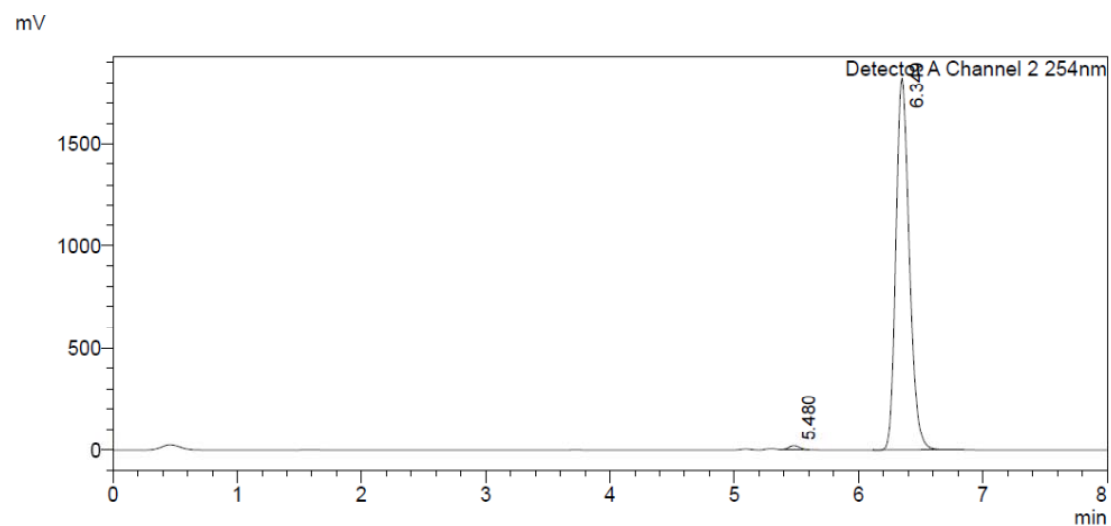
3dc



<Peak Table>

Detector A Channel 2 254nm

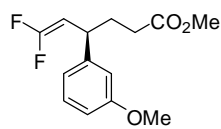
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.482	6299548	962577	50.034		M	
2	6.356	6290916	855120	49.966		M	
Total		12590464	1817698				



<Peak Table>

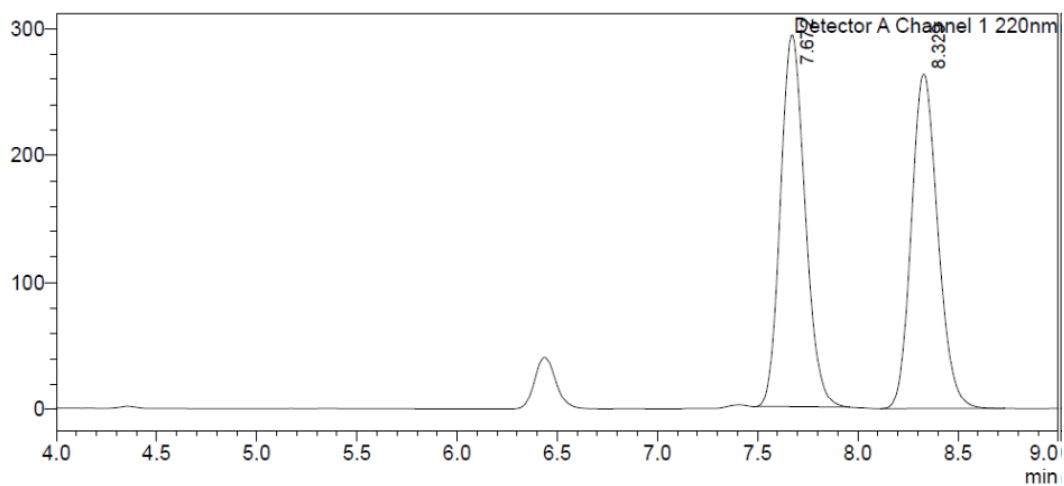
Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.480	110740	18985	0.805		M	
2	6.349	13651318	1822772	99.195		M	
Total		13762057	1841756				



3ea

mV

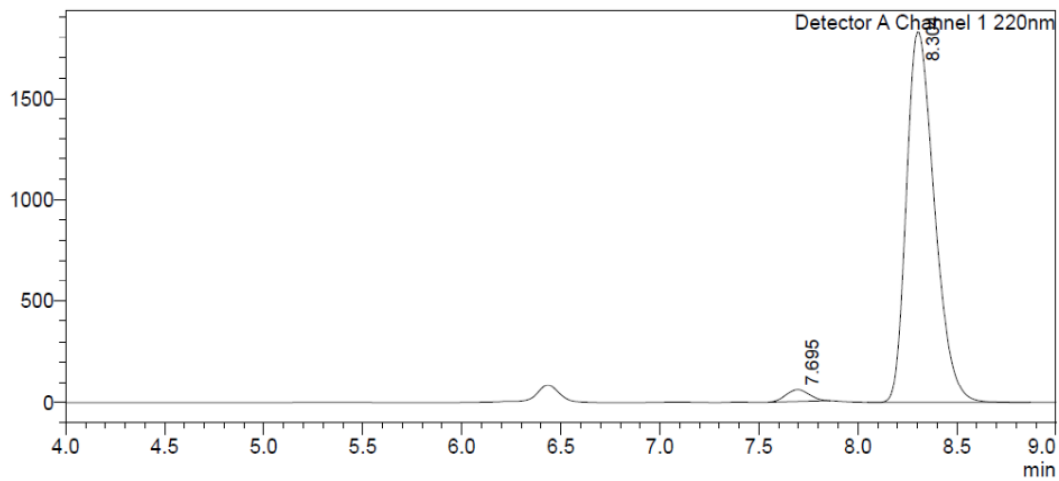


<Peak Table>

Detector A Channel 1 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.672	2502178	293407	50.726		M	
2	8.329	2430535	263760	49.274		M	
Total		4932713	557167				

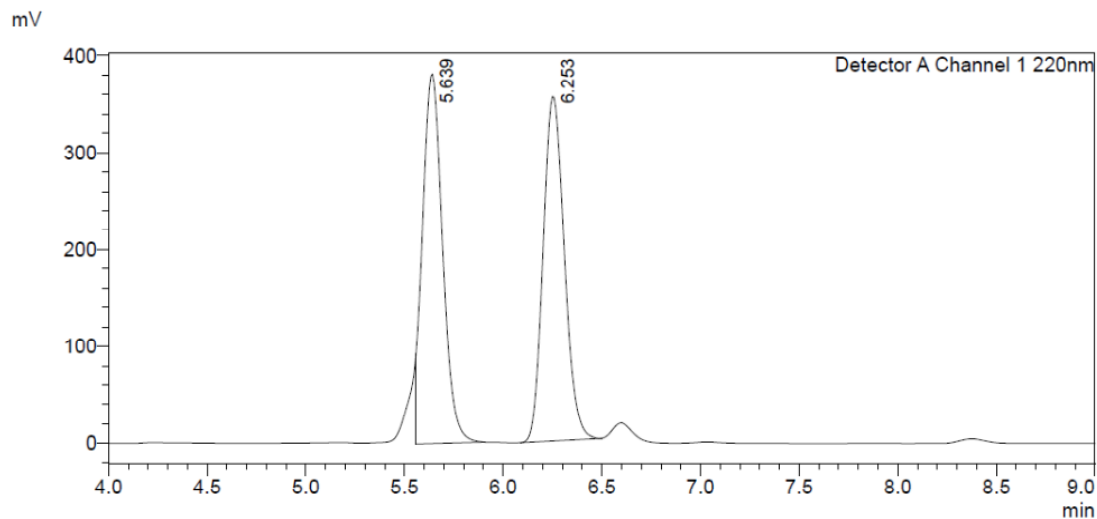
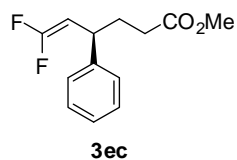
mV



