Supporting Information for

Difluoromethylene Insertion into Fluoroalkyl Copper Complexes

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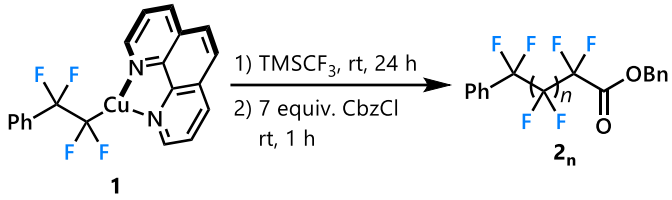
General Information

All reactions were performed under an atmosphere of nitrogen (1 atm) unless otherwise stated. All reagents were used as received. Anhydrous solvents were purchased and were stored in a nitrogen filled glove box with MS4A. Column chromatography was performed using Biotage Isolera One with the indicated solvent as an eluent. ^{1}H, ^{13}C and ^{19}F NMR spectroscopy was recorded on Bruker Avance III NMR spectrometer. Chemical shifts are reported in ppm from the solvent resonance as an internal standard (^{1}H: $CDCl_3$, δ = 7.26 ppm; ^{13}C: $CDCl_3$: δ = 77.36 ppm) or an external standard (^{19}F: $CFCl_3$, δ = 0 ppm). NMR data are reported as follows: chemical shifts, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br: broad signal), coupling constant (Hz), and integration. ^{13}C NMR spectroscopy was recorded with complete proton decoupling. The signals derived from $^{13}CF_2$ were not assigned due to multiple coupling with fluorine atoms. High resolution mass spectra were obtained on JEOL JMS-T700EI. Recycling Preparative High Performance Liquid Chromatography (HPLC) was performed on Japan Analytical Industry LC9225NEXT equipped with JAIGEL-1H and JAIGEL-2H by using chloroform as an eluent. Single crystal X-ray diffraction data were collected with a Rigaku XtaLAB Synergy diffractometer equipped with a HyPix-6000HE detector. Fluoroalkyl copper; (phen)$CuCF_2CF_2Ph$ was prepared by the procedure reported in our previous report[1]. Fluoroalkyl copper; (phen)$CuCF_3$ was prepared by the reported procedure[2].

Caution: Tetrafluoroethylene (TFE) is suspected to be carcinogens and is explosive. The reaction mixture must be handled in a well-ventilated fume hood. The handling of TFE should be guided by a chemist having technical skills in this area of fluorine chemistry.

Experimental Details

Optimization of the reaction conditions (Table 1)



1 **2$_n$**

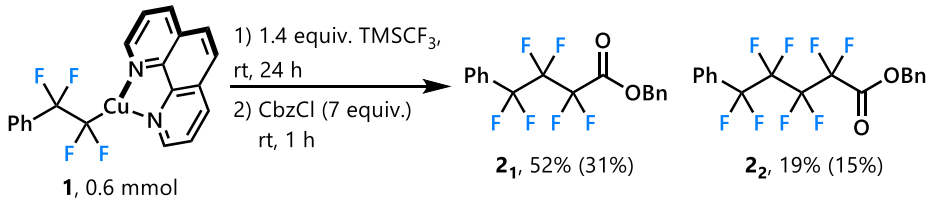
0.02 mmol scale reaction

To a screw cap test tube containing a stirring bar, (phen)CuCF_2CF_2Ph (0.02 mmol, 8 mg), the additive, and solvent (0.2 mL) were added. To this mixture, $TMSCF_3$ was added and stirred at room temperature for 24 hours. After the addition of CbzCl (0.14 mmol, 0.02 mL), the reaction mixture was stirred at room temperature for 1 hour. Volatiles in reaction mixture were removed under reduced pressure. $CDCl_3$ and $PhCF_3$ (internal standard, 0.04 mmol, 5 µL) were added to the tube, and the precipitate in the sample was removed by filtration. The NMR spectrum of the sample was measured to determine the NMR yield.

0.1 mmol scale reaction

To a vial containing a stirring bar, (phen)CuCF_2CF_2Ph (0.1 mmol, 42 mg), the additive, solvent (1 mL) was added. To this mixture, $TMSCF_3$ was added and stirred at room temperature for 24 hours. After the addition of CbzCl (0.7 mmol, 0.1 mL), the reaction mixture was stirred at room temperature for 1 hour. Volatiles in reaction mixture were removed under reduced pressure. $CDCl_3$ and $PhCF_3$ (internal standard, 0.08 mmol, 10 µL) were added to the tube, and the precipitate in the sample was removed by filtration. The NMR spectrum of the sample was measured to determine the NMR yield.

Isolation of 2_1 and 2_2 (0.6 mmol scale reaction)



1, 0.6 mmol

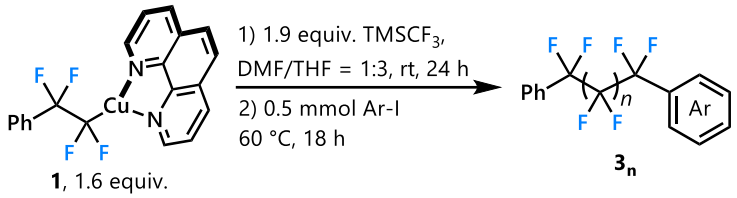
2_1, 52% (31%)

2_2, 19% (15%)

A screw cap test tube was charged with a stirring bar and (phen)CuCF_2CF_2Ph (**1**, 0.6 mmol, 250 mg). The complex was dissolved in DMF/THF mixed solvent (v/v'=1/3, 6 mL). To this mixture, $TMSCF_3$ (0.72 mmol, 107 µL) was added, and the reaction mixture was stirred at room temperature for 24 hours. After the addition of benzyl chloroformate (4.2 mmol, 0.59 mL), the reaction mixture was stirred at room temperature for 1 h. Afterwards, $PhCF_3$ (internal standard, 0.8 mmol, 100 µL) was added, and a portion of the mixture was added to a small test tube. To the tube, $CDCl_3$ was added, and precipitate was removed by filtration. The ^{19}F NMR spectrum of the sample was measured to determine the NMR yield. The reaction mixture was filtered and poured into a separatory funnel and diluted with Et_2O (45 mL). The organic layer was washed with H_2O (10 mL × 3) and brine (5 mL × 1), and dried over Na_2SO_4. After filtration and removal of the solvent under vacuum, the

residue was purified by HPLC using $CHCl_3$ to afford **2₂** (pale yellow oil, 35.9 mg, 15%), and the following flash column chromatography with hexane/ethyl acetate (v/v' = 97/3) as the eluent gave **2₁** (colorless oil, 66.8 mg, 31%): ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 5.36 (s, 2H), 7.40 (s, 5H), 7.48 (t, J = 7.6 Hz, 2H), 7.55 (d, J = 6.3 Hz, 3H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –110.4 (t, J_{FF} = 9.9 Hz, 2F), –118.1 (t, J_{FF} = 9.4 Hz, 2F), –123.6 (s, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 69.8 (t, J = 7.2 Hz), 127.1 (t, J = 6.5 Hz), 128.83, 128.87 (t, J = 25.7 Hz), 128.93, 129.1, 129.4, 132.1, 133.9, 159.7 (t, J = 29.7 Hz). One carbon is missing due to overlapping. HRMS(EI): m/z [M]$^+$ calcd for $C_{17}H_{12}F_6O_2$ 362.0736; found 362.0751. **2₂**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 5.36 (s, 2H), 7.39 (s, 5H), 7.49 (t, J = 7.5 Hz, 2H), 7.56 (d, J = 6.2 Hz, 3H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –110.9 (t, J_{FF} = 13.9 Hz, 2F), –118.6 (t, J_{FF} = 11.5 Hz, F), –121.7 (m, 2F), –122.3 (m, 2F). ^{13}C NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 70.0 (t, J = 6.7 Hz), 127.2 (t, J = 6.6 Hz), 128.9, 129.0, 129.2 (t, J = 51.3 Hz), 129.1, 129.4, 132.1, 133.7, 159.2 (t, J = 29.5 Hz). HRMS(EI): m/z [M]$^+$ calcd for $C_{18}H_{12}F_8O_2$ 412.0704; found 412.0717.

Substrate scope using $PhCF_2CF_2Cu(phen)$ (1) (Figure 2)

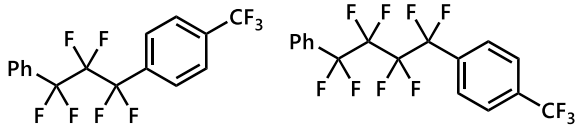


1, 1.6 equiv. **3ₙ**

General procedure A

A screw cap test tube was charged with a stirring bar and (phen)$CuCF_2CF_2Ph$ (**1**, 0.8 mmol, 340 mg). The complex was dissolved in DMF/THF mixed solvent (v/v'=1/3, 8 mL). To this mixture, $TMSCF_3$ (0.96 mmol, 140 μL) was added, and the reaction mixture was stirred at room temperature for 24 hours. After the addition of iodoarenes (0.5 mmol), the reaction mixture was stirred at 60 °C for 18 hours. After cooling the reaction mixture, $PhCF_3$ (internal standard, 0.8 mmol, 100 μL) was added, and a portion of the mixture was added to a small test tube. To the tube, $CDCl_3$ was added, and precipitate was removed by filtration. The ^{19}F NMR spectrum of the sample was measured to determine the NMR yield. The reaction mixture was filtered and poured into a separatory funnel and diluted with a mixture of Et_2O, ethyl acetate, and hexane (65 mL). The organic layer was washed with H_2O (10 mL × 3) and brine (5 mL × 1), and dried over Na_2SO_4. After filtration and removal of the solvent under vacuum, the residue was purified by HPLC using $CHCl_3$ as an eluent to afford the desired products **3₁** and **3₂**.

3a

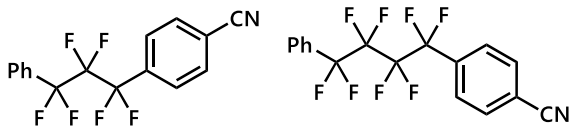


3a₁ **3a₂**

Following the general procedure A, the reaction with 4-iodobenzotrifluoride (136.7 mg, 0.5 mmol) was conducted to give **3a₁** in 47% (colorless oil, 87.9 mg, 69% NMR yield) and **3a₂** in 1% (colorless oil, 2.7 mg,

21% NMR yield). Extraction was performed with Et_2O (45 mL). **3a$_1$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.45–7.59 (m, 5H), 7.73 (t, J = 9.7 Hz, 4H). ^{19}F NMR (376 MHz, in CDCl3, rt, δ/ppm): –63.2 (s, 3F), –109.5 (t, J_{FF} = 12.3 Hz, 2F), –110.0 (t, J_{FF} = 12.0 Hz, 2F), –122.4 (s, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 125.2 (t, J = 272.8 Hz), 125.8 (d, J = 3.4 Hz), 127.1 (t, 6.5 Hz), 127.8 (t, J = 6.1 Hz), 128.8, 130.4 (t, J = 24.3 Hz), 131.8, 133.9 (q, J = 32.9 Hz), 134.5 (t, J = 25.1 Hz). HRMS(EI): m/z [M]$^+$ calcd for $C_{16}H_9F_9$ 372.0555; found 372.0560. **3a$_2$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.46–7.59(m, 5H), 7.74 (q, J = 13.3 Hz, 4H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –63.2 (s, 3F), –110.8 (t, J_{FF} = 14.1 Hz, 2F), –111.1 (t, J_{FF} = 13.7 Hz, 2F), –121.3 (m, 4F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 125.9 (t, J = 272.8 Hz), 125.9 (d, J = 3.5 Hz), 127.2 (t, J = 6.5 Hz), 127.9 (t, J = 5.5 Hz), 128.8, 129.8 (t, J = 24.1 Hz), 132.0, 133.7 (t, J = 24.4 Hz), 134.3 (q, J = 32.9 Hz). HRMS(EI): m/z [M]$^+$ calcd for $C_{17}H_9F_{11}$ 422.0523; found 422.0524.

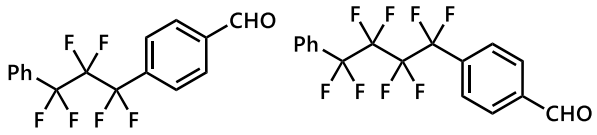
3b



3b$_1$ **3b$_2$**

Following the general procedure A, the reaction with 4-iodobenzonitrile (114.2 mg, 0.5 mmol) was conducted to give the **3b$_1$** in 47% (pale yellow oil, 77.7 mg, 78% NMR yield) and **3b$_2$** in 13% (pale yellow oil, 25.2 mg, 16% NMR yield). **3b$_1$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.45–7.57 (m, 5H), 7.71(d, J = 8.2 Hz, 2H), 7.78(d, J = 8.4 Hz, 2H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –109.5 (t, J = 12.5 Hz, 2F), –110.5 (t, J = 12.1 Hz, 2F), –122.4 (s, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 115.9, 118.0, 127.0 (t, J = 6.4 Hz), 128.0 (t, J = 6.6 Hz), 128.8, 130.1 (t, J = 24.3 Hz), 131.9, 132.5, 135.2 (t, J = 24.6 Hz). HRMS(EI): m/z [M]$^+$ calcd for $C_{16}H_9F_6N$ 329.0634; found 329.0636. **3b$_2$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.46–7.58 (m, 5H), 7.71(d, J = 8.4 Hz, 2H), 7.78(d, J = 8.5 Hz, 2H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –114.0 (t, J = 14.2 Hz, 2F), –114.7 (t, J = 13.8 Hz, 2F), –124.3 (m, 2F), –124.5 (m, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 116.2, 117.9, 127.2 (t, J = 6.4 Hz), 128.2 (t, J = 6.5 Hz), 128.9, 129.7 (t, J = 24.1 Hz), 132.1, 132.6, 134.5 (t, J = 25.0 Hz). HRMS(EI): m/z [M]$^+$ calcd for $C_{17}H_9F_8N$ 379.0602; found 379.0614.

3c

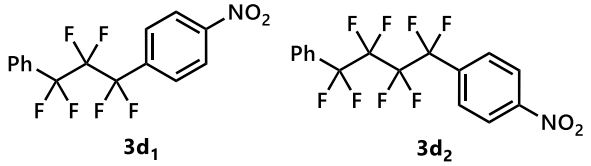


3c$_1$ **3c$_2$**

Following the general procedure A, the reaction with 4-iodobenzaldehyde (117.8 mg, 0.5 mmol) was conducted to give the **3c$_1$** in 51% (white solid, 83.8 mg, 65% NMR yield) and **3c$_2$** in 19% (white solid, 37.0 mg, 26% NMR yield). **3c$_1$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.44–7.58 (m, 5H), 7.77 (d, J = 8.1 Hz, 2H), 7.98 (d, J = 8.2 Hz, 2H), 10.1 (s, 1H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –109.7 (t, J_{FF} = 11.5 Hz, 2F), –110.2 (t, J_{FF} = 11.9 Hz, 2F), –122.5 (s, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 127.1 (t, J = 6.5 Hz), 128.0 (t, J = 6.5 Hz), 128.7, 129.8, 130.4 (t, J = 24.0 Hz), 131.8, 136.3 (t, J = 24.4 Hz), 138.6, 191.7 (d, J = 7.1

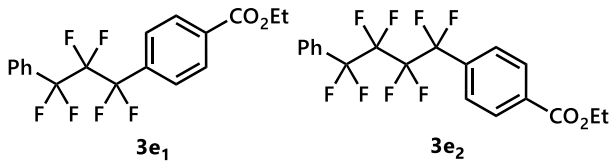
Hz). HRMS(EI): m/z $[M]^+$ calcd for $C_{16}H_{10}F_6O$ 332.0630; found 332.0633. **3c₂**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.46–7.58 (m, 5H), 7.77(d, *J* = 8.2 Hz, 2H), 7.99 (d, *J* = 8.2 Hz, 2H), 10.1 (s, 1H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –110.9 (t, J_{FF} = 13.5 Hz, 2F), –111.3 (t, J_{FF} = 13.7 Hz, 2F), –121.4 (m, 4F). ^{13}C NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 127.2 (t, *J* = 6.8 Hz), 128.1 (, *J* = 6.3 Hz), 128.8, 129.9, 130.6, 132.0, 135.5 (t, *J* = 24.2 Hz), 138.8, 191.6 (d, *J* = 7.0 Hz). HRMS(EI): m/z $[M]^+$ calcd for $C_{17}H_{10}F_8O$ 382.0598; found 382.0611.

3d



Following the general procedure A, the reaction with 1-iodo-4-nitrobenzene (125.1 mg, 0.5 mmol) was conducted to give the **3d₁** in 48% (yellow solid, 84.4 mg, 67% NMR yield) and **3d₂** in 12% (yellow solid, 23.4 mg, 18% NMR yield). **3d₁**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.46–7.57 (m, 5H), 7.78 (d, *J* = 8.8 Hz, 2H), 8.33 (d, *J* = 8.9 Hz, 2H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –109.6 (t, J_{FF} = 12.0 Hz, 2F), –110.1 (t, J_{FF} = 12.0 Hz, 2F), –122.4 (s, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 123.9, 127.0 (t, *J* = 6.3 Hz), 128.6 (t, *J* = 5.9 Hz), 128.8, 130.1 (t, *J* = 25.5 Hz), 132.0, 136.8 (t, *J* = 24.7 Hz), 150.1. HRMS(EI): m/z $[M]^+$ calcd for $C_{15}H_9F_6NO_2$ 349.0532; found 349.0538. **3d₂**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.46–7.58 (m, 5H), 7.80 (d, *J* = 8.7 Hz, 2H), 8.34 (d, *J* = 8.9 Hz, 2H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –110.8 (t, J_{FF} = 14.2 Hz, 2F), –111.1 (t, J_{FF} = 13.7 Hz, 2F), –121.1 (m, 2F), –121.2 (m, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 124.0, 127.1 (t, *J* = 6.3 Hz), 128.7 (t, *J* = 6.1 Hz), 128.9, 130.0 (t, *J* = 24.0 Hz), 132.1, 136.0 (t, *J* = 24.5 Hz), 150.3. HRMS(EI): m/z $[M]^+$ calcd for $C_{16}H_9F_8NO_2$ 399.0500; found, 399.0511.

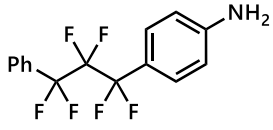
3e



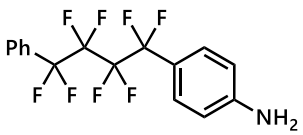
Following the general procedure A, the reaction with ethyl 4-iodobenzoate (140.0 mg, 0.5 mmol) was conducted to give the **3e₁** in 55% (pale yellow oil, 105.9 mg, 67% NMR yield) and **3e₂** in 18% (pale yellow oil, 38.3 mg, 24% NMR yield). **3e₁**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 1.41 (t, *J* = 7.0 Hz, 3H), 4.41 (q, *J* = 7.1 Hz, 2H), 7.44–7.68(m, 5H), 7.66 (d, *J* = 8.2 Hz, 2H), 8.14 (d, *J* = 8.3 Hz, 2H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –109.6 (t, J_{FF} = 12.6 Hz, 2F), –110.1 (t, J_{FF} = 12.0 Hz, 2F), –122.5 (s, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 14.5 (d, *J* = 4.3 Hz), 61.7 (t, *J* = 4.3 Hz), 127.1 (t, *J* = 6.4 Hz), 127.2 (t, *J* = 6.4 Hz), 128.7, 129.8, 130.5 (t, *J* = 23.7 Hz), 131.8, 133.6, 134.8 (t, *J* = 24.9 Hz), 165.9. HRMS(EI): m/z $[M]^+$ calcd for $C_{18}H_{14}F_6O_2$ 376.0893; found 376.0896. **3e₂**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 1.41 (t, *J* = 6.7 Hz, 3H), 4.41 (q, *J* = 7.1 Hz, 2H), 7.45–7.58 (m, 5H), 7.66 (d, *J* = 8.3 Hz, 2H), 8.14 (d, *J* = 8.3 Hz, 2H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –110.9 (t, J_{FF} = 13.7 Hz, 2F), –111.2 (t, J_{FF} = 13.7 Hz, 2F), –121.4– –121.4 (m, 2F),

–121.5– –121.6 (m, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 14.6 (d, J = 5.0 Hz), 61.8 (t, J = 4.8 Hz), 127.2 (t, J = 6.6 Hz), 127.3 (t, J = 6.4 Hz), 128.8, 129.9 (t, J = 25.9 Hz), 132.0, 133.9, 134.1 (t, J = 24.0 Hz), 165.9. HRMS(EI): m/z [M]$^+$ calcd for $C_{19}H_{14}F_8O_2$ 426.0861; found 426.0868.

3f



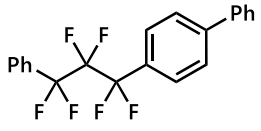
3f$_1$



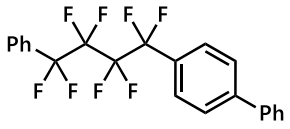
3f$_2$

Following the general procedure A, the reaction with 4-iodoaniline (110.9 mg, 0.5 mmol) was conducted for 24 hours to give the **3f$_1$** in 18% (brown oil, 28.4 mg, 42% NMR yield) and **3f$_2$** in 10% (brown solid, 18.4 mg, 17% NMR yield). **3f$_1$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 3.80 (br, 2H), 6.68 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 7.3 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.59 (d, J = 7.6 Hz, 2H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –108.3 (t, J_{FF} = 11.3 Hz, 2F), –109.6 (t, J_{FF} = 12.5 Hz, 2F), –122.7 (s, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 114.5, 127.1 (t, J = 6.0 Hz), 128.4 (t, J = 5.0 Hz), 128.6, 128.7 (t, J = 16.4 Hz), 130.1 (t, J = 24.3 Hz), 131.5, 149.3. HRMS(EI): m/z [M]$^+$ calcd for $C_{15}H_{11}F_6N$ 319.0790; found 319.0791. **3f$_2$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 3.90 (br, 2H), 6.68 (d, J = 7.5 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H), 7.46 (t, J = 7.5 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.58 (d, J = 7.7 Hz, 2H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –109.2 (m, 2F), –110.5 (t, J_{FF} = 12.8 Hz, 2F), –121.3 (t, J_{FF} = 13.7 Hz, 4F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 114.5, 127.2 (t, J = 6.4 Hz), 128.6, 128.7, 128.8 (t, J = 15.7 Hz), 130.2 (t, J = 24.4 Hz), 131.8, 149.6. HRMS(EI): m/z [M]$^+$ calcd for $C_{16}H_{11}F_8N$ 369.0758; found 369.0758.

3g



3g$_1$

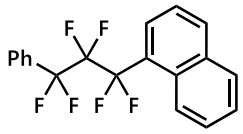


3g$_2$

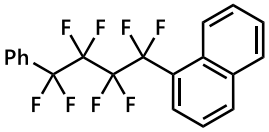
Following the general procedure A, the reaction with 4-iodobiphenyl (143.3 mg, 0.5 mmol) was conducted to give the **3g$_1$** in 51% (pale gray solid, 100.0 mg, 66% NMR yield) and **3g$_2$** in 16% (pale yellow solid, 34.5 mg, 19% NMR yield). **3g$_1$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.42 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.1 Hz, 4H), 7.55 (t, J = 7.3 Hz, 1H), 7.64 (d, J = 8.4 Hz, 4H), 7.69 (t, J = 9.8 Hz, 4H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –109.4 (t, J_{FF} = 12.4 Hz, 2F), –109.6 (t, J_{FF} = 12.5Hz, 2F), –122.5 (s, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 127.1 (t, J = 5.9 Hz), 127.3, 127.5, 127.6, 128.4, 128.7, 129.3, 129.6 (t, J = 23.8 Hz), 130.8 (t, J = 24.1 Hz), 131.7, 140.2, 144.6. HRMS(EI): m/z [M]$^+$ calcd for $C_{21}H_{14}F_6$ 380.0994; found 380.0999. **3g$_2$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.40 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.1 Hz, 4H), 7.55 (t, J = 7.2 Hz, 1H), 7.61 (d, J = 7.8 Hz, 4H), 7.67 (q, J = 8.5 Hz, 4H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –110.5 (t, J_{FF} = 13.6 Hz, 2F), –110.8 (t, J_{FF} = 13.1 Hz, 2F), –121.4 (m, 4F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 127.2 (t, J = 6.4 Hz), 127.5, 127.6, 127.7 (t, J = 7.0 Hz), 128.5, 128.8, 128.8 (t, J = 24.1 Hz), 129.3, 130.1 (t, J = 24.4 Hz), 131.9, 140.1, 144.9. HRMS(EI): m/z [M]$^+$ calcd for $C_{22}H_{14}F_8$ 430.0962; found

430.0975.

3h



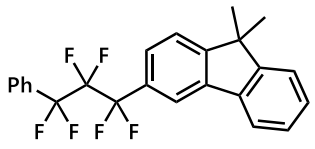
3h$_1$



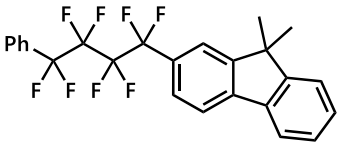
3h$_2$

Following the general procedure A, the reaction with 1-iodonaphthalene (125.8 mg, 0.5 mmol) was conducted to give the **3h$_1$** in 55% (pale yellow oil, 95.9 mg, 60% NMR yield) and **3h$_2$** in 11% (pale yellow oil, 22.2 mg, 14% NMR yield). **3h$_1$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.47–7.62 (m, 6H), 7.67 (d, J = 7.6 Hz, 2H), 7.84 (d, J = 7.3 Hz, 1H), 7.91 (d, J = 7.9 Hz, 1H), 8.02 (d, J = 8.2 Hz, 1H), 8.32 (d, J = 8.4 Hz, 1H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –103.3 (t, J_{FF} = 13.1 Hz, 2F), –109.6 (t, J_{FF} = 13.1 Hz, 2F), 120.5 (s, 2F). ^{13}C NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 124.54, 125.51,125.55,125.57,125.60,125.63,125.66, 125.7, 126.5 (t, J = 19.3 Hz), 127.1 (t, J = 6.4 Hz), 127.6, 128.0 (t, J = 9.9 Hz), 128.6, 129.2, 130.7, 130.7 (t, J = 24.3 Hz), 131.6, 133.1, 134.4. HRMS(EI): m/z $[M]^+$ calcd for $C_{19}H_{12}F_6$ 354.0838; found 354.0840. **3h$_2$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.56–7.61 (m, 8H), 7.82 (d, J = 7.3 Hz, 1H), 7.91 (d, J = 8.3 Hz, 1H), 8.03 (d, J = 8.2 Hz, 1H), 8.26 (d, J = 8.3 Hz, 1H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –104.3 (br, 2F), –110.5 (br, 2F), –119.6 (br, 2F), –121.6 (br, 2F). ^{13}C NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 124.6, 125.5 (br), 125.8 (t, J = 21.8 Hz), 126.6 (t, J = 6.2 Hz), 127.8, 128.3 (t, J = 9.8 Hz), 128.8, 129.2, 130.1(t, J = 24.4 Hz), 130.7, 131.9, 133.4, 134.4. One carbon was missing probably due to overlapping. HRMS(EI): m/z $[M]^+$ calcd for $C_{20}H_{12}F_8$ 404.0806; found 404.0801.

3i



3i$_1$

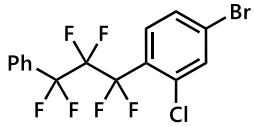


3i$_2$

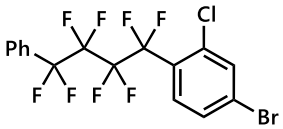
Following the general procedure A, the reaction with 2-iodo-9,9-dimethylfluorene (161.4 mg, 0.5 mmol) was conducted to give the **3i$_1$** in 53% (pale yellow oil, 112.3 mg, 67% NMR yield) and **3i$_2$** in 16% (pale yellow solid, 37.1 mg, 21% NMR yield). **3i$_1$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 1.52 (s, 6H), 7.40–7.42 (m, 2H), 7.47–7.65 (m, 8H), 7.76–7.81 (m, 2H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –108.6 (t, J_{FF} = 12.6 Hz, 2F), –109.6 (t, J_{FF} = 12.0 Hz, 2F), –122.4 (s, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 27.2 (d, J = 4.8 Hz), 47.4, 120.1, 121.0, 121.5, 123.1, 126.2 (t, J = 6.4), 127.1 (t, J = 6.2Hz), 127.5, 128.6, 128.7, 129.2 (t, J = 23.9 Hz), 130.9 (t, J = 24.3 Hz), 131.6, 138.2, 142.7,153.9, 154.5. HRMS(EI): m/z $[M]^+$ calcd for 420.1307; found 420.1309. **3i$_2$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 1.51 (s, 6H), 7.35–7.40 (m, 2H), 7.35–7.62 (m, 8H), 7.76–7.80 (m, 2H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –109.7 (t, J_{FF} = 14.6 Hz, 2F), –110.7 (t, J_{FF} = 14.2 Hz, 2F), –121.1 (m, 2F), –121.5 (m, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 27.2 (d, J = 6.7 Hz), 47.4, 120.1, 120.2, 121.0, 121.6, 123.1, 126.3 (t, J = 6.6 Hz), 127.2 (t, J = 5.5 Hz), 127.6, 128.5 (t, J =

24.4 Hz), 128.8, 130.1 (t, J = 24.1 Hz), 131.9, 138.1, 143.0, 154.0, 154.5. One carbon was missing probably due to overlapping. HRMS(EI): m/z $[M]^+$ calcd for $C_{24}H_{18}F_6$ 470.1275; found 470.1288.

3j



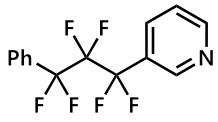
3j$_1$



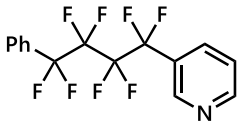
3j$_2$

Following the general procedure A, the reaction with 4-bromo-2-chloro-1-iodobenzene (158.7 mg, 0.5 mmol) was conducted to give the **3j$_1$** in 42% (yellow oil, 87.3 mg, 52% NMR yield) and **3j$_2$** in 8% (yellow oil, 19.1 mg, 12% NMR yield). **3j$_1$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.44–7.56 (m, 5H), 7.61 (d, J = 7.4 Hz, 2H), 7.66 (s, 1H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –106.3 (t, J_{FF} = 13.3 Hz, 2F), –109.9 (t, J_{FF} = 12.7 Hz, 2F), –120.7 (s, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 126.4, 126.8 (t, J = 6.3 Hz), 127.1 (t, J = 23.7 Hz), 128.4, 130.0, 130.2 (t, J = 23.9 Hz), 131.1 (t, J = 8.7 Hz), 131.5, 134.5 (t, J = 2.9 Hz), 134.6 (d, J = 3.3 Hz). HRMS(EI): m/z $[M]^+$ calcd for $C_{15}H_8BrClF_6$ 415.9397; found 415.9400. **3j$_2$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.44–7.55 (m, 5H), 7.59 (d, J = 7.5 Hz, 2H), 7.68 (s, 1H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –112.1 (t, J_{FF} = 14.7 Hz, 2F), –115.5 (t, J_{FF} = 14.1 Hz, 2F), –124.4 (m, 2F), –126.4 (m, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 126.8 (t, J = 23.7 Hz), 127.0, 127.2, 128.8, 129.9 (t, J = 24.3 Hz), 130.4, 131.5 (t, J = 8.3 Hz), 132.0, 135.0 (t, J = 2.7 Hz), 135.1 (d, J = 3.0 Hz). HRMS(EI): m/z $[M]^+$ calcd for $C_{16}H_8BrClF_8$ 465.9365; found 465.9369.

3k



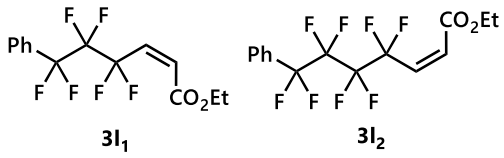
3k$_1$



3k$_2$

Following the general procedure A, the reaction with 3-iodopyridine (103.4 mg, 0.5 mmol) was conducted to give the **3k$_1$** in 52% (pale yellow oil, 80.5 mg, 67% NMR yield) and **3k$_2$** in 3% (pale yellow oil, 5.9 mg, 15% NMR yield). **3k$_1$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.39–7.58 (m, 6H), 7.89 (d, J = 8.3 Hz, 1H), 8.82 (d, J = 24.4 Hz, 2H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –109.6 (t, J_{FF} = 12.4 Hz, 2F), –110.5 (t, J_{FF} = 11.9 Hz, 2F), –122.7 (s, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 123.5, 127.0 (t, J = 6.6 Hz), 128.7, 130.3 (t, J = 24.2 Hz), 131.8, 134.9 (t, J = 6.2 Hz), 148.3 (t, J = 5.9 Hz), 152.8. One carbon is missing probably due to overlapping. HRMS(EI): m/z $[M]^+$ calcd for $C_{14}H_9F_6N$ 305.0634; found 305.0640. **3k$_2$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.44–7.59 (m, 6H), 7.89 (d, J = 8.0 Hz, 1H), 8.83 (d, J = 11.6 Hz, 2H), ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –110.9 (t, J_{FF} = 14.0 Hz, 2F), –111.6 (t, J_{FF} = 13.7 Hz , 2F), –121.3 (m, 2F), –121.6 (m, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 123.6, 127.2 (t, J = 6.9 Hz), 128.8, 129.7 (t, J = 24.5 Hz), 132.0, 135.0, 148.4, 153.0. One peak is missing due to an overlap. HRMS(EI): m/z $[M]^+$ calcd for $C_{15}H_9F_8N$ 355.0602; found 355.0595.

3l

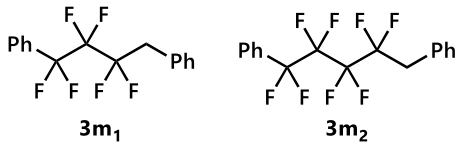


$3l_1$ **$3l_2$**

Following the general procedure A, the reaction with ethyl (Z)-3-iodoacrylate (111.8 mg, 0.5 mmol) was conducted to give the **$3l_1$** in 51% (pale yellow oil, 82.1 mg, 67% NMR yield). **$3l_1$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 1.28 (t, J = 7.2 Hz, 3H), 4.24 (q, J = 14.3 Hz, 2H), 5.94 (dt, J = 13.9 Hz, 1H), 6.34 (dt, J = 2.5 Hz, 12.8 Hz, 1H), 7.46–7.59 (m, 5H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –109.1 (q, J_{FF} = 12.1 Hz, 2F), –110.2 (t, J_{FF} = 10.9 Hz, 2F), –124.1 (s, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 14.2 (d, J = 4.2 Hz), 61.9 (t, J = 6.7 Hz), 124.5 (t, J = 23.6 Hz), 127.1 (t, J = 6.6 Hz), 128.8, 130.2 (t, J = 24.0 Hz), 130.7 (t, J = 5.0 Hz), 131.9, 164.8. HRMS(ESI): m/z $[M+Na]^+$ calcd for $C_{14}H_{12}F_6NaO_2$ 349.0634; found 349.06337.

We failed to isolate **$3l_2$** in pure form, but the presence of the compound was estimated by analysis of crude ^{19}F NMR (17% yield) and HRMS. **$3l_2$**: ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –109.9 (t, J_{FF} = 12.0 Hz, 2F), –110.8 (t, J_{FF} = 12.6 Hz, 2F), –121.7 (br, 2F), –122.8 (br, 2F). HRMS(ESI): m/z $[M+Na]^+$ calcd for $C_{15}H_{12}F_8O_2Na$ 399.0602; found 399.05988.

3m

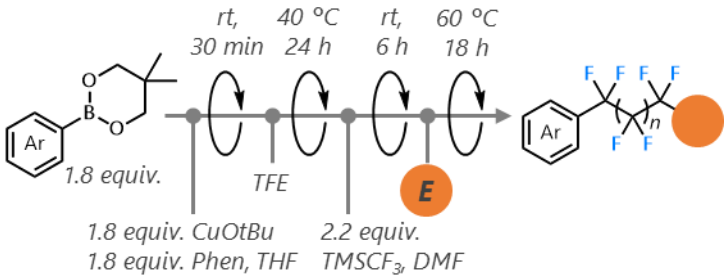


$3m_1$ **$3m_2$**

Following the modified general procedure A, the reaction with benzyl bromide (84.6 mg, 0.5 mmol) was conducted at 80 °C for 24 hours to give the **$3m_1$** in 42% (pale yellow solid, 65.5 mg, 61% NMR yield). **$3m_1$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 3.47 (t, J = 19.4 Hz, 2H), 7.40–7.72 (m, 10H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –110.0 (t, J_{FF} = 11.3 Hz, 2F), –112.3 (hepta, J = 11.2 Hz, 2F), –123.9 (s, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 37.6 (t, J = 21.9 Hz), 126.8 (t, J = 6.2 Hz), 127.6, 127.9, 128.4, 128.5, 129.9, 130.9, 131.4. HRMS(EI): m/z $[M]^+$ calcd for $C_{16}H_{12}F_6$, 318.0838; found 318.0848.

We failed to isolate **$3m_2$** in pure form, but the presence of the compound was estimated by analysis of crude ^{19}F NMR (7% yield) and HRMS. **$3m_1$**: ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –110.7 (br, 2F), –113.3 (br, 2F), –121.6 (br, 2F), –123.9 (br, 2F). HRMS(EI): m/z $[M]^+$ calcd for $C_{17}H_{12}F_8$ 368.0806; found 368.0807.

One-pot synthesis from aryl boronic acid esters (Figure 3)

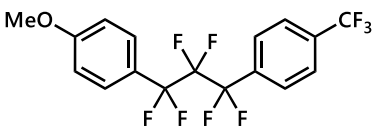


General procedure B

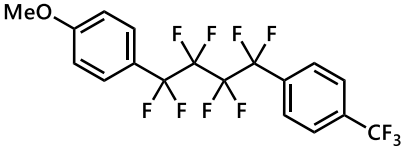
A solution of [CuO^{t}Bu] (0.90 mmol, 123 mg) and 1,10-phenanthroline (0.90 mmol, 162 mg) in THF (7 mL) was prepared in an autoclave reactor. To this solution, 5,5-dimethyl-2-aryl-1,3,2-dioxaborinane (0.90 mmol) was added, and then TFE (3.5 atm) was charged into the reactor. The reaction mixture was heated at 40 °C for 24 hours. After removal of TFE under reduced pressure, $TMSCF_3$ (1.1 mmol, 160 µL) and DMF (2.5 mL) were added to the reaction mixture followed by stirring for 6 hours at room temperature. Then, 4-iodobenzotrifluoride (0.50 mmol, 136 mg) was added, and the resultant solution was heated at 60 °C for 18 hours. After cooling the reaction mixture, $PhCF_3$ (internal standard, 0.8 mmol, 100 µL) was added, and a portion of the mixture was added to a small test tube. To the tube was added $CDCl_3$ and the resultant precipitate was removed by filtration. The ^{19}F NMR spectrum was measured to determine the NMR yield. The reaction mixture was filtered and poured into a separatory funnel and diluted with organic solvent (65 mL, Et_2O, ethyl acetate, and hexane). The organic layer was washed with H_2O (10 mL × 3) and brine (5 mL × 1), and dried over Na_2SO_4. After filtration and removal of the solvent under vacuum, the residue was purified by HPLC with $CHCl_3$ to afford the desired products.

Compounds **4** were prepared by the same procedure except for use of halogenating agent (1.8 mmol) instead of 4-iodobenzotrifluoride, and the yields were calculated based on the amount of aryl boronic acid ester.

3n



3n$_1$

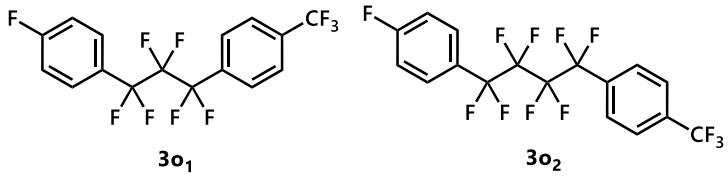


3n$_2$

Following the general procedure B, the reaction with 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane[3] (200.1 mg, 0.5 mmol) was conducted to give the **3n$_1$** in 46% (pale yellow solid, 91.2 mg, 62% NMR yield) and **3n$_2$** in 13% (pale yellow solid, 33.3 mg, 17% NMR yield). **3n$_1$**: ^1H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 3.84 (s, 3H), 6.90 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 7.73 (s, 4H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –63.3 (s, 3F), –108.5 (t, J_{FF} = 12.3 Hz, 2F), –110.2 (t, J_{FF} = 11.6 Hz, 2F), –122.7 (s, 2F). ^{13}C {^1H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 55.3 (d, J = 8.0 Hz), 113.8, 122.0 (t, J = 25.7 Hz), 124.9 (t, J = 272.8 Hz), 125.4, 127.4 (t, J = 6.4 Hz), 128.3 (t, J = 6.3 Hz), 133.4 (t, J = 32.8 Hz), 134.2 (t, J = 25.4 Hz), 162.0. HRMS(EI): m/z [M]+ calcd for $C_{17}H_{11}F_9O$, 402.0661; found 402.0659. **3n$_2$**: ^1H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 3.85 (s, 3H), 6.96 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.74 (q, J = 8.3, 12.5 Hz, 4H). ^{19}F NMR (376 MHz,

in $CDCl_3$, rt, δ/ppm): –63.2 (s, 3F), –109.8 (t, J_{FF} = 11.8 Hz, 2F), –111.2 (t, J_{FF} = 13.3 Hz, 2F), –121.4 (m, 4F). ^{13}C {^1H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 55.7 (d, J = 8.9 Hz), 114.2, 121.8 (t, J = 24.6 Hz), 125.2 (t, J = 272.6 Hz), 125.9 (d, J = 3.8 Hz), 127.9 (t, J = 5.8 Hz), 128.8 (t, J = 5.8 Hz), 133.8 (t, J = 24.7 Hz), 134.2 (t, J = 33.2 Hz), 162.5. HRMS(EI): m/z [M]$^+$ calcd for $C_{18}H_{11}F_{11}O$ 452.0629; found 452.0632.

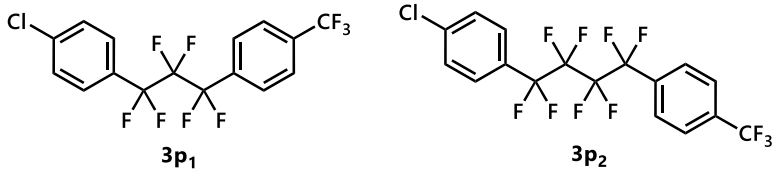
3o



3o$_1$ **3o$_2$**

Following the general procedure B, the reaction with 2-(4-fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane[3] (189.5 mg, 0.9 mmol) was conducted to give the **3o$_1$** in 33% (brown oil, 64.9 mg, 44% NMR yield) and **3o$_2$** in 9% (brown solid, 20.2 mg, 11% NMR yield, containing some impurities). **3o$_1$**: ^1H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.16 (t, J = 8.7 Hz, 2H), 7.57 (q, J = 8.7 Hz, 2H), 7.73 (q, J = 14.2 Hz, 4H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –63.3 (s, 3F), –108.2 (m, 1F), –108.9 (t, J = 12.3 Hz, 2F), –110.2 (t, J = 12.2 Hz, 2F), –122.5 (s, 2F). ^{13}C {^1H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 116.1 (d, J = 22.3 Hz), 125.2 (t, J = 272.4 Hz), 125.8 (q, J = 3.3 Hz), 126.4 (td, J = 25.0, 3.1 Hz), 127.8 (t, J = 6.1 Hz), 129.5 (q, J = 6.3, 14.8 Hz), 134.1 (t, J = 32.6 Hz), 134.3 (t, J = 24.6 Hz), 165.0 (d, J = 251.7 Hz). HRMS(EI): m/z [M]+ calcd for $C_{16}H_8F_{10}$ 390.0461; found 390.0461. **3o$_2$**: ^1H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.16 (t, J = 8.7 Hz, 2H), 7.58 (q, J = 5.1, 8.7 Hz, 2H), 7.74 (q, J_1 = 8.7 Hz, J_2 = 16.2 Hz, 4H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –63.2 (s, 3F), –107.7 (m, 1F), –110.1 (t, J_{FF} = 13.0 Hz, 2F), –111.2 (t, J_{FF} = 13.0 Hz, 2F), –121.3–121.4 (m, 4F). ^{13}C {^1H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 116.2 (d, J = 22.3 Hz), 125.1 (t, J = 272.9 Hz), 126.0 (td, J_1 = 11.2, 3.4 Hz), 127.9 (t, J = 5.8 Hz), 129.6 (q, J = 7.1 Hz), 133.6 (t, J = 24.5 Hz), 134.0 (t, J = 32.6 Hz), 165.1 (d, J = 252.1 Hz). One carbon was missing probably due to overlapping or low intensity. HRMS(EI): m/z [M]$^+$ calcd for $C_{17}H_8F_{12}$ 440.0429; found 440.0440.

3p

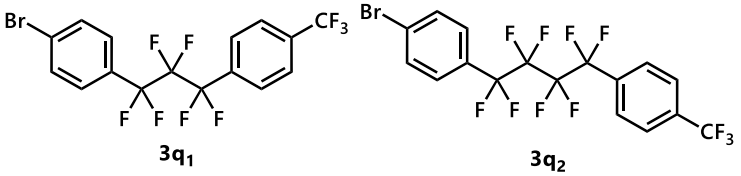


3p$_1$ **3p$_2$**

Following the general procedure B, the reaction with 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane[3] (205.7 mg, 0.9 mmol) was conducted to give the **3p$_1$** in 45% (pale yellow solid, 91.0 mg, 72% NMR yield) and **3p$_2$** in 6% (pale yellow solid, 12.5 mg containing certain amount of impurity, 15% NMR yield). **3p$_1$**: ^1H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.49 (q, J = 8.7, 23.7 Hz, 4H), 7.73 (q, J = 8.6, 14.6 Hz, 4H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –63.4 (s, 2F), –109.6 (t, J_{FF} = 12.5 Hz, 2F), –110.2 (t, J_{FF} = 11.8 Hz, 2F), –122.6 (s, 2F). ^{13}C {^1H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 125.2 (t, J = 272.2 Hz), 125.8 (d, J = 3.5 Hz), 127.8 (t, J = 6.3 Hz), 128.9, 129.2, 133.8 (t, J = 32.8 Hz), 134.2 (t, J = 24.3 Hz), 138.4. One carbon was missing probably due to overlapping. HRMS(EI): m/z [M]$^+$ calcd for $C_{16}H_8ClF_9$ 406.0165; found 406.0178. **3p$_2$**: ^1H NMR (400

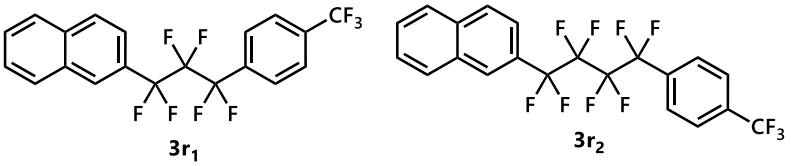
MHz, in $CDCl_3$, rt, δ/ppm): 7.49 (q, J = 8.7 Hz, 4H), 7.74 (q, J = 8.5 Hz, 4H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –63.3 (s, 3F), –110.8 (t, J_{FF} = 13.4 Hz, 2F), –111.2 (t, J_{FF} = 14.0 Hz, 2F), –121.4 (q, J = 12.2 Hz, 4F). ^{13}C NMR spectrum of the pure sample was not obtained due to low yield of the product and low intensity of the signals coupling with ^{19}F nuclei. HRMS(EI): m/z $[M]^+$ calcd for $C_{17}H_8ClF_{11}$ 456.0133; found 456.0131.

3q



Following the general procedure B, the reaction with 2-(4-bromophenyl)-5,5-dimethyl-1,3,2-dioxaborinane[3] (244.5 mg, 0.9 mmol) was conducted to give the **3q$_1$** in 46% (pale yellow solid, 103.8 mg, 67% NMR yield) and **3q$_2$** in 13% (pale yellow solid, 27.4 mg, 17% NMR yield). **3q$_1$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.44 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.73 (q, J = 8.4 Hz, 4H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –63.4 (s, 3F), –109.8 (t, J_{FF} = 12.3 Hz, 2F), –110.2 (t, J_{FF} = 11.9 Hz, 2F), –122.6 (s, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 125.2 (t, J = 272.9 Hz), 125.8 (d, J = 3.7 Hz), 126.8 (t, J = 1.9 Hz), 127.8 (t, J = 6.2 Hz), 128.7 (t, J = 6.4 Hz), 129.4 (t, J = 24.7 Hz), 132.2, 133.8 (t, J = 32.4 Hz), 134.2 (t, J = 25.0 Hz). HRMS(EI): m/z $[M]^+$ calcd for $C_{16}H_8BrF_9$ 449.9660; found 449.9668. **3q$_2$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.44 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 7.74 (q, J = 8.5 Hz, 4H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –63.3 (s, 3F), –111.0 (t, J_{FF} = 12.8 Hz, 2F), –111.3 (t, J_{FF} = 12.8 Hz, 2F), –121.3– –121.5 (m, 4F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 125.1 (dq, J = 4.4 Hz), 126.8 (dq, J = 4.0 Hz), 127.1 (q, J = 5.4 Hz), 128.0 (q, J = 6.5 Hz), 128.7 (q, J = 5.6 Hz), 129.6 (q, J = 5.5 Hz), 131.4 (d, J = 5.5 Hz), 133.1 (d, J = 5.6 Hz). HRMS(EI): m/z $[M]^+$ calcd for $C_{17}H_8BrF_{11}$ 499.9628; found 499.9632.

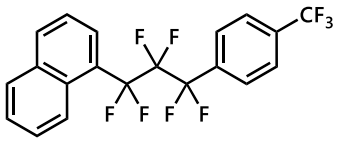
3r



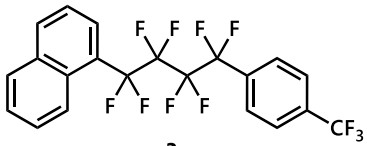
Following the general procedure B, the reaction with 5,5-dimethyl-2-(2-naphthyl)-1,3,2-dioxaborinane[3] (215.5 mg, 0.9 mmol) was conducted to give the **3r$_1$** in 55% (white solid, 114.5 mg, 79% NMR yield). ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.50–7.65 (m, 3H), 7.74 (s, 4H), 7.86–7.95 (m, 3H), 8.13 (s, 1H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –63.4 (s, 3F), –109.0 (t, J_{FF} = 11.7 Hz, 2F), –110.1 (t, J_{FF} = 11.6 Hz, 2F), –122.4 (s, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 123.1 (t, J = 5.7 Hz), 125.2 (t, J = 272.9 Hz), 125.8 (d, J = 3.6 Hz), 126.2, 127.3, 127.6, 127.8 (t, J = 7.0 Hz), 128.1, 128.2 (t, J = 84.4 Hz), 128.4, 128.8, 129.2, 132.6, 134.4 (t, J = 24.1 Hz), 134.8. HRMS(EI): m/z $[M]^+$ calcd for $C_{20}H_{11}F_9$ 422.0712; found 422.0723.

We failed to isolate **3r$_2$** in pure form, but the presence of the compound was estimated by HRMS of crude. **3r$_2$**: HRMS(EI): m/z $[M]^+$ calcd for $C_{21}H_{11}F_{11}$ 472.0680; found 472.0674.

3s



3s$_1$



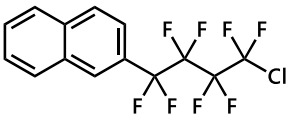
3s$_2$

Following the general procedure B with the modification of reaction time to 24 hours after addition of $TMSCF_3$, the reaction with 5,5-dimethyl-2-(1-naphthyl)-1,3,2-dioxaborinane[3] (217.6 mg, 0.9 mmol) was conducted to give the **3s$_1$** in 59% (brown oil, 122.5 mg, 78% NMR yield). **3s$_1$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.51–7.62 (m, 3H), 7.76 (q, J_1 = 8.8 Hz, J_2 = 13.6 Hz, 4H), 7.82 (d, J = 7.1 Hz, 1H), 7.90 (d, J = 7.7 Hz, 1H), 8.02 (d, J = 8.2 Hz, 1H), 8.27 (d, J = 8.2 Hz, 1H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –63.2 (s, 3F), –103.2 (t, J_{FF} = 13.1 Hz, 2F), –110.1 (t, J_{FF} = 12.8 Hz, 2F), –120.6 (s, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 122.5 (t, J = 272.0 Hz), 124.5, 125.4 (dq, J = 3.1 Hz), 125.7 (d, J = 3.3 Hz), 126.0 (t, J = 22.5 Hz), 126.5, 127.7, 127.8 (t, J = 7.1 Hz), 128.0 (t, J = 10.0 Hz), 129.2, 130.6, 133.3, 133.8 (t, J = 33.3 Hz), 134.4, 134.5 (t, J = 24.4 Hz). HRMS(EI): m/z $[M]^+$ calcd for $C_{20}H_{11}F_9$ 422.0712; found 422.0712.

We failed to isolate **3s$_2$**, which was observed in the crude reaction mixture (NMR yield was 7%), in pure form in this single experiment. Instead, collection of samples of several trials and purification with HPLC gave analytically meaningful sample as a brown solid. ^{13}C NMR spectrum of the pure sample was not obtained due to low yield of the product and low intensity of the signals coupling with ^{19}F nuclei. **3s$_2$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.52–7.61 (m, 3H), 7.75 (s, 4H), 7.81 (d, J = 7.0 Hz, 1H), 7.91 (d, J = 8.3 Hz, 1H), 8.03 (d, J = 8.2 Hz, 1H), 8.23 (d, J = 7.9 Hz, 1H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –63.3 (s, 3F), –104.6 (t, J_{FF} = 14.7 Hz, 2F), –111.1 (t, J_{FF} = 14.5 Hz, 2F), –119.5 (m, 2F), –121.5– –121.7 (m, 2F). HRMS(EI): m/z $[M]^+$ calcd for $C_{21}H_{11}F_{11}$ 472.0680; found 472.0681.

4a

4a$_1$

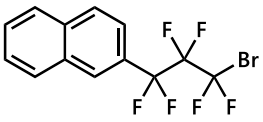


4a$_2$

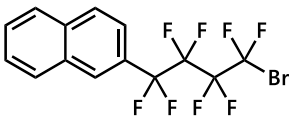
Following the general procedure B using 5,5-dimethyl-2-(2-naphthyl)-1,3,2-dioxaborinane (217.6 mg, 0.9 mmol), the reaction with *p*-toluenesulfonyl chloride (344.3 mg, 1.8 mmol) was conducted to give the **4a$_1$** in 43% (yellow solid, 120.7 mg, 52% NMR yield). **4a$_1$**: ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.58–7.65 (m, 3H), 7.94 (q, J = 8.1 Hz, 3H), 8.15 (s, 1H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –66.7 (t, J_{FF} = 13.2 Hz, 2F), –109.4 (t, J_{FF} = 13.0 Hz, 2F), –120.2 (s, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 122.9, 127.0 (t, J = 24.1 Hz), 127.5, 128.0 (t, J = 7.3 Hz), 128.1, 128.5, 129.0, 129.2, 132.6, 134.9. HRMS(EI): m/z $[M]^+$ calcd for $C_{13}H_7ClF_6$ 312.0135; found 312.0132.

4a$_2$ was not characterized due to low intensity and complexity of crude ^{19}F NMR spectrum.

4b



4b$_1$

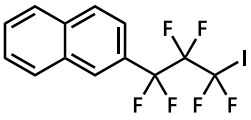


4b$_2$

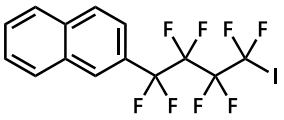
Following the general procedure B using 5,5-dimethyl-2-(2-naphthyl)-1,3,2-dioxaborinane (217.6 mg, 0.9 mmol), the reaction with *N*-bromosuccinimide (234.9 mg, 1.8 mmol) was conducted to give the **4b** in 38% (yellow solid, 118.7 mg, 41% NMR yield). ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.58–7.65 (m, 3H), 7.90-7.95 (m, 3H), 8.14 (s, 1H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –64.7 (tt, J = 13.6, 2.7 Hz, 2F), –112.2 (t, J_{FF} = 13.3 Hz, 2F), –120.2 (s, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 122.9 (t, J = 5.7 Hz), 127.1 (t, J = 24.1 Hz), 127.4, 128.0 (t, J = 7.0 Hz), 128.2, 128.5, 129.0, 129.2, 132.6, 134.9. HRMS(EI): m/z $[M]^+$ calcd for $C_{13}H_7BrF_6$ 355.9630; found 355.9631.

4b$_2$ was not characterized due to low intensity and complexity of crude ^{19}F NMR spectrum.

4c



4c$_1$

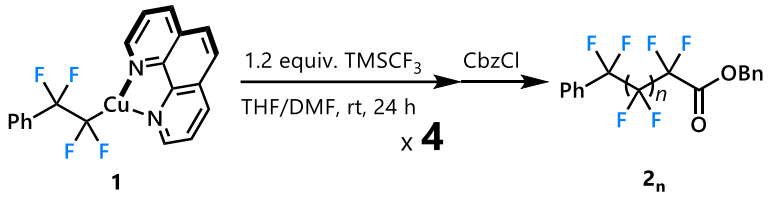


4c$_2$

Following the general procedure B using 5,5-dimethyl-2-(2-naphthyl)-1,3,2-dioxaborinane (217.6 mg, 0.9 mmol), the reaction with I_2 (454.7 mg, 1.8 mmol) was conducted to give the **4c$_1$** in 44% (orange solid, 160.8 mg, 52% NMR yield). ^{1}H NMR (400 MHz, in $CDCl_3$, rt, δ/ppm): 7.60–7.65 (m, 3H), 7.91–7.94 (m, 3H), 8.15 (s, 1H). ^{19}F NMR (376 MHz, in $CDCl_3$, rt, δ/ppm): –59.8 (m, 2F), –111.8 (t, J_{FF} = 13.7 Hz, 2F), –116.0 (t, J_{FF} = 4.9 Hz, 2F). ^{13}C {^{1}H} NMR (100.6 MHz, in $CDCl_3$, rt, δ/ppm): 122.9 (t, J = 5.6 Hz), 127.3 (t, J = 24.1 Hz), 127.4, 127.9 (t, J = 6.8 Hz), 128.1, 128.5, 128.9, 129.2, 132.5, 134.9. HRMS(EI): m/z $[M]^+$ calcd for $C_{13}H_7F_6I$ 403.9491; found 403.9508.

4c$_2$ was not characterized due to low intensity and complexity of crude ^{19}F NMR spectrum.

