

Operationally Simple Hydrotrifluoromethylation of Alkene with Sodium Triflate Enabled by Ir-Photoredox Catalysis

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1. General Information

A. Materials:

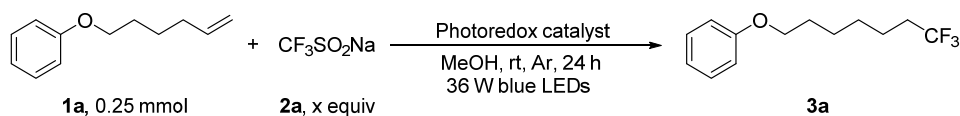
All reactions were conducted in oven-dried Schlenk tubes under argon atmosphere (purity $\geq 99.99\%$) unless otherwise mentioned. Reagents were commercially supplied and used as received. The photocatalyst Ir[dF(CF₃)ppy]₂(dtbpy)PF₆ was synthesized according to literature. (Reference: Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D.; Rohl, R.; Pascal, R. A.; Malliaras, G. G.; Bernhard, S. *Chem. Mater.* **2005**, *17*, 5712.) Organic solutions were concentrated under reduced pressure on Buchi rotary evaporator.

B. Analytical Methods:

Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. Infrared (IR) spectras were obtained using a Bio-Rad FTS-40 spectrometer. Data are represented as frequency of absorption (cm⁻¹). ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker Avance III HD400 spectrometer at ambient temperature. Data for ¹H-NMR are reported as follows: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant (Hz), and integration. Data for ¹³C-NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). High Resolution Mass Spectra (HRMS) were recorded using a JEOL JMS-700 spectrometer.

2. Optimization of Reaction Conditions

Table S1. Effects of the amount of reagents^{a,b}



Entry	Photoredox catalyst	2a	MeOH	Yield (%) ^b
1	1 mmol% Ir[dF(CF ₃)ppy] ₂ (dtbpy)PF ₆	3.0 equiv	2 mL	52%
2	2 mmol% Ir[dF(CF ₃)ppy] ₂ (dtbpy)PF ₆	3.0 equiv	2 mL	61%
3	3 mmol% Ir[dF(CF ₃)ppy] ₂ (dtbpy)PF ₆	3.0 equiv	2 mL	62%
4	2 mmol% Ir[dF(CF ₃)ppy] ₂ (dtbpy)PF ₆	2.0 equiv	2 mL	64%
5	2 mmol% Ir[dF(CF ₃)ppy] ₂ (dtbpy)PF ₆	1.5 equiv	2 mL	55%
6	2 mmol% Ir[dF(CF ₃)ppy] ₂ (dtbpy)PF ₆	2.0 equiv	3 mL	81%
8	2 mmol% Ir[dF(CF ₃)ppy] ₂ (dtbpy)PF ₆	2.0 equiv	4 mL	78%

^a Reaction conditions: **1a** (0.25 mmol), CF₃SO₂Na (x equiv), photoredox catalyst, and MeOH, reaction mixture was stirred under the irradiation of a 36 W blue LEDs at room temperature for 24 h under Ar atmosphere. ^b GC yields using benzophenone as an internal standard.

3. Measurement of Quantum Yield

Determination of the light intensity at 415 nm:

According to the procedure of Glorius,¹ the photon flux of the blue LEDs ($\lambda_{\text{max}} = 415 \text{ nm}$) was determined by standard ferrioxalate actinometry. 1,10-phenanthroline buffer solution was prepared by dissolving phenanthroline (25 mg) and sodium acetate (5.63 g) in H₂SO₄ (25 ml, 0.5 M). A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (0.737 g) in H₂SO₄ (10 ml, 0.05 M). Both solutions were stored in the dark. To determine the photon flux of the blue LEDs, the ferrioxalate solution (1.0 ml) was placed in a cuvette and irradiated for 90 seconds by the blue LEDs. After irradiation, the phenanthroline solution (0.175 ml) was added to the cuvette and the mixture was stirred in the dark for 1 hour to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared

according to the above procedures and the absorbance at 510 nm was measured. Conversion could be calculated using eq 1.

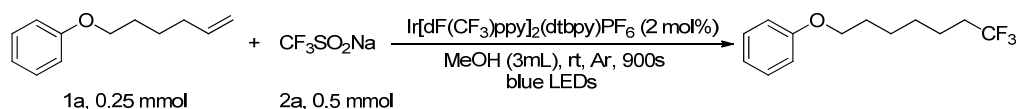
$$\text{mol Fe}^{2+} = \frac{V * \Delta A}{1 * \epsilon} \quad (1)$$

The V is the total volume (0.001175 L) of the solution after addition of phenanthroline, ΔA is the difference absorbance at 510 nm between the irradiated and non-irradiated solutions, ϵ is the molar absorptivity at 510 nm ($11,100 \text{ L mol}^{-1} \text{ cm}^{-1}$),² and 1 is the path length (1.000 cm); the mol Fe^{2+} was calculated (average of three experiments) to be 1.149×10^{-7} mol.

The photon flux can be calculated using eq 2. Φ_1 is the quantum yield for the ferrioxalate actinometer (1.1 for a 0.15 M solution at $\lambda = 420 \text{ nm}$),^{3,4} t_1 is the time (90.0 s), and f is the fraction of light absorbed at $\lambda = 420 \text{ nm}$.

$$\text{Photon flux} = \frac{\text{mol Fe}^{2+}}{\Phi_1 * t_1 * f} \quad (2)$$

Determination of quantum yield:



Olefins **1a** (0.25 mmol), $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (2 mol %, 5.6 mg), and $\text{CF}_3\text{SO}_2\text{Na}$ (0.5 mmol, 78 mg) were placed in a transparent Schlenk tube equipped with a stirring bar in a glove-box, then the solvent MeOH (3 mL) were added. The reaction mixture was stirred in dark for 3 minutes to ensure that the materials is completely dissolved and the mixture is homogeneous. After this time, 1 ml of the reaction mixture was taken into the same quartz cuvette used before. The cuvette was capped with a PTFE stopper and sealed with Parafilm M®. The sample was stirred and irradiated by the blue LEDs for 900 s. After irradiation, the yield of product was determined by GC analysis to be 1.3%. The quantum yield was determined using eq 3.

$$\Phi_2 = \frac{\text{mol prod}}{\text{flux} * t_2 * f} = \frac{\text{mol prod} * \Phi_1 * t_1}{\text{mol Fe}^{2+} * t_2} \quad (3)$$

The t_2 is the time (900 s). Finally, the quantum yield Φ_2 (1.3%) for the reaction was calculated to be 3.1.

References

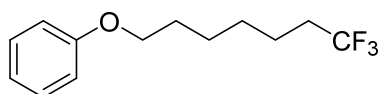
1. L. Candish, L. Pitzer, A. Gómez-Suárez, F. Glorius, *Chem. Eur. J.* **2016**, DOI: 10.1002/chem.201600421.
2. C. G. Hatchard, C. A. Parker, *Proc. Roy. Soc. (London)* **1956**, A23, 518.
3. W. J. Choi, S. Choi, K. Ohkubo, S. Fukuzumi, E. J. Cho, Y. You, *Chem. Sci.* **2015**, 6, 1454.
4. M. A. Cismesia, T. P. Yoon, *Chem. Sci.* **2015**, 6, 5426.

4. Experimental procedures and spectral data

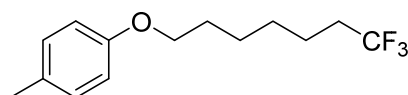
General Procedure:

Olefins (0.25 mmol), Ir[dF(CF₃)ppy]₂(dtbpy)PF₆ (2 mol %, 5.6 mg), and CF₃SO₂Na (0.5 mmol, 78 mg) were placed in a transparent Schlenk tube equipped with a stirring bar. The solvent MeOH (3 mL) were added under Ar atmosphere. The reaction mixture was stirred under the irradiation of a 36 W blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 24 h. After 24 h, the mixture was quenched with water and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel (ethyl acetate : petroleum ether).

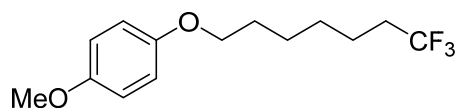
Spectral data



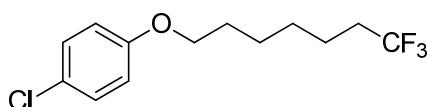
((7,7,7-trifluoroheptyl)oxy)benzene (3a) Following general procedure, the product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 77 % yield as a colorless liquid (50 mg). IR (ν) = 3063, 2948, 2873, 1736, 1587, 1249, 1144, 1050, 861, 834, 755, 692, 655 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.28 (t, *J* = 8.0 Hz, 2H), 6.99 – 6.83 (m, 3H), 3.95 (t, *J* = 6.4 Hz, 2H), 2.18 – 1.99 (m, 2H), 1.84 – 1.74 (m, 2H), 1.67 – 1.38 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 157.98, 128.41, 126.21 (d, *J* = 276.3 Hz), 119.54, 113.41, 66.50, 32.63 (q, *J* = 28.3 Hz), 28.01, 27.43, 24.73, 20.80 (q, *J* = 2.9 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -66.37. GC-MS: *m/z* 246 (M⁺). HRMS (ESI) calcd for C₁₃H₁₈F₃O [M+H]⁺: 247.1304, found 247.1301.



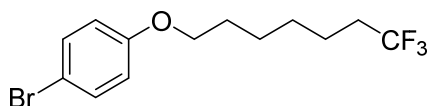
1-methyl-4-((7,7,7-trifluoroheptyl)oxy)benzene (3b) Following general procedure, the product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 82 % yield as a colorless liquid (53 mg). IR (ν) = 3442, 2943, 2868, 1536, 1444, 1175, 816 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.06 (d, *J* = 8.2 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 3.91 (t, *J* = 6.4 Hz, 2H), 2.27 (s, 3H), 2.15 – 1.98 (m, 2H), 1.81 – 1.72 (m, 2H), 1.64 – 1.35 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 156.96, 129.91, 129.79, 127.30 (d, *J* = 276.2 Hz), 114.35, 67.74, 33.69 (q, *J* = 28.3 Hz), 29.11, 28.50, 25.78, 21.87 (q, *J* = 2.9 Hz), 20.46. ¹⁹F NMR (376 MHz, CDCl₃) δ -66.39. GC-MS: *m/z* 260 (M⁺). HRMS (ESI) calcd for C₁₄H₂₀F₃O [M+H]⁺: 261.1461, found 261.1460.



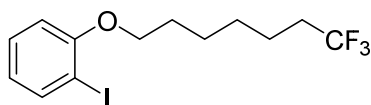
1-methoxy-4-((7,7,7-trifluoroheptyl)oxy)benzene (3c) Following general procedure, the product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 82 % yield as a colorless liquid (56 mg). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* 2012, **51**, 12551). IR (ν) = 3045, 2943, 2863, 2061, 1507, 1468, 1443, 1232, 1141, 1042, 825, 742, 655 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 6.85 – 6.79 (m, 4H), 3.90 (t, $J = 6.4$ Hz, 2H), 3.76 (s, 3H), 2.16 – 1.98 (m, 2H), 1.81 – 1.70 (m, 2H), 1.65 – 1.36 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 153.78, 153.23, 127.31 (d, $J = 276.2$ Hz), 115.42, 114.65, 68.34, 55.71, 33.68 (q, $J = 28.3$ Hz), 29.17, 28.51, 25.78, 21.87 (q, $J = 2.8$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -66.40.



1-chloro-4-((7,7,7-trifluoroheptyl)oxy)benzene (3d) Following general procedure, the product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 71 % yield as a colorless liquid (50 mg). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* 2012, **51**, 12551). IR (ν) = 3468, 2942, 2863, 2698, 1713, 1256, 1132, 1039, 721 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.22 (d, $J = 9.0$ Hz, 2H), 6.81 (d, $J = 9.0$ Hz, 2H), 3.91 (t, $J = 6.4$ Hz, 2H), 2.16 – 2.00 (m, 2H), 1.82 – 1.72 (m, 2H), 1.65 – 1.39 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.65, 129.30, 127.24 (d, $J = 276.3$ Hz), 125.40, 115.72, 68.00, 33.65 (q, $J = 28.4$ Hz), 28.95, 28.44, 25.71, 21.83 (q, $J = 2.9$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -66.38.

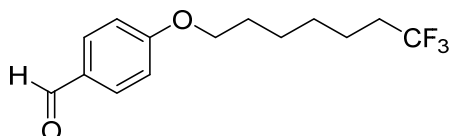


1-bromo-4-((7,7,7-trifluoroheptyl)oxy)benzene (3e) Following general procedure, the product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 74 % yield as a colorless liquid (60 mg). IR (ν) = 2949, 2871, 1730, 1247, 1049, 825, 666 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.36 (d, $J = 9.0$ Hz, 2H), 6.76 (d, $J = 9.0$ Hz, 2H), 3.91 (t, $J = 6.4$ Hz, 2H), 2.17 – 1.99 (m, 2H), 1.84 – 1.72 (m, 2H), 1.67 – 1.37 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.14, 132.23, 127.22 (d, $J = 276.3$ Hz), 116.25, 112.67, 67.93, 33.65 (q, $J = 28.4$ Hz), 28.92, 28.44, 25.70, 21.82 (q, $J = 2.9$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -66.38. GC-MS: m/z 324 (M⁺). HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{17}\text{BrF}_3\text{O}$ [M+H]⁺: 325.0409, found 325.0401.

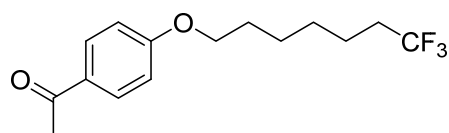


1-iodo-2-((7,7,7-trifluoroheptyl)oxy)benzene (3f) Following general procedure, the product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 80 % yield as a colorless liquid (74 mg). IR (ν) = 3062, 2942, 2872, 1582,

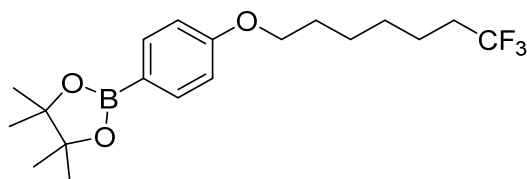
1466, 1252, 1140, 1049, 749, 651 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.76 (dd, $J = 7.8, 1.6$ Hz, 1H), 7.27 (ddd, $J = 8.3, 7.4, 1.6$ Hz, 1H), 6.79 (dd, $J = 8.2, 1.2$ Hz, 1H), 6.69 (td, $J = 7.7, 1.3$ Hz, 1H), 4.00 (t, $J = 6.2$ Hz, 2H), 2.17 – 2.01 (m, 2H), 1.89 – 1.79 (m, 2H), 1.66 – 1.39 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.49, 139.42, 129.43, 127.26 (d, $J = 276.3$ Hz), 122.40, 112.01, 86.66, 68.82, 33.65 (q, $J = 28.3$ Hz), 28.82, 28.36, 25.80, 21.82 (q, $J = 2.9$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -66.34. GC-MS: m/z 372 (M⁺). HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{17}\text{F}_3\text{IO}$ [M+H]⁺: 373.0271, found 325.0269.



4-((7,7,7-trifluoroheptyl)oxy)benzaldehyde (3g) Following general procedure, the product was purified by flash column chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 20), obtained in 78 % yield as a colorless liquid (53 mg). IR (ν) = 3542, 2954, 2738, 1729, 1437, 1160, 829 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 9.88 (s, 1H), 7.83 (d, $J = 8.7$ Hz, 2H), 6.99 (d, $J = 8.7$ Hz, 2H), 4.05 (t, $J = 6.4$ Hz, 2H), 2.17 – 2.01 (m, 2H), 1.89 – 1.76 (m, 2H), 1.66 – 1.41 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 190.85, 164.13, 132.01, 129.83, 127.21 (d, $J = 276.3$ Hz), 114.72, 68.11, 33.63 (q, $J = 28.4$ Hz), 28.81, 28.40, 25.67, 21.81 (q, $J = 2.9$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -66.37. GC-MS: m/z 274 (M⁺). HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{18}\text{F}_3\text{O}_2$ [M+H]⁺: 275.1253, found 275.1252.

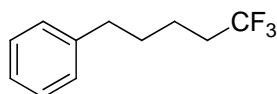


1-(4-((7,7,7-trifluoroheptyl)oxy)phenyl)ethanone (3h) Following general procedure, the product was purified by flash column chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 20), obtained in 88 % yield as a white solid (63 mg). IR (ν) = 3444, 2951, 2872, 1734, 1679, 1436, 1254, 1168, 832 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.9$ Hz, 2H), 6.91 (d, $J = 8.9$ Hz, 2H), 4.02 (t, $J = 6.4$ Hz, 2H), 2.55 (s, 3H), 2.17 – 2.00 (m, 2H), 1.87 – 1.75 (m, 2H), 1.66 – 1.41 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.82, 162.99, 130.60, 130.19, 127.21 (d, $J = 276.3$ Hz), 114.10, 67.94, 33.63 (q, $J = 28.3$ Hz), 28.84, 28.41, 26.33, 25.68, 21.81 (q, $J = 2.9$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -66.38. GC-MS: m/z 288 (M⁺). HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{20}\text{F}_3\text{O}_2$ [M+H]⁺: 289.1410, found 289.1413.

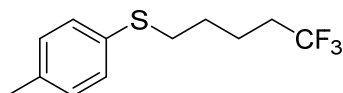


4,4,5,5-tetramethyl-2-(4-((7,7,7-trifluoroheptyl)oxy)phenyl)-1,3,2-dioxaborolane

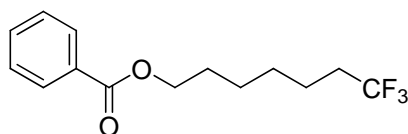
(3i) Following general procedure, the product was purified by flash column chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 50), obtained in 52 % yield as a colorless liquid (48 mg). IR (ν) = 3037, 2978, 1605, 1362, 1249, 1143, 1091, 860, 834, 655 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 3.98 (t, J = 6.4 Hz, 2H), 2.15 – 1.99 (m, 2H), 1.84 – 1.74 (m, 2H), 1.65 – 1.53 (m, 2H), 1.54 – 1.39 (m, 4H), 1.33 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.63, 136.52, 127.24 (q, J = 276.3 Hz), 113.83, 83.54, 67.45, 33.66 (q, J = 28.3 Hz), 28.96, 28.45, 25.72, 24.86, 21.83 (q, J = 2.8 Hz). (one carbon signal is overlapped) ^{19}F NMR (376 MHz, CDCl_3) δ -66.38. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{29}\text{BF}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 373.2156, found 373.2157.



(5,5,5-trifluoropentyl)benzene (3j) Following general procedure, the product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 85 % yield as a colorless liquid (43 mg). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* 2013, **52**, 2198). IR (ν) = 3443, 3063, 2955, 1735, 1453, 1257, 1054, 880, 699 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.30 (t, J = 7.4 Hz, 2H), 7.20 (dd, J = 13.9, 7.2 Hz, 3H), 2.65 (t, J = 7.5 Hz, 2H), 2.19 – 2.02 (m, 2H), 1.78 – 1.54 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.68, 128.39, 128.33, 127.14 (d, J = 273.2 Hz), 125.79, 35.48, 33.59 (q, J = 28.4 Hz), 30.46, 21.51 (q, J = 2.9 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -66.32.

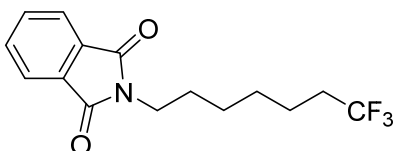


p-tolyl(5,5,5-trifluoropentyl)sulfane (3k) Following general procedure, the product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 65 % yield as a colorless liquid (40 mg). IR (ν) = 2948, 2924, 2874, 1493, 1391, 1133, 824 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.25 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 2.88 (t, J = 6.8 Hz, 2H), 2.32 (s, 3H), 2.16 – 1.98 (m, 2H), 1.74 – 1.60 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 136.41, 132.23, 130.34, 129.75, 127.04 (d, J = 276.3 Hz), 34.04, 33.33 (q, J = 28.6 Hz), 28.22, 21.01 (q, J = 3.2 Hz). (one carbon signal is overlapped) ^{19}F NMR (376 MHz, CDCl_3) δ -66.35. GC-MS: m/z 248 (M+). HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{16}\text{F}_3\text{S}$ $[\text{M}+\text{H}]^+$: 249.0919, found 249.0915.

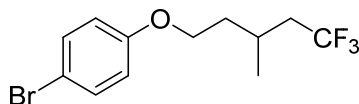


7,7,7-trifluoroheptyl benzoate (3n) Following general procedure, the product was purified by flash column chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 50), obtained in 63 % yield as a colorless liquid (43 mg). The compound data

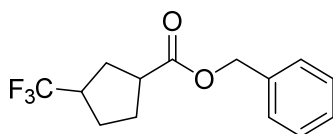
was in agreement with the literature (Ref. *J. Am. Chem. Soc.* 2013, **135**, 2505). IR (ν) = 3063, 2945, 2862, 1453, 1274, 1142, 973, 713 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 7.2$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.8$ Hz, 2H), 4.32 (t, $J = 6.5$ Hz, 2H), 2.16 – 1.97 (m, 2H), 1.84 – 1.71 (m, 2H), 1.66 – 1.37 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.64, 132.89, 130.40, 129.53, 128.36, 127.21 (d, $J = 276.2$ Hz), 64.80, 33.64 (q, $J = 28.4$ Hz), 28.49, 28.37, 25.73, 21.81 (q, $J = 2.9$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -66.40.



2-(7,7,7-trifluoroheptyl)isoindoline-1,3-dione (3o) Following general procedure, the product was purified by flash column chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 10), obtained in 75 % yield as a white solid (56 mg). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* 2013, **52**, 2198). IR (ν) = 3066, 3007, 2950, 1252, 1088, 1038 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.88 – 7.82 (m, 2H), 7.72 (dd, $J = 5.5, 3.0$ Hz, 2H), 3.69 (t, $J = 7.2$ Hz, 2H), 2.18 – 1.95 (m, 2H), 1.75 – 1.64 (m, 2H), 1.62 – 1.50 (m, 2H), 1.48 – 1.31 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.41, 133.88, 132.07, 127.14 (d, $J = 276.0$ Hz), 123.16, 37.74, 33.58 (q, $J = 28.3$ Hz), 28.31, 28.21, 26.39, 21.72 (q, $J = 2.9$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -66.42.



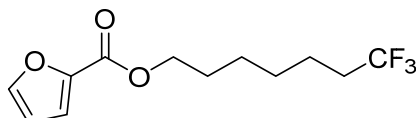
1-bromo-4-((5,5,5-trifluoro-3-methylpentyl)oxy)benzene (3p) Following general procedure, the product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 68 % yield as a colorless liquid (53 mg). IR (ν) = 3452, 3048, 2941, 1732, 1612, 1497, 1281, 811, 409 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.33 (m, 2H), 6.79 – 6.73 (m, 2H), 4.05 – 3.85 (m, 2H), 2.28 – 2.08 (m, 2H), 2.07 – 1.85 (m, 2H), 1.74 – 1.64 (m, 1H), 1.08 (d, $J = 6.3$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.88, 132.24, 127.01 (d, $J = 278.8$ Hz), 116.22, 112.89, 65.57, 40.22 (q, $J = 27.3$ Hz), 35.73, 25.01 (q, $J = 3.0$ Hz), 19.56. ^{19}F NMR (376 MHz, CDCl_3) δ -63.21. GC-MS: m/z 310 (M⁺). HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{15}\text{BrF}_3\text{O}$ [M+H]⁺: 311.0253, found 311.0252.



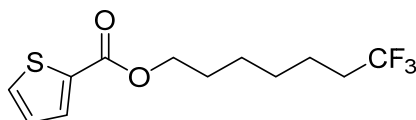
benzyl 3-(trifluoromethyl)cyclopentanecarboxylate (3q) Following general procedure, the product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 66 % yield as a colorless liquid (45 mg). The ratio of

trans/cis (5:1) was determined by GC-MS.

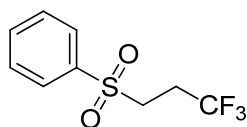
For trans structure: IR (ν) = 2957, 1780, 1454, 1384, 1271, 1160, 750, 697 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.32 (m, 5H), 5.12 (s, 2H), 3.01 – 2.91 (m, 1H), 2.86 – 2.72 (m, 1H), 2.70 – 2.64 (m, 1H), 2.22 – 2.12 (m, 1H), 2.07 – 1.96 (m, 2H), 1.93 – 1.82 (m, 1H), 1.80 – 1.68 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 174.93, 135.83, 128.94, 128.59, 128.52, 128.28, 128.12, 128.08, 128.05, 66.45, 42.23 (q, J = 27.3 Hz), 41.51, 29.83, 29.35 (q, J = 2.0 Hz), 25.86 (q, J = 3.0 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -71.53. GC-MS: m/z 272 (M⁺). HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{16}\text{F}_3\text{O}_2$ [M+H]⁺: 273.1097, found 273.1100.



7,7,7-trifluoroheptyl furan-2-carboxylate (3r) Following general procedure, the product was purified by flash column chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 50), obtained in 62 % yield as a colorless liquid (41 mg). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Chem.*, 2013, **52**, 2198). IR (ν) = 2944, 1713, 1504, 1419, 1257, 1077, 722, 655, 565 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.58 (d, J = 0.7 Hz, 1H), 7.18 (d, J = 3.4 Hz, 1H), 6.52 (dd, J = 3.4, 1.7 Hz, 1H), 4.31 (t, J = 6.6 Hz, 2H), 2.16 – 1.99 (m, 2H), 1.82 – 1.70 (m, 2H), 1.65 – 1.52 (m, 2H), 1.51 – 1.38 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.79, 146.24, 144.77, 127.19 (q, J = 276.2 Hz), 117.78, 111.80, 64.73, 33.60 (q, J = 28.4 Hz), 28.42, 28.29, 25.56, 21.76 (q, J = 2.4 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -66.44.

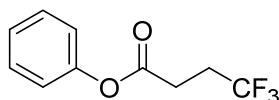


7,7,7-trifluoroheptyl thiophene-2-carboxylate (3s) Following general procedure, the product was purified by flash column chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 50), obtained in 79 % yield as a colorless liquid (55 mg). IR (ν) = 2969, 1489, 1245, 1139, 1052, 822, 646, 506 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.80 (dd, J = 3.7, 1.2 Hz, 1H), 7.56 (dd, J = 5.0, 1.2 Hz, 1H), 7.11 (dd, J = 4.9, 3.8 Hz, 1H), 4.30 (t, J = 6.6 Hz, 2H), 2.15 – 1.99 (m, 2H), 1.81 – 1.71 (m, 2H), 1.65 – 1.53 (m, 2H), 1.51 – 1.37 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.32, 133.95, 133.34, 132.29, 132.29, 127.21 (q, J = 276.3 Hz), 64.97, 33.65 (q, J = 28.3 Hz), 28.46, 28.34, 25.66, 21.81 (q, J = 2.4 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -66.38. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{16}\text{F}_3\text{O}_2\text{S}$ [M+H]⁺: 281.0818, found 281.0816.

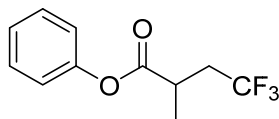


((3,3,3-trifluoropropyl)sulfonyl)benzene (3t) Following general procedure, the product was purified by flash column chromatography on silica gel (ethyl acetate :

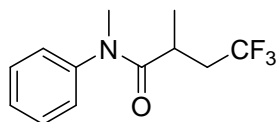
petroleum ether = 1 : 5), obtained in 55 % yield as a white solid (33 mg). The compound data was in agreement with the literature (Ref. *Archiv. Biochem. Biophys.* 1998, **263**, 178). IR (ν) = 3443, 2947, 2872, 1730, 1591, 1390, 1248, 823, 655 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 7.2$ Hz, 2H), 7.65 (t, $J = 7.5$ Hz, 1H), 7.55 (t, $J = 7.7$ Hz, 2H), 3.28 – 3.17 (m, 2H), 2.58 – 2.41 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.07, 134.47, 129.70, 128.11, 125.41 (d, $J = 276.5$ Hz), 49.35 (q, $J = 2.9$ Hz), 28.04 (q, $J = 31.5$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -65.94.



phenyl 4,4,4-trifluorobutanoate (3u) Following general procedure, the product was purified by flash column chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 20), obtained in 58 % yield as a colorless liquid (32 mg). IR (ν) = 3066, 2969, 1739, 1593, 1493, 943, 718 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.39 (t, $J = 7.9$ Hz, 2H), 7.26 (d, $J = 6.4$ Hz, 1H), 7.08 (d, $J = 8.0$ Hz, 2H), 2.96 – 2.79 (m, 2H), 2.68 – 2.47 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.60, 150.38, 129.56, 127.80, 126.43 (d, $J = 276.0$ Hz), 121.35, 29.37 (q, $J = 30.2$ Hz), 27.35 (q, $J = 3.3$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -66.89. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{10}\text{F}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 219.0627, found 219.0626.

