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Highly Regioselective Gold-Catalyzed Formal Hydration of Propargylic *gem*-Difluorides

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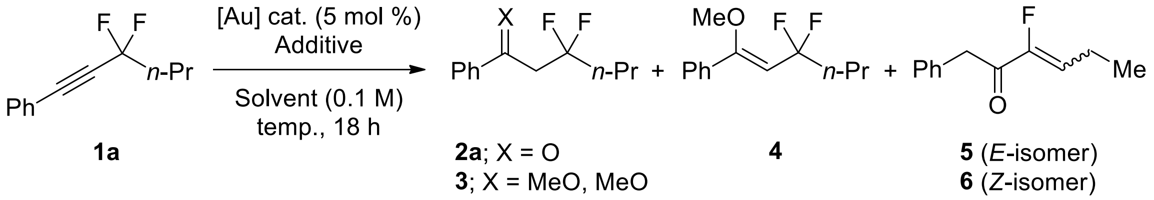
1. General information

The following includes general experimental procedures, specific details for representative reactions, and isolation and spectroscopic information for the new compounds prepared. All reactions were carried out under an argon atmosphere with dry solvents. Et_2O, THF, CH_3CN, CH_2Cl_2 and toluene were purified using a Vacuum Atmospheres Inc. Solvent Purification System. All other commercially available compounds were used as received. Thin-layer chromatography (TLC) analysis of reaction mixtures was performed using Silicycle silica gel 60 Å F254 TLC plates, and visualized under UV or by staining with either potassium permanganate, *p*-anisaldehyde or phosphomolybdic acid. Flash column chromatography was carried out on Silicycle silica gel 60 Å, 230–400 mesh. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ at ambient temperature using Agilent DD2 500 and Varian Inova 400 spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm downfield of tetramethylsilane and are respectively referenced to tetramethylsilane (δ = 0.00 ppm) and residual solvent (δ = 77.16 ppm). For ^{19}F NMR, $CFCl_3$ is used as the external standard. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sext = sextet, m = multiplet, bs = broad signal. High-resolution mass spectra were obtained on a LC/MS–TOF Agilent 6210 using electrospray ionization (ESI) or atmospheric pressure photoionization (APPI). Infrared spectra were recorded using a Thermo Scientific Nicolet 380 FT-IR spectrometer. Melting points were recorded on a Stanford Research System OptiMelt capillary melting point apparatus and are uncorrected.

2. Optimization of the gold-catalyzed formal hydration reaction

Table S1. Selected optimization data using propargylic difluoride **1**.[a]



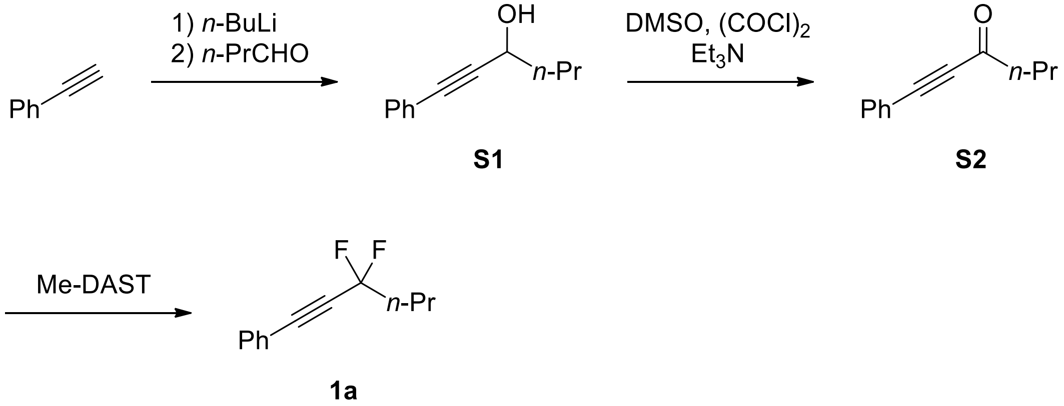
Entry	[Au] cat.	Solvent	Temp [°C]	Additive (mol %)	Conversion [%][b]	Yield [%][b]					Yield of **2a** + **3** + **4** [%][b]
						2a	**3**	**4**	**5**	**6**	
1	$AuCl_3$	CH_2Cl_2/MeOH (1:1)	40	-	48	17	-	-	7	5	17
2	Ph_3PAuCl	CH_2Cl_2/MeOH (1:1)	40	-	16	-	-	-	6	5	-
3	Ph_3PAuCl	CH_2Cl_2/MeOH (1:1)	40	AgOTf (5)	100	17	15	-	-	-	32
4	Ph_3PAuCl	MeOH	40	AgOTf (5)	100	7	20	-	-	-	27
5	Ph_3PAuCl	PhMe/MeOH (1:1)	40	AgOTf (5)	100	20	19	-	-	-	39
6	Ph_3PAuCl	$CHCl_3$/MeOH (1:1)	40	AgOTf (5)	21	6	-	-	2	-	6
7	Ph_3PAuCl	THF/MeOH (1:1)	40	AgOTf (5)	100	57	21	-	-	-	78
8	Ph_3PAuCl	THF/MeOH (1:1)	21	AgOTf (5)	100	55	25	4	-	-	84
9	Ph_3PAuCl	THF/MeOH (1:1)	0	AgOTf (5)	79	2	5	71	1	-	79
10	Ph_3PAuCl	THF/MeOH (1:1)	21	$Ag(NTf)_2$ (5)	100	44	13	24	-	-	81
11	$(naph)_3PAuCl$	THF/MeOH (1:1)	21	AgOTf (5)	100	38	4	23	-	-	65
12	Me_2SAuCl	THF/MeOH (1:1)	21	AgOTf (5)	37	18	-	10	-	-	28
13	IMesAuCl	THF/MeOH (1:1)	21	AgOTf (5)	100	54	3	22	-	-	79
14	**Ph_3PAuCl**	**THF/MeOH (9:1)**	**21**	**AgOTf (5)**	**100**	**27**	**33**	**39**	**-**	**-**	**99 (82)**[c]

[a] The optimized conditions are shown in bold.

[b] NMR yield estimated by ^{19}F NMR analysis of the crude mixture after an aqueous work-up (sat. aq. $NaHCO_3$) using 2-fluoro-4-nitrotoluene as the internal standard.

[c] Isolated yield of **2a** after an acidic treatment (3 N HCl/CH_2Cl_2, 21 °C, 3 h).

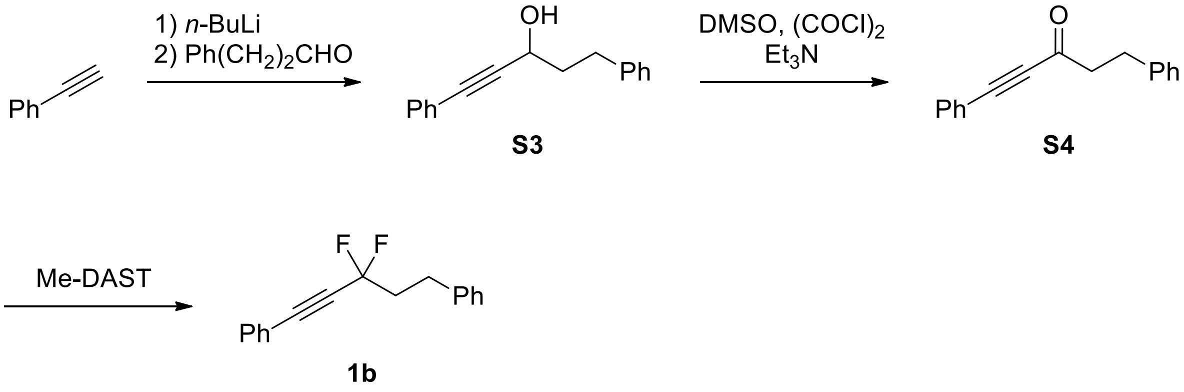
3. Preparation of propargylic *gem*-difluorides



1-Phenylhex-1-yn-3-ol (S1). To a -78 °C solution of phenylacetylene (4.0 mL, 36.4 mmol) in THF (120 mL) was added *n*-BuLi (2.5 mol/L in hexanes, 16.0 mL, 40.0 mmol) and the mixture was stirred at -78 °C for 30 minutes, and then at room temperature for 30 minutes. The solution was brought back to -78 °C and butyraldehyde (3.93 mL, 43.7 mmol) was added. The mixture was stirred at room temperature for 1 hour, after which saturated $NaHCO_3$ was added. The mixture was extracted with Et_2O (3x), washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (5.70 g, 90%) was isolated as a pale yellow oil by flash chromatography using 80% CH_2Cl_2/hexanes. Spectroscopic data was in agreement with the literature.[1]

1-Phenylhex-1-yn-3-one (S2). To a -78 °C solution of oxalyl chloride (1.11 mL, 12.9 mmol) in CH_2Cl_2 (90 mL) was added DMSO (1.83 mL, 25.8 mmol) and stirring was continued at -78 °C for 15 minutes. A solution of 1-phenylhex-1-yn-3-ol (**S1**, 761 mg, 2.65 mmol) in CH_2Cl_2 (17 mL) was slowly added and the resulting solution was stirred at -78 °C for 15 minutes. Et_3N (9.0 mL, 64.5 mmol) was added, the solution was stirred at -78 °C for 20 minutes, and then allowed to reach room temperature over 40 minutes. Saturated $NaHCO_3$ was added and stirring was continued for 30 minutes. The resulting mixture was extracted with CH_2Cl_2 (3x), dried over Na_2SO_4 and concentrated *in vacuo*. The desired product (1.55 g, 84%) was isolated as a yellow oil by flash chromatography using 2% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[2]

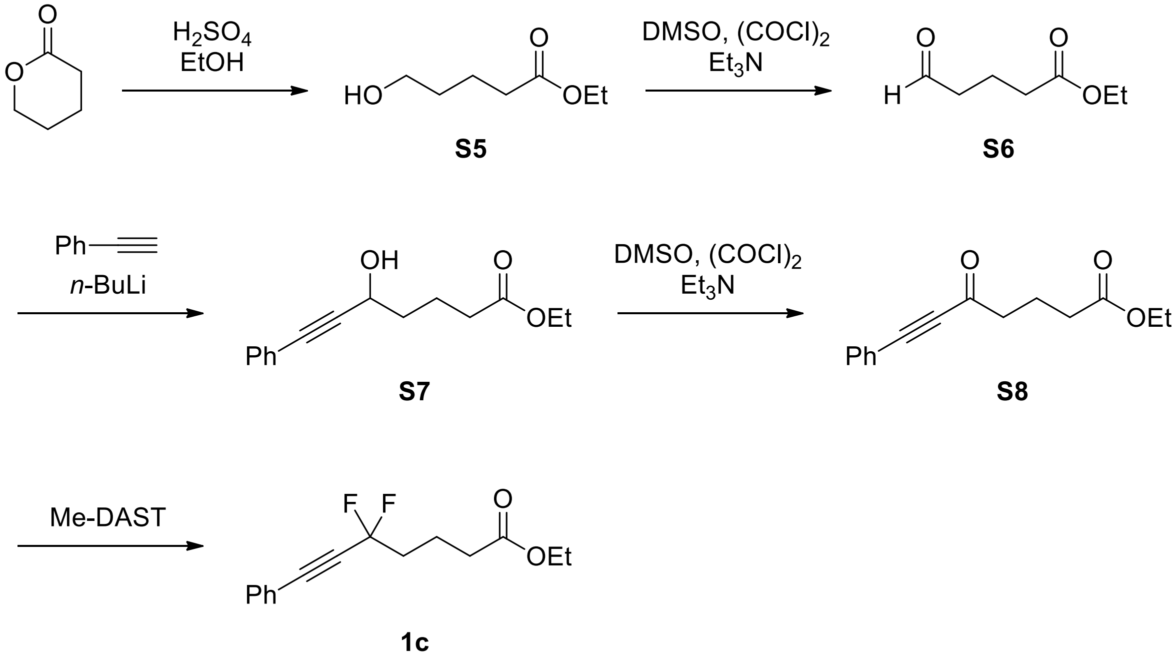
(3,3-Difluorohex-1-yn-1-yl)benzene (1a). 1-Phenylhex-1-yn-3-one (**S2**, 353 mg, 2.05 mmol) was charged into a polypropylene vial. Me-DAST (0.50 mL, 5.12 mmol) was added and the mixture was stirred at 45 °C for 72 hours. It was brought back to 0 °C, diluted with EtOAc and poured into a stirring mixture of EtOAc and saturated $NaHCO_3$. The mixture was stirred for 30 minutes, after which the organic layer was separated, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (114 mg, 29%) was isolated as a colorless oil by flash chromatography using hexanes. IR (ATR, ZnSe) ν = 2968, 2936, 2878, 2242, 1490, 1323, 1171, 993, 754, 688 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.50 (d, 2H, J = 6.9 Hz), 7.42-7.39 (m, 1H), 7.35 (t, 2H, J = 7.5 Hz), 2.11 (m, 2H), 1.71-1.62 (m, 2H), 1.03 (t, 3H, J = 7.5 Hz); ^{19}F NMR ($CDCl_3$, 470 MHz) δ -82.1 (t, 2F, J = 14.9 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 132.2 (t, $J_{C\text{-}F}$ = 2.4 Hz), 129.9, 128.6, 120.5 (t, $J_{C\text{-}F}$ = 2.8 Hz), 115.5 (t, $J_{C\text{-}F}$ = 232 Hz), 86.7 (t, $J_{C\text{-}F}$ = 6.9 Hz), 82.0 (t, $J_{C\text{-}F}$ = 40.8 Hz), 41.5 (t, $J_{C\text{-}F}$ = 26.0 Hz), 16.6 (t, $J_{C\text{-}F}$ = 3.9 Hz), 13.8; HRMS-ESI calcd for $C_{12}H_{12}F$ $[M-F]^+$ 175.0918; found 175.0934.



1,5-Diphenylpent-1-yn-3-ol (S3). To a -78 °C solution of phenylacetylene (4.0 mL, 36.5 mmol) in THF (100 mL) was added *n*-BuLi (2.5 mol/L in hexanes, 13.4 mL, 33.4 mmol) and the mixture was stirred at -78 °C for 30 minutes, and then at room temperature for 30 minutes. The solution was brought back to -78 °C and hydrocinnamaldehyde (4.0 mL, 30.4 mmol) was added. The mixture was stirred at room temperature for 1 hour, after which saturated $NaHCO_3$ was added. The mixture was extracted with Et_2O (3x), washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (3.74 g, 52%) was isolated as a pale yellow oil by flash chromatography using 5% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[3]

1,5-Diphenylpent-1-yn-3-one (S4). To a -78 °C solution of oxalyl chloride (0.49 mL, 5.75 mmol) in CH_2Cl_2 (40 mL) was added DMSO (0.82 mL, 11.5 mmol) and stirring was continued at -78 °C for 15 minutes. A solution of 1,5-diphenylpent-1-yn-3-ol (**S3**, 1132 mg, 4.79 mmol) in CH_2Cl_2 (8 mL) was slowly added and the resulting solution was stirred at -78 °C for 15 minutes. Et_3N (4.0 mL, 28.7 mmol) was added, the solution was stirred at -78 °C for 20 minutes, and then allowed to reach room temperature over 40 minutes. Saturated $NaHCO_3$ was added and stirring was continued for 30 minutes. The resulting mixture was extracted with CH_2Cl_2 (3x), dried over Na_2SO_4 and concentrated *in vacuo*. The desired product (1073 mg, 96%) was isolated as a yellow oil by flash chromatography using 10% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[4]

(3,3-Difluoropent-1-yne-1,5-diyl)dibenzene (1b). 1,5-Diphenylpent-1-yn-3-one (**S4**, 515 mg, 2.20 mmol) was charged into a polypropylene vial. Me-DAST (0.54 mL, 5.50 mmol) was added and the mixture was stirred at 65 °C for 72 hours. It was brought back to 0 °C, diluted with EtOAc and poured into a stirring mixture of EtOAc and saturated $NaHCO_3$. The mixture was stirred for 30 minutes, after which the organic layer was separated, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (91 mg, 16%) was isolated as a colorless oil by flash chromatography using hexanes. IR (ATR, ZnSe) ν = 3064, 3028, 2934, 2240, 1491, 1162, 1044, 953, 754, 688 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.51-7.50 (m, 2H), 7.44-7.40 (m, 2H), 7.38-7.35 (m, 2H), 7.33-7.30 (m, 2H), 7.25-7.21 (m, 3H), 2.97-2.94 (m, 2H), 2.51-2.42 (m, 2H); ^{19}F NMR ($CDCl_3$, 470 MHz) δ -82.8 (t, J = 14.7 Hz, 2F); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 139.9, 132.1 (t, $J_{C\text{-}F}$ = 2.2 Hz), 129.9, 128.6, 128.5, 128.3, 126.4, 120.2 (t, $J_{C\text{-}F}$ = 2.6 Hz), 114.8 (t, $J_{C\text{-}F}$ = 233 Hz), 87.1 (t, $J_{C\text{-}F}$ = 6.9 Hz), 81.5 (t, $J_{C\text{-}F}$ = 40.5 Hz), 41.2 (t, $J_{C\text{-}F}$ = 26.5 Hz), 29.2 (t, $J_{C\text{-}F}$ = 3.8 Hz); HRMS-ESI calcd for $C_{17}H_{18}F_2N$ $[M+NH_4]^+$ 274.1402; found 274.1400.



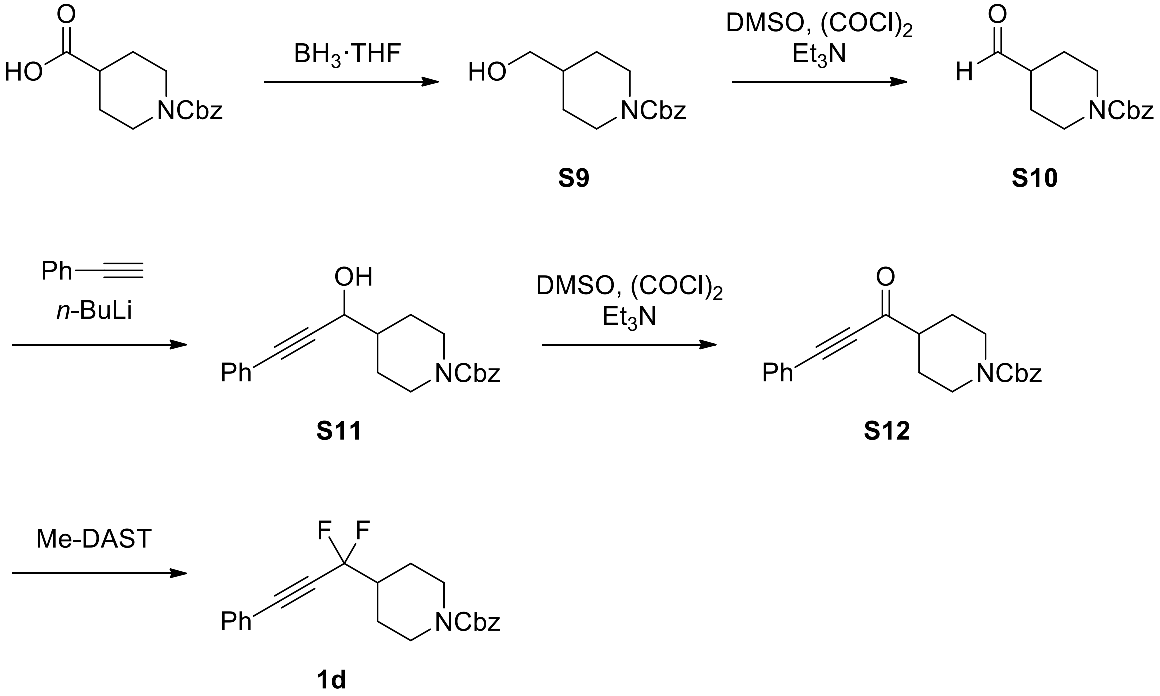
Ethyl 5-hydroxypentanoate (S5). To a solution of δ-valerolactone (1.85 mL, 20.0 mmol) in dry ethanol (40 mL) was added sulfuric acid (2 drops). The mixture was heated to reflux for 5 hours, after which it was brought to 0 °C. $NaHCO_3$ (200 mg) was added and the suspension was stirred for 10 minutes. The solids were filtered off, and ethanol was removed *in vacuo*. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The desired product (2.21 g, 76%) was isolated as a pale yellow oil by flash chromatography using 5% $MeOH/CH_2Cl_2$. Spectroscopic data was in agreement with the literature.[5]

Ethyl 5-oxopentanoate (S6). To a -78 °C solution of oxalyl chloride (1.55 mL, 18.1 mmol) in CH_2Cl_2 (140 mL) was added DMSO (2.57 mL, 36.2 mmol) and stirring was continued at -78 °C for 15 minutes. A solution of ethyl 5-hydroxypentanoate (**S5**, 2.21 g, 15.1 mmol) in CH_2Cl_2 (11 mL) was slowly added and the resulting solution was stirred at -78 °C for 15 minutes. Et_3N (12.6 mL, 90.6 mmol) was added, the solution was stirred at -78 °C for 20 minutes, and then allowed to reach room temperature over 40 minutes. Saturated $NaHCO_3$ was added and stirring was continued for 30 minutes. The resulting mixture was extracted with CH_2Cl_2 (3x), dried over Na_2SO_4 and concentrated *in vacuo*. The desired product (1.80 g, 82%) was isolated as a pale yellow oil by flash chromatography using 20% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[6]

Ethyl 5-hydroxy-7-phenylhept-6-ynoate (S7). To a -78 °C solution of phenylacetylene (0.60 mL, 5.50 mmol) in THF (17 mL) was added *n*-BuLi (2.5 mol/L in hexanes, 2.2 mL, 5.50 mmol) and the mixture was stirred at -78 °C for 30 minutes, and then at room temperature for 30 minutes. The solution was brought back to -78 °C and ethyl 5-oxopentanoate (**S6**, 721 mg, 5.00 mmol) was added. The mixture was stirred at room temperature for 1 hour, after which saturated $NaHCO_3$ was added. The mixture was extracted with Et_2O (3x), washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (1.02g, 83%) was isolated as a yellow oil by flash chromatography using 10% EtOAc/hexanes. IR (ATR, ZnSe) ν = 3421, 2938, 2202, 1730, 1713, 1489, 1151, 1025, 755, 691 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.32-7.30 (m, 2H), 4.62 (q, 1H, *J* = 5.8 Hz), 4.14 (q, 2H, *J* = 7.1 Hz), 2.40 (t, 2H, *J* = 6.8 Hz), 2.12 (dd, 1H, *J* = 5.7, 2.2 Hz), 1.92-1.82 (m, 4H), 1.26 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 131.8, 128.6, 128.5, 122.6, 89.8, 85.2, 62.6, 60.5, 37.2, 34.0, 20.8, 14.4; HRMS-ESI calcd for $C_{15}H_{17}O_2$ $[M+H]^+$-$[H_2O]$ 229.1223; found 229.1229.

Ethyl 5-oxo-7-phenylhept-6-ynoate (S8). To a -78 °C solution of oxalyl chloride (0.36 mL, 4.21 mmol) in CH_2Cl_2 (25 mL) was added DMSO (0.60 mL, 8.42 mmol) and stirring was continued at -78 °C for 15 minutes. A solution of ethyl 5-hydroxy-7-phenylhept-6-ynoate (**S7**, 864 mg, 3.51 mmol) in CH_2Cl_2 (10 mL) was slowly added and the resulting solution was stirred at -78 °C for 15 minutes. Et_3N (2.9 mL, 21.0 mmol) was added, the solution was stirred at -78 °C for 20 minutes, and then allowed to reach room temperature over 40 minutes. Saturated $NaHCO_3$ was added and stirring was continued for 30 minutes. The resulting mixture was extracted with CH_2Cl_2 (3x), dried over Na_2SO_4 and concentrated *in vacuo*. The desired product (805 mg, 94%) was isolated as a yellow oil by flash chromatography using 10% EtOAc/hexanes. IR (ATR, ZnSe) ν = 2979, 2198, 1729, 1666, 1374, 1159, 1095, 1026, 757, 688 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, 2H, *J* = 7.0 Hz), 7.46 (t, 2H, *J* = 7.5 Hz), 7.39 (t, 2H, *J* = 7.6 Hz), 4.15 (q, 2H, *J* = 7.1 Hz), 2.76 (t, 2H, *J* = 7.2 Hz), 2.40 (t, 2H, *J* = 7.3 Hz), 2.06 (p, 2H, *J* = 7.3 Hz), 1.27 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.1, 173.1, 133.2, 130.9, 128.8, 120.0, 91.1, 87.8, 60.6, 44.5, 33.3, 19.3, 14.4; HRMS-ESI calcd for $C_{15}H_{17}O_3$ $[M+H]^+$ 245.1172; found 245.1175.

Ethyl 5,5-difluoro-7-phenylhept-6-ynoate (1c). Ethyl 5-oxo-7-phenylhept-6-ynoate (**S8**, 393 mg, 1.61 mmol) was charged into a polypropylene vial. Me-DAST (0.39 mL, 4.02 mmol) was added and the mixture was stirred at 55 °C for 24 hours. It was brought back to 0 °C, diluted with EtOAc and poured into a stirring mixture of EtOAc and saturated $NaHCO_3$. The mixture was stirred for 30 minutes, after which the organic layer was separated, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (87 mg, 20%) was isolated as a pale yellow oil by flash chromatography using 5% EtOAc/hexanes. IR (ATR, ZnSe) ν = 2980, 2241, 1731, 1490, 1324, 1162, 1109, 968, 756, 689 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51 (m, 2H, *J*= 7.1 Hz), 7.41 (m, 1H), 7.36 (t, 2H, *J*= 7.4 Hz), 4.15 (q, 2H, *J* = 7.2 Hz), 2.43 (t, 2H, *J* = 7.4 Hz), 2.25-2.16 (m, 2H), 1.98 (p, 2H, *J* = 7.5 Hz), 1.26 (t, 3H, *J* = 7.1 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -82.2 (t, 1F, *J* = 28.3 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 132.3 (t, J_{C-F} = 2.2 Hz), 130.0, 128.6, 120.3 (t, J_{C-F} = 2.6 Hz), 115.1 (t, J_{C-F} = 232 Hz), 87.1 (t, J_{C-F} = 6.8 Hz), 81.5 (t, J_{C-F} = 40.6 Hz), 60.6, 38.7 (t, J_{C-F} = 26.7 Hz), 33.4, 18.6 (t, J_{C-F} = 3.8 Hz), 14.4; HRMS-ESI calcd for $C_{15}H_{16}FO_2$ $[M-F]^+$ 247.1129; found 247.1126.



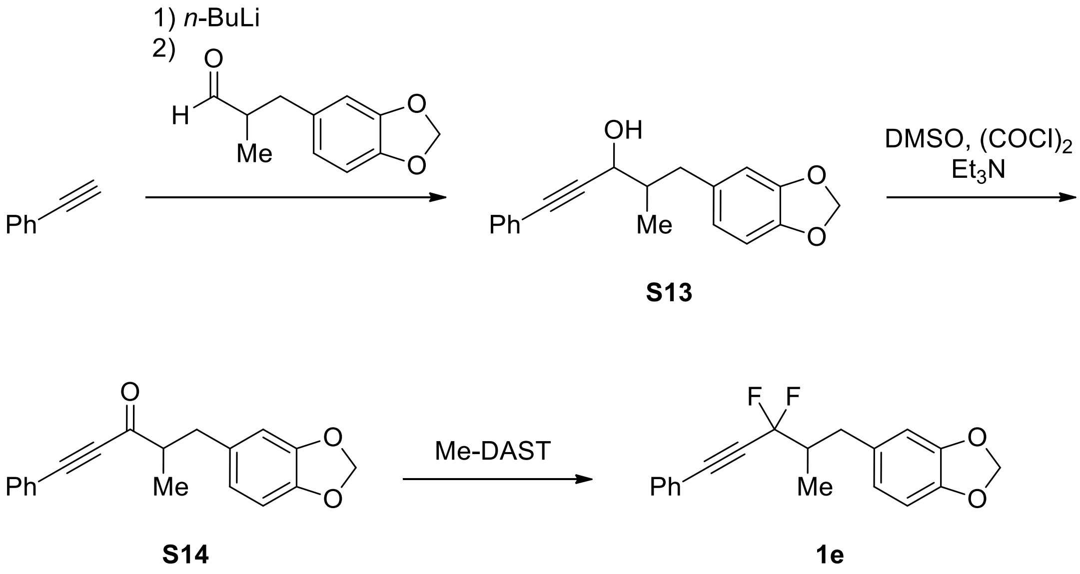
Benzyl 4-(hydroxymethyl)piperidine-1-carboxylate (S9). To a solution of 1-((benzyloxy)carbonyl)piperidine-4-carboxylic acid (1.79 g, 6.80 mmol) in THF (26 mL), was aded BH_3-THF (1 M in THF, 8.16 mL, 8.16 mmol) at 0 °C and the mixture was stirred at room temperature for 1 hour. CH_3OH (15 mL) was then added and the volatiles were removed under vacuum. The residue was taken up in EtOAc and saturated $NaHCO_3$ was added. The layers were separated, and the organic layer was dried with $MgSO_4$ and concentrated *in vacuo*. Spectroscopic data was in agreement with the literature.[7]

Benzyl 4-formylpiperidine-1-carboxylate (S10). To a -78 °C solution of oxalyl chloride (0.39 mL, 4.51 mmol) in CH_2Cl_2 (20 mL) was added DMSO (0.64 mL, 9.03 mmol) and stirring was continued at -78 °C for 15 minutes. A solution of benzyl 4-(hydroxymethyl)piperidine-1-carboxylate (**S9**, 938 mg, 3.76 mmol) in CH_2Cl_2 (18 mL) was slowly added and the resulting solution was stirred at -78 °C for 15 minutes. Et_3N (3.15 mL, 22.6 mmol) was added, the solution was stirred at -78 °C for 20 minutes, and then allowed to reach room temperature over 40 minutes. Saturated $NaHCO_3$ was added and stirring was continued for 30 minutes. The resulting mixture was extracted with CH_2Cl_2 (3x), dried over $MgSO_4$ and concentrated *in vacuo*. The desired product (724 mg, 78%) was isolated as a pale yellow oil by flash chromatography using 30% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[7]

Benzyl 4-(1-hydroxy-3-phenylprop-2-yn-1-yl)piperidine-1-carboxylate (S11). To a -78 °C solution of phenylacetylene (0.34 mL, 3.12 mmol) in THF (7 mL) was added *n*-BuLi (2.5 mol/L in hexanes, 1.25 mL, 3.12 mmol) and the mixture was stirred at -78 °C for 30 minutes, and then at room temperature for 30 minutes. The solution was brought back to -78 °C and a solution of benzyl 4-formylpiperidine-1-carboxylate (**S10**, 702 mg, 2.84 mmol) in THF (3 mL) was added. The mixture was stirred at room temperature for 1 hour, after which saturated $NaHCO_3$ was added. The mixture was extracted with Et_2O (3x), washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The desired compound (854 mg, 86%) was isolated as a yellow oil by flash chromatography using 40% EtOAc/hexanes. IR (ATR, ZnSe) ν = 3236, 2984, 2895, 1625, 1398, 1200, 906, 724, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42-7.40 (m, 2H), 7.35-7.28 (m, 8H), 5.14 (s, 2H), 4.42 (d, 2H, *J* = 6.0 Hz), 4.29 (d, 2H, *J* = 26.6 Hz), 2.79 (br s, 2H), 2.45 (br s, 1H), 1.96-1.76 (m, 3H), 1.50-1.30 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.4, 136.9, 131.8, 128.63, 128.56, 128.4, 128.0, 127.9, 122.5, 88.4, 86.3, 67.2, 66.7, 43.9, 42.7, 28.0, 27.5; HRMS-ESI calcd for $C_{22}H_{24}NO_3$ $[M+H]^+$ 350.1751; found 350.1748.

Benzyl 4-(3-phenylpropioloyl)piperidine-1-carboxylate (S12). To a -78 °C solution of oxalyl chloride (0.20 mL, 2.36 mmol) in CH_2Cl_2 (11.5 mL) was added DMSO (0.34 mL, 4.73 mmol) and stirring was continued at -78 °C for 15 minutes. A solution of benzyl 4-(1-hydroxy-3-phenylprop-2-yn-1-yl)piperidine-1-carboxylate (**S11**, 688 mg, 1.97 mmol) in CH_2Cl_2 (8.5 mL) was slowly added and the resulting solution was stirred at -78 °C for 15 minutes. Et_3N (1.65 mL, 11.8 mmol) was added, the solution was stirred at -78 °C for 20 minutes, and then allowed to reach room temperature over 40 minutes. Saturated $NaHCO_3$ was added and stirring was continued for 30 minutes. The resulting mixture was extracted with CH_2Cl_2 (3x), dried over $MgSO_4$ and concentrated *in vacuo*. The desired product (377 mg, 55%) was isolated as a pale orange oil by flash chromatography using hexanes. IR (ATR, ZnSe) ν = 2777, 2195, 1660, 1419, 1307, 1260, 1216, 1107, 1012, 685 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.58-7.56 (m, 2H), 7.48-7.44 (m, 1H), 7.40-7.29 (m, 7H), 5.14 (s, 2H), 4.17 (br s, 2H), 2.98 (t, 2H, *J* = 10.5 Hz), 2.66 (tt, 1H, *J* = 10.9, 3.9 Hz), 2.05 (br s, 1H), 1.78-1.65 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.1, 155.2, 136.8, 133.1, 131.0, 128.7, 128.5, 128.1, 127.9, 119.7, 92.5, 86.8, 67.2, 49.9, 43.3, 27.4; HRMS-ESI calcd for $C_{22}H_{22}NO_3$ $[M+H]^+$ 348.1594; found 348.1589.

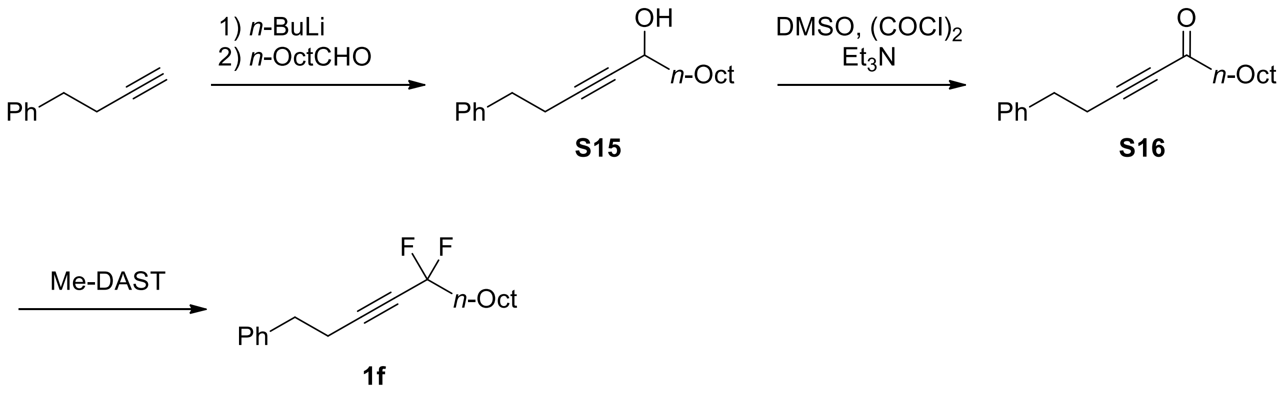
Benzyl 4-(1,1-difluoro-3-phenylprop-2-yn-1-yl)piperidine-1-carboxylate (1d). Benzyl 4-(3-phenylpropioloyl)piperidine-1-carboxylate (**S12**, 216 mg, 0.622 mmol) was charged into a polypropylene vial. Me-DAST (0.152 mL, 1.55 mmol) was added and the mixture was stirred at 55 °C for 24 hours. It was brought back to 0 °C, diluted with EtOAc and poured into a stirring mixture of EtOAc and saturated $NaHCO_3$. The mixture was stirred for 30 minutes, after which the organic layer was separated, dried over $MgSO_4$ and concentrated *in vacuo*. The desired compound (98 mg, 43%) was isolated as a pale yellow oil by flash chromatography using 10% EtOAc/hexanes. IR (ATR, ZnSe) ν = 2931, 2862, 2239, 1694, 1427, 1319, 1278, 1225, 1132, 1022, 786, 688 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50-7.48 (m, 2H), 7.43-7.40 (m, 1H), 4.37-4.28 (m, 7H), 5.15 (s, 2H), 4.34 (br s, 2H), 2.80 (s, 2H), 2.18 (pt, 1H, J = 11.9, 3.5 Hz), 1.95 (d, 2H, J = 10.5 Hz), 1.67-1.40 (m, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ -89.2 (dd, J = 47.5, 11.0 Hz, 2F); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.3, 136.8, 132.3 (t, $J_{C\text{-}F}$ = 2.1 Hz), 130.1, 128.62, 128.61, 128.1, 128.0, 120.1 (t, $J_{C\text{-}F}$ = 2.6 Hz), 116.4 (t, $J_{C\text{-}F}$ = 234 Hz), 88.1 (t, $J_{C\text{-}F}$ = 6.7 Hz), 80.3 (t, $J_{C\text{-}F}$ = 40.5 Hz), 67.3, 44.9 (t, $J_{C\text{-}F}$ = 25.8 Hz), 43.3, 25.5; HRMS-ESI calcd for $C_{22}H_{22}F_2NO_2$ $[M+H]^+$ 370.1613; found 370.1600.



5-(Benzo[*d*][1,3]dioxol-5-yl)-4-methyl-1-phenylpent-1-yn-3-ol (S13). To a -78 °C solution of phenylacetylene (0.60 mL, 5.50 mmol) in THF (17 mL) was added *n*-BuLi (2.5 mol/L in hexanes, 2.2 mL, 5.50 mmol) and the mixture was stirred at -78 °C for 30 minutes, and then at room temperature for 30 minutes. The solution was brought back to -78 °C and 2-methyl-3-(3,4-methylenedioxyphenyl)-propanal (0.83 mL, 5.00 mmol) was added. The mixture was stirred at room temperature for 1 hour, after which saturated $NaHCO_3$ was added. The mixture was extracted with Et_2O (3x), washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (1.10 g, 75%) was isolated as a colorless oil by flash chromatography using 10% EtOAc/hexanes. IR (ATR, ZnSe) ν = 3399, 2876, 1487, 1241, 1186, 1035, 928, 800, 754, 689 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.47-7.43 (m, 2H), 7.34-7.30 (m, 3H), 6.75-6.71 (m, 2H), 6.67 (t, 1H, *J* = 7.6 Hz), 5.93 (s, 2H), 4.51-4.73 (m, 1H), 2.94-2.81 (m, 1H), 2.51-2.46 (m, 2H), 2.14-2.04 (m, 1H), 1.91-1.83 (m, 1H), 1.05 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 147.71, 147.67, 145.92, 145.91, 134.4, 134.1, 131.9, 131.8, 128.61, 128.58, 128.48, 128.46, 122.72, 122.74, 122.21, 122.15, 109.7, 109.6, 108.3, 108.2, 100.9, 89.2, 88.4, 86.5, 86.1, 66.7, 66.4, 42.0, 41.8, 39.1, 38.5, 15.0, 14.7; HRMS-ESI calcd for $C_{19}H_{17}O_2$ $[M+H]^+$-$[H_2O]$ 277.1223; found 277.1203.

5-(Benzo[*d*][1,3]dioxol-5-yl)-4-methyl-1-phenylpent-1-yn-3-one (S14). To a -78 °C solution of oxalyl chloride (0.38 mL, 4.42 mmol) in CH_2Cl_2 (30 mL) was added DMSO (0.63 mL, 8.83 mmol) and stirring was continued at -78 °C for 15 minutes. A solution of 5-(benzo[*d*][1,3]dioxol-5-yl)-4-methyl-1-phenylpent-1-yn-3-ol (**S13**, 1083 mg, 3.68 mmol) in CH_2Cl_2 (7 mL) was slowly added and the resulting solution was stirred at -78 °C for 15 minutes. Et_3N (3.1 mL, 22.1 mmol) was added, the solution was stirred at -78 °C for 20 minutes, and then allowed to reach room temperature over 40 minutes. Saturated $NaHCO_3$ was added and stirring was continued for 30 minutes. The resulting mixture was extracted with CH_2Cl_2 (3x), dried over Na_2SO_4 and concentrated *in vacuo*. The desired product (949 mg, 88%) was isolated as a yellow oil by flash chromatography using 5% EtOAc/hexanes. IR (ATR, ZnSe) ν = 2969, 2877, 2195, 1661, 1487, 1441, 1243, 1035, 927, 733 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.58 (d, 2H, *J* = 7.1 Hz), 7.46 (t, 1H, *J* = 7.5 Hz), 7.39 (t, 2H, *J* = 7.5 Hz), 6.74-6.70 (m, 2H), 6.66 (m, 1H), 5.91 (s, 2H), 3.14 (dd, 1H, *J* = 13.8, 6.4 Hz), 2.93 (sext, 1H, *J* = 6.9 Hz), 2.65 (dd, 1H, *J* = 13.8, 7.9 Hz), 1.23 (d, 3H, *J* = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 191.2, 147.7, 146.2, 133.2, 132.8, 130.9, 128.8, 122.2, 120.1, 109.5, 108.3, 101.0, 92.2, 87.2, 50.8, 38.6, 15.9; HRMS-ESI calcd for $C_{19}H_{17}O_3$ $[M+H]^+$ 293.1172; found 293.1176.

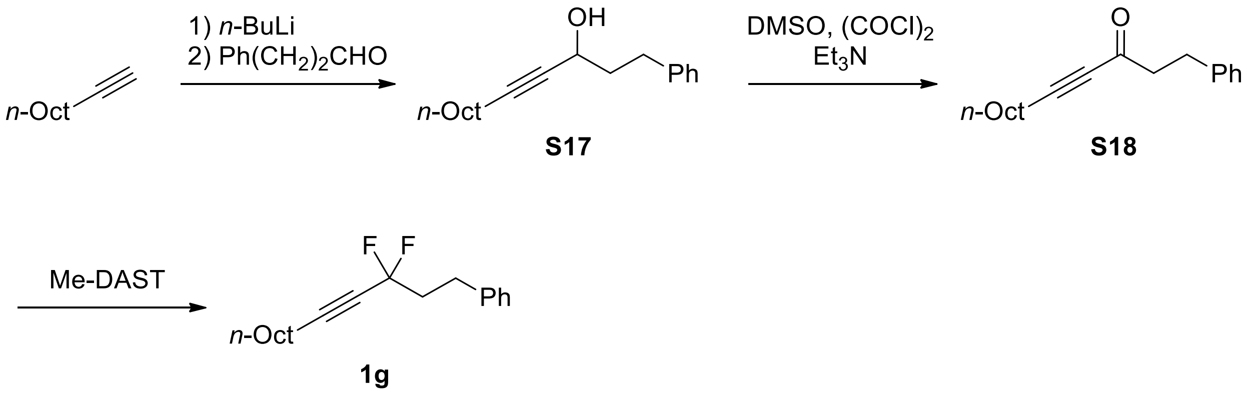
5-(3,3-Difluoro-2-methyl-5-phenylpent-4-yn-1-yl)benzo[*d*][1,3]dioxole (1e). 5-(Benzo[*d*][1,3]dioxol-5-yl)-4-methyl-1-phenylpent-1-yn-3-one (**S14**, 610 mg, 2.09 mmol) was charged into a polypropylene vial. Me-DAST (0.51 mL, 5.22 mmol) was added and the mixture was stirred at 45 °C for 24 hours. It was brought back to 0 °C, diluted with EtOAc and poured into a stirring mixture of EtOAc and saturated $NaHCO_3$. The mixture was stirred for 30 minutes, after which the organic layer was separated, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (295 mg, 45%) was isolated as a pale yellow oil by flash chromatography using hexanes. IR (ATR, ZnSe) ν = 2977, 2882, 2238, 1488, 1442, 1245, 1032, 983, 927, 755 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, 2H, *J* = 7.0 Hz), 7.40 (t, 1H, *J* = 7.4 Hz), 7.35 (t, 2H, *J* = 7.3 Hz), 6.74 (d, 1H, *J* = 7.9 Hz), 6.68 (s, 1H), 6.64 (d, 1H, *J* = 7.9 Hz), 5.90 (s, 2H), 3.14 (m, 1H), 2.41-2.35 (m, 2H), 1.06 (d, 3H, *J* = 6.2 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -88.5 (t, 2F, *J* = 10.9 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 146.2, 132.9, 132.3 (t, $J_{C\text{-}F}$ = 2.2 Hz), 130.0, 128.6, 122.3, 120.3 (t, $J_{C\text{-}F}$ = 2.6 Hz), 117.5 (t, $J_{C\text{-}F}$ = 235 Hz), 109.6, 108.3, 101.0, 87.7 (t, $J_{C\text{-}F}$ = 6.7 Hz), 80.9 (t, $J_{C\text{-}F}$ = 40.6 Hz), 44.5 (t, $J_{C\text{-}F}$ = 24.4 Hz), 36.4 (t, $J_{C\text{-}F}$ = 3.3 Hz), 13.0 (t, $J_{C\text{-}F}$ = 3.3 Hz); HRMS-ESI calcd for. $C_{19}H_{16}FO_2$ $[M-F]^+$ 295.1129; found 295.1125.



1-Phenyltridec-3-yn-5-ol (S15). To a -78 °C solution of 4-phenyl-1-butyne (0.77 mL, 5.50 mmol) in THF (17 mL) was added *n*-BuLi (2.5 mol/L in hexanes, 2.2 mL, 5.50 mmol) and the mixture was stirred at -78 °C for 30 minutes, and then at room temperature for 30 minutes. The solution was brought back to -78 °C and nonanal (0.86 mL, 5.00 mmol) was added. The mixture was stirred at room temperature for 1 hour, after which saturated $NaHCO_3$ was added. The mixture was extracted with Et_2O (3x), washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (1.27 g, 93%) was isolated as a colorless oil by flash chromatography using 20% EtOAc/hexanes. IR (ATR, ZnSe) ν = 3291, 2922, 2853, 2212, 1672, 1454, 1339, 1029, 745, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.29 (t, 2H, *J* = 7.5 Hz), 7.22-7.20 (m, 3H), 4.32 (q, 1H, *J* = 6.4 Hz), 2.82 (t, 2H, *J* = 7.5 Hz), 2.51 (td, 2H, *J* = 7.5, 2.0 Hz), 1.41-1.36 (m, 3H), 1.32-1.24 (m, 10H), 0.88 (t, 3H, *J* = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 140.7, 128.6, 128.5, 126.4, 84.8, 82.3, 62.9, 38.3, 35.2, 32.0, 29.7, 29.5, 29.4, 25.3, 22.8, 21.0, 14.3; HRMS-ESI calcd for $C_{19}H_{27}$ $[M+H]^+$-$[H_2O]$ 255.2107; found 255.2095.

1-Phenyltridec-3-yn-5-one (S16). To a -78 °C solution of oxalyl chloride (0.43 mL, 5.02 mmol) in CH_2Cl_2 (35 mL) was added DMSO (0.71 mL, 10.0 mmol) and stirring was continued at -78 °C for 15 minutes. A solution of 1-phenyltridec-3-yn-5-ol (**S15**, 1.14 g, 4.19 mmol) in CH_2Cl_2 (7 mL) was slowly added and the resulting solution was stirred at -78 °C for 15 minutes. Et_3N (3.5 mL, 25.1 mmol) was added, the solution was stirred at -78 °C for 20 minutes, and then allowed to reach room temperature over 40 minutes. Saturated $NaHCO_3$ was added and stirring was continued for 30 minutes. The resulting mixture was extracted with CH_2Cl_2 (3x), dried over Na_2SO_4 and concentrated *in vacuo*. The desired product (1.03 g, 91%) was isolated as a colorless oil by flash chromatography using 5% EtOAc/hexanes. IR (ATR, ZnSe) ν = 2925, 2853, 2211, 1669, 1495, 1454, 1242, 1158, 746, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.31 (t, 2H, *J* = 7.4 Hz), 7.25-7.21 (m, 3H), 2.89 (t, 2H, *J* = 7.5 Hz), 2.66 (t, 2H, *J* = 7.5 Hz), 2.48 (t, 2H, *J* = 7.5 Hz), 1.63-1.58 (m, 2H), 1.31-1.27 (m, 10H), 0.88 (t, 3H, *J* = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 188.6, 139.8, 128.7, 128.5, 126.8, 93.0, 81.5, 45.7, 34.1, 31.9, 29.4, 29.2, 29.1, 24.2, 22.8, 21.3, 14.3; HRMS-ESI calcd for $C_{19}H_{27}O$ $[M+H]^+$ 271.2056; found 271.2030.

(5,5-Difluorotridec-3-yn-1-yl)benzene (1f). 1-Phenyltridec-3-yn-5-one (**S16**, 865 mg, 3.20 mmol) was charged into a polypropylene vial. Me-DAST (0.78 mL, 8.00 mmol) was added and the mixture was stirred at 55 °C for 18 hours. It was brought back to 0 °C, diluted with EtOAc and poured into a stirring mixture of EtOAc and saturated $NaHCO_3$. The mixture was stirred for 30 minutes, after which the organic layer was separated, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (334 mg, 36%) was isolated as a colorless oil by flash chromatography using hexanes. IR (ATR, ZnSe) ν = 2926, 2855, 2254, 1455, 1341, 1194, 1008, 929, 747, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.30 (t, 2H, *J* = 7.4 Hz), 7.25-7.20 (m, 3H), 2.86 (t, 2H, *J* = 7.5 Hz), 2.56 (tt, 2H, *J* = 7.4, 4.8 Hz), 1.99-1.90 (m, 2H), 1.48-1.42 (m, 2H), 1.32-1.25 (m, 10H), 0.89 (t, 3H, *J* = 6.8 Hz); ^{19}F NMR ($CDCl_3$, 470 MHz) δ -81.3 (tt, 2F, *J* = 14.4, 4.5 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 140.0, 128.6, 128.5, 126.7, 115.2 (t, J_{C-F} = 231 Hz), 87.7 (t, J_{C-F} = 6.6 Hz), 74.9 (t, J_{C-F} = 40.4 Hz), 39.5 (t, J_{C-F} = 26.2 Hz), 34.3 (t, J_{C-F} = 1.9 Hz), 32.0, 29.4, 29.3, 29.1, 23.0 (t, J_{C-F} = 3.5 Hz), 22.8, 20.7 (t, J_{C-F} = 2.3 Hz), 14.3 ; HRMS-ESI calcd for $C_{19}H_{30}F_2N$ $[M+NH_4]^+$ 310.2341; found 310.2343.

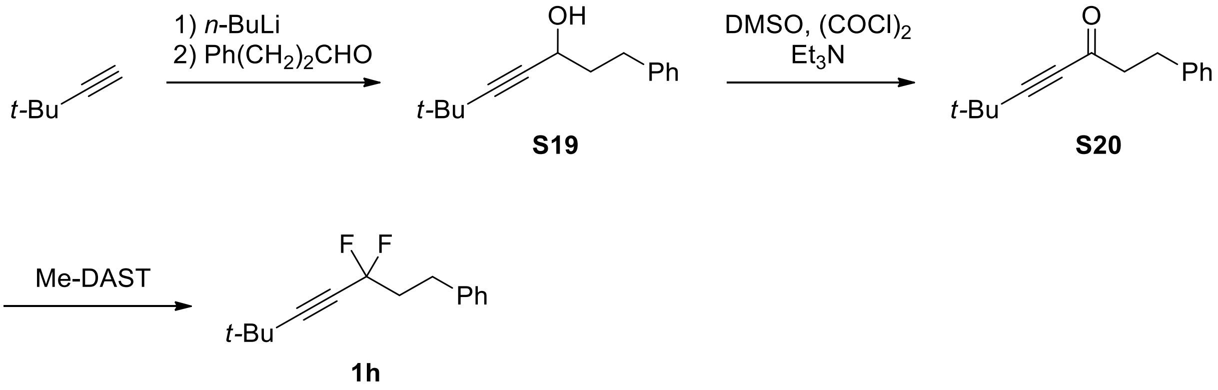


1-Phenyltridec-4-yn-3-ol (S17). To a -78 °C solution of 1-decyne (6.6 mL, 36.5 mmol) in THF (100 mL) was added *n*-BuLi (2.5 mol/L in hexanes, 13.4 mL, 33.4 mmol) and the mixture was stirred at -78 °C for 30 minutes, and then at room temperature for 30 minutes. The solution was brought back to -78 °C and hydrocinnamaldehyde (4.0 mL, 30.4 mmol) was added. The mixture was stirred at room temperature for 1 hour, after which saturated $NaHCO_3$ was added. The mixture was extracted with Et_2O (3x), washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (3.81 g, 46%) was isolated as a yellow oil by flash chromatography using 5% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[8]

1-Phenyltridec-4-yn-3-one (S18). To a -78 °C solution of oxalyl chloride (1.64 mL, 19.1 mmol) in CH_2Cl_2 (80 mL) was added DMSO (2.00 mL, 28.6 mmol) and stirring was continued at -78 °C for 15 minutes. A solution of 1-phenyltridec-4-yn-3-ol (**S17**, 2.60 g, 9.54 mmol) in CH_2Cl_2 (15 mL) was slowly added and the resulting solution was stirred at -78 °C for 15 minutes. Et_3N (8.0 mL, 57.3 mmol) was added, the solution was stirred at -78 °C for 20 minutes, and then allowed to reach room temperature over 40 minutes. Saturated $NaHCO_3$ was added and stirring was continued for 30 minutes. The resulting mixture was extracted with CH_2Cl_2 (3x), dried over Na_2SO_4 and concentrated *in vacuo*. The desired product (2.49 g, 97%) was isolated as a yellow oil by flash chromatography using 2% EtOAc/hexanes. IR (ATR, ZnSe) ν = 2925, 2855, 2212, 1673, 1454, 1243, 1159, 770, 738, 697cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.31-7.27 (m, 2H), 7.22-7.18 (m, 3H), 3.00-2.96 (m, 2H), 2.87 (m, 2H), 2.36 (t, 2H, *J* = 7.1 Hz), 1.61-1.53 (m, 2H), 1.41-1.36 (m, 2H), 1.32-1.27 (m, 8H), 0.88 (t, 3H, *J* = 6.7 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 187.3, 140.5, 128.6, 128.5, 126.4, 95.2, 80.9, 47.1, 31.9, 30.1, 29.3, 29.1, 29.0, 27.8, 22.8, 19.1, 14.2; HRMS-ESI calcd for $C_{19}H_{27}O$ $[M+H]^+$ 271.2056; found 271.2046.

(3,3-Difluorotridec-4-yn-1-yl)benzene (1h). 1-Phenyltridec-4-yn-3-one (**S18**, 1.00 g, 3.67 mmol) was charged into a polypropylene vial. Me-DAST (0.90 mL, 9.18 mmol) was added and the mixture was stirred at 55 °C for 24 hours. It was brought back to 0 °C, diluted with EtOAc and poured into a stirring mixture of EtOAc and saturated $NaHCO_3$. The mixture was stirred for 30 minutes, after which the organic layer was separated, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (284 mg, 26%) was isolated as a colorless oil by flash chromatography using hexanes. IR (ATR, ZnSe) ν = 2927, 2856, 2252, 1307, 1121, 1044, 934, 909, 734, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.32-7.29 (m, 2H), 7.23-7.20 (m, 3H), 2.89-2.85 (m, 2H), 2.38-2.25 (m, 4H), 1.59-1.53 (m, 2H), 1.43-1.37 (m, 2H), 1.32-1.27 (m, 8H), 0.88 (t, 3H, *J* = 6.7 Hz); ^{19}F NMR ($CDCl_3$, 470 MHz) δ -81.7 (tt, *J* = 14.5, 4.5 Hz, 2F); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 140.2, 128.7, 128.5, 126.4, 114.6 (t, J_{C-F} = 232 Hz), 89.4 (t, J_{C-F} = 6.6 Hz), 73.9 (t, J_{C-F} = 40.0 Hz), 41.4 (t, J_{C-F} = 26.9 Hz), 31.9, 29.4 (t, J_{C-F} = 4.0 Hz), 29.3, 29.1, 28.9, 27.9 (t,

$J_{C\text{-}F}$ = 3.8 Hz), 22.8, 18.5 (t, $J_{C\text{-}F}$ = 2.2 Hz), 14.2; HRMS-ESI calcd for $C_{19}H_{30}F_2N$ $[M+NH_4]^+$ 310.2341; found 310.2332.



S19

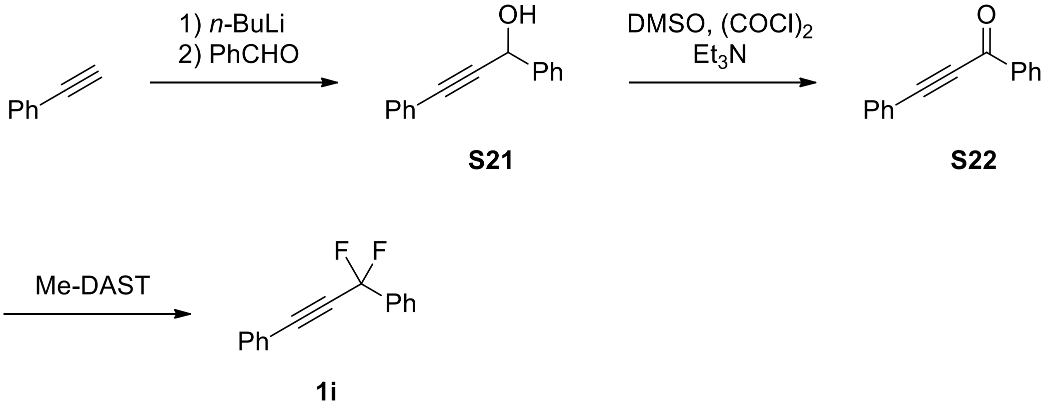
S20

1h

6,6-Dimethyl-1-phenylhept-4-yn-3-ol (S19). To a -78 °C solution of 3,3-dimethyl-1-butyne (0.80 mL, 6.50 mmol) in THF (20 mL) was added *n*-BuLi (2.5 mol/L in hexanes, 2.6 mL, 6.50 mmol) and the mixture was stirred at -78 °C for 30 minutes, and then at room temperature for 30 minutes. The solution was brought back to -78 °C and hydrocinnamaldehyde (0.86 mL, 5.91 mmol) was added. The mixture was stirred at room temperature for 1 hour, after which saturated $NaHCO_3$ was added. The mixture was extracted with Et_2O (3x), washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (470 mg, 37%) was isolated as a colorless oil by flash chromatography using 10% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[9]

6,6-Dimethyl-1-phenylhept-4-yn-3-one (S20). To a -78 °C solution of oxalyl chloride (0.22 mL, 2.57 mmol) in CH_2Cl_2 (15 mL) was added DMSO (0.36 mL, 5.14 mmol) and stirring was continued at -78 °C for 15 minutes. A solution of 6,6-dimethyl-1-phenylhept-4-yn-3-ol (**S19**, 463 mg, 2.14 mmol) in CH_2Cl_2 (6 mL) was slowly added and the resulting solution was stirred at -78 °C for 15 minutes. Et_3N (1.8 mL, 12.8 mmol) was added, the solution was stirred at -78 °C for 20 minutes, and then allowed to reach room temperature over 40 minutes. Saturated $NaHCO_3$ was added and stirring was continued for 30 minutes. The resulting mixture was extracted with CH_2Cl_2 (3x), dried over Na_2SO_4 and concentrated *in vacuo*. The desired product (396 mg, 86%) was isolated as a colorless oil by flash chromatography using 5% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[10]

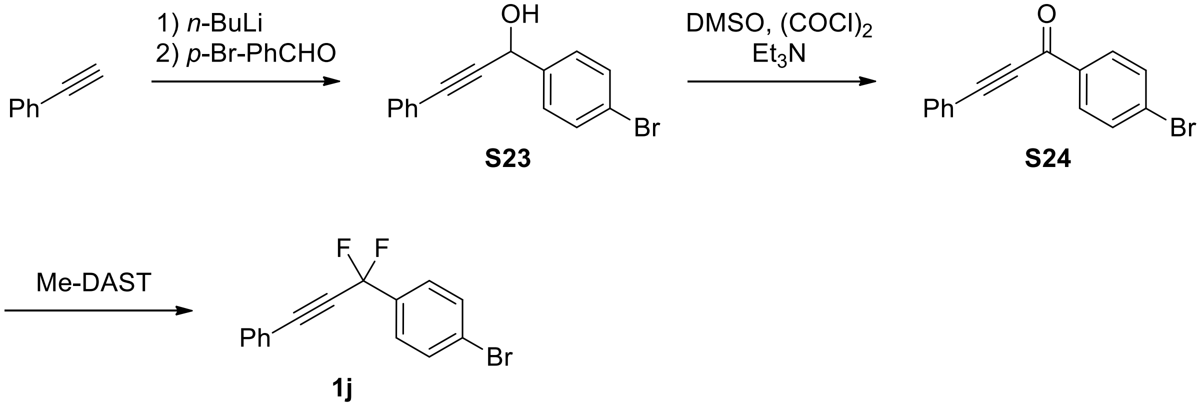
(3,3-Difluoro-6,6-dimethylhept-4-yn-1-yl)benzene (1h). 6,6-Dimethyl-1-phenylhept-4-yn-3-one (**S20**, 333 mg, 1.55 mmol) was charged into a polypropylene vial. Me-DAST (0.38 mL, 3.89 mmol) was added and the mixture was stirred at 45 °C for 24 hours. It was brought back to 0 °C, diluted with EtOAc and poured into a stirring mixture of EtOAc and saturated $NaHCO_3$. The mixture was stirred for 30 minutes, after which the organic layer was separated, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (128 mg, 35%) was isolated as a colorless oil by flash chromatography using hexanes. IR (ATR, ZnSe) ν = 3029, 2971, 2869, 2248, 1455, 1307, 1167, 1044, 899, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.30 (t, 2H, *J* = 7.5 Hz), 7.23-7.20 (m, 3H), 2.87-2.84 (m, 2H), 2.37-2.28 (m, 2H), 1.26 (s, 3H); ^{19}F NMR ($CDCl_3$, 470 MHz) δ -81.9 (t, 2F, *J* = 14.3 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 140.3, 128.7, 128.5, 126.4, 114.7 (t, $J_{C\text{-}F}$ = 232 Hz), 96.9 (t, $J_{C\text{-}F}$ = 6.7 Hz), 72.5 (t, $J_{C\text{-}F}$ = 40.1 Hz), 41.5 (t, $J_{C\text{-}F}$ = 26.9 Hz), 30.4 (t, $J_{C\text{-}F}$ = 1.9 Hz), 29.5 (t, $J_{C\text{-}F}$ = 3.8 Hz), 27.5 (t, $J_{C\text{-}F}$ = 2.0 Hz); HRMS-ESI calcd for $C_{15}H_{18}F$ $[M\text{-}F]^+$ 217.1387; found 217.1363.



1,3-Diphenylprop-2-yn-1-ol (S21). To a -78 °C solution of phenylacetylene (0.60 mL, 5.50 mmol) in THF (17 mL) was added *n*-BuLi (2.5 mol/L in hexanes, 2.2 mL, 5.50 mmol) and the mixture was stirred at -78 °C for 30 minutes, and then at room temperature for 30 minutes. The solution was brought back to -78 °C and benzaldehyde (0.51 mL, 5.00 mmol) was added. The mixture was stirred at room temperature for 1 hour, after which saturated $NaHCO_3$ was added. The mixture was extracted with Et_2O (3x), washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (893 mg, 86%) was isolated as a colorless oil by flash chromatography using 10% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[11]

1,3-Diphenylprop-2-yn-1-one (S22). To a -78 °C solution of oxalyl chloride (0.44 mL, 5.09 mmol) in CH_2Cl_2 (35 mL) was added DMSO (0.72 mL, 10.2 mmol) and stirring was continued at -78 °C for 15 minutes. A solution of 1,3-diphenylprop-2-yn-1-ol (**S21**, 883 mg, 4.24 mmol) in CH_2Cl_2 (7 mL) was slowly added and the resulting solution was stirred at -78 °C for 15 minutes. Et_3N (3.5 mL, 25.4 mmol) was added, the solution was stirred at -78 °C for 20 minutes, and then allowed to reach room temperature over 40 minutes. Saturated $NaHCO_3$ was added and stirring was continued for 30 minutes. The resulting mixture was extracted with CH_2Cl_2 (3x), dried over Na_2SO_4 and concentrated *in vacuo*. The desired product (627 mg, 72%) was isolated as a pale yellow oil by flash chromatography using 5% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[12]

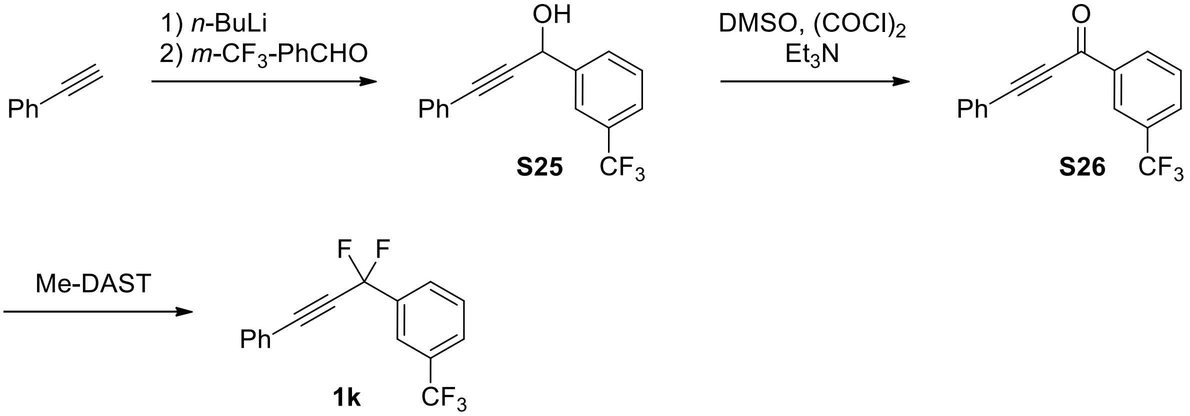
(3,3-Difluoroprop-1-yne-1,3-diyl)dibenzene (1i). 1,3-Diphenylprop-2-yn-1-one (**S22**, 512 mg, 2.48 mmol) was charged into a polypropylene vial. Me-DAST (0.61 mL, 6.21 mmol) was added and the mixture was stirred at 65 °C for 72 hours. It was brought back to 0 °C, diluted with EtOAc and poured into a stirring mixture of EtOAc and saturated $NaHCO_3$. The mixture was stirred for 30 minutes, after which the organic layer was separated, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (108 mg, 19%) was isolated as a colorless oil by flash chromatography using hexanes. Spectroscopic data was in agreement with the literature.[13]



1-(4-Bromophenyl)-3-phenylprop-2-yn-1-ol (S23). To a -78 °C solution of phenylacetylene (0.60 mL, 5.50 mmol) in THF (17 mL) was added *n*-BuLi (2.5 mol/L in hexanes, 2.2 mL, 5.50 mmol) and the mixture was stirred at -78 °C for 30 minutes, and then at room temperature for 30 minutes. The solution was brought back to -78 °C and *p*-bromobenzaldehyde (925 mg, 5.00 mmol) was added. The mixture was stirred at room temperature for 1 hour, after which saturated $NaHCO_3$ was added. The mixture was extracted with Et_2O (3x), washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (1.35 g, 94%) was isolated as a pale yellow oil by flash chromatography using 25% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[12]

1-(4-Bromophenyl)-3-phenylprop-2-yn-1-one (S24). To a -78 °C solution of oxalyl chloride (0.27 mL, 3.18 mmol) in CH_2Cl_2 (20 mL) was added DMSO (0.45 mL, 6.36 mmol) and stirring was continued at -78 °C for 15 minutes. A solution of 1-(4-bromophenyl)-3-phenylprop-2-yn-1-ol (**S23**, 761 mg, 2.65 mmol) in CH_2Cl_2 (7 mL) was slowly added and the resulting solution was stirred at -78 °C for 15 minutes. Et_3N (2.2 mL, 15.9 mmol) was added, the solution was stirred at -78 °C for 20 minutes, and then allowed to reach room temperature over 40 minutes. Saturated $NaHCO_3$ was added and stirring was continued for 30 minutes. The resulting mixture was extracted with CH_2Cl_2 (3x), dried over Na_2SO_4 and concentrated *in vacuo*. The desired product (688 mg, 91%) was isolated as a pale yellow solid by flash chromatography using 2% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[14]

1-Bromo-4-(1,1-difluoro-3-phenylprop-2-yn-1-yl)benzene (1j). 1-(4-Bromophenyl)-3-phenylprop-2-yn-1-one (**S24**, 237 mg, 0.831 mmol) was charged into a polypropylene vial. Me-DAST (0.20 mL, 2.08 mmol) was added and the mixture was stirred at 75 °C for 24 hours. It was brought back to 0 °C, diluted with EtOAc and poured into a stirring mixture of EtOAc and saturated $NaHCO_3$. The mixture was stirred for 30 minutes, after which the organic layer was separated, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (25 mg, 10%) was isolated as a colorless oil by flash chromatography using hexanes. Spectroscopic data was in agreement with the literature.[13]

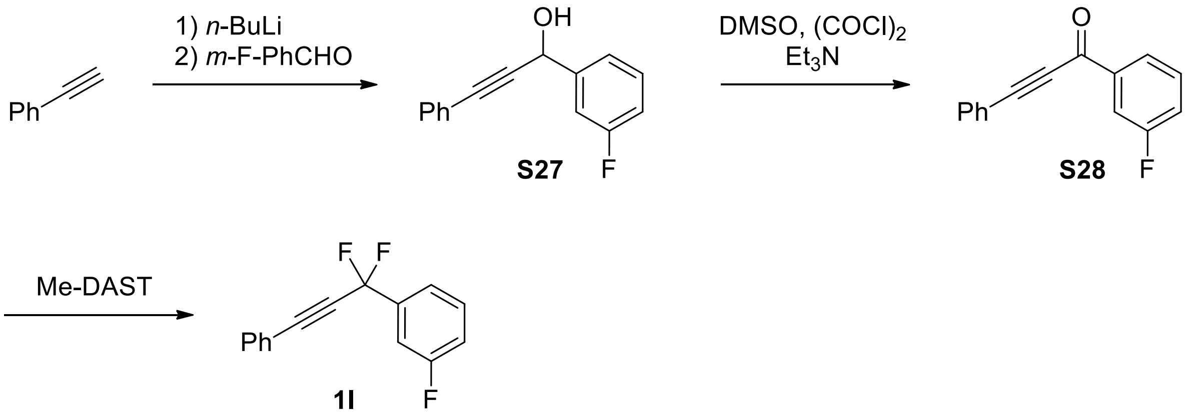


3-Phenyl-1-(3-(trifluoromethyl)phenyl)prop-2-yn-1-ol (S25). To a -78 °C solution of phenylacetylene (0.60 mL, 5.50 mmol) in THF (17 mL) was added *n*-BuLi (2.5 mol/L in hexanes, 2.2 mL, 5.50 mmol) and the mixture was stirred at -78 °C for 30 minutes, and then at room temperature for 30 minutes. The solution was brought back to -78 °C and 3-(trifluoromethyl)benzaldehyde (0.67 mL, 5.00 mmol) was added. The mixture was stirred at room temperature for 1 hour, after which saturated $NaHCO_3$ was added. The mixture was extracted with Et_2O (3x), washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (1271 mg, 92%) was isolated as a pale yellow oil by flash chromatography using 20% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[15]

3-Phenyl-1-(3-(trifluoromethyl)phenyl)prop-2-yn-1-one (S26). To a -78 °C solution of oxalyl chloride (0.46 mL, 5.40 mmol) in CH_2Cl_2 (35 mL) was added DMSO (0.77 mL, 10.8 mmol) and stirring was continued at -78 °C for 15 minutes. A solution of 3-phenyl-

1-(3-(trifluoromethyl)phenyl)prop-2-yn-1-ol (**S25**, 1243 mg, 4.50 mmol) in CH_2Cl_2 (10 mL) was slowly added and the resulting solution was stirred at -78 °C for 15 minutes. Et_3N (3.8 mL, 27.0 mmol) was added, the solution was stirred at -78 °C for 20 minutes, and then allowed to reach room temperature over 40 minutes. Saturated $NaHCO_3$ was added and stirring was continued for 30 minutes. The resulting mixture was extracted with CH_2Cl_2 (3x), dried over Na_2SO_4 and concentrated *in vacuo*. The desired product (1052 mg, 85%) was isolated as a yellow solid by flash chromatography using 5% EtOAc/hexanes. mp 58-60 °; IR (ATR, ZnSe) ν = 3069, 2203, 1645, 1332, 1276, 1160, 1111, 927, 758, 687 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.41 (d, 1H, *J* = 7.8 Hz), 7.88 (d, 1H, *J* = 7.8 Hz), 7.70-7.66 (m, 3H), 7.52 (t, 1H, *J* = 7.5 Hz), 7.44 (t, 2H, *J* = 7.5 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.9 (s, 3F); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.5, 137.4, 133.3, 132.7, 131.5 (q, J_{C-F} = 33.0 Hz), 131.3, 130.5, (q, J_{C-F} = 3.7 Hz), 129.5, 128.9, 126.4 (q, J_{C-F} = 3.9 Hz), 123.7 (q, J_{C-F} = 273 Hz), 119.8, 94.6, 86.5; HRMS-ESI calcd for $C_{16}H_{10}F_3O$ $[M+H]^+$ 275.0678; found 275.0668.

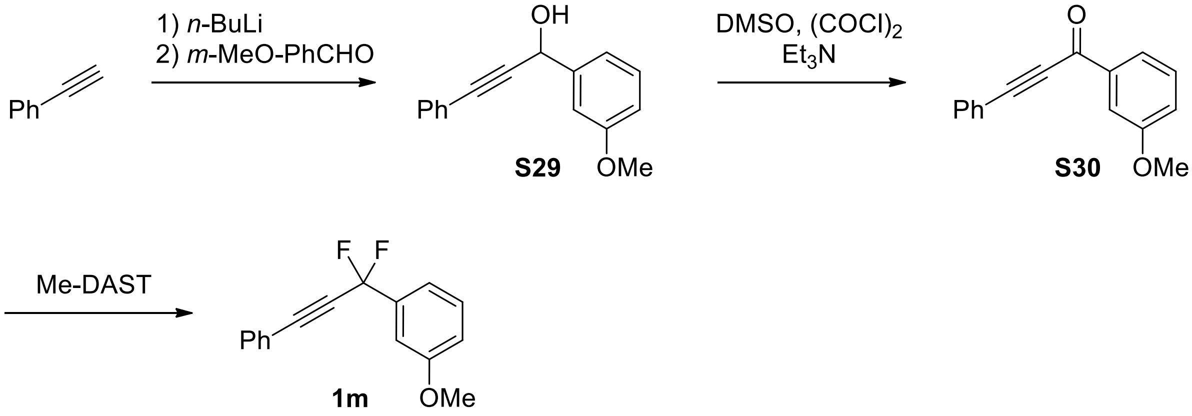
1-(1,1-Difluoro-3-phenylprop-2-yn-1-yl)-3-(trifluoromethyl)benzene (1k). 3-Phenyl-1-(3-(trifluoromethyl)phenyl)prop-2-yn-1-ol (**S26**, 361 mg, 1.32 mmol) was charged into a polypropylene vial. Me-DAST (0.32 mL, 3.29 mmol) was added and the mixture was stirred at 65 °C for 72 hours. It was brought back to 0 °C, diluted with EtOAc and poured into a stirring mixture of EtOAc and saturated $NaHCO_3$. The mixture was stirred for 30 minutes, after which the organic layer was separated, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (110 mg, 28%) was isolated as a colorless oil by flash chromatography using hexanes. IR (ATR, ZnSe) ν = 3084, 2239, 1491, 1445, 1335, 1276, 1121, 1017, 905, 687 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.94 (d, 1H, *J* = 7.8 Hz), 7.76 (d, 1H, *J* = 7.7 Hz), 7.62 (t, 1H, *J* = 7.8 Hz), 7.55 (d, 2H, *J* = 7.2 Hz), 7.44 (t, 1H, *J* = 7.4 Hz), 7.38 (t, 2H, *J* = 7.4 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.8 (s, 3F), -75.6 (s, 2F); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.3 (t, J_{C-F} = 28.9 Hz), 132.2 (t, J_{C-F} = 2.2 Hz), 131.2 (q, J_{C-F} = 32.9 Hz), 130.3, 129.3, 128.9 (m), 128.6, 127.5 (m), 123.6 (q, J_{C-F} = 272 Hz), 122.5 (m), 119.7 (J_{C-F} = 2.8 Hz), 111.9 (t, J_{C-F} = 232 Hz), 89.6 (t, J_{C-F} = 6.0 Hz), 81.1 (t, J_{C-F} = 41.5 Hz); HRMS-APPI calcd for $C_{16}H_{10}F_5$ $[M+H]^+$ 297.0697; found 297.0672.



1-(3-Fluorophenyl)-3-phenylprop-2-yn-1-ol (S27). To a -78 °C solution of phenylacetylene (0.60 mL, 5.50 mmol) in THF (17 mL) was added *n*-BuLi (2.5 mol/L in hexanes, 2.2 mL, 5.50 mmol) and the mixture was stirred at -78 °C for 30 minutes, and then at room temperature for 30 minutes. The solution was brought back to -78 °C and 3-fluorobenzaldehyde (0.53 mL, 5.00 mmol) was added. The mixture was stirred at room temperature for 1 hour, after which saturated $NaHCO_3$ was added. The mixture was extracted with Et_2O (3x), washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (1088 mg, 96%) was isolated as a pale yellow oil by flash chromatography using 20% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[15]

1-(3-Fluorophenyl)-3-phenylprop-2-yn-1-one (S28). To a -78 °C solution of oxalyl chloride (0.46 mL, 5.40 mmol) in CH_2Cl_2 (35 mL) was added DMSO (0.77 mL, 10.8 mmol) and stirring was continued at -78 °C for 15 minutes. A solution of 1-(3-fluorophenyl)-3-phenylprop-2-yn-1-ol (**S27**, 1243 mg, 4.50 mmol) in CH_2Cl_2 (10 mL) was slowly added and the resulting solution was stirred at -78 °C for 15 minutes. Et_3N (3.8 mL, 27.0 mmol) was added, the solution was stirred at -78 °C for 20 minutes, and then allowed to reach room temperature over 40 minutes. Saturated $NaHCO_3$ was added and stirring was continued for 30 minutes. The resulting mixture was extracted with CH_2Cl_2 (3x), dried over Na_2SO_4 and concentrated *in vacuo*. The desired product (1052 mg, 85%) was isolated a yellow solid by flash chromatography using 10% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[16]

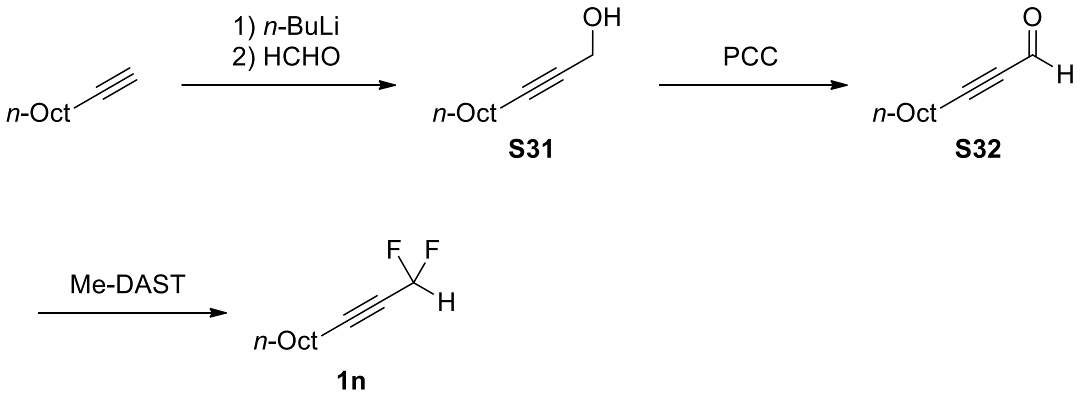
1-(1,1-Difluoro-3-phenylprop-2-yn-1-yl)-3-fluorobenzene (1l). 1-(3-Fluorophenyl)-3-phenylprop-2-yn-1-one (**S28**, 319 mg, 1.42 mmol) was charged into a polypropylene vial. Me-DAST (0.35 mL, 3.56 mmol) was added and the mixture was stirred at 65 °C for 72 hours. It was brought back to 0 °C, diluted with EtOAc and poured into a stirring mixture of EtOAc and saturated $NaHCO_3$. The mixture was stirred for 30 minutes, after which the organic layer was separated, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (87 mg, 25%) was isolated as a colorless oil by flash chromatography using hexanes. IR (ATR, ZnSe) ν = 3065, 2238, 1597, 1488, 1448, 1298, 1118, 1013, 877, 685 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.55-7.53 (m, 3H), 7.47-7.42 (m, 3H), 7.39-7.36 (m, 2H), 7.19 (td, J = 8.3, 1.9 Hz); ^{19}F NMR ($CDCl_3$, 470 MHz) δ -75.3 (s, 2F), -111.5 (m, 1F); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 162.7 (d, J_{C-F} = 248 Hz), 138.6 (td, J_{C-F} = 29.0, 7.6 Hz), 132.3 (t, J_{C-F} = 2.3 Hz), 130.5 (d, J = 8.1 Hz), 130.3, 128.7, 121.3 (td, J_{C-F} = 4.7, 3.1 Hz), 120.0 (t, J_{C-F} = 2.8 Hz), 117.9 (dt, J_{C-F} = 21.1, 1.6 Hz), 113.0 (dt, J_{C-F} = 23.9, 4.5 Hz), 112.0 (td, J_{C-F} = 232, 2.4 Hz), 89.3 (t, J_{C-F} = 6.0 Hz), 81.4 (t, J_{C-F} = 41.5 Hz); HRMS-ESI calcd for $C_{15}H_9F_2$ $[M-F]^+$ 227.0667; found 227.0663.



1-(3-Methoxyphenyl)-3-phenylprop-2-yn-1-ol (S29). To a -78 °C solution of phenylacetylene (0.60 mL, 5.50 mmol) in THF (17 mL) was added *n*-BuLi (2.5 mol/L in hexanes, 2.2 mL, 5.50 mmol) and the mixture was stirred at -78 °C for 30 minutes, and then at room temperature for 30 minutes. The solution was brought back to -78 °C and *m*-anisaldehyde (0.61 mL, 5.00 mmol) was added. The mixture was stirred at room temperature for 1 hour, after which saturated $NaHCO_3$ was added. The mixture was extracted with Et_2O (3x), washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (852 mg, 72%) was isolated as a pale yellow oil by flash chromatography using 20% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[11]

1-(3-Methoxyphenyl)-3-phenylprop-2-yn-1-one (S30). To a -78 °C solution of oxalyl chloride (0.37 mL, 4.29 mmol) in CH_2Cl_2 (25 mL) was added DMSO (0.61 mL, 8.58 mmol) and stirring was continued at -78 °C for 15 minutes. A solution of 1-(3-methoxyphenyl)-3-phenylprop-2-yn-1-ol (**S29**, 852 mg, 3.58 mmol) in CH_2Cl_2 (11 mL) was slowly added and the resulting solution was stirred at -78 °C for 15 minutes. Et_3N (3.0 mL, 21.5 mmol) was added, the solution was stirred at -78 °C for 20 minutes, and then allowed to reach room temperature over 40 minutes. Saturated $NaHCO_3$ was added and stirring was continued for 30 minutes. The resulting mixture was extracted with CH_2Cl_2 (3x), dried over Na_2SO_4 and concentrated *in vacuo*. The desired product (758 mg, 90%) was isolated as an orange oil by flash chromatography using 10% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[13]

1-(1,1-Difluoro-3-phenylprop-2-yn-1-yl)-3-methoxybenzene (1m). 1-(3-Methoxyphenyl)-3-phenylprop-2-yn-1-one (**S30**, 237 mg, 0.831 mmol) was charged into a polypropylene vial. Me-DAST (0.20 mL, 2.08 mmol) was added and the mixture was stirred at 75 °C for 24 hours. It was brought back to 0 °C, diluted with EtOAc and poured into a stirring mixture of EtOAc and saturated $NaHCO_3$. The mixture was stirred for 30 minutes, after which the organic layer was separated, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (25 mg, 10%) was isolated as a colorless oil by flash chromatography using hexanes. Spectroscopic data was in agreement with the literature.[13]

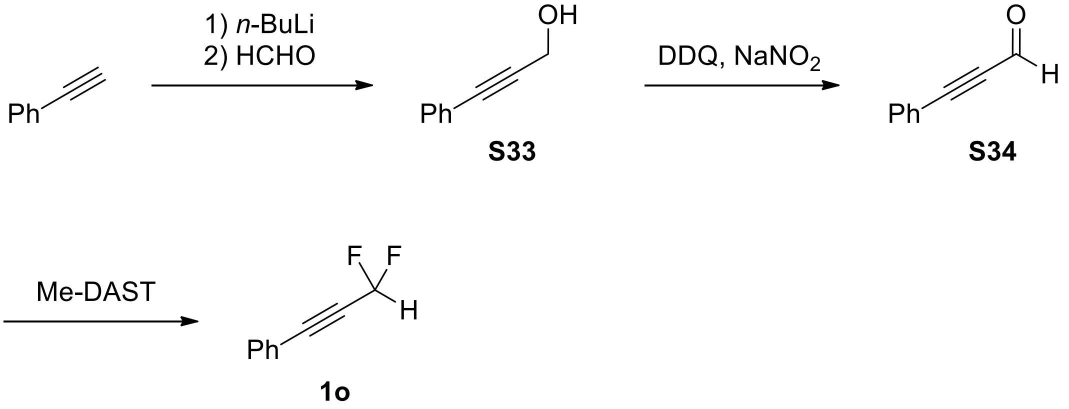


Undec-2-yn-1-ol (S31). To a -78 °C solution of 1-decyne (1.59 mL, 8.80 mmol) in THF (27 mL) was added *n*-BuLi (2.5 mol/L in hexanes, 3.5 mL, 8.80 mmol) and the mixture was stirred at -78 °C for 30 minutes, and then at room temperature for 30 minutes. The solution was brought back to -78 °C and paraformaldehyde (240 mg, 8.00 mmol) was added. The mixture was stirred at room temperature for 1 hour, after which saturated $NaHCO_3$ was added. The mixture was extracted with Et_2O (3x), washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (1072 mg, 80%) was isolated as a colorless oil by flash chromatography using 10% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[17]

Undec-2-ynal (S32). PCC was charged into a round-bottom flask, after which CH_2Cl_2 (25 mL) was added, and the resulting suspension was stirred for 30 minutes at room temperature. A solution of undec-2-yn-1-ol (**S31**, 1068 mg, 6.35 mmol) in CH_2Cl_2 (7 mL) was then added dropwise, and the resulting mixture was stirred at room temperature for 1 hour. The solution was then filtered through a short pad of silica, washing with CH_2Cl_2. The solvent was removed *in vacuo*. The desired compound (723 mg, 68%) was isolated as a yellow oil by flash chromatography using 5% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[17]

1,1-Difluoroundec-2-yne (1n). Undec-2-ynal (**S32**, 643 mg, 3.87 mmol) was charged into a polypropylene vial. Me-DAST (0.94 mL, 9.67 mmol) was added and the mixture was stirred at room temperature for 18 hours. It was then brought to 0 °C, diluted with EtOAc and poured into a stirring mixture of EtOAc and saturated $NaHCO_3$. The mixture was stirred for 30 minutes, after which the organic layer was separated, dried over

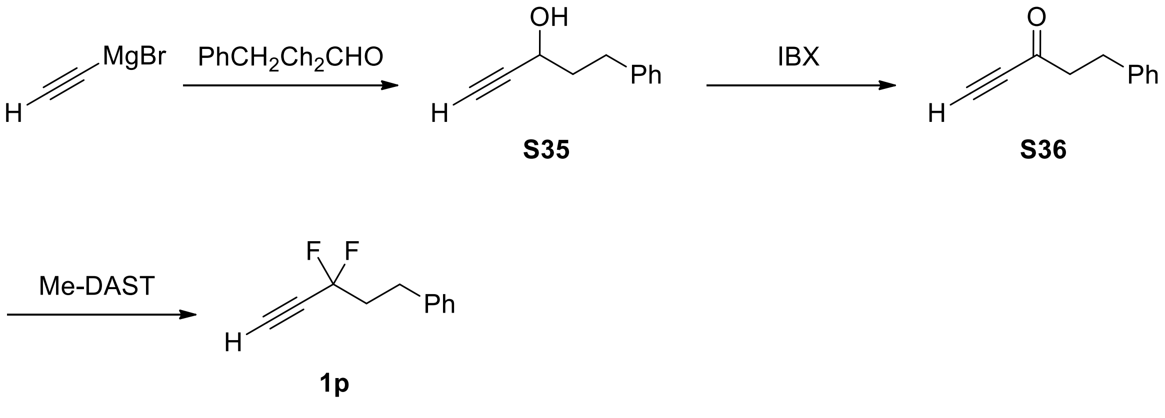
Na_2SO_4 and concentrated *in vacuo*. The desired compound (380 mg, 52%) was isolated as a colorless oil by flash chromatography using hexanes. IR (ATR, ZnSe) ν = 2925, 2856, 2338, 2254, 1459, 1372, 1165, 1038, 835, 723 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.17 (t, 1H, J = 55.6 Hz), 2.30-2.25 (m, 2H), 1.55 (p, 2H, J = 7.3 Hz), 1.38 (p, 2H, J = 6.7 Hz), 1.32-1.24 (m, 8H); ^{19}F NMR ($CDCl_3$, 470 MHz) δ -103.9 (dt, 2F, J = 56.0, 5.3 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 104.0 (t, J_{C-F} = 231 Hz), 91.0 (t, J_{C-F} = 7.0 Hz), 72.3 (t, J_{C-F} = 33.5 Hz), 31.9, 29.3, 29.1, 28.9, 27.8 (t, J_{C-F} = 2.3 Hz), 22.8, 18.5 (t, J_{C-F} = 2.6 Hz), 14.2; HRMS-ESI calcd for $C_{22}H_{40}F_2N$ $[2M+NH_4]^+$ 394.3091; found 394.3119.



3-Phenylprop-2-yn-1-ol (S33). To a -78 °C solution of phenylacetylene (0.90 mL, 8.20 mmol) in THF (20 mL) was added *n*-BuLi (2.5 mol/L in hexanes, 3.3 mL, 8.20 mmol) and the mixture was stirred at -78 °C for 30 minutes, and then at room temperature for 30 minutes. The solution was brought back to -78 °C and paraformaldehyde (224 mg, 7.45 mmol) was added. The mixture was stirred at room temperature for 1 hour, after which saturated $NaHCO_3$ was added. The mixture was extracted with Et_2O (3x), washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (861 mg, 87%) was isolated as a colorless oil by flash chromatography using 20% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[18]

3-Phenylpropiolaldehyde (S34). DDQ (148 mg, 0.651 mmol) was charged into a round-bottom flask, after which CH_2Cl_2 (25 mL) and AcOH (3 mL) were added, followed by a solution of 3-phenylprop-2-yn-1-ol (**S33**, 860 mg, 6.51 mmol) in CH_2Cl_2 (5 mL). $NaNO_2$ (45 mg, 0.651 mmol) was added in one portion, and the mixture was stirred under air and at room temperature for 22 hours. The solution was then filtered through a short pad of silica, washing with CH_2Cl_2. The solvent was removed *in vacuo*. The desired compound (575 mg, 68%) was isolated as a yellow oil by flash chromatography using 10% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[19]

(3,3-Difluoroprop-1-yn-1-yl)benzene (1o). 3-Phenylpropiolaldehyde (**S34**, 296 mg, 2.27 mmol) was charged into a polypropylene vial. Me-DAST (0.56 mL, 5.69 mmol) was added and the mixture was stirred at room temperature for 18 hours. It was then brought to 0 °C, diluted with EtOAc and poured into a stirring mixture of EtOAc and saturated $NaHCO_3$. The mixture was stirred for 30 minutes, after which the organic layer was separated, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (157 mg, 45%) was isolated as a colorless oil by flash chromatography using hexanes. IR (ATR, ZnSe) ν = 3063, 2975, 2248, 2221, 1490, 1369, 1258, 1086, 967, 687 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.52 (d, 2H, J = 7.2 Hz), 7.43 (t, 1H, J = 7.4 Hz), 7.37 (t, 2H, J = 7.4 Hz), 6.42 (t, 1H, J = 55.1 Hz); ^{19}F NMR ($CDCl_3$, 470 MHz) δ -105.3 (t, 2F, J = 54.8 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 132.3 (t, $J_{C\text{-}F}$ = 2.7 Hz), 130.3, 128.7, 120.0 (t, $J_{C\text{-}F}$ = 3.1 Hz), 104.4 (t, $J_{C\text{-}F}$ = 232 Hz), 88.6 (t, $J_{C\text{-}F}$ = 7.3 Hz), 79.9 (t, $J_{C\text{-}F}$ = 33.9 Hz); HRMS-ESI calcd for $C_9H_7F_2$ $[M+H]^+$ 153.0510; found 153.0517.



5-Phenylpent-1-yn-3-ol (S35). To a 0 °C solution of hydrocinnamaldehyde (1.46 mL, 10 mmol) in Et_2O (20 mL) was slowly added ethynylmagnesium bromide (0.5 mol/L in THF, 24 mL, 12 mmol), and the resulting mixture was stirred at 0 °C for 30 minutes, and then at room temperature for 2 hours. Saturated NH_4Cl was added and the mixture was extracted with Et_2O (3x), washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The desired compound (1.40 g, 88%) was isolated as a pale yellow oil by flash chromatography using 20% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[20]

5-Phenylpent-1-yn-3-one (S36). To a 30 °C solution of 5-phenylpent-1-yn-3-ol (**S35**, 728 mg, 4.54 mmol) in THF (7 mL) and DMSO (29 mL) was added 2-iodoxybenzoic acid (IBX, 3.82 g, 13.6 mmol). The resulting mixture was stirred at 30 °C for 5 hours, after which water was added and stirring was continued for 10 minutes. The suspension was filtered to remove the solids. It was then extracted with Et_2O, washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The desired compound (636 mg, 89%) was isolated as a pale yellow oil by flash chromatography using 10% EtOAc/hexanes. Spectroscopic data was in agreement with the literature.[21]

(3,3-Difluoropent-4-yn-1-yl)benzene (1p). 5-Phenylpent-1-yn-3-one (**S36**, 574 mg, 3.46 mmol) was charged into a polypropylene vial. Me-DAST (0.85 mL, 8.66 mmol) was added and the mixture was stirred at 55 °C for 5 hours. It was brought back to 0 °C, diluted with EtOAc and poured into a stirring mixture of EtOAc and saturated $NaHCO_3$. The mixture was stirred for 30 minutes, after which the organic layer was separated, dried over Na_2SO_4 and concentrated *in vacuo*. The desired compound (267 mg, 43%) was isolated as a colorless oil by flash chromatography using hexanes. IR (ATR, ZnSe) ν = 3302, 3030, 2937, 2135, 1455, 1303, 1171, 1047, 952, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.31 (t, 2H, *J* = 7.4 Hz), 7.24-7.20 (m, 2H), 2.90-2.87 (m, 2H), 2.81 (t, 1H, *J* = 5.0 Hz), 2.41-2.32 (m, 2H); ^{19}F NMR ($CDCl_3$, 470 MHz) δ -84.7 (td, 2F, *J* = 14.4, 5.2 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 139.8, 128.8, 128.4, 126.6, 113.9 (t, $J_{C\text{-}F}$ = 234 Hz), 76.5 (t, $J_{C\text{-}F}$ = 40.9 Hz), 75.6 (t, $J_{C\text{-}F}$ = 6.9 Hz), 41.0 (t, $J_{C\text{-}F}$ = 25.8 Hz), 29.1 (t, $J_{C\text{-}F}$ = 4.1 Hz); HRMS-ESI calcd for $C_{11}H_{10}F$ $[M-F]^+$ 161.0761; found 161.0784.

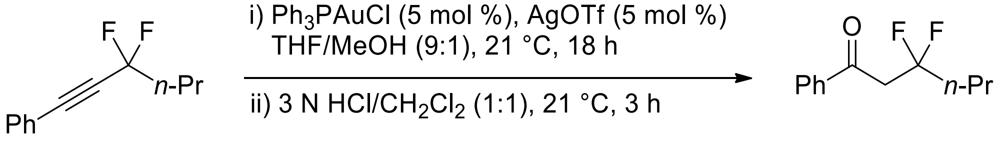
4. Gold-catalyzed formal hydration of propargylic *gem*-difluorides

General procedure A for the gold-catalyzed formal hydration of propargylic *gem*-difluorides: Chloro(triphenylphosphine)gold(I) (5 mol %) and silver trifluoromethane-sulfonate (5 mol %) were charged into a glass vial. A magnetic stir bar was added, and then the vial was sealed and flushed with argon, after which a solution of the propayglic *gem*-difluoride (1 equiv) in THF/MeOH (9:1, 0.1 M) was added. The vial was wrapped with aluminum foil, and the reaction mixture was stirred at room temperature for 18 hours. The reaction was then transferred to a round-bottom flask, using CH_2Cl_2 to rinse the vial. The volatiles were removed *in vacuo*, after which 3 mL of CH_2Cl_2 and 3 mL of HCl 3 N were added. The mixture was stirred at room temperature for 3 hours. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 two more times. The combined organic layers were washed with water, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was the purified by flash chromatography.

General procedure B for the gold-catalyzed formal hydration of propargylic *gem*-difluorides: Chloro(triphenylphosphine)gold(I) (5 mol %) and silver trifluoromethane-sulfonate (5 mol %) were charged into a glass vial. A magnetic stir bar was added, and then the vial was sealed and flushed with argon, after which a solution of the propayglic *gem*-difluoride (1 equiv) in THF/MeOH (9:1, 0.1 M) was added. The vial was wrapped with aluminum foil, and the reaction mixture was stirred at room temperature for 18 hours. The reaction was then transferred to a round-bottom flask, using CH_2Cl_2 to rinse the vial. The volatiles were removed *in vacuo*, after which 3 mL of CH_2Cl_2 and 3 mL of HCl 3 N were added. The mixture was stirred at room temperature for 24 hours. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 two more times. The combined organic layers were washed with water, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was the purified by flash chromatography.

General procedure C for the gold-catalyzed formal hydration of propargylic *gem*-difluorides: Chloro(triphenylphosphine)gold(I) (5 mol %) and silver trifluoromethane-sulfonate (5 mol %) were charged into a glass vial. A magnetic stir bar was added, and then the vial was sealed and flushed with argon, after which a solution of the propayglic *gem*-difluoride (1 equiv) in THF/MeOH (9:1, 0.1 M) was added. The vial was wrapped with aluminum foil, and the reaction mixture was stirred at 40 °C for 48 hours. The reaction was then transferred to a round-bottom flask, using CH_2Cl_2 to rinse the vial. The volatiles were removed *in vacuo*, after which 3 mL of CH_2Cl_2 and 3 mL of HCl 3 N were added. The mixture was stirred at room temperature for 3 hours. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 two more times. The combined organic layers were washed with water, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was the purified by flash chromatography.

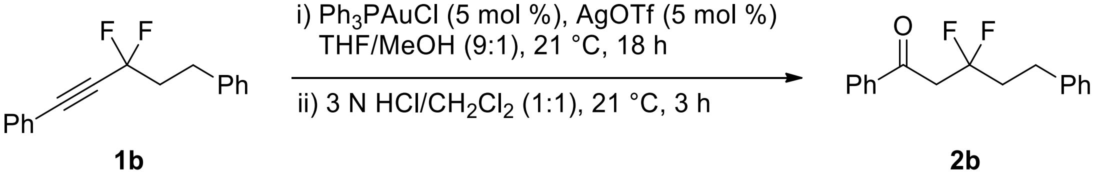
General procedure D for the gold-catalyzed formal hydration of propargylic *gem*-difluorides: Chloro(triphenylphosphine)gold(I) (5 mol %) and silver trifluoromethanesulfonate (5 mol %) were charged into a glass vial. A magnetic stir bar was added, and then the vial was sealed and flushed with argon, after which a solution of the propayglic *gem*-difluoride (1 equiv) in THF/MeOH (9:1, 0.1 M) was added. The vial was wrapped with aluminum foil, and the reaction mixture was stirred at 40 °C for 48 hours. The reaction was then transferred to a round-bottom flask, using CH_2Cl_2 to rinse the vial. The volatiles were removed *in vacuo*, after which 3 mL of CH_2Cl_2 and 3 mL of HCl 3 N were added. The mixture was stirred at room temperature for 24 hours. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 two more times. The combined organic layers were washed with water, dried over Na_2SO_4 and concentrated *in vacuo.* The residue was the purified by flash chromatography.



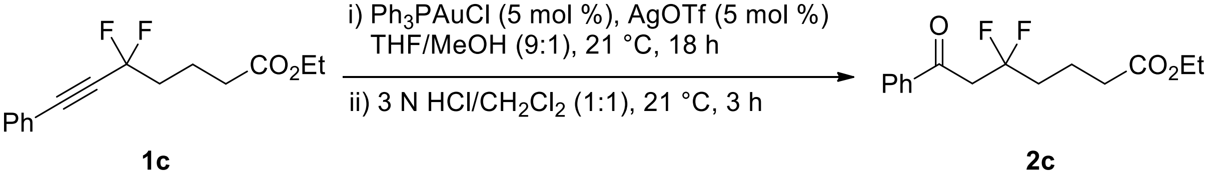
1a **2a**

3,3-Difluoro-1-phenylhexan-1-one (2a). Following general procedure A for the gold-catalyzed formal hydration of propargylic *gem*-difluoride **1a** on a 0.154 mmol scale, the desired product (26.9 mg, 82%) was isolated as a colorless oil by flash chromatography using 5% EtOAc/hexanes. IR (ATR, ZnSe) ν = 2966, 2935, 2878, 1683, 1449, 1139, 984, 861, 753, 687 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.97 (d, 2H, *J* = 8.2 Hz), 7.60 (t, 1H, *J* = 7.4 Hz), 7.49 (t, 2H, *J* = 7.8 Hz), 3.54 (t, 2H, *J* = 14.5 Hz), 2.11-2.01 (m, 2H), 1.59-

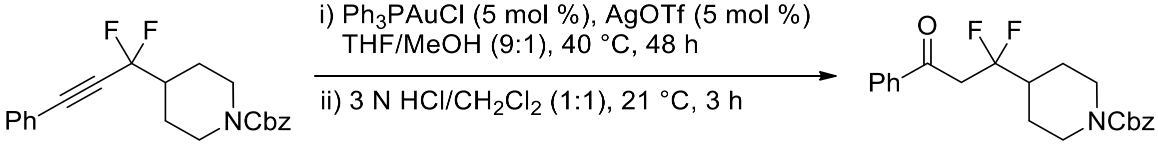
1.52 (sext, 2H, J = 7.5 Hz), 0.98 (t, 3H, J = 7.4 Hz); ^{19}F NMR (CDCl$_3$, 470 MHz) δ -91.5 (p, 2F, J = 16.1 Hz); ^{13}C NMR (CDCl$_3$, 126 MHz) δ 194.0 (t, $J_{C\text{-}F}$ = 5.7 Hz), 136.9 (t, $J_{C\text{-}F}$ = 1.7 Hz), 133.8, 128.9, 128.7, 123.2 (t, $J_{C\text{-}F}$ = 242 Hz), 44.6 (t, $J_{C\text{-}F}$ = 26.7 Hz), 38.4 (t, $J_{C\text{-}F}$ = 23.8 Hz), 15.9 (t, $J_{C\text{-}F}$ = 4.8 Hz), 14.0. HRMS-ESI calcd for $C_{12}H_{15}F_2O$ [M+H]$^+$ 213.1086; found 213.1085.



