

Supporting Information

Mono-Fluorinated Alkyne-Derived SAMs on Oxide-Free Si(111) Surfaces: Preparation, Characterization and Tuning of the Si Workfunction

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EXPERIMENTAL SECTION

Materials

Tetrahydro-2-(2-propynyloxy)-2H-pyran (THP, Aldrich, 98%), n-butyllithium (BuLi, 1.6 M in hexane, Aldrich), *p*-toluenesulfonic acid monohydrate (PTSA, Aldrich, 98%), potassium fluoride (KF, Sigma, +99.5%), 18-crown-6 (Fluka, +99.0%), 2-decyn-1-ol (Aldrich, 97%), 1-bromoundecane (Aldrich, 98%), 1-bromopentadecane (Aldrich, 97%), potassium tert-butoxide (*t*-BuOK, Aldrich) pyridine (Acros Organics, reagent ACS), Acetonitrile (Acros Organics, +99.5%), methanol (MeOH, VWR, +99.8%), 1,3-diaminopropane (Aldrich, +99%), 9-dodecyn-1-ol (ABCR, 97%), silica gel 60 (Fluka) and *p*-toluenesulfonyl chloride (TsCl, Molekula) were used as received. Tetrahydrofuran (THF, VWR, 99%) was distilled from sodium benzophenone and stored on sodium wires. Hexamethylphosphoramide (HMPA, Aldrich, 99%) was dried over Linde type molecular sieves of 4Å. Dichloromethane (DCM, Fisher Chemical, +99%) was distilled before use.

Analysis

All reactions were monitored by thin layer chromatography (TLC) and carried out on 0.25 mm silica gel PET foil plates with a medium pore size of 60 Å and a fluorescent indicator of 254 nm. Vanillin coloring reagent and heat were used as developing agents. The synthesized compounds were purified by automatic column chromatography with the Biotage Isolera One UV-VIS Flash Purification System using Biotage SNAP Cartridges (KP-Sil 50 g or 100 g).

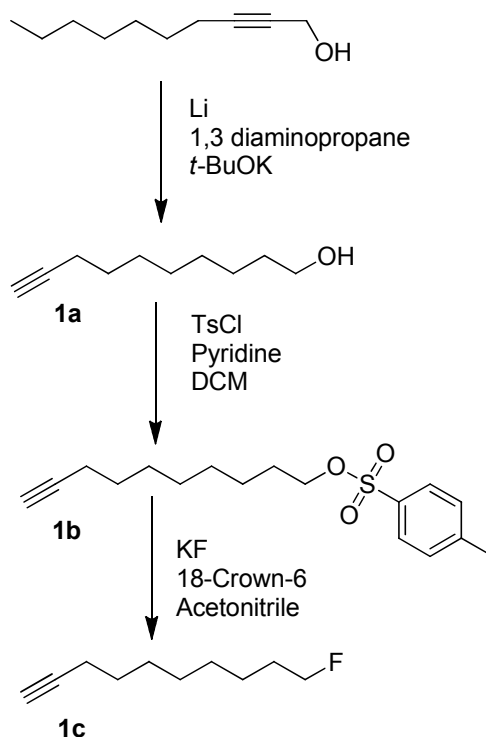
¹H-NMR (400 MHz) and ¹³C-NMR (100 MHz) spectra were recorded on a Bruker 400 MHz spectrometer with CDCl₃ as solvent and internal standard (¹H-NMR: 7.26 ppm and ¹³C-NMR: 77.16 ppm). In the reported data below the following abbreviations are used: s =

singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet. Chemical shifts are reported in ppm. High resolution mass spectra were recorded using Electron Spray Ionization (ESI) or Direct Analysis in Real Time (DART) ionization coupled to a high resolution mass spectrometer from Thermo Scientific. Samples were measured in acetone.

Attenuated total reflectance (ATR) infrared spectra of pure compounds were recorded on a Alpha-P spectrometer from Bruker. The wavenumbers are reported in reciprocal centimeters and the appearances are denoted as weak (w), medium (m) or strong (s).

The purities of the synthesized compounds were checked with GC-MS using an Agilent HP-5MS column (30 m \times 0.250 mm \times 0.25 μ m). If necessary, the final products were subsequently purified by preparative HPLC using an Altima C₁₈ column (250 \times 22 mm) to afford 100% pure compounds.

Synthesis of 10-fluorodec-1-yne



Dec-9-yn-1-ol (1a)

To a three-necked round-bottom flask, which was flushed with nitrogen and closed with a calcium chloride tube, small pieces of Li (2.73 g, 389.28 mmol) and 186 ml of 1,3-diaminopropane were added. The mixture was allowed to stir and heated in an oil bath at 70 °C until the blue color discharges (1 h) and a white suspension was formed. After cooling down to room temperature, potassium tert-butoxide (29.12 g, 259.52 mmol) was added to the mixture. The mixture was stirred for 20 min and then dec-2-yn-1-ol (10 g, 64.88 mmol) was added. Residual dec-2-yn-1-ol was washed into the mixture with a small portion of 1,3-diaminopropane (15 ml). The reaction mixture was stirred overnight at room temperature. Plenty of ice water was added to the reaction mixture and the mixture was extracted with ether three times. The organic layers were combined, washed with brine and water and dried over anhydrous MgSO_4 . The solvent was removed under reduced pressure. The residue was

purified by automatic column chromatography (heptane : ethyl acetate = 5:1) to afford dec-9-yn-1-ol (7.44 g, 48.23 mmol, 74%) as a clear oil. The reaction was monitored with TLC (heptane : ethyl acetate = 5:1).

$^1\text{H-NMR}$ (δ_{ppm}): 3.60-3.57 (t, 2H, R-CH₂-OH), 2.17-2.12 (dt, 2H, R-CH₂-C \equiv C-H), 1.95 (s, 1H, R-OH), 1.92-1.90 (t, 1H, R-C \equiv C-H), 1.56-1.46 (m, 4H, alkyl), 1.39-1.30 (m, 8H, alkyl). $^{13}\text{C-NMR}$ (δ_{ppm}): 84.77 (1C, R-C \equiv C-H), 68.19 (1C, R-C \equiv C-H), 62.90 (1C, R-CH₂-OH), 32.77 (1C, alkyl), 29.23 (1C, alkyl), 29.20 (1C, alkyl), 28.72 (1C, alkyl), 28.50 (1C, alkyl), 25.76 (1C, alkyl), 18.42 (1C, alkyl). IR (cm⁻¹): 3346 (m, OH), 3307, 624 (m, s, C \equiv C-H), 2928, 2855, 1463 (s, s, m, CH₂), 2117 (w, C \equiv C). MS (DART): calculated for C₁₀H₂₂ON (M + NH₄) 172.1696, found 172.1695.

Dec-9-ynyl 4-methylbenzenesulfonate (1b)

To a 250 ml three-necked round-bottom flask, flushed with nitrogen, was added dec-9-yn-1-ol (7.34 g, 47.62 mmol) at 0 °C, to dichloromethane (58 ml) and pyridine (7.6 ml). The mixture was stirred at 25 °C for 10 min. The flask was cooled down to 0 °C with an ice bath and p-toluenesulfonyl chloride (13.57 g, 71.43 mmol) was added to the reaction mixture. The mixture was stirred at 0 °C for 1 hour and then overnight at room temperature. The reaction was quenched with 35 ml of water at 0 °C and then warmed to 23 °C. The resulting layers were separated and the aqueous layer was washed with DCM. The combined organic layers were washed with brine and water and dried over MgSO₄. The solvent was removed by rotary evaporation. The crude extract was purified with automatic column chromatography (heptane : ethyl acetate = 13:1). The solvents were removed under reduced pressure to afford a white solid of dec-9-ynyl 4-methylbenzenesulfonate (10.25 g, 33.23 mmol, 70%). The reaction was monitored with TLC (heptane : ethyl acetate = 9:1).

$^1\text{H-NMR}$ (δ_{ppm}): 7.80-7.78 (d, 2H, Ph), 7.36-7.34 (d, 2H, Ph), 4.04-4.00 (t, 2H, R-CH₂-OTs), 2.45 (s, 3H, R-Ph-CH₃), 2.19-2.14 (m, 2H, R-CH₂-C \equiv C-H), 1.94-1.93 (t, 1H, R-C \equiv C-H), 1.67-1.60 (m, 2H, alkyl), 1.53-1.46 (m, 2H, alkyl), 1.39-1.27 (m, 8H, alkyl). $^{13}\text{C-NMR}$ (δ_{ppm}): 144.58 (1C, Ph), 133.28 (1C, Ph), 129.76 (2C, Ph), 127.84 (2C, Ph), 84.57 (1C, R-C \equiv C-H), 70.58 (1C, R-CH₂-OTs), 68.12 (1C, R-C \equiv C-H), 28.77, 28.75, 28.71, 28.48, 28.32 (5C, alkyl), 25.23 (1C, alkyl), 21.58 (1C, R-CH₃), 18.31 (1C, alkyl). IR (cm⁻¹): 3290, 662 (m, s, C \equiv C-H), 2930, 2857, 1464 (m, m, m, CH₂), 2116 (w, C \equiv C), 1174, 1356 (s, s, S=O). MS (DART): calculated for C₁₇H₂₈O₃NS (M + NH₄) 326.1784, found 326.1785.

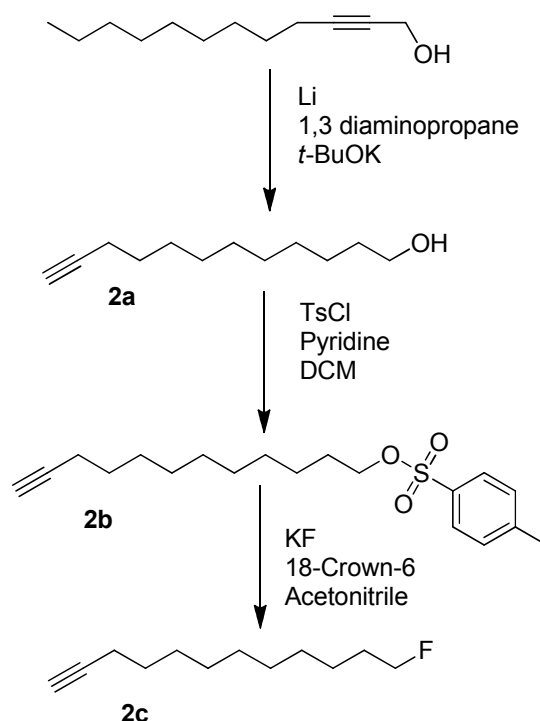
10-Fluorodec-1-yne (1c)

In a three-necked round-bottom flask, equipped with a condenser and a dropping funnel, potassium fluoride (3.86 g, 66.48 mmol) and 18-crown-6 (17.56 g, 66.48 mmol) were dissolved in 60 ml of acetonitrile. Nitrogen was flushed through the mixture. The solution was heated to 60 °C with an oil bath. A solution of dec-9-ynyl 4-methylbenzenesulfonate (10.11 g, 33.24 mmol) in 65 ml of acetonitrile was drop wise added. The solution was refluxed for 24 h and after that, additional equivalents of potassium fluoride (1.93 g, 33.24 mmol) and 18-crown-6 (8.78 g, 33.24 mmol) were added. The reaction mixture was refluxed for another 24 h. The solvent was removed by rotary evaporation. The residue was dissolved in ether and washed with water. The organic layers was dried with MgSO₄ and the solvent was removed under reduced pressure. The residue was purified by automatic column chromatography (heptane) to afford 10-fluorodec-1-yne (3.80 g, 24.33 mmol, 73%) as a clear oil. The reaction was monitored with TLC (heptane).

$^1\text{H-NMR}$ (δ_{ppm}) 4.43-4.40 (t, 1H, F-CH₂-R), 4.32-4.28 (t, 1H, F-CH₂-R), 2.13-2.09 (dt, 2H, R-CH₂-C \equiv C-H), 1.87-1.85 (t, 1H, R-C \equiv C-H), 1.70-1.55 (m, 2H, alkyl), 1.49-1.42 (m, 2H, alkyl), 1.35-1.27 (m, 8H, alkyl). $^{13}\text{C-NMR}$ (δ_{ppm}): 85.10, 83.47 (1C, F-CH₂-R), 84.79 (1C, R-

$\text{C}\equiv\text{C-H}$), 68.23 (1C, $\text{R-C}\equiv\text{C-H}$), 30.62-30.43 (1C, $\text{R-CH}_2\text{-CH}_2\text{-F}$), 29.23 (1C, alkyl), 29.10 (1C, alkyl), 28.75 (1C, alkyl), 28.75 (1C, alkyl), 25.28-25.24 (1C, $\text{R-CH}_2\text{-CH}_2\text{-CH}_2\text{-F}$), 18.51 (1C, alkyl). IR (cm^{-1}): 3304, 627 (m, s, $\text{C}\equiv\text{C-H}$), 2931, 2858, 1464 (s, s, m, CH_2), 2118 (w, $\text{C}\equiv\text{C}$). MS (DART): calculated for $\text{C}_{10}\text{H}_{21}\text{NF}$ ($\text{M} + \text{NH}_4$) 174.1653, found 174.1655.

Synthesis of 12-fluorododec-1-yne



Dodec-11-yn-1-ol (2a)

The procedure described for dec-9-yn-1-ol (**1a**) was used with 9-dodecyn-1-ol (12.00 g, 65.83 mmol), lithium (2.74 g, 390.59 mmol), potassium *tert*-butoxide (29.5 g, 262.90 mmol) and 187 ml of 1,3-diaminopropane to afford dodec-11-yn-1-ol (10.44 g, 57.27 mmol, 87%).

$^1\text{H-NMR}$ (δ_{ppm}): 3.61-3.57 (t, 2H, $\text{R-CH}_2\text{-OH}$), 2.17-2.12 (dt, 2H, $\text{R-CH}_2\text{-C}\equiv\text{C-H}$), 1.91-1.90 (t, 1H, $\text{R-C}\equiv\text{C-H}$), 1.77 (s, 1H, R-OH), 1.56-1.45 (m, 4H, alkyl), 1.38-1.26 (m, 12H, alkyl). $^{13}\text{C-NMR}$ (δ_{ppm}): 84.71 (1C, $\text{R-C}\equiv\text{C-H}$), 68.04 (1C, $\text{R-C}\equiv\text{C-H}$), 62.89 (1C, $\text{R-CH}_2\text{-OH}$), 29.23 (1C, alkyl), 29.10 (1C, alkyl), 28.75 (1C, alkyl), 28.75 (1C, alkyl), 25.28-25.24 (1C, $\text{R-CH}_2\text{-CH}_2\text{-CH}_2\text{-F}$), 18.51 (1C, alkyl).

CH₂-OH), 32.72 (1C, alkyl), 29.49 (1C, alkyl), 29.36 (2C, alkyl), 29.03, 28.69, 28.44, 25.70, 18.34 (5C, alkyl). IR (cm⁻¹): 3310, 628 (m, s, C≡C-H), 2924, 2853, 1463 (s, s, m, CH₂), 2118 (w, C≡C). MS (DART): calculated for C₁₂H₂₆ON (M + NH₄) 200.2009, found 200.2010.

Dodec-11-ynyl 4-methylbenzenesulfonate (2b)

The procedure described for dec-9-ynyl 4-methylbenzenesulfonate (**1b**) was used with dodec-11-yn-1-ol (10.42 g, 57.16 mmol), pyridine (9.25 ml, 114.45 mmol), 69 ml of dichloromethane and p-toluenesulfonyl chloride (16.36 g, 86.11 mmol) to give dodec-11-ynyl 4-methylbenzenesulfonate (12.57 g, 37.36 mmol, 65%).