<Peak Table>

Detector A Channel 1 220nm

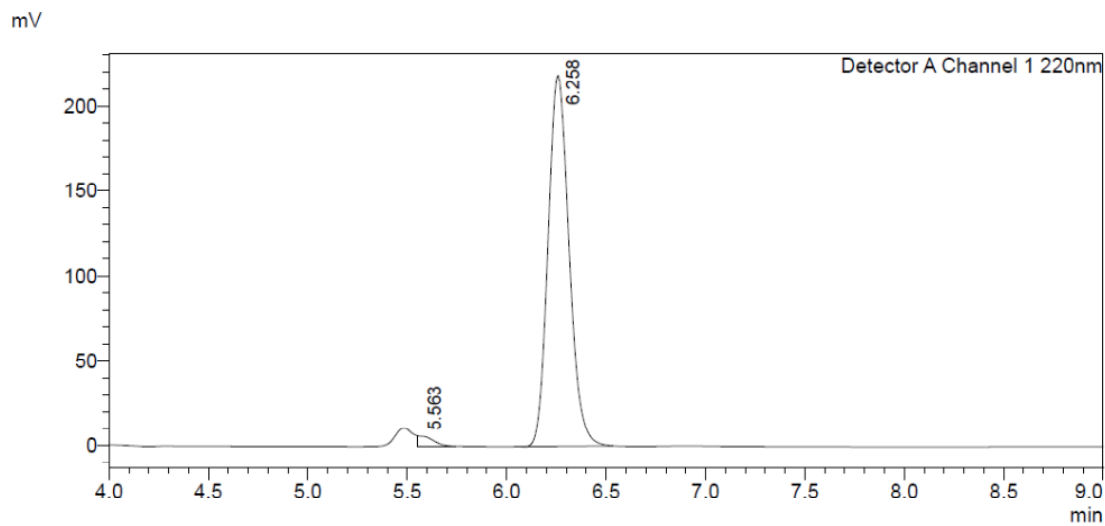
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.695	473763	57847	2.561		M	
2	8.304	18024341	1826824	97.439		M	
Total		18498104	1884671				



<Peak Table>

Detector A Channel 1 220nm

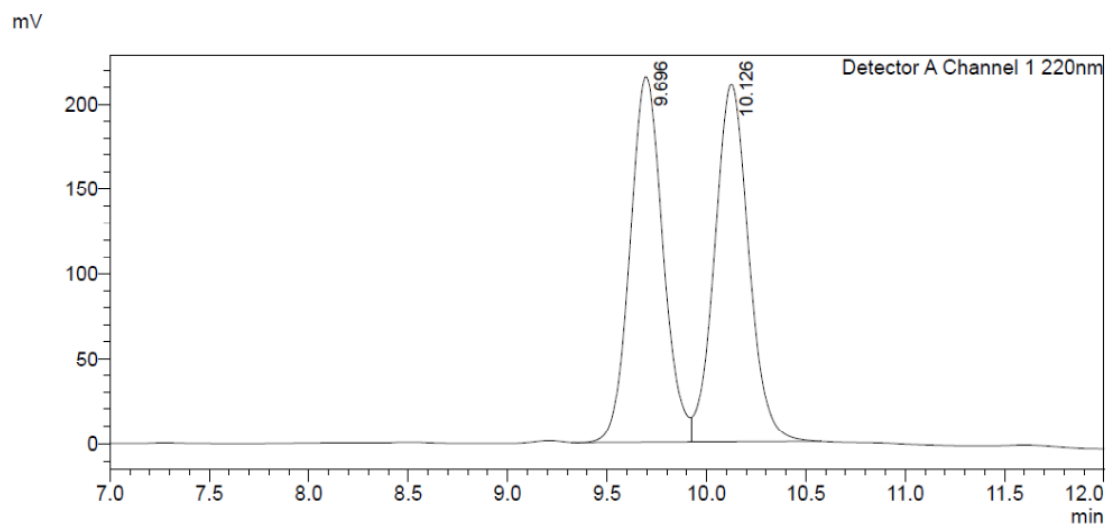
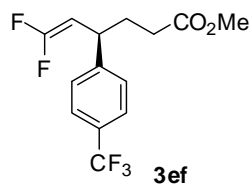
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.639	2661151	381404	50.047		M	
2	6.253	2656166	355424	49.953		M	
Total		5317317	736827				



<Peak Table>

Detector A Channel 1 220nm

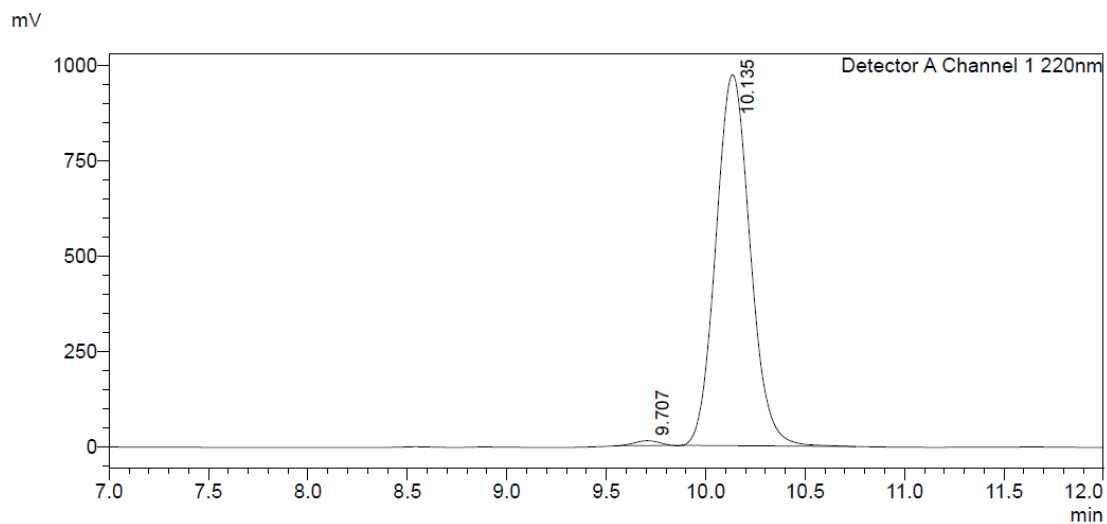
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.563	32431	6111	1.978		M	
2	6.258	1607100	218779	98.022		M	
Total		1639531	224890				



<Peak Table>

Detector A Channel 1 220nm

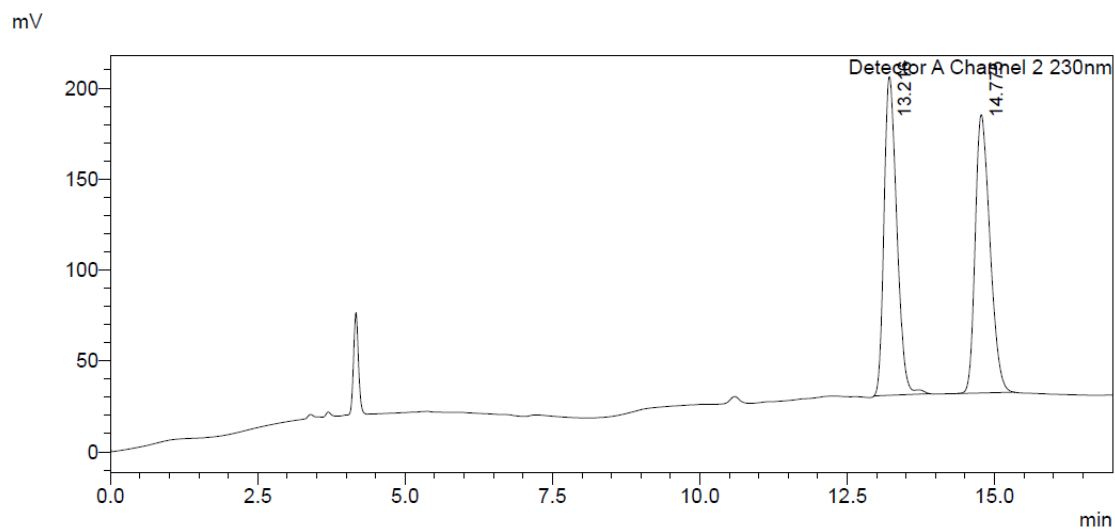
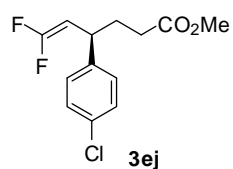
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.696	2487720	215896	49.739		M	
2	10.126	2513794	211226	50.261		V M	
Total		5001514	427122				



