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Exploiting the Inductive Effect of the Trifluoromethyl Group: Regioselective Gold-Catalyzed Hydration of 2,2,2-Trifluoroethyl-substituted Alkynes.

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1. General information

The following includes general experimental procedures, specific details for representative reactions, isolation and spectroscopic information for the new compounds prepared. All commercial compounds were used as received. Solvents were used as purchased unless stated as dry. THF, CH_2Cl_2 and toluene were purified using a Vacuum Atmospheres Inc. Solvent Purification System. For gold complexes synthesis, all chlorinated solvents (including the deuterated ones) were neutralized prior to use by filtration through dried basic alumina. All air and water sensitive reactions were carried out under argon atmosphere. Reactions were monitored by TLC on pre-coated plates (Silicycle silica gel 60 Å F254 230-240 mesh) and products were visualized under 254 nm UV light followed by staining with $KMnO_4$. Purification by flash column chromatography was carried out on silica gel (Silicycle silica gel 60 Å F254) or on Biotage® Isolera One Flash Chromatography System using SiliaSep silica gel cartridges. All reported yields are based on weighted mass of desired product, except if stated otherwise. Elemental analyses were performed at Université de Namur, rue de Bruxelles, 55 B-5000 Namur, Belgium. NMR spectra were recorded on an Agilent DD2 500 spectrometer, a Varian Inova 400 spectrometer, a Bruker Avance 400 Ultrashield or a Bruken Avance 300 Ultrashield in the indicated solvent at 298 K. Chemical shifts for ^{1}H and ^{13}C spectra are reported on the delta scale in ppm and were referenced to TMS (δ_H = 0 ppm, δ_C = 0 ppm) or residual solvent signal when not present ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.2 ppm). For ^{19}F, calibration was performed using a unified scale[1] or using $CFCl_3$ as external standard. Resonances are reported as follows: chemical shift (δ ppm), multiplicity (s = singulet, d = doublet, t = triplet, q = quartet, p = quintet, h = heptuplet, m = multiplet, br. s = broad signal), coupling constant (Hz), integration. High-resolution mass (HRMS) spectra were obtained on a LC/MS-TOF Agilent 6210 using electrospray ionization (ESI) and atmospheric pressure photoionization (APPI). Infrared spectra were recorded on an ABB MB3000 FT-IR spectrometer. Melting points were measured on a Stanford Research System OptiMelt

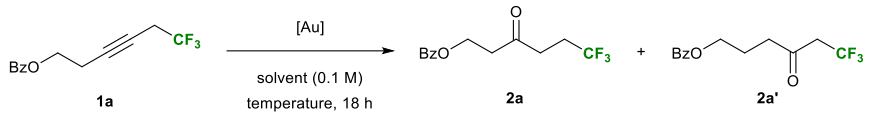
[1] R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow and P. Granger, *Pure Appl. Chem.*, 2001, **73**, 1795–1818.

MPA100 automated melting point apparatus and are uncorrected. Terminal alkynes were synthesized following procedures from literature.[2]

[2] R. Gauthier, N. V. Tzouras, Z. Zhang, S. Bédard, M. Saab, L. Falivene, K. van Hecke, L. Cavallo, S. P. Nolan and J.-F. Paquin, *Chem. Eur. J.*, 2021, **28**, e202103886.

2. Full optimization results

Table **SI1** Full optimization data using 2,2,2-trifluoroethyl-substituted alkyne **1a**.



Entry	[Au] (mol%)	Additive (mol%)	Solvent	Conv. (%)[a]	Yield (%)[a]	Ratio (**2a**:**2a'**)[b]
1	[Au(PPh$_3$)Cl] (2)	AgOTf (2)	THF/H$_2$O (9:1)	88	83	95:5
2	[Au(PPh$_3$)Cl] (2)	AgNTf$_2$ (2)	THF/H$_2$O (9:1)	68	66	96:4
3	[Au(IPr)Cl] (5)	AgOTf (5)	THF/H$_2$O (9:1)	100	98	94:6
4	[Au(IPr)OH] (5)	-	THF/H$_2$O (9:1)	16	6	99:1
5	[Au(IPr)(OTf)] (5)	-	THF/H$_2$O (9:1)	100	97	94:6
6	[Au(IPr)(OTf)] (1)	-	THF/H$_2$O (9:1)	100	94	94:6
7	[Au(IPr)(NTf$_2$)] (1)	-	THF/H$_2$O (9:1)	100	97	94:6
8	[Au(IPr)OH] (1)	-	THF/H$_2$O (9:1)	0	0	-
9	[Au(IPr)OH] (1)	HBF$_4$ (1)	THF/H$_2$O (9:1)	87	84	94:6
10	[Au(IPr)OH] (1)	TFA (drop)	THF/H$_2$O (9:1)	43	39	95:5
11	[Au(IPr)OH] (1)	HOTf (1)	THF/H$_2$O (9:1)	100	100	94:6
12	[{Au(IPr)}$_2$(μOH)][BF$_4$] (1)	-	THF/H$_2$O (9:1)	62	60	94:6
13	[Au(IPr)(4-methoxyphenyl)] (1)	-	THF/H$_2$O (9:1)	0	0	-
14	[Au(IPr)(cbz)] (1)	-	THF/H$_2$O (9:1)	1	0	-
15	[Au(IPr*)OH] (1)	-	THF/H$_2$O (9:1)	8	6	-
16	[Au(IPr*)(OTf)] (1)	-	THF/H$_2$O (9:1)	100	97	93:7
17	[Au(IPr^{Cl})(OTf)] (1)	-	THF/H$_2$O (9:1)	100	99	95:5
18	[Au(SIPr)(OTf)] (1)	-	THF/H$_2$O (9:1)	79	70	93:7
19	[Au(IPr)(MeCN)][BF$_4$] (1)	-	THF/H$_2$O (9:1)	38	38	94:6
20	[Au(IPr^{Cl})(MeCN)][BF$_4$] (1)	-	THF/H$_2$O (9:1)	28	27	96:4
21[c]	[Au(IPr)(MeCN)][BF$_4$] (1)	-	dioxane/H$_2$O (2:1)	100	90	96:4
22	[Au(IPr^{Cl})(MeCN)][BF$_4$] (1)	-	dioxane/H$_2$O (2:1)	89	81	96:4
23	[Au(IPr)(OTf)] (1)	-	THF/H$_2$O (9:1)	99	98	95:5
24	[Au(IPr)(OTf)] (1)	-	THF/H$_2$O (5:1)	100	100	94:6
25	[Au(IPr)(OTf)] (1)	-	THF/H$_2$O (2:1)	100	97	94:6
26	[Au(IPr)(OTf)] (1)	-	dioxane/H$_2$O (9:1)	100	94	95:5
27	[Au(IPr)(OTf)] (1)	-	dioxane/H$_2$O (2:1)	100	87	95:5
28	[Au(IPr)(OTf)] (1)	-	CH$_3$CN/H$_2$O (9:1)	14	10	89:11
29	[Au(IPr)(OTf)] (1)	-	Et$_2$O/H$_2$O (9:1)	36	33	95:5
30	[Au(IPr)(OTf)] (1)	-	EtOAc/H$_2$O (9:1)	100	96	94:6
31	[Au(IPr)(OTf)] (1)	-	EtOAc /H$_2$O (5:1)	96	94	94:6
32	[Au(IPr)(OTf)] (1)	-	EtOAc /H$_2$O (2:1)	47	44	94:6
33	[Au(IPr)(OTf)] (0.5)	-	EtOAc /H$_2$O (9:1)	94	90	94:6
34	[Au(IPr)(OTf)] (1)	-	EtOAc /H$_2$O (9:1)	100	100 (89)[d]	94:6
35	[Au(IPr)(OTf)] (1)	-	EtOAc /H$_2$O (9:1)	100	98	95:5
36	[Au(IPr)(OTf)] (1)	-	EtOAc /H$_2$O (9:1)	100	99	94:6
37	-	HOTf (1)	EtOAc /H$_2$O (9:1)	10	0	-
38	-	-	EtOAc /H$_2$O (9:1)	0	0	-

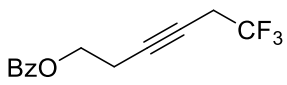
[a] Conversions of **1a** and yields of **2a** + **2a'** were estimated by ^{19}F NMR analysis of the crude mixture after workup using 2-fluoro-4-nitrotoluene as internal standard. [b] Ratio of **2a**:**2a'** estimated by ^{19}F NMR analysis of the crude mixture after workup. [c] The reaction was carried out at 60 °C. [d] Isolated yield of **2a** + **2a'** (94:6).

We started the optimization by testing gold complexes bearing a triphenylphosphine ligand (entries 1-2). While giving an excellent regioselectivity (95:5 avec 96:4 respectively), the conversions and yields were not satisfactory. We then tried different gold-IPr catalysts at 5 mol% (entries 3-5). With the chloride (entry 3), silver triflate was added to activate the catalyst. Chloride (entry 3) and triflate (entry 5) counterion gave excellent yields (98% et and 97%, respectively), but the hydroxide (entry 4) gave a better regioselectivity (99:1) despite the very low yield of 6%. Reducing the catalyst loading to 1 mol% did not significantly reduce the yield using [Au(IPr)(OTf)] (entry 6). The bistriflimide counterion gave similar result (entry 7). To improve the regioselectivity, we then tried using [Au(IPr)OH] with different activation methods (entries 8-11). Triflic acid proved to be efficient in activating the catalyst (entry 11), but the result was identical to the already activated catalyst bearing a triflate as the counterion. No improvement in the regioselectivity was observed. We then did a catalyst screening (entries 12-20) using different counterions and NHCs. However, none of these catalysts could improve the ratio of **2a** and **2a'**. Conversions and yields are also variable. Complexes bearing an acetonitrile ligand were also used in a 2:1 dioxane/H_2O mixture (entries 21-22). The catalysts were more active in this solvent, but the selectivity was still not affected. In a reaction carried out at 60 °C (entry 23), the conversion was not complete, so 70 °C was kept for the optimized conditions. The optimization of solvents (entries 24-32) showed that 9:1 EtOAc/H_2O was as good as THF/H_2O mixtures. EtOAc was selected for safety and environmental reasons. Lowering the catalyst loading resulted in reduced conversion (entry 33), so 1 mol% of gold catalyst was found necessary. Entries 34-36 just show that the reaction is reproductible. A first control experiment was done using only triflic acid without gold complex (entry 37). No product was observed in this case. Finally, another control experiment without gold complex or other activator gave no conversion (entry 38). These two control experiments support a gold-catalyzed process.

3. General procedure for the synthesis of trifluoroethylated alkynes

Modified Sonogashira coupling conditions

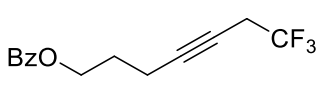
Following a modified procedure from Xu and collaborators,[3] $Pd(dba)_2$ (10 mol%), DPEPhos (20 mol%) and DABCO (2 equiv) were weighted in an oven-dried round bottom flask and purged with argon for 15 minutes. A solution of terminal alkyne (1 equiv) in dry toluene (0.5 M) was then added, followed by CF_3CH_2I (2 equiv). The reaction mixture was vigorously stirred at 80 °C for 24 h. The suspension is then cooled to room temperature and filtered over a Celite pad. The flask and the pad were rinsed with EtOAc or Et_2O (for more volatile compounds). The filtrate was washed with 3 M HCl (1x), saturated $NaHCO_3$ (1x) and brine (1x), dried over Na_2SO_4, filtered and evaporated *in vacuo*. The crude material was purified by flash silica gel chromatography.



6,6,6-Trifluorohex-3-yn-1-yl benzoate (1a)

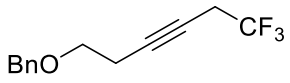
Prepared according to the general procedure on a 2.00 mmol scale, the desired product (434 mg, 1.69 mmol, 85%) was isolated as a yellow oil after purification by flash column chromatography (5% Et_2O/hexanes). ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.07–8.04 (m, 2H), 7.59–7.55 (m, 1H), 7.47–7.43 (m, 2H), 4.41 (t, *J* = 6.8 Hz, 2H), 3.02 (qt, *J* = 9.6, 2.4 Hz, 2H), 2.67 (tt, *J* = 6.8, 2.4 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.9 (t, *J* = 9.7 Hz, 3F). Data are in accordance with the one described in the literature.[3]

[3] Y.-S. Feng, C.-Q. Xie, W.-L. Qiao and H.-J. Xu, *Org. Lett.*, 2013, **15**, 936-939.



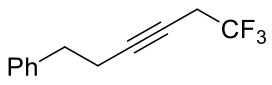
7,7,7-Trifluorohept-4-yn-1-yl benzoate (1b)

Prepared according to the general procedure on a 0.99 mmol scale, the desired product (164 mg, 0.61 mmol, 61%) was isolated as a yellow oil after automated flash purification (0–5% EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.06–8.03 (m, 2H), 7.59–7.54 (m, 1H), 7.48–7.41 (m, 2H), 4.41 (t, *J* = 6.3 Hz, 2H), 2.99 (qt, *J* = 9.7, 2.4 Hz, 2H), 2.39 (tt, *J* = 7.0, 2.4 Hz, 2H), 1.99 (tt, *J* = 7.0, 6.3 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -67.0 (t, *J* = 9.6 Hz, 3F). Data are in accordance with the one described in the literature.[4]



(((6,6,6-Trifluorohex-3-yn-1-yl)oxy)methyl)benzene (1c)

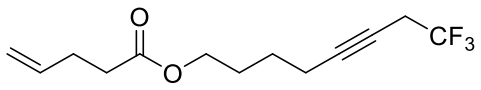
Prepared according to the general procedure on a 1.03 mmol scale, the desired product (154 mg, 0.64 mmol, 62%) was isolated as a yellow oil after purification by automated flash purification (0–5% EtOAc/hexanes). FT-IR ν (cm^{-1}) = 2864, 1366, 1281, 1254, 1155, 1138, 1107, 908, 696; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.37–7.33 (m, 4H), 7.32–7.27 (m, 1H), 4.56 (s, 2H), 3.58 (t, *J* = 6.9 Hz, 2H), 3.01 (qt, *J* = 9.7, 2.4 Hz, 2H), 2.51 (tt, *J* = 6.9, 2.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 138.0, 128.4, 127.73, 127.69, 124.4 (q, J_{C-F} = 276.5 Hz), 81.8, 73.0, 69.4 (q, J_{C-F} = 5.0 Hz), 68.1, 26.2 (q, J_{C-F} = 34.8 Hz), 20.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.9 (t, *J* = 9.9 Hz, 3F); HRMS (APPI-TOF) m/z calcd for $C_{13}H_{14}F_3O$ $[M+H]^+$ 243.0991; found 243.0983.



(6,6,6-Trifluorohex-3-yn-1-yl)benzene (1d)

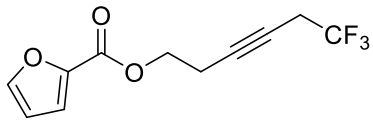
Prepared according to the general procedure on a 1.54 mmol scale, the desired product (232 mg, 1.09 mmol, 71%) was isolated as a colorless oil after purification by flash column chromatography (hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.33–7.26 (m, 2H), 7.24–7.18 (m, 3H), 2.99 (qt, *J* = 9.7, 2.4 Hz, 2H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.47 (tt, *J* = 7.5, 2.4 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.9 (t, *J* = 9.9 Hz, 3F). Data are in accordance with the one described in the literature.[5]

[4] E.-J. Han, Y. Sun, Q. Shen, Q.-Y. Chen, Y. Guo and Y.-G. Huang, *Org. Chem. Front.*, 2015, **2**, 1379-1387.
[5] C.-B. Liu, W. Meng, F. Li, S. Wang, J. Nie and J.-A. Ma, *Angew. Chem. Int. Ed.*, 2012, **51**, 6227-6230.



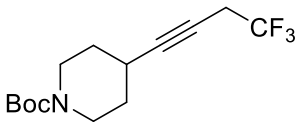
8,8,8-Trifluorooct-5-yn-1-yl pent-4-enoate (1e)

Prepared according to the general procedure on a 1.48 mmol scale, the desired product (204 mg, 0.78 mmol, 53%) was isolated as a yellow oil after purification by flash column chromatography (5–10 % EtOAc/hexanes). FT-IR ν (cm^{-1}) = 2953, 2939, 1734, 1641, 1281, 1155, 1138, 1109, 995, 908; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 5.83 (ddt, *J* = 16.7, 10.4, 6.3 Hz, 1H), 5.06 (ddt, *J* = 17.2, 1.7, 1.6 Hz, 1H), 5.01 (ddt, *J* = 10.3, 1.5, 1.3 Hz, 1H), 4.10 (t, *J* = 6.4 Hz, 2H), 3.00 (qt, *J* = 9.7, 2.4 Hz, 2H), 2.44–2.35 (m, 4H), 2.23 (tt, *J* = 7.0, 2.4 Hz, 2H), 1.78–1.69 (m, 2H), 1.63–1.56 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 173.1, 136.7, 124.4 (q, J_{C-F} = 276.6 Hz), 115.5, 84.2, 68.8 (q, J_{C-F} = 5.1 Hz), 63.8, 33.6, 28.9, 27.7, 26.1 (q, J_{C-F} = 34.7 Hz), 24.9, 18.2; ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -67.0 (t, *J* = 9.8 Hz, 3F); HRMS (ESI-TOF) m/z calcd for $C_{13}H_{18}F_3O_2$ $[M+H]^+$ 263.1253; found 263.1246.



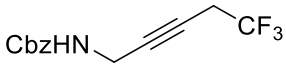
6,6,6-Trifluorohex-3-yn-1-yl furan-2-carboxylate (1f)

Prepared according to the general procedure on a 1.79 mmol scale, the desired product (296 mg, 1.20 mmol, 67%) was isolated as a colorless oil after purification by flash column chromatography (50% CH_2Cl_2/hexanes). FT-IR ν (cm^{-1}) = 2968, 2361, 1718, 1474, 1281, 1254, 1107, 885, 760, 656; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.59 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.20 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.52 (dd, *J* = 3.5, 1.7 Hz, 1H), 4.39 (t, *J* = 6.9 Hz, 2H), 3.02 (qt, *J* = 9.6, 2.4 Hz, 2H), 2.66 (tt, *J* = 6.9, 2.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 158.4, 146.6, 144.4, 124.3 (q, J_{C-F} = 276.6 Hz), 118.3, 111.9, 80.2, 70.3 (q, J_{C-F} = 5.1 Hz), 62.4, 26.1 (q, J_{C-F} = 34.8 Hz), 19.3; ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -68.9 (t, *J* = 9.6 Hz, 3F); HRMS (ESI-TOF) m/z calcd for $C_{11}H_{10}F_3O_3$ $[M+H]^+$ 247.0577; found 247.0562.



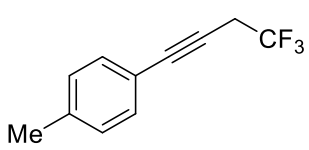
tert-Butyl-4-(4,4,4-trifluorobut-1-yn-1-yl)piperidine-1-carboxylate (1g)

Prepared according to the general procedure on a 1.58 mmol scale, the desired product (310 mg, 1.06 mmol, 67%) was isolated as a yellow oil after two purifications by flash column chromatography (0–2.5% EtOAc/toluene and 0–5% EtOAc/CH_2Cl_2). FT-IR ν (cm^{-1}) = 2932, 1690, 1420, 1366, 1256, 1157, 1140, 1109; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 3.69–3.61 (m, 2H), 3.21 (ddd, J = 13.5, 8.3, 3.5 Hz, 2H), 3.02 (qd, J = 9.6, 2.2 Hz, 1H), 2.59 (ddtq, J = 8.1, 6.1, 4.1, 2.2 Hz, 1H), 1.76 (ddd, J = 16.3, 7.2, 3.9 Hz, 2H), 1.62–1.51 (m, 2H), 1.45 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 154.8, 124.3 (q, J_{C-F} = 276.6 Hz), 86.7, 79.5, 69.9 (q, J_{C-F} = 4.9 Hz), 42.0 (br. d, J_{C-F} = 86.4 Hz), 31.1, 28.4, 26.8, 26.1 (q, J_{C-F} = 34.4 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -67.0 (t, J = 9.7 Hz, 3F); HRMS (APPI-TOF) m/z calcd for $C_{14}H_{21}F_3NO_2$ $[M+H]^+$ 292.1519; found 292.1540.



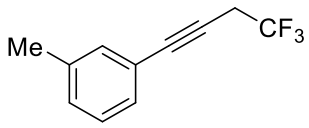
Benzyl (5,5,5-trifluoropent-2-yn-1-yl)carbamate (1h)

Prepared according to the general procedure on a 1.28 mmol scale, the desired product (219 mg, 0.807 mmol, 63%) was isolated as a pale yellow solid after purification by automated flash purification (0–15% EtOAc/hexanes). FT-IR ν (cm^{-1}) = 3300, 1684, 1543, 1246, 1146, 1109; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.38–7.30 (m, 5H), 5.12 (s, 2H), 4.96 (br. s, 1H), 4.03–3.98 (m, 2H), 3.03 (qt, J = 9.6, 2.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 155.9, 136.2, 128.6, 128.3, 128.2, 124.1 (q, J_{C-F} = 276.6 Hz), 80.4, 71.9 (q, J_{C-F} = 5.1 Hz), 67.2, 31.0, 26.1 (q, J_{C-F} = 34.8 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.5 (t, J = 9.7 Hz, 3F); HRMS (ESI-TOF) m/z calcd for $C_{13}H_{13}F_3NO_2$ $[M+H]^+$ 272.0893; found 272.0876.



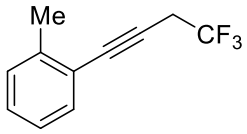
(6,6,6-Trifluorohex-3-yn-1-yl)benzene (1i)

Prepared according to the general procedure on a 1.93 mmol scale, the desired product (220 mg, 1.11 mmol, 57%) was isolated as a colorless oil after purification by flash column chromatography (hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.35–7.33 (m, 2H), 7.14–7.10 (m, 2H), 3.26 (q, *J* = 9.6 Hz, 2H), 2.35 (s, 3H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.5 (t, *J* = 9.7 Hz, 3F). Data are in accordance with the one described in the literature.[3]



1-Methyl-3-(4,4,4-trifluorobut-1-yn-1-yl)benzene (1j)

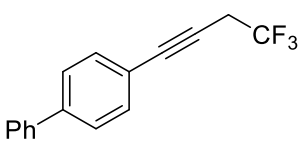
Prepared according to the general procedure on a 1.85 mmol scale, the desired product (223 mg, 1.13 mmol, 61%) was isolated as a colorless oil after purification by flash column chromatography (hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.28–7.27 (m, 1H), 7.27–7.24 (m, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.16–7.13 (m, 1H), 3.26 (q, *J* = 9.5 Hz, 2H), 2.33 (s, 3H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.5 (t, *J* = 9.6 Hz, 3F). Data are in accordance with the one described in the literature.[6]



1-Methyl-2-(4,4,4-trifluorobut-1-yn-1-yl)benzene (1k)

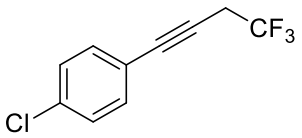
Prepared according to the general procedure on a 2.75 mmol scale, the desired product (354 mg, 1.79 mmol, 65%) was isolated as a colorless oil after purification by flash column chromatography (hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.44–7.38 (m, 1H), 7.27–7.17 (m, 2H), 7.15–7.11 (m, 1H), 3.31 (q, *J* = 9.5 Hz, 2H), 2.43 (s, 3H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.6 (t, *J* = 9.6 Hz, 3F). Data are in accordance with the one described in the literature.[6]

[6] Y. Miyake, S.-I. Ota, M. Shibata, K. Nakajima and Y. Nishibayashi, *Chem. Commun.*, 2013, **49**, 7809-7811.



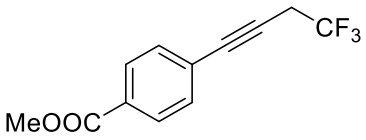
4-Ethynyl-1,1'-biphenyl (1l)

Prepared according to the general procedure on a 1.95 mmol scale, the desired product (322 mg, 1.24 mmol, 63%) was isolated as a white solid after purification by flash column chromatography (hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.59–7.50 (m, 6H), 7.46–7.42 (m, 2H), 7.38–7.34 (m, 1H), 3.29 (q, *J* = 9.6 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.4 (t, *J* = 9.5 Hz, 3F). Data are in accordance with the one described in the literature.[3]



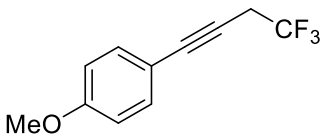
1-Chloro-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (1m)

Prepared according to the general procedure on a 3.38 mmol scale, the desired product (497 mg, 2.27 mmol, 67%) was isolated as a colorless oil after purification by flash column chromatography (hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.41–7.34 (m, 2H), 7.31–7.28 (m, 2H), 3.26 (q, *J* = 9.5 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.4 (t, *J* = 9.6 Hz, 3F). Data are in accordance with the one described in the literature.[6]



Methyl 4-(4,4,4-trifluorobut-1-yn-1-yl)benzoate (1n)

Prepared according to the general procedure on a 1.89 mmol scale, the desired product (305 mg, 1.26 mmol, 67%) was isolated as a yellow oil after purification by flash column chromatography (5% EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.00–7.97 (m, 2H), 7.52–7.49 (m, 2H), 3.92 (s, 3H), 3.30 (q, *J* = 9.5 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.3 (t, *J* = 9.5 Hz, 3F). Data are in accordance with the one described in the literature.[3]

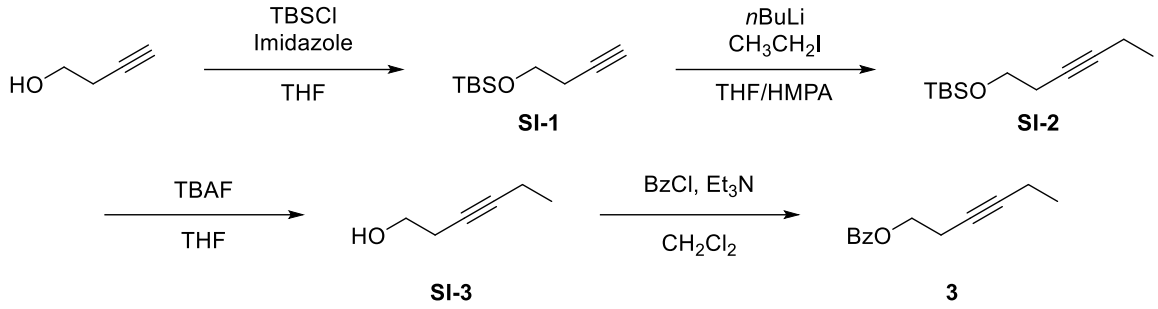


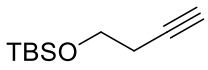
1-Methoxy-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (1o)

Prepared according to the general procedure on a 1.01 mmol scale, the desired product (118 mg, 0.55 mmol, 55%) was isolated as a colorless oil after purification by automated flash purification (0–5% EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.40–7.36 (m, 2H), 6.85–6.82 (m, 2H), 3.81 (s, 3H), 3.25 (q, *J* = 9.6 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.6 (t, *J* = 9.7 Hz, 3F). Data are in accordance with the one described in the literature.[3]

4. Synthesis of other alkynes

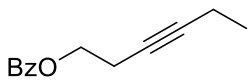
Alkyne **3** was synthesized through the following pathway:





(But-3-yn-1-yloxy)(tert-butyl)dimethylsilane (SI-1)

Imidazole (428 mg, 6.29 mmol, 1.25 equiv) and TBSCl (956 mg, 6.34 mmol, 1.25 equiv) were added over a solution of 3-butyn-1-ol (0.38 mL, 5.02 mmol, 1 equiv) in dry CH_2Cl_2 (17 mL, 0.3 M) cooled to 0 °C. The ice bath was removed and the reaction was heated to room temperature. After 1 hour, saturated NH_4Cl was added. The phases were separated and the aqueous layer was extracted with CH_2Cl_2 (2x). Combined organic layers were dried over Na_2SO_4, filtered and evaporated *in vacuo*. The desired product (492 mg, 2.67 mmol, 53%) was isolated as a colorless oil after purification by automated flash purification (0–5% EtOAc/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 3.74 (t, *J* = 7.1 Hz, 2H), 2.40 (td, *J* = 7.1, 2.7 Hz, 2H), 1.96 (t, *J* = 2.7 Hz, 2H), 0.90 (s, 9H), 0.07 (s, 6H). Data are in accordance with the one described in the literature.[7]



(But-3-yn-1-yloxy)(tert-butyl)dimethylsilane (3)

n-Butyllithium (2.5 M in hexanes, 1.6 mL, 4 mmol, 1.5 equiv) was added dropwise over a solution of **SI-1** (481 mg, 2.61 mmol, 1 equiv) in dry THF (5.2 mL, 0.5 M) cooled to -78 °C. After 20 minutes, HMPA (2.6 mL, 1 vol.) was added. After 30 minutes, iodoethane (0.25 mL, 3.11 mmol, 1.2 equiv) was added dropwise. After 20 minutes, the cooling bath was removed and the reaction was heated to room temperature. After 2 hours, saturated NH_4Cl and Et_2O were added. The phases were separated and the aqueous layer was extracted with Et_2O (2x). Combined organic layers were washed with brine (1x), dried over Na_2SO_4, filtered and evaporated *in vacuo*. Product **SI-2** was used for next step without further purification.