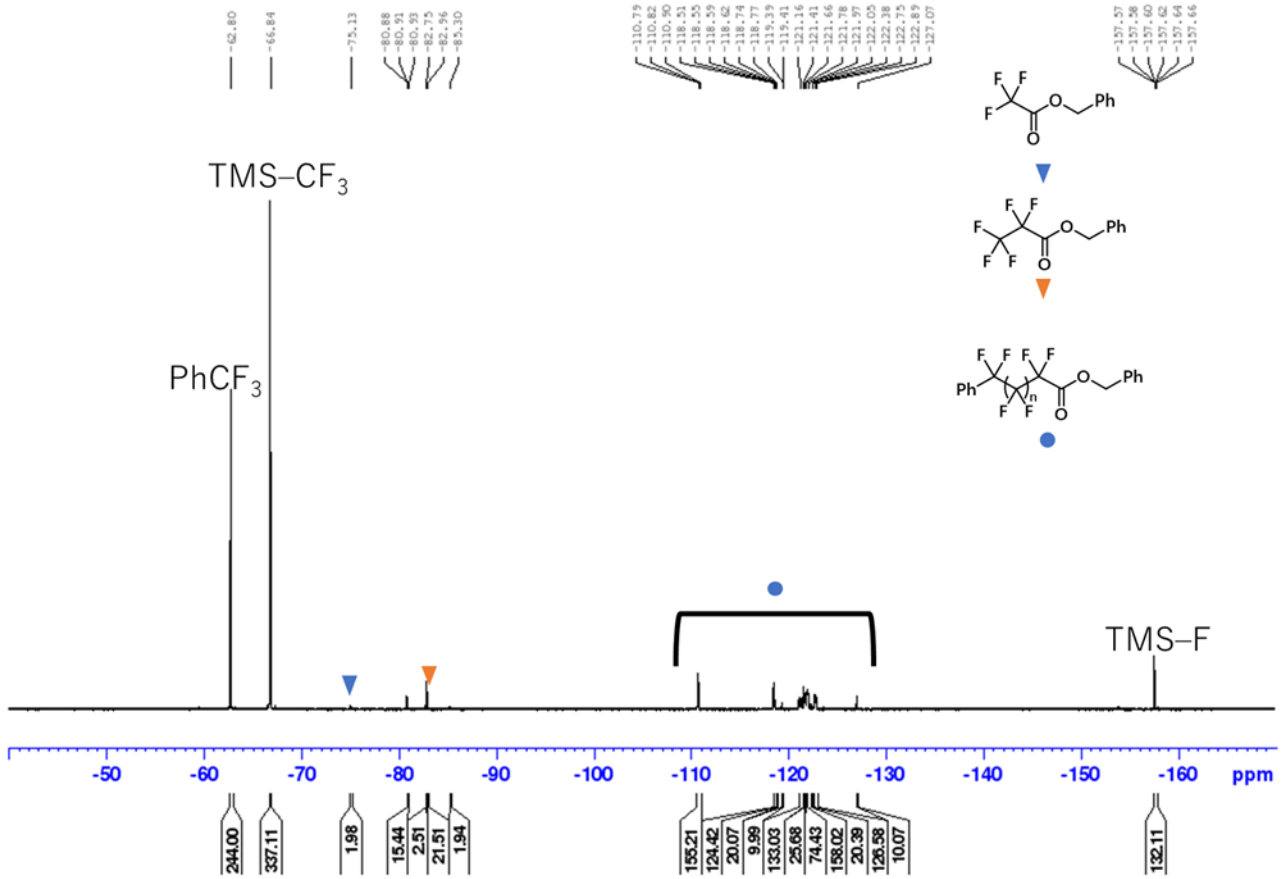
Further elongation of fluoroalkyl chain (Figure 4)



Experimental procedure

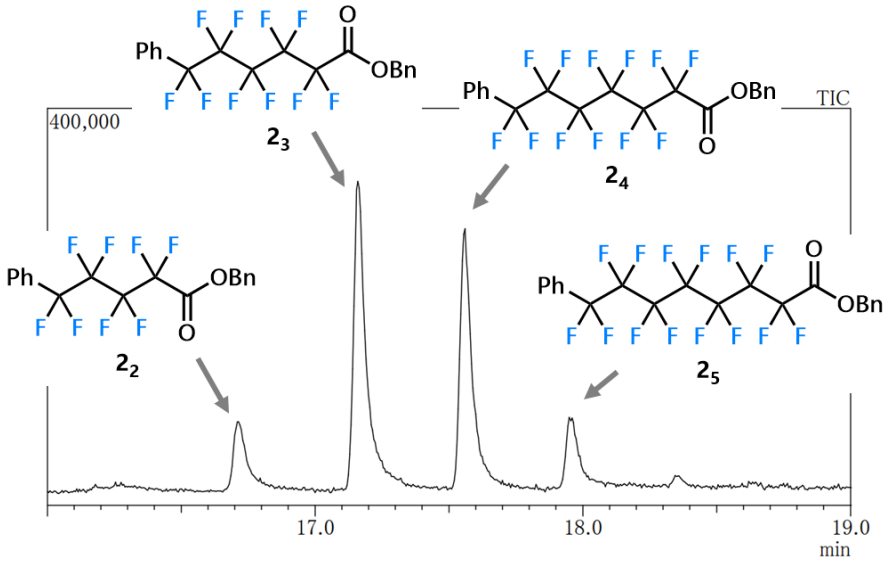
In a vial, **1** (42 mg, 0.1 mmol) was dissolved in DMF/THF = 1:3 (1 mL). To this solution was added $TMSCF_3$ (18 μL, 0.12 mmol). The reaction mixture was stirred for 24 hours at room temperature. Then, the sequence of addition of $TMSCF_3$ and stirring 24 hours was repeated three times (total amount of $TMSCF_3$ was 0.48 mmol). The reaction mixture was added CbzCl (0.7 mmol, 0.1 mL) and stirred for 1 hour at room temperature. The crude product was analyzed by ^{19}F NMR, GCMS, and HRMS.

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



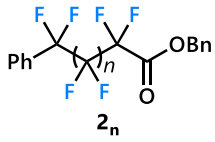
Analysis of ^{19}F NMR revealed that a significant amount of $TMSCF_3$ was remained.

Analysis of GCMS (low resolution) chart



Product	m/z $[M]^+$ calculated	found
$\mathbf{2_2}$	412.0704	412
$\mathbf{2_3}$	462.0672	462
$\mathbf{2_4}$	512.0640	512
$\mathbf{2_5}$	562.0608	562

HRMS (EI)



Product	m/z $[M]^+$ calculated	found
$\mathbf{2_3}$	462.0672	462.0664
$\mathbf{2_4}$	512.0640	512.0634
$\mathbf{2_5}$	562.0608	562.0599
$\mathbf{2_6}$	612.0576	612.0579
$\mathbf{2_7}$	662.0544	662.0563
$\mathbf{2_8}$	712.0512	712.0516

Crystallographic studies of 3b$_n$

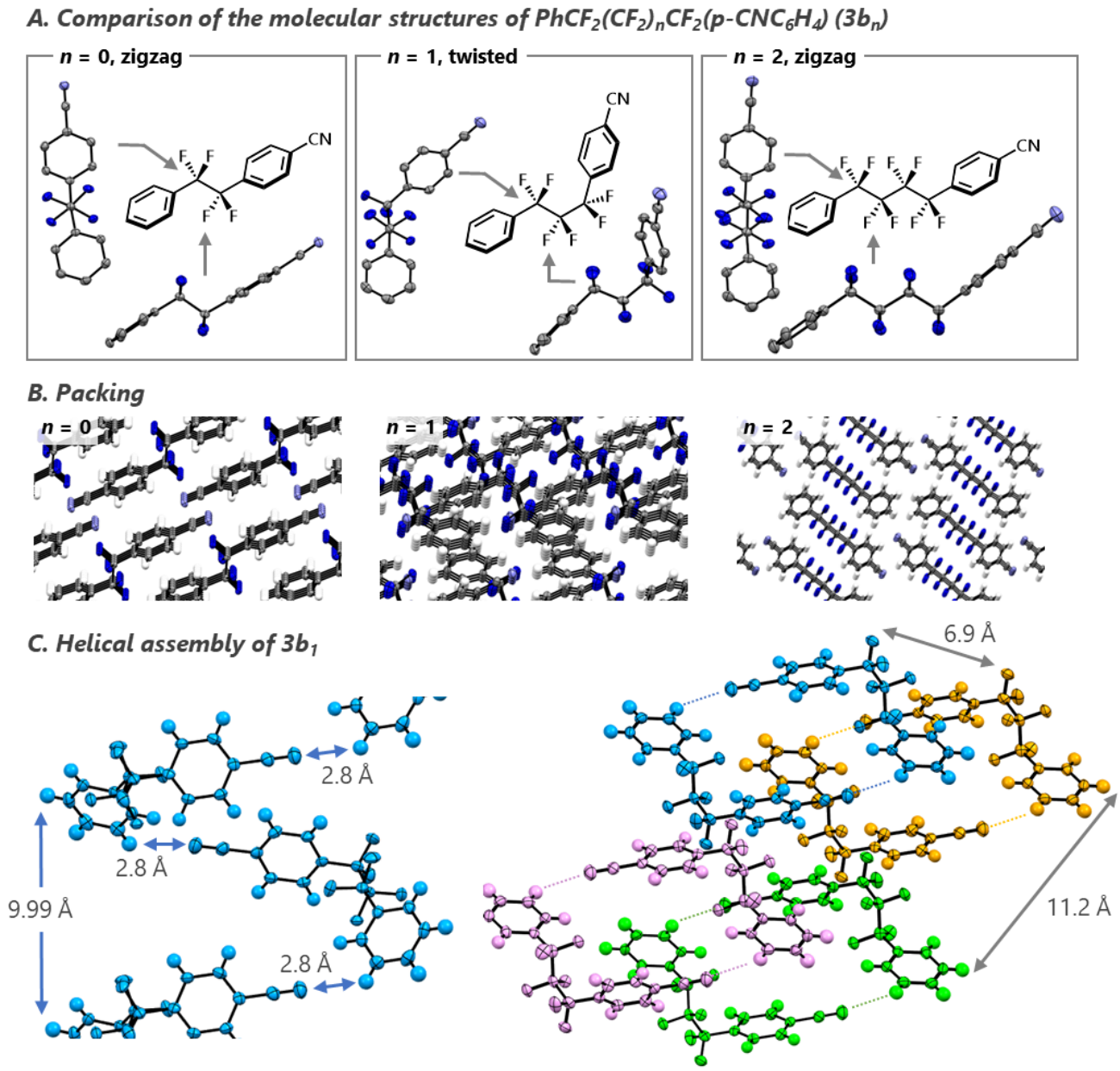
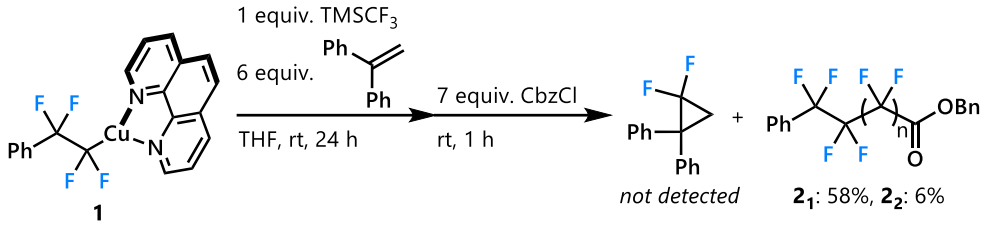


Figure S1. The crystallographic studies of 3b$_0$, 3b$_1$, and 3b$_2$.

3b$_0$ was synthesized by following the literature procedure.[1] The single crystals suitable for X-ray studies were prepared by recrystallization from hot hexane solutions.

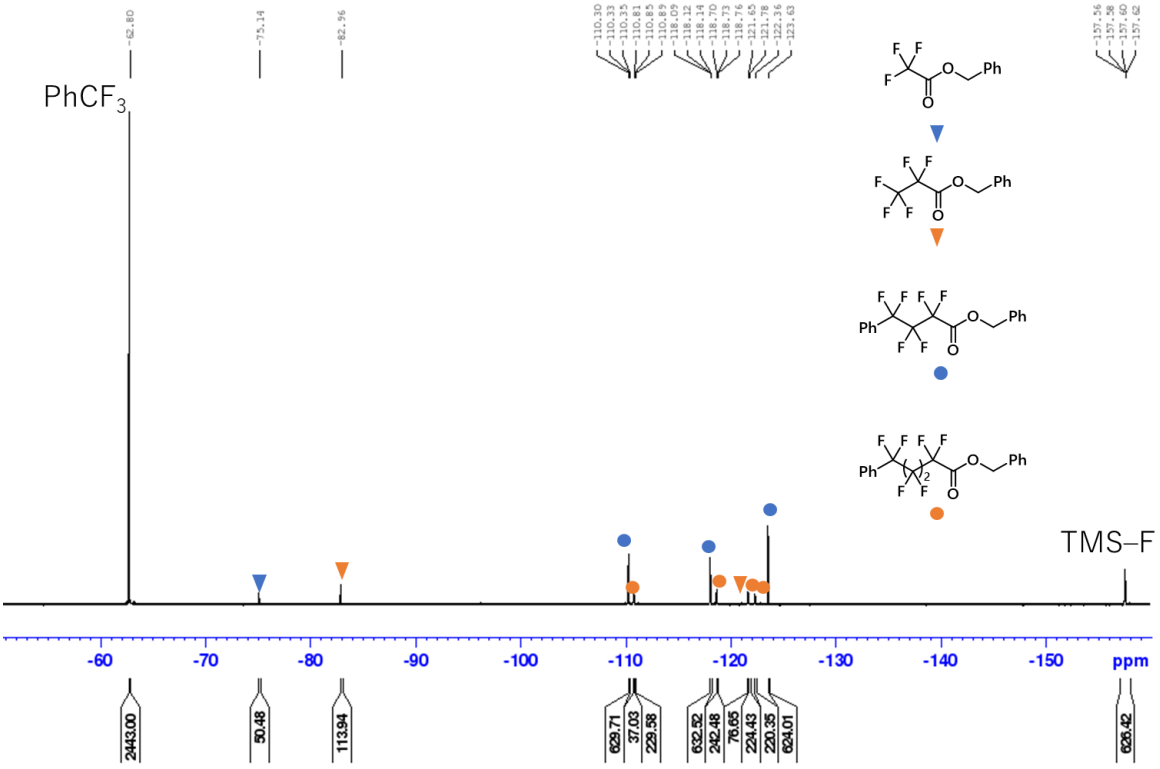
Mechanistic studies

Reaction in the presence of 1,1-diphenylethylene



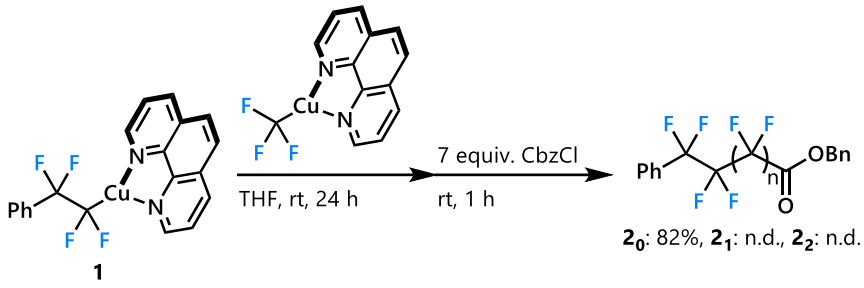
To a screw cap test tube, (phen)$CuCF_2CF_2Ph$ (**1**, 0.02 mmol, 8 mg) was added, followed by addition of THF (0.2 mL) and 1,1-diphenyl ethylene (0.12 mmol, 21 µL). To this mixture, $TMSCF_3$ (0.02 mmol, 3 µL) was added and stirred at room temperature for 24 hours. After the addition of CbzCl (0.14 mmol, 0.02 mL), the reaction mixture was stirred at room temperature for 1 hour. $CDCl_3$ and $PhCF_3$ (internal standard, 0.04 mmol, 5 µL) was added to the tube, and the precipitation in the sample was removed though filtration. Then NMR spectrum of the sample was measured, and the NMR yield was calculated to be 58% for $\mathbf{2_1}$ and 6% for $\mathbf{2_2}$. The corresponding difluorocyclopropane or TFE was not observed.

The ^{19}F NMR (376 MHz, $CDCl_3$) analysis of crude reaction mixture



When we performed the reaction to isolate **2**, we checked the ^{19}F NMR spectrum of the crude reaction mixture. In addition to the desired products $\mathbf{2_1}$ and $\mathbf{2_2}$, we observed formation of $CbzCF_3$[4] and $CbzCF_2CF_3$[5] of which precursor would be $CuCF_3$ and $CuCF_2CF_3$, respectively. It is unclear whether the copper species are ligated by Phen or not.

The reaction using (Phen)$CuCF_3$ instead of $TMSCF_3$



$\mathbf{2_0}$: 82%, $\mathbf{2_1}$: n.d., $\mathbf{2_2}$: n.d.

To a vial containing a stirring bar, (phen)$CuCF_2CF_2Ph$ **(**42 mg, 0.1 mmol), (phen)$CuCF_3$ (31.8 mg, 0.1 mmol), and THF (1 mL) was added. To this mixture, $TMSCF_3$ was added and stirred at room temperature for 24 hours. After the addition of CbzCl (0.7 mmol, 0.1 mL), the reaction mixture was stirred at room temperature for 1 hour. Volatiles in reaction mixture were removed under reduced pressure. $CDCl_3$ and $PhCF_3$ (internal standard, 0.08 mmol, 10 μL) were added to the tube, and the precipitate in the sample was removed by filtration. The NMR spectrum of the sample was measured to determine the NMR yield.

The reaction gave $\mathbf{2_0}$ in 84% yield indicating that (phen)$CuCF_3$ is not a major source of difluorocarbene or carbenoid.

References

[1] H. Saijo, M. Ohashi, S. Ogoshi *J. Am. Chem. Soc.* **2014**, *136*, 15158.

[2] H. Morimoto, T. Tsubogo, N. D. Litvinas, J. F. Hartwig *Angew. Chem. Int. Ed.* **2011**, *50*, 3793.

[3] T. O. Ronson, E. Renders, B. F. Van Steijvoort, X. Wang, C. C. D. Wybon, H. Prokopcová, L. Meerpoel, B. U. W. Maes *Angew. Chem. Int. Ed.* **2019***, 58,* 482.

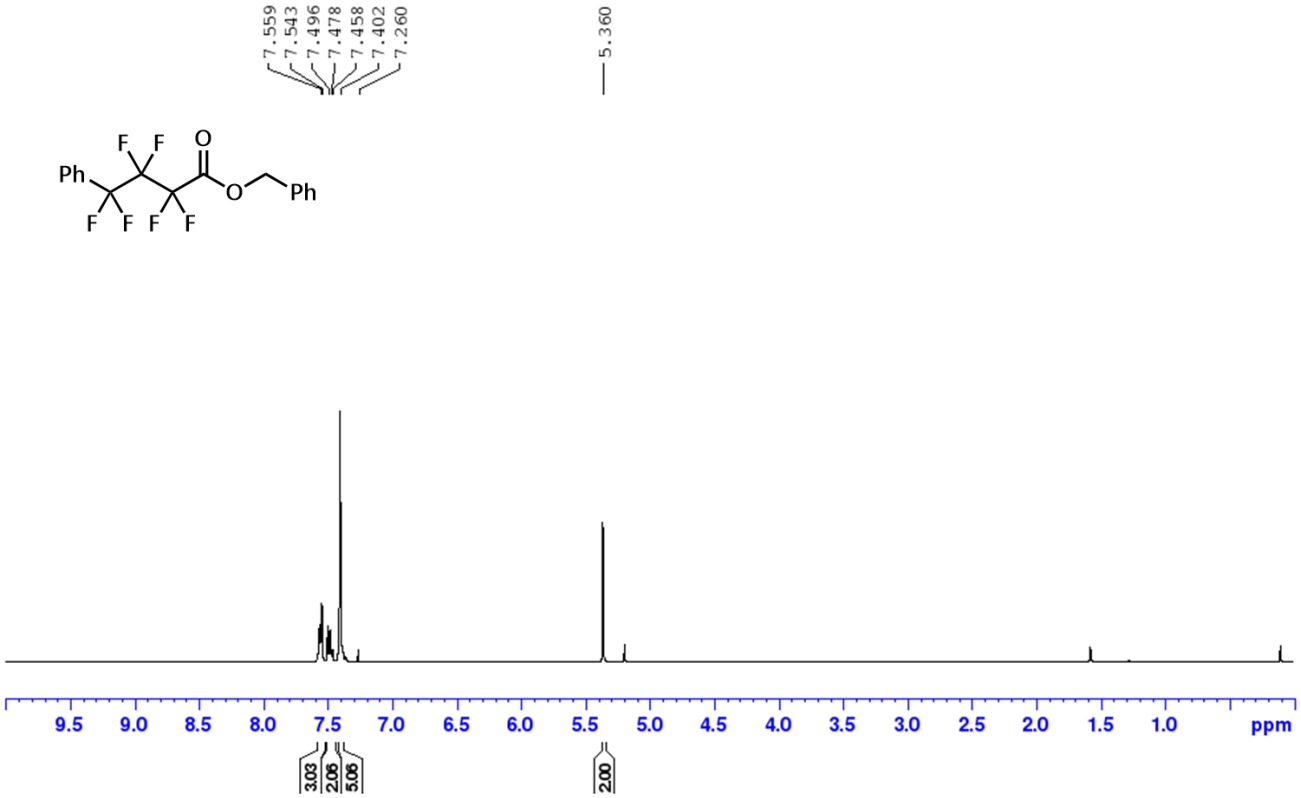
[4] M. Hitt, A. N. Vedernikov *Org. Lett.* **2022**, *24*, 7737.

[5] K. Hajimu, H. A. Hamouda, N. Ishikawa *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1694.

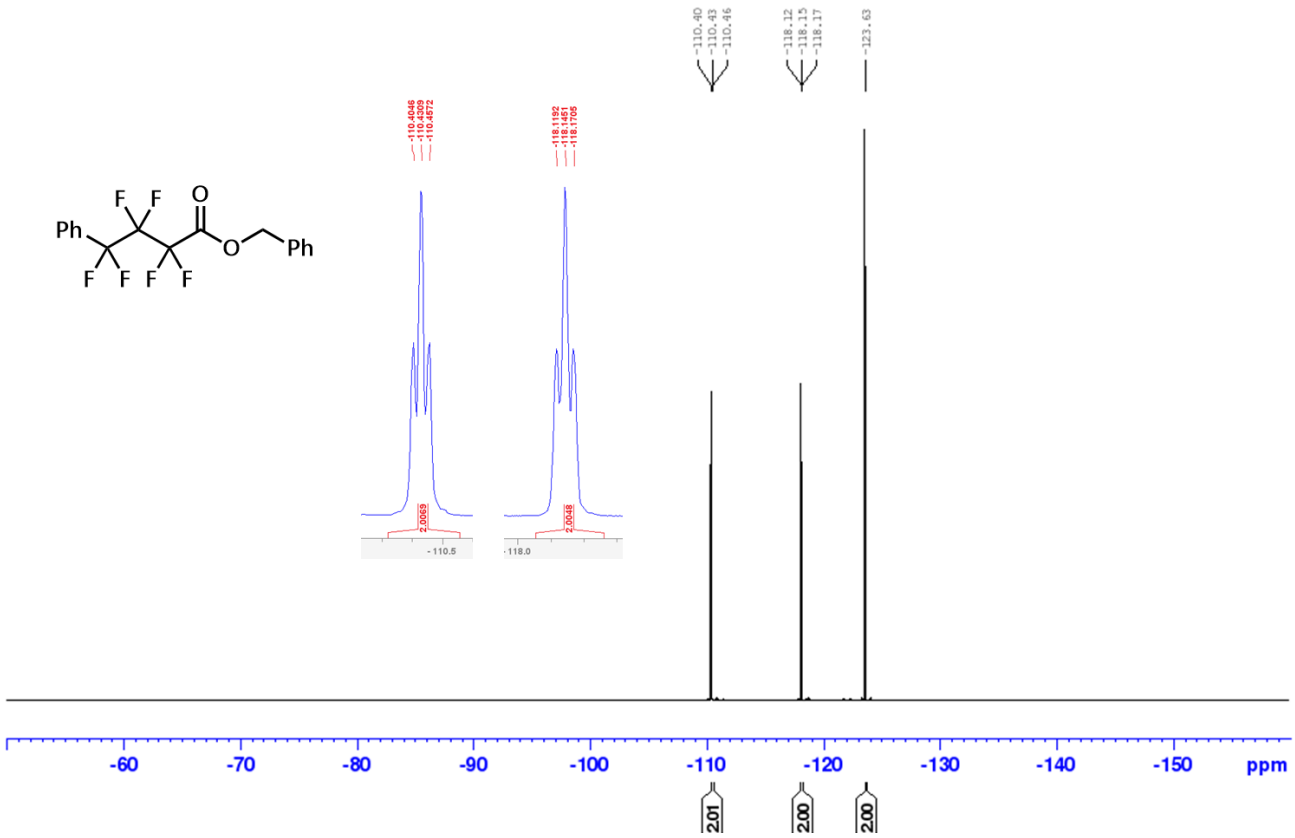
Spectrum Data

2_1

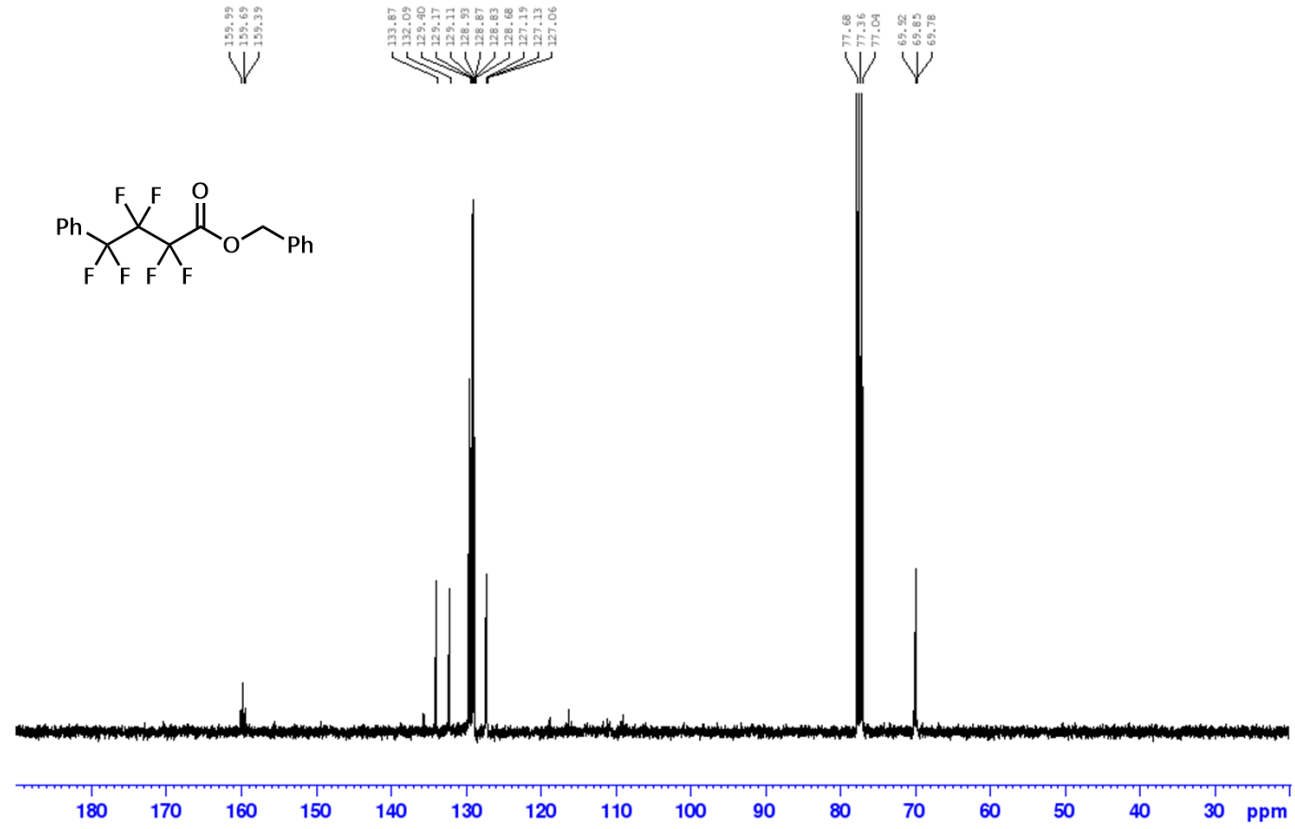
^{1}H NMR (400 MHz, $CDCl_3$)



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

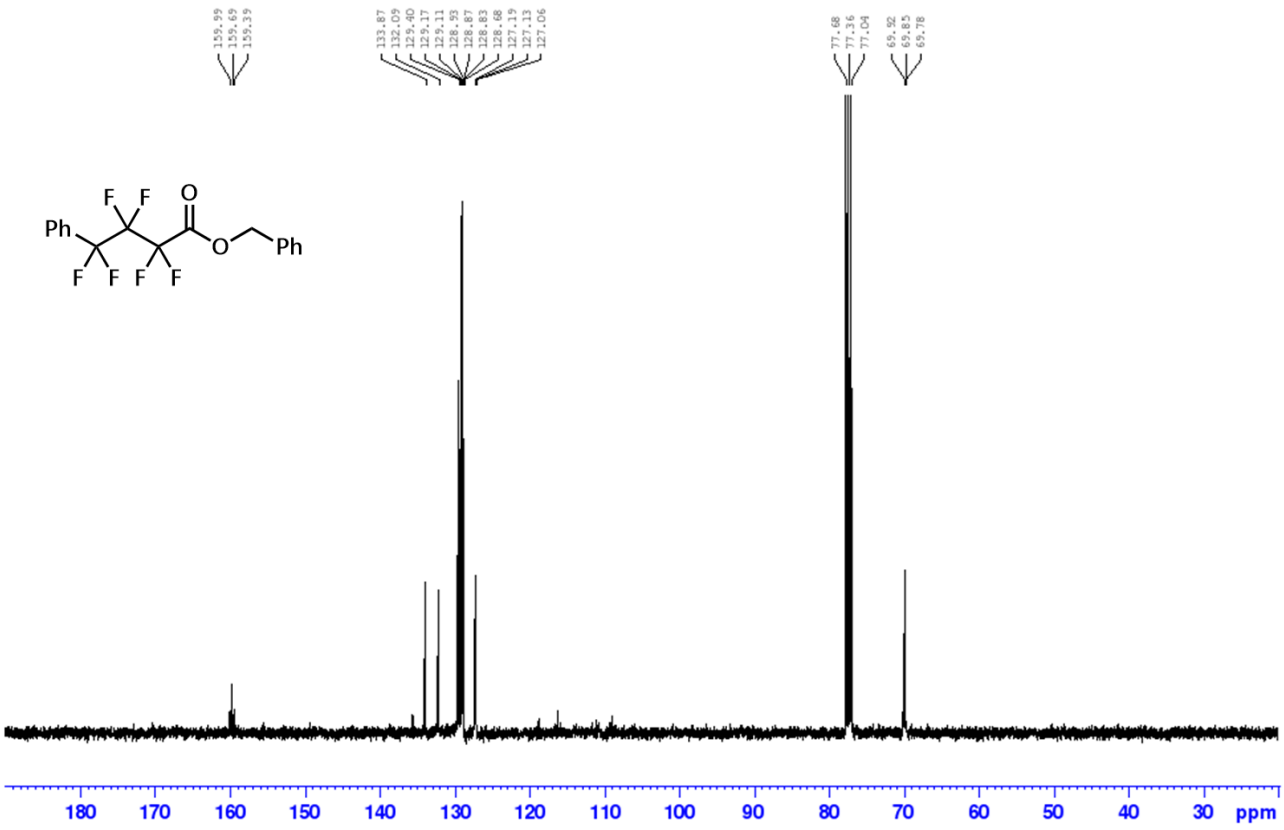


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

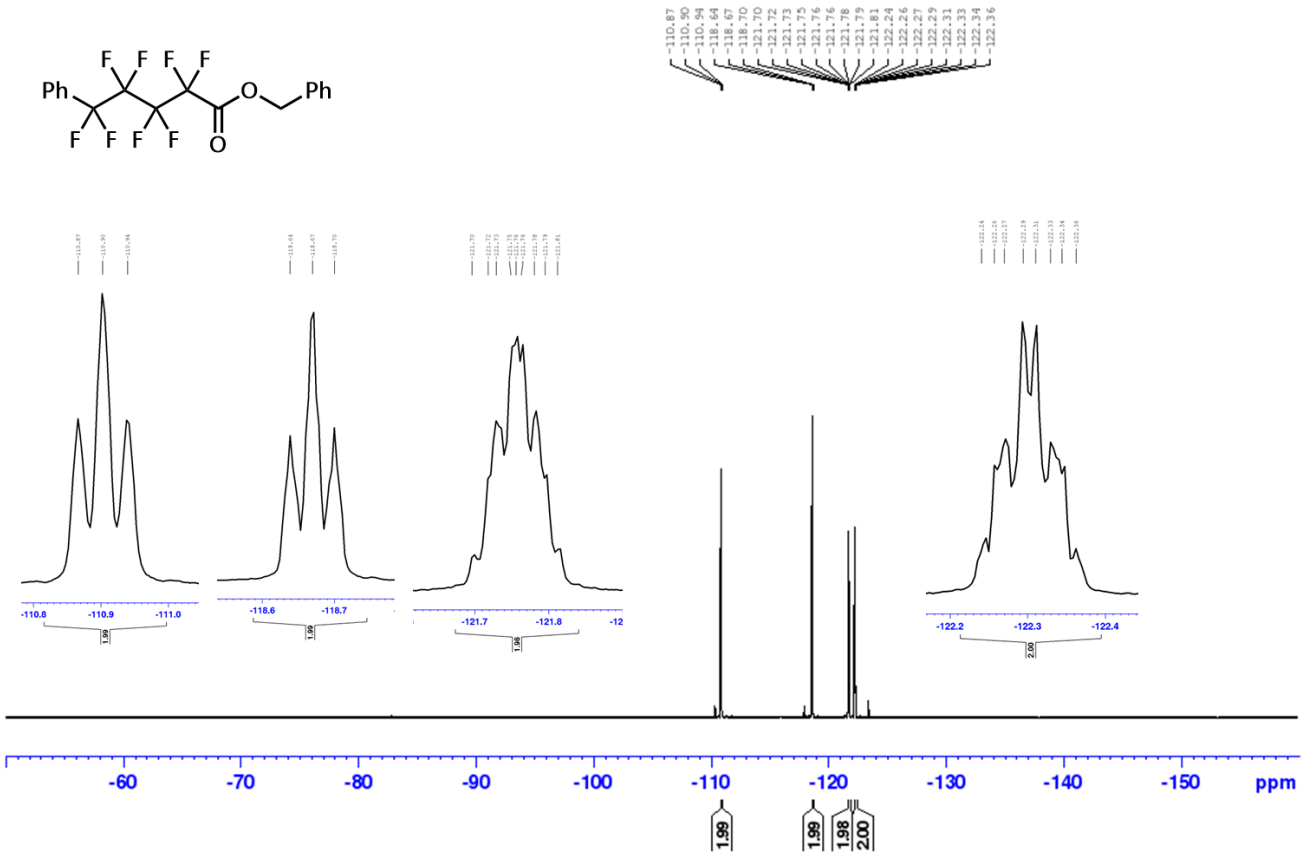


2_2

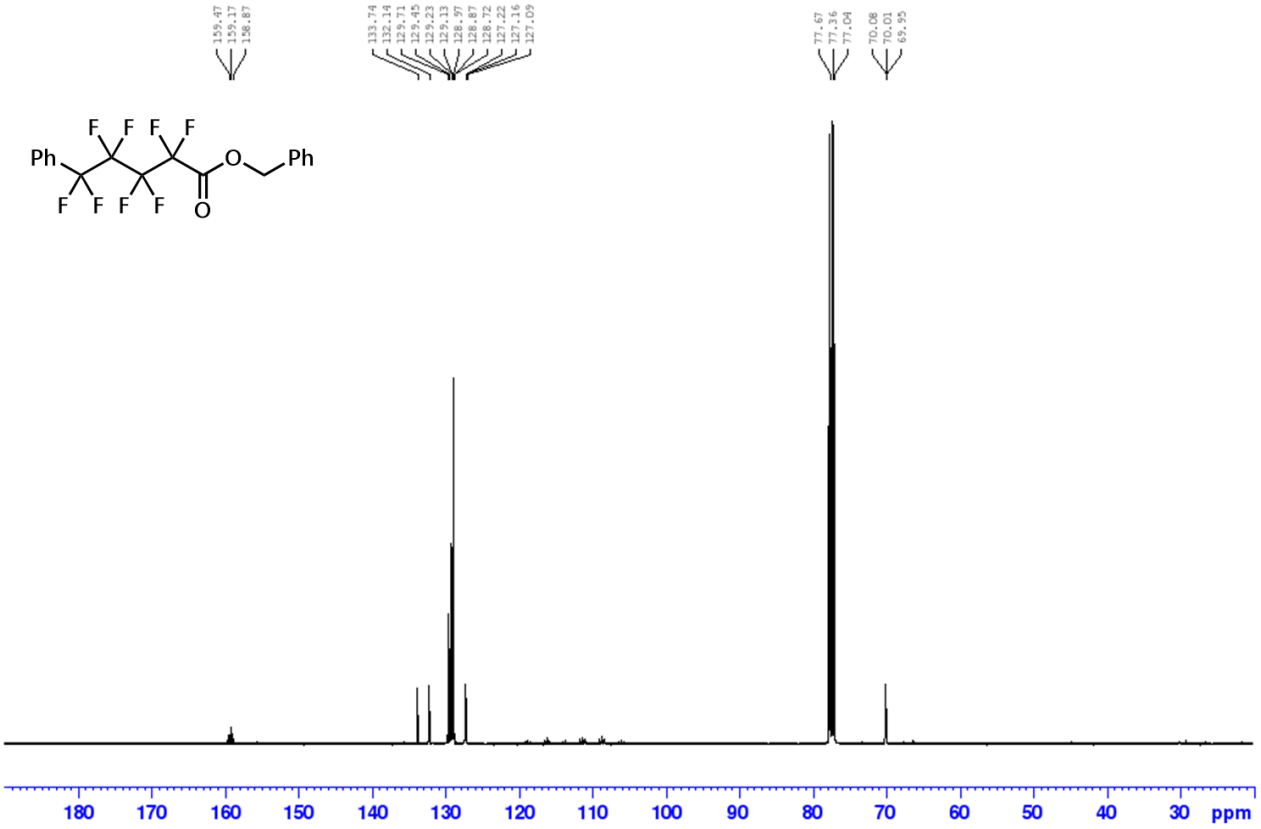
^{1}H NMR (400 MHz, $CDCl_3$)



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

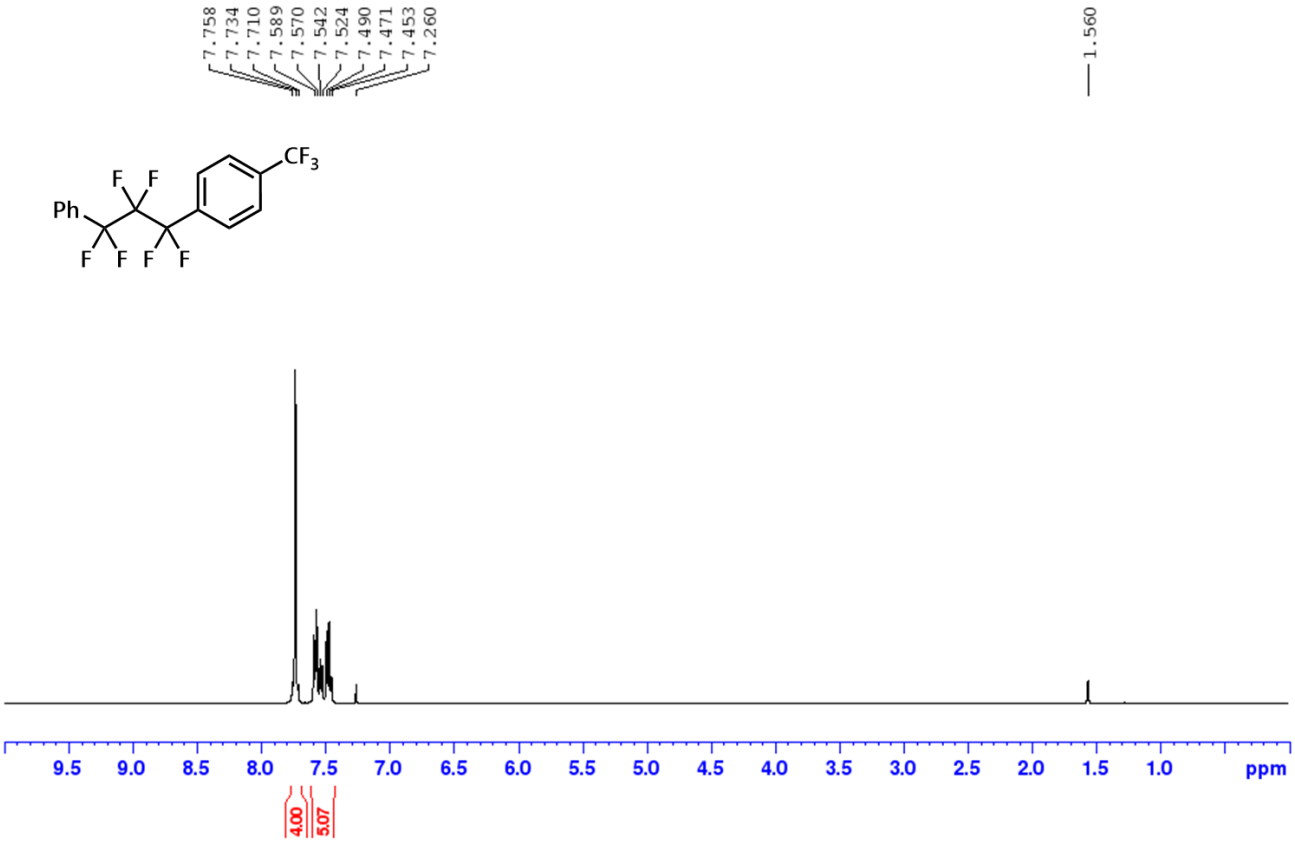


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

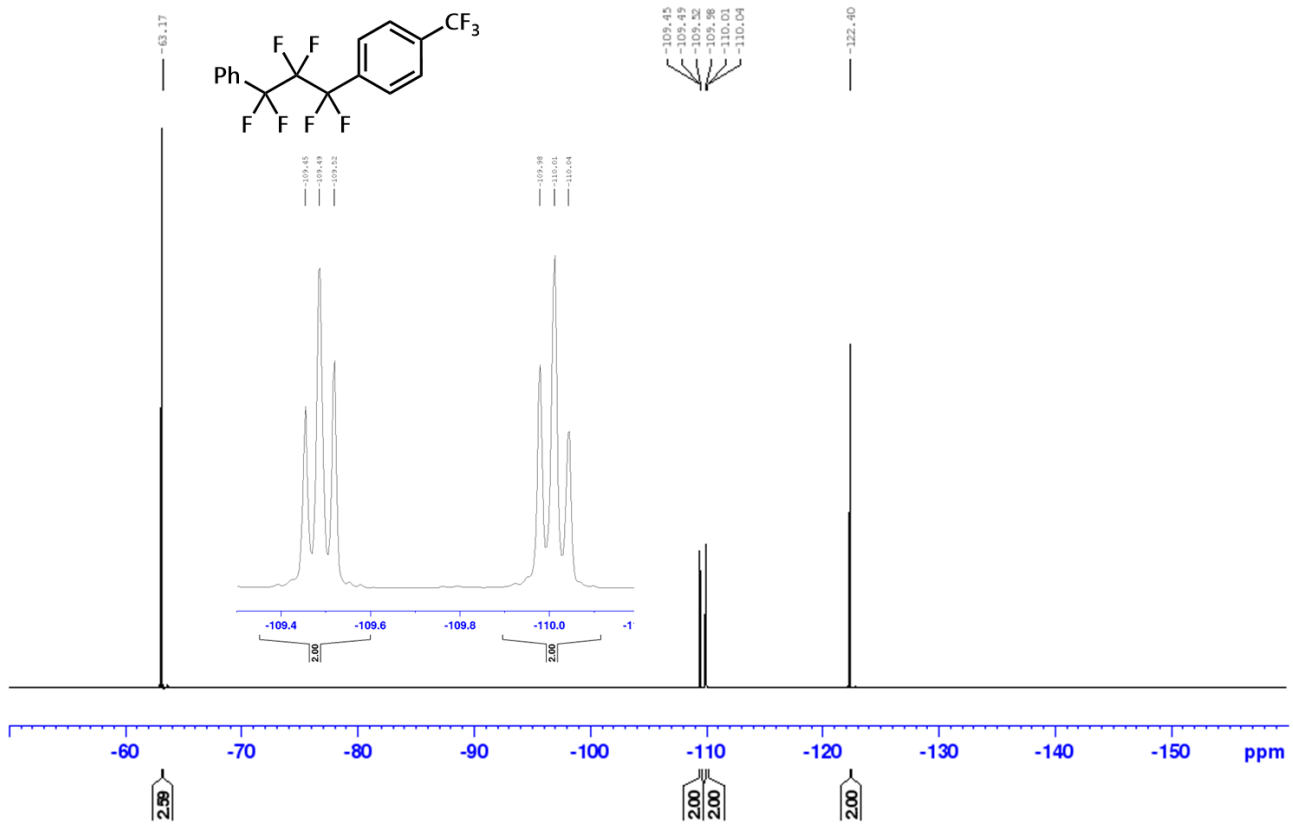


3a$_1$

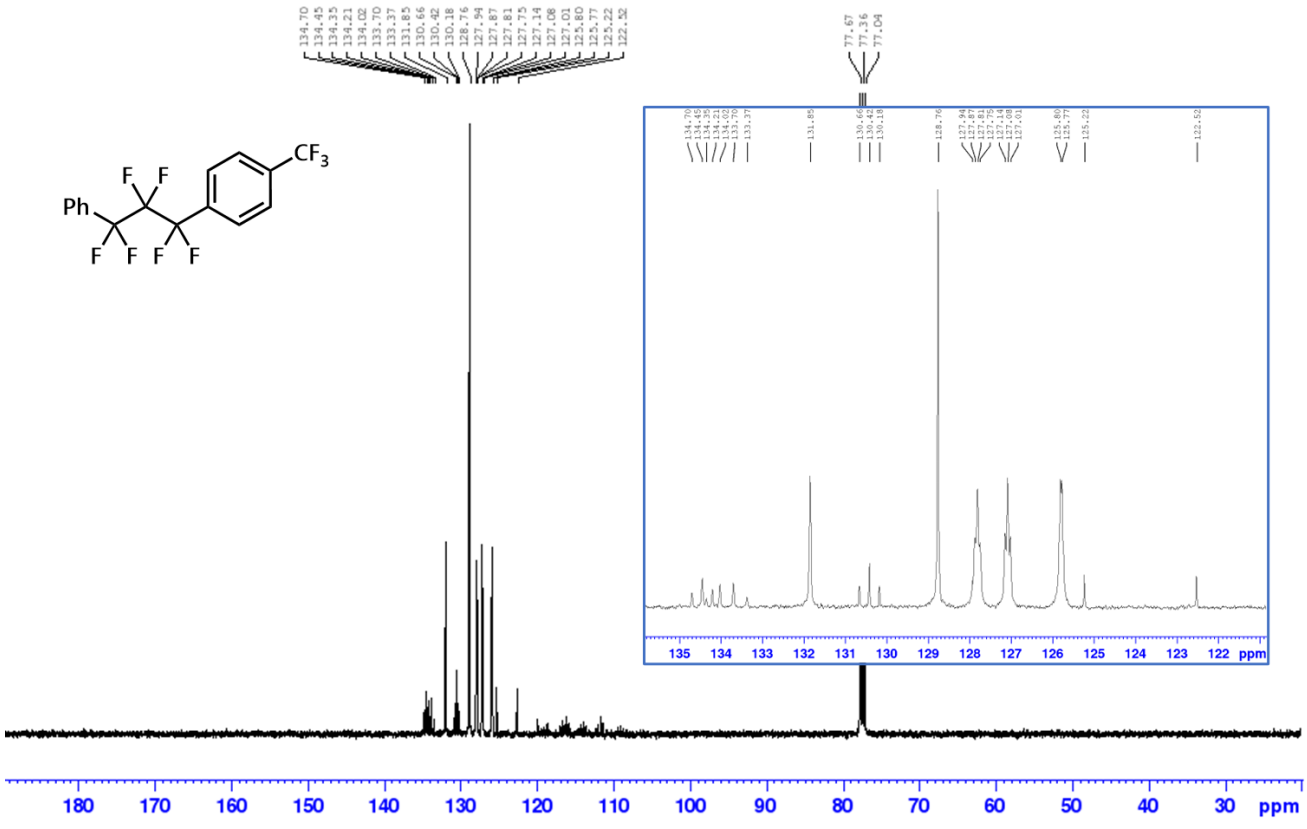
^{1}H NMR (400 MHz, $CDCl_3$)



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

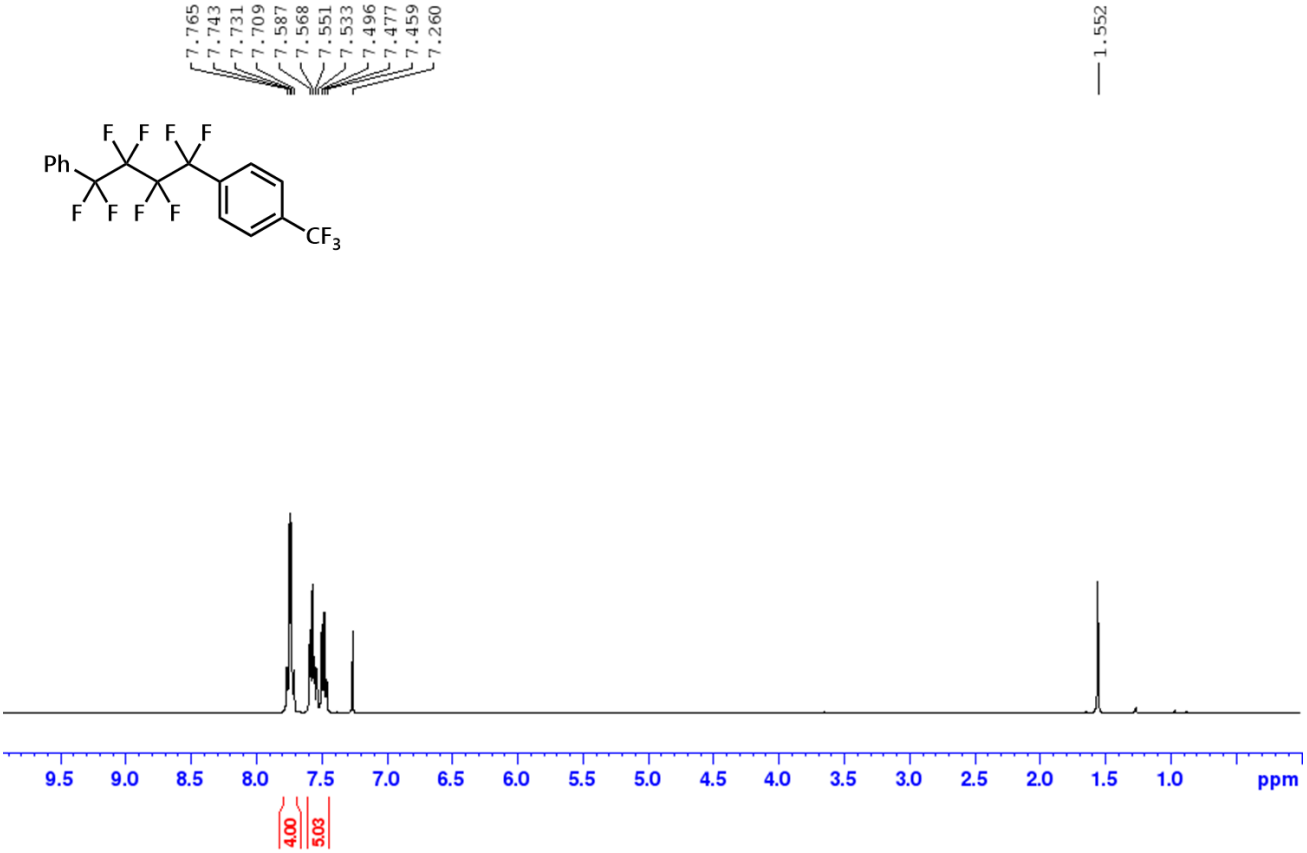


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

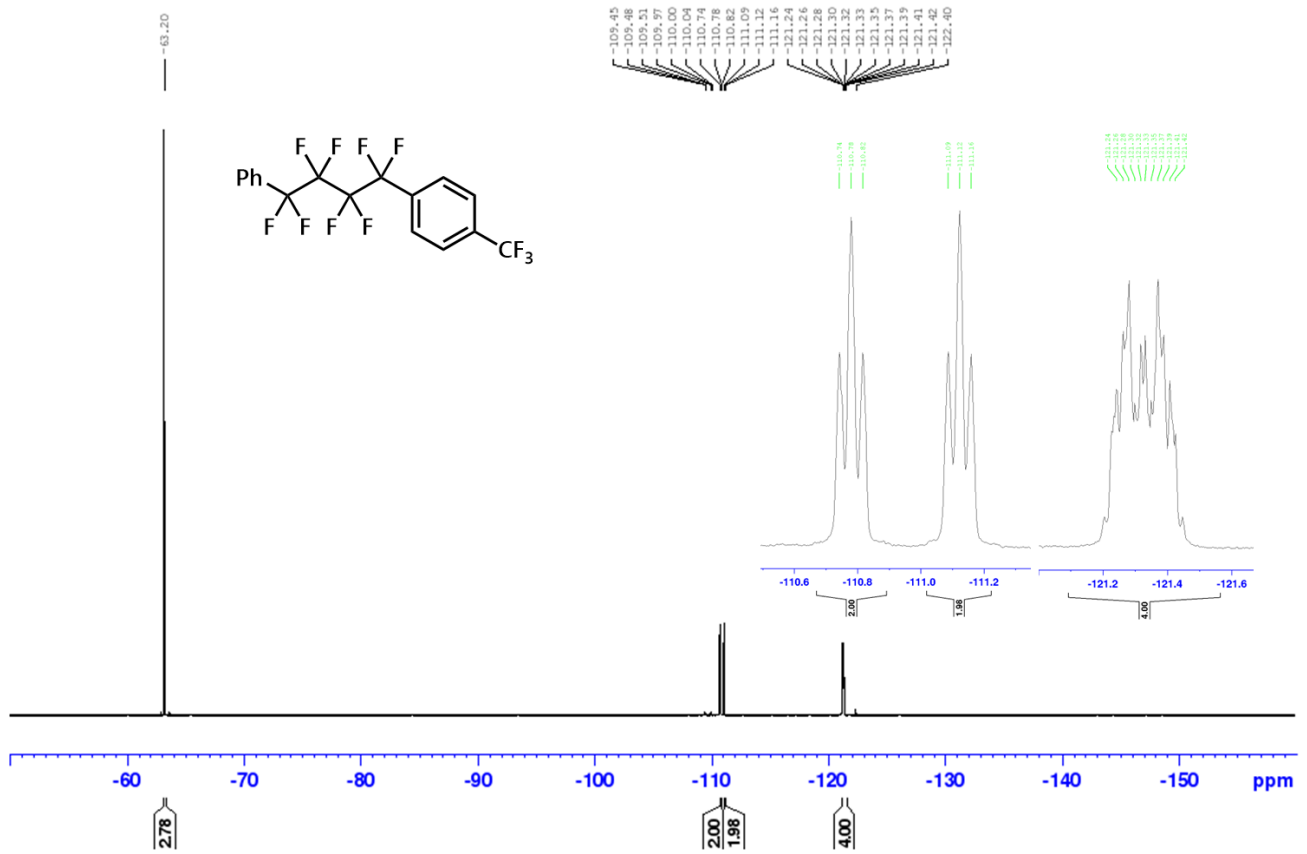


3a₂

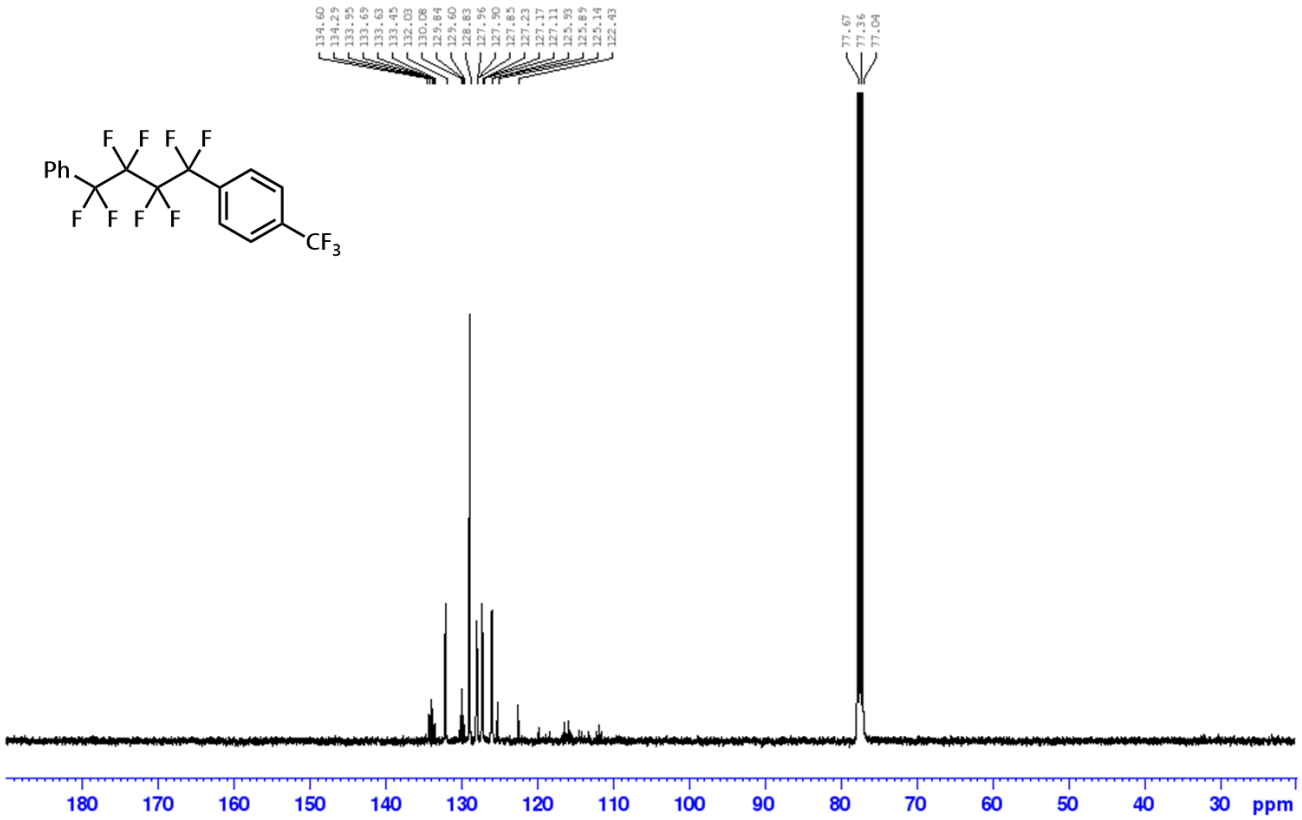
^{1}H NMR (400 MHz, $CDCl_3$)



