Electronic Supplementary Material (ESI) for ChemComm.

Light-Promoted Metal-Free Cross Dehydrogenative Couplings on Ethers Mediated by NFSI: Reactivity and Mechanistic Insights

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I. General information

All reagents were obtained from commercial sources and used as received, except for the propargyl alcohol which was distilled prior to use. Solvents were dried and distilled prior to use. NMR analyses were carried out on Bruker avanceIII-600 (600 MHz for proton, 151 MHz for ^{13}C), Bruker avanceII-400 (400 MHz for proton, 101 MHz for ^{13}C), and Bruker avanceIII-300 (300 MHz for proton, 75 MHz for ^{13}C) spectrometers in deuterated chloroform as solvent. The chemical shifts (δ) for carbon and proton are given compared to the residual solvent peak and are expressed in ppm. The ESI-TOF mass spectra (low and high resolution) were recorded at the CESAMO analytical center (Institut des Sciences Moléculaires, Université Bordeaux) on a QSTAR Elite spectrometer from Applied Biosystem. Results are expressed in weight percent.

II. ^{1}H and ^{19}F NMR spectra of the intermediate monofluorinated ethers

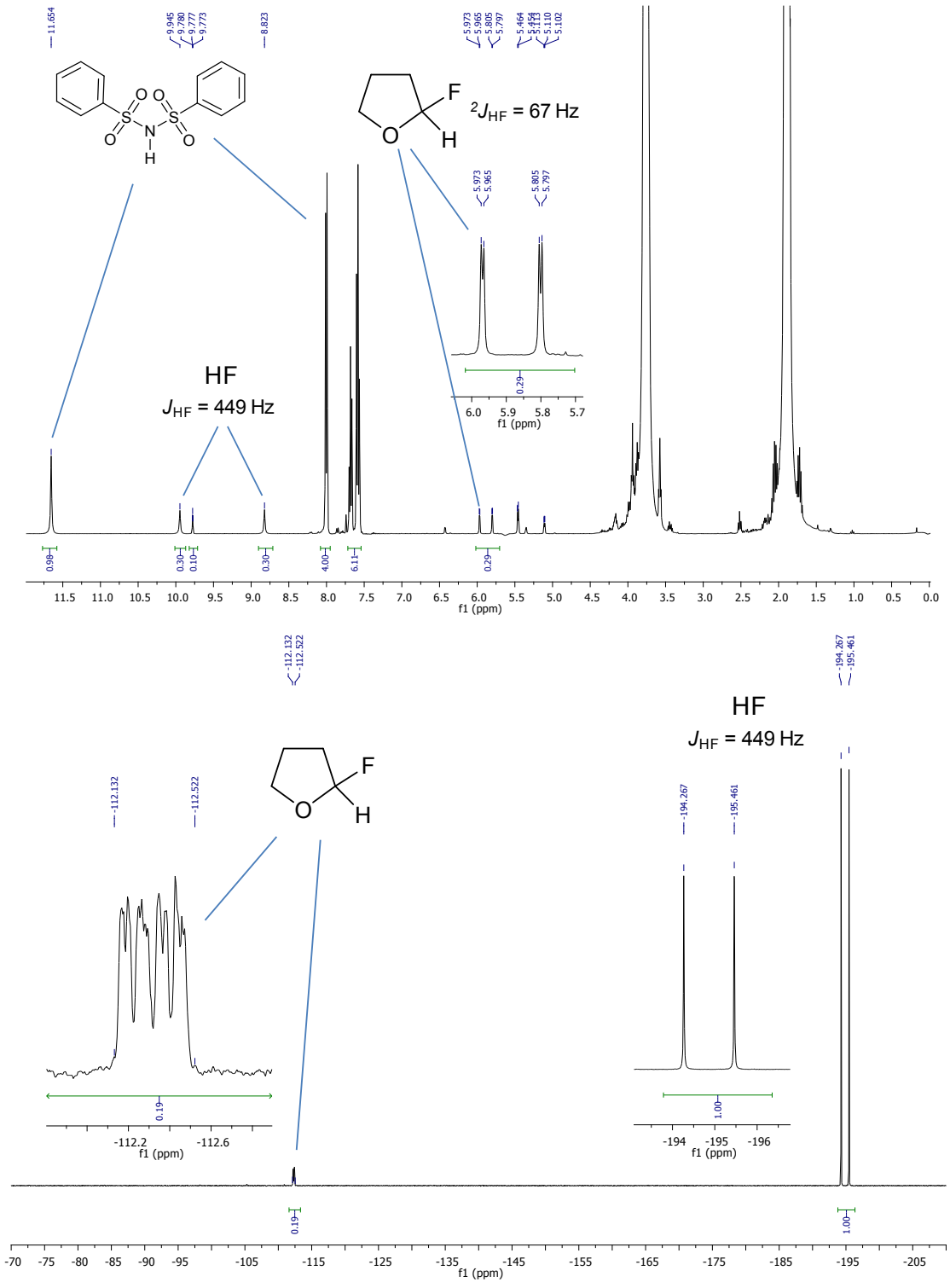


Figure S1: ^{1}H (400 MHz) ^{19}F (376 MHz) NMR spectra of the BP photo-promoted reaction between NFSI and THF after 10 min of irradiation. Conditions: $CDCl_3$ (0.4 mL, NMR tube), THF (0.1 mL, 1 mmol), NFSI (0.1 mmol), BP (2 mol%), 20 °C, degassing Ar bubbling (20 min), *hv* (320-390 nm, low pressure Hg lamp, type TLC, 6W).

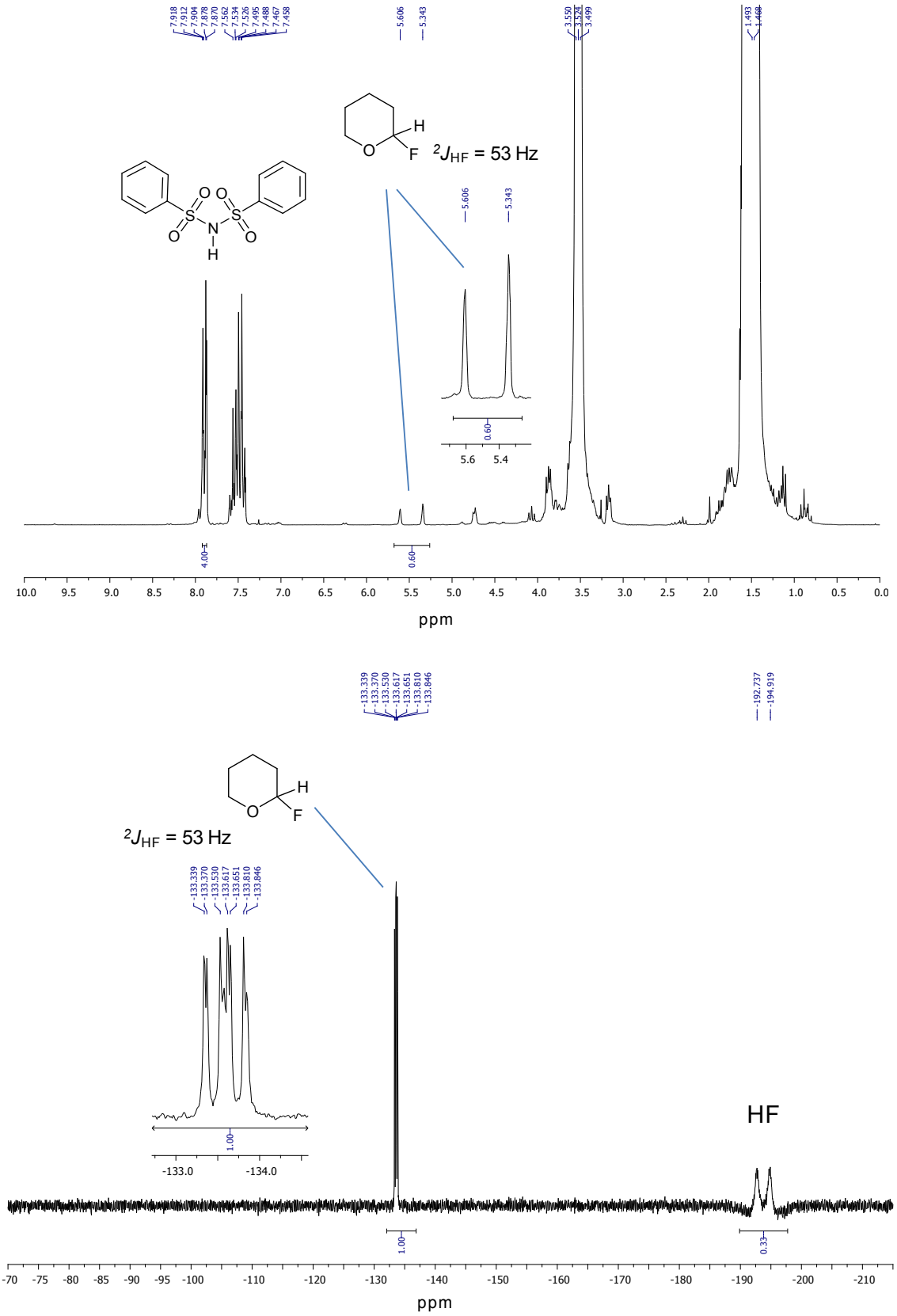


Figure S2: ^{1}H (200 MHz) ^{19}F (188 MHz) NMR spectra of the BP photo-promoted reaction between NFSI and THP after 10 min of irradiation. Conditions: $CDCl_3$ (0.4 mL, NMR tube), THP (0.1 mL, 1 mmol), NFSI (0.1 mmol), BP (2 mol%), 20 °C, degassing Ar bubbling (20 min), *hv* (320-390 nm, low pressure Hg lamp, type TLC, 6W).

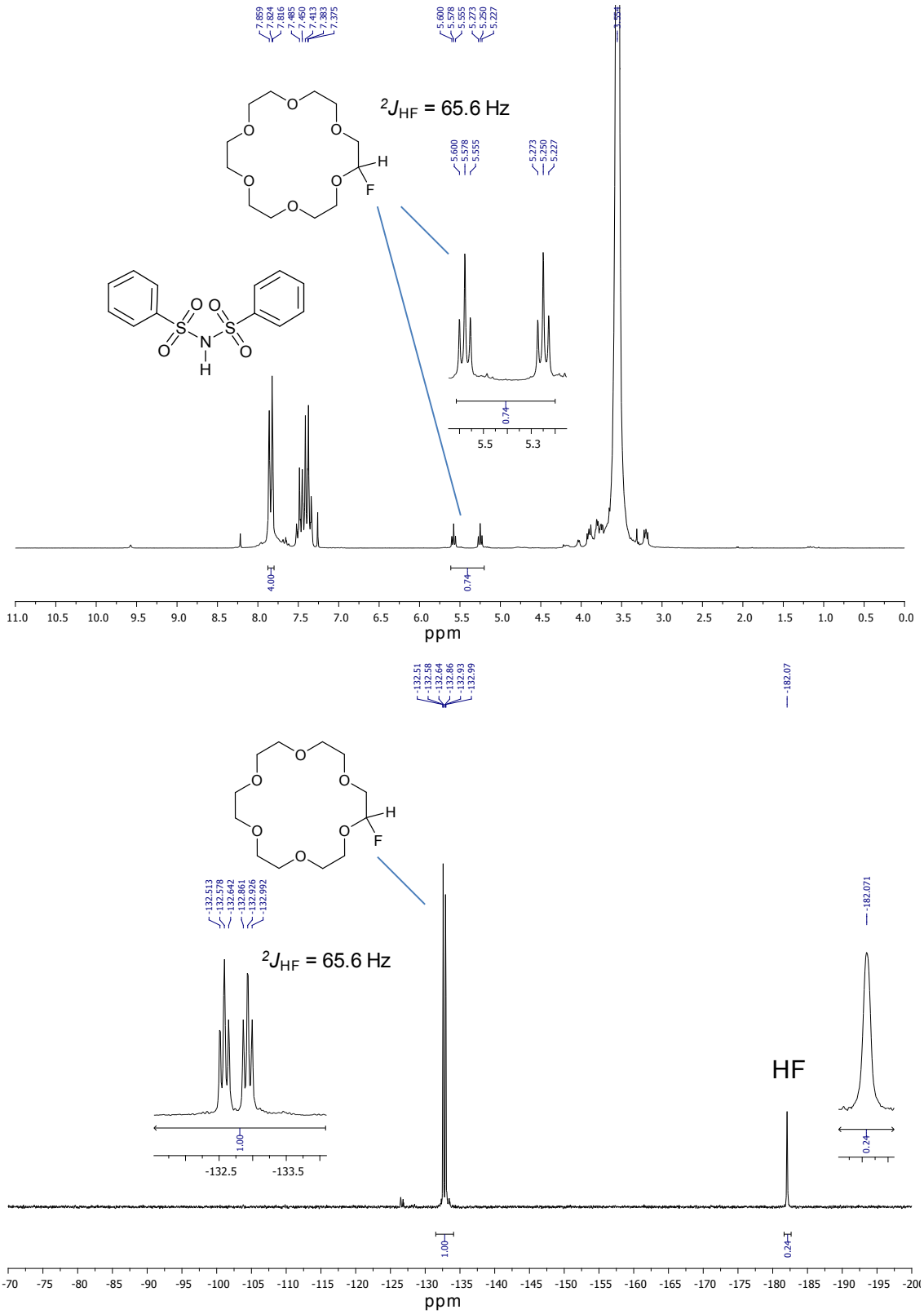


Figure S3: ^{1}H (200 MHz) ^{19}F (188 MHz) NMR spectra of the BP photo-promoted reaction between NFSI and 1,4,7,10,13,16-hexaoxacyclooctadecane after 30 min of irradiation. Conditions: $CDCl_3$ (0.5 mL, NMR tube), 1,4,7,10,13,16-hexaoxacyclooctadecane (0.2 mmol), NFSI (0.1 mmol), BP (5 mol%), 20 °C, degassing Ar bubbling (20 min), *hv* (320-390 nm, low pressure Hg lamp, type TLC, 6W).

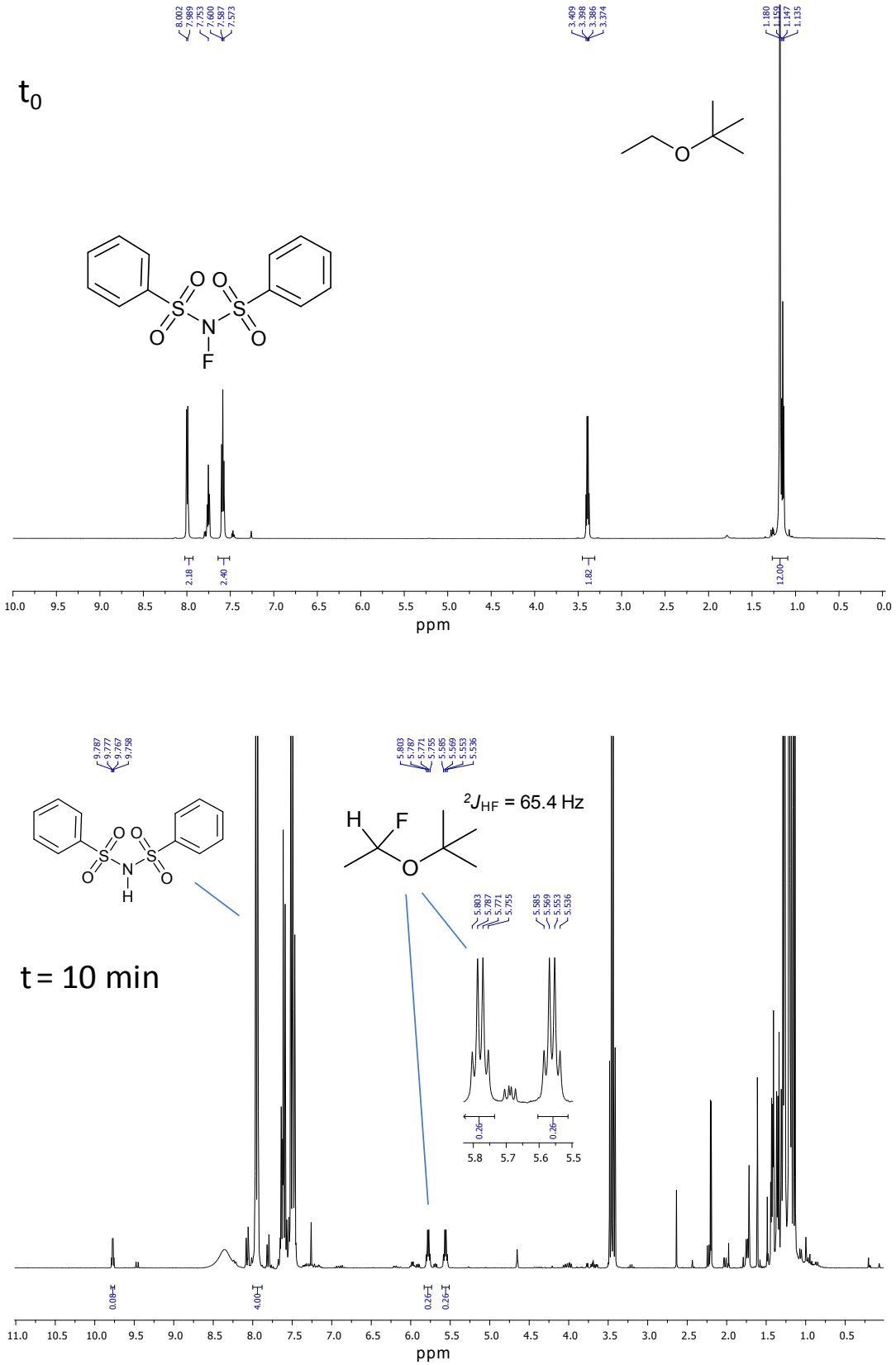


Figure S4: ^{1}H (300 MHz) NMR spectra of the BP photo-promoted reaction between NFSI and ETBE at t_0 and after 10 min of irradiation. Conditions: $CDCl_3$ (0.5 mL, NMR tube), ETBE (0.2 mmol), NFSI (0.1 mmol), BP (5 mol%), 20 °C, degassing Ar bubbling (20 min), *hv* (320-390 nm, low pressure Hg lamp, type TLC, 6W).

