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Synthesis of Fluoroolefin Derivatives by Nickel(II)–Catalyzed trifluorovinylation and 1,2,2-Trifluoroethylation of cinnamyl alcohols

Haifeng Wu,^{a,b} Min Zhou,^b Li Qiao,^{b,*} and Pengfei Zhang ^{a,b,*}

^a College of Pharmaceutical Science, Zhejiang University of Technology, Hangzhou, 310014, China ^b College of Material, Chemistry and Chemical Engineering, Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou, 311121, China

Email: 11837066@zju.edu.cn (Qiao, L.), pfzhang@hznu.edu.cn (Zhang, P.)

Supporting Information

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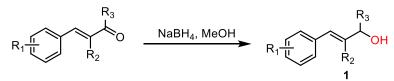
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1. General Information

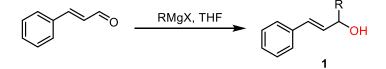
Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. All reactions were performed in a heating mantle in a sealed tube unless otherwise noted. Thin-layer chromatography was performed using silica gel 60 F254 and visualized using UV light. Column chromatography was performed with silica gel (mesh 300–400). ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded on a Bruker Avance 600 MHz spectrometer in CDCl₃ with Me₄Si as an internal standard. Data were reported as follows: chemical shift in ppm (δ), multiplicity (s =singlet, d = doublet, t = triplet, q = quartet, br = broad, and m = multiplet), coupling constant in hertz (Hz) and integration. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC (silica gel 60 F254) plates. Compounds for HRMS were analyzed by positive-mode electrospray ionization (ESI) using an Agilent 6530 QTOF mass spectrometer.

2. General Procedure

2.1 General procedure for the synthesis of allyl alcohol 1



Method A: The mixture of acrolein derivatives (10 mmol) in methanol (20 mL) was cooled down to 0 °C. Then, sodium borohydride (15 mmol, 568 mg) was added in five batches, and the resulting mixture was stirred for 2 h. After completion of the reaction as indicated by TLC, the reaction mixture was then quenched with saturated NaHCO₃ solution and extracted with EtOAc (3×25 mL). Organic layers were dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (200-300 mesh silica gel) to afford product **1**.



Method B: The mixture of acrolein derivatives (5 mmol) in anhydrous THF (10 mL) was cooled down to 0 °C. Then, the RMgX (6 mmol, 1.2 equiv.) was added, and the resulting mixture was

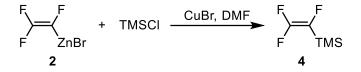
stirred for 3 h. After completion, the reaction mixture was then quenched with diluted HCl solution (5%, 10 mL) and extracted with EtOAc (3×10 mL). Organic layers were dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (200-300 mesh silica gel) to afford product 1.

2.2 General procedure for the synthesis of organozinc reagent TFVZ

$$F = \begin{cases} F \\ F \\ Br \end{cases} + Zn \xrightarrow{DMF} F \\ F \\ ZnBr \end{cases}$$

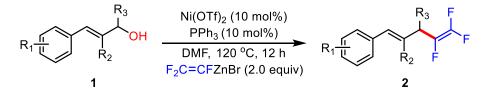
To a mixture of zinc dust (2.5 mol, 16.3 g) and anhydrous DMF (250 mL), was dropwise added 1-bromo-1,2,2-trifluoroethylene (21 mol, 34g) through a dry-ice condenser. Then, the resulting mixture was stirred at room temperature for 3 h. The mixture was used without further purification. The molar concentration of organozinc reagent in DMF is 0.84 mol/L.

2.3 General procedure for the synthesis of organosilicon reagent TFVTMS



To the DMF solution of organozinc reagent 2 (1 mol, 1.2 mL) was dropwise added dry chlorotrimethylsilane (2 mol, 217 mg), and the resulting mixture was cooled down to 0 °C. After the addition of CuBr (10 mol%, 14 mg) to the system, the mixture was stirred overnight. Then, an amount of ethylene glycol was then added to the reaction mixture, to ensure that all the chlorotrimethylsilane was removed from the reaction mixture, thus making isolation of the final product more efficient. The reaction mixture was then stirred overnight. Flash distillation of the reaction mixture followed by slow, careful fractional distillation afford the organosilicon reagent TFVTMS as a colorless liquid.

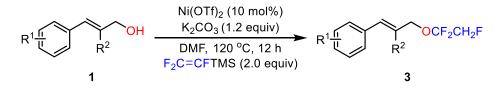
2.4 General procedure for the synthesis of 2



To a mixture of allyl alcohols (0.2 mmol), TFVZ (0.4 mmol, 25% in DMF, w/w), PPh₃ (10 mol%, 5.24 mg) was added Ni(CF₃SO₃)₂ (10 mol%, 7.14 mg). The resulting mixture was than sealed and

stirred for 12 h at 120 °C under air condition. After completion of the reaction as indicated by TLC, the reaction mixture was then cooled to room temperature and extracted with EtOAc (3×10 mL) and H₂O (5 mL). Organic layers were dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (200-300 mesh silica gel) with petroleum ether and ethyl acetate (v/v 20/1) as the eluent to give the pure product **2**.

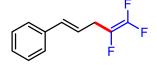
2.5 General procedure for the synthesis of 3



To a mixture of allyl alcohols (0.2 mmol), TFVTMS (0.4 mmol, 62 mg), K_2CO_3 (120 mol%, 33 mg) was added Ni(CF₃SO₃)₂ (10 mol%, 7.14 mg). The resulting mixture was than stirred for 12 h at 120 °C under air condition. After completion of the reaction, the reaction mixture was cooled to room temperature and extracted with ethyl acetate (3×10 mL) and H₂O (5 mL). The organic phase was dried over anhydrous Na₂SO₄. The crude residue was obtained after evaporation of the solvent in vacuum, and the residue was purified by flash chromatography with petroleum ether and ethyl acetate (v/v 20/1) as the eluent to give the pure product **3**.

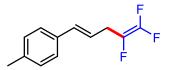
3. Characterization of Products

(E)-(4,5,5-trifluoropenta-1,4-dien-1-yl)benzene (2a)



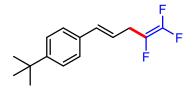
Obtained as a white liquid (38 mg, 97% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.36 (d, *J* = 7.5 Hz, 2H), 7.31 (dd, *J* = 10.3, 4.9 Hz, 2H), 7.25 – 7.21 (m, 1H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.14 (dt, *J* = 15.8, 6.6 Hz, 1H), 3.27 – 3.08 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 155.6-150.7 (m), 136.6, 133.5, 128.6, 128.5-128.1 (m), 127.7, 126.5, 121.9, 29.4 (dd, *J* = 20.2, 2.5 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -105.0 (dd, *J* = 84.8, 33.0 Hz), -123.9 (dd, *J* = 113.0, 88.0 Hz), -173.2 (dd, *J* = 113.0, 33.0 Hz); HRMS (ESI+): Calculated for C₁₁H₉F₃: [M+H]⁺ 199.0729, Found 199.0732.

(*E*)-1-methyl-4-(4,5,5-trifluoropenta-1,4-dien-1-yl)benzene (2b)



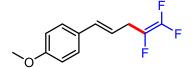
Obtained as a white liquid (41 mg, 96% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.25 (d, J = 7.9 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 6.50 (d, J = 15.8 Hz, 1H), 6.09 (dt, J = 15.6, 6.6 Hz, 1H), 3.20 – 3.11 (m, 2H), 2.33 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 153.2 (ddd, J = 286.7, 273.2, 46.6 Hz), 137.6, 133.86, 133.4, 129.3, 128.2 (ddd, J = 197.9, 147.4, 29.1 Hz), 126.2, 120.8, 29.4 (dd, J = 22.2, 2.2 Hz), 21.2. ¹⁹F NMR (471 MHz, CDCl₃) δ -105.2 (dd, J = 87.2, 32.6 Hz), -124.0 (dd, J = 114.4, 87.1 Hz), -173.2 (dd, J = 114.4, 32.6 Hz); HRMS (ESI+): Calculated for C₁₂H₁₁F₃: [M+H]⁺ 213.0886, Found 231.0893.

(*E*)-1-(tert-butyl)-4-(4,5,5-trifluoropenta-1,4-dien-1-yl)benzene (2c)



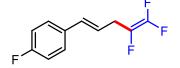
Obtained as a white liquid (47 mg, 93% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.34 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 6.52 (d, J = 15.8 Hz, 1H), 6.10 (dt, J = 15.8, 6.7 Hz, 1H), 3.24 – 3.08 (m, 2H), 1.31 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 150.9, 133.9, 133.3, 126. 0, 125.5, 121.1, 34.6, 31.3, 29.4 (dd, J = 22.2, 2.1 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -105.1 (dd, J = 87.0, 32.6 Hz), -124.0 (dd, J = 114.5, 86.9 Hz), -173.2 (dd, J = 114.5, 32.4 Hz); HRMS (ESI+): Calculated for C₁₅H₁₇F₃: [M+H]⁺ 255.1355, Found 255.1367.

(E)-1-methoxy-4-(4,5,5-trifluoropenta-1,4-dien-1-yl)benzene (2d)



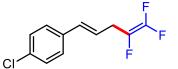
Obtained as a white liquid (44 mg, 96% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.24 – 7.19 (m, 2H), 6.81 – 6.74 (m, 2H), 6.39 (d, *J* = 15.8 Hz, 1H), 5.91 (dt, *J* = 15.8, 6.7 Hz, 1H), 3.71 (s, 3H), 3.11 – 3.03 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 159.3, 153.2 (ddd, *J* = 286.5, 273.1, 46.6 Hz), 132.9, 129.5, 127.5 (ddd, *J* = 235.2, 52.8, 15.2 Hz), 127.5, 119.6, 114.0, 55.3, 29.3 (dd, *J* = 22.2, 2.1 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -105.2 (dd, *J* = 87.2, 32.4 Hz), -124.1 (dd, *J* = 114.4, 87.3 Hz), -173.2 (dd, J = 114.4, 32.7 Hz); HRMS (ESI+): Calculated for C₁₂H₁₁F₃O: [M+H]⁺ 229.0835, Found 229.0825.

(E)-1-fluoro-4-(4,5,5-trifluoropenta-1,4-dien-1-yl)benzene (2e)



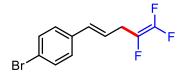
Obtained as a white liquid (39 mg, 90% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.32 (dd, J = 8.6, 5.4 Hz, 2H), 7.02 – 6.98 (m, 2H), 6.49 (d, J = 15.8 Hz, 1H), 6.06 (dt, J = 15.8, 6.6 Hz, 1H), 3.23 – 3.12 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 162.4 (d, J = 246.9 Hz), 153.2 (ddd, J = 286.7, 273.2, 46.4 Hz), 132.8 (d, J = 3.3 Hz), 132.3, 127.8 (d, J = 8.0 Hz), 127.2 (ddd, J = 235.3, 53.0, 15.6 Hz), 121.7, 115.5 (d, J = 21.6 Hz), 29.3 (dd, J = 22.3, 2.1 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -104.9 (dd, J = 86.7, 32.8 Hz), -114.3 (s), -123.8 (dd, J = 114.6, 86.6 Hz), -173.3 (dd, J = 114.6, 32.7 Hz); HRMS (ESI+): Calculated for C₁₁H₈F₄: [M+H]⁺ 217.0635, Found 271.0641.

(E)-1-chloro-4-(4,5,5-trifluoropenta-1,4-dien-1-yl)benzene (2f)



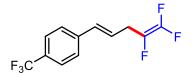
Obtained as a white liquid (46 mg, 99% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.29 – 7.25 (m, 4H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.12 (dt, *J* = 15.8, 6.6 Hz, 1H), 3.22 – 3.13 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 156.5 – 149.4 (m), 135.1, 133.4, 132.3, 128.8, 127.5, 127.1 (ddd, *J* = 235.5, 53.0, 15.7 Hz), 122.7, 29.3 (dd, *J* = 22.3, 2.1 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -104.7 (dd, *J* = 86.4, 32.9 Hz), -123.7 (dd, *J* = 114.7, 86.3 Hz), -173.3 (dd, *J* = 114.6, 32.9 Hz); HRMS (ESI+): Calculated for C₁₁H₈ClF₃: [M+H]⁺ 233.0339, Found 233.0329.

(E)-1-bromo-4-(4,5,5-trifluoropenta-1,4-dien-1-yl)benzene (2g)



Obtained as a white liquid (52 mg, 93% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.45 – 7.40 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.47 (d, *J* = 15.9 Hz, 1H), 6.14 (dt, *J* = 15.8, 6.6 Hz, 1H), 3.21 – 3.12 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 153.2 (ddd, *J* = 286.8, 273.5, 46.2 Hz), 135.6, 132.4, 131.7, 127.8, 127.1 (ddd, J = 68.6, 40.7, 15.7 Hz), 122.8, 121.5, 29.3 (dd, J = 22.3, 2.1 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ -104.7 (dd, J = 86.4, 32.9 Hz), -123.6 (dd, J = 114.7, 86.3 Hz), -173.3 (dd, J = 114.6, 32.9 Hz); HRMS (ESI+): Calculated for C₁₁H₈BrF₃: [M+H]⁺ 276.9834, Found 276.9830.

(E)-1-(trifluoromethyl)-4-(4,5,5-trifluoropenta-1,4-dien-1-yl)benzene (2h)



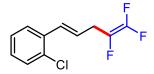
Obtained as a white liquid (45 mg, 85% yield); M.p. 189-190 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.60 (s, 1H), 7.51 (dd, J = 14.8, 7.7 Hz, 2H), 7.44 – 7.41 (m, 1H), 6.57 (d, J = 15.9 Hz, 1H), 6.23 (dt, J = 15.9, 6.6 Hz, 1H), 3.21 (dddd, J = 21.7, 8.1, 4.0, 2.6 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 153.2 (ddd, J = 287.3, 273.5, 46.2 Hz), 137.4, 132.2, 131.1 (d, J = 32.3 Hz), 129.4, 129.1, 126.9 (ddd, J = 235.5, 53.0, 15.8 Hz), 125.2, 124.6 – 122.0 (m), 29.3 (dd, J = 22.3, 2.1 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -62.8 (s), -104.5 (dd, J = 86.0, 33.0 Hz), -123.5 (dd, J = 114.8, 85.9 Hz), -173.3 (dd, J = 114.7, 33.0 Hz); HRMS (ESI+): Calculated for C₁₂H₈F₆: [M+H]⁺ 267.0603, Found 267.0596.

(E)-1-methoxy-2-(4,5,5-trifluoropenta-1,4-dien-1-yl)benzene (2j)



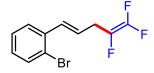
Obtained as a white liquid (43 mg, 95% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.40 (dd, J = 7.6, 1.4 Hz, 1H), 7.25 – 7.17 (m, 1H), 6.93 – 6.90 (m, 1H), 6.88-6.82 (m, 2H), 6.16 (dt, J = 15.9, 6.7 Hz, 1H), 3.84 (s, 3H), 3.25 – 3.11 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 156.6, 153.2 (ddd, J = 286.2, 273.1, 46.6 Hz), 128.8, 128.5, 127.4 (ddd, J = 52.8, 40.2, 26.3 Hz), 126.9, 126.9, 125.7, 122.5, 120.7, 110.9, 55.4, 29.8 (dd, J = 22.2, 2.1 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -105.3 (dd, J = 87.3, 32.5 Hz), -124.0 (dd, J = 114.5, 87.2 Hz), -173.1 (dd, J = 114.4, 32.5 Hz); HRMS (ESI+): Calculated for C₁₂H₁₁F₃O: [M+H]⁺ 229.0835, Found 229.0833.

