

Trifluoromethylation of Unactivated Alkenes with Me₃SiCF₃ and *N*-Iodosuccinimide

Xinkan Yang and Gavin Chit Tsui*

Table of Contents

General Experimental	S1
Materials.....	S1
Instrumentation.....	S1
Experimental Procedures.....	S2
Mechanistic Studies.....	S8
Optimization Studies.....	S13
Characterization Data	S16
Spectra.....	S28

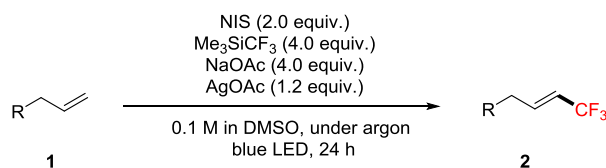
General Experimental. Unless otherwise noted, reactions were carried out under argon in a 25mL round-bottom flask with magnetic stirring. Analytical thin layer chromatography (TLC) was performed with EM Science silica gel 60 F254 aluminum plates. Visualization was done under a UV lamp (254 nm) and by immersion in ethanolic phosphomolybdic acid (PMA) or potassium permanganate (KMnO₄), followed by heating using a heat gun. Organic solutions were concentrated by rotary evaporation at 23–35 °C. Purification of reaction products were generally done by flash column chromatography with Grace Materials Technologies 230–400 mesh silica gel.

Materials. Anhydrous DMSO was purchased from J&K Scientific. NIS was purchased from Dieckmann then recrystallized from hexane : dioxane (2 : 1), then filtration and dried under reduced pressure for overnight.. AgOAc was purchased from Acros. DMF was dried over Solvent Purification System then bubbled with argon for 24 h. Other chemicals for substrates preparation were purchased from Acros, J&K Scientific, Aldrich and Dikemann.

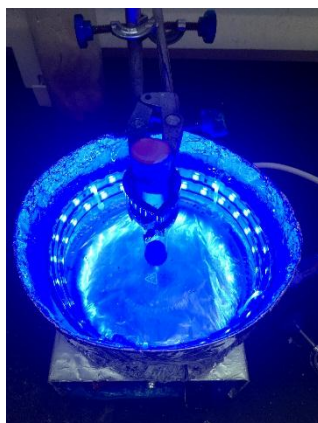
Instrumentation. Proton nuclear magnetic resonance spectra (¹H NMR) spectra, carbon nuclear magnetic resonance spectra (¹³C NMR) and fluorine nuclear magnetic resonance spectra (¹⁹F NMR) were recorded at 23 °C on a Bruker 400 spectrometer in CDCl₃ (400 MHz for ¹H, 101 MHz for ¹³C and 376 MHz for ¹⁹F) and Bruker 500 spectrometer in CDCl₃ (500 MHz for ¹H, 126 MHz for ¹³C and 470 MHz for ¹⁹F). Chemical shifts for protons were reported as parts per million in δ scale using solvent residual peak (CHCl₃: 7.26 ppm) or tetramethylsilane (0.00 ppm) as internal standards. Chemical shifts of ¹³C NMR spectra were reported in ppm from the central peak of CDCl₃ (77.16 ppm) on the δ scale. Chemical shifts of ¹⁹F NMR are reported as parts per million in δ scale using benzotrifluoride (-63.72 ppm) as internal standards. Data are represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintuplet, sx = sextet, sp = septuplet, m = multiplet, br = broad), and coupling constant (*J*, Hz). High resolution mass spectra (HRMS) were obtained on a Finnigan MAT 95XL GC Mass Spectrometer or a Thermo Scientific Q Exactive Focus Mass Spectrometer or Bruker 9.4T FTICR Mass Spectrometer. The control experiment results were obtained on a Shimadzu GCMS-QP2010 SE GC MS Spectrometer.

Experimental Procedures:

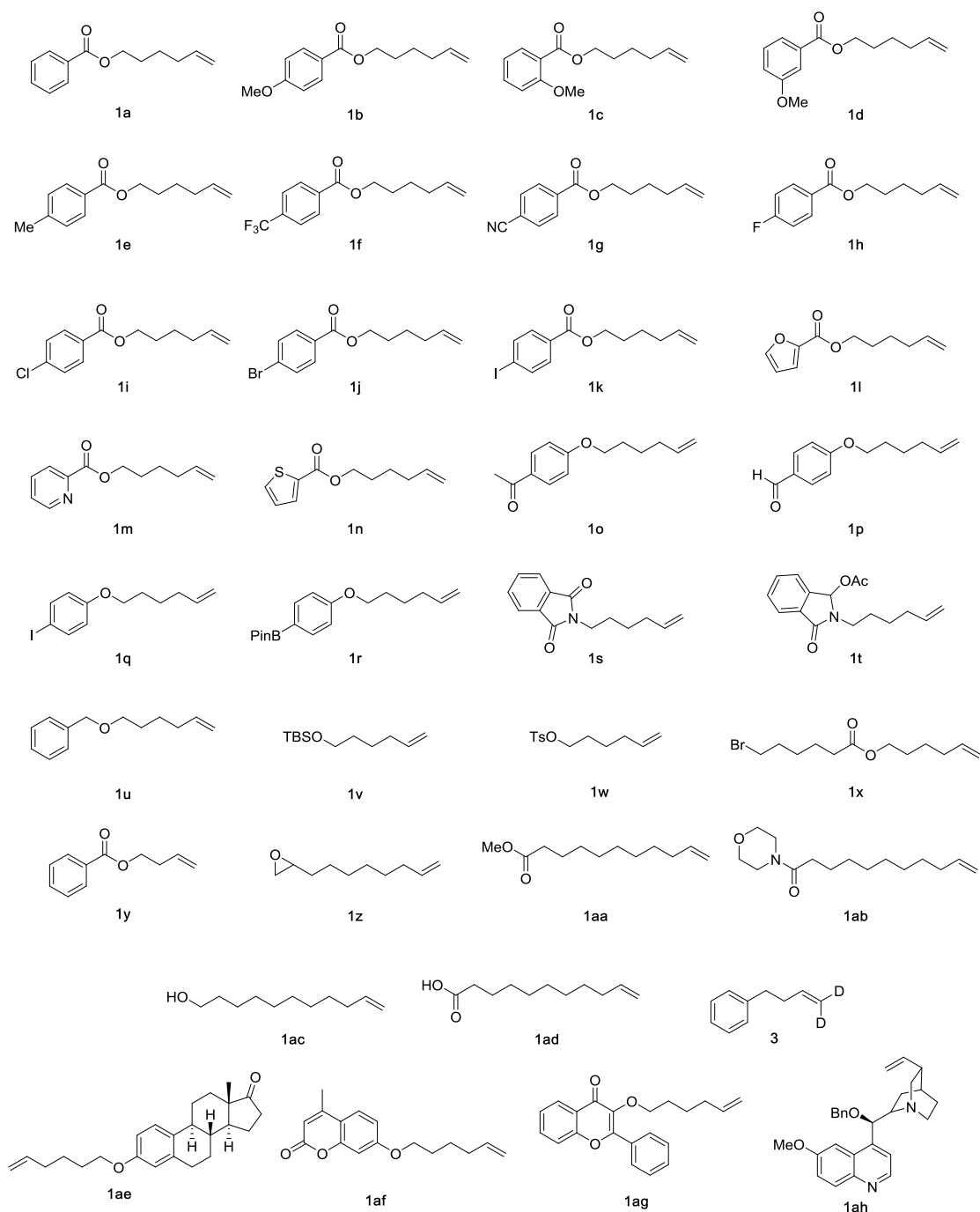
General procedure (*cf.* Scheme 2):



To a glass tube equipped with a magnetic stir bar were added alkene **1** (0.3 mmol), NIS (0.6 mmol), NaOAc (1.2 mmol) and AgOAc (0.36 mmol). The tube was then sealed with a septum, evacuated and refilled with argon for three times. Anhydrous DMSO (3.0 mL) was added via a syringe and the solution was further evacuated and refilled with argon for three times. Finally, Me₃SiCF₃ (180 μL, 0.4 mmol) was added dropwise to the solution. The tube was sealed and placed under a 16 W blue LED light trip at room temperature and stirred for 24 h (see picture below). The *E/Z* ratio was determined by ¹⁹F NMR of the crude mixture. The reaction was quenched with H₂O, extracted with diethyl ether for three times. The organic layers were combined, washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product.



Substrates:

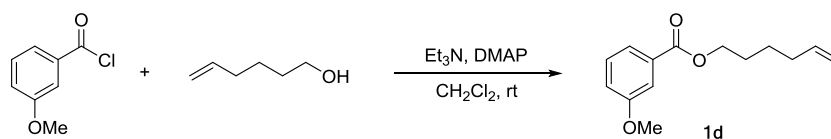


Alkenes **1a-1c**, **1e**, **1g-1s**, **1u-1y**, **1ab**, **1ae-1ah** were synthesized according to the literature procedures.¹ **1z**, **1aa**, **1ac**, **1ad** were commercially available. **1t** was synthesized from **1s**, **1d** and **1f** were synthesized by esterification from corresponding benzoyl chloride and 5-hexene-1-ol. **3** was synthesized according to the literature reported procedure.²

1 (a) Zhu, L.; Wang, L. S.; Li, B.; Fu, B.; Zhang, C. P.; Li, W. *Chem. Commun.* **2016**, 52, 6371. (b) Lin, Q.-Y.; Xu, X.-H.; Zhang, K.; Qing, F.-L. *Angew. Chem., Int. Ed.* **2016**, 55, 1479. (c) Liu, Z.-Q.; Liu, D. *J. Org. Chem.* **2017**, 82, 1649. (d) Braun, M.-G.; Doyle, A. G. *J. Am. Chem. Soc.* **2013**, 135, 12990. (e) Wu, X.; Chu, L.; Qing, F.-L. *Angew. Chem., Int. Ed.* **2013**, 52, 2198. (f) Ren, Y.; Zheng, X.; Zhang, X. *Synlett* **2018**, 29, 1028. (g) Ma, G.; Wan, W.; Hu, Q.; Jiang, H.; Wang, J.; Zhu, S.; Hao, J. *Chem. Commun.* **2014**, 50, 7527.

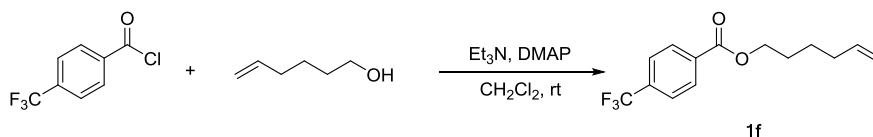
2 Shaw, M. H.; Croft, R. A.; Whittingham, W. G.; Bower, J. F. *J. Am. Chem. Soc.* **2015**, 137, 8054.

Preparation of hex-5-en-1-yl 3-methoxybenzoate (1d):



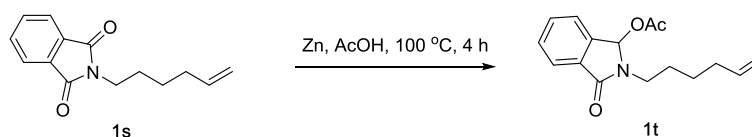
To a solution of 5-hexene-1-ol (0.48 mL, 4.0 mmol), Et₃N (1.11 mL, 8.0 mmol), DMAP (49.0 mg, 0.4 mmol) in CH₂Cl₂ (10 mL) was added dropwise with a solution of 3-Methoxybenzoyl chloride (0.89 mL, 6.0 mmol) in CH₂Cl₂ (4.0 mL) at 0 °C, the resulting mixture was vigorously stirred at room temperature and monitored the reaction by TLC. After completion, treated with sat. NaHCO₃ aq. then stirred at room temperature for another 20 mins. Et₂O was added, the organic layer was separated, washed with water, the combined extracts were washed with brine, dried over anhydrous Na₂SO₄, Filtered and evaporated the solvent, the residue was directly purified by flash chromatography to deliver the desired product **1d** as a colorless oil (930 mg, 4.0 mmol, 100% yield), R_f = 0.60 (hexane : EtOAc = 5 : 1). **¹H NMR** (400 MHz, CDCl₃): δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.56 (s, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.09 (dd, *J* = 8.4 Hz, *J* = 2.8 Hz, 1H), 5.87-5.77 (m, 1H), 5.06-4.96 (m, 2H), 4.32 (t, *J* = 6.6 Hz, 2H), 3.85 (s, 3H), 2.16-2.10 (m, 2H), 1.82-1.75 (m, 2H), 1.59-1.51 (m, 2H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 166.6, 159.6, 138.4, 131.9, 129.5, 122.0, 119.4, 115.0, 114.2, 65.1, 55.5, 33.4, 28.3, 25.4 ppm. **HRMS** m/z (APCI): calcd. for C₁₄H₁₉O₃ [M+H]⁺ : 235.1329; found: 235.1324.

Preparation of hex-5-en-1-yl 4-(trifluoromethyl)benzoate (1f):



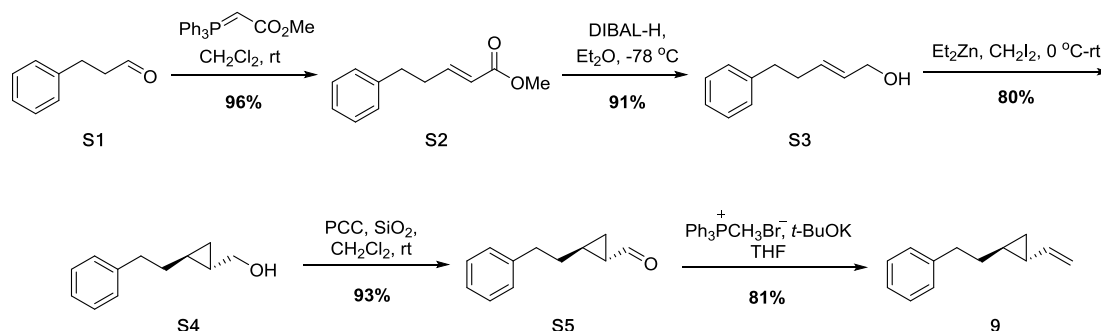
To a solution of 5-hexene-1-ol (0.24 mL, 2.0 mmol), Et₃N (0.56 mL, 4.0 mmol), DMAP (24.4 mg, 0.2 mmol) in CH₂Cl₂ (5.0 mL) was added dropwise with a solution of 4-trifluoromethylbenzoyl chloride (626 mg, 3.0 mmol) in CH₂Cl₂ (2.0 mL) at 0 °C, the resulting mixture was vigorously stirred at room temperature and monitored the reaction by TLC. After completion, treated with sat. NaHCO₃ aq. then stirred at room temperature for another 20 mins. Et₂O was added, the organic layer was separated, washed with water, the combined extracts were washed with brine, dried over anhydrous Na₂SO₄. Filtered and evaporated the solvent, the residue was directly purified by flash chromatography to deliver the desired product **1f** as a colorless oil (510 mg, 1.88 mmol, 94% yield), R_f = 0.70 (hexane : EtOAc = 5 : 1). **¹H NMR** (400 MHz, CDCl₃): δ 8.15 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 5.87-5.77 (m, 1H), 5.06-4.97 (m, 2H), 4.36 (t, *J* = 6.6 Hz, 2H), 2.16-2.11 (m, 2H), 1.84-1.77 (m, 2H), 1.59-1.52 (m, 2H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 165.6, 138.3, 134.5 (q, *J*_{C-F} = 32.6 Hz), 133.8, 130.1, 125.5 (q, *J*_{C-F} = 3.7 Hz), 123.8 (q, *J*_{C-F} = 273.6 Hz), 115.1, 65.6, 33.4, 28.2, 25.4 ppm. **¹⁹F NMR** (376 MHz, CDCl₃): δ: -64.11 (s, 3F). **HRMS** m/z (APCI): calcd. for C₁₄H₁₆F₃O₂ [M+H]⁺ : 273.1097; found: 273.1098.

Preparation of 2-(hex-5-en-1-yl)-3-oxoisindolin-1-yl acetate (**1t**):



A solution of **1s** (190 mg, 0.83 mmol), Zn (124 mg, 1.91 mmol) dust in acetic acid (4.2 mL) was heated to reflux for 4 hours, then cool down to room temperature. Most of acetic acid was removed under reduced pressure, then the residue was directly purified by column chromatography to afford the product **1t** (153 mg, 0.56 mmol, 68% yield) as a yellow oil. $R_f = 0.20$ (hexane : EtOAc = 5 : 1). **¹H NMR** (400 MHz, CDCl₃): δ 7.78-7.76 (m, 1H), 7.55-7.47 (m, 3H), 6.98 (s, 1H), 5.80-5.69 (m, 1H), 5.00-4.90 (m, 2H), 3.76-3.69 (m, 1H), 3.28-3.21 (m, 1H), 2.14 (s, 3H), 2.09-2.03 (m, 2H), 1.70-1.54 (m, 2H), 1.45-1.37 (m, 2H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 171.2, 167.8, 140.9, 138.4, 132.3, 132.1, 130.3, 123.8, 123.5, 114.9, 81.2, 40.2, 33.3, 27.7, 26.1, 21.1 ppm. **HRMS** m/z (APCI): calcd. for C₁₆H₂₀NO₃ [M+H]⁺: 274.1438; found: 274.1437.

Preparation of (2-(2-vinylcyclopropyl)ethyl)benzene (**9**):



To a stirred solution of **S1** (670 mg, 5.0 mmol) in CH₂Cl₂ (20.0 mL), Wittig ylide (2.0 g, 6.0 mmol) was added at room temperature under argon atmosphere, then stirred at room temperature for 24 h. the solvent was evaporated and the residue was directly purified by column chromatography to afford **S2** as a colorless oil (840 mg, 4.8 mmol, 96% yield, E / Z = 91 : 9). $R_f = 0.60$ (hexane : EtOAc = 8 : 1). The spectral data are in full accordance with the literature report.³

To a stirred solution of **S2** (840 mg, 4.78 mmol) in Et₂O (48.0 mL), DIBAL-H (1.0 M in hexane, 9.6 mL, 9.6 mmol) was added at -78 °C under argon atmosphere, then stirred at -78 °C for 2 h. Carefully quenched with saturated aqueous solution of sodium/potassium tartrate, then stirred for extra 1 h at room temperature. Extracted with Et₂O for three times, then the organic layers were combined and washed with brine, dried over anhydrous Na₂SO₄. Filtered and evaporated the solvent, the residue was directly purified by flash chromatography to deliver the desired product **S3** as a light yellow oil (435 mg, 4.4 mmol, 91% yield, E / Z = 91 : 9). $R_f = 0.20$ (hexane : EtOAc = 5 : 1). The spectral data are in full accordance with the literature report.³

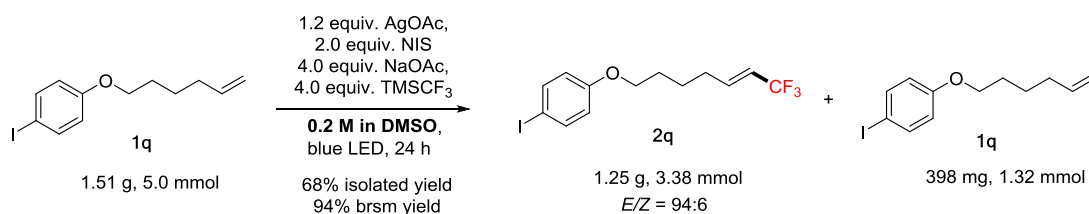
Under argon, **S3** (405 mg, 2.5 mmol) in dry CH₂Cl₂ (7.5 mL) was treated with Et₂Zn (1.0 M in hexane, 3.1 mmol, 3.1 mmol) at 0 °C, the suspension was stirred at 0 °C for 30 mins. In a second flask, Et₂Zn (1.0 M in hexane, 3.1 mmol, 3.1 mmol) was added to CH₂I₂ (0.4 mL, 5.0 mmol) in dry CH₂Cl₂

(15.0 mL) and stirred for 30 min at 0 °C. The contents of the first flask were transferred into the second flask at 0 °C and the mixture was stirred at room temperature until the substrate was completely consumed. Slowly quenched with sat. NH₄Cl aq., when an emulsion formed, 2 M HCl aq. was added slowly until the solution became clear. Extracted with CH₂Cl₂ for three times, then the organic layers were combined and washed with brine, dried over anhydrous Na₂SO₄. Filtered and evaporated the solvent, the residue was directly purified by flash chromatography to deliver the desired product **S4** as a light yellow oil. (350 mg, 2.0 mmol, 80% yield, dr (anti : syn) = 95 : 5). R_f = 0.22 (hexane : EtOAc = 5 : 1). **¹H NMR** (400 MHz, CDCl₃): δ 7.32-7.28 (m, 2H), 7.21-7.18 (m, 3H), 3.44-3.36 (m, 2H), 2.79-5.67 (m, 2H), 1.66 (s, 1H), 1.69-1.51 (m, 2H), 0.88-0.80 (m, 1H), 0.67-0.59 (m, 1H), 0.42-0.32 (m, 2H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 142.3, 128.5, 128.4, 125.8, 67.0, 35.9, 35.4, 21.4, 16.9, 9.0 ppm.

To a stirred solution of **S4** (350 mg, 2.0 mmol) in CH₂Cl₂ (10.0 mL) was added PCC (650 mg, 3.0 mmol) and silica gel (1.0 g) at room temperature under argon atmosphere, then stirred at room temperature and monitored by TLC. After completion, the solvent was evaporated and the residue was directly purified by column chromatography to afford the desired product **S5** as a colorless oil: (334 mg, 1.9 mmol, 93% yield, dr (anti : syn) = 95 : 5). R_f = 0.4 (hexane : EtOAc = 2 : 1). **¹H NMR** (400 MHz, CDCl₃): δ 8.97 (d, *J* = 5.6 Hz, 1H), 7.31-7.28 (m, 2H), 7.22-7.16 (m, 3H), 2.73 (d, *J* = 7.4 Hz, 2H), 1.76-1.59 (m, 3H), 1.51-1.46 (m, 1H), 1.31-1.27 (m, 1H), 0.95-0.90 (m, 1H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 201.0, 141.4, 128.5, 128.5, 126.1, 35.4, 34.5, 30.5, 22.3, 14.8 ppm.

Under argon, to a suspension of Wittig ylide (1.37 g, 3.84 mmol) in THF (2.0 mL) was quickly added *t*-BuOK (430 mg, 3.84 mmol), then stirred at room temperature for 30 mins, after that, the reaction system was cooled to 0 °C, a THF (2.0 mL) solution of **S5** (334 mg, 1.92 mmol) was added dropwise, then warmed to room temperature and stirred for overnight. Quenched with water, extracted with Et₂O for three times, then the organic layers were combined and washed with brine, dried over anhydrous Na₂SO₄. Filtered and evaporated the solvent, the residue was directly purified by flash chromatography to deliver the desired product **9** as a colorless oil. (270 mg, 1.55 mmol, 81% yield, dr (anti : syn) = 95 : 5). R_f = 0.90 (hexane : EtOAc = 5 : 1). **¹H NMR** (400 MHz, CDCl₃): δ 7.34-7.32 (m, 2H), 7.26-7.24 (m, 3H), 5.48-5.39 (m, 1H), 5.08 (d, *J* = 16.8 Hz, 1H), 4.90 (d, *J* = 10.0 Hz, 1H), 2.79-2.76 (m, 2H), 1.69-1.63 (m, 2H), 1.26-1.21 (m, 1H), 0.88-0.85 (m, 1H), 0.67-0.57 (m, 2H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 142.4, 142.1, 128.6, 128.4, 125.8, 111.3, 35.9, 35.8, 22.7, 20.8, 14.0 ppm. **HRMS** *m/z* (APCI): calcd. for C₁₃H₁₇ [M+H]⁺ : 173.1325; found: 173.1324.

Gram scale synthesis:



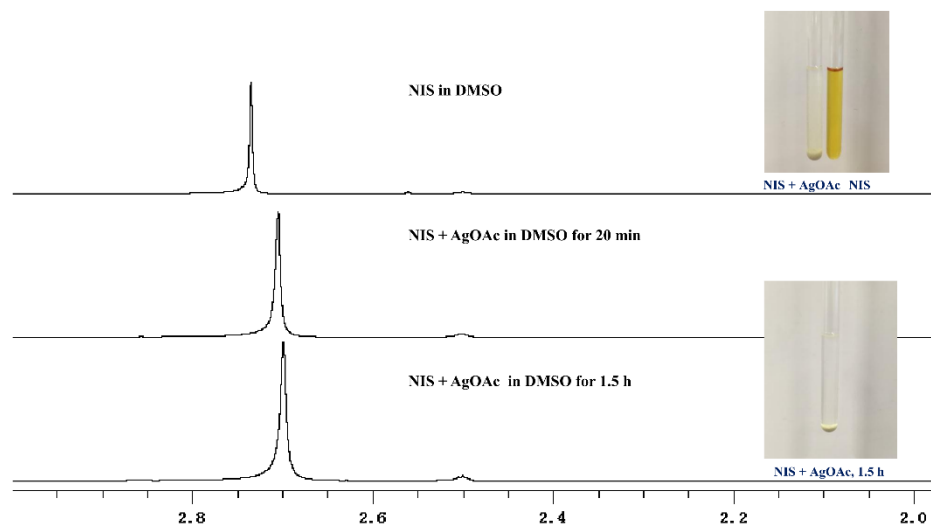
Under argon, to a 50 mL round bottom flask equipped with a magnetic stir bar was added alkene **1q** (1.51 g, 5.0 mmol), NIS (2.25 g, 10.0 mmol), NaOAc (1.64 g, 20.0 mmol) and AgOAc (1.0 g, 6.0 mmol). Then the tube was sealed with a septum, evacuated and refilled with argon for three times. Dry DMSO (25 mL) was added via syringe and the solution was again evacuated and refilled with argon for three times. Then Me₃SiCF₃ (3.0 mL, 20.0 mmol) was added dropwise to the above solution. The flask was sealed and placed under a 16 W blue LED light trip at room temperature and stirred for 24 h. The *E/Z* ratio (94:6) was determined by ¹⁹F NMR of the crude mixture. Then quenched with H₂O, extracted with diethyl ether for three times. The organic layers were combined, washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product **2q** as a colorless oil (1.25 g, 3.38 mmol, 68%, *E/Z* = 93:7, 398 mg **1q** was recovered, 94% brsm yield). R_f = 0.40 (hexane).

Mechanistic Studies:

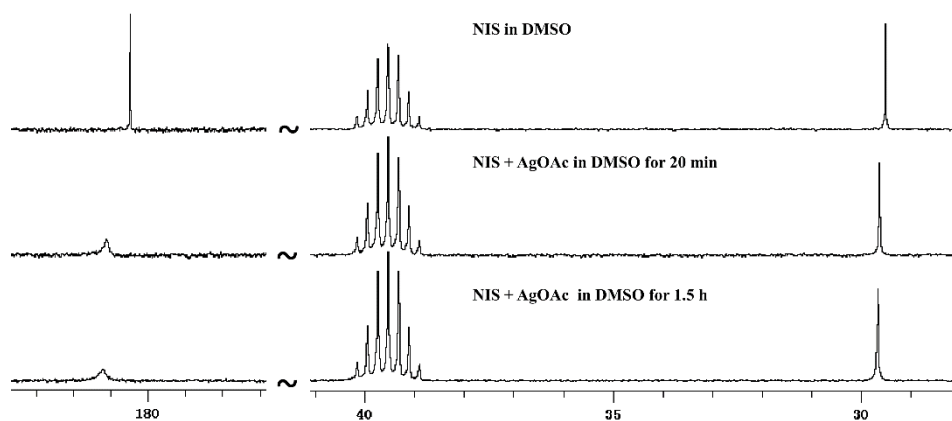
NMR experiments:

Under argon, to an NMR tube charged with AgOAc (10.0 mg, 0.06 mmol), NIS (22.5 mg, 0.1 mmol), DMSO- d_6 (0.5 mL) was added, then sealed with a septum. The mixture was evacuated and refilled with argon for three times, sealed and sonicated for 5 mins, then directly run the ^1H NMR and ^{13}C NMR experiments on the set time.

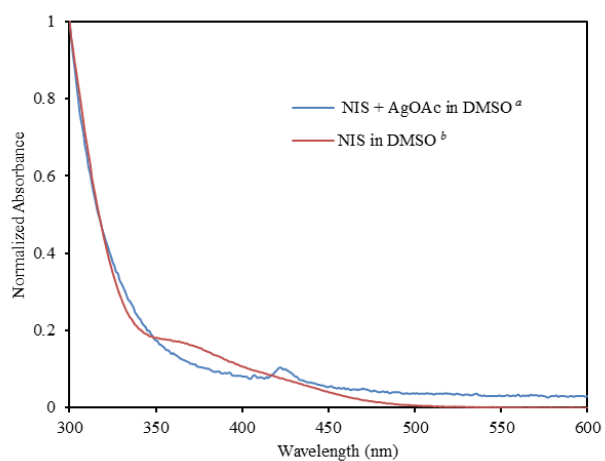
^1H NMR experiment



^{13}C NMR experiment

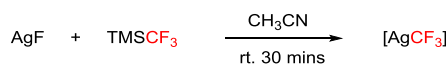


UV-Vis absorption spectra (recorded on a Varian CARY 1E UV-vis spectrophotometer):

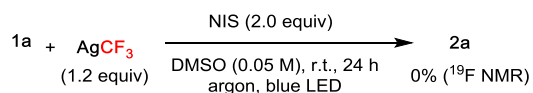


Note: ^aNIS/AgOAc (1:0.6) in DMSO (0.0025 M) under argon atmosphere. ^bNIS in DMSO (0.0025 M) under argon atmosphere.

[AgCF₃] experiment (cf. eq 1):

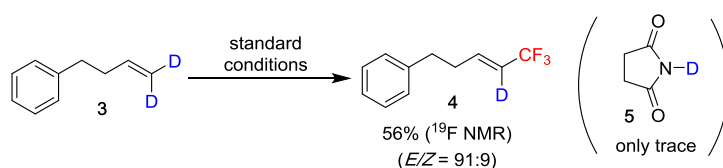


The preparation of [AgCF₃] was according to literature reported procedure.⁴ To an oven-dried glass tube equipped with a stir bar was added AgF (63.5 mg, 0.5 mmol), CH₃CN (3.0 mL) and TMSCF₃ (71 mg, 0.5 mmol). After the mixture was stirred at rt for 30 min, a dark brown suspension [AgCF₃] was formed. This suspension was immediately used without further purification. The preparation should be avoided from the light due to the photosensitivity of [AgCF₃].



Under argon, to a glass tube equipped with a magnetic stir bar was added alkene **1a** (20.4 mg, 0.1 mmol), NIS (45.0 mg, 0.2 mmol). Then the tube was sealed with a septum, evacuated and refilled with argon for three times. Dry DMSO (2.0 mL) was added via syringe and the solution was again evacuated and refilled with argon for three times. Then the above freshly prepared [AgCF₃] (0.33 M in CH₃CN, 0.36 mL, 0.12 mmol) was added dropwise to the above solution. The tube was sealed and placed under a 16 W blue LED light trip at room temperature and stirred for 24 h. The result was analyzed by ¹⁹F NMR using benzotrifluoride as the internal standard.

Labeling experiment (cf. eq 2):



Under argon, to a glass tube equipped with a magnetic stir bar was added alkene **3** (40.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), NaOAc (98.4 mg, 1.2 mmol) and AgOAc (60.2 mg, 0.36 mmol). Then the tube was sealed with a septum, evacuated and refilled with argon for three times. Dry DMSO (3.0 mL) was added via syringe and the solution was again evacuated and refilled with argon for three times. Then Me₃SiCF₃ (180 μL, 0.4 mmol) was added dropwise to the above solution. The tube was sealed and placed under a 16 W blue LED light trip at room temperature and stirred for 24 h. The yield and *E/Z* ratio (91:9) were determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. Then quenched with H₂O, extracted with diethyl ether for three times. The organic layers were combined, washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product **4** as a colorless oil (56% ¹⁹F NMR yield, *E/Z* = 93:7). *R*_f = 0.60 (hexane). Major isomer: **¹H NMR** (500 MHz, CDCl₃): δ 7.32 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 2H), 6.44-6.40 (m, 1H), 2.77 (t, *J* = 7.8 Hz, 2H), 2.51-2.48 (m, 2H) ppm. **¹³C NMR** (126 MHz, CDCl₃): δ 140.6, 139.7 (q, *J*_{C-F} = 6.6 Hz), 128.7, 128.5, 126.5, 123.1 (q, *J*_{C-F} = 269.6 Hz), 119.0 (m), 34.5, 33.3 ppm. **¹⁹F NMR** (470 MHz, CDCl₃): δ *E* isomer: -65.00 (s, 3F), *Z* isomer: -59.23 (s, 3F) ppm. **HRMS** *m/z* (EI): calcd. for C₁₁H₁₁DF₃ [*M*]⁺: 201.0870; found: 201.0872. The isotopic purity of **4** and succinimide **5** was determined by Shimadzu GCMS-QP2010 SE GC MS Spectrometer.

4 Zeng, Y.; Zhang, L.; Zhao, Y.; Ni, C.; Zhao, J.; Hu, J. *J. Am. Chem. Soc.* **2013**, *135*, 2955.

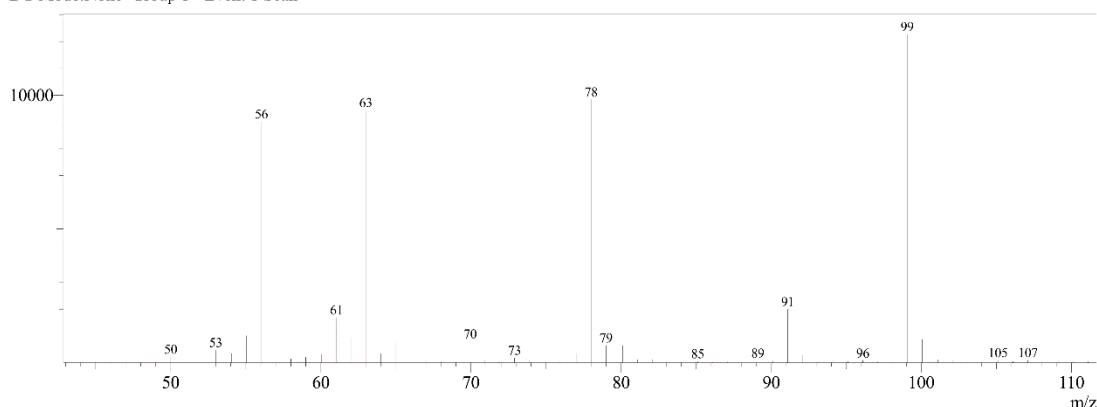
The EI-MS spectrum of succinimide 5 obtained from the labeling experiment:

Line#:1 R.Time:6.180(Scan#:219)

MassPeaks:429

RawMode:Single 6.180(219) BasePeak:99.05(12280)

BG Mode:None Group 1 - Event 1 Scan



The relative intensity of m/z 99 (93.5% isotopic purity) and m/z 100 are 12280 and 858 respectively.

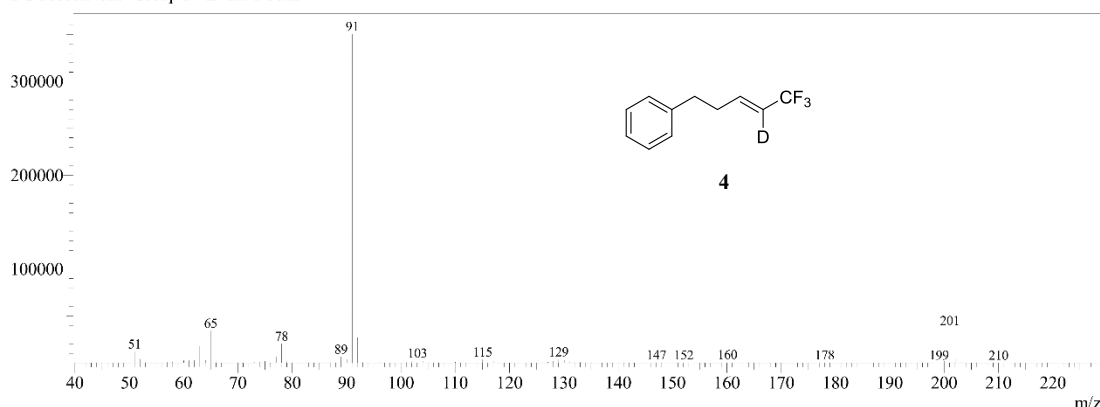
The EI-MS spectrum of succinimide 4 obtained from the labeling experiment:

Line#:1 R.Time:5.660(Scan#:167)

MassPeaks:451

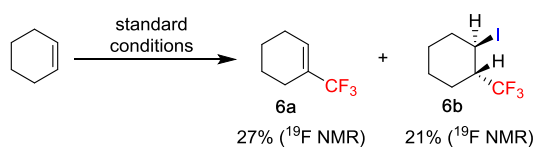
RawMode:Averaged 5.610-5.700(162-171) BasePeak:91.05(350761)

BG Mode:None Group 1 - Event 1 Scan



The relative intensity of m/z 200 and m/z 201 (95.3% isotopic purity) are 37049 and 1826 respectively.

Cyclohexene experiment (cf. eq3):



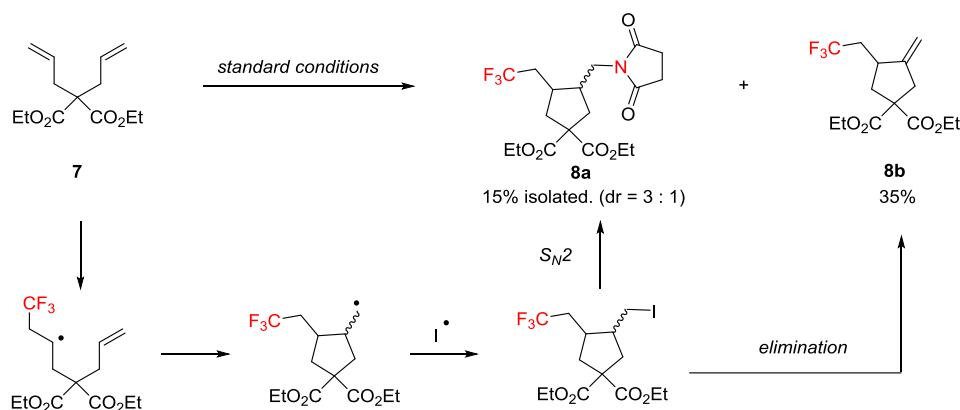
Under argon, to a glass tube equipped with a magnetic stir bar was added NIS (135 mg, 0.6 mmol), NaOAc (98.4 mg, 1.2 mmol) and AgOAc (60.2 mg, 0.36 mmol). Then the tube was sealed with a septum, evacuated and refilled with argon for three times. Dry DMSO (3.0 mL) was added via syringe and the solution was again evacuated and refilled with argon for three times. Then cyclohexene (31 μ L, 0.3 mmol) and Me₃SiCF₃ (180 μ L, 0.4 mmol) was added dropwise to the above solution sequentially. The tube was sealed and placed under a 16 W blue LED light trip at room temperature and stirred for 24 h. The result was analyzed by ¹⁹F NMR using benzotrifluoride as the internal standard. Then quenched with H₂O,

extracted with diethyl ether for three times. The organic layers were combined, washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product.

6a: 27% ¹⁹F NMR yield, ¹⁹F NMR (376 MHz, CDCl₃): δ -70.67 (s, 3F) ppm.

6b: 21 % ¹⁹F NMR yield, R_f = 0.70 (hexane). ¹H NMR (500 MHz, CDCl₃): δ 4.40-4.35 (m, 1H), 2.58-2.50 (m, 1H), 2.32-2.27 (m, 1H), 2.11-1.96 (m, 2H), 1.80-1.73 (m, 1H), 1.68-1.57 (m, 2H), 1.50-1.38 (m, 2H) ppm. ¹⁹F NMR (376 MHz, CDCl₃): δ -69.40 (d, *J* = 7.5 Hz, 3F) ppm. The spectral data are in full accordance with the literature report.⁵

Radical clock cyclization experiment (cf. eq 4):



Under argon, to a glass tube equipped with a magnetic stir bar was added alkene **7** (72 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), NaOAc (98.4 mg, 1.2 mmol) and AgOAc (60.2 mg, 0.36 mmol). Then the tube was sealed with a septum, evacuated and refilled with argon for three times. Dry DMSO (3.0 mL) was added via syringe and the solution was again evacuated and refilled with argon for three times. Then Me₃SiCF₃ (180 μL, 0.4 mmol) was added dropwise to the above solution sequentially. The tube was sealed and placed under a 16 W blue LED light trip at room temperature and stirred for 24 h. The result was analyzed by ¹⁹F NMR using benzonitrile as the internal standard. Then quenched with H₂O, extracted with diethyl ether for three times. The organic layers were combined, washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product.

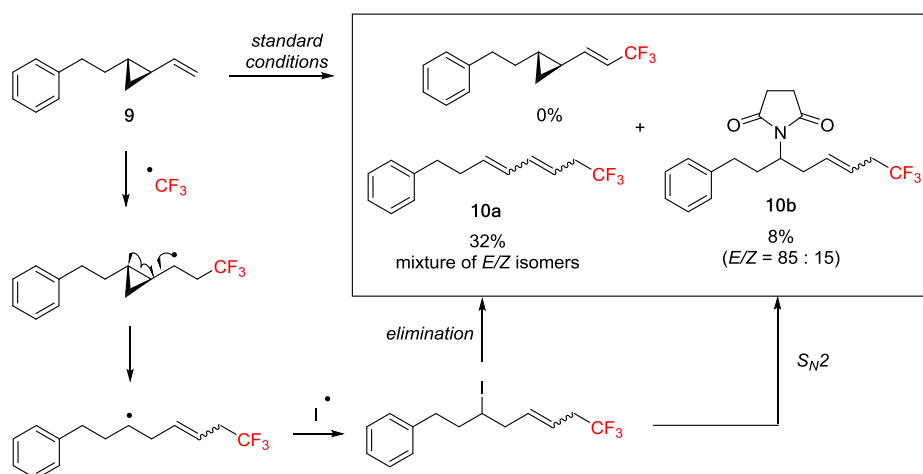
8a: (18 mg, 0.044 mmol, 15% yield, dr = 3 : 1), R_f = 0.30 (hexane : EtOAc = 1 : 1). Major isomer: ¹H NMR (500 MHz, CDCl₃): δ 4.19-4.14 (m, 4H), 3.48-3.38 (m, 2H), 2.70 (s, 4H), 2.56-2.51 (m, 1H), 2.46-2.39 (m, 1H), 2.38-2.32 (m, 2H), 2.16-2.08 (m, 1H), 2.05-2.00 (m, 2H), 1.98-1.92 (m, 1H), 1.23 (t, *J* = 7.5 Hz, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 177.4, 172.2, 172.2, 127.1 (q, *J*_{C-F} = 278.2 Hz), 62.0, 61.9, 58.4, 43.9, 40.5, 38.9, 38.3, 36.8, 35.4, 33.1 (q, *J*_{C-F} = 28.2 Hz), 28.2, 14.1 ppm. ¹⁹F NMR (470 MHz, CDCl₃): δ -65.32 (t, *J* = 10.6 Hz, 3F) ppm. HRMS *m/z* (APCI): calcd. for C₁₈H₂₅F₃NO₆ [M+H]⁺: 408.1629; found: 408.1628.

8b: (32.0 mg, 0.11 mmol, 35% yield), R_f = 0.50 (hexane : EtOAc = 5 : 1). ¹H NMR (500 MHz, CDCl₃): δ 4.99 (s, 1H), 4.82 (s, 1H), 4.17 (q, *J* = 6.0 Hz, 4H), 3.02 (d, *J* = 17.5 Hz, 1H), 2.89 (d, *J* = 17.0 Hz, 1H), 2.82-2.76 (m, 1H), 2.69-2.64 (m, 1H), 2.50-2.40 (m, 1H), 2.07-1.99 (m, 1H), 1.91 (t, *J* = 11.8 Hz, 1H), 1.21 (t, *J* = 7.0 Hz, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 171.4, 150.0, 126.8 (q, *J*_{C-F} = 278.2 Hz), 107.2, 61.7, 58.4, 40.2, 39.8, 37.9 (q, *J*_{C-F} = 28.1 Hz), 36.3 (q, *J*_{C-F} = 2.6 Hz), 14.0 ppm. ¹⁹F

5 Beniazza, R.; Molton, F.; Duboc, C.; Tron, A.; McClenaghan, N. D.; Lastecoueres, D.; Vincent, J. M. *Chem. Commun.* **2015**, 51, 9571–9574.

NMR (470 MHz, CDCl₃): δ -65.58 (t, J = 11.0 Hz, 3F) ppm. The spectral data are in full accordance with the literature report.⁶

Radical clock ring-opening experiment (cf. eq 5):



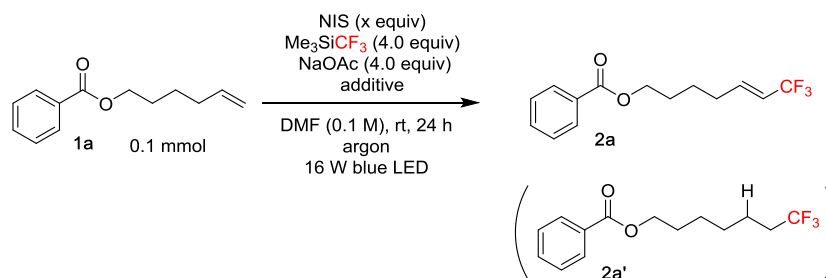
Under argon, to a glass tube equipped with a magnetic stir bar was added alkene **9** (51.6 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), NaOAc (98.4 mg, 1.2 mmol) and AgOAc (60.2 mg, 0.36 mmol). Then the tube was sealed with a septum, evacuated and refilled with argon for three times. Dry DMSO (3.0 mL) was added via syringe and the solution was again evacuated and refilled with argon for three times. Then Me₃SiCF₃ (180 μ L, 0.4 mmol) was added dropwise to the above solution sequentially. The tube was sealed and placed under a 16 W blue LED light trip at room temperature and stirred for 24 h. The result was analyzed by ¹⁹F NMR using benzonitrile as the internal standard. Then quenched with H₂O, extracted with diethyl ether for three times. The organic layers were combined, washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product.

10a: (23.0 mg, 0.096 mmol, 32% yield), R_f = 0.40 (hexane). Major isomer: **¹H NMR** (400 MHz, CDCl₃): δ 7.31 (t, J = 7.2 Hz, 2H), 7.23-7.19 (m, 3H), 6.23-6.20 (m, 1H), 6.13-6.06 (m, 1H), 5.81-5.73 (m, 1H), 5.53-5.45 (m, 1H), 2.89-2.79 (m, 2H), 2.73 (t, J = 7.8 Hz, 2H), 2.44 (t, J = 8.0 Hz, 2H) ppm. **¹³C NMR** (126 MHz, CDCl₃): δ 141.7, 137.0, 135.1, 129.8, 128.5, 128.5, 126.1, 126.1 (q, $J_{\text{C-F}}$ = 276.3 Hz), 118.5 (q, $J_{\text{C-F}}$ = 3.5 Hz), 37.4 (q, $J_{\text{C-F}}$ = 29.9 Hz), 35.7, 34.5 ppm. **¹⁹F NMR** (376 MHz, CDCl₃): δ -67.41 (t, J = 10.7 Hz, 3F) ppm. **HRMS** m/z (APCI): calcd. for C₁₄H₁₅F₃ [M+H]⁺ : 241.1199; found: 241.1198.

10b: (8.0 mg, 0.024 mmol, 8% yield), R_f = 0.30 (hexane : EtOAc = 2 : 1). Major isomer: **¹H NMR** (400 MHz, CDCl₃): δ 7.26 (t, J = 7.4 Hz, 2H), 7.18-7.13 (m, 3H), 5.57-5.50 (m, 1H), 5.40-6.33 (m, 1H), 4.27-4.17 (m, 1H), 2.83-2.61 (m, 4H), 2.41-2.22 (m, 1H), 2.55-2.46 (m, 2H), 2.36 (s, 4H), 1.97-1.88 (m, 1H) ppm. **¹³C NMR** (126 MHz, CDCl₃): δ 177.8, 144.1, 134.2, 128.5, 128.4, 126.2, 126.0 (q, $J_{\text{C-F}}$ = 276.9 Hz), 121.4 (q, $J_{\text{C-F}}$ = 3.5 Hz), 52.1, 37.3 (q, $J_{\text{C-F}}$ = 29.6 Hz), 35.1, 33.5, 31.7, 27.8 ppm. **¹⁹F NMR** (376 MHz, CDCl₃): δ -67.78 (t, J = 10.7 Hz, 3F) ppm. **HRMS** m/z (APCI): calcd. for C₁₈H₂₀F₃NO₂ [M+H]⁺ : 340.1519; found: 340.1518.

Optimization Studies:

Table S1. Optimization studies (part 1).

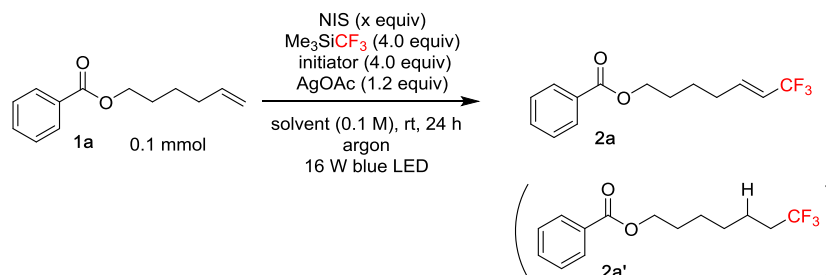


entry	x	additive (equiv)	yield (<i>E/Z</i>) ^a
1	3.0	none	2a 38% (94:6); 2a' 5%
2 ^b	3.0	none	2a 0%; 2a' 0%
3	3.0 ^c	none	2a 0%; 2a' 0%
4	3.0 ^d	none	2a 0%; 2a' 0%
5	3.0 ^e	none	2a 0%; 2a' 0%
6	3.0 ^f	none	2a trace; 2a' 0%
7	4.0	none	2a 62% (92:8); 2a' 6%
8 ^g	4.0	none	2a 0%; 2a' 0%
9	5.0	none	2a 42% (93:7); 2a' 4%
10	3.0	Ru(bpy) ₃ Cl ₂ ·6H ₂ O (0.025)	2a 53% (93:7); 2a' 5%
11	3.0	Ru(bpy) ₃ Cl ₂ ·6H ₂ O (0.05)	2a 45% (93:7); 2a' 5%
12	3.0	Ru(bpy) ₃ Cl ₂ ·6H ₂ O (0.10)	2a 15% (93:7); 2a' 1%
13	3.0	AgNO ₃ (0.2)	2a 38% (93:7); 2a' 2%
14	3.0	AgNO ₃ (0.4)	2a 39% (93:7); 2a' 2%
15	3.0	AgNO ₃ (1.0)	2a 73% (93:7); 2a' 5%
16 ^h	3.0	AgNO ₃ (1.2)	2a 73% (93:7); 2a' 5%
17	3.0	AgNO ₃ (2.0)	2a 74% (92:8); 2a' 5%
18	3.0	AgF (1.0)	2a 50% (94:6); 2a' 6%
19	3.0	Ag ₂ O (1.0)	2a 63% (93:7); 2a' 5%
20	3.0	AgOAc (1.0)	2a 73% (92:8); 2a' 6%
21^h	3.0	AgOAc (1.2)	2a 73% (93:7) ; 2a' 5%
22	3.0	Ag ₂ CO ₃ (1.0)	2a 49% (94:6); 2a' 1%
23	3.0	AgPF ₆ (1.0)	2a 15% (94:6); 2a' 5%
24	3.0	AgOTf (1.0)	2a 18% (93:7); 2a' 2%
25	3.0	CuCl (1.0)	2a trace; 2a' 2%
26	3.0	FeCl ₃ (1.0)	2a 0%; 2a' 0%
27	3.0	FeCl ₂ (1.0)	2a 0%; 2a' 0%
28 ⁱ	3.0	AgNO ₃ (1.0)	2a 66% (92:8); 2a' 6%
29 ^j	3.0	AgNO ₃ (1.0)	2a 64% (91:9); 2a' 5%
30 ^k	3.0	AgNO ₃ (1.0)	2a 26% (92:8); 2a' 5%

^aYield and *E/Z* ratio were determined by ¹⁹F NMR analysis of the crude mixture using benzotrifluoride as the internal standard. ^bOpen to air. ^cUsed *N*-bromosuccinimide (NBS) instead. ^dUsed *N*-chlorosuccinimide (NCS) instead. ^eUsed iodine (I₂) instead. ^fUsed iodo- monoacetate (IOAc) instead.

^gAdded TEMPO (2.0 equiv). ^hImproved reproducibility. ⁱTMSCF₃/NaOAc (5.0/5.0 equiv).
^jTMSCF₃/NaOAc (3.0/3.0 equiv). ^kTMSCF₃/NaOAc (2.0/2.0 equiv).

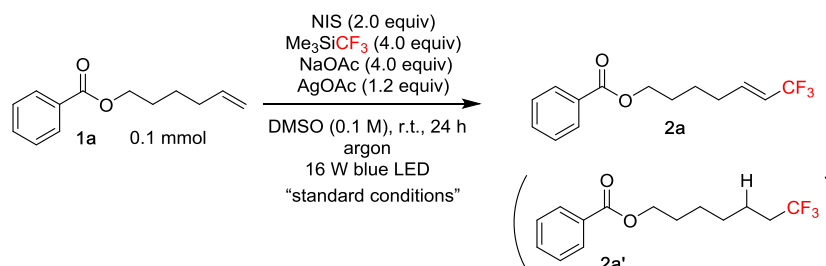
Table S2. Optimization studies (part 2).



entry	x	initiator	solvent	yield (<i>E/Z</i>) ^a
1	3.0	NaOAc	DMF	2a 73% (93:7); 2a' 5%
2	3.0	NaOAc	DMSO	2a 76% (93:7); 2a' 0%
3	3.0	NaOAc	MeCN	2a 33% (96:4); 2a' 0%
4	3.0	NaOAc	1,4-dioxane	2a 0%; 2a' 0%
5	2.0	NaOAc	DMSO	2a 76% (93:7); 2a' 0%
6	2.0	Na ₂ CO ₃	DMSO	2a 69% (93:7); 2a' 0%
7	2.0	NaHCO ₃	DMSO	2a 56% (91:9); 2a' 0%
8	2.0	sodium phenoxide	DMSO	2a 0%; 2a' 0%
9	2.0	sodium benzoate	DMSO	2a 74% (93:7); 2a' 0%
10	2.0	NaH ₂ PO ₄	DMSO	2a 44% (94:6); 2a' 0%
11	2.0	Na ₂ HPO ₄	DMSO	2a trace; 2a' 0%
12	2.0	NaF	DMSO	2a trace; 2a' 0%
13	2.0	NH ₄ OAc	DMSO	2a trace; 2a' 0%
14	2.0	Bu ₄ NOAc	DMSO	2a 49% (92:8); 2a' 0%
15	2.0	KOAc	DMSO	2a 75% (92:8); 2a' 0%
16	2.0	LiOAc	DMSO	2a 75% (92:8); 2a' 0%
17	2.0	K ₂ CO ₃	DMSO	2a trace; 2a' 0%
18	2.0	Et ₃ N	DMSO	2a trace; 2a' 0%
19 ^b	2.0	NaOAc	DMSO	2a 61% (95:5); 2a' 0%
20 ^c	2.0	NaOAc	DMSO	2a 74% (93:7); 2a' 0%
21 ^d	2.0	NaOAc	DMSO	2a 68% (94:6); 2a' 0%
22 ^e	2.0	NaOAc	DMSO	2a 72% (92:8); 2a' 0%

^aYield and *E/Z* ratio were determined by ¹⁹F NMR analysis of the crude mixture using benzotrifluoride as the internal standard. ^bUsed 4 W blue LED instead. ^cUsed 24 W white CFL bulb instead. ^d0.2 M in DMSO. ^e0.05 M in DMSO.

