

Organoselenium-Catalyzed Oxidative Allylic Fluorination with Electrophilic N-F Reagent

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1. General Considerations

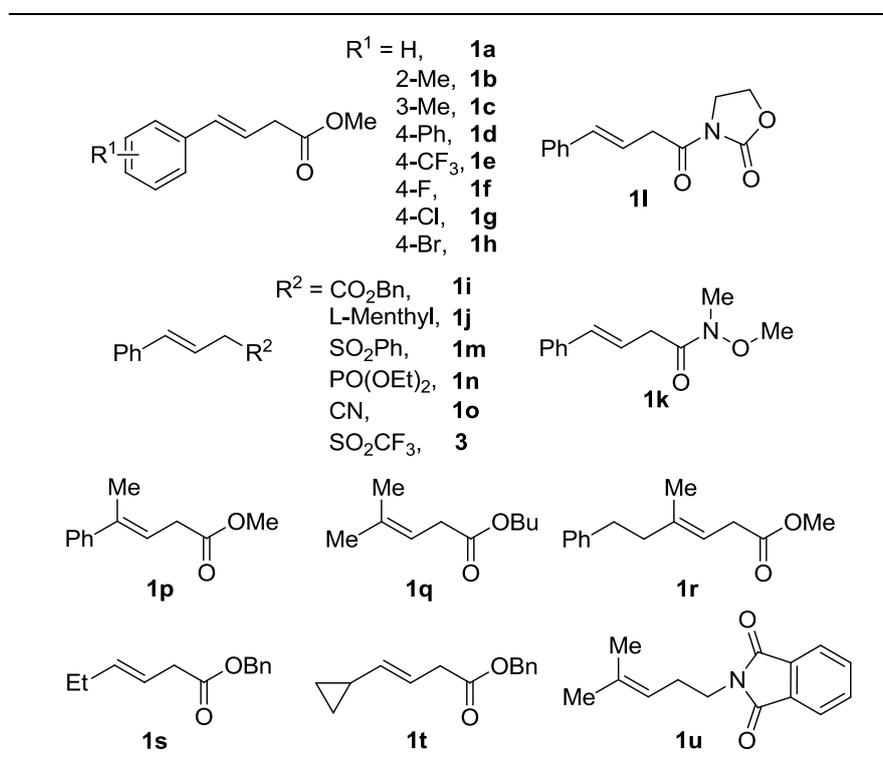
Unless otherwise noted, commercial reagents were purchased from Alfa Aesar, TCI, J&K, Energy, Macklin or Adamas and used without further purification. Reaction solvents THF, DCM and MeCN were purified by PureSolv MD-5 (Innovative Technology). DCE and CHCl_3 were dried over CaH_2 prior to use. All reactions were carried out with oven-dried glassware and all catalytic reactions were set up in glovebox. Analytical thin layer chromatography was performed on 0.20 mm silica gel HSGF-254 plates (Huanghai, China), and visualized under 254 nm UV light or by staining with potassium permanganate. Column chromatography was performed on 200-300 mesh silica gel (Huanghai, China).

^1H , ^{19}F , $^{13}\text{C}\{^1\text{H}\}$ and ^{77}Se NMR spectra were recorded using Bruker ARX 400 MHz spectrometer or Bruker Avance III 500 MHz spectrometer at ambient temperature. All NMR spectra are referenced to the residual solvent signal (CHCl_3 : $\delta\text{H} = 7.26$ and $\delta\text{C} = 77.16$). Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration. Data for $^{13}\text{C}\{^1\text{H}\}$ NMR are reported as follows: chemical shift (δ ppm), multiplicity (d = doublet, t = triplet, q = quartet), coupling constant (Hz).

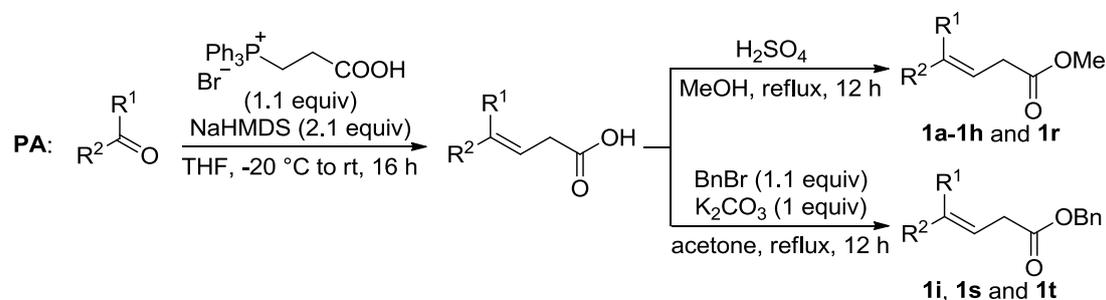
High resolution mass spectra (HRMS) were recorded on Thermo MAT95XP mass spectrometer at analytical center of Sun Yat-Sen University.

2. Experimental Procedures

2.1 Synthesis of Substrates



Substrates $\mathbf{1j}$, $\mathbf{1n}$ and $\mathbf{1u}$ were synthesized according to the literature procedure.



General procedure of method A (PA):

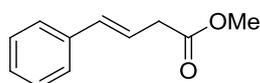
An oven-dried 50 mL Schlenk flask with a stir bar was charged with (2-carboxyethyl)triphenylphosphonium bromide (3.2 g, 7.7 mmol). The flask was evacuated and back-filled with nitrogen. Then anhydrous THF (15 mL) was added via syringe and the suspension was cooled to $-20\text{ }^\circ\text{C}$. To the colorless suspension was added NaHMDS (5.9 mL, 14.7 mmol, 2.5 M in THF) dropwise via syringe over 5 min. The resulting orange solution was stirred at $-20\text{ }^\circ\text{C}$ for 30 min and became homogeneous gradually. Then a solution of aldehyde or ketone (7 mmol) in anhydrous THF (2 mL) was added via syringe at $-20\text{ }^\circ\text{C}$. The resulting mixture was allowed to warm to room temperature and stirred overnight, after which the heterogeneous mixture was quenched with H₂O (50 mL) and washed with DCM (50 mL \times 2). The aqueous phase was acidified to pH = 1 by aqueous 1M HCl solution, and then extracted with EA (60

mL \times 3). The organic extracts were dried over anhydrous Na_2SO_4 , filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (200-300 mesh silica gel) to afford the olefinic acid.

Methyl esterification: To a 50 mL round-bottom flask equipped with a stir bar and Graham condenser were added olefinic acid and MeOH (0.5 M solution). Then, concentrated sulphuric acid (7% solution, *v/v*) was added dropwise. After being stirred at reflux for 12 h, the resulting mixture was quenched with saturated aqueous NaHCO_3 solution (20 mL) carefully and stirred for additional 1 h. The resulting biphasic mixture was extracted with DCM (25 mL \times 3). The organic extracts were dried over anhydrous Na_2SO_4 , filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (200-300 mesh silica gel) to afford the olefinic ester.

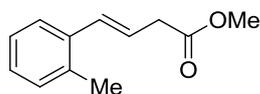
Benzyl esterification: A 25 mL round-bottom flask equipped with a stir bar and Graham condenser was charged with olefinic acid (1.6 mmol), K_2CO_3 (221 mg, 1.6 mmol) and acetone (5 mL). Then, BnBr (209 μL , 1.8 mmol) was added and the heterogeneous mixture was stirred at reflux for 17 h. The resulting mixture was diluted with Et_2O (40 mL) and washed with brine. The organic phase was dried over anhydrous Na_2SO_4 , filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (200-300 mesh silica gel) to afford the benzyl ester.

(*E*)-Methyl 4-phenylbut-3-enoate (**1a**)



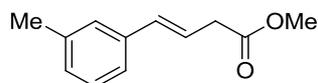
Prepared according to **PA**. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.37 (d, $J = 7.5$ Hz, 2H), 7.31 (t, $J = 7.5$ Hz, 2H), 7.25 – 7.20 (m, 1H), 6.50 (d, $J = 15.9$ Hz, 1H), 6.30 (dt, $J = 14.9, 7.1$ Hz, 1H), 3.72 (s, 3H), 3.26 (d, $J = 7.1$ Hz, 2H). The ^1H NMR spectrum was in accordance with that reported in the reference.³

(*E*)-Methyl 4-(*o*-tolyl)but-3-enoate (**1b**)



Prepared according to **PA**. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.40 (m, 1H), 7.22 – 7.07 (m, 3H), 6.70 (d, $J = 15.7$ Hz, 1H), 6.24 – 6.12 (m, 1H), 3.73 (s, 3H), 3.29 (d, $J = 7.1$ Hz, 2H), 2.34 (s, 3H). The ^1H NMR spectrum was in accordance with that reported in the reference.³

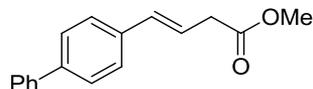
(*E*)-Methyl 4-(*p*-tolyl)but-3-enoate (**1c**)



Prepared according to **PA**. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.24 – 7.15 (m, 3H), 7.06 (d, $J = 7.1$ Hz, 1H), 6.47 (d, $J = 15.9$ Hz, 1H), 6.29 (dt, $J = 15.8, 7.1$ Hz, 1H), 3.72 (s, 3H), 3.26 (dd, $J = 7.1, 1.2$ Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz,

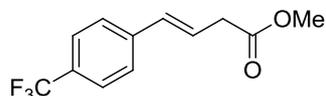
CDCl₃) δ 172.16, 138.21, 136.91, 133.70, 128.57, 128.50, 127.11, 123.62, 121.57, 52.03, 38.39, 21.50. HRMS (ESI) m/z calcd for C₁₂H₁₅O₂ [M + H]⁺: 191.1067, found: 191.1067.

(*E*)-Methyl 4-([1,1'-biphenyl]-4-yl)but-3-enoate (**1d**)



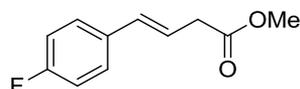
Prepared according to **PA**. Pale yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.53 (m, 4H), 7.44 (t, J = 8.2 Hz, 4H), 7.34 (t, J = 7.4 Hz, 1H), 6.54 (d, J = 15.9 Hz, 1H), 6.35 (dt, J = 15.9, 7.1 Hz, 1H), 3.74 (s, 3H), 3.29 (dd, J = 7.1, 1.3 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 172.11, 140.84, 140.50, 136.02, 133.20, 128.92, 127.44, 127.38, 127.07, 126.87, 121.93, 52.08, 38.44. HRMS (ESI) m/z calcd for C₁₇H₁₇O₂ [M + H]⁺: 253.1223, found: 253.1225.

(*E*)-Methyl 4-(4-(trifluoromethyl)phenyl)but-3-enoate (**1e**)



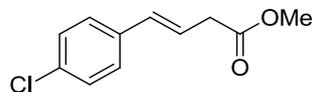
Prepared according to **PA**. White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 6.53 (d, J = 16.0 Hz, 1H), 6.47 – 6.35 (m, 1H), 3.73 (s, 3H), 3.29 (d, J = 6.9 Hz, 2H). The ¹H NMR spectrum was in accordance with that reported in the reference.³

(*E*)-Methyl 4-(4-fluorophenyl)but-3-enoate (**1f**)



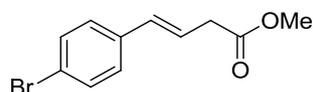
Prepared according to **PA**. Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.36 (dd, J = 7.5, 5.9 Hz, 2H), 7.08 – 6.97 (m, 2H), 6.48 (d, J = 15.9 Hz, 1H), 6.30 – 6.18 (m, 1H), 3.74 (s, 3H), 3.27 (d, J = 7.1 Hz, 2H). The ¹H NMR spectrum was in accordance with that reported in the reference.³

(*E*)-Methyl 4-(4-chlorophenyl)but-3-enoate (**1g**)



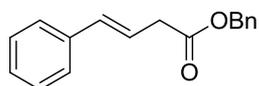
Prepared according to **PA**. White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.27 (m, 4H), 6.44 (d, J = 15.9 Hz, 1H), 6.33 – 6.21 (m, 1H), 3.72 (s, 3H), 3.25 (d, J = 7.0 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 171.94, 135.45, 133.34, 132.42, 128.83, 127.63, 122.53, 52.11, 38.26. HRMS (ESI) m/z calcd for C₁₁H₁₂ClO₂ [M + H]⁺: 211.0520, found: 211.0523.

(*E*)-Methyl 4-(4-bromophenyl)but-3-enoate (**1h**)



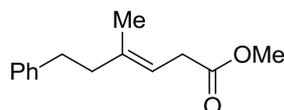
Prepared according to **PA**. White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, $J = 8.4$ Hz, 2H), 7.23 (d, $J = 8.3$ Hz, 2H), 6.43 (d, $J = 16.0$ Hz, 1H), 6.35 – 6.23 (m, 1H), 3.72 (s, 3H), 3.24 (d, $J = 6.8$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.89, 135.87, 132.46, 131.77, 127.95, 122.66, 121.47, 52.12, 38.26. HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{12}\text{BrO}_2$ [$\text{M} + \text{H}$] $^+$: 255.0015, found: 255.0019.

(*E*)-Benzyl 4-phenylbut-3-enoate (**1i**)



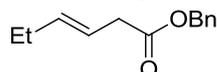
Prepared according to **PA**. White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.34 (m, 7H), 7.31 (t, $J = 7.5$ Hz, 2H), 7.28 – 7.20 (m, 1H), 6.50 (d, $J = 15.9$ Hz, 1H), 6.37 – 6.25 (m, 1H), 5.17 (s, 2H), 3.31 (d, $J = 7.0$ Hz, 2H). The ^1H NMR spectrum was in accordance with that reported in the reference.⁴

Methyl 4-methyl-6-phenylhex-3-enoate (**1r**) (*E/Z* = 1.8:1)



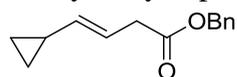
Prepared according to **PA**. Colorless oil. Major isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.29 (d, $J = 7.6$ Hz, 2H), 7.18 (d, $J = 7.5$ Hz, 3H), 5.35 (t, $J = 7.1$ Hz, 1H), 3.68 (s, 3H), 3.06 (d, $J = 7.0$ Hz, 2H), 2.78 – 2.70 (m, 2H), 2.38 – 2.27 (m, 2H), 1.69 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.90, 142.21, 138.73, 128.48, 128.40, 125.89, 116.27, 51.87, 41.53, 34.59, 33.70, 16.64. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{19}\text{O}_2$ [$\text{M} + \text{H}$] $^+$: 219.1380, found: 219.1377.

(*E*)-Benzyl hex-3-enoate (**1s**)

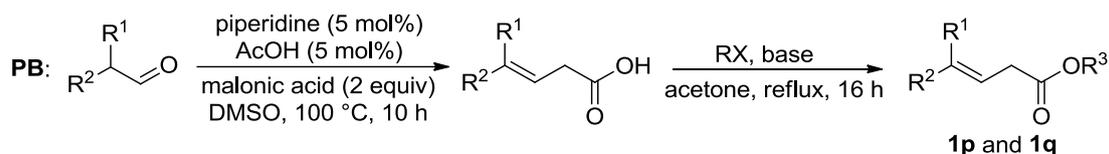


Prepared according to **PA** (the corresponding olefinic acid is commercial available). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.28 (m, 5H), 5.62 (dt, $J = 15.2$, 5.9 Hz, 1H), 5.58 – 5.49 (m, 1H), 5.13 (s, 2H), 3.13 – 3.03 (m, 2H), 2.06 (p, $J = 6.5$ Hz, 2H), 0.99 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.19, 136.67, 136.12, 128.68, 128.33, 128.30, 120.54, 66.46, 38.19, 25.65, 13.59. HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{17}\text{O}_2$ [$\text{M} + \text{H}$] $^+$: 205.1223, found: 205.1224.

Benzyl 4-cyclopropylbut-3-enoate (**1t**) (*E/Z* = 2:1)



Prepared according to **PA**. Colorless oil. Major isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.29 (m, 5H), 5.68 – 5.57 (m, 1H), 5.13 (s, 2H), 5.12 – 5.05 (m, 1H), 3.07 (d, $J = 7.0$ Hz, 2H), 1.46 – 1.34 (m, 1H), 0.73 – 0.65 (m, 2H), 0.42 – 0.32 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.06, 138.50, 137.59, 128.67, 128.33, 128.30, 119.11, 66.47, 38.06, 13.72, 6.66. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{O}_2$ [$\text{M} + \text{H}$] $^+$: 217.1223, found: 217.1225.



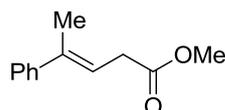
General procedure of method B (**PB**):

An oven-dried 10 mL Schlenk flask with a stir bar was evacuated and back-filled with nitrogen. Then anhydrous DMSO (500 μ L), AcOH (11.6 μ L, 0.2 mmol) and piperidine (20 μ L, 0.2 mmol) was added successively and the resulting mixture was stirred at room temperature. After 5 min, another portion of anhydrous DMSO (4 mL), aldehyde (4 mmol) and malonic acid (833 mg, 8 mmol) was added. The reaction was performed at room temperature for 20 min and then at 100 $^{\circ}$ C for 10 h with evolution of carbon dioxide. Then the homogeneous mixture was allowed to cool to room temperature and diluted with Et₂O (50 mL) and washed with H₂O (50 mL \times 3). The organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (200-300 mesh silica gel) to afford the olefinic acid.

Methyl esterification: A 25 mL round-bottom flask equipped with a stir bar and Graham condenser was charged with olefinic acid (1.6 mmol), Cs₂CO₃ (261 mg, 0.8 mmol) and acetone (5 mL). Then MeI (199 μ L, 3.2 mmol) was added and the heterogeneous mixture was stirred at reflux for 17 h. The resulting mixture was diluted with Et₂O (40 mL) and washed with brine. The organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (200-300 mesh silica gel) to afford the methyl ester.

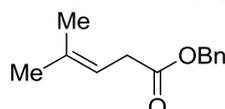
Benzyl esterification is same as **PA**.

(*E*)-Methyl 4-phenylpent-3-enoate (**1p**)

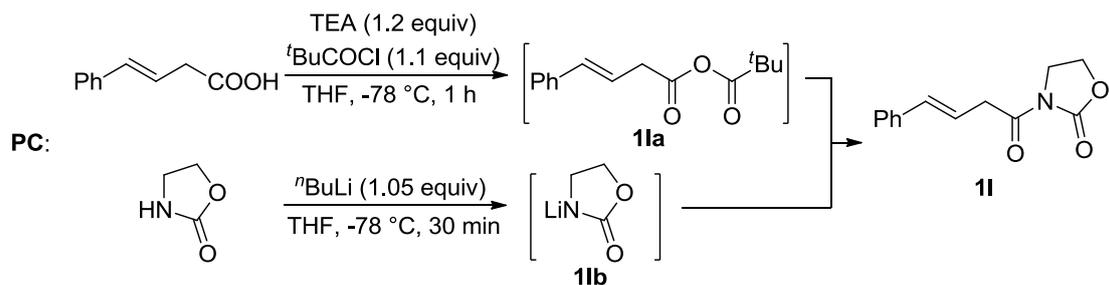


Prepared according to **PB**. Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.22 (m, 1H), 5.93 (t, *J* = 7.0 Hz, 1H), 3.31 (d, *J* = 7.1 Hz, 2H), 2.07 (s, 3H). The ¹H NMR spectrum was in accordance with that reported in the reference.⁵

Benzyl 4-methylpent-3-enoate (**1q**)

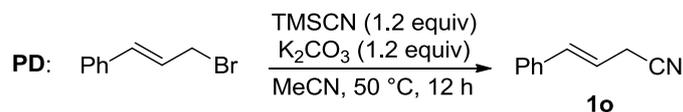


Prepared according to **PB** (NMM (1.1 equiv) was used instead of AcOH and piperidine). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.28 (m, 5H), 5.33 (t, *J* = 7.0 Hz, 1H), 5.12 (s, 2H), 3.09 (d, *J* = 7.0 Hz, 2H), 1.75 (s, 3H), 1.63 (s, 3H). The ¹H NMR spectrum was in accordance with that reported in the reference.⁶



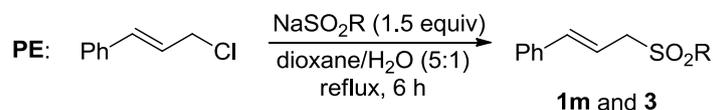
An oven-dried 50 mL Schlenk flask with a stir bar was charged with 2-oxazolidone (218 mg, 2.5 mmol). The flask was evacuated and back-filled with nitrogen. Then anhydrous THF (5 mL) was added via syringe and the solution was cooled to $-78\text{ }^{\circ}\text{C}$. To the colorless solution was added $n\text{BuLi}$ (1.6 mL, 2.6 mmol, 1.6 M in hexane) dropwise over 5 min. Then the heterogeneous mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 45 min to afford a solution of **11b**.

To another oven-dried 50 mL Schlenk flask with a stir bar was added (*E*)-4-phenylbut-3-enoic acid (406 mg, 2.5 mmol). The flask was evacuated and back-filled with nitrogen. Then anhydrous THF (30 mL) was added via syringe and the solution was cooled to $-78\text{ }^{\circ}\text{C}$. To the colorless solution were added TEA (416 μL , 3 mmol) and pivaloyl chloride (338 μL , 2.8 mmol). Then the mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 15 min and at $0\text{ }^{\circ}\text{C}$ for 45 min. The resulting anhydride **11a** was transferred via cannula over 30 min to the solution of **11b** and the mixture was allowed to warm to room temperature. After being stirred for additional 16 h, the resulting mixture was quenched with saturated NH_4Cl (50 mL) and extract with DCM (50 mL \times 3). The organic extracts were dried over anhydrous Na_2SO_4 , filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (200-300 mesh silica gel) to afford **11** as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, $J = 7.5$ Hz, 2H), 7.31 (t, $J = 7.3$ Hz, 2H), 7.23 (t, $J = 7.2$ Hz, 1H), 6.57 (d, $J = 16.0$ Hz, 1H), 6.44 – 6.31 (m, 1H), 4.43 (t, $J = 8.0$ Hz, 2H), 4.04 (t, $J = 8.0$ Hz, 2H), 3.88 (d, $J = 6.9$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.43, 153.60, 137.01, 134.24, 128.66, 127.73, 126.49, 121.30, 62.25, 42.70, 39.15. HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{NO}_3$ [$\text{M} + \text{H}$] $^+$: 232.0968, found: 232.0971.



An oven-dried 10 mL Schlenk flask with a stir bar was charged with K_2CO_3 (332 mg, 2.4 mmol). The flask was evacuated and back-filled with nitrogen. Then anhydrous MeCN (4 mL), cinnamyl bromide (394 mg, 2 mmol) and TMSCN (301 μL , 2 mmol) were added successively and the resulting mixture was stirred at room temperature for 12 h. The resulting mixture was quenched with saturated $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ (20 mL) and extract with DCM (50 mL \times 3). The organic extracts were dried over anhydrous Na_2SO_4 , filtered and concentrated *in vacuo*. The residual was purified by flash

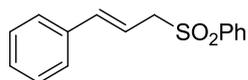
column chromatography (200-300 mesh silica gel) to afford **1o** as a pale yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.27 (m, 5H), 6.74 (d, $J = 15.8$ Hz, 1H), 6.06 (dt, $J = 15.8, 5.7$ Hz, 1H), 3.30 (dd, $J = 5.6, 1.6$ Hz, 2H). The ^1H NMR spectrum was in accordance with that reported in the reference.⁷



General procedure of method E (**PE**):

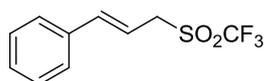
A 50 mL round-bottom flask equipped with a stir bar and Graham condenser was charged with sodium sulfinate (6 mmol), dioxane/ H_2O (24 mL, $v/v = 5:1$) and cinnamyl chloride (570 μL , 4 mmol) successively. Then the reaction was performed at reflux for 6 h. The resulting mixture was diluted with Et_2O (50 mL) and washed with brine. The organic phase was dried over anhydrous Na_2SO_4 , filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (200-300 mesh silica gel) to afford the olefinic sulfone.

(Cinnamylsulfonyl)benzene (**1m**)

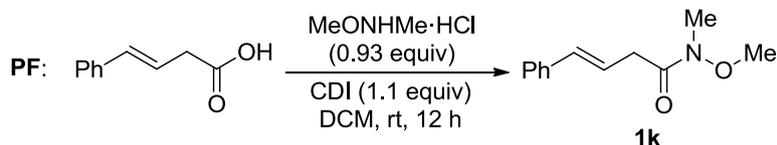


Prepared according to **PE**. White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 7.5$ Hz, 2H), 7.64 (t, $J = 7.4$ Hz, 1H), 7.54 (t, $J = 7.7$ Hz, 2H), 7.34 – 7.27 (m, 5H), 6.37 (d, $J = 15.8$ Hz, 1H), 6.17 – 6.03 (m, 1H), 3.95 (d, $J = 7.5$ Hz, 2H). The ^1H NMR spectrum was in accordance with that reported in the reference.⁸

(*E*)-(3-((Trifluoromethyl)sulfonyl)prop-1-en-1-yl)benzene (**3**)



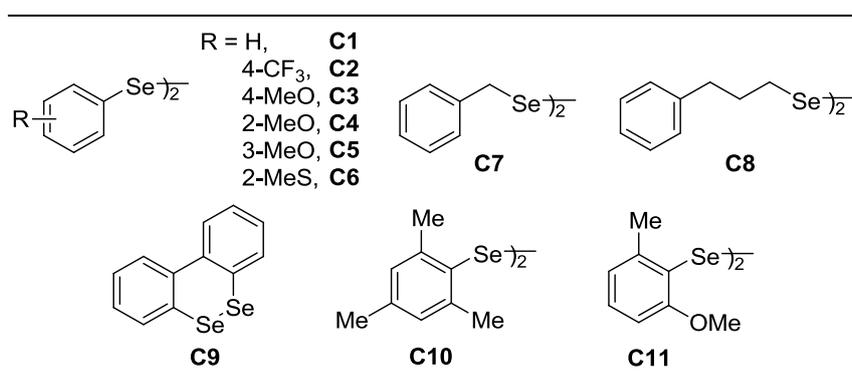
Prepared according to **PE**. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, $J = 7.7$ Hz, 2H), 7.32 (t, $J = 7.4$ Hz, 2H), 7.26 – 7.23 (m, 1H), 6.62 (d, $J = 15.9$ Hz, 1H), 6.37 (dt, $J = 15.8, 5.7$ Hz, 1H), 4.33 (d, $J = 5.7$ Hz, 2H). The ^1H NMR spectrum was in accordance with that reported in the reference.⁹



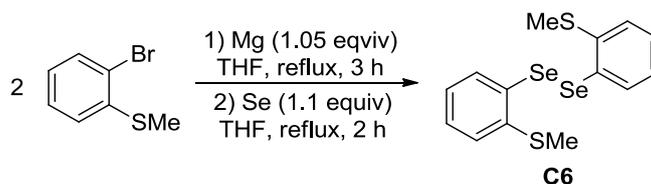
A 10 mL round-bottom flask with a stir bar was charged with (*E*)-4-phenylbut-3-enoic acid (162 mg, 1 mmol) and DCM (2 mL). Then 1,1'-carbon- yldiimidazole (178 mg, 1.1 mmol) was added carefully and the mixture was stirred at room temperature with evolution of carbon dioxide. After 10 min, $\text{MeONHMe}\cdot\text{HCl}$ (91 mg, 0.93 mmol) was added and the reaction was performed at room temperature for additional 12 h. The resulting mixture was concentrated *in vacuo* and purified by flash column

chromatography (200-300 mesh silica gel) to afford **1k** as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.38 (d, $J = 7.6$ Hz, 2H), 7.30 (t, $J = 7.5$ Hz, 2H), 7.21 (t, $J = 7.2$ Hz, 1H), 6.51 (d, $J = 16.0$ Hz, 1H), 6.42 – 6.30 (m, 1H), 3.73 (s, 3H), 3.39 (d, $J = 6.6$ Hz, 2H), 3.21 (s, 3H). The ^1H NMR spectrum was in accordance with that reported in the reference.¹⁰

2.2 Synthesis of Catalysts

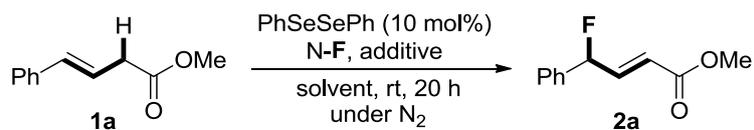


Catalysts **C1** and **C7** are commercial available. Synthesis of catalysts **C2**,¹¹ **C3-C5**,¹³ **C8**,¹¹ **C9**,¹² **C10**¹³ and **C11**¹³ was based on the literature procedure.



To an oven-dried 50 mL two-neck Schlenk flask equipped with a stir bar and Graham condenser was added magnesium turnings (102 mg, 4.2 mmol). The flask was then evacuated and back-filled with nitrogen. Then a solution of 2-bromothioanisole (203 mg, 1 mmol) in anhydrous THF (0.5 M solution) was added via syringe and the heterogeneous mixture was stirred at 40 °C to initiate the reaction. While the colorless solution turned gray, another portion of 2-bromothioanisole (609 mg, 3 mmol) in anhydrous THF (0.5 M solution) was added dropwise via syringe to maintain a gentle reflux. After being stirred at reflux for 3 h, the resulting Grignard reagent was cooled to room temperature. Then selenium powder (347 mg, 4.4 mmol) was added and the solution was heated to reflux for additional 2 h. The resulting mixture was equipped with an oxygen balloon and stirred vigorously overnight. Then the reaction was quenched with aqueous 1M HCl (50 mL) and extract with Et_2O (50 mL \times 3). The organic phase was dried over anhydrous Na_2SO_4 , filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (200-300 mesh silica gel) to afford 1,2-bis(2-(methylthio)phenyl)diselane as a yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 7.63 (dd, $J = 7.8, 1.3$ Hz, 1H), 7.32 (dd, $J = 7.7, 1.4$ Hz, 1H), 7.20 (td, $J = 7.5, 1.4$ Hz, 1H), 7.12 (td, $J = 7.6, 1.4$ Hz, 1H), 2.53 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.43, 133.28, 130.38, 130.33, 127.99, 127.90, 18.82. HRMS (APCI) m/z calcd for $\text{C}_7\text{H}_7\text{S}_2\text{Se}$ [$\text{M}/2$] $^-$: 202.9439, found: 202.9435.

2.3 Optimization of Condition with Alkene **1a**

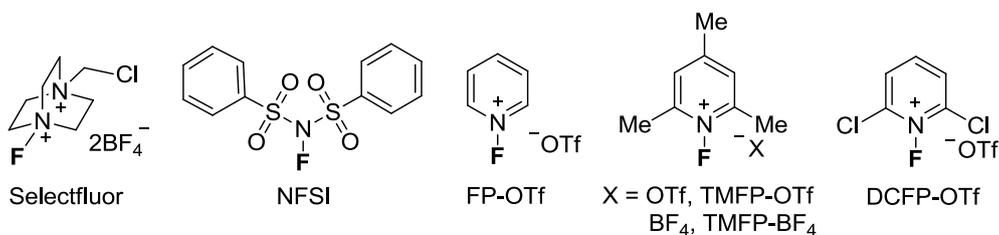


General procedure for the fluorination of **1a**:

A 1.5-mL vial equipped with a magnetic stir bar was charged with N-F reagents (0.06 mmol) and PhSeSePh (1.6 mg, 0.005 mmol). Then the vial was moved into glovebox. After dry DCE (350 μ L) and alkene **1a** (8.8 mg, 0.05 mmol) were added successively under inert gas, the vial was capped and removed from glovebox. The reaction was performed at room temperature for 20 h. Then the resulting mixture was quenched with H₂O (2 mL) and extracted with DCM (2 mL \times 3). The organic extracts were concentrated *in vacuo* and analyzed by ¹H NMR and ¹⁹F NMR in CDCl₃.

Table S1 Optimization of Alkene 1a

Entry	Oxidant (equiv)	Additive (equiv)	Solvent	Yield (%) ^a
1	Selectfluor (1.2)	-	DCM	0
2	NFSI (1.2)	-	DCM	0
3	FP-OTf (1.2)	-	DCM	0
4	DCFP-OTf (1.2)	-	DCM	0
5	TMFP-OTf (1.2)	-	DCM	83
6	TMFP-OTf (1.2)	-	DCE	84(85)
7	TMFP-OTf (1.2)	-	CHCl ₃	59
8	TMFP-OTf (1.2)	-	MeCN	56
9	TMFP-OTf (1.2)	-	CH ₃ NO ₂	trace
10	TMFP-OTf (1.2)	-	THF	0
11	TMFP-BF ₄ (1.2)	-	DCE	52
12	TMFP-OTf (1.2)	Et ₃ N•3HF (2.0)	DCE	47
13	TMFP-OTf (1.2)	pyridine•HF (2.0)	DCE	trace
14	TMFP-OTf (1.2)	LiF (2.0)	DCE	88
15	TMFP-OTf (1.2)	NaF (2.0)	DCE	86
16	TMFP-OTf (1.2)	KF (2.0)	DCE	82
17	TMFP-OTf (2.0)	-	DCE	86
18 ^b	TMFP-OTf (1.2)	-	DCE	66
19 ^c	TMFP-OTf (1.2)	-	DCE	0
20 ^d	TMFP-OTf (1.2)	-	DCE	22
21 ^e	TMFP-OTf (1.2)	-	DCE	0
22 ^f	TMFP-OTf (1.2)	-	DCE	0



^aDetermined by ¹⁹F NMR with benzotrifluoride as the internal standard. Yield of isolation on 0.1 mmol scale is provided in the parenthesis.

^bPhSeSePh (5 mol%) was used. ^cWithout catalyst. ^dUnder air. ^e1 mL DCE was used.

^fSe (20 mol%) was used instead of PhSeSePh.

2.4 Screening of Catalysts with or without TEMPO



General procedure for the fluorination of **1a** without TEMPO:

A 1.5-mL vial equipped with a magnetic stir bar was charged with TMFP-OTf (17.4

mg, 0.06 mmol) and diselenides (0.005 mmol). Then the vial was moved into glovebox. After dry DCE (350 μ L) and olefin **1a** (8.8 mg, 0.05 mmol) were added successively under inert gas, the vial was capped and removed from glovebox. The reaction was performed at room temperature for 20 h. Then the resulting mixture was quenched with H₂O (2 mL) and extracted with DCM (2 mL \times 3). The organic extracts were concentrated *in vacuo* and analyzed by ¹H NMR and ¹⁹F NMR in CDCl₃.