(E)-1-chloro-2-(4,5,5-trifluoropenta-1,4-dien-1-yl)benzene (2k)



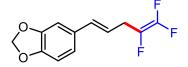
Obtained as a white liquid (43 mg, 92% yield); M.p. 149-150 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.49 (dd, J = 7.6, 1.7 Hz, 1H), 7.34 (dd, J = 7.7, 1.5 Hz, 1H), 7.24 – 7.14 (m, 2H), 6.93 (d, J = 15.8 Hz, 1H), 6.13 (dt, J = 15.8, 6.7 Hz, 1H), 3.27 – 3.17 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 153.2 (ddd, J = 287.1, 273.6, 46.5 Hz), 134.8, 132.9, 129.9, 129.7, 128.8, 127.1 (ddd, J = 235.6, 52.9, 15.8 Hz), 126.9 (d, J = 0.8 Hz), 124.8, 29.6 (dd, J = 22.3, 2.1 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -104.7 (dd, J = 86.3, 32.9 Hz), -123.6 (dd, J = 114.6, 86.2 Hz), -173.3 (dd, J = 114.7, 32.9 Hz); HRMS (ESI+): Calculated for C₁₁H₈ClF₃: [M+H]⁺ 233.0339, Found 233.0345.

(E)-1-bromo-2-(4,5,5-trifluoropenta-1,4-dien-1-yl)benzene (2l)



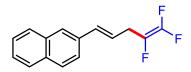
Obtained as a white liquid (52 mg, 93% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.45 – 7.40 (m, 2H), 7.25 – 7.19 (m, 2H), 6.47 (d, *J* = 15.9 Hz, 1H), 6.14 (dt, *J* = 15.8, 6.6 Hz, 1H), 3.21 – 3.12 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 153.2 (ddd, *J* = 287.0, 273.3, 46.3 Hz), 137.7, 135.6, 132.3, 131.7, 127.8, 127.1 (ddd, *J* = 68.6, 40.5, 15.7 Hz), 122.8, 121.5, 29.3 (dd, *J* = 22.3, 2.1 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -104.7 (dd, *J* = 86.3, 32.9 Hz), -123.6 (dd, *J* = 114.7, 86.2 Hz), -173.3 (dd, *J* = 114.6, 32.9 Hz); HRMS (ESI+): Calculated for C₁₁H₈BrF₃: [M+H]⁺ 276.9834, Found 276.9837.

(E)-5-(4,5,5-trifluoropenta-1,4-dien-1-yl)benzo[d][1,3]dioxole (2m)



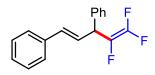
Obtained as a white liquid (40 mg, 83% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.26 (s, 2H), 6.90 (d, J = 1.5 Hz, 1H), 6.79 (dd, J = 8.0, 1.5 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 6.44 (d, J = 15.7 Hz, 1H), 5.96 (s, 1H), 3.15 (ddt, J = 21.9, 6.6, 4.0 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 148.1, 147.3, 133.1, 131.1, 120.9, 120.1, 108.3, 105.6, 101.1, 29.3 (dd, J = 22.2, 2.0 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -105.0 (dd, J = 87.1, 32.6 Hz), -123.9 (dd, J = 114.6, 86.8 Hz), -173.3 (dd, J = 114.4, 32.7 Hz); HRMS (ESI+): Calculated for C₁₂H₉F₃O₂: [M+H]⁺ 243.0627, Found 243.0622.

(E)-2-(4,5,5-trifluoropenta-1,4-dien-1-yl)naphthalene (2n)



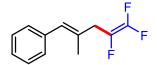
Obtained as a white liquid (47 mg, 95% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.81 – 7.76 (m, 3H), 7.71 (s, 1H), 7.57 (dd, J = 8.6, 1.7 Hz, 1H), 7.48 – 7.41 (m, 2H), 6.69 (d, J = 15.8 Hz, 1H), 6.27 (dt, J = 15.8, 6.6 Hz, 1H), 3.27 – 3.19 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 153.2 (ddd, J = 286.7, 273.2, 46.5 Hz), 134.1, 133.6, 133.6, 128.3, 128.0, 127.7, 128.5 – 126.0 (m), 125.96, 123.4, 122.3, 29.5 (dd, J = 22.2, 2.1 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -104.8 (dd, J = 86.6, 32.7 Hz), -123.7 (dd, J = 114.6, 86.6 Hz), -173.1 (dd, J = 114.5, 32.7 Hz); HRMS (ESI+): Calculated for C₁₅H₁₁F₃: [M+H]⁺ 249.0886, Found 249.0878.

(E)-(4,5,5-trifluoropenta-1,4-diene-1,3-diyl)dibenzene (20)

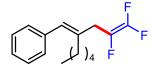


Obtained as a white liquid (51 mg, 93% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.42 – 7.36 (m, 4H), 7.35 – 7.30 (m, 5H), 7.25 (d, *J* = 6.2 Hz, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 6.50 – 6.38 (m, 1H), 4.63 – 4.46 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 153.3 (ddd, *J* = 288.7, 274.8, 46.4 Hz), 138.2, 136.5, 133.1, 123.0 (ddd, *J* = 48.2, 30.3, 11.8 Hz), 128.9, 128.7, 128.0, 127.95, 127.6, 126.5, 125.7, 45.3 (dd, *J* = 20.4, 1.9 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -104.6 (dd, *J* = 84.0, 32.5 Hz), -120.0 (dd, *J* = 114.3, 83.9 Hz), -178.4 (dd, *J* = 114.4, 32.6 Hz); HRMS (ESI+): Calculated for C₁₇H₁₃F₃: [M+H]⁺ 275.1042, Found 275.1066.

(E)-(4,5,5-trifluoro-2-methylpenta-1,4-dien-1-yl)benzene (2p)

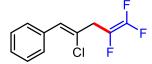


Obtained as a white liquid (28 mg, 65% yield); M.p. 172-173 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.36 – 7.30 (m, 2H), 7.25 – 7.21 (m, 3H), 6.41 (s, 1H), 3.16 – 3.08 (m, 2H), 1.89 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 137.5, 131.6, 128.8, 128.3, 128.1, 126.6, 36.7 (dd, J = 22.4, 2.3 Hz), 17.3; ¹⁹F NMR (471 MHz, CDCl₃) δ -104.3, -104.4, -104.5 (dd, J = 85.7, 32.5 Hz), -104.5, -104.6, -123.6, -123.8, -123.8 (dd, *J* = 114.5, 85.6 Hz), -123.8, -124.0, -171.9, -171.9, -172.0 (dd, *J* = 114.5, 32.6 Hz), -172.1, -172.17; HRMS (ESI+): Calculated for C₁₂H₁₁F₃: [M+H]⁺ 213.0886, Found 213.0895. (*E*)-(2-(2,3,3-trifluoroallyl)hept-1-en-1-yl)benzene (2q)



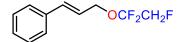
Obtained as a white liquid (40 mg, 75% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.31 (m, 2H), 7.26 – 7.17 (m, 3H), 6.40 (s, 1H), 3.12 (dd, *J* = 22.8, 2.6 Hz, 2H), 2.27 – 2.20 (m, 2H), 1.48 (td, *J* = 14.9, 7.4 Hz, 2H), 1.32 – 1.23 (m, 4H), 0.87 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 153.8 (ddd, *J* = 286.9, 272.9, 46.7 Hz), 137.5, 136.3 (d, *J* = 2.5 Hz), 128.6, 128.3, 128.2, 126.6, 33.8 (dd, *J* = 22.4, 2.3 Hz), 31.8, 30.4, 27.7, 22.4, 14.0; ¹⁹F NMR (471 MHz, CDCl₃) δ -104.5 (dd, *J* = 85.9, 32.5 Hz), -123.7 (dd, *J* = 114.4, 85.8 Hz), -171.7 (dd, *J* = 114.4, 32.4 Hz); HRMS (ESI+): Calculated for C₁₆H₁₉F₃: [M+H]⁺ 269.1512, Found 269.1505.

(Z)-(2-chloro-4,5,5-trifluoropenta-1,4-dien-1-yl)benzene (2r)



Obtained as a white liquid (36 mg, 78% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.61 (d, J = 7.4 Hz, 2H), 7.38 – 7.35 (m, 2H), 7.34 – 7.27 (m, 1H), 6.63 (s, 1H), 3.50 – 3.38 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 134.2, 129.1, 128.3, 128.2, 127.7, 38.0 (dd, J = 22.6, 2.4 Hz), 29.7; ¹⁹F NMR (471 MHz, CDCl₃) δ -102.3 (dd, J = 80.4, 33.3 Hz), -121.8 (dd, J = 114.7, 80.3 Hz), -173.9 (dd, J = 114.8, 33.4 Hz); HRMS (ESI+): Calculated for C₁₁H₈ClF₃: [M+H]⁺ 233.0339, Found 233.0348.

(E)-(3-(1,1,2-trifluoroethoxy)prop-1-en-1-yl)benzene (3a)



Obtained as a yellow liquid (39 mg, 90% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.33 (d, *J* = 7.4 Hz, 2H), 7.27 – 7.25 (m, 2H), 7.23 – 7.14 (m, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.20 (dt, *J* = 15.8, 6.4 Hz, 1H), 4.54 (dd, *J* = 6.4, 1.1 Hz, 2H), 4.48 (t, *J* = 8.5 Hz, 1H), 4.39 (t, *J* = 8.5 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 136.1, 134.3, 128.7, 128.2, 126.7, 122.9, 80.1 (dt, *J* = 182.3, 38.3 Hz), 64.5 (t, *J* =

6.6 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -78.9 - -87.4 (m), -225.4 - -241.7 (m); HRMS (ESI+): Calculated for C₁₁H₁₁F₃O: [M+H]⁺ 217.0835, Found 217.0850.

(E)-1-methyl-4-(3-(1,1,2-trifluoroethoxy)prop-1-en-1-yl)benzene (3b)

Obtained as a yellow liquid (37 mg, 80% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.29 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 6.63 (d, J = 15.9 Hz, 1H), 6.21 (dt, J = 15.8, 6.5 Hz, 1H), 4.59 (dd, J = 6.5, 1.1 Hz, 2H), 4.54 (t, J = 8.5 Hz, 1H), 4.45 (t, J = 8.5 Hz, 1H), 2.34 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 138.2, 134.4, 133.3, 129.3, 126.6, 121.8, 64.6, 21.2; ¹⁹F NMR (471 MHz, CDCl₃) δ -81.1 – -86.7 (m), -235.4 (tt, J = 46.2, 16.1 Hz); HRMS (ESI+): Calculated for C₁₂H₁₃F₃O: 231.0991, Found 231.0978.

(E)-1-methoxy-4-(3-(1,1,2-trifluoroethoxy)prop-1-en-1-yl)benzene (3c)

Obtained as a yellow liquid (47 mg, 95% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.34 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.61 (d, *J* = 15.8 Hz, 1H), 6.13 (dt, *J* = 15.7, 6.6 Hz, 1H), 4.58 (d, *J* = 6.6 Hz, 2H), 4.54 (t, *J* = 8.5 Hz, 1H), 4.45 (t, *J* = 8.5 Hz, 1H), 3.81 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 159.69, 134.16, 128.79 , 127.95, 120.58, 114.05, 80.09 (dt, *J* = 68.5, 38.3 Hz), 64.73, 55.31; ¹⁹F NMR (471 MHz, CDCl₃) δ -80.39 – -87.01 (m), -235.42 (s); HRMS (ESI+): Calculated for C₁₂H₁₃F₃O₂: [M+H]⁺ 247.0940, Found 247.0949.

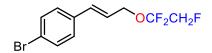
(E)-1-fluoro-4-(3-(1,1,2-trifluoroethoxy)prop-1-en-1-yl)benzene (3d)

Obtained as a yellow liquid (44 mg, 95% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.43 – 7.32 (m, 2H), 7.07 – 6.98 (m, 2H),, 6.63 (d, J = 15.9 Hz, 1H), 6.18 (dt, J = 15.8, 6.4 Hz, 1H), 4.59 (dd, J = 6.4, 1.3 Hz, 2H), 4.55 (t, J = 8.5 Hz, 1H), 4.46 (t, J = 8.5 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 162.7 (d, J = 247.7 Hz), 133.1, 132.2, 128.3 (d, J = 8.1 Hz), 122.7 (d, J = 2.2 Hz), 120.9 (d, J = 21.4 Hz), 115.6 (d, J = 21.7 Hz), 80.0 (dt, J = 182.2, 38.4 Hz), 64.3 (t, J = 6.6 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -83.9 (dt, J = 17.1, 8.7 Hz), -113.5 (ddd, J = 14.7, 9.1, 5.8 Hz), -224.6 - -247.8 (m); HRMS (ESI+): Calculated for C₁₁H₁₀F₄O: [M+H]⁺ 235.0741, Found 235.0755.

(*E*)-1-chloro-4-(3-(1,1,2-trifluoroethoxy)prop-1-en-1-yl)benzene (3e)

Obtained as a yellow liquid (36 mg, 72% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.38 – 7.28 (m, 4H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.24 (dt, *J* = 15.8, 6.3 Hz, 1H), 4.63 – 4.59 (m, 2H), 4.55 (t, *J* = 8.4 Hz, 1H), 4.46 (t, *J* = 8.4 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 134.6, 133.9, 132.9, 128.8, 127.9, 123.6, 64.2; ¹⁹F NMR (471 MHz, CDCl₃) δ -80.4 – -85.9 (m), -235.5 (td, *J* = 46.5, 23.4 Hz); HRMS (ESI+): Calculated for C₁₁H₁₀ClF₃O: [M+H]⁺ 251.0445, Found 251.0438.

(E)-1-bromo-4-(3-(1,1,2-trifluoroethoxy)prop-1-en-1-yl)benzene (3f)

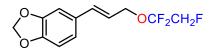


Obtained as a yellow liquid (52 mg, 90% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.43 – 7.36 (m, 2H), 7.27 – 7.11 (m, 2H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.19 (dt, *J* = 15.9, 6.3 Hz, 1H), 4.52 (dd, *J* = 6.3, 1.2 Hz, 2H), 4.48 (t, *J* = 8.4 Hz, 1H), 4.39 (t, *J* = 8.4 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 135.0, 132.9, 131.8, 128.2, 123.8, 122.1, 80.0 (d, *J* = 182.3 Hz), 64.2 (d, *J* = 6.7 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -83.9 (dt, *J* = 16.7, 8.5 Hz), -235.5 (tt, *J* = 46.2, 16.1 Hz); HRMS (ESI+): Calculated for C₁₁H₁₀BrF₃O: [M+H]⁺ 294.9940, Found 294.9952.

(E)-1-methoxy-2-(3-(1,1,2-trifluoroethoxy)prop-1-en-1-yl)benzene (3g)

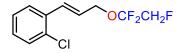
Obtained as a yellow liquid (47 mg, 95% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.43 (dd, J = 7.6, 1.6 Hz, 1H), 7.28 – 7.21 (m, 1H), 6.98 (d, J = 16.0 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 8.2 Hz, 1H), 6.29 (dt, J = 16.0, 6.5 Hz, 1H), 4.61 (dd, J = 6.5, 1.3 Hz, 2H), 4.54 (t, J = 8.6 Hz, 1H), 4.45 (t, J = 8.6 Hz, 1H), 3.85 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 157.0, 129.5, 129.3, 127.3, 125.0, 123.5, 123.3 – 118.5 (m), 120.7, 110.9, 80.1 (dt, J = 182.1, 38.2 Hz), 65.0 (t, J = 6.6 Hz), 55.45; ¹⁹F NMR (471 MHz, CDCl₃) δ -77.7 – -87.4 (m), -227.6 – -243.5 (m); HRMS (ESI+): Calculated for C₁₂H₁₃F₃O₂: [M+H]⁺ 247.0940, Found247.0929.

