

Supporting Information

Perfluoroalkoxylation Reaction via Dual Concurrent Catalysis

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1. General

• Instrumentation.

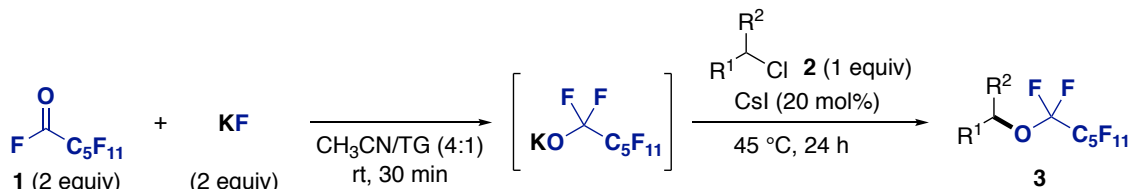
NMR spectra were obtained on a Bruker Ascend 400 spectrometer. Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in hertz (Hz). ^1H and ^{13}C spectra were referenced to tetramethylsilane as an internal standard. The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sep = septet, m = multiplet, brs = broad singlet, and brd = broad doublet. Melting points were determined with OptiMelt Automated Melting Point System and uncorrected. IR spectra were obtained on a JASCO FT/IR-4700 spectrophotometer. High resolution mass spectra were measured on a Bruker micrOTOF-II spectrometer using the APCI mode or the ESI mode. Low resolution mass spectra were obtained on either an Agilent 7890A/5975C or 7890B/5977A spectrometers using the EI mode. Yamazen medium pressure liquid chromatography (MPLC) system (EPCLC-W-Prep 2XY A-Type) and JAI Recycling Preparative HPLC (GPC) (LC-9110 II NEXT, mobile phase: chloroform) were used for purification of products.

• Materials.

Unless otherwise noted, materials were purchased from FUJIFILM Wako Pure Chemical Corporation, Tokyo Chemical Industry Co., Ltd., Sigma-Aldrich Co., LLC., and other commercial suppliers. Anhydrous MeCN was purchased from Kanto Chemical Co., Inc. Tetraglyme was distilled over Na/benzophenone and stored in an argon filled Schlenk tube. $\text{C}_5\text{F}_{11}\text{COF}$ was distilled under an argon atmosphere and stored in an argon-filled Schlenk tube. KF, KI, NaI, RbI, CsF, and CsI were finely ground using a mortar and pestle in an argon-filled glovebox, dried at 180 °C under reduced pressure ($< 2.0 \times 10^{-1}$ Torr) for a minimum of 12 hours outside of the box, and stored in a glovebox. All other chemicals were of reagent grade and used as received. Air- and moisture-sensitive manipulations were performed with standard Schlenk techniques under argon atmosphere. Medium pressure liquid chromatography was performed using the disposable Hi-flash premium silica column (w003-01) or amino column (w093-01) from Yamazen Co., and thin-layer chromatography was carried out on 0.25 mm Merck silica gel plates (60F-254).

2. Experimental Details

General Procedure



In an argon-filled glovebox, KF (58.1 mg, 1.0 mmol, 2.0 equiv) and CsI (26.0 mg, 0.10 mmol, 20 mol%) were added to a flame-dried 10 ml Schlenk tube, which was then taken out from the box. To the tube were added anhydrous MeCN (1.0 ml), anhydrous tetraglyme (0.25 ml), and C₅F₁₁COF (**1**) (316.1 mg, 1.0 mmol, 2.0 equiv) at rt, then the resultant mixture was stirred for 30 min before alkyl chloride (0.50 mmol, 1.0 equiv) was added. The reaction was stirred at 45 °C for 24 h, cooled to rt and quenched with H₂O, followed by extraction with Et₂O x 4. The combined organic layer was dried over MgSO₄, filtered and concentrated under reduced pressure.

Purification Method A

The crude residue was purified by MPLC (eluted typically with hexane or a mixture of hexane and CH₂Cl₂). If required, materials were further purified with GPC.

Purification Method B

To the crude residue dissolved in Et₂O was added 0.5 N NaOH aq. (2 ml), then the mixture was stirred overnight in order to hydrolyze perfluoroalkyl esters. The product was extracted with Et₂O x 4, dried over MgSO₄, filtered, and concentrated under reduced pressure, followed by purification with GPC.

Preparation of Substrates

Alkyl chlorides **2p**,¹ **2q**,² **2u**,³ **4d**,⁴ and **4f**⁵ were prepared from the corresponding alcohols according to the reported protocols. Other alkyl chlorides were all commercially available and were used as received.

1 Q. Huang, S. Z. Zard, *Org. Lett.*, 2017, **19**, 3895-3898.

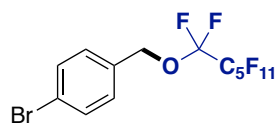
2 Q. Tian, J. Bai, B. Chen, G. Zhang, *Org. Lett.*, 2016, **18**, 1828-1831.

3 Y. Miura, S. Onogi, T. Fukuda, *Molecules*, 2012, **17**, 11877-11896.

4 B. Xu, U. K. Tambar, *ACS Catal.*, 2019, **9**, 4627-4631.

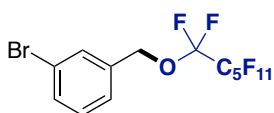
5 T. Y. R. Chen, M. R. Anderson, S. Grossman, D. G. Peters, *J. Org. Chem.*, 1987, **52**, 1231-1236.

1-bromo-4-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzene (3a)



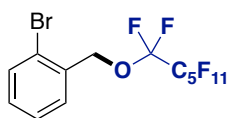
Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC), the titled compound was obtained as colorless oil in 67% yield (169.2 mg). **¹H NMR (400 MHz, CDCl₃):** δ 5.01 (s, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ 66.6 (t, *J* = 5.8 Hz), 110.3-110.7 (m), 114.3 (apparent t, *J* = 29.9 Hz), 115.9 (apparent t, *J* = 32.8 Hz), 117.0 (apparent t, *J* = 29.9 Hz), 118.8 (apparent t, *J* = 32.8 Hz), 119.7 (apparent t, *J* = 30.6 Hz), 123.2, 129.7, 132.1, 133.0. **¹⁹F NMR (376 MHz, CDCl₃):** δ -126.2- -126.1 (m, 2F), -125.14- -125.07 (m, 2F), -122.9 (brs, 2F), -122.3 (brs, 2F), -84.8 (brs, 2F), -80.8 (t, *J* = 9.2 Hz, 3F). **IR (ATR-IR):** 2963, 2898, 1492, 1333, 1195, 1145, 1097, 1072, 1014, 843, 804, 734, 708, 561, 573, 530, 502, 444, 424, 414 cm⁻¹. **¹. HRMS (APCI):** *m/z* calculated for C₁₃H₆BrF₁₃O [M]⁺ = 503.9389, found: 503.9378.

1-bromo-3-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzene (3b)



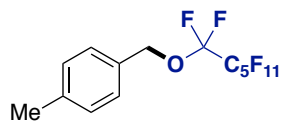
Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC), the titled compound was obtained as slightly yellowish oil in 51% yield (127.9 mg). **¹H NMR (400 MHz, CDCl₃):** δ 5.03 (s, 2H), 7.25-7.28 (m, 2H), 7.49-7.51 (m, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ 66.3 (t, *J* = 5.9 Hz), 110.1-110.9 (m), 114.3 (apparent t, *J* = 23.3 Hz), 115.9 (apparent t, *J* = 33.7 Hz), 117.0 (apparent t, *J* = 29.9 Hz), 118.0 (apparent t, *J* = 33.5 Hz), 119.7 (apparent t, *J* = 30.3 Hz), 122.9, 126.4, 130.5, 130.9, 132.2, 136.1. **¹⁹F NMR (376 MHz, CDCl₃):** δ. -126.2 (brs, 2F), -125.1 (brs, 2F), -122.9 (brs, 2F), -122.3 (brs, 2F), -85.0 (brs, 2F), -80.9 (brs, 3F). **IR (ATR-IR):** 3078, 2883, 1576, 1333, 1195, 1145, 1098, 1072, 991, 848, 773, 735, 709, 659, 570, 529, 467, 442, 409 cm⁻¹. **HRMS (APCI):** *m/z* calculated for C₁₃H₆BrF₁₃O [M]⁺ = 503.9389, found: 503.9379.

1-bromo-2-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzene (3c)



Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC), the titled compound was obtained as yellowish oil in 52% yield (132.0 mg). **¹H NMR (400 MHz, CDCl₃):** δ 5.17 (s, 2H), 7.23 (ddd, *J* = 7.6, 7.3, 1.2 Hz, 1H), 7.36 (ddd, *J* = 7.6, 7.6, 0.7 Hz, 1H), 7.42 (apparent d, *J* = 7.6 Hz, 1H), 7.59 (dd, *J* = 7.3, 0.7 Hz, 1H). **¹³C NMR (100 MHz, CDCl₃):** δ 66.9 (t, *J* = 5.9 Hz), 110.3-110.7 (m), 114.3 (apparent t, *J* = 29.1 Hz), 115.9 (apparent t, *J* = 32.8 Hz), 117.0 (apparent t, *J* = 30.3 Hz), 118.8 (apparent t, *J* = 37.0 Hz), 119.8 (apparent t, *J* = 29.1 Hz), 122.7, 127.9, 129.2, 130.3, 133.0, 133.5. **¹⁹F NMR (376 MHz, CDCl₃):** δ -126.2- -126.1 (m, 2F), -125.1 (brs, 2F), -122.9 (brs, 2F), -122.3 (brs, 2F), -85.3 (brs, 2F), -80.9 (t, *J* = 9.4 Hz, 3F). **IR (ATR-IR):** 3062, 2960, 1445, 1333, 1195, 1145, 1098, 1032, 813, 746, 708, 657, 570, 529, 453, 419, 410 cm⁻¹. **HRMS (APCI):** *m/z* calculated for C₁₃H₆BrF₁₃O [M]⁺ = 503.9389, found: 503.9371.

1-methyl-4-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzene (3d)

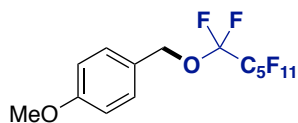


Following the Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC), the titled compound was obtained as colorless oil in 79% yield (173.1 mg). **¹H NMR (400 MHz, CDCl₃):** δ 2.35 (s, 3H), 5.01 (s, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ 21.3, 67.4 (t, *J* = 5.9 Hz), 110.3-110.7 (m), 114.3 (apparent t, *J* = 29.9 Hz), 115.9 (apparent t, *J* = 31.0 Hz), 117.1 (apparent t, *J* = 29.9 Hz), 118.8 (apparent t, *J* = 32.8 Hz), 119.7 (apparent t, *J* = 37.2 Hz), 128.3, 129.6, 131.0, 139.0. **¹⁹F NMR (376 MHz, CDCl₃):** δ -126.25- -126.16 (m, 2F), -125.2- -125.1 (m, 2F), -122.9 (brs, 2F), -122.3 (brs, 2F), -84.6 (brs, 2F), -80.9 (t, *J* = 10.2 Hz, 3F). **IR (ATR-IR):** 3001, 2920, 1333, 1195, 1146, 1096, 988, 911, 844, 797, 732, 709, 658, 573, 529, 475, 450, 435 cm⁻¹. **HRMS (APCI):** *m/z* calculated for C₁₄H₉F₁₃O [M]⁺ = 440.0440, found: 440.0442.

Large Scale Reaction:

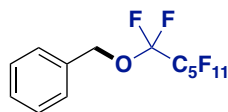
In an argon-filled glovebox, KF (581 mg, 10 mmol, 2.0 equiv) and CsI (260 mg, 1.0 mmol, 20 mol%) were added to a flame-dried 30 ml Schlenk tube, which was then taken out from the box. To the tube were added anhydrous MeCN (10 ml), anhydrous tetraglyme (2.5 ml), and C₃F₁₁COF (**1**) (3.16 g, 10 mmol, 2.0 equiv) at rt, then the resultant mixture was stirred for 30 min before 4-MeBnCl (703 mg, 5.0 mmol, 1.0 equiv) was added. The reaction was stirred at 45 °C for 24 h, cooled to rt and quenched with H₂O, followed by extraction with Et₂O x 4. The combined organic layer was dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by MPLC using hexane as an eluent, followed by a recycling preparative HPLC (GPC) afforded the product **9** as colorless oil in 70% yield (1.55 g).

1-methoxy-4-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzene (3e)



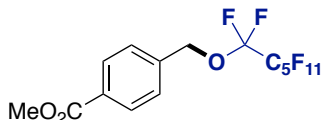
Following the Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, amino column was used), the titled compound was obtained as colorless oil in 74% yield (168.5 mg). **¹H NMR (400 MHz, CDCl₃):** δ 3.80 (s, 3H), 4.99 (s, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.8 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ 55.3, 67.4 (t, *J* = 5.9 Hz), 110.3-110.7 (m), 114.2 (3C, overlapped), 115.9 (apparent t, *J* = 31.0 Hz), 117.1 (apparent t, *J* = 29.9 Hz), 118.8 (apparent t, *J* = 32.8 Hz), 119.8 (apparent t, *J* = 33.6 Hz), 119.8 (apparent t, *J* = 29.8 Hz), 126.0, 130.1, 160.3. **¹⁹F NMR (376 MHz, CDCl₃):** δ -126.2- -126.1 (m, 2F), -125.13- -125.06 (m, 2F), -122.9 (brs, 2F), -122.3 (brs, 2F), -84.3 (brs, 2F), -80.8 (t, *J* = 9.2 Hz, 3F). **IR (ATR-IR):** 2836, 1615, 1518, 1305, 1194, 1173, 1144, 1091, 1037, 822, 706, 526, 469, 427, 411 cm⁻¹. **HRMS (APCI):** *m/z* calculated for C₁₄H₉F₁₃O₂ [M]⁺ = 456.0389, found: 456.0385.

(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzene (3f)



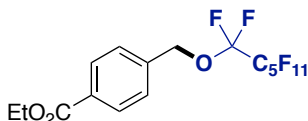
Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC), the titled compound was obtained as colorless oil in 53% yield (113.7 mg). **¹H NMR (400 MHz, CDCl₃):** δ 5.07 (s, 2H), 7.34-7.43 (m, 5H). **¹³C NMR (100 MHz, CDCl₃):** δ 67.3 (t, *J* = 5.9 Hz), 110.2-110.7 (m), 114.1 (apparent t, *J* = 29.9 Hz), 115.7 (apparent t, *J* = 33.6 Hz), 116.8 (apparent t, *J* = 29.9 Hz), 118.6 (apparent t, *J* = 41.3 Hz), 119.6 (apparent t, *J* = 29.9 Hz), 128.0, 128.9, 129.0, 133.9. **¹⁹F NMR (376 MHz, CDCl₃):** δ -126.22- -126.16 (m, 2F), -125.1 (brs, 2F), -122.9 (brs, 2F), -122.3 (brs, 2F), -84.7 (brs, 2F), -80.9 (t, *J* = 8.8 Hz, 3F). **IR (ATR-IR):** 3090, 3069, 3034, 1333, 1195, 1146, 1097, 989, 906, 840, 813, 734, 708, 695, 660, 570, 528, 479, 448, 427, 418 cm⁻¹. **HRMS (APCI):** *m/z* calculated for C₁₃H₇F₁₃O₂ [M]⁺⁺ = 426.0284, found: 426.0279.

methyl 4-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzoate (3g)



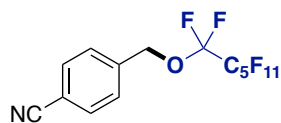
Following the **General procedure** and **Purification Method A** (eluent: hexane/CH₂Cl₂ 2:1), the titled compound was obtained as colorless oil in 51% yield (122.2 mg). **¹H NMR (400 MHz, CDCl₃):** δ 3.93 (s, 3H), 5.13 (s, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 8.08 (d, *J* = 8.1 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ 52.4, 66.5 (t, *J* = 5.9 Hz), 110.2-110.7 (m), 114.3 (apparent t, *J* = 29.2 Hz), 115.9 (apparent t, *J* = 32.8 Hz), 117.0 (apparent t, *J* = 29.9 Hz), 118.7 (apparent t, *J* = 32.8 Hz), 119.7 (apparent t, *J* = 29.9 Hz), 127.5, 130.2, 130.7, 138.8, 166.7. **¹⁹F NMR (376 MHz, CDCl₃):** δ -126.2- -126.1 (m, 2F), -125.14- -125.06 (m, 2F), -122.9 (brs, 2F), -122.3 (brs, 2F), -85.0 (brs, 2F), -80.8 (t, *J* = 10.3 Hz, 3F). **IR (ATR-IR):** 2960, 2855, 1726, 1438, 1333, 1281, 1194, 1145, 1098, 1021, 991, 844, 811, 755, 709, 661, 572, 531, 470, 458, 447, 422, 414 cm⁻¹. **HRMS (APCI):** *m/z* calculated for C₁₅H₁₀F₁₃O₃ [M+H]⁺ = 485.0417, found: 485.0400.

ethyl 4-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzoate (3h)



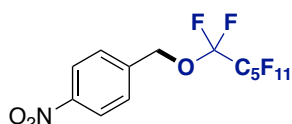
Following the **General procedure** and **Purification Method A** (eluent: hexane/CH₂Cl₂ 3:1), the titled compound was obtained as colorless oil in 50% yield (125.0 mg). **¹H NMR (400 MHz, CDCl₃):** δ 1.40 (t, *J* = 7.1 Hz, 3H), 4.39 (q, *J* = 7.1 Hz, 2H), 5.13 (s, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 8.08 (d, *J* = 8.1 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ 14.4, 61.3, 66.6 (t, *J* = 5.9 Hz), 110.3-110.7 (m), 114.3 (apparent t, *J* = 29.9 Hz), 115.9 (apparent t, *J* = 32.8 Hz), 117.0 (apparent t, *J* = 29.9 Hz), 118.8 (apparent t, *J* = 32.2 Hz), 119.8 (apparent t, *J* = 30.4 Hz), 127.5, 130.1, 131.1, 138.7, 166.2. **¹⁹F NMR (376 MHz, CDCl₃):** δ -126.2- -126.1 (m, 2F), -125.14- -125.07 (m, 2F), -122.9 (brs, 2F), -122.3 (brs, 2F), -85.0 (brs, 2F), -80.8 (t, *J* = 10.3 Hz, 3F). **IR (ATR-IR):** 2982, 2920, 2848, 1720, 1333, 1276, 1196, 1146, 1099, 1023, 852, 813, 755, 709, 661, 572, 529, 481, 436, 419, 404 cm⁻¹. **HRMS (APCI):** *m/z* calculated for C₁₆H₁₂F₁₃O₃ [M+H]⁺ = 499.0573, found: 499.0553.

4-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzonitrile (3i)



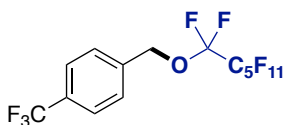
Following the **General procedure** and **Purification Method A** (eluent: hexane/CH₂Cl₂ 4:1), the titled compound was obtained as colorless oil in 53% yield (119.7 mg). **¹H NMR (400 MHz, CDCl₃):** δ 5.14 (s, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ 66.0 (t, *J* = 5.9 Hz), 110.3-110.6 (m), 112.9, 114.2 (apparent t, *J* = 30.6 Hz), 115.8 (apparent t, *J* = 32.8 Hz), 116.9 (apparent t, *J* = 30.6 Hz), 118.4, 118.7 (apparent t, *J* = 33.8 Hz), 119.7 (apparent t, *J* = 30.6 Hz), 128.0, 132.7, 139.1. **¹⁹F NMR (376 MHz, CDCl₃):** δ -126.2- -126.1 (m, 2F), -125.13- -125.06 (m, 2F), -122.9 (brs, 2F), -122.3 (brs, 2F), -85.1 (brs, 2F), -80.8 (t, *J* = 9.4 Hz, 3F). **IR (ATR-IR):** 3054, 2952, 2230, 1333, 1227, 1193, 1144, 1094, 1020, 989, 946, 913, 843, 821, 775, 745, 724, 708, 657, 609, 573, 547, 529, 476, 419 cm⁻¹. **HRMS (APCI):** *m/z* calculated for C₁₄H₇F₁₃NO [M+H]⁺ = 452.0315, found: 452.0297.

1-nitro-4-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzene (3j)



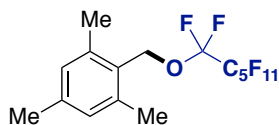
Following the **General procedure** and **Purification Method A** (eluent: hexane/CH₂Cl₂ 3:1), the titled compound was obtained as slightly yellowish oil in 56% yield (131.1 mg). **¹H NMR (400 MHz, CDCl₃):** δ 5.20 (s, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 8.28 (d, *J* = 8.6 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ 65.7 (t, *J* = 5.9 Hz), 110.2-110.7 (m), 114.2 (apparent t, *J* = 29.9 Hz), 115.8 (apparent t, *J* = 32.9 Hz), 117.0 (apparent t, *J* = 30.6 Hz), 118.7 (apparent t, *J* = 32.8 Hz), 119.7 (apparent t, *J* = 30.6 Hz), 124.2, 128.1, 140.9, 148.2. **¹⁹F NMR (376 MHz, CDCl₃):** δ -126.3- -126.2 (m, 2F), -125.1 (brs, 2F), -122.9 (brs, 2F), -122.3 (brs, 2F), -85.2 (brs, 2F), -80.9 (t, *J* = 9.6 Hz, 3F). **IR (ATR-IR):** 3082, 2957, 1610, 1527, 1349, 1195, 1145, 1098, 993, 854, 812, 769, 736, 709, 661, 571, 531, 474, 460, 437, 429, 415 cm⁻¹. **HRMS (APCI):** *m/z* calculated for C₁₃H₇F₁₃NO₃ [M+H]⁺ = 427.0213, found: 427.0214.

1-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)-4-(trifluoromethyl)benzene (3k)



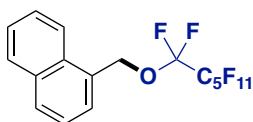
Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC), the titled compound was obtained as colorless oil in 55% yield (135.1 mg). **¹H NMR (400 MHz, CDCl₃):** δ 5.12 (s, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ 66.3 (t, *J* = 5.8 Hz), 110.4-110.7 (m), 114.3 (apparent t, *J* = 29.9 Hz), 115.9 (apparent t, *J* = 33.5 Hz), 117.0 (apparent t, *J* = 30.6 Hz), 118.8 (apparent t, *J* = 33.6 Hz), 119.8 (apparent t, *J* = 29.9 Hz), 122.7, 125.4, 125.9, 131.3 (q, *J* = 64.9 Hz), 137.9. **¹⁹F NMR (376 MHz, CDCl₃):** δ -126.2 (brs, 2F), -125.1 (brs, 2F), -122.9 (brs, 2F), -122.3 (brs, 2F), -85.1 (brs, 2F), -80.9 (apparent brd, *J* = 9.4 Hz, 3F), -62.9 (s, 3F). **IR (ATR-IR):** 2911, 1326, 1198, 1132, 1098, 1067, 1020, 823, 734, 708, 660, 594, 572, 529, 468, 440, 411 cm⁻¹. **HRMS (APCI):** *m/z* calculated for C₁₄H₆F₁₅O [M-F]⁺ = 475.0174, found: 475.0150.

1,3,5-trimethyl-2-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzene (3l)



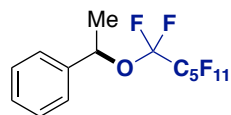
Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC), the titled compound was obtained as yellowish oil in 58% yield (135.2 mg). **¹H NMR (400 MHz, CDCl₃):** δ 2.28 (s, 3H), 2.35 (s, 6H), 5.13 (s, 2H), 6.89 (s, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ 19.2, 21.2, 62.1 (t, *J* = 6.2 Hz), 110.2-110.7 (m), 114.4 (apparent t, *J* = 29.9 Hz), 115.9 (apparent t, *J* = 32.8 Hz), 117.2 (apparent t, *J* = 29.9 Hz), 118.8 (apparent t, *J* = 33.5 Hz), 119.9 (apparent t, *J* = 29.2 Hz), 127.0, 129.3, 138.7, 139.6. **¹⁹F NMR (376 MHz, CDCl₃):** δ -126.4- -126.3 (m, 2F), -125.2 (brs, 2F), -123.1 (brs, 2F), -122.5 (brs, 2F), -85.4 (brs, 2F), -81.1 (t, *J* = 9.6 Hz, 3F). **IR (ATR-IR):** 3013, 2929, 1615, 1331, 1194, 1145, 1094, 984, 898, 853, 810, 782, 734, 707, 658, 529, 484, 465, 447, 437, 421, 410 cm⁻¹. **HRMS (APCI):** *m/z* calculated for C₁₆H₁₃F₁₃O [M]⁺ = 468.0753, found: 468.0757.

1-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)naphthalene (3m)



Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC), the titled compound was obtained as colorless oil in 63% yield (149.8 mg). **¹H NMR (400 MHz, CDCl₃):** δ 5.50 (s, 2H), 7.44 (dd, *J* = 8.1, 7.5 Hz, 1H), 7.50-7.58 (m, 3H), 7.88 (apparent d, *J* = 7.8 Hz, 2H), 7.96 (apparent d, *J* = 8.3 Hz, 1H). **¹³C NMR (100 MHz, CDCl₃):** δ 65.9 (t, *J* = 5.9 Hz), 110.3-110.7 (m), 114.5 (apparent t, *J* = 29.9 Hz), 115.9 (apparent t, *J* = 32.8 Hz), 117.3 (apparent t, *J* = 29.2 Hz), 118.8 (apparent t, *J* = 32.8 Hz), 120.0 (apparent t, *J* = 29.6 Hz), 123.2, 125.3, 126.3, 127.0, 127.6, 128.9, 129.4, 130.2, 131.5, 133.8. **¹⁹F NMR (376 MHz, CDCl₃):** δ -126.2- -126.1 (m, 2F), -125.1- -125.0 (m, 2F), -122.9 (brs, 2F), -122.3 (brs, 2F), -85.0 (brs, 2F), -80.8 (t, *J* = 9.6 Hz, 3F). **IR (ATR-IR):** 3062, 2896, 1331, 1195, 1145, 1097, 1038, 986, 904, 856, 792, 774, 735, 707, 660, 572, 529, 496, 459, 445, 421, 408 cm⁻¹. **HRMS (APCI):** *m/z* calculated for C₁₇H₉F₁₃O [M]⁺ = 476.0440, found: 476.0432.

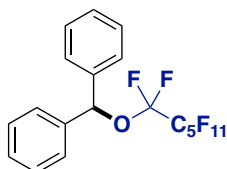
(1-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)ethyl)benzene (3n)



Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC) except for KF (3.0 equiv), **1** (3.0 equiv), and the reaction temperature (75 °C), the titled compound was obtained as slightly yellowish powder in 30% yield (151.0 mg). **Mp.: 90 °C.** **¹H NMR (400 MHz, CDCl₃):** δ 1.64 (d, *J* = 6.5 Hz, 3H), 5.52 (q, *J* = 6.5 Hz, 1H), 7.31-7.40 (m, 5H). **¹³C NMR (100 MHz, CDCl₃):** δ 23.9, 76.2 (t, *J* = 4.8 Hz), 110.3-110.7 (m), 114.3 (apparent t, *J* = 29.9 Hz), 115.9 (apparent t, *J* = 32.8 Hz), 117.1 (apparent t, *J* = 28.4 Hz), 118.8 (apparent t, *J* = 33.5 Hz), 119.8 (apparent t, *J* = 27.7 Hz), 125.7, 128.5, 128.8, 140.7. **¹⁹F NMR (376 MHz, CDCl₃):** δ -126.15- -126.07 (m, 2F), -125.5 (brs, 2F), -122.8 (brs, 2F), -122.2 (brs, 2F), -82.6 (apparent q, *J* = 11.1 Hz, 2F), -80.8 (t, *J* = 10.2 Hz, 3F). **IR (ATR-IR):** 3062, 2998, 2150, 1991, 1455, 1332, 1234, 1197, 1146, 1092, 1029, 991, 877, 842, 813, 759,

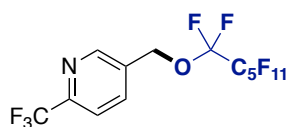
742, 708, 697, 659, 609, 567, 522, 507, 487, 473, 464, 442, 428, 418, 408 cm^{-1} . **HRMS (APCI):** m/z calculated for $\text{C}_{14}\text{H}_9\text{F}_{13}\text{O}$ $[\text{M}]^{++} = 440.0440$, found: 440.0454.

(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methylene)dibenzene (3o)



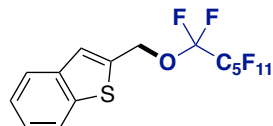
Following the **General procedure** and **Purification Method B** except for KF (3.0 equiv), **1** (3.0 equiv), and the reaction temperature (75 °C), the titled compound was obtained as fine white powder in 46% yield (114.9 mg). **Mp.:** 92 °C. **^1H NMR (400 MHz, CDCl_3):** δ 6.42 (s, 1H), 7.30-7.38 (m, 10H). **^{13}C NMR (100 MHz, CDCl_3):** δ 80.2 (t, $J = 4.4$ Hz), 110.1-111.0 (m), 114.4 (apparent t, $J = 29.9$ Hz), 115.9 (apparent t, $J = 32.8$ Hz), 117.2 (apparent t, $J = 29.2$ Hz), 118.8 (apparent t, $J = 32.8$ Hz), 119.9 (apparent t, $J = 29.9$ Hz), 126.9, 128.6, 128.8, 139.2. **^{19}F NMR (376 MHz, CDCl_3):** δ -126.2- -126.1 (m, 2F), -125.05- -124.97 (m, 2F), -122.8 (brs, 2F), -122.1 (brs, 2F), -82.1 (brs, 2F), -80.8 (t, $J = 10.2$ Hz, 3F). **IR (ATR-IR):** 2963, 2920, 2848, 2360, 1338, 1224, 1132, 1093, 1028, 907, 845, 789, 741, 694, 602, 573, 519, 501, 467, 449, 435, 420, 405 cm^{-1} . **HRMS (APCI):** m/z calculated for $\text{C}_{19}\text{H}_{11}\text{F}_{13}\text{O}$ $[\text{M}]^{++} = 502.0597$, found: 502.0572.

5-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)-2-(trifluoromethyl)pyridine (3p)



Following the **General procedure** and **Purification Method A** (eluent: hexane/ CH_2Cl_2 1:1), the titled compound was obtained as colorless oil in 67% yield (166.7 mg). **^1H NMR (400 MHz, CDCl_3):** δ 5.20 (s, 2H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 8.73 (s, 1H). **^{13}C NMR (100 MHz, CDCl_3):** δ 64.0 (t, $J = 5.9$ Hz), 110.3-110.7 (m), 114.3 (apparent t, $J = 30.3$ Hz), 115.9 (apparent t, $J = 32.8$ Hz), 117.0 (apparent t, $J = 30.3$ Hz), 118.8 (apparent t, $J = 32.8$ Hz), 119.8 (apparent t, $J = 30.6$ Hz), 120.1, 120.7, 122.8, 133.0, 136.7, 149.1 (q, $J = 67.2$ Hz). **^{19}F NMR (376 MHz, CDCl_3):** δ -126.6- -126.5 (m, 2F), -125.5- -125.4 (m, 2F), -123.2 (brs, 2F), -122.6 (brs, 2F), -85.8 (brs, 2F), -81.3 (t, $J = 10.2$ Hz, 3F), -68.6 (s, 3F). **IR (ATR-IR):** 2896, 1582, 1336, 1238, 1195, 1179, 1135, 1087, 1030, 993, 841, 754, 734, 708, 665, 649, 592, 532, 509, 482, 450, 436, 425, 413 cm^{-1} . **HRMS (APCI):** m/z calculated for $\text{C}_{13}\text{H}_6\text{F}_{16}\text{NO}$ $[\text{M}+\text{H}]^+ = 496.0188$, found: 496.0194.

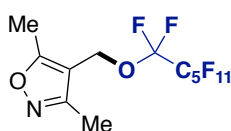
2-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzo[b]thiophene (3q)



Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC), the titled compound was obtained as fine white powder in 63% yield (151.0 mg). **Mp.:** 51 °C. **^1H NMR (400 MHz, CDCl_3):** δ 5.32 (s, 2H), 7.34 (s, 1H), 7.36-7.40 (m, 2H), 7.77-7.79 (m, 1H), 7.82-7.85 (m, 1H). **^{13}C NMR (100 MHz, CDCl_3):** δ 62.8 (t, $J = 5.9$ Hz), 110.3-110.7 (m), 114.2 (apparent t, $J = 25.5$ Hz), 115.9 (apparent t, $J = 32.8$ Hz), 116.9 (apparent t, $J = 29.9$ Hz), 118.7 (apparent t, $J = 30.5$ Hz),

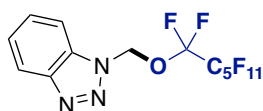
119.7 (apparent t, $J = 30.6$ Hz), 122.6, 124.2, 124.8, 125.1, 125.3, 136.5, 139.1, 140.8. **^{19}F NMR (376 MHz, CDCl_3):** δ -126.2- -126.1 (m, 2F), -125.1- -125.0 (m, 2F), -122.9 (brs, 2F), -122.3 (brs, 2F), -84.7 (brs, 2F), -80.8 (t, $J = 10.2$ Hz, 3F). **IR (ATR-IR):** 3062, 2886, 1329, 1192, 1140, 1097, 984, 918, 843, 825, 775, 746, 719, 708, 648, 564, 524, 497, 479, 461, 440, 423, 410 cm^{-1} . **HRMS (APCI):** m/z calculated for $\text{C}_{15}\text{H}_7\text{F}_{13}\text{OS}$ $[\text{M}]^{+} = 482.0005$, found: 481.9981.

3,5-dimethyl-4-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)isoxazole (3r)



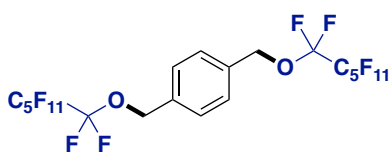
Following the **General procedure** and **Purification Method B**, the titled compound was obtained as yellowish oil in 69% yield (152.9 mg). **^1H NMR (400 MHz, CDCl_3):** δ 2.28 (s, 3H), 2.41 (s, 3H), 4.87 (s, 2H). **^{13}C NMR (100 MHz, CDCl_3):** δ 9.7, 11.0, 56.8 (t, $J = 6.4$ Hz), 108.2, 110.2-110.6 (m), 114.2 (apparent t, $J = 29.9$ Hz), 115.8 (apparent t, $J = 32.9$ Hz), 116.9 (apparent t, $J = 29.9$ Hz), 118.7 (apparent t, $J = 33.6$ Hz), 119.7 (apparent t, $J = 30.3$ Hz), 159.6, 169.0. **^{19}F NMR (376 MHz, CDCl_3):** δ -126.3- -126.2 (m, 2F), -125.2 (brs, 2F), -123.0 (brs, 2F), -122.5 (brs, 2F), -85.4 (brs, 2F), -80.9 (t, $J = 9.6$ Hz, 3F). **IR (ATR-IR):** 2883, 1642, 1430, 1333, 1235, 1194, 1145, 1097, 1039, 986, 903, 810, 778, 726, 708, 657, 571, 529, 459, 445, 431, 418, 406 cm^{-1} . **HRMS (APCI):** m/z calculated for $\text{C}_{12}\text{H}_9\text{F}_{13}\text{NO}_2$ $[\text{M}+\text{H}]^{+} = 446.0420$, found: 446.0414.

1-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)-1H-benzo[d][1,2,3]triazole (3s)



Following the **General procedure** and **Purification Method A** (eluent: hexane/ CH_2Cl_2 1:2), the titled compound was obtained as white solid in 76% yield (178.2 mg). **Mp.:** 78 °C. **^1H NMR (400 MHz, CDCl_3):** δ 6.55 (s, 2H), 7.47-7.52 (m, 1H), 7.61-7.65 (m, 2H), 8.14 (dd, $J = 8.3, 0.7$ Hz, 1H). **^{13}C NMR (100 MHz, CDCl_3):** δ 70.2 (t, $J = 6.6$ Hz), 109.0, 110.0-110.7 (m), 113.9 (apparent t, $J = 30.6$ Hz), 115.8 (apparent t, $J = 32.8$ Hz), 116.7 (apparent t, $J = 30.6$ Hz), 118.6 (apparent t, $J = 32.8$ Hz), 119.5 (apparent t, $J = 30.6$ Hz), 120.7, 125.1, 129.1, 132.6, 146.5. **^{19}F NMR (376 MHz, CDCl_3):** δ -126.2 (brd, $J = 8.3$ Hz, 2F), -125.2 (brs, 2F), -123.0 (brs, 2F), -122.4 (brs, 2F), -84.5 (brs, 2F), -80.8 (t, $J = 10.2$ Hz, 3F). **IR (ATR-IR):** 2889, 2356, 1193, 1143, 1096, 1038, 923, 782, 746, 709, 659, 528, 459, 445, 429, 420 cm^{-1} . **HRMS (APCI):** m/z calculated for $\text{C}_{13}\text{H}_7\text{F}_{13}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^{+} = 468.0376$, found: 468.0373. **Anal.:** Calcd: C, 33.42; H 1.29; N 8.99. Found: C, 33.56; H 1.31; N 9.26.

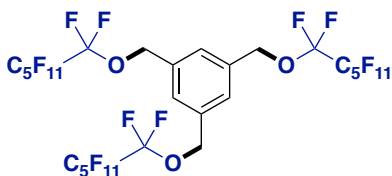
1,4-bis(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzene (3t)



Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC) except for KF (4.0 equiv), CsI (40 mol%), and **1** (4.0 equiv), the titled compound was obtained as colorless oil in 51% yield (198.8 mg). **^1H NMR**

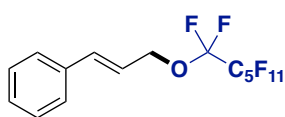
(400 MHz, CDCl₃): δ 5.07 (s, 4H), 7.37 (s, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 66.8 (brs), 110.4-110.7 (m), 114.3 (apparent t, J = 30.4 Hz), 115.9 (apparent t, J = 32.8 Hz), 117.1 (apparent t, J = 29.9 Hz), 118.8 (apparent t, J = 32.8 Hz), 119.8 (apparent t, J = 29.9 Hz), 128.3, 134.7. ¹⁹F NMR (376 MHz, CDCl₃): δ -126.4 (brs, 4F), -125.3 (brs, 4F), -123.1 (brs, 4F), -122.5 (brs, 4F), -85.1 (brs, 4F), -81.1 (brs, 6F). IR (ATR-IR): 2907, 1333, 1194, 1144, 1096, 1039, 990, 846, 801, 734, 708, 658, 573, 531, 450, 426 cm⁻¹. HRMS (APCI): m/z calculated for C₂₀H₈F₂₆O₂ [M]⁺⁺ = 774.0104, found: 774.0090.

1,3,5-tris(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzene (3u)



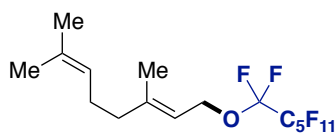
Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC), except for KF (6.0 equiv), CsI (30 mol%), **1** (6.0 equiv), and the reaction time (72 h), the titled compound was obtained as colorless oil in 47% yield (264.1 mg). ¹H NMR (400 MHz, CDCl₃): δ 5.09 (s, 6H), 7.33 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 66.4 (t, J = 5.9 Hz), 110.3-110.7 (m), 114.3 (apparent t, J = 29.9 Hz), 115.9 (apparent t, J = 32.9 Hz), 117.0 (apparent t, J = 30.3 Hz), 118.8 (apparent t, J = 32.8 Hz), 119.7 (apparent t, J = 29.9 Hz), 127.2, 135.5. ¹⁹F NMR (376 MHz, CDCl₃): δ -126.52- -126.46 (m, 2F), -125.3 (brs, 2F), -123.1 (brs, 2F), -122.6 (brs, 2F), -85.2 (brs, 2F), -81.2 (brs, 3F). IR (ATR-IR): 3047, 2904, 1465, 1333, 1193, 1144, 1098, 991, 853, 805, 773, 736, 719, 709, 659, 570, 528, 499, 471, 457, 439, 420, 410 cm⁻¹. HRMS (APCI): m/z calculated for C₂₇H₉F₃₉O₃ [M]⁺⁺ = 1121.9923, found: 1121.9869.

(E)-(3-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)prop-1-en-1-yl)benzene (5a)



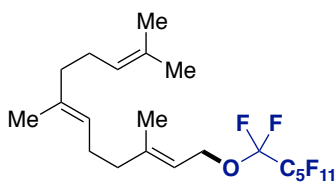
Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC), the titled compound was obtained as colorless oil in 74% yield (167.7 mg). ¹H NMR (400 MHz, CDCl₃): δ 4.68 (d, J = 6.6 Hz, 2H), 6.24 (dt J = 15.9, 6.6 Hz, 1H), 6.68 (d, J = 15.9 Hz, 1H), 7.26-7.41 (m, 5H). ¹³C NMR (100 MHz, CDCl₃): δ 66.5 (t, J = 5.8 Hz), 110.4-110.8 (m), 114.4 (apparent t, J = 29.6 Hz), 116.0 (apparent t, J = 33.6 Hz), 117.1 (apparent t, J = 29.9 Hz), 118.8 (apparent t, J = 32.8 Hz), 119.8 (apparent t, J = 29.9 Hz), 121.5, 127.0, 128.7, 128.9, 135.5, 135.8. ¹⁹F NMR (376 MHz, CDCl₃): δ -126.3- -126.2 (m, 2F), -125.2 (brs, 2F), -123.0 (brs, 2F), -122.4 (brs, 2F), -84.6 (brs, 2F), -80.9 (t, J = 9.6 Hz, 3F). IR (ATR-IR): 3034, 2963, 2896, 1332, 1195, 1145, 1095, 965, 910, 743, 707, 691, 659, 571, 530, 456, 443, 433, 416 cm⁻¹. HRMS (APCI): m/z calculated for C₁₅H₉F₁₃O [M]⁺⁺ = 452.0440, found: 452.0432.

(E)-3,7-dimethyl-1-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)octa-2,6-diene (5b)



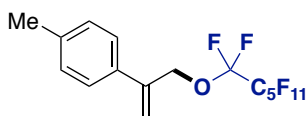
Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC) except for run in the dark at rt, the titled compound was obtained as colorless oil in 76% yield (180.1 mg). **¹H NMR (400 MHz, CDCl₃):** δ 1.60 (s, 3H), 1.68 (s, 3H), 1.71 (s, 3H), 2.06-2.13 (m, 4H), 4.56 (d, J = 7.3 Hz, 2H), 5.08 (t, J = 5.4 Hz, 1H), 5.36 (t, J = 7.3 Hz, 1H). **¹³C NMR (100 MHz, CDCl₃):** δ 16.3, 17.7, 25.7, 26.3, 39.7, 62.5 (t, J = 5.5 Hz), 110.5-110.8 (m), 114.5 (apparent t, J = 29.9 Hz), 116.0 (apparent t, J = 32.8 Hz), 117.1, 117.2 (apparent t, J = 29.9 Hz), 118.9 (apparent t, J = 32.8 Hz), 119.9 (apparent t, J = 29.9 Hz), 123.6, 132.3, 144.6. **¹⁹F NMR (376 MHz, CDCl₃):** δ -126.2 (brd, J = 10.2 Hz, 2F), -125.2 (brs, 2F), -123.0 (brs, 2F), -122.5 (brs, 2F), -84.5 (brs, 2F), -80.8 (t, J = 7.5 Hz, 3F). **IR (ATR-IR):** 2973, 2926, 2855, 1666, 1442, 1329, 1196, 1146, 1094, 985, 905, 811, 734, 707, 659, 529, 474, 459, 435, 415 cm⁻¹. **HRMS (APCI):** m/z calculated for C₁₆H₁₈F₁₃O [M+H]⁺ = 473.1145, found: 473.1129.

(2E,6E)-3,7,11-trimethyl-1-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)dodeca-2,6,10-triene (5c)



Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC) except for run in the dark at rt, the titled compound was obtained as colorless oil in 61% yield (165.3 mg). **¹H NMR (400 MHz, CDCl₃):** δ 1.60 (brs, 6H), 1.68 (s, 3H), 1.71 (s, 3H), 1.96-2.14 (m, 8H), 4.56 (d, J = 7.1 Hz, 2H), 5.10 (brs, 2H), 5.36 (d, J = 7.1 Hz, 1H). **¹³C NMR (100 MHz, CDCl₃):** δ 16.1, 16.4, 17.7, 25.8, 26.2, 26.9, 39.7, 39.9, 62.5 (t, J = 5.9 Hz), 110.4-110.7 (m), 114.4 (apparent t, J = 29.1 Hz), 116.0 (apparent t, J = 32.8 Hz), 117.0, 117.1 (apparent t, J = 29.8 Hz), 118.8 (apparent t, J = 32.8 Hz), 119.8 (apparent t, J = 29.9 Hz), 123.5, 124.4, 131.5, 135.9, 144.6. **¹⁹F NMR (376 MHz, CDCl₃):** δ -126.3- -126.2 (m, 2F), -125.2 (brs, 2F), -123.0 (brs, 2F), -122.5 (brs, 2F), -84.5 (brs, 2F), -80.9 (t, J = 10.0 Hz, 3F). **IR (ATR-IR):** 2982, 2918, 2848, 1663, 1330, 1236, 1196, 1146, 1094, 985, 906, 811, 734, 708, 659, 571, 531, 501, 449, 417 cm⁻¹. **HRMS (APCI):** m/z calculated for C₂₁H₂₆F₁₃O [M+H]⁺ = 541.1771, found: 541.1760.