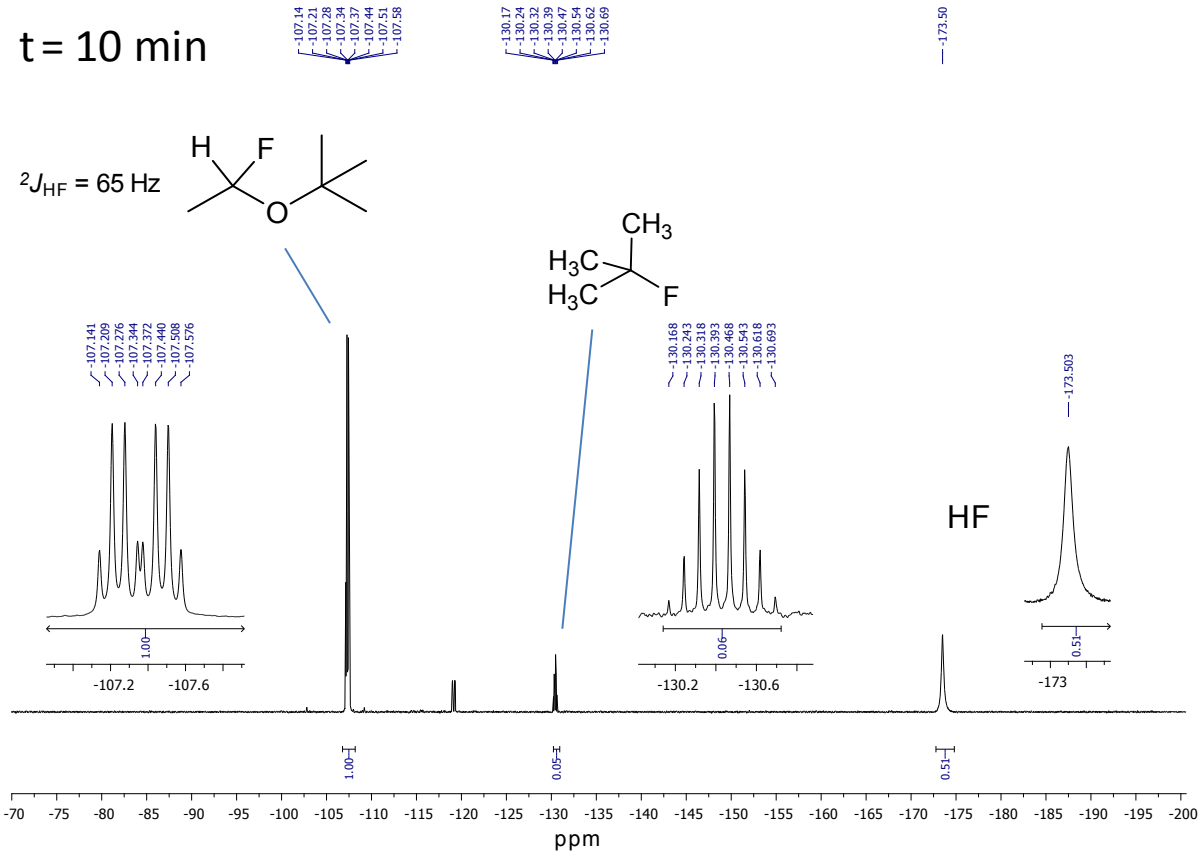
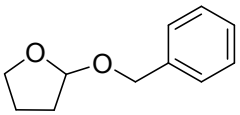


Figure S5: ^{19}F (282 MHz) NMR spectrum of the BP photo-promoted reaction between NFSI and ETBE after 10 min of irradiation. Conditions: $CDCl_3$ (0.5 mL, NMR tube), ETBE (0.2 mmol), NFSI (0.1 mmol), BP (5 mol%), 20 °C, degassing Ar bubbling (20 min), *hv* (320-390 nm, low pressure Hg lamp, type TLC, 6W).

III. Synthesis and characterization of compounds 1-13

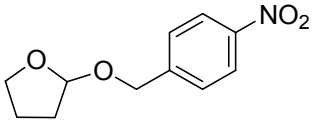
General Procedure: In a test tube, the benzophenone (BP) (2 mol%, 1.82 mg) and the *N*-fluorobis(phenyl)sulfonimide (NFSI) (157.5mg, 0.5 mmol) are dissolved in the ether of choice (THF, THP or 1,4-dioxane) (2 mL), and the tube capped with a rubber septum. The reaction mixture, protected from light by aluminum foil, is degassed by gentle argon bubbling for 20 minutes. The reaction is initiated by irradiating the tube at 320-390 nm using a low pressure Hg lamp (type Thin Layer Chromatography, 6W, set at 365 nm) placed at ~ 1 cm from the tube for 15-20 min. Then the nucleophile (0.6 mmol) is added with a syringe and the reaction is stirred at room temperature for 4 to 12 h without irradiation. The reaction mixture is concentrated under reduced pressure and purified by column chromatography on silica gel.

2-(benzyloxy)tetrahydrofuran (1): Synthesized according to the general procedure. After 15 min of irradiation at 20 °C the phenylmethanol was added (62.5 µL, 0.6 mmol) and the solution was stirred at 20 °C for 4 h. The residue was purified by flash chromatography over silica gel (Pentane/EtOAc, 90/10) to afford **1** as a colorless oil (70.6 mg, 79%).



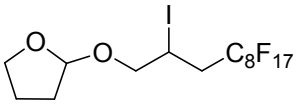
^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 7.38-7.27 (m, 5H), 5.27-5.20 (m, 1H), 4.74 (d, *J* = 11.7 Hz, 1H), 4.49 (d, *J* = 11.7 Hz, 1H), 4.03-3.87 (m, 2H), 2.12-1.78 (m, 4H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 138.3, 128.4, 127.9, 127.6, 103.2, 68.8, 67.1, 32.4, 23.5; **HRMS** (ESI): Calcd. for $C_{11}H_{14}O_2Na$ $[M+Na]^+$: 201.0886; Found: 201.0890.

2-((4-nitrobenzyl)oxy)tetrahydrofuran (2): Synthesized according to the general procedure. After 15 min of irradiation, the (4-nitrophenyl)methanol (92 mg, 0.6 mmol) was added and the solution was stirred for 4 h at 20 °C. The residue was purified by flash chromatography over silica gel (Pentane/EtOAc, 90/10) to afford **2** as a colorless oil (78 mg, 70%).



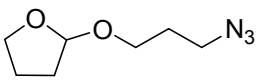
^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 8.21-8.11 (m, 2H), 7.52-7.41 (m, 2H), 5.24-5.17 (m, 1H), 4.78 (d, *J* = 13.5 Hz, 1H), 4.56 (d, *J* = 13.5 Hz, 1H), 3.98-3.81 (m, 2H), 2.12-1.76 (m, 4H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 147.3, 146.4, 127.8, 123.6, 103.7, 67.6, 67.4, 32.5, 23.5; **HRMS** (ESI): Calcd. for $C_{10}H_{11}N_3ONa$ $[M+Ag]^+$: 329.9896; Found: 329.9890.

2-((4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-2-iodoundecyl)oxy) tetrahydrofuran (3): Synthesized according to the general procedure. After 15 min of irradiation at 20 °C, the heptadecafluoro-2-iodoundecan-1-ol (362.5 mg, 0.6 mmol) was added and the solution was stirred for 6 h at 20 °C. The residue was purified by flash chromatography over silica gel (Pentane/EtOAc, 95/5) to afford **3** as a colorless oil (235 mg, 59%), and as a mixture of two diastereoisomers (1/1 ratio; measured by ^{1}H-NMR on the crude mixture).



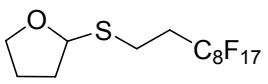
^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 5.21-5.09 (m, 1H, d1and d2), 4.46-4.29 (m, 1H, d1and d2), 3.99-3.76 (m, 3H, d1and d2), 3.75-3.58 (m, 1H, d1and d2), 3.17-2.88 (m, 1H, d1and d2), 2.80-2.50 (m, 1H, d1and d2), 2.08-1.78 (m, 4H, d1and d2); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm): **d1** = 104.74, 134.5, 72.8, 67.6, 37.8 (t, *J* = 21.6 Hz), 32.6, 23.5, 15.6, **d2** = 103.7, 71.5, 72.9, 67.5, 37.8 (q, *J* = 21.6 Hz), 32.5, 23.4, 15.1; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm):= -81.1 (t, *J* = 9.9 Hz), -113.8, -121.7, -122.1, -122.4, -122.9, -123.8, -126.3; **HRMS** (ESI): Calcd. for $C_{15}H_{12}F_{17}NaI$ $[M+Na]^+$: 696.9502; Found: 696.9510.

2-(3-azidopropoxy)tetrahydrofuran (4): Synthesized according to the general procedure. After 15 min of irradiation at 20 °C, the 3-azidopropan-1-ol (61 mg, 0.6 mmol) was added and the solution was stirred for 12 h at 20 °C. The residue was purified by flash chromatography over silica gel (Pentane/EtOAc, 90/10) to afford **4** as a colorless oil (56 mg, 65%).



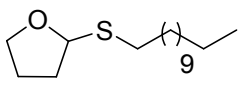
^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.47 (dd, *J* = 1.5 Hz and *J* = 4.2 Hz, 1H), 3.91-3.80 (m, 2H), 3.72 (tt, *J* = 6.3 Hz and *J* = 10.2 Hz, 1H), 3.44 (tt, *J* = 6.3 Hz and *J* = 9.9 Hz, 1H), 3.35 (t, *J* = 6.9 Hz, 2H), 2.05-1.76 (m, 6H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 104.0, 67.1, 63.8, 48.7, 32.4, 29.3, 23.6; **HRMS** (ESI): Calcd. for $C_7H_{13}N_3O_2Na$ $[M+Na]^+$: 194.0899; Found: 194.0905.

2-((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)thio)tetrahydrofuran (5): Synthesized according to the general procedure. After 20 min of irradiation at 20 °C, the heptadecafluorodecane-1-thiol (172 µL, 0.6 mmol) was added and the solution was stirred for 12 h at 20 °C. The residue was purified by flash chromatography over silica gel (Pentane/EtOAc, 98/02) to afford **5** as a colorless oil (256 mg, 93%).



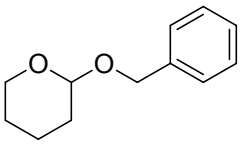
^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 5.38 (dd, *J* = 3.9 Hz and *J* = 7.5 Hz, 1H), 3.99-3.82 (m, 2H), 2.96-2.72 (m, 2H), 2.68-2.19 (m, 3H), 2.07-1.72 (m, 3H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 85.1, 67.0, 32.9 (t, *J* = 21.8 Hz), 32.7, 24.8, 22.4 (t, *J* = 4.4 Hz); **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm):= -81.3 (t, *J* = 9.9 Hz), -114.8, -122.0, -122.19, -122.21, -123.0, -123.7, -126.5; **HRMS** (ESI): Calcd. for $C_{14}H_{11}OF_{17}NaS$ $[M+Na]^+$: 573.0151; Found: 573.0158.

2-(dodecylthio)tetrahydrofuran (6): Synthesized according to the general procedure. After 15 min of irradiation at 20 °C, the dodecane-1-thiol (143.5 µL, 0.6 mmol) was added and the solution was stirred for 12 h at 20 °C. The residue was purified by flash chromatography over silica gel (Pentane 100% to Pentane/EtOAc, 99/1) to afford **6** as a colorless oil (112 mg, 82%).



^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 5.31 (dd, *J* = 4.2 Hz and *J* = 7.5 Hz, 1H), 3.96-3.81 (m, 2H), 2.72-2.49 (m, 2H), 2.31-2.16 (m, 1H), 2.02-1.90 (m, 1H), 1.87-1.72 (m, 2H), 1.67-1.52 (m, 2H), 1.43-1.14 (m, 18H), 0.85 (t, *J* = 6.3 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 84.5, 66.8, 32.7, 32.0, 31.3, 30.1, 29.8, 29.73, 29.70, 29.6, 29.4, 29.3, 29.1, 24.9, 22.8, 14.2; **HRMS** (ESI): Calcd. for $C_{16}H_{32}ONaS$ $[M+Na]^+$: 295.2066; Found: 295.2079.

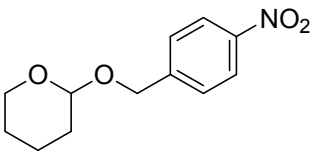
2-(benzyloxy)tetrahydro-2*H*-pyran (7): Synthesized according to the general procedure. After 15 min of irradiation at 20 °C, the phenylmethanol (62.5 µL, 0.6 mmol) was added and the solution was stirred for 4 h at 20 °C. The residue was purified by flash chromatography over silica gel (Pentane/EtOAc, 90/10) to afford **7** as a colorless oil (75.5 mg, 78%).



^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 7.43-7.27 (m, 5H), 4.81 (d, *J* = 12.0 Hz, 1H), 4.73 (t, *J* = 3.3 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.00-3.88 (m, 1H), 3.62-3.51 (m, 1H), 1.96-1.49 (m, 5H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 138.4, 128.4, 127.9, 127.6, 97.8, 68.9, 62.2, 30.7, 25.6, 19.4; **HRMS** (ESI): Calcd. for $C_{12}H_{16}O_2Na$ $[M+Na]^+$: 215.1042; Found: 215.1048.

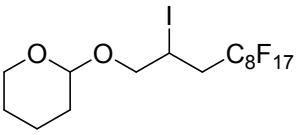
2-((4-nitrobenzyl)oxy)tetrahydro-2H-pyran (8): Synthesized according to the general procedure. After 15 min of irradiation at 20 °C, the (4-nitrophenyl)methanol (92 mg, 0.6 mmol) was added and the solution was stirred for 12 h at 20 °C. The residue was purified by flash

chromatography over silica gel (Pentane/EtOAc, 70/30) to afford **8** as a colorless oil (77 mg, 64%).



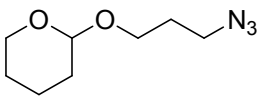
^{1}H-NMR ($CDCl_3$, 600 MHz) δ (ppm) = 8.27-8.08 (m, 2H), 7.56-7.43 (m, 2H), 4.86 (d, *J* = 13.8 Hz, 1H), 4.74-4.65 (m, 1H), 4.58 (d, *J* = 13.8 Hz, 1H), 3.85 (t, *J* = 10.8 Hz, 1H), 3.61-3.48 (m, 1H), 1.92-1.85 (m, 1H), 1.77-1.71 (m, 1H), 1.68-1.44 (m, 4H); **^{13}C-NMR** ($CDCl_3$, 150 MHz) δ (ppm) = 147.3, 146.2, 127.8, 123.6, 98.4, 67.7, 62.3, 30.5, 25.4, 19.3; **HRMS** (ESI): Calcd. for $C_{12}H_{15}NO_4$ $[M+H]^+$: 237.1001; Found: 237.1013.

2-(((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-iododecyl)oxy)methyl) tetrahydro-2H-pyran (9): Synthesized according to the general procedure. After 15 min of irradiation at 20 °C, the heptadecafluoro-2-iodoundecan-1-ol (362.5 mg, 0.6 mmol) was added and the solution was stirred for 5 h at 20 °C. The residue was purified by flash chromatography over silica gel (Pentane/EtOAc, 90/10) to afford **9** as a colorless oil (241 mg, 70%), and as a mixture of two diastereoisomers (1/1 ratio; measured by ^{1}H-NMR on the crude mixture).



^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.74-4.64 (m, 1H, d1and d2), 4.46-4.31 (m, 1H, d1and d2), 4.06-3.79 (m, 2H, d1and d2), 3.73-3.47 (m, 1H, d1and d2), 3.22-2.94 (m, 1H, d1and d2), 2.82-2.56 (m, 1H, d1and d2), 1.91-1.44 (m, 6H, d1and d2); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm): **d1** = 99.4, 72.9, 62.42, 37.9 (q, *J* = 22.3 Hz), 30.4, 25.48, 19.3, 15.5, **d2** = 98.4, 72.2, 62.40, 37.9 (q, *J* = 22.3 Hz), 30.4, 25.46, 19.2, 14.7; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm):= -81.0 (t, *J* = 9.9 Hz), -113.7, -121.7, -122.1, -122.4, -122.9, -123.8, -126.3; **HRMS** (ESI): Calcd. for $C_{16}H_{14}F_{17}OINa$ $[M+Na]^+$: 710.9665; Found: 710.9649.

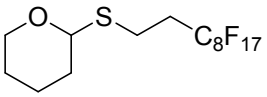
2-(3-azidopropoxy)tetrahydro-2H-pyran (10): Synthesized according to the general procedure. After 15 min of irradiation at 20 °C, the 3-azidopropan-1-ol (61 mg, 0.6 mmol) was added and the solution was stirred for 12 h at 20 °C. The residue was purified by flash chromatography over silica gel (Pentane/EtOAc, 90/10) to afford **10** as a colorless oil (67 mg, 72%).



^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.61-4.56 (m, 1H), 3.90-3.78 (m, 2H), 3.56-3.37 (m, 4H),1.93-1.65 (m, 4H), 1.63-1.48 (m, 4H); **^{13}C-**

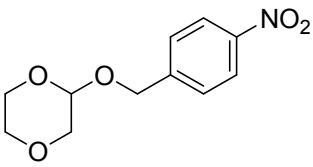
NMR ($CDCl_3$, 75 MHz) δ (ppm) = 99.1, 64.3, 62.5, 48.7, 30.8, 29.3, 25.6, 19.3; **HRMS** (ESI): Calcd. for $C_8H_{15}N_3O_2Na$ $[M+Na]^+$: 208.1056; Found: 208.1063.

2-((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)thio)tetrahydro-2H-pyran (11): Synthesized according to the general procedure. After 20 min of irradiation at 20 °C, the heptadecafluorodecane-1-thiol (172 µL, 0.6 mmol) was added and the solution stirred for 12 h at 20 °C. The residue was purified by flash chromatography over silica gel (Pentane/EtOAc, 99/1) to afford **11** as a colorless oil (233 mg, 83%).



^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.89 (dd, *J* = 3.6 Hz and *J* = 6.3 Hz, 1H), 4.12-4.01 (m, 1H), 3.58-3.47 (m, 1H), 2.95-2.71 (m, 2H), 2.64-2.27 (m, 2H), 2.03-1.90 (m, 1H), 1.86-1.74 (m, 1H), 1.72-1.51 (m, 4H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 83.0, 64.7, 32.9 (t, *J* = 21.7 Hz), 31.3, 25.7, 21.8, 21.6 (t, *J* = 4.4 Hz); **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -80.9 (t, *J* = 9.9 Hz), -114.6, -121.8, -121.97, -121.99, -122.8, -123.5, -126.2; **HRMS** (ESI): Calcd. for $C_{15}H_{13}OF_{17}NaS$ $[M+Na]^+$: 587.0307; Found: 587.0298.

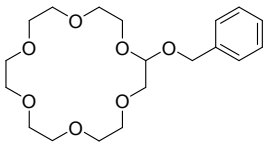
2-((4-nitrobenzyl)oxy)-1,4-dioxane (12): Synthesized according to the general procedure. After 20 min of irradiation at 20 °C, the (4-nitrophenyl)methanol (92 mg, 0.6 mmol) was added and the solution was stirred for 12 h at 20 °C. The residue was purified by flash chromatography over silica gel (Pentane/EtOAc, 70/30) to afford **12** as a colorless oil (99 mg, 83%).



^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 8.26-8.15 (m, 2H), 7.58-7.48 (m, 2H), 4.92 (d, *J* = 13.2 Hz, 1H), 4.72-4.60 (m, 2H), 4.11-3.98 (m, 1H), 3.80-3.69 (m, 3H), 3.66 (dd, *J* = 3.4 Hz and *J* = 11.8 Hz, 1H), 3.58 (dt, *J* = 3.8 Hz and *J* = 11.6 Hz, 1H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 147.1, 144.9, 127.6, 123.3, 94.9, 68.4, 67.8, 65.8, 61.2; **HRMS** (CI): Calcd. for $C_{11}H_{13}NO_5$ $[M]^{-\cdot}$: 239.07937; Found: 239.07914.

2-(benzyloxy)-1,4,7,10,13,16-hexaoxacyclooctadecane (13): Synthesized according to the general procedure from a mixture of NFSI (157.5 mg, 0.5 mmol), 1,4,7,10,13,16-hexaoxacyclooctadecane (264 mg, 1 mmol) and BP (2 mol%, 1.82 mg) in $CHCl_3$ (2 mL). After 20 min of irradiation at 20 °C, the phenylmethanol (62.5 µL, 0.6 mmol) was added and the

solution was stirred for 14 h at 20 °C. The residue was purified by flash chromatography over silica gel (CH_2Cl_2/MeOH, 98/02) to afford the compound **13** as a colorless oil (105 mg, 57%).



^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 7.36-7.31(m, 5H), 4.88 (t, *J* = 5.1 Hz, 1H), 4.65 (dd, *J* = 11.7 Hz and *J* = 28.2 Hz, 2H), 3.78-3.50 (m, 22H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 138.1, 128.5, 127.9, 127.7, 100.2, 72.6, 71.7, 71.0, 70.8, 70.66, 70.65, 70.63, 70.59, 70.49, 70.4, 68.5, 61.8; **HRMS** (ESI): Calcd. for $C_{19}H_{30}O_7Na$ $[M+Na]^+$: 393.1883; Found: 393.1888.