<Peak Table>

Detector A Channel 1 220nm

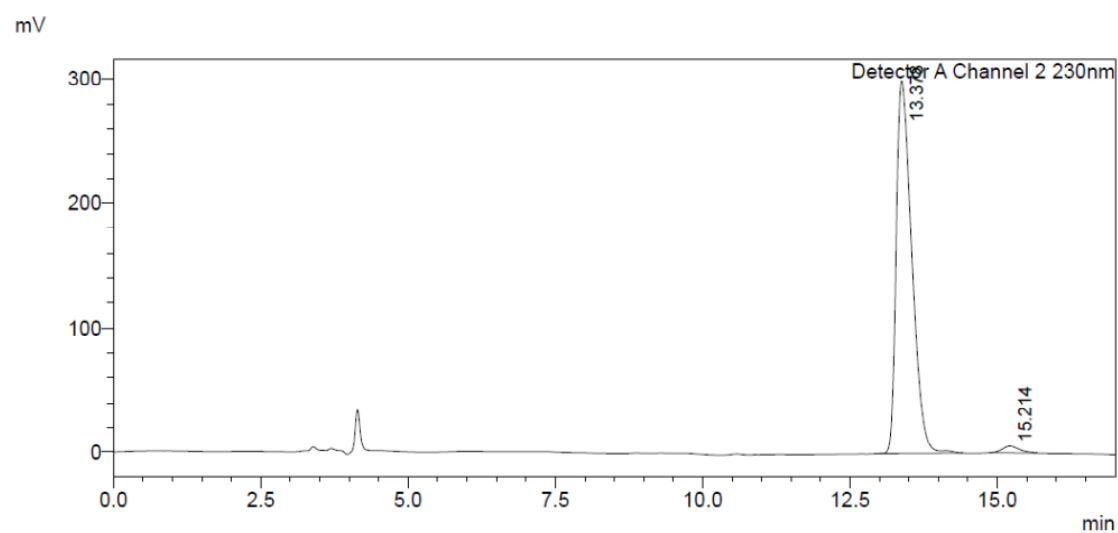
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.707	107143	12762	0.910		M	
2	10.135	11660498	972042	99.090		M	
Total		11767641	984804				



<Peak Table>

Detector A Channel 2 230nm

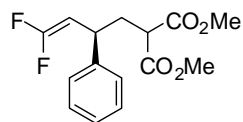
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.216	2646899	175270	49.806		M	
2	14.775	2667569	153029	50.194		M	
Total		5314468	328299				



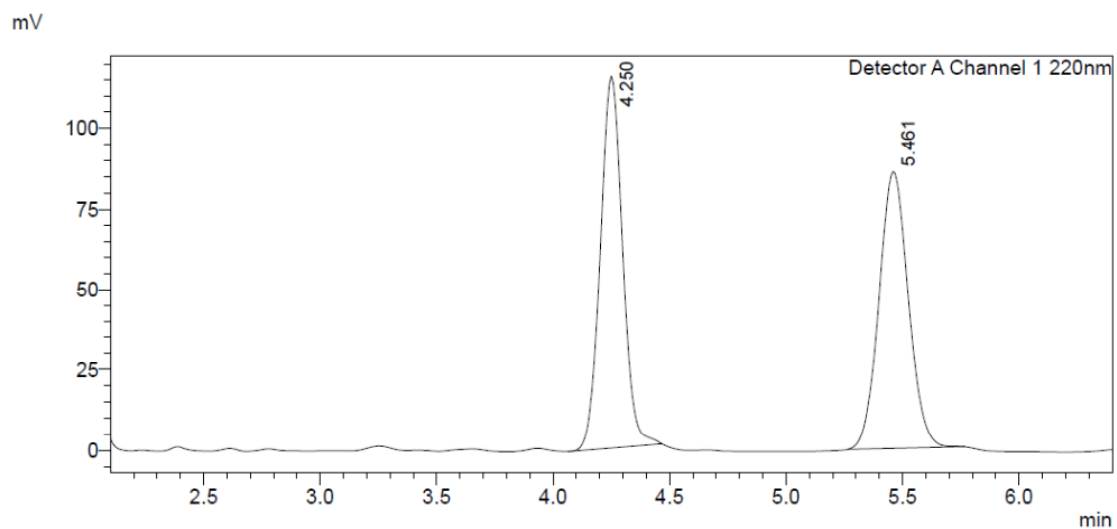
<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.378	5522722	299902	98.079		M	
2	15.214	108182	5376	1.921		M	
Total		5630904	305279				



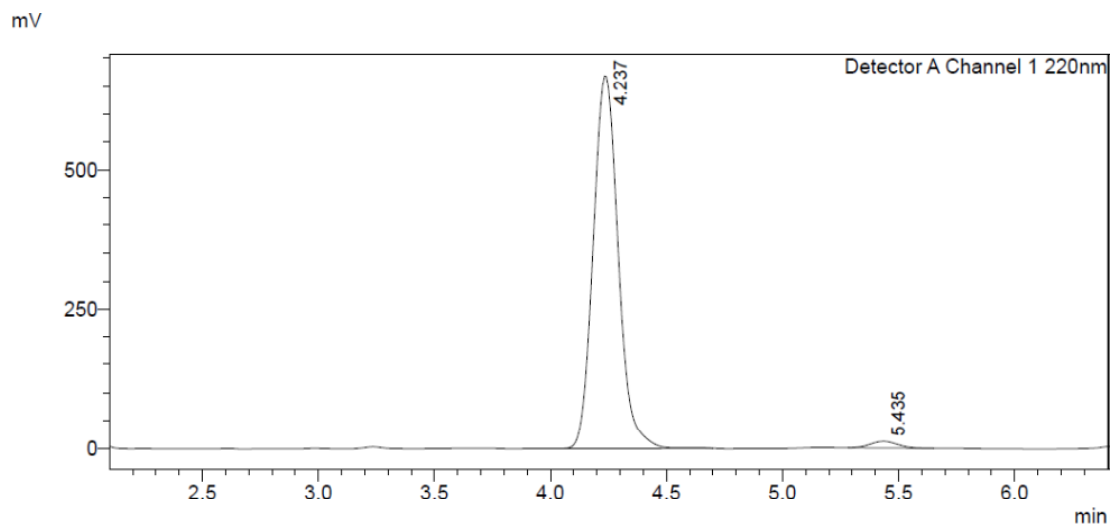
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<Peak Table>

Detector A Channel 1 220nm

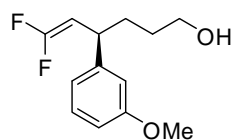
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.250	766469	115325	50.494		M	
2	5.461	751470	86090	49.506		M	
Total		1517938	201415				



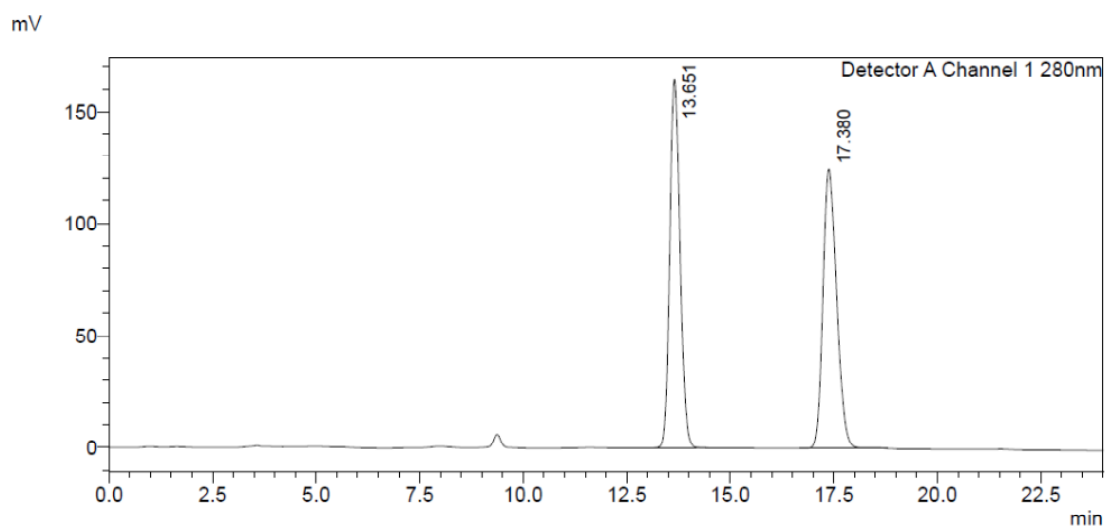
<Peak Table>

Detector A Channel 1 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.237	5002141	668799	98.148		M	
2	5.435	94379	11699	1.852		M	
Total		5096520	680498				