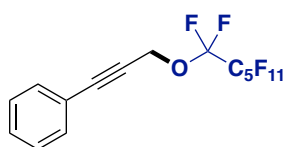
1-methyl-4-(3-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)prop-1-en-2-yl)benzene (5d)



Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC), the titled compound was obtained as colorless oil in 31% yield (71.8 mg). **¹H NMR (400 MHz, CDCl₃):** δ 2.35 (s, 3H), 4.88 (s, 2H), 5.38 (apparent s, 1H), 5.57 (apparent s, 1H), 7.15 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ

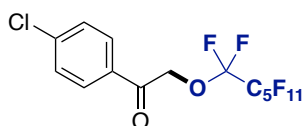
21.2, 67.0 (t, $J = 5.5$ Hz), 110.2-110.7 (m), 114.3 (apparent t, $J = 29.9$ Hz), 115.5, 115.9 (apparent t, $J = 32.8$ Hz), 117.1 (apparent t, $J = 29.5$ Hz), 118.9 (apparent t, $J = 32.8$ Hz), 119.8 (apparent t, $J = 29.9$ Hz), 125.9, 129.4, 134.6, 138.4, 140.8. **^{19}F NMR (376 MHz, CDCl_3):** δ -126.3 (brs, 2F), -125.2 (brs, 2F), -123.0 (brs, 2F), -122.4 (brs, 2F), -85.3 (brs, 2F), -80.9 (brs, 3F). **IR (ATR-IR):** 3094, 3034, 2138, 2038, 1750, 1518, 1333, 1197, 1146, 1096, 990, 910, 822, 735, 708, 659, 529, 439, 427, 415, 405 cm^{-1} . **HRMS (APCI):** m/z calculated for $\text{C}_6\text{H}_{12}\text{F}_{13}\text{N}_2\text{O}_6$ $[\text{M}+\text{H}]^+ = 467.0675$, found: 467.0683.

(3-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)prop-1-yn-1-yl)benzene (5f)



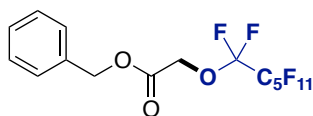
Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC) except for KF (3.0 equiv), **1** (3.0 equiv), and the reaction temperature (90 °C), the titled compound was obtained as colorless oil in 53% yield (119.1 mg). **^1H NMR (400 MHz, CDCl_3):** δ 4.89 (s, 2H), 7.30-7.38 (m, 3H), 7.46 (dd, $J = 8.5, 1.7$ Hz, 2H). **^{13}C NMR (100 MHz, CDCl_3):** δ 54.5 (t, $J = 29.8$ Hz), 80.9, 88.4, 110.4-110.7 (m), 114.3 (apparent t, $J = 29.9$ Hz), 115.9 (apparent t, $J = 32.8$ Hz), 117.1 (apparent t, $J = 29.9$ Hz), 118.8 (apparent t, $J = 32.8$ Hz), 119.8 (apparent t, $J = 30.3$ Hz), 121.8, 128.5, 129.3, 132.1. **^{19}F NMR (376 MHz, CDCl_3):** δ -126.2- -126.1 (m, 2F), -125.2- -125.1 (m, 2F), -122.9 (brs, 2F), -122.4 (brs, 2F), -85.5, (brs, 2F), -80.8 (t, $J = 9.4$ Hz, 3F). **IR (ATR-IR):** 2957, 2889, 2237, 1493, 1332, 1195, 1145, 1097, 990, 919, 846, 756, 707, 689, 659, 530, 477, 448, 430, 418, 406 cm^{-1} . **HRMS (APCI):** m/z calculated for $\text{C}_{15}\text{H}_7\text{F}_{13}\text{O}$ $[\text{M}]^{++} = 450.0284$, found: 450.0270.

1-(4-chlorophenyl)-2-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)ethan-1-one (5g)



Following the **General procedure** and **Purification Method A** (eluent: hexane/ CH_2Cl_2 3:1) except for run in the dark at rt, the titled compound was obtained as colorless oil in 17% yield (42.4 mg). **^1H NMR (400 MHz, CDCl_3):** δ 5.19 (s, 2H), 7.49 (d, $J = 8.6$ Hz, 2H), 7.86 (d, $J = 8.6$ Hz, 2H). **^{13}C NMR (100 MHz, CDCl_3):** δ 66.6 (t, $J = 4.0$ Hz), 110.1-110.5 (m), 114.2 (apparent t, $J = 31.0$ Hz), 115.9 (apparent t, $J = 33.2$ Hz), 116.9 (apparent t, $J = 30.3$ Hz), 118.7 (apparent t, $J = 32.9$ Hz), 119.7 (apparent t, $J = 30.3$ Hz), 129.52, 129.55, 132.2, 141.1, 189.2. **^{19}F NMR (376 MHz, CDCl_3):** δ -126.2- -126.1 (m, 2F), -125.0 (brs, 2F), -122.9 (brs, 2F), -122.3 (brs, 2F), -85.2 (brs, 2F), -80.8 (t, $J = 9.6$ Hz, 3F). **IR (ATR-IR):** 2957, 1714, 1592, 1405, 1335, 1197, 1145, 1095, 1014, 946, 815, 765, 735, 708, 658, 570, 526, 457, 443, 434, 418, 406 cm^{-1} . **HRMS (APCI):** m/z calculated for $\text{C}_{14}\text{H}_7\text{ClF}_{13}\text{O}_2$ $[\text{M}+\text{H}]^+ = 488.9922$, found: 448.9901.

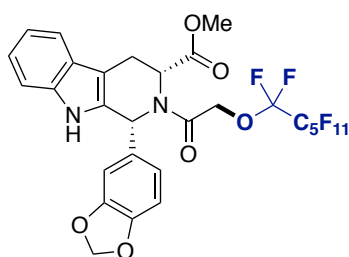
benzyl 2-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)acetate (5h)



Following the **General procedure** and **Purification Method A** (eluent: hexane/CH₂Cl₂ 4:1) except for KF (3.0 equiv), **1** (3.0 equiv), and the reaction temperature (75 °C), the titled compound was obtained as colorless oil in 49% yield (119.0 mg). **¹H NMR (400 MHz, CDCl₃):** δ 4.59 (s, 2H), 5.24 (s, 2H), 7.36 (brs, 5H). **¹³C NMR (100 MHz, CDCl₃):** δ 61.4 (t, *J* = 5.2 Hz), 67.7, 110.4-110.7 (m), 114.0 (apparent t, *J* = 30.3 Hz), 115.9 (apparent t, *J* = 32.8 Hz), 116.7 (apparent t, *J* = 30.7 Hz), 118.8 (apparent t, *J* = 32.7 Hz), 119.5 (apparent t, *J* = 30.2 Hz), 128.6, 128.8, 128.9, 134.8, 165.9. **¹⁹F NMR (376 MHz, CDCl₃):** δ -126.4- -126.3 (m, 2F), -125.2 (brs, 2F), -123.0 (brs, 2F), -122.4 (brs, 2F), -85.8 (brs, 2F), -81.0 (brs, 3F). **IR (ATR-IR):** 3032, 2954, 1773, 1750, 1336, 1193, 1145, 1102, 1038, 966, 848, 814, 736, 709, 658, 572, 529, 477, 455, 444, 433, 408 cm⁻¹. **HRMS (APCI):** *m/z* calculated for C₁₅H₉F₁₃NaO₃ [M+Na]⁺ = 507.0236, found: 507.0246.

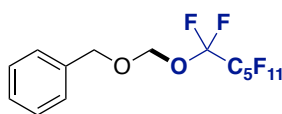
methyl

(1*R*,3*R*)-1-(benzo[*d*][1,3]dioxol-5-yl)-2-(2-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)acetyl)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole-3-carboxylate (5i)



Following the **General procedure** and **Purification Method A** (eluent: hexane/CH₂Cl₂ 1:1), except for KF (3.0 equiv), **1** (3.0 equiv), and the reaction temperature (75 °C), the titled compound was obtained as white solid in 27% yield (96.8 mg). **Mp.:** 68-93 °C (decomp.). **¹H NMR (400 MHz, CDCl₃):** δ 3.07 (dd, *J* = 15.6 Hz, 6.1 Hz, 1H), 3.19 (s, 3H), 3.67 (d, *J* = 15.6 Hz, 1H), 4.68 (brs, 1H), 4.79-4.86 (m, 2H), 5.88 (s, 2H), 6.62 (brs, 2H), 6.81 (brs, 1H), 6.87 (brs, 1H), 7.14-7.20 (m, 2H), 7.22-7.28 (m, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.91 (brs, 1H). **¹³C NMR (100 MHz, CDCl₃):** δ 21.6, 52.2, 52.48, 52.53, 63.8, 101.3, 107.4, 107.8, 110.2, 110.3-110.8 (m), 111.2, 114.1 (apparent t, *J* = 30.7 Hz), 115.8 (apparent t, *J* = 33.2 Hz), 116.9 (apparent t, *J* = 30.3 Hz), 118.69, 118.73 (apparent t, *J* = 36.8 Hz), 119.6 (apparent t, *J* = 30.6 Hz), 120.0, 122.8, 123.2, 126.3, 129.5, 132.6, 136.5, 147.6, 147.7, 165.0, 170.0. **¹⁹F NMR (376 MHz, CDCl₃):** δ -126.2 (brs, 2F), -124.9 (brs, 2F), -122.9 (brs, 2F), -122.3 (brs, 2F), -85.5 (apparent q, *J* = 23.3 Hz, 2F), -80.8 (brs, 3F). **IR (ATR-IR):** 3395, 2954, 1742, 1667, 1488, 1439, 1199, 1146, 1099, 1039, 935, 742, 710, 653, 530, 484, 466, 444, 420, 410 cm⁻¹. **HRMS (APCI):** *m/z* calculated for C₂₈H₂₀F₁₃N₂O₆ [M+H]⁺ = 727.1108, found: 727.1094.

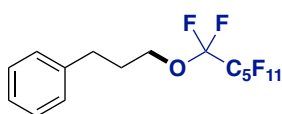
((((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methoxy)methyl)benzene (5j)



Following the **General procedure** and **Purification Method B** (mobile phase: CH₂Cl₂), except for run in the dark at rt, the titled compound was obtained as colorless oil in 26% yield (59.6 mg). **¹H NMR (400 MHz, C₆D₆):** δ 4.32 (s, 2H), 4.69 (s, 2H), 7.05-7.10 (m, 5H). **¹³C NMR (100**

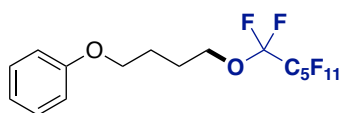
MHz, C₆D₆): δ 71.6, 91.2 (t, J = 5.1 Hz), 110.2-110.5 (m), 114.6 (apparent t, J = 29.9 Hz), 116.3 (apparent t, J = 32.8 Hz), 117.3 (apparent t, J = 29.9 Hz), 119.2 (apparent t, J = 32.9 Hz), 120.1 (apparent t, J = 29.9 Hz), 127.9, 128.4, 128.7, 136.3. **¹⁹F NMR (376 MHz, C₆D₆):** δ . -126.2- -126.1 (m, 2F), -125.3 (brs, 2F), -122.8 (brs, 2F), -122.2 (brs, 2F), -82.8 (brs, 2F), -80.8 (t, J = 10.2 Hz, 3F). **IR (ATR-IR):** 3032, 2946, 2883, 2820, 2359, 2161, 2015, 1981, 1772, 1642, 1455, 1382, 1239, 1208, 1149, 1105, 1041, 1026, 920, 864, 736, 697, 647, 563, 516, 505, 473, 460, 445, 437, 424, 405 cm⁻¹. **HRMS (ESI):** m/z calculated for C₁₄H₉F₁₃NaO₂ [M+Na]⁺ = 479.0287, found: 479.0272.

(3-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)propyl)benzene (5k)



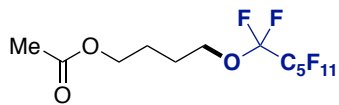
Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC) except for KF (3.0 equiv), CsI (30 mol%), **1** (3.0 equiv), the reaction temperature (90 °C), and the reaction time (48 h), the titled compound was obtained as slightly yellowish oil in 39% yield (88.2 mg). **¹H NMR (400 MHz, CDCl₃):** δ 1.98-2.05 (tt, J = 7.6, 6.2 Hz, 2H), 2.72 (t, J = 7.6 Hz, 2H), 4.03 (t, J = 6.2 Hz, 2H), 7.17-7.24 (m, 3H), 7.28-7.32 (m, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ 30.5, 31.6, 64.8 (t, J = 5.1 Hz), 110.4-110.6 (m), 114.2 (apparent t, J = 33.5 Hz), 115.9 (apparent t, J = 33.5 Hz), 117.0 (apparent t, J = 29.1 Hz), 118.8 (apparent t, J = 32.8 Hz), 119.7 (apparent t, J = 29.9 Hz), 126.4, 128.6, 128.7, 140.6. **¹⁹F NMR (376 MHz, CDCl₃):** δ -126.4- -126.3 (m, 2F), -125.5 (brs, 2F), -123.1 (brs, 2F), -122.5 (brs, 2F), -85.5 (brs, 2F), -81.1 (t, J = 9.6 Hz, 3F). **IR (ATR-IR):** 3032, 2848, 1335, 1235, 1196, 1145, 1097, 1039, 848, 772, 743, 707, 659, 569, 529, 501, 476, 443, 420, 410 cm⁻¹. **HRMS (APCI):** m/z calculated for C₁₅H₁₁F₁₃O [M]⁺ = 454.0597, found: 454.0576.

(4-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)butoxy)benzene (5l)



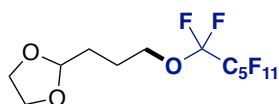
Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC) except for KF (3.0 equiv), CsI (30 mol%), **1** (3.0 equiv), the reaction temperature (90 °C), and the reaction time (48 h), the titled compound was obtained as colorless oil in 43% yield (104.2 mg). **¹H NMR (400 MHz, CDCl₃):** δ 1.85-1.94 (m, 4H), 3.99 (d, J = 5.6 Hz, 2H), 4.12 (d, J = 5.7 Hz, 2H), 6.89 (dd, J = 8.6, 1.9 Hz, 2H), 6.95 (apparent t, J = 7.3 Hz, 1H), 7.28 (dd, J = 8.6, 7.3 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ 25.6, 25.9, 65.5 (t, J = 5.1 Hz), 66.9, 110.3-110.7 (m), 114.2 (apparent t, J = 29.2 Hz), 114.5, 115.9 (apparent t, J = 32.8 Hz), 116.9 (apparent t, J = 29.9 Hz), 118.8 (apparent t, J = 32.8 Hz), 119.7 (apparent t, J = 29.5 Hz), 120.9, 129.6, 159.0. **¹⁹F NMR (376 MHz, CDCl₃):** δ -126.3- -126.2 (m, 2F), -125.4 (brs, 2F), -123.0 (brs, 2F), -122.5 (brs, 2F), -85.4 (brs, 2F), -80.9 (t, J = 9.4 Hz, 3F). **IR (ATR-IR):** 2948, 2873, 1602, 1498, 1335, 1234, 1195, 1145, 1093, 987, 753, 716, 707, 691, 660, 571, 529, 464, 451, 440, 427, 407 cm⁻¹. **HRMS (APCI):** m/z calculated for C₁₆H₁₄F₁₃O₂ [M+H]⁺ = 485.0781, found: 485.0763.

4-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)butyl acetate (5m)



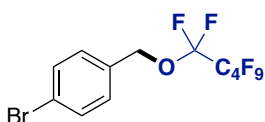
Following the **General procedure** and **Purification Method A** (eluent: hexane/CH₂Cl₂ 3:1), except for KF (3.0 equiv), CsI (30 mol%), **1** (3.0 equiv), the reaction temperature (90 °C), and the reaction time (48 h), the titled compound was obtained as colorless oil in 44% yield (99.3 mg). **¹H NMR (400 MHz, CDCl₃):** δ 1.70-1.83 (m, 4H), 2.06 (s, 3H), 4.09 (t, *J* = 6.0 Hz, 2H), 4.10 (t, *J* = 6.4 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ 20.9, 24.9, 25.7, 63.7, 65.2 (t, *J* = 5.1 Hz), 110.4-110.9 (m), 114.2 (apparent t, *J* = 29.8 Hz), 115.9 (apparent t, *J* = 26.6 Hz), 116.9 (apparent t, *J* = 29.9 Hz), 118.8 (apparent t, *J* = 32.8 Hz), 119.6 (apparent t, *J* = 29.5 Hz), 171.2. **¹⁹F NMR (376 MHz, CDCl₃):** δ. -126.2- -126.1 (m, 2F), -125.3 (brs, 2F), -122.9 (brs, 2F), -122.4 (brs, 2F), -85.4 (brs, 2F), -80.8 (t, *J* = 9.4 Hz, 3F). **IR (ATR-IR):** 2921, 2362, 2354, 2160, 2024, 1742, 1366, 1232, 1196, 1146, 1094, 1058, 1039, 986, 912, 846, 811, 771, 735, 718, 707, 659, 633, 605, 572, 529, 495, 484, 468, 456, 441, 405 cm⁻¹. **HRMS (APCI):** *m/z* calculated for C₁₂H₁₂F₁₃O₃ [M+H]⁺ = 451.0573, found: 451.0569.

2-(3-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)propyl)-1,3-dioxolane (5n)



Following the **General procedure** and **Purification Method A** (eluent: hexane/CH₂Cl₂ 3:1), except for KF (3.0 equiv), CsI (30 mol%), **1** (3.0 equiv), the reaction temperature (90 °C), and the reaction time (48 h), the titled compound was obtained as slightly yellowish oil in 38% yield (85.8 mg). **¹H NMR (400 MHz, CDCl₃):** δ 1.75-1.79 (m, 2H), 1.82-1.87 (m, 2H), 3.86-3.89 (m, 4H), 4.10 (t, *J* = 6.4 Hz, 2H), 4.91 (t, *J* = 8.2 Hz, 1H). **¹³C NMR (100 MHz, CDCl₃):** δ 23.4, 29.8, 65.1, 65.7 (t, *J* = 5.1 Hz), 103.8, 110.1-110.9 (m), 114.2 (apparent t, *J* = 29.9 Hz), 115.9 (apparent t, *J* = 32.8 Hz), 116.9 (apparent t, *J* = 29.9 Hz), 119.3 (apparent t, *J* = 33.2 Hz), 119.6 (apparent t, *J* = 29.6 Hz). **¹⁹F NMR (376 MHz, CDCl₃):** δ. -126.2 (brs, 2F), -125.3 (brs, 2F), -122.9 (brs, 2F), -122.4 (brs, 2F), -85.3 (brs, 2F), -80.9 (brs, 3F). **IR (ATR-IR):** 3852, 3745, 3545, 2962, 2189, 2051, 1972, 1409, 1336, 1237, 1197, 1145, 1095, 1029, 943, 802, 759, 735, 717, 708, 660, 572, 529, 500, 478, 467, 449, 436, 424 cm⁻¹. **HRMS (APCI):** *m/z* calculated for C₁₂H₁₂F₁₃O₃ [M+H]⁺ = 451.0573, found: 451.0571.

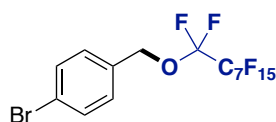
1-bromo-4-(((1,1,2,2,3,3,4,4,5,5,5-undecafluoropentyl)oxy)methyl)benzene (6a)



Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC), except for C₄F₉COF (266.0 mg, 1.0 mmol, 2.0 equiv) in lieu of **1**, the titled compound was obtained as colorless oil in 54% yield (123.3 mg). **¹H NMR (400 MHz, CDCl₃):** δ 5.02 (s, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ 66.6 (t, *J* = 5.9 Hz), 109.8-110.4 (m), 116.0 (apparent t, *J* = 32.8 Hz), 117.0 (apparent t, *J* = 29.9 Hz), 118.9 (apparent t, *J* = 32.8 Hz), 119.7 (apparent t, *J* = 29.9 Hz), 123.2, 129.7, 132.1, 133.0. **¹⁹F NMR (376 MHz, CDCl₃):** δ. -126.3 (brs 2F), -125.3 (brs,

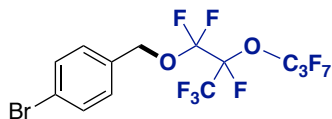
2F), -123.1 (brs, 2F), -84.9 (brs, 2F), -80.9 (t, $J = 18.4$ Hz, 3F). **IR (ATR-IR):** 3032, 2898, 2324, 2205, 2053, 2006, 1959, 1598, 1491, 1332, 1200, 1143, 1124, 1102, 1072, 1039, 1013, 951, 932, 873, 820, 803, 781, 744, 729, 704, 632, 598, 532, 503, 478, 464, 454, 438, 412 cm^{-1} . **HRMS (APCI):** m/z calculated for $\text{C}_{12}\text{H}_6\text{BrF}_{11}\text{O}$ $[\text{M}]^{+} = 453.9421$, found: 453.9404.

1-bromo-4-(((1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptafluorooctyl)oxy)methyl)benzene (6b)



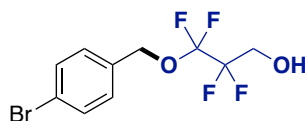
Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC), except for $\text{C}_7\text{F}_{15}\text{COF}$ (416.1 mg, 1.0 mmol, 2.0 equiv) in lieu of **1**, the reaction temperature (75 °C), the titled compound was obtained as colorless oil in 57% yield (173.0 mg). **^1H NMR (400 MHz, CDCl_3):** δ 5.02 (s, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 8.4$ Hz, 2H). **^{13}C NMR (100 MHz, CDCl_3):** δ 66.6 (t, $J = 5.5$ Hz), 110.1-110.3 (m), 113.3 (apparent t, $J = 32.1$ Hz), 113.5 (apparent t, $J = 32.7$ Hz), 114.3 (apparent t, $J = 29.9$ Hz), 115.9 (apparent t, $J = 32.8$ Hz), 117.1 (apparent t, $J = 29.9$ Hz), 118.8 (apparent t, $J = 32.8$ Hz), 119.8 (apparent t, $J = 29.9$ Hz), 123.2, 129.6, 132.1, 133.0. **^{19}F NMR (376 MHz, CDCl_3):** δ . -126.1 (brs 2F), -125.1 (brs, 2F), -123.7 (brs, 2F), -122.1- -121.9 (m, 6F), -84.8 (brs, 2F), -80.8 (t, $J = 10.9$ Hz, 3F). **IR (ATR-IR):** 3032, 2963, 2340, 2192, 2166, 2051, 2039, 1599, 1492, 1342, 1200, 1147, 1136, 1105, 1072, 1004, 878, 804, 764, 723, 704, 659, 597, 561, 531, 504, 472, 460, 441, 435, 425, 417, 402 cm^{-1} . **HRMS (APCI):** m/z calculated for $\text{C}_{15}\text{H}_6\text{BrF}_{17}\text{O}$ $[\text{M}]^{+} = 603.9325$, found: 603.9325.

1-bromo-4-(((1,1,2,3,3,3-hexafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propoxy)methyl)benzene (6c)



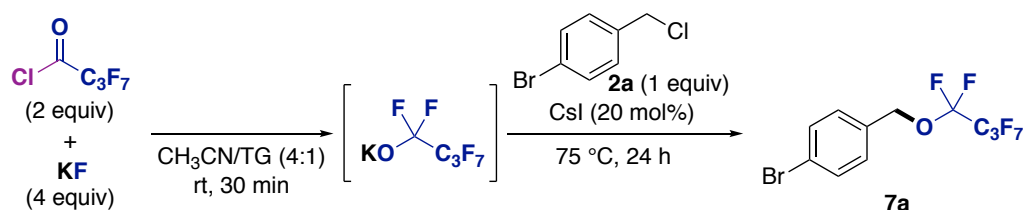
Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC), except for $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{COF}$ (332.0 mg, 1.0 mmol, 2.0 equiv) in lieu of **1**, the titled compound was obtained as colorless oil in 35% yield (91.7 mg). **^1H NMR (400 MHz, CDCl_3):** δ 5.01 (s, 2H), 7.20 (d, $J = 8.8$ Hz, 2H), 7.53 (d, $J = 8.8$ Hz, 2H). **^{13}C NMR (100 MHz, CDCl_3):** δ 66.8 (t, $J = 5.9$ Hz), 101.9 (apparent q, $J = 37.4$ Hz), 103.5-107.3 (m), 112.2-115.7 (m), 114.3-116.1 (m), 116.4-120.1 (m), 118.7 (apparent t, $J = 32.8$ Hz), 123.2, 129.5, 132.1, 132.9. **^{19}F NMR (376 MHz, CDCl_3):** δ . -144.4 (t, $J = 21.6$ Hz, 1F), -129.7 (brs 2F), -84.8 (brs, 2F), -81.7 (apparent q, $J = 112.4$ Hz, 2F), -81.3- -81.2 (m, 3F), -80.2- -80.1 (m, 3F). **IR (ATR-IR):** 3060, 2889, 2338, 2187, 2160, 2042, 2015, 1972, 1656, 1309, 1229, 1162, 1112, 1028, 989, 809, 754, 741, 696, 503, 487, 470, 464, 449, 415, 402 cm^{-1} . **HRMS (APCI):** m/z calculated for $\text{C}_{13}\text{H}_6\text{BrF}_{13}\text{O}_2$ $[\text{M}]^{+} = 519.9338$, found: 519.9316.

3-((4-bromobenzyl)oxy)-2,2,3,3-tetrafluoropropan-1-ol (6d)



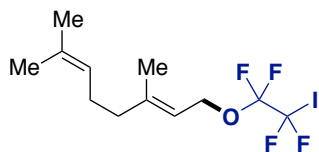
In an argon-filled glovebox, KF (58.1 mg, 1.0 mmol, 2.0 equiv) and CsI (26.0 mg, 0.10 mmol, 20 mol%) were added to a flame-dried 10 ml Schlenk tube, which was then taken out from the box. To the tube were added anhydrous MeCN (1.0 ml), anhydrous tetraglyme (0.25 ml), and MeOC(O)CF₂COF (156.1 mg, 1.0 mmol, 2.0 equiv) at rt, then the resultant mixture was stirred for 30 min before alkyl chloride (0.50 mmol, 1.0 equiv) was added. The reaction was stirred at 45 °C for 24 h, cooled to rt and quenched with H₂O, followed by extraction with Et₂O x 4. The combined organic layer was dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was dissolved in THF (3.0 ml) before DIBAL (142.2 mg, 1.0 mmol) was added at -78 °C. The mixture was stirred at rt for 12 h, quenched with saturated NH₄Cl aq., followed by extraction with Et₂O x 4. The combined organic layer was dried over MgSO₄, filtered and concentrated under reduced pressure, followed by purification according to **Purification Method A** (eluted with 100% CH₂Cl₂). The titled compound was obtained as white solid in 41% yield (62.6 mg). **Mp.**: 41 °C. **¹H NMR (400 MHz, CDCl₃)**: δ 2.28 (brs, 1H), 3.97 (t, *J* = 14.2 Hz, 2H), 4.96 (s, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃)**: δ 60.8 (t, *J* = 25.6 Hz), 65.8 (t, *J* = 6.2 Hz), 114.3 (tt, *J* = 35.0, 251.5 Hz), 118.3 (tt, *J* = 31.8, 270.9 Hz), 123.0, 129.7, 132.0, 133.6. **¹⁹F NMR (376 MHz, CDCl₃)**: δ. -125.9 (t, *J* = 14.2 Hz, 2F), -88.9 (brs, 2F). **IR (ATR-IR)**: 3389, 2963, 2929, 2356, 2054, 1596, 1488, 1408, 1385, 1346, 1227, 1194, 1186, 1176, 1124, 1098, 1085, 1067, 1006, 932, 837, 802, 795, 757, 713, 667, 637, 587, 578, 532, 497, 475, 461, 449, 418, 408 cm⁻¹. **HRMS (APCI)**: *m/z* calculated for C₁₀H₉BrF₄O₂ [M]⁺ = 315.9717, found: 315.9717.

1-bromo-4-((1,1,2,2,3,3,4,4,4-nonafluorobutoxy)methyl)benzene (7a)



In an argon-filled glovebox, KF (116.2 mg, 1.0 mmol, 4.0 equiv) and CsI (26.0 mg, 0.10 mmol, 20 mol%) were added to a flame-dried 10 ml Schlenk tube, which was then taken out from the box. To the tube were added anhydrous MeCN (1.0 ml), anhydrous tetraglyme (0.25 ml), and $\text{C}_3\text{F}_7\text{COCl}$ (232 mg, 1.0 mmol, 2.0 equiv) at rt, then the resultant mixture was stirred for 1 h before 4-BrBnCl (**6**) (102.7 mg, 0.50 mmol, 1.0 equiv) was added. The reaction was stirred at 75 °C for 24 h, cooled to rt and quenched with H_2O , followed by extraction with Et_2O x 4. The combined organic layer was dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by MPLC using hexane as an eluent, followed by a recycling preparative HPLC (GPC) to afford the product **7a** as slightly yellowish oil in 54% yield (110.0 mg). **^1H NMR (400 MHz, CDCl_3):** δ 5.01 (s, 2H), 7.22 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H). **^{13}C NMR (100 MHz, CDCl_3):** δ 66.6 (t, J = 5.9 Hz), 108.4-108.9 (m), 116.1 (apparent t, J = 32.9 Hz), 116.9 (apparent t, J = 29.9 Hz), 118.9 (apparent t, J = 32.8 Hz), 123.2, 129.7, 132.1, 132.9. **^{19}F NMR (376 MHz, CDCl_3):** δ -126.6 (brs, 2F), -126.2 (brs, 2F), -85.3 (brs, 2F), -81.1 (brs, 3F). **IR (ATR-IR):** 2963, 2892, 1491, 1304, 1206, 1139, 1104, 1072, 1014, 960, 882, 804, 786, 740, 687, 598, 533, 503, 444, 405 cm^{-1} . **HRMS (APCI):** m/z calculated for $\text{C}_{11}\text{H}_6\text{BrF}_9\text{O}$ $[\text{M}]^{++}$ = 403.9453, found: 403.9441.

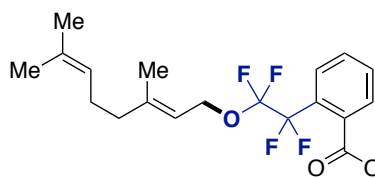
(E)-3,7-dimethyl-1-(1,1,2,2-tetrafluoro-2-iodoethoxy)octa-2,6-diene (8)



Following the **General procedure** and **Purification Method A** (eluted with 100% hexane, followed by GPC), except for ICF₂COF (223.9 mg, 1.0 mmol, 2.0 equiv) in lieu of **1**, run in the dark at rt, the titled compound was obtained as colorless oil in 62% yield (117.8 mg). ¹H

NMR (400 MHz, CDCl₃): δ 1.61 (s, 3H), 1.68 (s, 3H), 1.72 (s, 3H), 2.05-2.15 (m, 4H), 4.54 (d, *J* = 7.2 Hz, 2H), 5.08 (t, *J* = 6.8 Hz, 1H), 5.37 (t, *J* = 7.2 Hz, 1H). ¹³C **NMR (100 MHz, CDCl₃):** δ 16.6, 17.9, 25.8, 26.3, 39.7, 62.6 (t, *J* = 5.8 Hz), 92.7 (tt, *J* = 45.6, 317.5 Hz), 116.5 (tt, *J* = 28.4, 269.7 Hz), 117.3, 123.7, 132.2, 144.2. ¹⁹F **NMR (376 MHz, CDCl₃):** δ. -88.5 (t, *J* = 6.8 Hz, 2F), -62.4 (t, *J* = 6.8 Hz, 2F). **IR (ATR-IR):** 3442, 3222, 2366, 2190, 2167, 2156, 2048, 2022, 2009, 1977, 1652, 1275, 737, 670, 624, 595, 579, 553, 529, 509, 499, 490, 471, 456, 443, 431, 421, 410 cm⁻¹. **HRMS (APCI):** *m/z* calculated for C₁₂H₁₈F₄IO [M+H]⁺ = 381.0333, found: 381.0326.

methyl (E)-2-(2-((3,7-dimethylocta-2,6-dien-1-yl)oxy)-1,1,2,2-tetrafluoroethyl)benzoate (9)



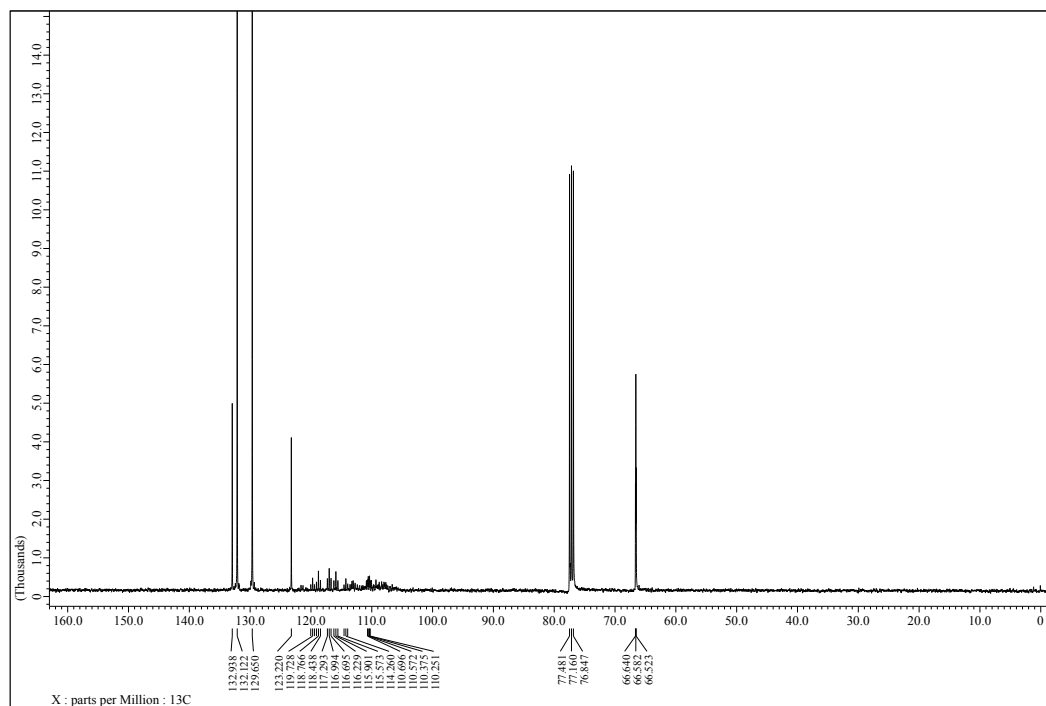
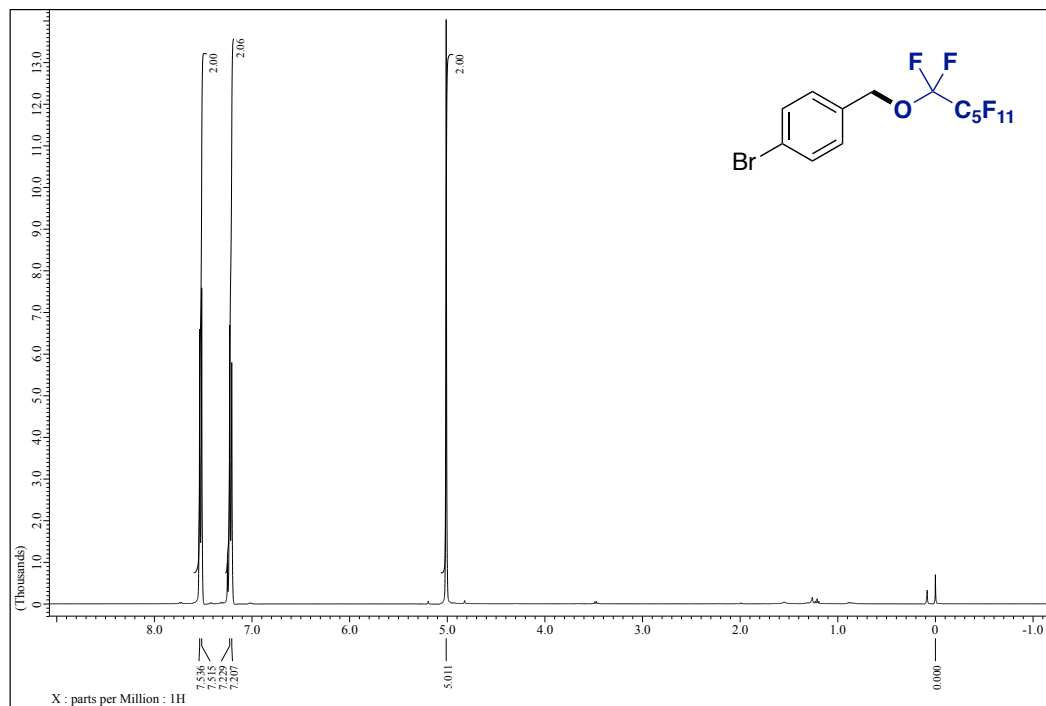
Under Ar atmosphere, **8** (171 mg, 0.45 mmol, 1.5 equiv) and DMPU (0.30 ml) were added to a flame-dried 10 ml Schlenk tube. To the tube, Et₂Zn (1.09 M in hexane; 275 μl, 0.30 mmol, 1.0 equiv) was added dropwise at rt, then the resultant mixture

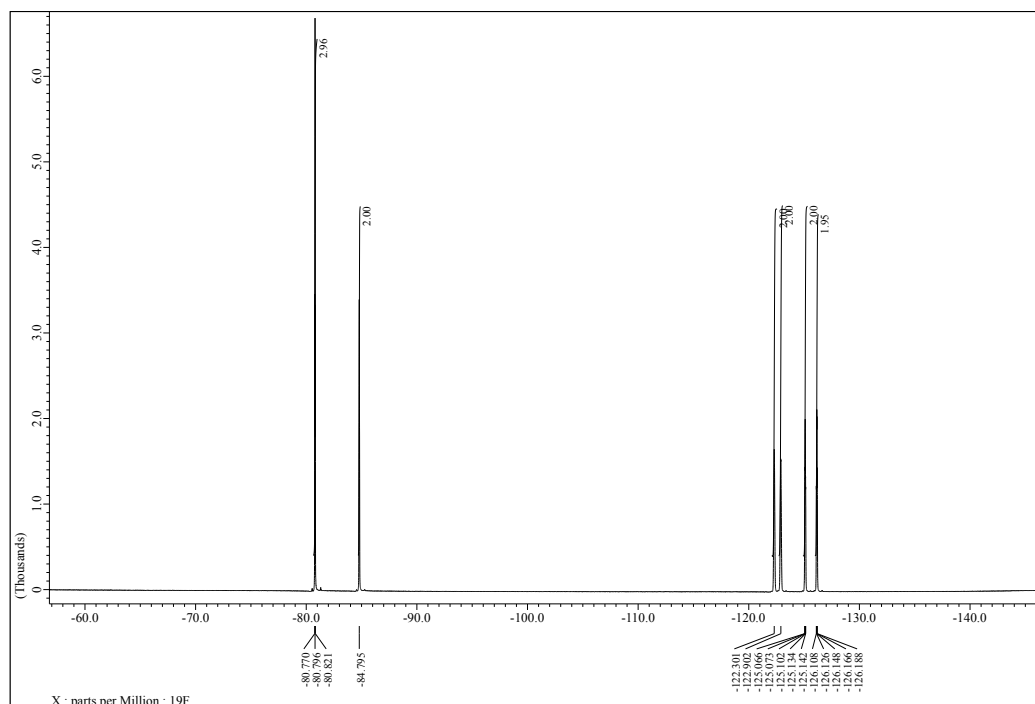
was stirred at rt for 15 min before methyl 2-iodobenzoate (78.6 mg, 0.30 mmol, 1.0 equiv) and CsI (5.7 mg, 0.030 mmol, 10 mol%) were added.⁶ The reaction was stirred at 90 °C for 16 h, cooled to rt and quenched with 1N HCl aq., followed by extraction with Et₂O x 4. The combined organic layer was dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified with GPC, and the titled compound was obtained as colorless oil in 32% yield (36.9 mg). ¹H **NMR (400 MHz, CDCl₃):** δ 1.60 (s, 3H), 1.65 (s, 3H), 1.67 (s, 3H), 2.01-2.10 (m, 4H), 3.89 (s, 3H), 4.48 (d, *J* = 7.2 Hz, 2H), 5.07 (t, *J* = 6.8 Hz, 1H), 5.32 (t, *J* = 7.2 Hz, 1H), 7.47-7.56 (m, 3H), 7.63-7.66 (m, 1H). ¹³C **NMR (100 MHz, CDCl₃):** δ 16.5, 17.8, 25.8, 26.3, 39.6, 52.8, 61.8 (t, *J* = 5.8 Hz), 114.7 (tt, *J* = 39.0, 253.7 Hz), 117.8, 118.8 (tt, *J* = 35.2, 270.5 Hz), 123.7, 128.1 (t, *J* = 24.8 Hz), 128.4, 128.8 (t, *J* = 7.3 Hz), 129.8, 131.0, 132.2, 133.3 (t, *J* = 2.9 Hz), 142.9, 169.1. ¹⁹F **NMR (376 MHz, CDCl₃):** δ -107.8 (brs, 2F), -87.9 (brs, 2F). **IR (ATR-IR):** 2952, 2911, 2848, 2363, 2031, 2010, 1739, 1667, 1433, 1384, 1299, 1278, 1182, 1150, 1072, 1045, 972, 910, 828, 759, 698, 657, 633, 585, 560, 528, 513, 503, 488, 456, 445, 424, 412 cm⁻¹. **HRMS (APCI):** *m/z* calculated for C₂₀H₂₄F₄O₃ [M]⁺⁺ = 388.1656, found: 388.1644.