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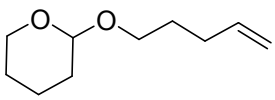
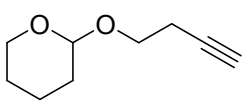
2*H*-Pyran, tetrahydro-2-(4-penten-1-yloxy) : (14) : Synthesized according to the general procedure. After 20 min of irradiation at 20 °C, the 4-Penten-1-ol (54.3 mg, 0.63 mmol) was added and the solution was stirred for 4 h at 20 °C. The residue was purified by flash chromatography over silica gel (Pentane/EtOAc, 90/10) to afford **14** as a colorless oil (52 mg, 61%).



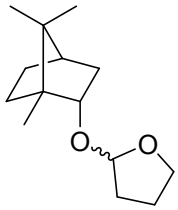
^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 5.94-5.80 (m, 1H), 5.10-4.97 (m, 2H), 4.61 (t, 1H), 3.94-3.75 (m, 2H), 3.57-3.40 (m, 2H), 2.22-2.14 (m, 2H), 1.91-1.52 (m, 8H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) =206.9, 138.4, 114.7, 67.0, 62.3, 31.0, 30.8, 30.5, 29.0, 25.5, 19.7; **HRMS** (ESI): Calcd. for $C_{10}H_{18}O_2Na$ $[M+Na]^+$: 193.1202; Found: 193.1199.

2-(3-Butynyloxy)tetrahydro-2*H*-pyran: (15) : Synthesized according to the general procedure. After 20 min of irradiation at 20 °C, the 3-Butyn-1-ol (54.1 mg, 0.75 mmol) was added and the solution was stirred for 4 h at 20 °C. The residue was purified by flash chromatography over silica gel (Pentane/EtOAc, 90/10) to afford **15** as a colorless oil (55 mg, 71%).



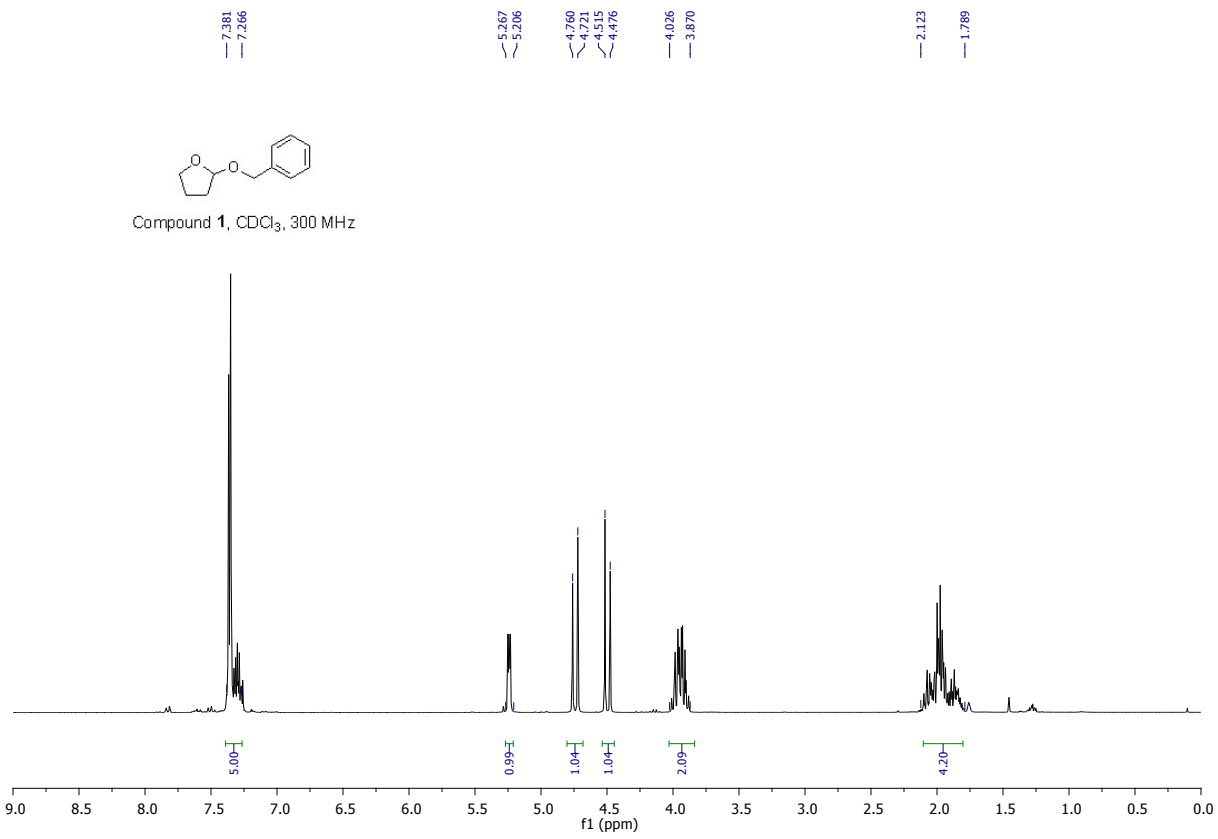
^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.65 (t, 1H), 3.92-3.80 (m, 2H), 3.61-3.48 (m, 2H), 2.52-2.47 (m, 2H), 1.97 (t, 1H), 1.85-1.50 (m, 7H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) =98.8, 81.5, 69.2, 65.6, 62.3, 30,6 25.5, 20.0, 19.5; **HRMS** (ESI): Calcd. for $C_{19}H_{14}O_2Na$ $[M+Na]^+$: 177.0894; Found: 177.0886.

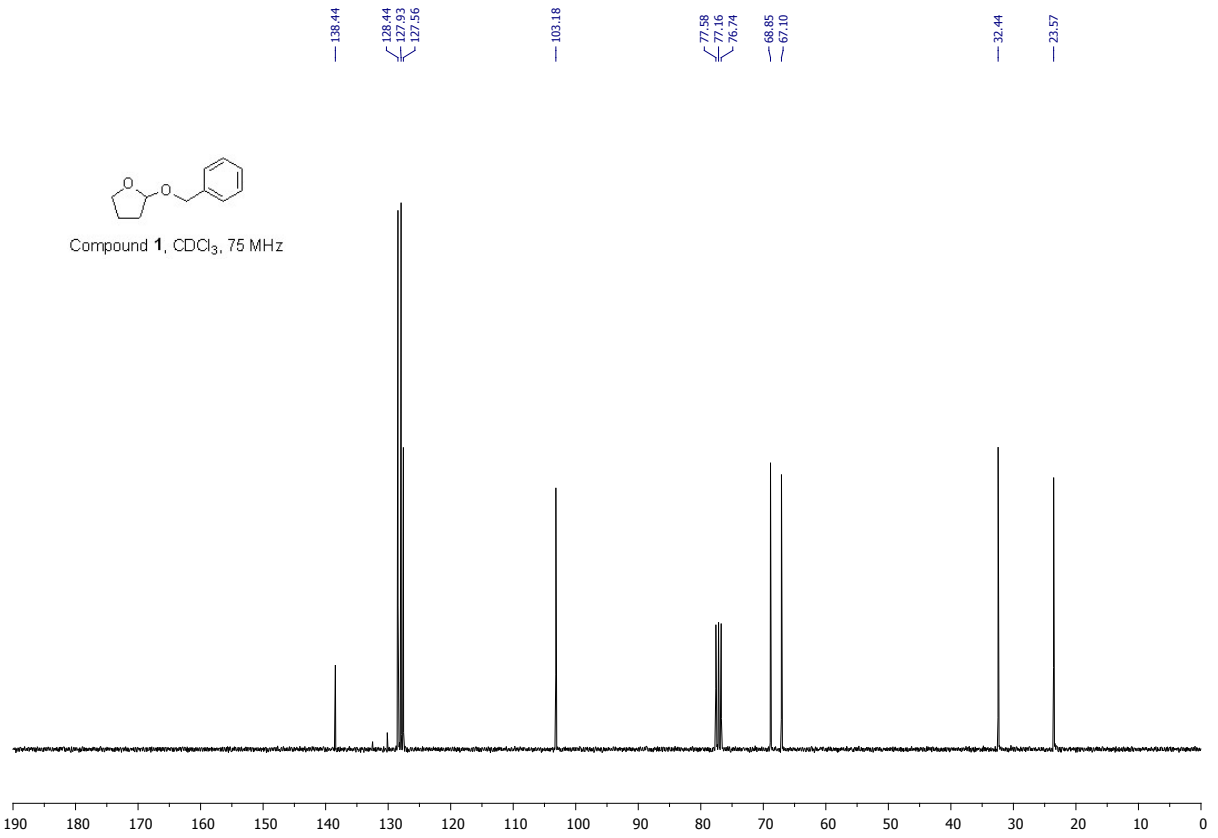
Borneol derivative (16) : Synthesized according to the general procedure. After 20 min of irradiation at 20 °C, Borneol (185 mg, 1.2 mmol) was added and the solution was stirred for 4 h at 20 °C. DCM was added and the reaction mixture was washed first with a saturated $NaHCO_3$ solution, twice with water and then with brine. After drying with $MgSO_4$ and solvent evaporation, the residue was purified by flash chromatography over silica gel (Pentane/EtOAc, 95/5) to afford **16** as a colorless oil (131 mg, 58%) and as a mixture of two diastereoisomers (~1/1 ratio; measured by ^{13}C-NMR after chromatography).

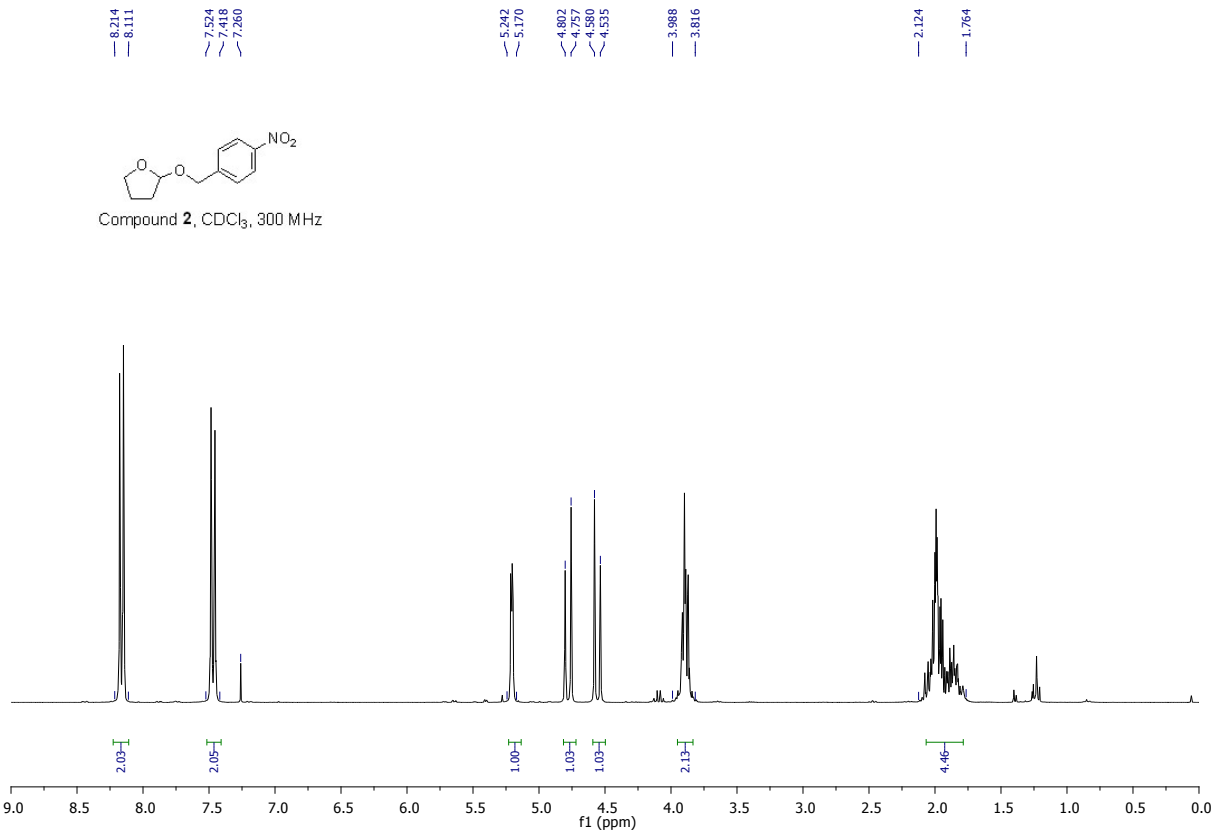


^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 5.17-5.13 (m, 1H), 3.95-3.73 (m, 3H), 2.27-2.10 (m, 1H), 2.06-1.58 (m, 7H), 1.25-1.15 (m, 2H), 1.09-0.95 (m, 1H), 0.87-0.84 (m, 9H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) =105.3, 101.6, 83.3; 79.3; 66.5; 66.3; 49.2; 48.7; 47.5; 47.3; 45.13; 45.09; 37.9; 35,7; 32.5; 28.3, 26.8, 26.70, 23.7, 23.5, 19.8, 18.9, 18.8, 13.8, 13.4; **HRMS** (ESI): Calcd. for $C_{14}H_{24}O_2Na$ $[M+Na]^+$: 247.1665; Found: 247.1668.

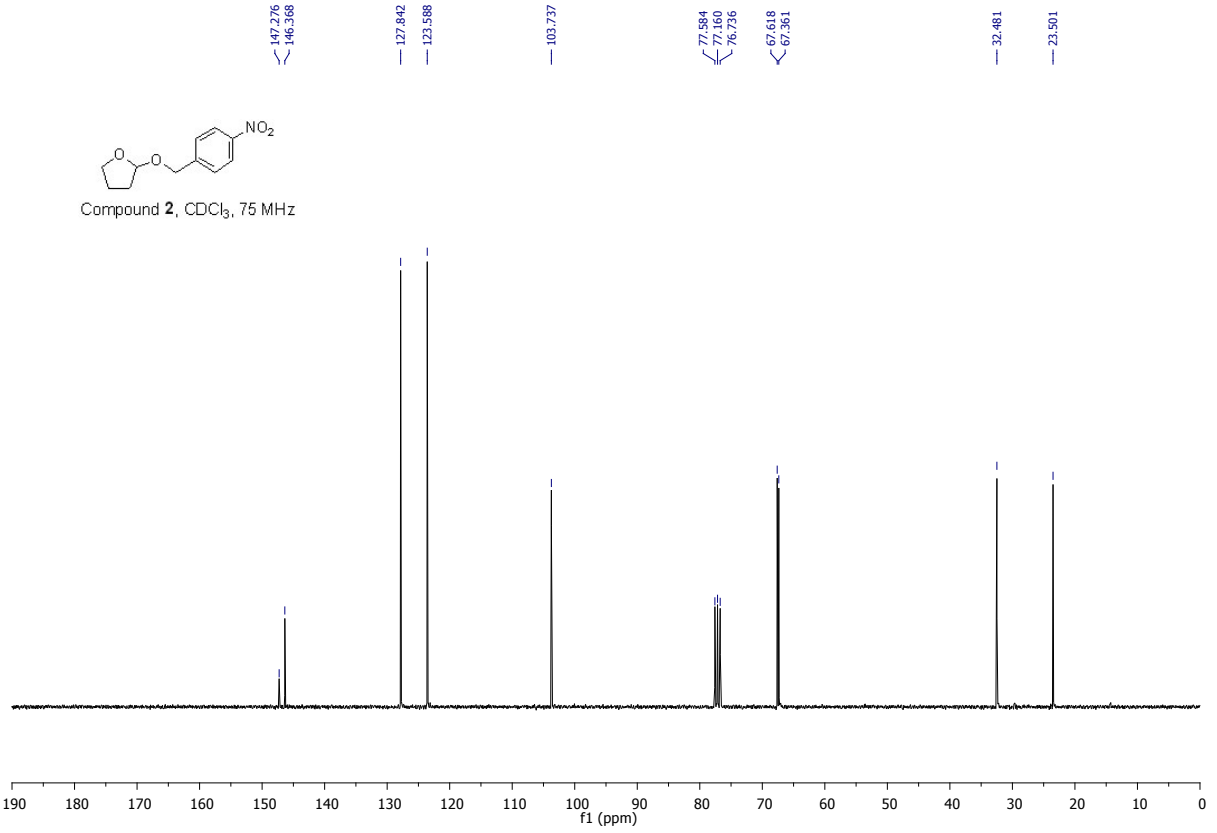
IV. ^{1}H, ^{13}C and ^{19}F NMR Spectra