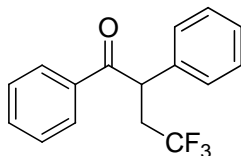


phenyl 4,4,4-trifluoro-2-methylbutanoate (3v) Following general procedure, the product was purified by flash column chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 20), obtained in 86 % yield as a colorless liquid (50 mg). IR (ν) = 3444, 2954, 1730, 1436, 1256, 1197, 1163, 828, 749, 690 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.38 (t, $J = 7.9$ Hz, 2H), 7.24 (t, $J = 7.9$ Hz, 1H), 7.07 (d, $J = 7.6$ Hz, 2H), 3.14 – 2.97 (m, 1H), 2.87 – 2.68 (m, 1H), 2.36 – 2.19 (m, 1H), 1.44 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 173.05, 150.52, 129.53, 126.30 (d, $J = 276.8$ Hz), 126.11, 121.33, 37.09 (q, $J = 28.9$ Hz), 34.28 (q, $J = 2.7$ Hz), 17.62. ^{19}F NMR (376 MHz, CDCl_3) δ -64.80. GC-MS: m/z 232 (M+). HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{12}\text{F}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 233.0784, found 233.0781.

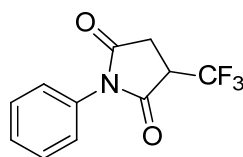


4,4,4-trifluoro-N,2-dimethyl-N-phenylbutanamide (3w) Following general procedure, The product was purified by flash column chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 20), obtained in 52 % yield as a colorless liquid (32 mg). IR (ν) = 3443, 2971, 2901, 2101, 1695, 1335, 1053, 832, 774 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.48 – 7.42 (m, 2H), 7.41 – 7.35 (m, 1H), 7.23 – 7.16 (m, 2H), 3.27 (s, 3H), 2.85 – 2.61 (m, 2H), 2.05 – 1.85 (m, 1H), 1.10 (d, $J = 6.5$ Hz, 3H). ^{13}C

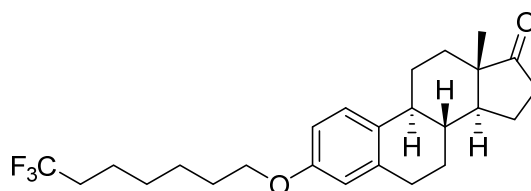
NMR (101 MHz, CDCl₃) δ 174.26, 143.50, 129.96, 128.21, 127.27, 126.45 (d, J = 277.0 Hz), 37.62, 37.57 (q, J = 28.1 Hz), 30.91 (q, J = 2.5 Hz), 18.75. ¹⁹F NMR (376 MHz, CDCl₃) δ -65.20. GC-MS: m/z 245 (M⁺). HRMS (ESI) calcd for C₁₂H₁₅F₃NO [M+H]⁺: 246.1100, found 246.1103.



4,4,4-trifluoro-1,2-diphenylbutan-1-one (3x) Following general procedure, the product was purified by flash column chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 20), obtained in 62 % yield as a white solid (43 mg). The compound data was in agreement with the literature (Ref. *Chem. Commun.* 2015, **51**, 7222). IR (ν) = 3063, 3029, 2954, 1732, 1434, 1382, 1260, 1159, 759, 699 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 7.2 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.31 (d, J = 4.3 Hz, 4H), 7.25 – 7.19 (m, 1H), 4.91 (dd, J = 7.7, 5.5 Hz, 1H), 3.42 – 3.19 (m, 1H), 3.41 – 3.22 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 196.75, 137.41, 135.67, 133.39, 129.36, 128.85, 128.69, 128.06, 127.86, 126.41 (d, J = 277.1 Hz), 47.18 (q, J = 2.4 Hz), 37.37 (q, J = 28.2 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -64.60.

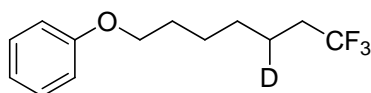


1-phenyl-3-(trifluoromethyl)pyrrolidine-2,5-dione (3y) Following general procedure, the product was purified by flash column chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 20), obtained in 21 % yield as a colorless liquid (13 mg). The compound data was in agreement with the literature (Ref. *J. Org. Chem.* 2014, **79**, 1386). IR (ν) = 2938, 1715, 1390, 1196, 1112, 682 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.50 (t, J = 7.4 Hz, 2H), 7.44 (t, J = 7.4 Hz, 1H), 7.28 (d, J = 7.4 Hz, 2H), 3.80 – 3.67 (m, 1H), 3.17 (dd, J = 18.7, 9.8 Hz, 1H), 3.04 (dd, J = 18.7, 5.1 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 172.42, 168.58, 131.03, 129.38, 129.26, 126.33, 123.76 (q, J = 277.4 Hz), 44.53 (q, J = 30.0 Hz), 29.61 (q, J = 2.4 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -68.76.



(8R,9S,13S,14S)-13-methyl-3-((7,7,7-trifluoroheptyl)oxy)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (3za) Following general procedure, the product was purified by flash column chromatography on silica gel

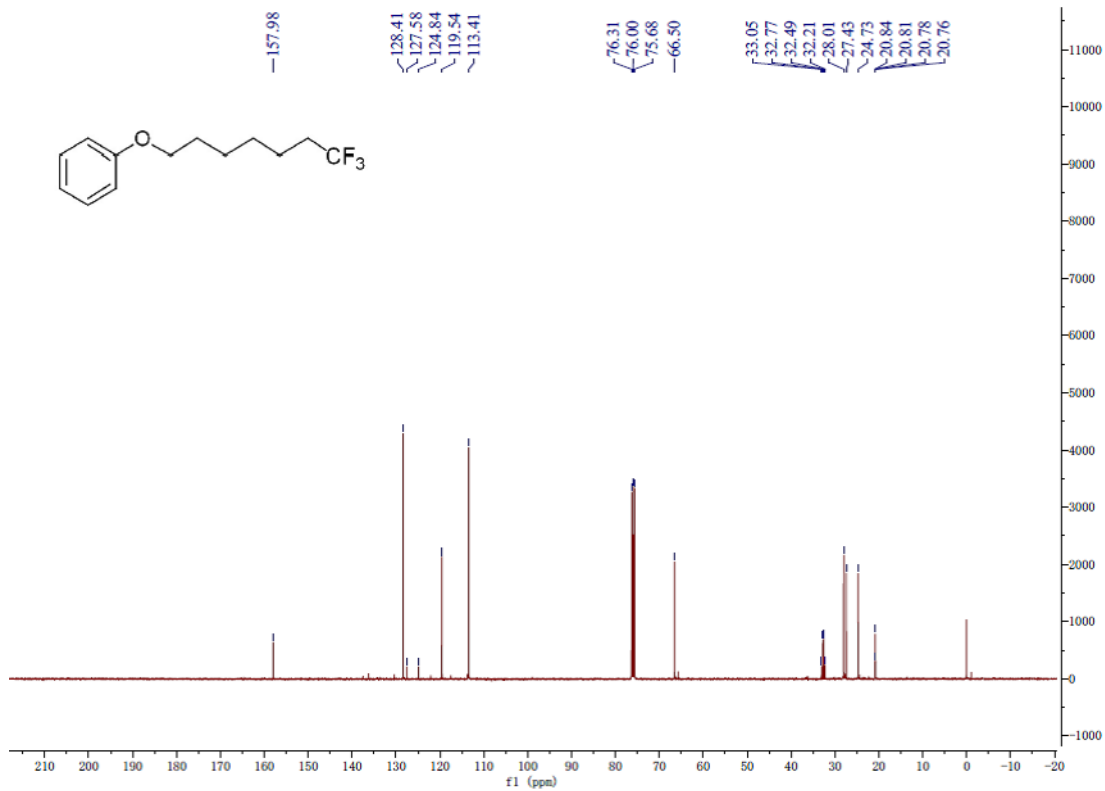
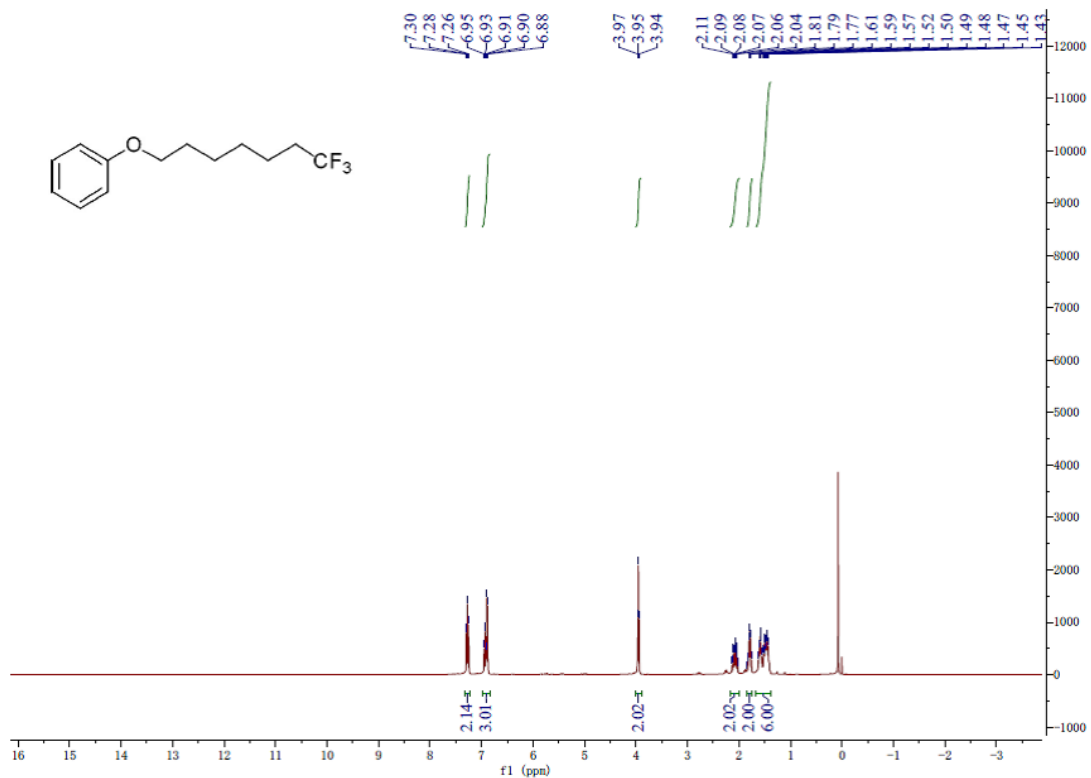
(ethyl acetate : petroleum ether = 1 : 50), obtained in 81 % yield as a white solid (86 mg). IR (ν) = 2945, 2866, 1730, 1582, 1474, 1396, 1297, 1255, 1181, 1121 cm^{-1} , 764 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.19 (d, $J = 8.6$ Hz, 1H), 6.70 (dd, $J = 8.6, 2.6$ Hz, 1H), 6.64 (d, $J = 2.5$ Hz, 1H), 3.93 (t, $J = 6.4$ Hz, 2H), 2.95 – 2.83 (m, 2H), 2.54 – 2.46 (m, 1H), 2.43 – 2.34 (m, 1H), 2.30 – 1.90 (m, 8H), 1.84 – 1.71 (m, 2H), 1.68 – 1.36 (m, 11H), 0.90 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 220.86, 157.08, 137.74, 131.98, 127.26 (d, $J = 276.3$ Hz), 126.34, 114.56, 112.10, 67.61, 50.45, 48.02, 44.01, 38.39, 35.90, 33.67 (q, $J = 28.3$ Hz), 31.60, 29.68, 29.07, 28.45, 26.58, 25.94, 25.76, 21.84 (q, $J = 2.8$ Hz), 21.60, 13.87. ^{19}F NMR (376 MHz, CDCl_3) δ -66.35. GC-MS: m/z 422 (M^+). HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{34}\text{F}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 423.2505, found 423.2504.

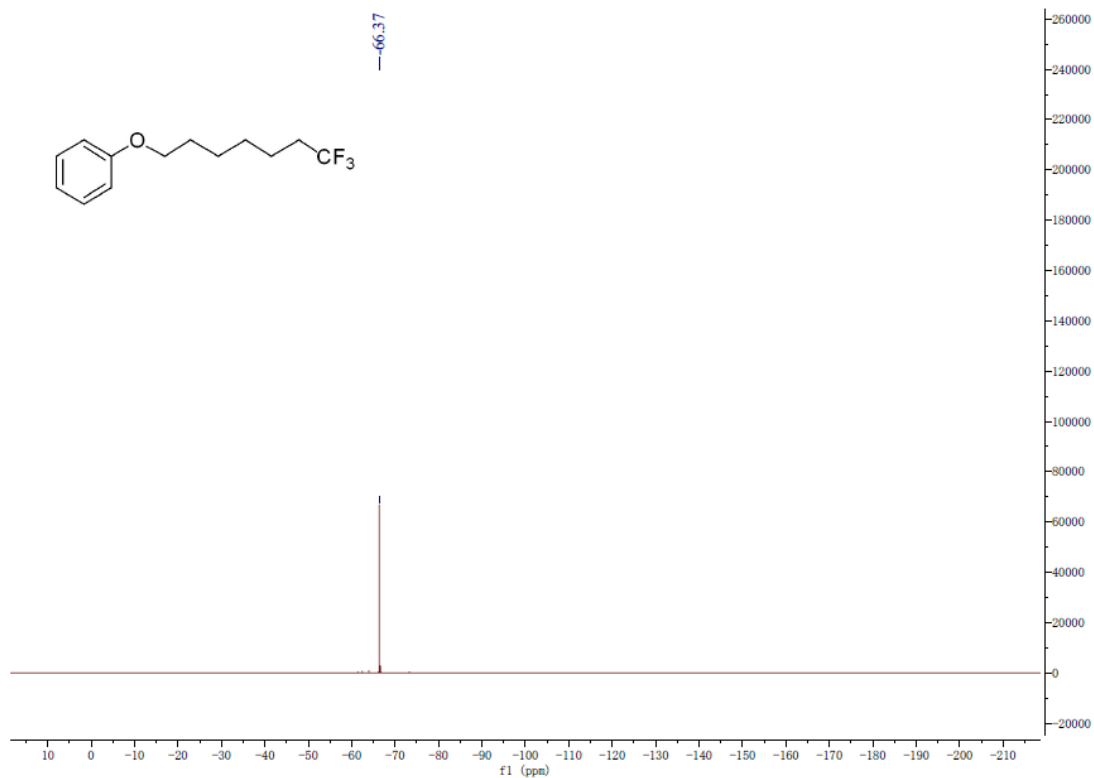


((7,7,7-trifluoroheptyl)oxy)benzene (3a-D) Following general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 52% yield as a white solid (32 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.27 (t, $J = 7.7$ Hz, 2H), 6.98 – 6.83 (m, 3H), 3.95 (t, $J = 6.3$ Hz, 2H), 2.18 – 1.97 (m, 2H), 1.92 – 1.69 (m, 2H), 1.68 – 1.36 (m, 5H).

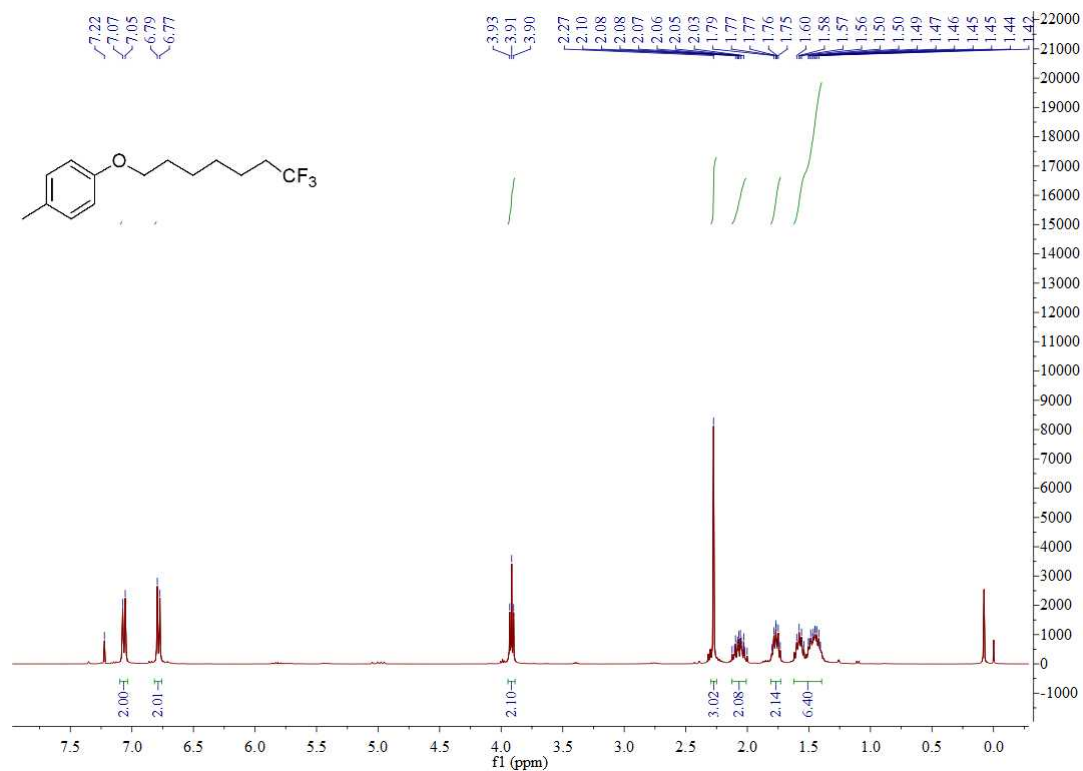
4. ^1H , ^{13}C and ^{19}F NMR spectra

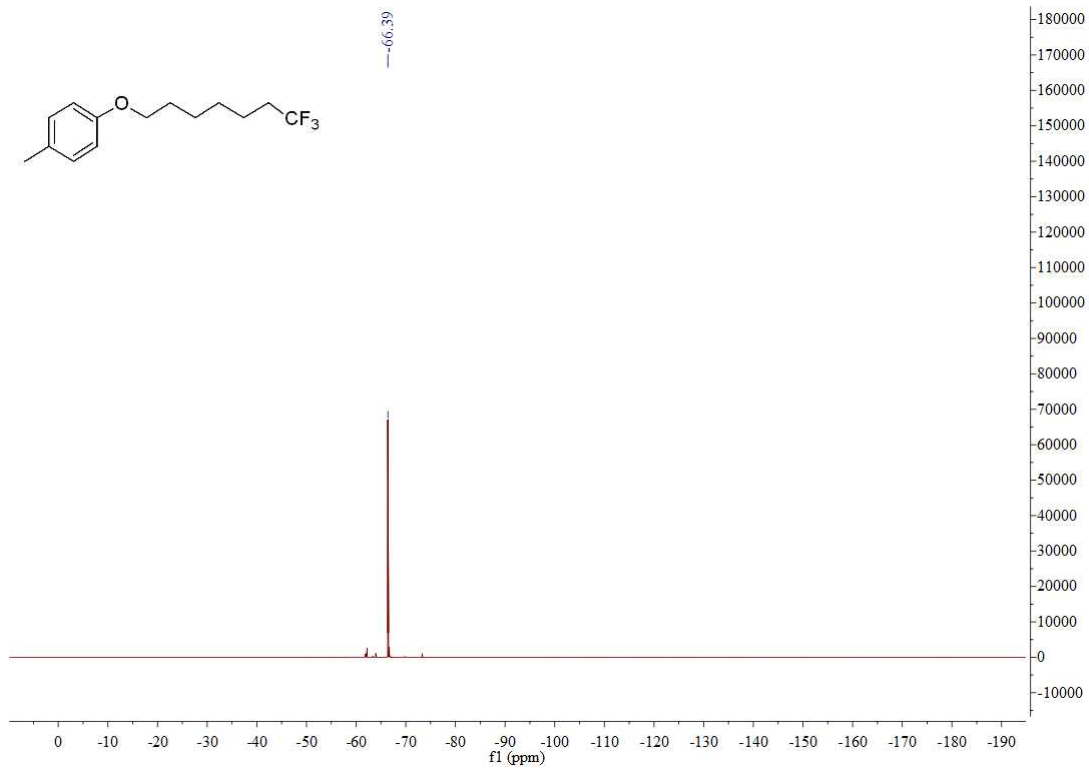
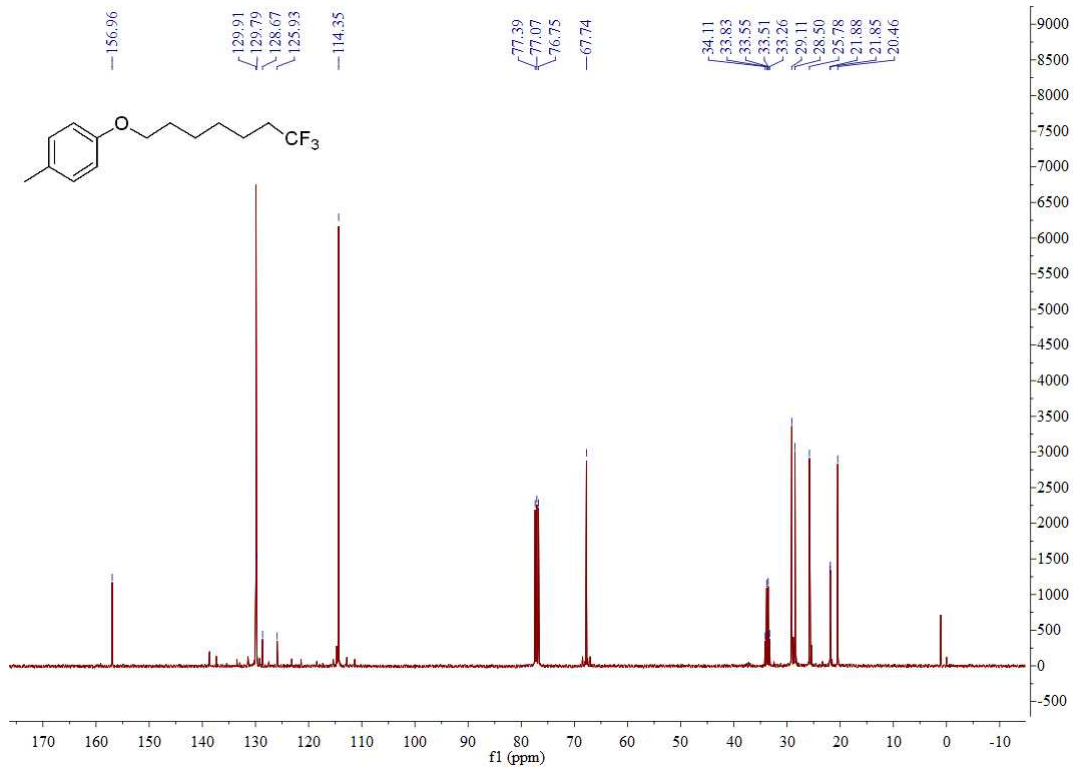
((7,7,7-trifluoroheptyl)oxy)benzene (**3a**)



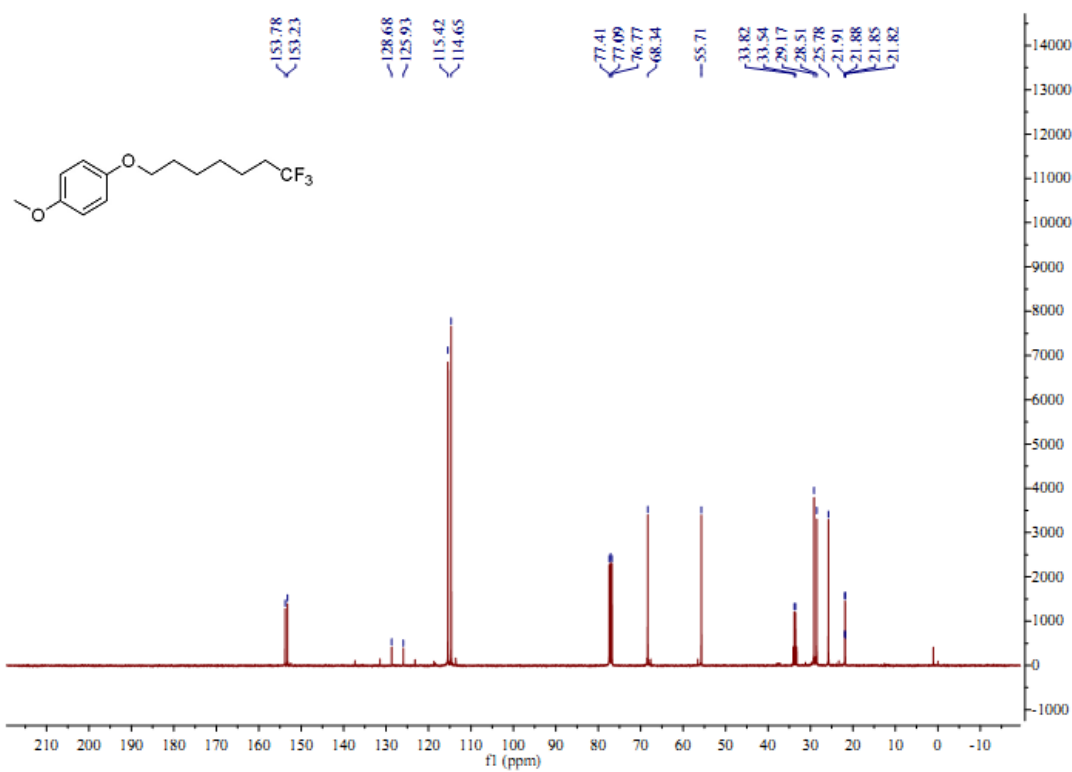
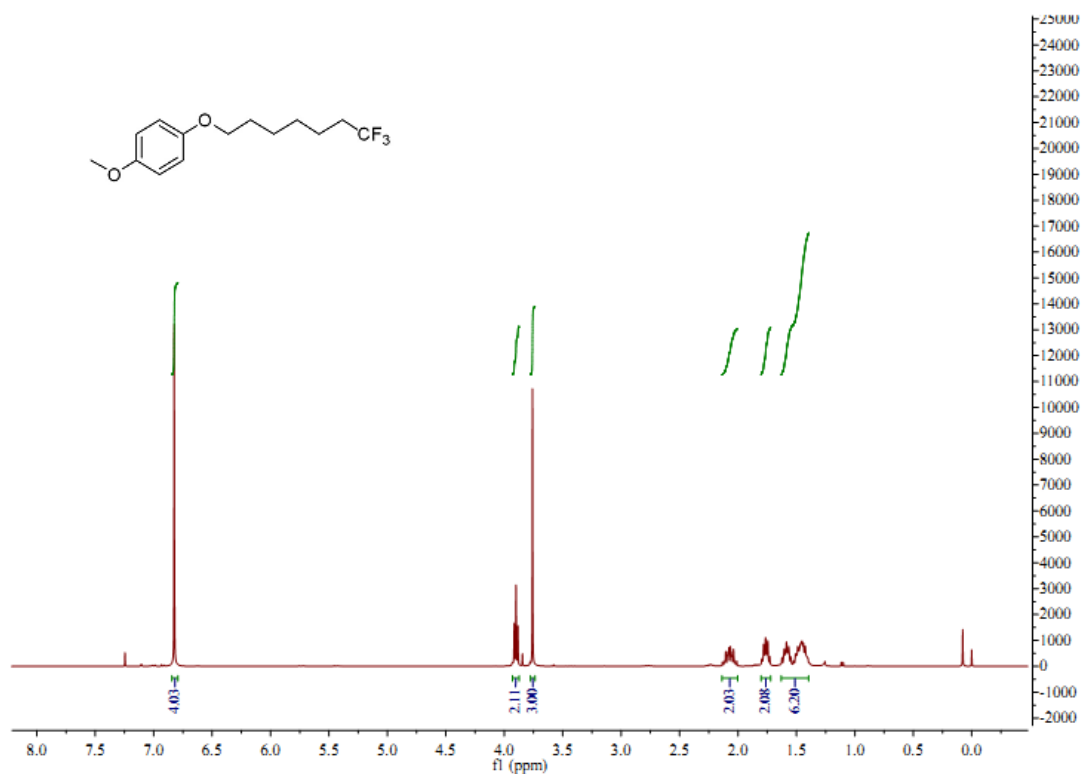