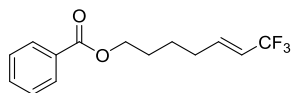
Table S3. Control experiments.



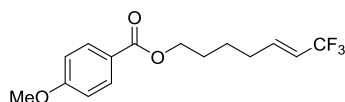
entry	change from the "standard conditions"	yield (<i>E/Z</i>) ^a
1	none	2a 76% (93:7); 2a' 0%
2 ^b	no NIS	2a 0%; 2a' 0%
3	1.0 equiv NIS	2a 37% (94:6); 2a' trace
4	no AgOAc	2a 7%; 2a' 3%
5	no NaOAc	2a 30% (94:6); 2a' 0%
6	no NaOAc, 5.2 equiv AgOAc	2a 15% (93:7); 2a' 4%
7	no irradiation	2a 8%; 2a' 0%
8	no irradiation, 80 °C	2a 13% (92:8); 2a' 0%

^aYield and *E/Z* ratio were determined by ¹⁹F NMR analysis of the crude mixture using benzotrifluoride as the internal standard. ^bDetected the formation of AgCF₃ mainly.

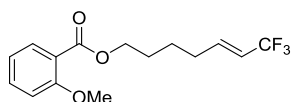
Characterization Data:



2a: 7,7,7-trifluorohept-5-en-1-yl benzoate. Prepared according to the general procedure. Reaction was run using **1a** (61.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μ L, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (94:6) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.25 mmol, 68.5 mg, 84 %, *E/Z* = 92:8), *R*_f = 0.60 (hexane : EtOAc = 5 : 1). E isomer: ¹H NMR (400 MHz, CDCl₃): δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 6.42-6.35 (m, 1H), 5.69-5.60 (m, 1H), 4.34 (t, *J* = 6.4 Hz, 2H), 2.26-2.21 (m, 2H), 1.84-1.76 (m, 2H), 1.65-1.58 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 166.7, 140.1 (q, *J*_{C-F} = 6.5 Hz), 133.1, 130.4, 129.6, 128.5, 123.1 (q, *J*_{C-F} = 270.0 Hz), 119.0 (q, *J*_{C-F} = 33.4 Hz), 64.6, 31.1, 28.2, 24.6 ppm. ¹⁹F NMR (376 MHz, CDCl₃): δ E isomer: -64.86 (s, 3F), Z isomer: -58.94 (s, 3F) ppm. The spectral data are in full accordance with the literature report.⁷

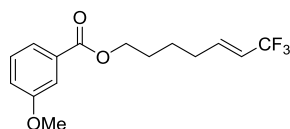


2b: 7,7,7-trifluorohept-5-en-1-yl 4-methoxybenzoate. Prepared according to the general procedure. Reaction was run using **1b** (70.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μ L, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (94:6) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.26 mmol, 77.0 mg, 85 %, *E/Z* = 92:8), *R*_f = 0.40 (hexane : EtOAc = 5 : 1). E isomer: ¹H NMR (400 MHz, CDCl₃): δ 7.98 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.39-6.35 (m, 1H), 5.67-5.58 (m, 1H), 4.29 (t, *J* = 6.4 Hz, 2H), 3.83 (s, 3H), 2.28-2.15 (m, 2H), 1.80-1.73 (m, 2H), 1.62-1.55 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 166.4, 163.4, 140.2 (q, *J*_{C-F} = 6.6 Hz), 131.6, 123.1 (q, *J*_{C-F} = 270.0 Hz), 122.8, 118.9 (q, *J*_{C-F} = 33.4 Hz), 113.7, 64.2, 55.4, 31.1, 28.3, 24.6 ppm. ¹⁹F NMR (376 MHz, CDCl₃): δ E isomer: -64.84 (s, 3F), Z isomer: -58.93 (s, 3F) ppm. HRMS *m/z* (APCI): calcd. for C₁₅H₁₈F₃O₃ [M+H]⁺ : 303.1203; found: 303.1202.

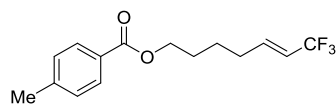


2c: 7,7,7-trifluorohept-5-en-1-yl 2-methoxybenzoate. Prepared according to the general procedure. Reaction was run using **1c** (70.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μ L, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (93:7) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.25 mmol, 76.1 mg, 84 %, *E/Z* = 92:8), *R*_f = 0.40 (hexane : EtOAc = 5 : 1). E isomer: ¹H NMR (400 MHz, CDCl₃): δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 6.97-6.94 (m, 2H), 6.40-

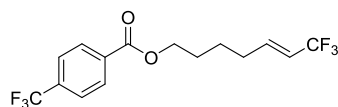
6.33 (m, 1H), 5.66-5.59 (m, 1H), 4.29 (t, $J = 6.4$ Hz, 2H), 3.86 (s, 3H), 2.28-2.15 (m, 2H), 1.79-1.72 (m, 2H), 1.62-1.55 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 166.3, 159.1, 140.2 (q, $J_{\text{C-F}} = 6.5$ Hz), 133.5, 131.5, 123.1 (q, $J_{\text{C-F}} = 270.0$ Hz), 120.2, 120.1, 118.7 (q, $J_{\text{C-F}} = 33.3$ Hz), 112.0, 64.3, 55.8, 30.9, 28.1, 24.5 ppm. ^{19}F NMR (376 MHz, CDCl_3): δ E isomer: -64.86 (s, 3F), Z isomer: -58.94 (s, 3F) ppm. HRMS m/z (APCI): calcd. for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 303.1203; found: 303.1202.



2d: 7,7,7-trifluorohept-5-en-1-yl 3-methoxybenzoate. Prepared according to the general procedure. Reaction was run using **1d** (70.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me_3SiCF_3 (180 μL , 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (93:7) was determined by ^{19}F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.20 mmol, 60.0 mg, 66 %, *E/Z* = 91:9, R_f = 0.40 (hexane : EtOAc = 5 : 1). E isomer: ^1H NMR (400 MHz, CDCl_3): δ 7.63 (d, $J = 7.6$ Hz, 2H), 7.56 (s, 1H), 7.34 (t, $J = 8.0$ Hz, 1H), 7.34 (dd, $J = 8.4$ Hz, $J = 2.0$ Hz, 1H), 6.42-6.34 (m, 1H), 5.68-5.61 (m, 1H), 4.33 (t, $J = 6.4$ Hz, 2H), 3.84 (s, 3H), 2.26-2.20 (m, 2H), 1.83-1.76 (m, 2H), 1.64-1.57 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 166.6, 159.7, 140.1 (q, $J_{\text{C-F}} = 6.5$ Hz), 131.7, 129.5, 123.1 (q, $J_{\text{C-F}} = 270.1$ Hz), 122.0, 119.4, 119.0 (q, $J_{\text{C-F}} = 33.3$ Hz), 114.3, 64.7, 55.5, 31.1, 28.2, 24.6 ppm. ^{19}F NMR (376 MHz, CDCl_3): δ E isomer: -64.85 (s, 3F), Z isomer: -58.93 (s, 3F) ppm. HRMS m/z (APCI): calcd. for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 303.1203; found: 303.1203.

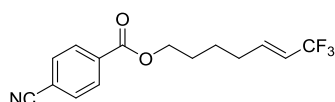


2e: 7,7,7-trifluorohept-5-en-1-yl 4-methylbenzoate. Prepared according to the general procedure. Reaction was run using **1e** (65.4 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me_3SiCF_3 (180 μL , 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (96:4) was determined by ^{19}F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.25 mmol, 70.4 mg, 82 %, *E/Z* = 93:7, R_f = 0.60 (hexane : EtOAc = 5 : 1). E isomer: ^1H NMR (400 MHz, CDCl_3): δ 7.83 (d, $J = 8.0$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 6.32-6.25 (m, 1H), 5.86-5.50 (m, 1H), 4.22 (t, $J = 6.4$ Hz, 2H), 2.30 (s, 3H), 2.12-2.10 (m, 2H), 1.73-1.66 (m, 2H), 1.54-1.47 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 166.7, 143.7, 140.2 (q, $J_{\text{C-F}} = 6.6$ Hz), 129.6, 129.2, 127.6, 123.1 (q, $J_{\text{C-F}} = 270.0$ Hz), 118.9 (q, $J_{\text{C-F}} = 33.4$ Hz), 64.3, 31.1, 28.2, 24.6, 21.7 ppm. ^{19}F NMR (376 MHz, CDCl_3): δ E isomer: -64.85 (s, 3F), Z isomer: -58.94 (s, 3F) ppm. HRMS m/z (APCI): calcd. for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 287.1253; found: 287.1253.

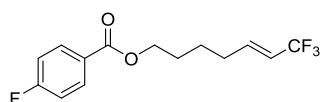


2f: 7,7,7-trifluorohept-5-en-1-yl 4-(trifluoromethyl)benzoate. Prepared according to the general procedure. Reaction was run using **1f** (81.6 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me_3SiCF_3 (180 μL , 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z*

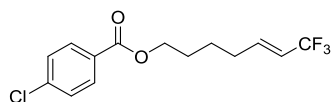
ratio (96:4) was determined by ^{19}F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.20 mmol, 69.4 mg, 68 %, E/Z = 93:7), R_f = 0.60 (hexane : EtOAc = 5 : 1). E isomer: ^1H NMR (400 MHz, CDCl_3): δ 8.14 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 6.42-6.34 (m, 1H), 5.69-5.60 (m, 1H), 4.37 (t, J = 6.4 Hz, 2H), 2.27-2.21 (m, 2H), 1.86-1.78 (m, 2H), 1.65-1.58 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 165.5, 140.0 (q, $J_{\text{C-F}}$ = 6.6 Hz), 134.6 (q, $J_{\text{C-F}}$ = 32.7 Hz), 133.6, 130.1, 125.5 (q, $J_{\text{C-F}}$ = 3.8 Hz), 123.8 (q, $J_{\text{C-F}}$ = 273.7 Hz), 123.1 (q, $J_{\text{C-F}}$ = 270.1 Hz), 119.1 (q, $J_{\text{C-F}}$ = 33.4 Hz), 65.2, 31.1, 28.2, 24.6 ppm. ^{19}F NMR (376 MHz, CDCl_3): δ E isomer: -63.98 (s, 3F), -64.86 (s, 3F), Z isomer: -63.96 (s, 3F), -58.91 (s, 3F) ppm. HRMS m/z (APCI): calcd. for $\text{C}_{15}\text{H}_{15}\text{F}_6\text{O}_2$ $[\text{M}+\text{H}]^+$: 341.0971; found: 341.0970.



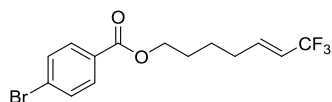
2g: 7,7,7-trifluorohept-5-en-1-yl 4-cyanobenzoate. Prepared according to the general procedure. Reaction was run using **1g** (68.7 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me_3SiCF_3 (180 μL , 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (96:4) was determined by ^{19}F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.17 mmol, 51.7 mg, 58 %, E/Z = 93:7), R_f = 0.20 (hexane : EtOAc = 8 : 1). Major isomer: ^1H NMR (400 MHz, CDCl_3): δ 8.11 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 6.40-6.33 (m, 1H), 5.67-5.60 (m, 1H), 4.35 (t, J = 6.4 Hz, 2H), 2.23-2.20 (m, 2H), 1.84-1.77 (m, 2H), 1.63-1.56 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 165.0, 139.9 (q, $J_{\text{C-F}}$ = 6.5 Hz), 134.1, 132.3, 130.1, 123.0 (q, $J_{\text{C-F}}$ = 270.1 Hz), 119.0 (q, $J_{\text{C-F}}$ = 33.4 Hz), 118.0, 116.4, 65.4, 31.0, 28.1, 24.5 ppm. ^{19}F NMR (376 MHz, CDCl_3): δ E isomer: -64.85 (s, 3F), Z isomer: -58.91 (s, 3F) ppm. The spectral data are in full accordance with the literature report.⁸



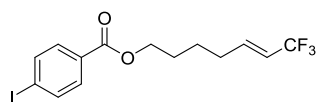
2h: 7,7,7-trifluorohept-5-en-1-yl 4-fluorobenzoate. Prepared according to the general procedure. Reaction was run using **1h** (66.6 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me_3SiCF_3 (180 μL , 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (95:5) was determined by ^{19}F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.25 mmol, 71.3 mg, 82 %, E/Z = 92:8), R_f = 0.60 (hexane : EtOAc = 5 : 1). E isomer: ^1H NMR (400 MHz, CDCl_3): δ 8.06-8.02 (m, 2H), 7.10 (t, J = 8.6 Hz, 2H), 6.40-6.35 (m, 1H), 5.68-5.59 (m, 1H), 4.32 (t, J = 6.4 Hz, 2H), 2.25-2.21 (m, 2H), 1.82-1.75 (m, 2H), 1.63-1.56 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 165.8 (d, $J_{\text{C-F}}$ = 254.7 Hz), 165.7, 140.1 (q, $J_{\text{C-F}}$ = 6.6 Hz), 132.2 (d, $J_{\text{C-F}}$ = 9.3 Hz), 126.6, 123.1 (q, $J_{\text{C-F}}$ = 270.1 Hz), 119.0 (q, $J_{\text{C-F}}$ = 33.3 Hz), 115.6 (d, $J_{\text{C-F}}$ = 22.1 Hz), 64.7, 31.1, 28.2, 24.6 ppm. ^{19}F NMR (376 MHz, CDCl_3): δ E isomer: -106.65 (s, 1F), -64.85 (s, 3F), Z isomer: -106.74 (s, 1F), -58.93 (s, 3F) ppm. HRMS m/z (APCI): calcd. for $\text{C}_{14}\text{H}_{15}\text{F}_4\text{O}_2$ $[\text{M}+\text{H}]^+$: 291.1003; found: 291.1007.



2i: 7,7,7-trifluorohept-5-en-1-yl 4-chlorobenzoate. Prepared according to the general procedure. Reaction was run using **1i** (71.4 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μ L, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (92:8) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.24 mmol, 73.4 mg, 80 %, *E/Z* = 92:8), *R*_f = 0.60 (hexane : EtOAc = 5 : 1). E isomer: **¹H NMR** (400 MHz, CDCl₃): δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 6.42-6.34 (m, 1H), 5.68-5.59 (m, 1H), 4.32 (t, *J* = 6.4 Hz, 2H), 2.26-2.20 (m, 2H), 1.83-1.74 (m, 2H), 1.63-1.56 (m, 2H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 165.8, 140.0 (q, *J*_{C-F} = 6.6 Hz), 139.5, 131.0, 128.8, 128.8, 123.1 (q, *J*_{C-F} = 270.1 Hz), 119.0 (q, *J*_{C-F} = 33.4 Hz), 64.8, 31.1, 28.2, 24.6 ppm. **¹⁹F NMR** (376 MHz, CDCl₃): δ E isomer: -64.85 (s, 3F), Z isomer: -58.92 (s, 3F) ppm. **HRMS** *m/z* (APCI): calcd. for C₁₄H₁₅ClF₃O₂ [M+H]⁺ : 307.0707; found: 307.0707.

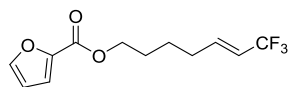


2j: 7,7,7-trifluorohept-5-en-1-yl 4-bromobenzoate. Prepared according to the general procedure. Reaction was run using **1j** (84.6 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μ L, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (95:5) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.26 mmol, 90.3 mg, 86 %, *E/Z* = 92:8), *R*_f = 0.60 (hexane : EtOAc = 5 : 1). E isomer: **¹H NMR** (400 MHz, CDCl₃): δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 6.41-6.33 (m, 1H), 5.67-5.59 (m, 1H), 4.31 (t, *J* = 6.4 Hz, 2H), 2.23-2.21 (m, 2H), 1.82-1.75 (m, 2H), 1.62-1.55 (m, 2H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 165.9, 140.0 (q, *J*_{C-F} = 6.6 Hz), 131.8, 131.1, 129.3, 128.1, 123.1 (q, *J*_{C-F} = 270.2 Hz), 119.0 (q, *J*_{C-F} = 33.4 Hz), 64.8, 31.1, 28.2, 24.6 ppm. **¹⁹F NMR** (376 MHz, CDCl₃): δ E isomer: -64.86 (s, 3F), Z isomer: -58.93 (s, 3F) ppm. **HRMS** *m/z* (APCI): calcd. for C₁₄H₁₅BrF₃O₂ [M+H]⁺ : 351.0202; found: 351.0209.

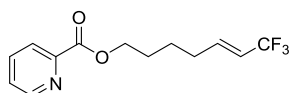


2k: 7,7,7-trifluorohept-5-en-1-yl 4-iodobenzoate. Prepared according to the general procedure. Reaction was run using **1k** (99.0 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μ L, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (93:7) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.25 mmol, 99.1 mg, 83 %, *E/Z* = 92:8), *R*_f = 0.60 (hexane : EtOAc = 5 : 1). E isomer: **¹H NMR** (400 MHz, CDCl₃): δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H), 6.41-6.33 (m, 1H), 5.67-5.59 (m, 1H), 4.31 (t, *J* = 6.4 Hz, 2H), 2.24-2.19 (m, 2H), 1.82-1.75 (m, 2H), 1.62-1.55 (m, 2H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 166.1, 140.0 (q, *J*_{C-F} = 6.5 Hz), 137.8, 131.1, 129.8, 123.1 (q, *J*_{C-F} = 270.1 Hz), 119.0 (q, *J*_{C-F} = 33.3 Hz), 100.8, 64.8, 31.1, 28.2, 24.6 ppm. **¹⁹F NMR** (376 MHz, CDCl₃): δ

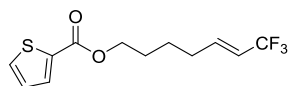
E isomer: -64.85 (s, 3F), Z isomer: -58.92 (s, 3F) ppm. **HRMS** *m/z* (APCI): calcd. for C₁₄H₁₅F₃IO₂ [M+H]⁺: 399.0063; found: 399.0067.



2l: 7,7,7-trifluorohept-5-en-1-yl furan-2-carboxylate. Prepared according to the general procedure. Reaction was run using **1l** (58.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μ L, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (93:7) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.13 mmol, 33.0 mg, 42 %, *E/Z* = 92:8), *R*_f = 0.70 (hexane : EtOAc = 5 : 1). E isomer: **¹H NMR** (400 MHz, CDCl₃): δ 7.56 (s, 1H), 7.16 (d, *J* = 3.2 Hz, 1H), 7.72 (dd, *J* = 2.0 Hz, 1H), 6.40-6.32 (m, 1H), 5.67-5.58 (m, 1H), 4.30 (t, *J* = 6.4 Hz, 2H), 2.24-2.18 (m, 2H), 1.80-1.73 (m, 2H), 1.61-1.53 (m, 2H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 158.8, 146.4, 144.8, 140.1 (q, *J*_{C-F} = 6.6 Hz), 123.1 (q, *J*_{C-F} = 270.1 Hz), 119.0 (q, *J*_{C-F} = 33.4 Hz), 118.0, 111.9, 64.5, 31.0, 28.2, 24.5 ppm. **¹⁹F NMR** (376 MHz, CDCl₃): δ E isomer: -64.86 (s, 3F), Z isomer: -58.94 (s, 3F) ppm. The spectral data are in full accordance with the literature report.⁹



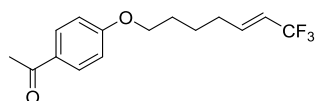
2m: 7,7,7-trifluorohept-5-en-1-yl picolinate. Prepared according to the general procedure. Reaction was run using **1m** (61.5 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μ L, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (93:7) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.14 mmol, 37.7 mg, 46 %, *E/Z* = 93:7), *R*_f = 0.30 (hexane : EtOAc = 2 : 1). E isomer: **¹H NMR** (400 MHz, CDCl₃): δ 8.72 (d, *J* = 4.0 Hz, 1H), 8.08 (d, *J* = 7.6 Hz, 1H), 7.81 (t, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 6.2 Hz, 1H), 6.37-6.29 (m, 1H), 5.64-5.57 (m, 1H), 4.39 (t, *J* = 6.6 Hz, 2H), 2.18-2.15 (m, 2H), 1.85-1.78 (m, 2H), 1.60-1.53 (m, 2H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 165.3, 149.9, 148.1, 140.0 (q, *J*_{C-F} = 6.5 Hz), 137.1, 127.0, 125.2, 123.0 (q, *J*_{C-F} = 270.2 Hz), 118.9 (q, *J*_{C-F} = 33.4 Hz), 65.5, 31.0, 28.1, 24.4 ppm. **¹⁹F NMR** (376 MHz, CDCl₃): δ E isomer: -64.84 (s, 3F), Z isomer: -58.92 (s, 3F) ppm. **HRMS** *m/z* (APCI): calcd. for C₁₃H₁₅F₃NO₂ [M+H]⁺: 274.1049; found: 274.1047.



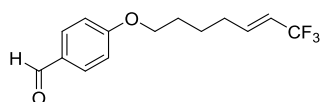
2n: 7,7,7-trifluorohept-5-en-1-yl thiophene-2-carboxylate. Prepared according to the general procedure. Reaction was run using **1n** (63.0 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μ L, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (93:7) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.25 mmol, 68.4 mg, 82 %, *E/Z* = 91:9), *R*_f = 0.60 (hexane : EtOAc = 5 : 1). E

⁹ Parsons, A. T.; Senecal, T. D.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2012**, *51*, 2947.

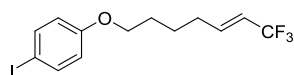
isomer: **¹H NMR** (400 MHz, CDCl₃): δ 7.80 (dd, *J* = 3.6 Hz, *J* = 1.2 Hz, 1H), 7.56 (dd, *J* = 4.8 Hz, *J* = 1.2 Hz, 1H), 7.11 (t, *J* = 4.4 Hz, 1H), 6.42-6.35 (m, 1H), 5.69-5.60 (m, 1H), 4.31 (t, *J* = 6.4 Hz, 2H), 2.24-2.21 (m, 2H), 1.82-1.75 (m, 2H), 1.64-1.56 (m, 2H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 162.3, 140.1 (q, *J*_{C-F} = 6.6 Hz), 133.9, 133.5, 132.4, 127.8, 123.1 (q, *J*_{C-F} = 270.2 Hz), 118.9 (q, *J*_{C-F} = 33.3 Hz), 64.7, 31.0, 28.2, 24.5 ppm. **¹⁹F NMR** (376 MHz, CDCl₃): δ E isomer: -64.85 (s, 3F), Z isomer: -58.93 (s, 3F) ppm. **HRMS** *m/z* (APCI): calcd. for C₁₂H₁₄F₃O₂S [M+H]⁺: 279.0661; found: 279.0664.



2o: 1-(4-((7,7,7-trifluorohept-5-en-1-yl)oxy)phenyl)ethan-1-one. Prepared according to the general procedure. Reaction was run using **1o** (65.4 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (75.2 mg, 0.45 mmol), Me₃SiCF₃ (180 μL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (92:8) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.20 mmol, 57.5 mg, 67 %, *E/Z* = 93:7), *R*_f = 0.30 (hexane : EtOAc = 5 : 1). E isomer: **¹H NMR** (500 MHz, CDCl₃): δ 7.92 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.41-6.39 (m, 1H), 5.67-5.63 (m, 1H), 4.03 (t, *J* = 6.0 Hz, 2H), 2.55 (s, 3H), 2.26-2.23 (m, 2H), 1.85-1.81 (m, 2H), 1.68-1.64 (m, 2H) ppm. **¹³C NMR** (126 MHz, CDCl₃): δ 196.9, 163.0, 140.2 (q, *J*_{C-F} = 6.4 Hz), 130.7, 130.4, 123.1 (q, *J*_{C-F} = 269.6 Hz), 119.0 (q, *J*_{C-F} = 33.3 Hz), 114.2, 67.8, 31.2, 28.6, 26.5, 24.7 ppm. **¹⁹F NMR** (470 MHz, CDCl₃): δ E isomer: -64.84 (m, 3F), Z isomer: -58.91 (d, *J* = 8.5, 3F) ppm. **HRMS** *m/z* (APCI): calcd. for C₁₅H₁₈F₃O₂ [M+H]⁺: 287.1253; found: 287.1254.

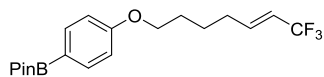


2p: 4-((7,7,7-trifluorohept-5-en-1-yl)oxy)benzaldehyde. Prepared according to the general procedure. Reaction was run using **1p** (61.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (75.2 mg, 0.45 mmol), Me₃SiCF₃ (180 μL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (93:7) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.18 mmol, 49.0 mg, 60 %, *E/Z* = 92:8), *R*_f = 0.30 (hexane : EtOAc = 5 : 1). E isomer: **¹H NMR** (400 MHz, CDCl₃): δ 9.86 (s, 1H), 7.81 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.42-6.35 (m, 1H), 5.68-5.60 (m, 1H), 4.04 (t, *J* = 6.2 Hz, 2H), 2.30-2.23 (m, 2H), 1.87-1.80 (m, 2H), 1.68-1.60 (m, 2H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 190.9, 164.1, 140.1 (q, *J*_{C-F} = 6.6 Hz), 132.1, 130.0, 123.1 (q, *J*_{C-F} = 270.1 Hz), 118.9 (q, *J*_{C-F} = 33.3 Hz), 114.8, 67.9, 31.1, 28.5, 24.6 ppm. **¹⁹F NMR** (376 MHz, CDCl₃): δ E isomer: -64.84 (s, 3F), Z isomer: -58.90 (s, 3F) ppm. **HRMS** *m/z* (APCI): calcd. for C₁₄H₁₆F₃O₂ [M+H]⁺: 273.1097; found: 273.1097.



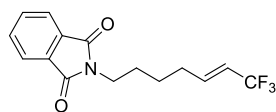
2q: 1-iodo-4-((7,7,7-trifluorohept-5-en-1-yl)oxy)benzene. Prepared according to the general procedure. Reaction was run using **1q** (90.6 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (94:6) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a

colorless oil (0.26 mmol, 96.6 mg, 87 %, *E/Z* = 92:8), *R*_f = 0.60 (hexane : EtOAc = 5 : 1). E isomer: ¹H NMR (400 MHz, CDCl₃): δ 7.55 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.45-6.37 (m, 1H), 5.70-5.61 (m, 1H), 3.93 (t, *J* = 6.2 Hz, 2H), 2.26-2.21 (m, 2H), 1.84-1.77 (m, 2H), 1.67-1.58 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 158.9, 140.3 (q, *J*_{C-F} = 6.6 Hz), 138.3, 123.1 (q, *J*_{C-F} = 270.1 Hz), 118.9 (q, *J*_{C-F} = 33.3 Hz), 117.0, 82.7, 67.6, 31.2, 28.6, 24.6 ppm. ¹⁹F NMR (376 MHz, CDCl₃): δ E isomer: -64.83 (s, 3F), Z isomer: -58.92 (s, 3F) ppm. HRMS *m/z* (APCI): calcd. for C₁₃H₁₄F₃IO [M]⁺ : 370.0036; found: 370.0034.

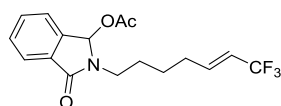


2r: 4,4,5,5-tetramethyl-2-(4-((7,7,7-trifluorohept-5-en-1-yl)oxy)phenyl)-1,3,2-dioxaborolane.

Prepared according to the general procedure. Reaction was run using **1r** (90.6 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (96:4) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by preparative TLC (hexane/EtOAc) and obtained a colorless oil (0.17 mmol, 61.05 mg, 55 %, *E/Z* = 93:7), *R*_f = 0.30 (hexane : EtOAc = 10 : 1). E isomer: ¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.44-6.36 (m, 1H), 5.68-5.60 (m, 1H), 4.00 (t, *J* = 6.2 Hz, 2H), 2.26-2.21 (m, 2H), 1.85-1.78 (m, 2H), 1.68-1.61 (m, 2H), 1.34 (s, 12H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 161.6, 140.3 (q, *J*_{C-F} = 6.5 Hz), 136.7, 123.2 (q, *J*_{C-F} = 270.1 Hz), 118.9 (q, *J*_{C-F} = 33.4 Hz), 113.9, 83.7, 67.3, 31.2, 28.7, 25.0, 24.7 ppm. ¹⁹F NMR (376 MHz, CDCl₃): δ E isomer: -64.84 (s, 3F), Z isomer: -58.93 (s, 3F) ppm. HRMS *m/z* (APCI): calcd. for C₁₉H₂₇BF₃O₃ [M+H]⁺ : 371.2003; found: 371.2003.

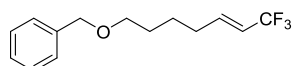


2s: 2-(7,7,7-trifluorohept-5-en-1-yl)isoindoline-1,3-dione. Prepared according to the general procedure. Reaction was run using **1q** (68.7 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (93:7) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.13 mmol, 38.4 mg, 43 %, *E/Z* = 93:7), *R*_f = 0.40 (hexane : EtOAc = 5 : 1). E isomer: ¹H NMR (500 MHz, CDCl₃): δ 7.83-7.82 (m, 2H), 7.71-7.69 (m, 2H), 6.36-6.31 (m, 1H), 5.62-5.58 (m, 1H), 3.69 (t, *J* = 7.0 Hz, 2H), 2.20-2.18 (m, 2H), 1.73-1.67 (m, 2H), 1.51-1.47 (m, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ 168.5, 140.0 (q, *J*_{C-F} = 6.6 Hz), 134.1, 132.2, 123.3 123.2 (q, *J*_{C-F} = 269.8 Hz), 118.9 (q, *J*_{C-F} = 33.3 Hz), 37.6, 31.0, 28.1, 25.3 ppm. ¹⁹F NMR (470 MHz, CDCl₃): δ E isomer: -64.84 (m, 3F), Z isomer: -58.91 (d, *J* = 8.5, 3F) ppm. The spectral data are in full accordance with the literature report.⁷

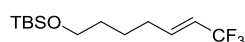


2t: 3-oxo-2-(7,7,7-trifluorohept-5-en-1-yl)isoindolin-1-yl acetate. Prepared according to the general procedure. Reaction was run using **1t** (81.9 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (94:6) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal

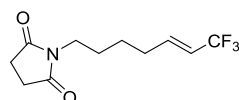
standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.22 mmol, 75.7 mg, 74 %, *E/Z* = 92:8), *R*_f = 0.30 (hexane : EtOAc = 5 : 1). E isomer: **¹H NMR** (400 MHz, CDCl₃): δ 7.79-7.77 (m, 1H), 7.56-7.49 (m, 3H), 6.98 (s, 1H), 6.36-6.29 (m, 1H), 5.64-5.55 (m, 1H), 3.76-3.68 (m, 1H), 3.33-3.26 (m, 1H), 2.20-2.17 (m, 2H), 2.14 (s, 3H), 1.71-1.60 (m, 2H), 1.53-1.44 (m, 2H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 171.2, 168.0, 140.9, 140.1 (q, *J*_{C-F} = 6.6 Hz), 132.5, 132.0, 130.4, 123.9, 123.6, 123.1 (q, *J*_{C-F} = 270.1 Hz), 118.9 (q, *J*_{C-F} = 33.3 Hz), 81.2, 40.0, 31.0, 27.8, 25.2, 21.1 ppm. **¹⁹F NMR** (376 MHz, CDCl₃): δ E isomer: -64.82 (s, 3F), Z isomer: -58.87 (s, 3F) ppm. **HRMS** *m/z* (APCI): calcd. for C₁₇H₁₉F₃NO₃ [M+H]⁺: 342.1312; found: 342.1317.



2u: ((7,7,7-trifluorohept-5-en-1-yl)oxy)methylbenzene. Prepared according to the general procedure. Reaction was run using **1u** (57.0 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (94:6) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.19 mmol, 49.5 mg, 64 %, *E/Z* = 92:8), *R*_f = 0.60 (hexane : EtOAc = 8 : 1). E isomer: **¹H NMR** (400 MHz, CDCl₃): δ 7.39-7.26 (m, 5H), 6.43-6.35 (m, 1H), 5.67-5.58 (m, 1H), 4.52 (s, 2H), 3.50 (t, *J* = 6.2 Hz, 2H), 2.22-2.15 (m, 2H), 1.70-1.63 (m, 2H), 1.60-1.54 (m, 2H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 140.6 (q, *J*_{C-F} = 6.6 Hz), 138.6, 128.5, 127.8, 127.7, 123.2 (q, *J*_{C-F} = 270.0 Hz), 118.7 (q, *J*_{C-F} = 33.2 Hz), 73.1, 70.0, 31.3, 29.3, 24.8 ppm. **¹⁹F NMR** (376 MHz, CDCl₃): δ E isomer: -64.83 (s, 3F), Z isomer: -58.94 (s, 3F) ppm. The spectral data are in full accordance with the literature report.¹⁰

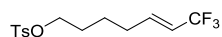


2v: tert-butyldimethyl((7,7,7-trifluorohept-5-en-1-yl)oxy)silane. Prepared according to the general procedure. Reaction was run using **1v** (64.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (92:8) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.19 mmol, 52.3 mg, 62 %, *E/Z* = 93:7), *R*_f = 0.30 (hexane). E isomer: **¹H NMR** (400 MHz, CDCl₃): δ 6.41-6.34 (m, 1H), 5.65-5.57 (m, 1H), 3.62 (t, *J* = 6.0 Hz, 2H), 2.19-2.17 (m, 2H), 1.54-1.49 (m, 2H), 0.90 (s, 9H), 0.05 (s, 6H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 140.7 (q, *J*_{C-F} = 6.6 Hz), 123.3 (q, *J*_{C-F} = 270.0 Hz), 118.6 (q, *J*_{C-F} = 33.3 Hz), 62.9, 32.2, 31.4, 26.1, 24.5, 18.5, -5.2 ppm. **¹⁹F NMR** (376 MHz, CDCl₃): δ E isomer: -64.85 (s, 3F), Z isomer: -58.98 (s, 3F) ppm. The spectral data are in full accordance with the literature report.⁷

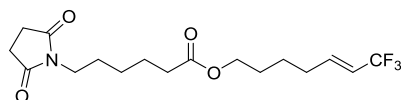


2w: 1-(7,7,7-trifluorohept-5-en-1-yl)pyrrolidine-2,5-dione. Prepared according to the general procedure. Reaction was run using **1w** (76.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (92:8) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and

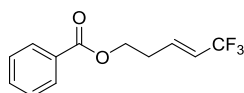
obtained a colorless oil (0.18 mmol, 44.8 mg, 60 %, $E/Z = 93:7$), $R_f = 0.30$ (hexane : EtOAc = 2 : 1). E isomer: $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.35-6.27 (m, 1H), 5.63-5.54 (m, 1H), 3.48 (t, $J = 7.2$ Hz, 2H), 2.68 (s, 4H), 2.17-2.14 (m, 2H), 1.60-1.53 (m, 2H), 1.45-1.36 (m, 2H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 177.4, 140.0 (q, $J_{\text{C-F}} = 6.6$ Hz), 123.0 (q, $J_{\text{C-F}} = 270.2$ Hz), 118.9 (q, $J_{\text{C-F}} = 33.4$ Hz), 38.4, 30.9, 28.2, 27.2, 25.2 ppm. $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ E isomer: -64.84 (s, 3F), Z isomer: -58.90 (s, 3F) ppm. **HRMS** m/z (APCI): calcd. for $\text{C}_{11}\text{H}_{15}\text{F}_3\text{NO}_2$ $[\text{M}+\text{H}]^+$: 250.1049; found: 250.1046.



2w': (E)-7,7,7-trifluorohept-5-en-1-yl 4-methylbenzenesulfonate. Prepared according to the general procedure. Reaction was run using **1w** (76.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me_3SiCF_3 (180 μL , 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (91:9) was determined by $^{19}\text{F NMR}$ of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.045 mmol, 14.5 mg, 15 %, $E/Z = 90:10$), $R_f = 0.40$ (hexane : EtOAc = 8 : 1). E isomer: $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.78 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 6.32-6.24 (m, 1H), 5.60-5.53 (m, 1H), 4.03 (t, $J = 6.2$ Hz, 2H), 2.44 (s, 3H), 2.13-2.08 (m, 2H), 1.69-1.62 (m, 2H), 1.51-1.43 (m, 2H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 145.0, 139.7 (q, $J_{\text{C-F}} = 6.6$ Hz), 133.1, 130.0, 128.0, 123.0 (q, $J_{\text{C-F}} = 270.1$ Hz), 119.1 (q, $J_{\text{C-F}} = 33.4$ Hz), 70.1, 30.7, 28.3, 24.0, 21.7 ppm. $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ E isomer: -64.90 (s, 3F), Z isomer: -58.95 (s, 3F) ppm. The spectral data are in full accordance with the literature report.¹¹



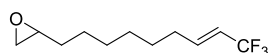
2x: 7,7,7-trifluorohept-5-en-1-yl 6-(2,5-dioxopyrrolidin-1-yl)hexanoate. Prepared according to the general procedure. Reaction was run using **1x** (82.8 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me_3SiCF_3 (180 μL , 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (91:9) was determined by $^{19}\text{F NMR}$ of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.23 mmol, 85.0 mg, 78 %, $E/Z = 92:8$), $R_f = 0.30$ (hexane : EtOAc = 2 : 1). E isomer: $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.33-6.26 (m, 1H), 5.59-5.53 (m, 1H), 3.99 (t, $J = 6.6$ Hz, 2H), 3.41 (t, $J = 7.4$ Hz, 2H), 2.62 (s, 4H), 2.22 (t, $J = 7.4$ Hz, 2H), 2.15-2.12 (m, 2H), 1.60-1.42 (m, 8H), 1.28-1.22 (m, 2H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 177.3, 173.4, 140.1 (q, $J_{\text{C-F}} = 6.5$ Hz), 123.0 (q, $J_{\text{C-F}} = 270.1$ Hz), 118.7 (q, $J_{\text{C-F}} = 33.4$ Hz), 63.8, 38.5, 33.9, 30.9, 28.1, 28.1, 28.0, 27.3, 26.3, 24.4 ppm. $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ E isomer: -64.85 (s, 3F), Z isomer: -58.94 (s, 3F) ppm. **HRMS** m/z (APCI): calcd. for $\text{C}_{17}\text{H}_{24}\text{F}_3\text{NO}_4$ $[\text{M}+\text{H}]^+$: 364.1730; found: 364.1735.



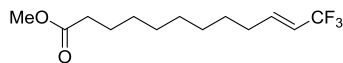
2y: 5,5,5-trifluoropent-3-en-1-yl benzoate. Prepared according to the general procedure. Reaction was run using **1y** (52.8 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me_3SiCF_3 (180 μL , 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (90:10) was determined by $^{19}\text{F NMR}$ of the crude mixture with benzotrifluoride as the internal standard. The product

11 Xu, J.; Fu, Y.; Luo, D.-F.; Jiang, Y.-Y.; Xiao, B.; Liu, Z.-J.; Gong, T.-J.; Liu, L. *J. Am. Chem. Soc.* **2011**, *133*, 15300.

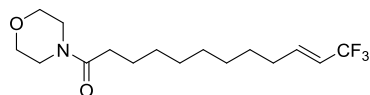
was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.19 mmol, 46.8 mg, 64 %, *E/Z* = 90:10), R_f = 0.40 (hexane : EtOAc = 8 : 1). E isomer: **¹H NMR** (400 MHz, CDCl₃): δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 6.50-6.42 (m, 1H), 5.83-5.74 (m, 1H), 4.43 (t, *J* = 6.4 Hz, 2H), 2.67-2.61 (m, 2H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 166.5, 136.3 (q, J_{C-F} = 6.7 Hz), 133.3, 129.7, 128.6, 128.5, 125.5 (q, J_{C-F} = 270.3 Hz), 121.1 (q, J_{C-F} = 33.7 Hz), 62.7, 31.1 ppm. **¹⁹F NMR** (376 MHz, CDCl₃): δ E isomer: -65.23 (s, 3F), Z isomer: -59.18 (s, 3F) ppm. **HRMS** *m/z* (APCI): calcd. for C₁₂H₁₂F₃O₂ [M+H]⁺ : 245.0784; found: 245.0781.



2z: 2-(9,9,9-trifluoronon-7-en-1-yl)oxirane. Prepared according to the general procedure. Reaction was run using **1z** (46.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μL, 1.2 mol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (93:7) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.22 mmol, 48.0 mg, 72 %, *E/Z* = 93:7), R_f = 0.70 (hexane : EtOAc = 5 : 1). E isomer: **¹H NMR** (400 MHz, CDCl₃): δ 6.40-6.31 (m, 1H), 5.63-5.54 (m, 1H), 2.90-2.86 (m, 1H), 2.72 (t, *J* = 4.6 Hz, 1H), 2.45-2.43 (m, 1H), 2.14-2.10 (m, 2H), 1.53-1.39 (m, 6H), 1.36-1.31 (m, 4H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 140.8 (q, J_{C-F} = 6.6 Hz), 123.2 (q, J_{C-F} = 270.1 Hz), 118.4 (q, J_{C-F} = 33.2 Hz), 52.4, 47.1, 32.5, 31.5, 29.2, 29.0, 27.9, 26.0 ppm. **¹⁹F NMR** (376 MHz, CDCl₃): δ E isomer: -64.88 (s, 3F), Z isomer: -58.99 (s, 3F) ppm. The spectral data are in full accordance with the literature report.¹²

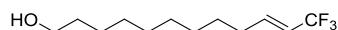


2aa: methyl-12,12,12-trifluorododec-10-enoate. Prepared according to the general procedure. Reaction was run using **1aa** (59.4 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μL, 1.2 mol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (94:6) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.23 mmol, 60.6 mg, 76 %, *E/Z* = 92:8), R_f = 0.70 (hexane : EtOAc = 5 : 1). E isomer: **¹H NMR** (400 MHz, CDCl₃): δ 6.40-6.32 (m, 1H), 5.63-5.56 (m, 1H), 3.66 (s, 3H), 2.30 (t, *J* = 7.6 Hz, 2H), 2.15-2.12 (m, 2H), 1.63-1.59 (m, 2H), 1.44-1.40 (m, 2H), 1.33-1.25 (m, 8H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 174.4, 140.9 (q, J_{C-F} = 6.6 Hz), 123.3 (q, J_{C-F} = 270.0 Hz), 118.4 (q, J_{C-F} = 33.2 Hz), 51.6, 34.2, 31.5, 29.3, 29.2, 29.2, 29.1, 28.0, 25.0 ppm. **¹⁹F NMR** (376 MHz, CDCl₃): δ E isomer: -64.82 (s, 3F), Z isomer: -58.96 (s, 3F) ppm. **HRMS** *m/z* (APCI): calcd. for C₁₃H₂₂F₃O₂ [M+H]⁺ : 267.1566; found: 267.1570.

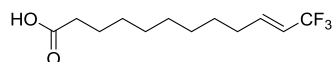


2ab: 12,12,12-trifluoro-1-morpholinododec-10-en-1-one. Prepared according to the general procedure. Reaction was run using **1ab** (75.9 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μL, 1.2 mol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (92:8) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard.

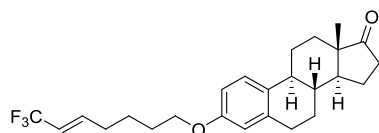
The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.20 mmol, 64.5 mg, 67 %, *E/Z* = 92:8), R_f = 0.30 (hexane : EtOAc = 1 : 1). E isomer: **¹H NMR** (500 MHz, CDCl₃): δ 6.36-6.31 (m, 1H), 5.59-5.54 (m, 1H), 3.66-3.62 (m, 4H), 3.59-3.57 (m, 2H), 3.45-3.40 (m, 2H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.14-2.10 (m, 2H), 1.63-1.59 (m, 2H), 1.44-1.38 (m, 2H), 1.33-1.21 (m, 8H) ppm. **¹³C NMR** (126 MHz, CDCl₃): δ 171.9, 140.9 (q, J_{C-F} = 6.6 Hz), 123.2 (q, J_{C-F} = 269.5 Hz), 118.3 (q, J_{C-F} = 33.1 Hz), 67.0, 66.7, 46.1, 41.9, 33.1, 31.5, 29.4, 29.3, 29.2, 29.0, 28.0, 25.2 ppm. **¹⁹F NMR** (470 MHz, CDCl₃): δ E isomer: -64.80 (m, 3F), Z isomer: -58.95 (d, *J* = 8.5, 3F) ppm. **HRMS** *m/z* (APCI): calcd. for C₁₆H₂₇F₃NO₂ [M+H]⁺ : 322.1988; found: 322.1983.



2ac: 12,12,12-trifluorododec-10-en-1-ol. Prepared according to the general procedure. Reaction was run using **1ac** (51.0 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μL, 1.2 mol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (92:8) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.24 mmol, 57.0 mg, 80 %, *E/Z* = 92:8), R_f = 0.40 (hexane : EtOAc = 2 : 1). E isomer: **¹H NMR** (400 MHz, CDCl₃): δ 6.39-6.31 (m, 1H), 5.62-5.53 (m, 1H), 3.61 (t, *J* = 6.6 Hz, 2H), 2.14-2.10 (m, 2H), 1.79 (s, 1H), 1.58-1.51 (m, 2H), 1.43-1.37 (m, 2H), 1.34-1.24 (m, 10H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 140.9 (q, J_{C-F} = 6.6 Hz), 123.2 (q, J_{C-F} = 269.9 Hz), 118.4 (q, J_{C-F} = 33.2 Hz), 63.1, 32.8, 31.5, 29.6, 29.5, 29.4, 29.1, 28.0, 25.8 ppm. **¹⁹F NMR** (376 MHz, CDCl₃): δ E isomer: -64.81 (s, 3F), Z isomer: -58.95 (s, 3F) ppm. The spectral data are in full accordance with the literature report.¹³



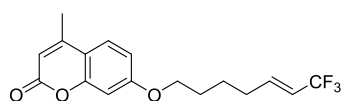
2ad: 12,12,12-trifluorododec-10-enoic acid. Prepared according to the general procedure. Reaction was run using **1ad** (55.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me₃SiCF₃ (180 μL, 1.2 mol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (92:8) was determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.21 mmol, 53.7 mg, 71 %, *E/Z* = 92:8), R_f = 0.40 (hexane : EtOAc = 2 : 1). E isomer: **¹H NMR** (500 MHz, CDCl₃): δ 6.40-6.34 (m, 1H), 5.63-5.56 (m, 1H), 2.35 (t, *J* = 7.5 Hz, 2H), 2.14-2.12 (m, 2H), 1.66-1.60 (m, 2H), 1.45-1.40 (m, 2H), 1.39-1.26 (m, 8H) ppm. **¹³C NMR** (126 MHz, CDCl₃): δ 180.5, 140.9 (q, J_{C-F} = 6.6 Hz), 123.3 (q, J_{C-F} = 269.4 Hz), 118.5 (q, J_{C-F} = 33.3 Hz), 34.2, 31.6, 29.3, 29.2, 29.1, 29.0, 28.0, 24.7 ppm. **¹⁹F NMR** (470 MHz, CDCl₃): δ E isomer: -64.81 (m, 3F), Z isomer: -58.90 (d, *J* = 8.5, 3F) ppm. **HRMS** *m/z* (APCI): calcd. for C₁₂H₂₀F₃O₂ [M+H]⁺ : 253.1410; found: 253.1409.



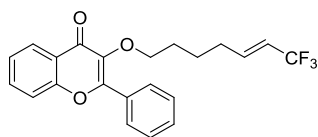
2ae: (8R,9S,13S,14S)-13-methyl-3-((7,7,7-trifluorohept-5-en-1-yl)oxy)6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one. Prepared according to the general procedure. Reaction was run using **1ae** (105.6 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (75.2 mg, 0.45 mmol), Me₃SiCF₃ (180 μL, 1.2 mol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio

¹³ Wu, X.; Chu, L.; Qing, F.-L. *Angew. Chem., Int. Ed.* **2013**, *52*, 2198.

(94:6) was determined by ^{19}F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.14 mmol, 58.0 mg, 46 %, $E/Z = 92:8$, 51.0 mg **1ae** was recovered, 94 % brsm yield), $R_f = 0.30$ (hexane : EtOAc = 8 : 1). E isomer: ^1H NMR (500 MHz, CDCl_3): δ 7.20 (d, $J = 8.5$ Hz, 1H), 6.71 (d, $J = 8.0$ Hz, 1H), 6.65 (s, 1H), 6.42-6.39 (m, 1H), 5.67-5.62 (m, 1H), 3.96 (t, $J = 6.0$ Hz, 2H), 2.92-2.89 (m, 2H), 2.51 (dd, $J = 9.3$ Hz, 2H), 2.41-2.38 (m, 1H), 2.30-2.21 (m, 2H), 2.18-2.11 (m, 1H), 2.09-2.00 (m, 2H), 1.96 (d, $J = 10.5$ Hz, 1H), 1.83-1.78 (m, 2H), 1.68-1.56 (m, 4H), 1.54-1.40 (m, 4H), 0.91 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 221.0, 157.0, 140.4 (q, $J_{\text{C-F}} = 6.6$ Hz), 137.8, 132.1, 126.4, 123.1 (q, $J_{\text{C-F}} = 270.3$ Hz), 118.8 (q, $J_{\text{C-F}} = 33.2$ Hz), 114.6, 112.1, 67.4, 50.5, 48.1, 44.1, 38.4, 35.9, 31.7, 31.2, 29.7, 28.7, 26.6, 26.0, 24.7, 21.7, 13.9 ppm. ^{19}F NMR (470 MHz, CDCl_3): δ E isomer: -64.84 (m, 3F), Z isomer: -58.95 (d, $J = 8.5$, 3F) ppm. HRMS m/z (APCI): calcd. for $\text{C}_{25}\text{H}_{32}\text{F}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 421.2349; found: 421.2347.

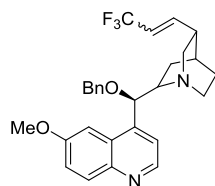


2af: 4-methyl-7-((7,7,7-trifluorohept-5-en-1-yl)oxy)-2H-chromen-2-one. Prepared according to the general procedure. Reaction was run using **1af** (77.4 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (75.2 mg, 0.45 mmol), Me_3SiCF_3 (180 μL , 1.2 mol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (93:7) was determined by ^{19}F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.21 mmol, 68.5 mg, 70 %, $E/Z = 94:6$), $R_f = 0.30$ (hexane : EtOAc = 5 : 1). E isomer: ^1H NMR (500 MHz, CDCl_3): δ 7.45 (d, $J = 8.5$ Hz, 1H), 6.81 (d, $J = 8.5$ Hz, 1H), 6.74 (s, 1H), 6.39-6.36 (m, 1H), 6.08 (s, 1H), 5.67-5.61 (m, 1H), 3.99 (t, $J = 6.3$ Hz, 2H), 2.35 (s, 3H), 2.25-2.20 (m, 2H), 1.85-1.79 (m, 2H), 1.66-1.60 (m, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ 162.0, 161.3, 155.3, 152.7, 140.1 (q, $J_{\text{C-F}} = 6.6$ Hz), 125.6, 123.1 (q, $J_{\text{C-F}} = 269.5$ Hz), 118.9 (q, $J_{\text{C-F}} = 33.3$ Hz), 113.6, 112.6, 111.9, 101.3, 68.1, 31.1, 28.4, 24.5, 18.7 (q, $J_{\text{C-F}} = 2.4$ Hz) ppm. ^{19}F NMR (376 MHz, CDCl_3): δ E isomer: -64.84 (s, 3F), Z isomer: -58.91 (s, 3F) ppm. HRMS m/z (APCI): calcd. for $\text{C}_{17}\text{H}_{18}\text{F}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 327.1201; found: 327.1203.



2ag: 4-methyl-7-((7,7,7-trifluorohept-5-en-1-yl)oxy)-2H-chromen-2-one. Prepared according to the general procedure. Reaction was run using **1ag** (96.0 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (75.2 mg, 0.45 mmol), Me_3SiCF_3 (180 μL , 1.2 mol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (93:7) was determined by ^{19}F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.28 mmol, 107.1 mg, 92%, $E/Z = 92:8$), $R_f = 0.60$ (hexane : EtOAc = 5 : 1). E isomer: ^1H NMR (400 MHz, CDCl_3): δ 8.23 (d, $J = 8.0$ Hz, 1H), 8.06-8.03 (m, 2H), 7.63 (t, $J = 7.8$ Hz, 1H), 7.50-7.47 (m, 4H), 7.35 (t, $J = 7.4$ Hz, 1H), 6.33-6.25 (m, 1H), 5.58-5.49 (m, 1H), 4.04 (t, $J = 6.2$ Hz, 2H), 2.13-2.07 (m, 2H), 1.72-1.65 (m, 2H), 1.54-1.47 (m, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ 175.2, 156.0, 155.3, 140.5, 140.4 (q, $J_{\text{C-F}} = 6.4$ Hz), 133.5, 131.0, 130.7, 128.7, 128.4, 125.8, 124.7, 124.2, 123.1 (q, $J_{\text{C-F}} = 269.5$ Hz), 118.5 (q, $J_{\text{C-F}} = 33.3$ Hz), 118.0, 72.1, 30.9, 29.3, 24.3 ppm. ^{19}F NMR

(376 MHz, CDCl₃): δ E isomer: -64.82 (s, 3F), Z isomer: -58.94 (s, 3F) ppm. **HRMS** m/z (APCI): calcd. for C₂₂H₂₀F₃O₃ [M+H]⁺ : 389.1357; found: 389.1359.