6 H. Kato, K. Hirano, D. Kurauchi, N. Toriumi, M. Uchiyama, *Chem. Eur. J.*, 2015, **21**, 3895-3900.

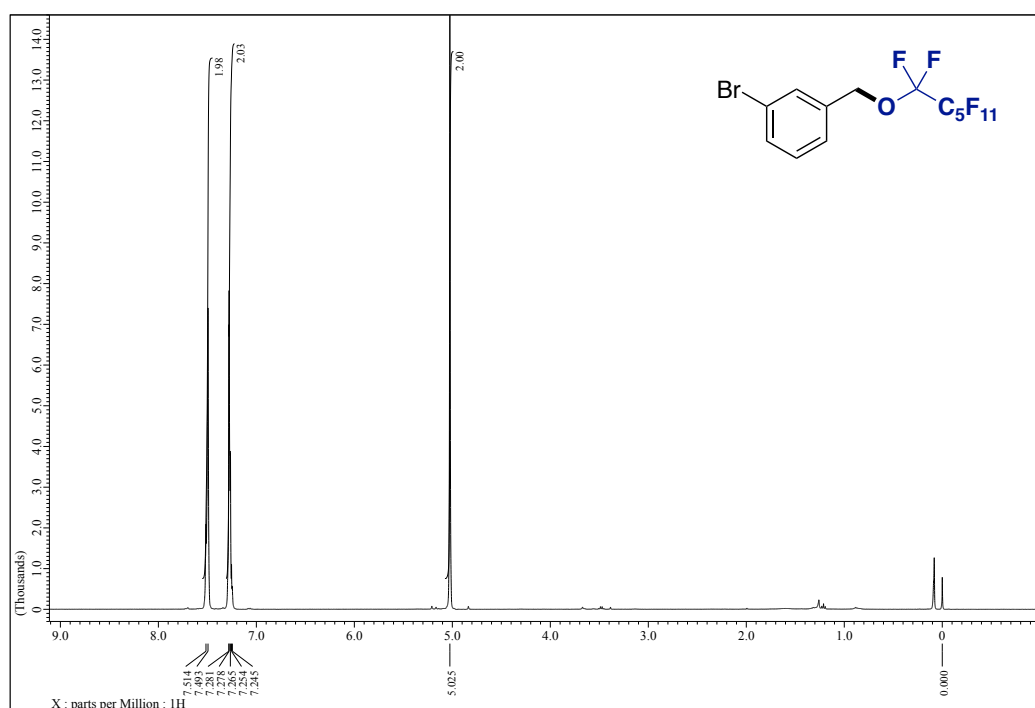
3. NMR Spectra

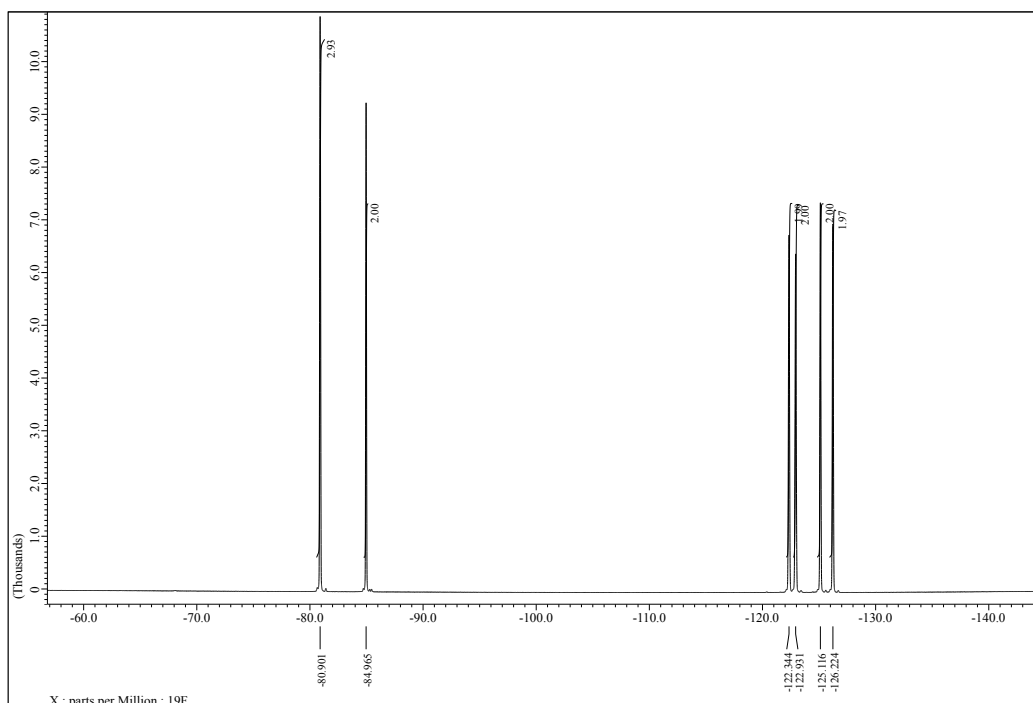
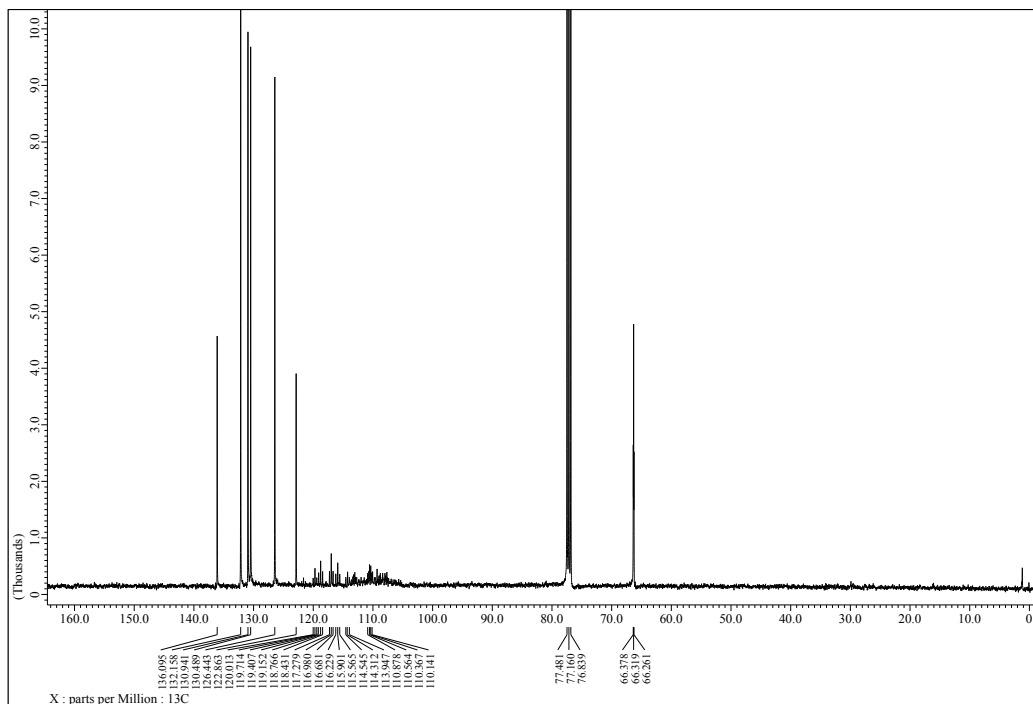
1-bromo-4-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzene (3a)



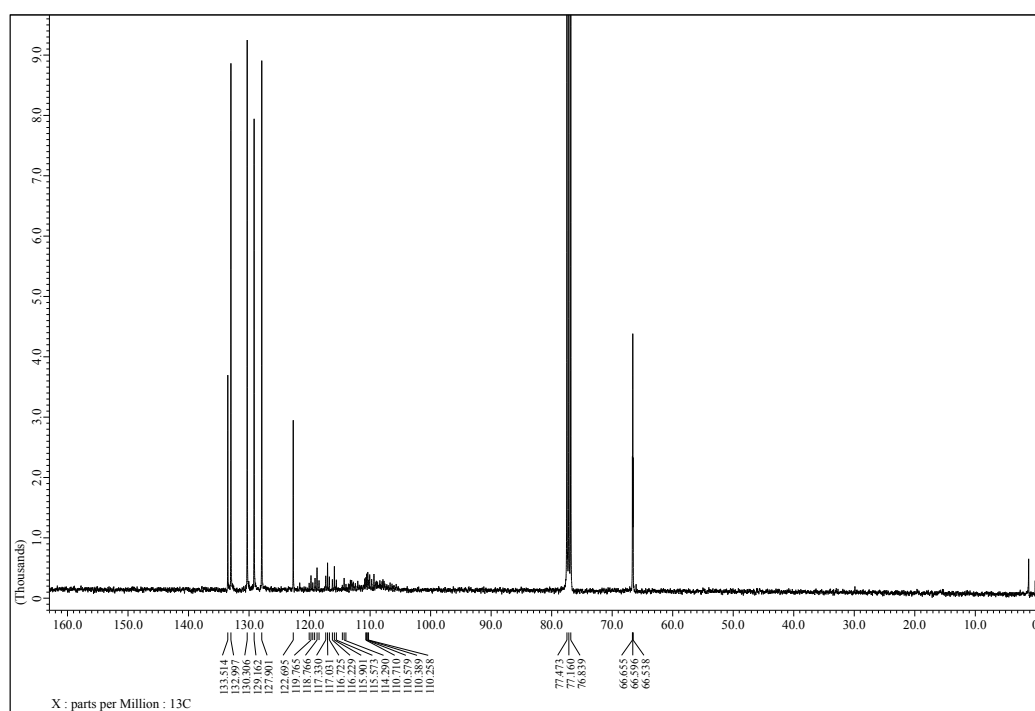
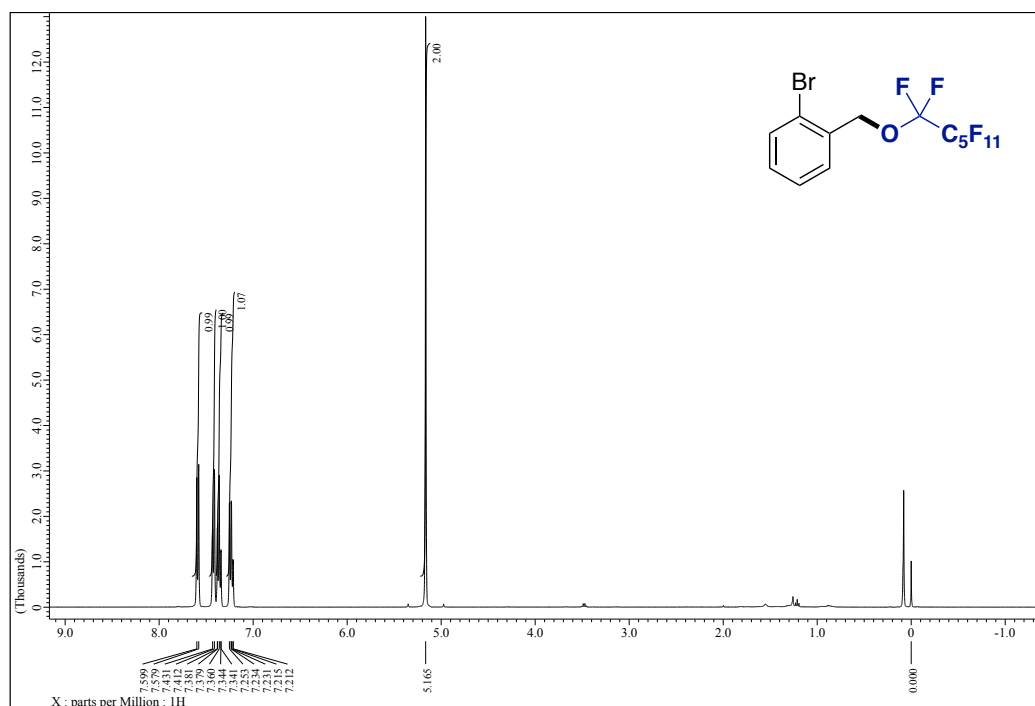


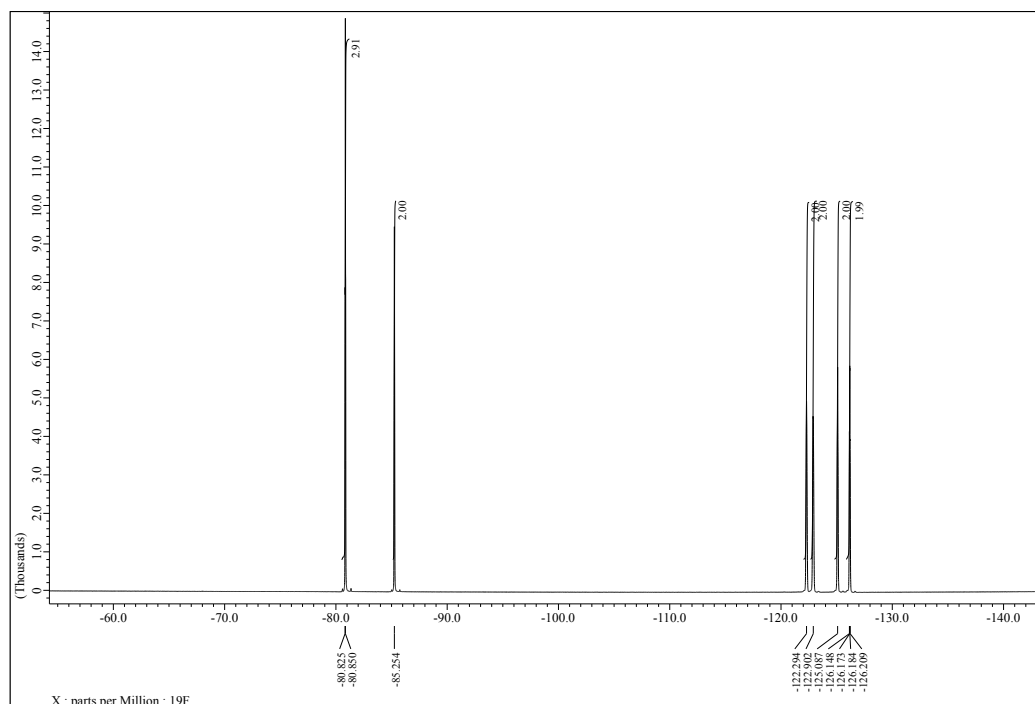
1-bromo-3-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzene (3b)



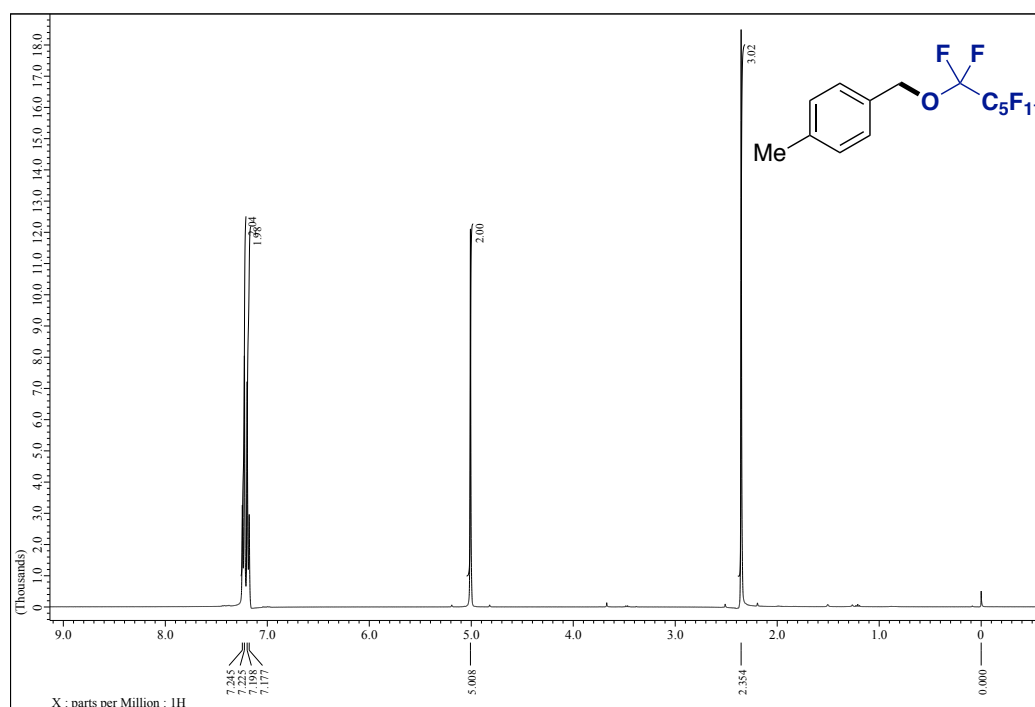


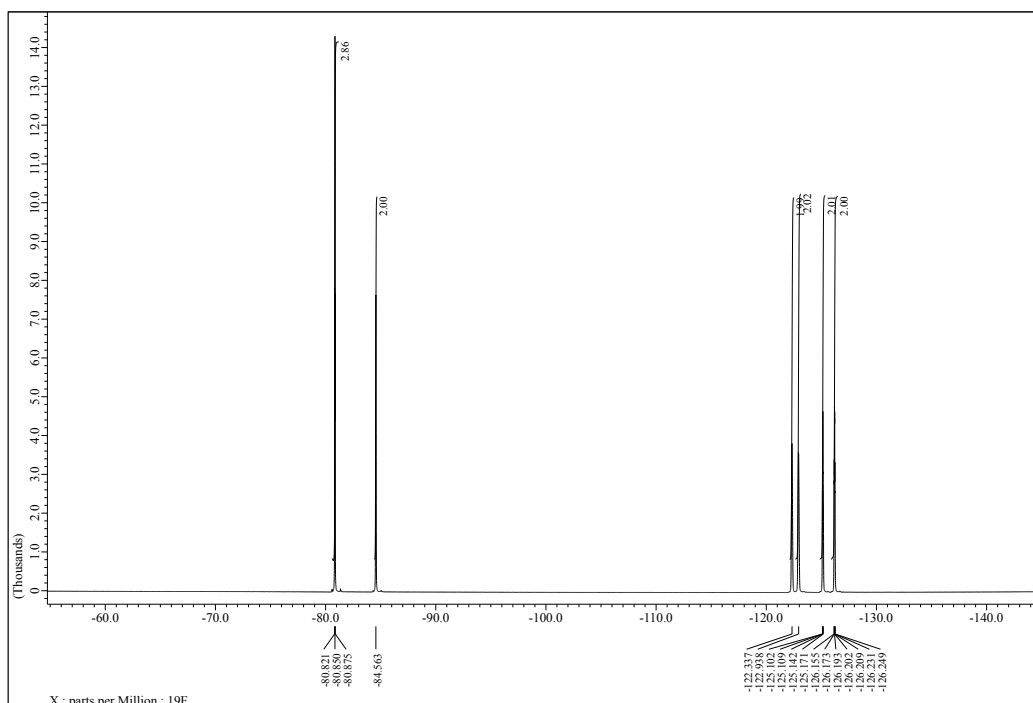
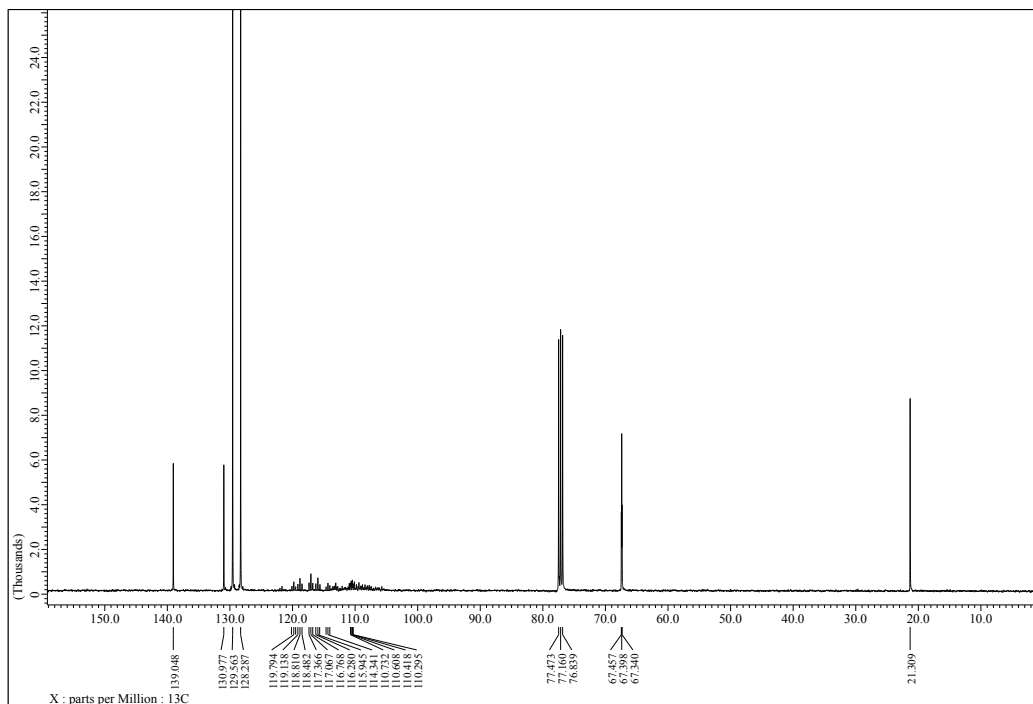
1-bromo-2-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzene (3c)



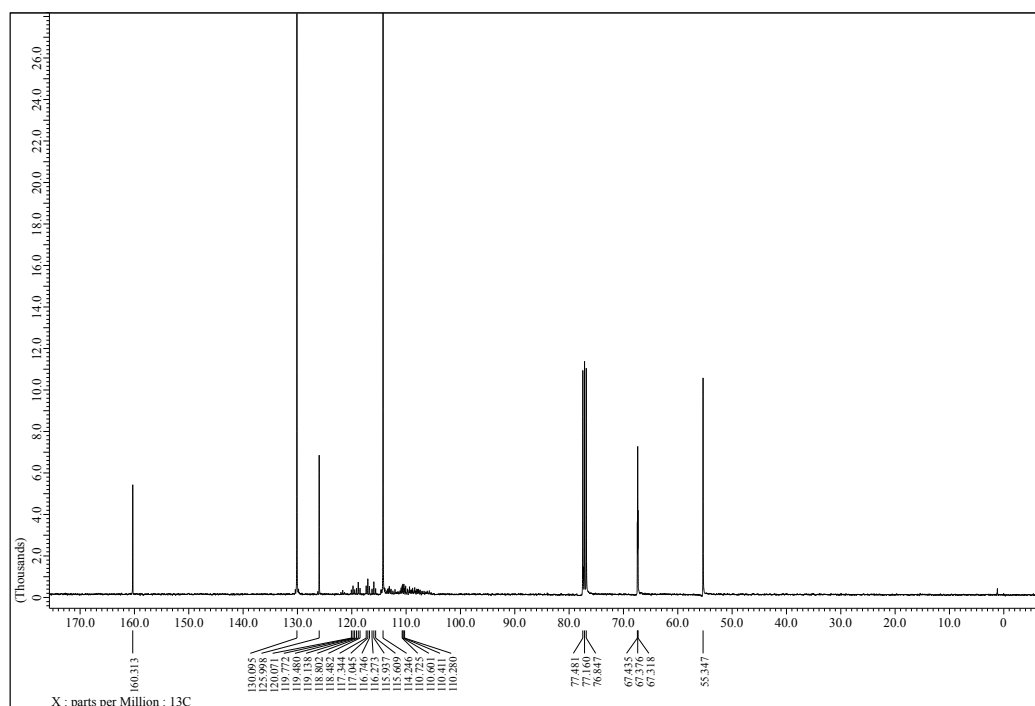
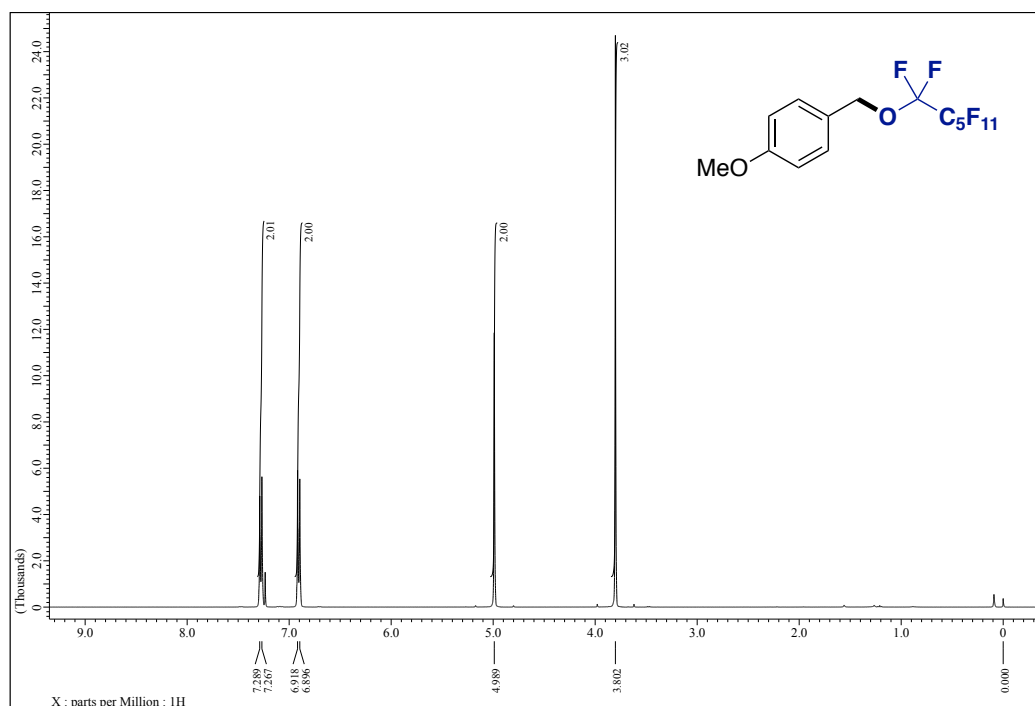


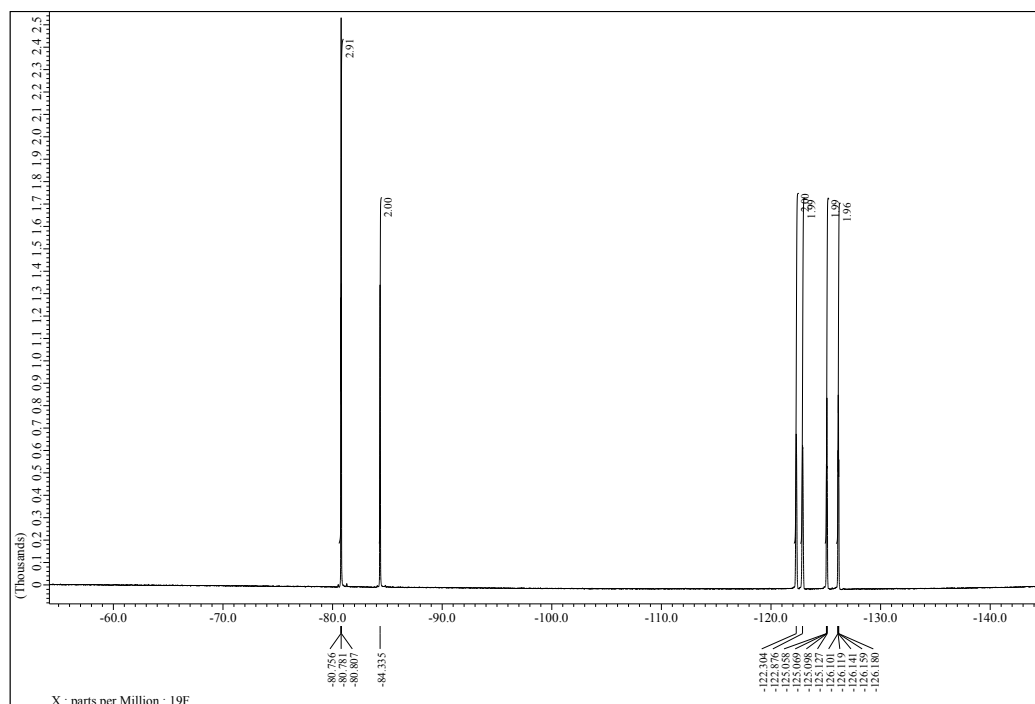
1-methyl-4-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzene (3d)



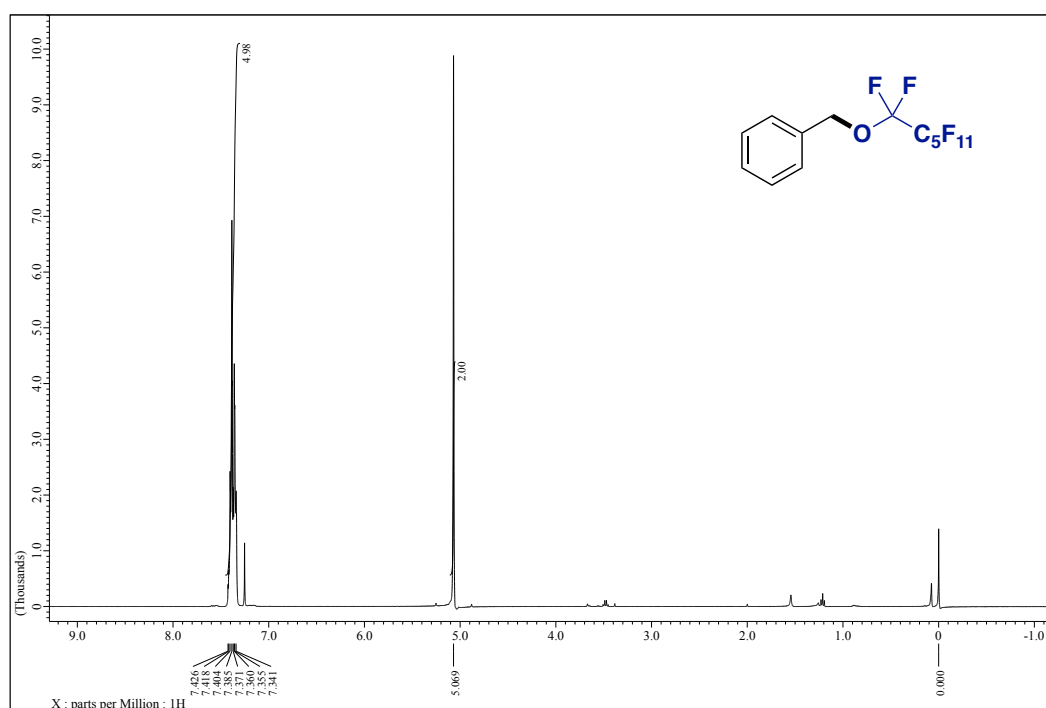


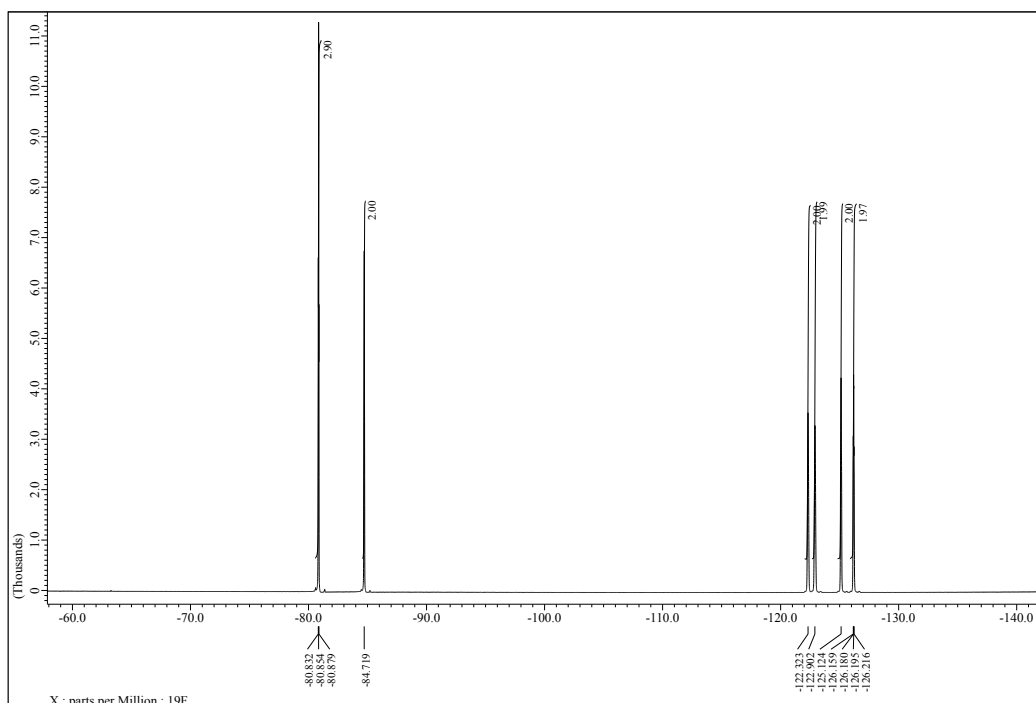
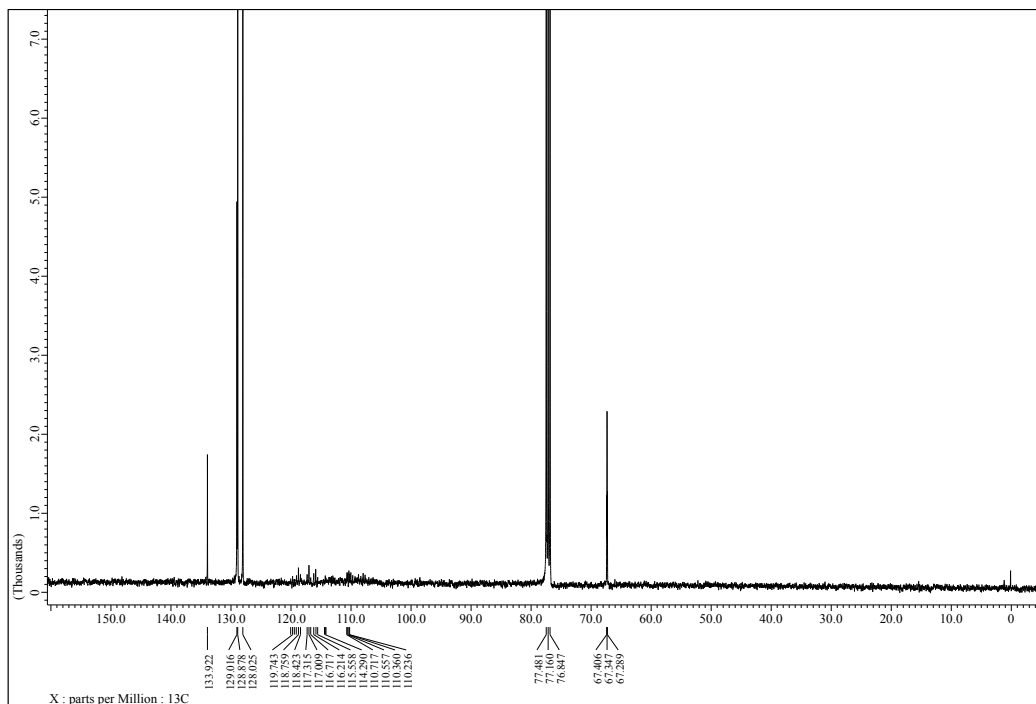
1-methoxy-4-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzene (3e)



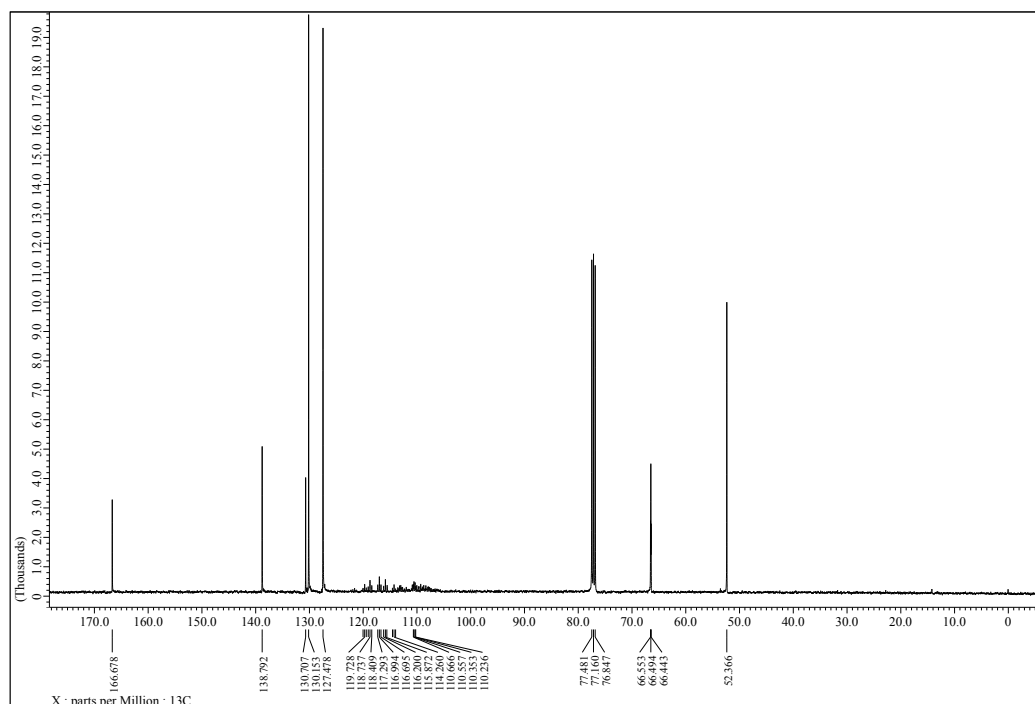
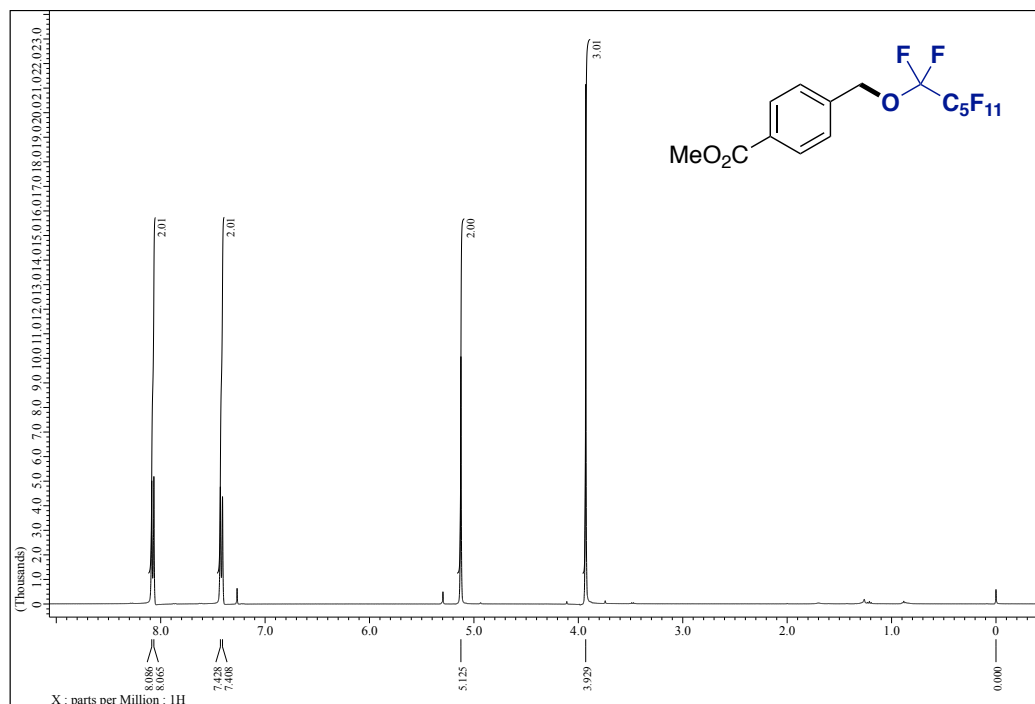


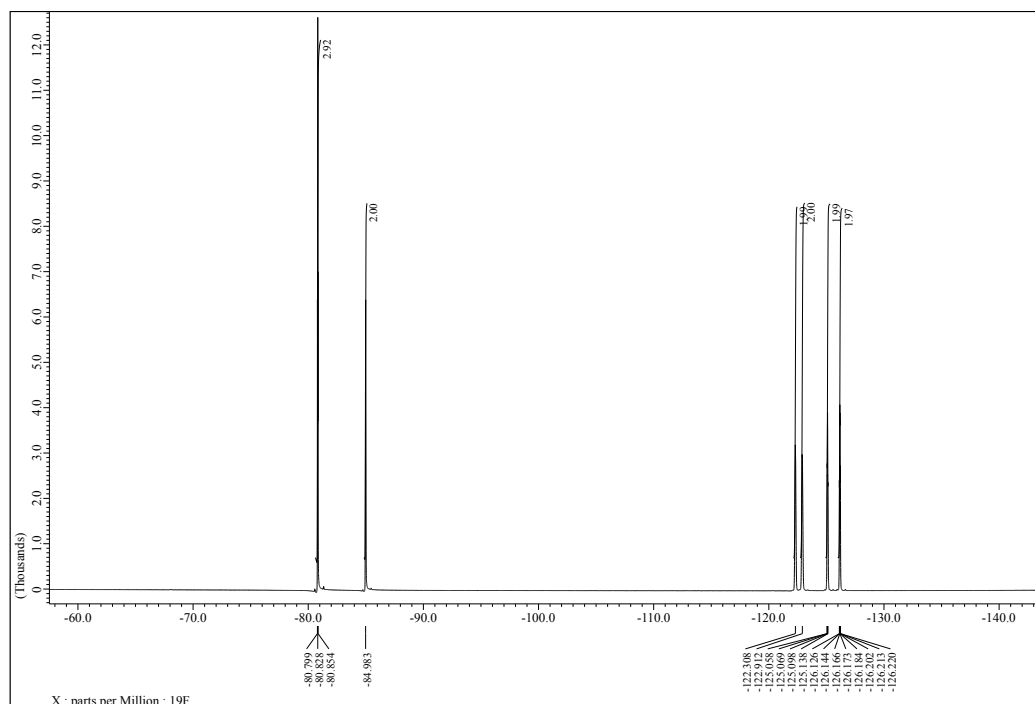
(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzene (3f)



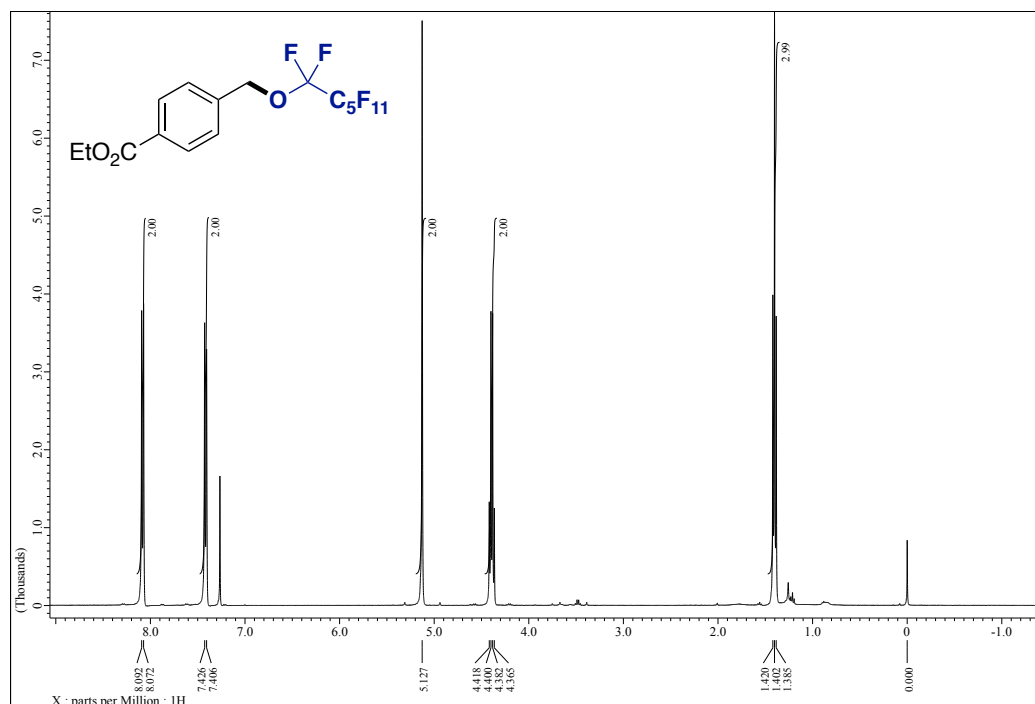


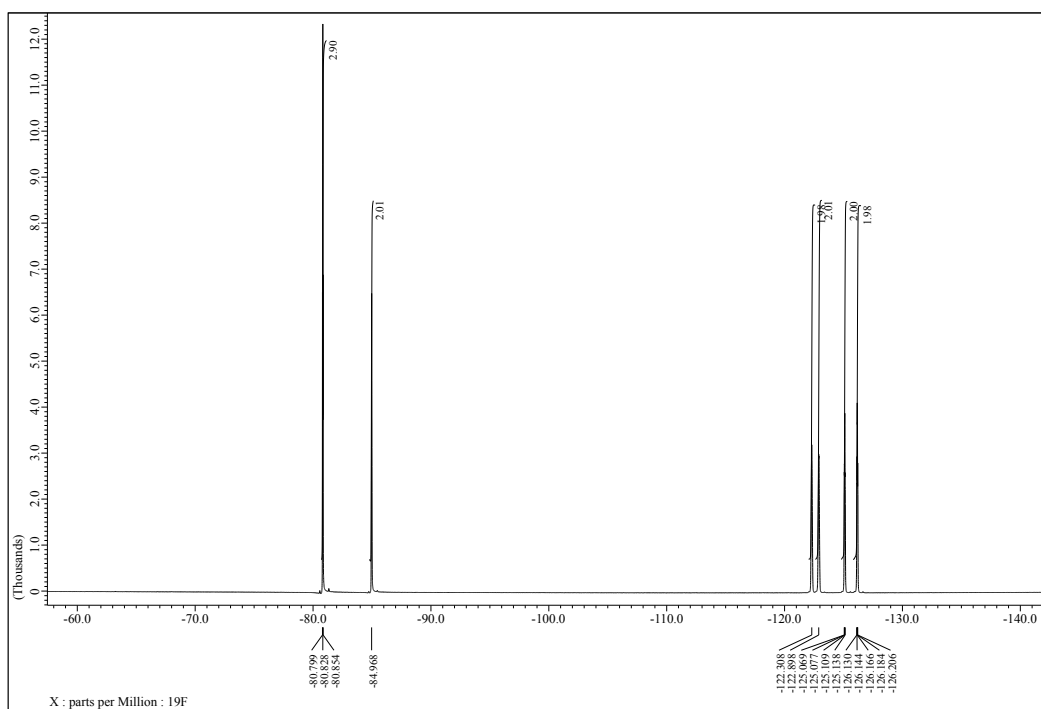
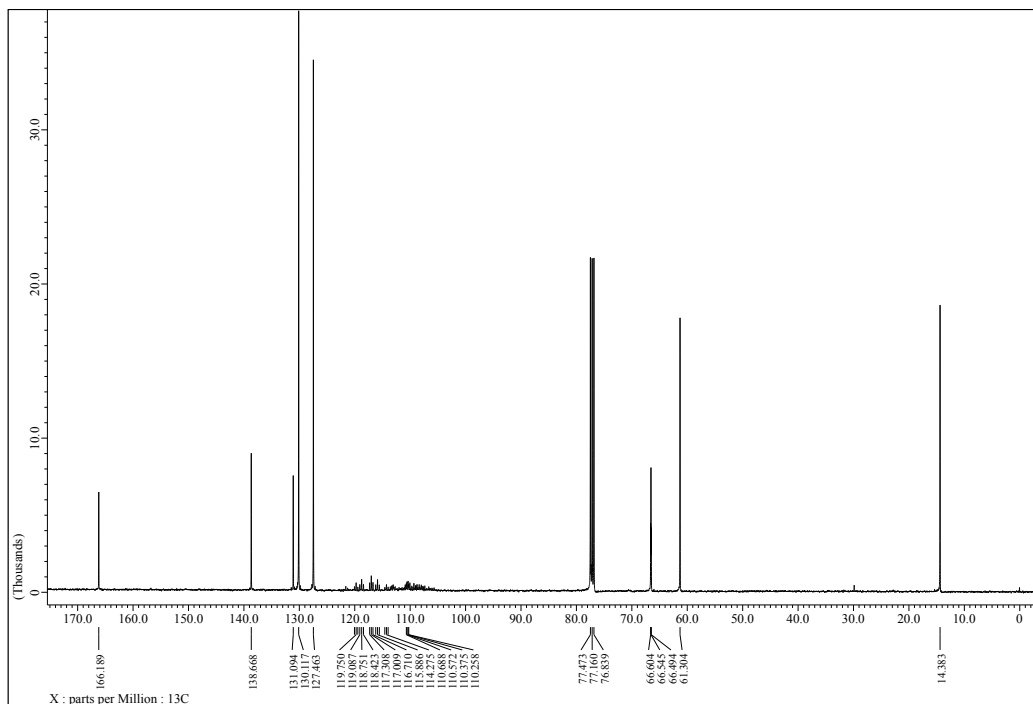
methyl 4-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzoate (3g)



