Radical Pentafluoroethylation of Unactivated Alkenes Using $CuCF_2CF_3$

Xinkan Yang and Gavin Chit Tsui*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR.

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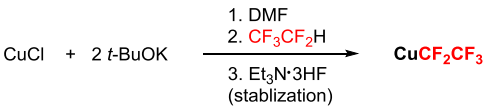
General Experimental. Analytical thin layer chromatography (TLC) was performed with EM Science silica gel 60 F254 aluminum plates. Visualization was done under a UV lamp (254 nm) and by immersion in ethanolic phosphomolybdic acid (PMA) or potassium permanganate ($KMnO_4$), followed by heating using a 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. Halocarbon 125-Pentafluoroethane (Purity: 99.0% min., 9.1kg in 16 L size cylinder) was purchased from SCIENTIFIC GAS ENGINEERING CO., LTD. Copper(I) chloride (extra pure, 99.99%) was purchased from Acros. Potassium *tert*-butoxide (97%) was purchased from Alfa Aesar. Anhydrous DMF and TREAT·HF was purchased from J&K Scientific. Other chemicals for substrates preparation were purchased from Acros, J&K Scientific, Aldrich and Dikemann.

Instrumentation. Proton nuclear magnetic resonance spectra (^{1}H NMR) spectra, carbon nuclear magnetic resonance spectra (^{13}C NMR) and fluorine nuclear magnetic resonance spectra (^{19}F NMR) were recorded at 23 °C on a Bruker 400 spectrometer in $CDCl_3$ (400 MHz for ^{1}H, 101 MHz for ^{13}C and 376 MHz for ^{19}F) and Bruker 500 spectrometer in $CDCl_3$ (500 MHz for ^{1}H, 126 MHz for ^{13}C and 470 MHz for ^{19}F). Chemical shifts for protons were reported as parts per million in δ scale using solvent residual peak ($CHCl_3$: 7.26 ppm) or tetramethylsilane (0.00 ppm) as internal standards. Chemical shifts of ^{13}C NMR spectra were reported in ppm from the central peak of $CDCl_3$ (77.16 ppm) on the δ scale. Chemical shifts of ^{19}F 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 Bruker SolariX 9.4T ICR Mass Spectrometer or Thermo Q Exactive Focus Orbitrap Mass Spectrometer. The melting points were obtained on a Stuart™ SMP40 automatic melting point apparatus. The control experiment results were obtained on a Shimadzu GCMS-QP2010 SE GC MS Spectrometer.

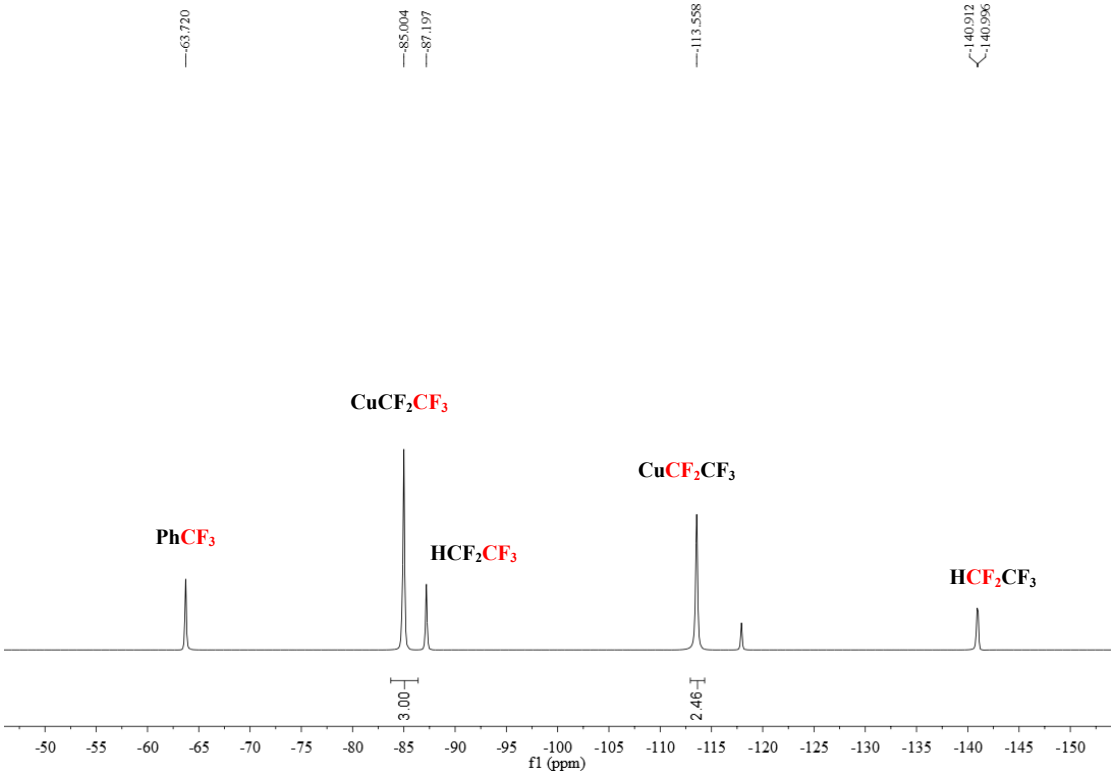
Experimental Procedures:

Modified procedure for the preparation of pentafluoroethane-derived [$CuCF_2CF_3$] reagent:[1]



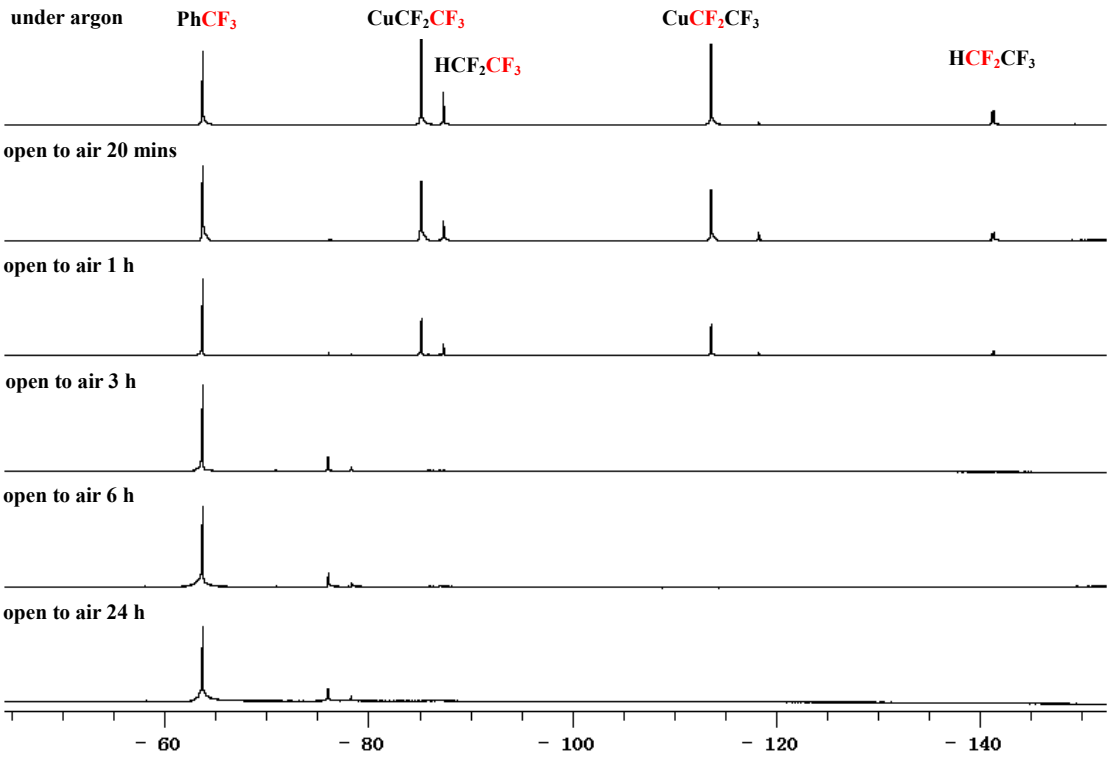
In a glove box, to a glass tube was charged CuCl (200 mg, 2.0 mmol), *t*-BuOK (472 mg, 4.0 mmol) and a stirrer bar. The flask was sealed with a septum, brought out of the glove box and put under an argon atmosphere. Degassed DMF (1.0 mL) was added *via* syringe and the mixture was vigorously stirred at room temperature for 30 min. Then pentafluoroethane (CF_3CF_2H) was bubbled into the mixture by using a needle connected to the CF_3CF_2H cylinder at room temperature for 2.5 min. After removing the CF_3CF_2H inlet, the mixture was stirred for 5 min and $Et_3N{\cdot}3HF$ (326 μL, 2.0 mmol) was slowly added under argon and the mixture was stirred for another 5 min. A slightly greyish yellow solution with white precipitates was obtained as the [$CuCF_2CF_3$] solution in DMF (~87%, ~0.90 M).

^{19}F NMR of freshly prepared $CuCF_2CF_3$ reagent (in DMF, under argon, internal standard = $PhCF_3$):

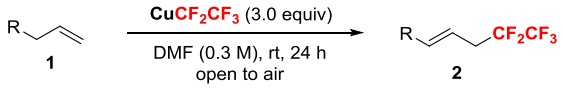


1 Lishchynskyi, A.; Grushin, V. V. *J. Am. Chem. Soc.* **2013**, *135*, 12584.

^{19}F NMR of the $CuCF_2CF_3$ reagent (0.1 M in DMF) over time when open to air:

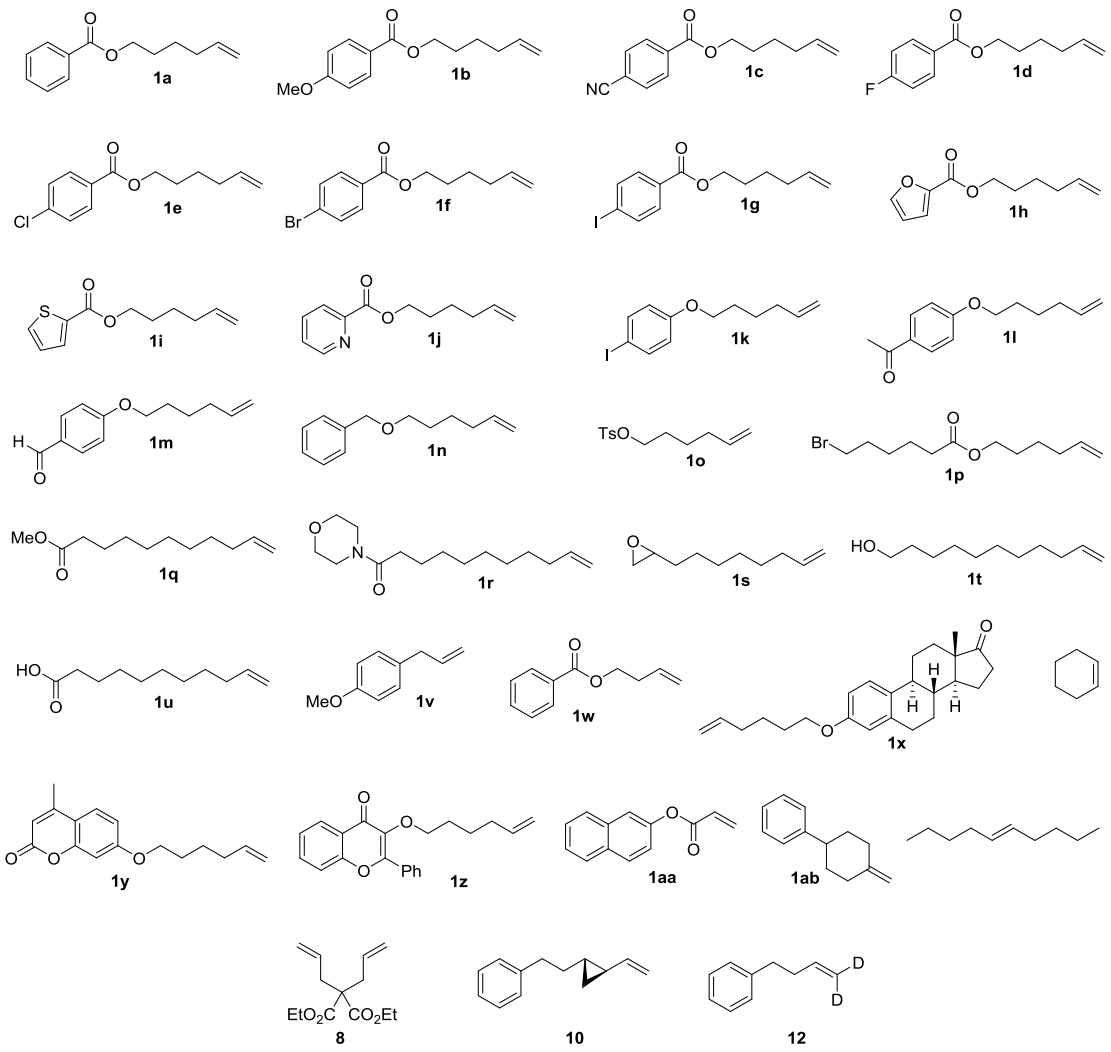


General procedure (*cf.* Scheme 2):



Under air, to a glass tube equipped with a magnetic stir bar and alkene **1** (0.3 mmol) was added above freshly prepared [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF) at 0 °C. Then the tube was warmed to room temperature and stirred for 24 h. The color slowly changed from greyish yellow to dark red. The E/Z ratio was determined by ^{19}F NMR of the crude mixture. The reaction mixture was quenched with aq. sat. sodium potassium tartrate, extracted with diethyl ether three times. The organic layers were combined, washed with water then brine, dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product **2**.

Substrates 1:



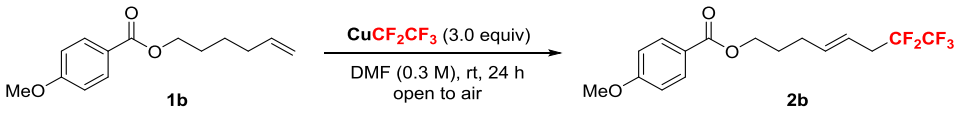
Alkenes **1a-1p**, **1r**, **1w-1ab, 10, 12** were synthesized according to literature procedure.[2] **1q**, **1s-1v**, **1ac-1ad, 8** were commercially available.

2 (a) Yang, X.; Tsui, G. C. *Org. Lett.* **2019**, *21*, 1521. (b) Ye, K.-Y.; McCallum, T.; Lin, S. *J. Am. Chem. Soc.* **2019**, *141*, 9548−9554. (c) Rigby, C. L.; Dixon, D. J. *Chem. Commun.* **2008**, *32*, 3798.

1 mmol scale reaction (*cf.* Scheme 2, compound 2b):

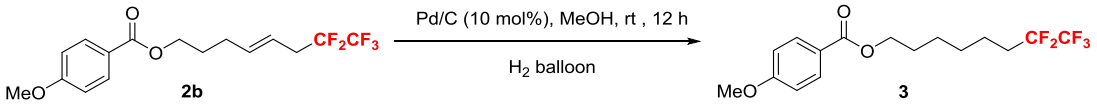
Large scale (14 mmol) preparation of pentafluoroethane-derived [$CuCF_2CF_3$] reagent:

In a glove box, to a 25 mL round-bottom flask was charged CuCl (1.40 g, 14 mmol), *t*-BuOK (3.30 g, 28.0 mmol) and a stirrer bar. The flask was sealed with a septum, brought out of the glove box and put under an argon atmosphere. Degassed DMF (7.0 mL) was added *via* syringe with a water bath, then the water bath was removed and the mixture was vigorously stirred at room temperature for 45 min. Pentafluoroethane (CF_3CF_2H) was bubbled into the mixture by using a needle connected to the CF_3CF_2H cylinder at room temperature for 5 min. After removing the CF_3CF_2H inlet, the mixture was stirred for 5 min and $Et_3N{\cdot}3HF$ (2.30 mL, 14 mmol) was slowly added under argon and the mixture was stirred for another 5 min. A slightly greyish yellow solution with white precipitates was obtained as the [$CuCF_2CF_3$] solution in DMF (~0.90 M).

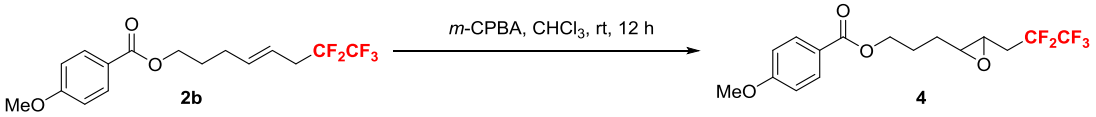


Under air, to a 50 mL glass tube equipped with a magnetic stir bar and alkene **1b** (234 mg, 1.0 mmol) was added above freshly prepared [$CuCF_2CF_3$] (3.30 mL, 3.0 mmol in DMF) at 0 °C. Then the tube was warmed to room temperature and stirred for 24 h. The color slowly changed from greyish yellow to dark red. The E/Z ratio was determined by ^{19}F NMR of the crude mixture. The reaction mixture was quenched with aq. sat. sodium potassium tartrate, extracted with diethyl ether three times. The organic layers were combined, washed with water then brine, dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product **2b** as a colorless oil (289 mg, 0.82 mmol, 82%, E/Z = 95:5, allylic : vinylic = 27 : 1). R_f = 0.40 (Hexane : Et_2O = 5 : 1).

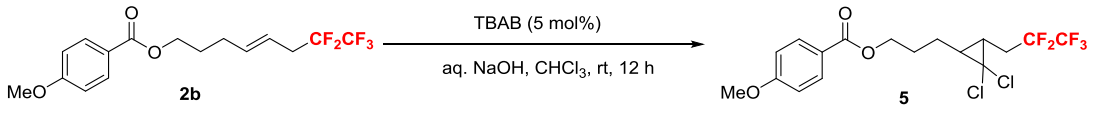
Further transformations (*cf.* Scheme 3):



To a 10 mL round-bottom flask equipped with a magnetic stir bar and **2b** (70.4 mg, 0.2 mmol) was added MeOH (4.0 mL) and Pd/C (21.1 mg, 0.02 mmol), the mixture was evacuated and refilled with H_2 for three times. Then stirred at room temperature for 12 h under a H_2 balloon. After completion (monitored by TLC), filtered and washed with dichloromethane for three times, the combined filtrate was concentrated by rotary evaporator. The crude residue was directly purified by flash column chromatography on silica gel to afford the desired product **3** (0.18 mmol, 63.7 mg, 90 %) as a colorless oil. R_f = 0.5 (hexane : Et_2O = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 4.28 (t, J = 6.6 Hz, 2H), 3.84 (s, 3H), 2.08-1.94 (m, 2H), 1.77 (m, 2H), 1.61 (m, 2H), 1.51-1.41 (m, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.5, 163.4, 131.6, 123.2, 119.3 (qt, $J_{C\text{-}F}$ = 286.3 Hz, $J_{C\text{-}F}$ = 36.6 Hz), 115.9 (tq, $J_{C\text{-}F}$ = 252.3 Hz, $J_{C\text{-}F}$ = 37.6 Hz), 113.7, 64.6, 55.4, 30.7 (t, $J_{C\text{-}F}$ = 22.2 Hz), 28.8, 28.6, 25.8, 20.3 (t, $J_{C\text{-}F}$ = 3.4 Hz) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -86.43 (s, 3F), -119.21 (t, J = 18.4 Hz, 2F). **HRMS** m/z (ESI): calcd. for $C_{16}H_{19}F_5O_3Na$ $[M+Na]^+$: 377.1147; found: 377.1144.



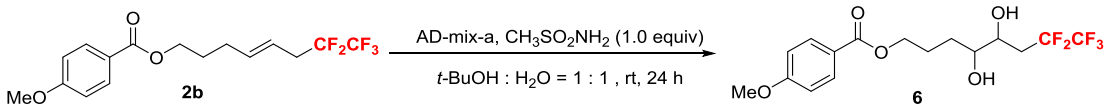
Followed a literature procedure [3]: a solution of *m*-CPBA (119 mg, 0.48 mmol) in $CHCl_3$ (1.6 mL) was added to a solution of **2b** (70.4 mg, 0.2 mmol) in $CHCl_3$ (0.6 mL) at 0 °C and then warmed to room temperature. After the solution was stirred for 12 h, CH_2Cl_2 was added, the organic phase was washed with sat. aq. $Na_2S_2O_3$ and $NaHCO_3$, then brine, dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The residue was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained product **4** (0.14 mmol, 52.2 mg, 71 %, dr = 93 : 7) as a yellow solid, melting point: 38.0–38.7 °C, R_f = 0.2 (hexane : Et_2O = 5 : 1). Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 4.32 (td, J = 6.4 Hz, J = 2.0 Hz, 2H), 3.83 (s, 3H), 2.98 (t, J = 5.6 Hz, 1H), 2.84 (t, J = 5.6 Hz, 1H), 2.44-2.29 (m, 1H), 2.25-2.11 (m, 1H), 1.96-1.85 (m, 2H), 1.82-1.74 (m, 1H), 1.71-1.64 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.3, 163.5, 131.6, 122.7, 119.2 (qt, $J_{C\text{-}F}$ = 286.2 Hz, $J_{C\text{-}F}$ = 35.8 Hz), 114.9 (tq, $J_{C\text{-}F}$ = 253.7 Hz, $J_{C\text{-}F}$ = 38.7 Hz), 113.7, 63.9, 57.4, 55.4, 50.7 (t, $J_{C\text{-}F}$ = 5.2 Hz), 34.6 (t, $J_{C\text{-}F}$ = 21.7 Hz), 28.4, 25.2 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -86.37 (s, 3F), -117.15 (m, 2F). **HRMS** m/z (ESI): calcd. for $C_{16}H_{17}F_5O_4Na$ $[M+Na]^+$: 391.0939; found: 391.0937.



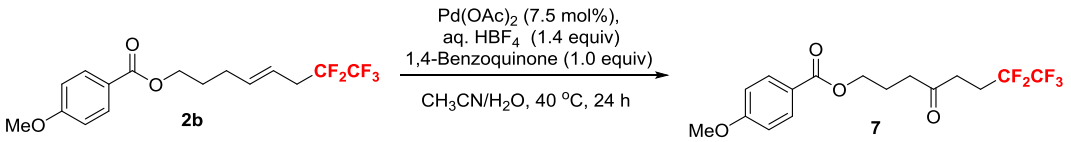
Followed a literature procedure [3]: a glass tube charge with a stirred bar was added **2b** (70.4 mg,

3 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.

0.2 mmol), TBAB (3.2 mg, 0.01 mmol) and 17 M aq. NaOH (1.2 mL, 20.0 mmol), then $CHCl_3$ (0.3 mL/0.3 mL) was added in two portions. The mixture was stirred at room temperature until **2b** was fully consumed (monitored by GC MS). Diluted with H_2O and CH_2Cl_2, extracted with CH_2Cl_2 for three times. The combined organic phase was washed with H_2O and brine, dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The residue was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained product **5** (0.18 mmol, 78.1 mg, 90 %, dr = 93 : 7) as a yellowish liquid, R_f = 0.5 (hexane : Et_2O = 5 : 1). Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.34 (t, *J* = 6.4 Hz 2H), 3.84 (s, 3H), 2.64-2.50 (m, 1H), 2.16-2.02 (m, 1H), 2.00-1.91 (m, 2H), 1.75 (q, *J* = 7.3 Hz, 2H), 1.47-1.37 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.4, 163.5, 131.7, 122.7, 119.0 (qt, $J_{C\text{-}F}$ = 286.5 Hz, $J_{C\text{-}F}$ = 35.9 Hz), 115.2 (tq, $J_{C\text{-}F}$ = 252.9 Hz, $J_{C\text{-}F}$ = 38.1 Hz), 113.7, 64.2, 63.9, 55.5, 35.3, 31.6 (t, $J_{C\text{-}F}$ = 21.9 Hz), 28.1 (t, $J_{C\text{-}F}$ = 4.0 Hz), 27.5, 26.8 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -86.23 (s, 3F), -118.10 (m, 2F). **HRMS** m/z (ESI): calcd. for $C_{17}H_{17}Cl_2F_5O_3$ $[M+Na]^+$: 457.0367; found: 457.0368.



Followed a literature procedure [3]: a glass tube equipped with a stirred bar was charge with *t*-BuOH (1.0 mL), H_2O (1.0 mL), AD-mix-α (280 mg) and CH_3SO_2Na (19.0 mg, 0.2 mmol). The mixture was stirred until both phases were clear. Then **2b** (70.4 mg, 0.2 mmol) was added at once and the heterogenous slurry was stirred until the **2b** was fully consumed. The reaction was quenched at 0 °C by adding Na_2SO_3 (3.0 g), then warm to room temperature and stirred for 1 h, extracted with EtOAc for three times. The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The crude residue was purified by flash column chromatography on silica gel (hexane/acetone) and obtained product **6** (0.18 mmol, 71.0 mg, 92 %, dr > 20 : 1) as a white solid, melting point: 82.6–83.4 °C, R_f = 0.4 (hexane : acetone = 5 : 1). Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.30 (t, *J* = 6.4 Hz, 2H), 3.99 (s, 1H), 3.82 (s, 3H), 3.54 (s, 1H), 3.33 (d, *J* = 17.2 Hz, 1H), 3.13 (d, *J* = 12.8 Hz, 1H), 2.49-2.19 (m, 2H), 1.98-1.89 (m,1H), 1.88-1.78 (m, 1H), 1.66 (q, *J* = 7.2 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 167.0, 163.6, 131.7, 122.4, 119.0 (qt, $J_{C\text{-}F}$ = 286.4 Hz, $J_{C\text{-}F}$ = 36.2 Hz), 115.8 (tq, $J_{C\text{-}F}$ = 254.0 Hz, $J_{C\text{-}F}$ = 38.1 Hz), 113.7, 73.8, 67.6, 64.6, 55.5, 35.0 (t, $J_{C\text{-}F}$ = 20.6 Hz), 29.9, 25.2 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -86.83 (s, 3F), -117.77 (m, 2F). **HRMS** m/z (ESI): calcd. for $C_{16}H_{19}F_5O_5$ $[M+Na]^+$: 409.1045; found: 409.1042.



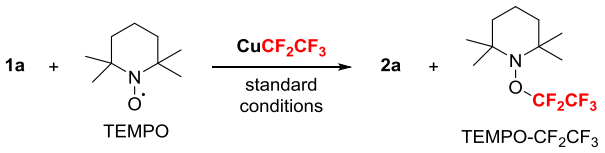
Followed a literature procedure [4]: to a glass tube charges with a stirred bar was added $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), 1,4-benzoquinone (21.6 mg, 0.2 mmol). A mixture of MeCN (0.88 mL) and water (0.10 mL) was added followed by addition of 32% aq. HBF_4 solution (60 μL). Then **2b** (70.4 mg, 0.2 mmol) was added at once and the homogeneous dark red solution was stirred for 24 h at 40

4 Lerch, M. M.; Morandi, B.; Wickens, Z. K.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2014**, *53*, 8654.

°C. Diluted with sat. aq. NaCl solution, extracted with CH_2Cl_2. The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The crude product was then further purified by flash column chromatography on silica gel (hexane/EtOAc) to furnish the desired pure product **7** (0.10 mmol, 38.3 mg, 52 %, rr > 20 : 1) as a white solid, melting point: 64.5–65.2 °C, R_f = 0.3 (hexane : EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.30 (t, *J* = 6.2 Hz, 2H), 3.84 (s, 3H), 2.72 (t, *J* = 7.8 Hz, 2H), 2.62 (t, *J* = 7.2 Hz, 2H), 2.41-2.28 (m, 2H), 2.10-2.03 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 206.1, 166.4, 163.6, 131.7, 122.5, 119.1 (qt, $J_{C\text{-}F}$ = 286.2 Hz, $J_{C\text{-}F}$ = 36.3 Hz), 115.6 (tq, $J_{C\text{-}F}$ = 252.6 Hz, $J_{C\text{-}F}$ = 38.0 Hz), 113.7, 63.7, 55.5, 39.2, 33.6, 24.8 (t, $J_{C\text{-}F}$ = 22.1 Hz), 23.0 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -86.49 (s, 3F), -119.30 (t, *J* = 18.4 Hz, 2F). **HRMS** m/z (ESI): calcd. for $C_{16}H_{17}F_5O_4Na$ $[M+Na]^+$: 391.0939; found: 391.0936.

Mechanistic studies:

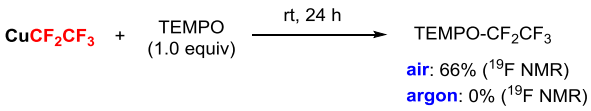
TEMPO trapping experiments (*cf.* Eqs. 4a and 4b).



Equiv of TEMPO	Yield (19F NMR) of **2a***	Yield (19F NMR) of TMEPO-CF_2CF_3**
1.0	59%	47%
2.0	15%	45%
3.0	0%	33%

* Based on **1a**. ** Based on TEMPO.

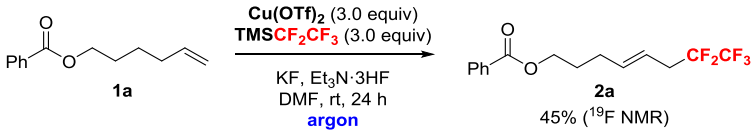
Under air, to a glass tube equipped with a magnetic stir bar was added alkene **1a** (20.4 mg, 0.1 mmol), TEMPO (15.6 mg for 1.0 equiv; 31.2 mg for 2.0 equiv; 46.8 mg for 3.0 equiv), then freshly prepared [$CuCF_2CF_3$] (0.33 mL, 0.90 mmol in DMF) was added dropwise at 0 °C. The tube was warmed to room temperature and stirred for 24 h. The crude yield of each equation was analyzed by ^{19}F NMR using benzotrifluoride as the internal standard. **TEMPO-CF_2CF_3: ^{19}F NMR** (376 MHz, $CDCl_3$): δ -84.80 (s, 3F), -85.81 (s, 2F). **HRMS** m/z (APCI): calcd. for $C_{11}H_{19}F_5NO$ $[M+H]^+$: 276.1381; found: 276.1380. The spectral data are in full accordance with the literature report.[5]



Under air or argon, to a glass tube equipped with a magnetic stir bar and TEMPO (46.8 mg, 0.3 mmol) was added freshly prepared [$CuCF_2CF_3$] (0.33 mL, 0.90 mmol in DMF) dropwise at 0 °C. Then the tube was warmed to room temperature and stirred for 24 h. The crude yield of under air or argon condition was analyzed by ^{19}F NMR using benzotrifluoride as the internal standard.

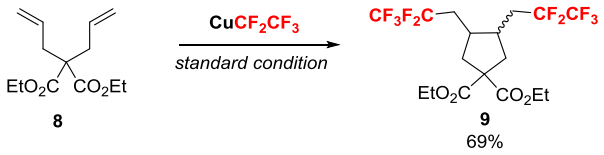
5 (a) Hartmann, M.; Li, Y.; Studer, A. *Org. Biomol. Chem.* **2016**, *14*, 206; (b) Xu, J.; Qiao, L.; Ying, B.; Zhu, X.; Shen, C.; Zhang, P. *Org. Chem. Front.* **2017**, *4*, 1116.

Using $Cu(OTf)_2$ and $TMSCF_2CF_3$ (*cf.* Eq. 4c):

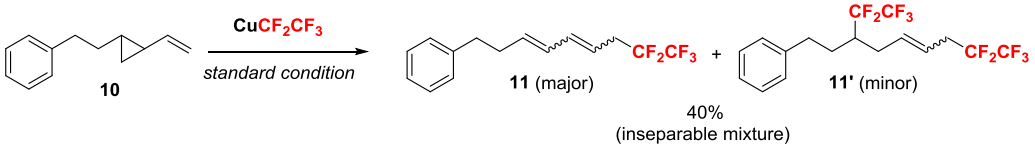


Under argon, to a glass tube equipped with a magnetic stir bar was added **1a** (20.4 mg, 0.1 mmol), $Cu(OTf)_2$ (108.5 mg, 0.3 mmol), KF (17.4 mg, 0.3 mmol), $Et_3N{\cdot}HF$ (32.6 μL, 0.2 mmol) and degassed DMF (0.33 mL), followed by addition of $TMSCF_2CF_3$ (53 μL, 0.3 mmol) dropwise at 0 °C. Then the tube was warmed to room temperature and stirred for 24 h. The crude yield was analyzed by ^1F NMR using benzotrifluoride as the internal standard.

Radical clock experiments (*cf.* Eqs. 4d and 4e).