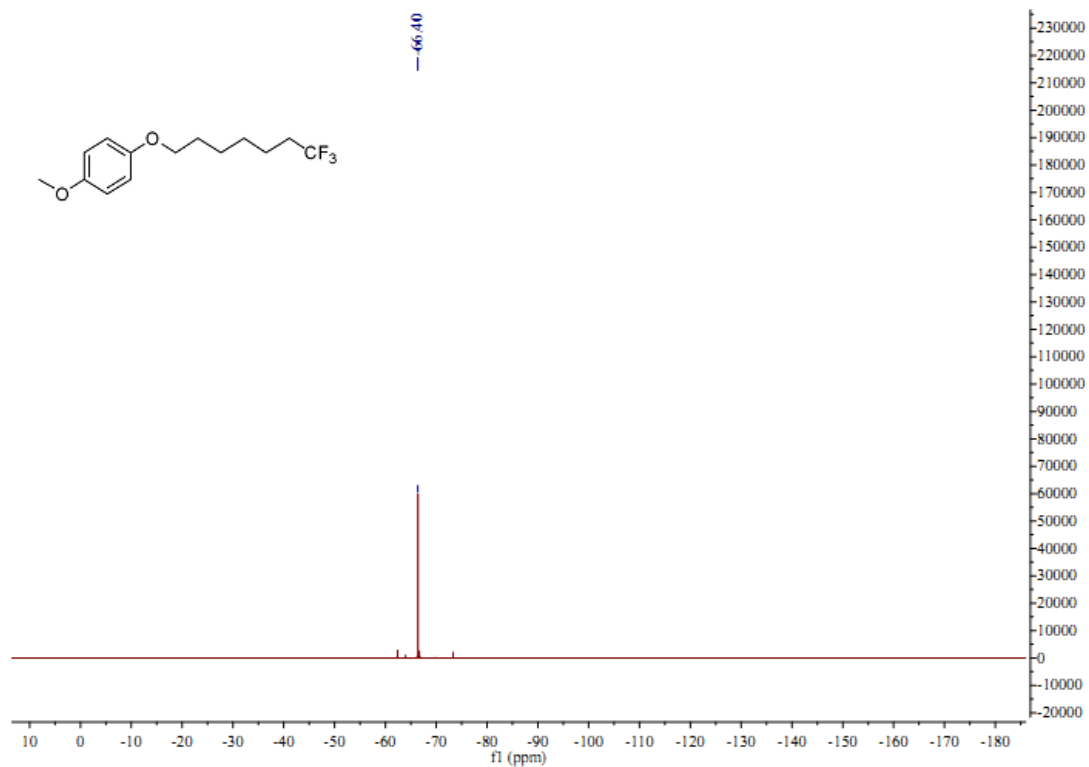
1-methyl-4-((7,7,7-trifluoroheptyl)oxy)benzene (3b)



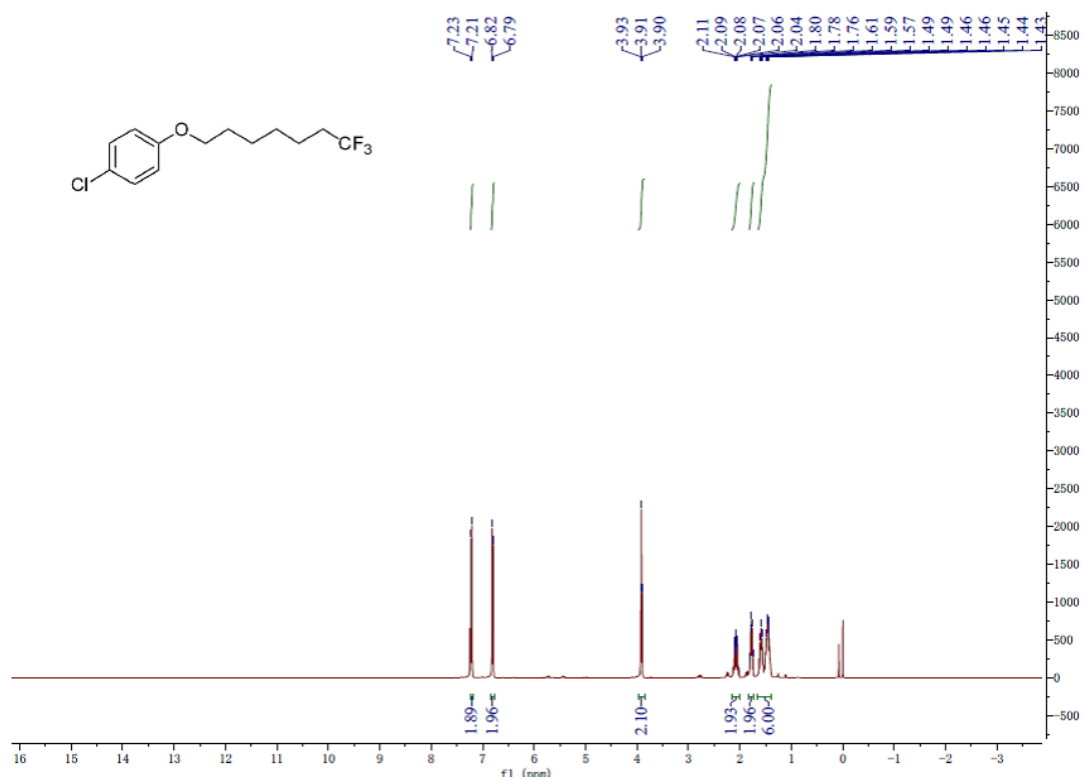


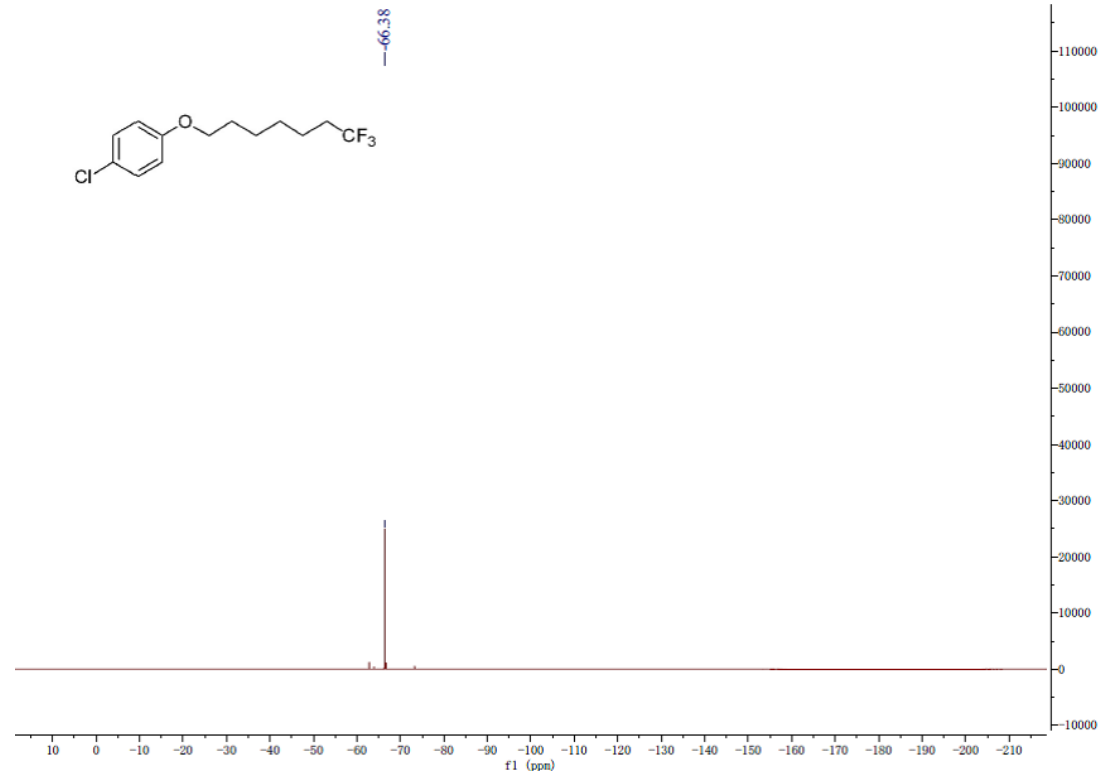
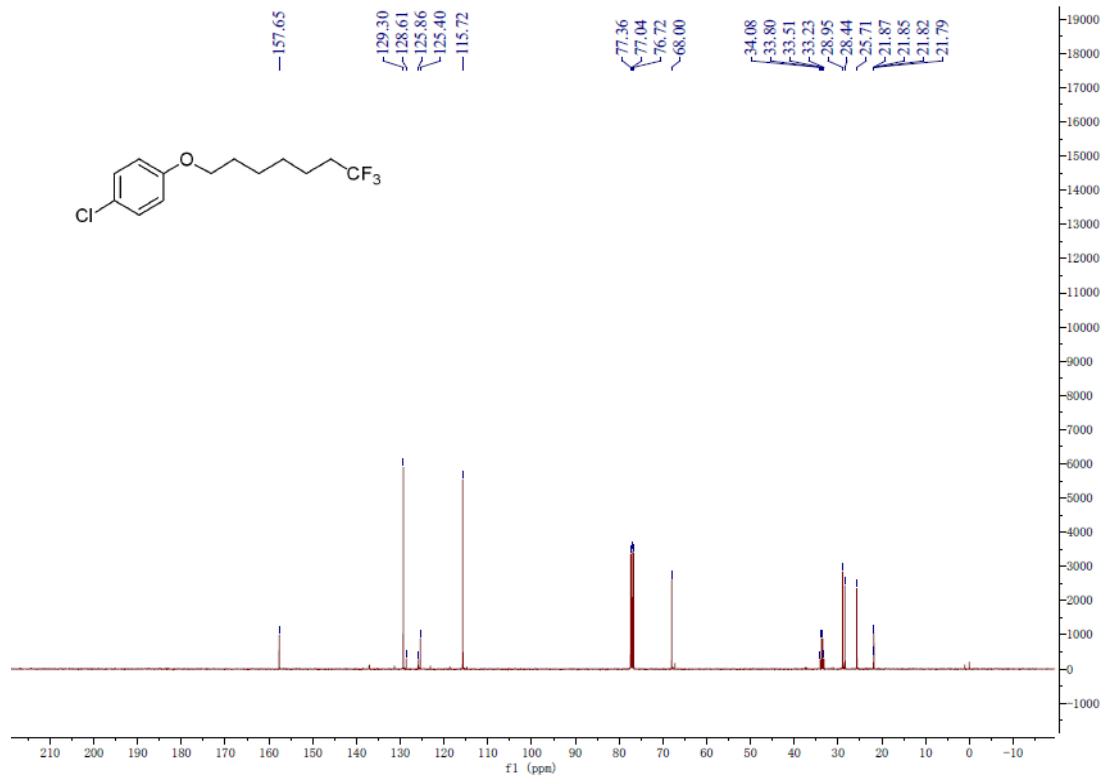
1-methoxy-4-((7,7,7-trifluoroheptyl)oxy)benzene (3c)



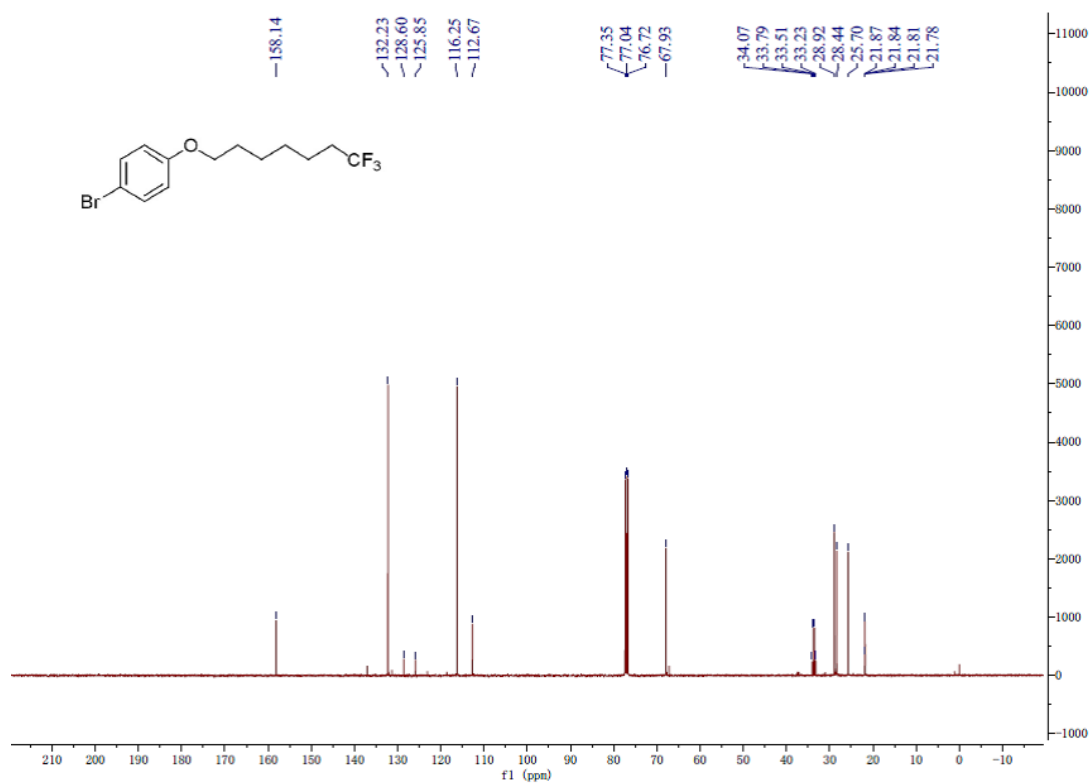
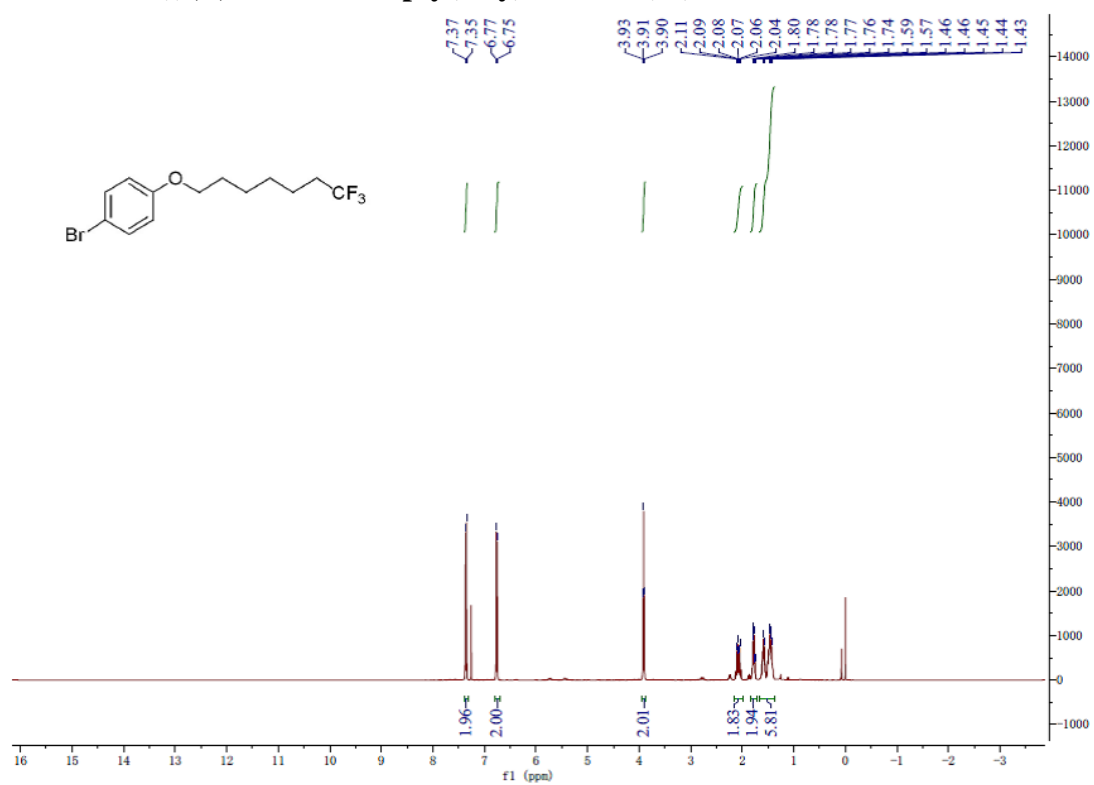


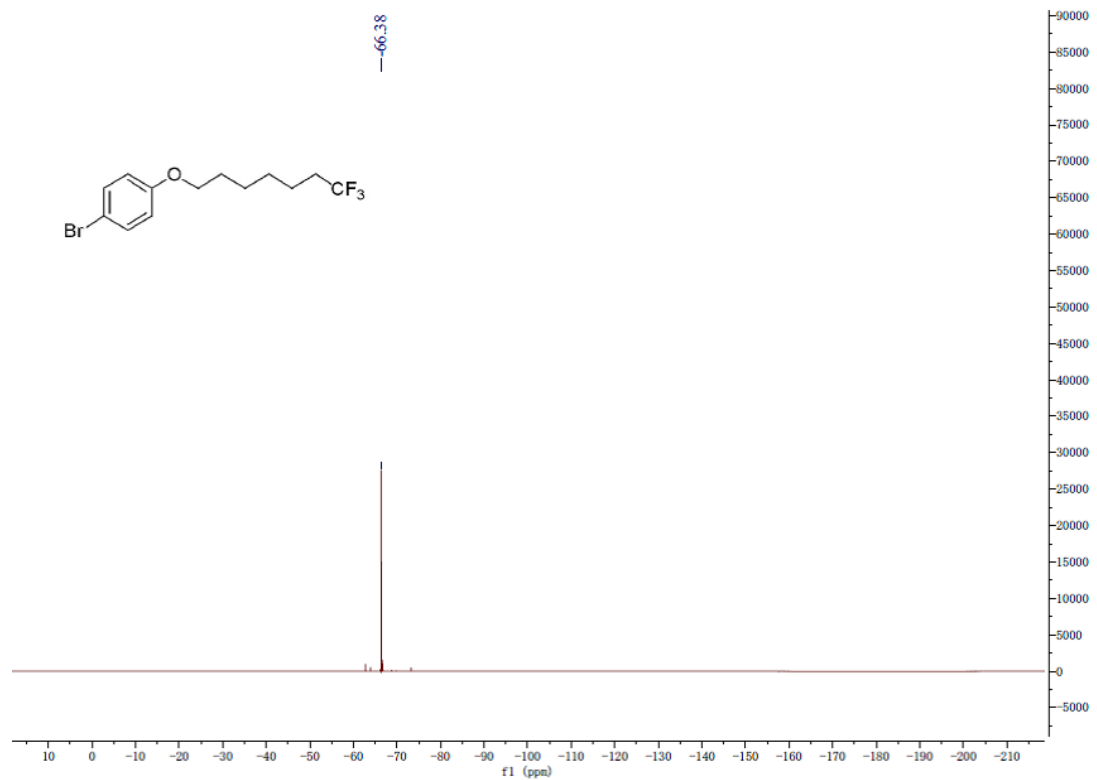
1-chloro-4-((7,7,7-trifluoroheptyl)oxy)benzene (3d)



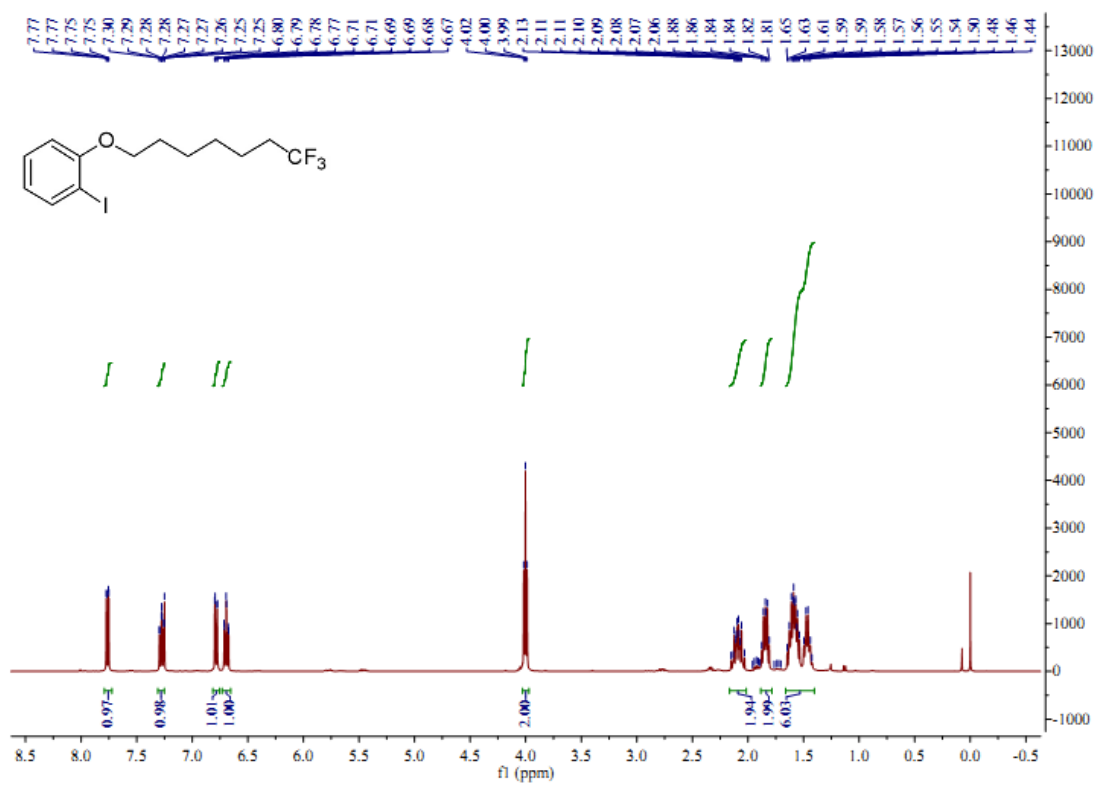


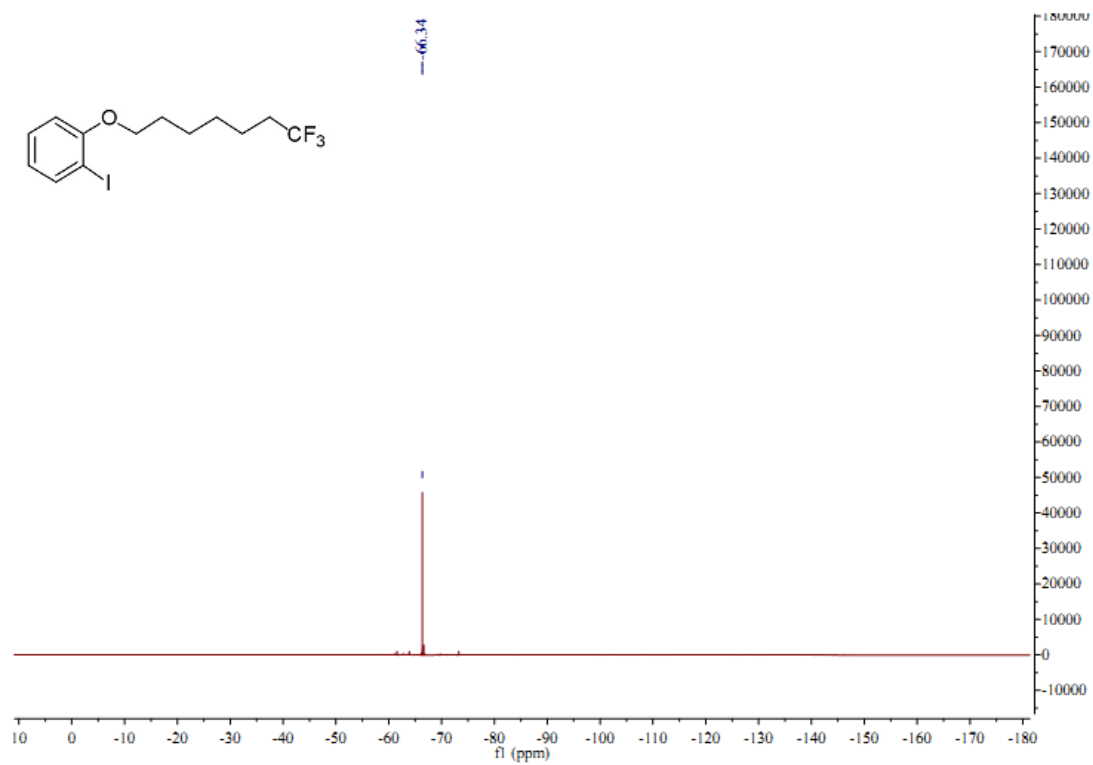
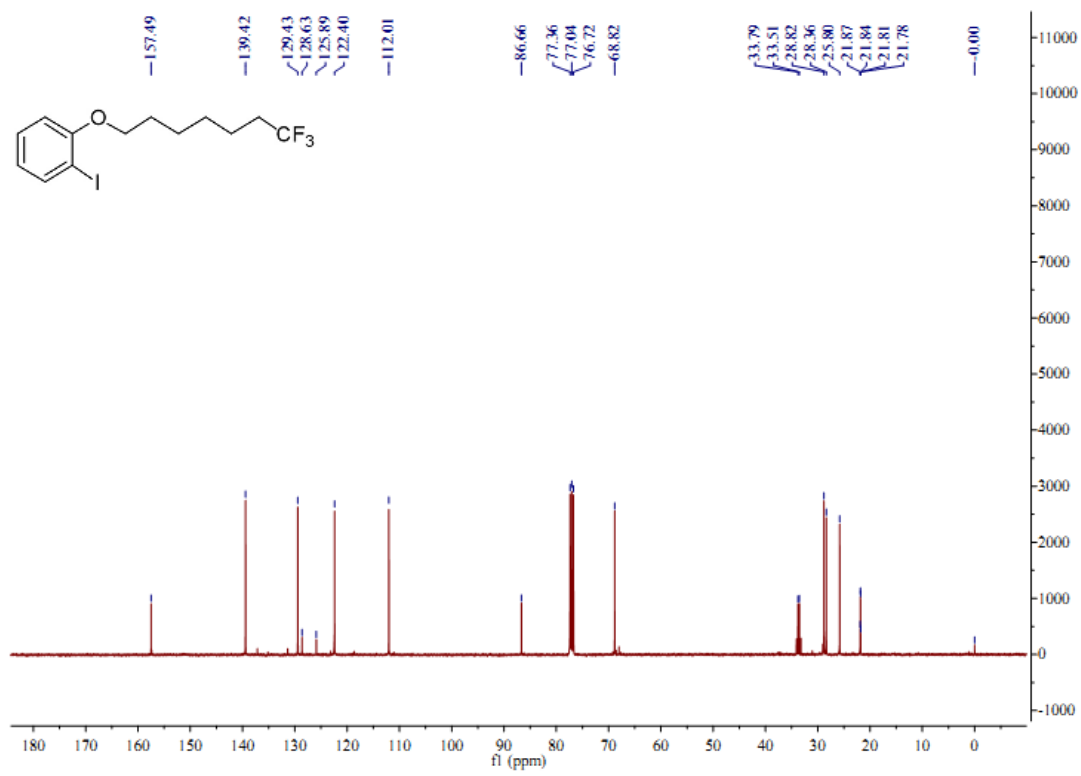
1-bromo-4-((7,7,7-trifluoroheptyl)oxy)benzene (3e)