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

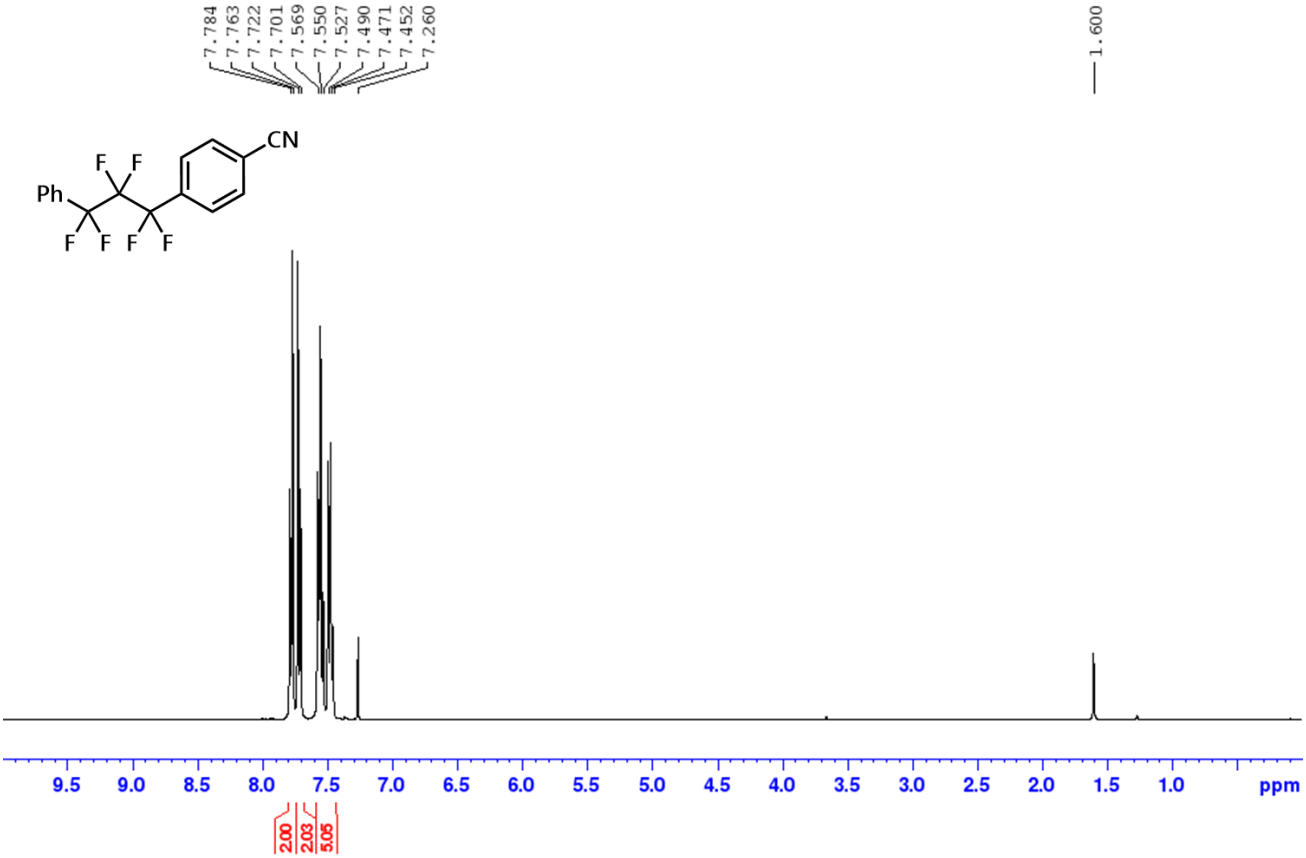


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

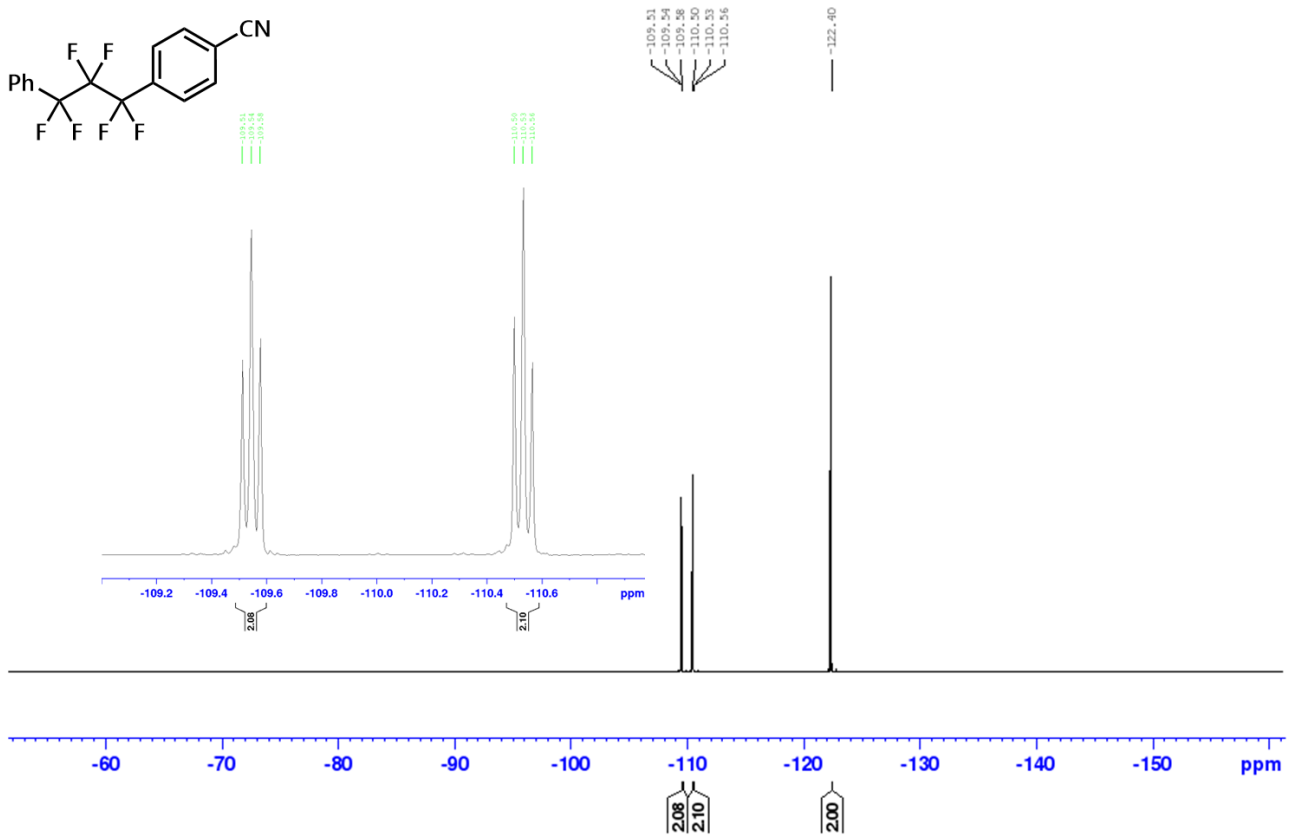


3b₁

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



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



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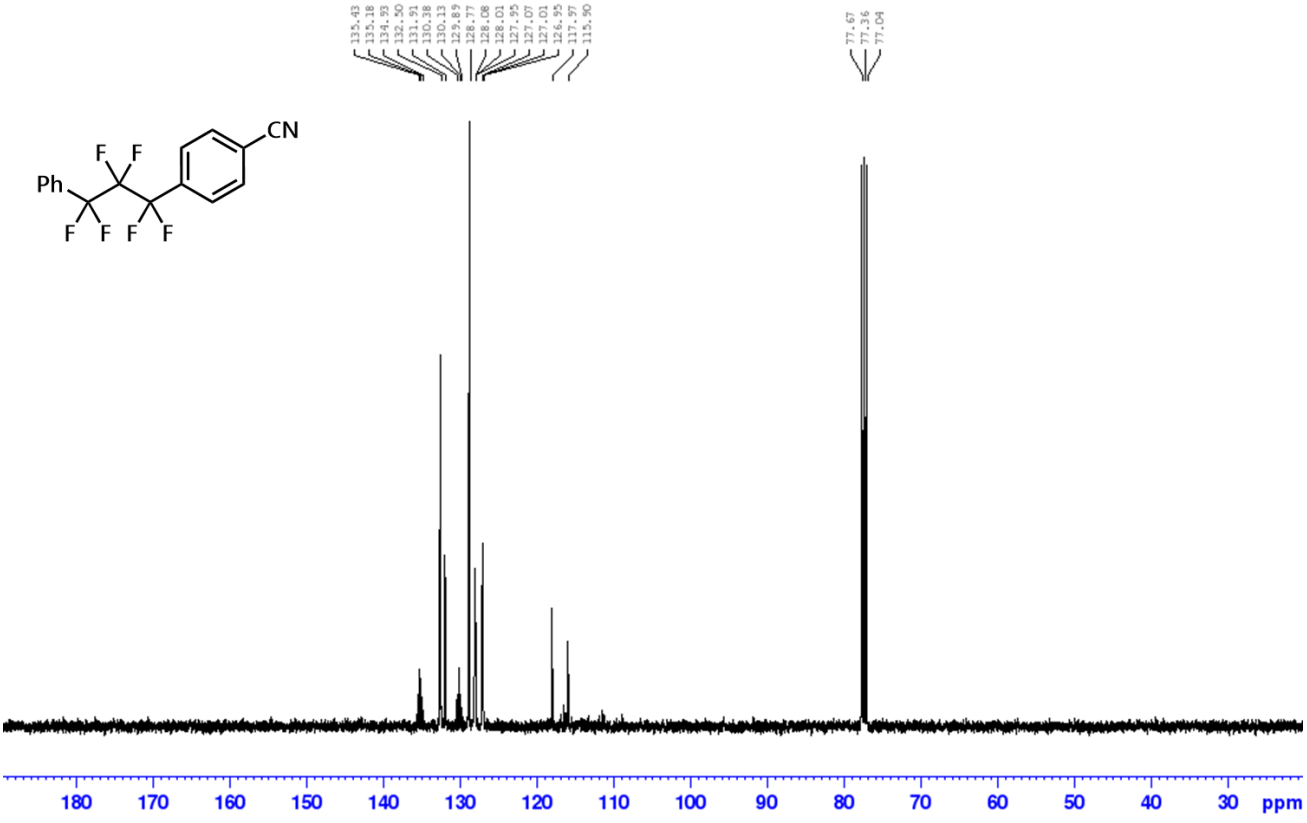
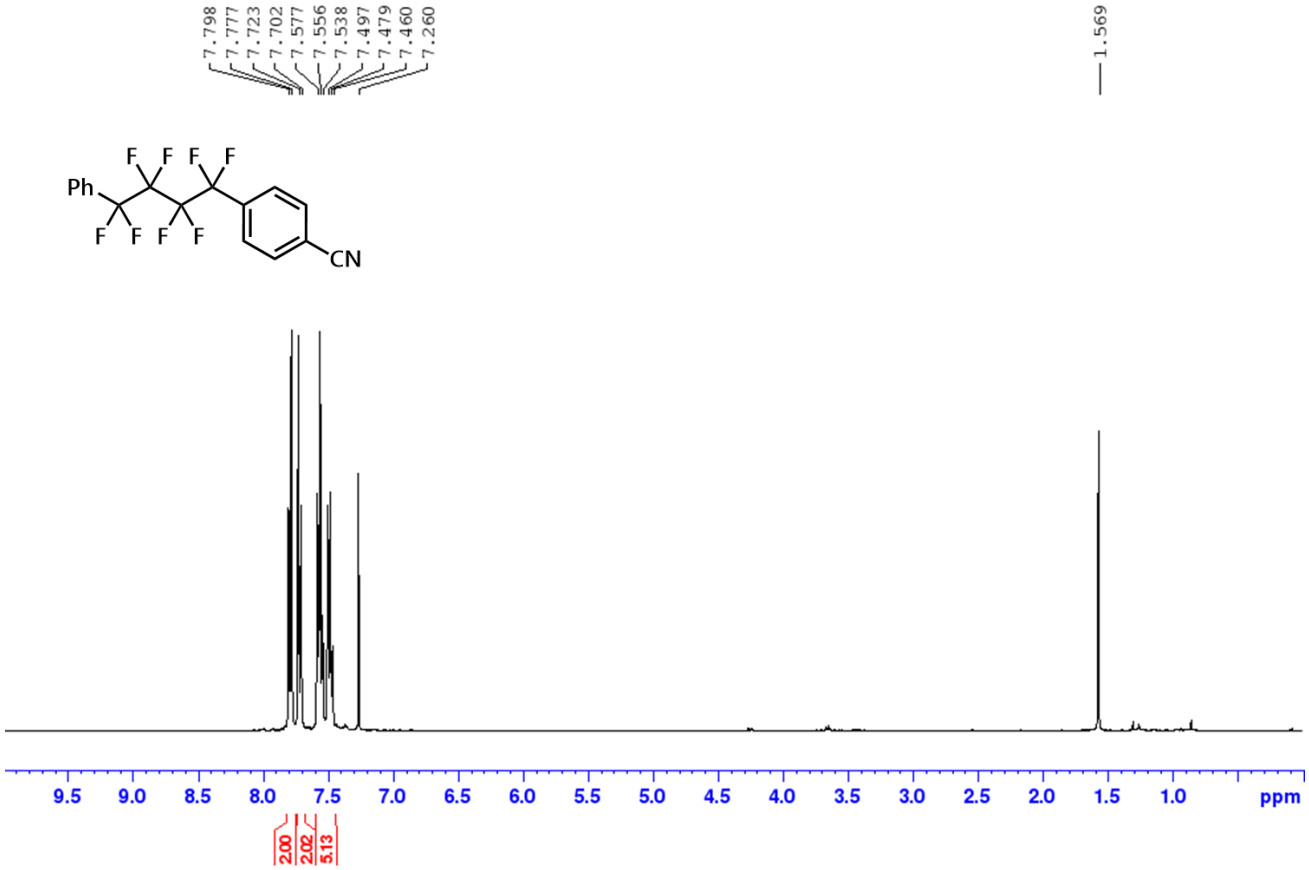
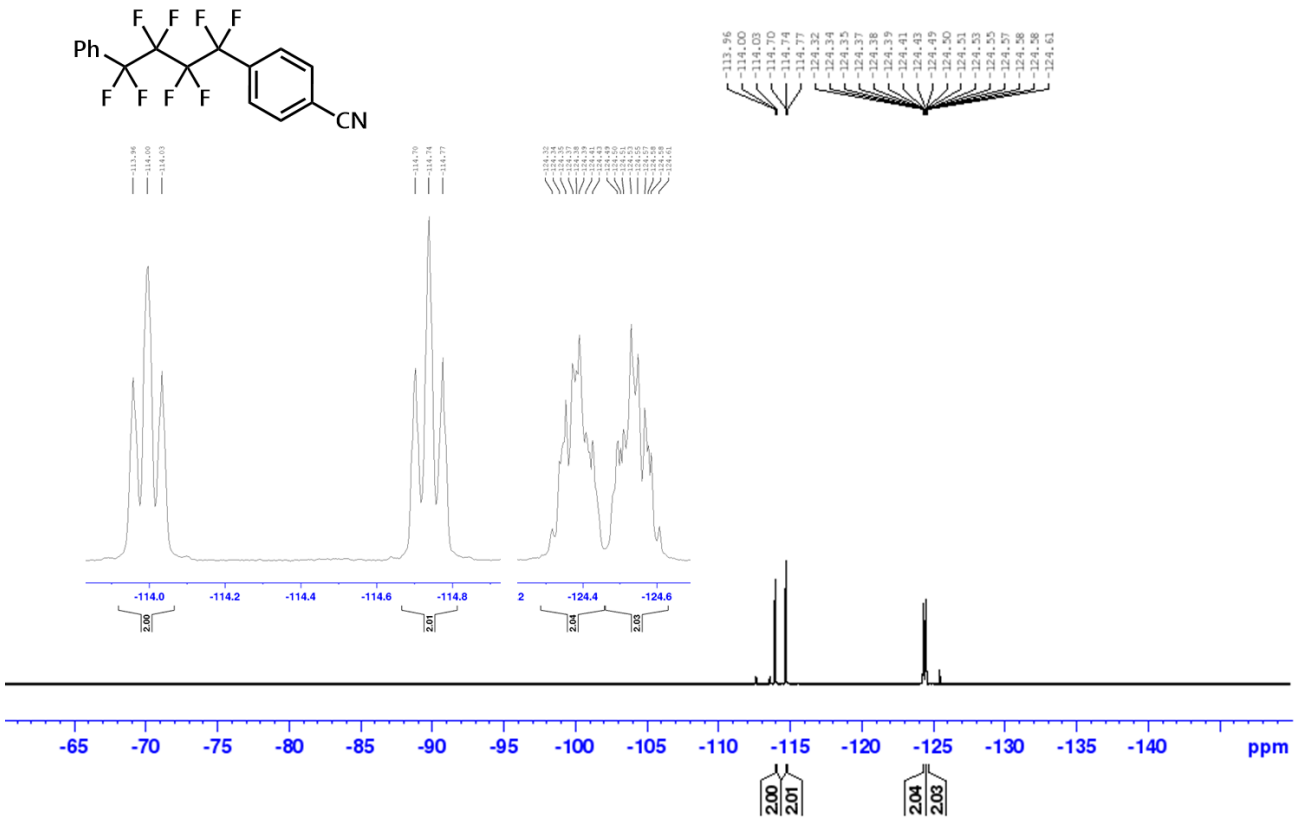


3b₂

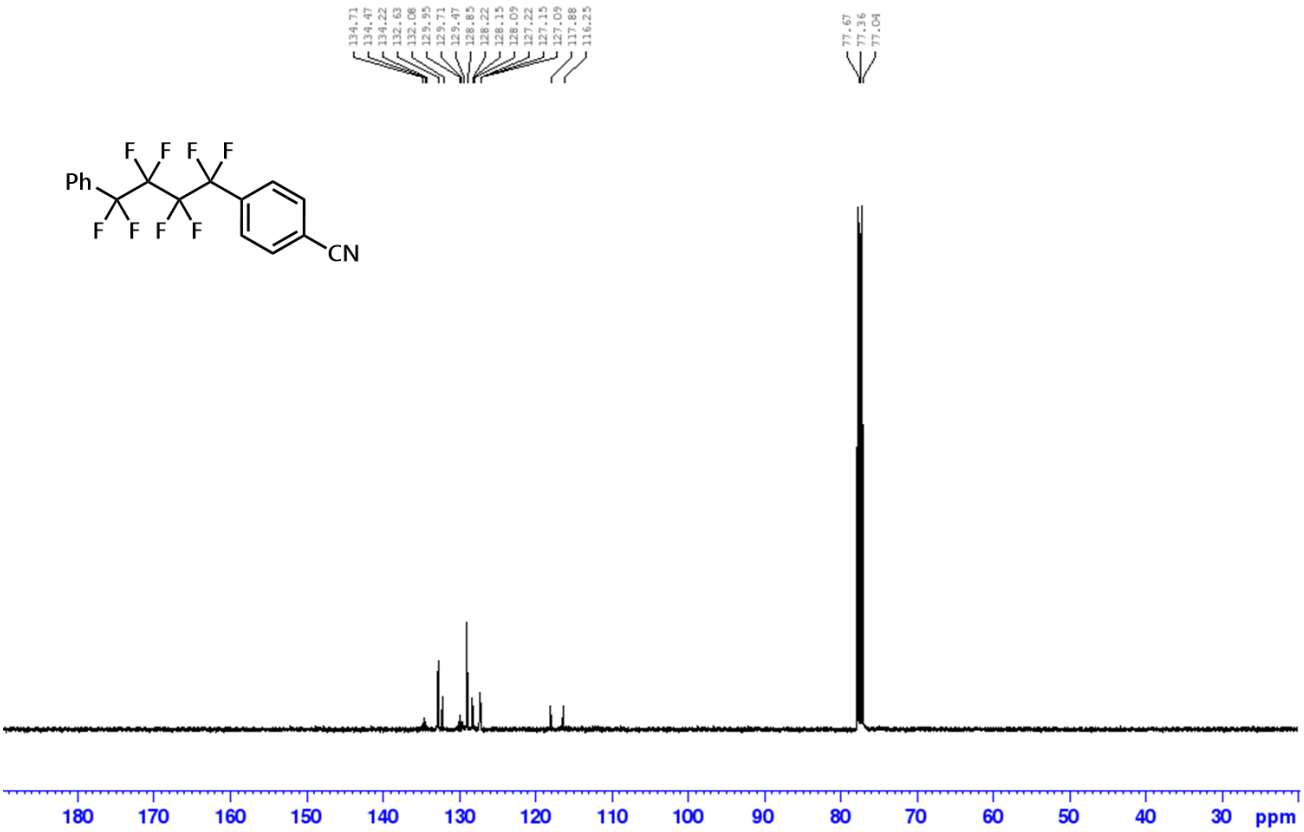
^{1}H NMR (400 MHz, $CDCl_3$)



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

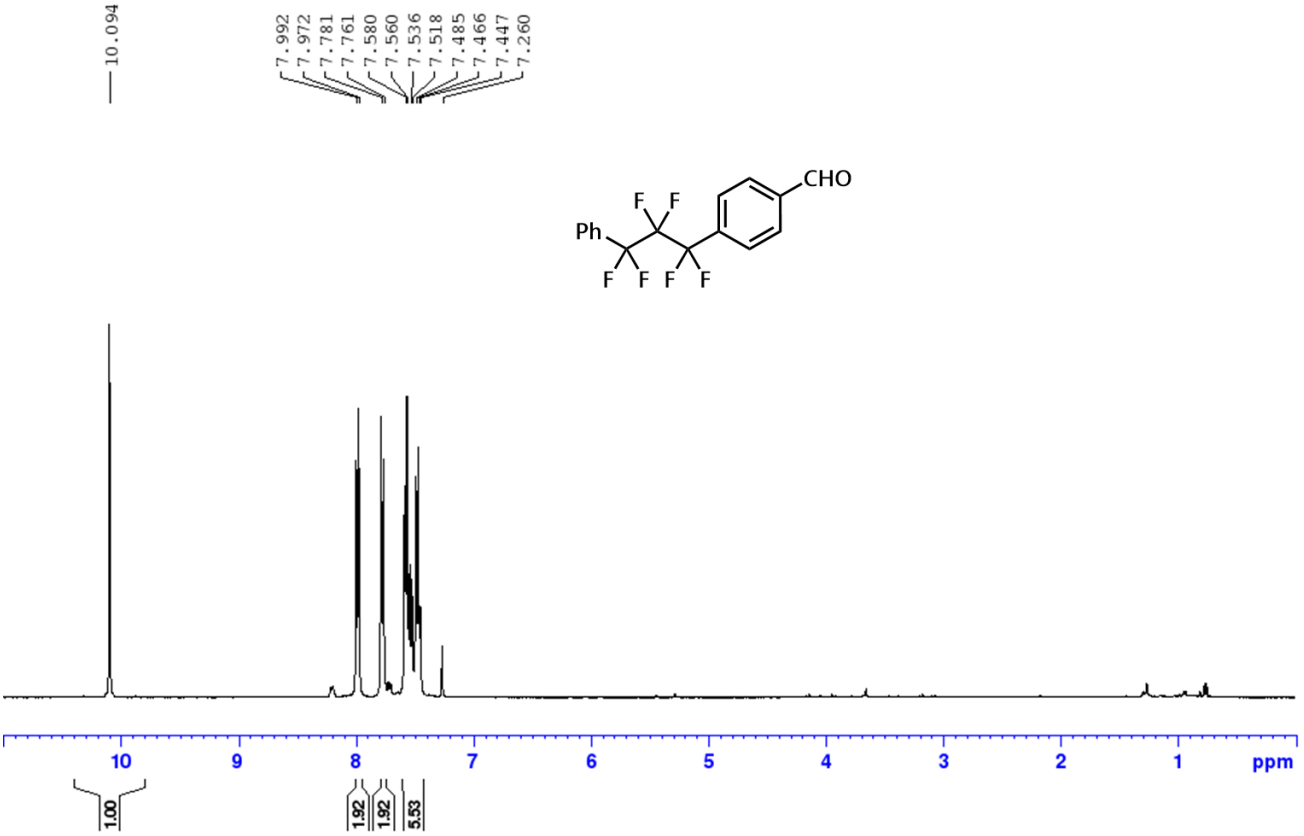


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)



3c₁

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



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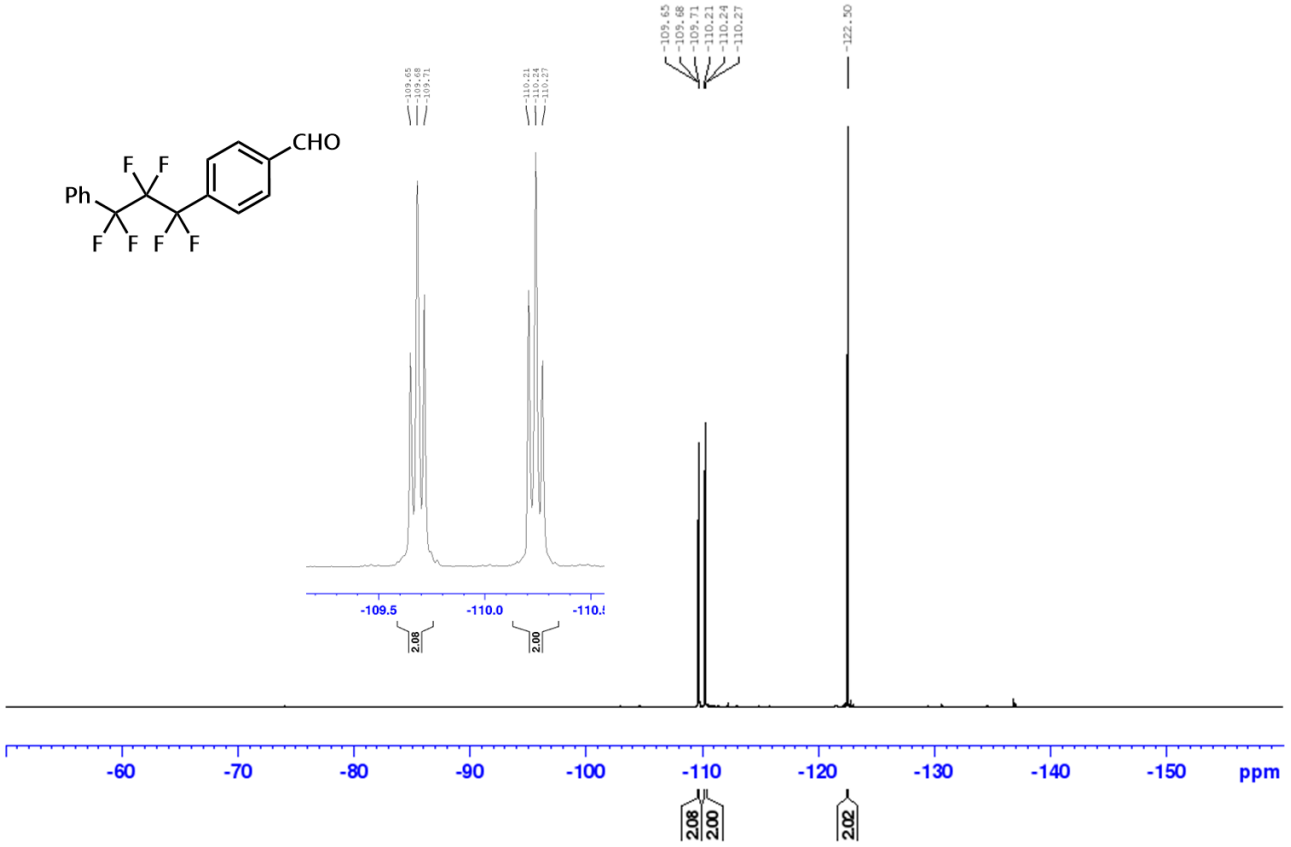
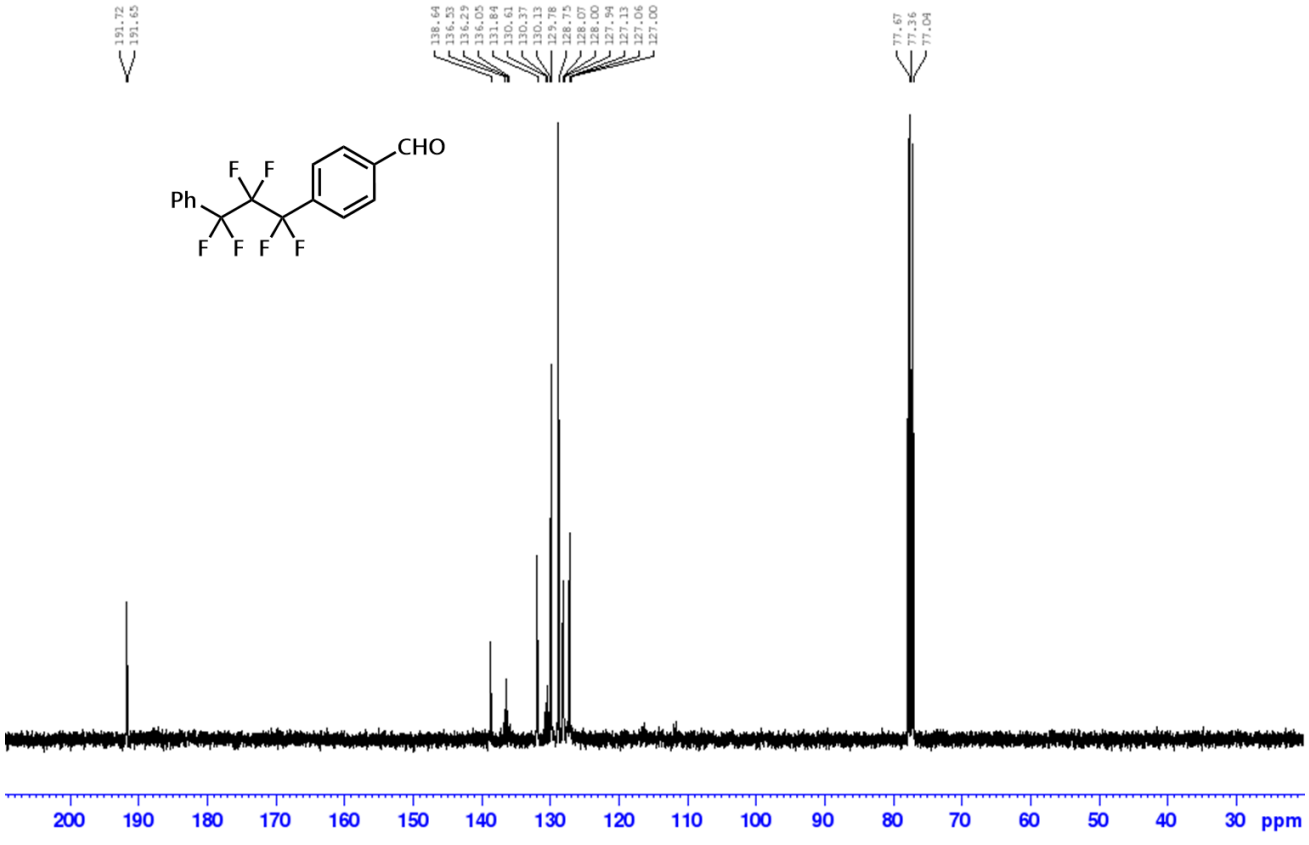
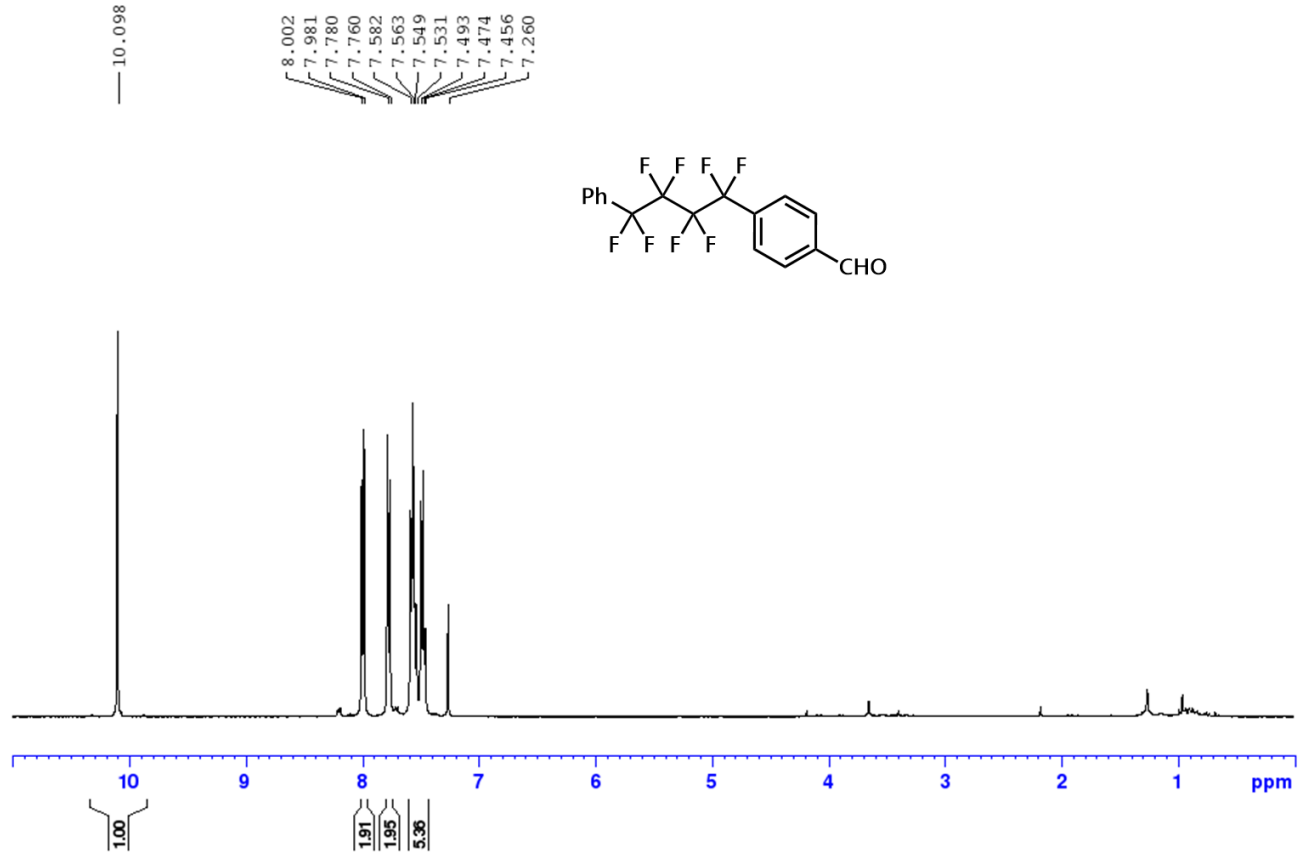


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)



3c₂

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



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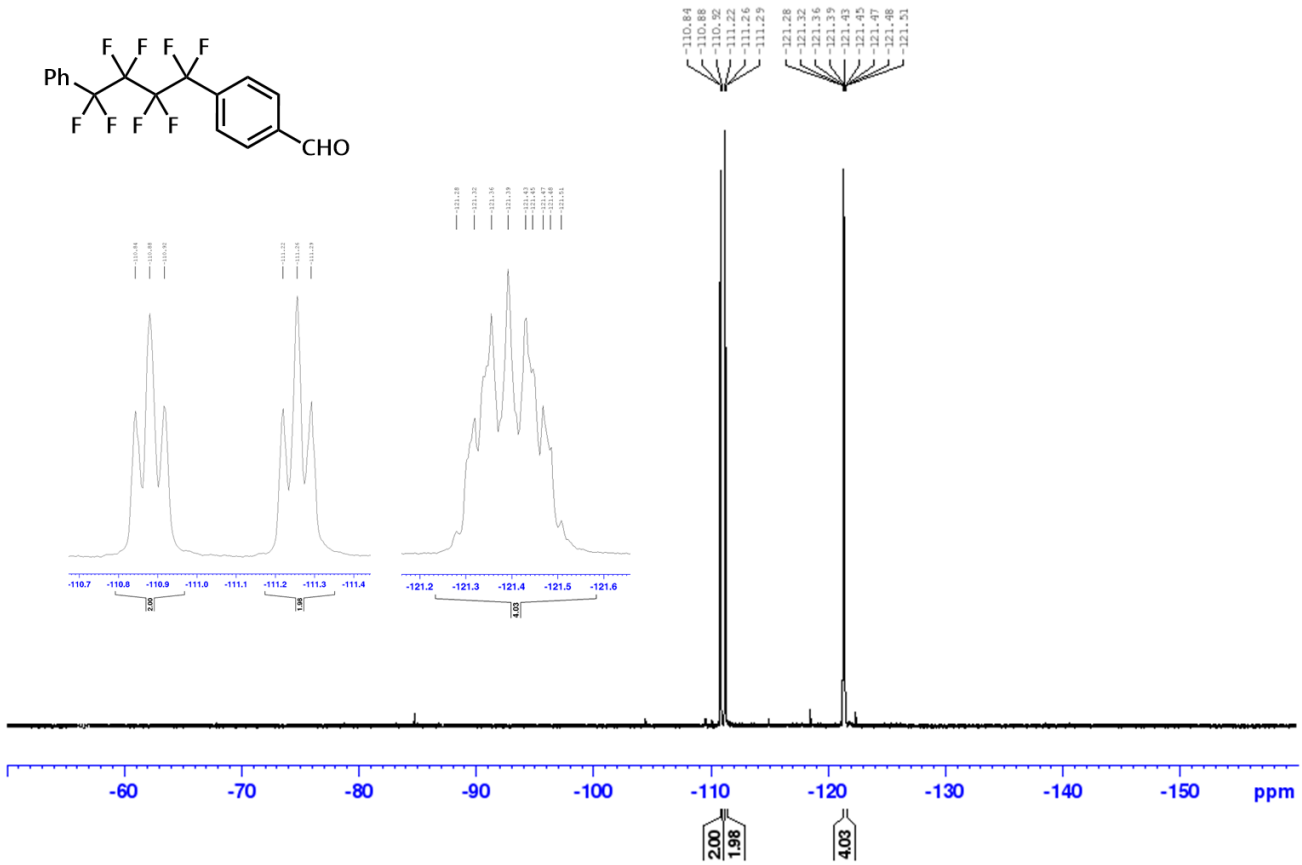

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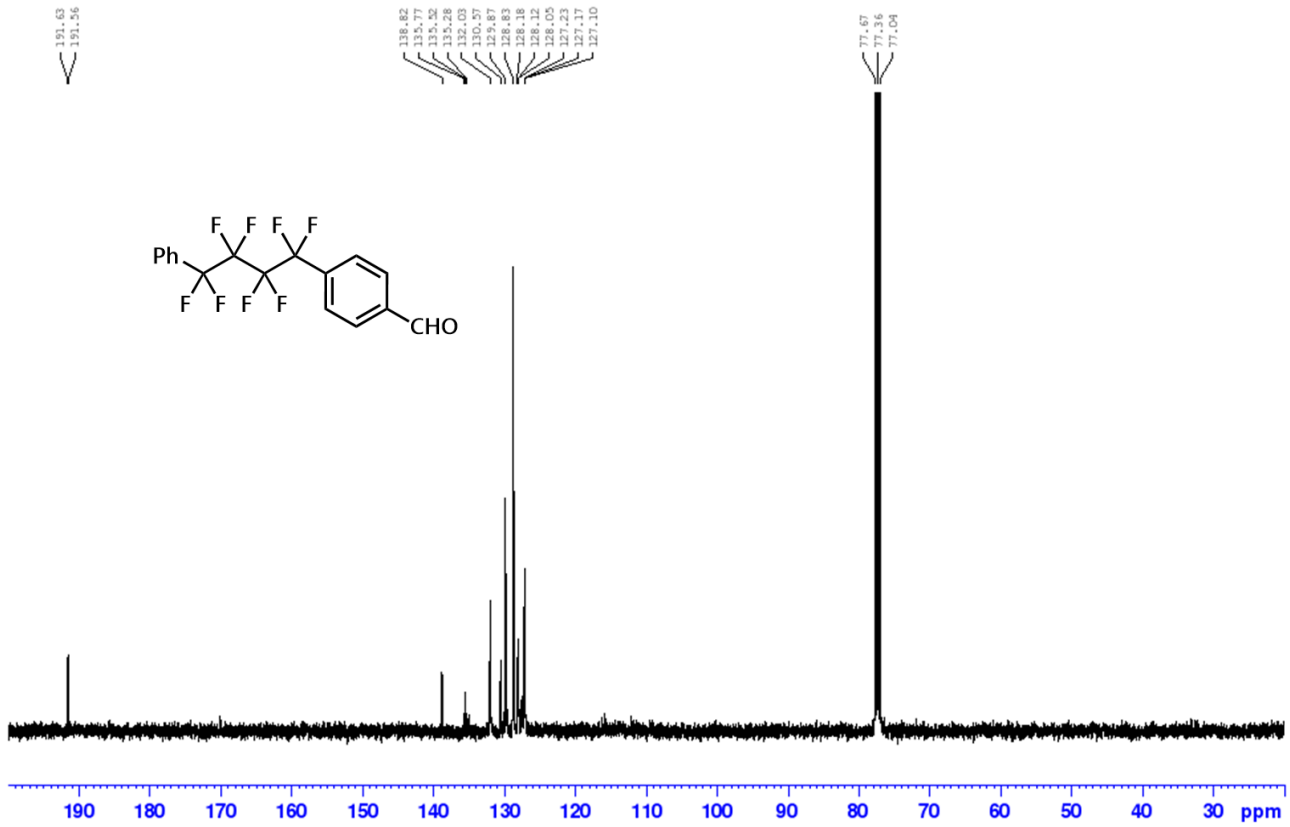

3d₁

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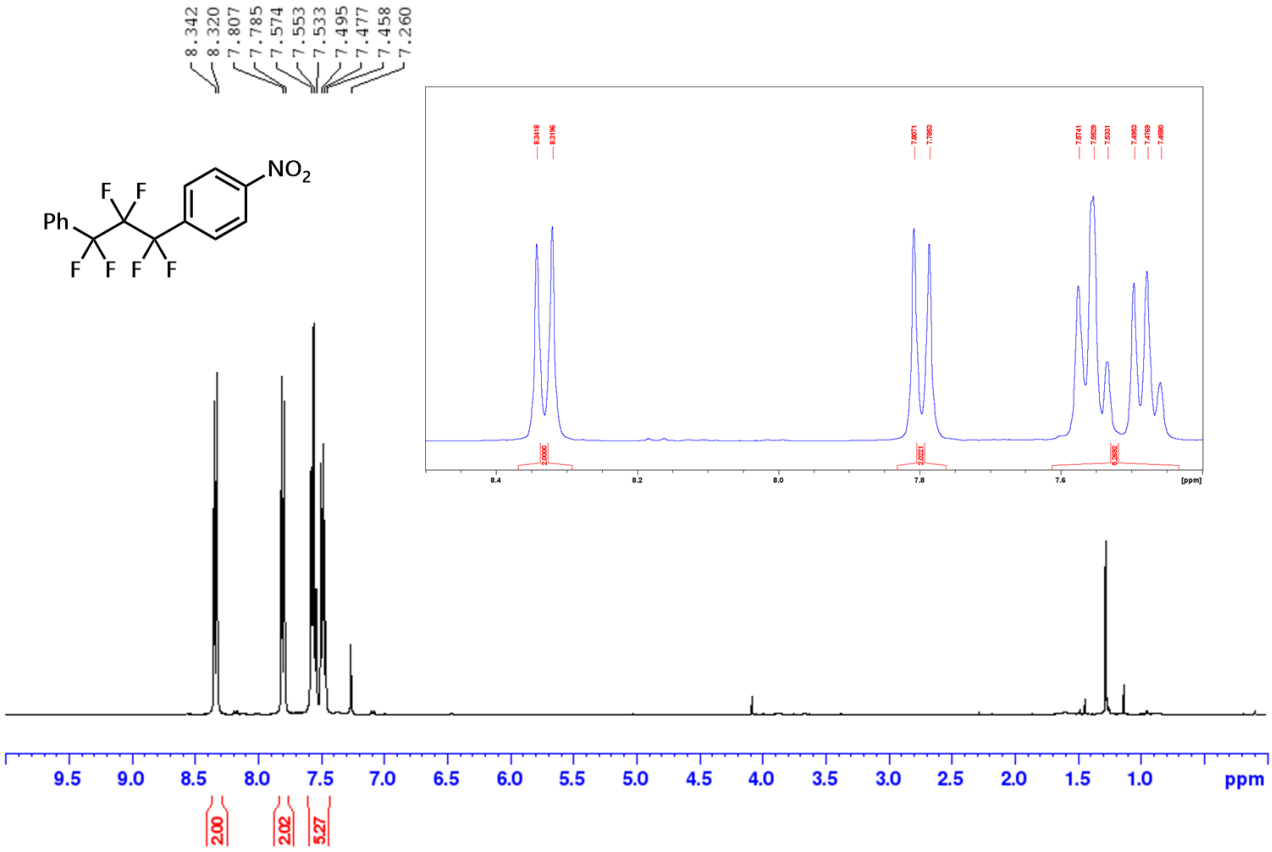

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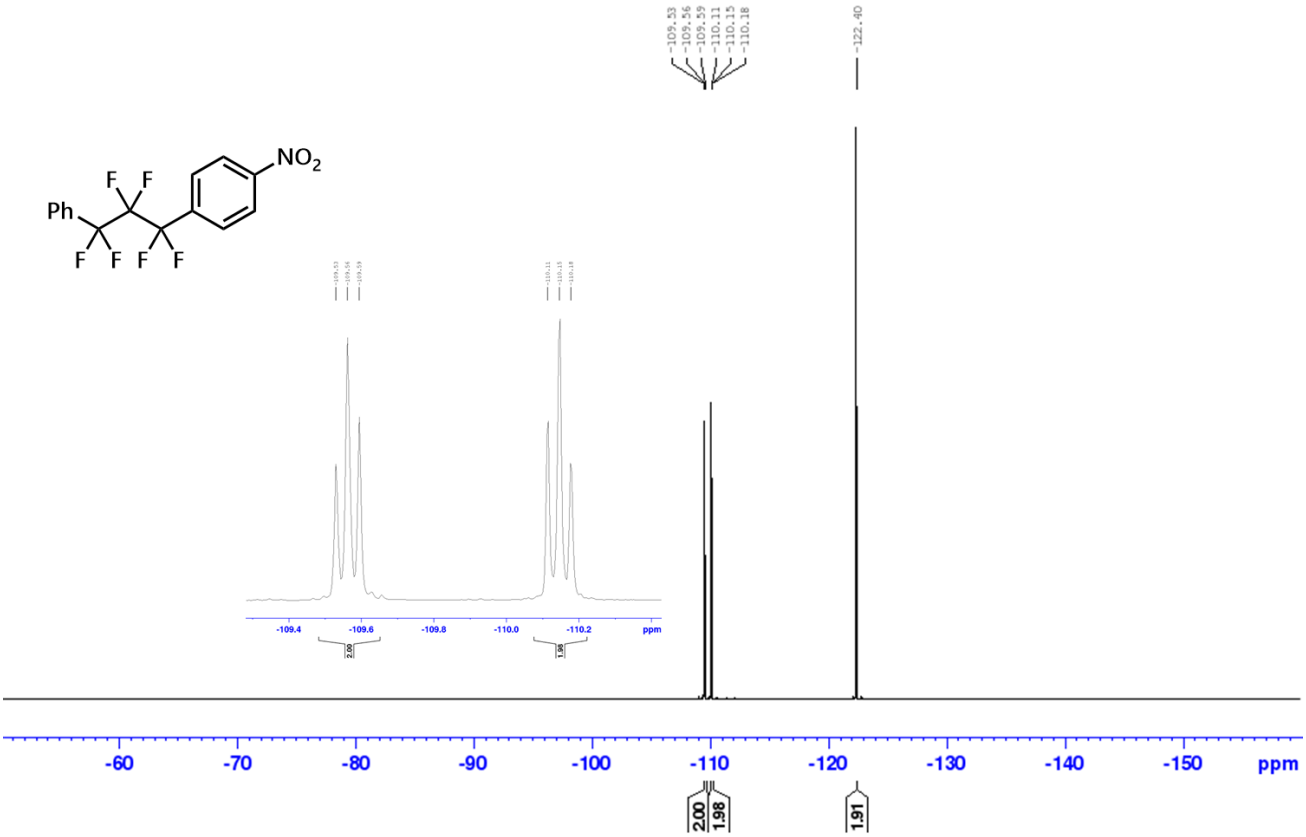

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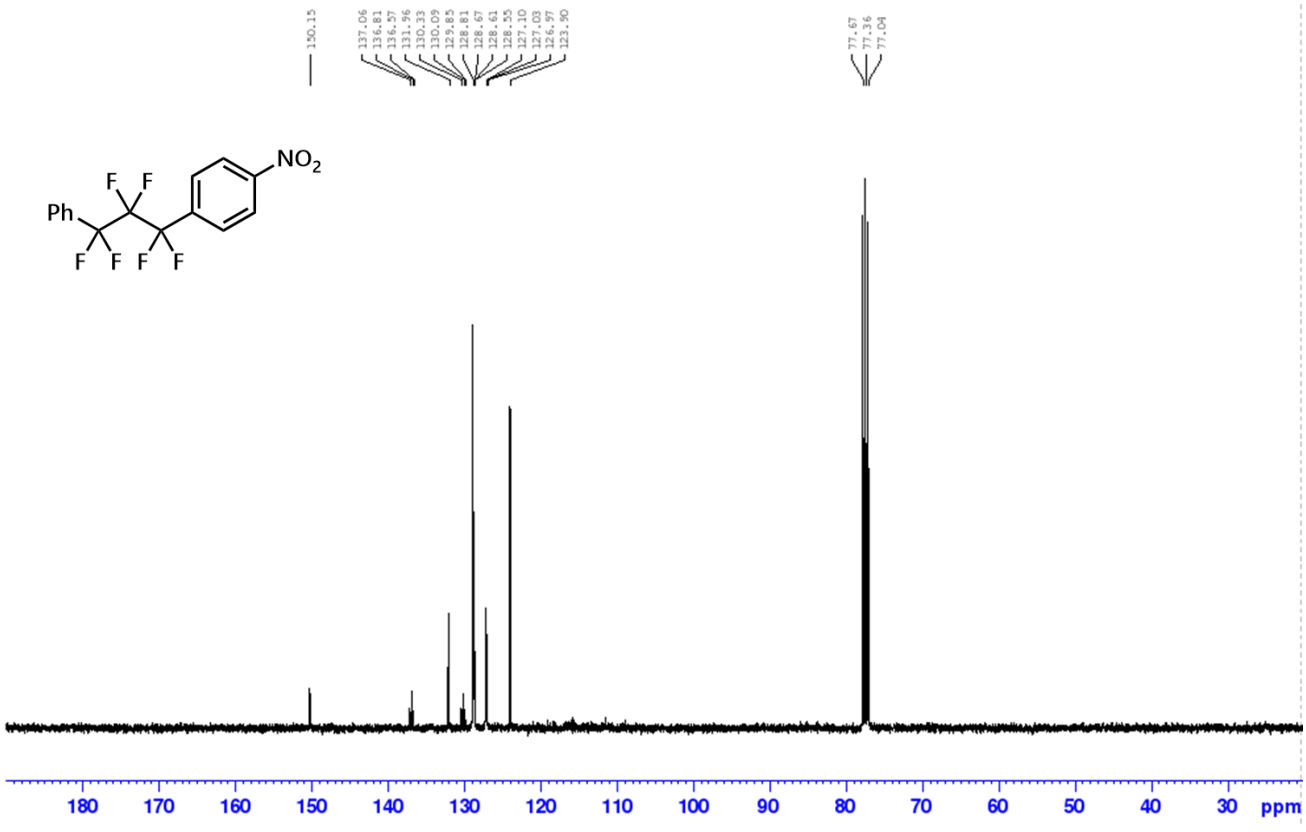
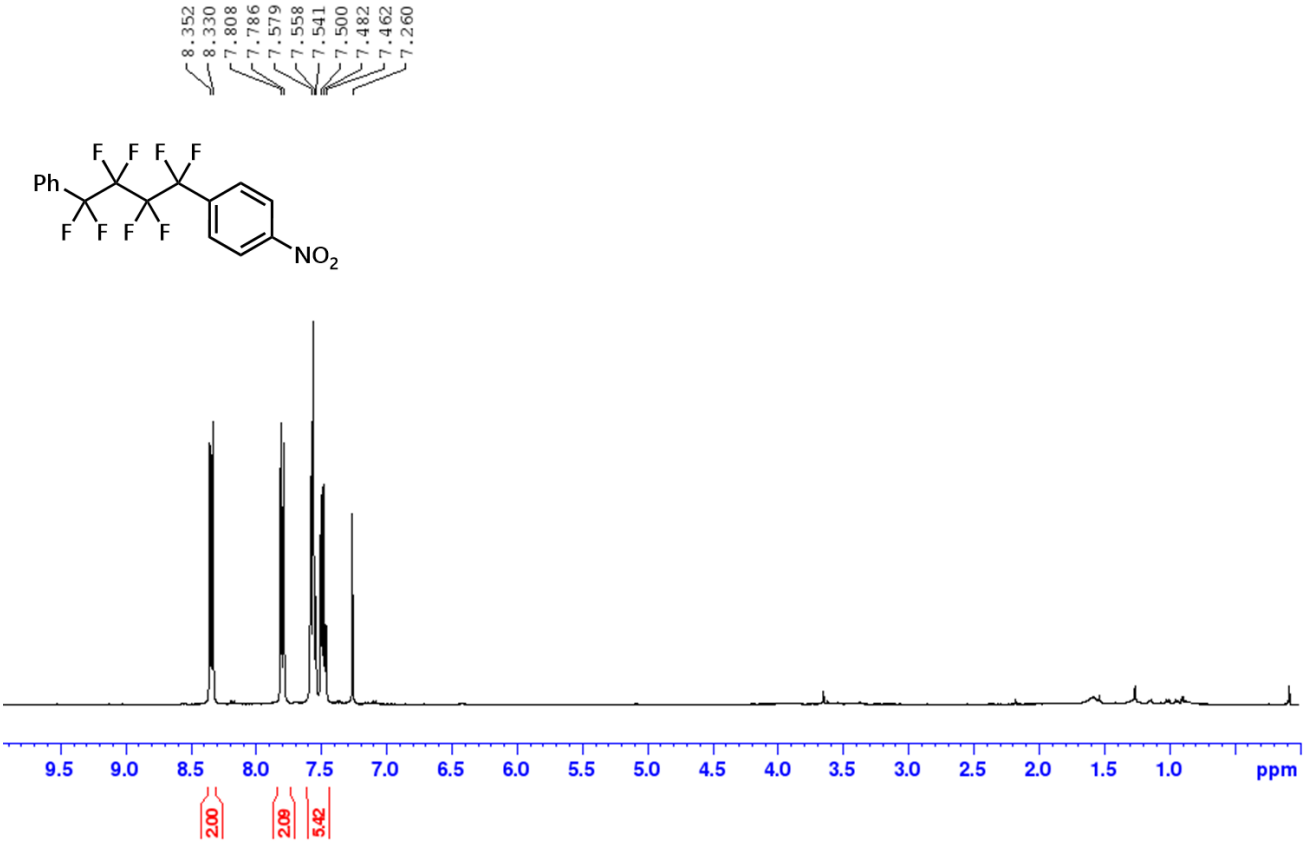


3d₂

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



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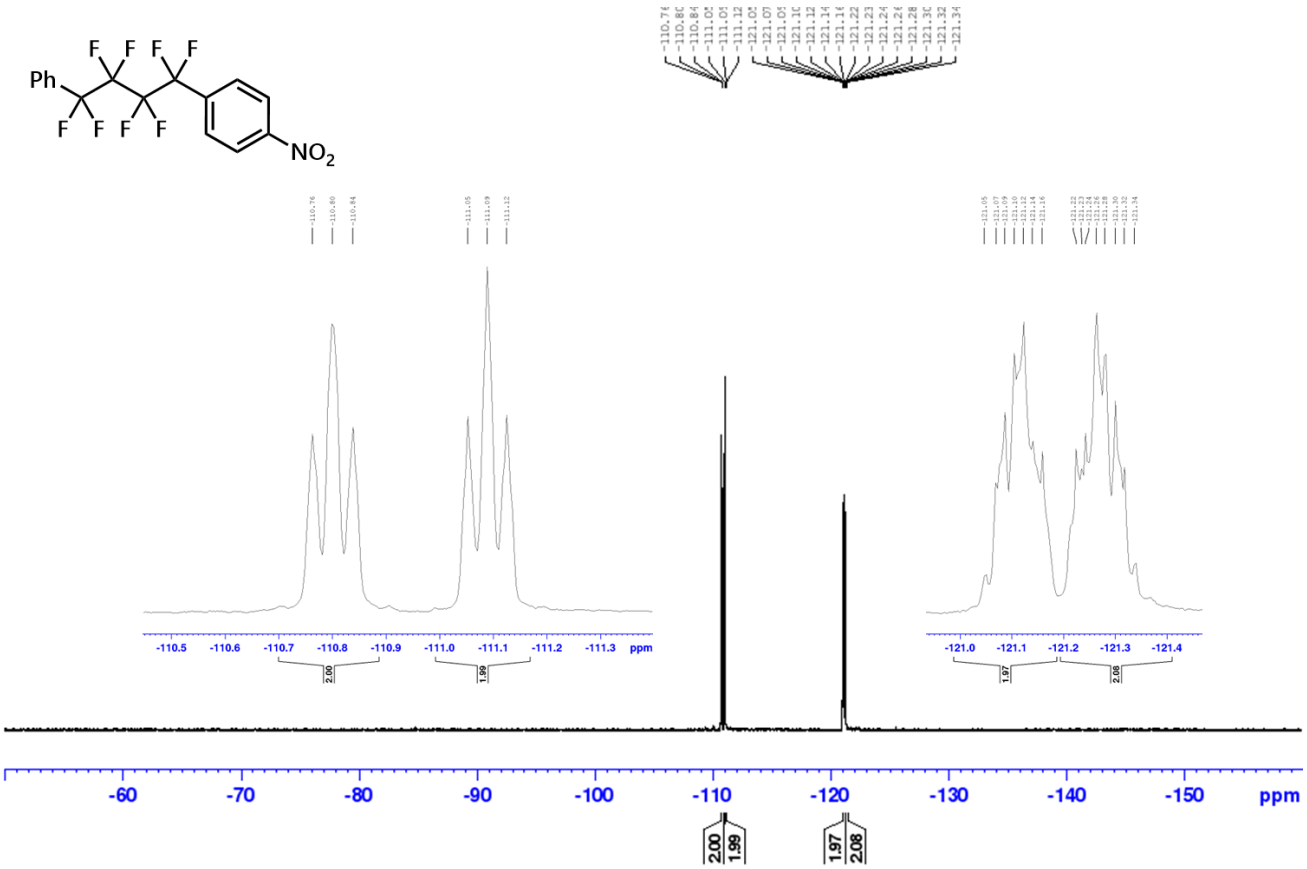