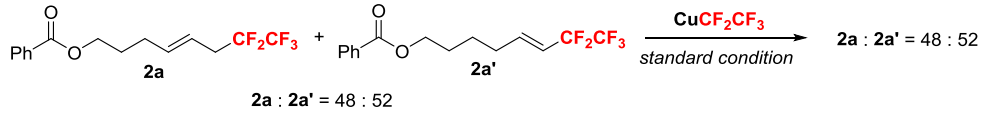
Under air, to a glass tube equipped with a magnetic stir bar and **8** (72.0 mg, 0.3 mmol) was added freshly prepared [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF) dropwise at 0 °C. Then the tube was warmed to room temperature and stirred for 24 h. The reaction mixture was quenched with aq. sat. sodium potassium tartrate, extracted with diethyl ether three times. The organic layers were combined, washed with water then brine, dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel (hexane/Et_2O) to afford an inseparable mixture of **9** and **8** (**9** : 0.21 mmol, dr = 9 : 1, determined by GC MS; **8** : 0.066 mmol, **9** + **8** total 114 mg, **9** : **8** = 3.2 : 1) as a colorless oil. R_f = 0.5 (hexane : EtOAc = 5 : 1). **Compound 9 (major diasteromer)**: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.19-4.11 (m, 4H), 2.55-2.49 (m, 4H), 2.25-2.18 (m, 2H), 2.03-1.94 (m, 4H), 1.23-1.19 (m, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 172.5, 172.0, 119.1 (qt, J_{C-F} = 286.3 Hz, J_{C-F} = 36.2 Hz), 115.9 (tq, J_{C-F} = 254.0 Hz, J_{C-F} = 37.7 Hz), 62.0, 61.9, 38.7, 38.7, 35.4, 29.6 (t, J_{C-F} = 21.6 Hz), 14.0, 13.9 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -86.91 (s, 3F), -118.26 (m, 2F). **HRMS** m/z (APCI): calcd. for $C_{17}H_{21}F_{10}O_4$ $[M+H]^+$: 479.1275; found: 479.1275.



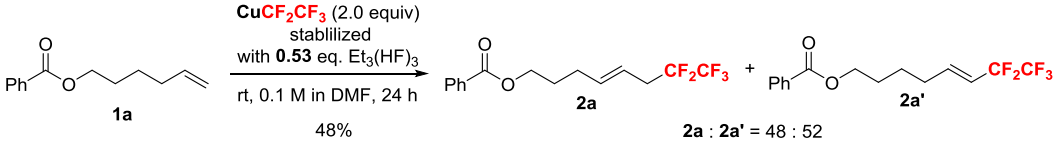
Under air, to a glass tube equipped with a magnetic stir bar and **10** (51.6 mg, 0.3 mmol) was added freshly prepared [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF) dropwise at 0 °C. Then the tube was warmed to room temperature and stirred for 24 h. The reaction mixture was quenched with aq. sat. sodium potassium tartrate, extracted with diethyl ether three times. The organic layers were combined, washed

with water then brine, dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel (hexane) to afford an inseparable mixture of **11** and **11'** (total about 0.12 mmol, 38 mg) as a colorless oil. R_f = 0.8 (hexane : Et_2O = 10 : 1). Major isomer of **11**: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 (t, J = 7.4 Hz, 2H), 7.49-7.43 (m, 3H), 6.53-6.43 (m, 1H), 6.39-6.28 (m, 1H), 6.06-5.99 (m, 1H), 5.79-5.72 (m, 1H), 3.11-3.04 (m, 2H), 3.01-2.97 (m, 2H), 2.69 (q, J = 7.7 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 141.7, 137.5, 135.2, 129.7, 128.5, 128.5, 126.1, 119.2 (qt, $J_{C\text{-}F}$ = 286.9 Hz, $J_{C\text{-}F}$ = 36.0 Hz), 114.9 (tq, $J_{C\text{-}F}$ = 253.2 Hz, $J_{C\text{-}F}$ = 36.4 Hz), 117.4 (t, $J_{C\text{-}F}$ = 17.6 Hz), 35.7, 34.7 (t, $J_{C\text{-}F}$ = 22.6 Hz), 34.5 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -85.97 (s, 3F), -118.22 (t, J = 17.7 Hz, 2F). **HRMS** m/z (APCI): calcd. for $C_{15}H_{16}F_5$ $[M+H]^+$: 291.1167; found: 291.1167. **Compound 11'**: **HRMS** m/z (ESI): calcd. for $C_{17}H_{17}F_{10}$ $[M+H]^+$: 411.1165; found: 411.1169.

Control experiments (*cf.* Eq. 4f).

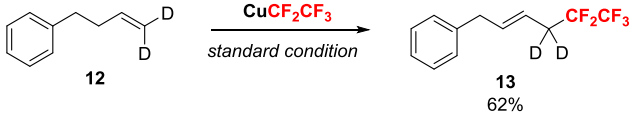


Under air, to a glass tube equipped with a magnetic stir bar and **2a** and **2a'** (32.2 mg, 0.1 mmol, **2a** : **2a'** = 48 : 52) was added freshly prepared [$CuCF_2CF_3$] (0.33 mL, 0.90 mmol in DMF) dropwise at 0 °C. The tube was warmed to room temperature and stirred for 24 h. The crude **2a**/**2a'** ratio was analyzed by ^{19}F NMR using benzotrifluoride as the internal standard.



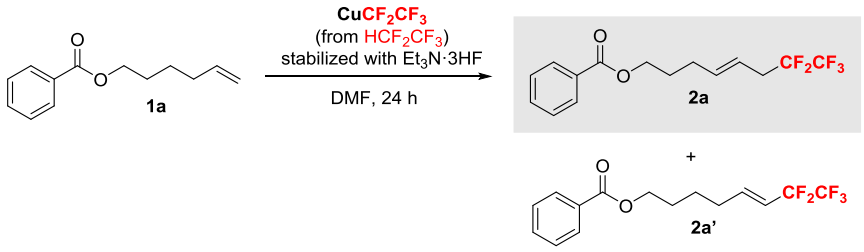
Preparation of 2a': Under air, to a glass tube equipped with a magnetic stir bar was added **1a** (20.4 mg, 0.1 mmol) and DMF (0.78 mL). Then freshly prepared [$CuCF_2CF_3$] (0.22 mL, 0.90 mmol in DMF, stabilized with 0.53 equiv $Et_3N{\cdot}HF$) was added dropwise at room temperature. The tube was stirred for 24 h at room temperature. Quenched with aq. sat. sodium potassium tartrate, extracted with diethyl ether three times. The organic layers were combined, washed with water then brine, dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel (hexane/Et_2O) to afford an inseparable mixture of **2a** and **2a'** (15.4 mg, 0.048 mmol, **2a : 2a'** = 48 : 52, R_f = 0.6 (hexane : Et_2O = 8 : 1)) as a colorless oil. **Compound 2a': ^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.05 (d, J = 7.5 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 6.47-6.39 (m, 1H), 5.67-5.57 (m, 1H), 4.34 (t, J = 6.4 Hz, 2H), 2.30-2.22 (m, 2H), 1.82-1.77 (m, 2H), 1.67-1.59 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.7, 142.5 (t, $J_{C\text{-}F}$ = 8.7 Hz), 133.0, 130.5, 129.6, 128.5, 119.1 (qt, $J_{C\text{-}F}$ = 286.3 Hz, $J_{C\text{-}F}$ = 38.5 Hz), 117.2 (t, $J_{C\text{-}F}$ = 23.2 Hz), 112.2 (tq, $J_{C\text{-}F}$ = 250.7 Hz, $J_{C\text{-}F}$ = 38.5 Hz), 64.5, 31.6, 28.2, 24.7 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$): *E* isomer: δ -86.53 (s, 3F), -116.24 (d, J = 11.7 Hz, 2F). **HRMS** m/z (APCI): calcd. for $C_{15}H_{16}F_5O_2$ $[M+H]^+$: 323.1065; found: 323.1066.

Using D-labeled substrate (*cf.* Eq. 4g):



Under air, to a glass tube equipped with a magnetic stir bar and alkene **12** (40.2 mg, 0.3 mmol, 92% D incorporation) was added freshly prepared [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF) at 0 °C. Then was warmed to room temperature and stirred for 24 h. Quenched with aq. sat. sodium potassium tartrate, extracted with diethyl ether three times. The organic layers were combined, washed with water then brine, dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The crude residue was purified by flash column chromatography on silica gel (hexane) to afford the desired product **13** (0.19 mmol, 46.9 mg, 90% D incorporation, R_f = 0.6 (hexane)) as a colorless oil. **Compound 13: ^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40 (t, J = 7.4 Hz, 2H), 7.27-7.20 (m, 3H), 5.90 (dt, J = 15.2 Hz, J = 6.8 Hz, 1H), 5.51 (d, J = 15.2 Hz, 1H), 3.44 (d, J = 6.8 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 139.6, 137.4, 128.7, 126.4, 119.3 (qt, $J_{C\text{-}F}$ = 286.6 Hz, $J_{C\text{-}F}$ = 36.3 Hz), 118.1, 114.9 (tq, $J_{C\text{-}F}$ = 252.8 Hz, $J_{C\text{-}F}$ = 36.7 Hz), 39.1 ppm. (one carbon missing due to overlap) **^{19}F NMR** (376 MHz, $CDCl_3$): δ -85.94 (s, 3F), -118.56 (s, 2F). **HRMS** m/z (APCI): calcd. for $C_{12}H_9D_2F_5$ $[M]^+$: 253.0979; found: 253.0982.

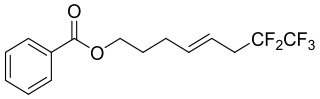
Table S1. Optimization studies[a]



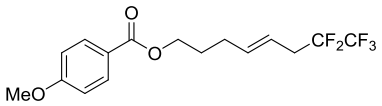
entry	equiv of $Et_3N·3HF$ (based on Cu)	equiv of $CuCF_2CF_3$	oxidant (equiv)	conc. (M)	yield of **2a**+**2a'** (%)[b]	ratio of **2a**:**2a'**[b]
1	0.53	2.0	air	0.1	59	1:1.3
2	0.75	2.0	air	0.1	59	5.5:1
3	1.0	2.0	air	0.1	59	19:1
4	1.2	2.0	air	0.1	42	19:1
5	1.0	2.0	air	0.2	67	21:1
6	1.0	2.0	air	0.3	69	22:1
7	1.0	2.0	air	0.4	71	22:1
8[c]	1.0	2.0	air	0.4	78	21:1
9[c,d]	1.0	2.0	air	0.4	56	25:1
10[c,e]	1.0	2.0	none	0.4	<5	-
11[c,e]	1.0	2.0	AgOAc (2.0)	0.4	37	14:1
12[c,e]	1.0	2.0	$PhI(OAc)_2$ (2.0)	0.4	77	11:1
13[c,e]	1.0	2.0	DDQ (2.0)	0.4	<5	-
14[c,e]	1.0	2.0	1,4-Benzoquinone (2.0)	0.4	<5	-
15[c,e]	1.0	2.0	Di-*tert*-butyl peroxide (2.0)	0.4	28	27:1
16[c]	1.0	2.0	O_2 balloon	0.4	46	15:1
17[c,f]	1.0	2.0	air	0.4	64	16:1
18[c]	1.0	1.5	air	0.4	68	19:1
19[c]	**1.0**	**3.0**	**air**	**0.3**	**88 (87)[g]**	**20:1**
20[c]	1.0	4.0	air	0.23	87	16:1

[a]Unless specified otherwise, reactions were carried out using 0.1 mmol **1a** at room temperature open to air. [b]Determined by ^1H NMR analysis of the crude mixture. [c]$CuCF_2CF_3$ was added at 0 °C then the reaction mixture was warmed to room temperature. [d]$CuCF_2CF_3$ was stabilized with 0.33 equiv Olah's reagent (HF-pyridine). [e]Under argon. [f]At 50 °C. [g]Isolated yield at 0.3 mmol scale (**2a**:**2a'** = 20:1; *E*/*Z* of **2a** = 92:8).

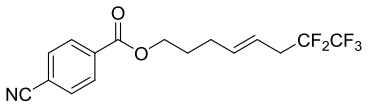
Characterization Data:



2a: (E)-7,7,8,8,8-pentafluorooct-4-en-1-yl benzoate. Prepared according to the general procedure. Reaction was run using **1a** (61.2 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a colorless oil (0.26 mmol, 84.0 mg, 87 %, *E/Z* = 92 : 8, allylic : vinylic = 20 : 1), R_f = 0.6 (hexane : Et_2O = 8 : 1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 5.78-5.72 (m, 1H), 5.49-5.43 (m, 1H), 4.33 (t, *J* = 6.5 Hz, 2H), 2.74 (td, *J* = 17.6 Hz, *J* = 7.5 Hz, 2H), 2.24 (q, *J* = 7.2 Hz, 2H), 1.87 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 166.6, 137.4, 133.0, 130.4, 129.6, 128.4, 119.3 (qt, $J_{C\text{-}F}$ = 286.1 Hz, $J_{C\text{-}F}$ = 36.3 Hz), 117.7 (t, $J_{C\text{-}F}$ = 4.3 Hz), 114.8 (tq, $J_{C\text{-}F}$ = 252.3 Hz, $J_{C\text{-}F}$ = 37.0 Hz), 64.2, 34.6 (t, $J_{C\text{-}F}$ = 22.5 Hz), 29.1, 28.1 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.93 (s, 3F), -118.37 (t, *J* = 17.4 Hz, 2F); *Z* isomer: δ -86.16 (s, 3F), -118.21 (t, *J* = 17.9 Hz, 2F). **HRMS** m/z (ESI): calcd. for $C_{15}H_{15}F_5O_2Na$ $[M+Na]^+$: 345.0884; found: 345.0881.

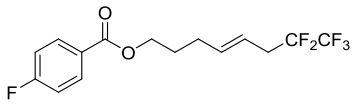


2b: (E)-7,7,8,8,8-pentafluorooct-4-en-1-yl 4-methoxybenzoate. Prepared according to the general procedure. Reaction was run using **1b** (70.2 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a colorless oil (0.26 mmol, 89.8 mg, 85 %, *E/Z* = 91 : 9, allylic : vinylic = 23 : 1), R_f = 0.5 (hexane : Et_2O = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 5.78-5.70 (m, 1H), 5.48-5.41 (m, 1H), 4.29 (t, *J* = 6.6 Hz, 2H), 3.83 (d, *J* = 1.2 Hz, 3H), 2.74 (td, *J* = 17.6 Hz, *J* = 7.2 Hz, 2H), 2.22 (q, *J* = 7.2 Hz, 2H), 1.84 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.4, 163.5, 137.5, 131.6, 122.9, 119.2 (qt, $J_{C\text{-}F}$ = 286.6 Hz, $J_{C\text{-}F}$ = 36.4 Hz), 117.6 (t, $J_{C\text{-}F}$ = 4.3 Hz), 114.8 (tq, $J_{C\text{-}F}$ = 252.7 Hz, $J_{C\text{-}F}$ = 37.2 Hz), 113.7, 63.9, 55.4, 34.6 (t, $J_{C\text{-}F}$ = 22.5 Hz), 29.1, 28.2 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.78 (s, 3F), -118.23 (t, *J* = 17.4 Hz, 2F); *Z* isomer: δ -85.99 (s, 3F), -118.05 (t, *J* = 17.9 Hz, 2F). **HRMS** m/z (ESI): calcd. for $C_{16}H_{17}F_5O_3Na$ $[M+Na]^+$: 375.0990; found: 375.0987.

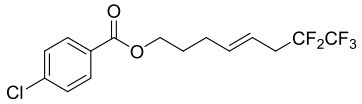


2c: (E)-7,7,8,8,8-pentafluorooct-4-en-1-yl 4-cyanobenzoate. Prepared according to the general procedure. Reaction was run using **1c** (68.7 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a colorless oil (0.23 mmol, 79.1 mg, 76 %, *E/Z* = 92 : 8, allylic : vinylic > 50 : 1), R_f = 0.4 (hexane : Et_2O = 5 : 1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 5.76-5.70 (m, 1H), 5.48-5.42 (m, 1H), 4.34 (t, *J* = 6.5 Hz, 2H), 2.73 (td, *J* = 17.6 Hz, *J* = 7.0 Hz, 2H), 2.23 (q, *J* = 7.2 Hz, 2H), 1.87 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 165.0, 137.1, 134.2, 132.3, 130.1, 119.3 (qt, $J_{C\text{-}F}$ = 286.1 Hz, $J_{C\text{-}F}$ = 36.2 Hz), 118.0, 117.9 (t, $J_{C\text{-}F}$ = 4.2 Hz), 116.4, 114.8 (tq, $J_{C\text{-}F}$ = 252.5 Hz, $J_{C\text{-}F}$ = 37.0 Hz), 65.0, 34.5 (t, $J_{C\text{-}F}$ = 22.4 Hz), 29.0, 27.9 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.78

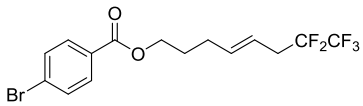
(s, 3F), -118.22 (t, J = 17.4 Hz, 2F); *Z* isomer: δ -86.01 (s, 3F), -118.05 (t, J = 17.9 Hz, 2F). **HRMS** m/z (APCI): calcd. for $C_{16}H_{15}F_5NO_2$ $[M+H]^+$: 348.1018; found: 348.1017.



2d: (E)-7,7,8,8,8-pentafluorooct-4-en-1-yl 4-fluorobenzoate. Prepared according to the general procedure. Reaction was run using **1d** (66.6 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a colorless oil (0.24 mmol, 82.6 mg, 81 %, *E/Z* = 92 : 8, allylic : vinylic = 24 : 1), R_f = 0.6 (hexane : Et_2O = 8 : 1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.06-8.03 (m, 2H), 7.73 (t, J = 8.0 Hz, 2H), 5.77-5.71 (m, 1H), 5.48-5.42 (m, 1H), 4.31 (t, J = 6.3 Hz, 2H), 2.74 (td, J = 17.5 Hz, J = 7.0 Hz, 2H), 2.23 (q, J = 7.2 Hz, 2H), 1.86 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 165.9 (d, $J_{C\text{-}F}$ = 254.8 Hz), 165.7, 137.4, 132.2 (d, $J_{C\text{-}F}$ = 9.3 Hz), 126.7 (d, $J_{C\text{-}F}$ = 2.9 Hz), 119.3 (qt, $J_{C\text{-}F}$ = 286.6 Hz, $J_{C\text{-}F}$ = 36.3 Hz), 117.8 (t, $J_{C\text{-}F}$ = 4.5 Hz), 115.6 (d, $J_{C\text{-}F}$ = 22.1 Hz), 114.9 (tq, $J_{C\text{-}F}$ = 252.9 Hz, $J_{C\text{-}F}$ = 37.2 Hz), 64.4, 34.6 (t, $J_{C\text{-}F}$ = 22.5 Hz), 29.1, 28.1 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.78 (s, 3F), -106.79 (m, 1F), -118.22 (t, J = 17.4 Hz, 2F); *Z* isomer: δ -86.01 (s, 3F), -106.71 (m, 1F), -118.06 (t, J = 17.7 Hz, 2F). **HRMS** m/z (APCI): calcd. for $C_{15}H_{15}F_6O_2$ $[M+H]^+$: 341.0971; found: 341.0971.

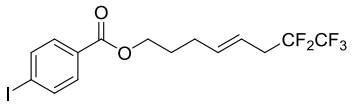


2e: (E)-7,7,8,8,8-pentafluorooct-4-en-1-yl 4-chlorobenzoate. Prepared according to the general procedure. Reaction was run using **1e** (71.4 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a colorless oil (0.25 mmol, 87.6 mg, 82 %, *E/Z* = 92 : 8, allylic : vinylic = 48 : 1), R_f = 0.6 (hexane : Et_2O = 8 : 1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.96 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 5.77-5.71 (m, 1H), 5.48-5.42 (m, 1H), 4.31 (t, J = 6.5 Hz, 2H), 2.74 (td, J = 17.5 Hz, J = 7.0 Hz, 2H), 2.23 (q, J = 7.2 Hz, 2H), 1.86 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 165.8, 139.5, 137.3, 131.0, 128.9, 128.8, 119.2 (qt, $J_{C\text{-}F}$ = 286.1 Hz, $J_{C\text{-}F}$ = 36.4 Hz), 117.8 (t, $J_{C\text{-}F}$ = 4.3 Hz), 114.8 (tq, $J_{C\text{-}F}$ = 252.5 Hz, $J_{C\text{-}F}$ = 37.2 Hz), 64.5, 34.6 (t, $J_{C\text{-}F}$ = 22.4 Hz), 29.1, 28.0 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.79 (s, 3F), -118.23 (t, J = 17.4 Hz, 2F); *Z* isomer: δ -86.00 (s, 3F), -118.10 (t, J = 17.7 Hz, 2F). **HRMS** m/z (APCI): calcd. for $C_{15}H_{15}ClF_5O_2$ $[M+H]^+$: 357.0675; found: 357.0674.

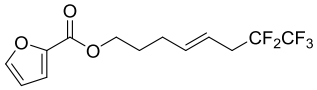


2f: (E)-7,7,8,8,8-pentafluorooct-4-en-1-yl 4-bromobenzoate. Prepared according to the general procedure. Reaction was run using **1f** (84.6 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a colorless oil (0.25 mmol, 100.8 mg, 84 %, *E/Z* = 92 : 8, allylic : vinylic = 24 : 1), R_f = 0.6 (hexane : Et_2O = 8 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 5.77-5.70 (m, 1H), 5.49-5.41 (m, 1H), 4.31 (t, J = 6.4 Hz, 2H), 2.74 (td, J = 17.6 Hz, J = 7.2 Hz, 2H), 2.22 (q, J = 7.1 Hz, 2H), 1.86 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 165.9, 137.3, 131.8, 131.2, 129.3, 128.1,

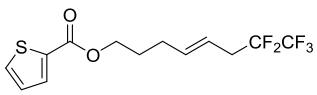
119.2 (qt, $J_{C\text{-}F}$ = 286.1 Hz, $J_{C\text{-}F}$ = 36.3 Hz), 117.8 (t, $J_{C\text{-}F}$ = 4.2 Hz), 114.8 (tq, $J_{C\text{-}F}$ = 252.4 Hz, $J_{C\text{-}F}$ = 37.2 Hz), 64.5, 34.6 (t, $J_{C\text{-}F}$ = 22.4 Hz), 29.1, 28.0 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.78 (s, 3F), -118.23 (t, *J* = 17.7 Hz, 2F); *Z* isomer: δ -86.00 (s, 3F), -118.05 (t, *J* = 17.9 Hz, 2F). **HRMS** m/z (APCI): calcd. for $C_{15}H_{15}BrF_5O_2$ $[M+H]^+$: 401.0170; found: 401.0168.



2g: (E)-7,7,8,8,8-pentafluorooct-4-en-1-yl 4-iodobenzoate. Prepared according to the general procedure. Reaction was run using **1g** (99.0 mg, 0.3 mmol), $[CuCF_2CF_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a colorless oil (0.22 mmol, 96.8 mg, 72 %, *E/Z* = 93 : 7, allylic : vinylic > 50 : 1, the product was contaminated by ~5% cross-coupled side product), R_f = 0.6 (hexane : Et_2O = 8 : 1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 5.77-5.71 (m, 1H), 5.48-5.42 (m, 1H), 4.31 (t, *J* = 6.4 Hz, 2H), 2.74 (td, *J* = 17.5 Hz, *J* = 7.0 Hz, 2H), 2.22 (q, *J* = 7.0 Hz, 2H), 1.86 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 166.2, 137.8, 137.3, 131.1, 129.9, 119.2 (qt, $J_{C\text{-}F}$ = 286.3 Hz, $J_{C\text{-}F}$ = 36.2 Hz), 117.8 (t, $J_{C\text{-}F}$ = 4.2 Hz), 114.8 (tq, $J_{C\text{-}F}$ = 252.3 Hz, $J_{C\text{-}F}$ = 37.2 Hz), 100.8, 64.5, 34.6 (t, $J_{C\text{-}F}$ = 22.6 Hz), 29.1, 28.0 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.78 (s, 3F), -118.25 (t, *J* = 17.7 Hz, 2F); *Z* isomer: δ -86.00 (s, 3F), -118.06 (t, *J* = 17.9 Hz, 2F). **HRMS** m/z (APCI): calcd. for $C_{15}H_{15}IF_5O_2$ $[M+H]^+$: 449.0031; found: 449.0031.

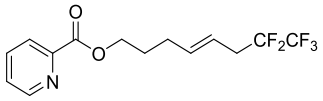


2h: (E)-7,7,8,8,8-pentafluorooct-4-en-1-yl furan-2-carboxylate. Prepared according to the general procedure. Reaction was run using **1h** (58.2 mg, 0.3 mmol), $[CuCF_2CF_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a colorless oil (0.20 mmol, 60.8 mg, 65 %, *E/Z* = 92 : 8, allylic : vinylic = 20 : 1), R_f = 0.6 (hexane : Et_2O = 8 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 (s, 1H), 7.15 (d, *J* = 3.6 Hz, 1H), 6.49 (dd, *J* = 1.6 Hz, 2H), 5.75-5.68 (m, 1H), 5.47-5.39 (m, 1H), 4.29 (t, *J* = 6.6 Hz, 2H), 2.72 (td, *J* = 17.2 Hz, *J* = 6.8 Hz, 2H), 2.20 (q, *J* = 7.1 Hz, 2H), 1.83 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 158.8, 146.4, 144.8, 137.3, 119.2 (qt, $J_{C\text{-}F}$ = 286.1 Hz, $J_{C\text{-}F}$ = 36.3 Hz), 117.9, 117.8 (t, $J_{C\text{-}F}$ = 4.4 Hz), 114.8 (tq, $J_{C\text{-}F}$ = 252.4 Hz, $J_{C\text{-}F}$ = 37.3 Hz), 111.9, 64.2, 34.6 (t, $J_{C\text{-}F}$ = 22.5 Hz), 29.0, 28.0 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.78 (s, 3F), -118.23 (t, *J* = 17.7 Hz, 2F); *Z* isomer: δ -86.00 (s, 3F), -118.06 (t, *J* = 17.7 Hz, 2F). **HRMS** m/z (ESI): calcd. for $C_{13}H_{13}F_5O_3Na$ $[M+Na]^+$: 335.0677; found: 335.0673.

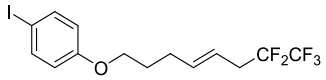


2i: (E)-7,7,8,8,8-pentafluorooct-4-en-1-yl thiophene-2-carboxylate. Prepared according to the general procedure. Reaction was run using **1i** (63.0 mg, 0.3 mmol), $[CuCF_2CF_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a colorless oil (0.21 mmol, 68.9 mg, 70 %, *E/Z* = 92 : 8, allylic : vinylic > 50 : 1), R_f = 0.6 (hexane : Et_2O = 8 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 3.6 Hz, 1H), 7.54 (d, *J* = 5.2 Hz, 1H), 7.09 (t, *J* =

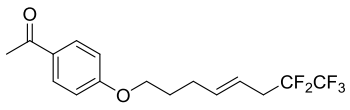
4.0 Hz, 1H), 5.77-5.70 (m, 1H), 5.49-5.42 (m, 1H), 4.30 (t, J = 6.4 Hz, 2H), 2.72 (td, J = 17.6 Hz, J = 7.2 Hz, 2H), 2.22 (q, J = 7.2 Hz, 2H), 1.84 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 162.3, 137.4, 134.0, 133.5, 132.4, 127.8, 119.3 (qt, $J_{C\text{-}F}$ = 286.5 Hz, $J_{C\text{-}F}$ = 36.4 Hz), 117.8 (t, $J_{C\text{-}F}$ = 4.4 Hz), 114.8 (tq, $J_{C\text{-}F}$ = 252.4 Hz, $J_{C\text{-}F}$ = 37.3 Hz), 64.4, 34.6 (t, $J_{C\text{-}F}$ = 22.5 Hz), 29.1, 28.1 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.78 (s, 3F), -118.23 (t, J = 17.7 Hz, 2F); *Z* isomer: δ -85.96 (s, 3F), -118.02 (t, J = 17.9 Hz, 2F). **HRMS** m/z (ESI): calcd. for $C_{13}H_{13}F_5O_2SNa$ $[M+Na]^+$: 351.0449; found: 351.0445.



2j: (E)-7,7,8,8,8-pentafluorooct-4-en-1-yl picolinate. Prepared according to the general procedure. Reaction was run using **1j** (61.5 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.23 mmol, 72.7 mg, 75 %, *E/Z* = 97 : 3, allylic : vinylic = 9 : 1), R_f = 0.4 (hexane : EtOAc = 2 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.73 (d, J = 4.0 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.81 (t, J = 7.6 Hz, 1H), 7.45 (m, 1H), 5.75-5.68 (m, 1H), 5.46-5.38 (m, 1H), 4.39 (t, J = 6.8 Hz, 2H), 2.71 (td, J = 17.6 Hz, J = 7.2 Hz, 2H), 2.21 (q, J = 7.2 Hz, 2H), 1.90 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 165.3, 150.0, 148.2, 137.3, 137.1, 127.0, 125.2, 119.2 (qt, $J_{C\text{-}F}$ = 286.1 Hz, $J_{C\text{-}F}$ = 36.4 Hz), 117.7 (t, $J_{C\text{-}F}$ = 4.3 Hz), 114.8 (tq, $J_{C\text{-}F}$ = 252.4 Hz, $J_{C\text{-}F}$ = 37.2 Hz), 65.2, 34.6 (t, $J_{C\text{-}F}$ = 22.4 Hz), 29.0, 28.0 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.79 (s, 3F), -118.25 (t, J = 17.7 Hz, 2F); *Z* isomer: δ -86.01 (s, 3F), -118.07 (t, J = 17.4 Hz, 2F); vinyl isomer: -86.39 (s, 3F), -116.14 (d, J = 11.7 Hz, 2F). **HRMS** m/z (ESI): calcd. for $C_{14}H_{15}F_5NO_2$ $[M+H]^+$: 324.1018; found: 324.1012.

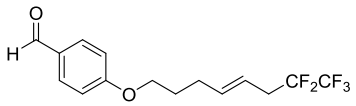


2k: (E)-1-iodo-4-((7,7,8,8,8-pentafluorooct-4-en-1-yl)oxy)benzene. Prepared according to the general procedure. Reaction was run using **1k** (90.6 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a colorless oil (0.24 mmol, 102.1 mg, 81 %, *E/Z* = 91 : 9, allylic : vinylic = 20 : 1), R_f = 0.9 (hexane : Et_2O = 10 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.0 Hz, 2H), 6.67 (d, J = 8.0 Hz, 2H), 5.79-5.72 (m, 1H), 5.49-5.42 (m, 1H), 3.92 (t, J = 6.4 Hz, 2H), 2.76 (td, J = 17.6 Hz, J = 7.2 Hz, 2H), 2.26 (q, J = 7.1 Hz, 2H), 1.88 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 159.0, 138.3, 137.7, 119.3 (qt, $J_{C\text{-}F}$ = 286.6 Hz, $J_{C\text{-}F}$ = 36.3 Hz), 117.7 (t, $J_{C\text{-}F}$ = 4.4 Hz), 117.0, 114.9 (tq, $J_{C\text{-}F}$ = 252.8 Hz, $J_{C\text{-}F}$ = 37.2 Hz), 82.7, 67.1, 34.7 (t, $J_{C\text{-}F}$ = 22.5 Hz), 29.0, 28.5 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.76 (s, 3F), -118.22 (t, J = 17.7 Hz, 2F); *Z* isomer: δ -85.97 (s, 3F), -118.03 (t, J = 17.9 Hz, 2F). **HRMS** m/z (ESI): calcd. for $C_{14}H_{14}F_5IO$ $[M]^+$: 420.0004; found: 420.0000.

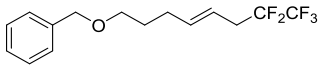


2l: (E)-1-(4-((7,7,8,8,8-pentafluorooct-4-en-1-yl)oxy)phenyl)ethan-1-one. Prepared according to the general procedure. Reaction was run using **1l** (65.4 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a yellow oil (0.26 mmol, 85.7 mg, 85 %, *E/Z* = 92 : 8, allylic : vinylic > 50 : 1), R_f = 0.6 (hexane :

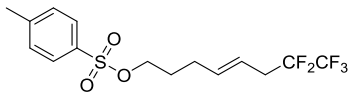
Et_2O = 2 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.77-5.69 (m, 1H), 5.46-5.39 (m, 1H), 3.99 (t, *J* = 6.4 Hz, 2H), 2.73 (td, *J* = 17.6 Hz, *J* = 7.2 Hz, 2H), 2.51 (s, 3H), 2.25 (q, *J* = 7.1 Hz, 2H), 1.88 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 196.8, 163.0, 137.5, 130.6, 130.3, 119.2 (qt, J_{C-F} = 286.3 Hz, J_{C-F} = 36.2 Hz), 117.7 (t, J_{C-F} = 4.1 Hz), 114.8 (tq, J_{C-F} = 252.4 Hz, J_{C-F} = 37.3 Hz), 114.1, 67.2, 34.5 (t, J_{C-F} = 22.4 Hz), 28.9, 28.3, 26.3 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.76 (s, 3F), -118.19 (t, *J* = 17.4 Hz, 2F); *Z* isomer: δ -85.98 (s, 3F), -118.02 (t, *J* = 17.9 Hz, 2F). **HRMS** m/z (ESI): calcd. for $C_{16}H_{17}F_5O_2Na$ $[M+Na]^+$: 359.1041; found: 359.1039.