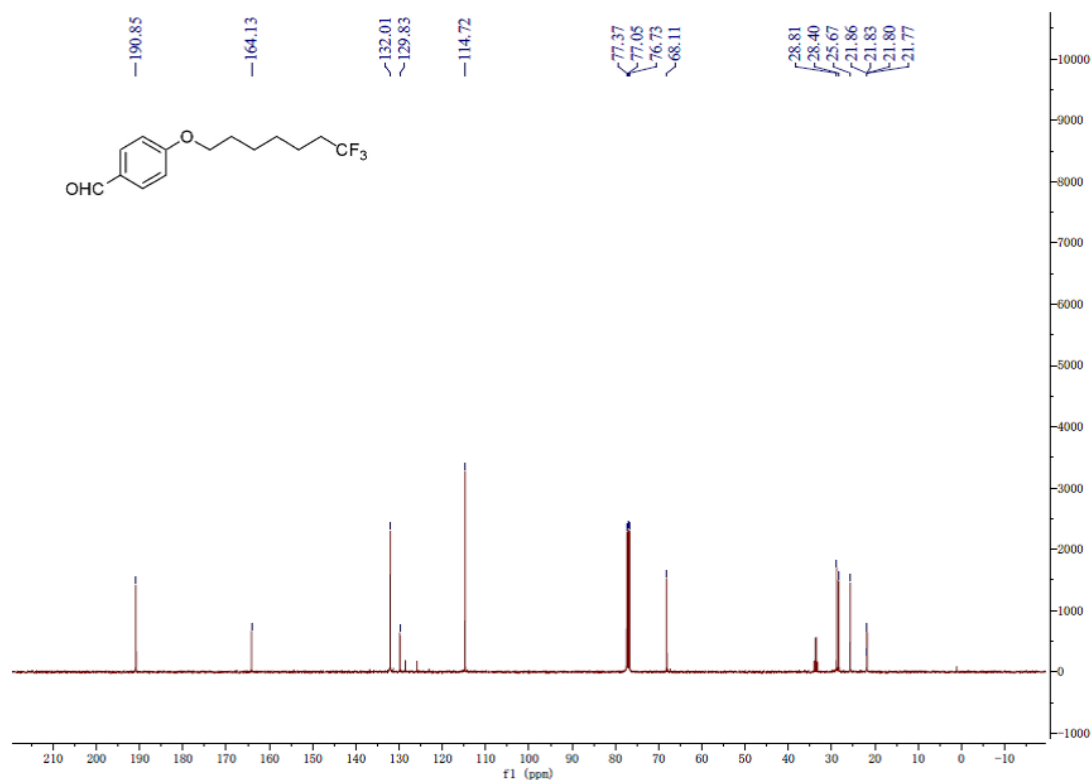
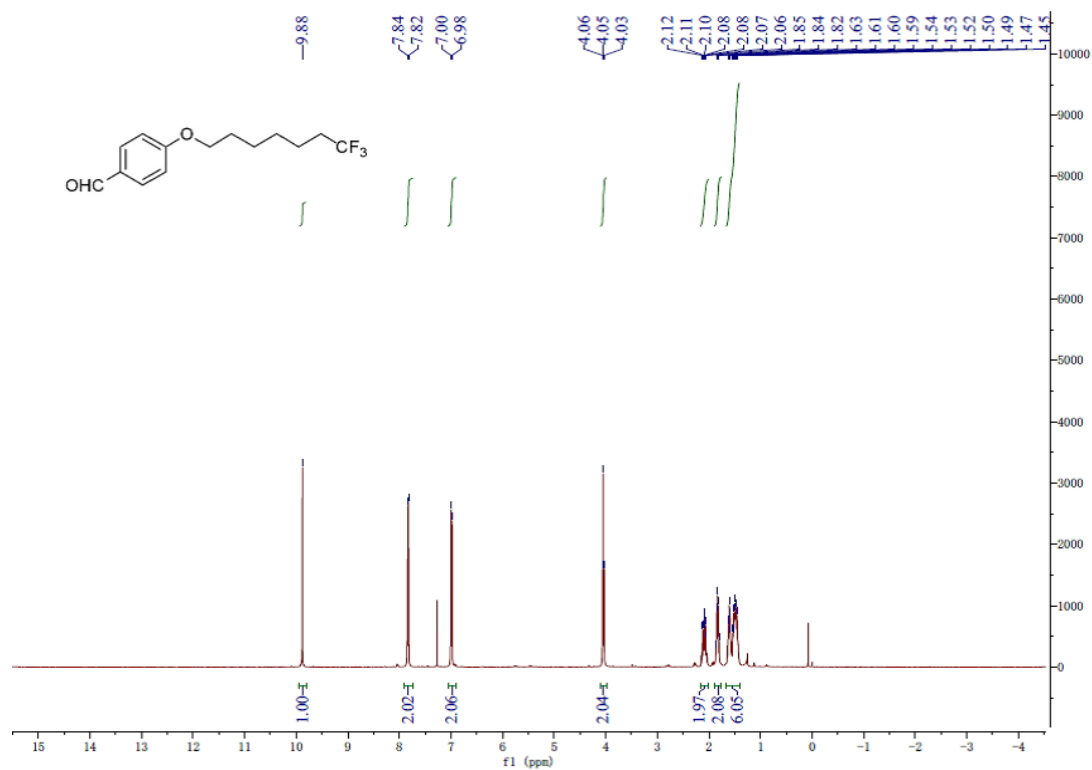


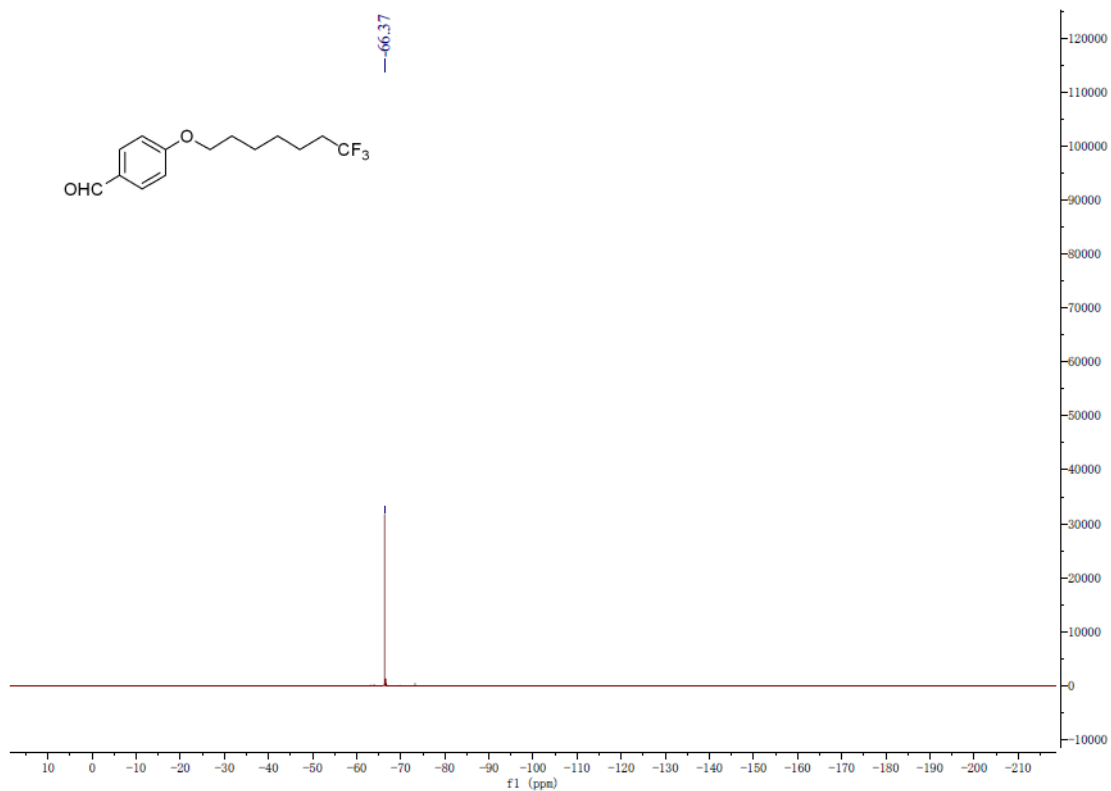
1-iodo-2-((7,7,7-trifluoroheptyl)oxy)benzene (3f)



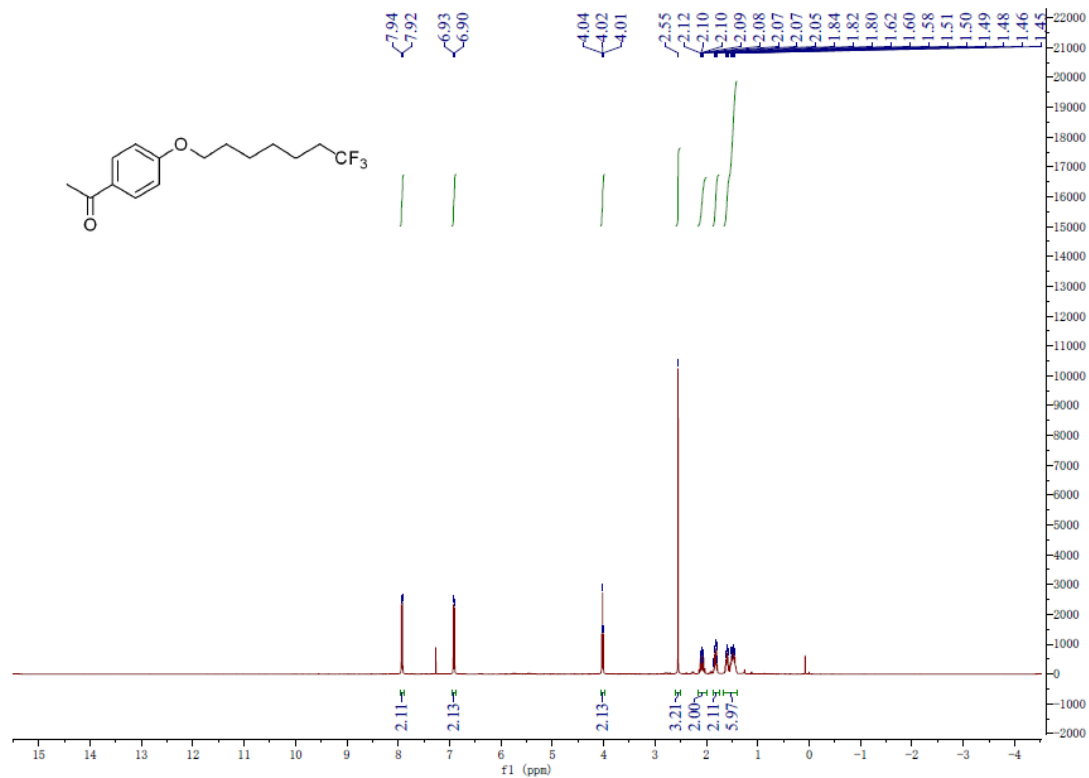


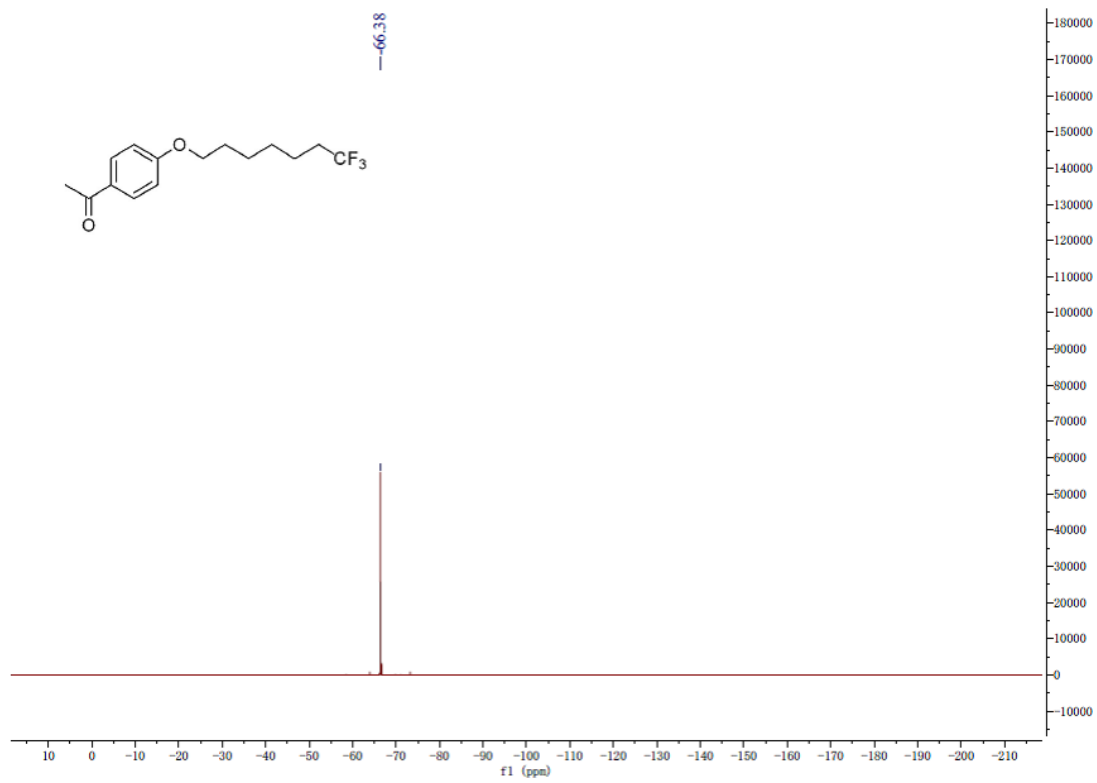
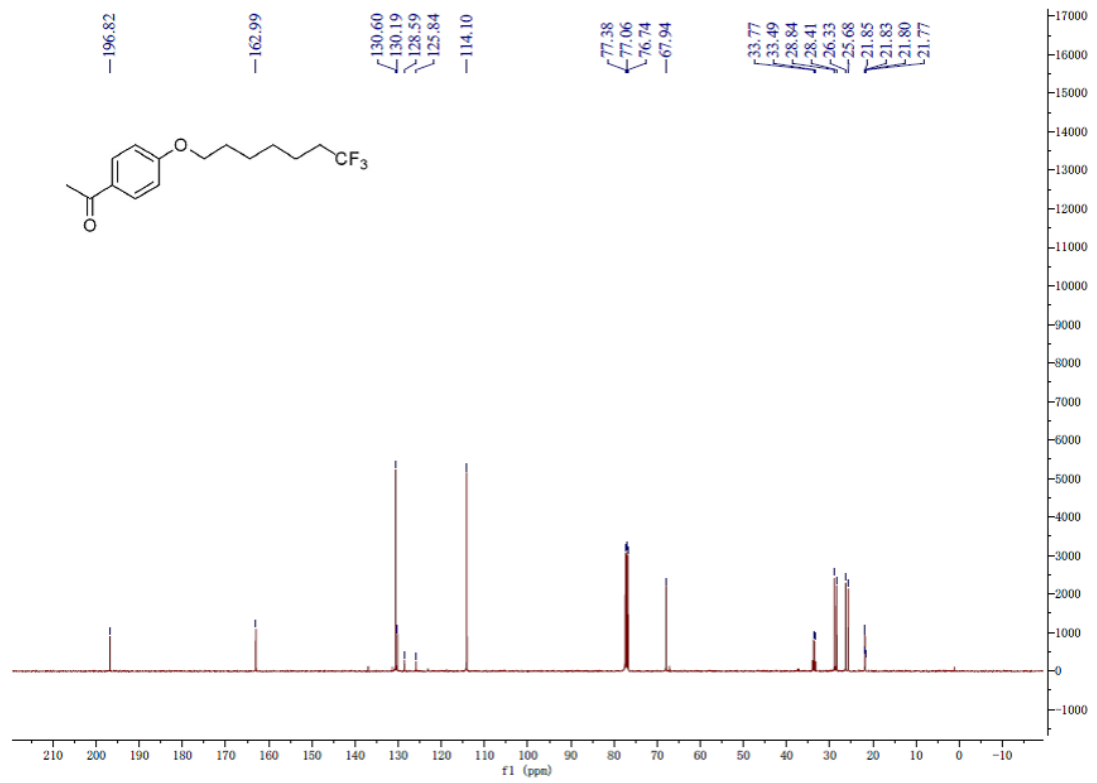
4-((7,7,7-trifluoroheptyl)oxy)benzaldehyde (3g)



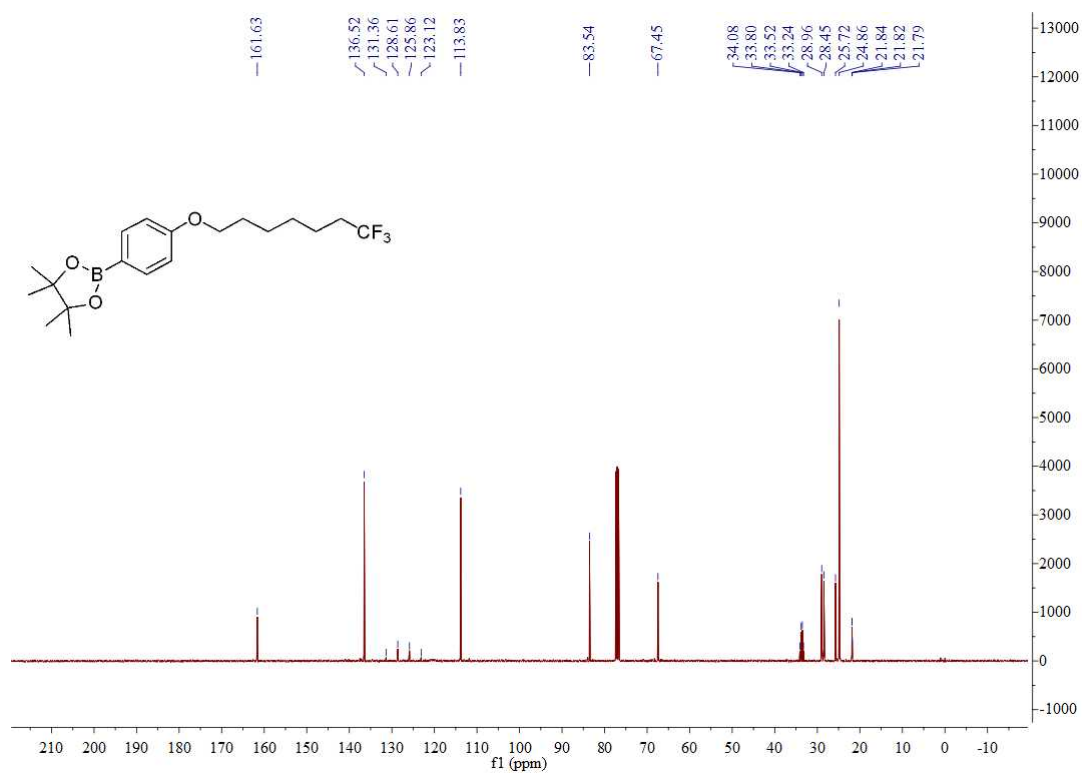
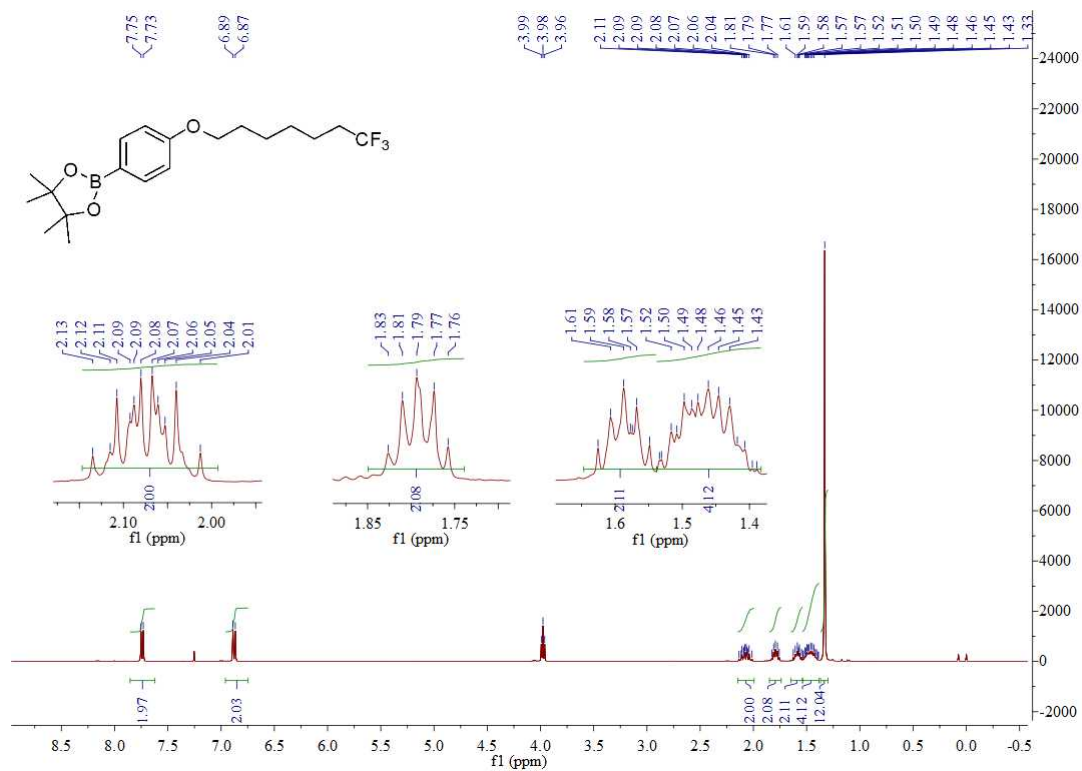


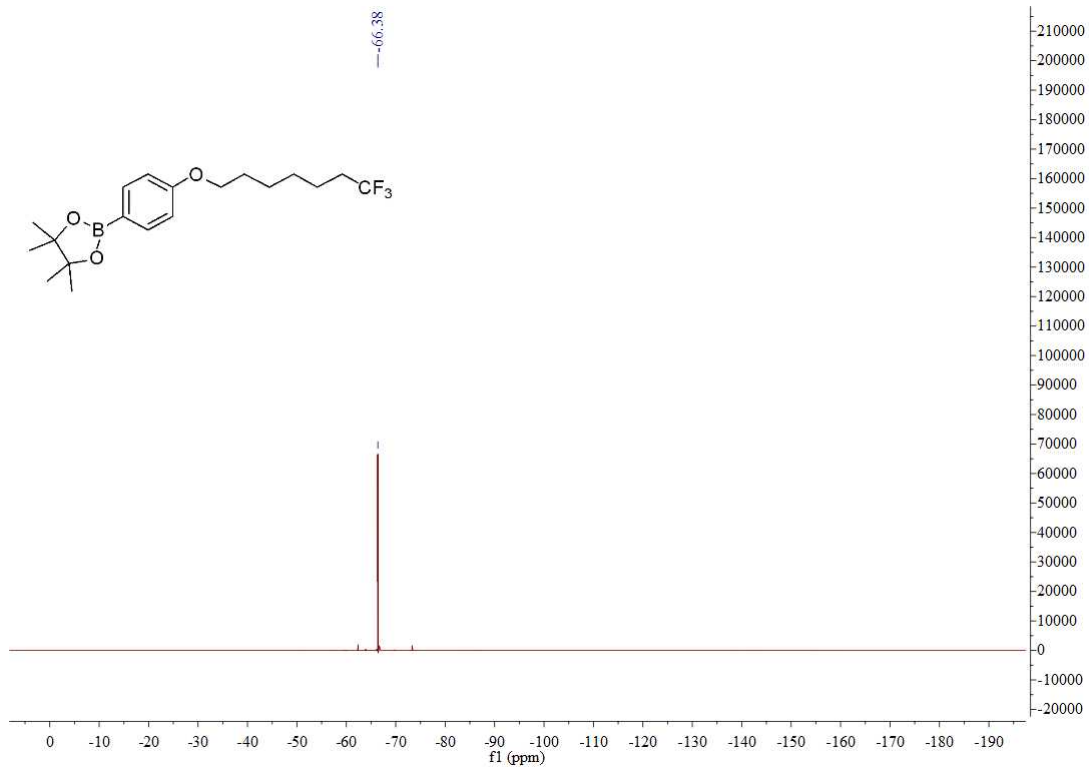
1-(4-((7,7,7-trifluoroheptyl)oxy)phenyl)ethanone (3h)



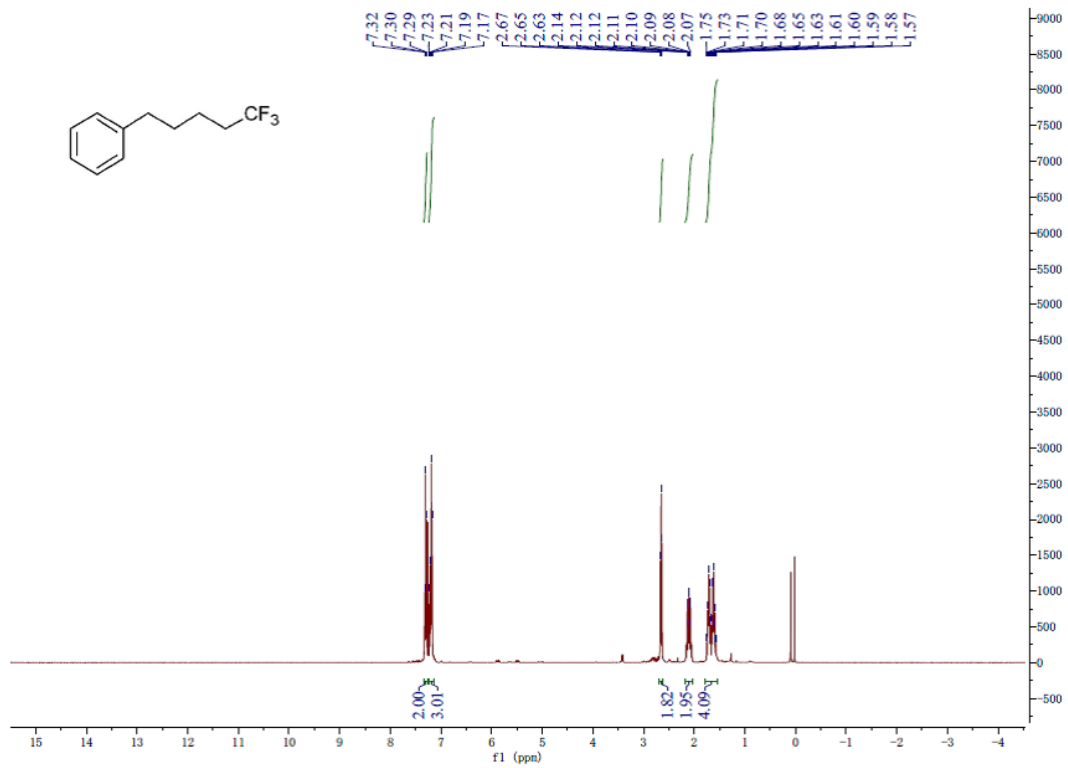


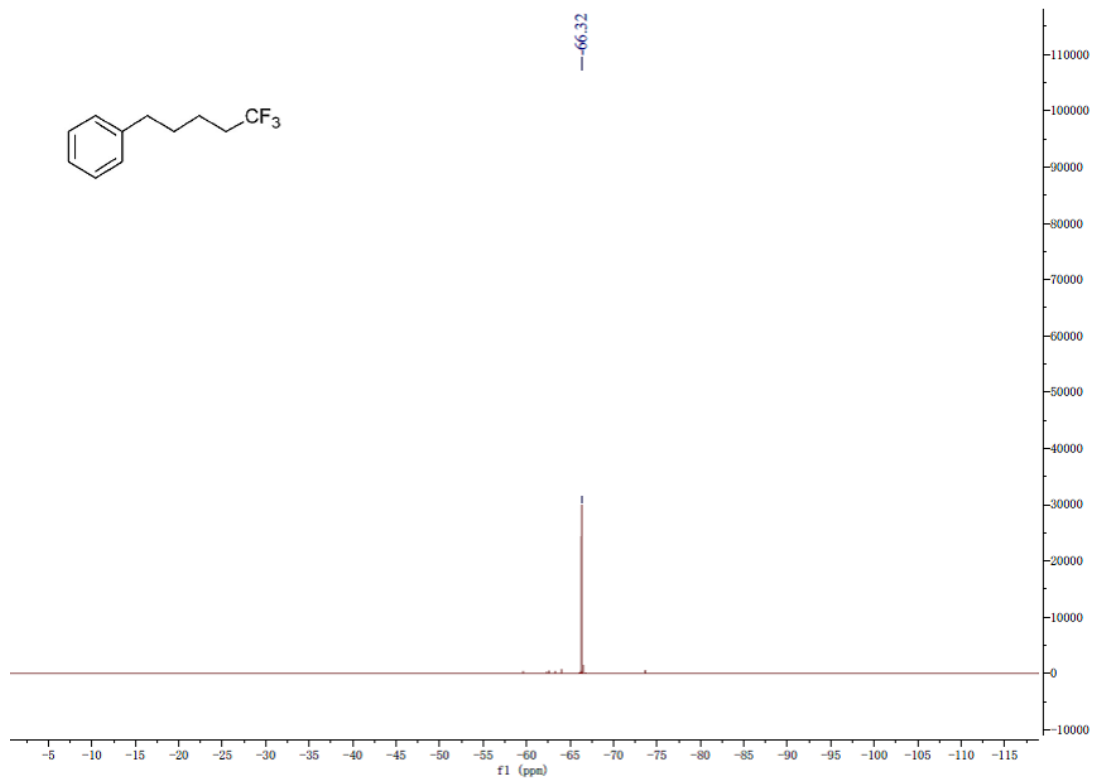
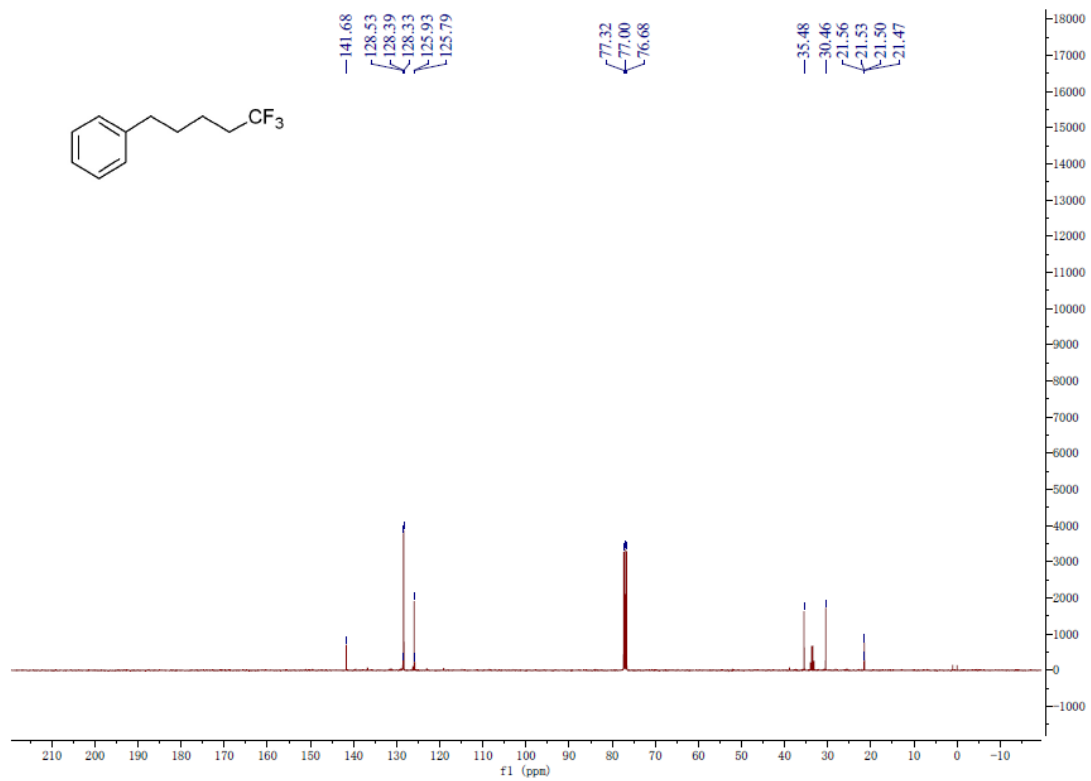
4,4,5,5-tetramethyl-2-(4-((7,7,7-trifluoroheptyl)oxy)phenyl)-1,3,2-dioxaborolane (3i)