[7] K. Ravindar, M. S. Reddy and P. Deslongchamps, *Org. Lett.*, 2011, **13**, 3178-3181.

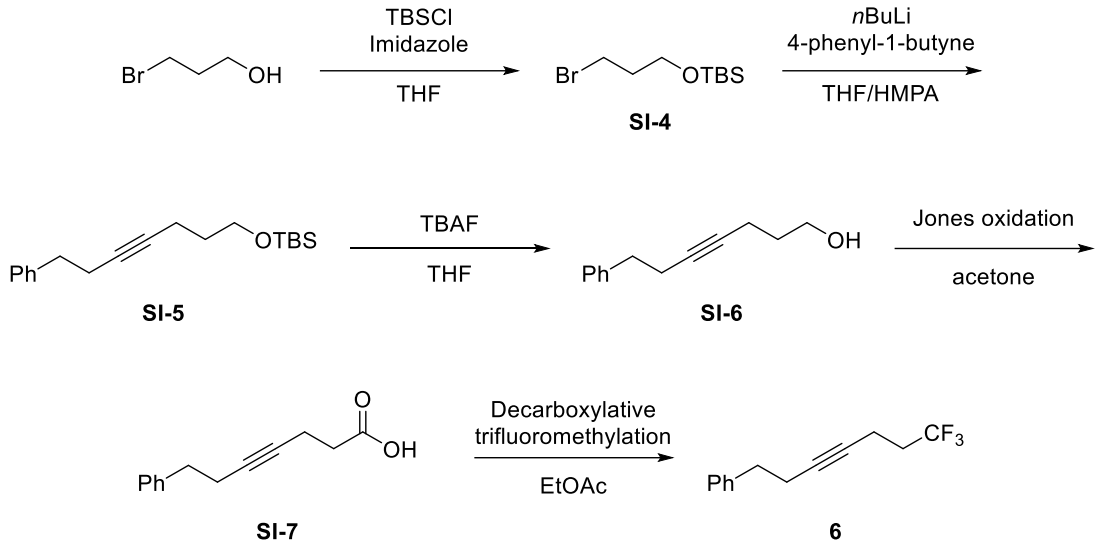
TBAF (1 M in THF, 4 mL, 4 mmol, 1.5 equiv) was added dropwise over a solution of **SI-2** in dry THF (2.6 mL, 1 M) at room temperature. After 1 hour, 1 M HCl and Et_2O were added. The phases were separated and the aqueous layer was extracted with Et_2O (2x). Combined organic layers dried over Na_2SO_4, filtered and evaporated *in vacuo*. Product **SI-3** was used for next step without further purification.

Benzyl chloride (0.46 mL, 3.96 mmol, 1.5 equiv) was added dropwise over a solution of **SI-3** and triethylamine (0.73 mL, 5.24 mmol, 2 equiv) in dry CH_2Cl_2 (26 mL, 0.1 M) cooled to 0 °C. After 15 minutes, the ice bath was removed and the reaction was heated to room temperature. After 24 hours, H_2O was added. The phases were separated and the aqueous layer was extracted with CH_2Cl_2 (2x). Combined organic layers were dried over Na_2SO_4, filtered and evaporated *in vacuo*. The desired product **3** (457 mg, 2.26 mmol, 87% over 3 steps) was isolated as a yellow oil after purification by automated flash purification (0–5% EtOAc/hexanes). FT-IR ν (cm^{-1}) = 2976, 1718, 1267, 1109, 1026, 708 ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.08–8.05 (m, 2H), 7.58–7.54 (m, 1H), 7.46–7.42 (m, 2H), 4.38 (t, *J* = 7.1 Hz, 2H), 2.62 (tt, *J* = 7.0, 2.4 Hz, 2H), 2.16 (qt, *J* = 7.5, 2.4 Hz, 2H), 1.11 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 166.4, 133.0, 130.2, 129.7, 128.3, 83.5, 74.8, 63.3, 19.4, 14.1, 12.4; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{15}O_2$ $[M+H]^+$ 203.1067; found 203.1073.

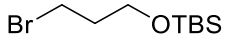
Alkyne **5** was synthesized following literature procedure.[8]

[8] M. Cloutier, M. Roudias and J.-F. Paquin, *Org. Lett.*, 2019, **21**, 3866-3870.

Alkyne **6** was synthesized through the following pathway:

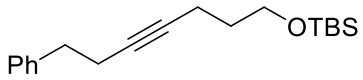


(3-Bromopropoxy)(tert-butyl)dimethylsilane (SI-4)



Following a modified procedure from Salvadori *et al.*,[9] 3-bromobutan-1-ol (1.35 mL, 14.9 mmol, 1 equiv) was added on a solution of TBSCl (2.94 g, 19.5 mmol, 1.3 equiv) and imidazole (2.34 g, 34.4 mmol, 2.3 equiv) in dry THF (30 mL, 0.5 M). After 3 hours, the solvent was evaporated *in vacuo*. The residue was solubilized in CH_2Cl_2 and H_2O, the phases were separated and the aqueous layer was extracted with CH_2Cl_2 (2x). Combined organic layers were washed with brine (1x), dried over Na_2SO_4, filtered and evaporated *in vacuo*. The desired product (2.15 g, 8.49 mmol, 57%) was isolated as a colorless oil after purification by automated flash purification (hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 3.74 (t, *J* = 5.7 Hz, 2H), 3.52 (t, *J* = 6.5 Hz, 2H), 2.03 (tt, *J* = 6.4, 5.7 Hz, 2H), 0.90 (s, 9H), 0.07 (s, 6H). Data are in accordance with the one described in the literature.[10]

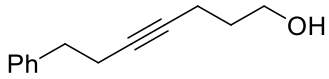
[9] C. Trapella, C. Fischetti, M. Pela, I Lazzari, R. Guerrini, G. Calo, A. Rizzi, V. Camarda, D. G. Lambert, J. McDonald, D. Regoli and S. Salvadori, *Bioorg. Med. Chem.*, 2009, **17**, 5080-5095.
[10] C. M. Thompson, C. A. Quinn and P. J. Hergenrother, *J. Med. Chem.*, 2009, **52**, 117-125.



tert-Butyldimethyl((7-phenylhept-4-yn-1-yl)oxy)silane (SI-5)

Following a procedure from van der Donk *et al.*[11] on **SI-4** (1.26 g, 4.98 mmol, 1 equiv), the desired product (496 mg, 1.64 mmol, 33%) was isolated as a colorless oil after purification by flash column chromatography (25% CH_2Cl_2/hexanes). FT-IR ν (cm^{-1}) = 2928, 2856, 1472, 1256, 1101, 833, 773; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.31–7.26 (m, 2H), 7.22–7.18 (m, 3H), 1.72–1.59 (m, 3H), 3.65 (t, *J* = 6.1 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.43 (tt, *J* = 7.6, 2.4 Hz, 2H), 2.22 (tt, *J* = 7.0, 2.4 Hz, 2H), 1.66 (tt, *J* = 7.1, 6.1 Hz, 2H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 141.0, 128.4, 126.2, 80.5, 79.6, 61.7, 35.6, 32.1, 26.0, 21.0, 18.4, 15.1, -5.3; HRMS (ESI-TOF) m/z calcd for $C_{19}H_{31}OSi$ $[M+H]^+$ 303.2139; found 303.2133.

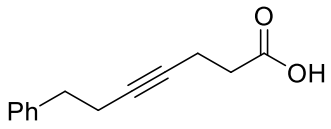
7-Phenylhept-4-yn-1-ol (SI-6)



Following a procedure from van der Donk *et al.*[11] on **SI-5** (421 mg, 1.39 mmol, 1 equiv), the desired product (249 mg, 1.32 mmol, 95%) was isolated as a colorless oil after purification by flash column chromatography (25% EtOAc/hexanes). FT-IR ν (cm^{-1}) = 2928, 1495, 1454, 1053, 696; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.32–7.27 (m, 2H), 7.23–7.18 (m, 3H), 3.69 (t, *J* = 6.1 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.44 (tt, *J* = 7.5, 2.4 Hz, 2H), 2.26 (tt, *J* = 6.9, 2.4 Hz, 2H), 1.70 (p, *J* = 6.6 Hz, 2H), 1.56 (br. s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 140.9, 128.5, 128.3, 126.2, 80.2, 80.1, 61.9, 35.4, 31.5, 20.9, 15.3; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{17}O$ $[M+H]^+$ 189.1274; found 189.1280.

[11] C. Jacquot, C. M. McGinley, E. Plata, T. R. Holman and W. A. van der Donk, *Org. Biomol. Chem.*, 2008, **6**, 5080-5095.

7-Phenylhept-4-ynoic acid (SI-7)

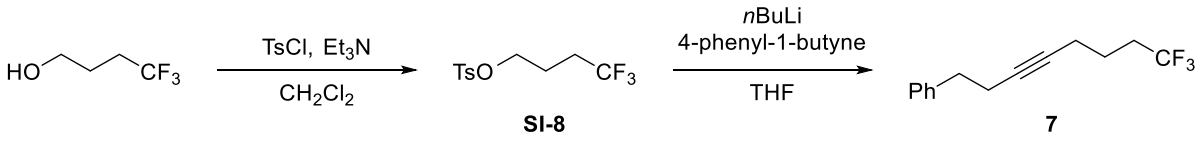


Following a procedure from Li *et al.*[12] on **SI-6** (630 mg, 3.34 mmol, 1 equiv), the desired product (537 mg, 2.66 mmol, 79%) was obtained as a white solid (no purification needed). FT-IR ν (cm^{-1}) = 2970, 1695, 1300, 1215, 949; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 11.52 (br. s, 1H), 7.31–7.25 (m, 2H), 7.24–7.15 (m, 3H), 2.78 (t, *J* = 7.4 Hz, 2H), 2.58–2.50 (m, 2H), 2.49–2.39 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 178.6, 140.8, 128.5, 128.3, 126.2, 80.6, 78.6, 35.3, 33.8, 20.9, 14.4; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{13}O_2$ $[M-H]^-$ 201.0921; found 201.0918.

(7,7,7-Trifluorohept-3-yn-1-yl)benzene (6)

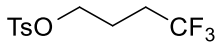
Following a procedure from MacMillan *et al.*[13] on **SI-7** (242 mg, 1.20 mmol, 1 equiv), the desired product (44 mg, 0.194 mmol, 16%) was isolated as a colorless oil after purification by flash column chromatography (1% Et_2O/hexanes). FT-IR ν (cm^{-1}) = 2928, 1385, 1254, 1130, 1111, 698; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.32–7.27 (m, 2H), 7.24–7.19 (m, 3H), 2.79 (t, *J* = 7.4 Hz, 2H), 2.47–2.37 (m, 4H), 2.32–2.22 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 140.7, 128.4, 128.3, 126.9 (q, J_{C-F} = 276.9 Hz), 126.3, 80.9, 77.2, 35.2, 33.7 (q, J_{C-F} = 28.8 Hz), 20.8, 12.4 (q, J_{C-F} = 3.9 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -67.0 (t, *J* = 10.5 Hz, 3F); HRMS (APPI-TOF) m/z calcd for $C_{13}H_{13}F_3$ $[M^*]^+$ 226.0964; found 226.0959.

Alkyne **7** was synthesized through the following pathway:



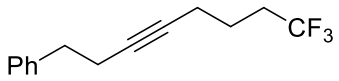
[12] C. L. Tung, C. T. T. Wong, E. Y. M. Fung and X. Li, *Org. Lett.*, 2016, **18**, 2600-2603.
[13] J. A. Kautzy, T. Wang, R. W. Evans and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2018, **140**, 6522-6536.

4,4,4-Trifluorobutyl 4-methylbenzenesulfonate (SI-8)



TsCl (440 mg, 2.31 mmol, 1.1 equiv) was added on a solution of 4,4,4-trifluorobutan-1-ol (0.22 mL, 2.08 mmol, 1 equiv), triethylamine (0.32 mL, 2.30 mmol, 1.1 equiv) and DMAP (26 mg, 0,213 mmoL, 0,1 equiv) in dry CH_2Cl_2 (7 mL, 0.3 M). After 2 hours, 3 M aqueous HCl was added. The phases were separated and the aqueous layer was extracted with CH_2Cl_2 (2x). Combined organic layers were dried over Na_2SO_4, filtered and evaporated *in vacuo*. The desired product (483 mg, 1.71 mmol, 82%) was isolated as a colorless oil after purification by automated flash purification (0-10% EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.81–7.78 (m, 2H), 7.38–7.35 (m, 2H), 4.09 (t, J = 6.1 Hz, 2H), 2.46 (s, 3H), 2.22–2.11 (m, 2H), 1.95–1.89 (m, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.4 (t, J = 10.7 Hz, 3F). Data are in accordance with the one described in the literature.[14]

[14] L. Lempke, A. Ernst, F. Kahl, R. Weberskirch and N. Krause, *Adv. Synth. Catal.*, 2016, **358**, 1491-1499.



(8,8,8-Trifluorooct-3-yn-1-yl)benzene (7)

In a microwave tube, *n*-butyllithium (2.5 M in hexanes, 0.58 mL, 1.45 mmol, 1.4 equiv) was added dropwise over a solution of 4-phenyl-1-butyne (0.21 mL, 1.49 mmol, 1.5 equiv) in dry THF (8 mL, 0.2 M) cooled to -78 °C. After 15 minutes, the cooling bath was removed and the reaction was heated to room temperature. After 1 hour, a solution of **SI-8** (291 mg, 1.03 mmol, 1 equiv) in dry THF (2 mL, 0.5 M) was added. The reaction was then capped and heated to 70 °C. After 17 hours, the reaction was cooled to room temperature and saturated NH_4Cl and Et_2O were added. The phases were separated and the aqueous layer was extracted with Et_2O (2x). Combined organic layers were washed with brine (1x), dried over Na_2SO_4, filtered and evaporated *in vacuo*. The desired product (167 mg, 0.695 mmol, 67%) was isolated as a colorless oil after purification by automated flash purification (0-3% EtOAc/hexanes). FT-IR ν (cm^{-1}) = 2947, 1389, 1256, 1130, 1111, 1014, 698; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.31–7.27 (m, 2H), 7.24–7.19 (m, 3H), 2.80 (t, *J* = 7.5 Hz, 2H), 2.45 (tt, *J* = 7.5, 2.4 Hz, 2H), 2.23 (tt, *J* = 6.7, 2.4 Hz, 2H), 2.16–2.06 (m, 2H), 1.73–1.66 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 140.8, 128.4, 128.3, 127.2 (q, J_{C-F} = 276.1 Hz), 126.3, 80.9, 79.0, 35.3, 32.7 (q, J_{C-F} = 28.7 Hz), 21.4 (q, J_{C-F} = 3.0 Hz), 20.8, 17.9; ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.2 (t, *J* = 10.9 Hz, 3F); HRMS (APPI-TOF) m/z calcd for $C_{14}H_{15}F_3$ $[M^*]^+$ 240.1120; found 240.1123.

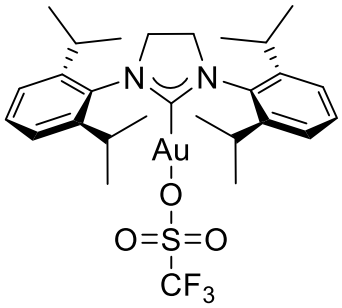
Oct-3-yn-1-ylbenzene (SI-9)

Methyllithium (1.6 M in Et_2O, 0.62 mL, 0.992 mmol, 1 equiv) was added dropwise over a solution of 4-phenyl-1-butyne (0.14 mL, 0.996 mmol, 1 equiv) in dry THF (2 mL, 0.5 M) cooled to 0 °C. After 10 minutes, a solution of 1-bromoethane (0.11 mL, 1.02 mmol, 1 equiv) in HMPA (1 mL, 1 vol.) was added dropwise. The cooling bath was removed and the reaction was heated to room temperature. After 4 hours, saturated NH_4Cl and Et_2O were added. The phases were separated and the aqueous layer was extracted with Et_2O (2x). Combined organic layers were washed with brine (1x), dried over Na_2SO_4, filtered and evaporated *in vacuo*. The desired product (75 mg, 0.403 mmol, 40%) was isolated as a colorless oil after purification by automated flash purification (0-5% toluene/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.30–7.26 (m, 2H), 7.23–7.18 (m, 3H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.44 (tt, *J* = 7.5, 2.4 Hz, 2H), 2.14 (tt, *J* = 7.1, 2.4 Hz, 2H), 1.50–1.32 (m, 4H), 0.90 (t, *J* = 7.3 Hz, 3H). Data are in accordance with the one described in the literature.[15]

[15] H. Yoneyama, K. Uemura, Y. Usami and S. Harusawa, *Tetrahedron*, 2017, **73**, 6109-6117.

5. Synthesis of gold complexes

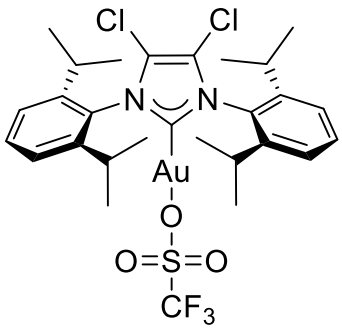
Except for the following, [Au(Acetonyl)(IPr^{Cl})],[16] [Au(NHC)(OTf)] complexes,[17] [Au(MeCN)(IPr^{Cl})][BF_4],[18] [Au(SIPr)(OH)][18] and all other gold complexes[2] were synthesized following literature procedures.



[Au(SIPr)(OTf)]

A 20-mL screwcap vial equipped with a septum cap and a stirring bar was charged with [Au(OH)(IPrCl)] (200 mg, 0.331 mmol, 1 equiv.) and chloroform (3.0 mL). To the resulting stirred solution was added HOTf (52.1 mg, 30.7 μL, 0.347 mmol, 1.05 equiv.) via a micropipette. After stirring at room temperature for 10 minutes, the mixture was microfiltered using a syringe filter for the removal of particles stemming from minor decomposition, the solvent was removed under vacuum and pentane (5.0 mL) was added to the residue. The resulting mixture was filtered, and the solid product was washed with pentane and dried under vacuum. The product was obtained as a white, microcrystalline solid in 98% yield (238 mg, 0.323 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.46 (t, J = 7.8 Hz, 2H), 7.26 (d, J = 7.8 Hz, 4H), 4.14 (s, 4H), 2.99 (hept, J = 6.8 Hz, 4H), 1.40 (d, J = 6.8 Hz, 12H), 1.34 (d, J = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 185.0, 146.6, 130.5, 124.9, 121.8, 53.6, 29.2, 25.0, 24.4. The CF_3 signal was not clearly detected, as it is a low intensity quadruplet (C-F coupling) at approximately 120 ppm; ^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) = -77.2. Data are in accordance with the one described in the literature.[19]

[16] D. Gasperini, A. Collado, A. Gómez-Suárez, D. B. Cordes, A. M. Z. Slawin and S. P. Nolan, *Chem. Eur. J.*, 2015, **21**, 4242-4252.
[17] T. A. C. A. Bayrakdar, F. Nahra, O. Zugazua, L. Eykens, D. Ormerod and S. P. Nolan, *Green Chem.*, 2020, **22**, 2598-2604.
[18] R. M. P. Veenboer, D. Gasperini, F. Nahra, D. B. Cordes, A. M. Z. Slawin, C. S. J. Cazin, and S. P. Nolan, *Organometallics*, 2017, **36**, 3645-3653.
[19] M. Gatto, A. Del Zotto, J. Segato and D. Zuccaccia, *Organometallics*, 2018, **37**, 4685-4591.

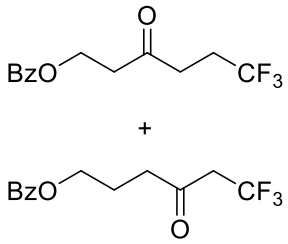


[Au(IPr^{Cl})(OTf)]

A 20-mL screwcap vial equipped with a septum cap and a stirring bar was charged with [Au(Acetonyl)(IPrCl)] (300 mg, 0.422 mmol, 1 equiv.) and DCM (3.0 mL). To the resulting stirred solution was added HOTf (66.4 mg, 39.2 μL, 0.443 mmol, 1.05 equiv.) via a micropipette. After stirring at room temperature for 10 minutes, the mixture was microfiltered using a syringe filter for the removal of particles stemming from minor decomposition, the solvent was removed under vacuum and pentane (5.0 mL) was added to the residue. The resulting mixture was filtered, and the solid product was washed with pentane and dried under vacuum. The product was obtained as a white, microcrystalline solid in 93% yield (317 mg, 0.395 mmol). Elemental analysis: calcd (%) for $C_{28}H_{34}AuCl_2F_3N_2O_3S$: C 41.85, H 4.27, N 3.49; found: C 41.97, H 4.08, N 3.05; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.60 (t, J = 7.8 Hz, 2H), 7.36 (d, J = 7.8 Hz, 4H), 2.39 (hept, J = 6.7 Hz, 4H), 1.33 (d, J = 6.9 Hz, 12H), 1.27 (d, J = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 161.9, 146.1, 132.2, 130.8, 124.9, 119.8, 29.4, 24.5, 23.7. The CF_3 signal was not clearly detected, as it is a low intensity quadruplet (C-F coupling) at approximately 120 ppm; ^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) = -77.1.

6. General procedure for the hydration of alkynes

[Au(IPr)(OTf)] (1 mol%) was added over a solution of alkyne (0.2 mmol) in EtOAc/H_2O (9:1, 0.1 M) in a 5 mL glass tube. The tube was sealed and heated to 70 °C. After 18 h, saturated $NaHCO_3$ was added. The phases were separated and the aqueous layer was extracted with EtOAc (2x). Combined organic layers were dried over Na_2SO_4, filtered and evaporated *in vacuo*. The crude material only contained the two desired regioisomers. If the regioisomers could be isolated, a silica gel flash chromatography was performed.

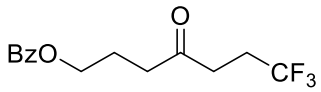


6,6,6-Trifluoro-3-oxohexyl benzoate + 6,6,6-Trifluoro-4-oxohexyl benzoate (94:6) (2a+2a')

Prepared according to the general procedure on a 0.219 mmol scale, the desired product (mixture of 94:6 of regioisomers determined by ^{19}F NMR) (53.3 mg, 0.194 mmol, 89%) was isolated as a colorless oil after purification by flash column chromatography (15% EtOAc/hexanes). ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.05–7.96 (m, 2H, **2a+2a'**), 7.60–7.53 (m, 1H, **2a+2a'**), 7.48–7.40 (m, 2H, **2a+2a'**), 4.61 (t, *J* = 6.2 Hz, 1.88H, **2a**), 4.35 (t, *J* = 6.2 Hz, 0.12H, **2a'**), 3.26 (q, *J* = 10.4 Hz, 0.11H, **2a'**), 2.93 (t, *J* = 6.2 Hz, 1.89H, **2a**), 2.77 (dd, *J* = 8.5 Hz, 1.88H, **2a**), 2.72 (t, *J* = 7.0 Hz, 0.13H, **2a'**), 2.46 (qdd, *J* = 10.7, 8.3, 6.9 Hz, 1.85H, **2a**), 2.11 (tt, *J* = 7.0, 6.4 Hz, 0.12H, **2a'**); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -62.4 (t, *J* = 10.5 Hz, 0.18F, **2a'**), -66.6 (t, *J* = 10.8 Hz, 2.82F, **2a**). Data are in accordance with the one described in the literature.[20]

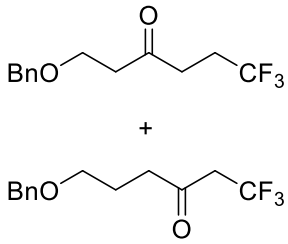
[20] M. M. Lerch, B. Morandi, Z. K. Wickens and R. H. Grubbs, *Angew. Chem. Int. Ed.*, 2014, **53**, 8654-8658.

1-(Benzyloxy)-6,6,6-trifluorohexan-3-one (2b)



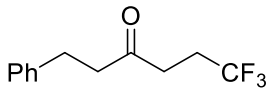
Prepared according to the general procedure on a 0.208 mmol scale, the desired product (48.8 mg, 0.169 mmol, 81%) was isolated as a colorless oil after purification by flash chromatography (30% Et_2O/hexanes). FT-IR ν (cm^{-1}) = 2962, 1715, 1315, 1271, 1107, 959, 710; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.03–8.01 (m, 2H), 7.59–7.55 (m, 1H), 7.47–7.43 (m, 2H), 4.35 (t, *J* = 6.3 Hz, 2H), 2.71 (t, *J* = 7.8 Hz, 2H), 2.63 (t, *J* = 7.2 Hz, 2H), 2.48–2.35 (m, 2H), 2.10 (p, *J* = 6.7 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 205.9, 166.5, 133.1, 130.1, 129.5, 128.4, 126.9 (q, J_{C-F} = 276.0 Hz), 63.9, 39.1, 35.1 (q, J_{C-F} = 2.5 Hz), 27.9 (q, J_{C-F} = 29.9 Hz), 22.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.6 (t, *J* = 10.9 Hz, 3F); HRMS (ESI-TOF) m/z calcd for $C_{14}H_{16}F_3O_3$ $[M+H]^+$ 289.1046; found 289.1023.

1-(Benzyloxy)-6,6,6-trifluorohexan-3-one + 6-(benzyloxy)-1,1,1-trifluorohexan-3-one (96:4) (2c+2c')



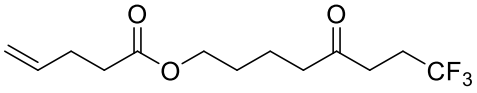
Prepared according to the general procedure on a 0.202 mmol scale, the desired product (mixture of 96:4 of regioisomers determined by ^{19}F NMR) (51.4 mg, 0.197 mmol, 98%) was isolated as a colorless oil after purification by flash column chromatography (25% Et_2O/hexanes). ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.37–7.33 (m, 2H, **2c+2c'**), 7.32–7.27 (m, 3H, **2c+2c'**), 4.51 (s, 1.91H, **2c**), 4.47 (s, 0.09H, **2c'**), 3.75 (t, *J* = 6.1 Hz, 1.92H, **2c**), 3.49 (t, *J* = 5.9 Hz, 0.09H, **2c'**), 3.21 (q, *J* = 10.5 Hz, 0.08H, **2c'**), 2.76–2.71 (m, 3.85H, **2c**), 2.65 (t, *J* = 7.0 Hz, 0.09H, **2c'**), 2.46–2.36 (m, 1.89H, **2c**), 1.93 (tt, *J* = 7.1, 6.0 Hz, 0.09H, **2c'**); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -62.5 (t, *J* = 10.5 Hz, 0.13F, **2c'**), -66.6 (t, *J* = 10.8 Hz, 2.87F, **2c**). Data are in accordance with the one described in the literature.[20]

6,6,6-Trifluoro-1-phenylhexan-3-one (2d)



Prepared according to the general procedure on a 0.178 mmol scale, the desired product (35.6 mg, 0.155 mmol, 87%) was isolated as a colorless oil after purification by flash chromatography (5% EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.31–7.27 (m, 2H), 7.24–7.15 (m, 3H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.78 (t, *J* = 7.5 Hz, 2H), 2.64 (dd, *J* = 8.6, 6.7 Hz, 2H), 2.40 (qdd, *J* = 10.8, 8.5, 6.9 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.6 (t, *J* = 10.8 Hz, 3F). Data are in accordance with the one described in the literature.[21]

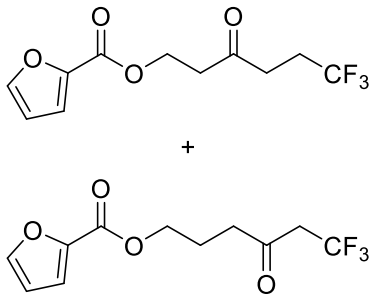
1 mmol scale procedure: [Au(IPr)(OTf) (7,4 mg, 10.1 µmol, 1 mol%) was added over a solution of alkyne (212 mg, 1.00 mmol, 1 equiv) in EtOAc/H_2O (9:1, 10 mL, 0.1 M) in a 20 mL glass tube. The tube was sealed and heated to 70 °C. After 18 h, saturated $NaHCO_3$ was added. The phases were separated and the aqueous layer was extracted with EtOAc (2x). Combined organic layers were dried over Na_2SO_4, filtered and evaporated *in vacuo*. The desired product (206 mg, 0.895 mmol, 89%) was isolated as a colorless oil after purification by flash column chromatography (5% EtOAc/hexanes). Spectral data are in accordance with the one described above.



8,8,8-Trifluoro-5-oxooctyl pent-4-enoate (2e)

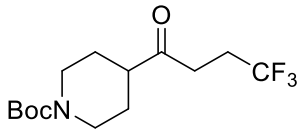
Prepared according to the general procedure on a 0.203 mmol scale, the desired product (mixture of 97:3 of regioisomers determined by ^{19}F NMR) (56.1 mg, 0.200 mmol, 99%) was obtained as a yellow oil (no purification needed). The characterization of the major regioisomer only is shown. FT-IR ν (cm^{-1}) = 2959, 1722, 1310, 1256, 1140, 1109, 916; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 5.82 (ddt, *J* = 16.7, 10.4, 6.3 Hz, 1H), 5.06 (ddt, *J* = 17.2, 1.7, 1.6 Hz, 1H), 5.00 (ddt, *J* = 10.3, 1.4, 1.3 Hz, 1H), 4.08 (t, *J* = 6.1 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.50 (t, *J* = 7.0 Hz, 2H), 2.45–2.35 (m, 6H), 1.72–1.59 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 206.5, 173.1, 136.7, 127.0 (q, J_{C-F} = 275.6 Hz), 115.5, 63.8, 42.1, 34.9 (q, J_{C-F} = 2.5 Hz), 33.5, 28.9, 28.0, 27.9 (q, J_{C-F} = 29.8 Hz), 20.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.6 (t, *J* = 10.8 Hz, 3F); HRMS (ESI-TOF) m/z calcd for $C_{13}H_{23}F_3NO_3$ $[M+NH_4]^+$ 298.1625; found 298.1615.