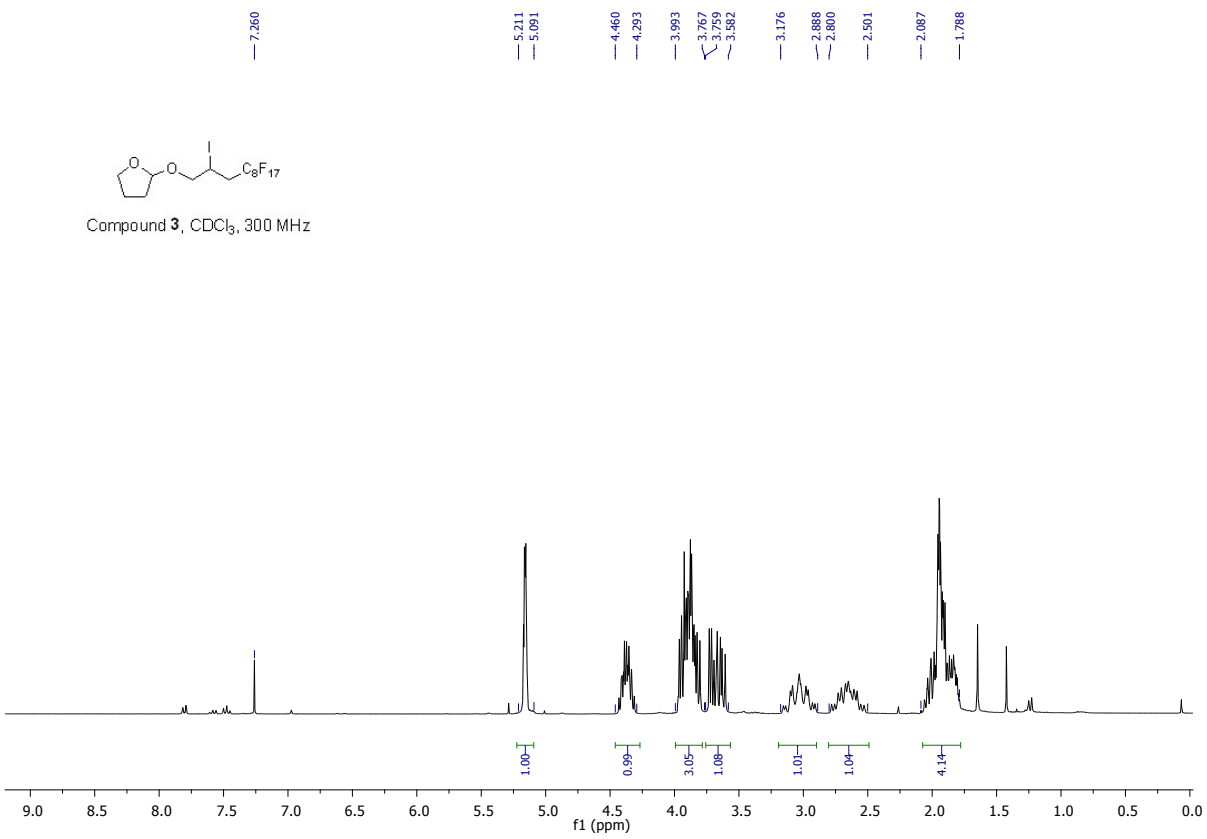




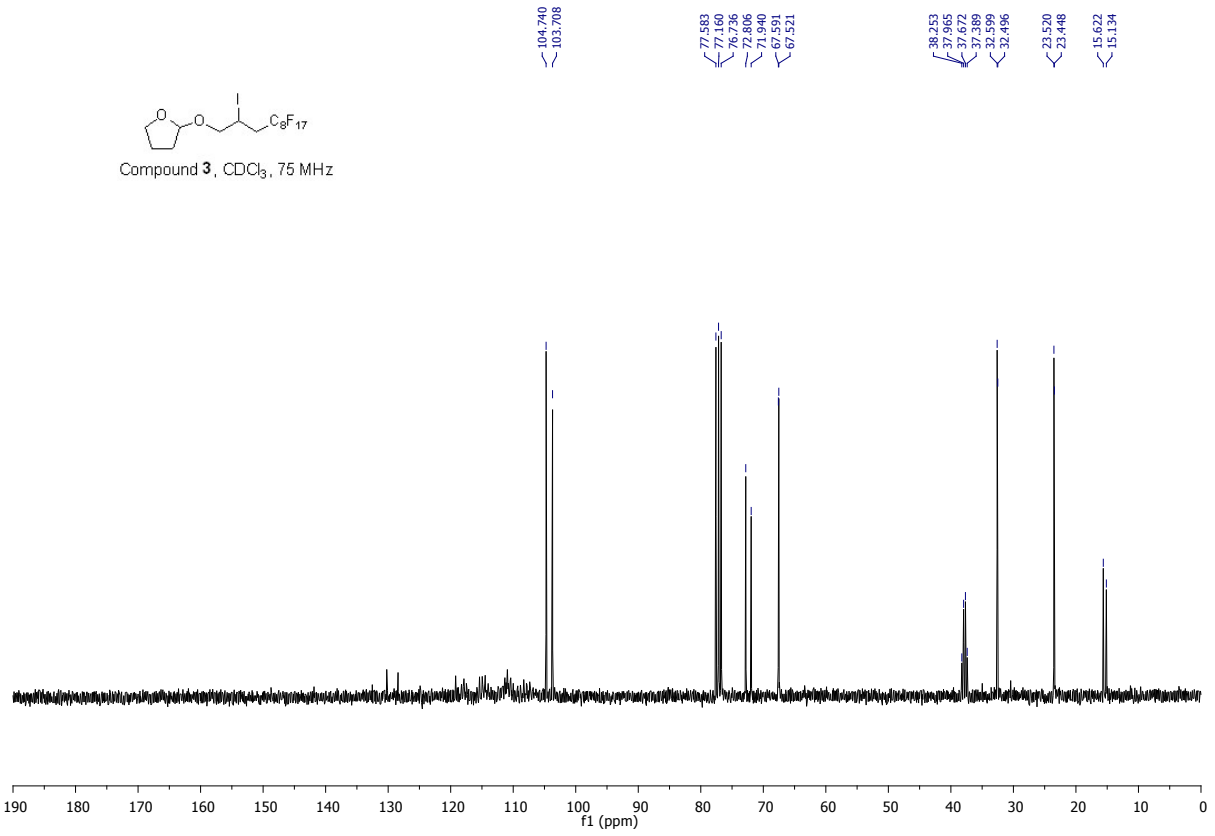
Compound **2**, $CDCl_3$, 300 MHz



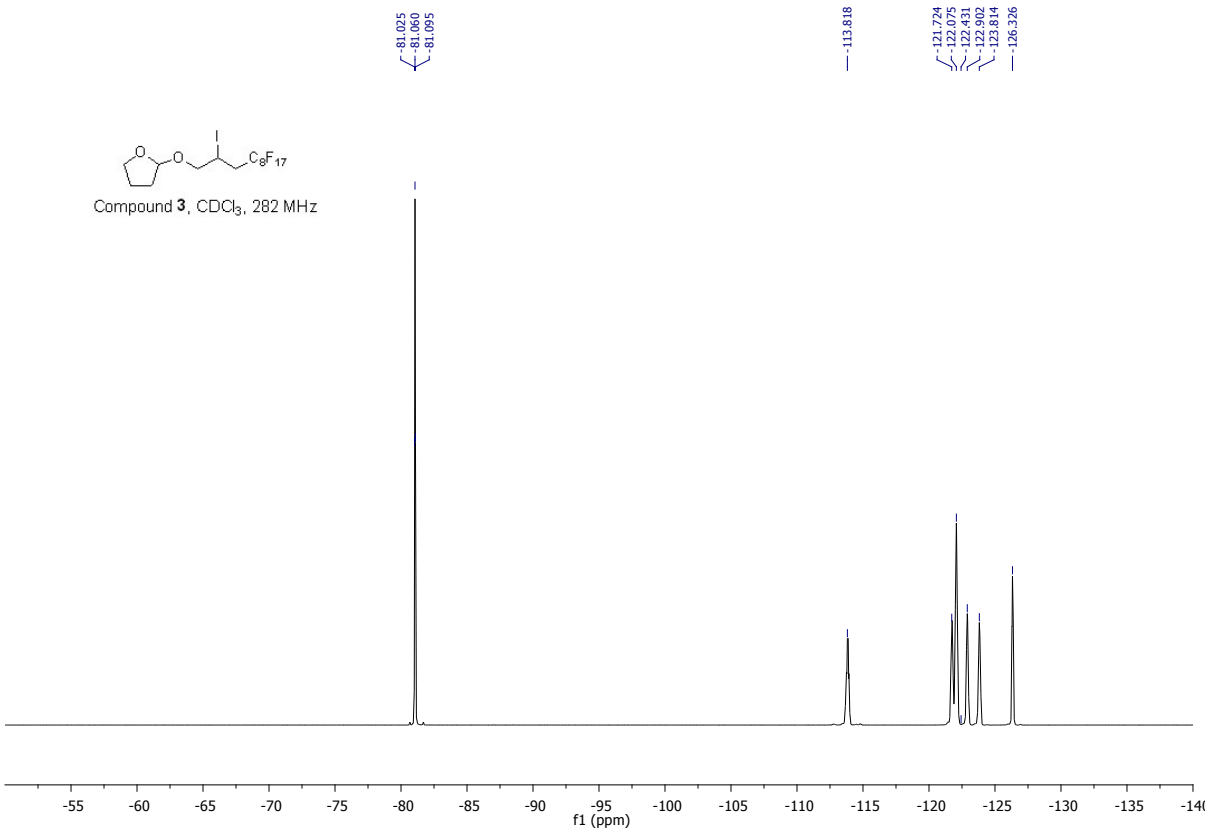
Compound **2**, $CDCl_3$, 75 MHz

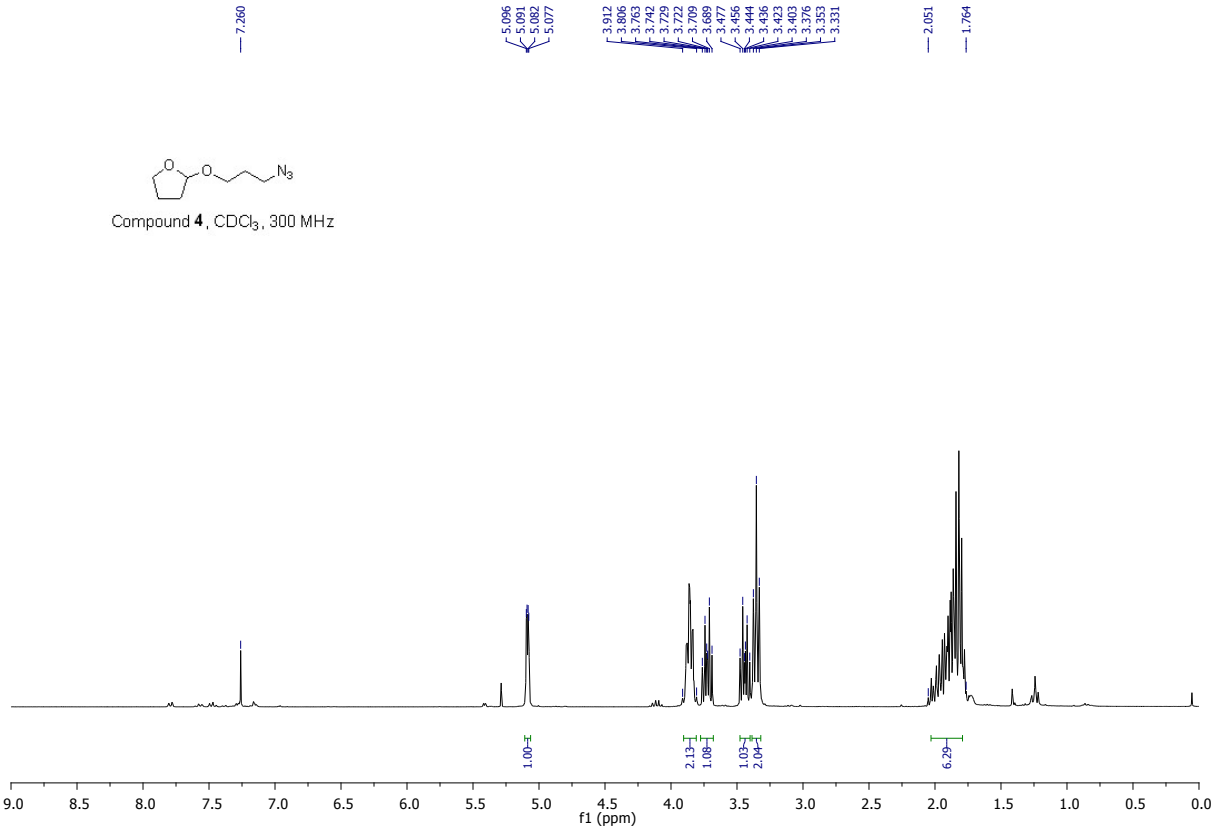


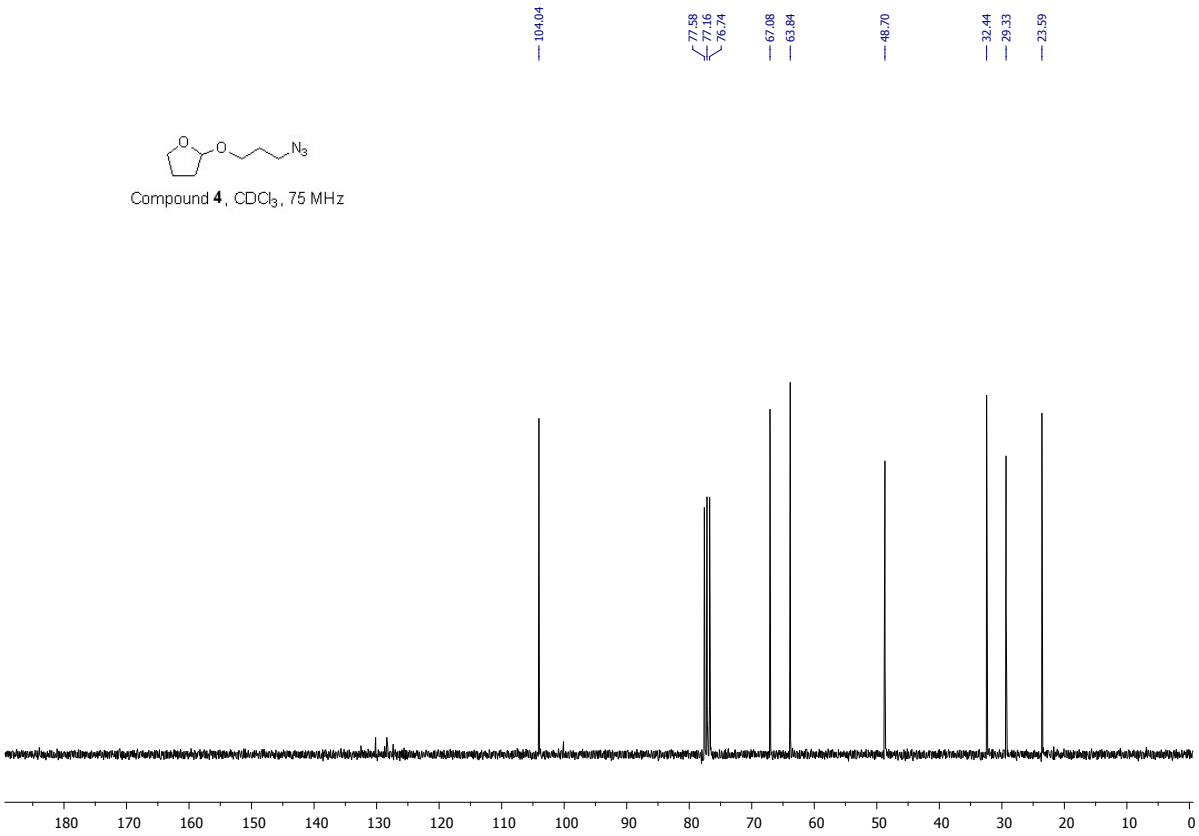
Compound **3**, $CDCl_3$, 300 MHz



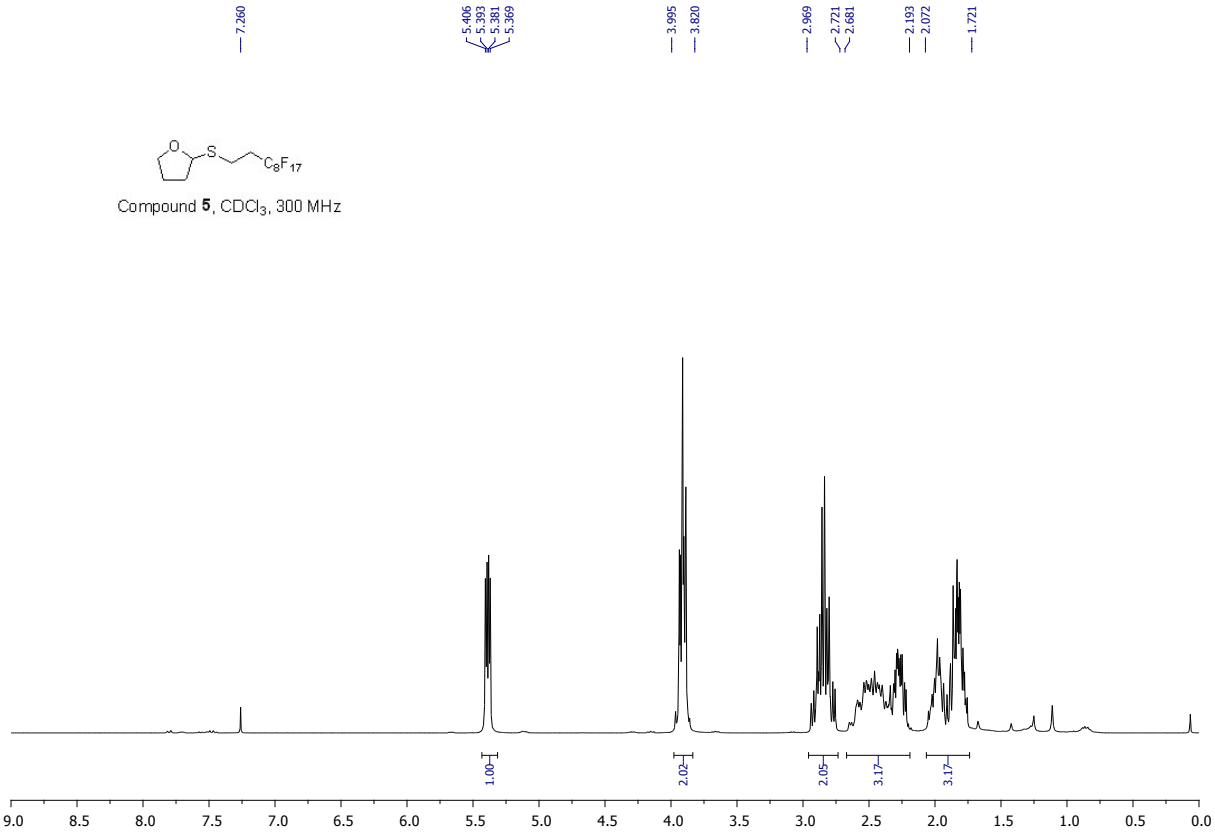
Compound **3**, $CDCl_3$, 75 MHz


-81.025
-81.060
-81.095
-113.818
-121.724
-122.075
-122.431
-122.902
-123.814
-126.326
Compound 3, CDCl3, 282 MHz
f1 (ppm)

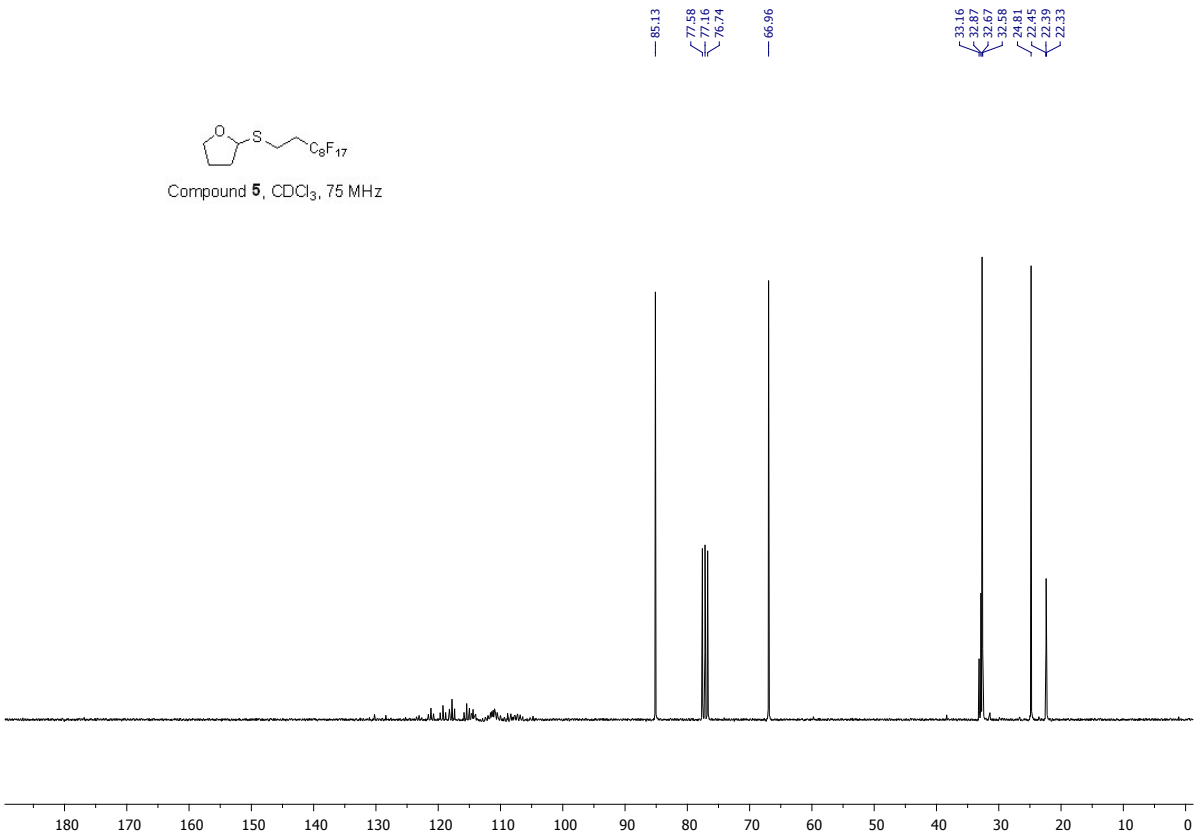

7.260
5.096
5.091
5.082
5.077
3.912
3.806
3.763
3.742
3.729
3.722
3.709
3.689
3.477
3.456
3.444
3.436
3.423
3.403
3.376
3.353
3.331
2.051
1.764
Compound 4, CDCl3, 300 MHz
1.00
2.13
1.08
1.03
2.04
6.29
f1 (ppm)