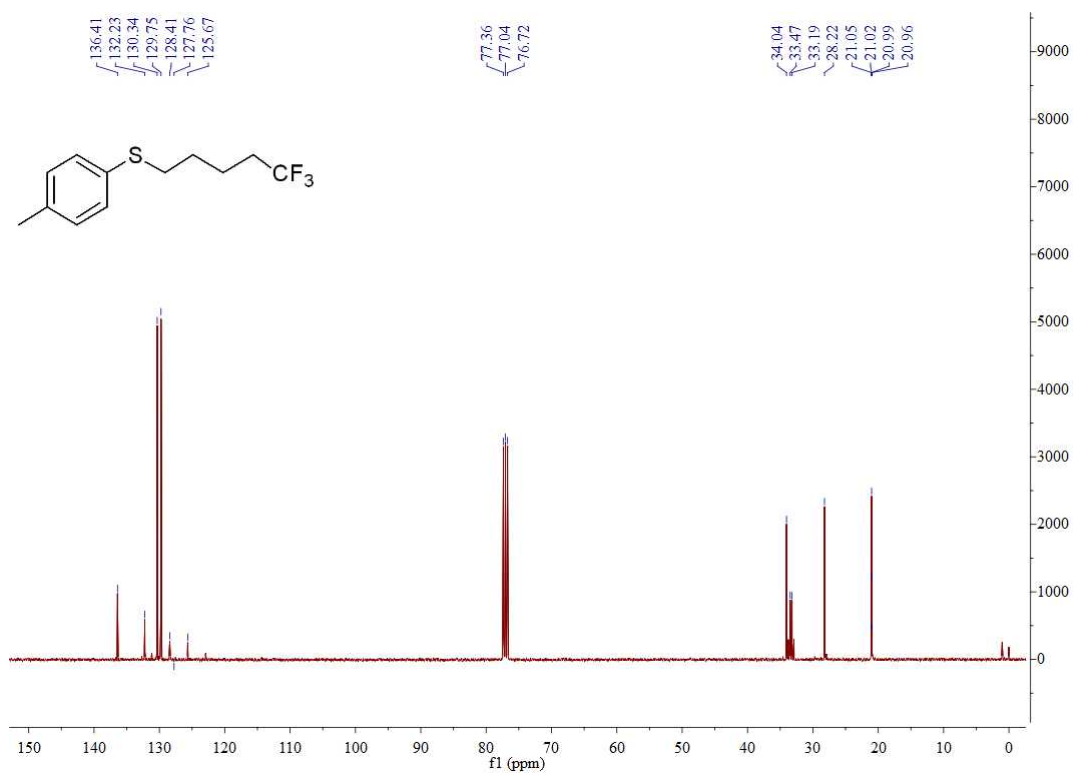
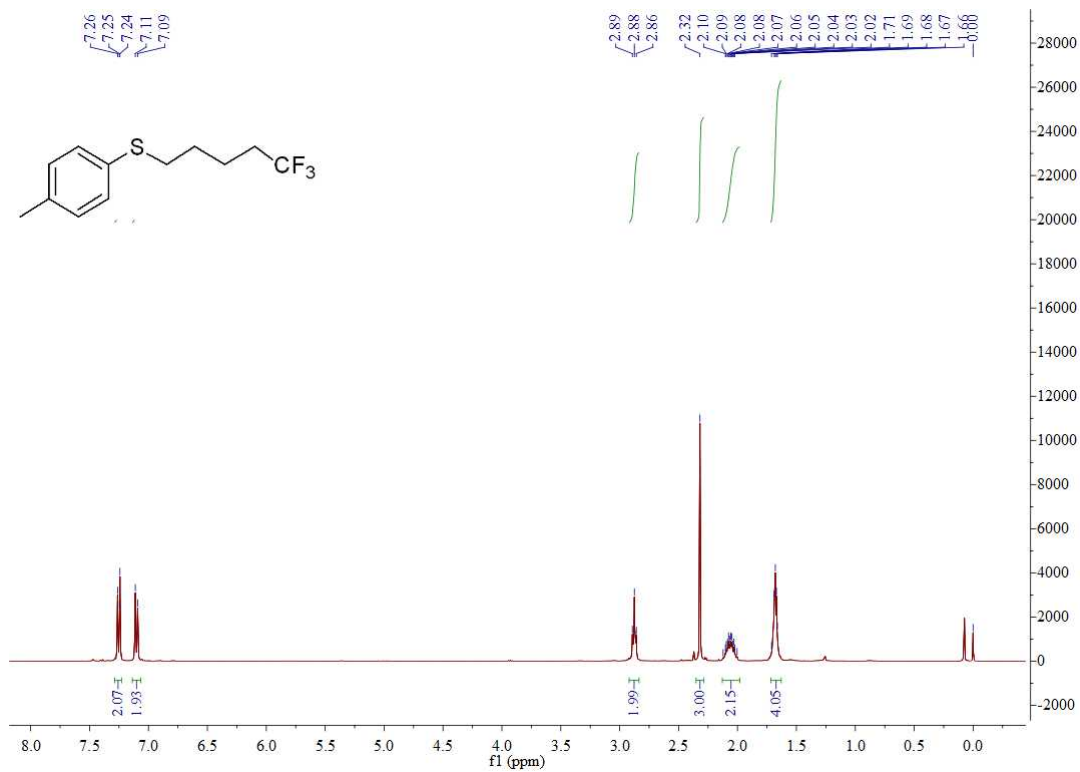


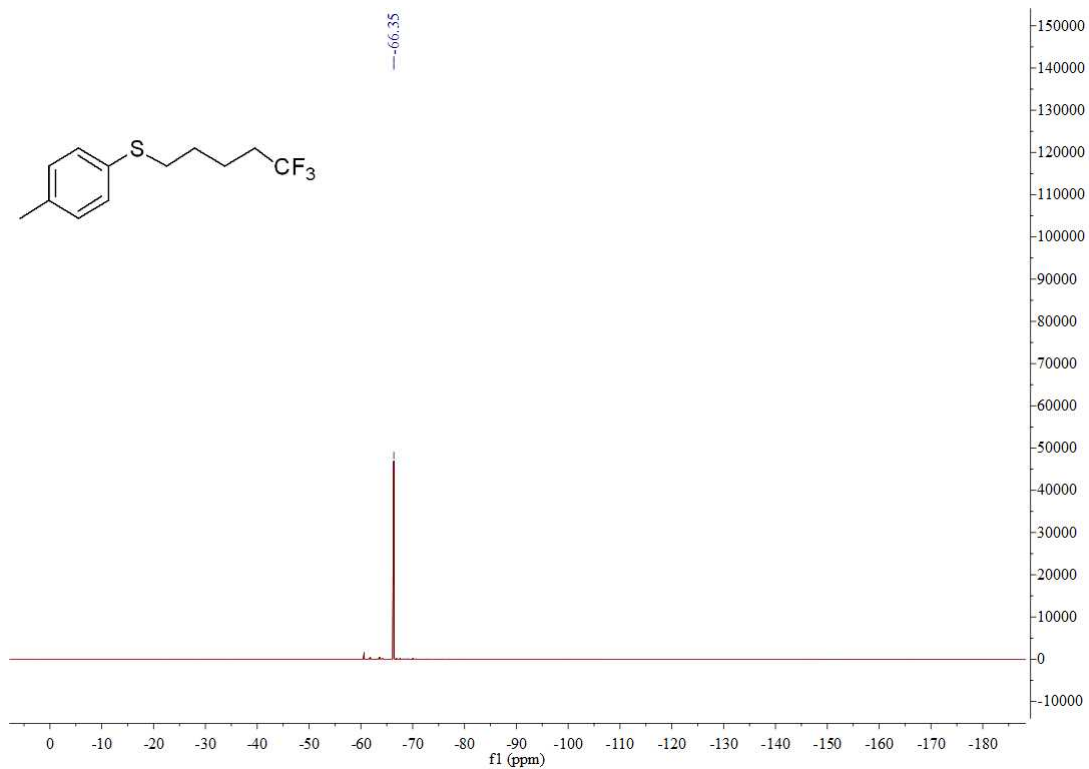
(5,5,5-trifluoropentyl)benzene (3j)



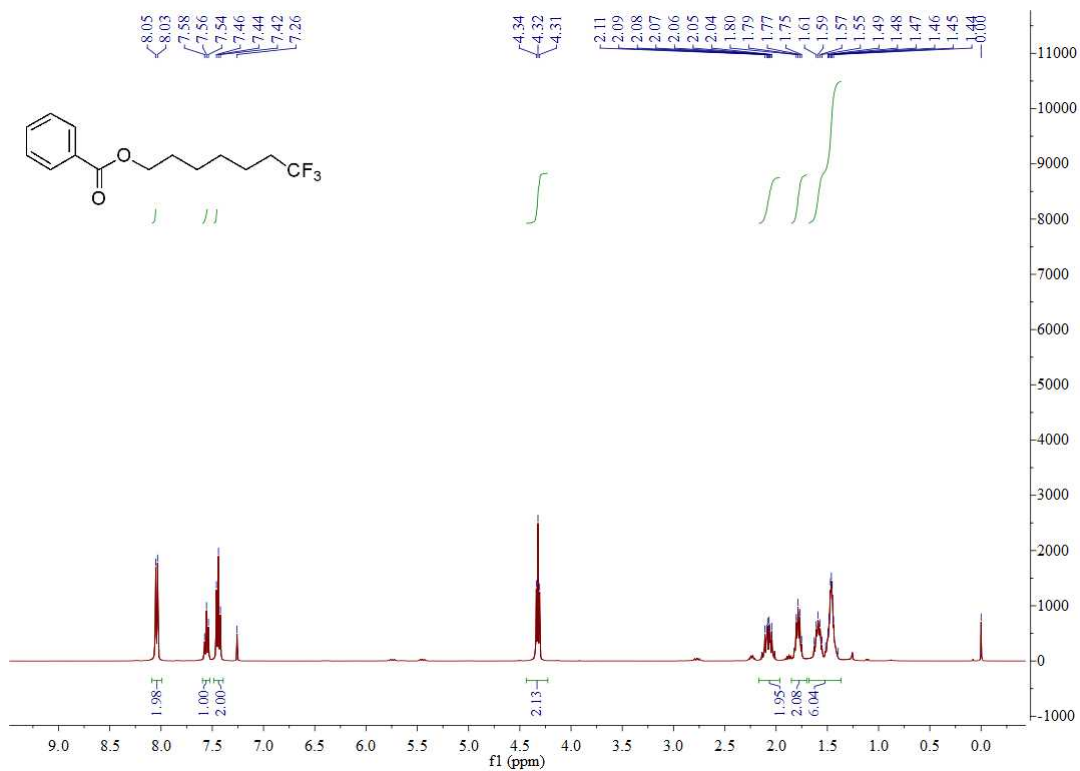


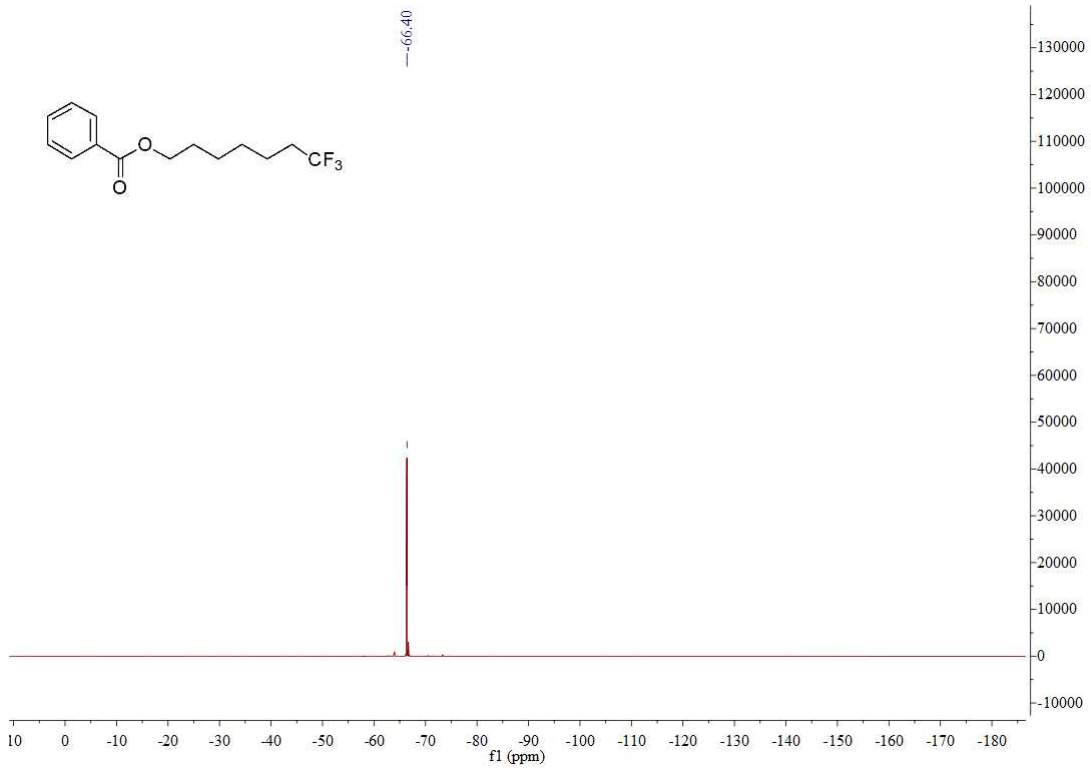
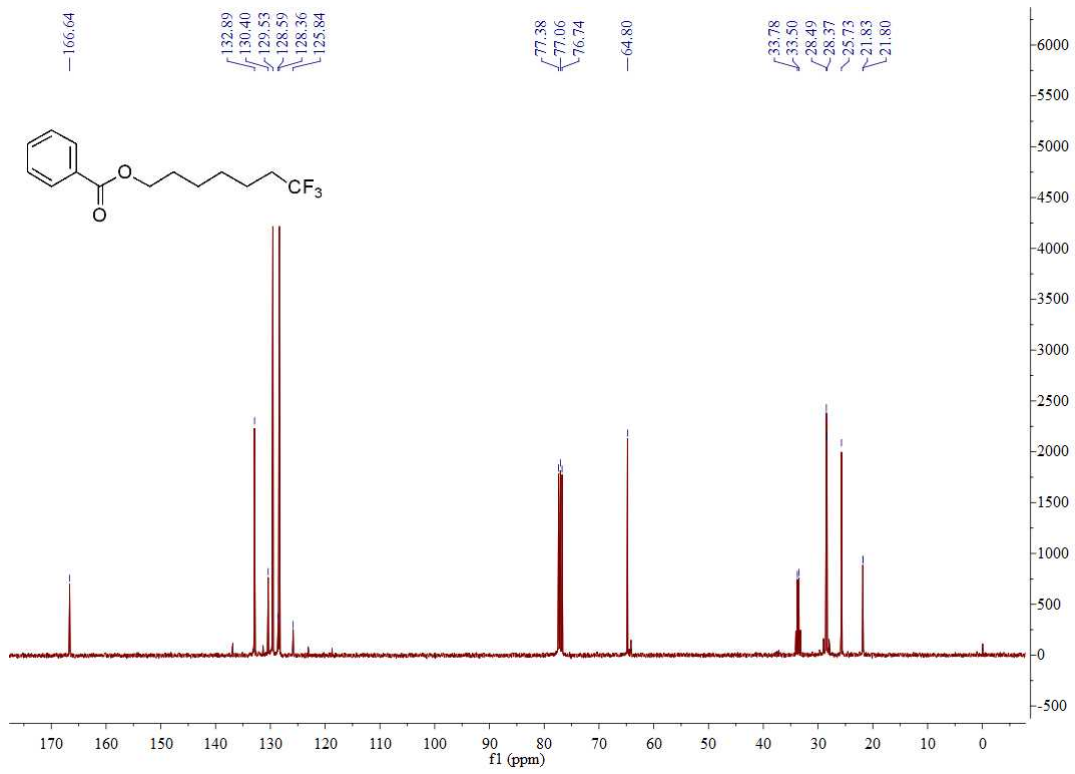
p-tolyl(5,5,5-trifluoropentyl)sulfane (3k)



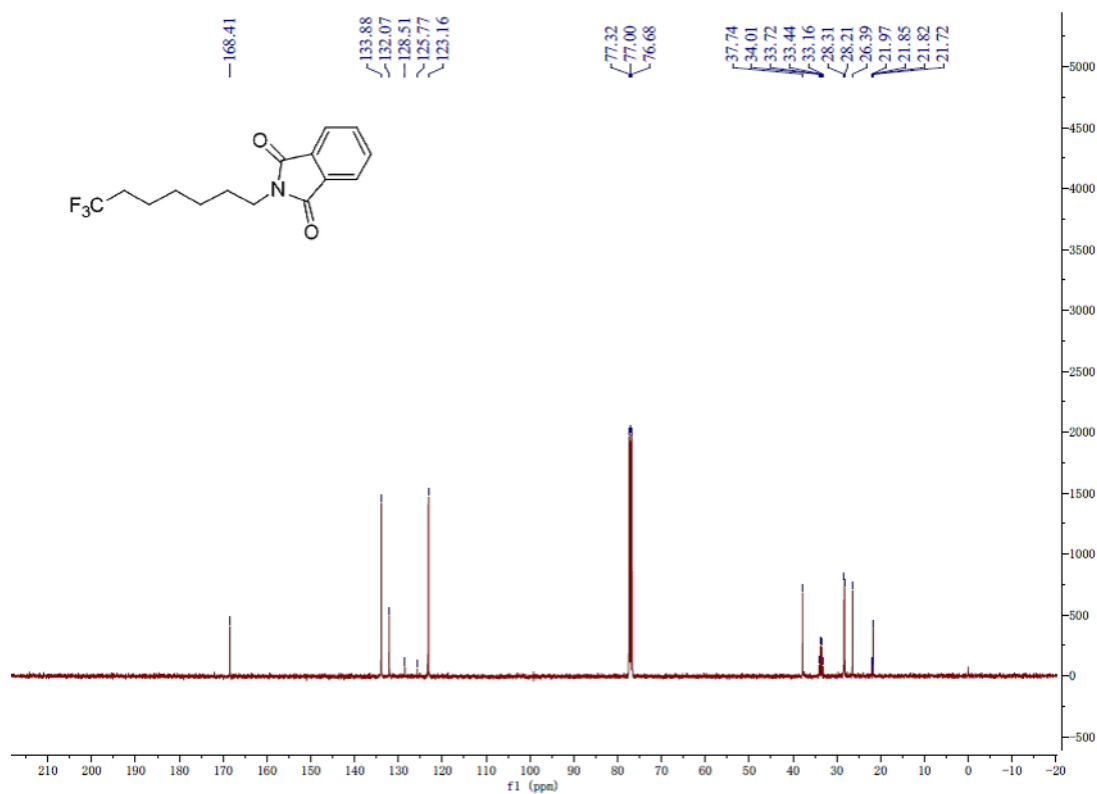
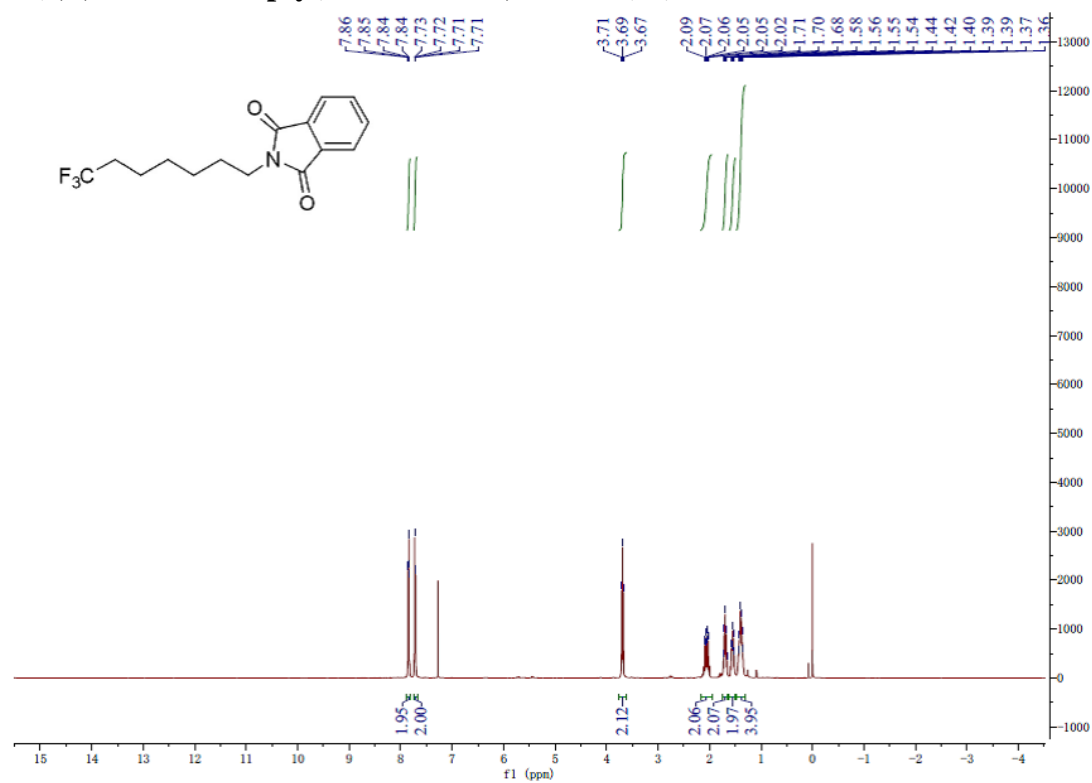


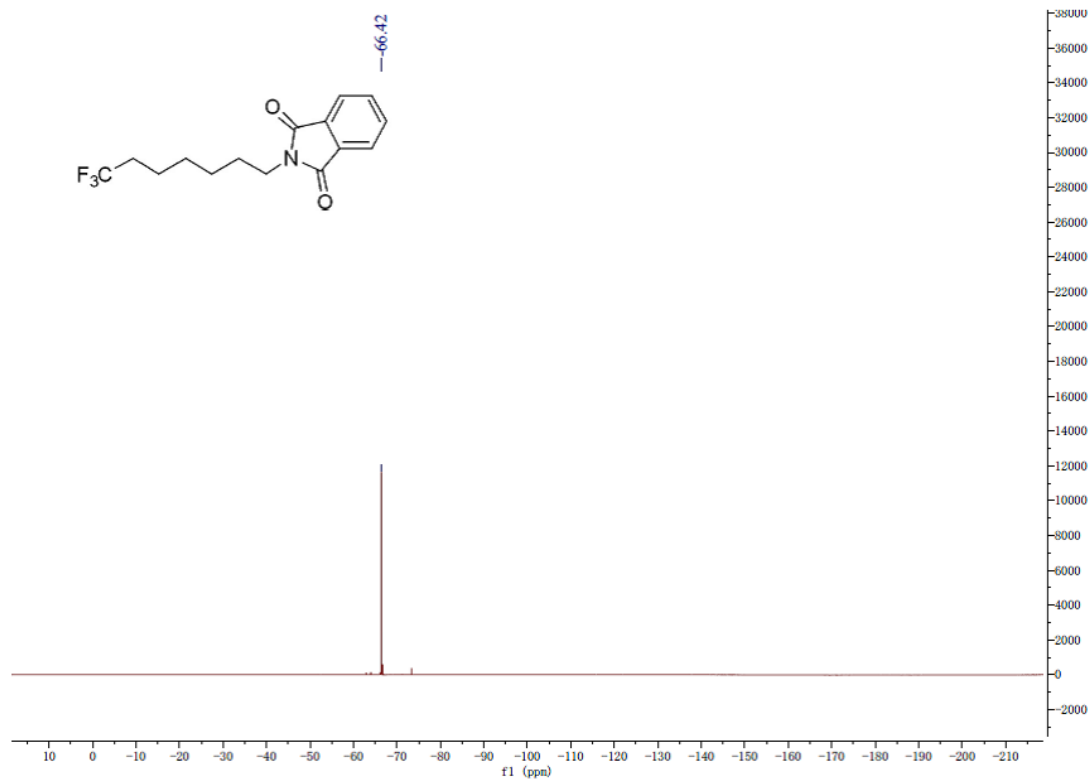
7,7,7-trifluoroheptyl benzoate (3n)