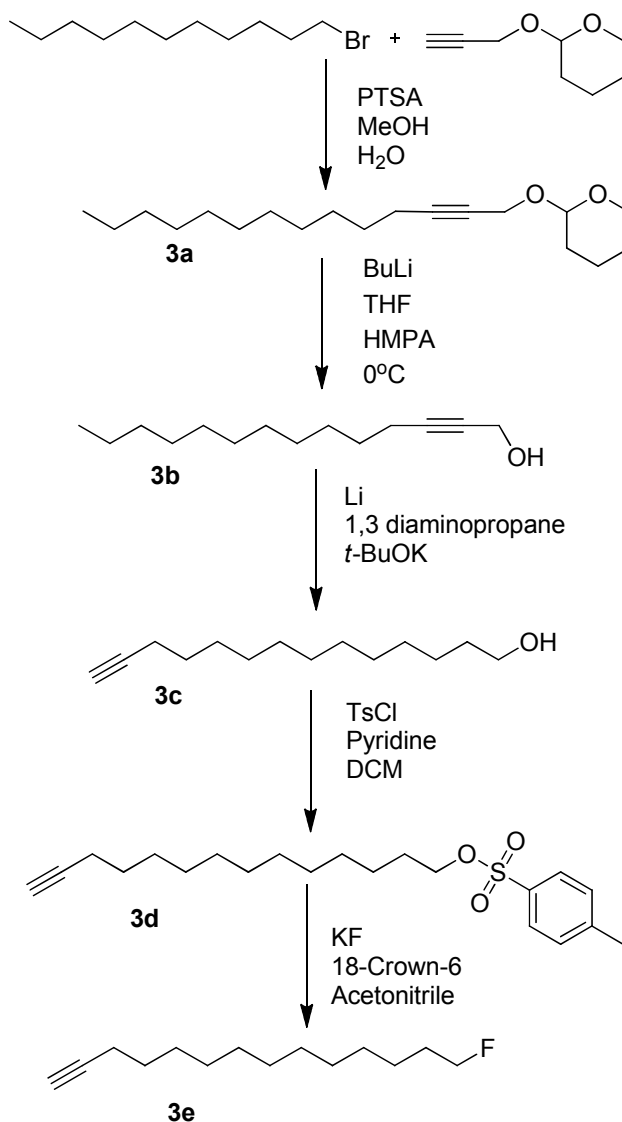
¹H-NMR (δ_{ppm}): 7.74-7.72 (d, 2H, Ph), 7.30-7.28 (d, 2H, Ph), 3.97-3.94 (t, 2H, R-CH₂-OTs), 2.39 (s, 3H, R-Ph-CH₃), 2.13-2.12 (dt, 2H, R-CH₂-C≡C-H), 1.92 (t, 1H, R-CH₂-C≡C-H), 1.60-1.53 (quin, 2H, alkyl), 1.48-1.41 (quin, 2H, alkyl), 1.37-1.23 (m, 12H, alkyne) ¹³C-NMR (δ_{ppm}): 144.55 (1C, Ph), 133.27 (1C, Ph), 129.74 (2C, Ph), 127.82 (2C, Ph), 84.67 (1C, R-C≡C-H), 70.62 (1C, R-CH₂-OTs), 68.04 (s, 1C, R-C≡C-H), 29.24 (2C, alkyl), 28.95, 28.82, 28.76, 28.63, 28.40 (5C, alkyl), 25.26 (1C, alkyl), 21.57 (1C, alkyl), 18.33 (1C, alkyl). IR (cm⁻¹): 3292, 664 (m, s, C≡C-H), 2927, 2855, 1465 (s, s, m, CH₂), 2116 (w, C≡C), 1176, 1359 (s, s, S=O). MS (DART): calculated for C₁₉H₃₂O₃NS (M + NH₄) 354.2097, found 354.2102.

12-Fluorotetradec-1-yne (2c)

The procedure described for 10-fluorodec-1-yne (**1c**) was used with dodec-11-ynyl 4-methylbenzenesulfonate (12.57 g, 37.36 mmol), potassium fluoride (4.33 g, 74.53 mmol and 2.17 g, 37.36 mmol), 18-crown-6 (19.7 g, 74.53 mmol and 9.85 g, 37.36 mmol) and 60 and 75 ml of acetonitrile to afford 12-fluorododec-1-yne (6.63 g, 35.98 mmol, 95%). The product was purified with subsequently automatic column chromatography and preparative HPLC to afford a colorless oil.

^1H -NMR (δ_{ppm}): 4.51-4.48 (t, 1H, F-CH₂-R), 4.39-4.36 (t, 1H, F-CH₂-R), 2.20-2.16 (dt, 2H, R-CH₂-C \equiv C-H), 1.94-1.93 (t, 1H, R-C \equiv C-H), 1.72-1.64 (m, 2H, alkyl), 1.54-1.51 (m, 2H, alkyl), 1.41-1.30 (m, 12H, alkyl). ^{13}C -NMR (δ_{ppm}): 85.00, 83.37 (1C, F-CH₂-R), 84.74 (1C, R-C \equiv C-H), 68.02 (1C, R-C \equiv C-H), 30.48-30.29 (1C, R-CH₂-CH₂-F), 29.41, 29.34, 29.18, 29.03, 28.70, 28.46 (6C, alkyl), 25.28-25.24 (1C, R-CH₂-CH₂-CH₂-F), 18.51 (1C, alkyl). IR (cm⁻¹): 3305, 627 (m, s, C \equiv C-H), 2927, 2855, 1464 (s, s, m, CH₂), 2117 (w, C \equiv C). MS (DART): calculated for C₁₂H₂₅NF (M + NH₄) 202.1966, found 202.1969.

Synthesis of 14-fluorotetradec-1-yne



2-Tetradec-2-ynoxytetrahydropyran (3a)

In an oven-dried 500 ml three-necked round-bottom flask, a solution of tetrahydro-2-(2-propynyloxy)-2H-pyran (11.95 ml, 85.00 mmol) in 212 ml of dry THF was cooled to 0 °C in an ice bath. The mixture was flushed with nitrogen and the round-bottom flask was closed with a calcium chloride tube. The mixture was treated with *n*-butyllithium in hexane (16.02 ml of a 1.6 M solution) Thereafter, 1-bromoundecane (18.97 ml, 85.00 mmol) in 149 ml of

dry HMPA was added at 0 °C. The reaction mixture was stirred overnight at room temperature. The reaction was quenched with 50 ml of saturated aqueous NH₄Cl solution and extracted with heptane. The combined organic layers were washed with demineralized water and dried over MgSO₄. The solvent was removed by rotary evaporation. Remaining starting material was removed using a with silica gel filled glass filter (heptane). After that, the residue was purified by automatic column chromatography (heptane: ethyl acetate = 9:1). The solvents were removed under reduced pressure to afford 2-tetradec-2-ynoxytetrahydropyran (8.26 g, 28.05 mmol, 33%) as a clear oil. The reaction was monitored with TLC (heptane : ethyl acetate = 9:1).

¹H-NMR (δ_{ppm}): 4.82-4.80 (t, 1H, R-O-CH-O-R), 4.30-4.18 (tq, 2H, R-C≡C-CH₂-O-R), 3.88-3.82, 3.55-3.50 (m, 2H, R-O-CR-O-CH₂-CH₂-R), 2.23-2.19 (tt, 2H, R-CH₂-C≡C-R), 1.897-1.47 (m, 6H, alkyl), 1.38-1.26 (m, 18H, alkyl), 0.90-0.86 (t, 3H, R-CH₃). ¹³C-NMR (δ_{ppm}): 96.81 (1C, R-O-CH-O-R), 86.94 (1C, R-C≡C-CH₂-O-R), 75.89 (1C, R-C≡C-CH₂-O-R), 62.16 (1C, R-C≡C-CH₂-O-R), 54.82 (1C, R-O-CR-O-CH₂-CH₂-R), 32.07, 30.49, 29.77, 29.68, 29.49, 29.29, 29.05, 28.79, 25.57, 22.84, 19.32, 18.99 (13C, alkyl and ring structure), 14.25 (1C, R-CH₃). IR (cm⁻¹): 2922, 2852, 1463 (s, s, m, CH₂), 2217 (w, C≡C), 1117 (s, C-O). MS (DART): calculated for C₁₉H₃₈O₂N (M + NH₄) 312.2897, found 312.2902.

Tetradec-2-yn-1-ol (3b)

The reaction was carried out in a 250 ml three-necked round-bottom flask which was flushed with nitrogen gas and closed with a calcium chloride tube. *p*-Toluenesulfonic acid monohydrate (1.87 g, 9.85 mmol) was added to a solution of 2-tetradec-2-ynoxytetrahydropyran (5.80 g, 19.70 mmol) and 100 ml of methanol. The reaction mixture was stirred overnight at room temperature. The reaction was checked with TLC (heptane: ethyl acetate 8:2). If still starting material remains, another portion of PTSA can be added.

The reaction was quenched with 10 ml of ice cold demineralized water. The methanol was removed by rotary evaporation. More water was added and the mixture was extracted with ether. The organic layers were washed with saturated NaCl solution and dried over anhydrous MgSO_4 . The solvent was removed under reduced pressure and the remaining residue was purified by automatic column chromatography (heptane: ethyl acetate = 9:1) to give tetradec-2-yn-1-ol (3.05 g, 14.51 mmol, 74%) as a white wax-like solid. The reaction was monitored with TLC (heptane : ethyl acetate = 8:2).

^1H -NMR (δ_{ppm}): 4.27-4.25 (td, 2H, $\text{RC}\equiv\text{C}-\text{CH}_2-\text{OH}$), 2.24-2.19 (tt, 2H, $\text{R}-\text{CH}_2-\text{C}\equiv\text{CR}$), 1.55-1.49 (quin, 2H, $\text{R}-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{CR}$), 1.40-1.27 (m, 17H, alkyl/ $\text{R}-\text{OH}$), 0.91-0.87 (t, 3H, $\text{R}-\text{CH}_3$). ^{13}C -NMR (δ_{ppm}): 86.88 (1C, $\text{R}-\text{C}\equiv\text{C}-\text{CH}_2-\text{OH}$), 78.42 (1C, $\text{RC}\equiv\text{C}-\text{CH}_2-\text{OH}$), 51.63 (1C, $\text{R}-\text{CH}_2-\text{OH}$), 32.07, 29.77, 29.67, 29.48, 29.30, 29.03, 28.77, 22.83, 18.89 (10C, alkyl), 14.26 (1C, $\text{R}-\text{CH}_3$). IR (cm^{-1}): 3294 (m, OH), 2955, 2871 (m, m, CH_3), 2915, 2849, 1470 (s, s, s, CH_2), 2119 (w, $\text{C}\equiv\text{C}$). MS (DART): calculated for $\text{C}_{14}\text{H}_{30}\text{ON}$ ($\text{M} + \text{NH}_4$) 228.2322, found 228.2324.

Tetradec-13-yn-1-ol (3c)

The procedure described for dec-9-yn-1-ol (**1a**) was used with tetradec-2-yn-1-ol (5.81 g, 27.64 mmol), lithium (1.16 g, 165.84 mmol), potassium *tert*-butoxide (12.40 g, 110.56 mmol) and 79 ml of 1,3-diaminopropane to afford tetradec-13-yn-1-ol (4.80 g, 22.84 mmol, 83%)

^1H -NMR (δ_{ppm}): 3.67-3.63 (t, 2H, $\text{R}-\text{CH}_2-\text{OH}$), 2.19-2.13 (dt, 2H, $\text{R}-\text{CH}_2-\text{C}\equiv\text{C}-\text{H}$), 1.95-1.94 (t, 1H, $\text{RC}\equiv\text{C}-\text{H}$), 1.61-1.45 (m, 4H, alkyl), 1.41-1.28 (m, 17H, alkyl). ^{13}C -NMR (δ_{ppm}): 84.79 (1C, $\text{R}-\text{C}\equiv\text{C}-\text{H}$), 67.99 (1C, $\text{RC}\equiv\text{C}-\text{H}$), 62.92 (1C, $\text{R}-\text{CH}_2-\text{OH}$), 32.80 (1C, alkyl), 29.56, 29.54, 29.52, 29.46, 29.40, 29.07, 28.73, 28.48 (8C, alkyl) 25.72 (1C, alkyl), 1837 (1C, alkyl). IR (cm^{-1}): 3312 (m, OH), 3287, 628 (m, $\text{C}\equiv\text{C}-\text{H}$), 2923, 2853, 1462 (s, s, m,

CH₂), 2118 (w, C≡C). MS (DART): calculated for C₁₄H₃₀ON (M + NH₄) 228.2322, found 228.2321.

Tetradec-13-ynyl 4-methylbenzenesulfonate (3d)

The procedure described for dec-9-ynyl 4-methylbenzenesulfonate (**1b**) was used with tetradec-13-yn-1-ol (4.67 g, 22.22 mmol), pyridine (3.59 ml, 44.44 mmol), *p*-toluenesulfonylchloride (5.07 g, 26.69 mmol) and 27 ml of dichloromethane to give tetradec-13-ynyl 4-methylbenzenesulfonate (3.32 g, 9.12 mmol). The product was obtained with a good yield.

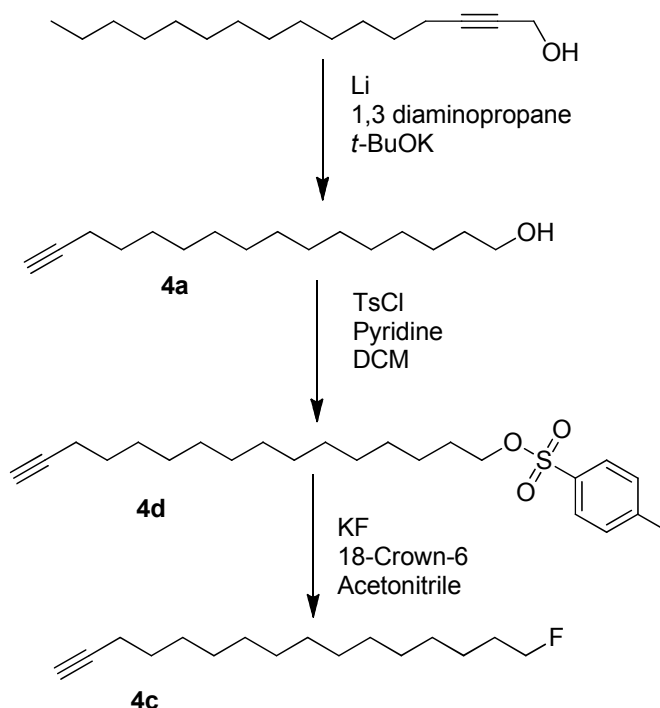
¹H NMR (δ_{ppm}): 7.80-7.78 (d, 2H, Ph), 7.35-7.33 (d, 2H, Ph), 4.03-4.00 (t, 2H, R-CH₂-OTs), 2.45 (s, 3H, R-Ph-CH₃), 2.2-2.16 (dt, 2H, R-CH₂-C≡C-H), 1.94-1.92 (t, 1H, RC≡C-H), 1.66-1.60 (quin, 2H, alkyl), 1.56-1.48 (quin, 2H, alkyl), 1.39-1.22 (m, 16H, alkyl). ¹³C NMR (δ_{ppm}): 144.56 (1C, Ph), 133.32 (1C, Ph), 129.76 (2C, Ph), 127.85 (2C, Ph), 84.73 (1C, R-C≡C-H), 70.66 (1C, R-CH₂-OTs), 68.02 (1C, RC≡C-H), 29.48 (1C, alkyl), 29.42 (2C, alkyl), 29.33, 29.05, 28.89, 28.80, 28.71, 28.46, 25.30, 21.59, 18.37 (9C, alkyl). IR (cm⁻¹): 3293, 663 (m, s, C≡C-H), 2918, 2851, 1471 (s, s, m, CH₂), 2116 (w, C≡C), 1173, 1354 (s, s, S=O). MS (DART): calculated for C₂₁H₃₆O₃NS (M + NH₄) 382.2410, found 382.2410.

14-Fluorotetradec-1-yne (3e)

The procedure described for 10-fluorodec-1-yne (**1c**) was used with tetradec-13-ynyl 4-methylbenzenesulfonate (3.20 g, 8.79 mmol), potassium fluoride (1.02g, 17.55 mmol and 0.51 g, 8.78 mmol), 18-crown-6 (4.64 g, 17.55 mmol and 2.32 g, 8.78 mmol) and 18 and 16 mol of acetonitrile to afford 14-fluorotetradec-1-yne (1.44 g, 6.78 mmol, 77%). The product was purified by preparative HPLC. A pure colorless oil was obtained.