2m: (E)-4-((7,7,8,8,8-pentafluorooct-4-en-1-yl)oxy)benzaldehyde. Prepared according to the general procedure. Reaction was run using **1m** (61.2 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a yellow oil (0.25 mmol, 81.1 mg, 84 %, *E/Z* = 93 : 7, allylic : vinylic > 50 : 1), R_f = 0.6 (hexane : Et_2O = 2 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.85 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 5.77-5.70 (m, 1H), 5.47-5.40 (m, 1H), 4.02 (t, *J* = 6.2 Hz, 2H), 2.74 (td, *J* = 17.2 Hz, *J* = 7.2 Hz, 2H), 2.26 (q, *J* = 7.1 Hz, 2H), 1.89 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 190.9, 164.1, 137.4, 132.0, 130.0, 119.2 (qt, J_{C-F} = 286.3 Hz, J_{C-F} = 36.4 Hz), 117.8 (t, J_{C-F} = 4.3 Hz), 114.8 (tq, J_{C-F} = 252.3 Hz, J_{C-F} = 37.2 Hz), 114.8, 67.3, 34.6 (t, J_{C-F} = 22.4 Hz), 28.9, 28.3 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.77 (s, 3F), -118.21 (t, *J* = 17.4 Hz, 2F); *Z* isomer: δ -86.00 (s, 3F), -118.04 (t, *J* = 17.9 Hz, 2F). **HRMS** m/z (ESI): calcd. for $C_{15}H_{16}F_5O_2$ $[M+H]^+$: 323.1065; found: 323.1061.

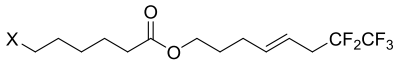


2n: (E)-(((7,7,8,8,8-pentafluorooct-4-en-1-yl)oxy)methyl)benzene. Prepared according to the general procedure. Reaction was run using **1n** (57.0 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a colorless oil (0.25 mmol, 76.7 mg, 83 %, *E/Z* = 91 : 9, allylic : vinylic = 31 : 1), R_f = 0.7 (hexane : Et_2O = 10 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38-7.34 (m, 4H), 7.33-7.28 (m, 1H), 5.76-5.69 (m, 1H), 5.46-5.38 (m, 1H), 4.52 (s, 2H), 3.50 (t, *J* = 6.4 Hz, 2H), 2.75 (td, *J* = 17.6 Hz, *J* = 7.2 Hz, 2H), 2.20 (q, *J* = 7.2 Hz, 2H), 1.74 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 138.7, 138.2, 128.5, 127.8, 127.7, 119.3 (qt, J_{C-F} = 286.7 Hz, J_{C-F} = 36.4 Hz), 117.1 (t, J_{C-F} = 4.4 Hz), 114.9 (tq, J_{C-F} = 252.8 Hz, J_{C-F} = 37.2 Hz), 73.1, 69.5, 34.7 (t, J_{C-F} = 22.5 Hz), 29.3, 29.1 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.77 (s, 3F), -118.24 (t, *J* = 17.6 Hz, 2F); *Z* isomer: δ -85.96 (s, 3F), -118.04 (t, *J* = 17.9 Hz, 2F). **HRMS** m/z (APCI): calcd. for $C_{15}H_{17}F_5ONa$ $[M+Na]^+$: 331.1091; found: 331.1089.



2o: (E)-7,7,8,8,8-pentafluorooct-4-en-1-yl 4-methylbenzenesulfonate. Prepared according to the general procedure. Reaction was run using **1o** (76.2 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a yellow oil (0.17 mmol, 62.5 mg, 56 %, *E/Z* = 92 : 8, allylic : vinylic > 50 : 1), R_f = 0.5 (hexane :

Et_2O = 2 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.61-5.53 (m, 1H), 5.34-5.27 (m, 1H), 4.00 (t, *J* = 6.4 Hz, 2H), 2.67 (td, *J* = 17.6 Hz, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 2.10 (q, *J* = 7.2 Hz, 2H), 1.72 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 145.0, 136.6, 133.1, 129.9, 128.0, 119.2 (qt, $J_{C\text{-}F}$ = 286.7 Hz, $J_{C\text{-}F}$ = 36.3 Hz), 118.2 (t, $J_{C\text{-}F}$ = 4.4 Hz), 114.7 (tq, $J_{C\text{-}F}$ = 252.8 Hz, $J_{C\text{-}F}$ = 37.1 Hz), 67.6, 34.5 (t, $J_{C\text{-}F}$ = 22.5 Hz), 28.3, 28.1, 21.6 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.82 (s, 3F), -118.28 (t, *J* = 17.6 Hz, 2F); *Z* isomer: δ -85.93 (s, 3F), -118.00 (t, *J* = 17.6 Hz, 2F). **HRMS** m/z (ESI): calcd. for $C_{15}H_{17}F_5O_3SNa$ $[M+Na]^+$: 395.0711; found: 395.0706.

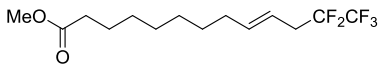


2p (X = Br) : **2p"** (X = Cl) = 5 : 3

2p/2p": (E)-7,7,8,8,8-pentafluorooct-4-en-1-yl 6-bromo/-Chlorohexanoate. Prepared according to the general procedure. Reaction was run using **1p** (82.8 mg, 0.3 mmol), $[CuCF_2CF_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained an inseparable mixture of **2p** and **2p**" as a colorless oil (**2p** : **2p"** = 5 : 3, total 0.20 mmol, 77.0 mg, 68 %, *E/Z* of **2p** = 93 : 7, *E/Z* of **2p"** = 93 : 7, allylic : vinylic > 50 : 1), R_f = 0.5 (hexane : Et_2O = 5 : 1).

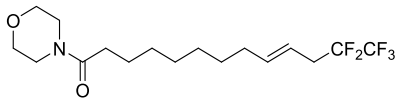
2p: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.72-5.65 (m, 1H), 5.44-5.37 (m, 1H), 4.05 (t, *J* = 6.6 Hz, 2H), 3.38 (t, *J* = 6.8 Hz, 2H), 2.72 (td, *J* = 17.6 Hz, *J* = 7.2 Hz, 2H), 2.30 (t, *J* = 7.4 Hz, 2H), 2.12 (q, *J* = 7.2 Hz, 2H), 1.85 (m, 2H), 1.71 (m, 2H), 1.63 (m, 2H), 1.46 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 173.5, 137.4, 119.2 (qt, $J_{C\text{-}F}$ = 286.1 Hz, $J_{C\text{-}F}$ = 36.4 Hz), 117.6 (t, $J_{C\text{-}F}$ = 4.3 Hz), 114.8 (tq, $J_{C\text{-}F}$ = 252.3 Hz, $J_{C\text{-}F}$ = 37.2 Hz), 63.6, 34.6 (t, $J_{C\text{-}F}$ = 22.5 Hz), 34.1, 33.5, 32.5, 29.0, 28.0, 27.7, 24.2 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.78 (s, 3F), -118.25 (t, *J* = 17.6 Hz, 2F); *Z* isomer: δ -85.96 (s, 3F), -118.03 (t, *J* = 17.9 Hz, 2F). **HRMS** m/z (ESI): calcd. for $C_{14}H_{20}BrF_5O_2Na$ $[M+Na]^+$: 417.0459; found: 417.0454.

2p": **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.72-5.65 (m, 1H), 5.44-5.37 (m, 1H), 4.05 (t, *J* = 6.6 Hz, 2H), 3.51 (t, *J* = 6.6 Hz, 2H), 2.72 (td, *J* = 17.6 Hz, *J* = 7.2 Hz, 2H), 2.30 (t, *J* = 7.4 Hz, 2H), 2.12 (q, *J* = 7.2 Hz, 2H), 1.77 (m, 2H), 1.71 (m, 2H), 1.63 (m, 2H), 1.45 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 173.5, 137.4, 119.2 (qt, $J_{C\text{-}F}$ = 286.1 Hz, $J_{C\text{-}F}$ = 36.4 Hz), 117.6 (t, $J_{C\text{-}F}$ = 4.3 Hz), 114.8 (tq, $J_{C\text{-}F}$ = 252.3 Hz, $J_{C\text{-}F}$ = 37.2 Hz), 63.6, 44.8, 34.6 (t, $J_{C\text{-}F}$ = 22.5 Hz), 34.1, 32.3, 29.0, 28.0, 26.5, 24.3 ppm.**^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.78 (s, 3F), -118.25 (t, *J* = 17.6 Hz, 2F); *Z* isomer: δ -85.96 (s, 3F), -118.03 (t, *J* = 17.9 Hz, 2F). **HRMS** m/z (ESI): calcd. for $C_{14}H_{20}ClF_5O_2Na$ $[M+Na]^+$: 373.0964; found: 373.0960.

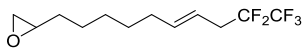


2q: methyl (E)-12,12,13,13,13-pentafluorotridec-9-enoate. Prepared according to the general procedure. Reaction was run using **1q** (59.4 mg, 0.3 mmol), $[CuCF_2CF_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a colorless oil (0.24 mmol, 76.8 mg, 81 %, *E/Z* = 94 : 6, allylic : vinylic = 33 : 1), R_f = 0.7 (hexane : Et_2O = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.70-5.62 (m, 1H), 5.38-5.30 (m, 1H), 3.63 (s, 3H), 2.70 (td, *J* = 17.6 Hz, *J* = 7.2 Hz, 2H), 2.27 (t, *J* = 7.6 Hz, 2H), 2.02 (q, *J* = 6.8 Hz, 2H), 1.59 (m, 2H), 1.34 (m, 2H), 1.31-1.23 (m, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 174.4, 138.9, 119.3 (qt, $J_{C\text{-}F}$ = 286.7 Hz, $J_{C\text{-}F}$ = 36.5 Hz), 116.5 (t, $J_{C\text{-}F}$ = 4.3 Hz), 114.9 (tq, $J_{C\text{-}F}$ = 252.6 Hz, $J_{C\text{-}F}$ = 37.1 Hz), 51.4, 34.7 (t, $J_{C\text{-}F}$ = 22.5 Hz), 34.1, 32.6, 29.2, 29.1, 28.9, 25.0 ppm (one carbon missing due to overlap). **^{19}F NMR** (470 MHz,

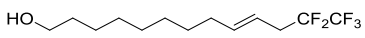
$CDCl_3$): *E* isomer: δ -85.76 (s, 3F), -118.26 (t, *J* = 17.6 Hz, 2F); *Z* isomer: δ -85.94 (s, 3F), -118.00 (t, *J* = 17.6 Hz, 2F). **HRMS** m/z (ESI): calcd. for $C_{14}H_{21}F_5O_2Na$ $[M+Na]^+$: 339.1354; found: 339.1351.



2r: (E)-12,12,13,13,13-pentafluoro-1-morpholinotridec-9-en-1-one. Prepared according to the general procedure. Reaction was run using **1r** (75.9 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a yellow oil (0.25 mmol, 91.3 mg, 82 %, *E/Z* = 93 : 7, allylic : vinylic = 28 : 1), R_f = 0.3 (hexane : EtOAc = 3 : 2). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.68-5.61 (m, 1H), 5.36-5.26 (m, 1H), 3.62 (t, *J* = 4.8 Hz, 4H), 3.57 (t, *J* = 4.4 Hz, 2H), 3.42 (t, *J* = 4.4 Hz, 2H), 2.69 (td, *J* = 17.6 Hz, *J* = 7.2 Hz, 2H), 2.26 (t, *J* = 7.6 Hz, 2H), 2.01 (q, *J* = 6.8 Hz, 2H), 1.58 (m, 2H), 1.33(m, 2H), 1.29-1.22 (m, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 171.9, 138.9, 119.2 (qt, J_{C-F} = 286.3 Hz, J_{C-F} = 36.4 Hz), 116.4 (t, J_{C-F} = 4.2 Hz), 114.9 (tq, J_{C-F} = 252.1 Hz, J_{C-F} = 37.0 Hz), 67.0, 66.7, 46.1, 41.9, 34.6 (t, J_{C-F} = 22.4 Hz), 33.1, 32.5, 29.4, 29.2, 28.9, 28.8, 25.2 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.77 (s, 3F), -118.22 (t, *J* = 17.6 Hz, 2F); *Z* isomer: δ -85.95 (s, 3F), -118.02 (t, *J* = 17.9 Hz, 2F). **HRMS** m/z (ESI): calcd. for $C_{17}H_{27}F_5NO_2$ $[M+H]^+$: 372.1957; found: 372.1953.

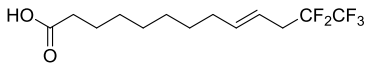


2s: (E)-2-(9,9,10,10,10-pentafluorodec-6-en-1-yl)oxirane. Prepared according to the general procedure. Reaction was run using **1s** (46.2 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a colorless oil (0.22 mmol, 60.4 mg, 74 %, *E/Z* = 92 : 8, allylic : vinylic = 45 : 1), R_f = 0.7 (hexane : Et_2O = 5 : 2). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.71-5.64 (m, 1H), 5.39-5.32 (m, 1H), 2.90-2.85 (m, 1H), 2.71 (td, *J* = 17.8 Hz, *J* = 6.8 Hz, 2H), 2.74-2.69 (m, 1H), 2.43 (dd, *J* = 4.8 Hz, *J* = 2.8 Hz, 1H), 2.05 (q, *J* = 6.7 Hz, 2H), 1.54-1.30 (m, 8H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 138.8, 119.3 (qt, J_{C-F} = 286.6 Hz, J_{C-F} = 36.4 Hz), 116.7 (t, J_{C-F} = 4.3 Hz), 114.9 (tq, J_{C-F} = 252.6 Hz, J_{C-F} = 37.2 Hz), 52.4, 47.1, 34.7 (t, J_{C-F} = 22.5 Hz), 32.5, 32.5, 28.9, 25.9 ppm (one carbon missing due to overlap). **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.76 (s, 3F), -118.26 (t, *J* = 17.6 Hz, 2F); *Z* isomer: δ -85.94 (s, 3F), -118.00 (t, *J* = 17.6 Hz, 2F). **HRMS** m/z (APCI): calcd. for $C_{12}H_{18}F_5O$ $[M+H]^+$: 273.1272; found: 273.1271.

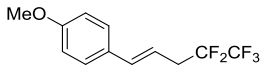


2t: (E)-12,12,13,13,13-pentafluorotridec-9-en-1-ol. Prepared according to the general procedure. Reaction was run using **1t** (51.0 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a colorless oil (0.24 mmol, 70.0 mg, 81 %, *E/Z* = 92 : 8, allylic : vinylic = 48 : 1), R_f = 0.3 (hexane : EtOAc = 3 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.71-5.64 (m, 1H), 5.38-5.31 (m, 1H), 3.60 (t, *J* = 6.6 Hz, 2H), 2.71 (td, *J* = 17.6 Hz, *J* = 7.2 Hz, 2H), 2.04 (s, 1H), 2.03 (q, *J* = 6.8 Hz, 2H), 1.53 (m, 2H), 1.34 (m, 2H), 1.32-1.22 (m, 8H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 139.0, 119.3 (qt, J_{C-F} = 286.1 Hz, J_{C-F} = 36.4 Hz), 116.5 (t, J_{C-F} = 4.3 Hz), 114.9 (tq, J_{C-F} = 252.6 Hz, J_{C-F} = 37.0 Hz), 63.0, 34.7 (t, J_{C-F} = 22.4 Hz), 32.8, 32.6, 29.5, 29.5, 29.1, 29.0, 25.8 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.76 (s, 3F), -118.26 (t, *J* = 17.4 Hz, 2F); *Z* isomer: δ -85.95 (s, 3F), -117.99 (t, *J* = 17.6 Hz, 2F). **HRMS** m/z (APCI): calcd. for

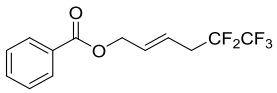
$C_{13}H_{22}F_5O$ $[M+H]^+$: 289.1585; found: 289.1583.



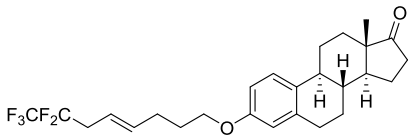
2u: (E)-12,12,13,13,13-pentafluorotridec-9-enoic acid. Prepared according to the general procedure. Reaction was run using **1u** (55.2 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a yelow oil (0.24 mmol, 72.5 mg, 80 %, *E/Z* = 97 : 3, allylic : vinyl = 13 : 1), R_f = 0.2 (hexane : EtOAc = 2 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.56 (s, 1H), 5.73-5.65 (m, 1H), 5.40-5.33 (m, 1H), 2.73 (td, *J* = 17.6 Hz, *J* = 7.2 Hz, 2H), 2.34 (t, *J* = 7.4 Hz, 2H), 2.05 (q, *J* = 6.9 Hz, 2H), 1.63 (m, 2H), 1.35 (m, 2H), 1.33-1.24 (m, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 180.7, 139.0, 119.3 (qt, J_{C-F} = 286.1 Hz, J_{C-F} = 36.4 Hz), 116.6 (t, J_{C-F} = 4.3 Hz), 115.0 (tq, J_{C-F} = 252.3 Hz, J_{C-F} = 37.0 Hz), 34.7 (t, J_{C-F} = 22.4 Hz), 34.2, 32.6, 29.2, 29.2, 28.9, 28.9, 24.8 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.77 (s, 3F), -118.28 (t, *J* = 17.6 Hz, 2F); *Z* isomer: δ -85.97 (s, 3F), -118.03 (t, *J* = 17.9 Hz, 2F). **HRMS** m/z (APCI): calcd. for $C_{13}H_{18}F_5O_2$ $[M-H]^-$: 301.1232; found: 301.1232.



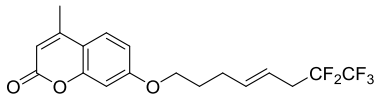
2v: (E)-1-methoxy-4-(4,4,5,5,5-pentafluoropent-1-en-1-yl)benzene. Prepared according to the general procedure. Reaction was run using **1v** (44.4 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a colorless oil (0.17 mmol, 44.7 mg, 56 %, *E/Z* = 98 : 2, allylic : vinylic > 50 : 1), R_f = 0.5 (hexane : Et_2O = 10 : 1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.02-5.96 (m, 1H), 3.82 (s, 3H), 2.95 (td, *J* = 17.5 Hz, *J* = 7.5 Hz, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 159.7, 136.6, 129.2, 127.8, 119.3 (qt, J_{C-F} = 286.1 Hz, J_{C-F} = 36.2 Hz), 114.9 (tq, J_{C-F} = 252.4 Hz, J_{C-F} = 37.2 Hz), 114.2, 113.9 (t, J_{C-F} = 4.4 Hz), 55.4, 35.0 (t, J_{C-F} = 22.5 Hz) ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.75 (s, 3F), -117.96 (t, *J* = 17.4 Hz, 2F). **HRMS** m/z (APCI): calcd. for $C_{12}H_{12}F_5O$ $[M+H]^+$: 267.0802; found: 267.0806.



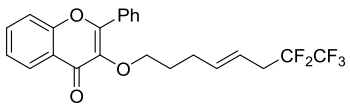
2w: (E)-5,5,6,6,6-pentafluorohex-2-en-1-yl benzoate. Prepared according to the general procedure. Reaction was run using **1w** (52.8 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a colorless oil (0.18 mmol, 52.9 mg, 60 %, *E/Z* = 98 : 2, allylic : vinylic = 7 : 1 by crude ^{1}H NMR, vinylic isomer was separated by column chromatography), R_f = 0.7 (hexane : Et_2O = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 6.01-5.95 (m, 1H), 5.86-5.79 (m, 1H), 4.84 (d, *J* = 6.0 Hz, 2H), 2.85 (td, *J* = 17.6 Hz, *J* = 6.8 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.3, 133.2, 132.2, 130.1, 129.8, 128.5, 121.4 (t, J_{C-F} = 4.4 Hz), 119.2 (qt, J_{C-F} = 286.6 Hz, J_{C-F} = 36.1 Hz), 114.7 (tq, J_{C-F} = 253.6 Hz, J_{C-F} = 37.7 Hz), 64.4, 34.4 (t, J_{C-F} = 22.6 Hz) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$): *E* isomer: δ -85.87 (s, 3F), -118.05 (t, *J* = 17.3 Hz, 2F). **HRMS** m/z (ESI): calcd. for $C_{13}H_{11}F_5O_2Na$ $[M+Na]^+$: 317.0571; found: 317.0570.



2x: (8R,9S,13S,14S)-13-methyl-3-(((E)-6-((1,2,2,2-tetrafluoro-2l5-vinyl)-l2-fluoranyl)hex-4-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 **1x** (105.6 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a white solid, melting point: 98.7–99.4 °C (0.28 mmol, 131.1 mg, 93 %, *E/Z* = 95 : 5, allylic : vinylic = 30 : 1), R_f = 0.4 (hexane : Et_2O = 3 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 8.8 Hz, 1H), 6.74 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1H), 6.67 (d, *J* = 2.4 Hz, 1H), 5.83-5.76 (m, 1H), 5.52-5.46 (m, 1H), 3.96 (d, *J* = 6.4 Hz, 2H), 2.97-2.87 (m, 2H), 2.79 (td, *J* = 17.6 Hz, *J* = 6.8 Hz, 2H), 2.79 (dd, *J* = 18.8 Hz, *J* = 8.8 Hz, 2H), 2.45-2.39 (m, 1H), 2.29 (q, *J* = 7.2 Hz, 2H), 2.22-1.95 (m, 4H), 1.89 (m, 2H), 1.70-1.42 (m, 6H), 0.94 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 220.8, 157.0, 137.8, 137.7, 132.0, 126.3, 119.2 (qt, $J_{C\text{-}F}$ = 286.3 Hz, $J_{C\text{-}F}$ = 36.4 Hz), 117.3 (t, $J_{C\text{-}F}$ = 4.3 Hz), 114.8 (tq, $J_{C\text{-}F}$ = 253.6 Hz, $J_{C\text{-}F}$ = 37.2 Hz), 114.5, 112.1, 66.8, 50.4, 48.0, 44.0, 38.4, 35.8, 34.5 (t, $J_{C\text{-}F}$ = 22.4 Hz), 31.6, 29.7, 29.0, 28.6, 26.6, 25.9, 21.6, 13.8 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.76 (s, 3F), -118.21 (t, *J* = 17.6 Hz, 2F); *Z* isomer: δ -85.97 (s, 3F), -118.01 (t, *J* = 17.9 Hz, 2F). **HRMS** m/z (ESI): calcd. for $C_{26}H_{31}F_5O_2$ $[M]^+$: 470.2239; found: 470.2231.

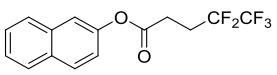


2y: (E)-4-methyl-7-((7,7,8,8,8-pentafluorooct-4-en-1-yl)oxy)-2H-chromen-2-one. Prepared according to the general procedure. Reaction was run using **1y** (77.4 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a yellow solid, melting point: 46.1–46.5 °C (0.22 mmol, 81.2 mg, 72 %, *E/Z* = 96 : 4, allylic : vinylic > 50 : 1), R_f = 0.3 (hexane : Et_2O = 2 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.8 Hz, 1H), 6.80 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1H), 6.72 (t, *J* = 2.0 Hz, 1H), 6.06 (s, 1H), 5.76-5.69 (m, 1H), 5.46-5.38 (m, 1H), 3.97 (t, *J* = 6.4 Hz, 2H), 2.73 (td, *J* = 17.6 Hz, *J* = 6.8 Hz, 2H), 2.34 (s, 3H), 2.25 (q, *J* = 7.1 Hz, 2H), 1.88 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 162.1, 161.3, 155.3, 152.7, 137.4, 125.6, 119.2 (qt, $J_{C\text{-}F}$ = 286.7 Hz, $J_{C\text{-}F}$ = 36.4 Hz), 117.7 (t, $J_{C\text{-}F}$ = 4.4 Hz), 114.8 (tq, $J_{C\text{-}F}$ = 252.7 Hz, $J_{C\text{-}F}$ = 37.2 Hz), 113.5, 112.5, 111.8, 101.4, 67.5, 34.5 (t, $J_{C\text{-}F}$ = 22.5 Hz), 28.9, 28.2, 18.6 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$): *E* isomer: δ -85.76 (s, 3F), -118.22 (t, *J* = 17.5 Hz, 2F); *Z* isomer: δ -85.97 (s, 3F), -118.04 (t, *J* = 17.7 Hz, 2F). **HRMS** m/z (ESI): calcd. for $C_{18}H_{17}F_5O_3Na$ $[M+Na]^+$: 399.0990; found: 399.0988.

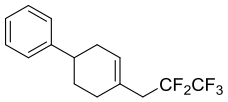


2z: (E)-3-((7,7,8,8,8-pentafluorooct-4-en-1-yl)oxy)-2-phenyl-4H-chromen-4-one. Prepared according to the general procedure. Reaction was run using **1z** (96.0 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a yellow oil (0.25 mmol, 110.4 mg, 84 %, *E/Z* = 95 : 5, allylic : vinylic =

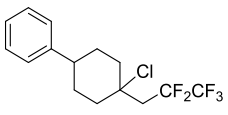
23 : 1), R_f = 0.6 (hexane : Et_2O = 3 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.0 Hz, 2H), 8.08-8.03 (m, 2H), 7.62 (t, *J* = 8.5 Hz, 1H), 7.52-7.47 (m, 3H), 7.38-7.33 (m, 1H), 5.67-5.59 (m, 1H), 5.29-5.22 (m, 1H), 4.03 (t, *J* = 6.4 Hz, 2H), 2.67 (td, *J* = 17.6 Hz, *J* = 6.8 Hz, 2H), 2.13 (q, *J* = 7.1 Hz, 2H), 1.77 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 175.1, 156.0, 155.3, 140.5, 137.8, 133.4, 131.0, 130.7, 128.7, 128.4, 125.7, 124.7, 124.2, 119.2 (qt, $J_{C\text{-}F}$ = 286.8 Hz, $J_{C\text{-}F}$ = 36.3 Hz), 118.0, 117.1 (t, $J_{C\text{-}F}$ = 4.3 Hz), 114.8 (tq, $J_{C\text{-}F}$ = 252.7 Hz, $J_{C\text{-}F}$ = 37.1 Hz), 71.8, 34.5 (t, $J_{C\text{-}F}$ = 22.4 Hz), 29.3, 28.9 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): *E* isomer: δ -85.79 (s, 3F), -118.21 (t, *J* = 17.6 Hz, 2F); *Z* isomer: δ -85.87 (s, 3F), -117.89 (t, *J* = 17.9 Hz, 2F). **HRMS** m/z (ESI): calcd. for $C_{23}H_{20}F_5O_3$ $[M+H]^+$: 439.1327; found: 439.1323.



2aa: naphthalen-2-yl 4,4,5,5,5-pentafluoropentanoate. Prepared according to the general procedure. Reaction was run using **1aa** (59.4 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/Et_2O) and obtained a colorless oil (0.06 mmol, 20.0 mg, 21 %), R_f = 0.7 (hexane : Et_2O = 5 : 1). **^{1}H NMR** (100 MHz, $CDCl_3$): δ 7.89-7.81 (m, 3H), 7.58 (d, *J* = 2.0 Hz, 1H), 7.54-7.46 (m, 2H), 7.23 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1H), 2.96 (t, *J* = 7.8 Hz, 2H), 2.65-2.52 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 170.0, 148.1, 133.8, 132.7, 129.7, 127.9, 127.8, 126.9, 126.1, 120.8, 119.1 (qt, $J_{C\text{-}F}$ = 285.6 Hz, $J_{C\text{-}F}$ = 35.9 Hz), 118.6, 115.3 (tq, $J_{C\text{-}F}$ = 252.8 Hz, $J_{C\text{-}F}$ = 38.2 Hz), 26.4 (t, $J_{C\text{-}F}$ = 22.1 Hz), 26.1 (t, $J_{C\text{-}F}$ = 3.8 Hz) ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): δ -86.39 (s, 3F), -119.57 (t, *J* = 18.1 Hz, 2F). **HRMS** m/z (ESI): calcd. for $C_{15}H_{11}F_5O_2Na$ $[M+Na]^+$: 341.0571; found: 341.0570.



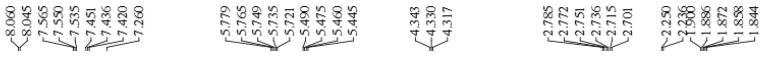
2ab: (4-(2,2,3,3,3-pentafluoropropylidene)cyclohexyl)benzene. Prepared according to the general procedure. Reaction was run using **1ab** (51.6 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane) and obtained a colorless oil (0.03 mmol, 8.7 mg, 10 %), R_f = 0.5 (hexane). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.25-7.21 (m, 3H), 5.77 (s, 1H), 2.81-2.68 (m, 3H), 2.38-2.27 (m, 2H), 2.23-2.15 (m, 2H), 1.98 (dd, *J* = 12.0 Hz, *J* = 2.0 Hz, 1H), 1.79 (qd, *J* = 12.0 Hz, *J* = 5.5 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 146.7, 129.7, 128.6, 127.0, 126.3, 119.3 (qt, $J_{C\text{-}F}$ = 286.4 Hz, $J_{C\text{-}F}$ = 36.2 Hz), 115.4 (tq, $J_{C\text{-}F}$ = 252.5 Hz, $J_{C\text{-}F}$ = 36.9 Hz), 39.5, 38.9 (t, $J_{C\text{-}F}$ = 21.7 Hz), 33.8, 30.0, 30.0 ppm. (one carbon missing due to overlap) **^{19}F NMR** (470 MHz, $CDCl_3$): δ -86.05 (s, 3F), -116.98 (m, 2F). **HRMS** m/z (APCI): calcd. for $C_{15}H_{16}F_5$ $[M+H]^+$: 291.1167; found: 291.1167.

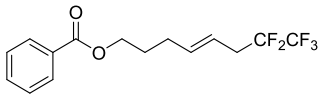


2ab": (4-chloro-4-(2,2,3,3,3-pentafluoropropyl)cyclohexyl)benzene. Prepared according to the general procedure. Reaction was run using **1ab** (51.6 mg, 0.3 mmol), [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane) and obtained a white solid, melting point: 71.3–71.8 °C (0.25 mmol, 82.2 mg, 84 %), R_f = 0.4 (hexane). **^{1}H NMR** (400

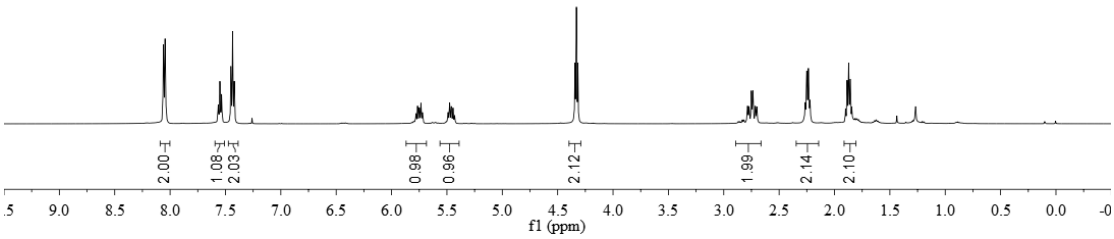
MHz, $CDCl_3$): δ 7.30 (d, J = 7.4 Hz, 2H), 7.24 (d, J = 7.2 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 2.65 (t, J = 19.6 Hz, 2H), 2.50 (tt, J = 12.0 Hz, J = 3.6 Hz, 1H), 2.22 (d, J = 12.4 Hz, 2H), 2.07 (q, J = 12.4 Hz, 2H), 1.93 (t, J = 13.2 Hz, 2H), 1.81 (d, J = 11.6 Hz, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 146.3, 128.6, 127.0, 126.5, 118.9 (qt, $J_{C\text{-}F}$ = 286.8 Hz, $J_{C\text{-}F}$ = 35.7 Hz), 115.4 (tq, $J_{C\text{-}F}$ = 257.0 Hz, $J_{C\text{-}F}$ = 37.3 Hz), 69.2, 44.6 (t, $J_{C\text{-}F}$ = 19.4 Hz), 43.2, 39.8, 29.4 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): δ -87.46 (s, 3F), -116.10 (t, J = 19.5 Hz, 2F). **HRMS** m/z (APCI): calcd. for $C_{15}H_{16}ClF_5$ $[M]^+$: 326.0855; found: 326.0860.