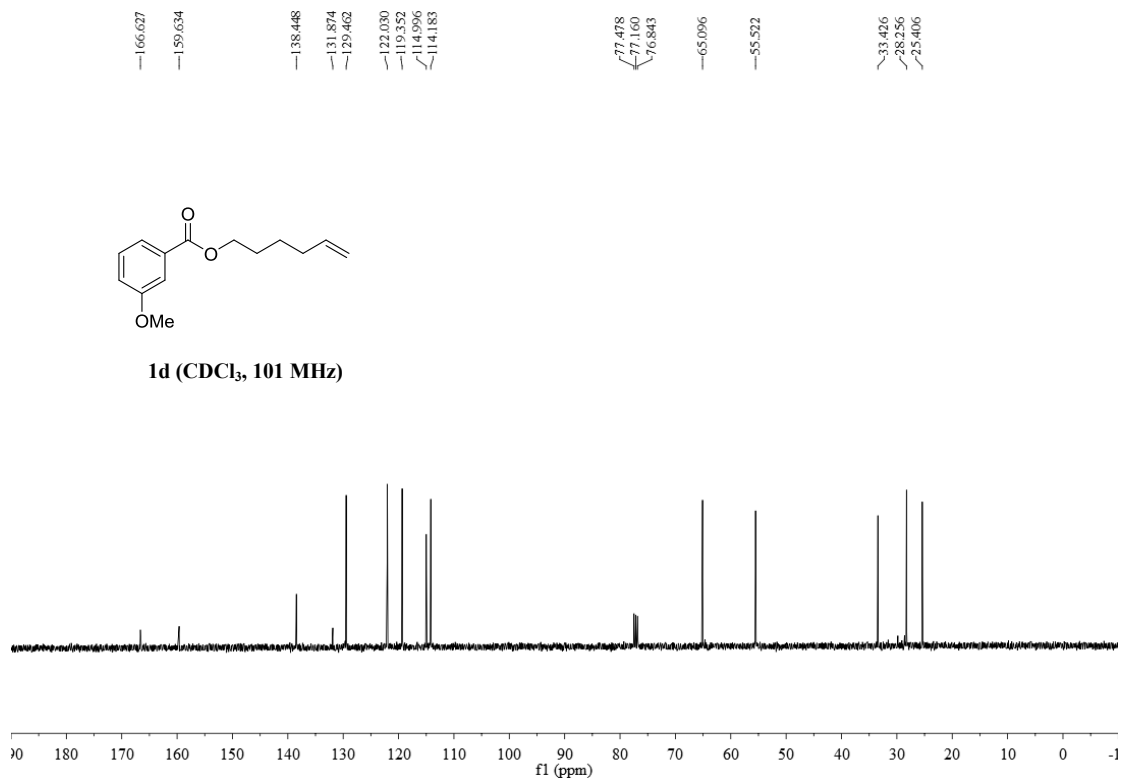
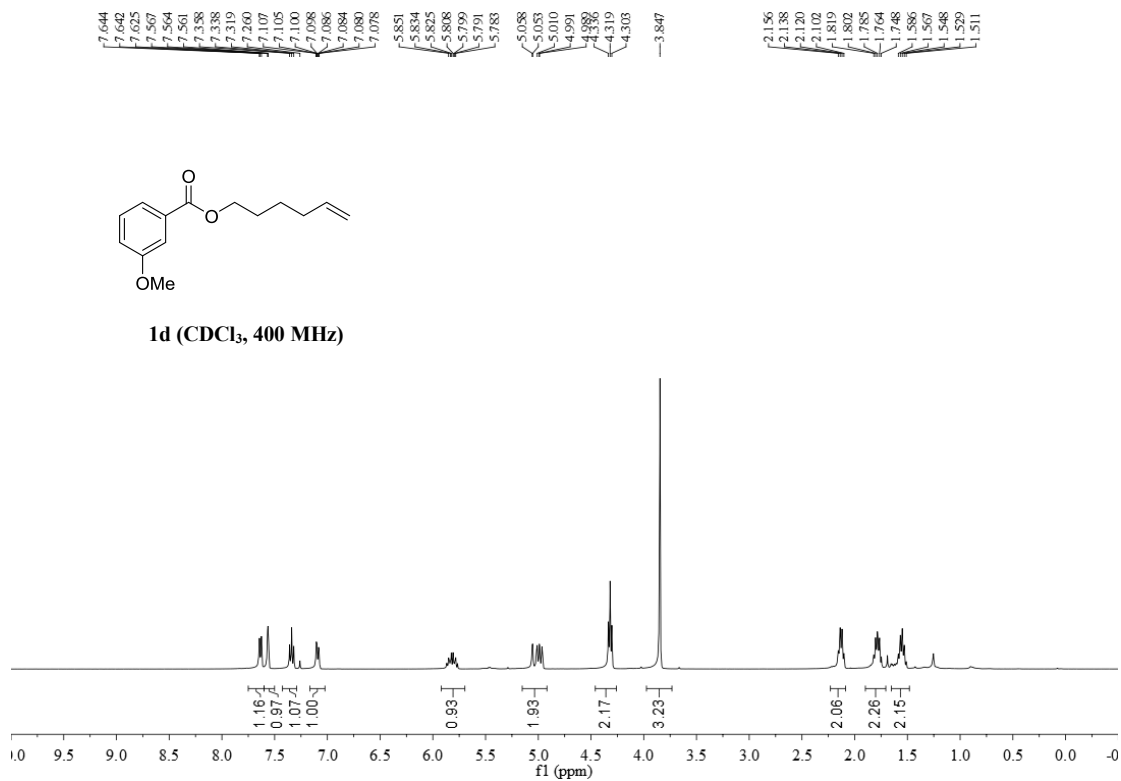


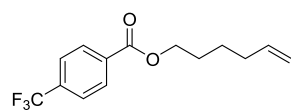
1ah: (1*S*,4*S*,5*S*)-2-((*R*)-(benzyloxy)(6-methoxyquinolin-4-yl)methyl)-5-(3,3,3-trifluoroprop-1-en-1-yl)quinuclidine. Prepared according to the general procedure. Reaction was run using **1ah** (124.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (75.2 mg, 0.45 mmol), Me₃SiCF₃ (180 μ L, 1.2 mol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The *E/Z* ratio (63:37) was determined by ¹⁹F NMR of the crude mixture with benzonitrile as the internal standard. The product was purified by preparative TLC and obtained a yellow oil (0.16 mmol, 78.1 mg, 54%, *E/Z* isomer can be separated by preparative TLC to afford pure compound respectively), *R*_f = 0.50 (CH₂Cl₂ : MeOH = 20 : 1).

E isomer: **¹H NMR** (400 MHz, CDCl₃): δ 8.78 (d, *J* = 4.4 Hz, 1H), 8.06 (d, *J* = 9.2 Hz, 1H), 7.60 (s, 1H), 7.52 (d, *J* = 4.0 Hz, 1H), 7.43 (d, *J* = 2.4 Hz, 1H), 7.10 (d, *J* = 2.4 Hz, 1H), 7.39-7.32 (m, 4H), 6.23-6.17 (m, 1H), 5.67-5.59 (m, 1H), 4.58-4.49 (m, 2H), 4.07 (s, 3H), 3.82 (s, 1H), 3.41-3.32 (m, 2H), 3.08-2.82 (m, 2H), 2.74-2.57 (m, 2H), 2.24-1.90 (m, 3H), 1.82-1.67 (m, 1H), 1.57 (t, *J* = 10.8 Hz, 1H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 158.9, 147.3, 144.9, 142.3 (m), 140.2 (m), 137.2, 132.0, 128.8, 128.3, 127.9, 127.2, 123.0, 122.5 (q, *J*_{C-F} = 6.4 Hz), 120.5 (m), 118.7, 101.1, 71.6, 60.1, 57.1, 55.1, 43.3, 36.9, 29.8, 27.2, 25.7, 20.5 ppm. **¹⁹F NMR** (376 MHz, CDCl₃): δ -64.53 (s, 3F) ppm. **HRMS** m/z (APCI): calcd. for C₂₈H₃₀F₃N₂O₂ [M+H]⁺ : 483.2254; found: 483.2252.

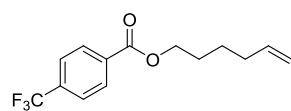
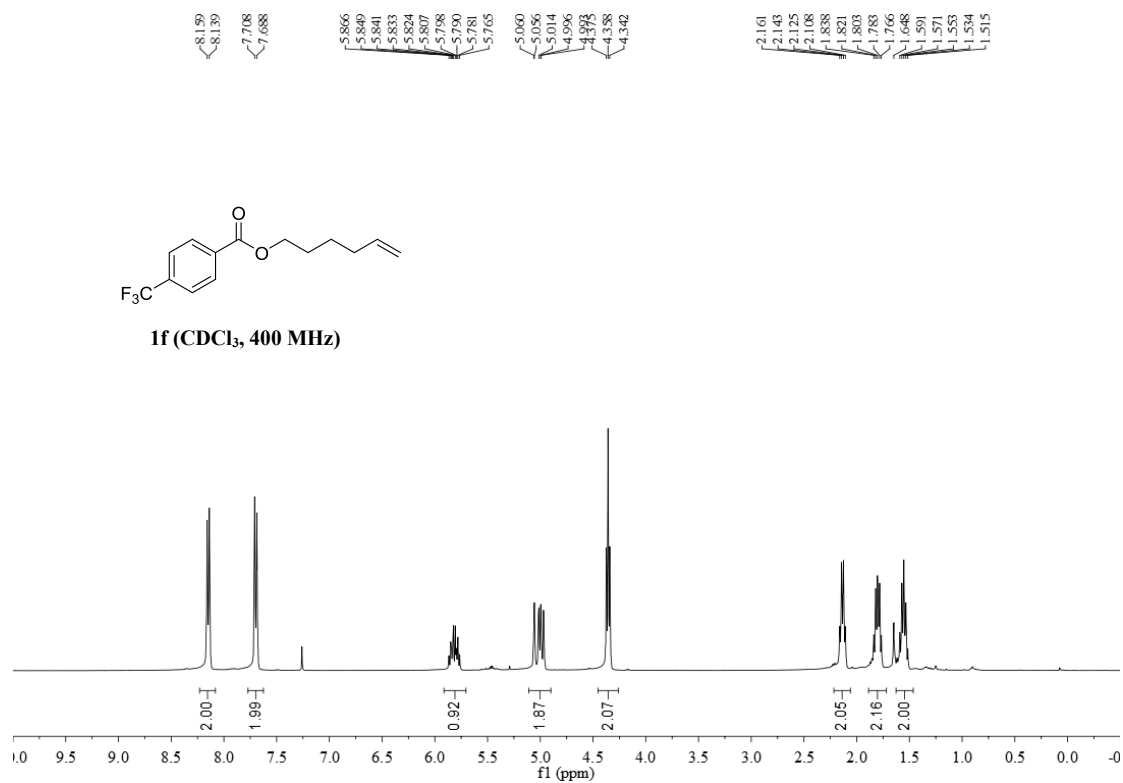
Z isomer: **¹H NMR** (400 MHz, CDCl₃): δ 8.76 (d, *J* = 4.0 Hz, 1H), 8.05 (d, *J* = 9.2 Hz, 1H), 7.52 (d, *J* = 3.6 Hz, 2H), 7.41-7.28 (m, 6H), 5.87 (t, *J* = 10.8 Hz, 1H), 5.58-5.53 (m, 1H), 4.55-4.48 (m, 2H), 4.01 (s, 3H), 3.71-3.58 (m, 2H), 3.34-3.25 (m, 2H), 3.02-2.80 (m, 2H), 2.74-2.62 (m, 1H), 2.10-1.81 (m, 3H), 1.66-1.59 (m, 2H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 158.6, 147.5, 144.8, 143.6 (m), 142.9 (m), 137.4, 132.0, 128.7, 128.1, 127.8, 127.3, 122.8 (q, *J*_{C-F} = 270.7 Hz), 122.6, 119.8 (m), 118.6, 101.1, 71.5, 60.3, 56.8, 56.7, 43.2, 34.0, 29.8, 27.2, 26.2, 20.8 ppm. **¹⁹F NMR** (376 MHz, CDCl₃): δ -58.73 (s, 3F) ppm. **HRMS** m/z (APCI): calcd. for C₂₈H₃₀F₃N₂O₂ [M+H]⁺ : 483.2254; found: 483.2253.

Spectrum:

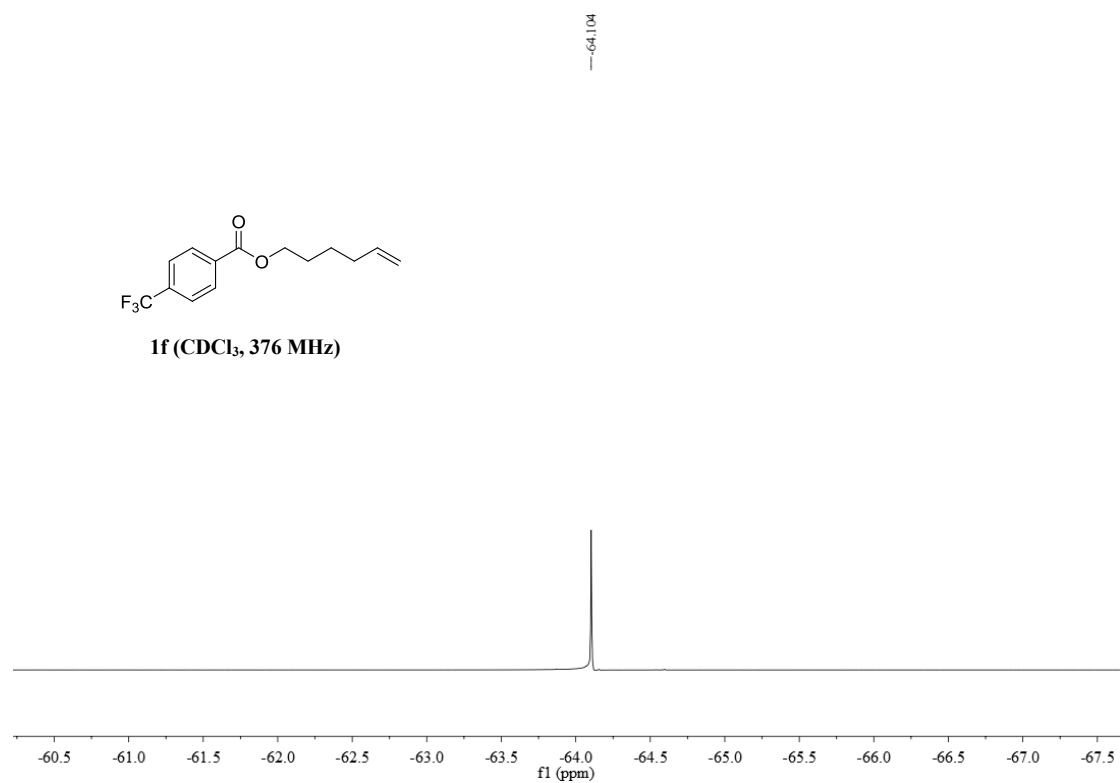


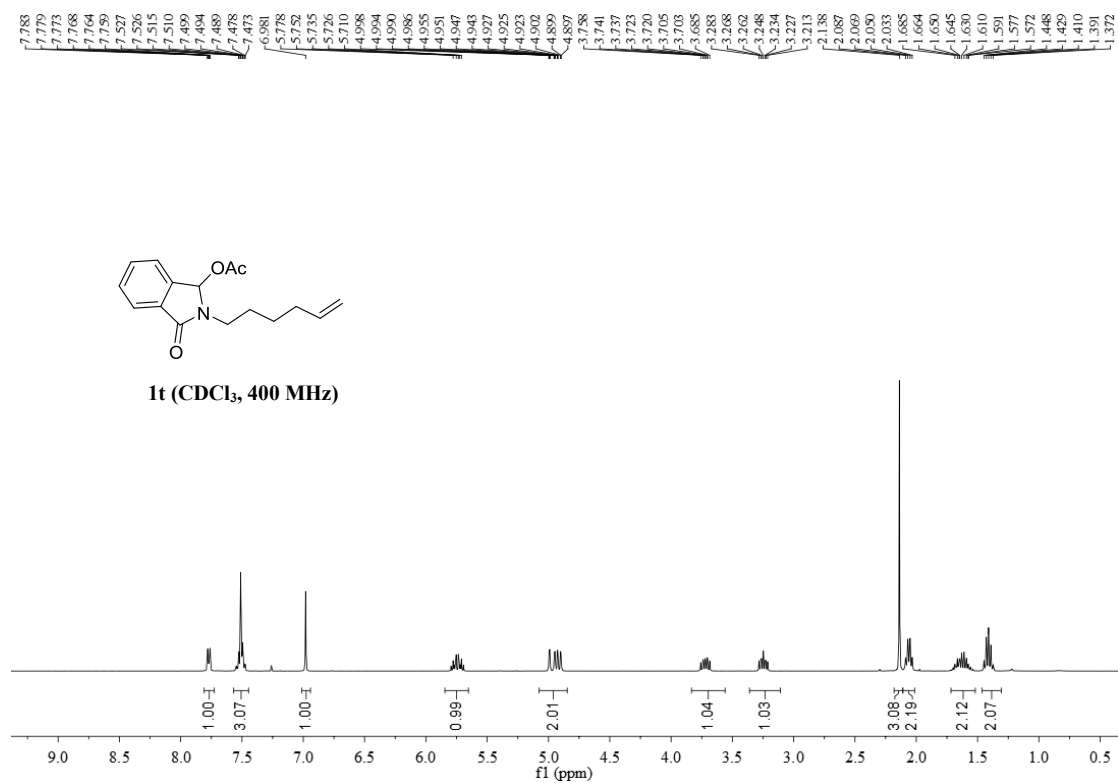
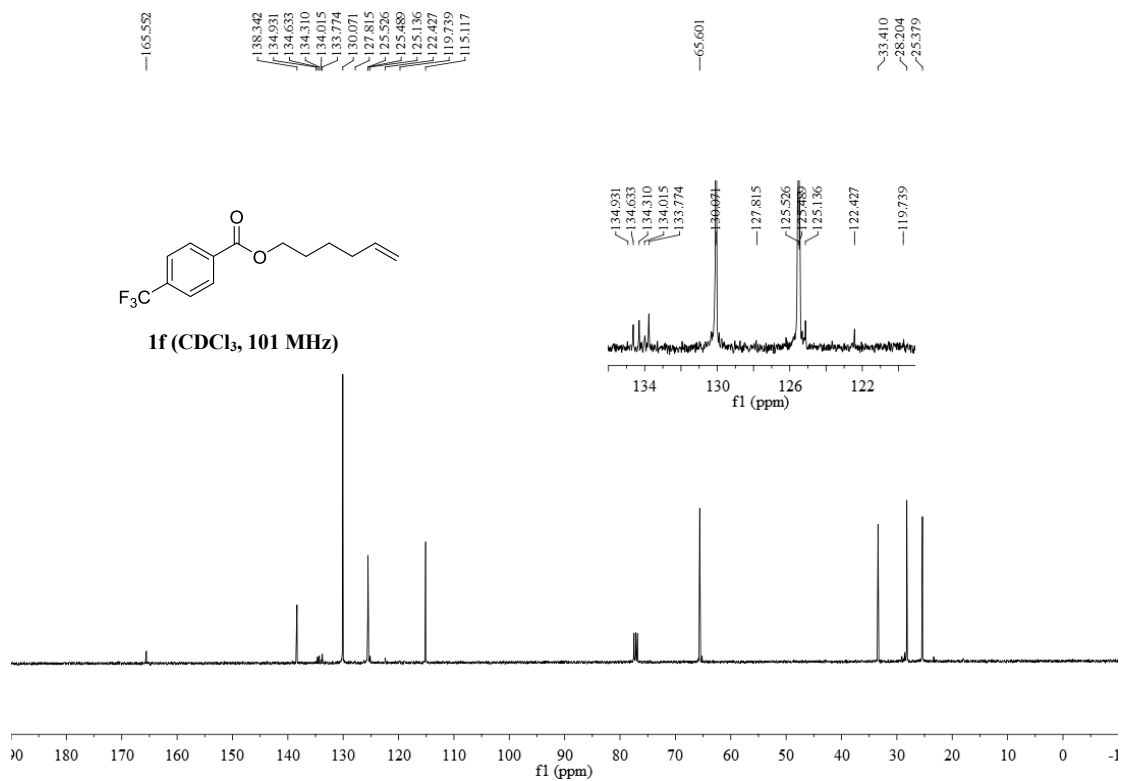


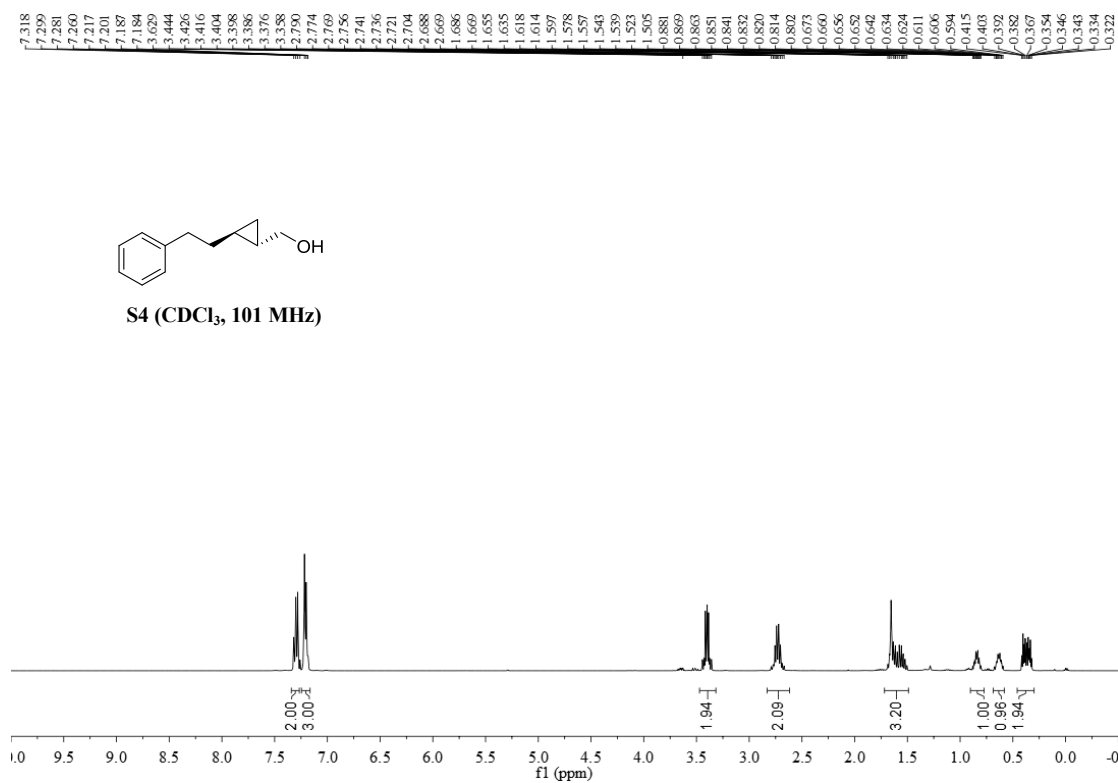
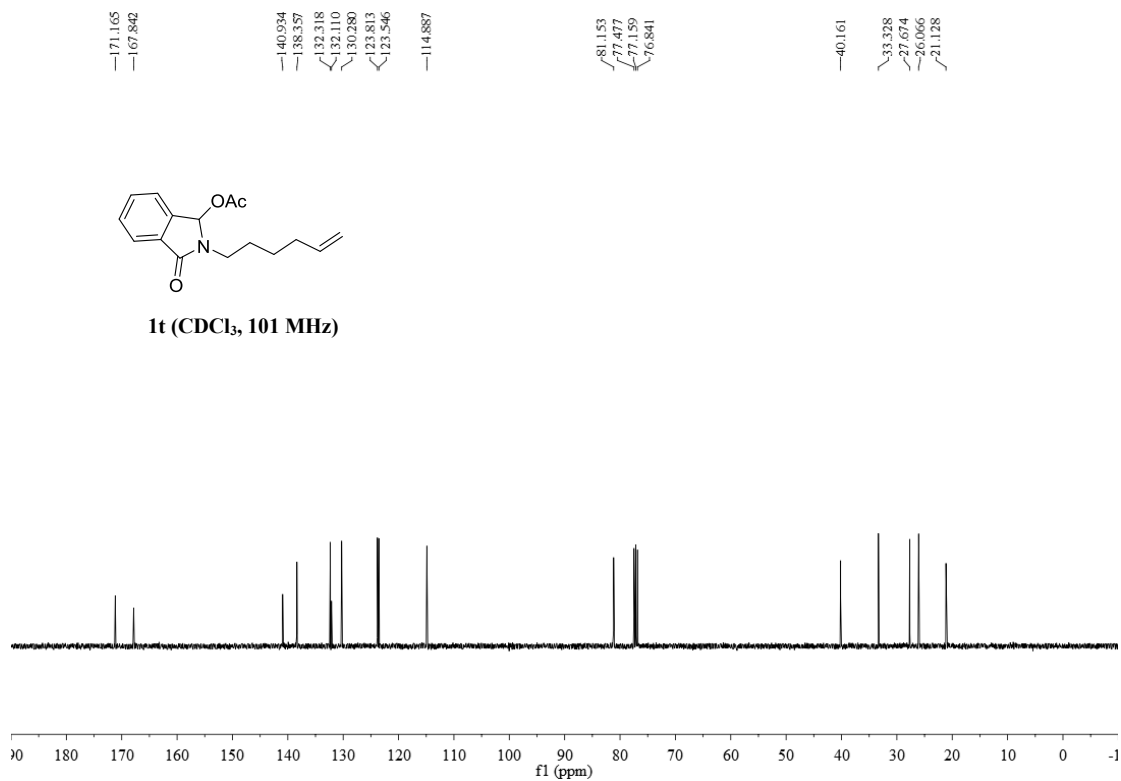
1f (CDCl₃, 400 MHz)

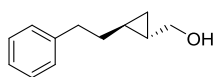


1f (CDCl₃, 376 MHz)

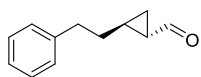
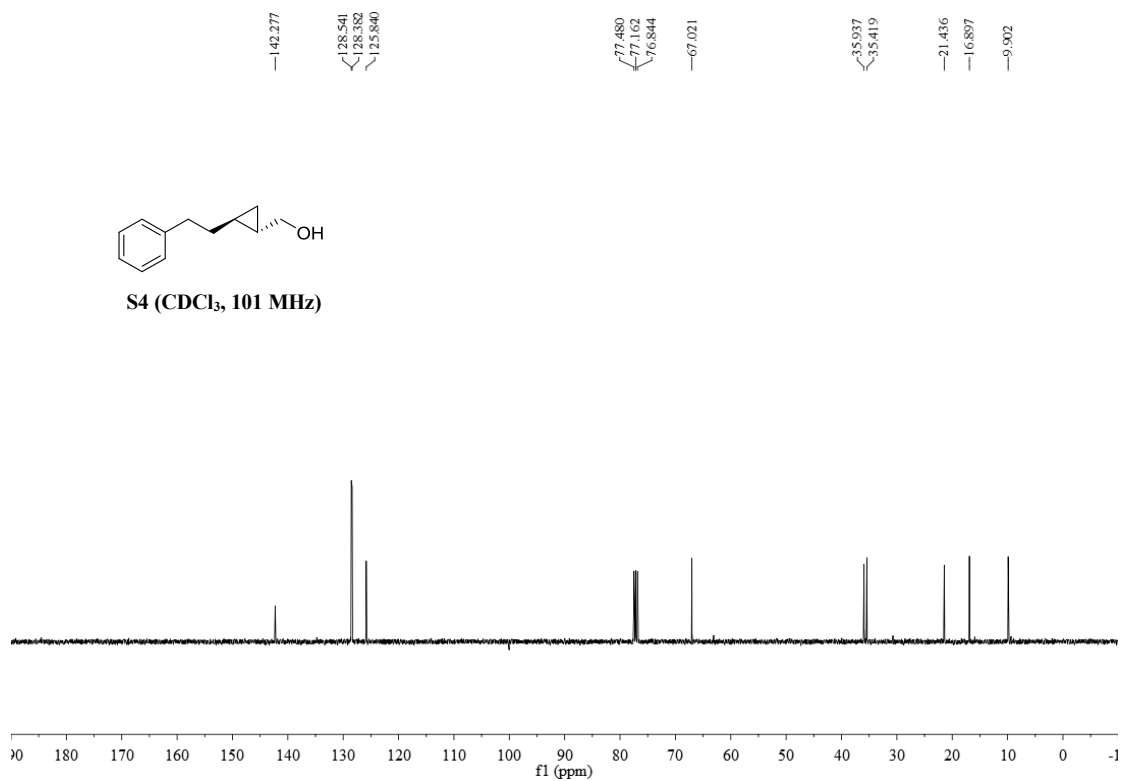




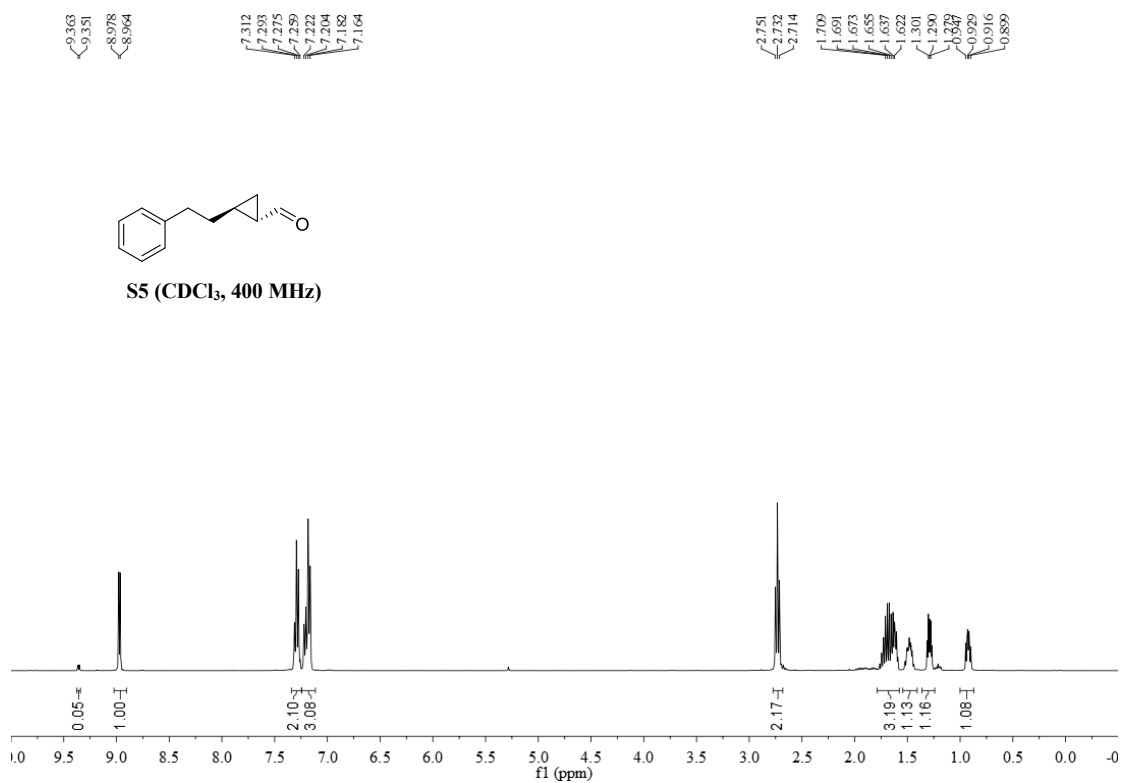


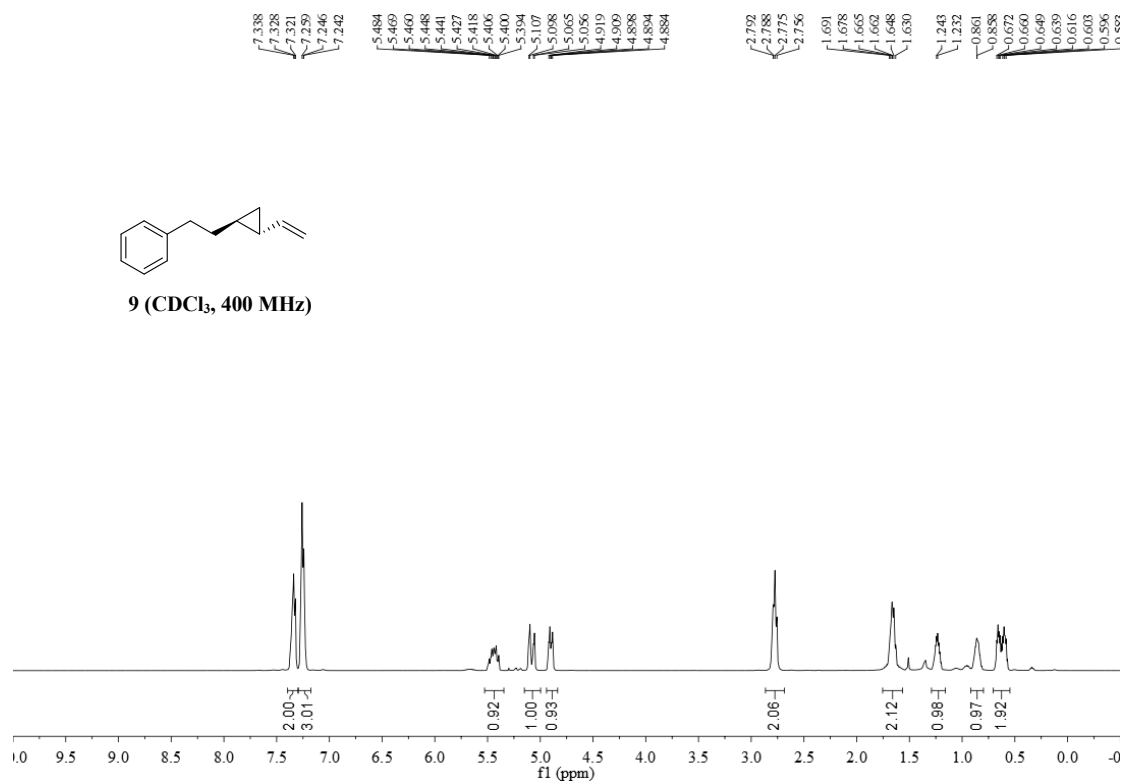
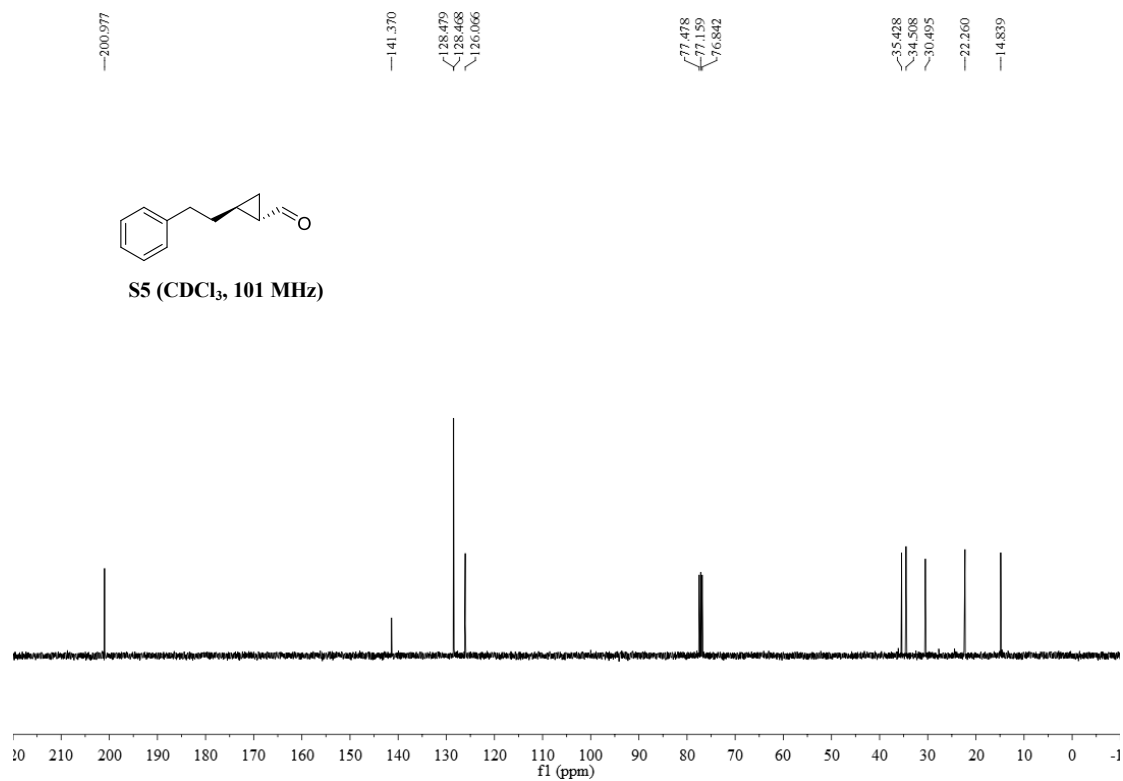


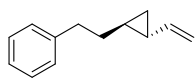
S4 (CDCl₃, 101 MHz)



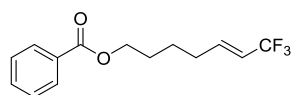
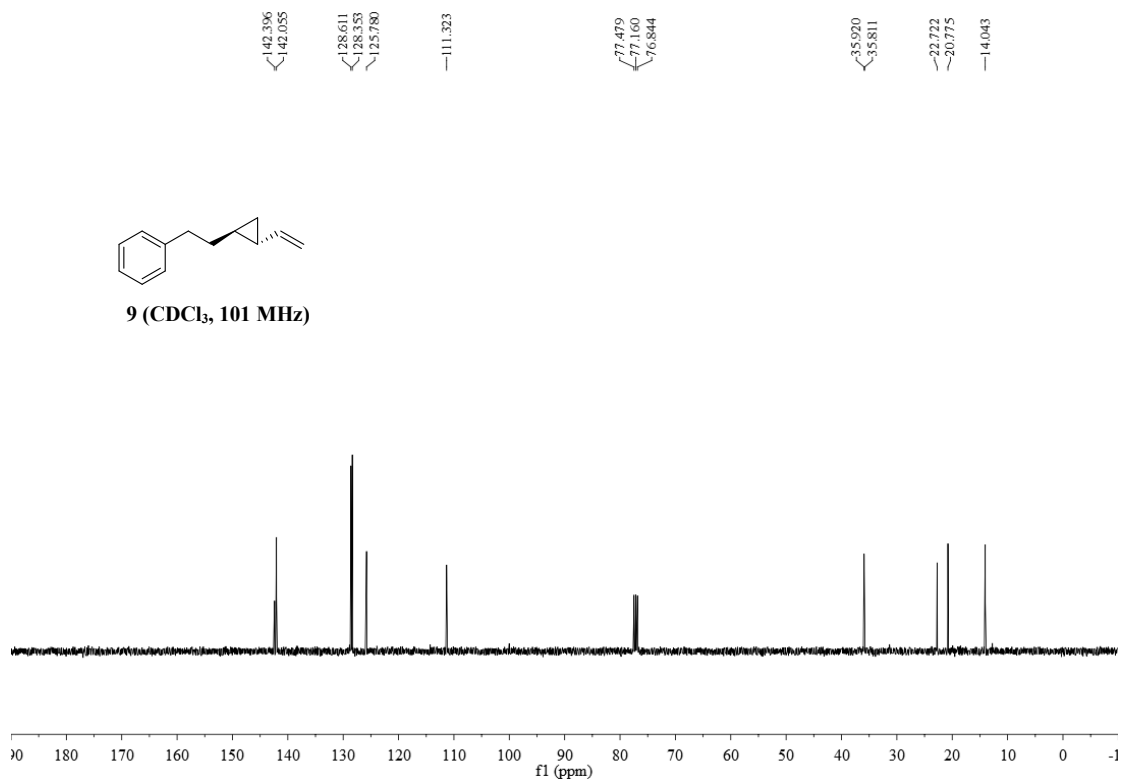
S5 (CDCl₃, 400 MHz)



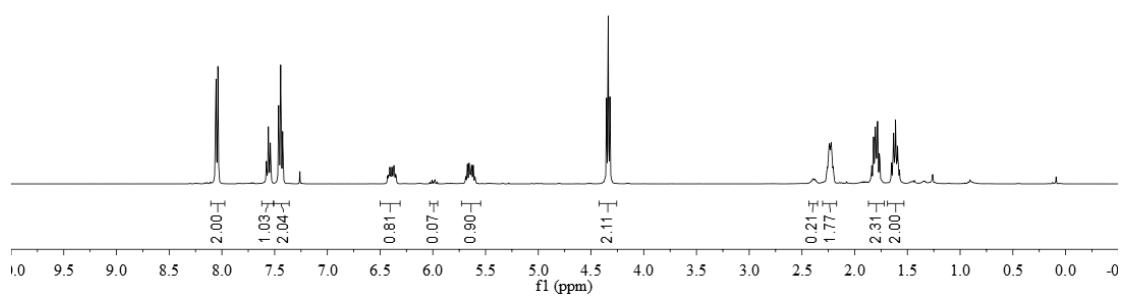


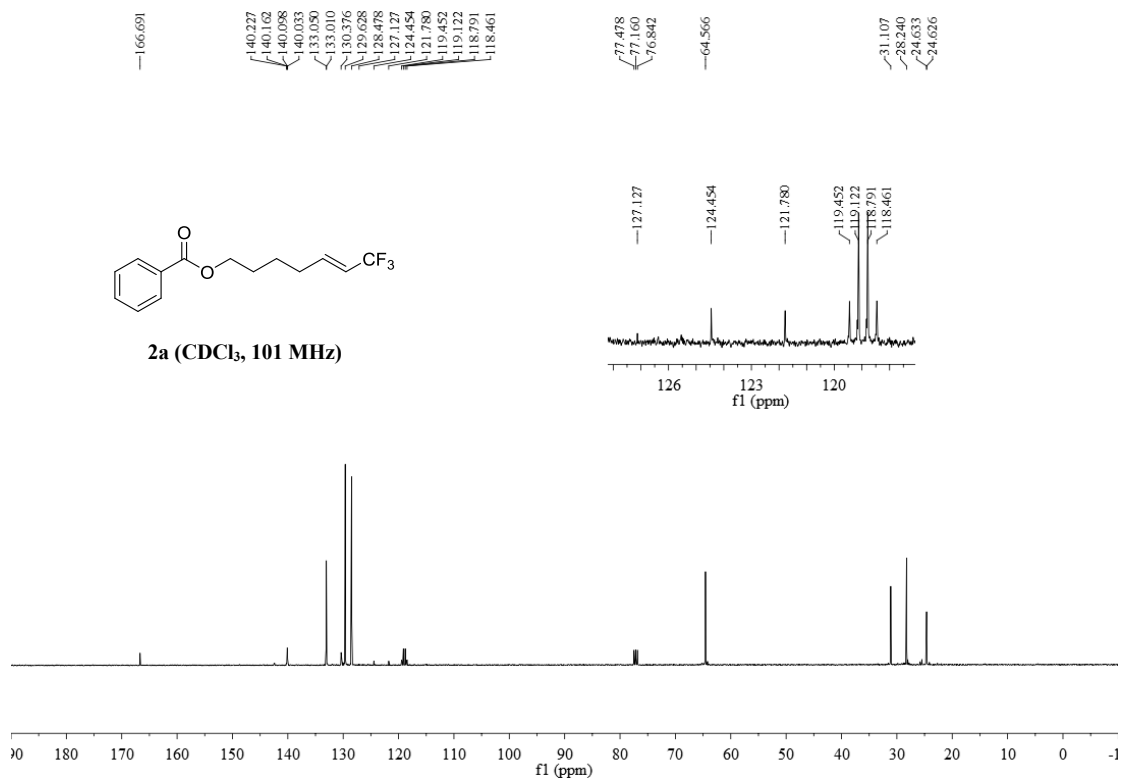
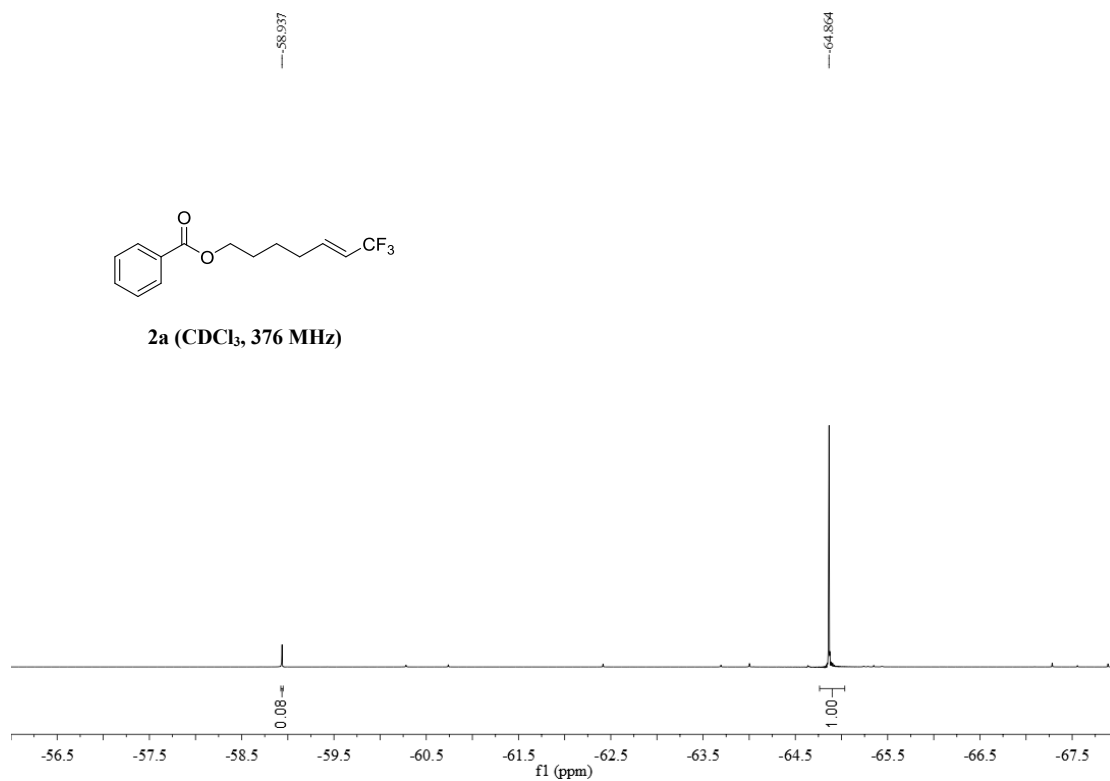


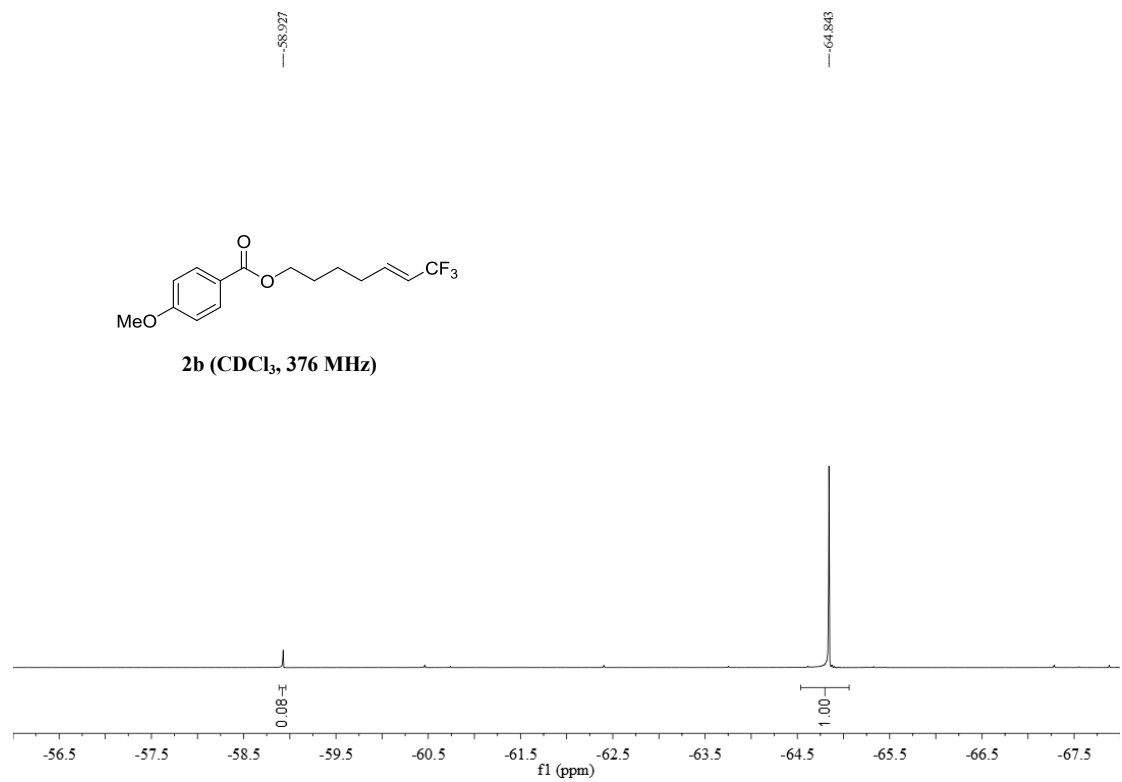
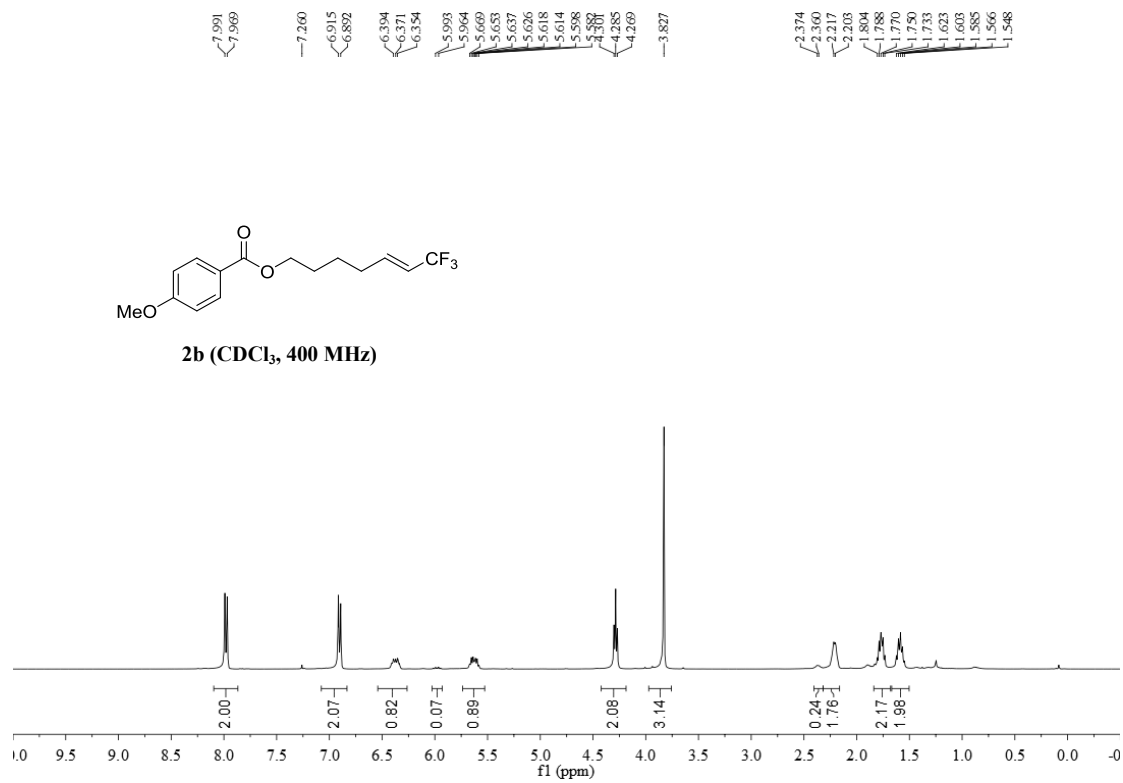
9 (CDCl₃, 101 MHz)