3,3-Difluoro-1,5-diphenylpentan-1-one (2b). Following general procedure A for the gold-catalyzed formal hydration of propargylic *gem*-difluoride **1b** on a 0.117 mmol scale, the desired product (23.2 mg, 72%) was isolated as a colorless oil by flash chromatography using 5% EtOAc/hexanes. IR (ATR, ZnSe) ν = 3062, 3028, 2933, 1683, 1449, 1363, 1049, 908, 731, 687 cm$^{-1;}$ ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.96-7.94 (m, 2H), 7.60 (t, 1H, J = 7.4 Hz), 7.49 (t, 2H, J = 7.8 Hz), 7.28 (t, 2H, J = 7.6 Hz), 7.22-7.17 (m, 3H), 3.57 (t, 2H, J = 14.4 Hz), 2.88-2.85 (m, 2H), 2.48-2.37 (m, 2H); ^{19}F NMR (CDCl$_3$, 470 MHz) δ -92.1 (p, 2F, J = 15.9 Hz); ^{13}C NMR (CDCl$_3$, 126 MHz) δ 193.8 (t, $J_{C\text{-}F}$ = 5.9 Hz), 140.5, 136.8 (t, $J_{C\text{-}F}$ = 1.7 Hz), 133.9, 128.9, 128.7, 128.6, 128.5, 126.4, 122.7 (t, $J_{C\text{-}F}$ = 243 Hz), 44.7 (t, $J_{C\text{-}F}$ = 26.6 Hz), 38.1 (t, $J_{C\text{-}F}$ = 24.0 Hz), 28.6 (t, $J_{C\text{-}F}$ = 5.1 Hz); HRMS-ESI calcd for $C_{17}H_{17}F_2O$ [M+H]$^+$ 275.1242; found 275.1244.

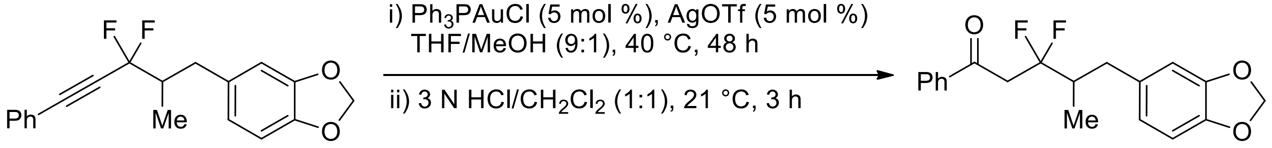


Ethyl 5,5-difluoro-7-oxo-7-phenylheptanoate (2c). Following general procedure A for the gold-catalyzed formal hydration of propargylic *gem*-difluoride **1c** on a 0.113 mmol scale, the desired product (26.8 mg, 84%) was isolated as a colorless oil by flash chromatography using 15% EtOAc/hexanes. IR (ATR, ZnSe) ν = 2982, 2256, 1729, 1688, 1449, 1367, 1182, 908, 728, 688 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, 2H, *J* = 8.5 Hz), 7.61 (t, 1H, *J* = 7.4 Hz), 7.49 (t, 2H, *J* = 7.8 Hz), 4.14 (q, 2H, *J* = 7.1 Hz), 3.56 (t, 2H, *J* = 14.4 Hz), 2.38 (t, 2H, *J* = 7.5 Hz), 2.21-2.11 (m, 2H), 1.91-1.84 m, 2H), 1.26 (t, 3H, *J* = 7.1 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -91.2 (m, 2F); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.8 (t, $J_{C\text{-}F}$ = 5.7 Hz), 173.1, 136.8, 133.9, 128.9, 128.6, 122.9 (t, $J_{C\text{-}F}$ = 243 Hz), 60.6, 44.6 (t, $J_{C\text{-}F}$ = 26.7 Hz), 35.6 (t, $J_{C\text{-}F}$ = 24.3 Hz), 33.7, 17.9 (t, $J_{C\text{-}F}$ = 5.0 Hz), 14.4; HRMS-APPI calcd for $C_{15}H_{19}F_2O_3$ $[M+H]^+$ 285.1297; found 285.1268.



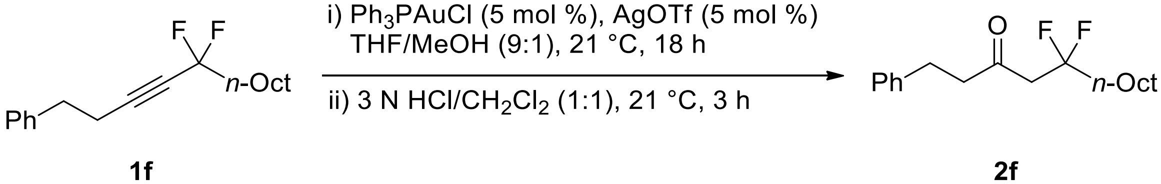
1d **2d**

Benzyl 4-(1,1-difluoro-3-oxo-3-phenylpropyl)piperidine-1-carboxylate (2d). Following general procedure C for the gold-catalyzed formal hydration of propargylic *gem*-difluoride **1d** on a 0.0812 mmol scale, the desired product (22.5 mg, 72%) was isolated as a colorless oil by flash chromatography using 20% EtOAc/hexanes. IR (ATR, ZnSe) ν = 3061, 2931, 2858, 1686, 1427, 1324, 1231, 1119, 1025, 748 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, 2H, *J* = 7.4 Hz), 7.61 (t, 1H, *J* = 7.4 Hz), 7.49 (t, 2H, *J* = 7.7 Hz), 7.37-7.31 (m, 5H), 5.13 (s, 2H), 4.30 (bs, 2H), 3.55 (t, 2H, *J* = 15.1 Hz), 2.77 (bs, 1H), 2.45-2.34 (m, 1H), 1.84 (d, 2H, *J* = 12.8 Hz), 1.54-1.47 (m, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ -99.7 (m, 2F); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.7 (t, $J_{C\text{-}F}$ = 5.5 Hz), 155.1, 136.7, 136.6, 133.9, 128.8, 128.5, 128.5, 128.0, 127.9, 123.2 (t, $J_{C\text{-}F}$ = 245 Hz), 67.1, 43.4, 42.3 (t, $J_{C\text{-}F}$ = 26.9 Hz), 41.4 (t, $J_{C\text{-}F}$ = 23.3 Hz), 24.8 (t, $J_{C\text{-}F}$ = 4.4 Hz); HRMS-APPI calcd for $C_{22}H_{24}F_2NO_3$ $[M+H]^+$ 388.1719; found 388.1696.



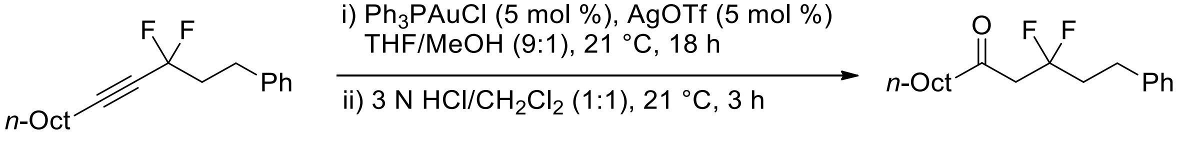
1e **2e**

5-(Benzo[*d*][1,3]dioxol-5-yl)-3,3-difluoro-2-methyl-1-phenylpentan-1-one (2e). Following general procedure C for the gold-catalyzed formal hydration of propargylic *gem*-difluoride **1e** on a 0.0954 mmol scale, the desired product (19.4 mg, 61%) was isolated as a colorless oil by flash chromatography using 7% EtOAc/hexanes. IR (ATR, ZnSe) ν = 2976, 2886, 1683, 1488, 1442, 1244, 1036, 927, 808, 686 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, 2H, *J* = 7.4 Hz), 7.60 (t, 1H, *J* = 7.4 Hz), 7.49 (t, 2H, *J* = 7.7 Hz), 6.72 (d, 1H, *J* = 7.9 Hz), 6.68 (s, 1H), 6.63 (d, 1H, *J* = 7.9 Hz), 5.90 (d, 1H, *J* = 10.9 Hz), 5.89 (d, 1H, *J* = 10.9 Hz), 3.58 (td, 2H, *J* = 15.8, 3.5 Hz), 3.06 (dd, 1H, *J* = 13.6, 3.9 Hz), 2.62-2.49 (m, 1H), 2.34 (dd, 1H, *J* = 13.5, 10.6 Hz), 0.98 (t, 3H, *J* = 6.9 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -99.0 (m, 2F); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.0 (t, *J* = 5.2 Hz), 147.8, 146.1, 137.0, 133.7, 133.3, 128.8, 128.7, 124.4 (t, $J_{C\text{-}F}$ = 246 Hz), 122.2, 109.6, 108.3, 101.0, 43.1 (t, $J_{C\text{-}F}$ = 26.8 Hz), 41.2 (t, $J_{C\text{-}F}$ = 22.4 Hz), 35.8 (t, $J_{C\text{-}F}$ = 4.8 Hz), 12.7 (t, $J_{C\text{-}F}$ = 4.8 Hz); HRMS-APPI calcd for $C_{19}H_{19}F_2O_3$ $[M+H]^+$ 333.1272; found 333.1297.



1f **2f**

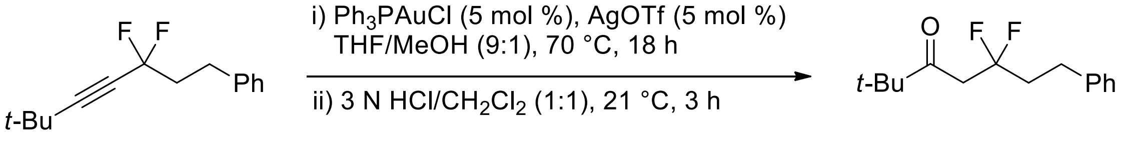
5,5-Difluoro-1-phenyltridecan-3-one (2f). Following general procedure A for the gold-catalyzed formal hydration of propargylic *gem*-difluoride **1f** on a 0.103 mmol scale, the desired product (28.3 mg, 89%) was isolated as a colorless oil by flash chromatography using 5% EtOAc/hexanes. IR (ATR, ZnSe) ν = 2954, 2916, 2848, 1715, 1372, 1150, 1026, 969, 921, 703 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.28 (t, 2H, *J* = 7.4 Hz), 7.21-7.17 (m, 3H), 2.97-2.84 (m, 6H), 1.94-1.84 (m, 2H), 1.46-1.39 (m, 2H), 1.32-1.24 (m, 10H), 0.88 (t, 3H, *J* = 6.9 Hz); ^{19}F NMR ($CDCl_3$, 470 MHz) -92.8 (p, 2F, *J* = 16.3 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 203.8 (t, $J_{C\text{-}F}$ = 4.4 Hz), 140.7, 128.7, 128.5, 126.3, 122.9 (t, $J_{C\text{-}F}$ = 242 Hz), 49.3 (t, $J_{C\text{-}F}$ = 26.2 Hz), 45.8 (t, $J_{C\text{-}F}$ = 2.1 Hz), 36.6 (t, $J_{C\text{-}F}$ = 24.1 Hz), 31.9, 29.5, 29.4, 29.3, 29.3, 22.8, 22.3 (t, $J_{C\text{-}F}$ = 4.5 Hz), 14.3; HRMS-ESI calcd for $C_{19}H_{29}F_2O$ $[M+H]^+$ 311.2181; found 311.2175.



1g

2g

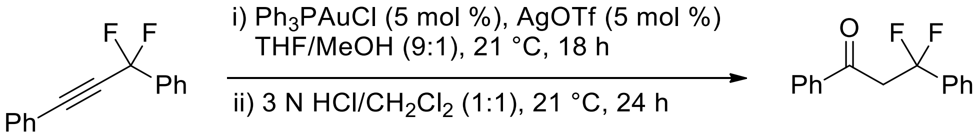
3,3-Difluoro-1-phenyltridecan-5-one (2g). Following general procedure A for the gold-catalyzed formal hydration of propargylic *gem*-difluoride **1g** on a 0.103 mmol scale, the desired product (26.8 mg, 84%) was isolated as a colorless oil by flash chromatography using 2% EtOAc/hexanes. IR (ATR, ZnSe) ν = 2953, 2925, 2855, 1721, 1530, 1350, 1072, 812, 724, 698 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.31-7.28 (m, 2H), 7.22-7.19 (m, 3H), 2.98 (t, 2H, J = 15.3 Hz), 2.83-2.79 (m, 2H), 2.48 (t, 2H, J = 7.3 Hz), 2.34-2.24 (m, 2H), 1.59-1.53 (m, 2H), 1.31-1.25 (m, 10H), 0.88 (t, 3H, J = 6.9 Hz); ^{19}F NMR (CDCl$_3$, 470 MHz) δ -93.3 (p, 2F, J = 16.2 Hz); ^{13}C NMR (CDCl$_3$, 126 MHz) δ 204.7 (t, $J_{C\text{-}F}$ = 4.6 Hz), 140.4, 128.7, 128.5, 126.4, 122.4 (t, $J_{C\text{-}F}$ = 242.7 Hz), 48.9 (t, $J_{C\text{-}F}$ = 26.0 Hz), 44.5 (t, $J_{C\text{-}F}$ = 1.9 Hz), 38.2 (t, $J_{C\text{-}F}$ = 24.1 Hz), 32.0, 29.5, 29.2, 29.2, 28.6 (t, $J_{C\text{-}F}$ = 5.0 Hz), 23.4, 22.8, 14.2; HRMS-ESI calcd for $C_{19}H_{29}F_2O$ [M+H]$^+$ 311.2181; found 311.2173.



1h

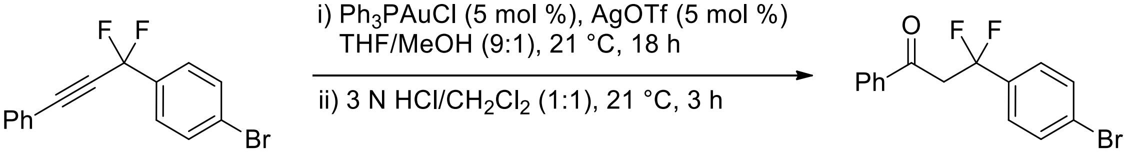
2h

5,5-Difluoro-2,2-dimethyl-7-phenylheptan-3-one (2h). Chloro(triphenylphosphine) gold(I) (3.1 mg, 0.0063 mmol, 5 mol %) and silver trifluoromethanesulfonate (1.6 mg, 0.0063 mmol, 5 mol %) were charged into a glass vial. A magnetic stir bar was added, and then the vial was sealed and flushed with argon, after which a solution of (3,3-difluoro-6,6-dimethylhept-4-yn-1-yl)benzene (**1h**, 30 mg, 0.127 mmol) in THF/MeOH (9:1, 1.27 mL) was added. The vial was wrapped with aluminum foil, and the reaction mixture was stirred at 70 °C for 18 hours. The reaction was then transferred to a round-bottom flask, using CH_2Cl_2 to rinse the vial. The volatiles were removed *in vacuo*, after which 3 mL of CH_2Cl_2 and 3 mL of HCl 3 N were added. The mixture was stirred at room temperature for 3 hours, at which point 2-fluoro-4-nitrotoluene (28.3 mg, 0.182 mmol) was added as an internal standard. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 two more times. The combined organic layers were washed with water, dried over Na_2SO_4 and concentrated *in vacuo*. An NMR yield of 7% was estimated by ^{19}F NMR analysis of the crude reaction mixture. ^{19}F NMR ($CDCl_3$, 470 MHz) δ -92.2 (p, 2F, J = 15.6 Hz, 0.0145 mmol, 7%).



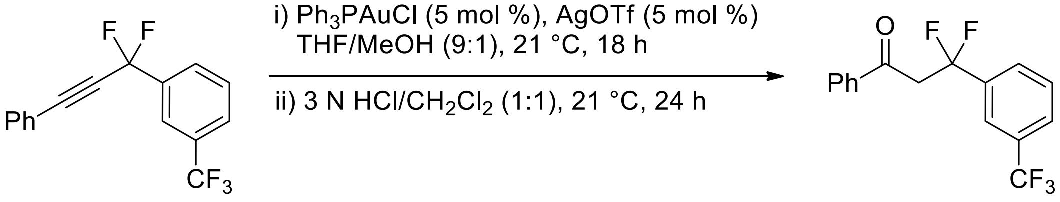
1i **2i**

3,3-Difluoro-1,3-diphenylpropan-1-one (2i). Following general procedure B for the gold-catalyzed formal hydration of propargylic *gem*-difluoride **1i** on a 0.131 mmol scale, the desired product (21.1 mg, 65%) was isolated as a white solid by flash chromatography using hexanes. mp 57-59 °C; IR (ATR, ZnSe) ν = 3061, 2924, 1692, 1596, 1311, 1209, 1147, 984, 819, 686 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, 2H, J = 8.5 Hz), 7.60-7.53 (m, 3H), 7.48-7.42 (m, 5H), 3.87 (t, 2H, J = 14.7 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -90.3 (t, 2F, J = 14.9 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.8 (t, J_{C-F} = 4.1 Hz), 136.7 (t, J_{C-F} = 1.4 Hz), 133.6, 130.0 (t, J_{C-F} = 1.9 Hz), 128.7, 128.5, 128.4, 127.2, 125.1 (t, J_{C-F} = 6.2 Hz), 120.5 (t, J_{C-F} = 245 Hz), 47.1 (t, J_{C-F} = 28.2 Hz; HRMS-APPI calcd for $C_{15}H_{12}FO$ [M-F]$^+$ 227.0867; found 227.0868.



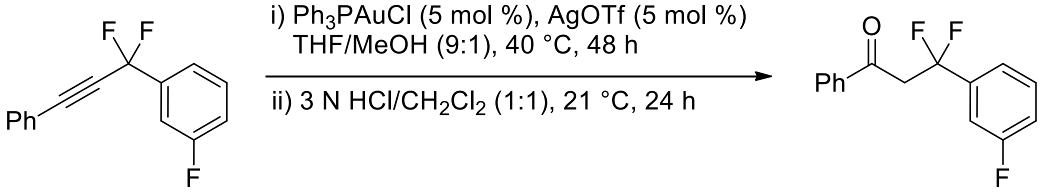
1j **2j**

3-(4-Bromophenyl)-3,3-difluoro-1-phenylpropan-1-one (2j). Following general procedure A for the gold-catalyzed formal hydration of propargylic *gem*-difluoride **1j** on a 0.0977 mmol scale, the desired product (26.0 mg, 82%) was isolated as a colorless oil by flash chromatography using 10% EtOAc/hexanes. IR (ATR, ZnSe) ν = 3061, 2923, 1675, 1488, 1312, 1208, 1008, 825, 757, 686 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, 2H, *J* = 7.6 Hz), 7.61-7.55 (m, 3H), 7.47 (t, 2H, *J* = 7.7 Hz), 7.42 (d, 2H, *J* = 8.3 Hz), 3.87 (t, 2H, *J* = 14.3 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -90.0 (t, 2F, *J* = 14.2 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.6 (t, $J_{C\text{-}F}$ = 4.5 Hz), 136.6, 135.6 (t, $J_{C\text{-}F}$ = 26.2 Hz), 133.9, 131.8, 128.9, 128.6, 127.2 (t, $J_{C\text{-}F}$ = 6.2 Hz), 124.6 (t, $J_{C\text{-}F}$ = 2.1 Hz), 120.4 (t, $J_{C\text{-}F}$ = 245 Hz), 47.0 (t, $J_{C\text{-}F}$ = 28.2 Hz); HRMS-APPI calcd for $C_{23}H_{12}BrF_2O$ [M+H]$^+$ 325.0034; found 325.0061.



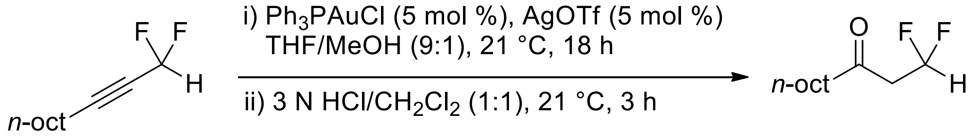
1k **2k**

3,3-Difluoro-1-phenyl-3-(3-(trifluoromethyl)phenyl)propan-1-one (2k). Following general procedure B for the gold-catalyzed formal hydration of propargylic *gem*-difluoride **1k** on a 0.101 mmol scale, the desired product (19.0 mg, 60%) was isolated as a colorless oil by flash chromatography using 30% DCM/hexanes. IR (ATR, ZnSe) ν = 2928, 1693, 1598, 1449, 1344, 1279, 1122, 1075, 908, 812 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, 2H, *J* = 7.3 Hz), 7.80 (s, 1H), 7.77 (d, 1H, *J* = 7.9 Hz), 7.70 (d, 1H, *J* = 7.8 Hz), 7.61-7.55 (m, 2H), 7.47 (t, 2H, *J* = 7.8 Hz), 3.92 (t, 2H, *J* = 14.3 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.8 (s, 3F), -90.4 (t, 2F, *J* = 14.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.4 (t, *J* = 4.7 Hz), 137.6 (t, *J* = 26.5 Hz), 136.5 (t, *J* = 1.7 Hz), 134.0, 131.1 (q, *J* = 32.9 Hz), 129.2, 128.9, 128.5, 127.0 (m), 123.8 (q, *J* = 272 Hz), 122.5 (m), 120.6 (t, *J* = 245 Hz), 47.0 (t, *J* = 27.9 Hz); HRMS-APPI calcd for $C_{16}H_{12}F_5O$ [M+H]$^+$ 315.0803; found 315.0773.



1l **2l**

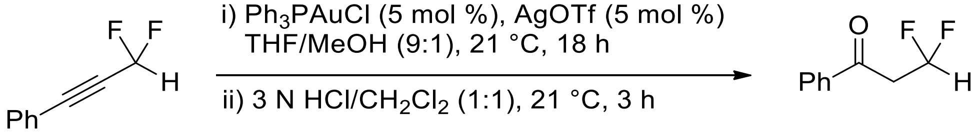
3,3-Difluoro-3-(3-fluorophenyl)-1-phenylpropan-1-one (2l). Following general procedure D for the gold-catalyzed formal hydration of propargylic *gem*-difluoride **1l** on a 0.122 mmol scale, the desired product (15.8 mg, 49%) was isolated as a pale orange oil by flash chromatography using 10% EtOAc/hexanes. IR (ATR, ZnSe) ν = 3066, 2934, 2851, 1689, 1593, 1321, 1221, 1184, 991, 872 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.90 (d, 2H, *J* = 7.6 Hz), 7.59 (t, 1H, *J* = 7.4 Hz), 7.47 (t, 2H, *J* = 7.7 Hz), 7.39 (q, 1H, *J* = 7.8 Hz), 7.32 (d, 1H, *J* = 7.7 Hz), 7.26 (d, 1H, *J* = 7.4 Hz), 7.12 (t, 1H, *J* = 8.1 Hz), 3.87 (t, 2H, *J* = 14.5 Hz); ^{19}F NMR (470 MHz, CDCl$_3$) δ -90.2 (t, 2F, *J* = 14.3 Hz), -111.8 (q, 1F, *J* = 8.3 Hz); ^{13}C NMR (126 MHz, CDCl$_3$) δ 192.5 (t, J_{C-F} = 4.3 Hz), 162.6 (d, J_{C-F} = 247.0 Hz), 138.8 (td, J_{C-F} = 26.4, 7.2 Hz), 133.9, 130.4 (d, J_{C-F} = 7.9 Hz), 128.9, 128.6, 121.1 (td, J_{C-F} = 6.3, 3.3 Hz), 119.9 (td, J_{C-F} = 245, 1.9 Hz), 118.7 (d, J_{C-F} = 21.3 Hz), 117.2 (d, J_{C-F} = 21.0 Hz), 112.9 (dt, J_{C-F} = 23.8, 6.5 Hz), 47.0 (t, J_{C-F} = 27.9 Hz); HRMS-APPI calcd for $C_{15}H_{11}F_2O$ [M-F]$^+$ 245.0772; found 245.0746.



1n **2n**

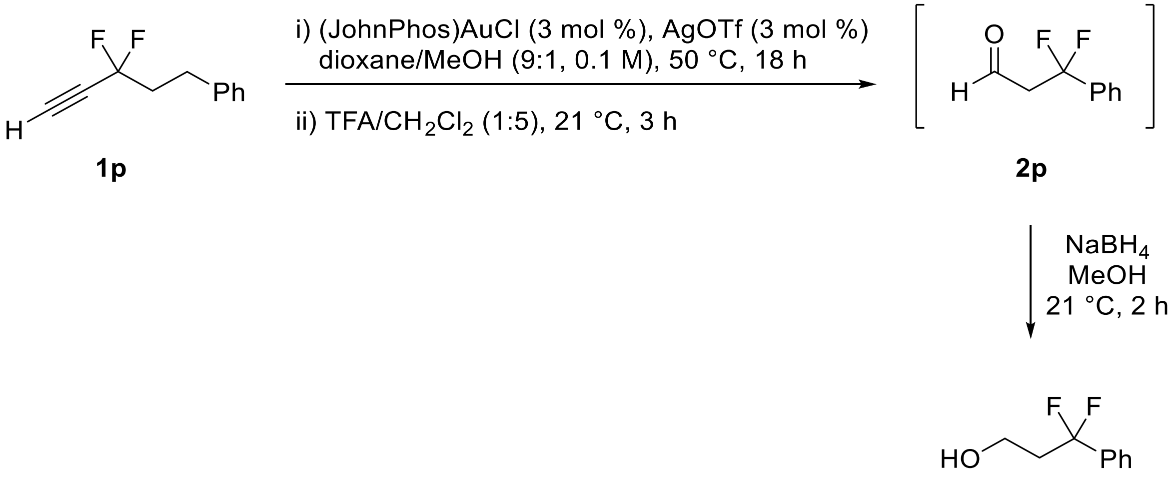
1,1-Difluoroundecan-3-one (2n). Following general procedure A for the gold-catalyzed formal hydration of propargylic *gem*-difluoride **1n** on a 0.159 mmol scale, the desired product (25.8 mg, 78%) was isolated as a colorless oil by flash chromatography using 3% EtOAc/hexanes. IR (ATR, ZnSe) ν = 2925, 2855, 1719, 1465, 1418, 1391, 1302, 1114, 1043, 1015 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.17 (t, 1H, *J* = 55.5), 2.31-2.25 (m, 2H), 1.55 (p. 2H, *J* = 7.7 Hz), 1.38 (p, 2H, *J* = 6.8 Hz), 1.32-1.24 (m, 8H), 0.89 (t, 3H, *J* = 6.9

Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -103.9 (dt, 2F, *J* = 56.0, 5.4 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 104.0 (t, $J_{C\text{-}F}$ = 231 Hz), 91.0 (t, $J_{C\text{-}F}$ = 7.0 Hz), 72.3 (t, $J_{C\text{-}F}$ = 33.5 Hz), 31.9, 29.3, 29.1, 28.9, 27.8 (t, $J_{C\text{-}F}$ = 2.2 Hz), 22.8, 18.5 (t, $J_{C\text{-}F}$ = 2.6 Hz), 14.2; HRMS-APPI calcd for $C_{11}H_{21}F_2O$ $[M+H]^+$ 207.1555; found 207.1526.



1o **2o**

3,3-Difluoro-1-phenylpropan-1-one (2o). Following general procedure A for the gold-catalyzed formal hydration of propargylic *gem*-difluoride **1o** on a 0.197 mmol scale, the desired product (21.6 mg, 64%) was isolated as a colorless oil by flash chromatography using 5% EtOAc/hexanes. IR (ATR, ZnSe) ν = 3063, 2930, 1685, 1597, 1421, 1325, 1215, 1118, 1036, 881 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, 2H, *J* = 8.5 Hz), 7.63 (t, 1H, *J* = 7.4 Hz), 7.51 (t, 2H, *J* = 7.8 Hz), 6.41 (tt, 1H, *J* = 55.5, 4.6 Hz), 3.55 (td, 2H, *J* = 15.2, 4.6 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -116.9 (dt, 2F, *J* = 55.1, 15.1 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.9 (t, $J_{C\text{-}F}$ = 6.6 Hz), 136.1 (t, $J_{C\text{-}F}$ = 1.8 Hz), 134.2, 129.0, 128.3, 115.0 (t, $J_{C\text{-}F}$ = 238.4 Hz), 43.1 (t, $J_{C\text{-}F}$ = 23.4 Hz); HRMS-APPI calcd for $C_9H_9F_2O$ $[M+H]^+$ 171.0616; found 171.0595.

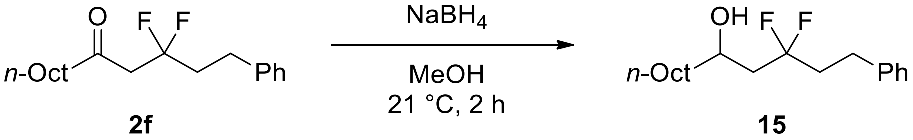


1p **2p** **16**

3,3-Difluoro-3-phenylpropanal (2p). (JohnPhos)AuCl (2.7 mg, 0.0050 mmol, 3 mol %) and silver trifluoromethanesulfonate (1.3 mg, 0.0050 mmol, 3 mol %) were charged into a glass vial. A magnetic stir bar was added, and then the vial was sealed and flushed with argon, after which a solution of (3,3-difluoropent-4-yn-1-yl)benzene (**1p**, 30 mg, 0.166 mmol) in dioxane/MeOH (9:1, 1.66 mL) was added. The vial was wrapped with aluminum foil, and the reaction mixture was stirred at 50 °C for 18 hours. The reaction was then transferred to a round-bottom flask, using CH_2Cl_2 to rinse the vial. The volatiles were removed *in vacuo*, after which 2.5 mL of CH_2Cl_2 and 0.5 mL of TFA were added. The mixture was stirred at room temperature for 3 hours and then quenched by the addition of H_2O. The resulting mixture was extracted with CH_2Cl_2 (3x), dried over Na_2SO_4 and concentrated *in vacuo*. Fluorobenzene (40 µL, 0.429 mmol) was added mixture as an internal standard and an NMR yield of 82% was estimated by ^{19}F NMR analysis of the crude reaction mixture. ^{19}F NMR ($CDCl_3$, 470 MHz) δ -94.6 (p, 2F, *J* = 16.5 Hz, 0.1370 mmol, 82%).

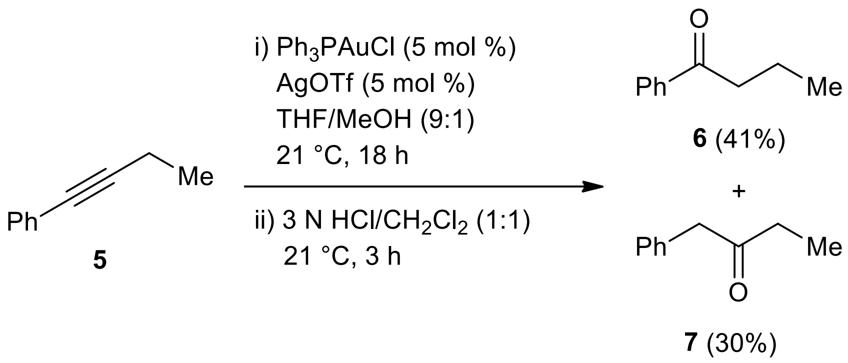
3,3-Difluoro-3-phenylpropan-1-ol (16). The crude reaction mixture was dissolved in MeOH (0.8 mL) and sodium borohydride (12.6 mg, 0.333 mmol) was added. The resulting mixture was stirred at room temperature for 2 hours. Water was added and the mixture was extracted with Et_2O (3x). The combined organic layers were washed with brine and concentrated *in vacuo*. The desired compound (23.1 mg, 69%) was isolated as a pale yellow oil by flash chromatography using 25% EtOAc/hexanes. IR (ATR, ZnSe) ν = 3357, 2934, 1497, 1455, 1379, 1054, 926, 845, 746, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.29 (m, 2H), 7.23-7.20 (m, 3H), 3.89 (t, 2H, *J* = 6.1 Hz), 2.85-2.81 (m, 2H), 2.25-2.13 (m, 4H), 1.59 (bs, 1H); ^{19}F NMR (470 MHz, $CDCl_3$) δ -97.8 (p, 2F, *J* = 16.7 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 128.7, 128.4, 126.4, 124.7 (t, $J_{C\text{-}F}$ = 241 Hz), 57.3 (t, $J_{C\text{-}F}$ = 5.5 Hz), 39.3 (t, $J_{C\text{-}F}$ = 24.2 Hz), 39.1 (t, $J_{C\text{-}F}$ = 25.0 Hz), 28.5 (t, $J_{C\text{-}F}$ = 5.2 Hz); HRMS-APPI calcd for $C_{11}H_{18}F_2NO$ $[M+NH_4]^+$ 218.1351; found 218.1344.

5. Reduction of 3,3-difluoroketone 2f

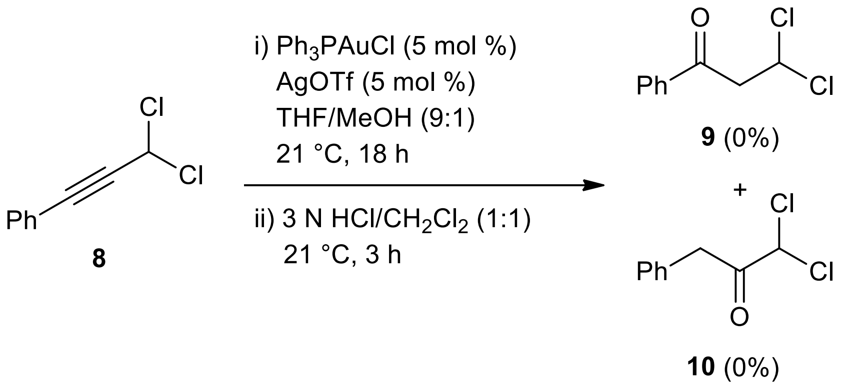


3,3-Difluoro-1-phenyltridecan-5-ol (8). To a stirring solution of 3,3-difluoro-1-phenyltridecan-5-one (26 mg, 0.0838 mmol) in MeOH (0.4 mL) was added sodium borohydride (6.3 mg, 0.168 mmol). The resulting mixture was stirred at room temperature for 2 hours. Water was added and the mixture was extracted with Et_2O (3x). The combined organic layers were washed with brine and concentrated *in vacuo*. The desired compound (24.3 mg, 93%) was isolated as a white solid by flash chromatography using 15% EtOAc/hexanes. mp 37-38 °C; IR (ATR, ZnSe) ν = 3385, 2955, 2916, 2849, 1456, 1386, 1149, 1030, 848, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, 2H, J = 7.5 Hz), 7.23-7.20 (m, 3H), 4.05-3.99 (m, 1H), 2.88-2.77 (m, 2H), 2.27-2.17 (m, 2H), 2.07-1.98 (m, 2H), 1.86 (m, 1H), 1.51-1.41 (m, 3H), 1.34-1.26 (m, 12H); ^{19}F NMR (470 MHz, $CDCl_3$) δ -96.7 (m, 2F); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.7, 128.7, 128.5, 126.4, 125.1 (t, $J_{C\text{-}F}$ = 241 Hz), 67.0 (t, $J_{C\text{-}F}$ = 4.3 Hz), 43.7 (t, J = 23.4 Hz), 39.2 (t, J = 25.0 Hz), 37.9, 32.0, 29.7, 29.6, 29.4, 28.6 (t, J = 5.2 Hz), 25.5, 22.8, 14.3; HRMS-APPI calcd for $C_{19}H_{34}F_2NO$ $[M+NH_4]^+$ 330.2603; found 330.2576.

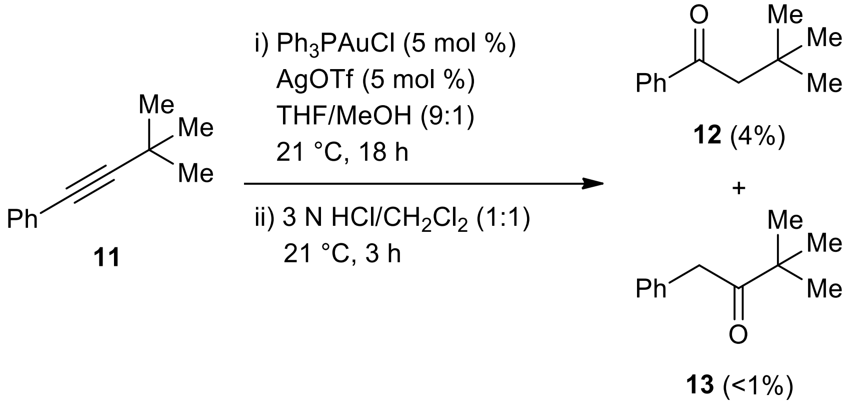
6. Hydration of non-fluorinated substrates



Chloro(triphenylphosphine)gold(I) (5.7 mg, 0.0115 mmol, 5 mol %) and silver trifluoromethanesulfonate (3.0 mg, 0.0115 mmol, 5 mol %) were charged into a glass vial. A magnetic stir bar was added, and then the vial was sealed and flushed with argon, after which a solution of 1-phenyl-1-butyne (**5**, 30 mg, 0.230 mmol) in THF/MeOH (9:1, 2.3 mL) was added. The vial was wrapped with aluminum foil, and the reaction mixture was stirred at room temperature for 18 hours. The reaction was then transferred to a round-bottom flask, using CH_2Cl_2 to rinse the vial. The volatiles were removed *in vacuo*, after which 3 mL of CH_2Cl_2 and 3 mL of HCl 3 N were added. The mixture was stirred at room temperature for 3 hours, at which point 1,4-dimethoxybenzene (11.3 mg, 0.0818 mmol) was added as an internal standard. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 two more times. The combined organic layers were washed with water, dried over Na_2SO_4 and concentrated *in vacuo*. Yields were estimated by NMR analysis of the crude reaction mixture. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.95 (**6**,[22] t, 2H, *J* = 7.3 Hz, 0.0956 mmol, 41%), 2.47 (**7**,[23] q, 2H, *J* = 7.3 Hz, 0.0680 mmol, 30%), 2.42 (**5**,[24] q, 2H, *J* = 7.5 Hz, 0.0422 mmol, 18%).

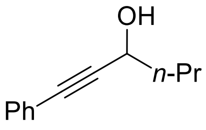


Chloro(triphenylphosphine)gold(I) (4.0 mg, 0.0081 mmol, 5 mol %) and silver trifluoromethanesulfonate (2.1 mg, 0.0081 mmol, 5 mol %) were charged into a glass vial. A magnetic stir bar was added, and then the vial was sealed and flushed with argon, after which a solution of (3,3-dichloroprop-1-yn-1-yl)benzene[25] (**8**, 30 mg, 0.162 mmol) in THF/MeOH (9:1, 1.6 mL) was added. The vial was wrapped with aluminum foil, and the reaction mixture was stirred at room temperature for 18 hours. The reaction was then transferred to a round-bottom flask, using CH_2Cl_2 to rinse the vial. The volatiles were removed *in vacuo*, after which 3 mL of CH_2Cl_2 and 3 mL of HCl 3 N were added. The mixture was stirred at room temperature for 3 hours, at which point 1,4-dimethoxybenzene (9.3 mg, 0.0673 mmol) was added as an internal standard. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 two more times. The combined organic layers were washed with water, dried over Na_2SO_4 and concentrated *in vacuo*. Yields were estimated by NMR analysis of the crude reaction mixture. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.49 (**8**,[25] s, 1H, 0.1600 mmol, 99%), 6.31 (**9**,[26] s, 1H, 0.0007 mmol, <1%).

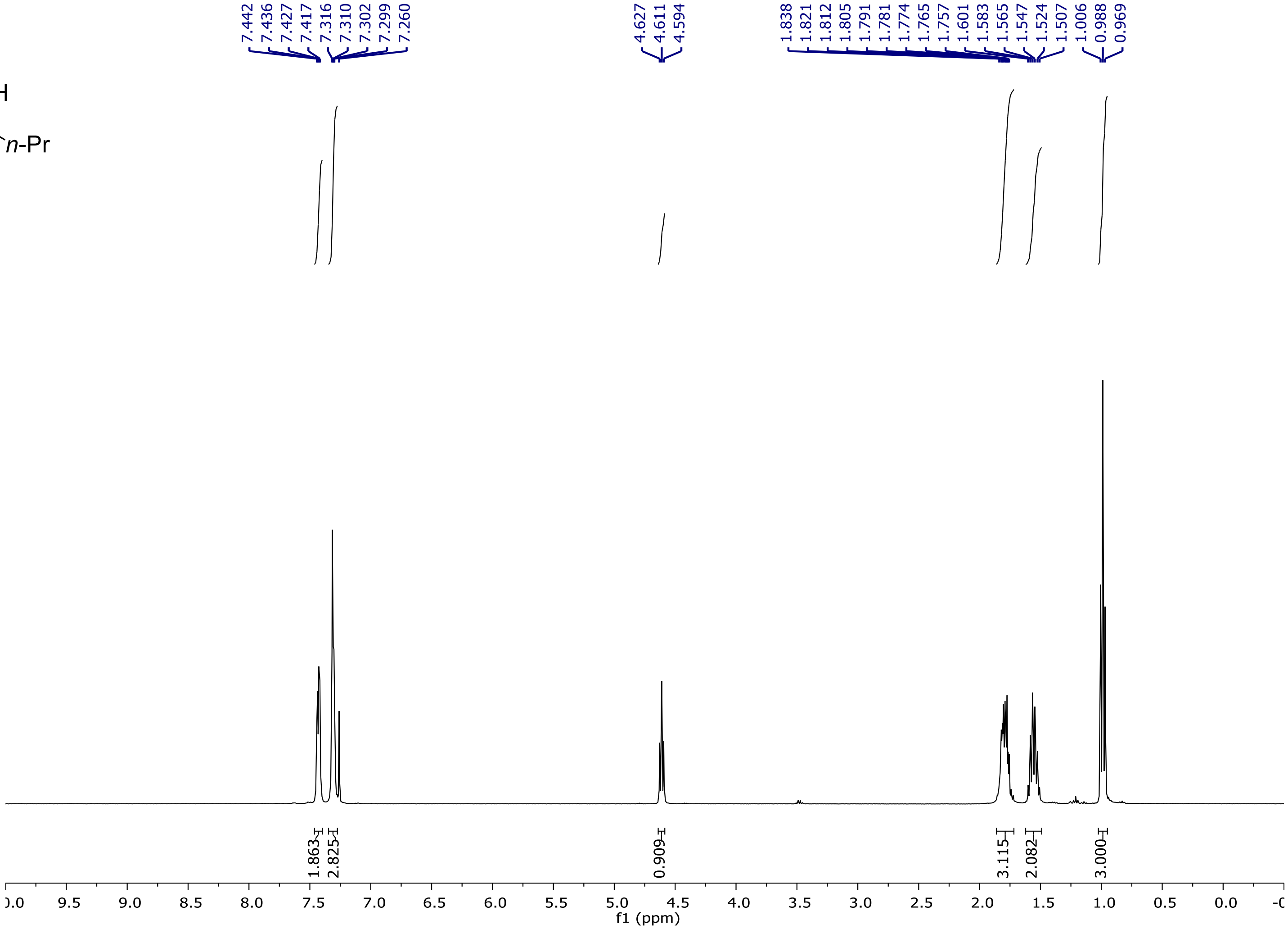


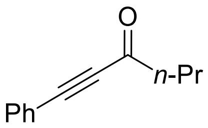
Chloro(triphenylphosphine)gold(I) (4.7 mg, 0.0095 mmol, 5 mol %) and silver trifluoromethanesulfonate (2.4 mg, 0.0095 mmol, 5 mol %) were charged into a glass vial. A magnetic stir bar was added, and then the vial was sealed and flushed with argon, after which a solution of (3,3-dimethylbut-1-yn-1-yl)benzene[27] (**11**, 30 mg, 0.190 mmol) in THF/MeOH (9:1, 1.9 mL) was added. The vial was wrapped with aluminum foil, and the reaction mixture was stirred at room temperature for 18 hours. The reaction was then transferred to a round-bottom flask, using CH_2Cl_2 to rinse the vial. The volatiles were removed *in vacuo*, after which 3 mL of CH_2Cl_2 and 3 mL of HCl 3 N were added. The mixture was stirred at room temperature for 3 hours, at which point 1,4-dimethoxybenzene (9.6 mg, 0.0695 mmol) was added as an internal standard. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 two more times. The combined organic layers were washed with water, dried over Na_2SO_4 and concentrated *in vacuo*. Yields were estimated by NMR analysis of the crude reaction mixture. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.32 (**11**,[27] s, 9H, 0.1787 mmol, 94%), 1.23 (**13**,[28] s, 9H, 0.0011 mmol, <1%), 1.06 (**12**,[29] 9H, 0.0072 mmol, 4%).

7. ^{1}H, ^{19}F and ^{13}C NMR spectra



S1

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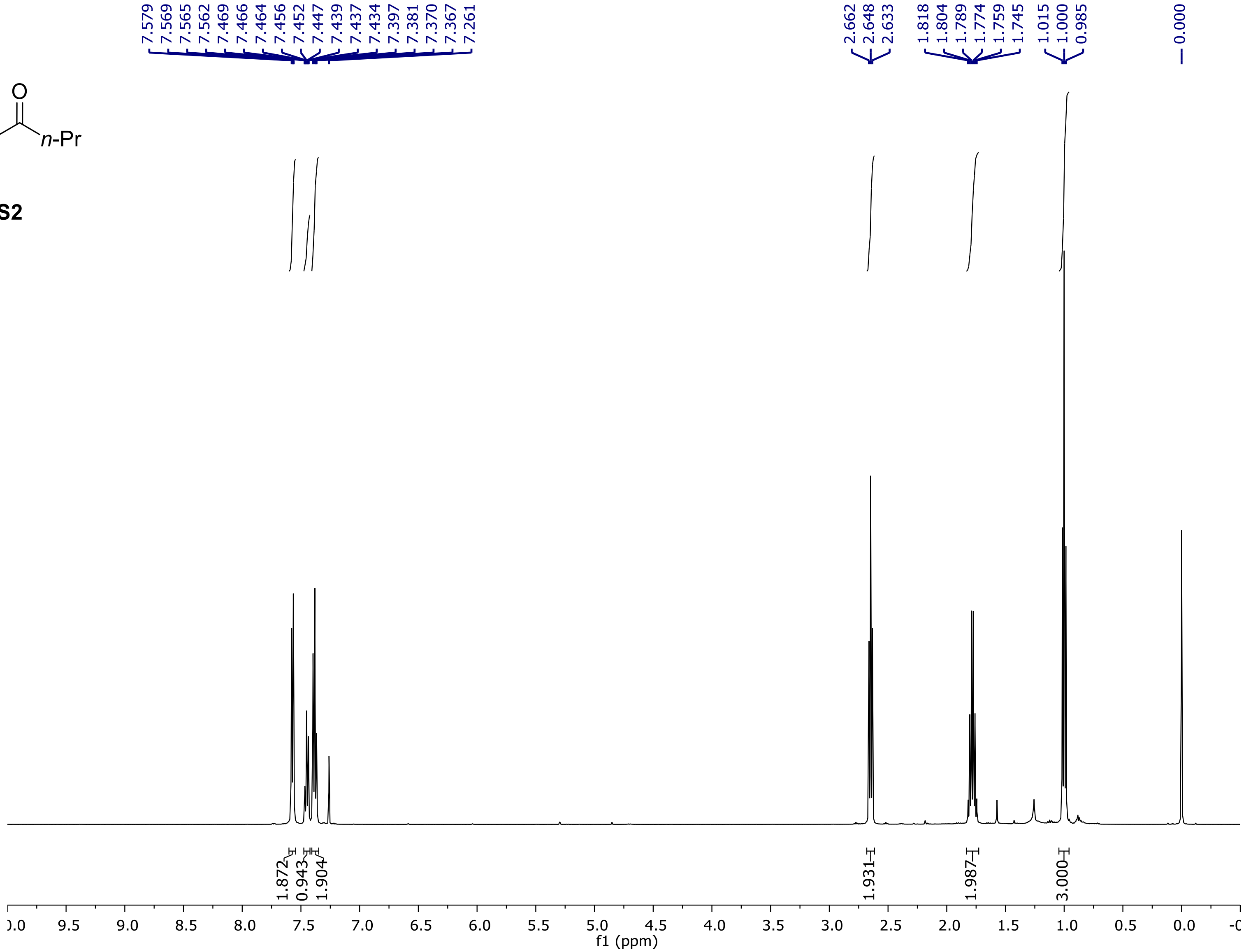
n-Pr
Ph

S2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7.261
2.662
2.648
2.633
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1.804
1.789
1.774
1.759
1.745
1.015
1.000
0.985
0.000
1.872
0.943
1.904
1.931
1.987
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9.5
9.0
8.5
8.0
7.5
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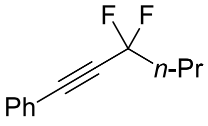
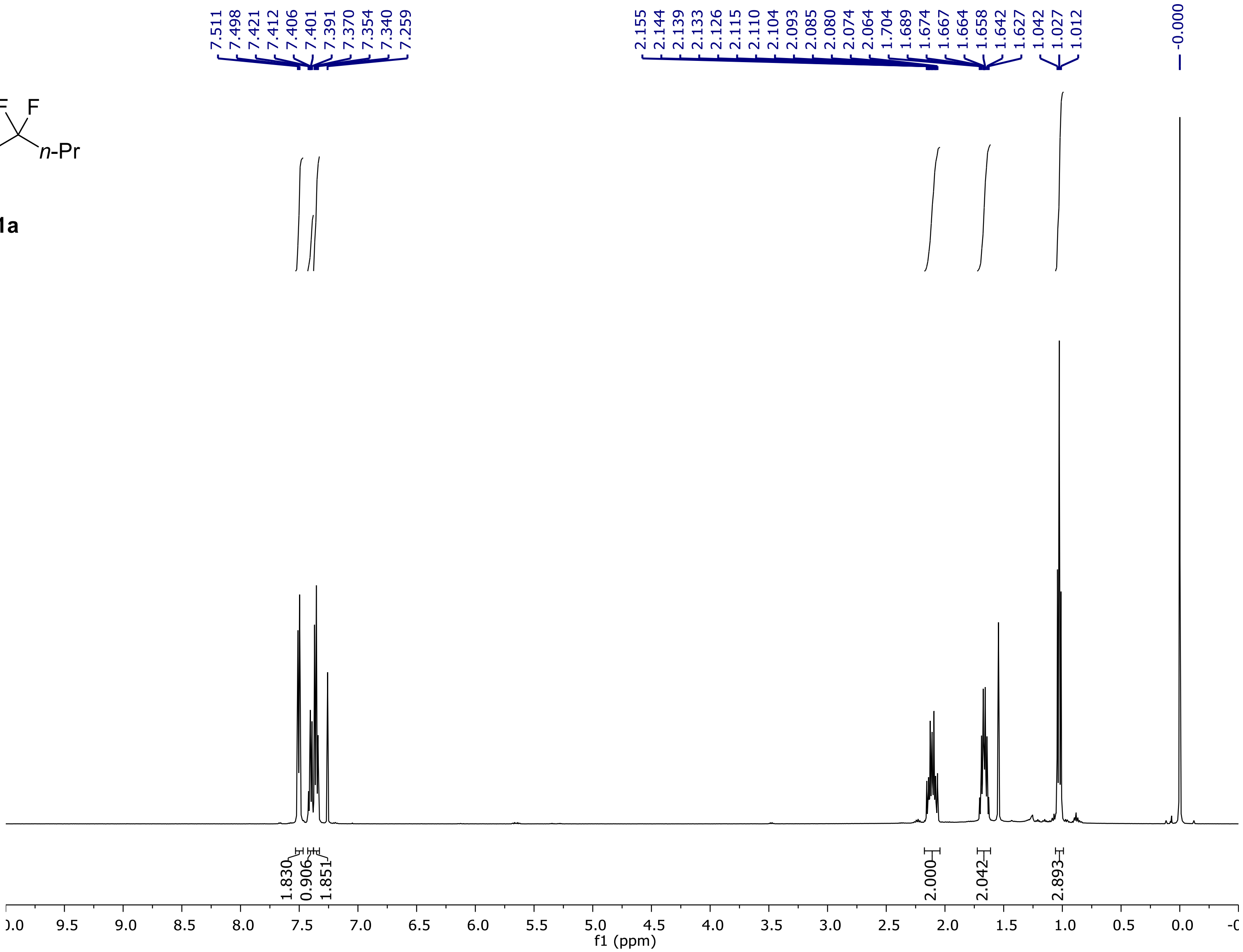
f1 (ppm)


F
F
n-Pr
Ph

1a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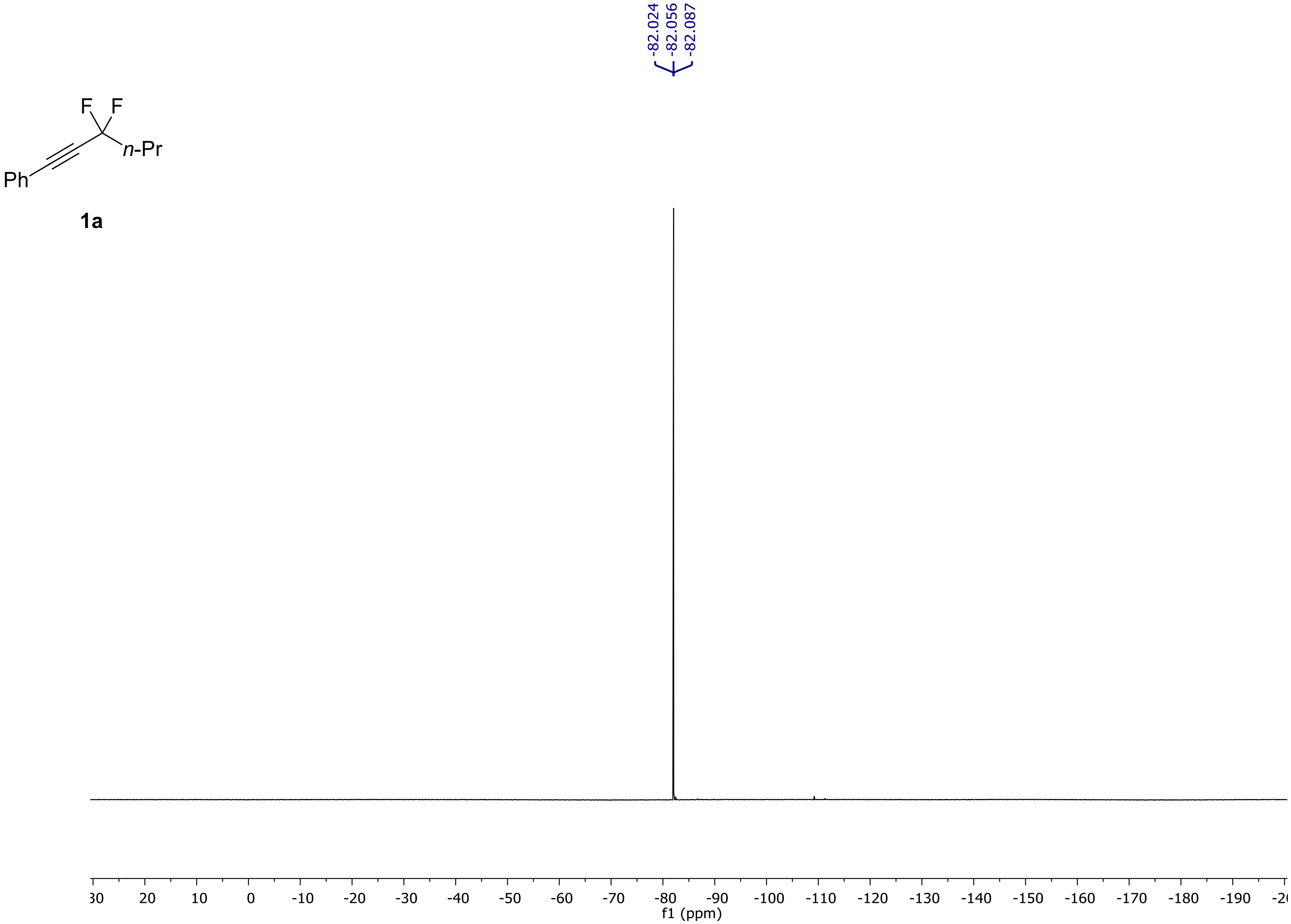
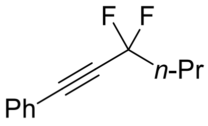
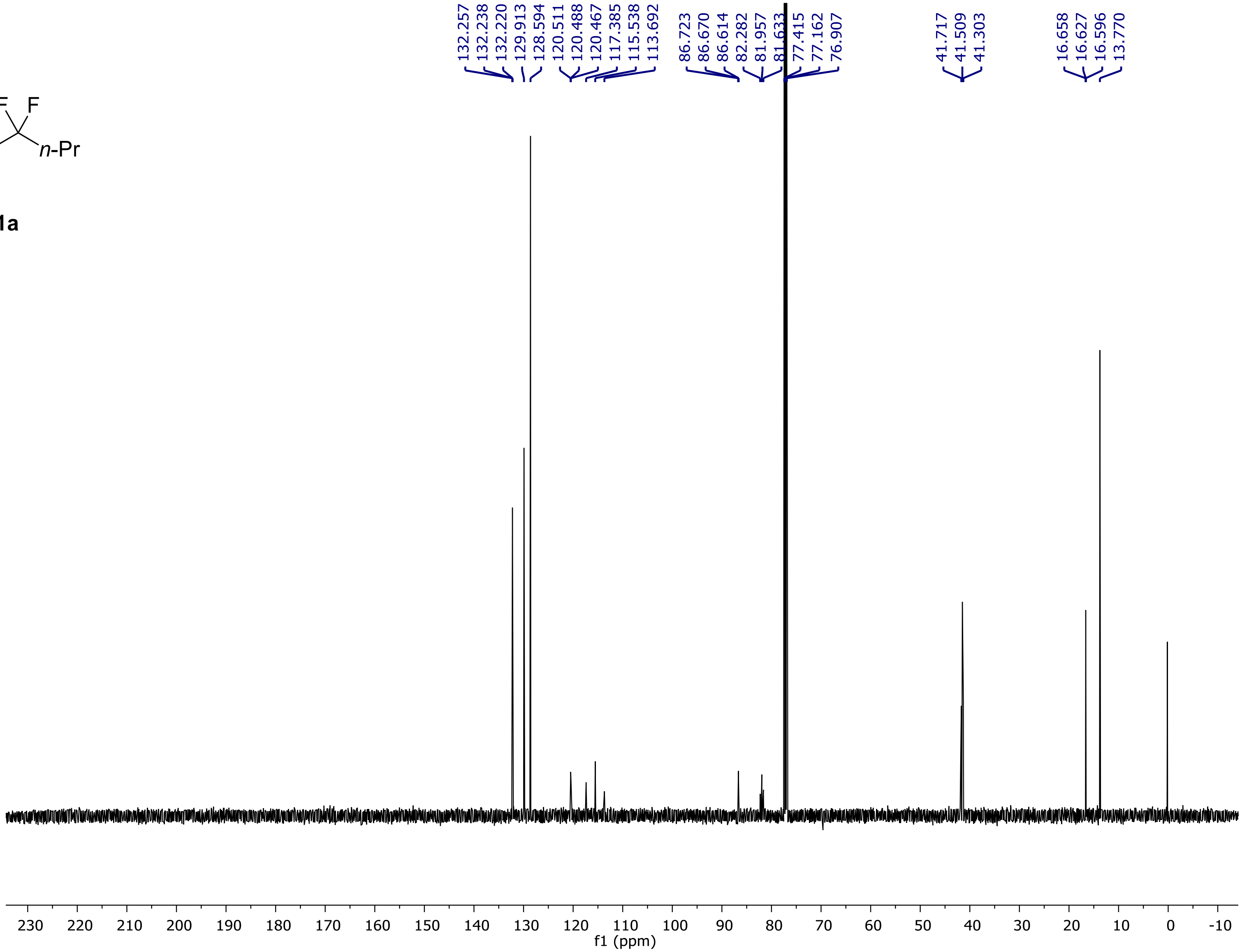
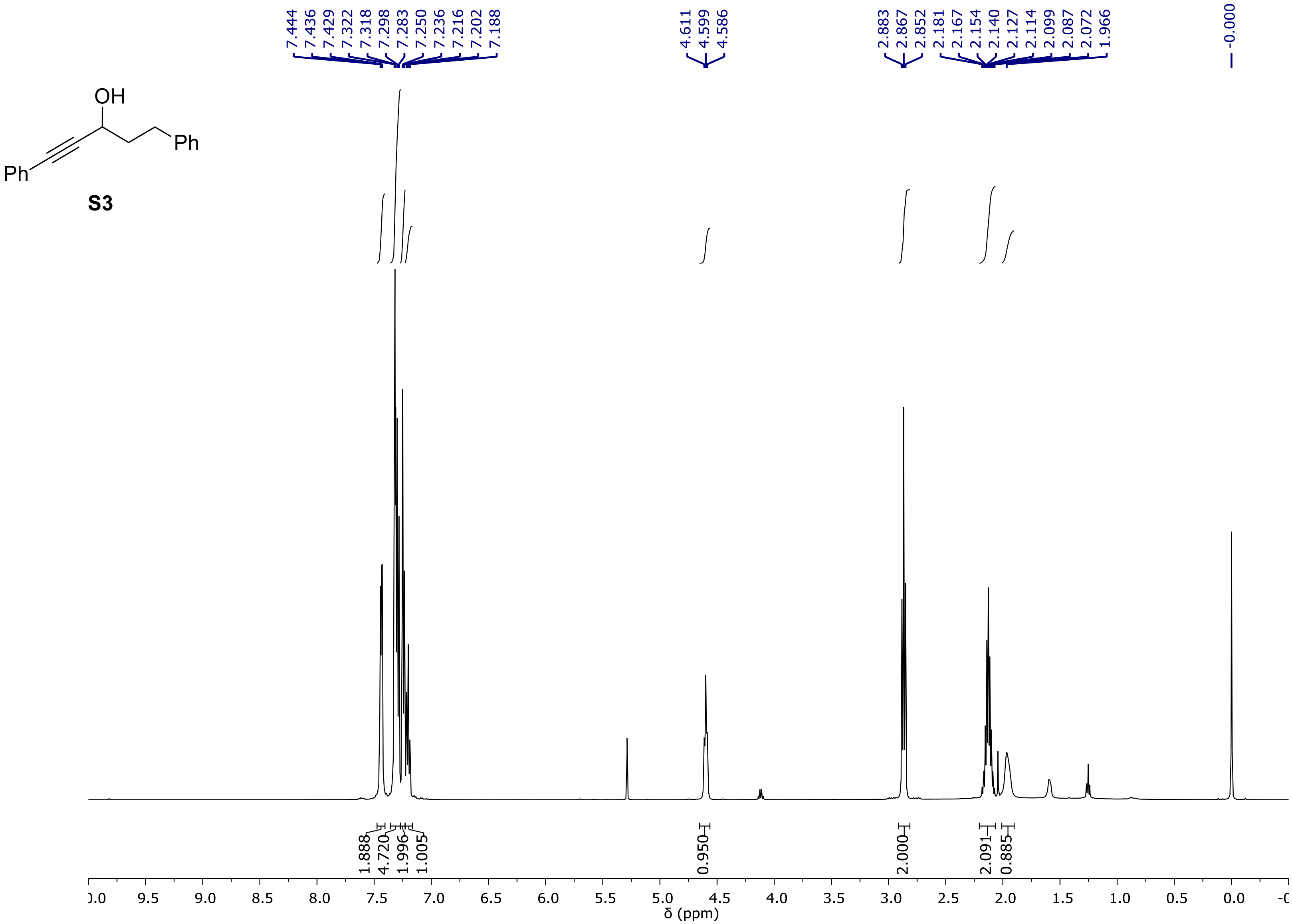
7.498
7.421
7.412
7.406
7.401
7.391
7.370
7.354
7.340
7.259
2.155
2.144
2.139
2.133
2.126
2.115
2.110
2.104
2.093
2.085
2.080
2.074
2.064
1.704
1.689
1.674
1.667
1.664
1.658
1.642
1.627
1.042
1.027
1.012
-0.000
1.830
0.906
1.851
2.000
2.042
2.893
).0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)


-82.024
-82.056
-82.087
F
F
n-Pr
Ph
1a
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


F
F
n-Pr
Ph

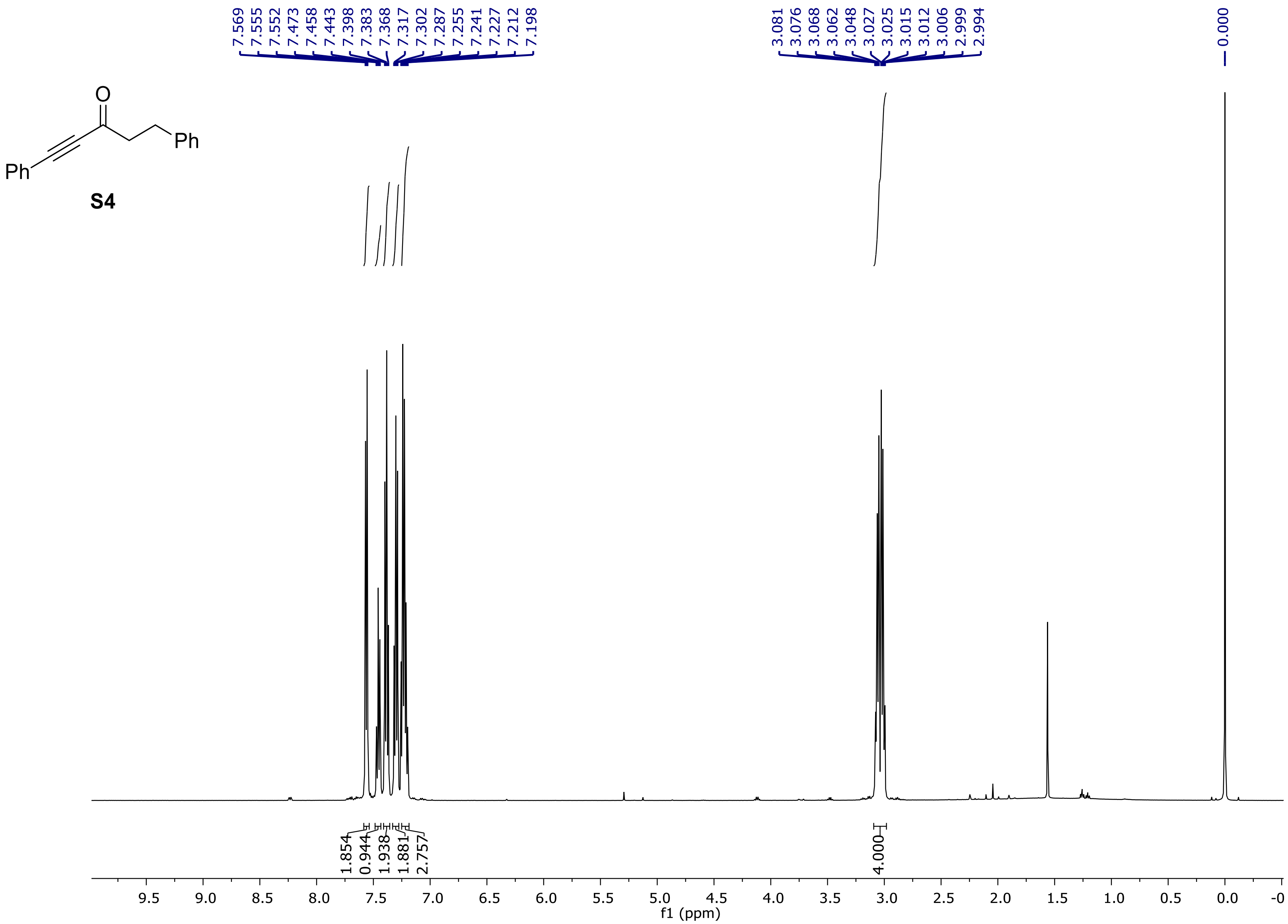
1a


132.257
132.238
132.220
129.913
128.594
120.511
120.488
120.467
117.385
115.538
113.692
86.723
86.670
86.614
82.282
81.957
81.633
77.415
77.162
76.907
41.717
41.509
41.303
16.658
16.627
16.596
13.770
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

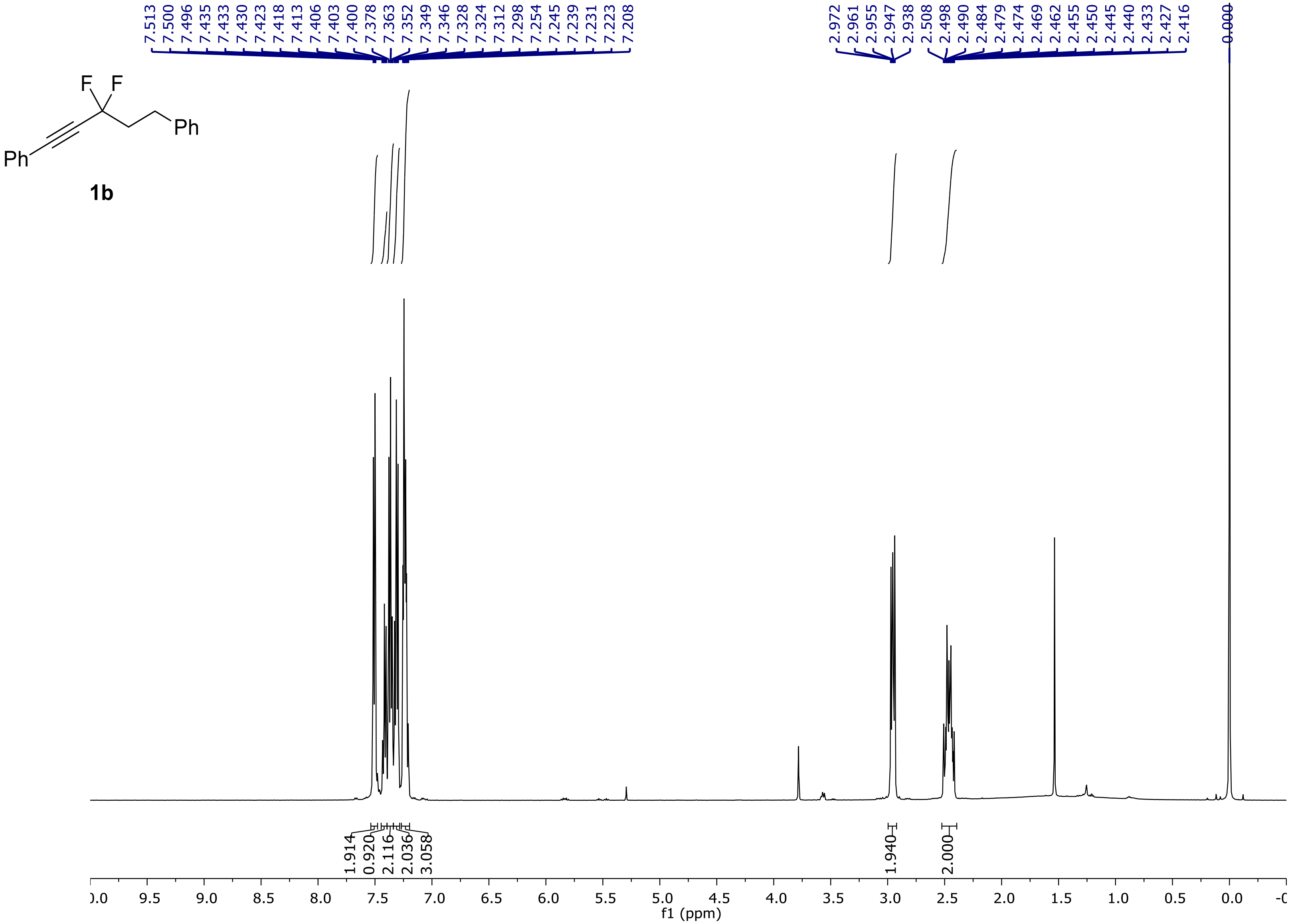

OH
Ph
Ph

S3

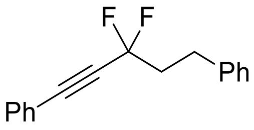
7.444
7.436
7.429
7.322
7.318
7.298
7.283
7.250
7.236
7.216
7.202
7.188
4.611
4.599
4.586
2.883
2.867
2.852
2.181
2.167
2.154
2.140
2.127
2.114
2.099
2.087
2.072
1.966
-0.000
1.888
4.720
1.996
1.005
0.950
2.000
2.091
0.885
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)


O
Ph
Ph
7.569
7.555
7.552
7.473
7.458
7.443
7.398
7.383
7.368
7.317
7.302
7.287
7.255
7.241
7.227
7.212
7.198
3.081
3.076
3.068
3.062
3.048
3.027
3.025
3.015
3.012
3.006
2.999
2.994
0.000
1.854
0.944
1.938
1.881
2.757
4.000
9.5
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
-0
f1 (ppm)

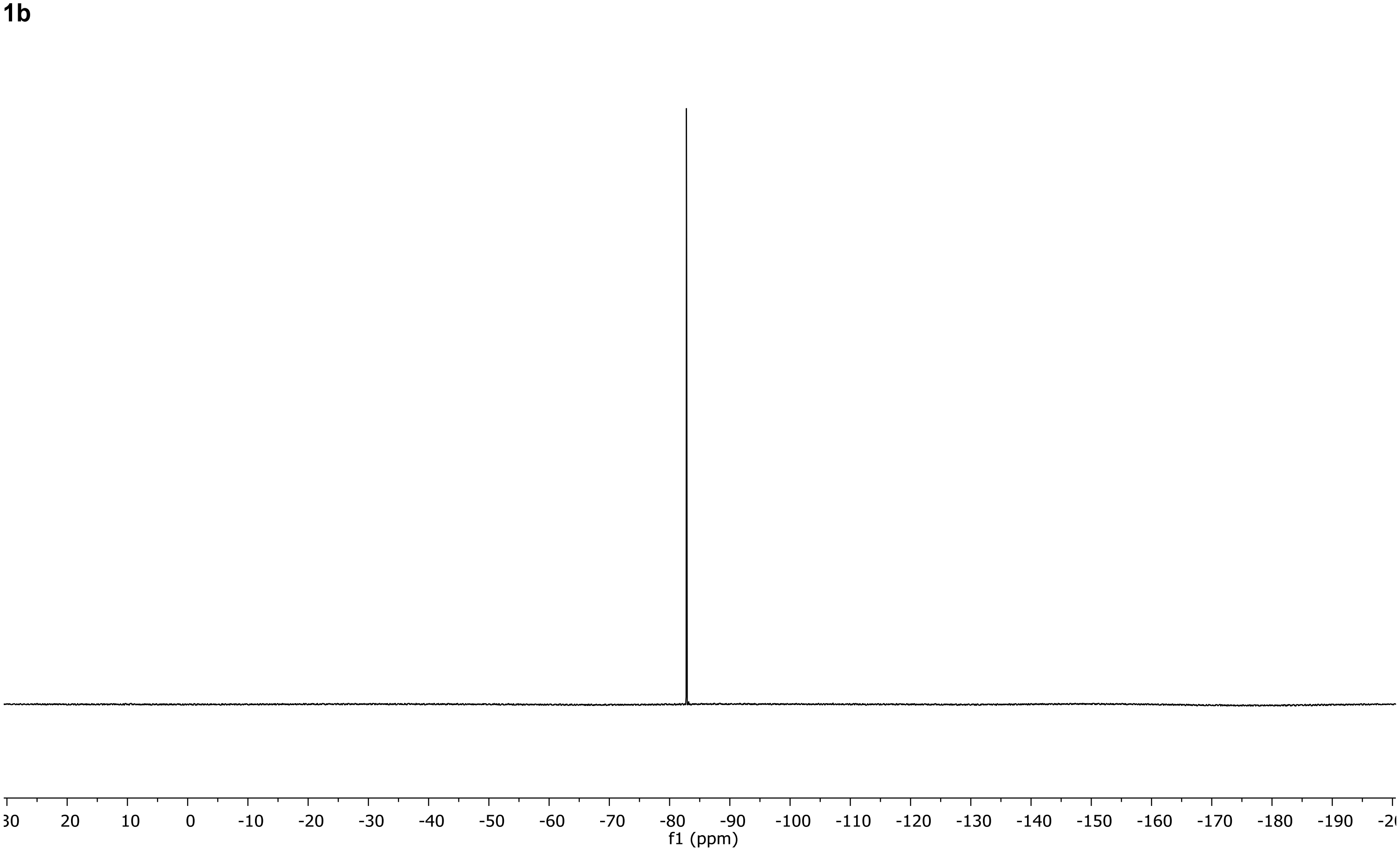
S4

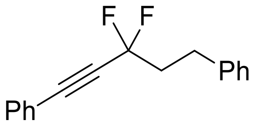

F
F
Ph
Ph
7.513
7.500
7.496
7.435
7.433
7.430
7.423
7.418
7.413
7.406
7.403
7.400
7.378
7.363
7.352
7.349
7.346
7.328
7.324
7.312
7.298
7.254
7.245
7.239
7.231
7.223
7.208
2.972
2.961
2.955
2.947
2.938
2.508
2.498
2.490
2.484
2.479
2.474
2.469
2.462
2.455
2.450
2.445
2.440
2.433
2.427
2.416
0.000
1.914
0.920
2.116
2.036
3.058
1.940
2.000
).0
9.5
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
-(
f1 (ppm)

1b

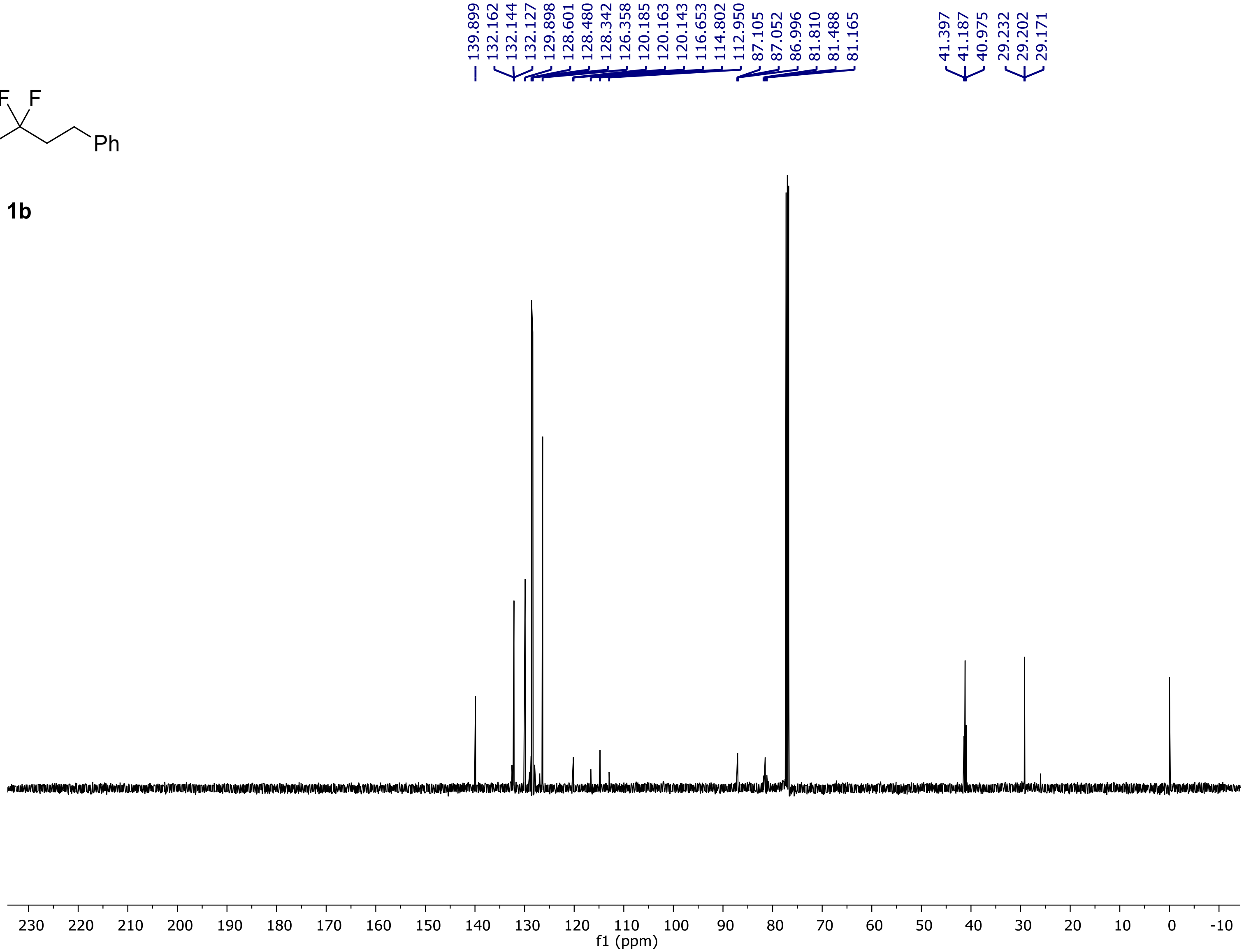

F
F
Ph
Ph

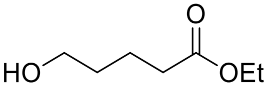
1b


-82.765
-82.796
-82.828
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

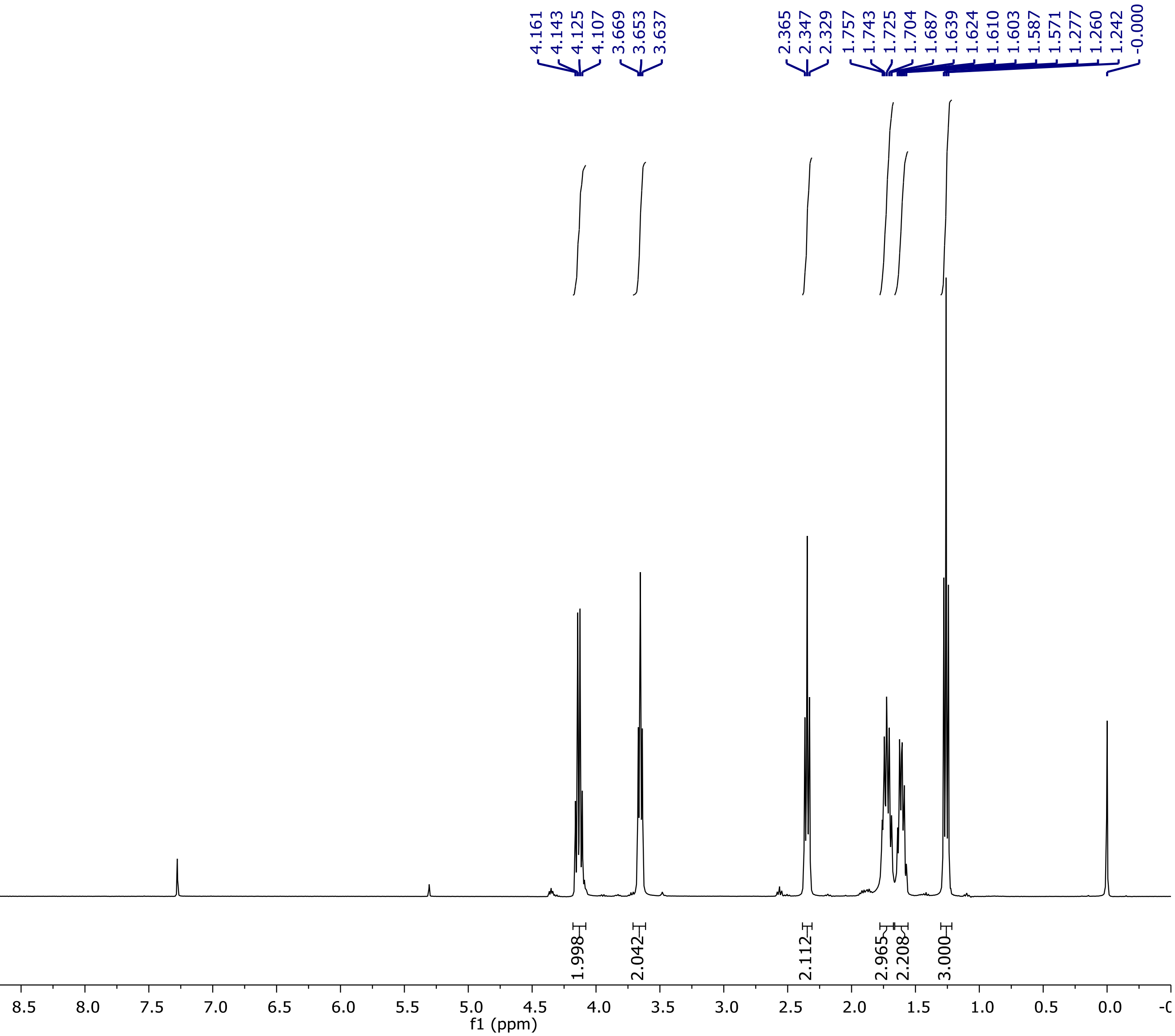

F
F
Ph
Ph

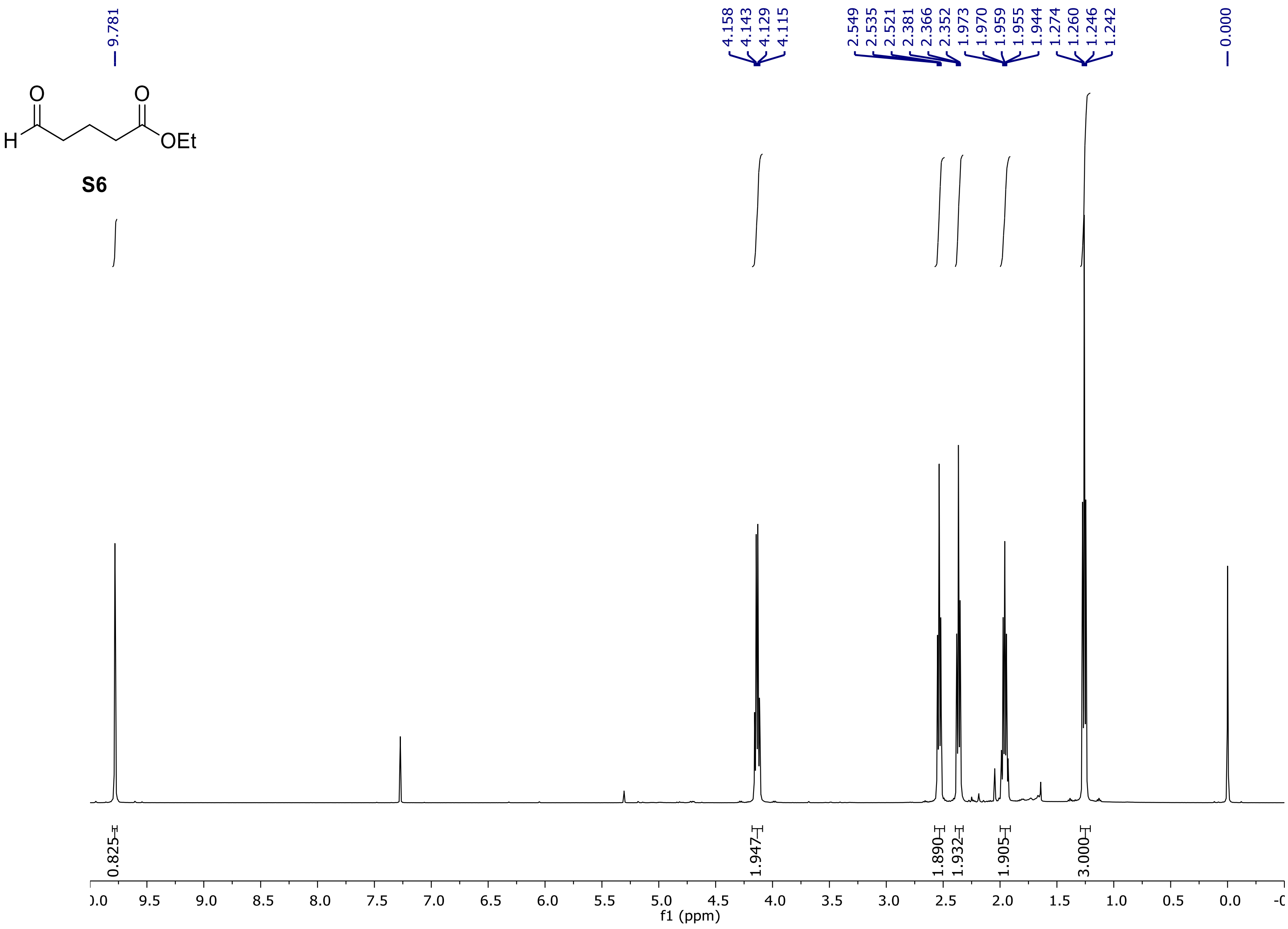
1b


139.899
132.162
132.144
132.127
129.898
128.601
128.480
128.342
126.358
120.185
120.163
120.143
116.653
114.802
112.950
87.105
87.052
86.996
81.810
81.488
81.165
41.397
41.187
40.975
29.232
29.202
29.171
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


HO
O
OEt

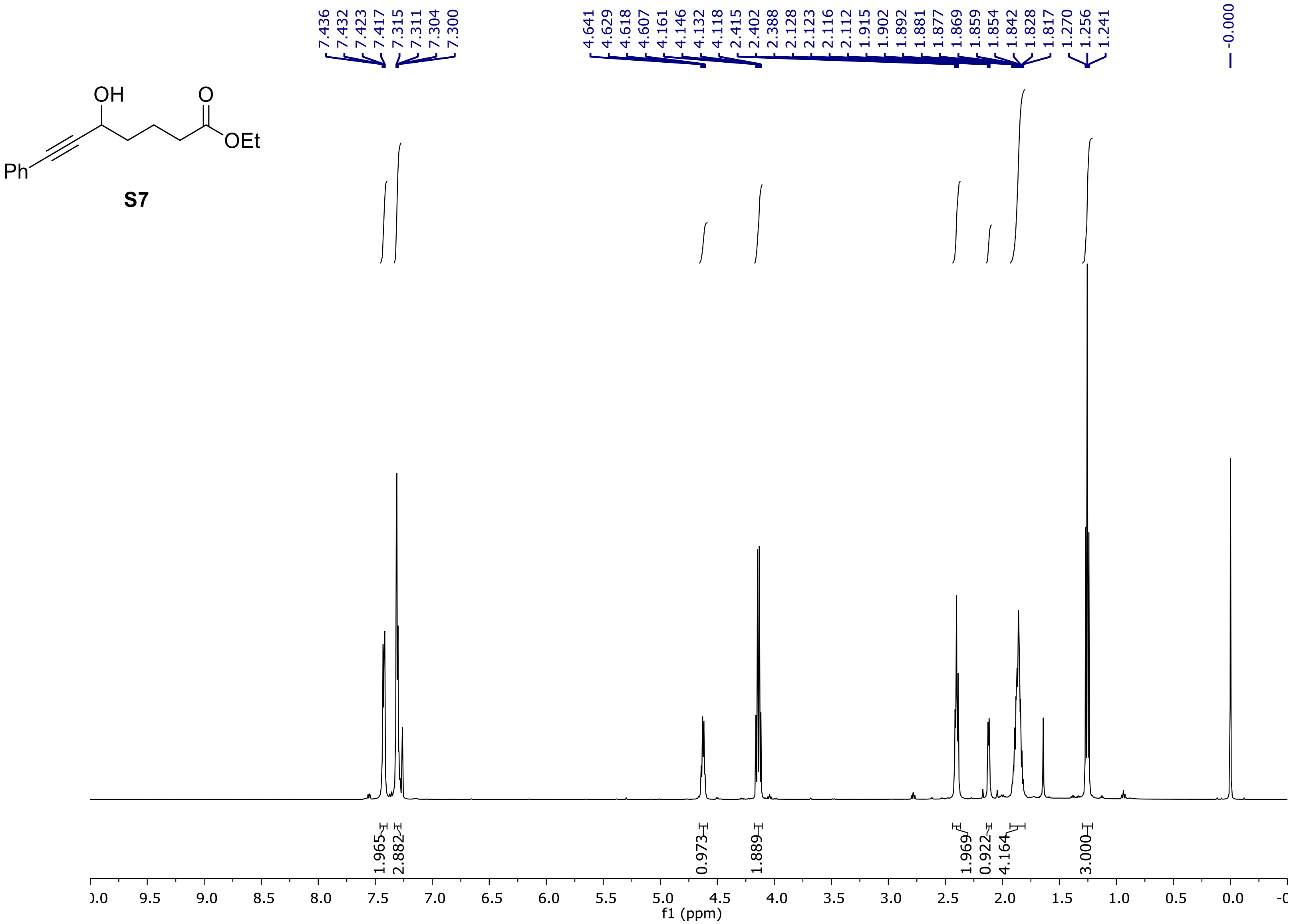
S5


4.161
4.143
4.125
4.107
3.669
3.653
3.637
2.365
2.347
2.329
1.757
1.743
1.725
1.704
1.687
1.639
1.624
1.610
1.603
1.587
1.571
1.277
1.260
1.242
-0.000
1.998
2.042
2.112
2.965
2.208
3.000
0.0
9.5
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
-0
f1 (ppm)



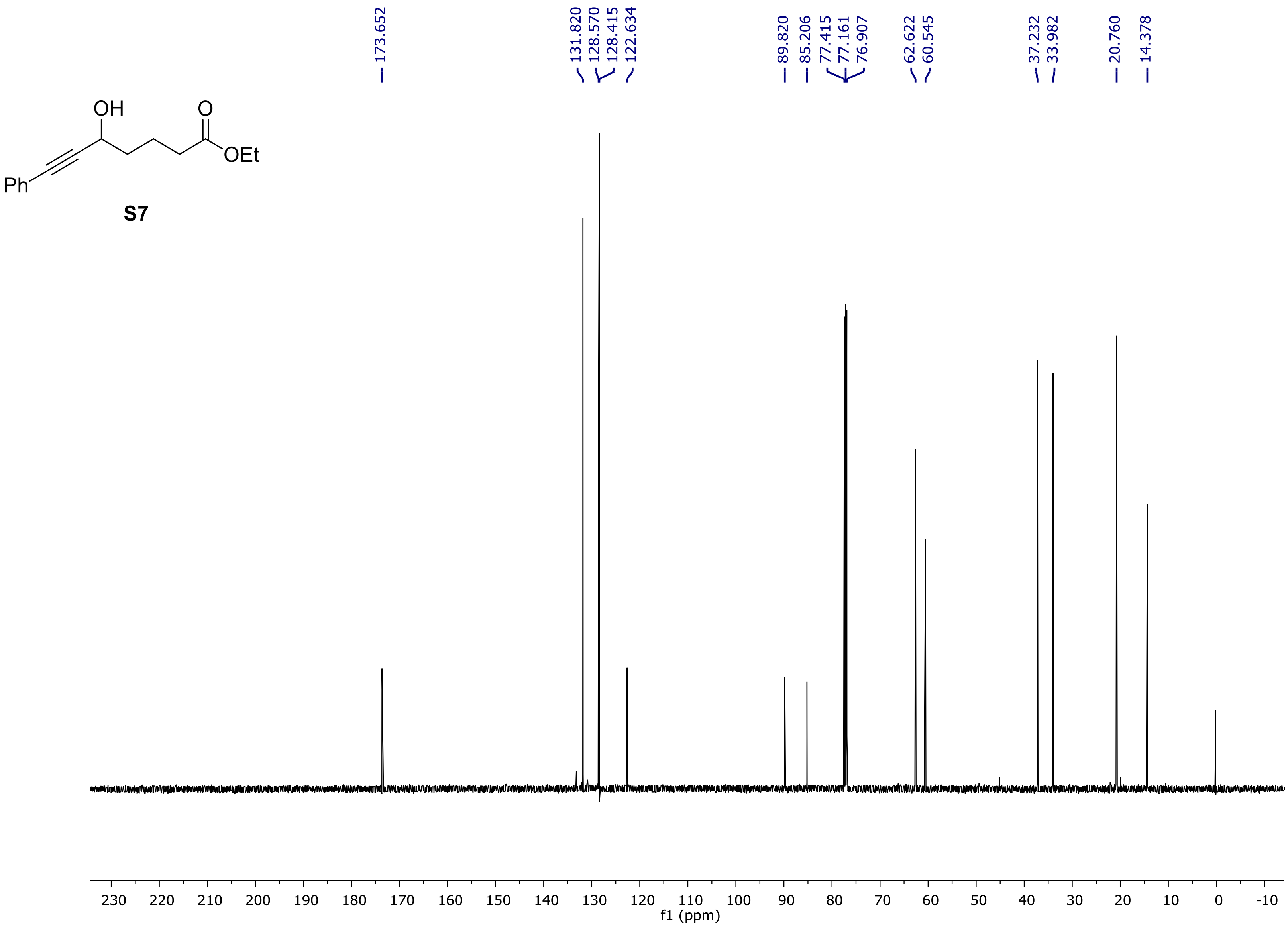
S6

9.781
4.158
4.143
4.129
4.115
2.549
2.535
2.521
2.381
2.366
2.352
1.973
1.970
1.959
1.955
1.944
1.274
1.260
1.246
1.242
0.000
0.825
1.947
1.890
1.932
1.905
3.000
9.5
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
f1 (ppm)

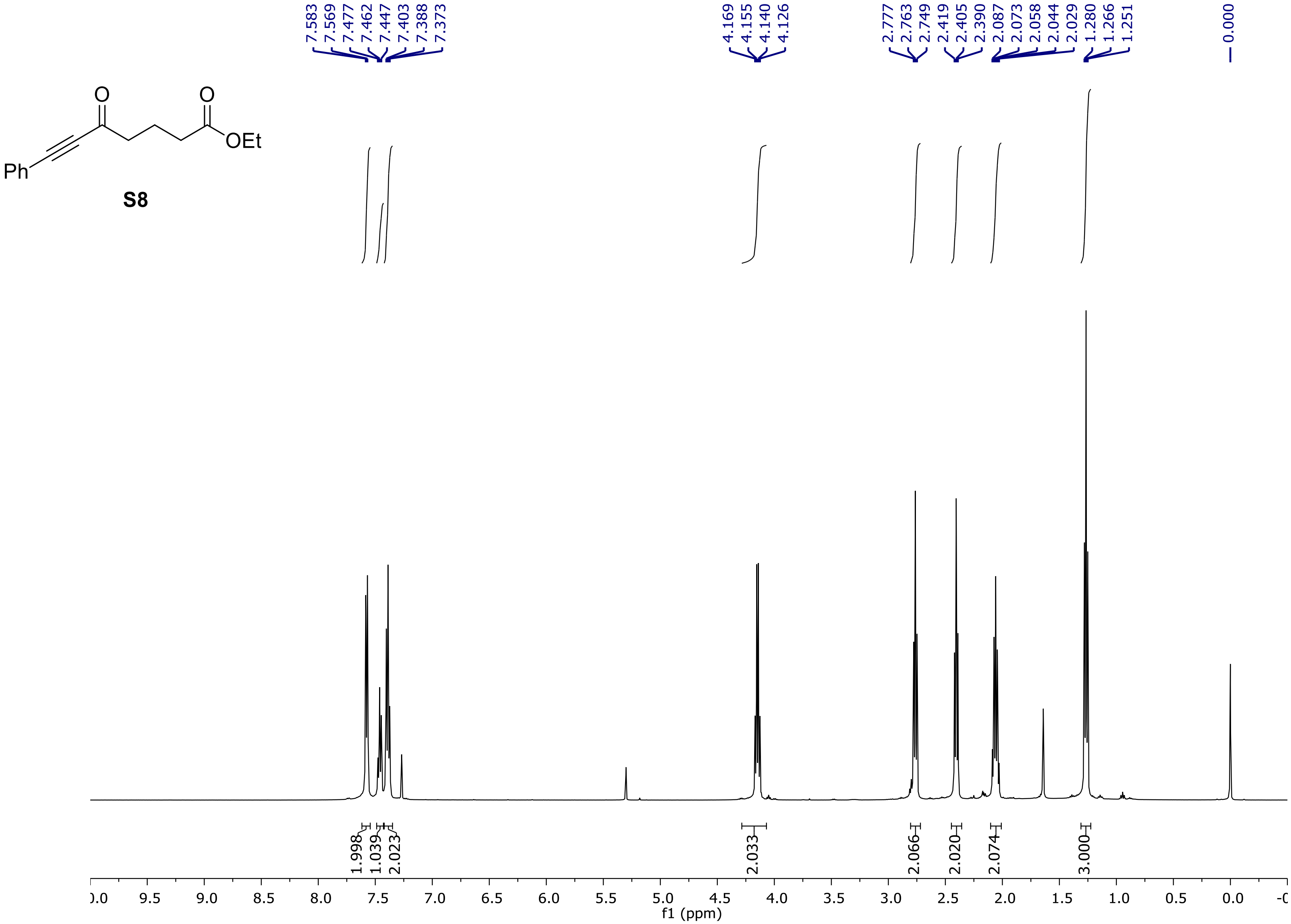

OH
O
OEt
Ph

S7

7.436
7.432
7.423
7.417
7.315
7.311
7.304
7.300
4.641
4.629
4.618
4.607
4.161
4.146
4.132
4.118
2.415
2.402
2.388
2.128
2.123
2.116
2.112
1.915
1.902
1.892
1.881
1.877
1.869
1.859
1.854
1.842
1.828
1.817
1.270
1.256
1.241
-0.000
1.965
2.882
0.973
1.889
1.969
0.922
4.164
3.000
).0
9.5
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
-(
f1 (ppm)

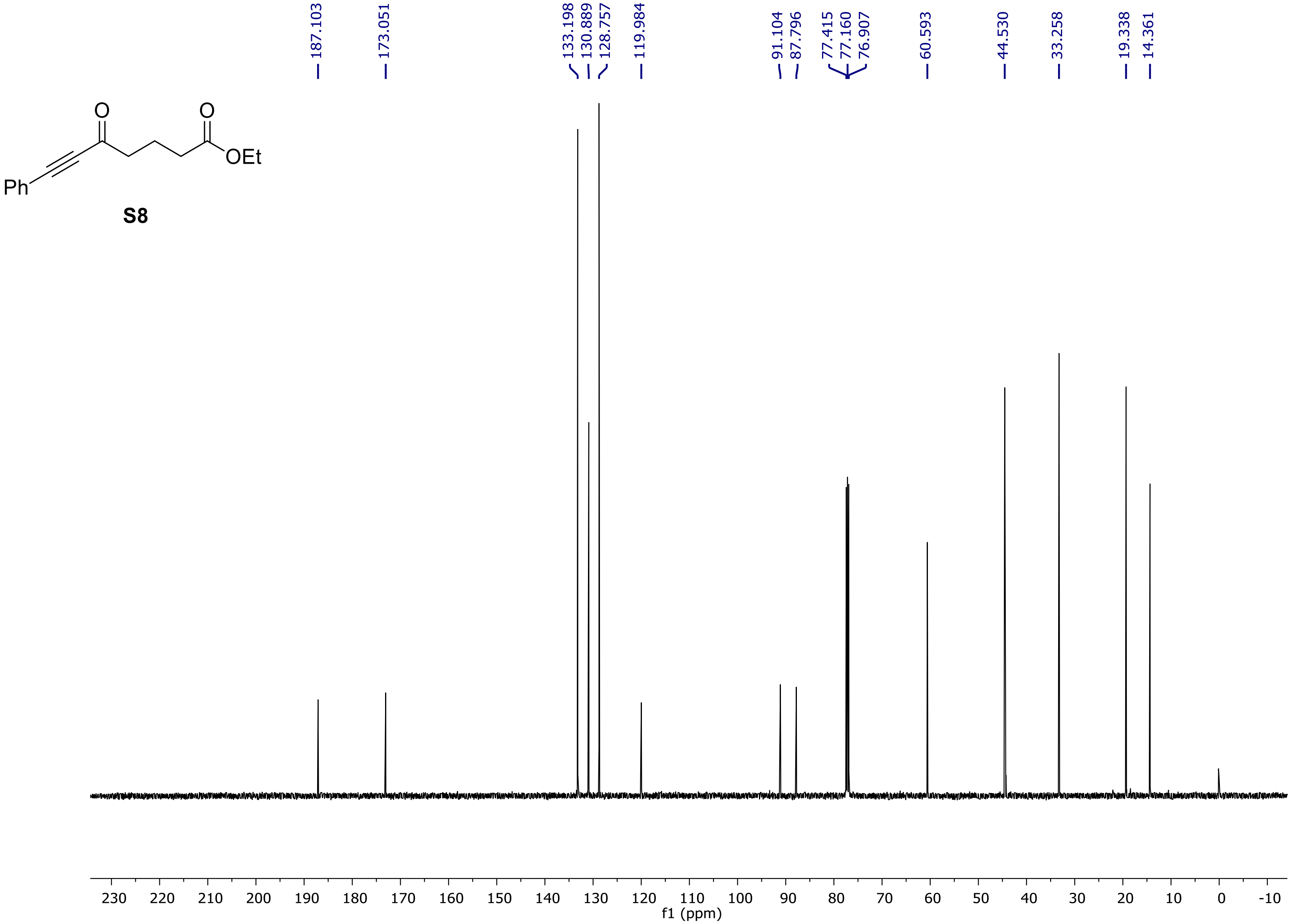

OH
O
OEt
Ph
173.652
131.820
128.570
128.415
122.634
89.820
85.206
77.415
77.161
76.907
62.622
60.545
37.232
33.982
20.760
14.378
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