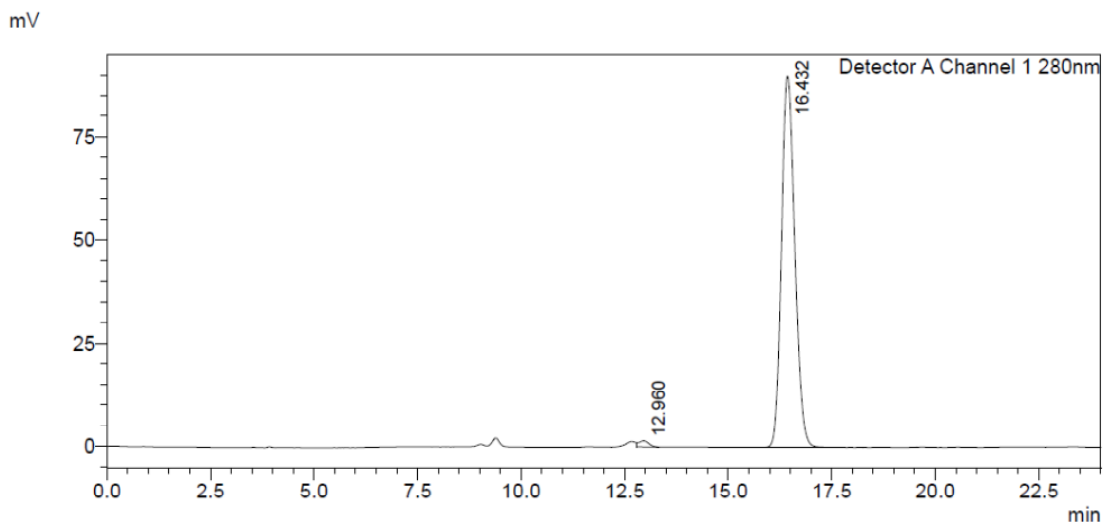
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<Peak Table>

Detector A Channel 1 280nm

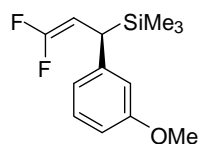
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.651	2849577	164954	49.811		M	
2	17.380	2871212	124509	50.189		M	
Total		5720789	289464				



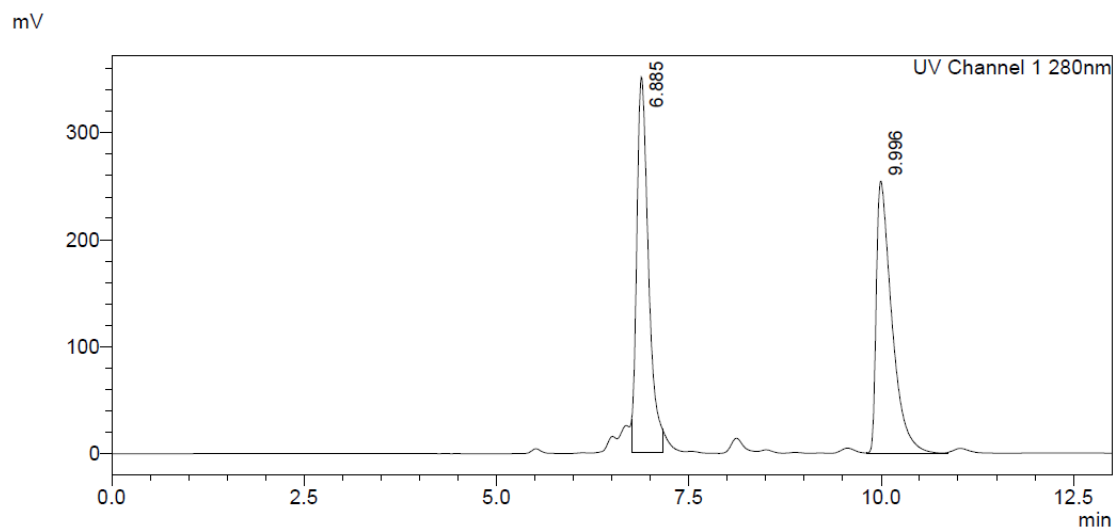
<Peak Table>

Detector A Channel 1 280nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.960	23521	1429	1.156		M	
2	16.432	2010947	90134	98.844		M	
Total		2034469	91562				



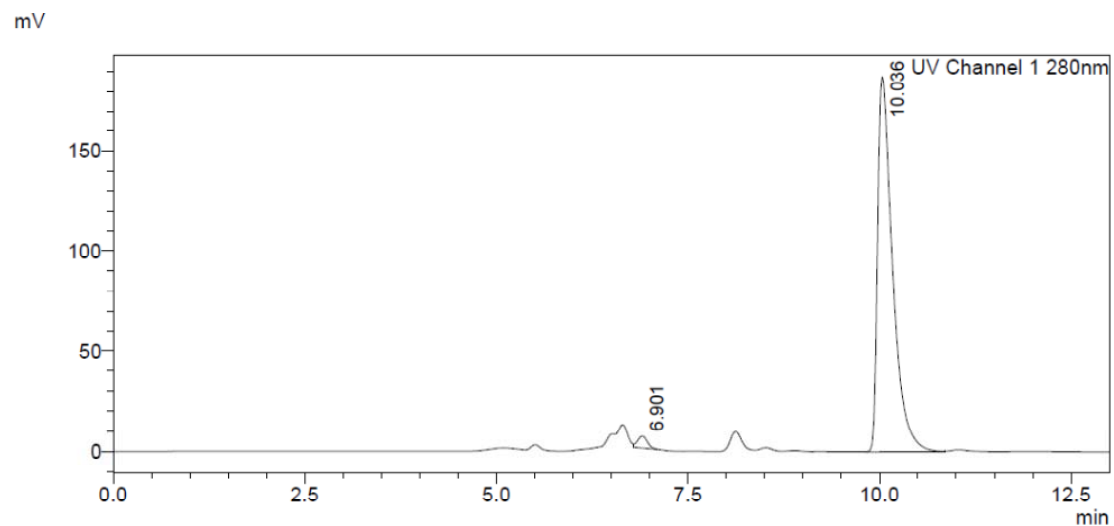
3ha



<Peak Table>

UV Channel 1 280nm

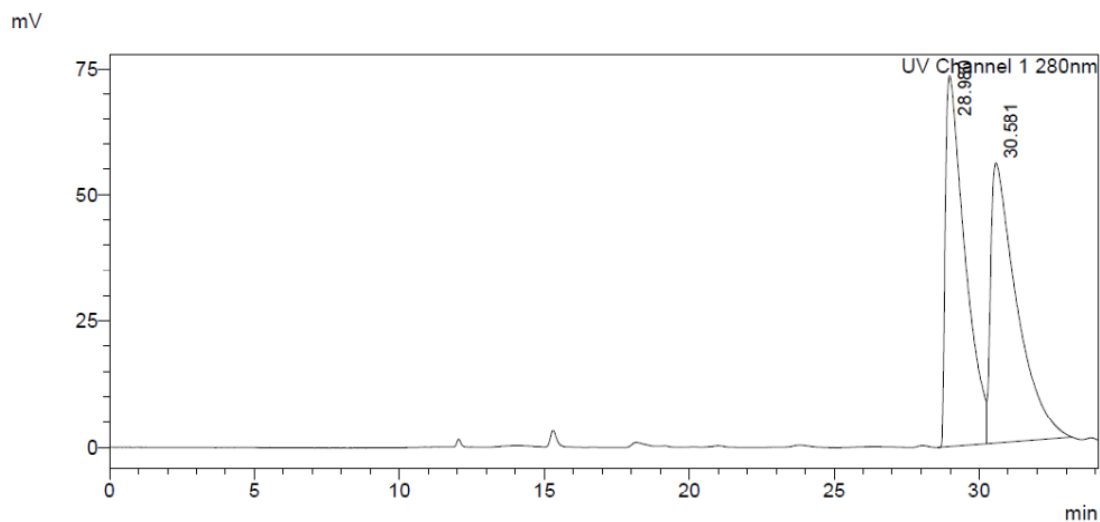
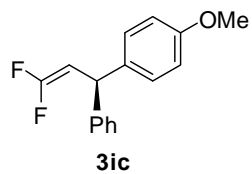
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.885	3689543	350815	50.441		M	
2	9.996	3625079	255117	49.559		M	
Total		7314622	605932				