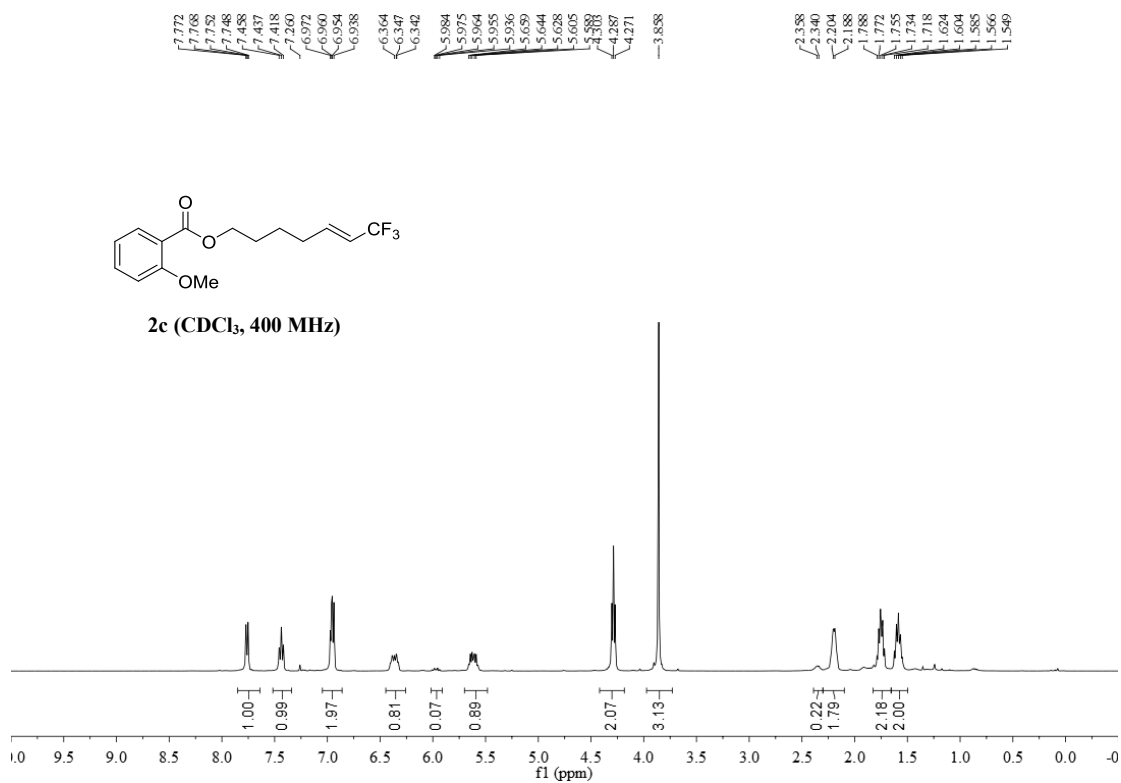
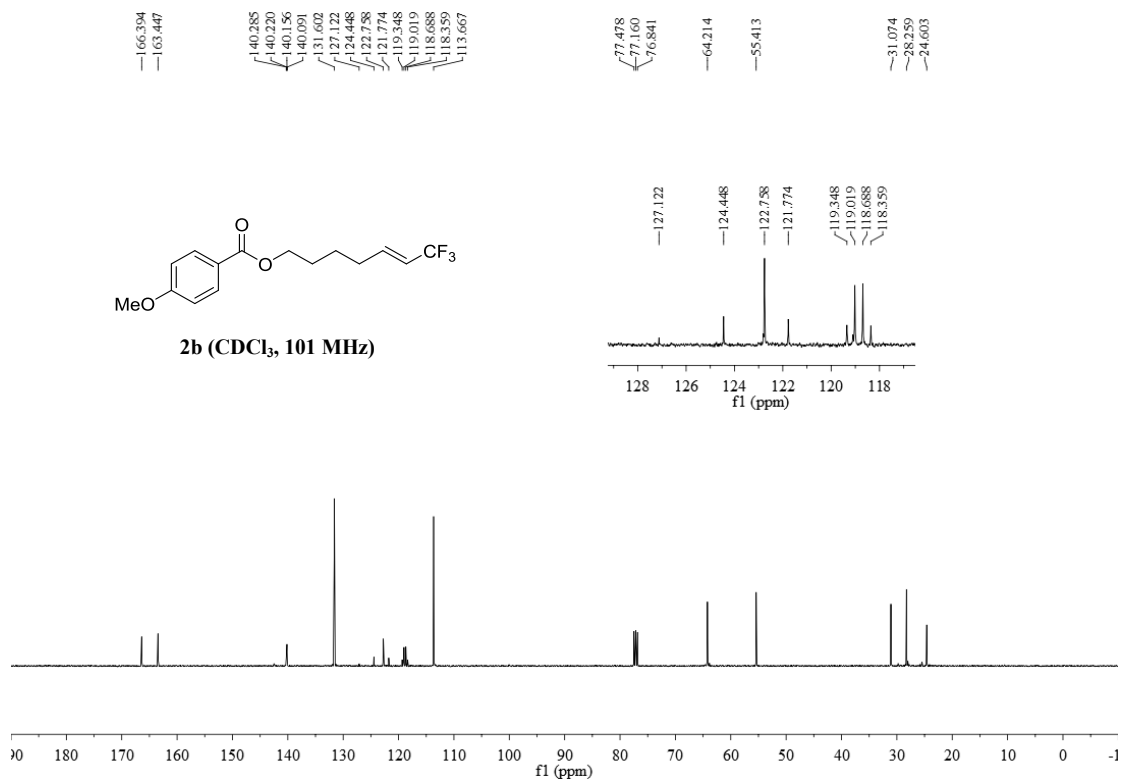


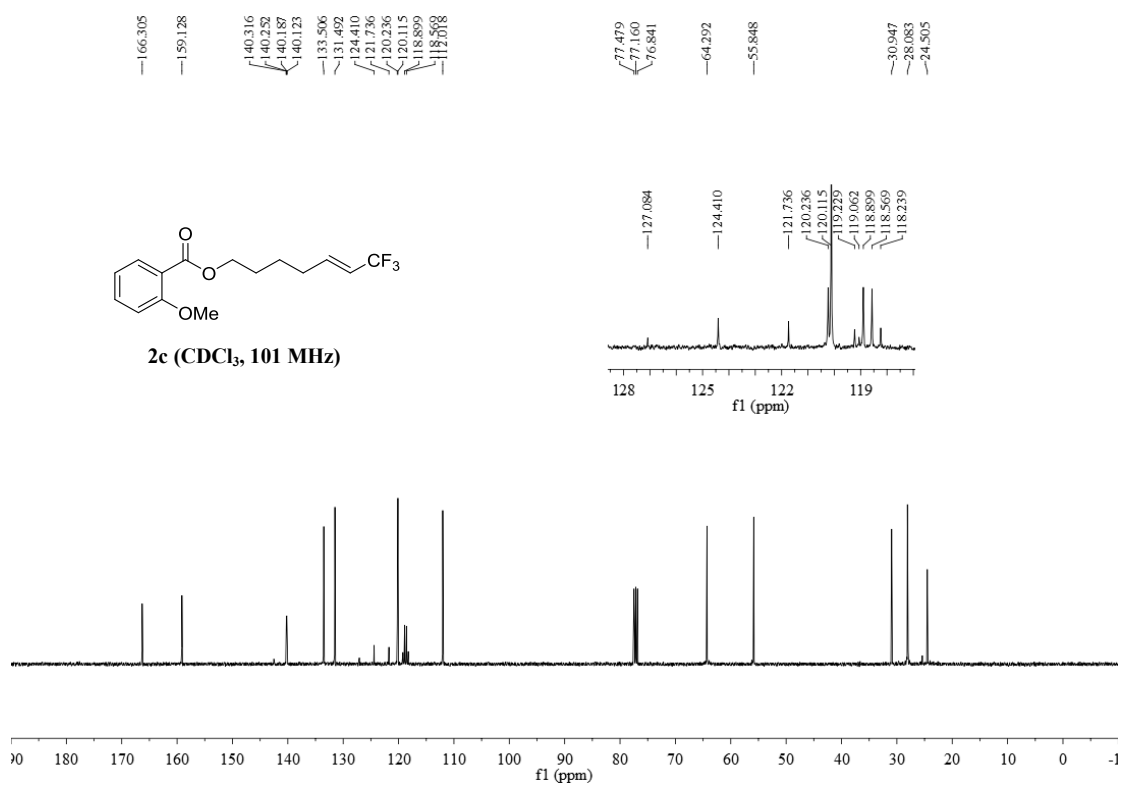
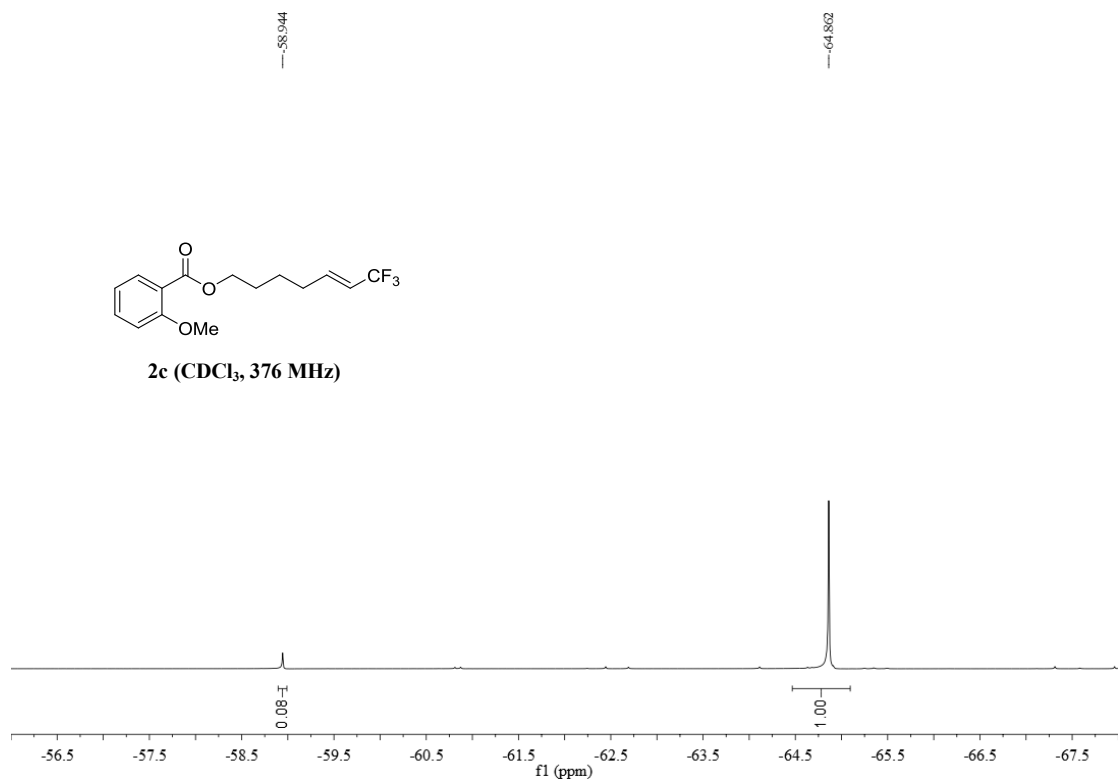
2a (CDCl₃, 400 MHz)

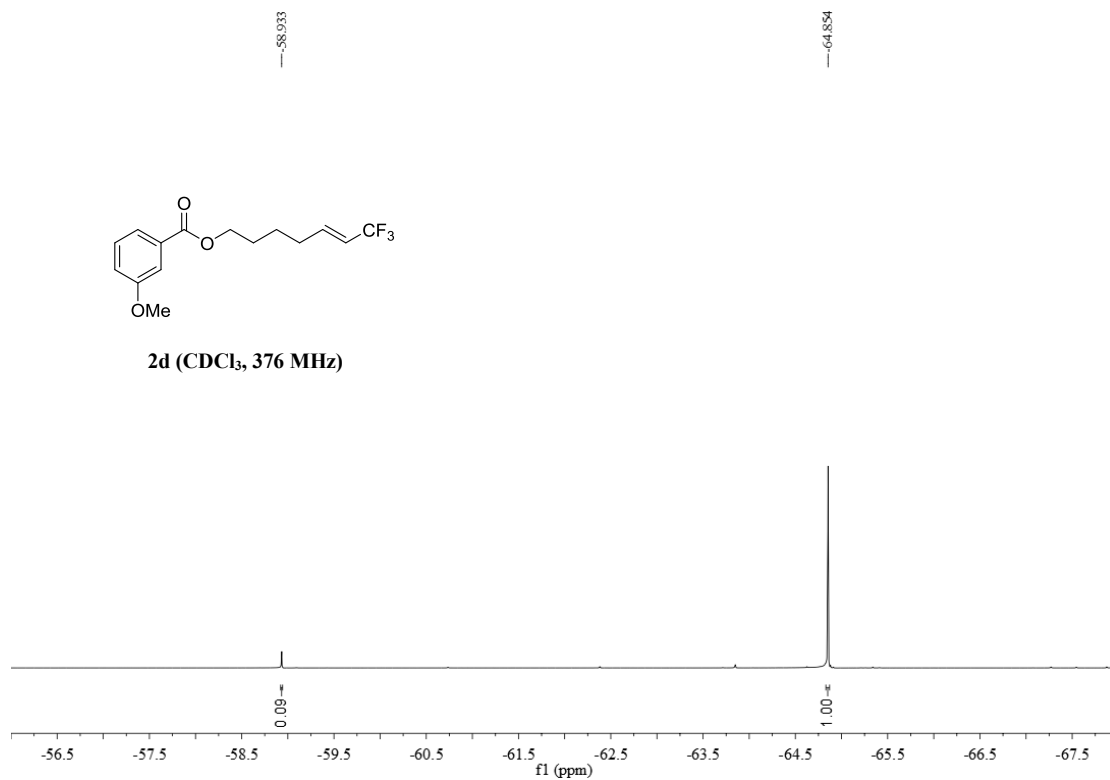
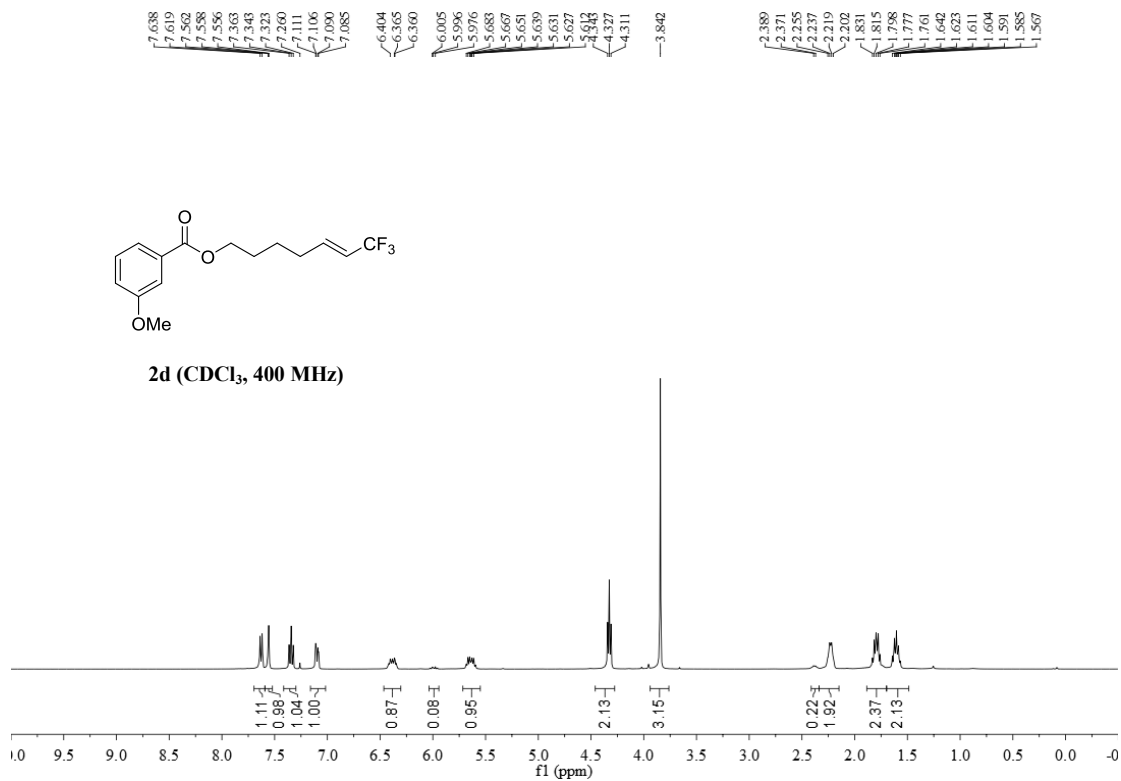


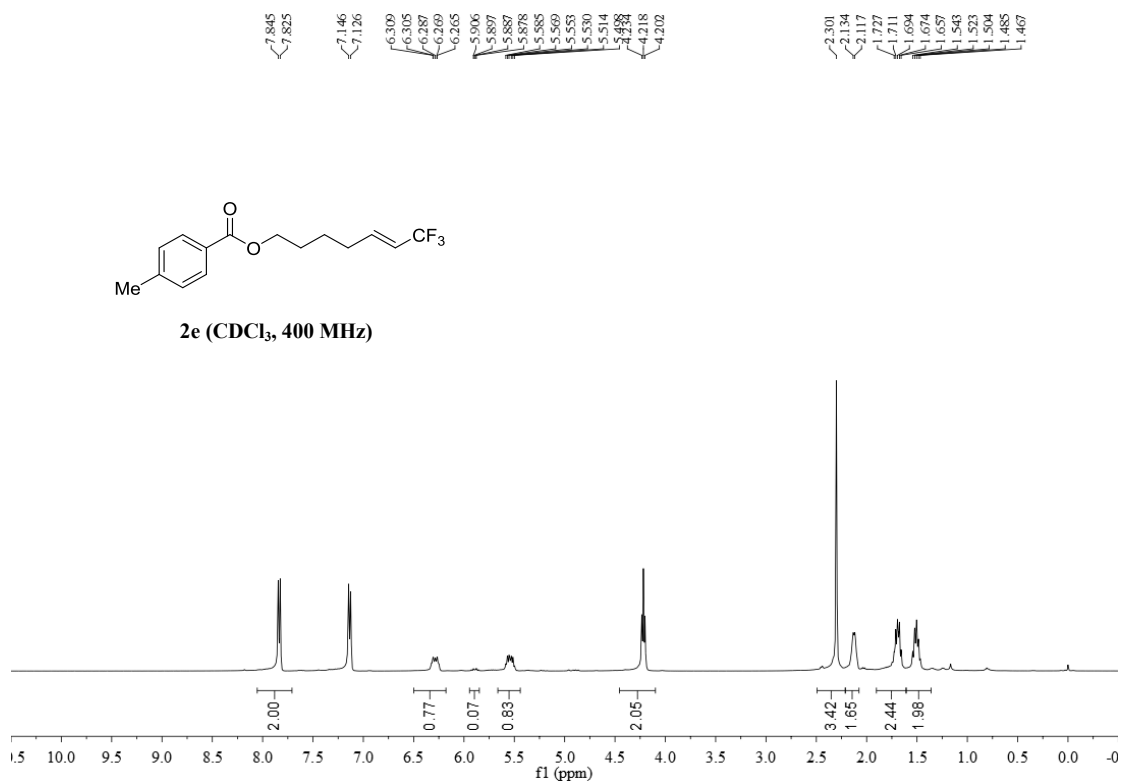
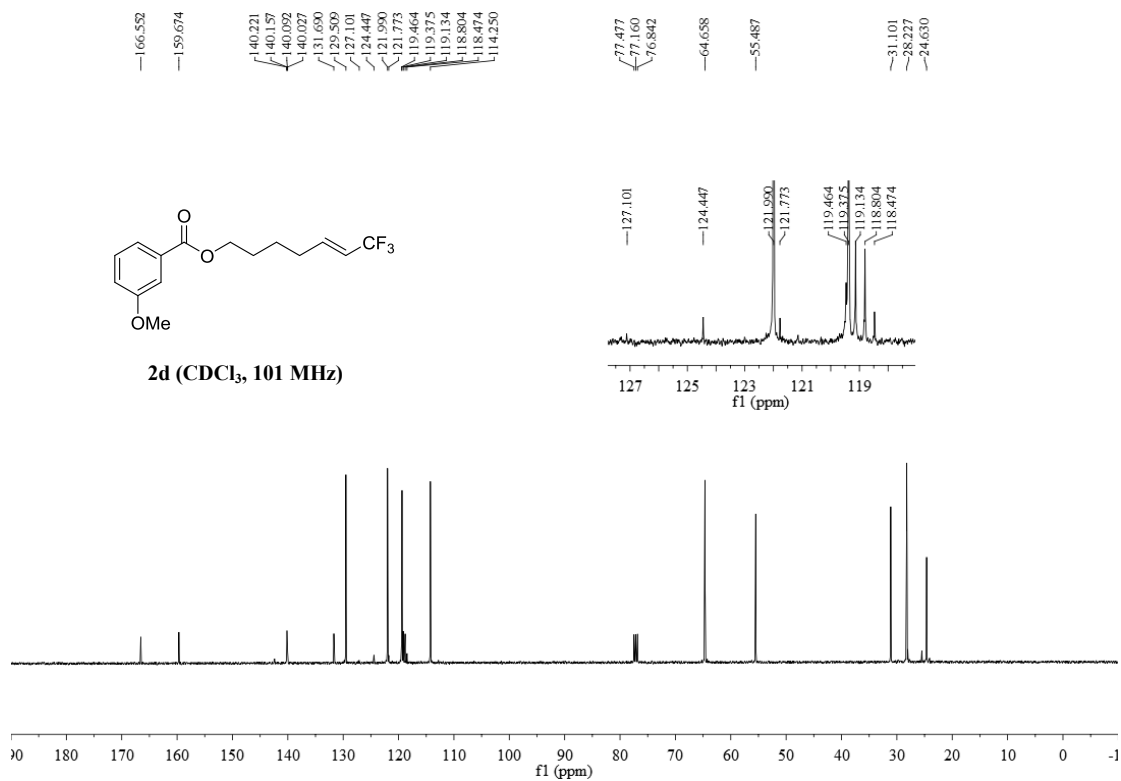


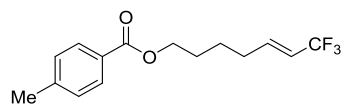




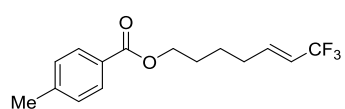
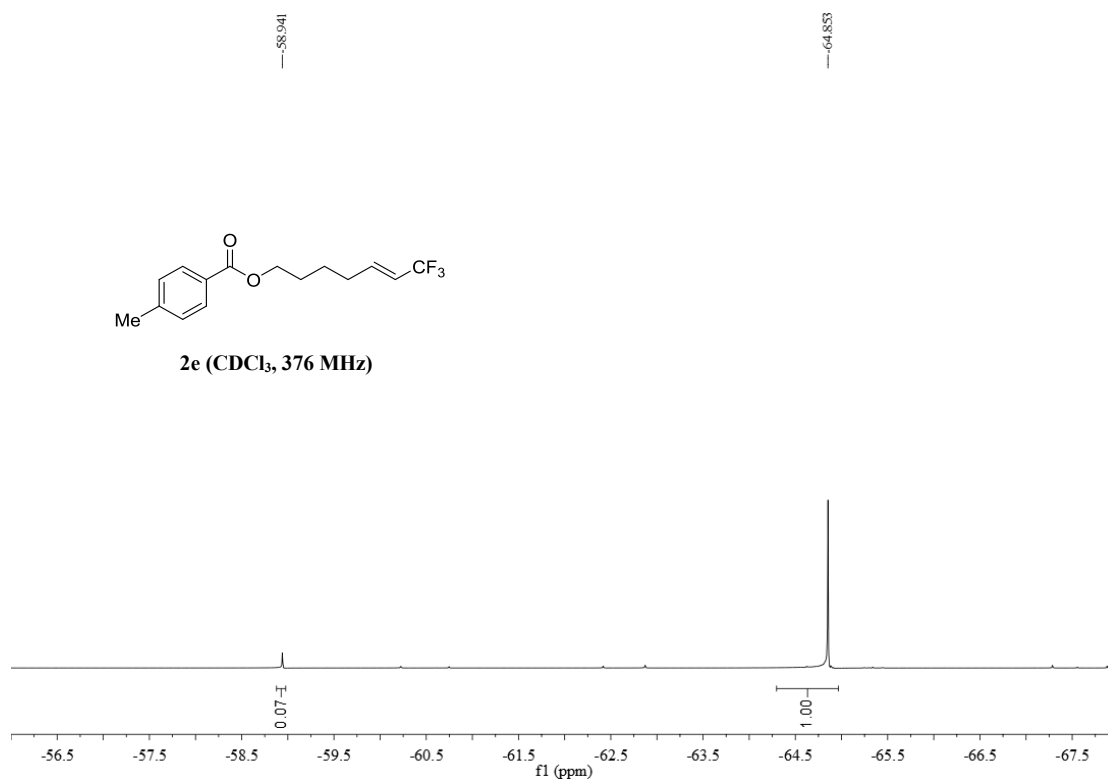




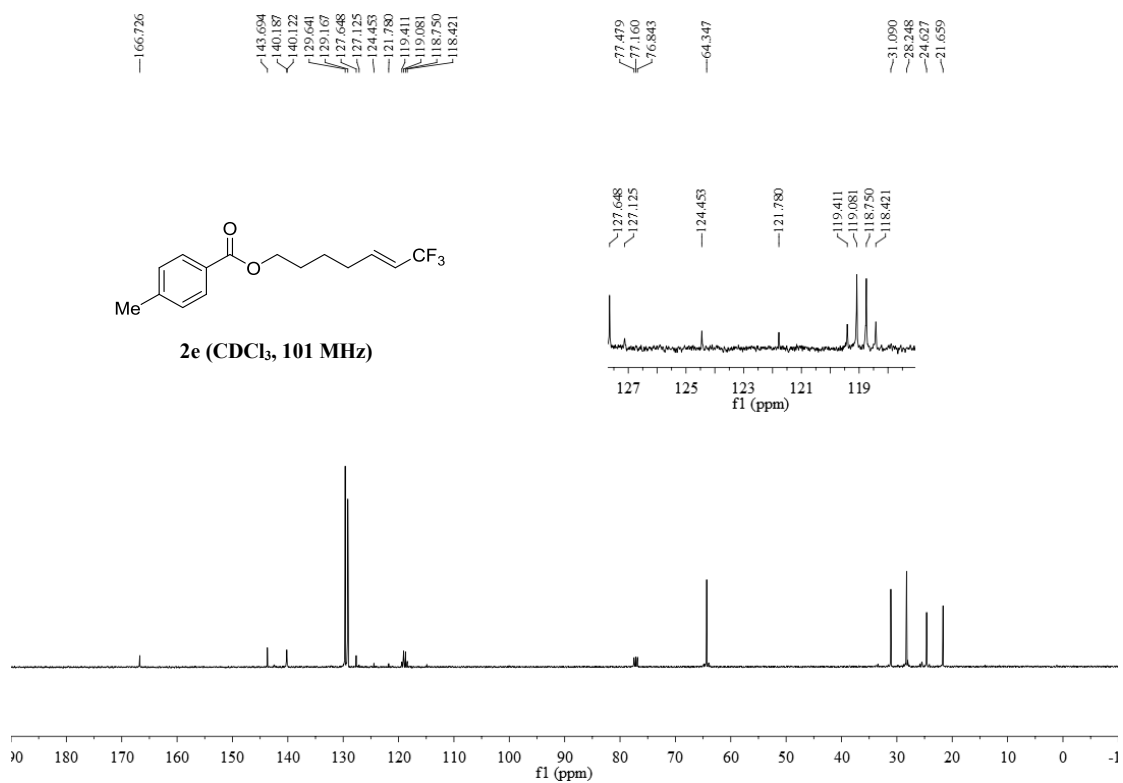


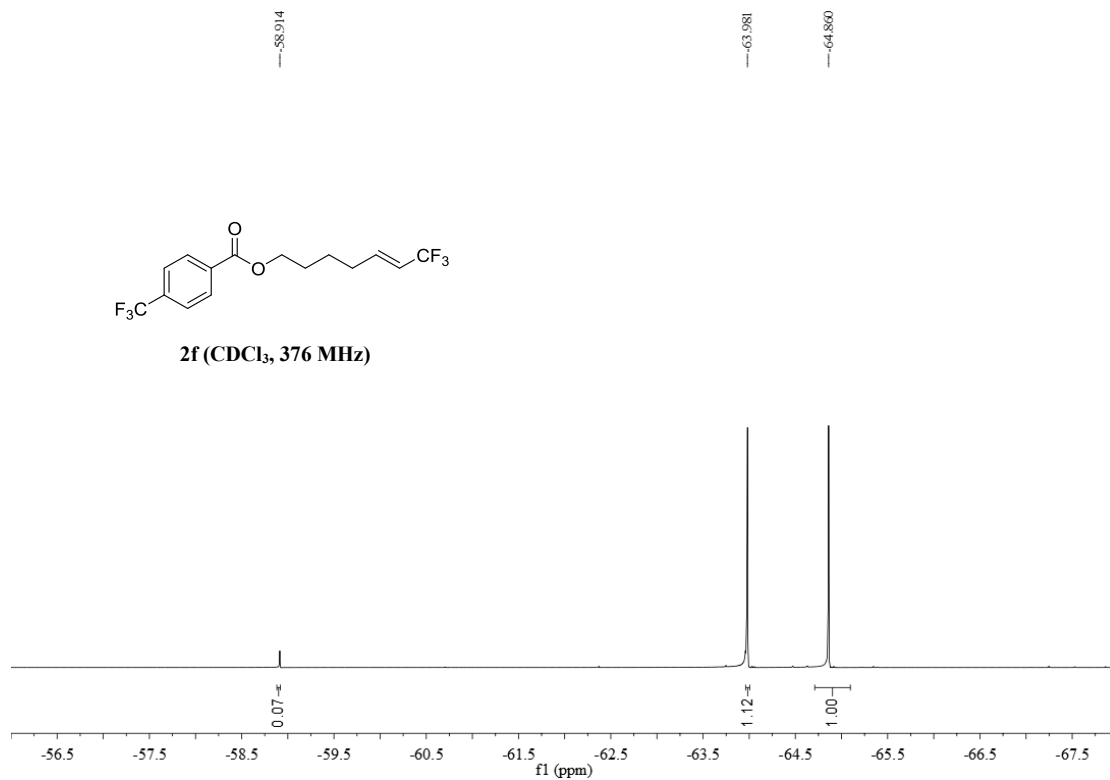
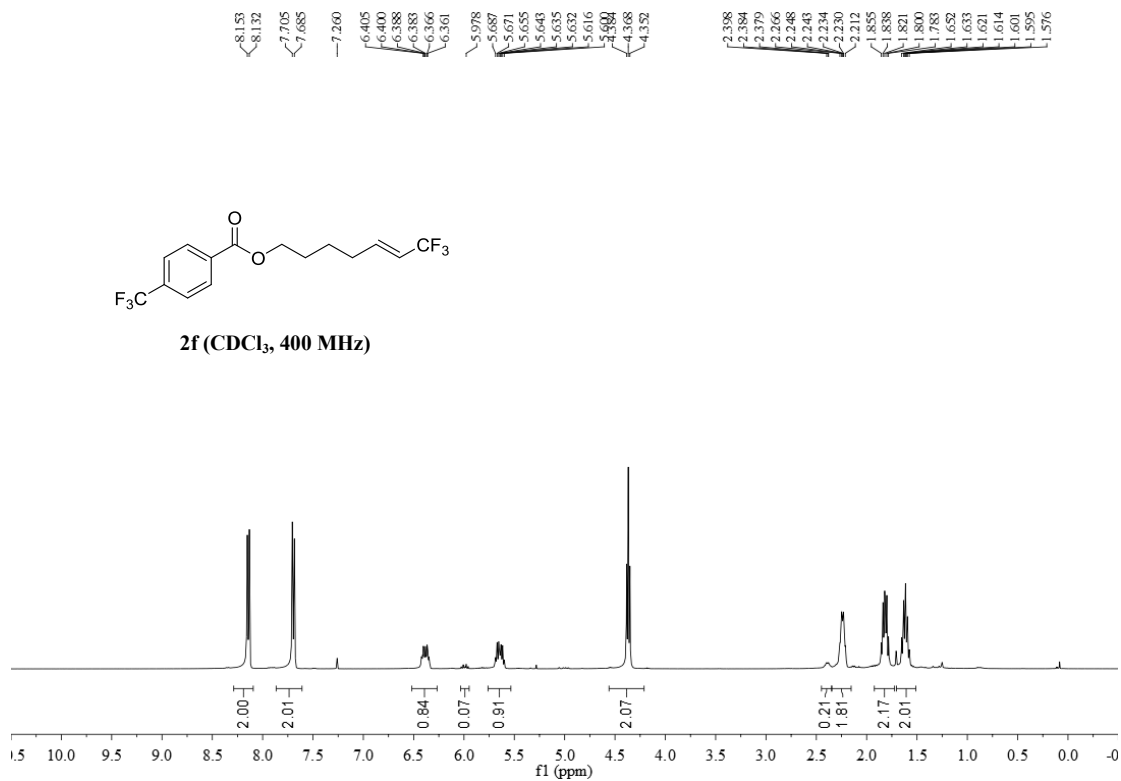


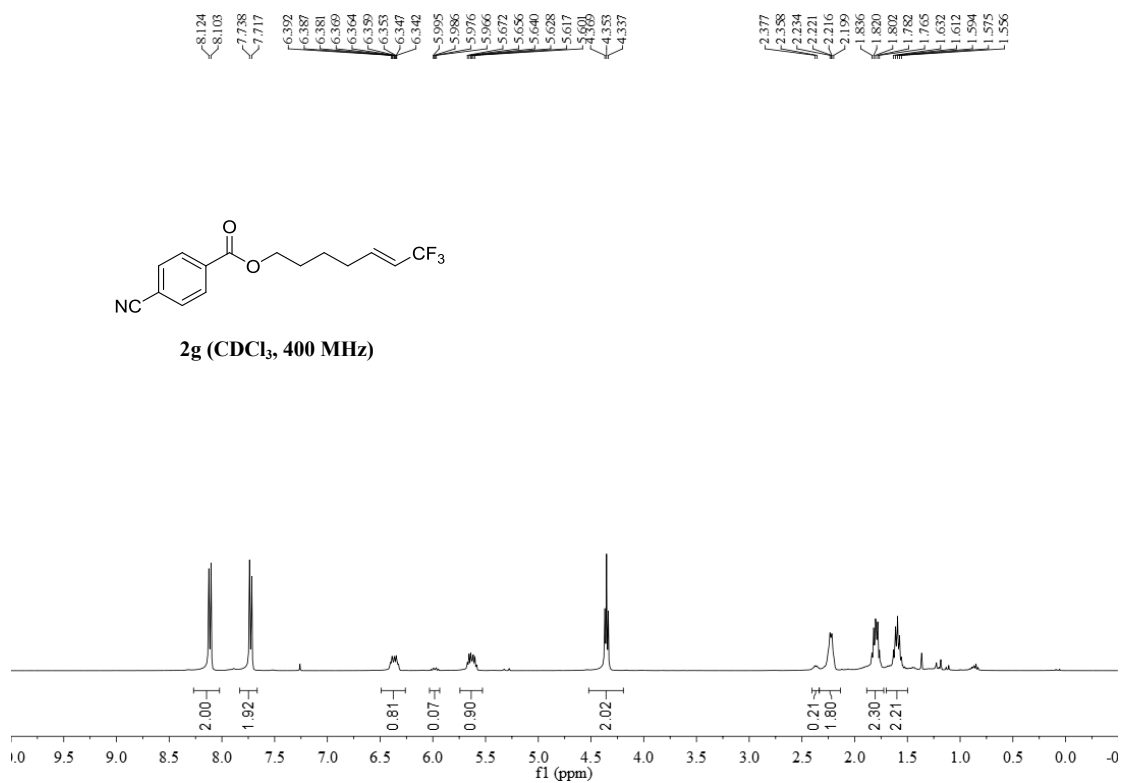
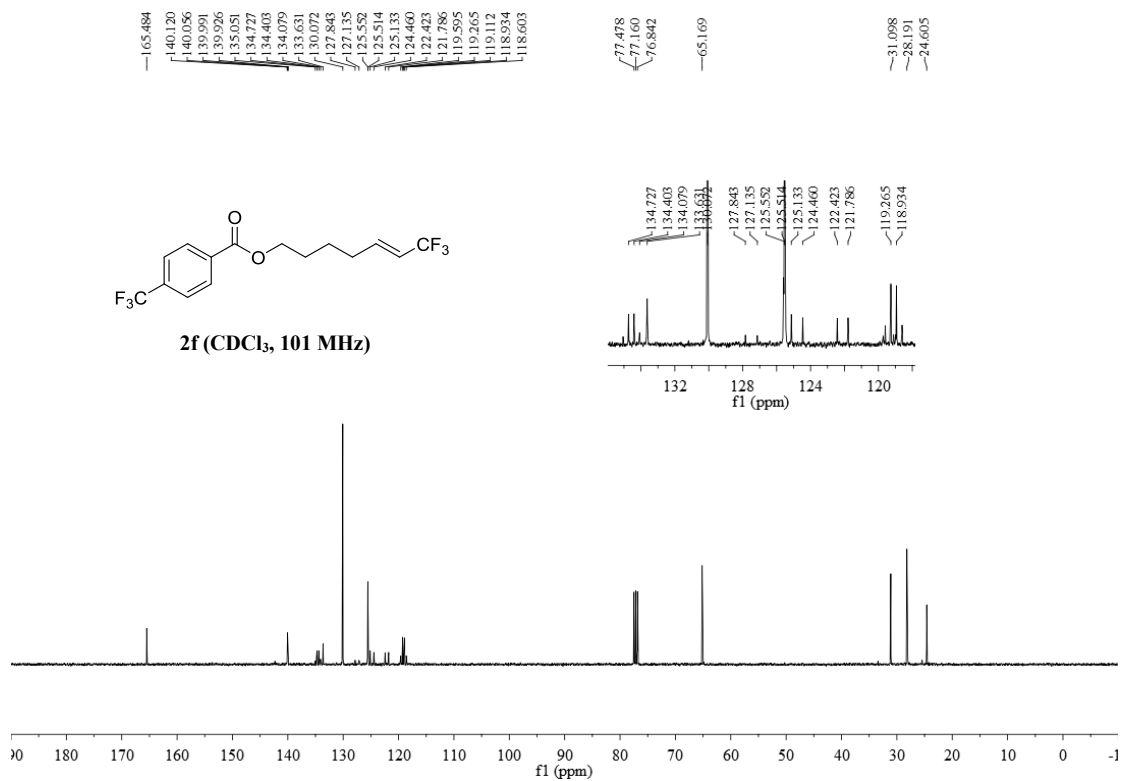
2e (CDCl₃, 376 MHz)

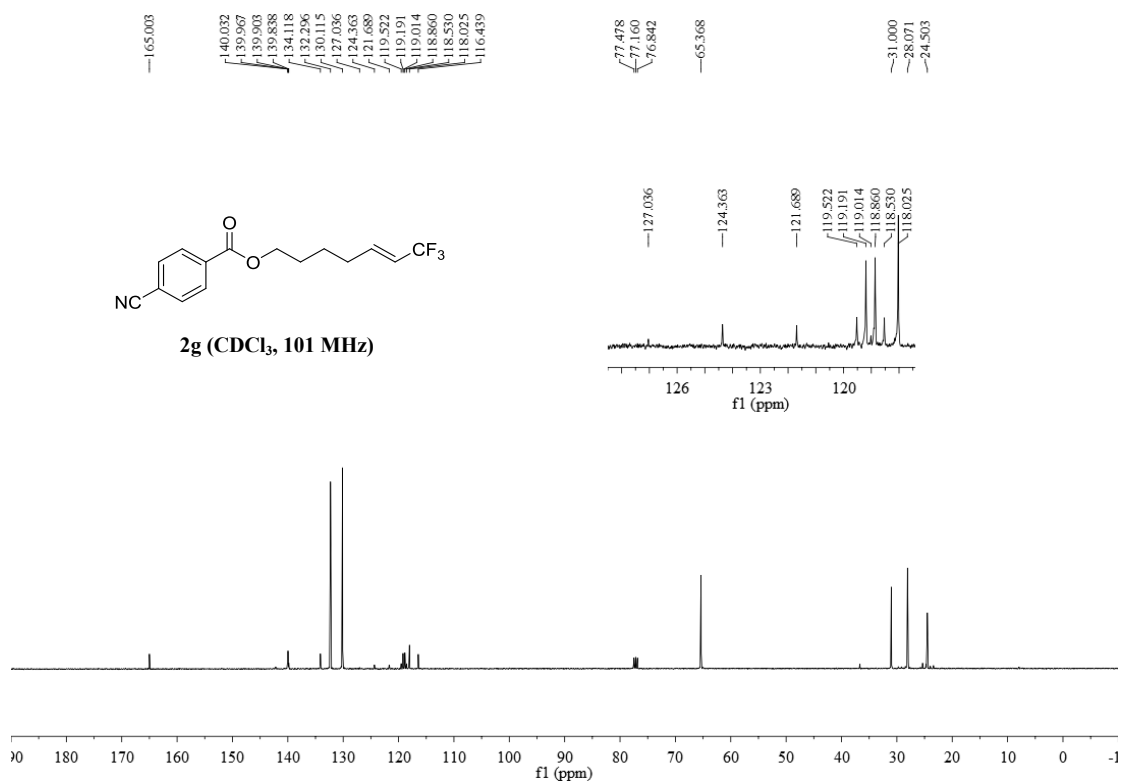
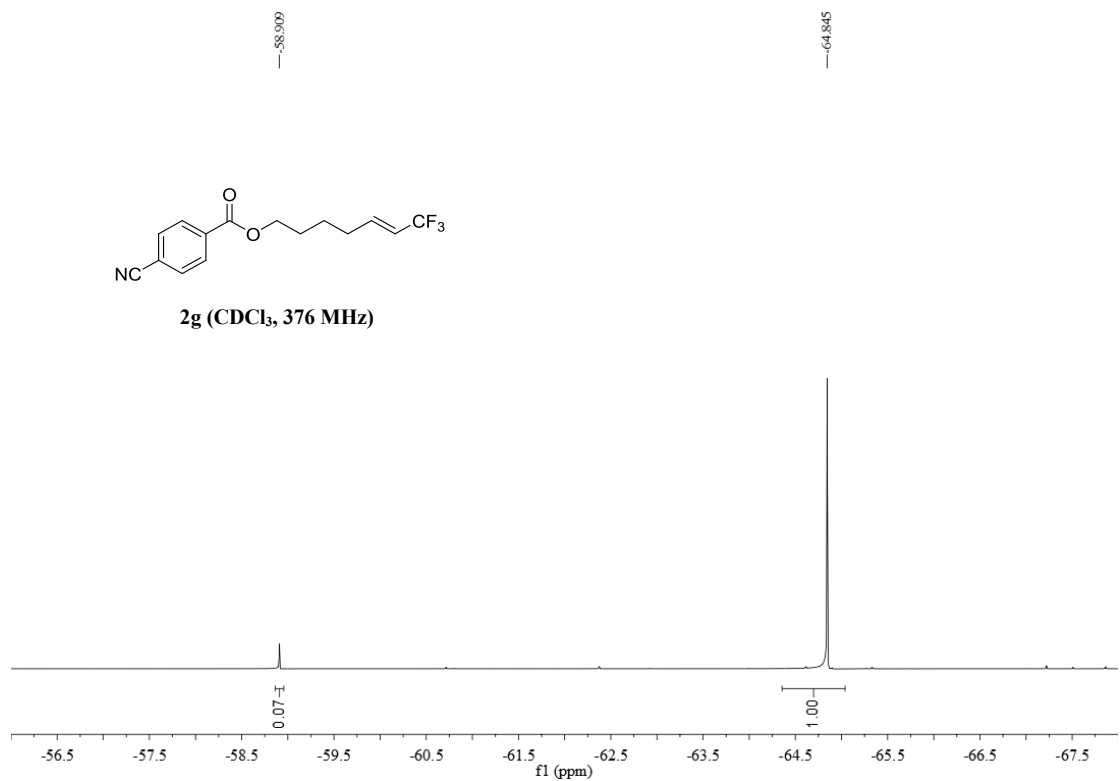


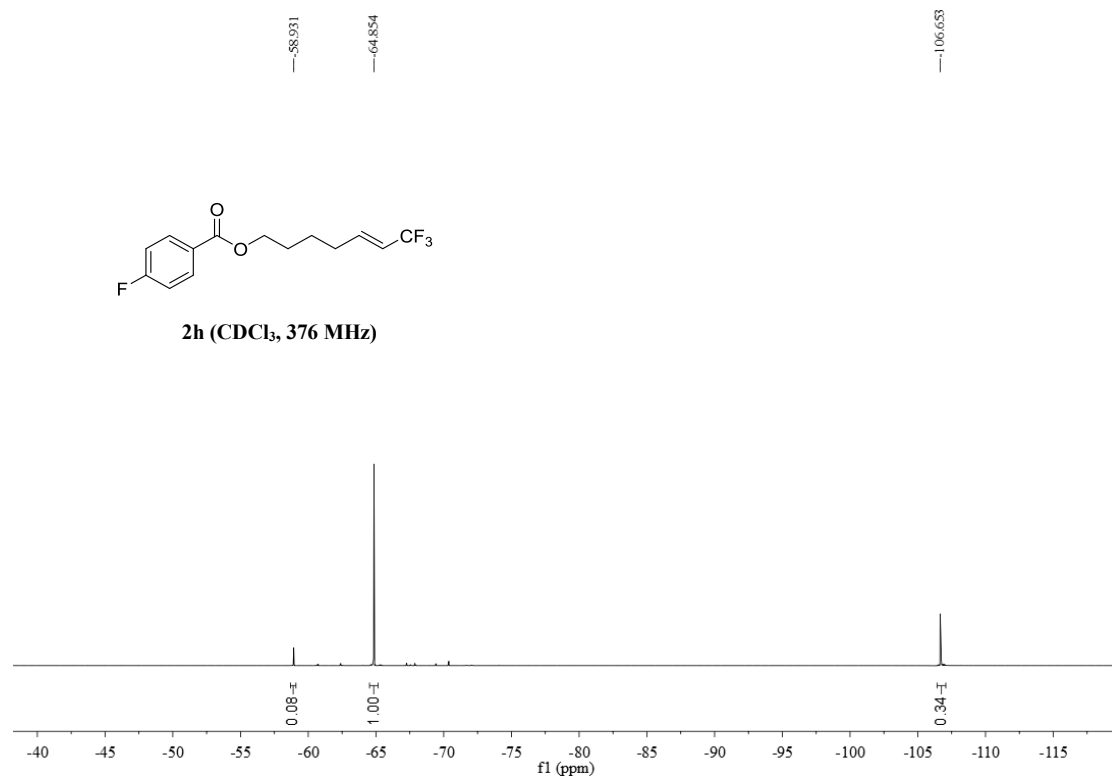
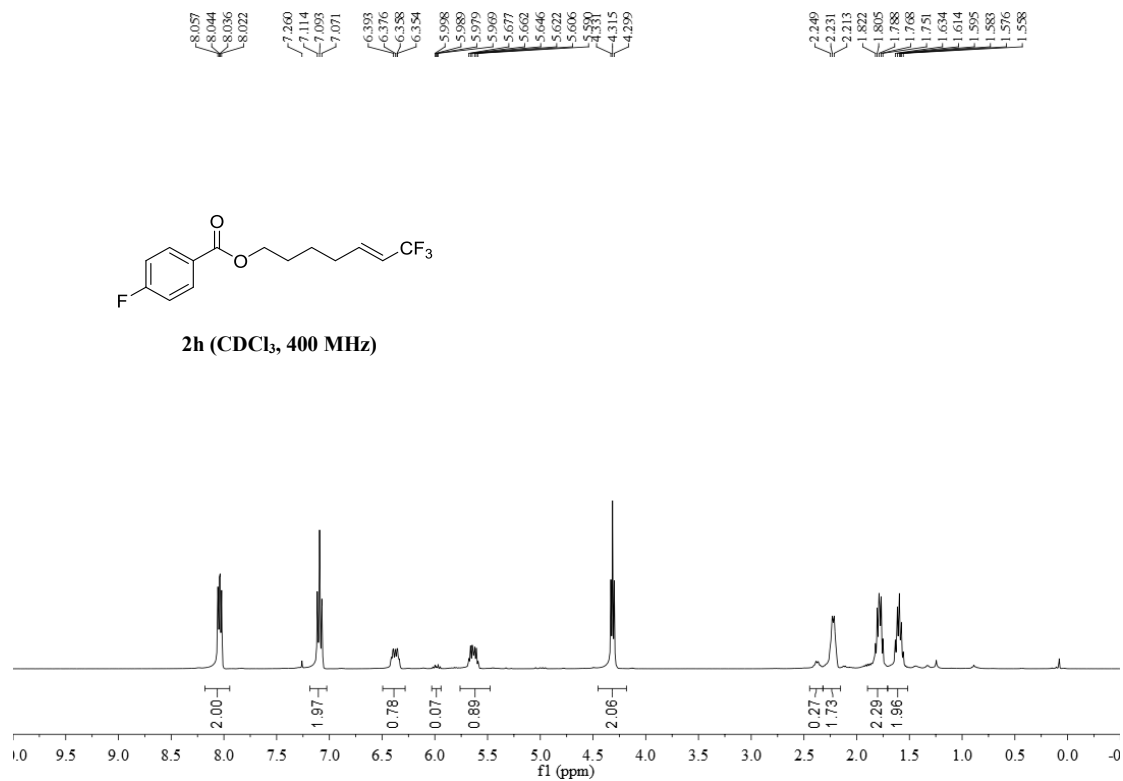
2e (CDCl₃, 101 MHz)

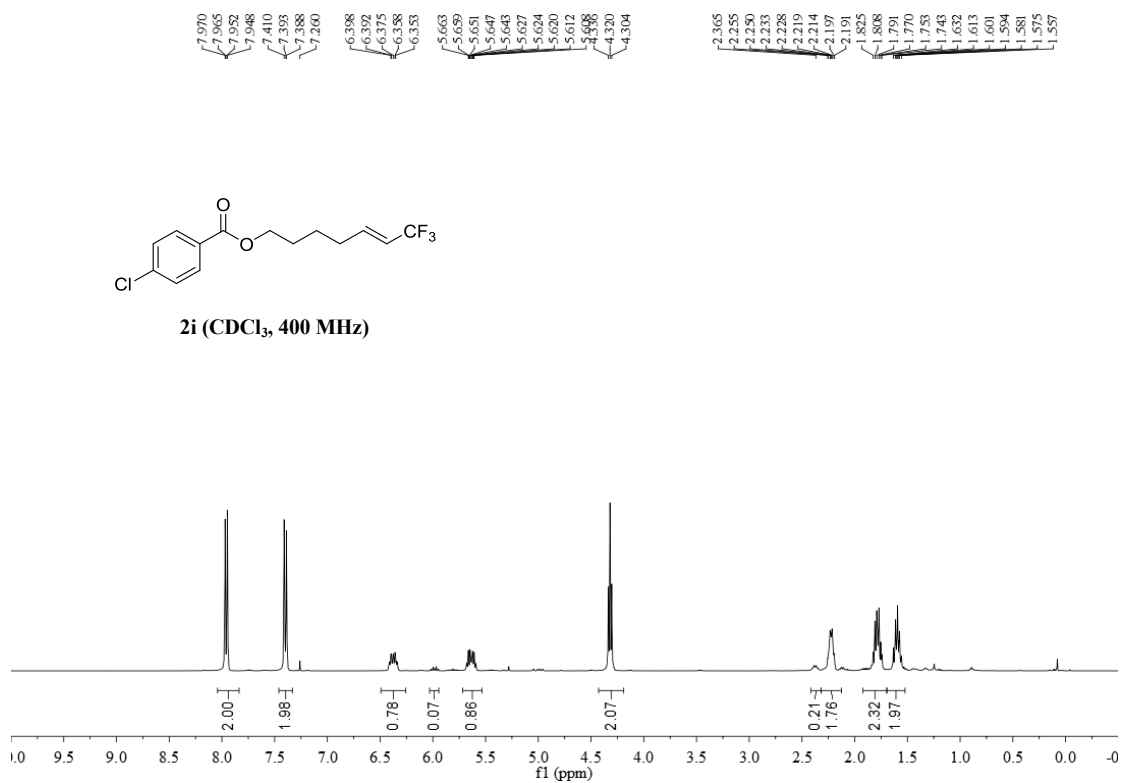
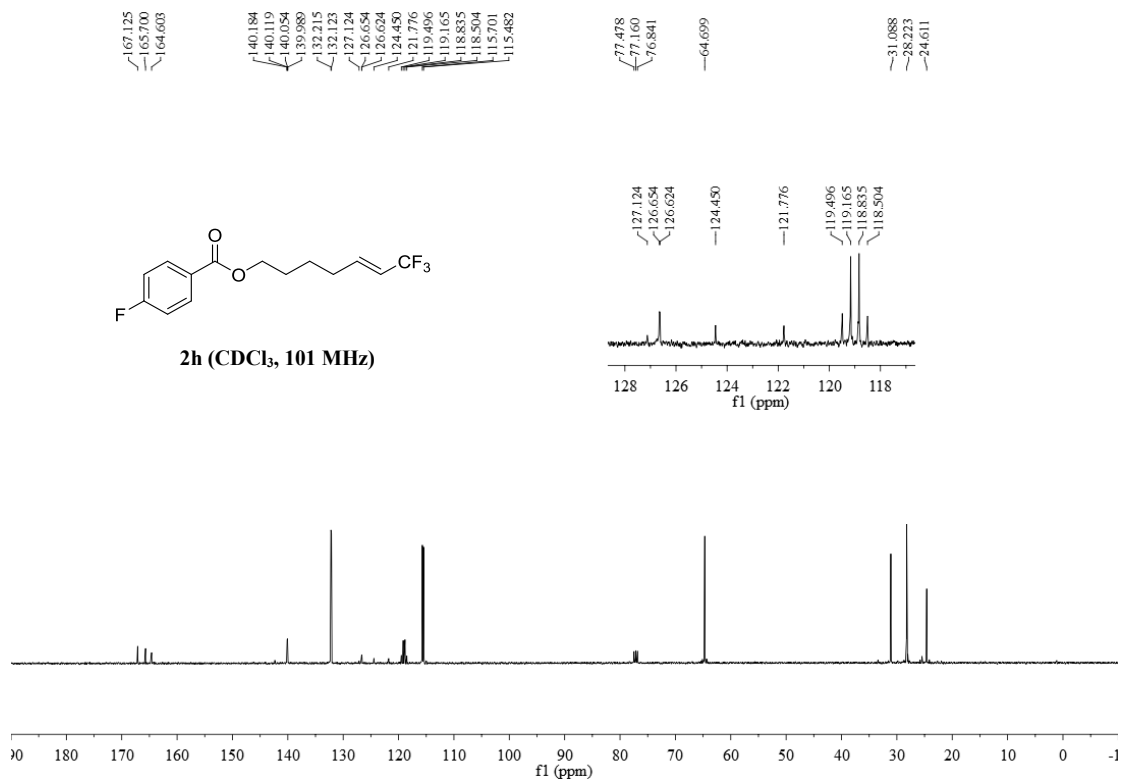