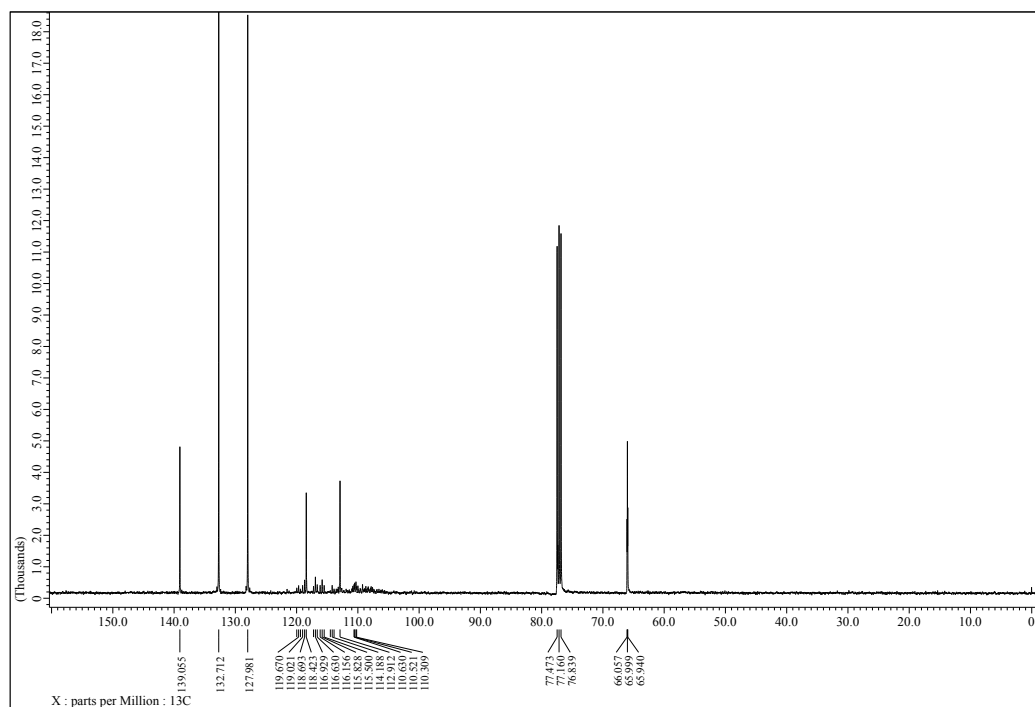
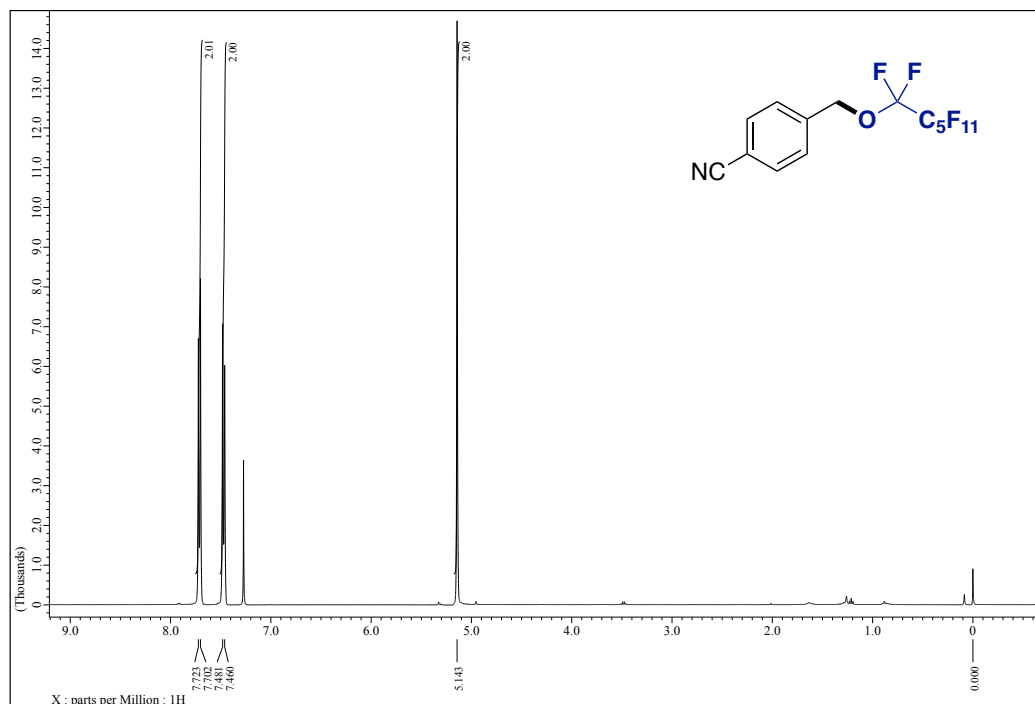


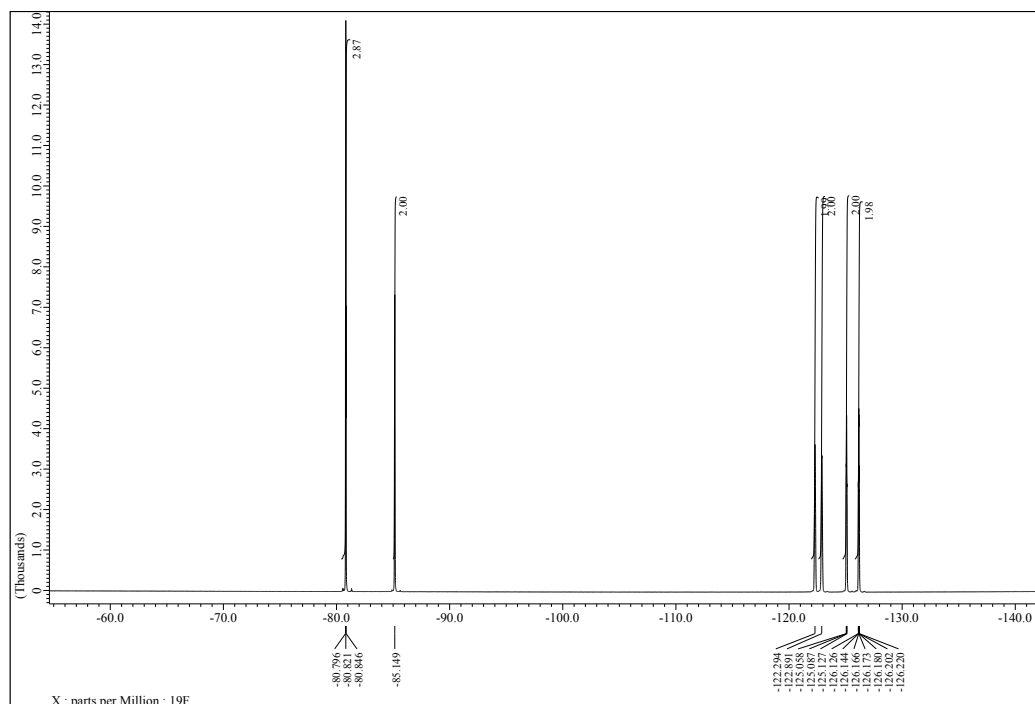
ethyl 4-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzoate (3h)



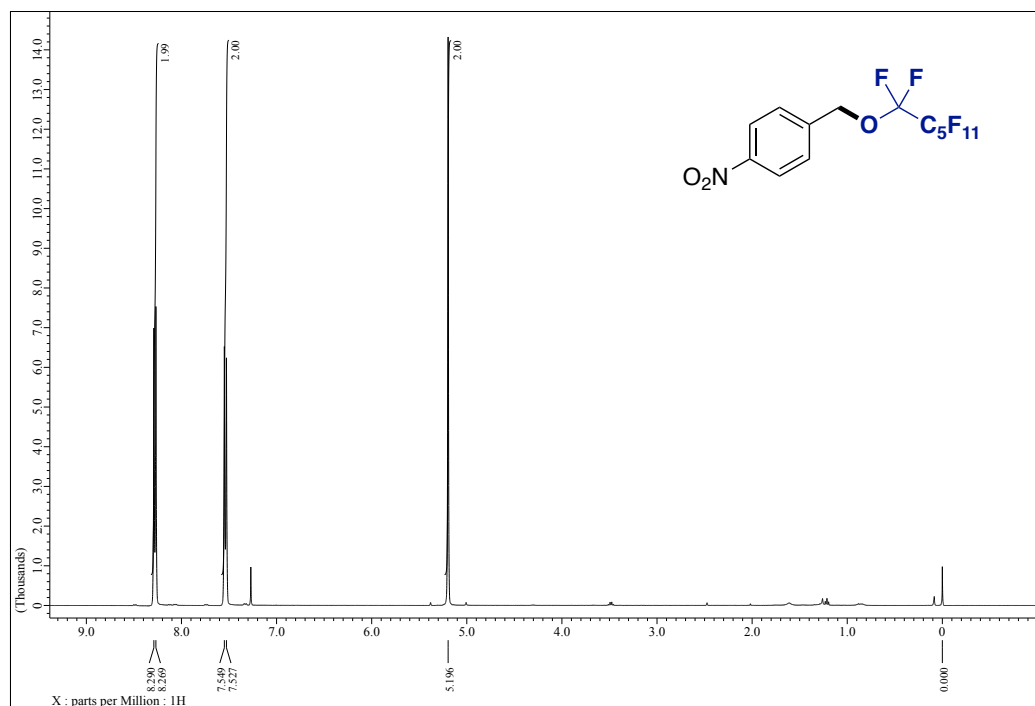


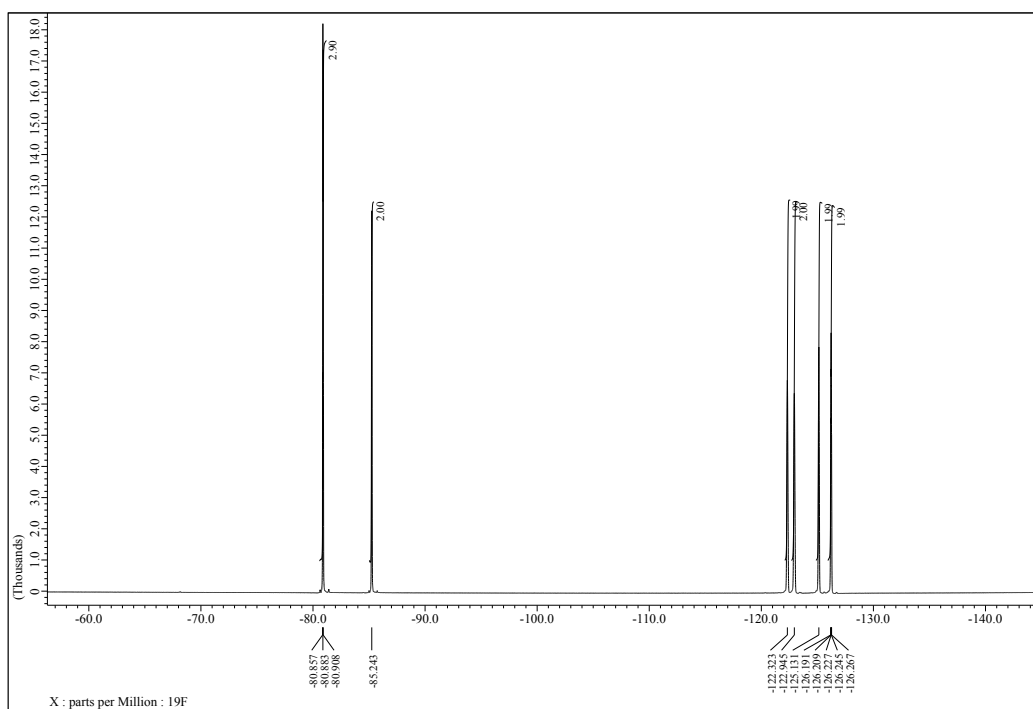
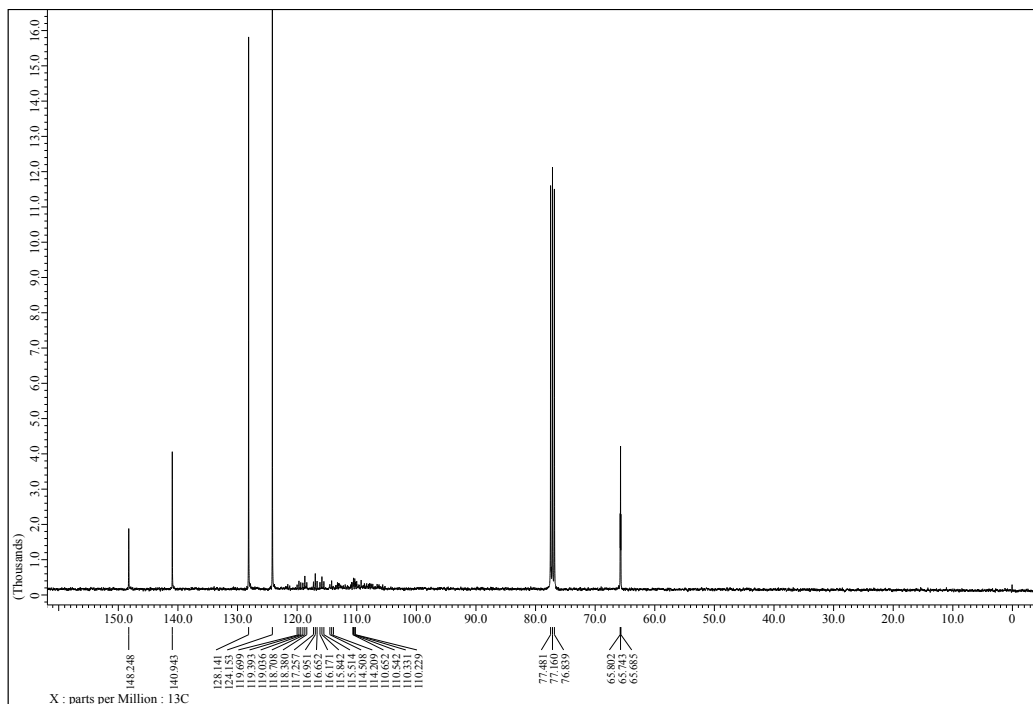
4-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzonitrile (3i)



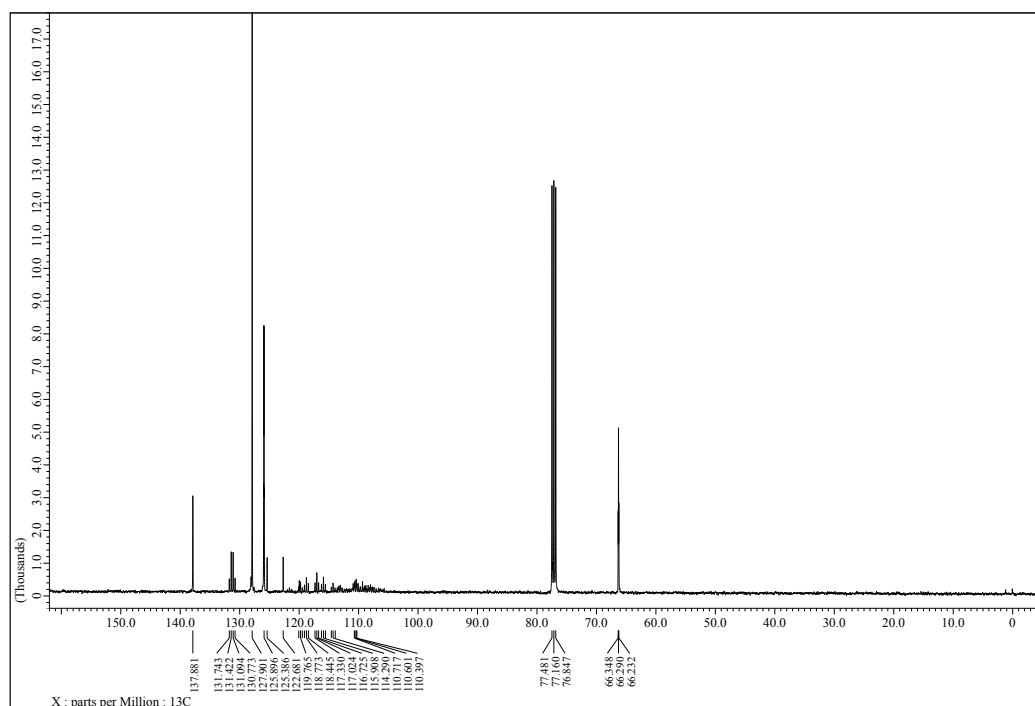
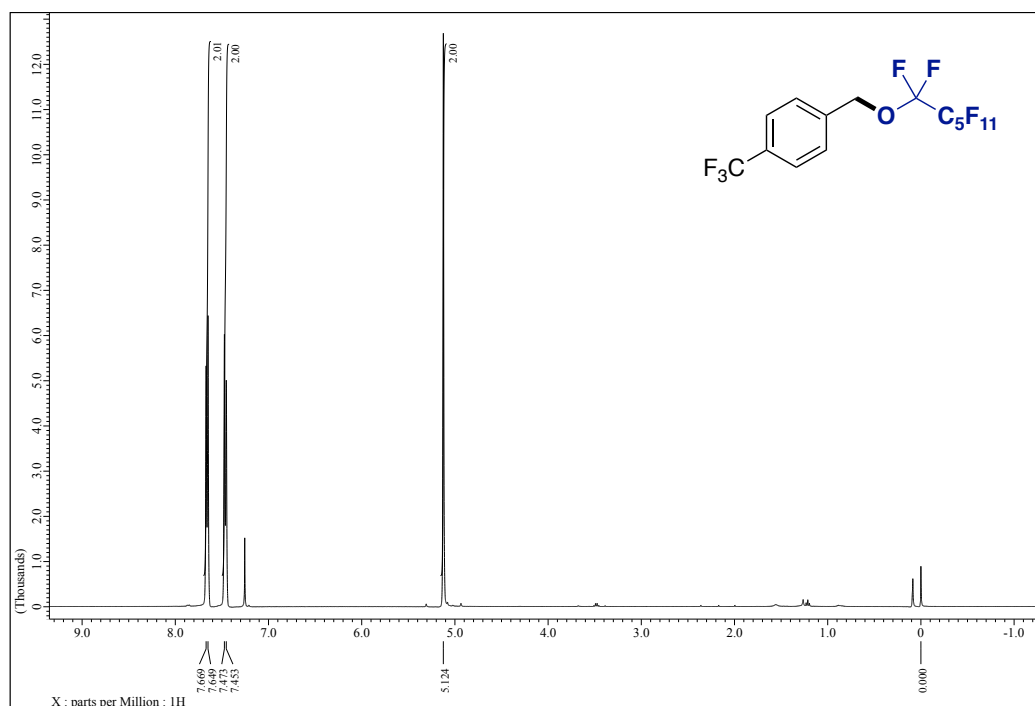


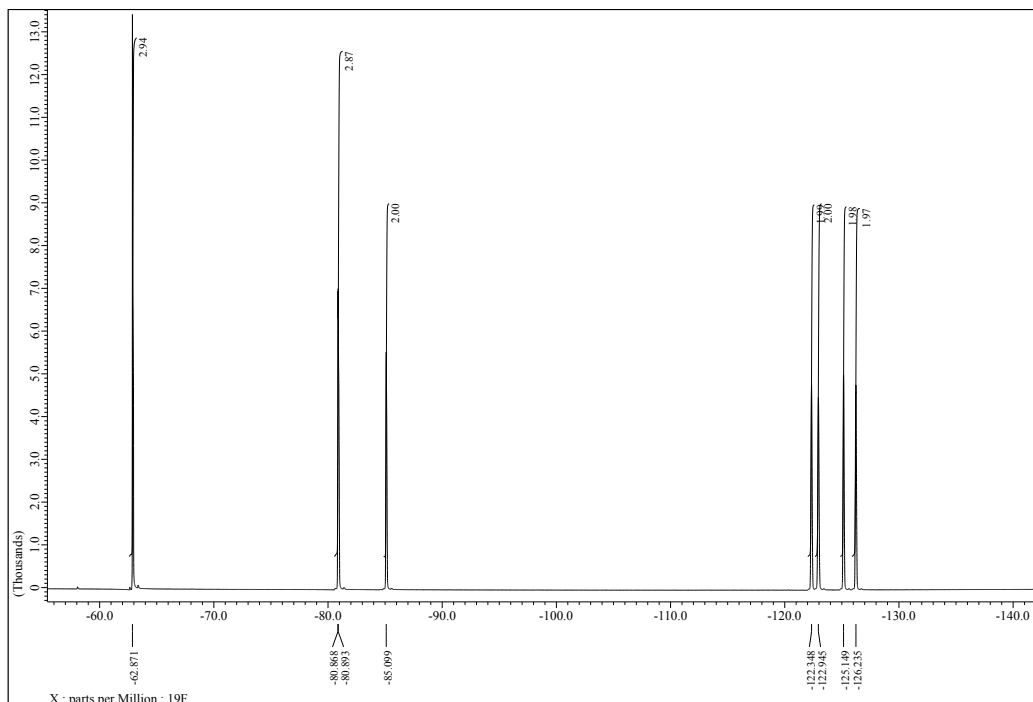
1-nitro-4-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzene (3j)



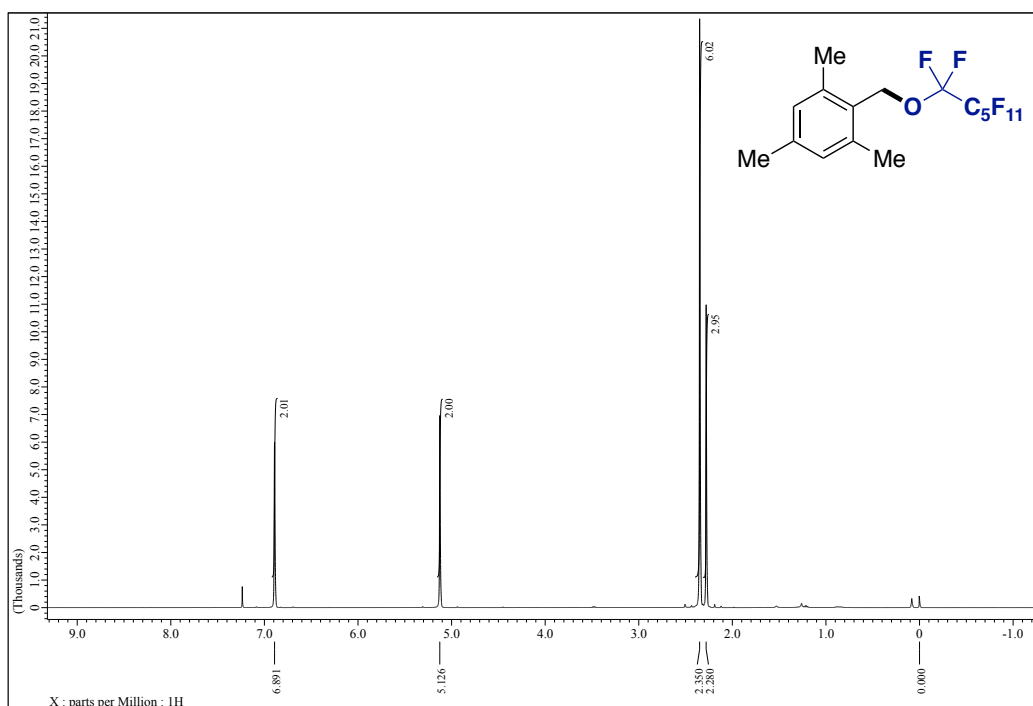


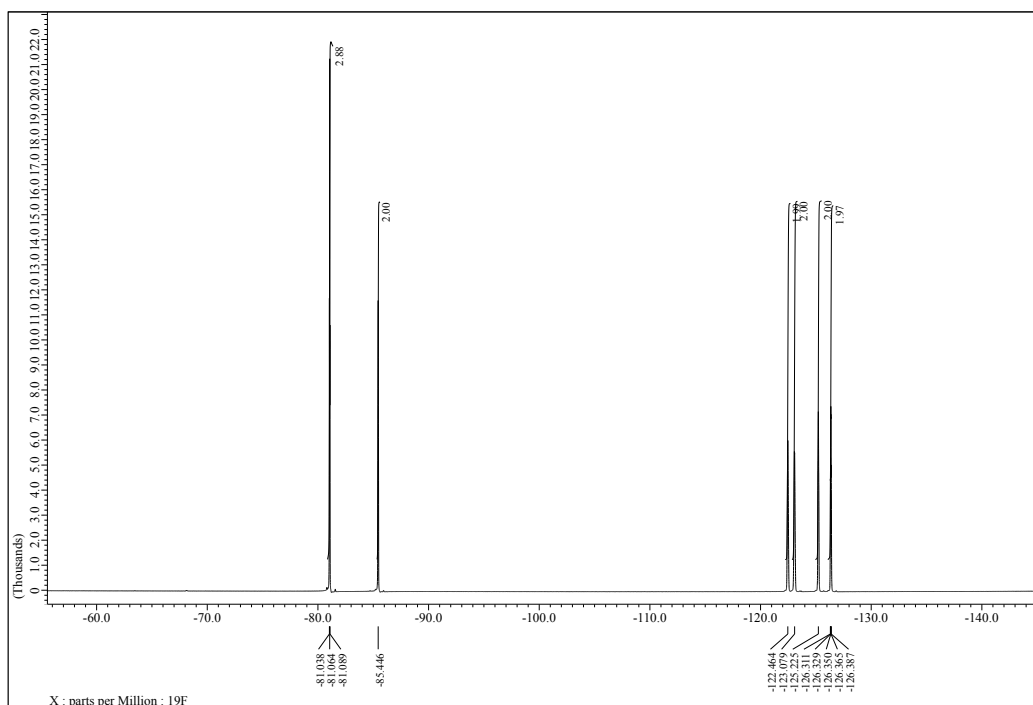
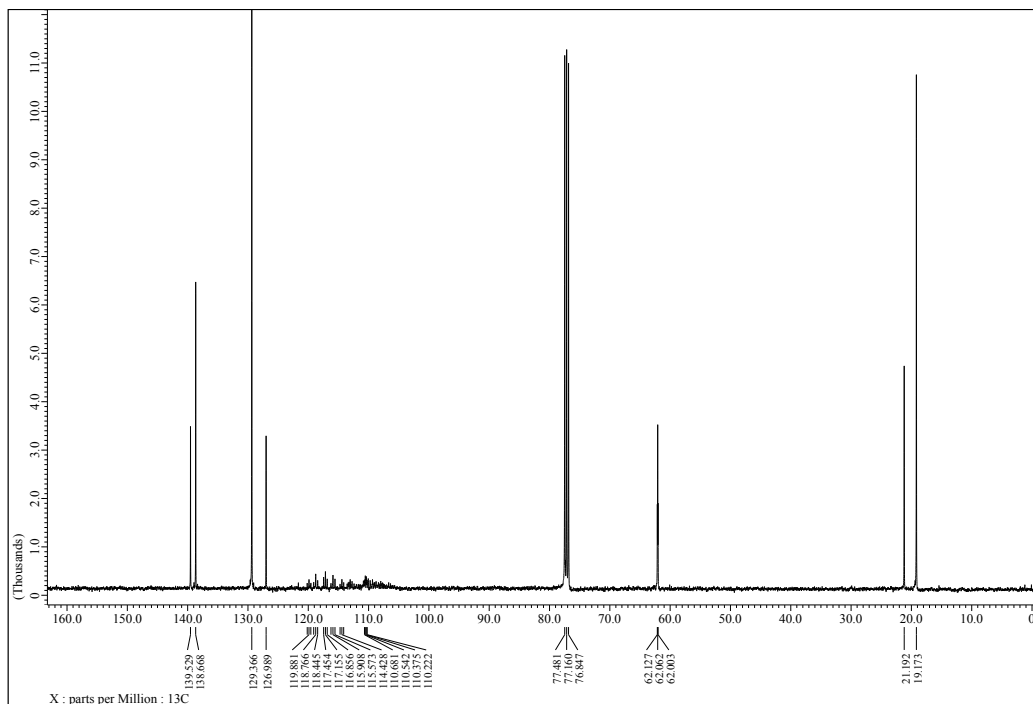
1-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)-4-(trifluoromethyl)benzene (3k)



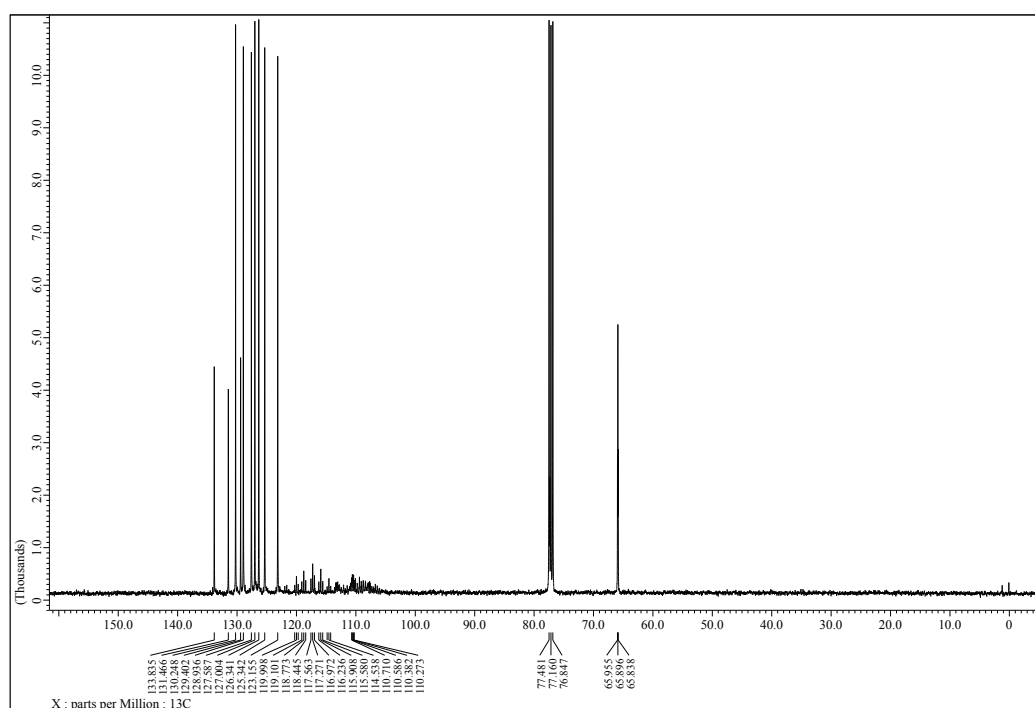
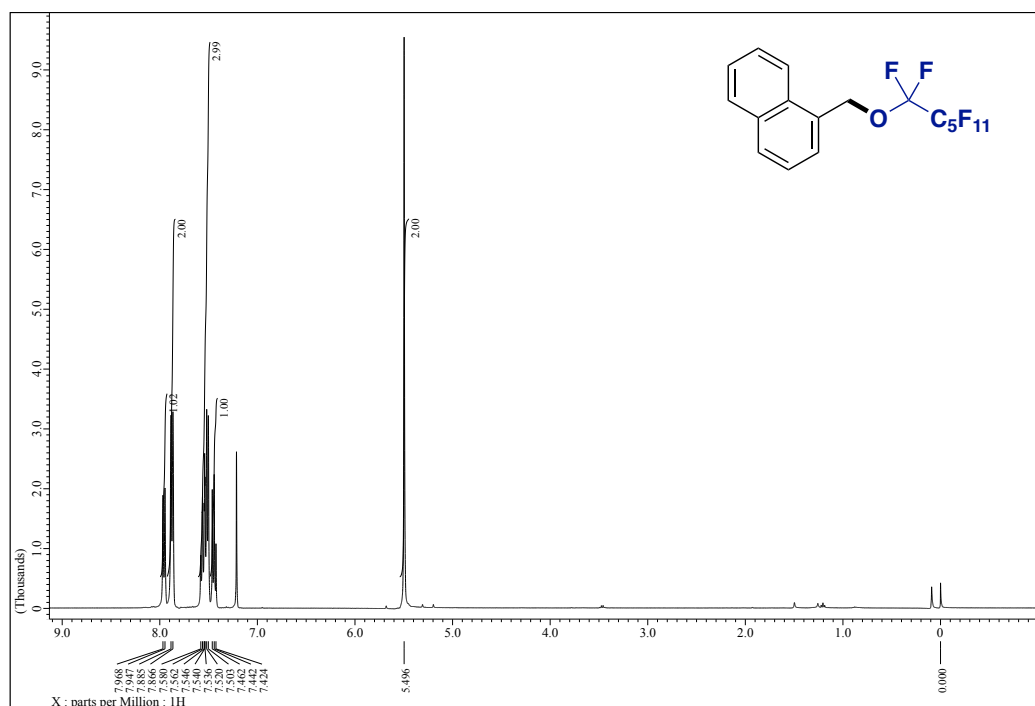


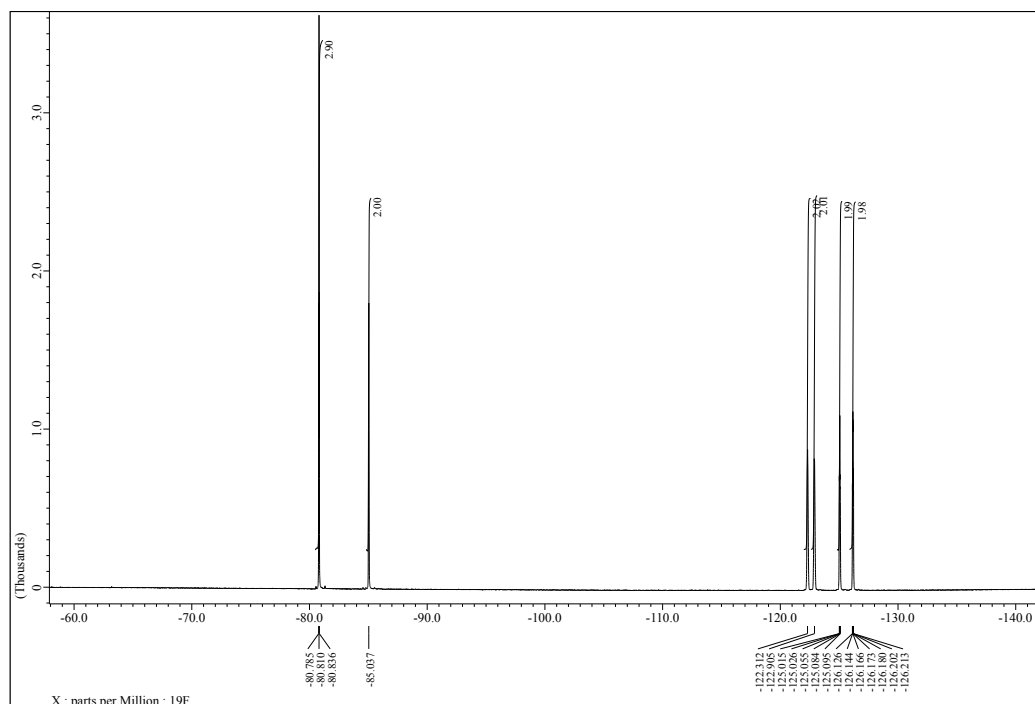
1,3,5-trimethyl-2-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzene (3I)



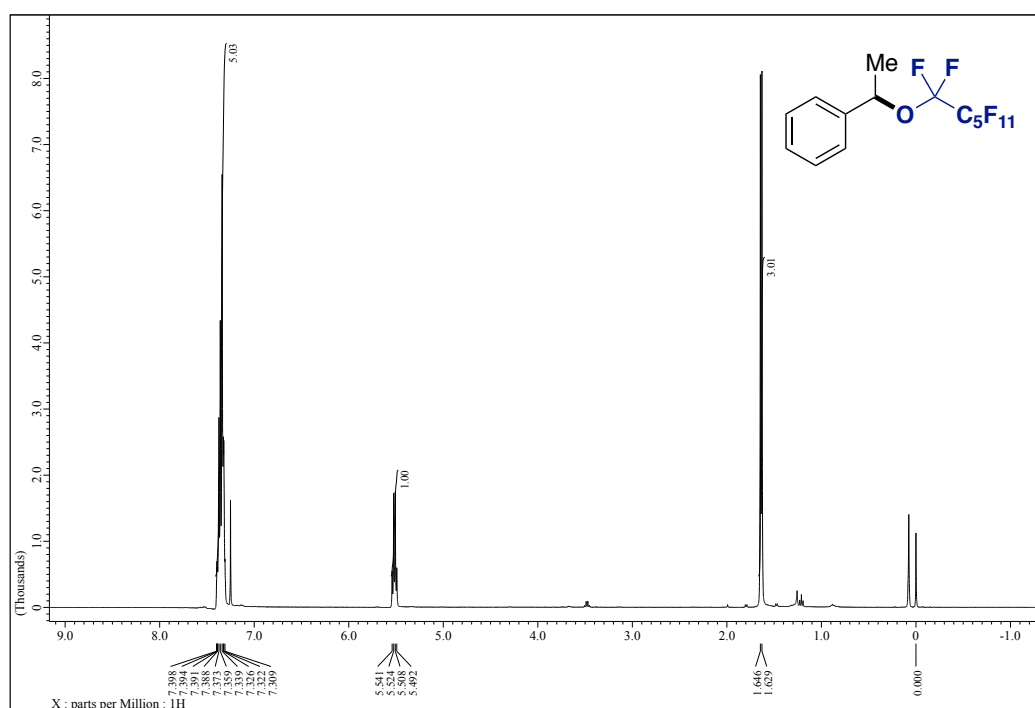


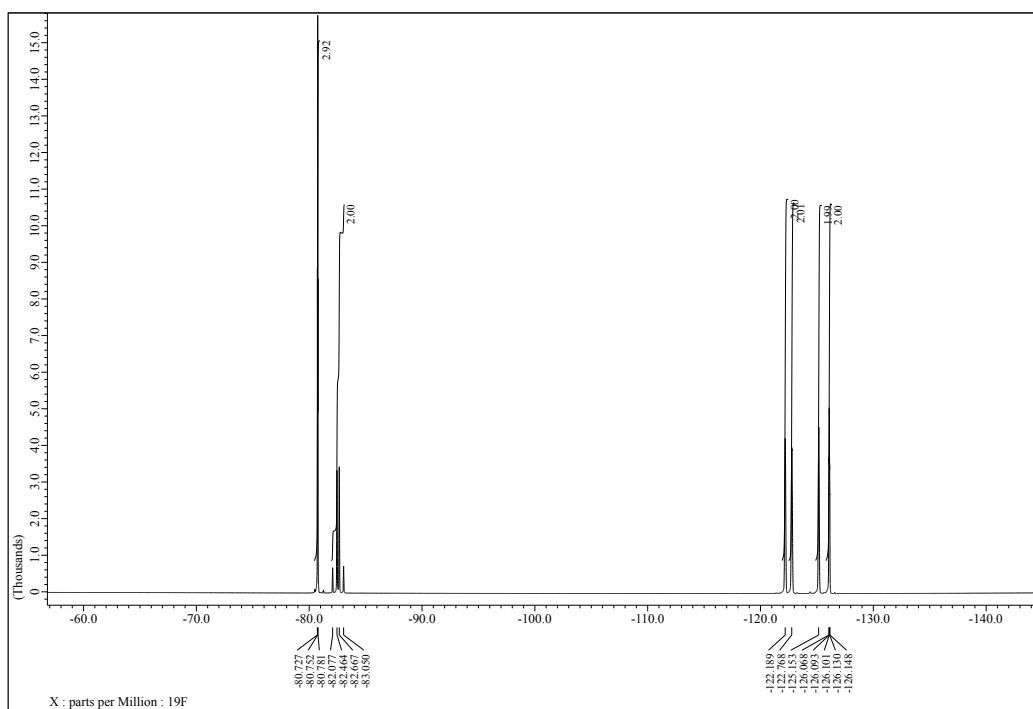
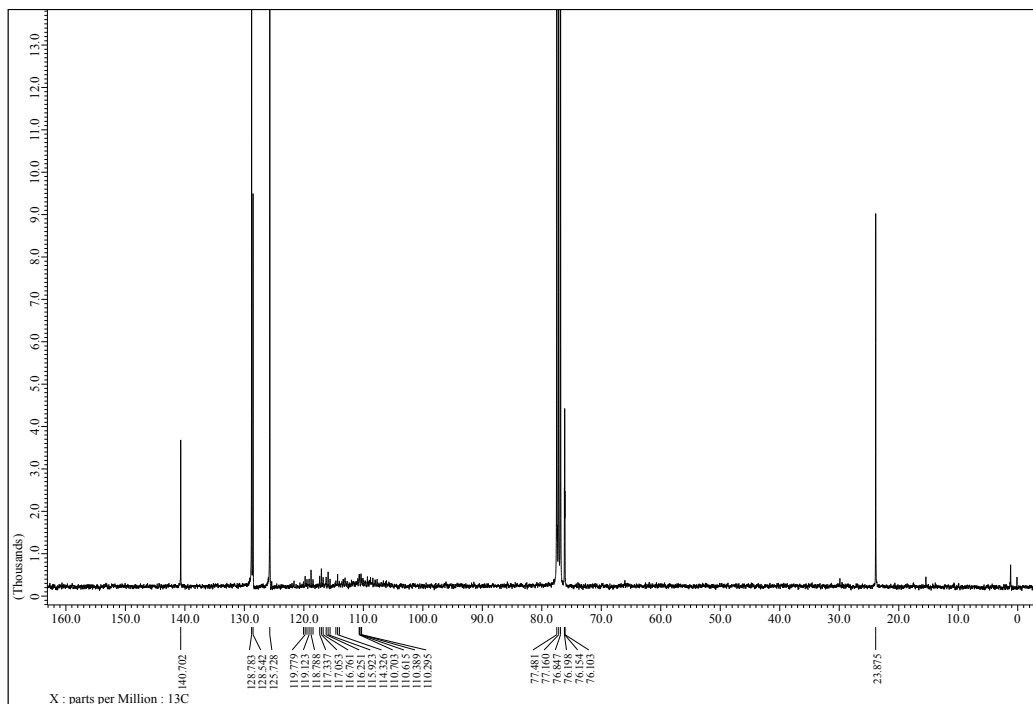
1-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)naphthalene (3m)



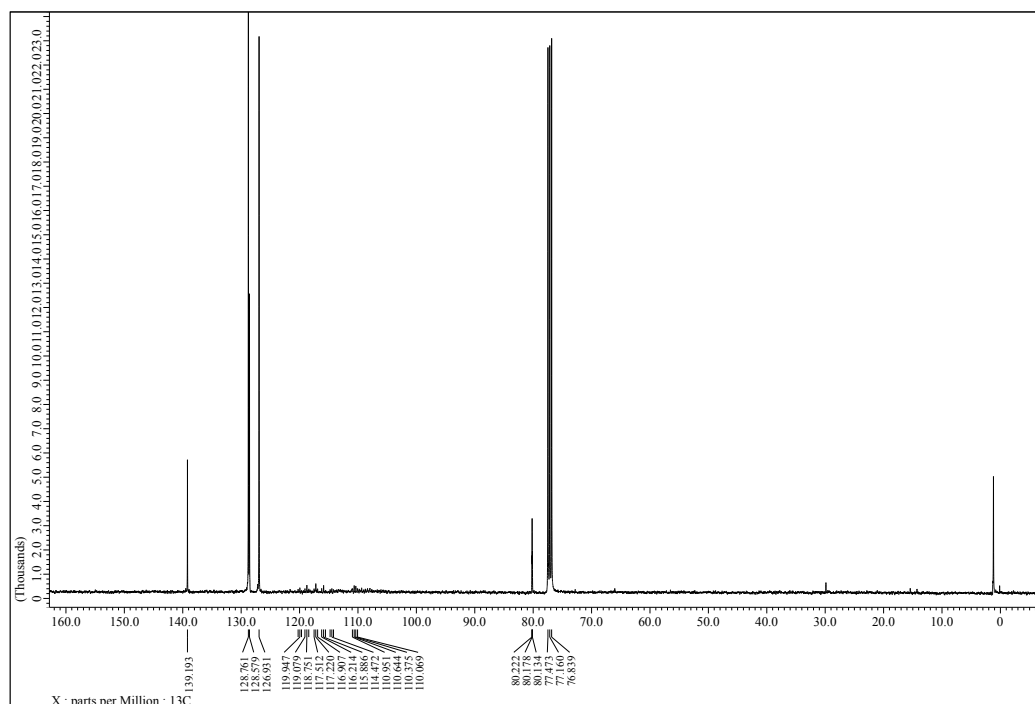
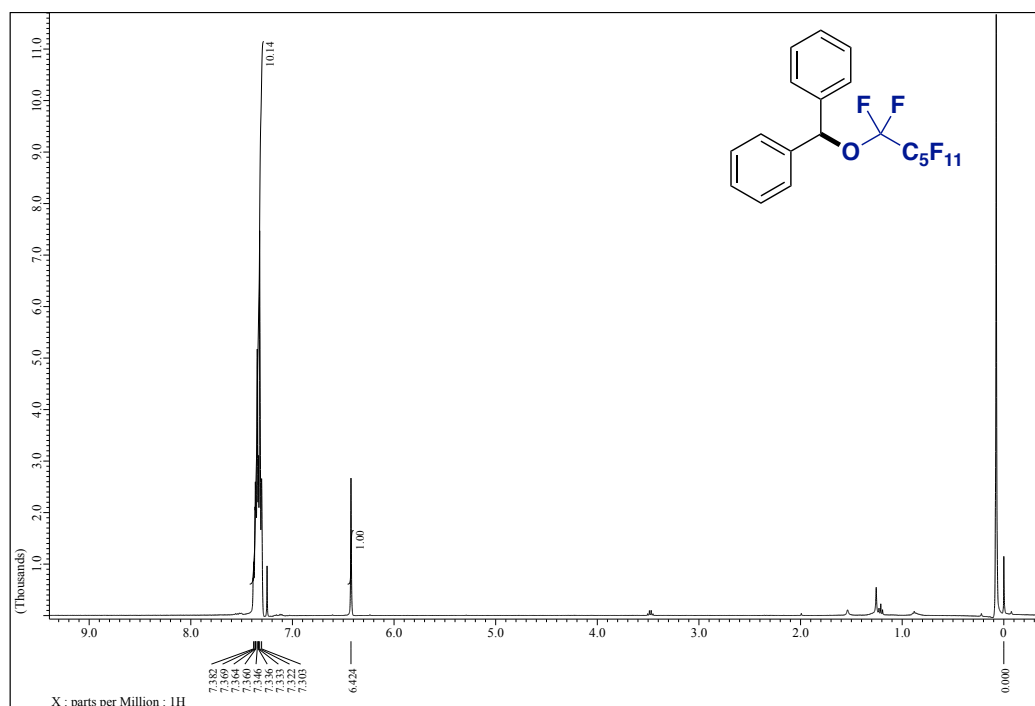