General procedure for the fluorination of **1a** with TEMPO:

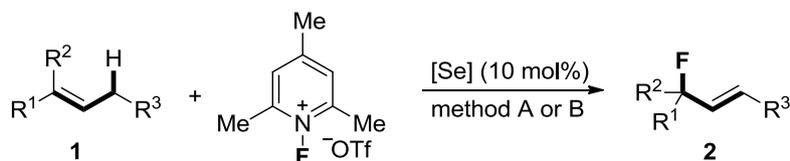
A 1.5-mL vial equipped with a magnetic stir bar was charged with TMFP-OTf (29.0 mg, 0.1 mmol) and diselenides (0.005 mmol). Then the vial was moved into glovebox. After TEMPO (3.9 mg, 0.025 mmol), dry DCE (350 μ L) and olefin **1a** (8.8 mg, 0.05 mmol) were added successively under inert gas, the vial was capped and removed from glovebox. The reaction was performed at room temperature for 20 h. Then the resulting mixture was quenched with H₂O (2 mL) and extracted with DCM (2 mL \times 3). The organic extracts were concentrated *in vacuo* and analyzed by ¹H NMR and ¹⁹F NMR in CDCl₃.

Table S2 Optimization of Catalysts with or without TEMPO

Entry	Catalyst	Yield (%) ^a	
		Without TEMPO	With TEMPO
1	C1	84	72
2	C2	53	44
3	C3	0	72
4	C4	0	81
5	C5	71	82
6	C6	70	36
7	C7	47	91
8	C8	63	77
9	C9	25	47
10	C10	81	41
11	C11	58	67

^aDetermined by ¹⁹F NMR with benzotrifluoride as the internal standard.

2.5 Synthesis of Allylic Fluorides via Electrophilic Selenium Catalysis



General procedure of method A (**MA**):

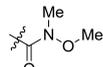
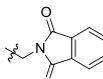
A 1.5-mL vial equipped with a magnetic stir bar was charged with TMFP-OTf (34.7 mg, 0.12 mmol) and **C1** (3.1 mg, 0.01 mmol). Then the vial was moved into glovebox. After dry DCE (500 μ L) and olefins **1** (0.1 mmol) was added successively under inert gas, the vial was capped and removed from glovebox. The reaction was

performed at room temperature for 20 h. Then the resulting mixture was concentrated *in vacuo* and purified by flash column chromatography (200-300 mesh silica gel) to afford the corresponding allylic fluorides **2**.

General procedure of method B (**MB**):

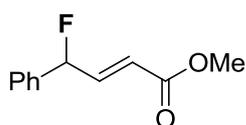
A 1.5-mL vial equipped with a magnetic stir bar was charged with TMFP-OTf (57.9 mg, 0.2 mmol), **C4** (3.4 mg, 0.01 mmol) or **C7** (3.7 mg, 0.01 mmol). Then the vial was moved into glovebox. After TEMPO (7.8 mg, 0.05 mmol) in dry DCE (500 μ L) and olefins **1** (0.1 mmol) were added successively under nitrogen atmosphere, the vial was capped and removed from glovebox. The reaction was performed at room temperature for 20 h. Then the resulting mixture was quenched with H₂O (2 mL) and extracted with DCM (2 mL \times 3). The organic extracts were concentrated *in vacuo* and purified by flash column chromatography (200-300 mesh silica gel) to afford the corresponding allylic fluorides **2**.

Table S3 Substrate Scope

Entry	R ¹	R ²	R ³	Yield (%) ^a	
				Method A ^a	Method B
1	Ph	H	CO ₂ Me	85	92
2	(2-Me)C ₆ H ₄	H	CO ₂ Me	80	83
3	(3-Me)C ₆ H ₄	H	CO ₂ Me	(43)	46
4	(4-Ph)C ₆ H ₄	H	CO ₂ Me	63	67
5	(4-CF ₃)C ₆ H ₄	H	CO ₂ Me	88	77
6	(4-F)C ₆ H ₄	H	CO ₂ Me	81	88
7	(4-Cl)C ₆ H ₄	H	CO ₂ Me	89	98
8	(4-Br)C ₆ H ₄	H	CO ₂ Me	88	84
9	Ph	Me	CO ₂ Me	72	76
10	PhCH ₂ CH ₂	Me	CO ₂ Me	(41)	74
11	Me	Me	CO ₂ Bn	(16)	77
12	Ph	H	CO ₂ Bn	79	97
13	Ph	H	L-Menthyl	71	89
14	Ph	H	oxazolidin-2-one	trace	74
15	Ph	H	CN	(18)	71
16	Ph	H	PO(OEt) ₂	(37)	59
17	Ph	H	SO ₂ Ph	(55)	97
18	Ph	H		trace	60
19	ethyl	H	CO ₂ Bn	(10)	59
20	cyclopropyl	H	CO ₂ Bn	(6)	68
21	Me	Me		(17)	69

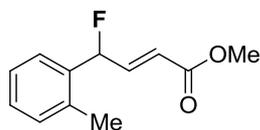
^aNMR yields were provided in the parenthesis and determined by ¹⁹F NMR with benzotrifluoride as the internal standard.

(*E*)-Methyl 4-fluoro-4-phenylbut-2-enoate (**2a**):



Prepared according to **MA** or **MB** (**C7** was used as the catalyst in **MB**). Flash column chromatography (eluent: PE/EA = 50:1, *v/v*) to afford **2a** (**MA**: 16.6 mg, 85%; **MB**: 18.0 mg, 92%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.37 (m, 3H), 7.35 (d, *J* = 7.0 Hz, 2H), 7.13 – 7.00 (m, 1H), 6.19 (d, *J* = 15.7 Hz, 1H), 6.02 (dd, *J* = 47.0, 3.0 Hz, 1H), 3.76 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.39, 144.50 (d, *J* = 22.0 Hz), 136.82 (d, *J* = 20.0 Hz), 129.42 (d, *J* = 2.3 Hz), 128.99, 126.77 (d, *J* = 5.7 Hz), 121.16 (d, *J* = 10.3 Hz), 91.92 (d, *J* = 175.3 Hz), 51.97. ¹⁹F NMR (377 MHz, CDCl₃) δ -173.46. The ¹H, ¹³C and ¹⁹F NMR spectra were in accordance with those reported in the reference.¹⁴

(*E*)-Methyl 4-fluoro-4-(*o*-tolyl)but-2-enoate (**2b**):



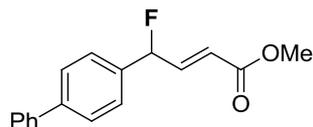
Prepared according to **MA** or **MB** (**C7** was used as the catalyst in **MB**). Flash column chromatography (eluent: PE/EA = 50:1, *v/v*) to afford **2b** (**MA**: 16.6 mg, 80%; **MB**: 17.3 mg, 83%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.18 (m, 4H), 7.13 – 7.00 (m, 1H), 6.33 – 6.12 (m, 2H), 3.76 (s, 3H), 2.38 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.43, 144.13 (d, *J* = 22.0 Hz), 135.78 (d, *J* = 4.0 Hz), 134.85 (d, *J* = 18.9 Hz), 130.98, 129.31 (d, *J* = 2.3 Hz), 126.90 (d, *J* = 7.1 Hz), 126.53, 121.21 (d, *J* = 10.0 Hz), 89.57 (d, *J* = 174.2 Hz), 51.96, 19.15. ¹⁹F NMR (377 MHz, CDCl₃) δ -176.64. HRMS (APCI) *m/z* calcd for C₁₂H₁₂FO₂ [M - H]⁻: 207.0827, found: 207.0825.

(*E*)-Methyl 4-fluoro-4-(*m*-tolyl)but-2-enoate (**2c**):



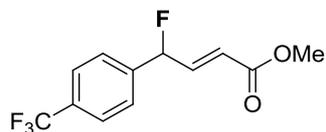
Prepared according to **MB** (**C7** was used as the catalyst). Flash column chromatography (eluent: PE/EA = 50:1, *v/v*) to afford **2c** (9.5 mg, 46%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.29 (t, *J* = 7.5 Hz, 1H), 7.22 – 7.12 (m, 3H), 7.11 – 6.99 (m, 1H), 6.18 (d, *J* = 15.7 Hz, 1H), 5.98 (dd, *J* = 47.1, 3.0 Hz, 1H), 3.76 (s, 3H), 2.37 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.46, 144.66 (d, *J* = 22.0 Hz), 138.82, 136.72 (d, *J* = 19.8 Hz), 130.17 (d, *J* = 2.3 Hz), 128.88, 127.40 (d, *J* = 5.6 Hz), 123.89 (d, *J* = 5.7 Hz), 121.01 (d, *J* = 10.2 Hz), 91.99 (d, *J* = 175.2 Hz), 51.96, 21.50. ¹⁹F NMR (377 MHz, CDCl₃) δ -173.19. HRMS (APCI) *m/z* calcd for C₁₂H₁₂FO₂ [M - H]⁻: 207.0827, found: 207.0827.

(*E*)-Methyl 4-([1,1'-biphenyl]-4-yl)-4-fluorobut-2-enoate (**2d**):



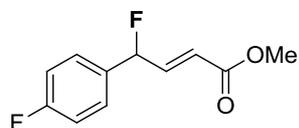
Prepared according to **MA** or **MB** (**C4** was used as the catalyst in **MB**). Flash column chromatography (eluent: PE/EA = 30:1, *v/v*) to afford **2d** (**MA**: 16.9 mg, 63%; **MB**: 18.1 mg, 67%) as a pale yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, $J = 7.8$ Hz, 2H), 7.59 (d, $J = 7.6$ Hz, 2H), 7.51 – 7.41 (m, 4H), 7.38 (t, $J = 7.2$ Hz, 1H), 7.17 – 7.03 (m, 1H), 6.23 (d, $J = 15.7$ Hz, 1H), 6.07 (dd, $J = 47.1, 3.8$ Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.39, 144.40 (d, $J = 22.1$ Hz), 142.49, 142.46, 140.51, 135.74 (d, $J = 20.0$ Hz), 129.00, 127.79 (d, $J = 6.2$ Hz), 127.31, 127.28 (d, $J = 5.6$ Hz), 121.35 (d, $J = 10.1$ Hz), 91.75 (d, $J = 175.2$ Hz), 51.99. ^{19}F NMR (377 MHz, CDCl_3) δ -172.92. The ^1H , ^{13}C and ^{19}F NMR spectra were in accordance with those reported in the reference.¹⁴

(*E*)-Methyl 4-fluoro-4-(4-(trifluoromethyl)phenyl)but-2-enoate (**2e**):



Prepared according to **MA** or **MB** (**C4** was used as the catalyst in **MB** and the reaction was performed at 40 °C for 2 d). Flash column chromatography (eluent: PE/EA = 40:1, *v/v*) to afford **2e** (**MA**: 23.0 mg, 88%; **MB**: 20.3 mg, 77%) as a pale yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 8.0$ Hz, 2H), 7.48 (d, $J = 7.9$ Hz, 2H), 7.02 (ddd, $J = 19.0, 15.7, 4.5$ Hz, 1H), 6.20 (d, $J = 15.7$ Hz, 1H), 6.08 (dd, $J = 46.9, 3.8$ Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.11, 143.43 (d, $J = 21.3$ Hz), 140.73 (d, $J = 20.2$ Hz), 131.48 (q, $J = 32.5$ Hz), 126.77 (d, $J = 6.2$ Hz), 126.02 (q, $J = 3.7$ Hz), 123.91 (q, $J = 272.2$ Hz), 121.95 (d, $J = 10.4$ Hz), 91.08 (d, $J = 177.0$ Hz), 52.12. ^{19}F NMR (377 MHz, CDCl_3) δ -62.78, -177.31. The ^1H , ^{13}C and ^{19}F NMR spectra were in accordance with those reported in the reference.¹⁴

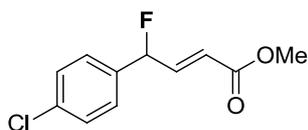
(*E*)-Methyl 4-fluoro-4-(4-fluorophenyl)but-2-enoate (**2f**):



Prepared according to **MA** or **MB** (**C7** was used as the catalyst in **MB**). Flash column chromatography (eluent: PE/EA = 40:1, *v/v*) to afford **2f** (**MA**: 18.6 mg, 81%; **MB**: 19.8 mg, 88%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.33 (dd, $J = 7.1, 5.5$ Hz, 2H), 7.13 – 6.97 (m, 3H), 6.18 (d, $J = 15.7$ Hz, 1H), 6.00 (dd, $J = 46.9, 2.8$ Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.27, 163.31 (dd, $J = 248.6, 2.7$ Hz), 144.09 (d, $J = 22.2$ Hz), 132.67 (dd, $J = 20.5, 3.2$ Hz), 128.88 (dd, $J = 8.4, 5.4$ Hz), 121.41 (d, $J = 10.1$ Hz), 116.01 (d, $J = 21.8$ Hz), 91.21 (d, $J = 175.5$ Hz), 52.00. ^{19}F NMR (377 MHz, CDCl_3) δ -111.80 (d, $J = 4.3$ Hz), -171.13 (d, $J = 4.4$ Hz). The

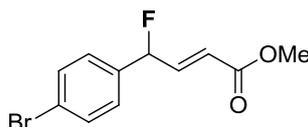
^1H , ^{13}C and ^{19}F NMR spectra were in accordance with those reported in the reference.¹⁴

(*E*)-Methyl 4-(4-chlorophenyl)-4-fluorobut-2-enoate (**2g**):



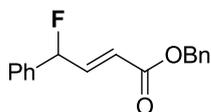
Prepared according to **MA** or **MB** (**C7** was used as the catalyst in **MB**). Flash column chromatography (eluent: PE/EA = 40:1, *v/v*) to afford **2g** (**MA**: 20.3 mg, 89%; **MB**: 22.4 mg, 98%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.38 (d, $J = 8.1$ Hz, 2H), 7.28 (d, $J = 8.2$ Hz, 2H), 7.08 – 6.94 (m, 1H), 6.17 (d, $J = 15.7$ Hz, 1H), 5.99 (dd, $J = 46.9, 4.1$ Hz, 1H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.23, 143.85 (d, $J = 21.9$ Hz), 135.33 (d, $J = 20.9$ Hz), 129.25, 128.15 (d, $J = 5.7$ Hz), 121.64 (d, $J = 10.1$ Hz), 91.17 (d, $J = 175.9$ Hz), 52.05. ^{19}F NMR (377 MHz, CDCl_3) δ -173.58. The ^1H , ^{13}C and ^{19}F NMR spectra were in accordance with those reported in the reference.¹⁴

(*E*)-Methyl 4-(4-bromophenyl)-4-fluorobut-2-enoate (**2h**):



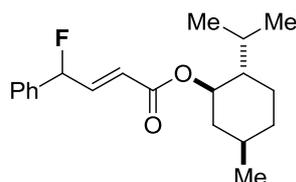
Prepared according to **MA** or **MB** (**C4** was used as the catalyst in **MB** and the mixture was stirred for 2 d). Flash column chromatography (eluent: PE/EA = 40:1, *v/v*) to afford **2h** (**MA**: 24.1 mg, 88%; **MB**: 22.8 mg, 84%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, $J = 8.1$ Hz, 2H), 7.22 (d, $J = 7.8$ Hz, 2H), 7.07 – 6.90 (m, 1H), 6.17 (d, $J = 15.7$ Hz, 1H), 5.98 (dd, $J = 46.9, 3.2$ Hz, 1H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.21, 143.77 (d, $J = 21.9$ Hz), 135.84 (d, $J = 20.5$ Hz), 132.20, 128.38 (d, $J = 5.7$ Hz), 123.59 (d, $J = 2.8$ Hz), 121.66 (d, $J = 10.2$ Hz), 91.21 (d, $J = 176.0$ Hz), 52.0. ^{19}F NMR (377 MHz, CDCl_3) δ -174.08. The ^1H , ^{13}C and ^{19}F NMR spectra were in accordance with those reported in the reference.¹⁴

(*E*)-Benzyl 4-fluoro-4-phenylbut-2-enoate (**2i**):



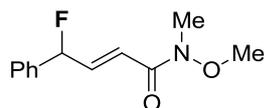
Prepared according to **MA** or **MB** (**C7** was used as the catalyst in **MB**). Flash column chromatography (eluent: PE/EA = 50:1, *v/v*) to afford **2i** (**MA**: 21.4 mg, 79%; **MB**: 26.1 mg, 97%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.31 (m, 10H), 7.17 – 7.04 (m, 1H), 6.24 (d, $J = 15.7$ Hz, 1H), 6.02 (dd, $J = 47.0, 3.5$ Hz, 1H), 5.21 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.70, 144.77 (d, $J = 22.0$ Hz), 136.78 (d, $J = 20.1$ Hz), 135.80, 129.39 (d, $J = 2.3$ Hz), 128.97, 128.70, 128.45, 128.43, 126.76 (d, $J = 5.7$ Hz), 121.33 (d, $J = 10.2$ Hz), 91.91 (d, $J = 175.3$ Hz), 66.69. ^{19}F NMR (377 MHz, CDCl_3) δ -173.43. HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{15}\text{FNaO}_2$ [$\text{M} + \text{Na}$] $^+$: 293.0948, found: 293.0946.

(*E*)-(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-fluoro-4-phenylbut-2-enoate (**2j**):



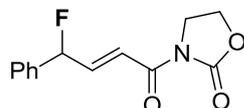
Prepared according to **MA** or **MB** (**C7** was used as the catalyst in **MB**). Flash column chromatography (eluent: PE/EA = 90:1, *v/v*) to afford **2j** (**MA**: 22.5 mg, 71%, *d.r.* = 1:1; **MB**: 28.3 mg, 89%, *d.r.* = 1:1) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.31 (m, 5H), 7.11 – 6.98 (m, 1H), 6.16 (d, *J* = 14.4 Hz, 1H), 6.02 (dd, *J* = 47.0, 2.0 Hz, 1H), 4.77 (td, *J* = 10.8, 4.2 Hz, 1H), 2.02 (d, *J* = 11.9 Hz, 1H), 1.95 – 1.81 (m, 1H), 1.69 (d, *J* = 12.5 Hz, 2H), 1.57 – 1.46 (m, 1H), 1.41 (t, *J* = 11.6 Hz, 1H), 1.16 – 0.95 (m, 2H), 0.95 – 0.83 (m, 7H), 0.76 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.58, 143.89 (d, *J* = 21.9 Hz), 136.95 (d, *J* = 20.2 Hz), 129.37, 128.97, 126.81 (d, *J* = 5.2 Hz), 122.22 (d, *J* = 6.6 Hz), 92.07 (d, *J* = 174.5 Hz), 74.79, 47.16, 40.98, 34.34, 31.52, 26.38, 23.57, 22.15, 20.89, 16.50. ¹⁹F NMR (377 MHz, CDCl₃) δ -177.94. HRMS (ESI) *m/z* calcd for C₂₀H₂₆FO₂ [M - H]⁻: 317.1922, found: 317.1920.

(*E*)-4-Fluoro-*N*-methoxy-*N*-methyl-4-phenylbut-2-enamide (**2k**):



Prepared according to **MB** (**C7** was used as the catalyst). Flash column chromatography (eluent: PE/EA = 5:1, *v/v*) to afford **2k** (13.3 mg, 60%) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.30 (m, 5H), 7.08 (ddd, *J* = 19.9, 15.5, 4.3 Hz, 1H), 6.78 (d, *J* = 15.5, 1H), 6.07 (dd, *J* = 47.3, 2.8 Hz, 1H), 3.73 (s, 3H), 3.27 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.90, 142.89 (d, *J* = 21.0 Hz), 137.16 (d, *J* = 20.0 Hz), 129.29 (d, *J* = 2.3 Hz), 128.90, 126.86 (d, *J* = 5.6 Hz), 118.81 (d, *J* = 9.5 Hz), 92.50 (d, *J* = 174.7 Hz), 62.06, 32.49. ¹⁹F NMR (377 MHz, CDCl₃) δ -172.25. The ¹H, ¹³C and ¹⁹F NMR spectra were in accordance with those reported in the reference.¹⁴

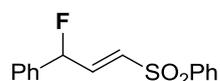
(*E*)-3-(4-Fluoro-4-phenylbut-2-enoyl)oxazolidin-2-one (**2l**):



Prepared according to **MB** (**C7** was used as the catalyst). Flash column chromatography (eluent: PE/EA = 3:1, *v/v*) to afford **2l** (18.4 mg, 74%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 15.5 Hz, 1H), 7.46 – 7.33 (m, 5H), 7.25 – 7.14 (m, 1H), 6.07 (dd, *J* = 47.1, 4.8 Hz, 1H), 4.43 (t, *J* = 8.0, 2H), 4.07 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 164.56, 153.40, 145.62 (d, *J* = 22.5 Hz), 136.88 (d, *J* = 20.5 Hz), 129.36 (d, *J* = 2.3 Hz), 128.98, 126.71 (d, *J* = 5.8 Hz), 120.20 (d, *J* = 10.2 Hz), 92.24 (d, *J* = 175.2 Hz), 62.28, 42.79. ¹⁹F NMR (377 MHz,

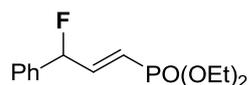
CDCl₃) δ -172.84. HRMS (ESI) m/z calcd for C₁₃H₁₁FNO₃ [M - H]⁻: 248.0728, found: 248.0728.

(*E*)-(1-Fluoro-3-(phenylsulfonyl)allyl)benzene (**2m**):



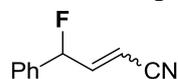
Prepared according to **MB** (**C4** was used as the catalyst, TMFP-OTf (72.4 mg, 0.25 mmol) was employed and the reaction was performed at 40 °C for 2 d). Flash column chromatography (eluent: PE/EA = 6:1, v/v) to afford **2m** (26.8 mg, 97%) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 7.6 Hz, 2H), 7.66 (t, J = 7.1 Hz, 1H), 7.57 (t, J = 7.4 Hz, 2H), 7.46 – 7.36 (m, 3H), 7.35 – 7.28 (m, 2H), 7.16 – 7.00 (m, 1H), 6.74 (d, J = 15.0 Hz, 1H), 6.06 (d, J = 46.9 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 142.14 (d, J = 22.0 Hz), 139.98, 135.56 (d, J = 19.6 Hz), 133.86, 130.95 (d, J = 9.2 Hz), 129.86 (d, J = 2.4 Hz), 129.56, 129.18, 127.97, 126.90 (d, J = 5.5 Hz), 91.04 (d, J = 178.8 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -173.18. HRMS (ESI) m/z calcd for C₁₅H₁₃FNaO₂S [M + Na]⁺: 299.0512, found: 299.0510.

(*E*)-Diethyl (3-fluoro-3-phenylprop-1-en-1-yl)phosphonate (**2n**):



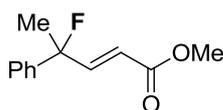
Prepared according to **MB** (**C4** was used as the catalyst). After standard work-up, the concentrated mixture was treated with NaBH₄ (1.5 mg) in THF (1 mL) and stirred for additional 10 h. Flash column chromatography (eluent: PE/EA = 1:1, v/v) to afford **2n** (16.1 mg, 59%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.30 (m, 5H), 6.97 – 6.77 (m, 1H), 6.14 – 5.88 (m, 2H), 4.15 – 4.03 (m, 4H), 1.32 (t, J = 7.1 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 148.43 (dd, J = 22.5, 5.8 Hz), 136.58 (d, J = 19.5 Hz), 129.41 (d, J = 2.3 Hz), 128.97, 126.77 (d, J = 5.7 Hz), 117.61 (dd, J = 188.0, 9.3 Hz), 92.42 (dd, J = 176.9, 22.2 Hz), 62.14 (d, J = 5.6 Hz), 16.48 (d, J = 6.4 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -174.17. The ¹H NMR spectrum was in accordance with that reported in the reference.¹⁵

4-Fluoro-4-phenylbut-2-enenitrile (**2o**):



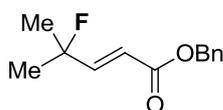
Prepared according to **MB** (**C4** was used as the catalyst). Flash column chromatography (eluent: PE/EA = 40:1, v/v) to afford **2o** (11.4 mg, 71%, *E/Z* = 3:1) as a pale yellow oil. Major isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.51 – 7.29 (m, 5H), 6.83 (ddd, J = 19.8, 16.3, 3.7 Hz, 1H), 6.10 – 5.90 (m, 1H), 5.78 (d, J = 16.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 150.54 (d, J = 21.6 Hz), 135.41 (d, J = 19.5 Hz), 129.99 (d, J = 2.4 Hz), 129.25, 126.91 (d, J = 5.4 Hz), 116.47, 100.41 (d, J = 14.0 Hz), 91.53 (d, J = 178.7 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -174.76. HRMS (ESI) m/z calcd for C₁₀H₇FN [M - H]⁻: 160.0568, found: 160.0570.

(*E*)-Methyl 4-fluoro-4-phenylpent-2-enoate (**2p**):



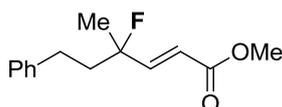
Prepared according to **MA** or **MB** (**C7** was used as the catalyst in **MB**). Flash column chromatography (eluent: PE/EA = 50:1, *v/v*) to afford **2p** (**MA**: 14.9 mg, 72%; **MB**: 15.9 mg, 76%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.29 (m, 5H), 7.12 (dd, *J* = 19.1, 15.7 Hz, 1H), 6.12 (d, *J* = 15.6 Hz, 1H), 3.75 (s, 3H), 1.83 (d, *J* = 22.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.76, 149.24 (d, *J* = 22.7 Hz), 141.46 (d, *J* = 22.4 Hz), 128.68, 128.29, 124.64 (d, *J* = 8.0 Hz), 118.91 (d, *J* = 10.5 Hz), 95.25 (d, *J* = 176.1 Hz), 51.91, 26.66 (d, *J* = 25.3 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -145.99. The ¹H, ¹³C and ¹⁹F NMR spectra were in accordance with those reported in the reference.¹⁴

(*E*)-Methyl 4-fluoro-4-methylpent-2-enoate (**2q**):



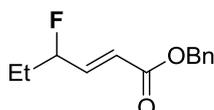
Prepared according to **MB** (**C4** was used as the catalyst). Flash column chromatography (eluent: PE/EA = 50:1, *v/v*) to afford **2q** (16.8 mg, 75%) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.29 (m, 5H), 6.99 (dd, *J* = 19.4, 15.8 Hz, 1H), 6.09 (d, *J* = 15.7 Hz, 1H), 5.20 (s, 2H), 1.48 (d, *J* = 21.1 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 166.31, 150.65 (d, *J* = 21.5 Hz), 135.92, 128.72, 128.43, 118.76 (d, *J* = 10.4 Hz), 93.49 (d, *J* = 171.4 Hz), 66.58, 26.98 (d, *J* = 24.8 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -142.10. HRMS (APCI) *m/z* calcd for C₁₃H₁₄FO₂ [M - H]⁻: 221.0983, found: 221.0983.

(*E*)-Methyl 4-fluoro-4-methyl-6-phenylhex-2-enoate (**2r**):



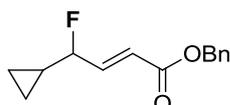
Prepared according to **MB** (**C4** was used as the catalyst). Flash column chromatography (eluent: PE/EA = 50:1, *v/v*) to afford **2r** (17.5 mg, 74%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.29 (t, *J* = 7.3 Hz, 2H), 7.23 – 7.14 (m, 3H), 6.95 (dd, *J* = 21.2, 15.7 Hz, 1H), 6.12 (d, *J* = 15.7 Hz, 1H), 3.78 (s, 3H), 2.74 (td, *J* = 13.0, 5.2 Hz, 1H), 2.67 – 2.56 (m, 1H), 2.15 – 1.90 (m, 2H), 1.52 (d, *J* = 21.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.68, 149.15 (d, *J* = 20.9 Hz), 141.25, 128.48, 128.27, 126.04, 119.50 (d, *J* = 10.6 Hz), 95.17 (d, *J* = 176.3 Hz), 51.77, 41.74 (d, *J* = 22.8 Hz), 29.74 (d, *J* = 4.4 Hz), 25.55 (d, *J* = 24.8 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -152.58. The ¹H, ¹³C and ¹⁹F NMR spectra were in accordance with those reported in the reference.¹⁴

(*E*)-Benzyl 4-fluorohex-2-enoate (**2s**):



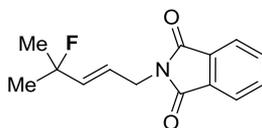
Prepared according to **MB** (**C4** was used as the catalyst). Flash column chromatography (eluent: PE/EA = 50:1, *v/v*) to afford **2s** (13.0 mg, 59%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.30 (m, 5H), 6.94 (ddd, *J* = 20.1, 15.8, 4.1 Hz, 1H), 6.12 (d, *J* = 15.8 Hz, 1H), 5.21 (s, 2H), 5.04 (ddd, *J* = 48.2, 9.5, 4.7 Hz, 1H), 1.86 – 1.67 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.94, 145.63 (d, *J* = 18.7 Hz), 135.93, 128.73, 128.44, 128.40, 121.06 (d, *J* = 11.0 Hz), 92.37 (d, *J* = 174.3 Hz), 66.59, 27.94 (d, *J* = 21.7 Hz), 8.93 (d, *J* = 5.4 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -185.66. HRMS (APCI) *m/z* calcd for C₁₃H₁₄FO₂ [M - H]⁻: 221.0983, found: 221.0983.

(*E*)-Benzyl 4-cyclopropyl-4-fluorobut-2-enoate (**2t**):



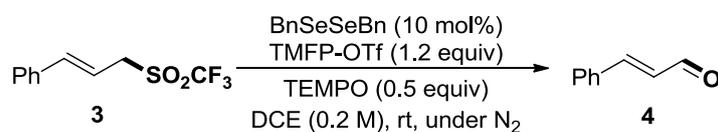
Prepared according to **MB** (**C4** was used as the catalyst). Flash column chromatography (eluent: PE/EA = 50:1, *v/v*) to afford **2t** (16.0 mg, 68%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.30 (m, 5H), 7.08 – 6.95 (m, 1H), 6.14 (d, *J* = 15.8 Hz, 1H), 5.21 (s, 2H), 4.51 – 4.32 (m, 1H), 1.19 – 1.05 (m, 1H), 0.74 – 0.60 (m, 2H), 0.59 – 0.48 (m, 1H), 0.45 – 0.31 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 165.97, 144.89 (d, *J* = 21.9 Hz), 135.93, 128.73, 128.46, 128.43, 121.17 (d, *J* = 10.0 Hz), 95.15 (d, *J* = 174.4 Hz), 66.64, 14.66 (d, *J* = 27.0 Hz), 3.64, 2.16 (d, *J* = 8.5 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -176.44. HRMS (APCI) *m/z* calcd for C₁₄H₁₄FO₂ [M - H]⁻: 233.0983, found: 233.0984.

(*E*)-2-(4-Fluoro-4-methylpent-2-en-1-yl)isoindoline-1,3-dione (**2u**):



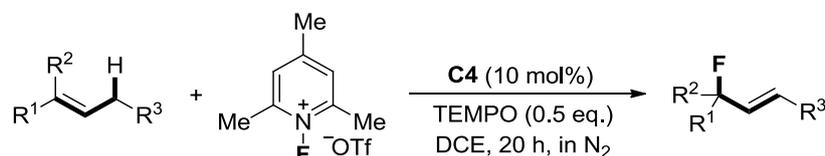
Prepared according to **MB** (**C4** was used as the catalyst). Flash column chromatography (eluent: PE/acetone = 40:1, *v/v*) to afford **2u** (17.1 mg, 69%) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.85 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.4, 3.0 Hz, 2H), 5.91 – 5.80 (m, 1H), 5.76 (dt, *J* = 11.9, 5.5 Hz, 1H), 4.28 (d, *J* = 4.8 Hz, 2H), 1.41 (d, *J* = 21.3 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 167.85, 137.50 (d, *J* = 22.3 Hz), 134.01, 132.11, 123.34, 122.05 (d, *J* = 10.5 Hz), 93.45 (d, *J* = 165.7 Hz), 38.91, 27.21 (d, *J* = 25.2 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -136.46. The ¹H, ¹³C and ¹⁹F NMR spectra were in accordance with those reported in the reference.¹⁶

2.6 Synthesis of Cinnamaldehyde (**4**) via Electrophilic Selenium Catalysis

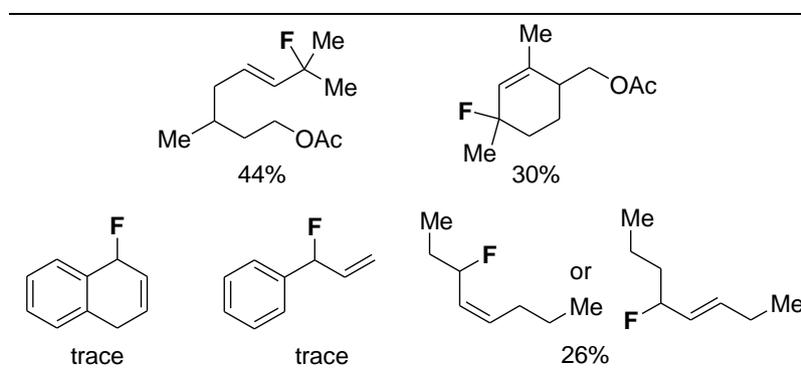


A 1.5-mL vial equipped with a magnetic stir bar was charged with TMFP-OTf (34.7 mg, 0.12 mmol) and **C7** (3.4 mg, 0.01 mmol). Then the vial was moved into glovebox. After TEMPO (7.8 mg, 0.05 mmol) in dry DCE (500 μ L) and olefin **3** (0.1 mmol) were added successively under nitrogen atmosphere, the vial was capped and removed from glovebox. The reaction was performed at room temperature for 20 h. Then the resulting mixture was quenched with H₂O (2 mL) and extracted with DCM (2 mL \times 3). The organic extracts were concentrated *in vacuo* and purified by flash column chromatography (200-300 mesh silica gel, eluent: PE/EA = 30:1, *v/v*) to afford **4** (12.2 mg, 92%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 9.74 (d, *J* = 7.7 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.55 – 7.43 (m, 4H), 6.75 (dd, *J* = 15.9, 7.7 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 193.58, 152.67, 133.88, 131.16, 128.99, 128.49, 128.38. The ¹H and ¹³C spectra were in accordance with those reported in the reference.¹⁷

2.7 Unsatisfied Results

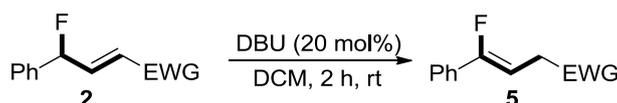


The fluorination was performed according to Method B with **C4** as the catalyst. The yield was determined by ¹⁹F NMR with benzotrifluoride as the internal standard.



Scheme S1 Selected Unsatisfied Results

2.8 Synthesis of Vinyl Fluorides via Olefin Isomerization

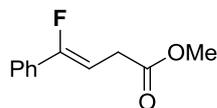


General procedure of the isomerization:

To a 4-mL vial equipped with a magnetic stir bar were added allylic fluorides **2** (0.08 mmol), DCM (1 mL) and DBU (2.4 μ L, 0.016 mmol) successively. The mixture was stirred at room temperature for 2 h. Then the reaction was quenched with aqueous 6M HCl solution (3 μ L) and concentrated *in vacuo*. The residue was purified by flash

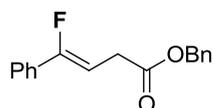
column chromatography (200-300 mesh silica gel) to afford the corresponding vinyl fluorides **5**.