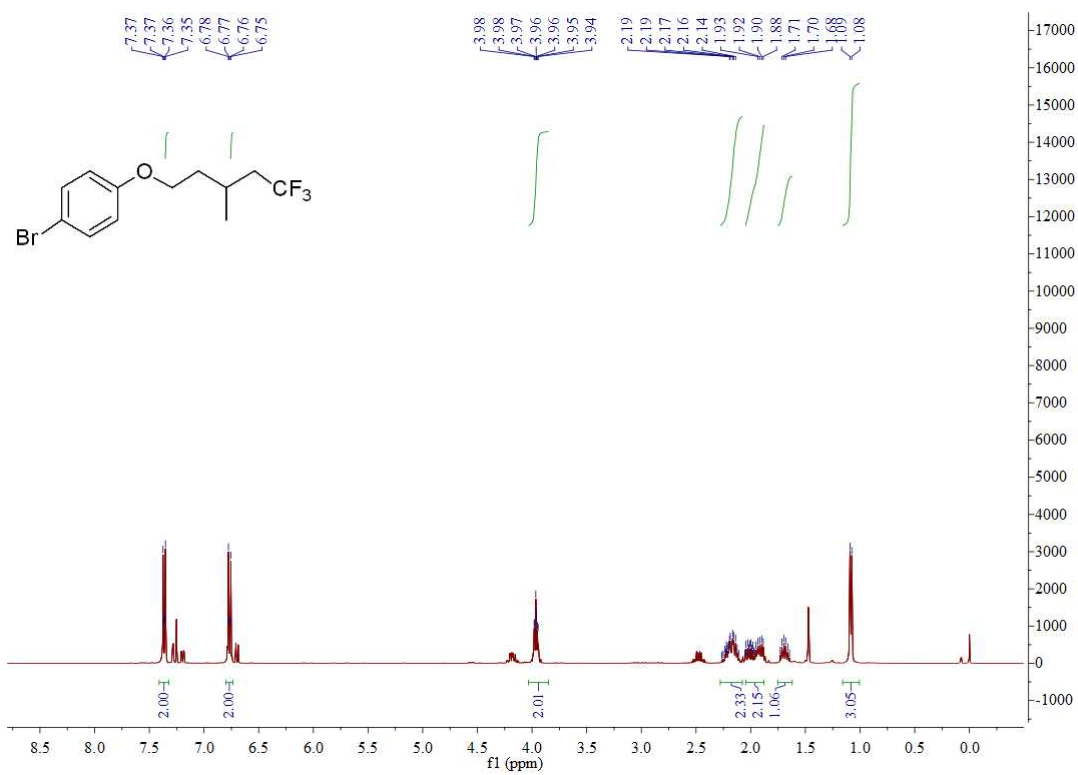


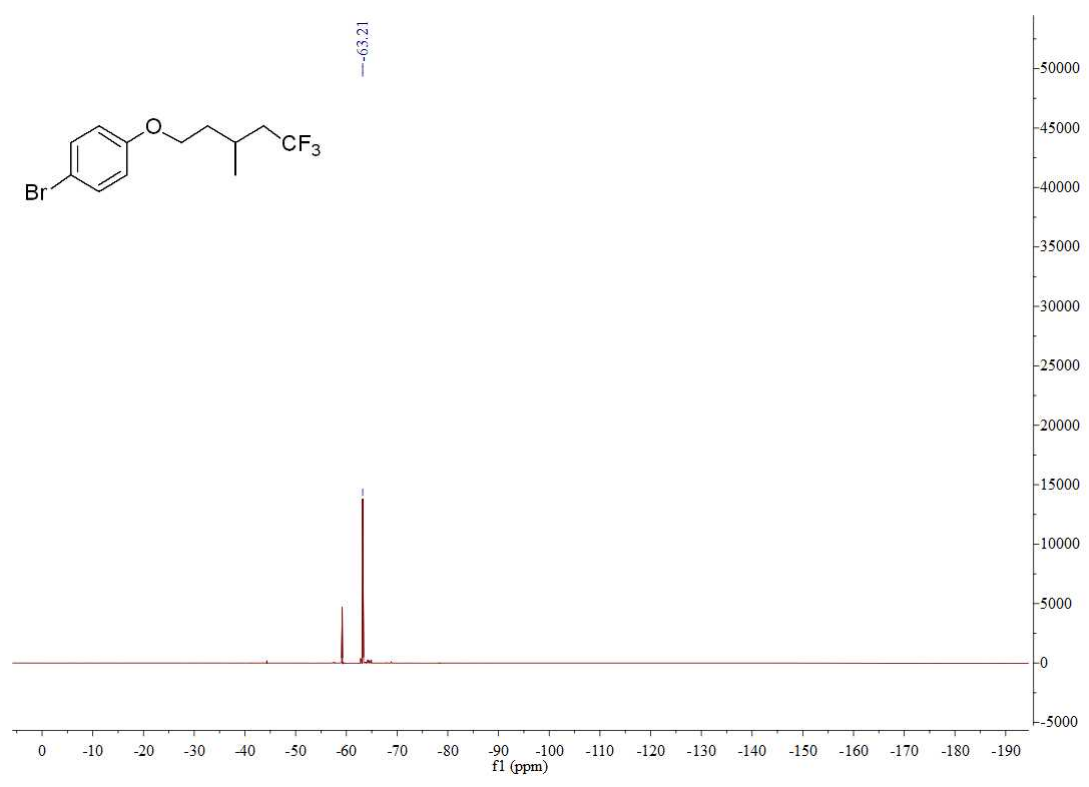
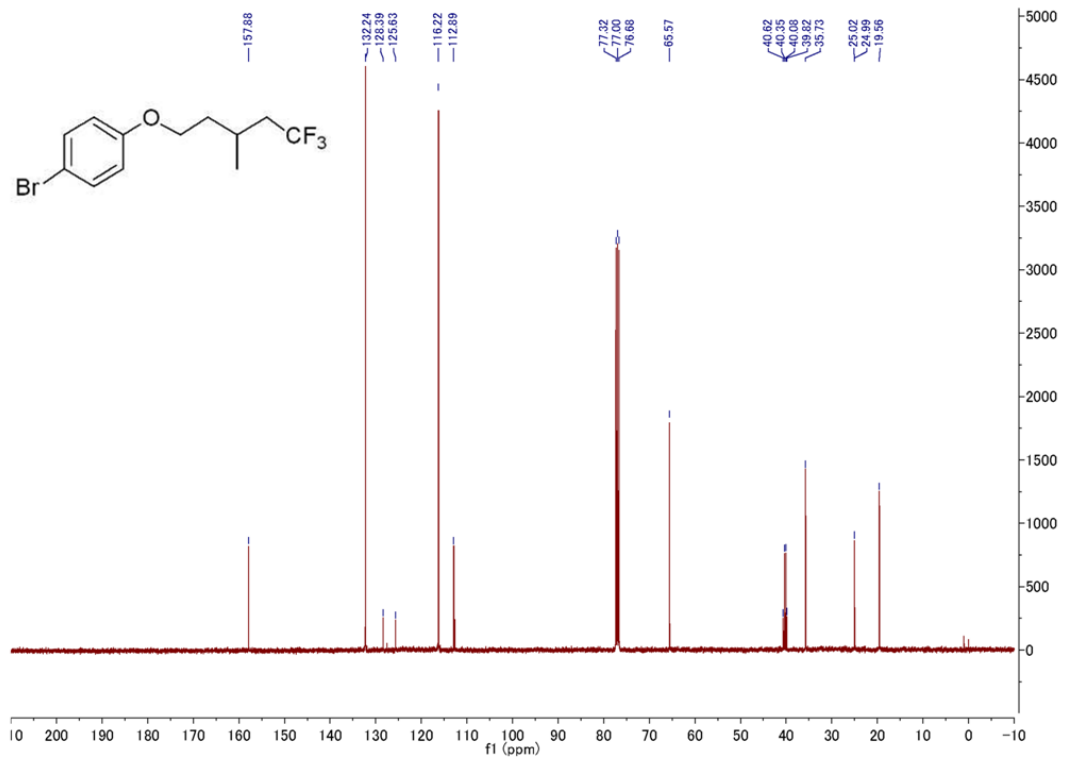
2-(7,7,7-trifluoroheptyl)isoindoline-1,3-dione (3o)



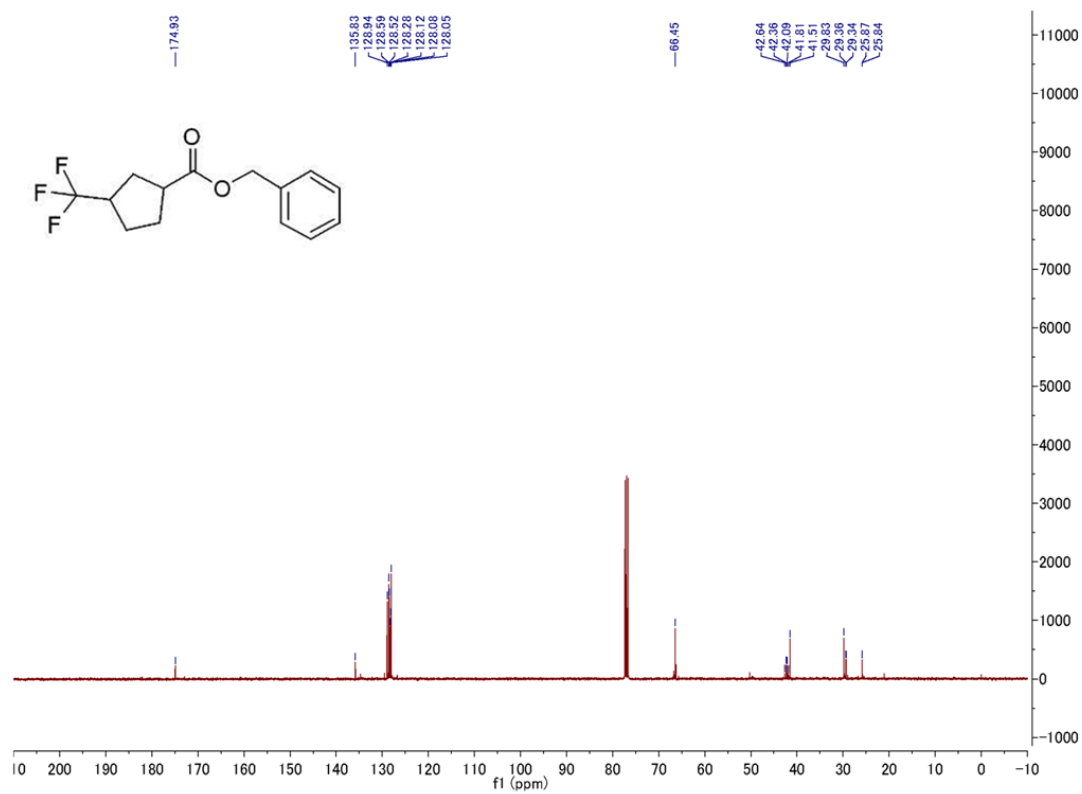
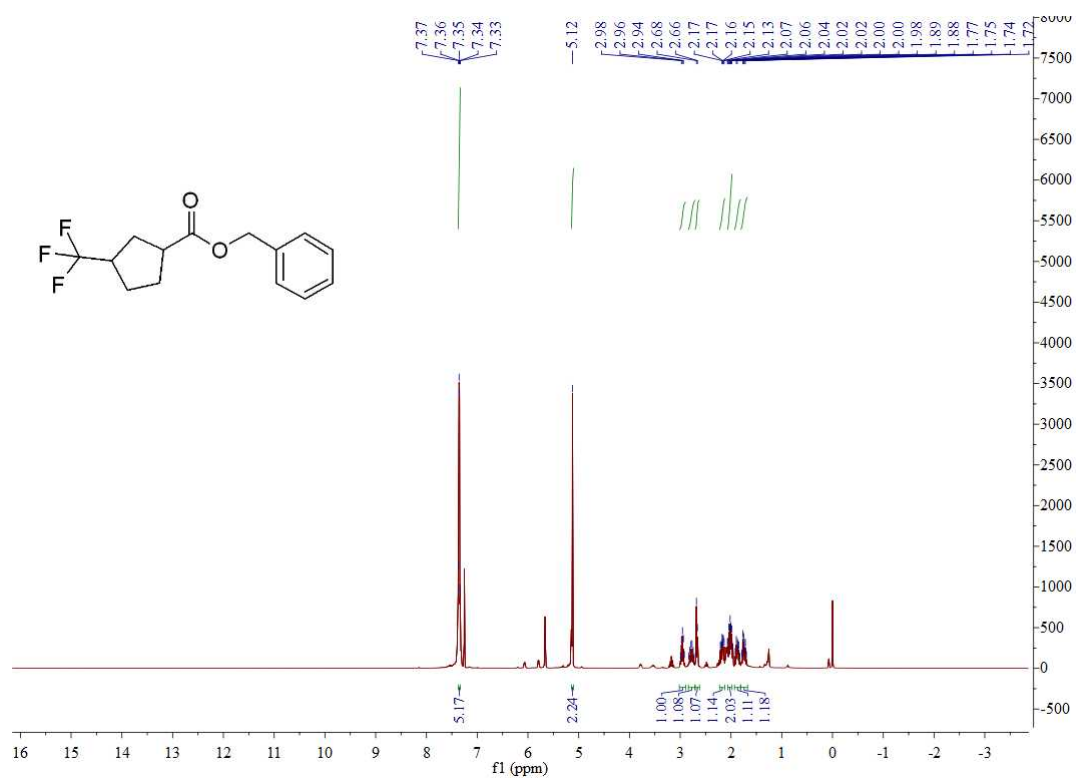


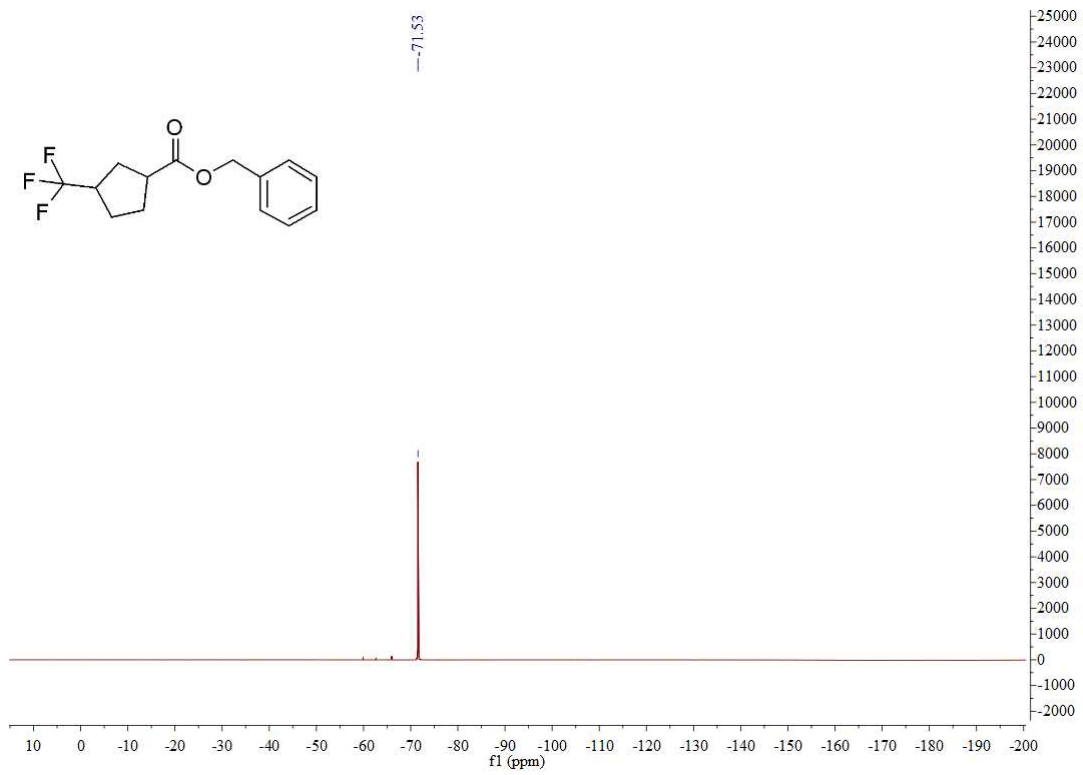
1-bromo-4-((5,5,5-trifluoro-3-methylpentyl)oxy)benzene (3p)



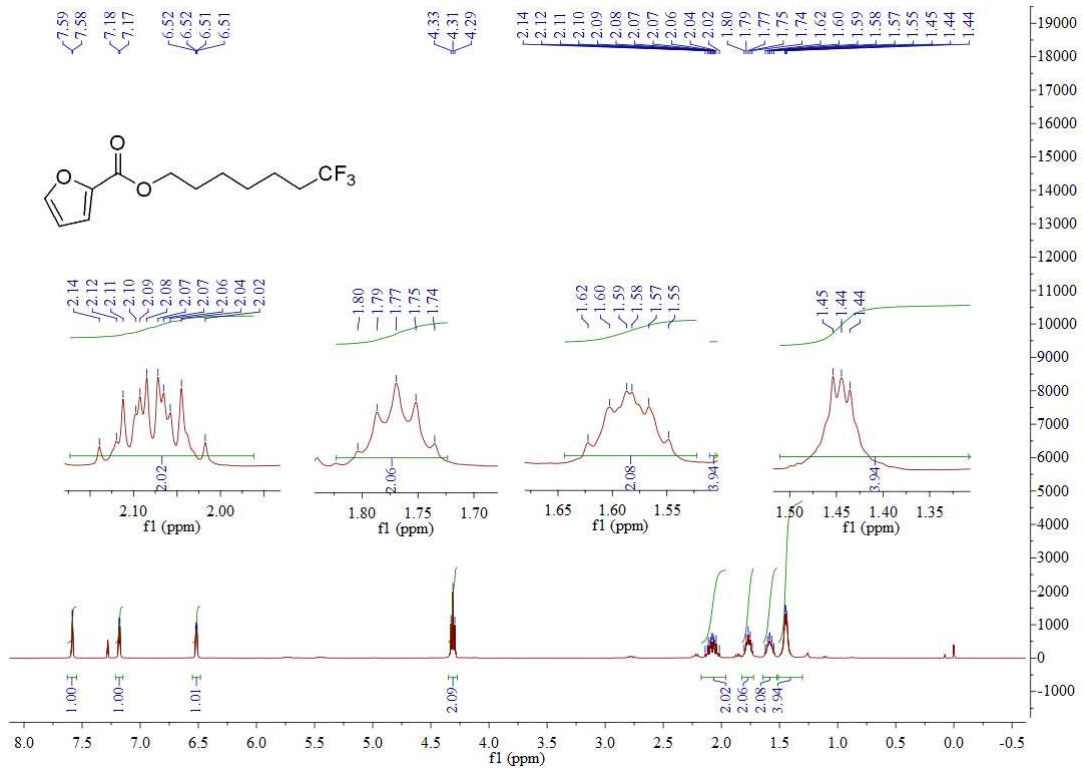


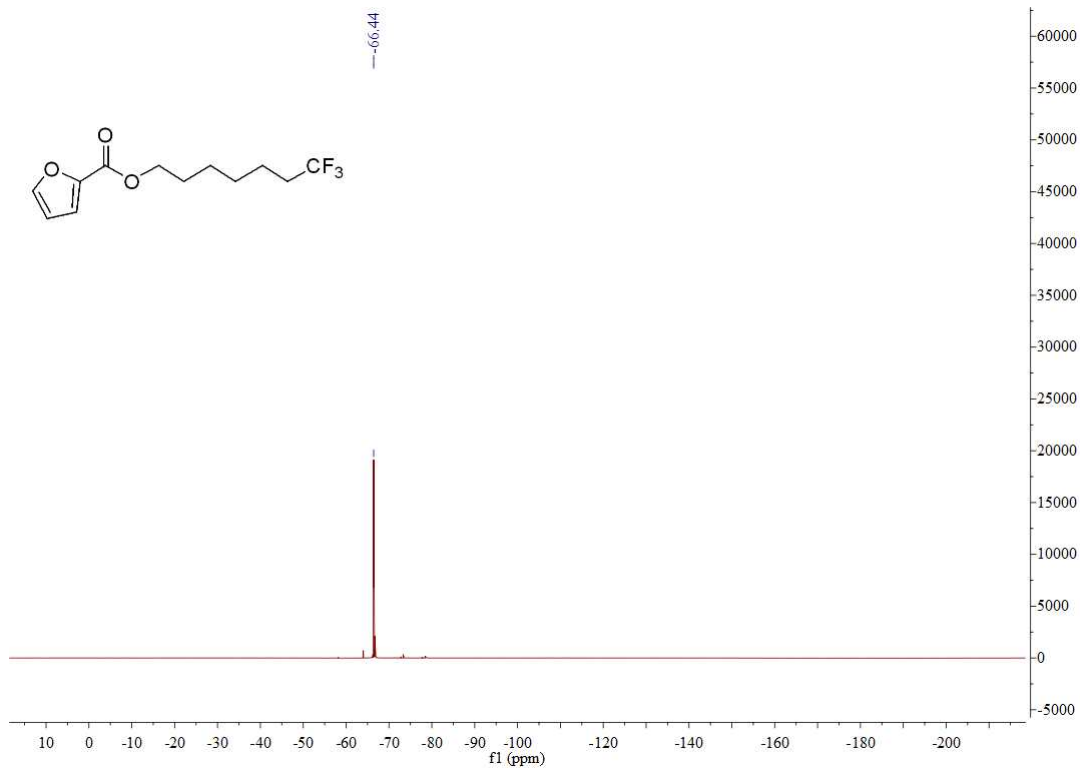
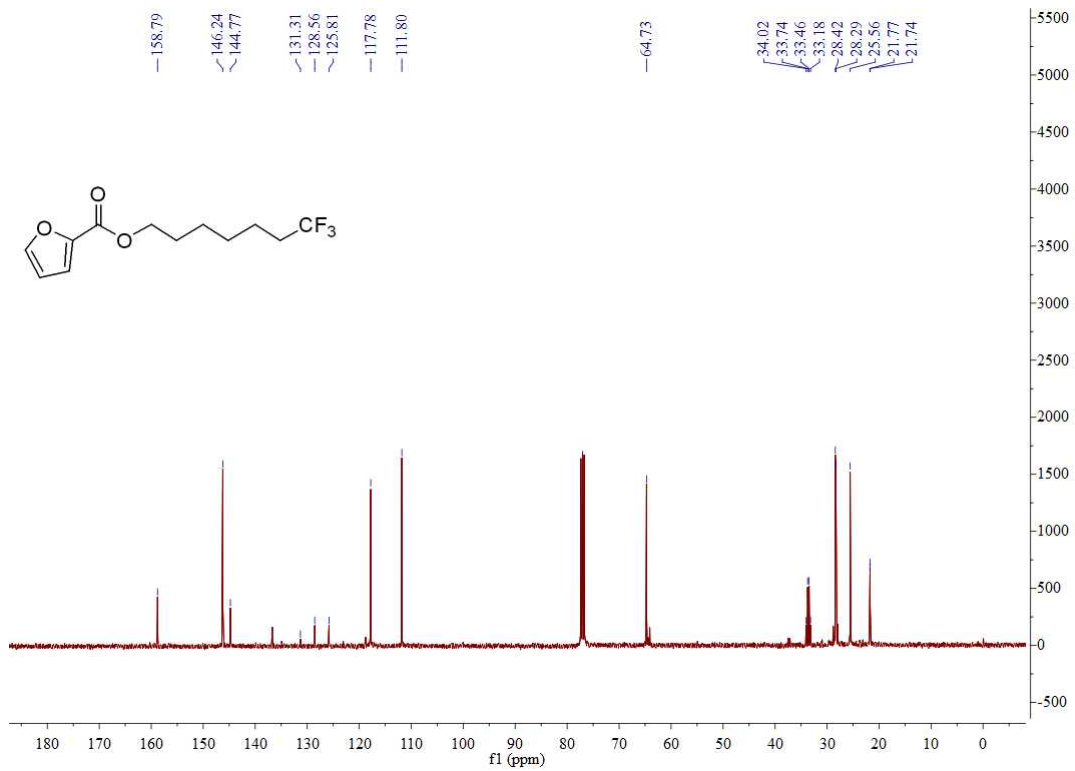
benzyl 3-(trifluoromethyl)cyclopentanecarboxylate (3q)



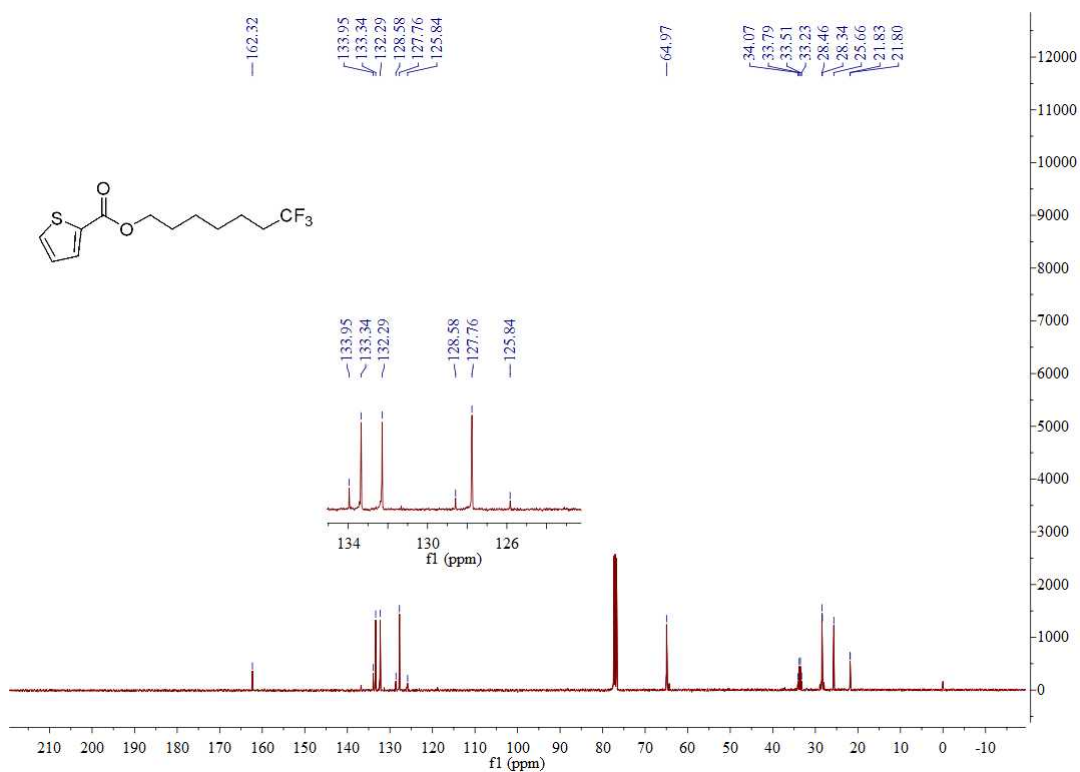
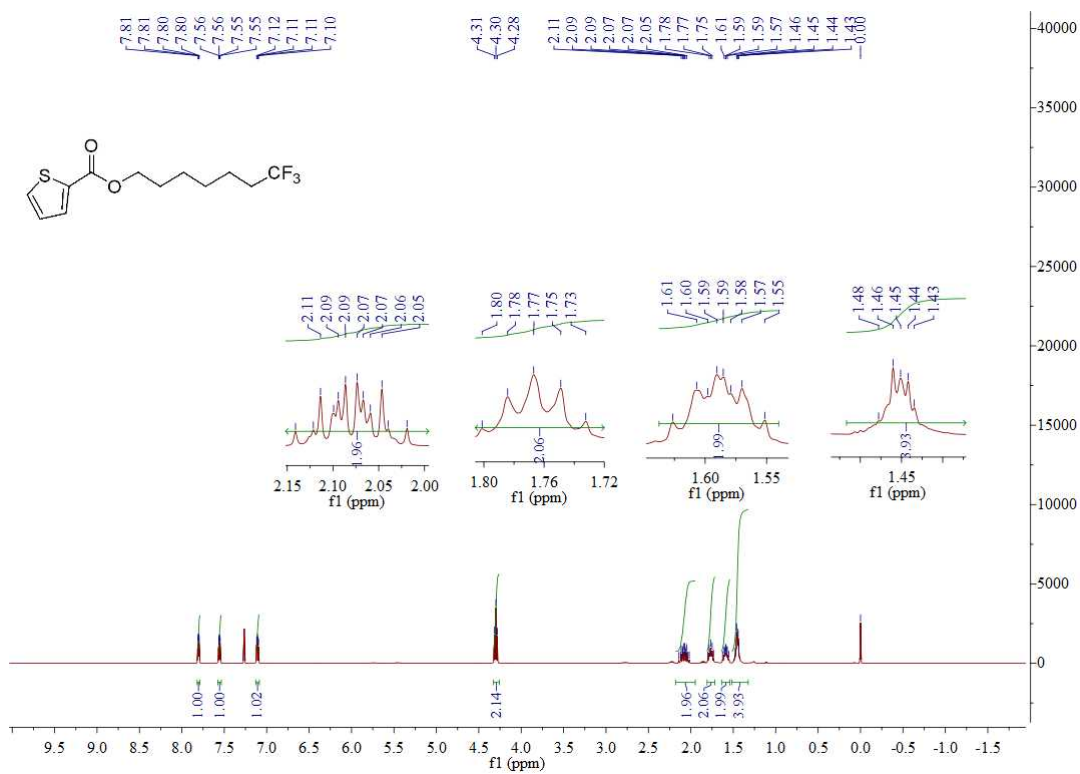


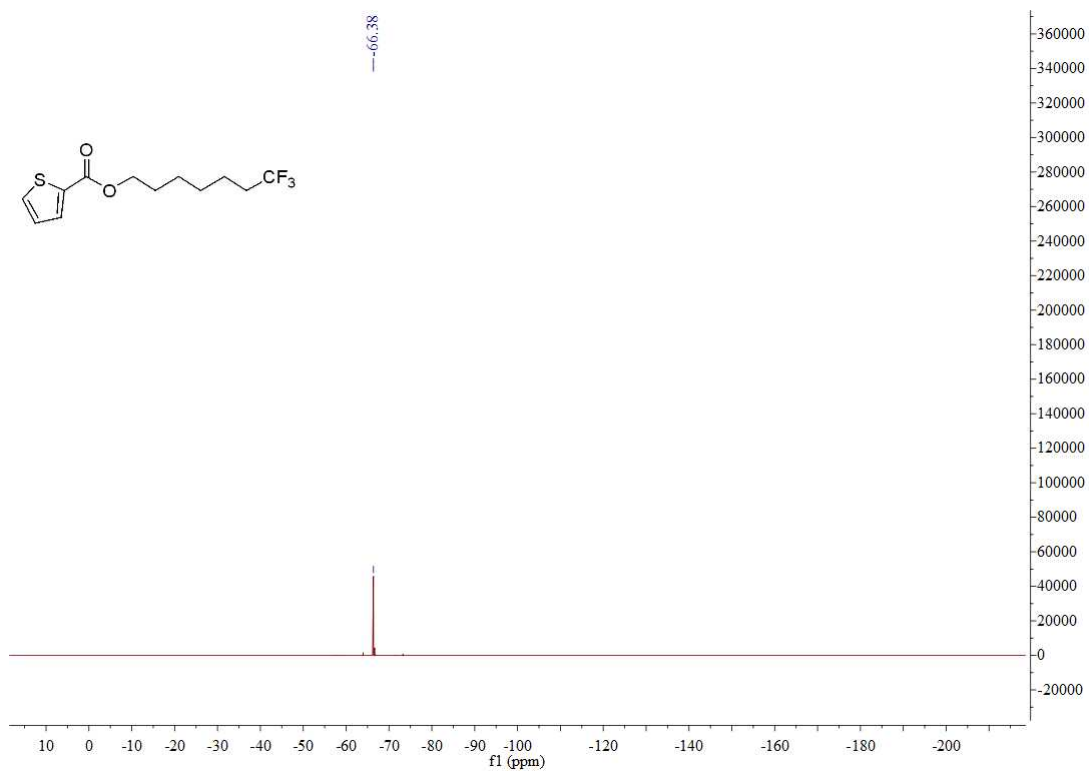
7,7,7-trifluoroheptyl furan-2-carboxylate (3r)