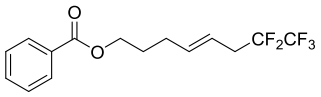
Spectra:



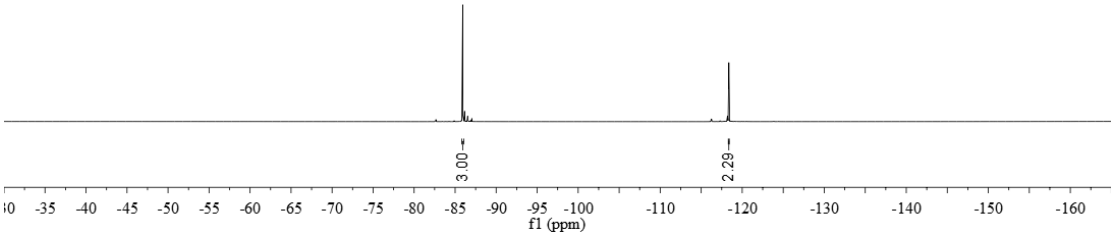


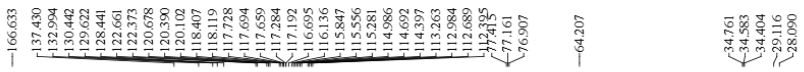
2a (^{1}H NMR $CDCl_3$, 500 MHz)

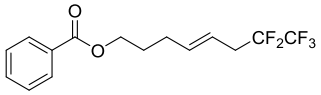




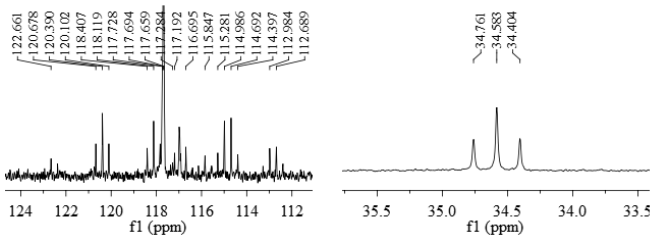
2a (^{19}F NMR, $CDCl_3$, 470 MHz)

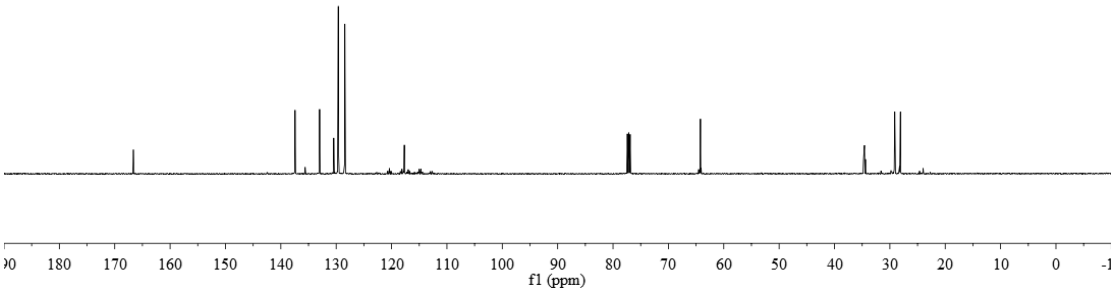


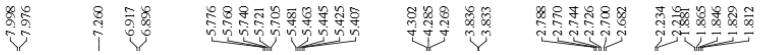


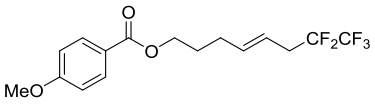


2a (^{13}C NMR, $CDCl_3$, 126 MHz)

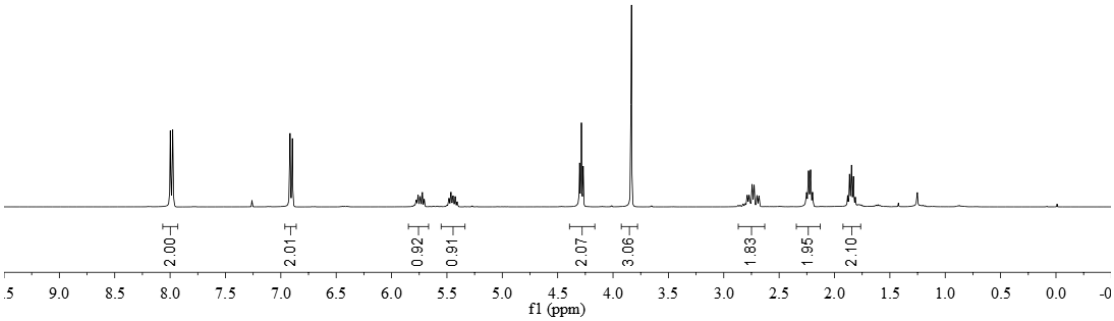


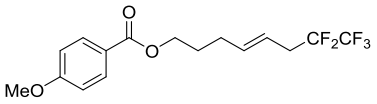




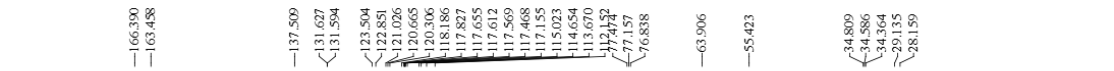


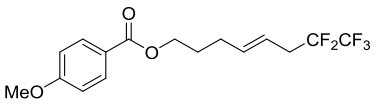
2b (^{1}H NMR, $CDCl_3$, 400 MHz)



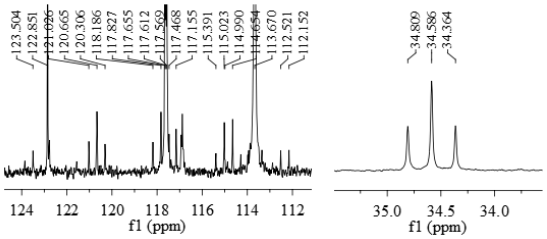


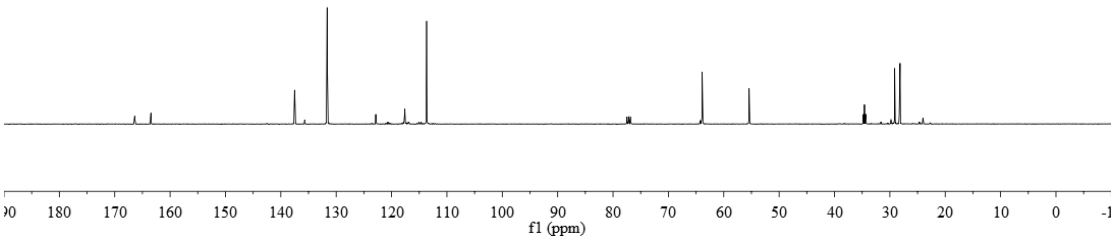
2b (^{19}F NMR, $CDCl_3$, 470 MHz)

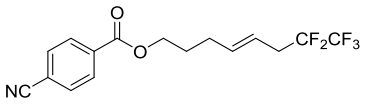




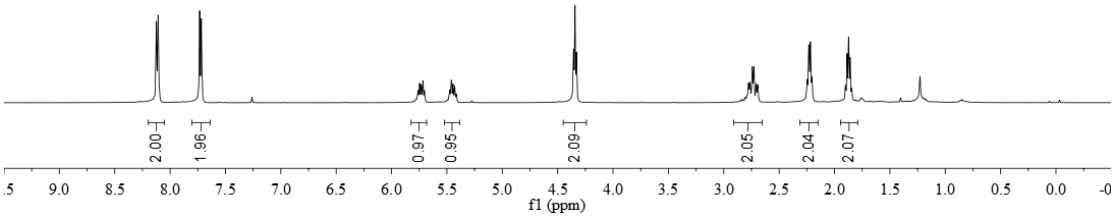
2b (^{13}C NMR, $CDCl_3$, 101 MHz)

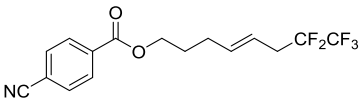




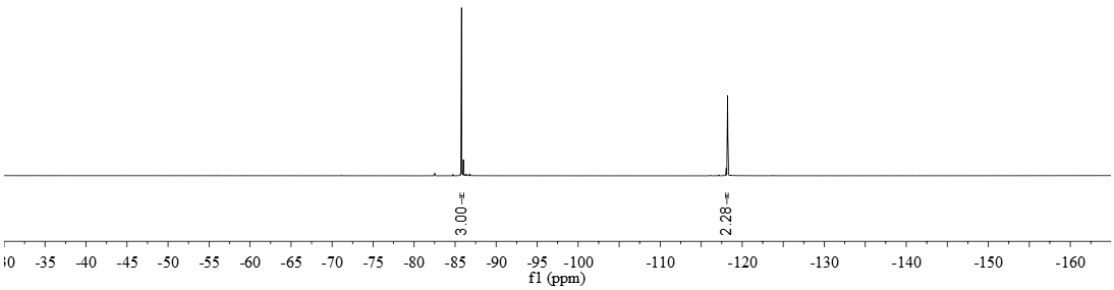


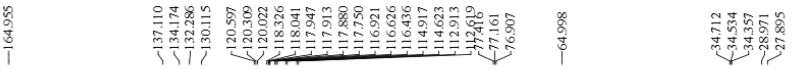
2c (^{1}H NMR, $CDCl_3$, 500 MHz)

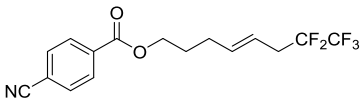




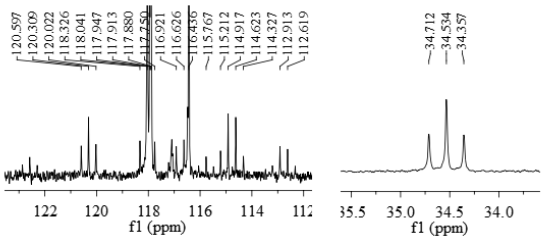
2c (^{19}F NMR, $CDCl_3$, 470 MHz)

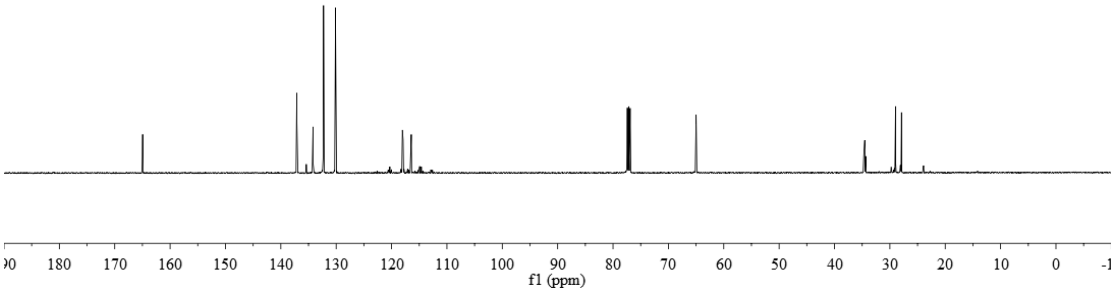


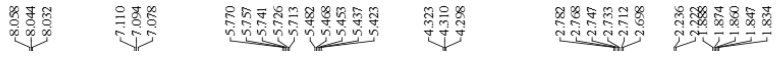


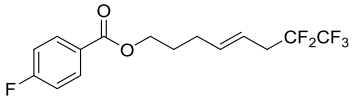


2c (^{13}C NMR, $CDCl_3$, 126 MHz)

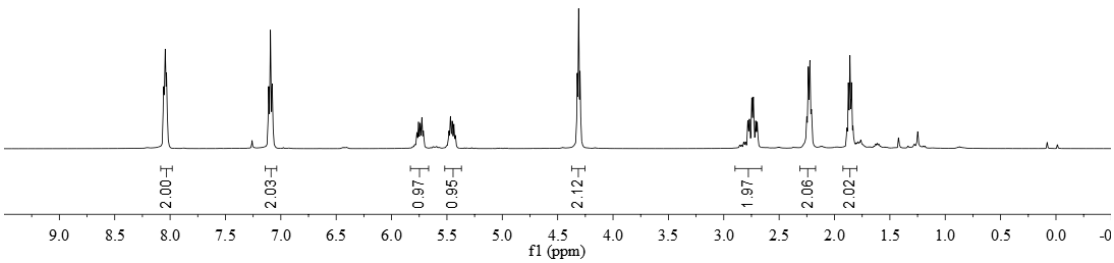


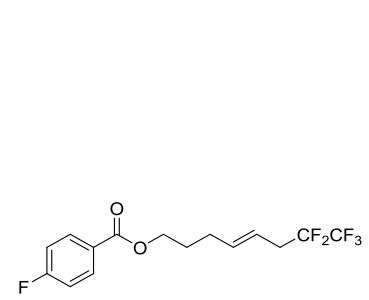




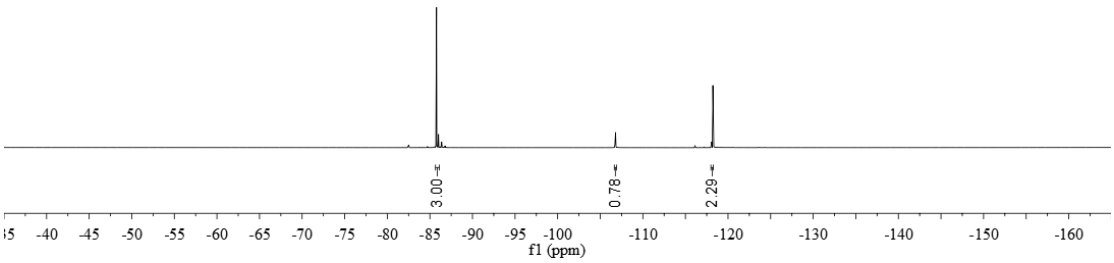


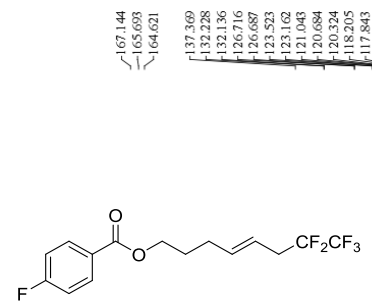
2d (^{1}H NMR, $CDCl_3$, 500 MHz)



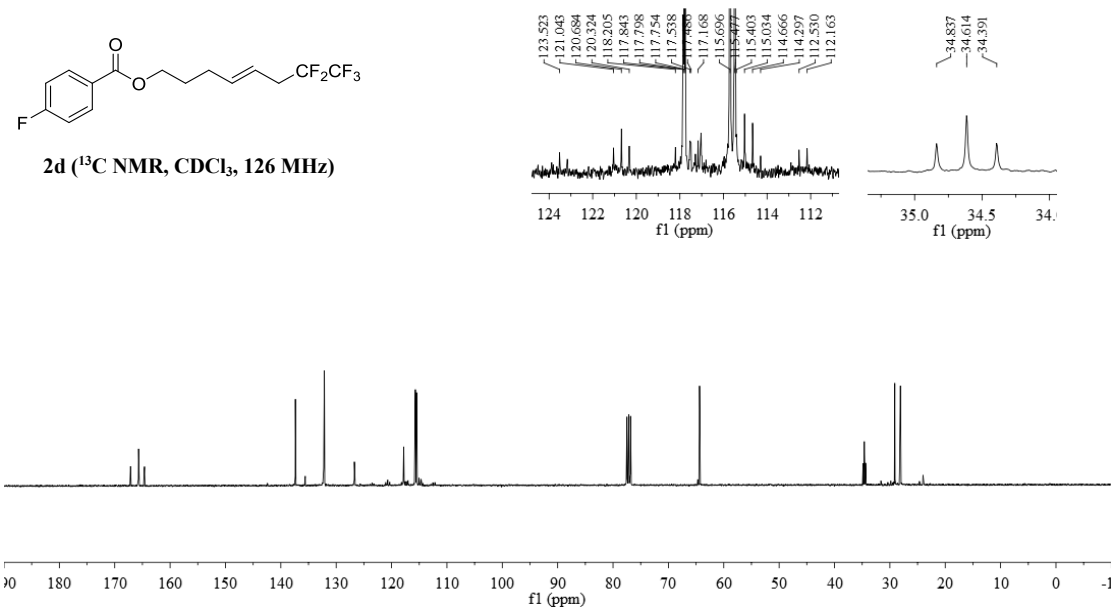


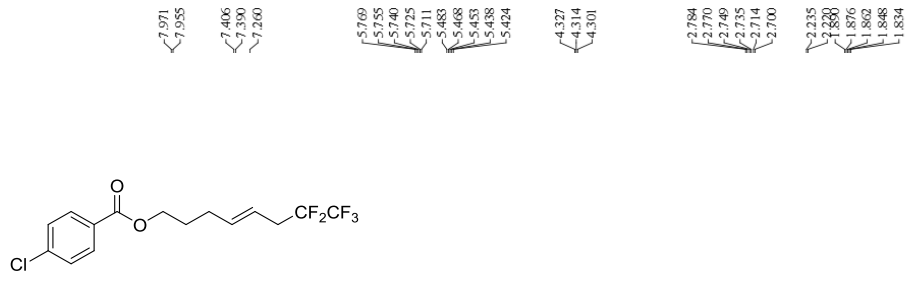
2d (^{19}F NMR, $CDCl_3$, 470 MHz)



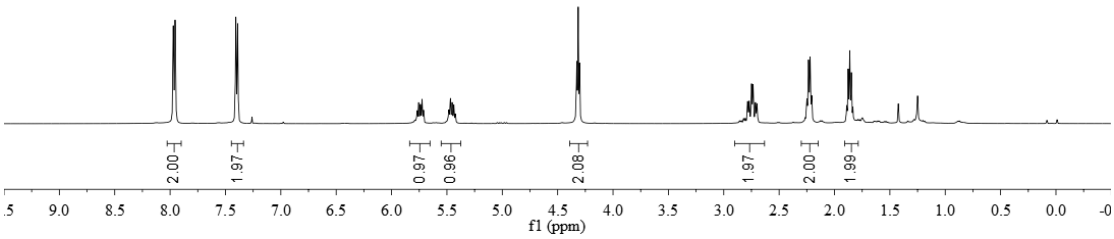


2d (^{13}C NMR, $CDCl_3$, 126 MHz)

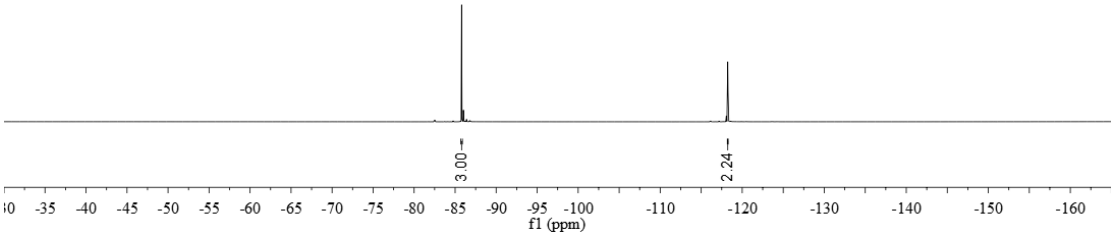


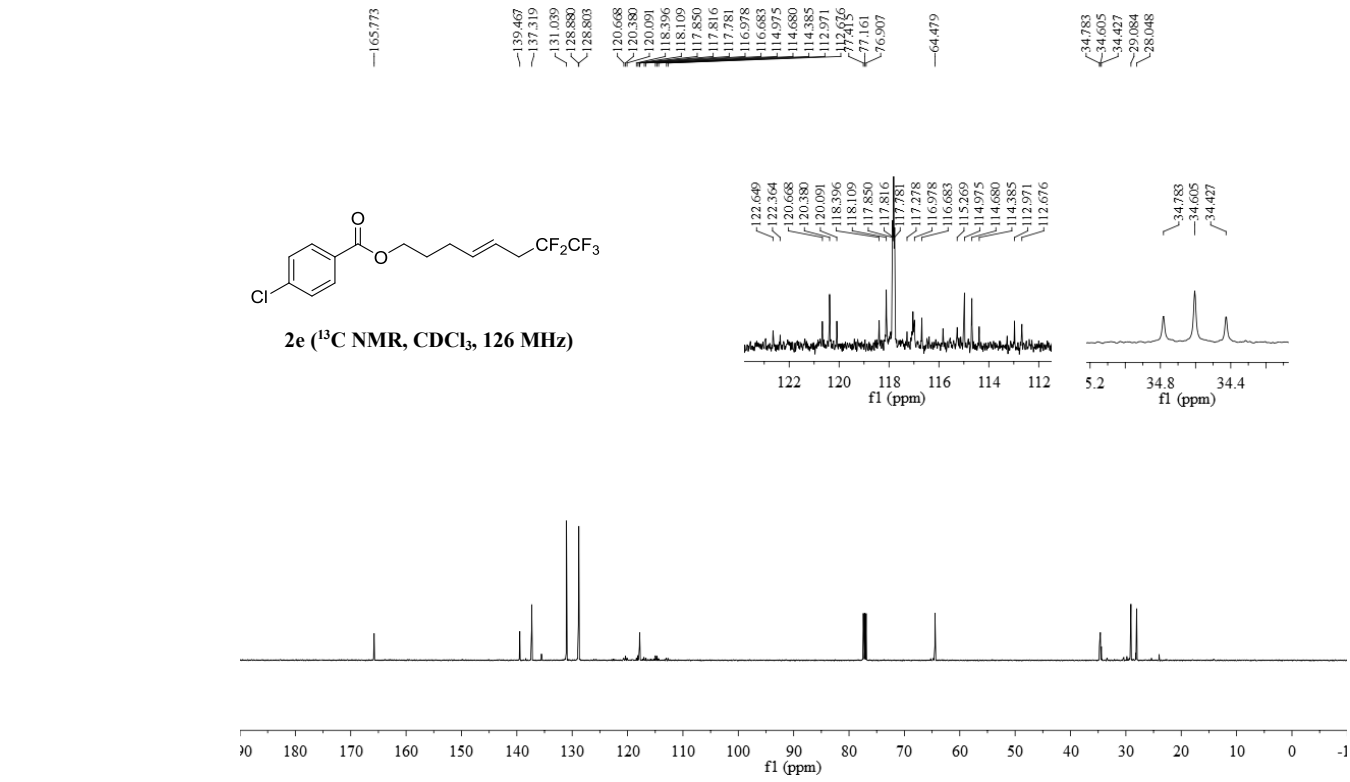


2e (^{1}H NMR, $CDCl_3$, 500 MHz)

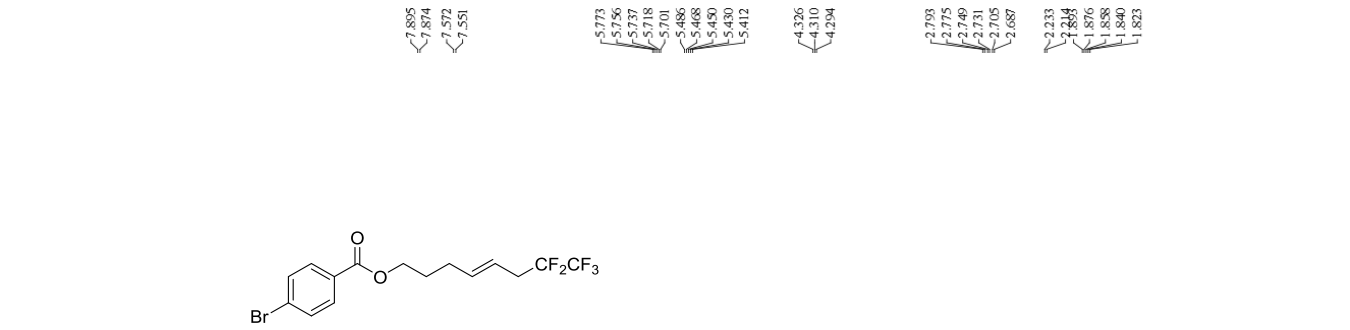


2e (^{19}F NMR, $CDCl_3$, 470 MHz)

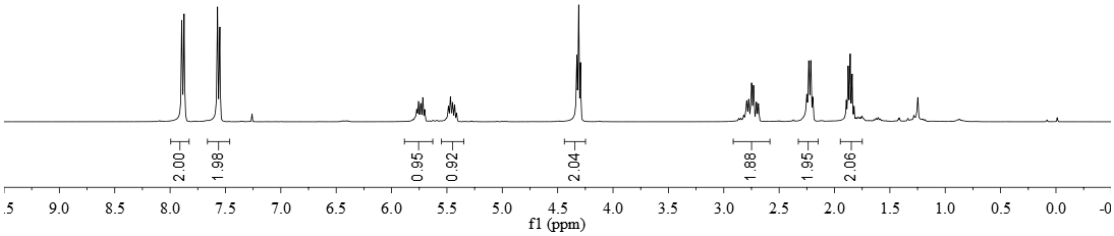


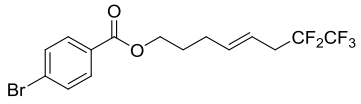


2e (^{13}C NMR, $CDCl_3$, 126 MHz)

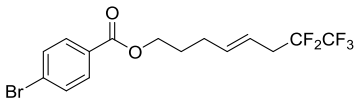


2f (^{1}H NMR, $CDCl_3$, 400 MHz)

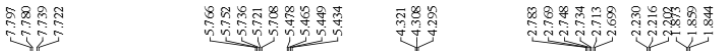


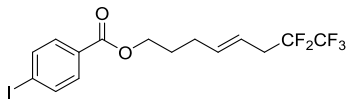


2f (^{19}F NMR, $CDCl_3$, 470 MHz)

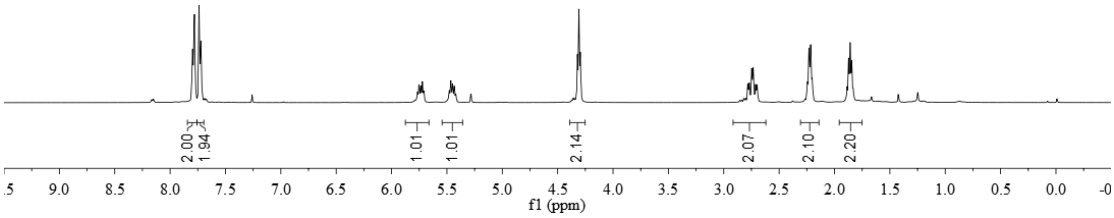


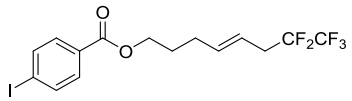
2f (^{13}C NMR, $CDCl_3$, 126 MHz)



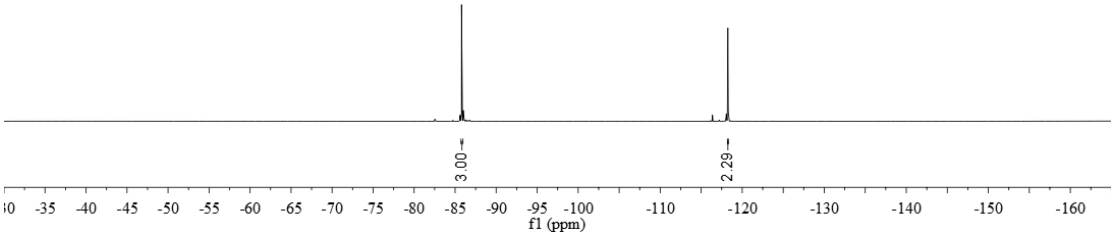


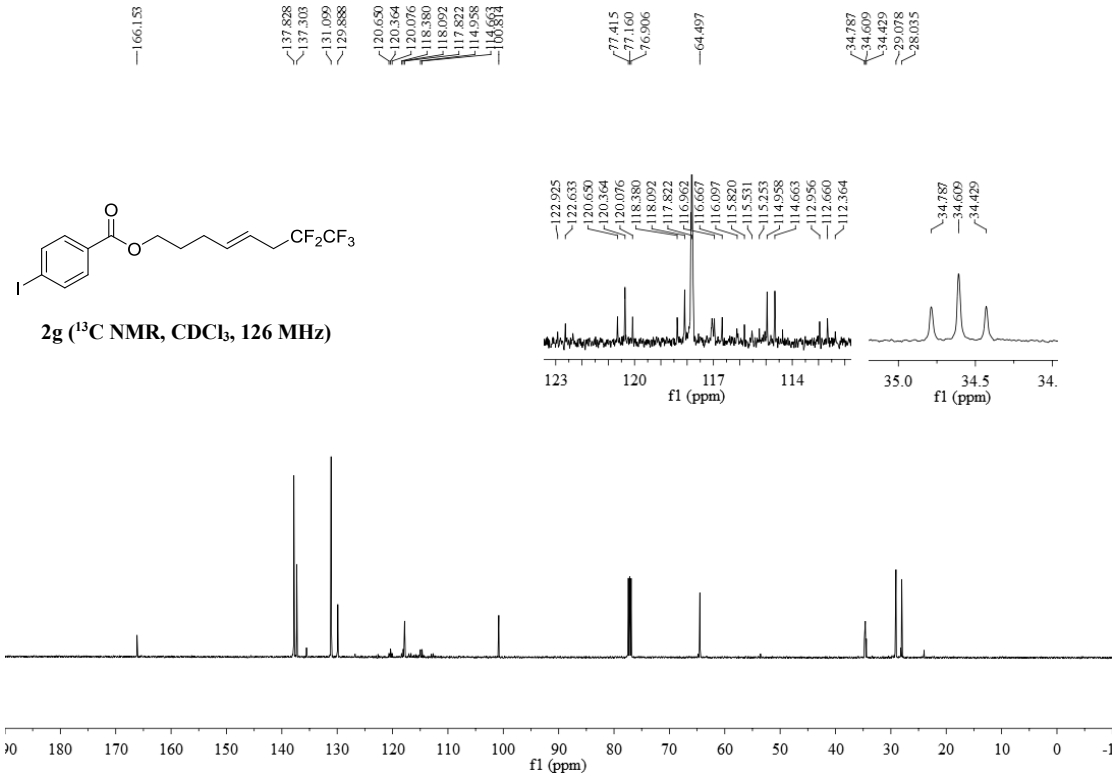
2g (^{1}H NMR, $CDCl_3$, 500 MHz)



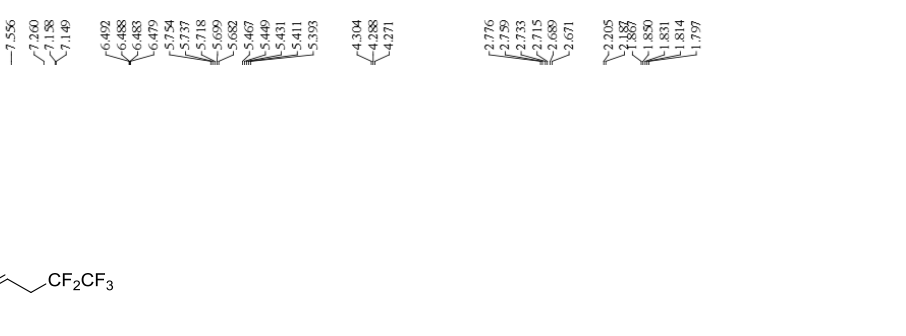


2g (^{19}F NMR, $CDCl_3$, 470 MHz)

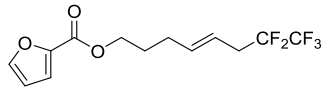




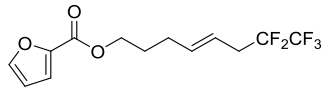
2g (^{13}C NMR, $CDCl_3$, 126 MHz)



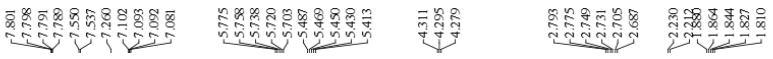
2h (^{1}H NMR, $CDCl_3$, 400 MHz)

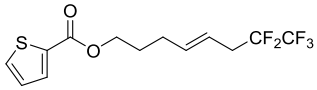


2h (^{19}F NMR, $CDCl_3$, 470 MHz)

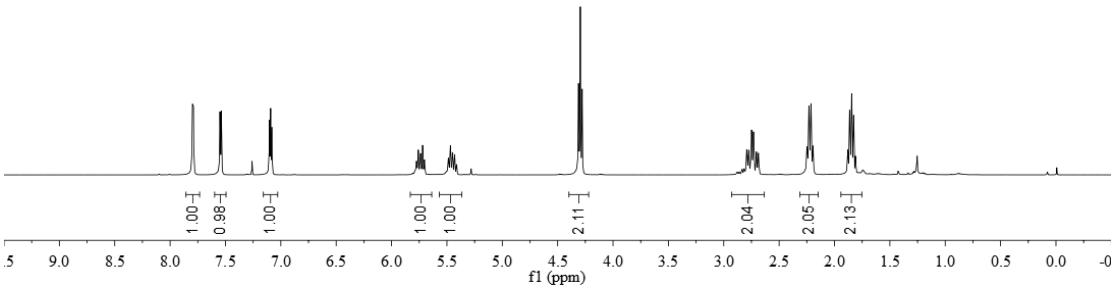


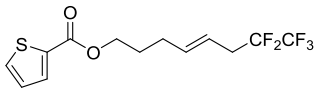
2h (^{13}C NMR, $CDCl_3$, 126 MHz)



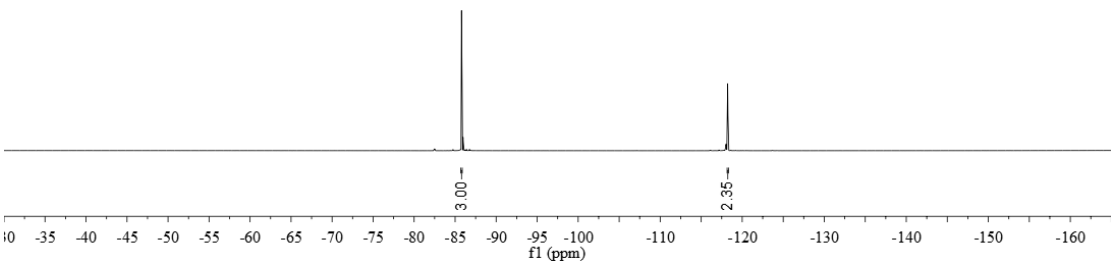


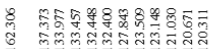
2i (^{1}H NMR, $CDCl_3$, 400 MHz)

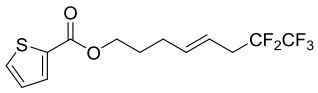




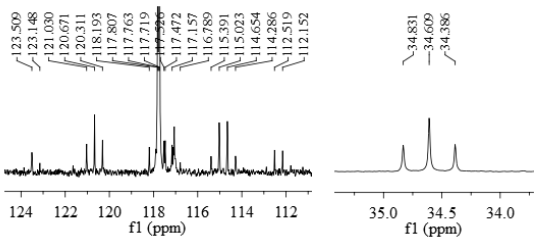
2i (^{19}F NMR, $CDCl_3$, 470 MHz)