[21] D. G. Kananovich, Y. A. Konik, D. M. Zubrytski, I. Järving and M. Lopp, *Chem. Commun.*, 2015, **51**, 8349-8352.



6,6,6-Trifluoro-3-oxohexyl furan-2-carboxylate + 6,6,6-trifluoro-4-oxohexyl furan-2-carboxylate (94:6) (2f+2f')

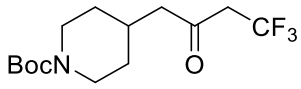
Prepared according to the general procedure on a 0.201 mmol scale, the desired product (mixture of 94:6 of regioisomers determined by ^{19}F NMR) (46.2 mg, 0.175 mmol, 87%) was isolated as a colorless oil after purification by flash column chromatography (40% Et_2O/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.59 (dd, *J* = 1.8, 0.9 Hz, 0.08H, **2f'**), 7.58 (dd, *J* = 1.8, 0.9 Hz, 0.87H, **2f**), 7.18 (dd, *J* = 3.5, 0.9 Hz, 0.08H, **2f'**), 7.16 (dd, *J* = 3.5, 0.9 Hz, 0.90H, **2f**), 6.53–6.52 (dd, *J* = 1.8, 0.9 Hz, 0.08H, **2f'**), 6.51 (dd, *J* = 3.5, 1.7 Hz, 0.90H, **2f**), 4.58 (t, *J* = 6.2 Hz, 1.87H, **2f**), 4.33 (t, *J* = 6.2 Hz, 0.13H, **2f'**), 3.27 (q, *J* = 10.5 Hz, 0.13H, **2f'**), 2.92 (t, *J* = 6.2 Hz, 1.89H, **2f**), 2.77 (dd, *J* = 8.5, 6.8 Hz, 1.88H, **2f**), 2.70 (t, *J* = 7.0 Hz, 0.14H, **2f'**), 2.45 (qdd, *J* = 10.8, 8.3, 6.9 Hz, 1.92H, **2f**), 2.09 (tt, *J* = 7.0, 6.2 Hz, 0.14H, **2f'**); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -62.4 (t, *J* = 10.5 Hz, 0.19F, **2f'**), -66.6 (t, *J* = 10.8 Hz, 2.81F, **2f**). Data for the major regioisomer are in accordance with the one described in the literature.[20]



***tert*-Butyl 4-(4,4,4-trifluorobutanoyl)piperidine-1-carboxylate (2g)**

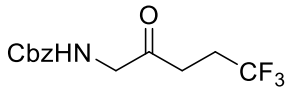
Prepared according to the general procedure on a 0.193 mmol scale, using 2 mol% of [Au(IPr)(OTf)] (2.9 mg, 3.95 μmol), the desired product (44 mg, 0.142 mmol, 74%) was isolated as a colorless oil after purification by flash column chromatography (40% Et_2O/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 4.13 (br s, 2H), 2.83–2.70 (m, 4H), 2.50 (tt, *J* = 11.5, 3.7 Hz, 1H), 2.42 (qt, *J* = 10.8, 7.6 Hz, 2H), 1.83 (br. d, *J* = 13.0 Hz, 2H), 1.60–1.49 (m, 2H), 1.46 (s, 9H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.6 (t, *J* = 10.8 Hz, 3F). Data are in accordance with the one described in the literature.[22]

[22] Y. A. Konik, M. Kudrjashova, N. Konrad, S. Kaabel, I. Järving, M. Lopp and D. G. Kananovich, *Org. Biomol. Chem.*, 2017, **15**, 4635-4643.



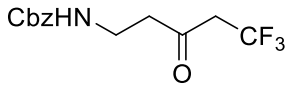
tert-Butyl 4-(4,4,4-trifluoro-2-oxobutyl)piperidine-1-carboxylate (2g')

The other regioisomer (**2g'**, 15 mg, 0.048 mmol, 25%) was isolated as a white solid after purification (see above). FT-IR ν (cm^{-1}) = 2922, 2854, 1728, 1674, 1416, 1273, 1126, 1040, 771, 636; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 4.08 (br. s, 2H), 3.20 (q, *J* = 10.4 Hz, 2H), 2.80–2.67 (m, 2H), 2.47 (d, *J* = 6.7 Hz, 2H), 2.09–1.98 (m, 1H), 1.69–1.62 (m, 2H), 1.45 (s, 9H), 1.12 (dt, *J* = 13.4, 9.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 199.0 (q, $J_{C\text{-}F}$ = 2.3 Hz), 154.8, 123.5 (q, $J_{C\text{-}F}$ = 277.1 Hz), 79.4, 49.9 (q, $J_{C\text{-}F}$ = 1.9 Hz), 46.9 (q, $J_{C\text{-}F}$ = 28.1 Hz), 31.7, 31.3, 30.3, 28.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -62.3 (t, *J* = 10.5 Hz, 3F); HRMS (APPI-TOF) m/z calcd for $C_{14}H_{23}F_3NO_3$ $[M+H]^+$ 310.1625; found 310.1646.



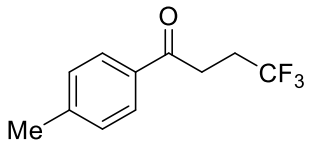
Benzyl (5,5,5-trifluoro-2-oxopentyl)carbamate (2h)

Prepared according to the general procedure on a 0.212 mmol scale, the desired product (48 mg, 0.166 mmol, 78%) was isolated as a white solid after purification by automated flash purification (40–70% Et_2O/hexanes). FT-IR ν (cm^{-1}) = 3333, 1726, 1688, 1539, 1250, 1219, 1148, 1043, 704; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.39–7.31 (m, 5H), 5.41 (br. s, 1H), 5.13 (s, 2H), 4.12 (d, *J* = 5.1 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.53–2.40 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 202.0, 156.1, 136.1, 128.6, 128.3, 128.1, 126.6 (q, $J_{C\text{-}F}$ = 275.7 Hz), 67.2, 50.5, 32.4 (q, $J_{C\text{-}F}$ = 2.7 Hz), 27.7 (q, $J_{C\text{-}F}$ = 30.2 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.7 (t, *J* = 10.6 Hz, 3F); HRMS (ESI-TOF) m/z calcd for $C_{13}H_{15}F_3NO_3$ $[M+H]^+$ 290.0999; found 290.1002.



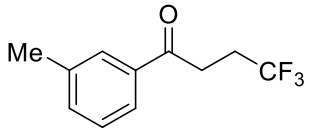
Benzyl (5,5,5-trifluoro-3-oxopentyl)carbamate (2h')

The other regioisomer (**2h'**, 8 mg, 0.028 mmol, 13%) was isolated as a white solid after purification (see above). FT-IR ν (cm^{-1}) = 3337, 1726, 1688, 1535, 1421, 1257, 1217, 1036, 698; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.38–7.30 (m, 5H), 5.19 (br. s, 1H), 5.08 (s, 2H), 3.47 (dt, *J* = 6.0, 5.9 Hz, 2H), 3.23 (q, *J* = 10.4 Hz, 2H), 2.80 (t, *J* = 5.7 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 199.5, 156.3, 136.3, 128.6, 128.2, 128.1, 123.4 (q, J_{C-F} = 277.0 Hz), 66.8, 46.5 (q, J_{C-F} = 28.6 Hz), 43.4, 35.2; ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -62.3 (t, *J* = 10.5 Hz, 3F); HRMS (ESI-TOF) m/z calcd for $C_{13}H_{15}F_3NO_3$ $[M+H]^+$ 290.0999; found 290.1002.



4,4,4-Trifluoro-1-(*p*-tolyl)butan-1-one (2i)

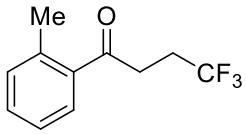
Prepared according to the general procedure on a 0.201 mmol scale, the desired product (39 mg, 0.180 mmol, 90%) was isolated as a white solid after purification by flash column chromatography (5% Et_2O/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.90–7.84 (m, 2H), 7.31–7.25 (m, 2H), 3.23 (dd, *J* = 7.8, 8.0 Hz, 2H), 2.65–2.52 (m, 2H), 2.42 (s, 3H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.4 (t, *J* = 10.9 Hz, 3F). Data are in accordance with the one described in the literature.[23]



4,4,4-Trifluoro-1-(*m*-tolyl)butan-1-one (2j)

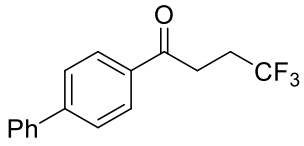
Prepared according to the general procedure on a 0.206 mmol scale, the desired product (39 mg, 0.180 mmol, 87%) was isolated as a colorless oil after purification by flash column chromatography (5% Et_2O/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.80–7.74 (m, 2H), 7.44–7.38 (m, 1H), 7.41–7.34 (m, 1H), 3.25 (dd, *J* = 9.2, 7.7 Hz, 2H), 2.66–2.52 (m, 2H), 2.43 (s, 3H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.4 (t, *J* = 10.8 Hz, 3F). Data are in accordance with the one described in the literature.[24]

[23] T.-P. Yang, Q. Li, J.-H. Lin and J.-C. Xiao, *Chem. Commun.*, 2014, **50**, 1077-1079.
[24] Y. Xiong, D. Chen, S. Zeng, C. Cheng, P. Wang, W. Deng, J. Xiang and N. Yi, *Synlett*, 2018, **29**, 2279-2282.



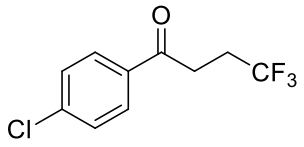
4,4,4-Trifluoro-1-(*o*-tolyl)butan-1-one (2k)

Prepared according to the general procedure on a 0.204 mmol scale, the desired product (44 mg, 0.204 mmol, 100%) was isolated as a colorless oil (no purification needed). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.68 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.41 (td, *J* = 7.5, 1.4 Hz, 1H), 7.31–7.26 (m, 2H), 3.19 (dd, *J* = 7.9, 7.5 Hz, 2H), 2.63–2.53 (m, 2H), 2.42 (s, 3H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.4 (t, *J* = 10.6 Hz, 3F). Data are in accordance with the one described in the literature.[25]



1-([1,1'-Biphenyl]-4-yl)-4,4,4-trifluorobutan-1-one (2l)

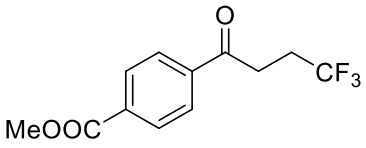
Prepared according to the general procedure on a 0.201 mmol scale, the desired product (52 mg, 0.187 mmol, 93%) was isolated as a white solid after purification by flash column chromatography (0–5% EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.06–8.03 (m, 2H), 7.72–7.70 (m, 2H), 7.65–7.62 (m, 2H), 7.50–7.46 (m, 2H), 7.43–7.40 (m, 1H), 3.30 (dd, *J* = 7.6, 7.9 Hz, 2H), 2.69–2.56 (m, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.4 (t, *J* = 10.3 Hz, 3F). Data are in accordance with the one described in the literature.[3]



1-([1,1'-Biphenyl]-4-yl)-4,4,4-trifluorobutan-1-one (2m)

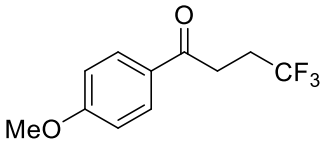
Prepared according to the general procedure on a 0.203 mmol scale, the desired product (43 mg, 0.182 mmol, 90%) was isolated as a white solid after purification by flash column chromatography (5% Et_2O/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.93–7.90 (m, 2H), 7.49–7.45 (m, 2H), 3.27–3.20 (m, 2H), 2.65–2.54 (m, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.4 (t, *J* = 10.8 Hz, 3F). Data are in accordance with the one described in the literature.[23]

[25] S. Park, J. M. Joo and E. J. Cho, *Eur. J. Org. Chem.*, 2015, 4093-4097.



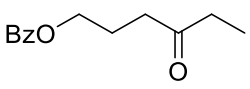
1-([1,1'-Biphenyl]-4-yl)-4,4,4-trifluorobutan-1-one (2n)

Prepared according to the general procedure on a 0.197 mmol scale, the desired product (47 mg, 0.181 mmol, 92%) was isolated as a white solid after purification by flash column chromatography (5–10% EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.17–8.14 (m, 2H), 8.06–8.00 (m, 2H), 3.96 (s, 3H), 3.29 (dd, *J* = 7.6, 8.0 Hz, 2H), 2.68–2.55 (m, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.4 (t, *J* = 10.8 Hz, 3F). Data are in accordance with the one described in the literature.[24]



1-([1,1'-Biphenyl]-4-yl)-4,4,4-trifluorobutan-1-one (2o)

Prepared according to the general procedure on a 0.198 mmol scale, the desired product (46 mg, 0.198 mmol, 100%) was isolated as a white solid (no purification needed). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.97–7.94 (m, 2H), 6.97–6.94 (m, 2H), 3.88 (s, 3H), 3.21 (dd, *J* = 7.8, 8.0 Hz, 2H), 2.65–2.51 (m, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.4 (t, *J* = 10.9 Hz, 3F). Data are in accordance with the one described in the literature.[26]

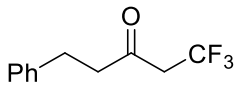


4-Oxohexyl benzoate (4')

Prepared according to the general procedure on a 0.196 mmol scale of **3**, using 2 mol% of [Au(IPr)(OTf)] (2.8 mg, 3.81 µmol), the crude mixture contained a 17:83 ratio of **4:4'**. Compound **4'** (19 mg, 0.086 mmol, 44%) was isolated as a colorless oil after purification by automated flash purification (0-7% EtOAc/toluene). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.05–8.01 (m, 2H), 7.61–7.52 (m, 1H), 7.47–7.42 (m, 2H), 4.33 (t, *J* = 6.3 Hz, 2H), 2.58 (t, *J* = 7.2 Hz, 2H), 2.46 (q, *J* = 7.3 Hz, 2H), 2.08 (tt, *J* = 6.8, 7.1 Hz, 2H), 1.03 (t, *J* = 7.3 Hz, 3H). Data are in accordance with the one described in the literature.[27] Compound **4** was identified on the crude mixture ^{1}H NMR from literature data (mixture of **4** and **4'**).[28]

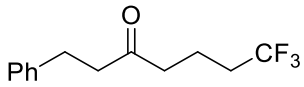
[26] P. Colbon, J. Ruan, M. Purdie and J. Xiao, *Org. Lett.*, 2010, **12**, 3670-367.
[27] Y. Zhao, W.-L. Yim, C. K. Tan and Y.-Y. Yeung, *Org. Lett.*, 2011, **13**, 4308-4311.
[28] B. Morandi, Z. K. Wickens and R. H. Grubbs, *Angew. Chem. Int. Ed.*, 2013, **52**, 2944-2948.

1,1,1-Trifluoro-5-phenylpentan-3-one (8)

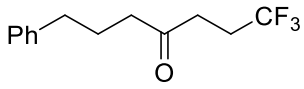


Prepared according to the general procedure on a 0.194 mmol scale of **5**, using 2 mol% of [Au(IPr)(OTf)] (2.9 mg, 3.95 μmol), the crude mixture contained **8** as the sole regioisomer (identified on the crude ^{1}H and ^{19}F NMR from literature data).[8]

7,7,7-Trifluoro-1-phenylheptan-3-one (9)



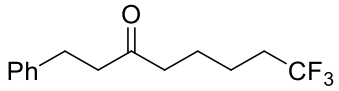
Prepared according to the general procedure on a 0.142 mmol scale of **6**, using 2 mol% of [Au(IPr)(OTf)] (2.2 mg, 2.99 μmol), the crude mixture contained a 74:26 ratio of **9:9'**. Compound **9** (23 mg, 0.094 mmol, 66%, contaminated with 6% of **9'**) was isolated as a colorless oil after purification by flash column chromatography (5% EtOAc/hexanes). Identity of **9** and **9'** was confirmed by COSY. FT-IR ν (cm^{-1}) = 2951, 1715, 1252, 1132, 748, 698; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.31–7.26 (m, 2H), 7.22–7.15 (m, 3H), 2.90 (t, J = 7.6 Hz, 2H), 2.73 (t, J = 7.6 Hz, 2H), 2.47 (t, J = 7.1 Hz, 2H), 2.12–2.01 (m, 2H), 1.87–1.78 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 208.5, 140.8, 128.6, 128.3, 127.0 (q, J_{C-F} = 276.5 Hz), 126.2, 44.3, 41.1, 32.8 (q, J_{C-F} = 28.8 Hz), 29.8, 16.0 (q, J_{C-F} = 3.2 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.2 (t, J = 10.9 Hz, 3F); HRMS (ESI-TOF) m/z calcd for $C_{13}H_{16}F_3O$ $[M+H]^+$ 245.1148; found 245.1147.



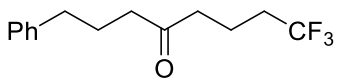
1,1,1-Trifluoro-7-phenylheptan-4-one (9')

The other regioisomer (**9'**, 6 mg, 0.025 mmol, 17%, contaminated with an unknown impurity) was isolated as a colorless oil after purification (see above). FT-IR ν (cm^{-1}) = 2937, 1718, 1256, 1142, 1095, 748, 698; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.31–7.26 (m, 2H), 7.22–7.15 (m, 3H), 2.65–2.61 (m, 4H), 2.48–2.34 (m, 4H), 1.99–1.89 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 206.8, 141.3, 128.47, 128.46, 127.0 (q, J_{C-F} = 275.1 Hz), 126.1, 41.9, 34.98, 34.95 (q, J_{C-F} = 2.6 Hz), 27.9 (q, J_{C-F} = 29.8 Hz), 25.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.6 (t, J = 10.9 Hz, 3F); HRMS (ESI-TOF) m/z calcd for $C_{13}H_{16}F_3O$ $[M+H]^+$ 245.1148; found 245.1145.

8,8,8-Trifluoro-1-phenyloctan-3-one (10)

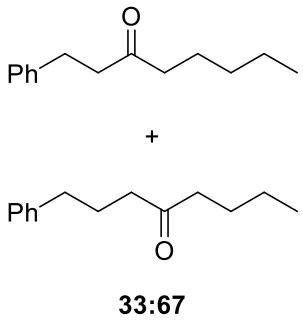


Prepared according to the general procedure on a 0.205 mmol scale of **7**, using 2 mol% of [Au(IPr)(OTf)] (3.0 mg, 4.08 µmol), the crude mixture contained a 42:58 ratio of **10:10'**. Compound **10** (11 mg, 0.043 mmol, 21%) was isolated as a colorless oil after purification by automated flash purification (50-100% toluene/hexanes). Identity of **10** and **10'** was confirmed by COSY. FT-IR ν (cm^{-1}) = 2947, 1713, 1375, 1134, 1256, 1030, 748; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.30–7.26 (m, 2H), 7.21–7.16 (m, 3H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.7 Hz, 2H), 2.41 (t, *J* = 7.1 Hz, 2H), 2.12–1.98 (m, 2H), 1.66–1.59 (m, 2H), 1.55–1.47 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 209.2, 140.9, 128.5, 128.3, 127.0 (q, J_{C-F} = 276.3 Hz), 126.2, 44.3, 42.4, 33.6 (q, J_{C-F} = 28.6 Hz), 29.8, 22.6, 21.5 (q, J_{C-F} = 2.9 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.4 (t, *J* = 10.8 Hz, 3F); HRMS (ESI-TOF) m/z calcd for $C_{14}H_{18}F_3O$ $[M+H]^+$ 259.1304; found 259.1314.



8,8,8-Trifluoro-1-phenyloctan-4-one (10')

The other regioisomer (**10'**, 15 mg, 0.058 mmol, 28%, contaminated with 4% of **10**) was isolated as a colorless oil after purification (see above). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.30–7.26 (m, 2H), 7.23–7.13 (m, 3H), 2.64–2.60 (m, 2H), 2.47 (t, *J* = 7.3 Hz, 2H), 2.41 (t, *J* = 7.4 Hz, 2H), 2.14–2.04 (m, 2H), 1.95–1.89 (m, 2H), 1.87–1.77 (m, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = -66.2 (t, *J* = 10.9 Hz, 3F). Data are in accordance with the one described in the literature.[29]



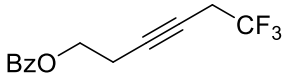
33:67

1-Phenyloctan-3-one + 1-phenyloctan-4-one (SI-10 + SI-10')

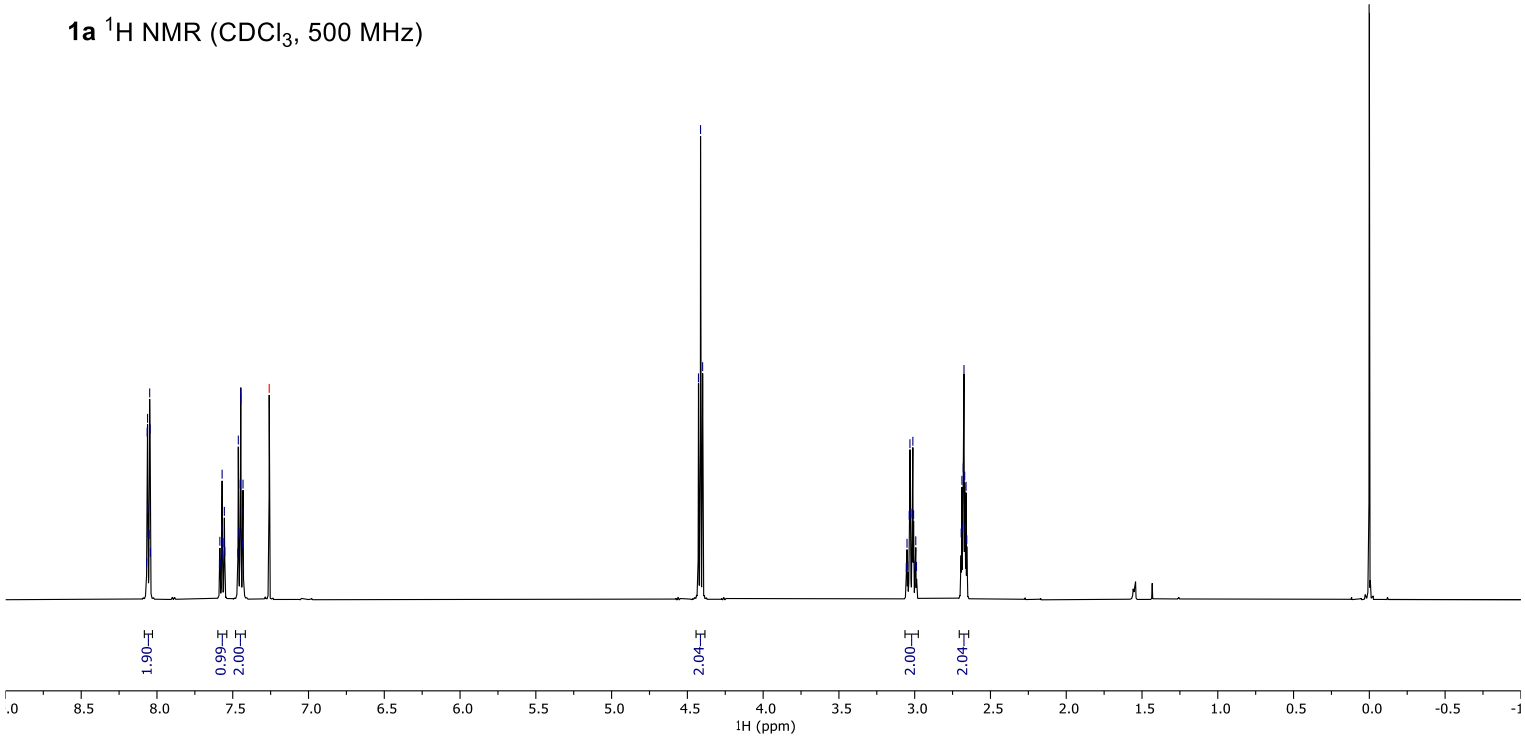
Prepared according to the general procedure on a 0.200 mmol scale of **SI-9**, using 2 mol% of [Au(IPr)(OTf)] (3.0 mg, 4.08 µmol), the crude mixture contained a 33:67 ratio of **SI-10:SI-10'**. Compound **SI-10**[30] and **SI-10'**[31] were identified with data from the literature.

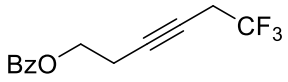
[29] J. Zhuo, Y. Zhang, Z. Li and C. Li, *ACS Catal.*, 2020, **10**, 3895-3903.
[30] E. W. Werner and M. S. Gisman, *J. Am. Chem. Soc.*, 2011, **133**, 9692-9695.
[31] J. C. Gilbert, D. H. Giamalva and U. Weerasooriya, *J. Org. Chem.*, 1983, **48**, 5251-5256.