^1H NMR (δ_{ppm}) 4.51-4.48 (t, 1H, F-CH₂-R), 4.39-4.36 (t, 1H, F-CH₂-CH₂), 2.21-2.16 (m, 2H, R-CH₂-C \equiv C-H), 1.94-1.93 (t, 1H, R-C \equiv C-H), 1.76-1.63 (m, 2H, alkyl), 1.57-1.49 (m, 2H, alkyl), 1.41-1.29 (m, 16H, alkyl). ^{13}C NMR (δ_{ppm}): 85.01, 83.38 (1C, F-CH₂-R), 84.76 (1C, R-C \equiv C-H), 68.00 (1C, R-C \equiv C-H), 30.50, 30.31 (1C, FCH₂-CH₂-R), 29.53, 29.48, 29.46, 29.22, 29.08, 28.74, 28.49 (8C, alkyl), 25.16, 25.11 (1C, FCH₂-CH₂-CH₂-R), 18.38 (1C, alkyl). IR (cm⁻¹): 3310, 626 (m, s, C \equiv C-H), 2924, 2854, 1465 (s, s, m, CH₂), 2119 (w, C \equiv C). MS (DART): calculated for C₁₄H₂₉NF (M + NH₄) 230.2279, found 230.2280.

Synthesis of 16-fluorohexadec-1-yne



Hexadec-15-yn-1-ol (4a)

The procedure described for dec-9-yn-1-ol (**1a**) was used with hexadec-7-yn-1-ol (20 g, 83.9 mmol), Lithium (3.49 g, 503.3 mmol), 1,3-diaminopropane (240 mL) and potassium *tert*-butoxide (37.6 g, 335.54 mmol) to give hexadec-15-yn-1-ol as a colorless oil (13.95 g, 58.51 mmol, 73%)

$^1\text{H-NMR}$ (δ_{ppm}) 3.62-3.59 (t, 2H, R-CH₂-OH), 2.17-2.13 (dt 2H, R-CH₂-C \equiv C-H), 1.91-1.90 (t, 1H, R-C \equiv C-H), 1.61 (s, 1H, R-OH), 1.56-1.46 (m, 4H, Alkyl), 1.38-1.24 (m, 20H, alkyl). $^{13}\text{C-NMR}$ (400 MHz, CDCl₃, δ_{ppm}): 85.08 (1C, R-C \equiv C-H), 68.34 (1C, C \equiv C-H), 63.29 (1C, R-CH₂-OH), 33.10 (1C, alkyl), 29.93, 29.92, 29.90 (5C, alkyl), 29.80 (1C, alkyl), 29.74 (1C, alkyl), 29.41 (1C, alkyl), 29.06 (1C, alkyl), 28.81 (1C, alkyl), 26.06 (1C, alkyl), 18.70 (1C, alkyl). IR (cm⁻¹): 3286, 628 (m, s, C \equiv C-H), 2917, 2849, 1472 (s, s, m, CH₂), 2114 (w, C \equiv C). MS (DART): calculated for C₁₆H₃₁O (M + H) 239.2375, found 239.2367.

Hexadec-15-ynyl 4-methylbenzenesulfonate (4b)

The procedure described for dec-9-ynyl (**1b**) was used with hexadec-15-yn-1-ol (10.00 g, 42.0 mmol) and *p*-toluenesulfonyl chloride (9.60 g, 50.4 mmol) to give hexadec-15-ynyl 4-methylbenzenesulfonate as a white solid (13.35 g, 34.04 mmol, 81%):

$^1\text{H-NMR}$ (δ_{ppm}): 7.79-7.77 (d, 2H, Ph), 7.34-7.32 (d, 2H, Ph), 4.03-3.99 (t, 2H, R-CH₂-OTs), 2.44 (s, 3H, R-Ph-CH₃), 2.19-2.15 (m 2H, R-CH₂-C \equiv C-H), 1.93-1.91 (t, 1H, R-C \equiv C-H), 1.65-1.58 (m, 2H, alkyl), 1.54-1.48 (m, 2H, alkyl), 1.41-1.21(m, 20H, alkyl). $^{13}\text{C NMR}$ (δ_{ppm}): 144.90 (1C, Ph), 133.67 (1C, Ph), 130.10 (1C, Ph), 128.19 (1C, Ph), 85.09 (1C, R-C \equiv C-H), 71.00 (1C, R-CH₂-OTs), 68.35 (1C, R-C \equiv C-H), 29.90, 29.89, 29.80, 29.79, 29.69, 29.42, 29.24, 29.15, 29.07, 28.82 (13C, alkyl), 25.64 (1C, alkyl), 21.92 (1C, alkyl), 18.71 (1C, alkyl). IR (cm⁻¹): 3288, 667 (m, s, C \equiv C-H), 2916, 2850, 1472 (s, s, m, CH₂), 2116 (w, C \equiv C), 1175, 1357 (s, s, S=O). MS (ESI): calculated for C₂₃H₃₆O₃NaS (M + Na) 415.2283, found 415.2273.

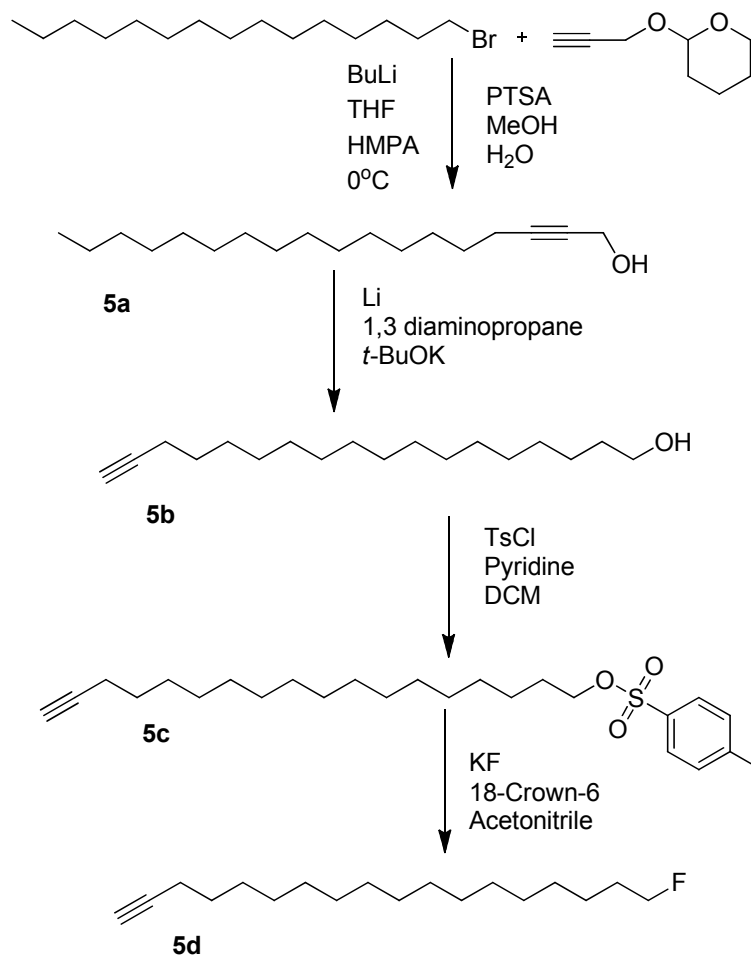
16-Fluorohexadec-1-yne (4c)

The procedure described for 10-fluorodec-1-yne (**1c**) was used with potassium tert-butoxide (3.26 g, 56.09 mmol and 1.62 g, 28.04 mmol) and 18-crown-6 (14.8 g, 56.09 mmol and 7.4 g, 28.04 mmol) in 50 ml of acetonitrile and hexadec-15-ynyl 4-methylbenzenesulfonate (11.0 g,

28.04 mmol) in 55 mL of acetonitrile to give 16-fluorohexadec-1-yne (6.40 g, 26.64 mmol, 95%) as a clear oil.

$^1\text{H-NMR}$ (δ_{ppm}) 4.49-4.46 (t, 1H, F-CH₂-R), 4.37-4.34 (t, 1H, F-CH₂-R), 2.19-2.15 (m, 2H, R-CH₂-C \equiv C-H), 1.92-1.91(t, 1H, R-C \equiv C-H), 1.74-1.61 (m, 2H, alkyl), 1.55-1.48 (m, 2H, alkyl), 1.40-1.26 (m, 20H, alkyl). $^{13}\text{C-NMR}$ (δ_{ppm}): 85.29, 83.66 (1C, F-CH₂-R), 85.05 (1C, R-C \equiv C-H), 68.35 (1C, R-C \equiv C-H), 30.86, 30.67 (1C, alkyl), 29.96, 29.93, 29.89, 29.85 (6C, alkyl), 29.59 (1C, alkyl), 29.45 (1C, alkyl), 29.10 (1C, alkyl), 28.85 (1C, alkyl), 25.52, 25.47 (1C, F-CH₂-CH₂-R), 18.73 (1C, alkyl). IR (cm⁻¹): 3311, 626 (m, s, C \equiv C-H), 2923, 2853, 1465 (s, s, m, CH₂), 2117 (w, C \equiv C). MS (ESI): calculated for C₁₆H₃₀NF (M + H) 241.2332, found 241.2325.

Synthesis of 18-fluorooctadec-1-yne



Octadec-2-yn-1-ol (5a)

The procedure described for 2-tetradec-2-ynoxytetrahydropyran (**3a**) was used with THP (11.91 g, 85.00 mmol) in 212 ml of dry THF, *n*-butyl lithium (10.89 g, 170.00 mmol) and 1-bromopentadecane (24.26 g, 85.00 mmol) in 149 ml of HMPA. The product was directly used in the next step without purification. The procedure described for tetradec-2-yn-1-ol (**3b**) was used with *p*-toluenesulfonic acid monohydrate (8.08 g, 42.50 mmol).

$^1\text{H-NMR}$ (δ_{ppm}): 4.26-4.25 (t, 2H, $\text{RC}\equiv\text{C-CH}_2\text{-OH}$), 2.23-2.19 (m, 2H, $\text{R-CH}_2\text{-C}\equiv\text{CR}$), 1.52-1.47 (quin, 2H, $\text{R-CH}_2\text{-CH}_2\text{-C}\equiv\text{CR}$), 1.39-1.26 (m, 25H, alkyl), 0.90-0.86 (t, 3H, R-CH_3). $^{13}\text{C-NMR}$ (δ_{ppm}): 86.66 (1C, $\text{RC}\equiv\text{C-CH}_2\text{-OH}$), 78.24 (1C, $\text{RC}\equiv\text{C-CH}_2\text{-OH}$), 51.41 (1C, $\text{R-CH}_2\text{-OH}$), 31.92 (1C, alkyl), 29.69 (3C, alkyl), 29.65 (3C, alkyl), 29.63, 29.52, 29.35, 29.14, 28.88 (5C, alkyl), 22.68, (1C, alkyl), 18.72 (1C, alkyl), 14.71 (1C, alkyl). IR (cm^{-1}): 3302 (m, OH), 2954, 2871 (m, m, CH_3), 2914, 2848, 1470 (s, s, s, CH_2), 2118 (w, $\text{C}\equiv\text{C}$). MS (DART): calculated for $\text{C}_{18}\text{H}_{38}\text{ON}$ ($\text{M} + \text{NH}_4$) 284.2948, found 284.2950.

Octadec-17-yn-1-ol (5b)

The procedure described for dec-9-yn-1-ol (**1a**) was used with lithium (0.39 g, 56.07 mmol), 29 mol of 1,3-diaminopropane, potassium tert-butoxide (4.53 g, 37.38 mmol) and octadec-2-yn-1-ol (2.49 g, 9.35 mmol) to give octadec-17-yn-1-ol (1.20 g, 4.51 mmol, 48%).

$^1\text{H-NMR}$ (δ_{ppm}): 3.64-3.61 (t, 2H, $\text{R-CH}_2\text{-OH}$), 2.19-2.15 (dt, 2H, $\text{R-CH}_2\text{-C}\equiv\text{C-H}$), 1.93-1.92 (t, 1H, $\text{RC}\equiv\text{C-H}$), 1.60-1.44 (m, 4H, alkyl), 1.40-1.25 (m, 25H, alkyl). $^{13}\text{C-NMR}$ (δ_{ppm}): 84.77 (1C, $\text{R-C}\equiv\text{C-H}$), 67.99 (1C, $\text{RC}\equiv\text{C-H}$), 62.91 (1C, $\text{R-CH}_2\text{-OH}$), 32.79 (1C, alkyl), 29.63, 29.58, 29.48, 29.42, 29.09, 28.74, 28.48 (13C, alkyl) 25.72 (1C, alkyl), 18.37 (1C, alkyl). IR (cm^{-1}): 3286, 628 (m, s, $\text{R-C}\equiv\text{C-H}$), 2917, 2849, 1472 (s, s, m, CH_2), 2115 (w, $\text{C}\equiv\text{C}$). MS (DART): calculated for $\text{C}_{18}\text{H}_{38}\text{ON}$ ($\text{M} + \text{NH}_4$) 284.2948, found 284.2953.

Octadec-17-ynyl-4-methylbenzenesulfonate (5c)

The procedure described for dec-9-ynyl 4-methylbenzenesulfonate (**1b**) was used with octadec-17-yn-1-ol (1.20 g, 4.51 mmol), pyridine (0.70 ml, 9.01 mmol), p-toluenesulfonylchloride (0.88 g, 4.61 mmol) and 50 ml of dichloromethane to give octadec-17-ynyl-4-methylbenzenesulfonate (1.20 g, 2.85 mmol, 63%).

^1H -NMR (δ_{ppm}): 7.79-7.77 (d, 2H, Ph), 7.35-7.32 (d, 2H, Ph), 4.03-4.00 (t, 2H, R-CH₂-OTs), 2.44 (s, 3H, R-Ph-CH₃), 2.19-2.15 (dt, 2H, R-CH₂-C \equiv C-H), 1.93-1.92 (t, 1H, R-CH₂-C \equiv C-H), 1.66-1.59 (quin, 2H, alkyl), 1.55-1.49 (quin, 2H, alkyl), 1.44-1.21 (m, 24H, alkyne)
 ^{13}C -NMR (δ_{ppm}): 144.56 (1C, Ph), 133.32 (1C, Ph), 129.76 (2C, Ph), 127.85 (2C, Ph), 84.73 (1C, R-C \equiv C-H), 70.67 (1C, R-CH₂-OTs), 68.02 (1C, R-C \equiv C-H), 29.61 (4C, alkyl), 29.57 (2C, alkyl), 29.47, 29.36, 29.09, 28.90, 28.80, 28.73, 28.48 (7C, alkyl), 25.30 (1C, alkyl), 21.58 (1C, alkyl), 18.37 (1C, alkyl). IR (cm⁻¹): 3293 (m, s, C \equiv C-H), 2916, 2850, 1471 (s, s, m, CH₂), 2115 (w, C \equiv C). MS (DART): calculated for C₂₅H₄₄NO₃S (M + NH₄) 438.3036, found 438.3032.