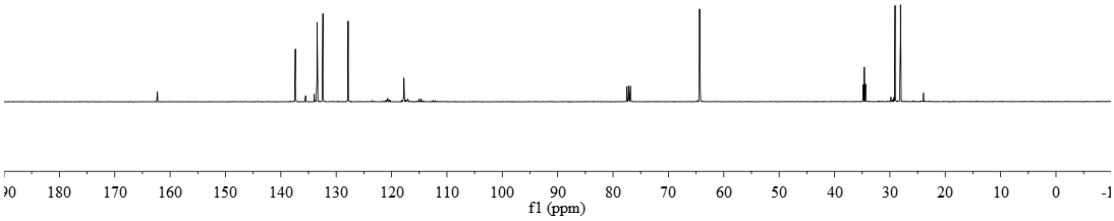


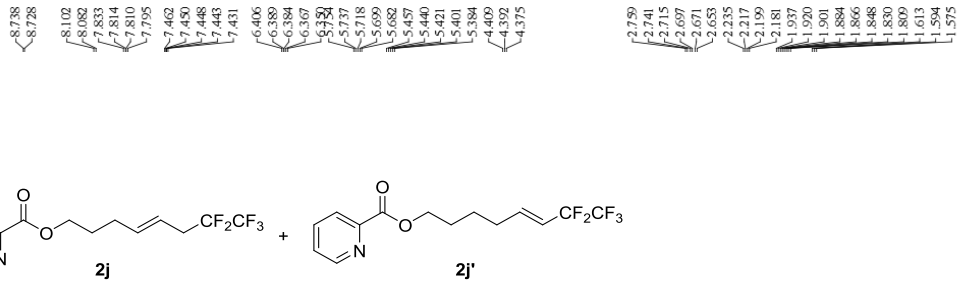




2i (^{13}C NMR, $CDCl_3$, 101 MHz)

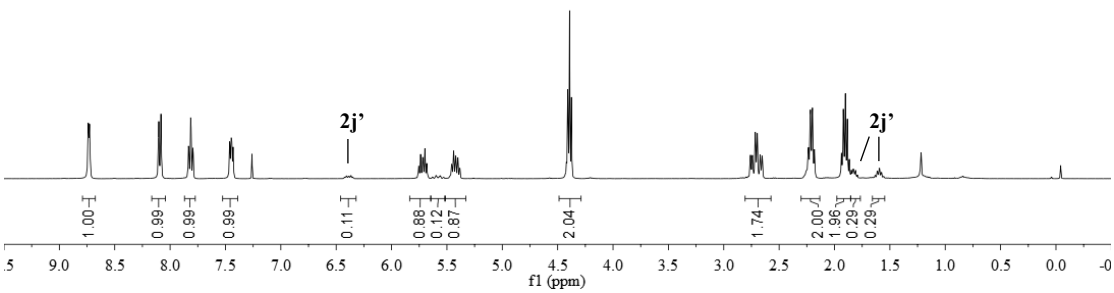


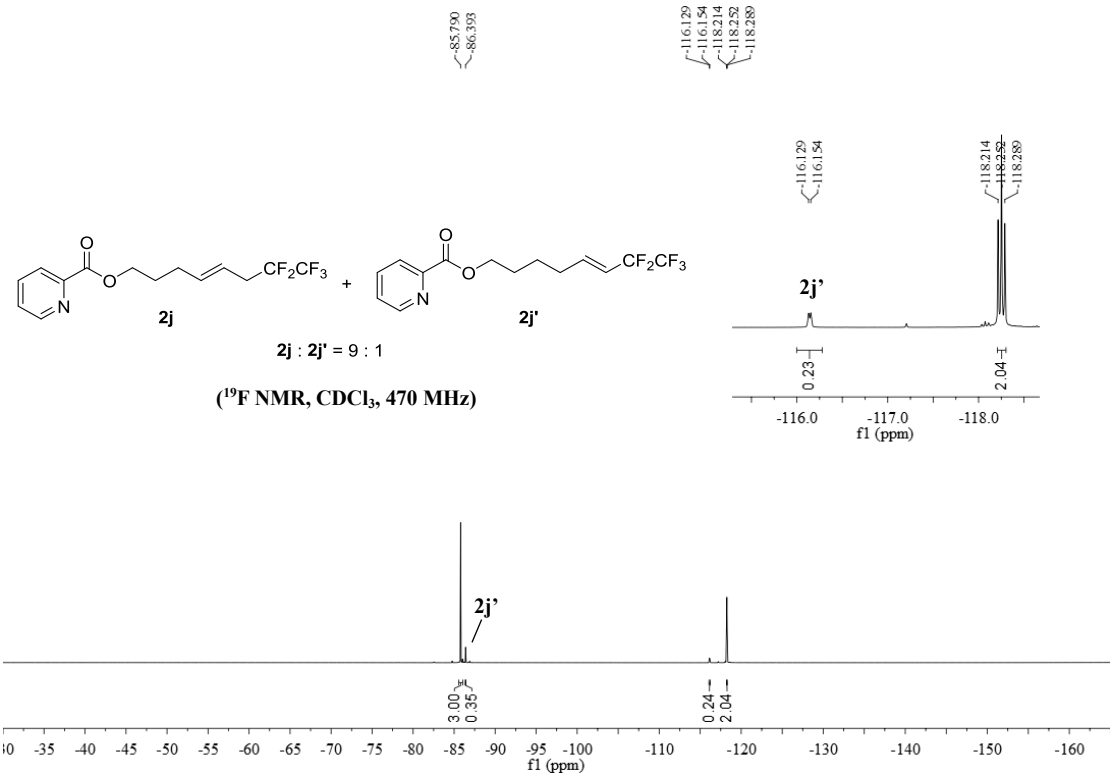




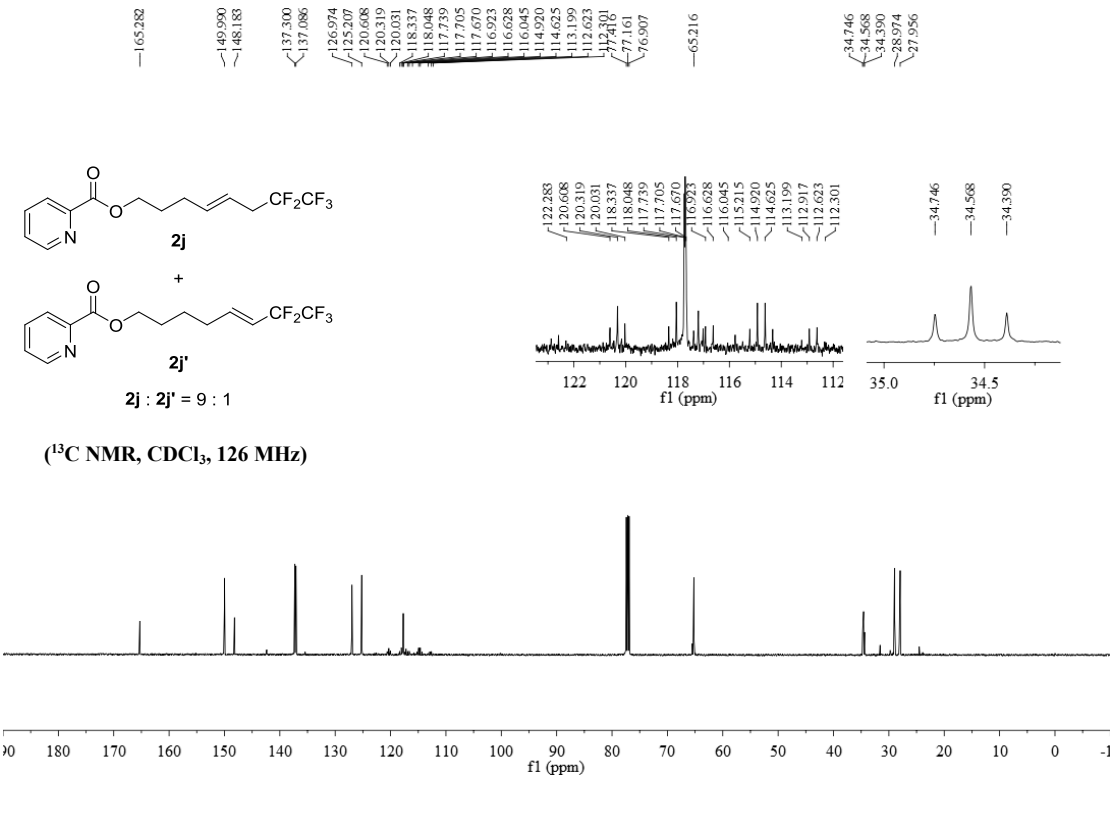
2j : **2j'** = 9 : 1

(^{1}H NMR, $CDCl_3$, 400 MHz)

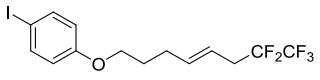




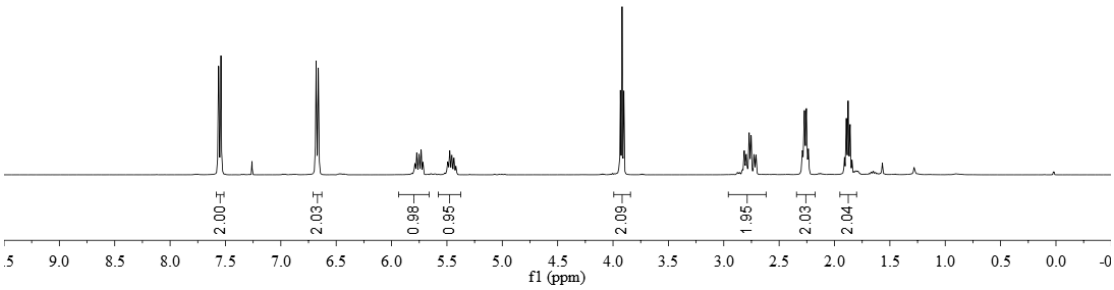
(**^{19}F NMR, $CDCl_3$, 470 MHz**)

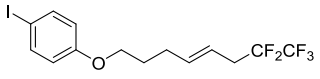


(**^{13}C NMR, $CDCl_3$, 126 MHz**)

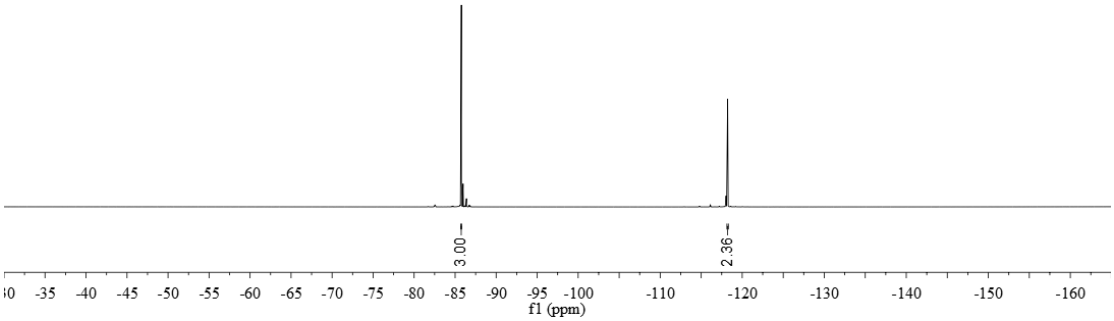


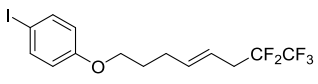
2k (^{1}H NMR, $CDCl_3$, 400 MHz)



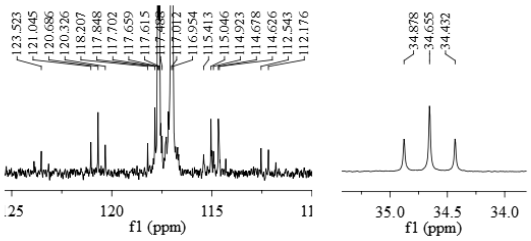


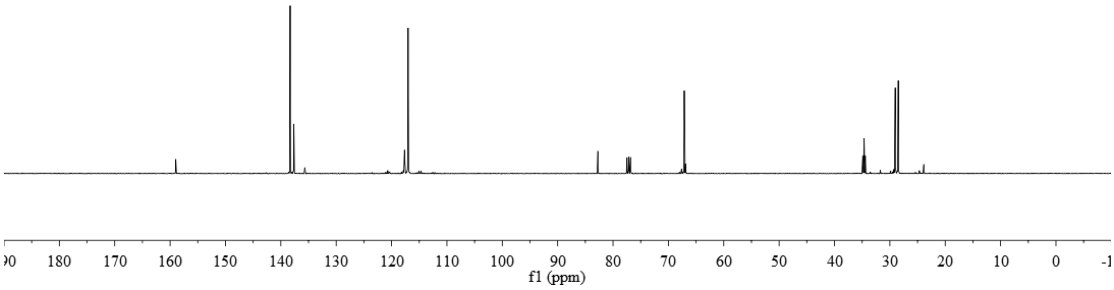
2k (^{19}F NMR, $CDCl_3$, 470 MHz)

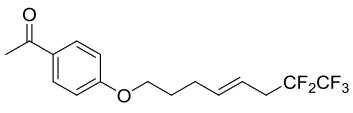




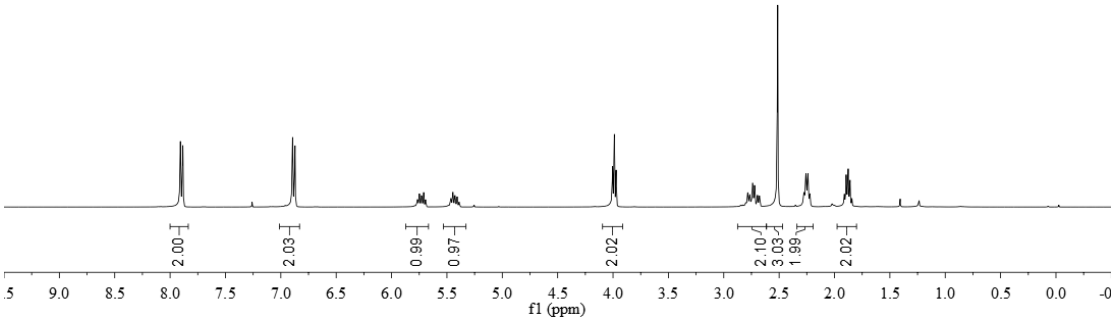
2k (^{13}C NMR, $CDCl_3$, 101 MHz)

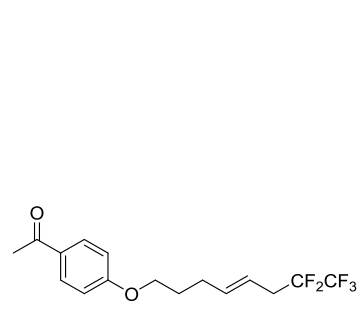




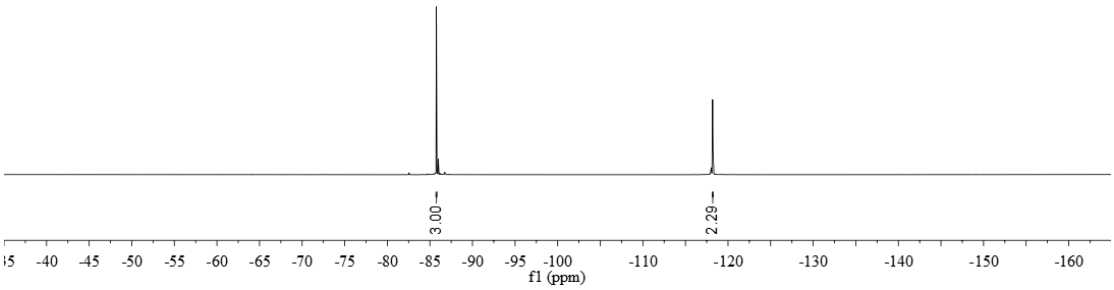


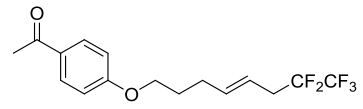
2l (^{1}H NMR, $CDCl_3$, 400 MHz)



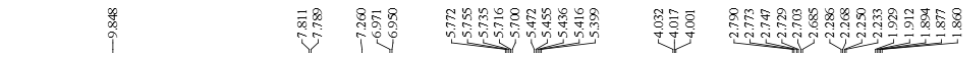


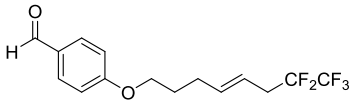
2l (^{19}F NMR, $CDCl_3$, 470 MHz)



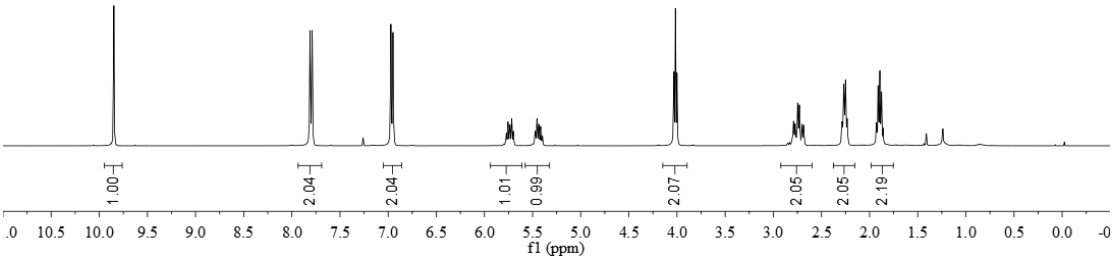


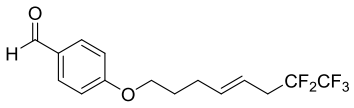
2l (^{13}C NMR, $CDCl_3$, 126 MHz)



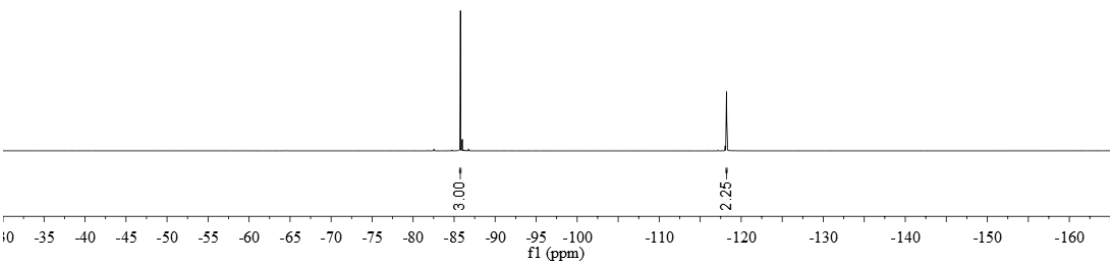


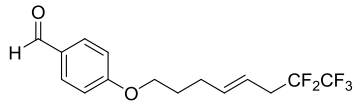
2m (^{1}H NMR, $CDCl_3$, 400 MHz)



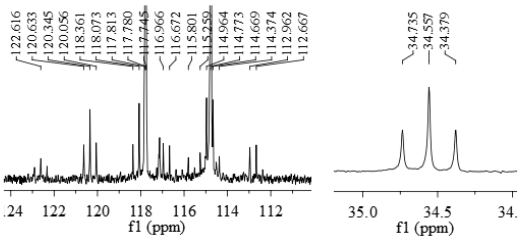


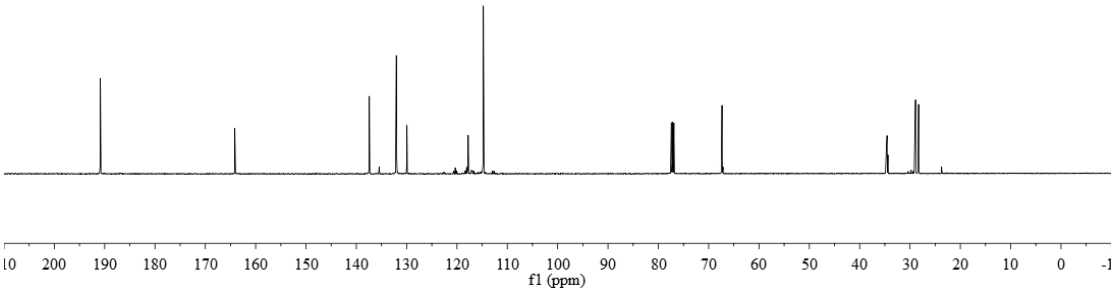
2m (^{19}F NMR, $CDCl_3$, 470 MHz)

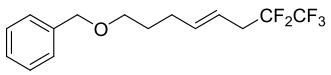




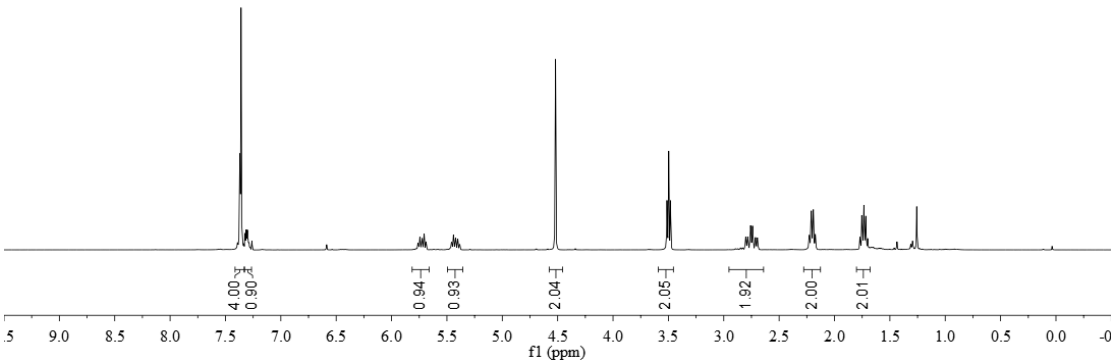
2m (^{13}C NMR, $CDCl_3$, 126 MHz)

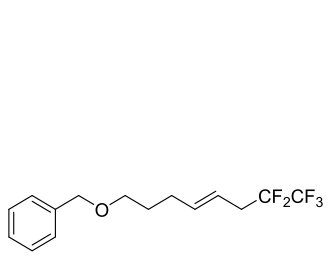




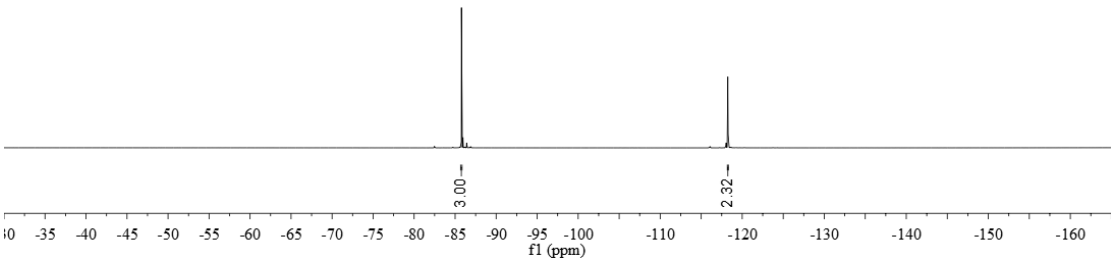


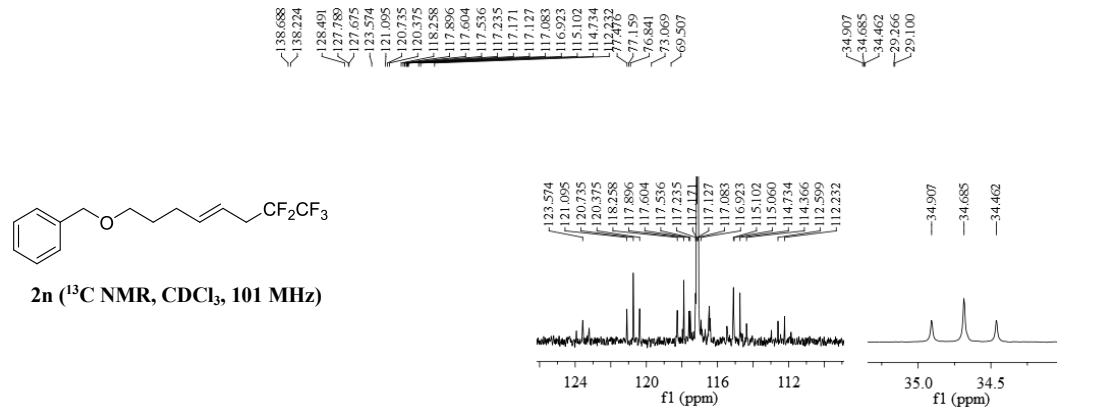
2n (^{1}H NMR, $CDCl_3$, 400 MHz)



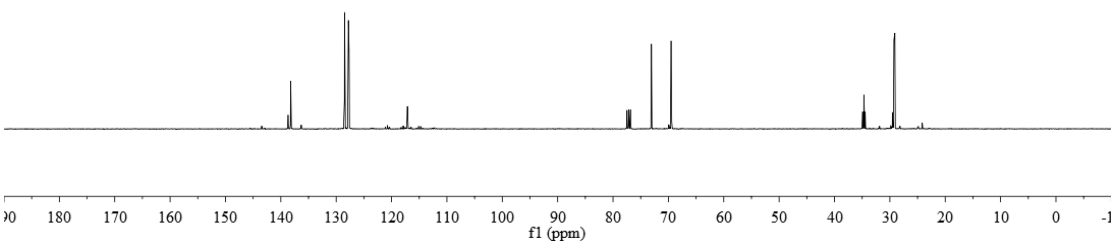


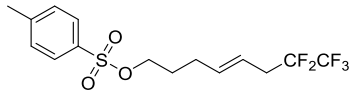
2n (^{19}F NMR, $CDCl_3$, 470 MHz)



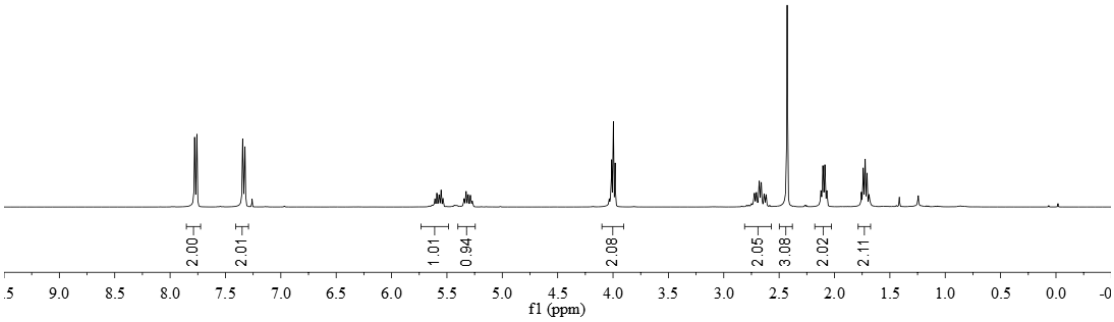


2n (^{13}C NMR, $CDCl_3$, 101 MHz)

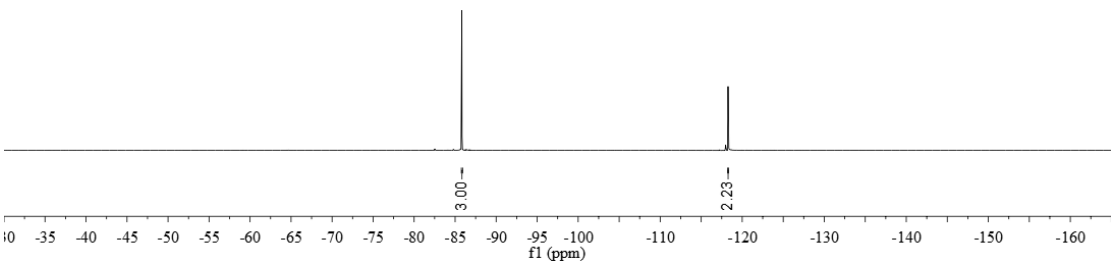


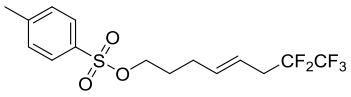


2o (^{1}H NMR, $CDCl_3$, 400 MHz)

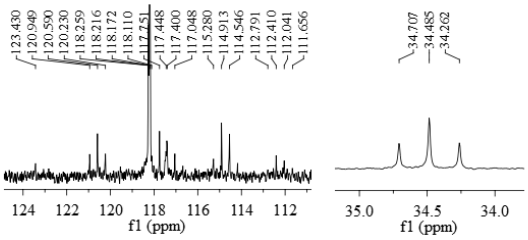


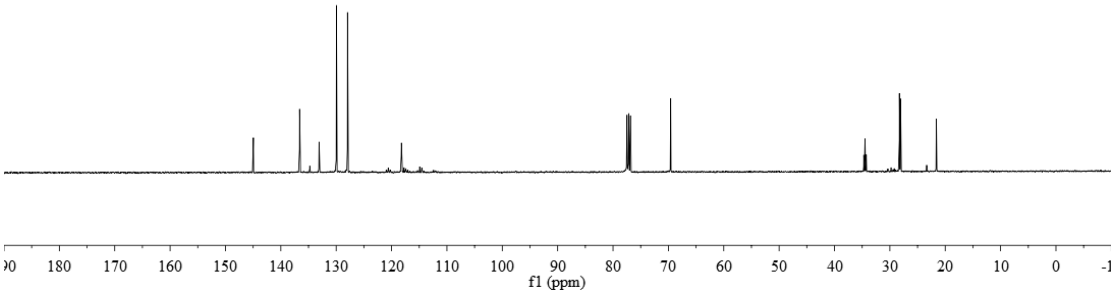
2o (^{19}F NMR, $CDCl_3$, 470 MHz)

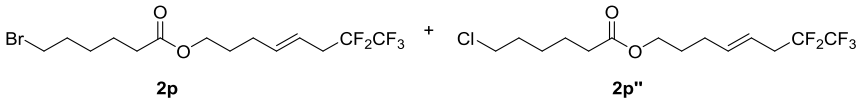




2o (^{13}C NMR, $CDCl_3$, 101 MHz)

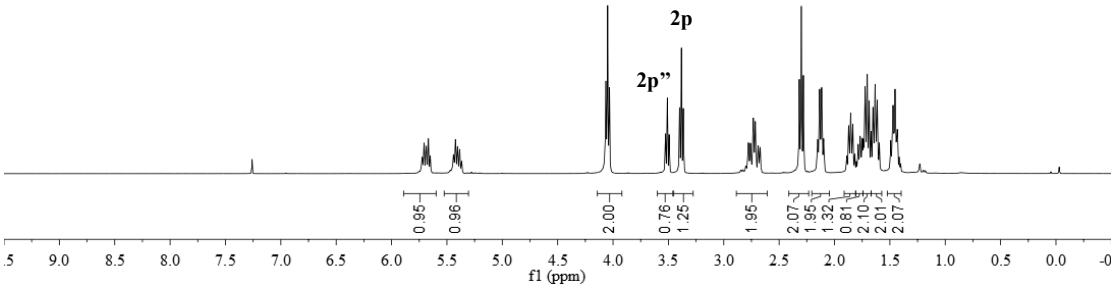


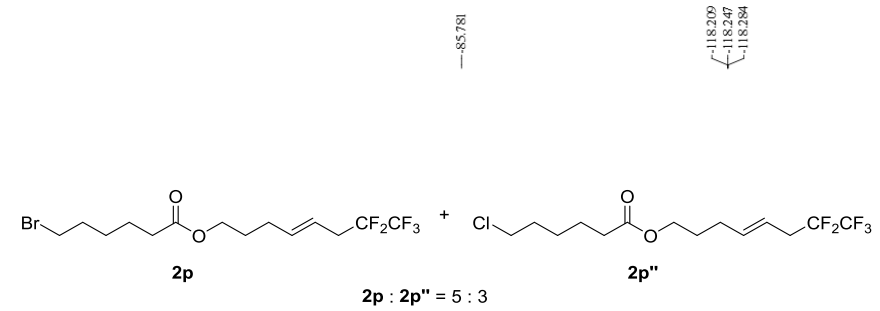




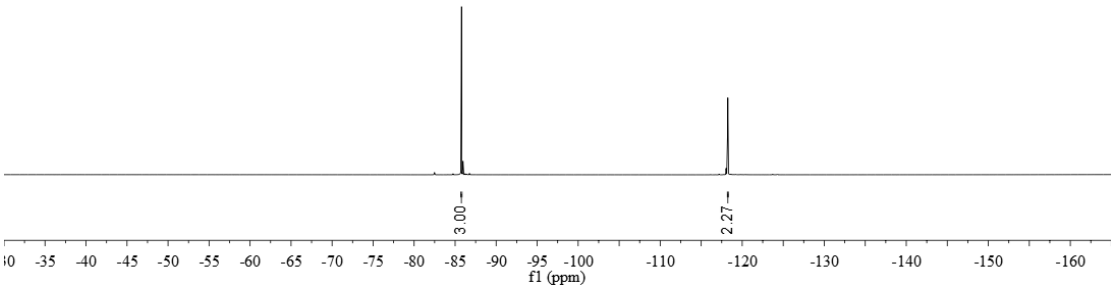
2p : **2p"** = 5 : 3

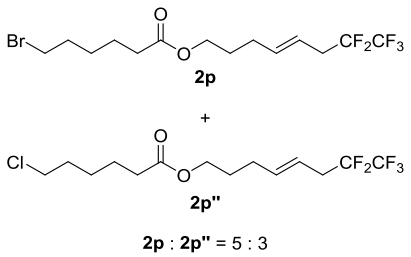
(^{1}H NMR, $CDCl_3$, 400 MHz)