7. NMR specta

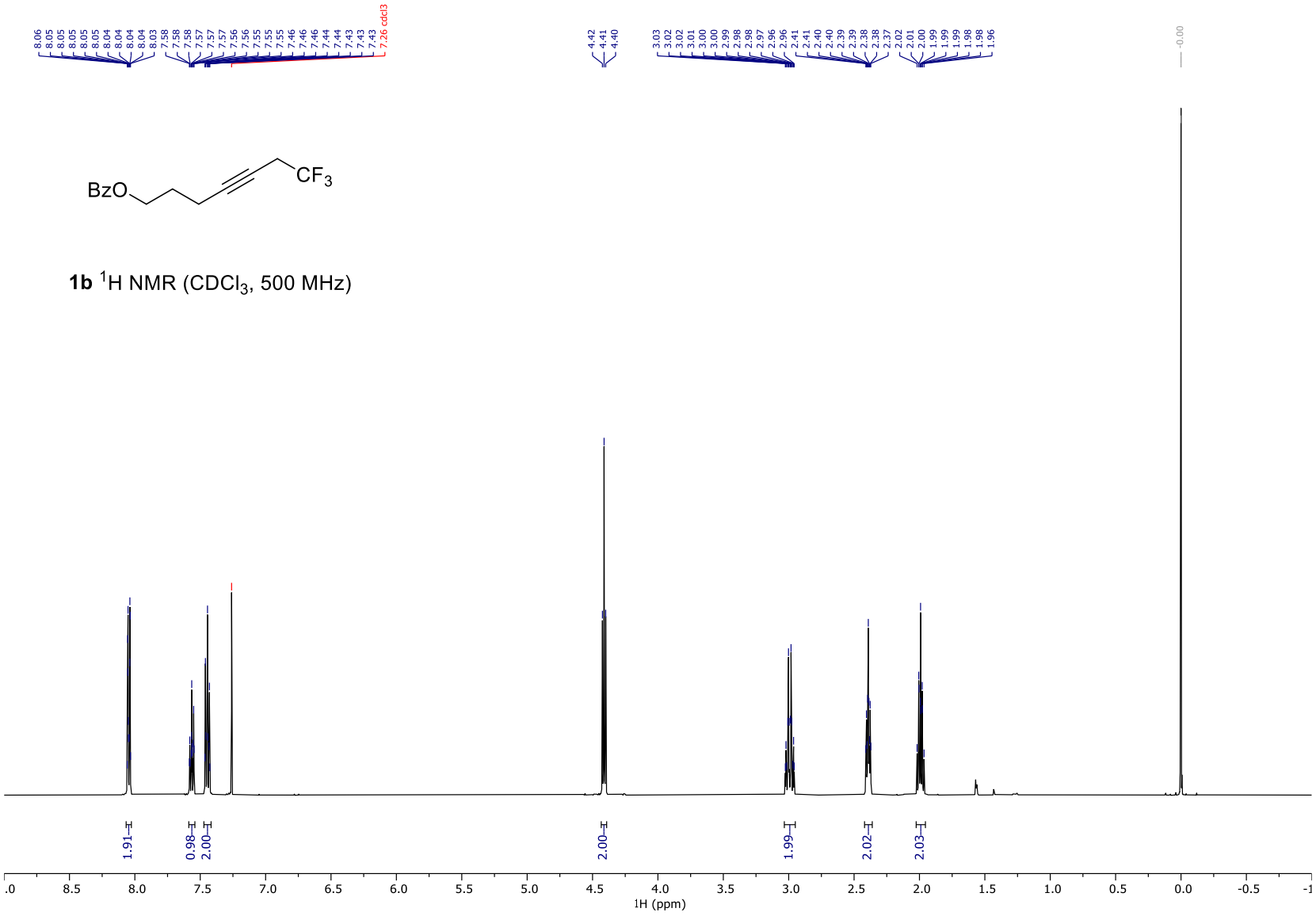


1a ^{1}H NMR ($CDCl_3$, 500 MHz)

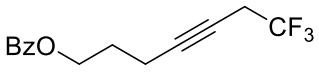




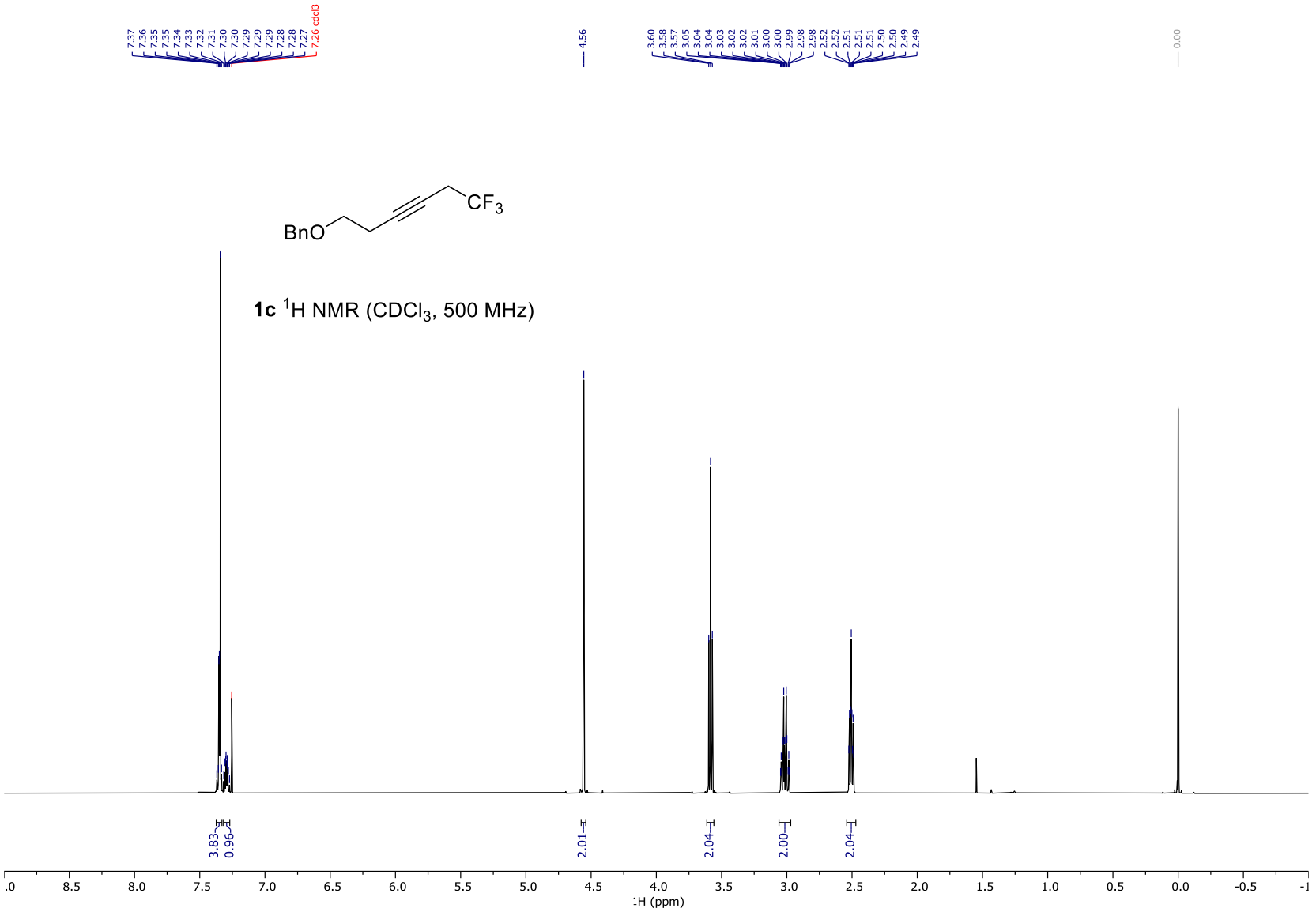
1a ^{19}F NMR ($CDCl_3$, 470 MHz)



1b ^{1}H NMR ($CDCl_3$, 500 MHz)



1b ^{19}F NMR ($CDCl_3$, 470 MHz)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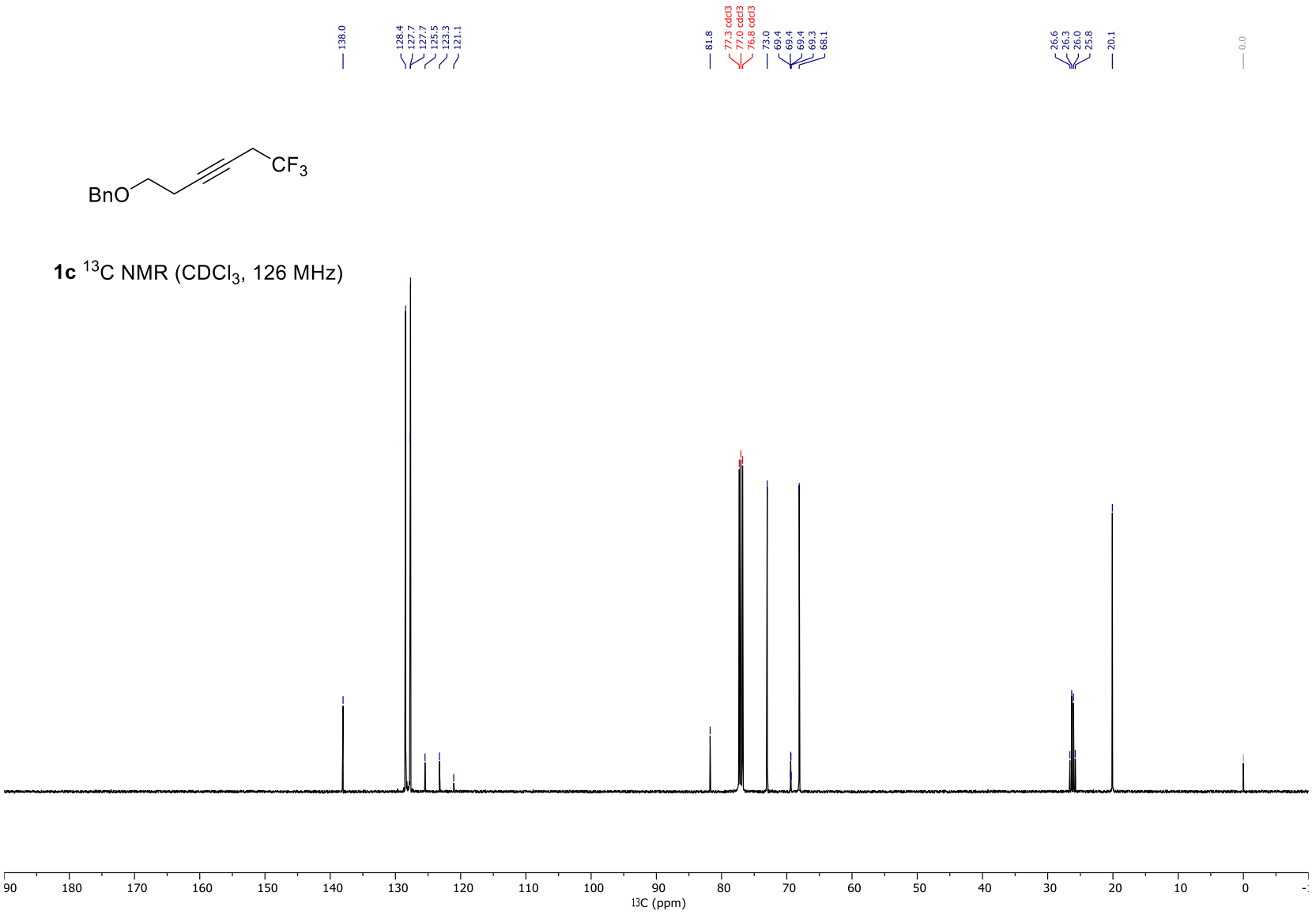
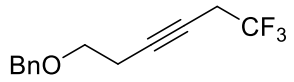
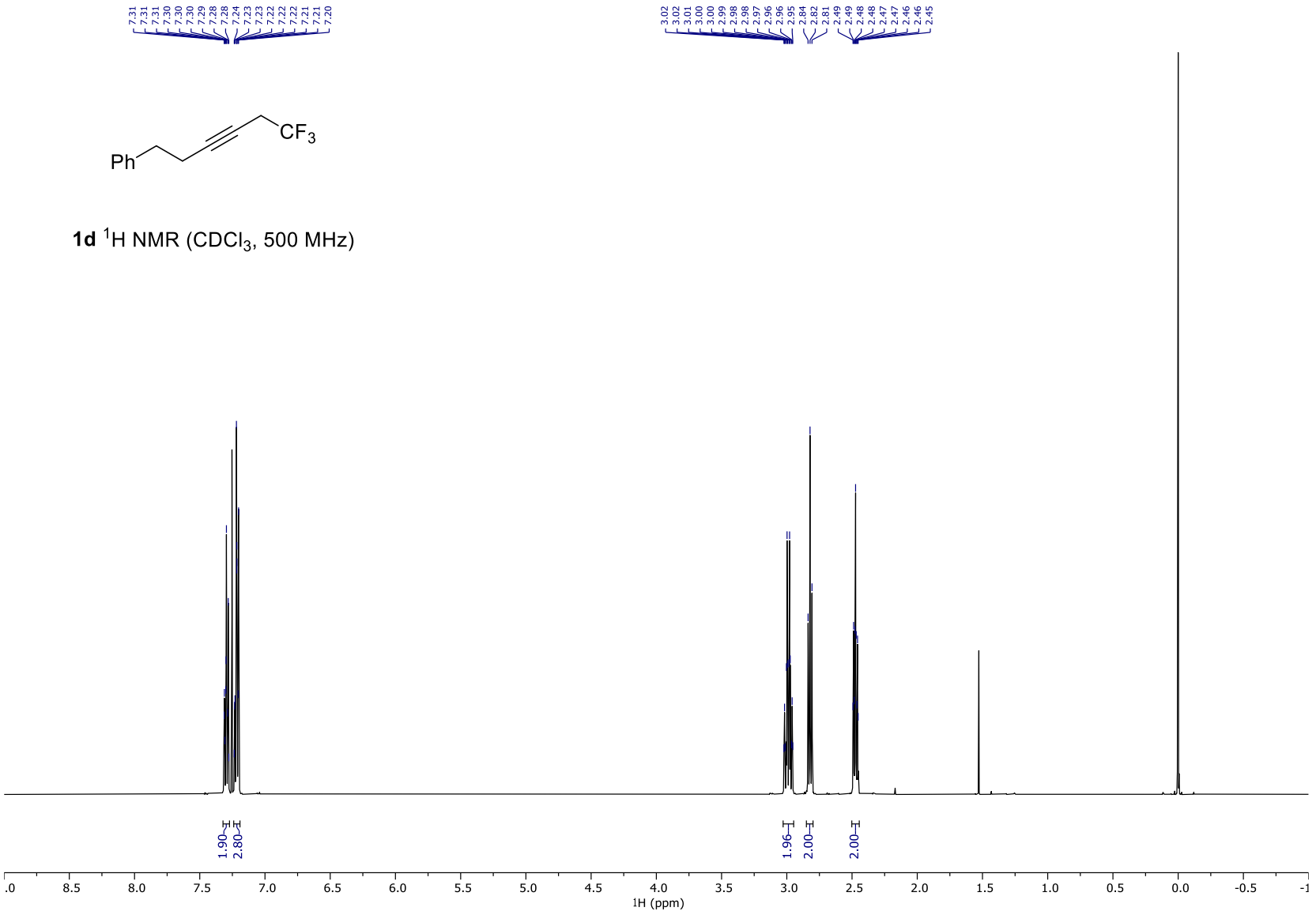
2.52
2.51
2.51
2.51
2.50
2.50
2.49
2.49
0.00
BnO
CF3
1c 1H NMR (CDCl3, 500 MHz)
3.83
0.96
2.01
2.04
2.00
2.04
1H (ppm)



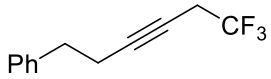
1c ^{13}C NMR ($CDCl_3$, 126 MHz)



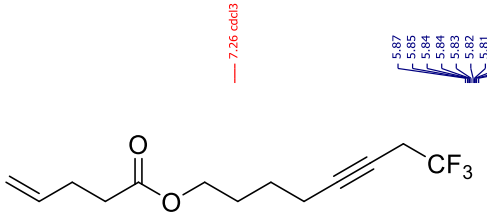
1c ^{19}F NMR ($CDCl_3$, 470 MHz)



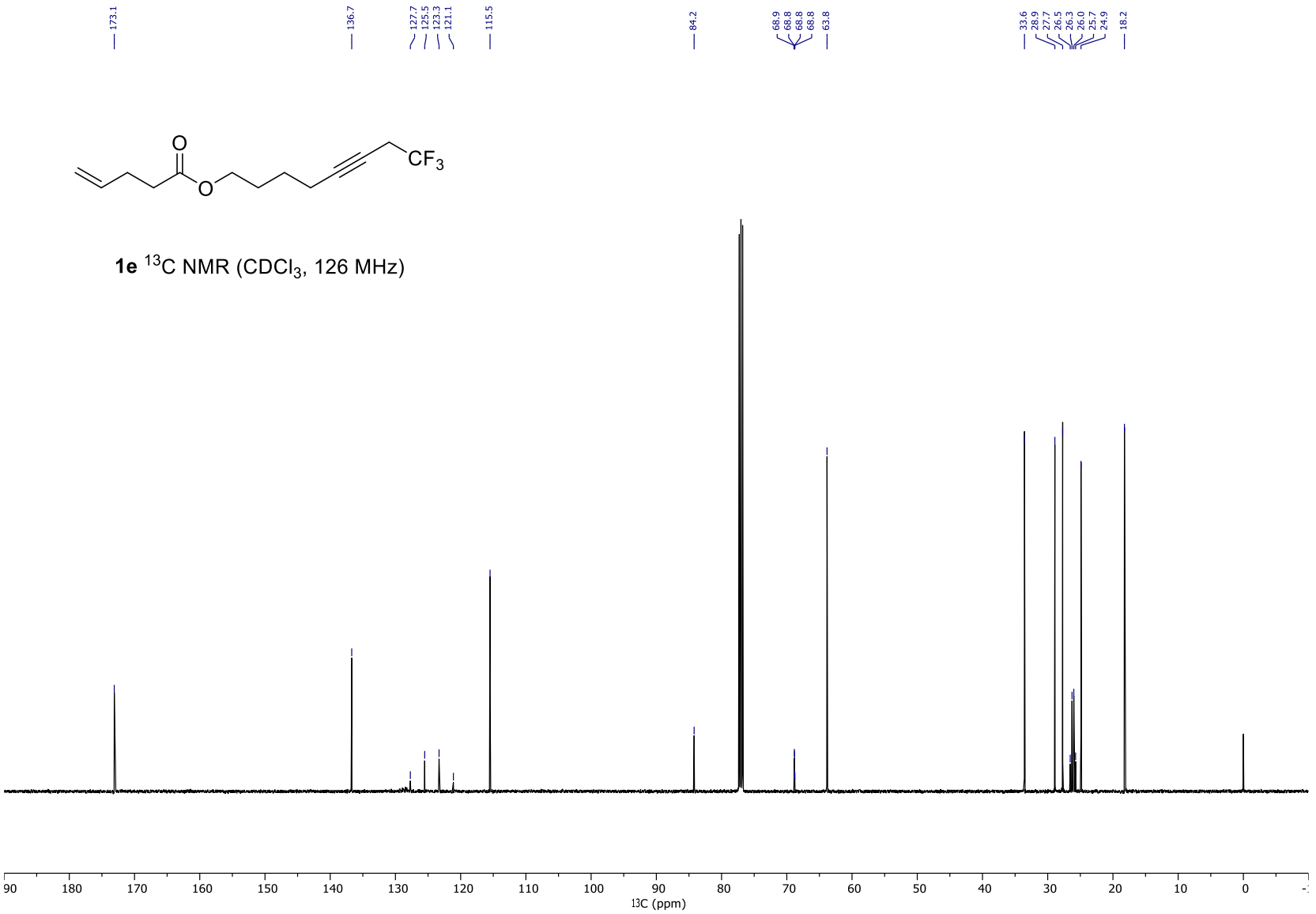
1d ^{1}H NMR ($CDCl_3$, 500 MHz)



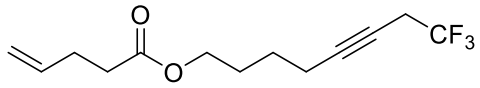
1d ^{19}F NMR ($CDCl_3$, 470 MHz)



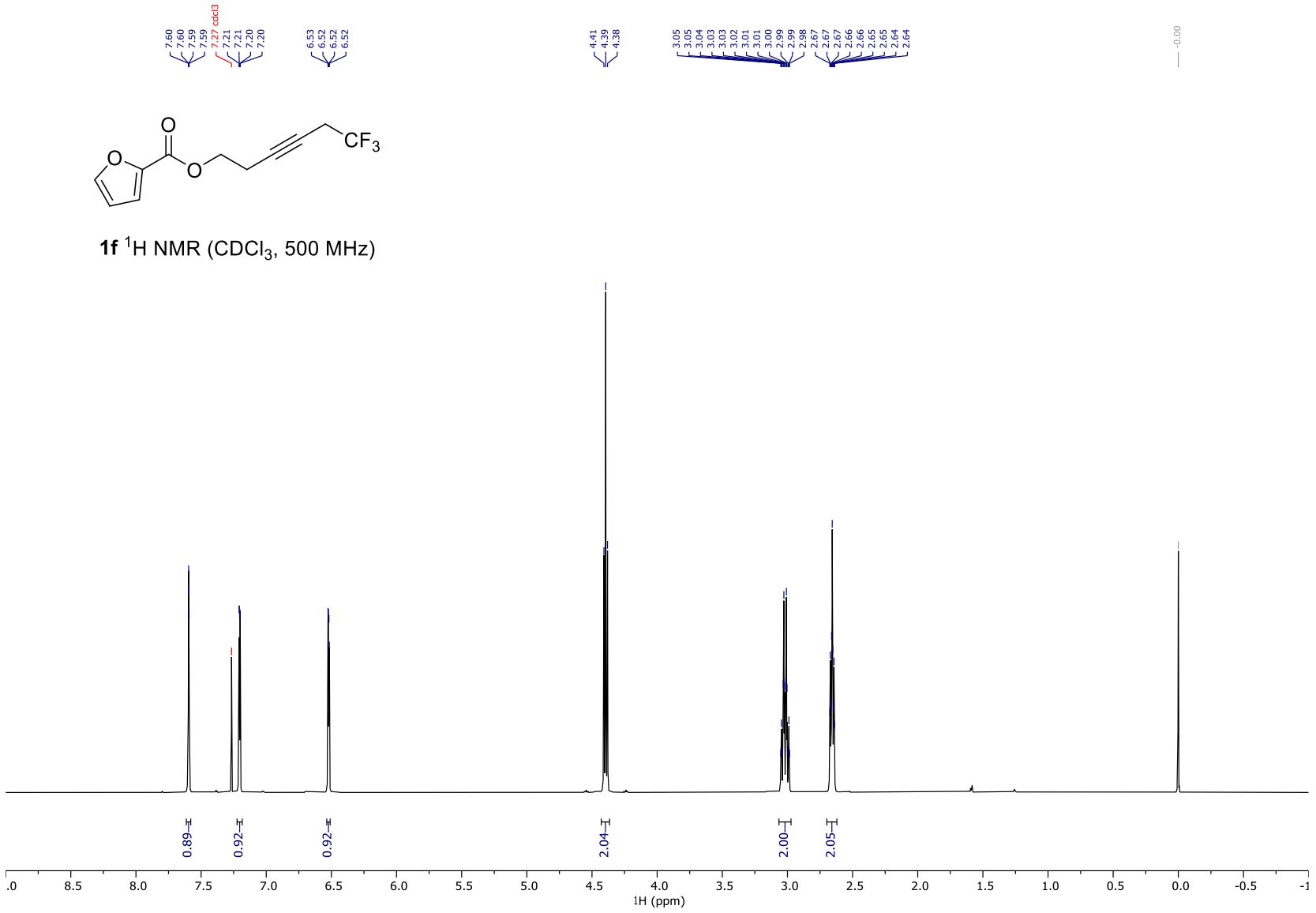
1e ^{1}H NMR ($CDCl_3$, 500 MHz)



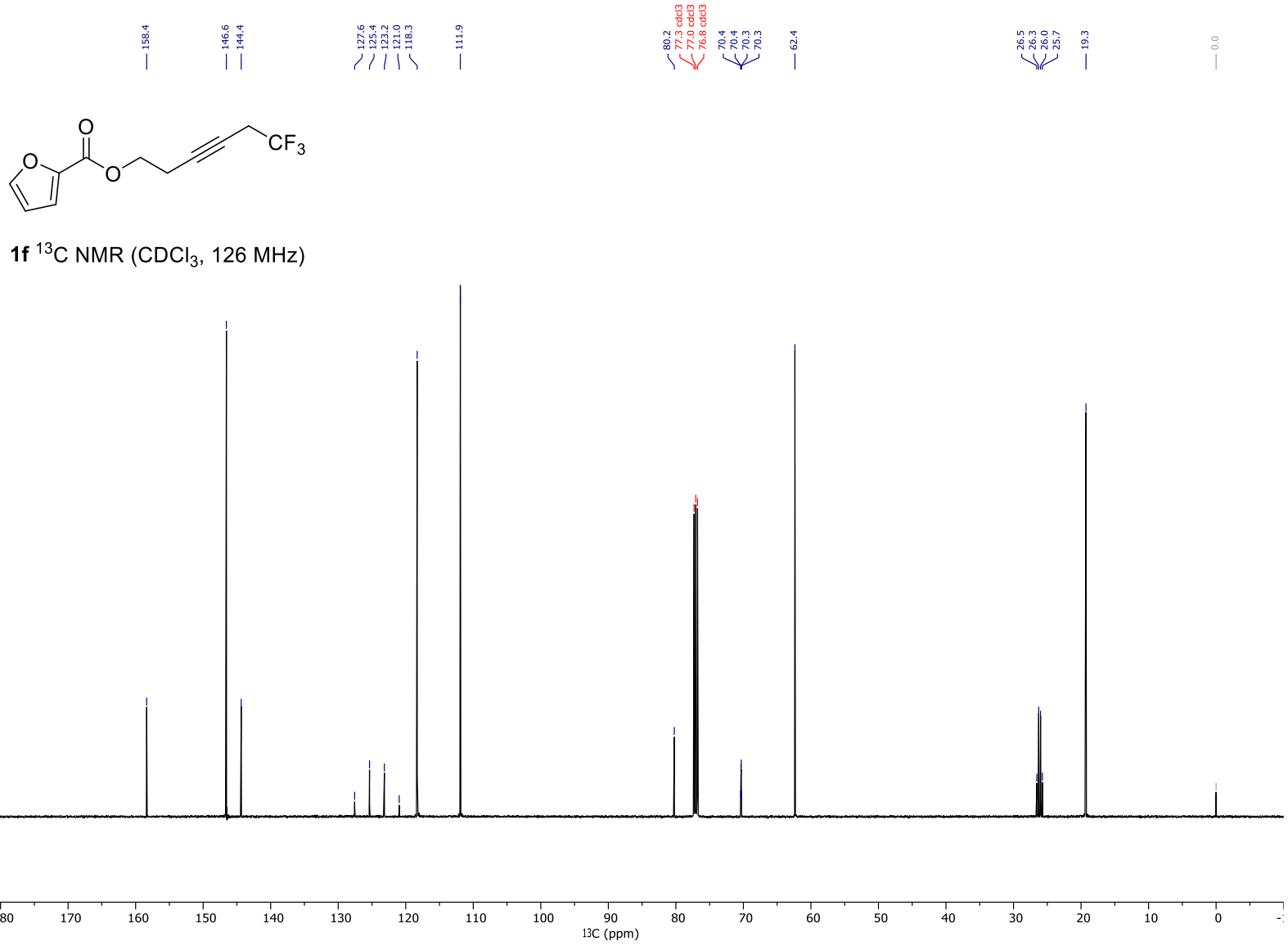
1e ^{13}C NMR ($CDCl_3$, 126 MHz)



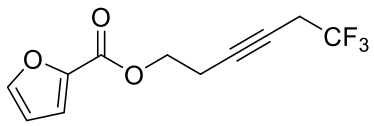
1e ^{19}F NMR ($CDCl_3$, 470 MHz)



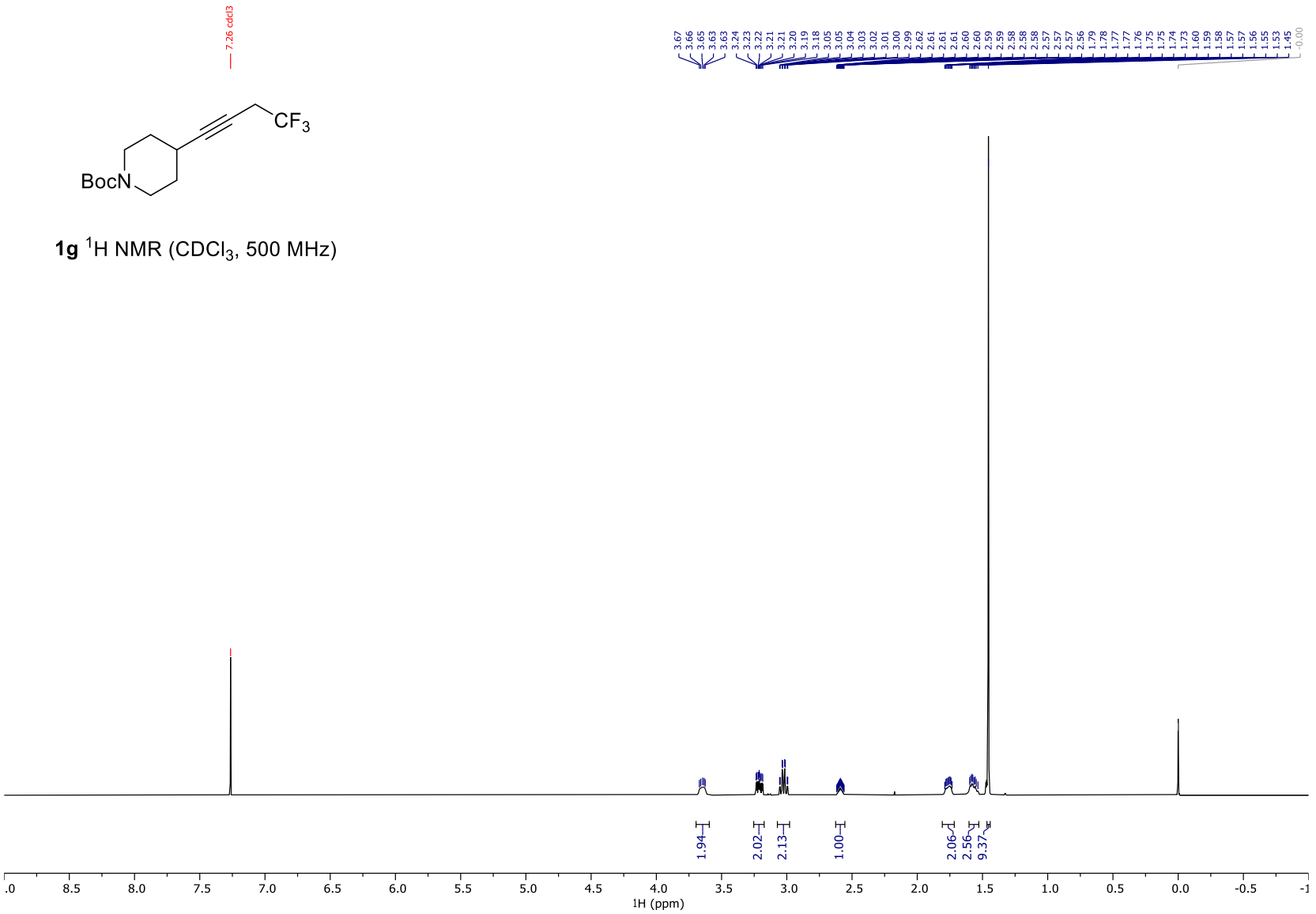
1f ^{1}H NMR ($CDCl_3$, 500 MHz)