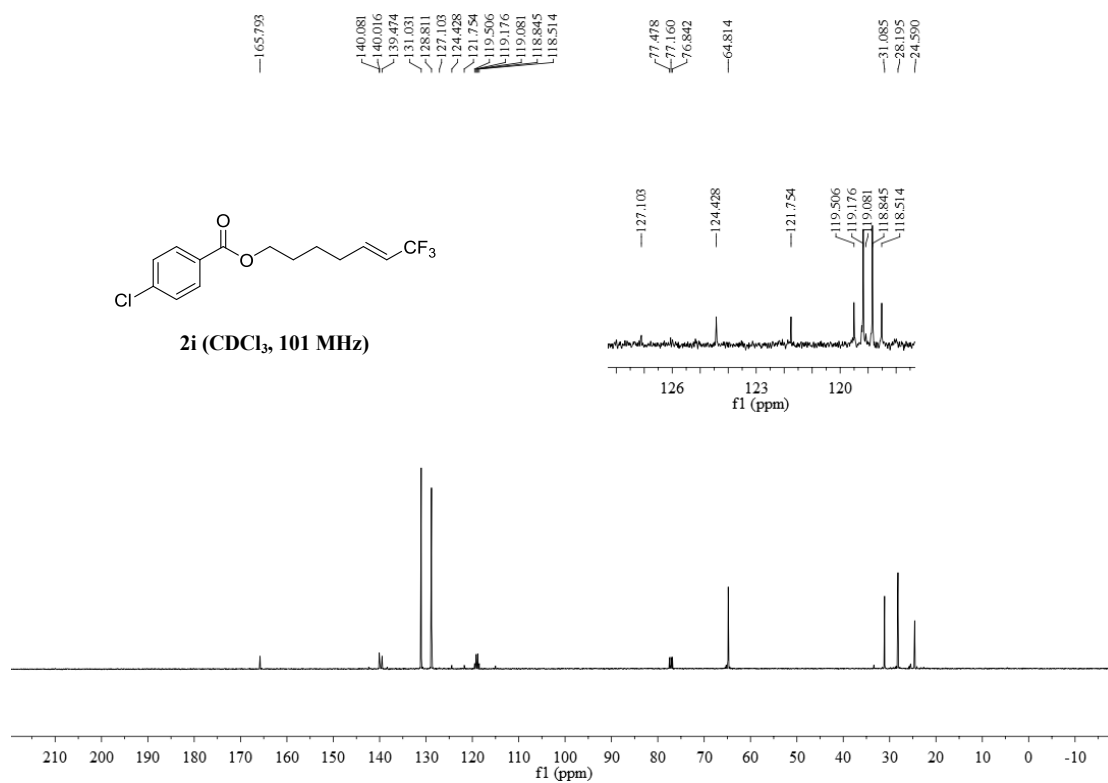
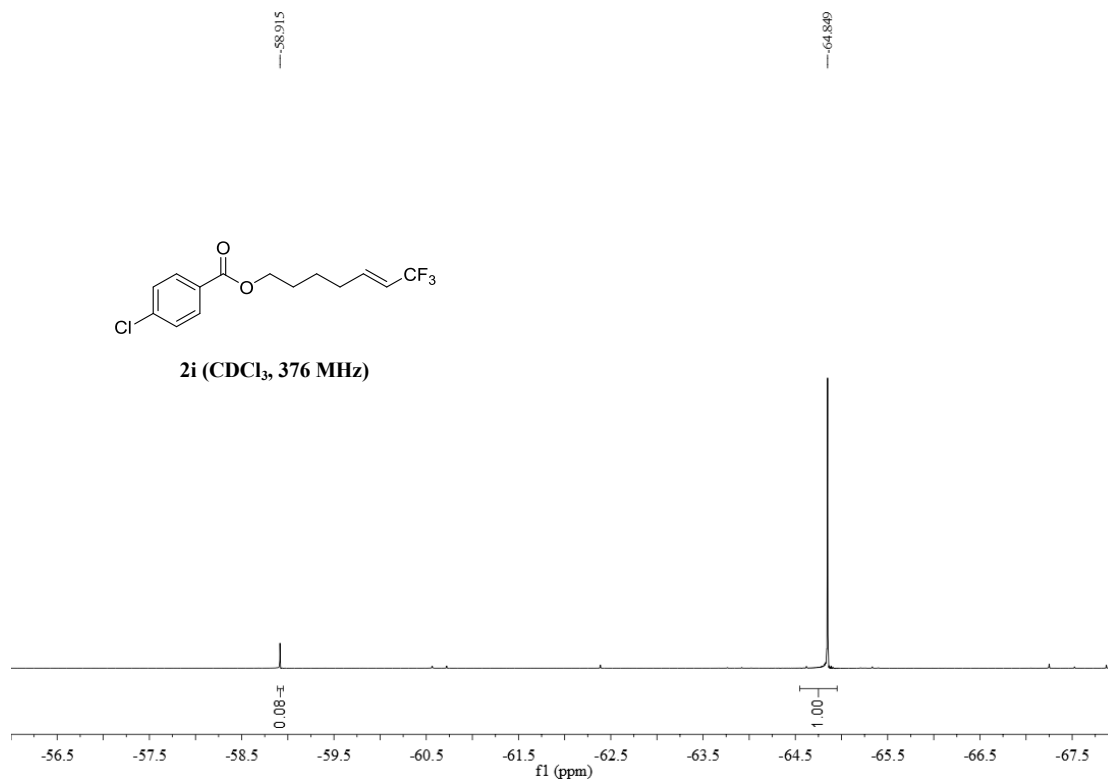


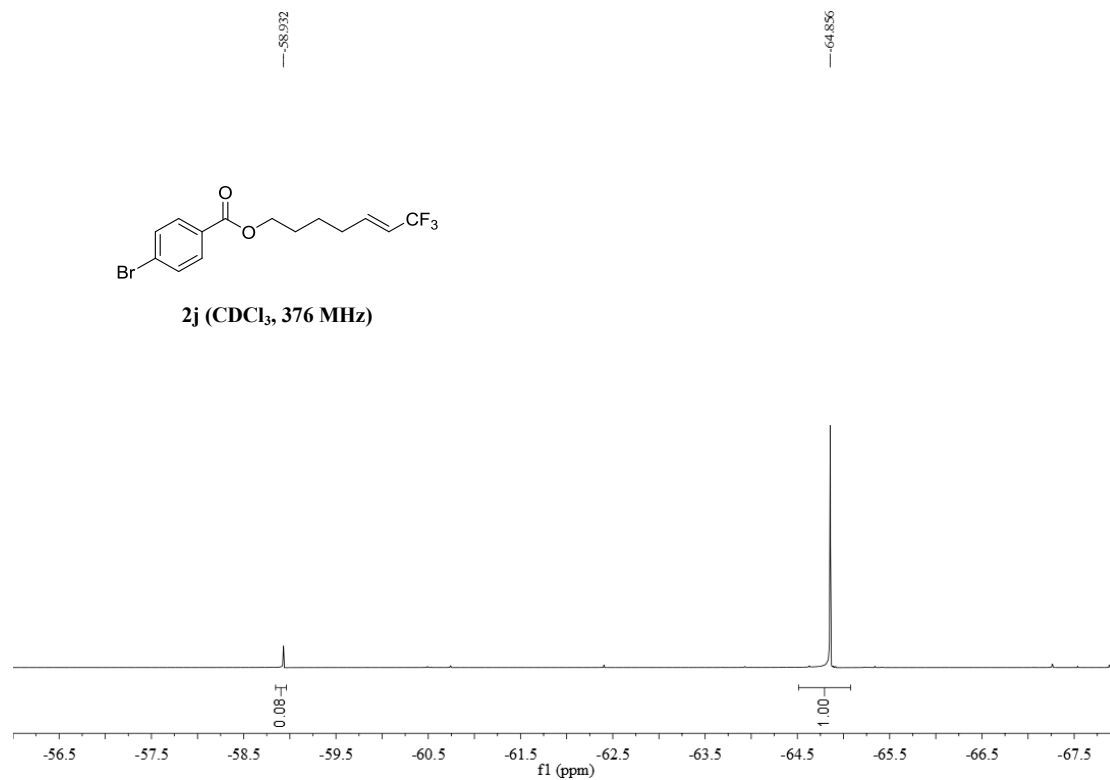
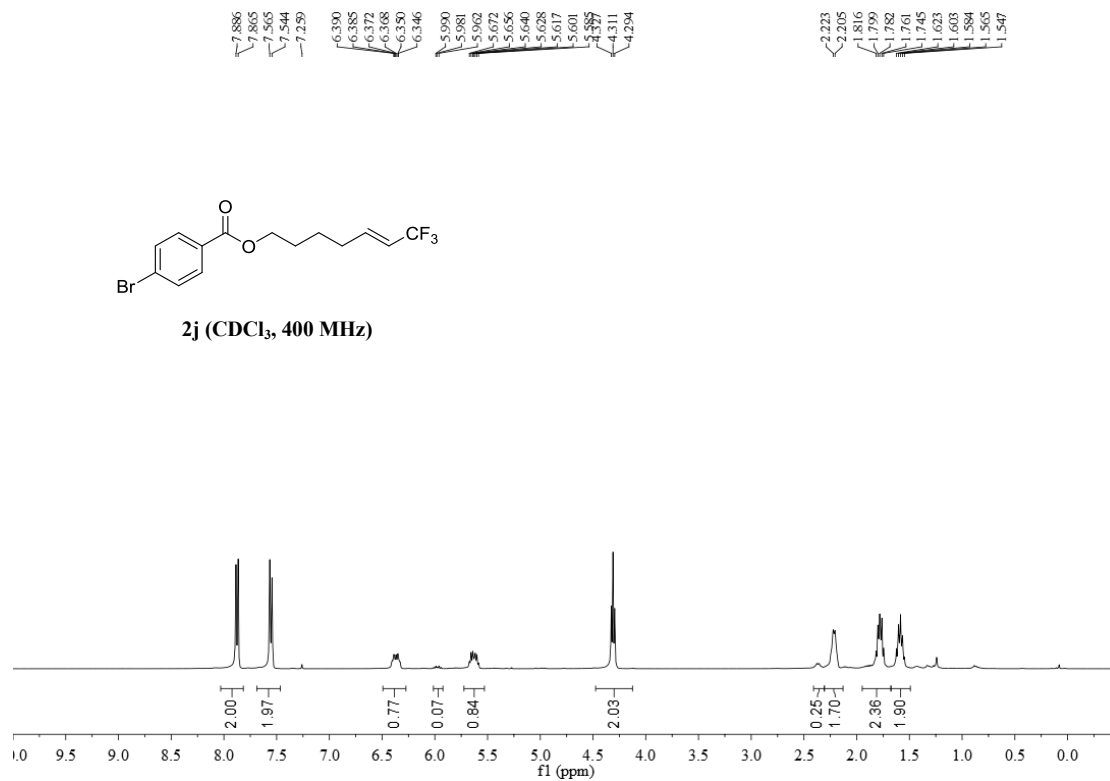


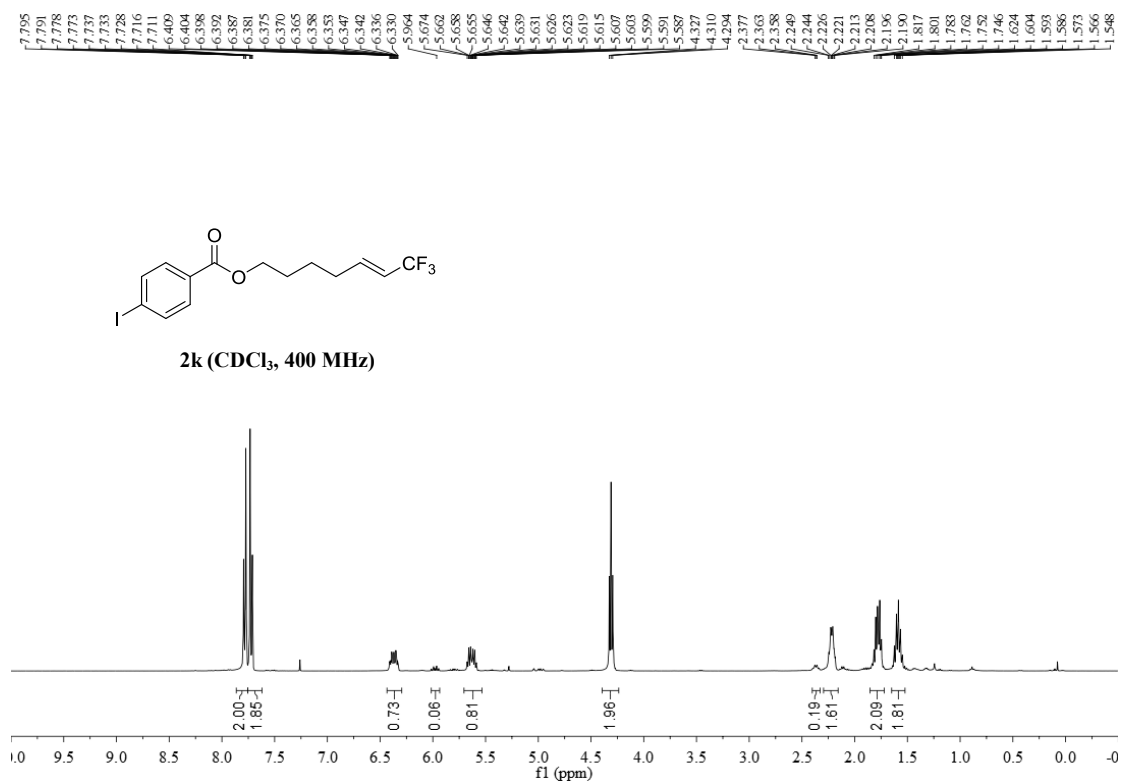
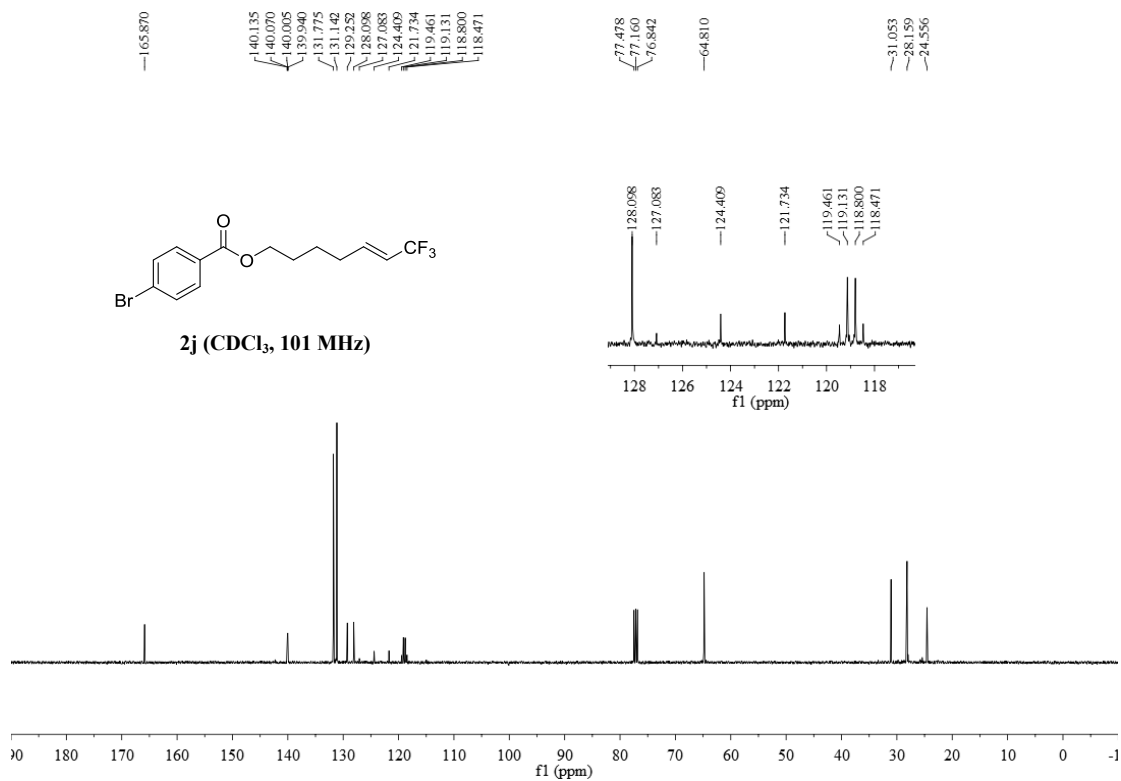


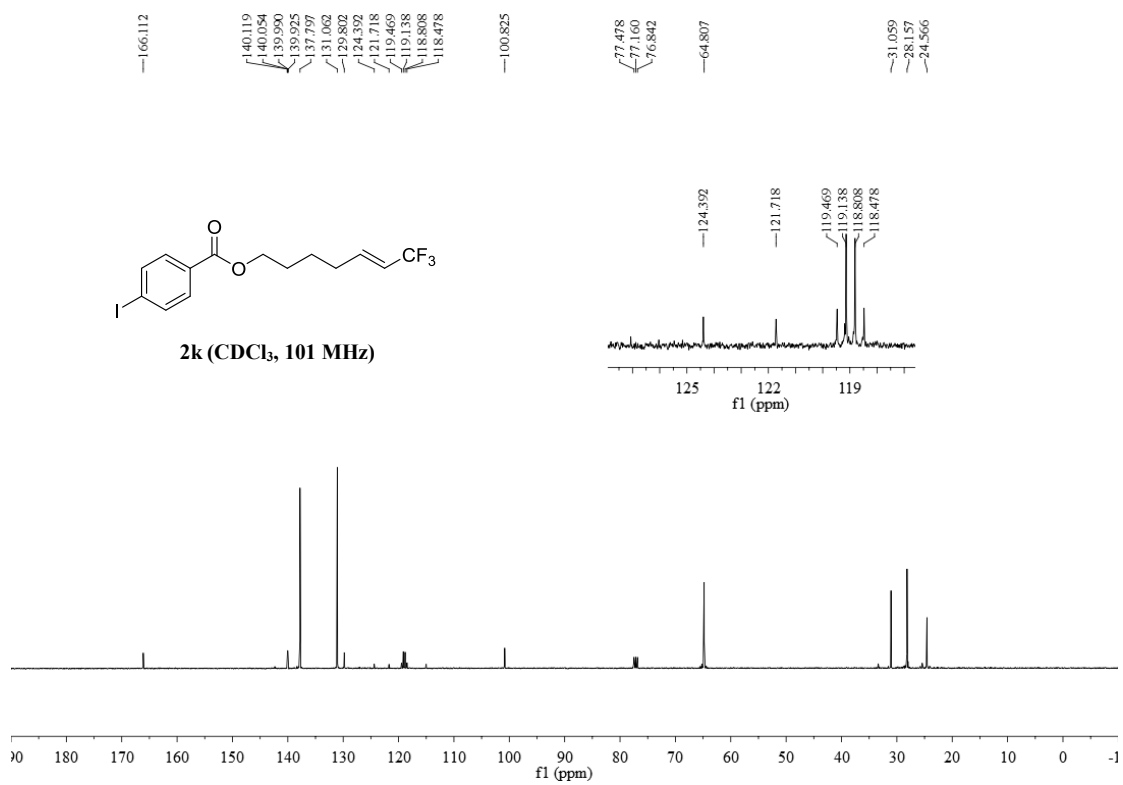
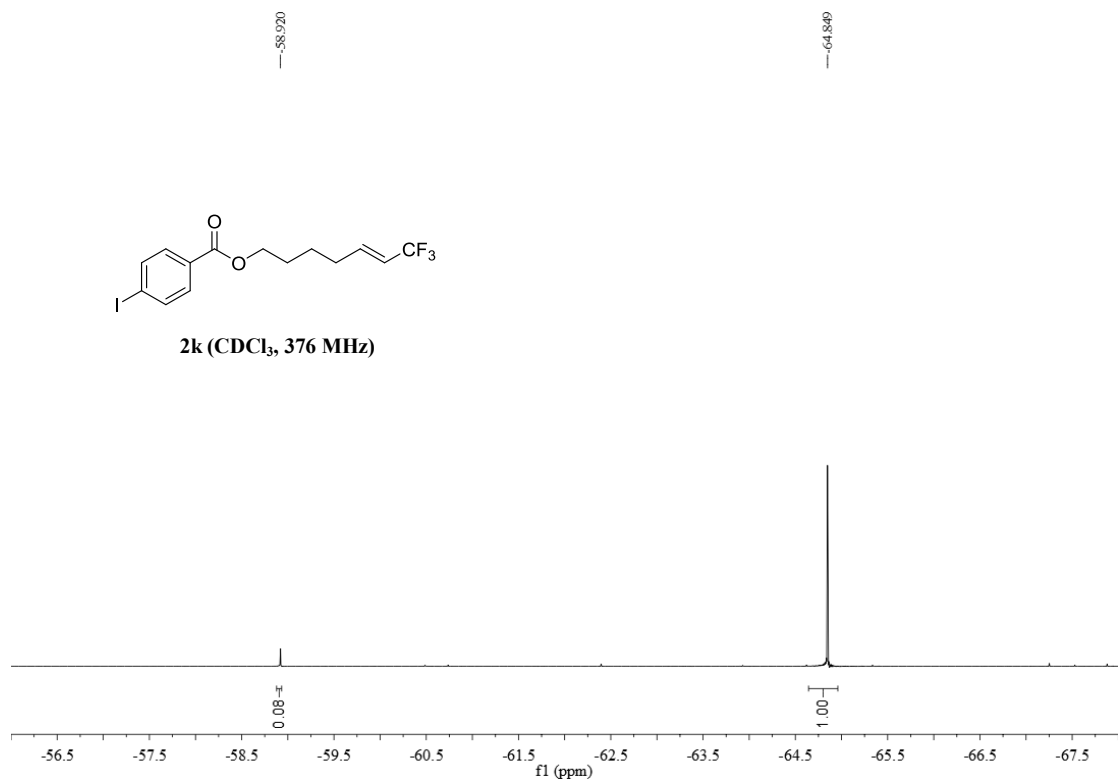


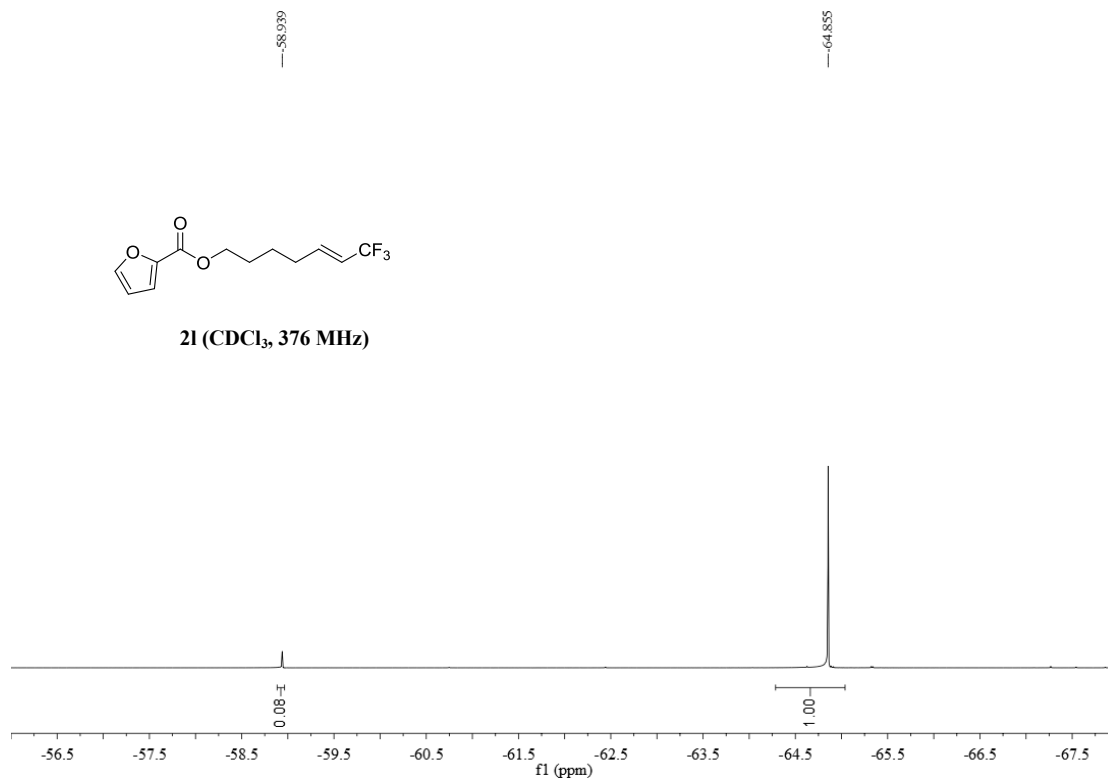
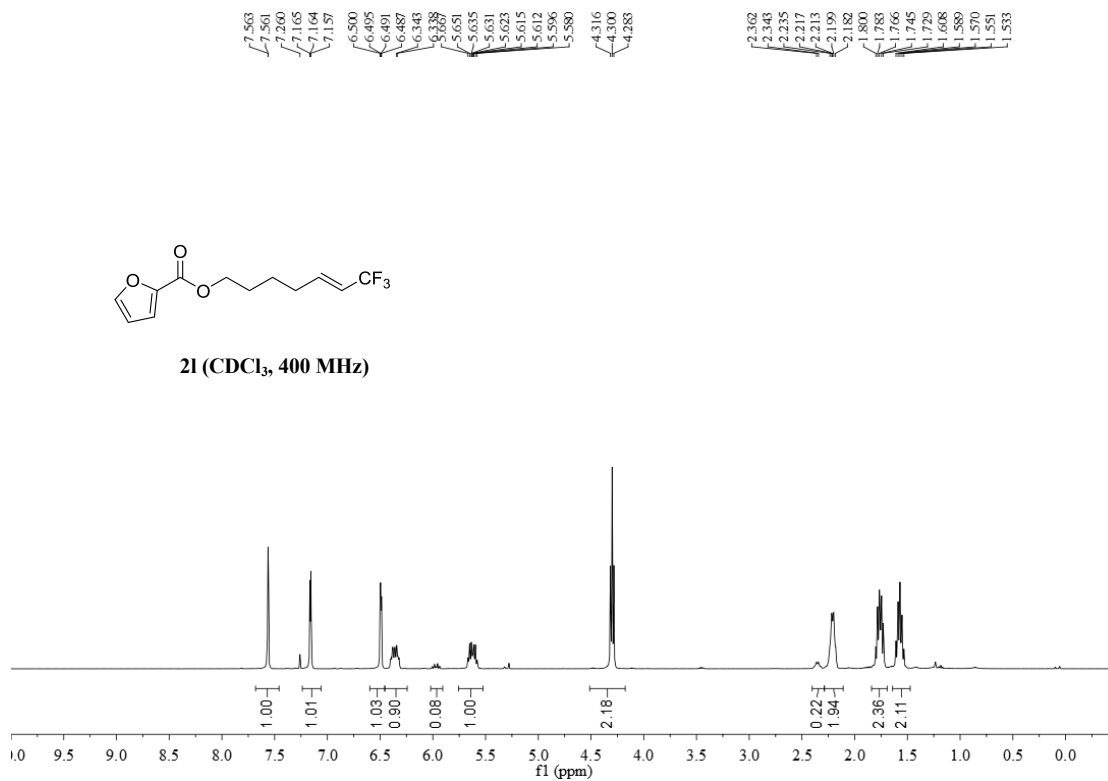


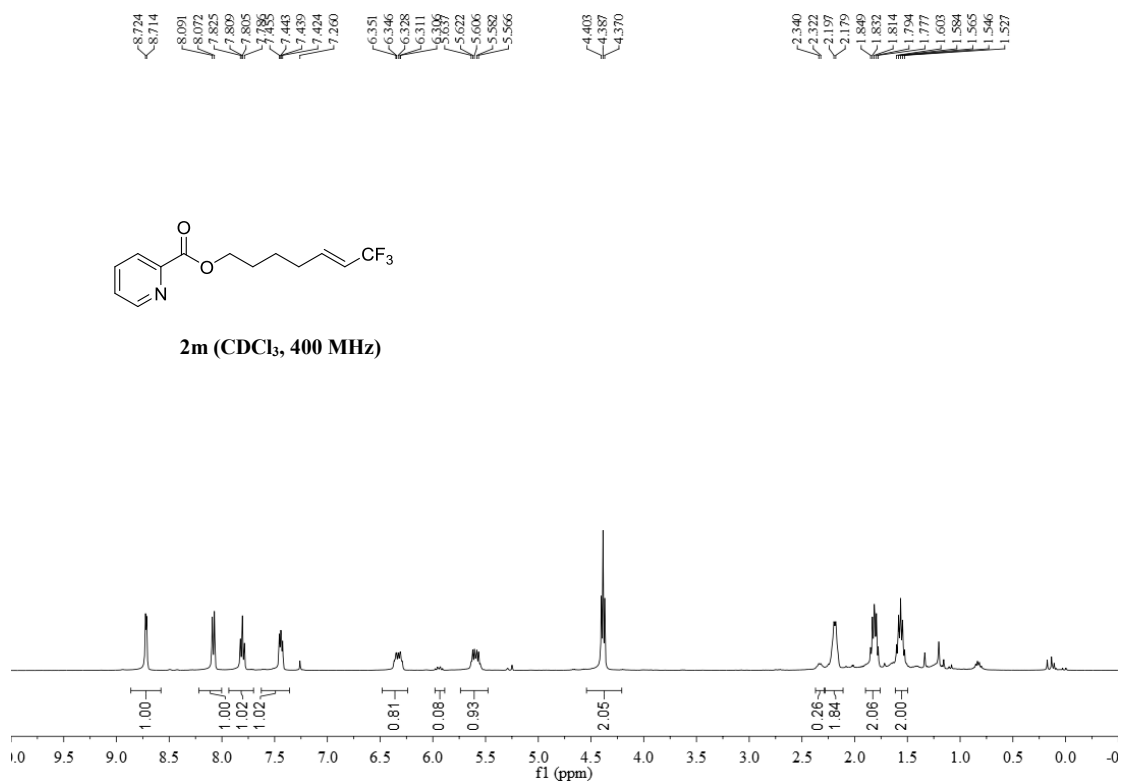
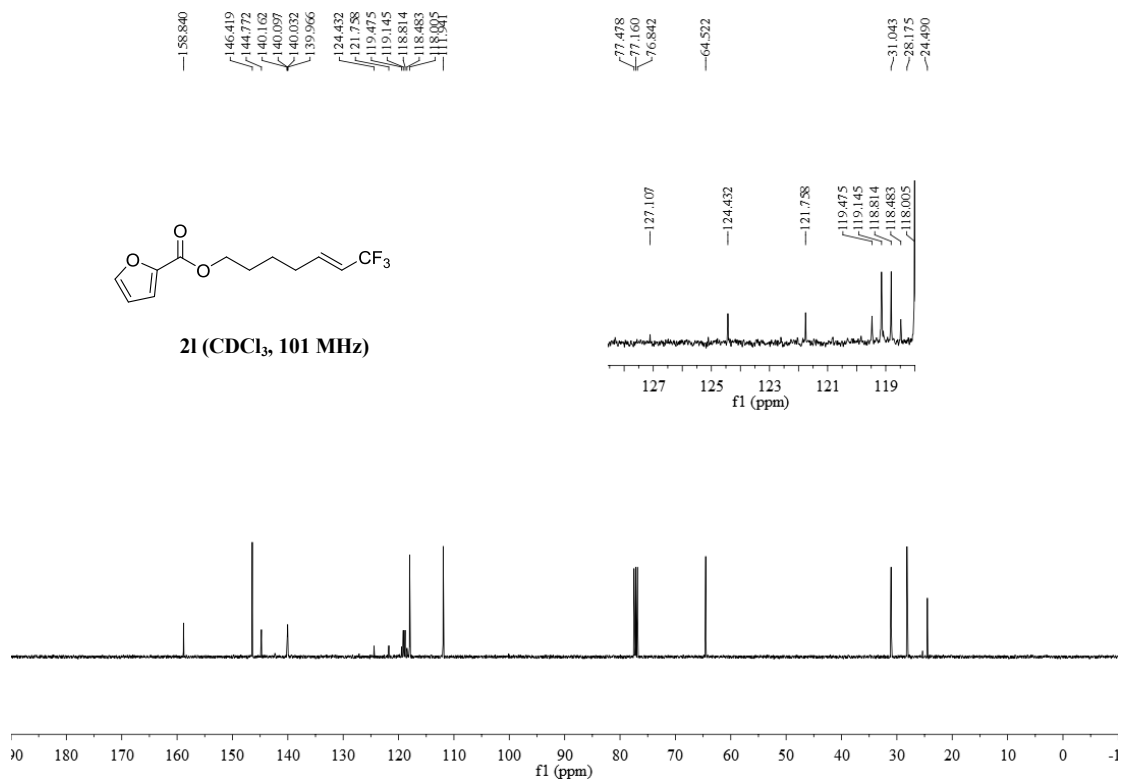


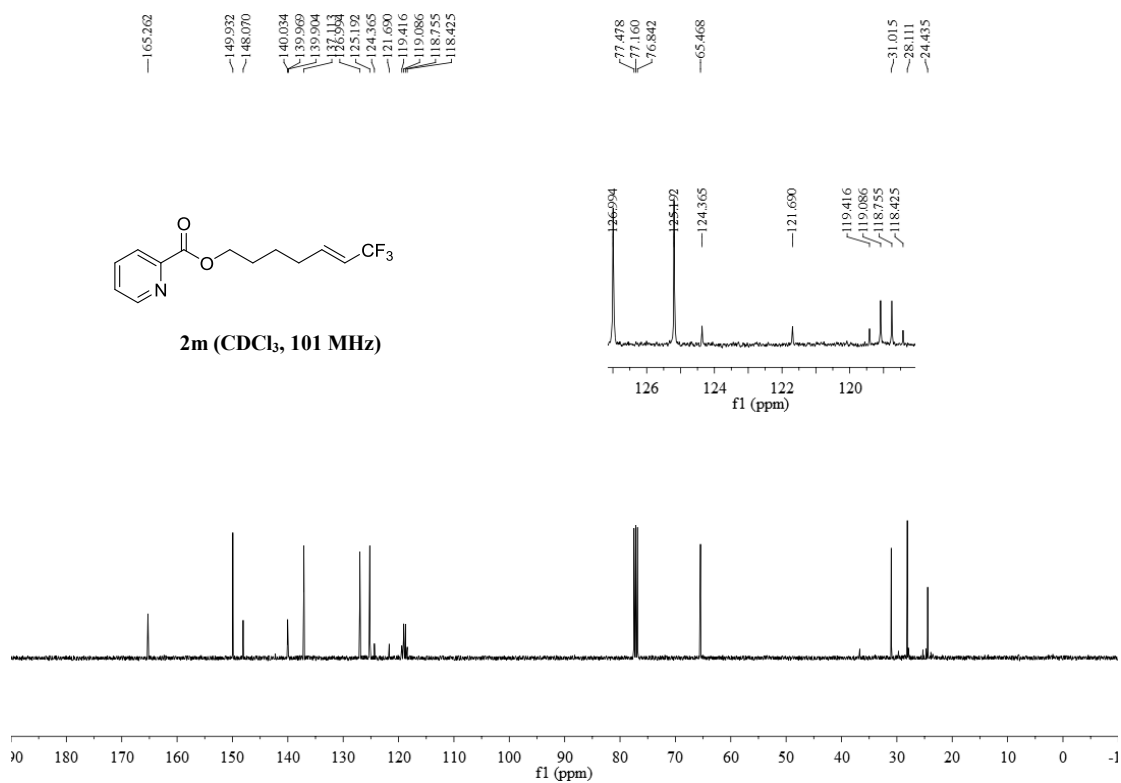
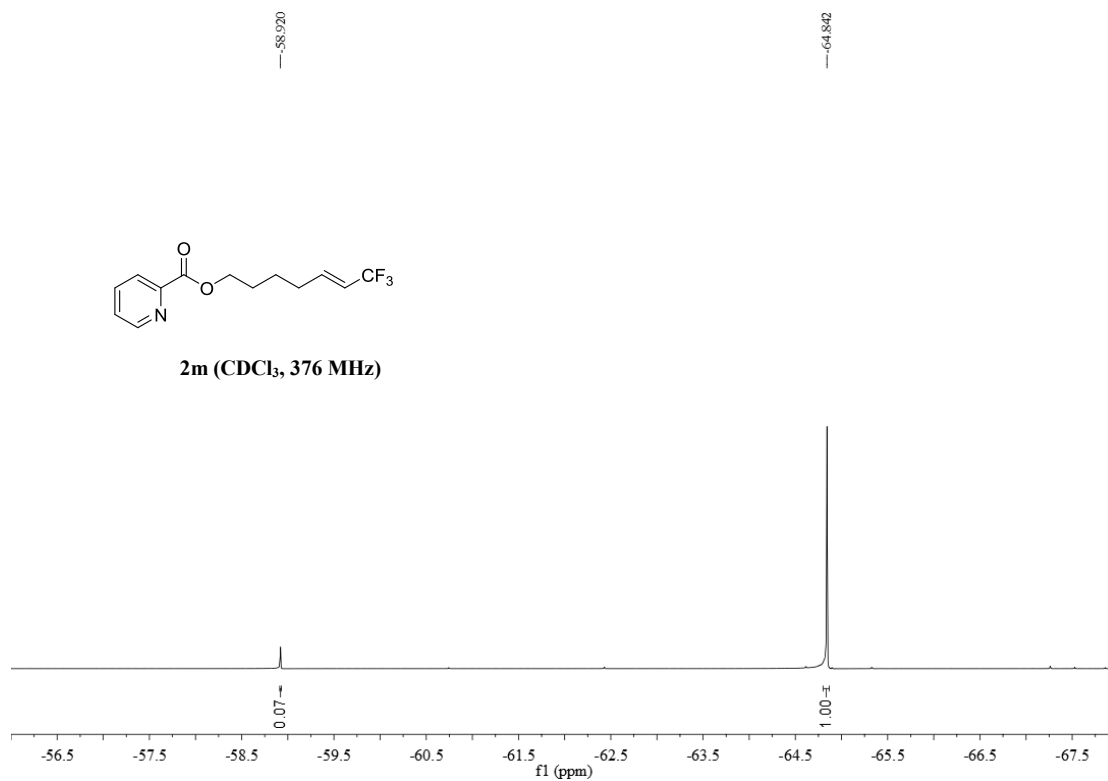


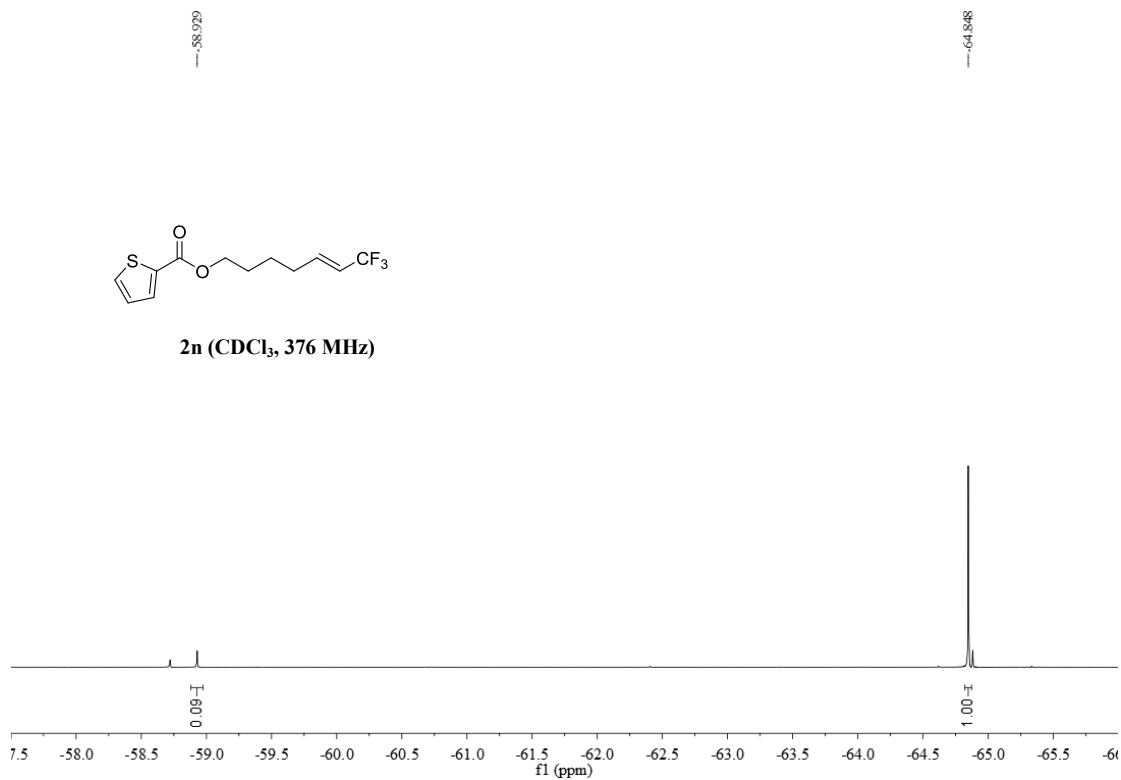
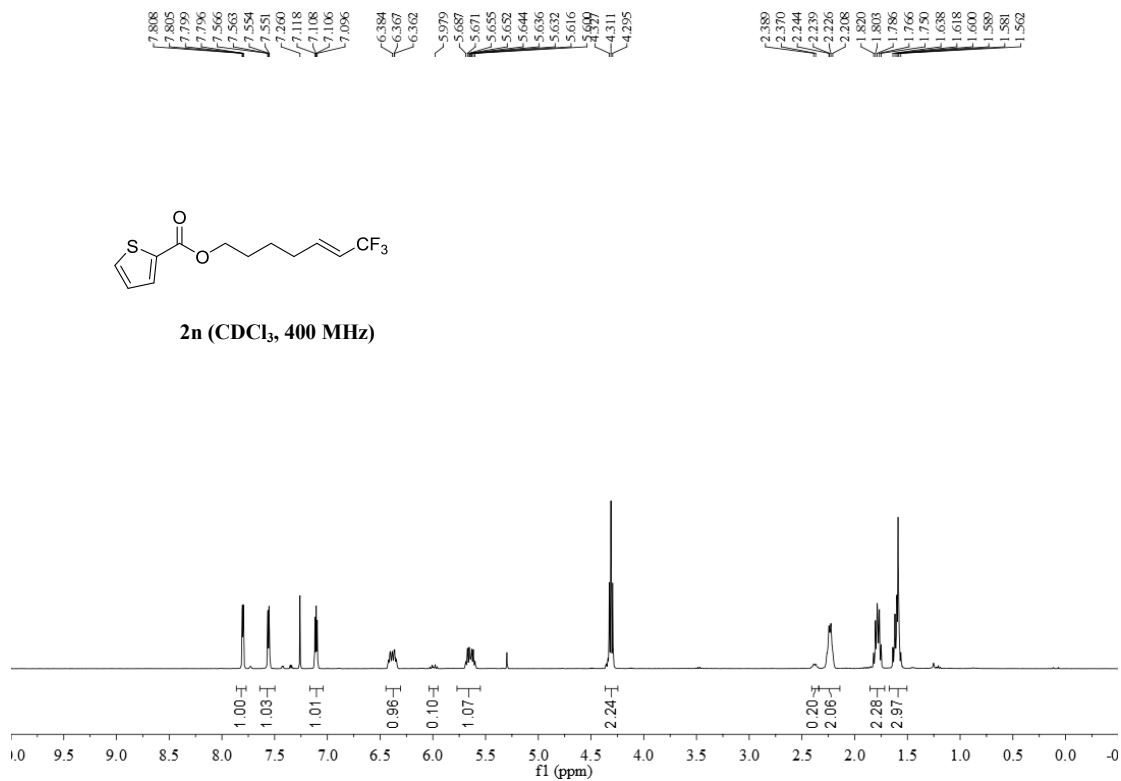


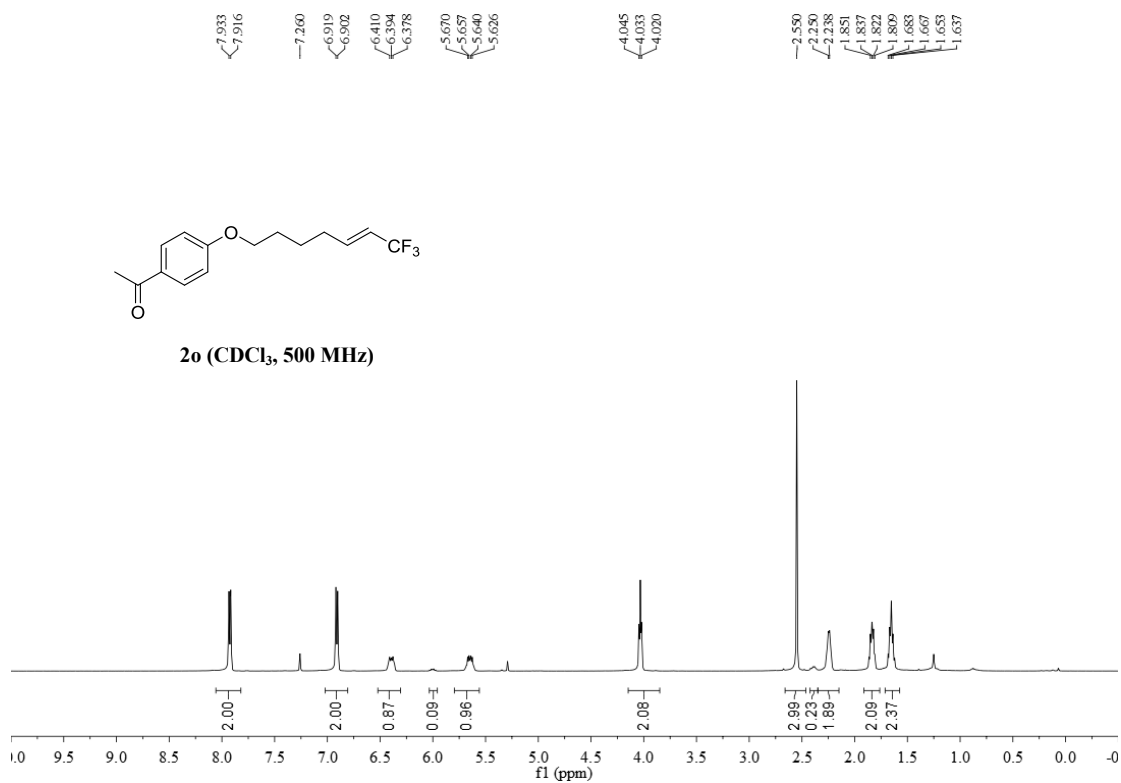
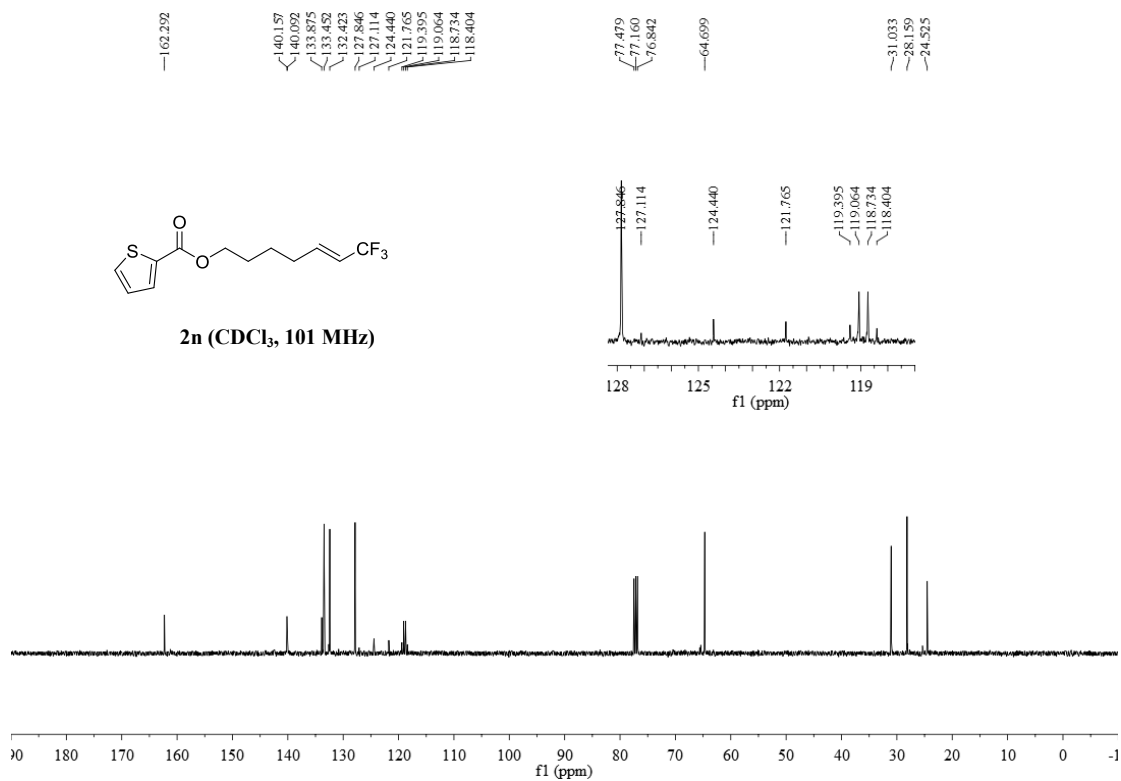


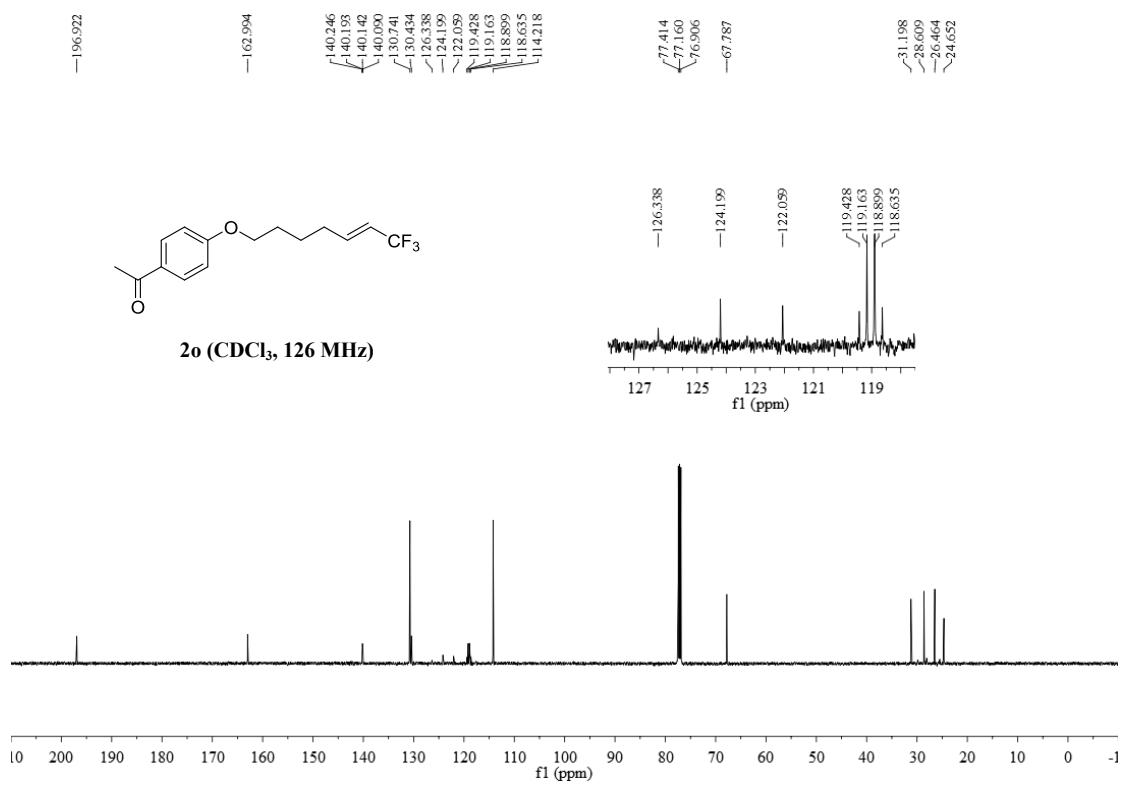
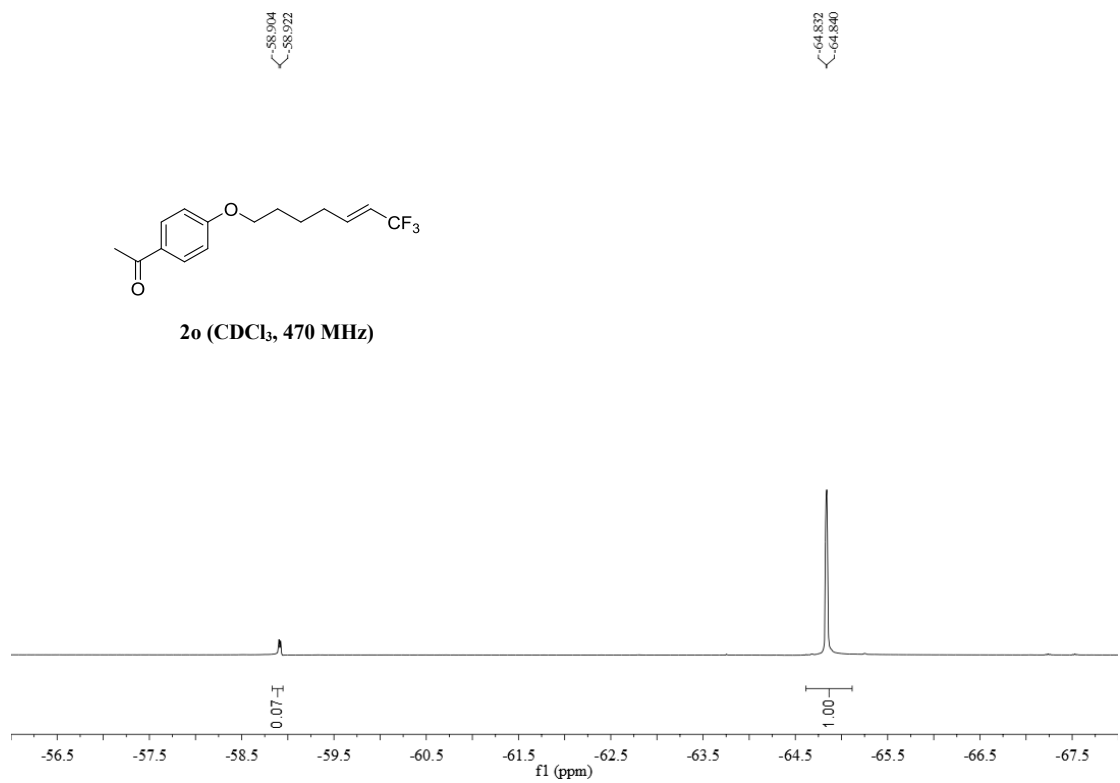