(E)-5-(3-(1,1,2-trifluoroethoxy)prop-1-en-1-yl)benzo[d][1,3]dioxole (3h)



Obtained as a yellow liquid (34 mg, 65% yield). ¹H NMR (500 MHz, CDCl₃) δ 6.93 (d, *J* = 1.5 Hz, 1H), 6.83 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.10 (dt, *J* = 15.8, 6.5 Hz, 1H), 5.96 (s, 2H), 4.58 (dd, *J* = 6.5, 1.1 Hz, 2H), 4.54 (t, *J* = 8.5 Hz, 1H), 4.45 (t, *J* = 8.5 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 148.1, 147.8, 134.2, 130.5, 121.6, 121.1, 108.3, 105.9, 101.2, 64.5; ¹⁹F NMR (471 MHz, CDCl₃) δ -80.7 – -88.1 (m), -235.43; HRMS (ESI+): Calculated for C₁₂H₁₁F₃O₃: [M+H]⁺ 261.0733, Found 261.0750.

(E)-1-chloro-2-(3-(1,1,2-trifluoroethoxy)prop-1-en-1-yl)benzene (3i)



Obtained as a yellow liquid (44 mg, 88% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.61 – 7.49 (m, 1H), 7.36 (dd, *J* = 4.8, 2.8 Hz, 1H), 7.26 – 7.18 (m, 2H), 7.06 (d, *J* = 15.8 Hz, 1H), 6.35 – 6.10 (m, 1H), 4.71 – 4.62 (m, 2H), 4.56 (td, *J* = 8.5, 3.3 Hz, 1H), 4.50 – 4.44 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 134.2, 133.3, 130.2, 129.8, 129.2, 127.1, 126.9, 125.8, 121.0 (td, *J* = 264.4, 21.4 Hz), 80.0 (dt, *J* = 182.3, 38.2 Hz), 64.3 (t, *J* = 6.6 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -83.9 (dt, *J* = 16.5, 8.4 Hz), -235.50; HRMS (ESI+): Calculated for C₁₁H₁₀ClF₃O: [M+H]⁺ 251.0445, Found 251.0459.

(E)-1-bromo-2-(3-(1,1,2-trifluoroethoxy)prop-1-en-1-yl)benzene (3j)

Obtained as a yellow liquid (50 mg, 85% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.54 – 7.39 (m, 2H), 7.31 – 7.20 (m, 2H), 6.60 (d, *J* = 15.8 Hz, 1H), 6.26 (dt, *J* = 15.7, 6.2 Hz, 1H), 4.59 (d, *J* = 6.2 Hz, 2H), 4.55 (td, *J* = 8.4, 1.1 Hz, 1H), 4.48 – 4.40 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 135.00, 132.90, 131.79, 128.17, 123.76, 122.07, 80.02(dt, *J* = 182.4, 38.4 Hz), 64.19 (t, *J* = 6.6 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -83.89 (dt, *J* = 16.4, 8.4 Hz), -235.45 (ddd, *J* = 46.2, 31.2, 16.1 Hz); HRMS (ESI+): Calculated for C₁₁H₁₀BrF₃O: [M+H]⁺ 294.9940 Found 294.9949.

(E)-(2-methyl-3-(1,1,2-trifluoroethoxy)prop-1-en-1-yl)benzene (3k)

OCF₂CH₂F

Obtained as a yellow liquid (42 mg, 92% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.35 – 7.32 (m, 2H), 7.28 (d, *J* = 7.3 Hz, 2H), 7.25 – 7.22 (m, 1H), 6.55 (s, 1H), 4.55 (t, *J* = 8.5 Hz, 1H), 4.52 – 4.41 (m, 3H), 1.91 (d, *J* = 0.9 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 136.9, 132.3, 128.95, 128.9, 128.2, 126.9, 121.0 (td, *J* = 264.0, 21.3 Hz), 80.1 (dt, *J* = 182.1, 38.4 Hz), 69.7 (t, *J* = 6.2 Hz), 15.3; ¹⁹F NMR (471 MHz, CDCl₃) δ -83.9 (dt, *J* = 16.7, 8.4 Hz), -235.4 (tt, *J* = 46.1, 16.2 Hz); HRMS (ESI+): Calculated for C₁₂H₁₃F₃O: [M+H]⁺ 231.0991, Found 231.0977.

(*E*)-(2-((1,1,2-trifluoroethoxy)methyl)hept-1-en-1-yl)benzene (3l)

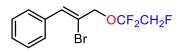
Obtained as a yellow liquid (52 mg, 90% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.35 – 7.30 (m, 2H), 7.26 – 7.22 (m, 3H), 6.56 (s, 1H), 4.56 (t, *J* = 8.5 Hz, 1H), 4.51 (s, 2H), 4.46 (t, *J* = 8.5 Hz, 1H), 2.31 – 2.26 (m, 2H), 1.58 – 1.40 (m, 2H), 1.34 – 1.21 (m, 4H), 0.87 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 136.9, 136.9, 129.1, 128.7, 128.2, 126.9, 121.0 (td, *J* = 264.1, 21.3 Hz), 80.1 (dt, *J* = 182.2, 38.4 Hz), 67.7 (t, *J* = 6.3 Hz), 31.9, 28.5, 27.7, 22.4, 14.0; ¹⁹F NMR (471 MHz, CDCl₃) δ -74.8 – -93.7 (m), -223.5 – -252.8 (m); HRMS (ESI+): Calculated for C₁₆H₂₁F₃O: [M+H]⁺ 287.1617, Found 287.1610.

(*E*)-(2-((1,1,2-trifluoroethoxy)methyl)oct-1-en-1-yl)benzene (3m)

OCF₂CH₂F

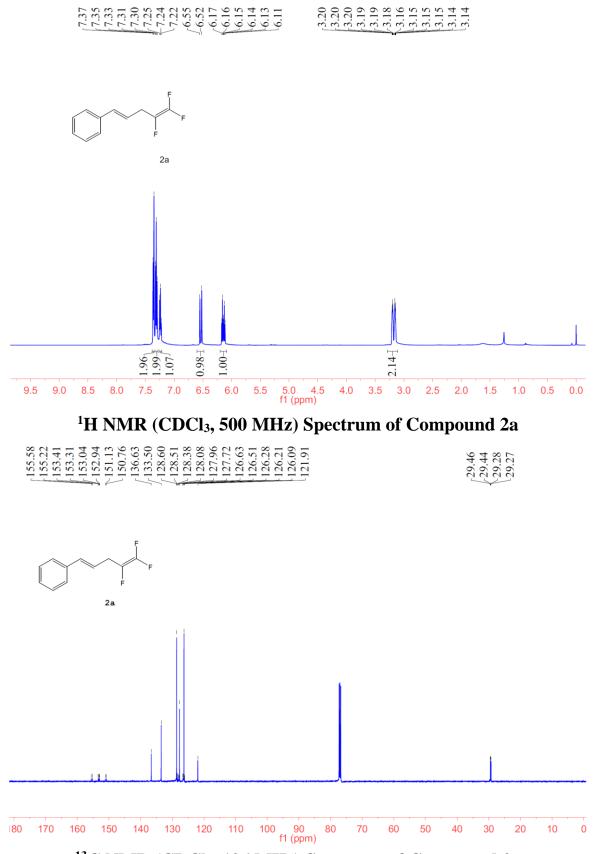
Obtained as a yellow liquid (48 mg, 80% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.36-7.31 (m, 2H), 7.26 – 7.22 (m, 3H), 6.56 (s, 1H), 4.56 (t, *J* = 8.5 Hz, 1H), 4.51 (d, *J* = 0.9 Hz, 2H), 4.47 (t, *J* = 8.5 Hz, 1H), 2.36 – 2.22 (m, 2H), 1.49 (dt, *J* = 11.2, 7.5 Hz, 2H), 1.36 – 1.21 (m, 6H), 0.87 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 136.9, 136.9, 129.1, 128.7, 128.2, 126.9, 80.1 (dt, *J* = 182.2, 38.3 Hz), 67.6 (t, *J* = 6.2 Hz), 31.5, 29.4, 28.5, 27.9, 22.6, 14.0; ¹⁹F NMR (471 MHz, CDCl₃) δ -81.5 – -85.6 (m), -228.7 – -237.6 (m); HRMS (ESI+): Calculated for C₁₇H₂₃F₃O: [M+H]⁺ 301.1774, Found 301.1774.

(Z)-(2-bromo-3-(1,1,2-trifluoroethoxy)prop-1-en-1-yl)benzene (3n)

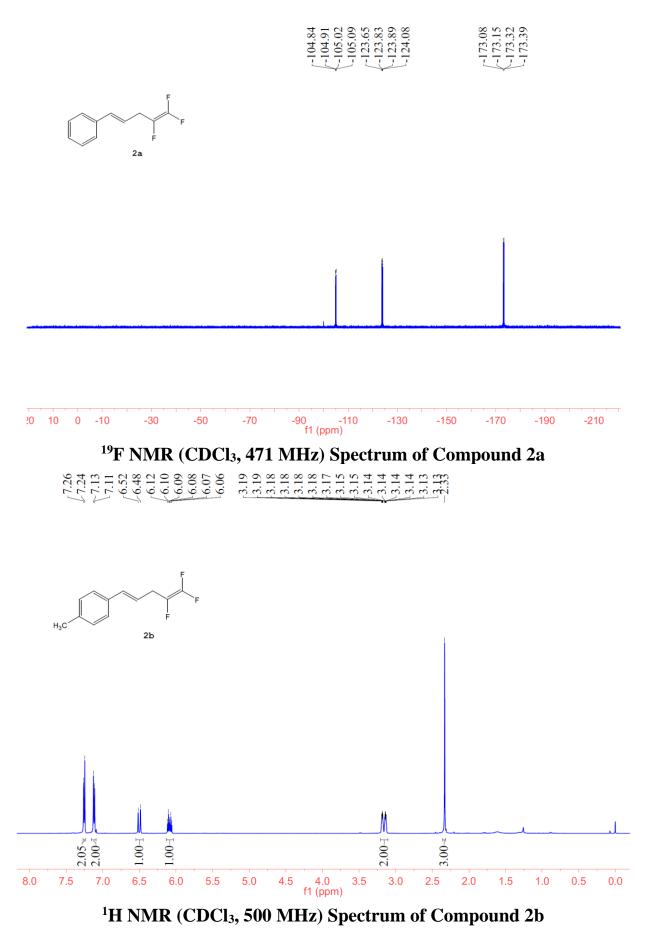


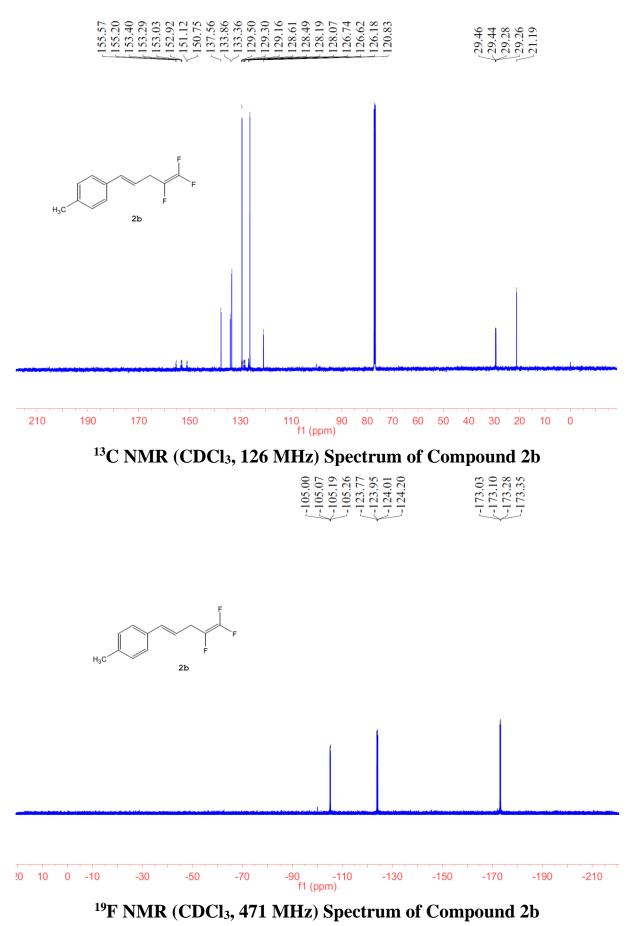
Obtained as a yellow liquid (35 mg, 60% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.46 (dd, J = 7.8, 1.6 Hz, 2H), 7.37 – 7.29 (m, 3H), 4.81 (s, 2H), 4.58 (t, J = 8.7 Hz, 1H), 4.48 (t, J = 8.7 Hz, 1H), 3.74 – 3.70 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 131.9, 128.9, 128.4, 120.0, 100.0, 87.2, 82.2, 79.8 (d, J = 182.7 Hz), 52.6 (t, J = 8.2 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -77.7 – -89.3 (m), -235.8; HRMS (ESI+): Calculated for C₁₁H₁₀BrF₃O: [M+H]⁺ 294.9940, Found 294.9950.

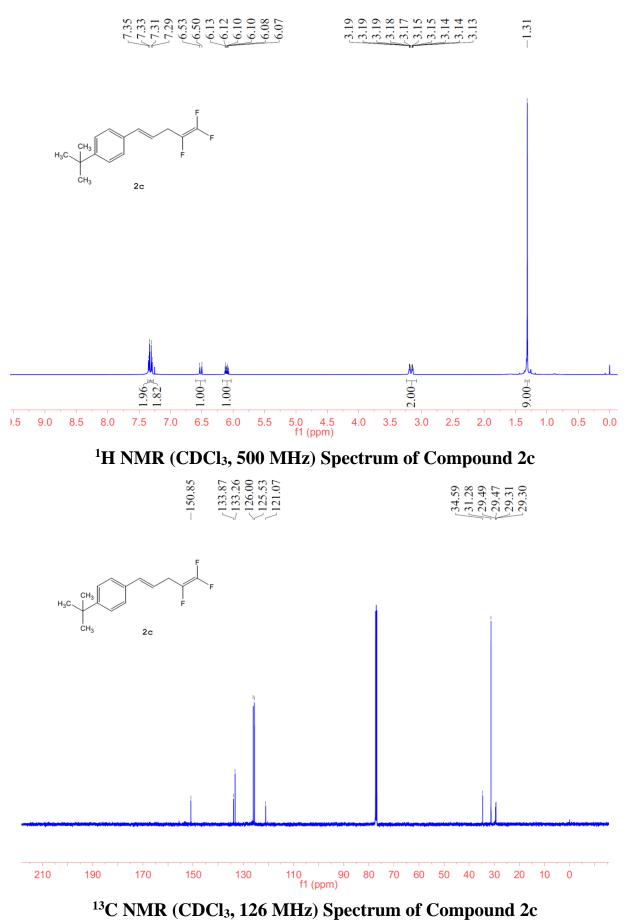
4. Copies of NMR Spectra

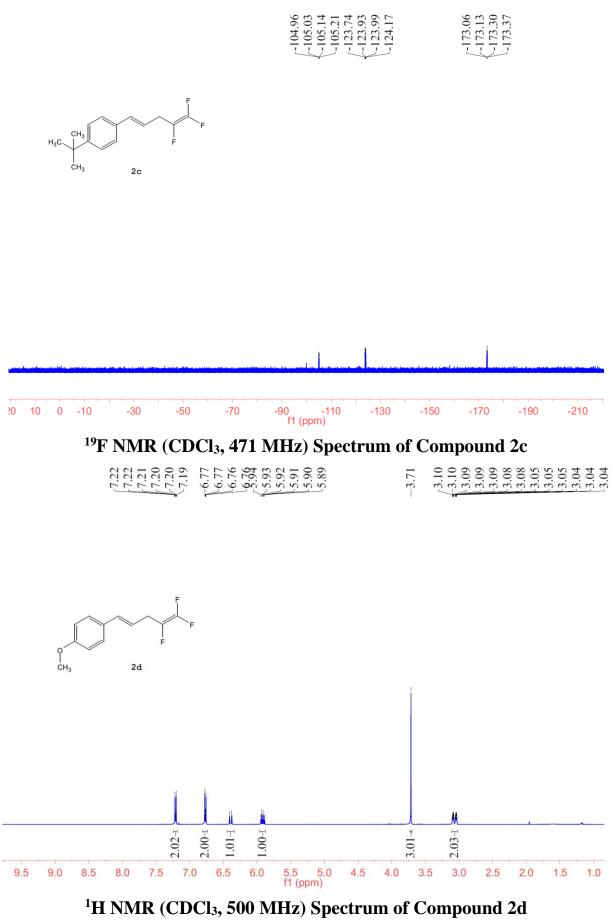


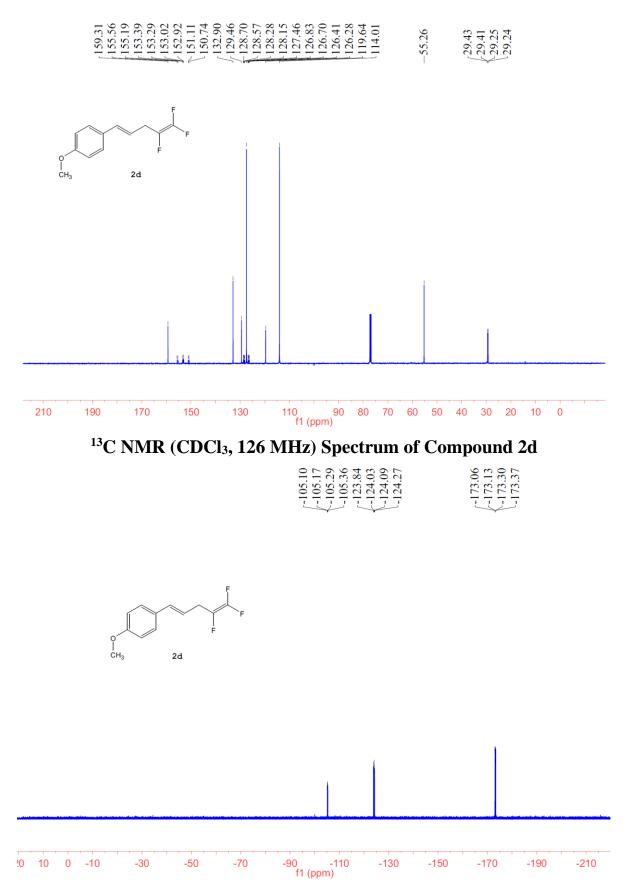
¹³C NMR (CDCl₃, 126 MHz) Spectrum of Compound 2a