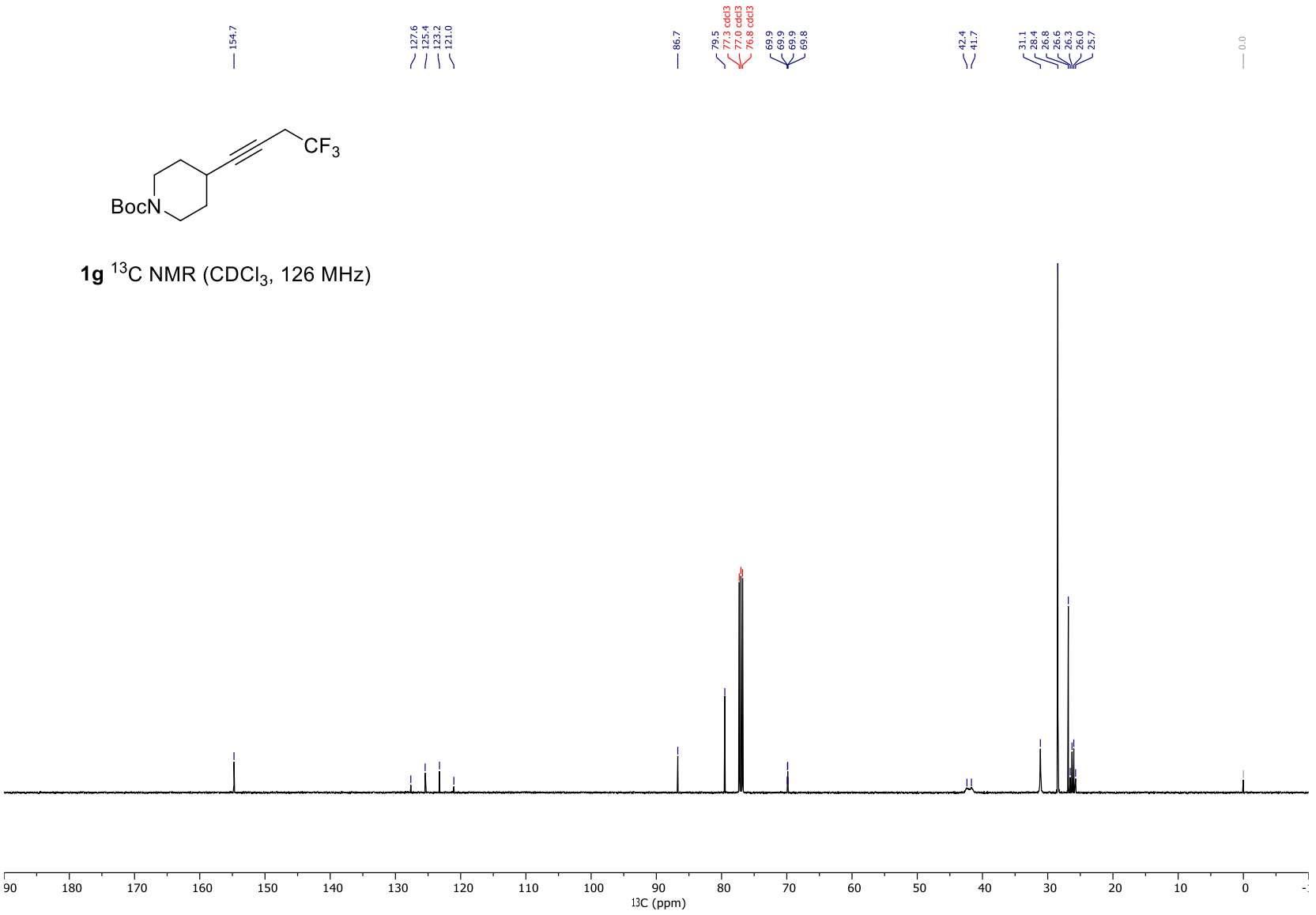
1f ^{13}C NMR ($CDCl_3$, 126 MHz)



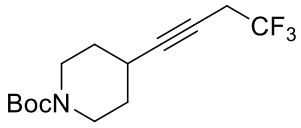
1f ^{19}F NMR ($CDCl_3$, 470 MHz)



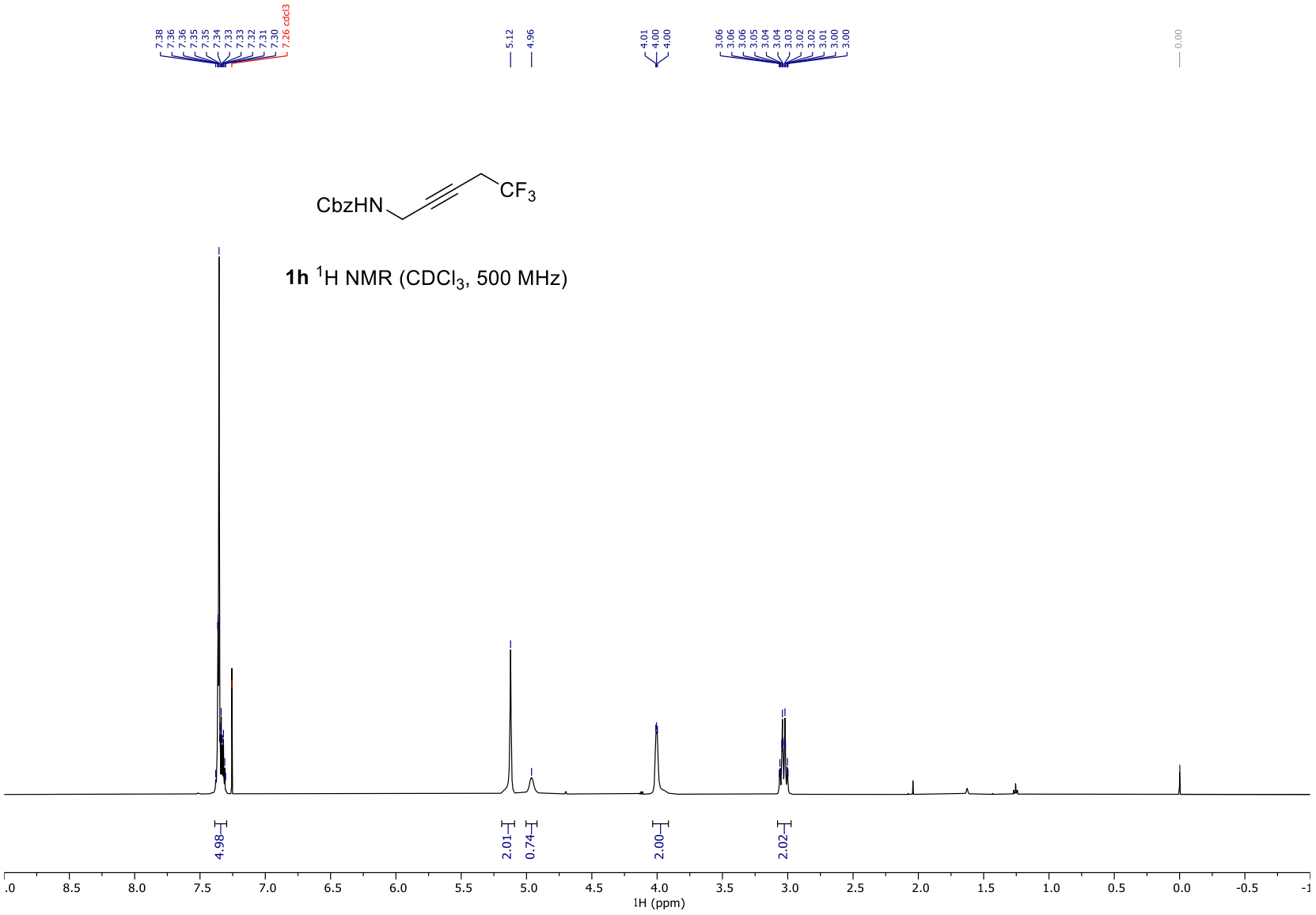
1g ^{1}H NMR ($CDCl_3$, 500 MHz)

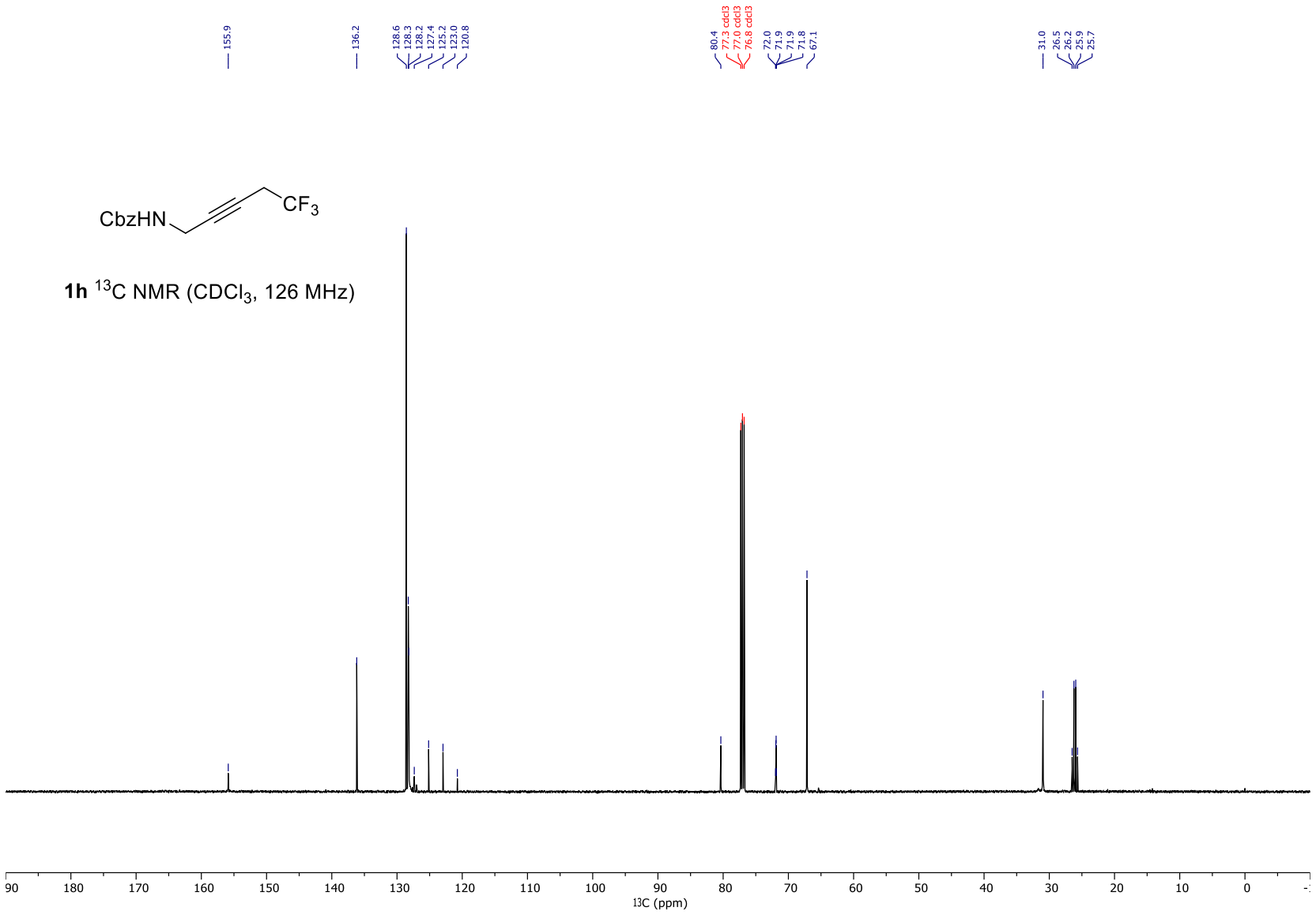


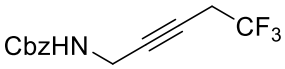
1g ^{13}C NMR ($CDCl_3$, 126 MHz)



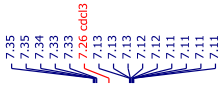
1g ^{19}F NMR ($CDCl_3$, 470 MHz)

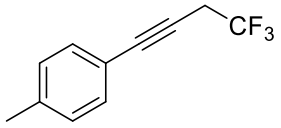

7.38
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.26 cdcl3
5.12
4.96
4.01
4.00
4.00
3.06
3.06
3.06
3.05
3.04
3.04
3.03
3.02
3.02
3.01
3.00
3.00
0.00
CbzHN
CF3
1h 1H NMR (CDCl3, 500 MHz)
4.98
2.01
0.74
2.00
2.02
1H (ppm)


155.9
136.2
128.6
128.3
128.2
127.4
125.2
123.0
120.8
80.4
77.3 cdcl3
77.0 cdcl3
76.8 cdcl3
72.0
71.9
71.9
71.8
67.1
31.0
26.5
26.2
25.9
25.7
CbzHN
CF3
1h 13C NMR (CDCl3, 126 MHz)
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
13C (ppm)

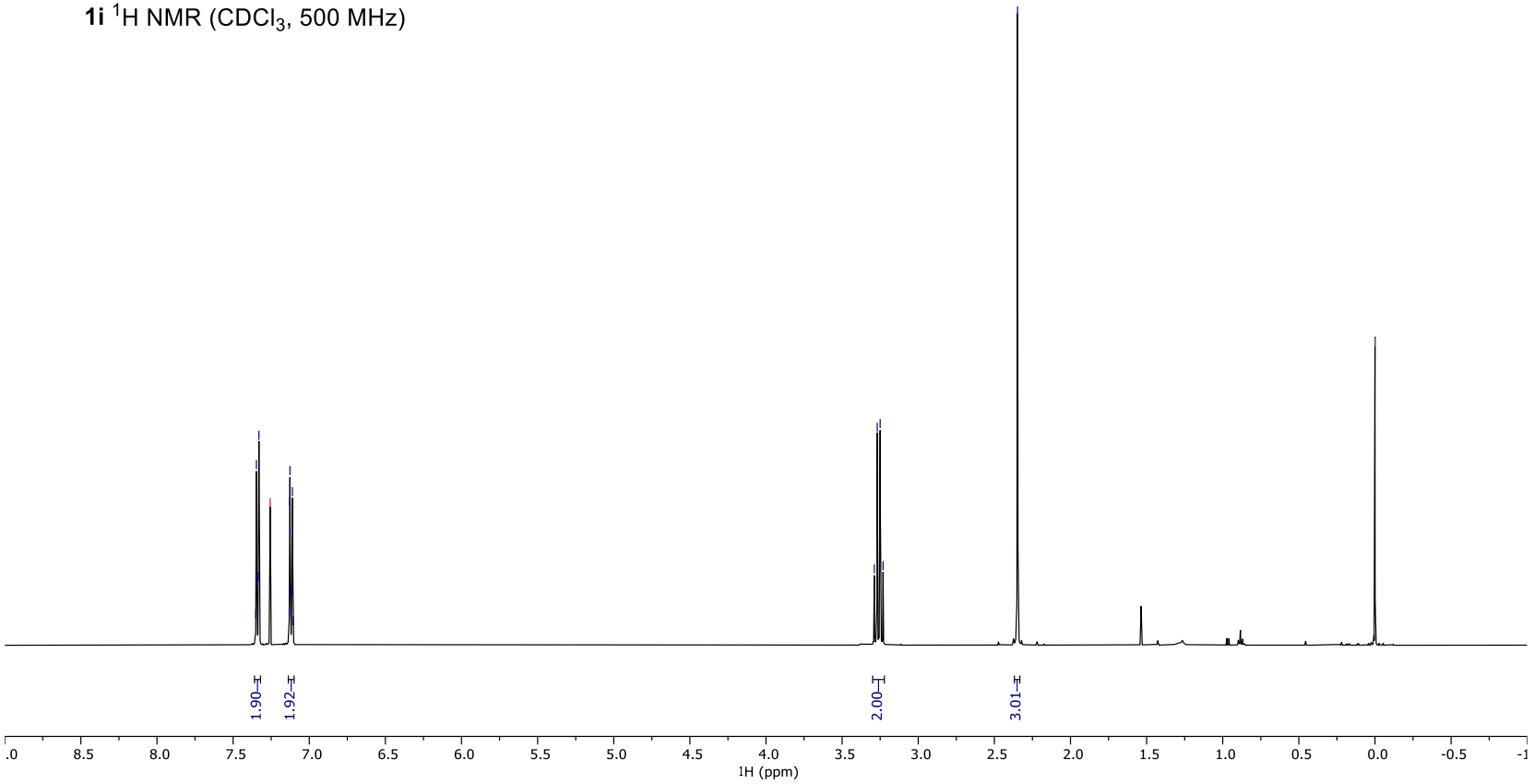


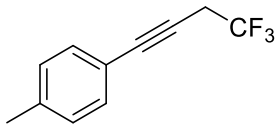
1h ^{19}F NMR ($CDCl_3$, 470 MHz)



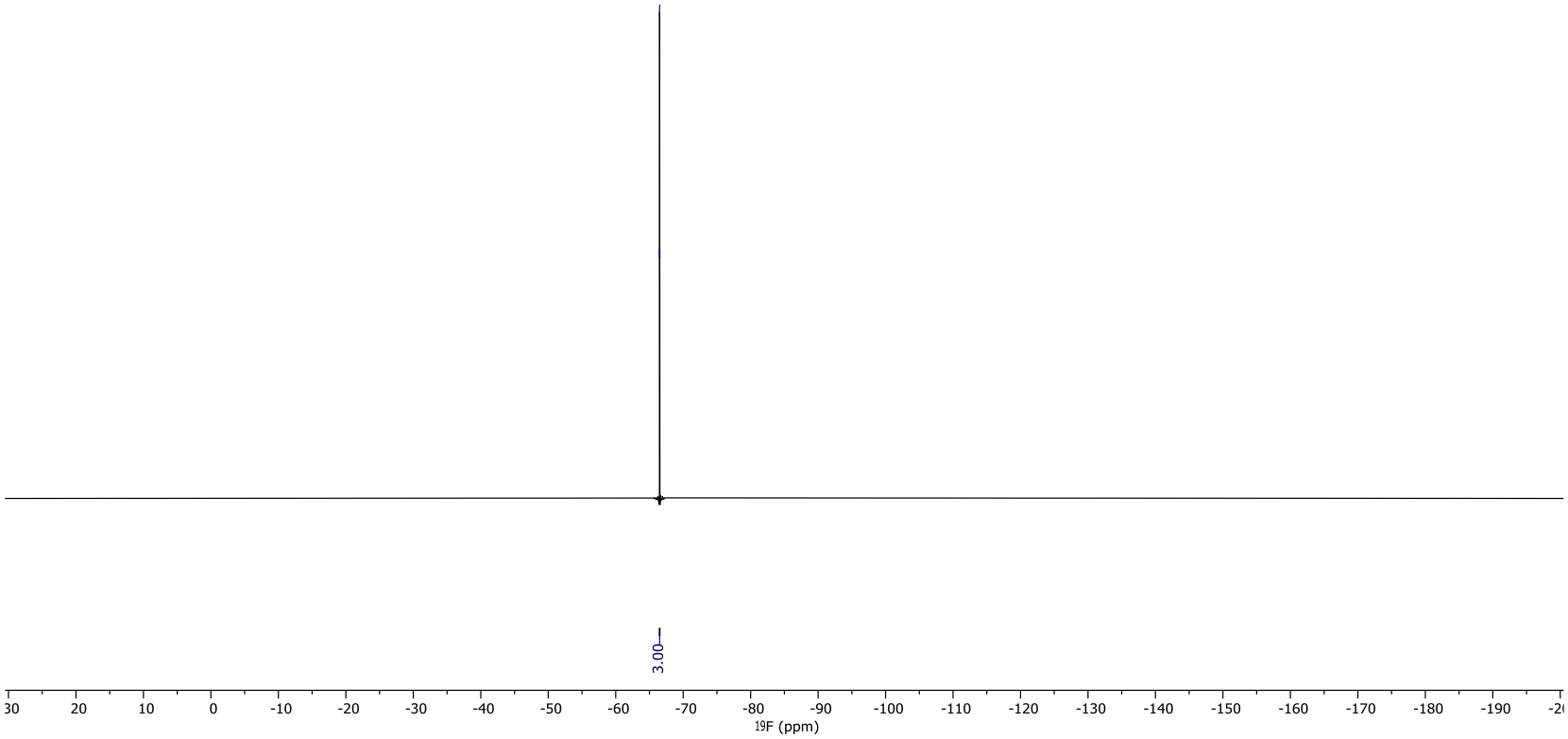


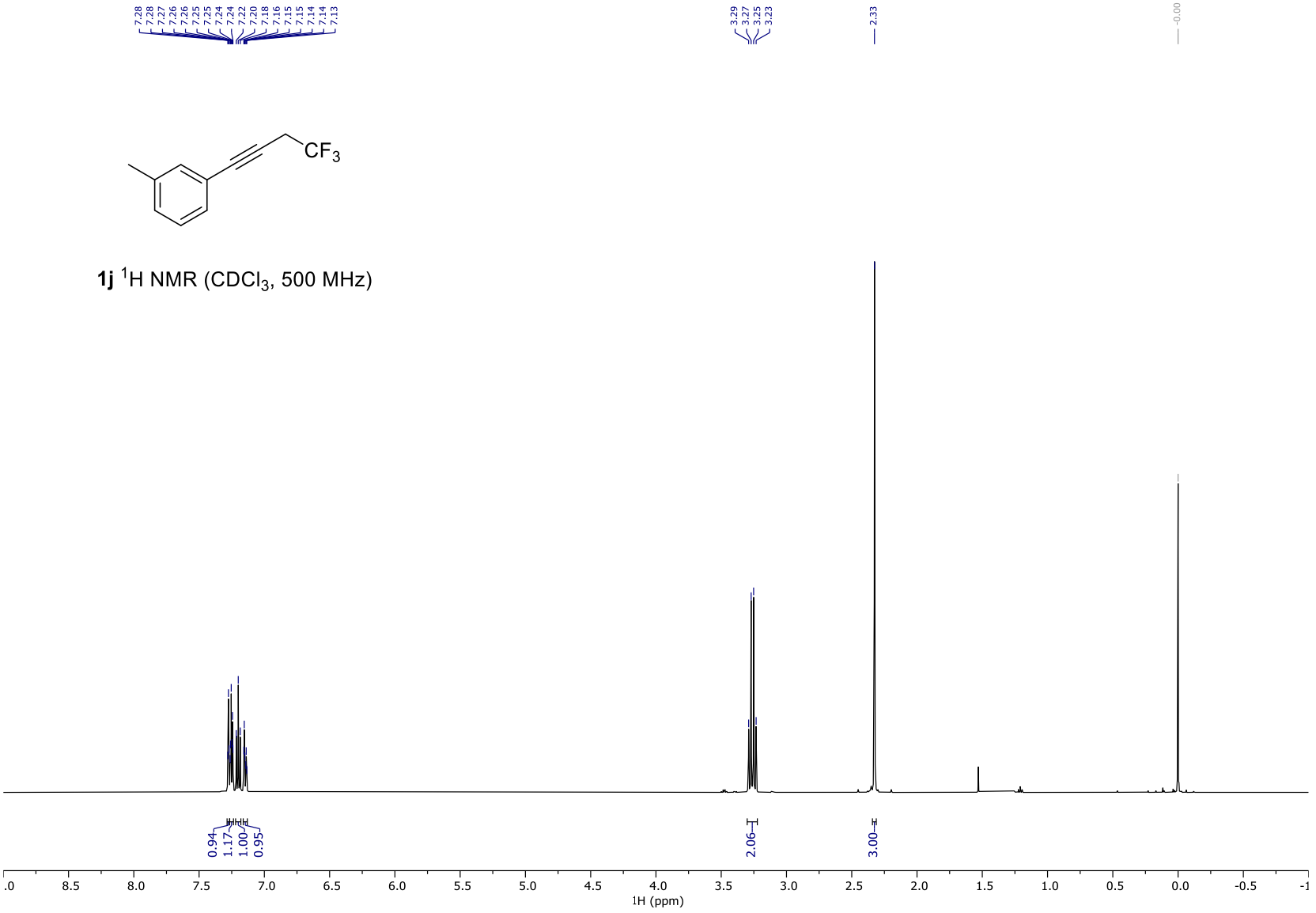
1i ^{1}H NMR ($CDCl_3$, 500 MHz)



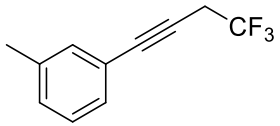


1i ^{19}F NMR ($CDCl_3$, 470 MHz)

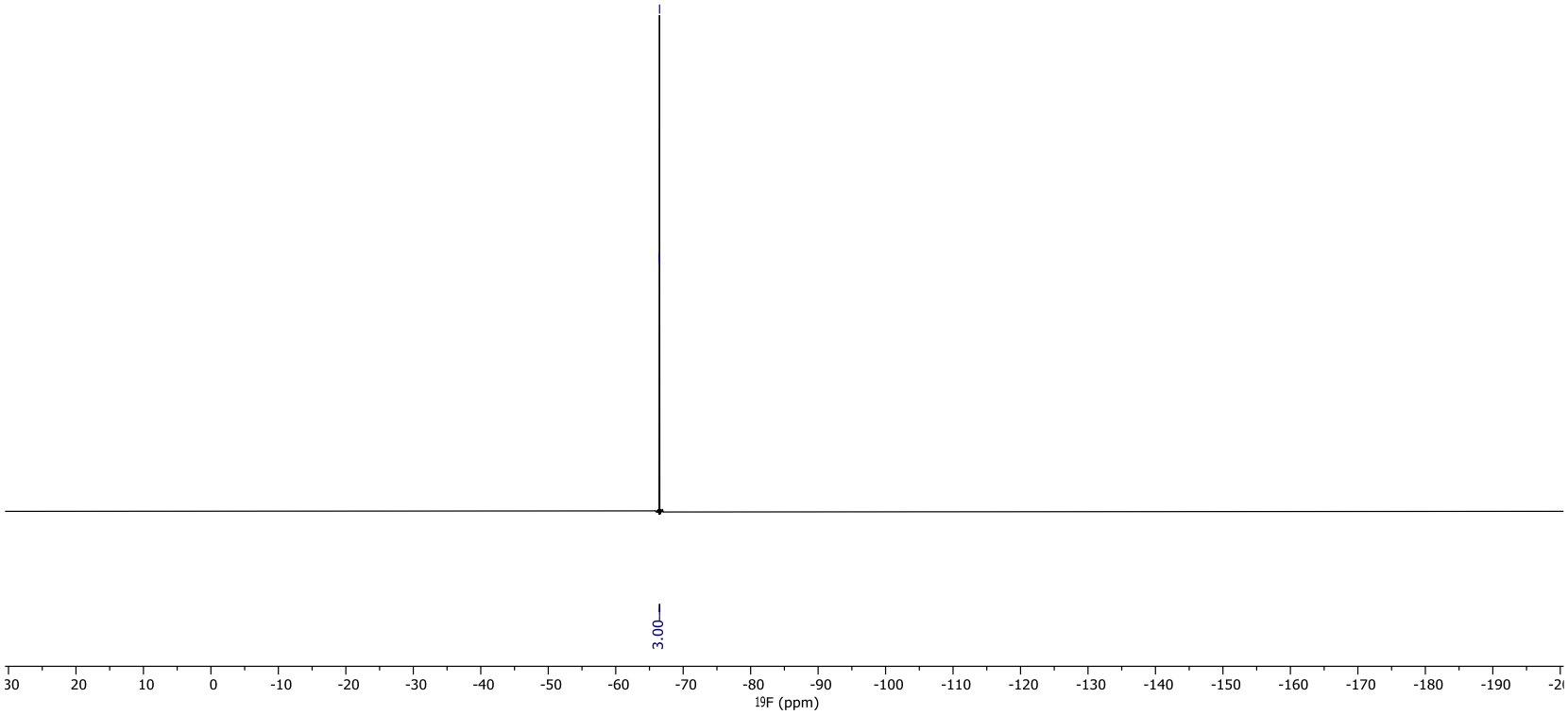


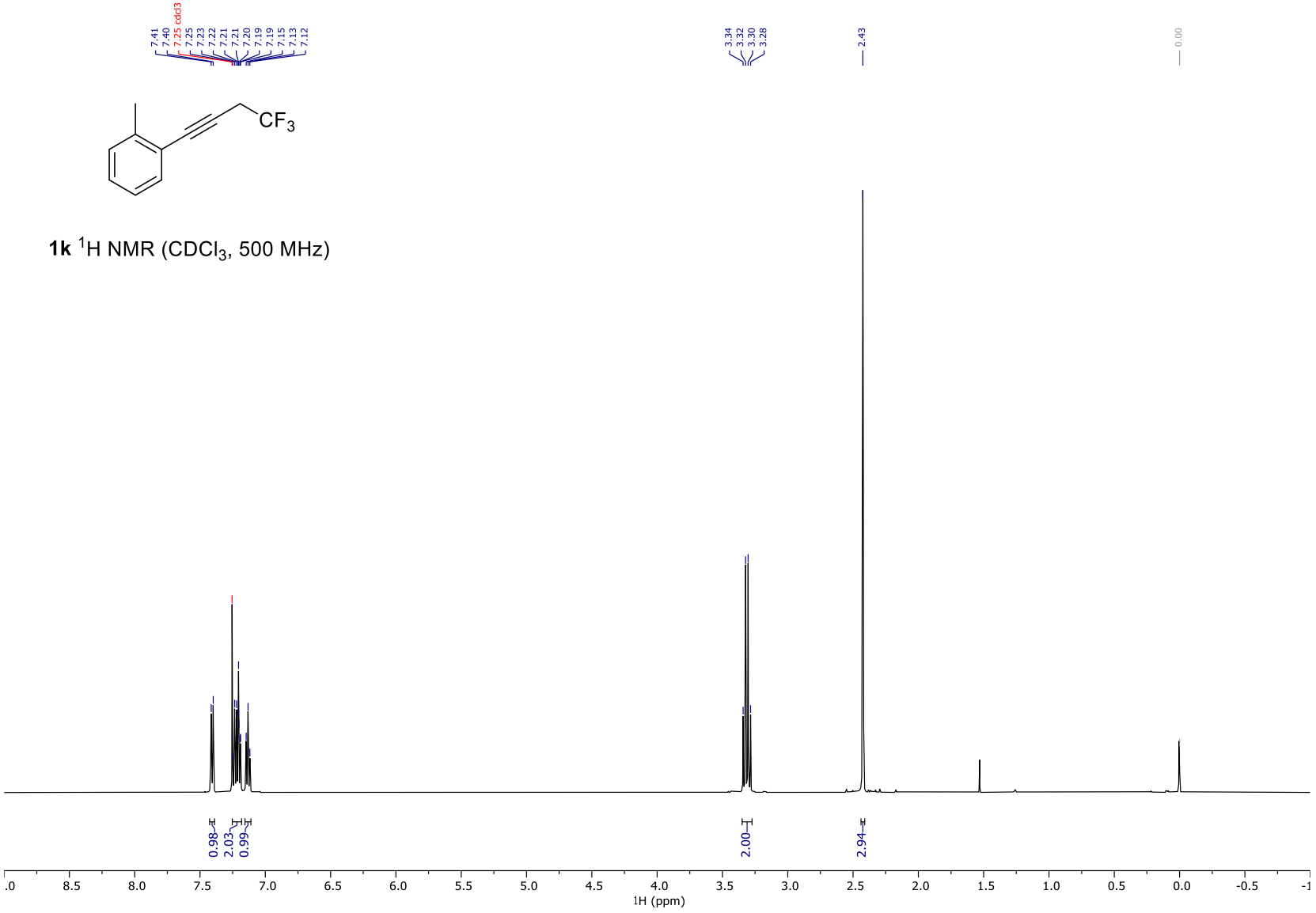


1j ^{1}H NMR ($CDCl_3$, 500 MHz)