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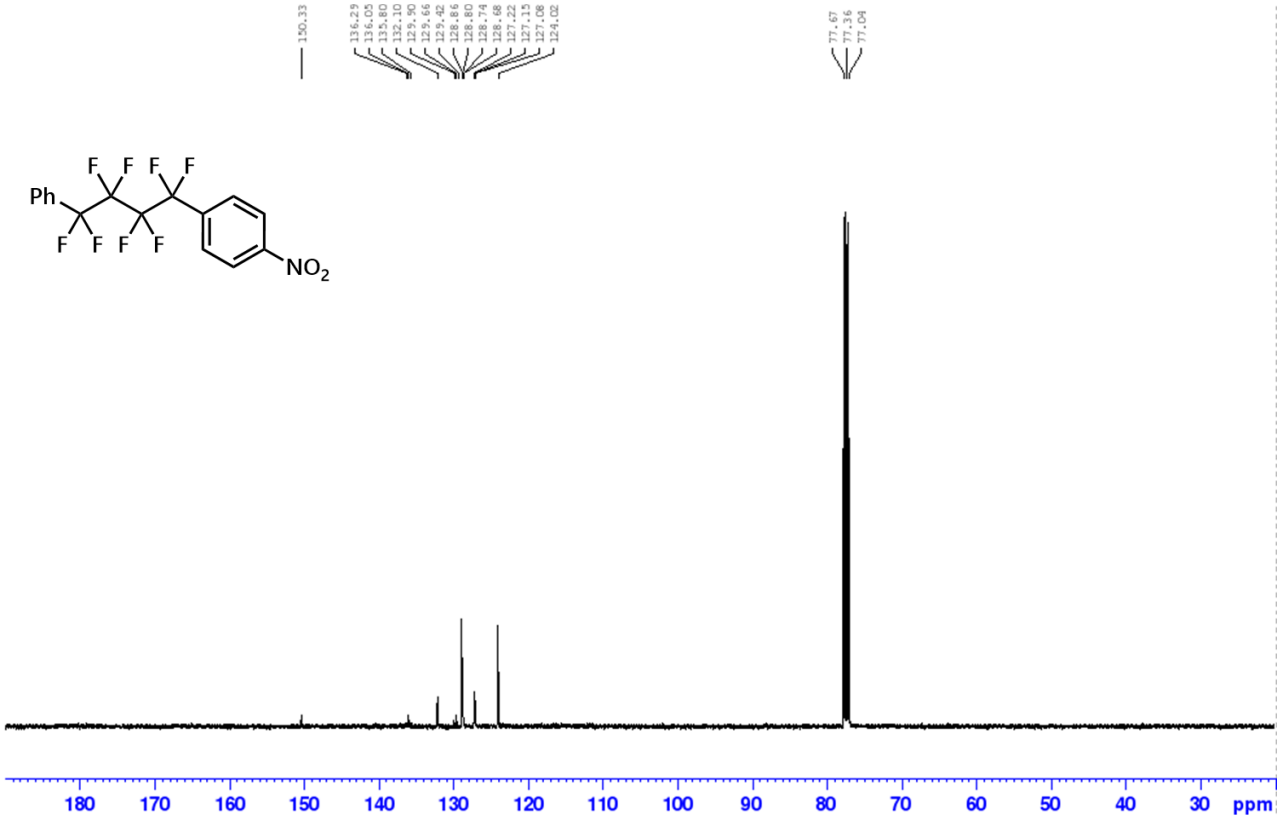
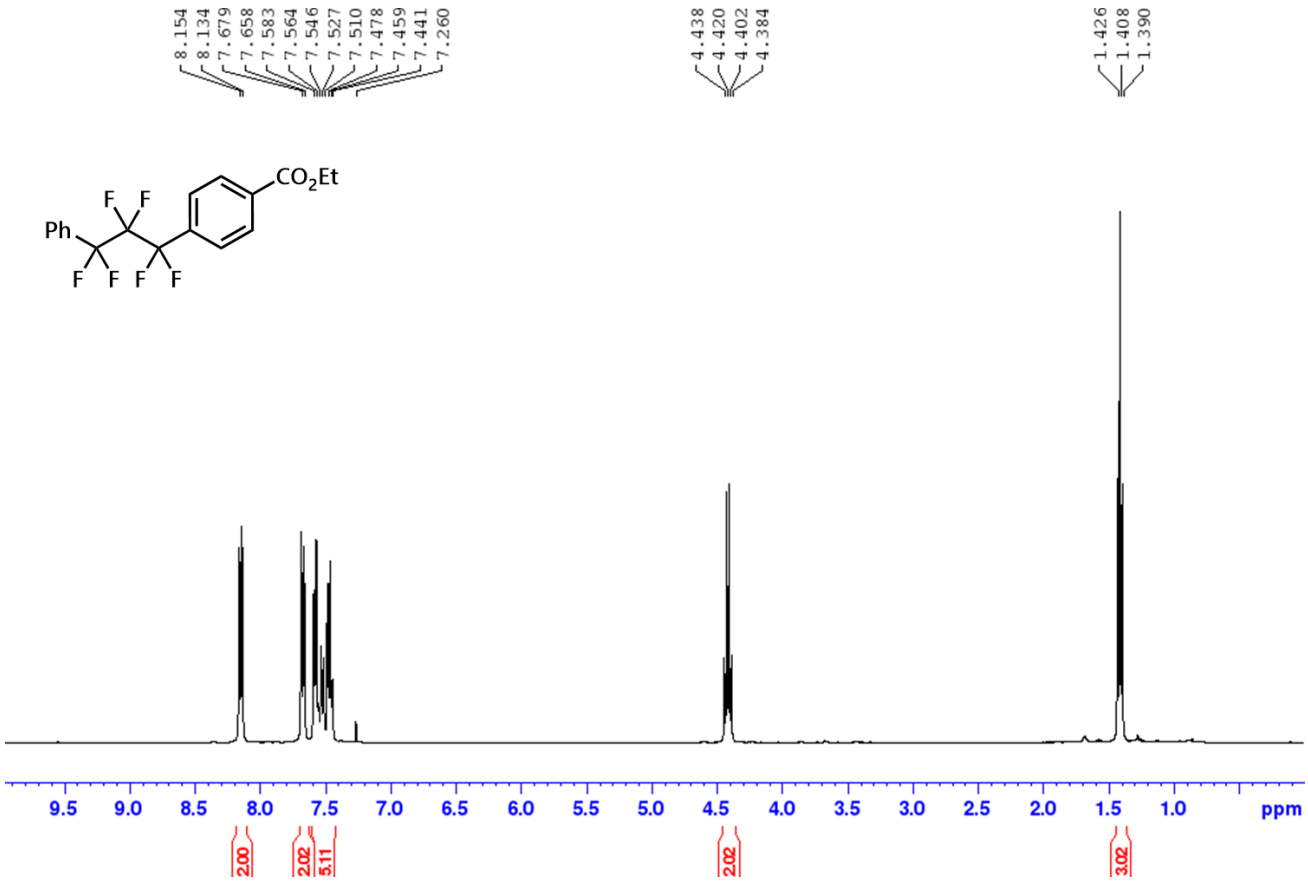


3e₁

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



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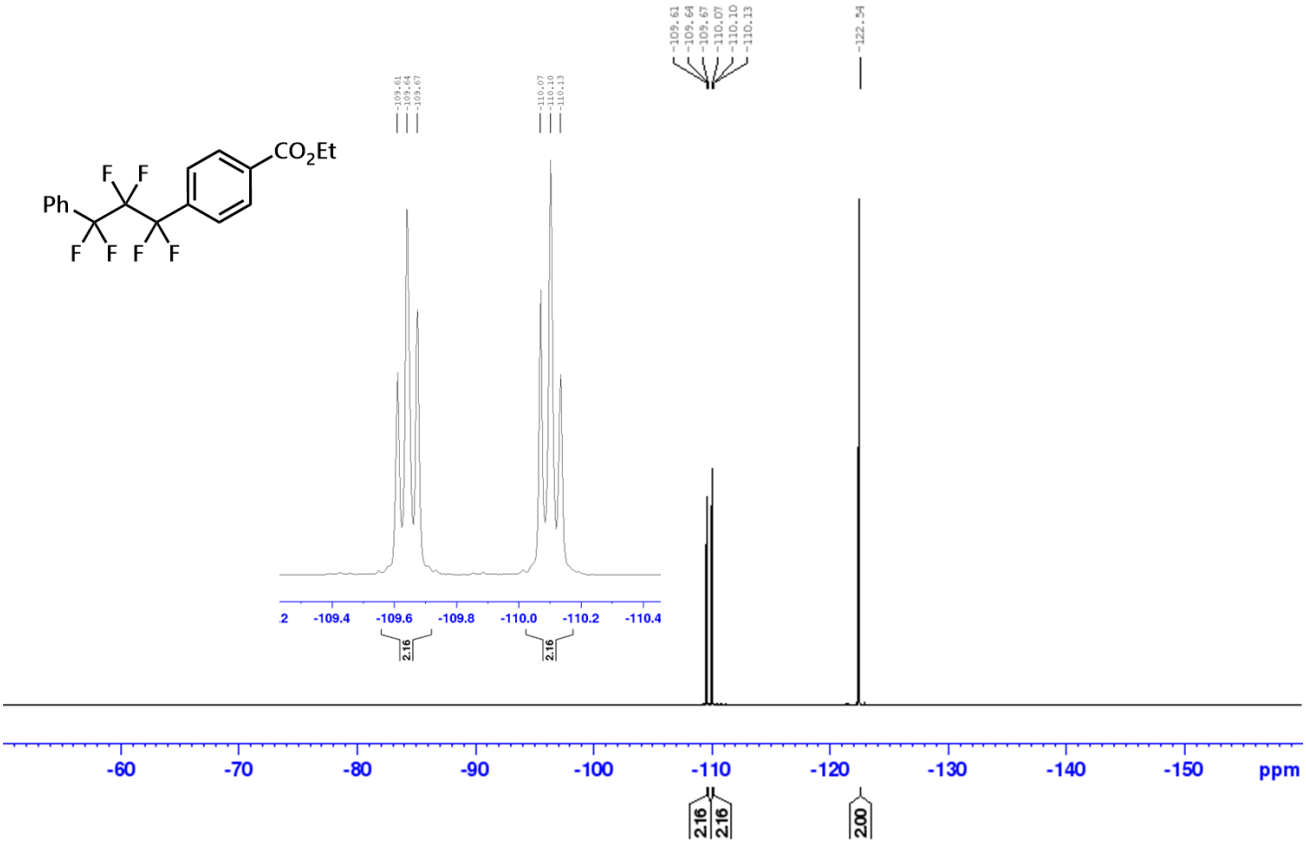

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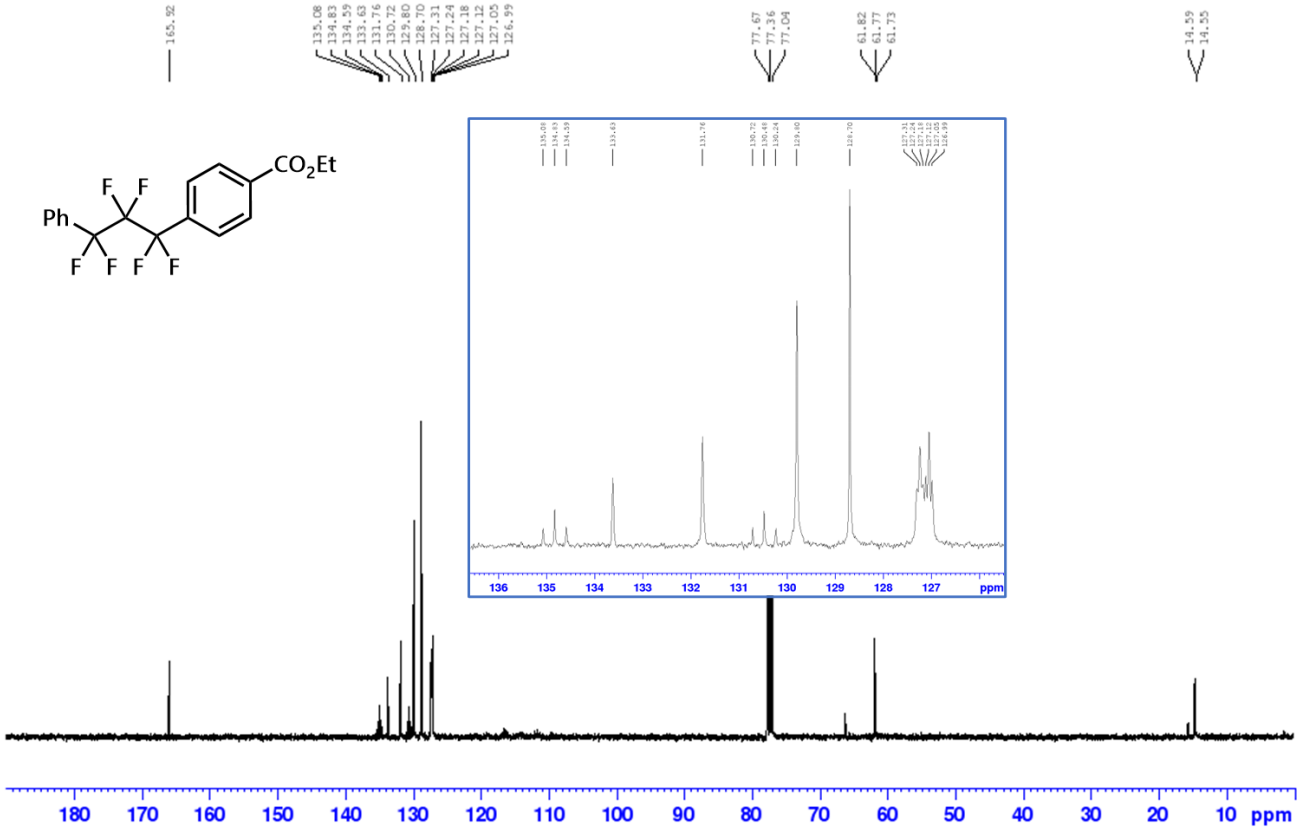
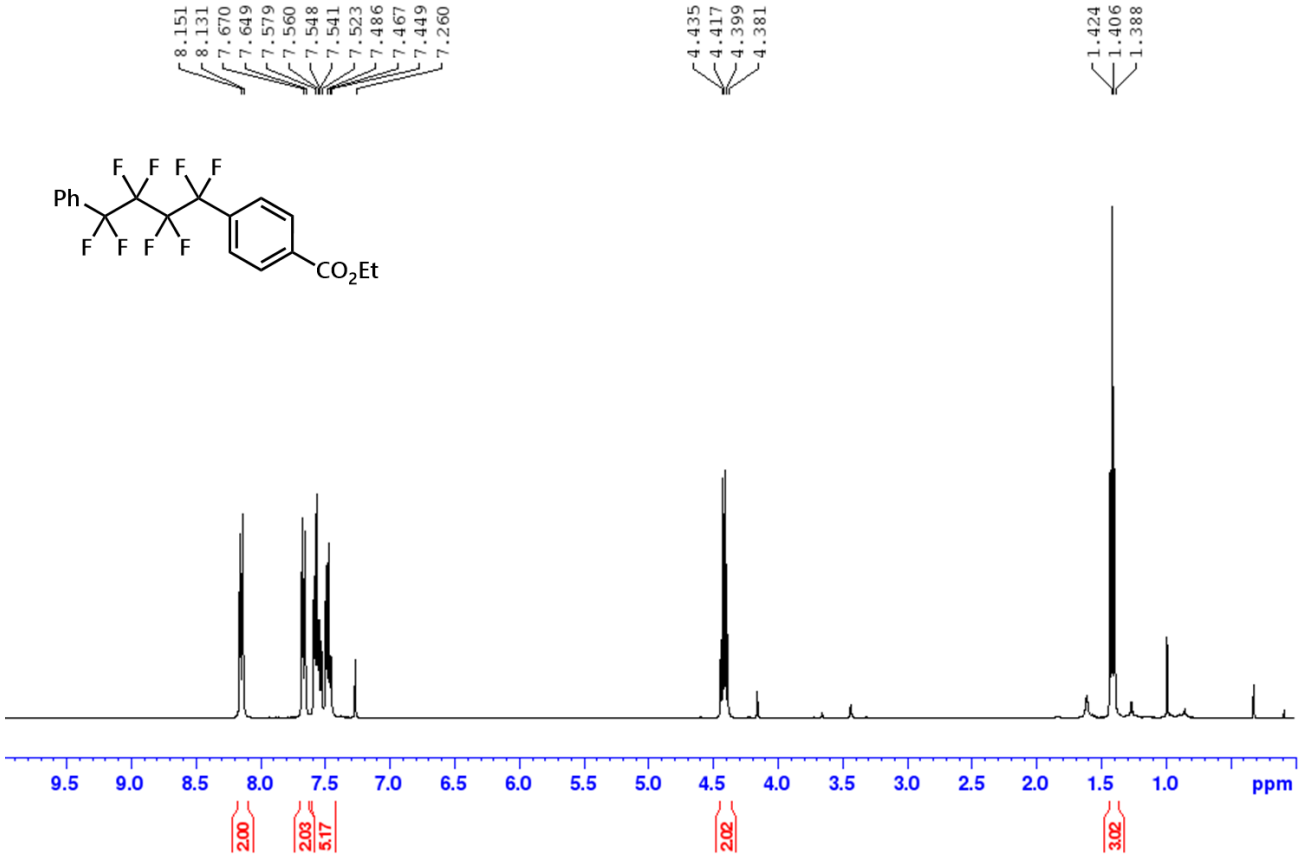


3e₂

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



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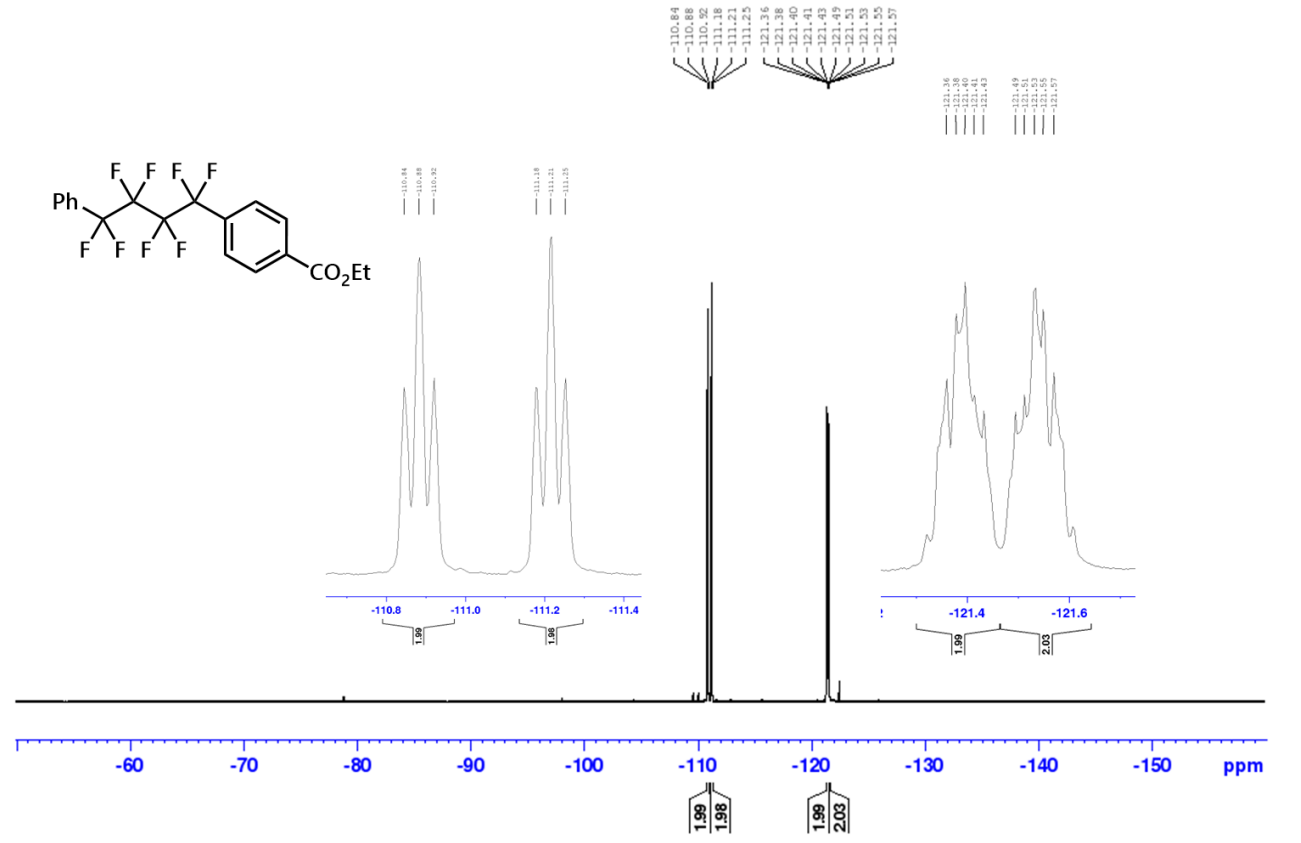
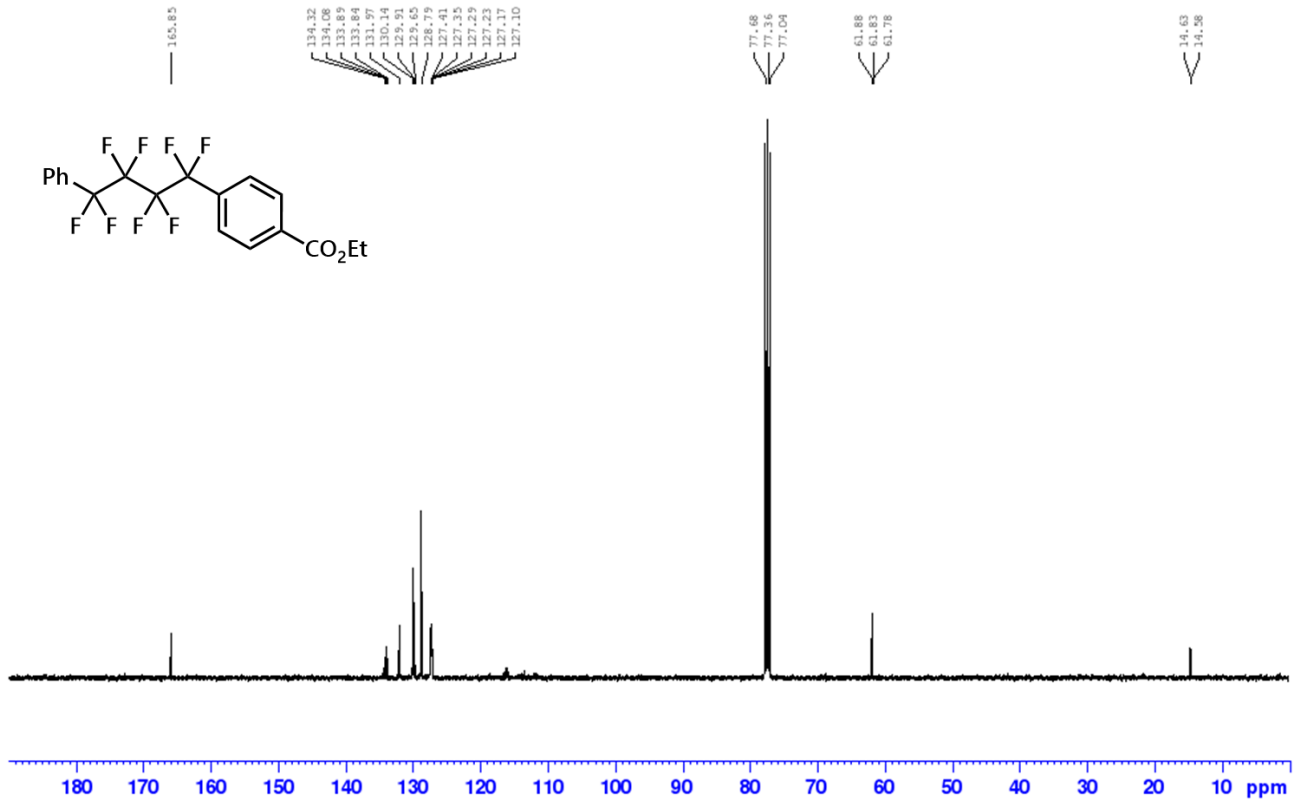
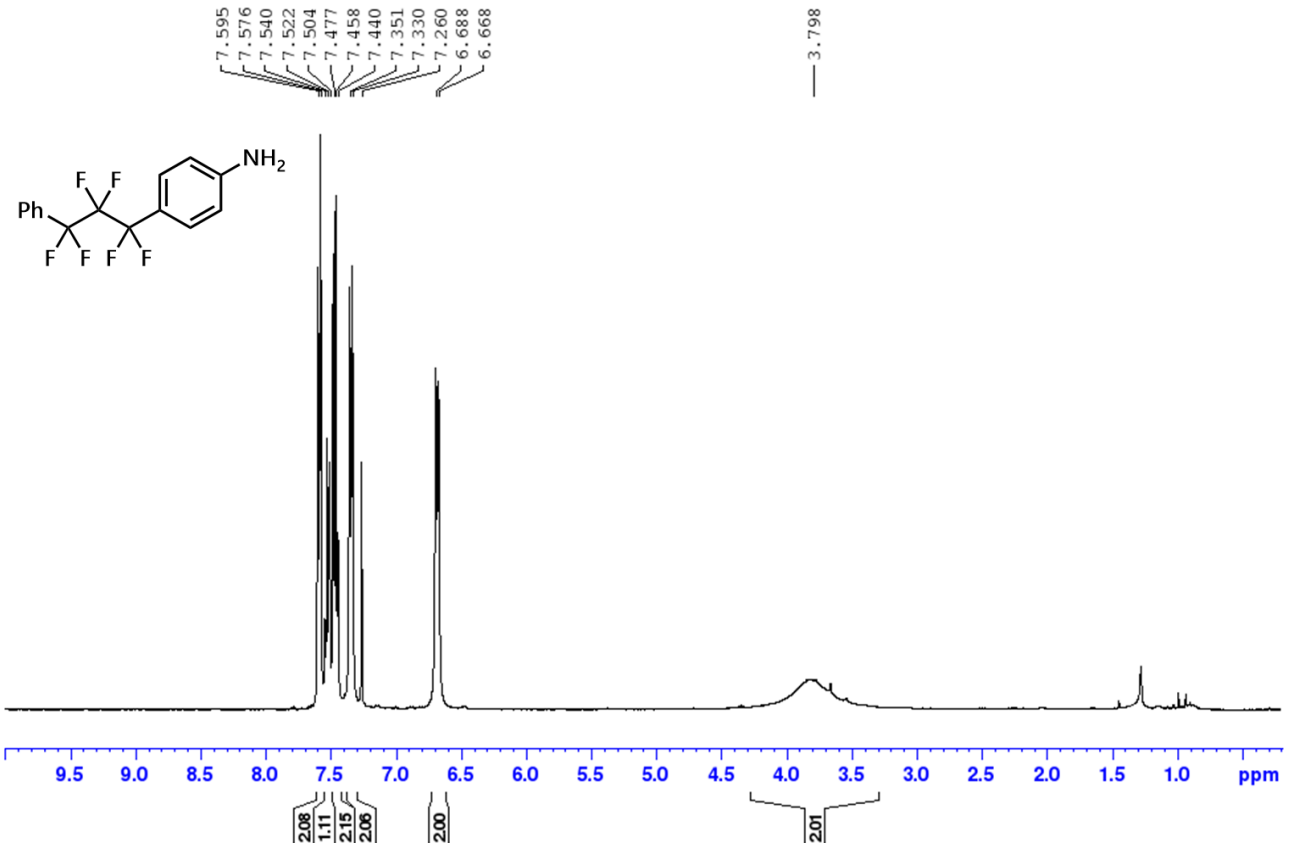


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

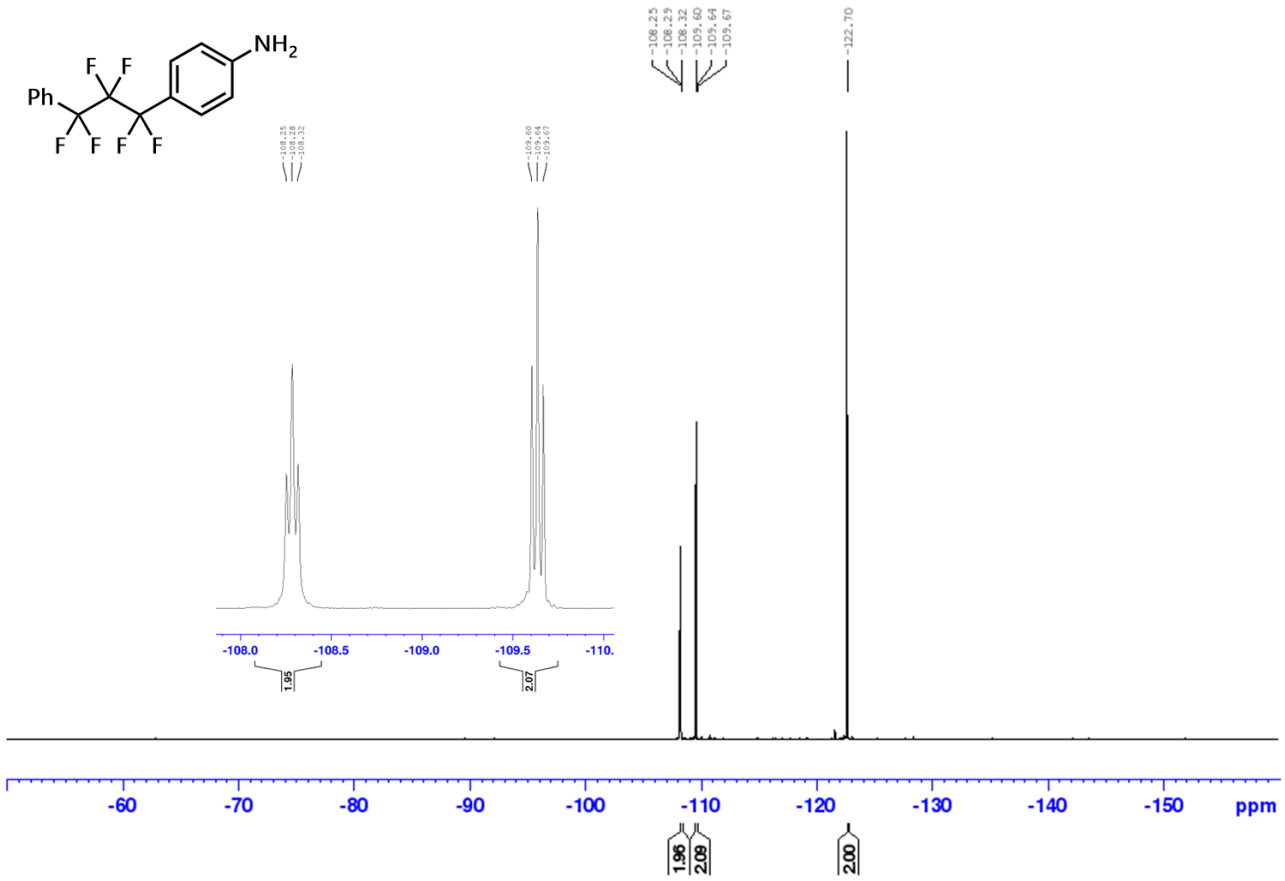


3f₁

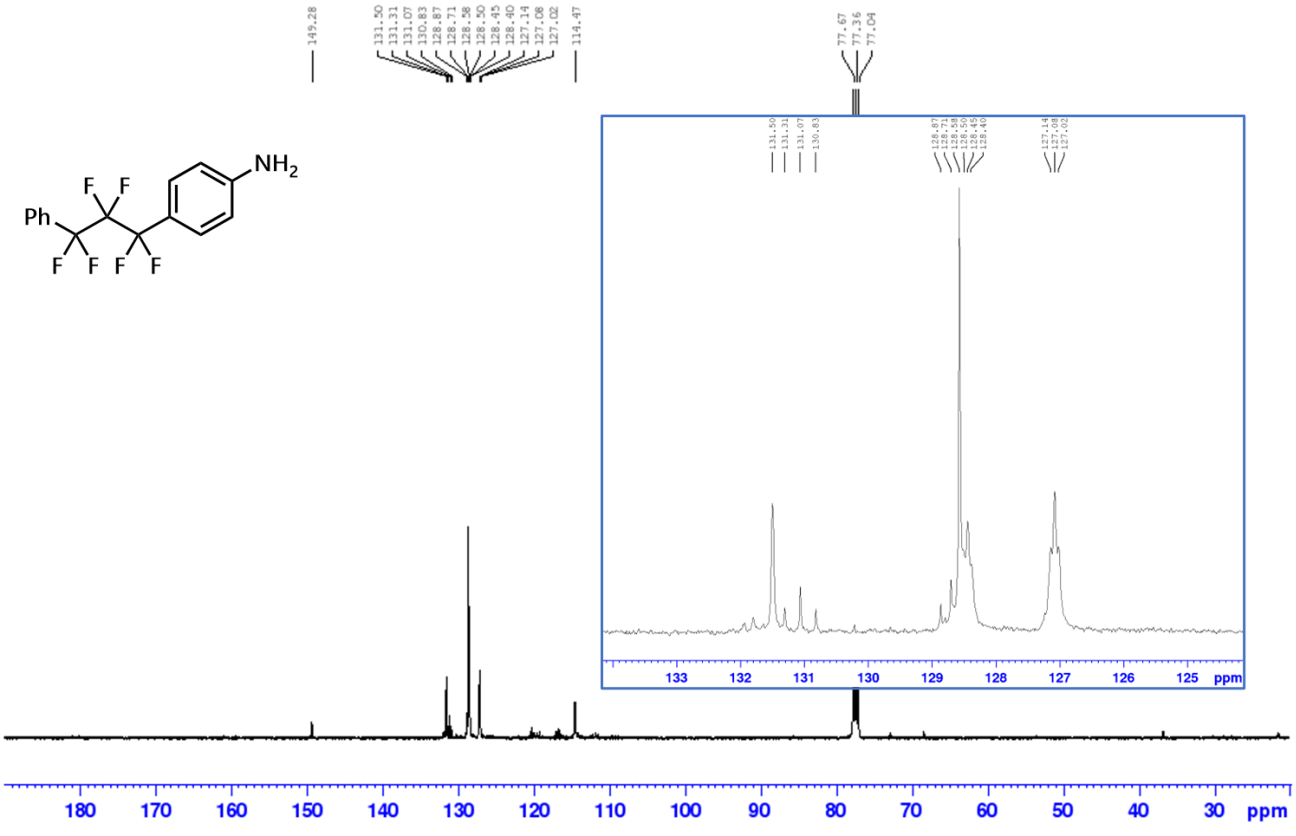
^{1}H NMR (400 MHz, $CDCl_3$)



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

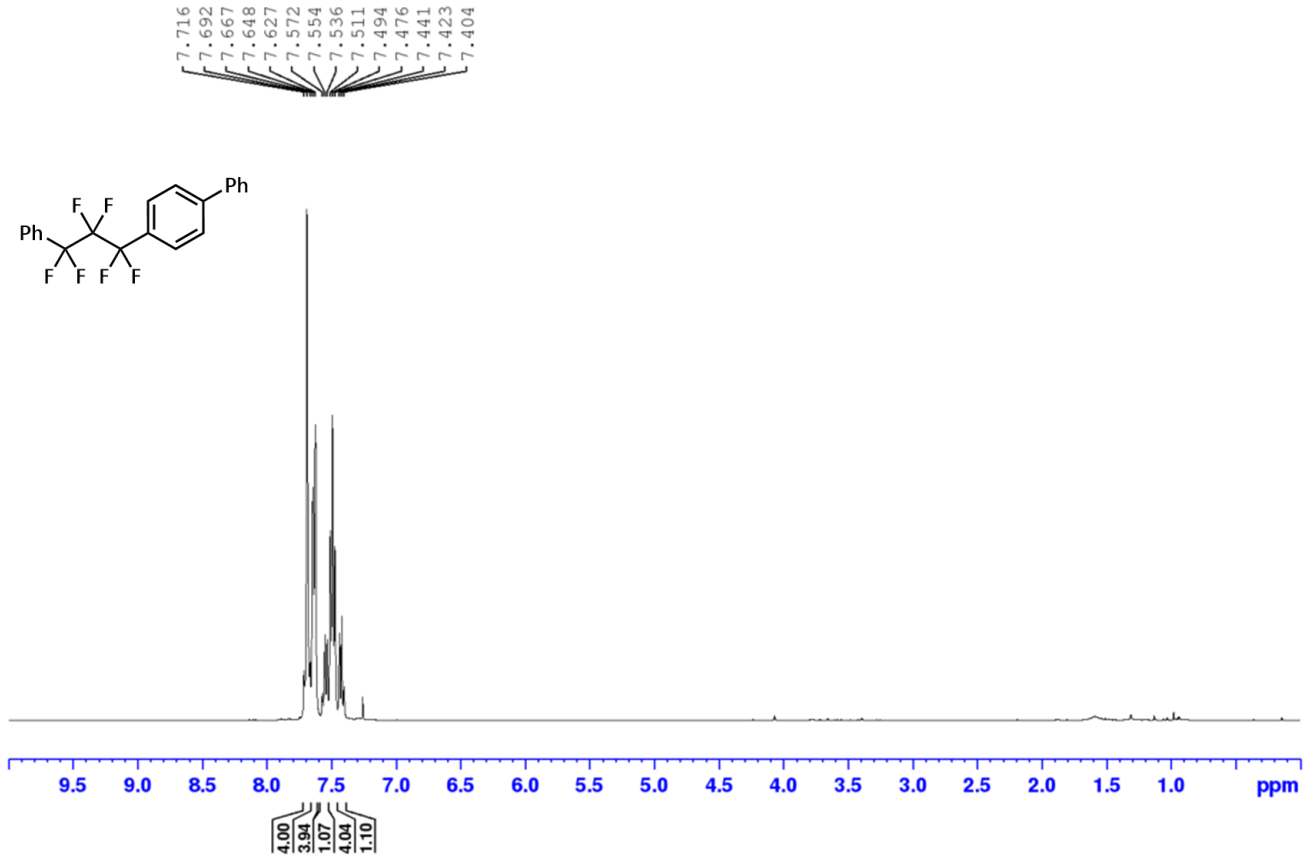


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)



3g₁

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



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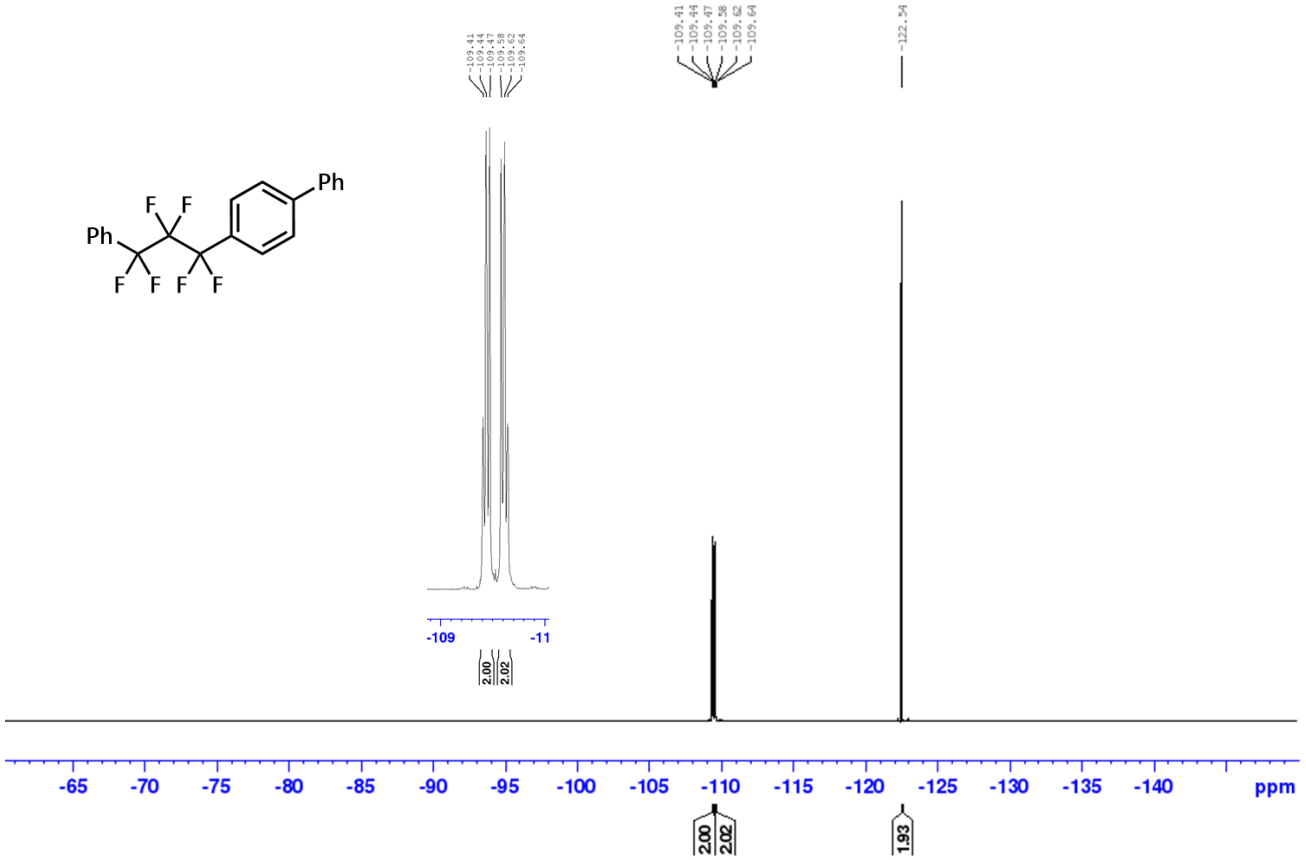
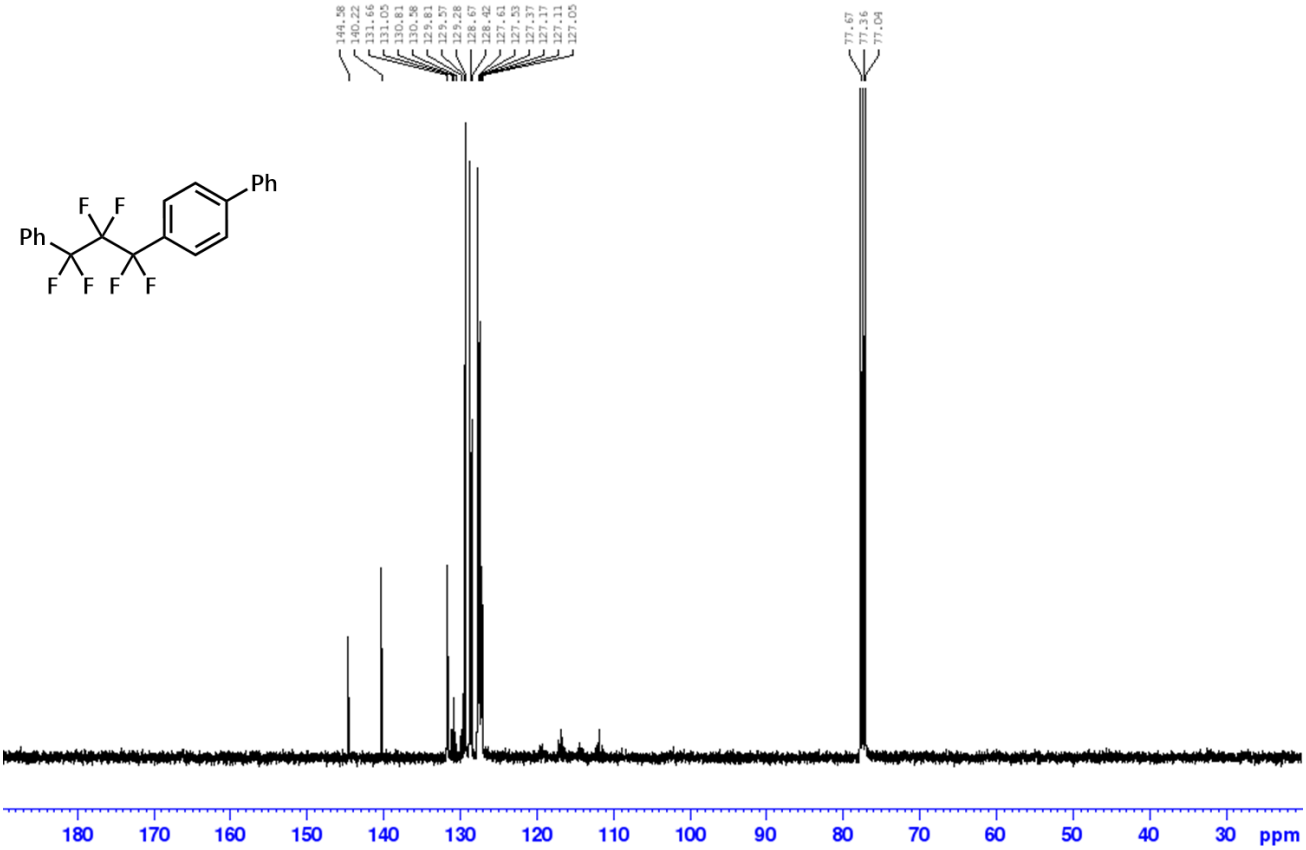
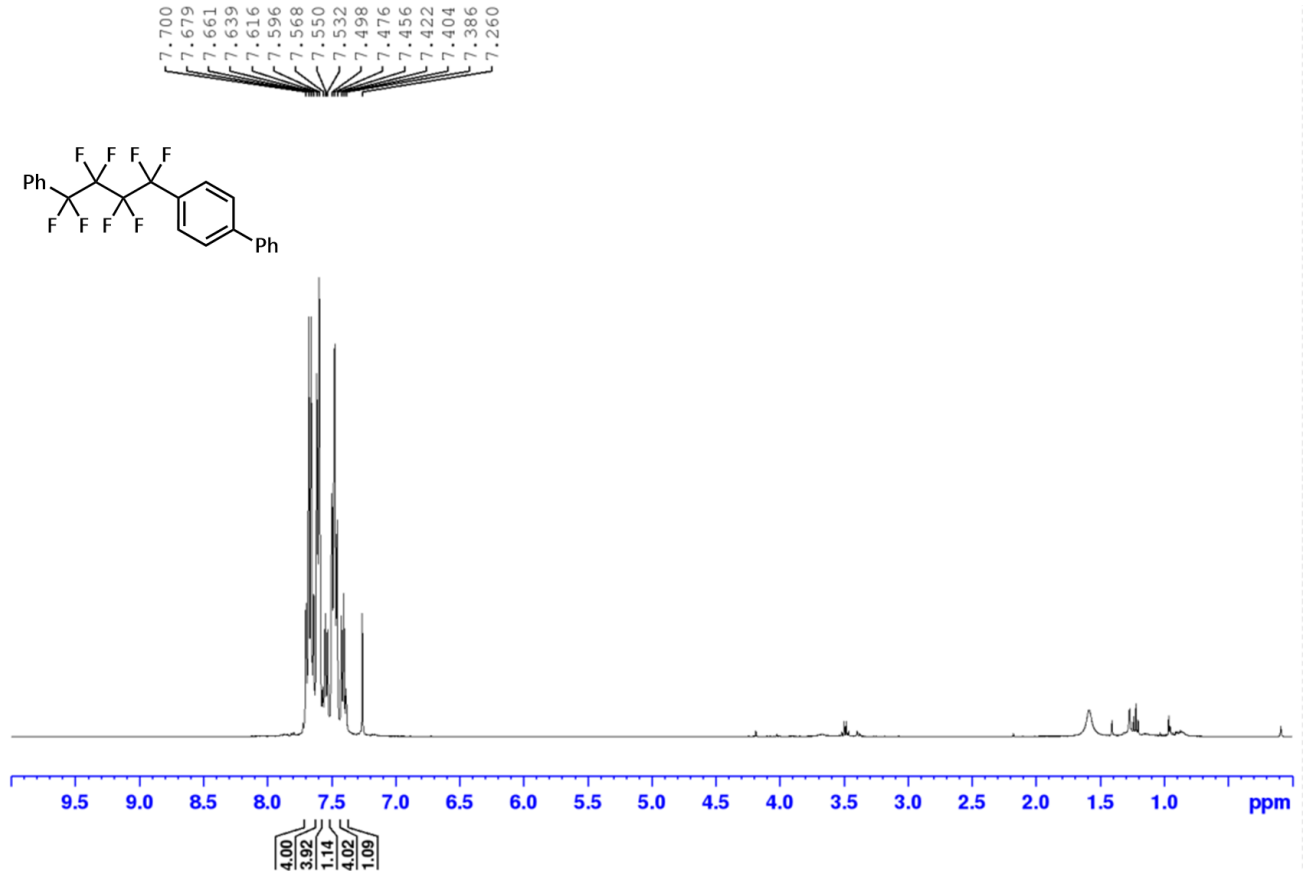


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

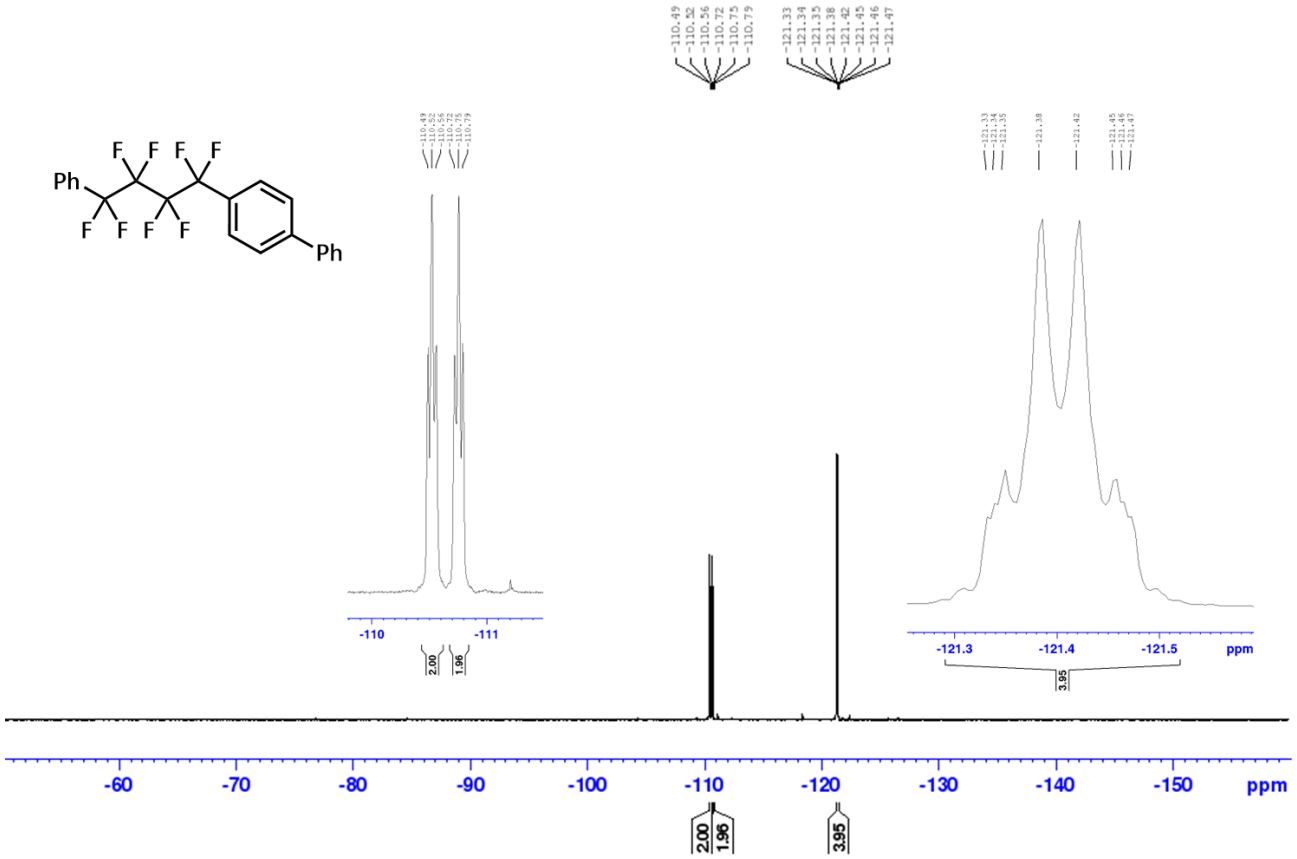


3g₂

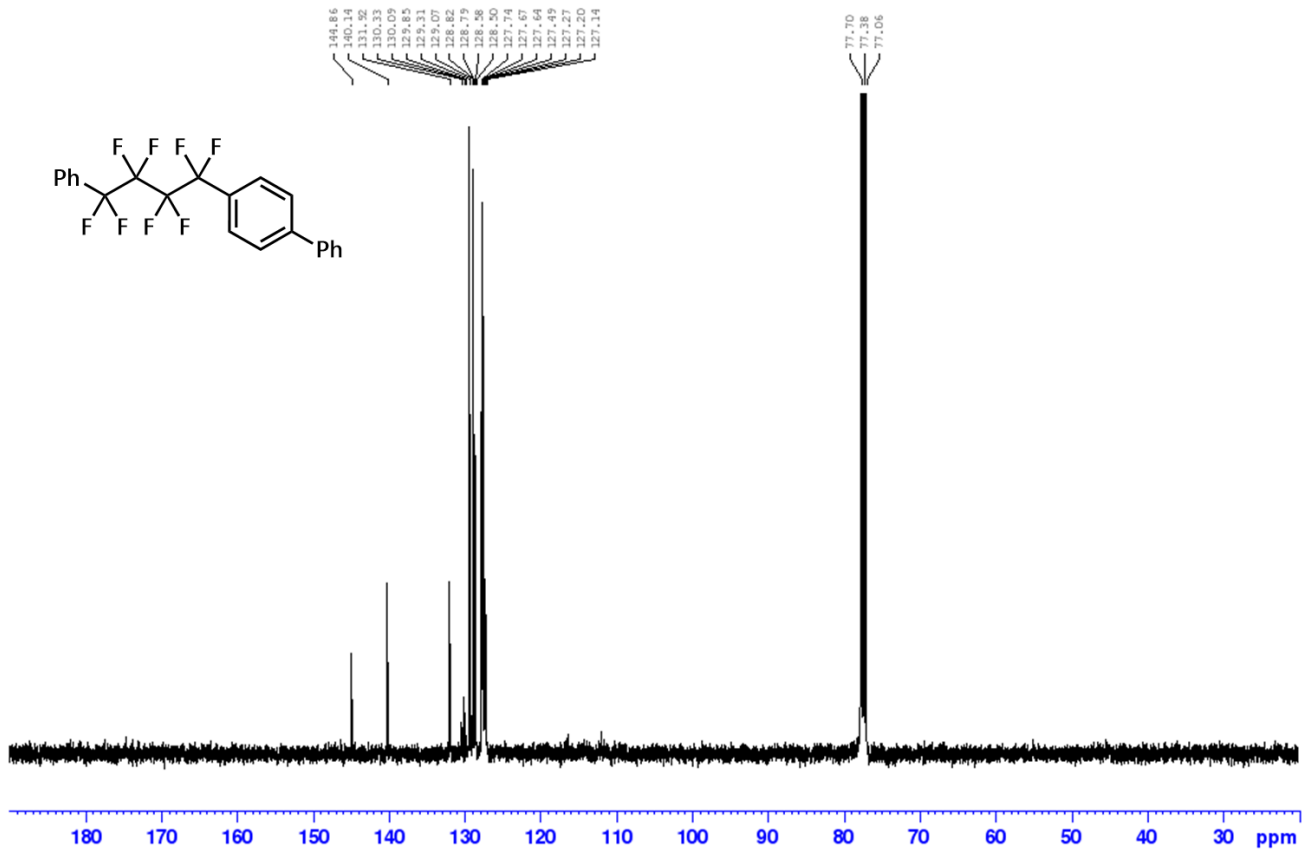
^{1}H NMR (400 MHz, $CDCl_3$)