<Peak Table>

UV Channel 1 280nm

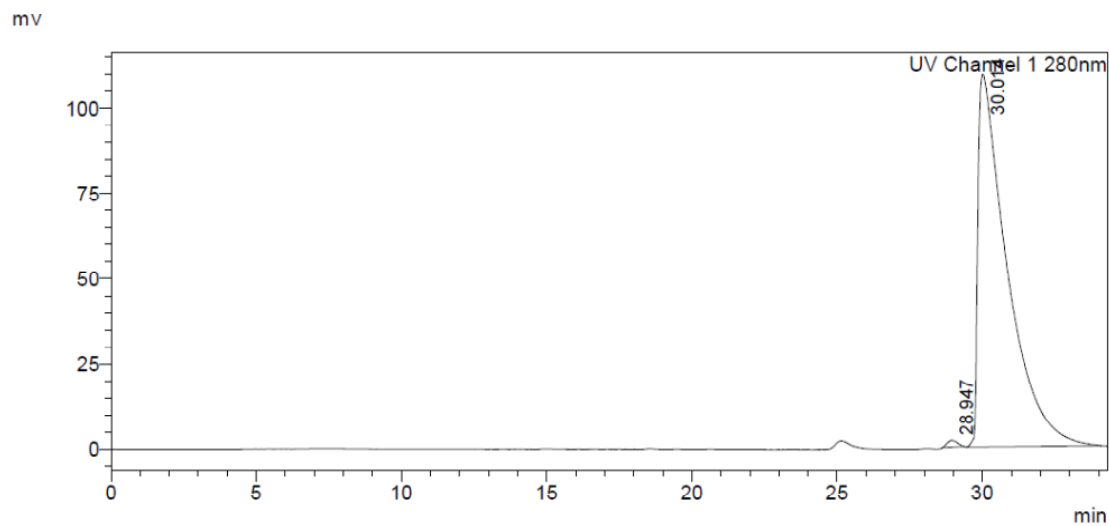
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.901	51881	5879	2.002		M	
2	10.036	2539657	187499	97.998		M	
Total		2591538	193378				



<Peak Table>

UV Channel 1 280nm

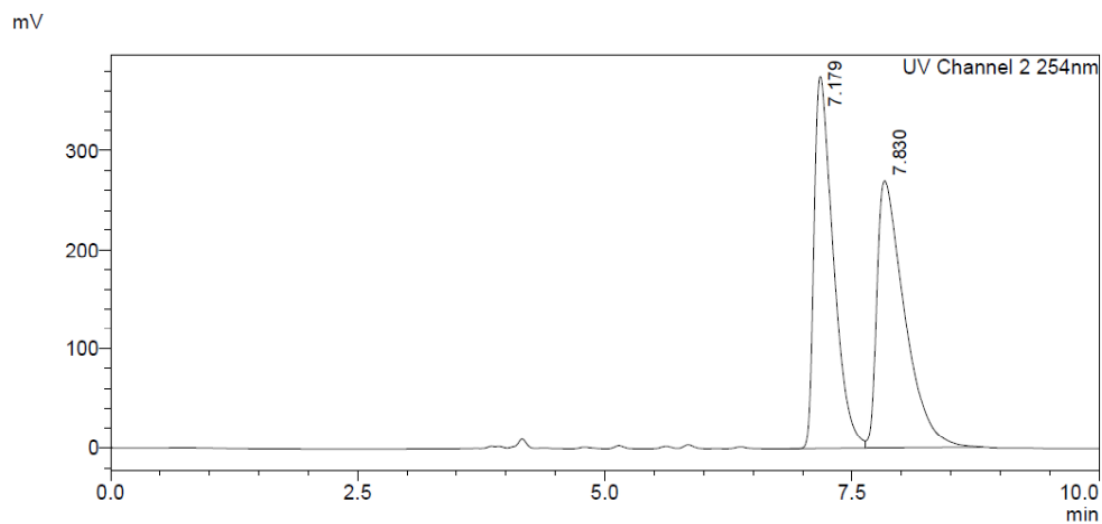
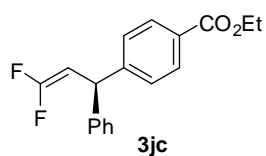
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	28.980	3442216	73523	49.890		M	
2	30.581	3457347	55316	50.110		V M	
Total		6899563	128839				



<Peak Table>

UV Channel 1 280nm

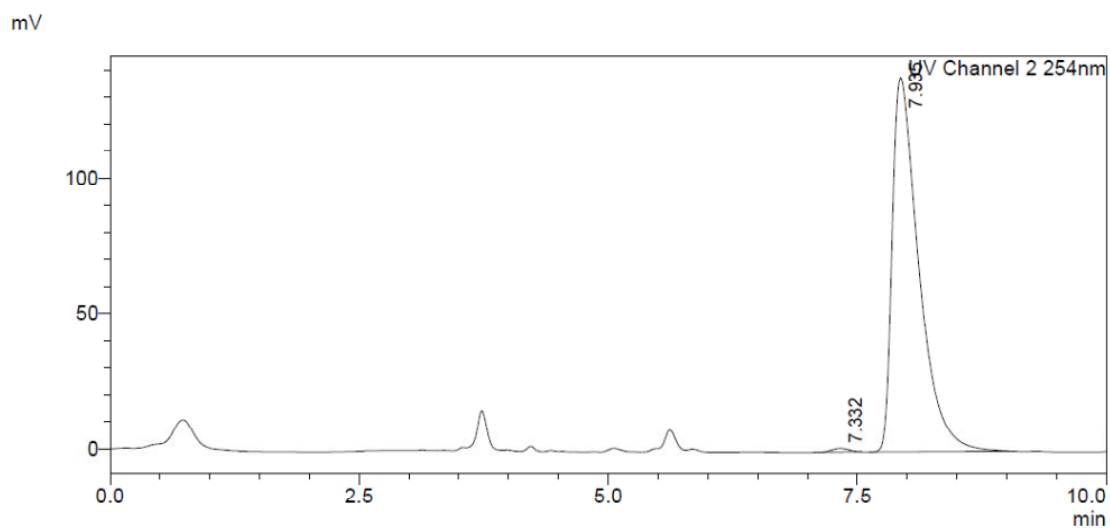
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	28.947	49044	2011	0.640		M	
2	30.014	7618139	109363	99.360		M	
Total		7667183	111375				