(Z)-Methyl 4-fluoro-4-phenylbut-3-enoate (**5a**):



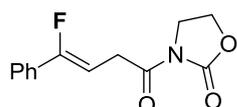
Prepared according to the general procedure. Flash column chromatography (eluent: PE/EA = 50:1, v/v) to afford **5a** (15.4 mg, 99%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, $J = 7.3$ Hz, 2H), 7.43 – 7.30 (m, 3H), 5.62 (dt, $J = 36.1, 7.2$ Hz, 1H), 3.73 (s, 3H), 3.36 (d, $J = 7.2$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.79, 158.37 (d, $J = 250.0$ Hz), 132.00 (d, $J = 28.4$ Hz), 129.19, 128.60 (d, $J = 1.8$ Hz), 124.37 (d, $J = 7.0$ Hz), 97.94 (d, $J = 16.2$ Hz), 52.18, 29.92 (d, $J = 6.1$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -117.00. HRMS (APCI) m/z calcd for $\text{C}_{11}\text{H}_{10}\text{FO}_2$ [$\text{M} - \text{H}$] $^-$: 193.0670, found: 193.0665.

(Z)-Benzyl 4-fluoro-4-phenylbut-3-enoate (**5b**):



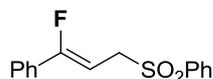
Prepared according to the general procedure. Flash column chromatography (eluent: PE/EA = 50:1, v/v) to afford **5b** (21.4 mg, 99%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, $J = 7.5$ Hz, 2H), 7.44 – 7.30 (m, 8H), 5.65 (dt, $J = 36.2, 7.2$ Hz, 1H), 5.18 (s, 2H), 3.42 (d, $J = 7.2$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.18, 158.43 (d, $J = 250.2$ Hz), 135.90, 132.00 (d, $J = 28.5$ Hz), 129.19, 128.73, 128.59 (d, $J = 1.5$ Hz), 128.45, 128.38, 124.39 (d, $J = 6.9$ Hz), 97.86 (d, $J = 16.1$ Hz), 66.87, 30.13 (d, $J = 6.1$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -116.66. HRMS (APCI) m/z calcd for $\text{C}_{17}\text{H}_{14}\text{FO}_2$ [$\text{M} - \text{H}$] $^-$: 269.0983, found: 269.0982.

(Z)-3-(4-Fluoro-4-phenylbut-3-enoyl)oxazolidin-2-one (**5c**):



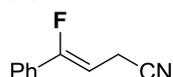
Prepared according to the general procedure. Flash column chromatography (eluent: PE/EA = 1:1, v/v) to afford **5c** (16.5 mg, 83%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, $J = 7.4$ Hz, 2H), 7.40 – 7.31 (m, 3H), 5.72 (dt, $J = 36.5, 7.0$ Hz, 1H), 4.44 (t, $J = 8.1$ Hz, 2H), 4.05 (t, $J = 8.0$ Hz, 2H), 3.96 (d, $J = 7.0$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.75, 158.72 (d, $J = 250.7$ Hz), 153.61, 132.04 (d, $J = 28.6$ Hz), 129.18, 128.58 (d, $J = 1.8$ Hz), 124.43 (d, $J = 7.0$ Hz), 97.21 (d, $J = 15.5$ Hz), 62.34, 42.71, 31.41 (d, $J = 5.6$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -116.12. HRMS (APCI) m/z calcd for $\text{C}_{13}\text{H}_{13}\text{FNO}_3$ [$\text{M} + \text{H}$] $^+$: 250.0874, found: 250.0873.

(Z)-(1-Fluoro-3-(phenylsulfonyl)prop-1-en-1-yl)benzene (**5d**):



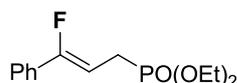
Prepared according to the modified general procedure (TEA (11.1 μ L, 0.08 mmol) was employed instead of DBU). Flash column chromatography (eluent: PE/EA = 7:1, v/v) to afford **5d** (21.8 mg, 99%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, J = 7.7 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.5 Hz, 2H), 7.46 – 7.32 (m, 5H), 5.50 (dt, J = 33.5, 8.1 Hz, 1H), 4.07 (d, J = 8.1 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.50 (d, J = 257.4 Hz), 138.58, 133.95, 130.84 (d, J = 27.9 Hz), 130.18, 129.22, 128.75 (d, J = 1.5 Hz), 128.49, 124.73 (d, J = 7.1 Hz), 92.62 (d, J = 15.4 Hz), 53.13 (d, J = 5.3 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -112.25. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{13}\text{FN}_2\text{O}_2\text{S}$ [$\text{M} + \text{Na}$] $^-$: 299.0512, found: 299.0509.

(Z)-4-Fluoro-4-phenylbut-3-enenitrile (**5e**):



Prepared according to the general procedure. Flash column chromatography (eluent: PE/EA = 50:1, v/v) to afford **5e** (11.1 mg, 86%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.57 – 7.48 (m, 2H), 7.44 – 7.35 (m, 3H), 5.41 (dt, J = 33.5, 7.2 Hz, 1H), 3.36 (d, J = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 160.08 (d, J = 254.6 Hz), 130.78 (d, J = 27.6 Hz), 130.07 (s), 128.79 (d, J = 1.9 Hz), 124.58 (d, J = 7.1 Hz), 117.47 (d, J = 1.9 Hz), 94.10 (d, J = 16.7 Hz), 13.21 (d, J = 8.8 Hz). HRMS (APCI) m/z calcd for $\text{C}_{10}\text{H}_7\text{NF}$ [$\text{M} - \text{H}$] $^-$: 160.0568, found: 160.0566.

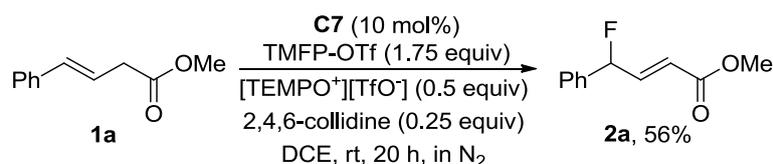
(Z)-Diethyl (3-fluoro-3-phenylallyl)phosphonate (**5f**):



Prepared according to the general procedure. Flash column chromatography (eluent: PE/EA = 50:1, v/v) to afford **5f** (21.3 mg, 98%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.58 – 7.47 (m, 1H), 7.40 – 7.29 (m, 1H), 5.46 (dq, J = 34.8, 7.6 Hz, 1H), 4.13 (p, J = 7.0 Hz, 1H), 2.83 (dd, J = 22.0, 8.0 Hz, 1H), 1.32 (t, J = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.01 (dd, J = 250.6, 14.8 Hz), 131.90 (dd, J = 28.6, 3.6 Hz), 129.25 (s), 128.62 (s), 124.30 (dd, J = 6.9, 1.4 Hz), 95.49 (dd, J = 17.0, 11.5 Hz), 62.28 (d, J = 6.6 Hz), 22.90 (dd, J = 142.7, 5.7 Hz), 16.55 (d, J = 5.9 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -117.06 (d, J = 10.8 Hz). HRMS (APCI) m/z calcd for $\text{C}_{13}\text{H}_{19}\text{FO}_3\text{P}$ [$\text{M} + \text{H}$] $^+$: 273.1050, found: 273.1052.

3. Mechanistic Studies

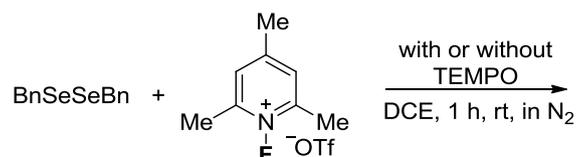
3.1 Influence of Oxoammonium Salt for Fluorination



A 1.5-mL vial equipped with a magnetic stir bar was charged with TMFP-OTf (25.4 mg, 0.088 mmol), **C7** (1.9 mg, 0.005 mmol) and $[\text{TEMPO}^+][\text{TfO}^-]$ (7.6 mg, 0.025

mmol). Then the vial was moved into glovebox. After dry DCE (350 μ L), olefins **1a** (8.8 mg, 0.05 mmol) and 2,4,6-collidine (1.6 μ L, 0.013 mmol) were added successively under nitrogen atmosphere, the vial was capped and removed from glovebox. The reaction was performed at room temperature for 20 h. Then the resulting mixture was quenched with H₂O (2 mL) and extracted with DCM (2 mL \times 3). The organic extracts were concentrated *in vacuo* and analyzed by ¹H NMR and ¹⁹F NMR in CDCl₃. Benzotrifluoride was used as the internal standard.

3.2 Influence of TEMPO for Oxidation of BnSeSeBn (C7)



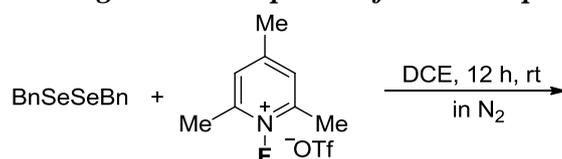
A 1.5-mL vial equipped with a magnetic stir bar was charged with TMFP-OTf (14.5 mg, 0.05 mmol), **C7** and TEMPO. Then the vial was moved into glovebox. After dry DCE (350 μ L) were added under inert gas, the vial was capped and removed from glovebox. The reaction was performed at room temperature for 1 h. Then the resulting mixture was quenched with H₂O (2 mL) and extracted with DCM (2 mL \times 3). The organic extracts were concentrated *in vacuo* and analyzed by ¹H NMR in CDCl₃. Benzyl benzoate was used as the internal standard.

Table S4 Influence of TEMPO for Oxidation of BnSeSeBn

Entry	Ratio of S.M.			Residual BnSeSeBn after 1 h ^a
	TMFP-OTf	BnSeSeBn	TEMPO	
1	1.25	1	0.5	91
2	1	1	0.5	95
3	1	1	-	36
4	1	0.5	0.5	46
5	1	0.5	-	2

^aDetermined by ¹H NMR with benzyl benzoate as the internal standard.

3.3 Analysis of the Resulting Selenium Species after Decomposition of C7

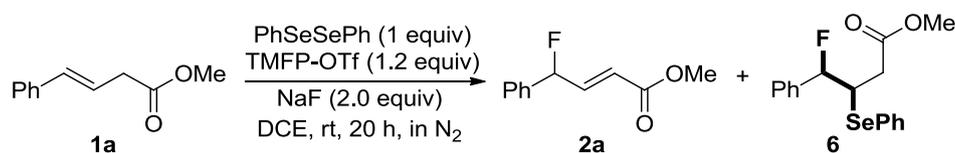


A 4-mL vial equipped with a magnetic stir bar was charged with TMFP-OTf (116 mg, 0.4 mmol) and **C7** (68.0 mg, 0.2 mmol). Then the vial was moved into glovebox. After dry DCE (1 mL) was added under inert gas, the vial was capped and removed from glovebox. The reaction was performed at room temperature for 12 h and stood for additional 30 min. Then the supernatant was poured out carefully and the insoluble black solid was washed with DCM (5 mL \times 3). The resulting selenium species was analyzed by melting point apparatus.

Table S5 Melting Point of the Resulting Selenium Species

Sample	Melting Point/ $^{\circ}$ C	Characteristic
resulting selenium species	220.5-221.0	black powder
99.99% selenium powder	221.2-221.7	black powder
ref. 18	221	-

3.4 Formation of Fluoroselenenylated Intermediate (6)



A 1.5-mL vial equipped with a magnetic stir bar was charged with TMFP-OTf (17.4 mg, 0.06 mmol), **C1** (1.6 mg, 0.005 mmol) and NaF (4.2 mg, 0.1 mmol). Then the vial was moved into glovebox. After dry DCE (350 μ L) and olefin **1a** (8.8 mg, 0.05 mmol) were added successively under inert gas, the vial was capped and removed from glovebox. The reaction was performed at room temperature for 20 h. Then the resulting mixture was quenched with H₂O (2 mL) and extracted with DCM (2 mL \times 3). The organic extracts were concentrated *in vacuo* and analyzed by ¹H NMR and ¹⁹F NMR in CDCl₃. Benzotrifluoride was used as the internal standard.

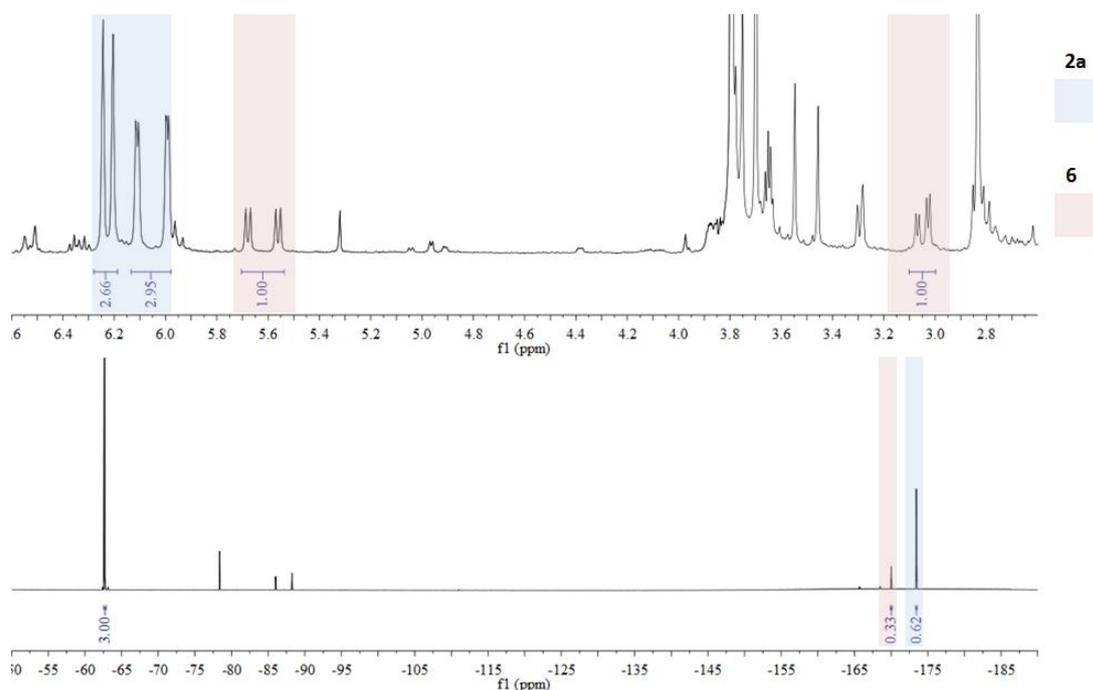


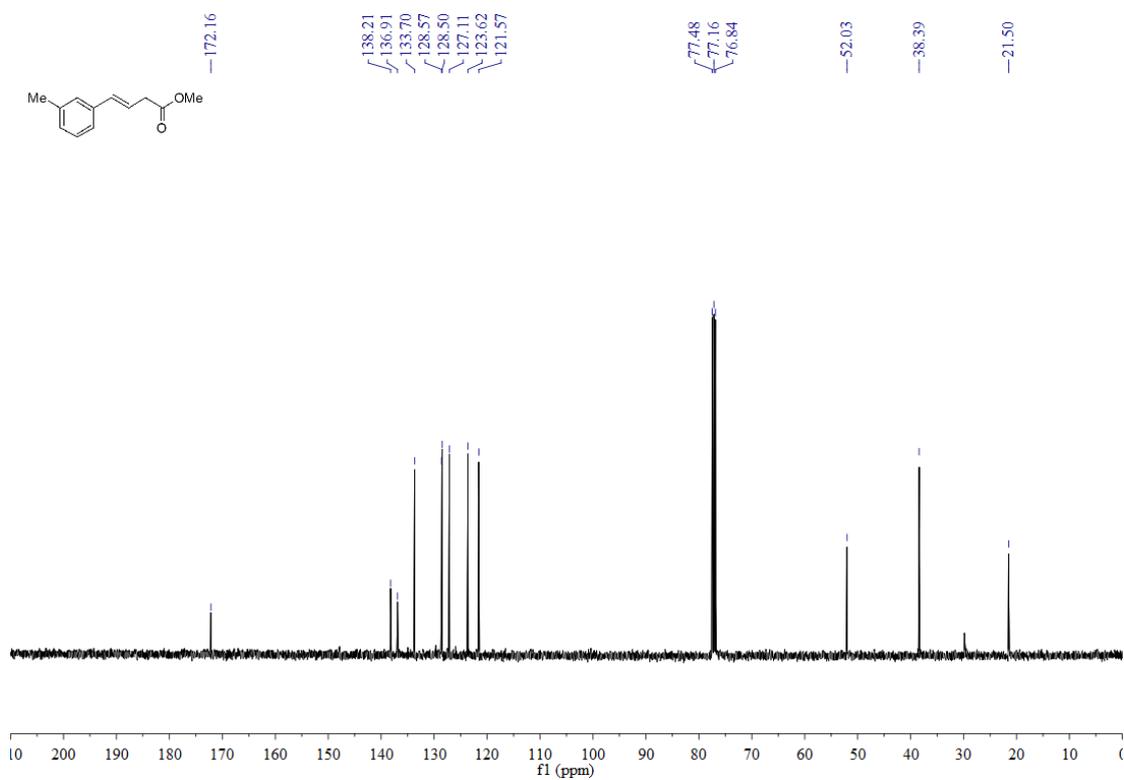
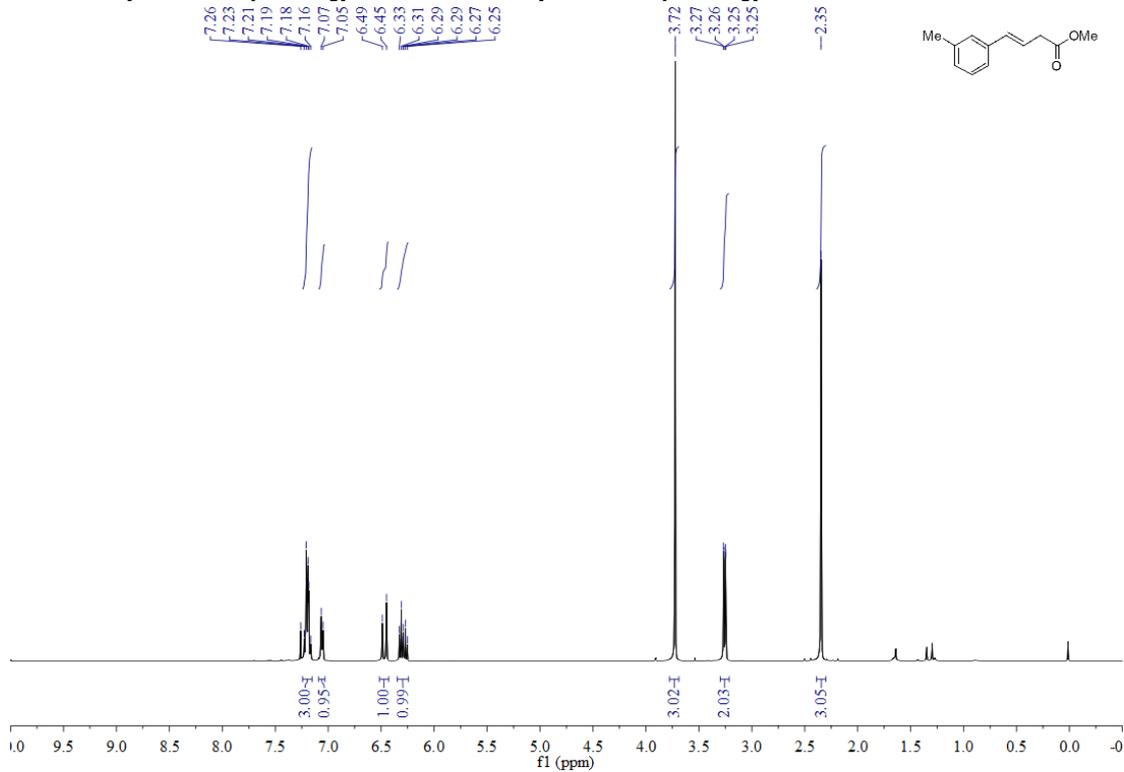
Figure S1 Extracts of the ¹H NMR (6.6 to 2.6 ppm) and ¹⁹F NMR (-50 to -190 ppm) Spectra of the Reaction Mixture

4. References

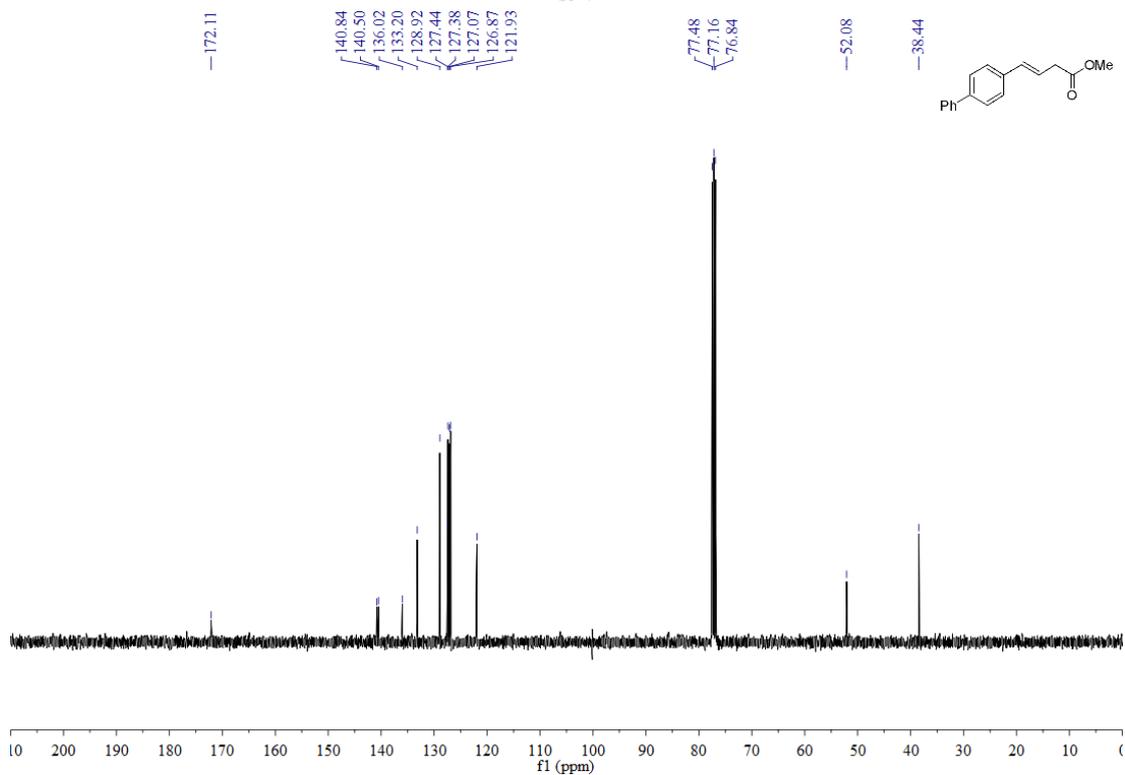
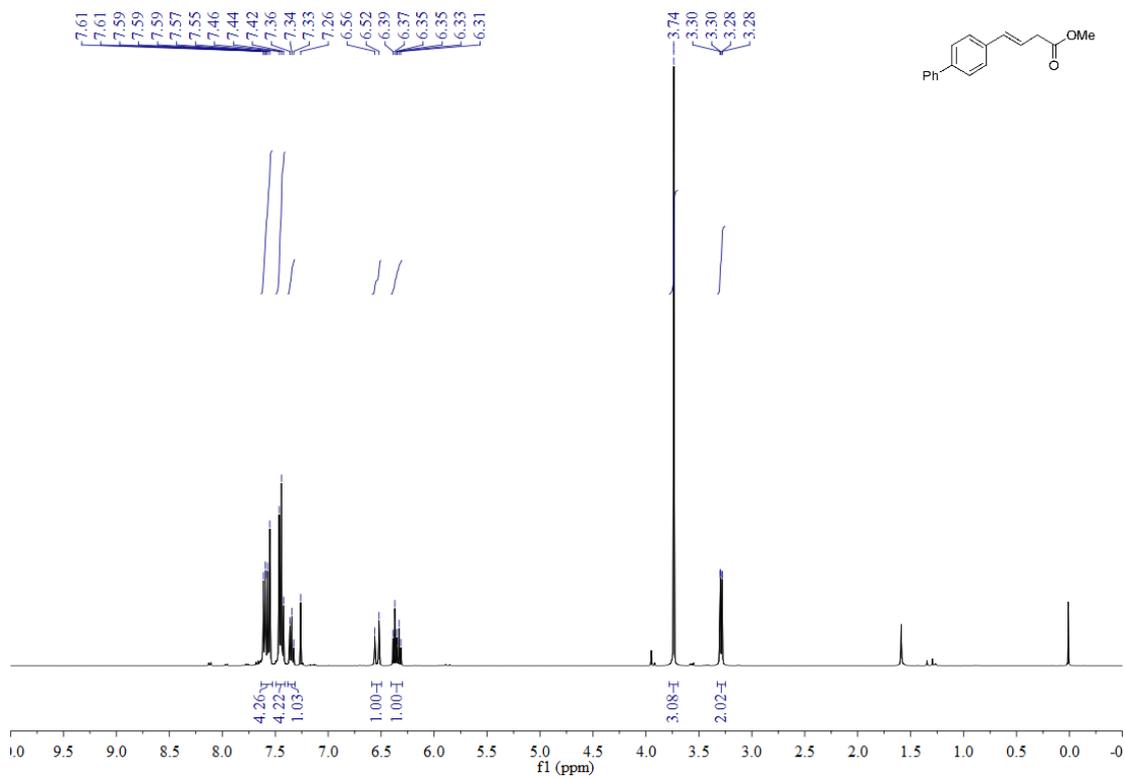
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5. NMR Spectra for New Compounds

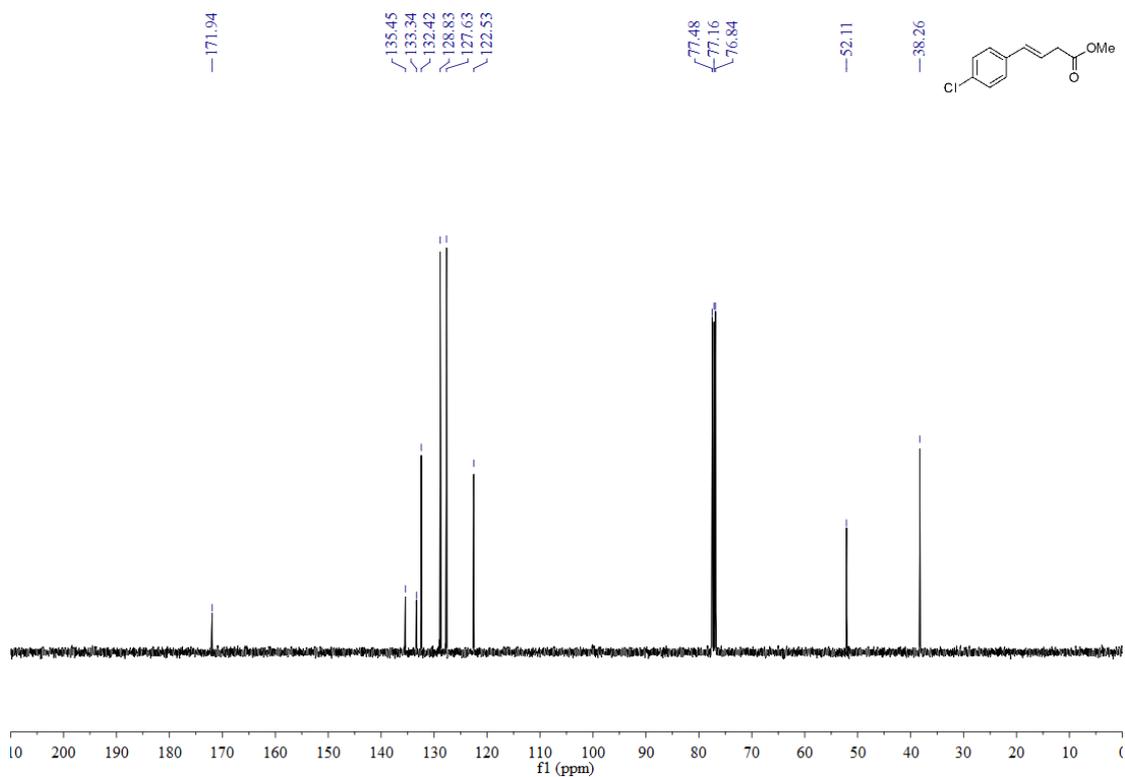
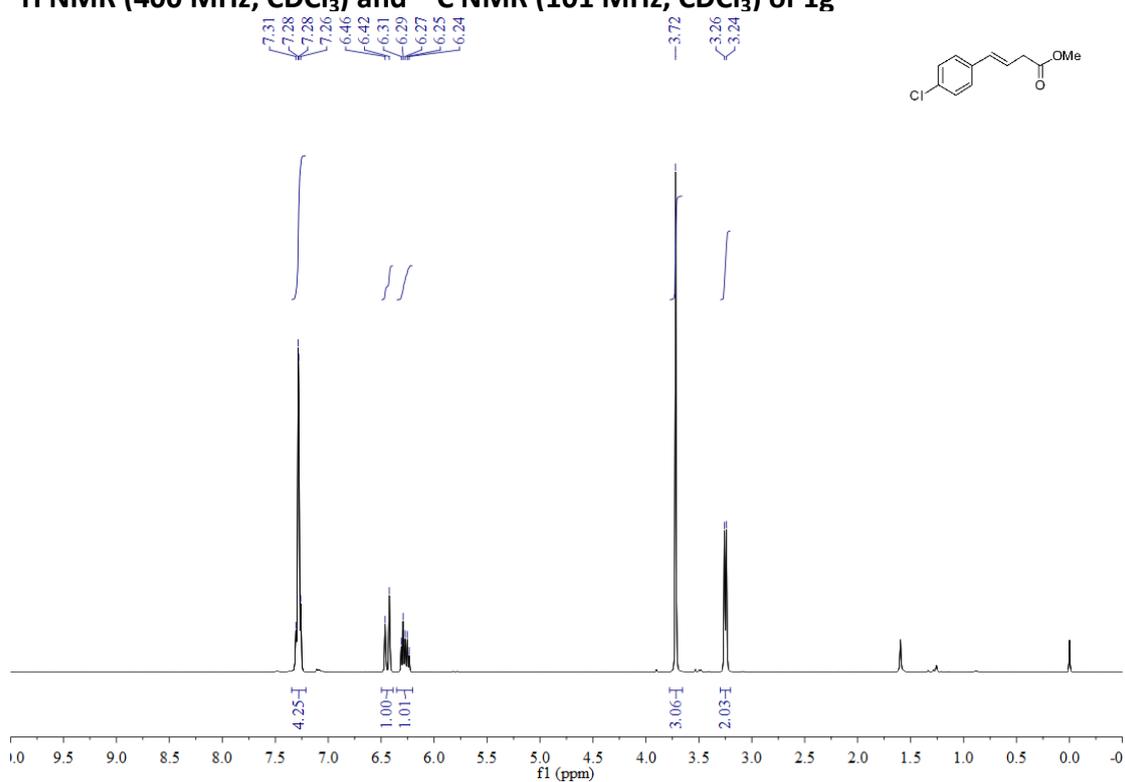
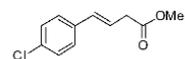
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (101 MHz, CDCl_3) of **1c**



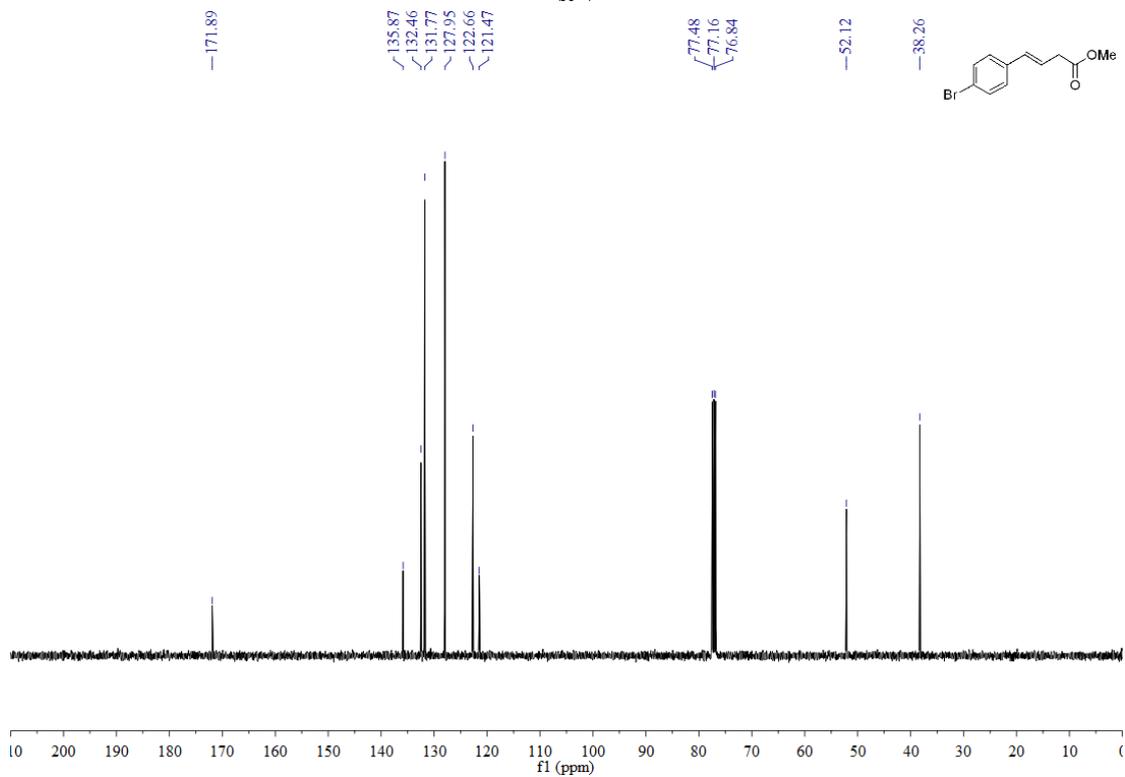
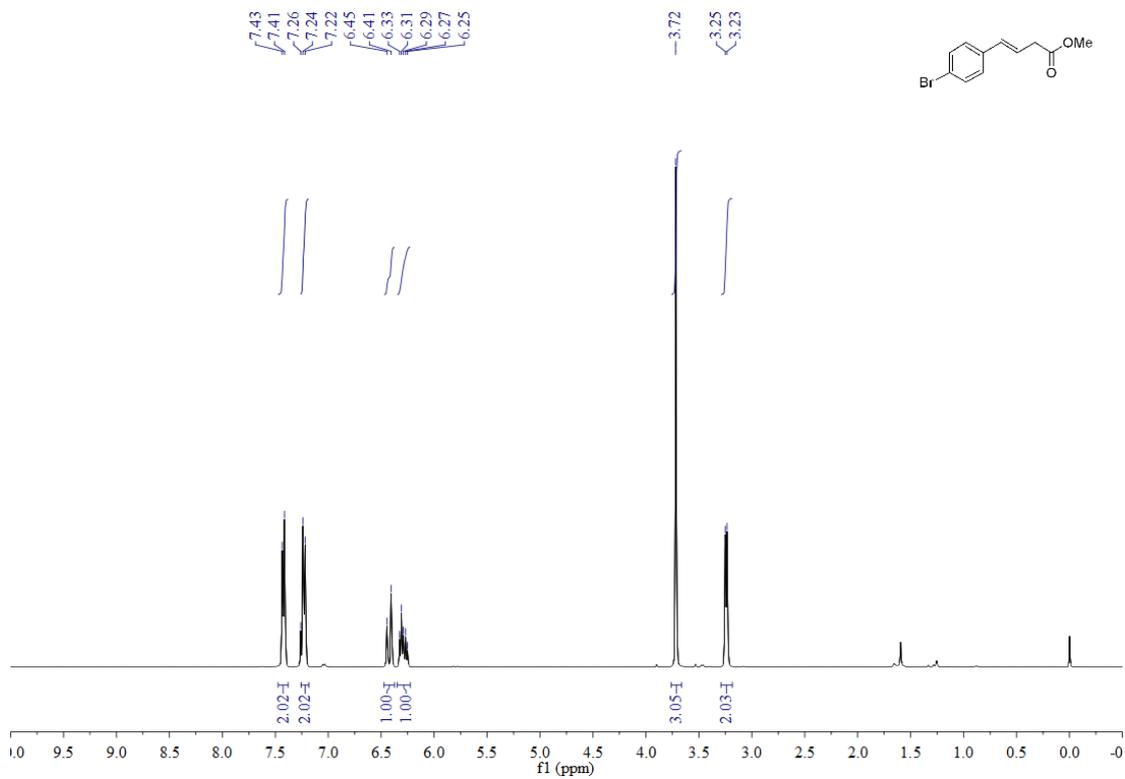
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 1d