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

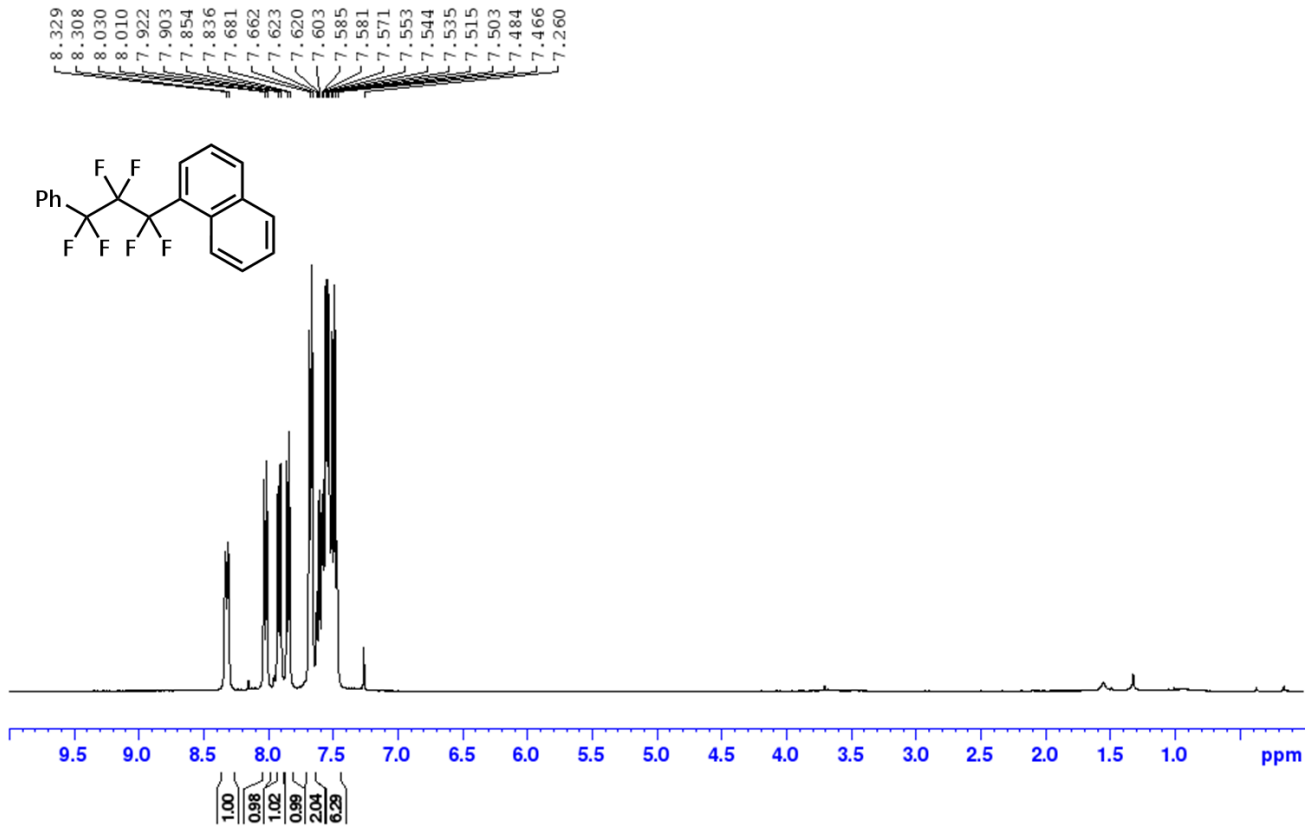


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

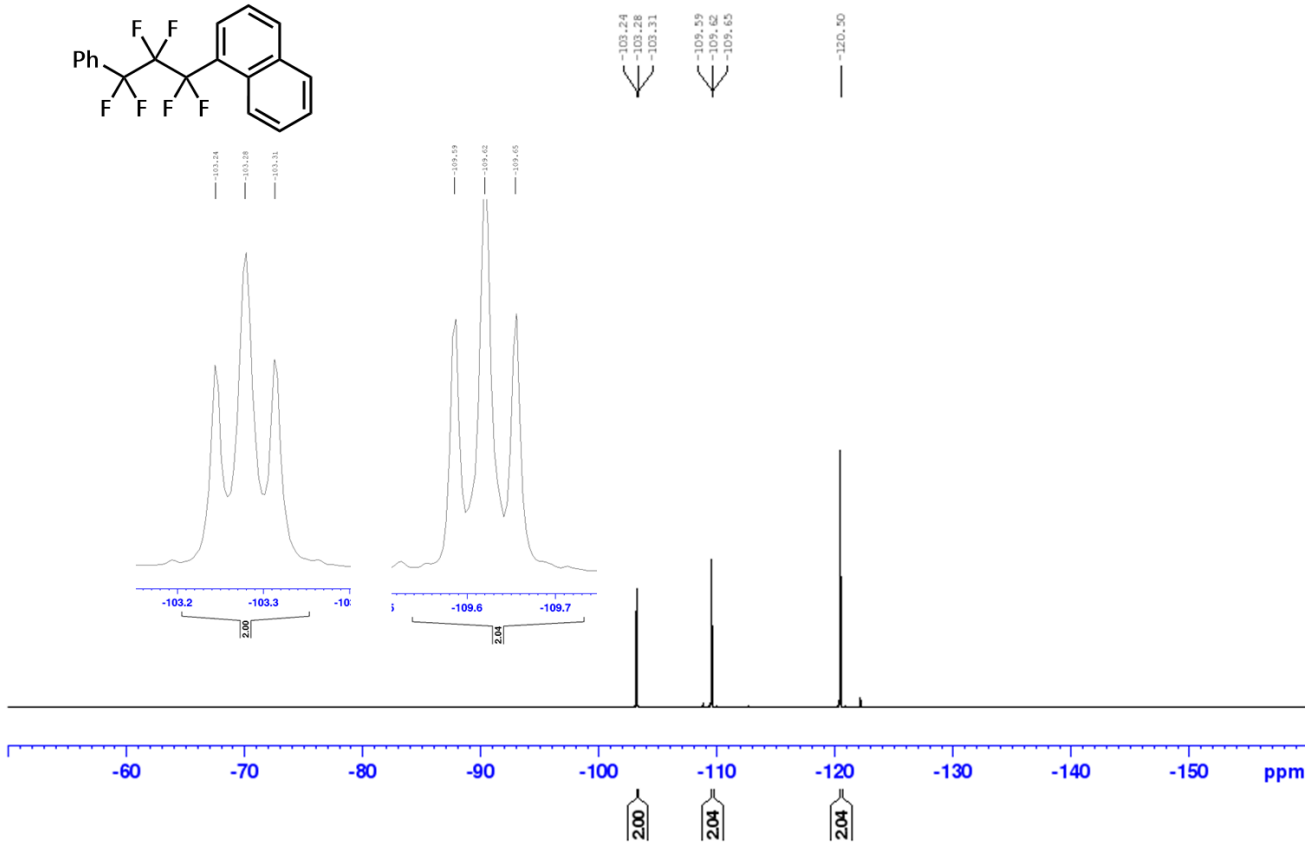


3h₁

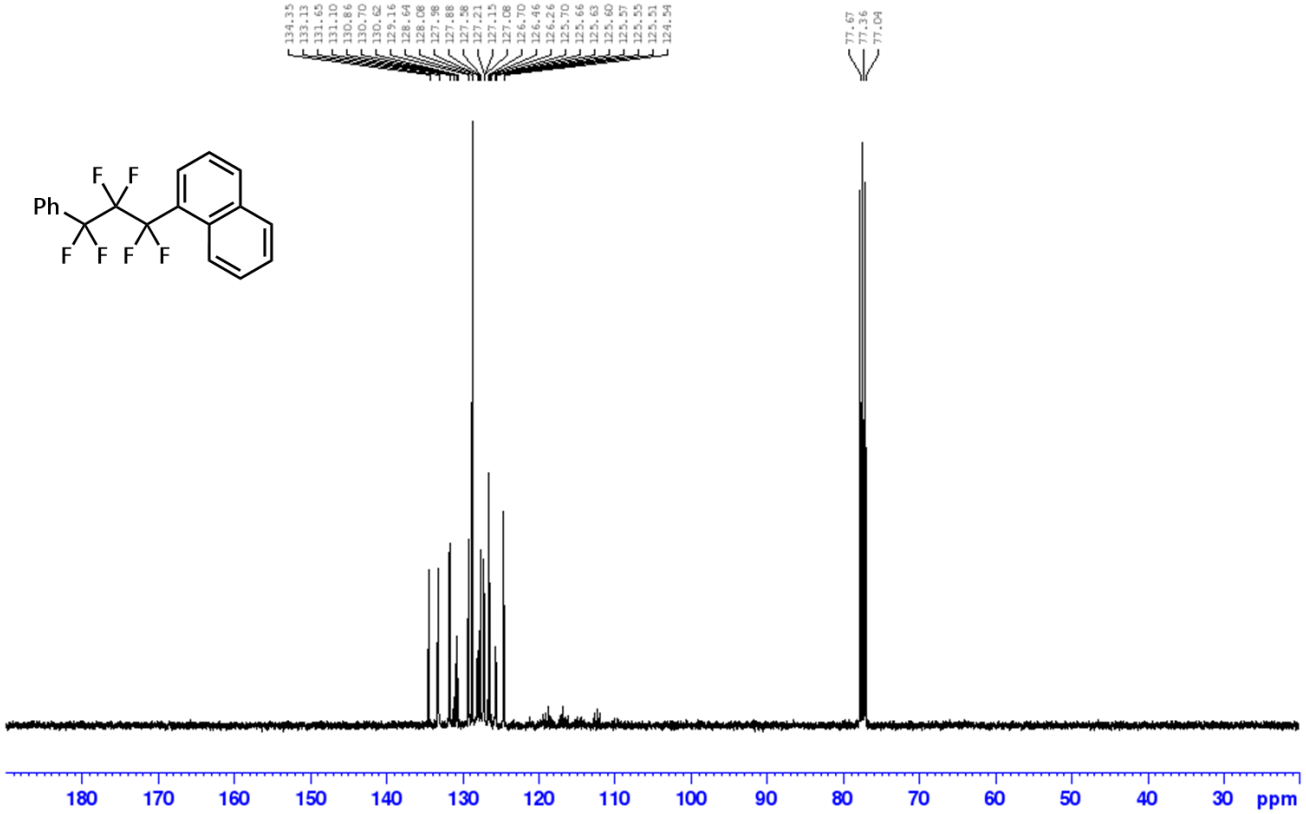
^{1}H NMR (400 MHz, $CDCl_3$)



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

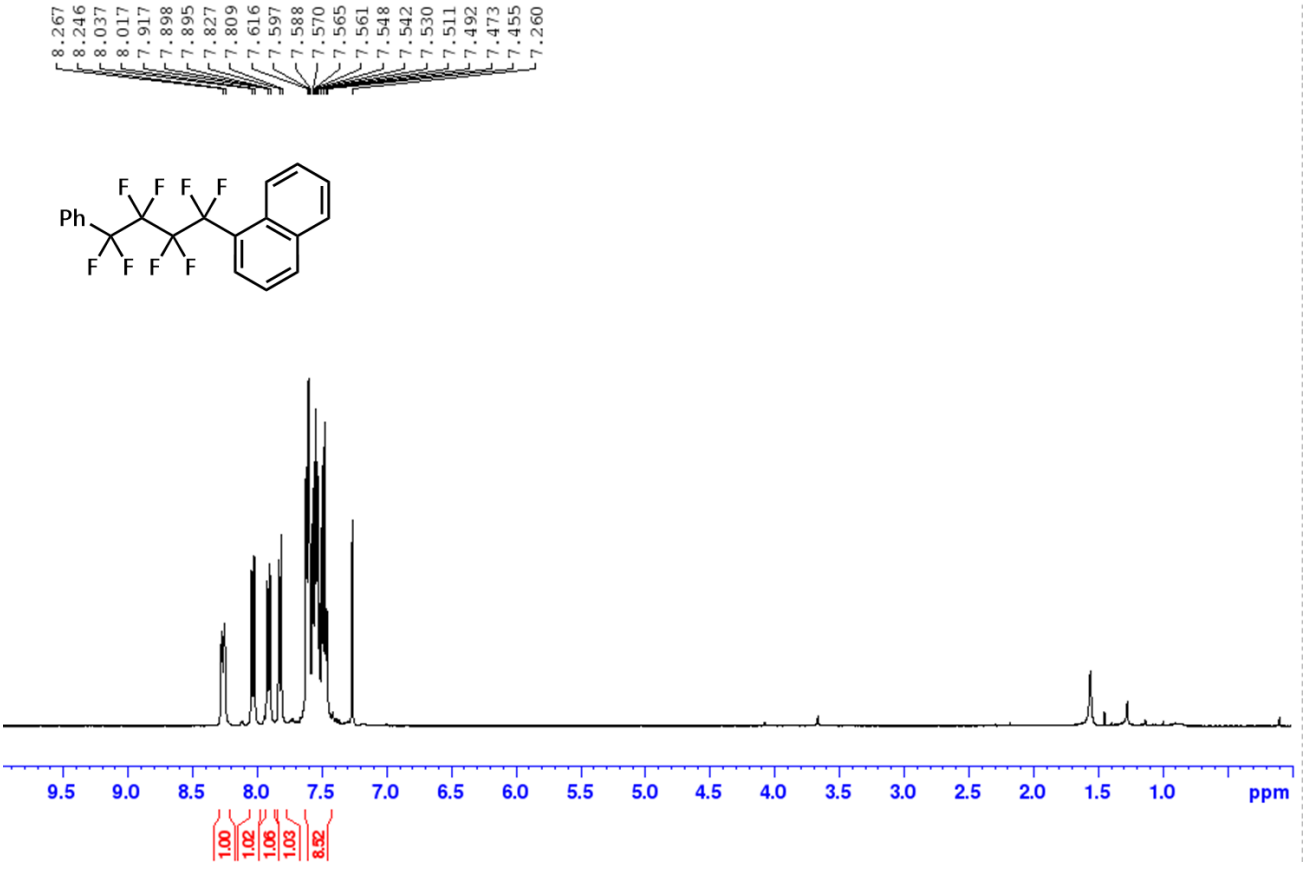


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

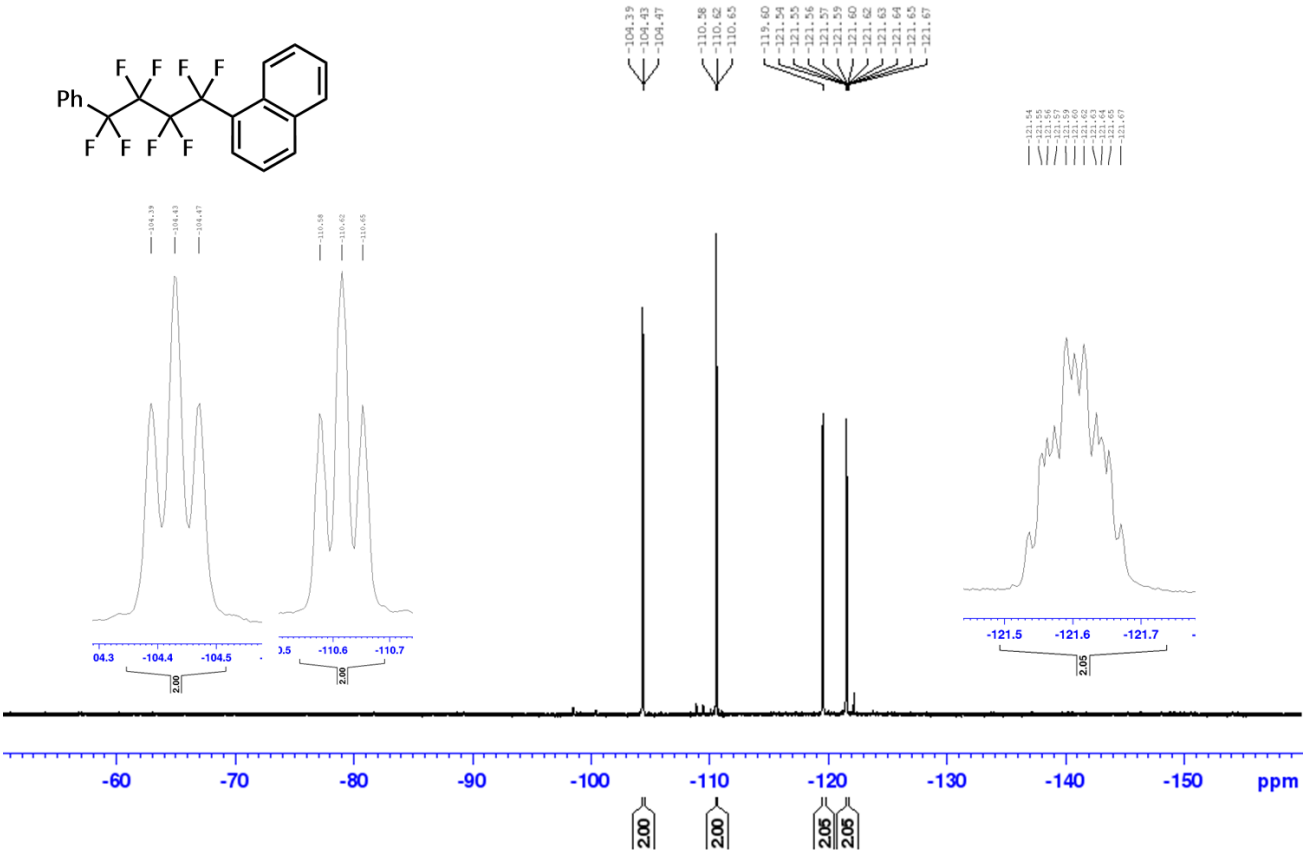


3h₂

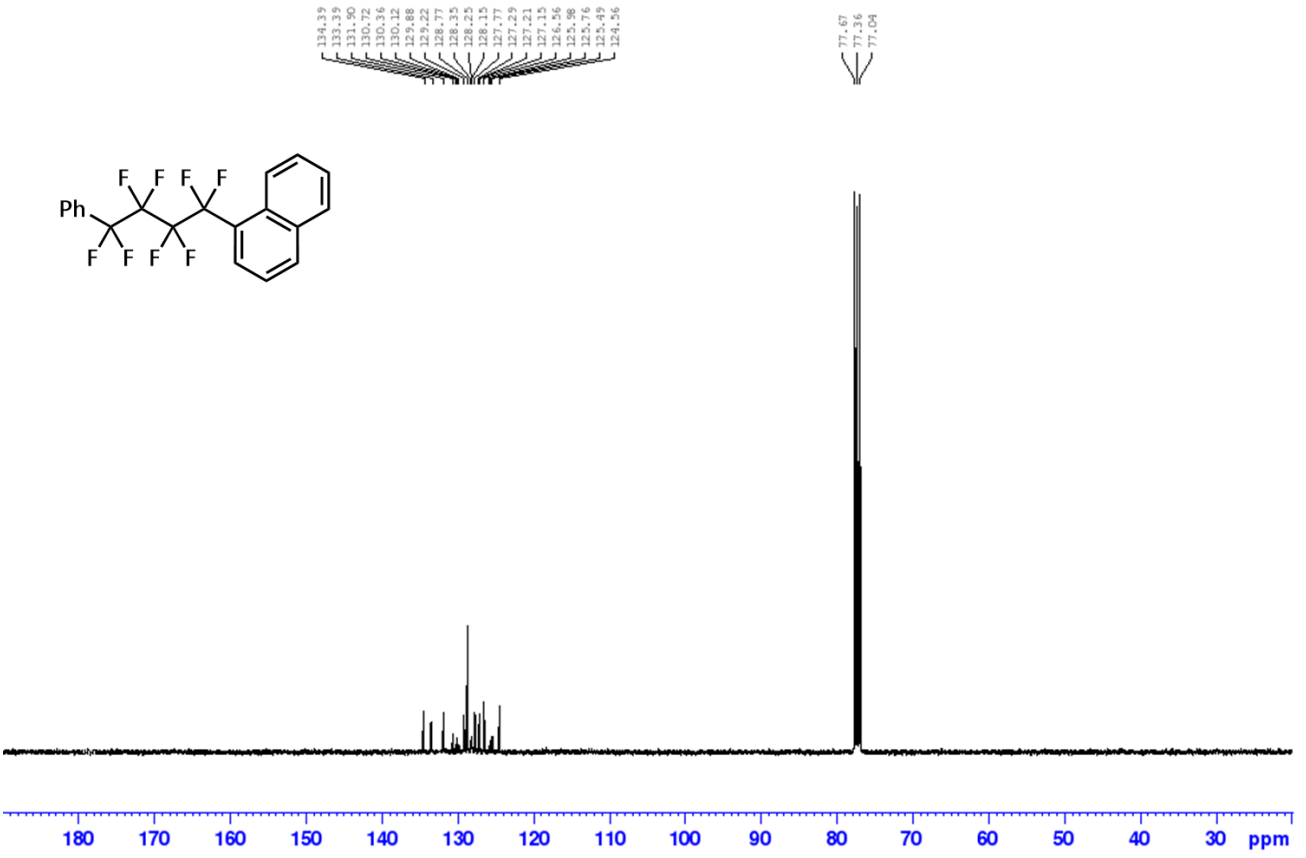
^{1}H NMR (400 MHz, $CDCl_3$)



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

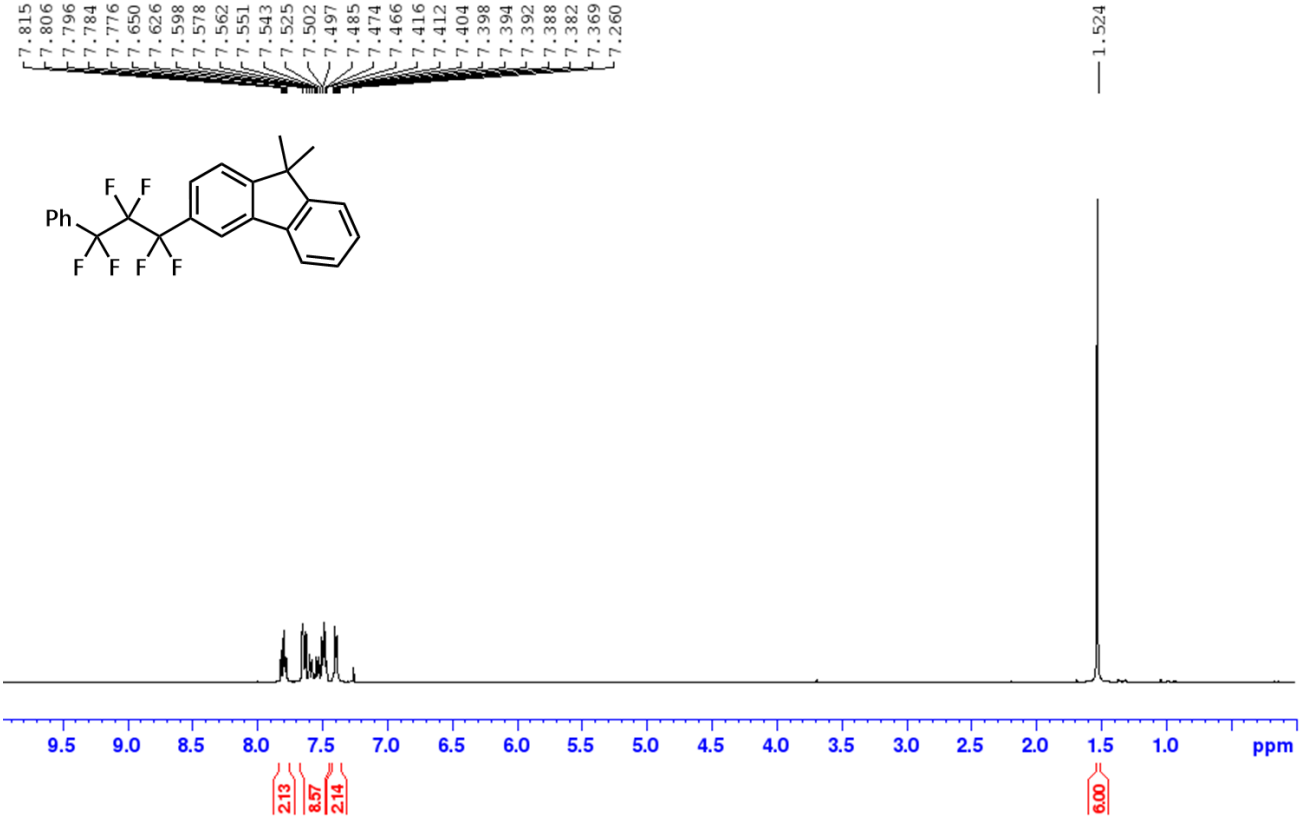


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

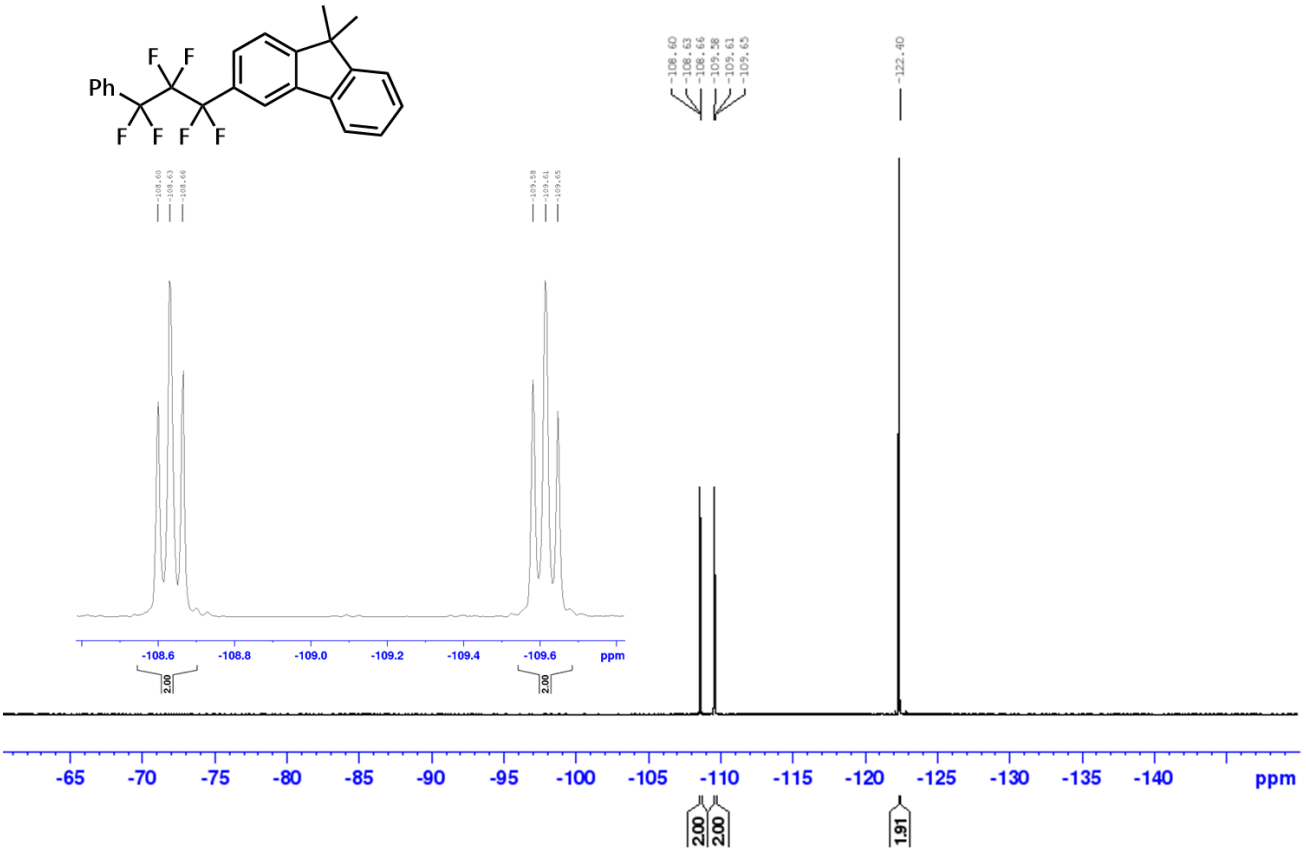


3i₁

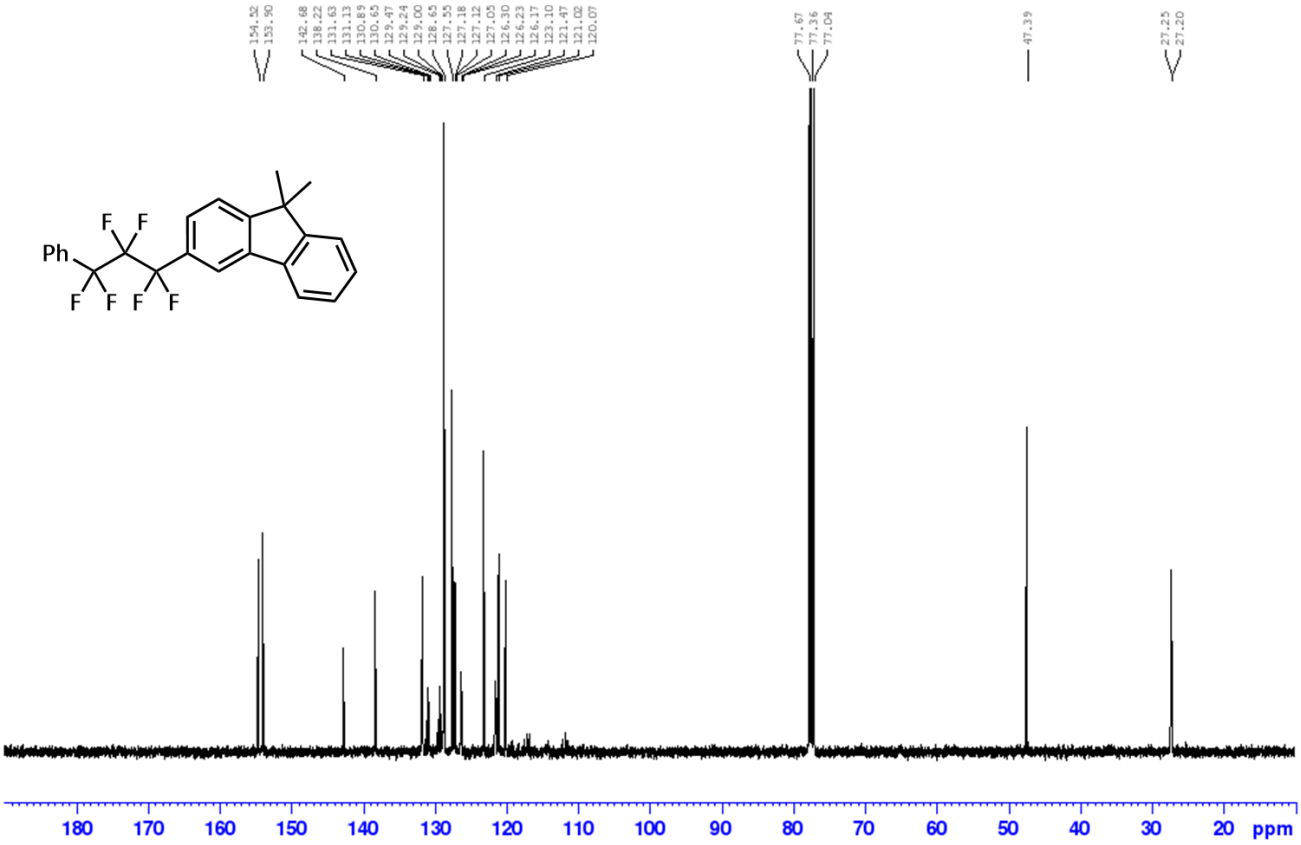
^{1}H NMR (400 MHz, $CDCl_3$)



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

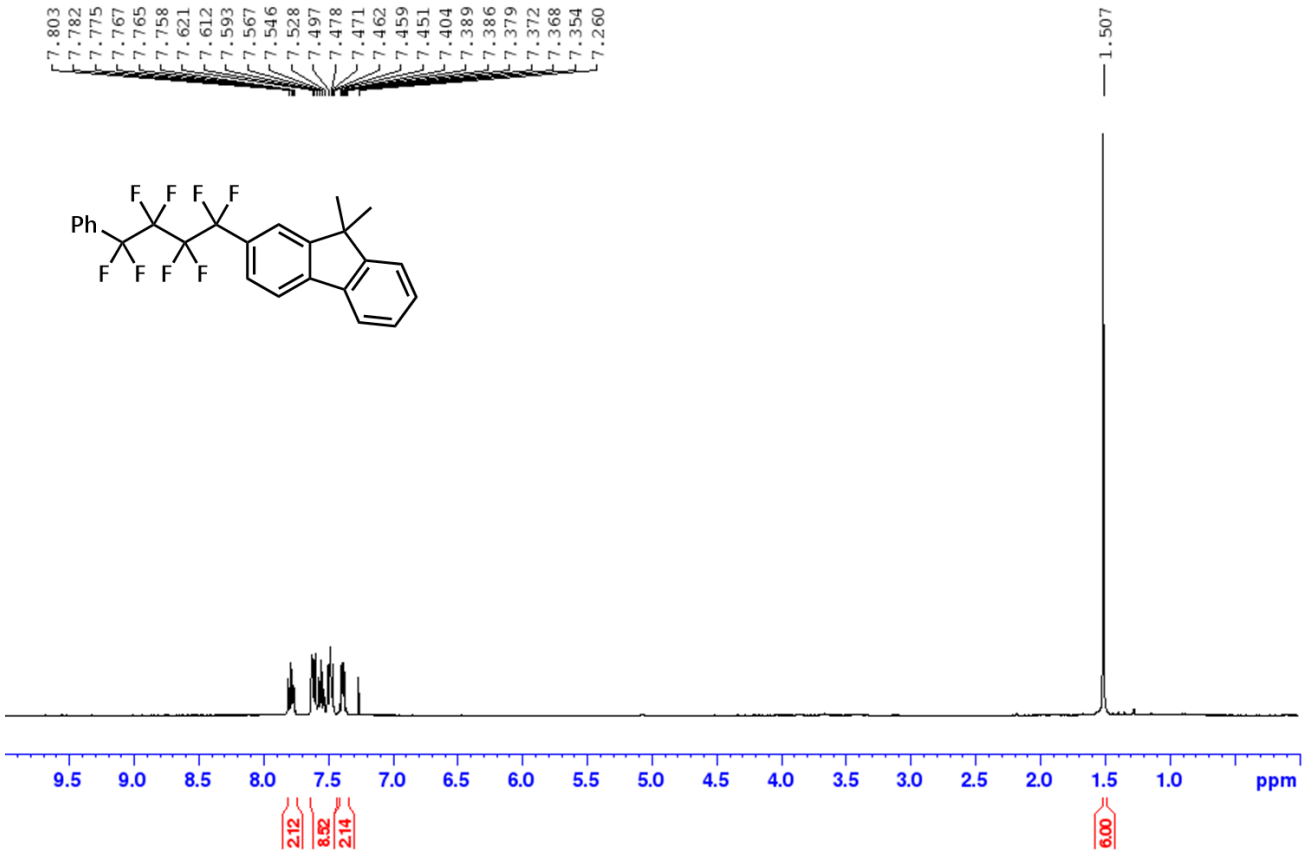


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

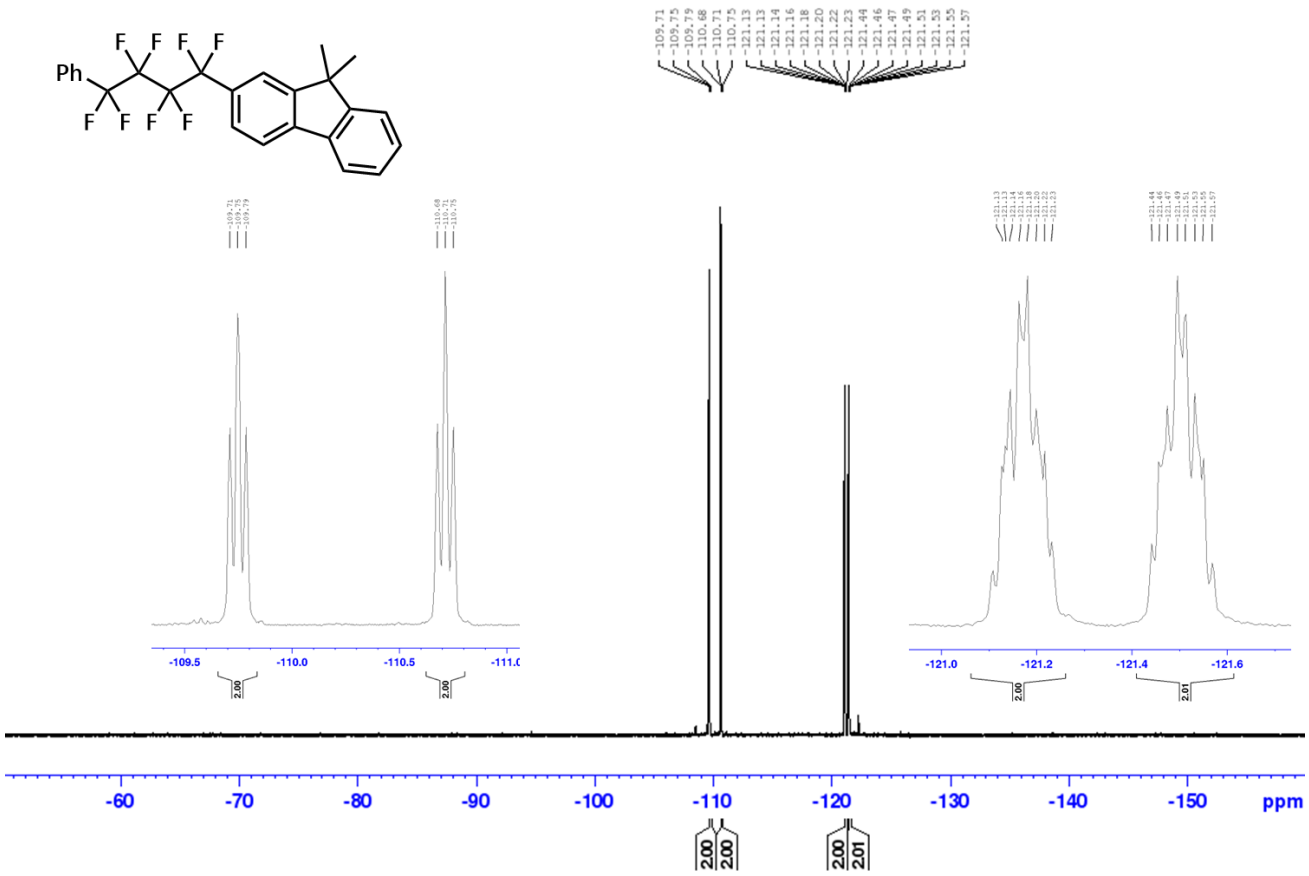


3i₂

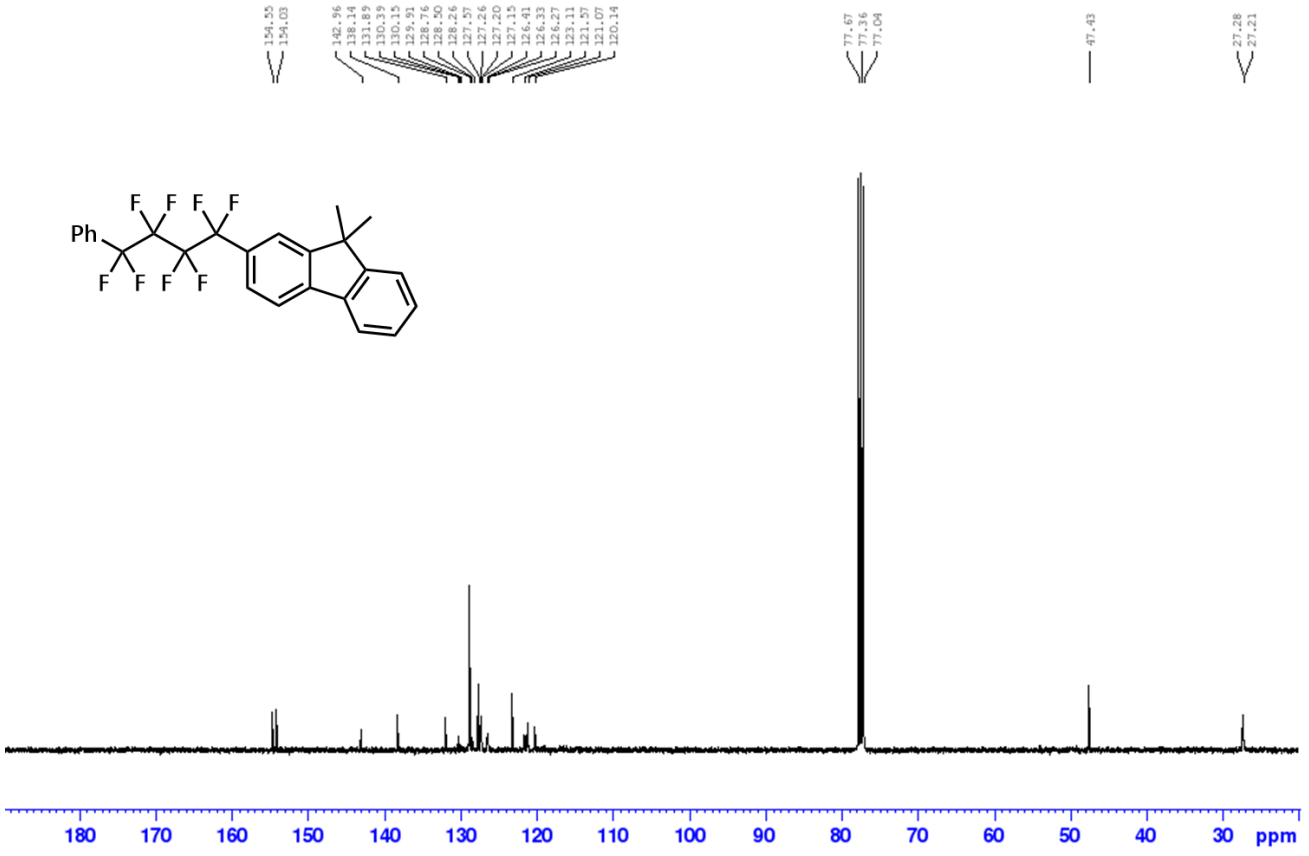
^{1}H NMR (400 MHz, $CDCl_3$)



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

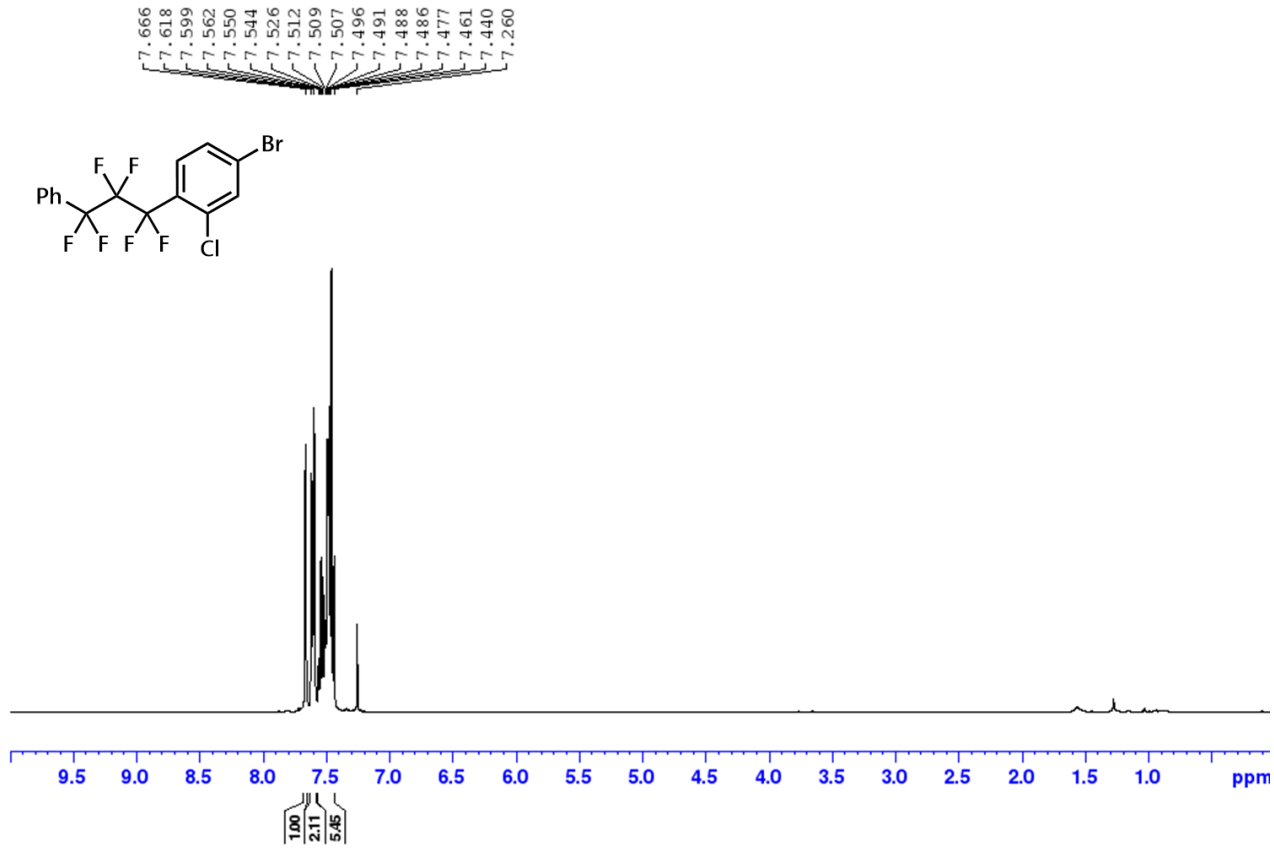


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

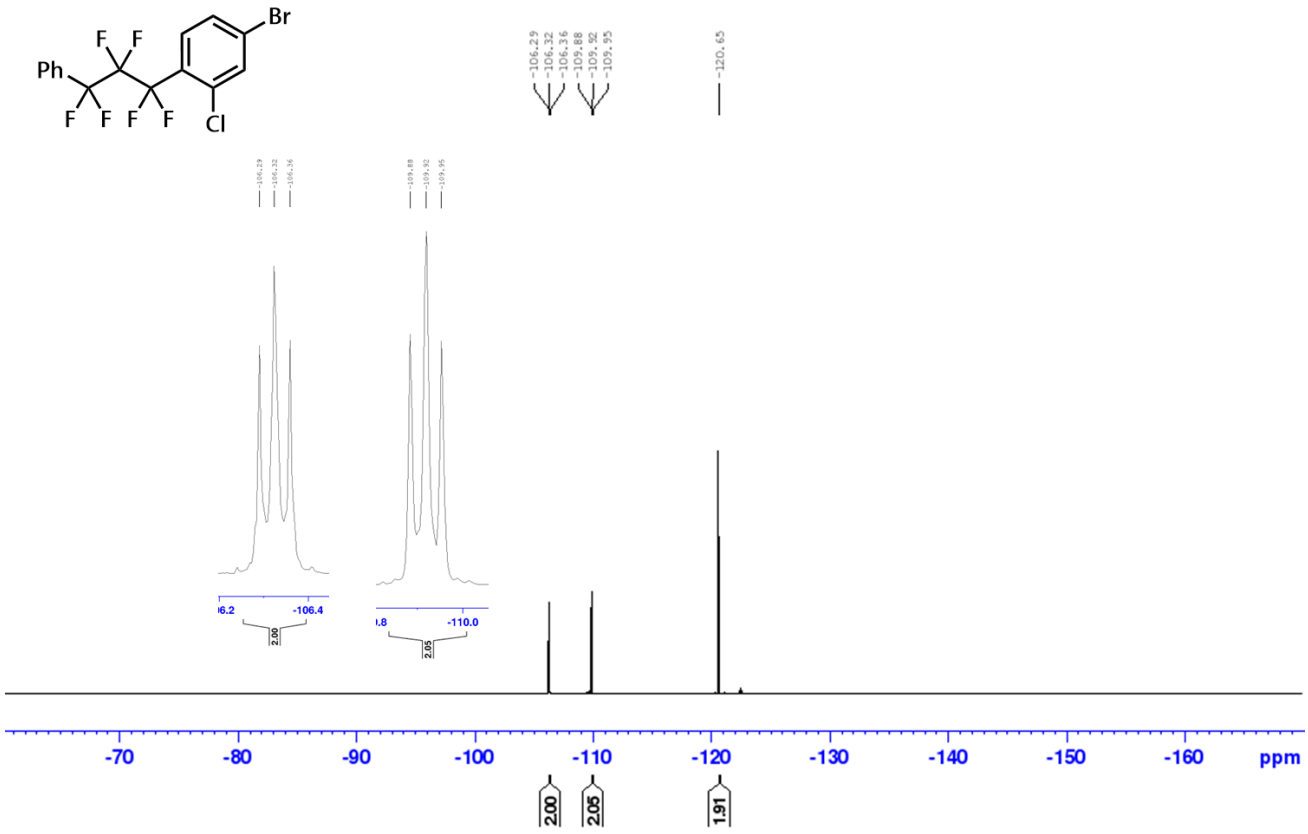


3j₁

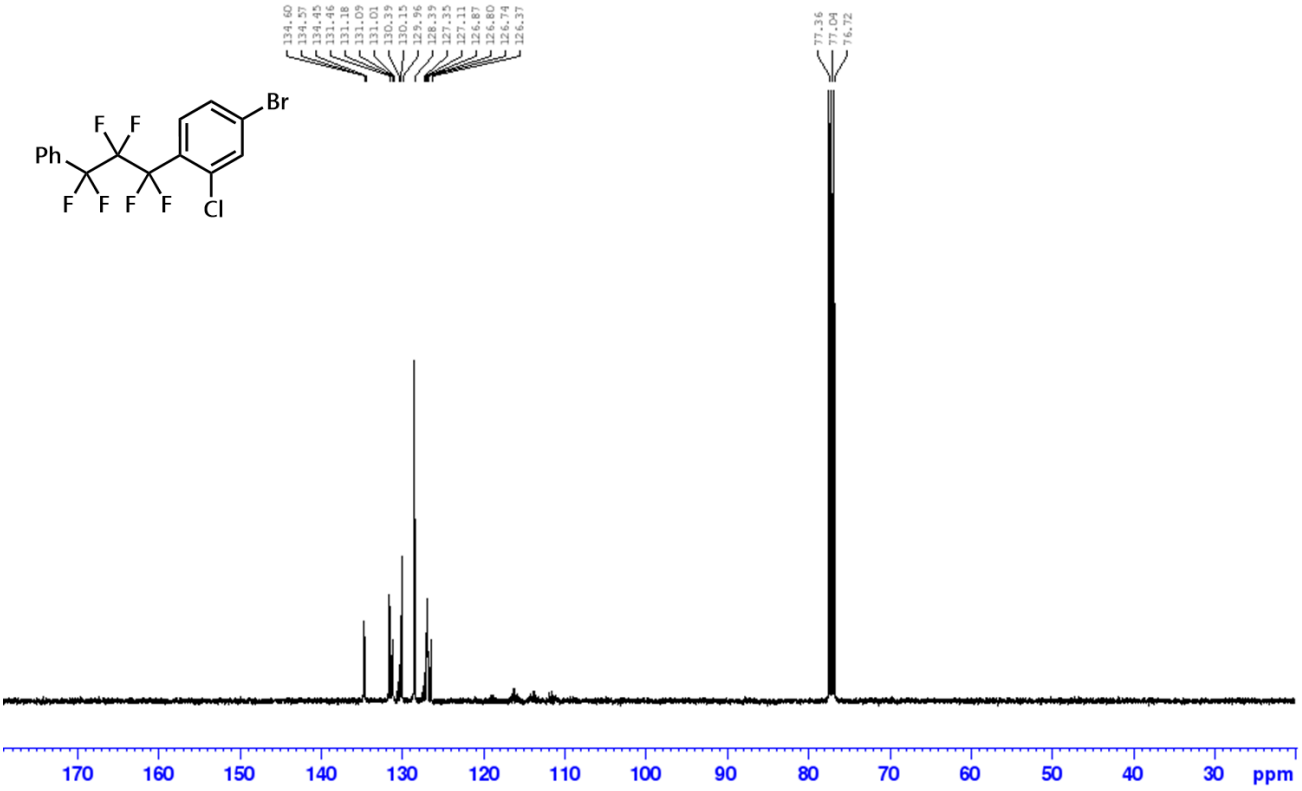
^{1}H NMR (400 MHz, $CDCl_3$)



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

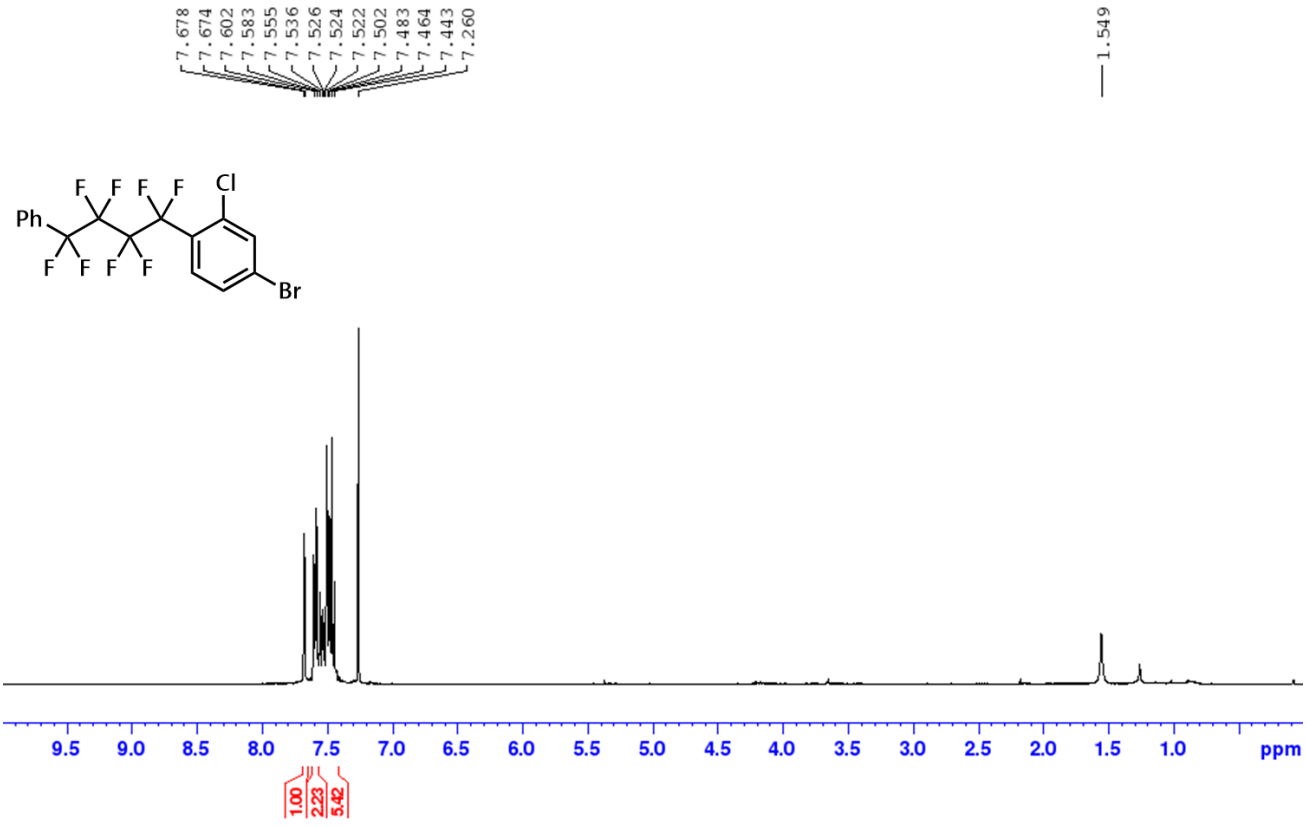


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

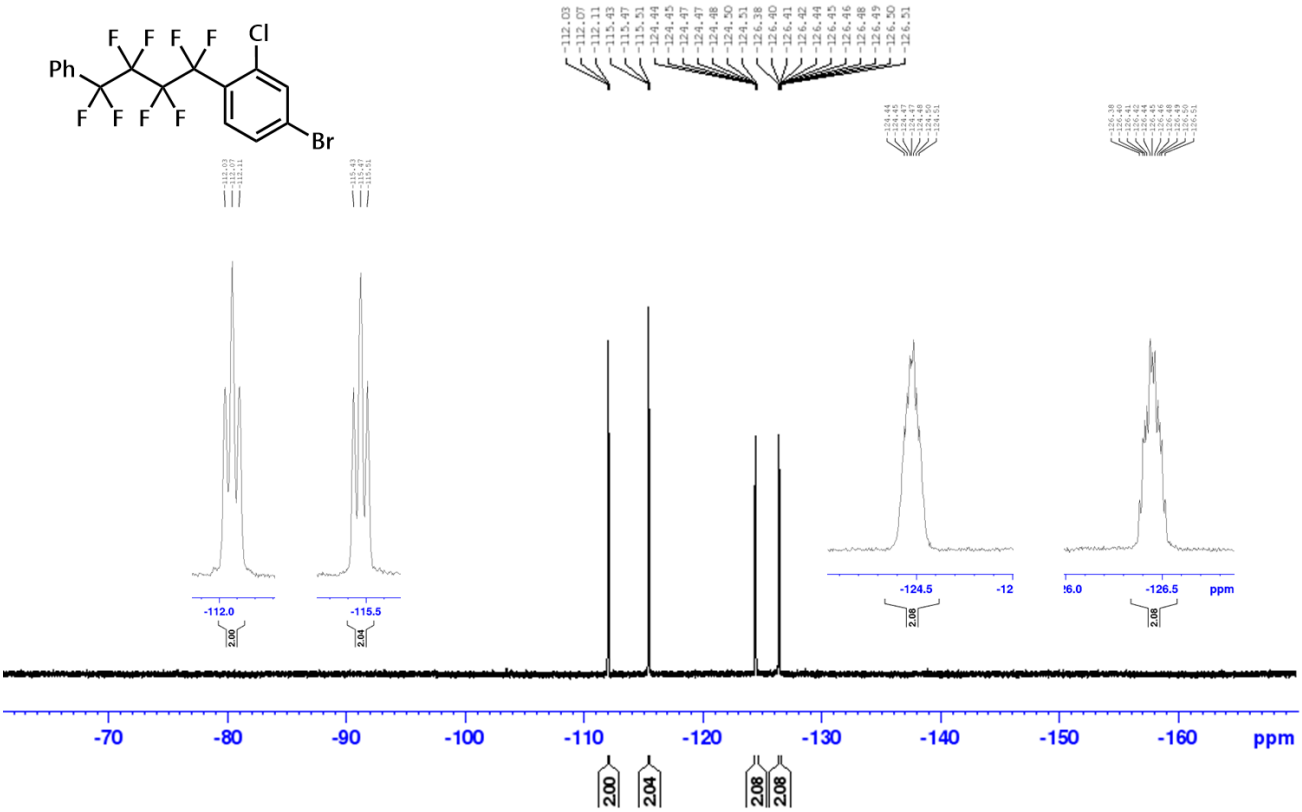


3j₂

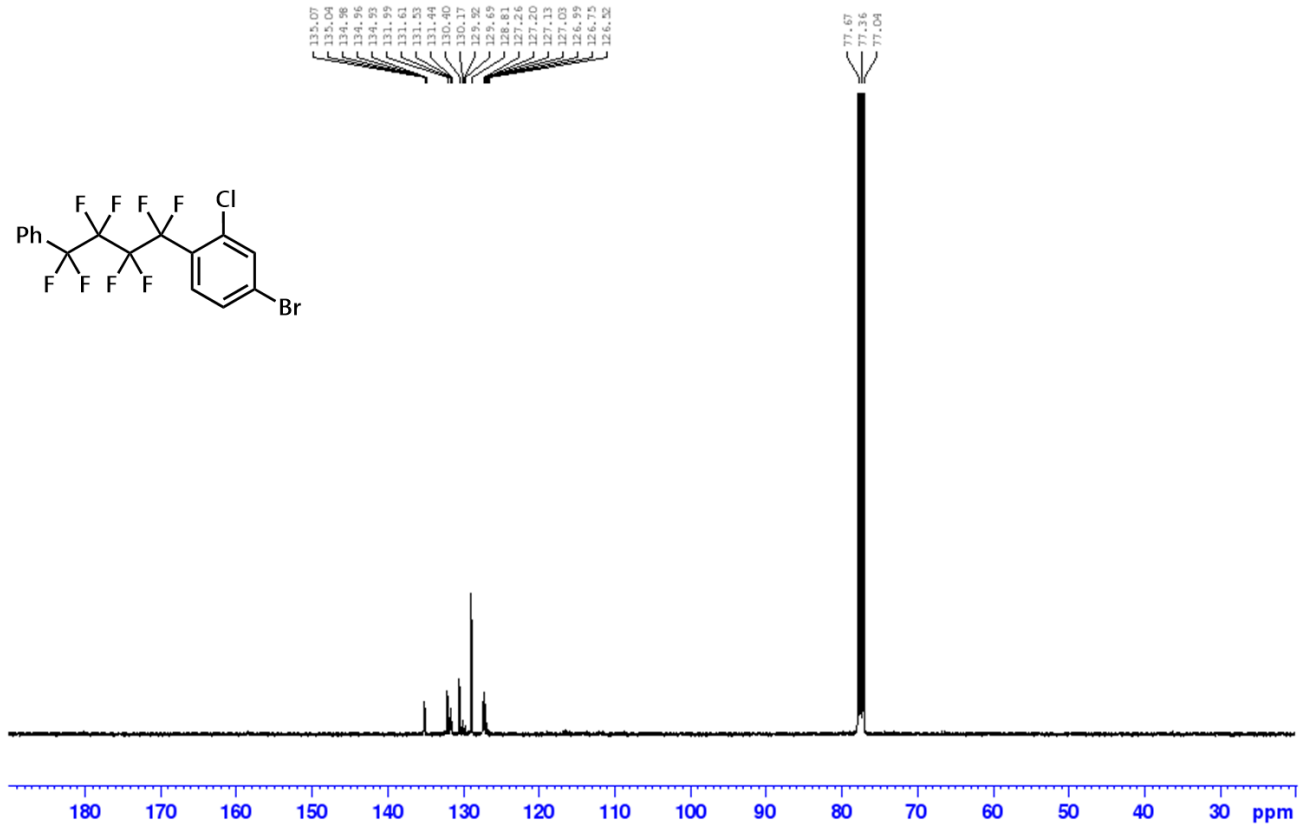
^{1}H NMR (400 MHz, $CDCl_3$)