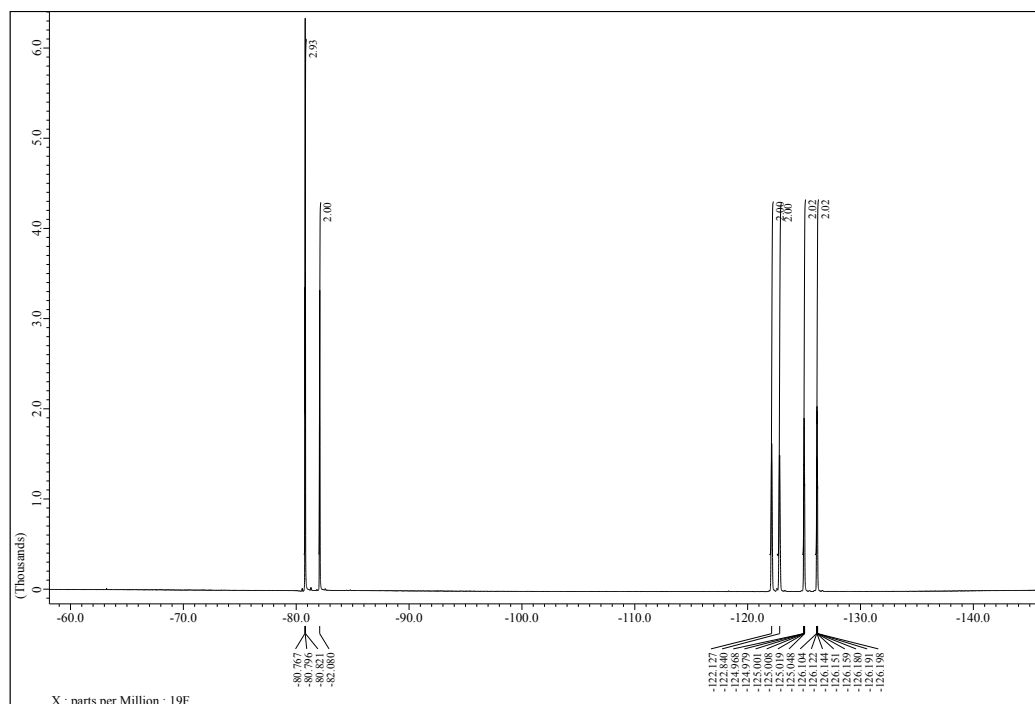
(1-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)ethyl)benzene (3n)



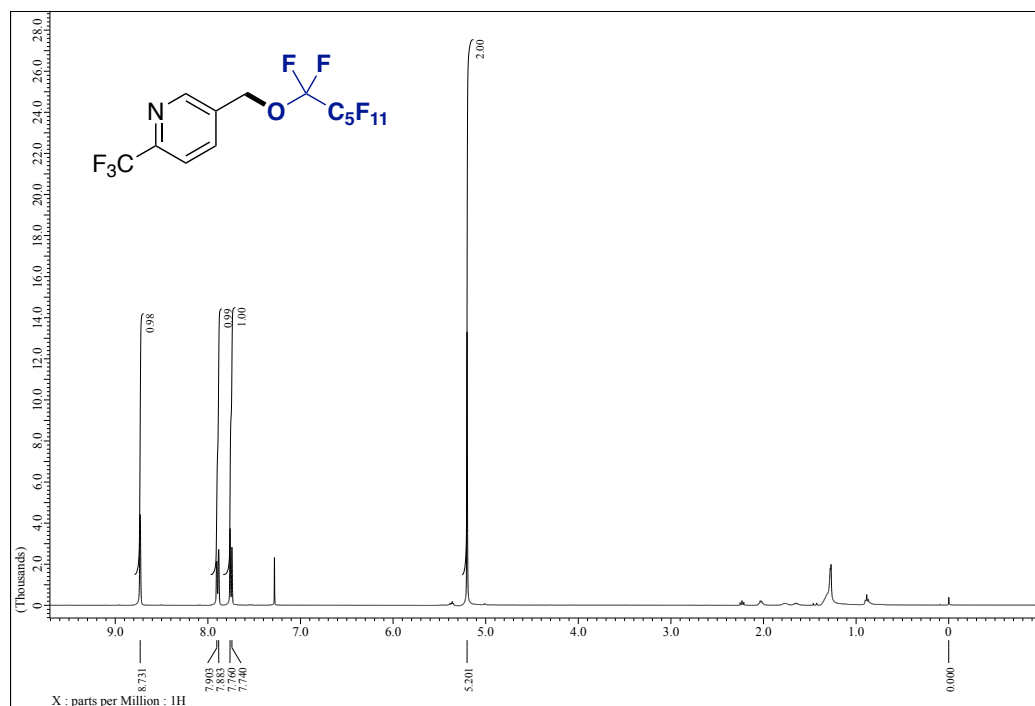


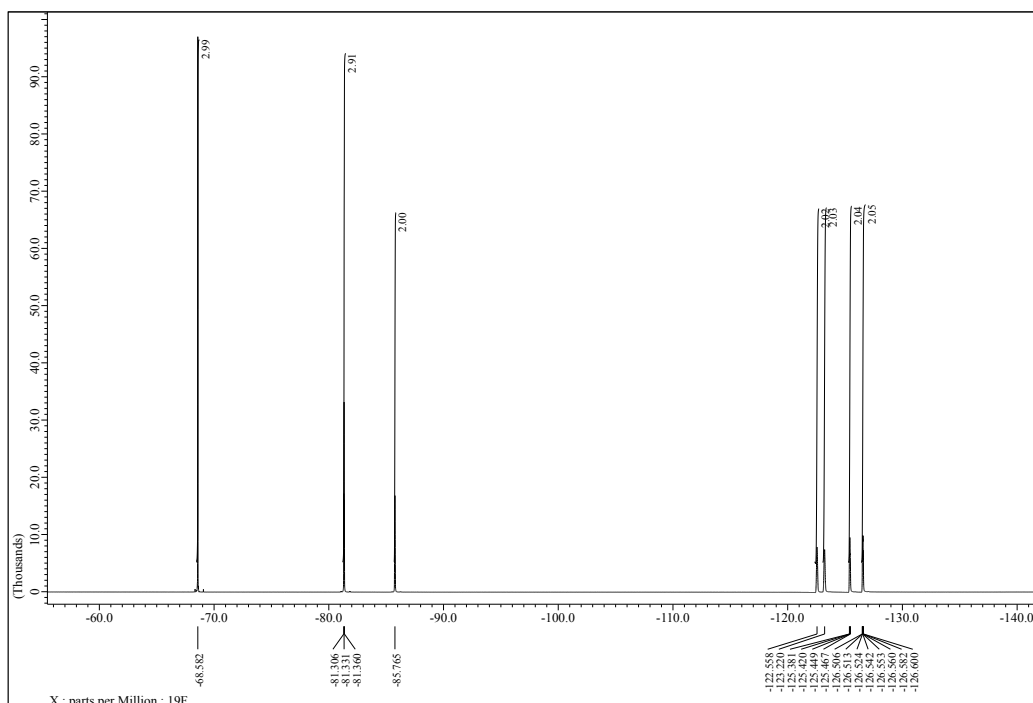
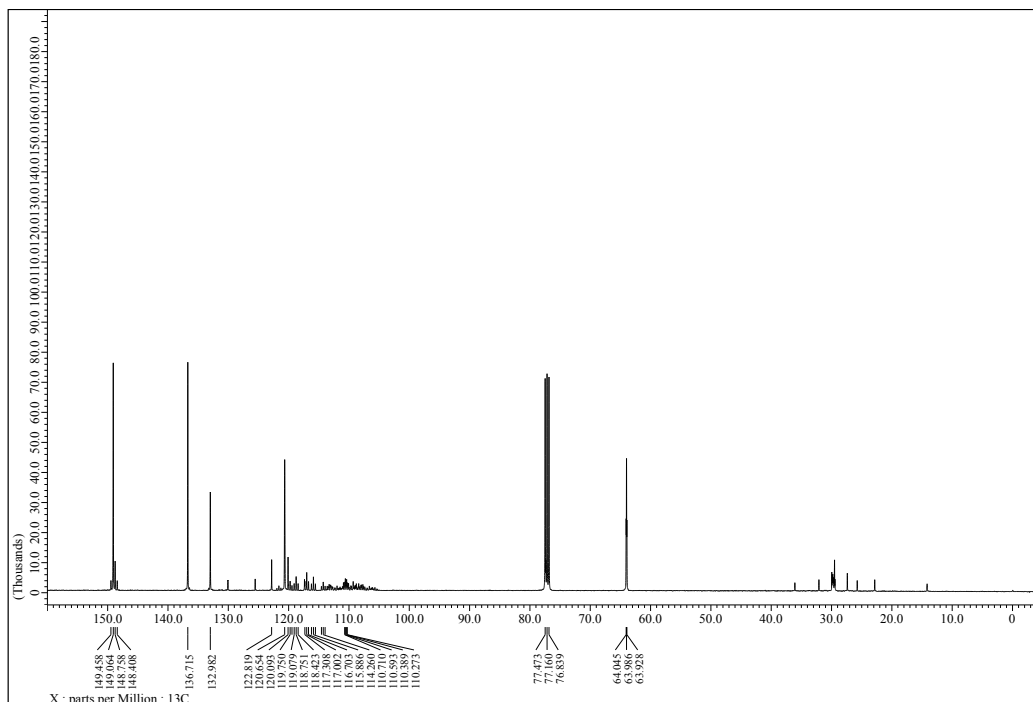
((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methylene)dibenzene (3o)



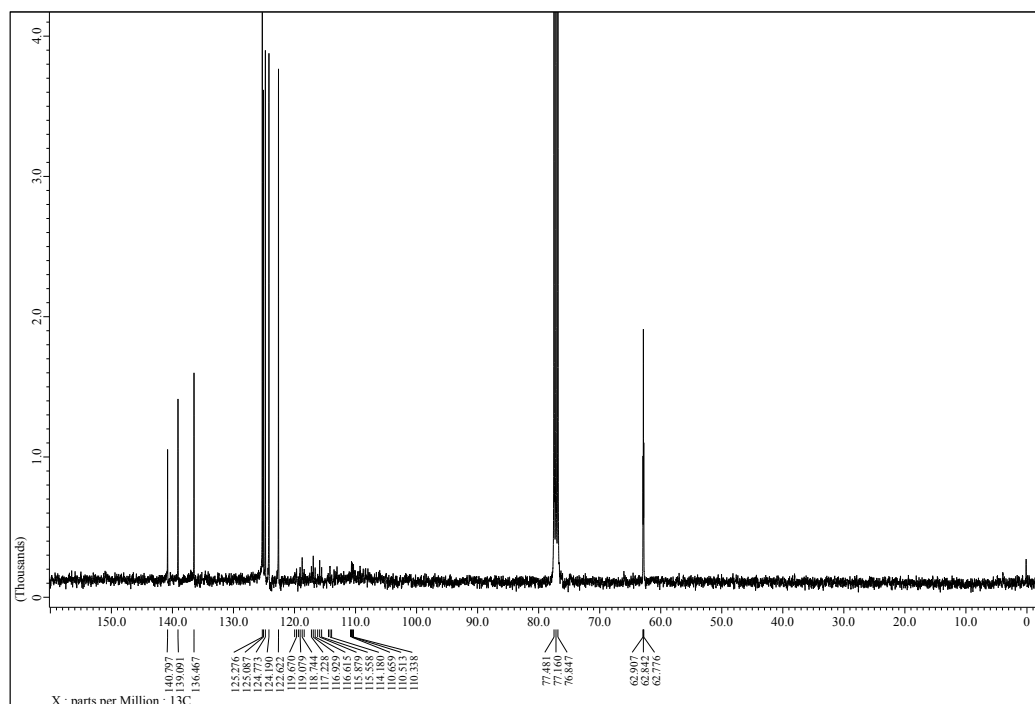
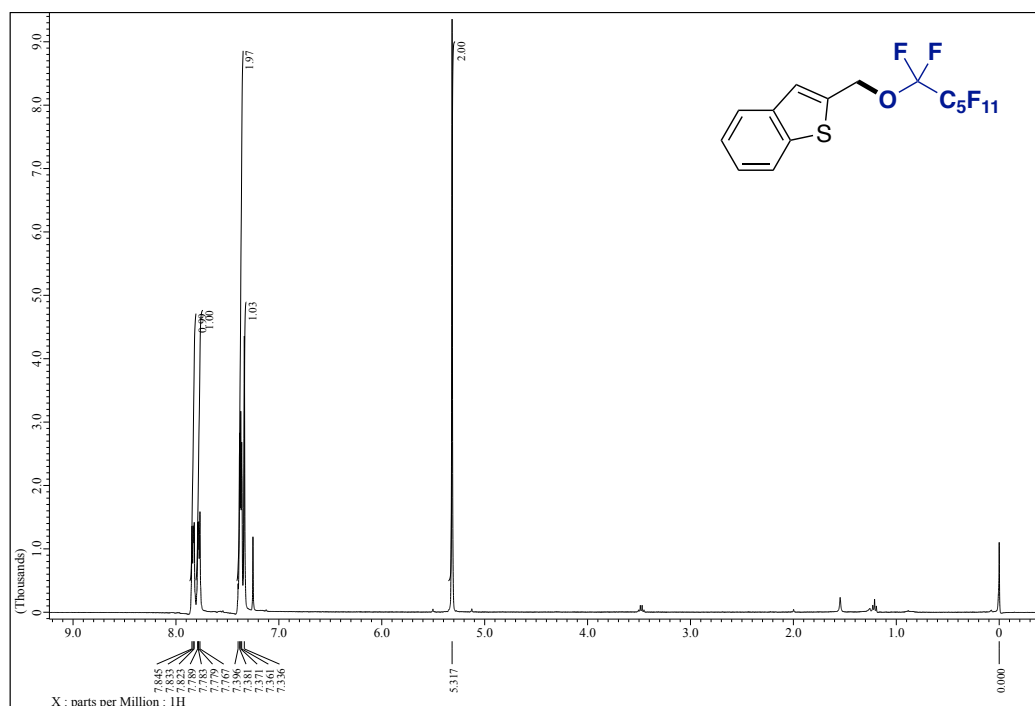


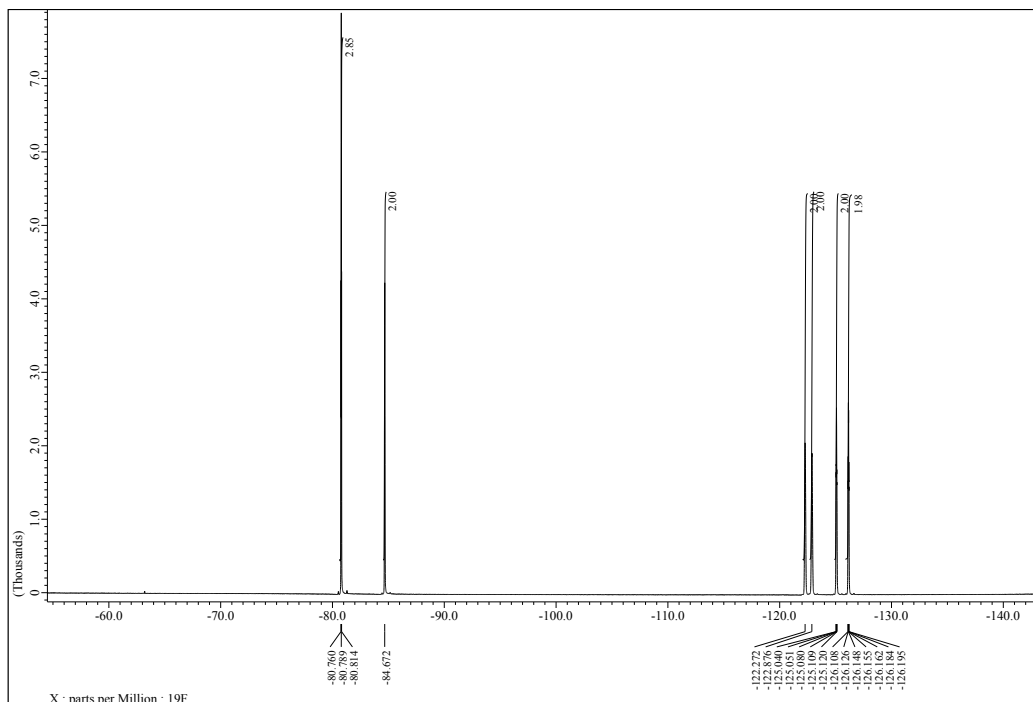
5-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)-2-(trifluoromethyl)pyridine (3p)



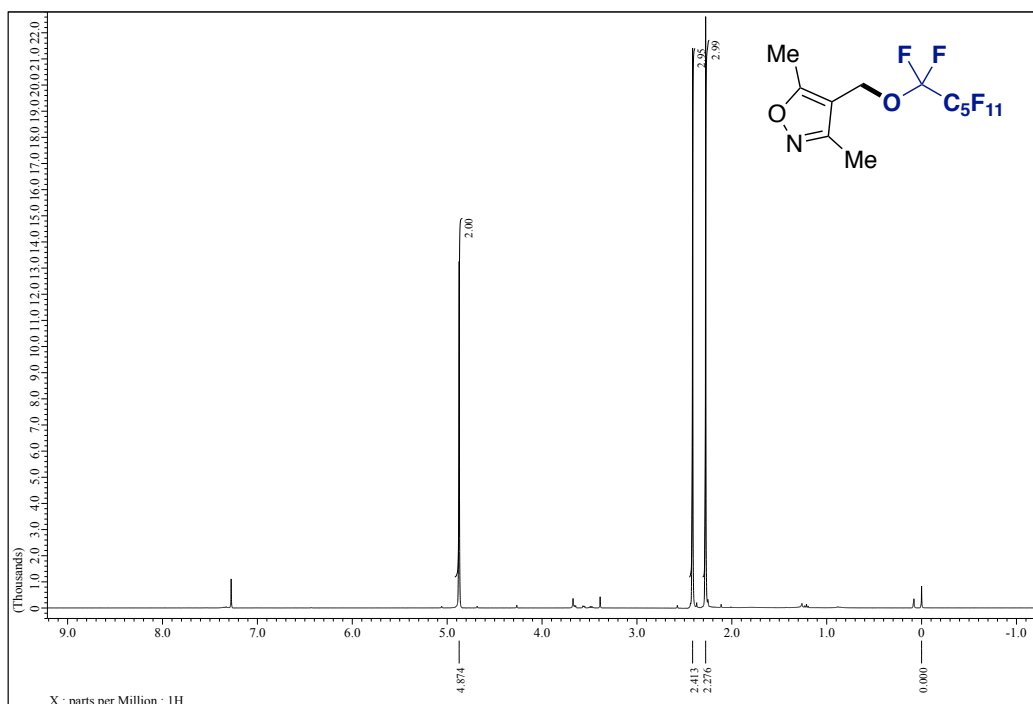


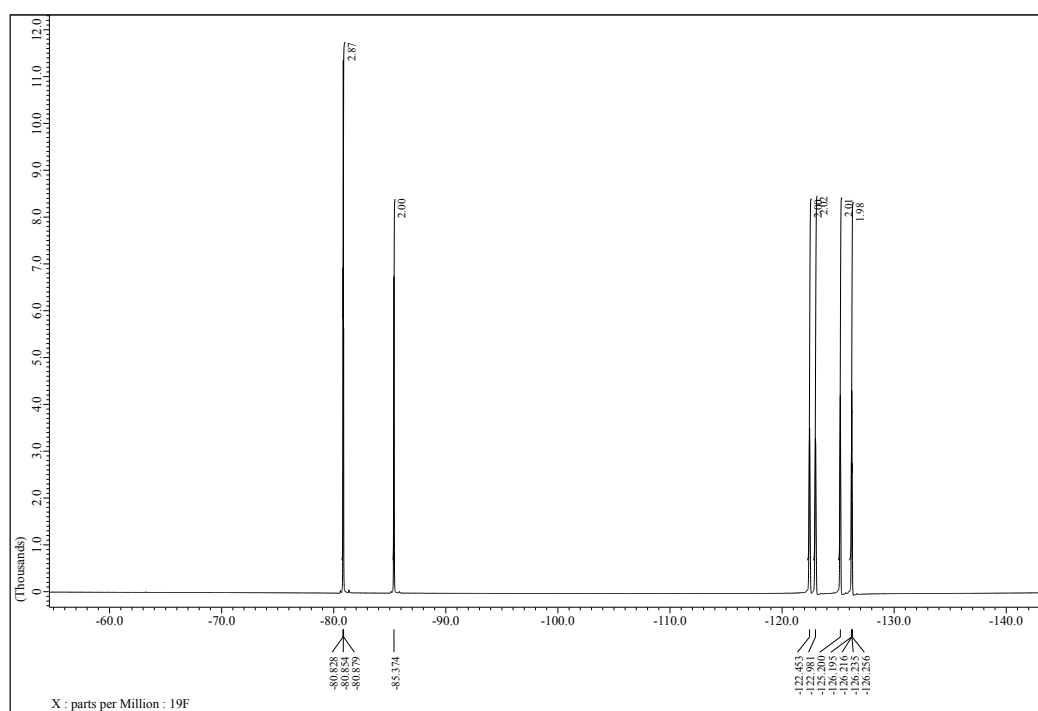
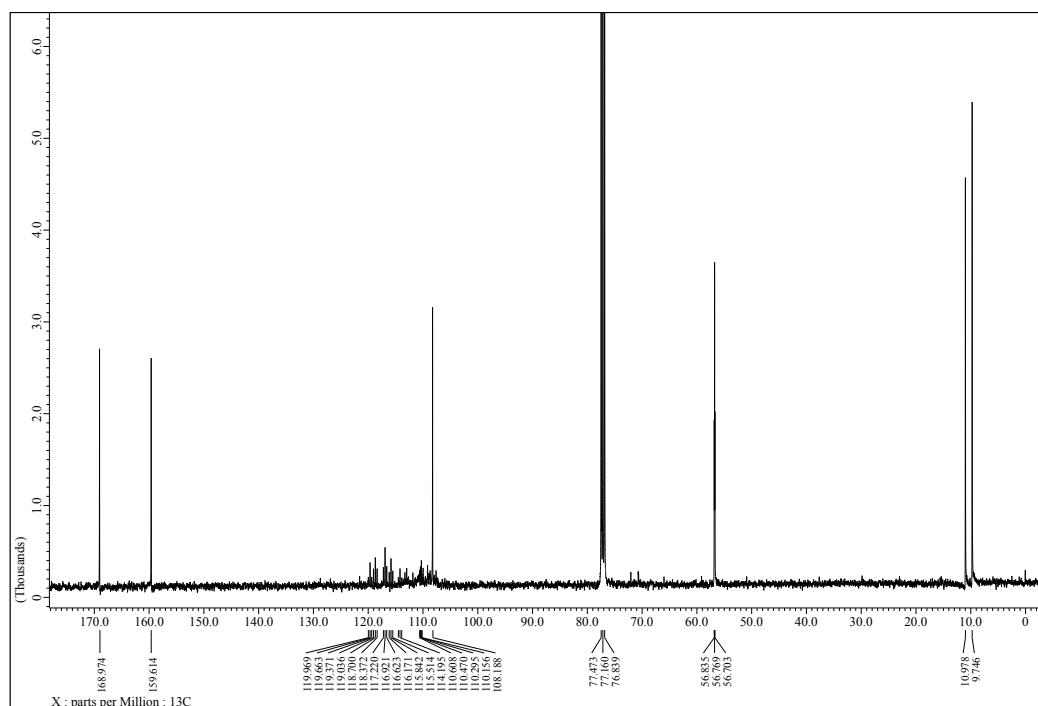
2-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzo[b]thiophene (3q)



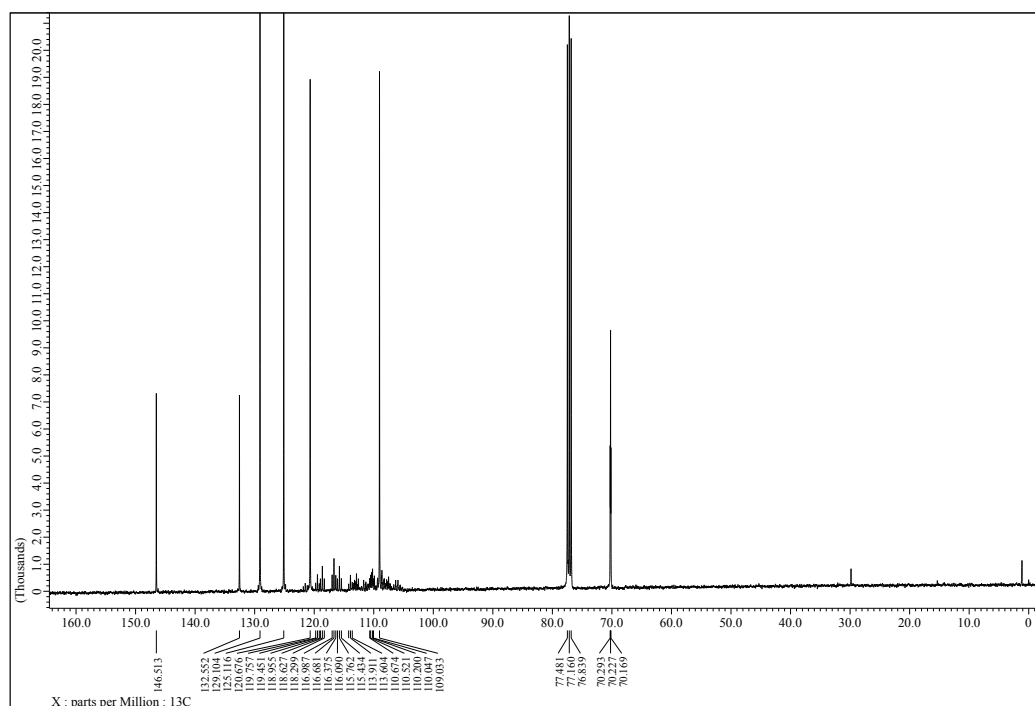
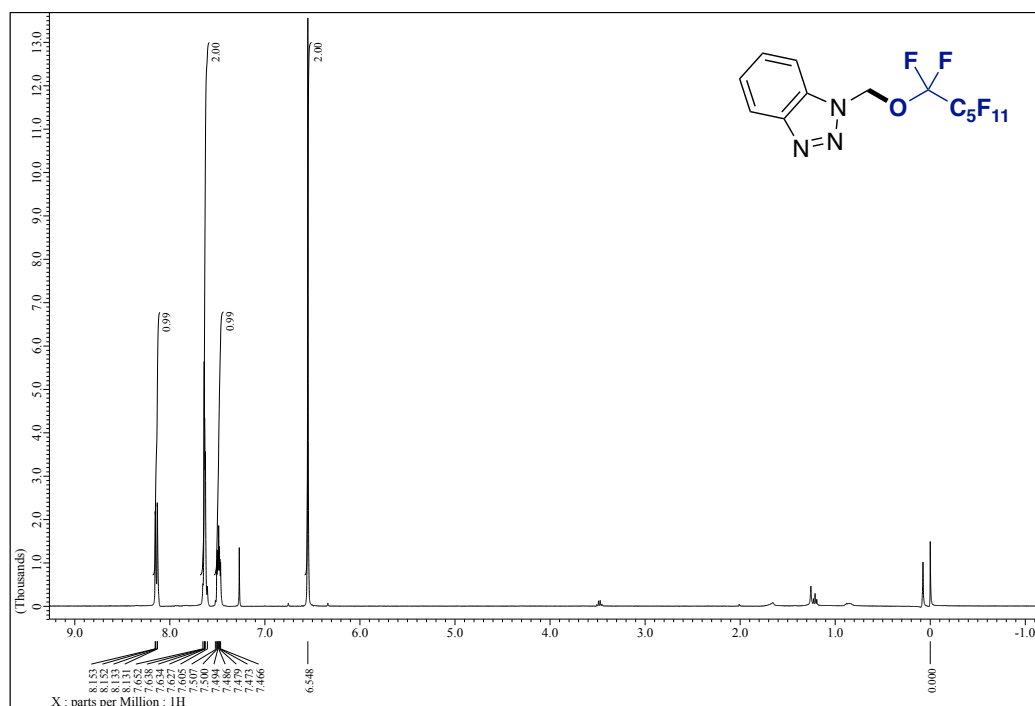


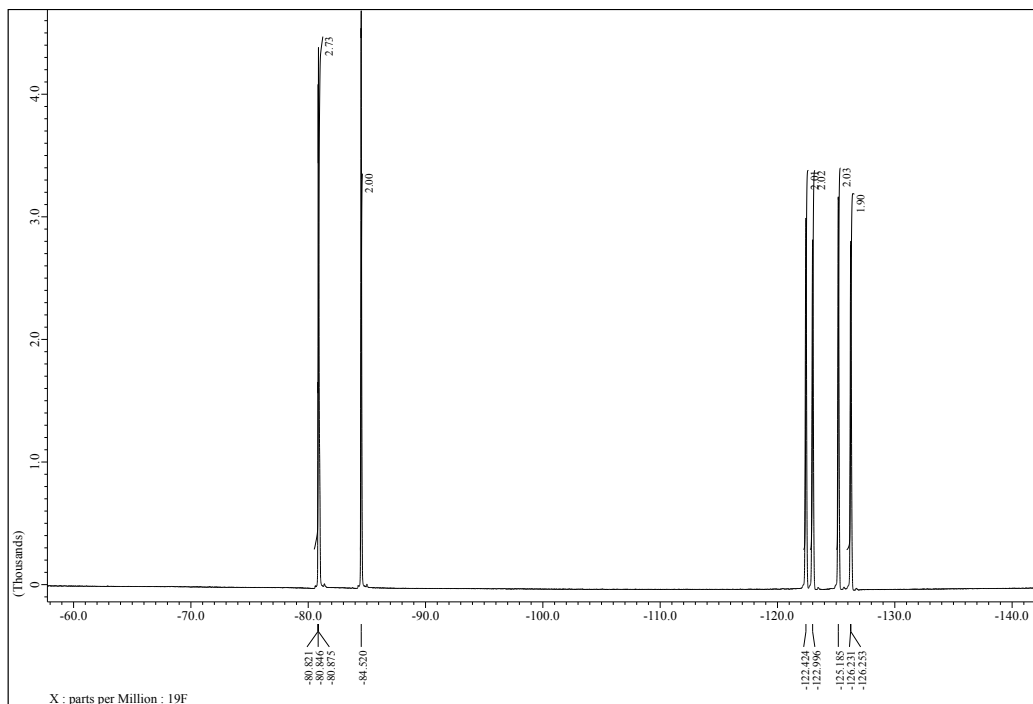
3,5-dimethyl-4-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)isoxazole (3r)



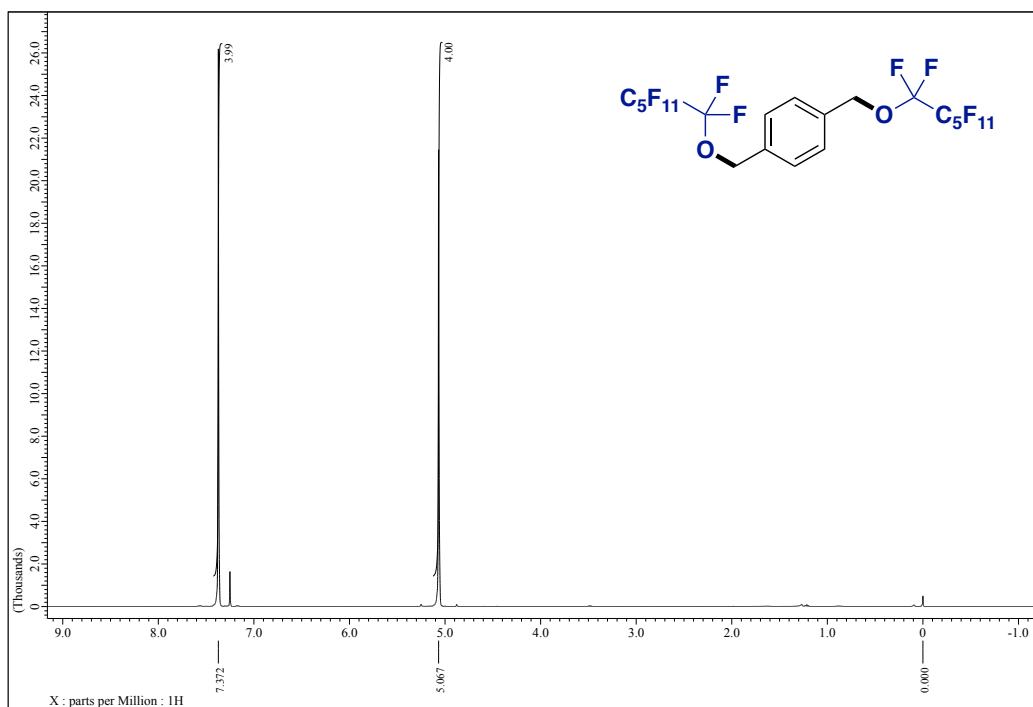


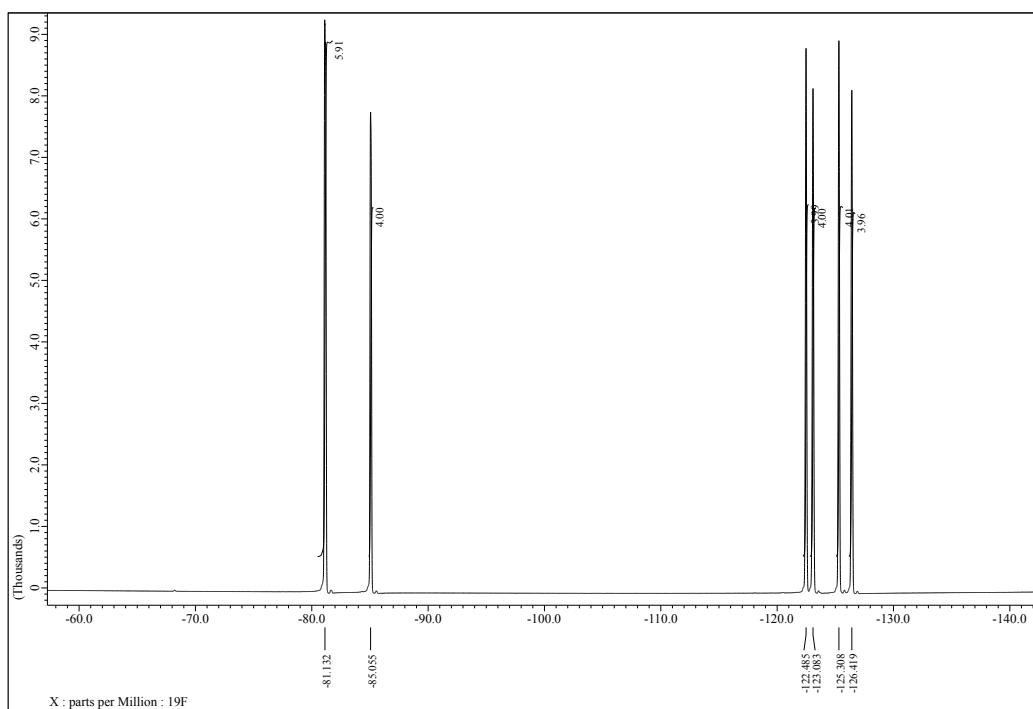
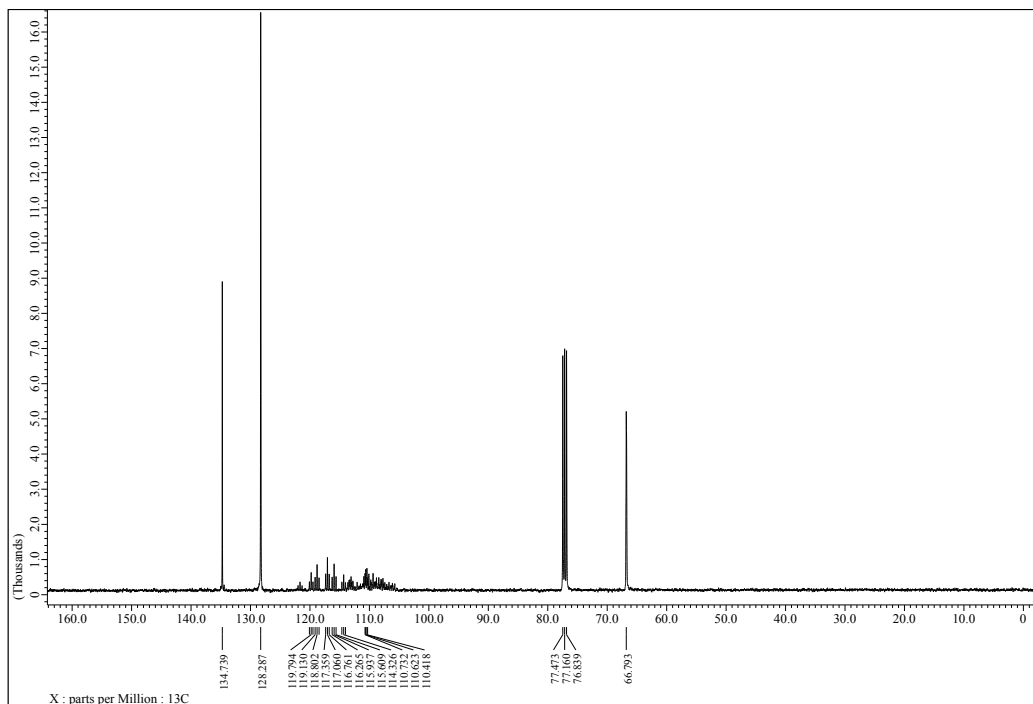
1-(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)-1*H*-benzo[d][1,2,3]triazole (3s)



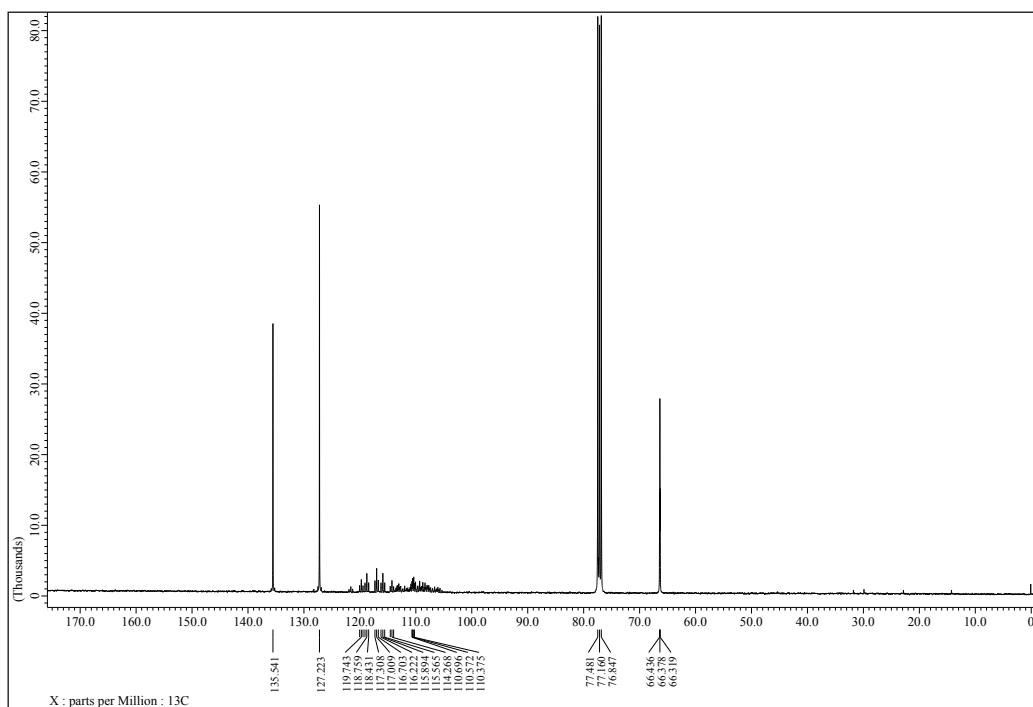
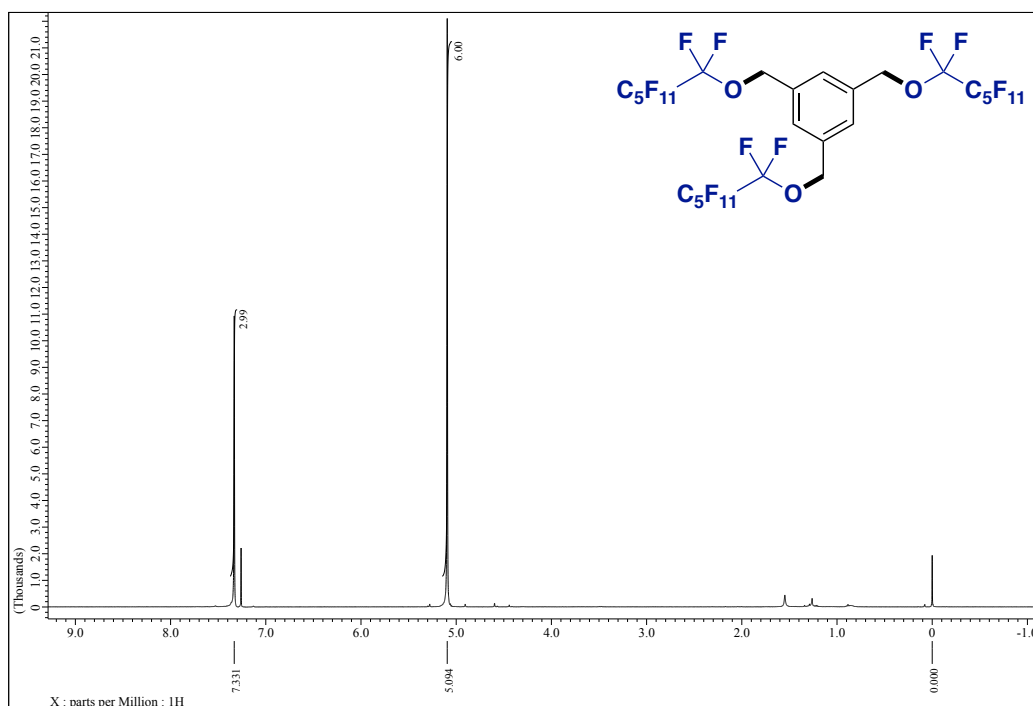