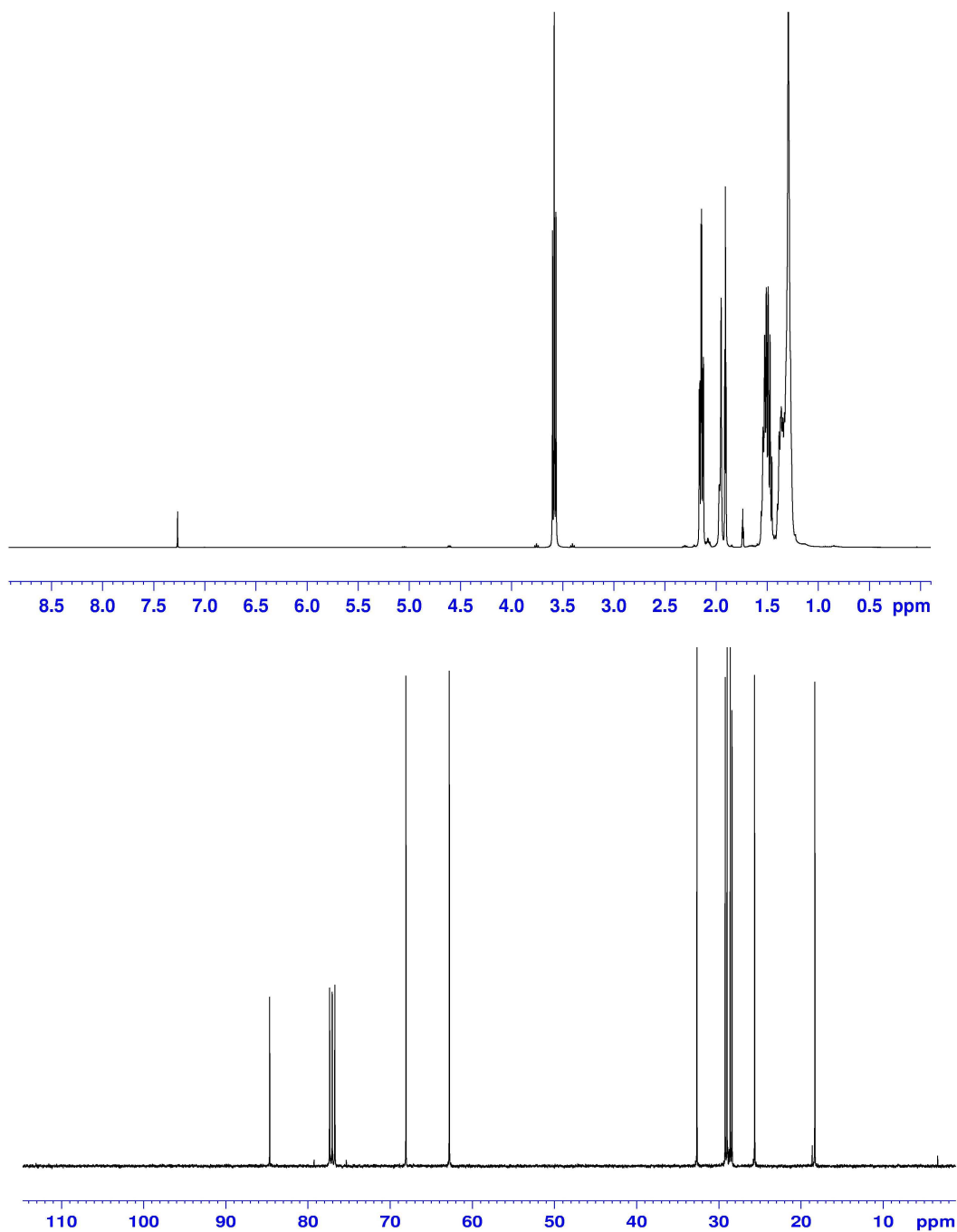
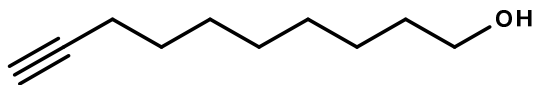
18-Fluorooctadec-1-yne (5d)

The procedure described for 10-fluorodec-1-yne (**1c**) was used with potassium tert-butoxide (3.26 g, 5.70 mmol and 1.62 g, 2.85 mmol) and 18-crown-6 (14.8 g, 5.70 mmol and 7.4 g, 2.85 mmol) in 10 ml of acetonitrile and hexadec-15-ynyl 4-methylbenzenesulfonate (1.2 g, 2.85 mmol) in 12 mL of acetonitrile to afford 18-fluorooctadec-1-yne (0.6 g, 2.23 mmol, 78%)

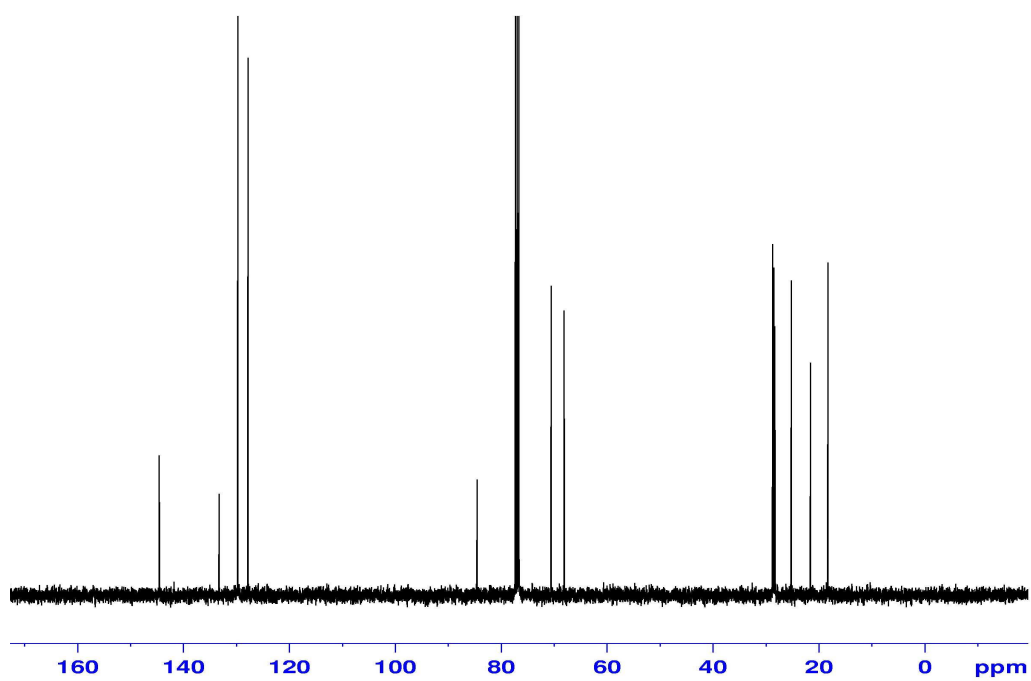
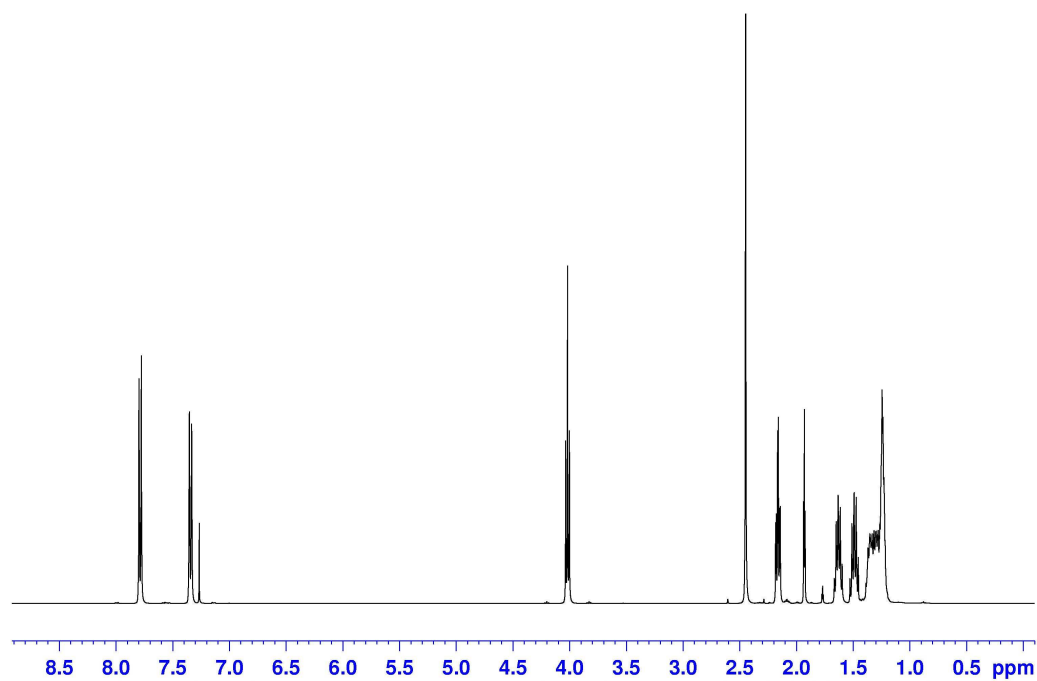
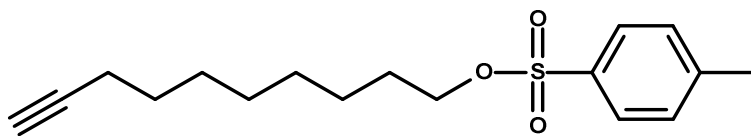
^1H -NMR (δ_{ppm}) 4.50-4.47 (t, 1H, F-CH₂-R), 4.38-4.35 (t, 1H, F-CH₂-R), 2.20-2.15 (m, 2H, R-CH₂-C \equiv C-H), 1.93-1.92 (t, 1H, R-C \equiv C-H), 1.75-1.62 (m, 2H, alkyl), 1.56-1.49 (quin, 2H, alkyl), 1.41-1.27 (m, 24H, alkyl). ^{13}C NMR (δ_{ppm}): 84.92, 83.28 (1C, F-CH₂-R), 84.67 (1C, R-C \equiv C-H), 67.98 (1C, R-C \equiv C-H), 30.50, 30.30 (1C, FCH₂-CH₂-R), 29.59, 29.57, 29.52, 29.49, 29.48, 29.22, 29.08, 28.74, 28.64, 28.48 (12C, alkyl), 25.16, 25.10 (1C, FCH₂-CH₂-CH₂-R), 18.36 (1C, alkyl). IR (cm⁻¹): 3311, 627 (m, s, C \equiv C-H), 2923, 2853, 1465 (s, s, m, CH₂), 2118 (w, C \equiv C). MS (DART): calculated for C₁₈H₃₇NF (M + NH₄) 286.2905, found 286.2915.

^1H & ^{13}C NMR-Spectra

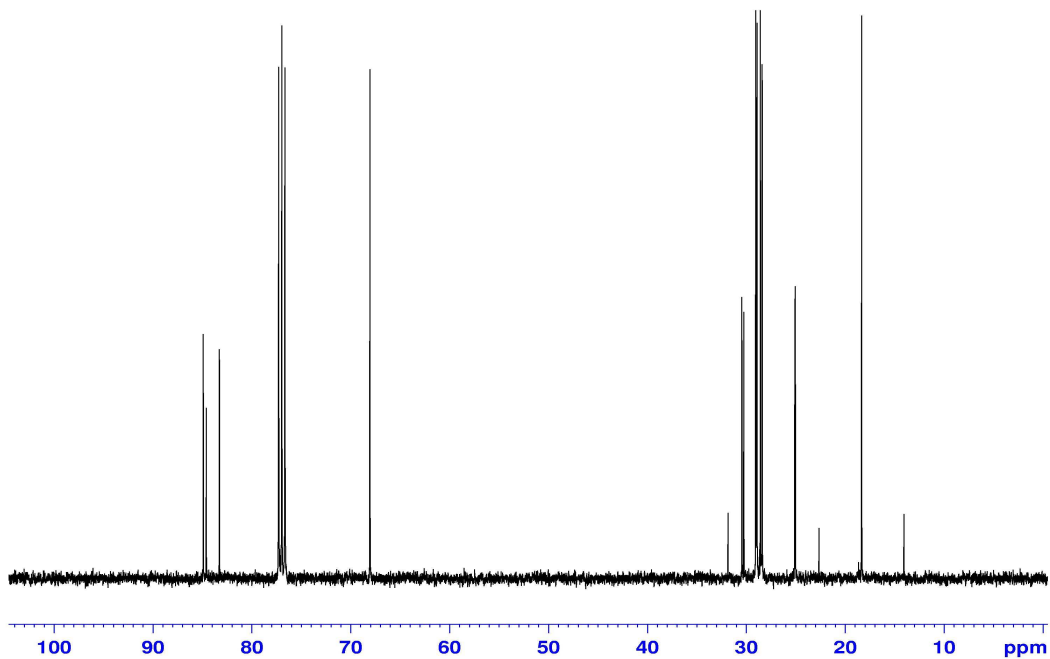
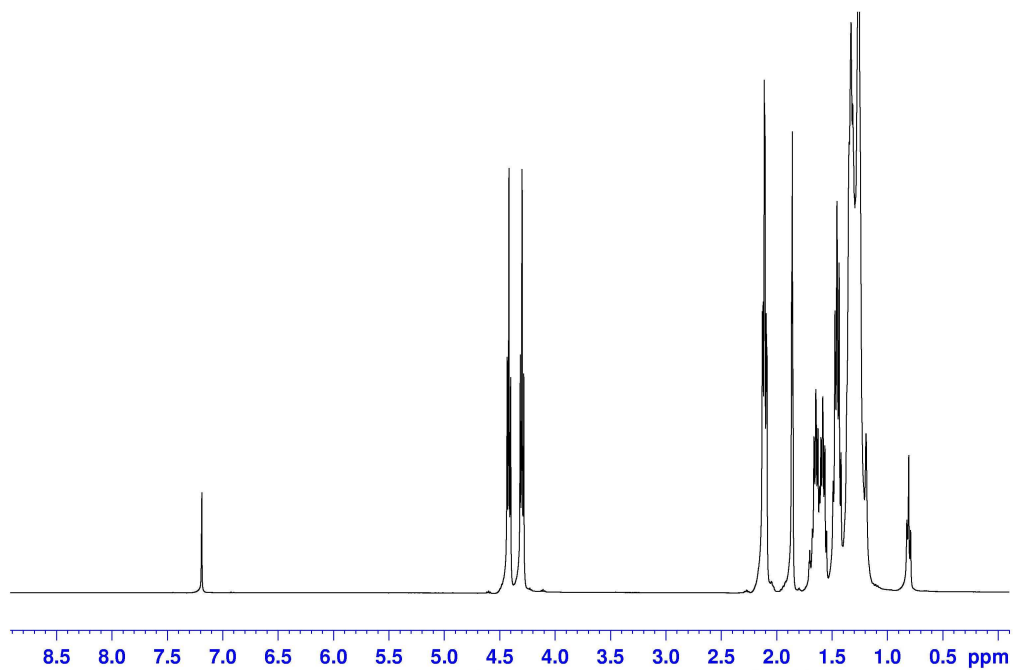
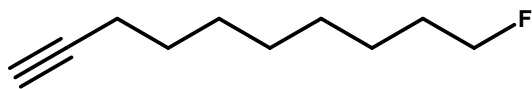
Dec-9-yn-1-ol (1a)