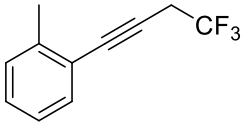


1j ^{19}H NMR ($CDCl_3$, 470 MHz)

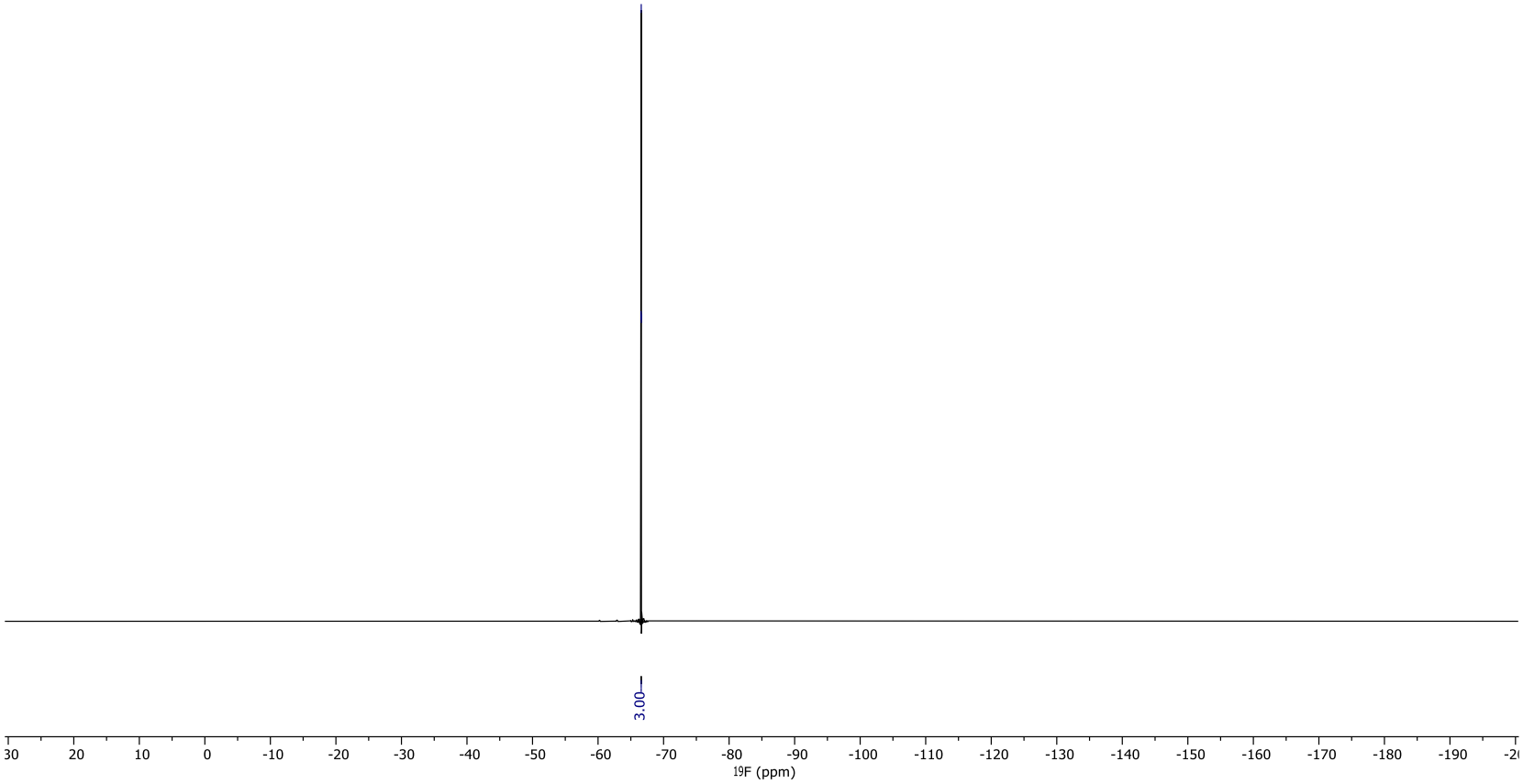


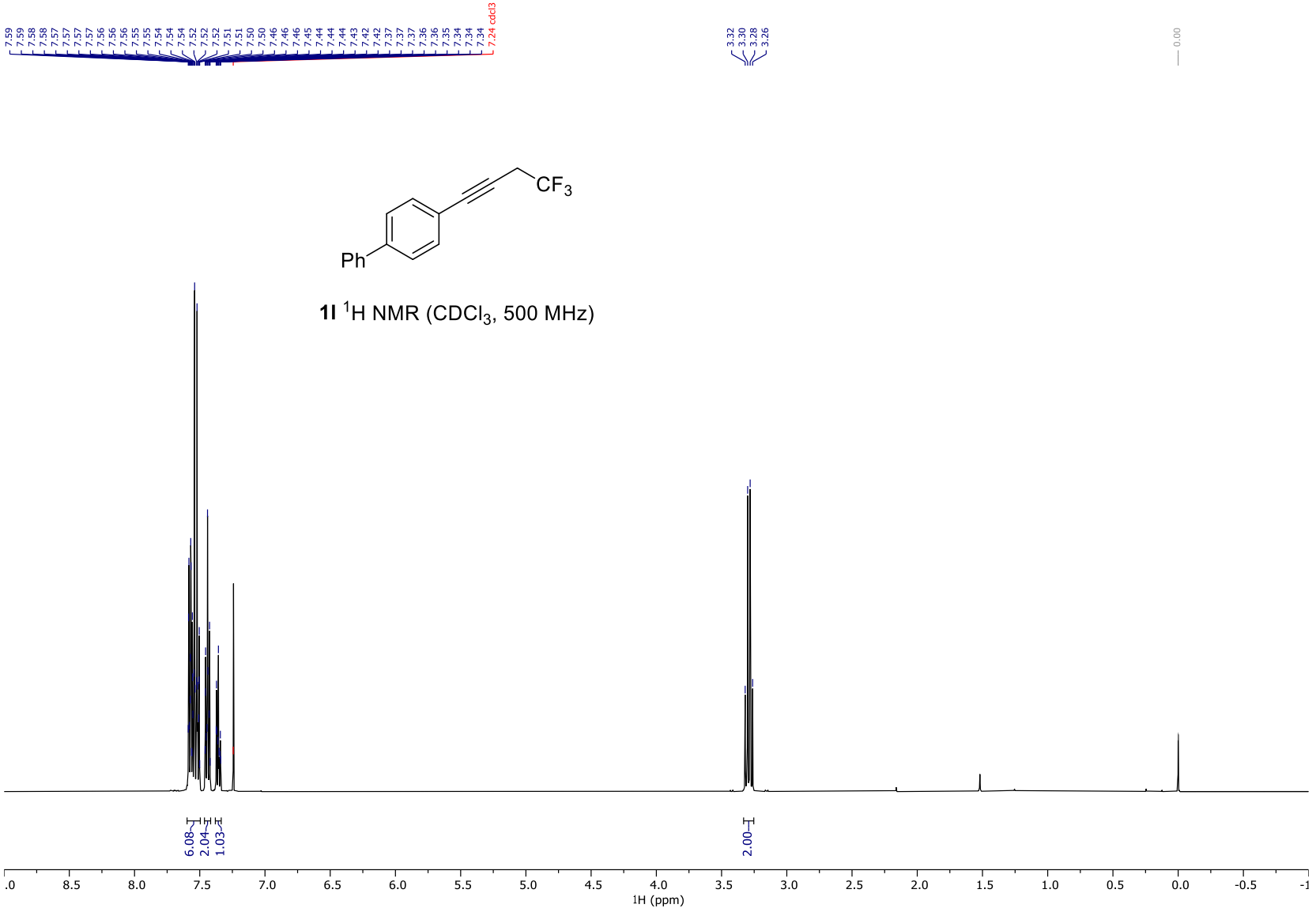


1k ^{1}H NMR ($CDCl_3$, 500 MHz)

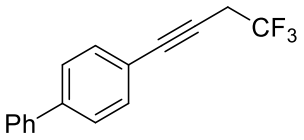


1k ^{19}F NMR ($CDCl_3$, 470 MHz)

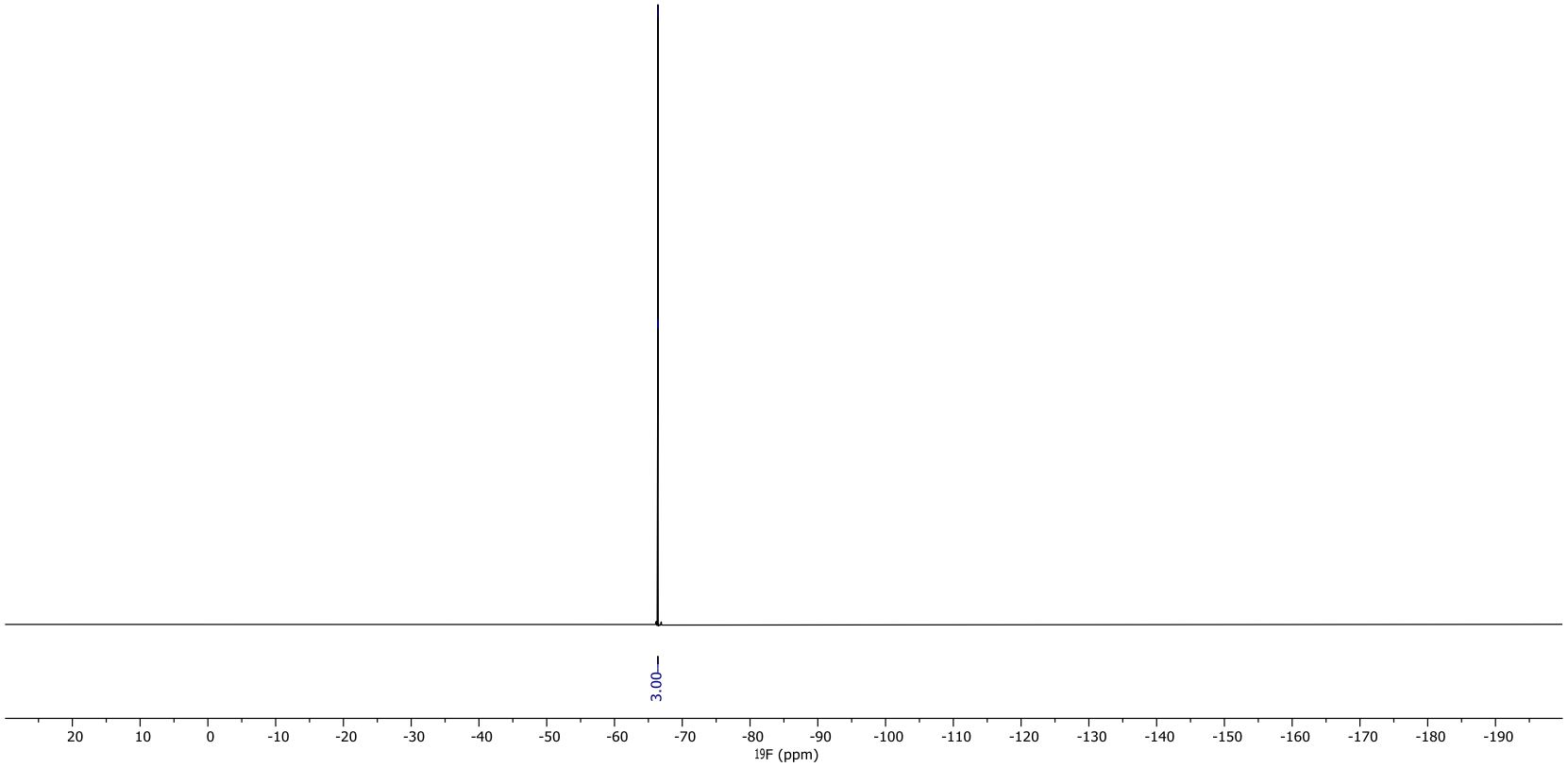


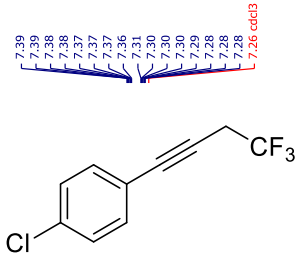


1l ^{1}H NMR ($CDCl_3$, 500 MHz)

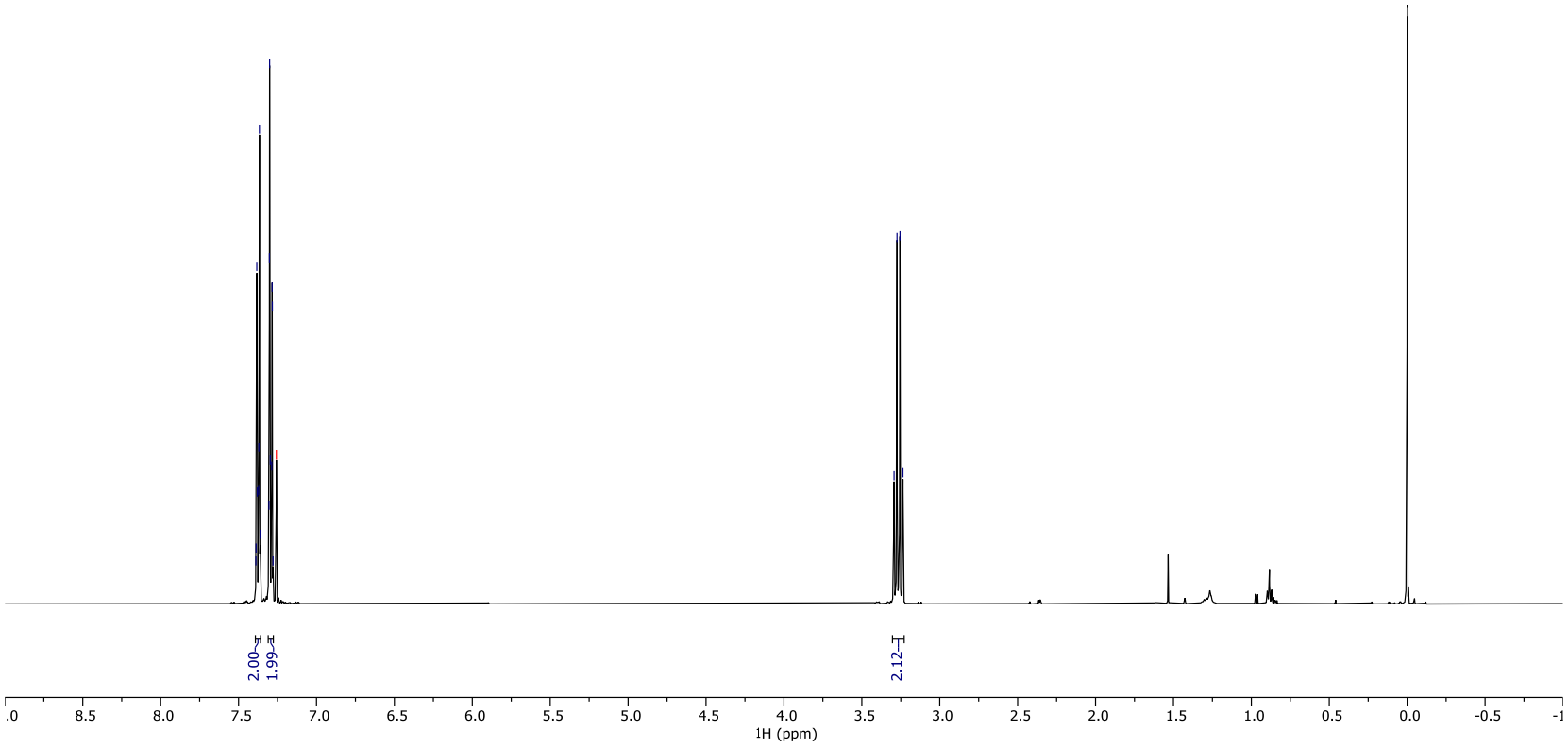


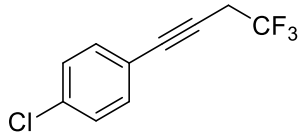
1l ^{19}F NMR ($CDCl_3$, 470 MHz)



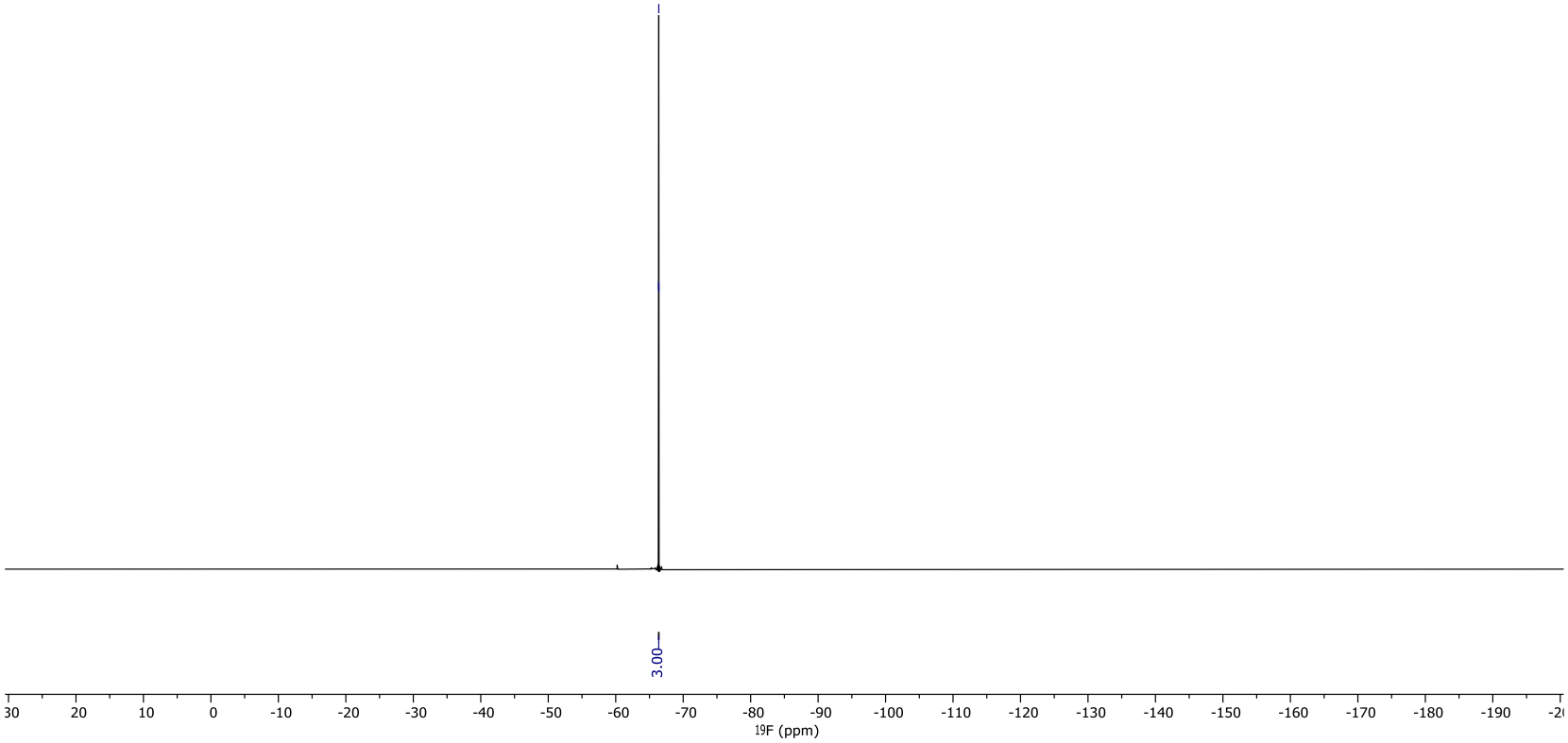


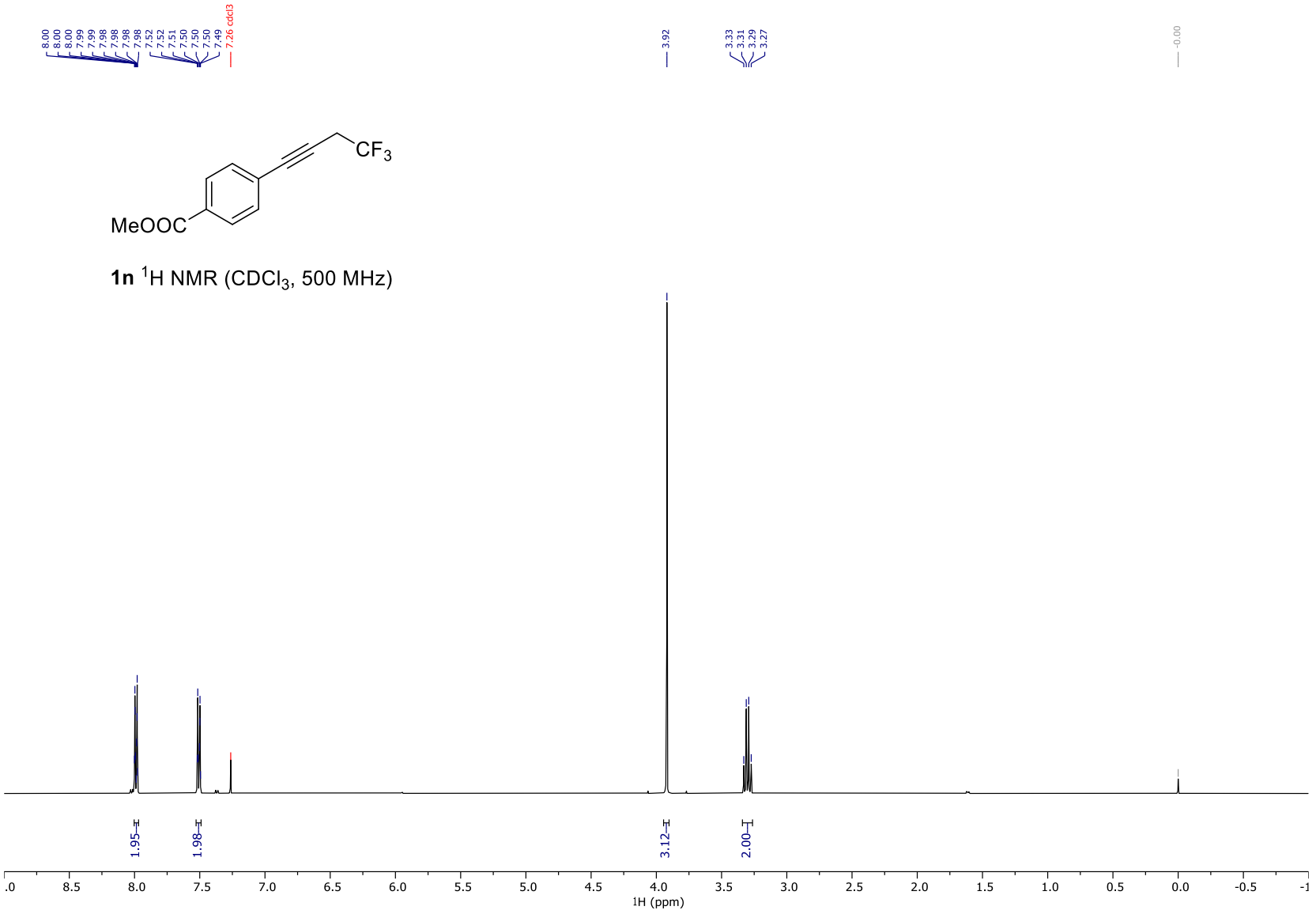
1m ^{1}H NMR ($CDCl_3$, 500 MHz)

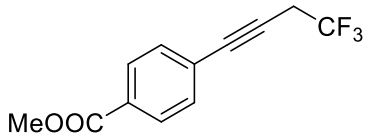




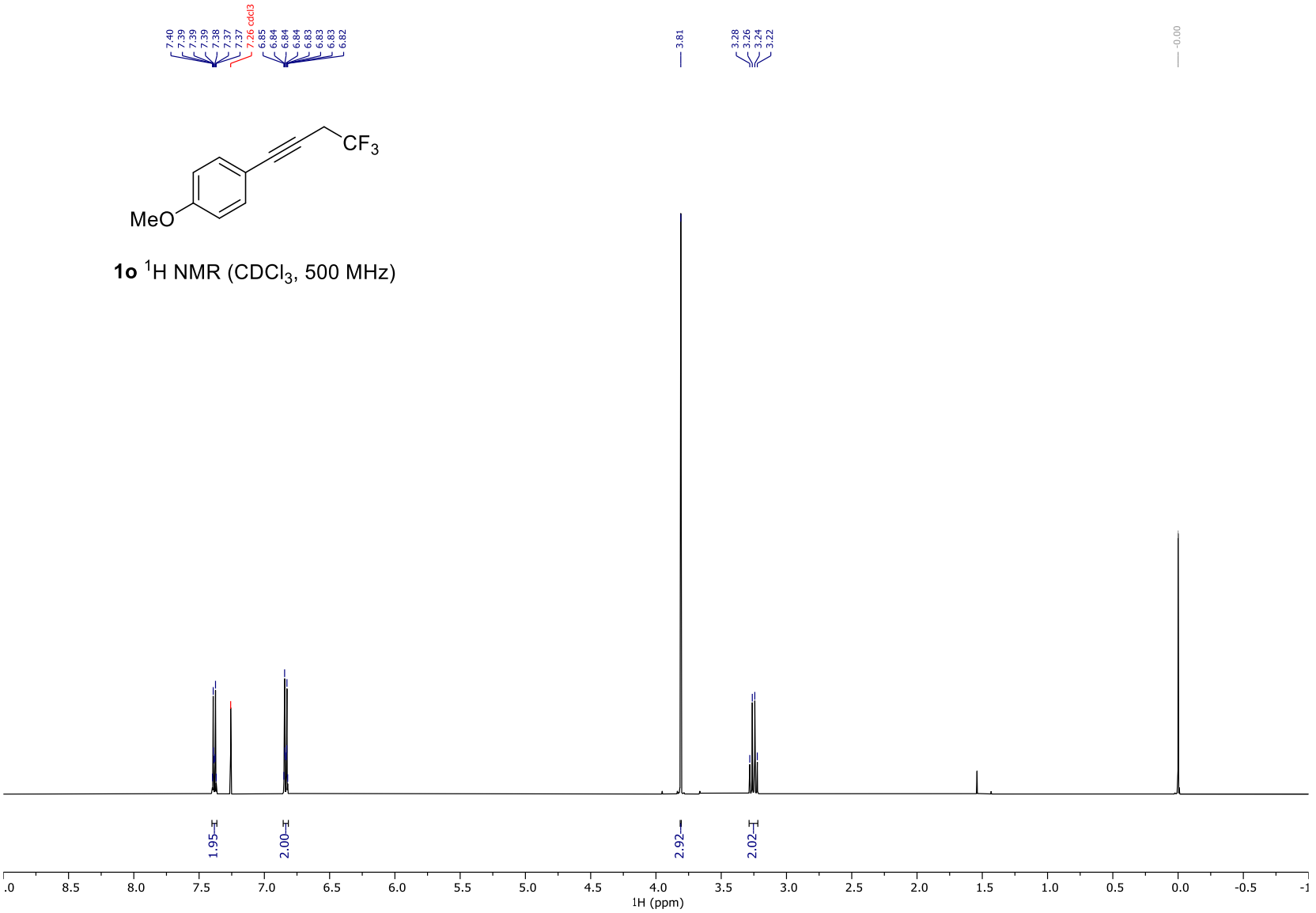
1m ^{19}F NMR ($CDCl_3$, 470 MHz)



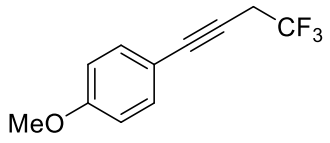

8.00
8.00
8.00
7.99
7.99
7.98
7.98
7.98
7.98
7.52
7.52
7.51
7.50
7.50
7.50
7.49
7.26 cdcl3
3.92
3.33
3.31
3.29
3.27
-0.00
CF3
MeOOC
1n 1H NMR (CDCl3, 500 MHz)
1.95
1.98
3.12
2.00
1H (ppm)