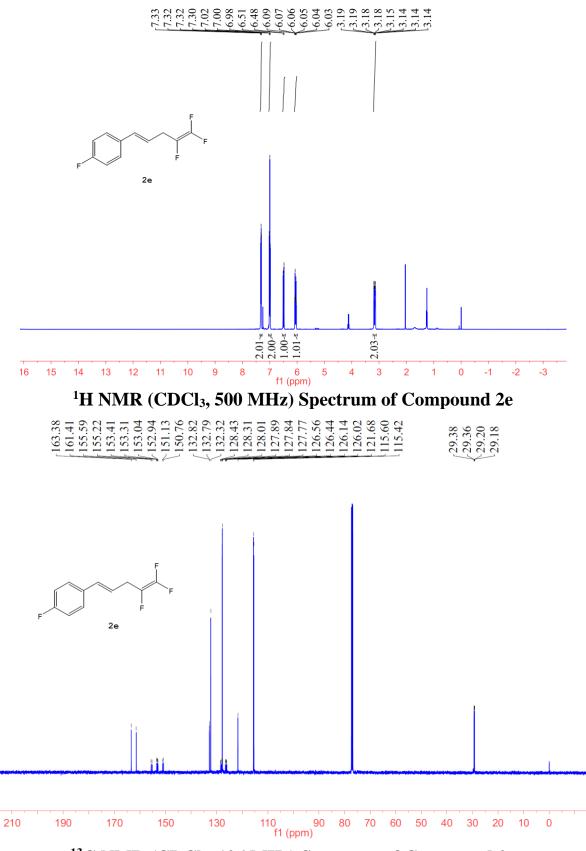




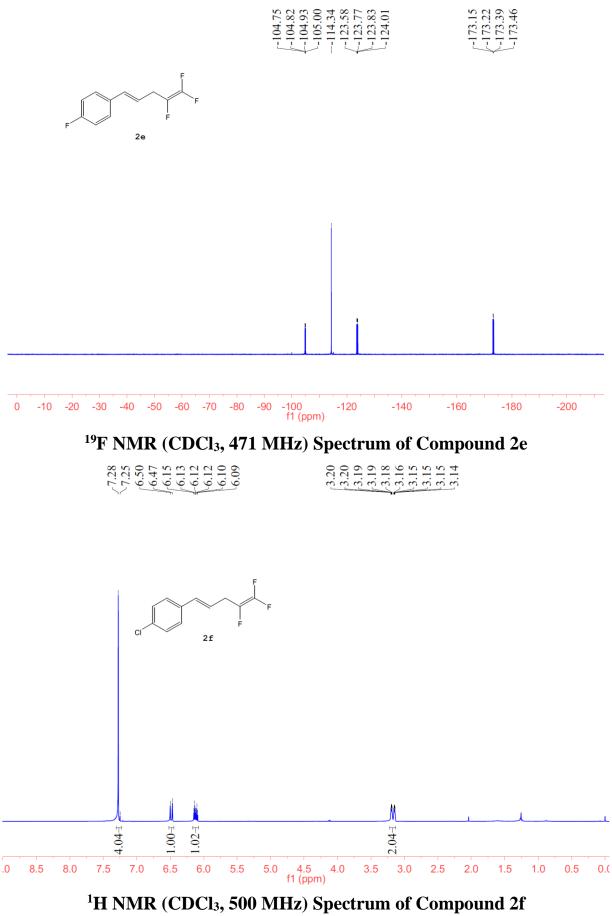


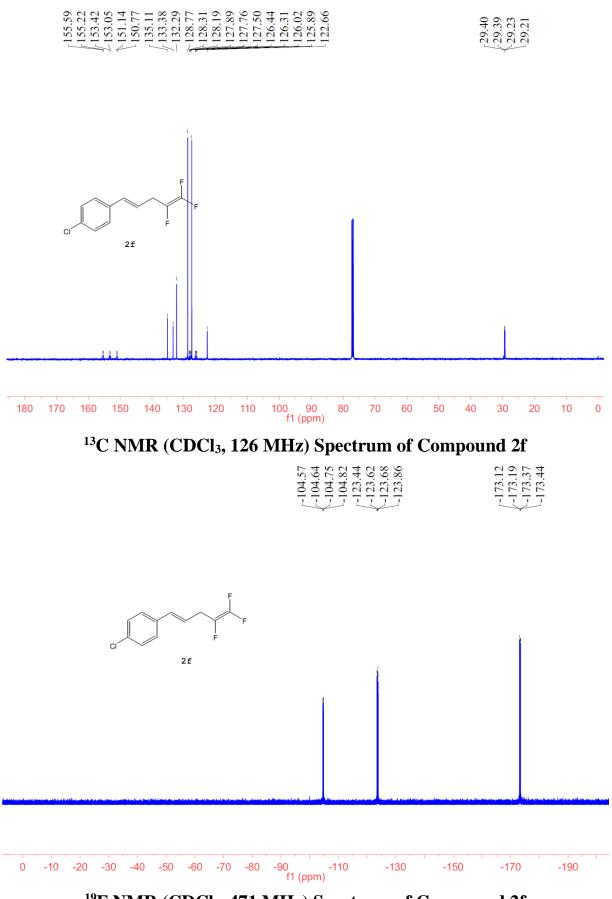


¹⁹F NMR (CDCl₃, 471 MHz) Spectrum of Compound 2d

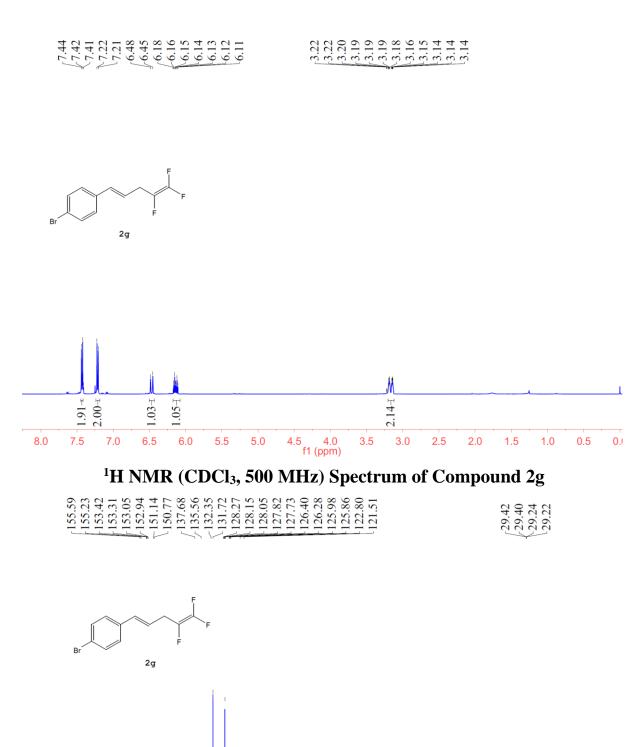


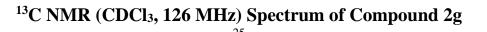
¹³C NMR (CDCl₃, 126 MHz) Spectrum of Compound 2e



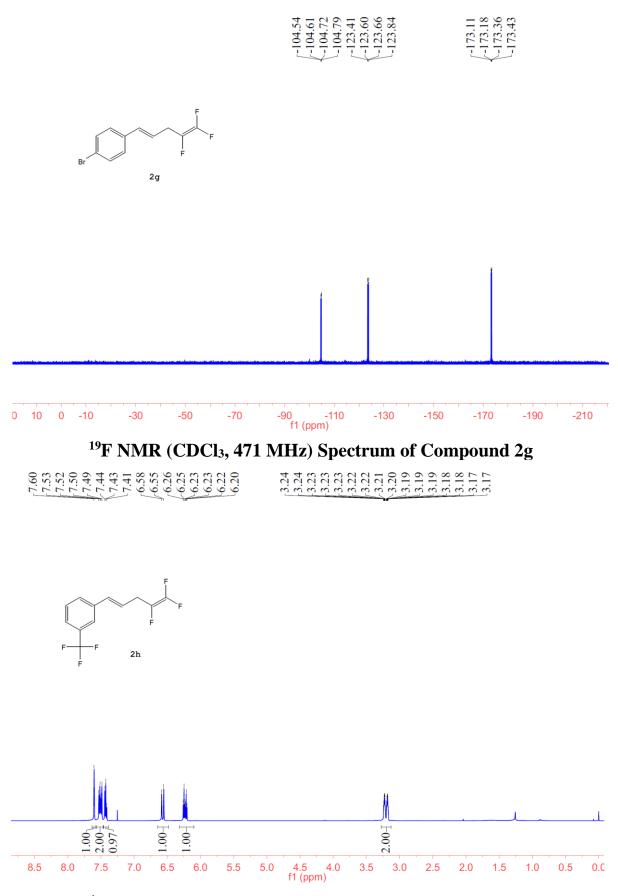


¹⁹F NMR (CDCl₃, 471 MHz) Spectrum of Compound 2f

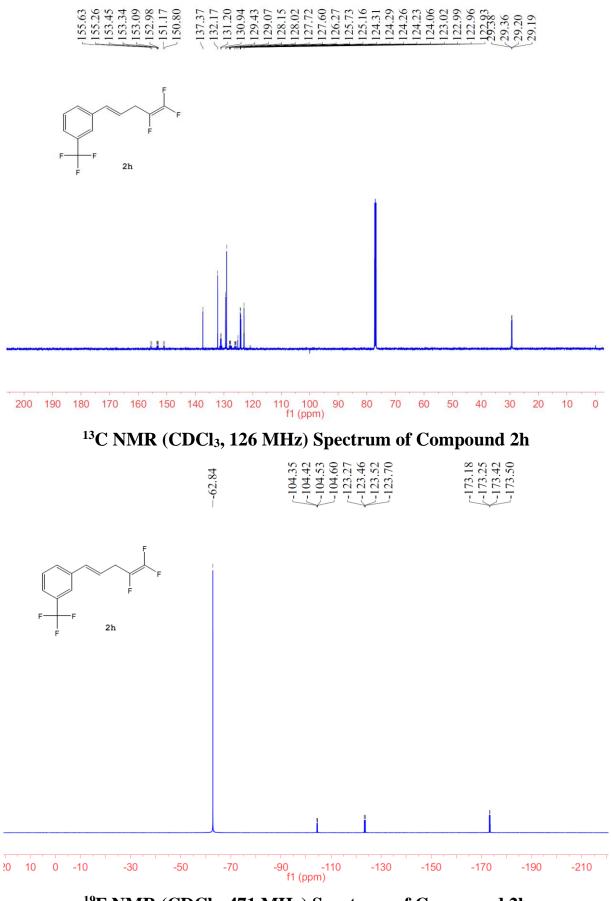




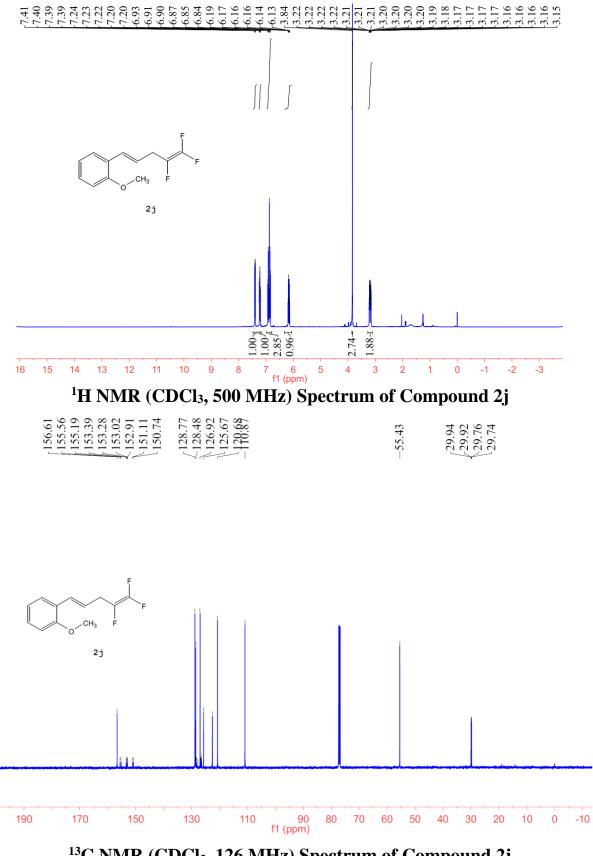
170 160 150 140 130 120 110 100 90 f1 (ppm)



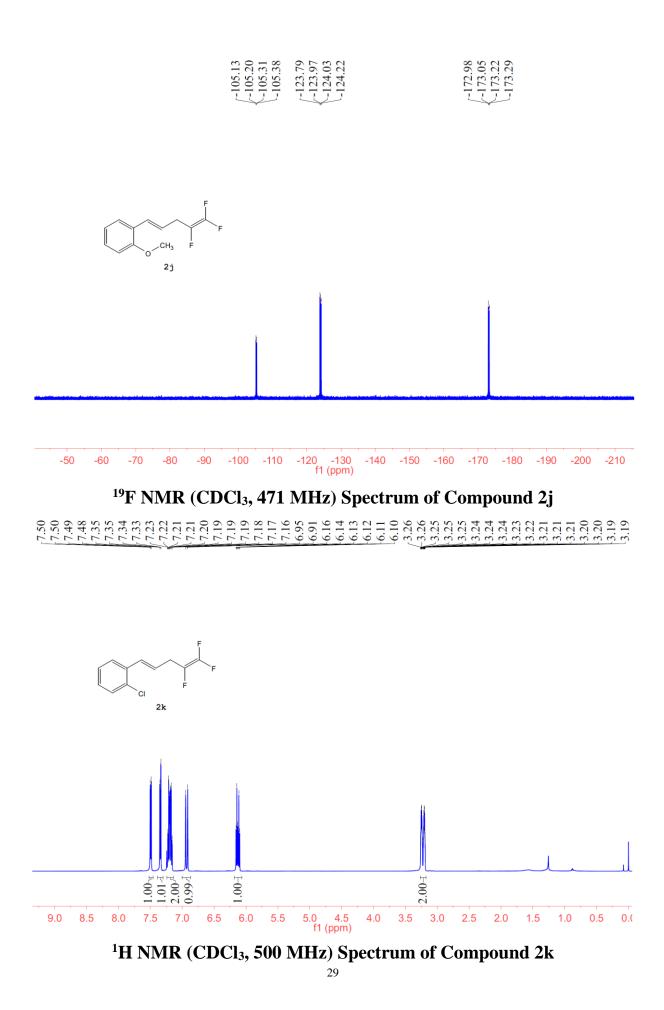
¹H NMR (CDCl₃, 500 MHz) Spectrum of Compound 2h