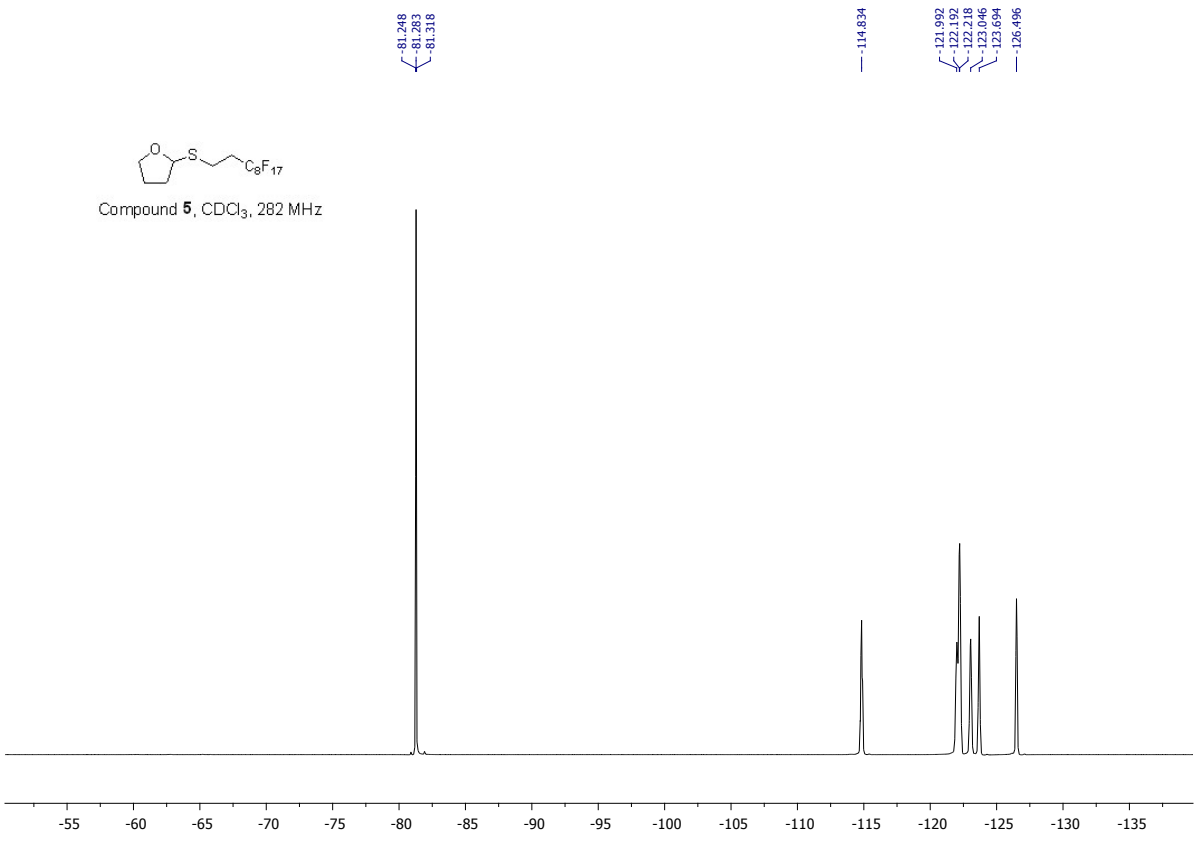
Compound **4**, $CDCl_3$, 75 MHz



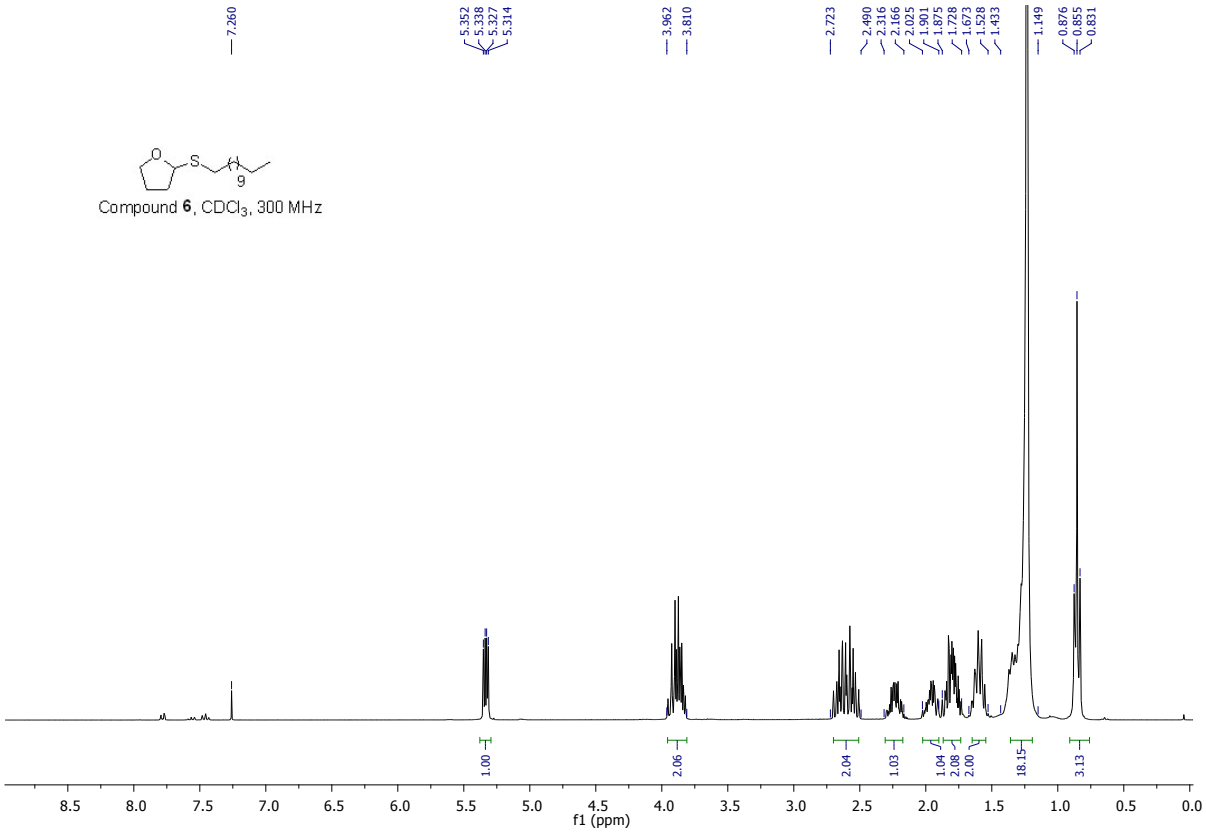
Compound **5**, $CDCl_3$, 300 MHz

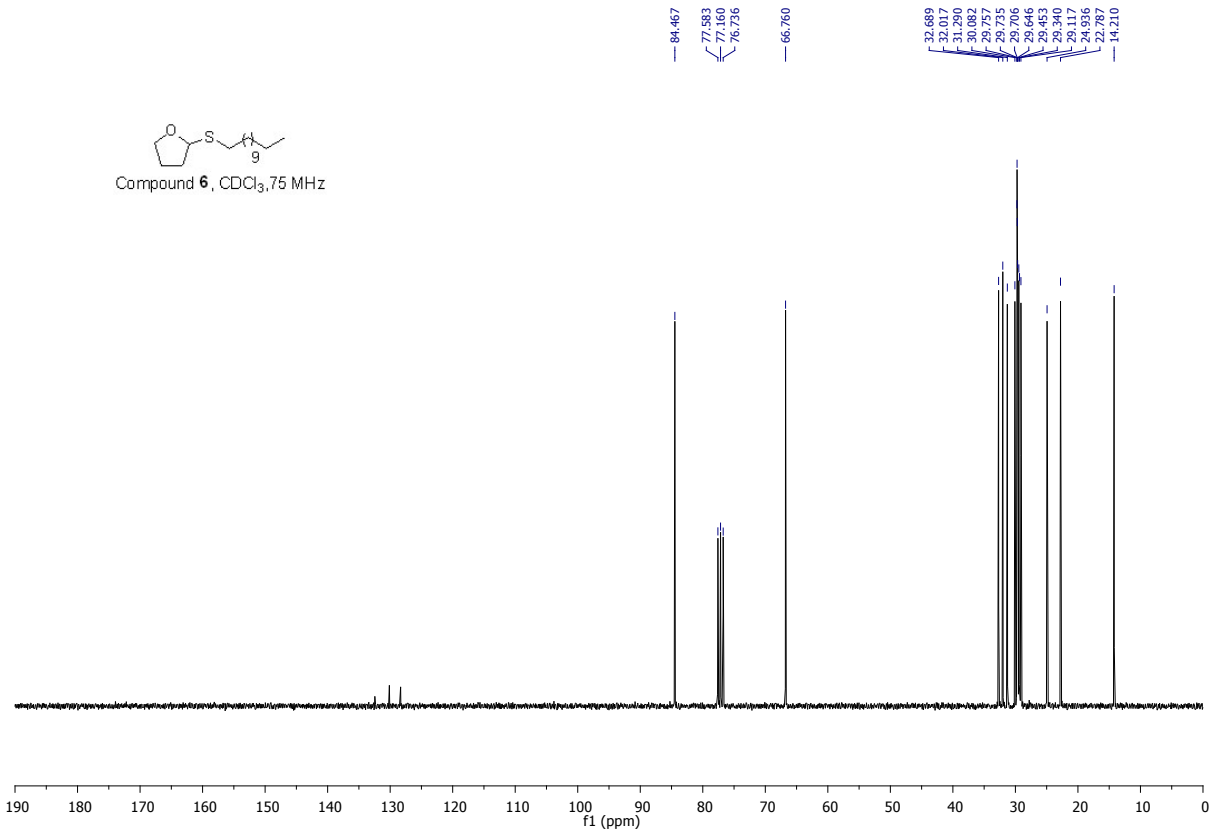


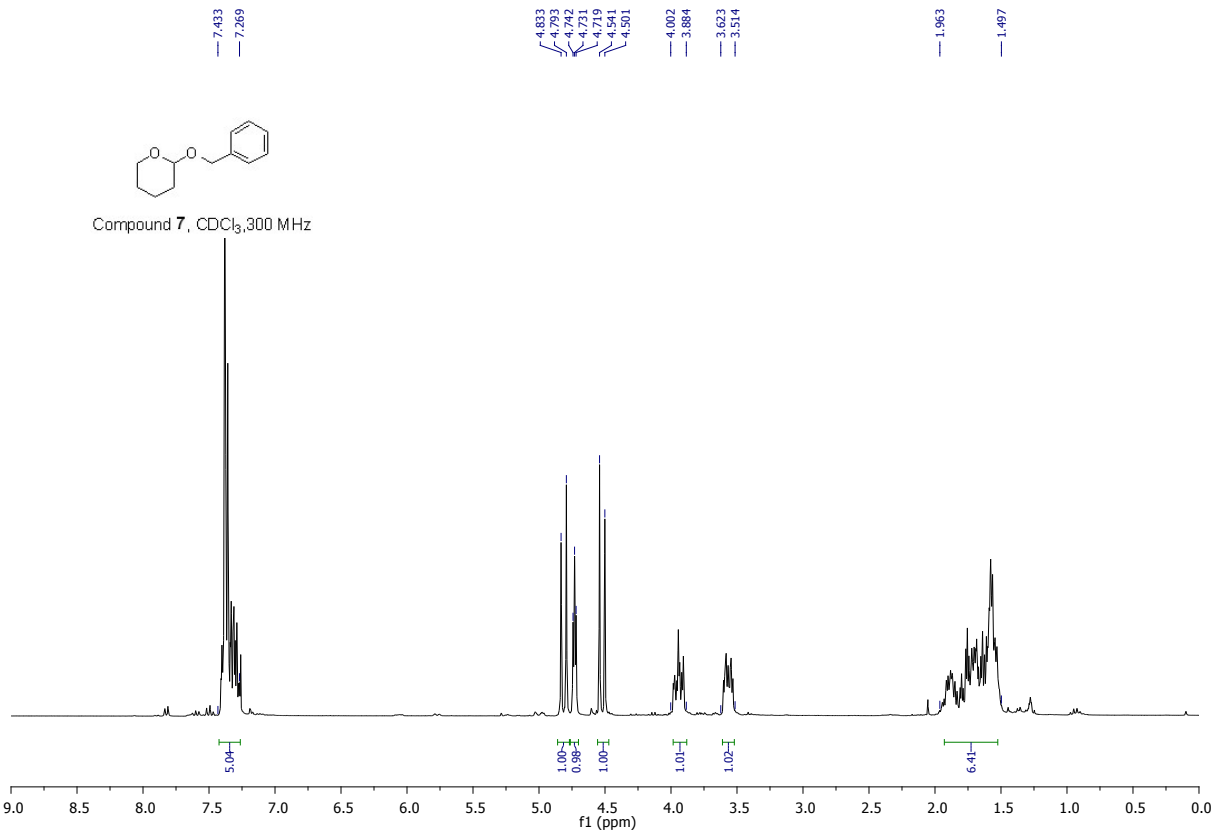
Compound **5**, $CDCl_3$, 75 MHz

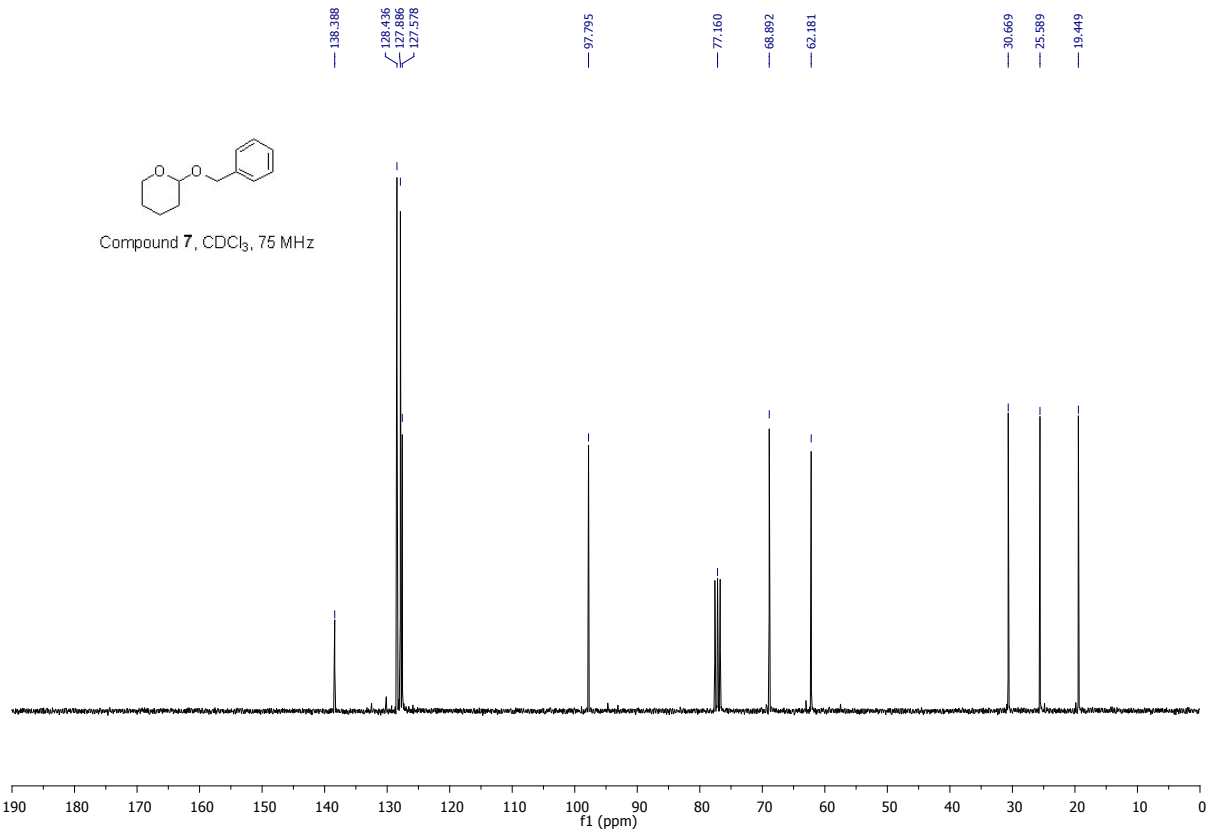


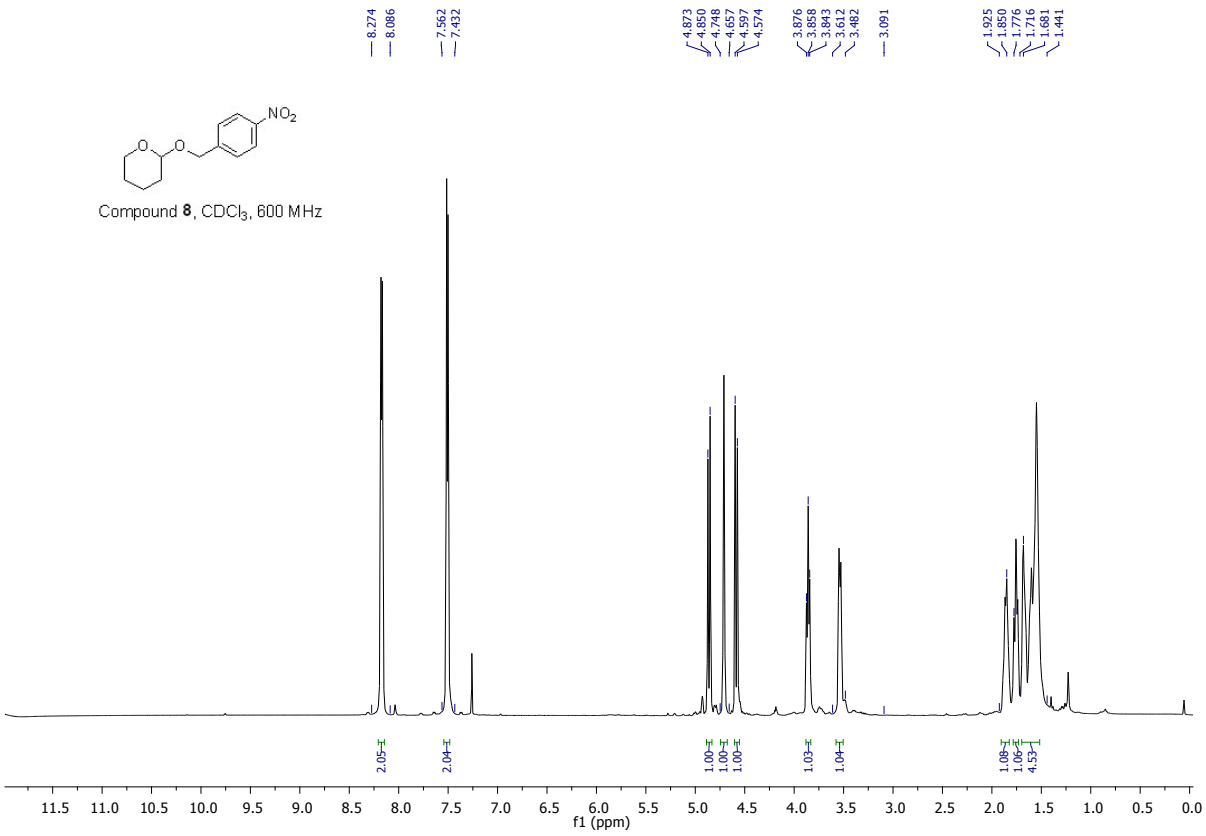
Compound **5**, $CDCl_3$, 282 MHz

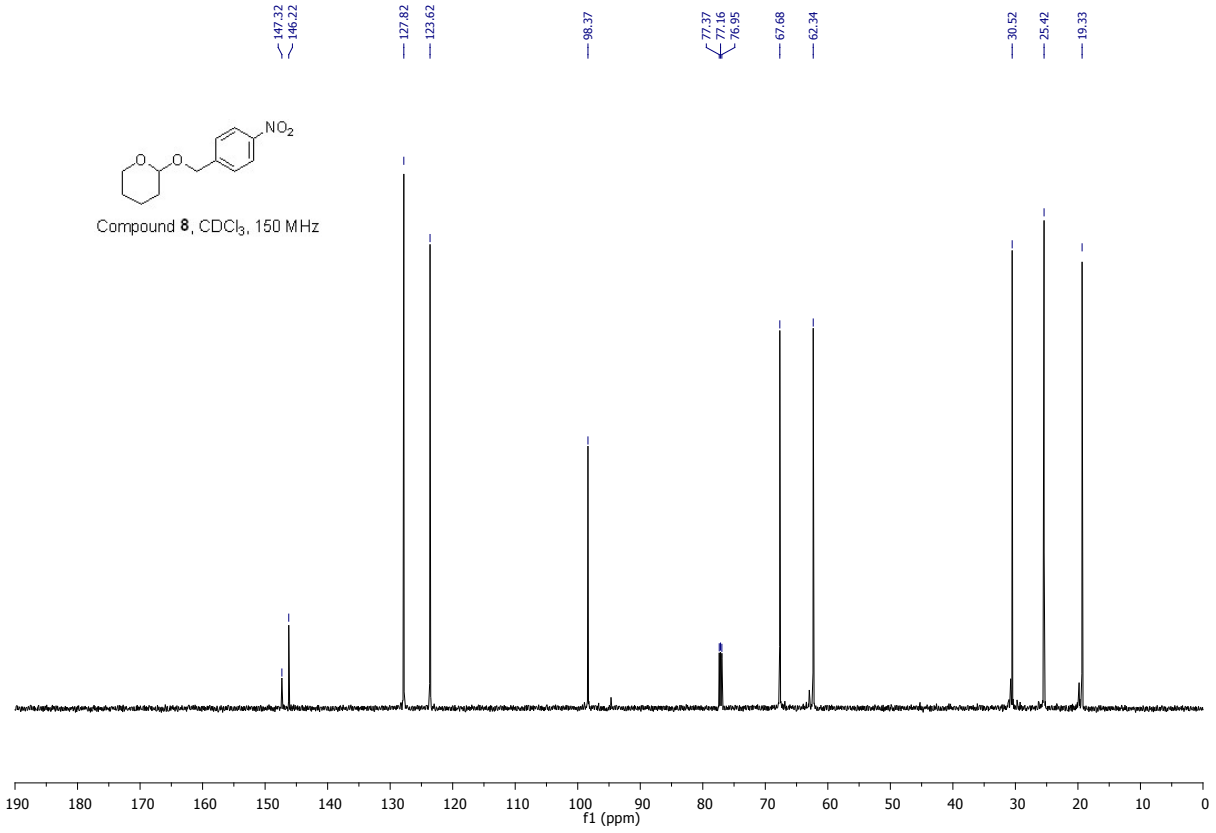

7.260
5.352
5.338
5.327
5.314
3.962
3.810
2.723
2.490
2.316
2.166
2.025
1.901
1.875
1.728
1.673
1.528
1.433
1.149
0.876
0.855
0.831
Compound 6, CDCl3, 300 MHz
1.00
2.06
2.04
1.03
1.04
2.08
2.00
18.15
3.13
f1 (ppm)

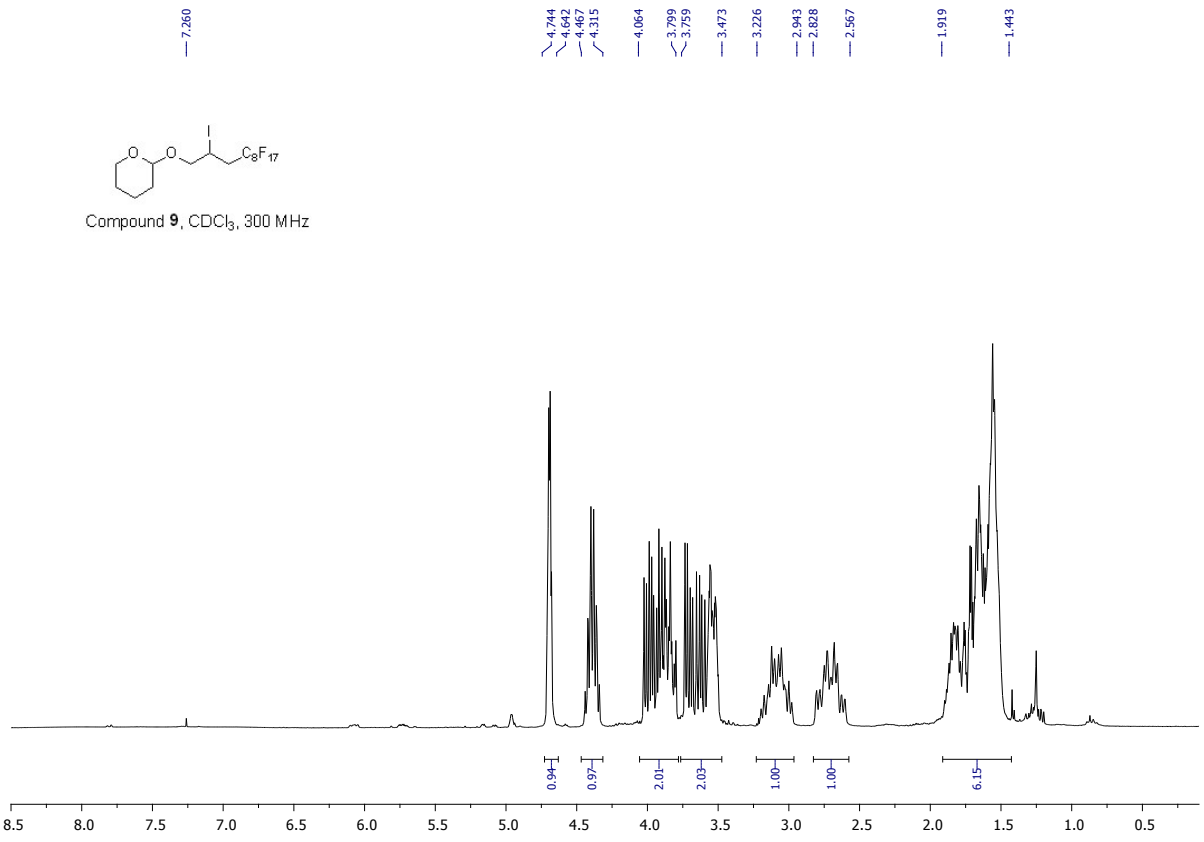

84.467
77.583
77.160
76.736
66.760
32.689
32.017
31.290
30.082
29.757
29.735
29.706
29.646