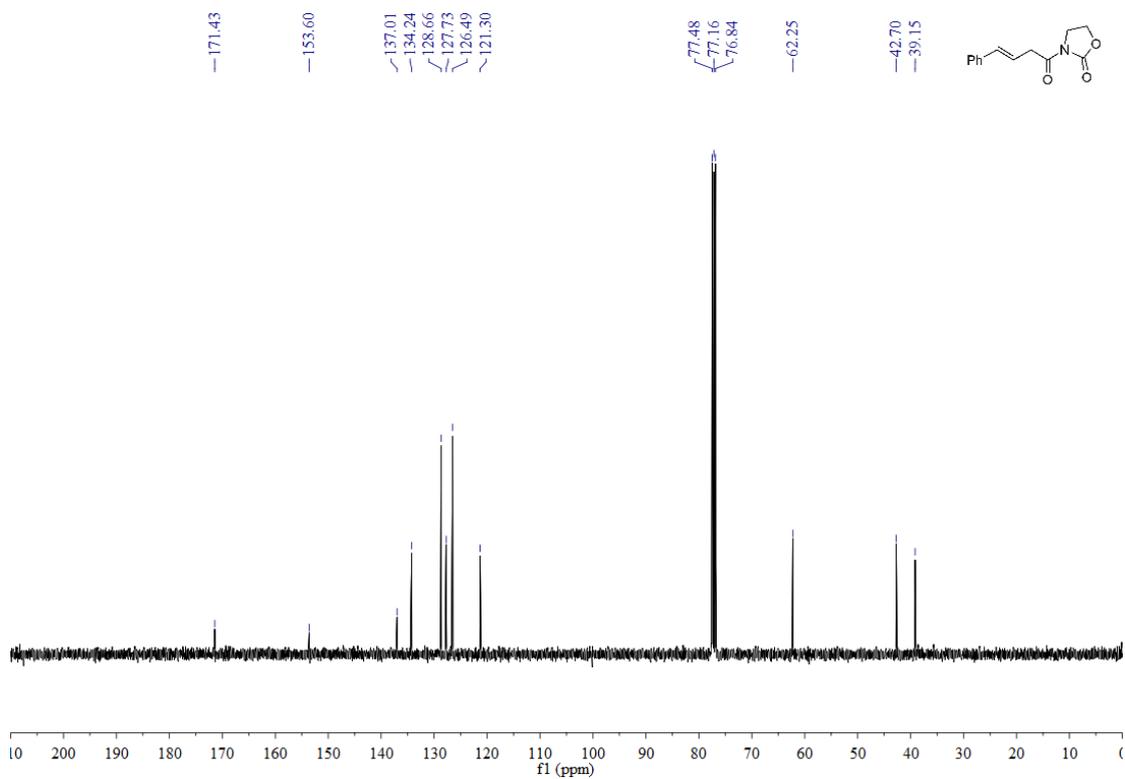
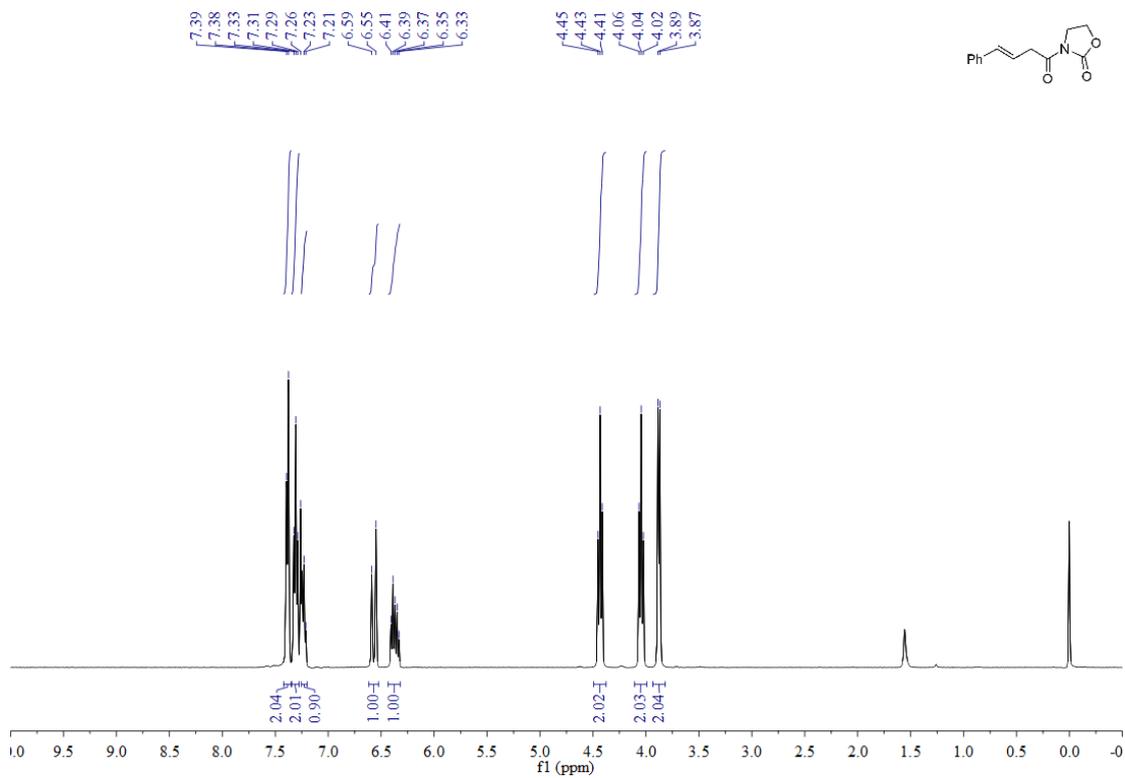
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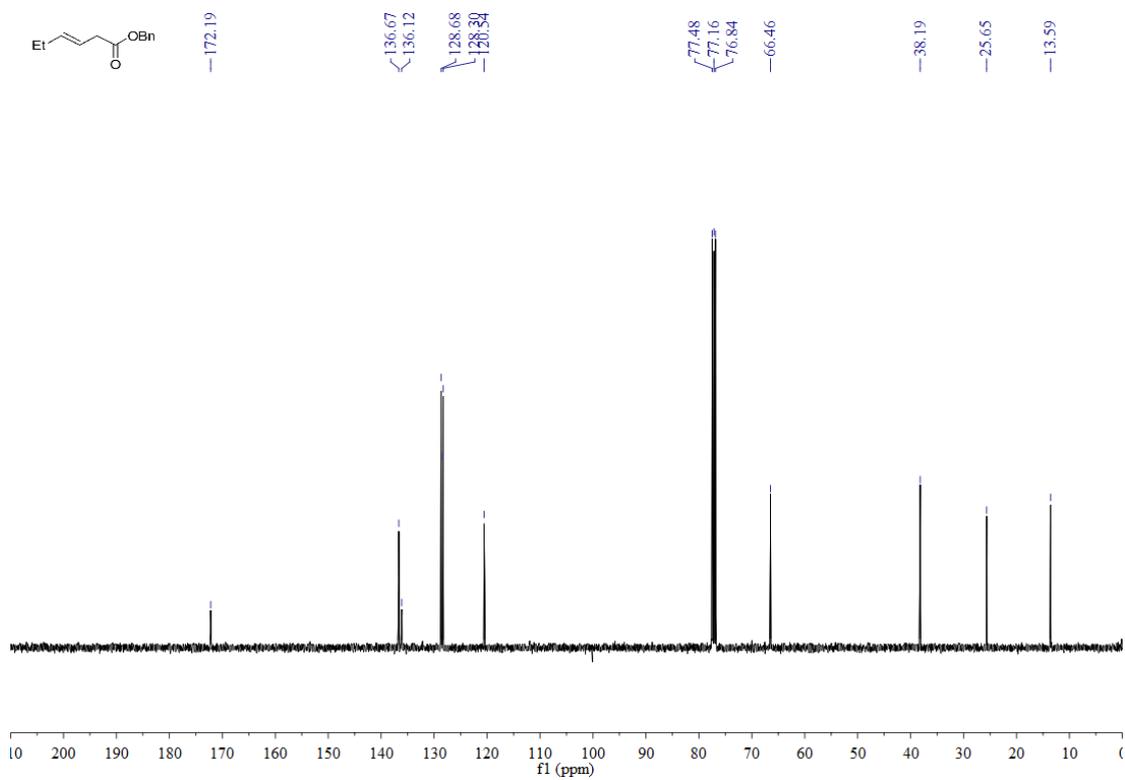
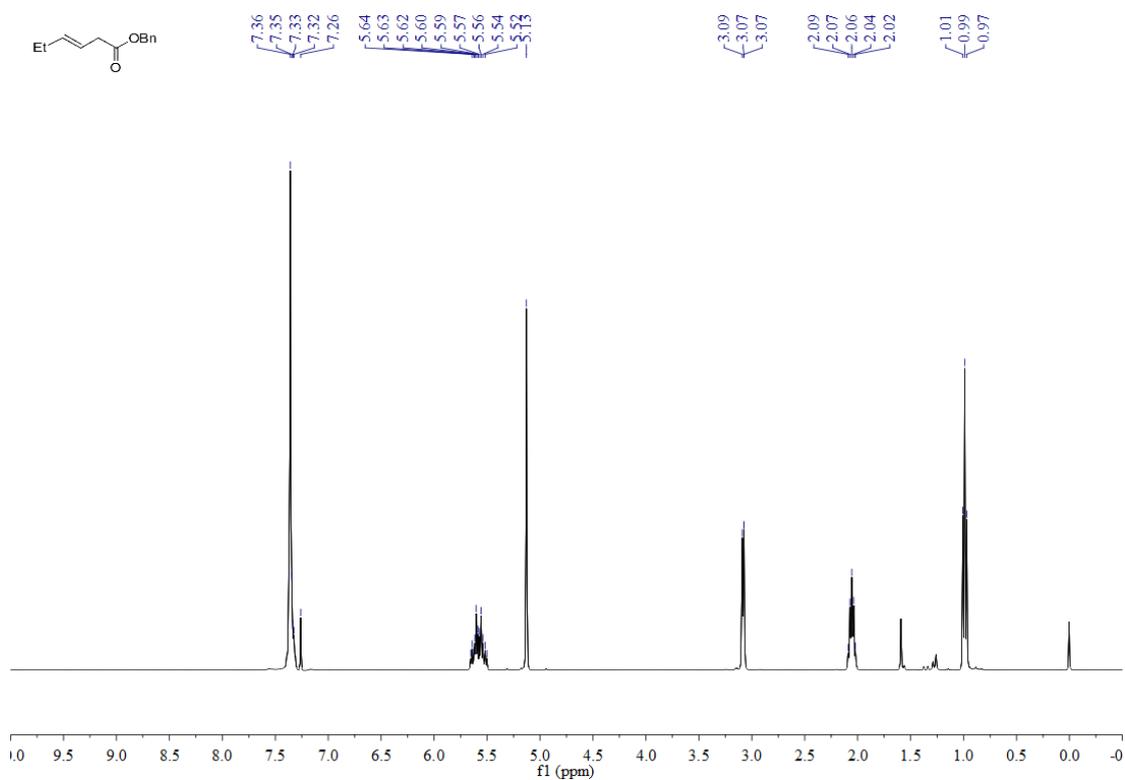
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (101 MHz, CDCl_3) of 1h



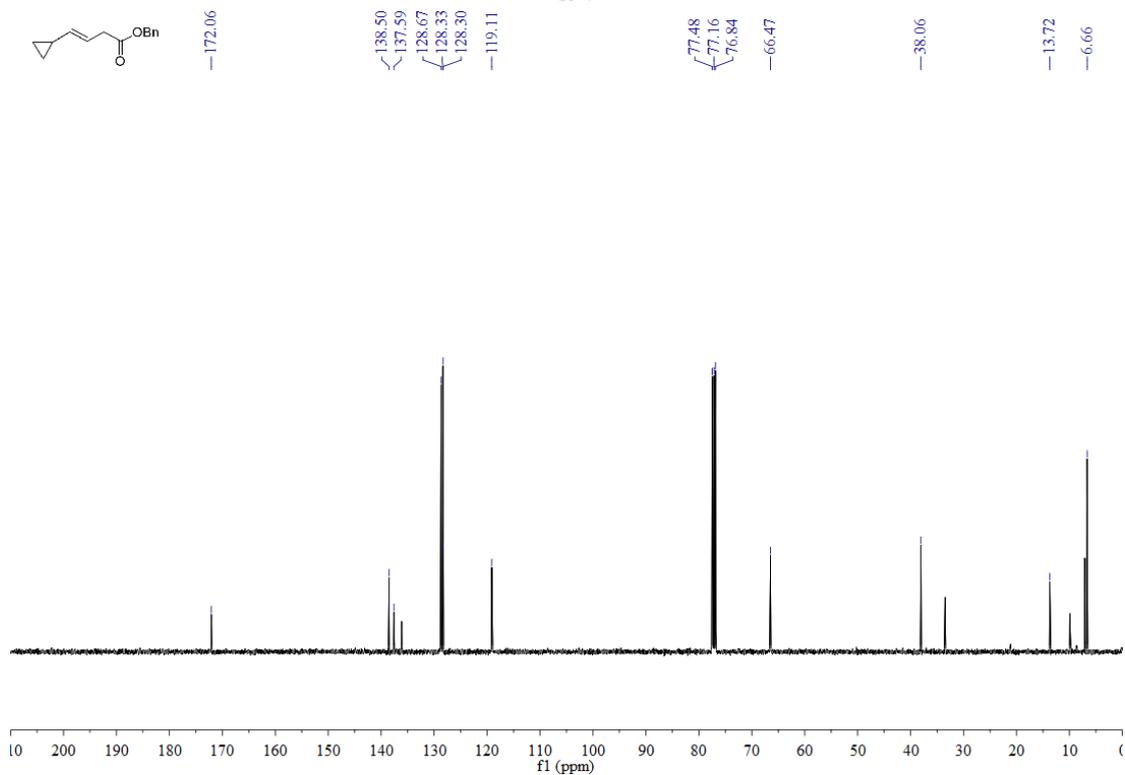
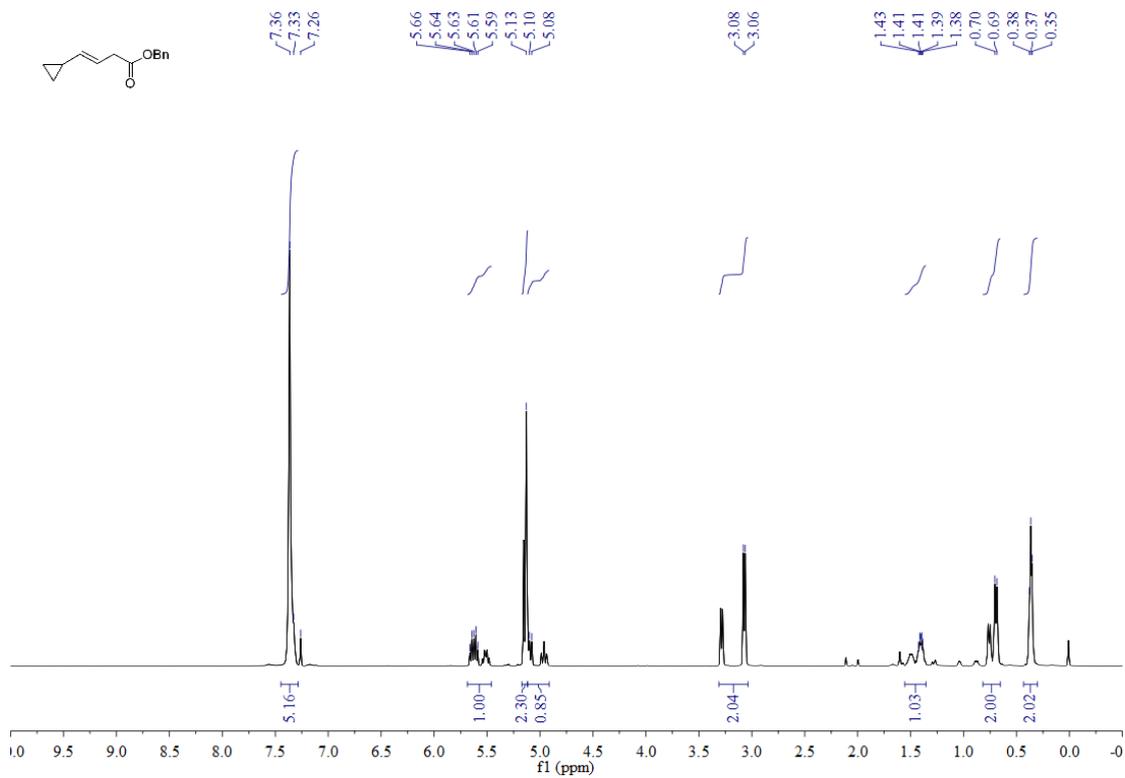
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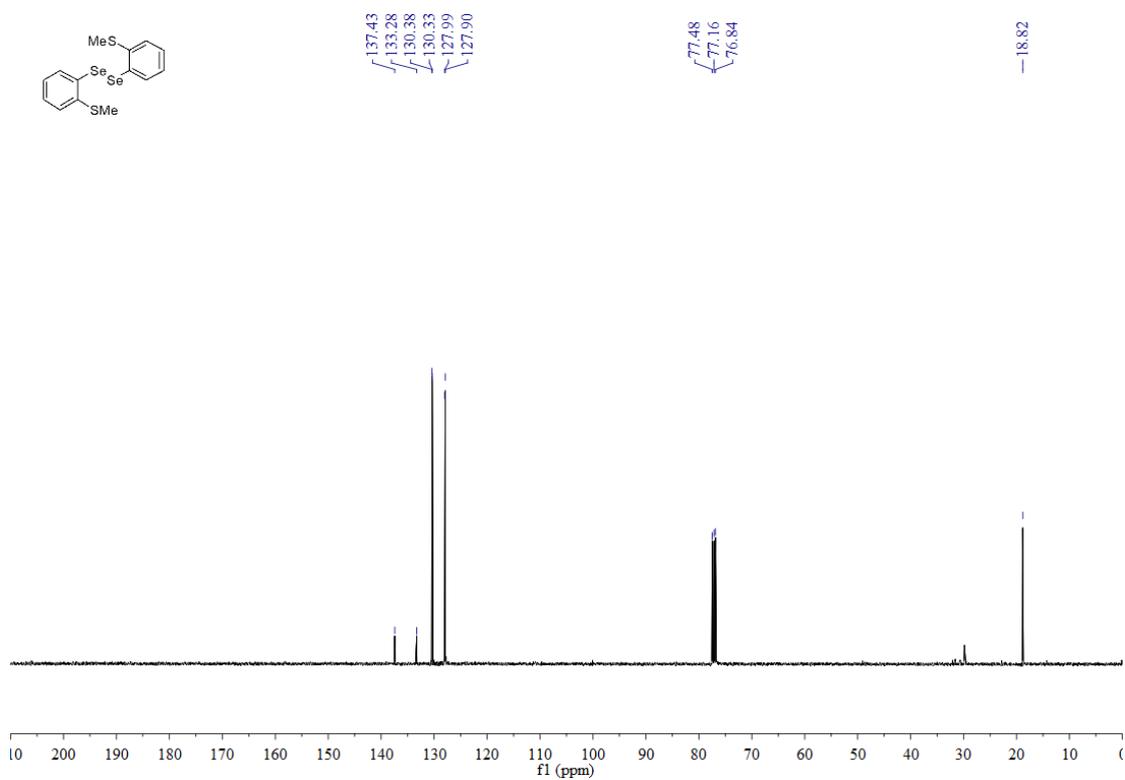
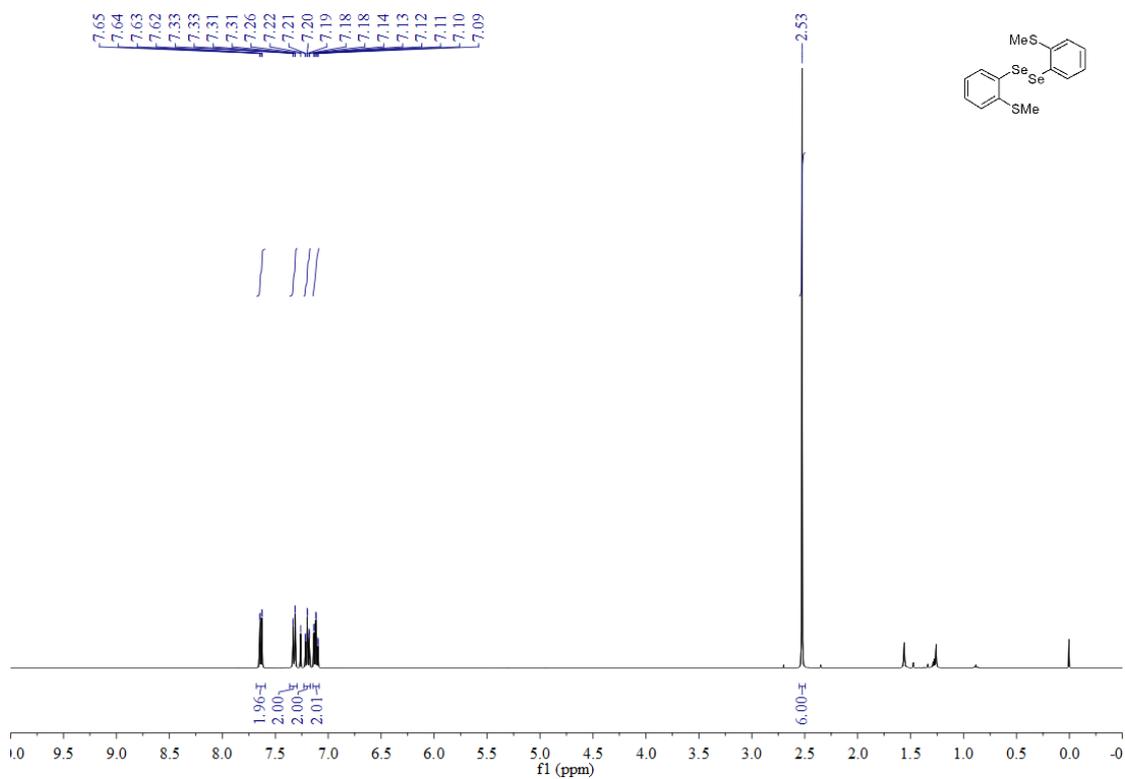
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (101 MHz, CDCl_3) of **1s**



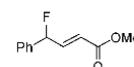
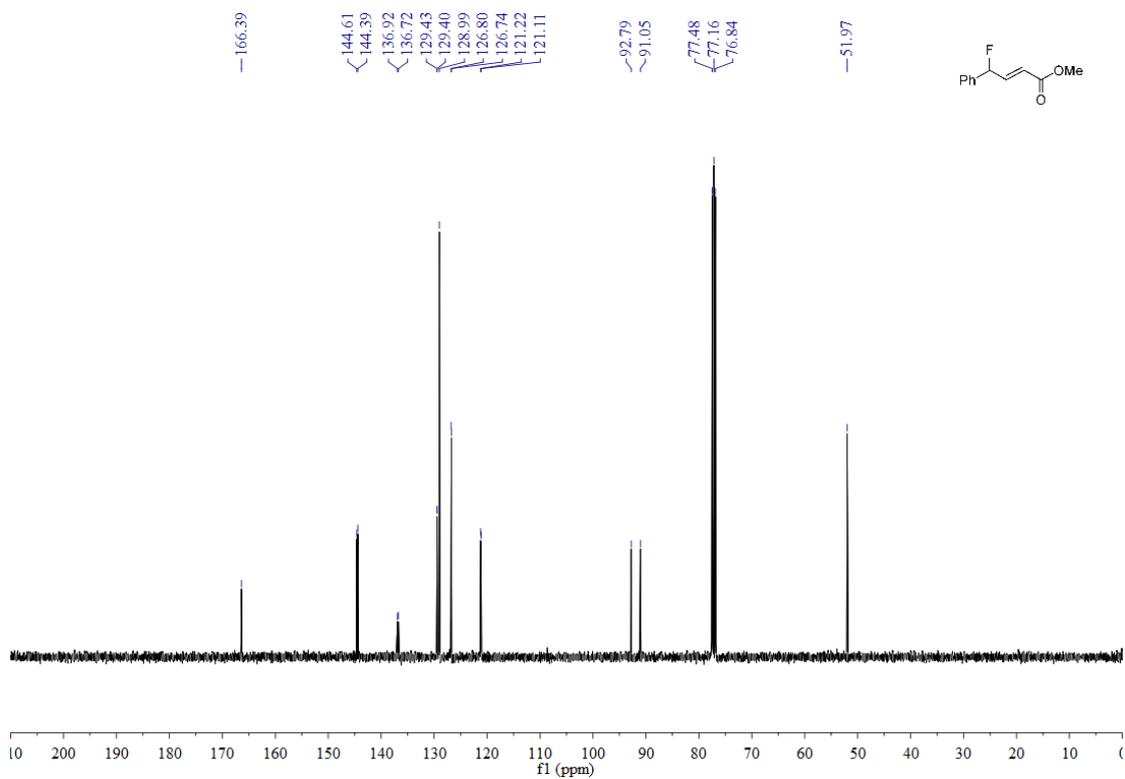
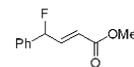
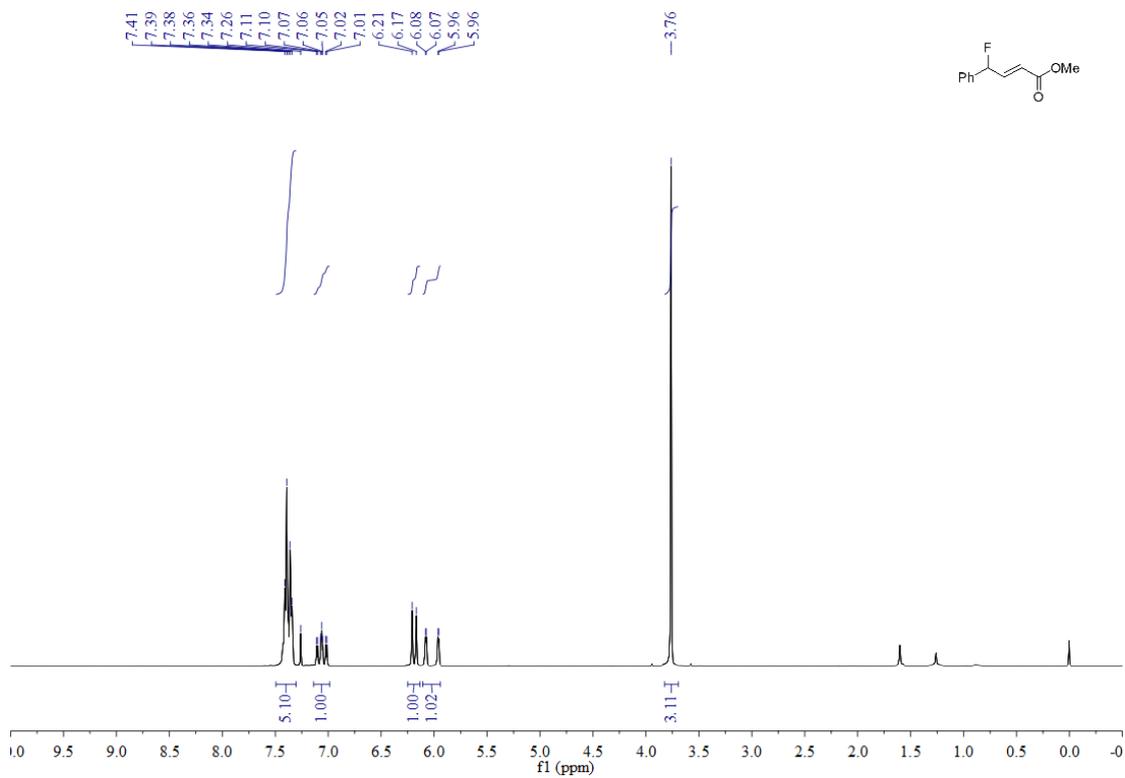
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 1t



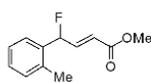
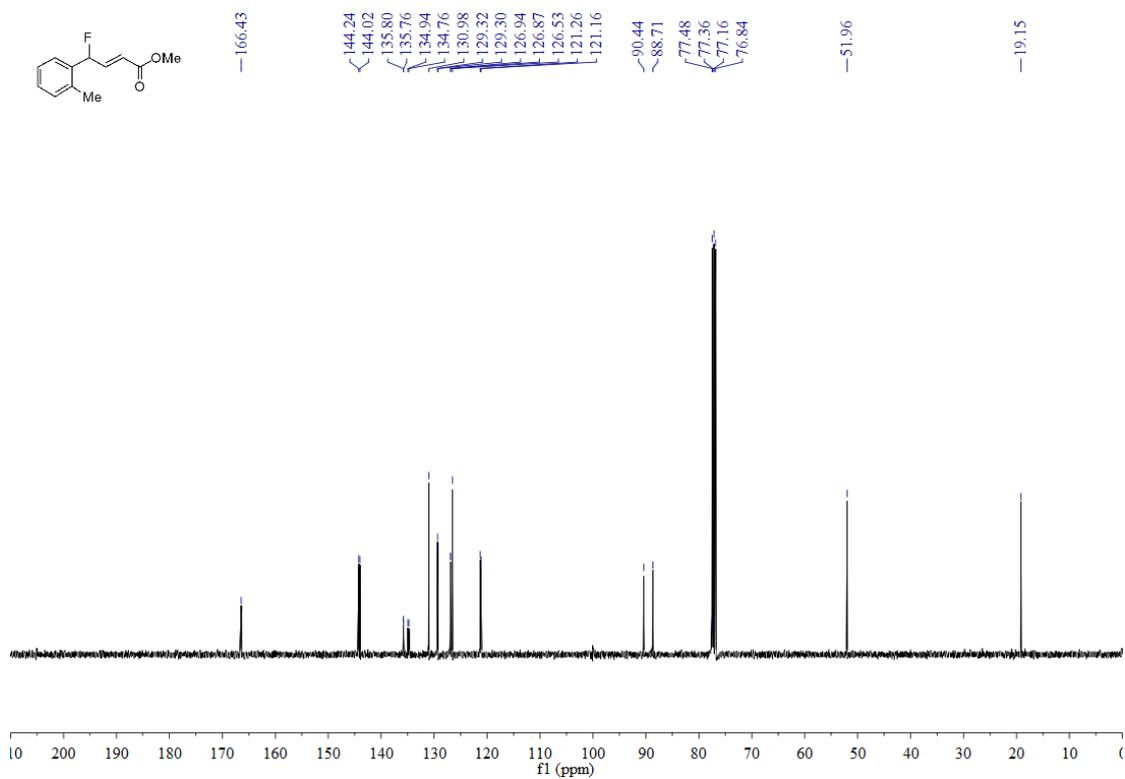
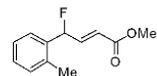
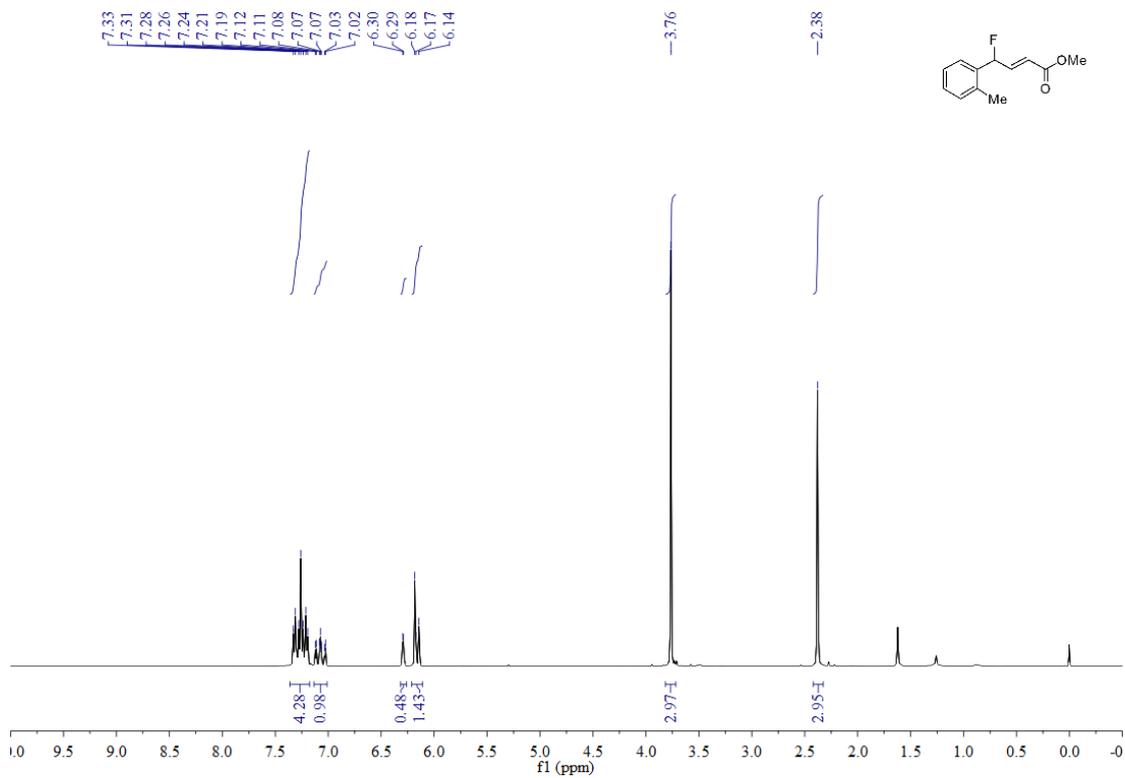
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (101 MHz, CDCl_3) of C6