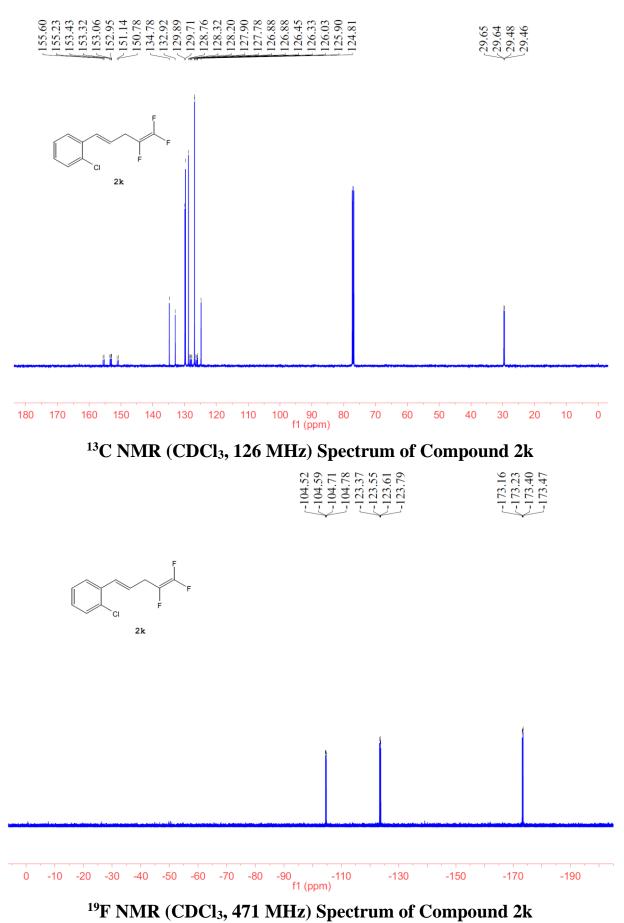


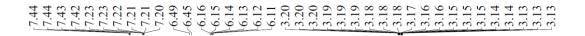
¹⁹F NMR (CDCl₃, 471 MHz) Spectrum of Compound 2h

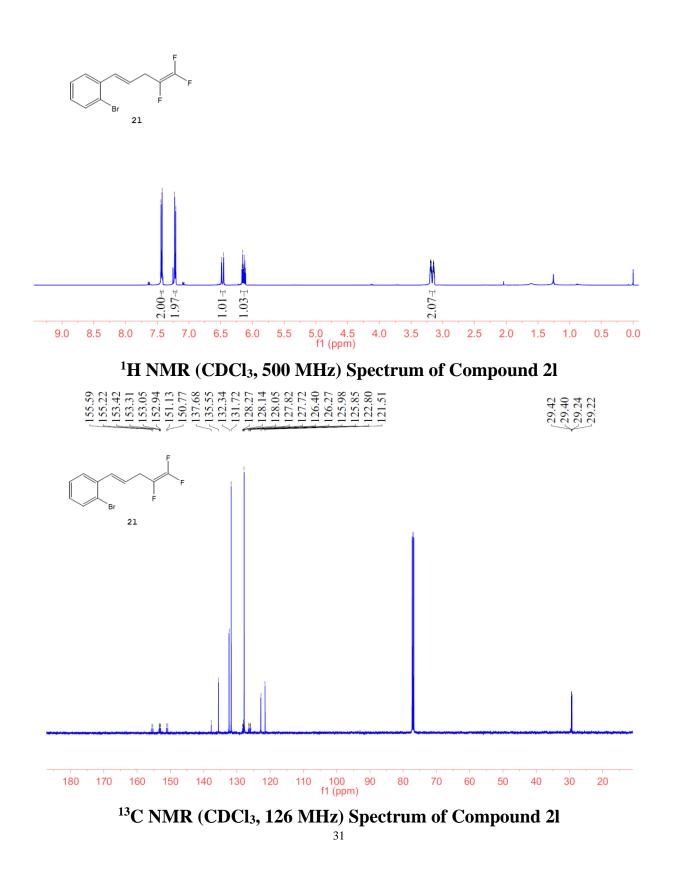


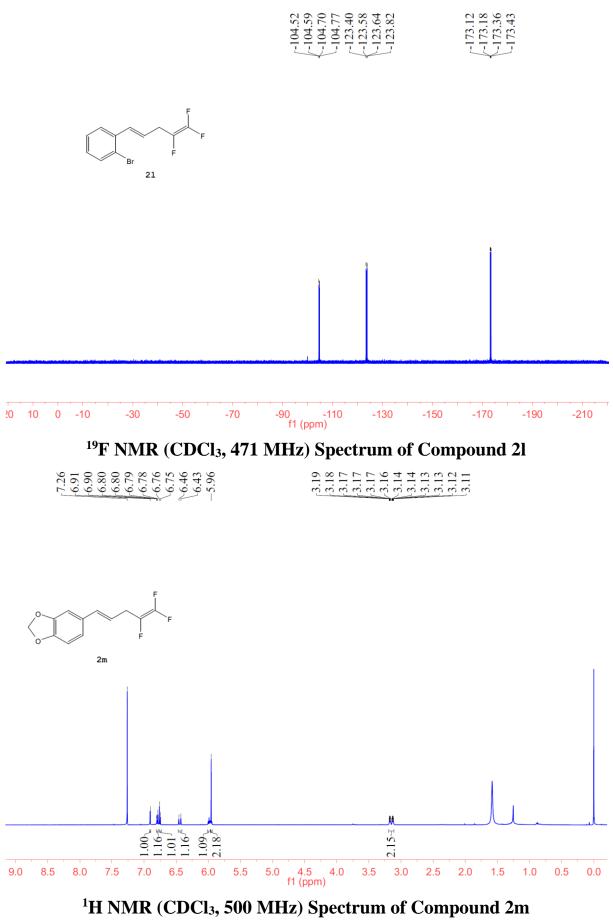
¹³C NMR (CDCl₃, 126 MHz) Spectrum of Compound 2j