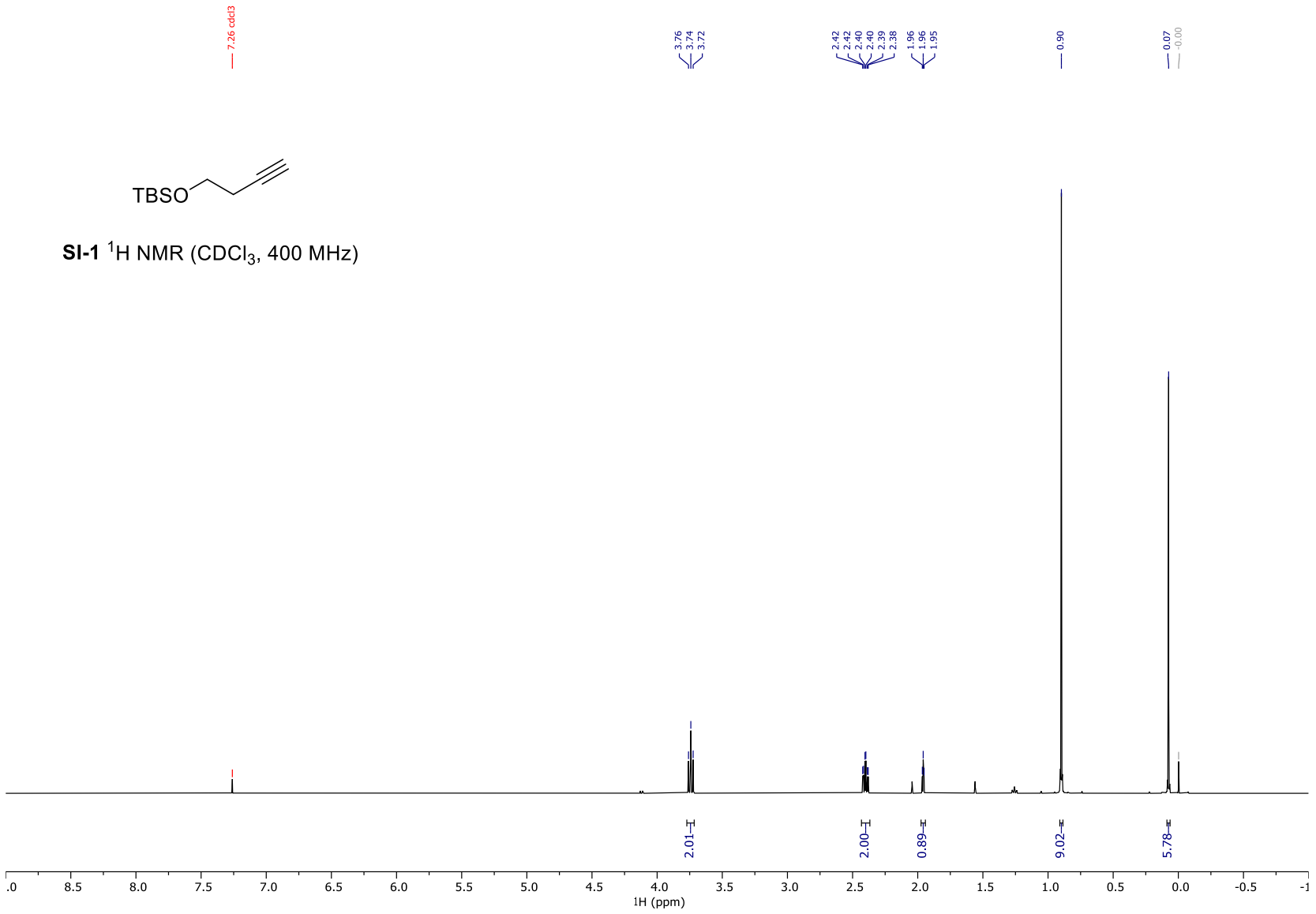
1n ^{19}F NMR ($CDCl_3$, 470 MHz)



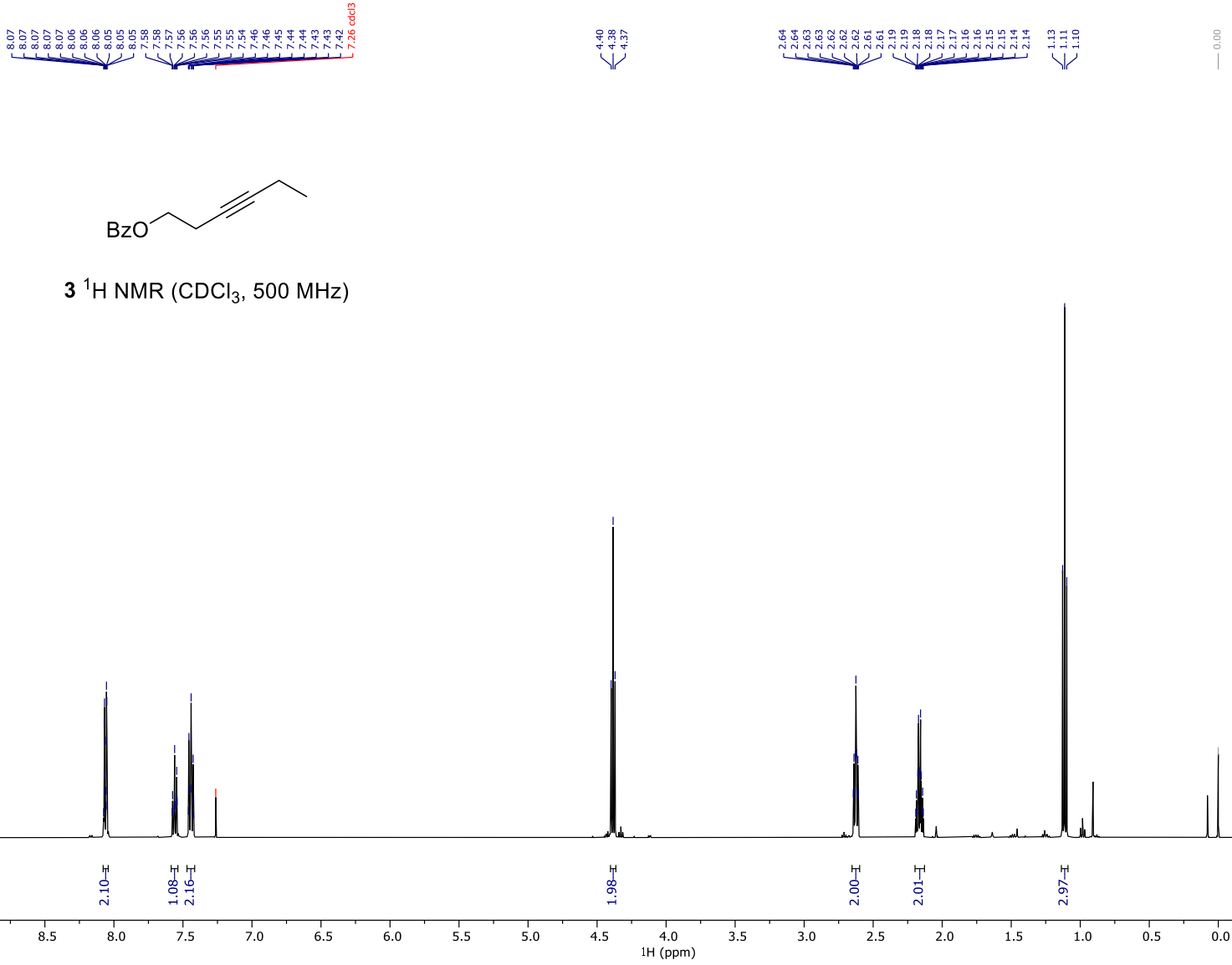
1o ^{1}H NMR ($CDCl_3$, 500 MHz)

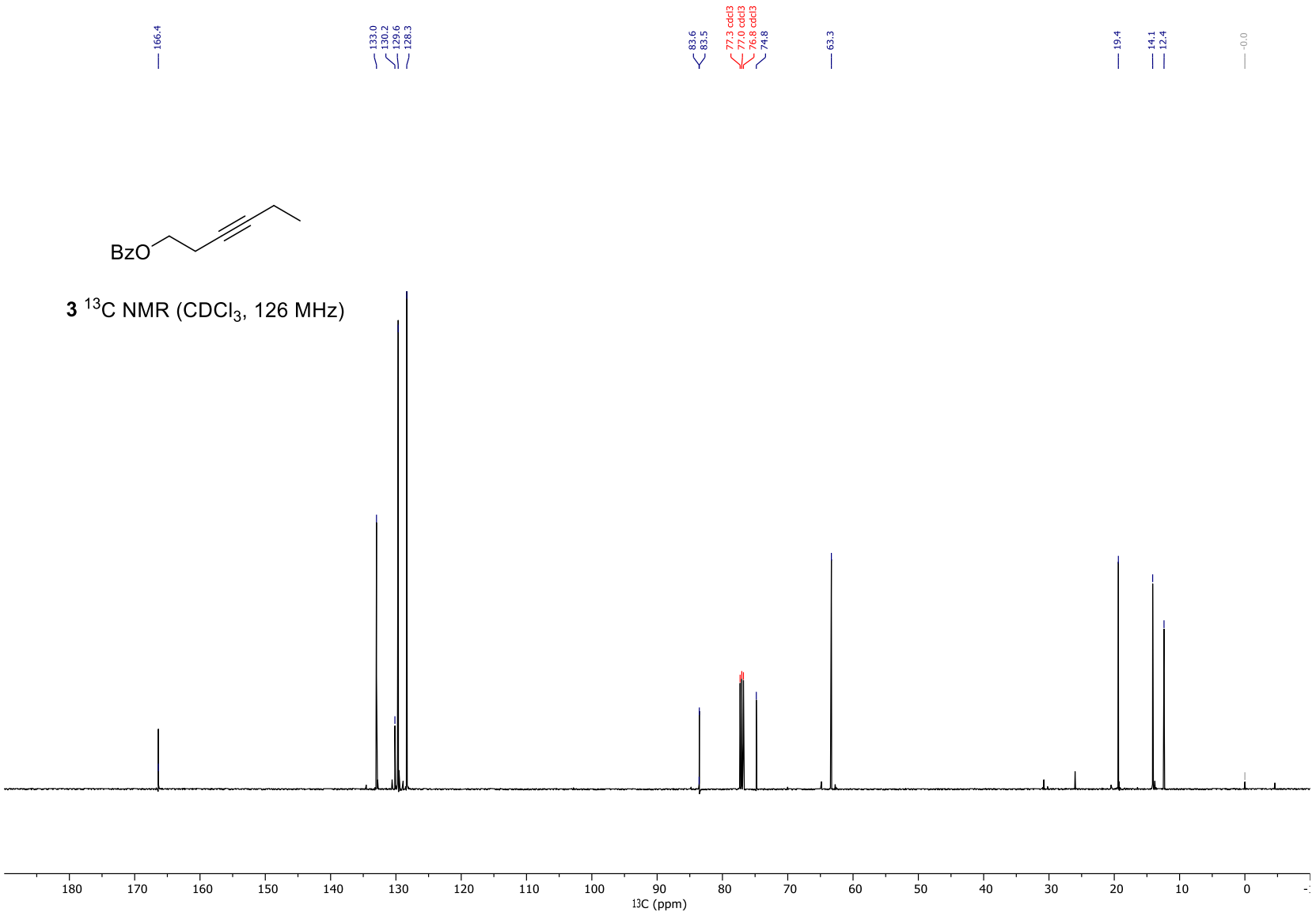


1o ^{19}F NMR ($CDCl_3$, 470 MHz)

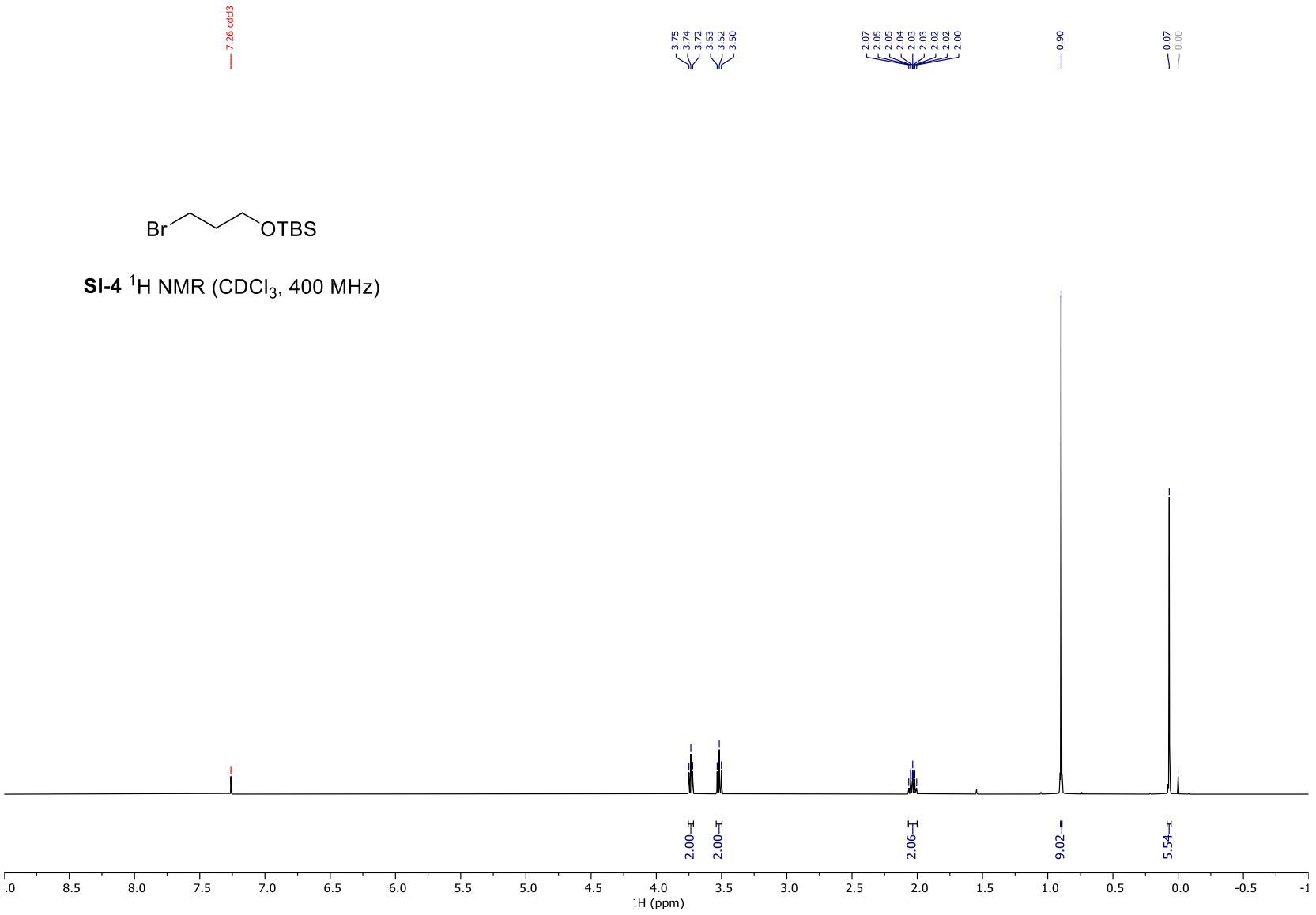


SI-1 ^{1}H NMR ($CDCl_3$, 400 MHz)

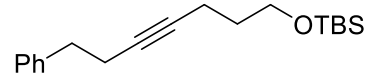

8.07 8.07 8.07 8.07 8.07 8.06 8.06 8.06 8.05 8.05 8.05 7.58 7.58 7.57 7.56 7.56 7.56 7.55 7.55 7.54 7.46 7.46 7.45 7.44 7.44 7.43 7.43 7.42 7.26 cdcl3
4.40 4.38 4.37
2.64 2.64 2.63 2.63 2.62 2.62 2.62 2.61 2.61 2.19 2.19 2.18 2.18 2.17 2.17 2.16 2.16 2.15 2.15 2.14 2.14
1.13 1.11 1.10
0.00
BzO
3 1H NMR (CDCl3, 500 MHz)
2.10 1.08 2.16 1.98 2.00 2.01 2.97
1H (ppm)



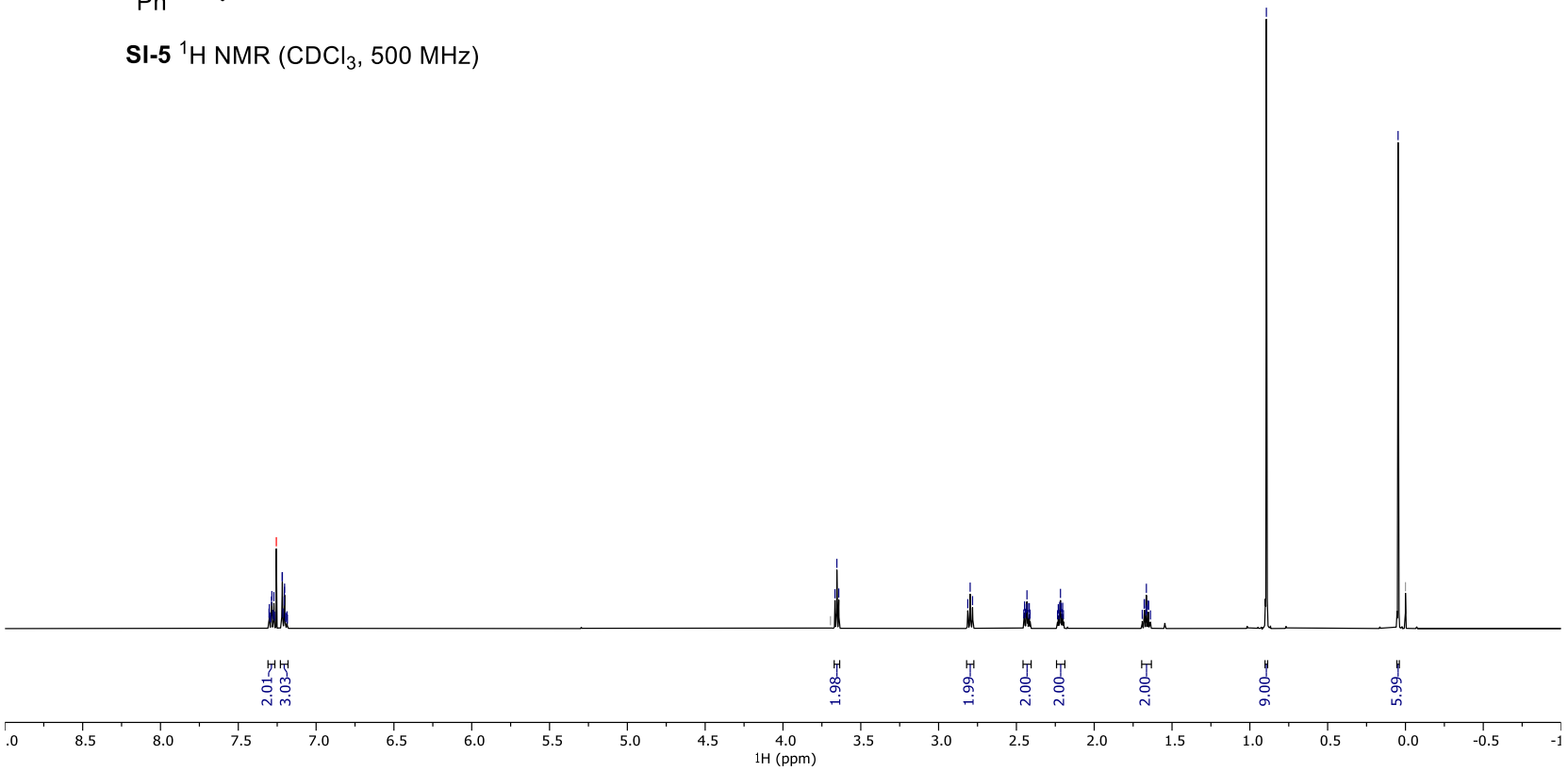
3 ^{13}C NMR ($CDCl_3$, 126 MHz)

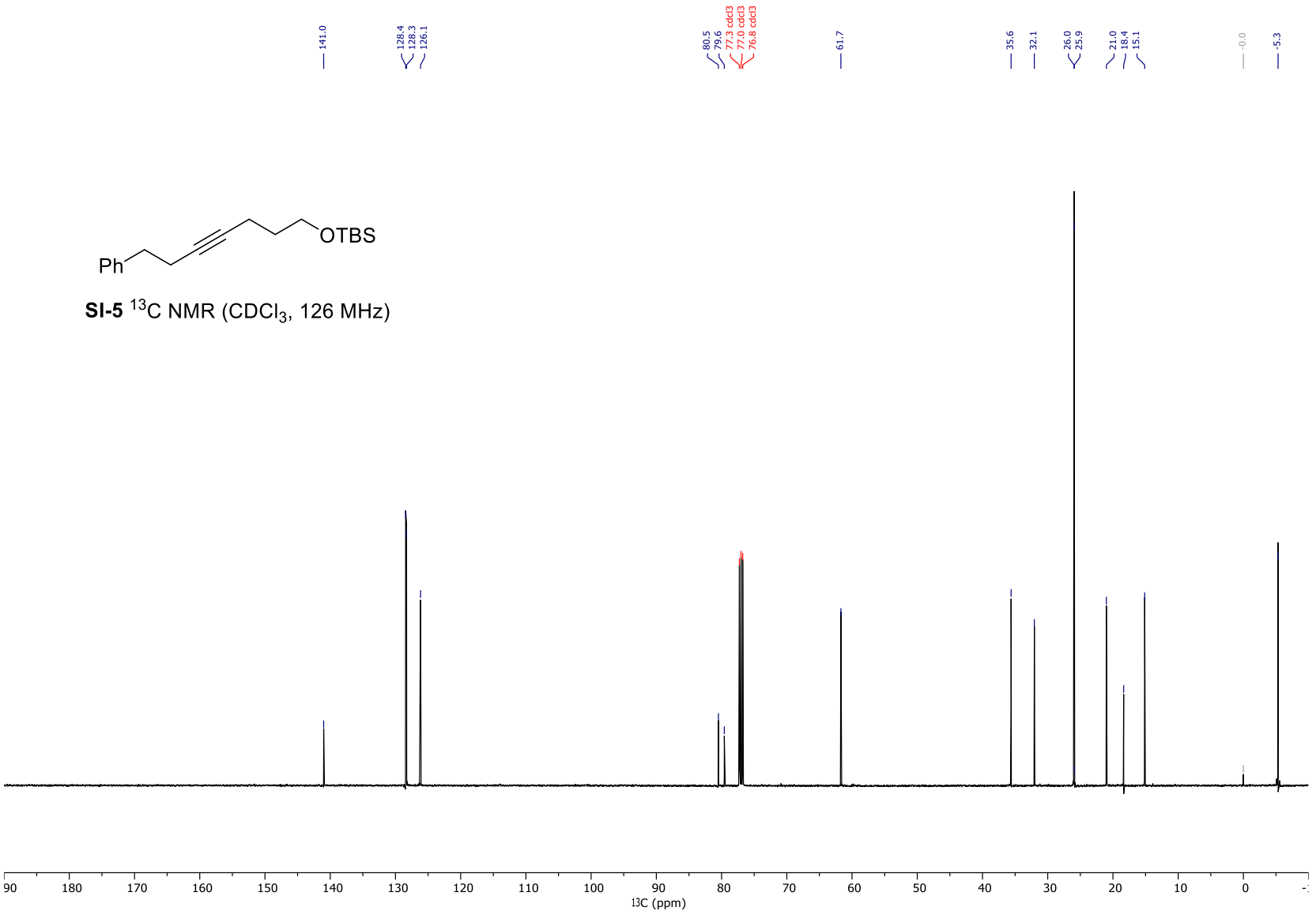


SI-4 ^{1}H NMR ($CDCl_3$, 400 MHz)

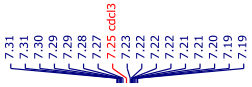


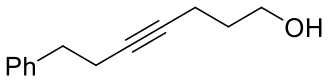
SI-5 ^{1}H NMR ($CDCl_3$, 500 MHz)



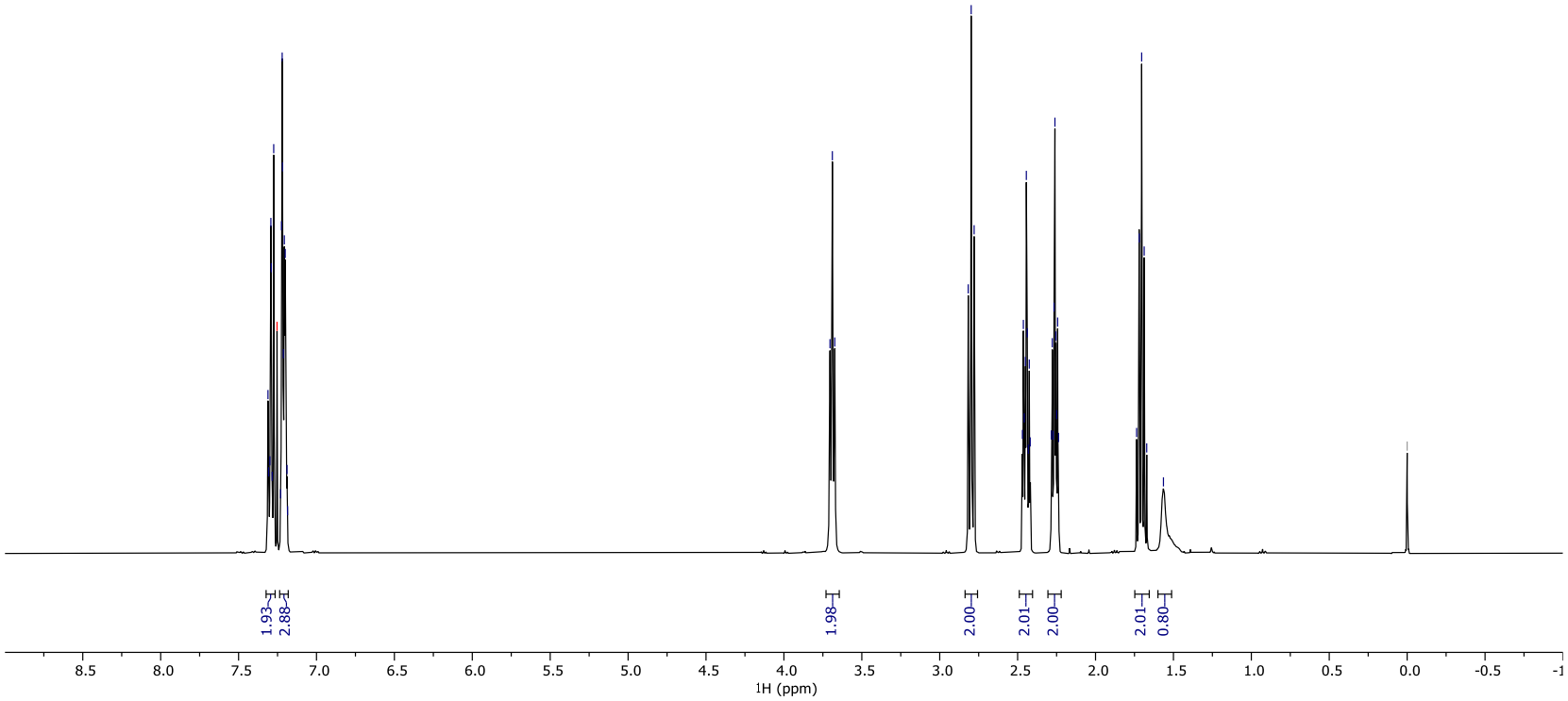


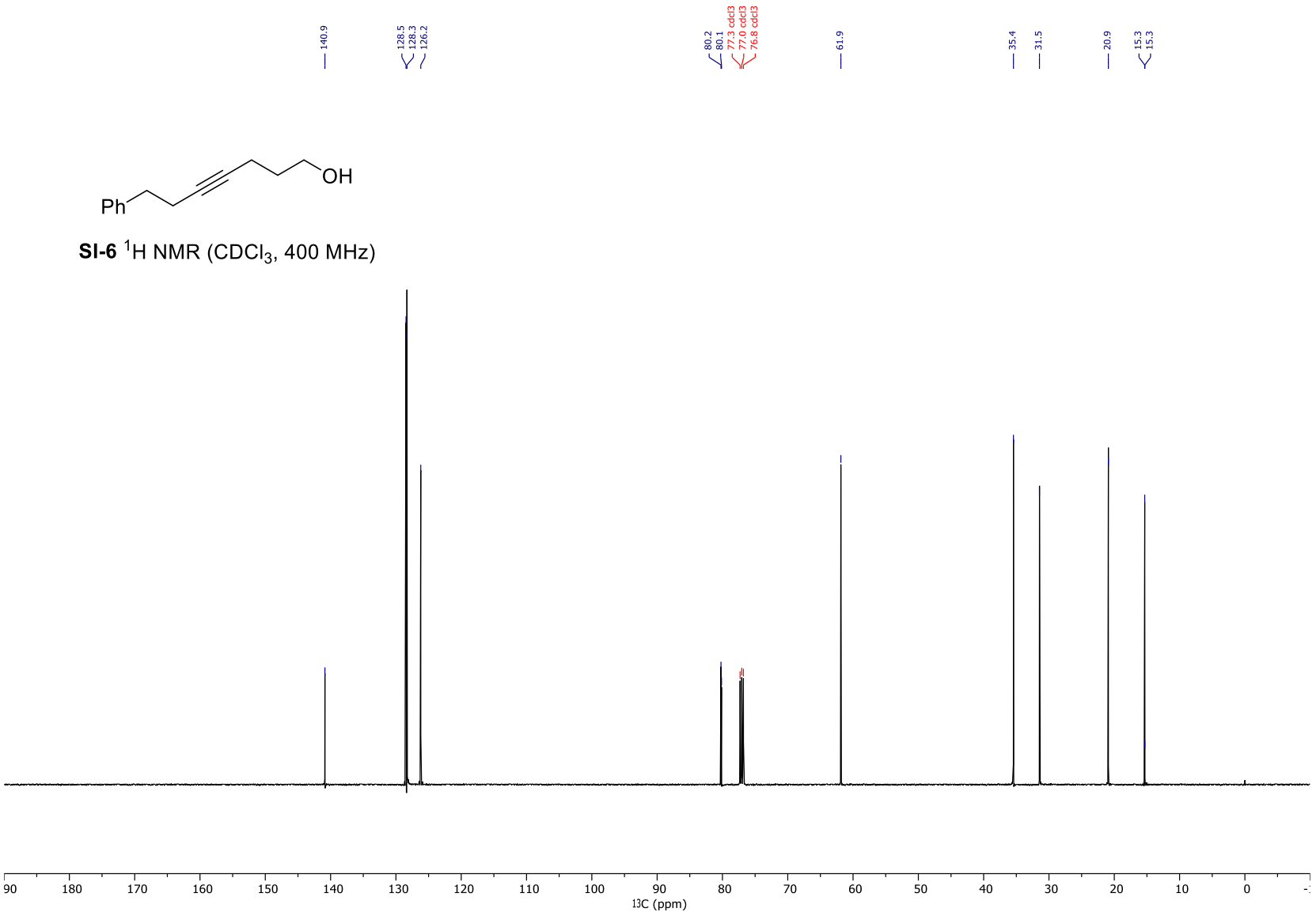
SI-5 ^{13}C NMR ($CDCl_3$, 126 MHz)