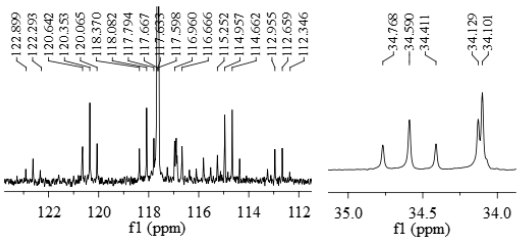




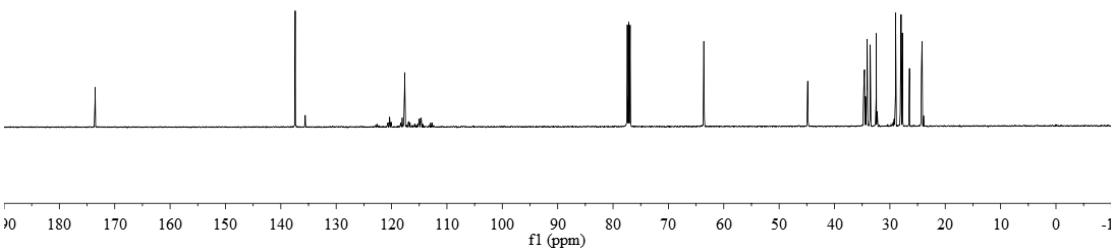
(^{19}F NMR, $CDCl_3$, 470 MHz)

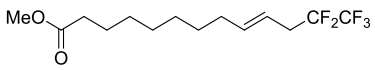




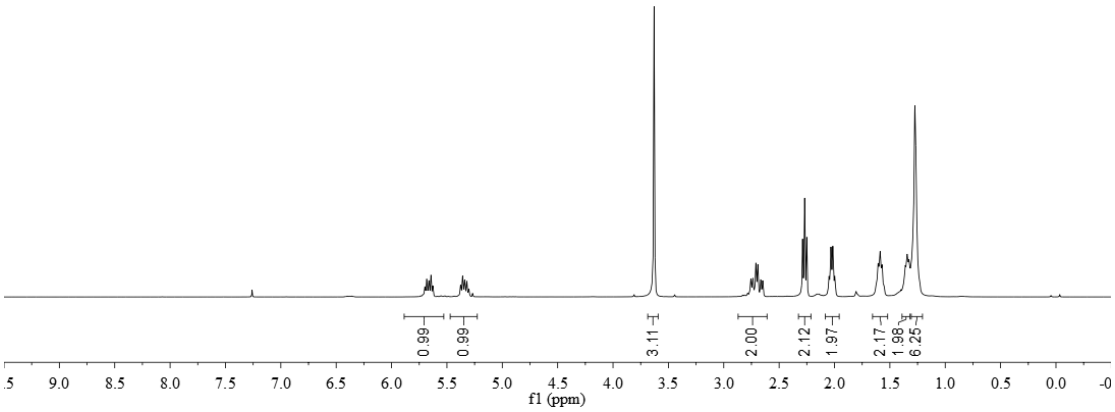


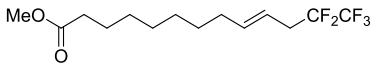
(^{13}C NMR, $CDCl_3$, 126 MHz)



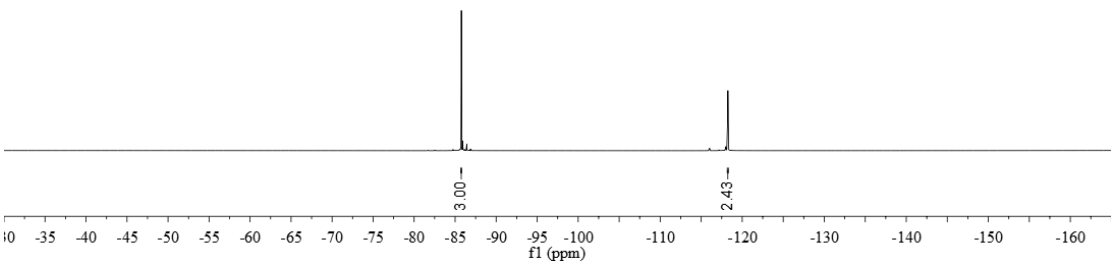


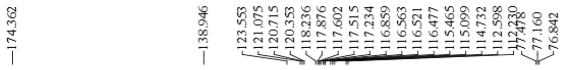
2q (^{1}H NMR, $CDCl_3$, 400 MHz)

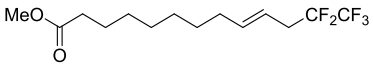




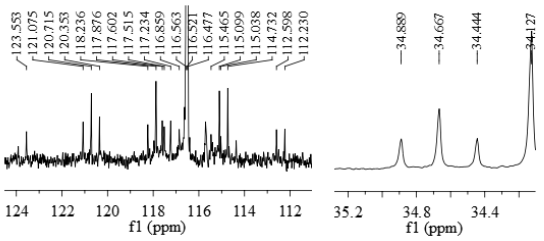
2q (^{19}F NMR, $CDCl_3$, 470 MHz)

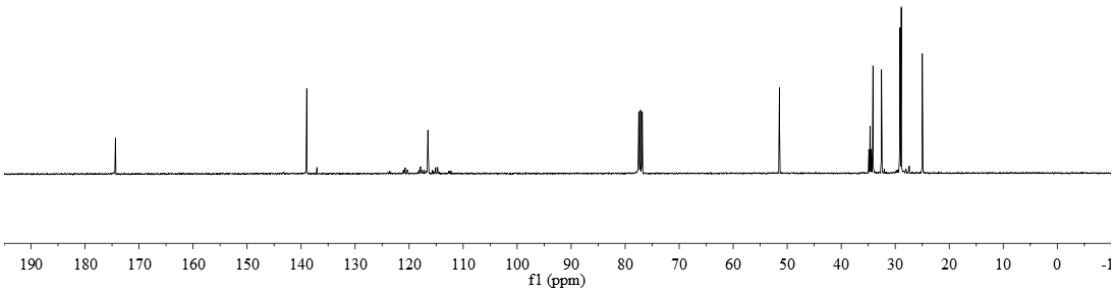


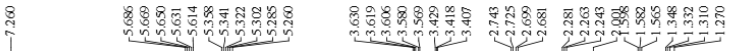


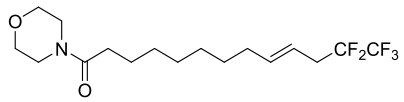


2q (^{13}C NMR, $CDCl_3$, 101 MHz)

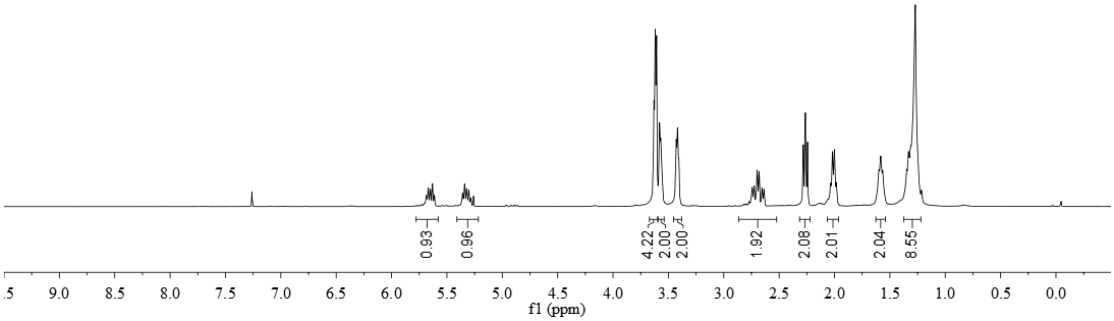


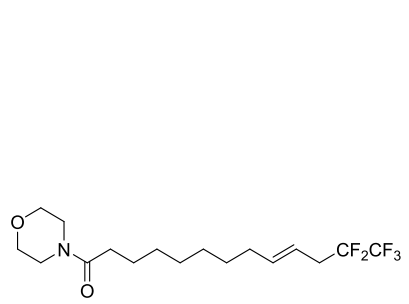




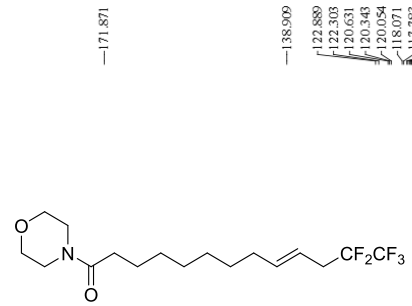


2r (^{1}H NMR, $CDCl_3$, 400 MHz)

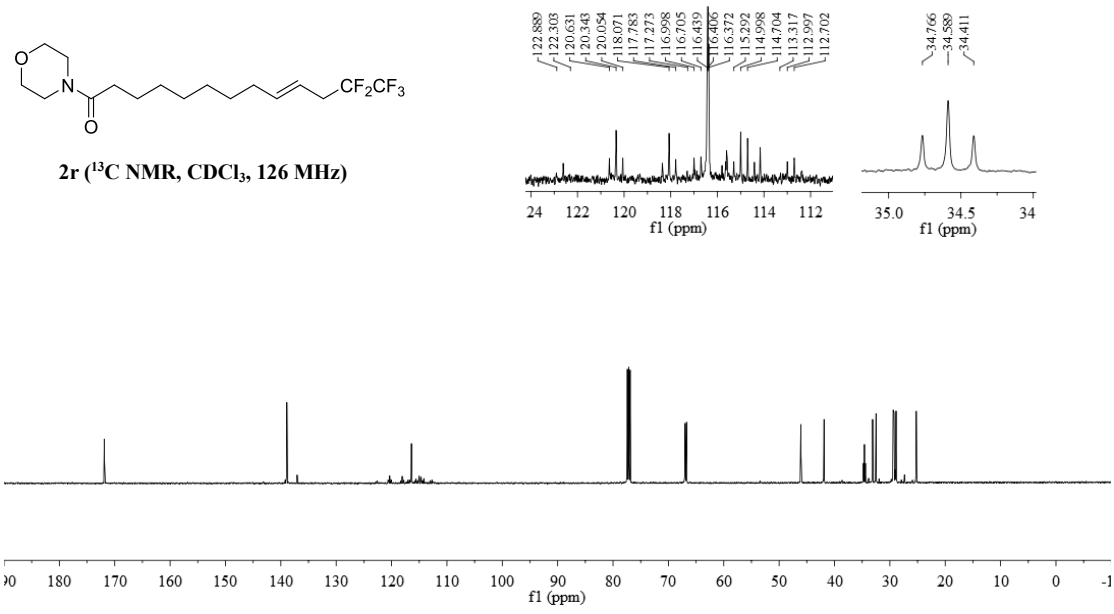


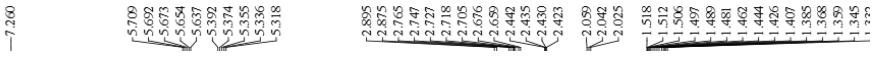


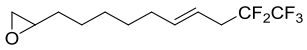
2r (^{19}F NMR, $CDCl_3$, 470 MHz)



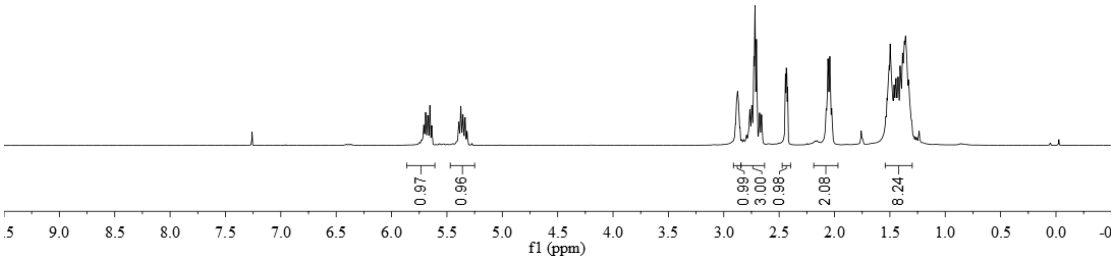
2r (^{13}C NMR, $CDCl_3$, 126 MHz)

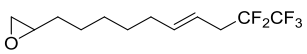




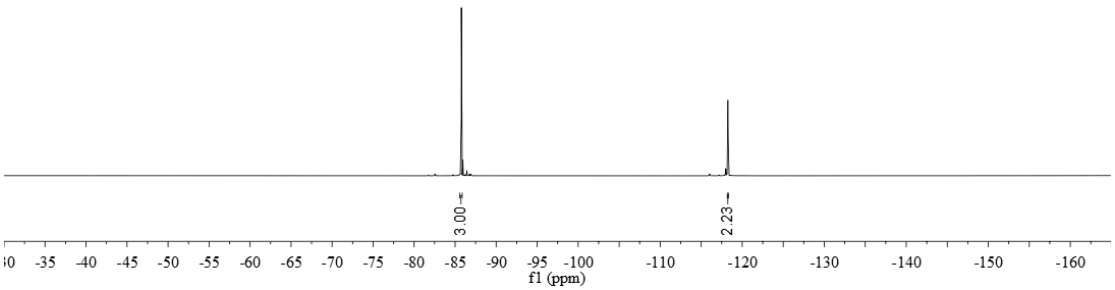


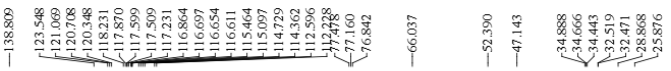
2s (^{1}H NMR, $CDCl_3$, 400 MHz)

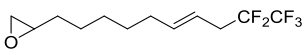




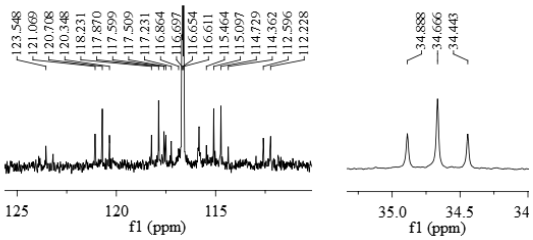
2s (^{19}F NMR, $CDCl_3$, 470 MHz)

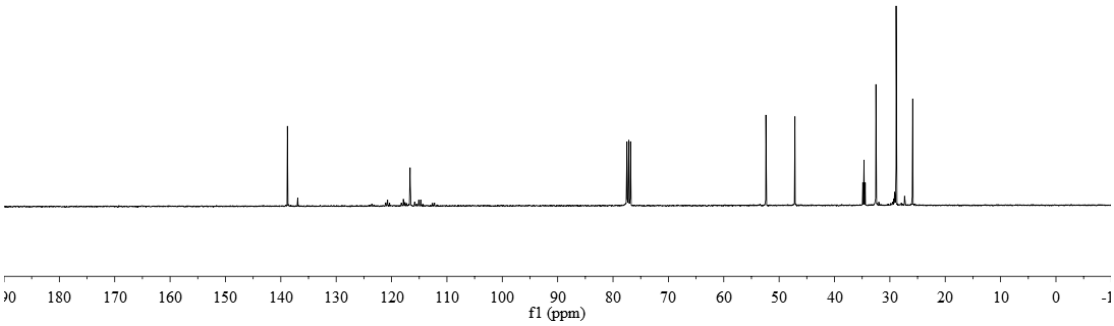


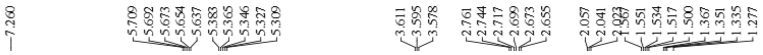


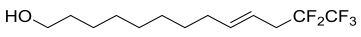


2s (^{13}C NMR, $CDCl_3$, 101 MHz)

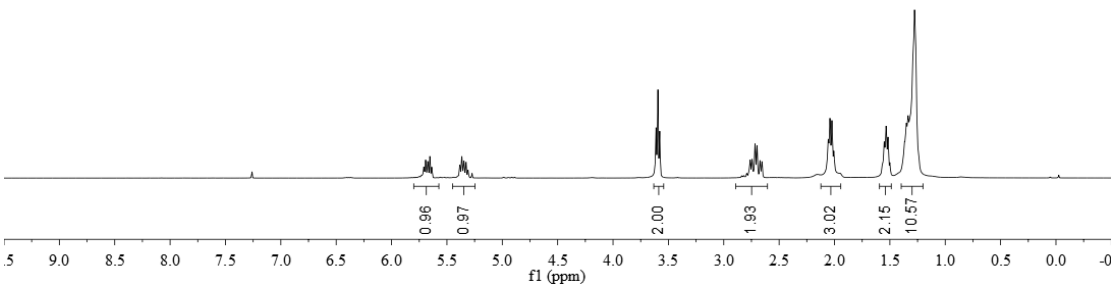


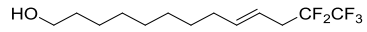




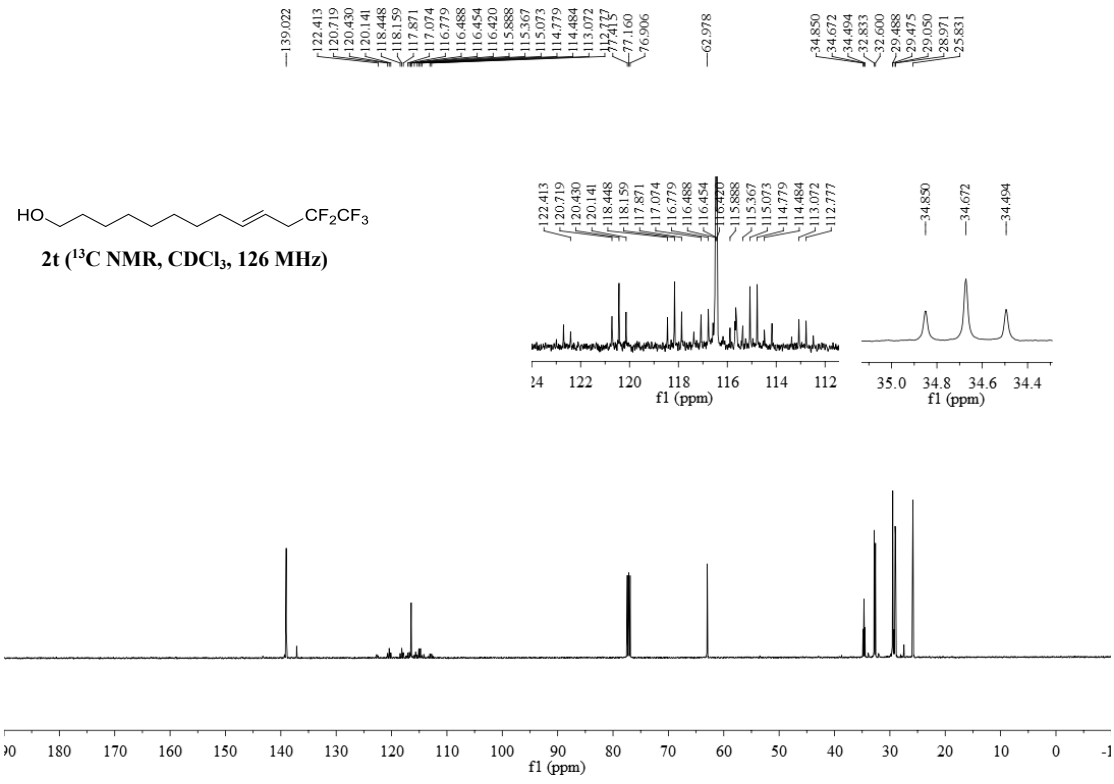


2t (^{1}H NMR, $CDCl_3$, 400 MHz)

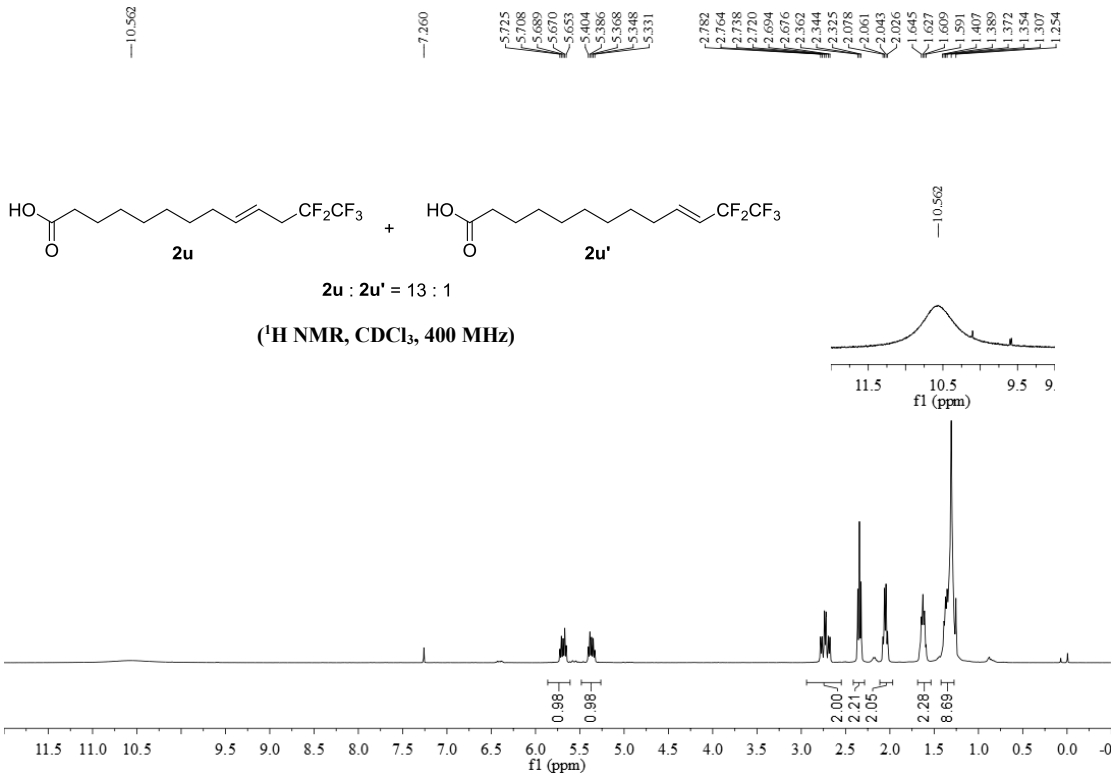


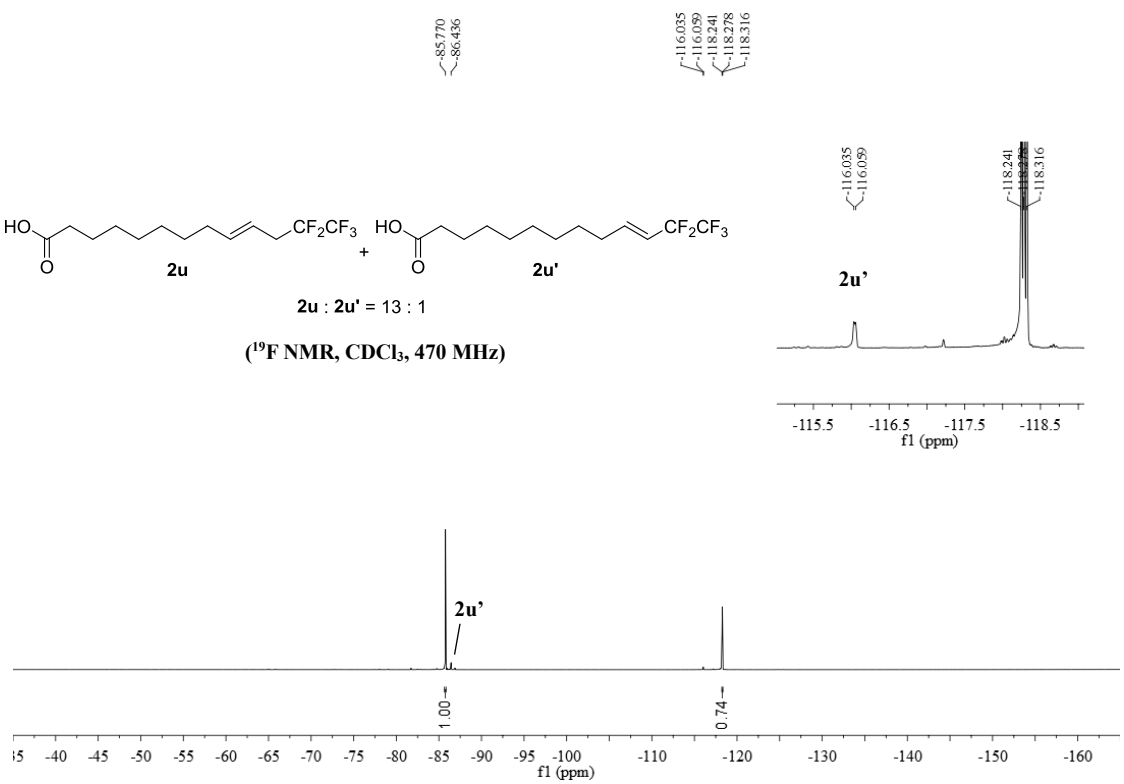


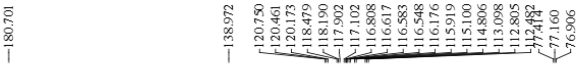
2t (^{19}F NMR, $CDCl_3$, 470 MHz)

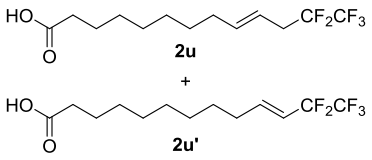


2t (^{13}C NMR, $CDCl_3$, 126 MHz)


10.562
7.260
5.725
5.708
5.689
5.670
5.653
5.404
5.386
5.368
5.348
5.331
2.782
2.764
2.738
2.720
2.694
2.676
2.362
2.344
2.325
2.078
2.061
2.043
2.026
1.645
1.627
1.609
1.591
1.407
1.389
1.372
1.354
1.307
1.254
HO
O
CF2CF3
2u
2u'
2u : 2u' = 13 : 1
(1H NMR, CDCl3, 400 MHz)
f1 (ppm)
0.98
0.98
2.00
2.21
2.05
2.28
8.69

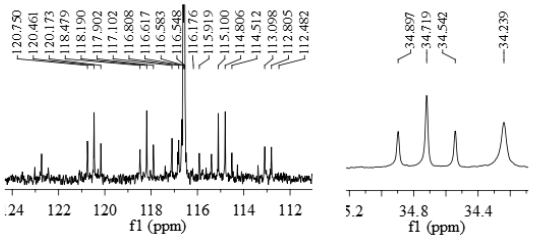

85.770
86.436
116.035
116.099
118.241
118.278
118.316
HO
O
CF2CF3
2u
2u'
2u : 2u' = 13 : 1
(19F NMR, CDCl3, 470 MHz)
2u'
f1 (ppm)
1.00
0.74

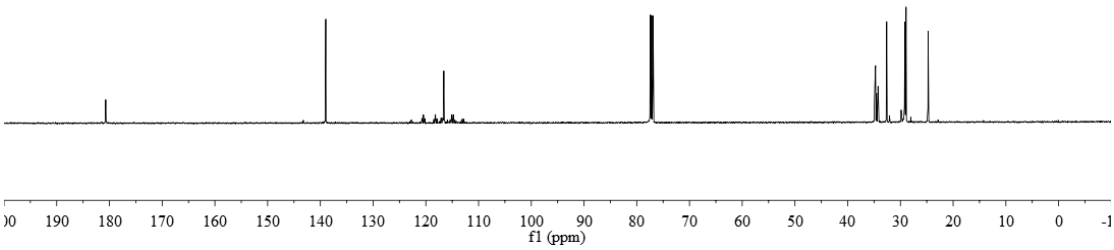


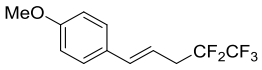


2u : **2u'** = 13 : 1

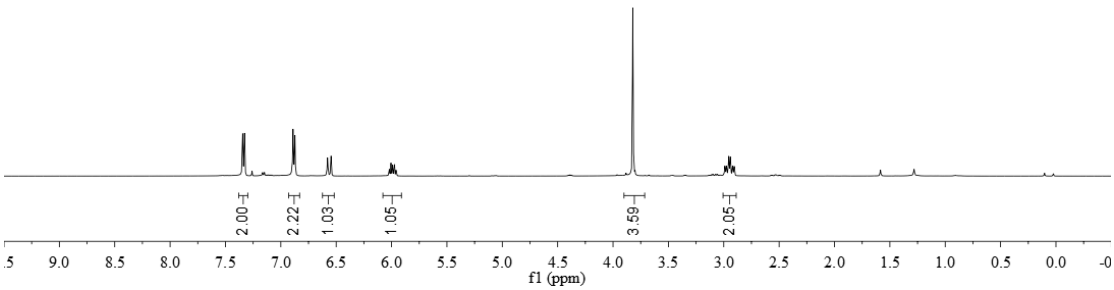
(^{13}C NMR, $CDCl_3$, 126 MHz)

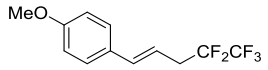




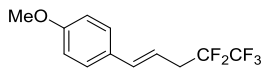


2v (^{1}H NMR, $CDCl_3$, 500 MHz)

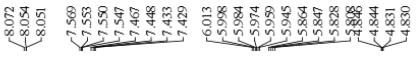


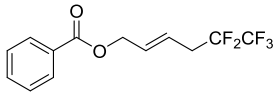


2v (^{19}F NMR, $CDCl_3$, 470 MHz)

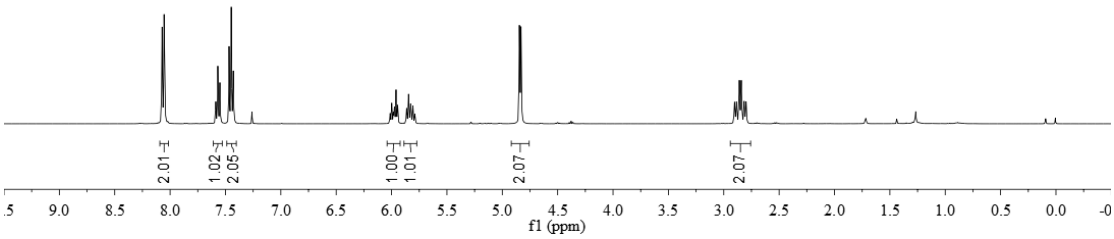


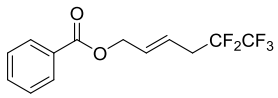
2v (^{13}C NMR, $CDCl_3$, 126 MHz)



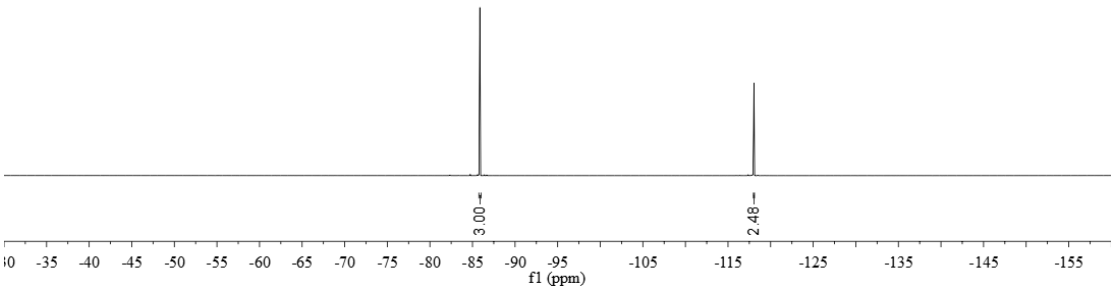


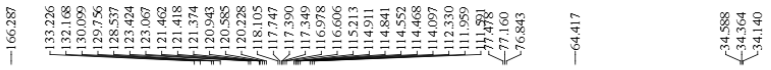
2w (^{1}H NMR, $CDCl_3$, 400 MHz)

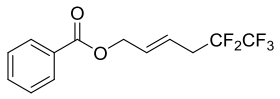




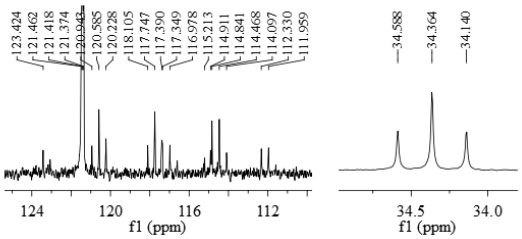
2w (^{19}F NMR, $CDCl_3$, 376 MHz)

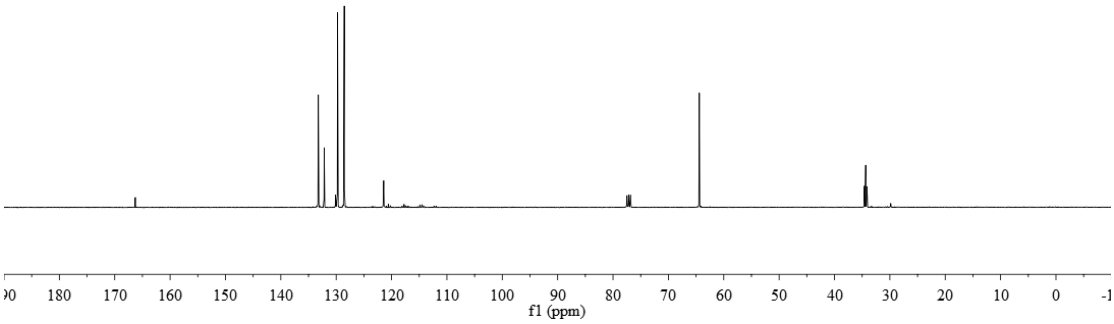


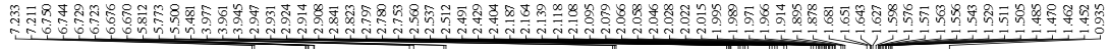


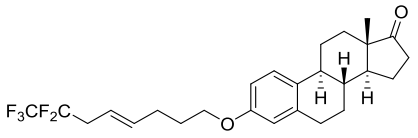


2w (^{13}C NMR, $CDCl_3$, 101 MHz)