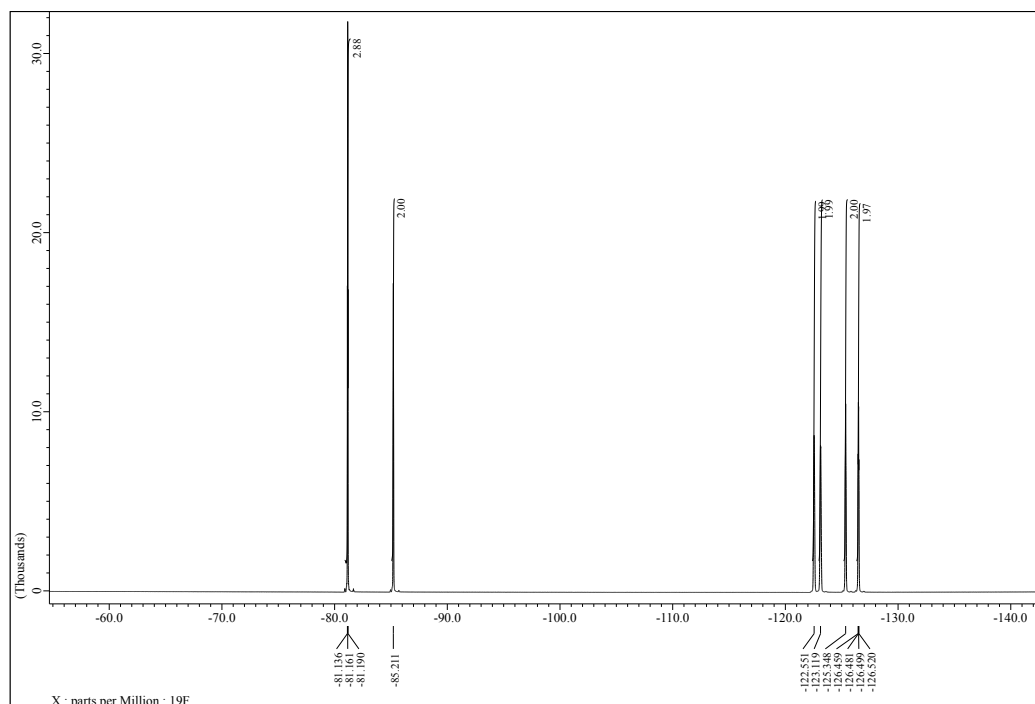
1,4-bis(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzene (3t)



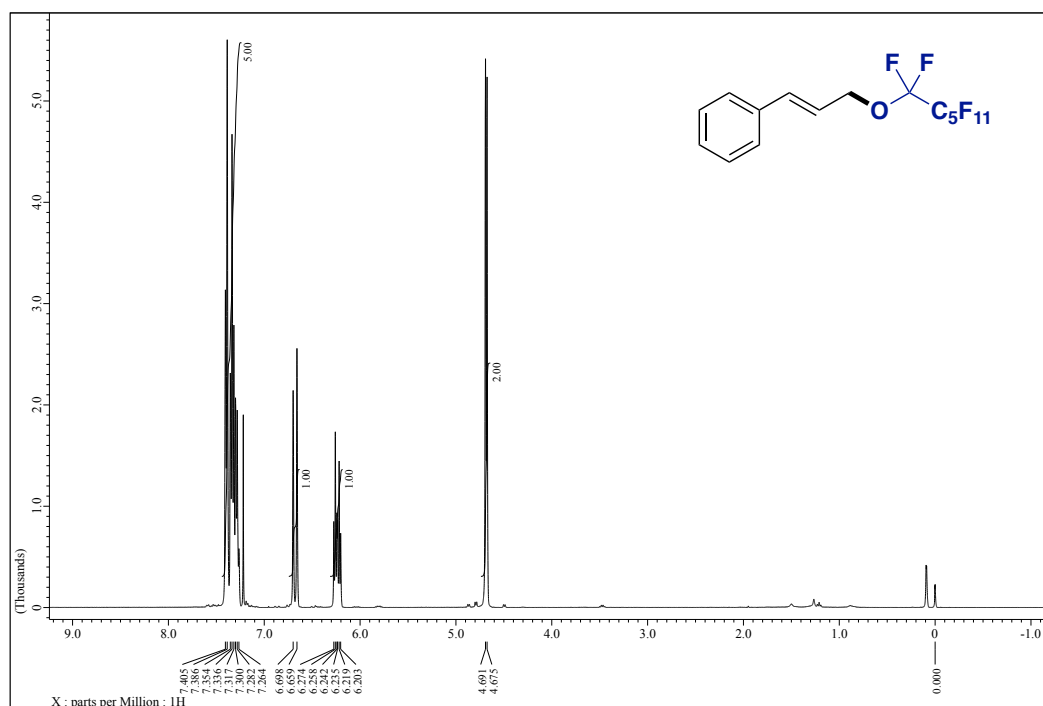


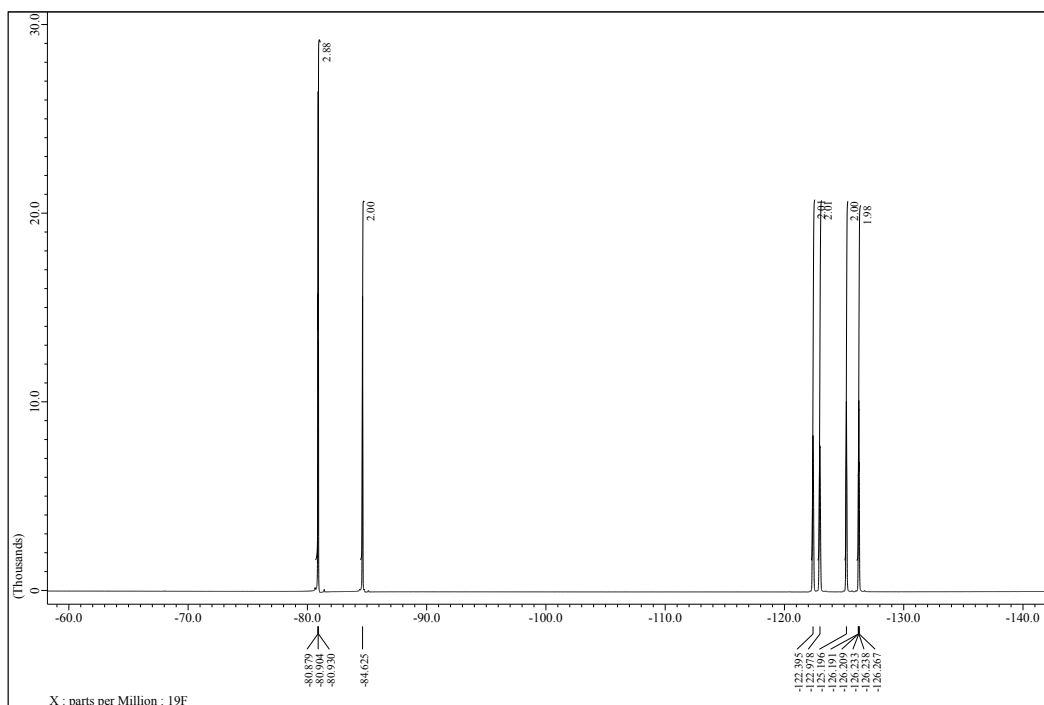
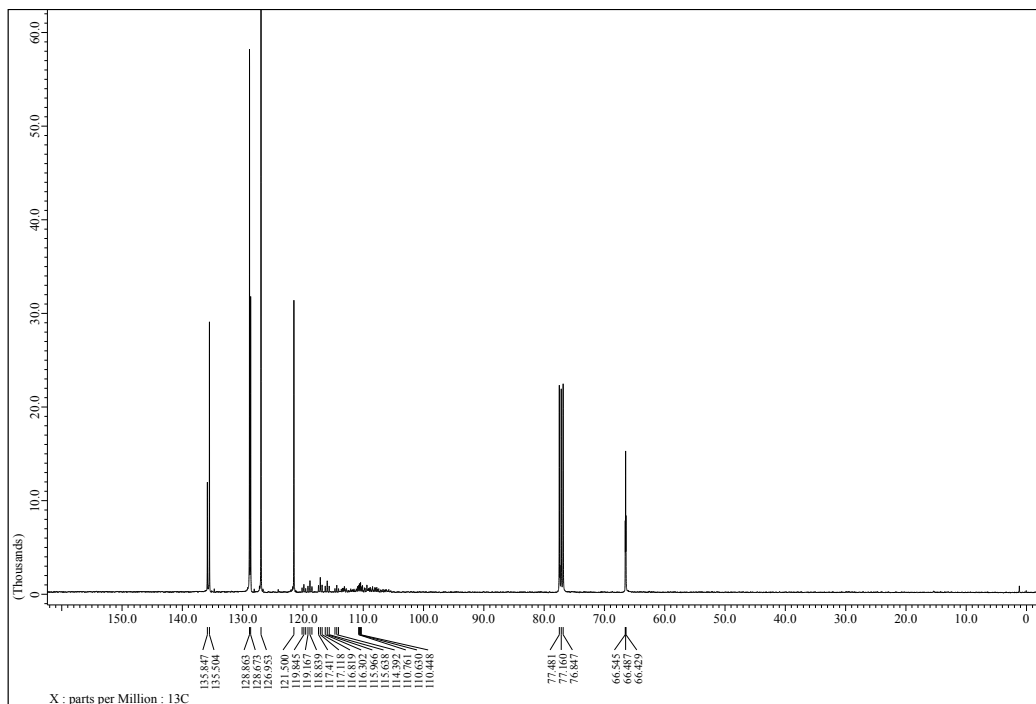
1,3,5-tris(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methyl)benzene (3u)



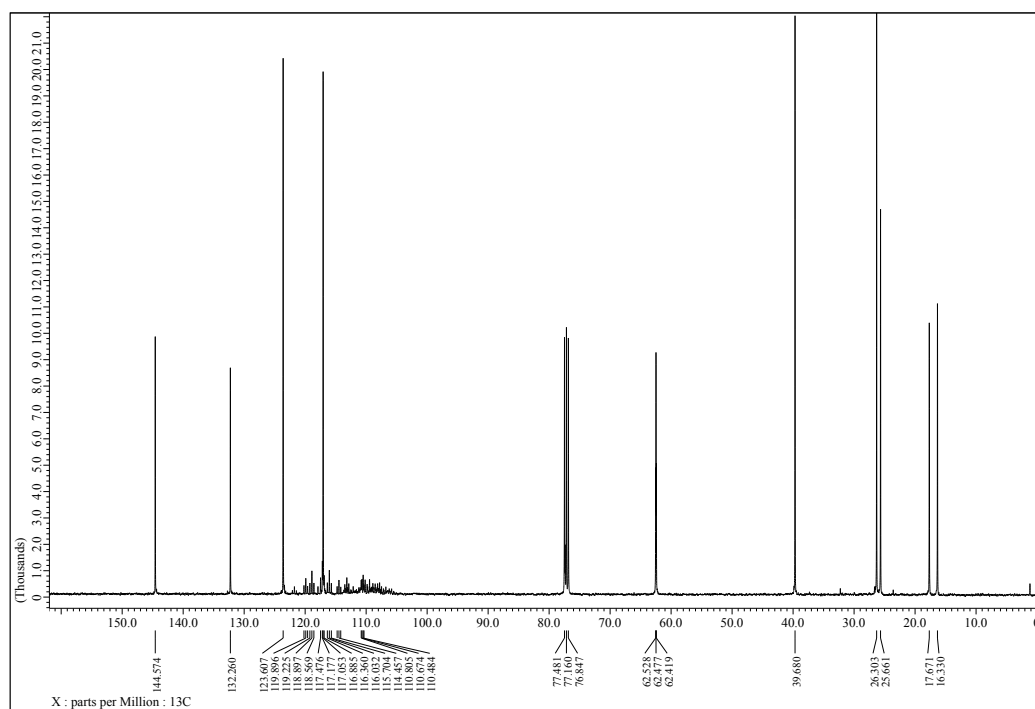
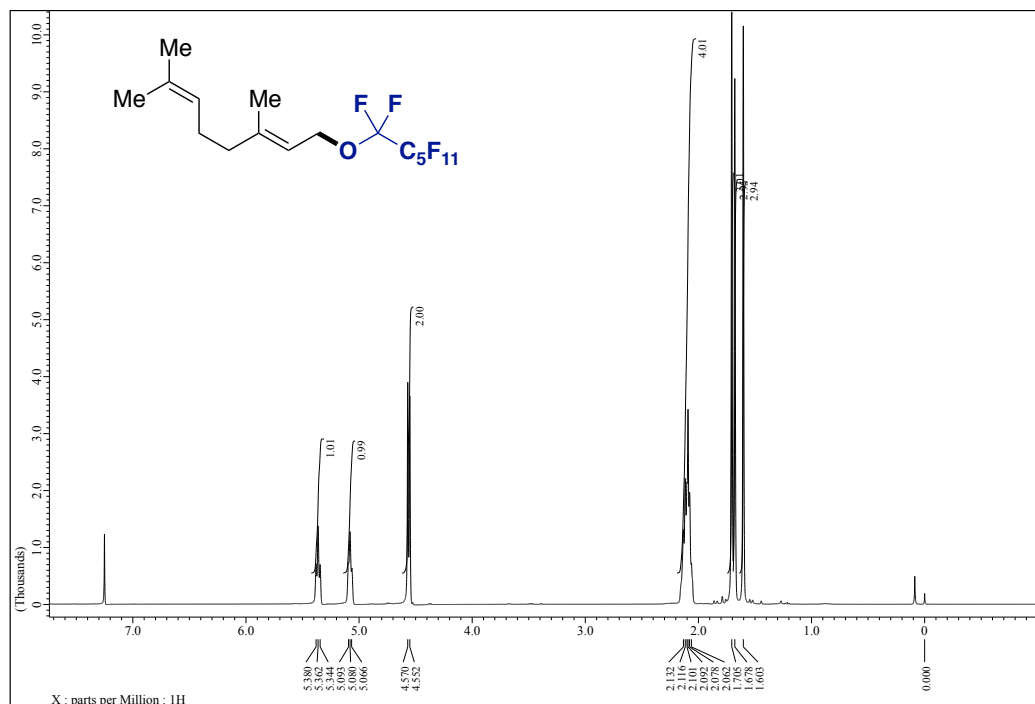


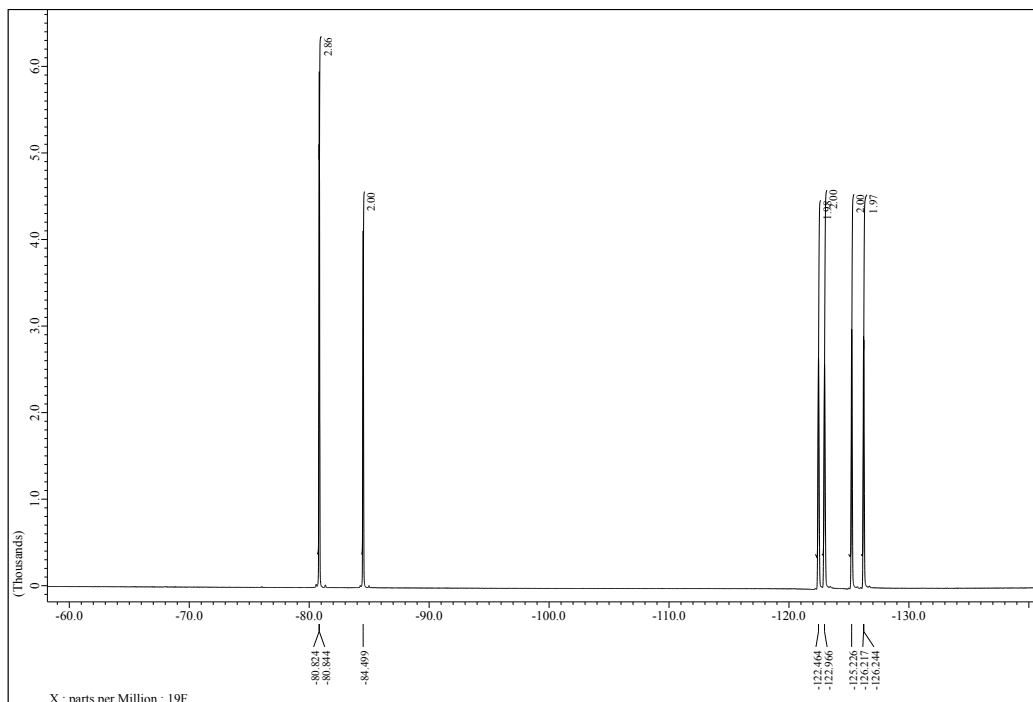
(E)-3-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)prop-1-en-1-yl)benzene (5a)



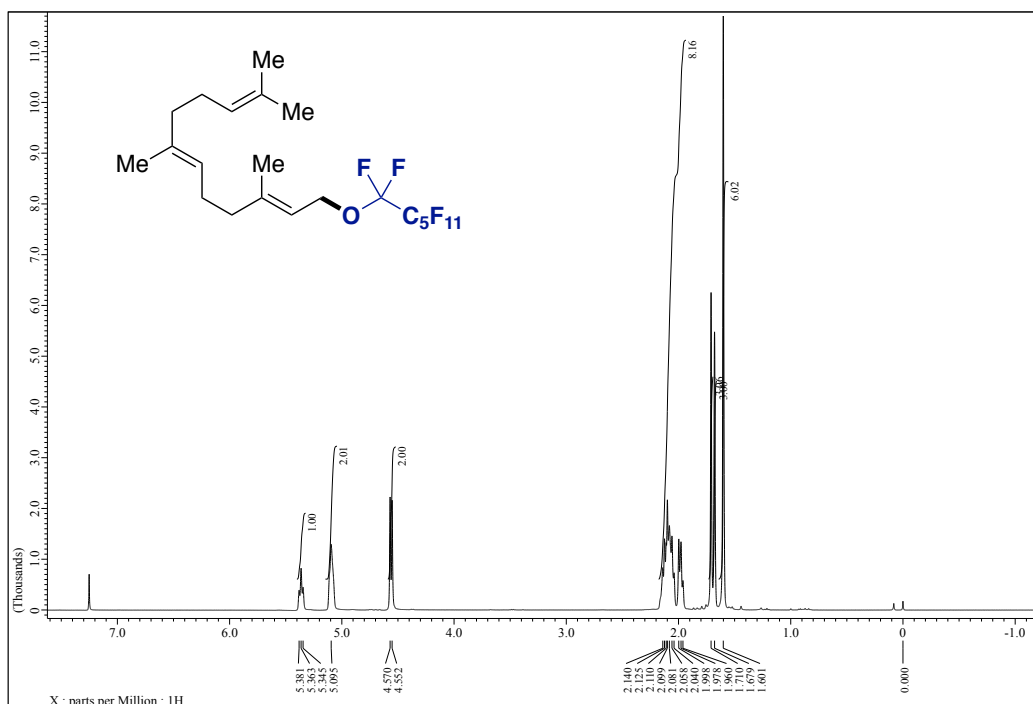


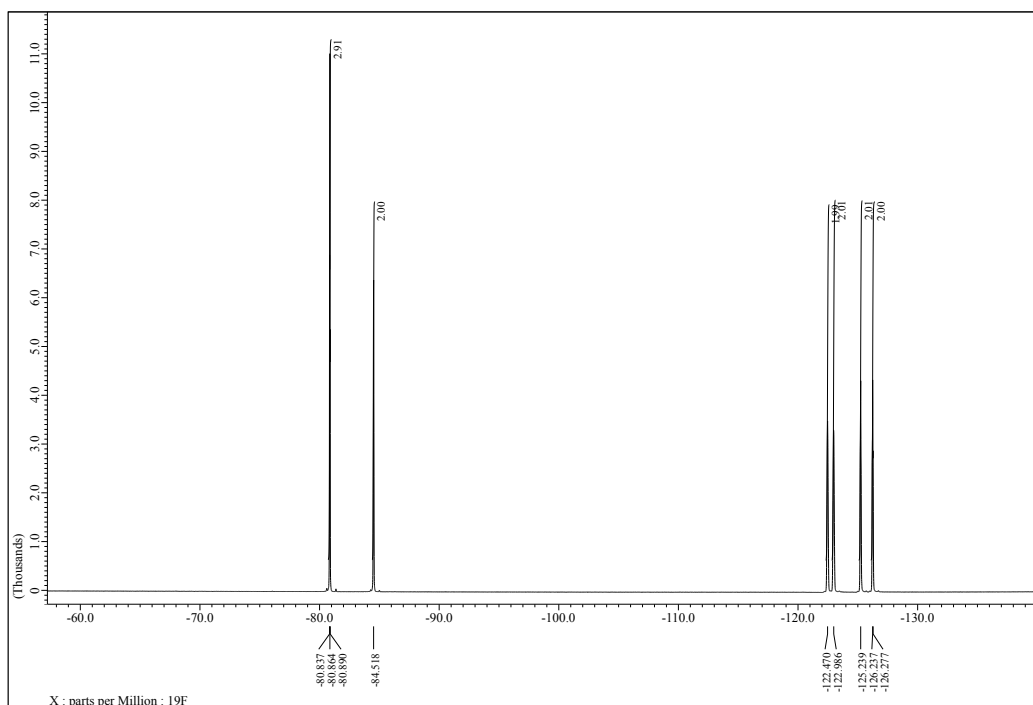
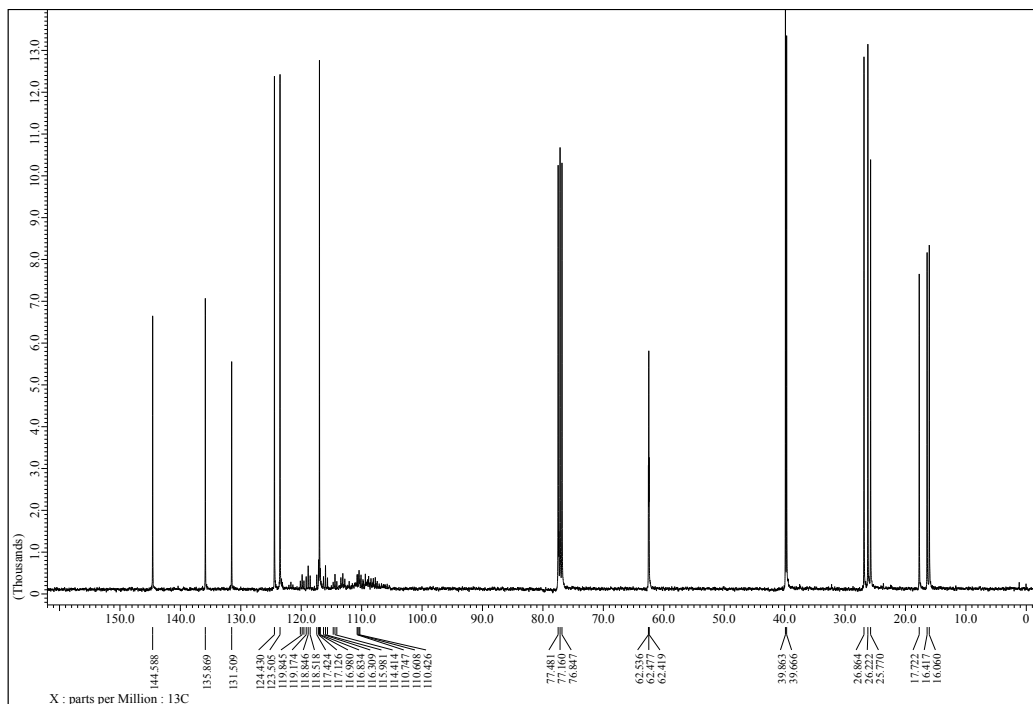
(E)-3,7-dimethyl-1-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)octa-2,6-diene (5b)



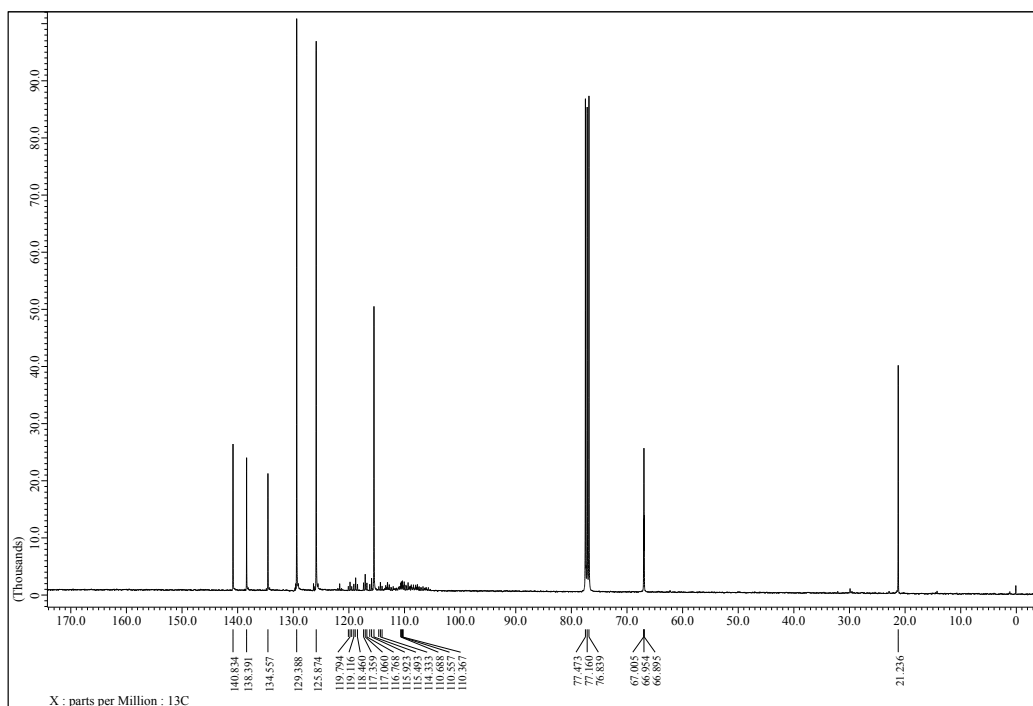
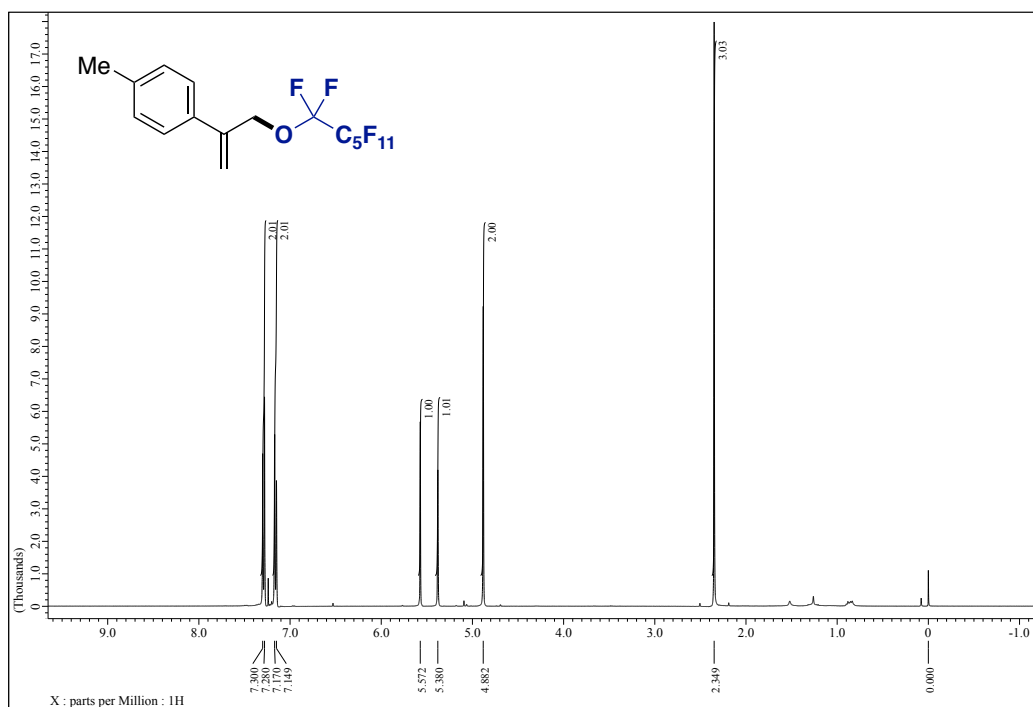


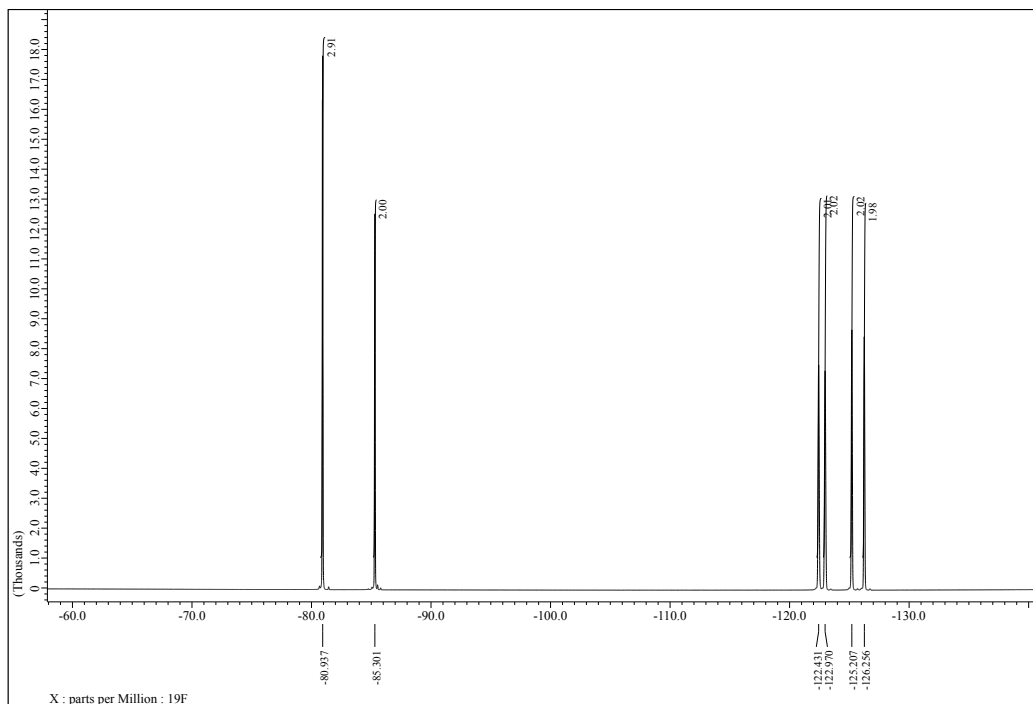
(2*E*,6*E*)-3,7,11-trimethyl-1-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)dodeca-2,6,10-triene (5c)



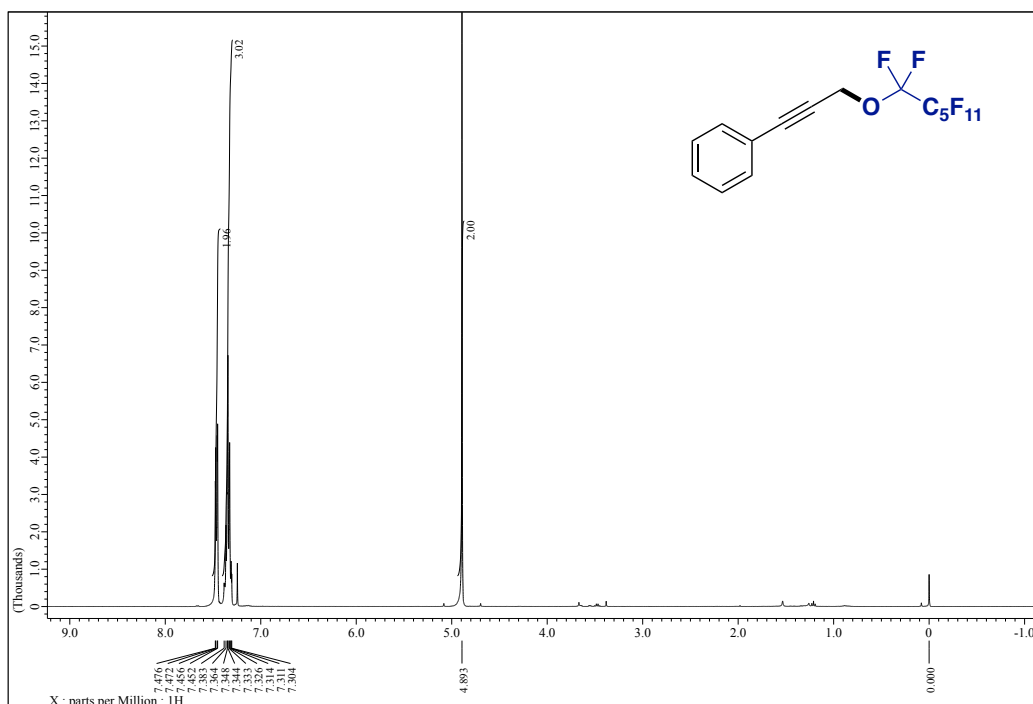


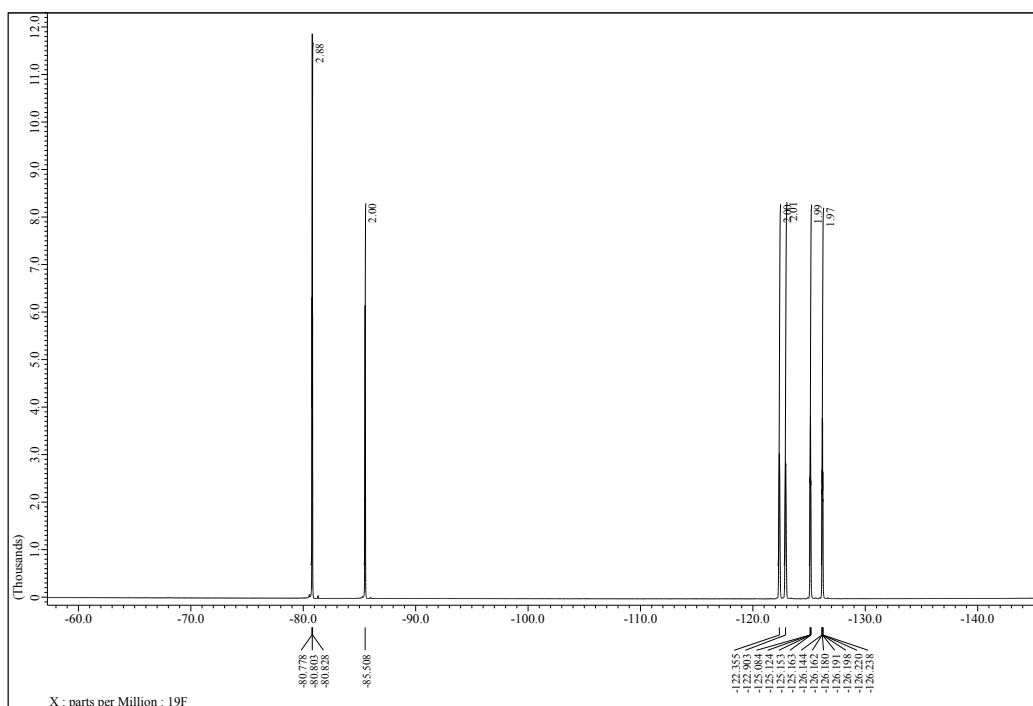
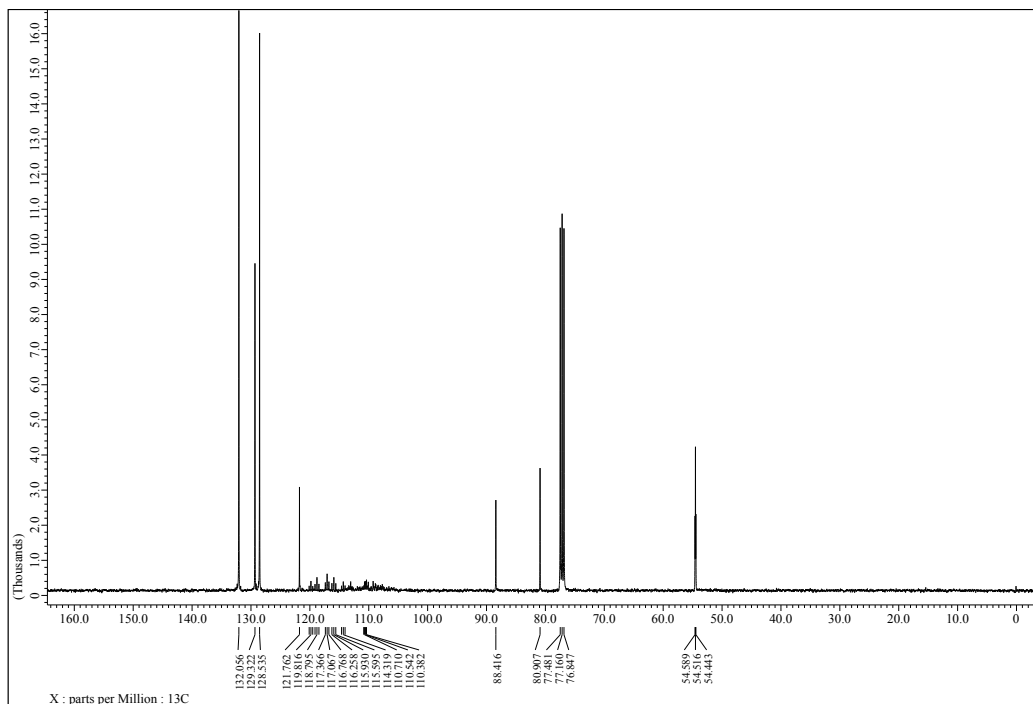
1-methyl-4-(3-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)prop-1-en-2-yl)benzene (5d)



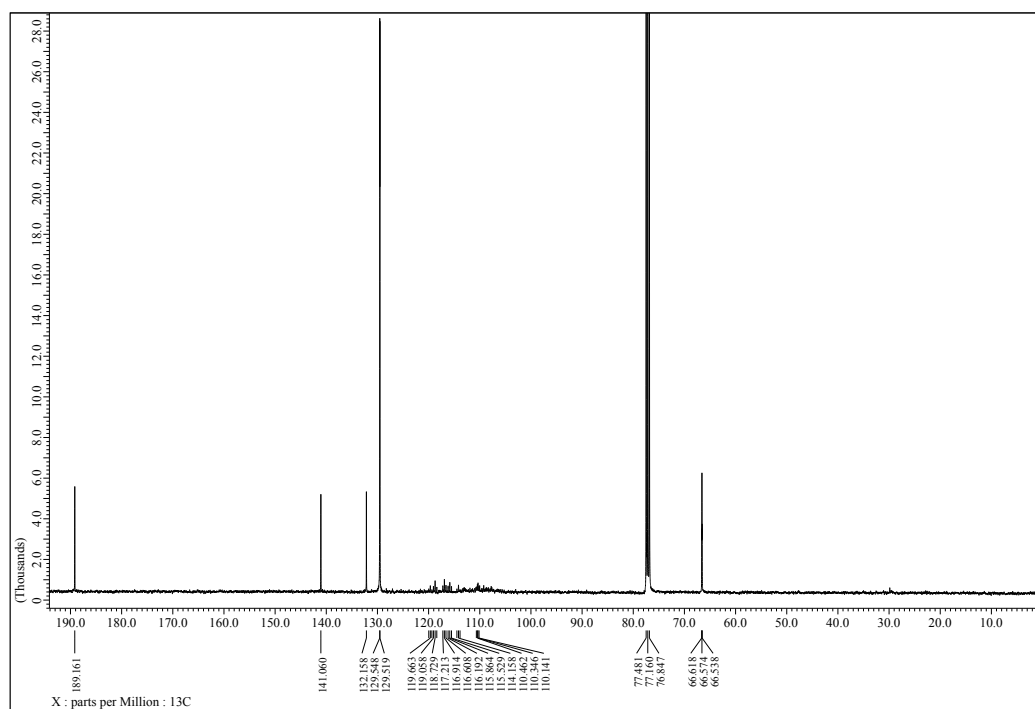
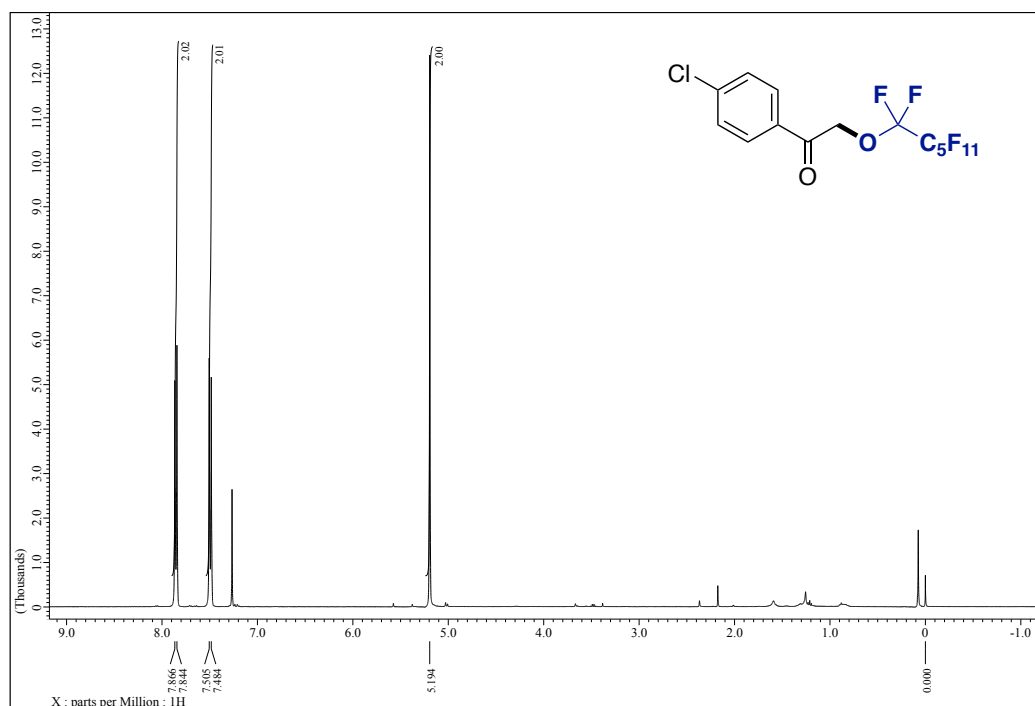


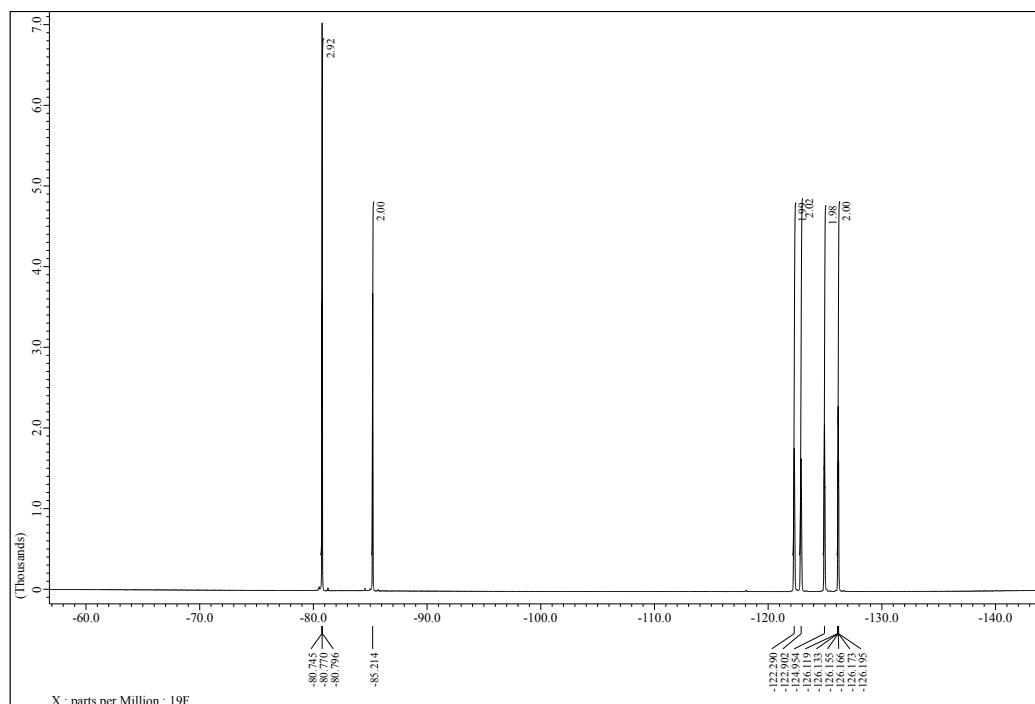
(3-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)prop-1-yn-1-yl)benzene (5f)