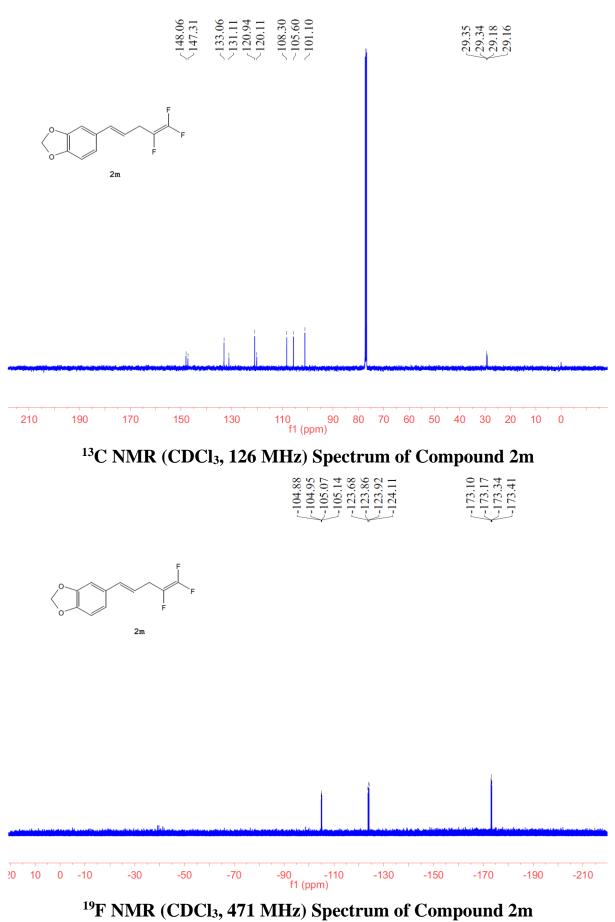


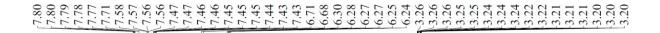


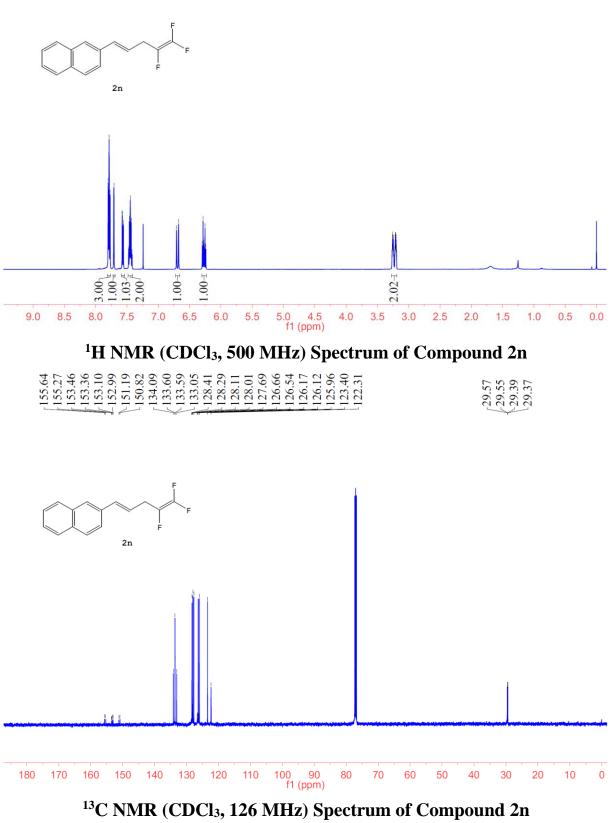


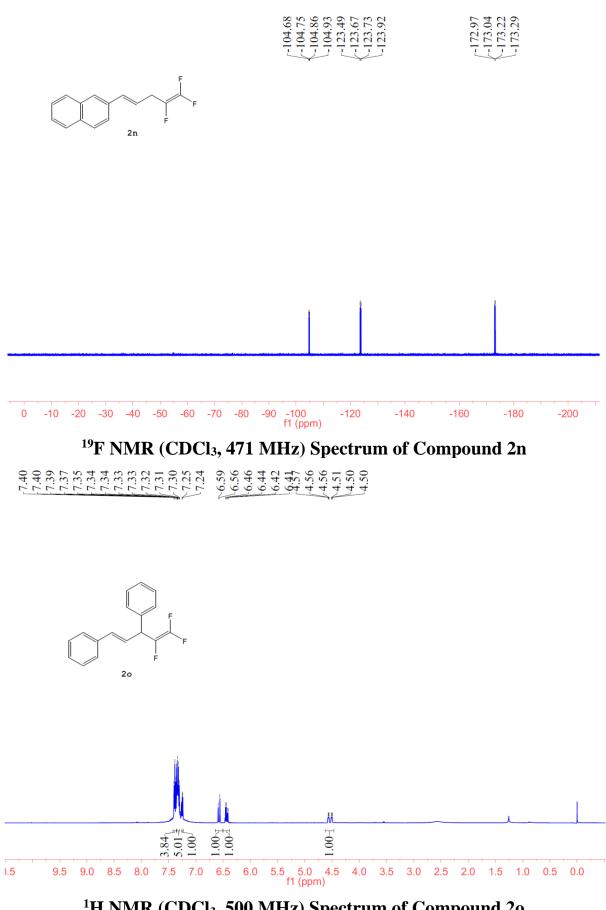




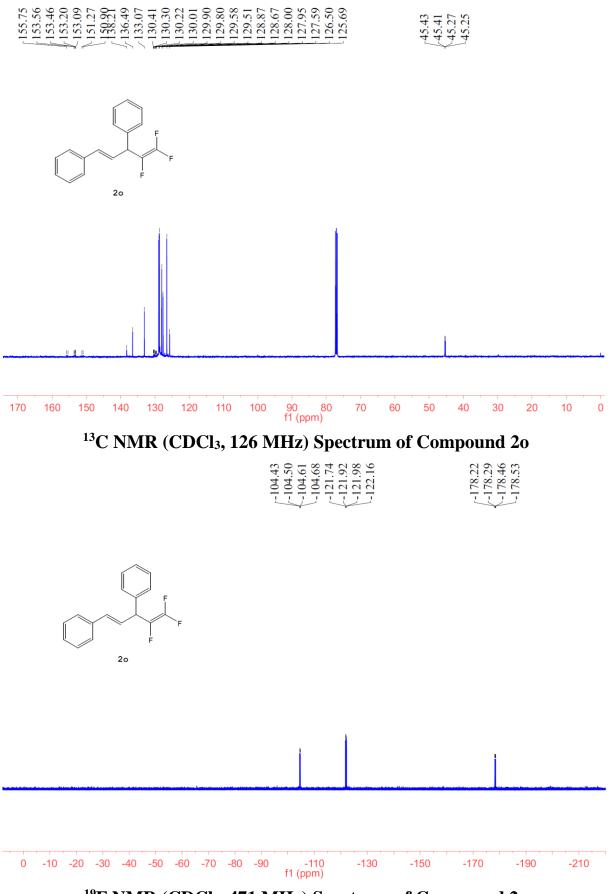




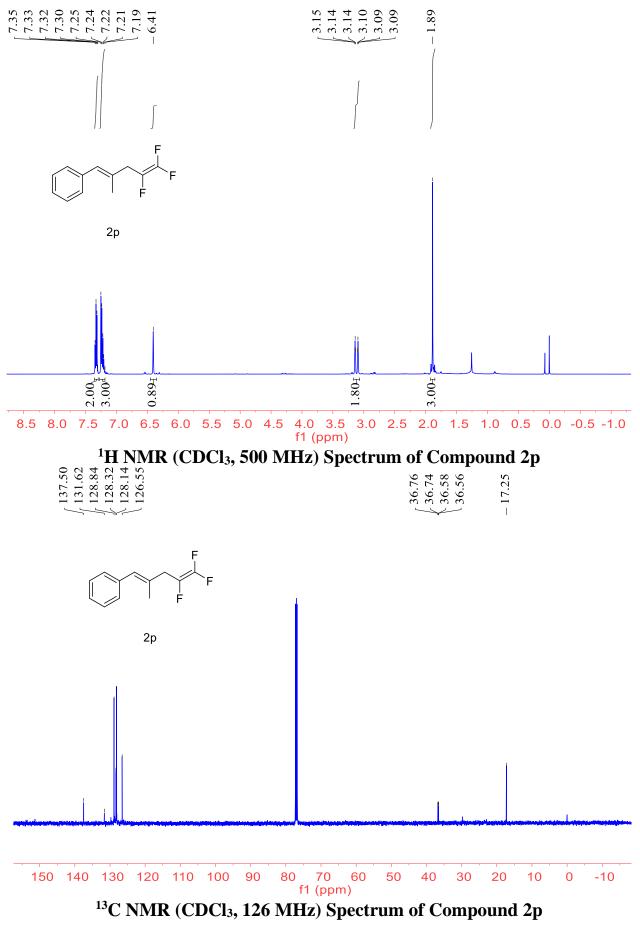


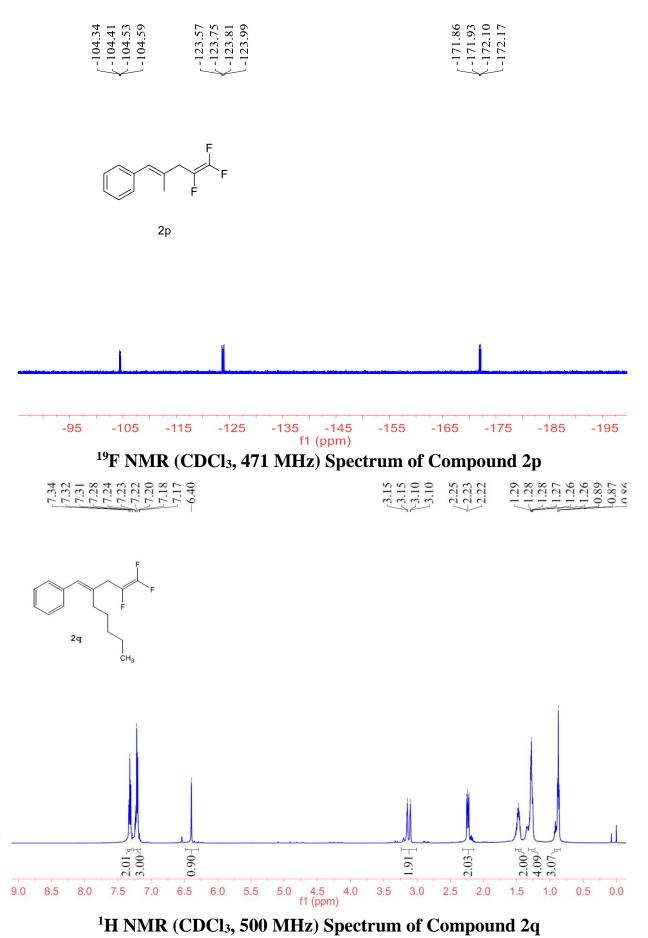


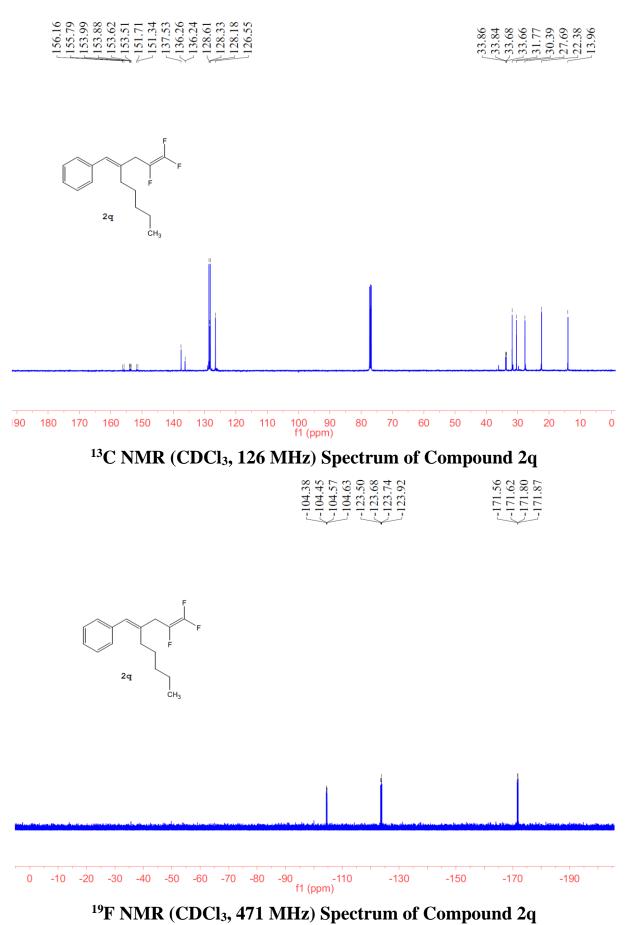
¹H NMR (CDCl₃, 500 MHz) Spectrum of Compound 20

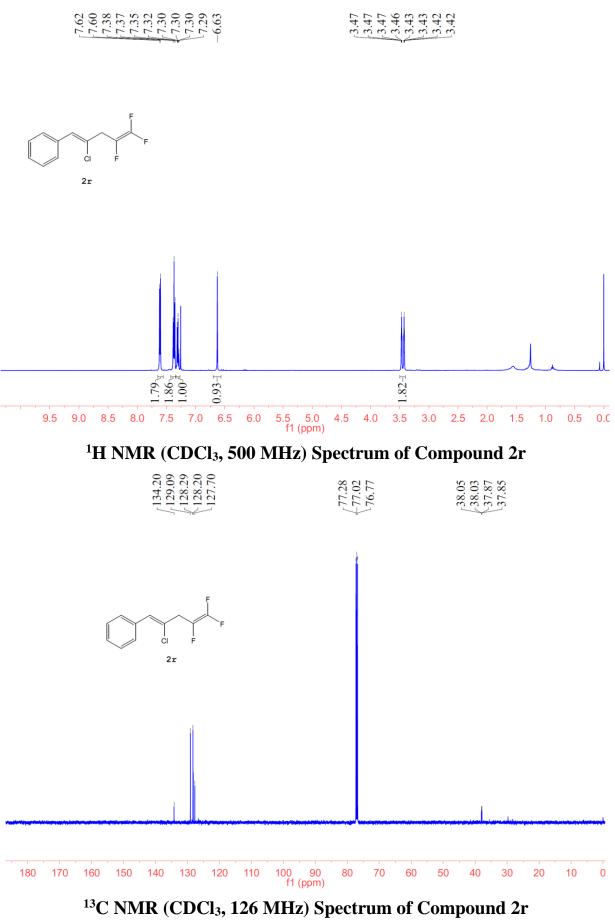


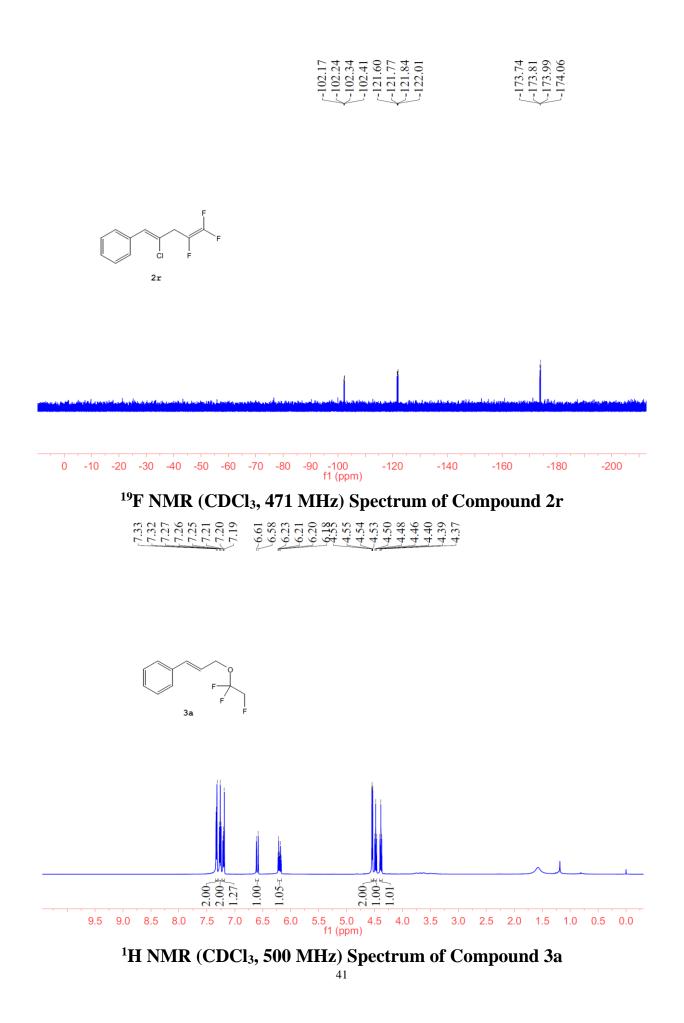
¹⁹F NMR (CDCl₃, 471 MHz) Spectrum of Compound 20