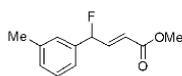
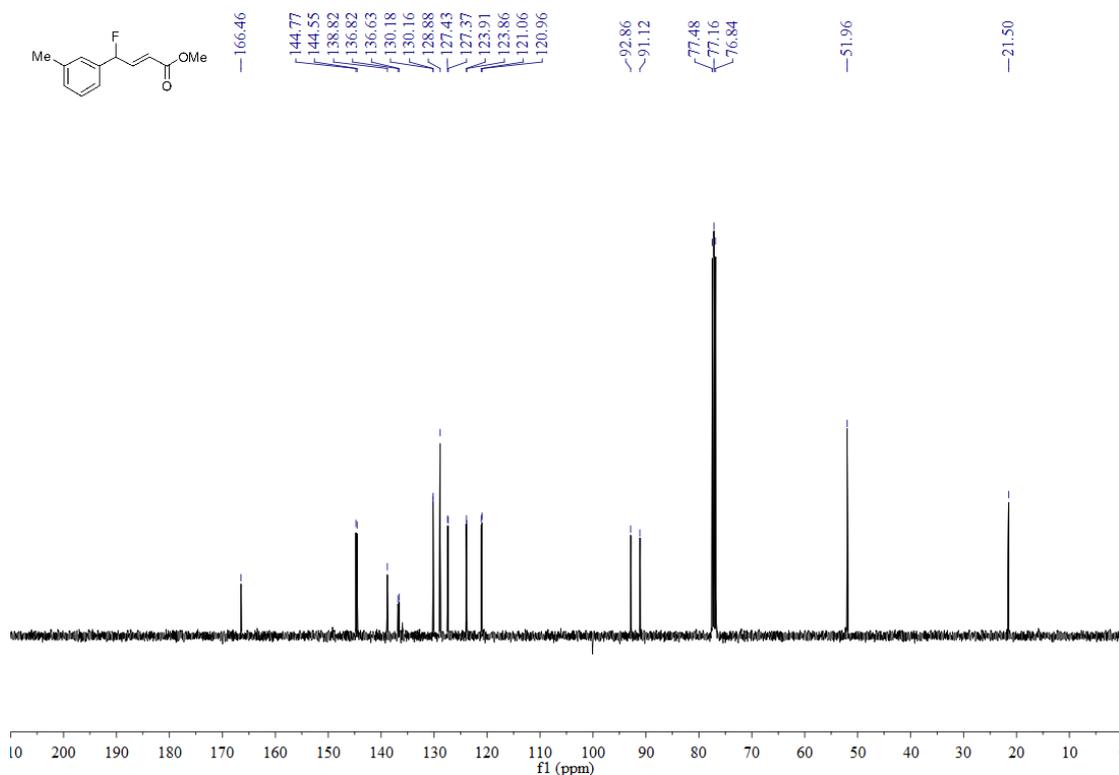
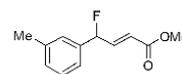
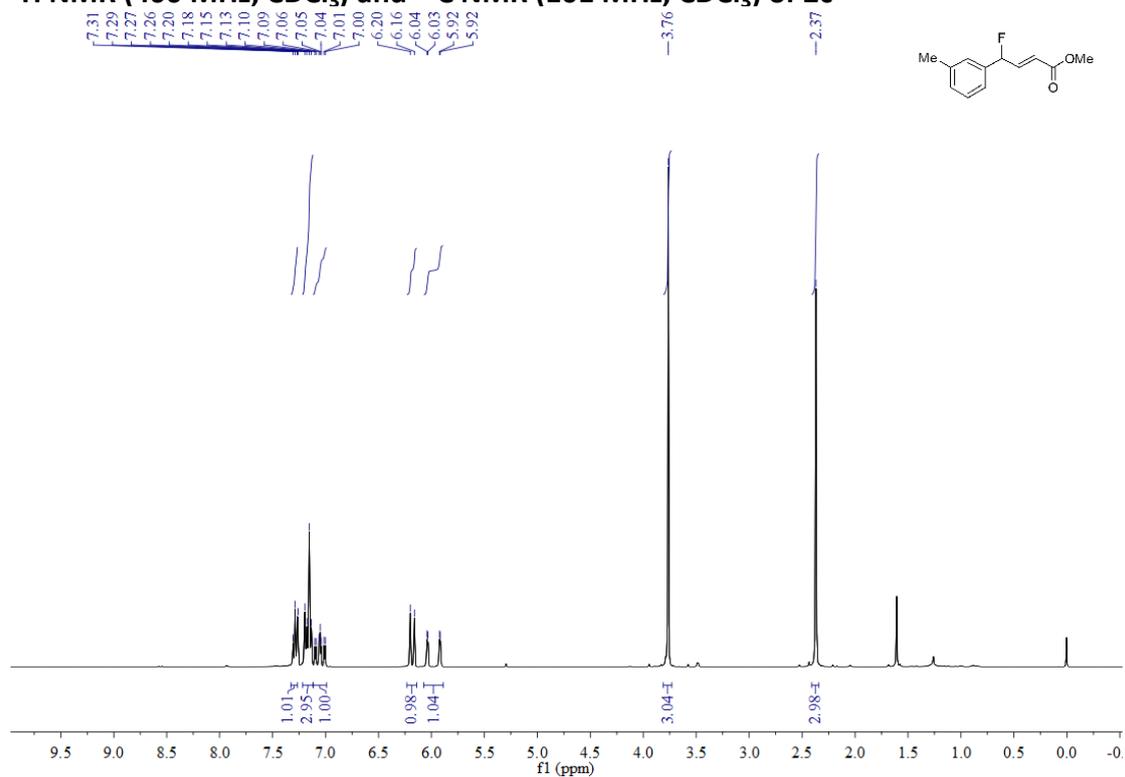
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 2a



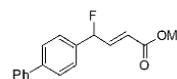
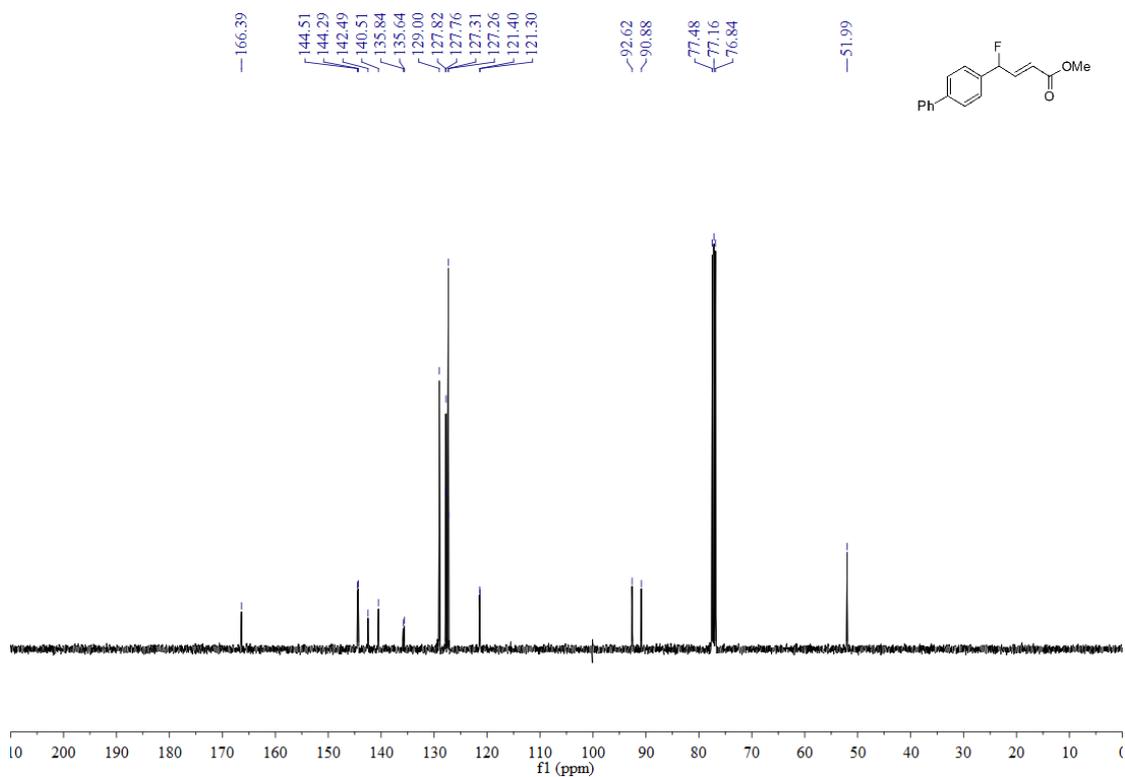
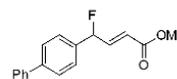
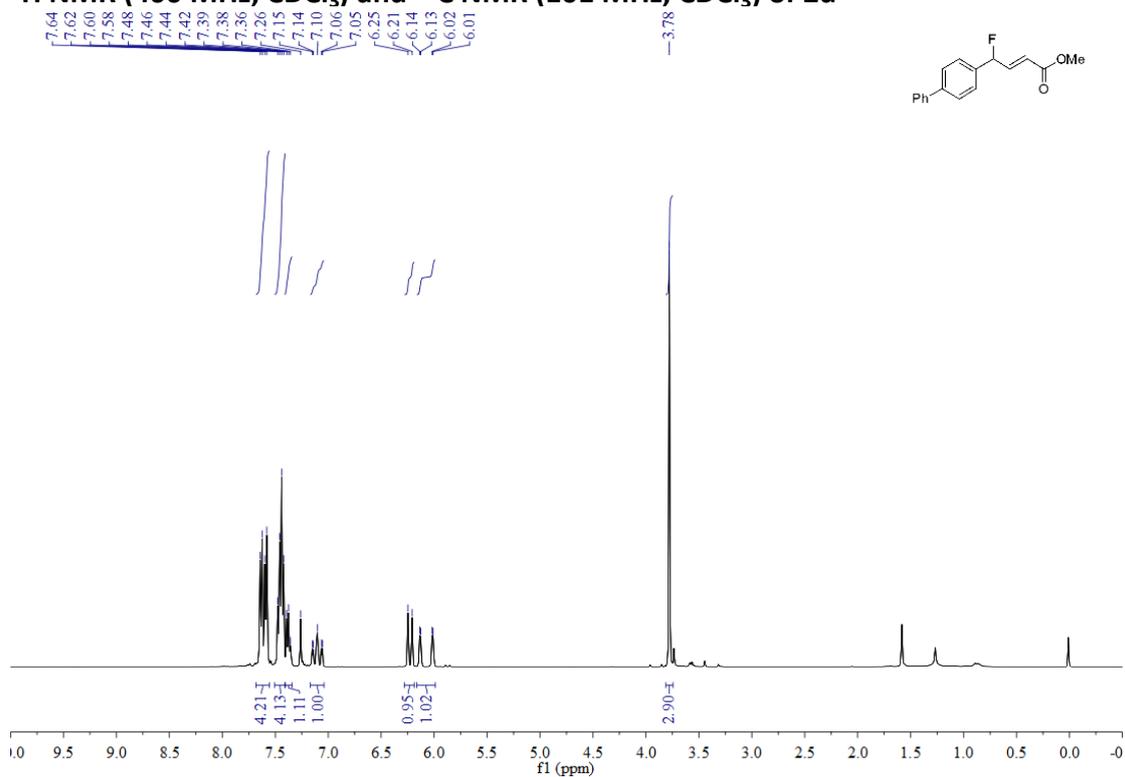
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (101 MHz, CDCl_3) of 2b



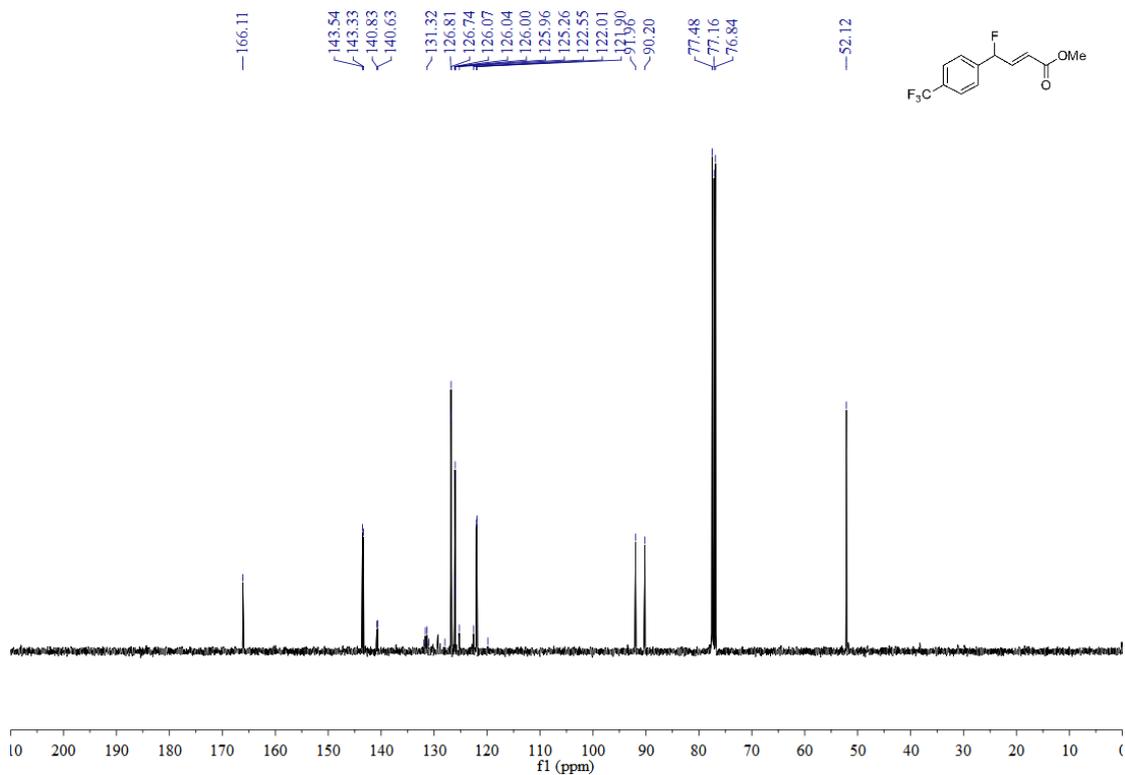
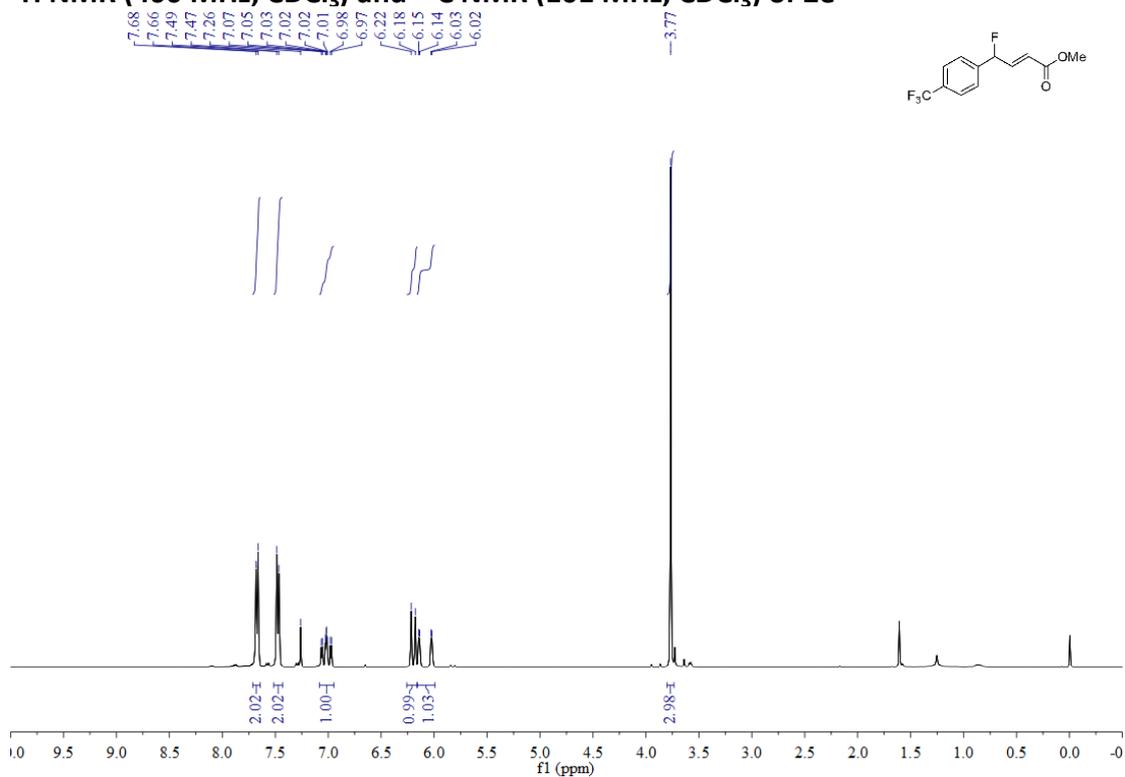
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 2c



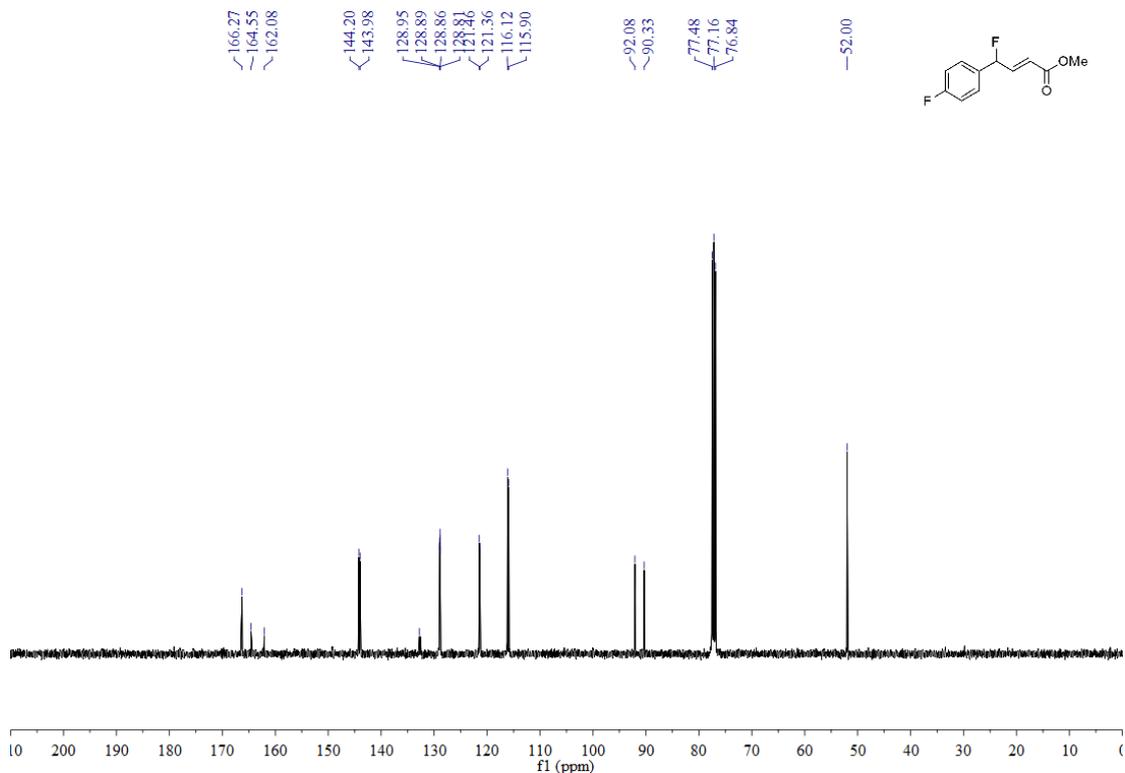
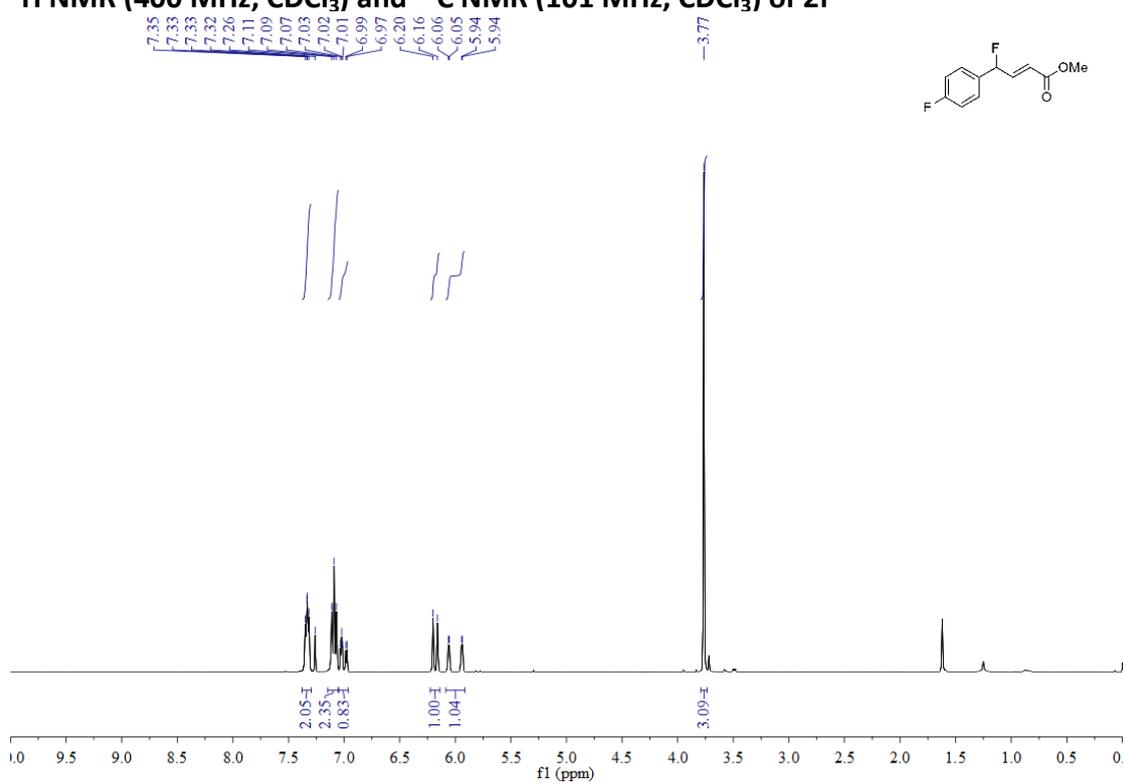
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 2d



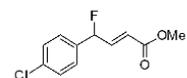
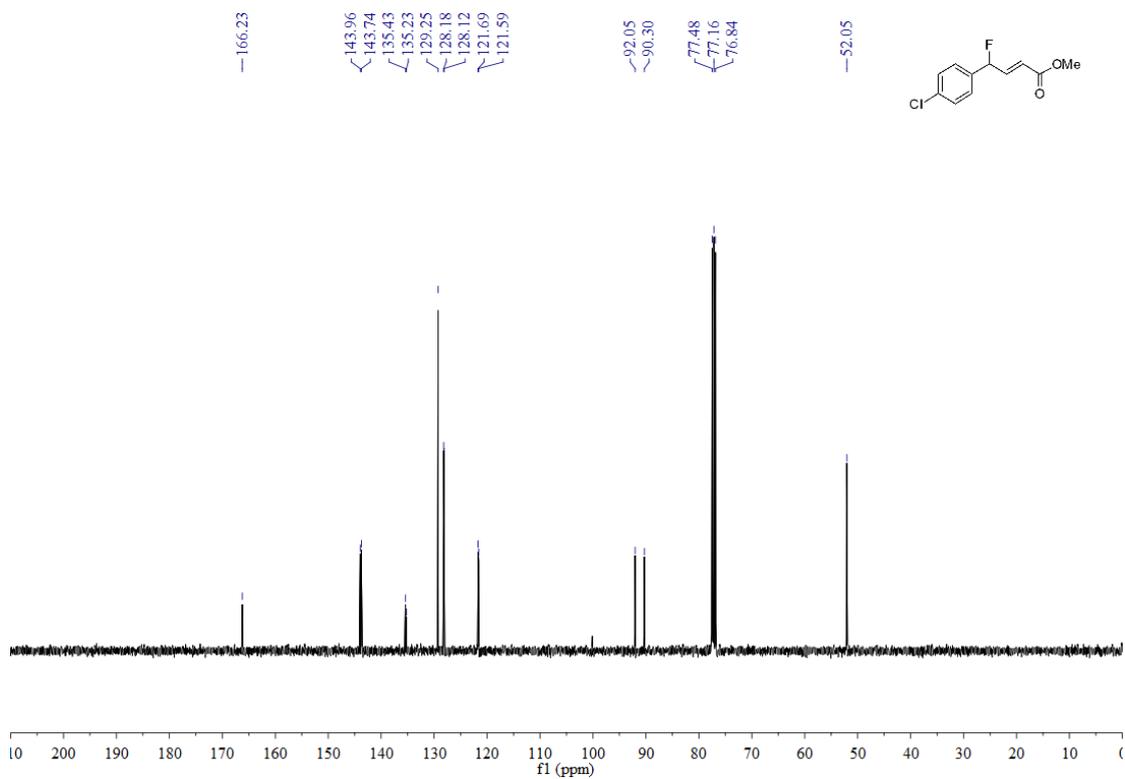
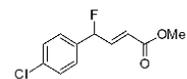
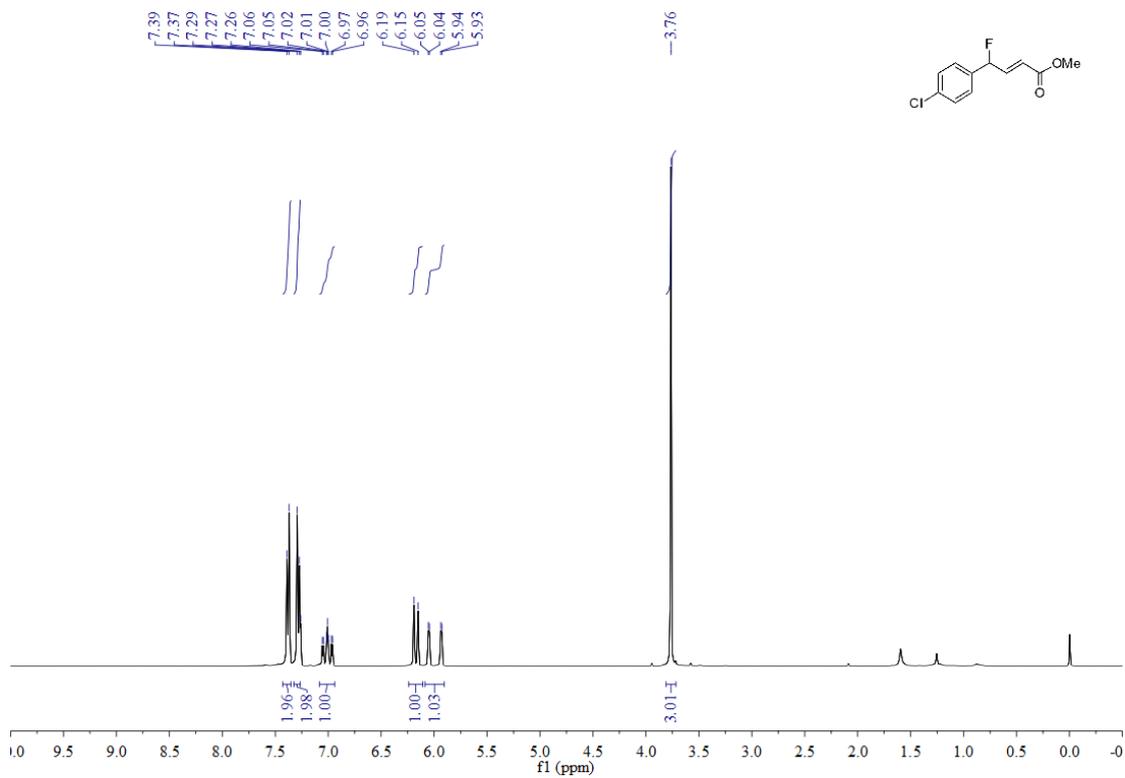
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 2e



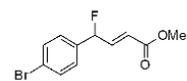
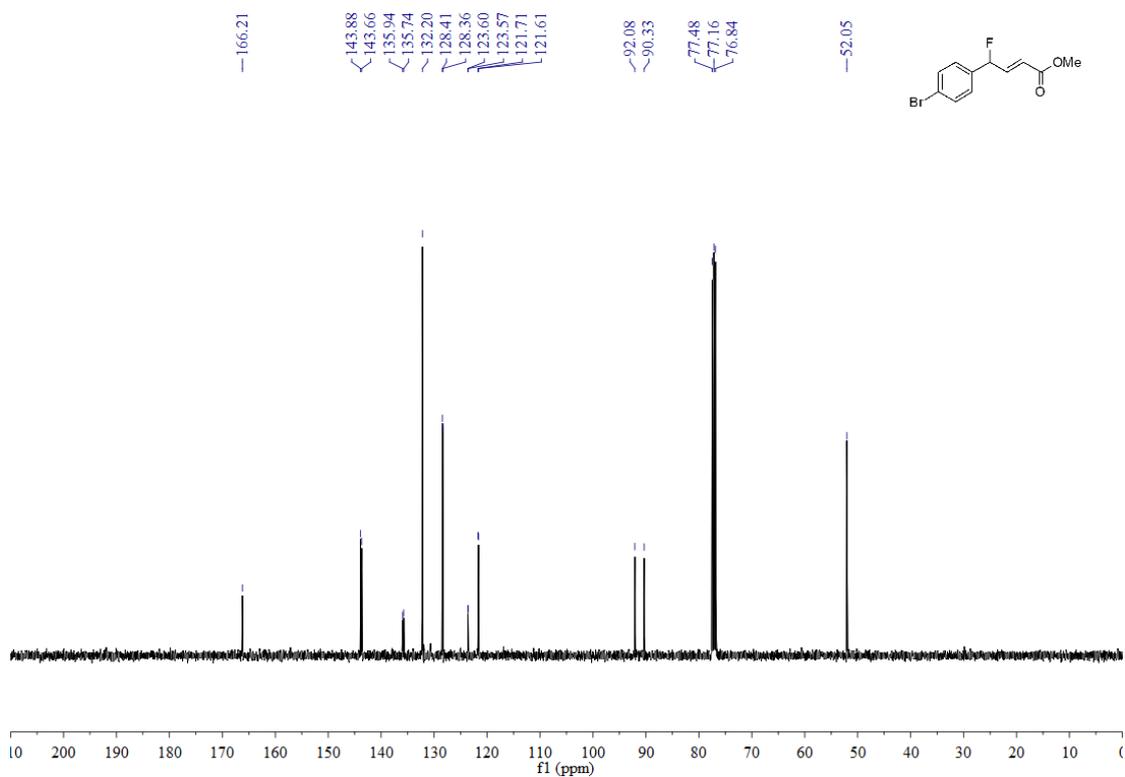
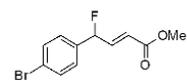
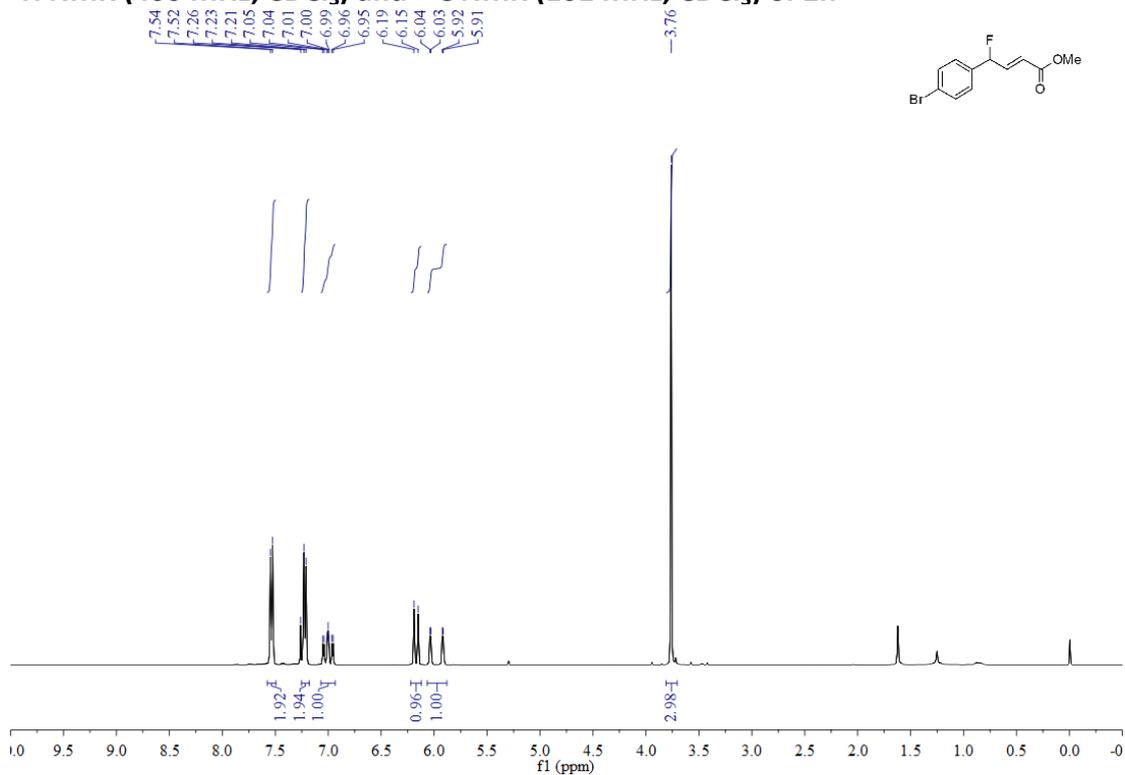
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 2f