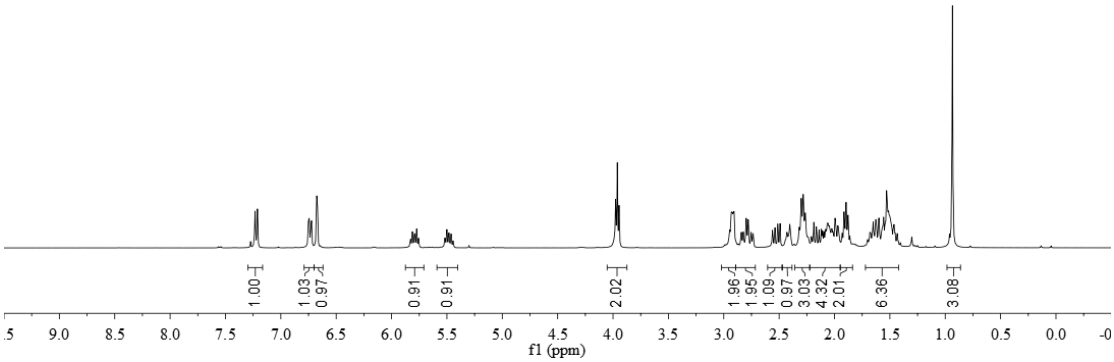


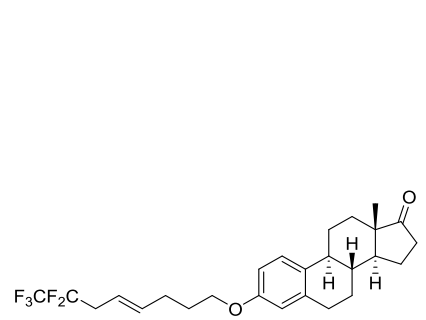




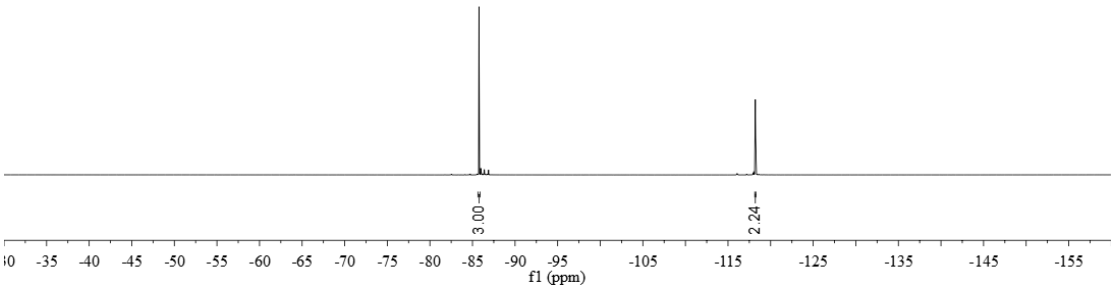


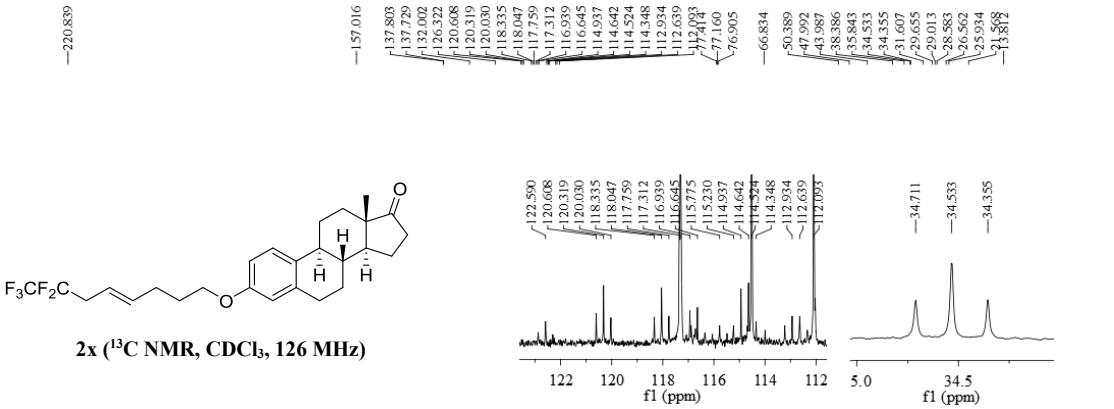
2x (^{1}H NMR, $CDCl_3$, 400 MHz)



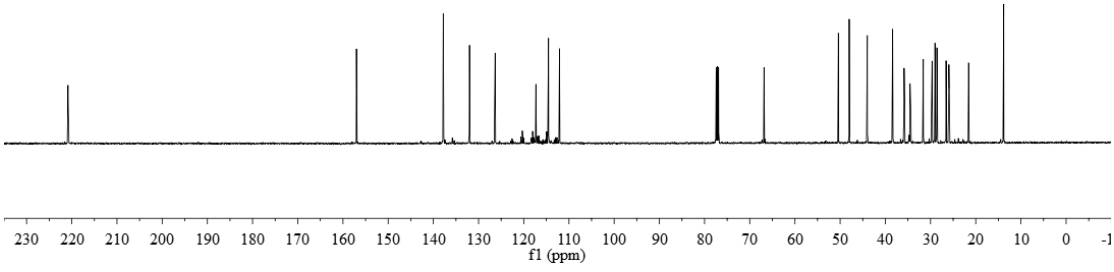


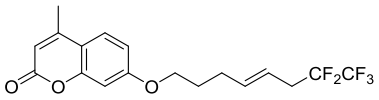
2x (^{19}F NMR, $CDCl_3$, 470 MHz)



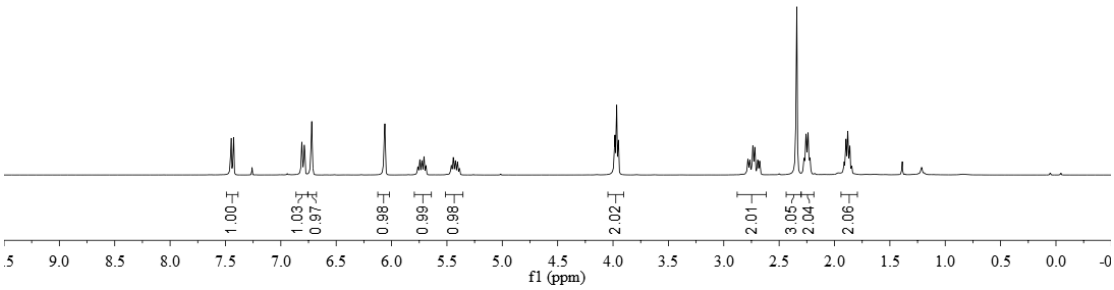


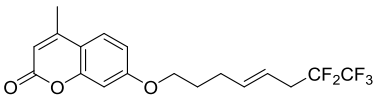
2x (^{13}C NMR, $CDCl_3$, 126 MHz)



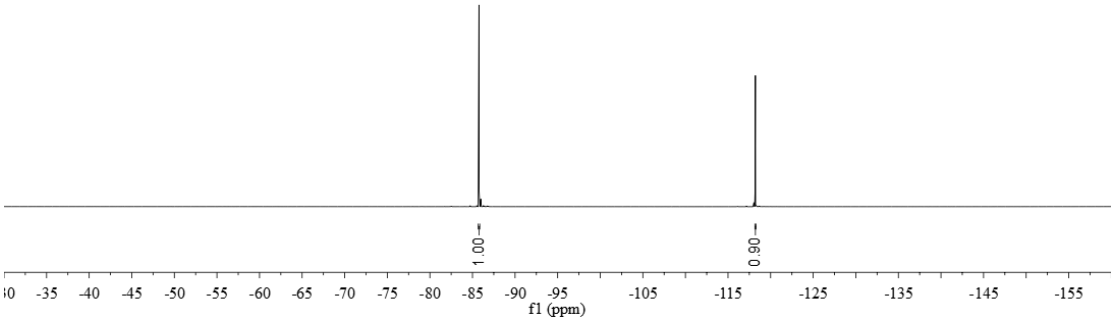


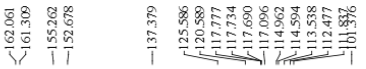
2y (^{1}H NMR, $CDCl_3$, 400 MHz)

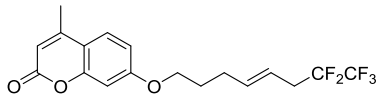




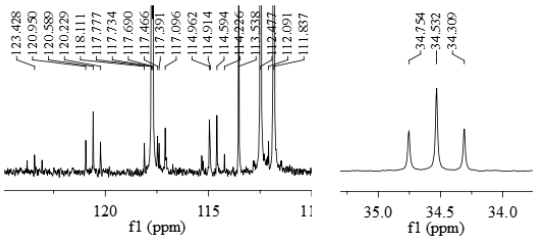
2y (^{19}F NMR, $CDCl_3$, 376 MHz)

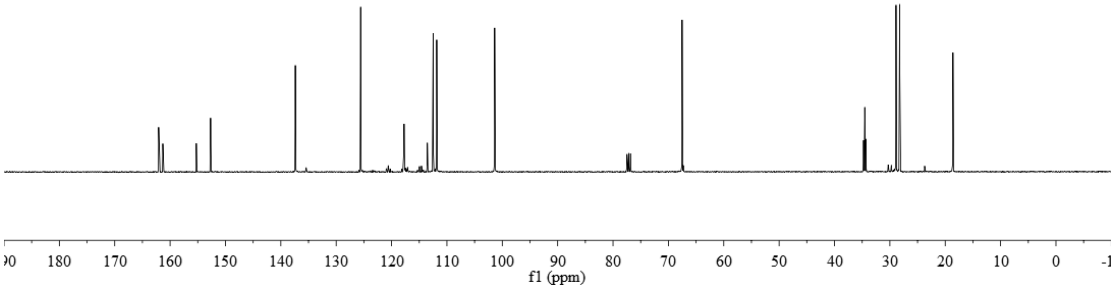


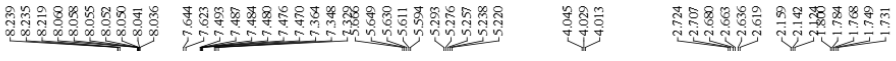


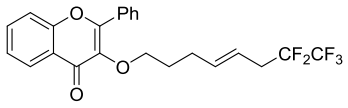


2y (^{13}C NMR, $CDCl_3$, 101 MHz)

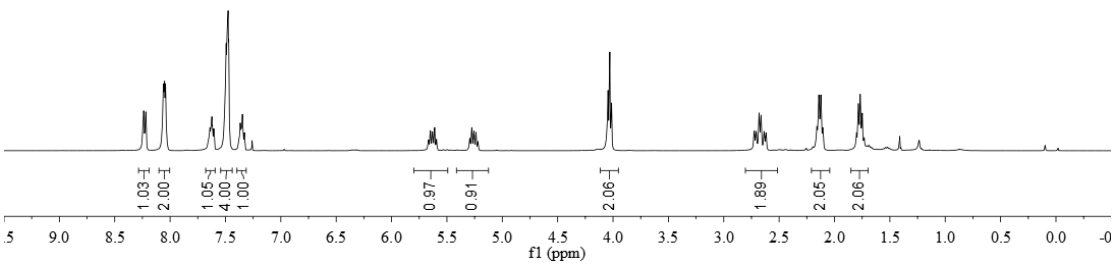


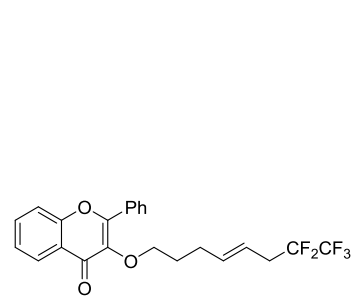




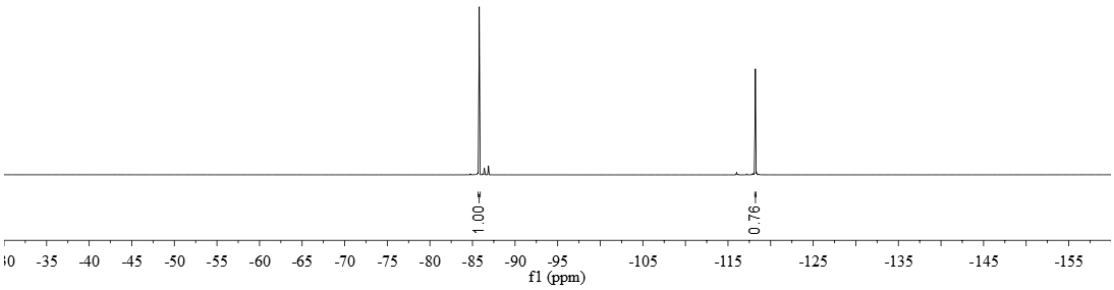


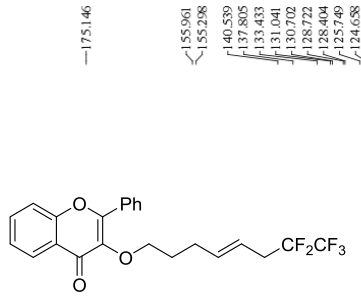
2z (^{1}H NMR, $CDCl_3$, 400 MHz)



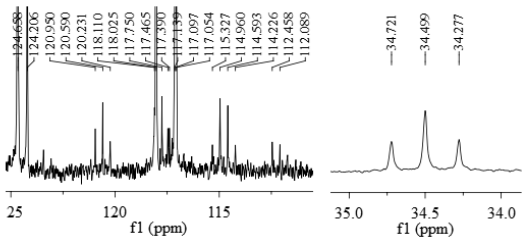


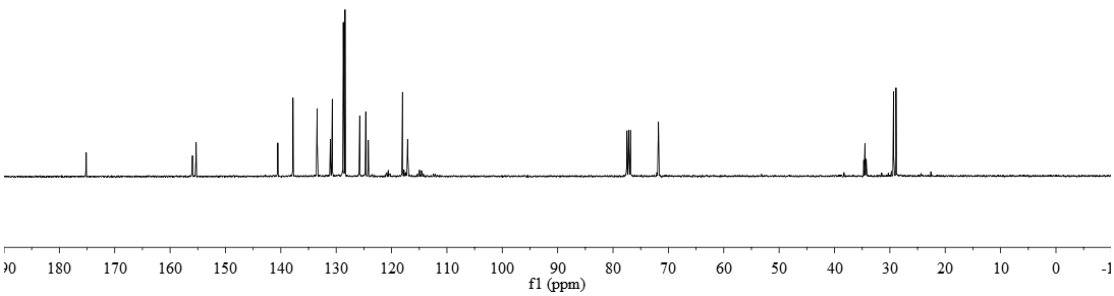
2z (^{19}F NMR, $CDCl_3$, 470 MHz)

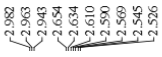


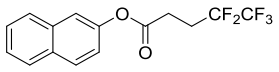


2z (^{13}C NMR, $CDCl_3$, 101 MHz)

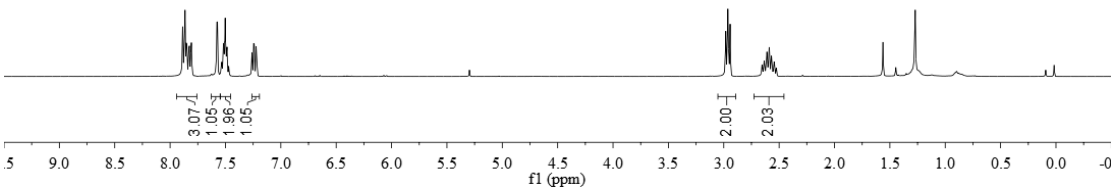


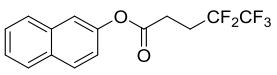




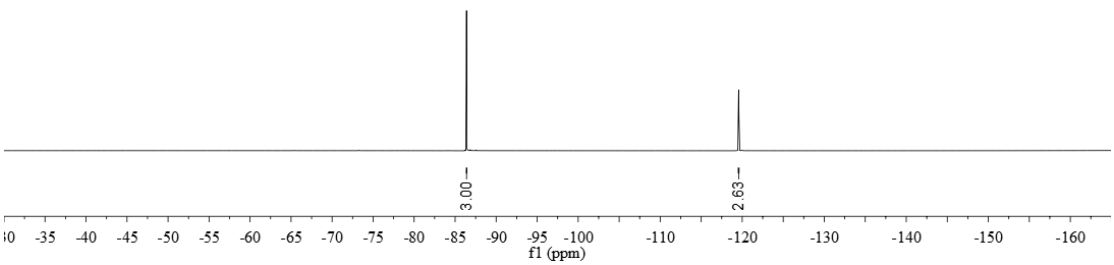


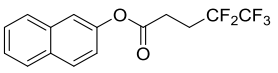
2aa (^{1}H NMR, $CDCl_3$, 100 MHz)



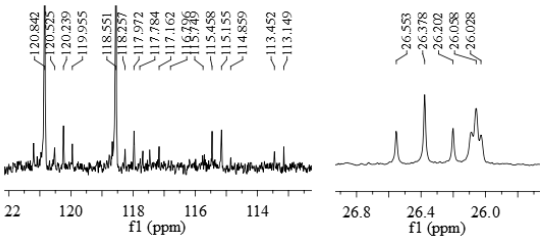


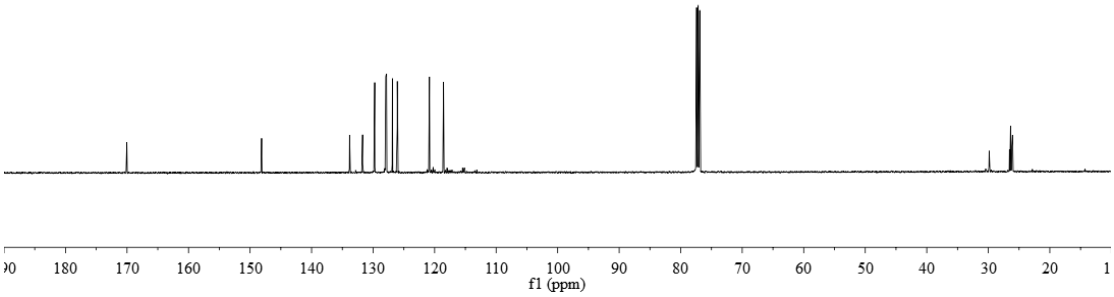
2aa (^{19}F NMR, $CDCl_3$, 470 MHz)

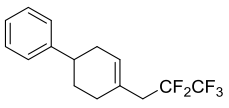




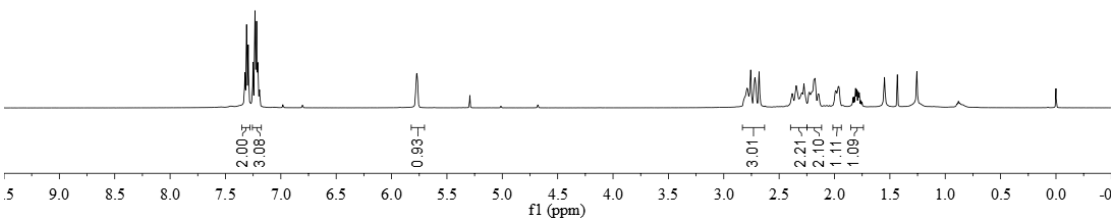
2aa (^{13}C NMR, $CDCl_3$, 126 MHz)

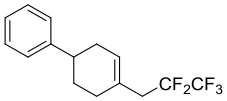




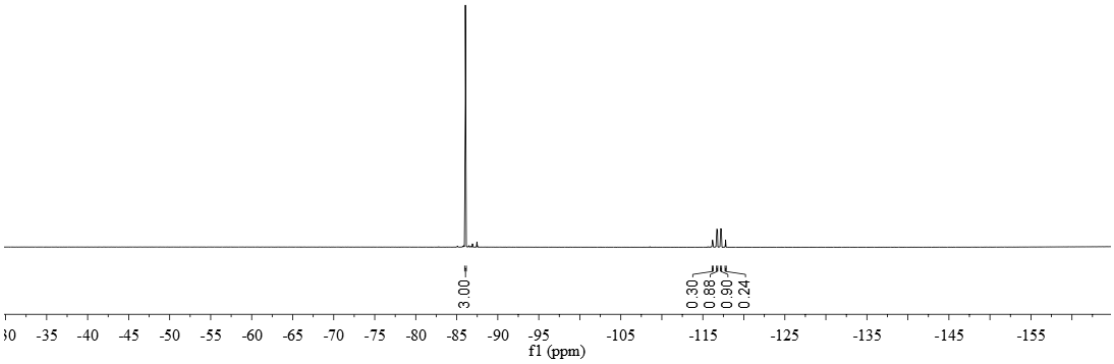


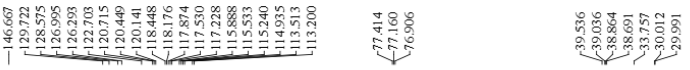
2ab (^{1}H NMR, $CDCl_3$, 500 MHz)

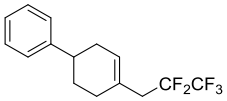




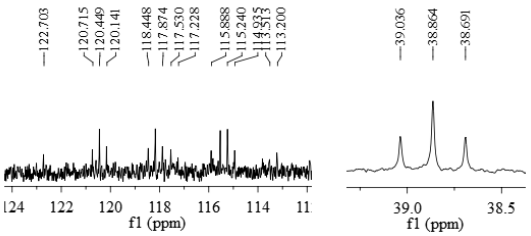
2ab (^{19}F NMR, $CDCl_3$, 470 MHz)

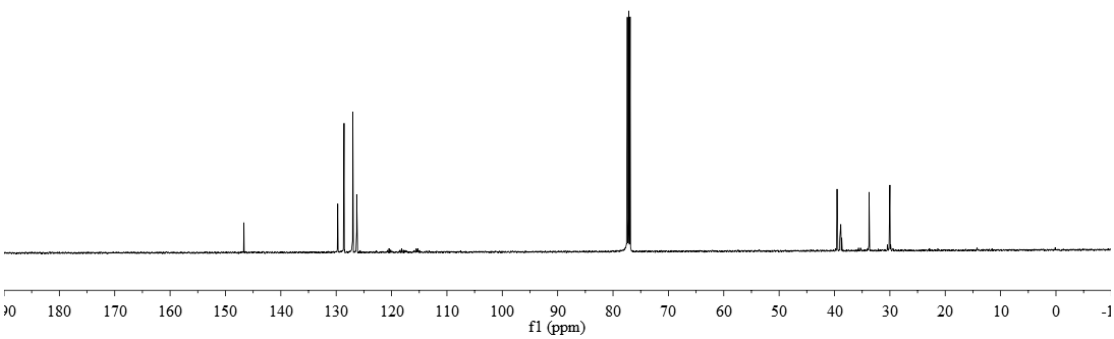


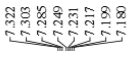


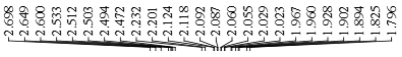


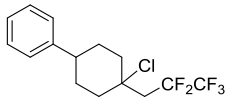
2ab (^{13}C NMR, $CDCl_3$, 126 MHz)



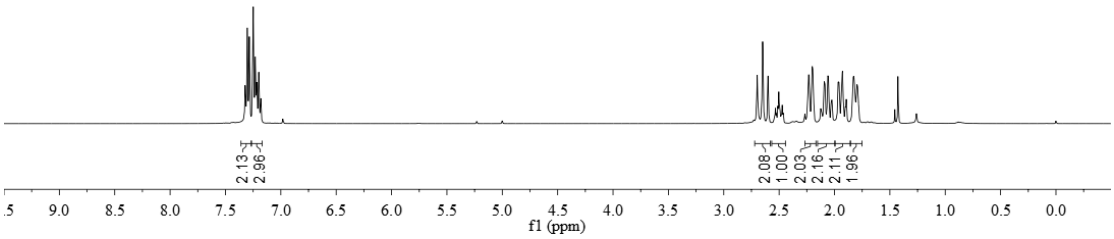


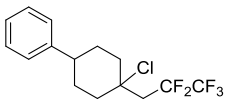




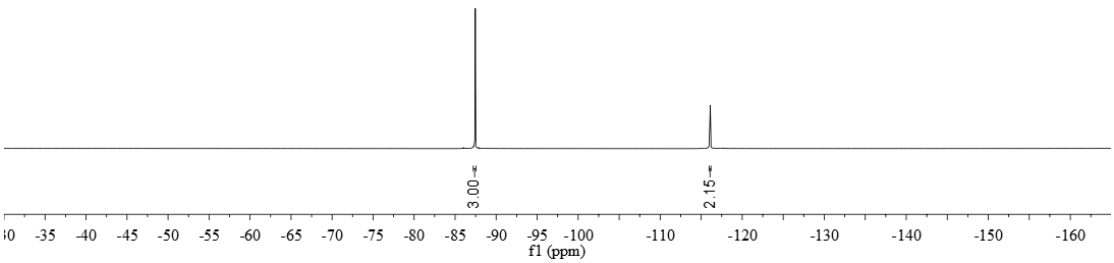


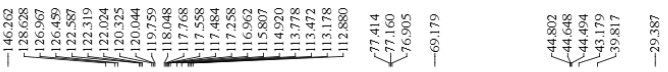
2ab" (^{1}H NMR, $CDCl_3$, 400 MHz)

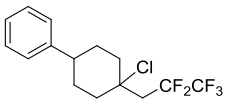




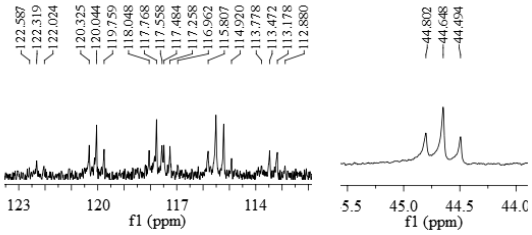
2ab" (^{19}F NMR, $CDCl_3$, 470 MHz)

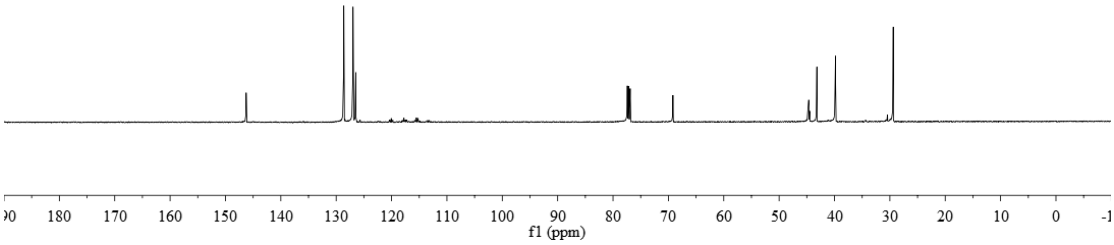


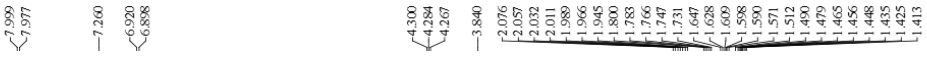


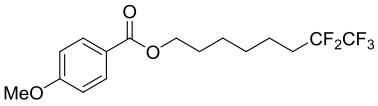


2ab" (^{13}C NMR, $CDCl_3$, 126 MHz)

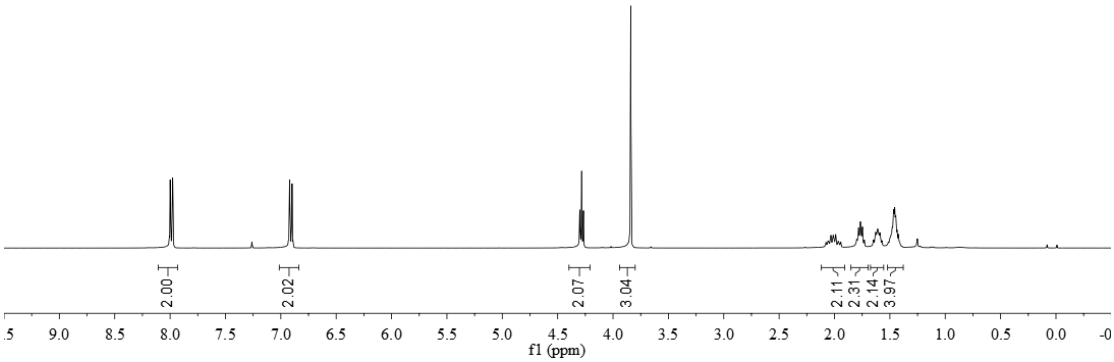


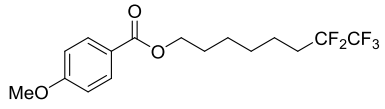




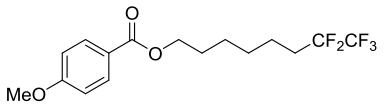


3 (^{1}H NMR, $CDCl_3$, 400 MHz)

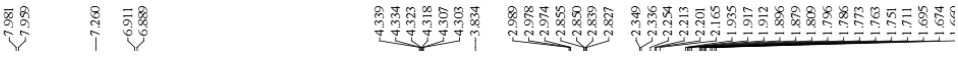


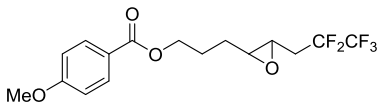


3 (^{19}F NMR, $CDCl_3$, 376 MHz)

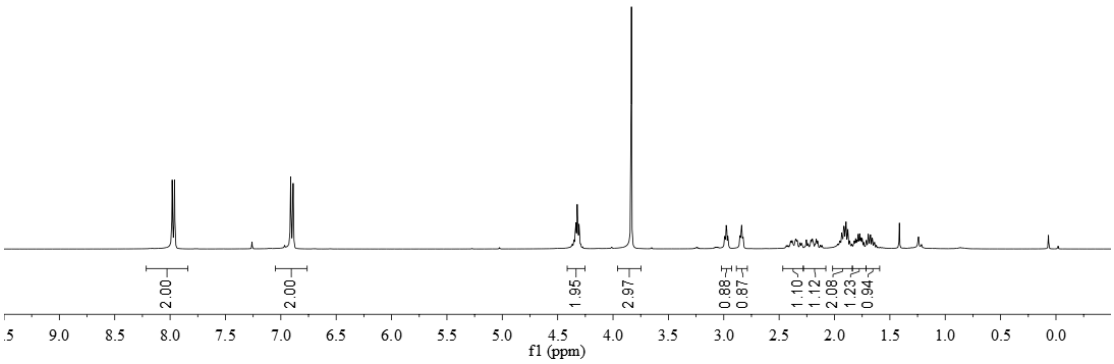


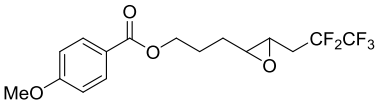
3 (^{13}C NMR, $CDCl_3$, 101 MHz)



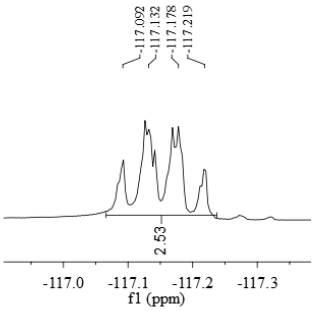


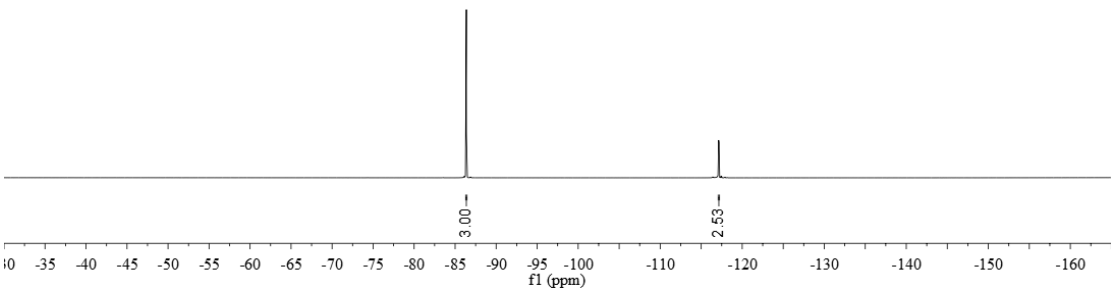
4 (^{1}H NMR, $CDCl_3$, 400 MHz)

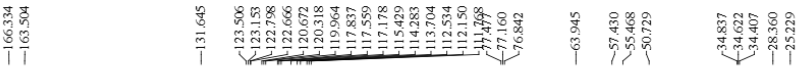


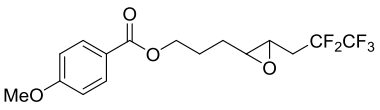


4 (^{19}F NMR, $CDCl_3$, 400 MHz)