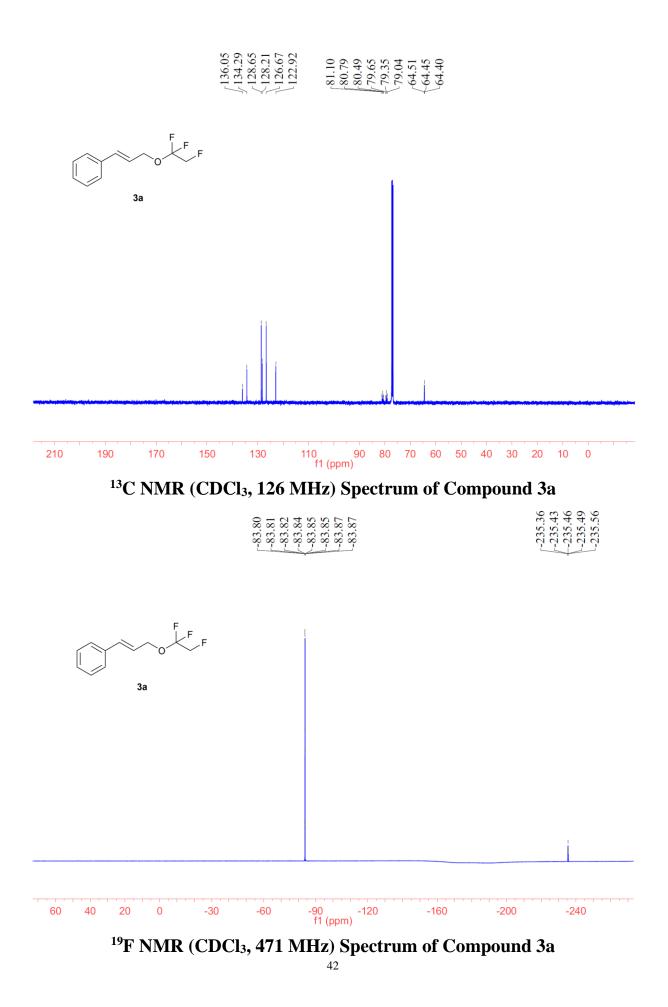


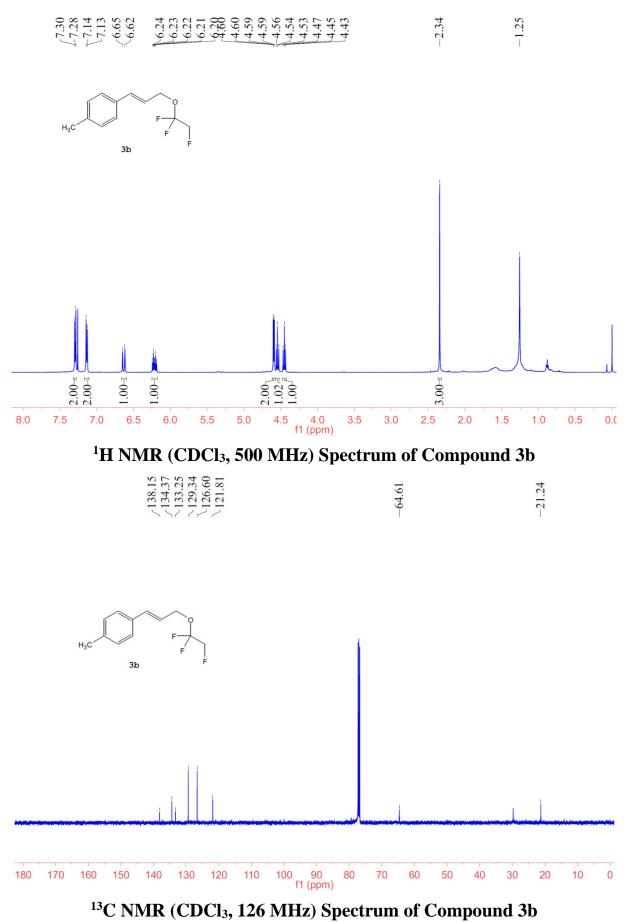


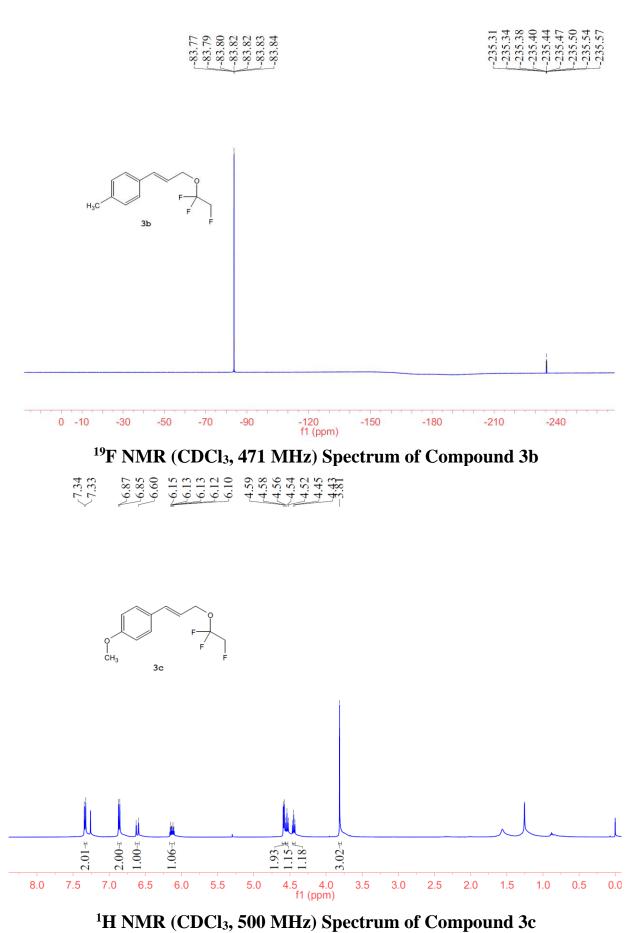


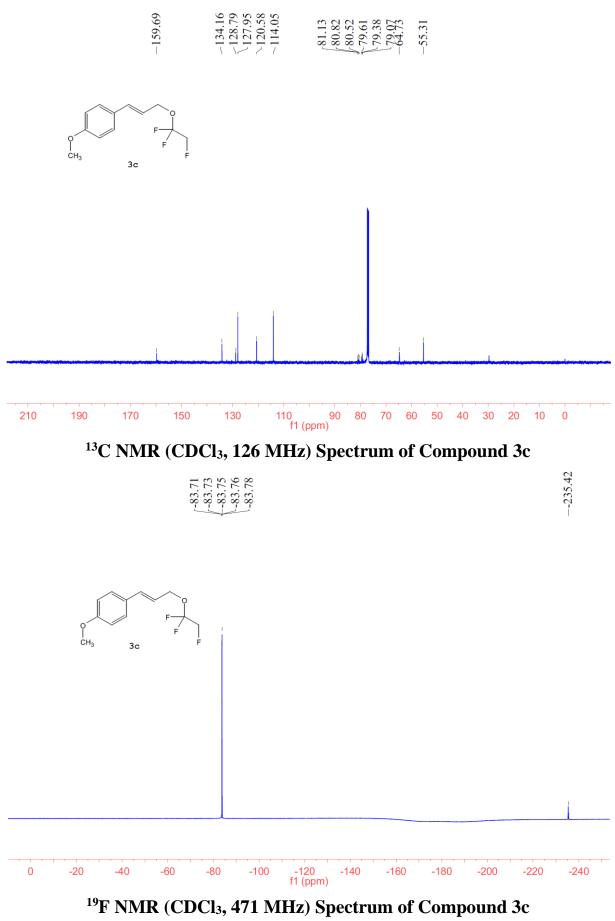


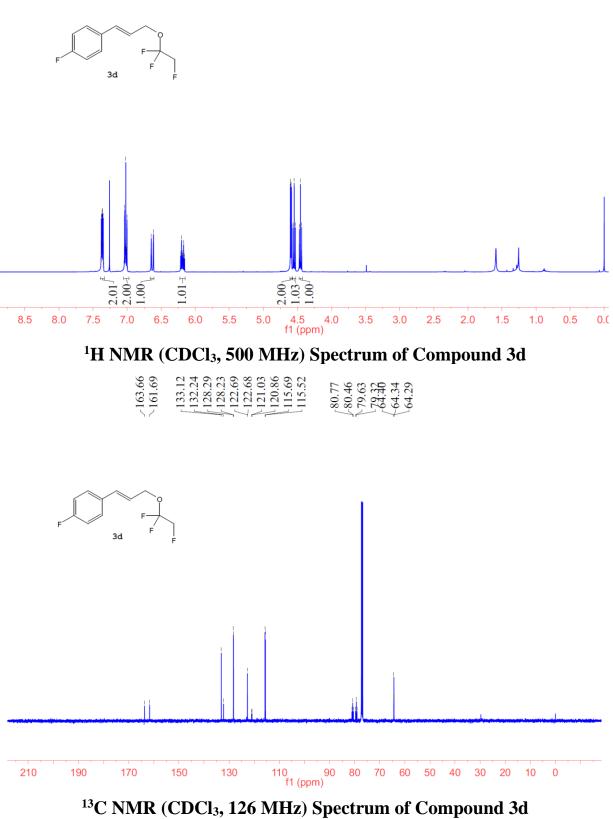


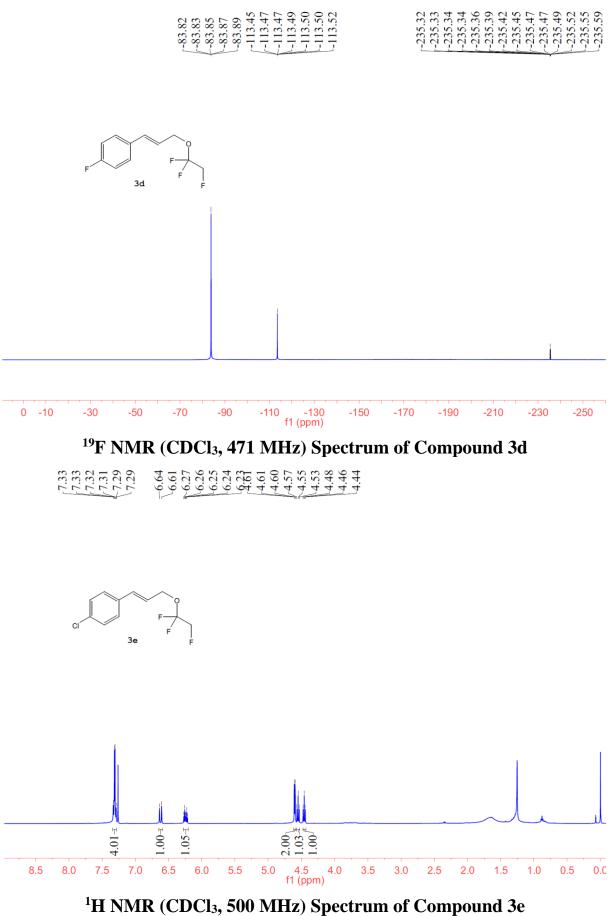


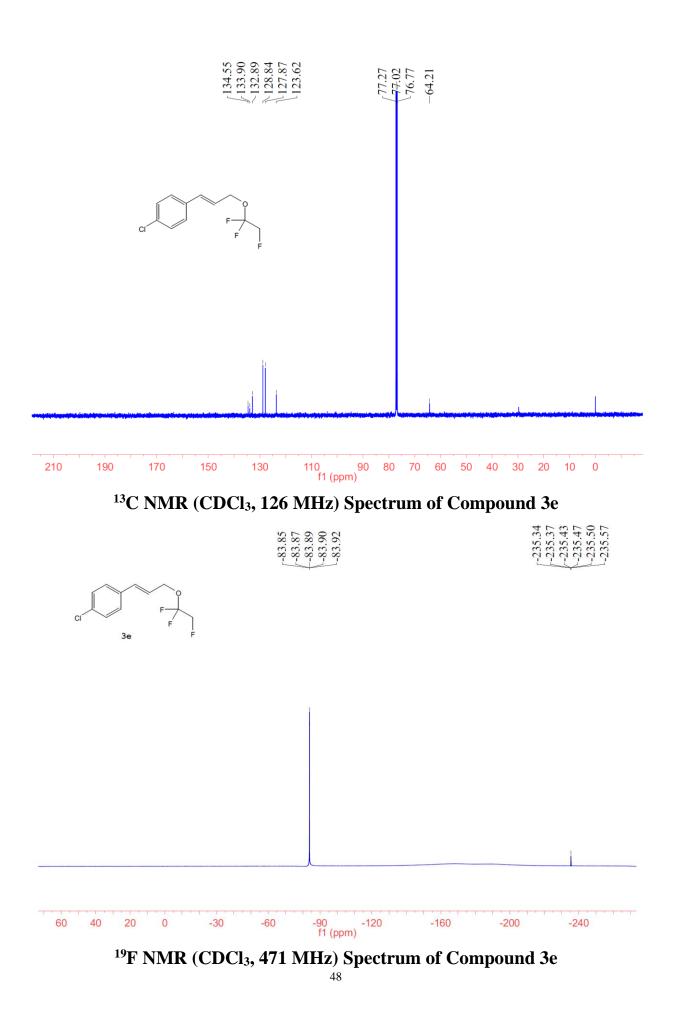


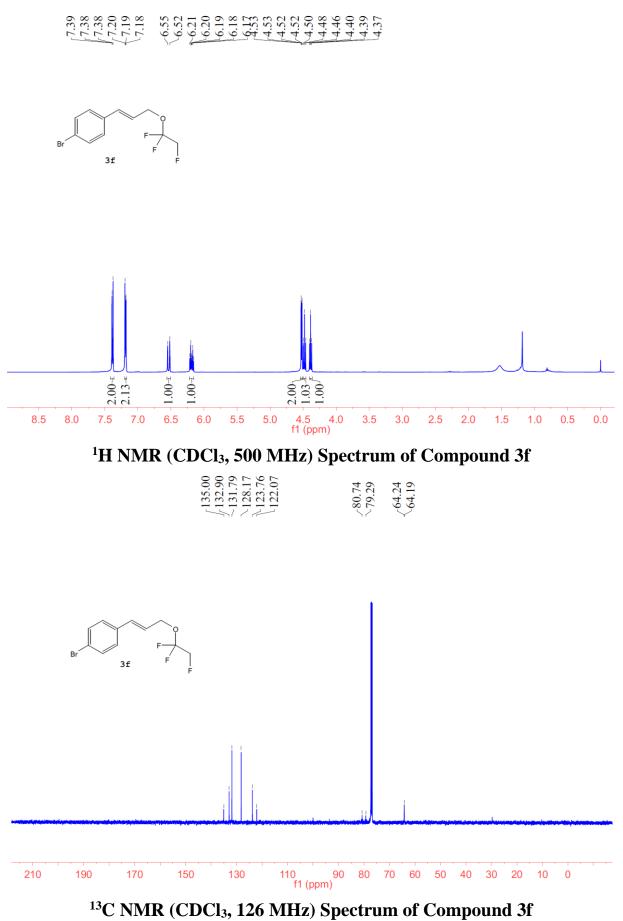


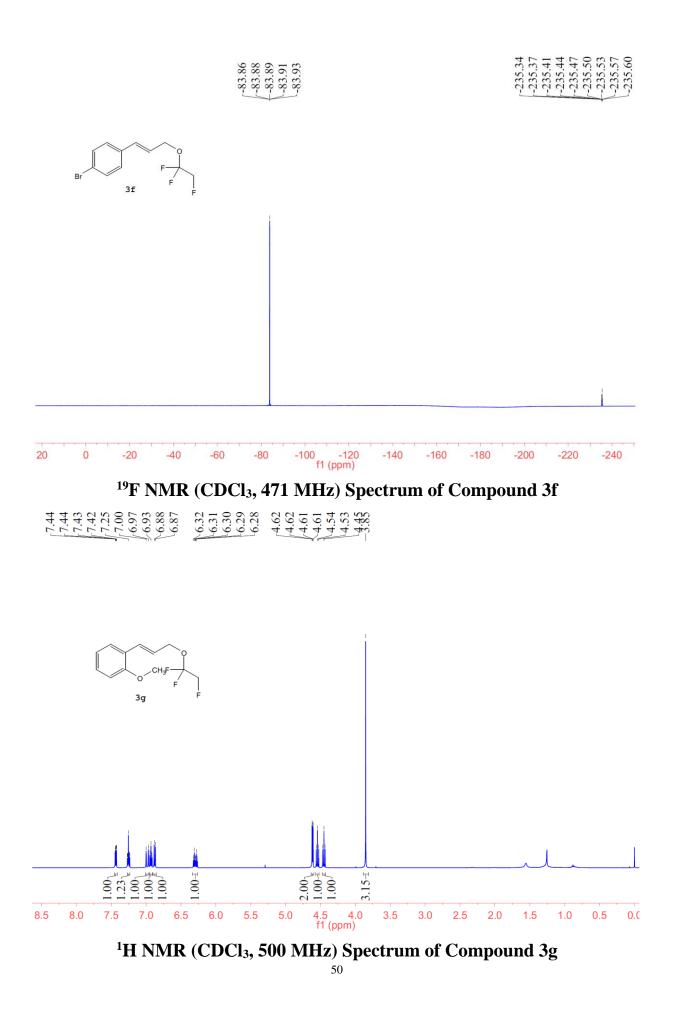


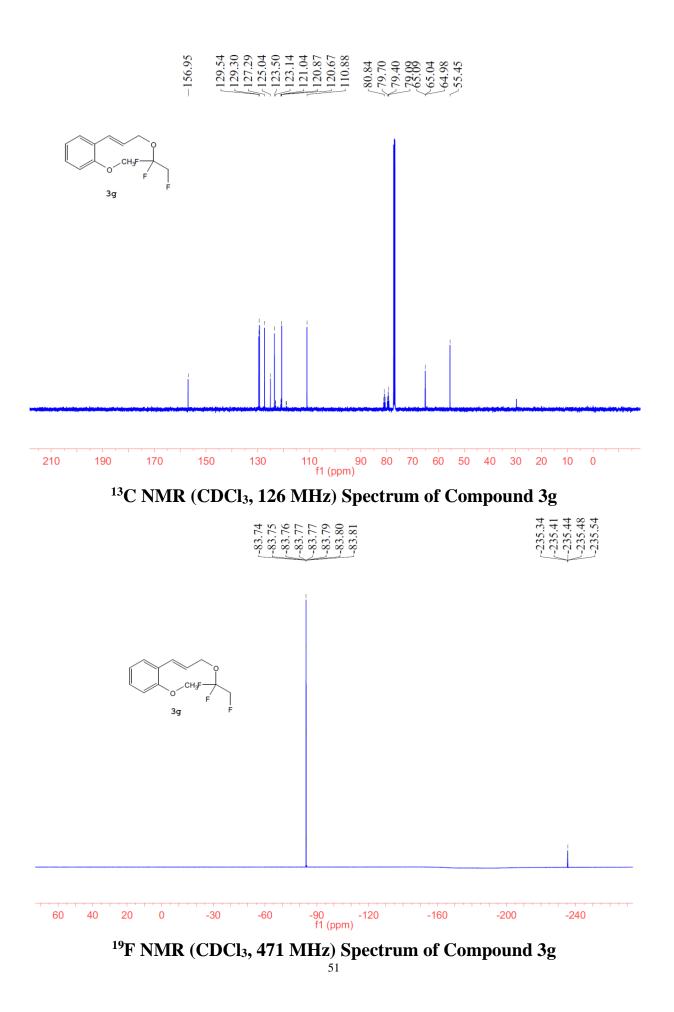




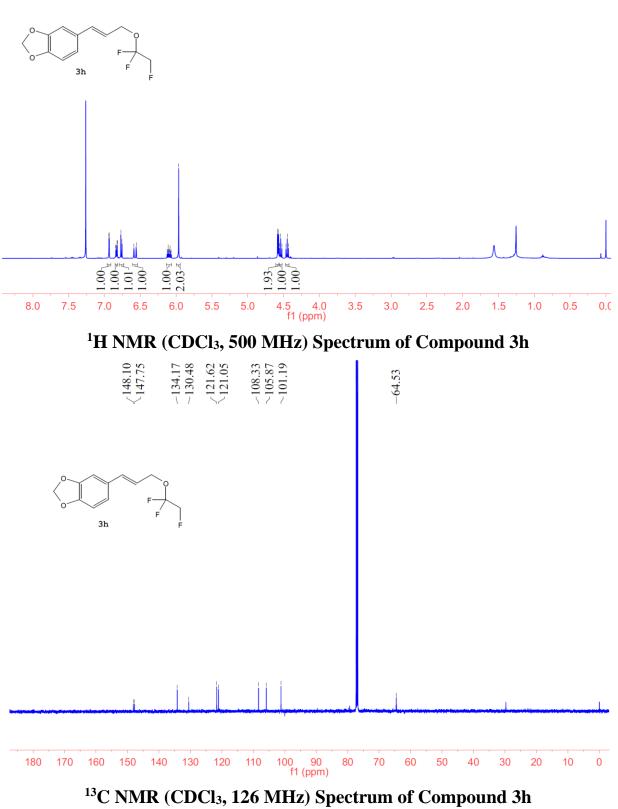




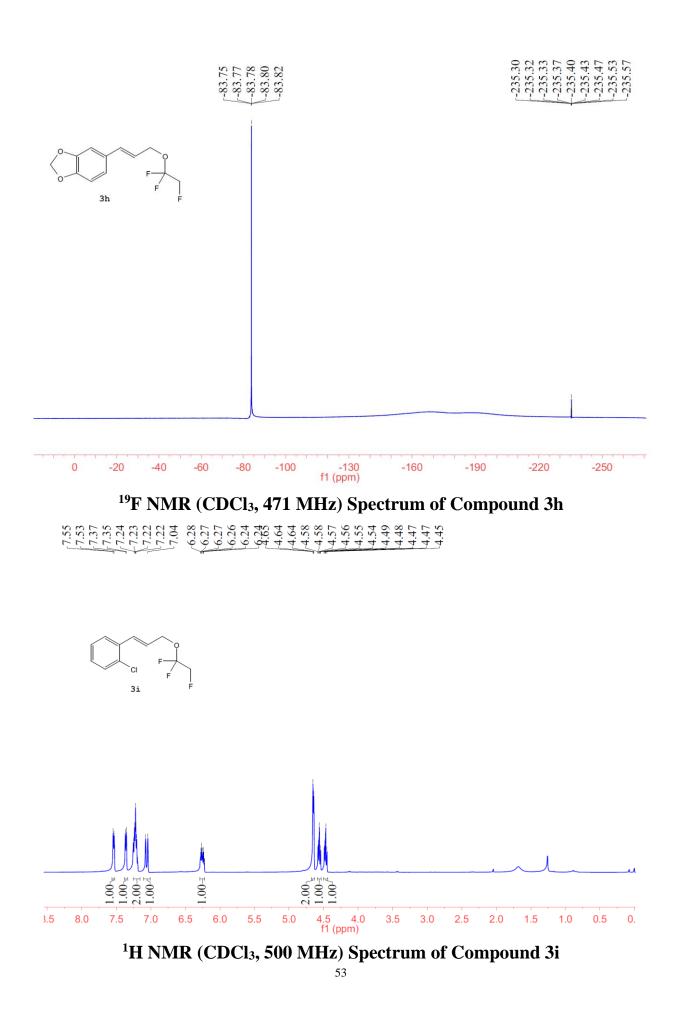


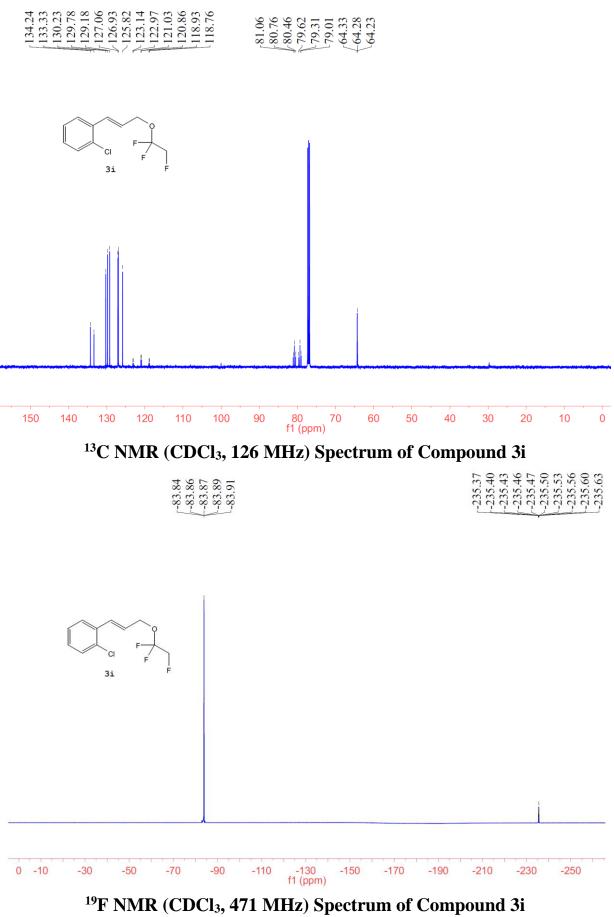


$\begin{array}{c} 6.94\\ 6.93\\ 6.93\\ 6.93\\ 6.93\\ 6.92\\ 6.92\\ 6.93\\ 6.92\\ 6.93\\ 6.56\\ 6.03\\ 6.56\\ 6.03\\ 6.56\\ 6.11\\ 6.56\\ 6.12\\ 6.56\\$