29.453
29.340
29.117
24.936
22.787
14.210
Compound 6, CDCl3,75 MHz
f1 (ppm)


7.433
7.269
4.833
4.793
4.742
4.731
4.719
4.541
4.501
4.002
3.884
3.623
3.514
1.963
1.497
Compound 7, CDCl3,300 MHz
5.04
1.00
0.98
1.00
1.01
1.02
6.41
f1 (ppm)

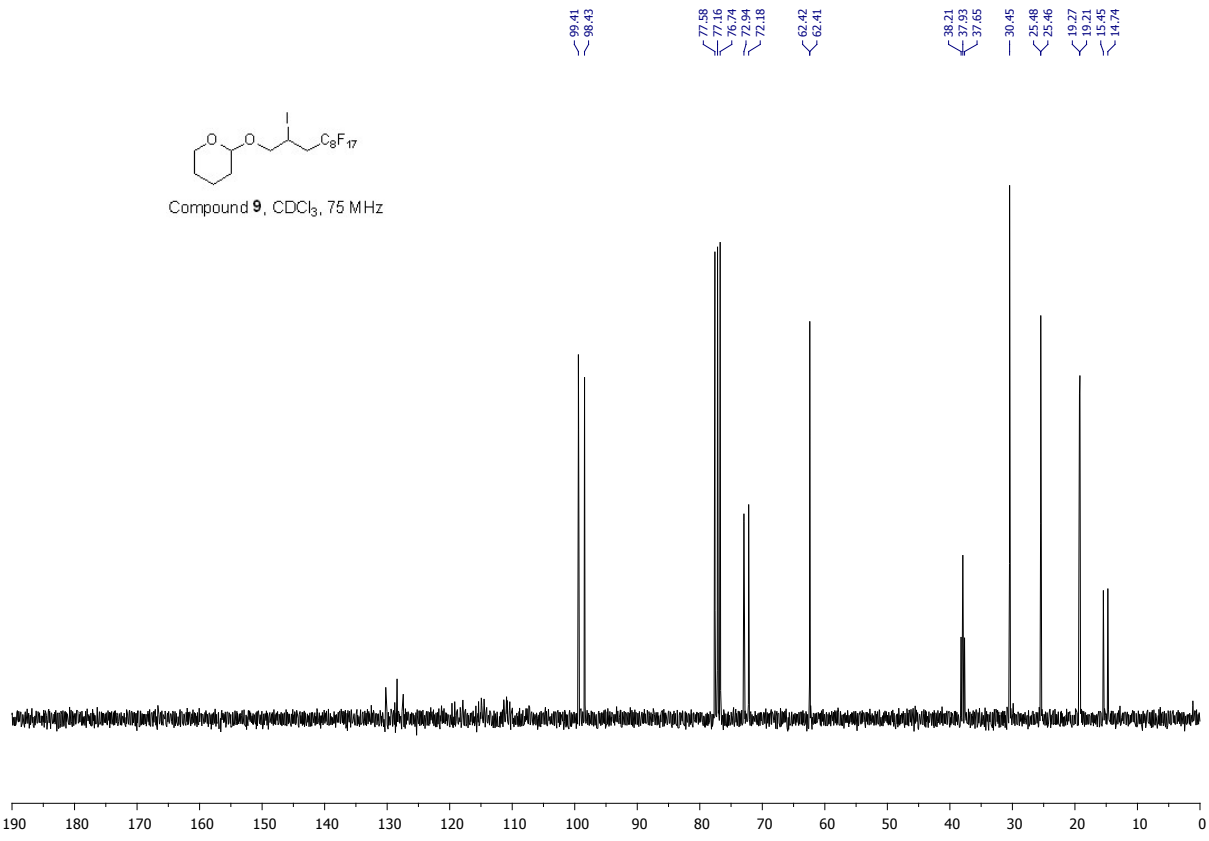

138.388
128.436
127.886
127.578
97.795
77.160
68.892
62.181
30.669
25.589
19.449
Compound 7, CDCl3, 75 MHz
f1 (ppm)


8.274
8.086
7.562
7.432
4.873
4.850
4.748
4.657
4.597
4.574
3.876
3.858
3.843
3.612
3.482
3.091
1.925
1.850
1.776
1.716
1.681
1.441
NO2
Compound 8, CDCl3, 600 MHz
2.05
2.04
1.00
1.00
1.00
1.03
1.04
1.08
1.06
4.53
f1 (ppm)

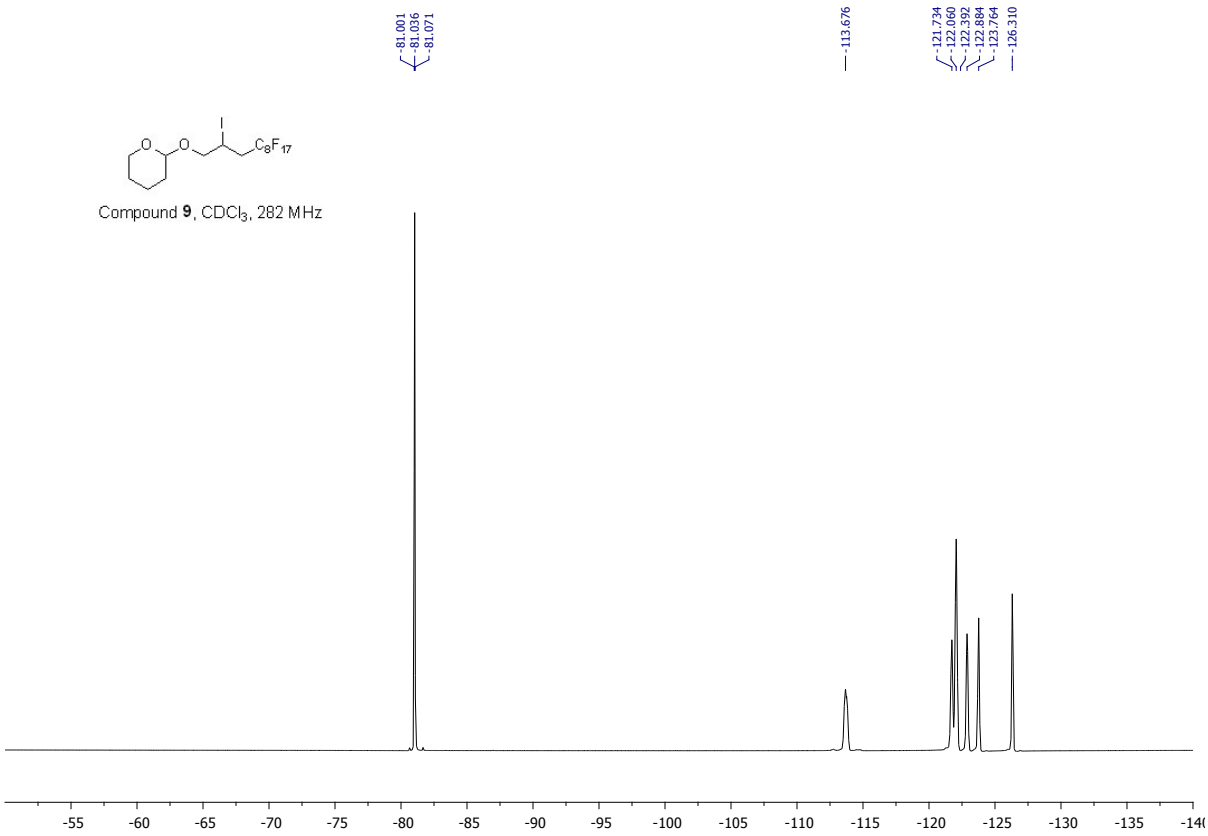

147.32
146.22
127.82
123.62
98.37
77.37
77.16
76.95
67.68
62.34
30.52
25.42
19.33
NO2
Compound 8, CDCl3, 150 MHz
f1 (ppm)