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

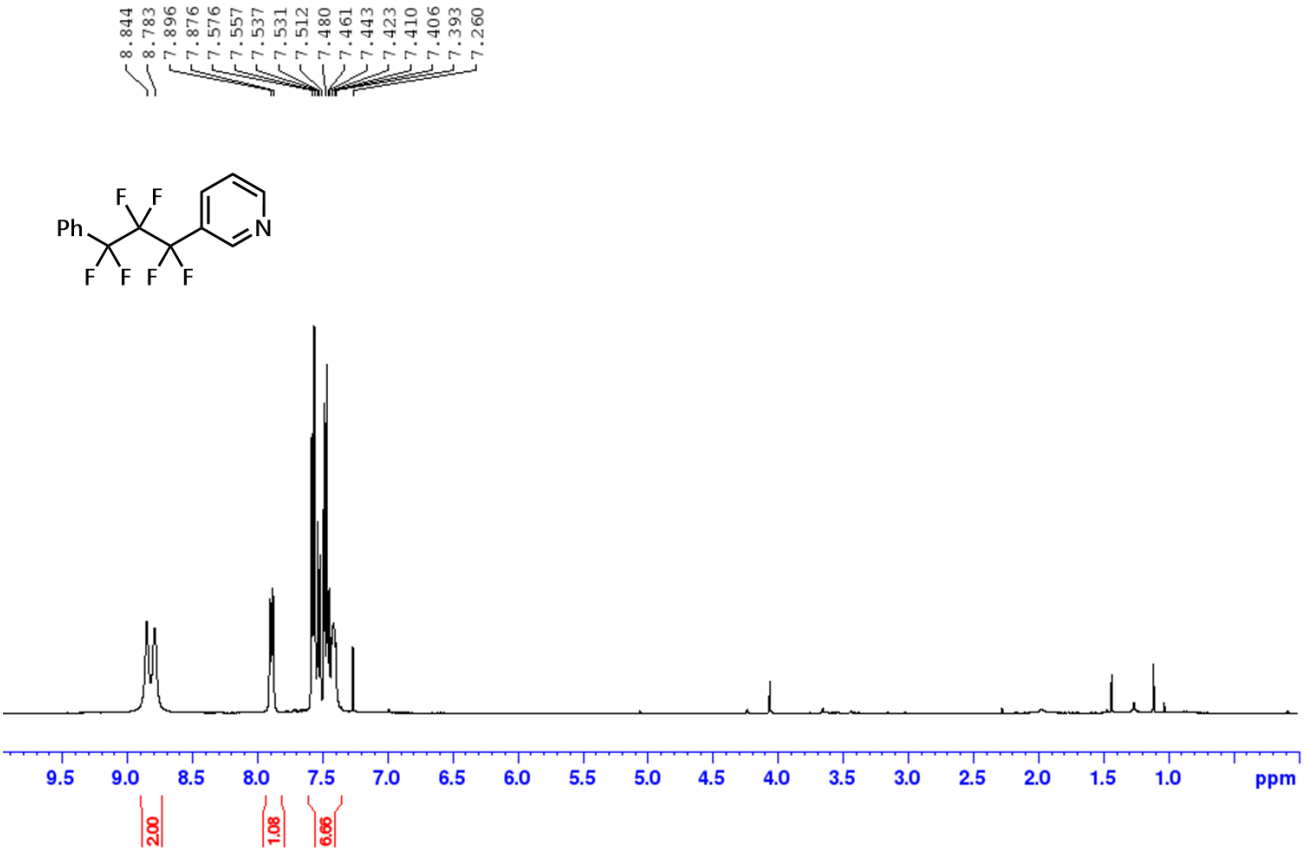


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

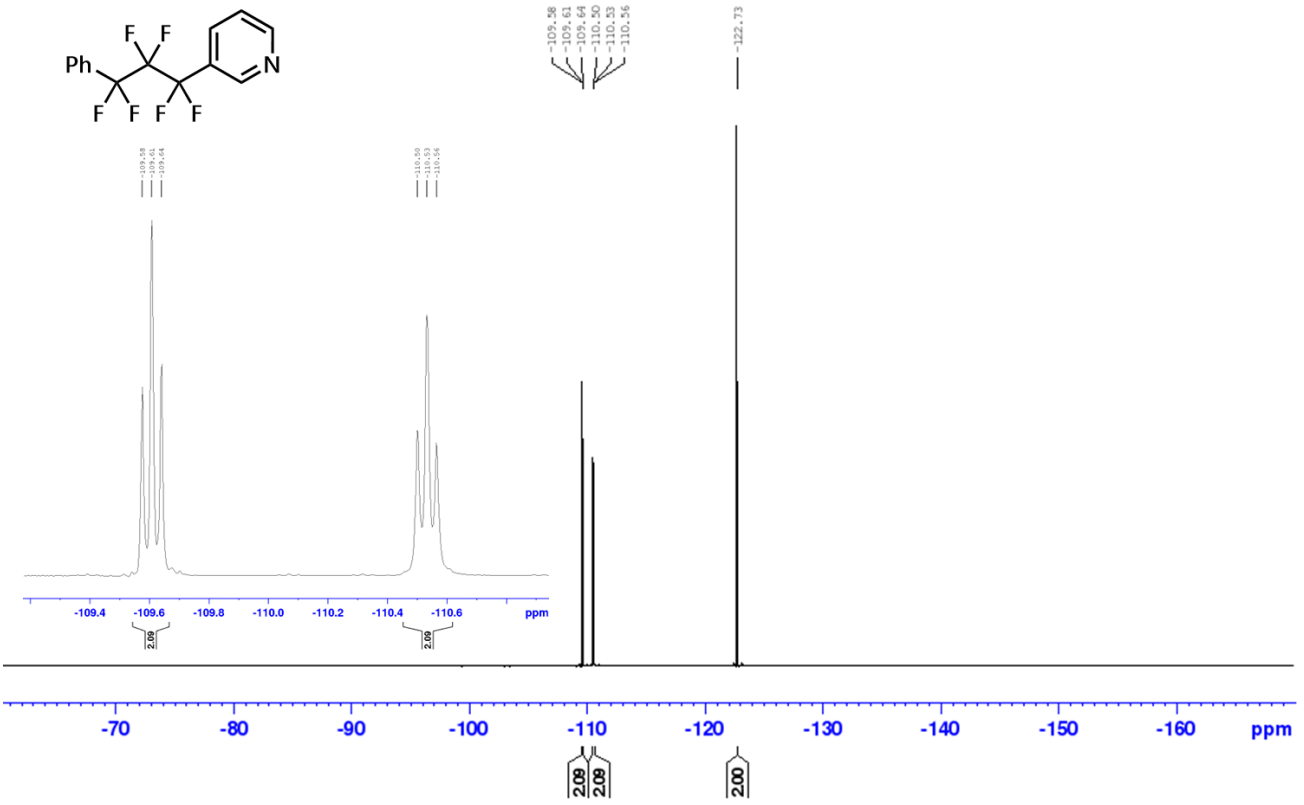


3k₁

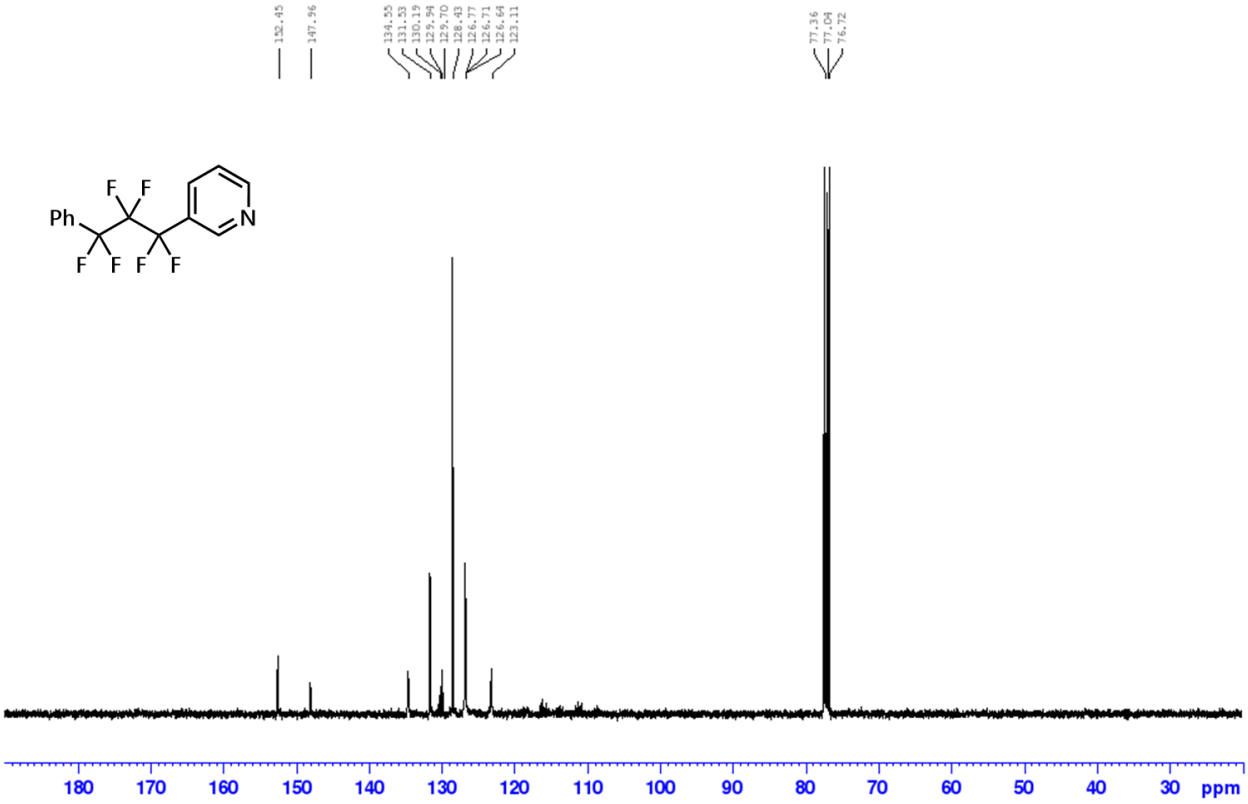
^{1}H NMR (400 MHz, $CDCl_3$)



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

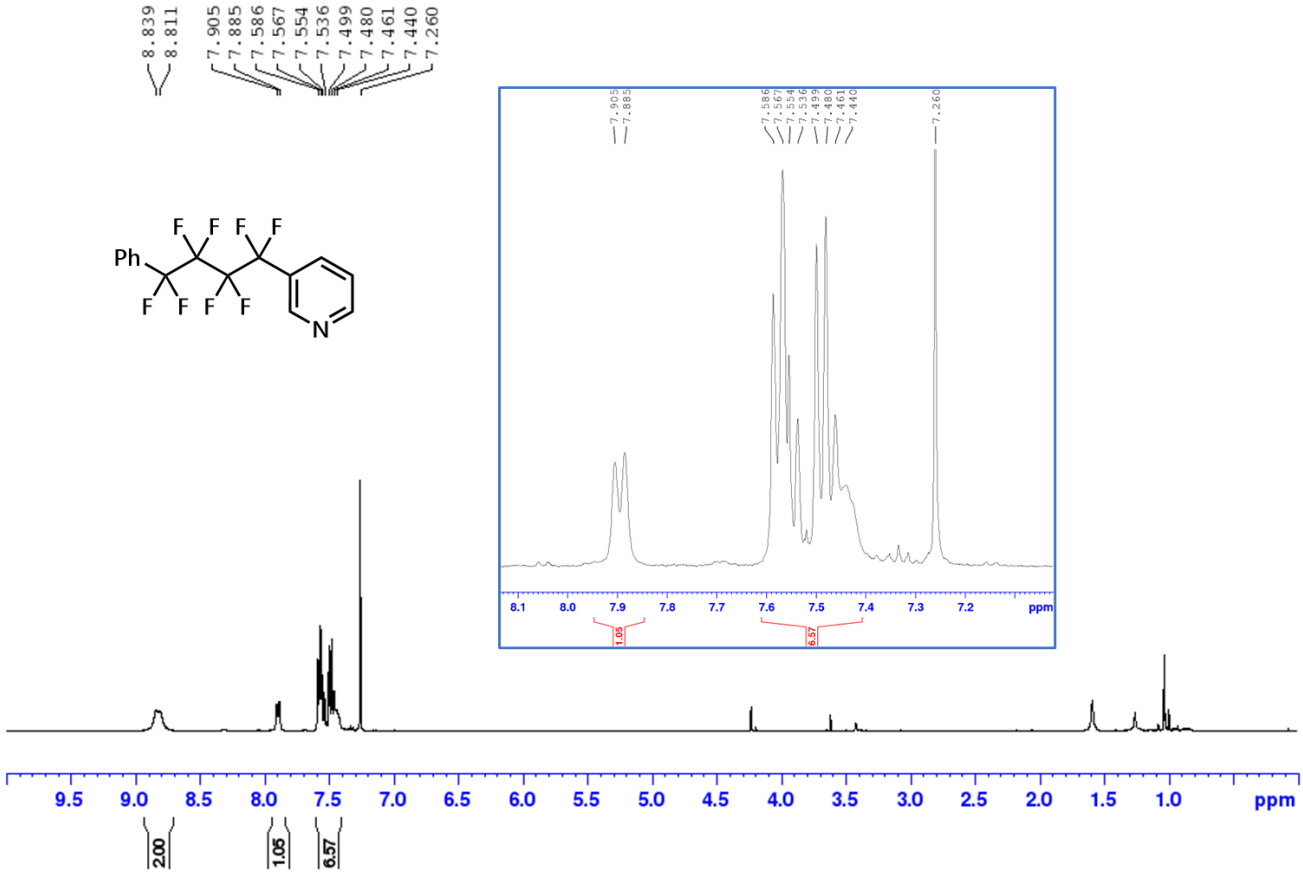


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

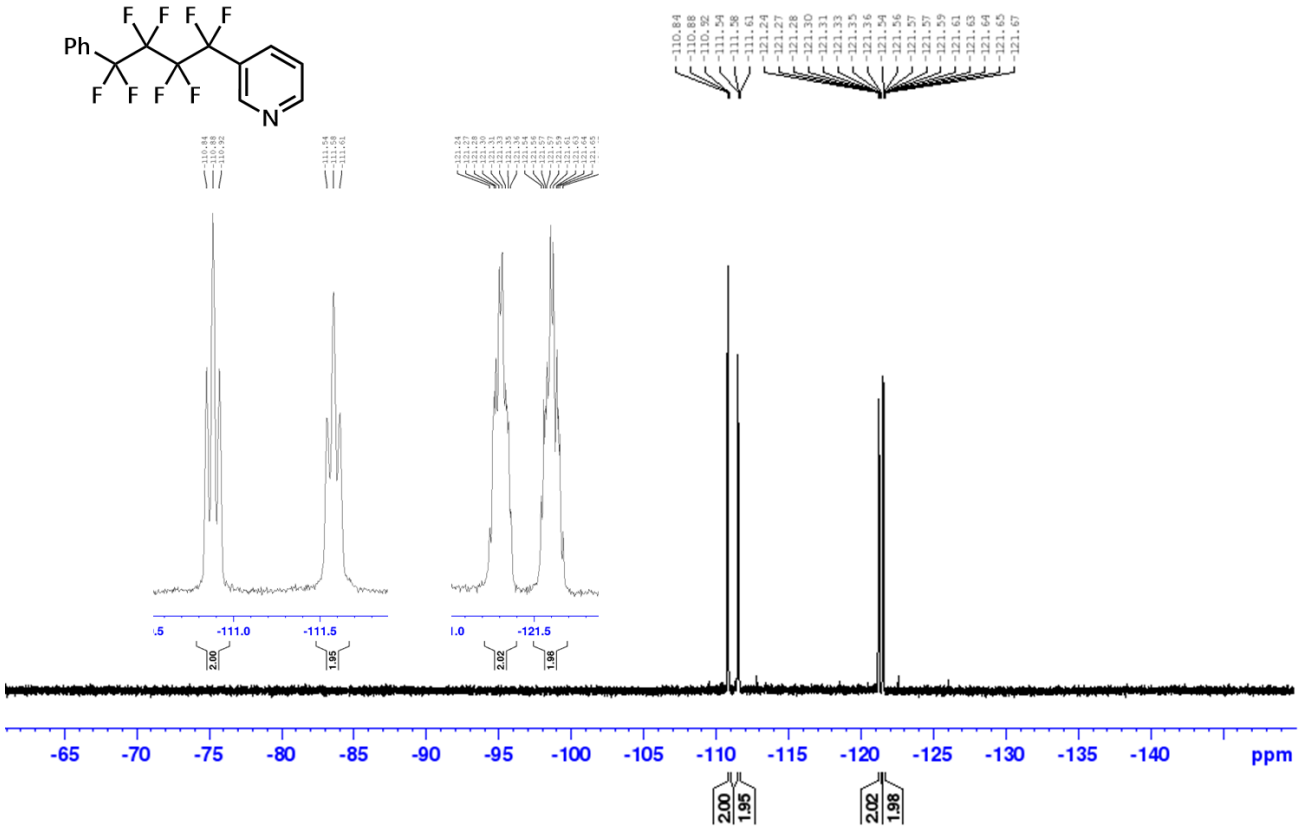


3k₂

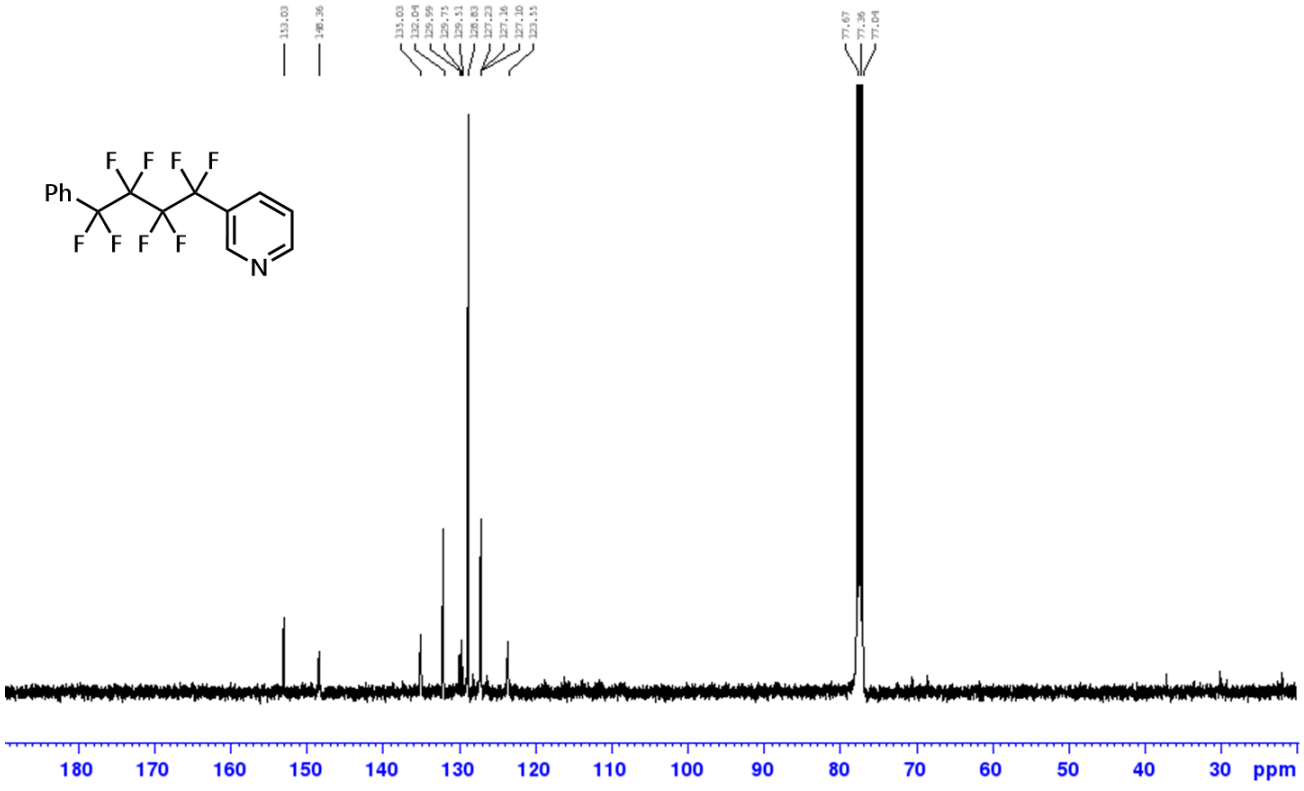
^{1}H NMR (400 MHz, $CDCl_3$)



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

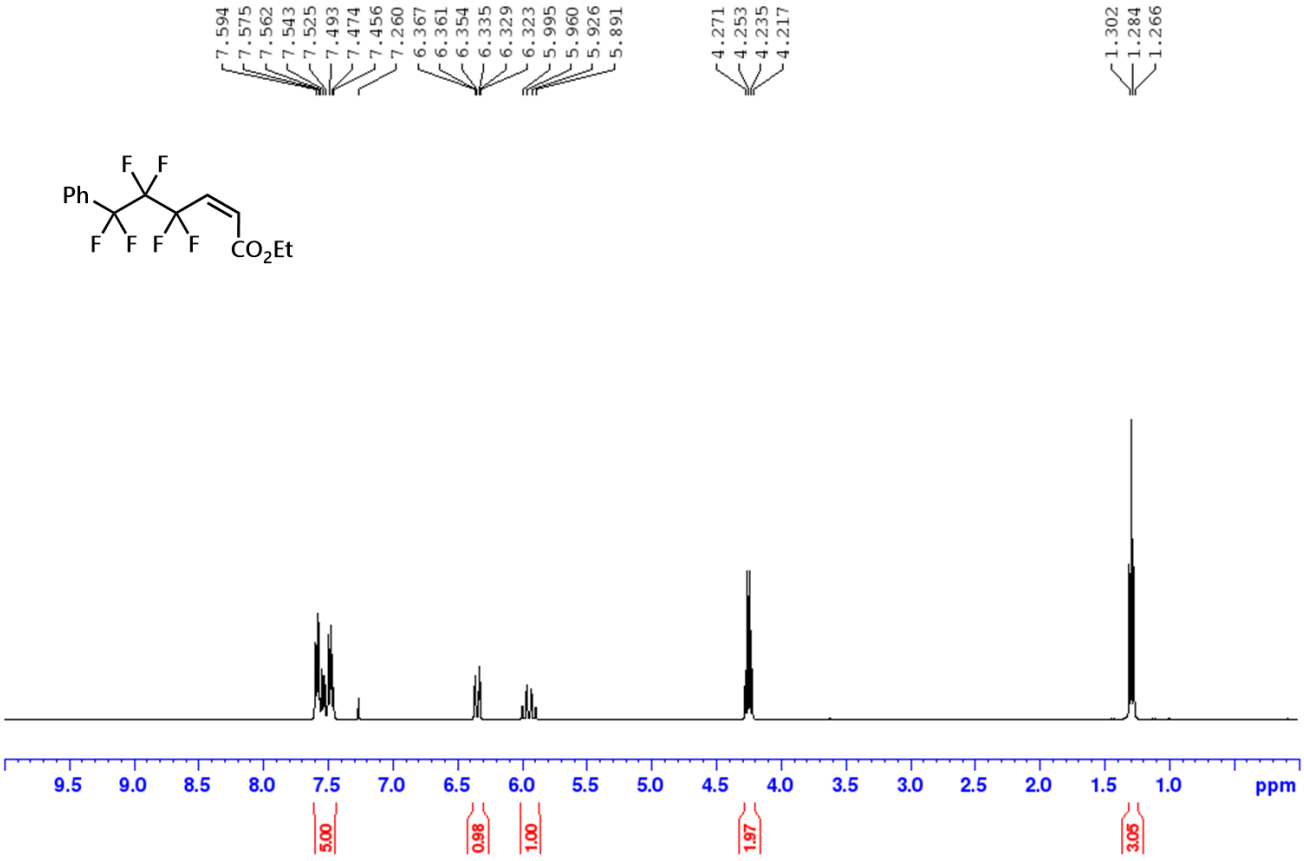


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

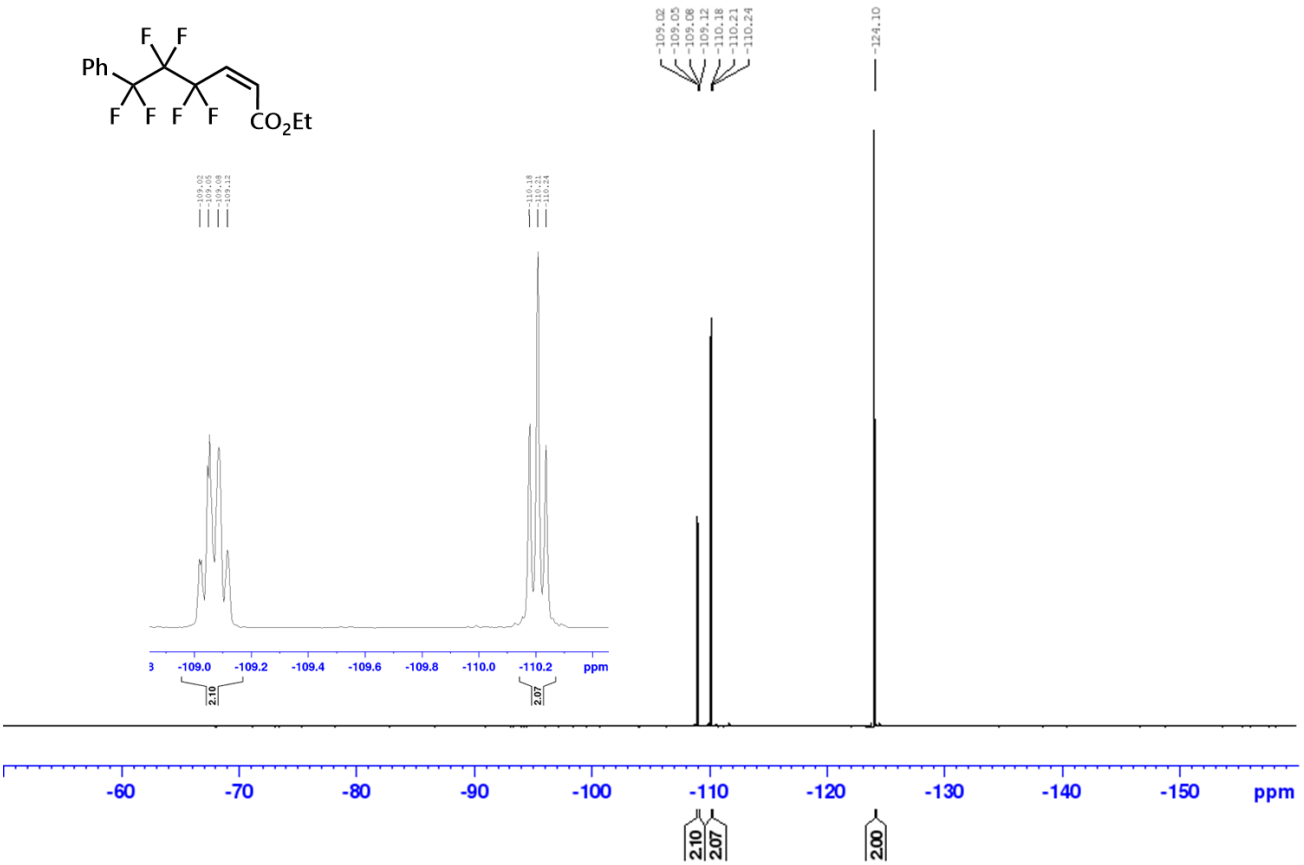


3l₁

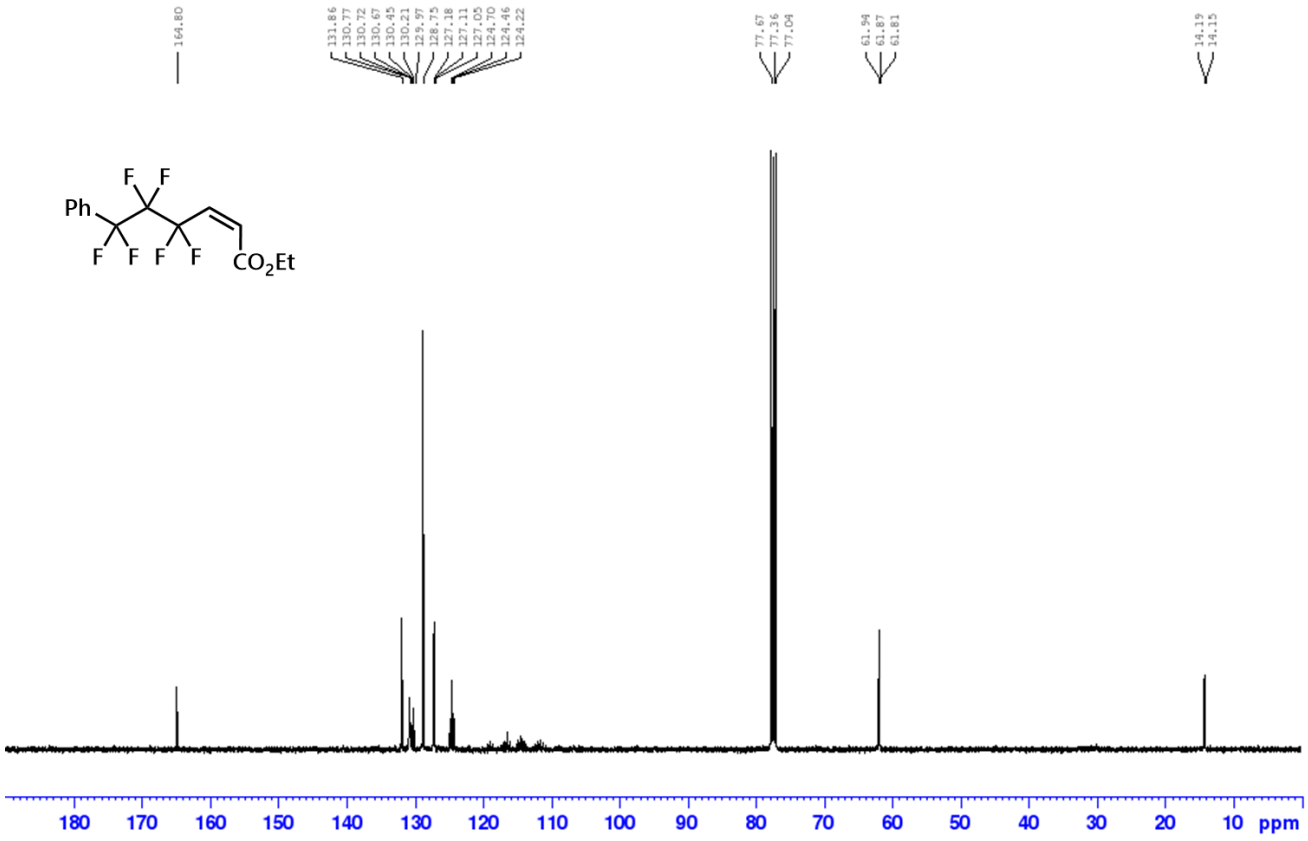
^{1}H NMR (400 MHz, $CDCl_3$)



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

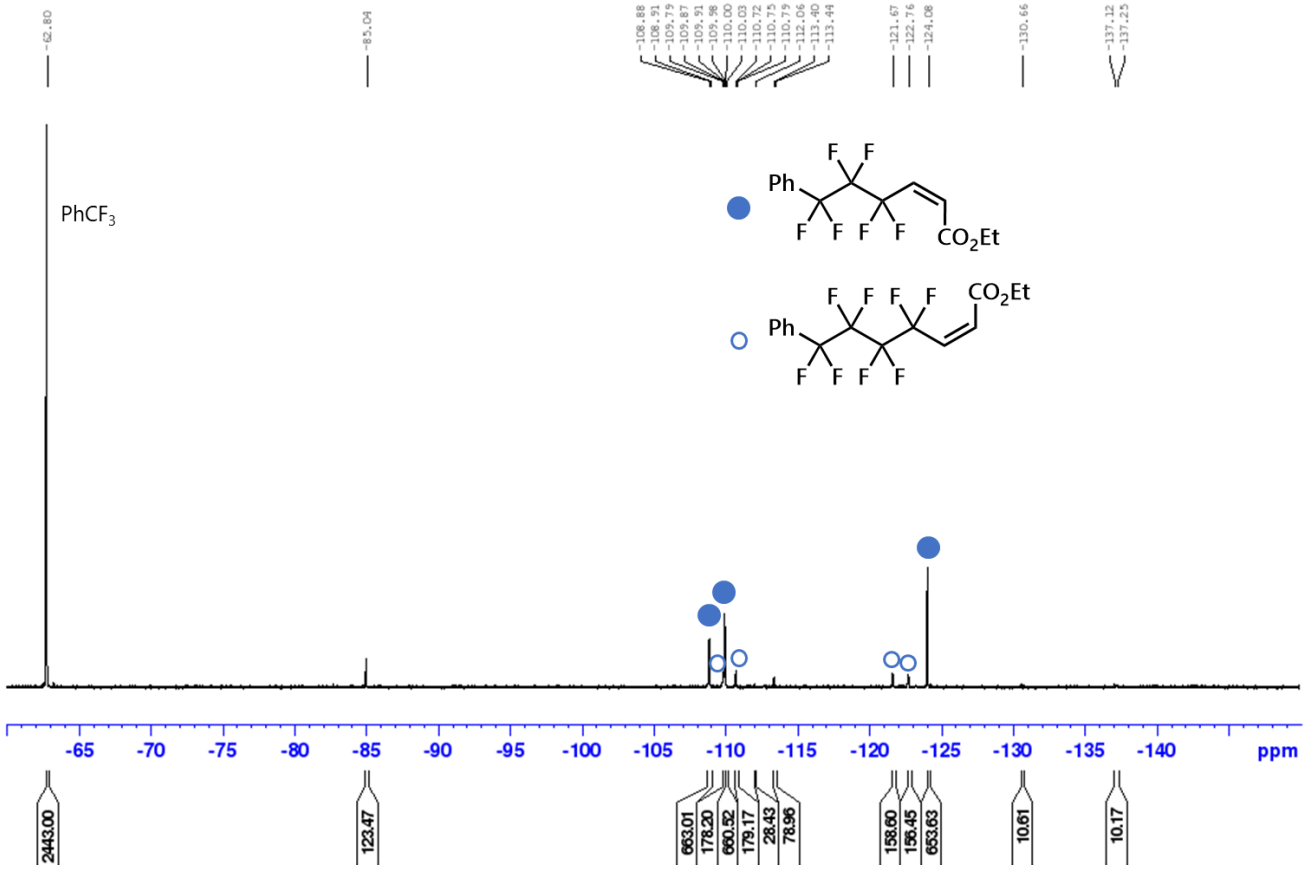


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)



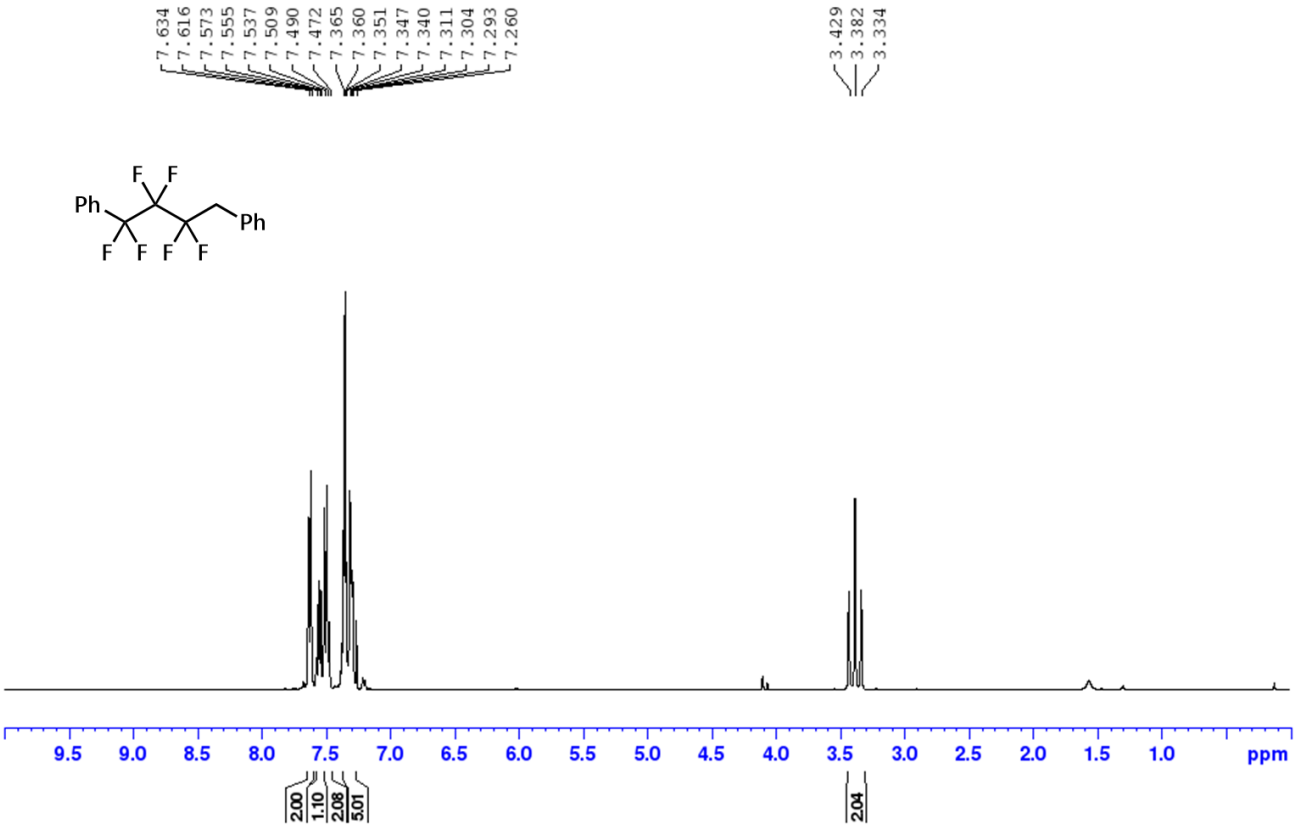
3l₂

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

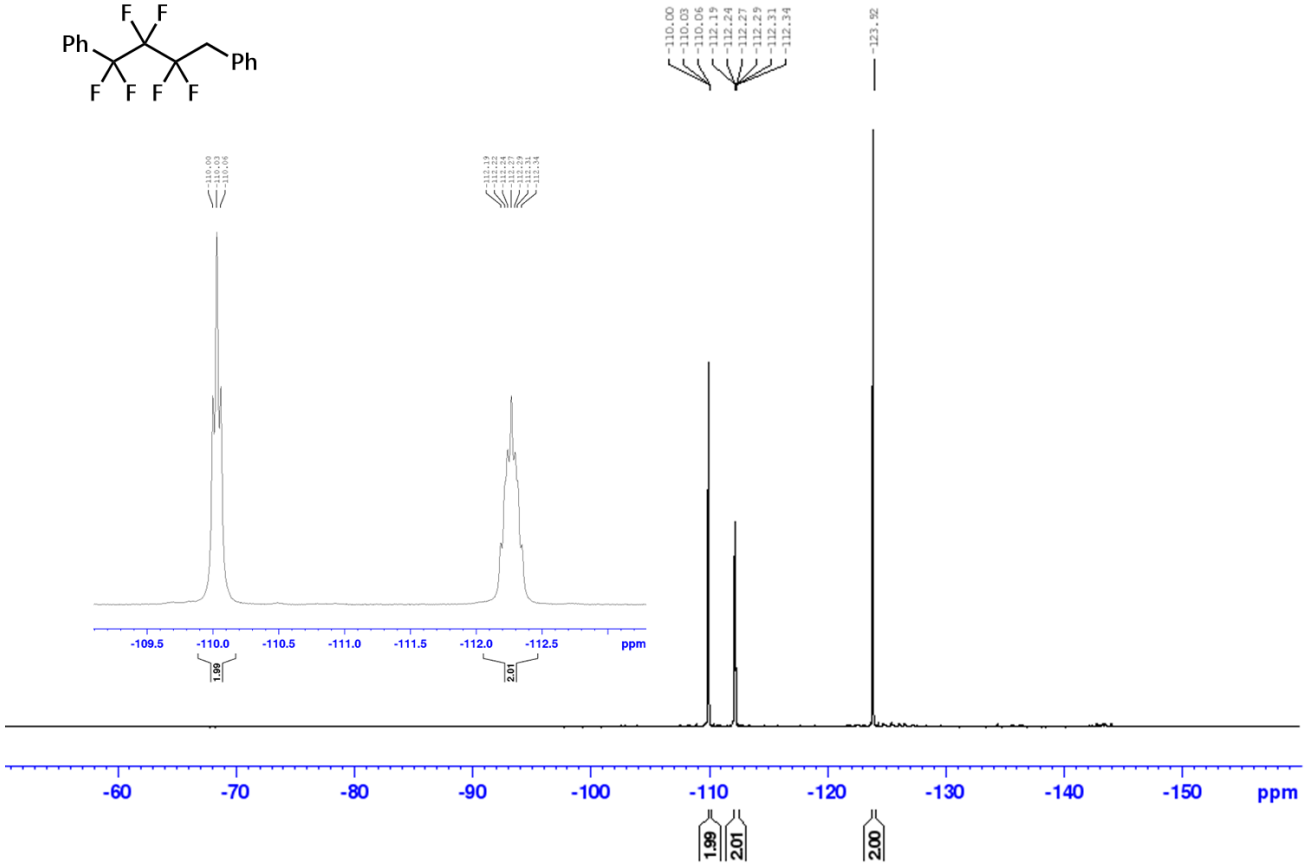


3m₁

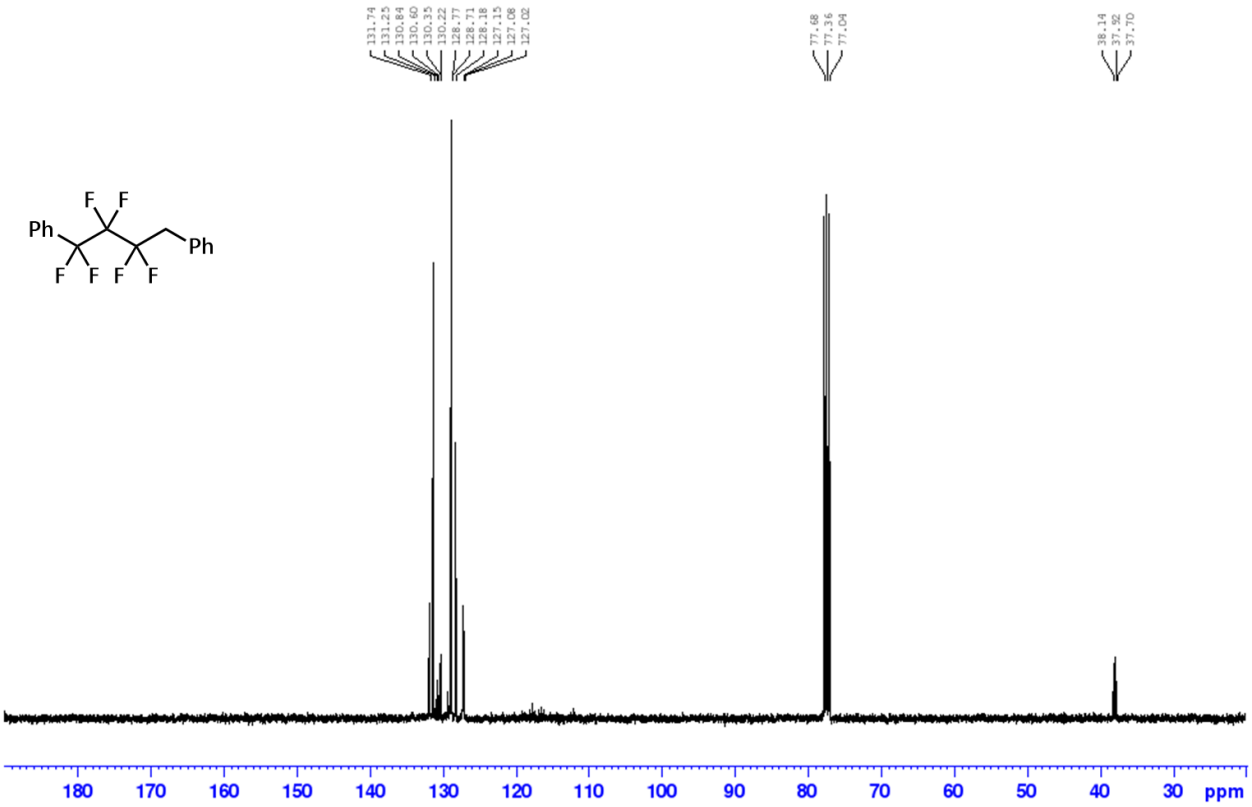
^{1}H NMR (400 MHz, $CDCl_3$)



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

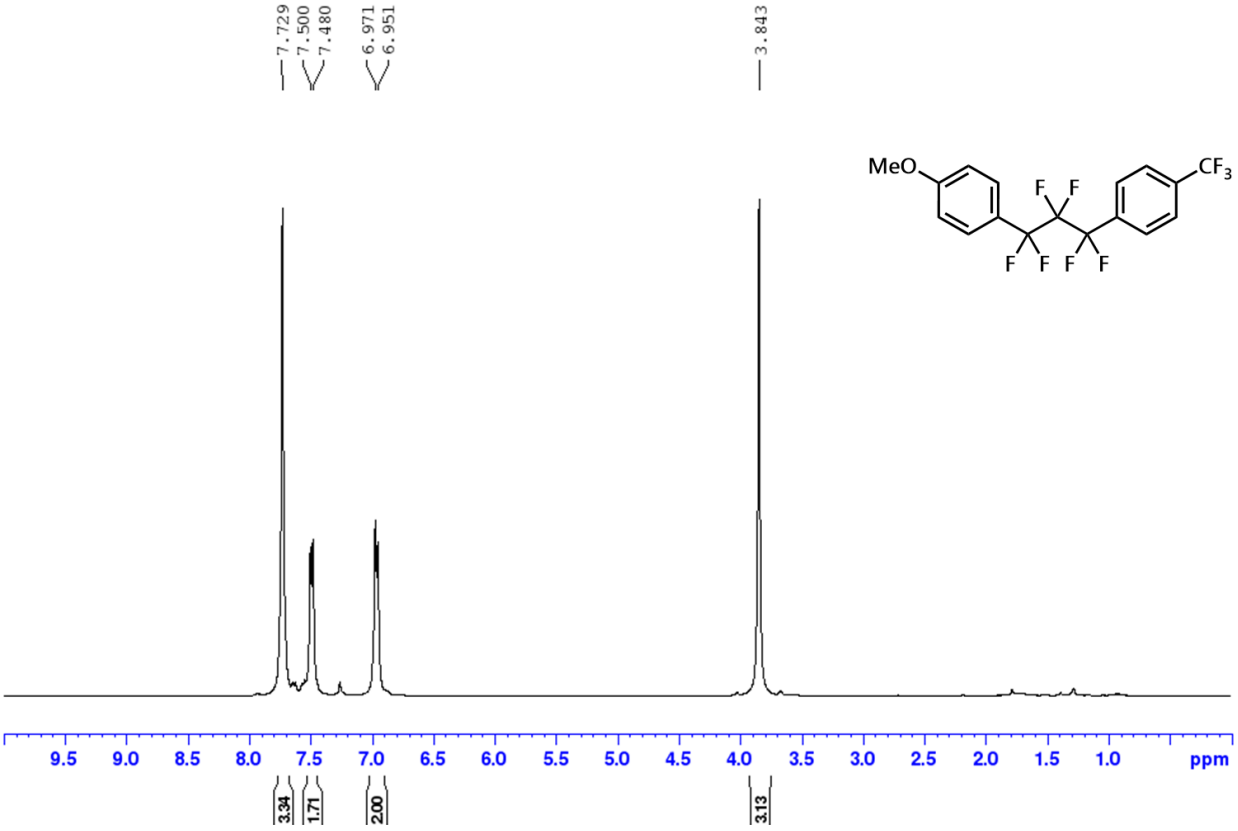


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

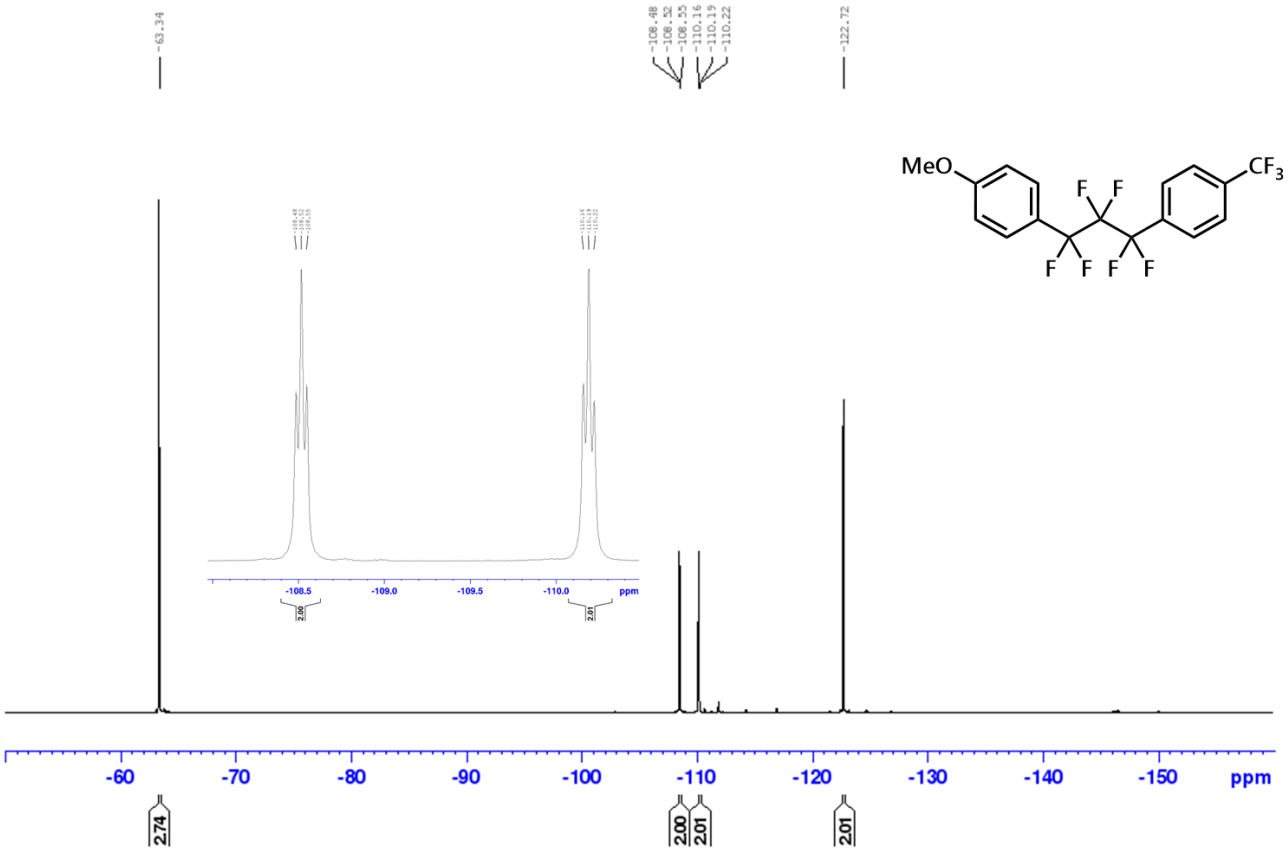


3n₁

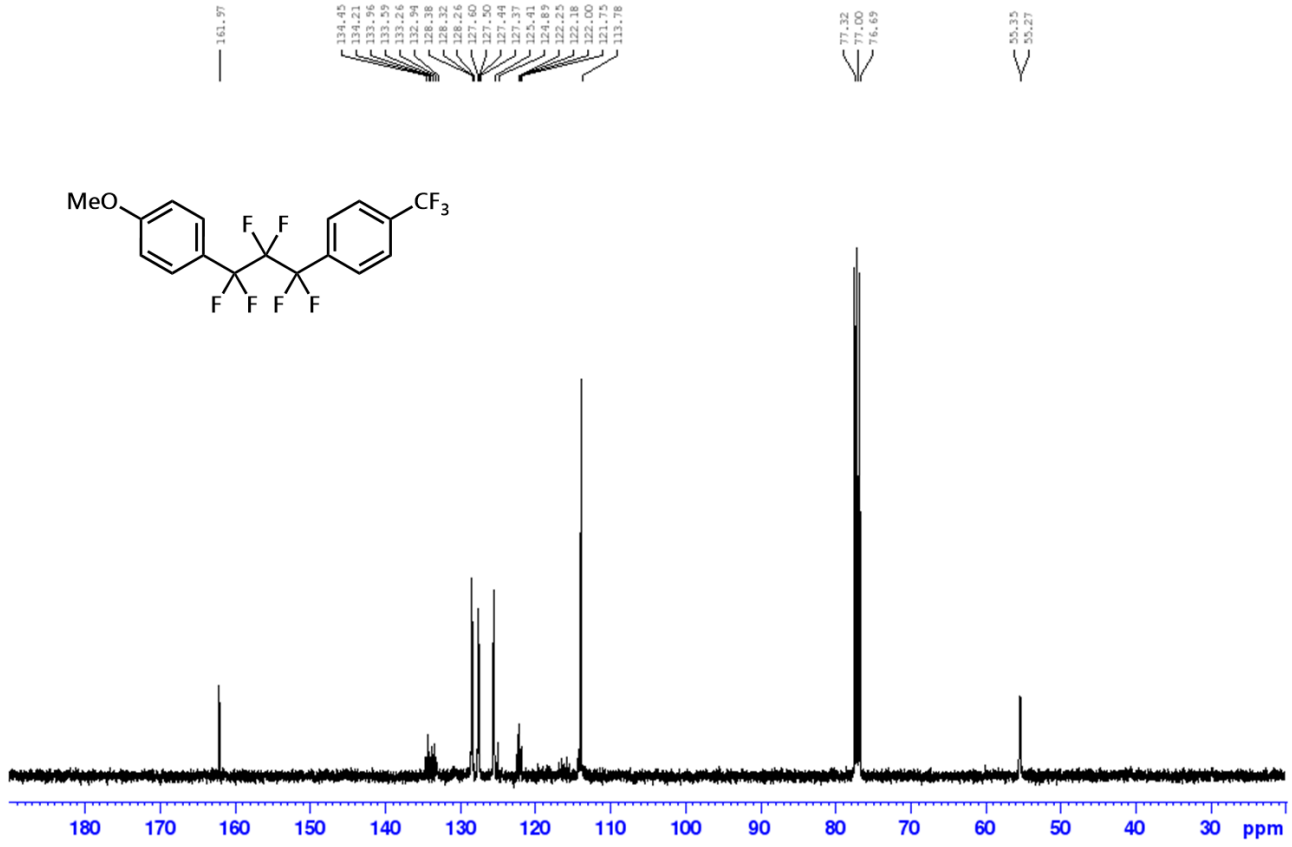
^{1}H NMR (400 MHz, $CDCl_3$)



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

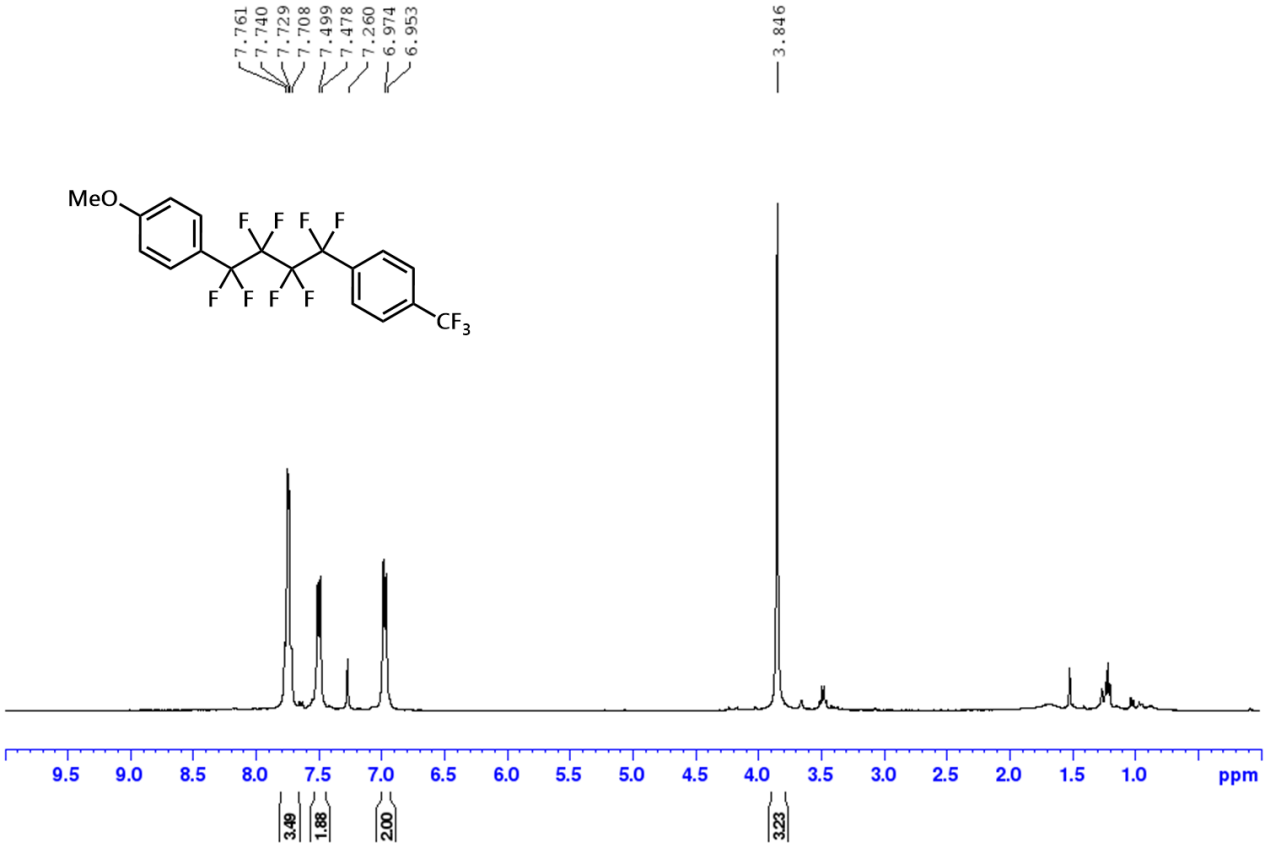


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

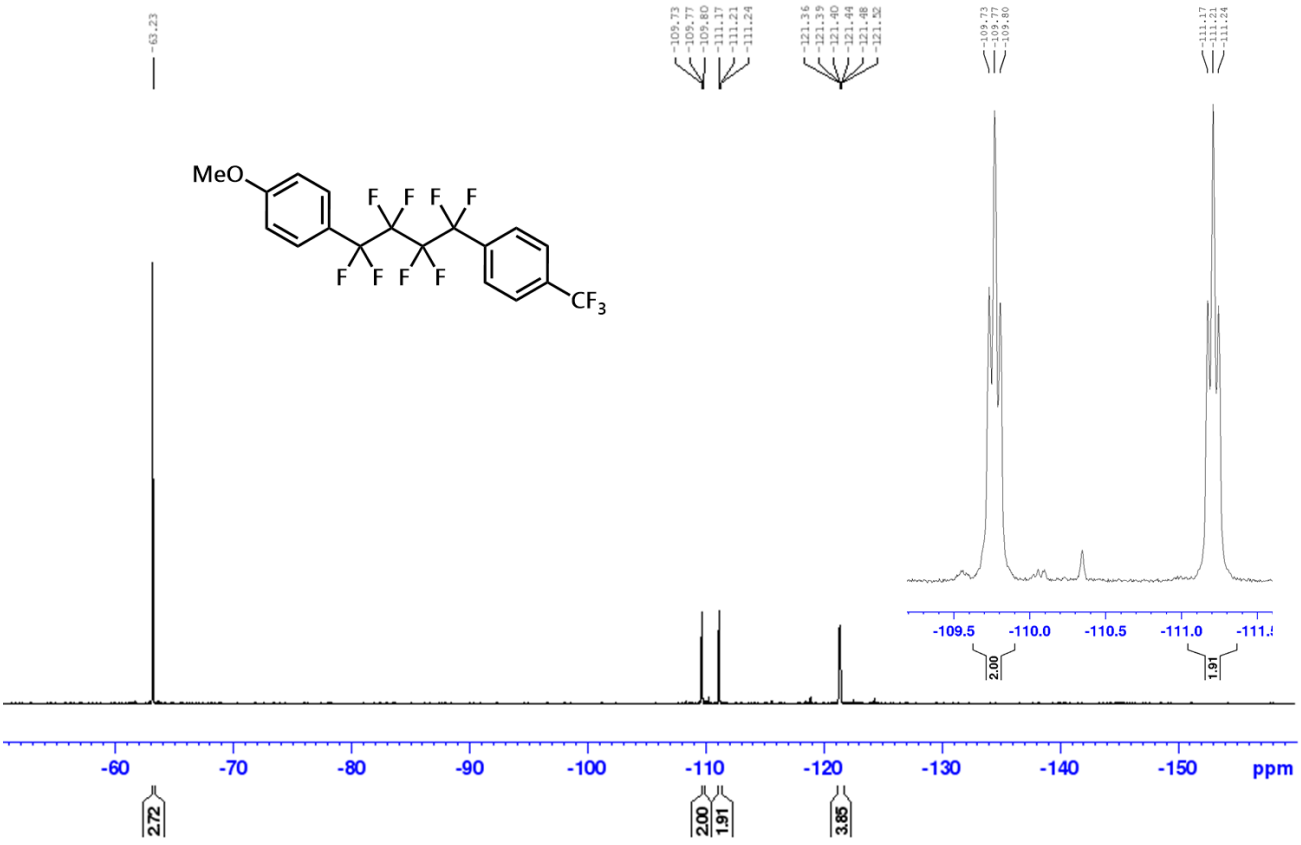


3n₂

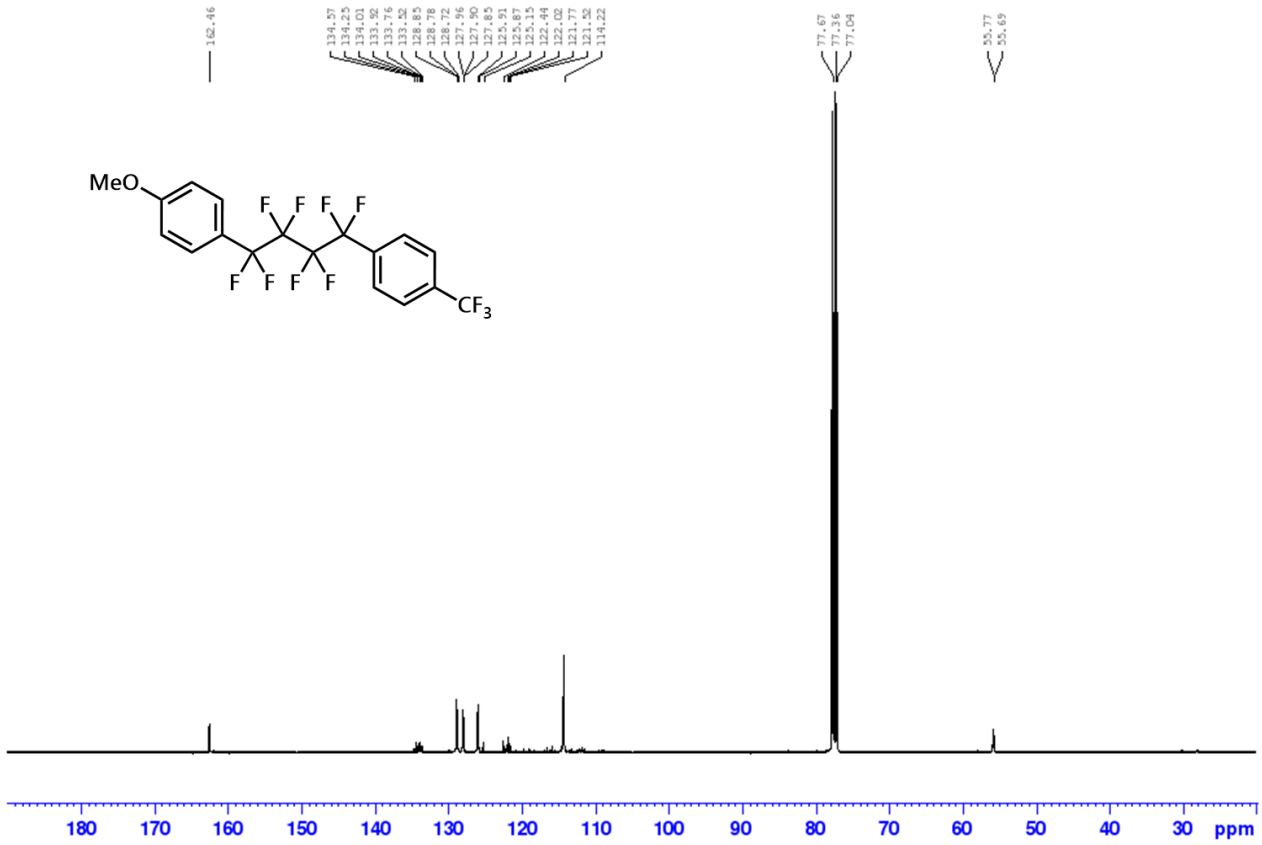
^{1}H NMR (400 MHz, $CDCl_3$)