<Peak Table>

UV Channel 2 254nm

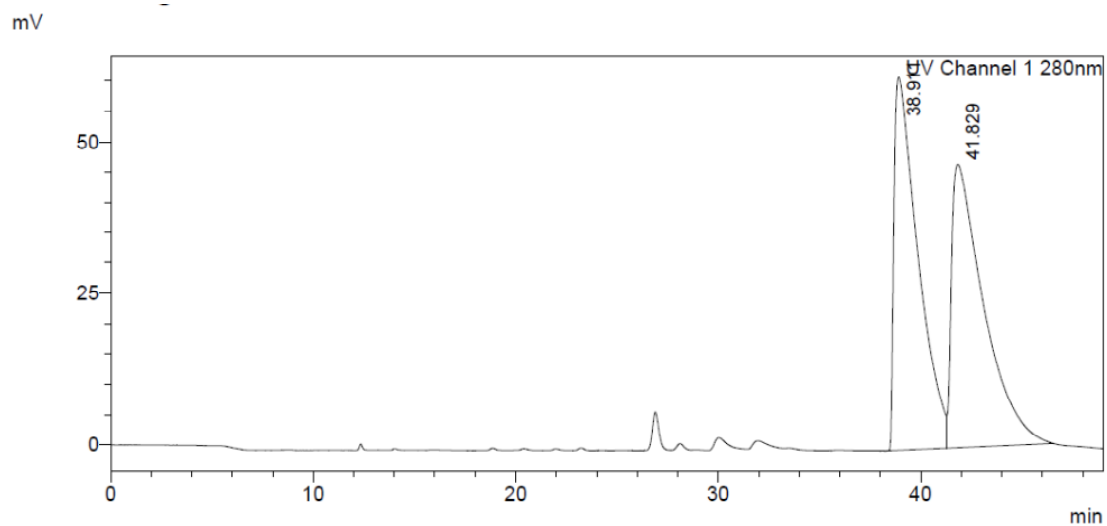
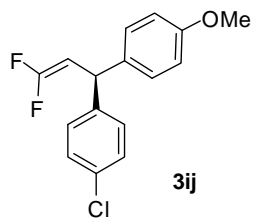
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.179	5072620	375132	49.139		M	
2	7.830	5250436	270141	50.861		V M	
Total		10323056	645273				



<Peak Table>

UV Channel 2 254nm

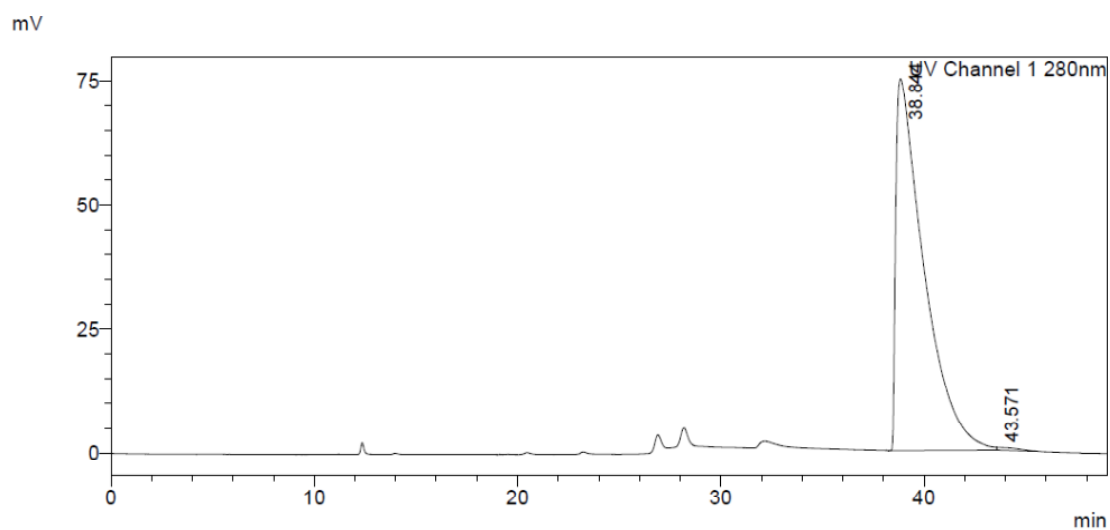
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.332	14914	1304	0.576		M	
2	7.935	2575238	138126	99.424		M	
Total		2590153	139430				



<Peak Table>

UV Channel 1 280nm

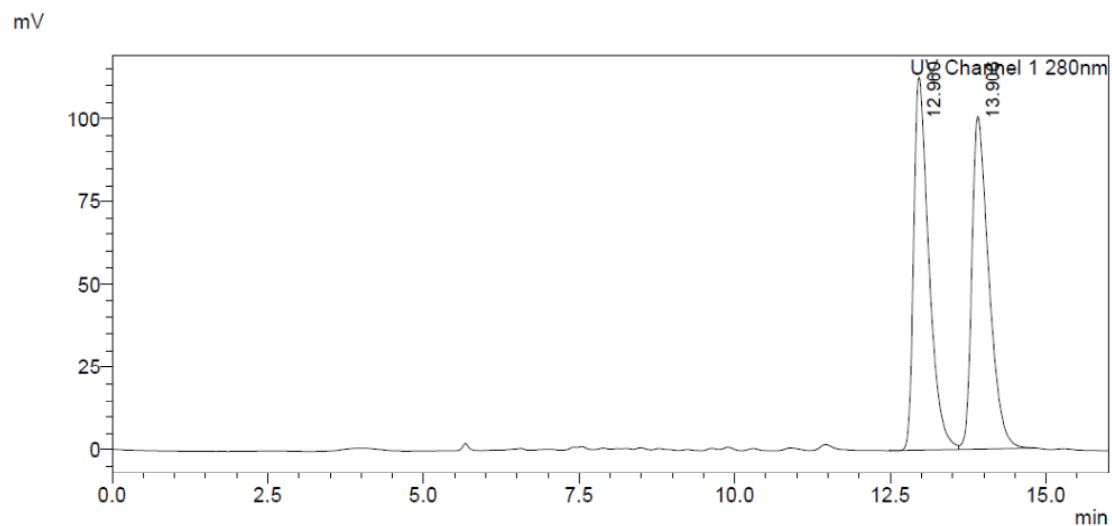
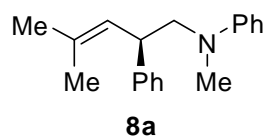
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	38.911	5052916	61428	49.487		M	
2	41.829	5157673	46706	50.513		V M	
Total		10210590	108134				



<Peak Table>

UV Channel 1 280nm

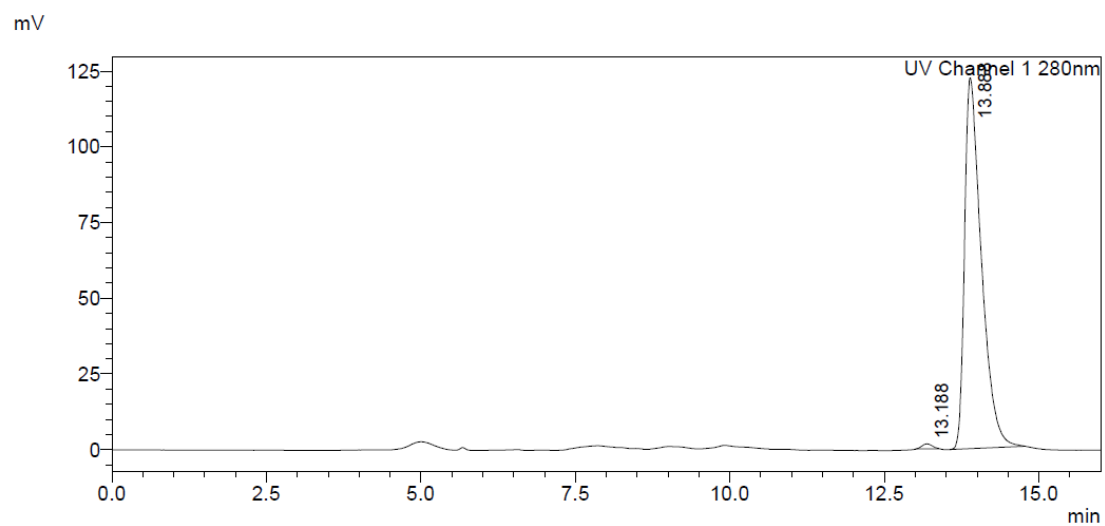
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	38.844	7189991	74918	99.452		M	
2	43.571	39589	561	0.548		M	
Total		7229580	75479				



<Peak Table>

UV Channel 1 280nm

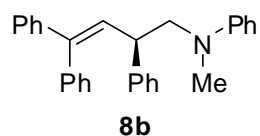
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.960	1915933	112734	50.011		M	
2	13.906	1915106	100462	49.989		V M	
Total		3831039	213197				