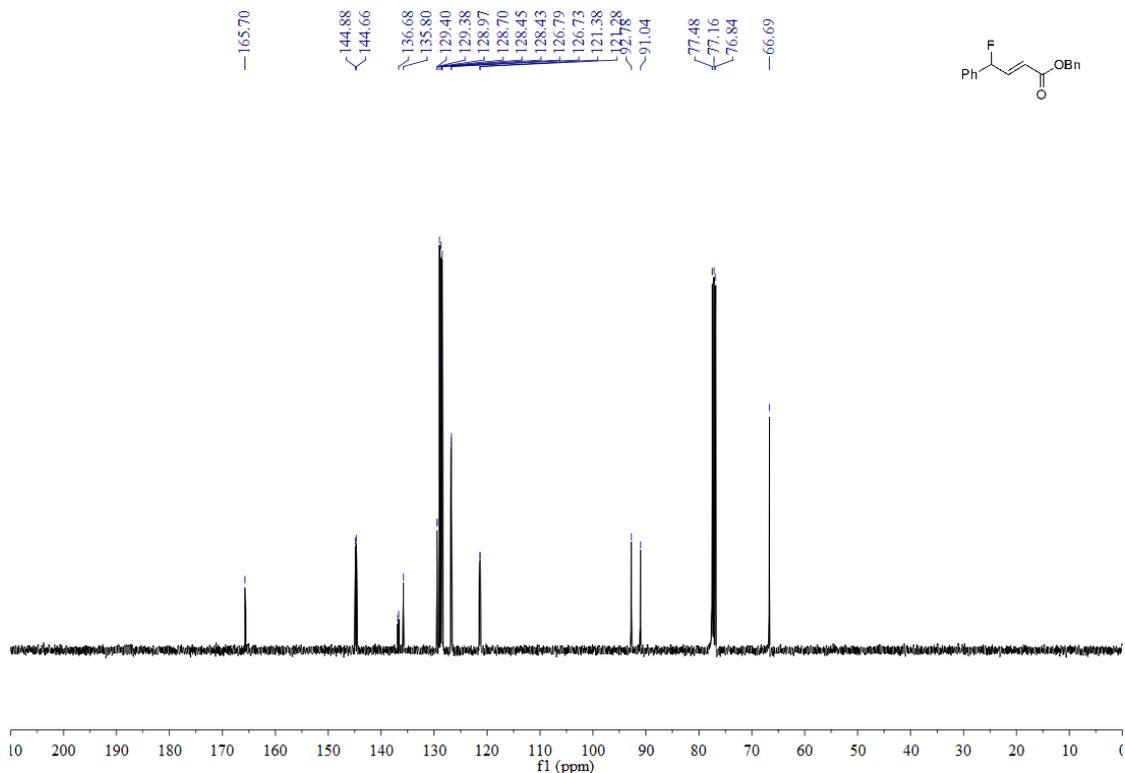
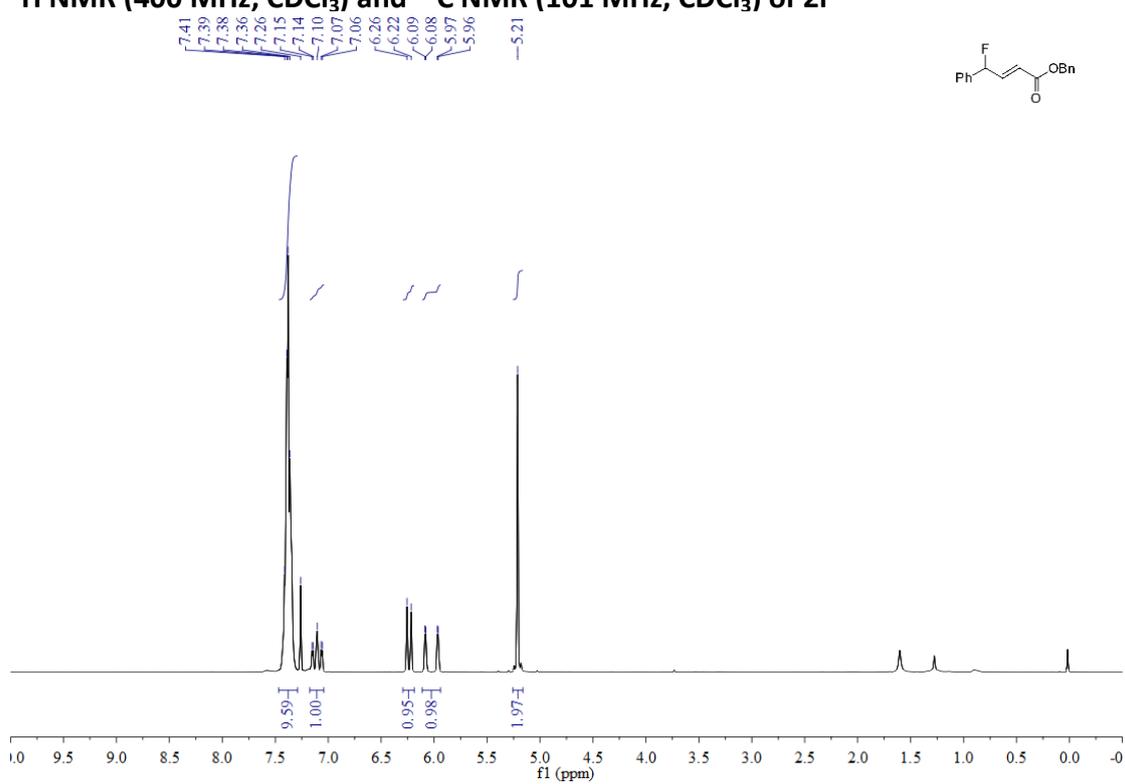
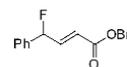
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (101 MHz, CDCl_3) of 2g



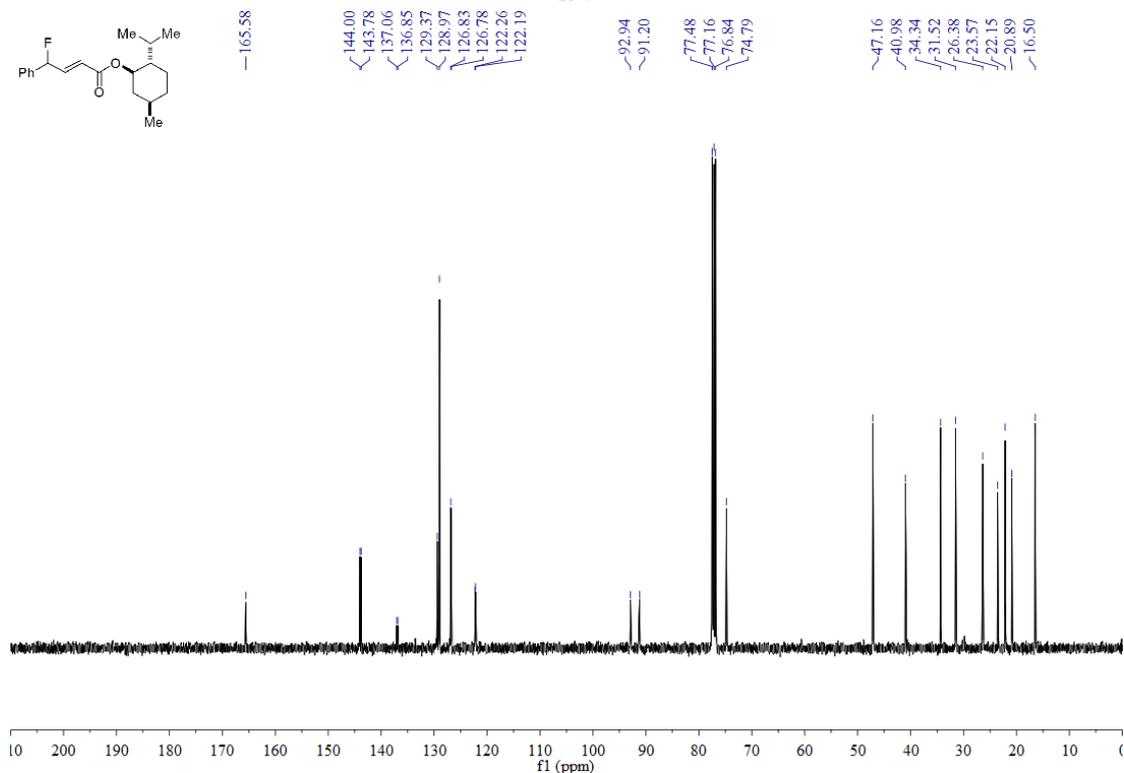
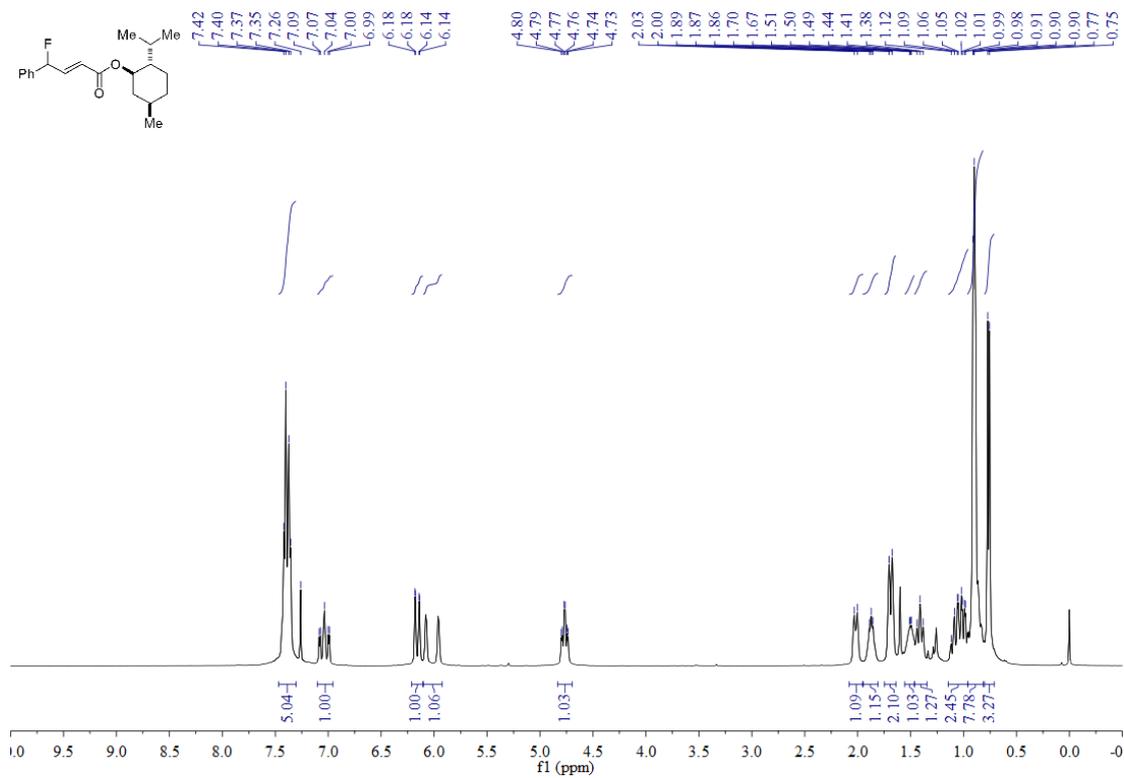
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 2h



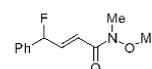
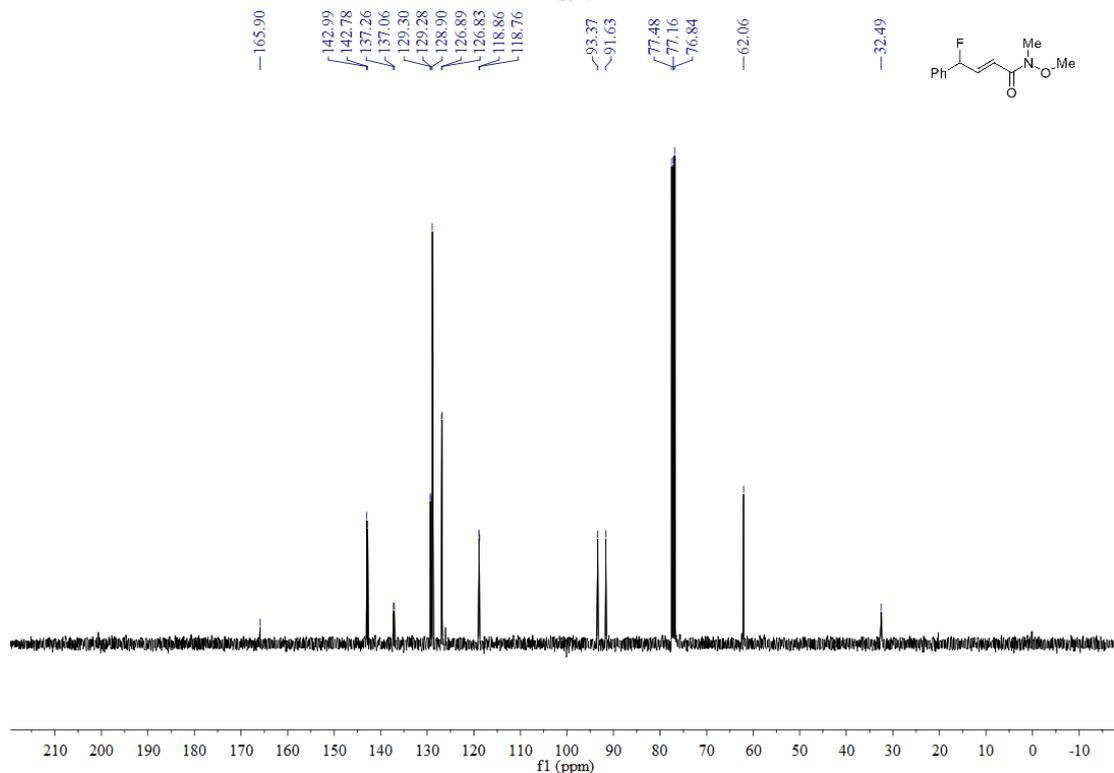
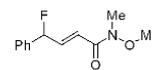
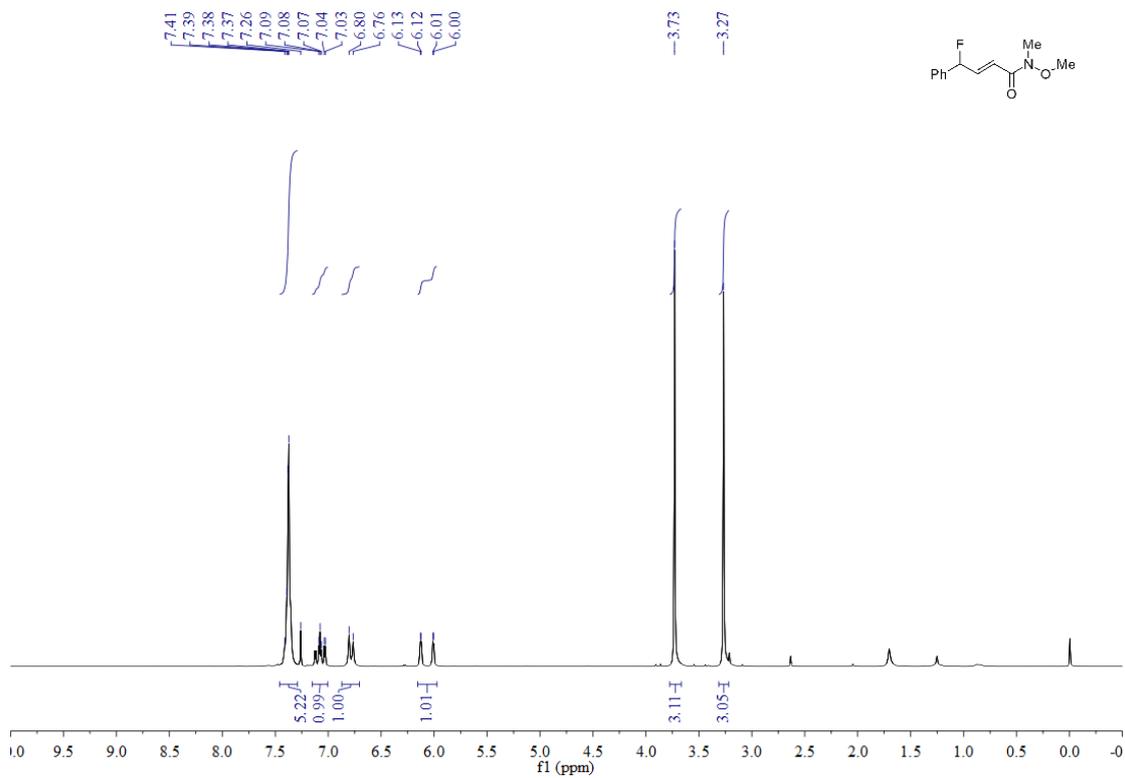
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 2i



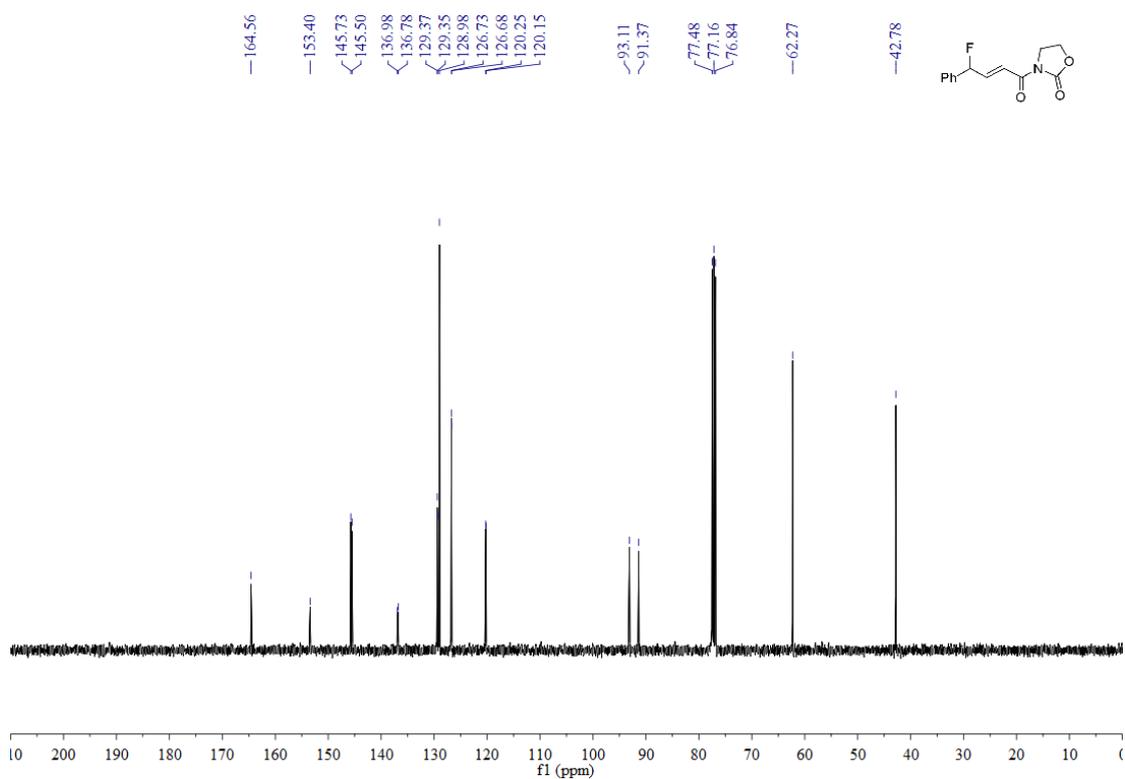
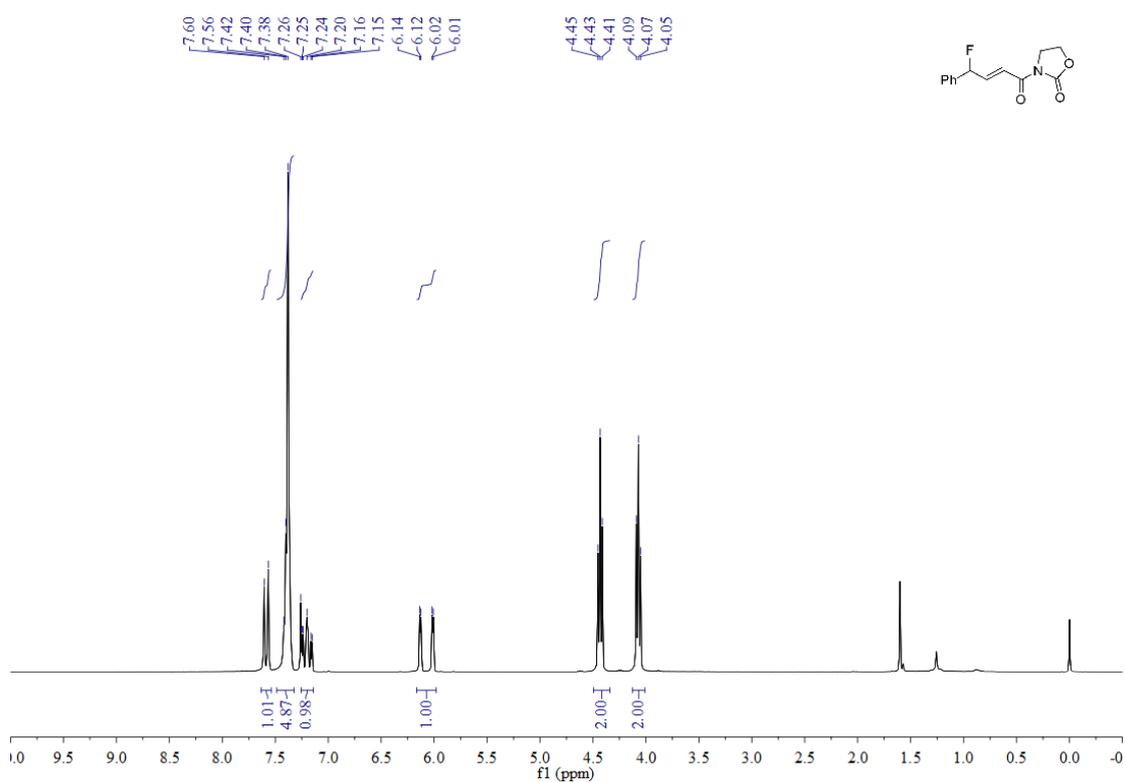
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 2j



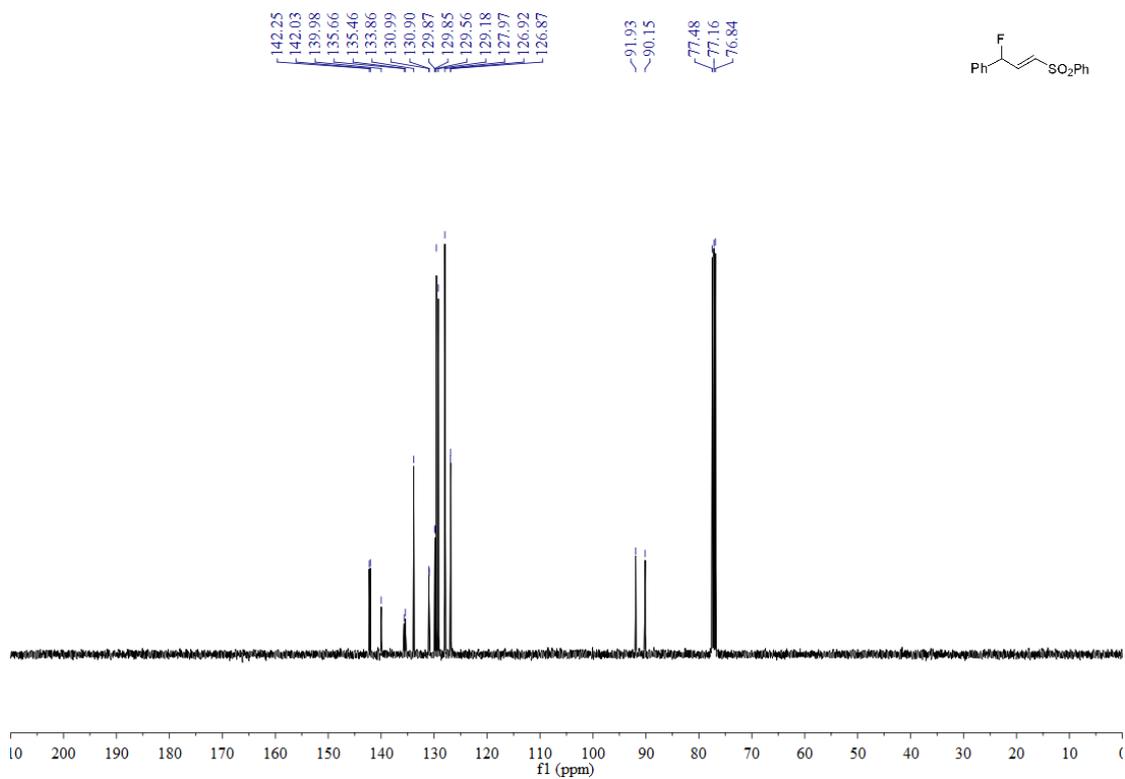
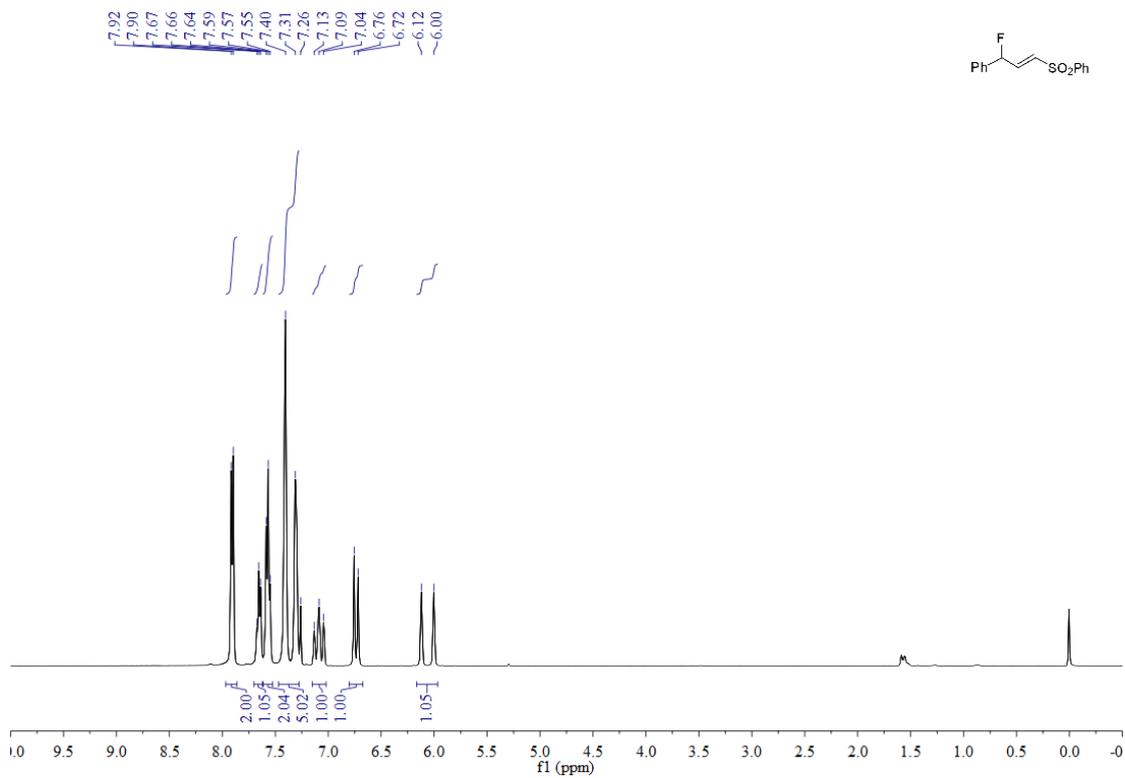
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (101 MHz, CDCl_3) of 2k



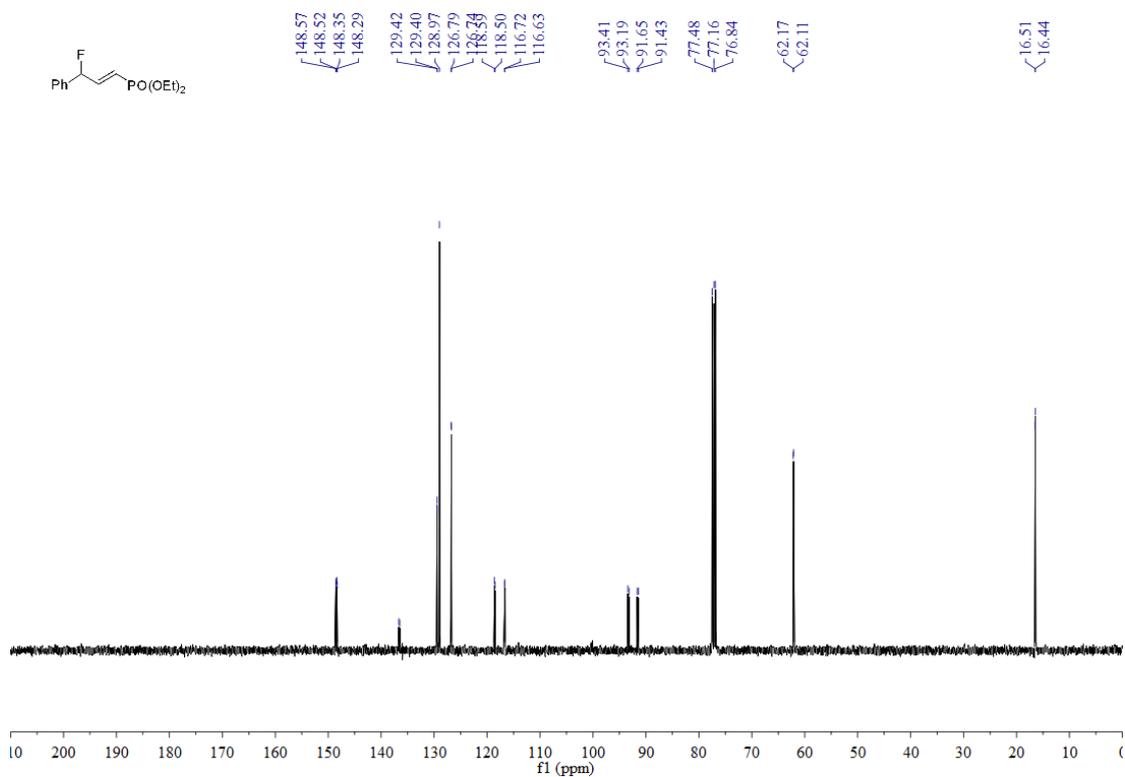
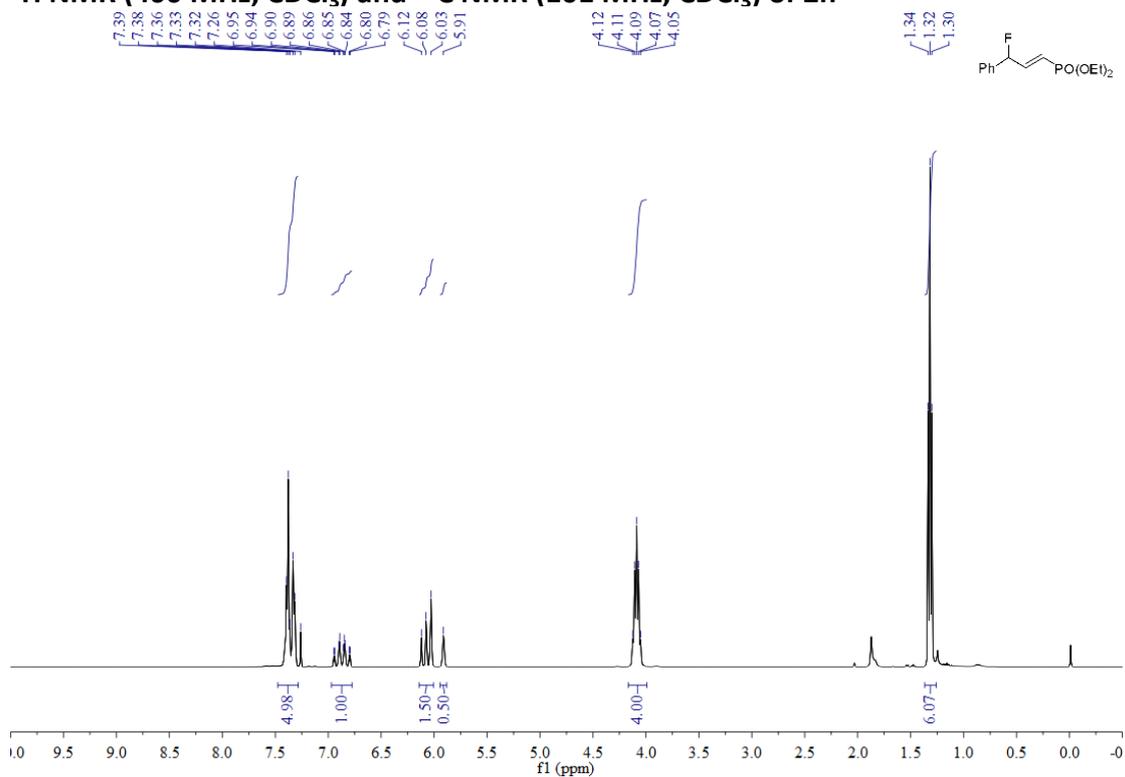
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 2I