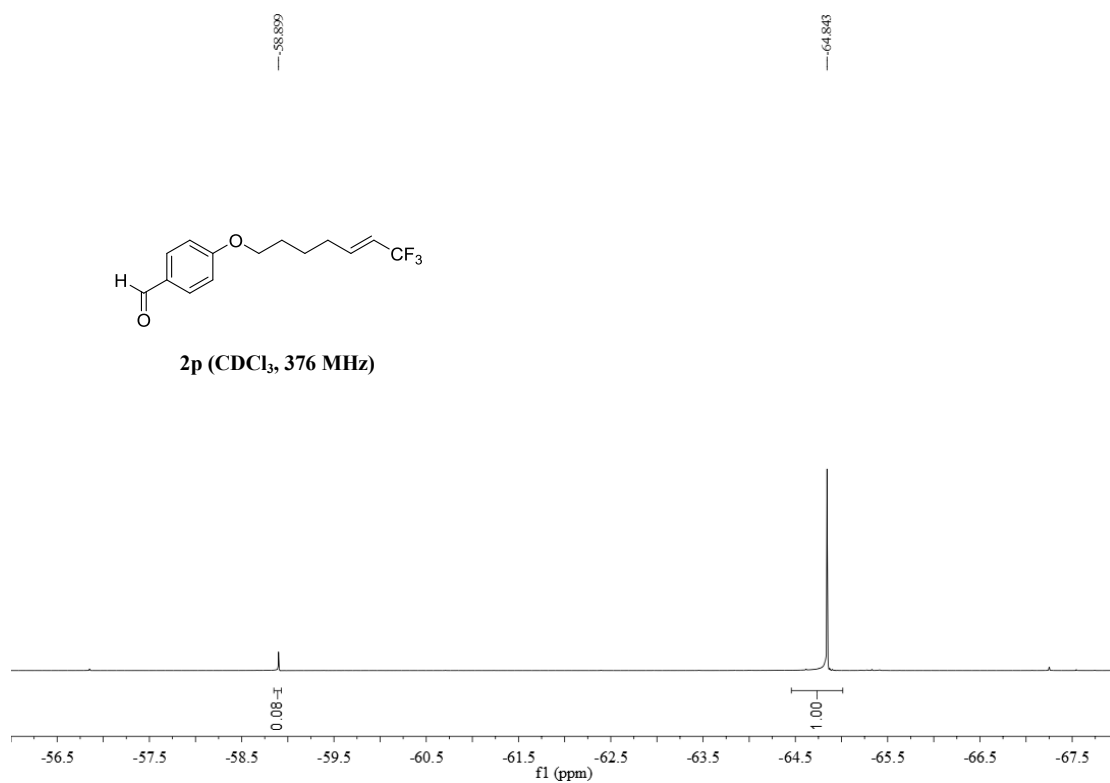
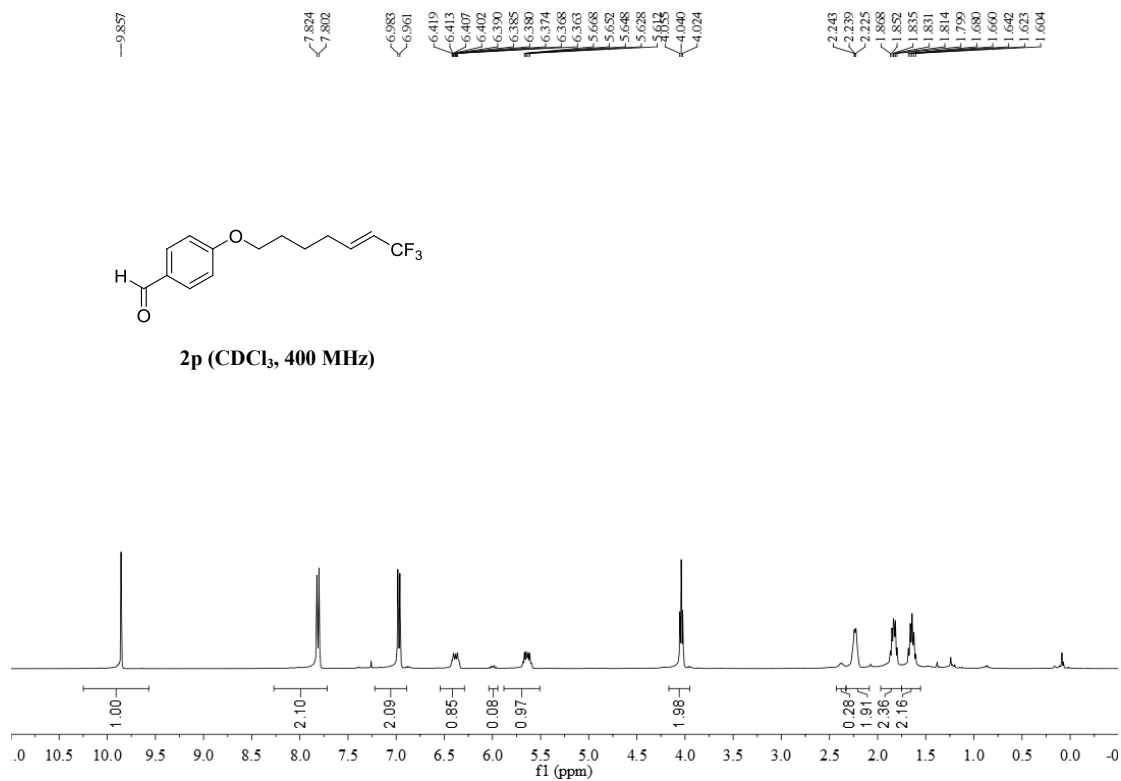


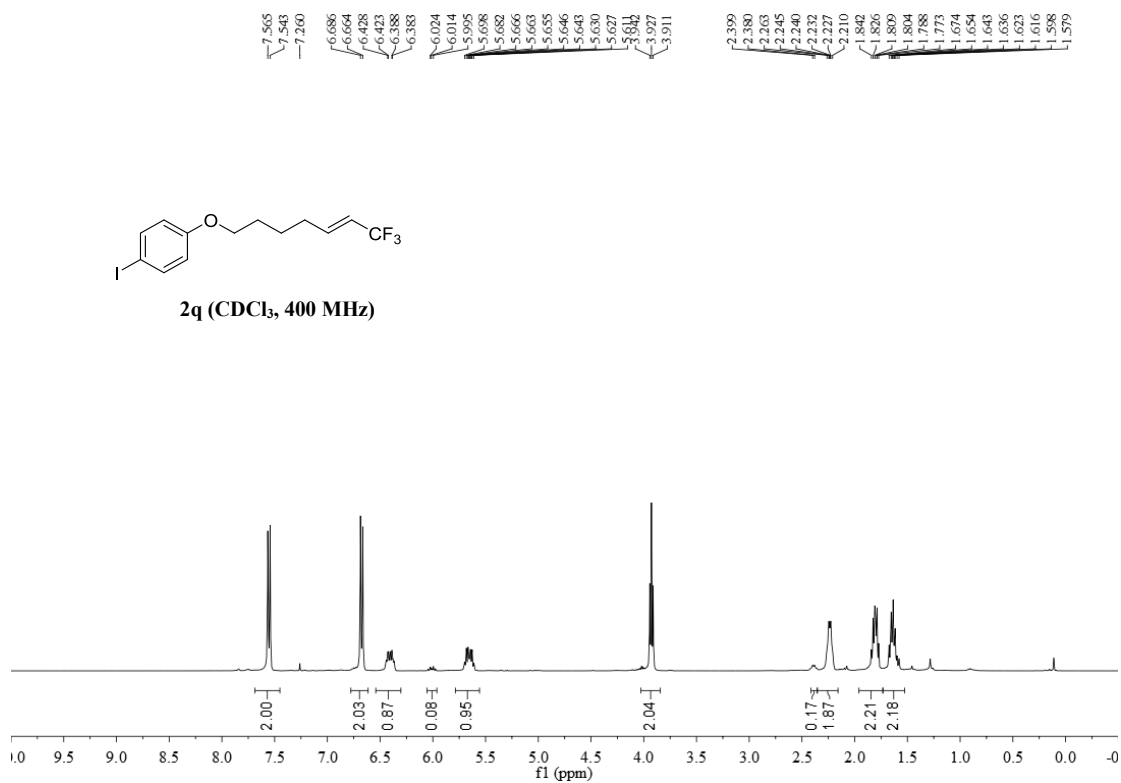
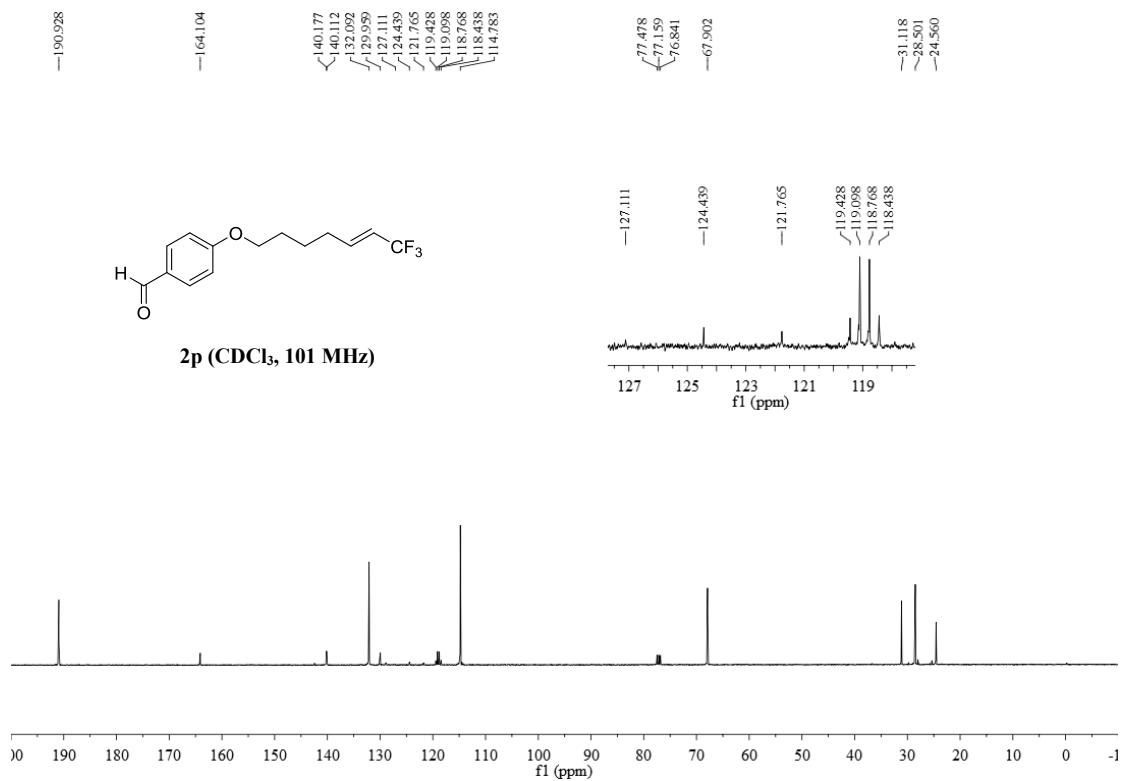


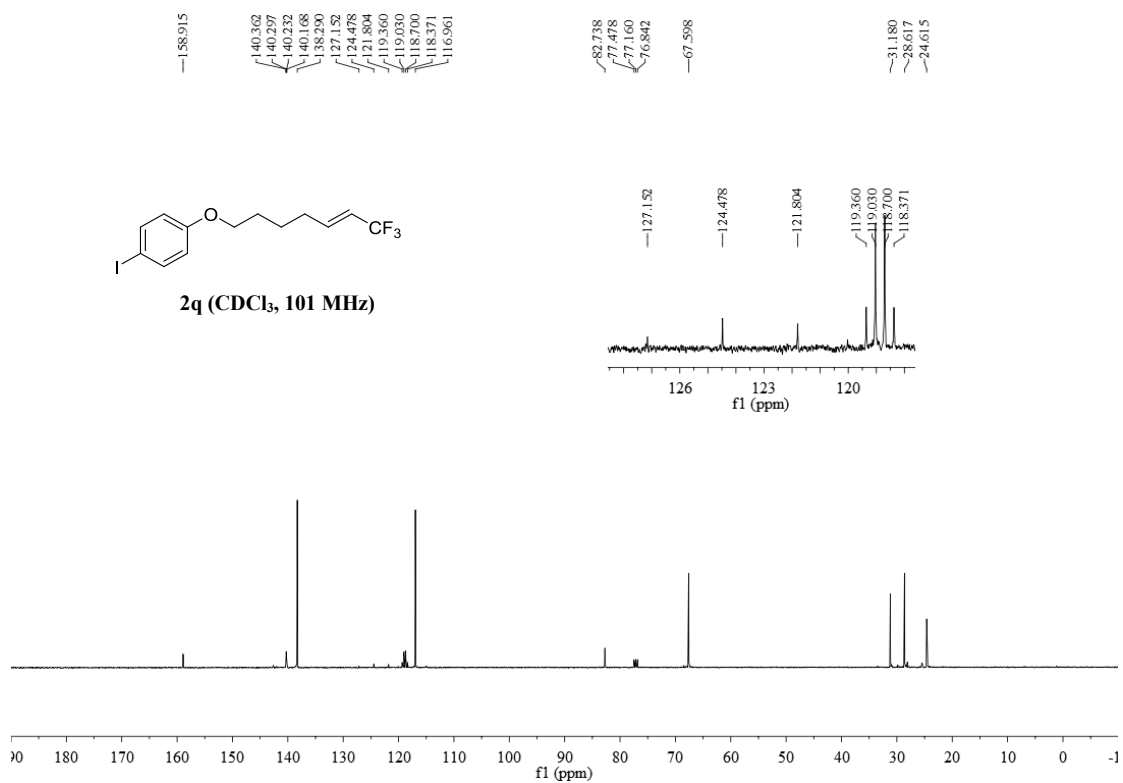
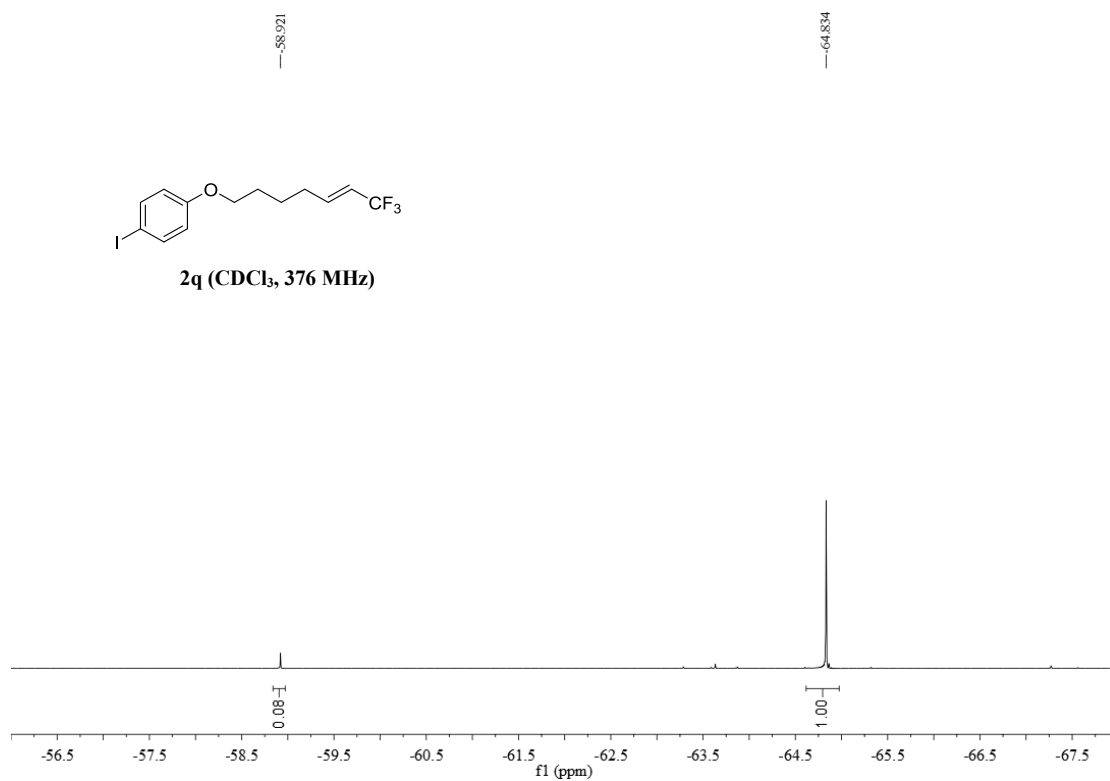


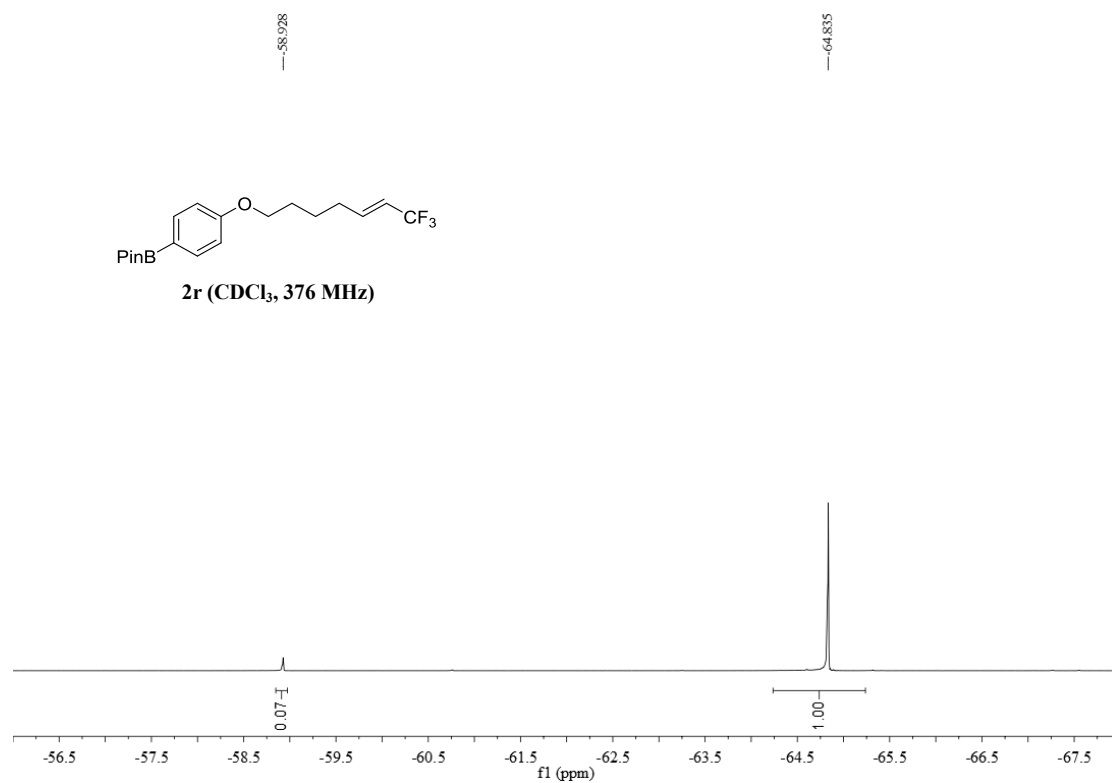
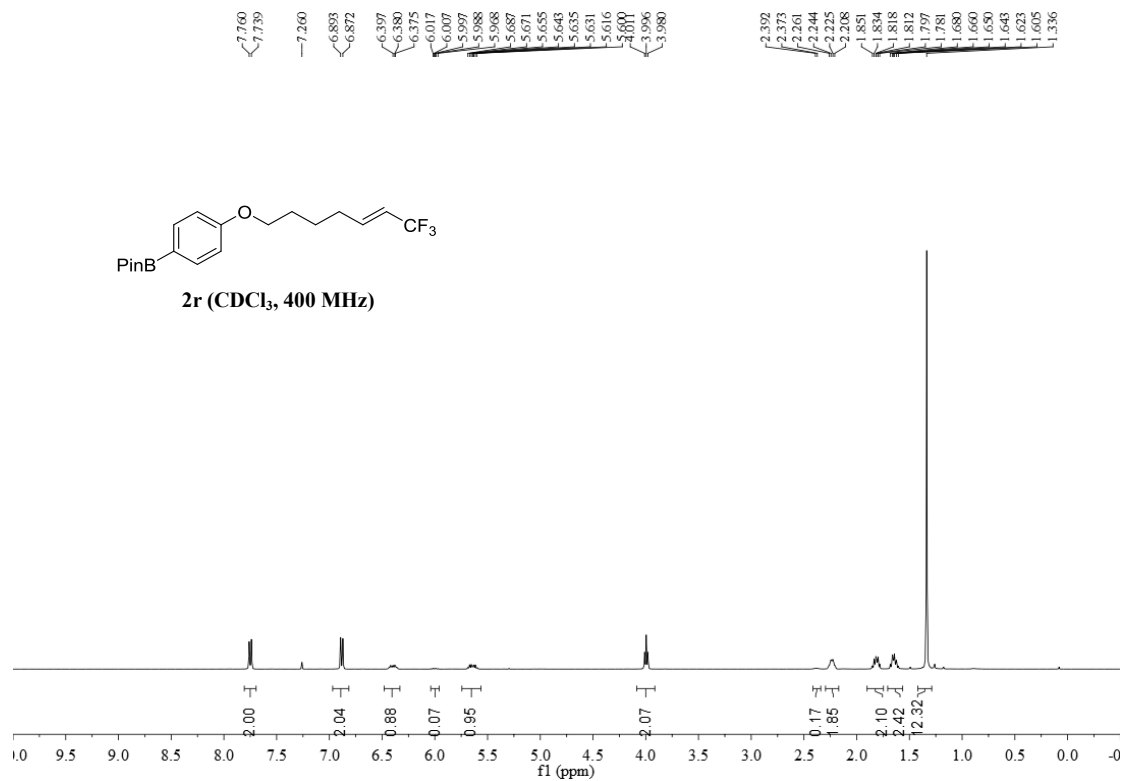


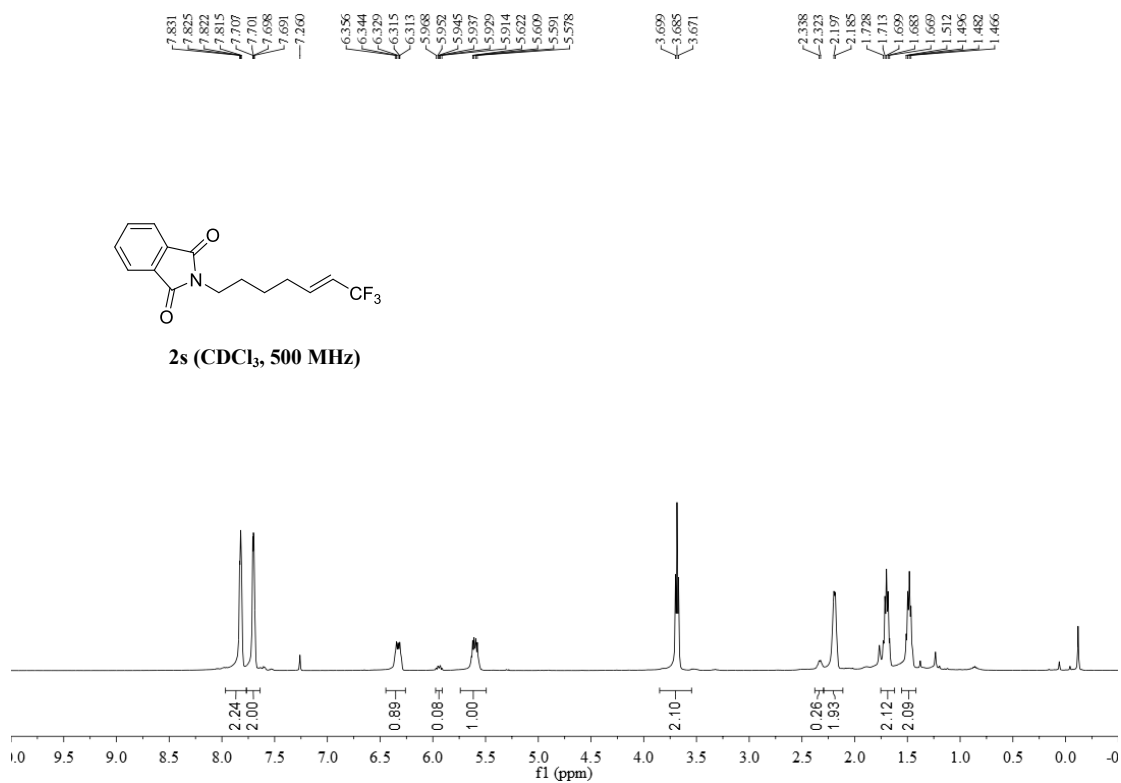
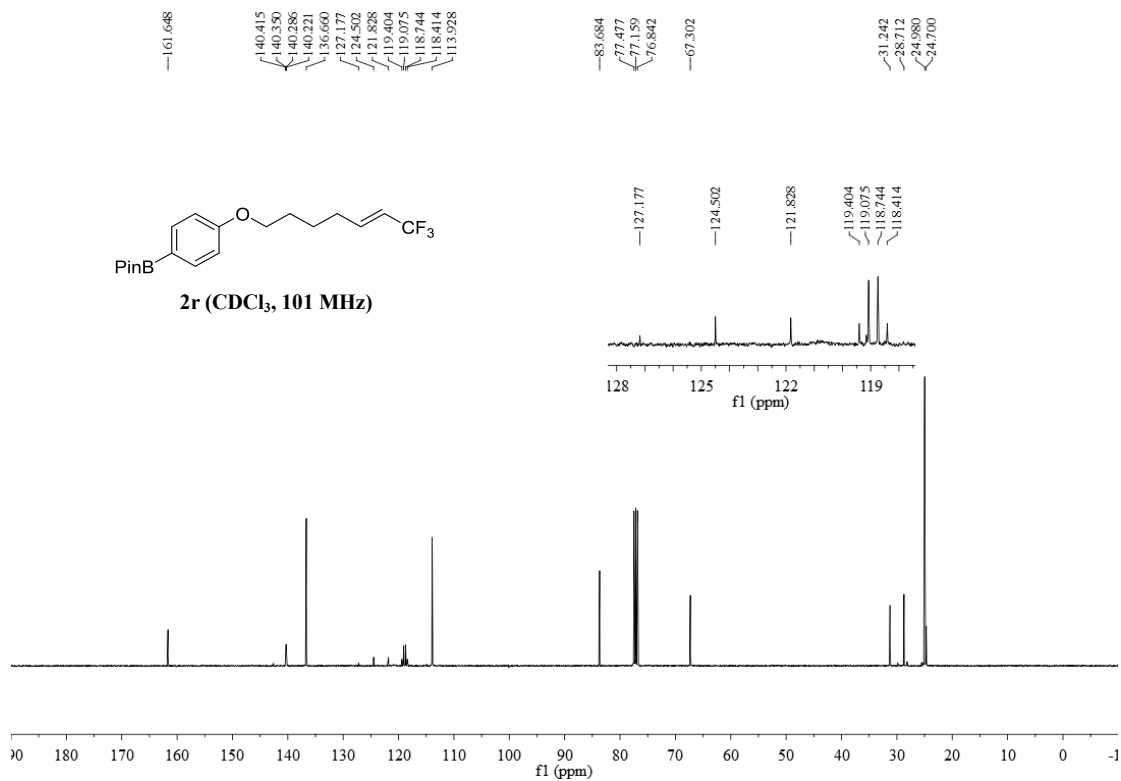


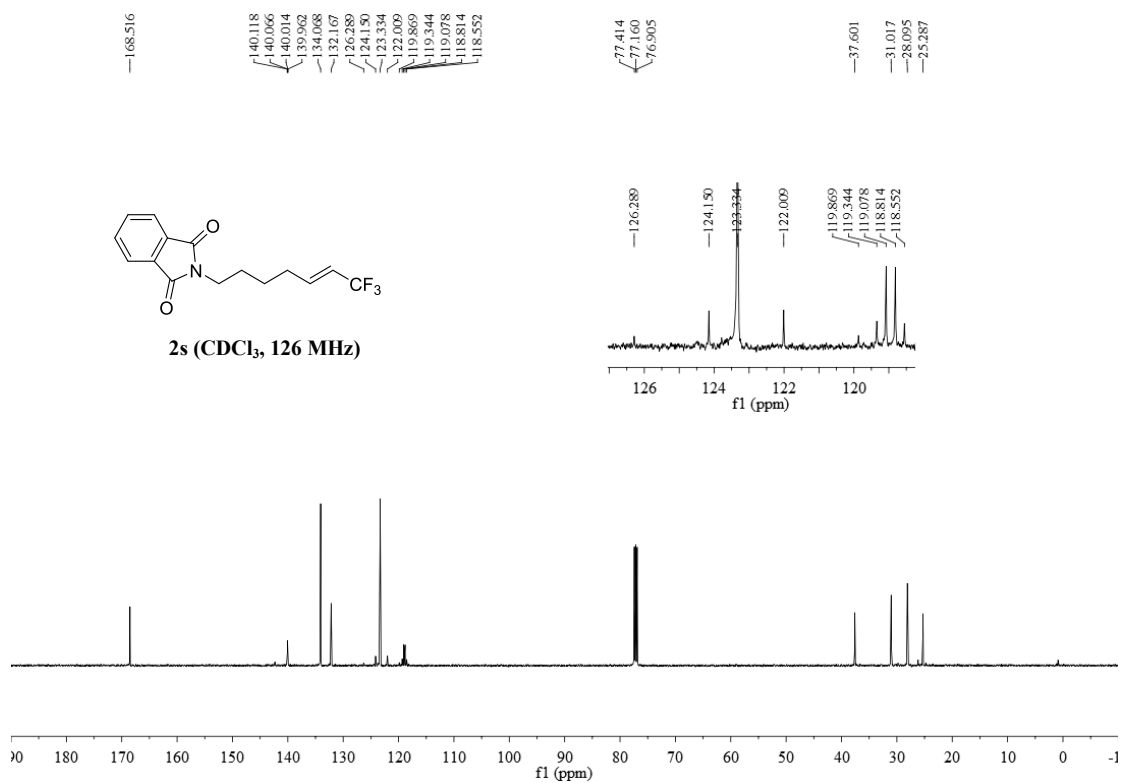
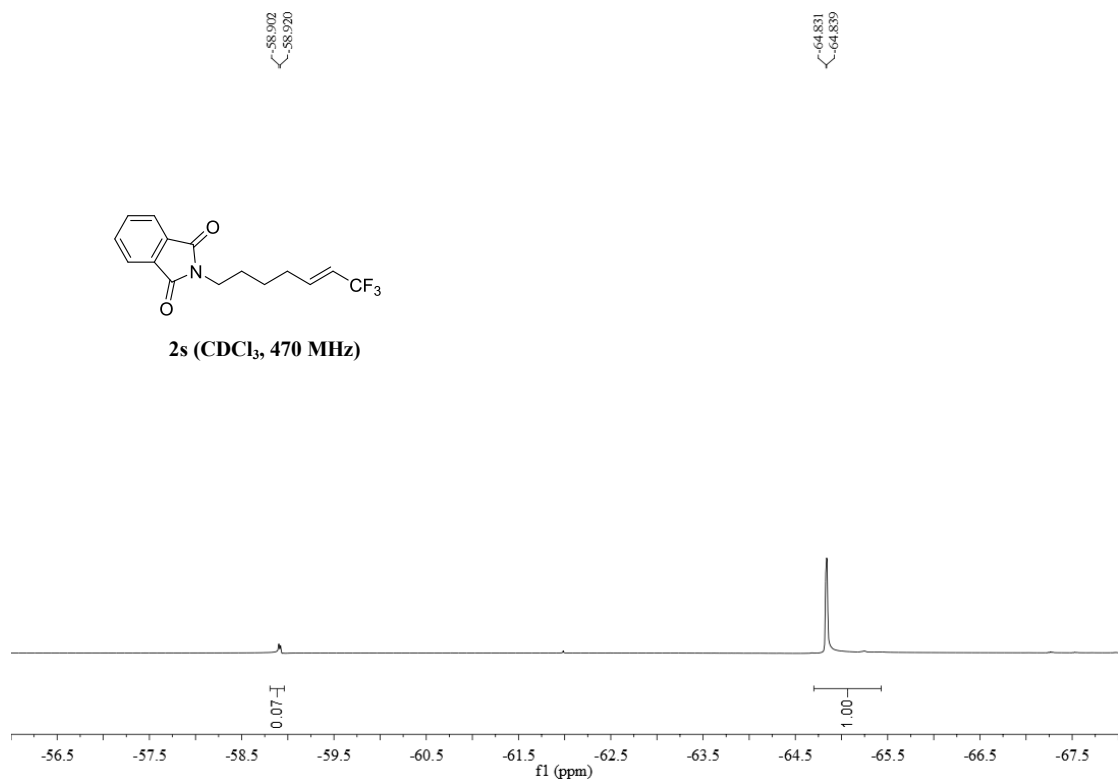


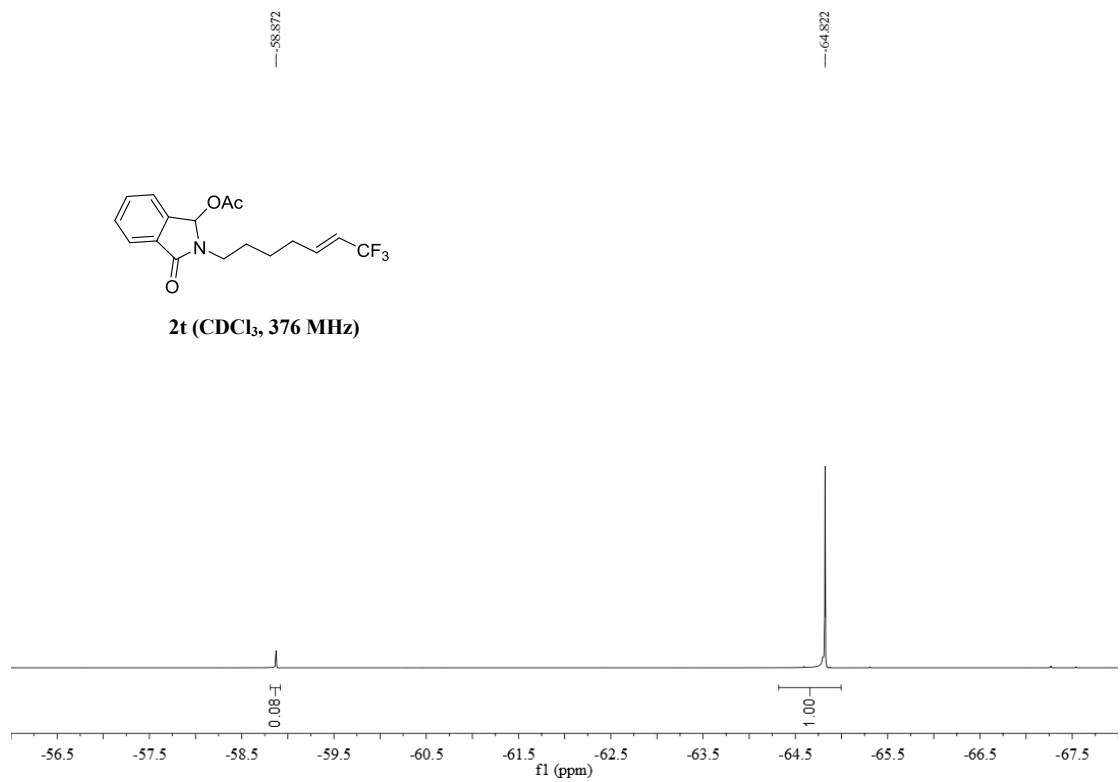
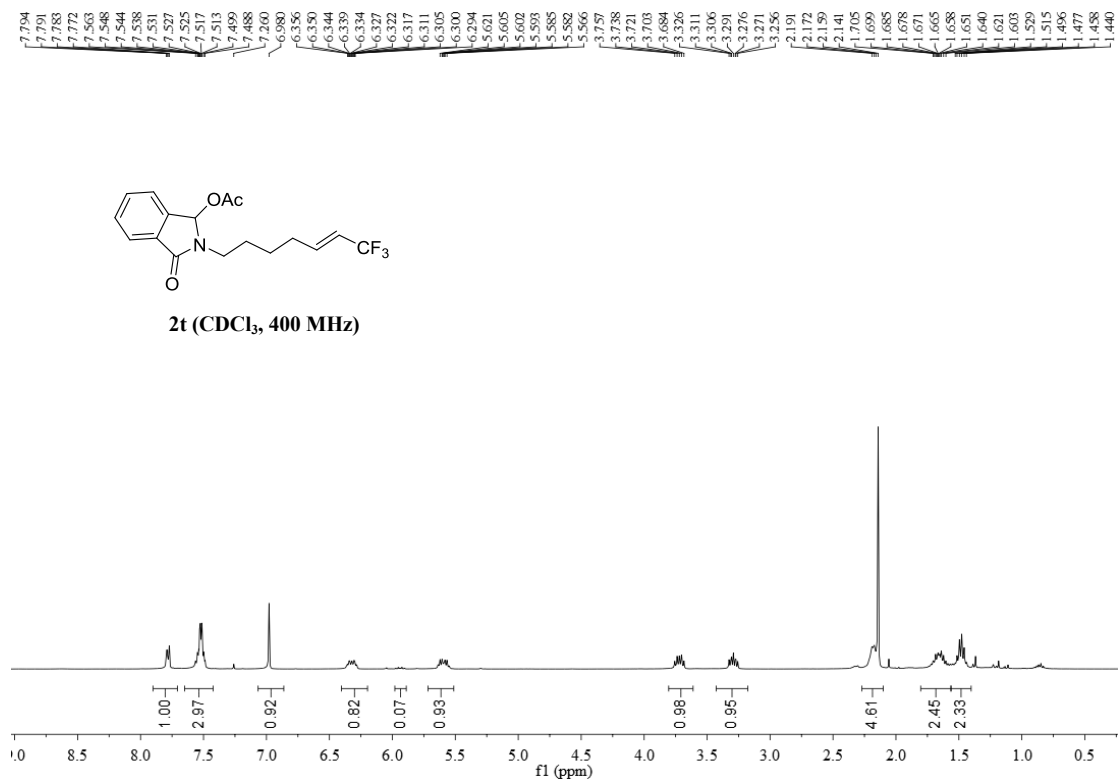


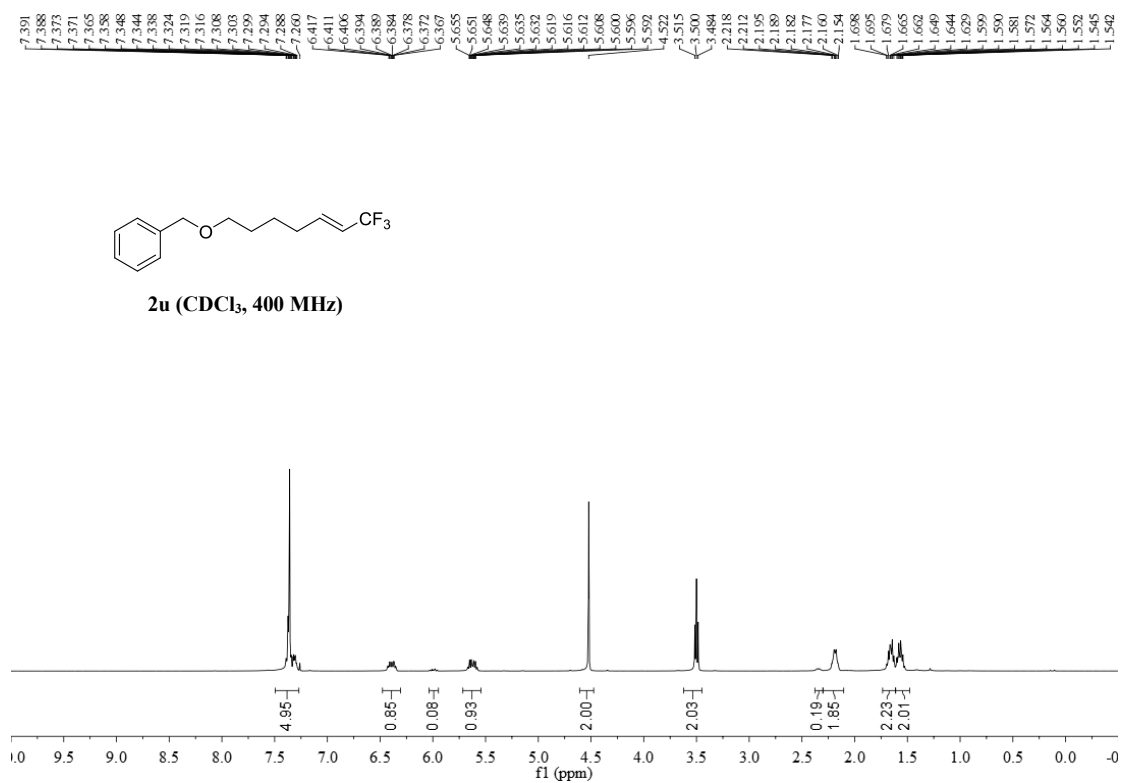
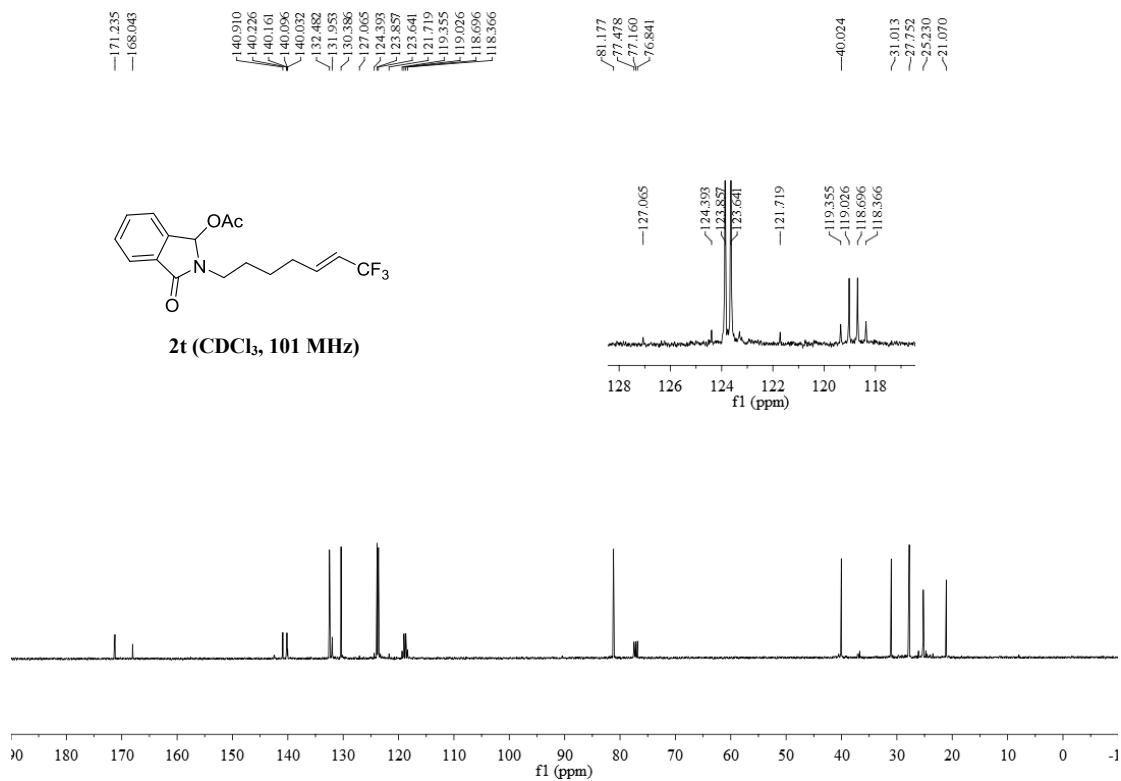


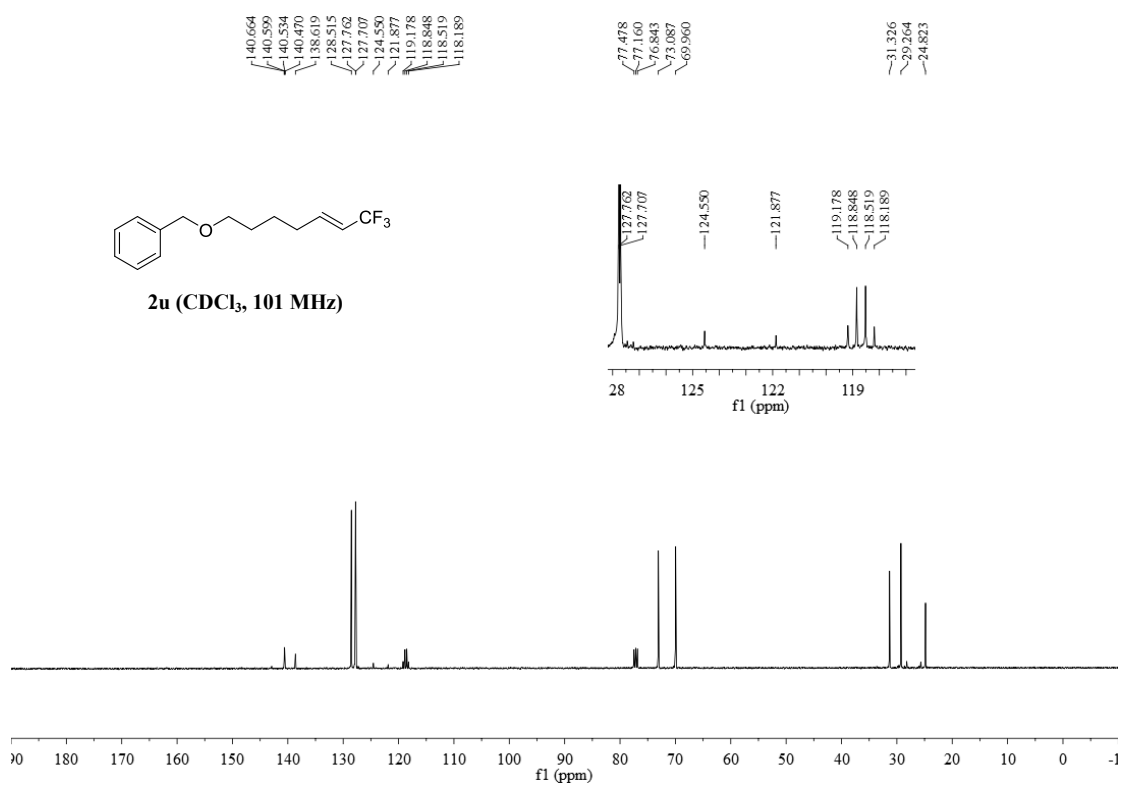
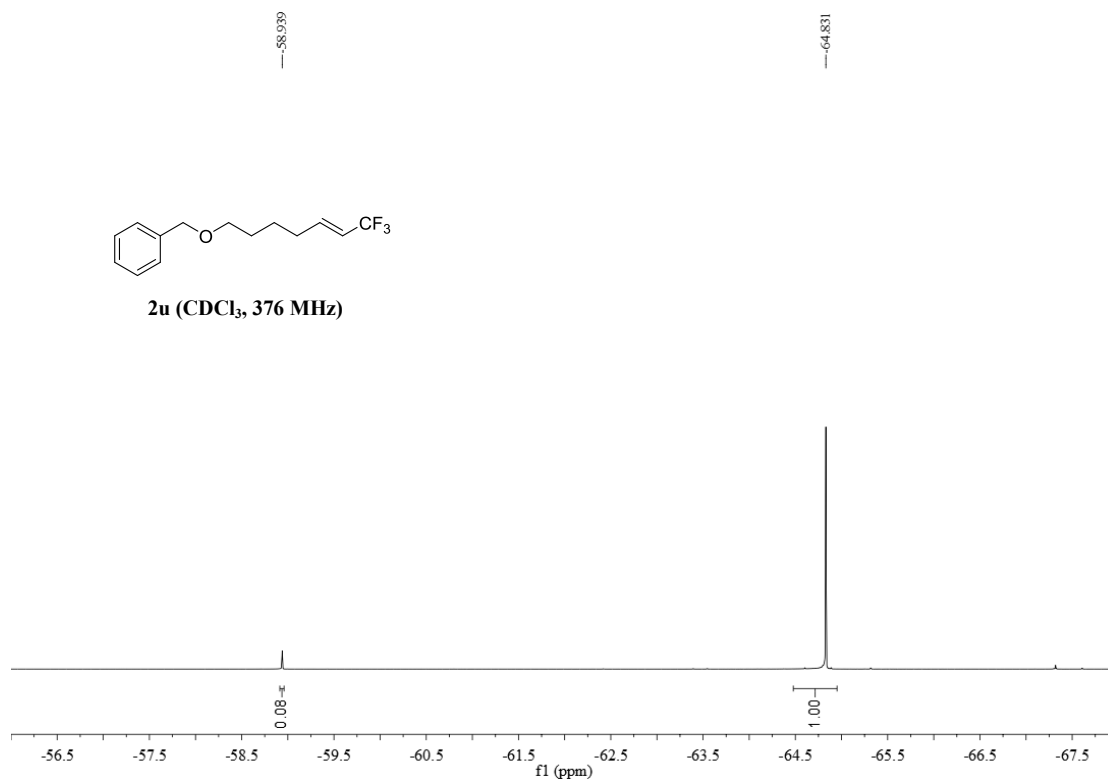


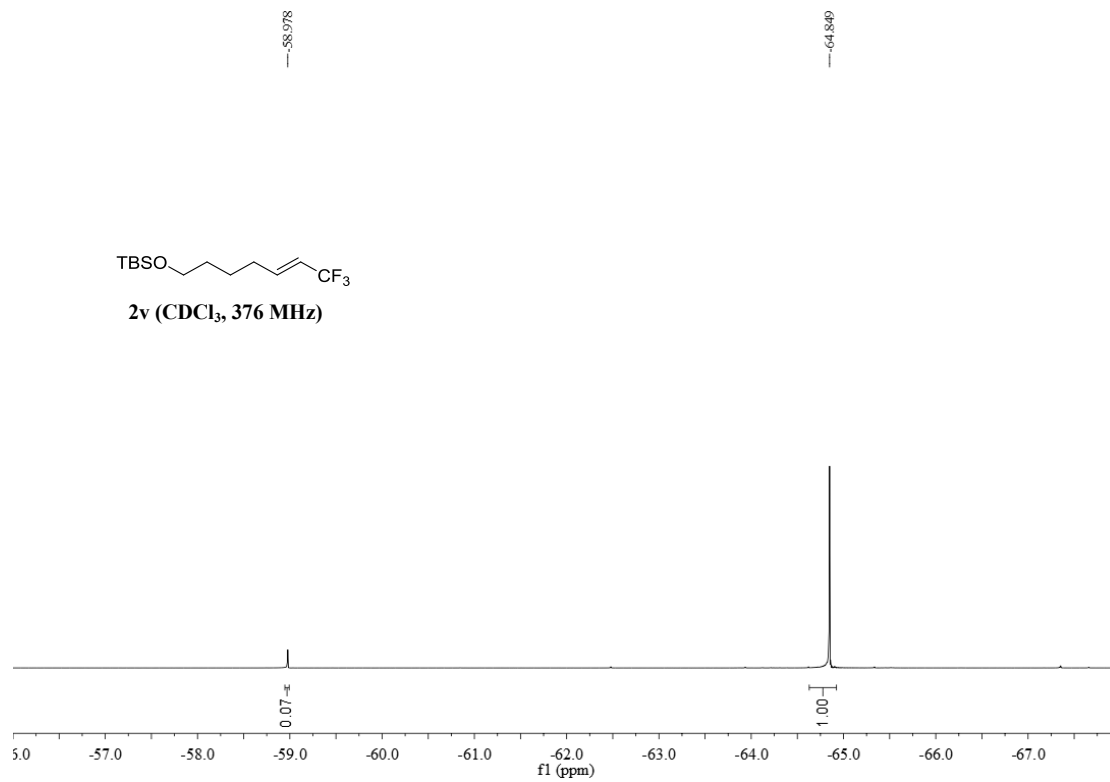
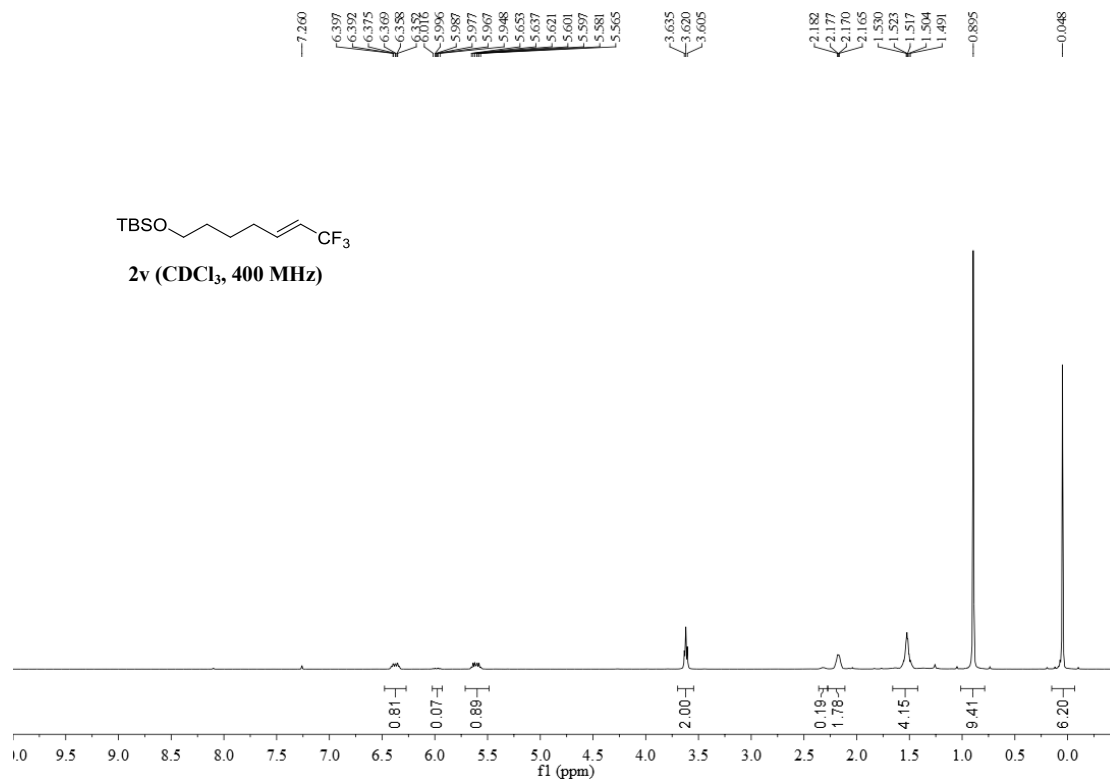