<Peak Table>

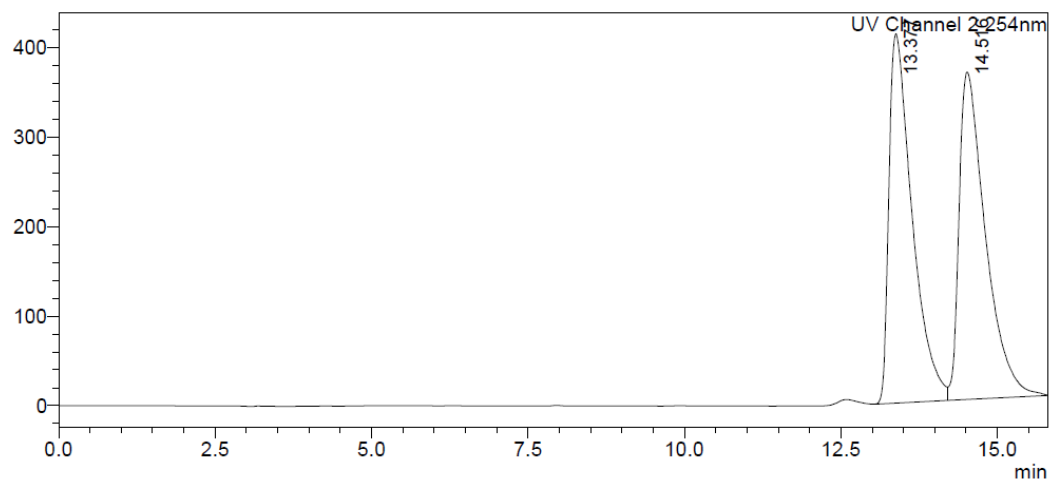
UV Channel 1 280nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.188	19411	1654	0.831		M	
2	13.888	2315757	122342	99.169		M	
Total		2335168	123995				



<Chromatogram>

mV

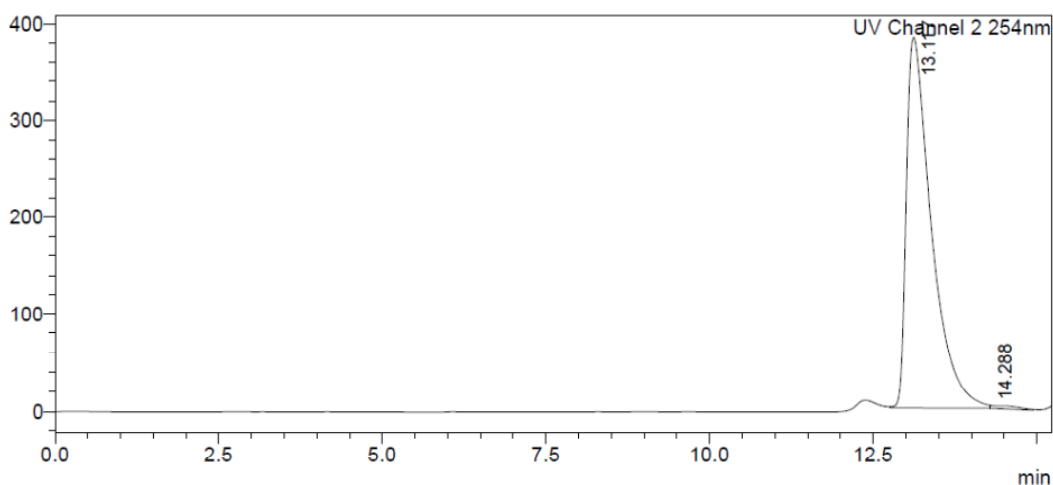


<Peak Table>

UV Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.377	10658343	412371	49.814		M	
2	14.516	10738133	365825	50.186		V M	
Total		21396476	778196				

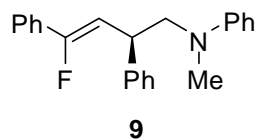
mV



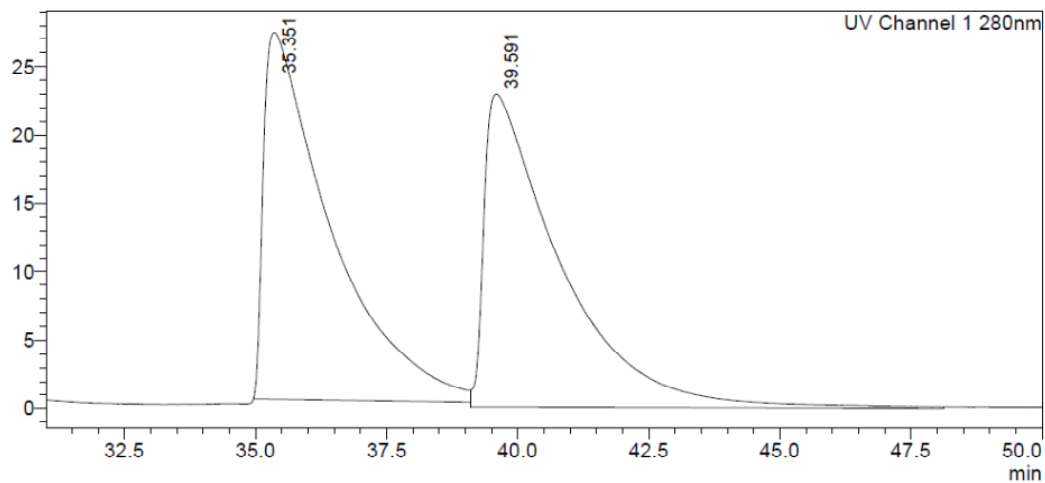
<Peak Table>

UV Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.117	10101078	382632	99.104		M	
2	14.288	91353	3023	0.896		M	
Total		10192431	385655				



mV

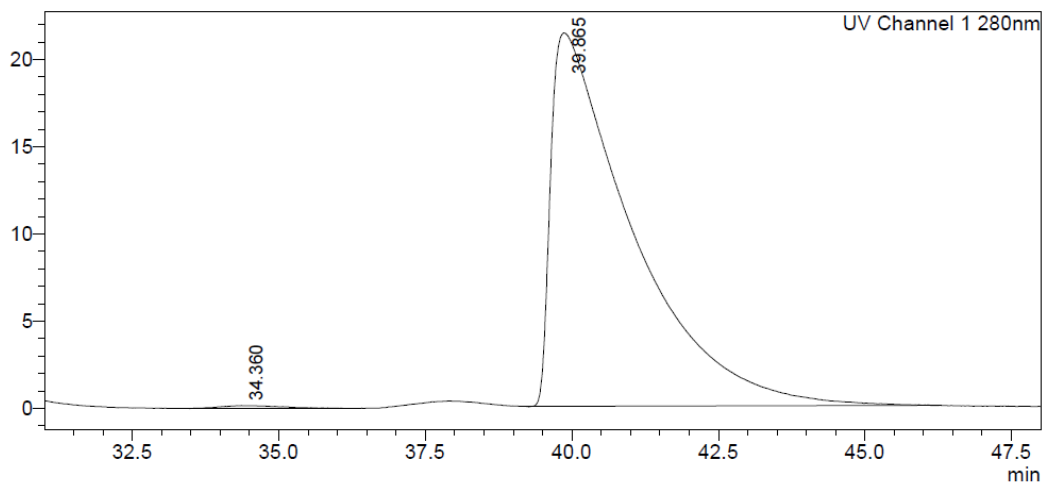


<Peak Table>

UV Channel 1 280nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	35.351	2382660	26814	50.631		M	
2	39.591	2323294	22902	49.369		M	
Total		4705954	49716				