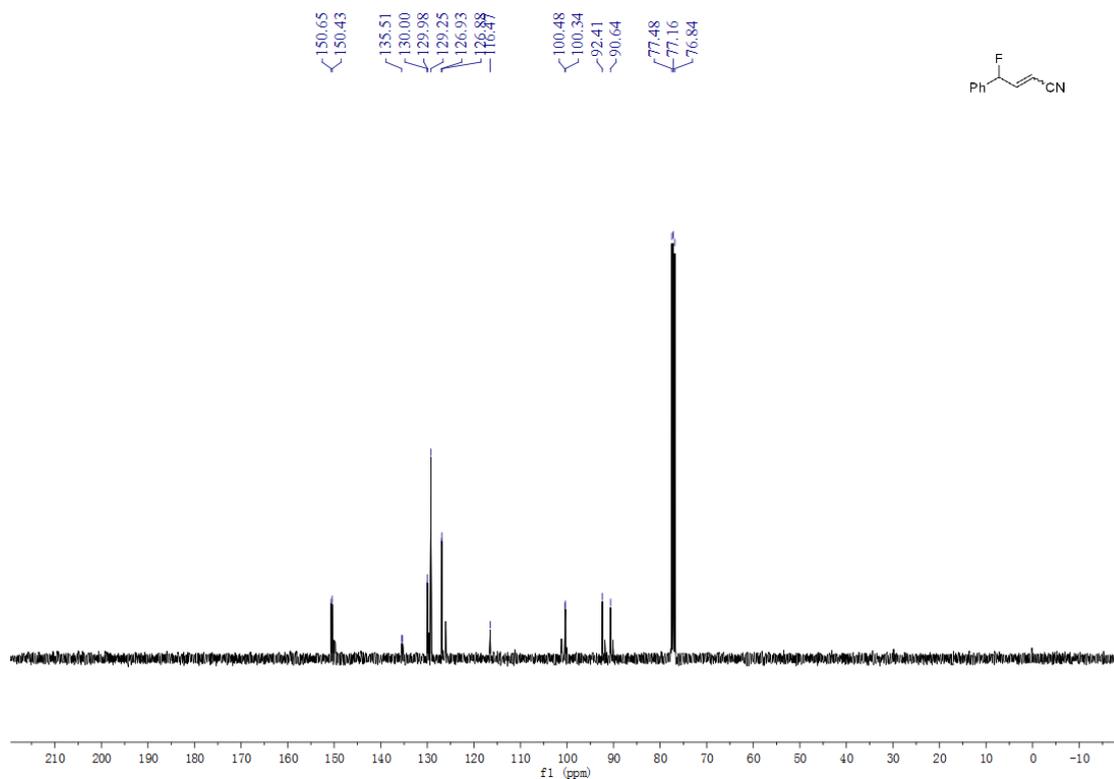
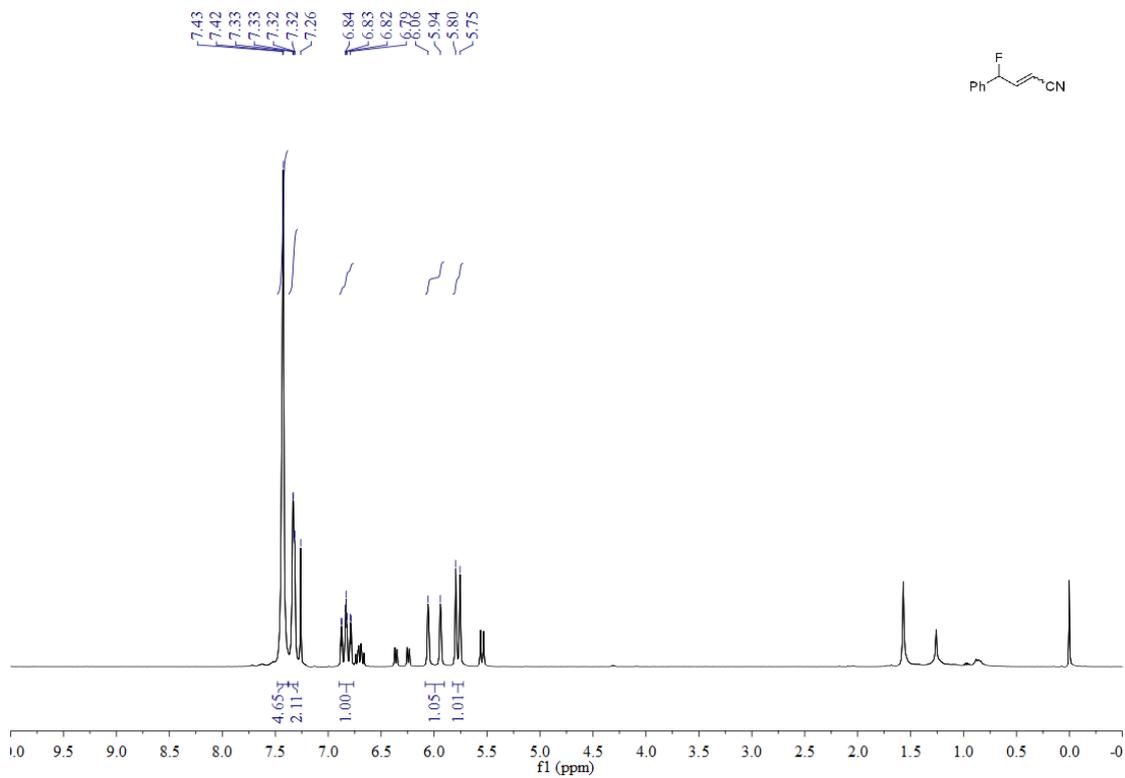
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 2m



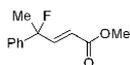
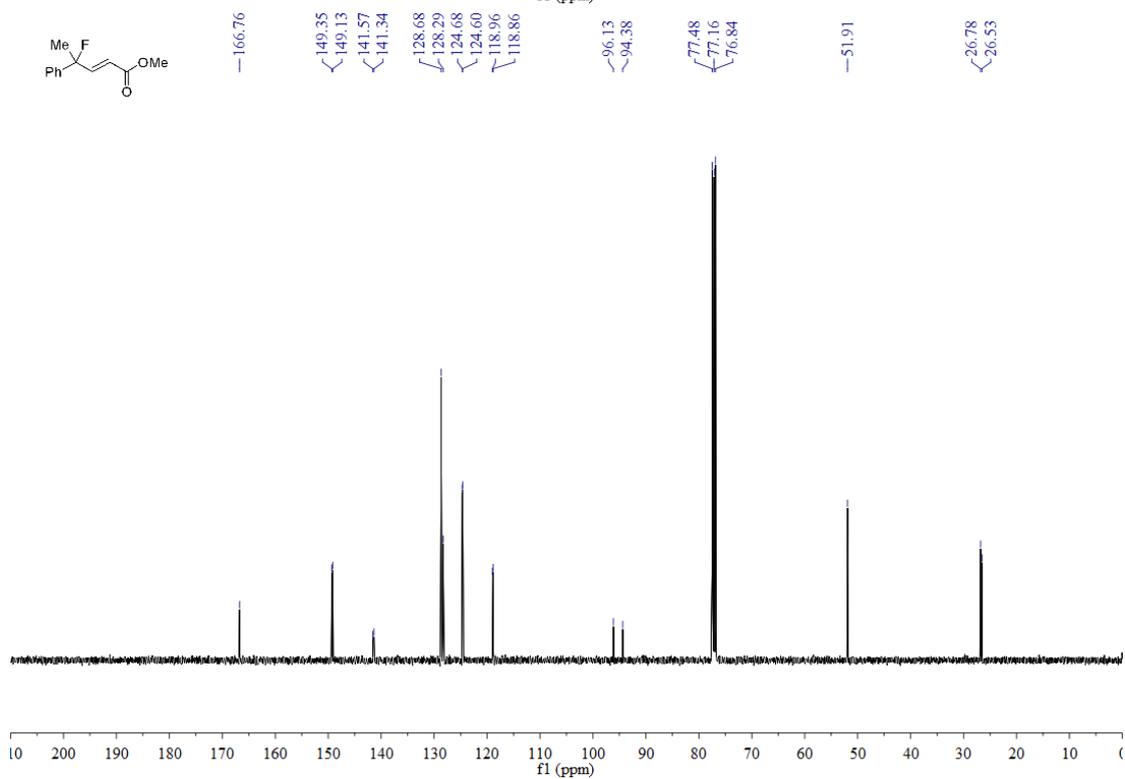
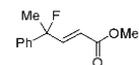
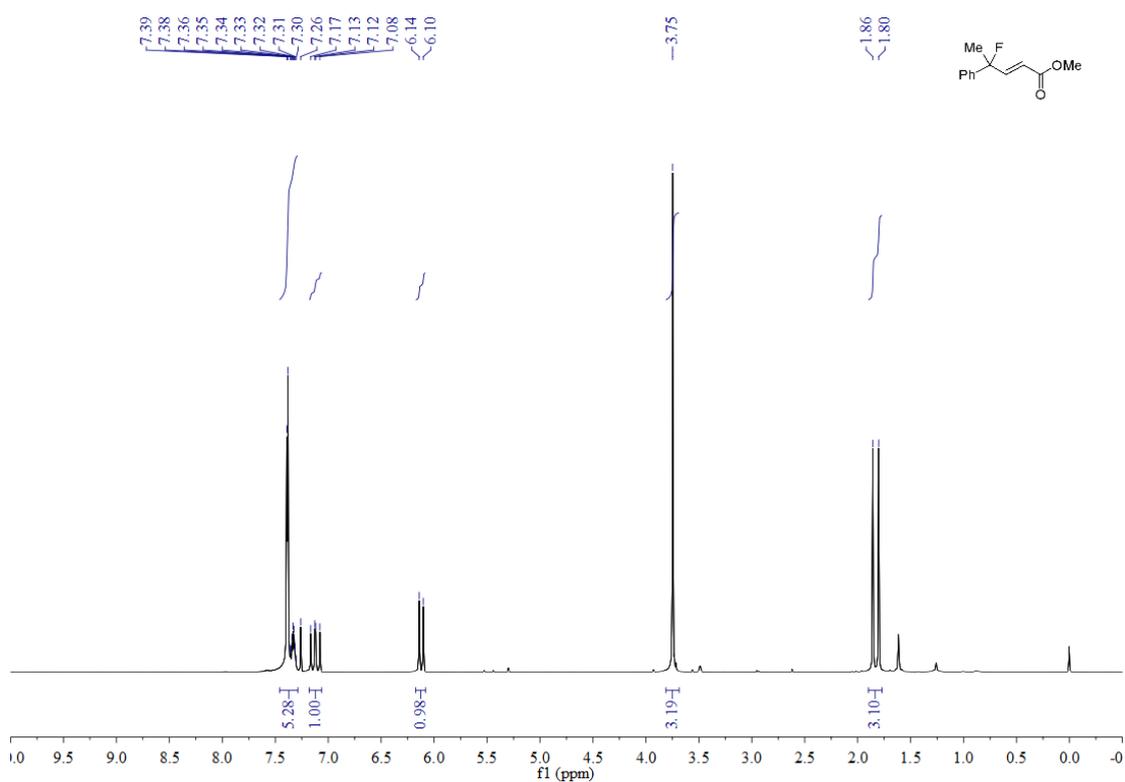
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 2n



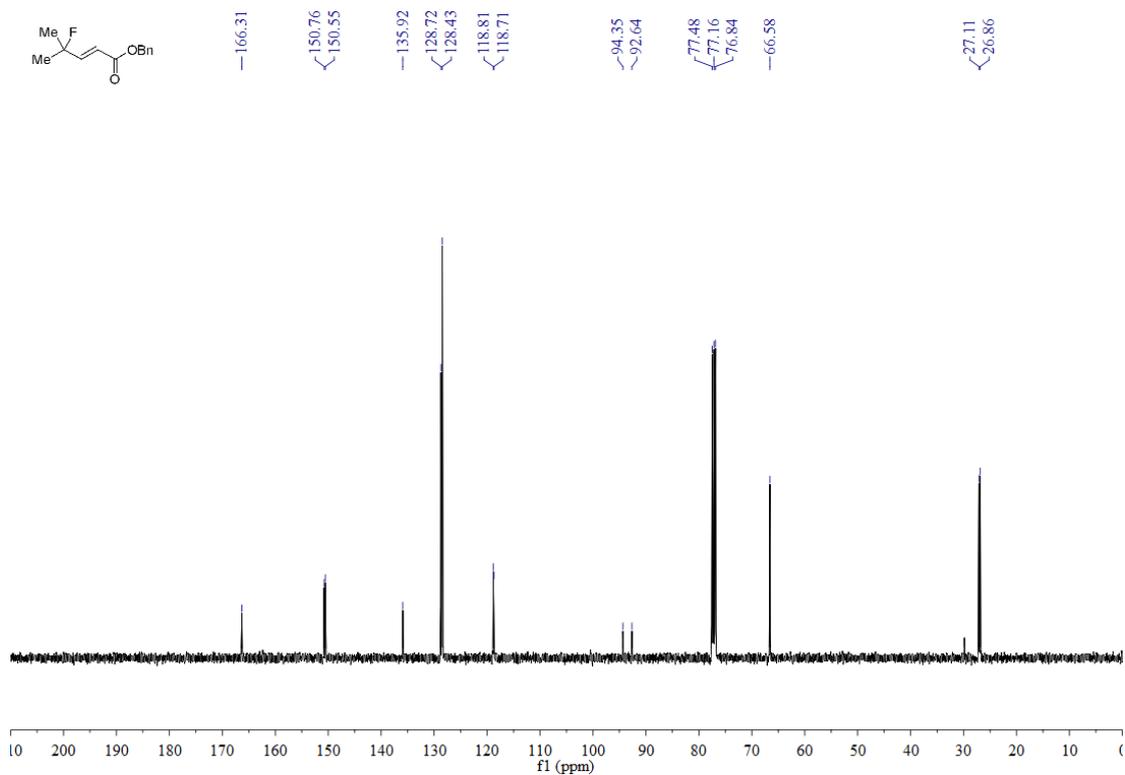
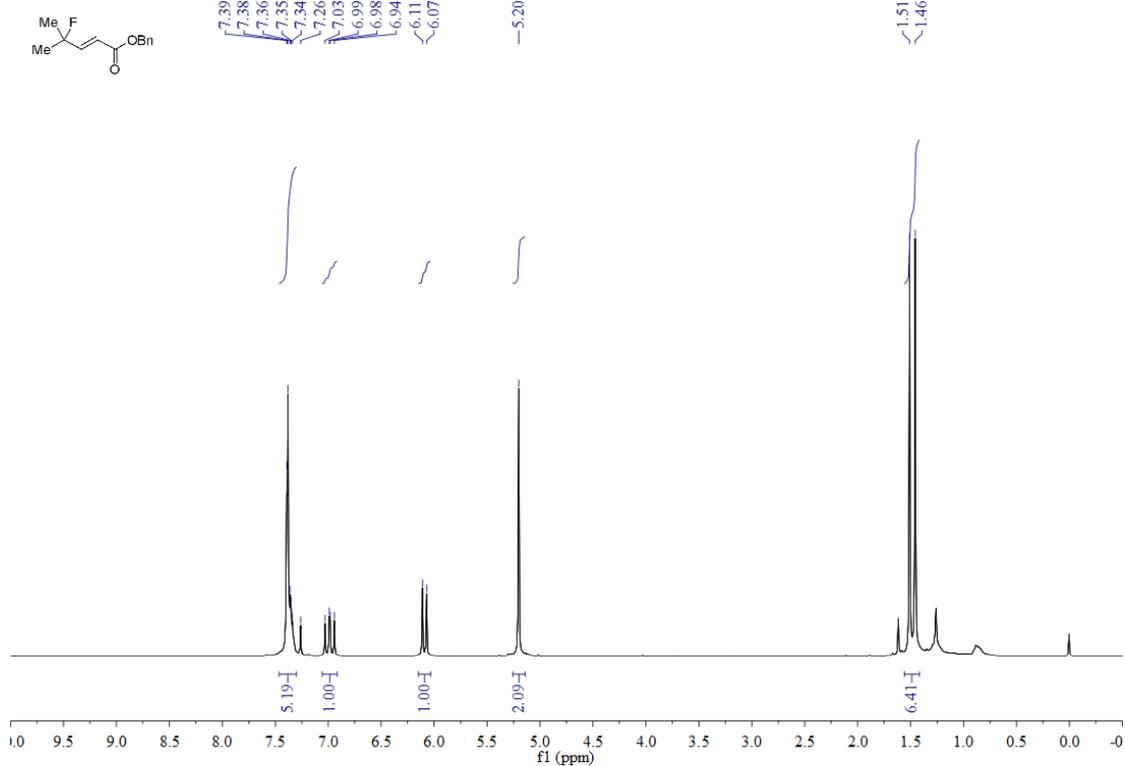
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (101 MHz, CDCl_3) of 2o



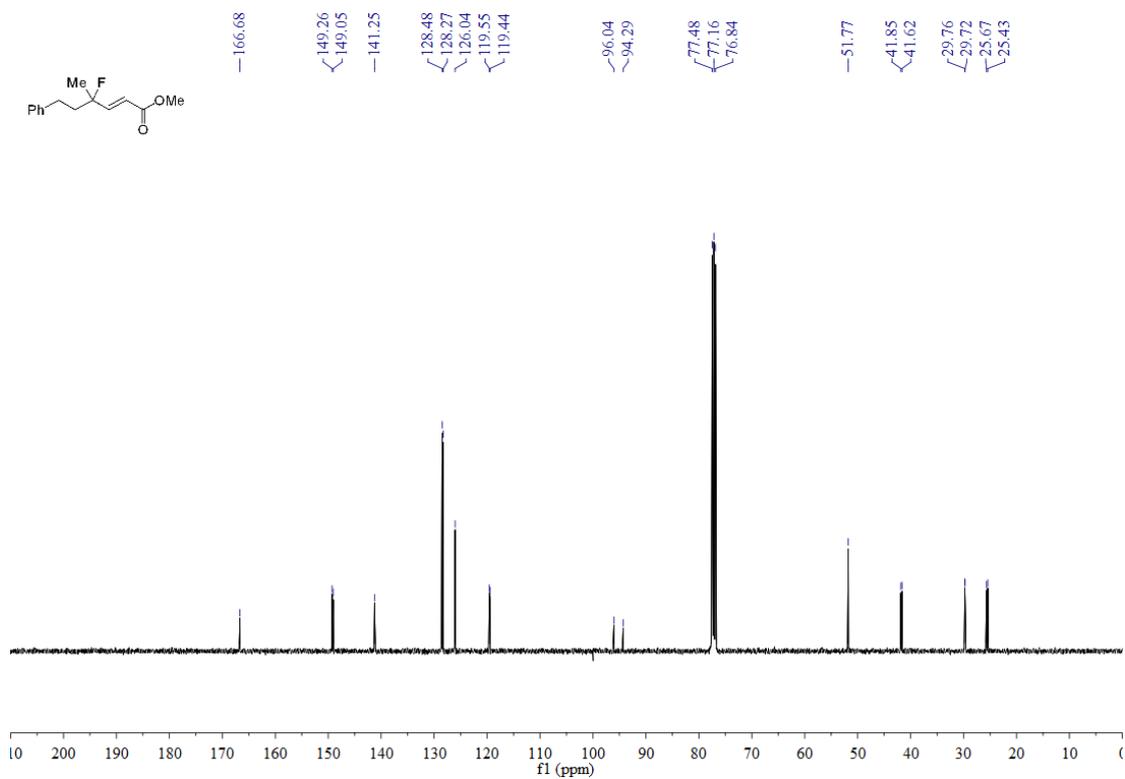
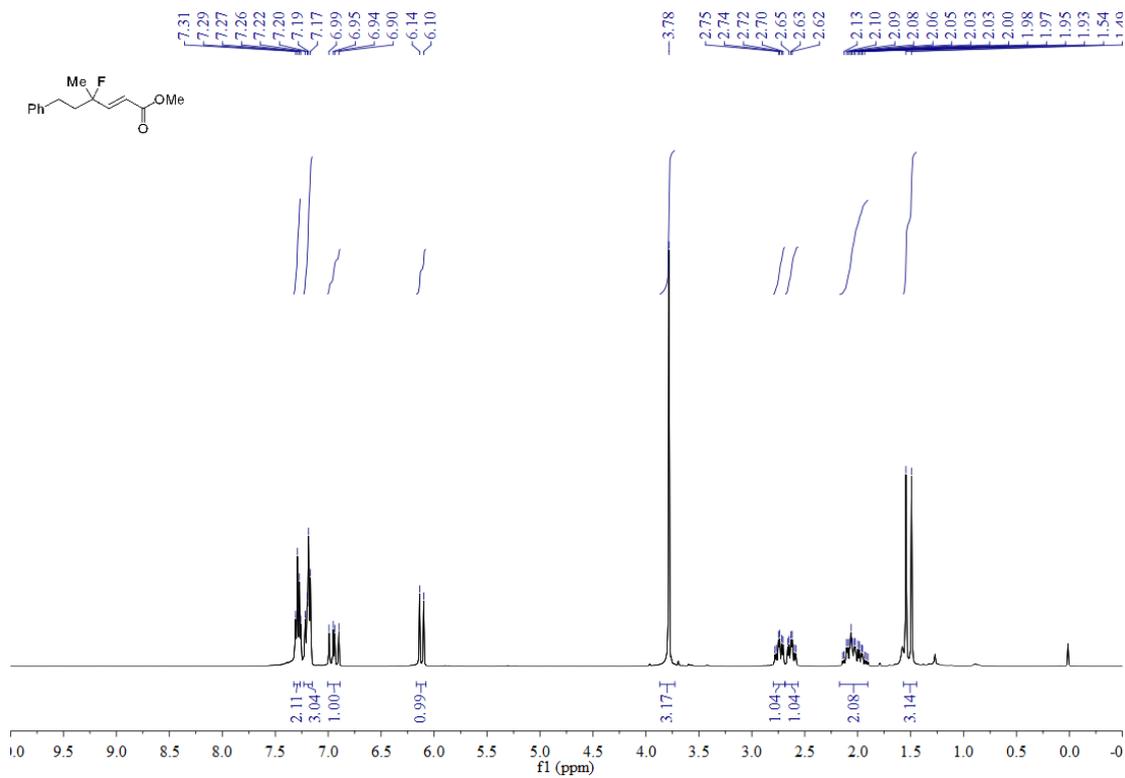
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (101 MHz, CDCl_3) of 2p



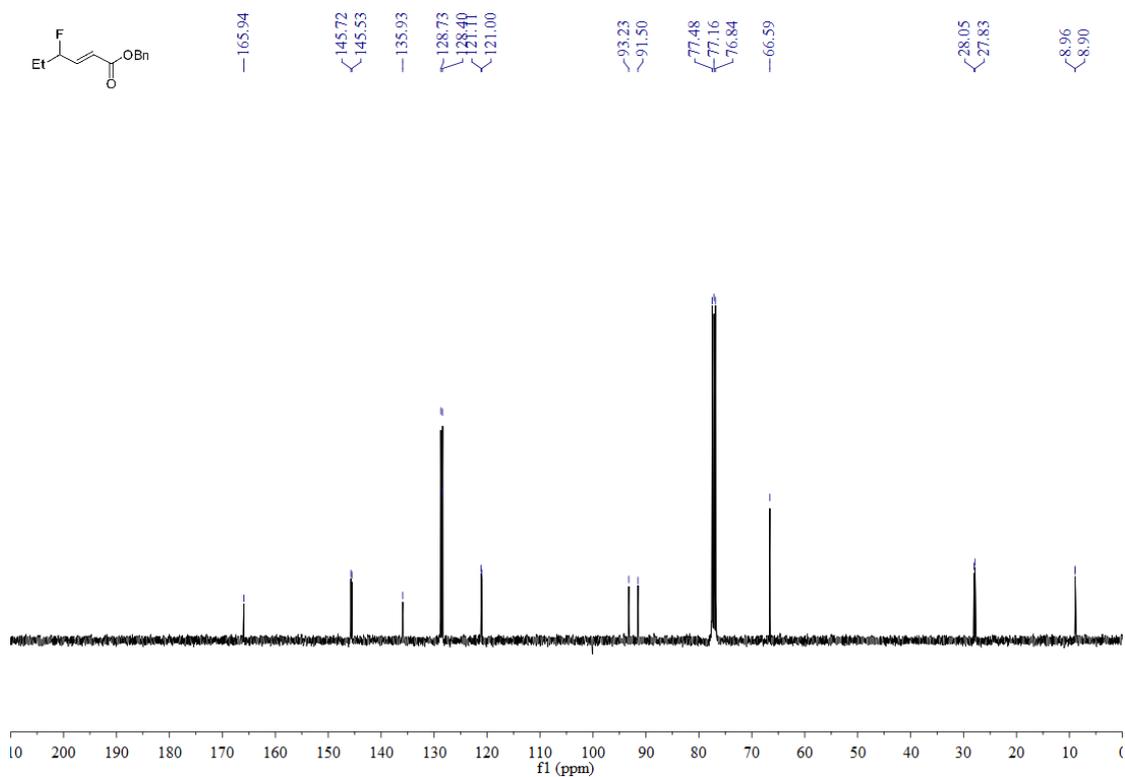
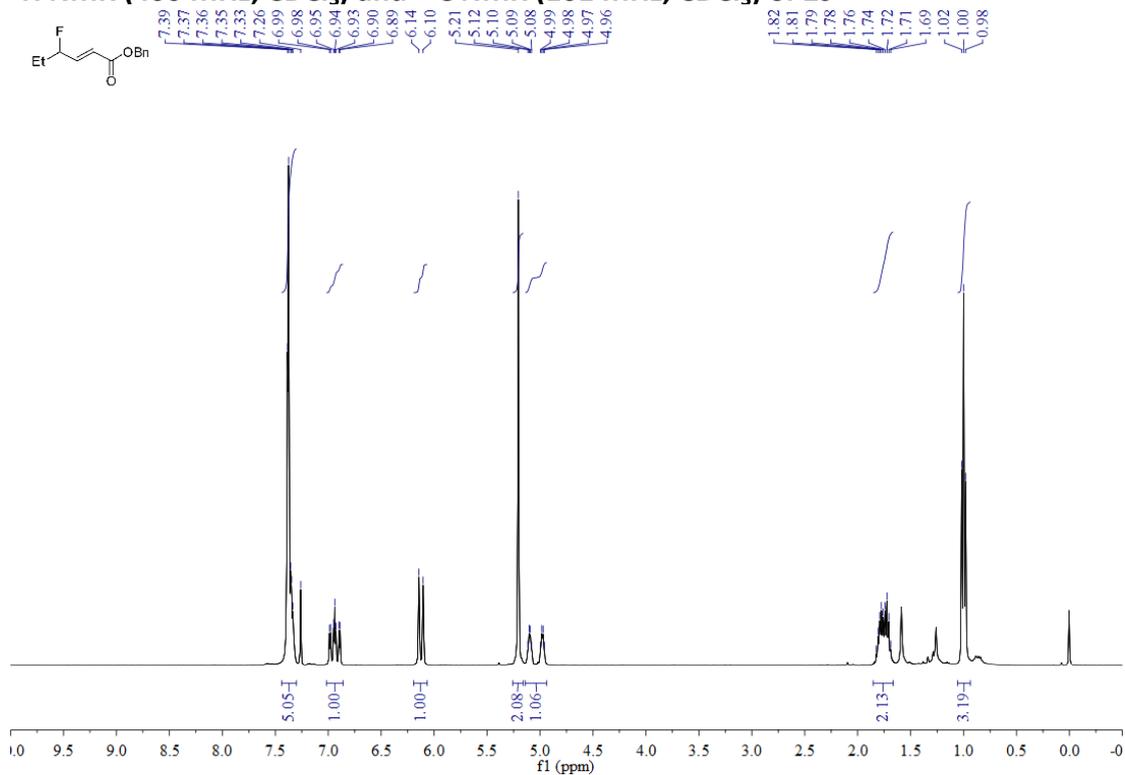
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (101 MHz, CDCl_3) of 2q



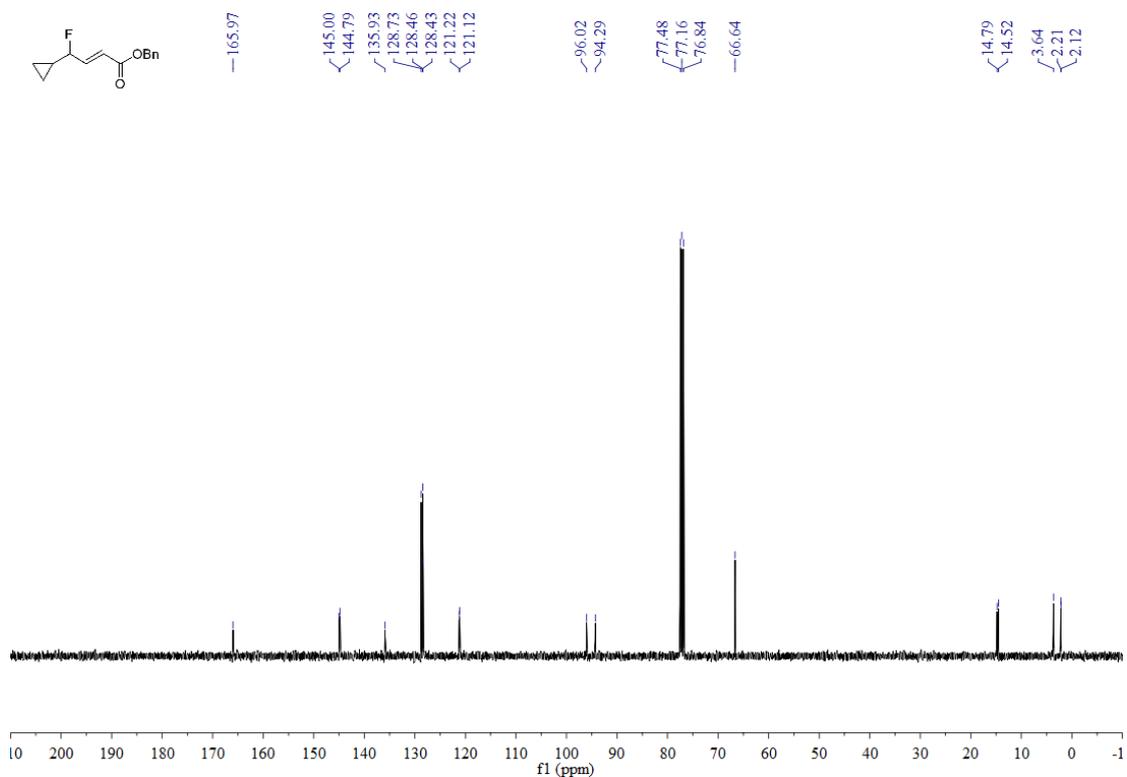
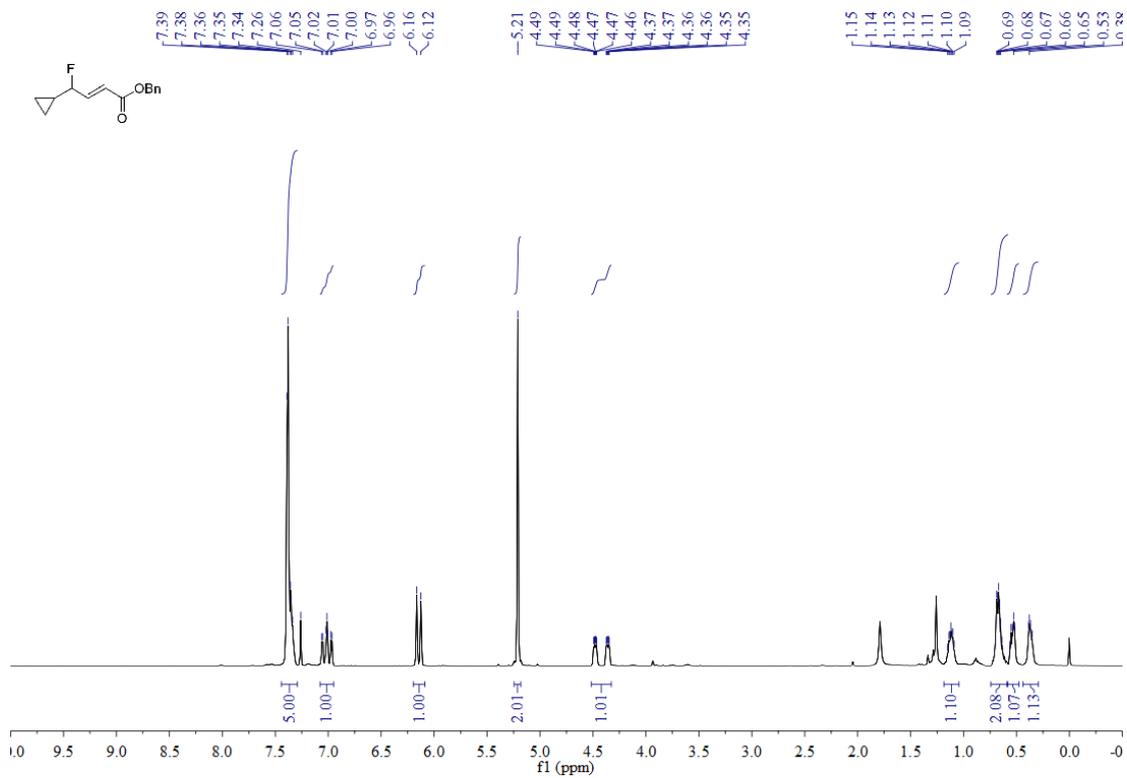
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 2r



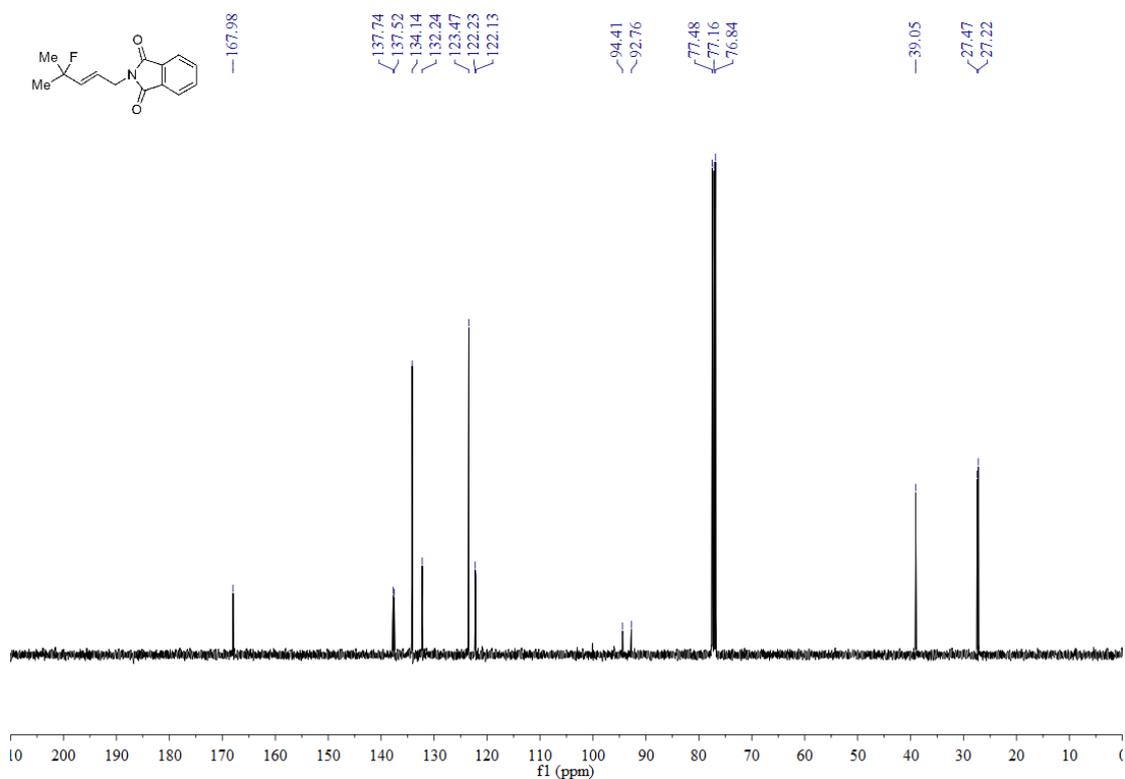
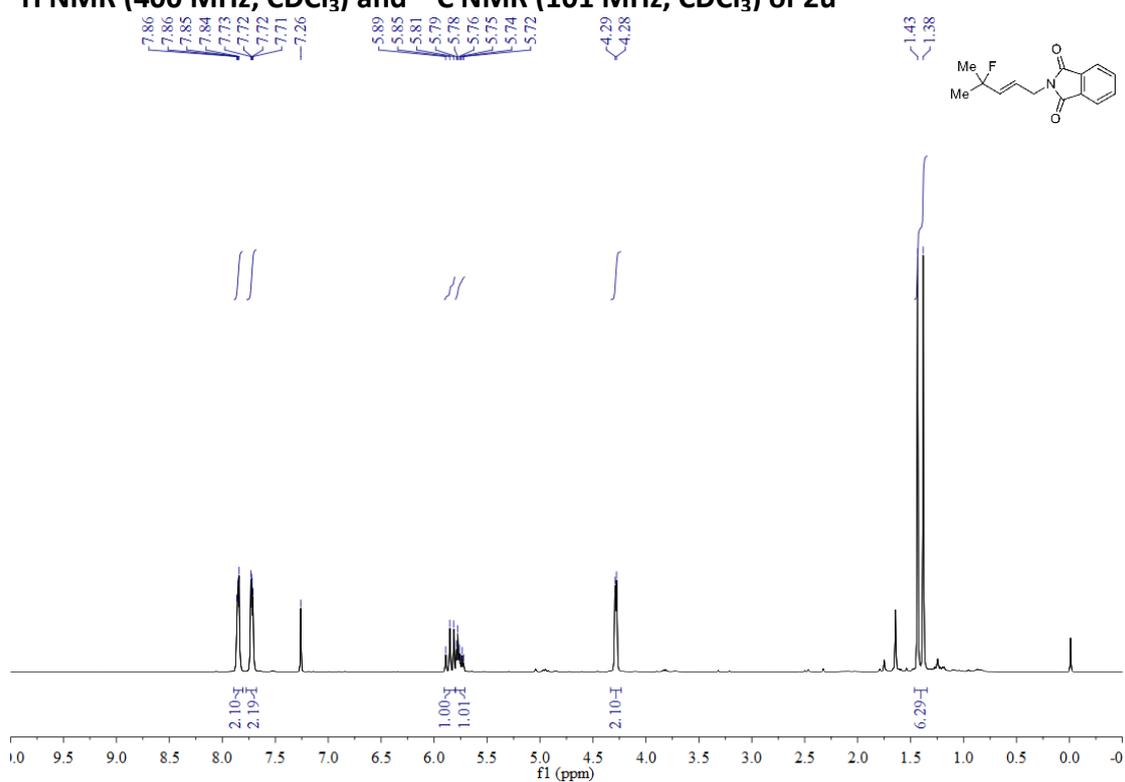
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 2s