S7


O
O
OEt
Ph

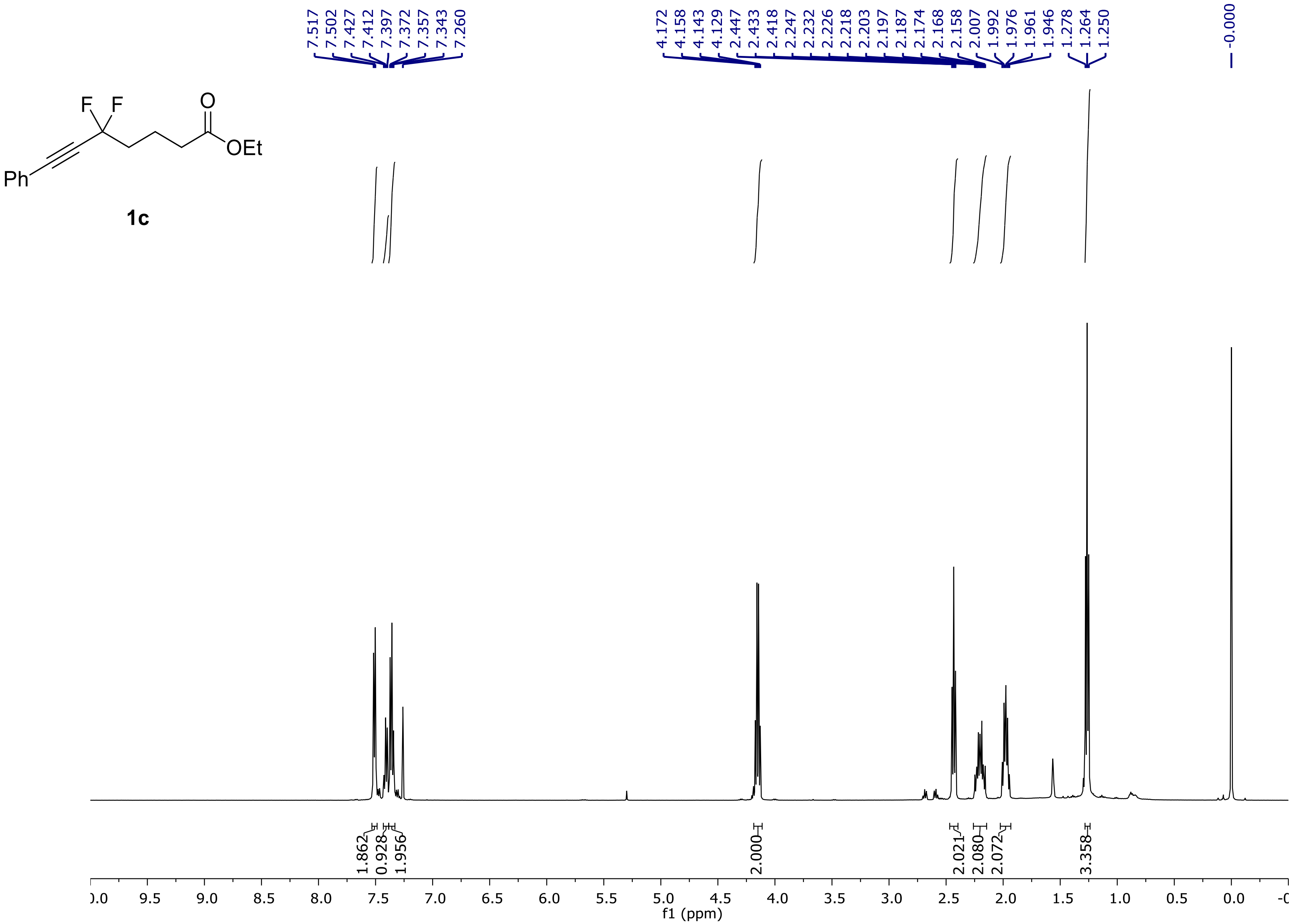
S8

7.583
7.569
7.477
7.462
7.447
7.403
7.388
7.373
4.169
4.155
4.140
4.126
2.777
2.763
2.749
2.419
2.405
2.390
2.087
2.073
2.058
2.044
2.029
1.280
1.266
1.251
0.000
1.998
1.039
2.023
2.033
2.066
2.020
2.074
3.000
0.0
9.5
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
-(
f1 (ppm)


O
O
Ph
OEt

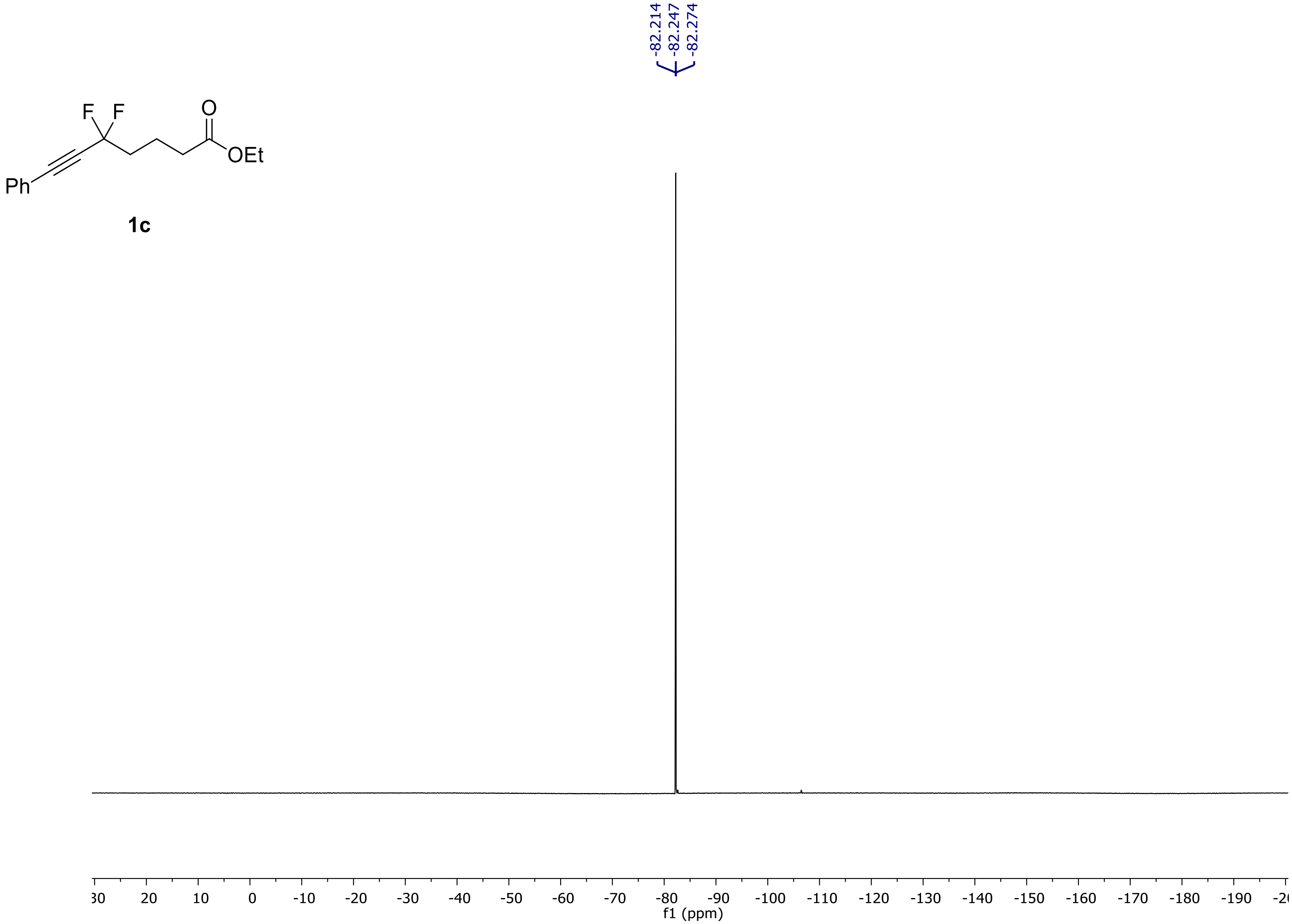
S8

187.103
173.051
133.198
130.889
128.757
119.984
91.104
87.796
77.415
77.160
76.907
60.593
44.530
33.258
19.338
14.361
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


F
F
O
OEt
Ph

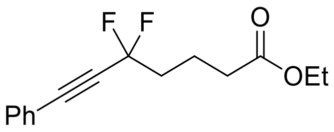
1c

7.517
7.502
7.427
7.412
7.397
7.372
7.357
7.343
7.260
4.172
4.158
4.143
4.129
2.447
2.433
2.418
2.247
2.232
2.226
2.218
2.203
2.197
2.187
2.174
2.168
2.158
2.007
1.992
1.976
1.961
1.946
1.278
1.264
1.250
-0.000
1.862
0.928
1.956
2.000
2.021
2.080
2.072
3.358
).0
9.5
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
-(
f1 (ppm)

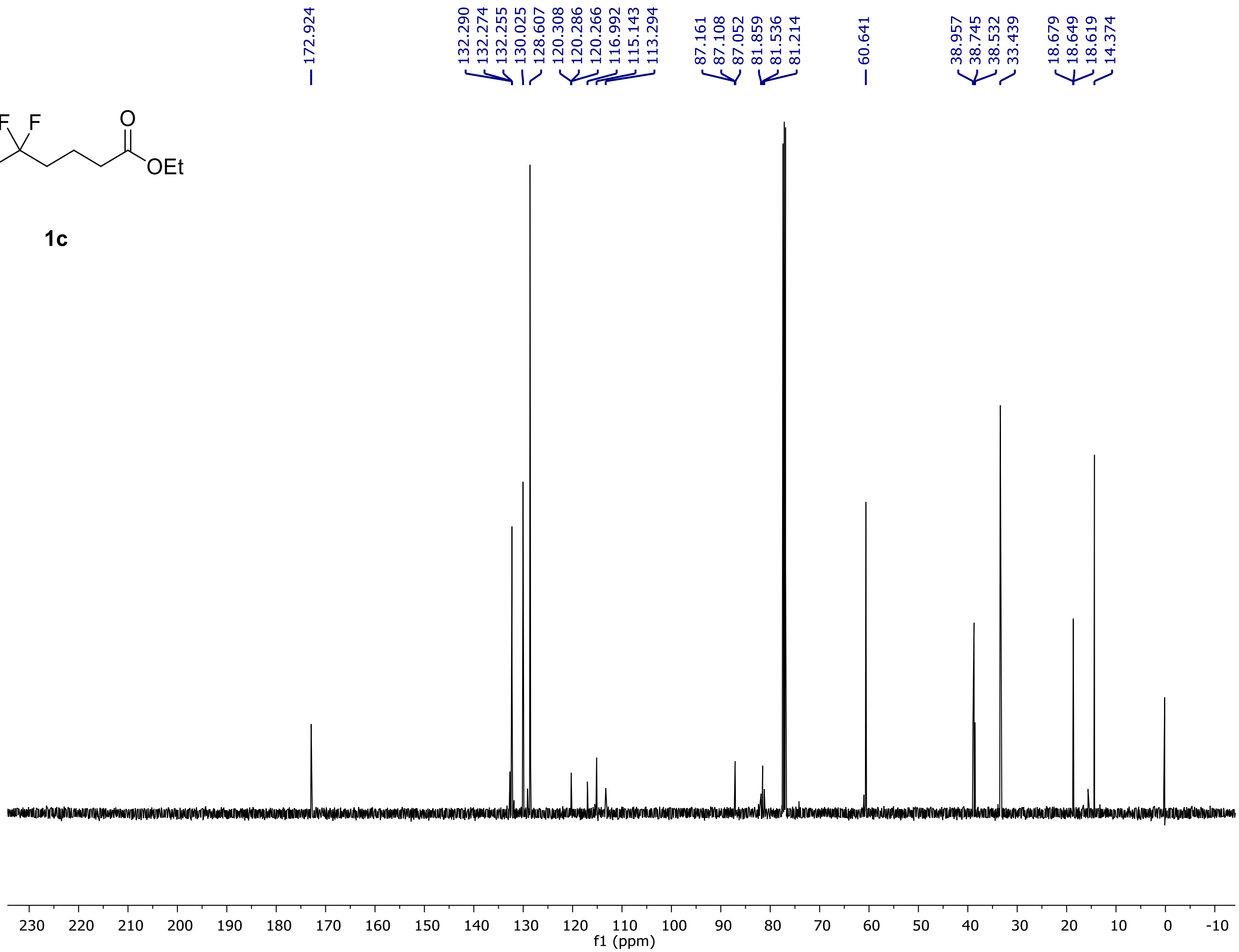

F
F
O
OEt
Ph

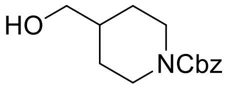
1c

-82.214
-82.247
-82.274
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

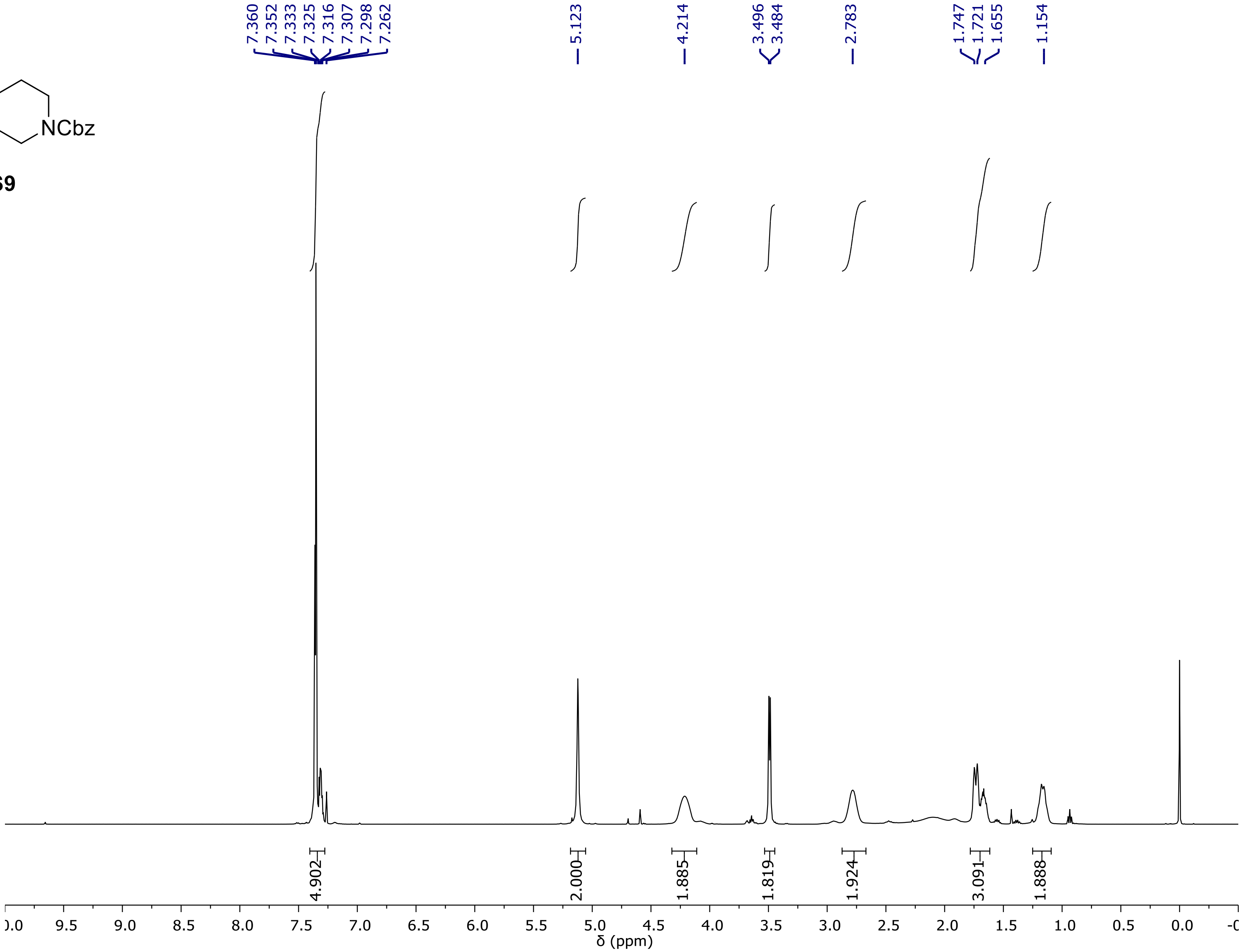

F
F
O
OEt
Ph

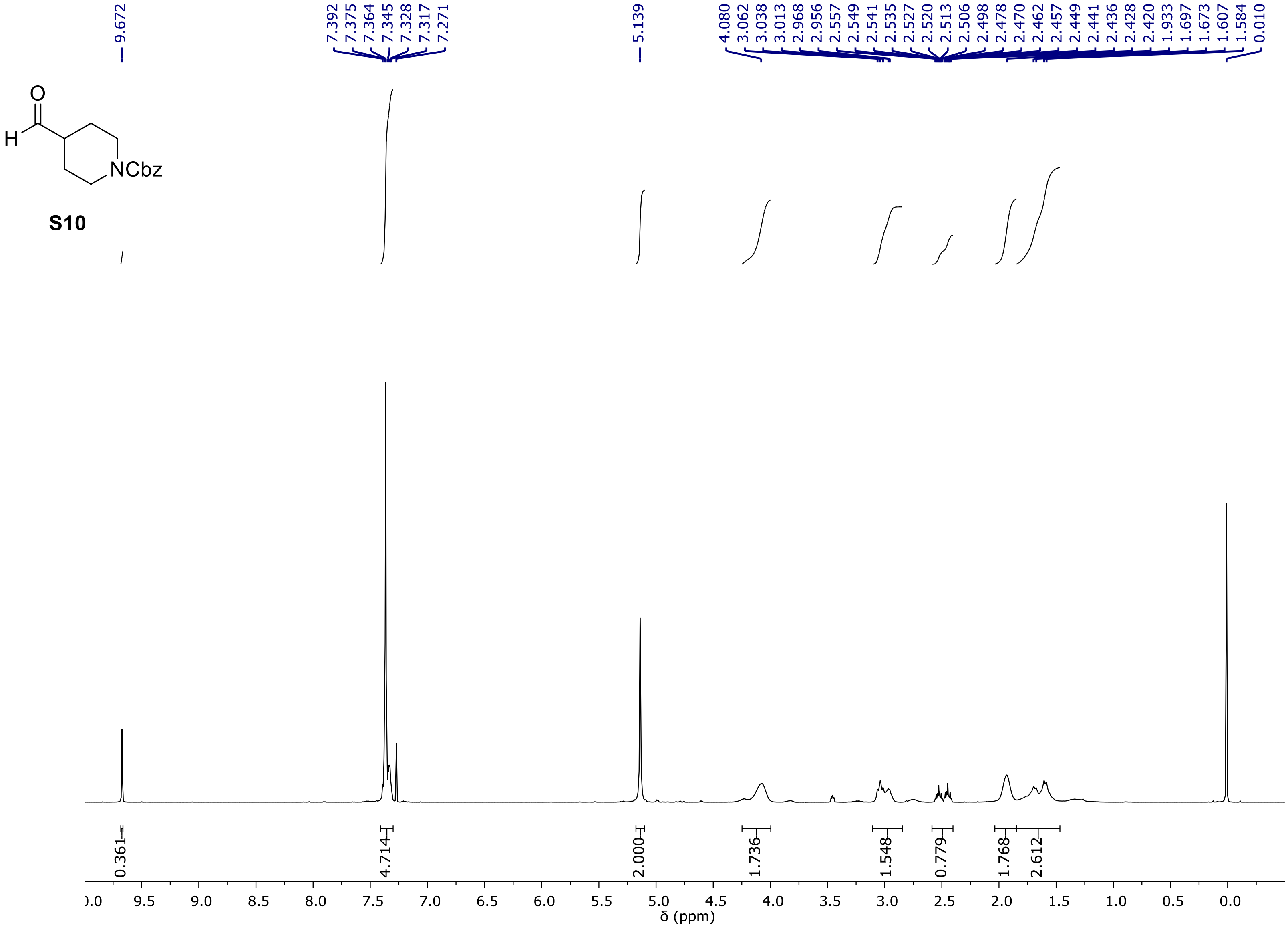
1c


172.924
132.290
132.274
132.255
130.025
128.607
120.308
120.286
120.266
116.992
115.143
113.294
87.161
87.108
87.052
81.859
81.536
81.214
60.641
38.957
38.745
38.532
33.439
18.679
18.649
18.619
14.374
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


HO
NCbz

S9

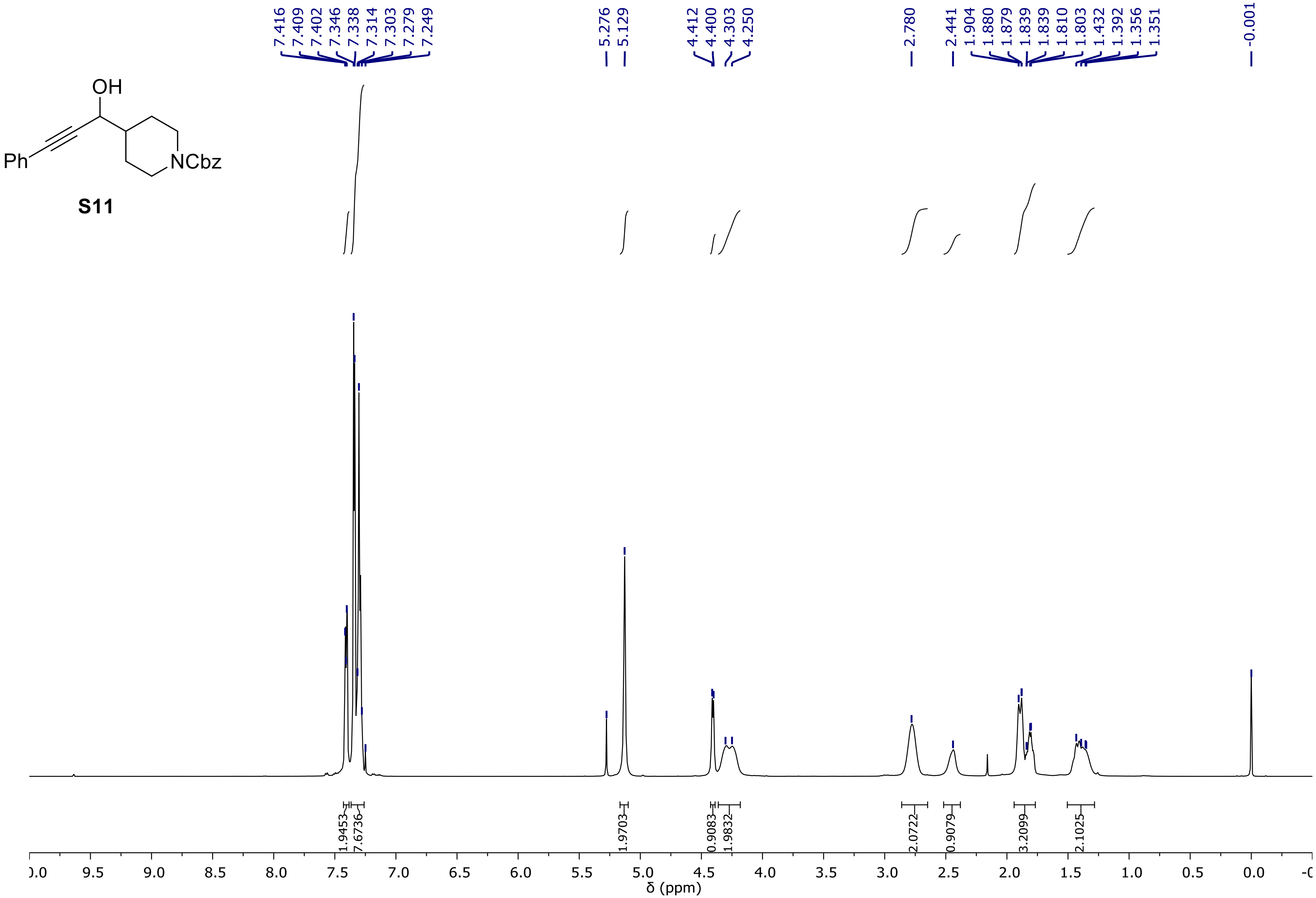

7.360
7.352
7.333
7.325
7.316
7.307
7.298
7.262
5.123
4.214
3.496
3.484
2.783
1.747
1.721
1.655
1.154
4.902
2.000
1.885
1.819
1.924
3.091
1.888
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)



O
H
NCbz

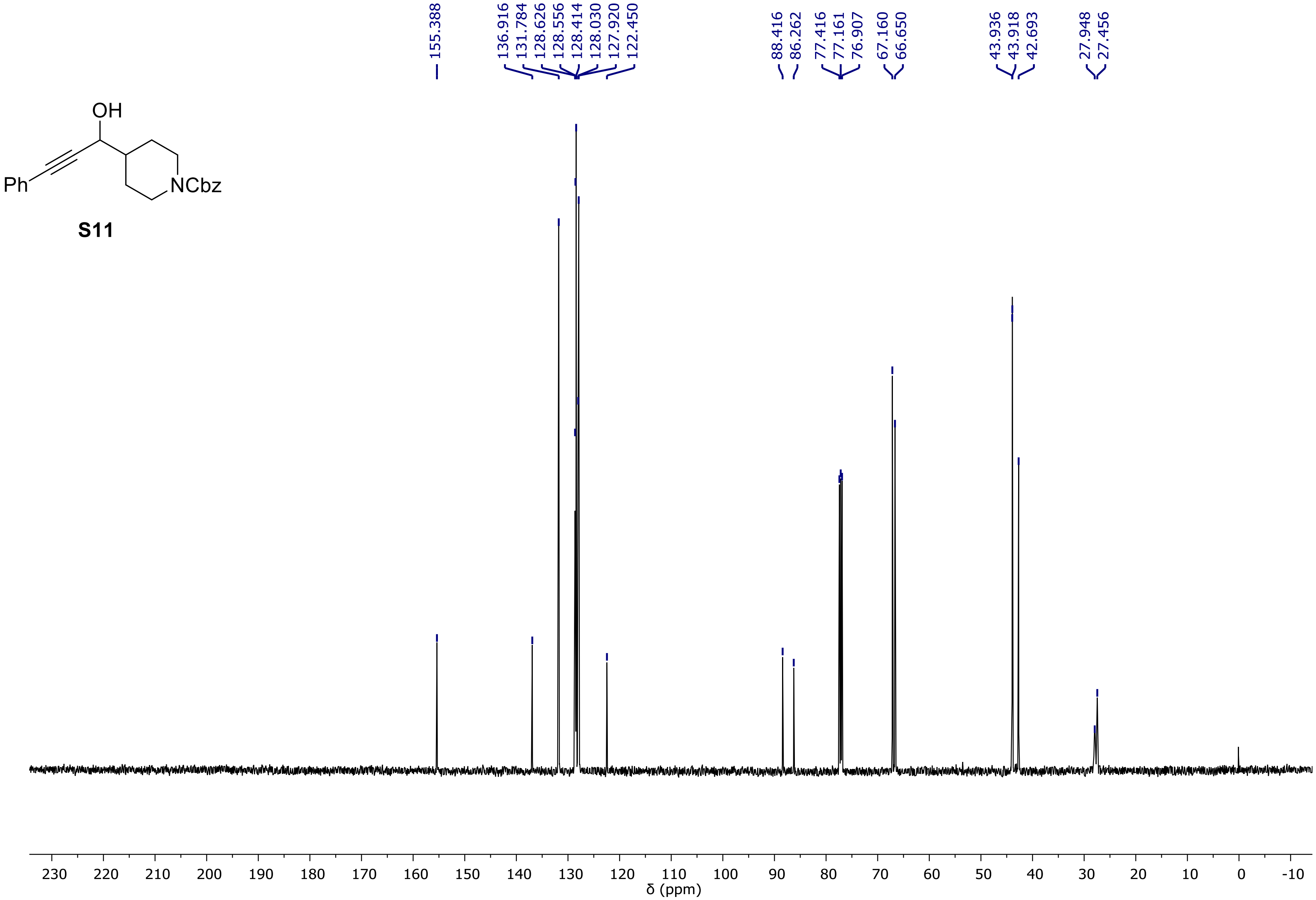
S10

9.672
7.392
7.375
7.364
7.345
7.328
7.317
7.271
5.139
4.080
3.062
3.038
3.013
2.968
2.956
2.557
2.549
2.541
2.535
2.527
2.520
2.513
2.506
2.498
2.478
2.470
2.462
2.457
2.449
2.441
2.436
2.428
2.420
1.933
1.697
1.673
1.607
1.584
0.010
0.361
4.714
2.000
1.736
1.548
0.779
1.768
2.612
0.0
9.5
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
δ (ppm)


OH
Ph
NCbz

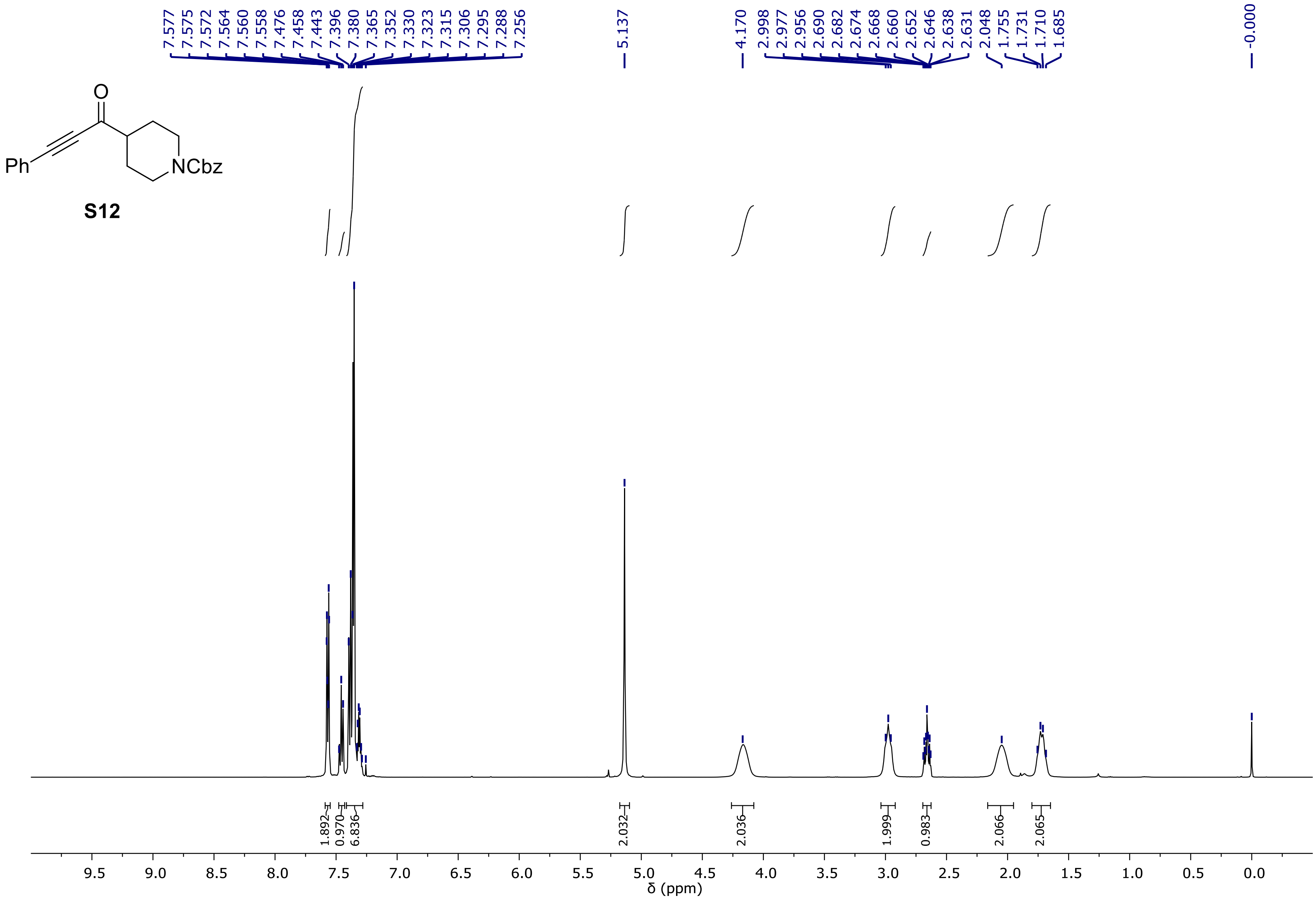
S11

7.416
7.409
7.402
7.346
7.338
7.314
7.303
7.279
7.249
5.276
5.129
4.412
4.400
4.303
4.250
2.780
2.441
1.904
1.880
1.879
1.839
1.839
1.810
1.803
1.432
1.392
1.356
1.351
-0.001
1.9453
7.6736
1.9703
0.9083
1.9832
2.0722
0.9079
3.2099
2.1025
9.5
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
δ (ppm)


OH
Ph
NCbz

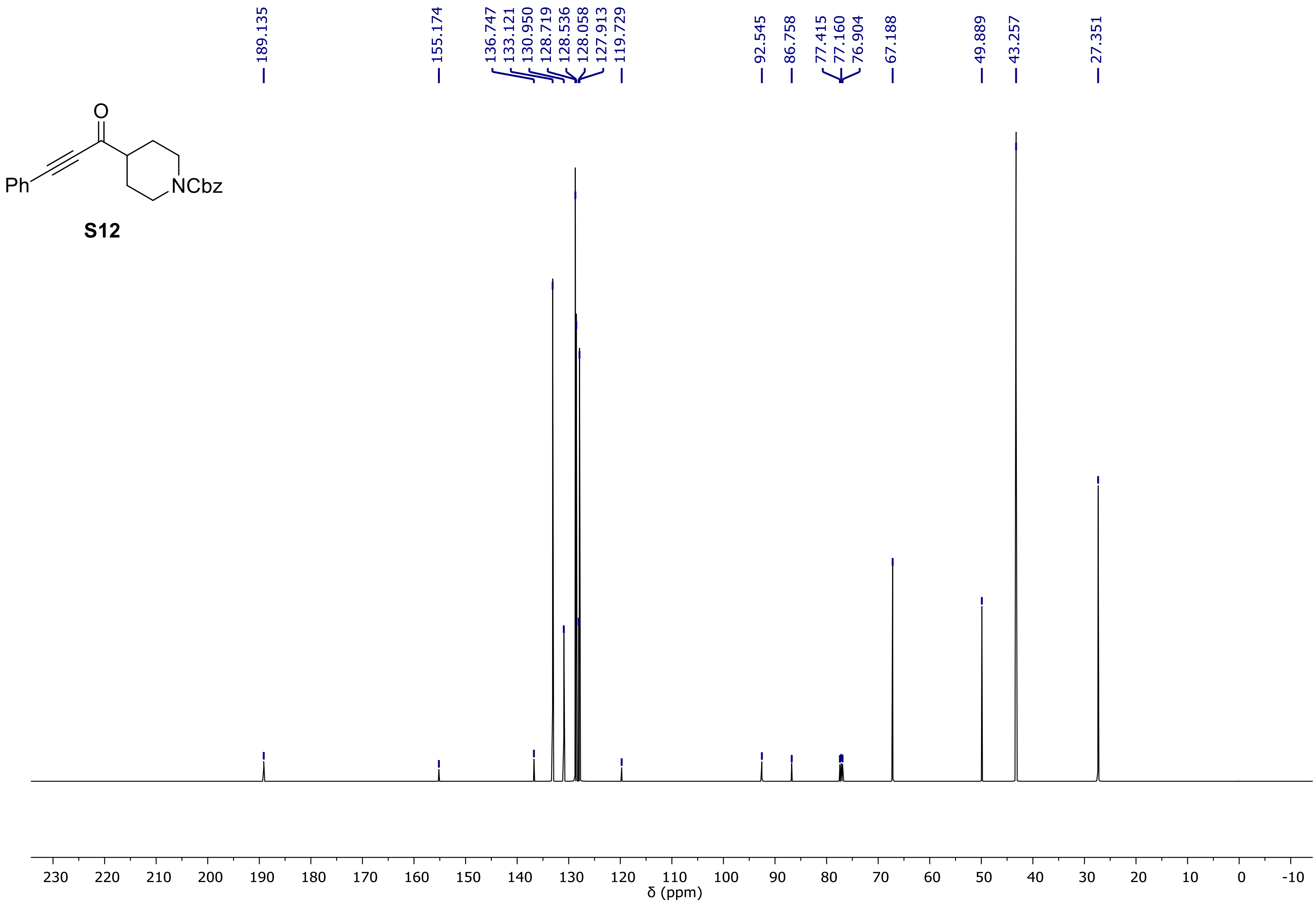
S11

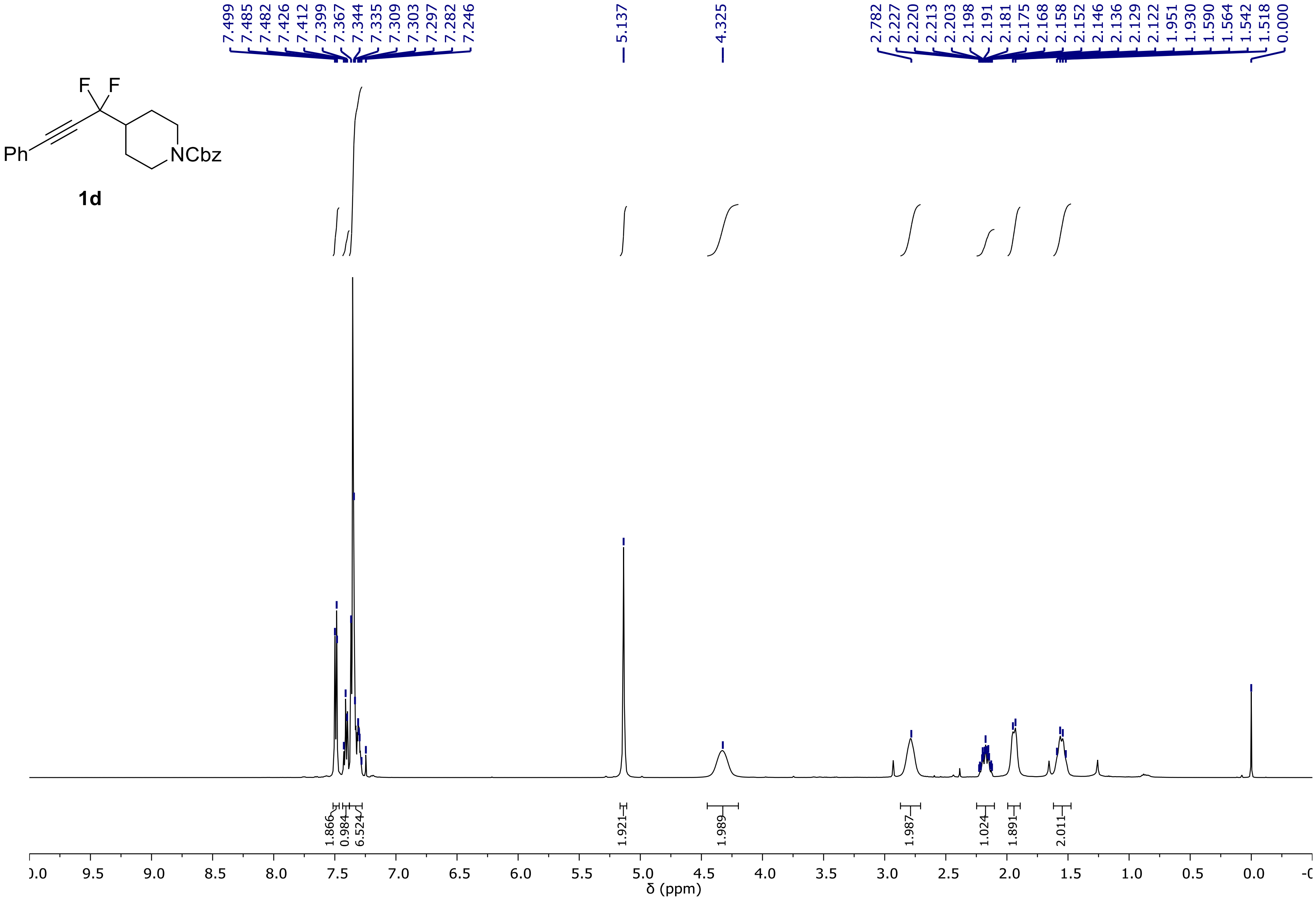
155.388
136.916
131.784
128.626
128.556
128.414
128.030
127.920
122.450
88.416
86.262
77.416
77.161
76.907
67.160
66.650
43.936
43.918
42.693
27.948
27.456
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)



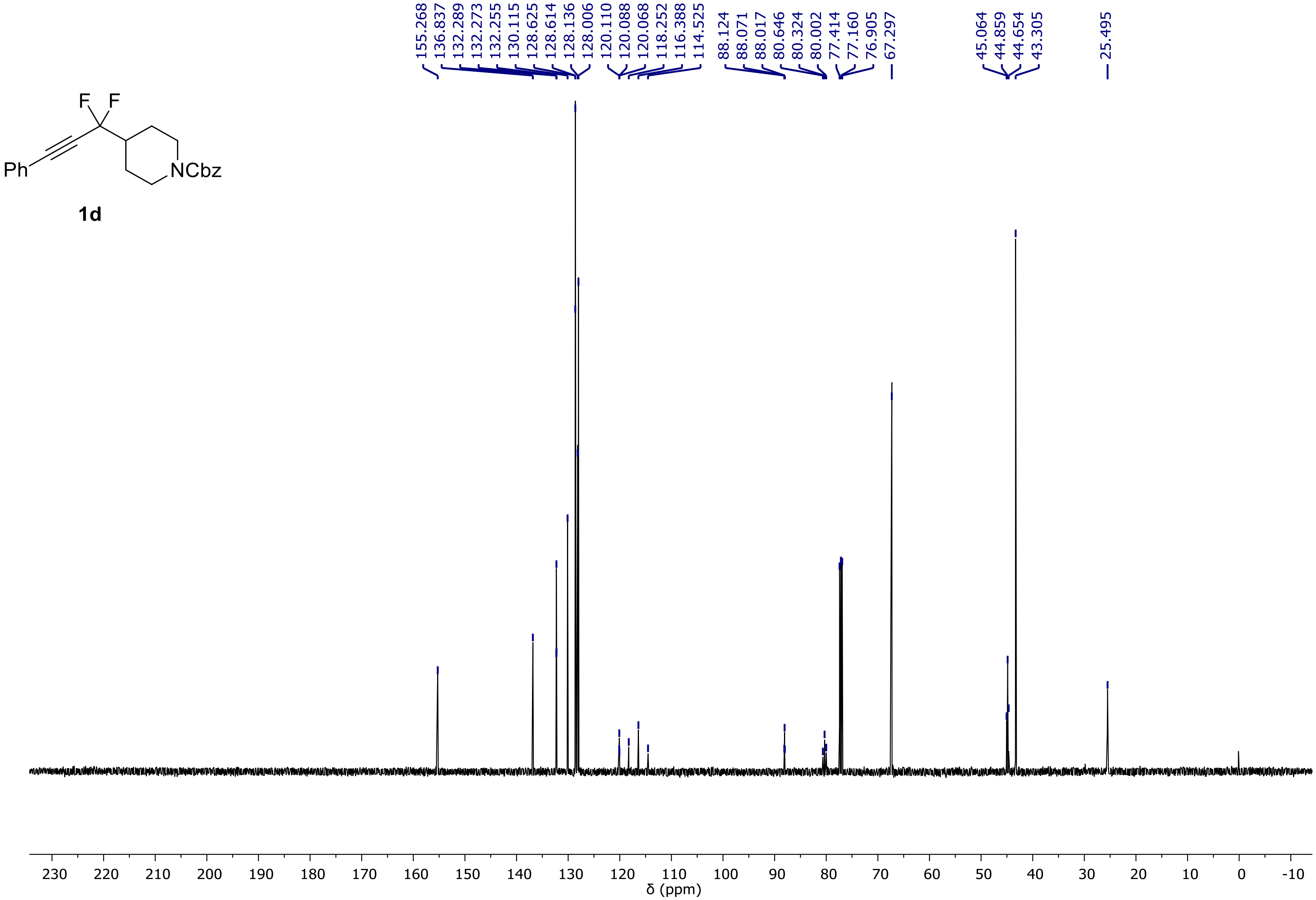
S12

O
Ph
NCbz
7.577
7.575
7.572
7.564
7.560
7.558
7.476
7.458
7.443
7.396
7.380
7.365
7.352
7.330
7.323
7.315
7.306
7.295
7.288
7.256
5.137
4.170
2.998
2.977
2.956
2.690
2.682
2.674
2.668
2.660
2.652
2.646
2.638
2.631
2.048
1.755
1.731
1.710
1.685
-0.000
1.892
0.970
6.836
2.032
2.036
1.999
0.983
2.066
2.065
9.5
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
δ (ppm)


S12
O
Ph
NCbz
189.135
155.174
136.747
133.121
130.950
128.719
128.536
128.058
127.913
119.729
92.545
86.758
77.415
77.160
76.904
67.188
49.889
43.257
27.351
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

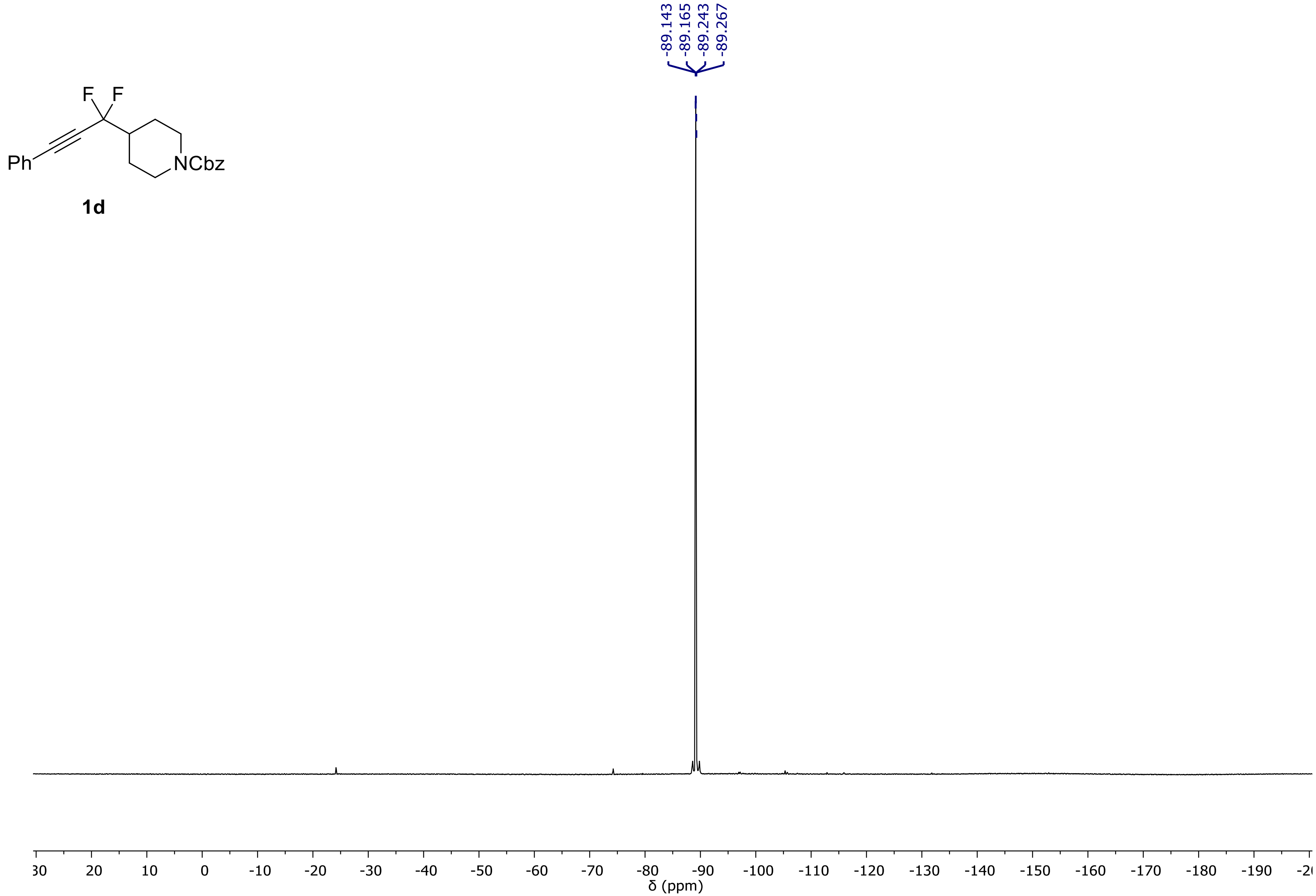

1d

F F
Ph
NCbz
7.499
7.485
7.482
7.426
7.412
7.399
7.367
7.344
7.335
7.309
7.303
7.297
7.282
7.246
5.137
4.325
2.782
2.227
2.220
2.213
2.203
2.198
2.191
2.181
2.175
2.168
2.158
2.152
2.146
2.136
2.129
2.122
1.951
1.930
1.590
1.564
1.542
1.518
0.000
1.866
0.984
6.524
1.921
1.989
1.987
1.024
1.891
2.011
0.0
9.5
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
δ (ppm)



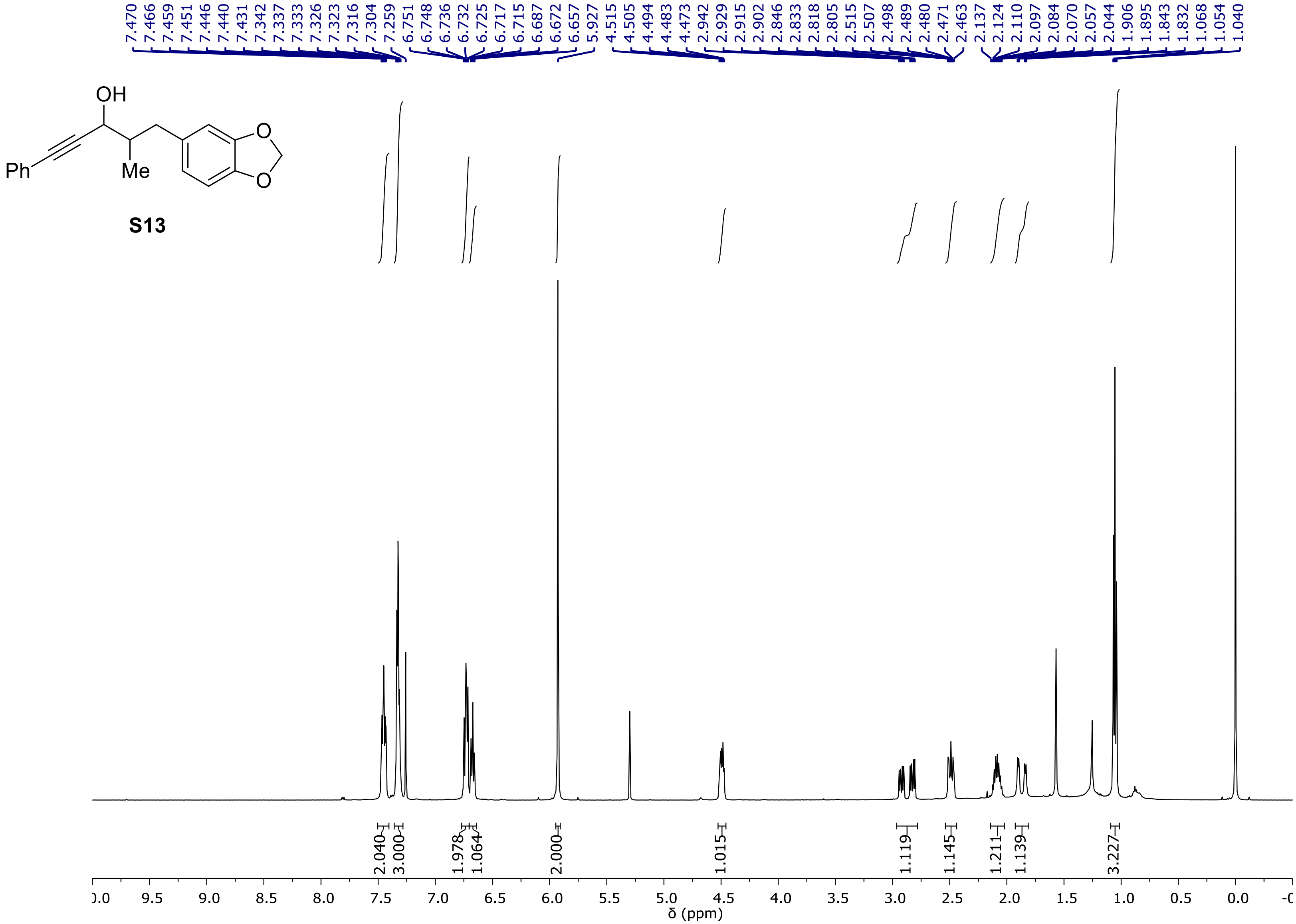
1d

155.268
136.837
132.289
132.273
132.255
130.115
128.625
128.614
128.136
128.006
120.110
120.088
120.068
118.252
116.388
114.525
88.124
88.071
88.017
80.646
80.324
80.002
77.414
77.160
76.905
67.297
45.064
44.859
44.654
43.305
25.495
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)


F
F
Ph
NCbz

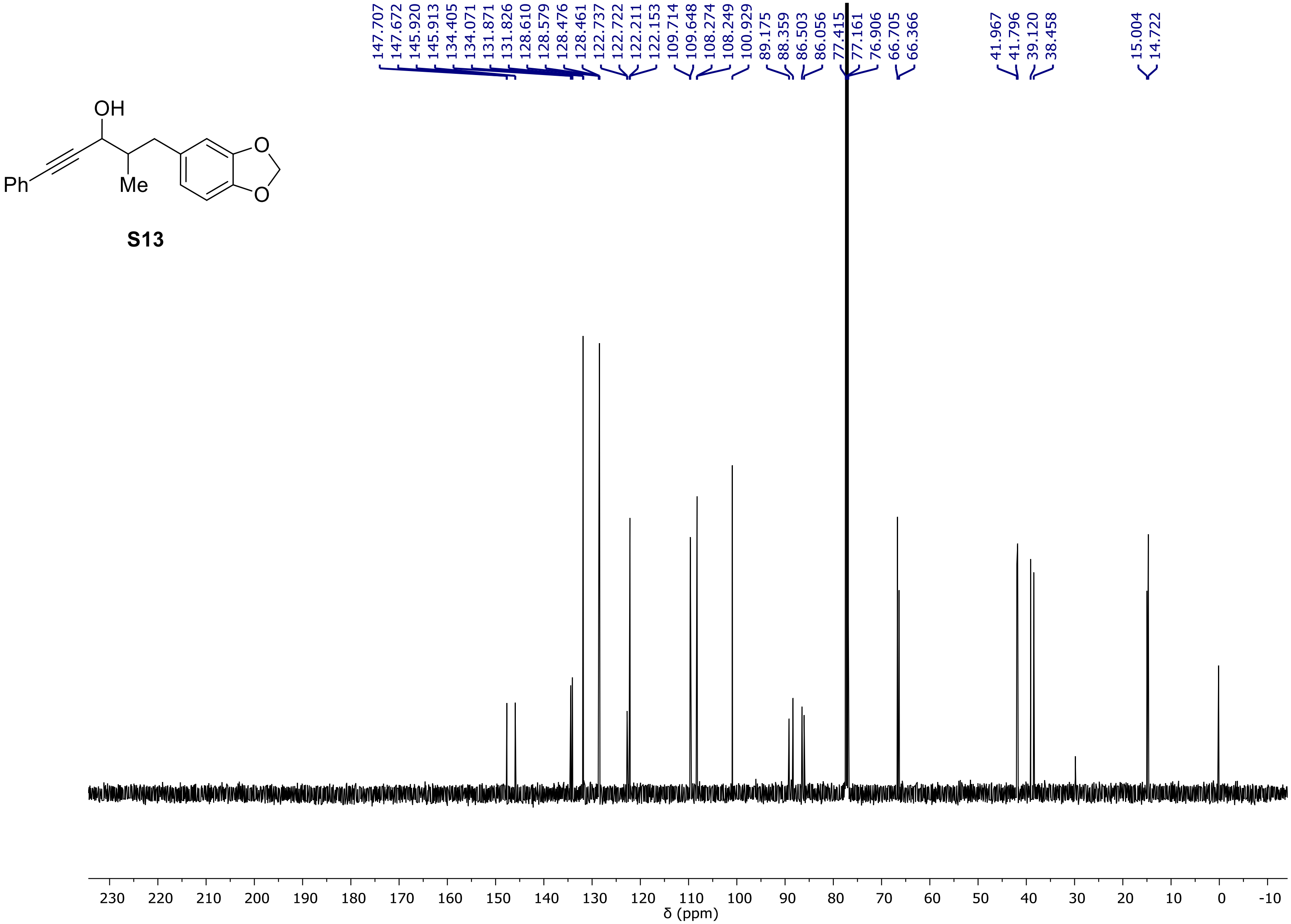
1d

-89.143
-89.165
-89.243
-89.267
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
δ (ppm)


OH
Ph
Me
O
O

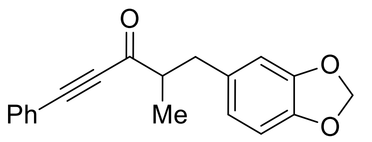
S13

7.470
7.466
7.459
7.451
7.446
7.440
7.431
7.342
7.337
7.333
7.326
7.323
7.316
7.304
7.259
6.751
6.748
6.736
6.732
6.725
6.717
6.715
6.687
6.672
6.657
5.927
4.515
4.505
4.494
4.483
4.473
2.942
2.929
2.915
2.902
2.846
2.833
2.818
2.805
2.515
2.507
2.498
2.489
2.480
2.471
2.463
2.137
2.124
2.110
2.097
2.084
2.070
2.057
2.044
1.906
1.895
1.843
1.832
1.068
1.054
1.040
2.040
3.000
1.978
1.064
2.000
1.015
1.119
1.145
1.211
1.139
3.227
).0
9.5
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
-(
δ (ppm)

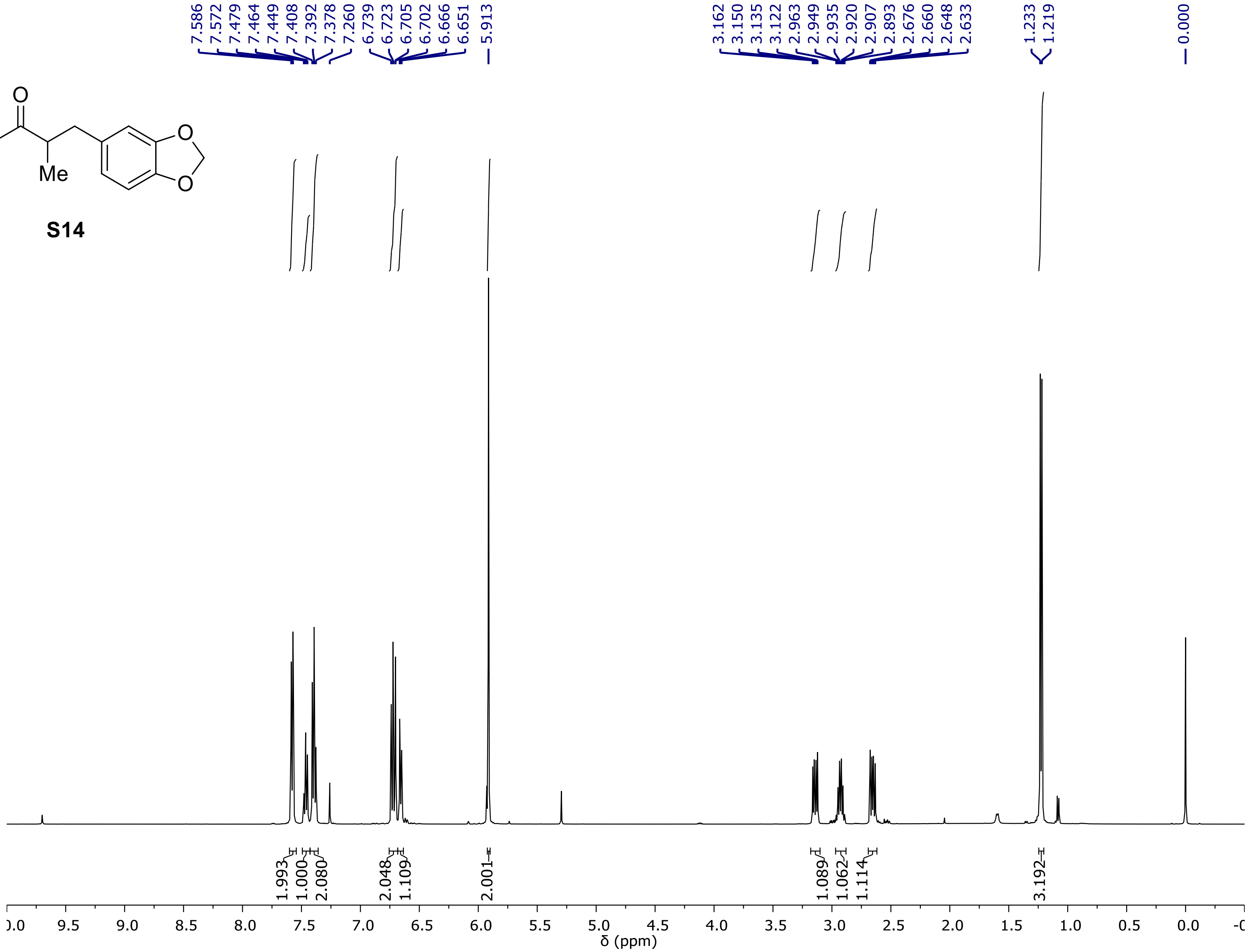

OH
Ph
Me
O
O

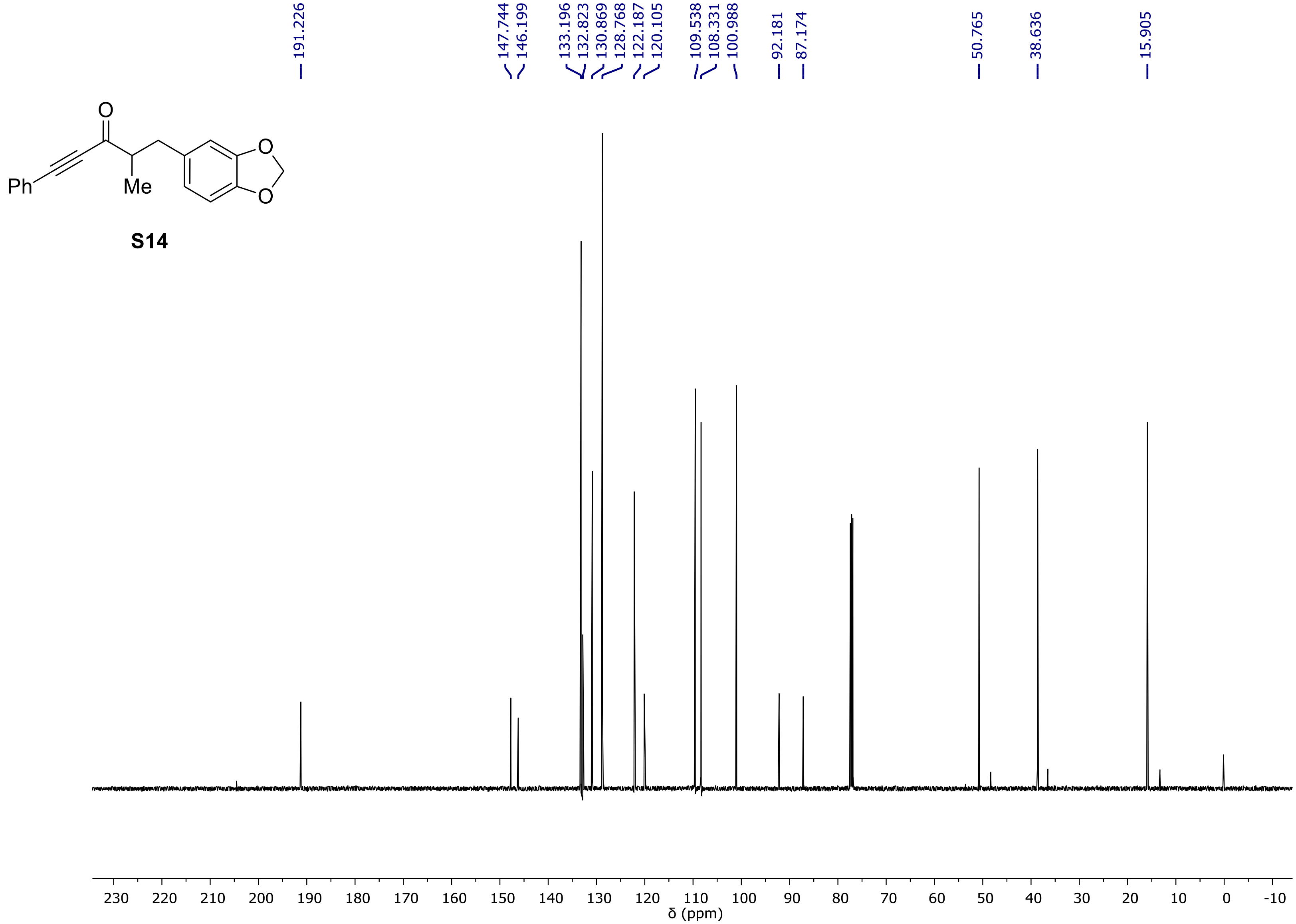
S13

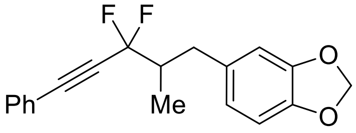
147.707
147.672
145.920
145.913
134.405
134.071
131.871
131.826
128.610
128.579
128.476
128.461
122.737
122.722
122.211
122.153
109.714
109.648
108.274
108.249
100.929
89.175
88.359
86.503
86.056
77.415
77.161
76.906
66.705
66.366
41.967
41.796
39.120
38.458
15.004
14.722
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)


O
Ph
Me
O
O

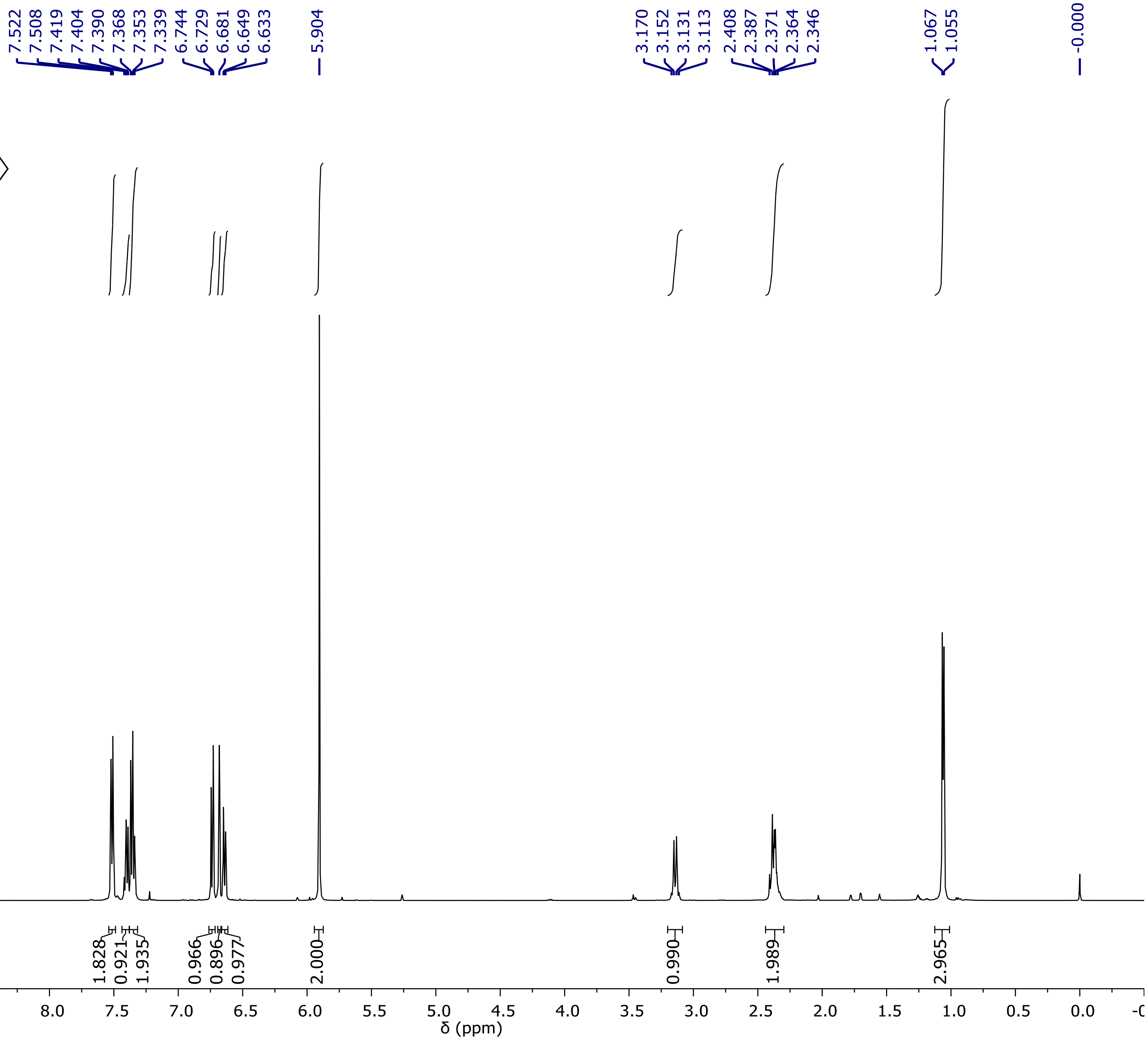
S14

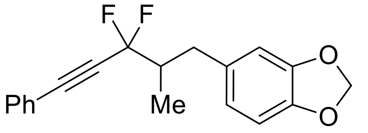

7.586
7.572
7.479
7.464
7.449
7.408
7.392
7.378
7.260
6.739
6.723
6.705
6.702
6.666
6.651
5.913
3.162
3.150
3.135
3.122
2.963
2.949
2.935
2.920
2.907
2.893
2.676
2.660
2.648
2.633
1.233
1.219
0.000
1.993
1.000
2.080
2.048
1.109
2.001
1.089
1.062
1.114
3.192
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)


191.226
147.744
146.199
133.196
132.823
130.869
128.768
122.187
120.105
109.538
108.331
100.988
92.181
87.174
50.765
38.636
15.905
O
Ph
Me
O
O
S14
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

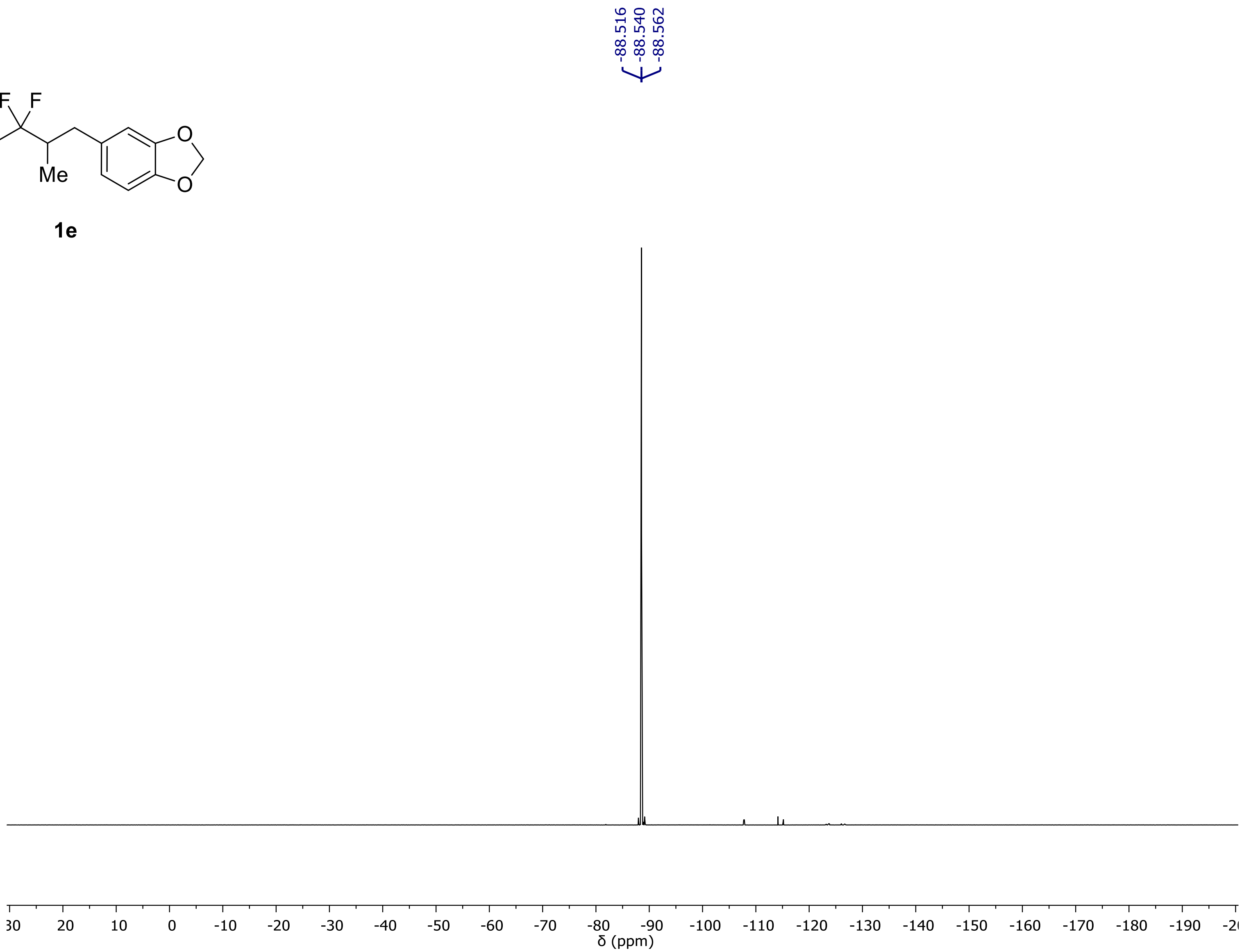

F
F
Ph
Me
O
O

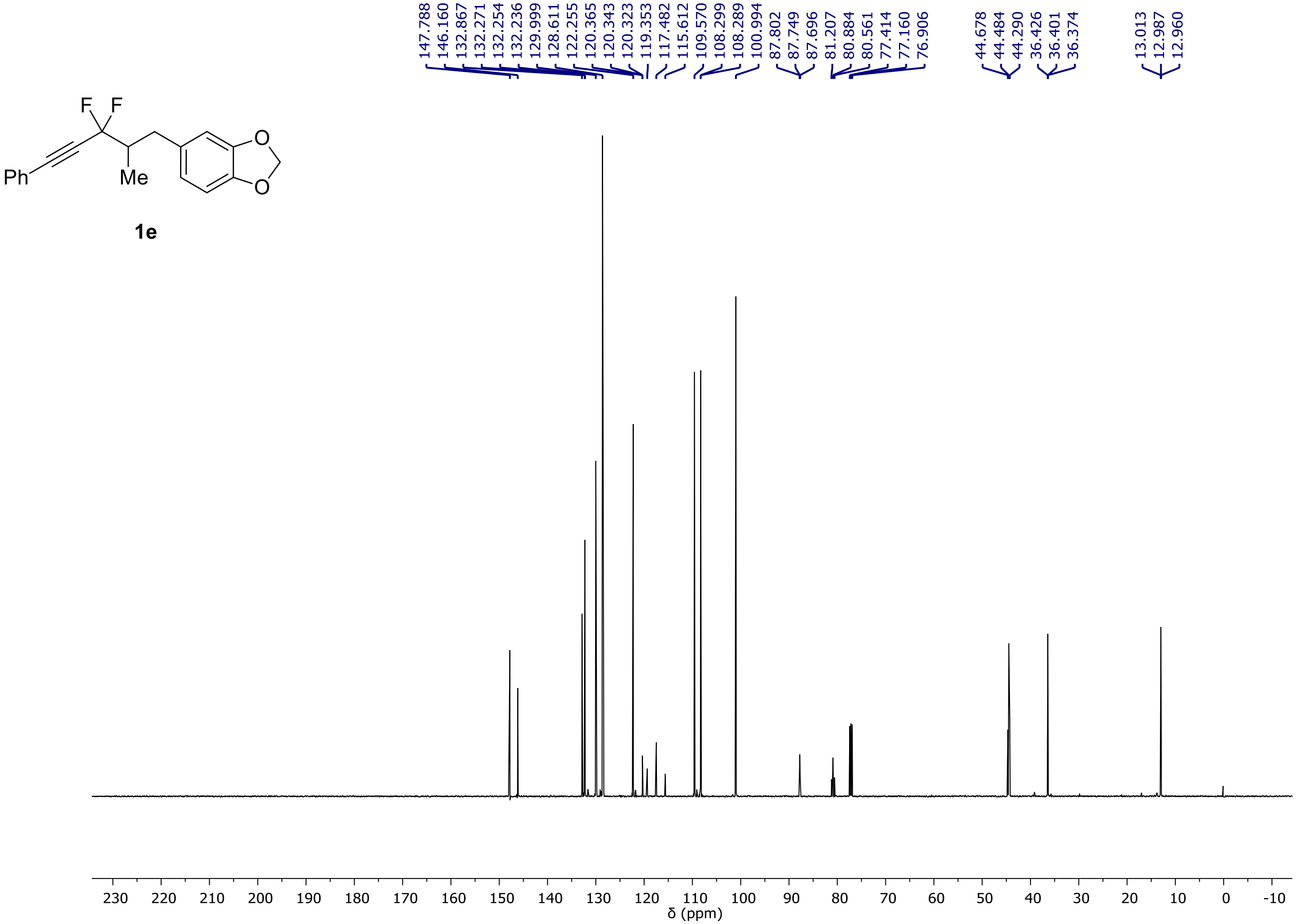
1e


7.522
7.508
7.419
7.404
7.390
7.368
7.353
7.339
6.744
6.729
6.681
6.649
6.633
5.904
3.170
3.152
3.131
3.113
2.408
2.387
2.371
2.364
2.346
1.067
1.055
-0.000
1.828
0.921
1.935
0.966
0.896
0.977
2.000
0.990
1.989
2.965
9.5
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
δ (ppm)


F
F
Ph
Me
O
O

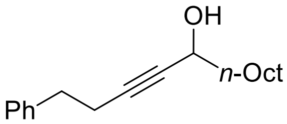
1e


-88.516
-88.540
-88.562
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
δ (ppm)

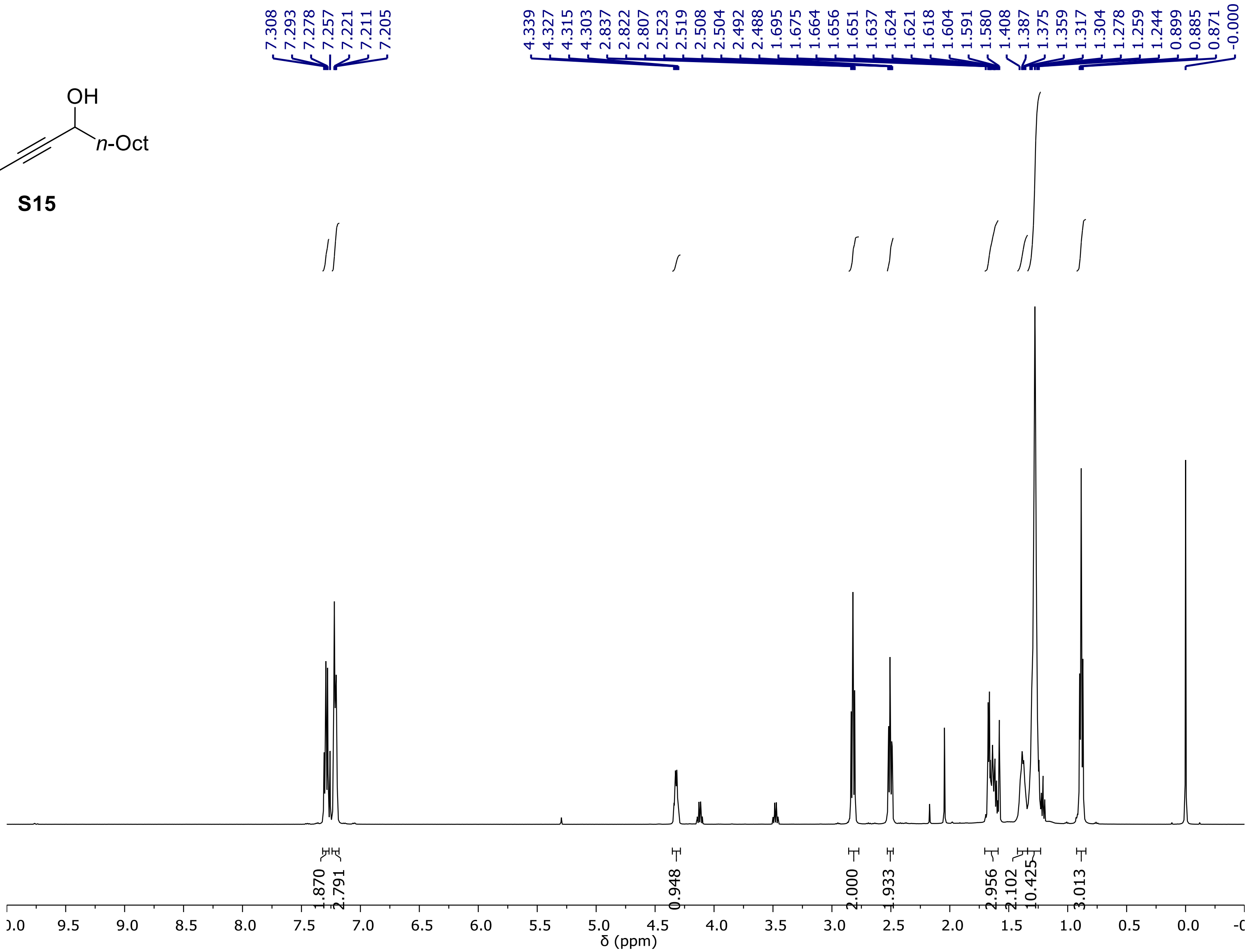


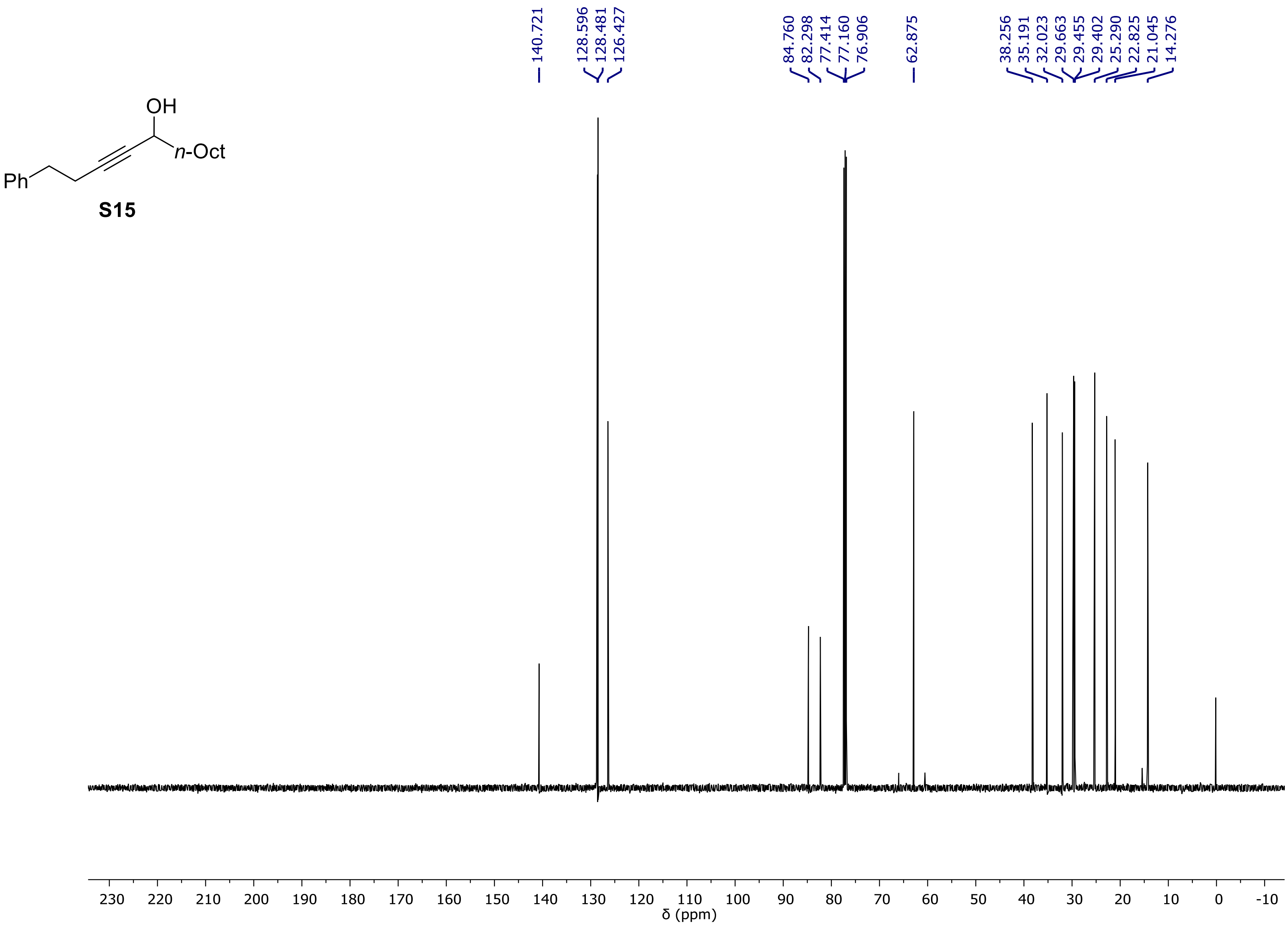
1e

147.788
146.160
132.867
132.271
132.254
132.236
129.999
128.611
122.255
120.365
120.343
120.323
119.353
117.482
115.612
109.570
108.299
108.289
100.994
87.802
87.749
87.696
81.207
80.884
80.561
77.414
77.160
76.906
44.678
44.484
44.290
36.426
36.401
36.374
13.013
12.987
12.960
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)


OH
n-Oct
Ph

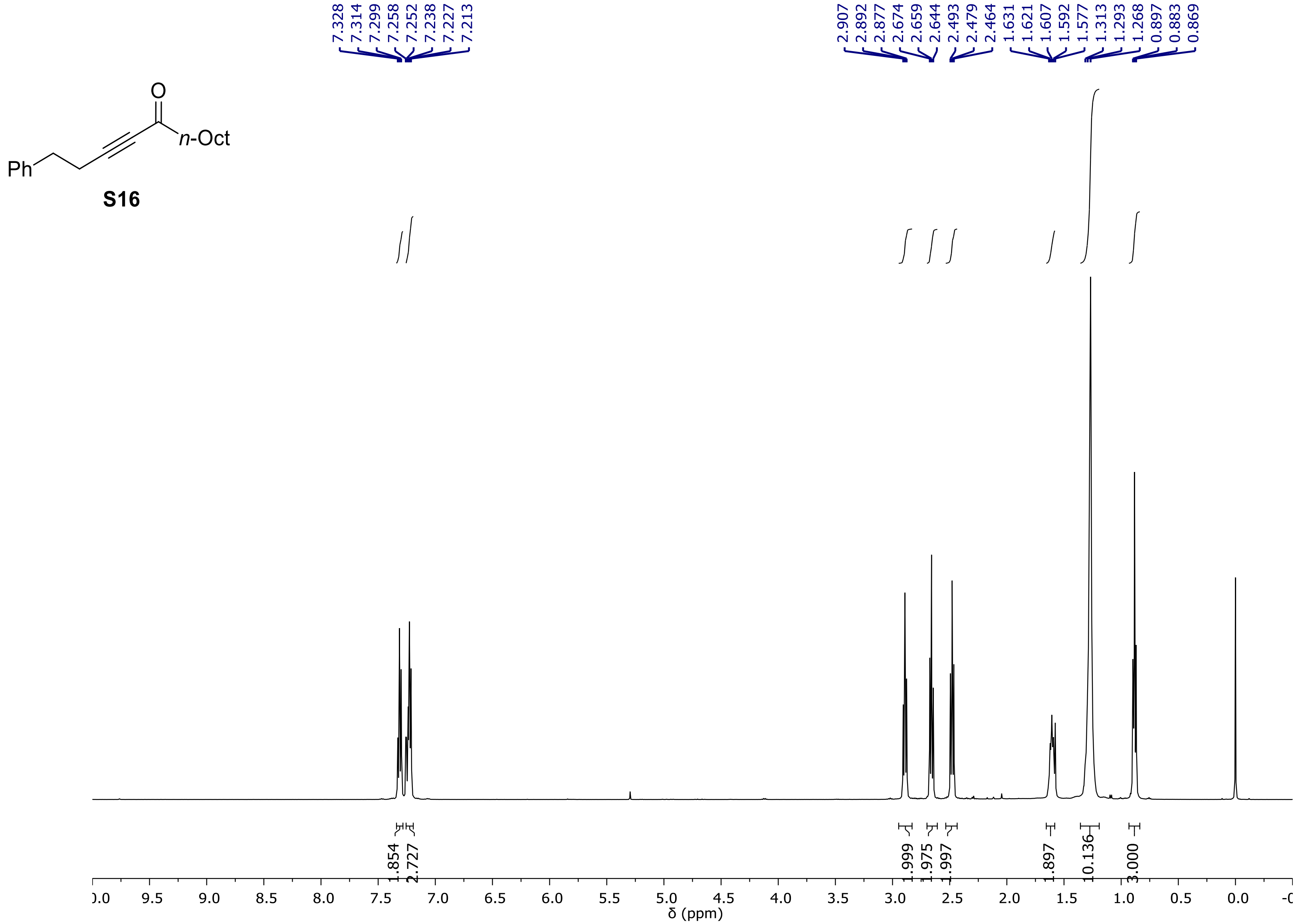
S15


7.308
7.293
7.278
7.257
7.221
7.211
7.205
4.339
4.327
4.315
4.303
2.837
2.822
2.807
2.523
2.519
2.508
2.504
2.492
2.488
1.695
1.675
1.664
1.656
1.651
1.637
1.624
1.621
1.618
1.604
1.591
1.580
1.408
1.387
1.375
1.359
1.317
1.304
1.278
1.259
1.244
0.899
0.885
0.871
-0.000
1.870
2.791
0.948
2.000
1.933
2.956
2.102
10.425
3.013
0.0
9.5
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
δ (ppm)

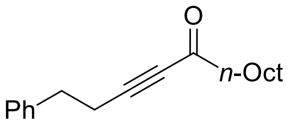

OH
n-Oct
Ph

S15

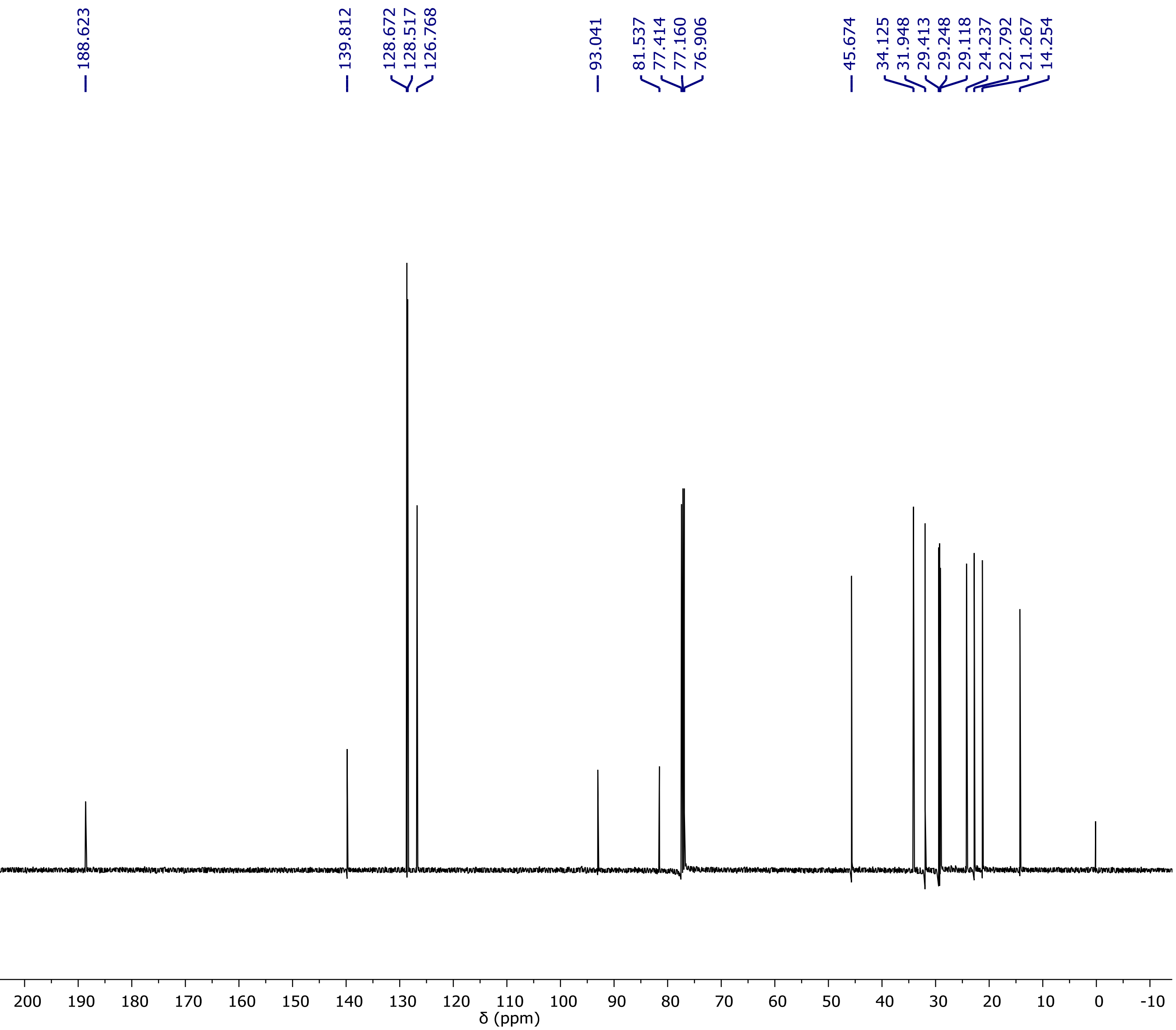
140.721
128.596
128.481
126.427
84.760
82.298
77.414
77.160
76.906
62.875
38.256
35.191
32.023
29.663
29.455
29.402
25.290
22.825
21.045
14.276
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

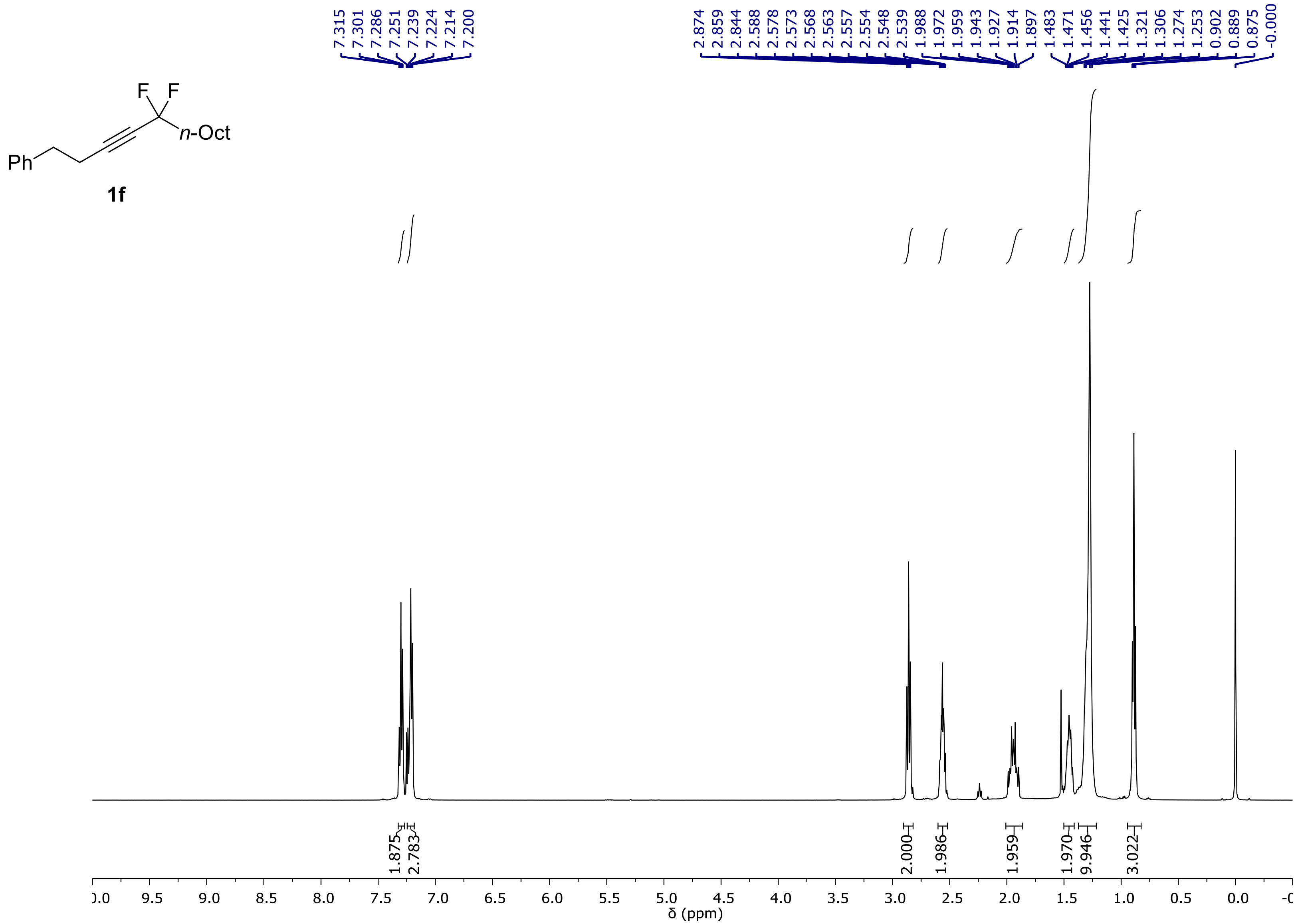

O
n-Oct
Ph
7.328
7.314
7.299
7.258
7.252
7.238
7.227
7.213
2.907
2.892
2.877
2.674
2.659
2.644
2.493
2.479
2.464
1.631
1.621
1.607
1.592
1.577
1.313
1.293
1.268
0.897
0.883
0.869
1.854
2.727
1.999
1.975
1.997
1.897
10.136
3.000
).0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
δ (ppm)

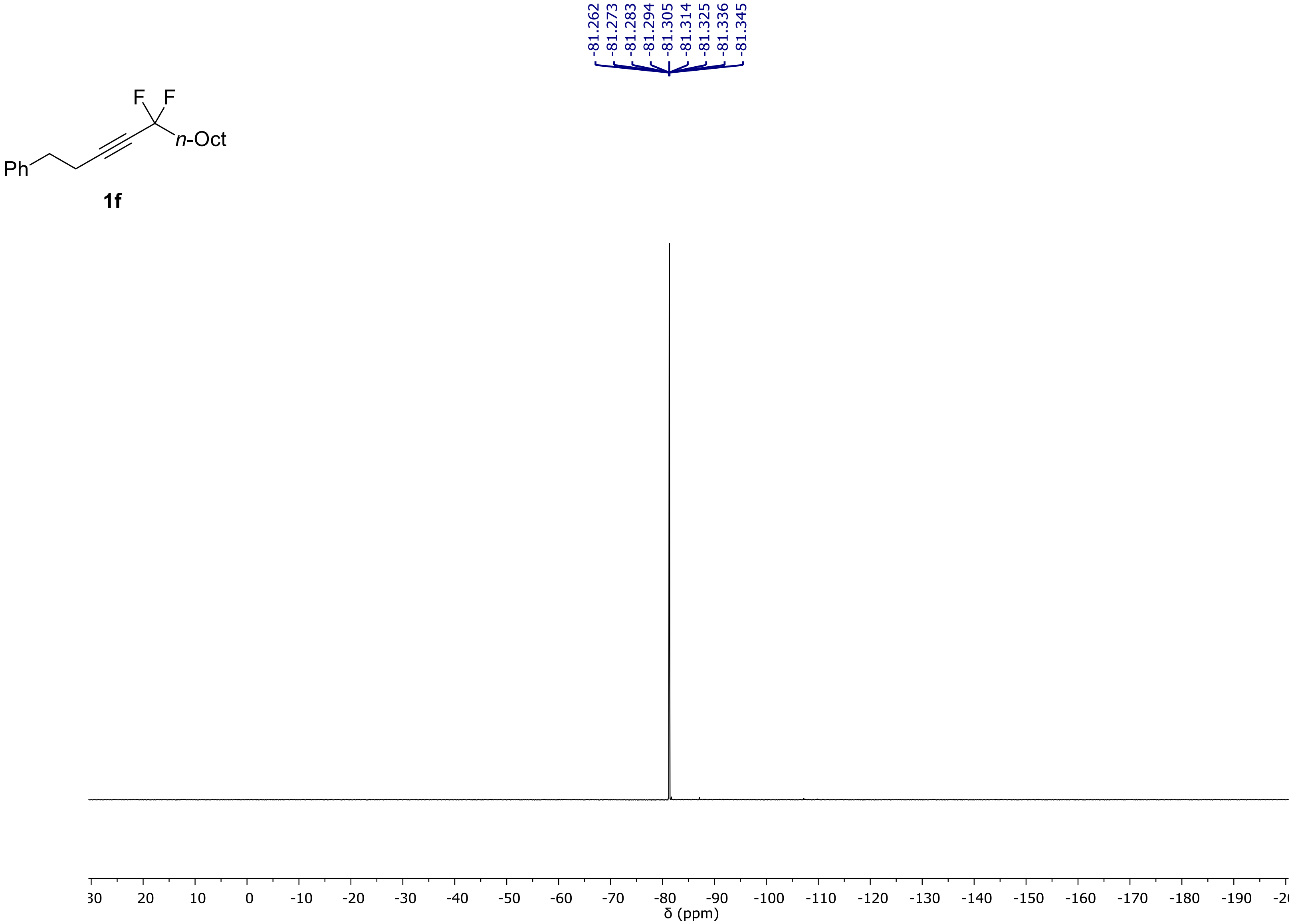
S16


O
n-Oct
Ph

S16

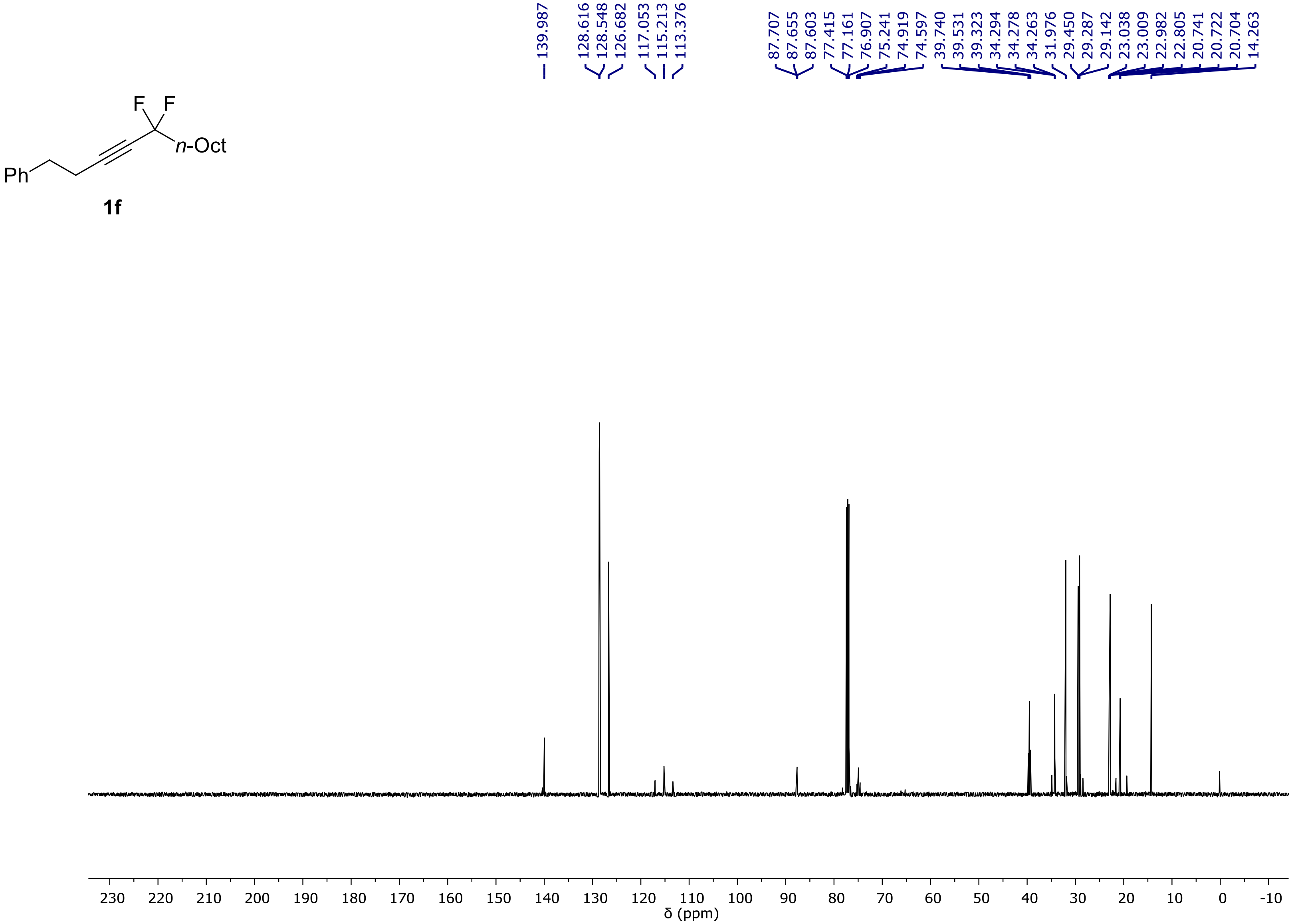

188.623
139.812
128.672
128.517
126.768
93.041
81.537
77.414
77.160
76.906
45.674
34.125
31.948
29.413
29.248
29.118
24.237
22.792
21.267
14.254
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)