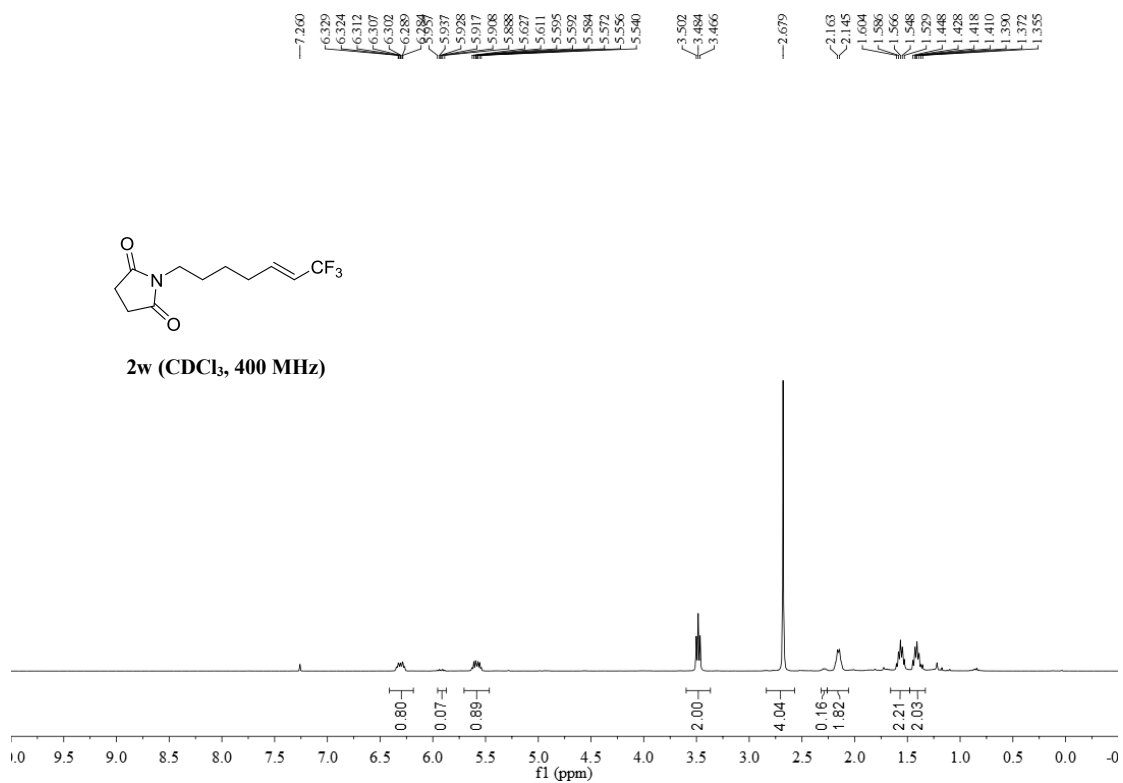
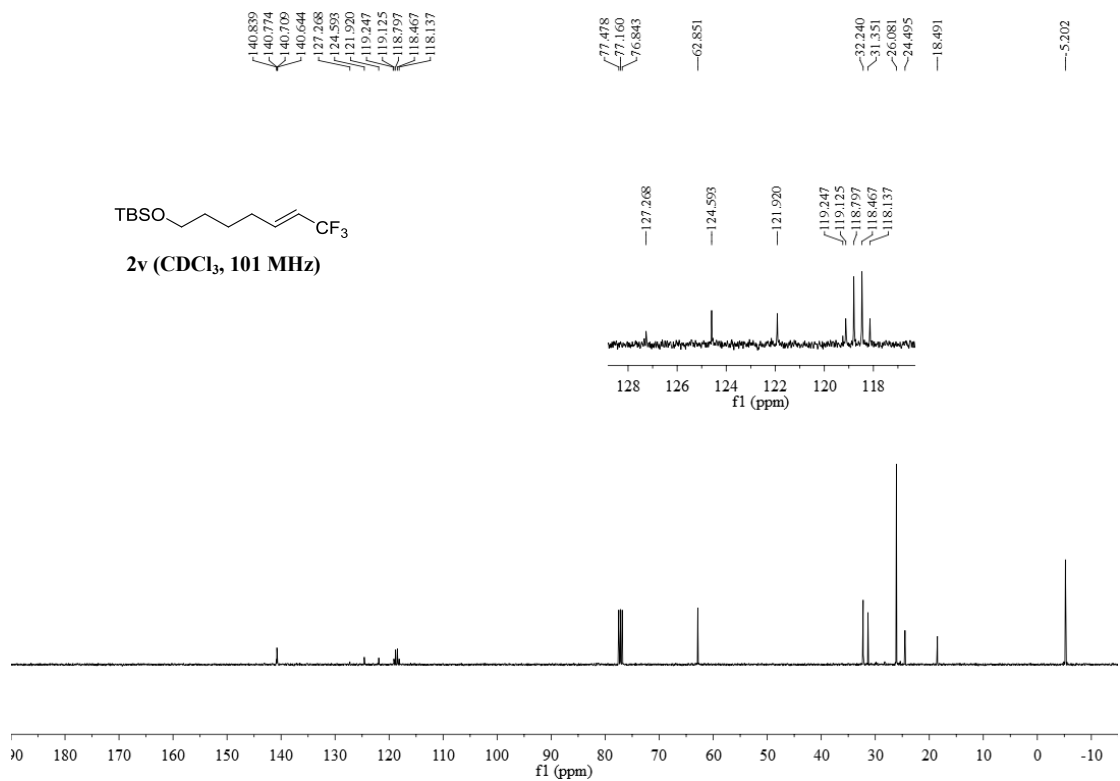


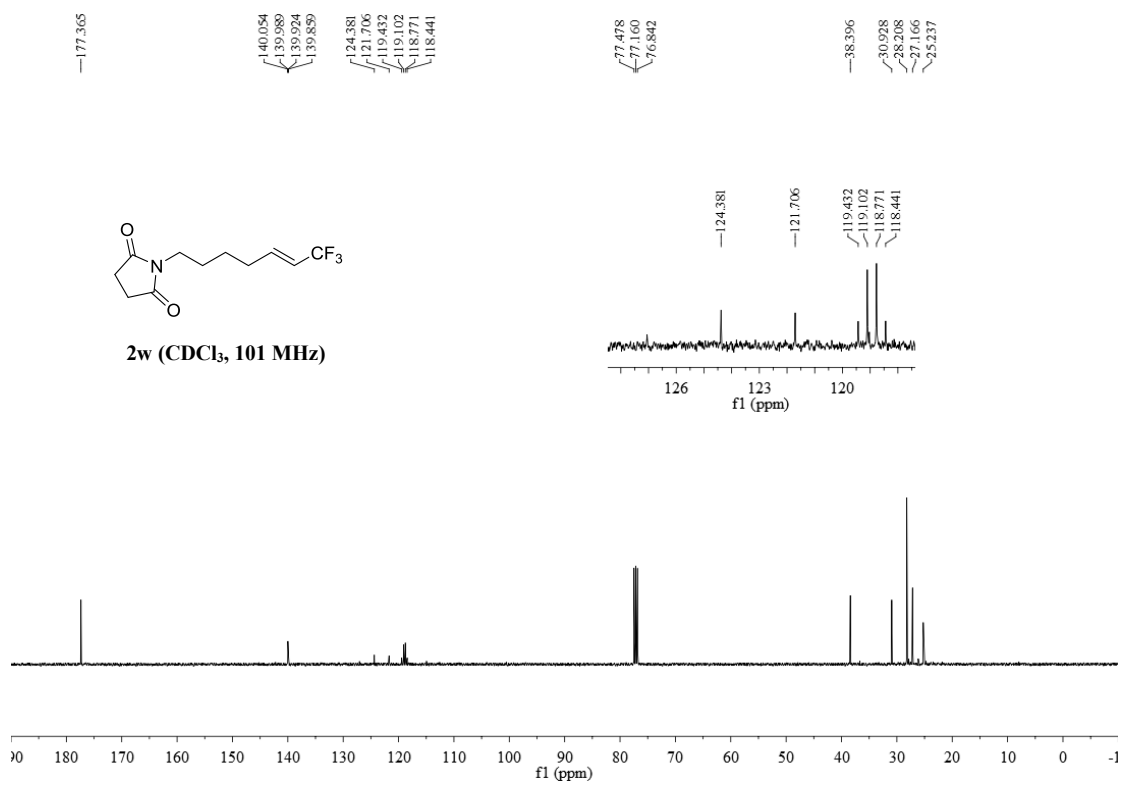
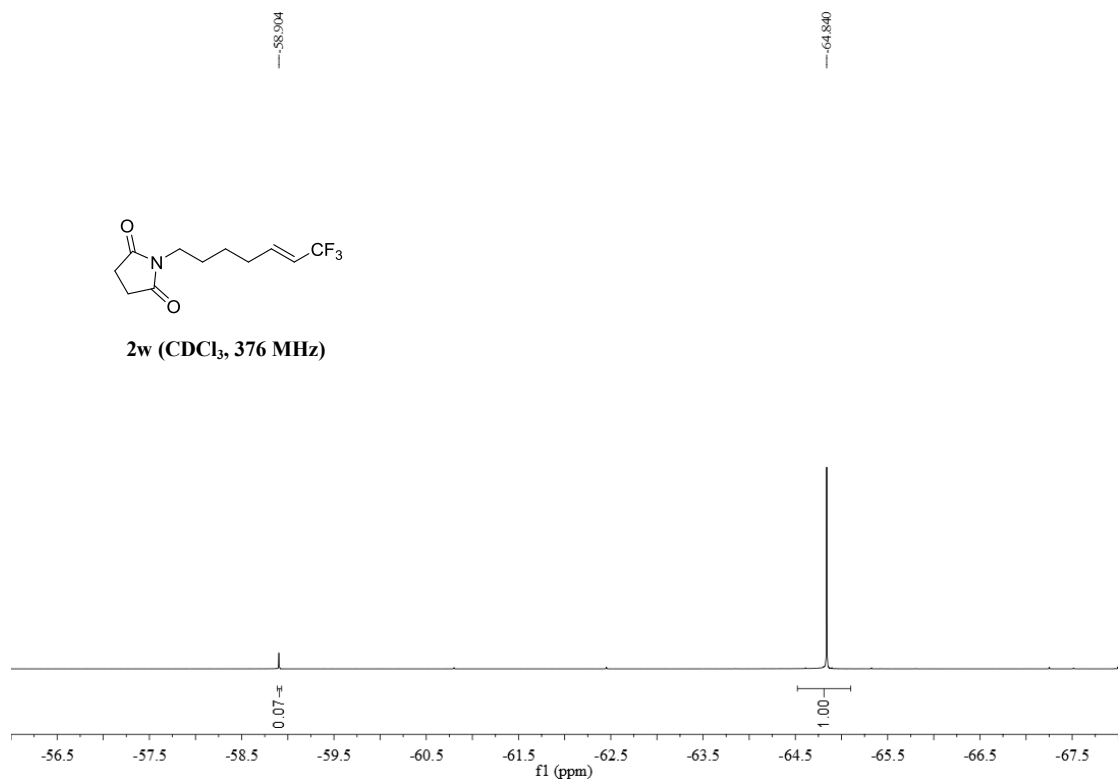


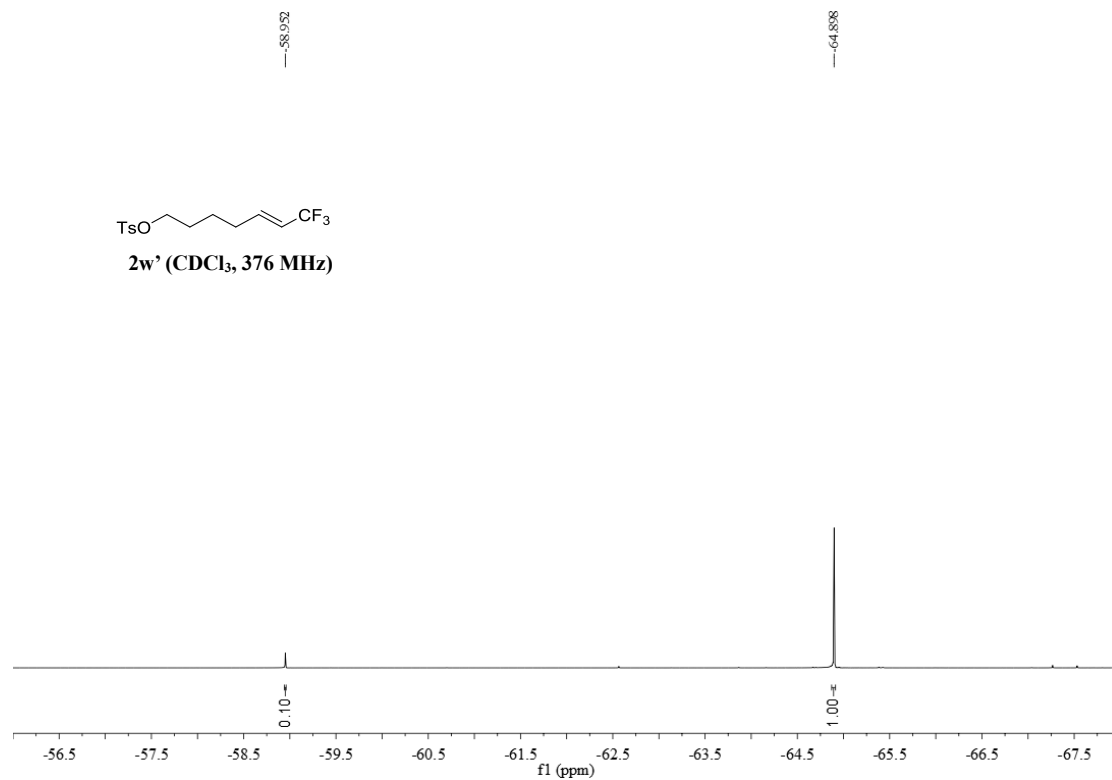
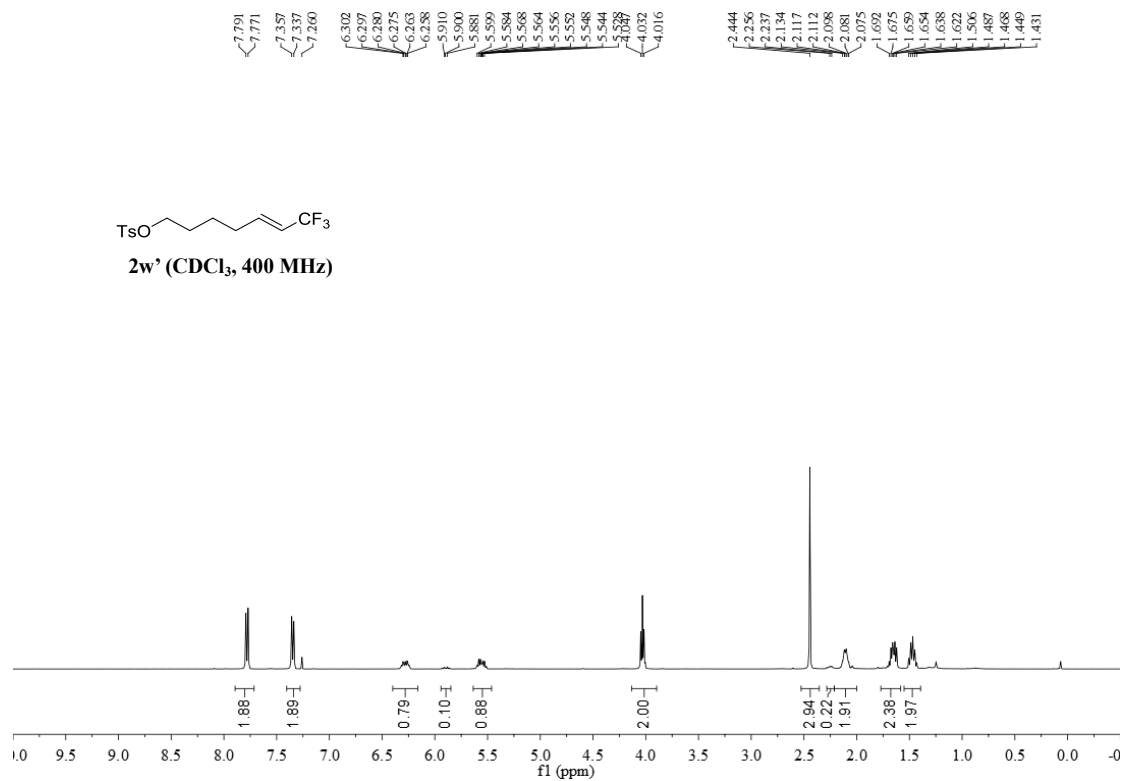


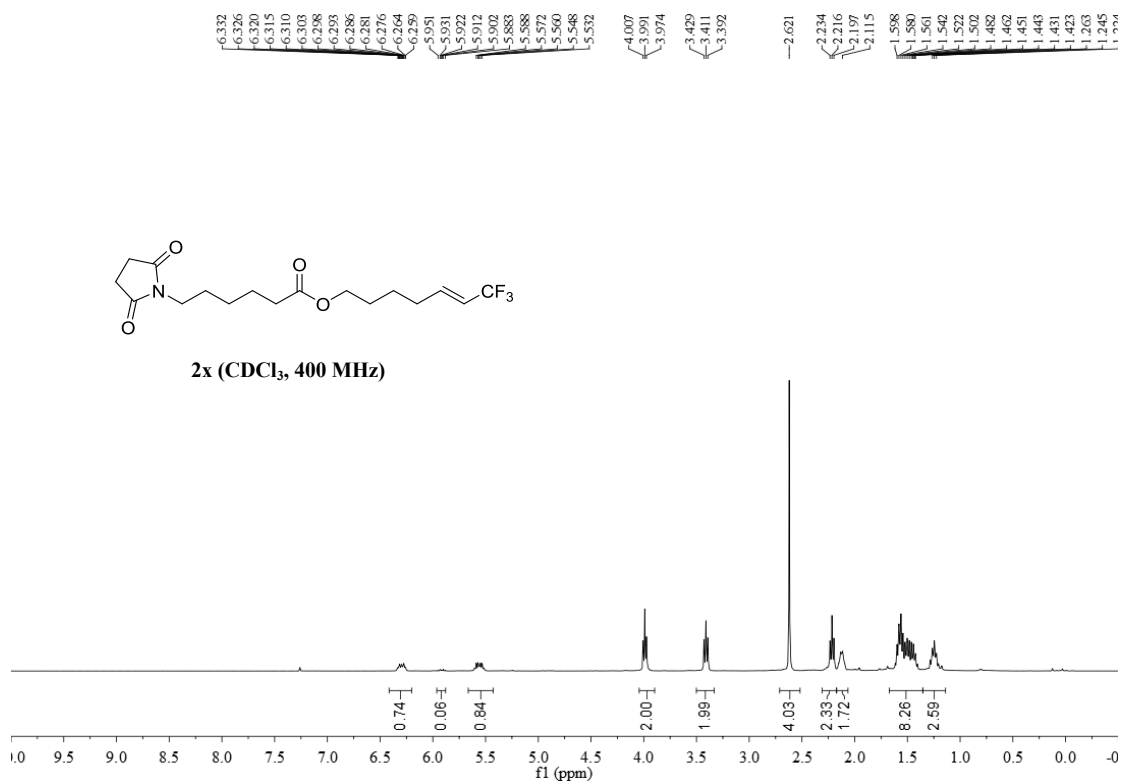
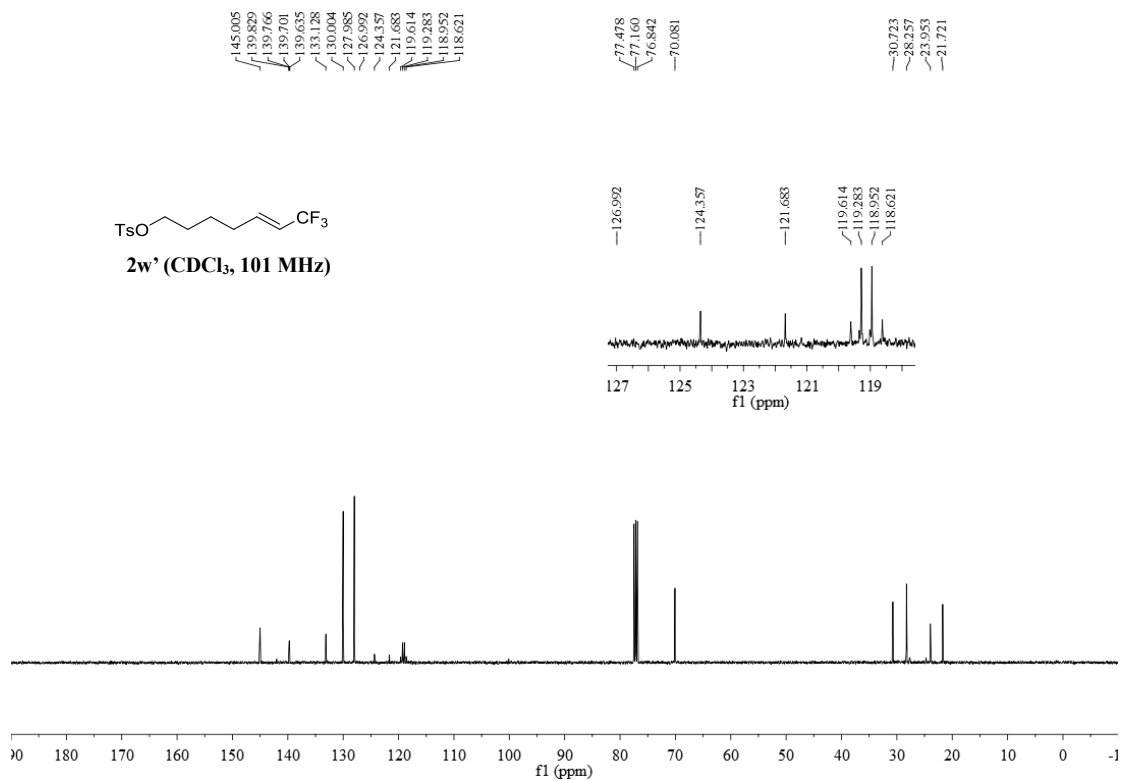


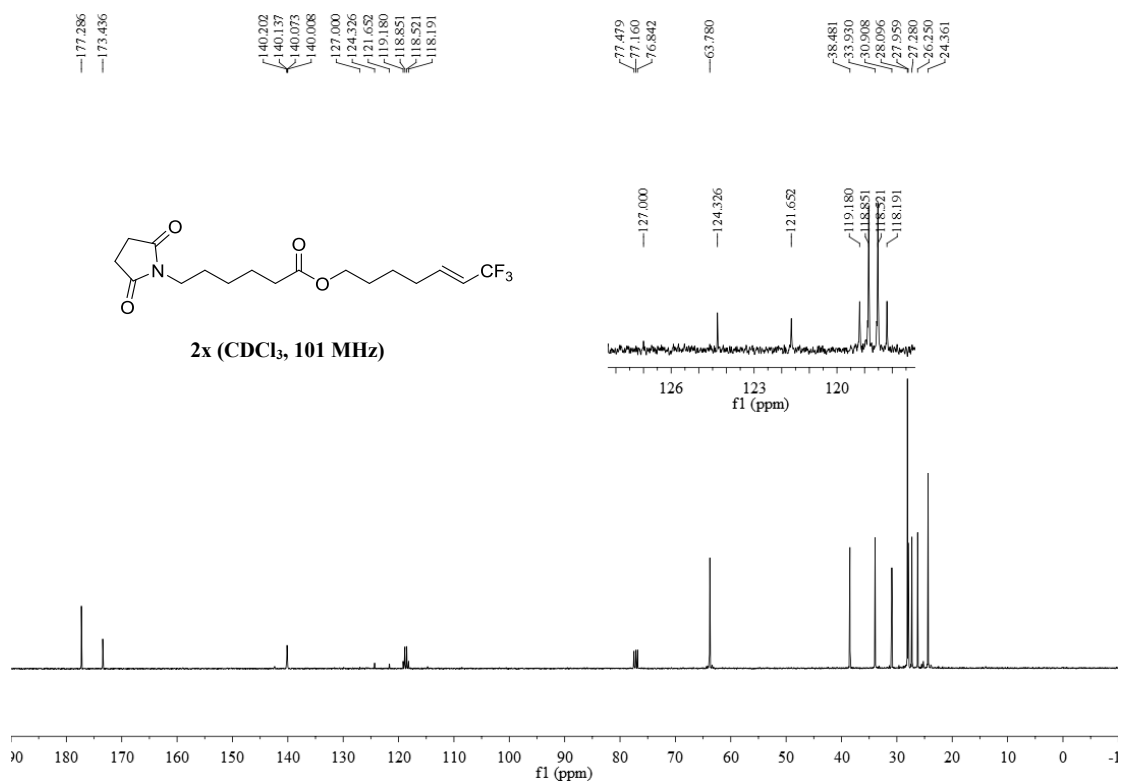
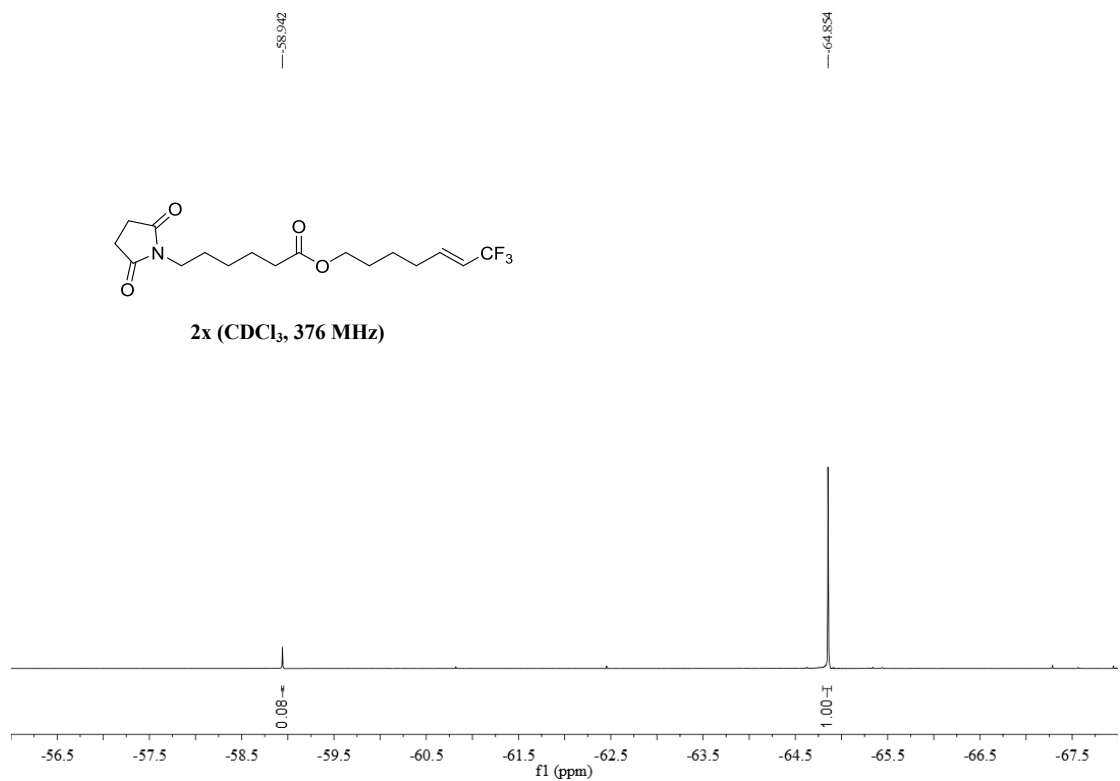


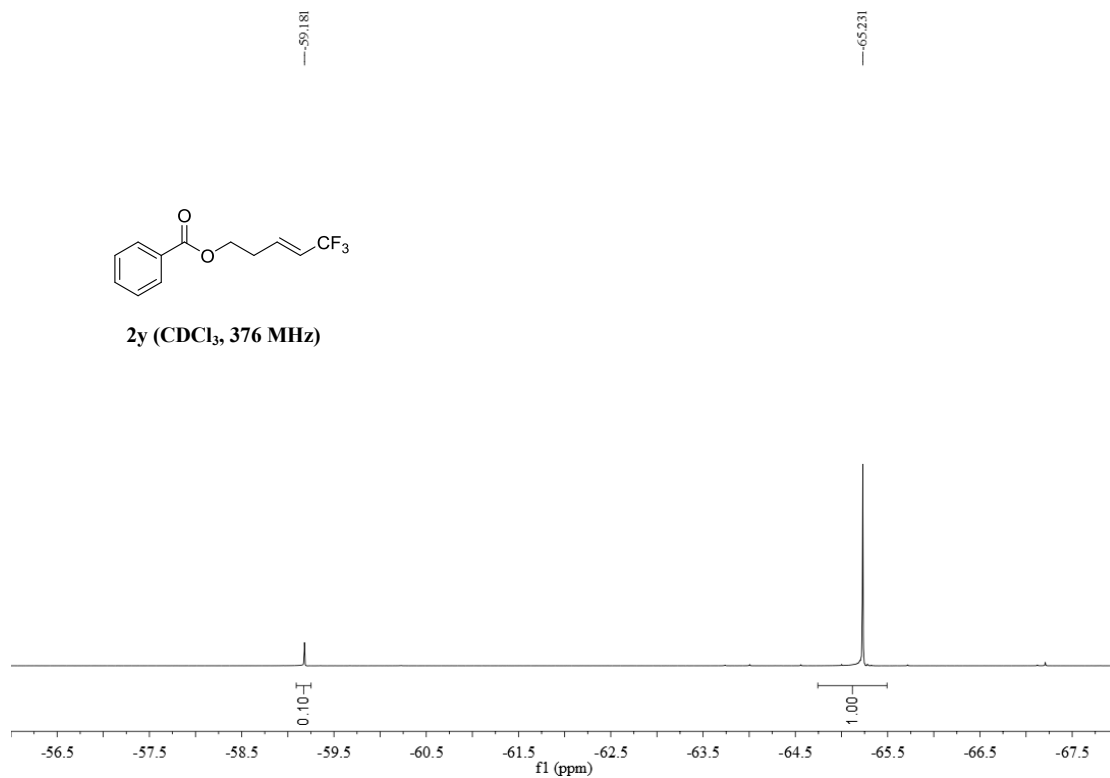
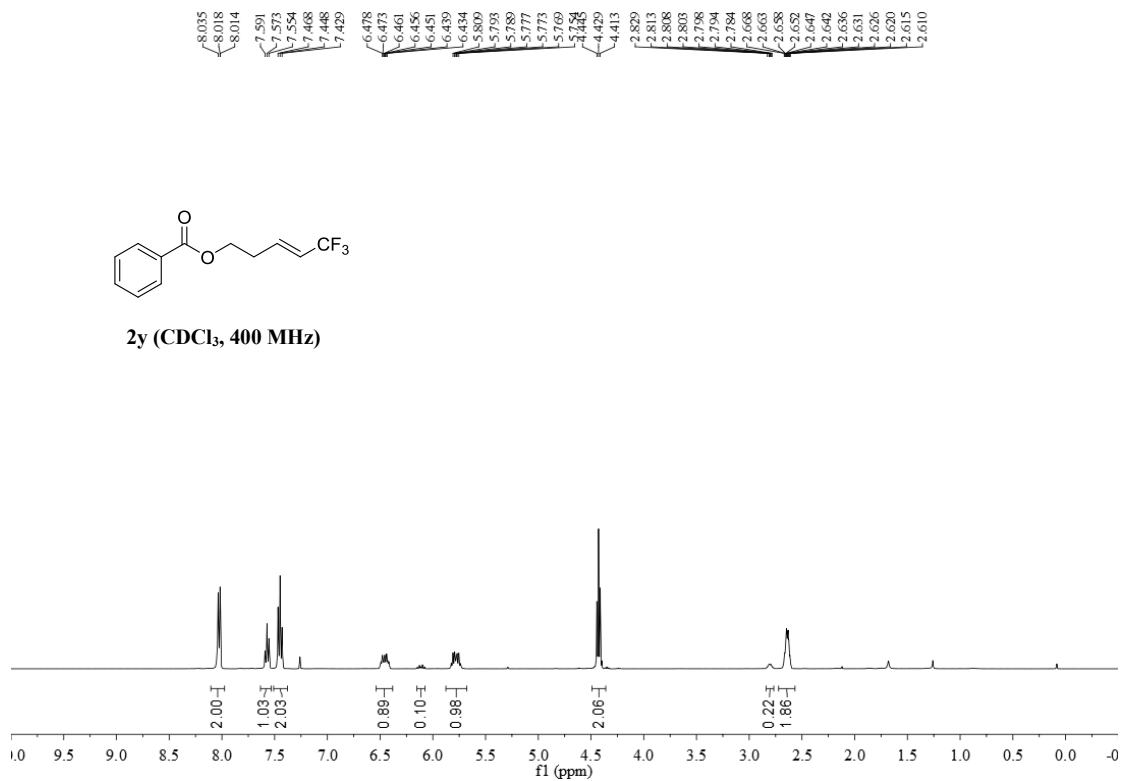


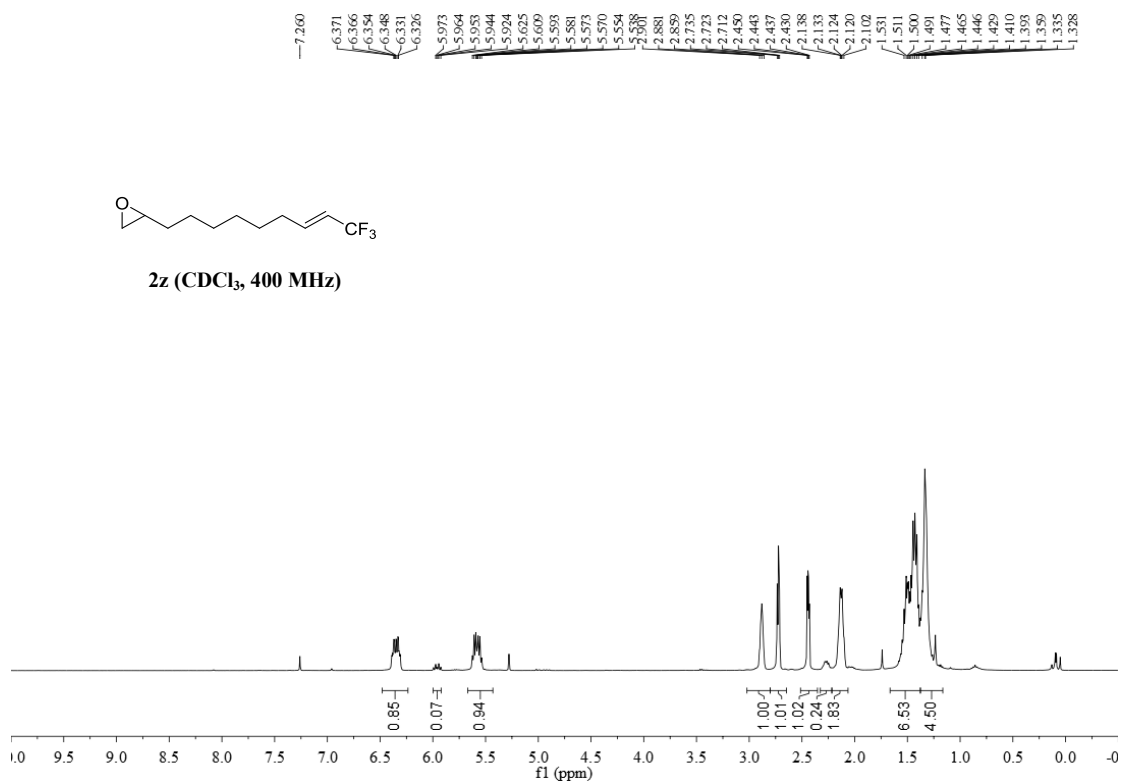
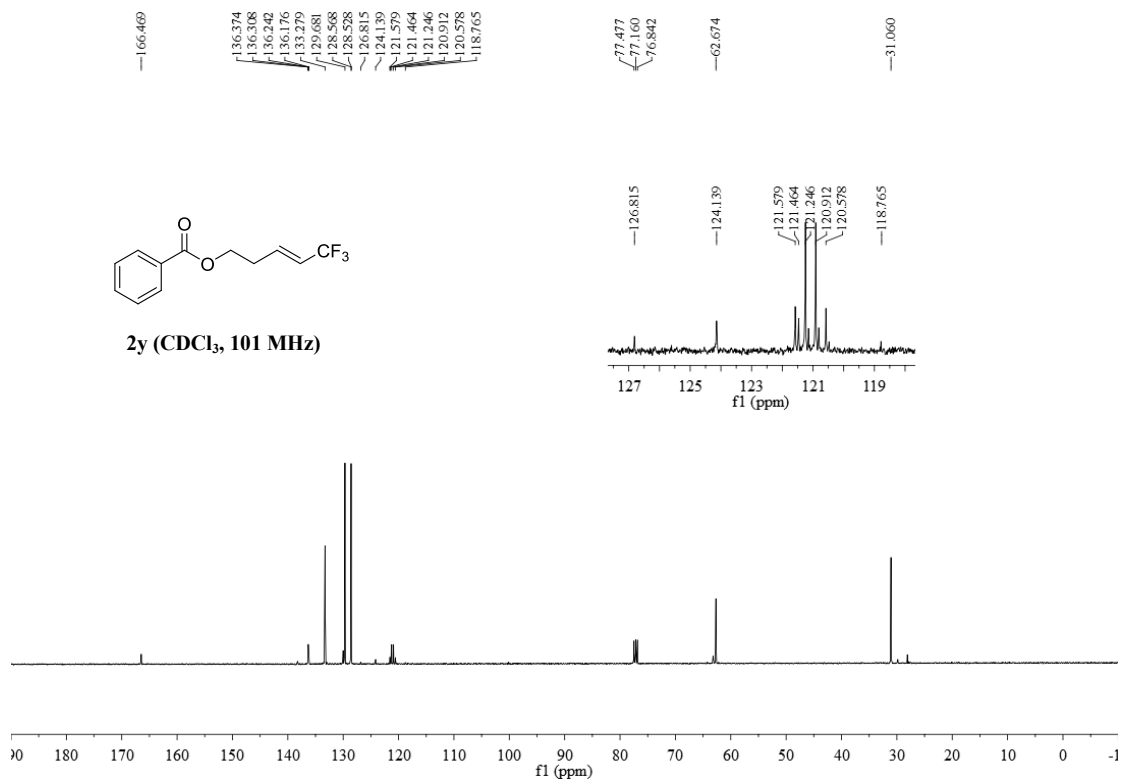


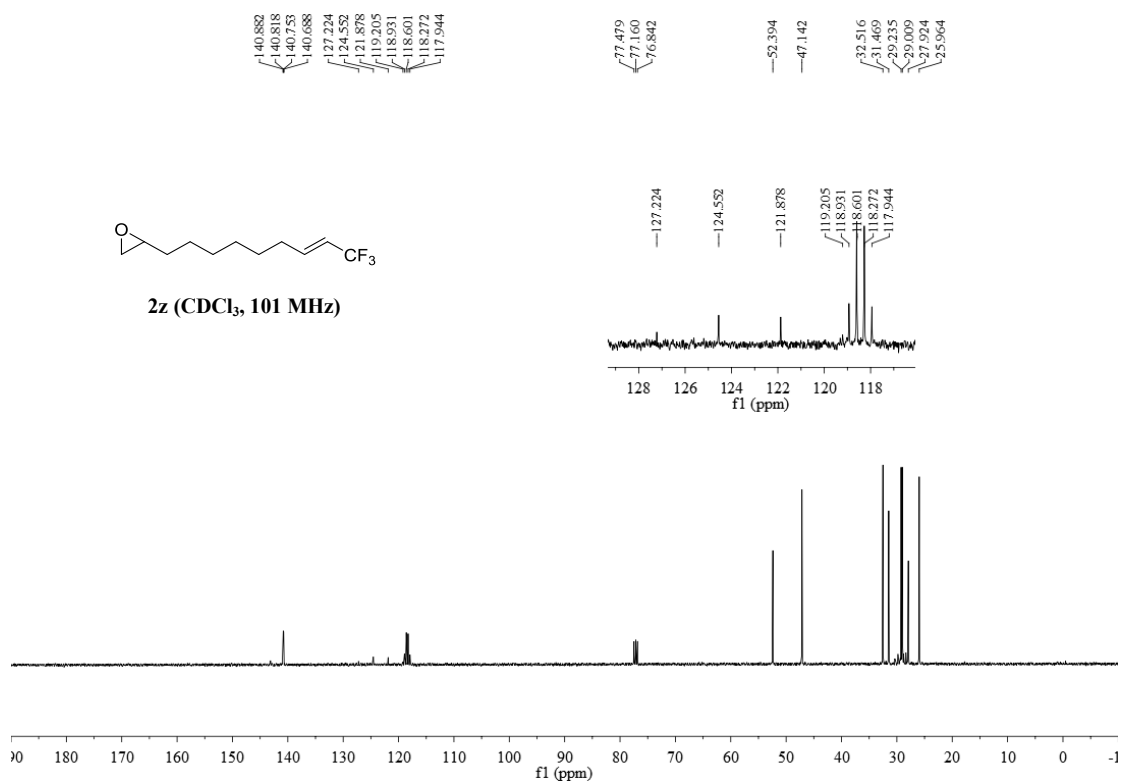
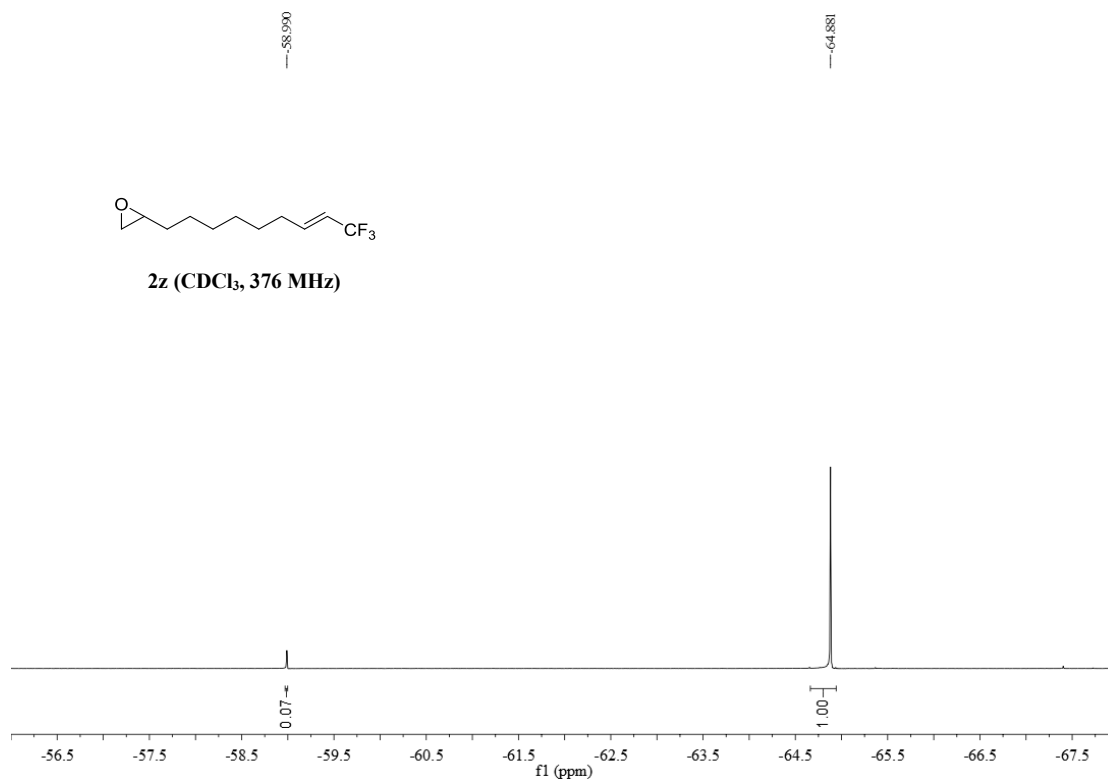


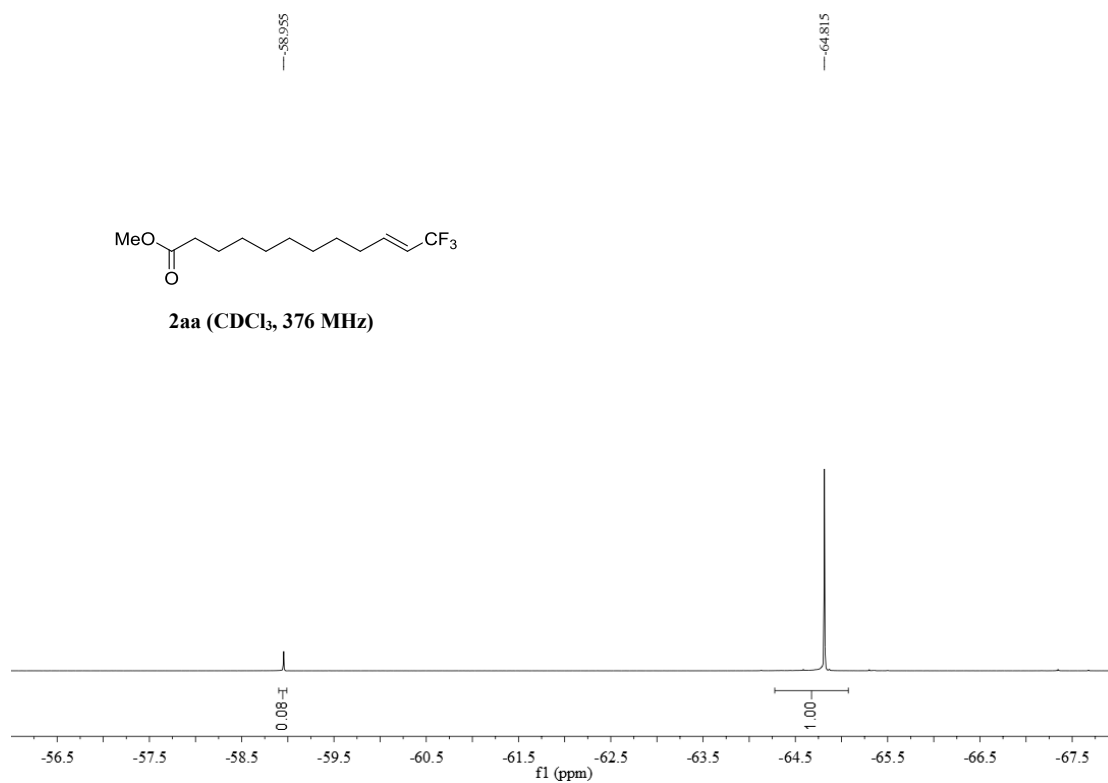
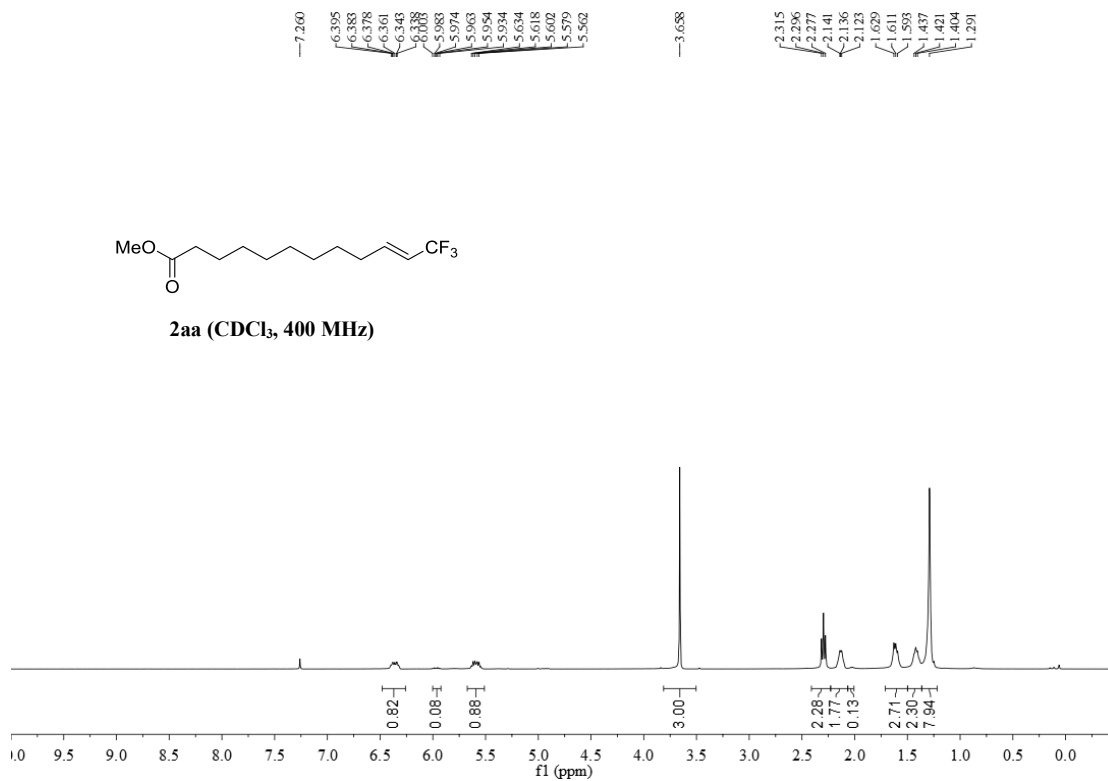


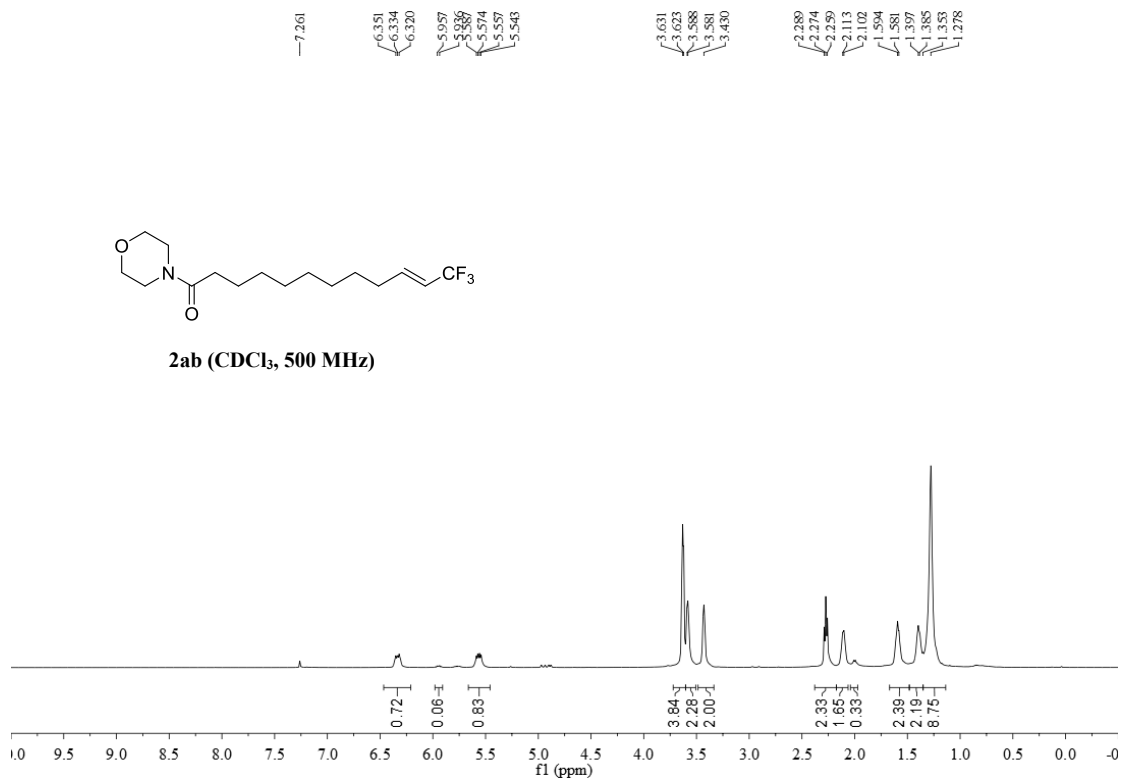
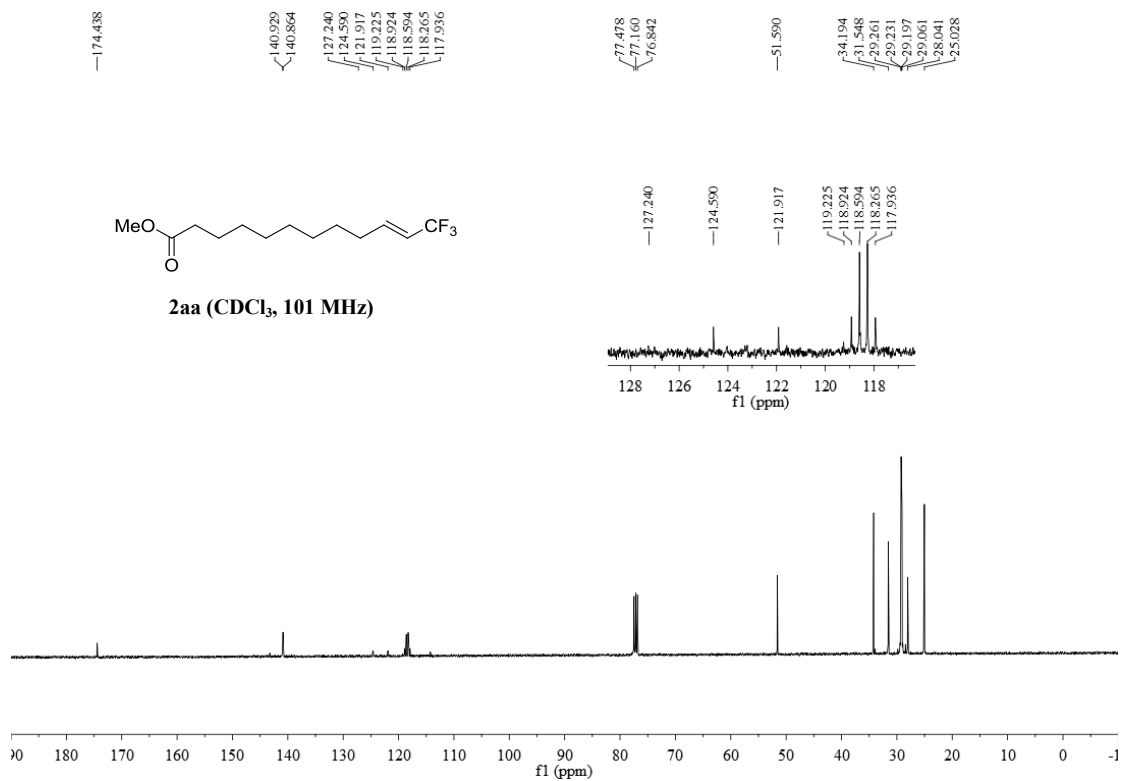