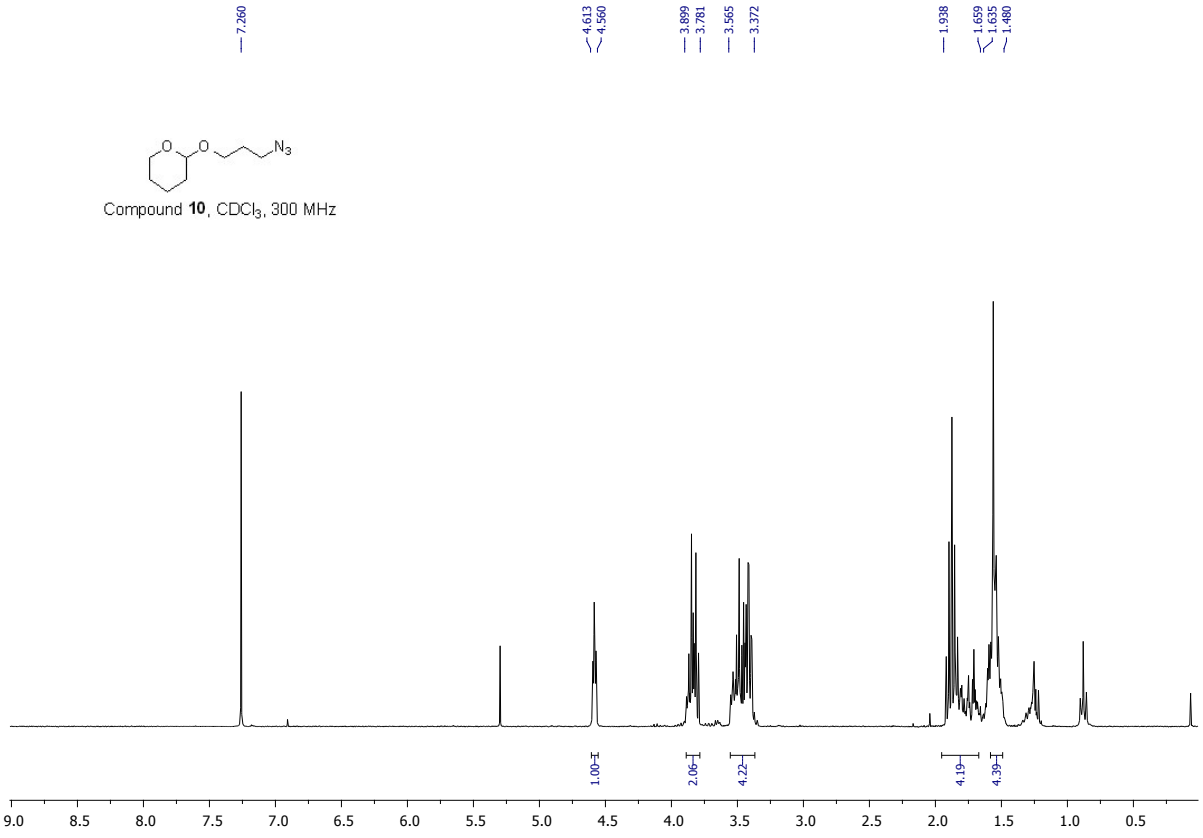


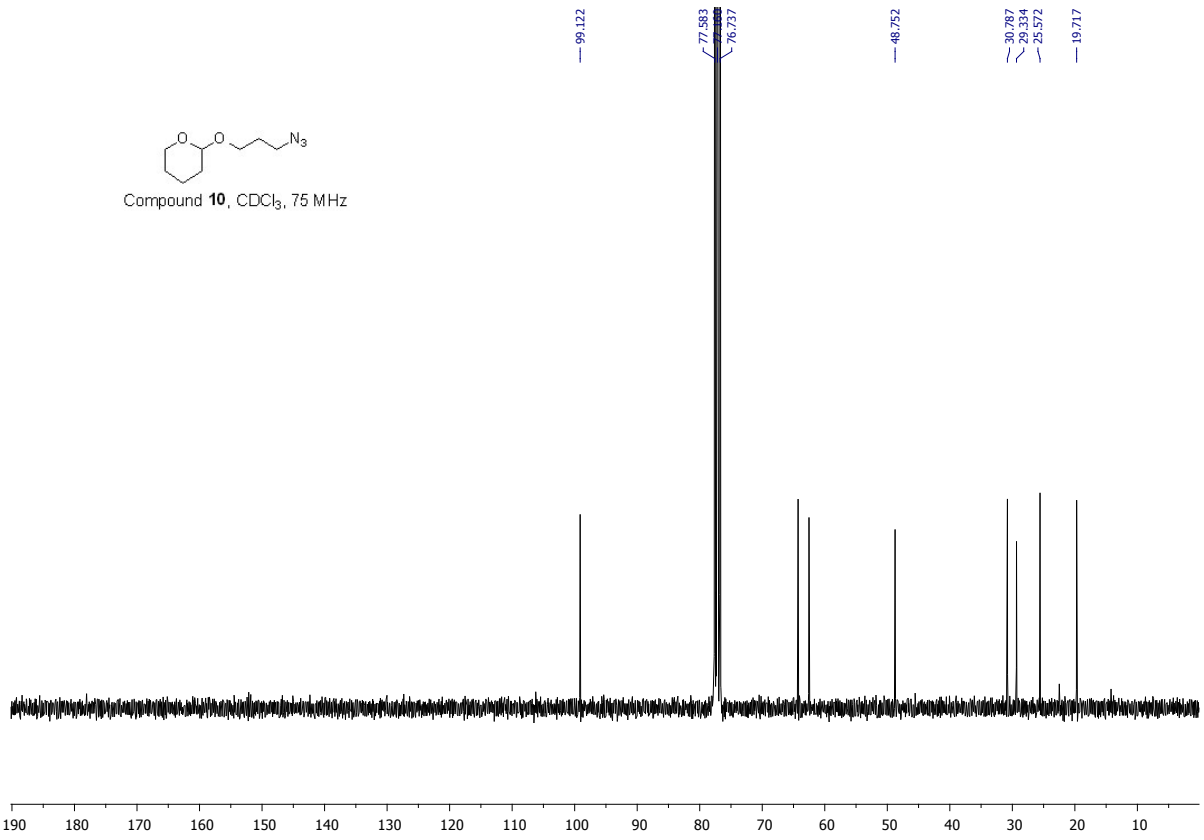
Compound **9**, $CDCl_3$, 300 MHz



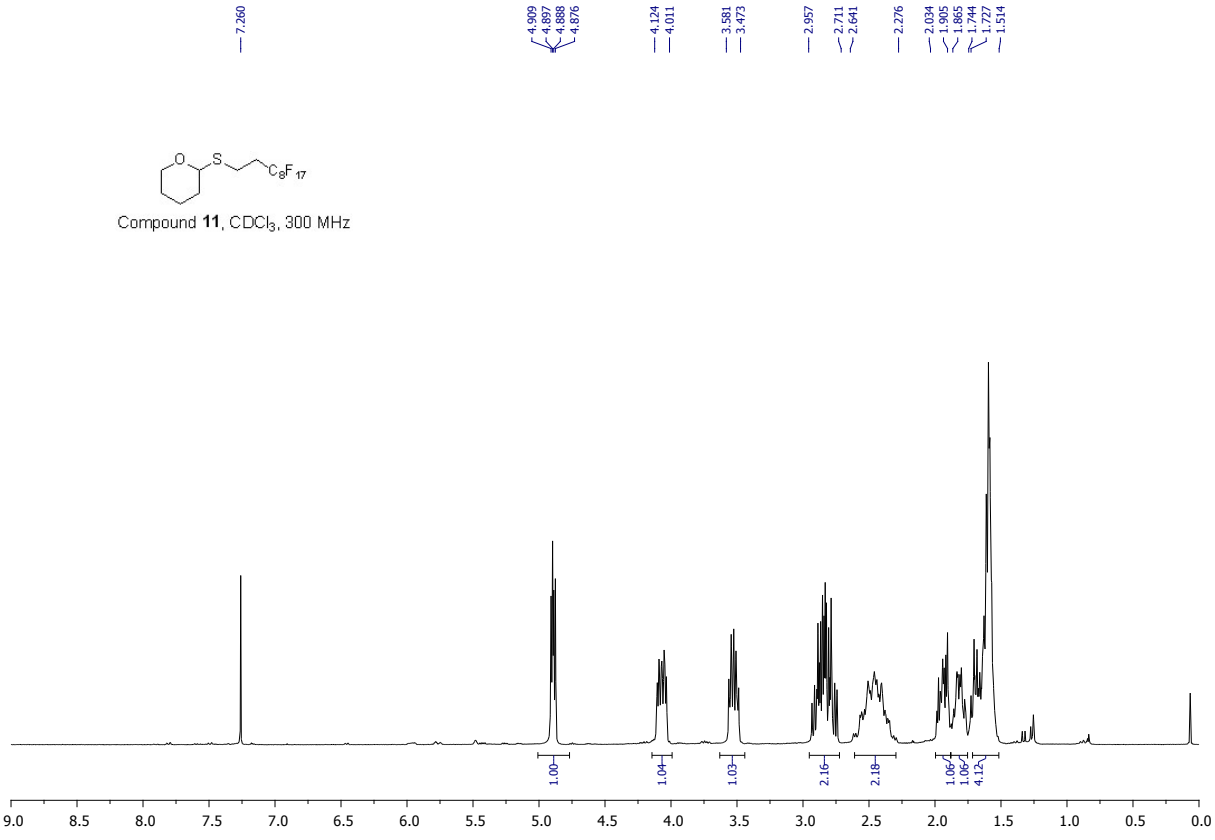
Compound **9**, $CDCl_3$, 75 MHz


-81.001
-81.036
-81.071
-113.676
-121.734
-122.060
-122.392
-122.884
-123.764
-126.310
Compound 9, CDCl3, 282 MHz
-55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135

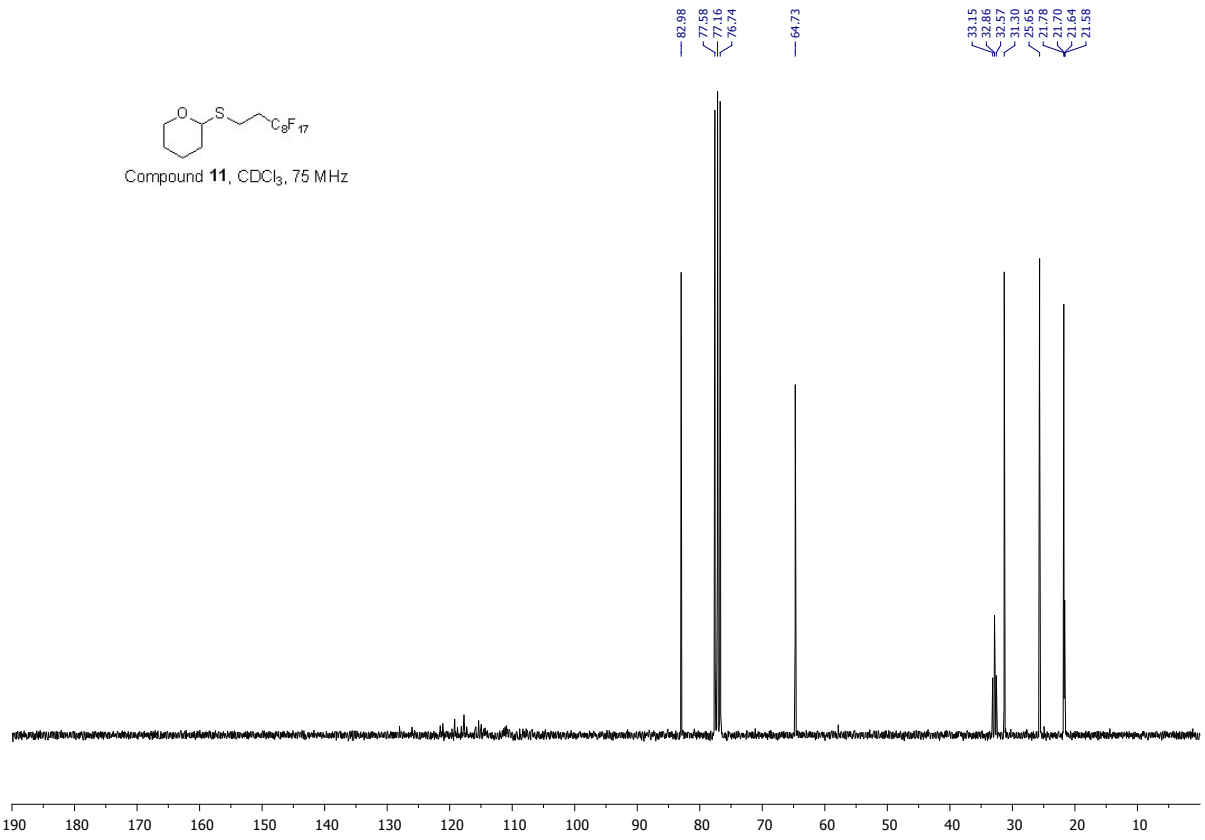

7.260
4.613
4.560
3.899
3.781
3.565
3.372
1.938
1.659
1.635
1.480
Compound 10, CDCl3, 300 MHz
1.00
2.06
4.22
4.19
4.39
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