F F
n-Oct
Ph
1f
7.315
7.301
7.286
7.251
7.239
7.224
7.214
7.200
2.874
2.859
2.844
2.588
2.578
2.573
2.568
2.563
2.557
2.554
2.548
2.539
1.988
1.972
1.959
1.943
1.927
1.914
1.897
1.483
1.471
1.456
1.441
1.425
1.321
1.306
1.274
1.253
0.902
0.889
0.875
-0.000
1.875
2.783
2.000
1.986
1.959
1.970
9.946
3.022
).0
9.5
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
-(
δ (ppm)


F
F
n-Oct
Ph

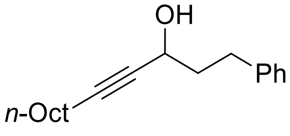
1f

-81.262
-81.273
-81.283
-81.294
-81.305
-81.314
-81.325
-81.336
-81.345
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
δ (ppm)

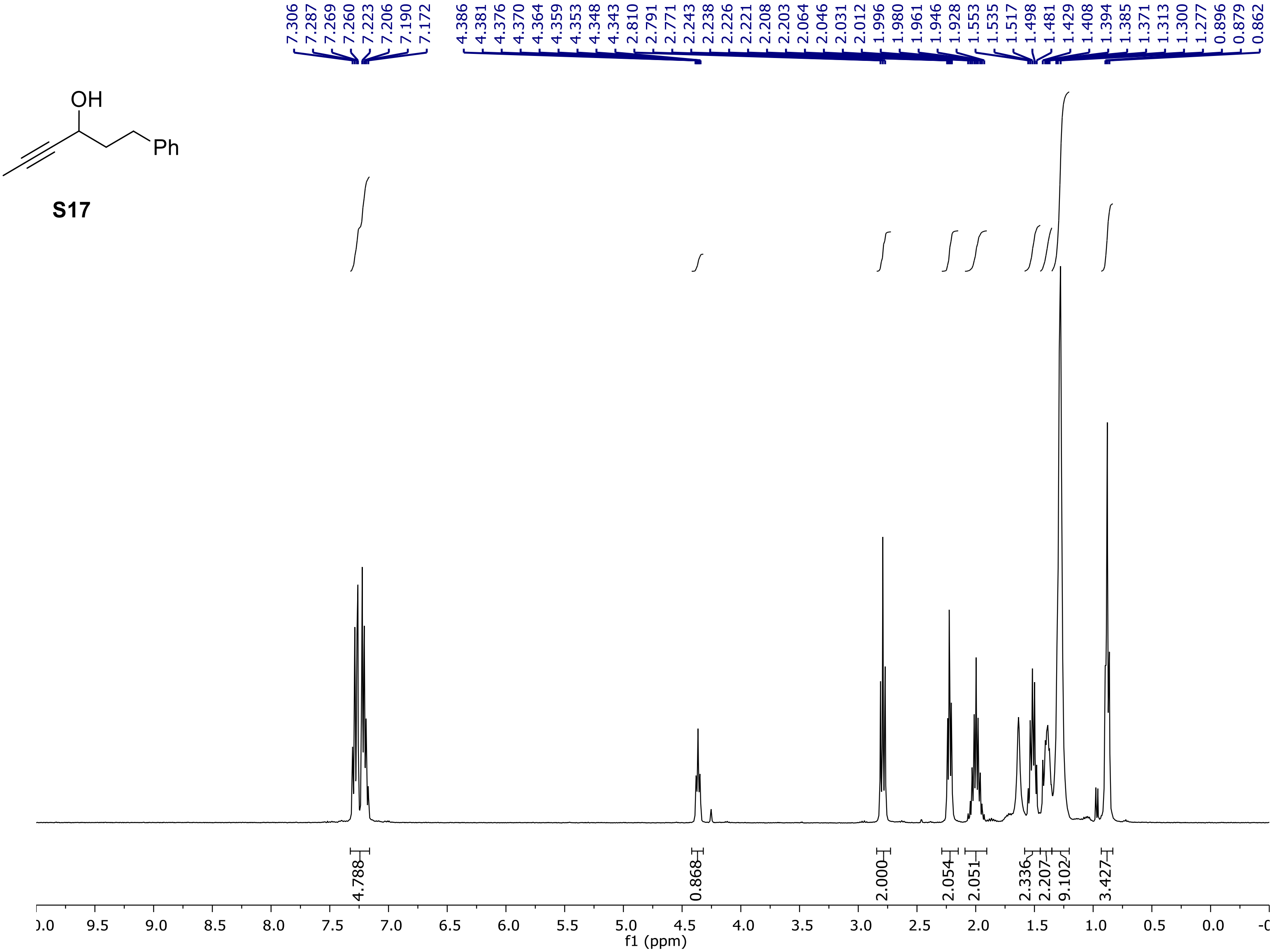

F
F
n-Oct
Ph

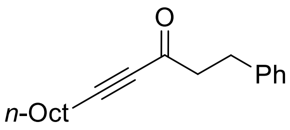
1f

139.987
128.616
128.548
126.682
117.053
115.213
113.376
87.707
87.655
87.603
77.415
77.161
76.907
75.241
74.919
74.597
39.740
39.531
39.323
34.294
34.278
34.263
31.976
29.450
29.287
29.142
23.038
23.009
22.982
22.805
20.741
20.722
20.704
14.263
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

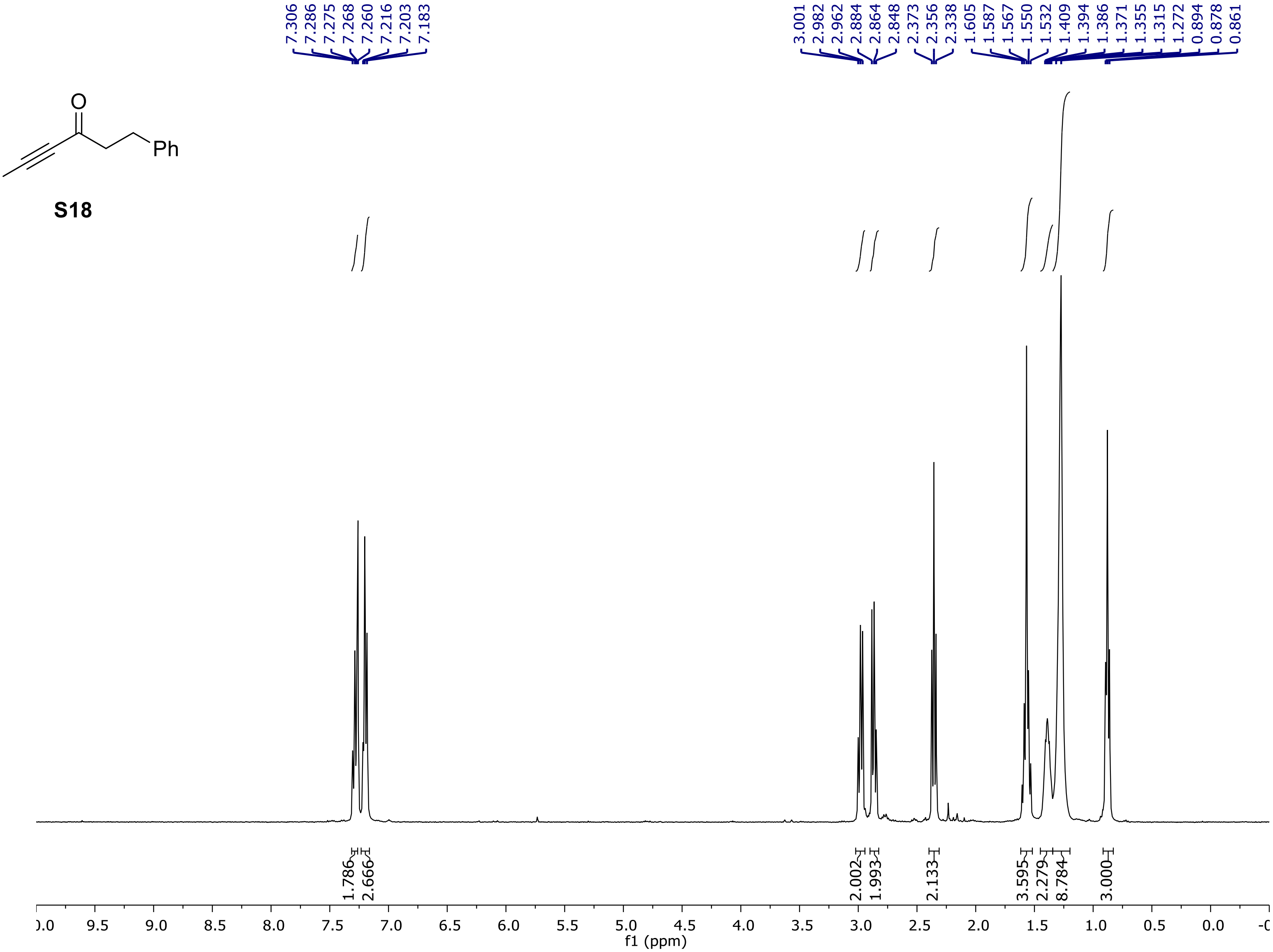

OH
Ph
n-Oct

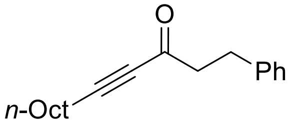
S17


7.306
7.287
7.269
7.260
7.223
7.206
7.190
7.172
4.386
4.381
4.376
4.370
4.364
4.359
4.353
4.348
4.343
2.810
2.791
2.771
2.243
2.238
2.226
2.221
2.208
2.203
2.064
2.046
2.031
2.012
1.996
1.980
1.961
1.946
1.928
1.553
1.535
1.517
1.498
1.481
1.429
1.408
1.394
1.385
1.371
1.313
1.300
1.277
0.896
0.879
0.862
4.788
0.868
2.000
2.054
2.051
2.336
2.207
9.102
3.427
0.0
9.5
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
-(
f1 (ppm)

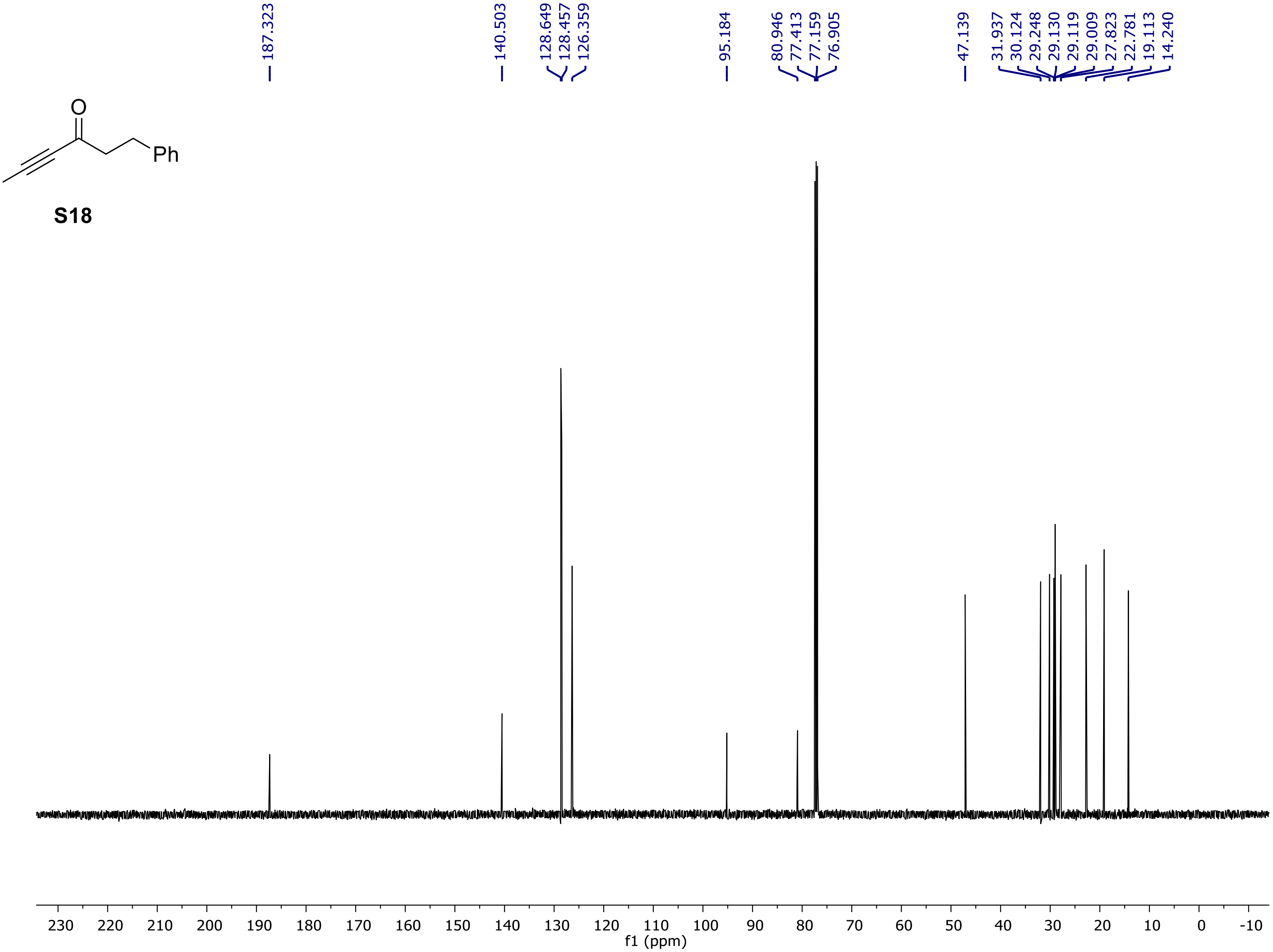

O
Ph
n-Oct

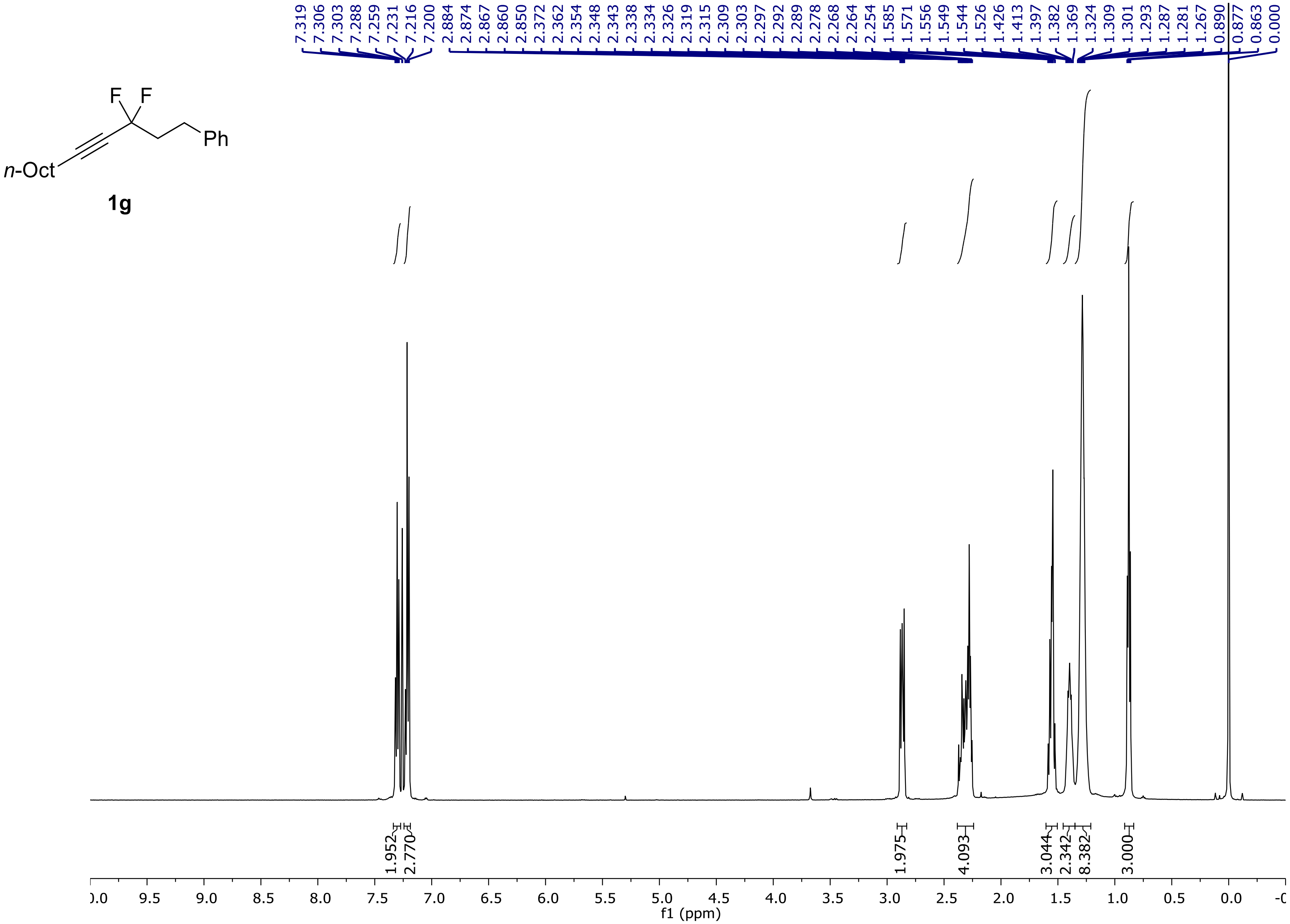
S18


7.306
7.286
7.275
7.268
7.260
7.216
7.203
7.183
3.001
2.982
2.962
2.884
2.864
2.848
2.373
2.356
2.338
1.605
1.587
1.567
1.550
1.532
1.409
1.394
1.386
1.371
1.355
1.315
1.272
0.894
0.878
0.861
1.786
2.666
2.002
1.993
2.133
3.595
2.279
8.784
3.000
9.5
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
f1 (ppm)


O
Ph
n-Oct

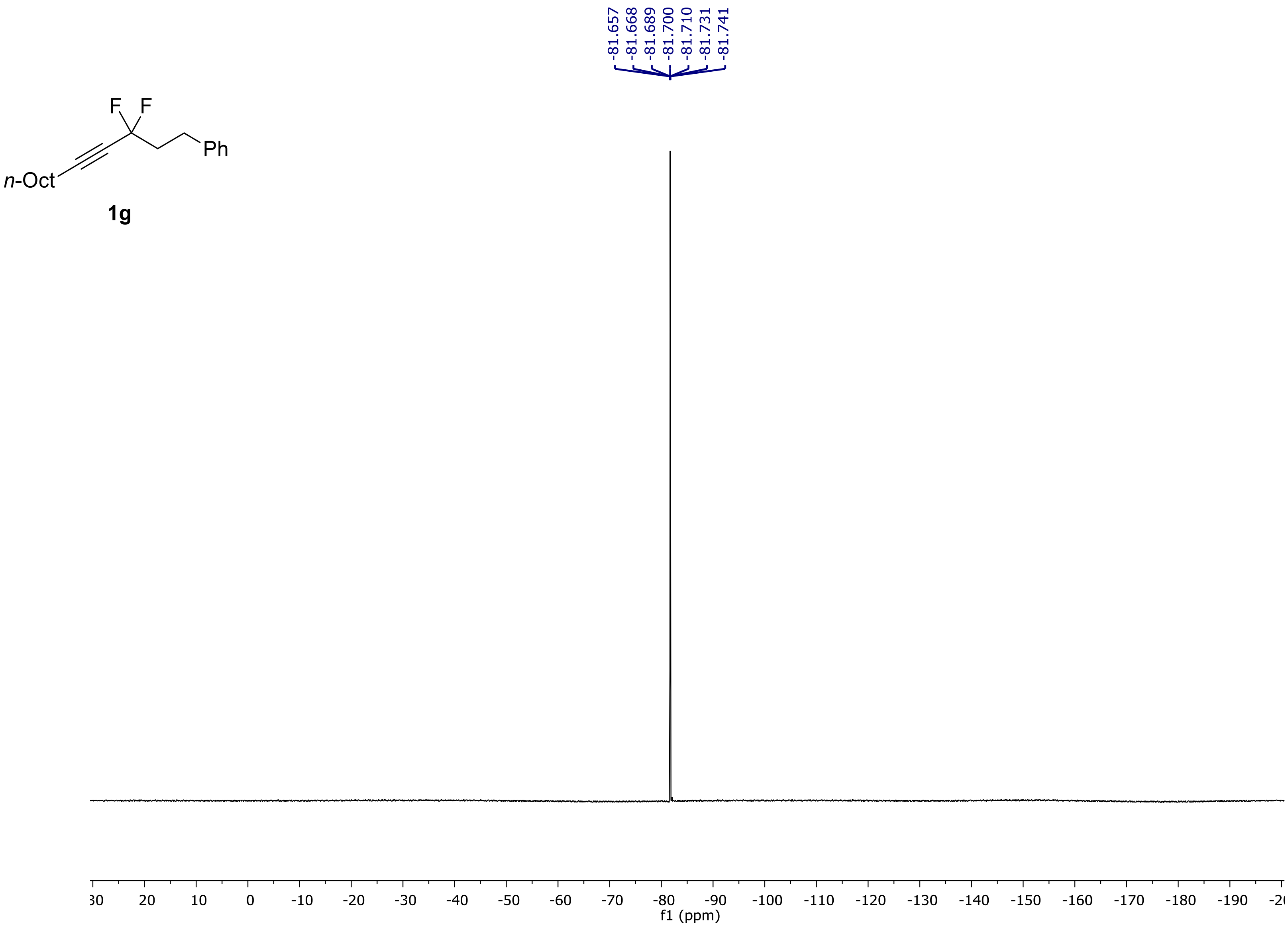
S18


187.323
140.503
128.649
128.457
126.359
95.184
80.946
77.413
77.159
76.905
47.139
31.937
30.124
29.248
29.130
29.119
29.009
27.823
22.781
19.113
14.240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

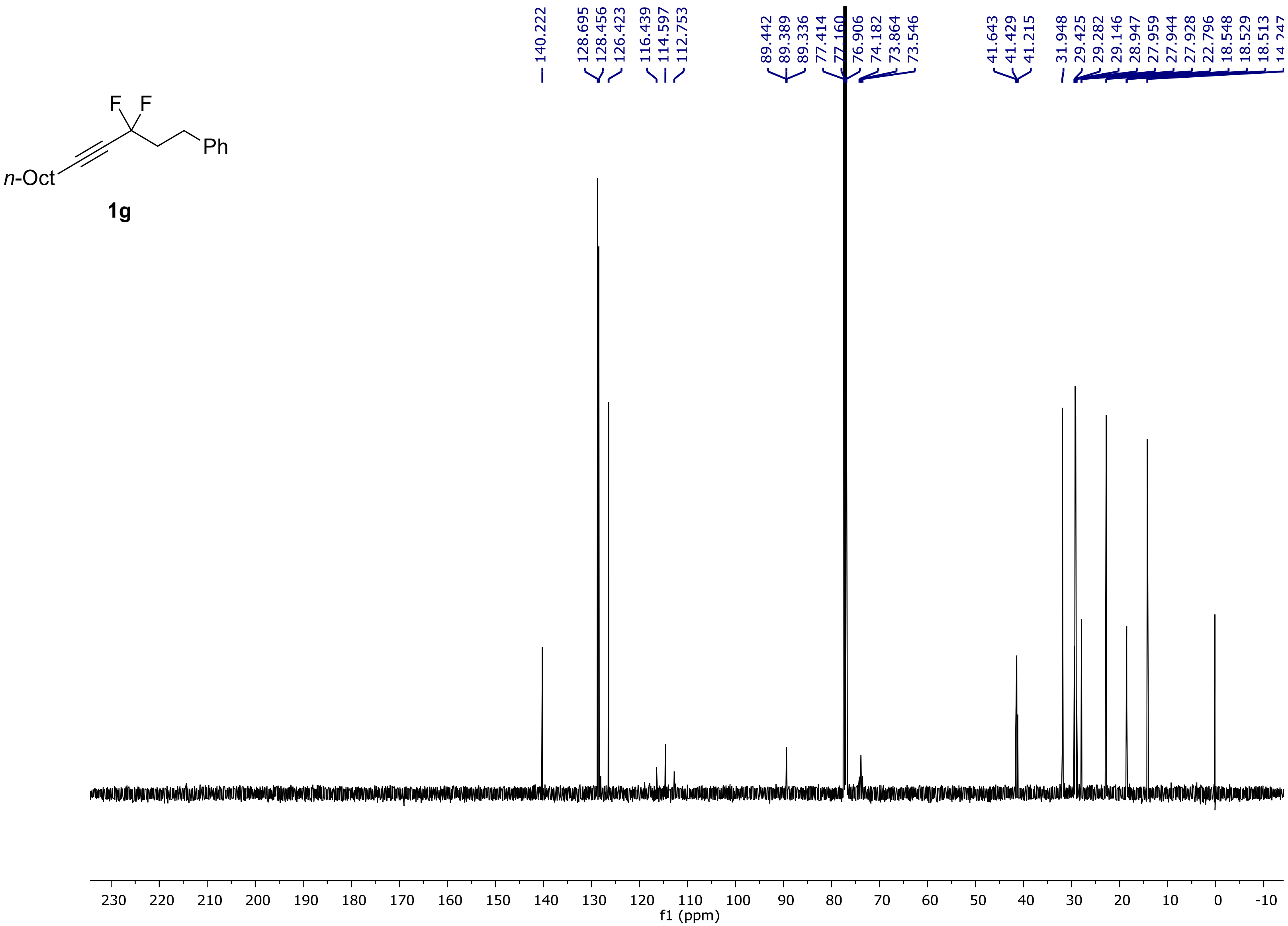

F
F
Ph
n-Oct

1g

7.319
7.306
7.303
7.288
7.259
7.231
7.216
7.200
2.884
2.874
2.867
2.860
2.850
2.372
2.362
2.354
2.348
2.343
2.338
2.334
2.326
2.319
2.315
2.309
2.303
2.297
2.292
2.289
2.278
2.268
2.264
2.254
1.585
1.571
1.556
1.549
1.544
1.526
1.426
1.413
1.397
1.382
1.369
1.324
1.309
1.301
1.293
1.287
1.281
1.267
0.890
0.877
0.863
0.000
1.952
2.770
1.975
4.093
3.044
2.342
8.382
3.000
9.5
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
f1 (ppm)

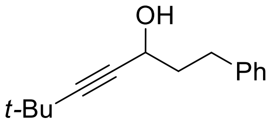

-81.657
-81.668
-81.689
-81.700
-81.710
-81.731
-81.741
F
F
Ph
n-Oct
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
f1 (ppm)

1g

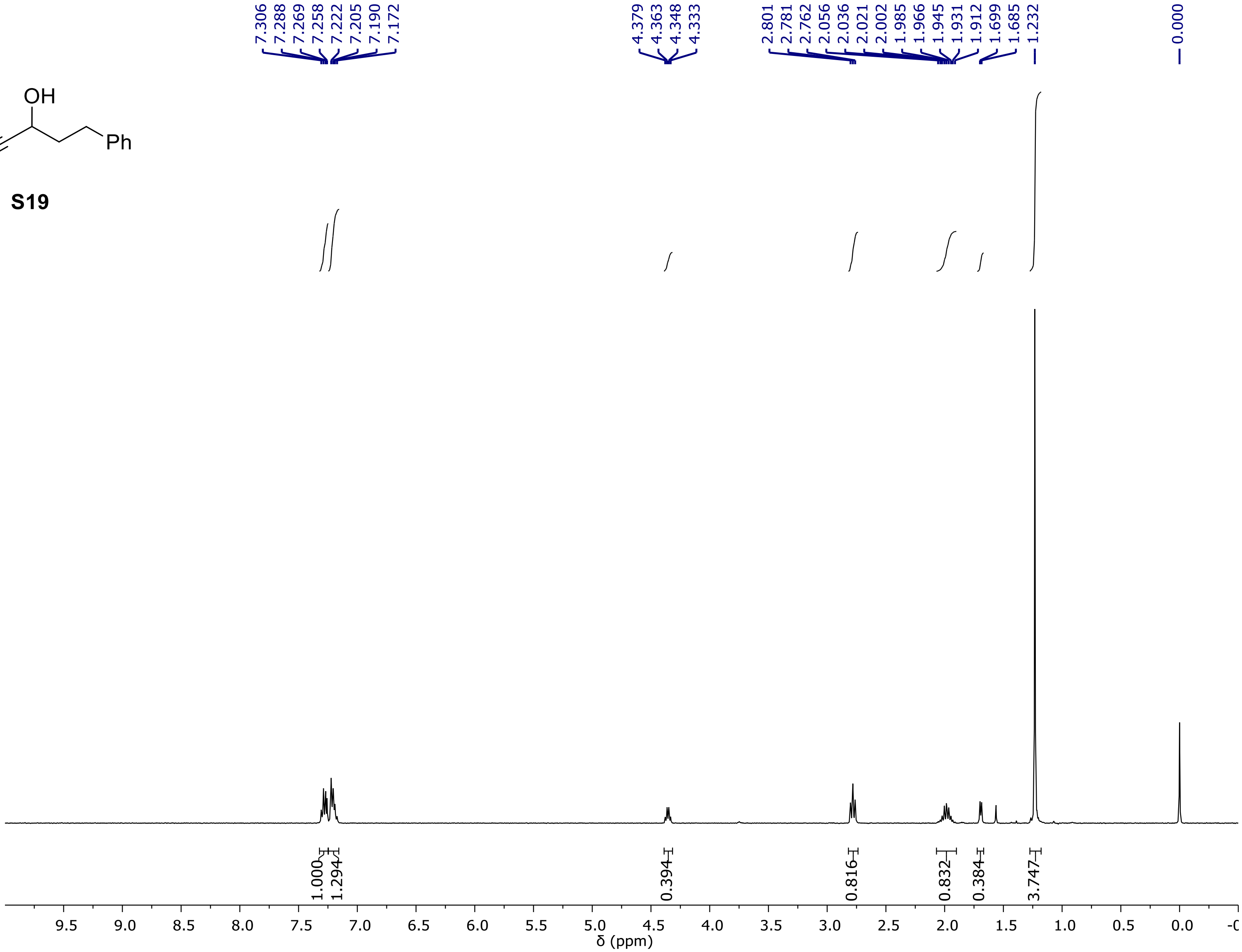

F
F
Ph
n-Oct

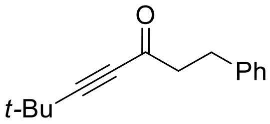
1g

140.222
128.695
128.456
126.423
116.439
114.597
112.753
89.442
89.389
89.336
77.414
77.160
76.906
74.182
73.864
73.546
41.643
41.429
41.215
31.948
29.425
29.282
29.146
28.947
27.959
27.944
27.928
22.796
18.548
18.529
18.513
14.247
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

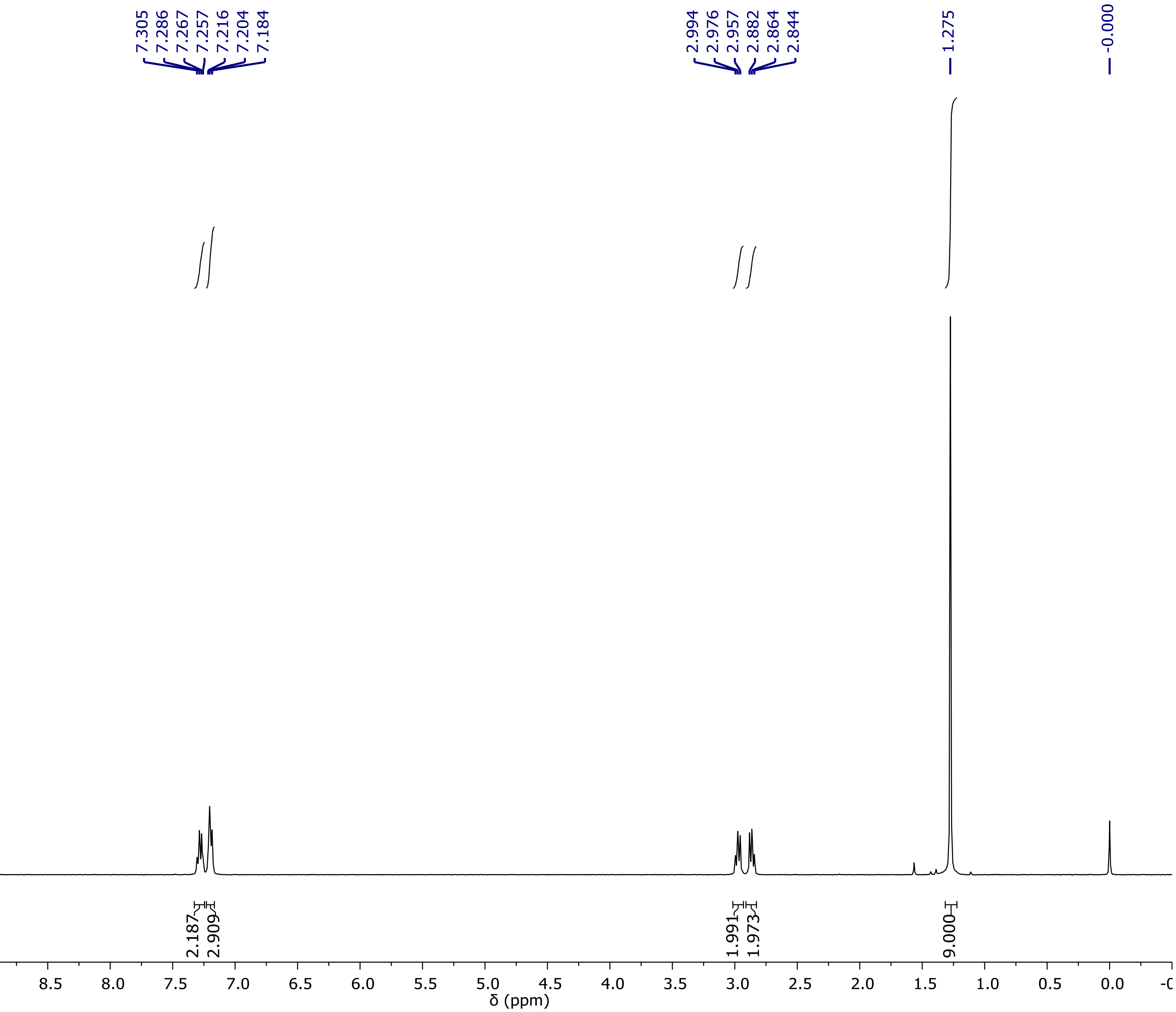

OH
Ph
t-Bu

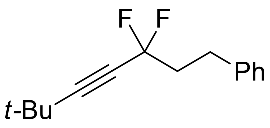
S19


7.306
7.288
7.269
7.258
7.222
7.205
7.190
7.172
4.379
4.363
4.348
4.333
2.801
2.781
2.762
2.056
2.036
2.021
2.002
1.985
1.966
1.945
1.931
1.912
1.699
1.685
1.232
0.000
1.000
1.294
0.394
0.816
0.832
0.384
3.747
9.5
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
δ (ppm)

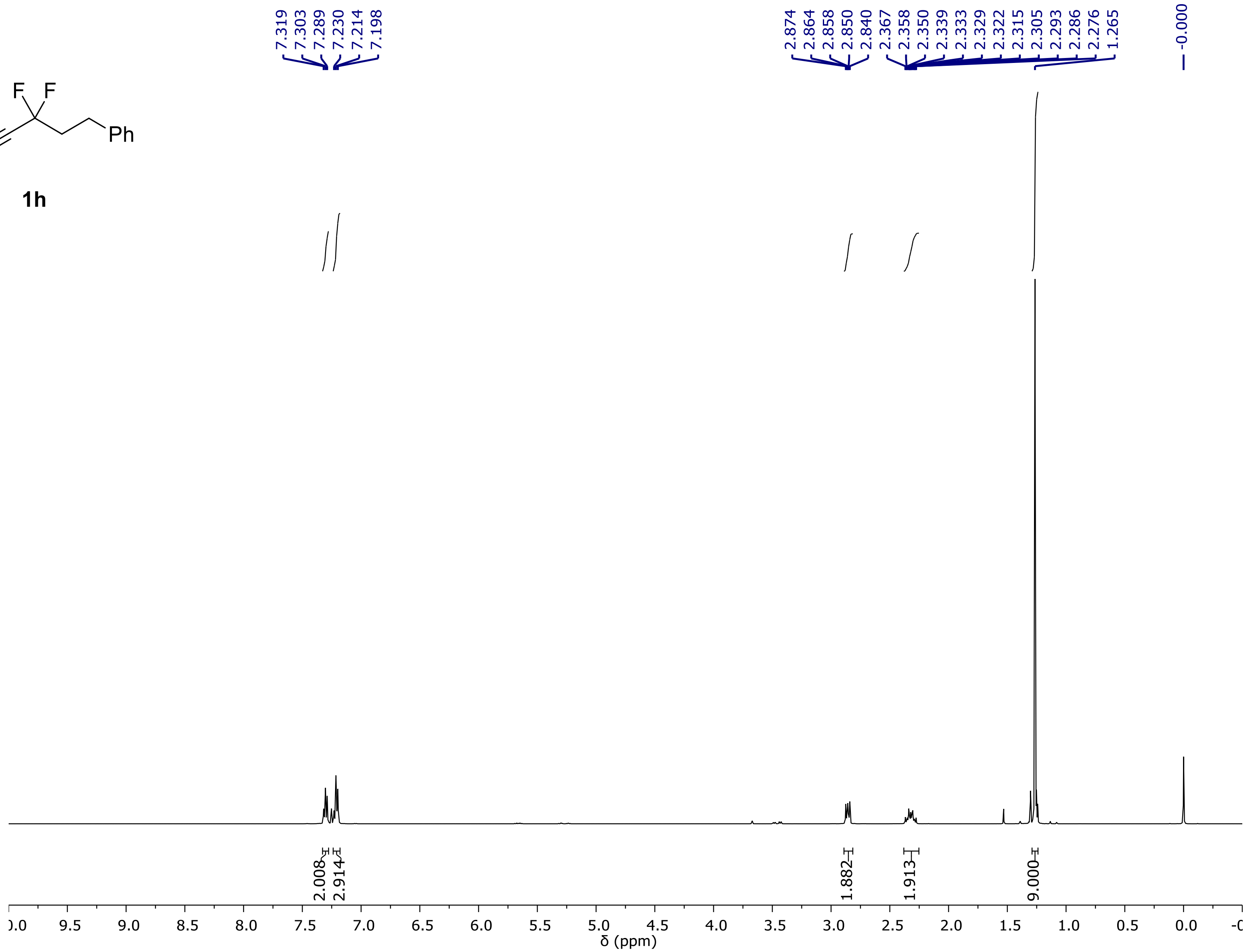

O
Ph
t-Bu

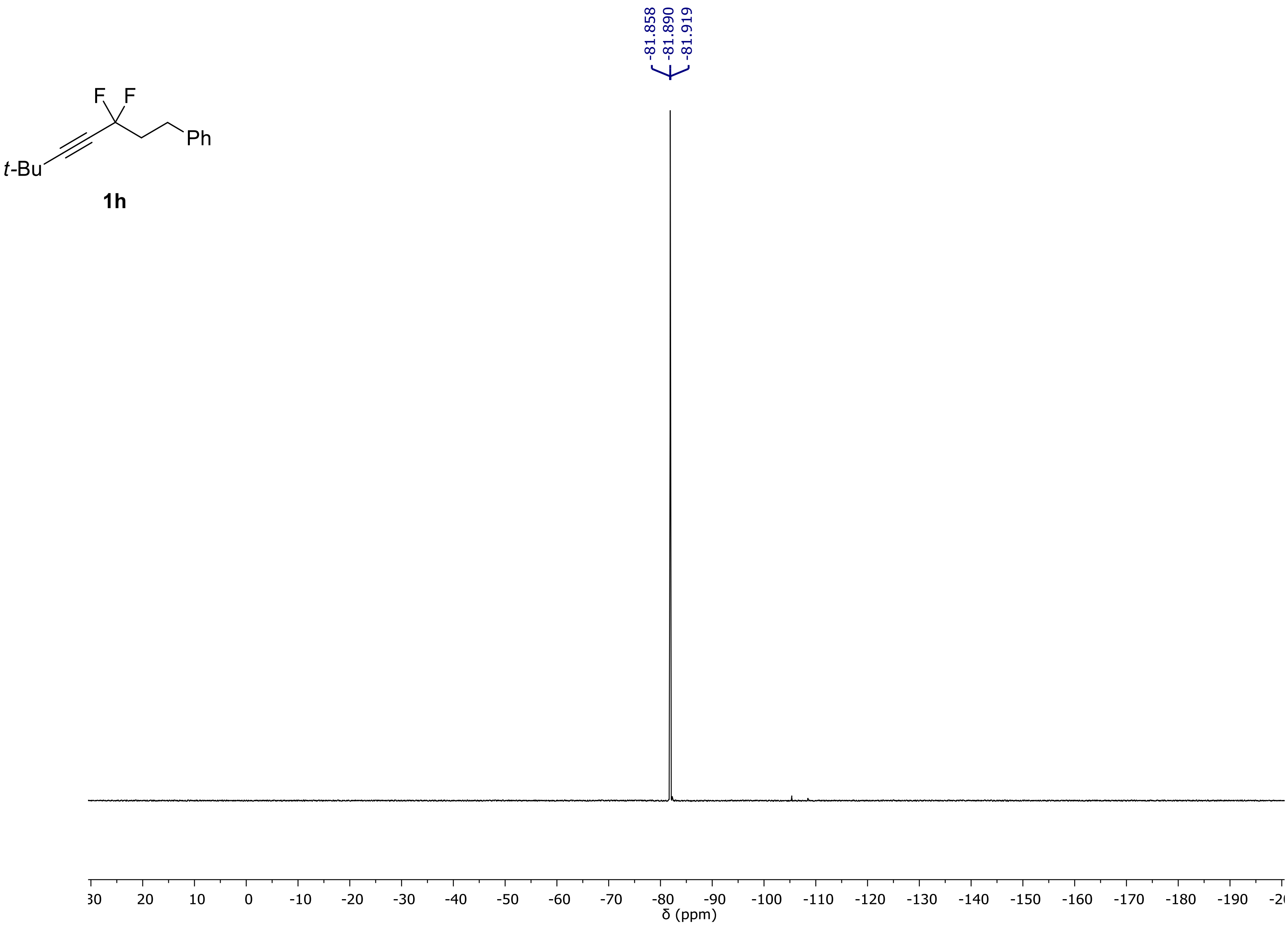
S20


7.305
7.286
7.267
7.257
7.216
7.204
7.184
2.994
2.976
2.957
2.882
2.864
2.844
1.275
-0.000
2.187
2.909
1.991
1.973
9.000
0.0
9.5
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
δ (ppm)

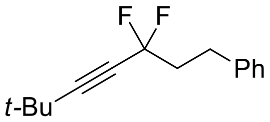

F
F
Ph
t-Bu

1h

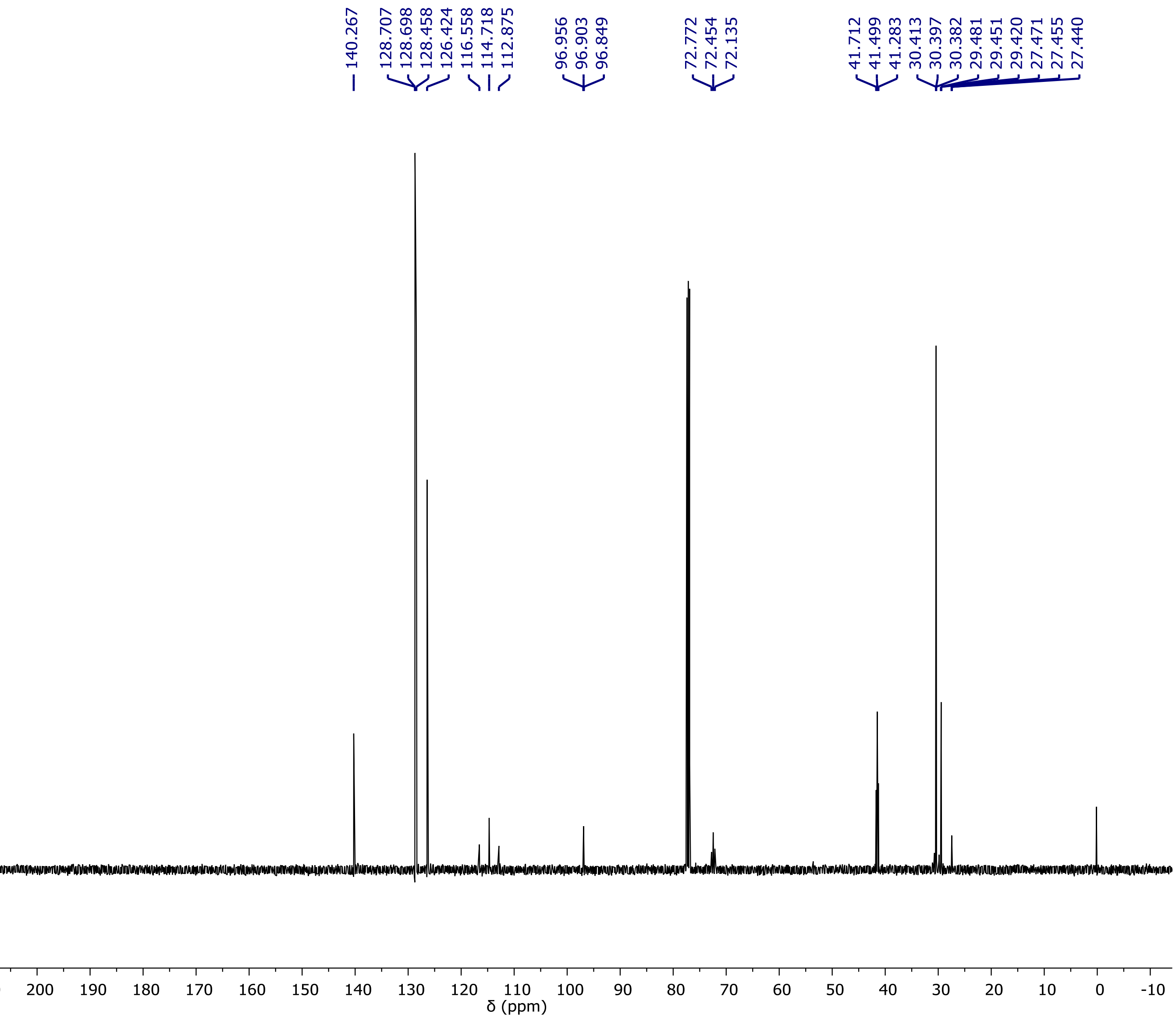

7.319
7.303
7.289
7.230
7.214
7.198
2.874
2.864
2.858
2.850
2.840
2.367
2.358
2.350
2.339
2.333
2.329
2.322
2.315
2.305
2.293
2.286
2.276
1.265
-0.000
2.008
2.914
1.882
1.913
9.000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
δ (ppm)

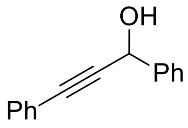

-81.858
-81.890
-81.919
F F
Ph
t-Bu
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
δ (ppm)

1h

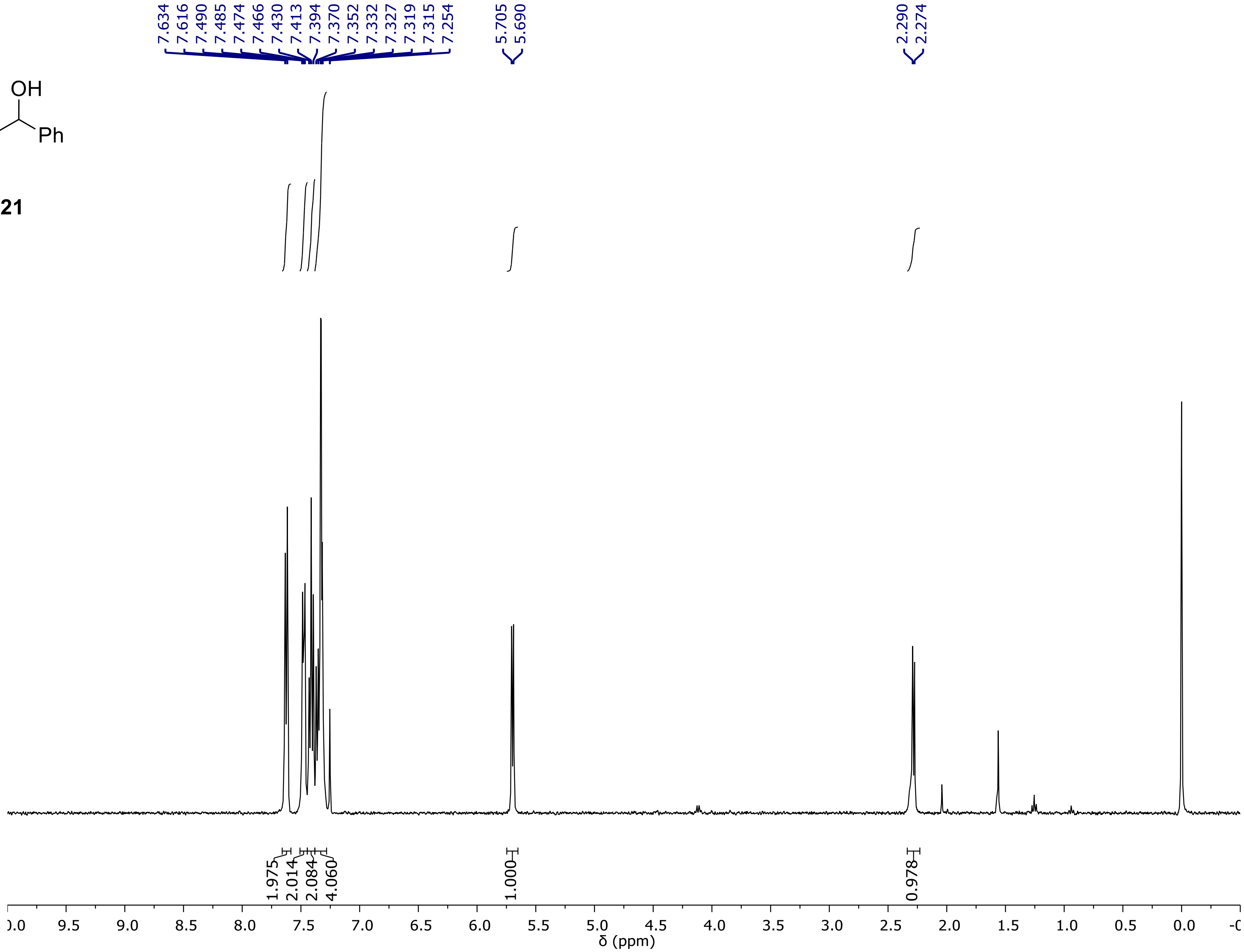

F
F
Ph
t-Bu

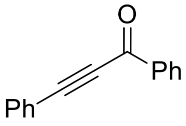
1h


140.267
128.707
128.698
128.458
126.424
116.558
114.718
112.875
96.956
96.903
96.849
72.772
72.454
72.135
41.712
41.499
41.283
30.413
30.397
30.382
29.481
29.451
29.420
27.471
27.455
27.440
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

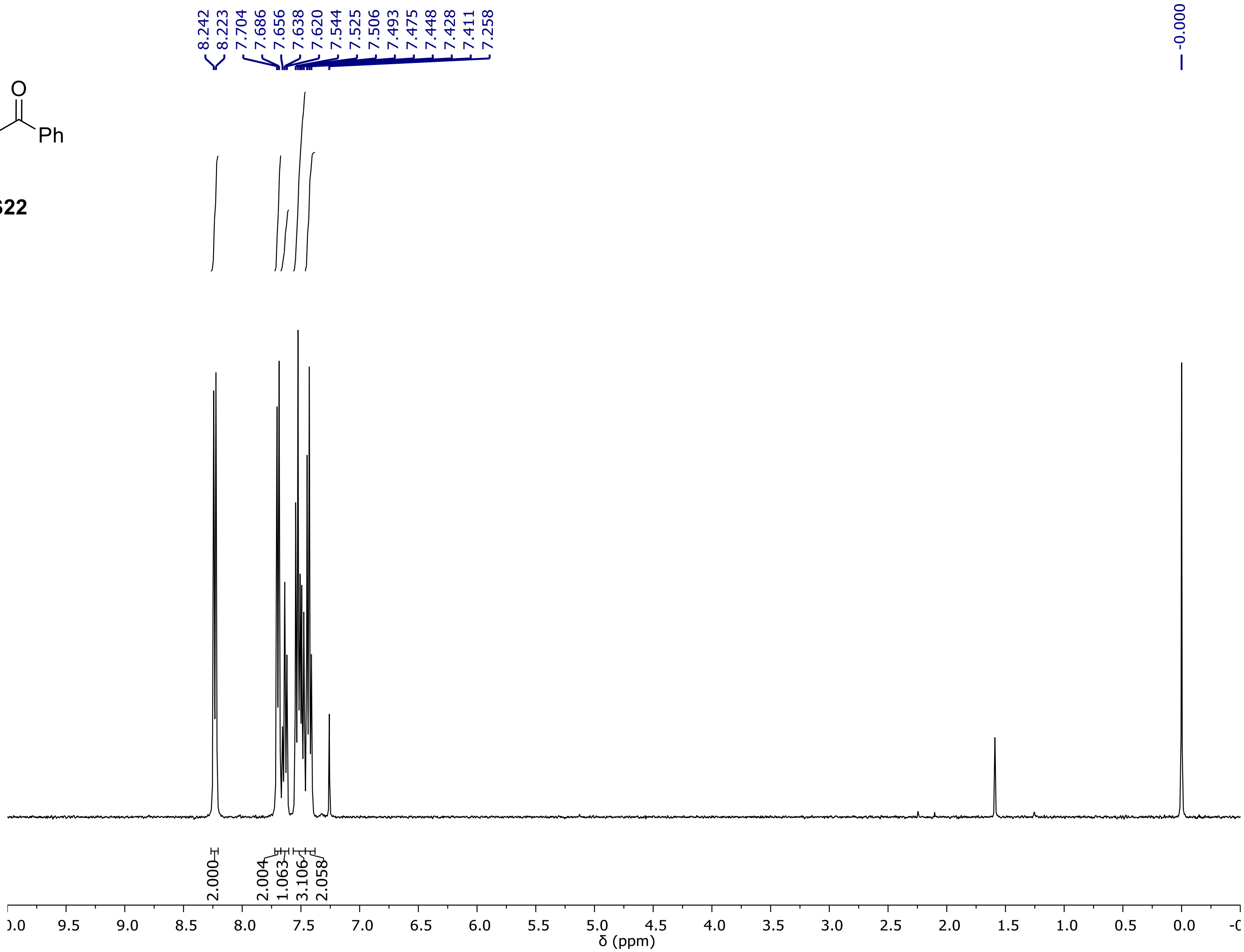

OH
Ph
Ph

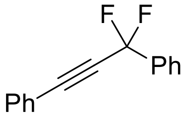
S21


7.634
7.616
7.490
7.485
7.474
7.466
7.430
7.413
7.394
7.370
7.352
7.332
7.327
7.319
7.315
7.254
5.705
5.690
2.290
2.274
1.975
2.014
2.084
4.060
1.000
0.978
9.5
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
δ (ppm)

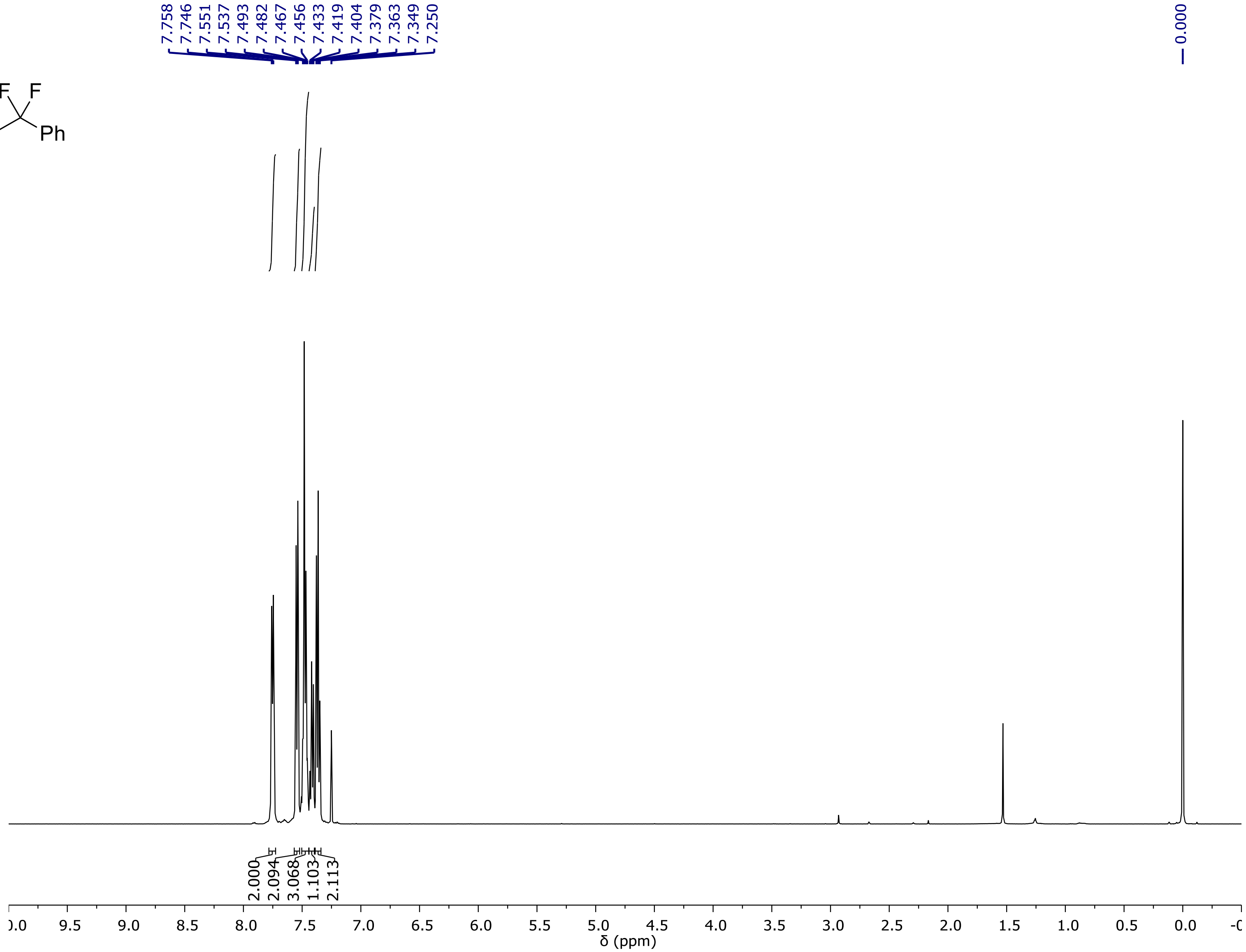

O
Ph
Ph

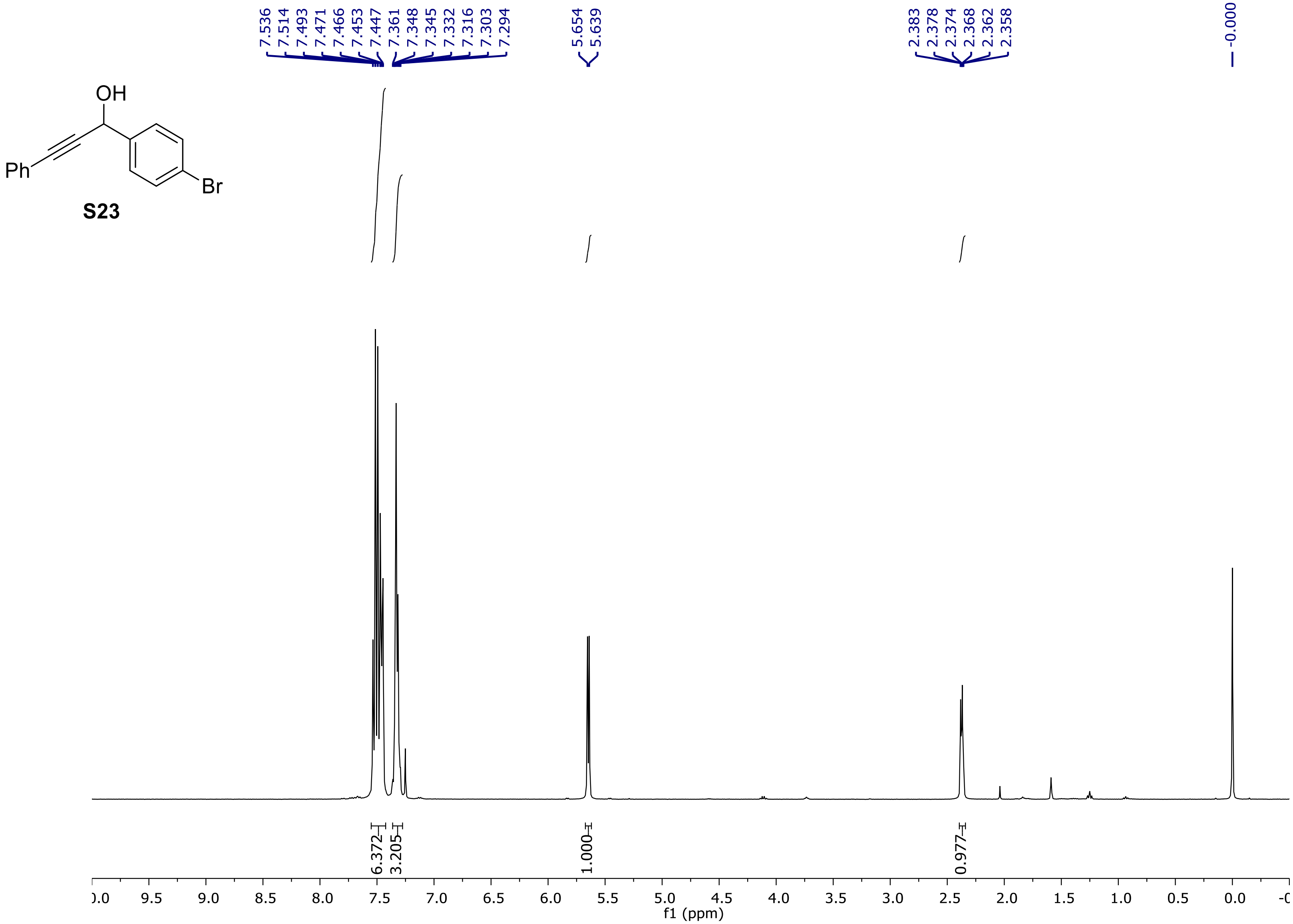
S22


8.242
8.223
7.704
7.686
7.656
7.638
7.620
7.544
7.525
7.506
7.493
7.475
7.448
7.428
7.411
7.258
-0.000
2.000
2.004
1.063
3.106
2.058
9.5
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
δ (ppm)


F
F
Ph
Ph

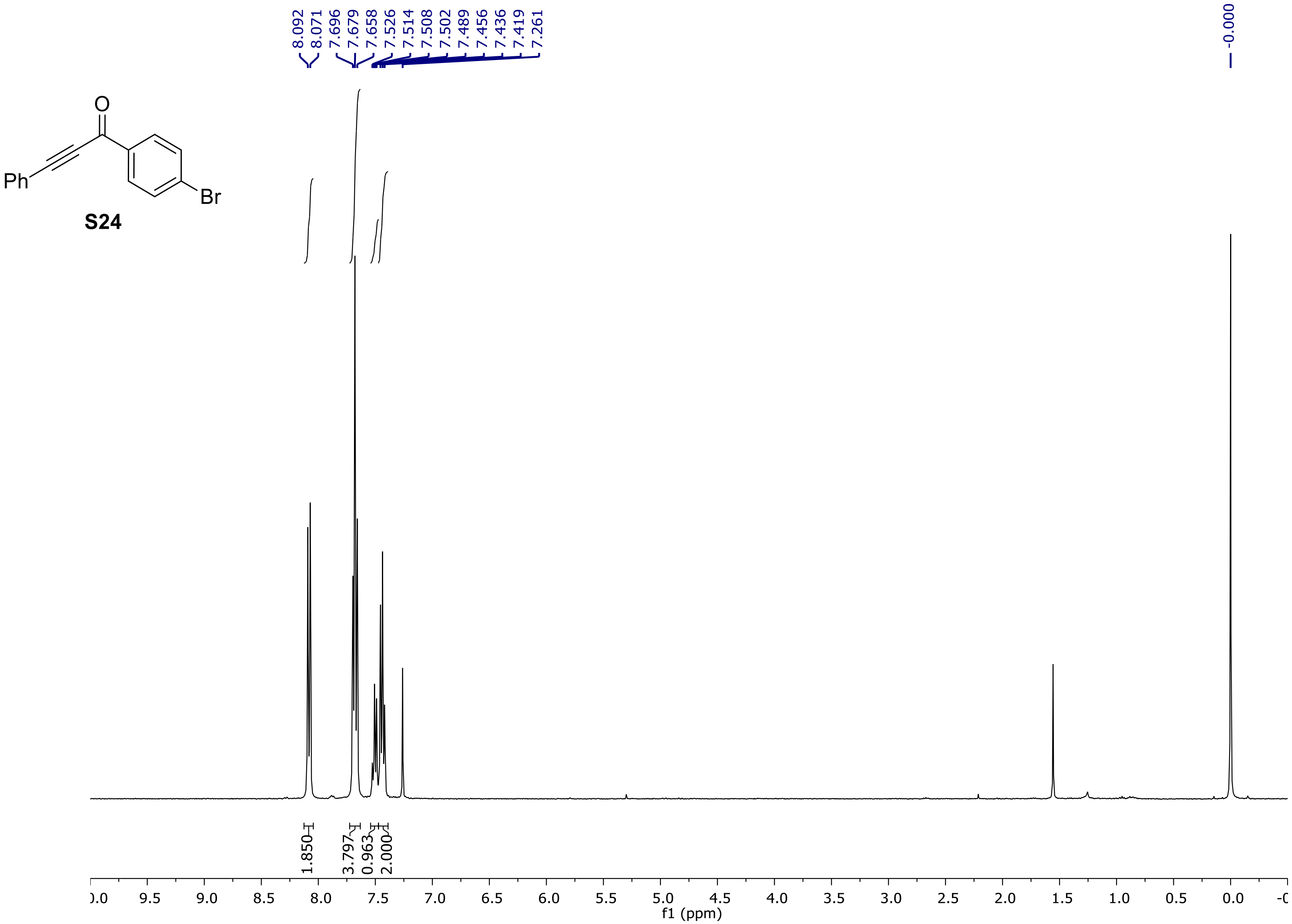
1i


7.758
7.746
7.551
7.537
7.493
7.482
7.467
7.456
7.433
7.419
7.404
7.379
7.363
7.349
7.250
0.000
2.000
2.094
3.068
1.103
2.113
9.5
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
δ (ppm)


OH
Ph
Br

S23

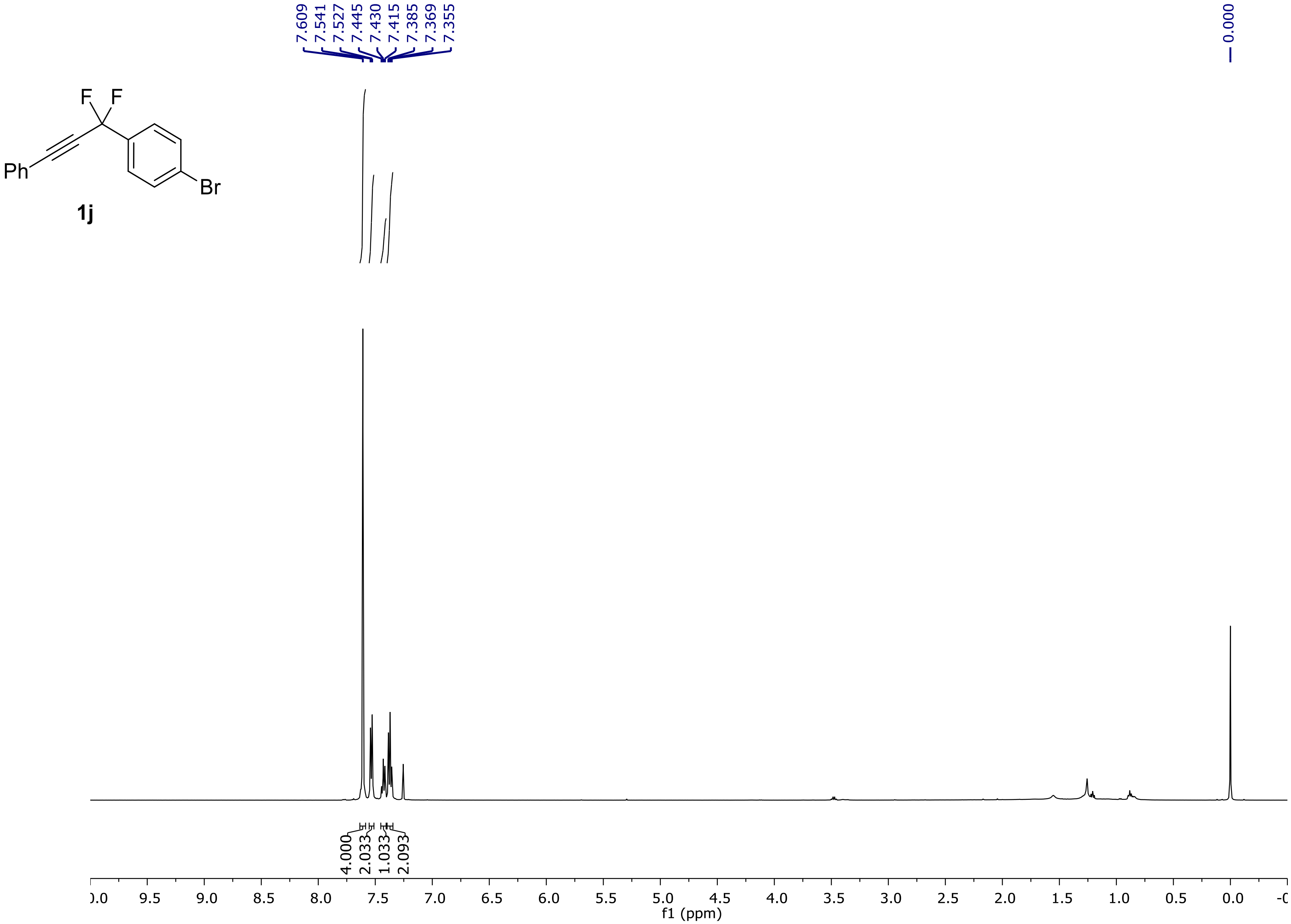
7.536
7.514
7.493
7.471
7.466
7.453
7.447
7.361
7.348
7.345
7.332
7.316
7.303
7.294
5.654
5.639
2.383
2.378
2.374
2.368
2.362
2.358
-0.000
6.372
3.205
1.000
0.977
).0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)

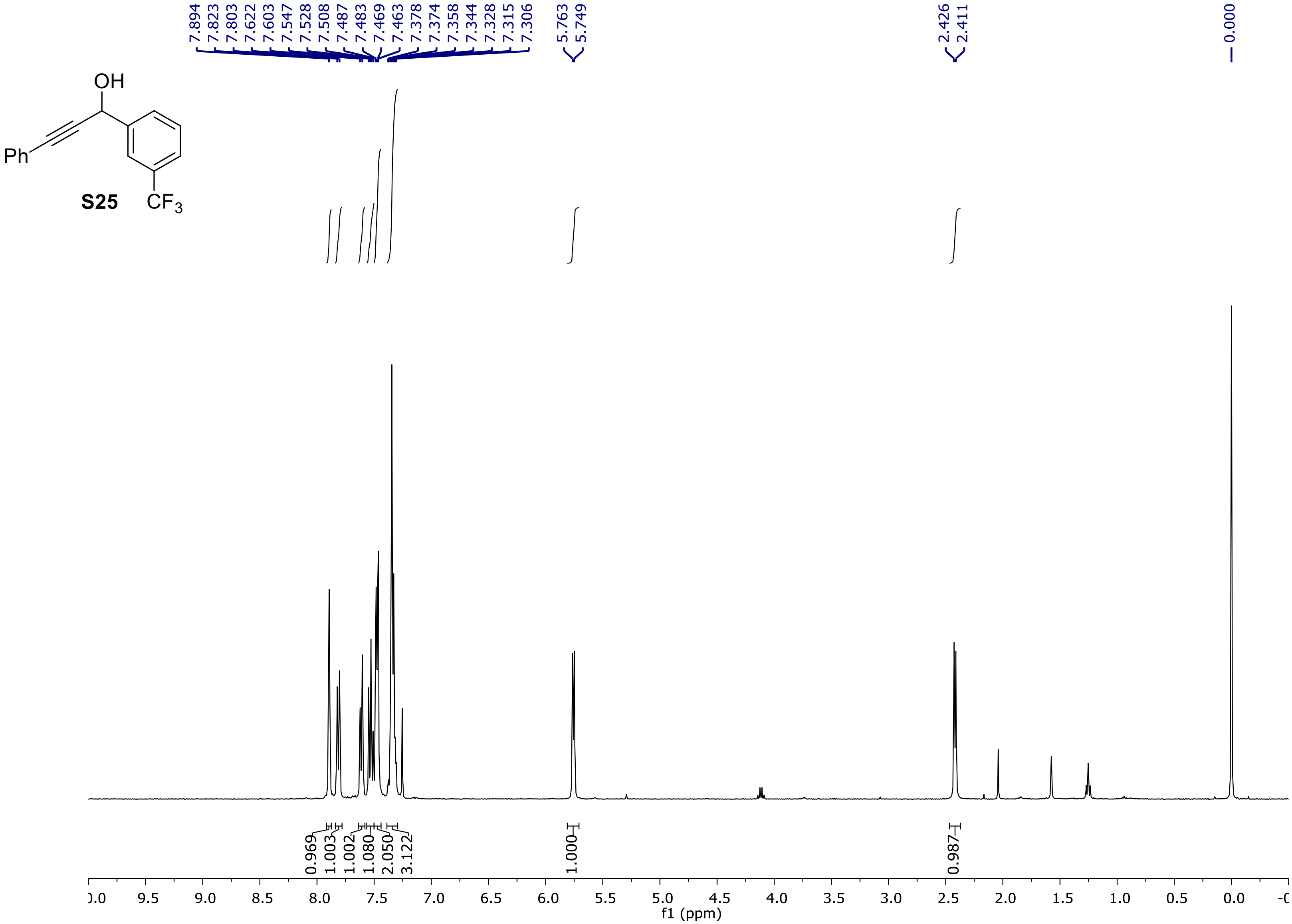

O
Ph
Br
8.092
8.071
7.696
7.679
7.658
7.526
7.514
7.508
7.502
7.489
7.456
7.436
7.419
7.261
-0.000
1.850
3.797
0.963
2.000
).0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)

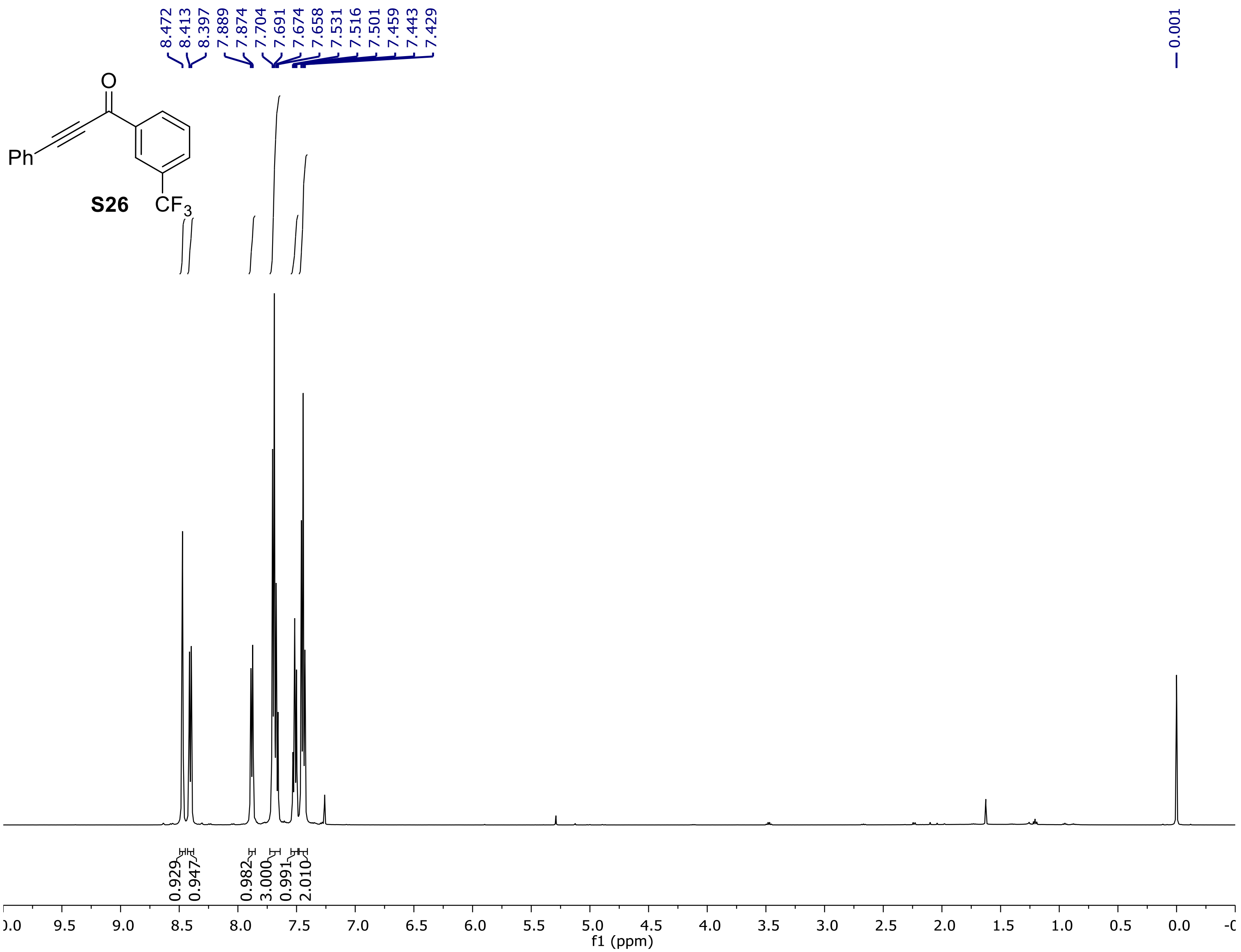
S24

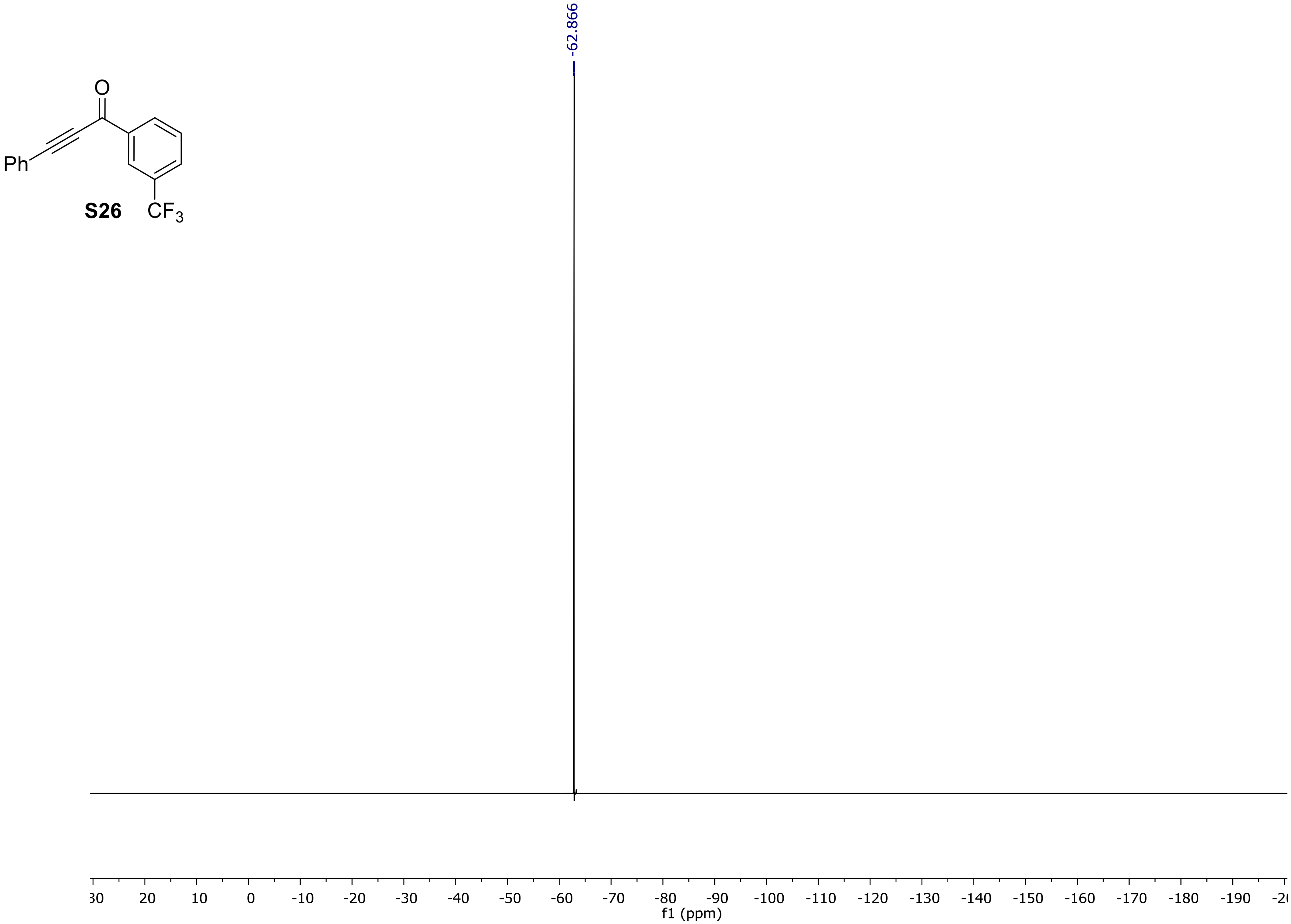
F
F
Ph
Br

1j

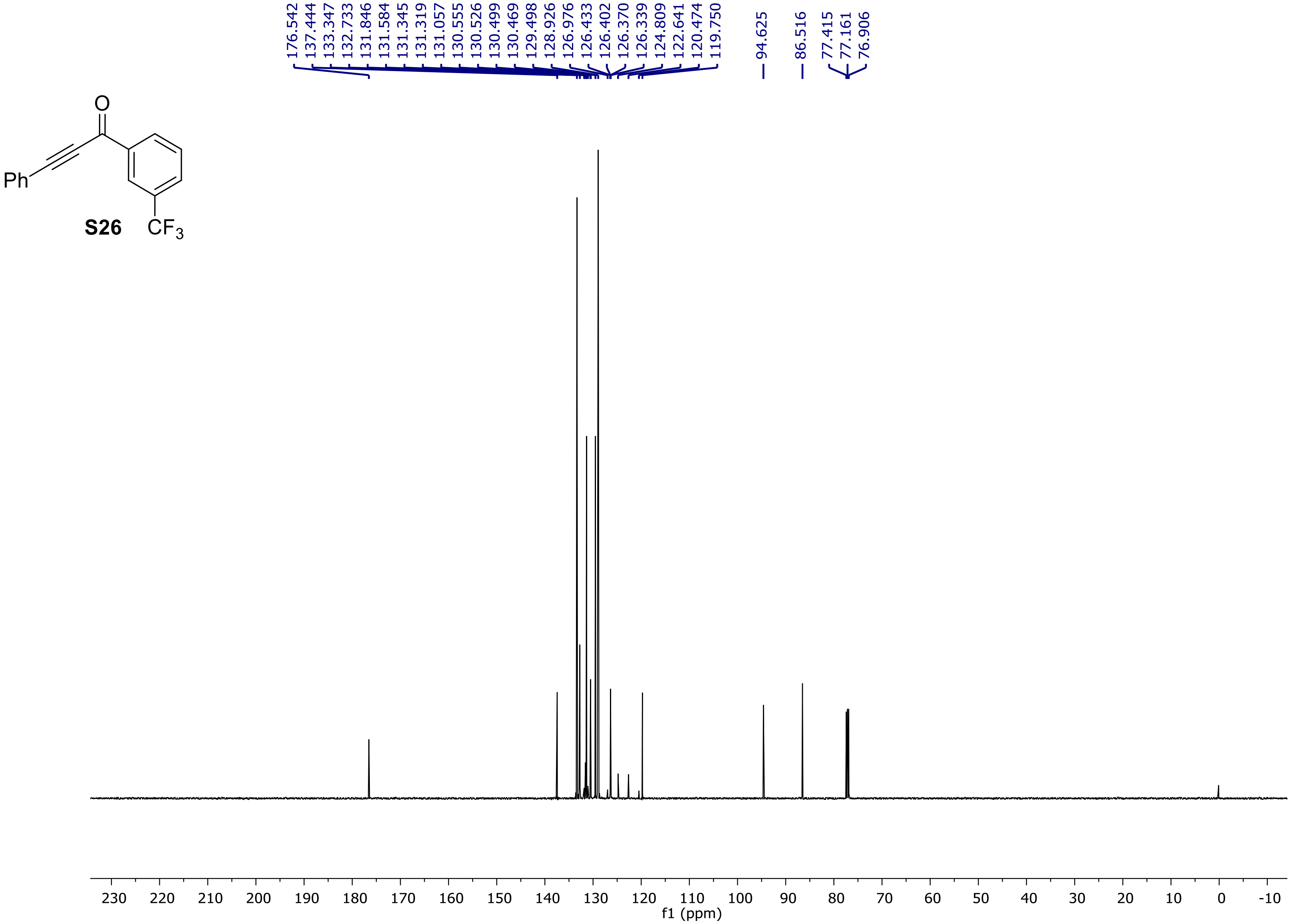

7.609
7.541
7.527
7.445
7.430
7.415
7.385
7.369
7.355
0.000
4.000
2.033
1.033
2.093
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


S25
OH
Ph
CF3
7.894
7.823
7.803
7.622
7.603
7.547
7.528
7.508
7.487
7.483
7.469
7.463
7.378
7.374
7.358
7.344
7.328
7.315
7.306
5.763
5.749
2.426
2.411
0.000
0.969
1.003
1.002
1.080
2.050
3.122
1.000
0.987
9.5
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
f1 (ppm)

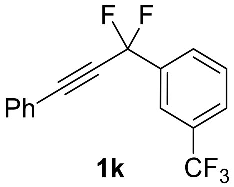

8.472
8.413
8.397
7.889
7.874
7.704
7.691
7.674
7.658
7.531
7.516
7.501
7.459
7.443
7.429
0.001
O
Ph
S26
CF3
0.929
0.947
0.982
3.000
0.991
2.010
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)



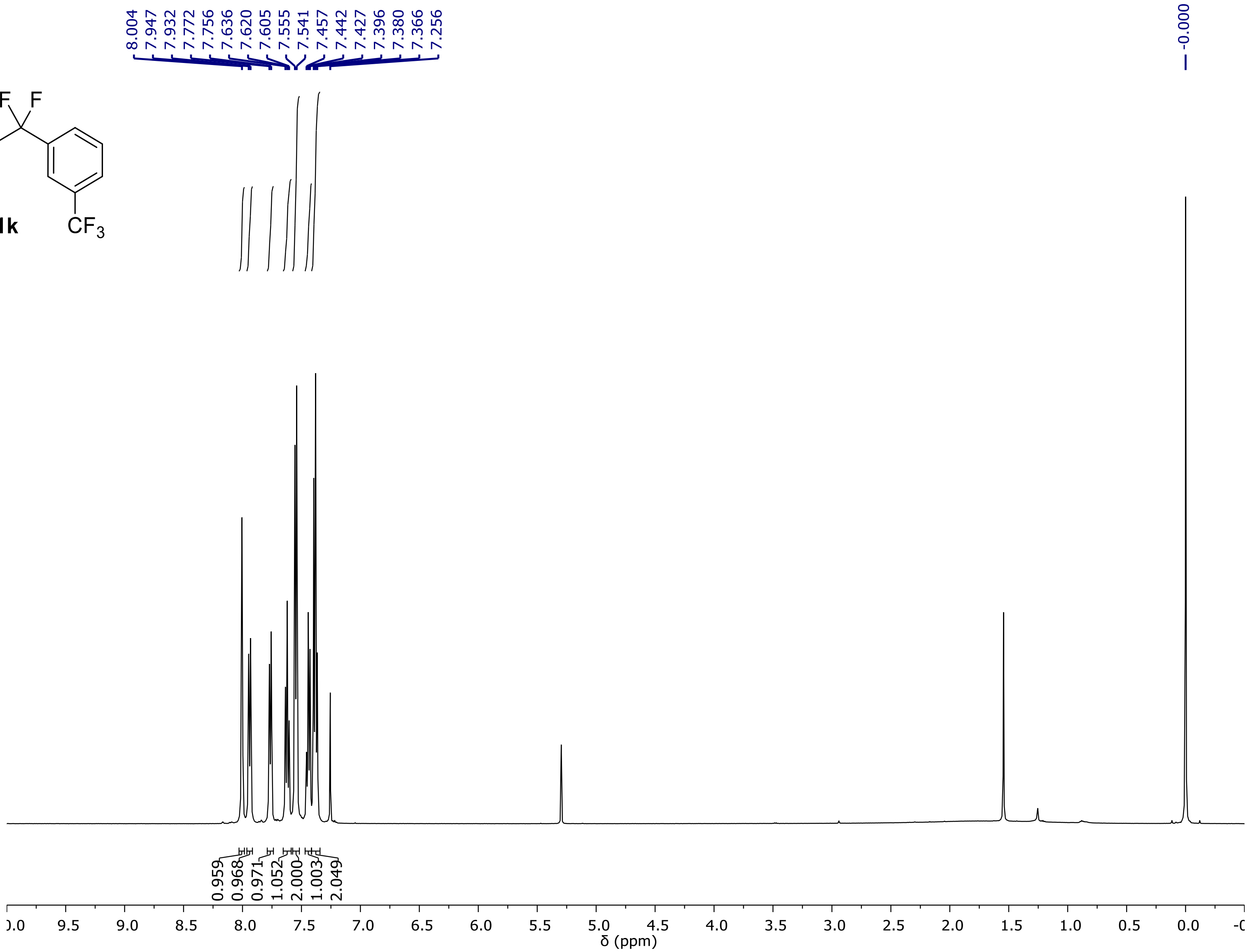
S26
-62.866
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

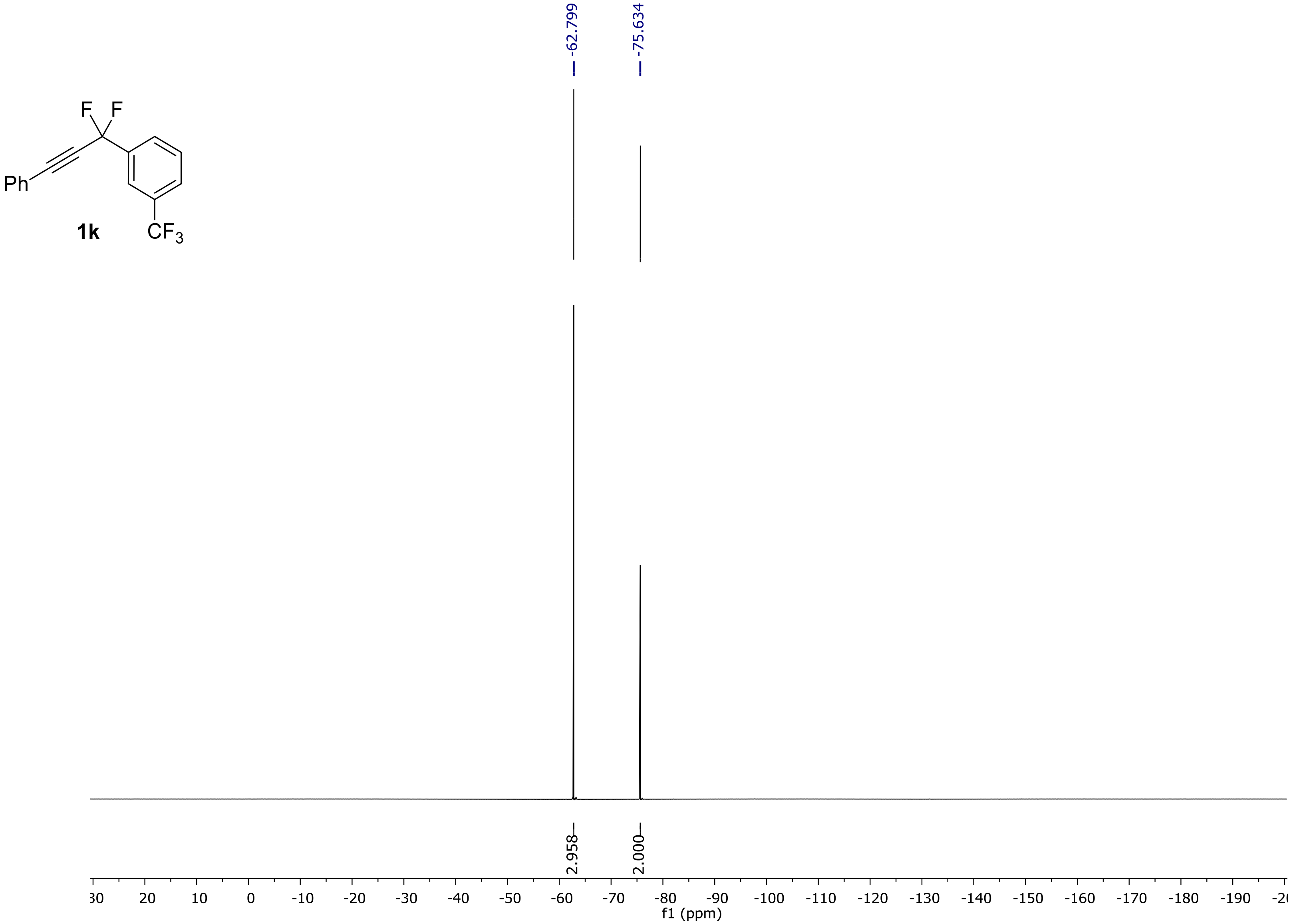

176.542
137.444
133.347
132.733
131.846
131.584
131.345
131.319
131.057
130.555
130.526
130.499
130.469
129.498
128.926
126.976
126.433
126.402
126.370
126.339
124.809
122.641
120.474
119.750
94.625
86.516
77.415
77.161
76.906
O
Ph
CF3
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

S26


F
F
Ph
CF3

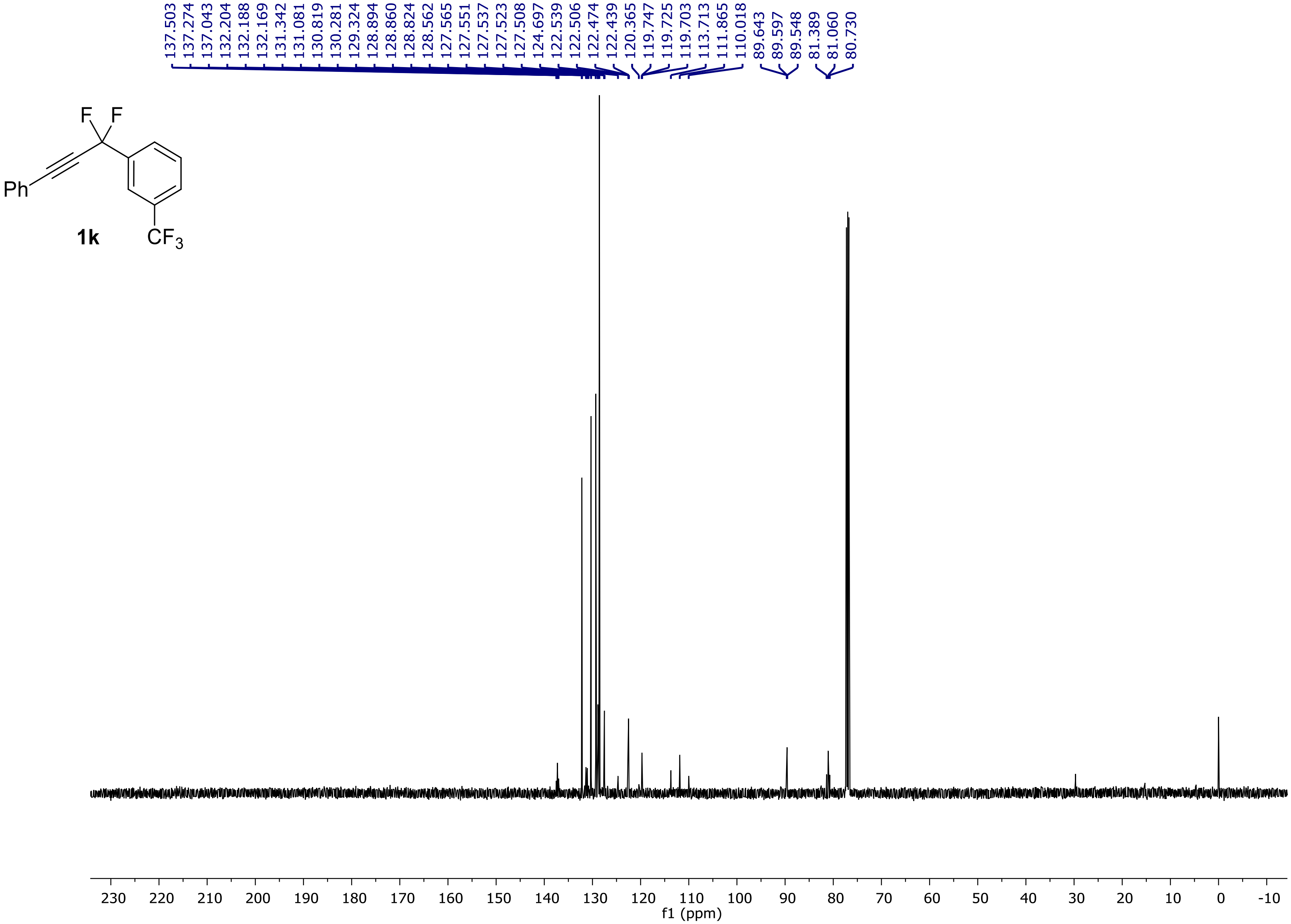
1k


8.004
7.947
7.932
7.772
7.756
7.636
7.620
7.605
7.555
7.541
7.457
7.442
7.427
7.396
7.380
7.366
7.256
-0.000
0.959
0.968
0.971
1.052
2.000
1.003
2.049
10.0
9.5
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
-0
δ (ppm)



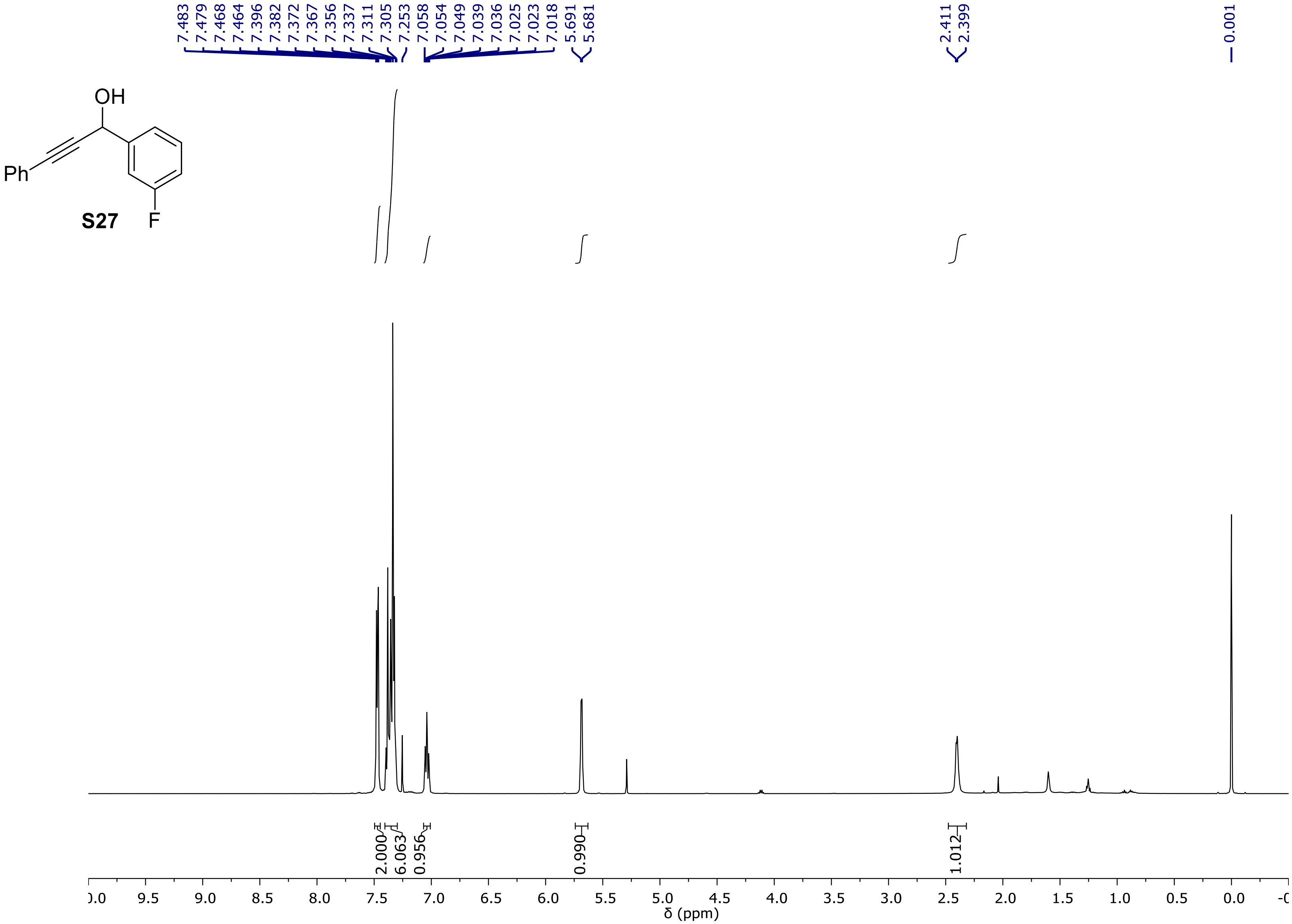
1k

-62.799
-75.634
2.958
2.000
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
f1 (ppm)