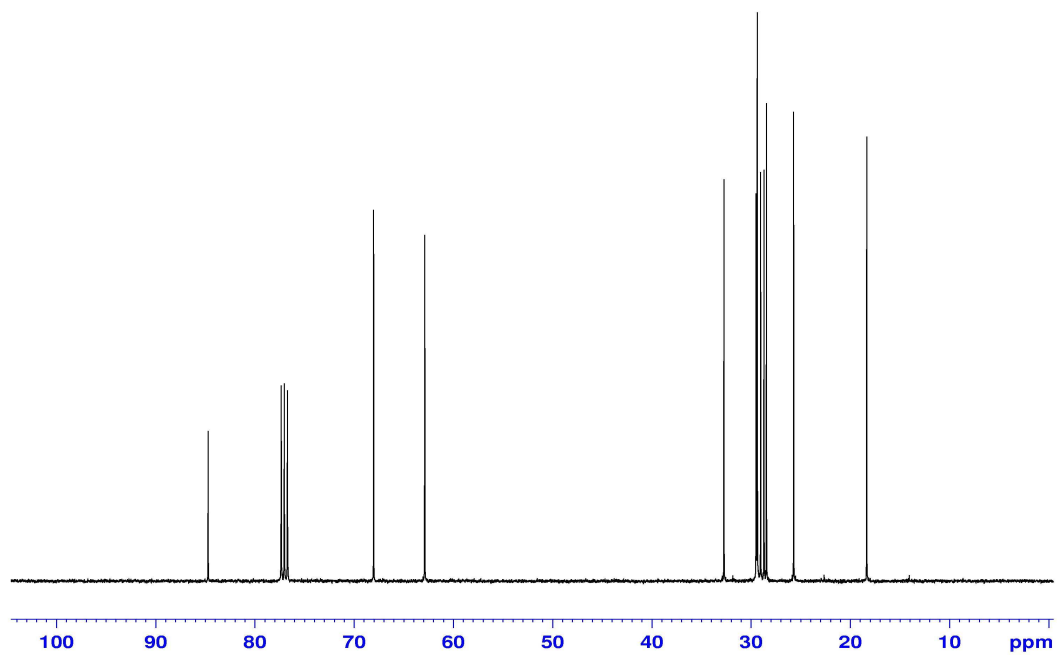
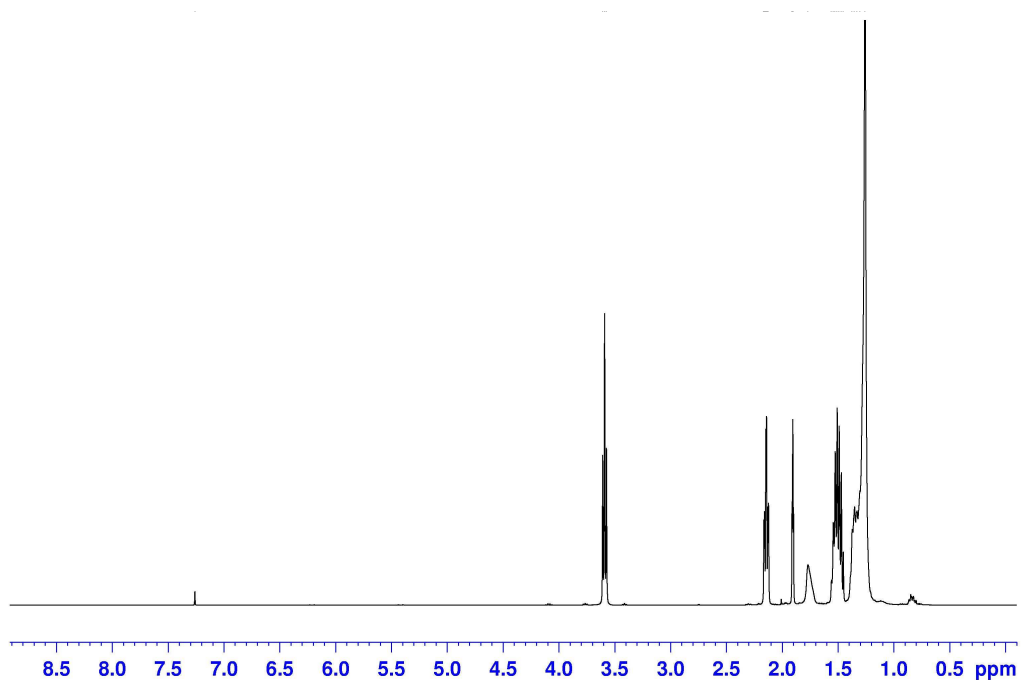
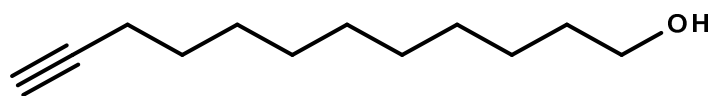
Dec-9-ynyl 4-methylbenzenesulfonate (1b)



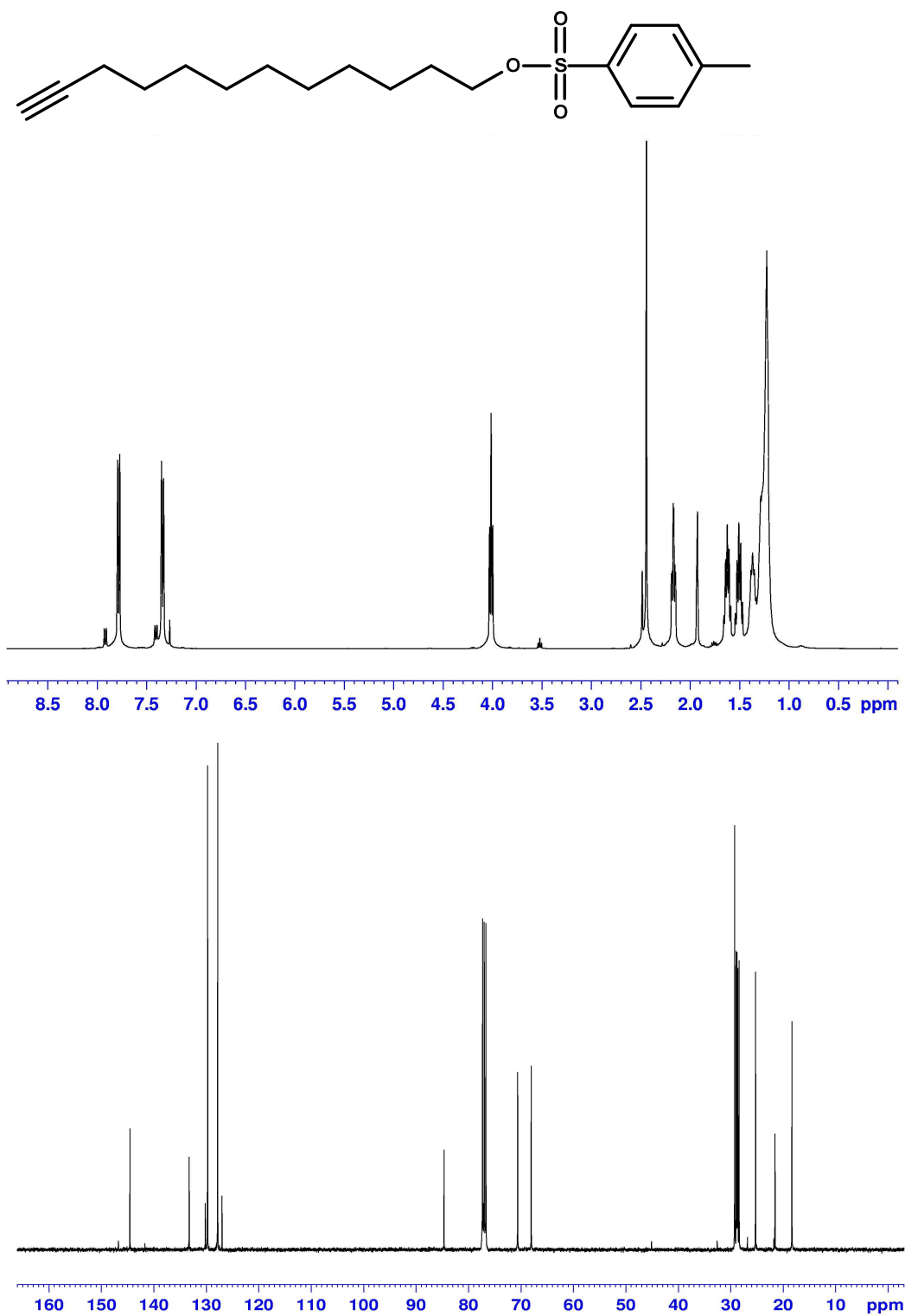
10-Fluorodec-1-yne (1c)



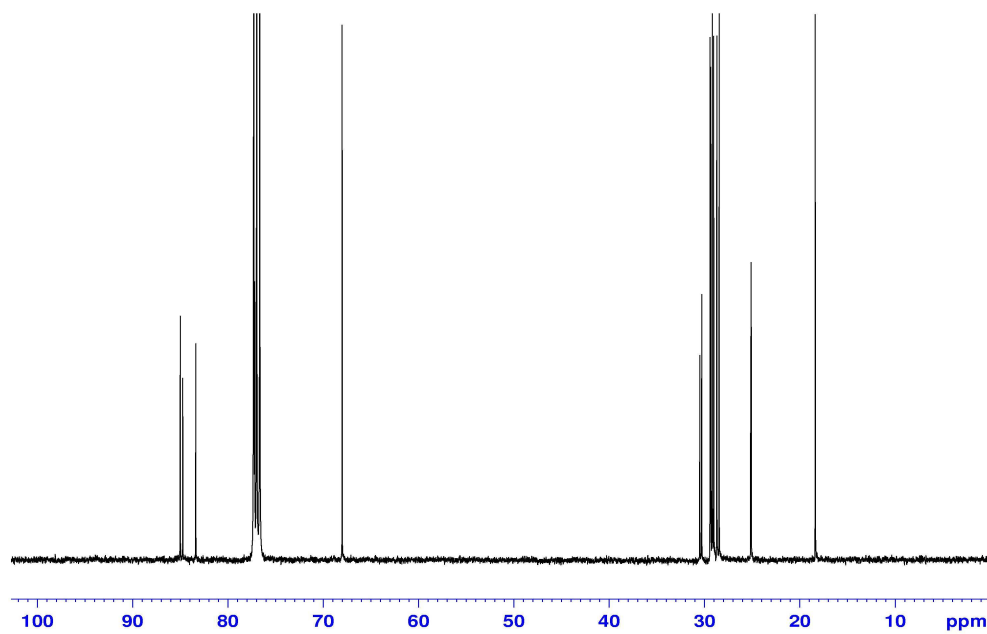
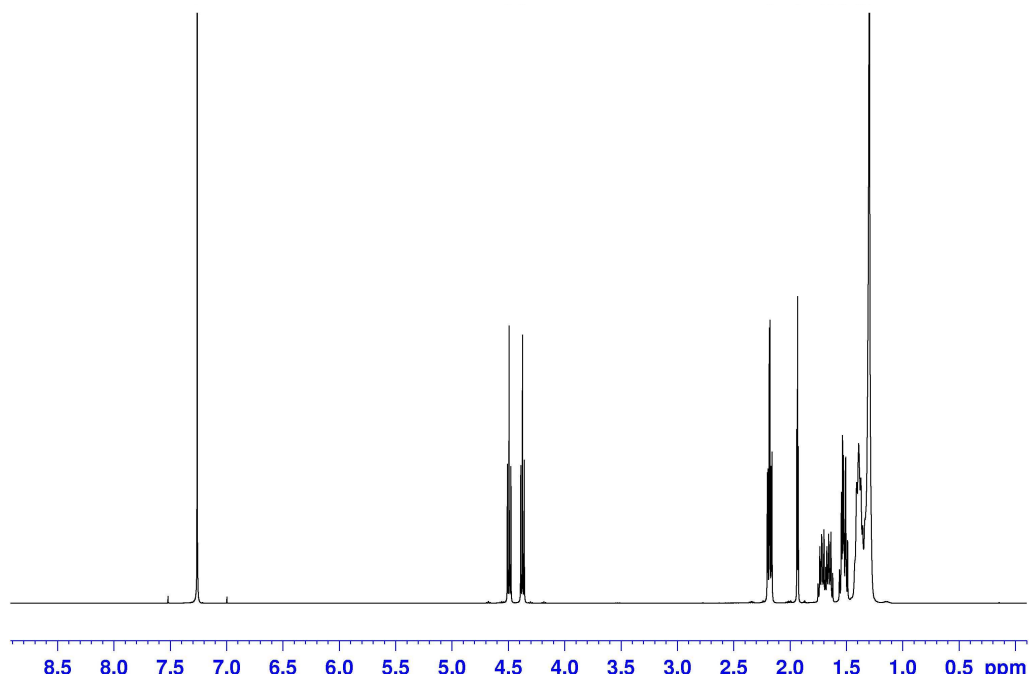
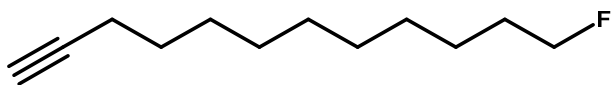
Dodec-11-yn-1-ol (2a)



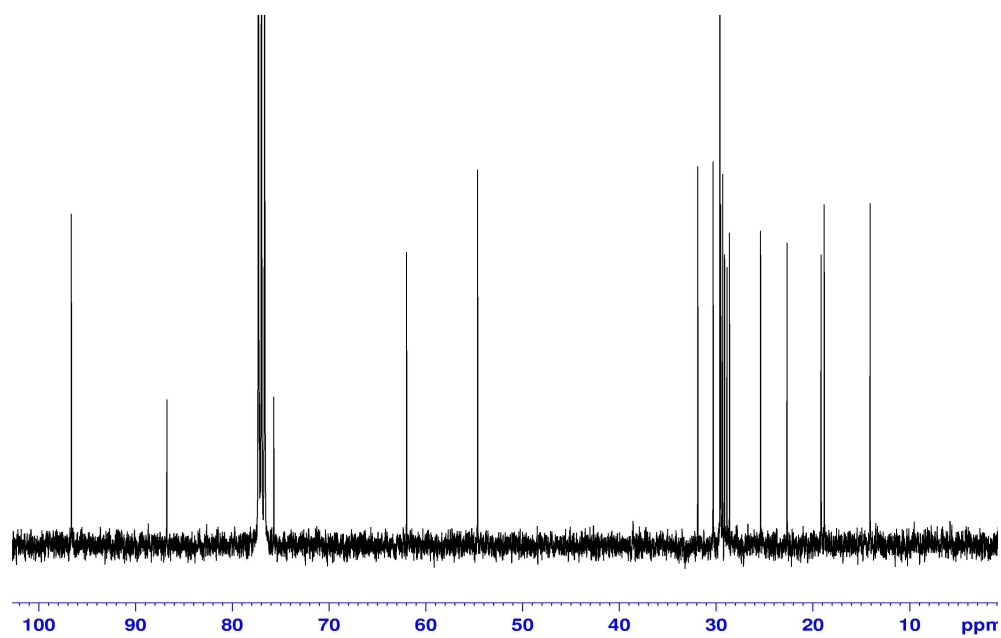
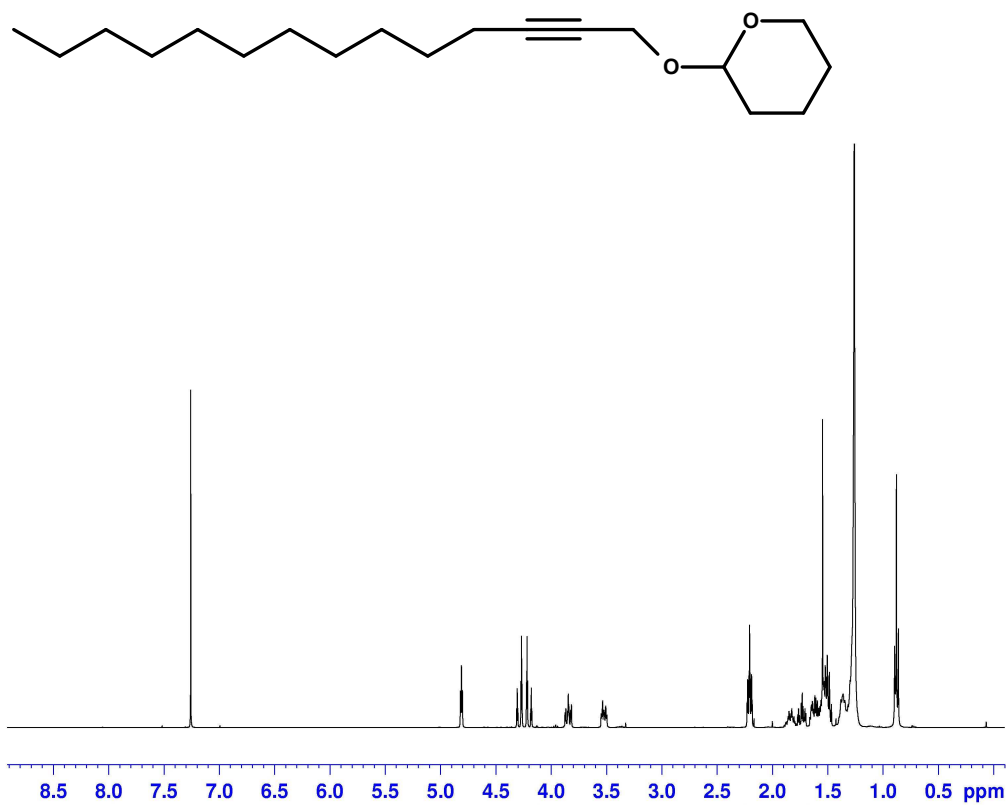
Dodec-11-ynyl 4-methylbenzenesulfonate (2b)