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

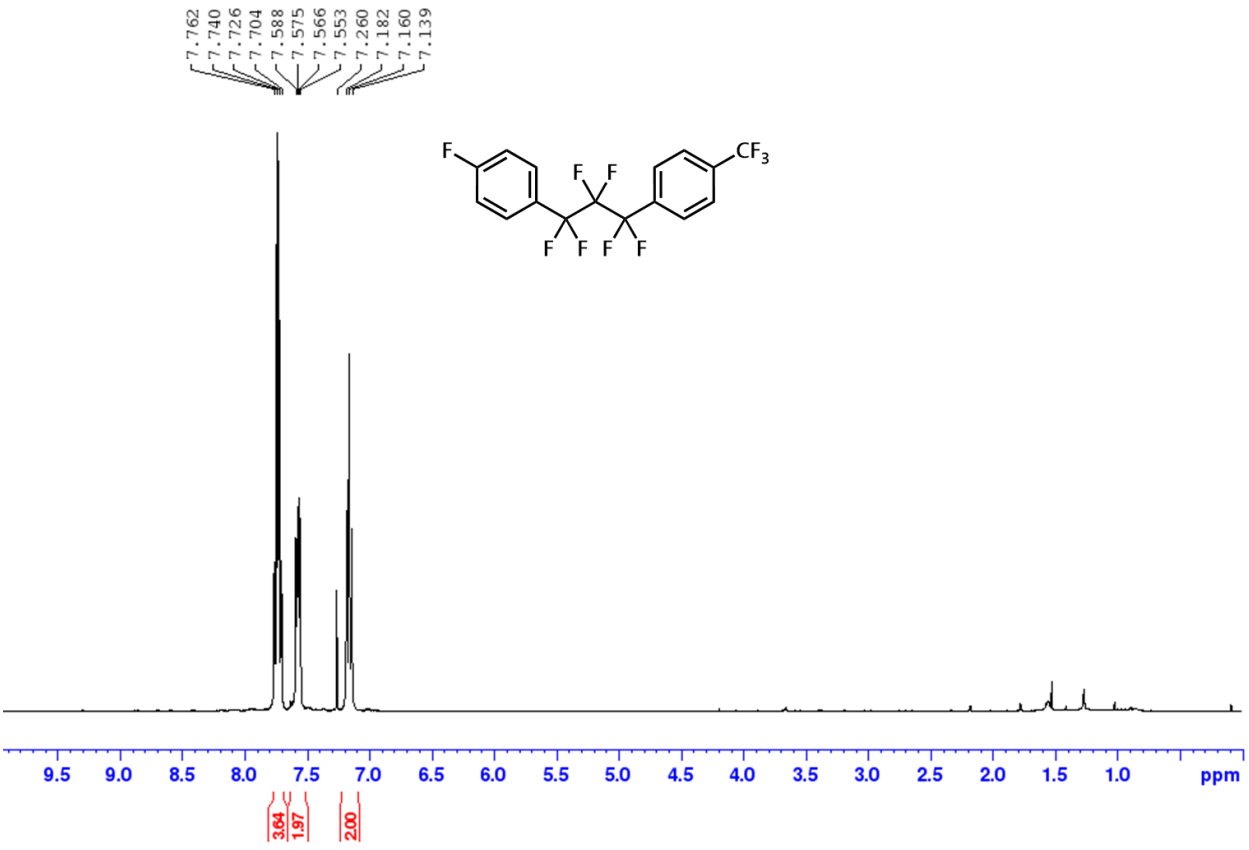


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

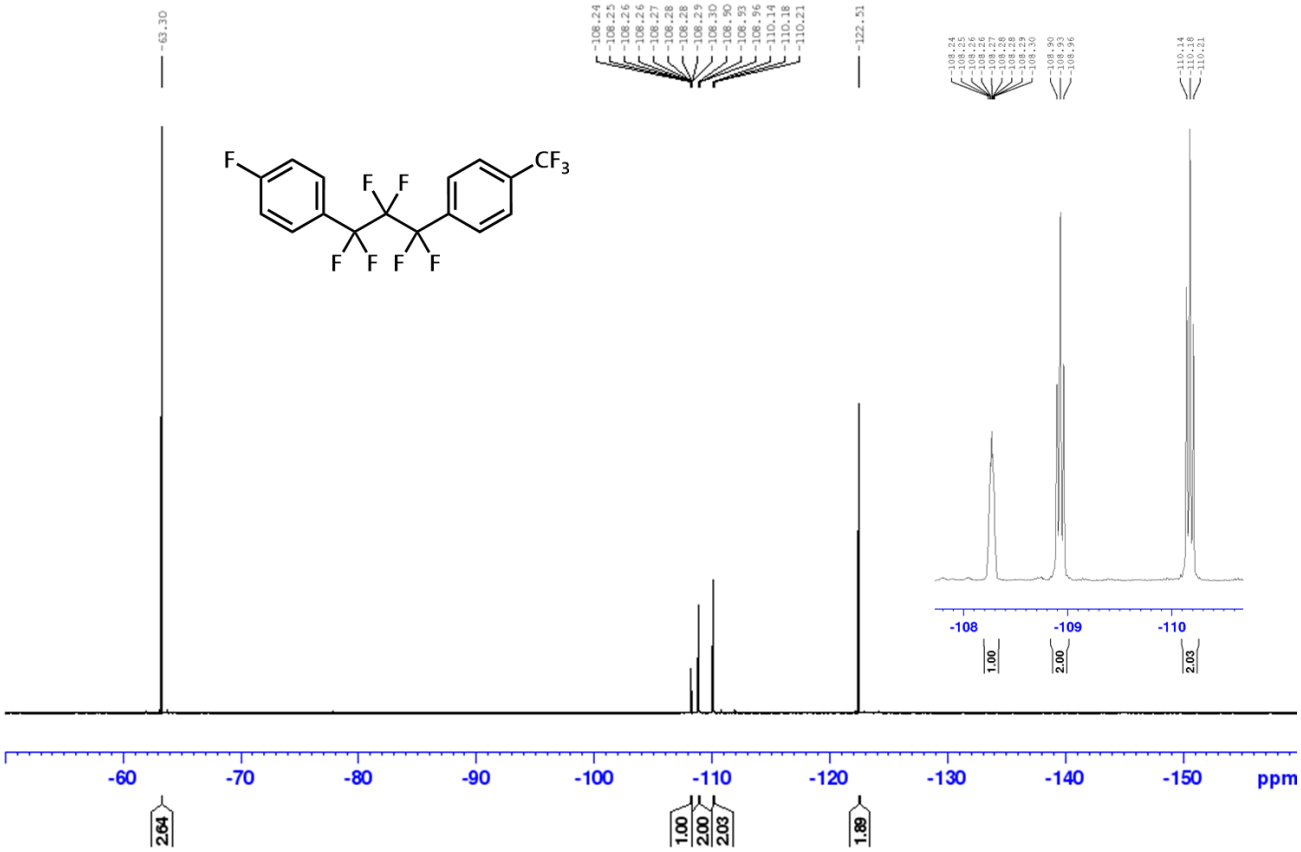


3o₁

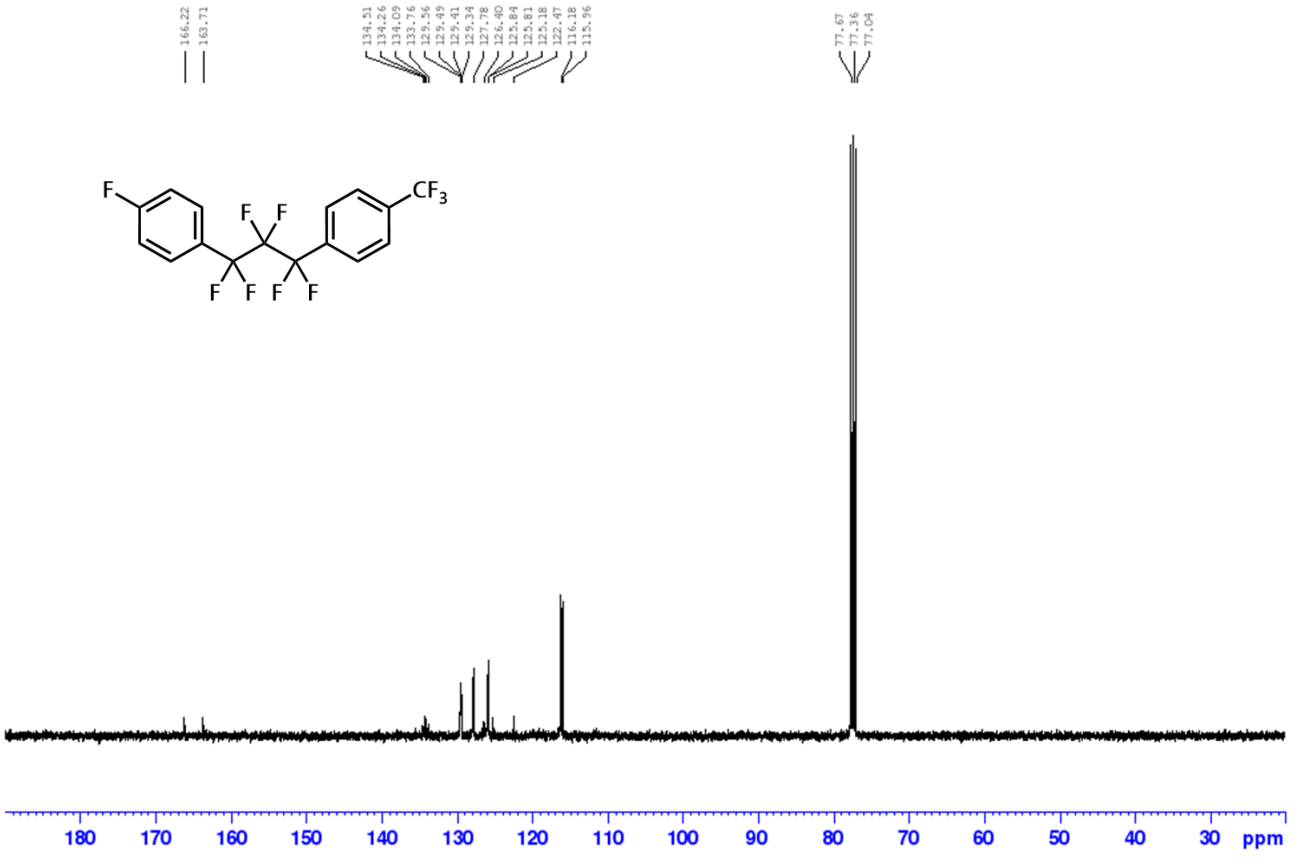
^{1}H NMR (400 MHz, $CDCl_3$)



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

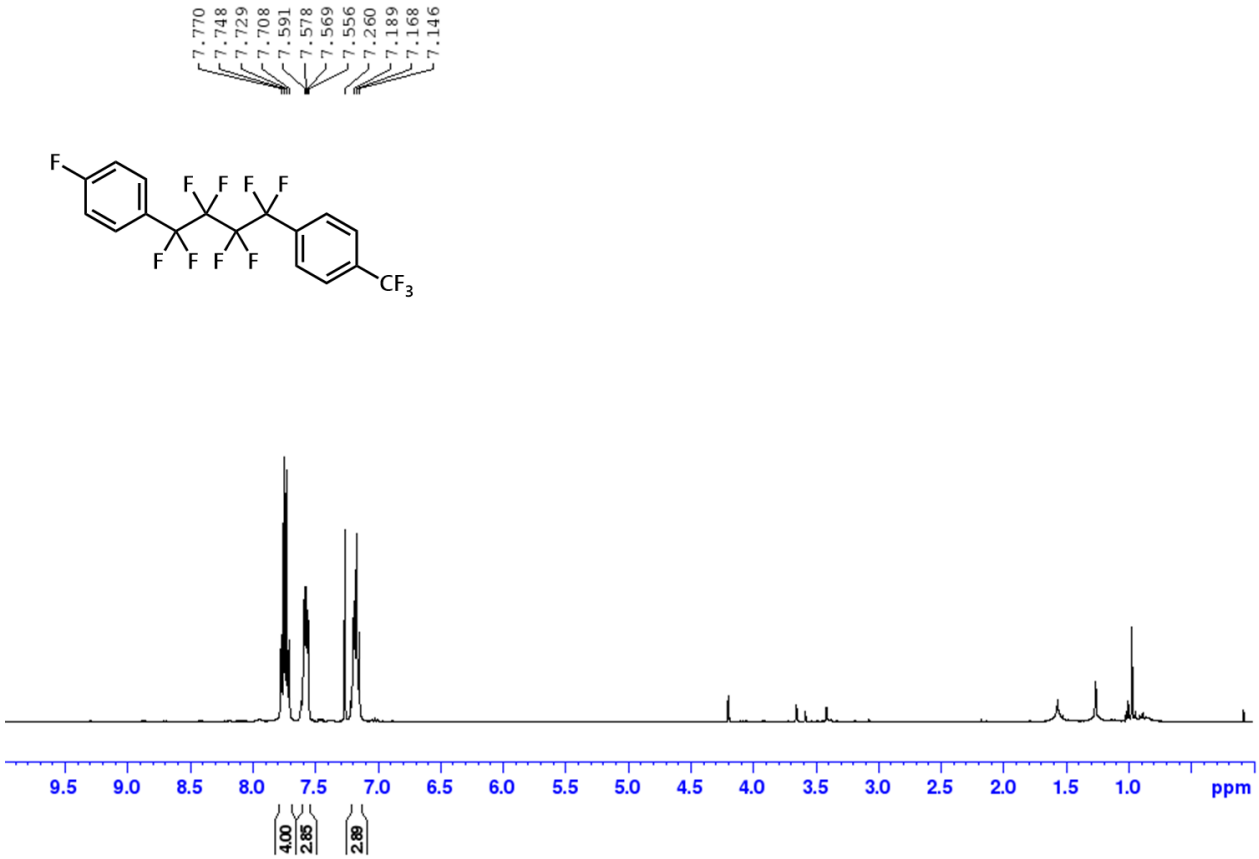


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

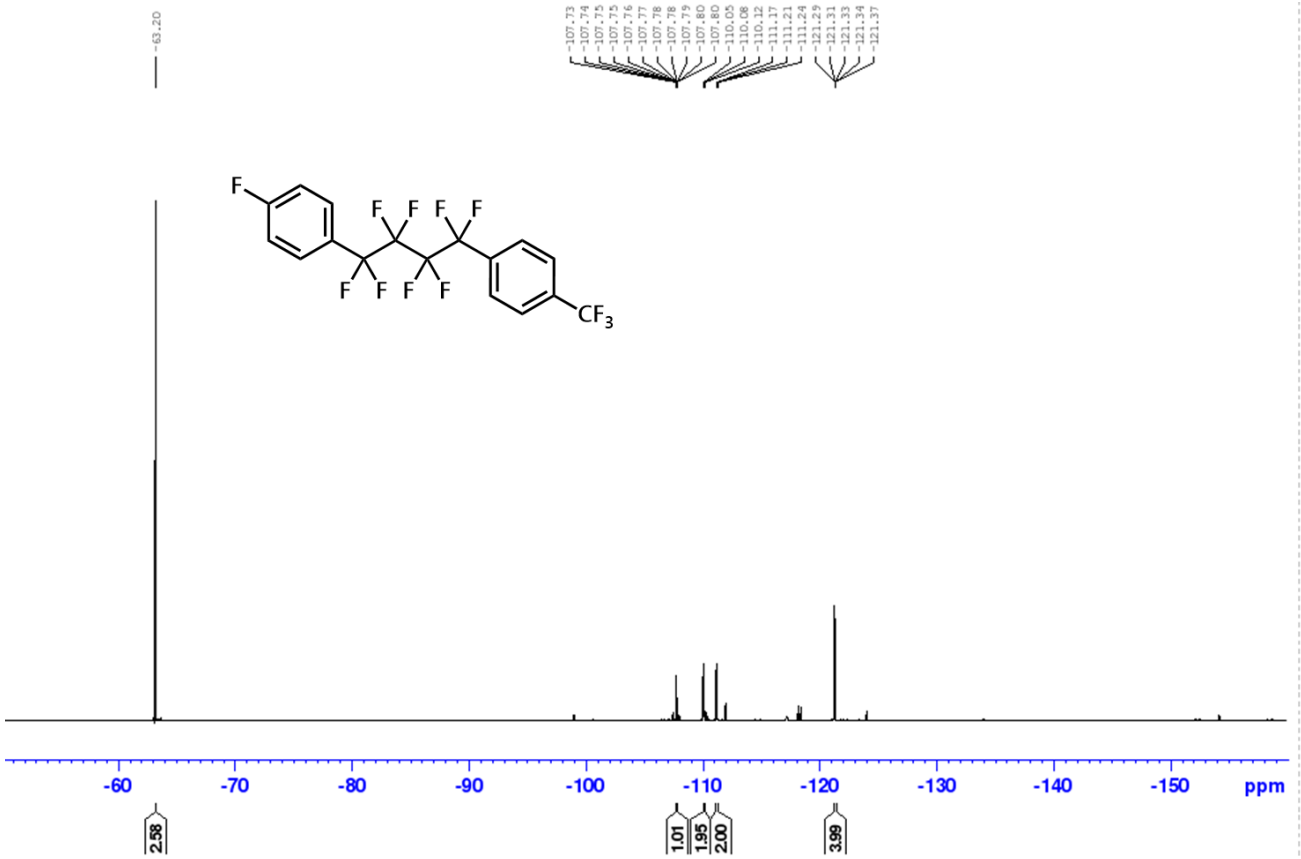


3o₂

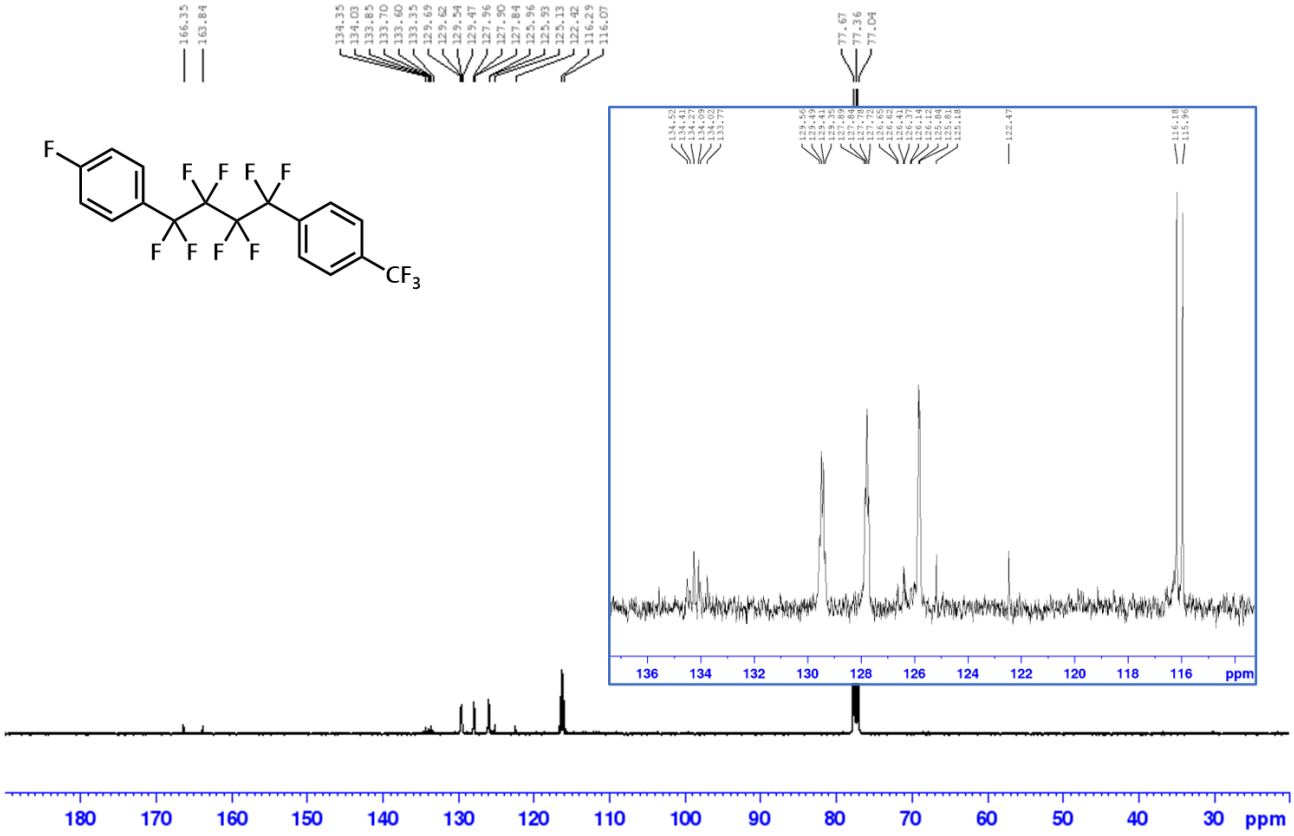
^{1}H NMR (400 MHz, $CDCl_3$)



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

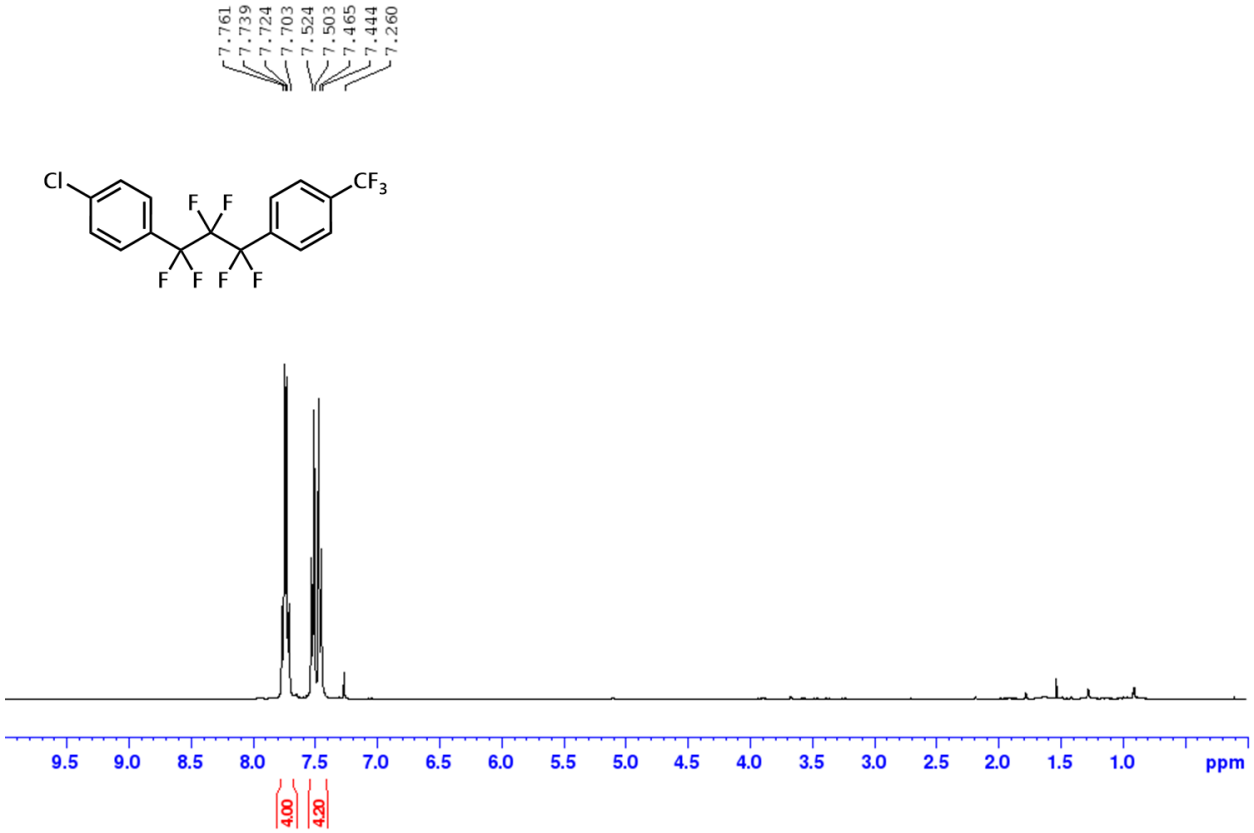


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

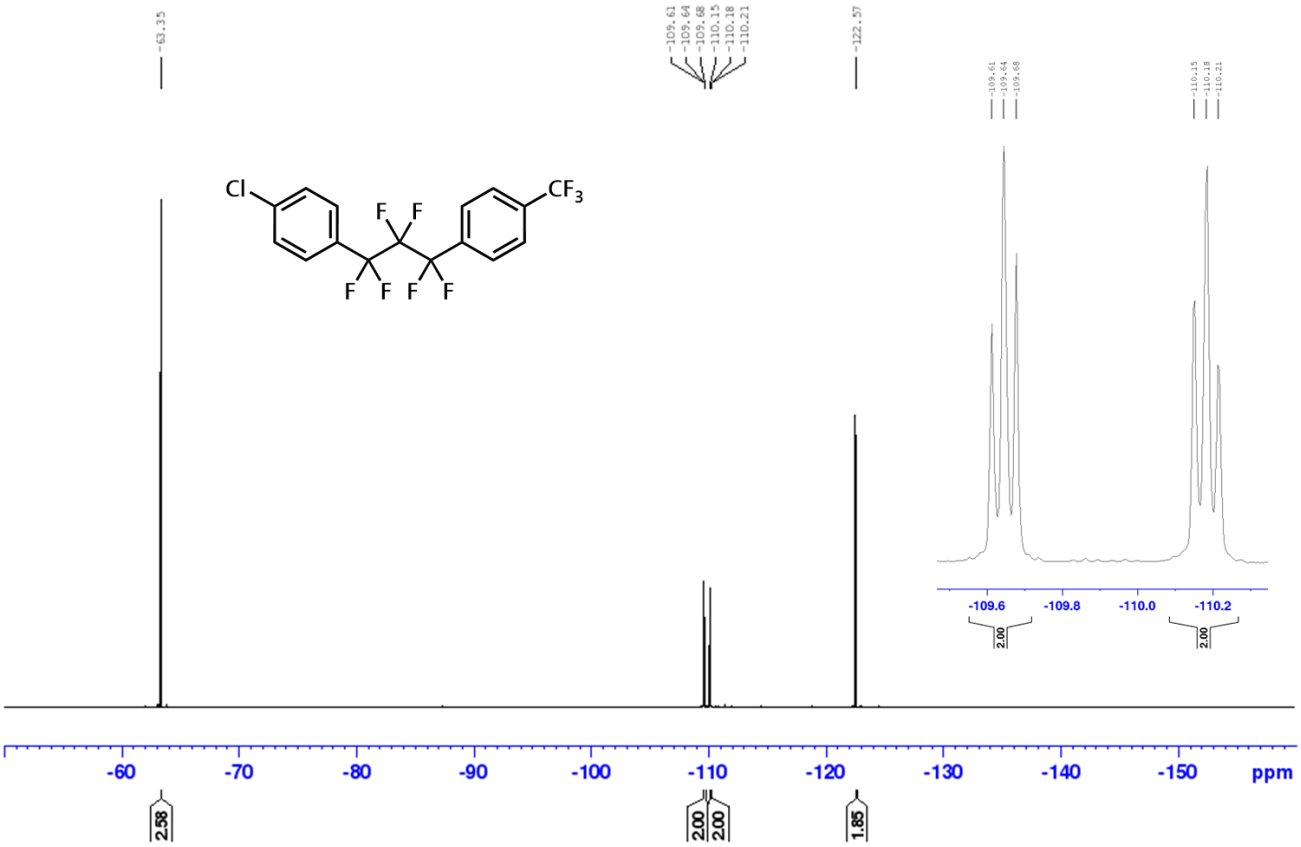


3p₁

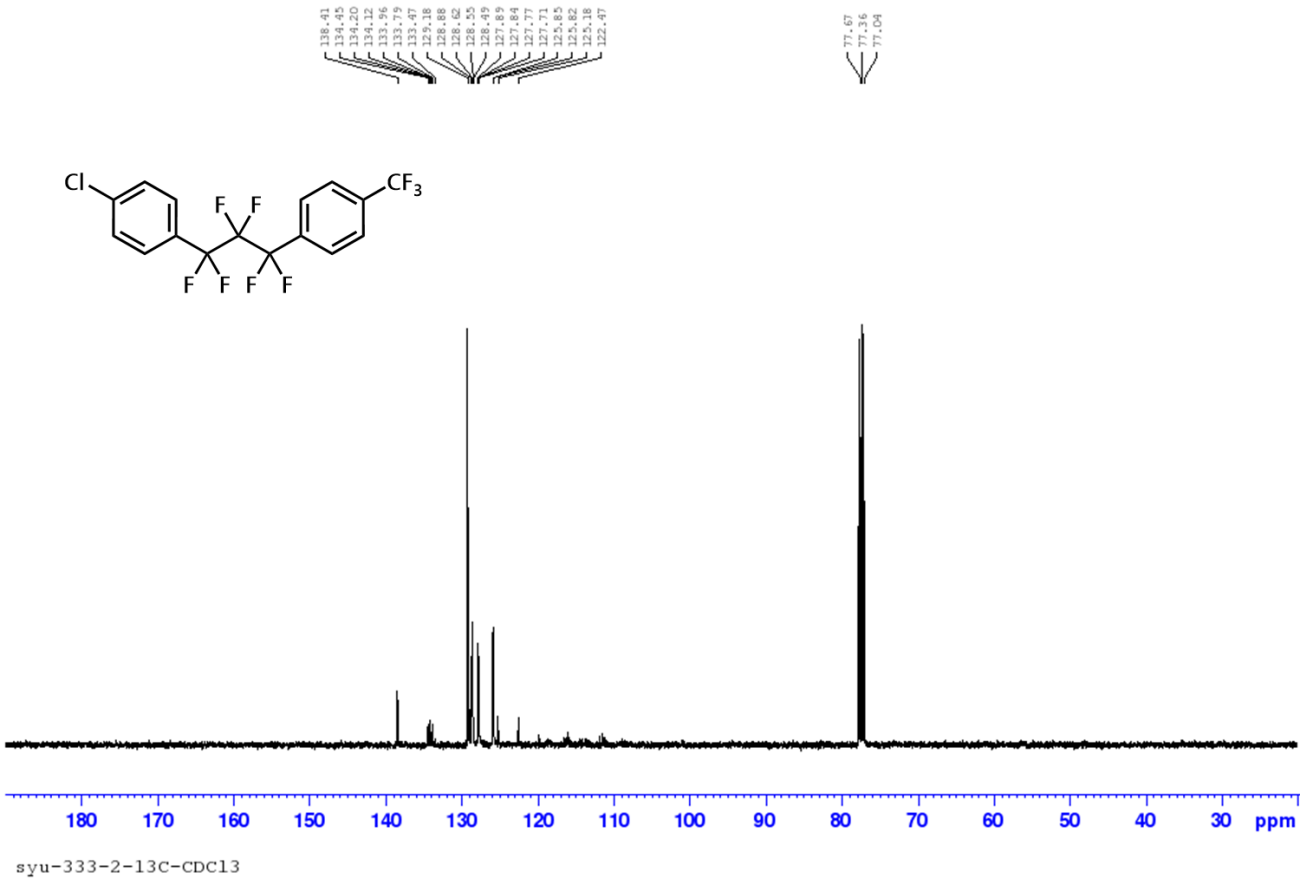
^{1}H NMR (400 MHz, $CDCl_3$)



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

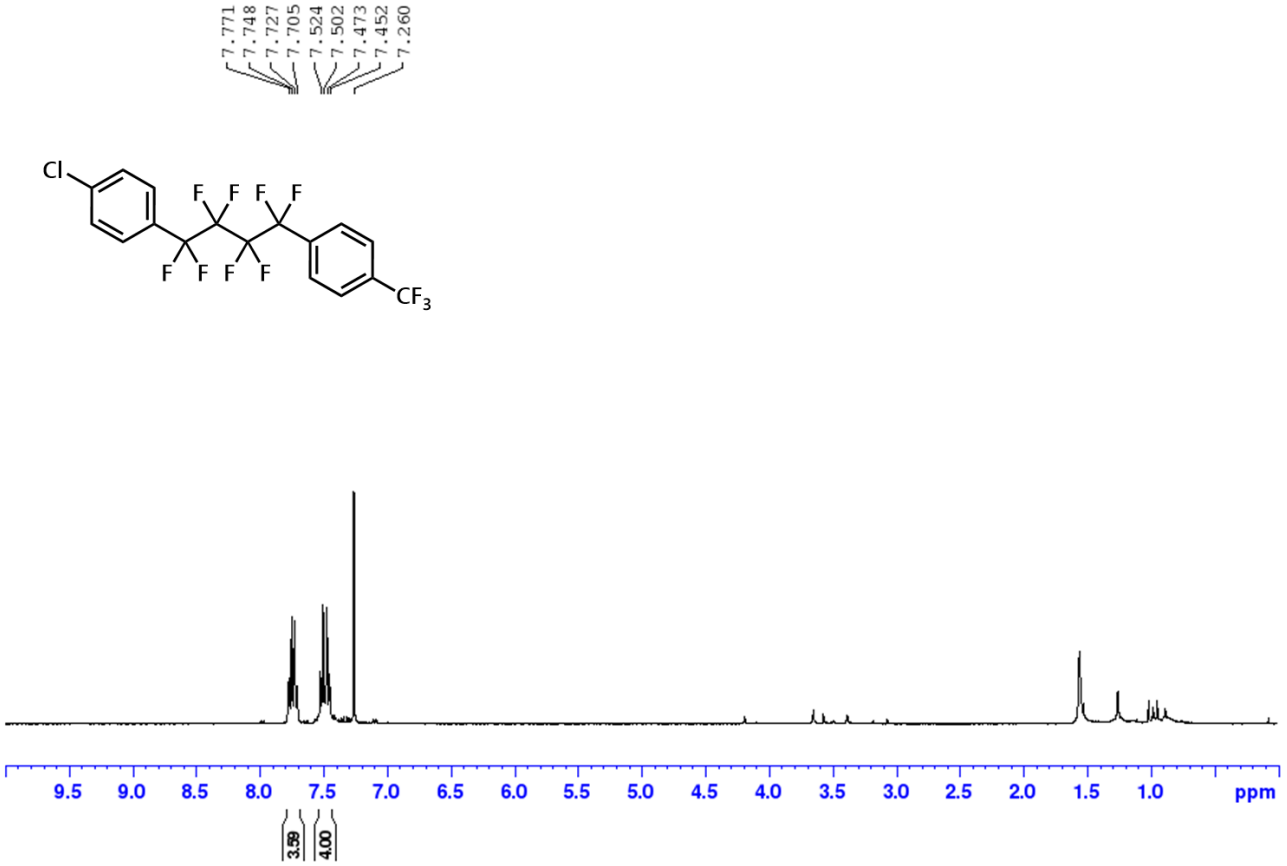


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

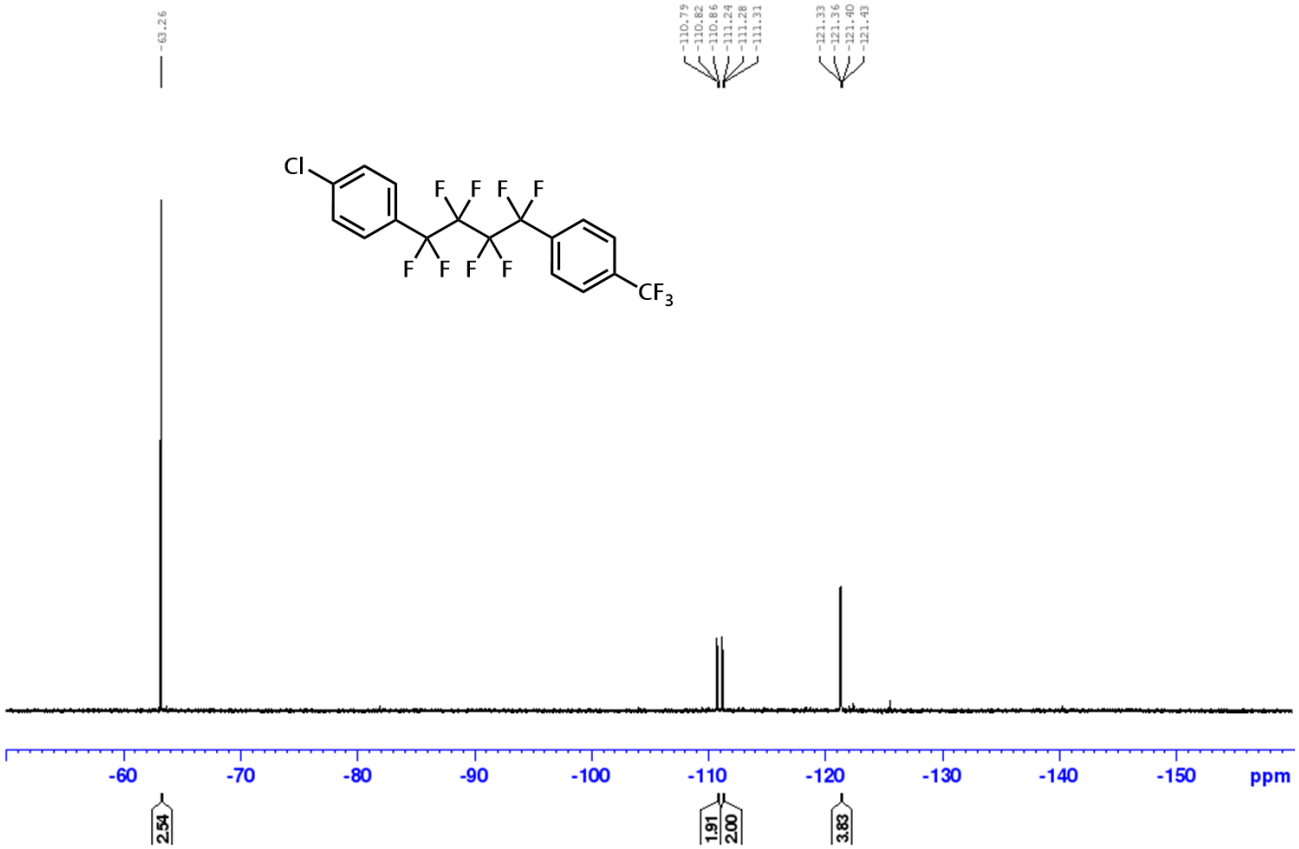


3p₂

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

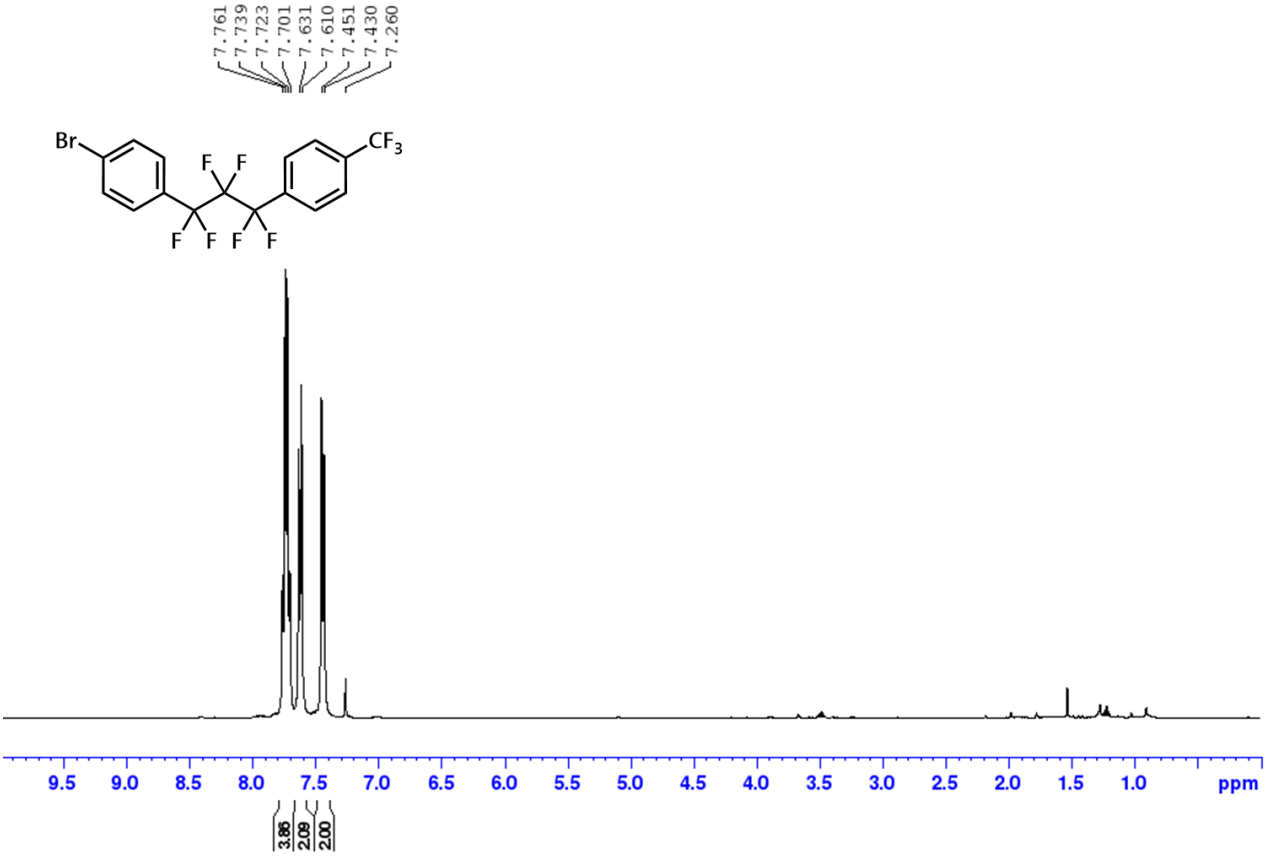


^{19}F NMR (376 MHz, $CDCl_3$):

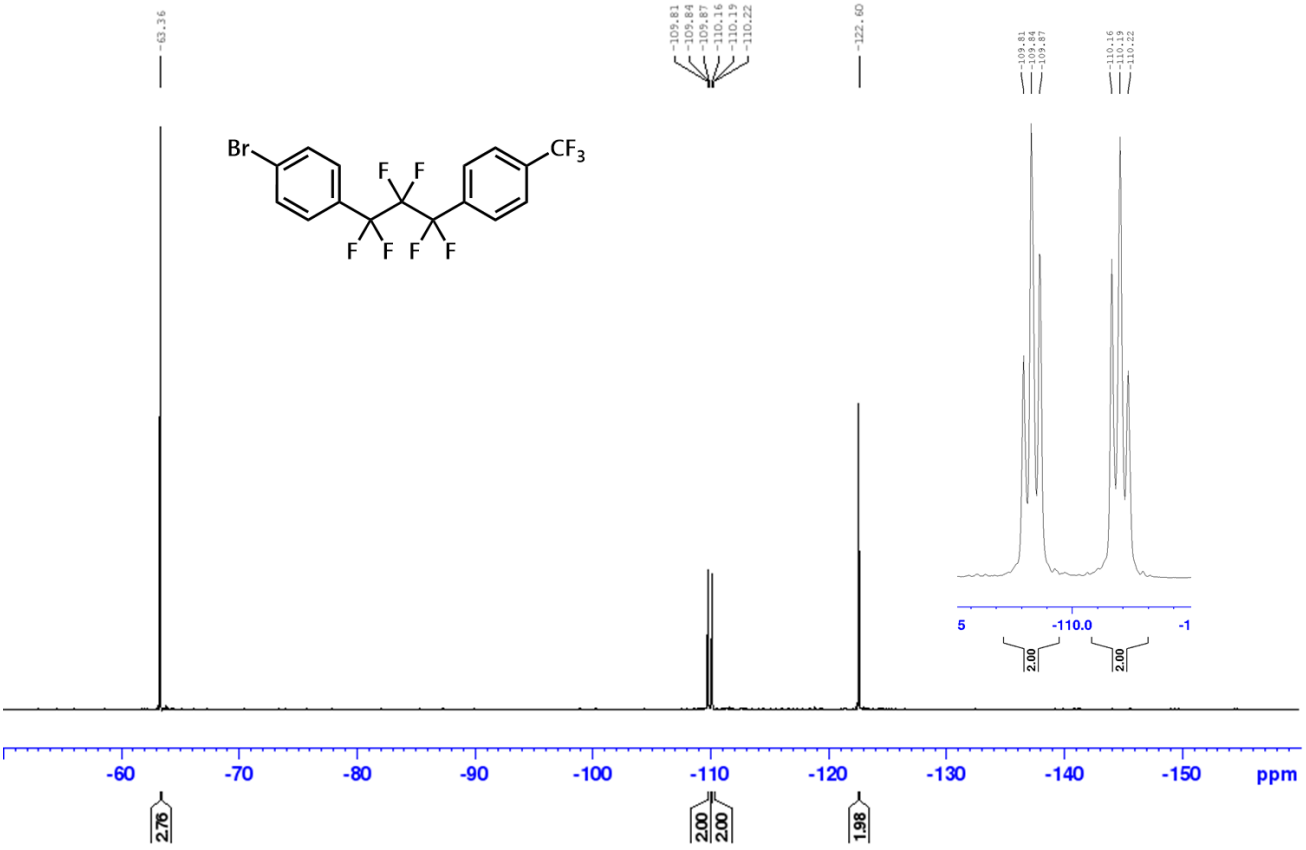


3q₁

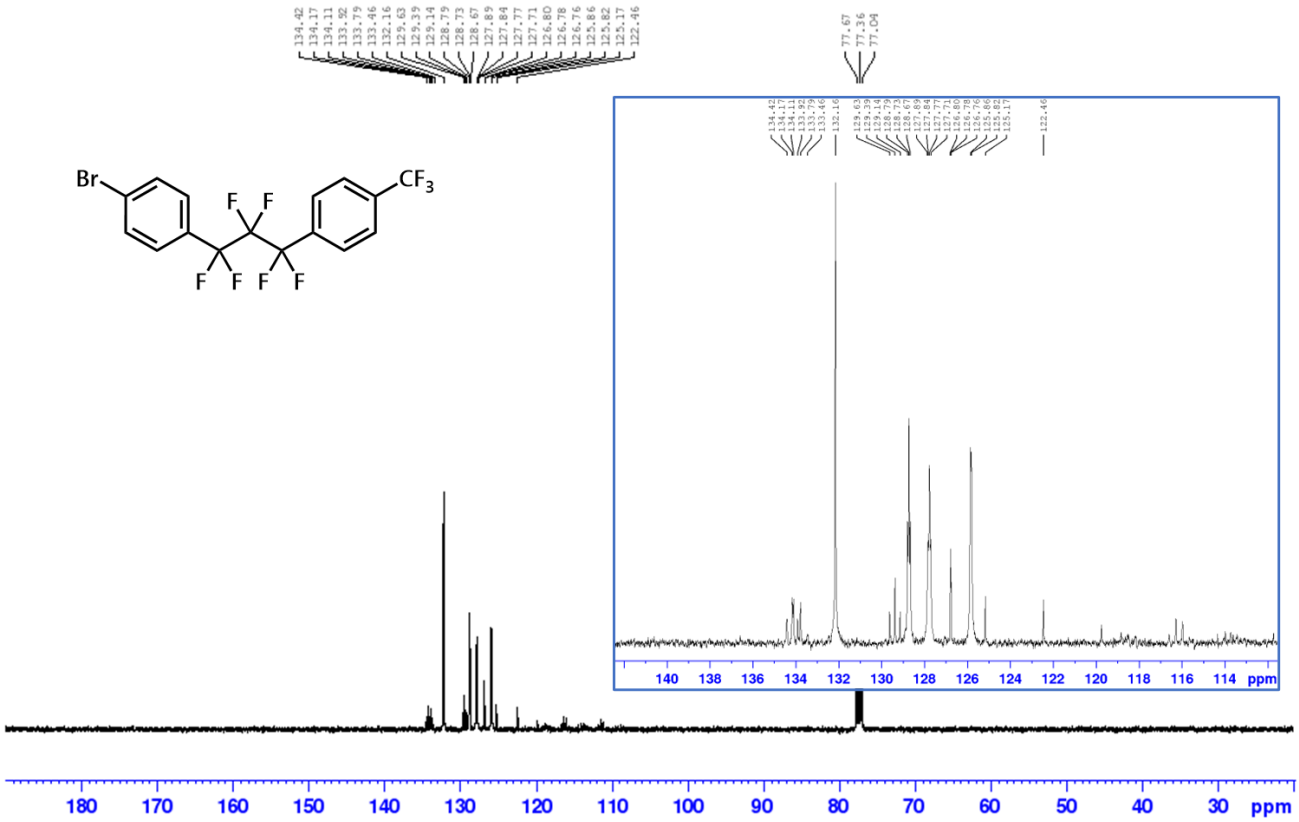
^{1}H NMR (400 MHz, $CDCl_3$)



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

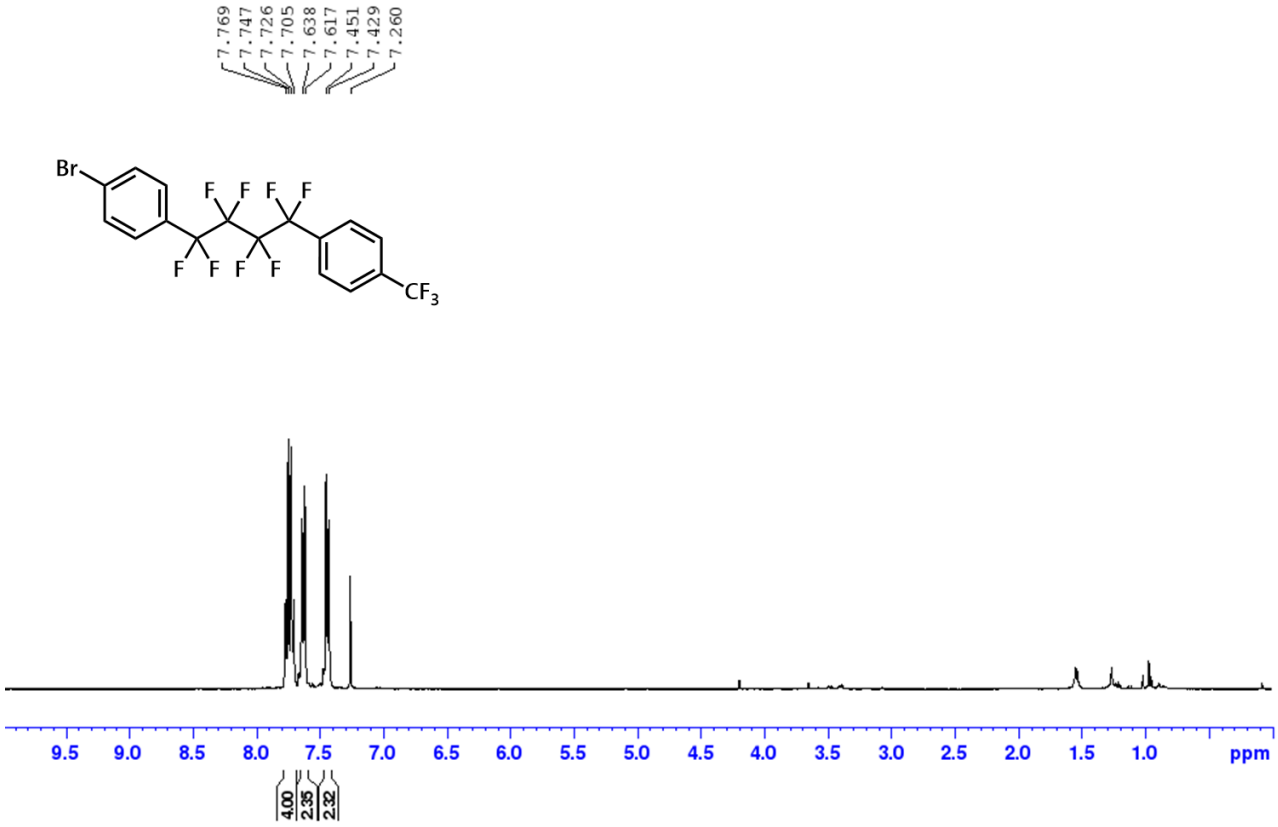


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

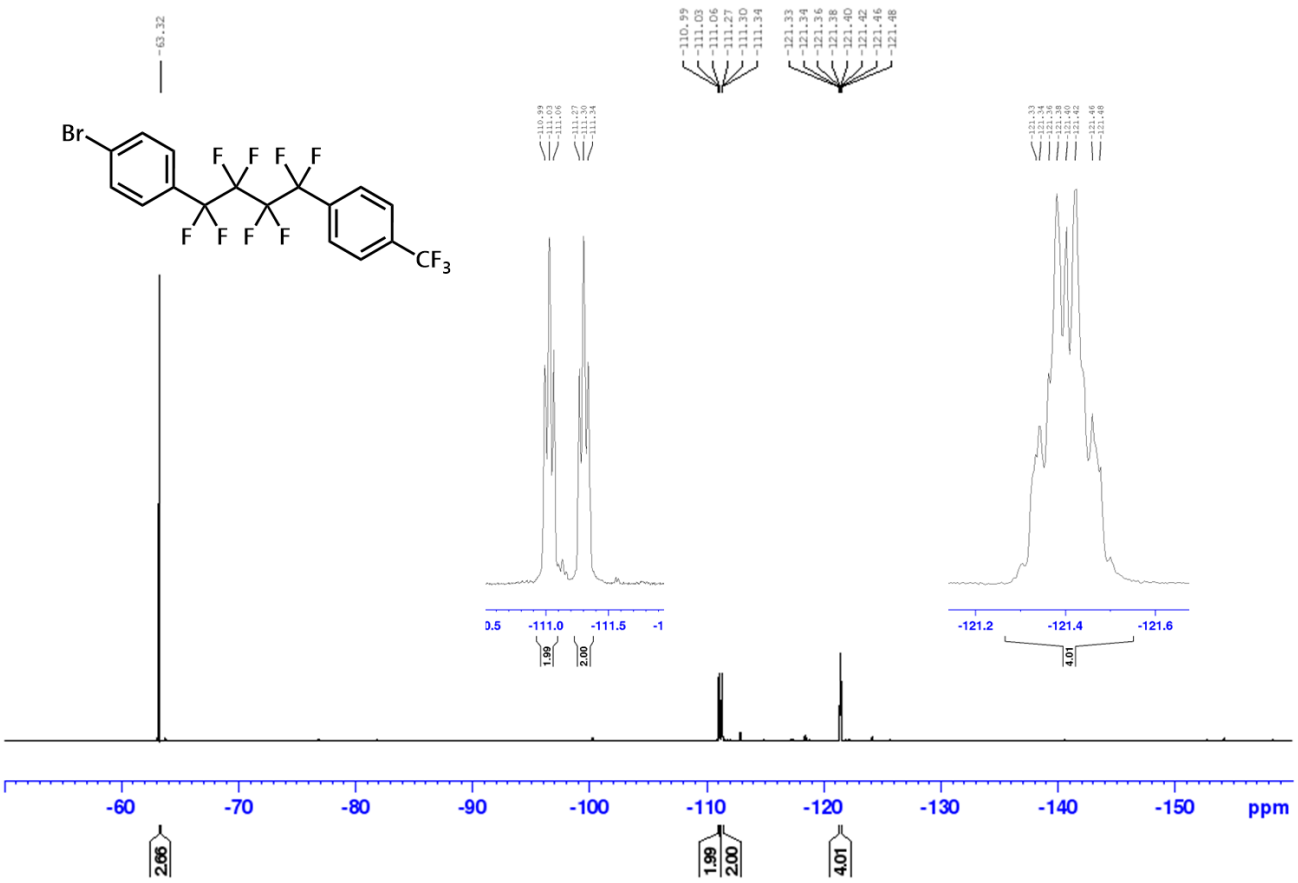


3q₂

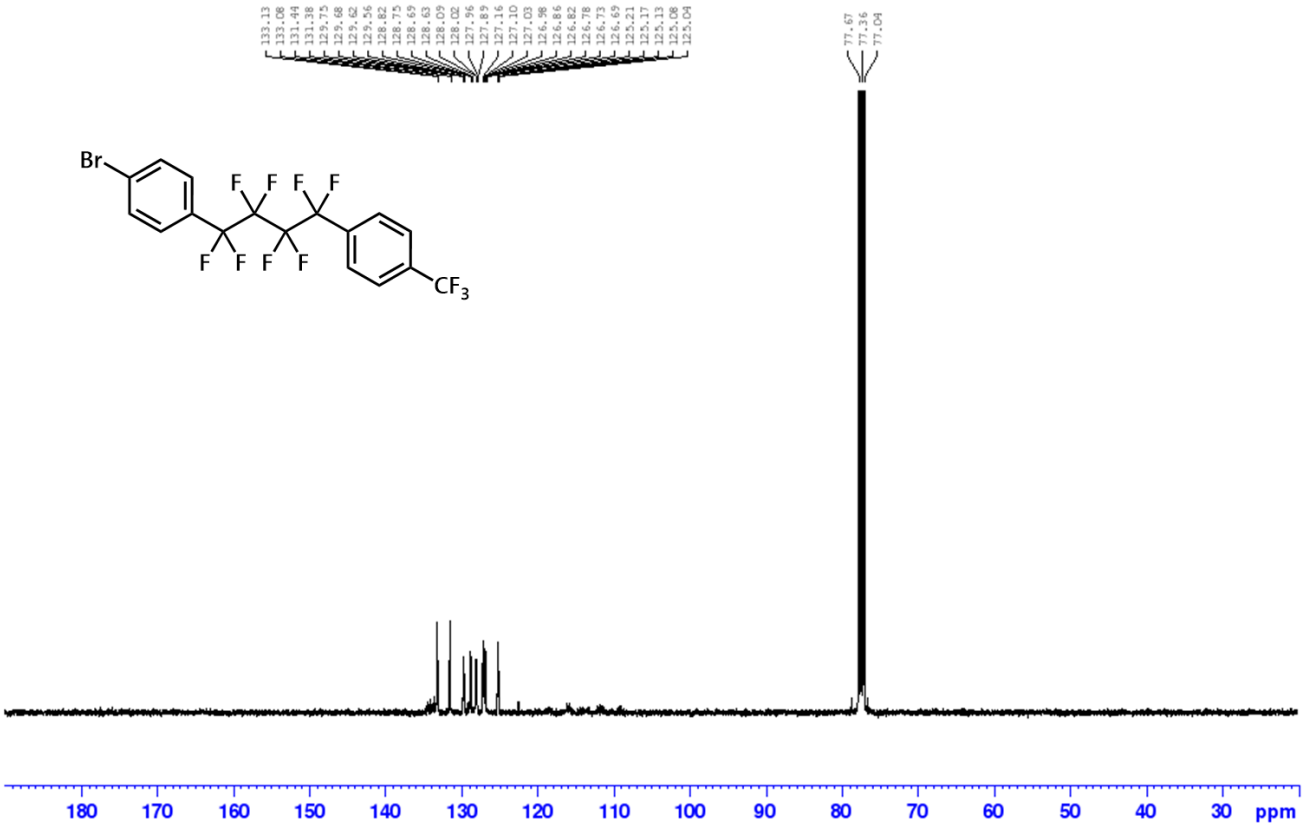
^{1}H NMR (400 MHz, $CDCl_3$)