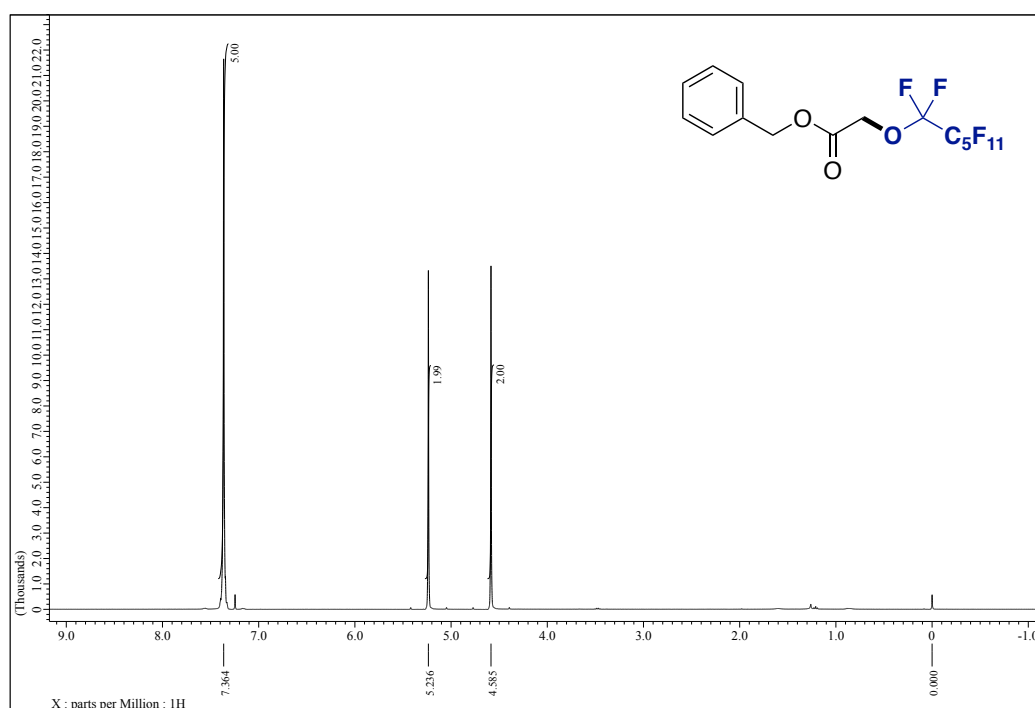


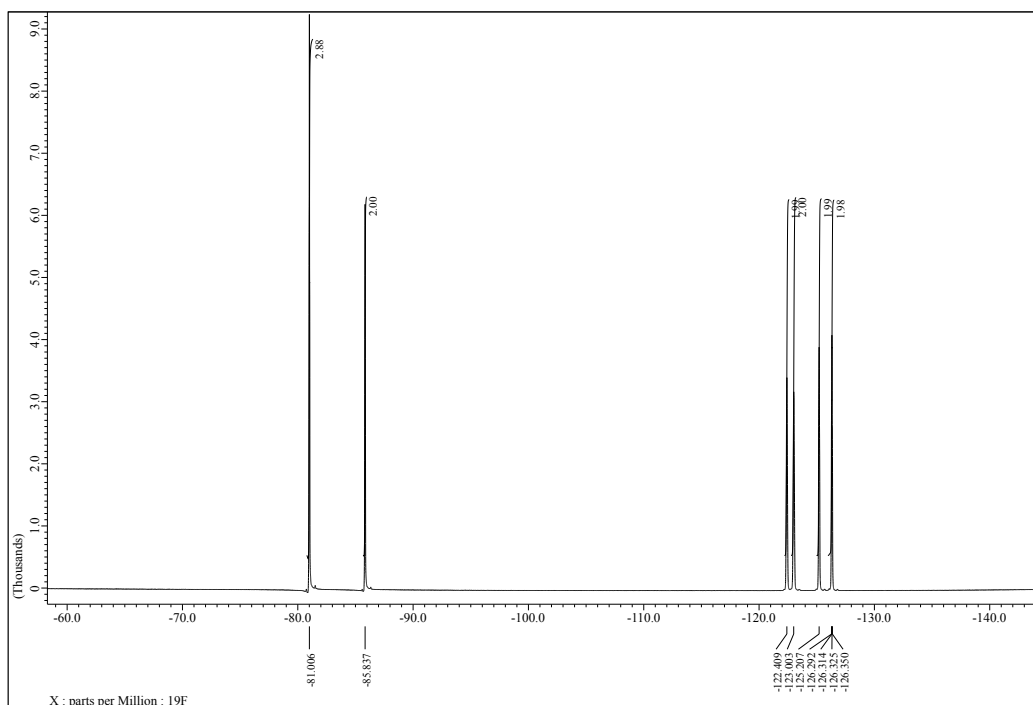
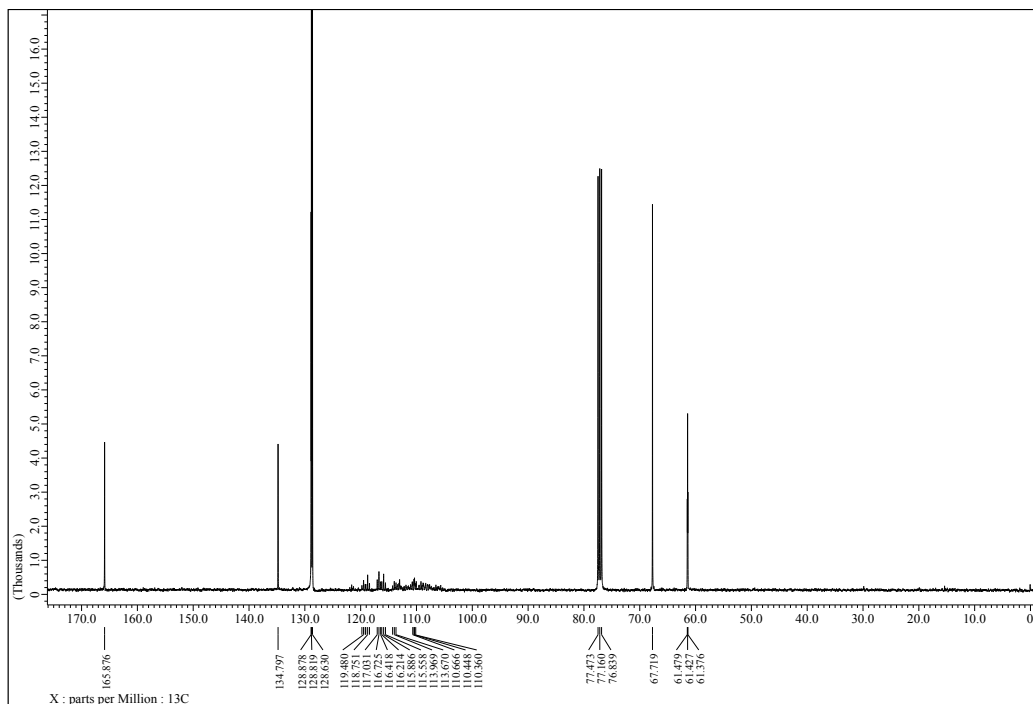
1-(4-chlorophenyl)-2-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)ethan-1-one (5g)



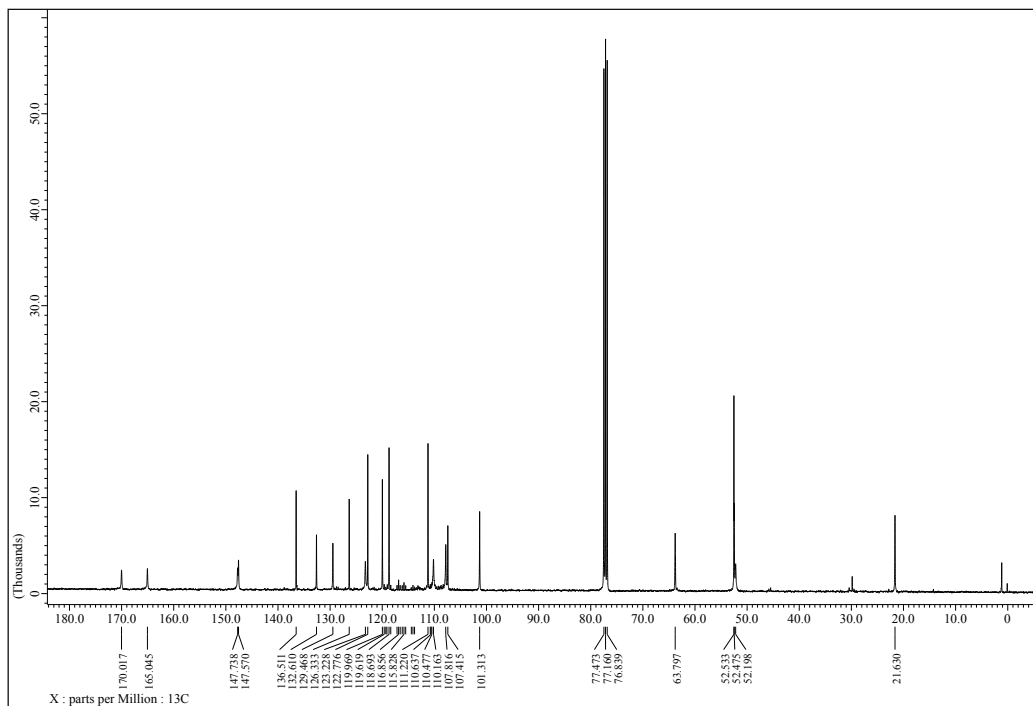
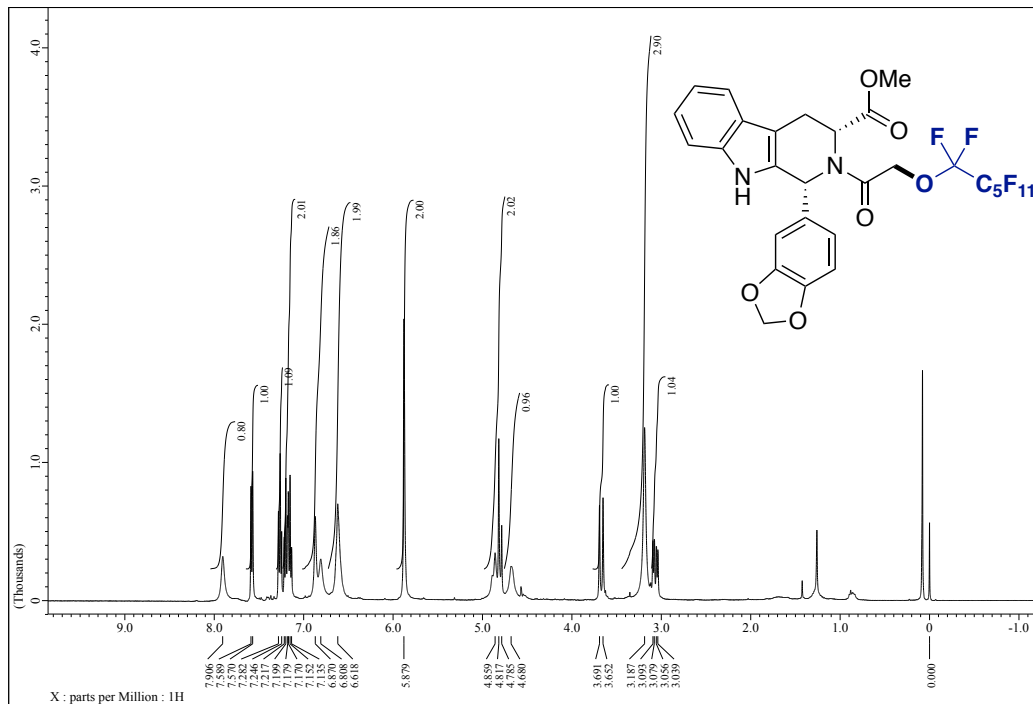


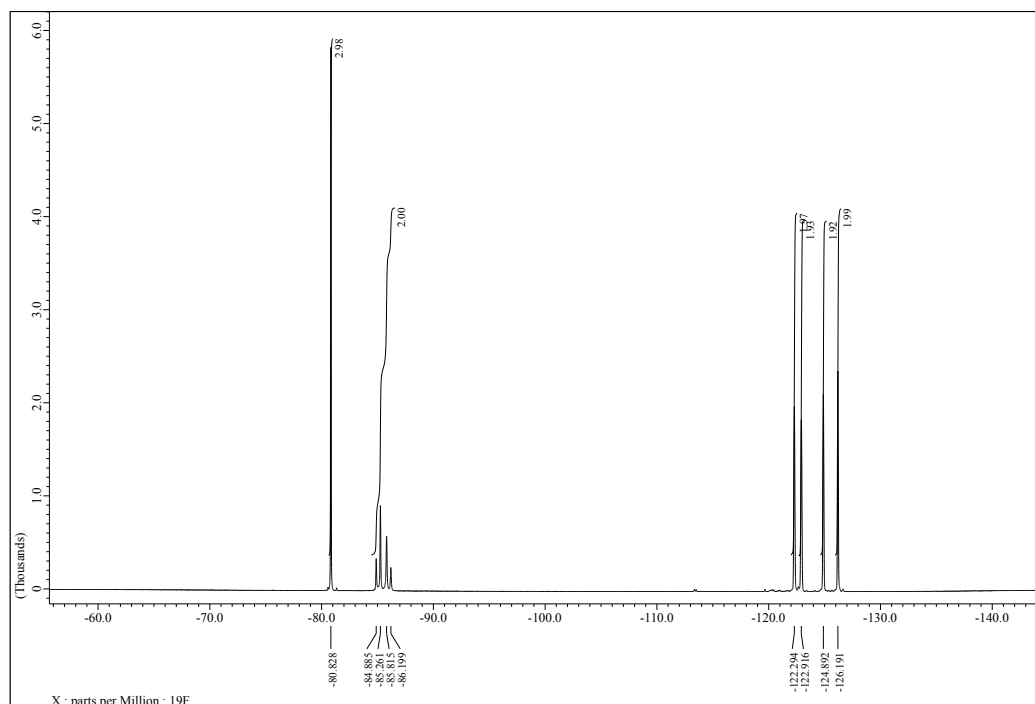
benzyl 2-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)acetate (5h)



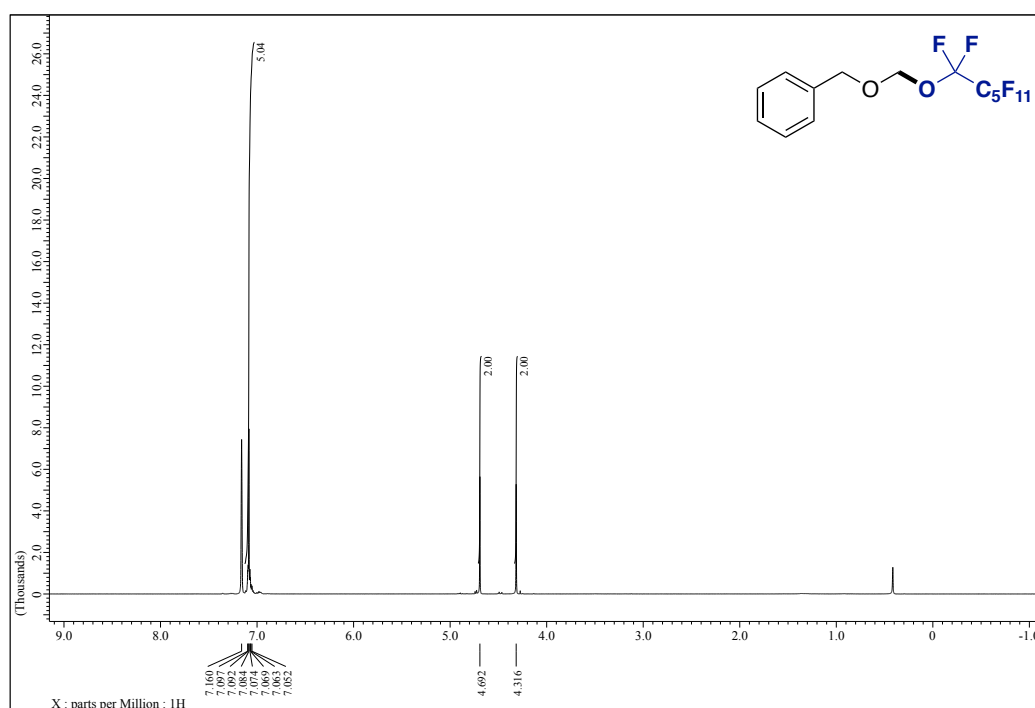


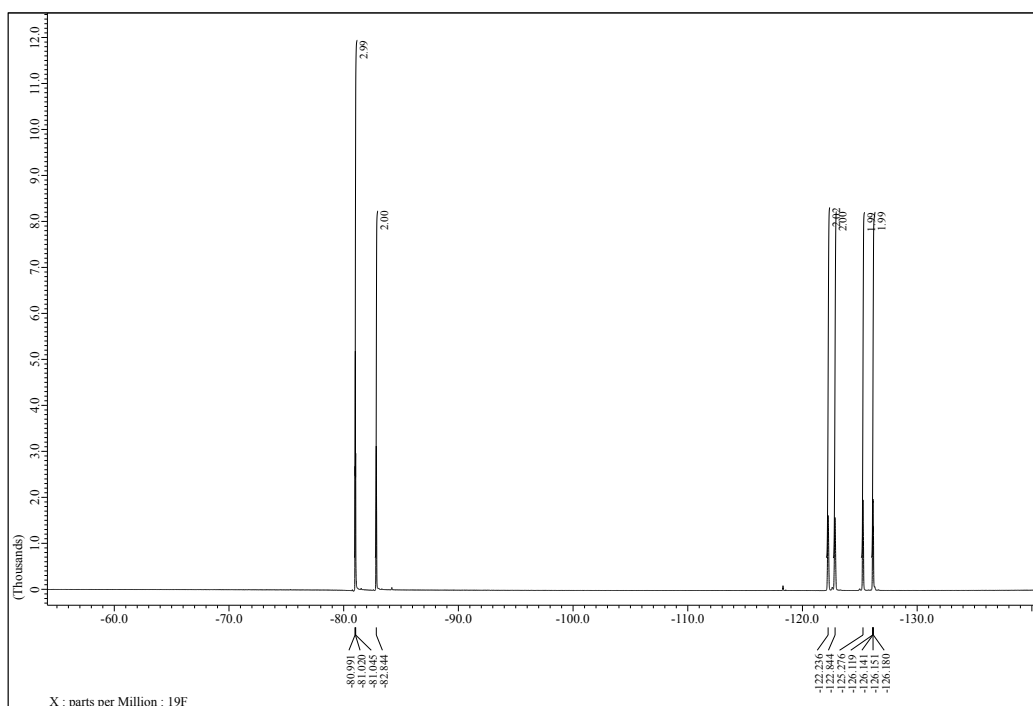
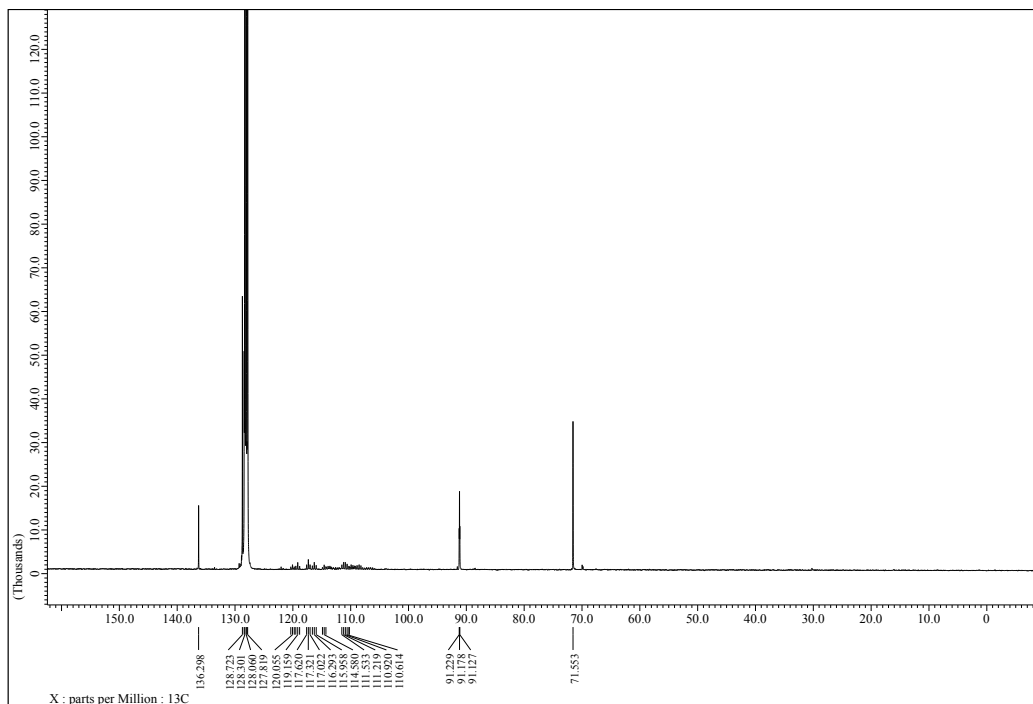
methyl (1*R*,3*R*)-1-(benzo[*d*][1,3]dioxol-5-yl)-2-(2-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)acetyl)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole-3-carboxylate (5i)



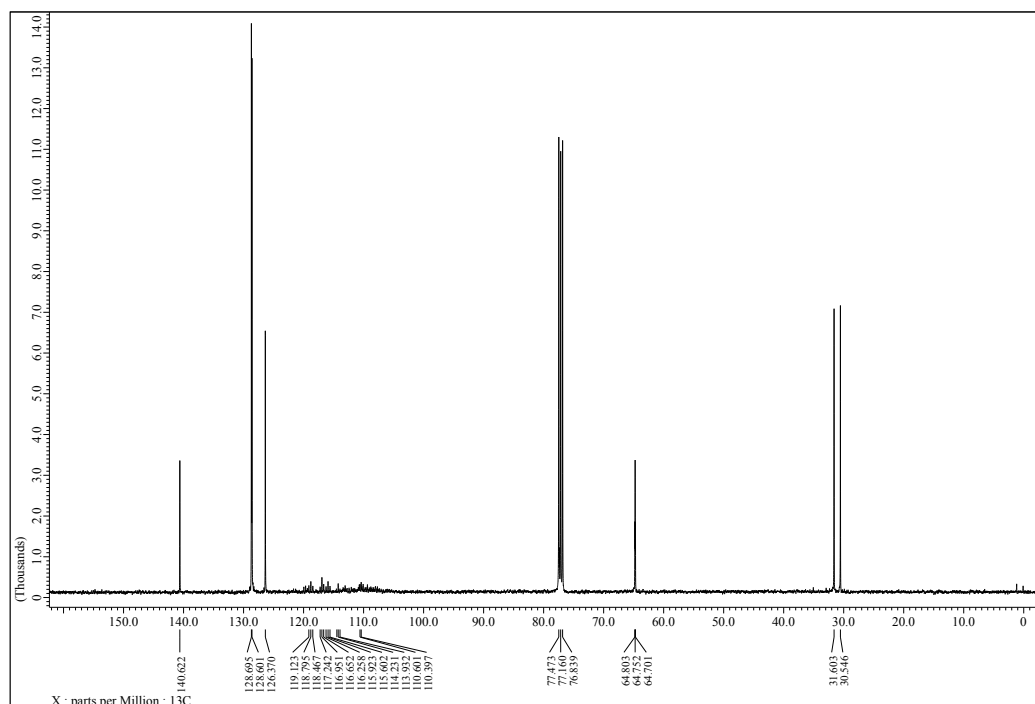
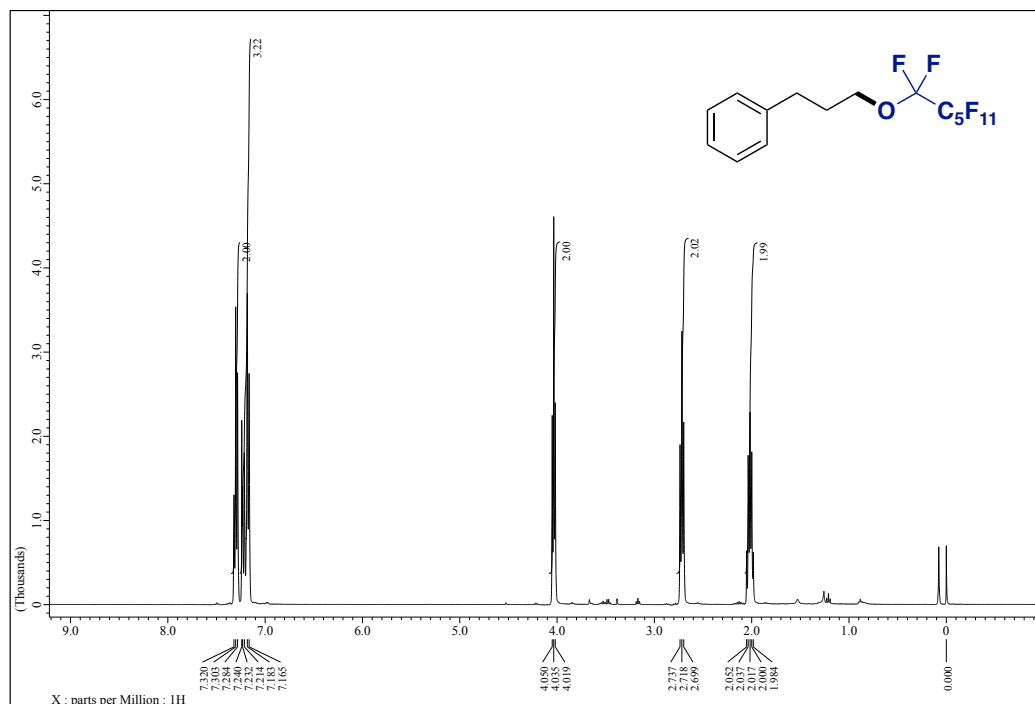


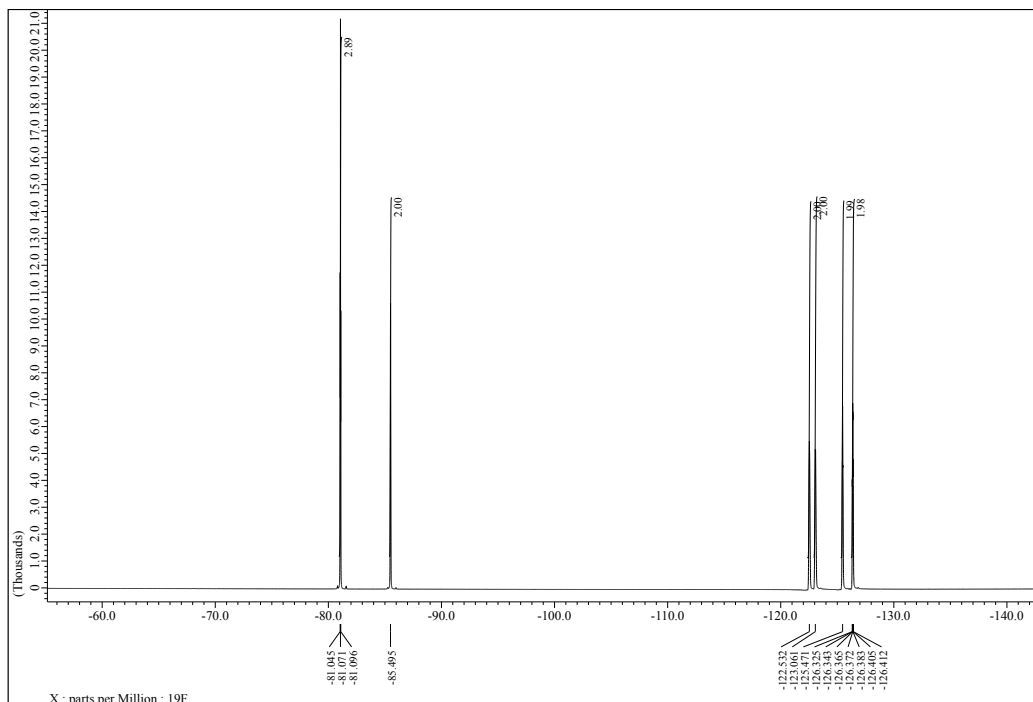
(((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)methoxy)methyl)benzene (5j)



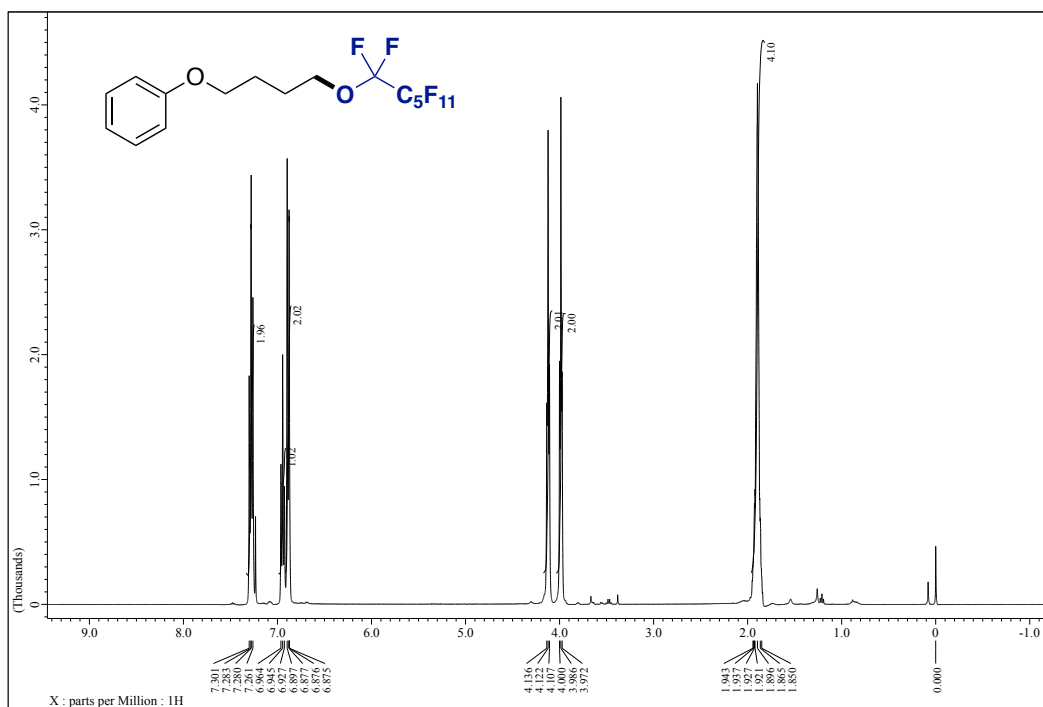


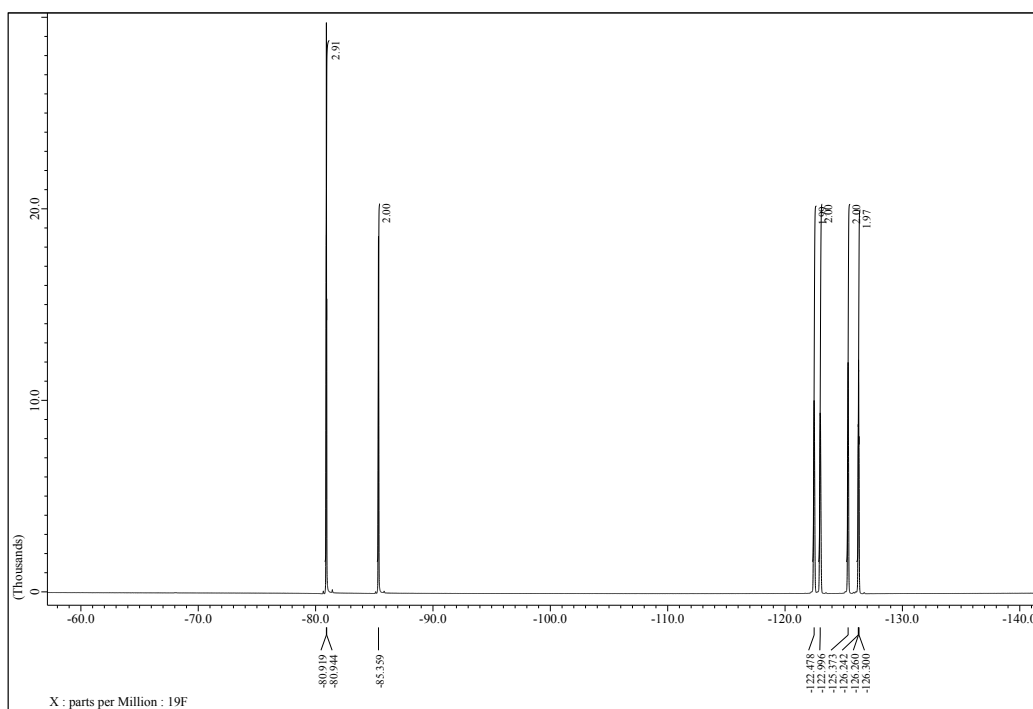
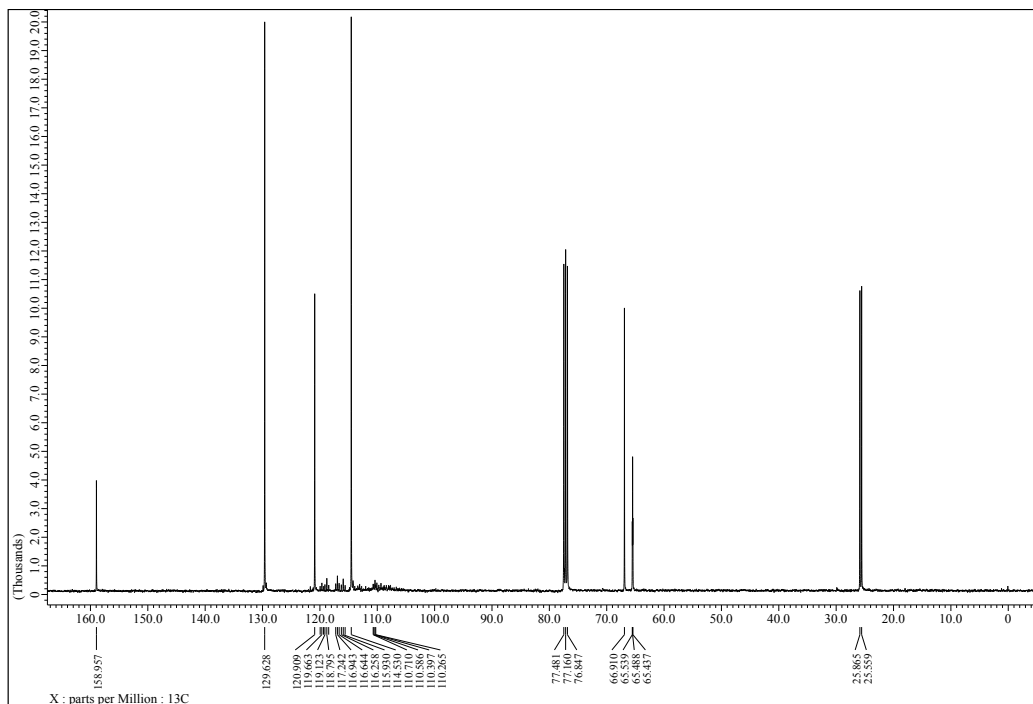
(3-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)propyl)benzene (5k)



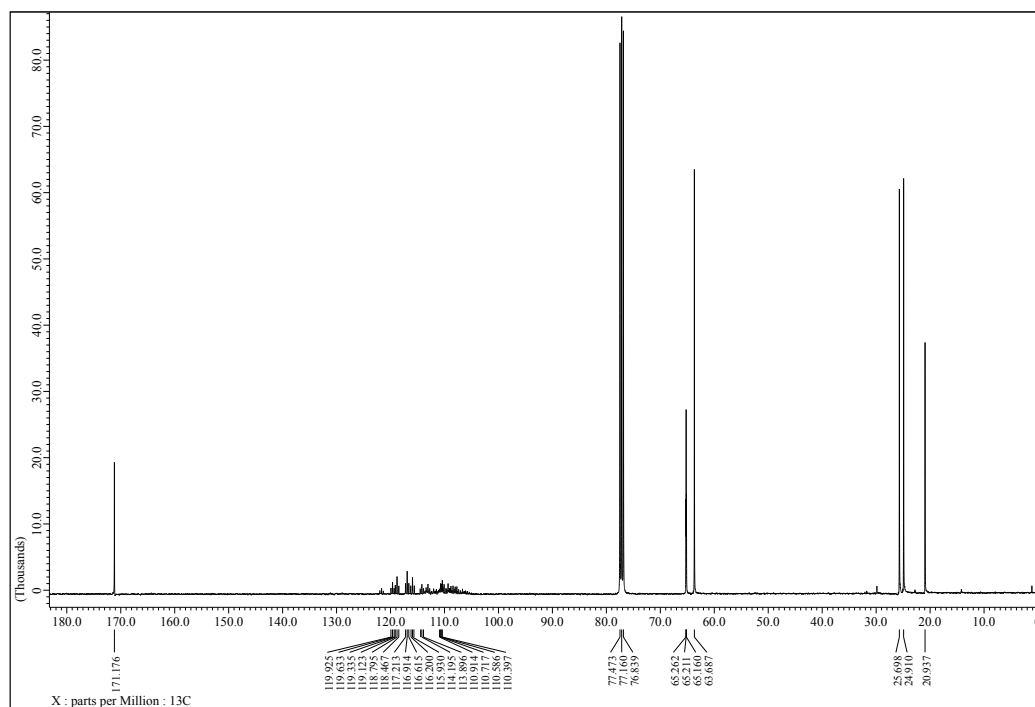
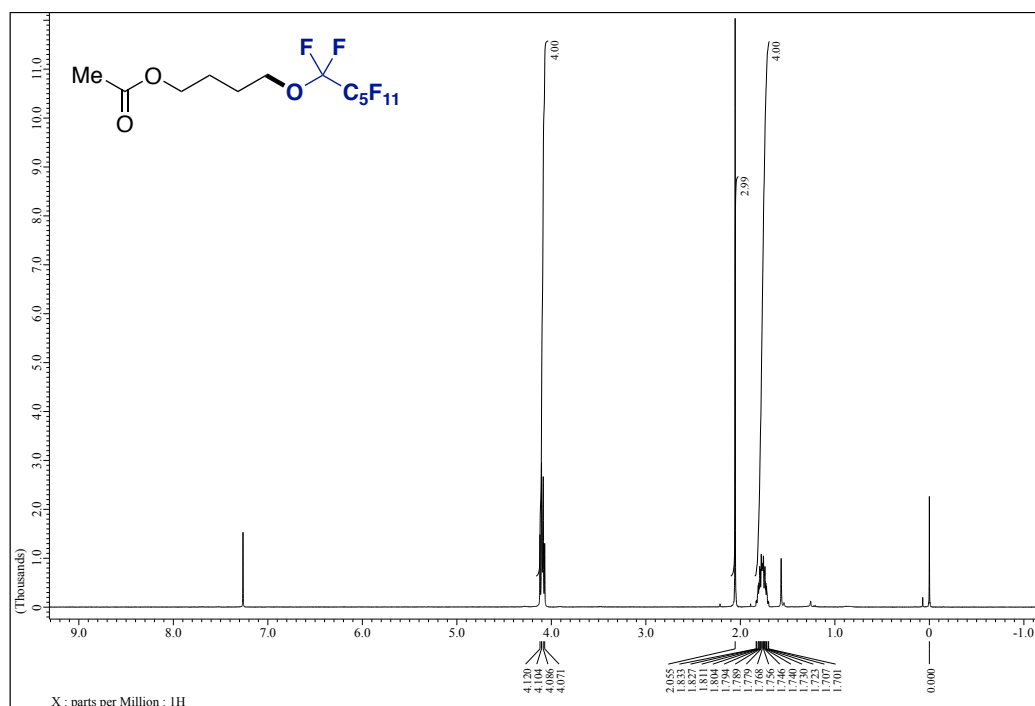


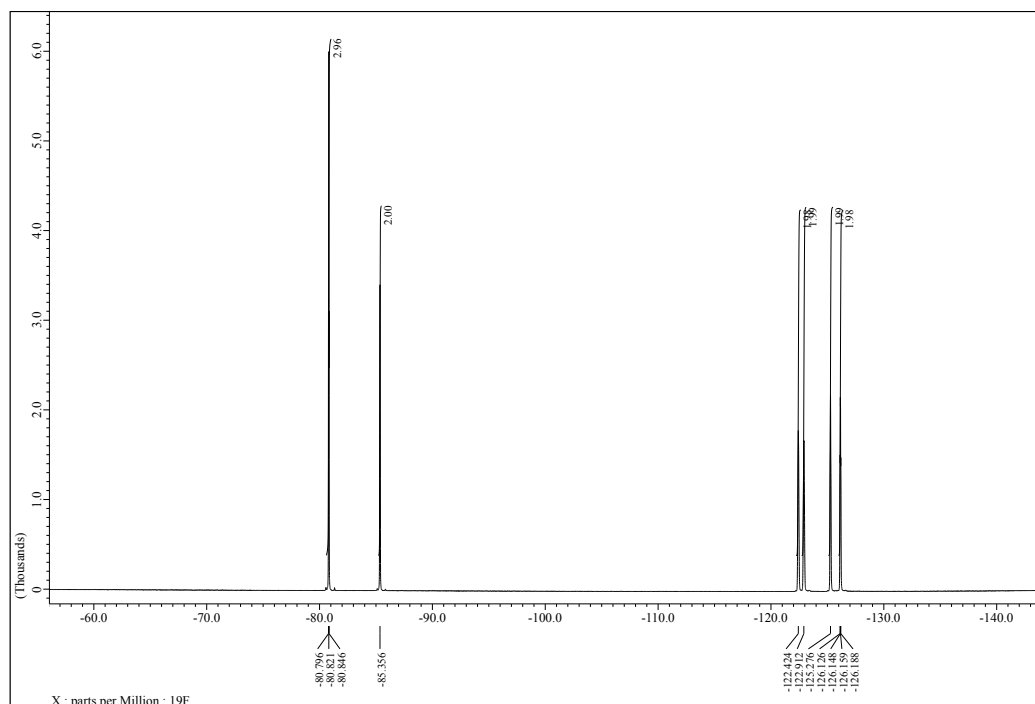
(4-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)butoxy)benzene (5l)



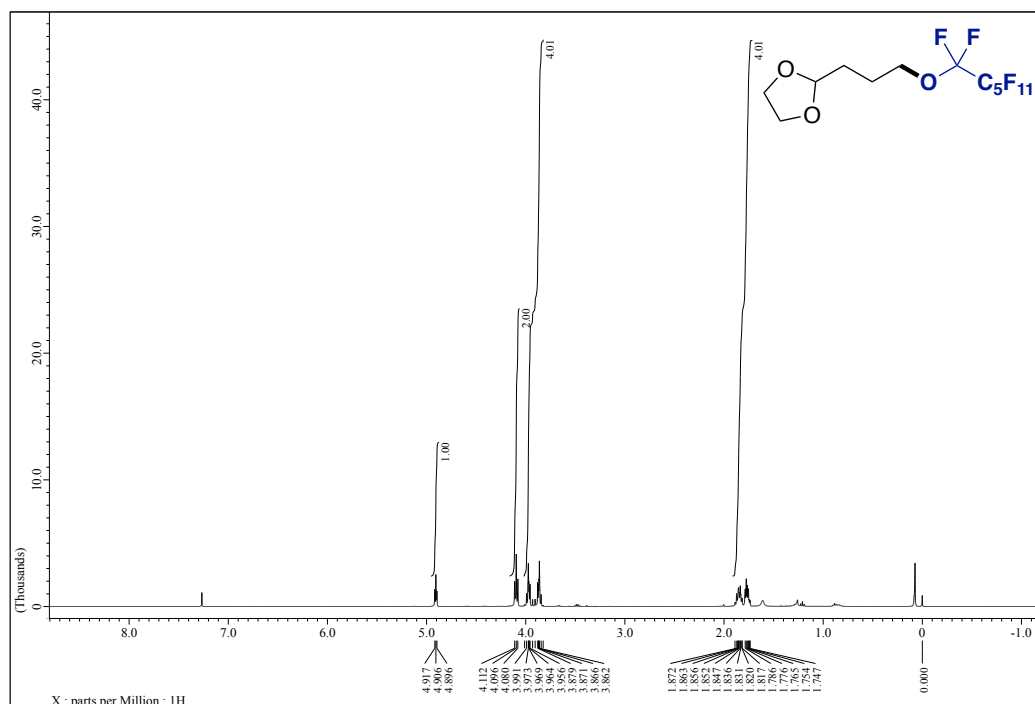


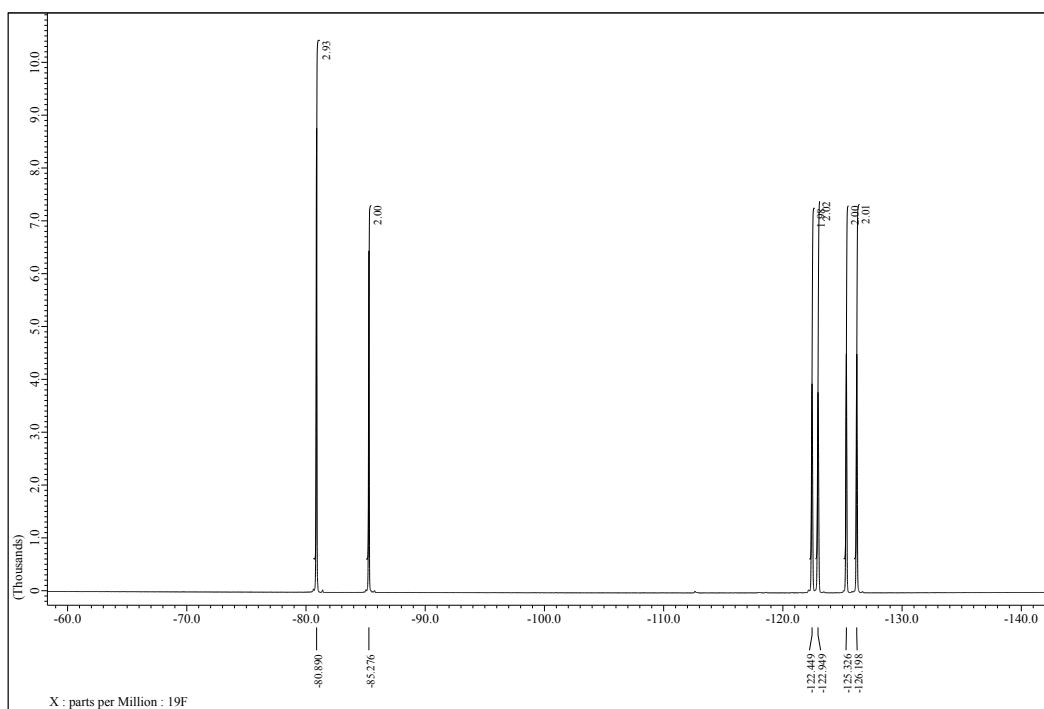
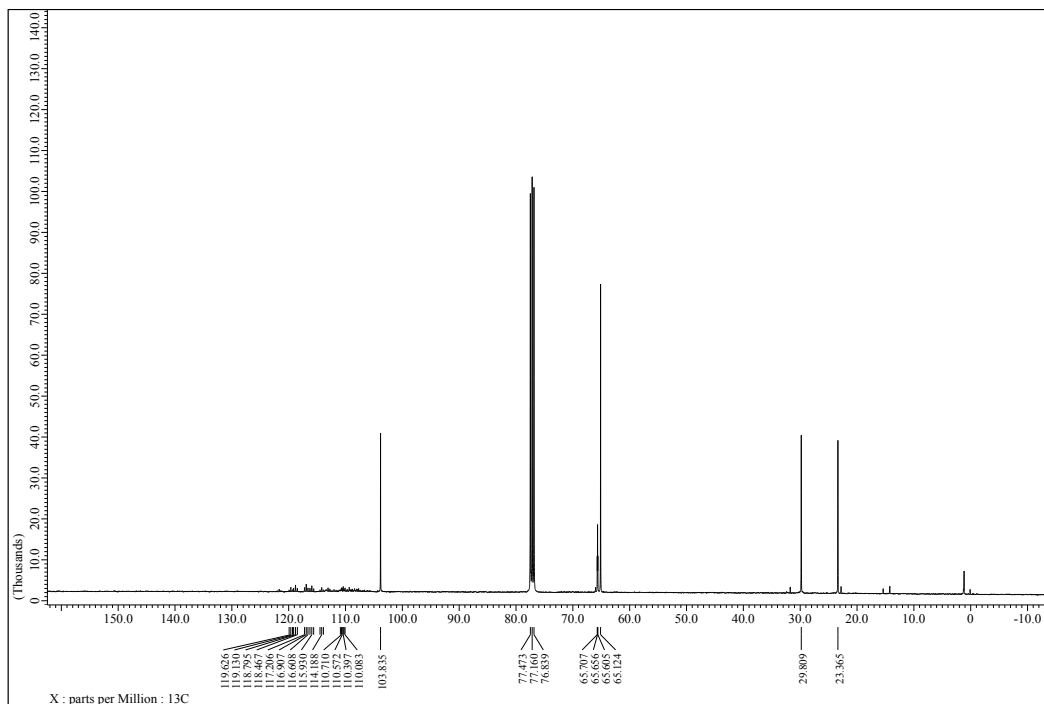
4-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)butyl acetate (5m)