F
F
Ph
CF3

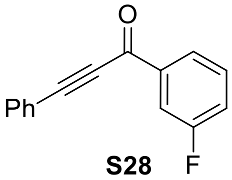
1k

137.503
137.274
137.043
132.204
132.188
132.169
131.342
131.081
130.819
130.281
129.324
128.894
128.860
128.824
128.562
127.565
127.551
127.537
127.523
127.508
124.697
122.539
122.506
122.474
122.439
120.365
119.747
119.725
119.703
113.713
111.865
110.018
89.643
89.597
89.548
81.389
81.060
80.730
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

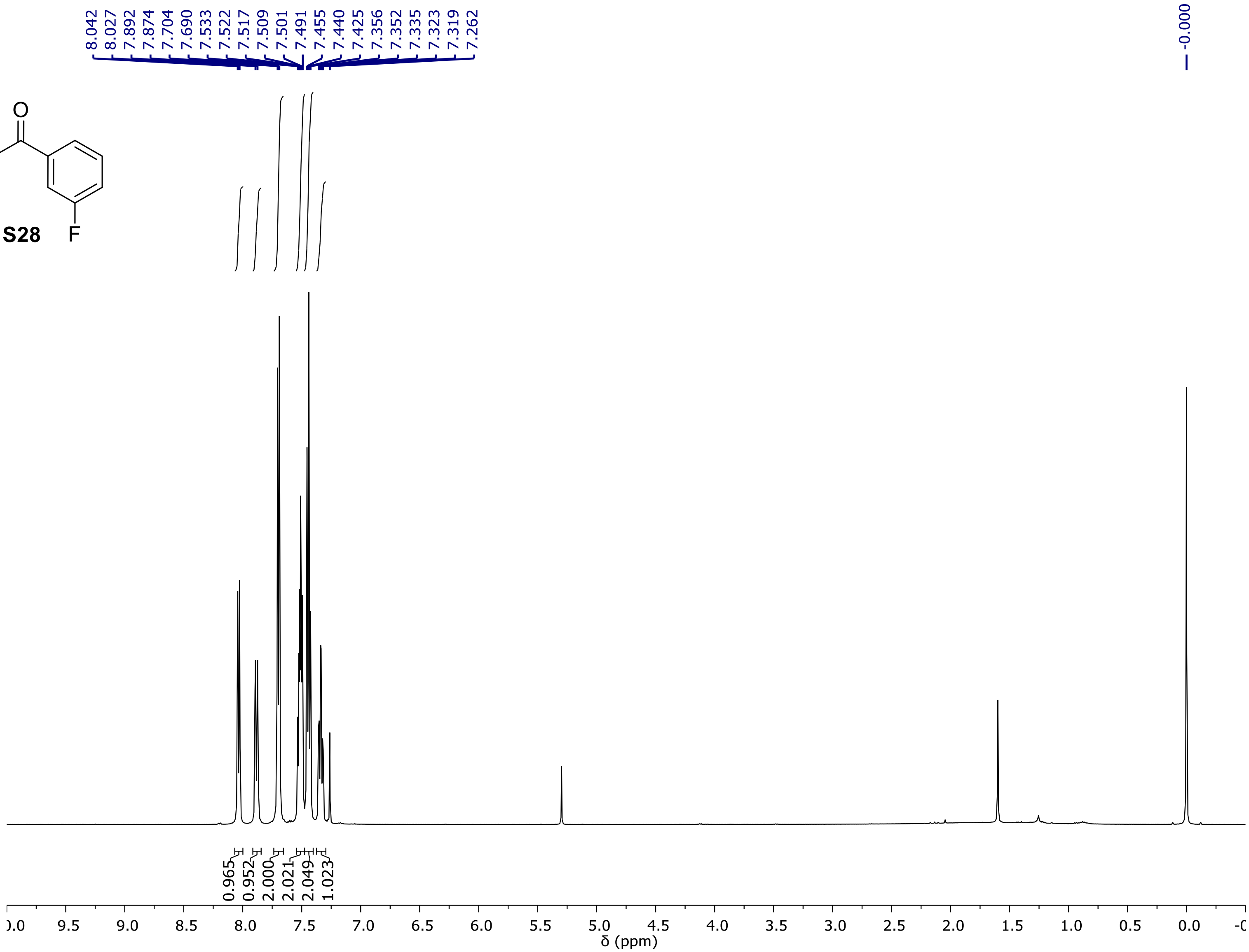

OH
Ph
F

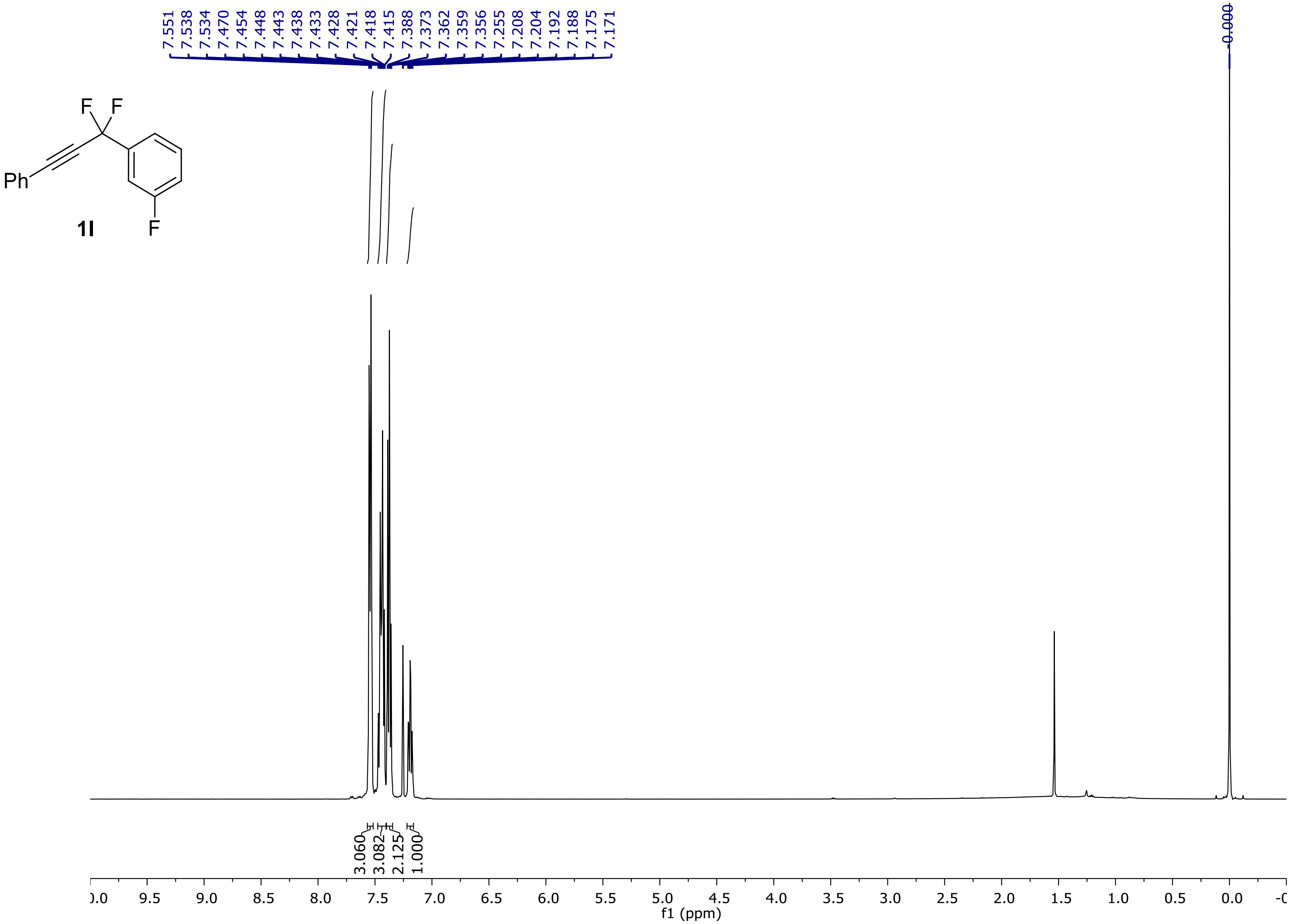
S27

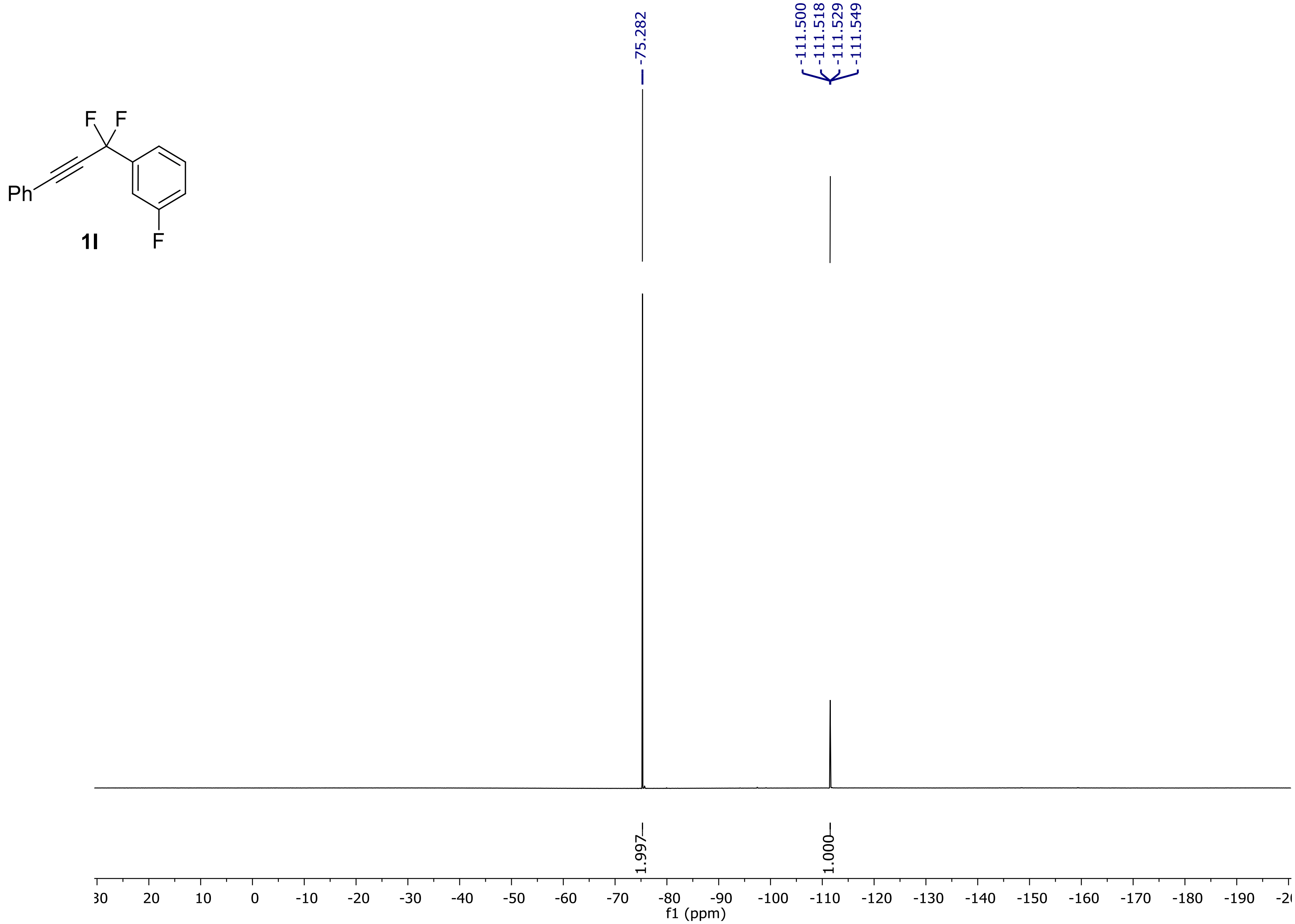
7.483
7.479
7.468
7.464
7.396
7.382
7.372
7.367
7.356
7.337
7.311
7.305
7.253
7.058
7.054
7.049
7.039
7.036
7.025
7.023
7.018
5.691
5.681
2.411
2.399
0.001
2.000
6.063
0.956
0.990
1.012
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)


O
Ph
F

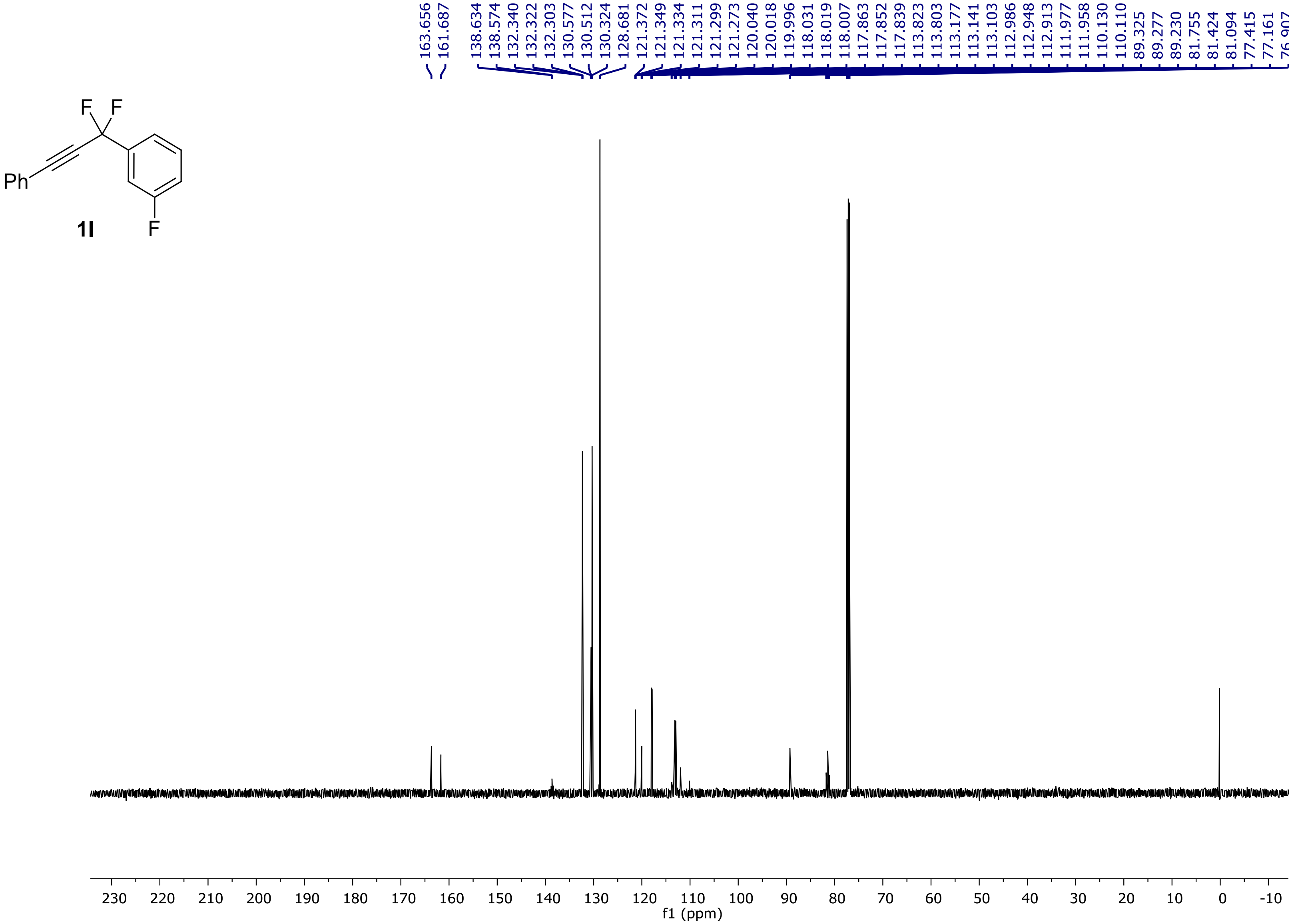
S28


8.042
8.027
7.892
7.874
7.704
7.690
7.533
7.522
7.517
7.509
7.501
7.491
7.455
7.440
7.425
7.356
7.352
7.335
7.323
7.319
7.262
-0.000
0.965
0.952
2.000
2.021
2.049
1.023
10.0
9.5
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
-0
δ (ppm)


1l
F
F
Ph
F
7.551
7.538
7.534
7.470
7.454
7.448
7.443
7.438
7.433
7.428
7.421
7.418
7.415
7.388
7.373
7.362
7.359
7.356
7.255
7.208
7.204
7.192
7.188
7.175
7.171
0.000
3.060
3.082
2.125
1.000
).0
9.5
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
-(
f1 (ppm)

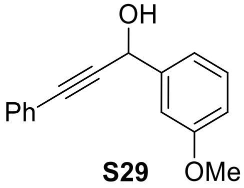

F
F
Ph
F
-75.282
-111.500
-111.518
-111.529
-111.549
1.997
1.000
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
f1 (ppm)

1l

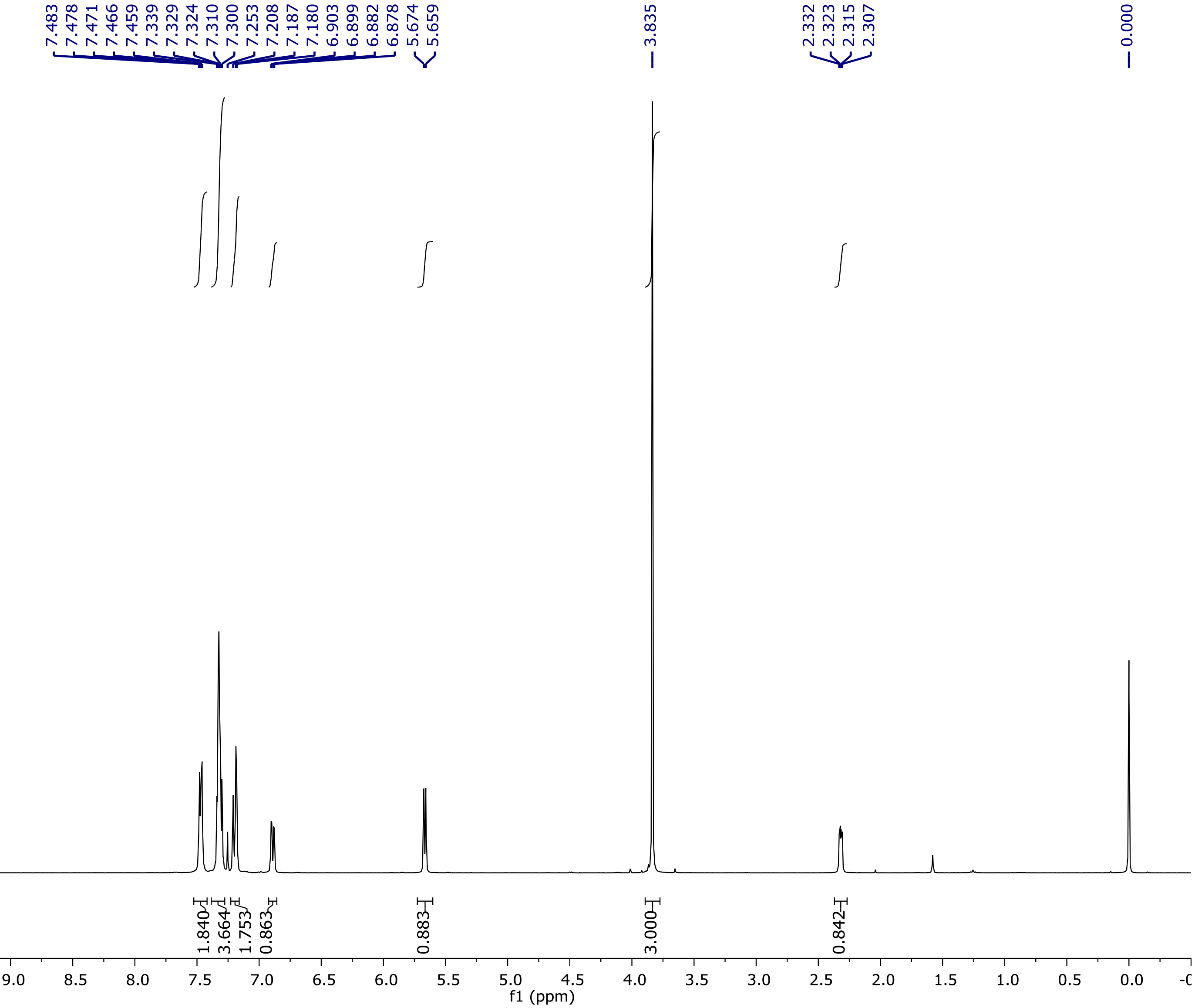

F
F
Ph
F

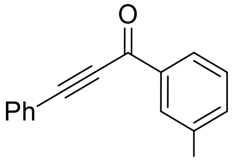
1l

163.656
161.687
138.634
138.574
132.340
132.322
132.303
130.577
130.512
130.324
128.681
121.372
121.349
121.334
121.311
121.299
121.273
120.040
120.018
119.996
118.031
118.019
118.007
117.863
117.852
117.839
113.823
113.803
113.177
113.141
113.103
112.986
112.948
112.913
111.977
111.958
110.130
110.110
89.325
89.277
89.230
81.755
81.424
81.094
77.415
77.161
76.907
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

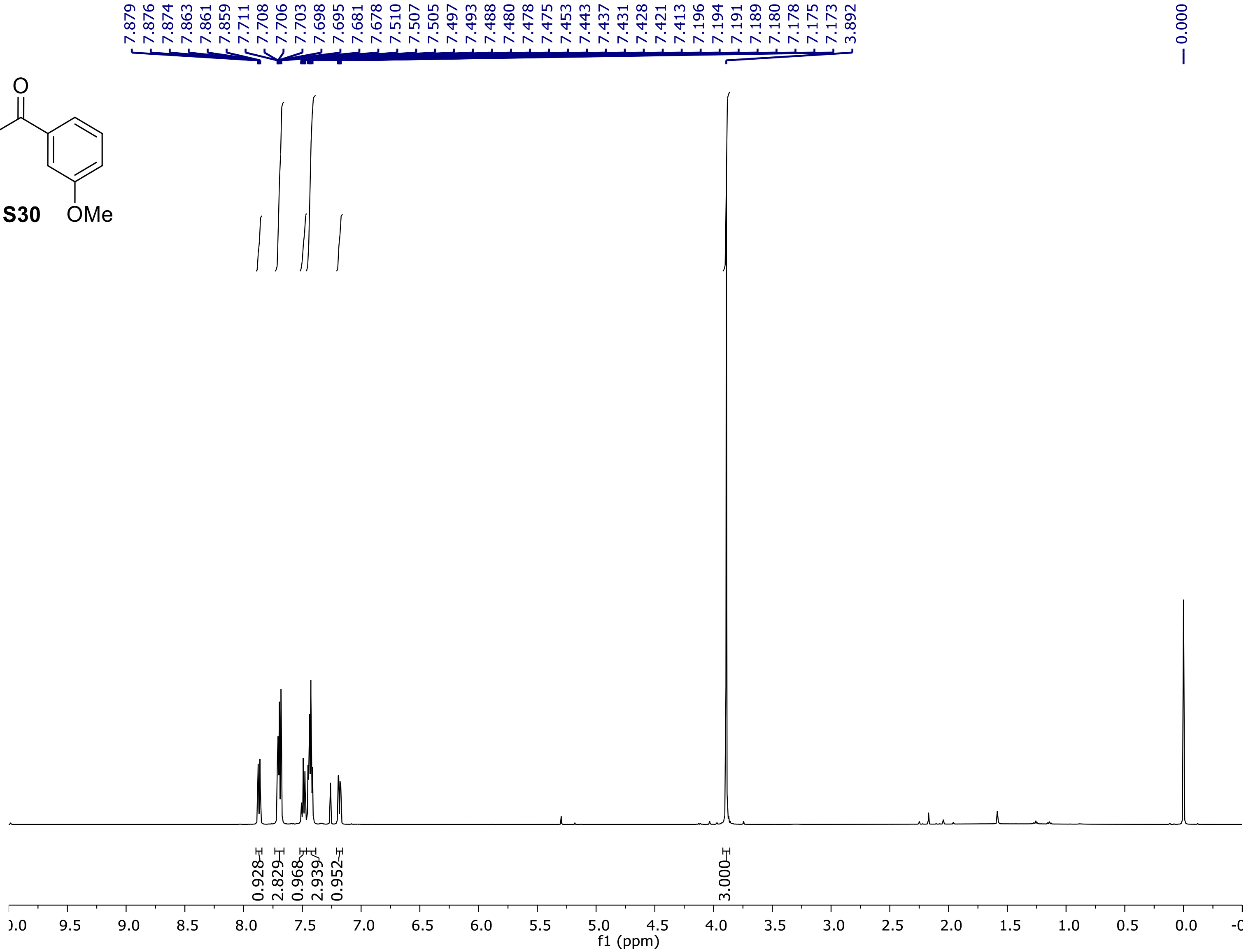

OH
Ph
OMe

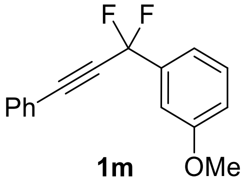
S29


7.483
7.478
7.471
7.466
7.459
7.339
7.329
7.324
7.310
7.300
7.253
7.208
7.187
7.180
6.903
6.899
6.882
6.878
5.674
5.659
3.835
2.332
2.323
2.315
2.307
0.000
1.840
3.664
1.753
0.863
0.883
3.000
0.842
0.0
9.5
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
f1 (ppm)

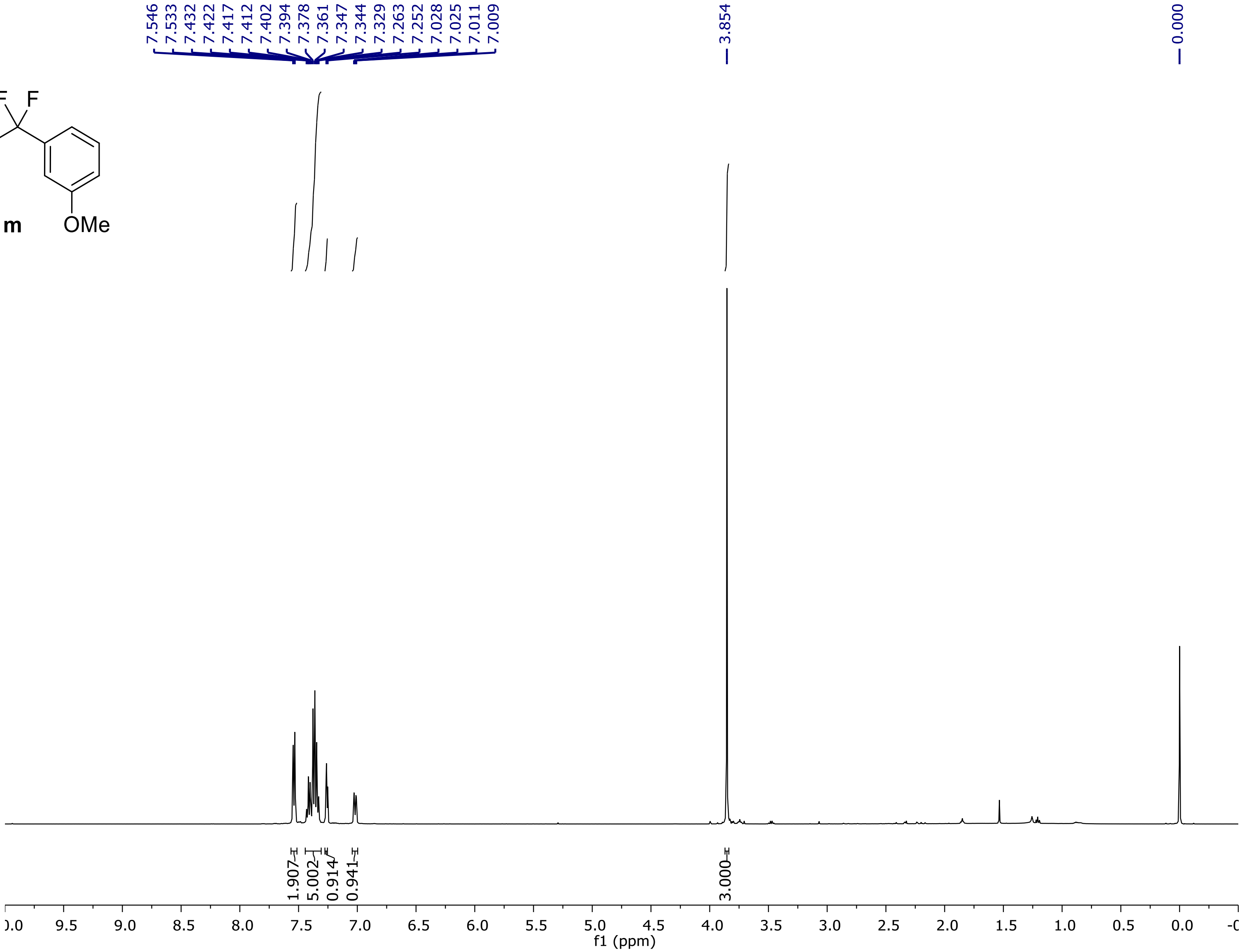

O
Ph
OMe

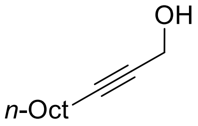
S30


7.879
7.876
7.874
7.863
7.861
7.859
7.711
7.708
7.706
7.703
7.698
7.695
7.681
7.678
7.510
7.507
7.505
7.497
7.493
7.488
7.480
7.478
7.475
7.453
7.443
7.437
7.431
7.428
7.421
7.413
7.196
7.194
7.191
7.189
7.180
7.178
7.175
7.173
3.892
0.000
0.928
2.829
0.968
2.939
0.952
3.000
).0
9.5
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
-(
f1 (ppm)

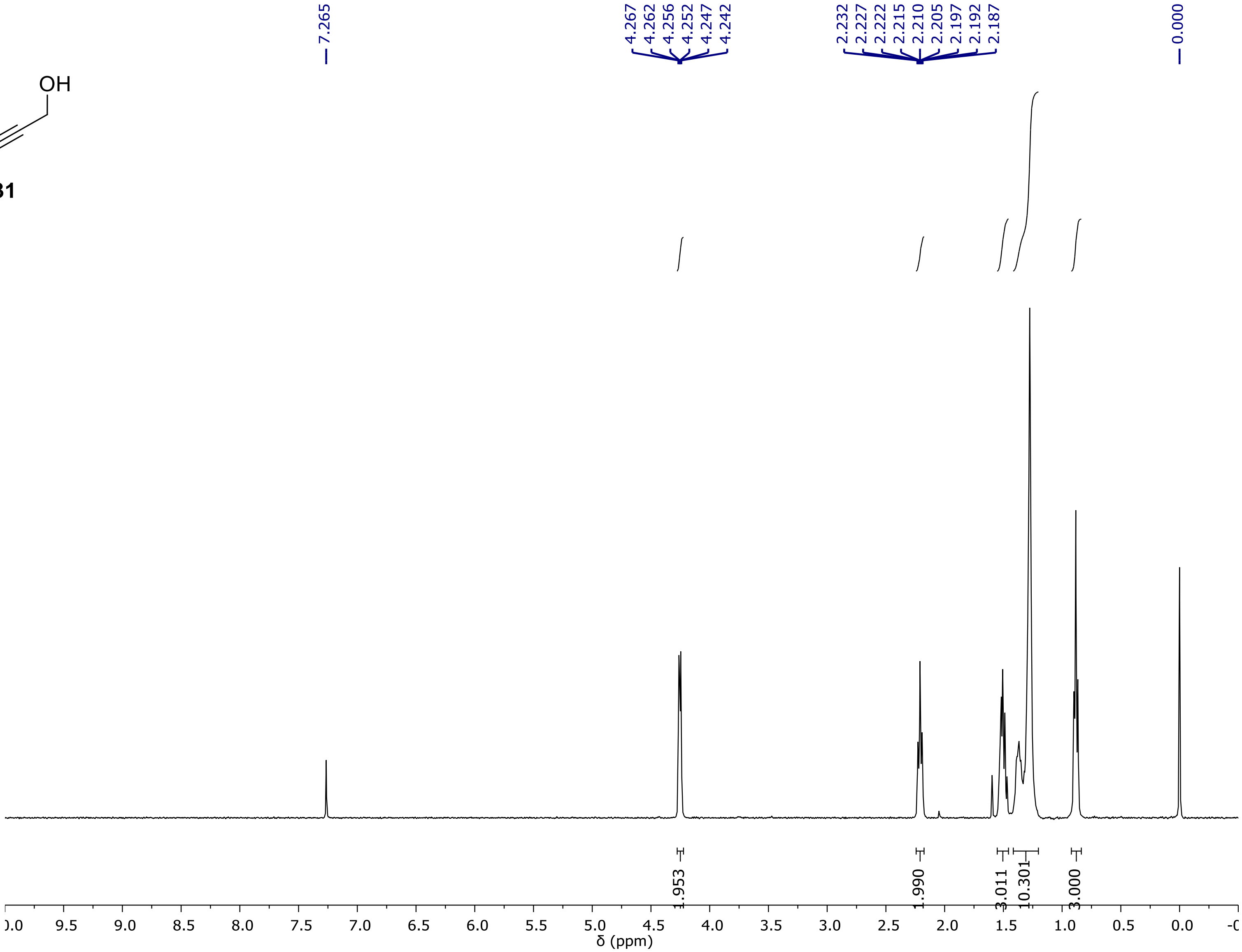

F
F
Ph
OMe

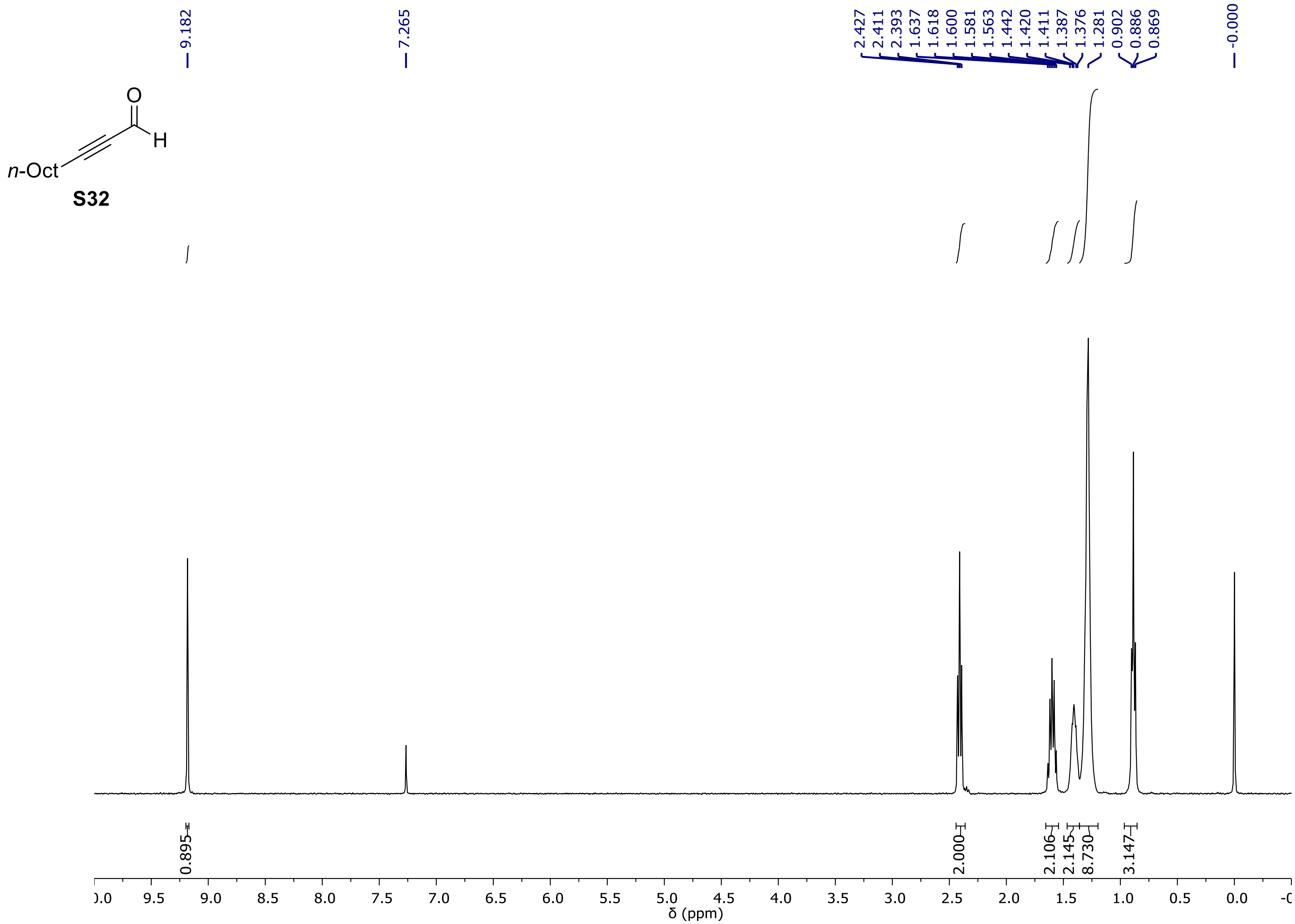
1m


7.546
7.533
7.432
7.422
7.417
7.412
7.402
7.394
7.378
7.361
7.347
7.344
7.329
7.263
7.252
7.028
7.025
7.011
7.009
3.854
0.000
1.907
5.002
0.914
0.941
3.000
10.0
9.5
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
-0
f1 (ppm)


OH
n-Oct

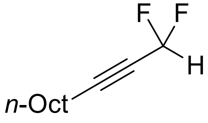
S31


7.265
4.267
4.262
4.256
4.252
4.247
4.242
2.232
2.227
2.222
2.215
2.210
2.205
2.197
2.192
2.187
0.000
1.953
1.990
3.011
10.301
3.000
0.0
9.5
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
δ (ppm)

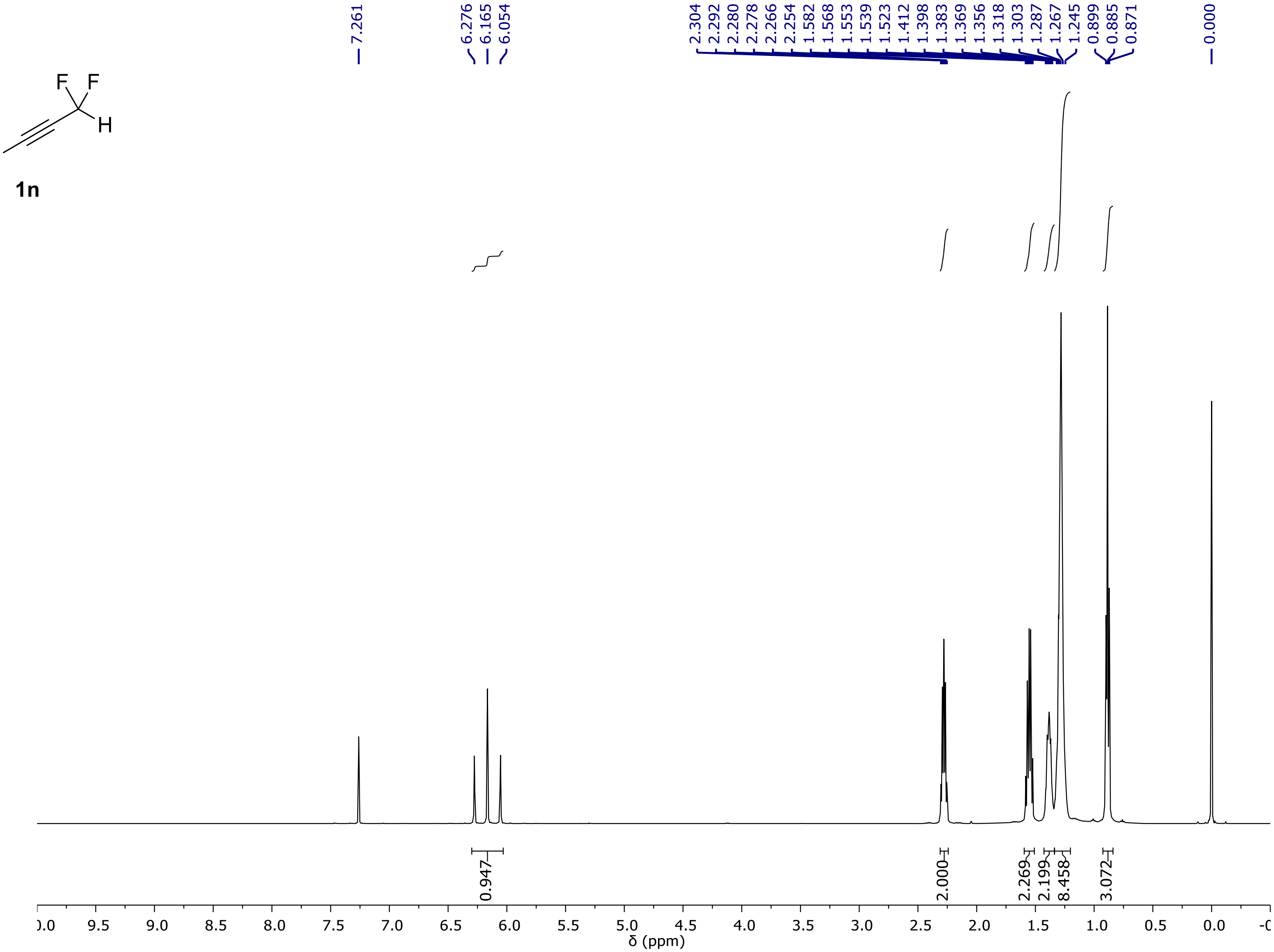


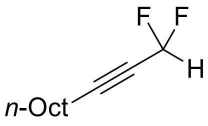
S32

n-Oct
O
H
9.182
7.265
2.427
2.411
2.393
1.637
1.618
1.600
1.581
1.563
1.442
1.420
1.411
1.387
1.376
1.281
0.902
0.886
0.869
-0.000
0.895
2.000
2.106
2.145
8.730
3.147
9.5
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
δ (ppm)

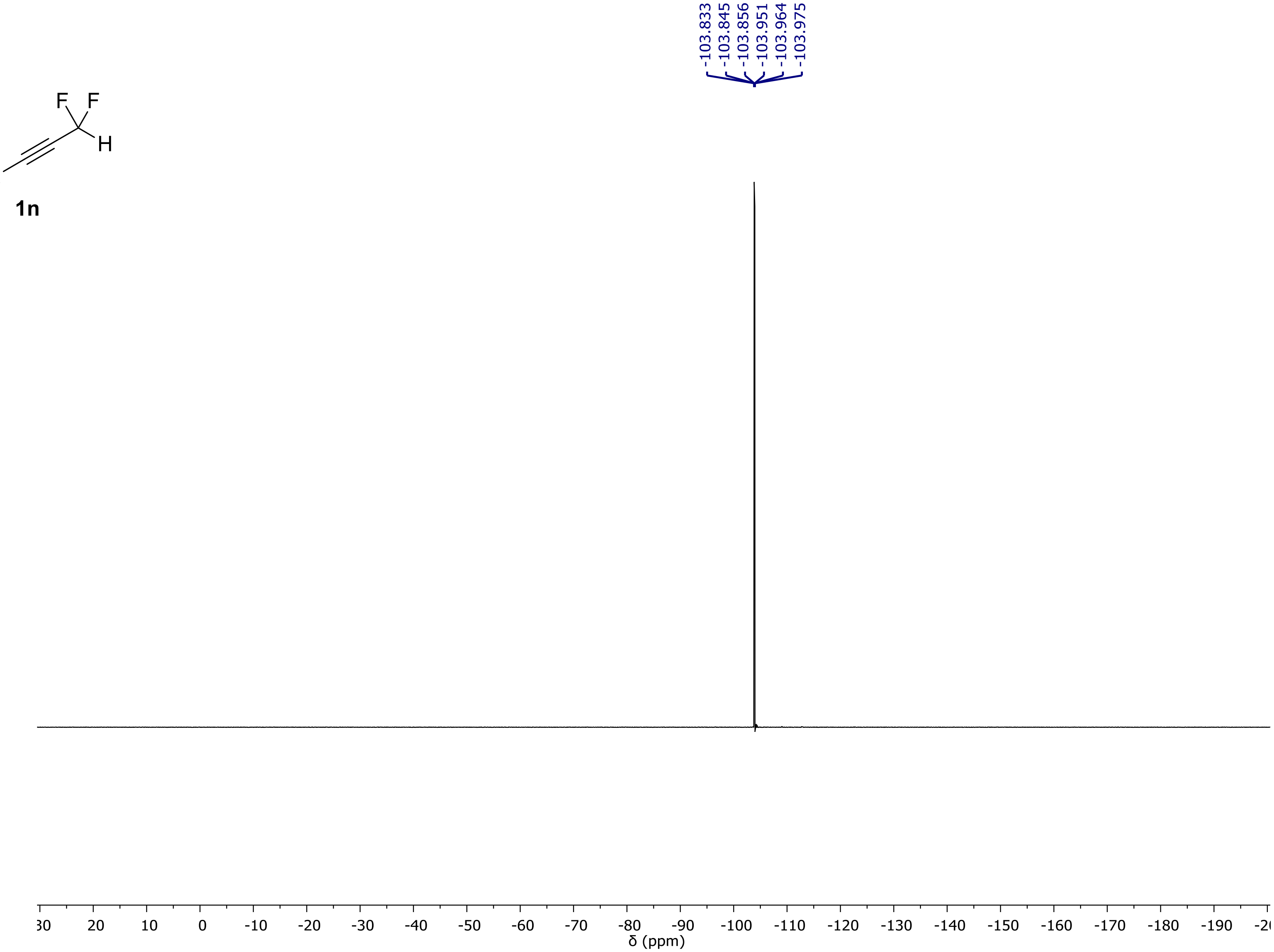

F F
H
n-Oct

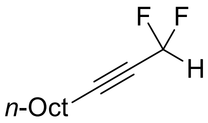
1n


7.261
6.276
6.165
6.054
2.304
2.292
2.280
2.278
2.266
2.254
1.582
1.568
1.553
1.539
1.523
1.412
1.398
1.383
1.369
1.356
1.318
1.303
1.287
1.267
1.245
0.899
0.885
0.871
0.000
0.947
2.000
2.269
2.199
8.458
3.072
).0
9.5
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
-(
δ (ppm)

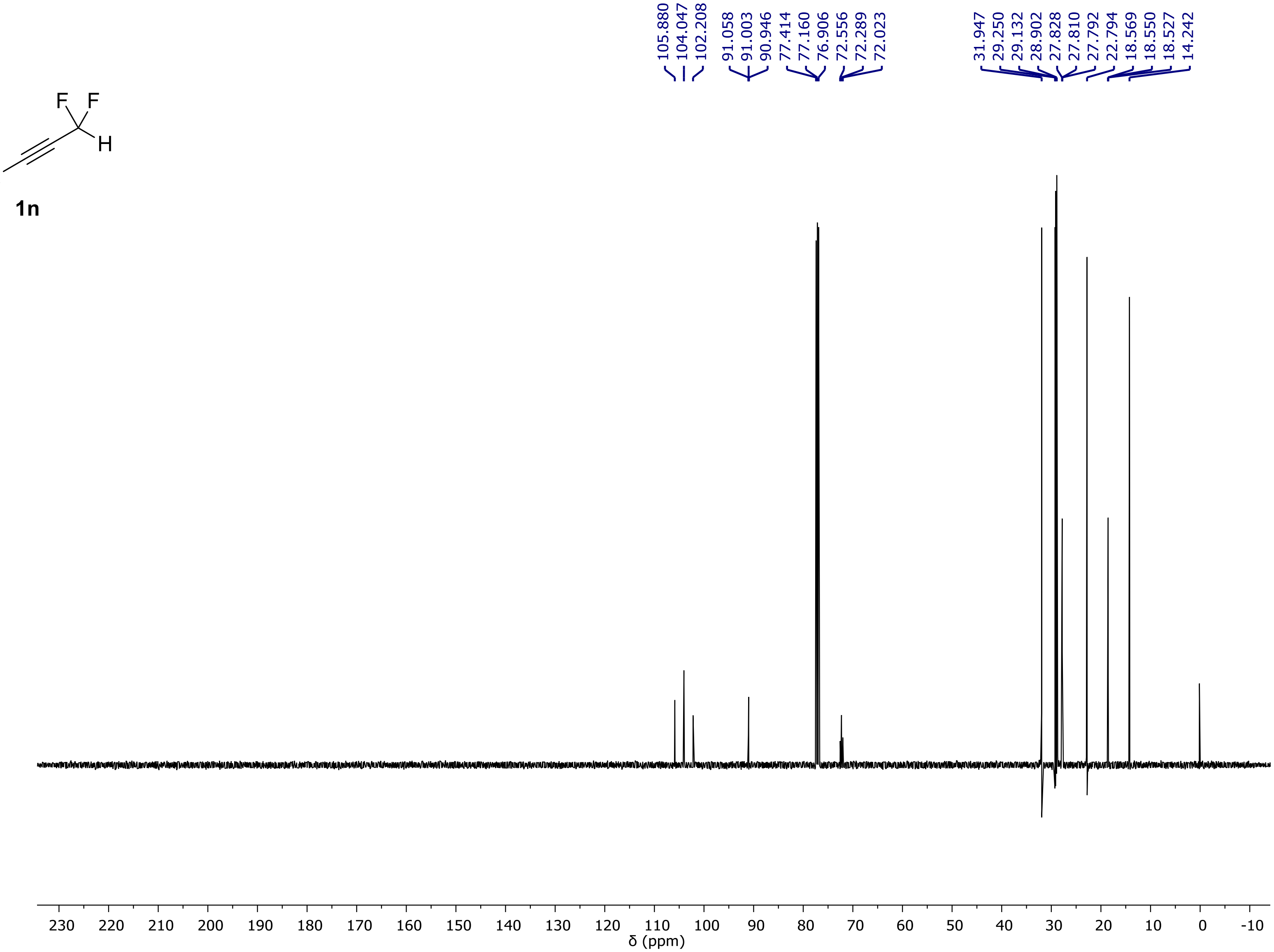

F
F
H
n-Oct

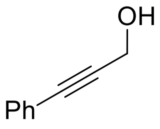
1n


-103.833
-103.845
-103.856
-103.951
-103.964
-103.975
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
δ (ppm)

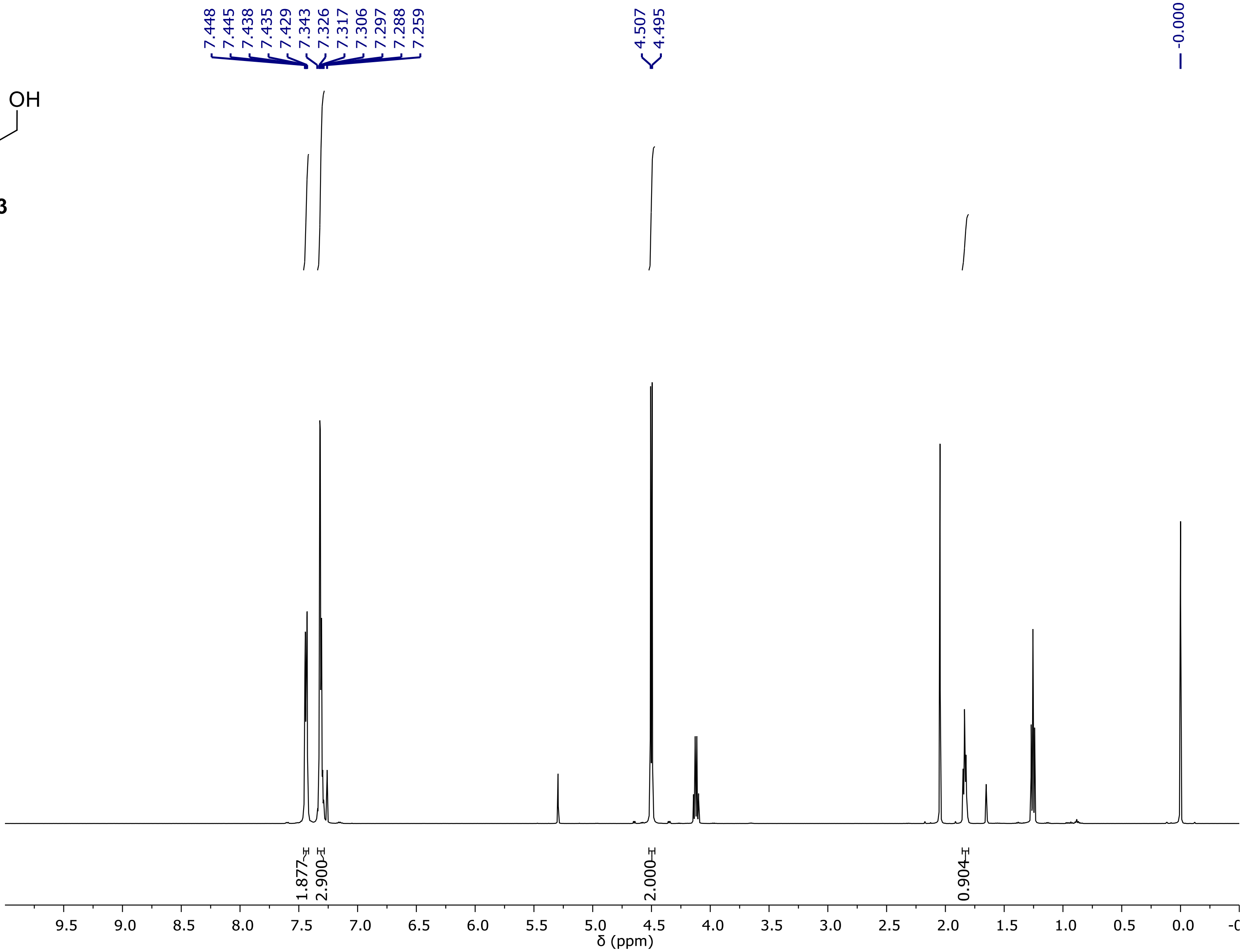

F
F
H
n-Oct

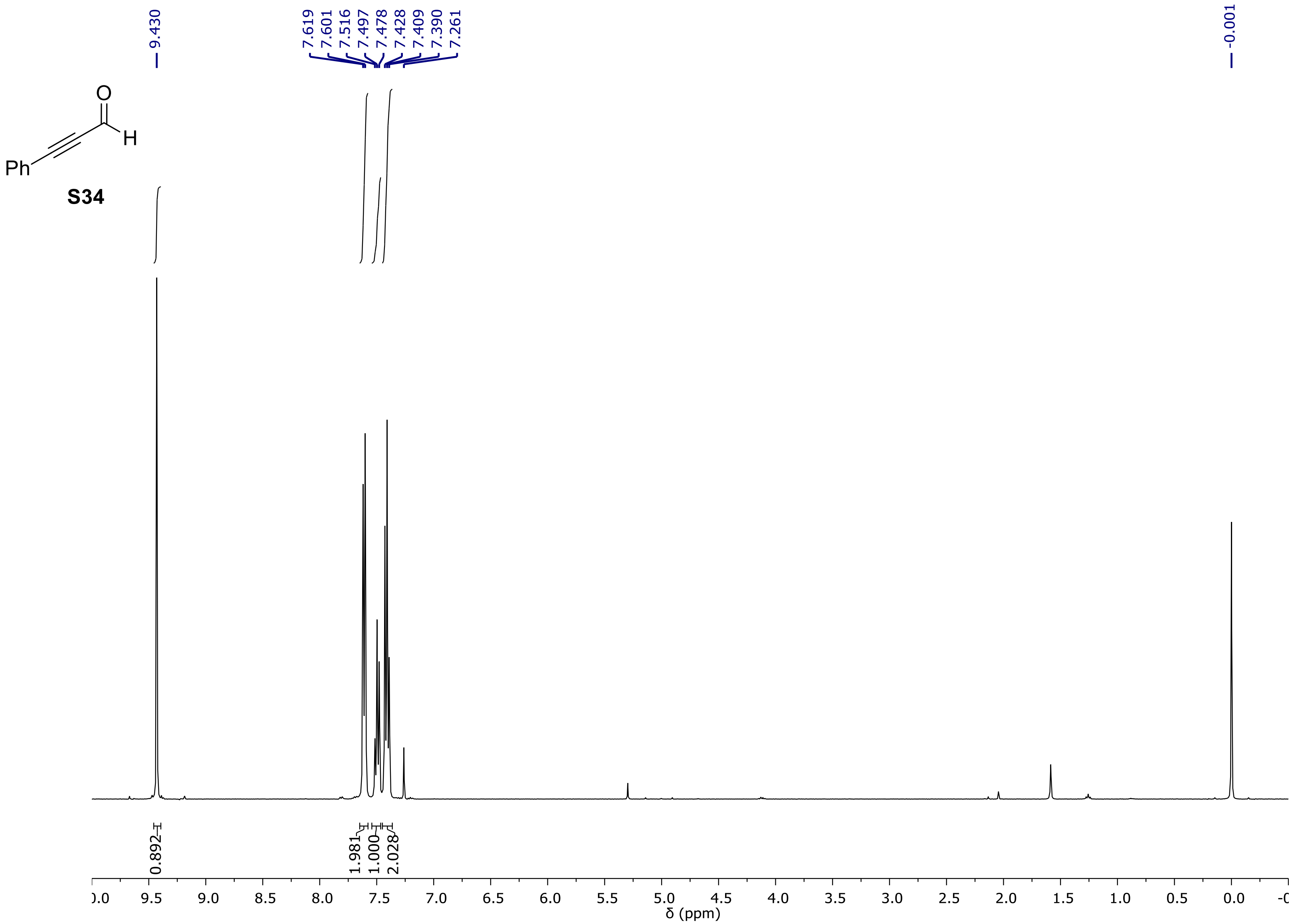
1n


105.880
104.047
102.208
91.058
91.003
90.946
77.414
77.160
76.906
72.556
72.289
72.023
31.947
29.250
29.132
28.902
27.828
27.810
27.792
22.794
18.569
18.550
18.527
14.242
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)


OH
Ph

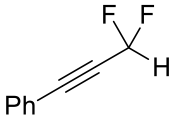
S33


7.448
7.445
7.438
7.435
7.429
7.343
7.326
7.317
7.306
7.297
7.288
7.259
4.507
4.495
-0.000
1.877
2.900
2.000
0.904
9.5
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
δ (ppm)

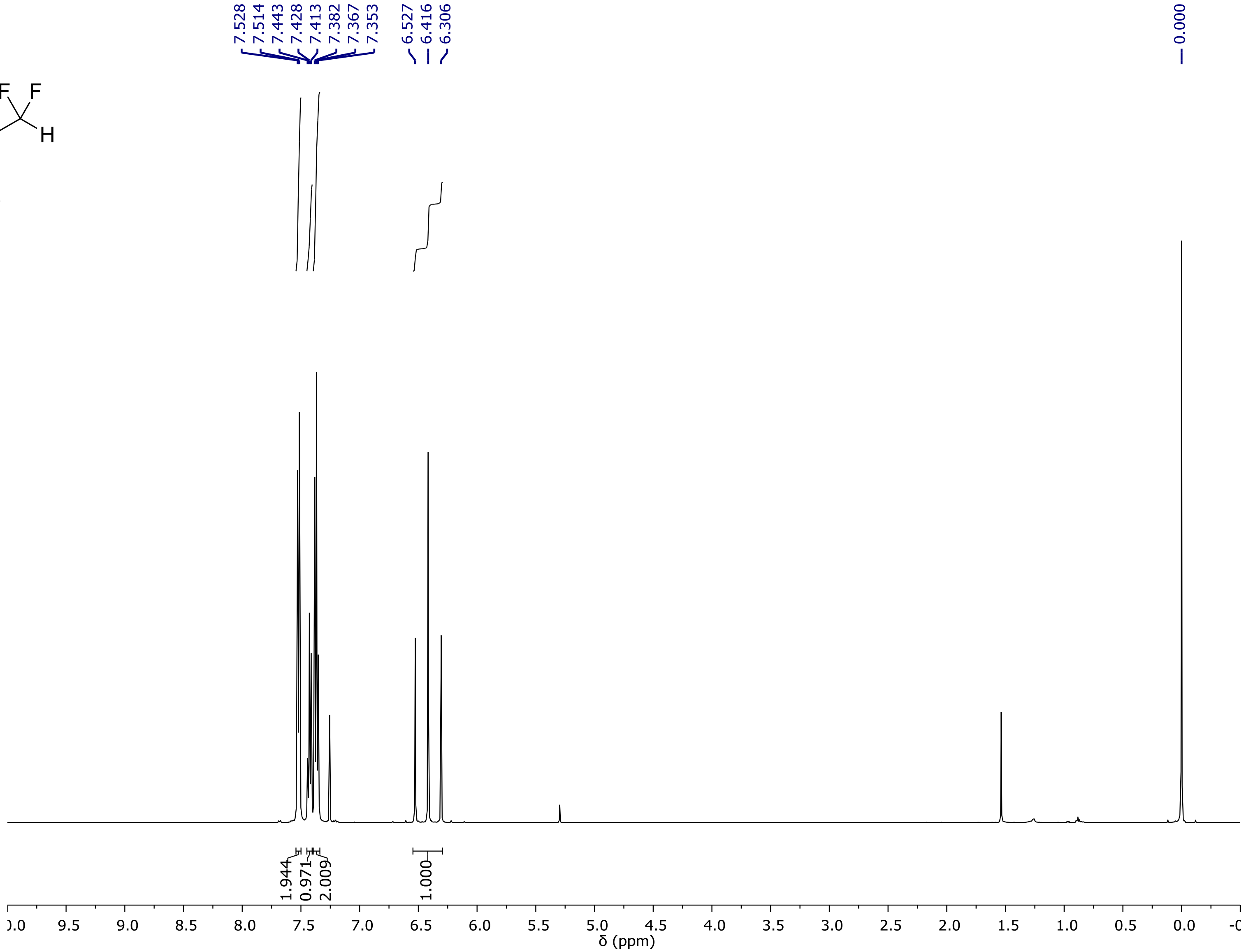


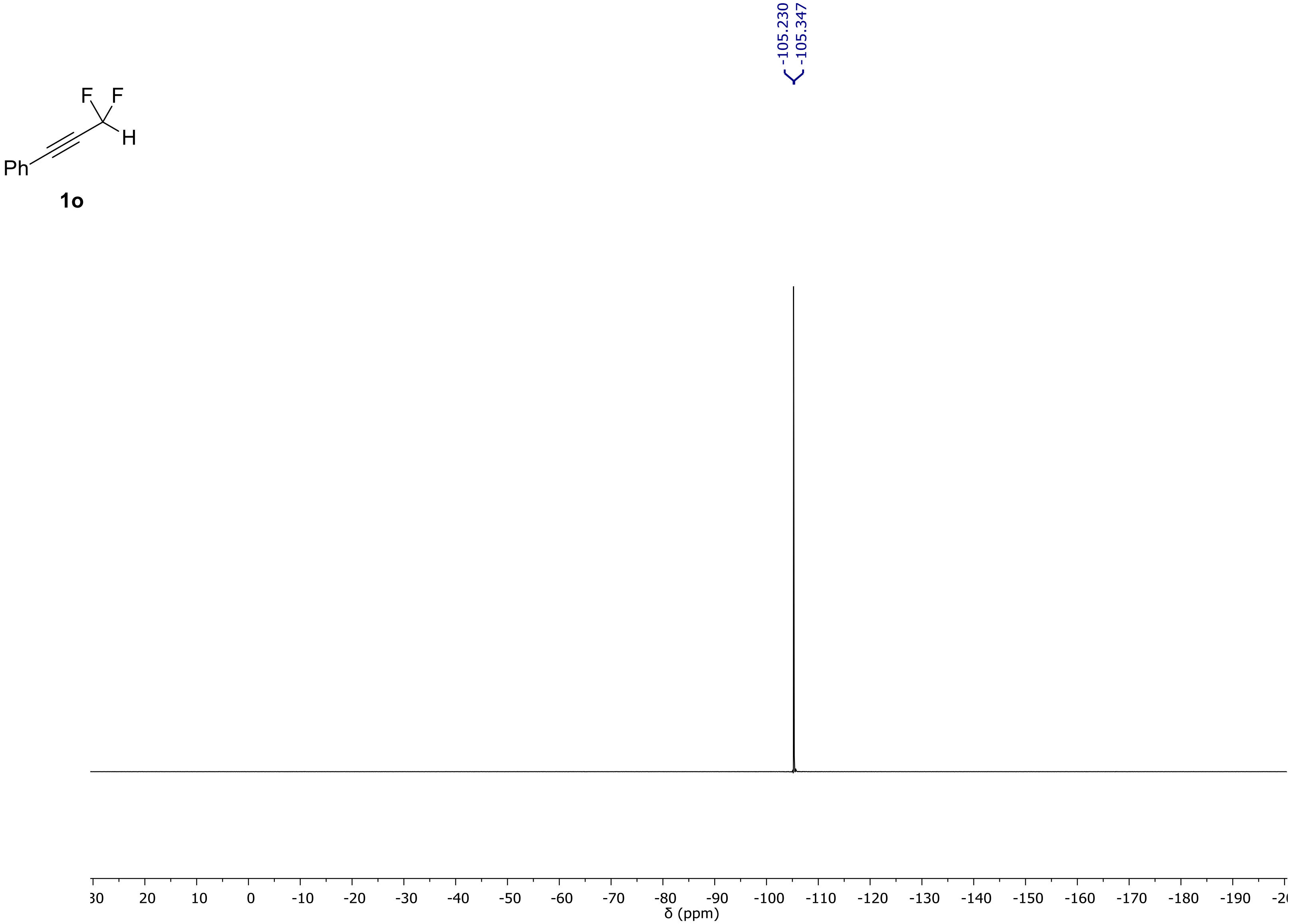
S34

O
H
Ph
9.430
7.619
7.601
7.516
7.497
7.478
7.428
7.409
7.390
7.261
-0.001
0.892
1.981
1.000
2.028
).0
9.5
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
-(
δ (ppm)

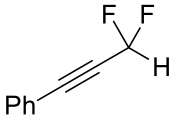

F
F
H
Ph

1o

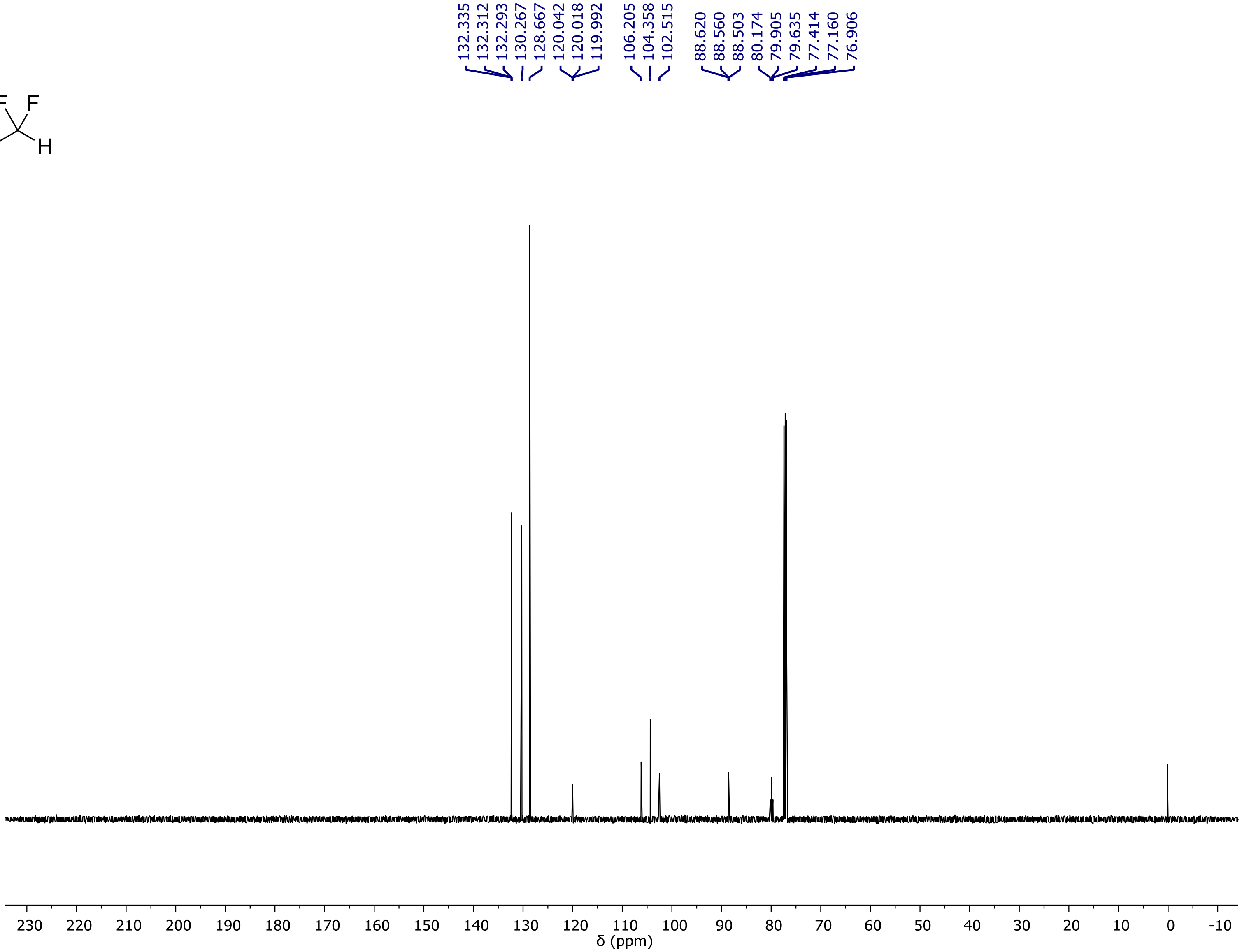

7.528
7.514
7.443
7.428
7.413
7.382
7.367
7.353
6.527
6.416
6.306
0.000
1.944
0.971
2.009
1.000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
δ (ppm)

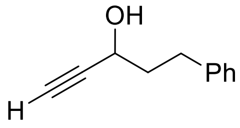

F
F
H
Ph
-105.230
-105.347
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
δ (ppm)

1o

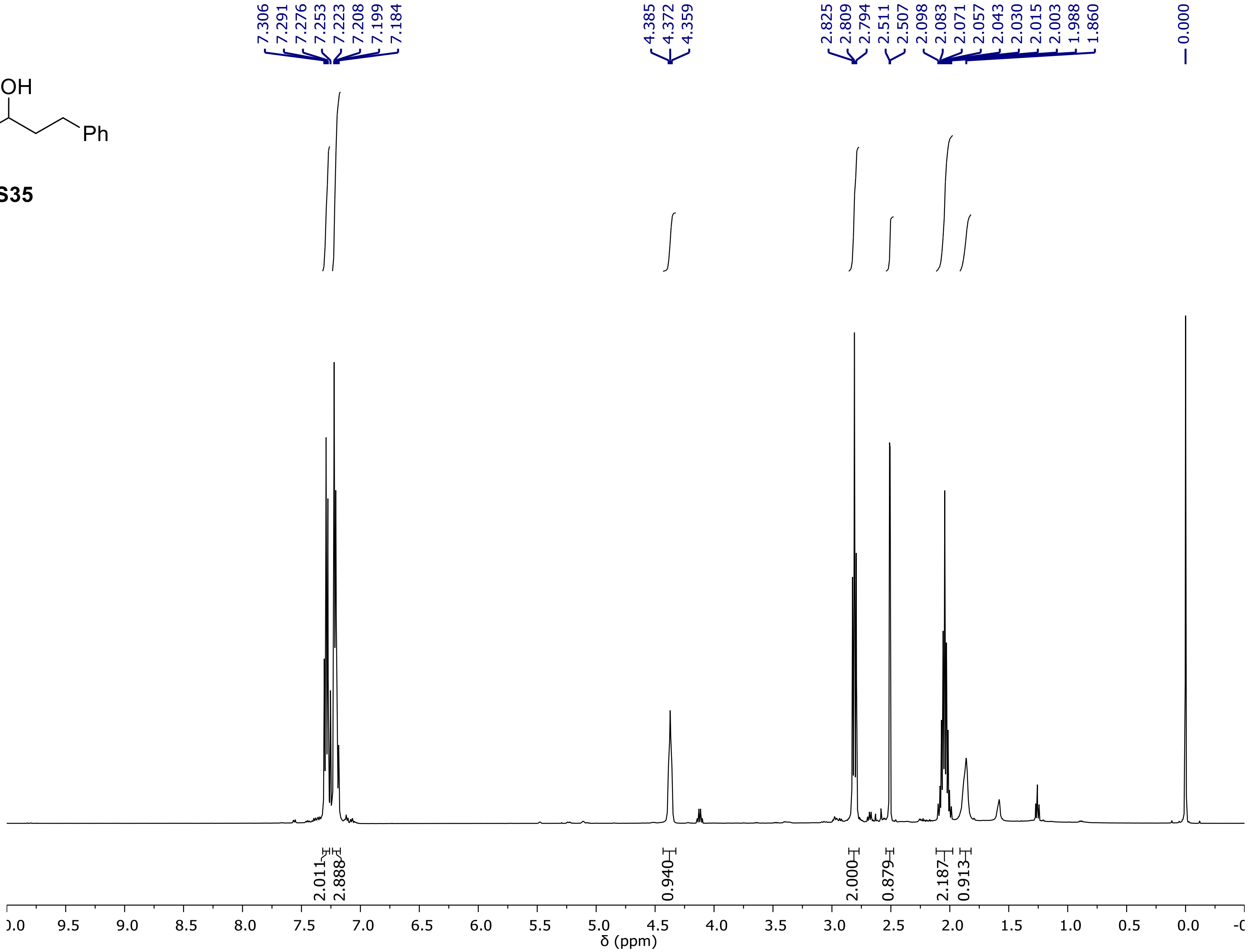

F
F
H
Ph

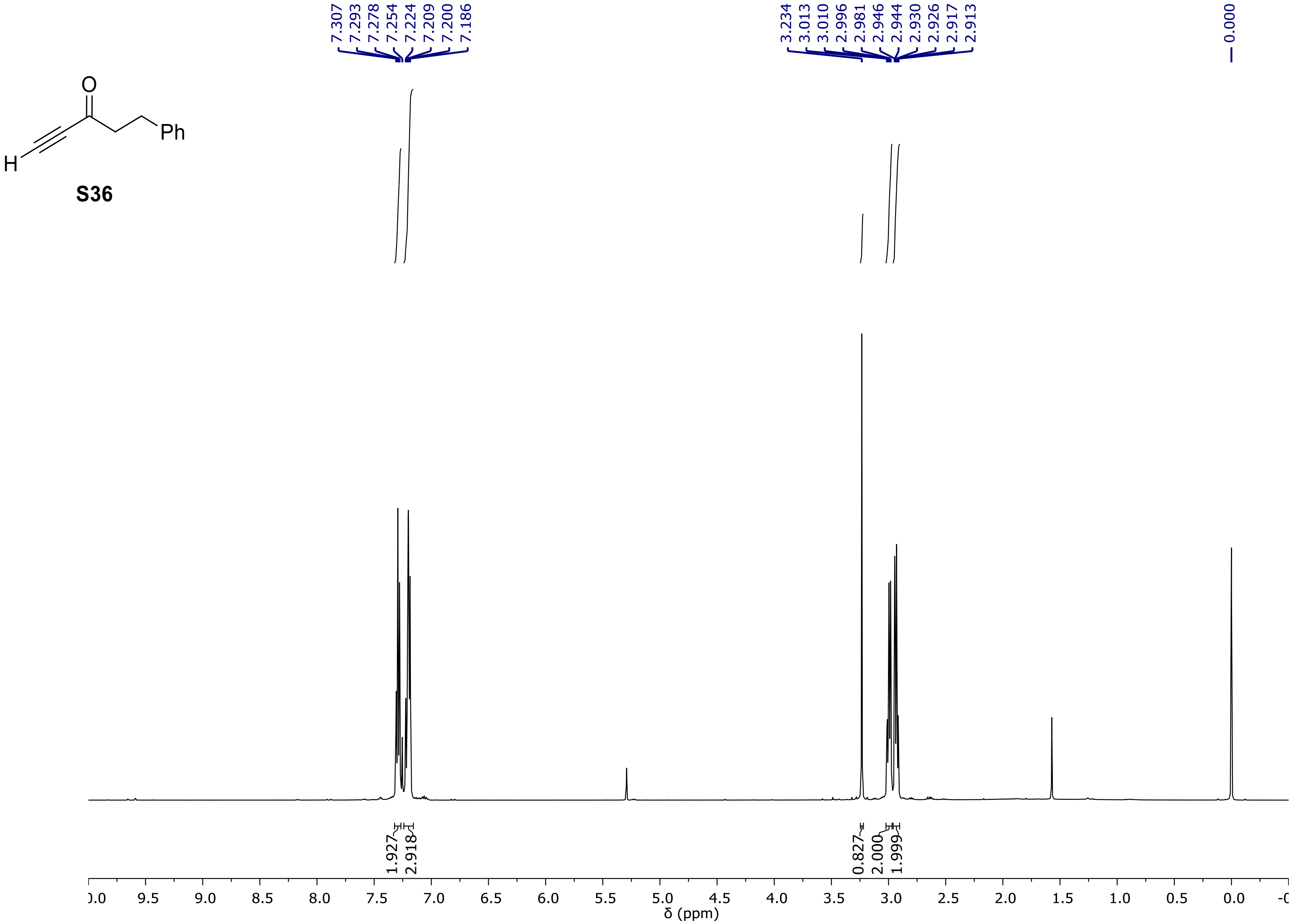
1o


132.335
132.312
132.293
130.267
128.667
120.042
120.018
119.992
106.205
104.358
102.515
88.620
88.560
88.503
80.174
79.905
79.635
77.414
77.160
76.906
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)


OH
H
Ph

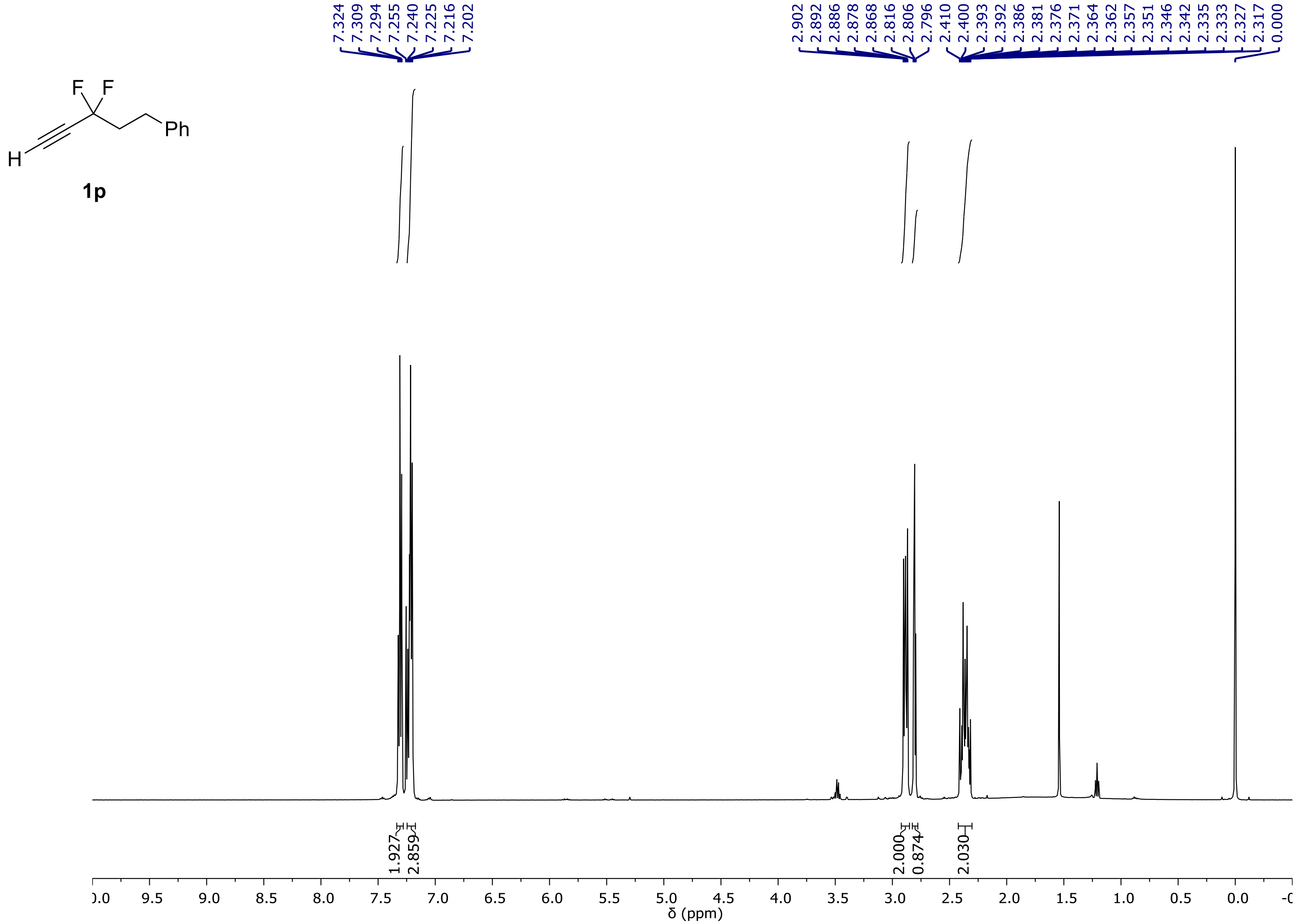
S35


7.306
7.291
7.276
7.253
7.223
7.208
7.199
7.184
4.385
4.372
4.359
2.825
2.809
2.794
2.511
2.507
2.098
2.083
2.071
2.057
2.043
2.030
2.015
2.003
1.988
1.860
0.000
2.011
2.888
0.940
2.000
0.879
2.187
0.913
).0
9.5
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
-(
δ (ppm)

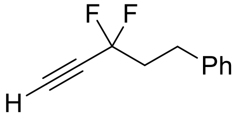

O
Ph
H

S36

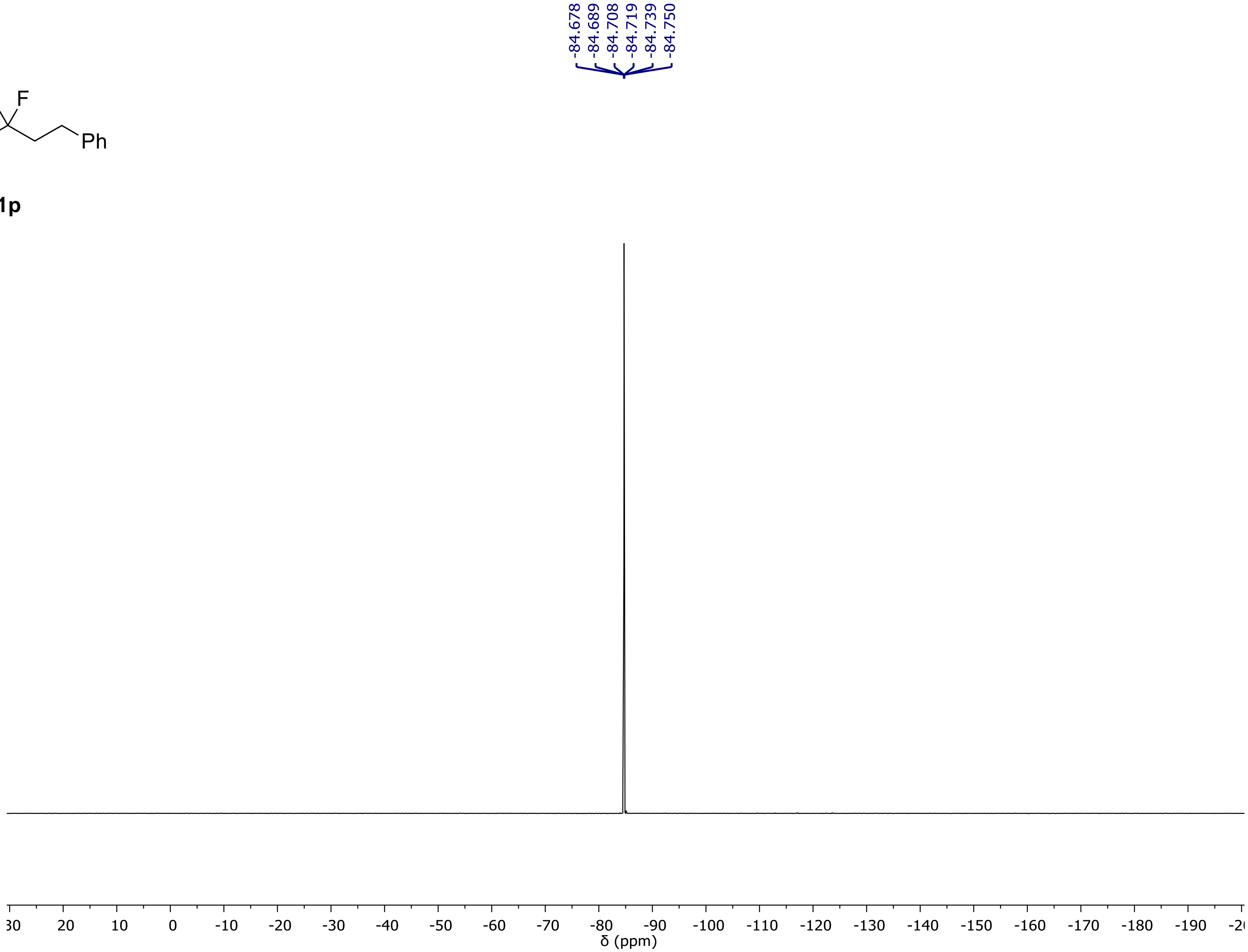
7.307
7.293
7.278
7.254
7.224
7.209
7.200
7.186
3.234
3.013
3.010
2.996
2.981
2.946
2.944
2.930
2.926
2.917
2.913
0.000
1.927
2.918
0.827
2.000
1.999
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

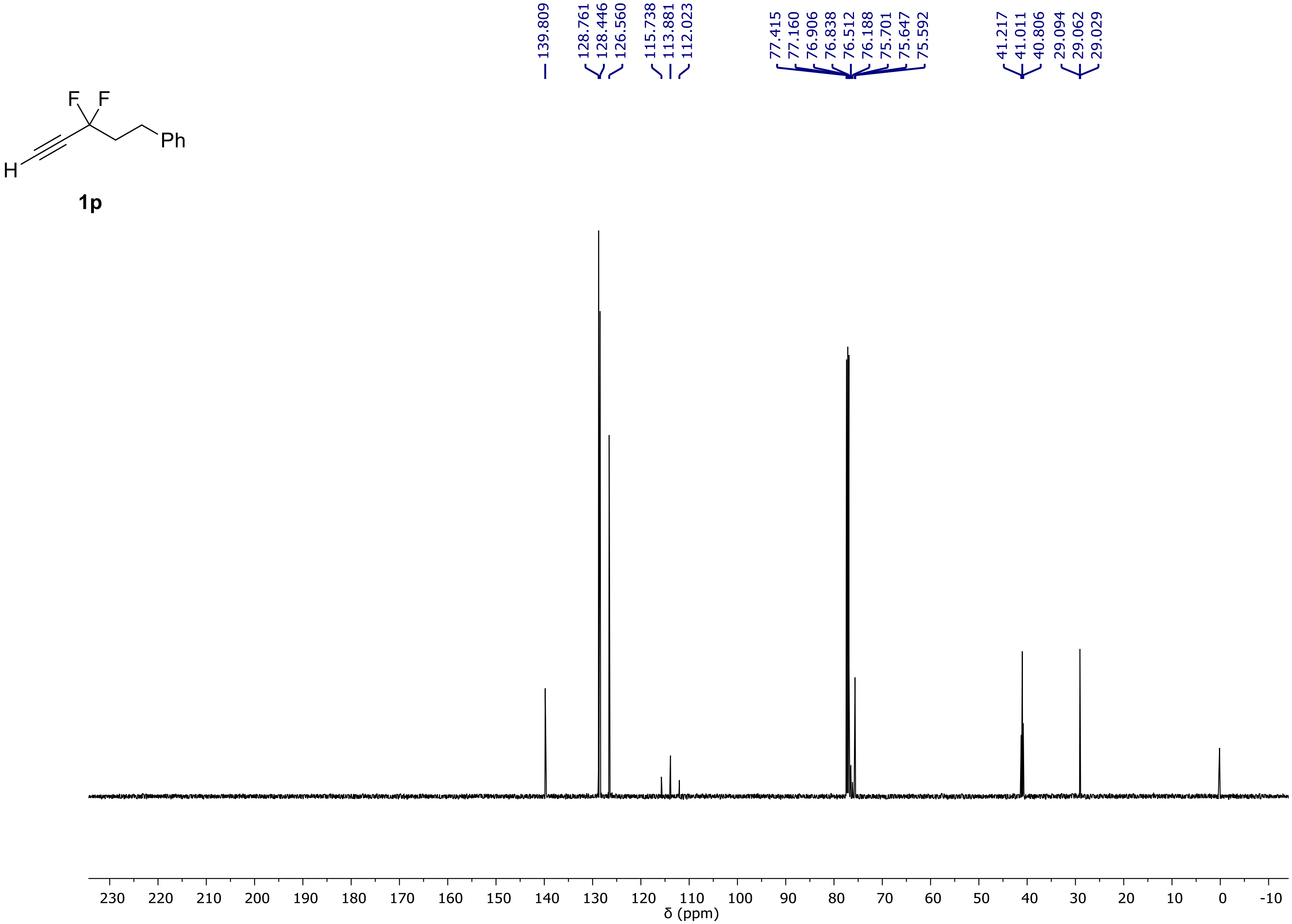

F F
Ph
H
7.324
7.309
7.294
7.255
7.240
7.225
7.216
7.202
2.902
2.892
2.886
2.878
2.868
2.816
2.806
2.796
2.410
2.400
2.393
2.392
2.386
2.381
2.376
2.371
2.364
2.362
2.357
2.351
2.346
2.342
2.335
2.333
2.327
2.317
0.000
1.927
2.859
2.000
0.874
2.030
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

1p


F
F
H
Ph

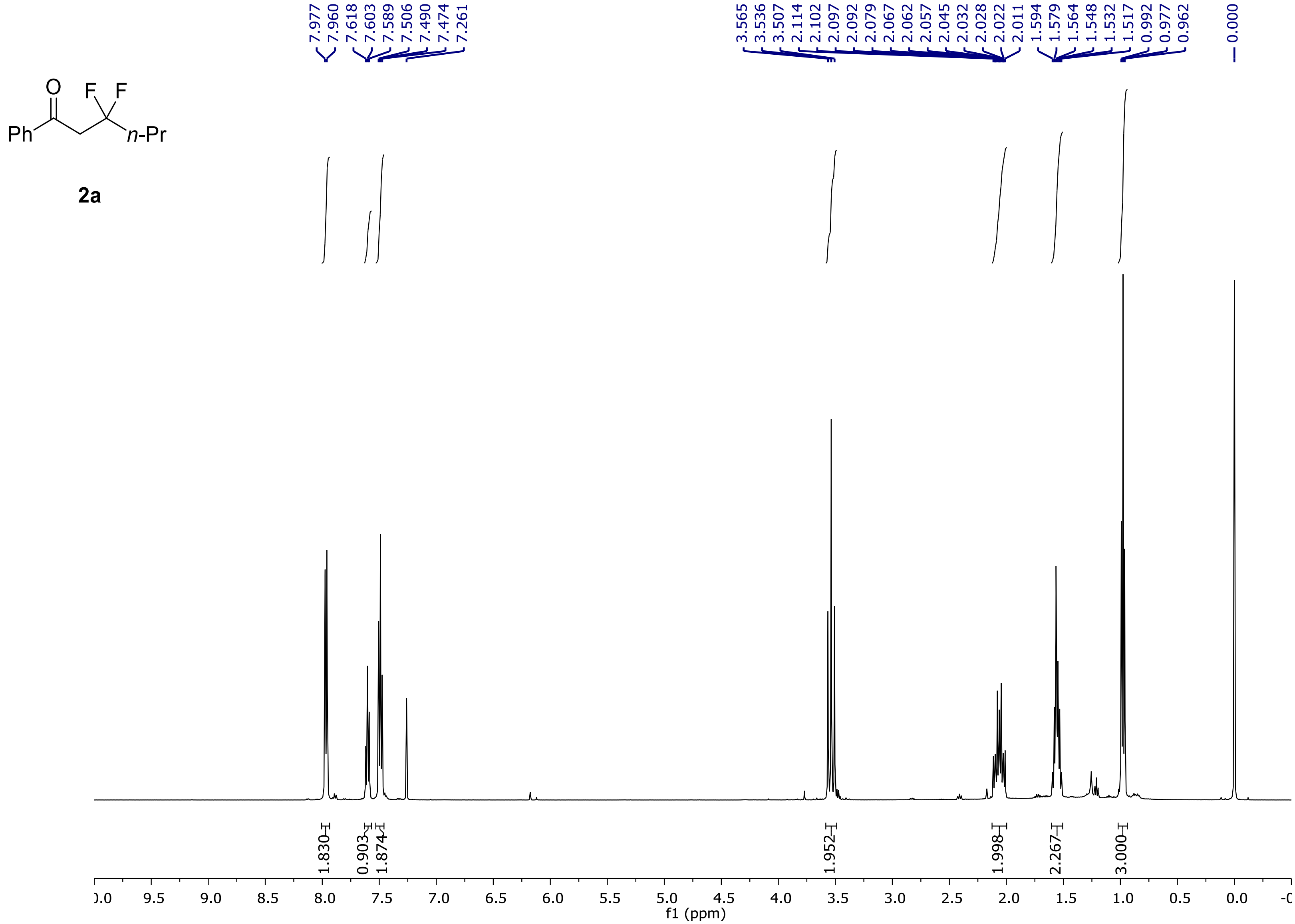
1p


-84.678
-84.689
-84.708
-84.719
-84.739
-84.750
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
δ (ppm)

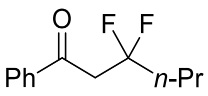

F
F
Ph
H

1p

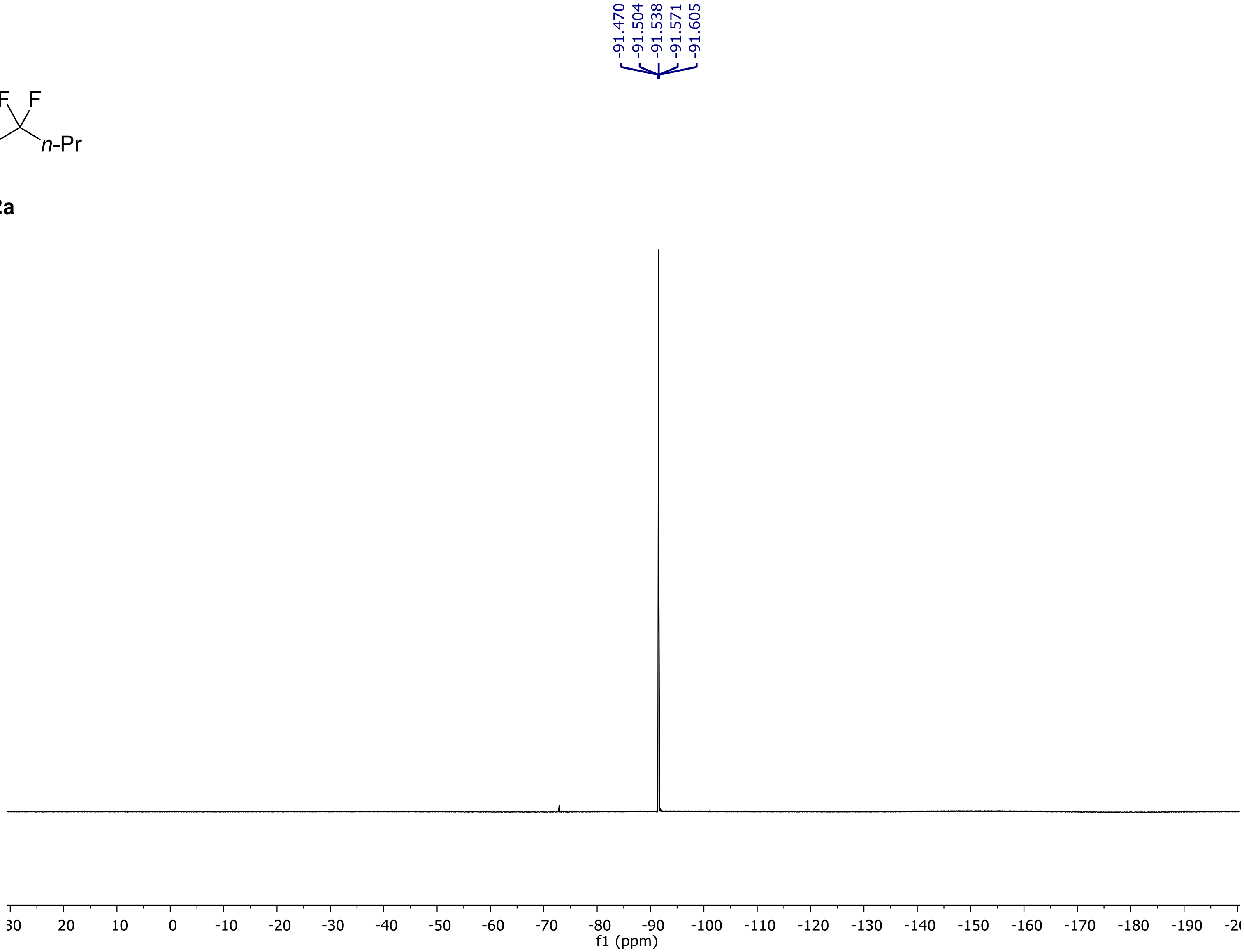
139.809
128.761
128.446
126.560
115.738
113.881
112.023
77.415
77.160
76.906
76.838
76.512
76.188
75.701
75.647
75.592
41.217
41.011
40.806
29.094
29.062
29.029
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

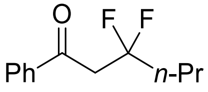

O
F
F
Ph
n-Pr
7.977
7.960
7.618
7.603
7.589
7.506
7.490
7.474
7.261
3.565
3.536
3.507
2.114
2.102
2.097
2.092
2.079
2.067
2.062
2.057
2.045
2.032
2.028
2.022
2.011
1.594
1.579
1.564
1.548
1.532
1.517
0.992
0.977
0.962
0.000
1.830
0.903
1.874
1.952
1.998
2.267
3.000
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2a

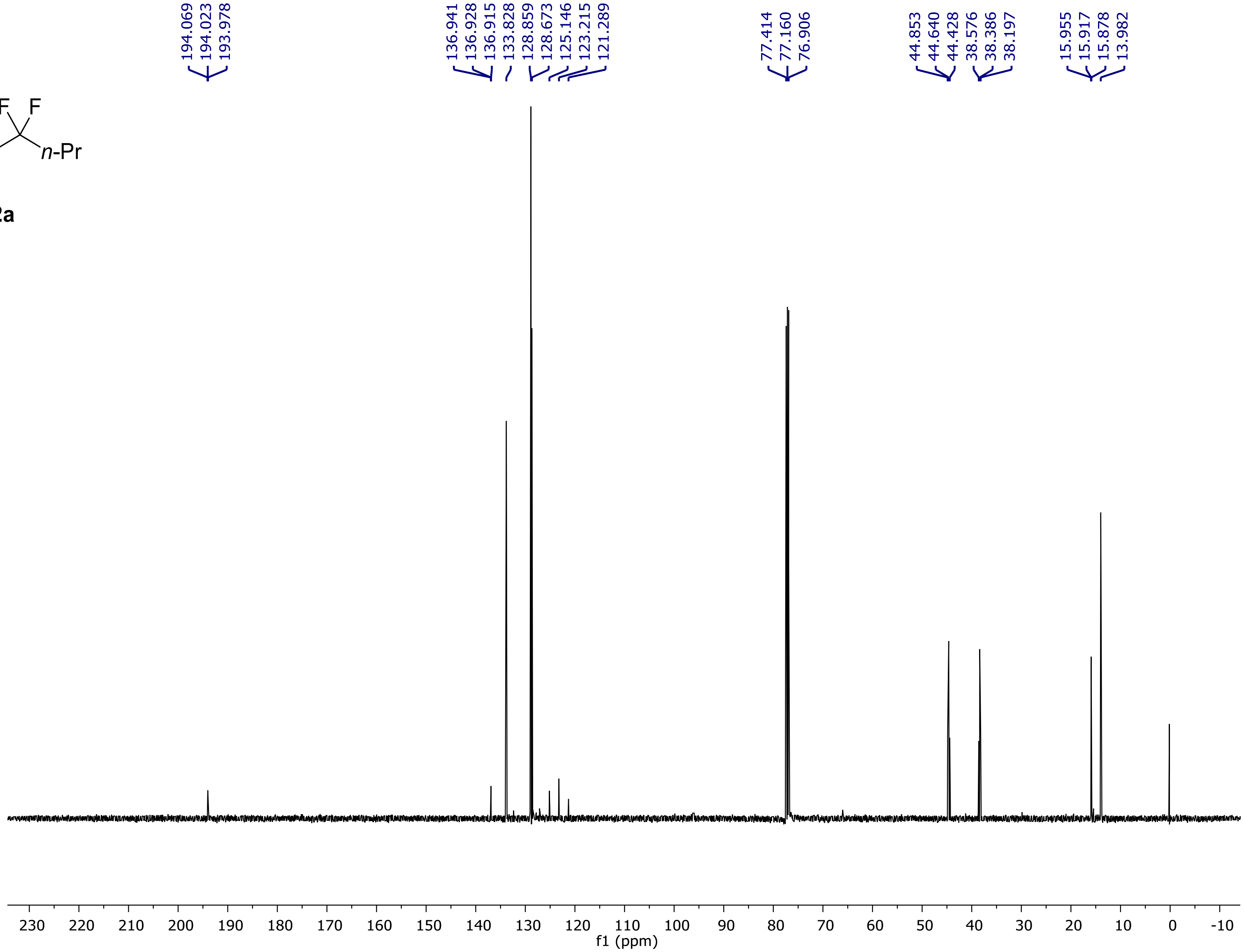


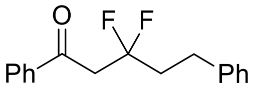
2a


-91.470
-91.504
-91.538
-91.571
-91.605
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

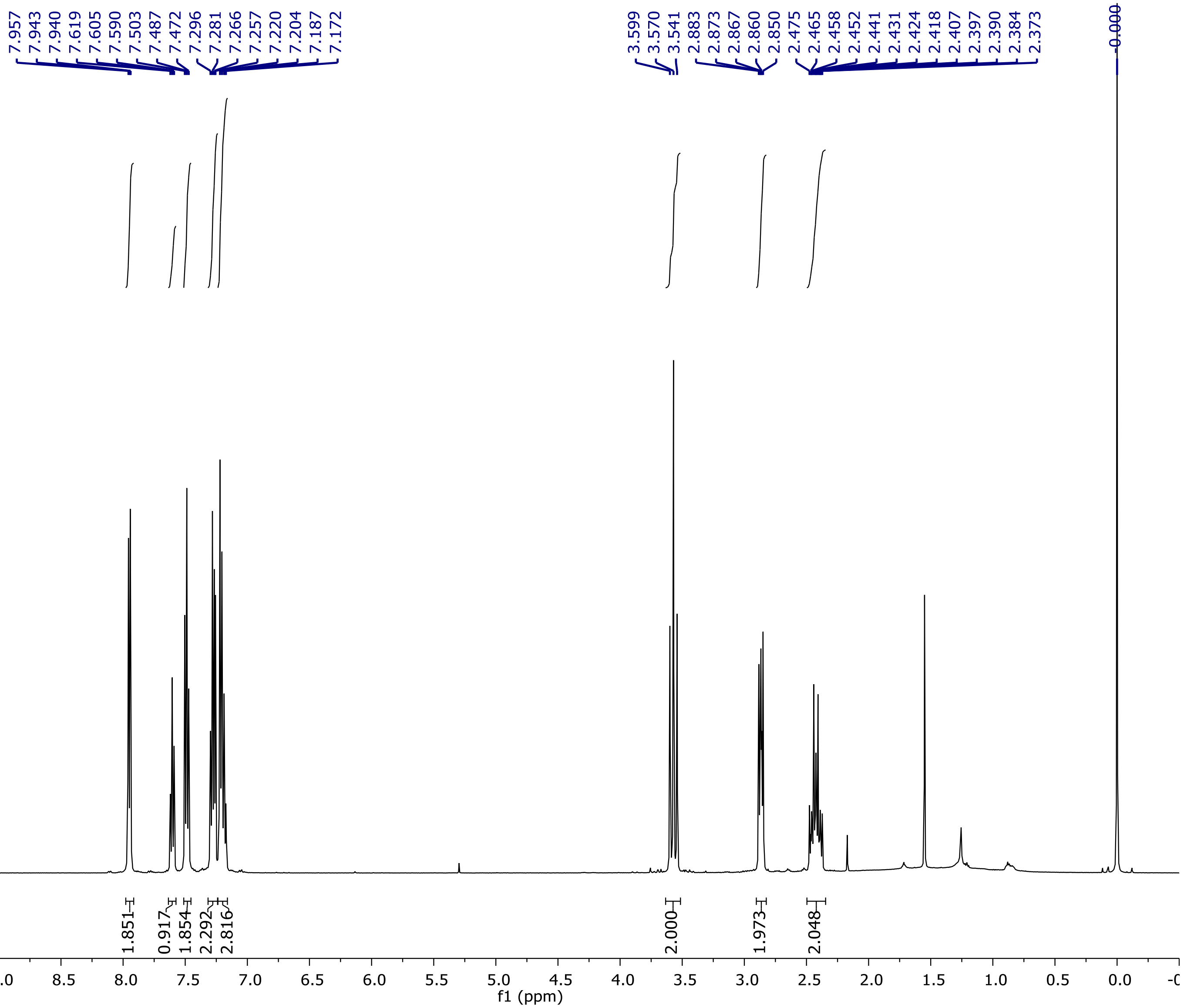

O
F
F
Ph
n-Pr

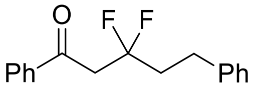
2a


194.069
194.023
193.978
136.941
136.928
136.915
133.828
128.859
128.673
125.146
123.215
121.289
77.414
77.160
76.906
44.853
44.640
44.428
38.576
38.386
38.197
15.955
15.917
15.878
13.982
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