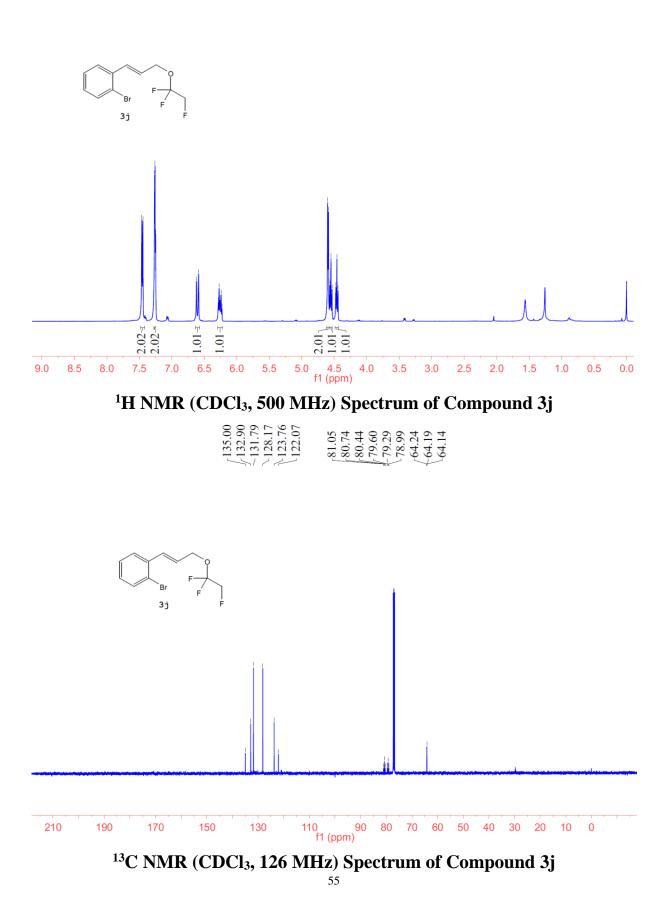


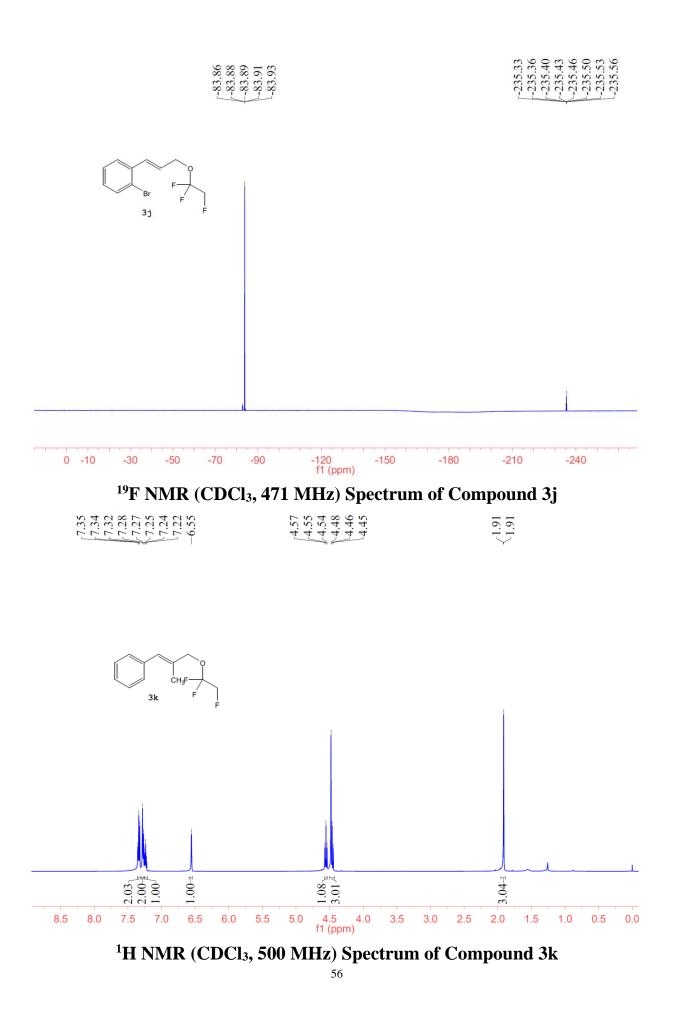
52

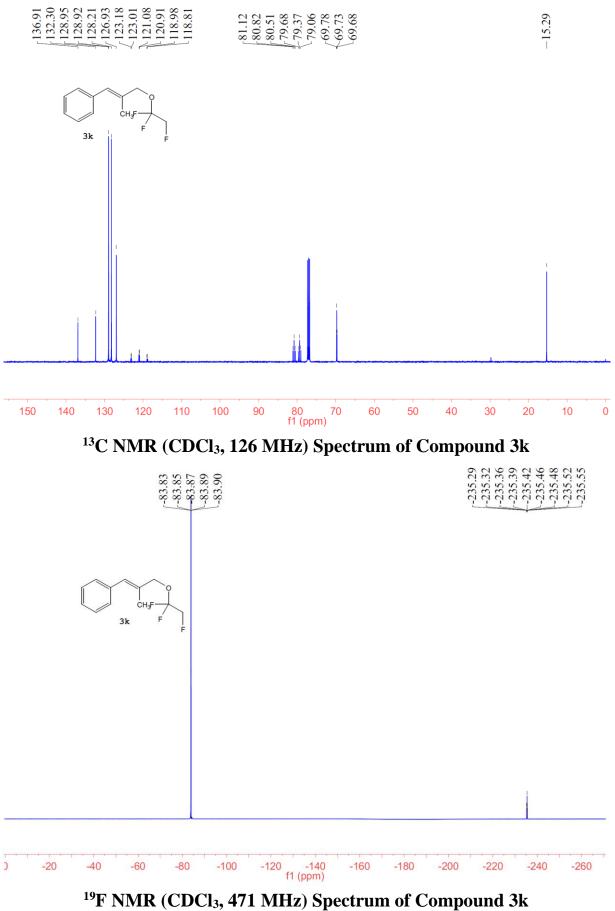




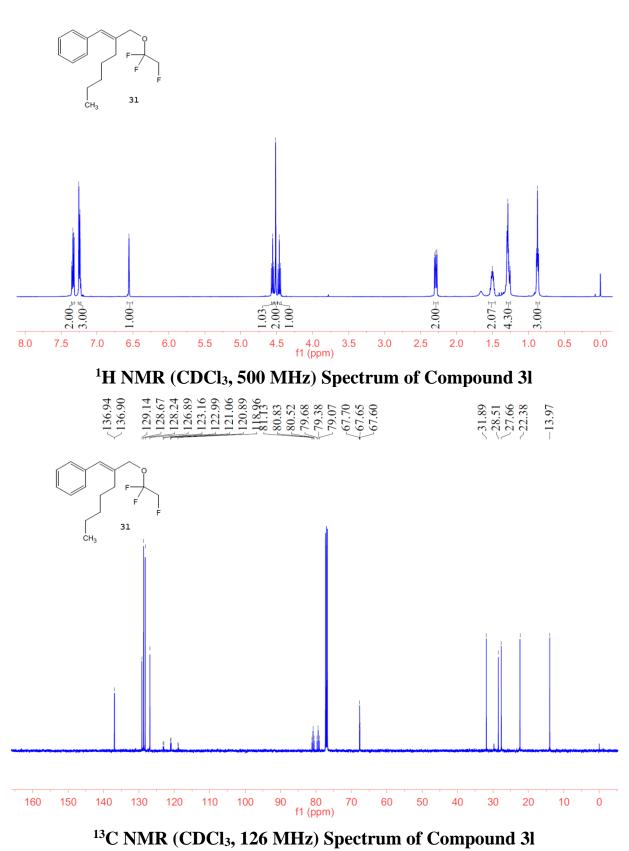
7.46 7.45 7.7.7 7.45 7.7.7 7.45 7.7.7 7.7.7 7.45 7.7.7

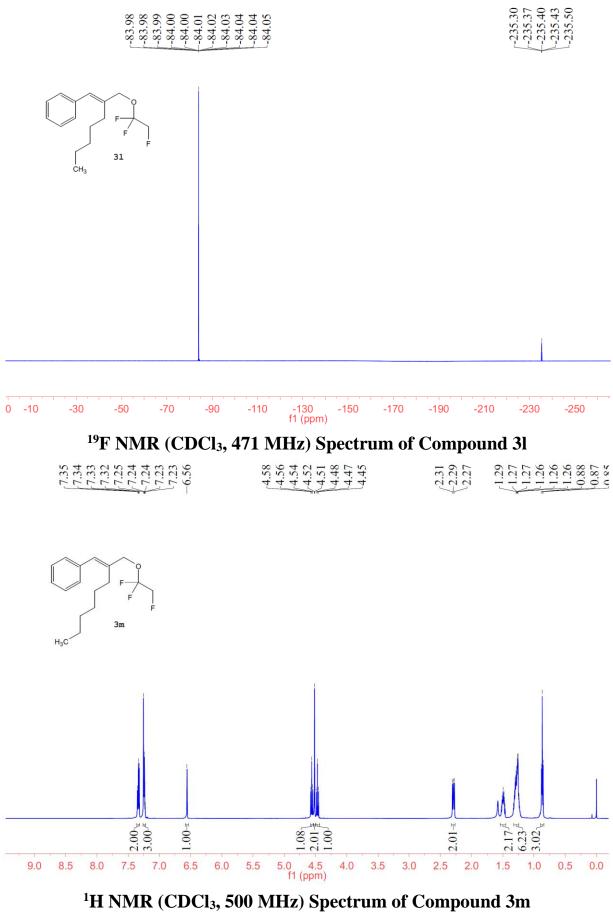


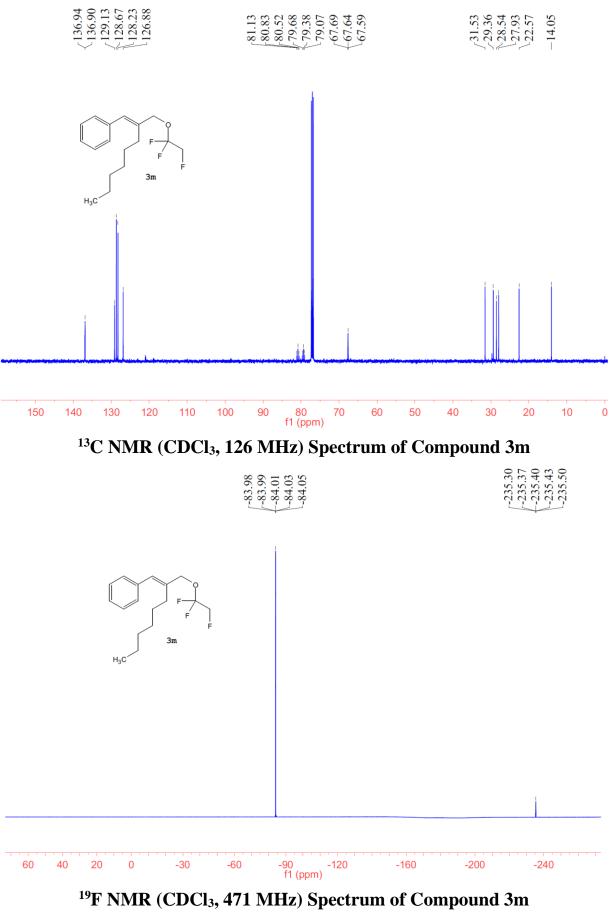




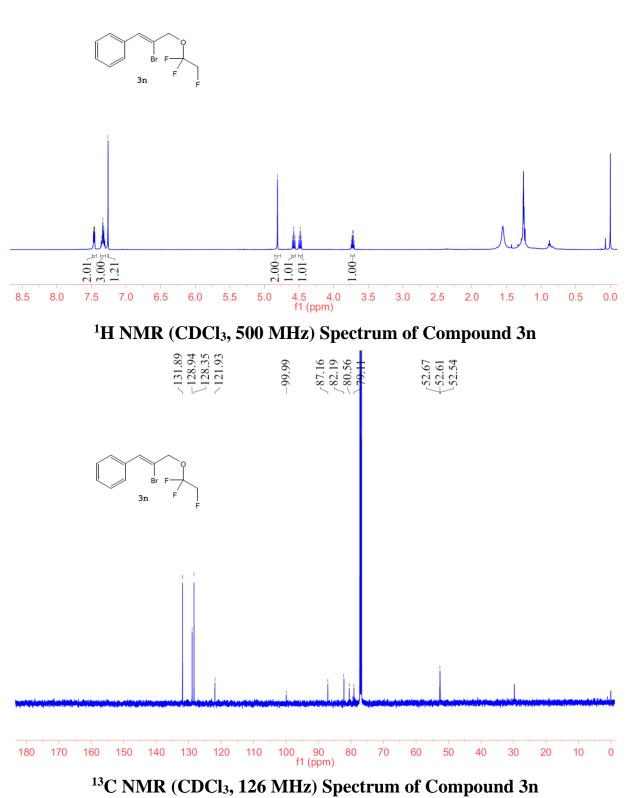
55 55 33 33 35 564 57 57 53 33 33 53	55 55 54 51 51 54 51 54 54 54 54 54 54 54 54 54 54 54 54 54	52 52 50	87 87 87 87 87 87 87 87 87 87 87 87 87 8
	4 4 4 4 4		

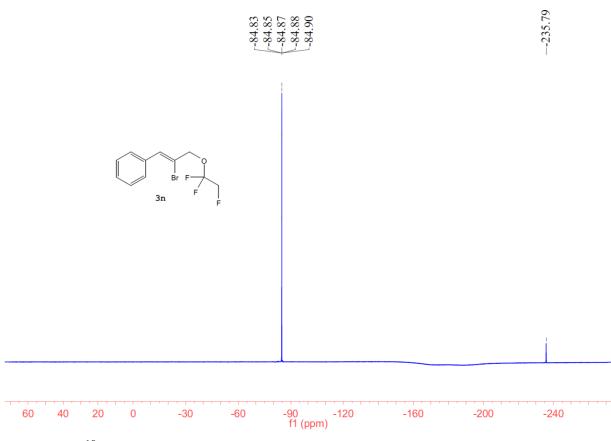












¹⁹F NMR (CDCl₃, 471 MHz) Spectrum of Compound 3n