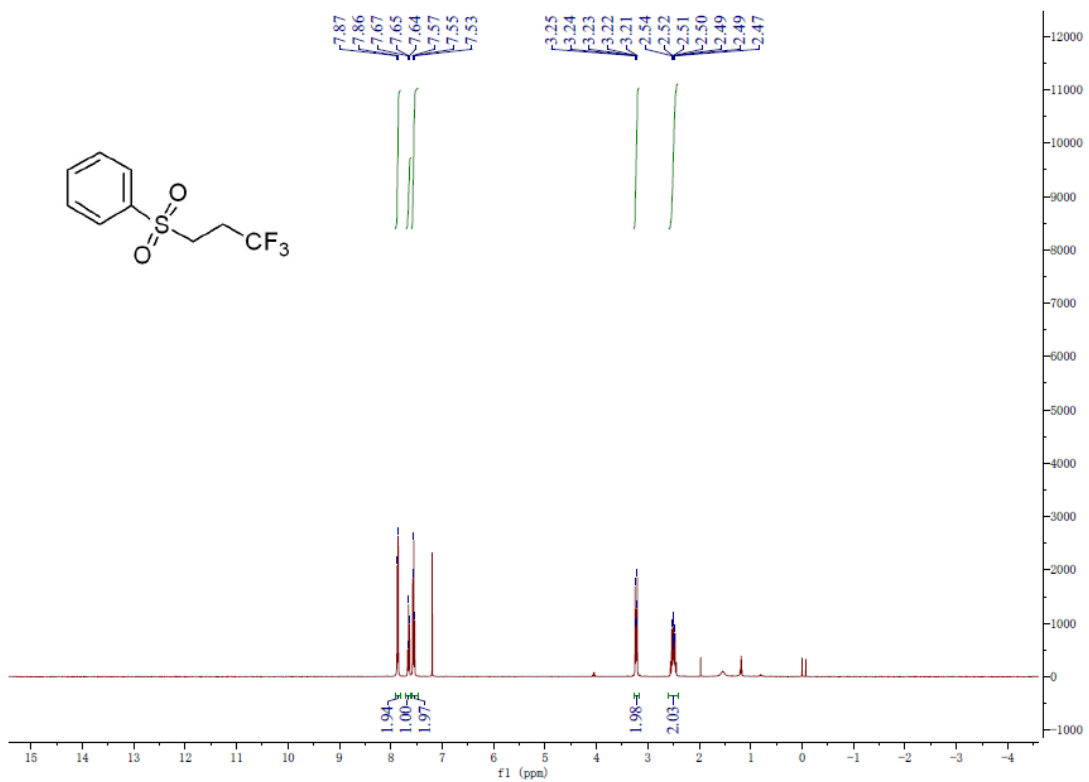


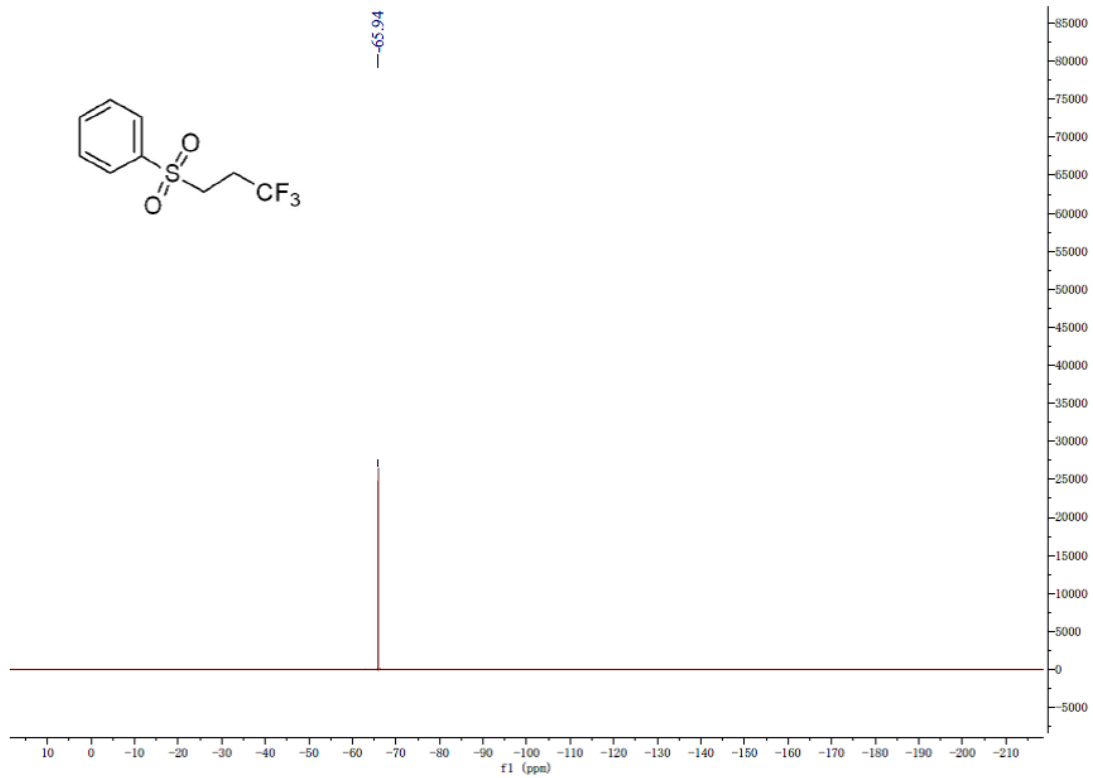
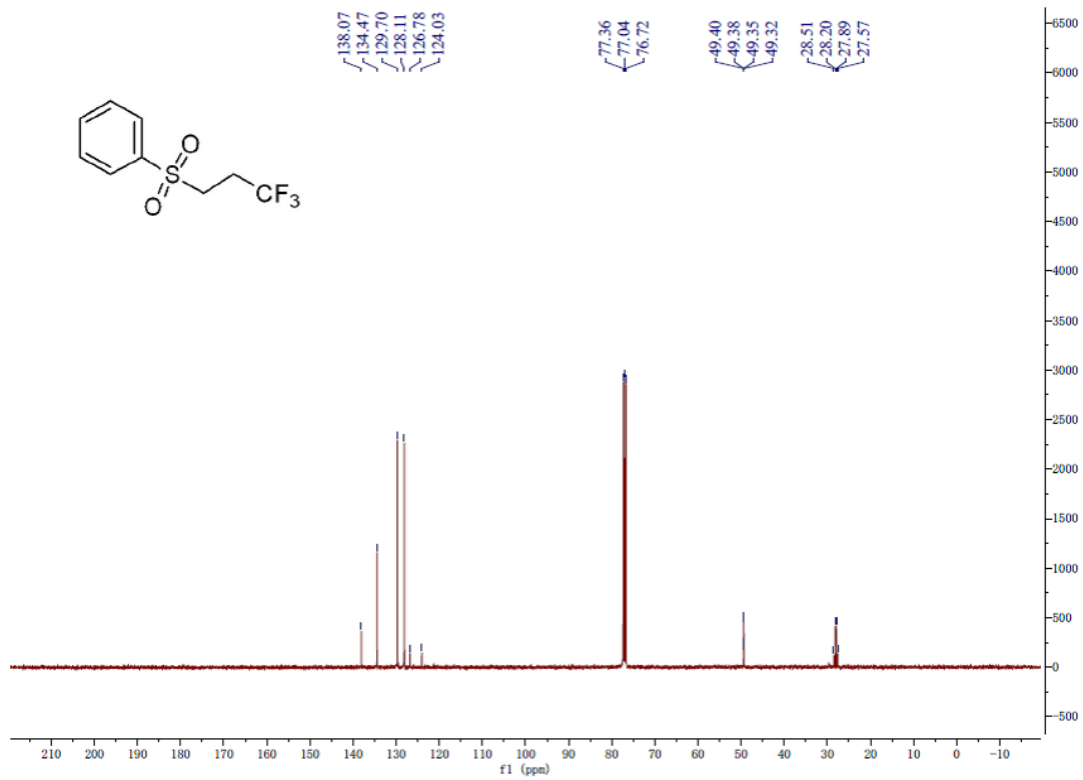
7,7,7-trifluoroheptyl thiophene-2-carboxylate (3s)



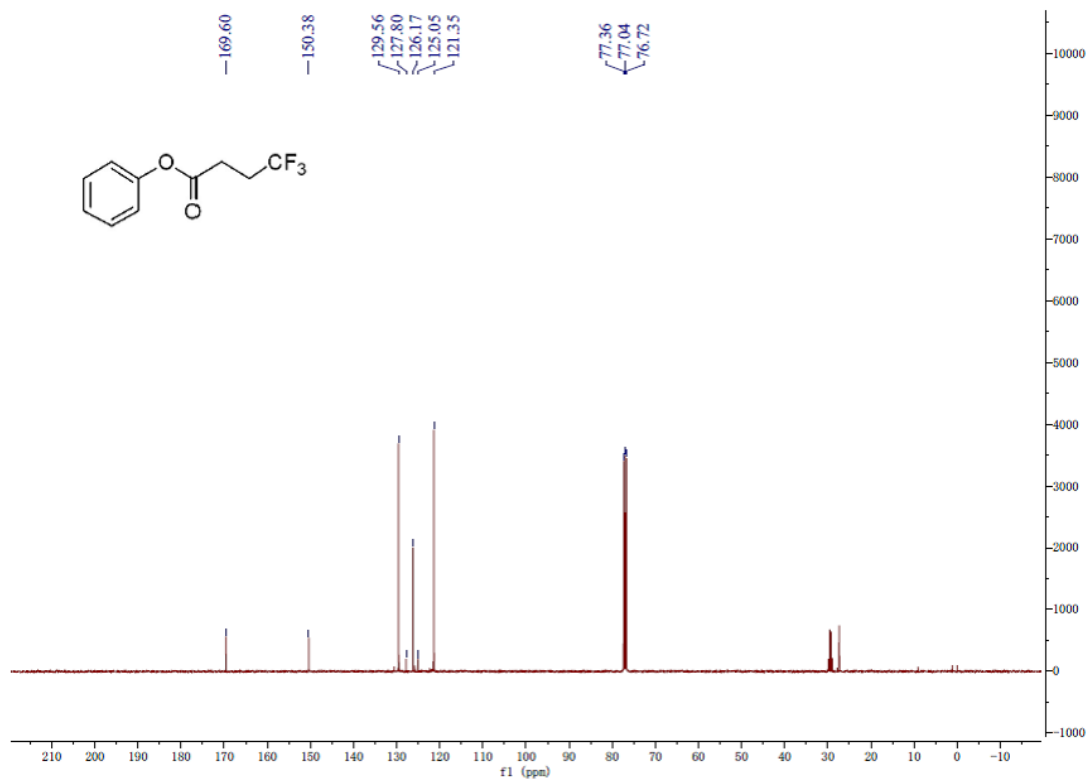
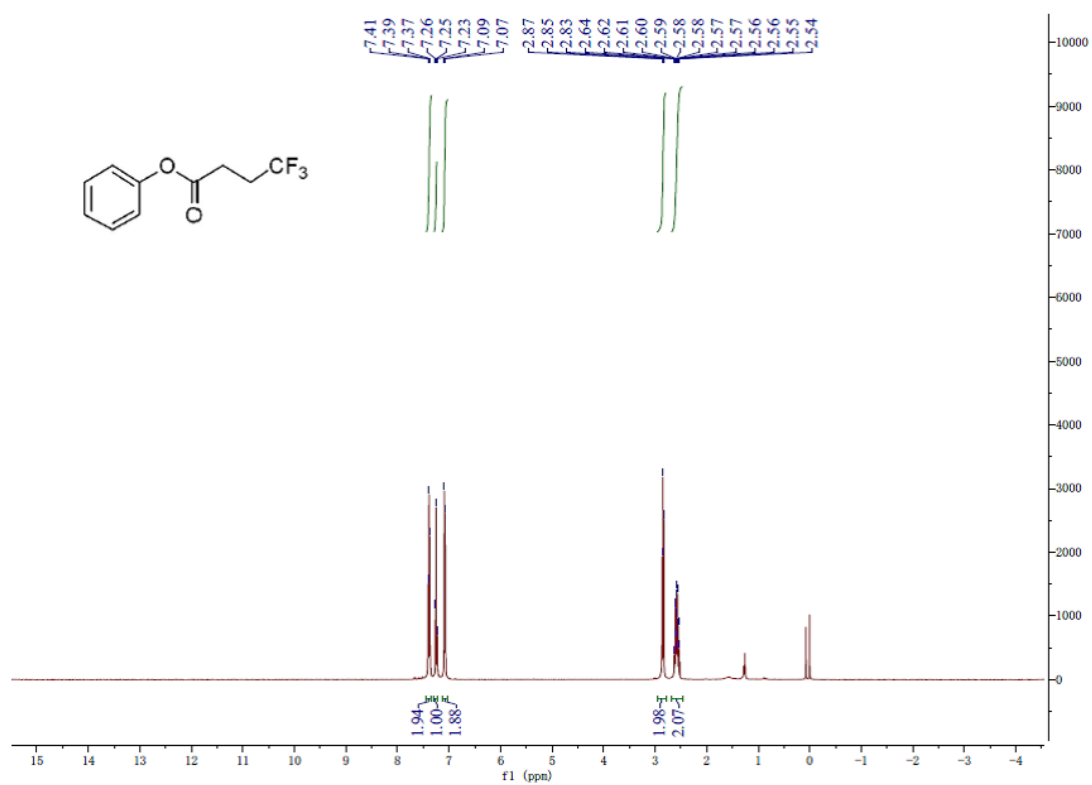


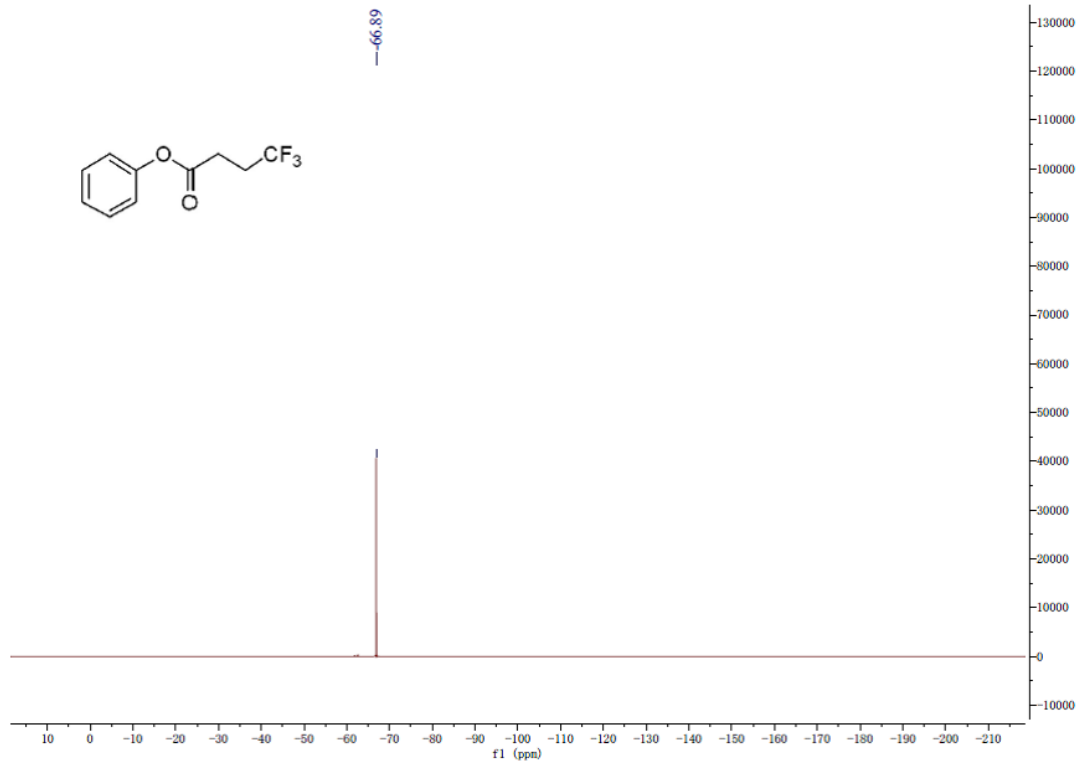
((3,3,3-trifluoropropyl)sulfonyl)benzene (3t)



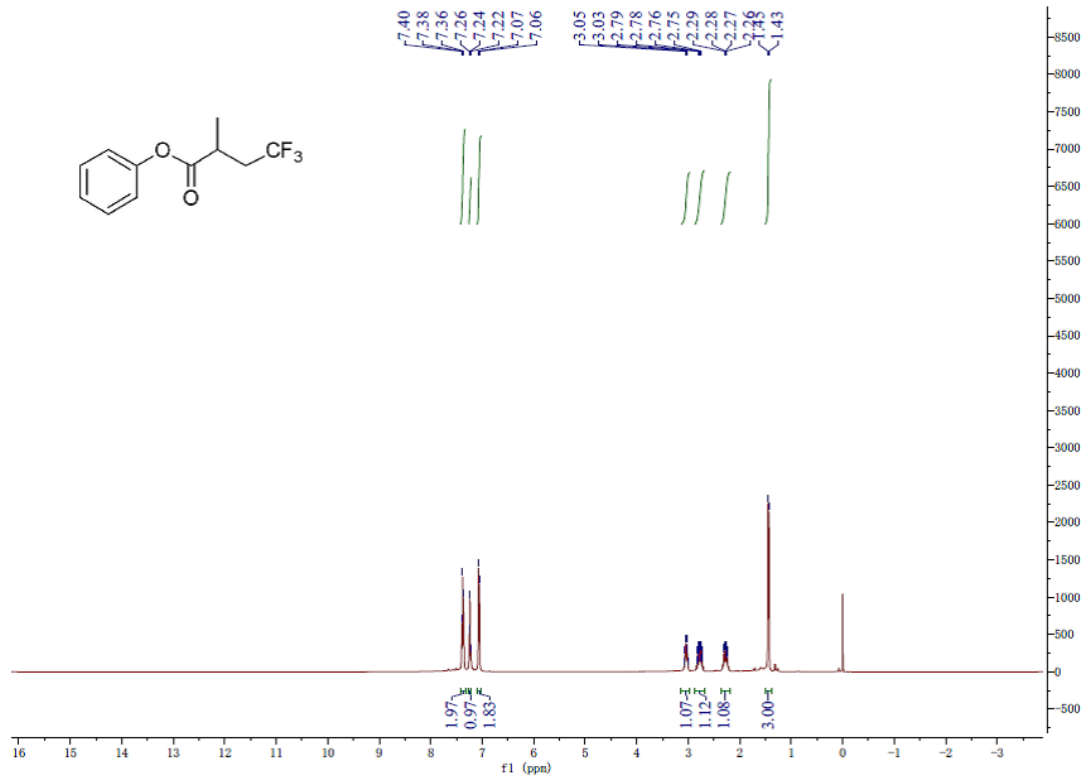


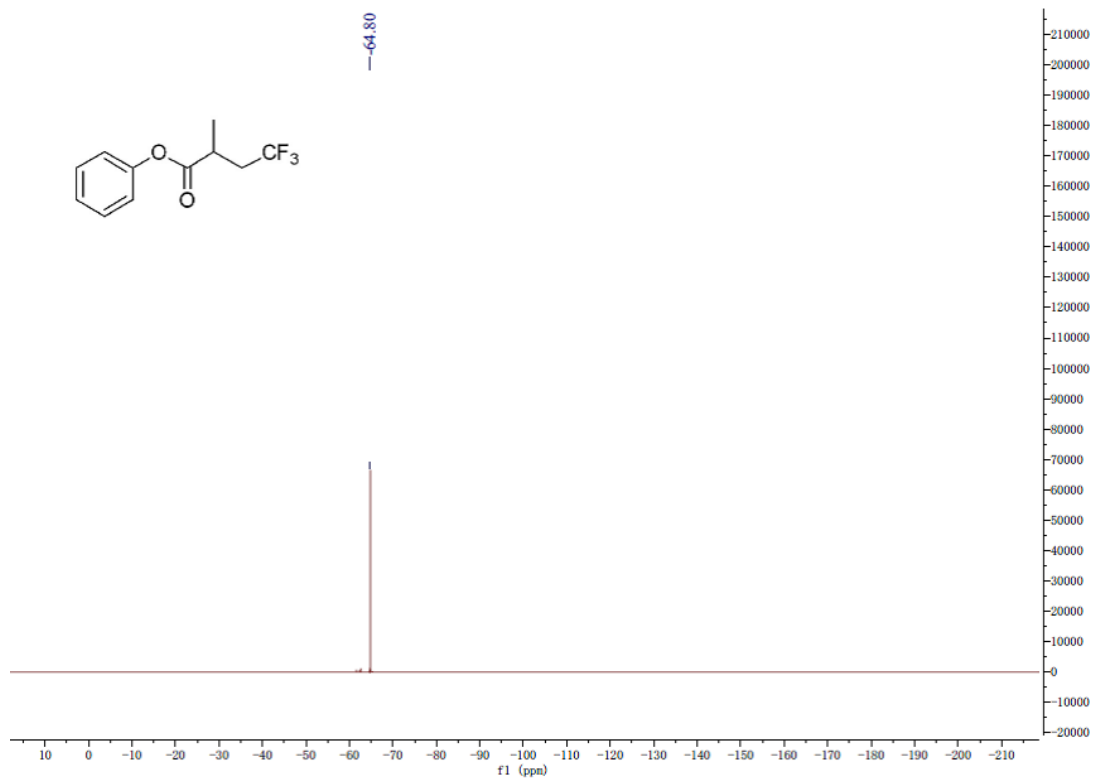
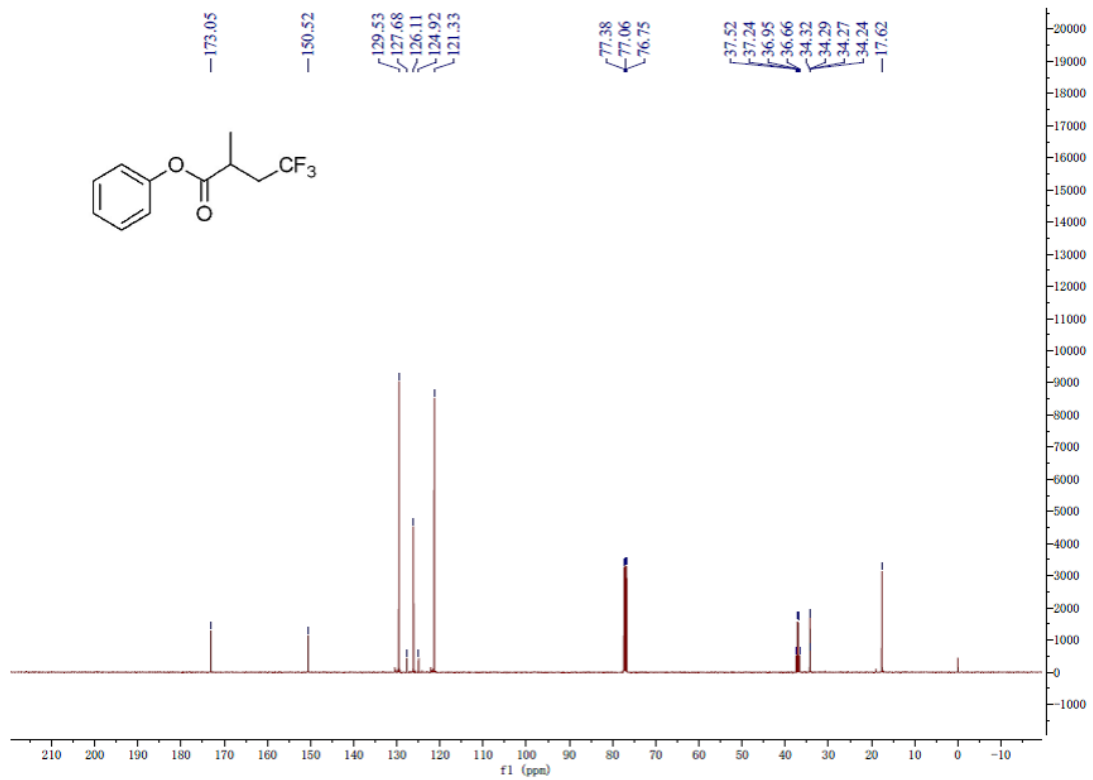
phenyl 4,4,4-trifluorobutanoate (3u)



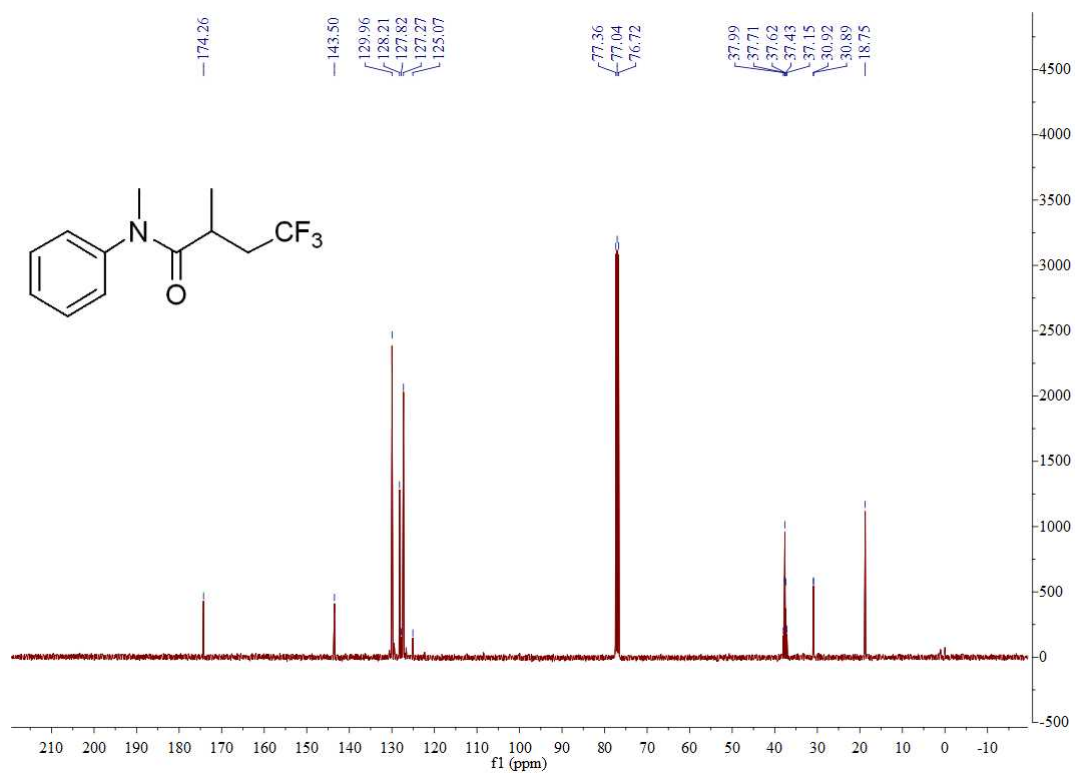
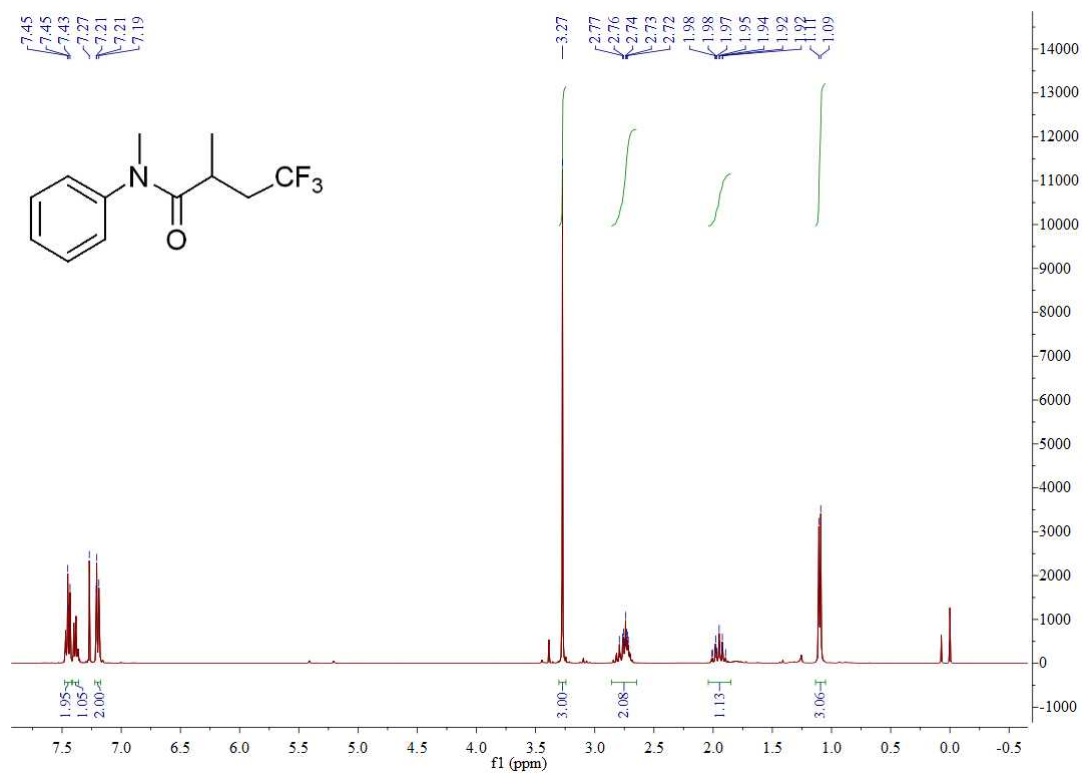