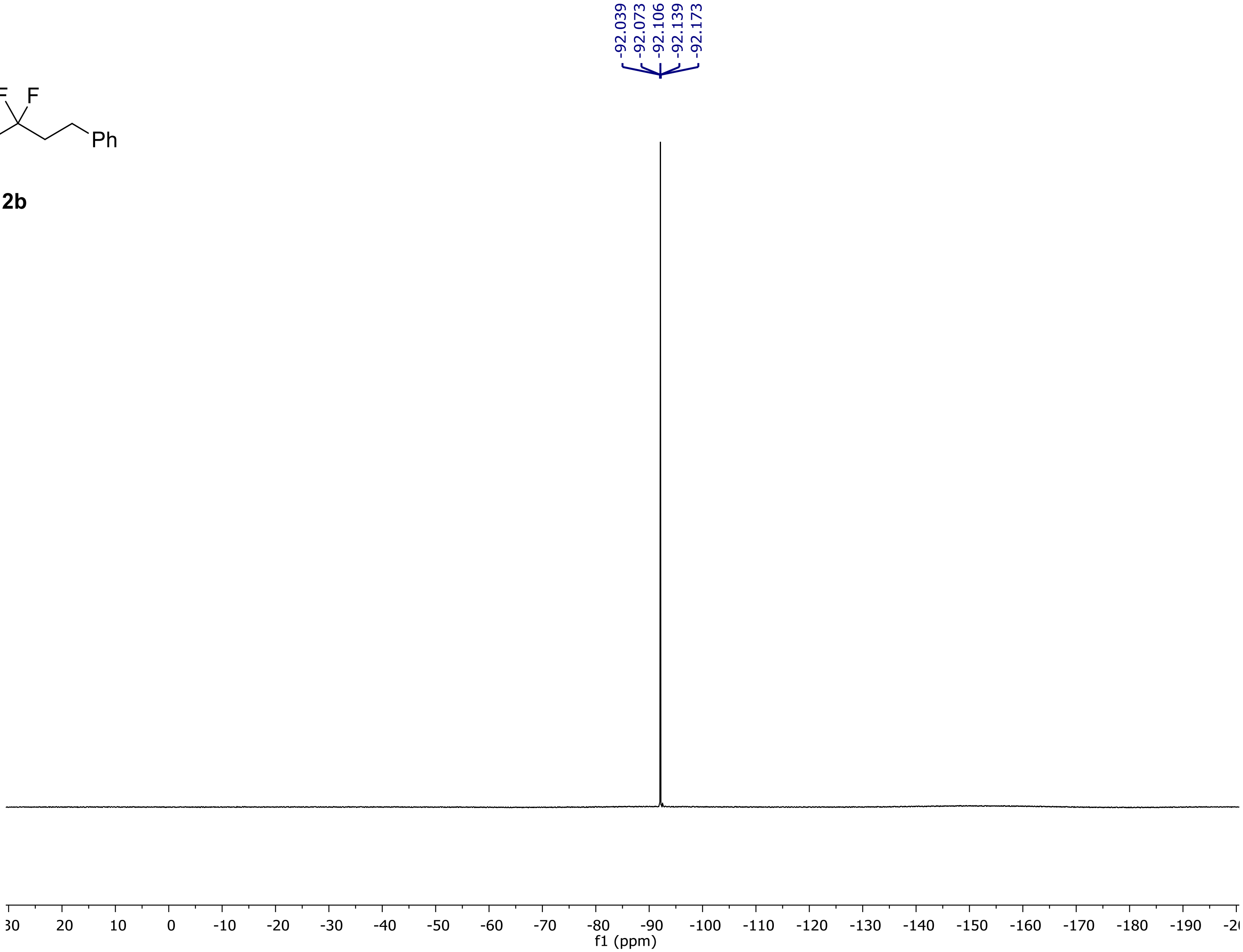

O
F
F
Ph
Ph

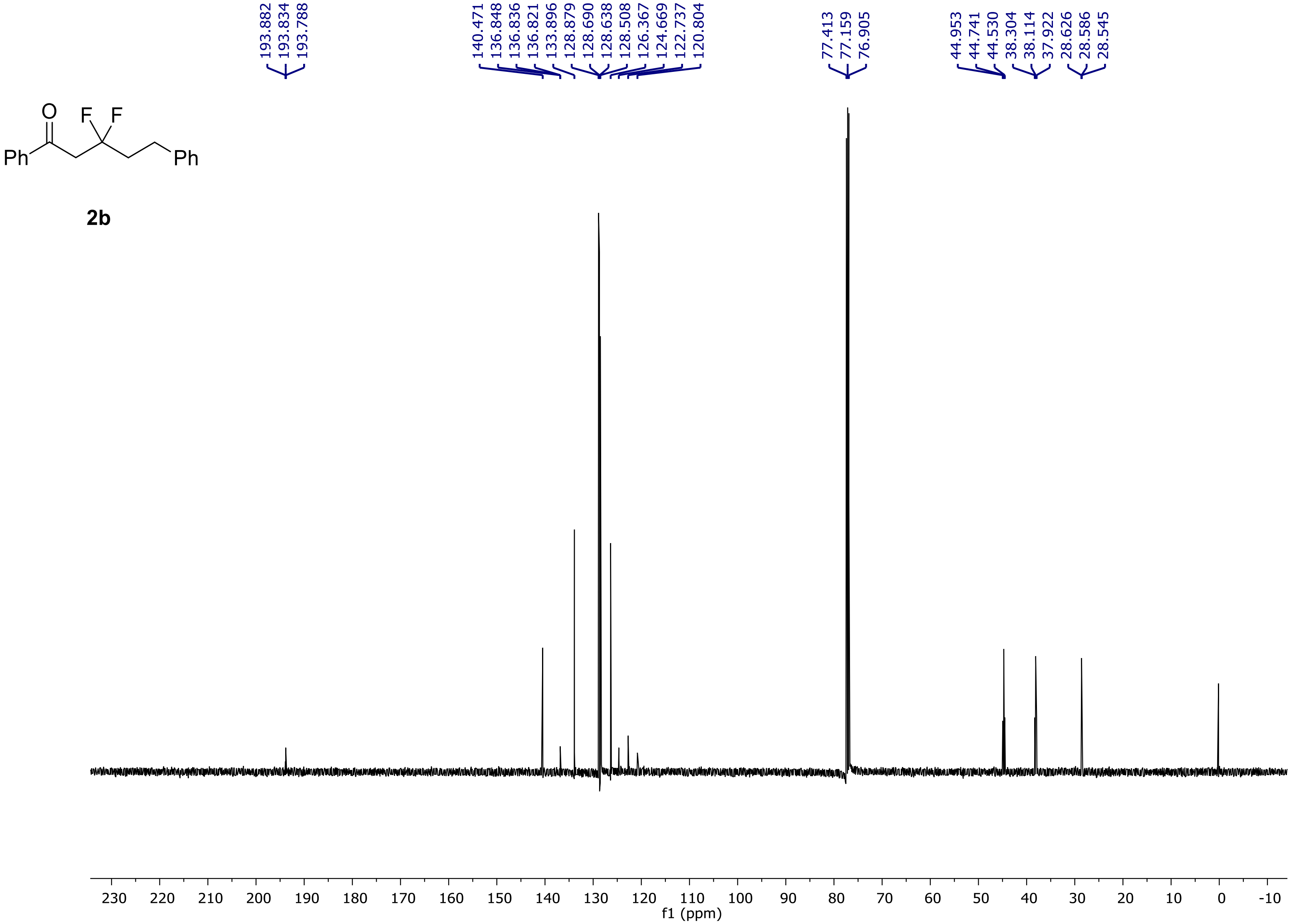
2b


7.957
7.943
7.940
7.619
7.605
7.590
7.503
7.487
7.472
7.296
7.281
7.266
7.257
7.220
7.204
7.187
7.172
3.599
3.570
3.541
2.883
2.873
2.867
2.860
2.850
2.475
2.465
2.458
2.452
2.441
2.431
2.424
2.418
2.407
2.397
2.390
2.384
2.373
0.000
1.851
0.917
1.854
2.292
2.816
2.000
1.973
2.048
9.5
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
f1 (ppm)


O
F
F
Ph
Ph

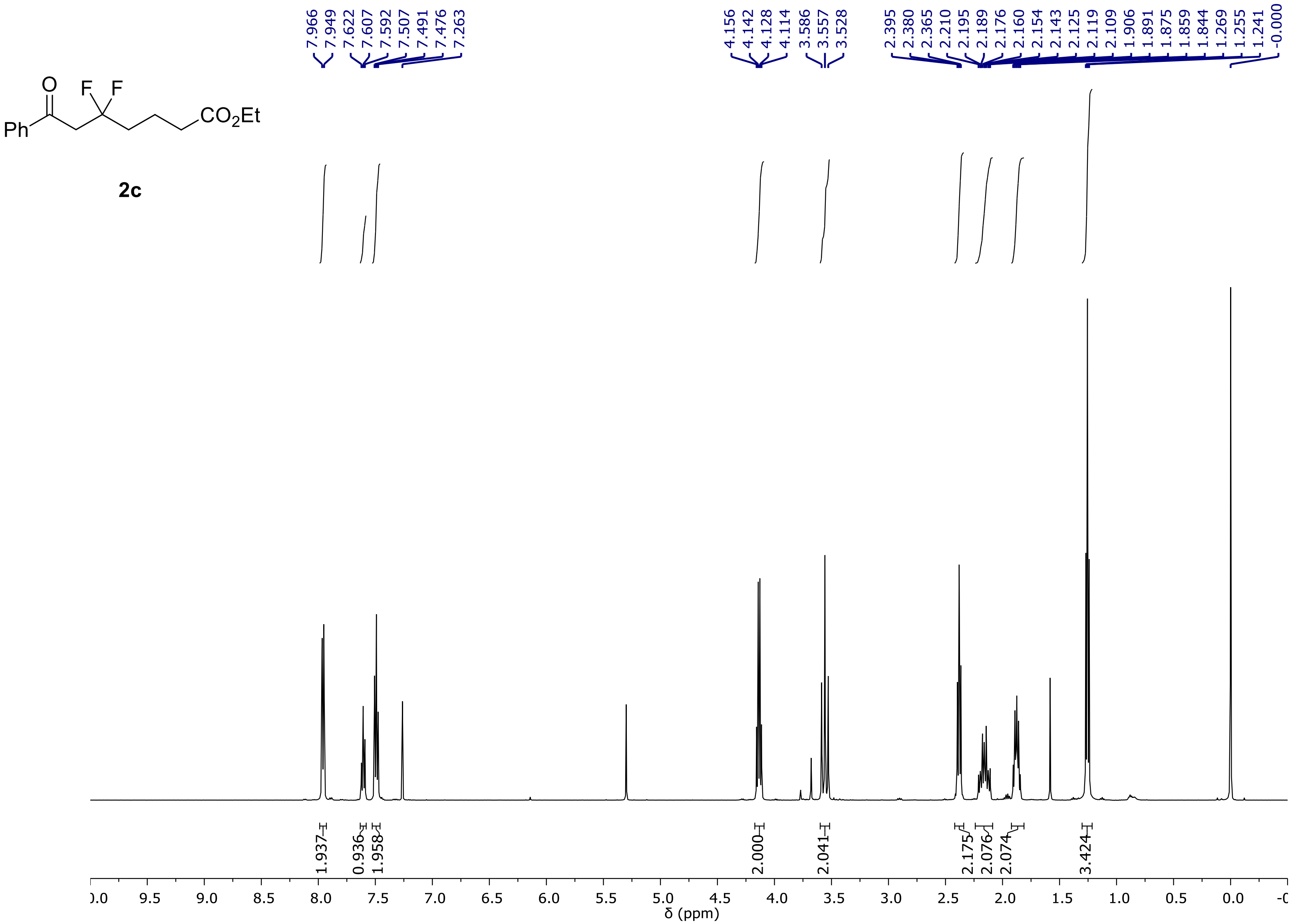
2b


-92.039
-92.073
-92.106
-92.139
-92.173
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
f1 (ppm)


O
F
F
Ph
Ph

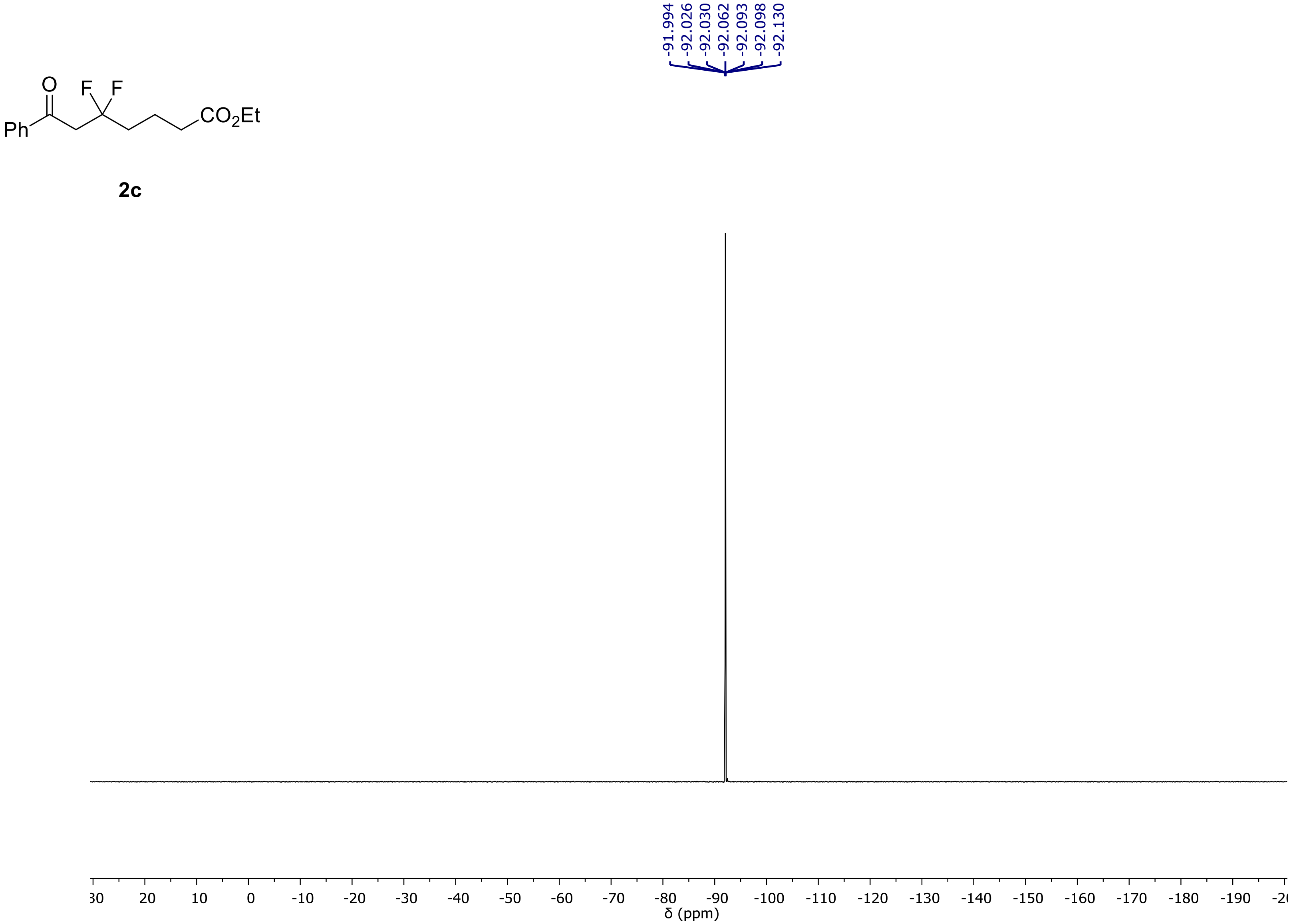
2b

193.882
193.834
193.788
140.471
136.848
136.836
136.821
133.896
128.879
128.690
128.638
128.508
126.367
124.669
122.737
120.804
77.413
77.159
76.905
44.953
44.741
44.530
38.304
38.114
37.922
28.626
28.586
28.545
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
F F
Ph
CO2Et

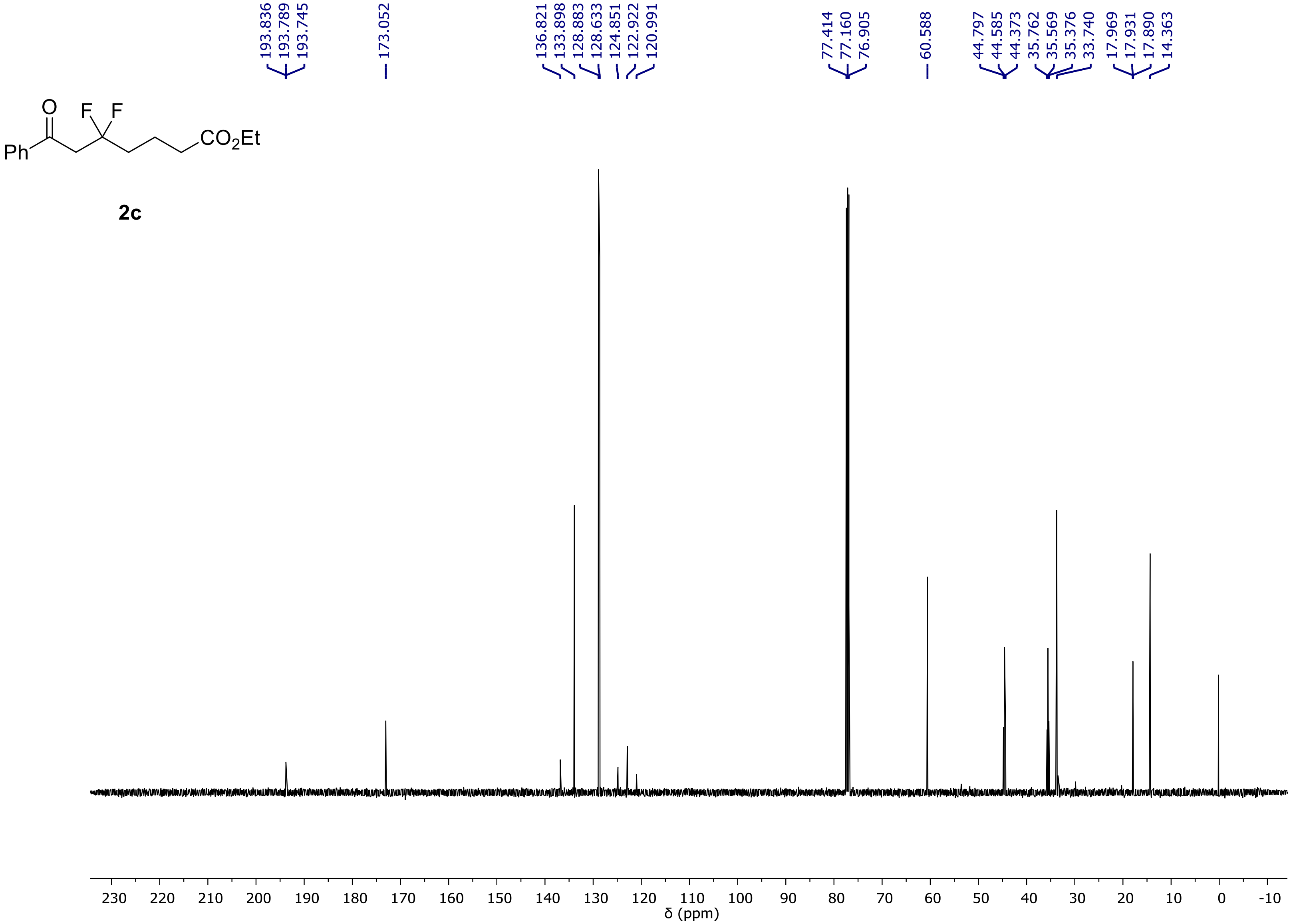
2c

7.966
7.949
7.622
7.607
7.592
7.507
7.491
7.476
7.263
4.156
4.142
4.128
4.114
3.586
3.557
3.528
2.395
2.380
2.365
2.210
2.195
2.189
2.176
2.160
2.154
2.143
2.125
2.119
2.109
1.906
1.891
1.875
1.859
1.844
1.269
1.255
1.241
-0.000
1.937
0.936
1.958
2.000
2.041
2.175
2.076
2.074
3.424
).0
9.5
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
-(
δ (ppm)



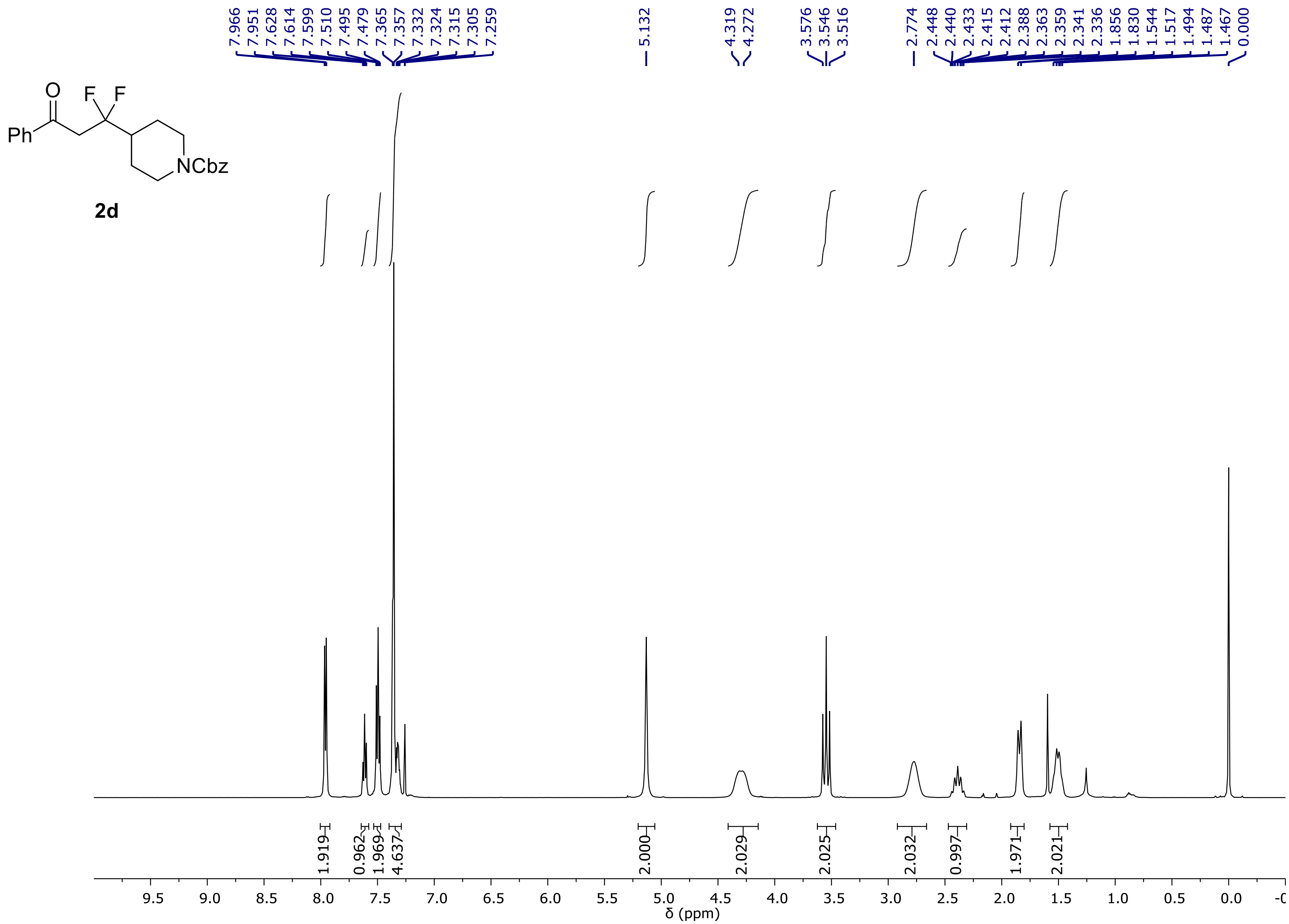
2c

-91.994
-92.026
-92.030
-92.062
-92.093
-92.098
-92.130
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
δ (ppm)

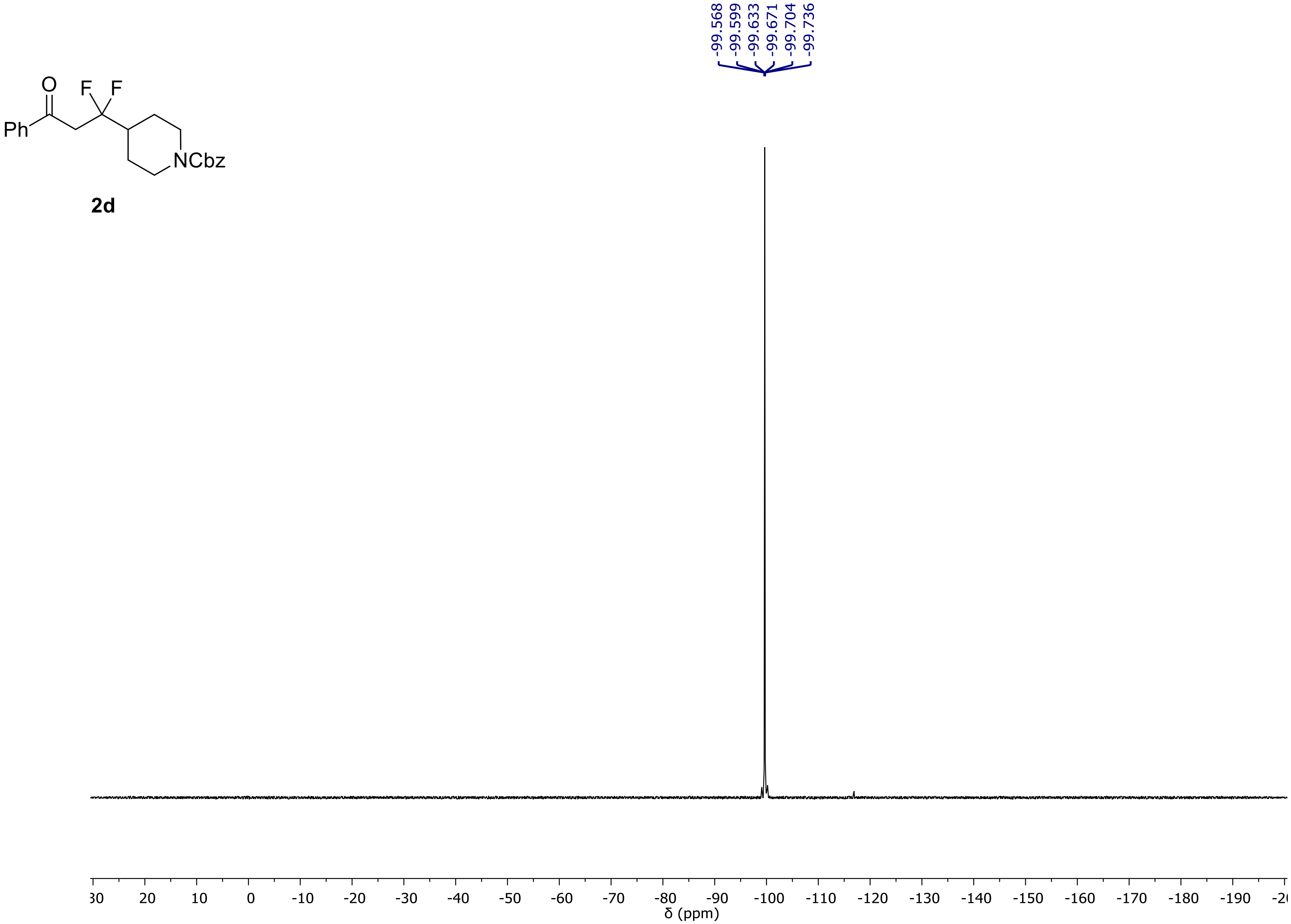

O
F
F
Ph
CO$_2$Et

2c

193.836
193.789
193.745
173.052
136.821
133.898
128.883
128.633
124.851
122.922
120.991
77.414
77.160
76.905
60.588
44.797
44.585
44.373
35.762
35.569
35.376
33.740
17.969
17.931
17.890
14.363
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

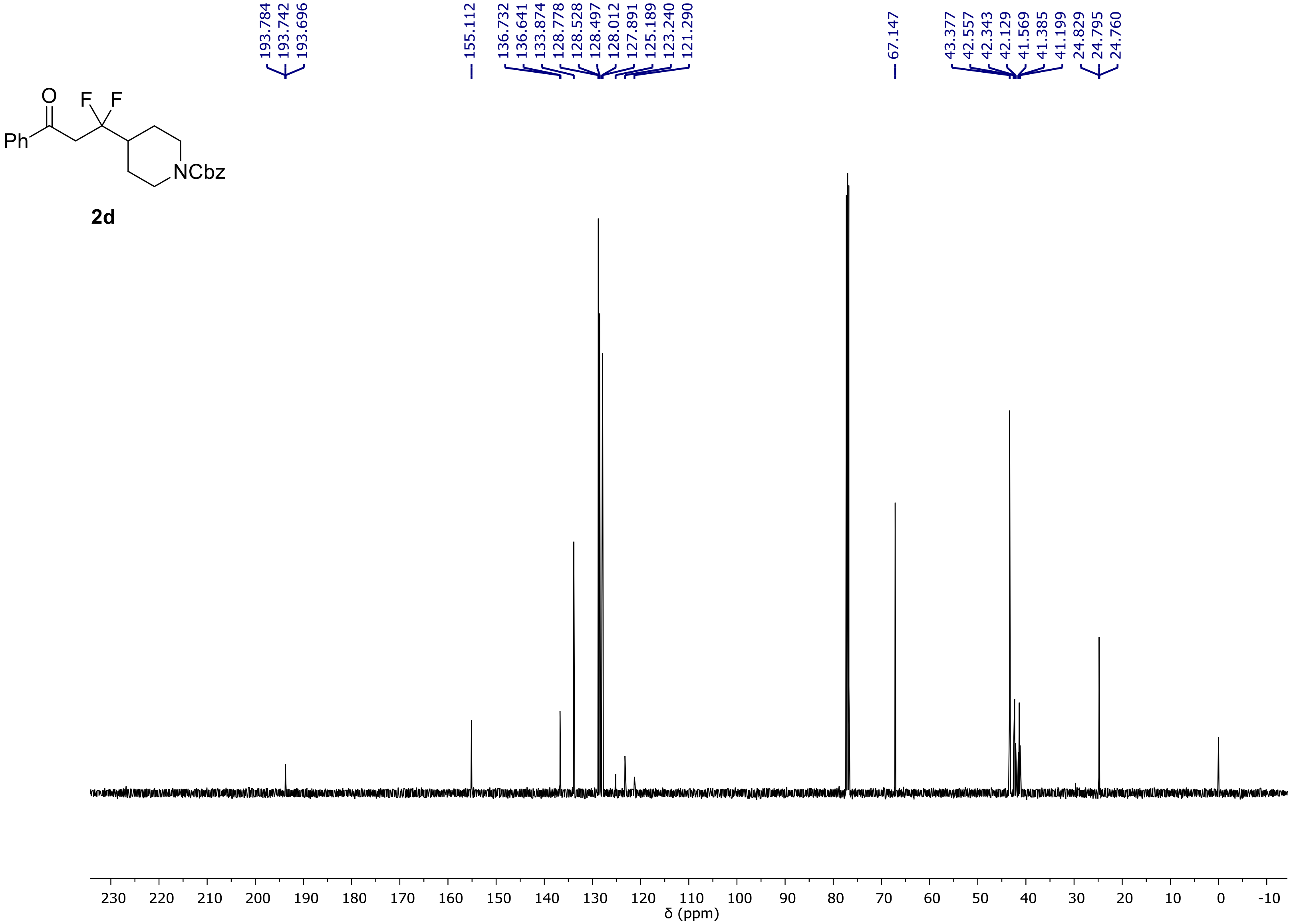

Ph
O
F
F
NCbz
7.966
7.951
7.628
7.614
7.599
7.510
7.495
7.479
7.365
7.357
7.332
7.324
7.315
7.305
7.259
5.132
4.319
4.272
3.576
3.546
3.516
2.774
2.448
2.440
2.433
2.415
2.412
2.388
2.363
2.359
2.341
2.336
1.856
1.830
1.544
1.517
1.494
1.487
1.467
0.000
1.919
0.962
1.969
4.637
2.000
2.029
2.025
2.032
0.997
1.971
2.021
9.5
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
δ (ppm)

2d


O
F
F
Ph
NCbz

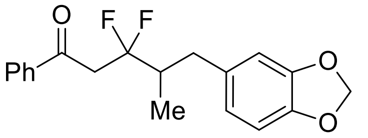
2d

-99.568
-99.599
-99.633
-99.671
-99.704
-99.736
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
δ (ppm)

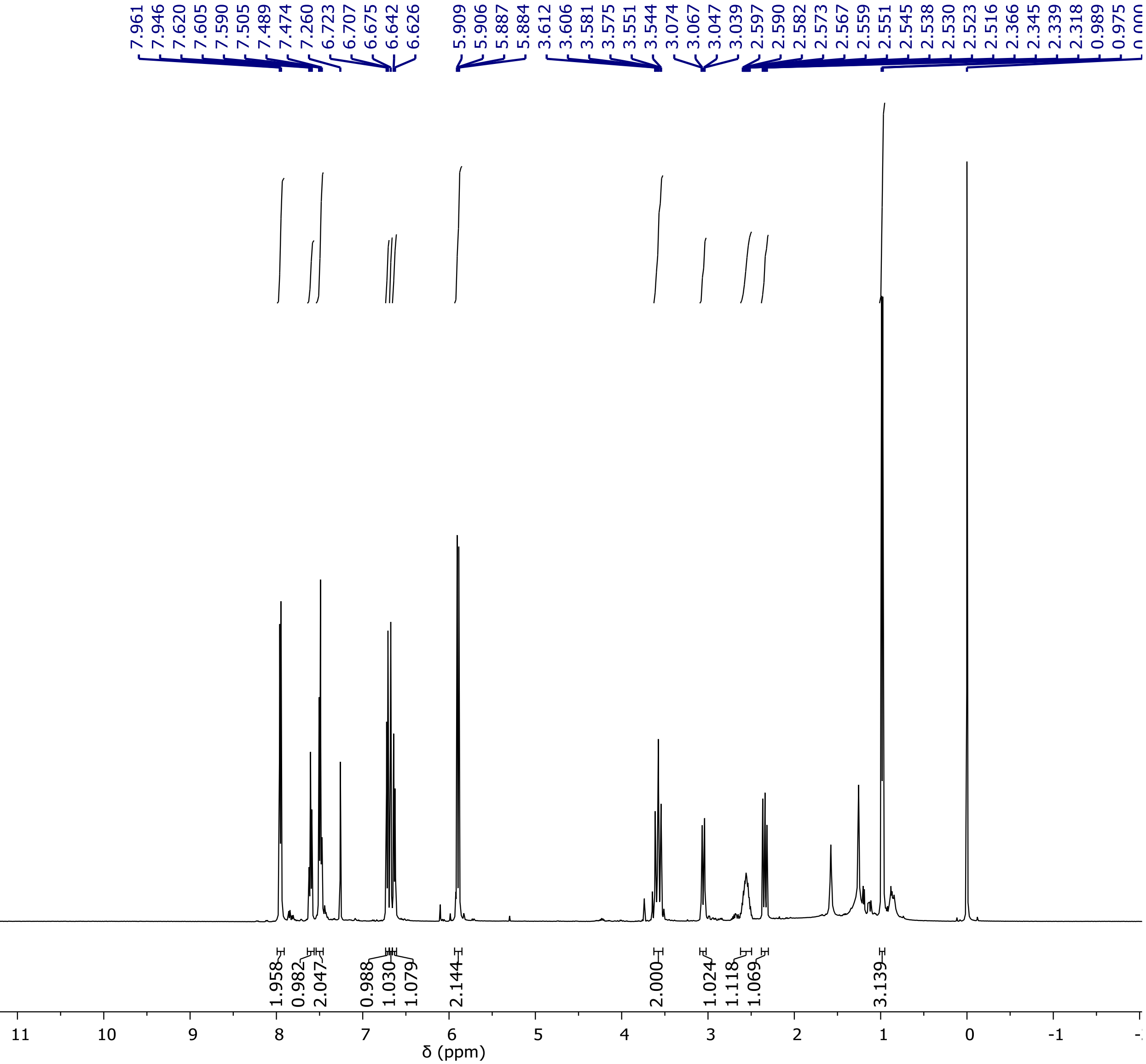

O
F
F
Ph
NCbz

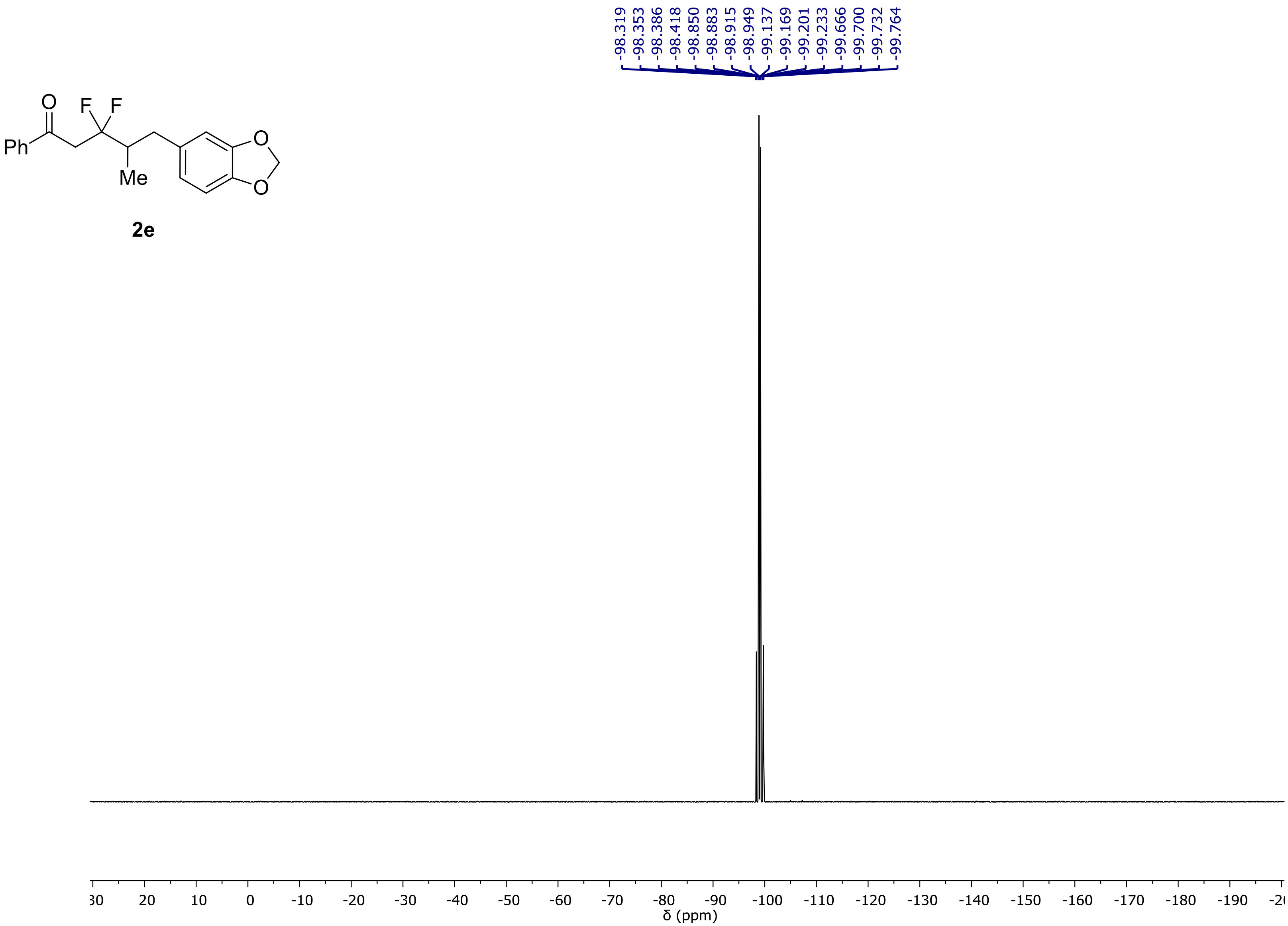
2d

193.784
193.742
193.696
155.112
136.732
136.641
133.874
128.778
128.528
128.497
128.012
127.891
125.189
123.240
121.290
67.147
43.377
42.557
42.343
42.129
41.569
41.385
41.199
24.829
24.795
24.760
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)


O
F
F
Ph
Me
O
O

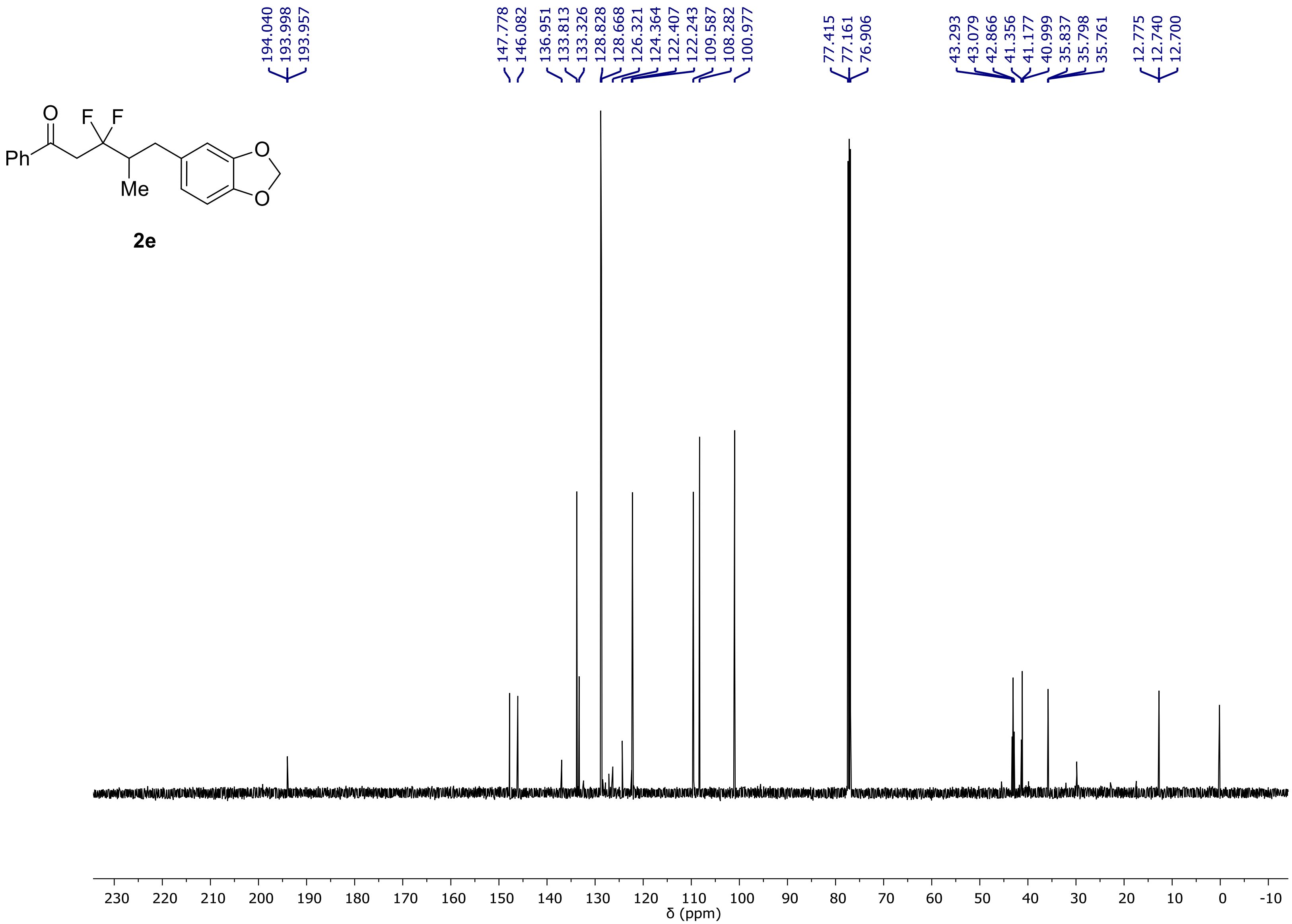
2e

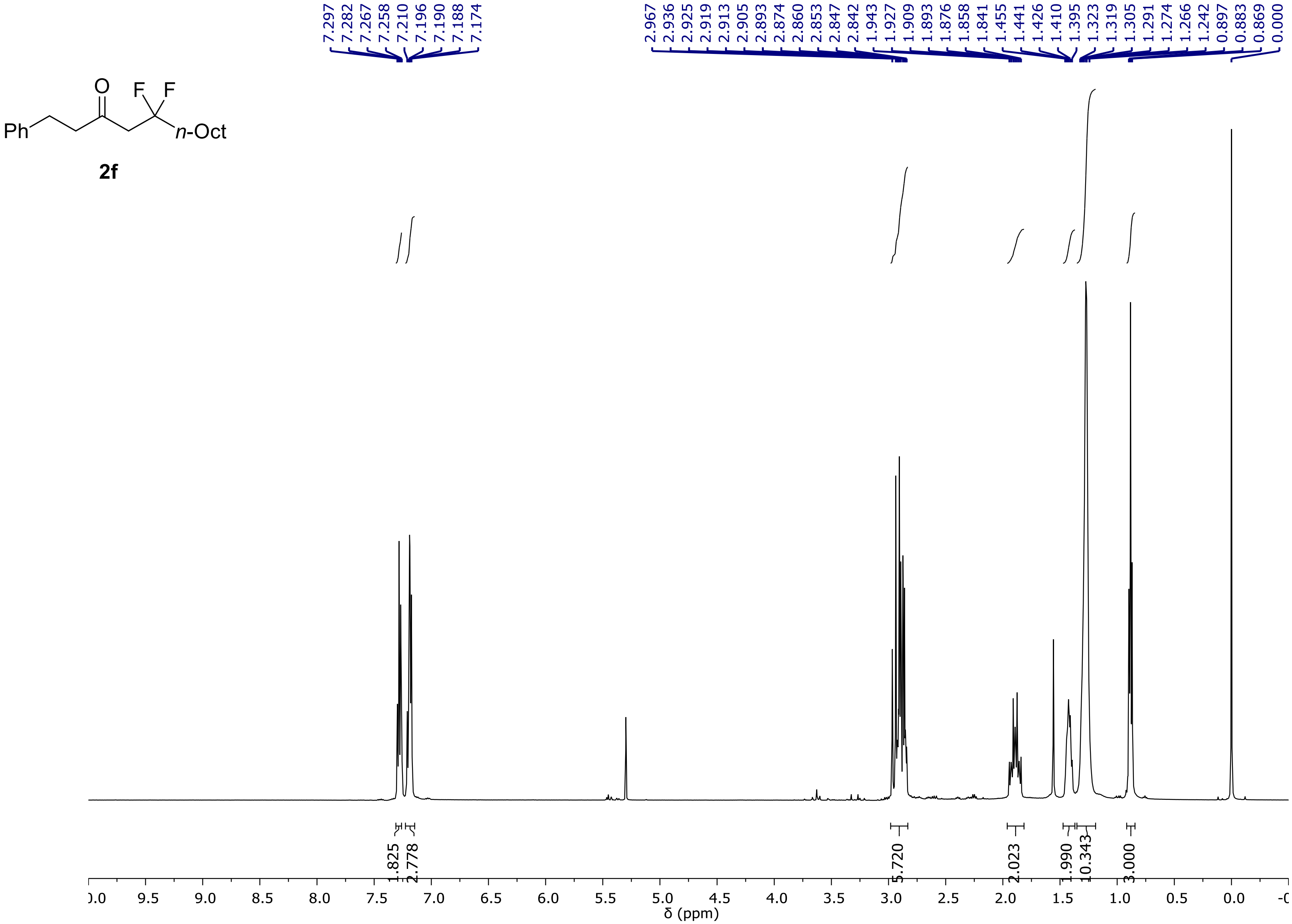

7.961
7.946
7.620
7.605
7.590
7.505
7.489
7.474
7.260
6.723
6.707
6.675
6.642
6.626
5.909
5.906
5.887
5.884
3.612
3.606
3.581
3.575
3.551
3.544
3.074
3.067
3.047
3.039
2.597
2.590
2.582
2.573
2.567
2.559
2.551
2.545
2.538
2.530
2.523
2.516
2.366
2.345
2.339
2.318
0.989
0.975
0.000
1.958
0.982
2.047
0.988
1.030
1.079
2.144
2.000
1.024
1.118
1.069
3.139
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


O
F
F
Ph
Me
O
O

2e

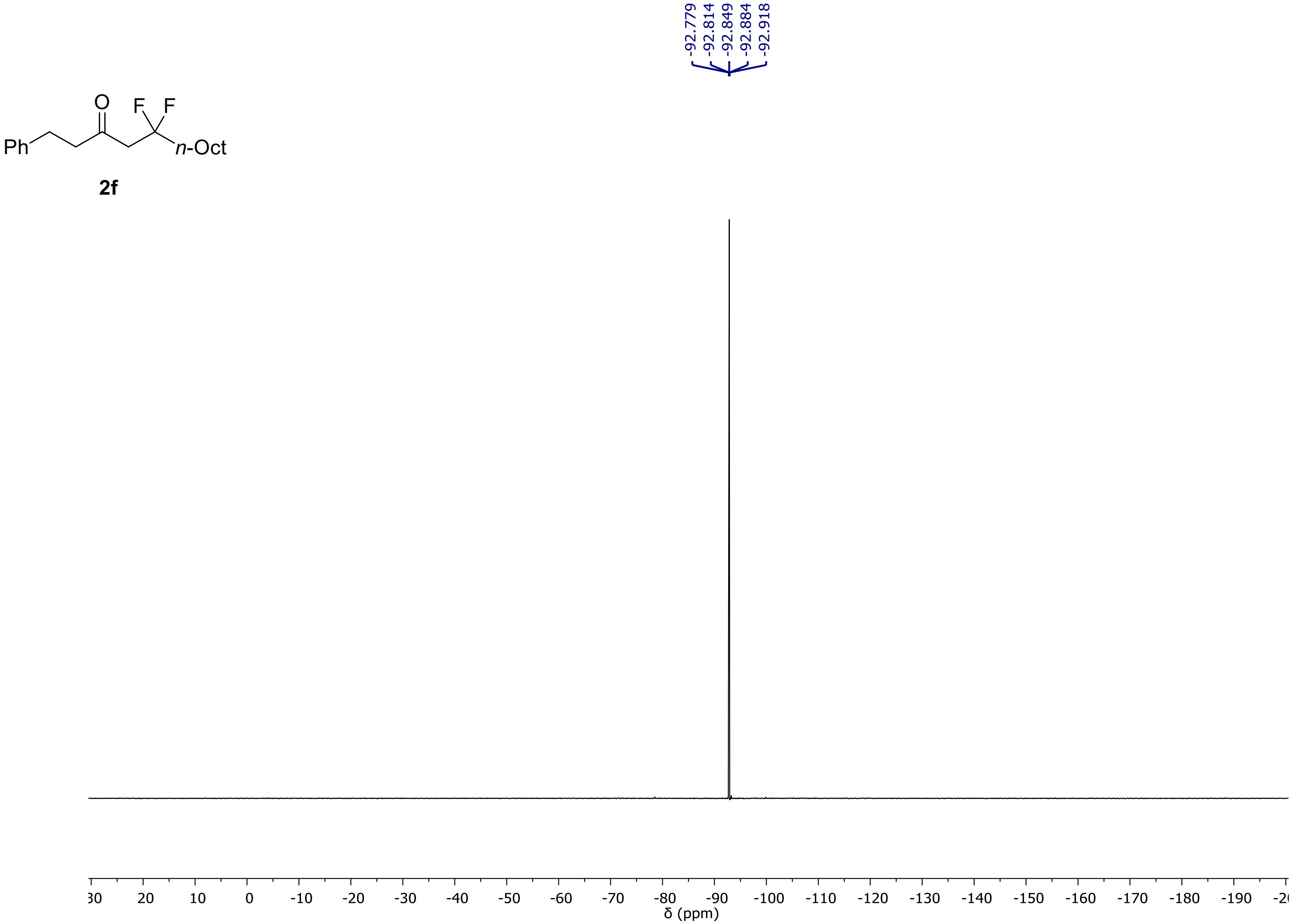
-98.319
-98.353
-98.386
-98.418
-98.850
-98.883
-98.915
-98.949
-99.137
-99.169
-99.201
-99.233
-99.666
-99.700
-99.732
-99.764
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
δ (ppm)


2e
O
F
F
Ph
Me
O
O
194.040
193.998
193.957
147.778
146.082
136.951
133.813
133.326
128.828
128.668
126.321
124.364
122.407
122.243
109.587
108.282
100.977
77.415
77.161
76.906
43.293
43.079
42.866
41.356
41.177
40.999
35.837
35.798
35.761
12.775
12.740
12.700
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)


O
F
F
Ph
n-Oct

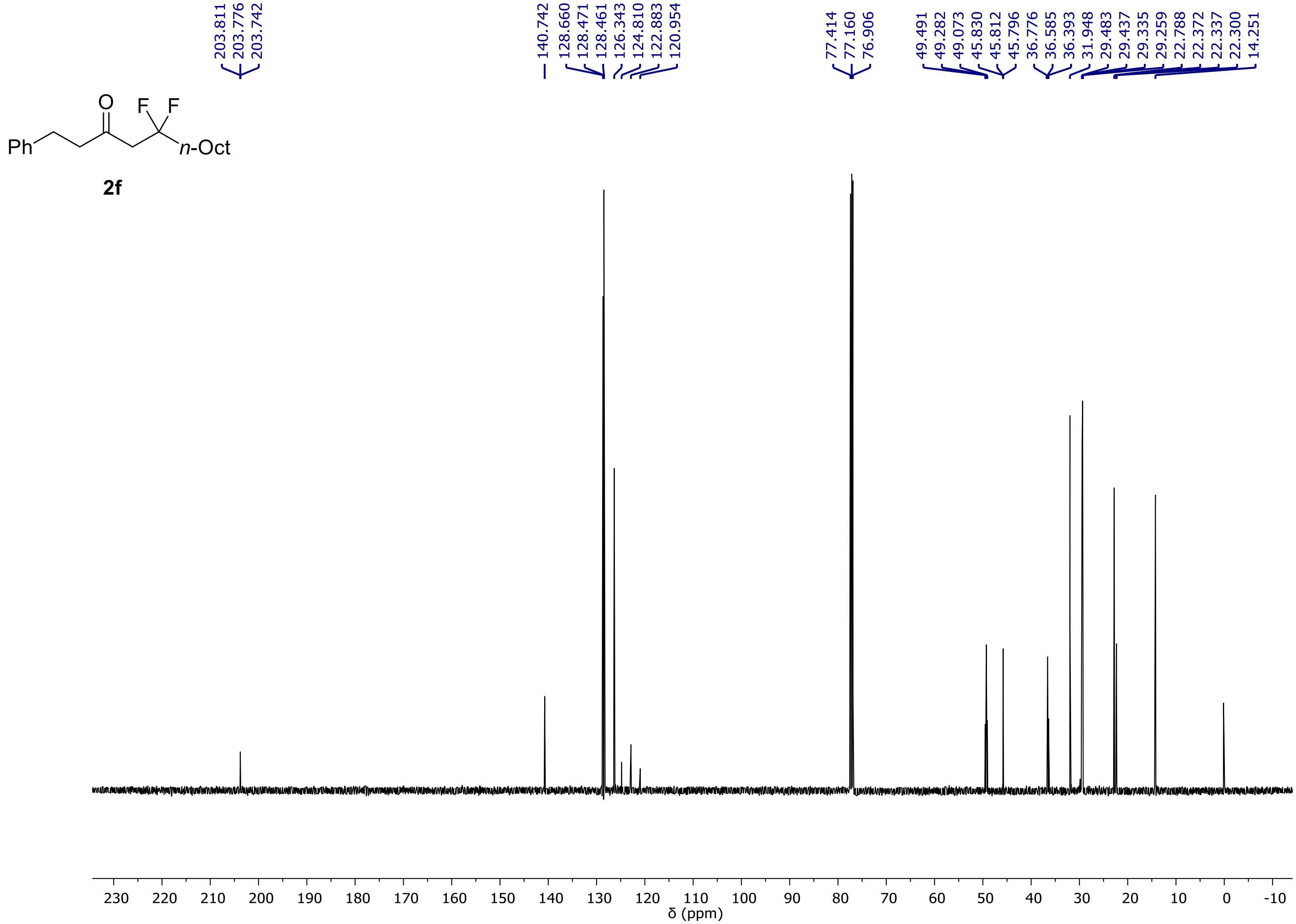
2f

7.297
7.282
7.267
7.258
7.210
7.196
7.190
7.188
7.174
2.967
2.936
2.925
2.919
2.913
2.905
2.893
2.874
2.860
2.853
2.847
2.842
1.943
1.927
1.909
1.893
1.876
1.858
1.841
1.455
1.441
1.426
1.410
1.395
1.323
1.319
1.305
1.291
1.274
1.266
1.242
0.897
0.883
0.869
0.000
1.825
2.778
5.720
2.023
1.990
10.343
3.000
0.0
9.5
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
-0
δ (ppm)

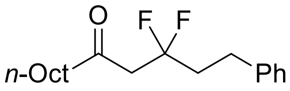


2f

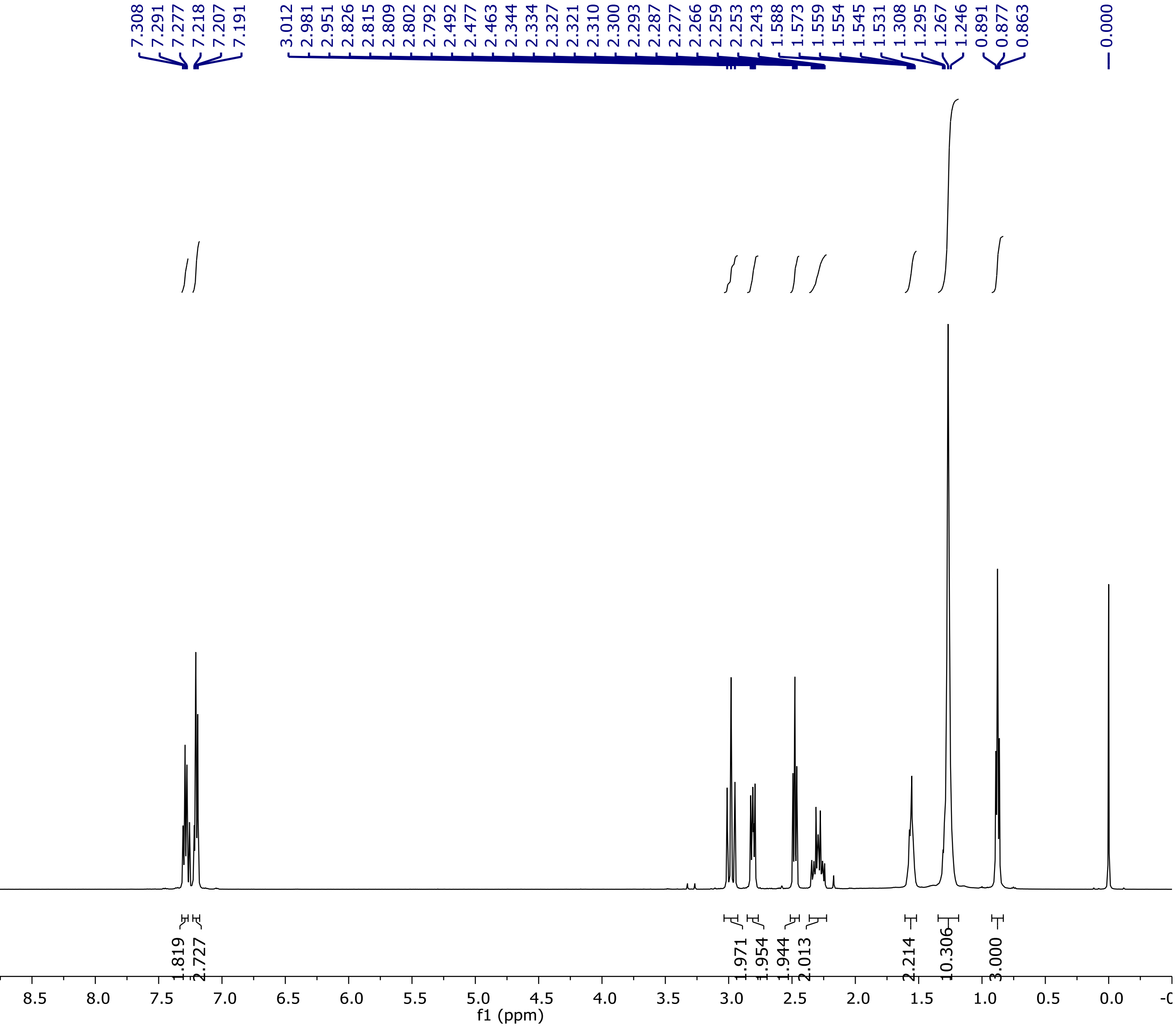
-92.779
-92.814
-92.849
-92.884
-92.918
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
δ (ppm)

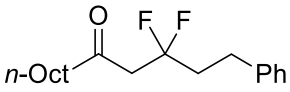

2f

Ph
O
F
F
n-Oct
203.811
203.776
203.742
140.742
128.660
128.471
128.461
126.343
124.810
122.883
120.954
77.414
77.160
76.906
49.491
49.282
49.073
45.830
45.812
45.796
36.776
36.585
36.393
31.948
29.483
29.437
29.335
29.259
22.788
22.372
22.337
22.300
14.251
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

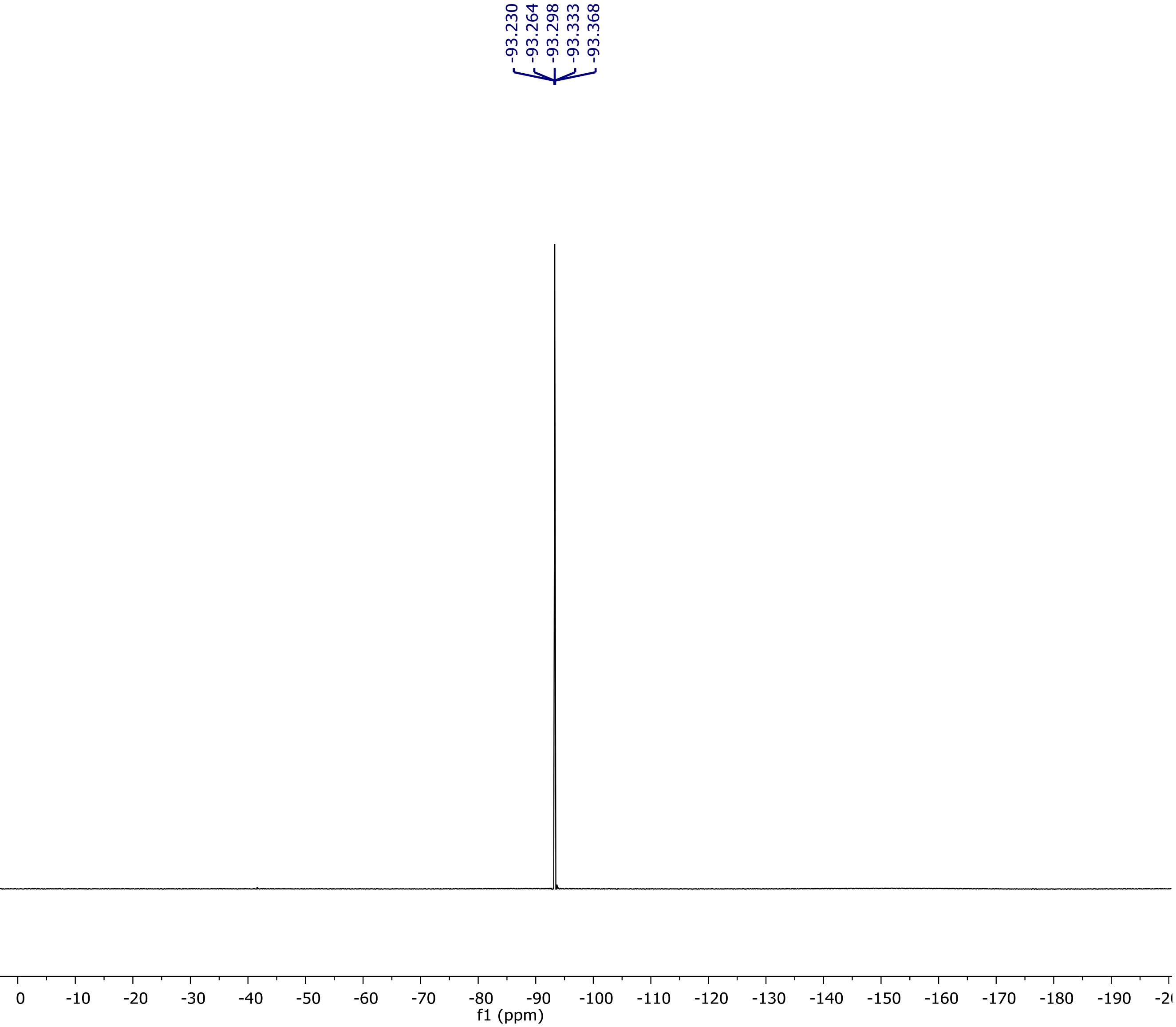

O
F
F
n-Oct
Ph

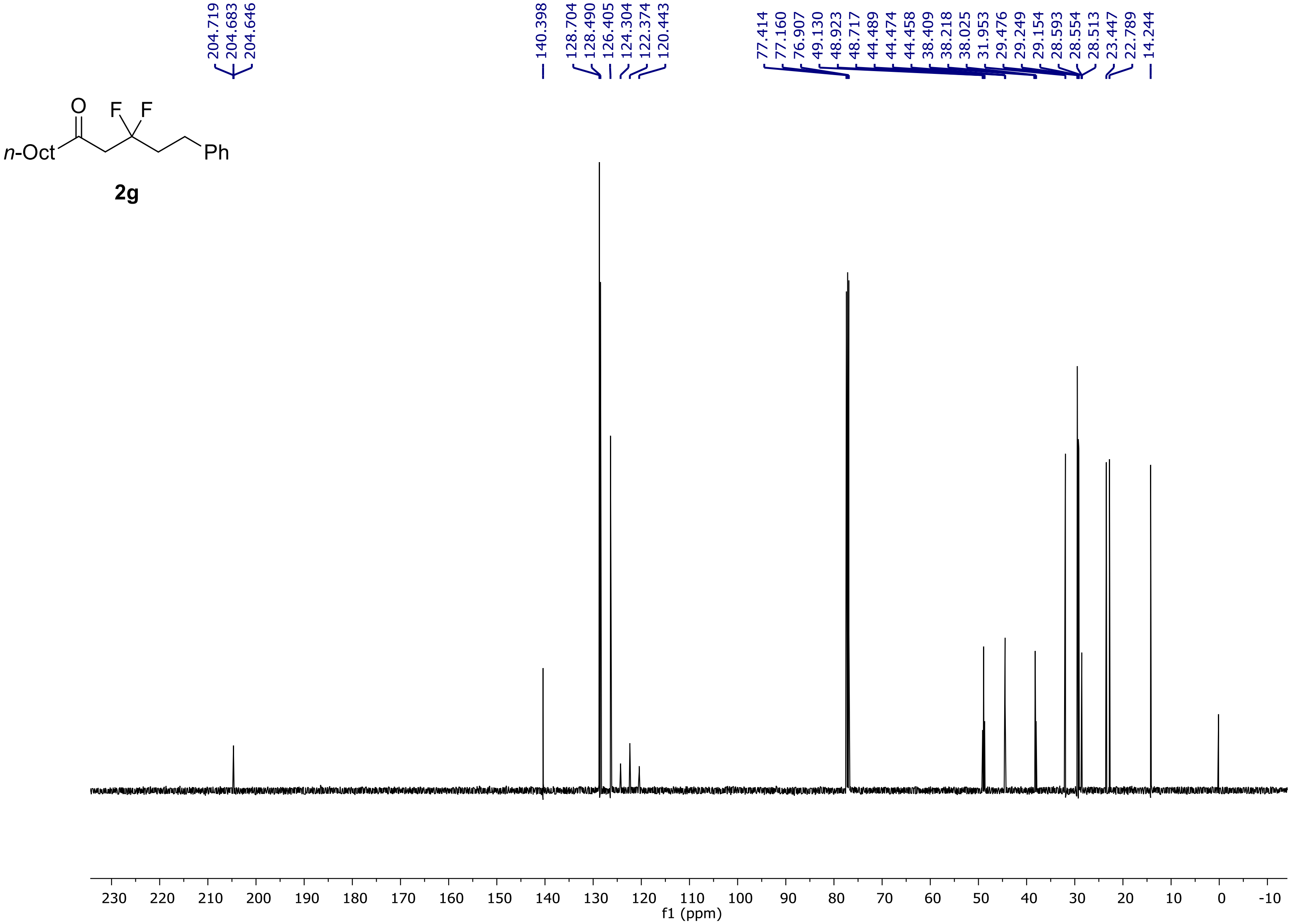
2g


7.308
7.291
7.277
7.218
7.207
7.191
3.012
2.981
2.951
2.826
2.815
2.809
2.802
2.792
2.492
2.477
2.463
2.344
2.334
2.327
2.321
2.310
2.300
2.293
2.287
2.277
2.266
2.259
2.253
2.243
1.588
1.573
1.559
1.554
1.545
1.531
1.308
1.295
1.267
1.246
0.891
0.877
0.863
0.000
1.819
2.727
1.971
1.954
1.944
2.013
2.214
10.306
3.000
0.0
9.5
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
f1 (ppm)

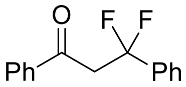

O
F
F
n-Oct
Ph

2g

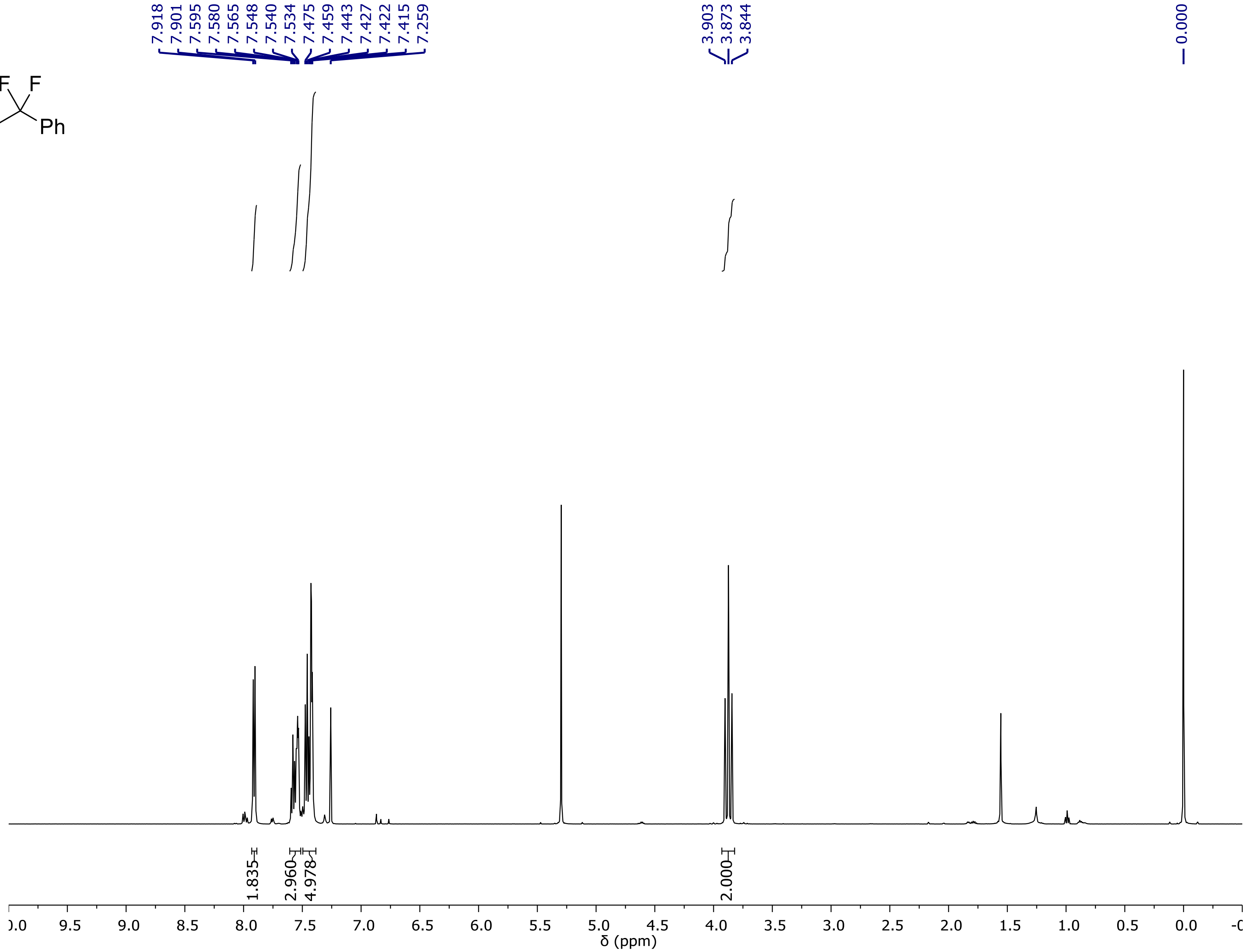

-93.230
-93.264
-93.298
-93.333
-93.368
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
f1 (ppm)

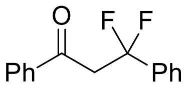

n-Oct
O
F
F
Ph
204.719
204.683
204.646
140.398
128.704
128.490
126.405
124.304
122.374
120.443
77.414
77.160
76.907
49.130
48.923
48.717
44.489
44.474
44.458
38.409
38.218
38.025
31.953
29.476
29.249
29.154
28.593
28.554
28.513
23.447
22.789
14.244
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

2g

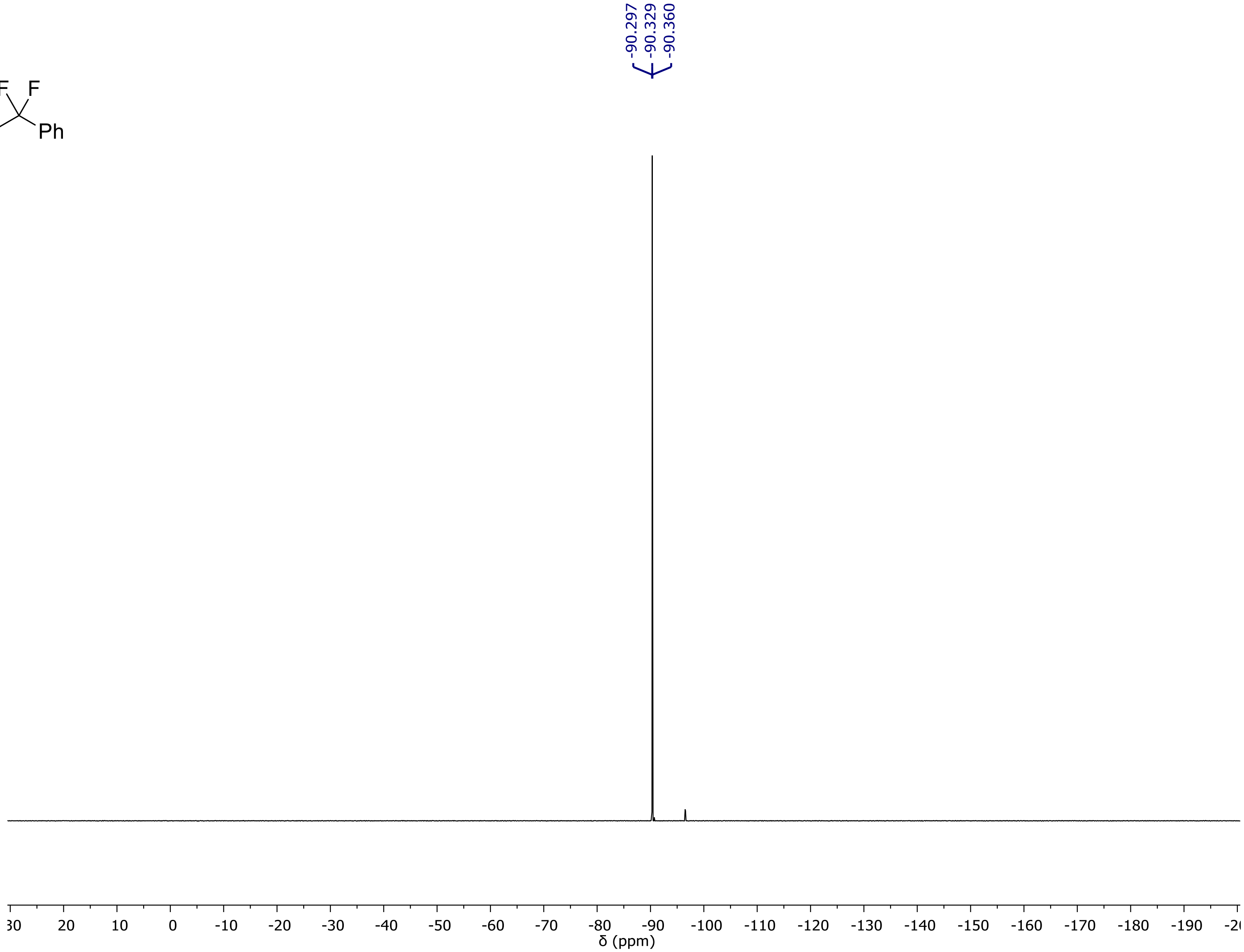


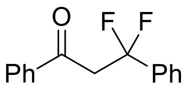
2i


7.918
7.901
7.595
7.580
7.565
7.548
7.540
7.534
7.475
7.459
7.443
7.427
7.422
7.415
7.259
3.903
3.873
3.844
0.000
1.835
2.960
4.978
2.000
9.5
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
δ (ppm)

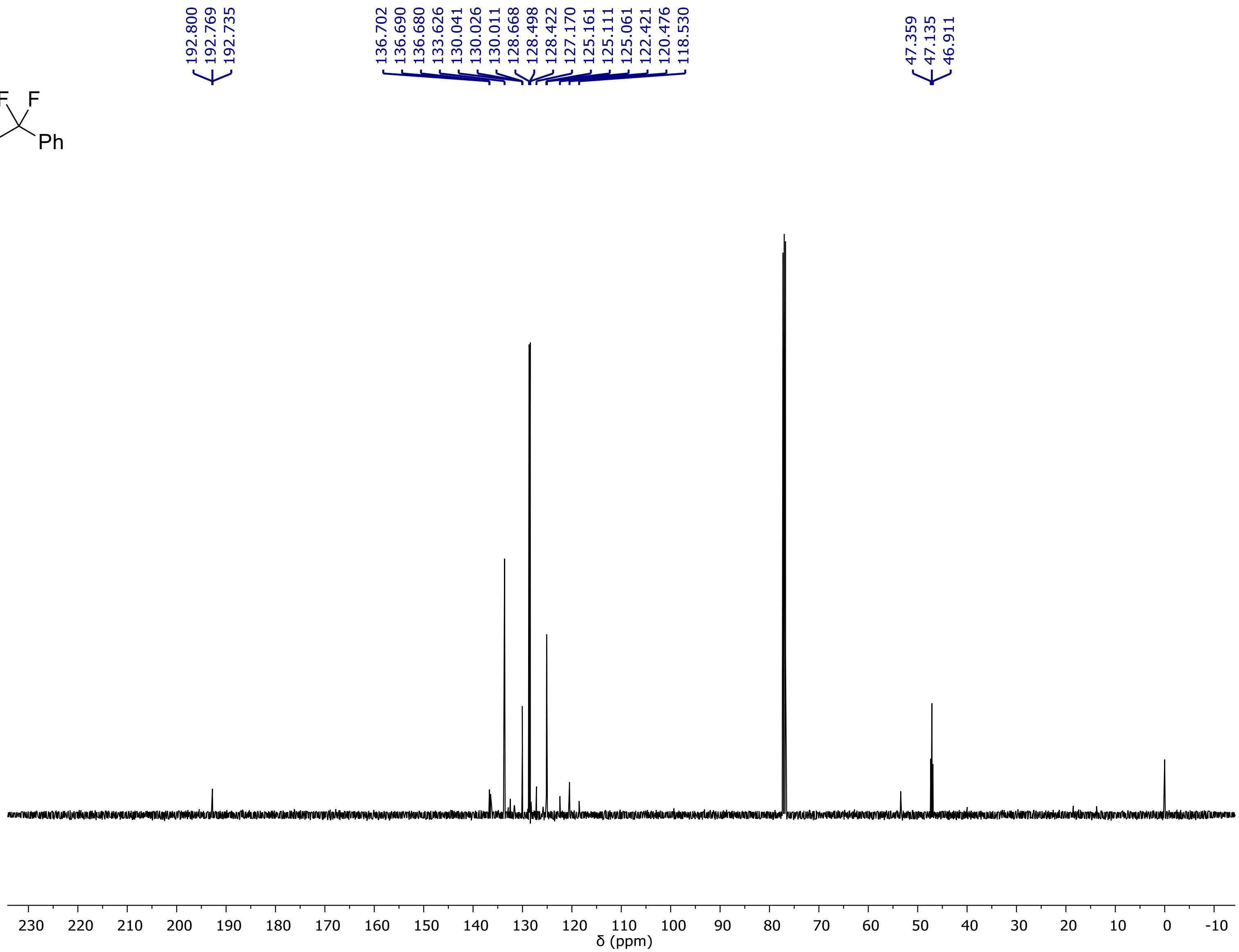


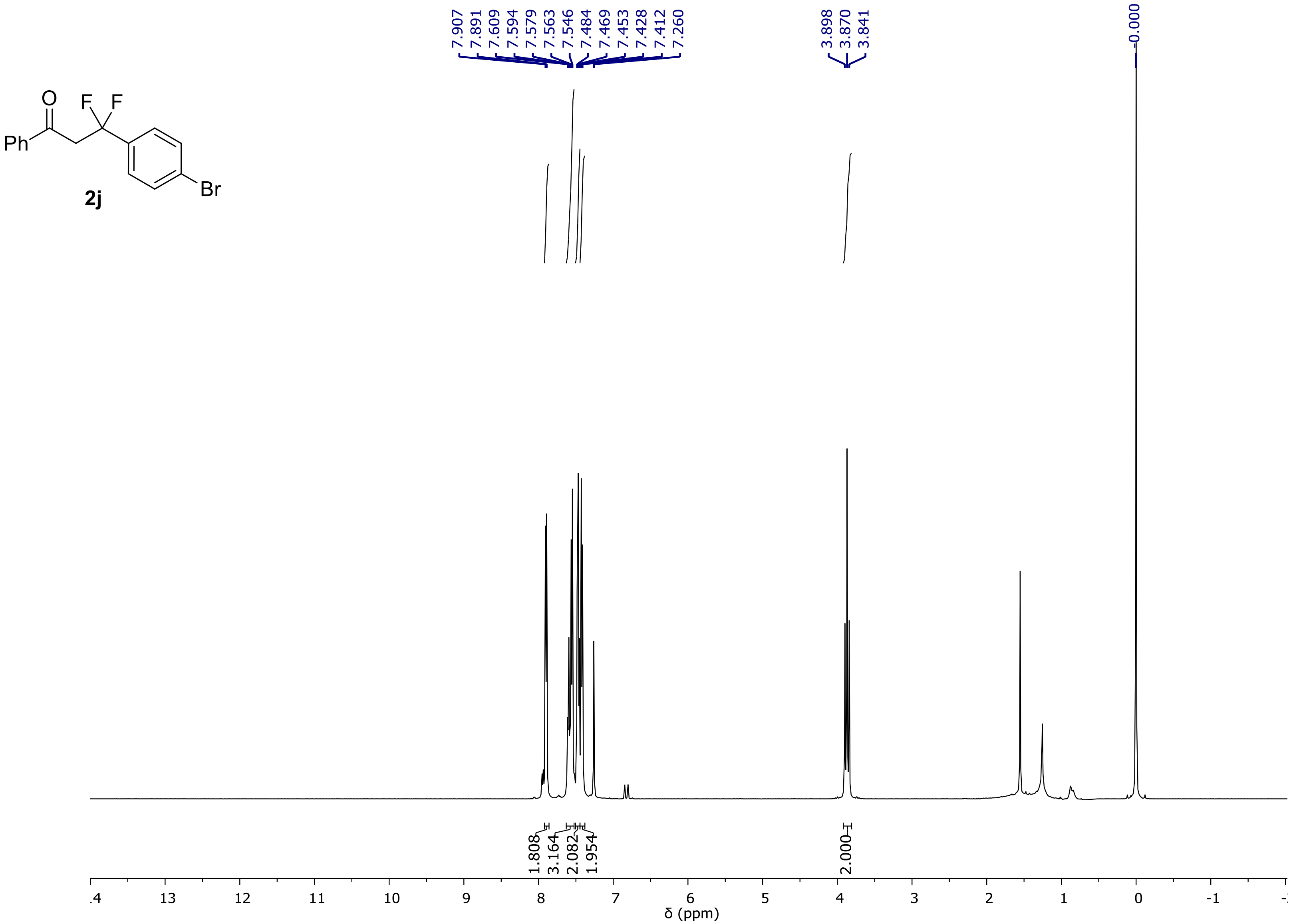
2i


-90.297
-90.329
-90.360
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
δ (ppm)


O
F
F
Ph
Ph

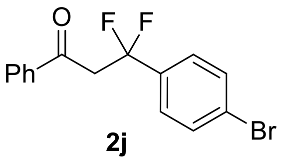
2i


192.800
192.769
192.735
136.702
136.690
136.680
133.626
130.041
130.026
130.011
128.668
128.498
128.422
127.170
125.161
125.111
125.061
122.421
120.476
118.530
47.359
47.135
46.911
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

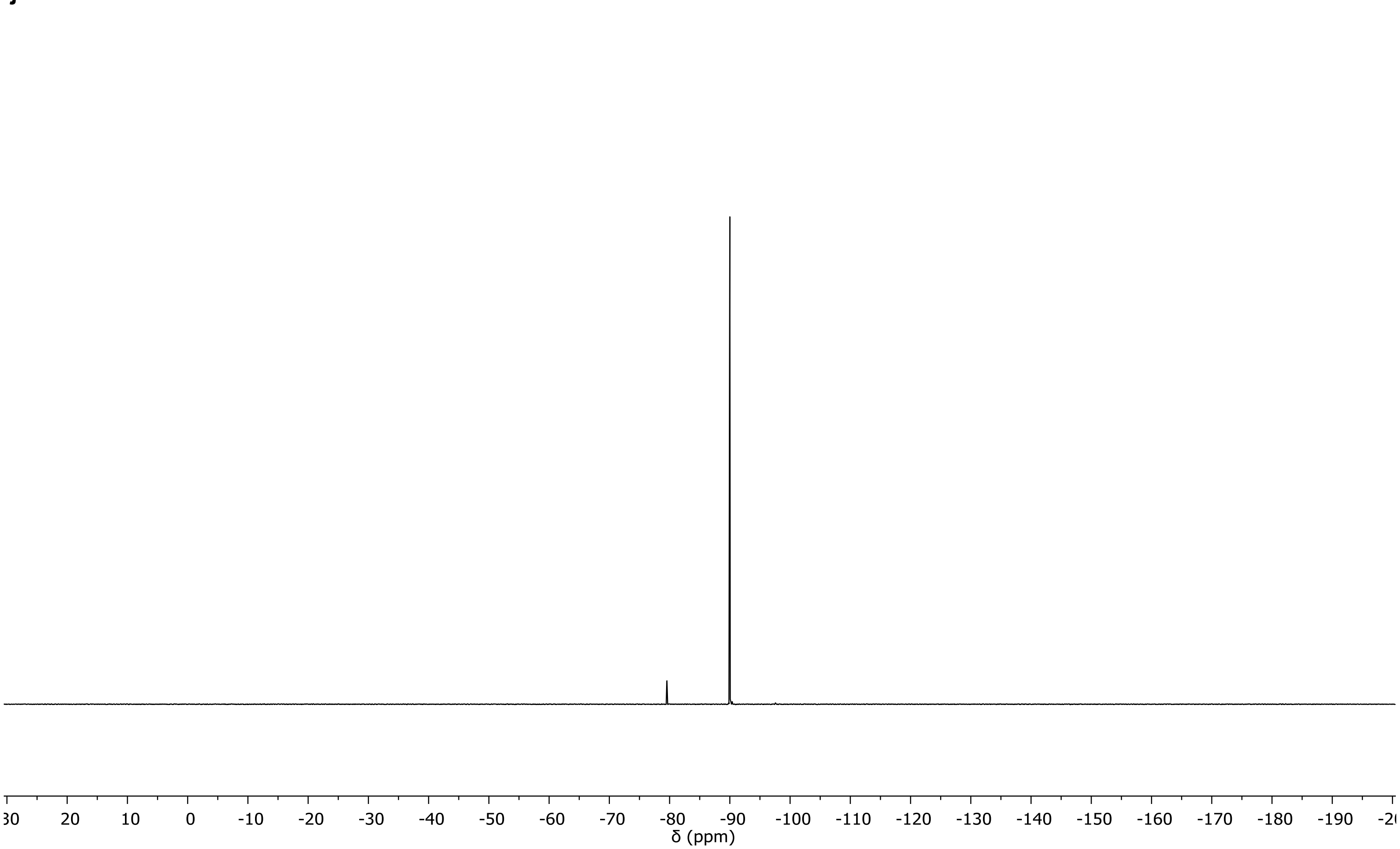

O
F
F
Ph
Br

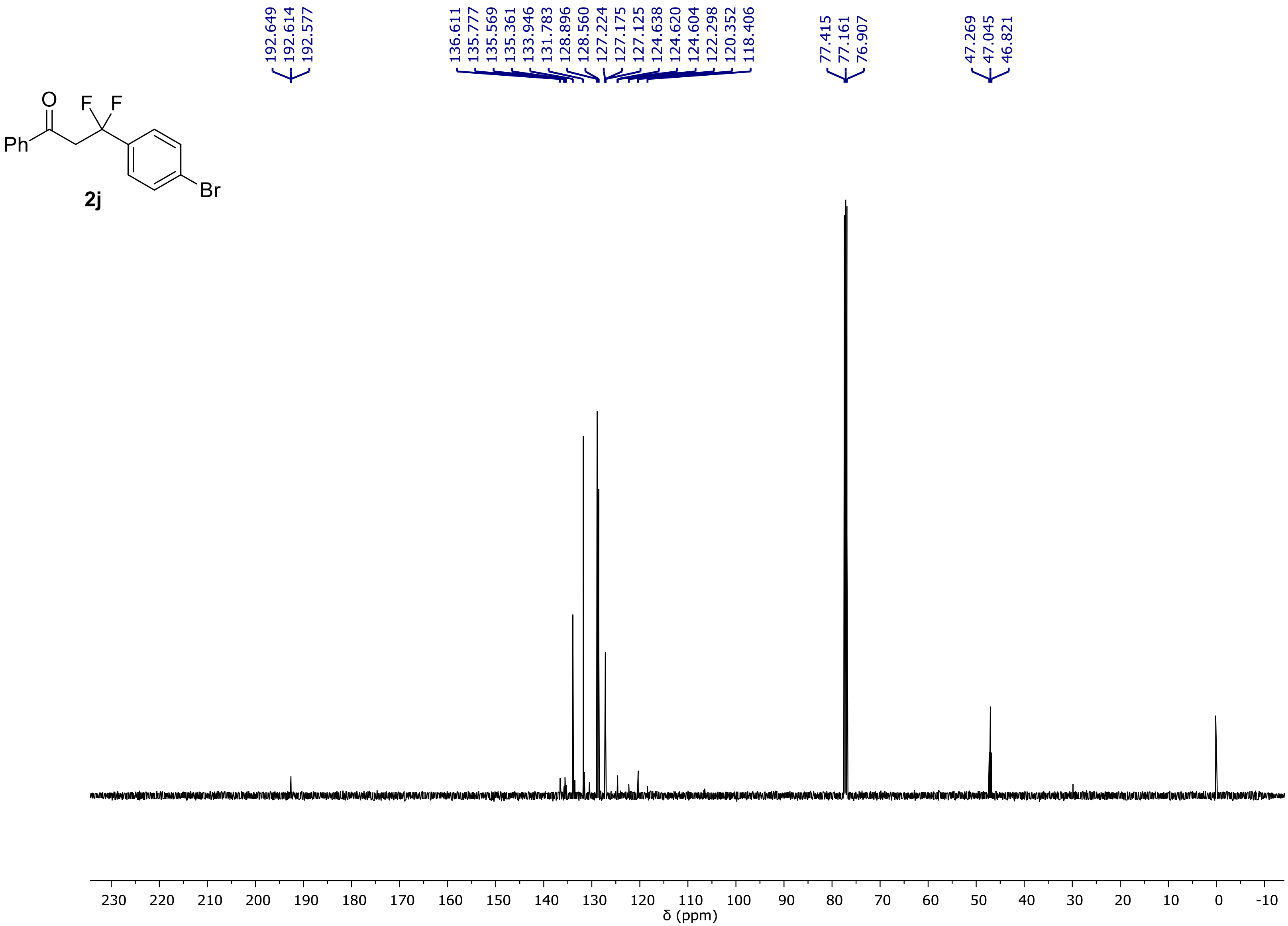
2j

7.907
7.891
7.609
7.594
7.579
7.563
7.546
7.484
7.469
7.453
7.428
7.412
7.260
3.898
3.870
3.841
0.000
1.808
3.164
2.082
1.954
2.000
.4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

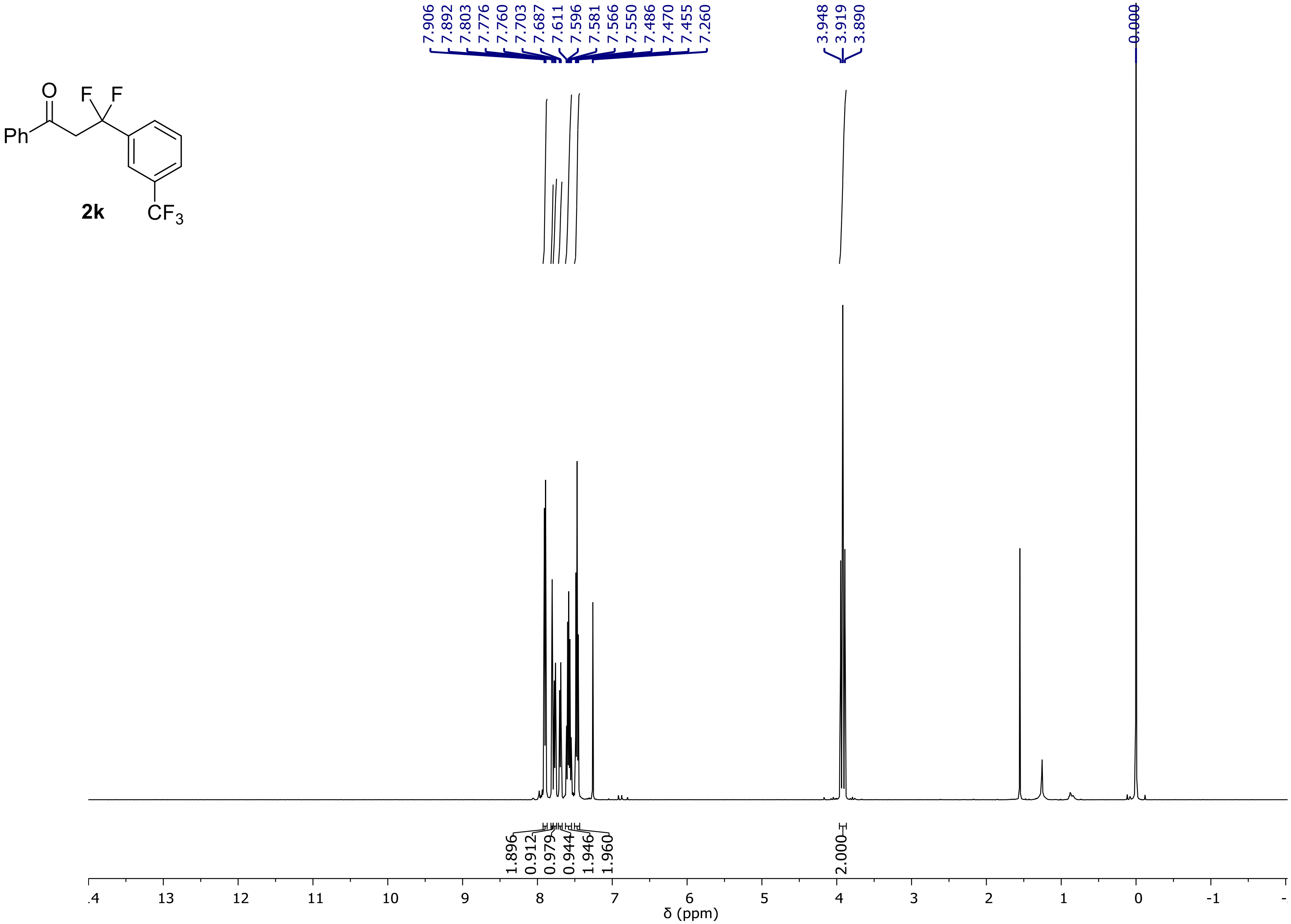

O
F
F
Ph
Br

2j


-89.968
-89.998
-90.029
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
δ (ppm)

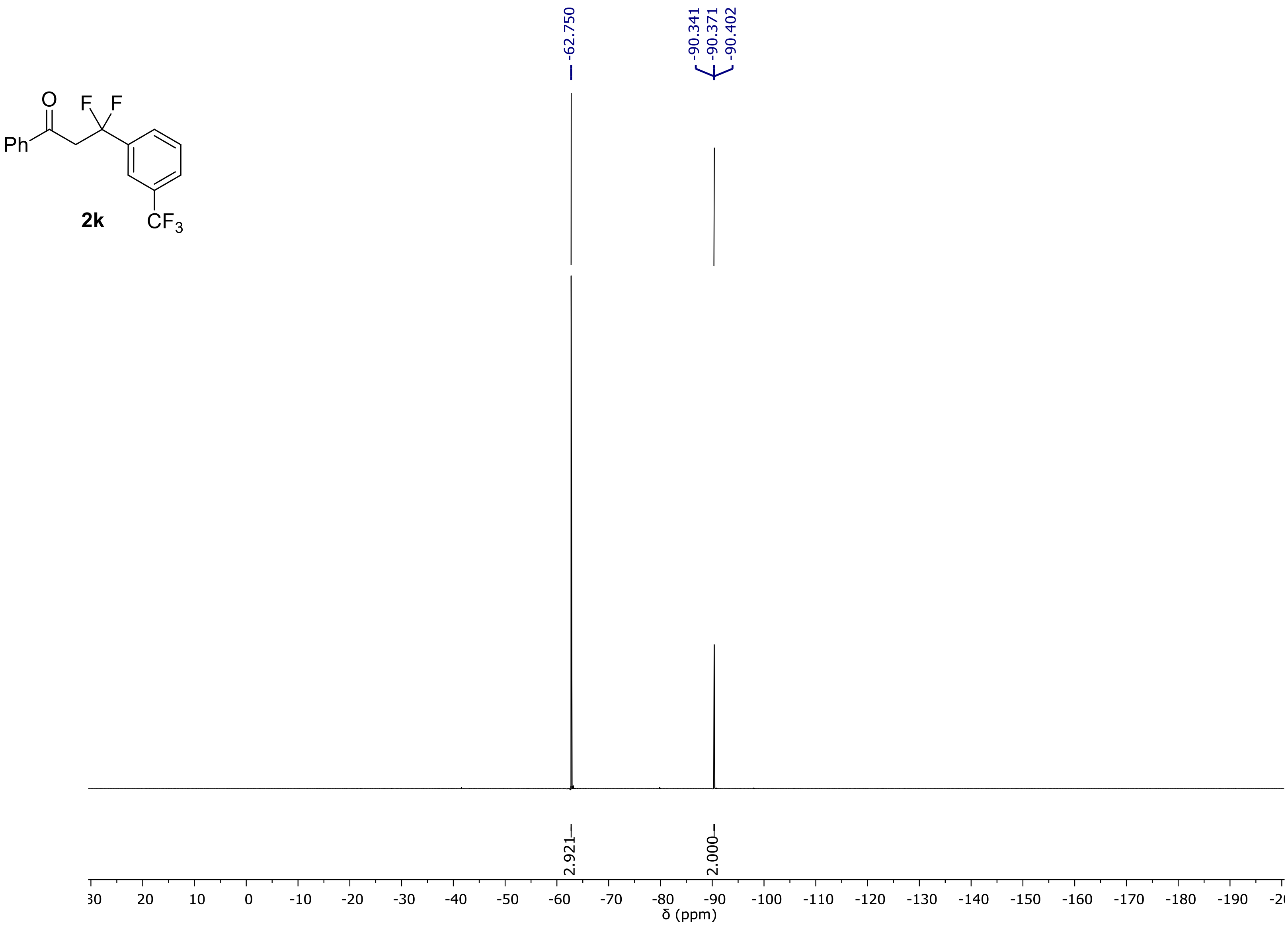

O
F
F
Ph
Br
192.649
192.614
192.577
136.611
135.777
135.569
135.361
133.946
131.783
128.896
128.560
127.224
127.175
127.125
124.638
124.620
124.604
122.298
120.352
118.406
77.415
77.161
76.907
47.269
47.045
46.821
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