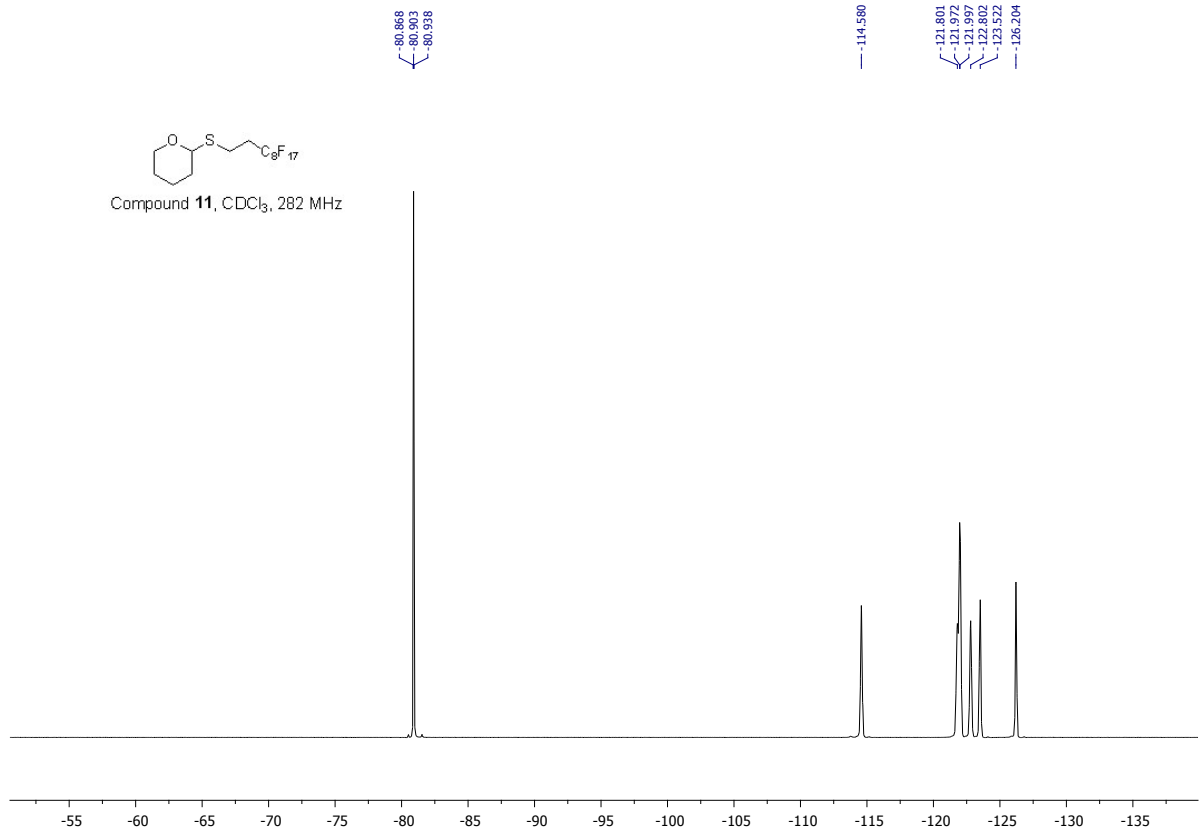


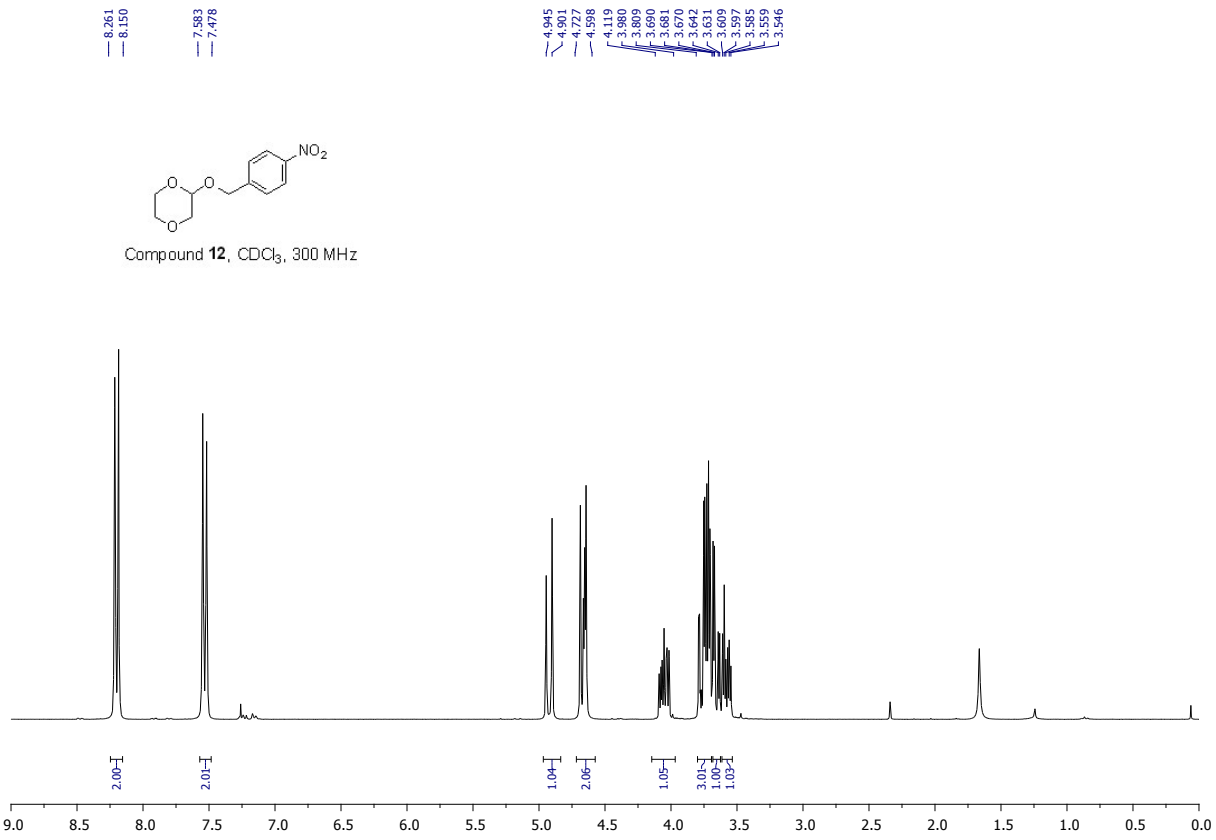
Compound **10**, $CDCl_3$, 75 MHz

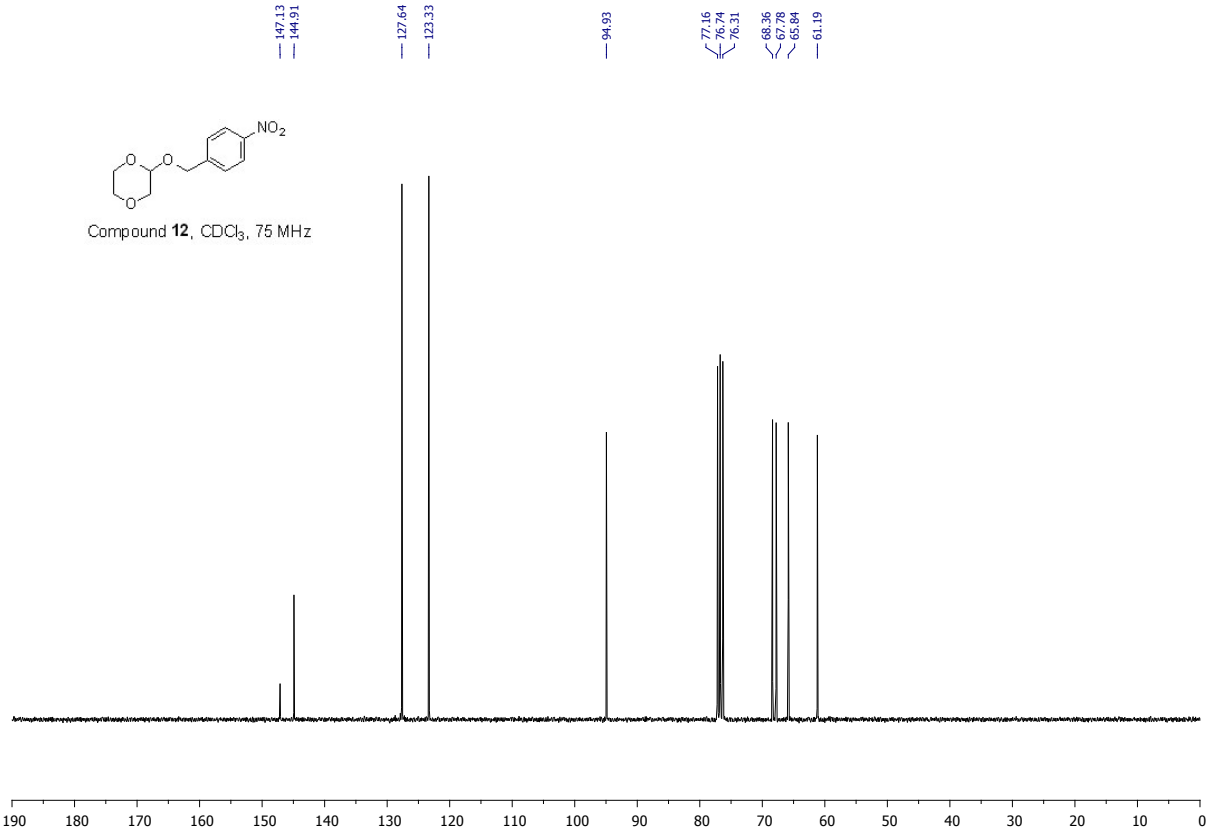


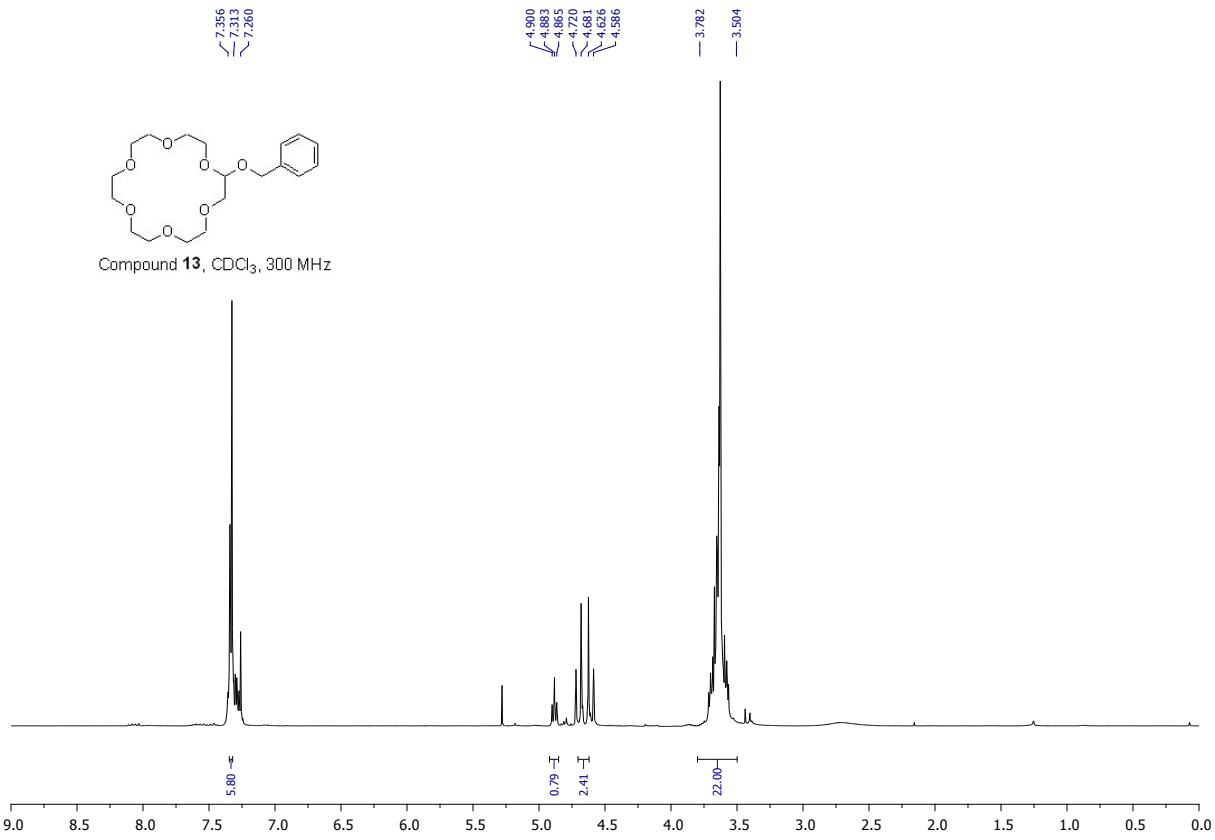
Compound **11**, $CDCl_3$, 300 MHz

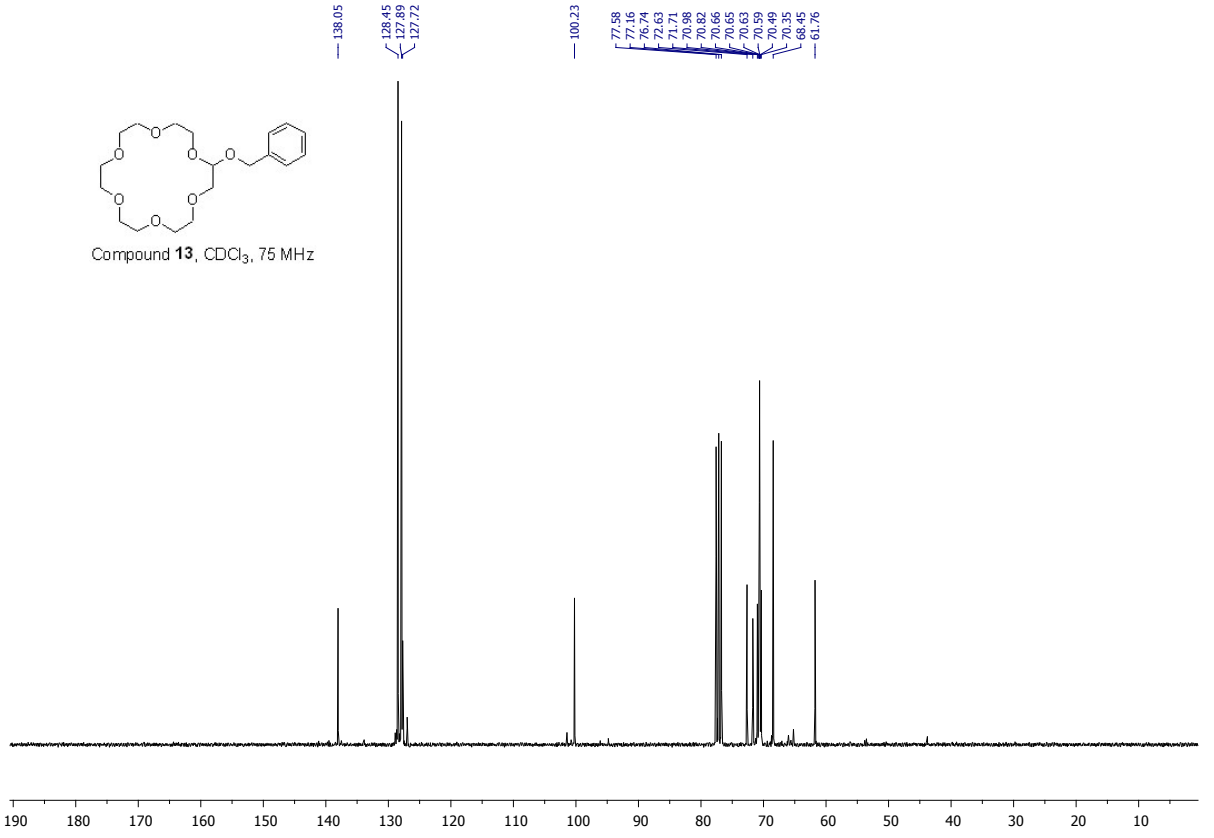

82.98
77.58
77.16
76.74
64.73
33.15
32.86
32.57
31.30
25.65
21.78
21.70
21.64
21.58
O
S
C_8F_{17}
Compound **11**, $CDCl_3$, 75 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

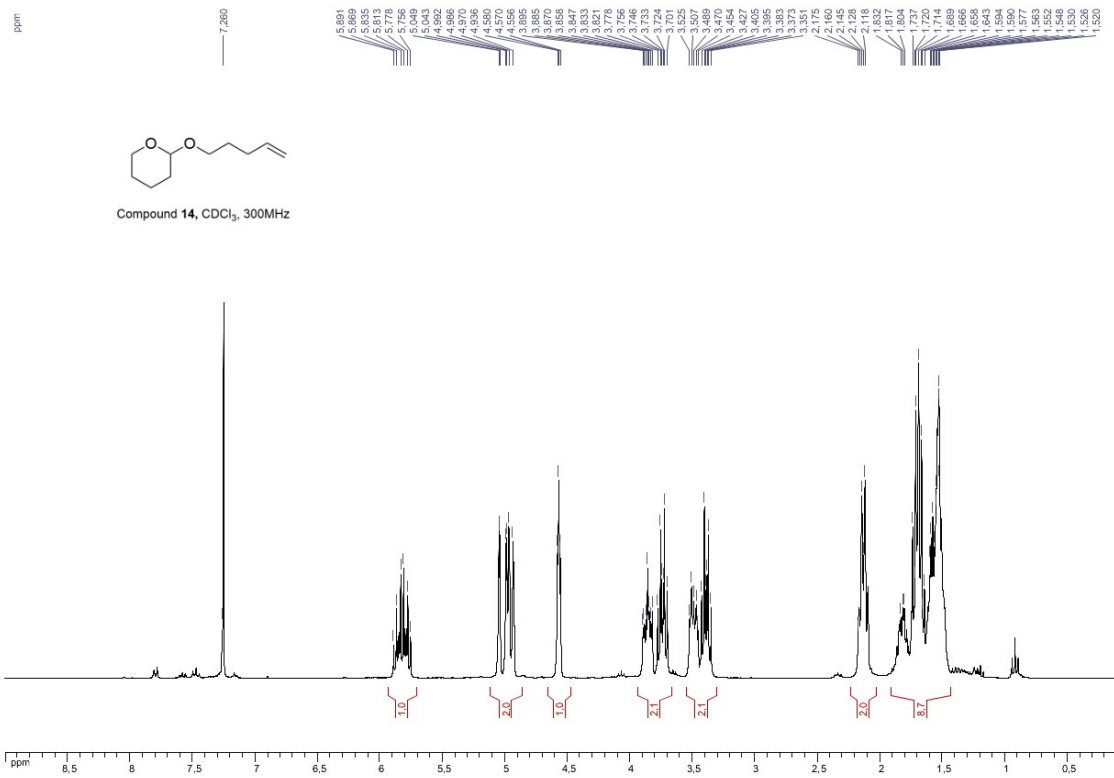

-80.868
-80.903
-80.938
-114.580
-121.801
-121.972
-121.997
-122.802
-123.522
-126.204
O
S
C_8F_{17}
Compound **11**, $CDCl_3$, 282 MHz
-55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135


8.261
8.150
7.583
7.478
4.945
4.901
4.727
4.598
4.119
3.980
3.809
3.690
3.681
3.670
3.642
3.631
3.609
3.597
3.585
3.559
3.546
NO2
Compound 12, CDCl3, 300 MHz
2.00
2.01
1.04
2.06
1.05
3.01
1.00
1.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

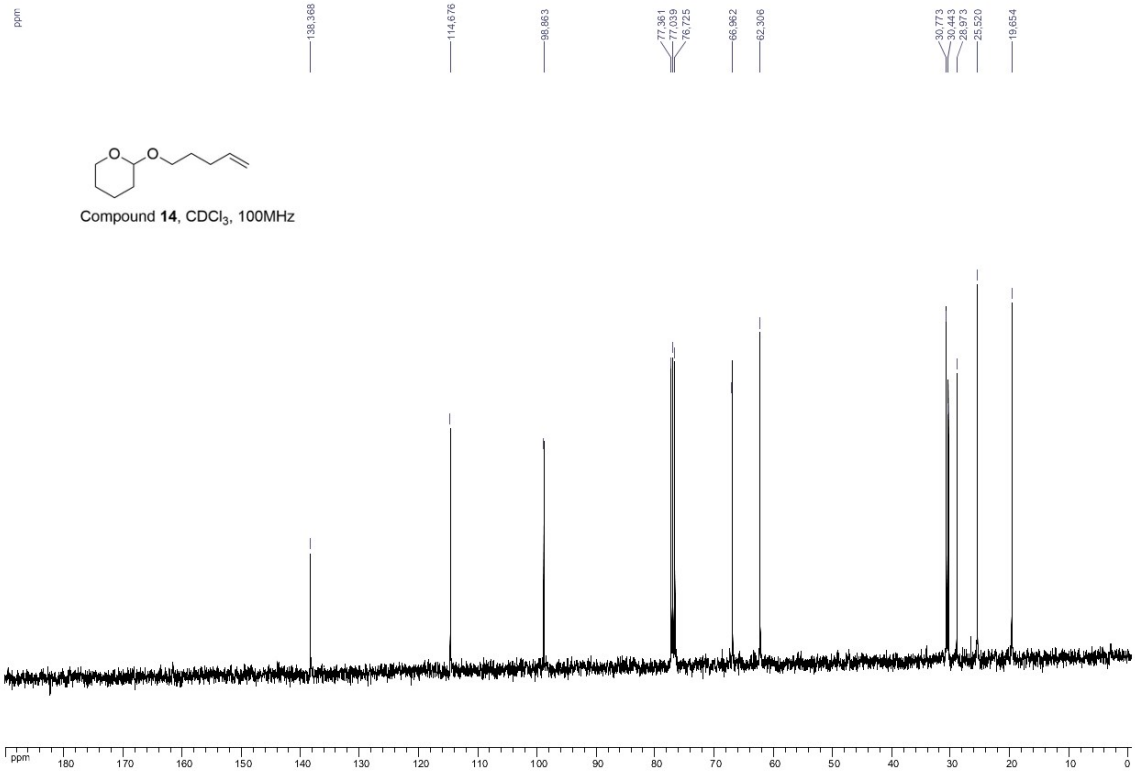

147.13
144.91
127.64
123.33
94.93
77.16
76.74
76.31
68.36
67.78
65.84
61.19
NO2
Compound 12, CDCl3, 75 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.356
7.313
7.260
4.900
4.883
4.865
4.720
4.681
4.626
4.586
3.782
3.504
Compound 13, CDCl3, 300 MHz
5.80
0.79
2.41
22.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

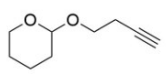

138.05
128.45
127.89
127.72
100.23
77.58
77.16
76.74
72.63
71.71
70.98
70.82
70.66
70.65
70.63
70.59
70.49
70.35
68.45
61.76
Compound 13, CDCl3, 75 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



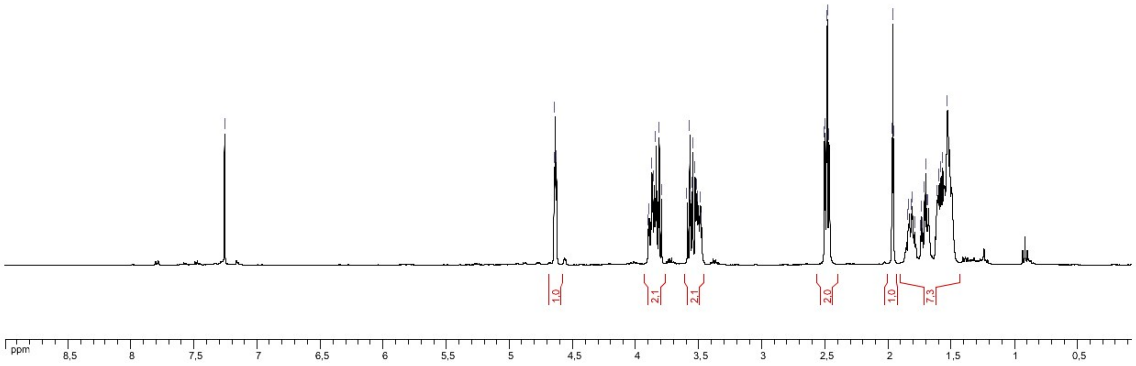
Compound **14,** $CDCl_3$, 300MHz

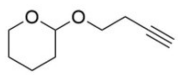


Compound **14**, $CDCl_3$, 100MHz

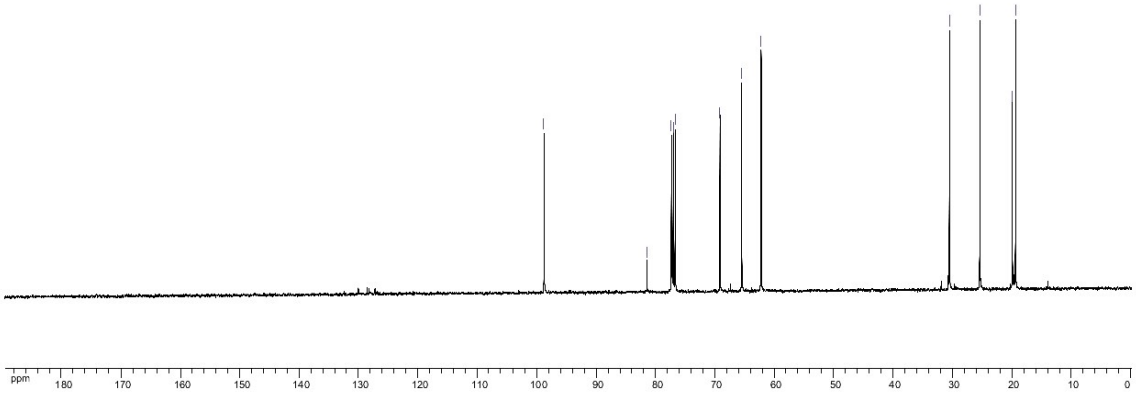


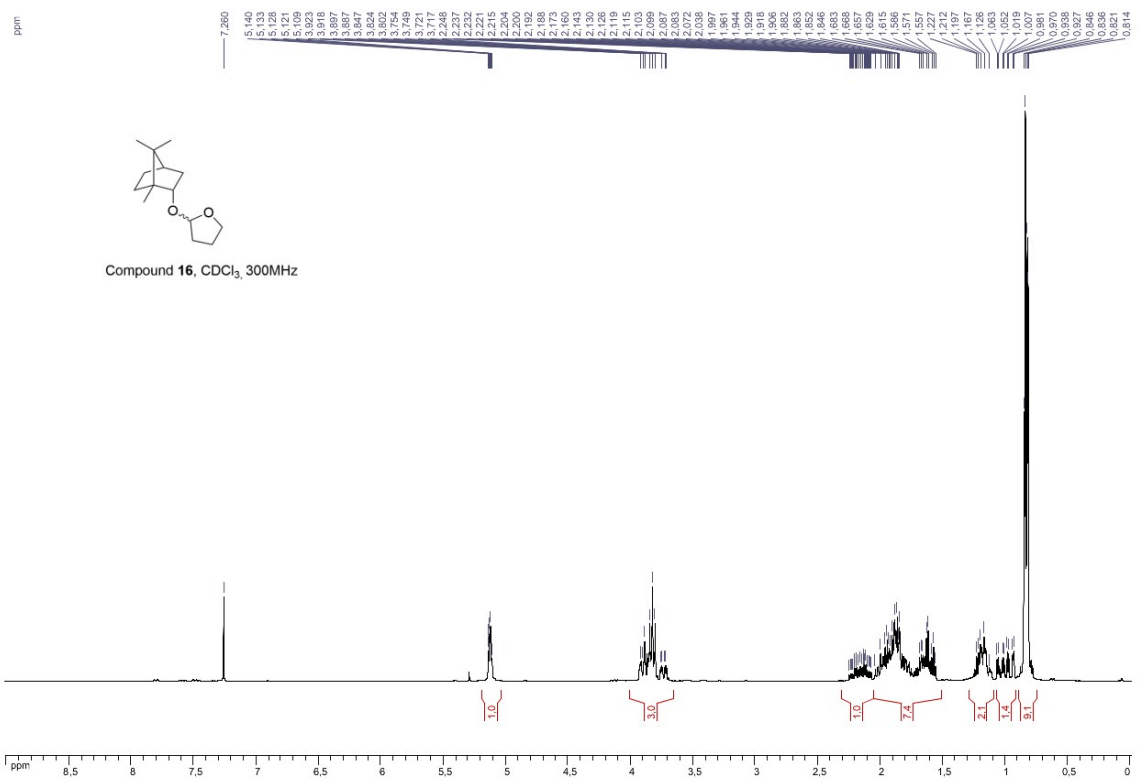
Compound **15**, $CDCl_3$, 400MHz



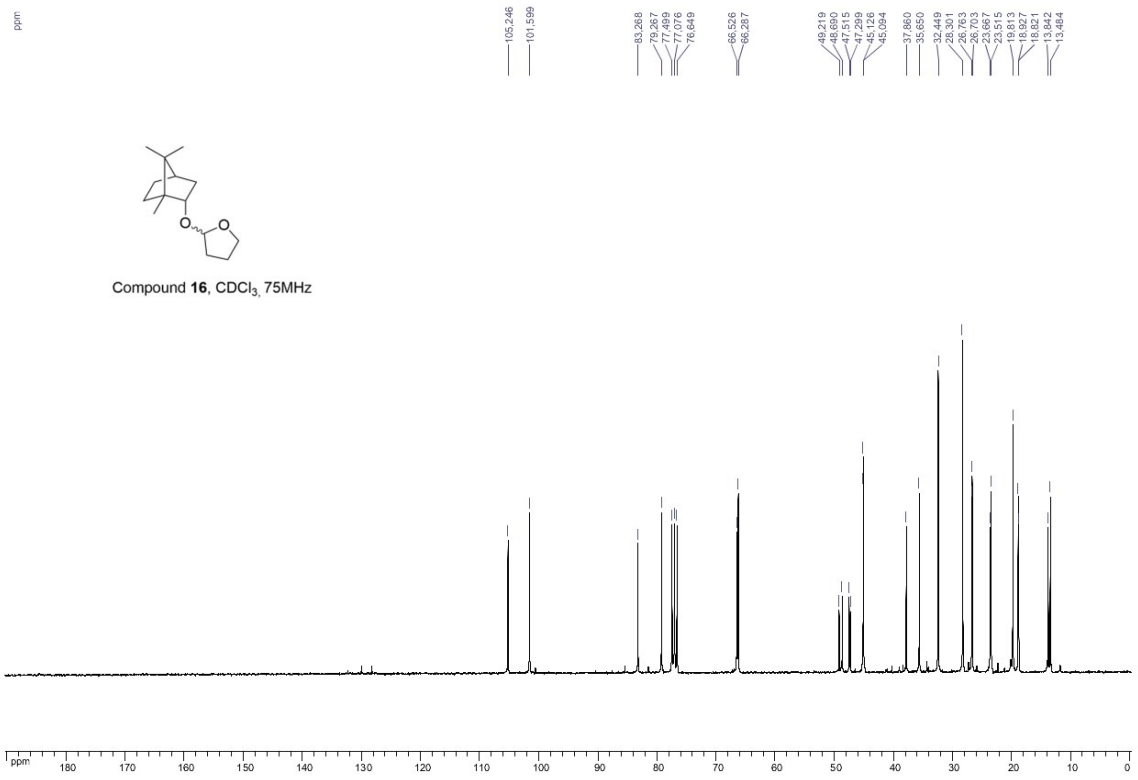


Compound **15**, $CDCl_3$, 100MHz





Compound **16**, $CDCl_3$, 300MHz



Compound **16**, $CDCl_3$, 75MHz