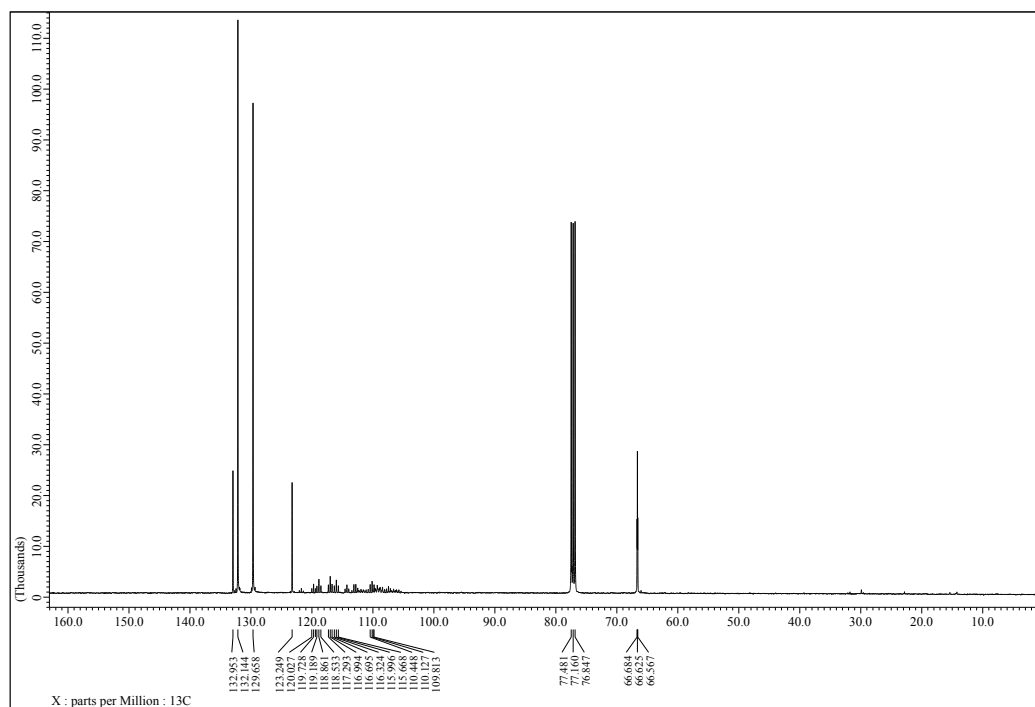
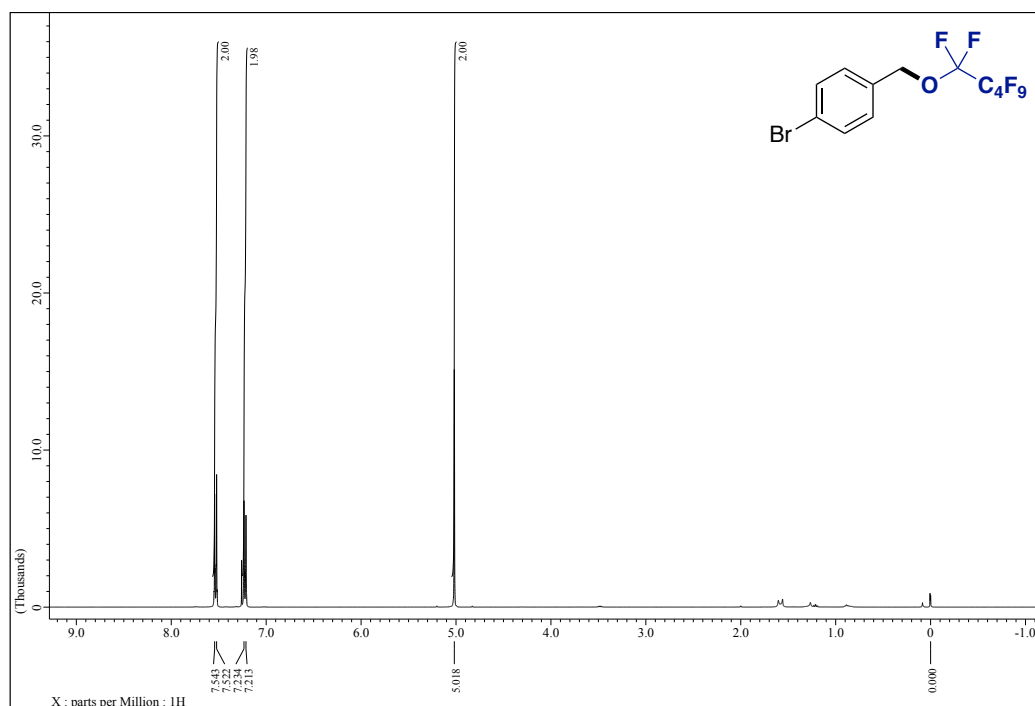


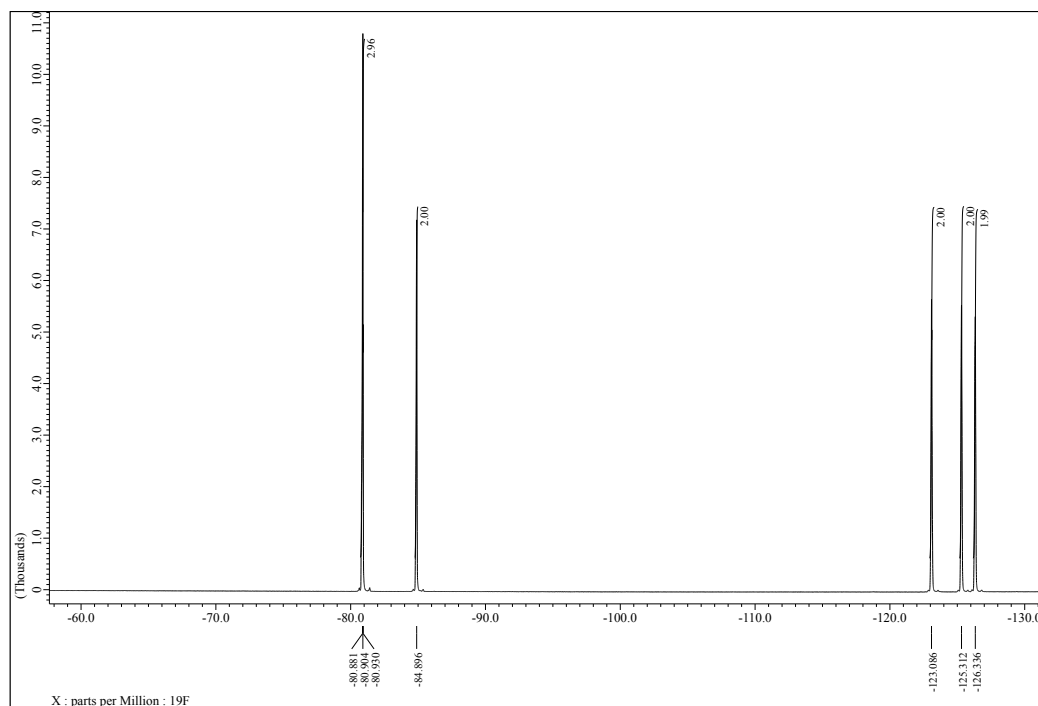
2-((1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy)propyl-1,3-dioxolane (5n)



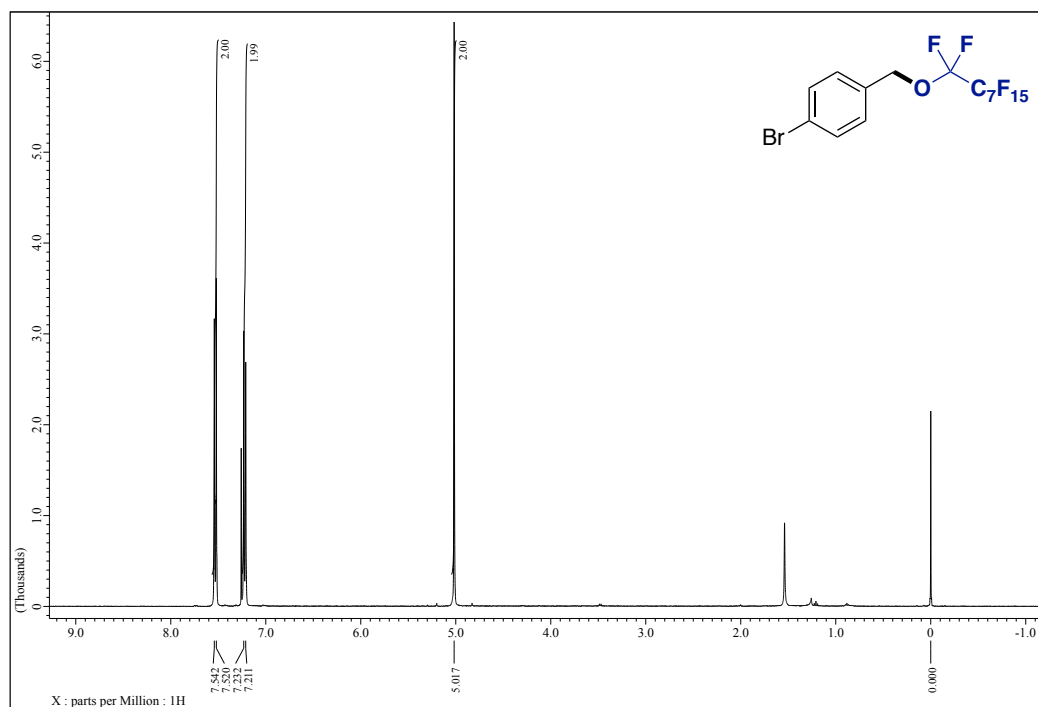


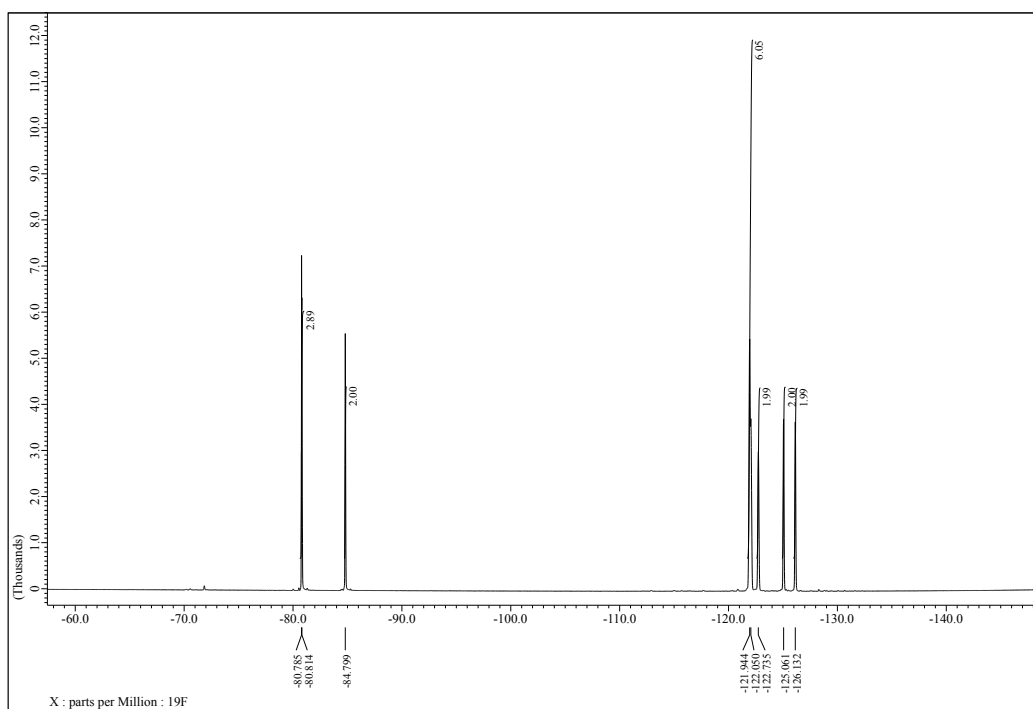
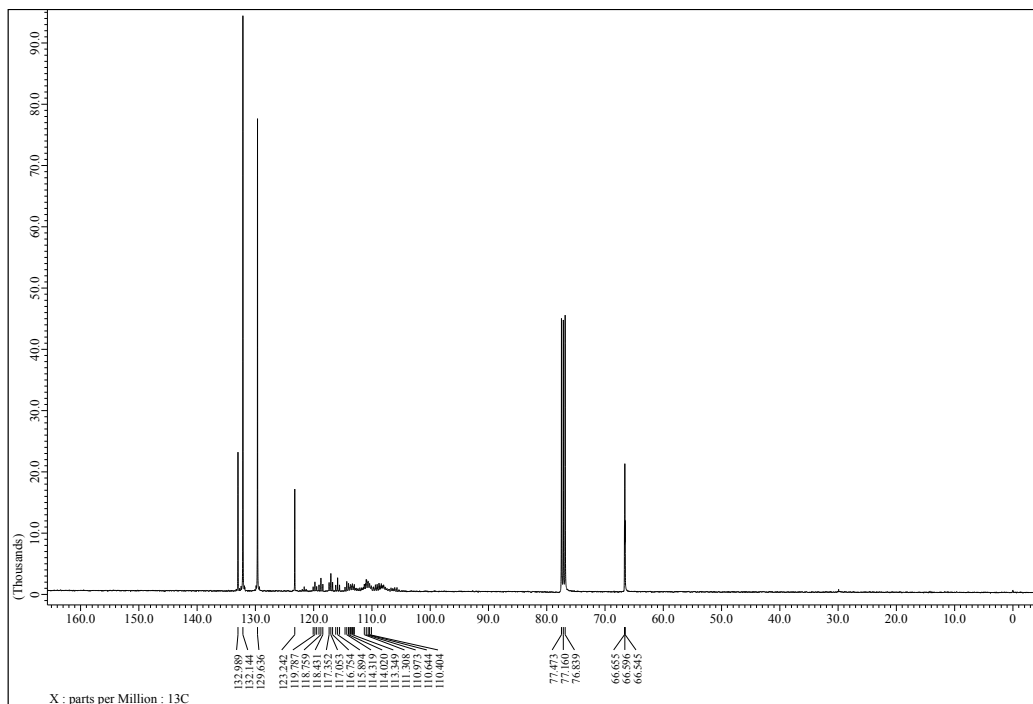
1-bromo-4-(((1,1,2,2,3,3,4,4,5,5,5-undecafluoropentyl)oxy)methyl)benzene (6a)



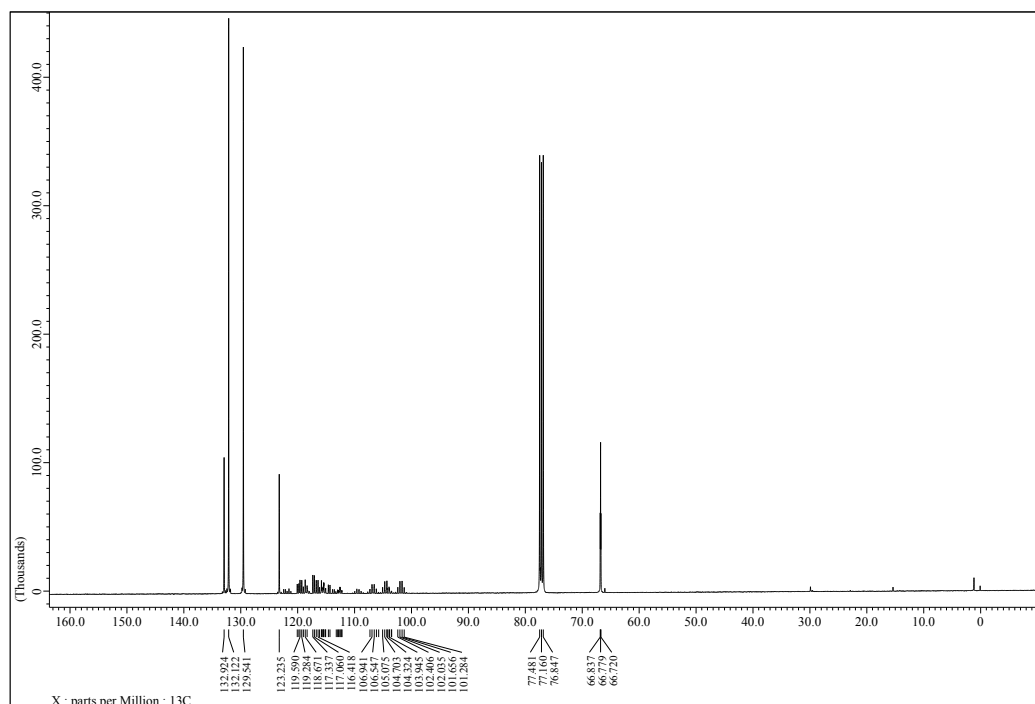
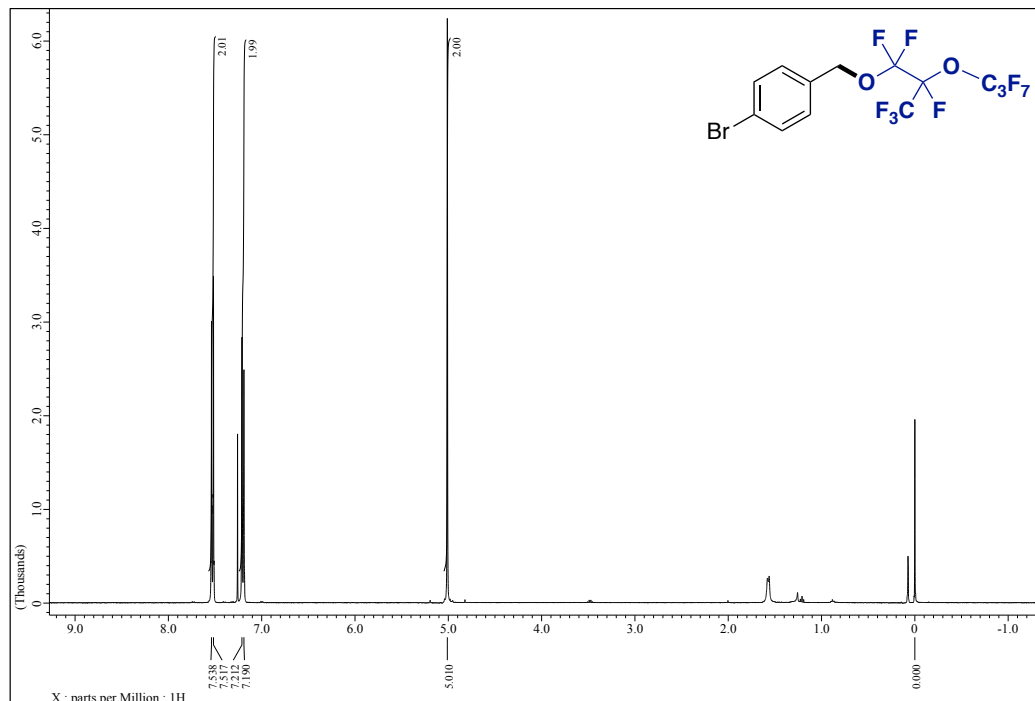


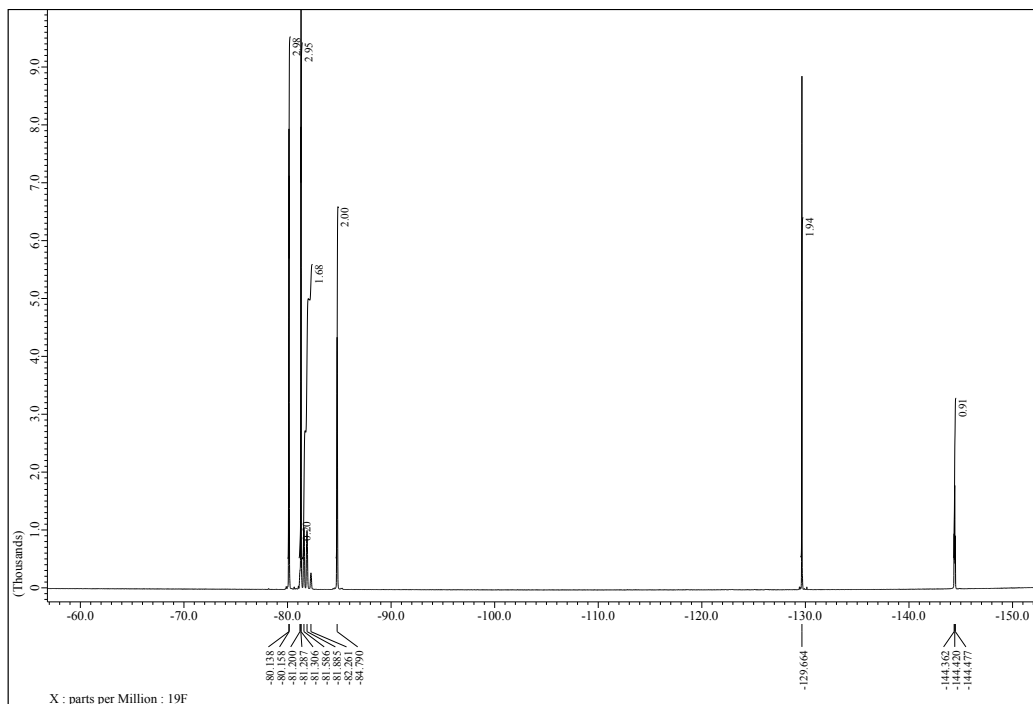
1-bromo-4-(((1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptafluorooctyl)oxy)methyl)benzene (6b)



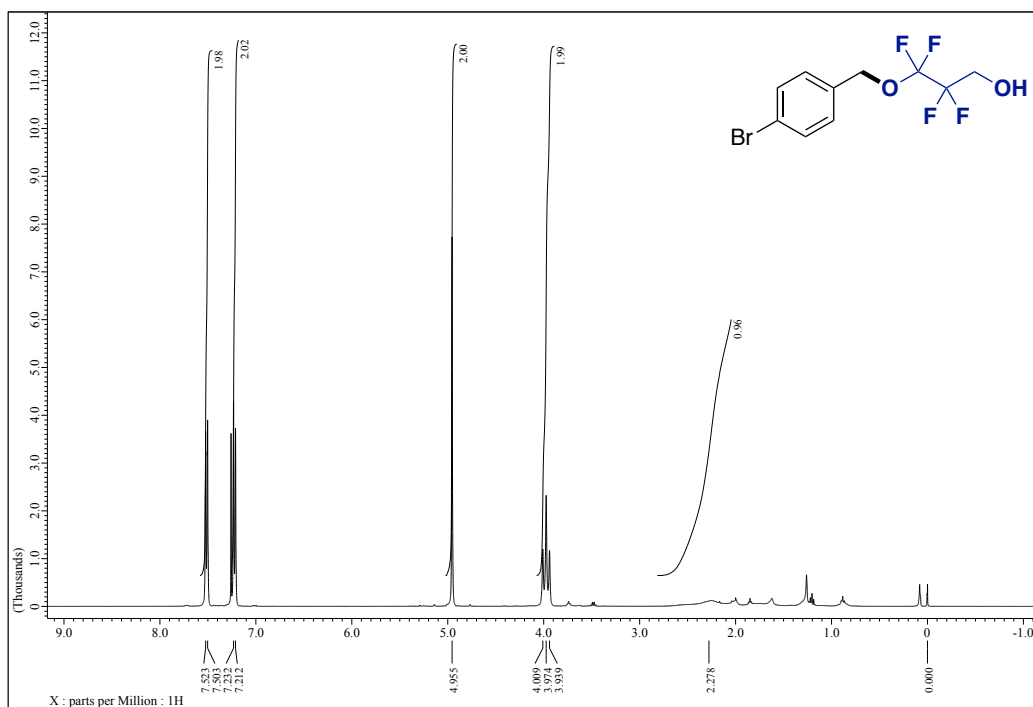


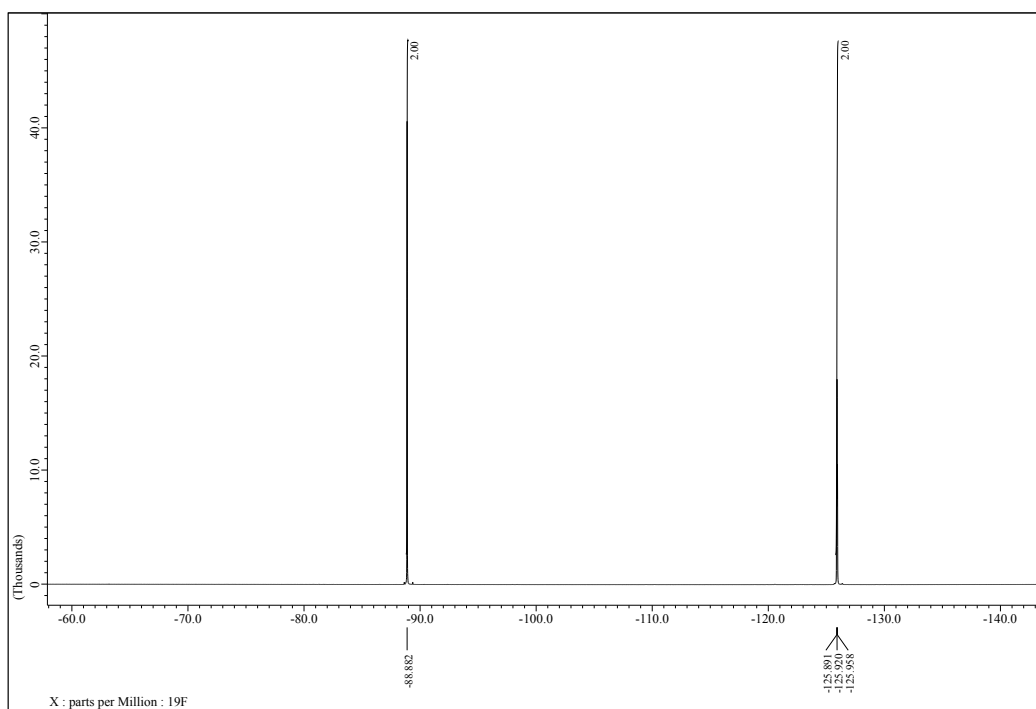
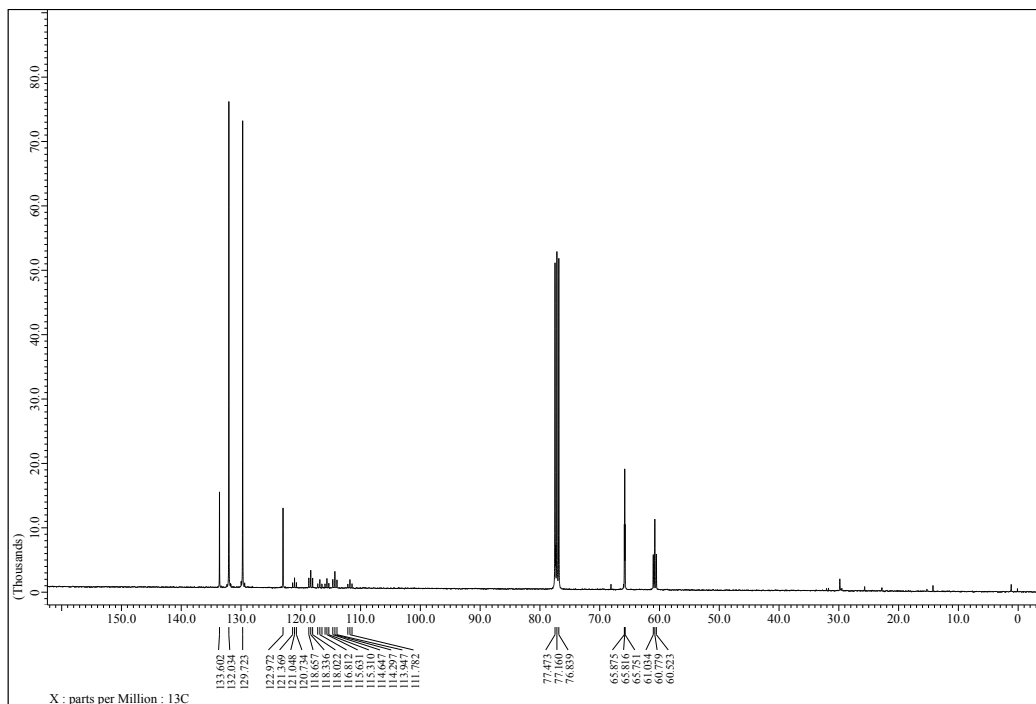
1-bromo-4-((1,1,2,3,3,3-hexafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propoxy)methyl)-benzene (6c)



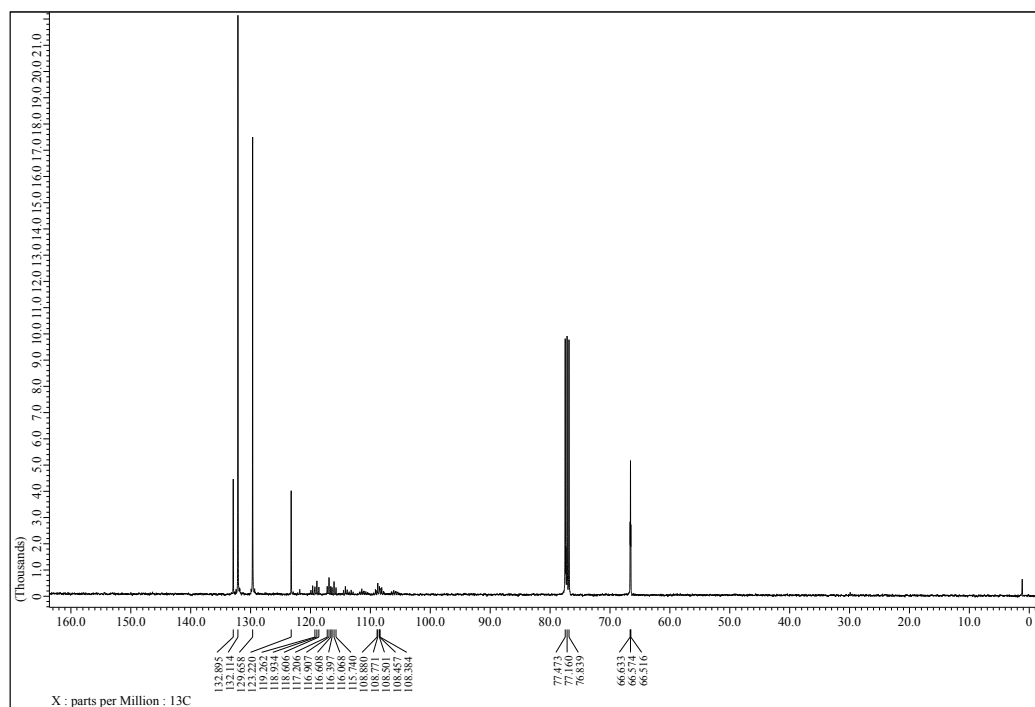
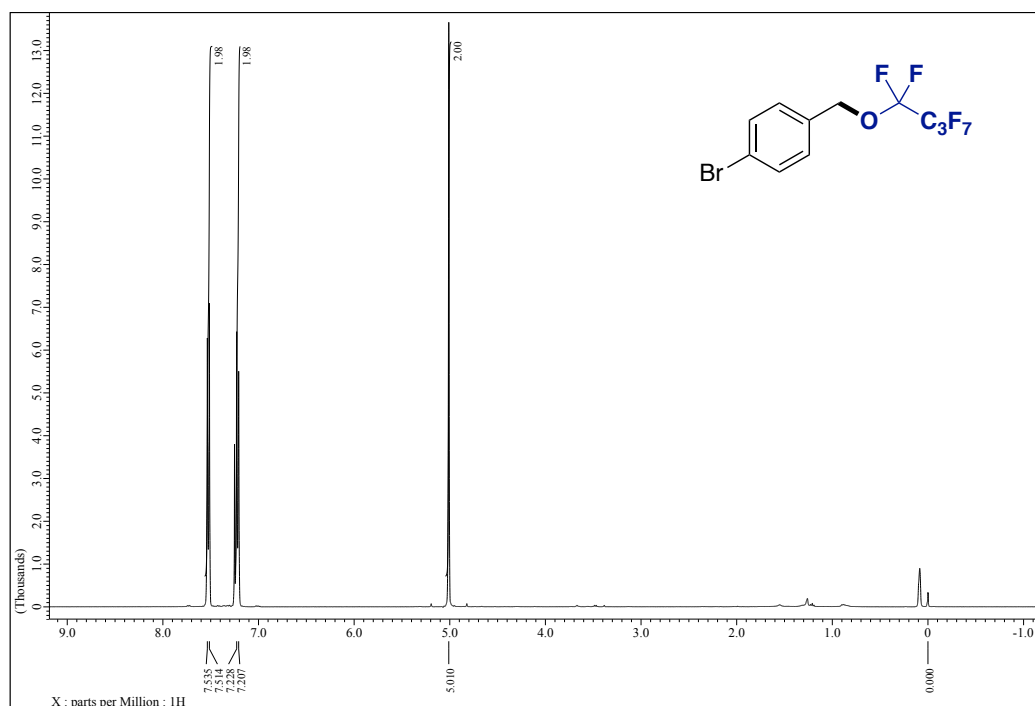


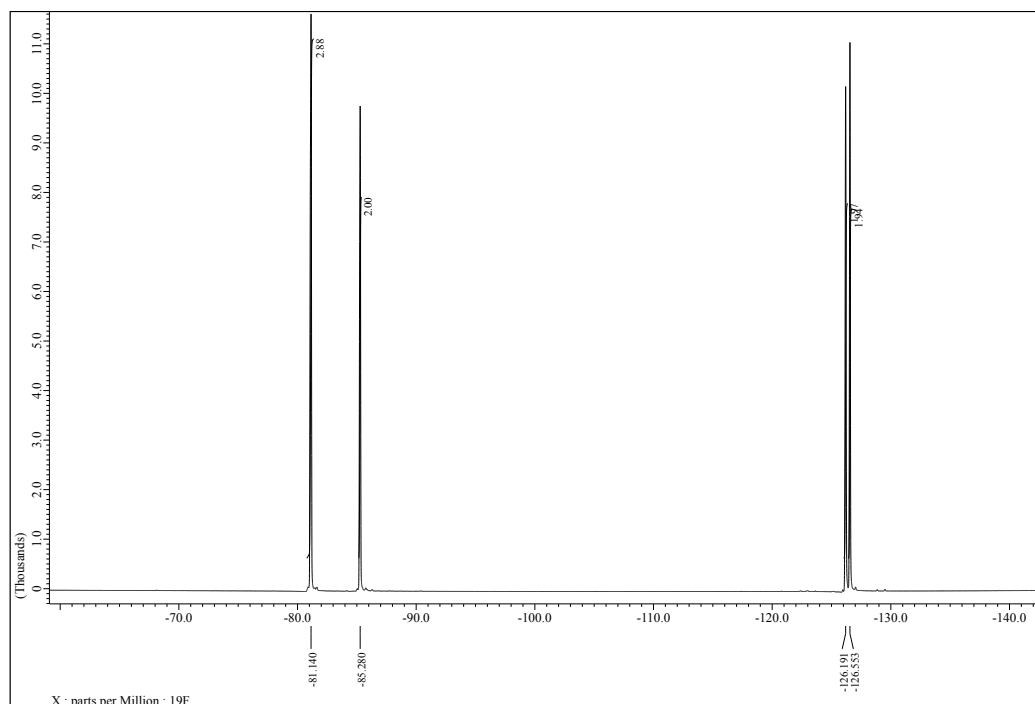
3-((4-bromobenzyl)oxy)-2,2,3,3-tetrafluoropropan-1-ol (6d)



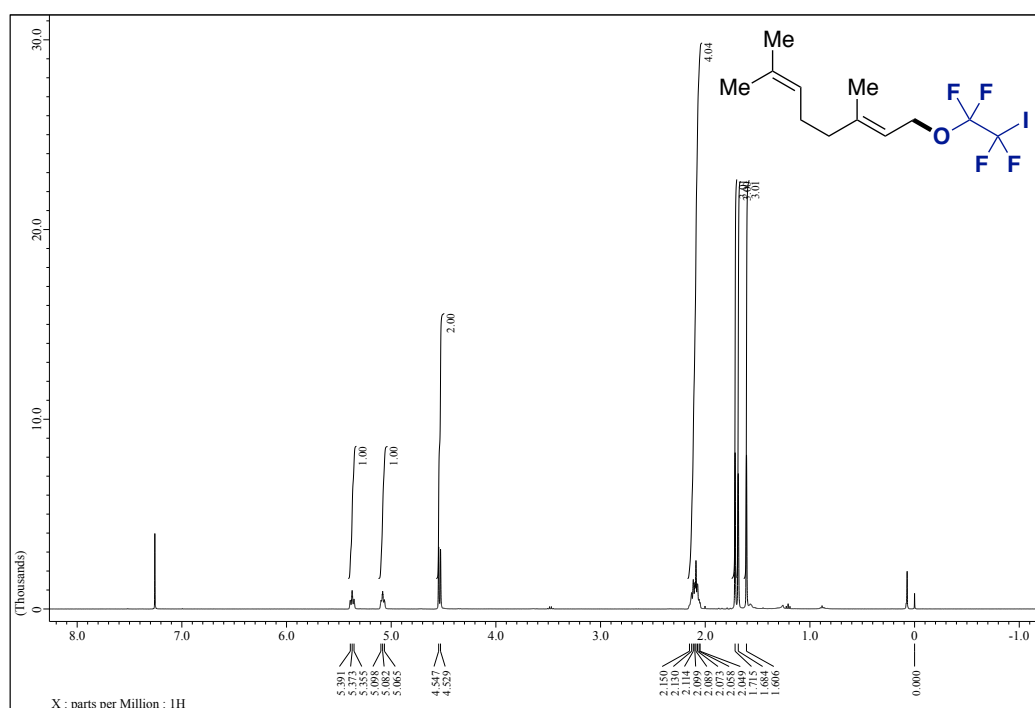


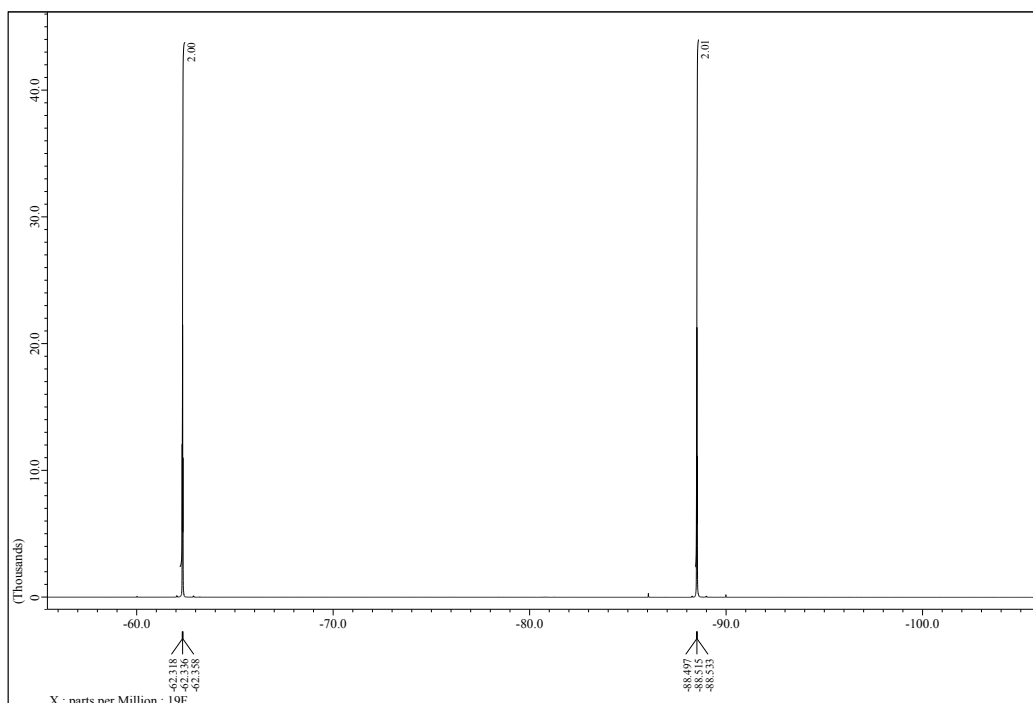
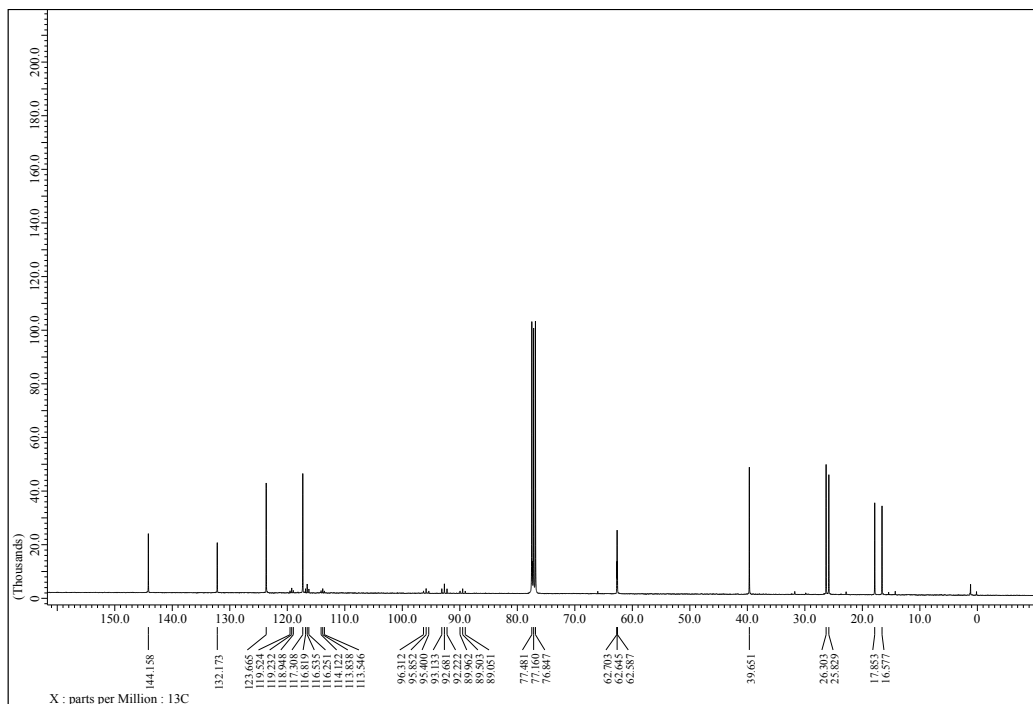
1-bromo-4-((1,1,2,2,3,3,4,4,4-nonafluorobutoxy)methyl)benzene (7a)





(*E*)-3,7-dimethyl-1-(1,1,2,2-tetrafluoro-2-iodoethoxy)octa-2,6-diene (8)





methyl (E)-2-(2-((3,7-dimethylocta-2,6-dien-1-yl)oxy)-1,1,2,2-tetrafluoroethyl)benzoate (9)