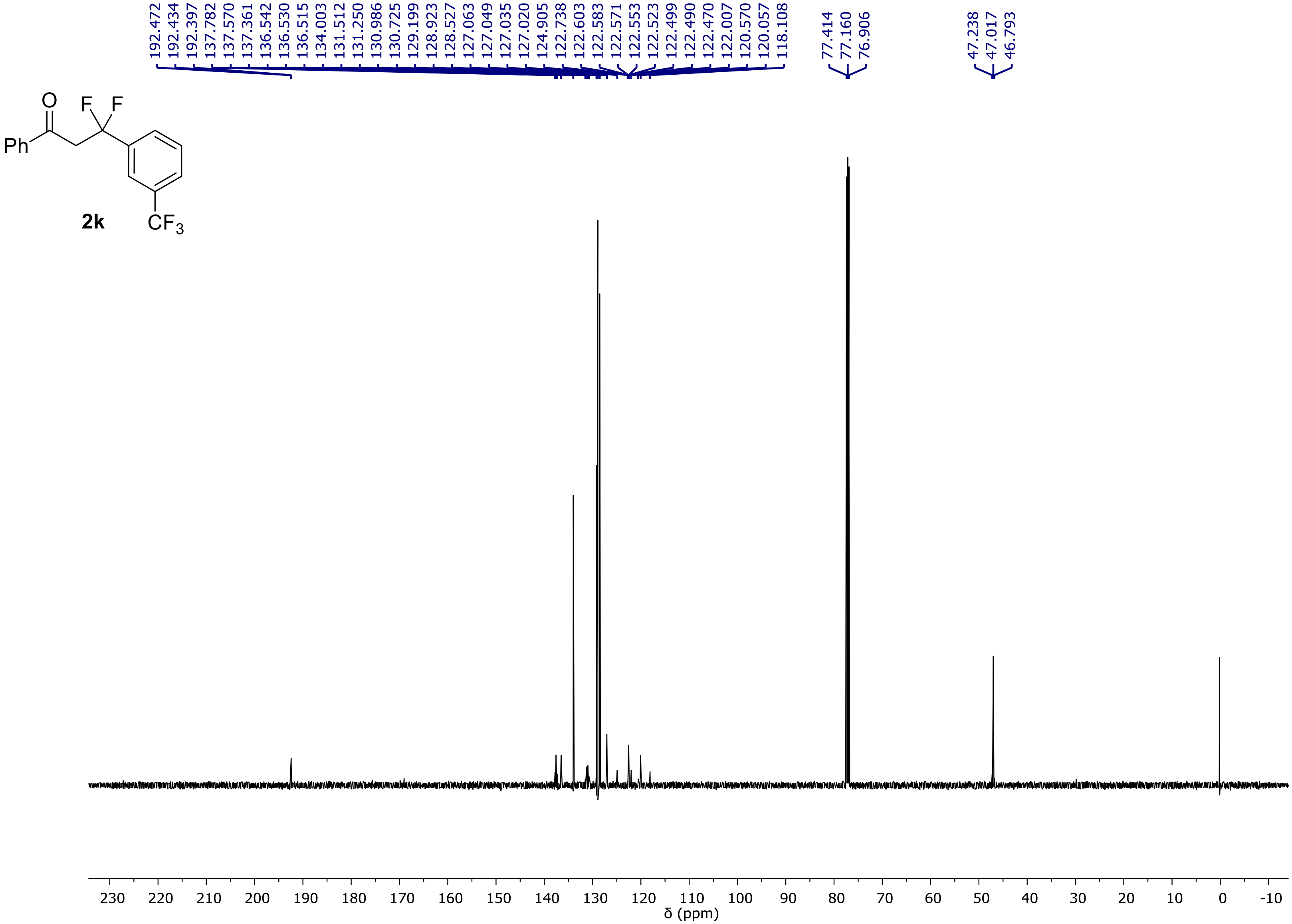
2j


O
F
F
Ph
CF3

2k

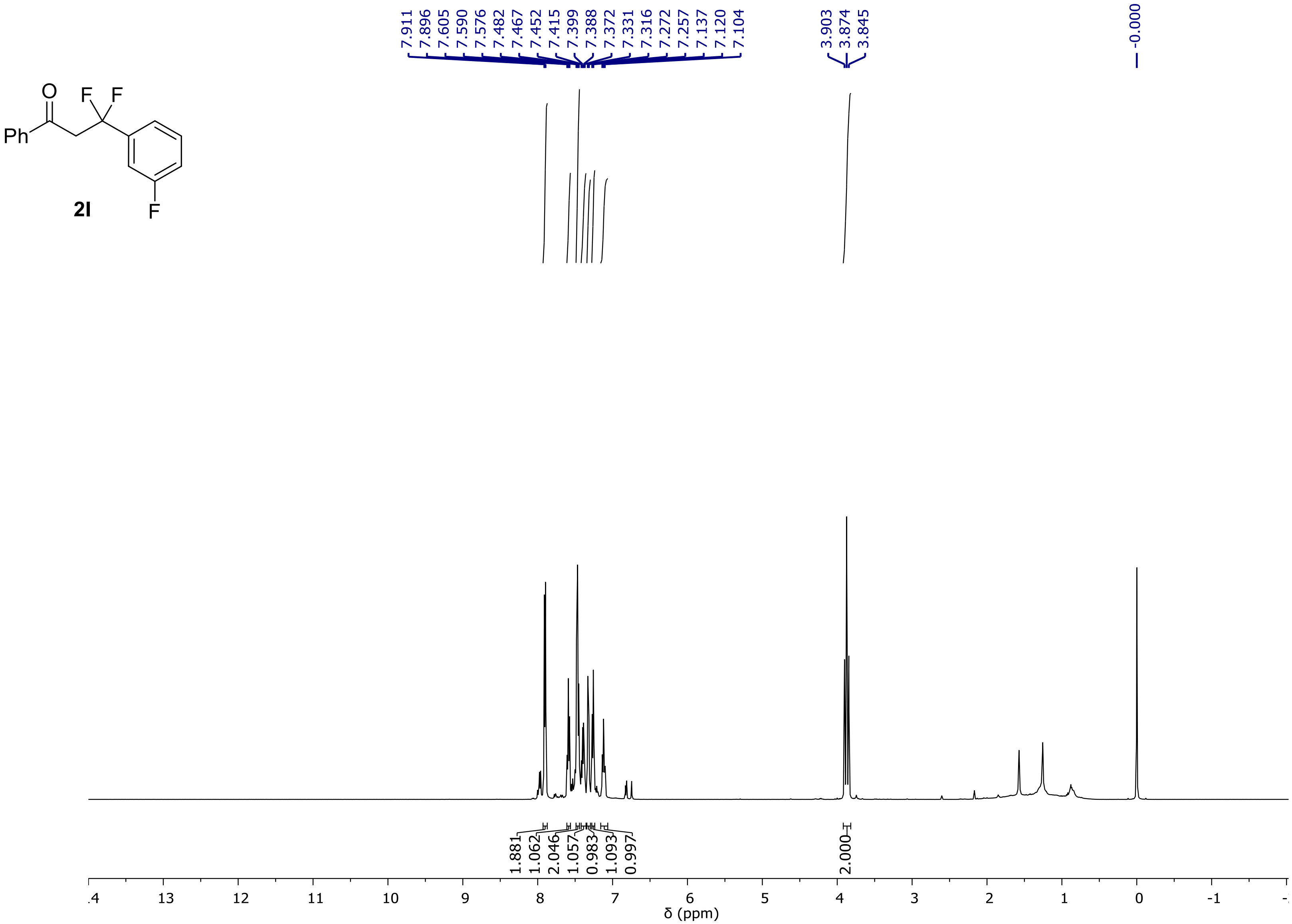
7.906
7.892
7.803
7.776
7.760
7.703
7.687
7.611
7.596
7.581
7.566
7.550
7.486
7.470
7.455
7.260
3.948
3.919
3.890
0.000
1.896
0.912
0.979
0.944
1.946
1.960
2.000
.4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-
δ (ppm)


-62.750
-90.341
-90.371
-90.402
O
F
F
Ph
CF3
2k
2.921
2.000
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
δ (ppm)



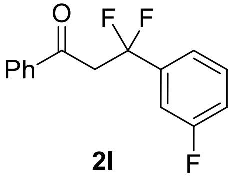
2k

192.472
192.434
192.397
137.782
137.570
137.361
136.542
136.530
136.515
134.003
131.512
131.250
130.986
130.725
129.199
128.923
128.527
127.063
127.049
127.035
127.020
124.905
122.738
122.603
122.583
122.571
122.553
122.523
122.499
122.490
122.470
122.007
120.570
120.057
118.108
77.414
77.160
76.906
47.238
47.017
46.793
O
F
F
Ph
CF3
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

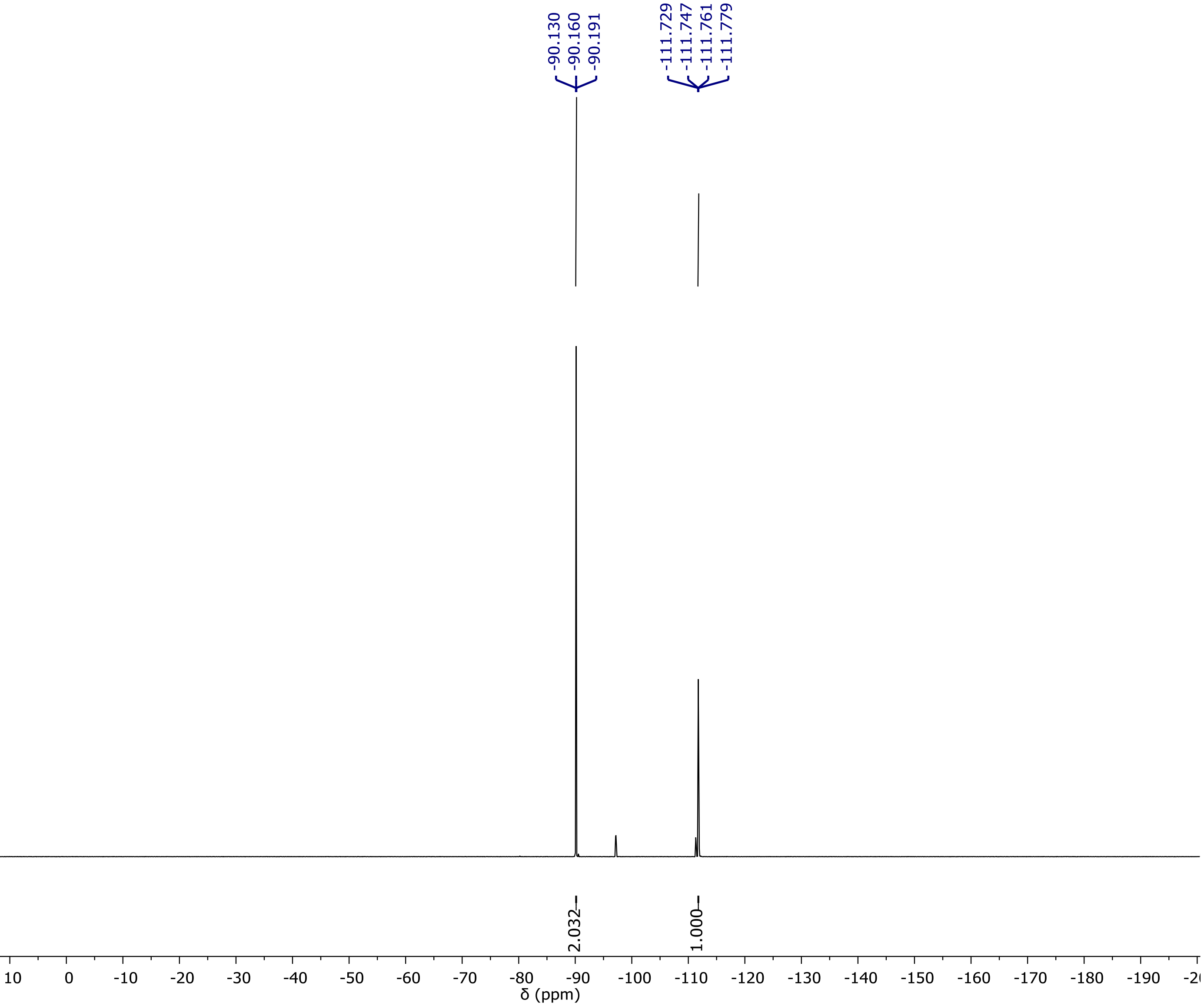

O
F
F
Ph
F

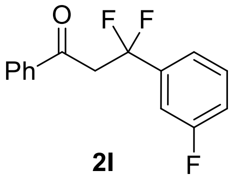
2l

7.911
7.896
7.605
7.590
7.576
7.482
7.467
7.452
7.415
7.399
7.388
7.372
7.331
7.316
7.272
7.257
7.137
7.120
7.104
3.903
3.874
3.845
-0.000
1.881
1.062
2.046
1.057
0.983
1.093
0.997
2.000
.4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-.
δ (ppm)

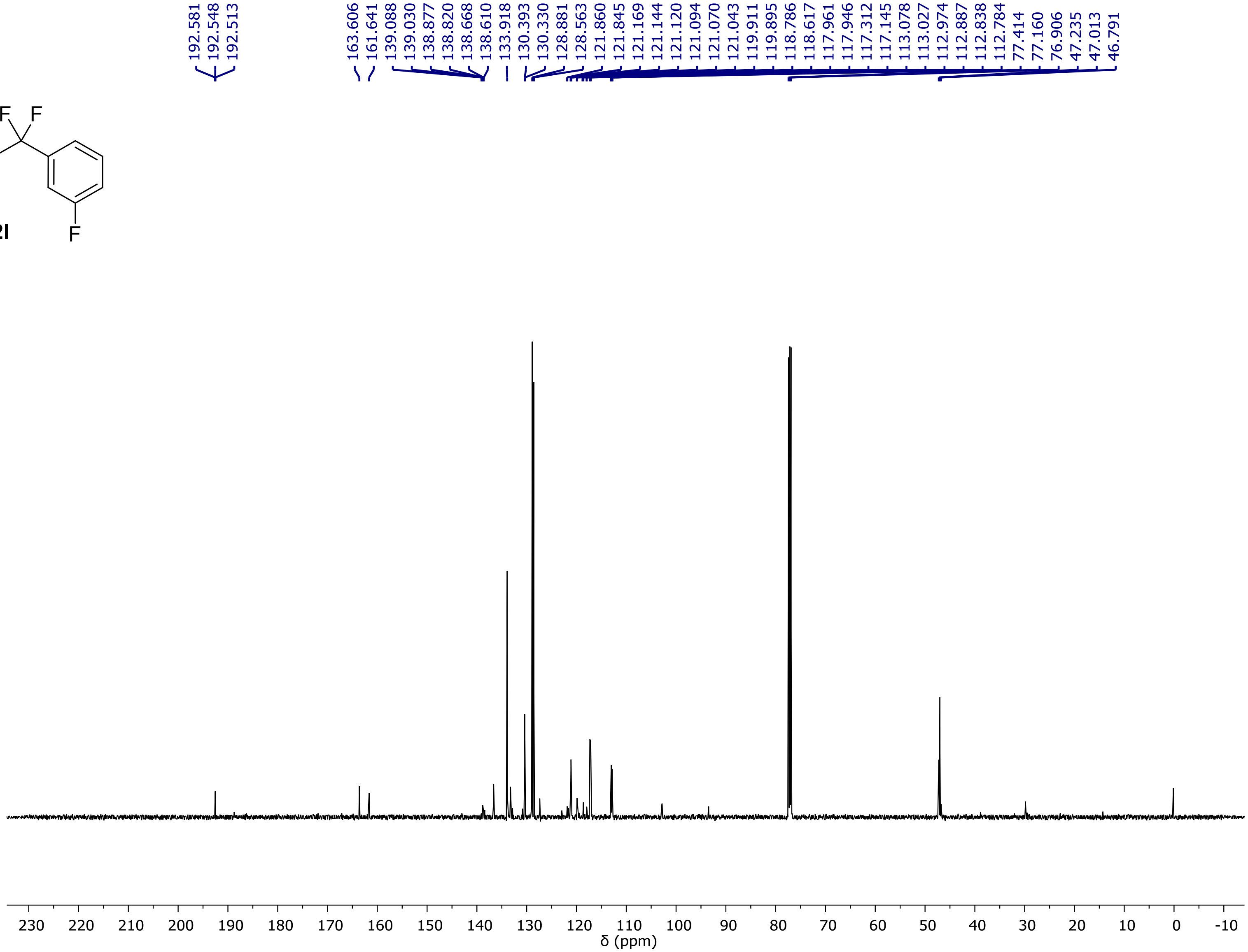


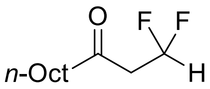
2l


-90.130
-90.160
-90.191
-111.729
-111.747
-111.761
-111.779
2.032
1.000
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
δ (ppm)


O
F
F
Ph
F

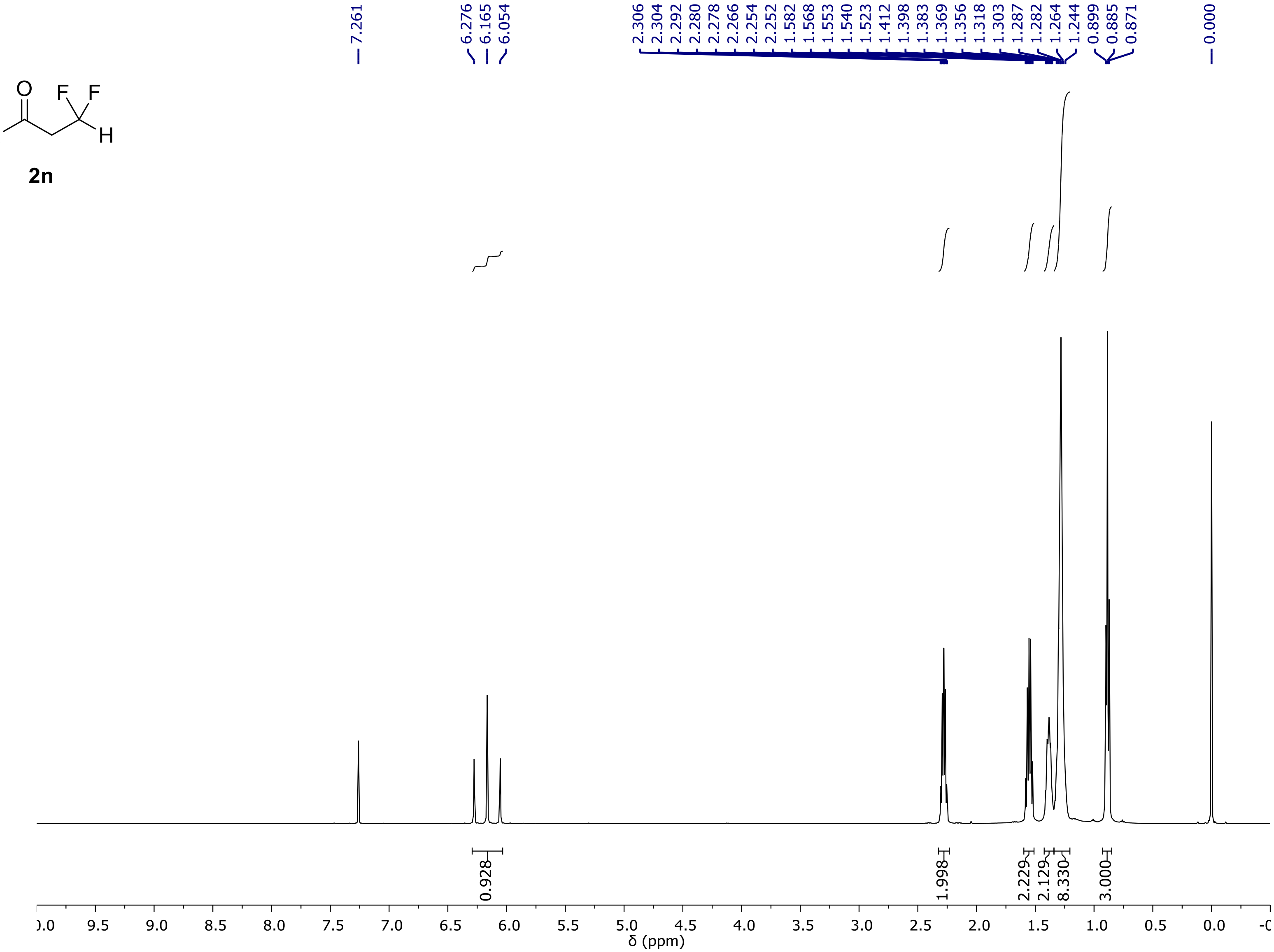
2l


192.581
192.548
192.513
163.606
161.641
139.088
139.030
138.877
138.820
138.668
138.610
133.918
130.393
130.330
128.881
128.563
121.860
121.845
121.169
121.144
121.120
121.094
121.070
121.043
119.911
119.895
118.786
118.617
117.961
117.946
117.312
117.145
113.078
113.027
112.974
112.887
112.838
112.784
77.414
77.160
76.906
47.235
47.013
46.791
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

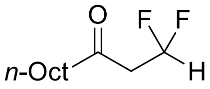


O
F
F
n-Oct
H

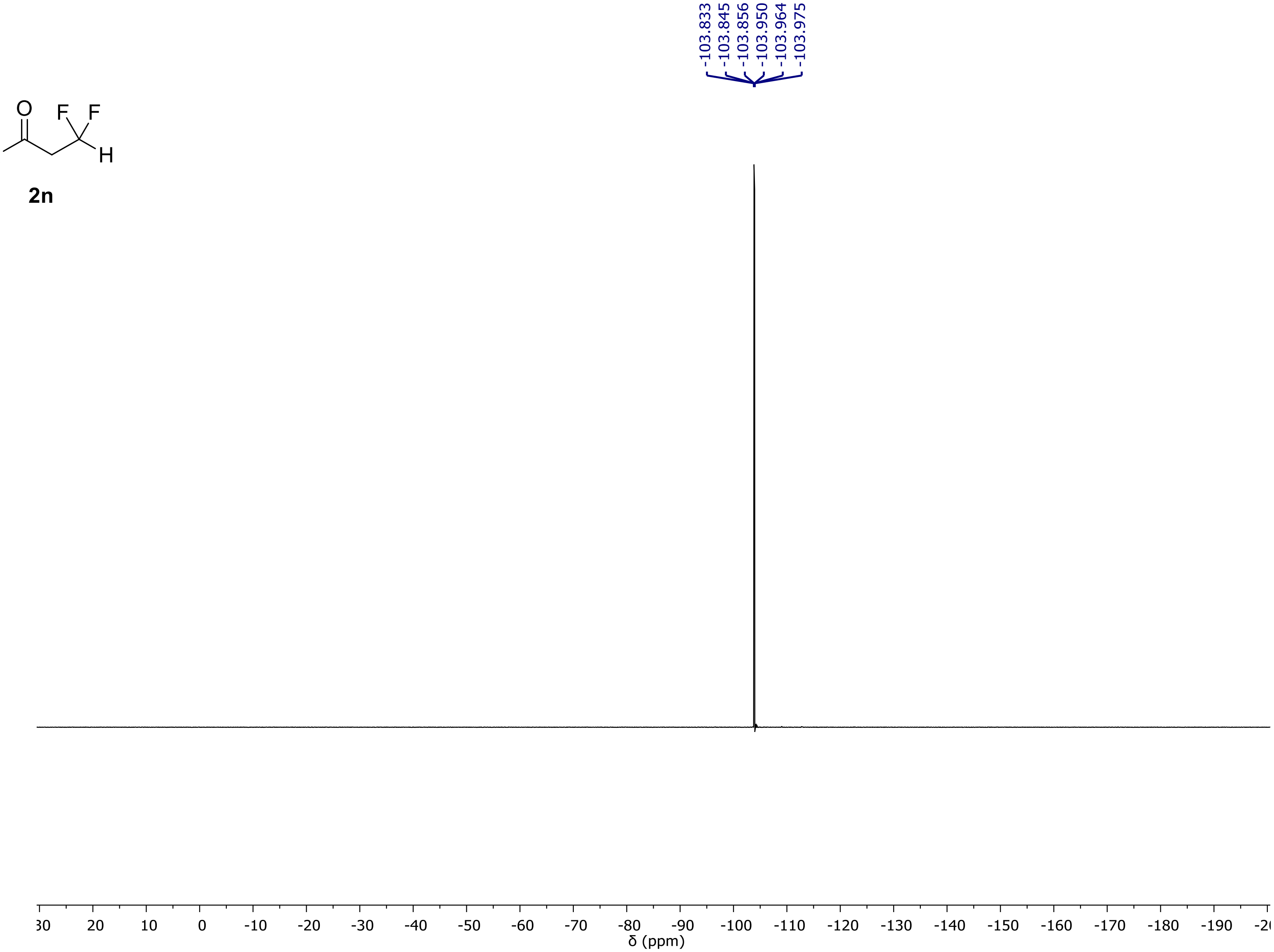
2n

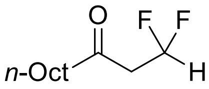


7.261
6.276
6.165
6.054
2.306
2.304
2.292
2.280
2.278
2.266
2.254
2.252
1.582
1.568
1.553
1.540
1.523
1.412
1.398
1.383
1.369
1.356
1.318
1.303
1.287
1.282
1.264
1.244
0.899
0.885
0.871
0.000
0.928
1.998
2.229
2.129
8.330
3.000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

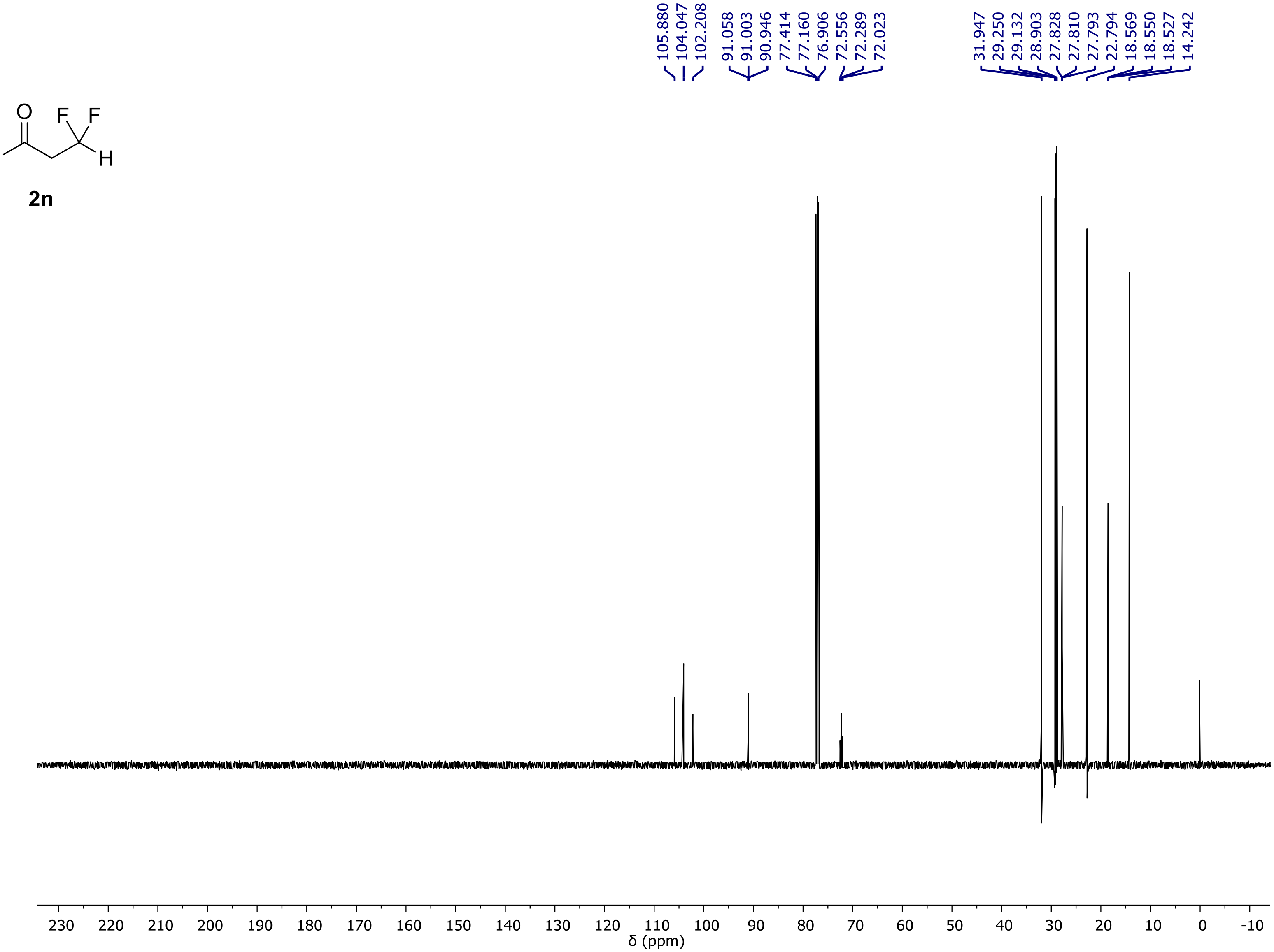

O
F
F
n-Oct
H

2n


-103.833
-103.845
-103.856
-103.950
-103.964
-103.975
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
δ (ppm)


O
F
F
n-Oct
H

2n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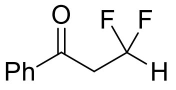
102.208
91.058
91.003
90.946
77.414
77.160
76.906
72.556
72.289
72.023
31.947
29.250
29.132
28.903
27.828
27.810
27.793
22.794
18.569
18.550
18.527
14.242
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)



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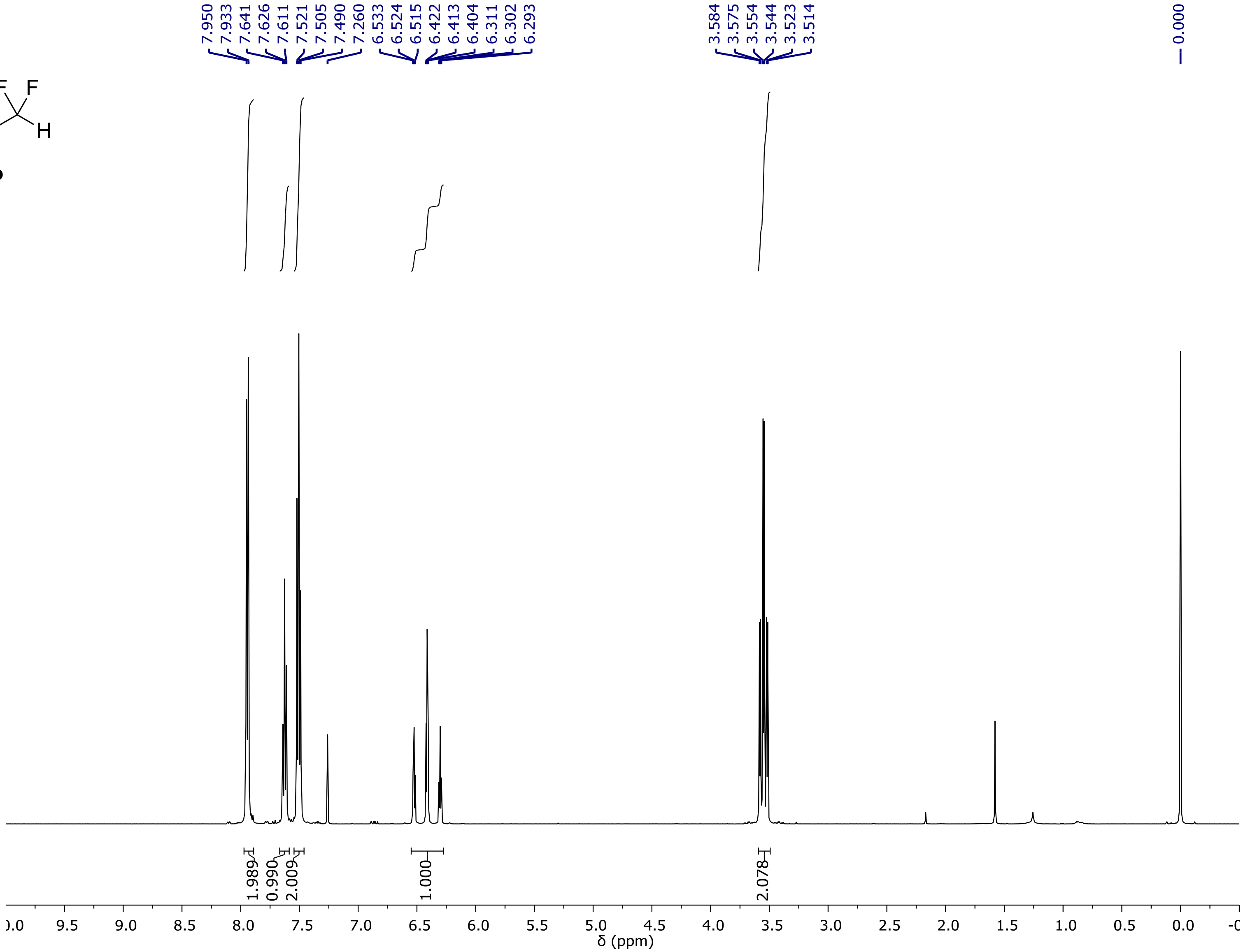
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7.933
7.641
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7.521
7.505
7.490
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6.533
6.524
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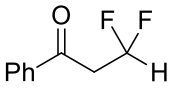
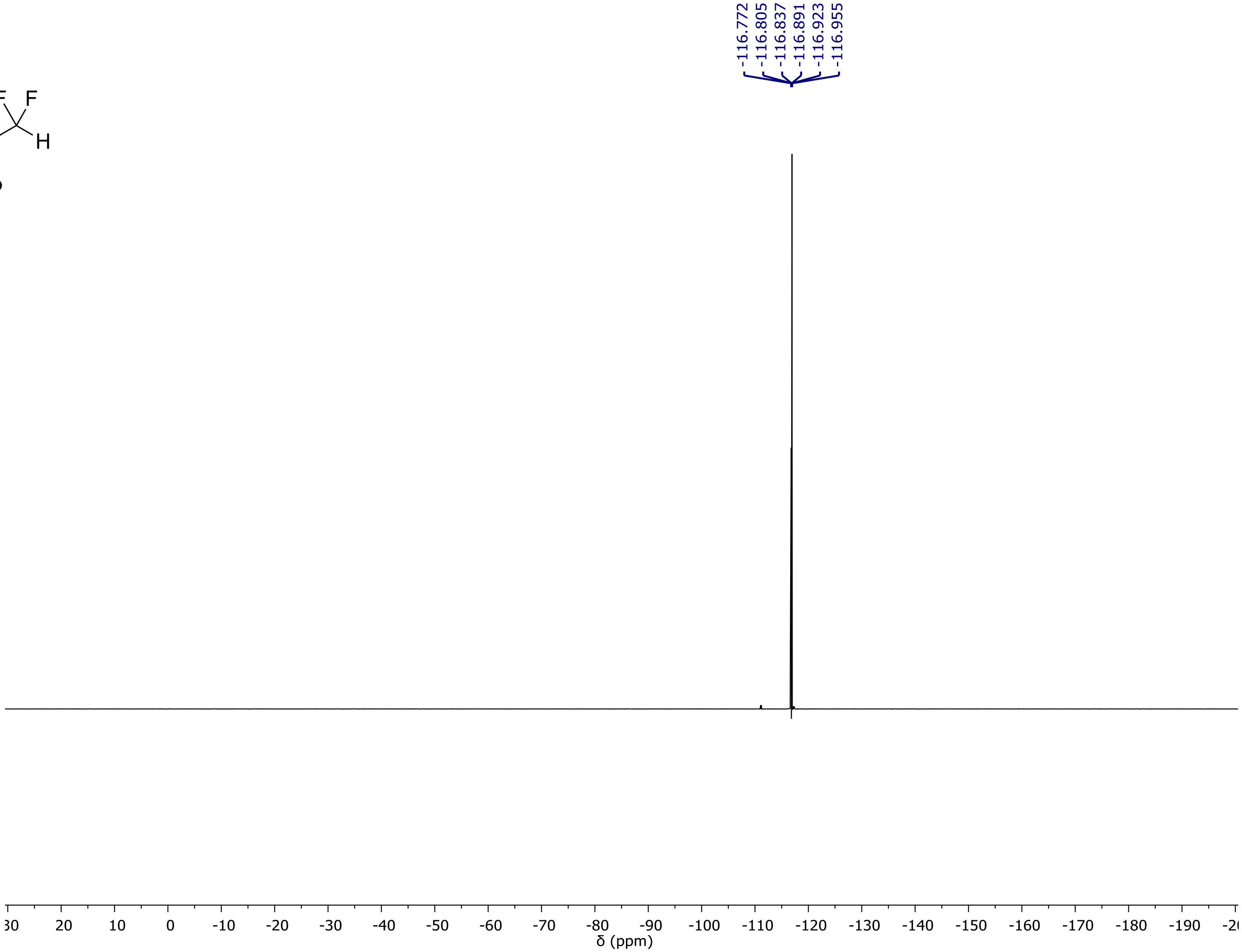
6.422
6.413
6.404
6.311
6.302
6.293
3.584
3.575
3.554
3.544
3.523
3.514
0.000
1.989
0.990
2.009
1.000
2.078
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)



2o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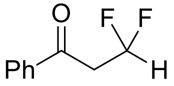
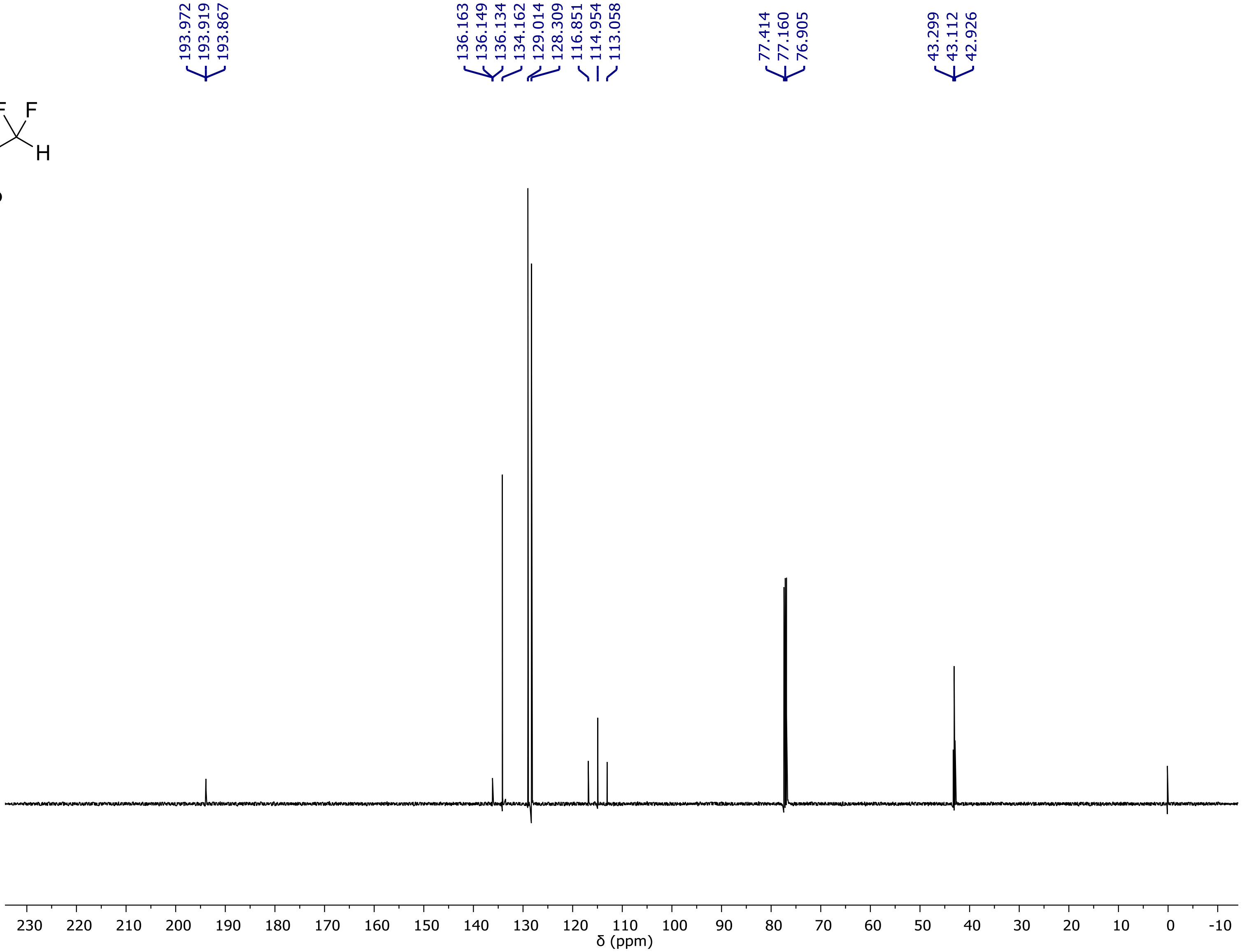
-116.805
-116.837
-116.891
-116.923
-116.955
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
δ (ppm)


O
F
F
Ph
H

2o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136.134
134.162
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128.309
116.851
114.954
113.058
77.414
77.160
76.905
43.299
43.112
42.926
230
220
210
200
190
180
170
160
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140
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120
110
100
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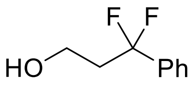
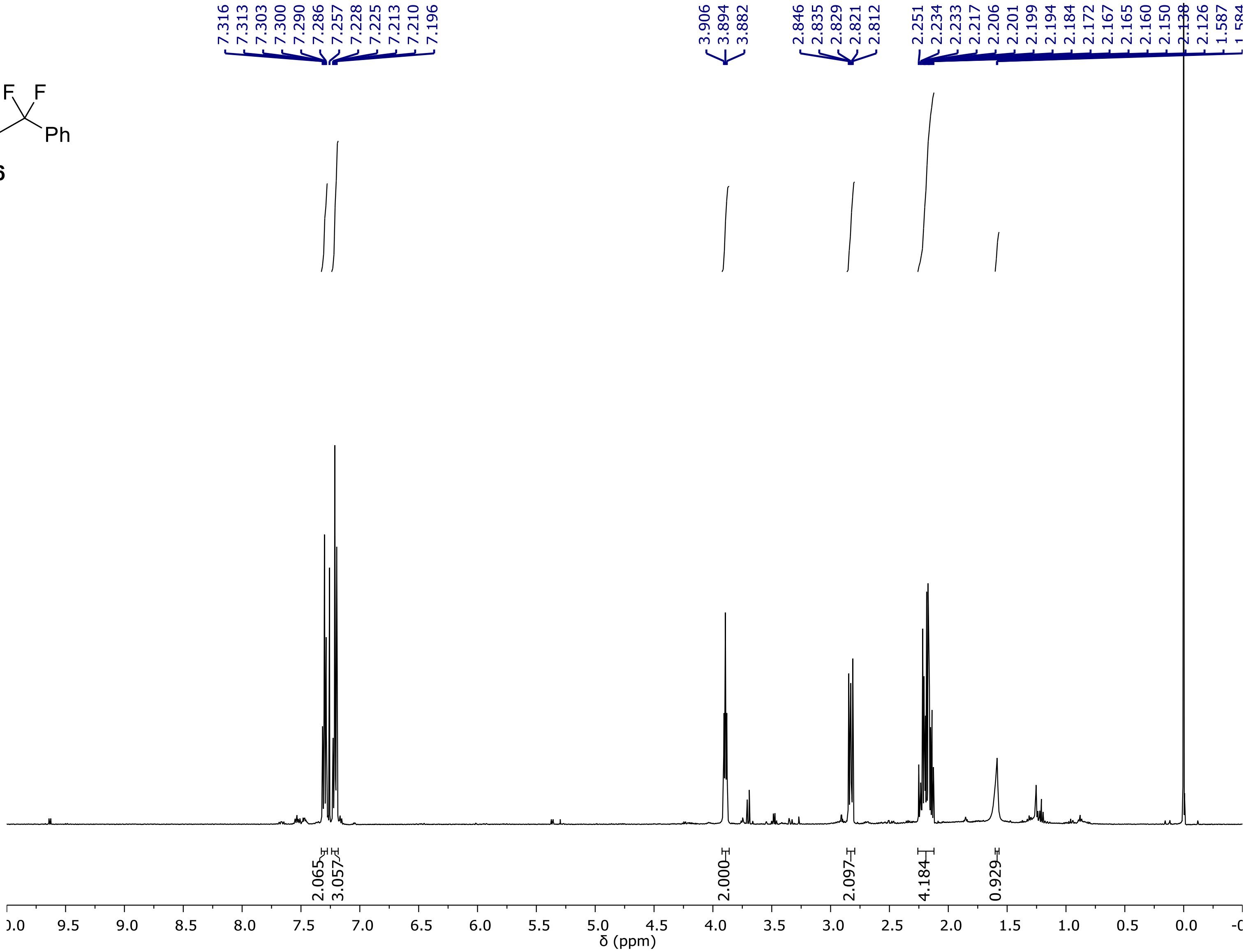
80
70
60
50
40
30
20
10
0
-10
δ (ppm)



16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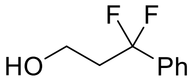
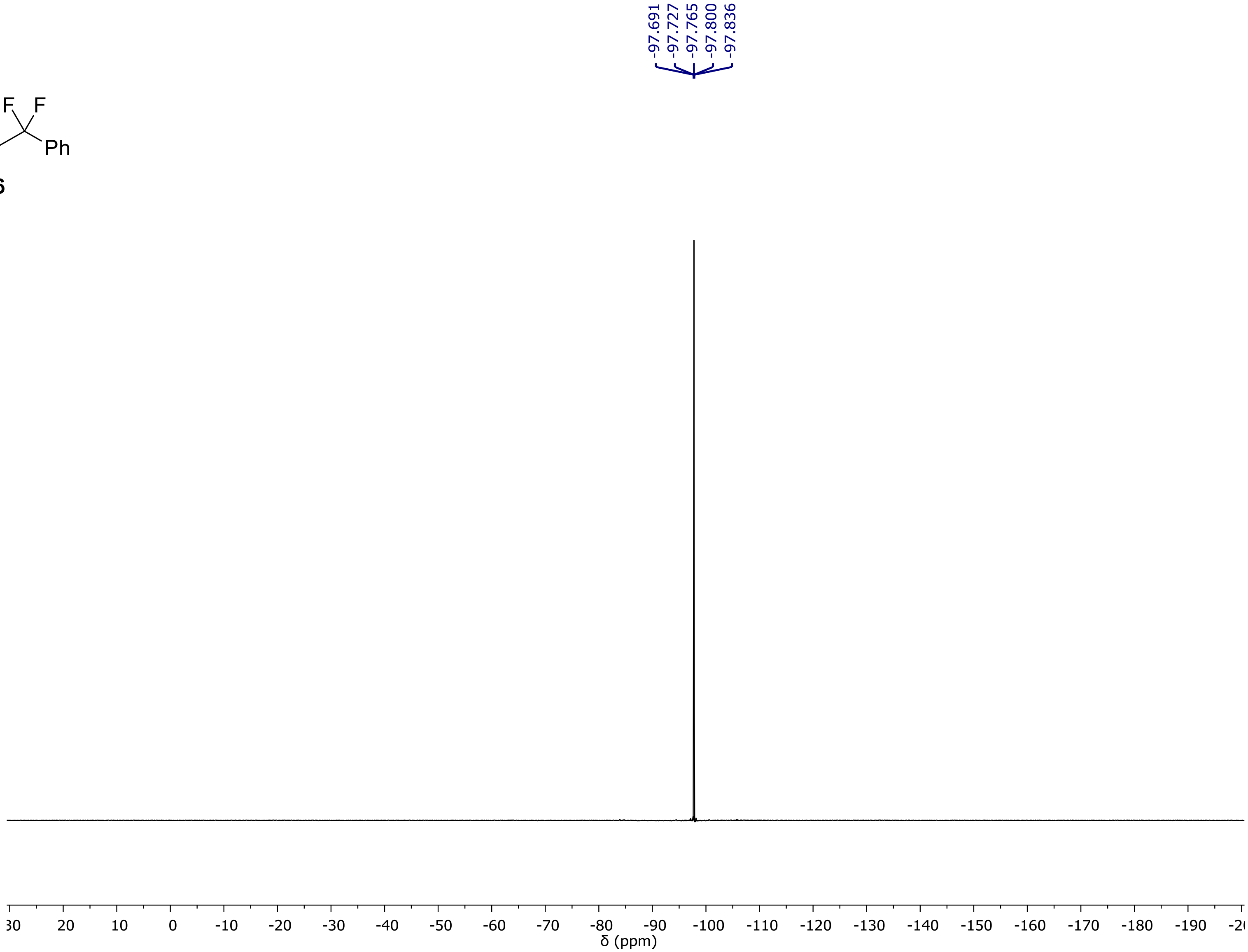
7.286
7.257
7.228
7.225
7.213
7.210
7.196
3.906
3.894
3.882
2.846
2.835
2.829
2.821
2.812
2.251
2.234
2.233
2.217
2.206
2.201
2.199
2.194
2.184
2.172
2.167
2.165
2.160
2.150
2.138
2.126
1.587
2.065
3.057
2.000
2.097
4.184
0.929
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

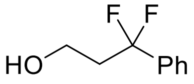


F
F
HO
Ph

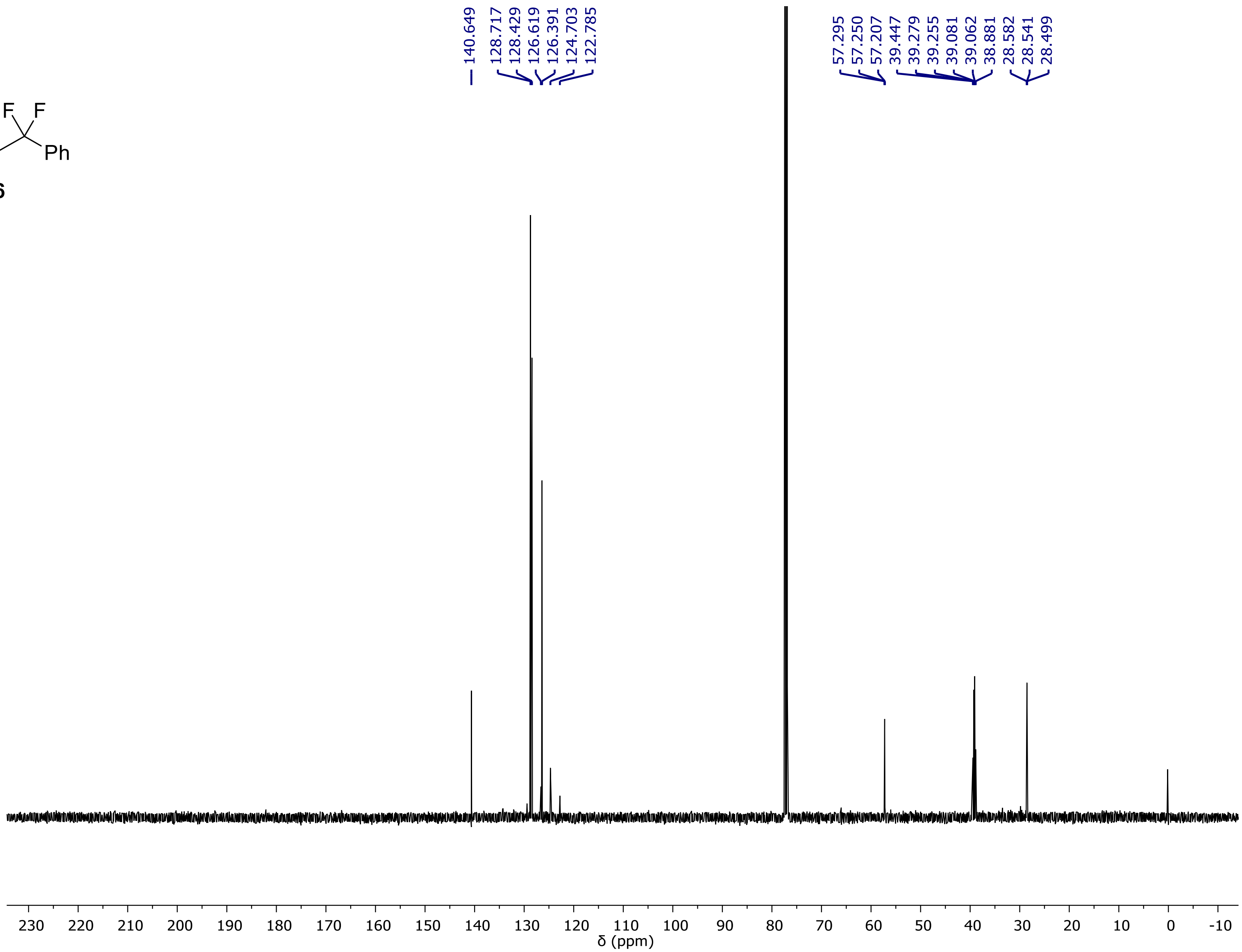
16



-97.691
-97.727
-97.765
-97.800
-97.836
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
δ (ppm)


F
F
HO
Ph

16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128.429
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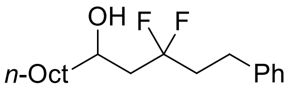
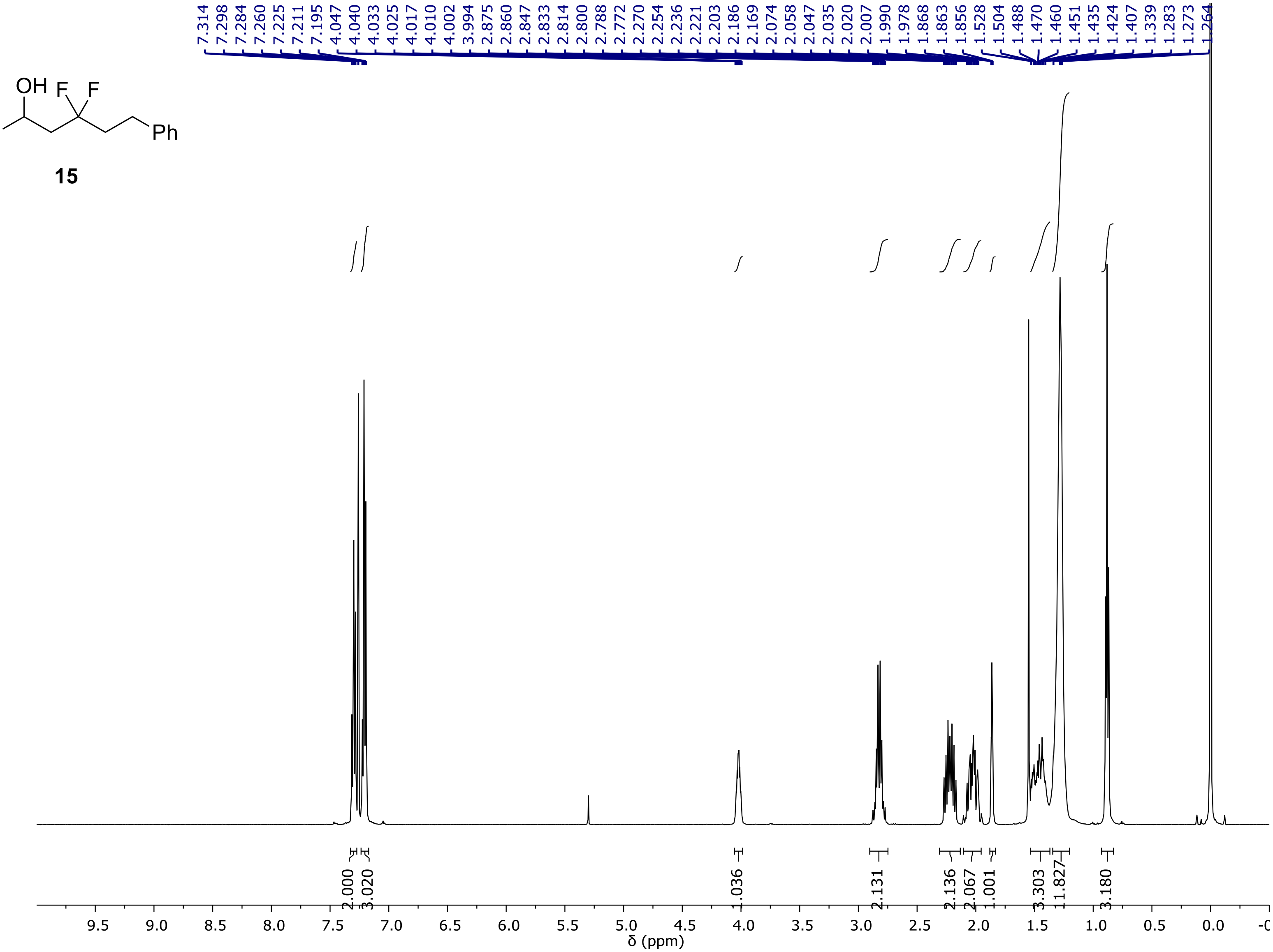
124.703
122.785
57.295
57.250
57.207
39.447
39.279
39.255
39.081
39.062
38.881
28.582
28.541
28.499
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)



OH
F
F
n-Oct
Ph

15



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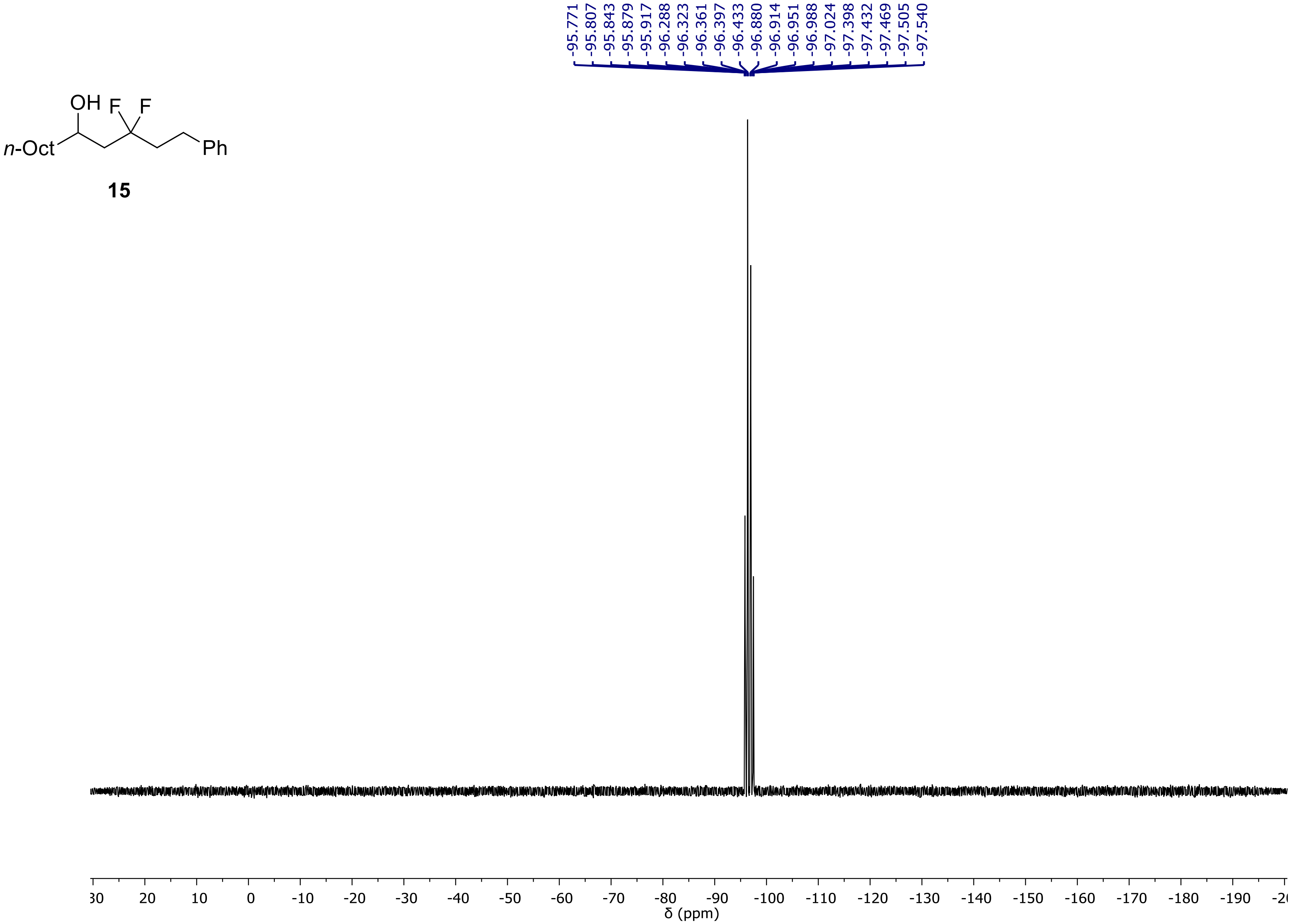
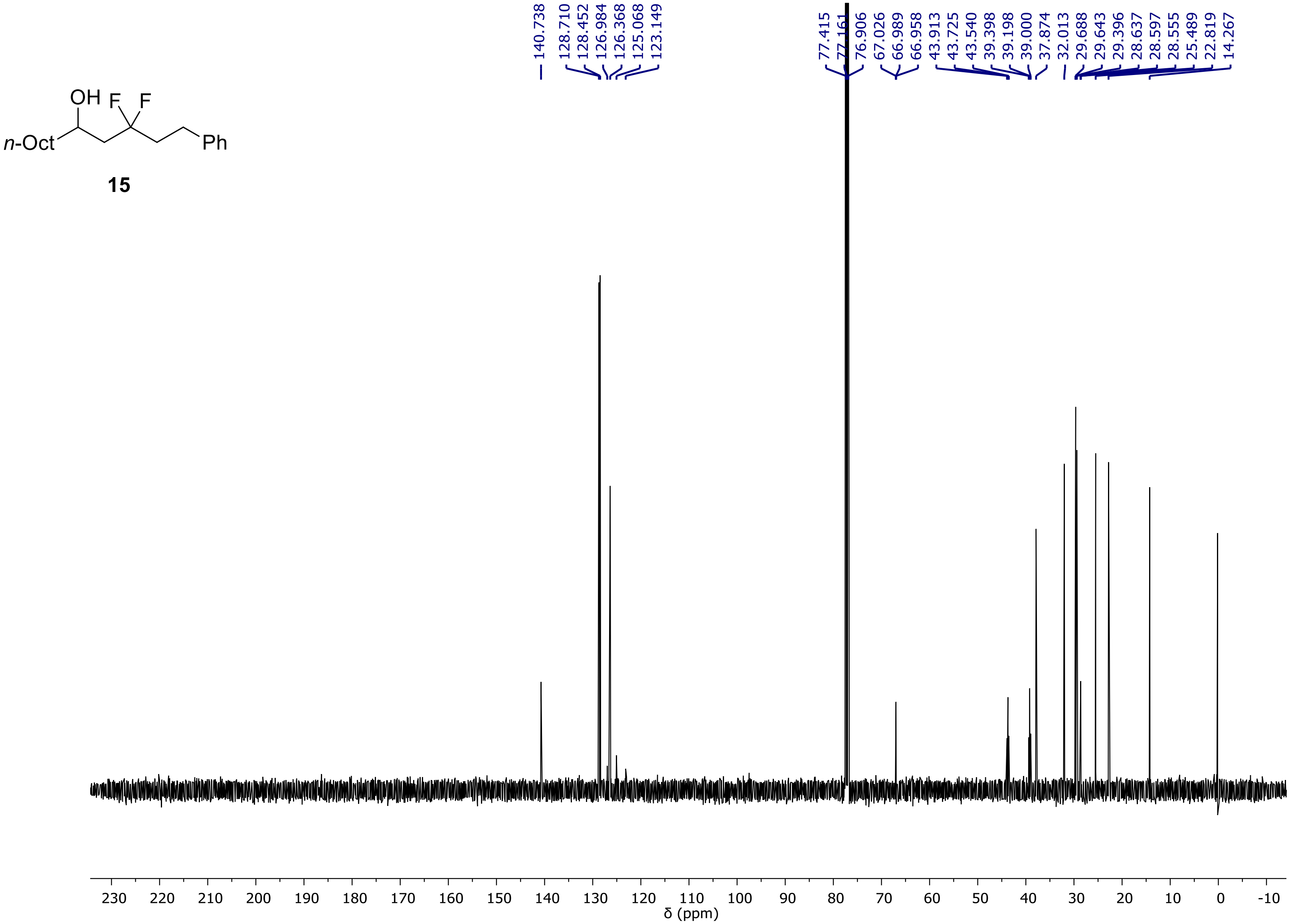
7.211
7.195
4.047
4.040
4.033
4.025
4.017
4.010
4.002
3.994
2.875
2.860
2.847
2.833
2.814
2.800
2.788
2.772
2.270
2.254
2.236
2.221
2.203
2.186
2.169
2.074
2.058
2.047
2.035
2.020
2.007
1.990
1.978
1.868
1.863
1.856
1.528
1.504
1.488
1.470
1.460
1.451
1.435
1.424
1.407
1.339
1.283
1.273
1.264
2.000
3.020
1.036
2.131
2.136
2.067
1.001
3.303
11.827
3.180
9.5
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
-
δ (ppm)


OH
F
F
n-Oct
Ph

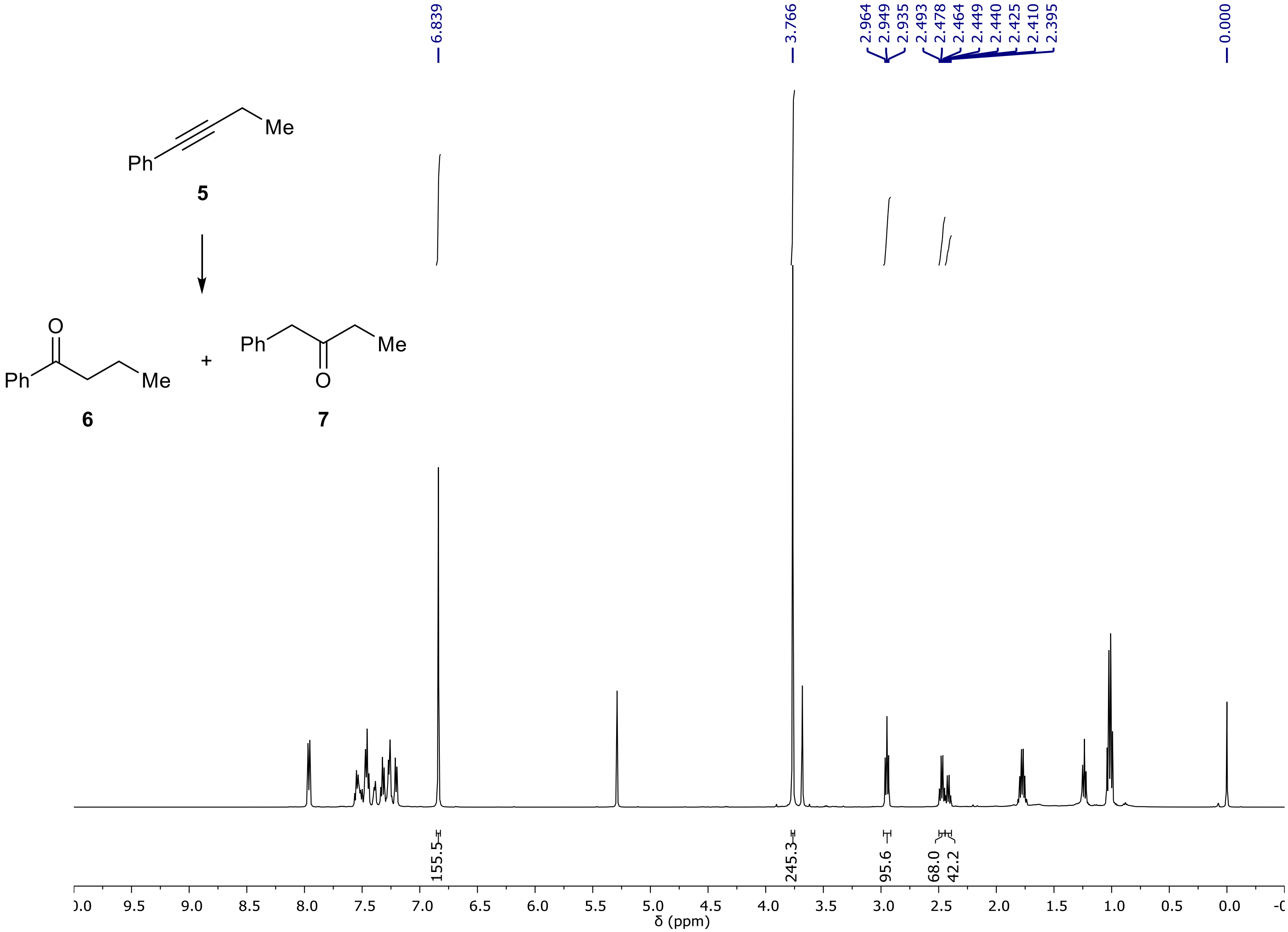
15

-95.771
-95.807
-95.843
-95.879
-95.917
-96.288
-96.323
-96.361
-96.397
-96.433
-96.880
-96.914
-96.951
-96.988
-97.024
-97.398
-97.432
-97.469
-97.505
-97.540
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
δ (ppm)


OH
F
F
n-Oct
Ph

15

140.738
128.710
128.452
126.984
126.368
125.068
123.149
77.415
77.161
76.906
67.026
66.989
66.958
43.913
43.725
43.540
39.398
39.198
39.000
37.874
32.013
29.688
29.643
29.396
28.637
28.597
28.555
25.489
22.819
14.267
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)



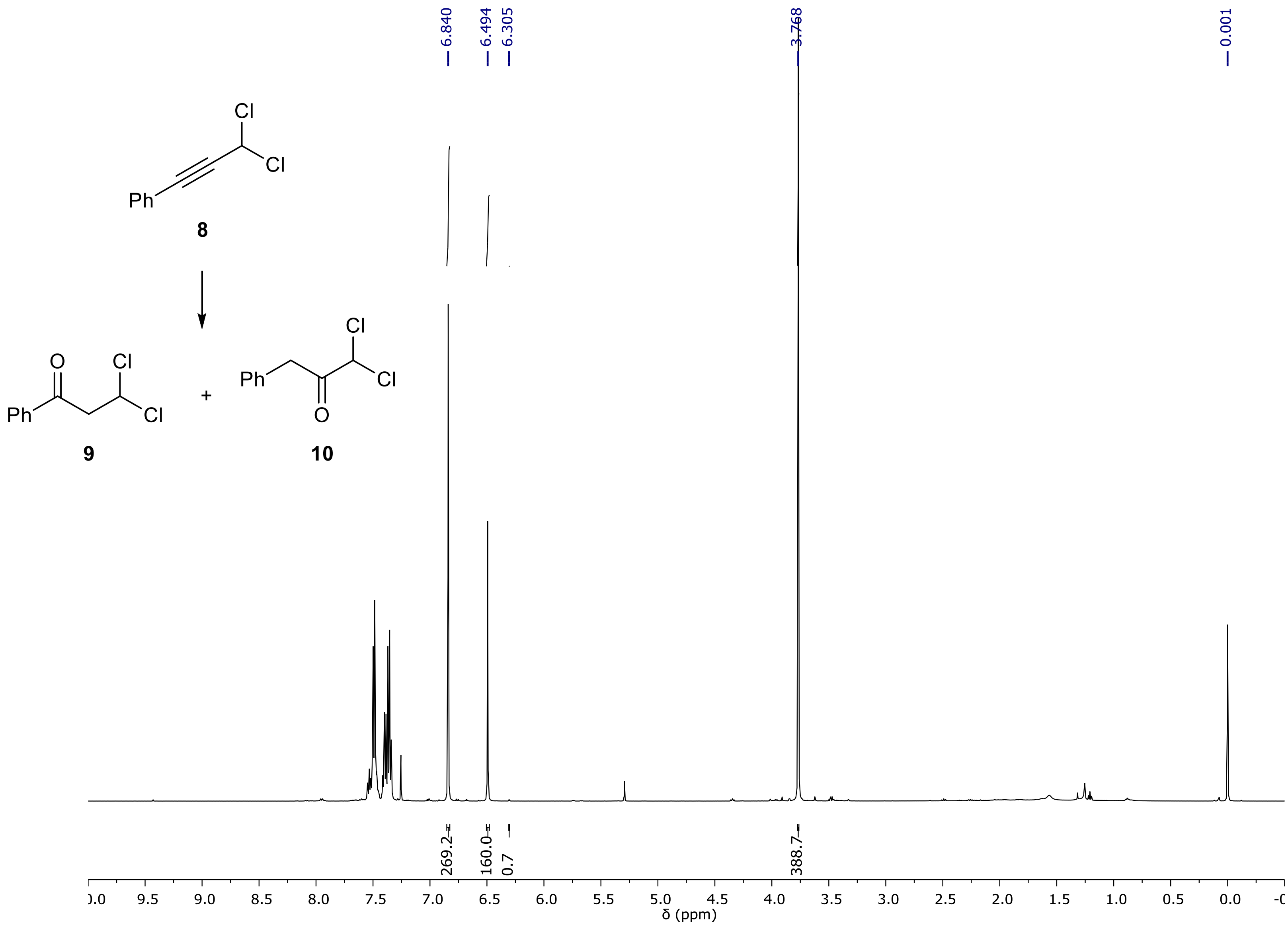
Ph
Me
Ph
Me
+
Ph
O
Me
O

5

6

7

6.839
3.766
2.964
2.949
2.935
2.493
2.478
2.464
2.449
2.440
2.425
2.410
2.395
0.000
155.5
245.3
95.6
68.0
42.2
).0
9.5
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
-(
δ (ppm)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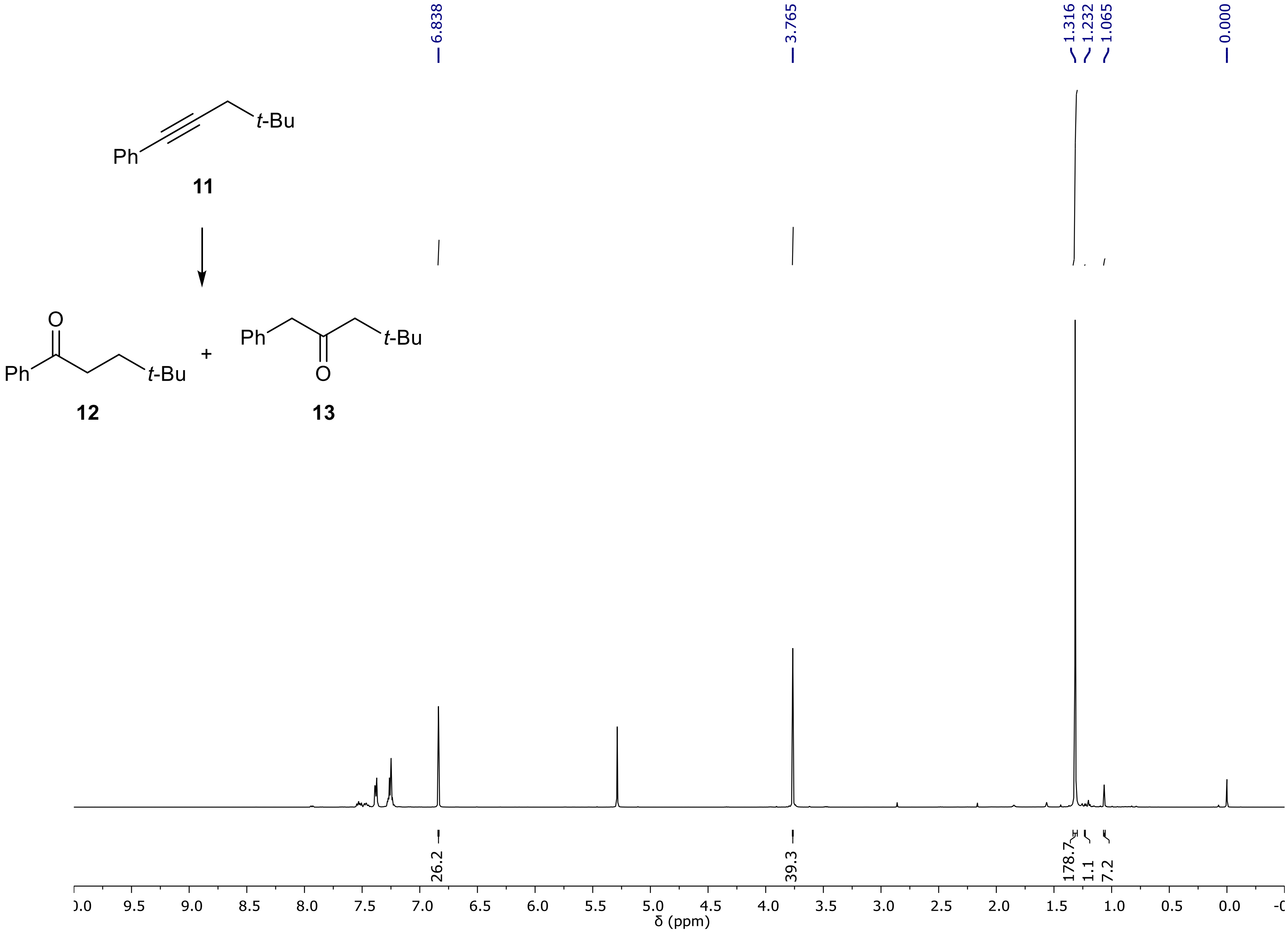
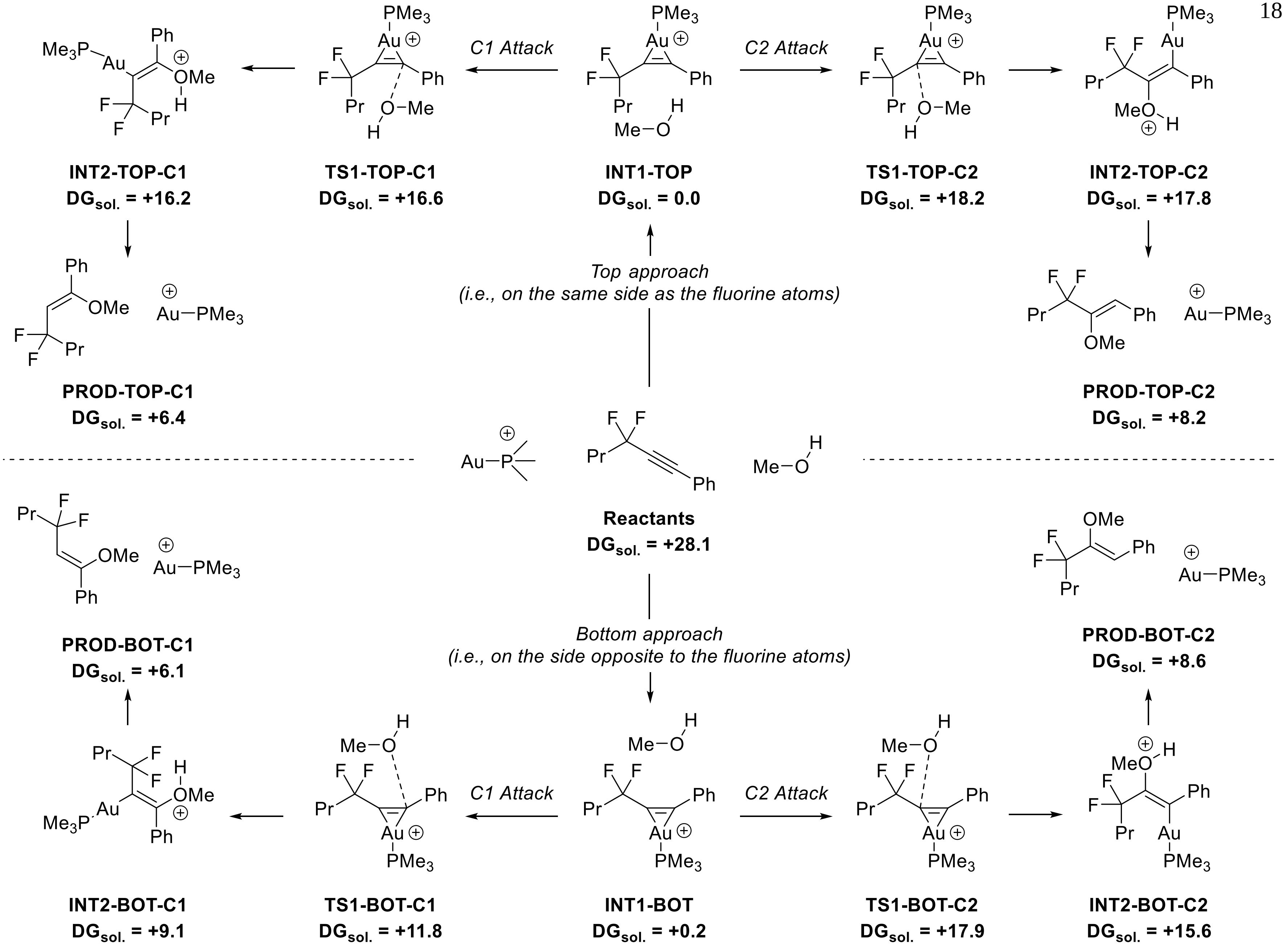
6.494
6.305
3.768
0.001
Cl
Cl
Ph
8
O
Cl
Ph
Cl
9
+
Cl
Ph
Cl
O
10
269.2
160.0
0.7
388.7
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)


Ph
t-Bu
11
O
Ph
t-Bu
12
+
Ph
t-Bu
O
13
6.838
3.765
1.316
1.232
1.065
0.000
26.2
39.3
178.7
1.1
7.2
9.5
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
δ (ppm)

8. DFT calculations

All computations were performed using the May 1, 2013 (R1) version of the GAMESS (US)[30] software package. The program MacMolPlt (version 7.7)[31] was used to help create the input files for each computation. Structure optimizations were performed using the standard convergence criteria of the GAMESS program. Vibrational frequency calculations were performed for all optimized structures in order to verify that the stationary points were true minima, and not transition structures or higher-order loci on the potential energy surface. Each structure was optimized and verified at the DFT level using the BP86 functional and the def2-TZVP basis set[32] obtained from the Basis Set Exchange[33] website. Scalar relativistic effects were introduced by using an effective core potential on gold to describe the innermost 60 electrons with the associated basis set. Solvation effects were considered using the SMD model[34] for ethanol to approximate the 1:1 THF/methanol solvent, by taking a mole fraction-weighted average of the published solvent descriptors.[35]



Scheme S1. Summary of the Structures Computed in this Study.

Table S1. Computed B2PLYP/def2-TZVP//BP86/def2-TZVP Energies for Confirmed Structures

	B2PLYP	**BP86**	
Species	**G(Total)[b]**	**E(Zero-Pt.)**	**G(Total) + E(Zero-Pt.)**
Alkyne-Reactant	-663.8840313651	0.201371	-663.6826603651
Au-Reactant	-596.2949125978	0.112989	-596.1819235978
Methanol	-115.6853347576	0.049466	-115.6358687576
INT1-BOT	-1260.2231678204	0.314107	-1259.9090608204
INT2-BOT-C1	-1375.9006210697	0.369918	-1375.5307030697
INT2-BOT-C2	-1375.8901970183	0.369856	-1375.5203410183
INT1-TOP	-1260.2246108570	0.315270	-1259.9093408570
INT2-TOP-C1	-1375.8884864940	0.369097	-1375.5193894940
INT2-TOP-C2	-1375.8862211619	0.369383	-1375.5168381619
TS1-BOT-C1	-1375.8925341358	0.366137	-1375.5263971358
TS1-BOT-C2	-1375.8827275847	0.366000	-1375.5167275847
TS1-TOP-C1	-1375.8857605657	0.366938	-1375.5188225657
TS1-TOP-C2	-1375.8829889908	0.366726	-1375.5162629908
PROD-BOT-C1	-779.6086992579	0.255142	-779.3535572579
PROD-BOT-C2	-779.6046433722	0.255136	-779.3495073722
PROD-TOP-C1	-779.6084088978	0.255273	-779.3531358978
PROD-TOP-C2	-779.6062960248	0.256042	-779.3502540248

[a] In hartree units.

[b] Total free energy in solution.

Table S2. Optimized Coordinates for [MeOH]

C	6.0	1.41056168	0.45835948	1.23810661
H	1.0	2.51315022	0.41635731	1.27327657
H	1.0	1.04618871	1.03020859	2.10936904
H	1.0	1.01840544	-0.56598091	1.30051684
O	8.0	0.93659759	1.01517749	-0.00165869
H	1.0	1.28722668	1.92084801	-0.08136030

Table S3. Vibrational Frequency Data for [MeOH]

MODE	FREQ(CM**-1)	SYMMETRY	RED. MASS	IR INTENS.
1	11.069	A	1.070703	0.655056
2	6.570	A	2.639427	0.140401
3	2.611	A	2.508256	0.327524
4	0.081	A	5.218692	0.000127
5	0.114	A	5.333318	0.000088
6	0.288	A	5.296226	0.003443
7	289.432	A	1.073498	4.034713
8	987.385	A	5.623363	3.836276
9	1057.961	A	1.171525	0.243237
10	1129.784	A	1.265742	0.009997
11	1341.504	A	1.264713	0.951008
12	1418.297	A	1.119372	0.092189
13	1425.685	A	1.051834	0.137198
14	1446.961	A	1.043279	0.210273
15	2926.720	A	1.033433	1.719422
16	2979.878	A	1.105969	1.722393
17	3042.396	A	1.100239	0.855622
18	3667.167	A	1.066191	1.616257

Table S4. Optimized Coordinates for [Au–PMe$_3^+$]

Au	79.0	-0.54488361	-2.27671814	0.01979788
P	15.0	-0.71031946	-0.04842601	0.18718940
C	6.0	-1.04239726	0.39768538	1.90722024
C	6.0	-2.07999086	0.51739067	-0.85204870
H	1.0	-1.90039647	0.24513951	-1.90131974
H	1.0	-2.16351652	1.61376154	-0.77367342
H	1.0	-3.02188206	0.06313577	-0.51594555
H	1.0	-0.21986878	0.06335580	2.55524349
H	1.0	-1.97628486	-0.07612522	2.24064803
H	1.0	-1.14122951	1.49297774	1.98351669
C	6.0	0.82897812	0.72883385	-0.35682344
H	1.0	1.66607833	0.39477822	0.27187780
H	1.0	0.72099197	1.82156646	-0.26353872
H	1.0	1.03710103	0.47803438	-1.40607369

Table S5. Vibrational Frequency Data for [Au–PMe$_3^+$]

```
MODE FREQ(CM**-1)  SYMMETRY  RED. MASS  IR INTENS.
   1      27.931     A        4.114688    0.073681
   2      12.148     A        3.273388    0.024593
   3       8.996     A        5.174014    0.103394
   4       0.134     A       19.693116    0.000002
   5       0.060     A       19.484114    0.000001
   6       0.119     A       19.682134    0.000001
   7     153.352     A        2.970574    0.001505
   8     167.252     A        2.942888    0.017991
   9     218.598     A        3.383841    0.019918
  10     241.286     A        1.357561    0.003142
  11     246.154     A        2.003442    0.015677
  12     255.738     A        1.895421    0.026184
  13     288.851     A        1.084134    0.007743
  14     311.776     A        1.088507    0.038881
  15     431.949     A        3.858296    1.514874
  16     650.165     A        4.325483    0.743348
  17     747.178     A        3.793125    0.424590
  18     762.652     A        3.745267    0.371387
  19     788.360     A        1.188329    0.037503
  20     853.200     A        1.312785    0.256210
  21     877.379     A        1.254160    0.166921
  22     951.654     A        1.459130    3.065824
  23     958.349     A        1.411705    1.647480
  24     978.231     A        1.384513    5.694196
  25    1276.063     A        1.188503    0.525288
  26    1307.397     A        1.173994    0.525592
  27    1332.128     A        1.154864    0.188035
  28    1369.026     A        1.047767    0.119289
  29    1389.347     A        1.045480    0.280591
  30    1403.894     A        1.044070    0.528822
  31    1418.729     A        1.047372    0.132399
  32    1424.481     A        1.046089    0.367168
  33    1446.357     A        1.039826    0.415548
  34    2976.485     A        1.032940    0.267169
  35    2977.091     A        1.033552    0.183149
  36    2978.781     A        1.033406    0.170264
  37    3059.555     A        1.101695    0.047741
  38    3060.686     A        1.102112    0.004798
  39    3063.012     A        1.102065    0.270041
  40    3071.819     A        1.103008    0.077371
  41    3079.590     A        1.103928    0.044395
  42    3080.033     A        1.104550    0.127705
```

Table S6. Optimized Coordinates for [Alkyne-SM]

C	6.0	-6.21062326	2.24436569	-2.99472475
C	6.0	-5.00535440	1.97153640	-2.09007311
H	1.0	-7.12877798	2.36279964	-2.39955759
H	1.0	-6.37704182	1.41926146	-3.70540047
H	1.0	-6.07307577	3.16757131	-3.58039713
H	1.0	-5.18699598	1.06571281	-1.49033785
H	1.0	-4.88125849	2.80327344	-1.37912118
C	6.0	-3.71770430	1.79771233	-2.90619755
H	1.0	-3.79961896	0.93576765	-3.58844066
C	6.0	-2.46310019	1.58702111	-2.06938410
H	1.0	-3.53589773	2.68264866	-3.53818965
F	9.0	-2.61395693	0.44809729	-1.26004815
F	9.0	-2.31155396	2.64596057	-1.16190517
C	6.0	-1.23540497	1.46099234	-2.84621882
C	6.0	-0.24825270	1.40943336	-3.55725074
C	6.0	0.90772885	1.39336419	-4.39000893
C	6.0	1.05431700	0.42336744	-5.40539694
C	6.0	1.90731680	2.37649465	-4.21944618
C	6.0	2.17589545	0.44814044	-6.23488808
C	6.0	3.02183652	2.39165330	-5.05751181
C	6.0	3.15811086	1.43167973	-6.06744051
H	1.0	0.28369194	-0.33822840	-5.53857136
H	1.0	1.79506063	3.12369370	-3.43158865
H	1.0	3.78741074	3.15881467	-4.92273712
H	1.0	2.28197026	-0.30266434	-7.02114820
H	1.0	4.03024721	1.45010006	-6.72486591

Table S7. Vibrational Frequency Data for [Alkyne-SM]

```
MODE FREQ(CM**-1)  SYMMETRY  RED. MASS  IR INTENS.
   1       25.160   A        4.137732    0.015562
   2       11.845   A        4.888321    0.002017
   3        6.328   A        5.556799    0.008277
   4        0.362   A        7.462007    0.000028
   5        0.227   A        7.459439    0.000005
   6        0.024   A        7.457074    0.000001
   7       32.799   A        3.978830    0.017022
   8       42.390   A        4.788582    0.025767
   9       83.382   A        5.207892    0.003898
  10       86.777   A        2.234788    0.024576
  11      119.029   A        3.753648    0.004879
  12      126.168   A        3.391840    0.011204
  13      171.887   A        6.490085    0.014616
  14      201.799   A        4.912720    0.132711
  15      245.202   A        1.149712    0.000229
  16      254.360   A        6.631141    0.009097
  17      310.854   A        3.539964    0.056168
  18      332.870   A        4.696733    0.045562
  19      355.260   A        3.439661    0.026962
  20      385.383   A        2.928879    0.001039
  21      425.864   A        7.321666    0.035043
  22      499.511   A        6.595759    0.057191
  23      520.033   A        5.515000    0.119864
  24      536.912   A        6.068321    0.363564
  25      560.029   A        7.327354    0.109936
  26      594.132   A        7.364800    0.887030
  27      625.074   A        6.658644    0.003260
  28      678.182   A        1.812848    1.712216
  29      726.409   A        4.064738    0.503070
  30      732.727   A        1.260828    0.101816
  31      747.758   A        1.912638    1.725864
  32      806.046   A        5.715899    1.683775
  33      817.674   A        2.124762    3.412984
  34      823.184   A        1.256790    0.030580
  35      891.717   A        1.911289    0.146573
  36      902.780   A        1.402231    0.115356
  37      906.625   A        1.818538    3.009760
  38      941.161   A        1.360008    0.006782
  39      965.481   A        1.282775    0.003500
  40      988.045   A        6.106649    0.272087
  41     1013.924   A        3.341638    2.458686
  42     1030.001   A        2.804734    0.093416
  43     1044.784   A        2.362167    2.493735
  44     1091.905   A        1.602378    0.203762
  45     1108.997   A        3.827880    6.376302
```

46	1109.443	A	1.864181	1.208350
47	1115.286	A	3.147304	3.589069
48	1165.120	A	1.082031	0.007953
49	1184.690	A	1.137398	0.004203
50	1230.907	A	1.262097	0.177582
51	1263.203	A	2.290849	0.719844
52	1297.892	A	1.166771	0.249186
53	1303.895	A	1.754738	1.737866
54	1310.791	A	2.262408	0.083607
55	1345.052	A	2.397260	0.025828
56	1351.754	A	1.422384	0.655263
57	1361.013	A	1.392645	0.713130
58	1424.251	A	1.037664	0.231689
59	1426.436	A	1.060175	0.177739
60	1430.535	A	1.057240	0.160506
61	1445.882	A	2.183758	0.255871
62	1453.328	A	1.097348	0.372111
63	1495.360	A	2.196875	0.836820
64	1571.459	A	5.058479	0.054648
65	1598.301	A	5.356626	0.001246
66	2245.309	A	11.998705	6.557196
67	2954.541	A	1.036088	0.815608
68	2967.575	A	1.059301	0.092932
69	2977.738	A	1.060019	0.997197
70	2996.775	A	1.100180	0.026951
71	3012.927	A	1.102730	0.039686
72	3027.112	A	1.102063	1.261194
73	3029.012	A	1.102920	1.419512
74	3100.340	A	1.086175	0.022088
75	3107.245	A	1.088456	0.064617
76	3114.825	A	1.092336	0.220409
77	3121.348	A	1.094857	0.278149
78	3125.231	A	1.097490	0.118436

Table S8. Optimized Coordinates for [INT1-BOT]

C	6.0	-3.21411204	2.12317348	0.93270832
C	6.0	-2.92452621	1.90787804	2.13075924
C	6.0	-2.78040123	2.10537696	-0.49830440
C	6.0	-2.57113934	1.60820925	3.46565008
C	6.0	-2.01132178	2.60362411	4.30325079
C	6.0	-2.74373960	0.28652480	3.94599581
C	6.0	-1.62473536	2.26883650	5.59761667
C	6.0	-2.34851766	-0.02874589	5.24193525
C	6.0	-1.79071832	0.95830780	6.06571484
H	1.0	-1.88280630	3.62006855	3.92641640
H	1.0	-1.19059920	3.03238797	6.24555779
H	1.0	-3.17692447	-0.47247639	3.29245210
H	1.0	-2.47499681	-1.04755616	5.61380291
H	1.0	-1.48152661	0.70282191	7.08214521
C	6.0	-2.83653402	3.45807910	-1.18742907
F	9.0	-3.58081841	1.18332911	-1.17067277
F	9.0	-1.49463904	1.57949364	-0.54571557
H	1.0	-3.88756084	3.78879547	-1.13878357
C	6.0	-2.33458996	3.45098400	-2.63731408
H	1.0	-2.25482345	4.16516924	-0.57308376
H	1.0	-2.90182447	2.70807838	-3.22001576
H	1.0	-1.27966380	3.13549137	-2.65818954
C	6.0	-2.47634459	4.83049488	-3.28556871
H	1.0	-3.52648497	5.16319704	-3.29763985
H	1.0	-2.12205482	4.81290436	-4.32732010
H	1.0	-1.88953602	5.59280062	-2.74841452
Au	79.0	-5.12048817	2.87549829	1.61205065
P	15.0	-7.22800684	3.74220037	1.93657994
C	6.0	-7.20264149	5.33709383	2.80991626
C	6.0	-8.29419327	2.63376141	2.90949583
H	1.0	-6.60882282	6.06656599	2.24160504
H	1.0	-6.75104618	5.21391916	3.80439186
H	1.0	-8.22933006	5.71708918	2.92502284
H	1.0	-8.39419842	1.66434789	2.40084863
H	1.0	-9.29246330	3.08291316	3.02740383
H	1.0	-7.85406303	2.46469188	3.90252709
C	6.0	-8.09004593	4.03780317	0.36209708
H	1.0	-7.51629972	4.74296761	-0.25595260
H	1.0	-9.08544064	4.46404839	0.56122351
H	1.0	-8.20952129	3.09645176	-0.19306393

Table S9. Vibrational Frequency Data for [INT1-BOT]

```
MODE FREQ(CM**-1)  SYMMETRY  RED. MASS  IR INTENS.
   1      19.946     A        5.733261    0.021557
   2       8.836     A        5.836321    0.031224
   3       7.039     A        5.073277    0.042065
   4       0.503     A       11.678887    0.000045
   5       0.228     A       11.653591    0.000002
   6       0.090     A       11.662452    0.000003
   7      22.865     A        4.486668    0.017281
   8      29.123     A        4.447233    0.026026
   9      34.417     A        4.154234    0.035891
  10      38.150     A        3.958754    0.003425
  11      39.971     A        5.411044    0.078157
  12      52.251     A        4.046677    0.007734
  13      68.607     A        5.673293    0.198023
  14      73.500     A        5.712531    0.021516
  15      89.256     A        2.029173    0.018980
  16     104.959     A        3.049902    0.004542
  17     117.166     A        4.909112    0.179489
  18     127.830     A        4.899258    0.145884
  19     165.678     A        2.811268    0.093399
  20     175.228     A        2.574004    0.050012
  21     183.362     A        1.304080    0.028109
  22     192.792     A        3.071009    0.040746
  23     204.971     A        5.898149    0.064540
  24     216.169     A        6.924164    0.062953
  25     221.712     A        1.132847    0.012678
  26     257.412     A        2.631345    0.059023
  27     260.830     A        1.655281    0.042075
  28     268.147     A        2.145210    0.109969
  29     272.571     A        2.560516    0.041624
  30     317.894     A        1.020934    0.005263
  31     318.753     A        3.228323    0.025790
  32     343.780     A        4.791459    1.306695
  33     362.580     A        3.965685    0.536318
  34     376.494     A        3.402286    0.206857
  35     388.436     A        2.906252    0.000385
  36     441.953     A        8.319310    0.025742
  37     502.541     A        6.343434    0.125725
  38     515.869     A        5.671520    1.011234
  39     534.408     A        8.073988    0.638621
  40     567.315     A        7.440110    0.330664
  41     607.815     A        6.687505    0.031411
  42     620.255     A        7.984644    6.307429
  43     659.181     A        4.261755    0.692728
  44     673.226     A        1.837308    1.591989
  45     726.932     A        1.250907    0.015413
```

46	735.601	A	3.808820	0.534865
47	736.305	A	3.711660	0.354244
48	737.786	A	4.262311	0.231153
49	756.373	A	1.793163	1.484688
50	784.168	A	1.195000	0.040156
51	807.517	A	5.266771	1.830429
52	836.455	A	1.258270	0.139971
53	838.207	A	1.666403	1.631150
54	840.397	A	1.280426	0.235843
55	846.282	A	1.260089	0.424067
56	895.405	A	2.045265	0.692711
57	928.876	A	2.385912	4.165220
58	931.723	A	1.370791	0.097377
59	935.985	A	1.438642	4.160134
60	945.942	A	1.451640	7.123954
61	951.823	A	1.404496	1.314532
62	966.655	A	1.371428	0.041772
63	982.800	A	5.235959	0.490124
64	986.513	A	1.346580	0.008513
65	1013.507	A	3.204822	3.025666
66	1020.935	A	2.300469	1.090637
67	1033.263	A	2.914687	1.300265
68	1083.507	A	1.593420	0.216360
69	1108.475	A	2.768112	5.097444
70	1115.827	A	1.864654	1.184871
71	1126.955	A	5.094318	4.624417
72	1165.736	A	1.091958	0.169501
73	1185.717	A	1.158671	0.511023
74	1235.598	A	1.415559	0.720700
75	1246.440	A	2.750012	0.551927
76	1275.502	A	1.202239	0.467514
77	1283.698	A	1.198538	0.422847
78	1298.978	A	1.317537	0.220474
79	1301.529	A	1.676432	0.016590
80	1303.365	A	1.182961	0.082790
81	1304.269	A	1.260252	0.183609
82	1335.783	A	3.606695	0.364758
83	1359.109	A	1.380197	0.393056
84	1367.252	A	1.356924	0.503158
85	1385.531	A	1.044656	0.194702
86	1389.159	A	1.048740	0.022945
87	1397.780	A	1.044791	0.017710
88	1406.691	A	1.044498	0.397437
89	1412.143	A	1.044878	0.579307
90	1414.463	A	1.082737	0.105620
91	1421.370	A	1.042170	0.194348
92	1430.193	A	1.042366	0.113736
93	1435.288	A	2.185074	0.732631

94	1441.132	A	1.037829	0.413387
95	1451.857	A	1.096804	0.305555
96	1476.506	A	2.063222	0.159032
97	1554.351	A	4.825087	0.011777
98	1580.700	A	5.198107	2.959092
99	2045.826	A	11.993597	21.615772
100	2955.500	A	1.036361	0.829543
101	2965.124	A	1.059361	0.194961
102	2970.823	A	1.033750	0.021980
103	2972.021	A	1.033898	0.010197
104	2974.182	A	1.033905	0.001932
105	2975.192	A	1.059516	1.114801
106	2995.163	A	1.100742	0.014033
107	3012.060	A	1.102631	0.030978
108	3026.826	A	1.103335	1.432173
109	3028.485	A	1.101435	1.213250
110	3056.264	A	1.101532	0.003152
111	3056.389	A	1.102686	0.004057
112	3056.929	A	1.102422	0.006694
113	3066.383	A	1.102490	0.000768
114	3069.904	A	1.103065	0.000357
115	3070.216	A	1.102547	0.004043
116	3106.035	A	1.086487	0.023350
117	3113.568	A	1.087971	0.054729
118	3119.811	A	1.091986	0.015574
119	3127.842	A	1.094781	0.064927
120	3130.872	A	1.097398	0.146945

Table S10. Optimized Coordinates for [TS1-BOT-C1]

C	6.0	-0.97962731	1.23378098	0.73202091
C	6.0	-0.87008125	0.66923940	1.89152396
C	6.0	0.02707388	1.29754305	-0.38778934
C	6.0	-1.52213764	0.18940629	3.07673120
C	6.0	-1.12914693	0.60655367	4.36721468
C	6.0	-2.59773493	-0.71670347	2.92913604
C	6.0	-1.81764984	0.13618100	5.48330116
C	6.0	-3.28055239	-1.17492163	4.05417347
C	6.0	-2.89256167	-0.75006539	5.33009720
H	1.0	-2.88425231	-1.04964530	1.92991233
H	1.0	-4.11458397	-1.86939108	3.93427062
H	1.0	-3.42775035	-1.11238372	6.21066141
C	6.0	-0.39914343	2.00896764	-1.65598416
F	9.0	0.42293358	-0.00996967	-0.69665343
F	9.0	1.20731735	1.90151215	0.11336775
H	1.0	-1.29008770	1.47918344	-2.03451681
C	6.0	0.68257105	2.08977318	-2.74082518
H	1.0	-0.73616397	3.01778126	-1.36421537
H	1.0	1.01083720	1.07414556	-3.01298976
H	1.0	1.56603563	2.61226511	-2.34157610
C	6.0	0.17759174	2.81716299	-3.98987556
H	1.0	-0.68751121	2.29954386	-4.43413353
H	1.0	0.96435010	2.87095666	-4.75755215
H	1.0	-0.13170971	3.84910035	-3.75855827
Au	79.0	-2.87435150	2.16847253	0.63993472
P	15.0	-4.88251495	3.27863383	0.47876379
C	6.0	-5.42239904	3.55150938	-1.24089420
C	6.0	-4.84296227	4.93095732	1.25047302
H	1.0	-5.55046701	2.58855844	-1.75560665
H	1.0	-4.66638565	4.13817167	-1.78154099
H	1.0	-6.37940359	4.09599113	-1.26044619
H	1.0	-4.57820797	4.84310293	2.31369686
H	1.0	-5.82566595	5.42045069	1.16607904
H	1.0	-4.08777523	5.55656433	0.75394911
C	6.0	-6.25711918	2.39339900	1.28752291
H	1.0	-6.41628981	1.41943896	0.80224830
H	1.0	-7.18478870	2.98188758	1.21669781
H	1.0	-6.02249289	2.21942949	2.34702444
O	8.0	0.98909152	0.14685060	2.29503441
C	6.0	1.27202463	-1.27947700	2.34238839
H	1.0	1.05026388	-1.76590478	1.38299549
H	1.0	0.64583027	-1.70108557	3.13697076
H	1.0	2.33114529	-1.41466594	2.60351253
H	1.0	1.52428949	0.57282096	1.59011734
H	1.0	-1.51639998	0.46573141	6.47981787
H	1.0	-0.29200944	1.29604006	4.48253059