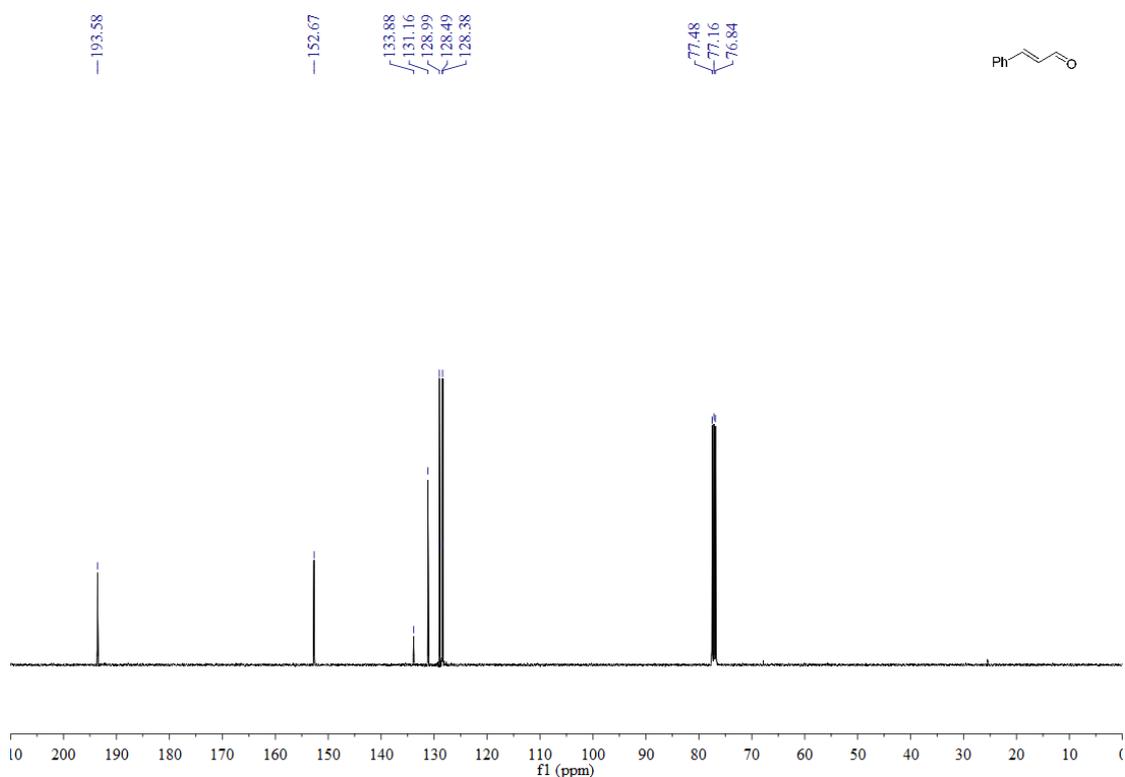
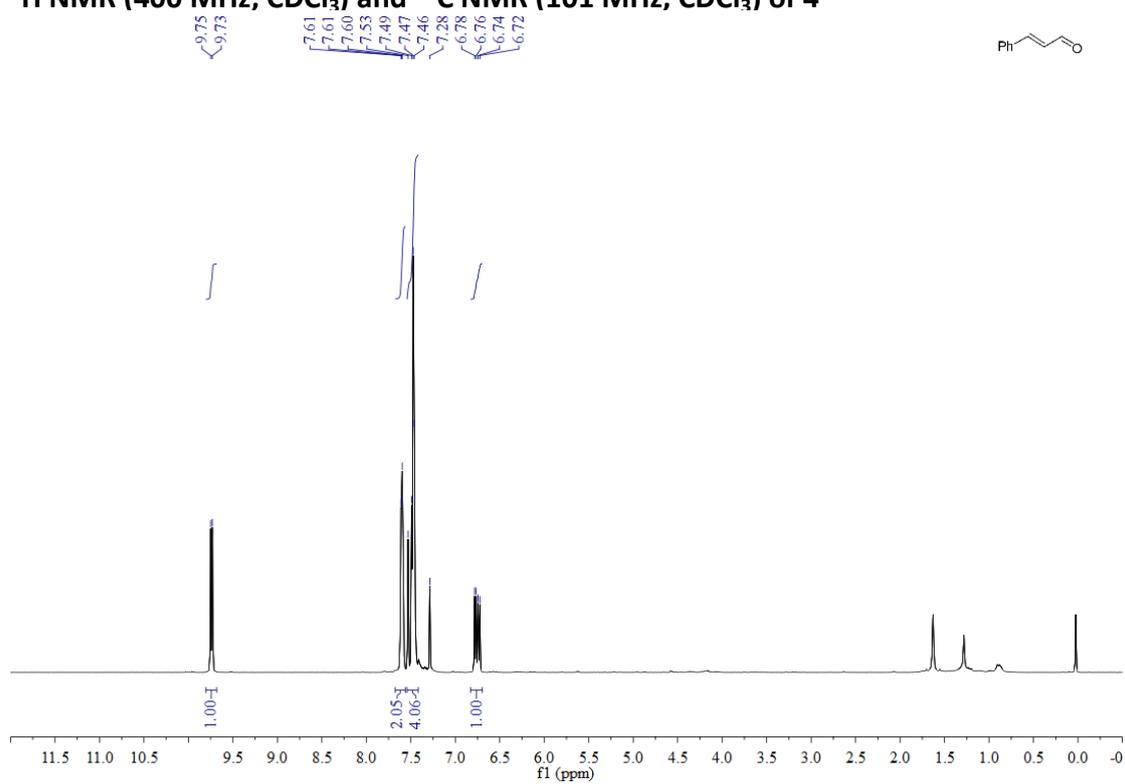
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (101 MHz, CDCl_3) of 2t



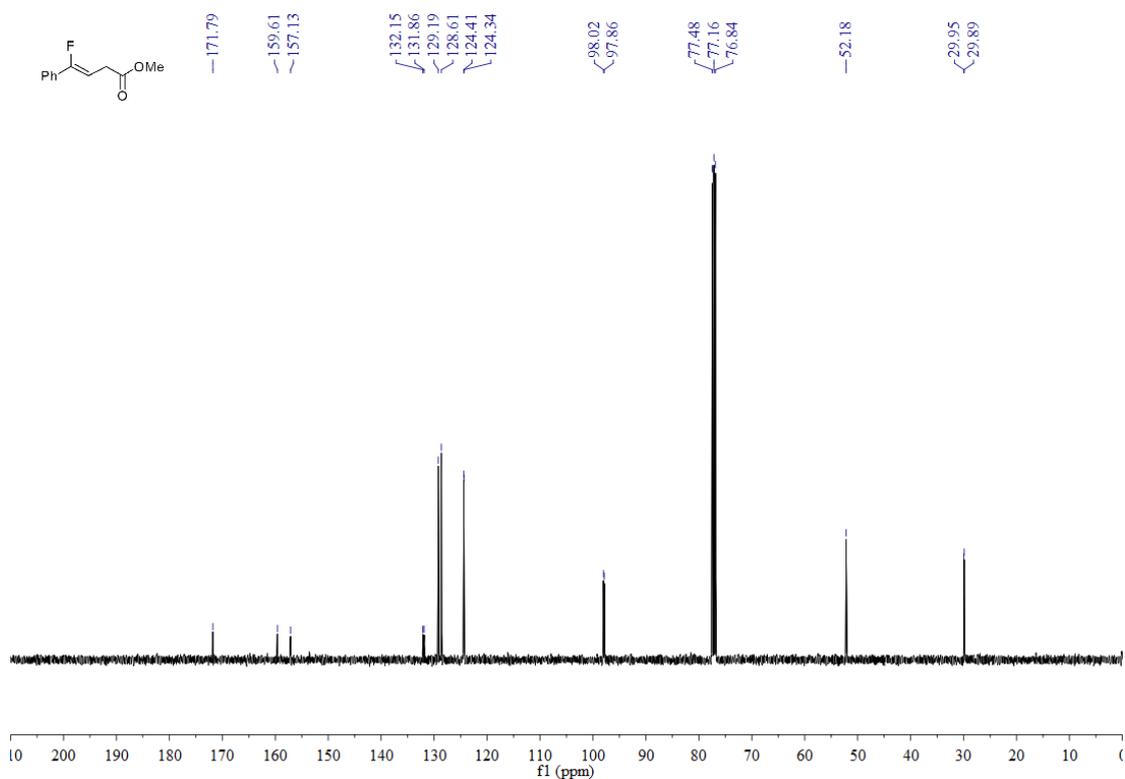
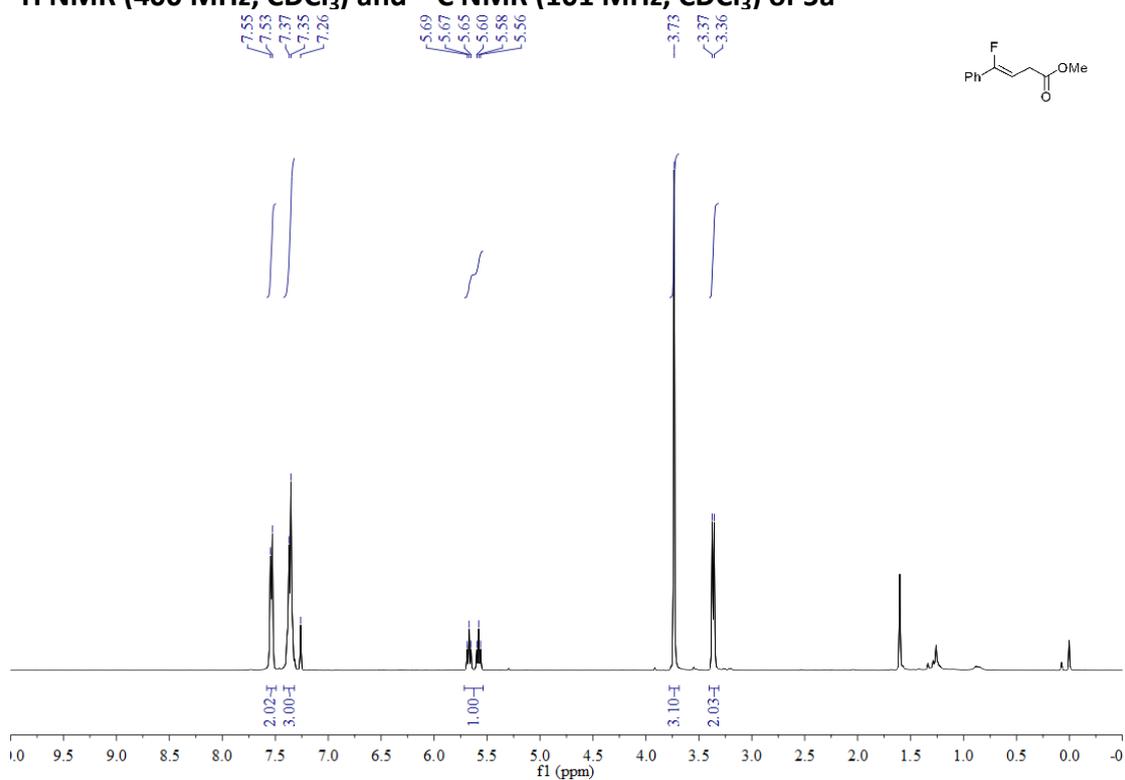
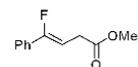
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 2u



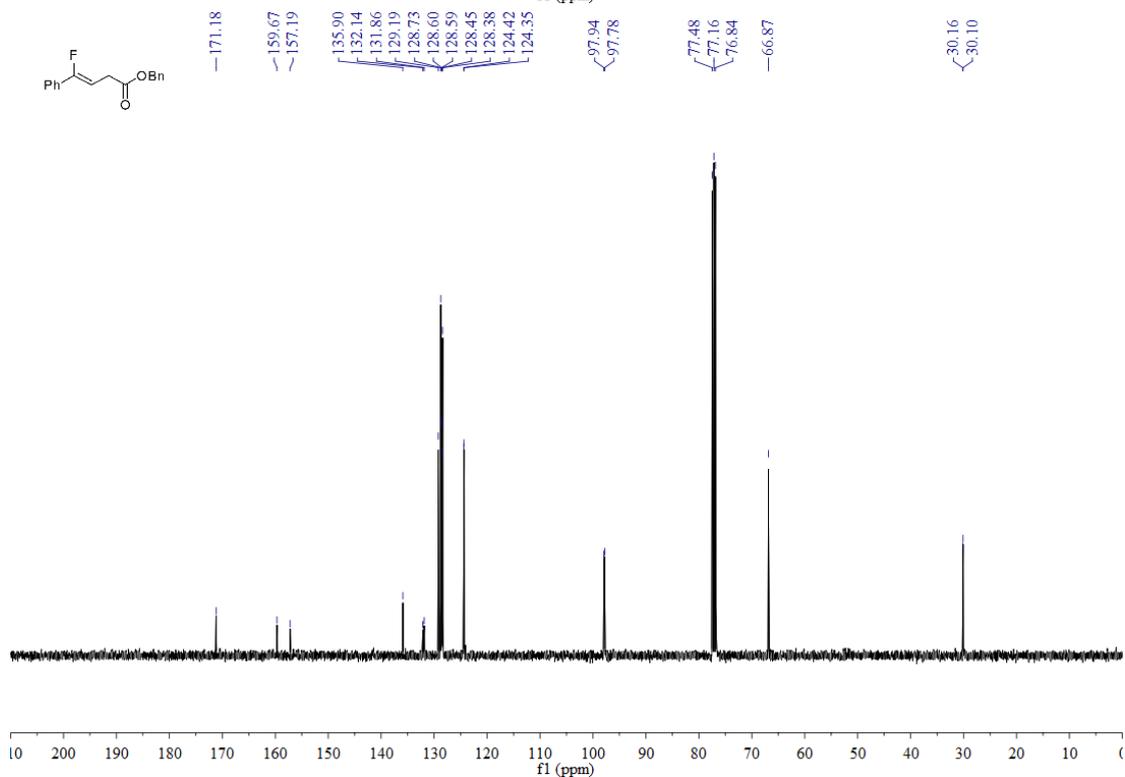
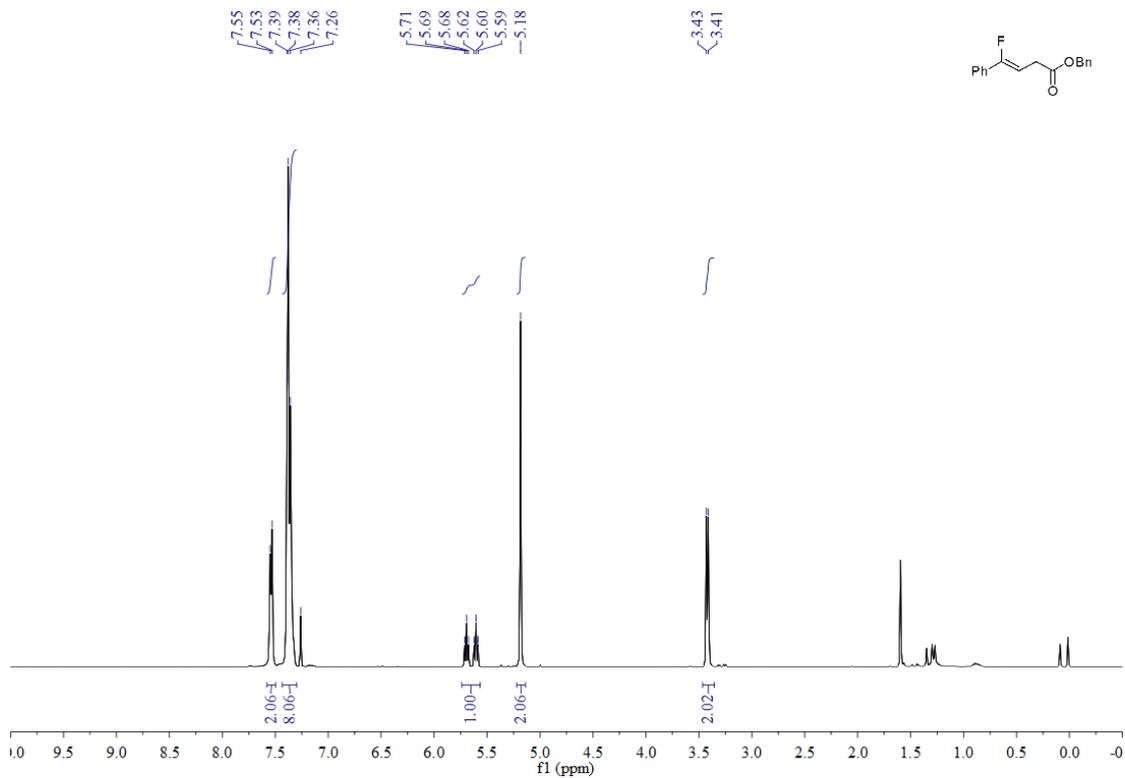
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 4



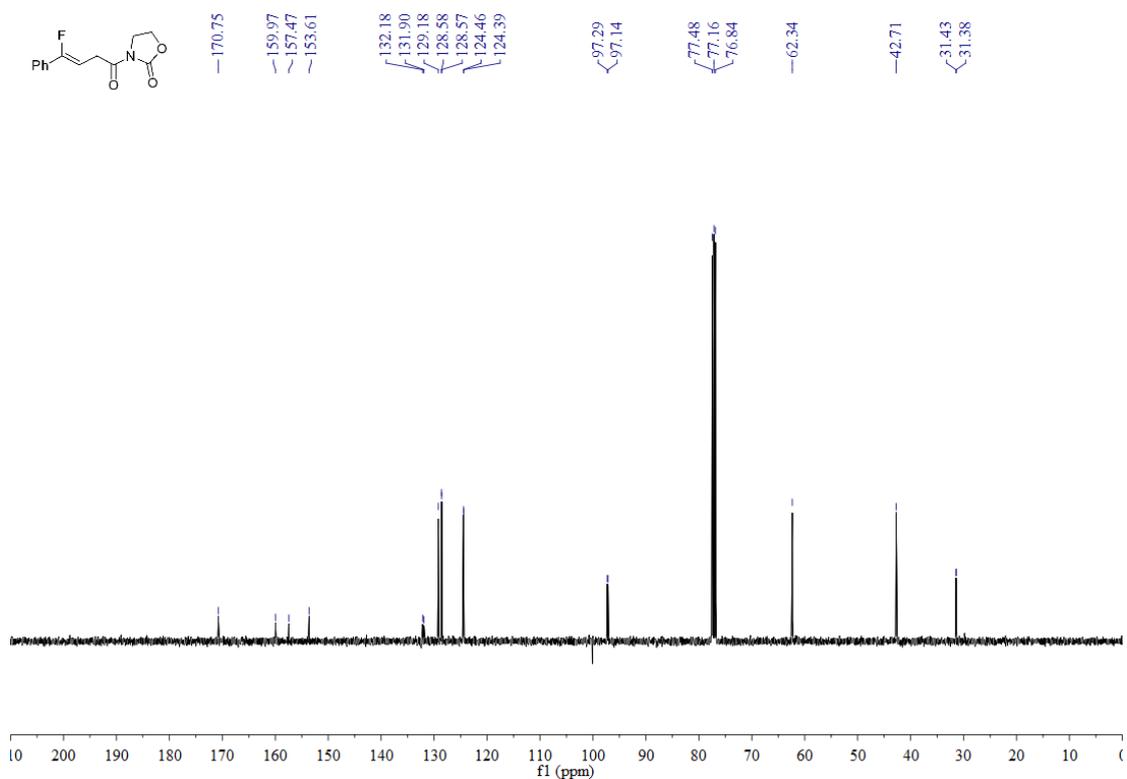
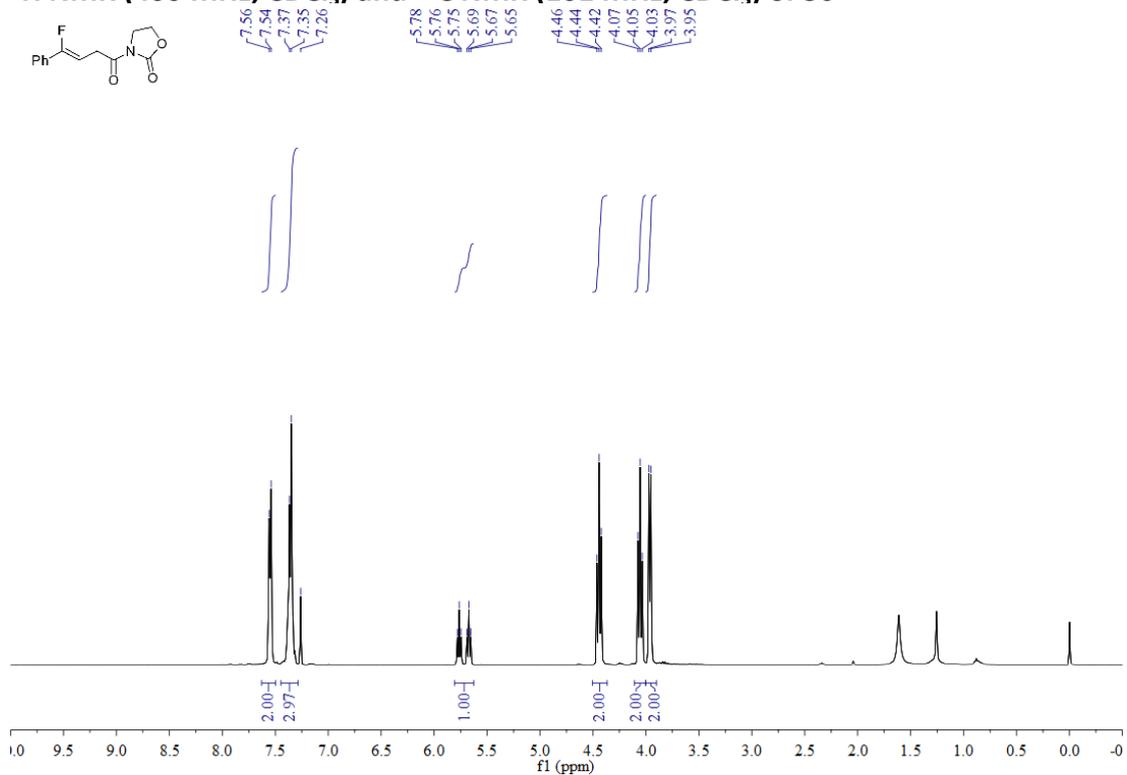
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 5a



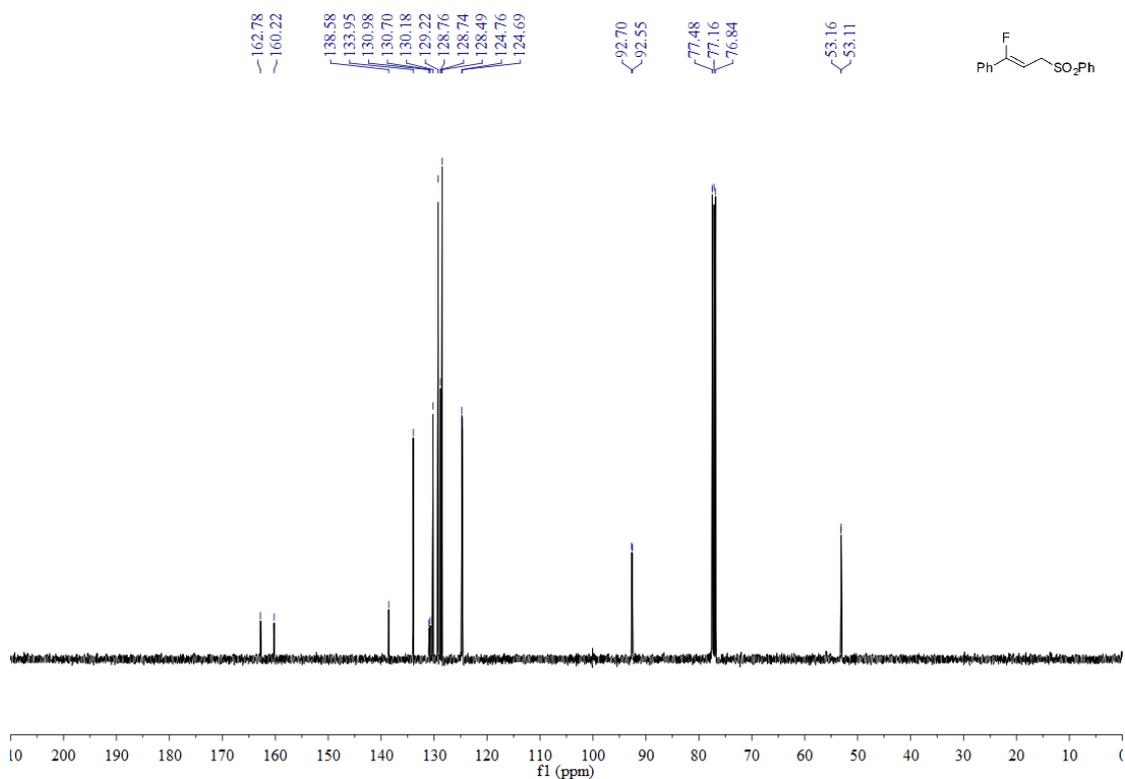
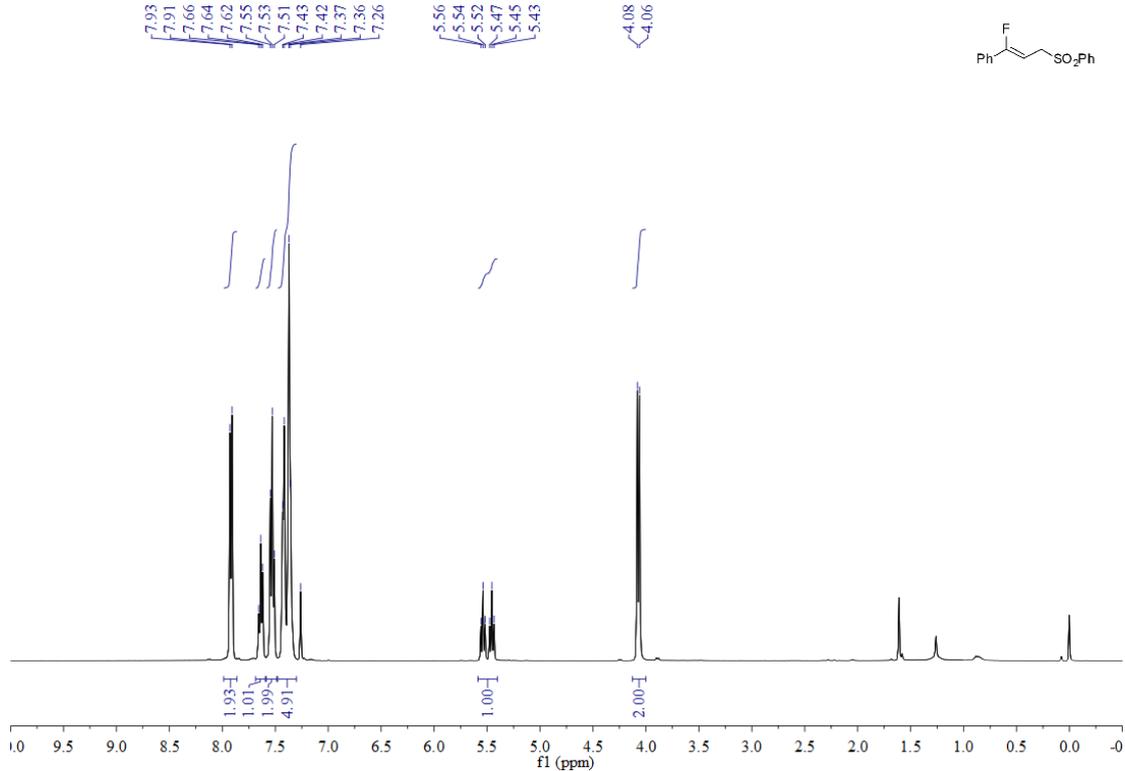
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (101 MHz, CDCl_3) of 5b



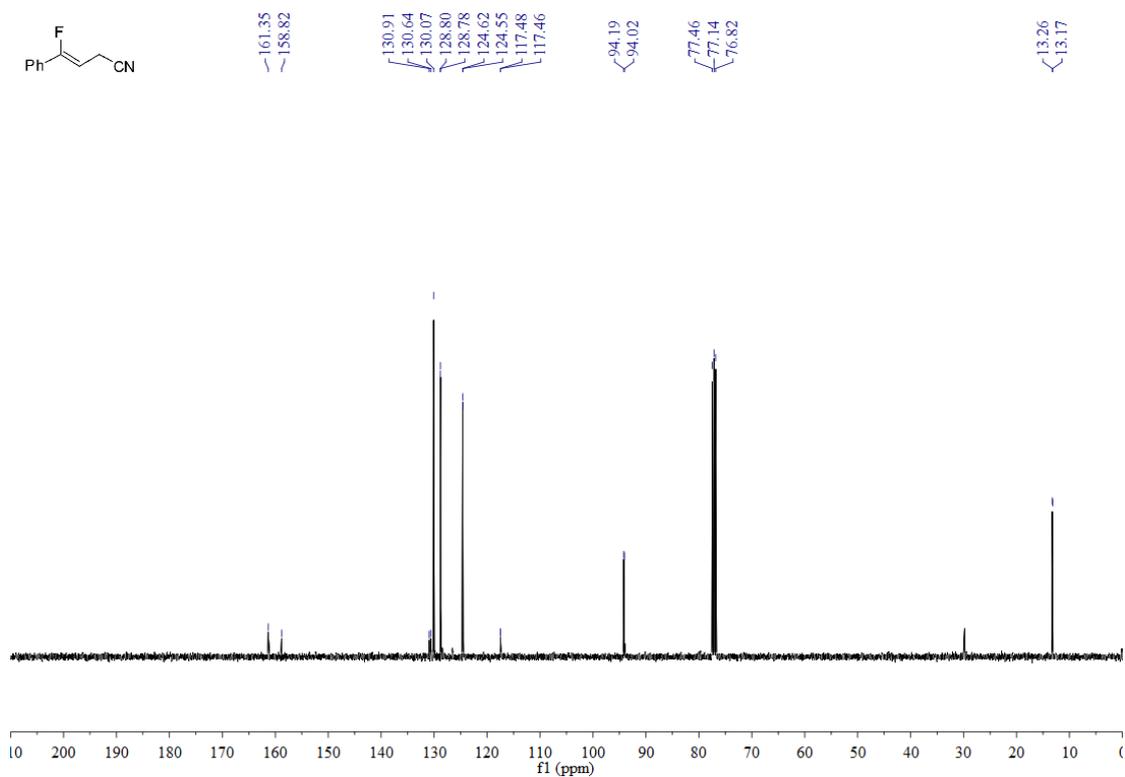
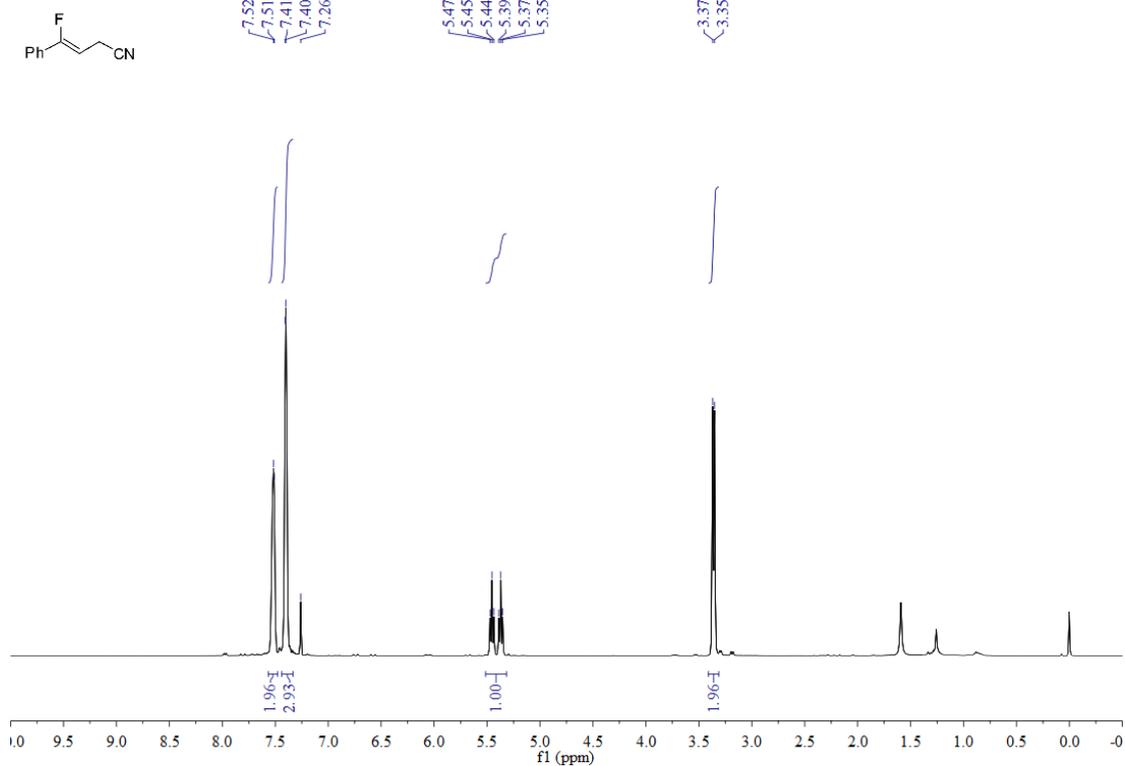
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 5c



¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 5d



¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (101 MHz, CDCl₃) of 5e



^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (101 MHz, CDCl_3) of 6f