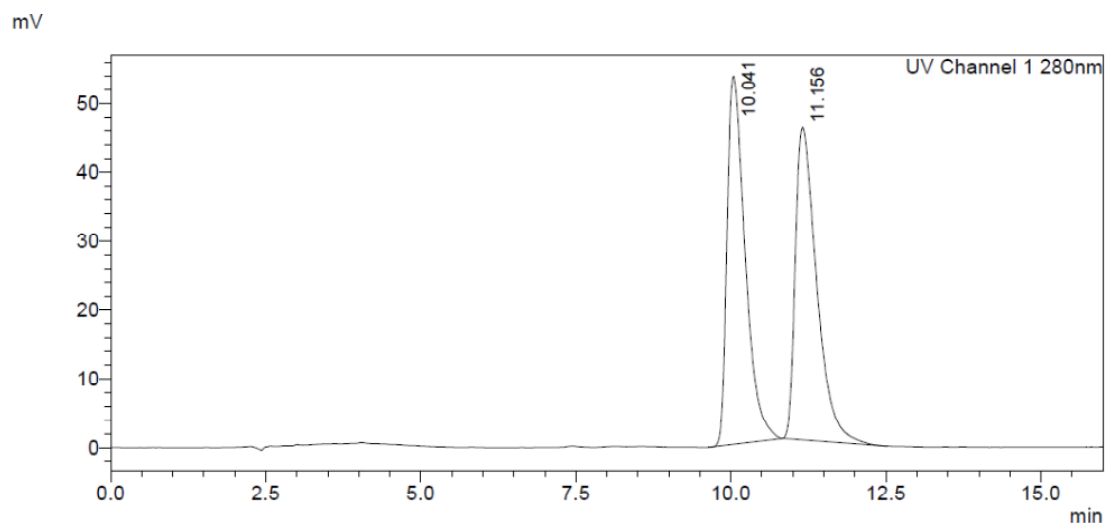
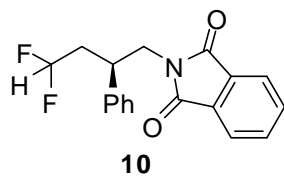
mV



<Peak Table>

UV Channel 1 280nm

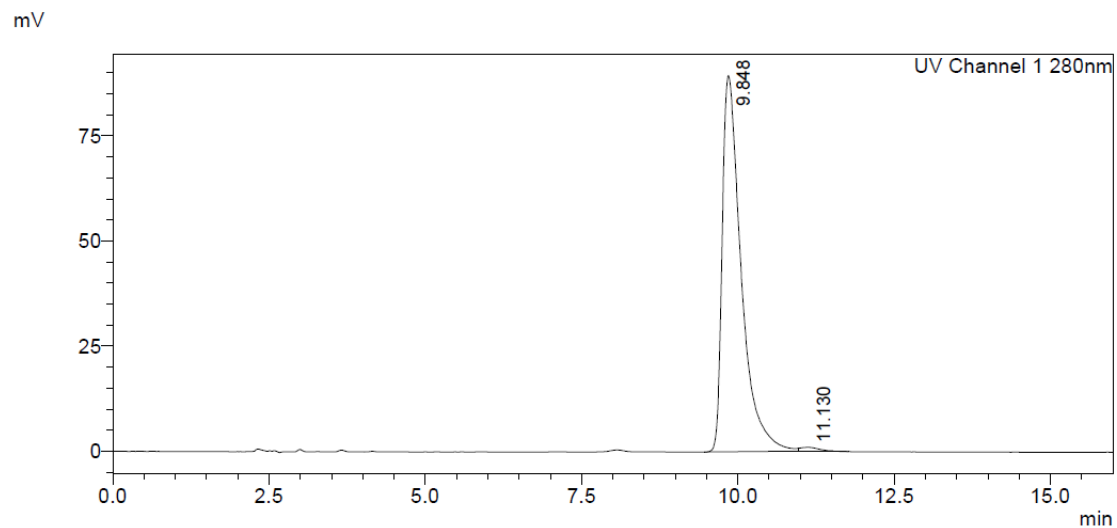
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	34.360	10904	151	0.526		M	
2	39.865	2062775	21400	99.474		M	
Total		2073679	21551				



<Peak Table>

UV Channel 1 280nm

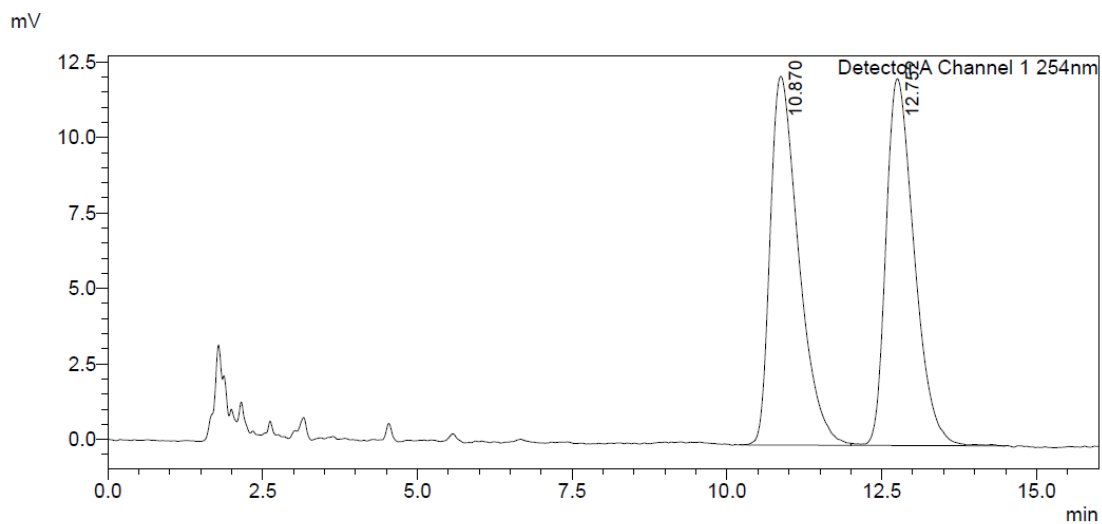
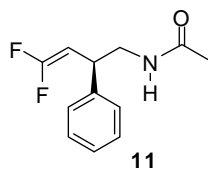
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.041	1086684	53525	49.981		M	
2	11.156	1087510	45360	50.019		M	
Total		2174194	98885				



<Peak Table>

UV Channel 1 280nm

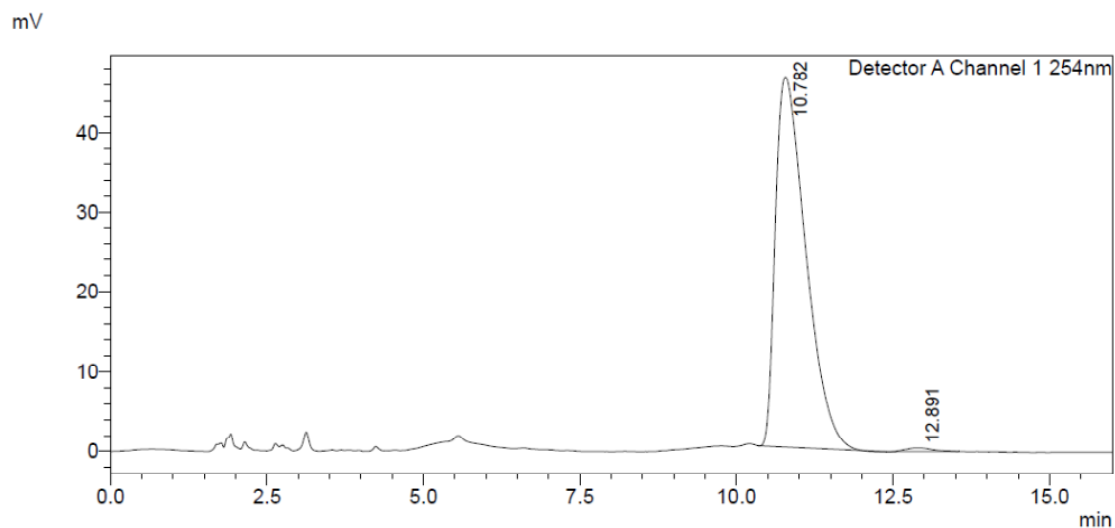
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.848	1889276	89454	99.033		M	
2	11.130	18444	905	0.967		M	
Total		1907720	90359				



<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.870	391756	12217	50.345		M	
2	12.752	386381	12148	49.655		V M	
Total		778137	24365				



<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.782	1565201	46395	99.152		M	
2	12.891	13387	468	0.848		M	
Total		1578588	46863				