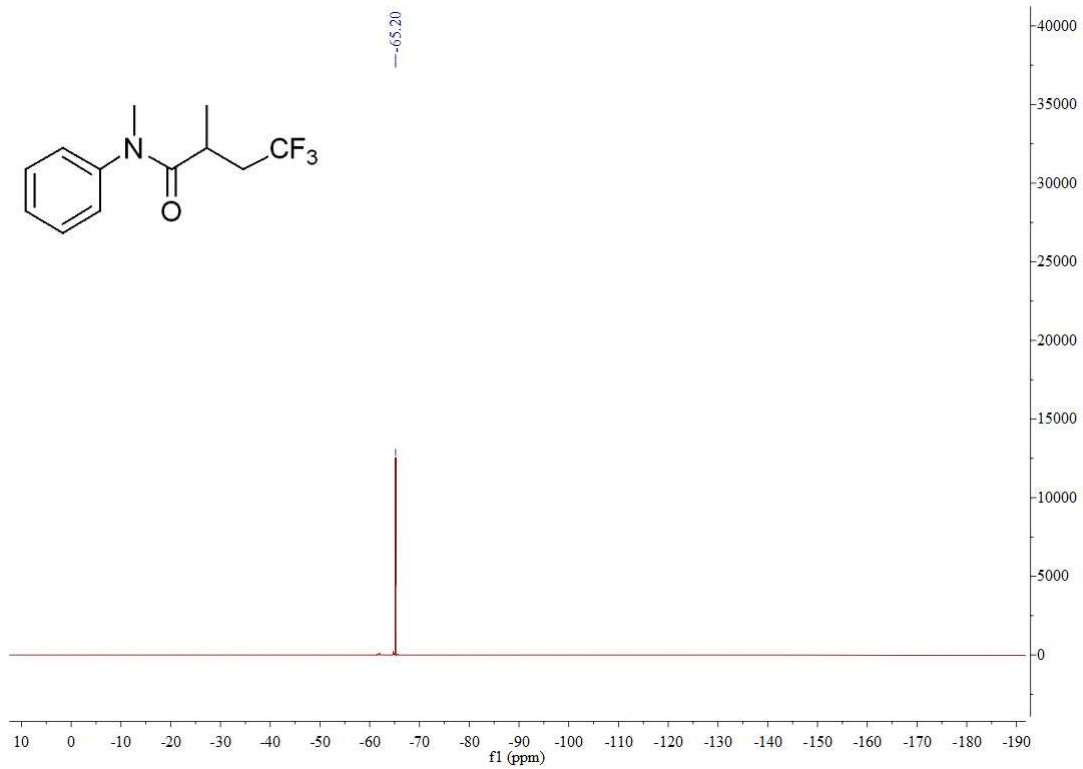
phenyl 4,4,4-trifluoro-2-methylbutanoate (3v)



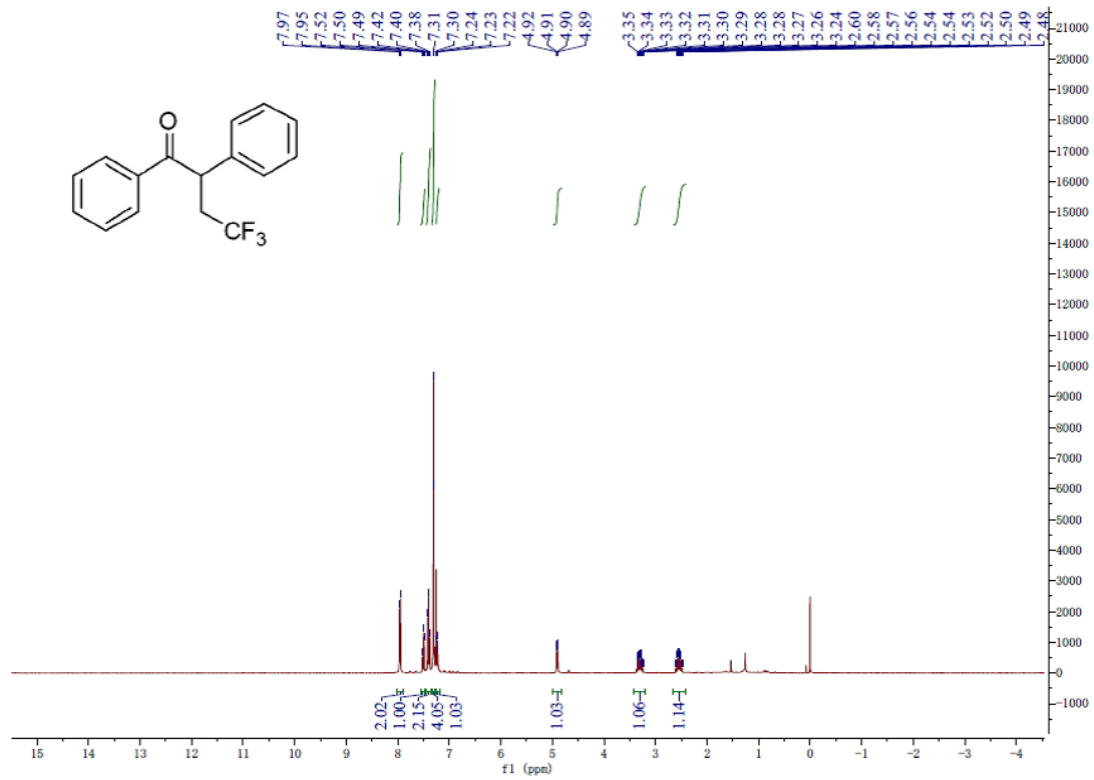


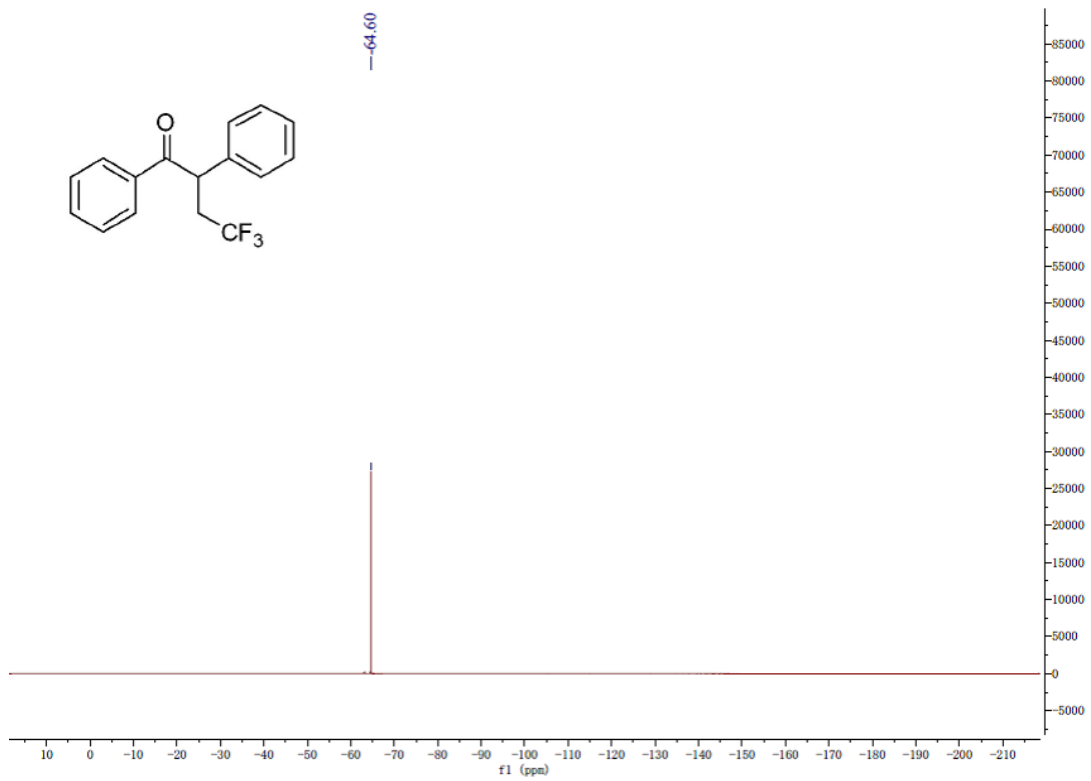
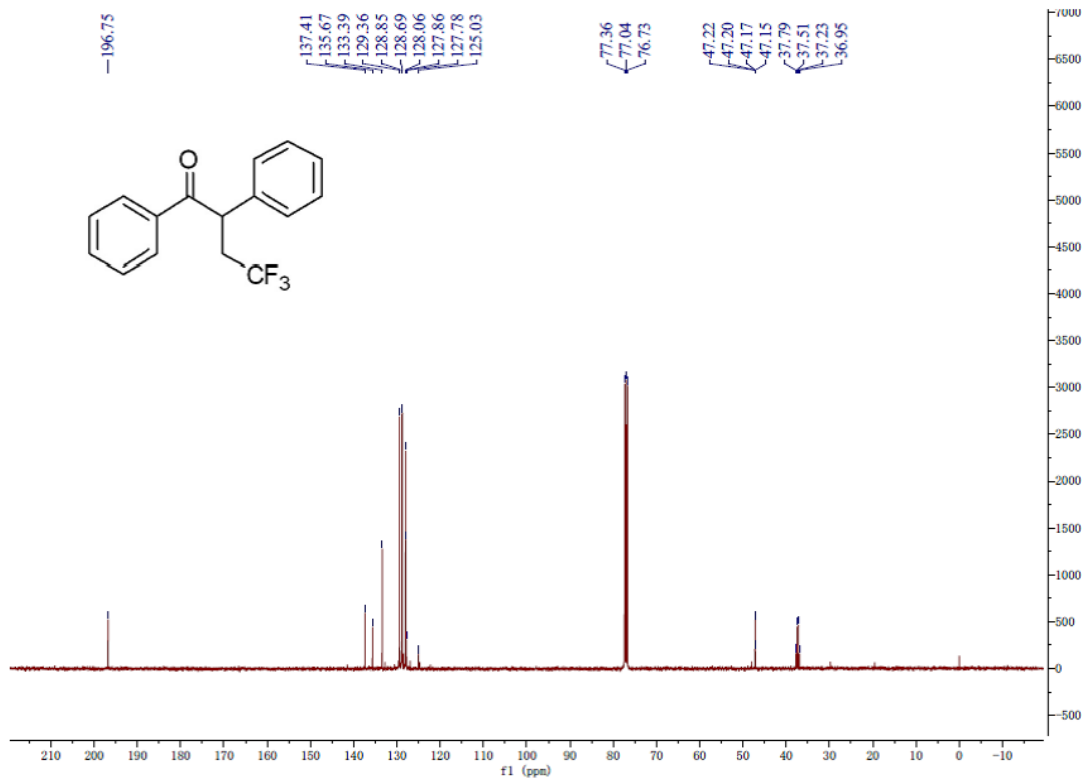
4,4,4-trifluoro-N,2-dimethyl-N-phenylbutanamide (3w)



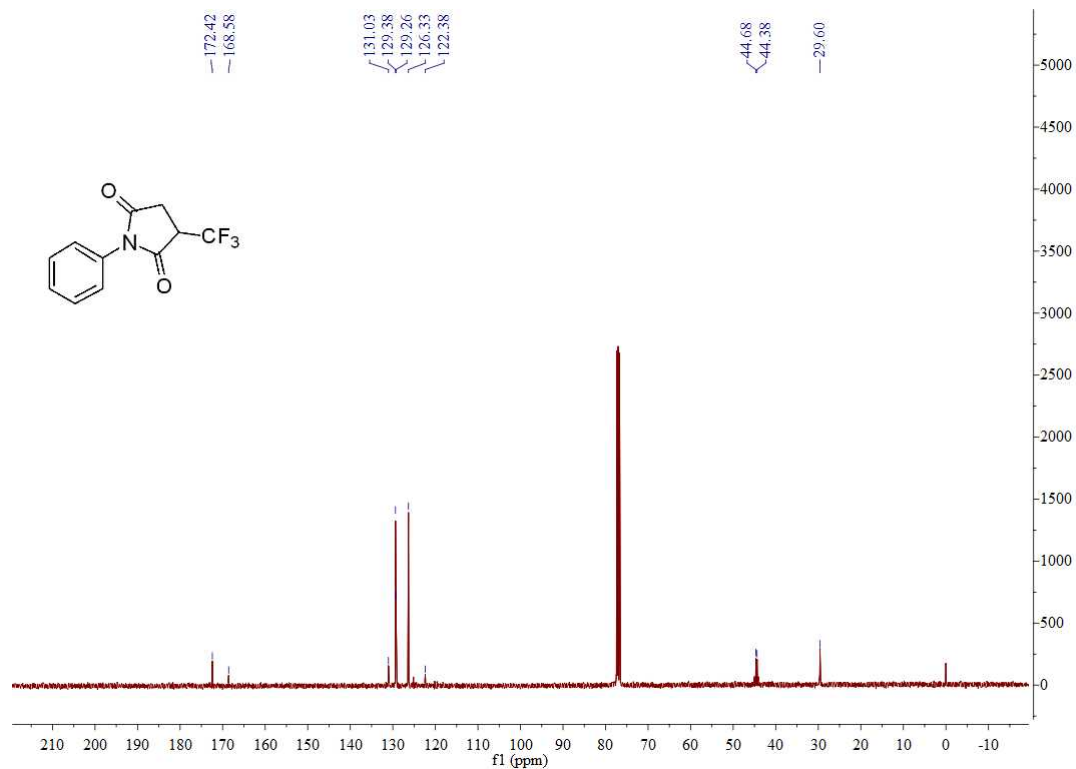
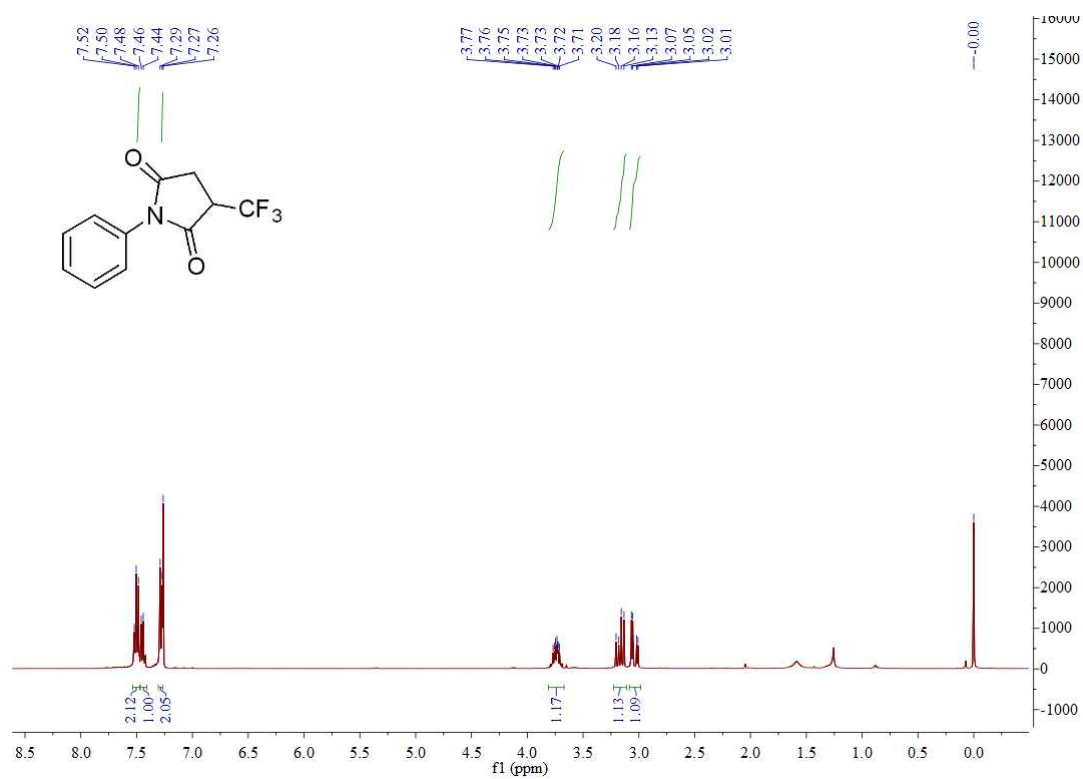


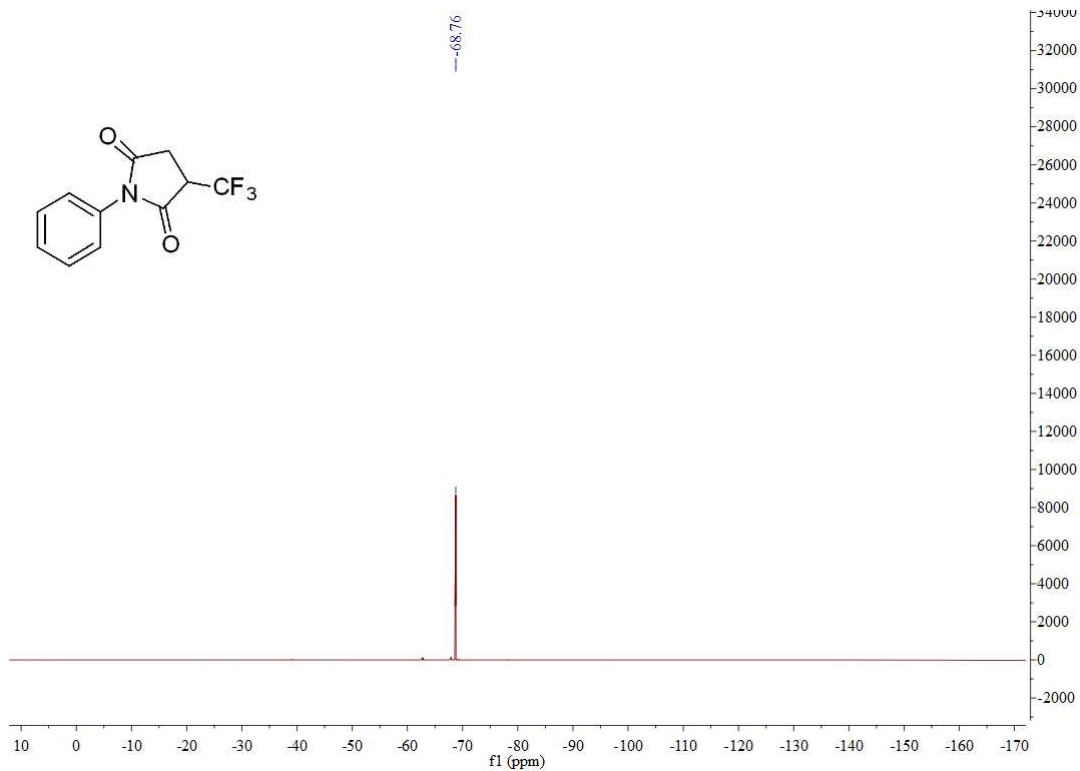
4,4,4-trifluoro-1,2-diphenylbutan-1-one (3x)



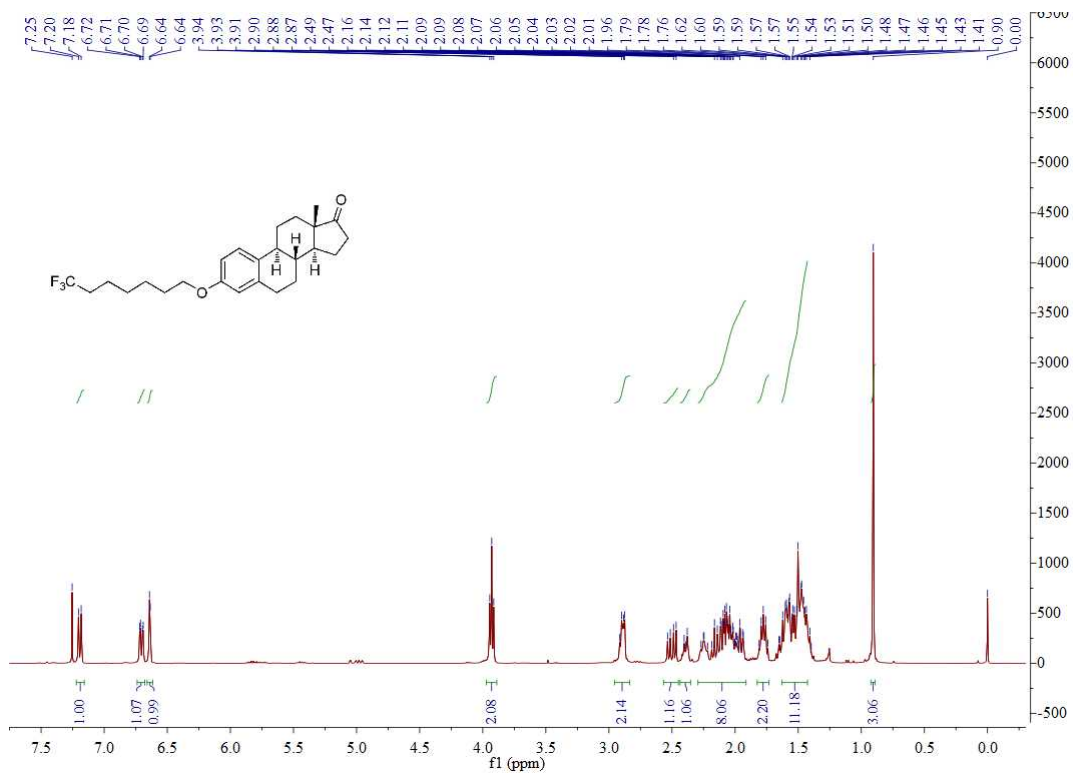


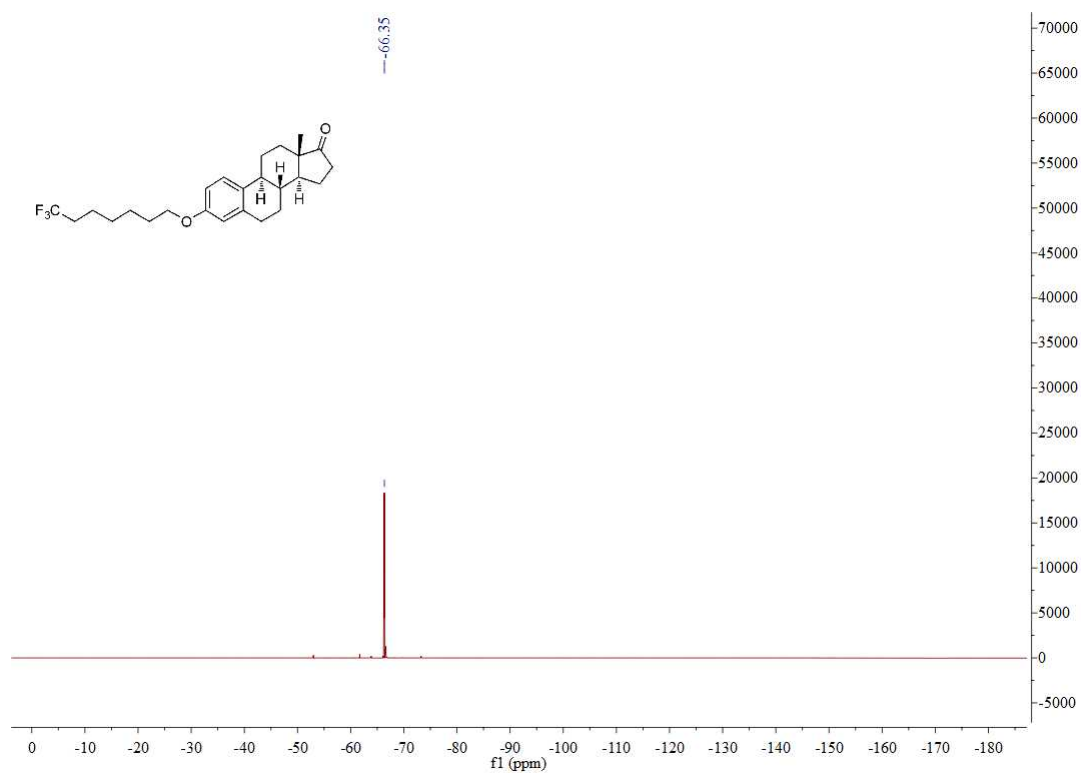
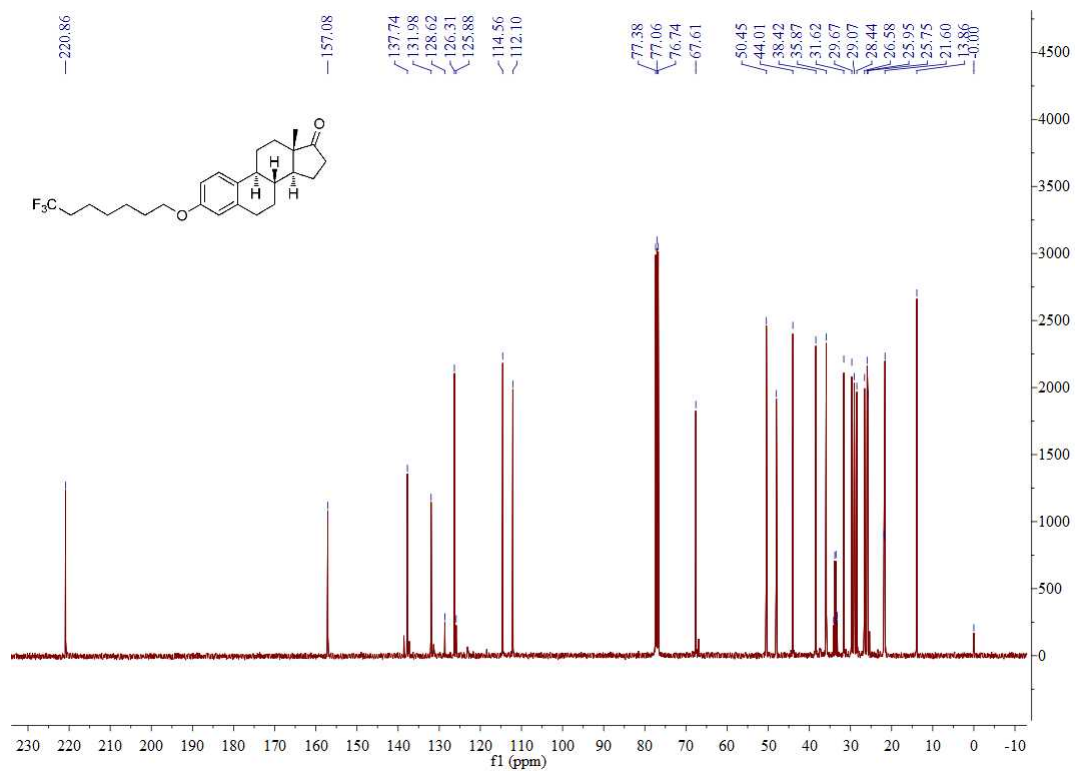
1-phenyl-3-(trifluoromethyl)pyrrolidine-2,5-dione (3y)





(8R,9S,13S,14S)-13-methyl-3-((7,7,7-trifluoroheptyl)oxy)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (3za)





((7,7,7-trifluoroheptyl)oxy)benzene (3a-D)