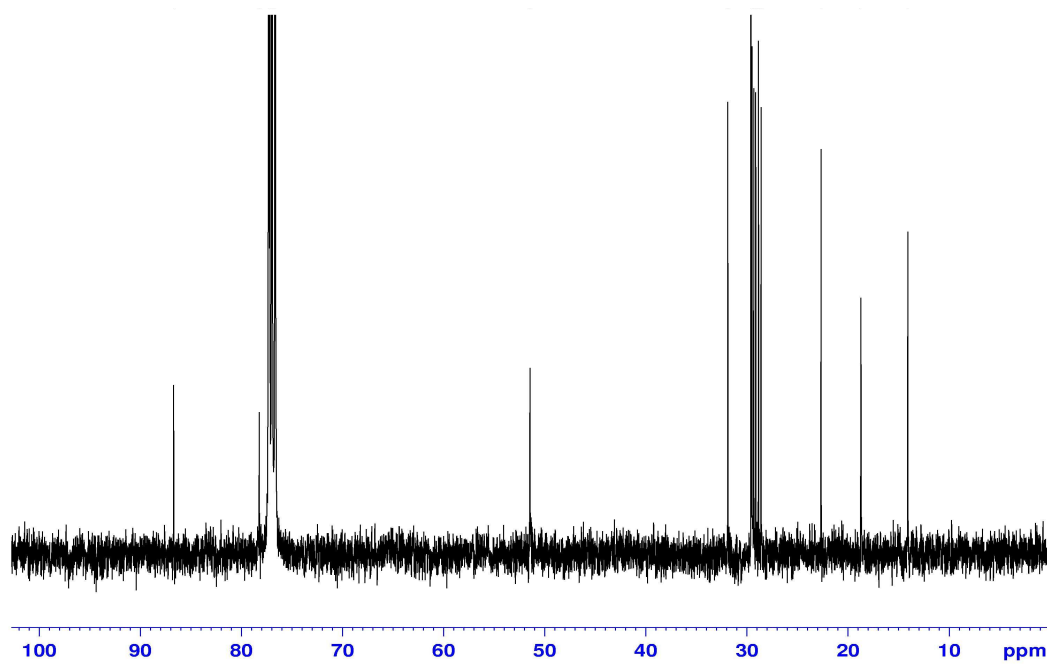
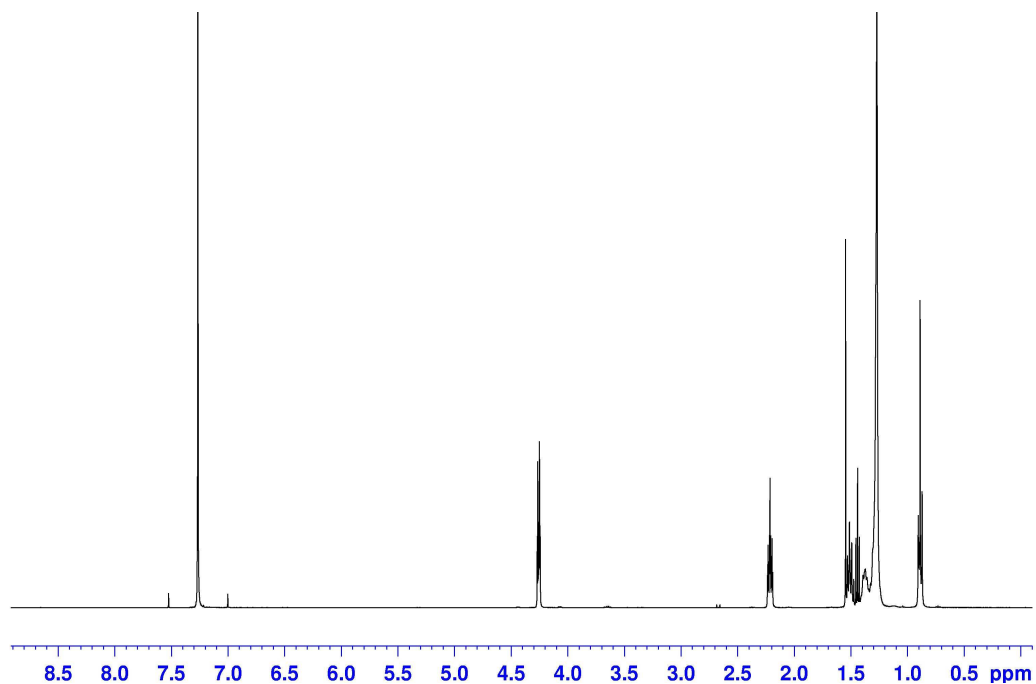
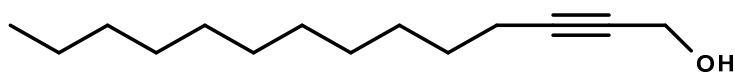
12-Fluorotetradec-1-yne (2c)



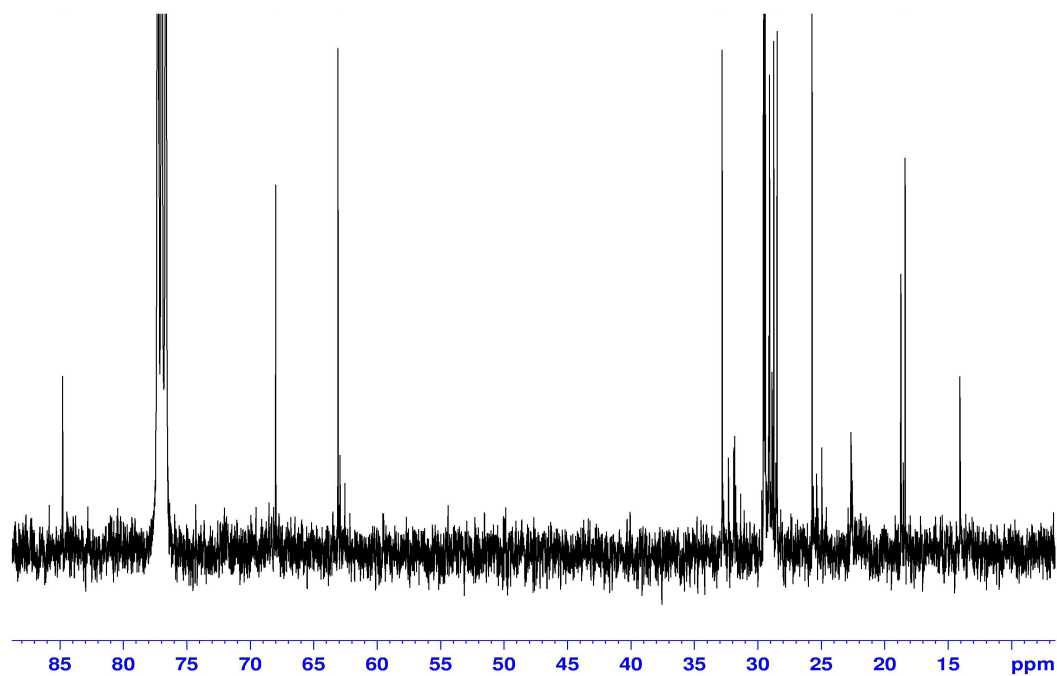
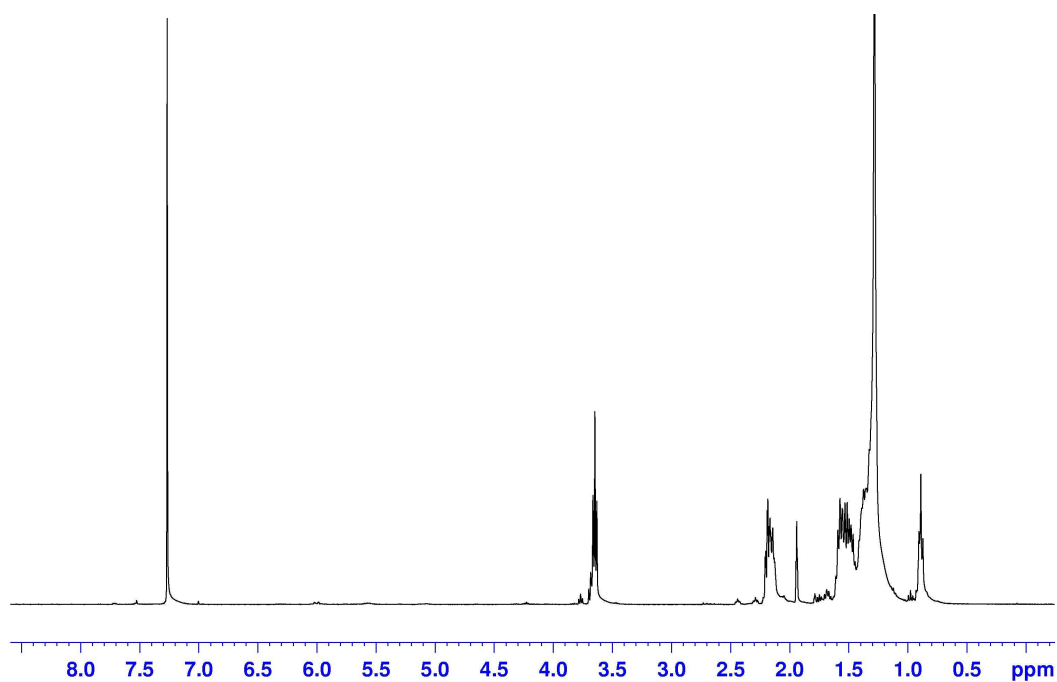
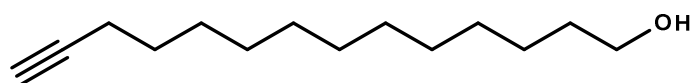
2-Tetradec-2-ynoxytetrahydropyran (3a)



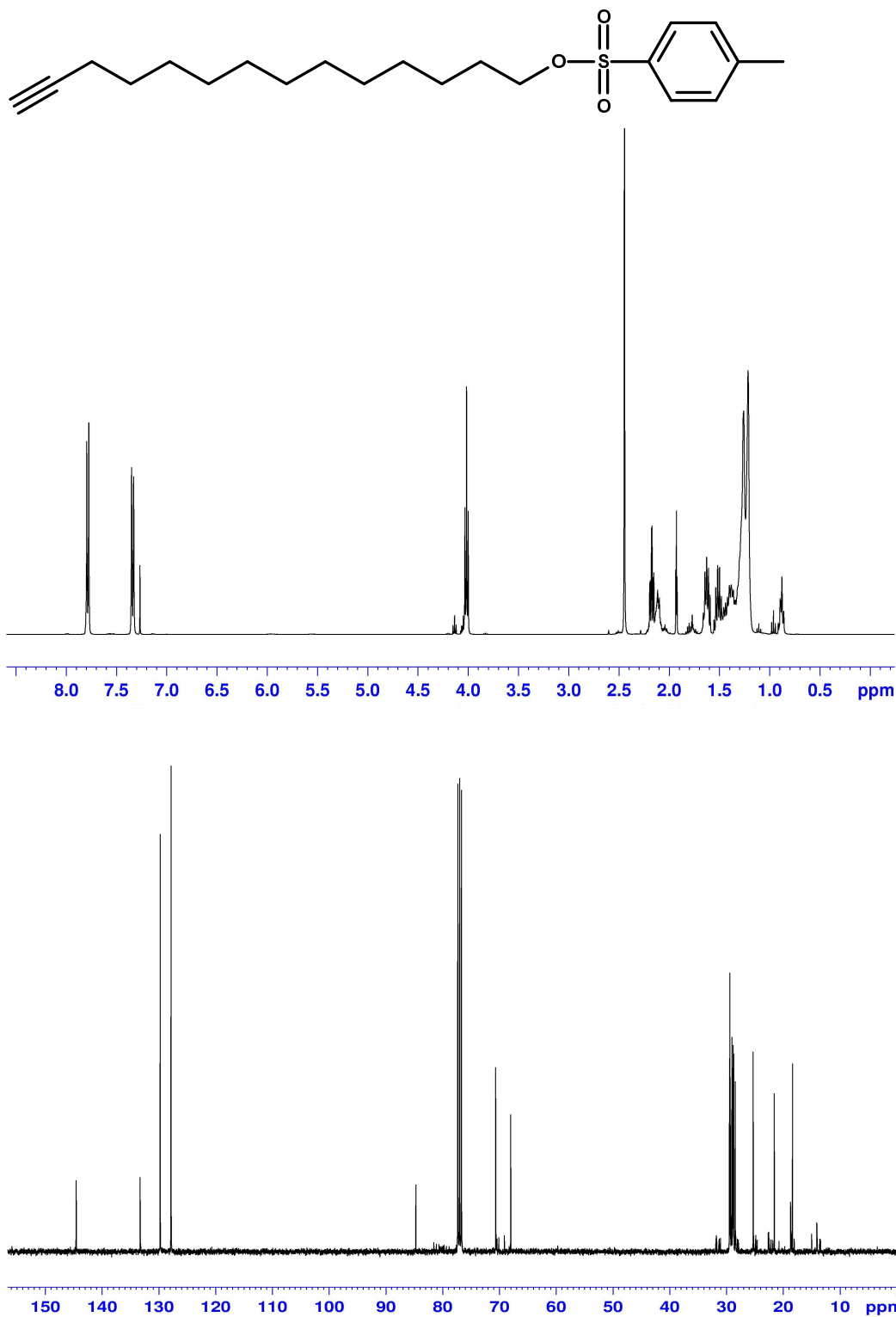
Tetradec-2-yn-1-ol (3b)



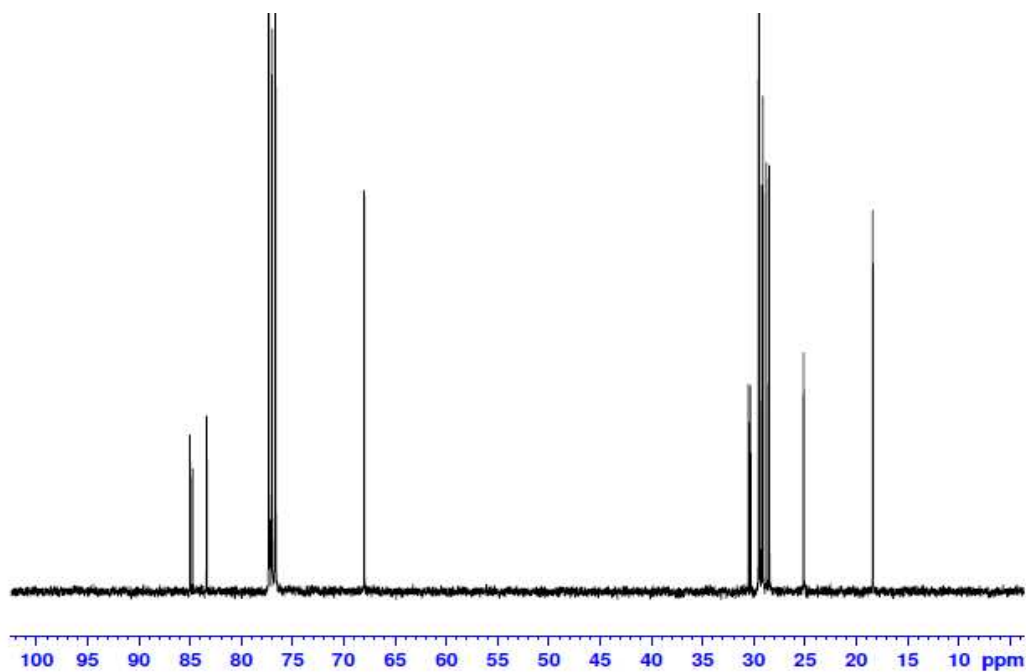
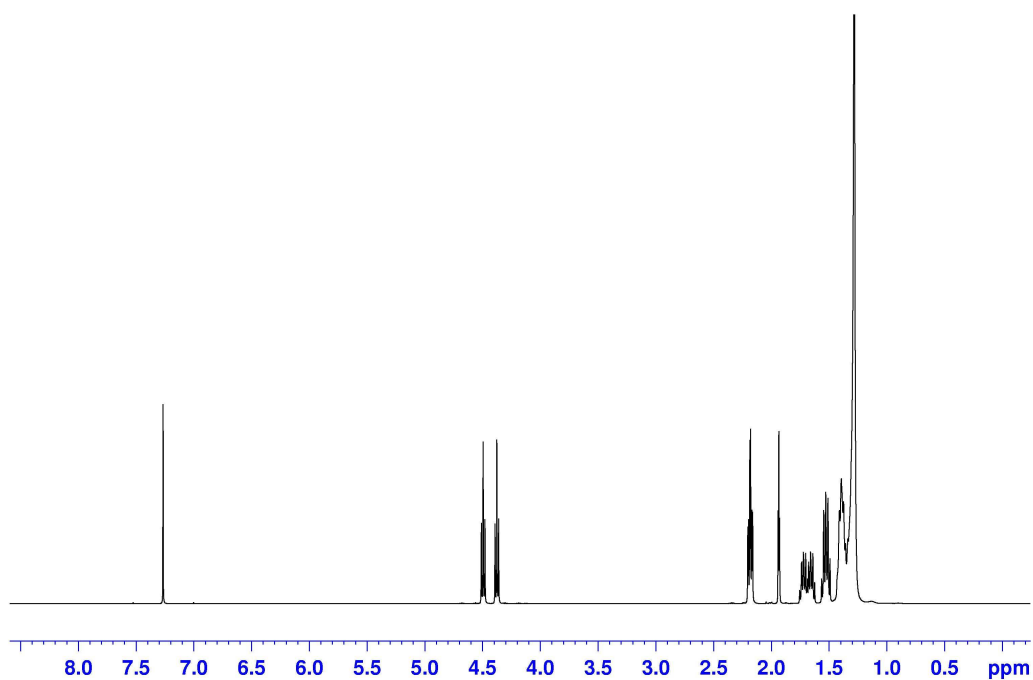
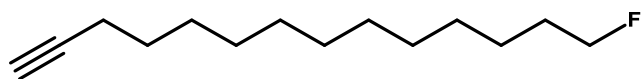
Tetradec-13-yn-1-ol (3c)