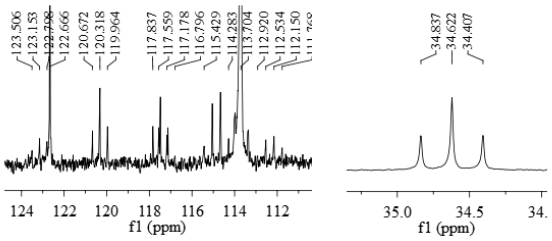


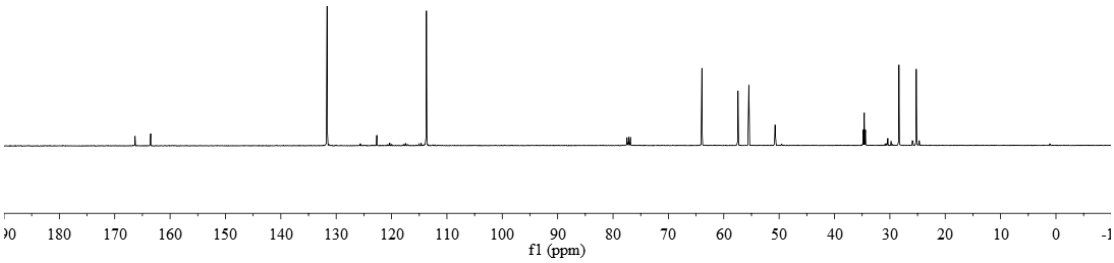


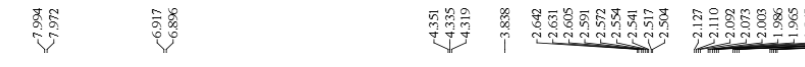


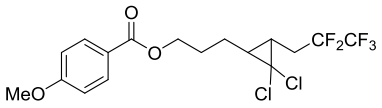


4 (^{13}C NMR, $CDCl_3$, 101 MHz)

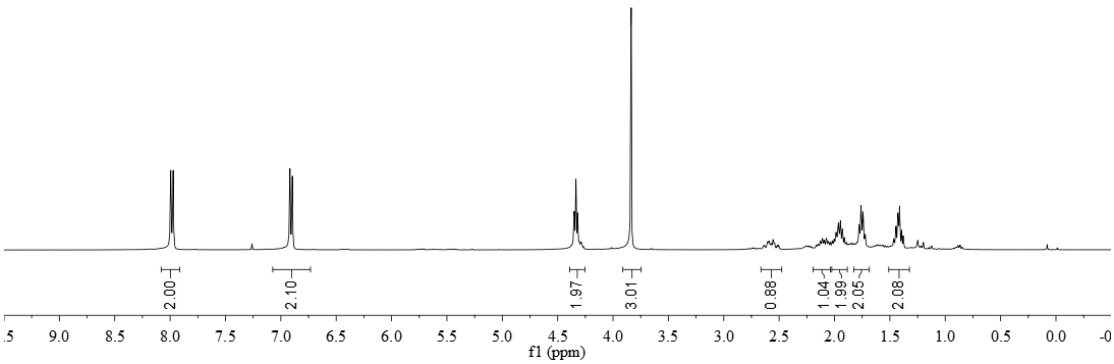


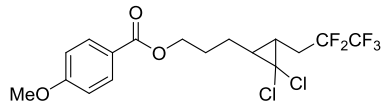




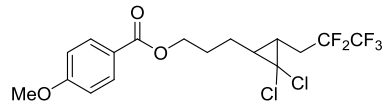


5 (^{1}H NMR, $CDCl_3$, 400 MHz)

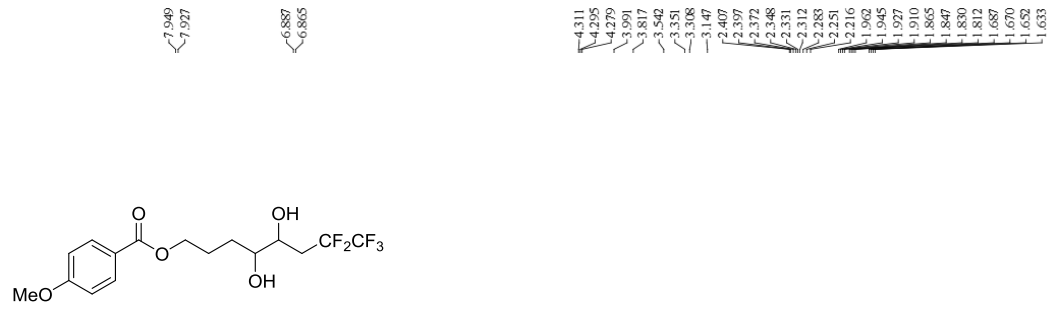




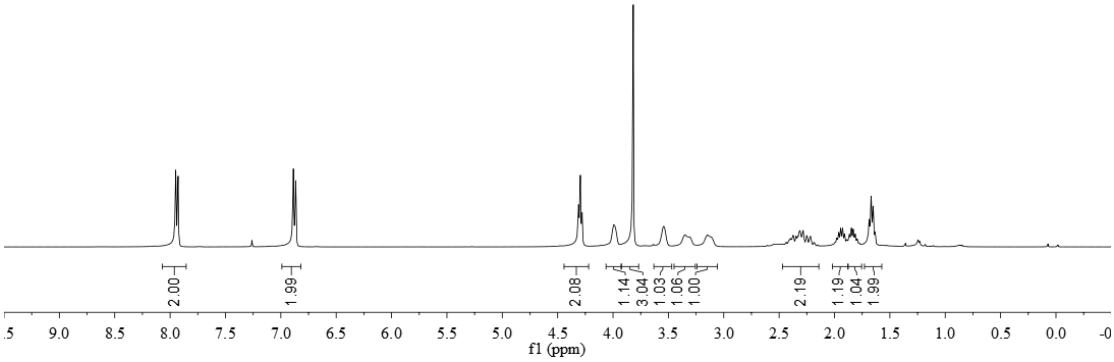
5 (^{19}F NMR, $CDCl_3$, 376 MHz)

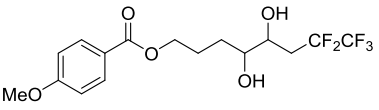


5 (^{13}C NMR, $CDCl_3$, 101 MHz)

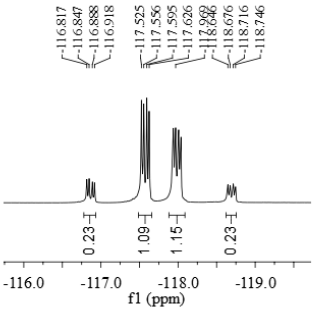


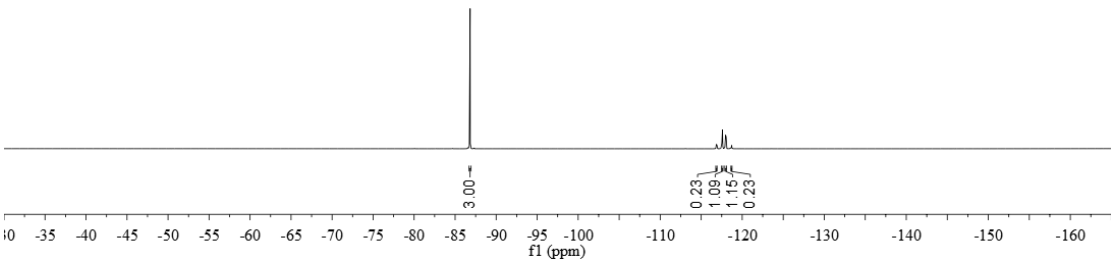
6 (^{1}H NMR, $CDCl_3$, 400 MHz)

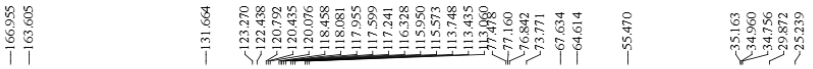


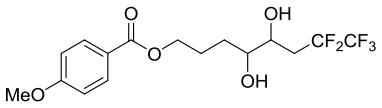


6 (^{19}F NMR, $CDCl_3$, 376 MHz)

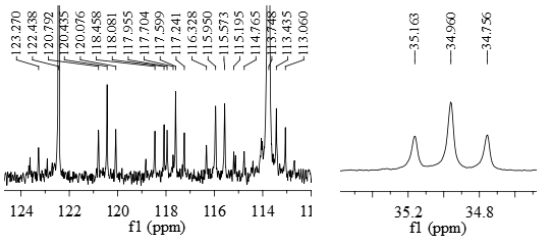


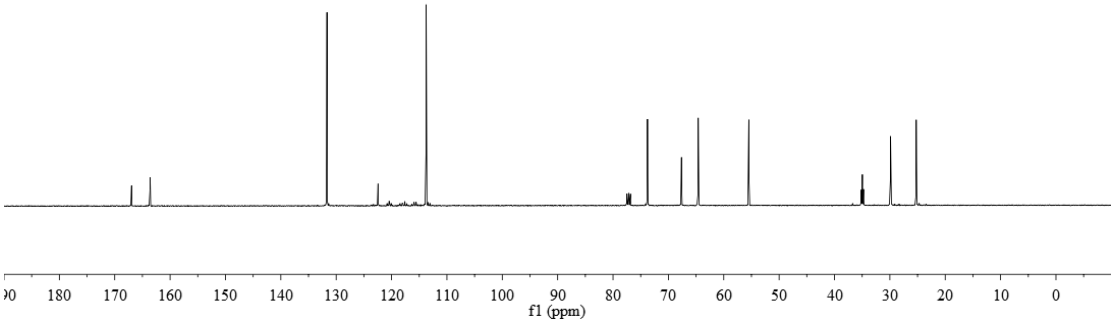


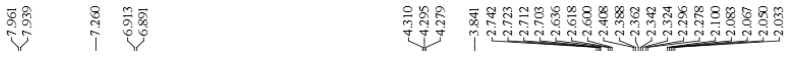


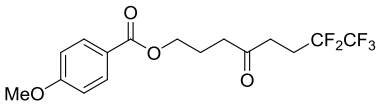


6 (^{13}C NMR, $CDCl_3$, 101 MHz)

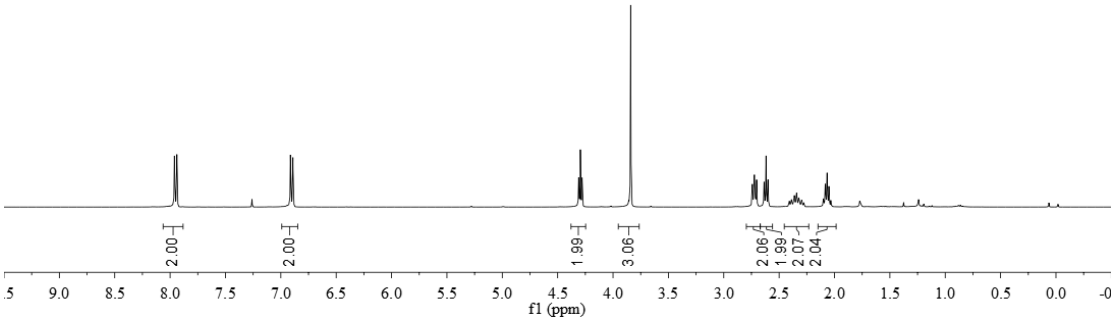


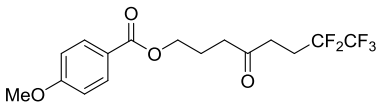




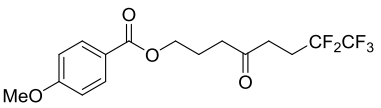


7 (^{1}H NMR, $CDCl_3$, 400 MHz)

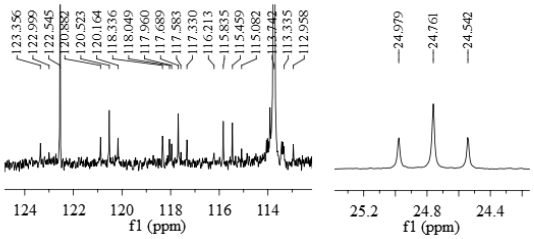


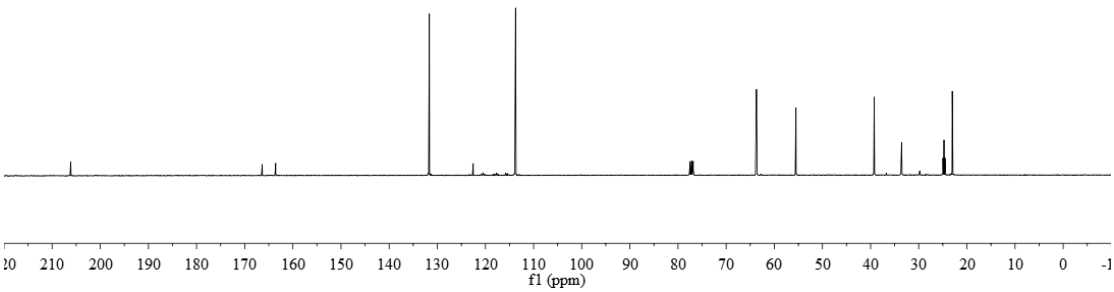


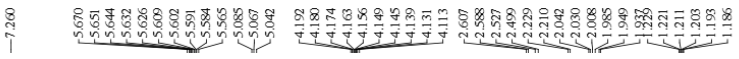
7 (^{19}F NMR, $CDCl_3$, 376 MHz)

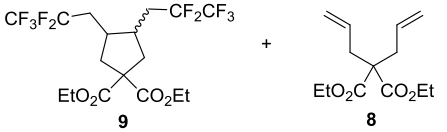


7 (^{13}C NMR, $CDCl_3$, 101 MHz)



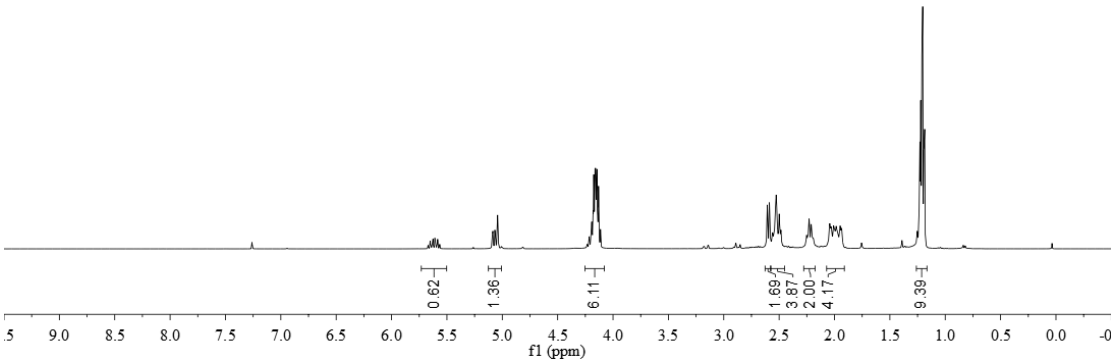


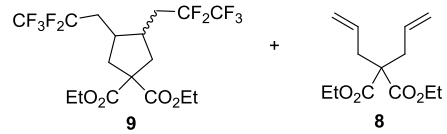




9 : **8** = 3.2 : 1

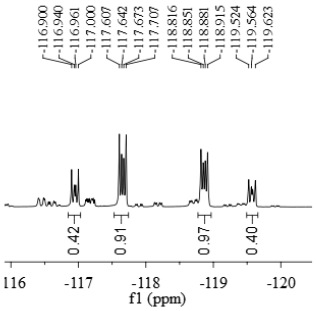
(**^{1}H NMR, $CDCl_3$, 400 MHz)**

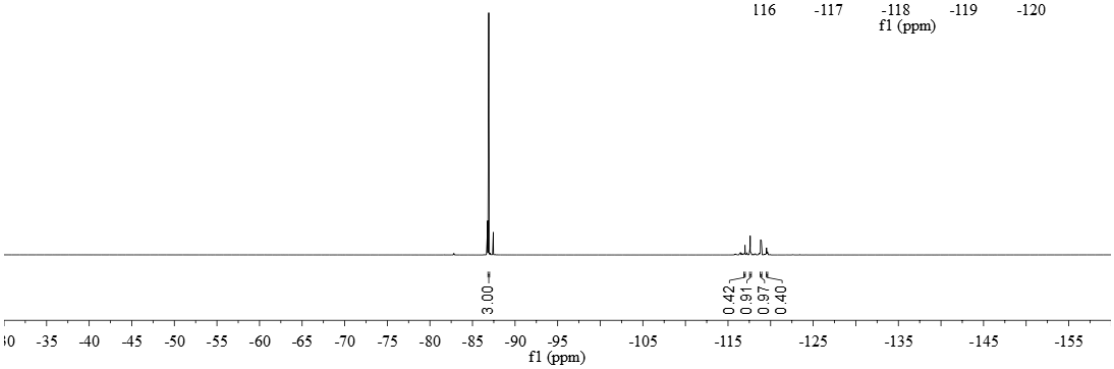


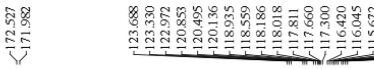


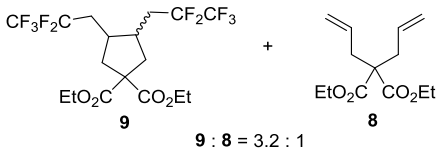
9 : **8** = 3.2 : 1

(**^{19}F NMR, $CDCl_3$, 376 MHz)**



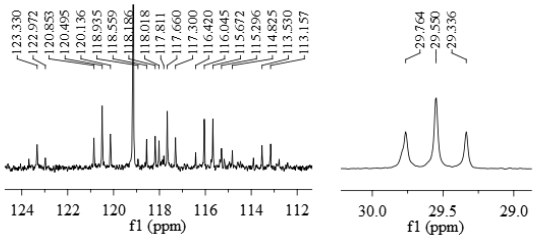


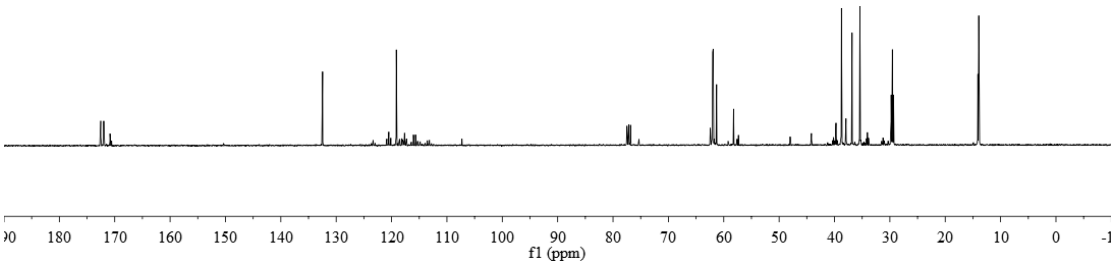


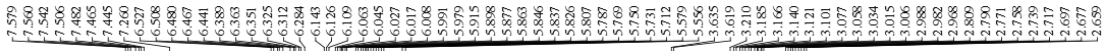


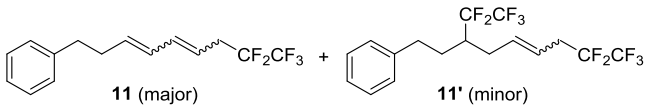
9 : **8** = 3.2 : 1

(**^{13}C NMR, $CDCl_3$, 101 MHz)**

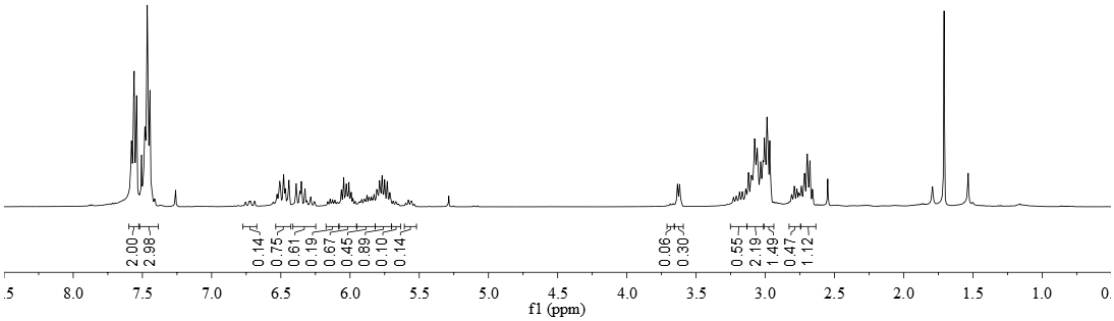


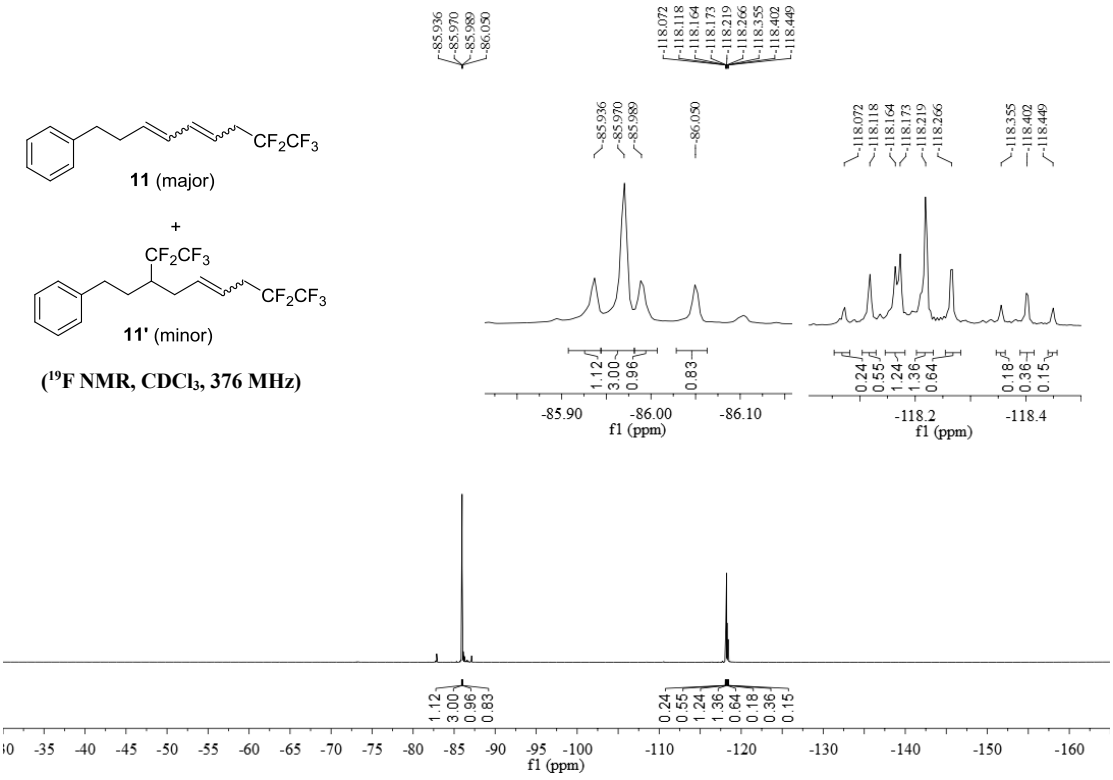




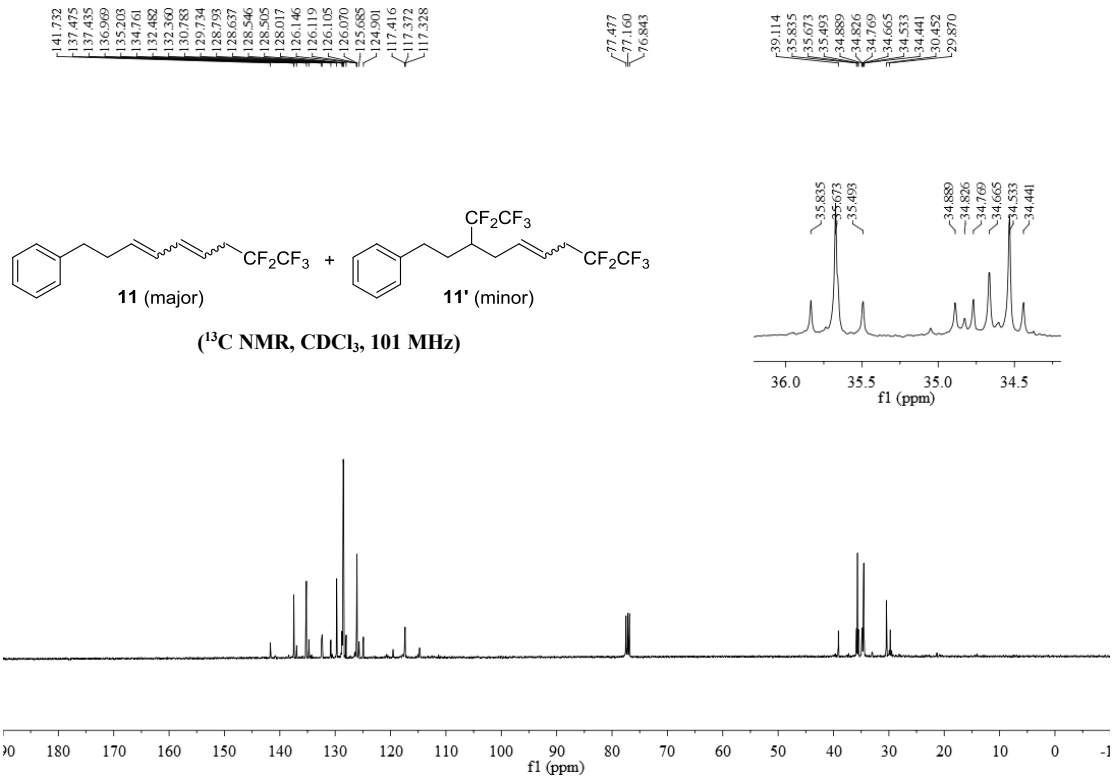


(**^{1}H NMR, $CDCl_3$, 400 MHz)**

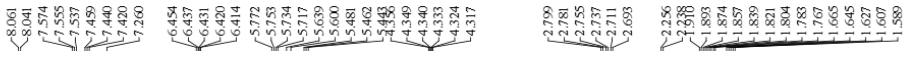


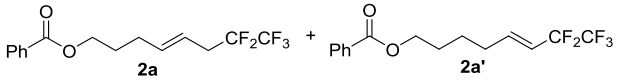


(^{19}F NMR, $CDCl_3$, 376 MHz)



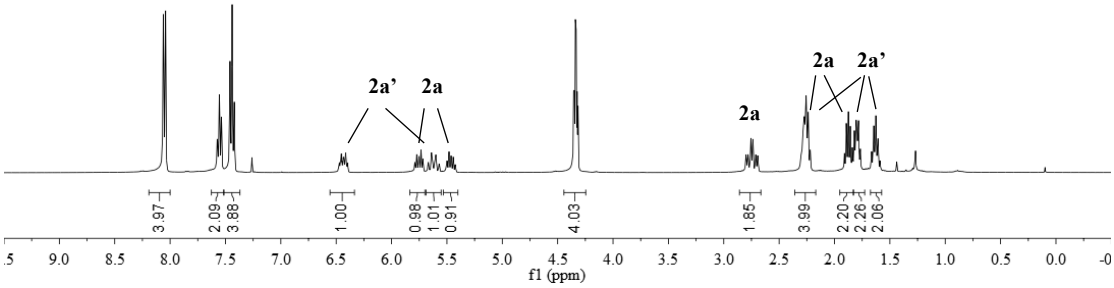
(^{13}C NMR, $CDCl_3$, 101 MHz)

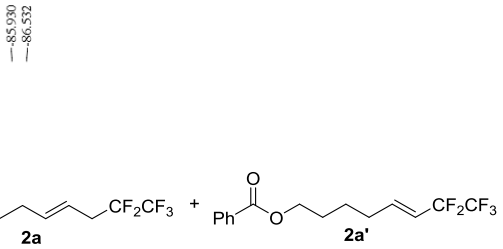




2a : **2a'** = 48 : 52

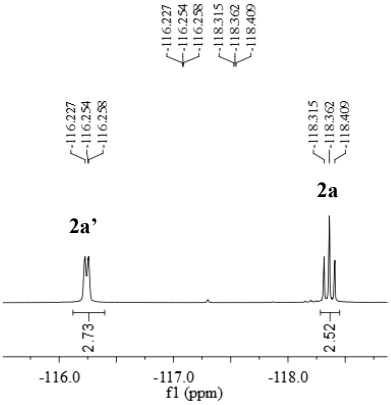
(^{1}H NMR, $CDCl_3$, 400 MHz)

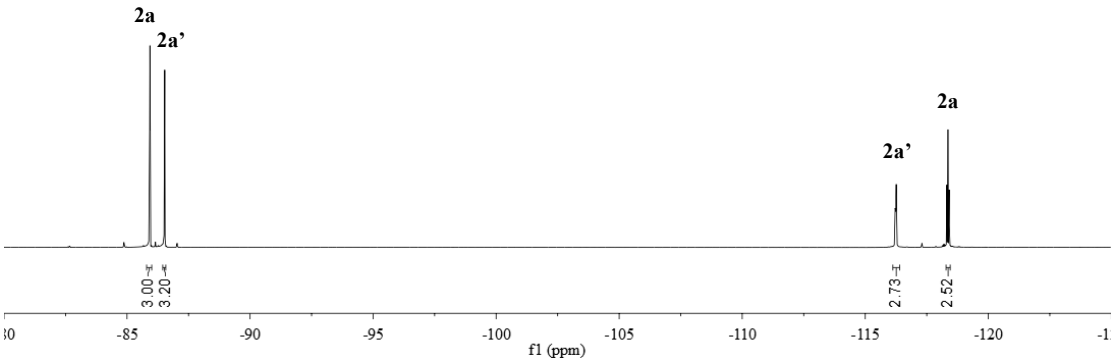


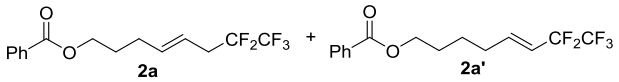


2a : **2a'** = 48 : 52

(^{19}F NMR, $CDCl_3$, 376 MHz)

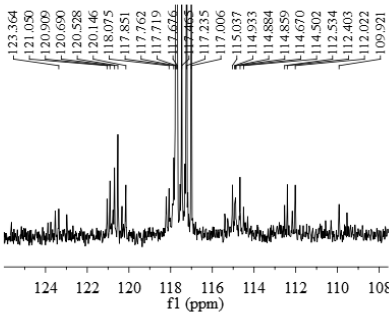


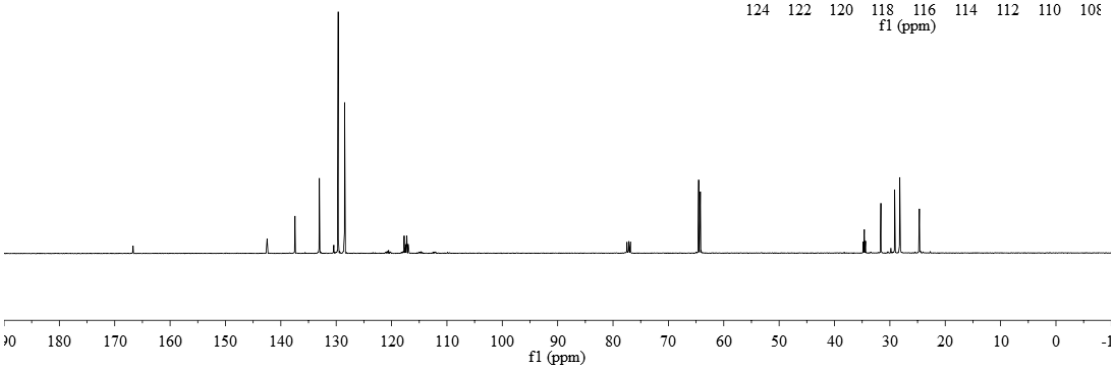


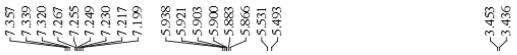


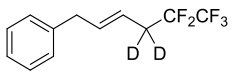
2a : **2a'** = 48 : 52

(^{13}C NMR, $CDCl_3$, 101 MHz)

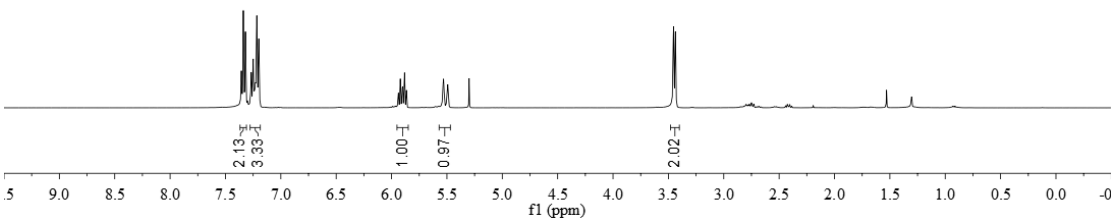


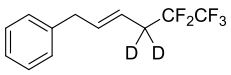




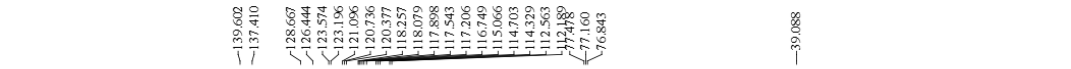


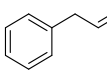
13 (^{1}H NMR, $CDCl_3$, 400 MHz)





13 (^{19}F NMR, $CDCl_3$, 376 MHz)





13 (^{13}C NMR, $CDCl_3$, 101 MHz)