Table S11. Vibrational Frequency Data for [TS1-BOT-C1]

```
MODE FREQ(CM**-1)  SYMMETRY  RED. MASS  IR INTENS.
   1    -197.909   A         7.718939   11.657297
   2      13.704   A         4.937498    0.006158
   3       8.967   A         5.334148    0.008229
   4       6.789   A         5.227823    0.004952
   5       0.792   A        10.907501    0.000035
   6       0.332   A        10.867178    0.000007
   7       0.283   A        10.824373    0.000007
   8      29.601   A         4.050334    0.110330
   9      36.230   A         4.413903    0.047442
  10      40.977   A         4.187276    0.021375
  11      49.395   A         4.437829    0.056085
  12      52.156   A         2.232232    0.068961
  13      56.692   A         3.209343    0.023483
  14      61.071   A         2.631652    0.055451
  15      78.448   A         4.240091    0.037775
  16      87.301   A         2.759240    0.001532
  17      98.908   A         3.941711    0.131946
  18     111.951   A         3.261819    0.048540
  19     114.565   A         2.331005    0.022859
  20     131.977   A         4.104793    0.084635
  21     156.048   A         3.702675    0.024702
  22     162.871   A         2.328022    0.006993
  23     170.120   A         1.351013    0.024018
  24     173.999   A         2.647904    0.072363
  25     179.857   A         2.268769    0.037382
  26     193.000   A         3.841342    0.024098
  27     199.829   A         4.066377    0.112504
  28     219.502   A         1.137503    0.003831
  29     223.835   A         5.448841    0.126470
  30     229.916   A         6.135159    0.597654
  31     245.622   A         3.476131    1.590786
  32     255.610   A         1.268673    0.013554
  33     267.595   A         2.563015    0.049323
  34     278.232   A         2.594436    0.103630
  35     282.319   A         5.269079    0.556734
  36     294.275   A         1.028780    0.001525
  37     325.691   A         3.351894    0.091379
  38     352.621   A         4.875219    0.905989
  39     357.719   A         3.949322    0.221799
  40     385.714   A         3.070676    0.099940
  41     392.404   A         2.854124    0.008181
  42     491.116   A         6.146771    1.079863
  43     507.948   A         4.201840    0.561899
  44     519.503   A         3.709968    0.852212
  45     542.833   A         4.225911    1.345752
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46     583.017    A        2.505054    2.891997
47     594.518    A        3.509602    2.373914
48     621.685    A        6.533607    0.239335
49     661.019    A        4.212655    0.571989
50     680.017    A        1.708199    2.066644
51     711.098    A        4.843552    1.441733
52     729.252    A        3.903046    0.508157
53     732.457    A        3.859198    0.476597
54     739.600    A        1.176839    0.084298
55     757.055    A        2.045118    1.037308
56     782.660    A        2.824820    1.868036
57     782.922    A        1.603511    0.740192
58     796.751    A        4.875653    2.161120
59     822.923    A        2.130072    2.508653
60     826.561    A        1.248760    0.001225
61     845.211    A        1.276062    0.338745
62     847.628    A        1.261196    0.274494
63     898.127    A        1.998634    0.402002
64     910.724    A        1.792939    2.136067
65     925.102    A        1.384165    0.073760
66     939.837    A        1.399194    1.292763
67     945.133    A        1.587365    8.996390
68     949.703    A        1.646304    4.147824
69     953.879    A        2.441773    0.628171
70     954.892    A        1.691115    0.256770
71     978.863    A        1.325620    0.009610
72     986.088    A        5.790351    0.408158
73    1015.364    A        3.106328    2.894811
74    1020.382    A        2.262493    0.661390
75    1038.079    A        2.958969    2.217029
76    1064.553    A        1.151547    1.171109
77    1081.037    A        1.528200    0.257245
78    1111.802    A        2.042034    2.022244
79    1117.415    A        2.488332    3.903513
80    1136.527    A        2.400707    2.793848
81    1138.675    A        1.471743    0.340412
82    1166.980    A        1.206233    0.005990
83    1183.289    A        1.126192    0.001334
84    1225.862    A        3.177250    0.293191
85    1237.494    A        1.269407    0.112180
86    1277.219    A        1.201231    0.392882
87    1285.089    A        1.202884    0.522585
88    1293.512    A        1.579290    0.096358
89    1296.393    A        1.506937    0.443379
90    1300.360    A        1.138200    0.247861
91    1305.353    A        1.188506    0.098457
92    1312.608    A        1.231854    0.694499
93    1336.852    A        4.780040    0.413413
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 94    1360.739    A          1.580096    1.082011
 95    1369.417    A          1.269964    0.246921
 96    1382.498    A          1.049473    0.048358
 97    1391.872    A          1.045625    0.011036
 98    1394.683    A          1.045189    0.094211
 99    1398.202    A          1.046136    0.555382
100    1410.273    A          1.085654    0.085586
101    1411.097    A          1.077274    0.258168
102    1411.273    A          1.073647    0.466264
103    1422.152    A          1.041168    0.319421
104    1426.157    A          1.051564    0.559812
105    1428.378    A          1.042809    0.094912
106    1437.618    A          1.039752    0.411470
107    1439.371    A          2.130526    0.488408
108    1449.533    A          1.051342    0.217617
109    1451.770    A          1.095962    0.377091
110    1471.740    A          2.175469    0.032764
111    1566.703    A          4.588947    0.080431
112    1581.967    A          5.619702    1.457577
113    1788.184    A         11.727779   23.283914
114    2955.106    A          1.036508    0.911267
115    2962.231    A          1.059454    0.451964
116    2970.011    A          1.033994    0.117641
117    2970.957    A          1.034446    0.027805
118    2971.831    A          1.034063    0.024438
119    2974.917    A          1.059502    1.140702
120    2978.798    A          1.030135    0.841700
121    2993.852    A          1.100017    0.015733
122    3009.743    A          1.102295    0.029589
123    3025.867    A          1.102524    1.455333
124    3027.604    A          1.102048    1.375816
125    3052.740    A          1.102084    0.004725
126    3053.326    A          1.102273    0.025365
127    3054.696    A          1.102351    0.086221
128    3058.052    A          1.107728    0.195112
129    3065.156    A          1.102523    0.001253
130    3066.169    A          1.102656    0.008624
131    3066.566    A          1.102307    0.000781
132    3090.841    A          1.105606    0.182281
133    3097.498    A          1.086706    0.016898
134    3108.731    A          1.088790    0.104577
135    3114.079    A          1.092564    0.245499
136    3123.431    A          1.095300    0.061644
137    3129.064    A          1.095102    0.103949
138    3541.451    A          1.067022    6.407213
```

Table S12. Optimized Coordinates for [INT2-BOT-C1]

C	6.0	-3.33144331	2.22003031	1.74513412
C	6.0	-2.77523685	1.97182763	2.94004583
C	6.0	-2.57866287	1.92554295	0.47134519
C	6.0	-3.30985594	1.98826778	4.30276680
C	6.0	-2.58014393	2.54848599	5.37154722
C	6.0	-4.58279800	1.43599391	4.55317879
C	6.0	-3.12908649	2.57752538	6.65423727
C	6.0	-5.12435484	1.47098875	5.83840561
C	6.0	-4.40161133	2.04478621	6.89047480
H	1.0	-1.59303606	2.98052573	5.19453478
H	1.0	-2.56245089	3.02371430	7.47453690
H	1.0	-5.13257313	0.95916319	3.73945379
H	1.0	-6.10914135	1.03467333	6.02042294
H	1.0	-4.82703161	2.06967545	7.89638424
C	6.0	-3.14218473	2.42788792	-0.83796144
F	9.0	-2.35846400	0.54645813	0.39042515
F	9.0	-1.21227753	2.45248938	0.59198165
H	1.0	-4.12022829	1.92938578	-0.95101625
C	6.0	-2.26061893	2.17268515	-2.06840730
H	1.0	-3.35392141	3.50345182	-0.72184628
H	1.0	-2.01744366	1.10035300	-2.13483882
H	1.0	-1.30568457	2.70829129	-1.95239544
C	6.0	-2.94879341	2.62364125	-3.35983348
H	1.0	-3.88932276	2.07496810	-3.52708697
H	1.0	-2.30026293	2.44626641	-4.23110247
H	1.0	-3.18715644	3.69915962	-3.33740163
Au	79.0	-5.21077442	3.11084557	1.63430679
P	15.0	-7.23415947	4.20819950	1.42858565
C	6.0	-8.28287315	3.52723575	0.09784053
C	6.0	-7.05072641	5.97884417	1.01918054
H	1.0	-8.52478409	2.47523355	0.30733386
H	1.0	-7.74554253	3.57497597	-0.86021239
H	1.0	-9.21983337	4.09849072	0.01081638
H	1.0	-6.50825167	6.49465942	1.82455206
H	1.0	-8.03482151	6.45391989	0.88836676
H	1.0	-6.47273970	6.08282423	0.09021471
C	6.0	-8.27654934	4.16579962	2.92681432
H	1.0	-8.50020409	3.12452817	3.19988322
H	1.0	-9.22230434	4.70329332	2.75868821
H	1.0	-7.74306297	4.63569546	3.76564050
O	8.0	-1.28167355	1.66593575	2.98388529
C	6.0	-0.83818281	0.28599742	3.34771633
H	1.0	-1.20115042	-0.41924980	2.59206796
H	1.0	-1.26533806	0.07855914	4.33146763
H	1.0	0.25485024	0.32926375	3.38680959
H	1.0	-0.92369437	1.95654941	2.08490634

Table S13. Vibrational Frequency Data for [INT2-BOT-C1]

```
MODE FREQ(CM**-1)  SYMMETRY  RED. MASS  IR INTENS.
   1      16.811     A        5.062861    0.011597
   2      10.868     A        5.566068    0.004013
   3       5.964     A        5.413425    0.001284
   4       0.601     A       10.894803    0.000003
   5       0.271     A       10.871508    0.000010
   6       0.143     A       10.823055    0.000007
   7      21.090     A        5.947539    0.008967
   8      31.746     A        4.636869    0.049458
   9      40.747     A        5.185696    0.087340
  10      55.961     A        4.996942    0.067360
  11      62.406     A        5.137505    0.015804
  12      66.497     A        2.925849    0.002623
  13      73.516     A        4.259316    0.050900
  14      76.739     A        4.721100    0.044603
  15     111.360     A        3.112026    0.005750
  16     126.533     A        2.996820    0.071122
  17     137.504     A        4.200312    0.122848
  18     149.532     A        3.568108    0.124242
  19     155.653     A        2.491771    0.029475
  20     167.929     A        3.348693    0.135414
  21     174.580     A        2.972490    0.004441
  22     186.613     A        4.193882    0.114927
  23     192.120     A        1.684645    0.021440
  24     193.243     A        1.908364    0.051028
  25     232.362     A        6.432119    0.067781
  26     233.009     A        5.733918    0.010708
  27     244.690     A        1.312279    0.019464
  28     248.648     A        3.708946    0.117854
  29     257.354     A        1.515286    0.031668
  30     265.197     A        2.189872    0.043002
  31     272.369     A        1.275679    0.012373
  32     277.984     A        1.247919    0.043621
  33     293.728     A        4.418885    0.713522
  34     307.632     A        3.832298    0.049727
  35     332.543     A        2.689103    0.135575
  36     344.376     A        1.177490    0.001635
  37     349.164     A        3.856771    0.527263
  38     387.180     A        3.194827    0.122068
  39     403.479     A        2.874202    0.026703
  40     424.917     A        4.146438    0.308355
  41     463.108     A        5.933665    0.550628
  42     495.773     A        9.052555    0.175657
  43     536.891     A        6.068767    0.745285
  44     587.196     A        6.441352    0.391382
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45      613.106     A          6.479320    0.297248
46      625.566     A          6.231534    3.603820
47      657.068     A          4.447458    0.760257
48      657.503     A          4.553795    1.484583
49      673.773     A          6.239032    3.053436
50      688.306     A          1.734389    2.249949
51      725.625     A          4.081735    0.525409
52      728.254     A          3.937777    0.469676
53      735.450     A          2.343892    1.609329
54      758.954     A          1.852715    1.956713
55      762.249     A          1.944020    1.885504
56      783.591     A          1.177451    0.000432
57      813.724     A          3.824695    4.500712
58      828.558     A          1.274893    0.196846
59      832.267     A          4.967294    1.866837
60      843.315     A          1.257326    0.274481
61      845.785     A          1.263478    0.429169
62      893.591     A          1.816997    0.896509
63      901.941     A          1.723290    0.294129
64      913.562     A          1.445980    0.108922
65      927.145     A          4.338935    3.043877
66      937.279     A          1.384784    1.280941
67      944.166     A          1.408258    1.147101
68      949.248     A          1.475354    5.690020
69      952.864     A          1.382049    0.520672
70      974.109     A          1.303734    0.022958
71      988.013     A          6.046083    0.172127
72     1009.781     A          2.388636    3.804828
73     1028.957     A          2.190364    0.380282
74     1033.364     A          2.168980    0.618937
75     1050.246     A          1.612958    2.971494
76     1090.860     A          1.632691    0.086607
77     1101.601     A          1.824271    0.648072
78     1120.261     A          2.554065    4.557079
79     1135.970     A          2.487607    3.160258
80     1144.541     A          1.365214    0.388349
81     1167.233     A          1.086475    0.028039
82     1184.040     A          1.147174    0.007639
83     1201.700     A          1.527019    0.995165
84     1241.434     A          1.956891    0.573543
85     1243.899     A          1.425305    0.074270
86     1276.322     A          1.204008    0.468574
87     1279.382     A          1.204737    0.434313
88     1295.365     A          1.308027    0.267716
89     1298.249     A          1.188718    0.030214
90     1313.173     A          1.941874    0.072631
91     1315.775     A          1.261969    0.515335
92     1342.750     A          2.768024    0.066884
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  93    1362.244    A         1.478586    0.791644
  94    1370.570    A         1.307050    0.369345
  95    1386.066    A         1.049389    0.045461
  96    1390.708    A         1.044526    0.047741
  97    1399.570    A         1.048417    0.143778
  98    1406.356    A         1.044164    0.454663
  99    1409.333    A         1.045217    0.424772
 100    1410.443    A         1.088998    0.160314
 101    1422.163    A         1.041787    0.442063
 102    1424.167    A         1.113063    0.479763
 103    1431.837    A         1.042975    0.073185
 104    1439.754    A         2.063738    0.354374
 105    1443.389    A         1.039972    0.411727
 106    1445.563    A         1.207235    0.765989
 107    1452.545    A         1.095175    0.343288
 108    1469.338    A         1.117429    0.414686
 109    1485.796    A         2.035830    0.729159
 110    1492.471    A         1.069045    0.307379
 111    1567.489    A         5.142882    0.167109
 112    1594.232    A         5.350099    0.352952
 113    1620.423    A         6.127318   10.956062
 114    2955.193    A         1.036424    0.933038
 115    2964.658    A         1.059695    0.330537
 116    2968.781    A         1.034265    0.163290
 117    2970.137    A         1.034355    0.044991
 118    2972.113    A         1.034205    0.044082
 119    2974.106    A         1.061090    1.094078
 120    2997.277    A         1.099070    0.046025
 121    3013.071    A         1.102058    0.125729
 122    3021.164    A         1.030864    3.075945
 123    3026.350    A         1.101946    1.317066
 124    3030.294    A         1.102334    1.181728
 125    3046.311    A         1.070822   21.128777
 126    3052.086    A         1.101747    0.044721
 127    3052.713    A         1.102171    0.107288
 128    3054.736    A         1.101943    0.069747
 129    3062.558    A         1.101995    0.036971
 130    3064.173    A         1.102331    0.011055
 131    3066.681    A         1.102340    0.019037
 132    3101.990    A         1.086197    0.023163
 133    3109.703    A         1.087914    0.038202
 134    3115.626    A         1.091411    0.244728
 135    3122.932    A         1.093539    0.160672
 136    3126.983    A         1.097721    0.078848
 137    3131.332    A         1.110548    0.025717
 138    3138.656    A         1.111666    0.031160
```

Table S14. Optimized Coordinates for [PROD-BOT-C1]

C	6.0	-2.91912580	2.41172886	1.87134922
C	6.0	-2.41281867	1.92524874	3.02907920
C	6.0	-2.23553824	2.41134953	0.54040867
C	6.0	-3.18404675	1.94109333	4.29925823
C	6.0	-2.56283998	2.36652136	5.48958111
C	6.0	-4.53994942	1.56882238	4.33483553
C	6.0	-3.28613210	2.43239141	6.68121052
C	6.0	-5.26088238	1.63406396	5.53008890
C	6.0	-4.63746548	2.06581879	6.70580339
H	1.0	-1.51245582	2.66653609	5.47009563
H	1.0	-2.79377723	2.77370763	7.59501171
H	1.0	-5.02443886	1.20887327	3.42395186
H	1.0	-6.31214714	1.33657742	5.54606009
H	1.0	-5.20199347	2.11239004	7.64008570
C	6.0	-3.15874982	2.74914837	-0.62314814
F	9.0	-1.62052107	1.17252111	0.29578957
F	9.0	-1.15879142	3.32951283	0.54271340
H	1.0	-3.98798418	2.02165747	-0.60297358
C	6.0	-2.48601818	2.75888205	-2.00010180
H	1.0	-3.60387611	3.73553419	-0.40752324
H	1.0	-2.04154229	1.77083743	-2.19942236
H	1.0	-1.65565586	3.48295522	-1.99866652
C	6.0	-3.47228956	3.11170030	-3.11760616
H	1.0	-4.30493593	2.39139152	-3.16006517
H	1.0	-2.97494578	3.10488248	-4.09975815
H	1.0	-3.90586019	4.11454487	-2.97181249
H	1.0	-3.90432239	2.87922573	1.89999330
O	8.0	-1.10847735	1.50654221	3.07379007
C	6.0	-0.84281492	0.24174513	3.72500968
H	1.0	-1.29806721	-0.58244747	3.15353727
H	1.0	-1.21408057	0.22058907	4.75986433
H	1.0	0.24829395	0.13095443	3.72623086

Table S15. Vibrational Frequency Data for [PROD-BOT-C1]

```
 MODE FREQ(CM**-1)  SYMMETRY  RED. MASS  IR INTENS.
    1      11.382    A         4.881925    0.014441
    2       5.930    A         4.669656    0.004608
    3       4.790    A         5.080237    0.007887
    4       0.439    A         7.090984    0.000051
    5       0.229    A         7.076987    0.000004
    6       0.020    A         7.064954    0.000002
    7      38.712    A         5.704458    0.063163
    8      50.542    A         4.578588    0.014656
    9      63.019    A         4.851984    0.003507
   10      74.281    A         3.011884    0.011977
   11     104.249    A         2.914246    0.028297
   12     123.186    A         1.499234    0.010231
   13     124.954    A         1.765908    0.008654
   14     135.953    A         2.489443    0.177424
   15     148.313    A         3.281491    0.089079
   16     186.090    A         5.039221    0.090431
   17     210.850    A         6.379160    0.008659
   18     242.346    A         4.966660    0.097297
   19     264.440    A         3.682997    0.094068
   20     277.651    A         1.179847    0.014086
   21     300.111    A         4.358710    0.460603
   22     328.980    A         3.339246    0.098848
   23     359.934    A         3.250951    0.037651
   24     401.661    A         2.939294    0.024439
   25     433.081    A         3.966600    0.148267
   26     469.923    A         5.329295    0.043022
   27     504.885    A         4.030814    0.422302
   28     511.026    A         7.292066    0.077179
   29     601.899    A         5.759828    0.703163
   30     606.806    A         6.027286    0.299966
   31     677.667    A         3.819319    0.175580
   32     691.862    A         1.638227    1.756669
   33     699.601    A         4.882121    0.536020
   34     739.555    A         1.266393    0.021442
   35     751.489    A         1.787314    0.979092
   36     766.378    A         4.234106    0.891509
   37     774.482    A         2.105637    0.977070
   38     795.837    A         4.593431    1.345759
   39     828.400    A         1.789352    3.724726
   40     833.323    A         1.250655    0.003023
   41     895.777    A         1.881752    0.439250
   42     910.105    A         1.570698    2.176756
   43     911.307    A         1.604881    1.098761
   44     949.050    A         1.367222    0.009251
   45     951.238    A         5.180575    0.189159
```

46	969.182	A	1.284325	0.013654
47	986.634	A	5.988636	0.053423
48	1018.555	A	2.611239	0.945646
49	1023.049	A	2.832259	1.006970
50	1035.255	A	3.063769	3.135183
51	1071.927	A	1.699726	1.042382
52	1077.589	A	2.069321	0.782199
53	1101.683	A	3.013708	1.815012
54	1112.840	A	1.779890	1.104199
55	1120.098	A	1.281404	0.119405
56	1149.757	A	1.071205	0.005330
57	1154.699	A	2.705701	4.989571
58	1168.406	A	1.211763	0.057082
59	1173.441	A	1.503895	1.143517
60	1234.896	A	1.321188	0.267416
61	1245.837	A	3.146660	4.221664
62	1285.266	A	1.521329	1.451120
63	1295.859	A	1.521751	0.335036
64	1299.198	A	1.119651	0.156278
65	1312.788	A	1.609224	1.553192
66	1331.883	A	5.458928	0.292971
67	1360.389	A	1.428169	0.385501
68	1367.484	A	1.408000	0.429570
69	1420.057	A	1.212764	0.134685
70	1424.650	A	1.080554	0.168153
71	1424.927	A	1.112999	0.429120
72	1431.646	A	1.146993	0.184120
73	1432.224	A	1.648565	0.713029
74	1437.493	A	1.061705	0.261800
75	1439.073	A	1.039461	0.389882
76	1458.185	A	1.098614	0.329672
77	1476.282	A	2.200244	0.285535
78	1565.566	A	5.649739	0.153805
79	1588.699	A	5.700465	0.033759
80	1620.106	A	8.061399	9.287689
81	2951.036	A	1.036138	1.036180
82	2958.923	A	1.033961	1.475742
83	2960.250	A	1.058909	0.171909
84	2972.523	A	1.059916	1.167591
85	2991.276	A	1.099508	0.051126
86	3006.611	A	1.102204	0.039136
87	3022.159	A	1.102388	1.525485
88	3025.571	A	1.102655	1.754590
89	3030.090	A	1.104821	0.894102
90	3077.562	A	1.103201	0.515586
91	3091.023	A	1.085713	0.093446
92	3096.669	A	1.087128	0.002746
93	3104.843	A	1.090205	0.184830

94	3110.573	A	1.093995	0.443726
95	3118.542	A	1.097568	0.280661
96	3122.270	A	1.089052	0.086084

Table S16. Optimized Coordinates for [TS1-BOT-C2]

C	6.0	0.13453862	1.37552285	0.50250876
C	6.0	-0.99947846	1.42750537	1.08620906
C	6.0	1.12580264	1.89319563	-0.48381680
C	6.0	-1.62500274	0.80987561	2.26797247
C	6.0	-2.62425542	-0.17196268	2.12782502
C	6.0	-1.23752284	1.22845113	3.55568647
C	6.0	-3.19728708	-0.74949503	3.26274467
C	6.0	-1.82604587	0.64955926	4.68328905
C	6.0	-2.80276155	-0.34160700	4.54192591
H	1.0	-0.48777342	2.01452518	3.67214489
H	1.0	-1.51561987	0.98001254	5.67730856
H	1.0	-3.25931454	-0.79119605	5.42631674
C	6.0	0.57730848	2.90124655	-1.48957288
F	9.0	1.68977690	0.82791239	-1.17486906
F	9.0	2.17558599	2.46453786	0.23372839
H	1.0	-0.22292797	2.39617395	-2.05477571
C	6.0	1.65344679	3.44392776	-2.44293761
H	1.0	0.11081750	3.72403955	-0.92445809
H	1.0	2.10892534	2.60917473	-2.99841952
H	1.0	2.45898938	3.91475677	-1.85765457
C	6.0	1.07144320	4.46373367	-3.42420125
H	1.0	0.28804192	4.02058363	-4.05954075
H	1.0	1.85725844	4.85188341	-4.08989668
H	1.0	0.62913281	5.32442951	-2.89749813
Au	79.0	-2.33504057	2.82669783	0.17317361
P	15.0	-4.03901196	4.20313215	-0.52197534
C	6.0	-3.86339784	4.80260134	-2.23224950
C	6.0	-4.20219564	5.68769932	0.52058333
H	1.0	-3.82927752	3.95196295	-2.92700934
H	1.0	-2.93272018	5.37798309	-2.33289766
H	1.0	-4.71433592	5.44998217	-2.49631119
H	1.0	-4.37440825	5.39156818	1.56509268
H	1.0	-5.04935646	6.30368900	0.18029958
H	1.0	-3.28179717	6.28675413	0.47189417
C	6.0	-5.65413189	3.36446834	-0.44437918
H	1.0	-5.64844131	2.46981406	-1.08303213
H	1.0	-6.45184803	4.04262400	-0.78558153
H	1.0	-5.86674356	3.05690360	0.58952254
O	8.0	1.40387607	0.01027968	1.34318721
C	6.0	1.01723933	-1.36004770	1.02860057
H	1.0	1.73890793	-2.04371047	1.49858677
H	1.0	1.06576753	-1.45832813	-0.06048401
H	1.0	0.00164736	-1.57926416	1.38475931
H	1.0	1.33075178	0.14644821	2.31010079
H	1.0	-3.96106172	-1.52147388	3.14428854
H	1.0	-2.94069314	-0.49027109	1.13203537

Table S17. Vibrational Frequency Data for [TS1-BOT-C2]

```
MODE FREQ(CM**-1)  SYMMETRY  RED. MASS  IR INTENS.
   1    -167.687     A        6.961760   10.868540
   2      17.540     A        5.051300    0.003574
   3       6.731     A        5.832188    0.006281
   4       5.466     A        5.752289    0.007835
   5       0.224     A       10.827998    0.000016
   6       0.197     A       10.856529    0.000005
   7       0.286     A       10.858694    0.000004
   8      31.430     A        4.013884    0.032863
   9      35.497     A        4.566534    0.038603
  10      42.647     A        3.958166    0.015129
  11      47.729     A        4.786280    0.065977
  12      50.967     A        5.086014    0.093688
  13      61.874     A        4.045512    0.036898
  14      71.020     A        4.589411    0.002772
  15      89.520     A        1.829178    0.054267
  16      92.574     A        2.287113    0.034048
  17     102.184     A        4.641554    0.038618
  18     106.432     A        3.375897    0.369663
  19     117.831     A        2.362934    0.042723
  20     126.332     A        2.927467    0.219660
  21     152.589     A        1.247701    0.038724
  22     162.279     A        2.393679    0.331831
  23     173.916     A        3.194001    0.029732
  24     176.387     A        2.680154    0.031474
  25     182.384     A        3.275370    0.000304
  26     196.320     A        2.559381    0.014798
  27     198.263     A        2.715555    0.119772
  28     203.085     A        1.444269    0.027274
  29     222.471     A        5.133560    0.098329
  30     230.794     A        3.574168    0.068117
  31     232.909     A        1.099257    0.017655
  32     248.261     A        6.049597    0.848557
  33     267.212     A        2.648718    0.043520
  34     270.107     A        4.125876    0.174116
  35     281.447     A        1.187747    0.008931
  36     302.466     A        2.506857    0.042308
  37     321.715     A        3.495724    0.131344
  38     352.561     A        3.964233    0.725606
  39     391.329     A        3.064315    0.057369
  40     391.796     A        3.374342    0.204614
  41     406.008     A        5.487343    2.287413
  42     463.866     A        3.904210    2.127011
  43     511.466     A        6.088268    0.264009
  44     529.662     A        6.530424    0.479734
  45     553.013     A        2.009937    3.307176
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46	585.329	A	5.936410	2.114587
47	595.732	A	2.688765	1.794337
48	614.746	A	6.150465	0.074188
49	630.952	A	4.352879	0.335858
50	661.453	A	4.164205	0.628525
51	689.676	A	1.854571	1.207884
52	732.130	A	3.738732	0.422120
53	736.557	A	3.722898	0.407528
54	737.531	A	2.888412	0.450908
55	750.374	A	1.221492	0.647219
56	751.546	A	2.358329	2.494402
57	780.524	A	1.185638	0.003237
58	811.078	A	6.138392	2.468466
59	829.492	A	1.291124	0.321043
60	831.005	A	1.246512	0.014760
61	843.348	A	1.844979	1.958595
62	848.029	A	1.272107	0.342593
63	892.129	A	2.012214	0.545049
64	905.851	A	1.386972	0.462675
65	930.292	A	1.892710	2.521615
66	935.700	A	1.484684	4.241412
67	940.049	A	1.643795	7.325209
68	944.854	A	3.351757	0.927094
69	949.936	A	1.399026	0.249778
70	951.673	A	1.508283	2.959077
71	967.100	A	1.280264	0.005632
72	986.439	A	6.024385	0.306094
73	1013.431	A	3.137659	3.754869
74	1028.863	A	2.467433	0.177051
75	1036.700	A	2.604809	1.296601
76	1070.190	A	1.148273	0.333614
77	1081.539	A	1.622169	0.326016
78	1103.465	A	2.962994	3.277096
79	1113.909	A	2.284524	2.029865
80	1119.361	A	2.418172	2.513441
81	1127.105	A	1.557391	1.432317
82	1163.341	A	1.082010	0.026532
83	1184.952	A	1.141068	0.030893
84	1200.232	A	4.076761	1.226927
85	1220.130	A	1.302887	0.149993
86	1269.098	A	1.507290	0.750786
87	1270.657	A	1.205578	0.459081
88	1279.435	A	1.204385	0.386034
89	1287.814	A	1.103913	0.027487
90	1297.065	A	1.188982	0.030592
91	1302.796	A	2.511488	0.005952
92	1328.174	A	1.497077	0.566519
93	1332.566	A	1.232045	0.731729

94	1337.602	A	2.092977	0.044299
95	1375.229	A	1.228233	0.117973
96	1375.587	A	1.049791	0.163127
97	1384.353	A	1.048044	0.075675
98	1394.313	A	1.043348	0.049026
99	1403.144	A	1.046464	0.466281
100	1407.609	A	1.045650	0.456927
101	1411.815	A	1.113093	0.212644
102	1414.103	A	1.074750	0.200252
103	1420.798	A	1.042260	0.301673
104	1431.030	A	1.058580	0.434173
105	1432.528	A	1.046543	0.088630
106	1434.636	A	2.131988	0.325784
107	1440.625	A	1.037010	0.437905
108	1446.072	A	1.042437	0.258540
109	1452.255	A	1.087908	0.279551
110	1483.056	A	2.064349	0.651320
111	1566.893	A	5.155370	0.104003
112	1586.159	A	5.352607	0.176770
113	1860.510	A	11.870031	3.693197
114	2957.011	A	1.036675	0.792435
115	2966.089	A	1.058212	0.102375
116	2967.885	A	1.035000	0.020867
117	2970.764	A	1.034805	0.026410
118	2975.362	A	1.034090	0.018940
119	2976.513	A	1.058924	1.279982
120	2978.900	A	1.031568	0.952810
121	2998.193	A	1.100551	0.018720
122	3016.771	A	1.102843	0.103776
123	3026.910	A	1.100369	0.987726
124	3030.047	A	1.104214	1.516899
125	3050.509	A	1.100689	0.004037
126	3051.453	A	1.100638	0.020127
127	3054.843	A	1.107696	0.254900
128	3056.759	A	1.101358	0.012180
129	3067.024	A	1.102706	0.001489
130	3067.983	A	1.102465	0.000771
131	3074.293	A	1.103631	0.003705
132	3096.220	A	1.085730	0.043314
133	3099.791	A	1.104570	0.201902
134	3101.120	A	1.087504	0.046565
135	3108.796	A	1.091115	0.142016
136	3114.178	A	1.094200	0.199966
137	3120.400	A	1.098124	0.217884
138	3606.590	A	1.066478	3.531377

Table S18. Optimized Coordinates for [INT2-BOT-C2]

C	6.0	-2.46706676	2.77266574	0.40554872
C	6.0	-3.22460675	2.68678069	1.50123596
C	6.0	-2.65643024	3.32210827	-0.98242313
C	6.0	-2.62833953	2.11243844	2.73969007
C	6.0	-3.15106368	0.93281668	3.30683899
C	6.0	-1.51559961	2.72899961	3.35997128
C	6.0	-2.56639266	0.37769356	4.44523907
C	6.0	-0.93983799	2.16647363	4.50879860
C	6.0	-1.45935571	0.98945600	5.04928541
H	1.0	-4.01435232	0.44965038	2.84416461
H	1.0	-2.98115540	-0.54034680	4.86767292
H	1.0	-1.15363753	3.69517827	2.99213338
H	1.0	-0.09125724	2.66373587	4.98361158
H	1.0	-1.01127565	0.55444497	5.94487429
C	6.0	-4.02103996	3.88535714	-1.32804728
F	9.0	-2.34001231	2.30248880	-1.89715385
F	9.0	-1.67103791	4.29023170	-1.20004261
H	1.0	-4.76147079	3.09031105	-1.14418447
C	6.0	-4.11926556	4.38442707	-2.77950001
H	1.0	-4.24648905	4.70190430	-0.62382233
H	1.0	-3.86663818	3.56412411	-3.46919203
H	1.0	-3.37577486	5.17953587	-2.94676924
C	6.0	-5.51847506	4.91403913	-3.10287404
H	1.0	-6.28510666	4.13247204	-2.97920084
H	1.0	-5.56977844	5.26737118	-4.14384222
H	1.0	-5.79175472	5.75870371	-2.45076942
Au	79.0	-5.20108032	3.28231239	1.75065780
P	15.0	-7.38148928	3.86509848	2.26103330
C	6.0	-8.48274708	4.06028891	0.81996572
C	6.0	-7.49199915	5.43607283	3.18461132
H	1.0	-8.51644230	3.12611556	0.24054159
H	1.0	-8.10787010	4.86053038	0.16656555
H	1.0	-9.50348854	4.31352758	1.14556336
H	1.0	-6.93209410	5.35419321	4.12721157
H	1.0	-8.54081059	5.67987585	3.41282344
H	1.0	-7.05669689	6.25137186	2.58972120
C	6.0	-8.20914078	2.63114262	3.32334995
H	1.0	-8.24248791	1.65698421	2.81477952
H	1.0	-9.23760509	2.94837379	3.55574560
H	1.0	-7.65130424	2.51398683	4.26328945
O	8.0	-1.01919973	2.29139209	0.52587843
C	6.0	-0.65763110	0.95028734	-0.05490049
H	1.0	-0.17072469	1.15155089	-1.01133835
H	1.0	0.03635020	0.48900476	0.65526313
H	1.0	-1.56946766	0.35542378	-0.16532330
H	1.0	-0.88864976	2.24935722	1.52313304

Table S19. Vibrational Frequency Data for [INT2-BOT-C2]

```
MODE FREQ(CM**-1)  SYMMETRY  RED. MASS   IR INTENS.
   1       23.200    A         4.806223    0.008688
   2       10.950    A         5.770906    0.002257
   3        8.258    A         6.496453    0.005449
   4        0.351    A        10.827034    0.000003
   5        0.200    A        10.839646    0.000001
   6        0.136    A        10.857002    0.000001
   7       33.077    A         5.140024    0.018560
   8       45.951    A         4.852663    0.047501
   9       49.292    A         5.357692    0.147954
  10       53.671    A         5.189309    0.081597
  11       60.523    A         4.660996    0.043712
  12       72.601    A         4.114285    0.018498
  13       74.759    A         3.966923    0.066892
  14       89.984    A         3.587622    0.103258
  15       97.374    A         2.049501    0.016524
  16      106.172    A         4.193729    0.127529
  17      111.811    A         4.470490    0.042841
  18      141.830    A         2.756117    0.042046
  19      163.703    A         3.210705    0.106485
  20      180.198    A         3.578185    0.052856
  21      185.633    A         3.850848    0.057073
  22      195.822    A         1.591392    0.001768
  23      201.991    A         4.356510    0.089027
  24      212.324    A         1.679141    0.018292
  25      220.571    A         3.872620    0.033412
  26      233.905    A         4.013546    0.050884
  27      236.727    A         1.148097    0.006819
  28      261.373    A         2.238384    0.014795
  29      262.054    A         2.012673    0.038926
  30      265.744    A         2.246855    0.023531
  31      278.561    A         2.598200    0.029949
  32      282.984    A         4.030832    0.261815
  33      296.156    A         2.998975    0.309067
  34      316.214    A         2.240764    0.427137
  35      327.101    A         1.024870    0.011061
  36      329.317    A         2.110921    0.025266
  37      365.041    A         3.642395    0.779120
  38      384.665    A         2.932191    0.091441
  39      400.565    A         2.952297    0.112891
  40      424.363    A         3.490700    0.006970
  41      471.977    A         4.428417    0.037896
  42      514.387    A         7.606413    0.533841
  43      536.045    A         5.106567    0.222110
  44      595.522    A         6.950230    0.286023
  45      627.618    A         6.602478    0.147407
```

46	648.382	A	8.542607	0.907676
47	658.540	A	4.396627	1.515737
48	668.231	A	6.819910	3.605652
49	692.298	A	4.310658	0.960253
50	700.446	A	1.523560	2.500903
51	727.067	A	3.886907	0.454350
52	732.205	A	1.151359	0.004897
53	738.264	A	4.148291	0.591212
54	747.745	A	2.888642	0.598171
55	776.543	A	1.174961	0.001706
56	784.048	A	3.189056	0.124251
57	810.021	A	5.323490	3.425949
58	825.291	A	1.993849	2.907738
59	835.151	A	1.278378	0.382759
60	836.890	A	1.323710	0.085027
61	857.521	A	1.249079	0.341320
62	866.669	A	2.503086	0.447470
63	887.253	A	1.859557	1.986432
64	908.491	A	1.441246	2.230648
65	910.031	A	1.776704	2.688700
66	931.500	A	1.829280	6.810275
67	935.640	A	1.539739	0.425487
68	937.476	A	1.427734	1.739694
69	956.454	A	1.412878	4.545282
70	957.748	A	1.396495	0.854915
71	973.514	A	1.313696	0.158303
72	989.878	A	5.148343	0.008067
73	1022.073	A	2.905928	0.406124
74	1039.870	A	2.231396	0.251818
75	1054.545	A	2.661489	2.412153
76	1089.926	A	1.613378	0.270980
77	1106.454	A	1.791158	1.183167
78	1119.494	A	2.682116	6.375634
79	1146.536	A	1.738241	0.364224
80	1159.847	A	2.426096	0.490778
81	1171.319	A	1.091617	0.011001
82	1185.255	A	1.158011	0.132933
83	1196.077	A	2.082970	0.401355
84	1207.531	A	1.719663	0.135804
85	1224.089	A	1.295747	0.124703
86	1274.309	A	1.204401	0.611819
87	1277.800	A	1.492673	0.529222
88	1279.909	A	1.200326	0.396874
89	1289.092	A	1.193464	0.294621
90	1298.136	A	1.183157	0.027040
91	1306.814	A	2.146934	0.088611
92	1336.735	A	1.639646	0.796233
93	1339.333	A	2.122737	0.666900

94	1370.355	A	1.231645	0.232753
95	1374.165	A	1.214238	2.094228
96	1390.983	A	1.050610	0.066491
97	1395.554	A	1.045687	0.024263
98	1400.167	A	1.047313	0.038372
99	1409.698	A	1.048357	0.544987
100	1410.703	A	1.089870	0.140012
101	1411.337	A	1.045740	0.509552
102	1418.853	A	1.066280	0.339386
103	1422.768	A	1.042096	0.352263
104	1433.320	A	1.043825	0.131496
105	1445.026	A	1.040378	0.411436
106	1447.548	A	1.872123	0.055376
107	1453.771	A	1.141825	0.465088
108	1455.869	A	1.091470	0.351044
109	1488.151	A	2.093428	0.867172
110	1558.417	A	1.087080	0.726179
111	1571.840	A	4.935257	0.177988
112	1595.527	A	5.286597	0.320059
113	1613.643	A	9.227275	1.001182
114	2957.540	A	1.036533	0.794939
115	2968.240	A	1.058701	0.170166
116	2968.733	A	1.034142	0.108633
117	2970.903	A	1.033410	0.094278
118	2974.513	A	1.033529	0.030282
119	2978.864	A	1.059783	1.243865
120	2998.858	A	1.099945	0.011589
121	3015.988	A	1.102495	0.137047
122	3027.716	A	1.029356	0.852803
123	3027.859	A	1.098505	1.328955
124	3030.309	A	1.103702	1.456976
125	3051.574	A	1.101983	0.062104
126	3053.965	A	1.102833	0.136237
127	3056.253	A	1.102694	0.076589
128	3058.063	A	1.073711	26.135737
129	3063.702	A	1.103273	0.055576
130	3064.729	A	1.102470	0.014029
131	3068.236	A	1.102563	0.017069
132	3071.652	A	1.087049	1.386017
133	3102.437	A	1.086881	0.054159
134	3109.402	A	1.089996	0.125403
135	3117.942	A	1.094290	0.203591
136	3124.179	A	1.097865	0.098798
137	3137.513	A	1.112378	0.010544
138	3154.981	A	1.110671	0.101234

Table S20. Optimized Coordinates for [PROD-BOT-C2]

C	6.0	-1.81616426	2.94442892	0.38422224
C	6.0	-2.64194489	2.29623365	1.23808086
C	6.0	-2.32926250	3.78470778	-0.77523321
C	6.0	-2.33002067	1.59743381	2.49222708
C	6.0	-3.12126970	0.49689457	2.88623762
C	6.0	-1.31465983	2.03546143	3.36886168
C	6.0	-2.87801600	-0.16748095	4.08949184
C	6.0	-1.08146369	1.37703347	4.57829285
C	6.0	-1.85305583	0.26643702	4.93903112
H	1.0	-3.92803144	0.15628010	2.23168325
H	1.0	-3.49415398	-1.02573133	4.36832762
H	1.0	-0.72835004	2.92109680	3.11511207
H	1.0	-0.29498497	1.73729265	5.24585819
H	1.0	-1.66439700	-0.25025567	5.88271475
C	6.0	-3.82798171	3.92607403	-0.97266710
F	9.0	-1.75803721	3.27985406	-1.95410633
F	9.0	-1.75749230	5.06176662	-0.63686514
H	1.0	-4.23995972	2.91714001	-1.13876712
C	6.0	-4.21497011	4.84419727	-2.14201903
H	1.0	-4.26527739	4.30819607	-0.03695818
H	1.0	-3.73429942	4.48879433	-3.06696272
H	1.0	-3.82990718	5.85910463	-1.95546949
C	6.0	-5.73213625	4.89830494	-2.34050083
H	1.0	-6.14354706	3.90333247	-2.57562423
H	1.0	-5.99632692	5.57068348	-3.17109847
H	1.0	-6.24555588	5.26723766	-1.43792367
H	1.0	-3.70095444	2.30448580	0.96960342
O	8.0	-0.44782844	2.97883940	0.40219417
C	6.0	0.27149761	1.74581623	0.62412167
H	1.0	1.22279513	1.85410011	0.08656237
H	1.0	0.47366777	1.57873714	1.69200718
H	1.0	-0.28959212	0.89145374	0.21788602

Table S21. Vibrational Frequency Data for [PROD-BOT-C2]

```
 MODE FREQ(CM**-1)  SYMMETRY  RED. MASS  IR INTENS.
    1      20.420    A        3.421959    0.001910
    2      11.996    A        5.192740    0.032266
    3       4.916    A        4.488589    0.000672
    4       0.530    A        7.129299    0.000049
    5       0.162    A        7.080500    0.000010
    6       0.260    A        7.046284    0.000002
    7      21.155    A        2.751698    0.028620
    8      33.723    A        2.700805    0.050406
    9      53.248    A        3.808266    0.007722
   10      66.368    A        3.760574    0.005394
   11      85.674    A        3.346185    0.028959
   12      99.100    A        2.968888    0.015452
   13     106.040    A        3.100958    0.086378
   14     135.613    A        3.880796    0.018435
   15     159.454    A        1.515851    0.052746
   16     211.570    A        3.558604    0.065106
   17     218.396    A        3.033670    0.025549
   18     221.641    A        1.290573    0.003493
   19     261.417    A        6.455568    0.101577
   20     284.268    A        5.889851    0.167959
   21     305.998    A        3.848007    0.021890
   22     330.039    A        4.442508    0.120437
   23     344.871    A        4.004470    0.053306
   24     363.539    A        3.911617    0.052544
   25     398.356    A        3.020802    0.015087
   26     422.411    A        4.221240    0.066721
   27     510.228    A        3.597348    0.621096
   28     518.094    A        5.708516    0.242102
   29     589.537    A        6.583379    0.412739
   30     623.912    A        6.427908    0.015810
   31     677.254    A        5.359644    0.118234
   32     692.492    A        1.745612    1.839405
   33     720.607    A        4.433313    0.220514
   34     725.672    A        1.196999    0.057835
   35     738.244    A        2.073069    1.205501
   36     808.763    A        4.309195    0.790565
   37     815.658    A        2.297432    3.444096
   38     817.172    A        3.136576    3.155272
   39     826.635    A        1.560205    0.374627
   40     838.042    A        1.323754    0.107683
   41     873.497    A        2.725527    0.198563
   42     904.983    A        1.509453    0.517740
   43     907.840    A        1.893385    2.225669
   44     926.045    A        2.279618    0.121843
   45     951.950    A        1.351559    0.012691
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46	967.683	A	1.267760	0.047499
47	991.391	A	6.213335	0.056512
48	1010.463	A	4.115883	2.752020
49	1032.065	A	2.783630	0.248971
50	1036.349	A	2.505729	1.042629
51	1086.603	A	2.282450	1.919664
52	1092.548	A	1.751902	0.848452
53	1108.738	A	1.855059	0.942081
54	1125.131	A	1.289454	0.963412
55	1142.024	A	4.423115	7.710218
56	1163.331	A	1.454947	0.842553
57	1167.231	A	1.089499	0.006156
58	1182.458	A	1.192483	0.226501
59	1186.068	A	2.194371	3.130879
60	1222.735	A	2.634592	0.104844
61	1230.865	A	1.276946	0.181817
62	1285.784	A	1.598934	0.843401
63	1289.742	A	1.093889	0.028866
64	1308.923	A	2.245307	1.637527
65	1335.266	A	1.358999	0.853458
66	1345.927	A	2.725207	0.404191
67	1352.246	A	1.832734	0.567629
68	1359.269	A	1.289178	0.404065
69	1411.169	A	1.092054	0.579327
70	1422.080	A	1.052861	0.022598
71	1426.104	A	1.063789	0.070931
72	1430.266	A	1.106540	0.110486
73	1431.578	A	1.038616	0.405479
74	1441.865	A	1.211471	0.258726
75	1444.467	A	1.099030	0.219751
76	1452.498	A	1.834967	0.709283
77	1492.214	A	2.166671	0.442549
78	1575.181	A	5.106928	0.049318
79	1598.835	A	5.454035	0.191966
80	1635.799	A	7.591239	1.646741
81	2952.299	A	1.036446	0.823139
82	2961.173	A	1.028665	1.142018
83	2964.772	A	1.058490	0.186877
84	2974.714	A	1.060073	1.118446
85	2994.132	A	1.100500	0.013491
86	3013.999	A	1.102419	0.154156
87	3024.009	A	1.100194	1.145285
88	3027.250	A	1.104318	1.520176
89	3035.782	A	1.106151	0.687675
90	3056.892	A	1.106022	0.543285
91	3089.668	A	1.086761	0.037032
92	3094.905	A	1.087625	0.003320
93	3096.718	A	1.086900	0.187045

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94    3103.126    A          1.090314    0.241990
95    3110.863    A          1.094581    0.479748
96    3117.099    A          1.097767    0.205958
```

Table S22. Optimized Coordinates for [INT1-TOP]

C	6.0	-2.75651002	2.32484818	1.23036313
C	6.0	-2.65874243	2.02120423	2.43895411
C	6.0	-2.16021442	2.41191030	-0.13614905
C	6.0	-2.50748038	1.64344776	3.79446793
C	6.0	-2.06998444	2.59176326	4.74994135
C	6.0	-2.75799251	0.30501455	4.18190289
C	6.0	-1.88175392	2.19661140	6.07061243
C	6.0	-2.55847740	-0.07173651	5.50690460
C	6.0	-2.12387419	0.86916661	6.44971371
H	1.0	-1.87729239	3.62140656	4.44335747
H	1.0	-1.54516661	2.92666340	6.80915642
H	1.0	-3.09430933	-0.42019588	3.43934488
H	1.0	-2.74462104	-1.10468256	5.80779314
H	1.0	-1.97106159	0.56830657	7.48851490
C	6.0	-0.64927304	2.24913669	-0.17116669
F	9.0	-2.53134513	3.63334632	-0.68858719
F	9.0	-2.77608252	1.44624484	-0.92837816
H	1.0	-0.22417094	3.02762318	0.48339146
C	6.0	-0.05337398	2.33616304	-1.58288252
H	1.0	-0.41328570	1.27761114	0.29339170
H	1.0	-0.32303509	3.30159354	-2.03968334
H	1.0	-0.49265501	1.55012548	-2.21710467
C	6.0	1.47007012	2.18591833	-1.55758178
H	1.0	1.94464219	2.98256397	-0.96258110
H	1.0	1.88407350	2.23967957	-2.57580733
H	1.0	1.77394426	1.21838737	-1.12649691
Au	79.0	-4.74274635	3.05692077	1.67857051
P	15.0	-6.85482883	3.97046041	1.68535638
C	6.0	-7.43384218	4.25030279	-0.01721030
C	6.0	-6.91614389	5.58182430	2.52689981
H	1.0	-7.49072886	3.29677987	-0.56082553
H	1.0	-6.73467922	4.91437864	-0.54424906
H	1.0	-8.43173218	4.71548557	-0.00448842
H	1.0	-6.61716557	5.47082615	3.57874537
H	1.0	-7.93767405	5.99033880	2.48496318
H	1.0	-6.22505951	6.28238010	2.03776050
C	6.0	-8.08959579	2.90676808	2.49462032
H	1.0	-8.10073376	1.91437995	2.02223277
H	1.0	-9.08751488	3.36215544	2.40543222
H	1.0	-7.84291363	2.78459764	3.55887127

Table S23. Vibrational Frequency Data for [INT1-TOP]

```
 MODE FREQ(CM**-1)  SYMMETRY  RED. MASS  IR INTENS.
    1      16.625     A        4.442826    0.015005
    2      12.139     A        5.671689    0.000259
    3       9.021     A        5.051961    0.032122
    4       0.488     A       11.758467    0.000015
    5       0.178     A       11.689789    0.000002
    6       0.082     A       11.677387    0.000004
    7      29.621     A        5.715109    0.031659
    8      33.988     A        5.761746    0.089831
    9      44.967     A        5.246984    0.087392
   10      57.886     A        3.854572    0.005159
   11      61.126     A        3.536297    0.004824
   12      64.670     A        4.540091    0.017596
   13      77.325     A        3.092507    0.049126
   14      87.290     A        6.858203    0.167241
   15     112.044     A        3.775845    0.037451
   16     124.418     A        4.983632    0.141181
   17     135.739     A        3.299426    0.061542
   18     138.201     A        4.043384    0.125131
   19     167.086     A        2.752029    0.075724
   20     173.670     A        1.056846    0.001455
   21     197.809     A        4.947578    0.013347
   22     203.870     A        3.246667    0.001833
   23     208.171     A        2.669061    0.023862
   24     222.269     A        4.978201    0.112576
   25     226.173     A        1.345339    0.001726
   26     249.719     A        1.500828    0.052487
   27     264.460     A        1.444854    0.054069
   28     275.031     A        2.547602    0.053645
   29     279.124     A        1.092801    0.001139
   30     293.568     A        8.942900    0.079429
   31     321.113     A        3.279463    0.011935
   32     346.741     A        5.023660    1.178971
   33     369.844     A        3.257743    0.025598
   34     382.875     A        3.596439    0.867663
   35     393.896     A        2.947422    0.005068
   36     470.939     A        7.522360    0.066998
   37     503.510     A        6.985327    0.084388
   38     521.446     A        5.459718    0.059811
   39     548.066     A        7.993235    3.308801
   40     571.530     A        8.780484    2.135476
   41     596.892     A        7.407923    0.132235
   42     620.574     A        6.709373    0.009667
   43     657.256     A        4.222737    0.746363
   44     683.044     A        2.102689    1.211624
   45     733.474     A        1.139348    0.036051
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46	736.443	A	3.305687	0.338009
47	738.947	A	4.006757	0.516275
48	745.871	A	5.033600	1.234565
49	762.704	A	1.625015	1.521637
50	780.005	A	1.175206	0.007181
51	817.416	A	6.025249	1.220726
52	840.288	A	1.682231	1.815059
53	843.297	A	1.294741	0.246293
54	843.457	A	1.284820	0.139662
55	850.801	A	1.272616	0.467939
56	896.974	A	1.976878	0.306364
57	927.874	A	2.259326	4.287588
58	936.959	A	1.454128	4.653973
59	943.297	A	1.408266	1.913943
60	945.404	A	1.351044	0.040799
61	950.364	A	1.435497	5.136852
62	982.332	A	1.344418	0.049847
63	987.813	A	6.053036	0.755539
64	996.764	A	1.298499	0.003635
65	1017.816	A	3.266522	2.595787
66	1030.192	A	2.330594	0.101980
67	1045.090	A	2.849755	1.850386
68	1094.177	A	1.634388	0.331897
69	1107.534	A	2.987403	7.861768
70	1117.423	A	1.971380	1.380720
71	1135.627	A	3.995335	3.887162
72	1174.597	A	1.088181	0.005552
73	1185.086	A	1.146214	0.332006
74	1234.752	A	1.275229	0.238960
75	1245.107	A	3.512256	0.844208
76	1280.296	A	1.198297	0.493069
77	1283.641	A	1.206129	0.554077
78	1294.359	A	1.448205	0.640495
79	1300.078	A	1.146221	0.197013
80	1302.266	A	1.188548	0.036220
81	1311.788	A	2.155178	0.060931
82	1351.597	A	2.095453	0.492584
83	1352.439	A	1.740120	0.641612
84	1369.819	A	1.237917	0.181002
85	1383.999	A	1.047661	0.039960
86	1386.143	A	1.047053	0.055549
87	1397.074	A	1.045547	0.224523
88	1400.419	A	1.044378	0.484724
89	1411.360	A	1.044668	0.521862
90	1421.723	A	1.043228	0.262519
91	1425.069	A	1.049391	0.035778
92	1431.665	A	1.066331	0.091377
93	1436.722	A	1.040103	0.395517

94	1439.655	A	2.296788	0.694291
95	1451.723	A	1.095448	0.465513
96	1487.303	A	2.111891	0.096828
97	1563.986	A	4.507624	0.027398
98	1591.446	A	5.266825	2.630248
99	2059.752	A	11.993856	19.180663
100	2955.115	A	1.036889	0.817948
101	2966.716	A	1.059084	0.242223
102	2974.724	A	1.033142	0.034185
103	2976.292	A	1.057338	0.765722
104	2976.357	A	1.036099	0.077127
105	2977.575	A	1.033445	0.009431
106	2995.899	A	1.100856	0.007457
107	3014.763	A	1.102764	0.133203
108	3027.800	A	1.104344	1.393863
109	3030.152	A	1.100656	1.016489
110	3059.133	A	1.103483	0.017060
111	3059.749	A	1.102980	0.007224
112	3060.421	A	1.103071	0.002098
113	3064.112	A	1.102177	0.001405
114	3070.267	A	1.102897	0.000004
115	3071.973	A	1.102623	0.000008
116	3107.494	A	1.087085	0.031582
117	3115.943	A	1.088881	0.053874
118	3123.269	A	1.092318	0.054131
119	3128.167	A	1.095388	0.082027
120	3133.645	A	1.097141	0.128340

Table S24. Optimized Coordinates for [TS1-TOP-C1]

C	6.0	-0.76115108	1.27584743	0.75356871
C	6.0	-0.67424184	0.64261752	1.88518119
C	6.0	0.14082177	1.48972774	-0.43171224
C	6.0	-1.46018827	0.28891560	3.05355525
C	6.0	-1.11401808	0.76001793	4.33617830
C	6.0	-2.58611989	-0.54486597	2.89340925
C	6.0	-1.90051401	0.41379333	5.43518877
C	6.0	-3.36355233	-0.88620055	4.00054121
C	6.0	-3.02264118	-0.40789056	5.27061129
H	1.0	-2.83943582	-0.92059785	1.90021837
H	1.0	-4.23547220	-1.53054845	3.86964178
H	1.0	-3.63266873	-0.67642748	6.13612318
C	6.0	1.56176162	0.93227047	-0.44933268
F	9.0	0.21514994	2.87202454	-0.63808388
F	9.0	-0.53391892	0.99043471	-1.55286086
H	1.0	2.10920858	1.36709249	0.40781423
C	6.0	2.34006643	1.24927640	-1.73848033
H	1.0	1.49818635	-0.16437526	-0.33482546
H	1.0	2.39940047	2.34119987	-1.86337209
H	1.0	1.78272235	0.85706151	-2.60270476
C	6.0	3.74945664	0.65312946	-1.72001266
H	1.0	4.34946251	1.04990613	-0.88548934
H	1.0	4.28015757	0.89308774	-2.65344954
H	1.0	3.72547817	-0.44447443	-1.62547433
Au	79.0	-2.67674589	2.18456793	0.61454767
P	15.0	-4.72298908	3.17933154	0.29060838
C	6.0	-5.15088987	3.31429672	-1.47760785
C	6.0	-4.84685040	4.87229347	0.95698786
H	1.0	-5.18929911	2.31278086	-1.92970312
H	1.0	-4.38758278	3.90463305	-2.00368977
H	1.0	-6.13054419	3.80072284	-1.60220218
H	1.0	-4.68135071	4.86407232	2.04378605
H	1.0	-5.84309673	5.29222822	0.74890757
H	1.0	-4.08414459	5.51186228	0.49091497
C	6.0	-6.09862280	2.25298738	1.05227852
H	1.0	-6.12371778	1.22761691	0.65694690
H	1.0	-7.06052923	2.74387789	0.83941221
H	1.0	-5.95834541	2.20012164	2.14163947
O	8.0	0.93484837	-0.14288026	2.31527042
C	6.0	0.89176553	-1.60107219	2.47891998
H	1.0	0.40993345	-2.07783079	1.61535597
H	1.0	0.32602948	-1.79877424	3.39448357
H	1.0	1.92192781	-1.95806599	2.59882402
H	1.0	1.56346345	0.07427809	1.59270883
H	1.0	-1.63680410	0.79040831	6.42580843
H	1.0	-0.23948325	1.40060723	4.46359158

Table S25. Vibrational Frequency Data for [TS1-TOP-C1]

```
 MODE FREQ(CM**-1)  SYMMETRY  RED. MASS  IR INTENS.
    1    -201.832     A        7.653998   13.361406
    2      12.809     A        5.328195    0.006650
    3      11.209     A        4.870474    0.010490
    4       6.809     A        5.054121    0.006200
    5       0.604     A       10.846556    0.000001
    6       0.257     A       10.821198    0.000015
    7       0.196     A       10.784171    0.000032
    8      27.783     A        3.991550    0.124192
    9      33.639     A        4.039637    0.035580
   10      36.016     A        4.933577    0.042593
   11      42.043     A        7.888580    0.082578
   12      51.643     A        4.872832    0.089393
   13      57.668     A        3.533335    0.028383
   14      61.946     A        4.121177    0.112311
   15      74.768     A        2.829752    0.004283
   16      84.407     A        4.281002    0.039537
   17      91.627     A        2.359414    0.009718
   18     115.873     A        4.061120    0.053191
   19     131.093     A        1.671924    0.033341
   20     136.178     A        2.084999    0.015989
   21     138.587     A        4.391328    0.093535
   22     162.470     A        2.490002    0.031800
   23     168.627     A        2.455997    0.005940
   24     177.679     A        3.345193    0.035345
   25     188.149     A        1.789670    0.004297
   26     195.980     A        1.678207    0.014418
   27     217.643     A        6.907257    0.019472
   28     227.157     A        4.310577    0.026772
   29     235.508     A        3.778284    0.008802
   30     250.207     A        1.245695    0.544425
   31     258.010     A        2.284888    0.037808
   32     260.835     A        1.331566    0.001804
   33     272.808     A        2.632205    0.073892
   34     278.487     A        3.833247    1.007268
   35     295.870     A        1.079321    0.001571
   36     319.836     A        4.429110    2.824775
   37     331.520     A        3.207584    0.089756
   38     347.598     A        3.937915    0.455148
   39     376.317     A        3.796344    0.048391
   40     380.281     A        3.308519    0.068980
   41     394.631     A        2.899465    0.032116
   42     504.688     A        7.436639    0.260498
   43     514.555     A        6.310587    1.388058
   44     532.473     A        5.014532    0.401155
   45     592.799     A        7.084446    0.393116
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46	598.479	A	6.643723	0.512074
47	622.842	A	7.515310	0.097718
48	651.676	A	7.299310	0.579911
49	658.575	A	4.413733	0.976603
50	687.282	A	1.673967	2.159913
51	727.241	A	3.884884	0.504416
52	732.756	A	3.850944	0.444723
53	750.986	A	1.533338	2.544969
54	754.333	A	1.731934	2.102677
55	766.274	A	2.841375	0.972047
56	778.517	A	1.181995	0.014099
57	790.451	A	1.546338	0.996719
58	821.095	A	3.001686	1.235366
59	831.911	A	1.897567	5.187326
60	833.153	A	1.298323	0.048998
61	835.010	A	1.299129	0.402141
62	837.958	A	1.346012	1.117136
63	897.368	A	2.035831	0.785372
64	921.049	A	1.416716	0.095099
65	927.029	A	3.185933	1.960099
66	934.857	A	1.422687	2.075196
67	936.339	A	1.496554	6.093848
68	941.396	A	1.872918	1.751723
69	945.642	A	1.447204	2.191661
70	957.521	A	1.370694	0.006815
71	977.721	A	1.311630	0.012566
72	985.827	A	5.834571	0.612753
73	1007.661	A	3.542281	3.439393
74	1020.376	A	2.129214	0.495198
75	1033.085	A	3.037539	0.494741
76	1074.193	A	1.518169	0.442947
77	1078.183	A	1.164822	1.946515
78	1105.449	A	2.603435	4.783602
79	1108.788	A	1.922243	1.491255
80	1137.415	A	4.035607	4.476012
81	1161.244	A	1.126935	0.008410
82	1162.601	A	1.220766	0.119772
83	1169.793	A	1.149507	0.073408
84	1209.704	A	3.341269	0.145332
85	1227.211	A	1.286859	0.088524
86	1270.094	A	1.200523	0.413230
87	1274.706	A	1.524868	0.845353
88	1280.757	A	1.199563	0.542472
89	1283.998	A	1.274970	0.428986
90	1295.060	A	1.514268	0.064651
91	1299.077	A	1.190354	0.075805
92	1310.902	A	1.132755	0.217040
93	1328.699	A	4.960041	0.263012

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 94    1333.365    A          1.549588    0.746040
 95    1367.150    A          1.227851    0.073615
 96    1385.044    A          1.049978    0.049459
 97    1391.241    A          1.046365    0.064956
 98    1396.659    A          1.044469    0.024086
 99    1401.768    A          1.046972    0.477940
100    1407.749    A          1.042955    0.563945
101    1420.978    A          1.040959    0.293663
102    1424.672    A          1.036236    0.124888
103    1431.305    A          2.183910    0.584882
104    1438.616    A          1.050772    0.679354
105    1439.401    A          1.041864    0.404441
106    1445.426    A          1.078637    0.128333
107    1451.827    A          1.086665    0.323790
108    1463.270    A          1.087028    0.156891
109    1471.394    A          2.181028    0.023353
110    1496.097    A          1.070838    0.224889
111    1563.940    A          5.279944    0.041059
112    1580.575    A          5.618283    0.637099
113    1775.289    A         11.643064   16.352117
114    2927.626    A          1.057433    1.056483
115    2956.192    A          1.036872    0.861874
116    2969.608    A          1.034230    0.101008
117    2970.870    A          1.033866    0.035404
118    2971.419    A          1.033671    0.009327
119    2979.191    A          1.063118    0.638652
120    2982.320    A          1.096862    0.262278
121    2995.679    A          1.029466    0.456779
122    3007.828    A          1.102330    0.114115
123    3030.033    A          1.101379    1.125014
124    3031.071    A          1.103897    1.273067
125    3049.963    A          1.101473    0.027517
126    3053.127    A          1.101833    0.015529
127    3054.547    A          1.102514    0.095114
128    3064.294    A          1.102360    0.003279
129    3065.501    A          1.102362    0.008600
130    3066.869    A          1.102792    0.004816
131    3084.611    A          1.108590    0.136145
132    3102.219    A          1.086529    0.009589
133    3107.484    A          1.106038    0.180270
134    3112.198    A          1.087898    0.055804
135    3115.833    A          1.091832    0.207467
136    3126.412    A          1.094593    0.116584
137    3129.417    A          1.096871    0.106005
138    3517.227    A          1.067049   11.229541
```

Table S26. Optimized Coordinates for [INT2-TOP-C1]

C	6.0	-3.17304158	2.29898119	1.74216211
C	6.0	-2.70623064	1.95555246	2.94064164
C	6.0	-2.49434948	2.16954660	0.39590520
C	6.0	-3.29006982	1.99271905	4.28857756
C	6.0	-2.59124756	2.58528590	5.35987759
C	6.0	-4.56102180	1.43286443	4.52022696
C	6.0	-3.16608095	2.63011742	6.63078499
C	6.0	-5.12896347	1.48213804	5.79424524
C	6.0	-4.43452263	2.08090115	6.85105276
H	1.0	-1.60579956	3.02647972	5.19466496
H	1.0	-2.62193871	3.09981251	7.45321941
H	1.0	-5.08980417	0.94739968	3.69809556
H	1.0	-6.11309385	1.03920209	5.96294355
H	1.0	-4.87959814	2.11602449	7.84800816
C	6.0	-1.05129898	1.67928910	0.23244530
F	9.0	-2.56826496	3.42505527	-0.22106847
F	9.0	-3.30769372	1.33390999	-0.38436681
H	1.0	-0.38609493	2.36364722	0.79979837
C	6.0	-0.54375440	1.65959609	-1.22378516
H	1.0	-0.97941053	0.65090013	0.63100255
H	1.0	-0.61363870	2.67420506	-1.64198732
H	1.0	-1.20856249	1.01842368	-1.82206583
C	6.0	0.89656854	1.15276814	-1.32405519
H	1.0	1.59435880	1.79414415	-0.76237243
H	1.0	1.22839665	1.14487302	-2.37307453
H	1.0	0.99519360	0.12630227	-0.93691105
Au	79.0	-5.07154131	3.19019365	1.63493276
P	15.0	-7.13688993	4.19783258	1.44142878
C	6.0	-8.16806030	3.46086788	0.12668285
C	6.0	-7.04866171	5.97393084	1.02792740
H	1.0	-8.36033249	2.40083885	0.34722909
H	1.0	-7.64349699	3.52447200	-0.83770287
H	1.0	-9.13069057	3.98901153	0.04546492
H	1.0	-6.51167965	6.51460552	1.82041705
H	1.0	-8.05699444	6.40272188	0.92133671
H	1.0	-6.49866676	6.10537910	0.08556394
C	6.0	-8.15740299	4.10696411	2.95253682
H	1.0	-8.31507683	3.05708790	3.23798299
H	1.0	-9.13622379	4.58418465	2.79044557
H	1.0	-7.64360332	4.61677933	3.78006411
O	8.0	-1.23272383	1.47505283	3.09909511
C	6.0	-0.99804103	0.09857937	3.63323808
H	1.0	-1.49451339	-0.63639128	2.98904896
H	1.0	-1.41004598	0.08913085	4.64470434
H	1.0	0.09014833	-0.02536702	3.65107799
H	1.0	-0.79232275	1.56768763	2.21501303

Table S27. Vibrational Frequency Data for [INT2-TOP-C1]

```
 MODE FREQ(CM**-1)  SYMMETRY  RED. MASS  IR INTENS.
    1      12.957    A         5.295988    0.013928
    2       9.600    A         4.662494    0.000361
    3       8.445    A         4.989991    0.005004
    4       0.445    A        10.920208    0.000027
    5       0.261    A        10.855017    0.000005
    6       0.231    A        10.847451    0.000005
    7      31.617    A         4.427432    0.091524
    8      44.803    A         4.136957    0.197888
    9      52.537    A         4.909341    0.054785
   10      59.486    A         4.011752    0.048205
   11      62.567    A         5.086182    0.012795
   12      74.759    A         8.399358    0.069135
   13      78.488    A         2.939179    0.000959
   14      89.427    A         4.517431    0.049462
   15     102.478    A         3.160923    0.165395
   16     112.118    A         2.107012    0.021264
   17     122.540    A         3.740138    0.122828
   18     142.235    A         4.897628    0.048106
   19     154.129    A         3.669881    0.040584
   20     171.675    A         3.406828    0.011931
   21     174.041    A         2.625729    0.035631
   22     177.369    A         1.458725    0.010836
   23     186.083    A         2.117234    0.002557
   24     195.066    A         3.238046    0.052560
   25     219.676    A         1.294597    0.030773
   26     225.720    A         1.084993    0.001327
   27     230.865    A         1.137166    0.001956
   28     235.740    A         3.848158    0.100821
   29     243.323    A         3.372329    0.005132
   30     246.840    A         4.021345    0.172435
   31     263.630    A         1.469111    0.051437
   32     264.468    A         2.156772    0.033358
   33     272.004    A         3.738268    0.456162
   34     274.281    A         2.818889    0.128757
   35     302.197    A         6.745968    0.478861
   36     341.309    A         2.984658    0.152351
   37     351.396    A         3.785933    0.495607
   38     382.794    A         2.964888    0.042771
   39     396.727    A         2.902778    0.121049
   40     409.593    A         4.002858    0.443949
   41     454.100    A         5.335232    2.167065
   42     512.354    A         7.864762    0.160459
   43     544.720    A         5.043893    1.347086
   44     573.099    A         7.236492    5.257907
   45     614.122    A         5.906310    0.542160
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46	622.148	A	6.341366	1.109433
47	653.632	A	7.125661	0.405384
48	659.450	A	4.186325	0.364671
49	683.362	A	6.054744	0.096972
50	685.440	A	1.780102	2.246008
51	726.124	A	3.978109	0.521117
52	728.519	A	3.851611	0.482259
53	755.741	A	2.072152	1.765638
54	764.120	A	1.346490	0.285040
55	778.874	A	1.597369	0.791244
56	781.469	A	1.186617	0.016366
57	793.601	A	2.294629	1.976213
58	813.281	A	7.080896	2.720549
59	823.223	A	1.259242	0.020812
60	837.039	A	2.087532	4.541720
61	837.483	A	1.303475	0.528633
62	840.075	A	1.279486	0.018119
63	892.423	A	2.539781	0.393047
64	904.492	A	1.408100	0.114537
65	928.550	A	2.589372	0.728814
66	936.301	A	1.398861	1.224031
67	942.067	A	1.459421	3.703343
68	946.388	A	1.427898	3.236477
69	948.167	A	1.386199	0.733979
70	958.070	A	1.561699	1.720438
71	973.072	A	1.303618	0.010977
72	989.657	A	6.095864	0.237865
73	1019.043	A	3.382325	4.200986
74	1035.144	A	2.860106	0.013931
75	1036.333	A	2.364507	0.612962
76	1091.715	A	1.629371	0.170135
77	1109.864	A	2.382053	3.790285
78	1114.049	A	2.116791	3.574068
79	1119.419	A	1.285678	0.175642
80	1144.569	A	1.478356	2.171210
81	1159.802	A	3.109074	2.507987
82	1173.211	A	1.090696	0.014340
83	1189.607	A	1.142342	0.030563
84	1216.196	A	3.631417	0.644699
85	1236.300	A	1.306429	0.166075
86	1272.731	A	1.205164	0.464889
87	1277.219	A	1.206103	0.412080
88	1279.805	A	1.531035	1.181333
89	1296.150	A	1.189907	0.027474
90	1304.776	A	1.236947	0.155284
91	1315.512	A	2.115521	0.076603
92	1343.782	A	1.508616	0.350083
93	1344.706	A	1.864333	0.398725

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  94    1366.261    A         1.255302    1.079404
  95    1372.518    A         1.224708    0.035373
  96    1387.709    A         1.049628    0.032888
  97    1392.098    A         1.045073    0.003108
  98    1395.343    A         1.046827    0.069507
  99    1402.117    A         1.117953    0.276100
 100    1403.607    A         1.044769    0.597362
 101    1409.048    A         1.046669    0.481463
 102    1418.513    A         1.040571    0.365449
 103    1435.534    A         1.038136    0.186210
 104    1438.880    A         1.039502    0.384533
 105    1440.318    A         1.085013    0.332779
 106    1445.481    A         1.550431    0.711296
 107    1446.273    A         1.248709    0.113946
 108    1451.257    A         1.068240    0.065573
 109    1467.133    A         1.098233    0.259933
 110    1489.691    A         2.095917    0.286485
 111    1570.750    A         5.085722    0.052929
 112    1596.783    A         5.326638    0.178298
 113    1655.922    A         9.825963    7.693807
 114    2891.877    A         1.061516    2.215804
 115    2956.880    A         1.036859    0.835782
 116    2967.972    A         1.034301    0.151495
 117    2969.800    A         1.034333    0.056881
 118    2972.459    A         1.097224    0.109663
 119    2973.264    A         1.033478    0.053913
 120    2983.982    A         1.060185    0.563777
 121    3010.734    A         1.101702    0.233992
 122    3019.415    A         1.028808    0.193366
 123    3031.954    A         1.102059    0.936094
 124    3035.339    A         1.103464    1.176201
 125    3049.885    A         1.102046    0.078905
 126    3051.491    A         1.101411    0.083788
 127    3055.225    A         1.102543    0.074606
 128    3060.351    A         1.101849    0.020416
 129    3063.379    A         1.102430    0.024991
 130    3064.667    A         1.102219    0.007694
 131    3102.546    A         1.086237    0.008208
 132    3112.147    A         1.088041    0.046782
 133    3116.921    A         1.091211    0.205147
 134    3124.154    A         1.094503    0.216850
 135    3124.921    A         1.108722    0.029462
 136    3128.233    A         1.097213    0.047729
 137    3147.597    A         1.110462    0.043914
 138    3341.416    A         1.068553   22.896028
```

Table S28. Optimized Coordinates for [PROD-TOP-C1]

C	6.0	-3.01657391	2.20094299	1.85496271
C	6.0	-2.44850588	1.82544076	3.02445769
C	6.0	-2.44406676	2.21731472	0.47646946
C	6.0	-3.19711041	1.89084446	4.30878592
C	6.0	-2.58100128	2.45385861	5.44323301
C	6.0	-4.52283192	1.43277383	4.41151762
C	6.0	-3.27989697	2.57020450	6.64516830
C	6.0	-5.21909761	1.54796231	5.61777830
C	6.0	-4.60159254	2.11650157	6.73697948
H	1.0	-1.55464876	2.82147598	5.37095690
H	1.0	-2.79226255	3.02004957	7.51345539
H	1.0	-5.00310421	0.96870512	3.54654193
H	1.0	-6.24675322	1.18314707	5.68631554
H	1.0	-5.14614582	2.20345831	7.68001413
C	6.0	-1.07915485	1.61997032	0.18996085
F	9.0	-2.44999647	3.56446171	0.03222892
F	9.0	-3.40203619	1.60176694	-0.36476412
H	1.0	-0.34397721	2.18351674	0.78378421
C	6.0	-0.68636805	1.62421596	-1.29440892
H	1.0	-1.07051361	0.59155387	0.58360881
H	1.0	-0.74248236	2.65049696	-1.69075286
H	1.0	-1.40827370	1.02389193	-1.86995268
C	6.0	0.72423452	1.06773782	-1.50644648
H	1.0	1.48155272	1.67757821	-0.98798704
H	1.0	0.98633820	1.05188823	-2.57557940
H	1.0	0.80990589	0.03623347	-1.12813950
H	1.0	-4.03523016	2.59368324	1.89879346
O	8.0	-1.11769068	1.49655306	3.08676291
C	6.0	-0.76633501	0.30038369	3.82179832
H	1.0	-1.24723482	-0.58309567	3.37286878
H	1.0	-1.04452908	0.36867669	4.88387060
H	1.0	0.32329327	0.21059729	3.73418689

Table S29. Vibrational Frequency Data for [PROD-TOP-C1]

```
MODE FREQ(CM**-1)  SYMMETRY  RED. MASS  IR INTENS.
   1      19.410     A        4.149181    0.033407
   2       4.637     A        5.379179    0.008042
   3       3.104     A        5.462856    0.013190
   4       0.340     A        7.089421    0.000030
   5       0.274     A        7.072600    0.000007
   6       0.160     A        7.058656    0.000007
   7      43.803     A        4.727690    0.022825
   8      57.994     A        4.551598    0.011669
   9      68.953     A        4.181757    0.019712
  10      80.962     A        3.555105    0.035442
  11      92.171     A        1.526337    0.058939
  12     110.146     A        2.137778    0.004849
  13     112.876     A        2.833067    0.021497
  14     125.844     A        2.015348    0.238120
  15     134.032     A        3.058511    0.011421
  16     189.129     A        5.320118    0.164081
  17     224.500     A        5.413932    0.153430
  18     239.016     A        4.877208    0.082348
  19     273.451     A        4.247712    0.283800
  20     276.547     A        1.121400    0.012966
  21     305.249     A        6.221282    0.150837
  22     329.482     A        3.253522    0.107283
  23     356.429     A        3.210261    0.008198
  24     404.438     A        2.982179    0.008374
  25     428.315     A        4.041185    0.129434
  26     478.282     A        4.915984    0.014830
  27     504.377     A        3.751614    0.494623
  28     511.637     A        8.117843    0.174869
  29     606.355     A        5.535352    0.695254
  30     608.625     A        5.872924    0.256791
  31     660.873     A        7.077608    0.348498
  32     672.287     A        3.968532    0.056912
  33     697.181     A        1.641611    1.707321
  34     724.884     A        1.260401    0.297953
  35     755.581     A        3.005093    2.242057
  36     770.299     A        3.900539    1.190691
  37     784.155     A        3.310525    1.153376
  38     801.031     A        2.192701    2.955981
  39     819.498     A        1.470698    1.712077
  40     839.223     A        1.252127    0.004357
  41     895.363     A        1.756215    1.105611
  42     906.966     A        1.843900    1.052326
  43     915.264     A        1.451160    0.096160
  44     952.302     A        4.095066    1.511077
  45     955.903     A        1.358180    0.011055
```

46	972.760	A	1.279426	0.010655
47	987.256	A	6.021449	0.175925
48	999.323	A	4.525605	8.876227
49	1026.881	A	2.382370	0.312516
50	1035.700	A	2.739342	1.895334
51	1057.347	A	3.176823	1.333939
52	1075.613	A	1.563157	0.295687
53	1104.524	A	2.285750	1.314898
54	1110.883	A	1.858973	1.280693
55	1131.983	A	1.278743	0.045628
56	1155.748	A	1.077426	0.001131
57	1163.317	A	1.452203	0.470887
58	1178.185	A	1.164384	0.045040
59	1195.565	A	2.604250	1.791256
60	1234.465	A	1.277347	0.172753
61	1245.512	A	3.094732	5.079341
62	1294.063	A	1.743320	1.190641
63	1297.083	A	1.092190	0.018144
64	1307.713	A	1.650920	1.051057
65	1317.857	A	1.522674	0.826377
66	1334.442	A	4.379360	0.148727
67	1360.673	A	1.500583	0.863751
68	1367.149	A	1.350544	0.388219
69	1407.057	A	1.104145	0.191920
70	1425.325	A	1.083820	0.195303
71	1426.966	A	1.173019	0.461252
72	1429.840	A	1.045836	0.161086
73	1435.737	A	1.950695	0.736164
74	1440.018	A	1.038597	0.361993
75	1445.794	A	1.084866	0.189351
76	1453.378	A	1.096462	0.348613
77	1485.941	A	2.137509	0.244591
78	1565.539	A	5.612815	0.100818
79	1595.500	A	5.465609	0.021512
80	1633.215	A	8.069326	6.128830
81	2952.304	A	1.036257	0.940229
82	2955.390	A	1.032436	1.536428
83	2967.904	A	1.059391	0.568482
84	2986.449	A	1.061104	0.673539
85	2995.155	A	1.100520	0.007525
86	3017.482	A	1.102668	0.802016
87	3024.091	A	1.100765	1.332311
88	3025.763	A	1.105387	0.848883
89	3031.536	A	1.103029	1.277709
90	3068.953	A	1.102891	0.453362
91	3089.672	A	1.085484	0.078365
92	3095.749	A	1.086660	0.004730
93	3101.988	A	1.090074	0.180594

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94    3103.929    A         1.088323    0.022756
95    3107.868    A         1.094095    0.504475
96    3116.080    A         1.097766    0.298907
```

Table S30. Optimized Coordinates for [TS1-TOP-C2]

C	6.0	-0.01969801	1.33146334	0.14182138
C	6.0	-0.98551273	1.38702774	0.97085512
C	6.0	0.69597054	1.82726502	-1.07627726
C	6.0	-1.37315810	0.72650790	2.22466540
C	6.0	-2.53676105	-0.06562992	2.28174901
C	6.0	-0.58444130	0.88398039	3.38073444
C	6.0	-2.87943792	-0.71825337	3.46711659
C	6.0	-0.94361210	0.23325326	4.56463718
C	6.0	-2.08634758	-0.57225055	4.61066389
H	1.0	0.29304630	1.53513718	3.35858130
H	1.0	-0.32627651	0.36079153	5.45672321
H	1.0	-2.36133885	-1.08035064	5.53747272
C	6.0	2.04429436	2.48704815	-0.83997774
F	9.0	-0.16871972	2.73095965	-1.69187045
F	9.0	0.81382960	0.77066451	-1.97608483
H	1.0	1.87398767	3.31627536	-0.13336089
C	6.0	2.71382856	2.99677730	-2.12474346
H	1.0	2.68835044	1.75488138	-0.33075935
H	1.0	2.03810811	3.69446349	-2.64406800
H	1.0	2.88642335	2.15145063	-2.80911279
C	6.0	4.04124069	3.69829440	-1.82508278
H	1.0	3.89687896	4.56842947	-1.16472816
H	1.0	4.50958252	4.06020069	-2.75280499
H	1.0	4.75682974	3.01978040	-1.33411741
Au	79.0	-2.44153380	2.83224249	0.33439669
P	15.0	-4.21547556	4.21303415	-0.11661427
C	6.0	-4.16531706	4.92559433	-1.79220498
C	6.0	-4.34231853	5.62204647	1.03009403
H	1.0	-4.17078447	4.12194300	-2.54218292
H	1.0	-3.24980402	5.52040339	-1.91957033
H	1.0	-5.03976631	5.57465506	-1.95686579
H	1.0	-4.44229698	5.25435400	2.06131411
H	1.0	-5.22222471	6.23687410	0.78415316
H	1.0	-3.43927479	6.24554682	0.96540082
C	6.0	-5.80525303	3.33176422	0.00433524
H	1.0	-5.83220243	2.50558472	-0.72027135
H	1.0	-6.64139462	4.01722383	-0.20488587
H	1.0	-5.92603302	2.91686225	1.01491094
O	8.0	1.34616959	-0.13417348	0.59213716
C	6.0	0.85724699	-1.46869695	0.26846257
H	1.0	1.60018790	-2.20516109	0.60560226
H	1.0	0.76056176	-1.51041543	-0.82090658
H	1.0	-0.11334556	-1.66666996	0.74355173
H	1.0	1.45727682	-0.06590483	1.56373787
H	1.0	-3.77567673	-1.34221041	3.49575925
H	1.0	-3.15640211	-0.18863942	1.39079773

Table S31. Vibrational Frequency Data for [TS1-TOP-C2]

```
MODE FREQ(CM**-1)  SYMMETRY  RED. MASS  IR INTENS.
   1    -168.251    A        7.542925   10.455012
   2      14.894    A        5.392147    0.001671
   3       9.350    A        5.198650    0.008306
   4       7.630    A        4.899315    0.002887
   5       0.328    A       10.863466    0.000007
   6       0.247    A       10.841770    0.000002
   7       0.249    A       10.846293    0.000015
   8      27.822    A        4.196404    0.071301
   9      34.720    A        4.852575    0.040685
  10      38.305    A        4.768815    0.036656
  11      40.741    A        4.613178    0.056697
  12      50.010    A        4.175076    0.025412
  13      62.980    A        5.160887    0.076994
  14      69.072    A        4.313689    0.063940
  15      72.061    A        4.186021    0.018728
  16      88.238    A        3.953451    0.031265
  17      94.673    A        3.495426    0.316248
  18     111.069    A        3.215987    0.082120
  19     121.658    A        2.642252    0.005123
  20     131.383    A        3.187116    0.060042
  21     152.628    A        1.550306    0.496430
  22     170.230    A        3.283875    0.051882
  23     174.553    A        3.983642    0.016603
  24     178.662    A        3.384161    0.032539
  25     187.516    A        3.289124    0.010587
  26     203.046    A        4.725704    0.032557
  27     218.543    A        3.995408    0.200948
  28     226.494    A        1.032148    0.001023
  29     237.640    A        6.809189    0.174732
  30     246.740    A        4.348066    0.419361
  31     249.467    A        2.004446    0.004520
  32     259.997    A        1.184199    0.010560
  33     271.918    A        1.085240    0.011003
  34     278.133    A        2.394539    0.033779
  35     288.089    A        2.254508    1.196278
  36     290.098    A        1.108174    0.032712
  37     314.286    A        3.352392    0.020194
  38     354.017    A        3.515426    0.186096
  39     357.348    A        3.742592    0.598820
  40     397.094    A        2.983545    0.009570
  41     426.800    A        9.013359    1.122595
  42     441.274    A        4.431094    0.026879
  43     509.526    A        5.515385    2.314937
  44     524.066    A        5.181739    0.520974
  45     549.363    A        6.273093    0.703951
```

46	568.491	A	1.891026	2.376667
47	589.087	A	2.850991	3.504997
48	610.957	A	6.315931	0.091409
49	644.881	A	5.655460	0.752442
50	658.874	A	4.227516	0.870758
51	693.348	A	1.884185	1.170153
52	730.347	A	3.848173	0.426166
53	733.371	A	3.859436	0.479747
54	738.228	A	1.163596	0.024955
55	741.523	A	2.786991	0.584389
56	753.149	A	2.976520	5.252235
57	782.549	A	1.176847	0.013745
58	803.544	A	5.582655	0.764936
59	833.675	A	1.690121	1.719685
60	837.910	A	1.239989	0.034732
61	840.907	A	1.268617	0.447998
62	848.762	A	1.265475	0.248691
63	890.262	A	1.994187	0.223224
64	909.110	A	1.379830	0.473420
65	928.392	A	2.284931	2.942317
66	938.523	A	1.412773	1.494508
67	942.792	A	1.853571	8.215884
68	948.384	A	2.388618	3.381255
69	951.718	A	1.506769	1.340942
70	954.616	A	1.526526	0.182532
71	969.923	A	1.282404	0.004837
72	985.034	A	5.904088	0.279597
73	1010.102	A	3.296795	2.246610
74	1025.544	A	2.490475	0.217107
75	1036.076	A	2.688862	1.277287
76	1083.157	A	1.576114	0.273272
77	1088.270	A	1.181284	0.500159
78	1107.854	A	2.589074	4.097135
79	1118.755	A	2.038934	0.806571
80	1123.920	A	4.763784	3.409259
81	1167.885	A	1.091527	0.013771
82	1172.094	A	1.227698	0.361248
83	1182.292	A	1.161061	0.112224
84	1207.505	A	3.638011	1.208742
85	1235.456	A	1.269833	0.246248
86	1272.745	A	1.202483	0.515421
87	1275.748	A	1.203362	0.539824
88	1294.006	A	1.202193	0.048546
89	1294.557	A	1.345942	0.627410
90	1301.241	A	2.130704	0.028766
91	1303.759	A	1.186726	0.422963
92	1320.121	A	1.220042	0.315146
93	1333.927	A	2.444258	0.046771

94	1348.489	A	1.402978	0.533573
95	1358.763	A	1.337721	0.463021
96	1381.697	A	1.048199	0.121249
97	1386.358	A	1.047708	0.072604
98	1392.110	A	1.044850	0.007014
99	1406.793	A	1.047420	0.488658
100	1407.932	A	1.046147	0.473749
101	1411.444	A	1.076010	0.124588
102	1415.098	A	1.042029	0.408517
103	1429.673	A	1.040469	0.411938
104	1432.149	A	1.041975	0.100721
105	1435.953	A	1.453718	0.254999
106	1437.383	A	1.395300	0.542676
107	1448.449	A	1.049570	0.309406
108	1453.048	A	1.094256	0.355526
109	1481.545	A	2.081543	0.820219
110	1509.137	A	1.095044	0.151182
111	1566.607	A	5.187308	0.134621
112	1584.815	A	5.309649	0.087696
113	1874.938	A	11.835041	4.502965
114	2954.845	A	1.036164	0.837784
115	2968.245	A	1.059515	0.320741
116	2973.306	A	1.034129	0.038297
117	2973.985	A	1.034707	0.011436
118	2974.886	A	1.034216	0.010304
119	2979.255	A	1.063356	0.585998
120	2981.231	A	1.031389	0.892372
121	3000.301	A	1.100370	0.005201
122	3023.125	A	1.102328	0.869574
123	3028.242	A	1.100637	0.988703
124	3037.397	A	1.101289	0.633293
125	3056.798	A	1.101787	0.007016
126	3057.834	A	1.107071	0.254991
127	3058.029	A	1.101773	0.005346
128	3058.476	A	1.101719	0.009631
129	3069.156	A	1.102721	0.000982
130	3073.415	A	1.102644	0.001696
131	3074.489	A	1.103241	0.001464
132	3097.339	A	1.085665	0.003538
133	3103.222	A	1.105608	0.173776
134	3103.898	A	1.087991	0.020766
135	3108.004	A	1.090808	0.215971
136	3116.554	A	1.094523	0.255599
137	3122.143	A	1.097893	0.190125
138	3584.061	A	1.066673	3.914224

Table S32. Optimized Coordinates for [INT2-TOP-C2]

C	6.0	-2.43141961	2.72709656	0.43247044
C	6.0	-3.15439367	2.52782416	1.53801727
C	6.0	-2.79850078	3.42279792	-0.86373746
C	6.0	-2.53139877	1.88339520	2.72052503
C	6.0	-3.05309677	0.69064772	3.25916696
C	6.0	-1.38129091	2.45186472	3.31971622
C	6.0	-2.43052793	0.07532977	4.34588051
C	6.0	-0.76706475	1.82966018	4.41543245
C	6.0	-1.28548563	0.63831234	4.92590332
H	1.0	-3.94716358	0.24796003	2.81473207
H	1.0	-2.84550738	-0.85198987	4.74756050
H	1.0	-1.02644026	3.43577290	2.99136257
H	1.0	0.10878386	2.29200912	4.87550926
H	1.0	-0.80837870	0.15393963	5.78027582
C	6.0	-1.74632728	3.50570154	-1.95835471
F	9.0	-3.22269154	4.71892166	-0.54816461
F	9.0	-3.94252491	2.79439902	-1.36586094
H	1.0	-0.83630204	3.95696378	-1.53172004
C	6.0	-2.20996761	4.30123615	-3.18943906
H	1.0	-1.49410665	2.47859645	-2.26540995
H	1.0	-2.45316195	5.33192635	-2.88941240
H	1.0	-3.13635159	3.85546851	-3.58350849
C	6.0	-1.14053571	4.32465267	-4.28489542
H	1.0	-0.20899510	4.79586840	-3.93259525
H	1.0	-1.49143255	4.89632511	-5.15766001
H	1.0	-0.89251053	3.30884480	-4.63253069
Au	79.0	-5.12009239	3.17736554	1.69537807
P	15.0	-7.28017759	3.96197987	1.97603571
C	6.0	-8.15080070	4.30962849	0.40958396
C	6.0	-7.34490347	5.53303957	2.90426540
H	1.0	-8.22344494	3.39537477	-0.19693361
H	1.0	-7.59634399	5.06472063	-0.16628742
H	1.0	-9.16535282	4.68749285	0.60902590
H	1.0	-6.92206383	5.39258432	3.90952110
H	1.0	-8.38421726	5.88281107	2.99868941
H	1.0	-6.75413275	6.29940939	2.38258719
C	6.0	-8.37631416	2.82219577	2.88793325
H	1.0	-8.45297146	1.86644721	2.34989810
H	1.0	-9.38251019	3.25500846	2.99733901
H	1.0	-7.96116924	2.62213516	3.88636756
O	8.0	-0.98107380	2.26778984	0.44186223
C	6.0	-0.66437346	0.92405093	-0.17184065
H	1.0	-0.11343706	1.12697184	-1.09321415
H	1.0	-0.03045694	0.39917281	0.55053335
H	1.0	-1.60358369	0.38820308	-0.34510452
H	1.0	-0.78858805	2.20001435	1.42634666

Table S33. Vibrational Frequency Data for [INT2-TOP-C2]

```
MODE FREQ(CM**-1)  SYMMETRY  RED. MASS  IR INTENS.
   1      15.032    A        5.074519    0.013523
   2      11.372    A        5.160072    0.007223
   3       7.712    A        5.304625    0.011919
   4       2.855    A        9.856849    0.001032
   5       0.586    A       10.783559    0.000012
   6       0.231    A       10.841918    0.000002
   7      36.956    A        3.830568    0.004391
   8      42.341    A        4.415904    0.134343
   9      43.188    A        4.063860    0.159891
  10      49.355    A        4.608524    0.035784
  11      58.324    A        3.313950    0.015833
  12      69.402    A        2.781237    0.028173
  13      73.000    A        4.290821    0.021970
  14      81.648    A        3.845133    0.024150
  15      85.080    A        5.524296    0.081533
  16     104.214    A        3.230677    0.017378
  17     118.593    A        4.329502    0.130017
  18     133.148    A        3.582390    0.024534
  19     158.233    A        3.708898    0.277630
  20     173.090    A        3.665652    0.058290
  21     184.394    A        3.594212    0.016316
  22     189.162    A        1.098484    0.016397
  23     191.230    A        3.423846    0.056740
  24     207.882    A        3.788506    0.011287
  25     220.178    A        4.396238    0.010330
  26     222.282    A        1.112820    0.000235
  27     226.303    A        3.787416    0.170907
  28     237.896    A        1.261373    0.011484
  29     259.490    A        2.767230    0.048102
  30     263.119    A        1.183755    0.009717
  31     266.883    A        3.507515    0.163989
  32     278.075    A        2.681639    0.066546
  33     292.358    A        4.953465    0.008758
  34     301.983    A        5.055908    0.298267
  35     332.255    A        3.215006    0.092159
  36     334.743    A        1.014138    0.000658
  37     367.266    A        3.502565    0.435942
  38     369.475    A        3.302197    0.101078
  39     402.663    A        3.020454    0.088307
  40     408.767    A        5.720011    0.714914
  41     467.542    A        4.527640    0.031913
  42     522.427    A        5.115435    0.222002
  43     533.247    A        7.701487    1.527729
  44     559.157    A        6.069795    0.176743
  45     625.561    A        6.543845    0.004167
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46	648.612	A	7.846061	0.701666
47	661.018	A	4.270137	0.896865
48	679.883	A	6.079644	1.369335
49	707.898	A	2.187901	3.318008
50	708.643	A	2.811352	0.725745
51	729.528	A	3.103792	0.524180
52	729.669	A	1.285712	0.097229
53	733.664	A	3.947043	0.513769
54	755.238	A	2.440373	0.671279
55	782.067	A	2.788689	1.261439
56	786.221	A	1.173793	0.018423
57	802.052	A	6.022238	6.631588
58	826.932	A	1.867441	2.077033
59	842.867	A	1.255596	0.232768
60	844.740	A	1.277683	0.314585
61	850.126	A	1.251920	0.315145
62	861.052	A	2.276330	1.598390
63	894.497	A	2.450658	1.556050
64	910.016	A	1.370469	1.138774
65	921.908	A	2.036779	3.090242
66	941.929	A	1.446339	1.881048
67	943.094	A	1.900098	2.967441
68	945.979	A	1.416274	0.624704
69	950.498	A	1.612161	6.090664
70	959.816	A	1.396277	0.473967
71	979.424	A	1.369215	0.068996
72	990.045	A	4.375536	0.016428
73	1027.706	A	2.829666	0.086755
74	1038.173	A	2.234741	0.306560
75	1057.144	A	2.484501	0.136620
76	1090.621	A	1.608672	0.199627
77	1112.216	A	1.839898	1.021141
78	1117.908	A	1.314399	0.535521
79	1131.149	A	2.685072	3.702789
80	1144.508	A	3.576981	2.216524
81	1168.862	A	1.098413	0.009518
82	1176.437	A	1.598425	0.016674
83	1186.610	A	1.149162	0.047848
84	1213.844	A	3.556371	0.488107
85	1234.779	A	1.255450	0.151777
86	1280.689	A	1.203371	0.428695
87	1285.848	A	1.202123	0.397503
88	1293.364	A	1.371488	0.737204
89	1303.790	A	1.188561	0.034324
90	1304.216	A	1.180256	0.125122
91	1307.610	A	1.966701	0.115865
92	1342.371	A	2.444659	0.373370
93	1352.306	A	1.569013	1.286990

94	1368.076	A	1.229408	0.179955
95	1371.017	A	1.217417	1.157749
96	1395.047	A	1.048287	0.021232
97	1398.342	A	1.048174	0.131656
98	1401.849	A	1.047197	0.077879
99	1411.355	A	1.044066	0.356514
100	1413.113	A	1.068093	0.725798
101	1417.067	A	1.088885	0.098107
102	1418.132	A	1.044752	0.500816
103	1424.297	A	1.042940	0.265019
104	1431.669	A	1.043836	0.125724
105	1437.516	A	1.039942	0.348224
106	1442.381	A	1.160208	0.424975
107	1446.402	A	1.843215	0.137231
108	1452.055	A	1.092587	0.248855
109	1480.101	A	1.060577	0.529806
110	1486.945	A	2.105220	0.799277
111	1571.446	A	5.119611	0.168895
112	1593.613	A	5.999060	0.084331
113	1596.271	A	7.713125	1.478706
114	2954.059	A	1.036311	0.939964
115	2968.976	A	1.033894	0.169265
116	2970.599	A	1.034052	0.073165
117	2971.145	A	1.058143	0.133115
118	2971.432	A	1.034051	0.025384
119	2981.633	A	1.059195	0.860746
120	3000.274	A	1.100569	0.063908
121	3012.523	A	1.029798	0.303647
122	3018.403	A	1.101350	0.298255
123	3027.553	A	1.100684	1.044087
124	3032.512	A	1.104582	1.340398
125	3052.060	A	1.101949	0.106087
126	3053.193	A	1.102517	0.087096
127	3054.022	A	1.102879	0.069734
128	3058.654	A	1.090100	1.798560
129	3061.631	A	1.102026	0.019045
130	3063.728	A	1.102523	0.028007
131	3064.487	A	1.102159	0.013892
132	3094.909	A	1.069502	25.090126
133	3104.374	A	1.086828	0.592442
134	3112.452	A	1.089495	0.088672
135	3114.227	A	1.111367	0.391820
136	3117.883	A	1.094298	0.235295
137	3127.209	A	1.097686	0.083272
138	3147.298	A	1.107223	0.276742

Table S34. Optimized Coordinates for [PROD-TOP-C2]

C	6.0	-1.78391743	3.02184176	0.40927899
C	6.0	-2.64071321	2.41108155	1.25904989
C	6.0	-2.26192713	3.93870020	-0.71200943
C	6.0	-2.34384847	1.65461433	2.48479414
C	6.0	-3.14788747	0.55551106	2.85506797
C	6.0	-1.31312907	2.05062747	3.36283350
C	6.0	-2.90022779	-0.14691077	4.03652811
C	6.0	-1.07504654	1.35507333	4.55004787
C	6.0	-1.86018622	0.24702494	4.88771915
H	1.0	-3.96659613	0.24477211	2.20032239
H	1.0	-3.52576661	-1.00411403	4.29777861
H	1.0	-0.71576834	2.93345571	3.12460303
H	1.0	-0.27554297	1.68486083	5.21784306
H	1.0	-1.67013252	-0.29960454	5.81413126
C	6.0	-2.00641346	3.43042159	-2.12261081
F	9.0	-1.61742961	5.17575884	-0.53716499
F	9.0	-3.61553884	4.21400213	-0.54698497
H	1.0	-0.93861562	3.16567612	-2.18372917
C	6.0	-2.37817931	4.42101049	-3.23415613
H	1.0	-2.57204771	2.49005318	-2.23489904
H	1.0	-1.81720054	5.35849953	-3.09266281
H	1.0	-3.44727302	4.67706680	-3.15730476
C	6.0	-2.08195400	3.85457039	-4.62541246
H	1.0	-1.01328135	3.61139631	-4.73996925
H	1.0	-2.34269023	4.58115959	-5.41008329
H	1.0	-2.65605903	2.93418860	-4.81823683
H	1.0	-3.69964433	2.52826262	1.01545382
O	8.0	-0.41862923	2.94064379	0.36044690
C	6.0	0.21170971	1.66126883	0.59135640
H	1.0	1.16248548	1.69590724	0.04332515
H	1.0	0.41259801	1.49351323	1.65909779
H	1.0	-0.41508687	0.84605610	0.20081681

Table S35. Vibrational Frequency Data for [PROD-TOP-C2]

```
 MODE FREQ(CM**-1)  SYMMETRY  RED. MASS  IR INTENS.
    1      17.774     A        4.954547    0.032524
    2       8.355     A        4.835616    0.005106
    3       4.333     A        5.353912    0.008549
    4       0.652     A        7.119431    0.000024
    5       0.311     A        7.056346    0.000031
    6       0.070     A        7.065124    0.000004
    7      48.735     A        6.031893    0.024578
    8      51.310     A        4.299162    0.013975
    9      70.863     A        3.832164    0.005692
   10     106.055     A        3.657406    0.008642
   11     114.204     A        4.879397    0.009821
   12     118.026     A        3.086944    0.049159
   13     136.606     A        1.692905    0.003564
   14     143.992     A        2.316840    0.082388
   15     189.612     A        2.042038    0.046561
   16     192.628     A        5.491879    0.019262
   17     228.552     A        2.421424    0.009698
   18     253.426     A        3.601484    0.246605
   19     272.345     A        1.802205    0.029653
   20     276.497     A        1.922852    0.027770
   21     314.845     A        3.359520    0.033312
   22     329.995     A        3.546847    0.033615
   23     351.707     A        4.452557    0.068014
   24     379.123     A        4.247564    0.077094
   25     400.115     A        3.068042    0.030861
   26     466.348     A        5.174400    0.073557
   27     494.349     A        4.108716    0.401361
   28     529.045     A        4.804324    0.168246
   29     560.109     A        6.372430    0.349698
   30     622.162     A        6.423799    0.008026
   31     651.283     A        5.898885    0.282953
   32     693.480     A        1.730903    1.681964
   33     719.363     A        4.557402    1.605985
   34     735.529     A        1.962944    0.938665
   35     747.200     A        1.157212    0.007889
   36     803.917     A        2.754320    1.193586
   37     807.621     A        2.546201    1.245972
   38     817.845     A        2.900789    1.923318
   39     836.962     A        1.305934    0.066591
   40     844.475     A        1.636288    1.348045
   41     887.947     A        2.167264    0.161588
   42     902.493     A        1.583926    0.304309
   43     924.886     A        2.548712    1.108346
   44     937.336     A        2.486240    2.350616
   45     949.930     A        1.360042    0.026668
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46      965.669    A         1.267840    0.043011
47      990.736    A         6.213469    0.000813
48     1023.425    A         2.945244    1.191618
49     1030.493    A         2.797954    0.742729
50     1036.666    A         2.705489    2.412333
51     1085.622    A         2.057866    0.536313
52     1089.109    A         1.953623    0.942067
53     1113.156    A         2.701833    2.379054
54     1125.360    A         1.259157    0.176394
55     1128.821    A         2.750302    4.133354
56     1164.225    A         1.207073    0.349341
57     1164.764    A         1.295825    0.454319
58     1178.504    A         2.348181    2.803936
59     1180.963    A         1.178687    0.249686
60     1223.451    A         2.776891    0.331268
61     1243.031    A         1.270852    0.277618
62     1298.275    A         1.773701    0.502151
63     1302.910    A         1.826116    2.060343
64     1305.846    A         1.116665    0.126199
65     1329.767    A         1.428719    0.984692
66     1344.356    A         3.448882    0.081310
67     1360.691    A         1.531506    0.775562
68     1370.053    A         1.287154    0.215352
69     1418.441    A         1.075586    0.319953
70     1422.357    A         1.077894    0.247117
71     1432.177    A         1.121153    0.112771
72     1433.654    A         1.047041    0.106611
73     1442.811    A         1.038283    0.377222
74     1444.161    A         1.607814    0.025801
75     1452.684    A         1.321548    0.904939
76     1458.163    A         1.095648    0.369714
77     1491.015    A         2.180186    0.493897
78     1572.817    A         5.171215    0.072760
79     1598.364    A         5.462786    0.311628
80     1633.169    A         7.790978    2.096962
81     2954.510    A         1.036340    0.893432
82     2963.437    A         1.029112    1.177332
83     2965.326    A         1.058889    0.189536
84     2974.761    A         1.061727    0.909305
85     2995.599    A         1.099114    0.024253
86     3015.570    A         1.101925    0.113653
87     3024.998    A         1.100814    1.201221
88     3027.916    A         1.103627    1.648498
89     3038.945    A         1.106583    0.610687
90     3058.444    A         1.105814    0.505989
91     3088.883    A         1.085957    0.023737
92     3094.196    A         1.087707    0.020206
93     3095.766    A         1.086520    0.068615
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94    3100.737    A         1.090693    0.267634
95    3108.580    A         1.094542    0.520240
96    3115.141    A         1.097976    0.241387
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