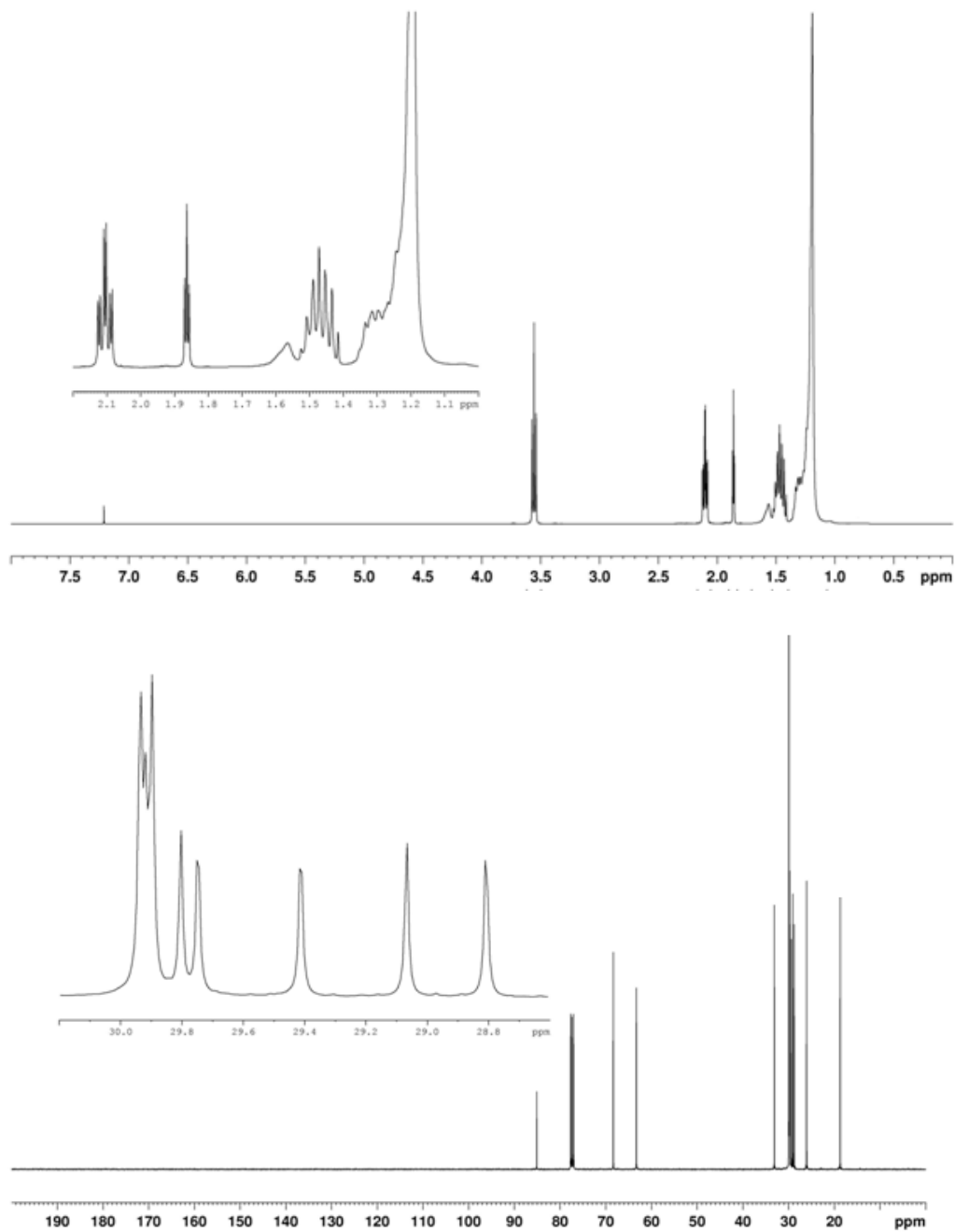
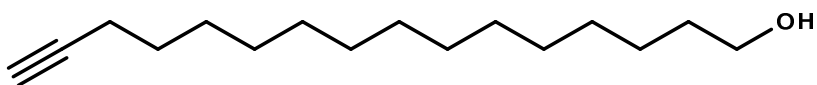
Tetradec-13-ynyl 4-methylbenzenesulfonate (3d)



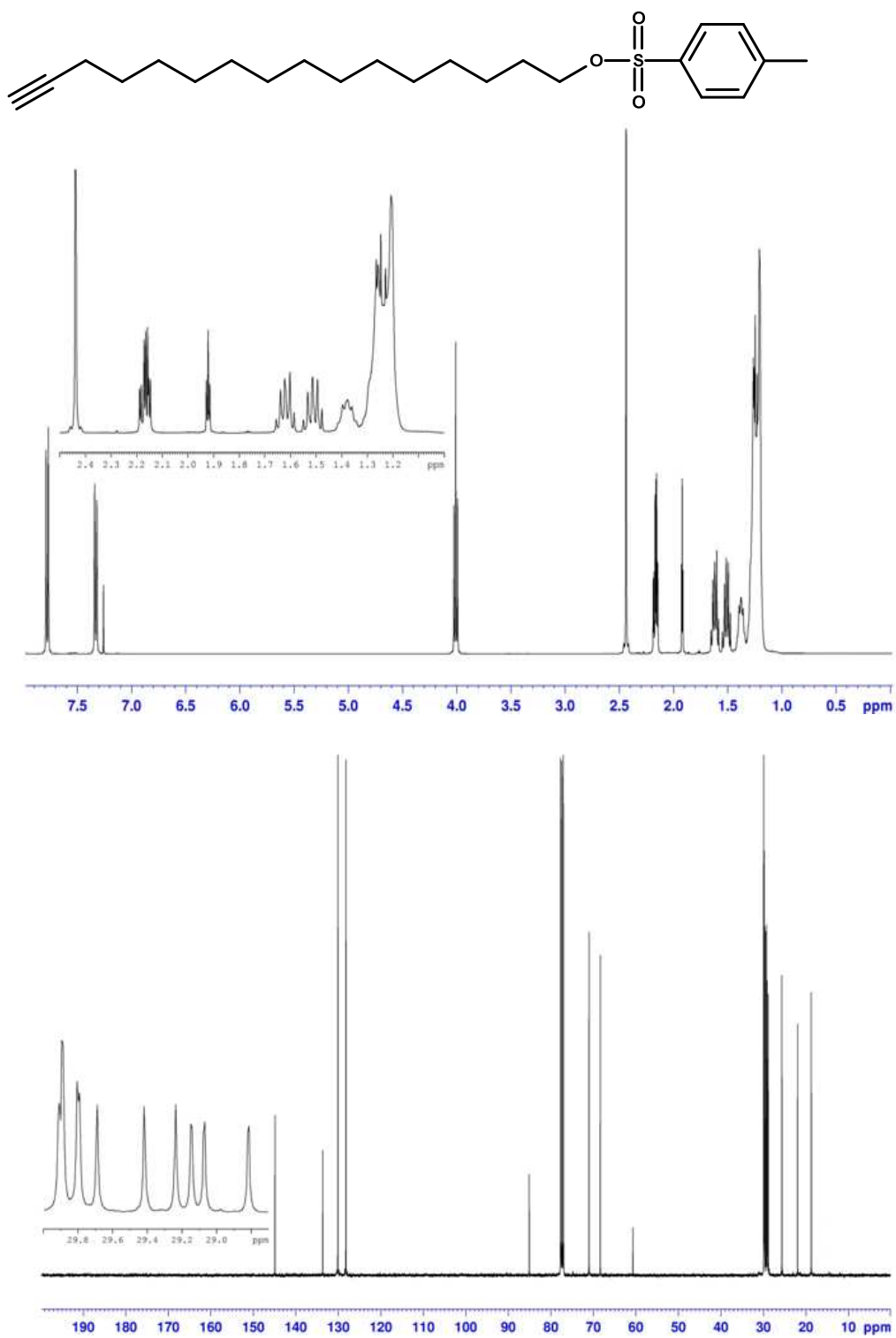
14-Fluorotetradec-1-yne (3e)



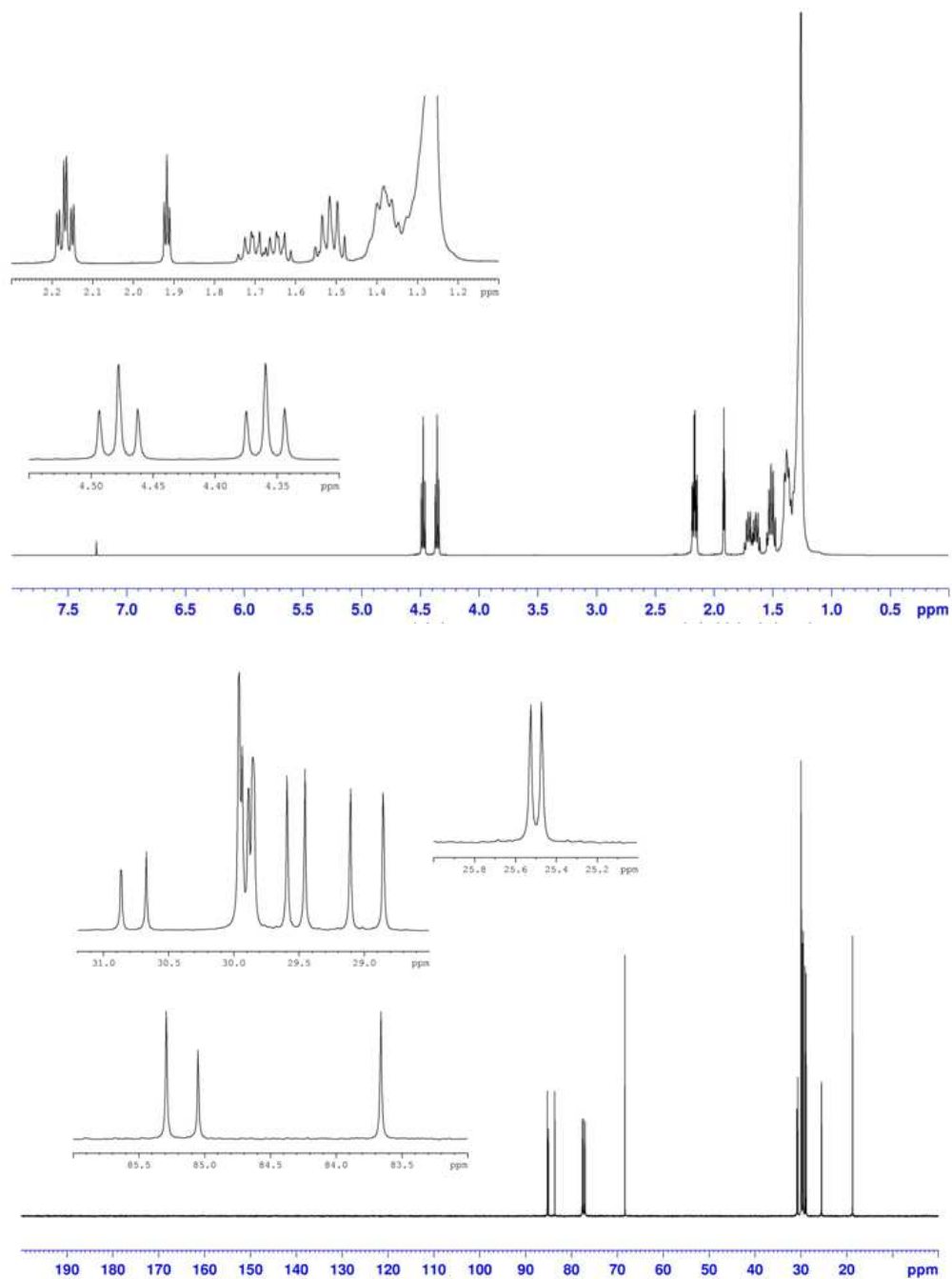
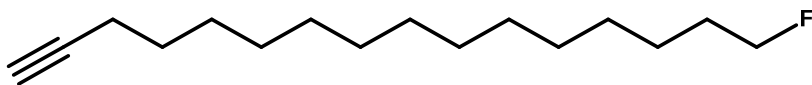
Hexadec-15-yn-1-ol (4a)



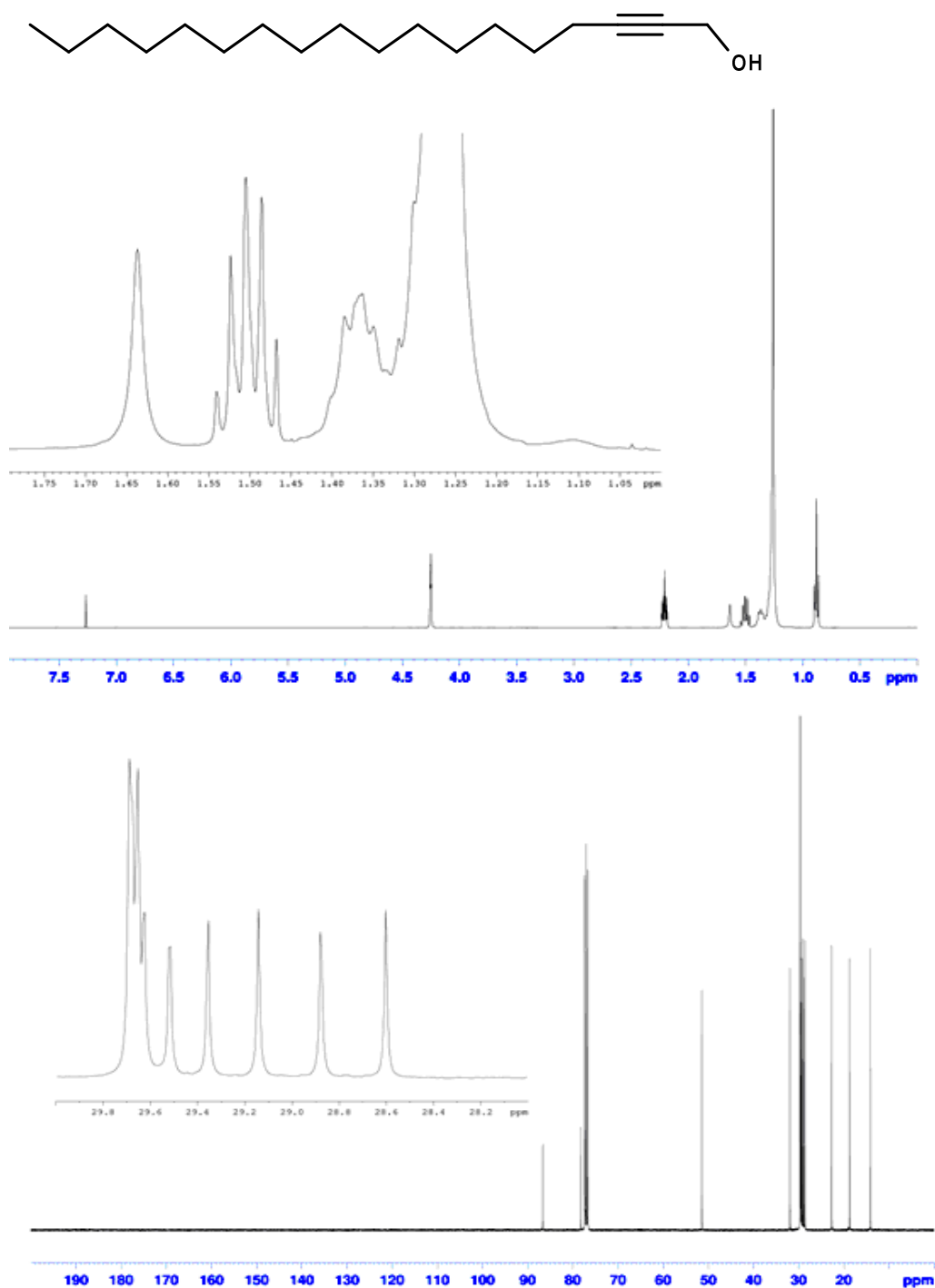
Hexadec-15-ynyl 4-methylbenzenesulfonate (4b)