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

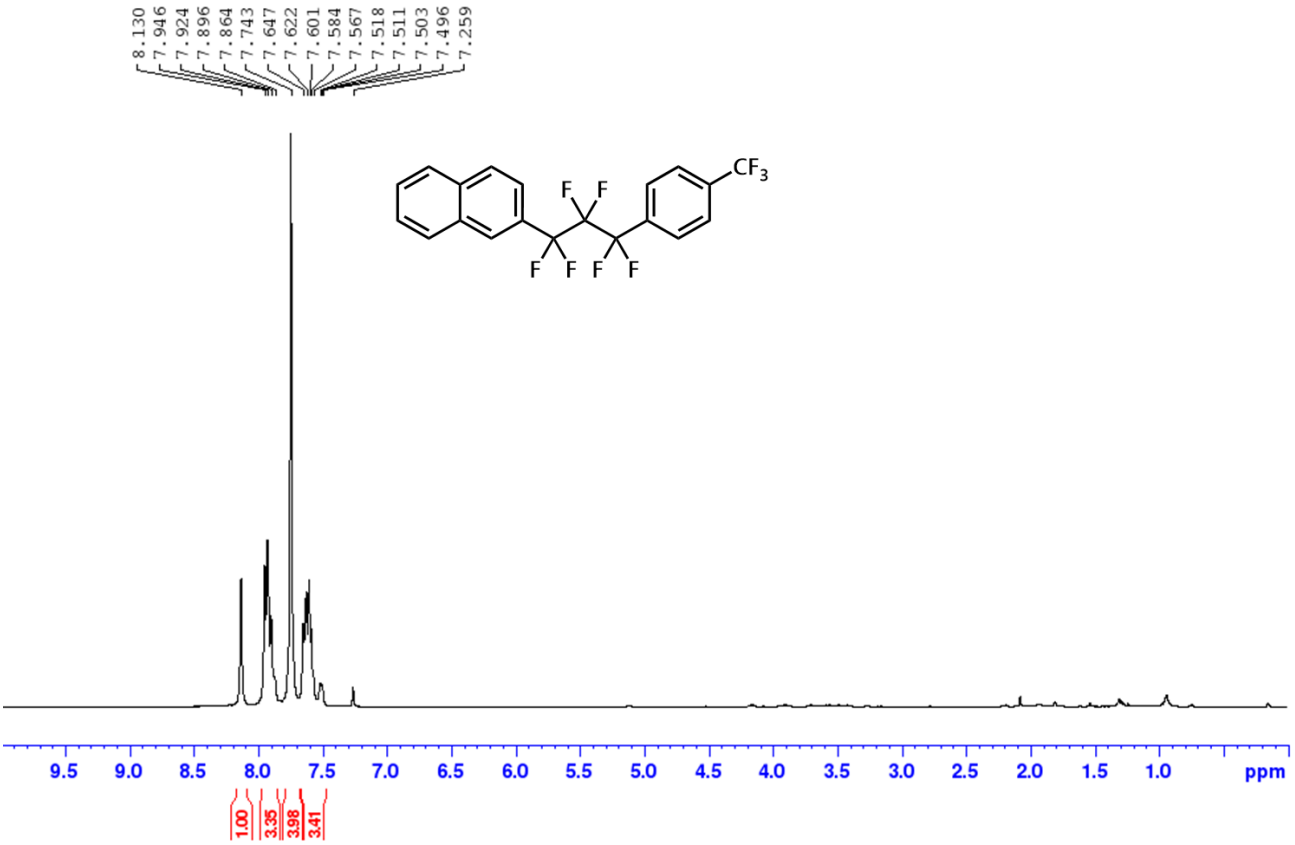


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

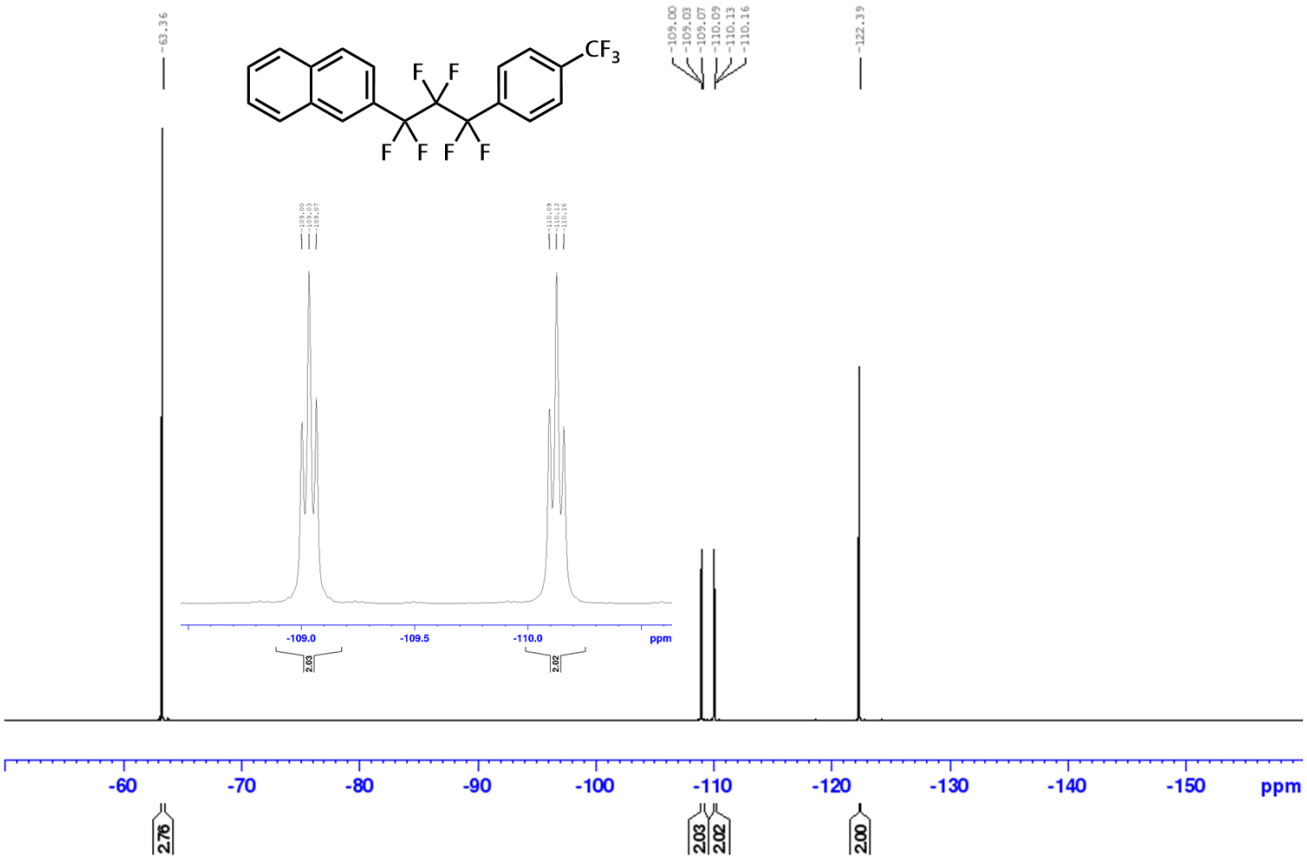


3r₁

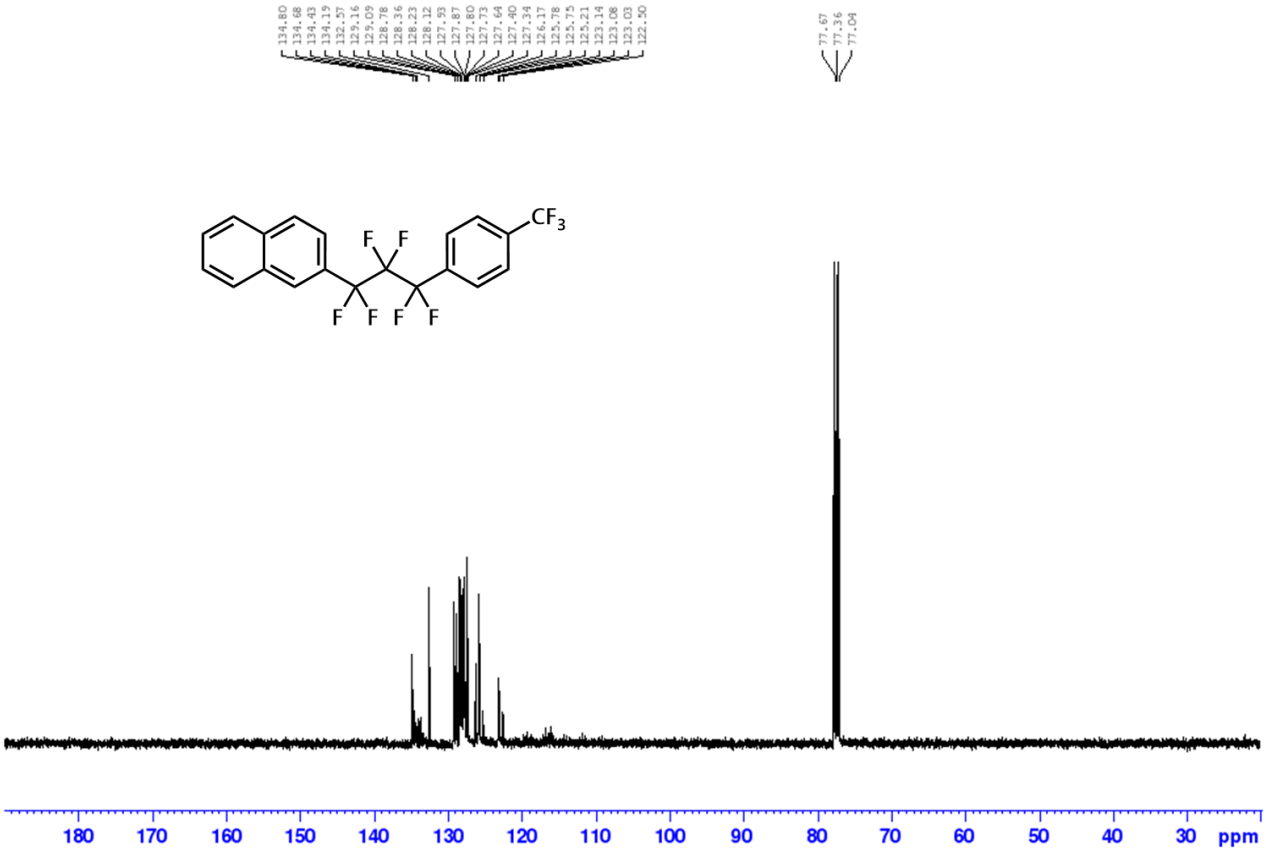
^{1}H NMR (400 MHz, $CDCl_3$)



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

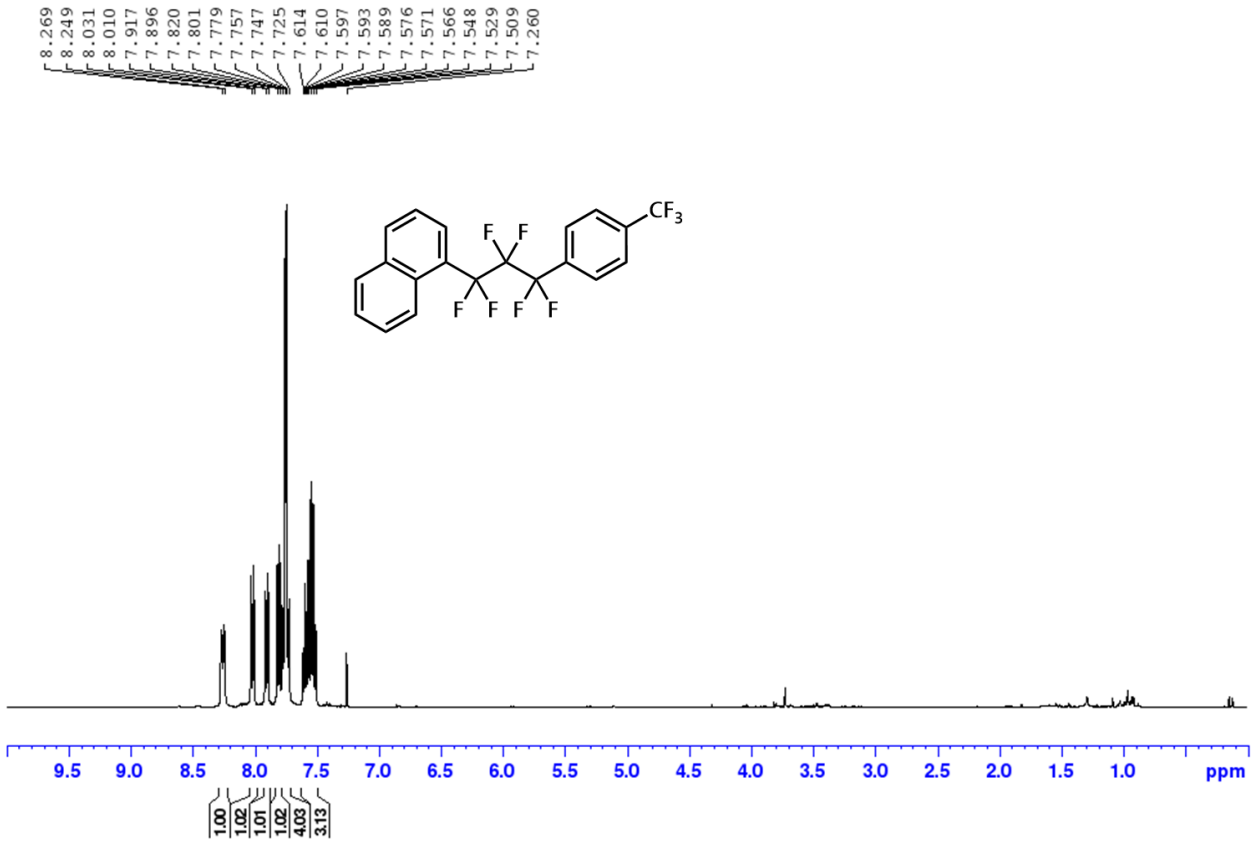


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

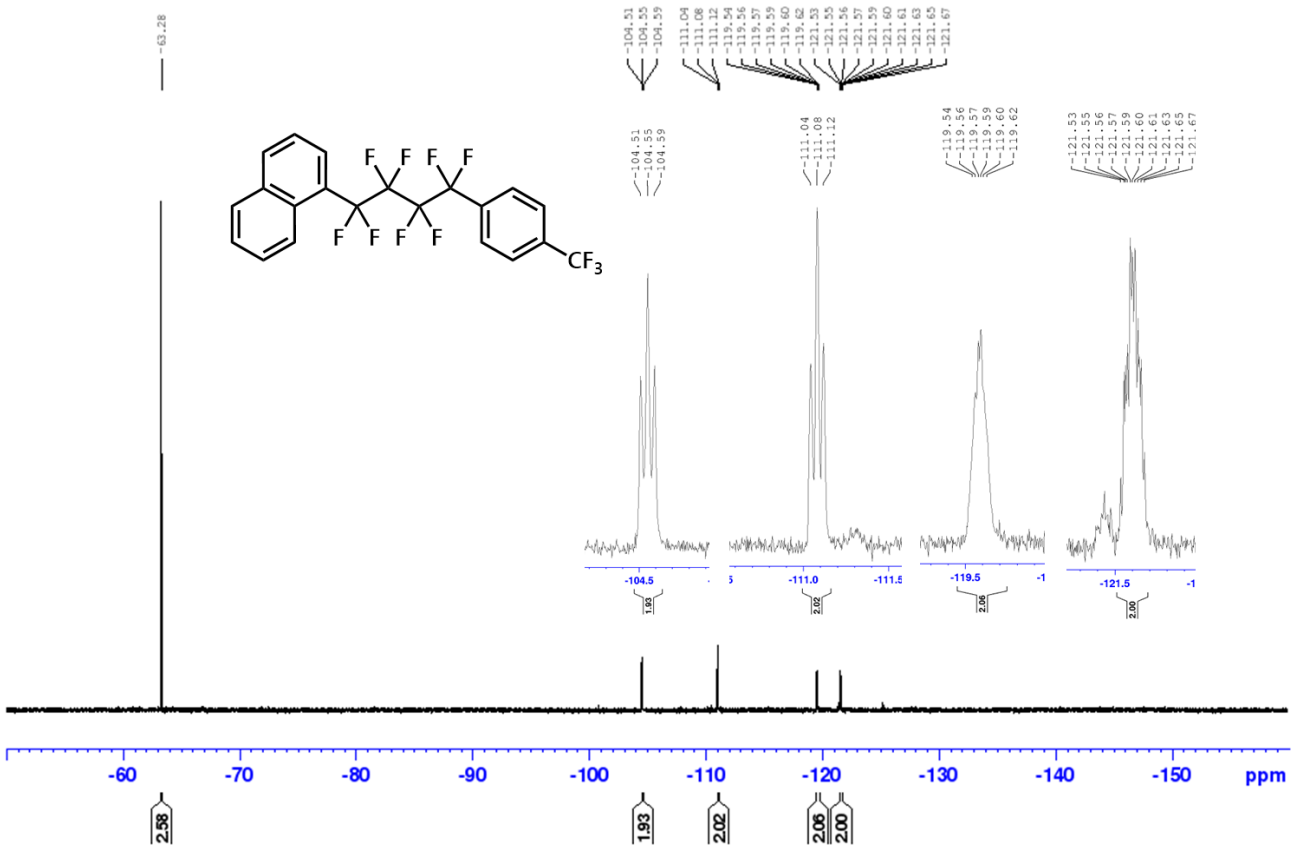


***3s*$_1$**

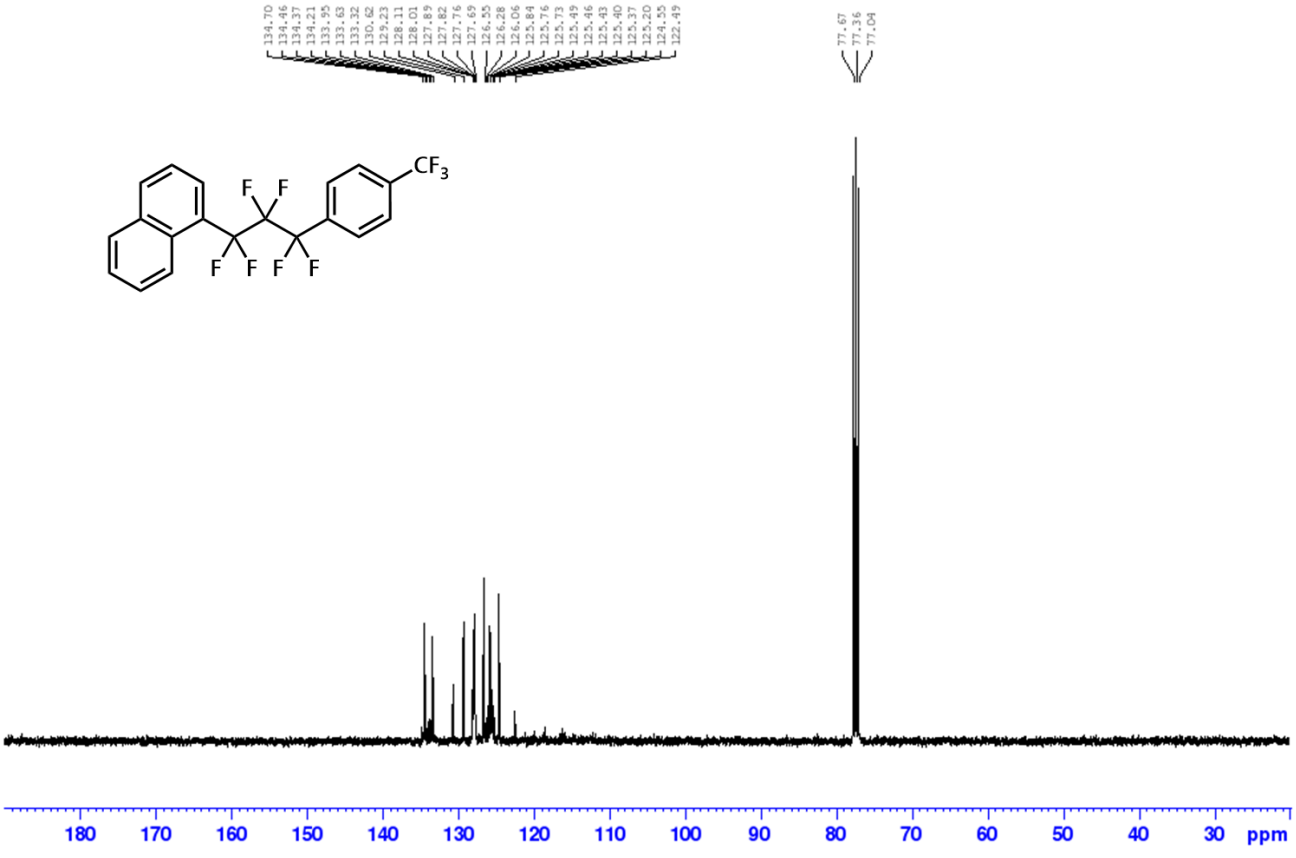
^{1}H NMR (400 MHz, $CDCl_3$)



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

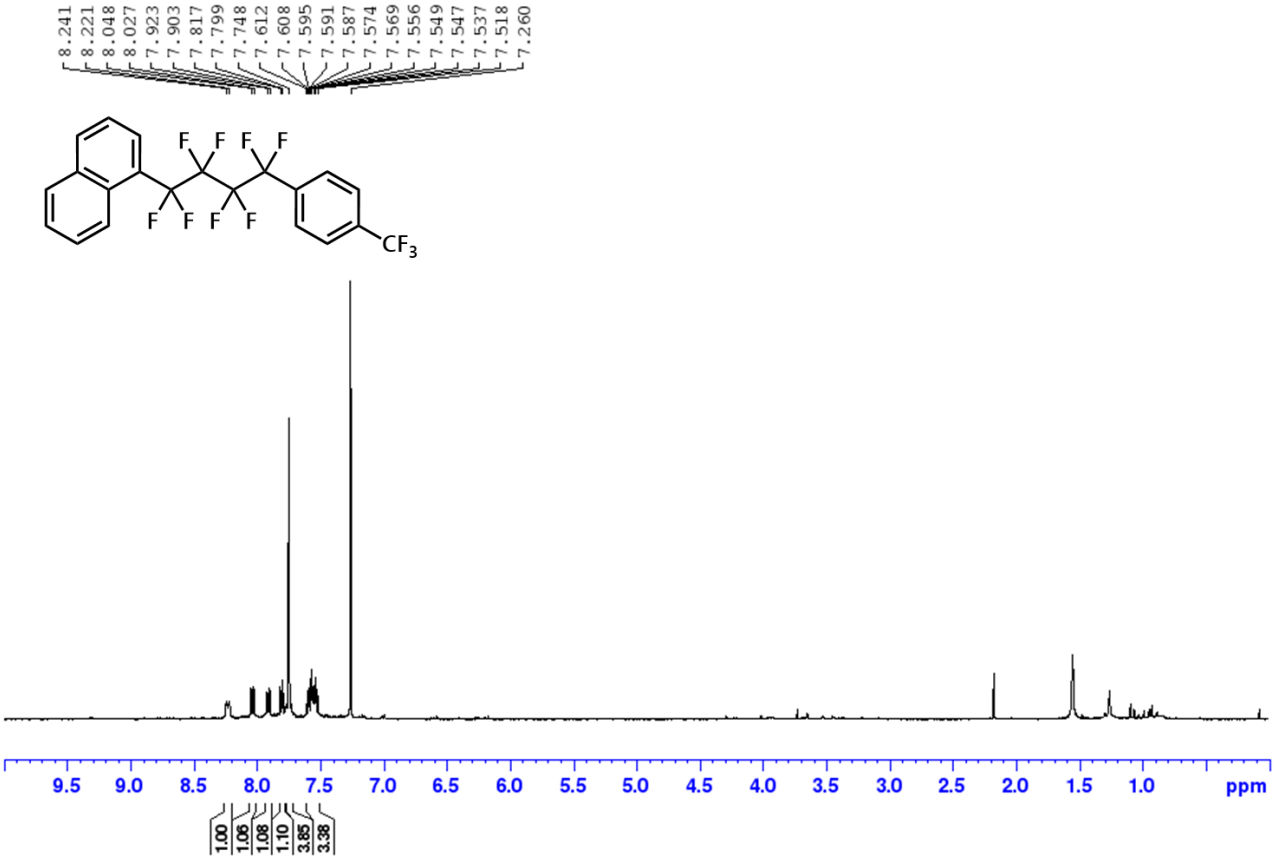


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

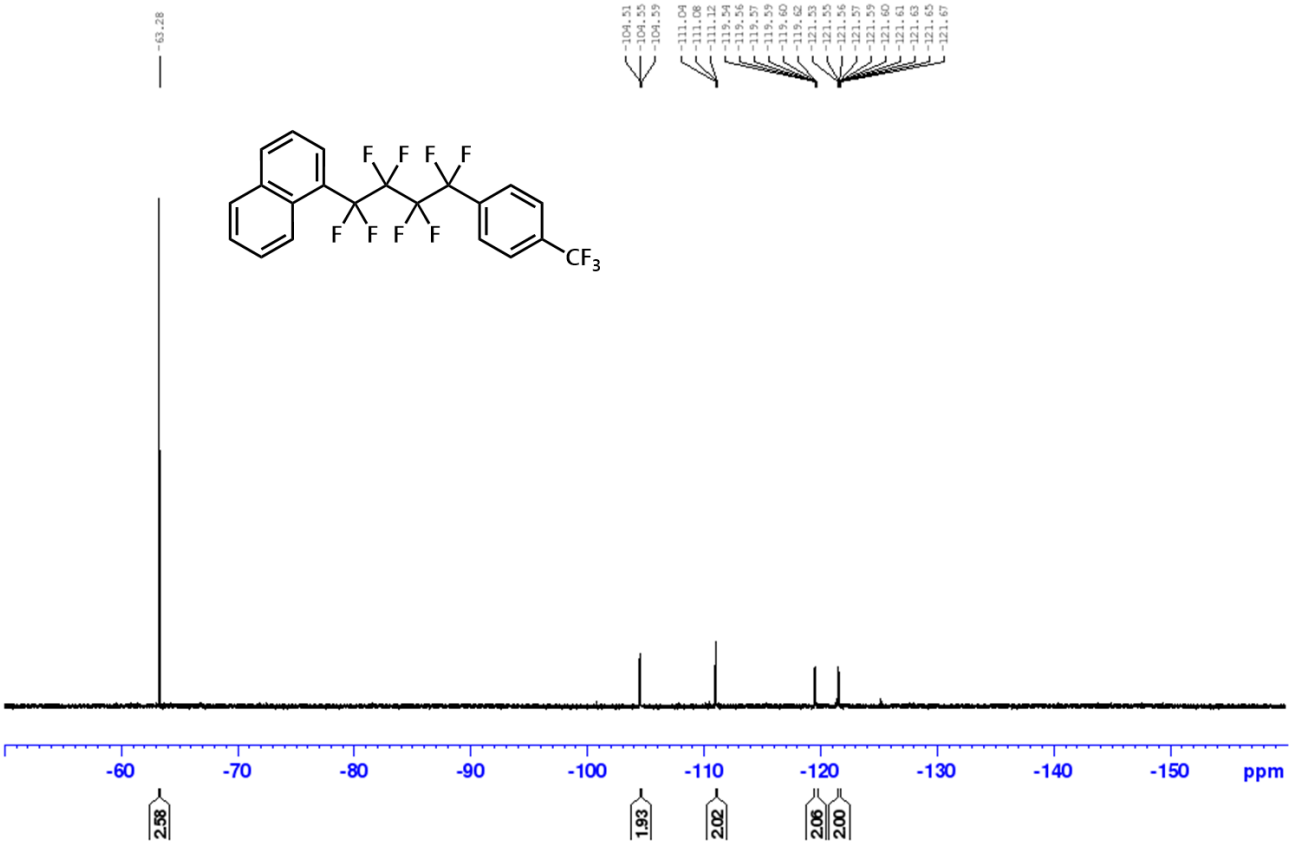


3s₂

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

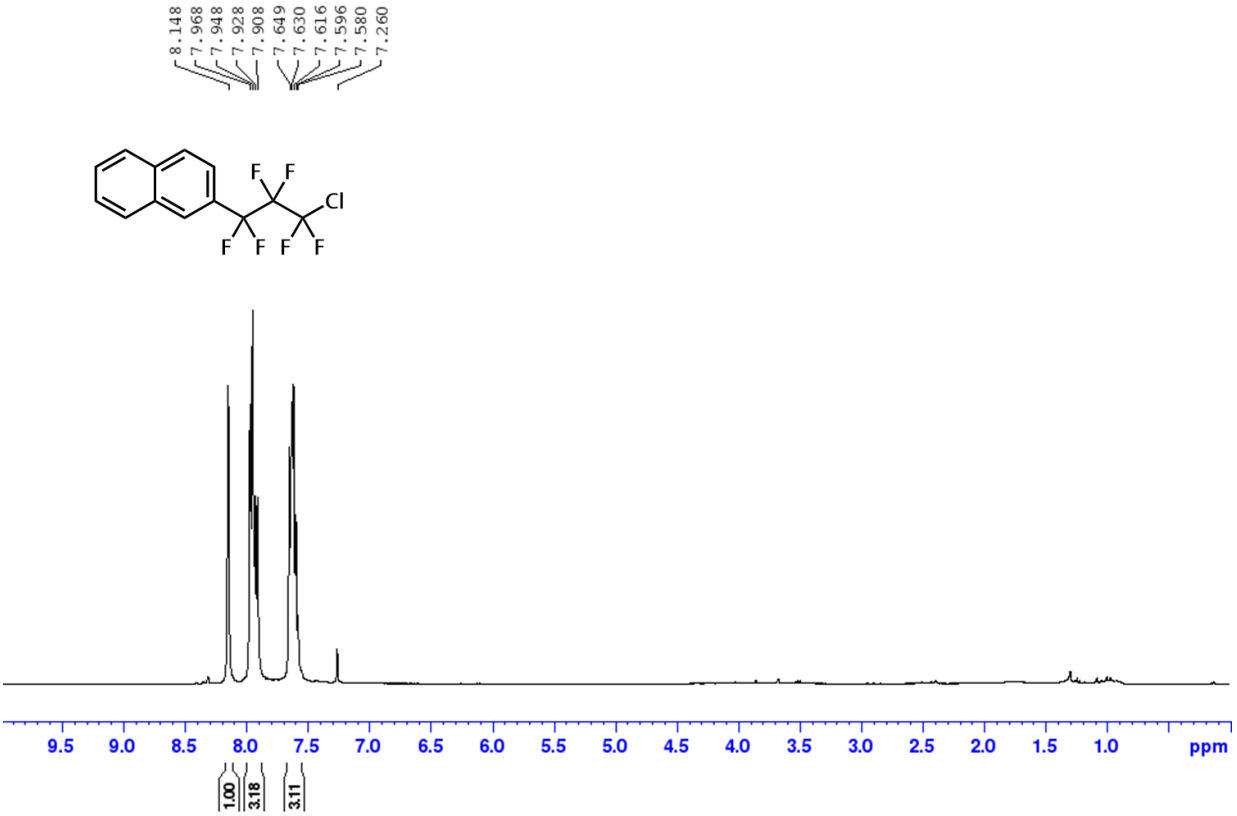


^{19}F NMR (376 MHz, $CDCl_3$):

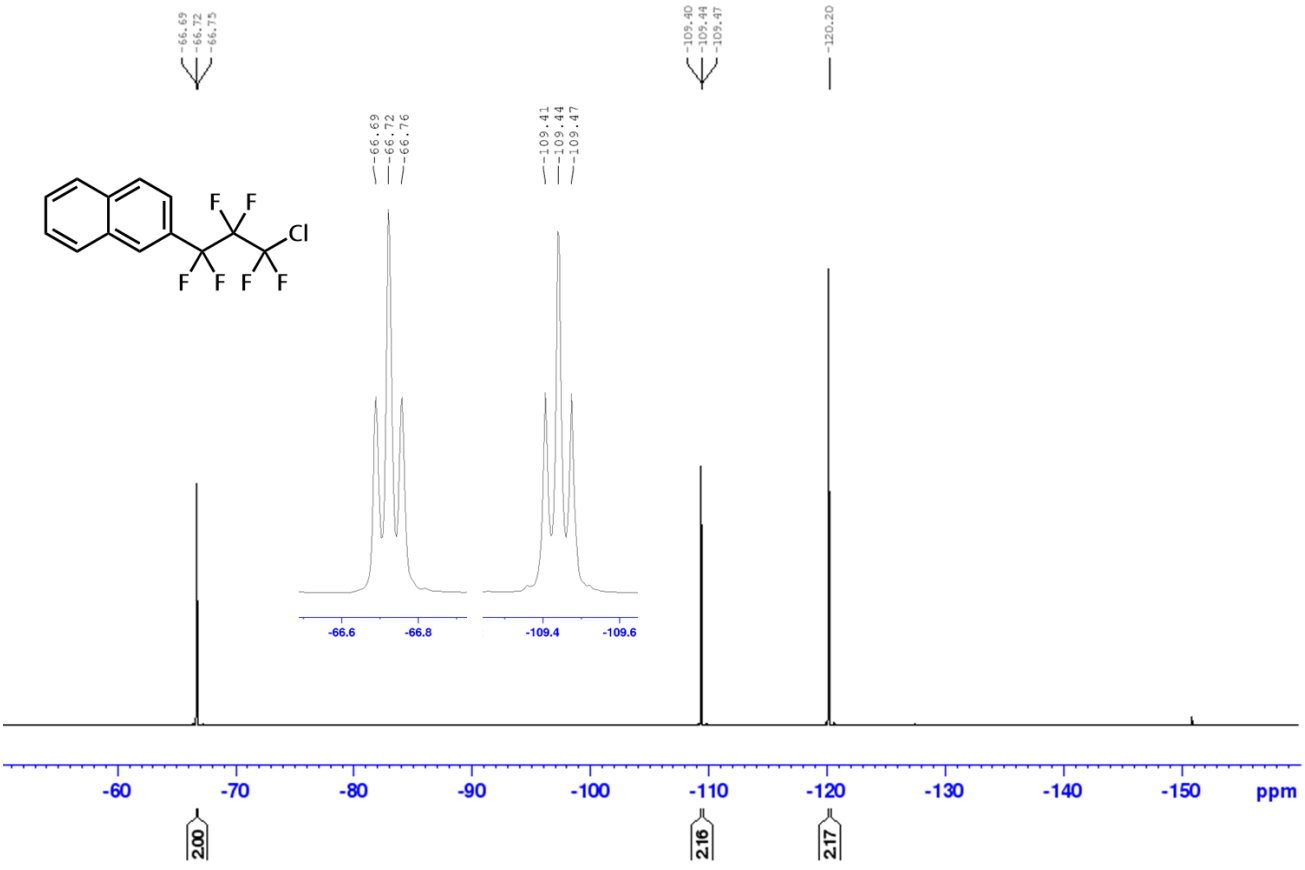


4a

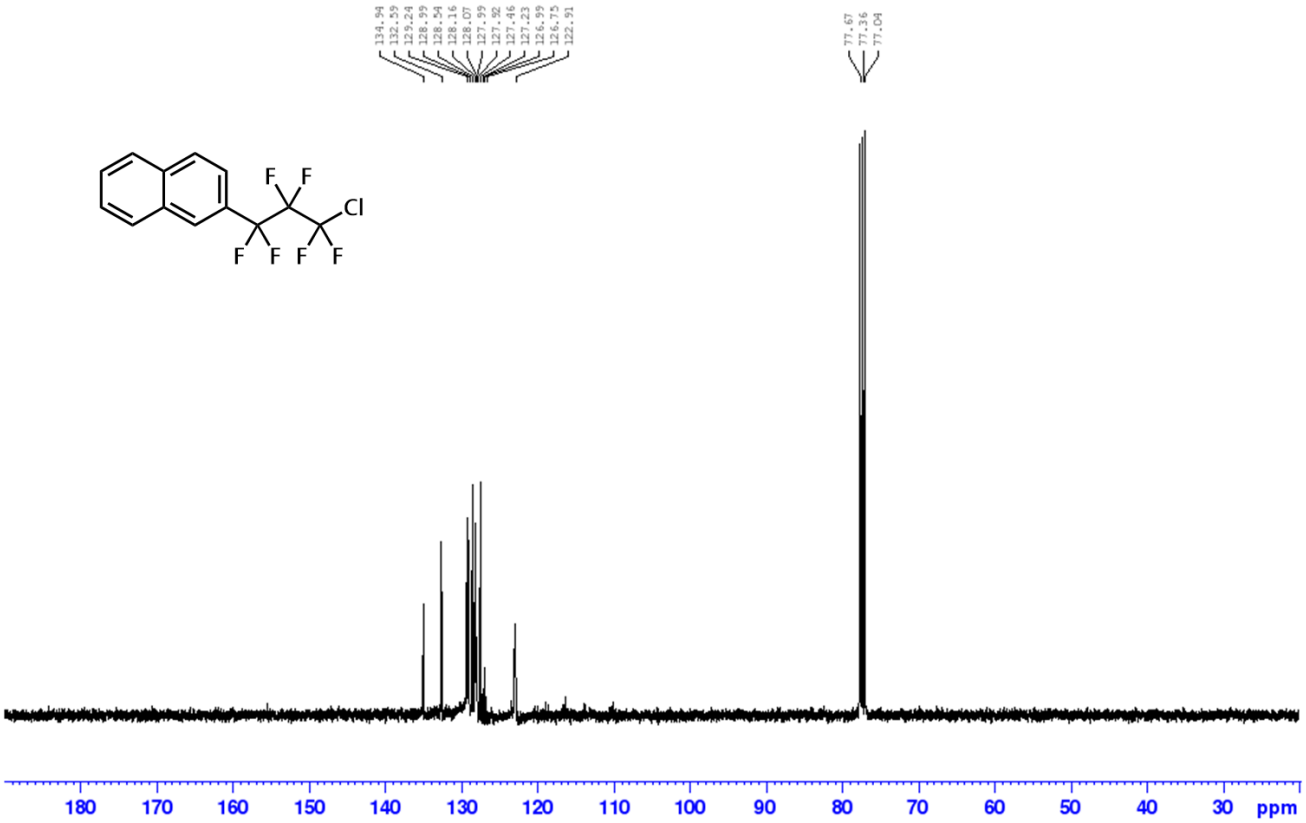
^{1}H NMR (400 MHz, $CDCl_3$)



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

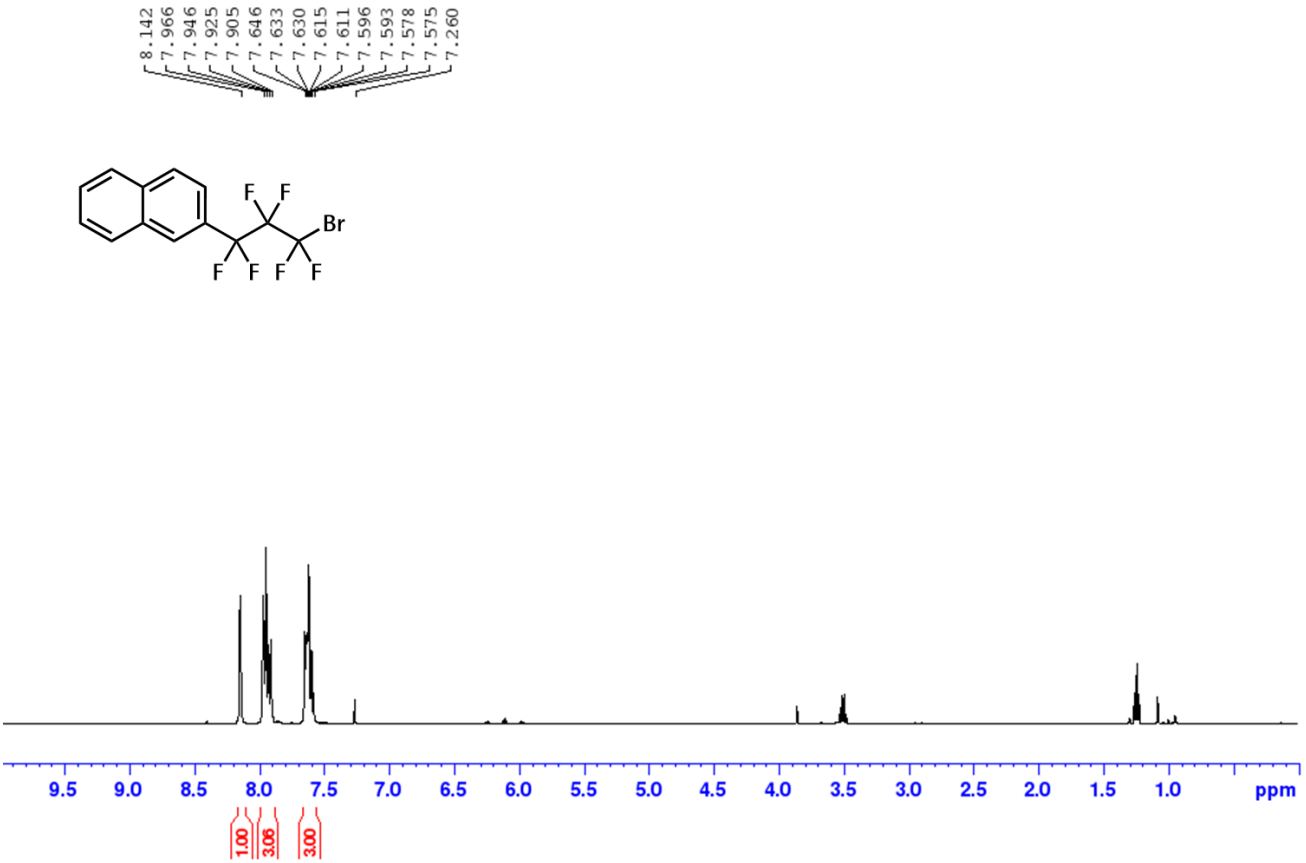


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

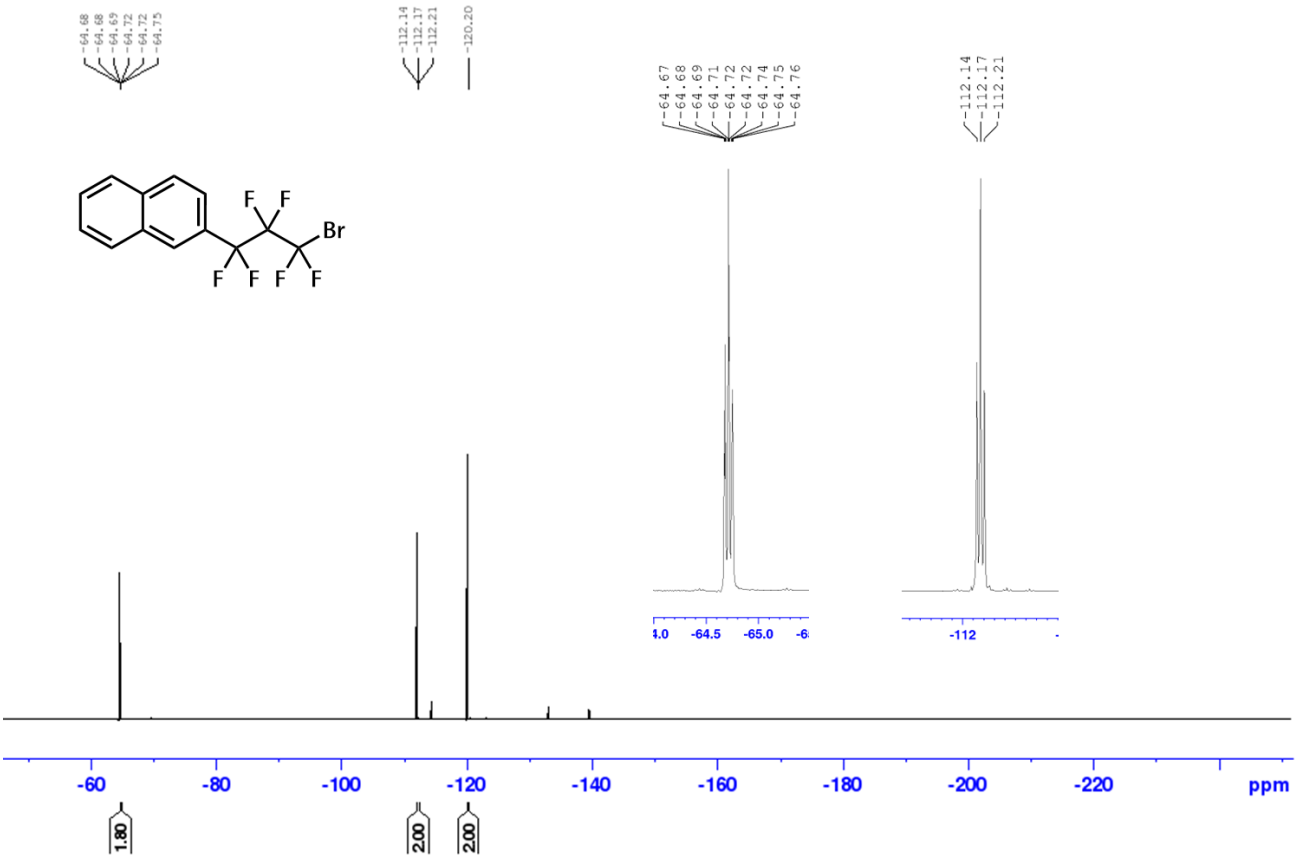


4b

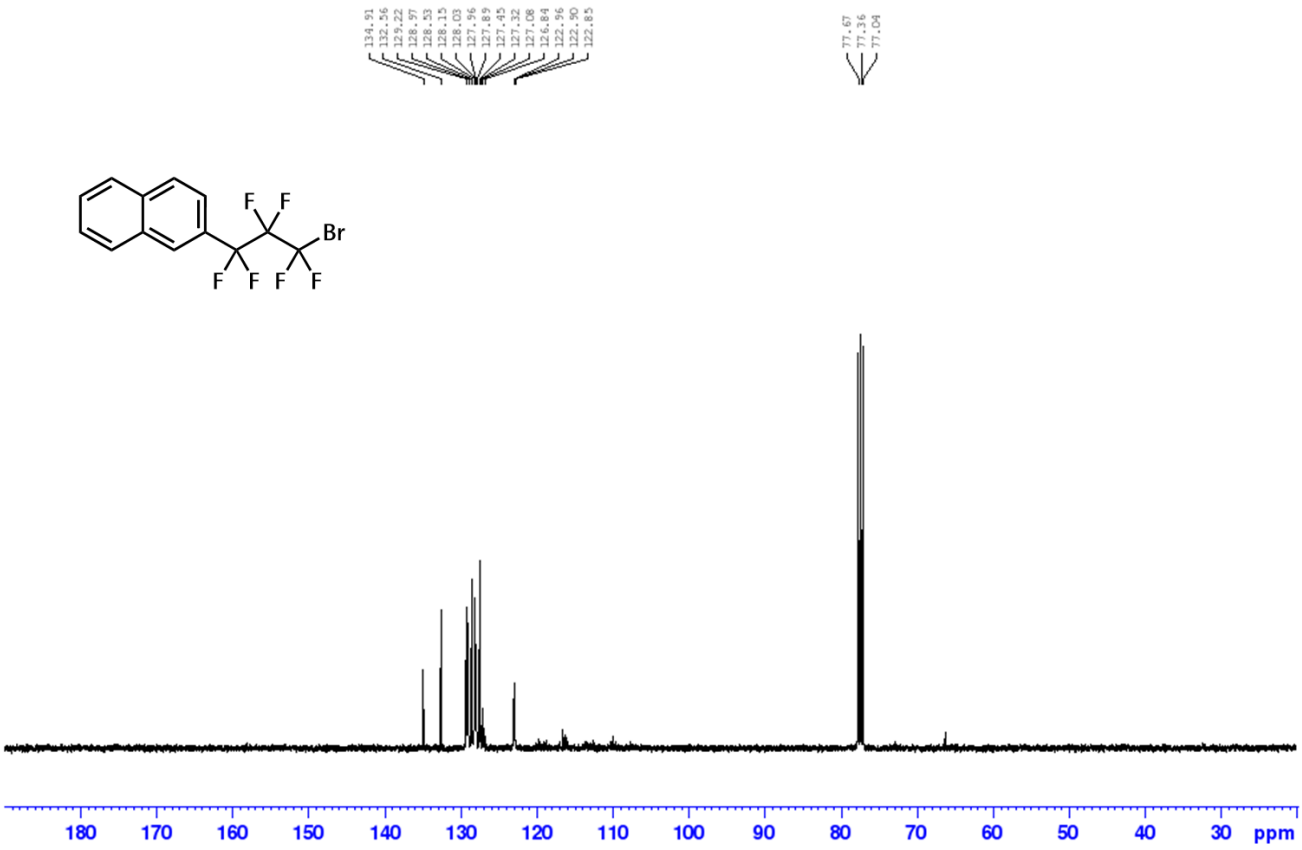
^{1}H NMR (400 MHz, $CDCl_3$)



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

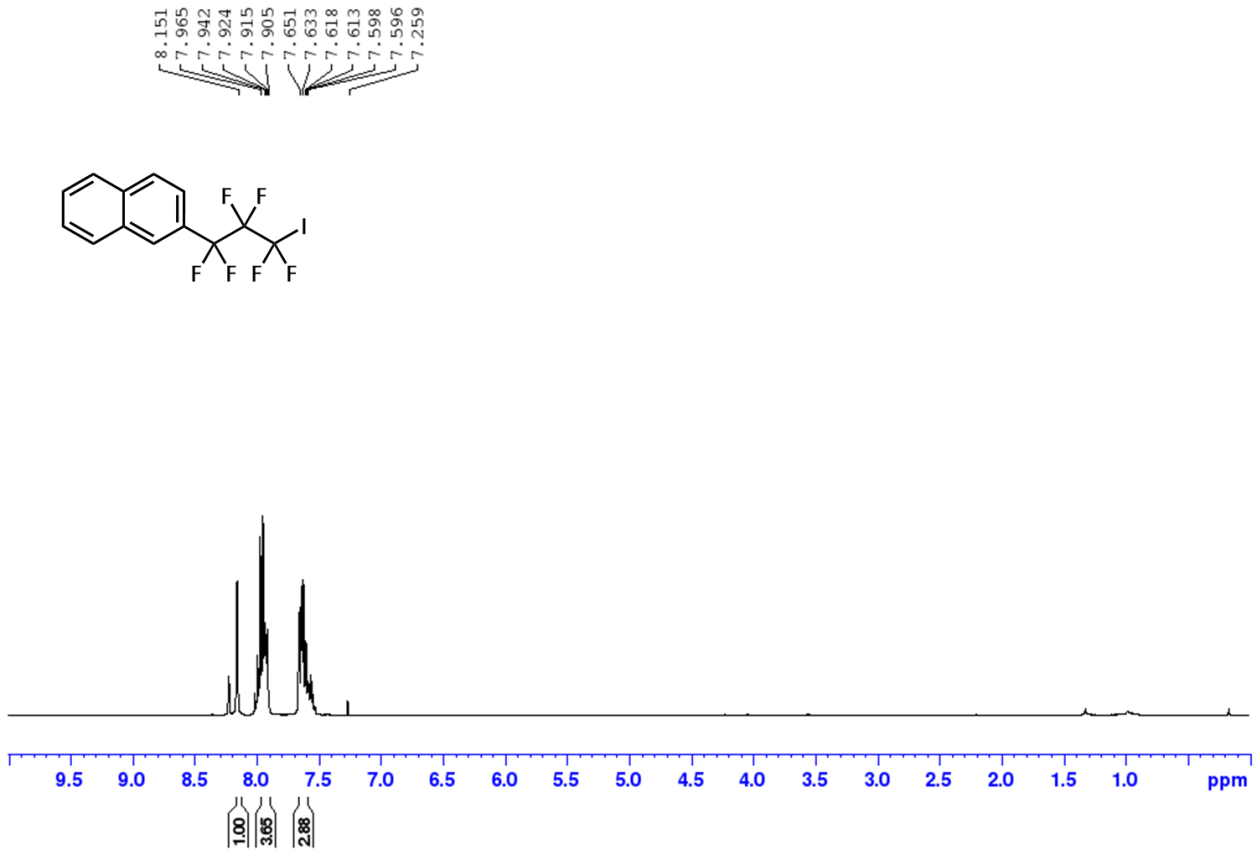


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)

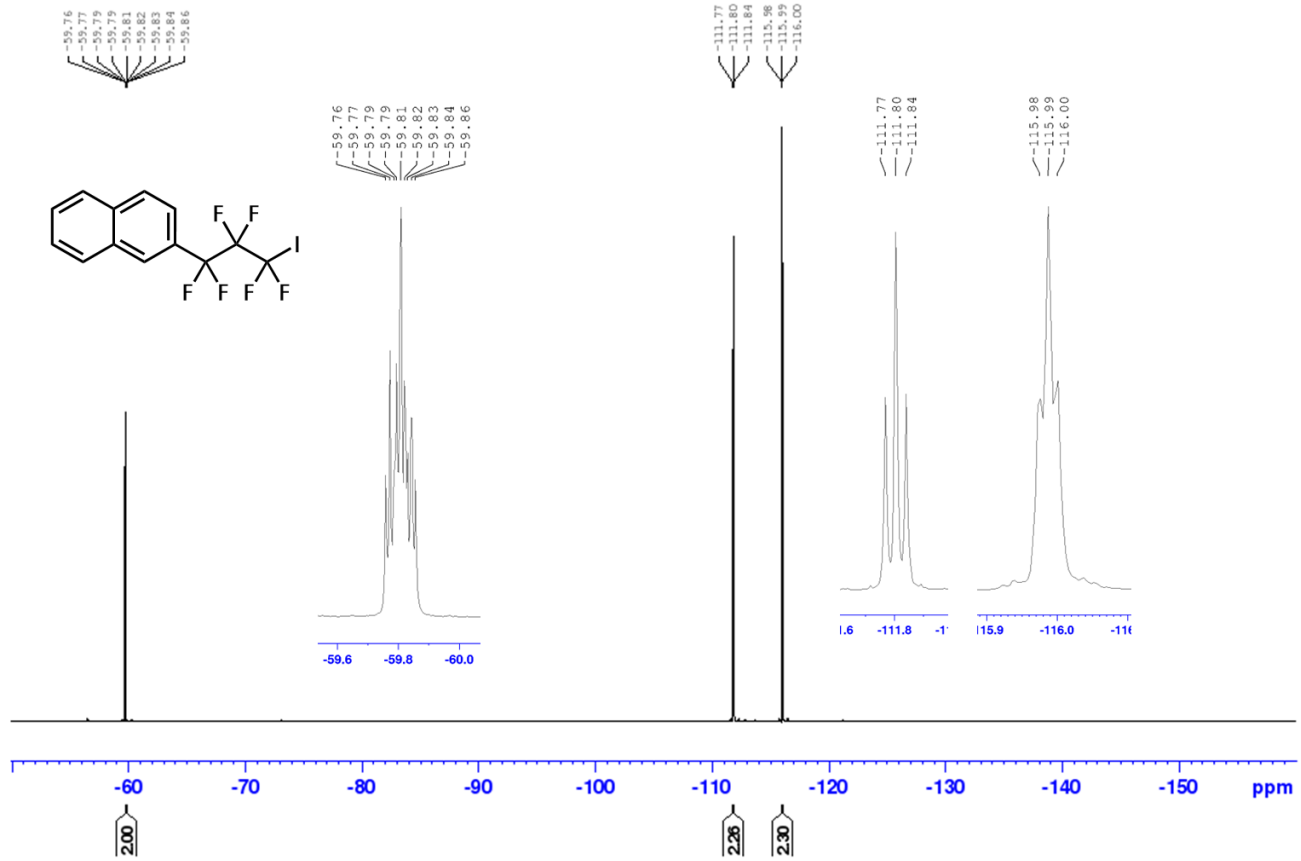


4c

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



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



^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$)