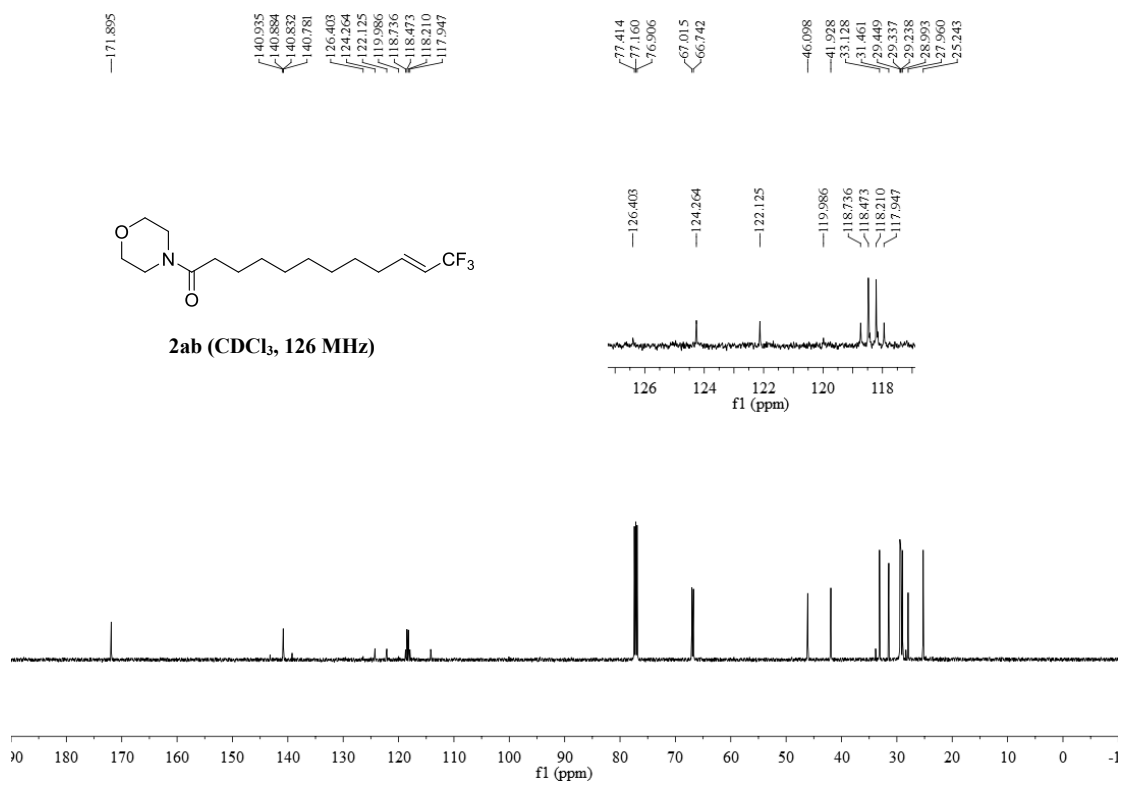
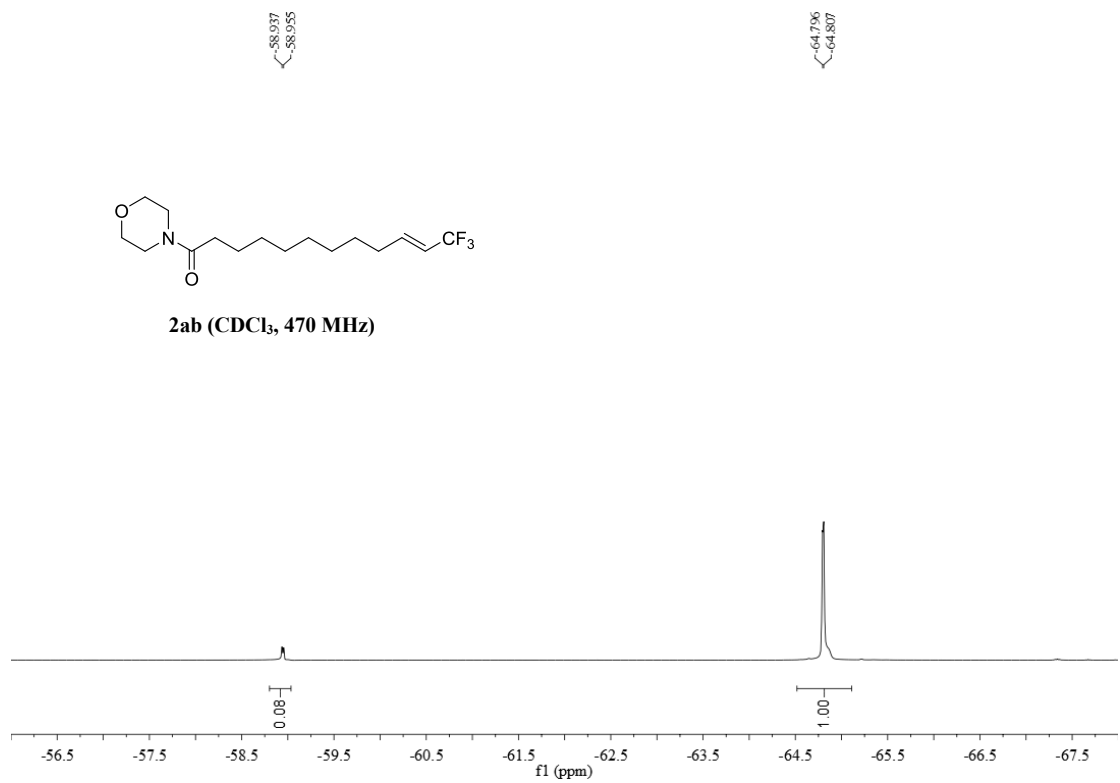


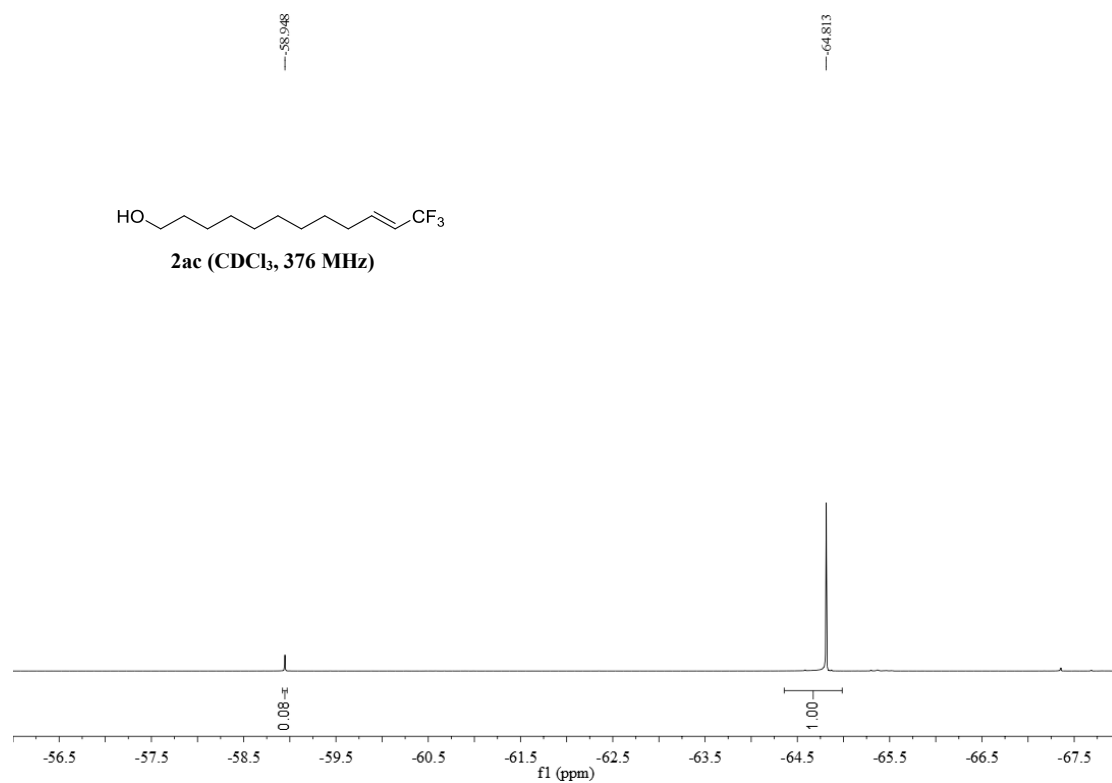
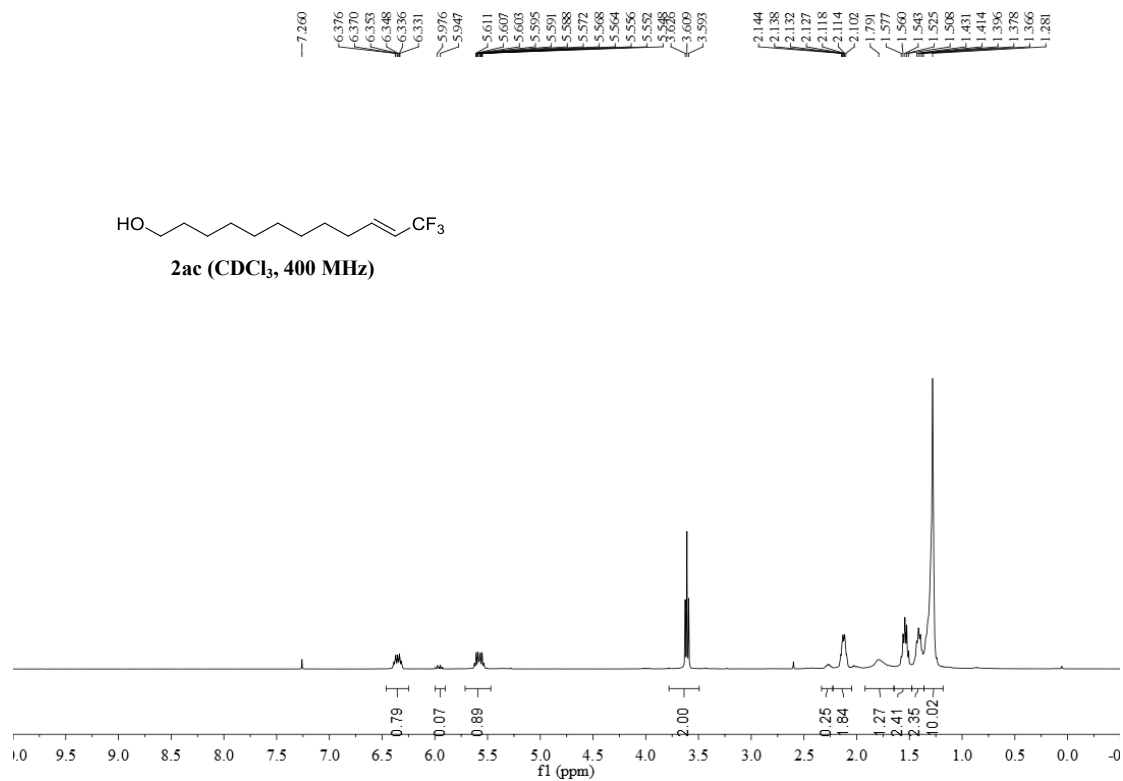


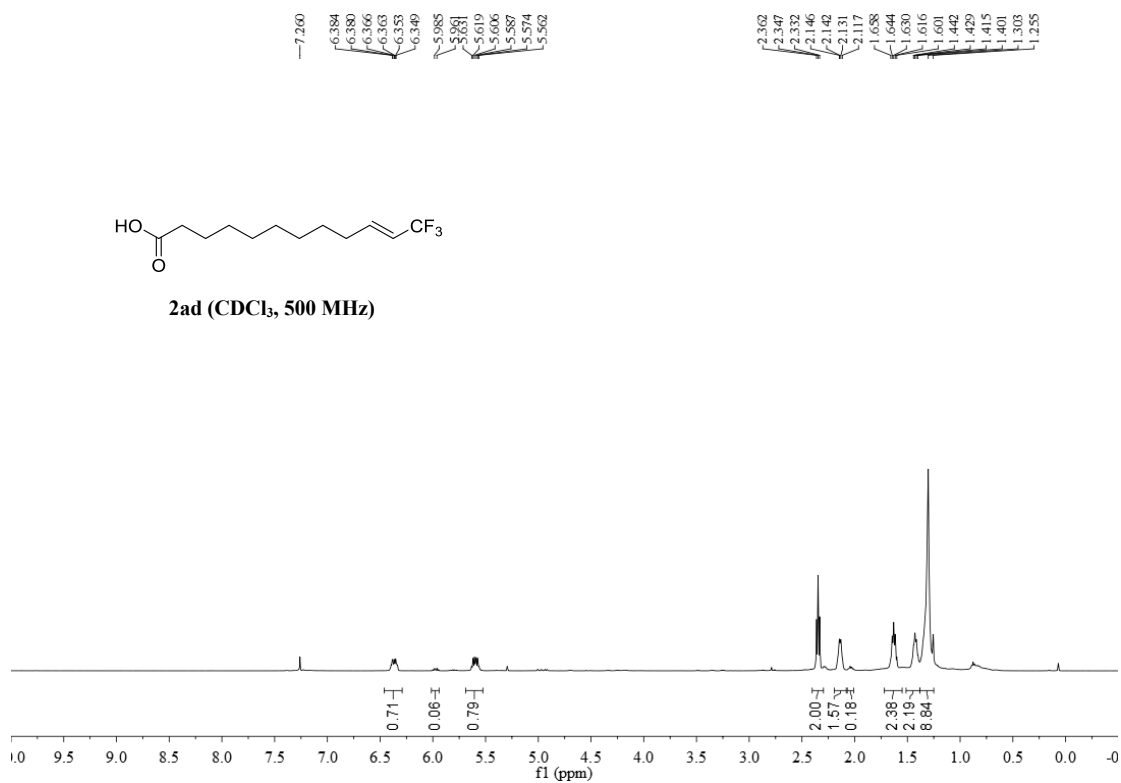
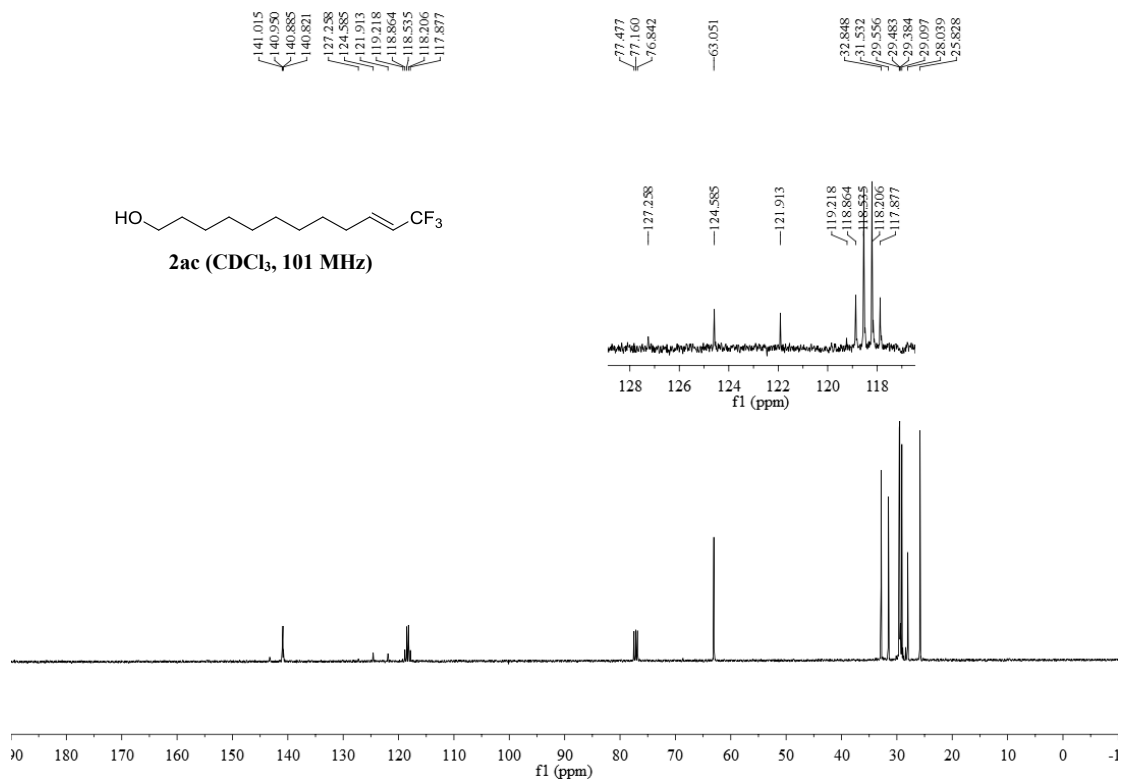


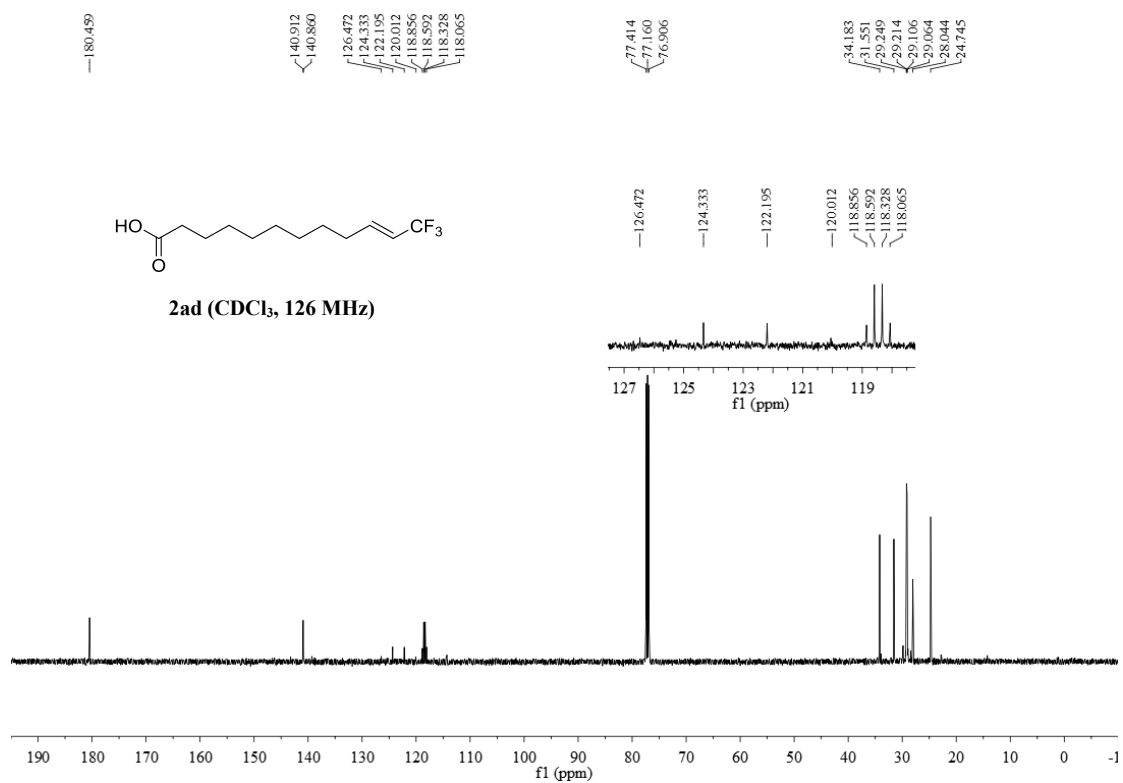
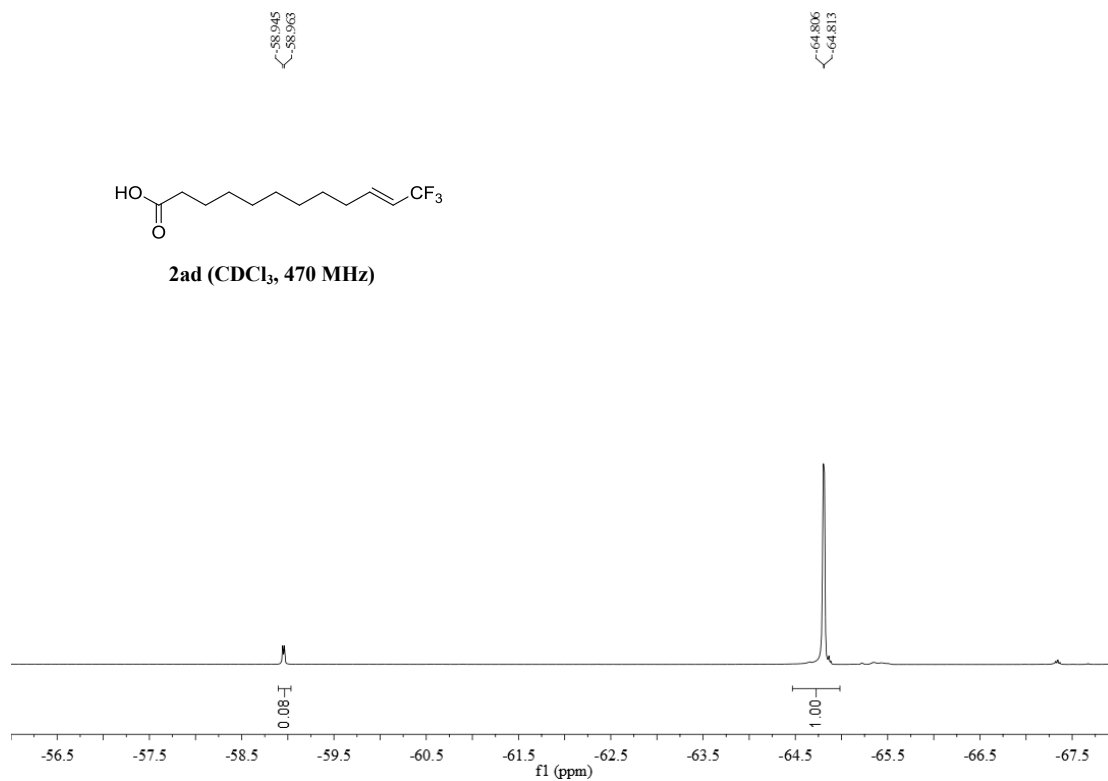


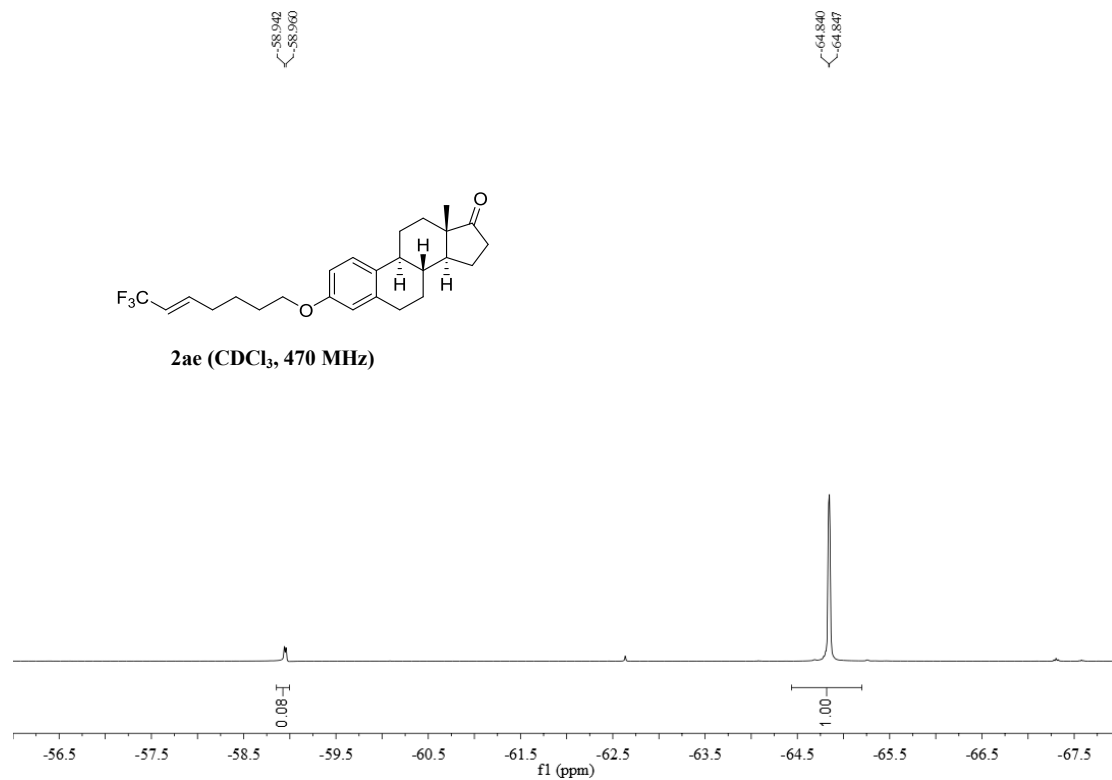
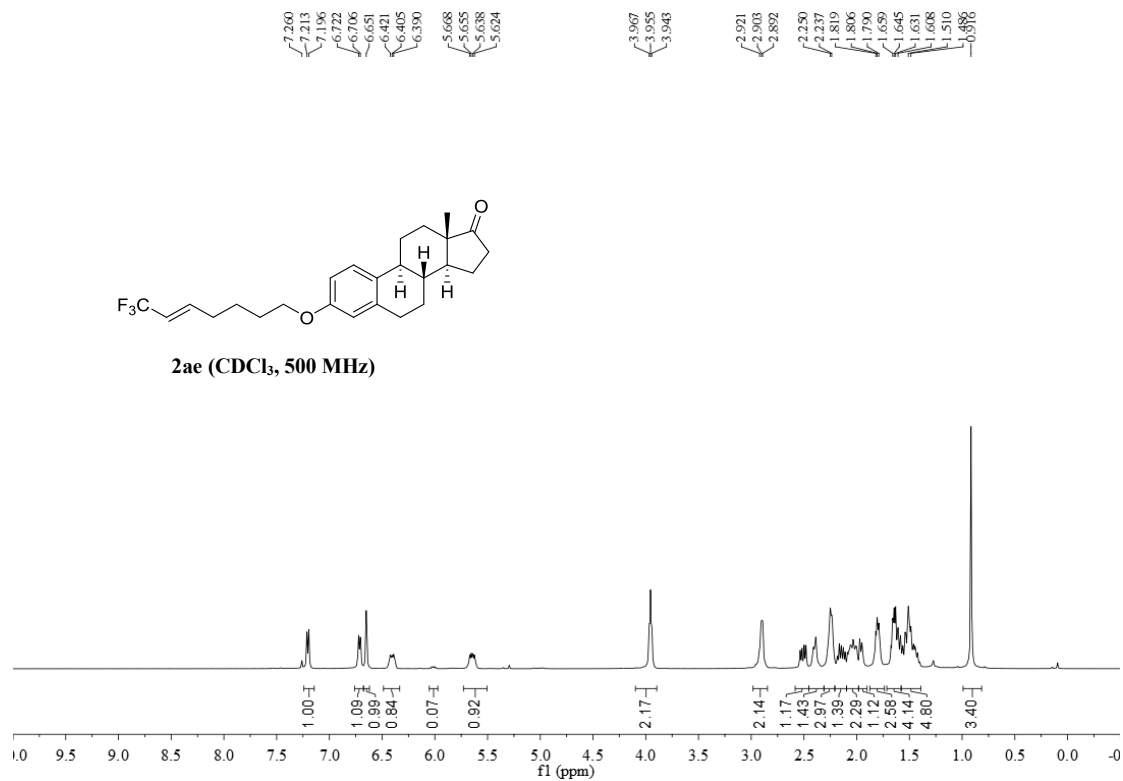


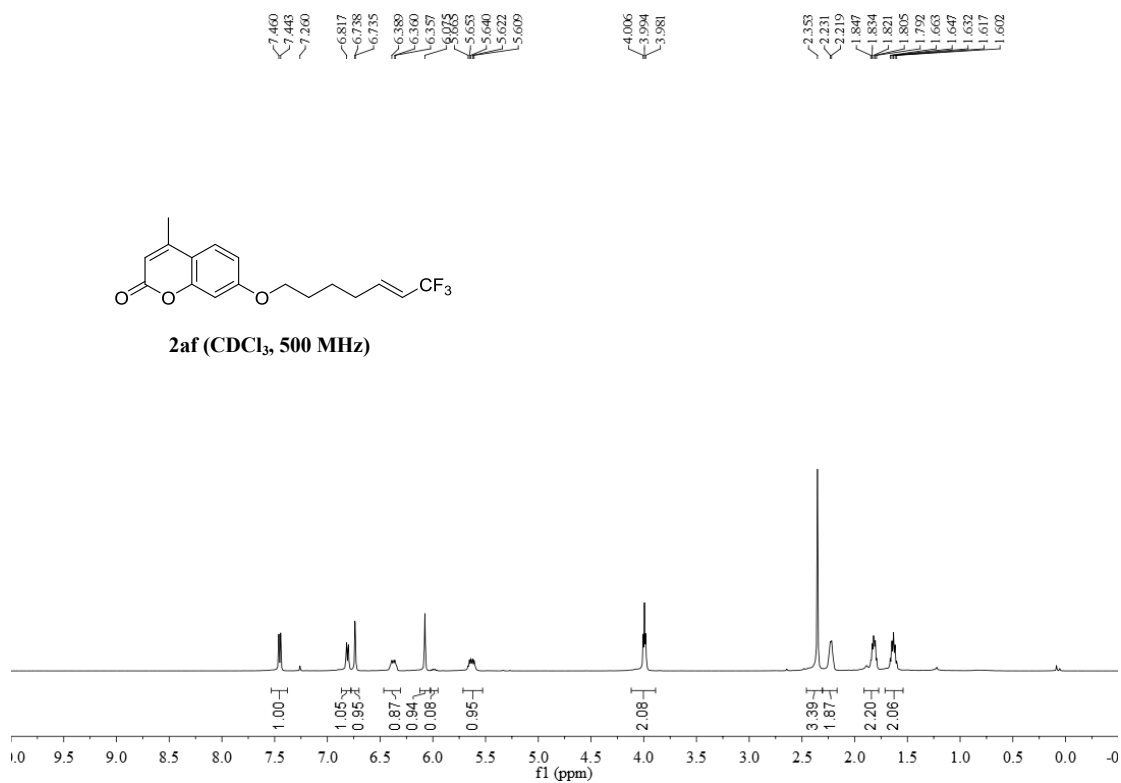
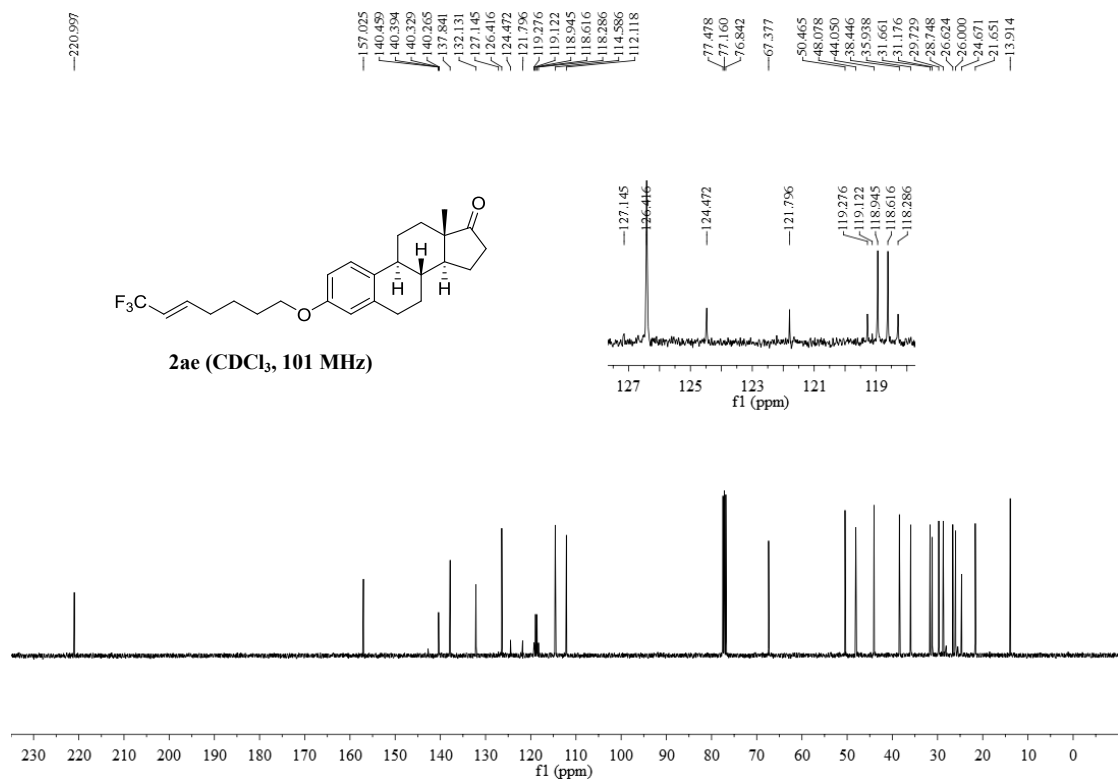


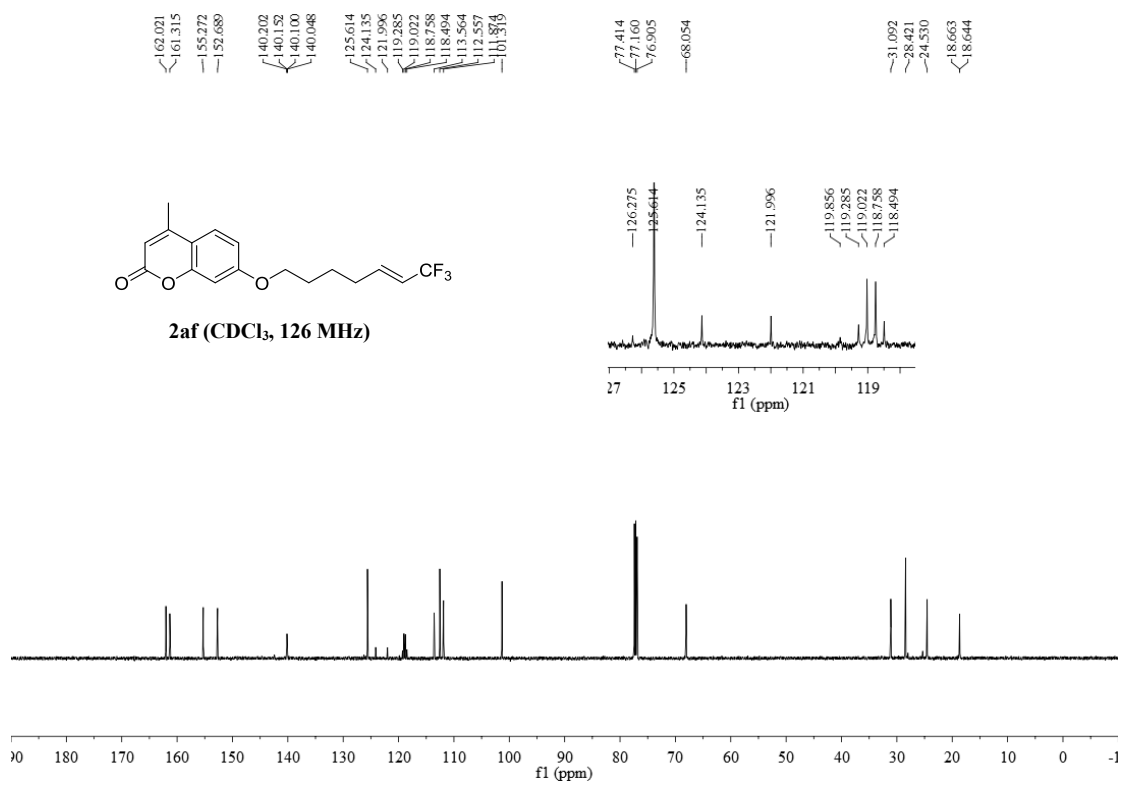
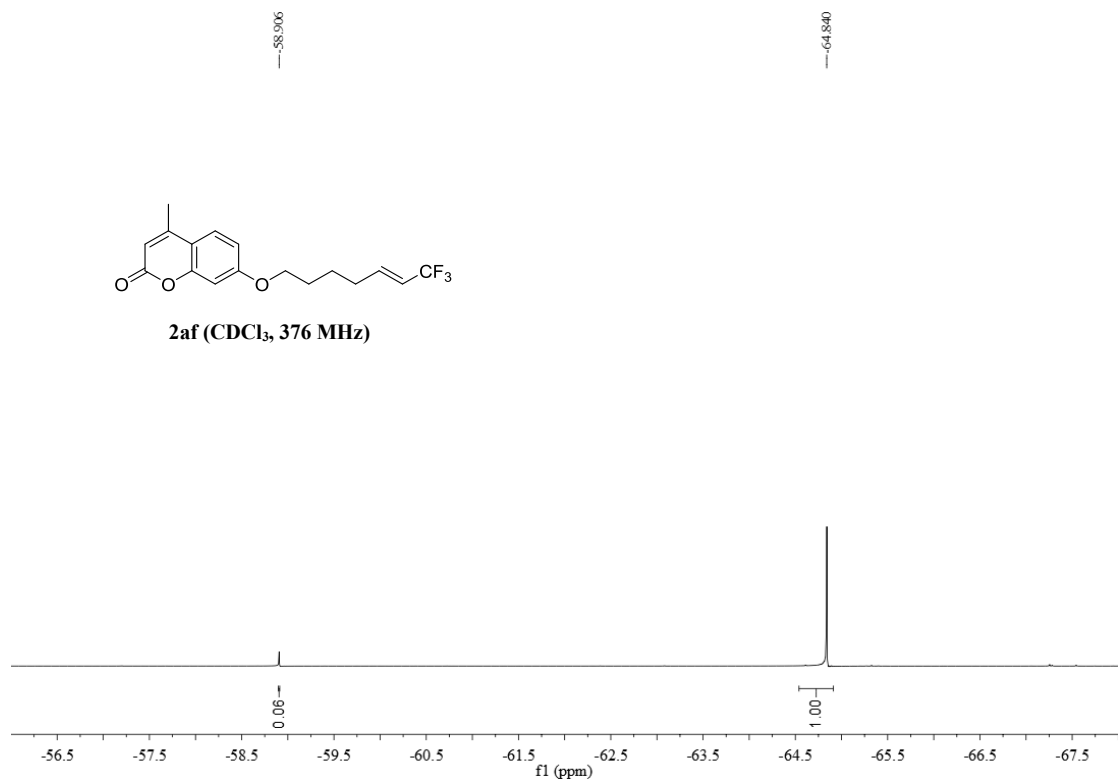




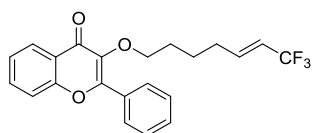




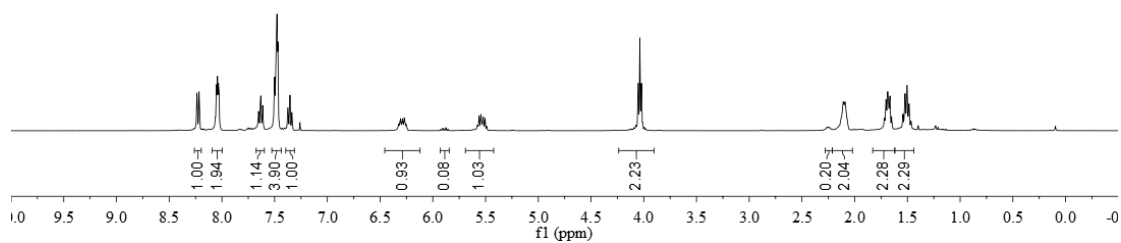




8.237
8.234
8.217
8.214
8.062
8.051
8.048
8.042
8.038
8.033
8.029
8.027
7.649
7.635
7.631
7.628
7.614
7.610
7.501
7.486
7.477
7.473
7.470
7.374
7.372
7.354
7.337
7.334
7.260
6.327
6.322
6.316
6.310
6.305
6.300
6.293
6.288
6.283
6.277
6.271
6.266
6.261
6.254
6.249
5.561
5.545
5.541
5.533
5.525
5.521
5.505
4.037
4.022
2.126
2.108
2.090
2.072
1.719
1.703
1.687
1.666
1.650
1.542
1.522
1.504
1.484
1.466

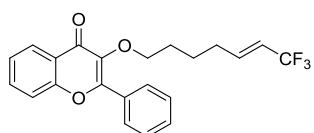


2ag (CDCl₃, 400 MHz)

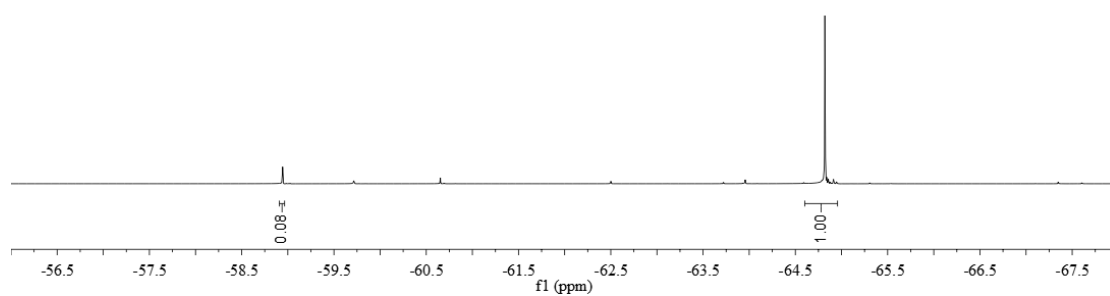


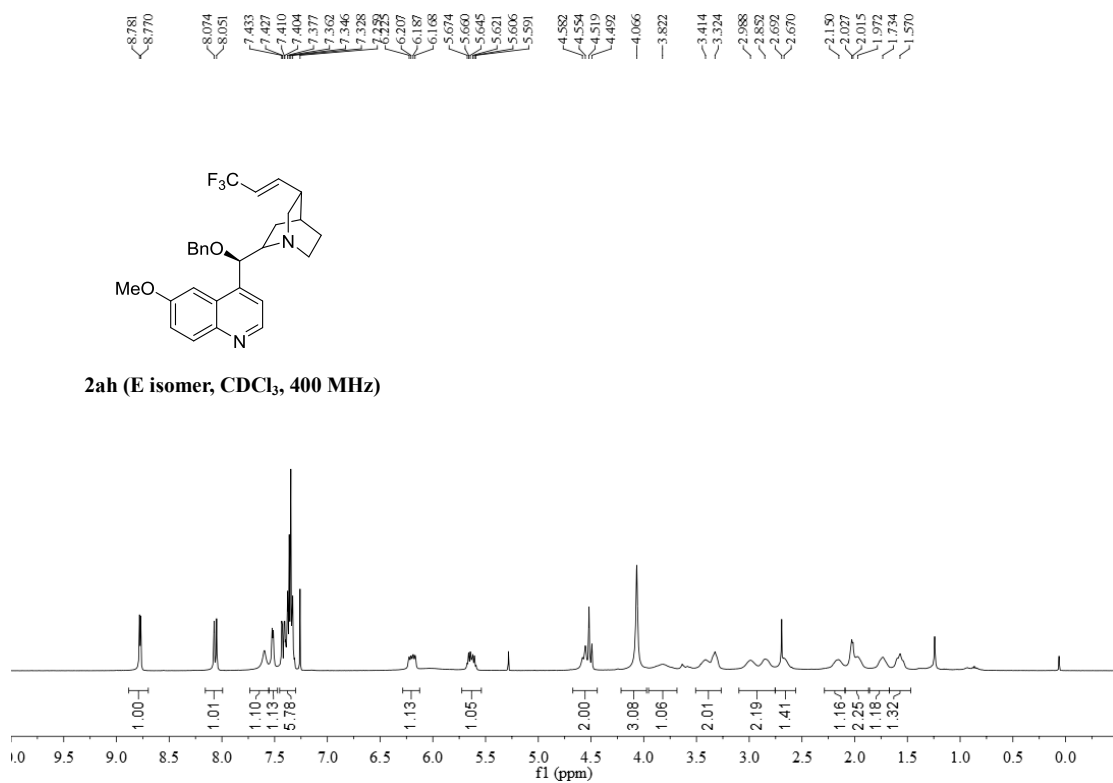
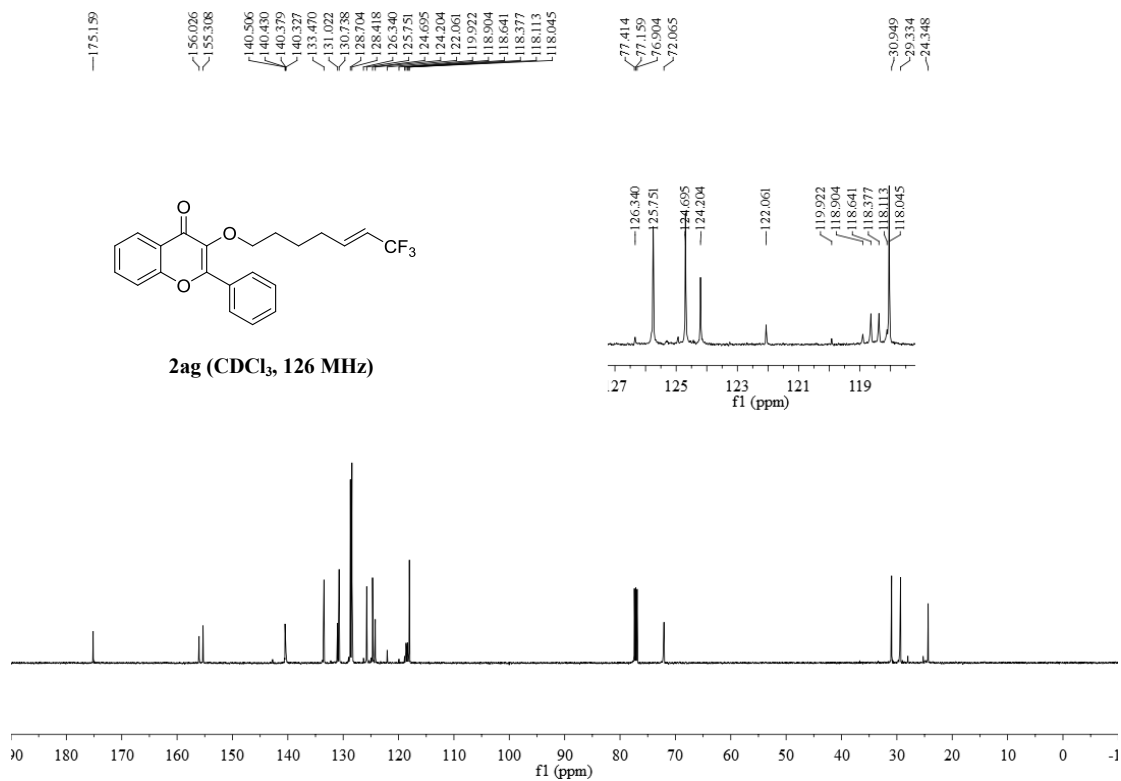
—58.944

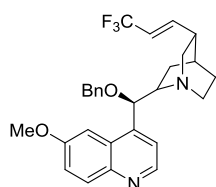
—64.820



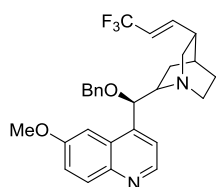
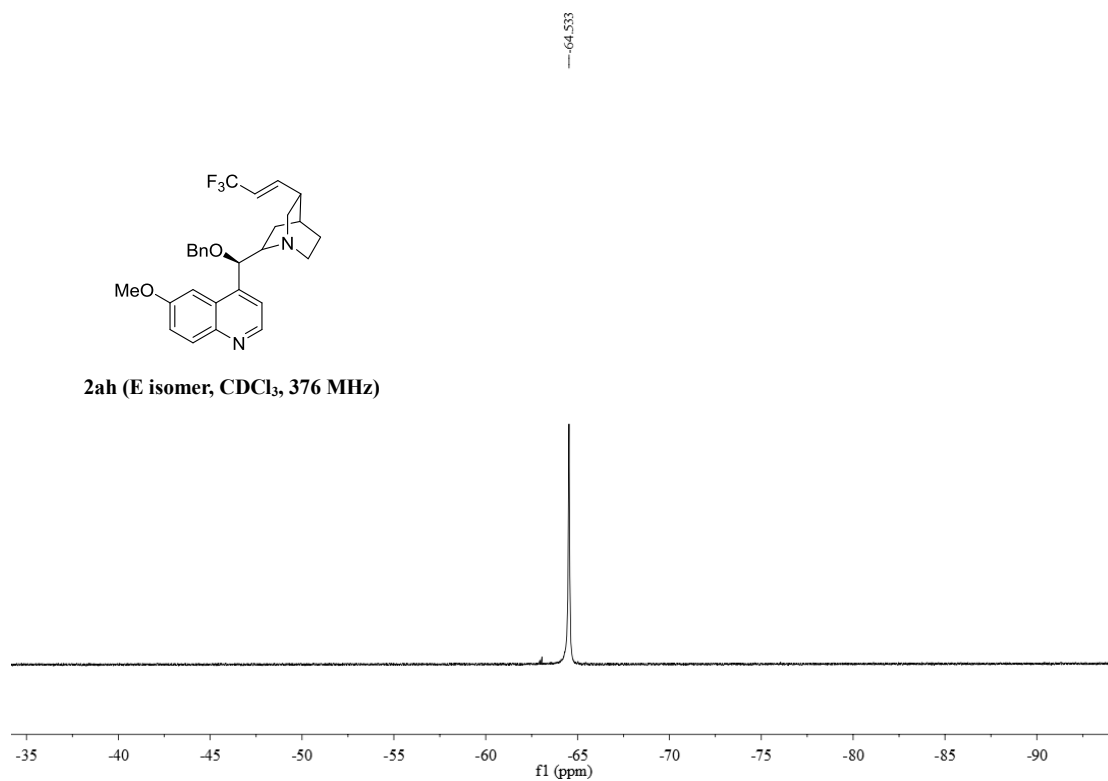
2ag (CDCl₃, 376 MHz)



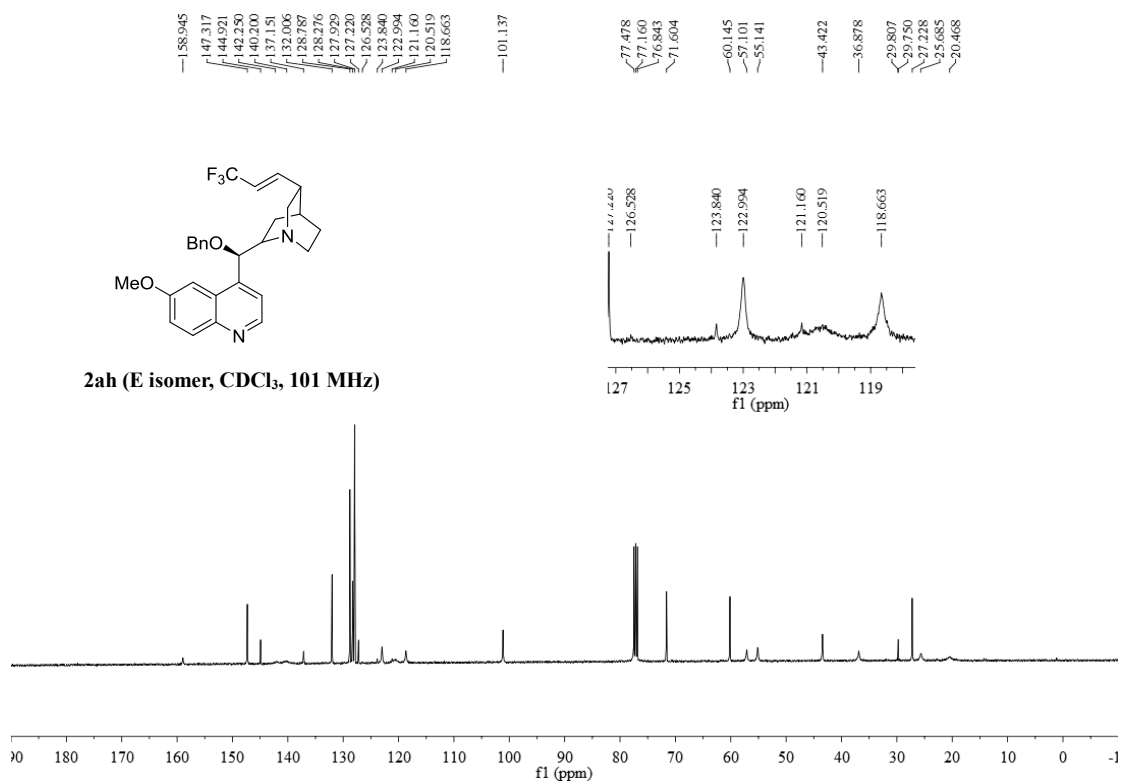


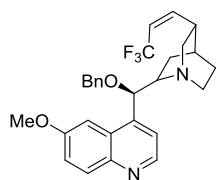


2ah (E isomer, CDCl₃, 376 MHz)

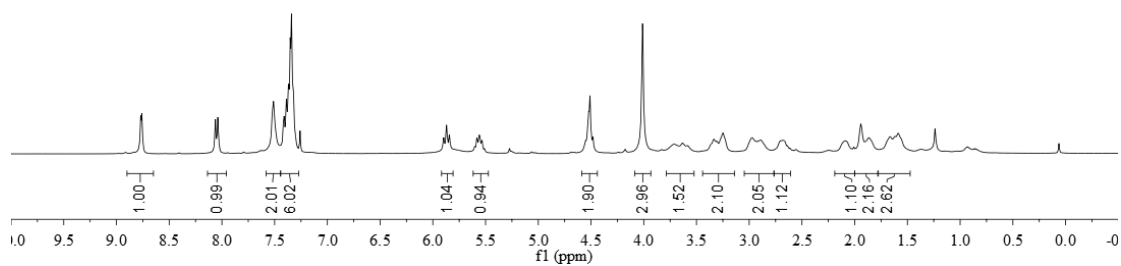


2ah (E isomer, CDCl₃, 101 MHz)

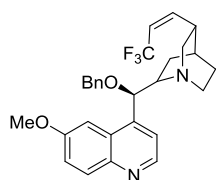




2ah (Z isomer, CDCl₃, 400 MHz)



—58.729



2ah (Z isomer, CDCl₃, 376 MHz)