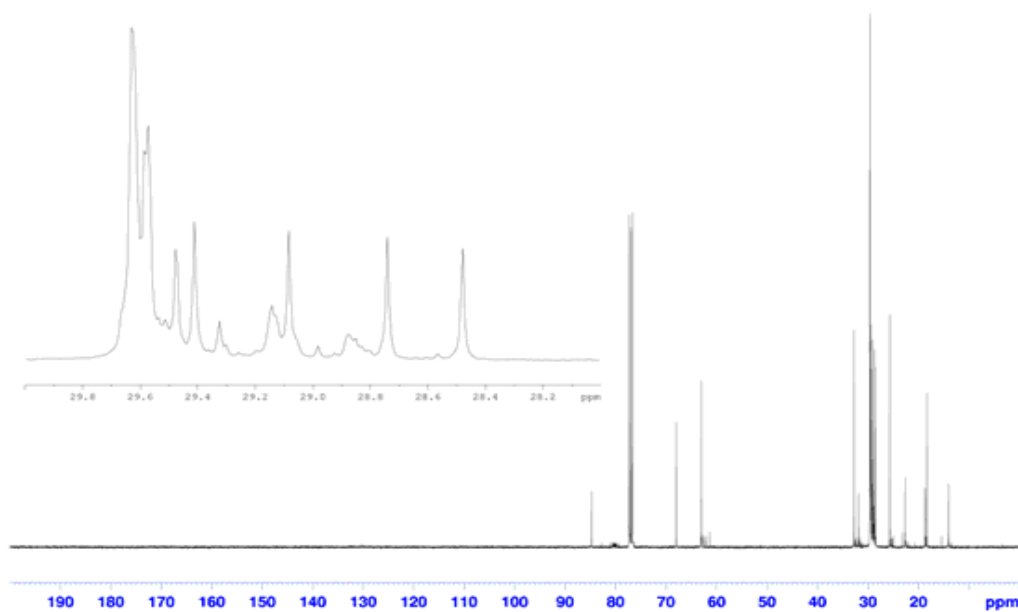
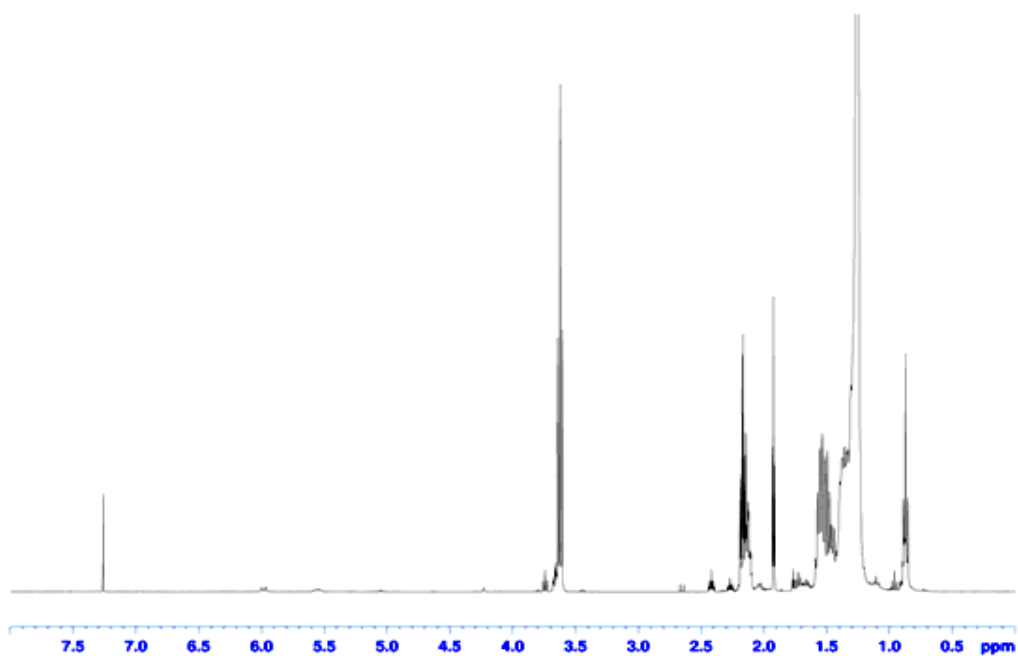
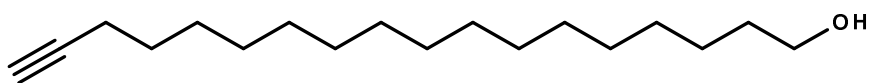
16-Fluorohexadec-1-yne (4c)



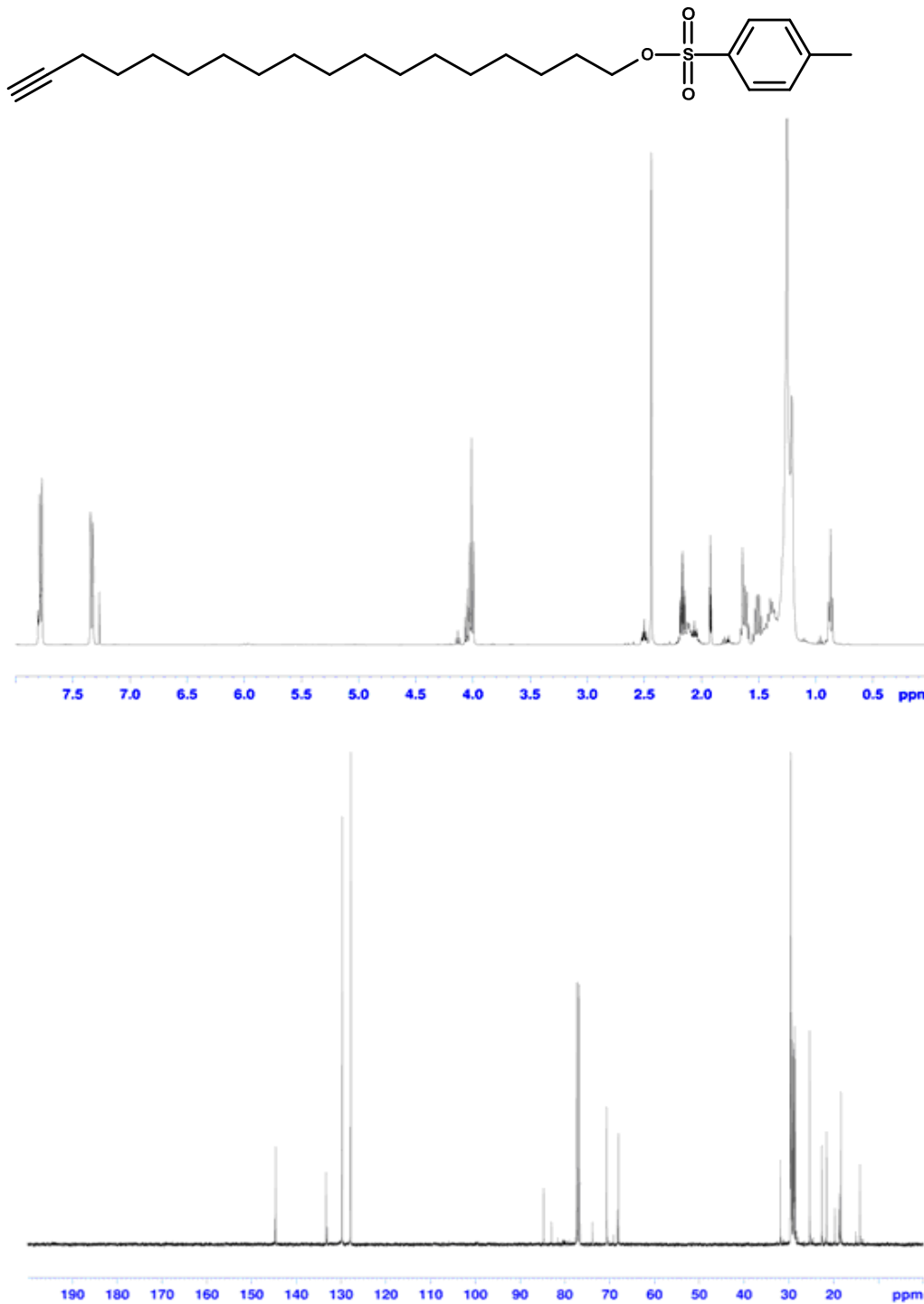
Octadec-2-yn-1-ol (5a)



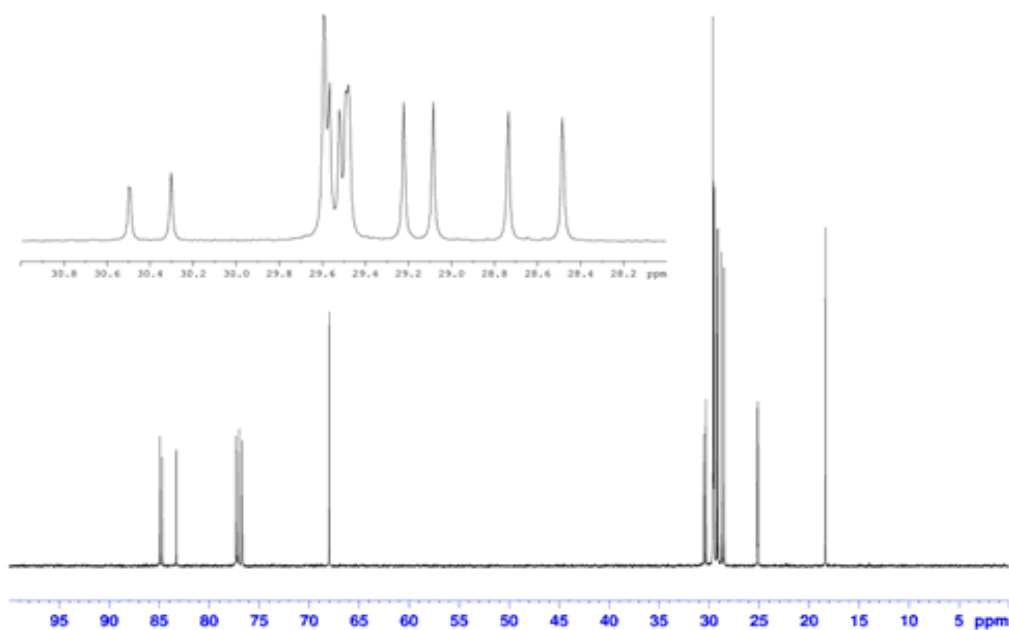
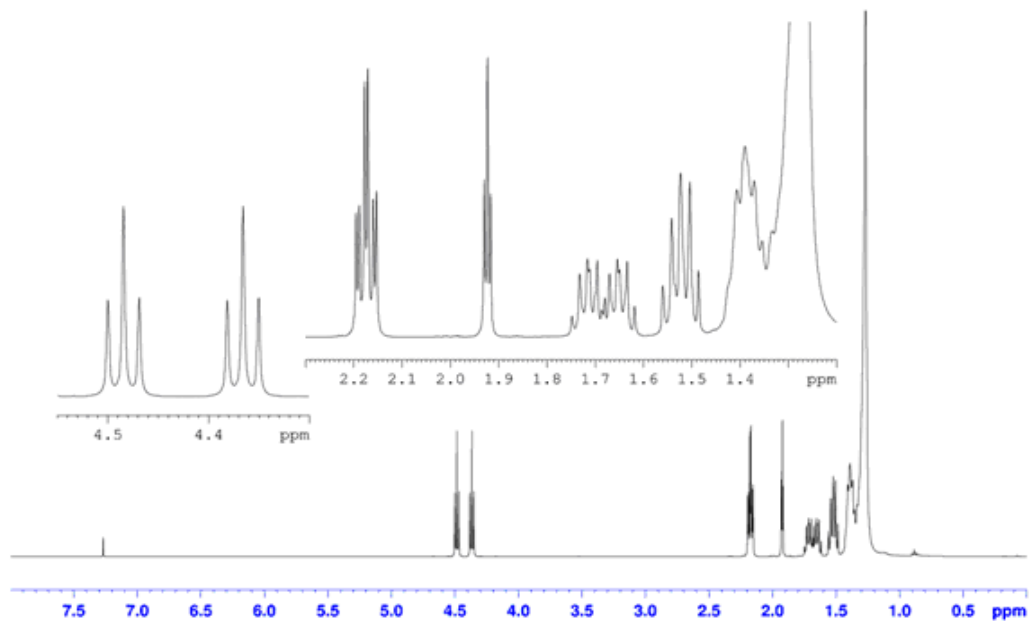
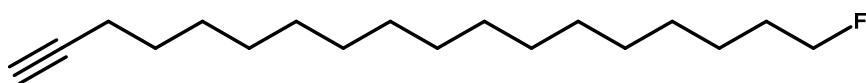
Octadec-17-yn-1-ol (5b)



Octadec-17-ynyl-4-methylbenzenesulfonate (5c)



18-Fluorooctadec-1-yne (5d)



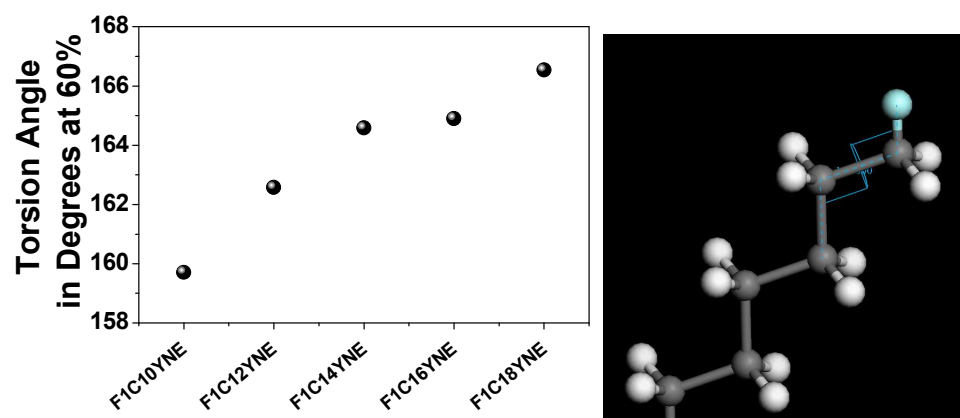


Figure. (Left) Simulation cells of surface coverage of 60 % after optimization and average torsional angle of C-C-C-F, (Right) torsional angle measured of C-C-C-F.