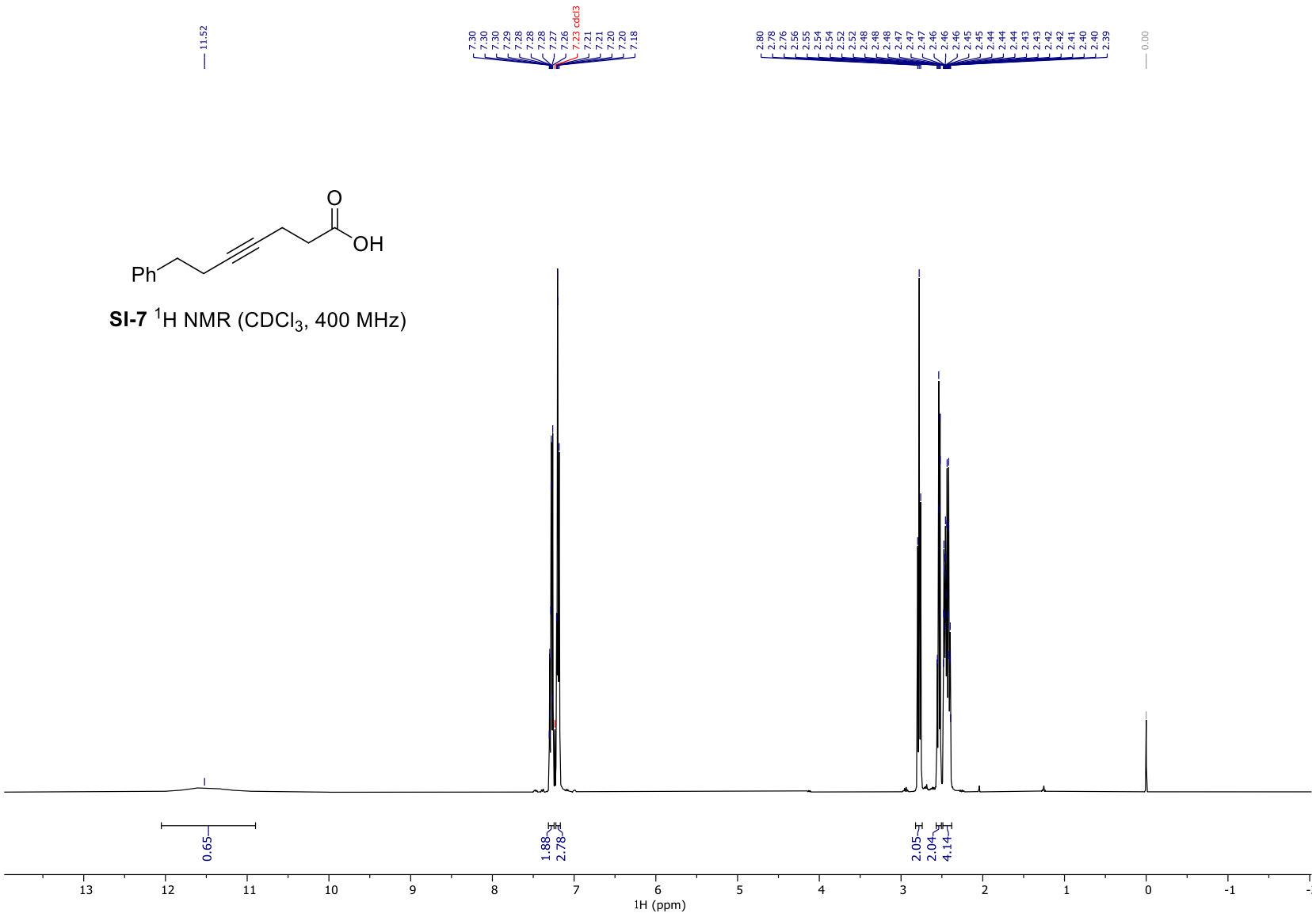


SI-6 ^{1}H NMR ($CDCl_3$, 400 MHz)

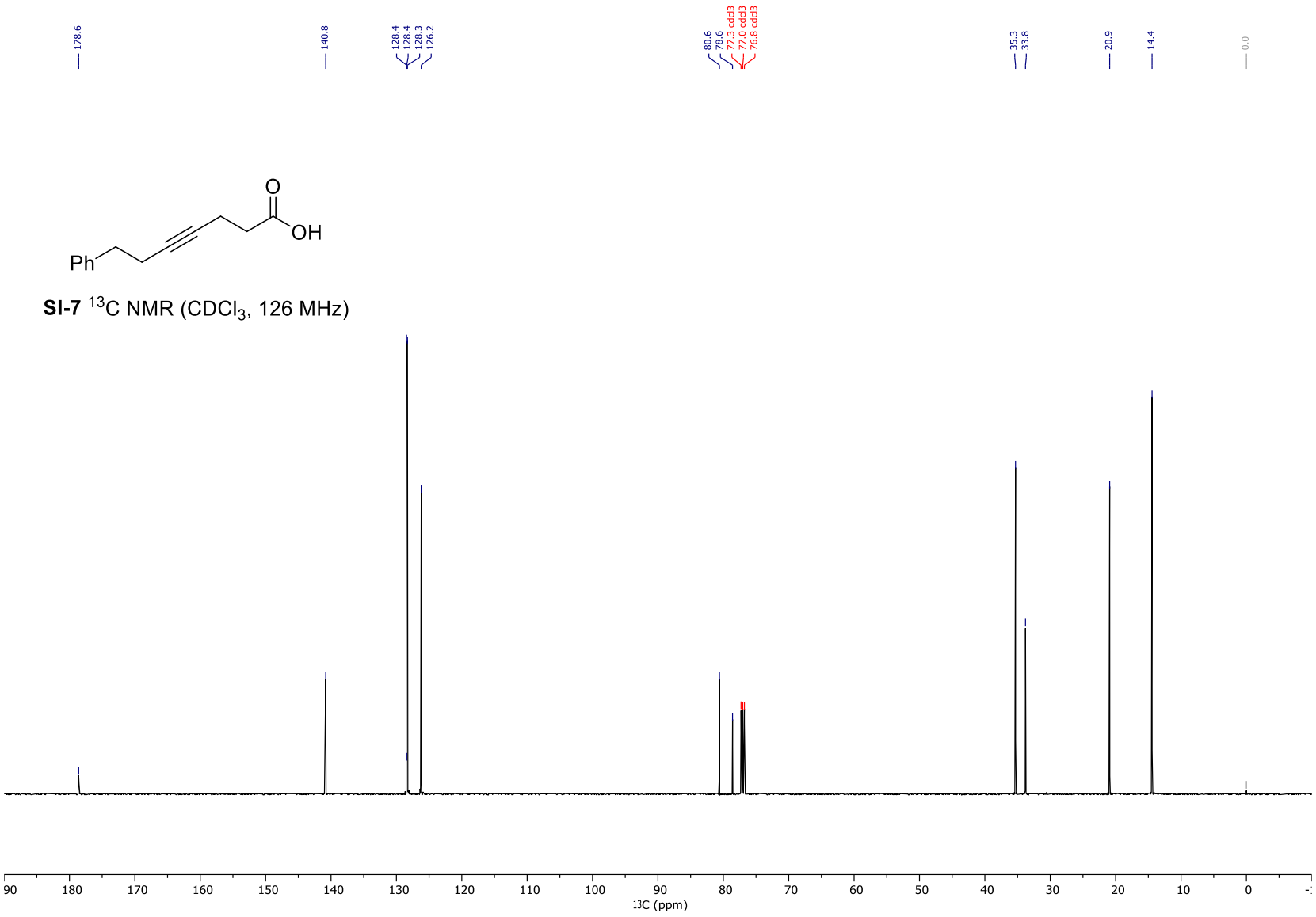




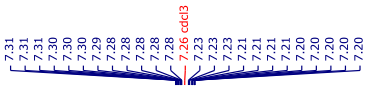
SI-6 ^{1}H NMR ($CDCl_3$, 400 MHz)



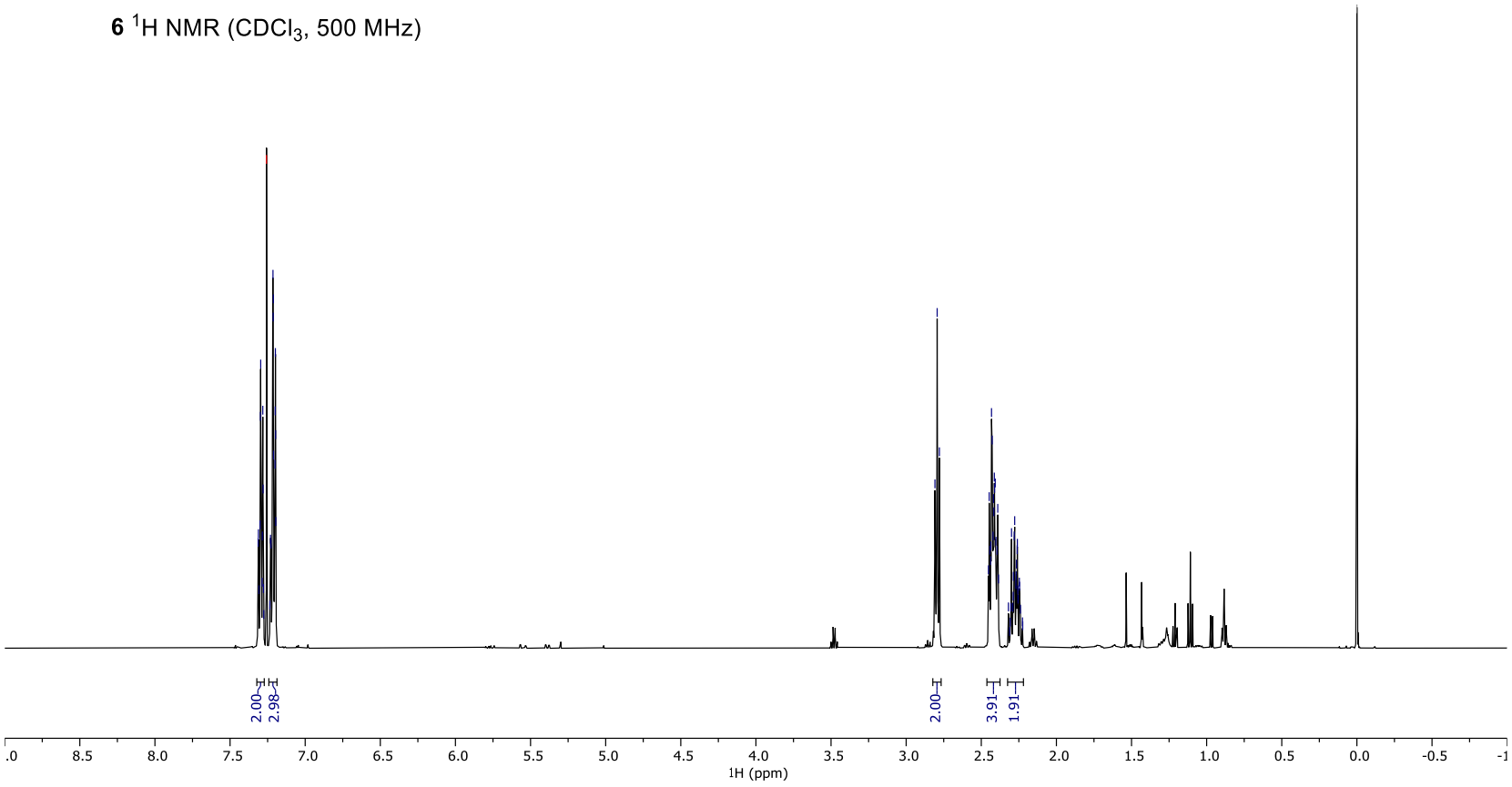
SI-7 ^{1}H NMR ($CDCl_3$, 400 MHz)

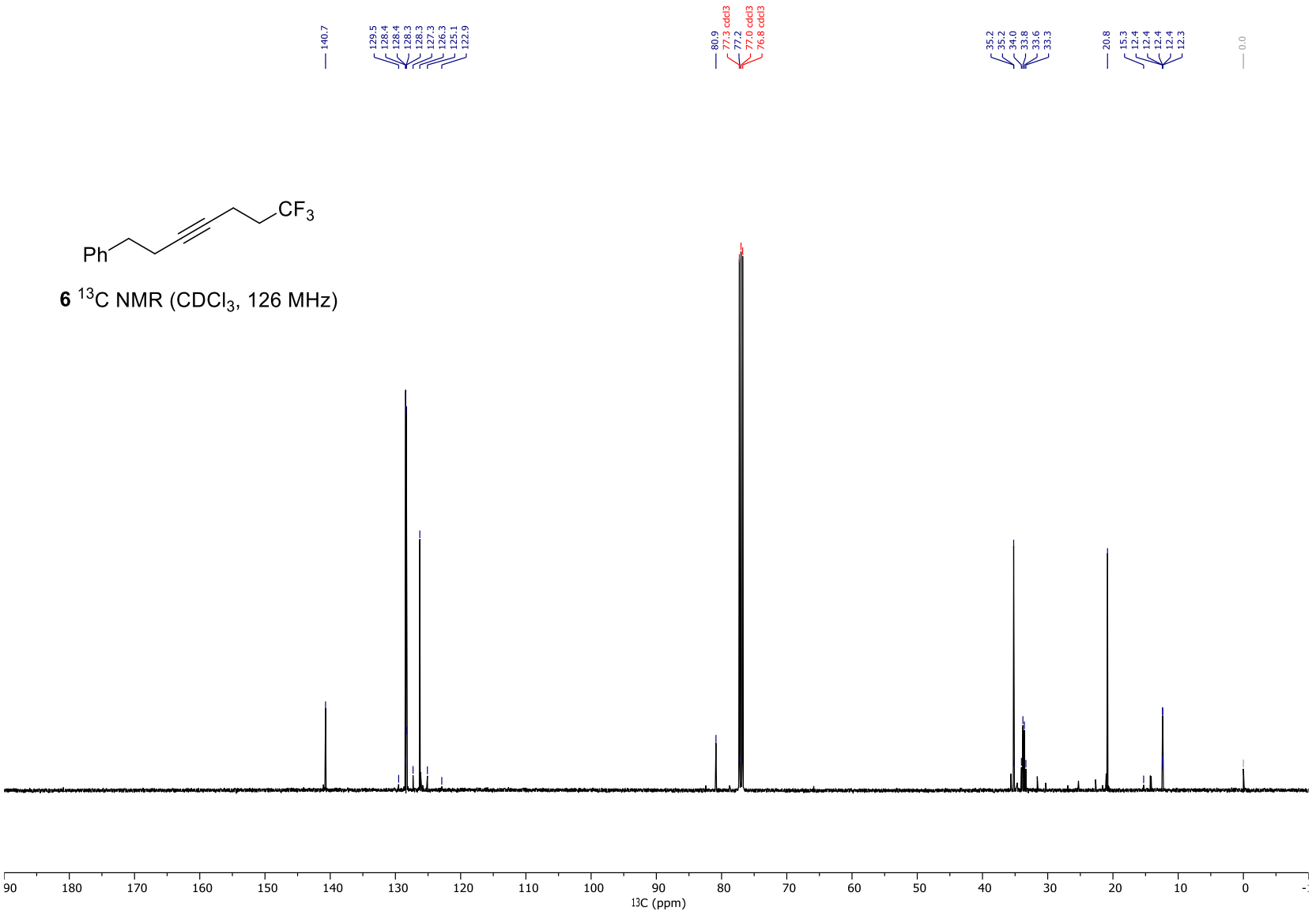


SI-7 ^{13}C NMR ($CDCl_3$, 126 MHz)



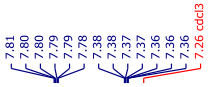
6 ^{1}H NMR ($CDCl_3$, 500 MHz)

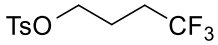




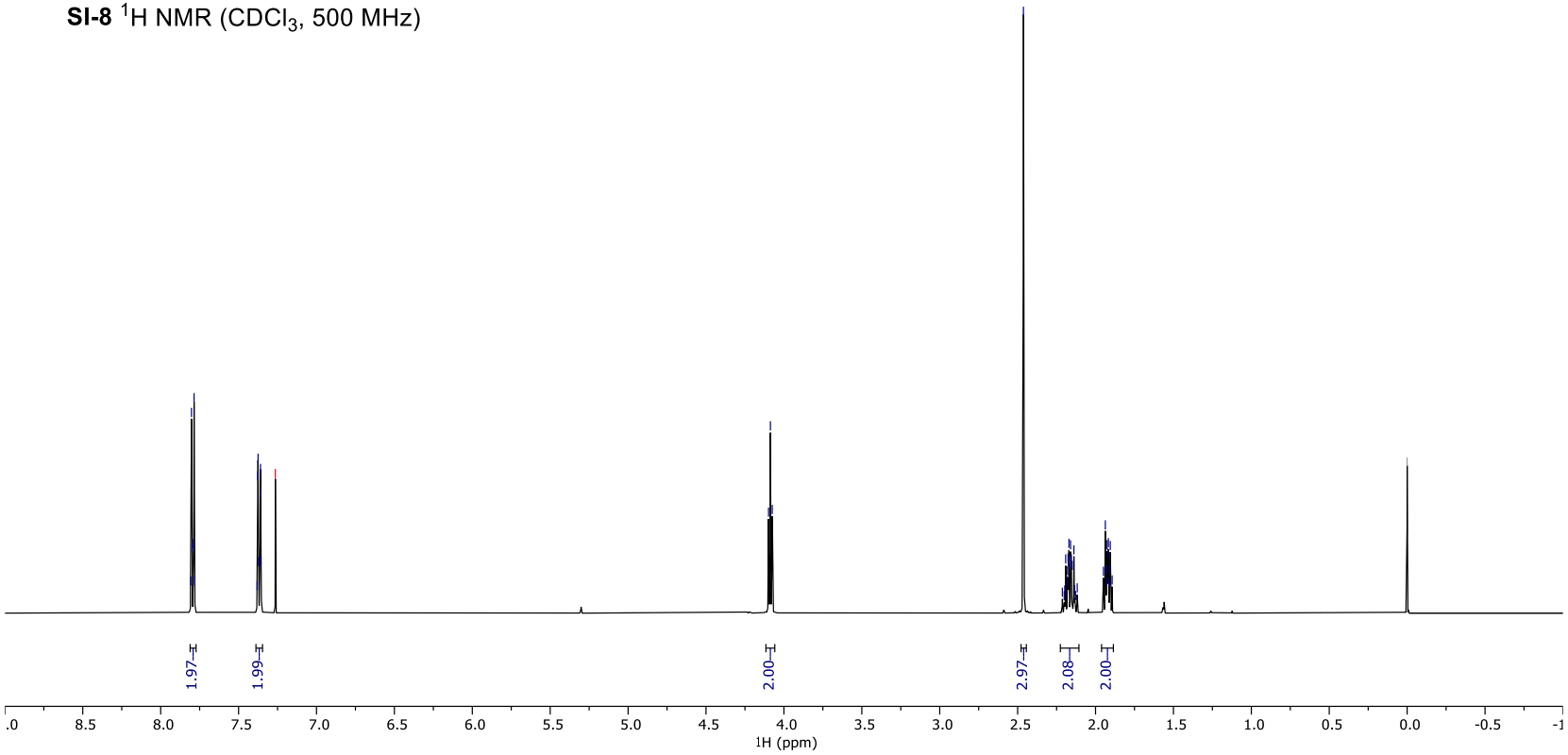
6 ^{13}C NMR ($CDCl_3$, 126 MHz)

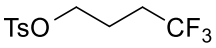
6 ^{19}F NMR ($CDCl_3$, 470 MHz)



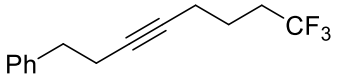


SI-8 ^{1}H NMR ($CDCl_3$, 500 MHz)

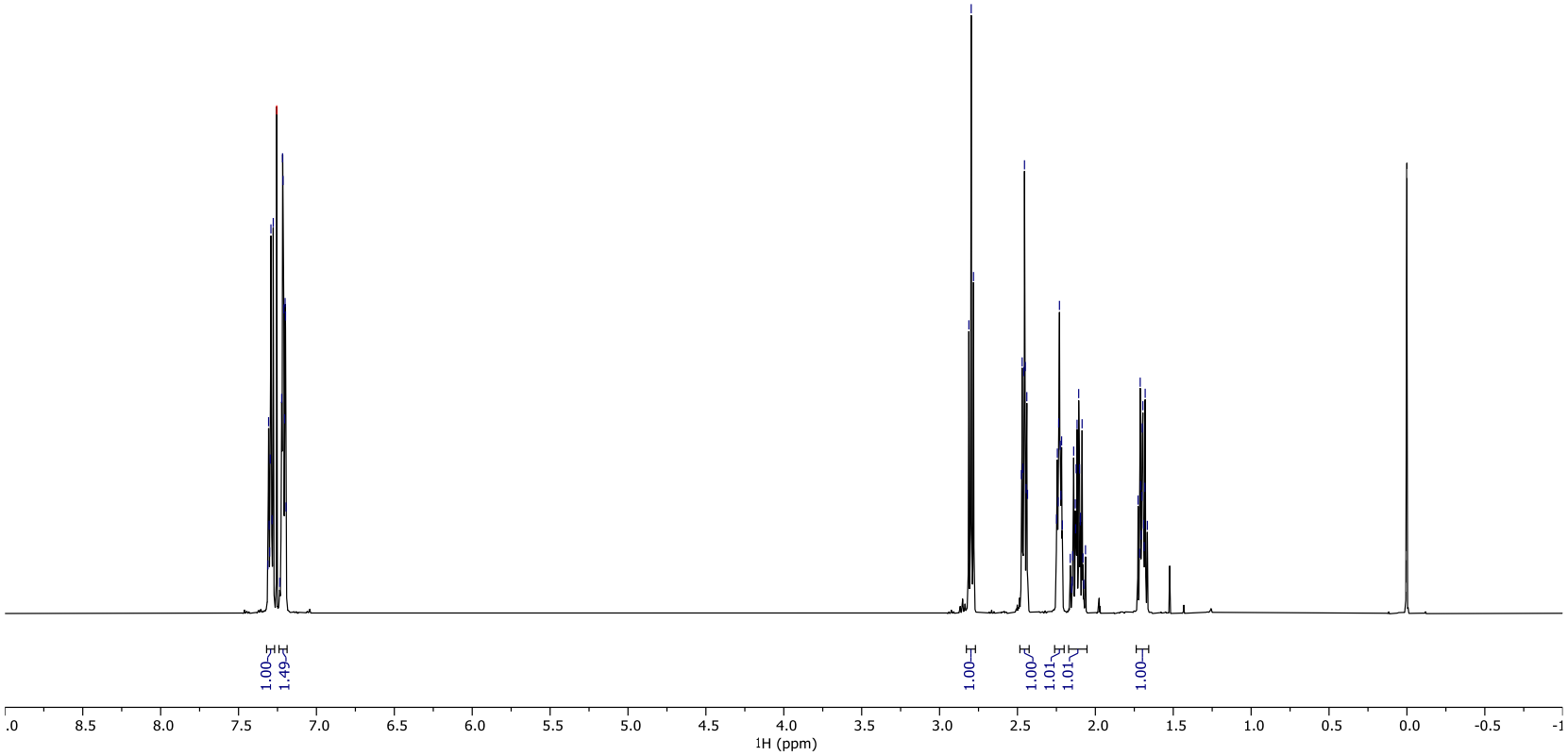


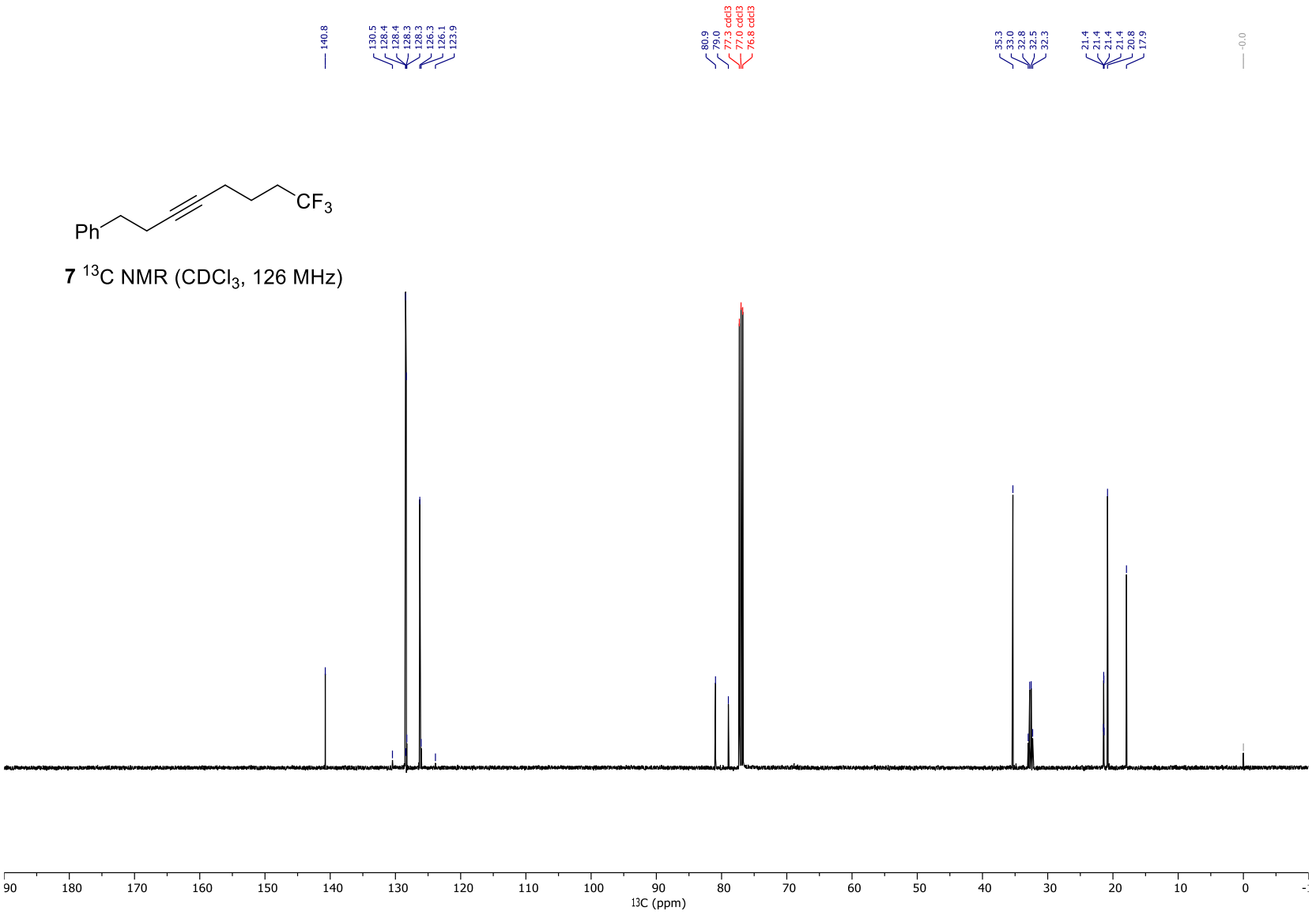


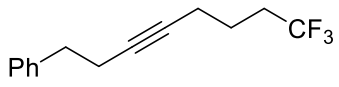
SI-8 ^{19}F NMR ($CDCl_3$, 470 MHz)



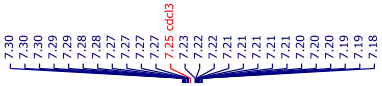
7 ^{1}H NMR ($CDCl_3$, 500 MHz)



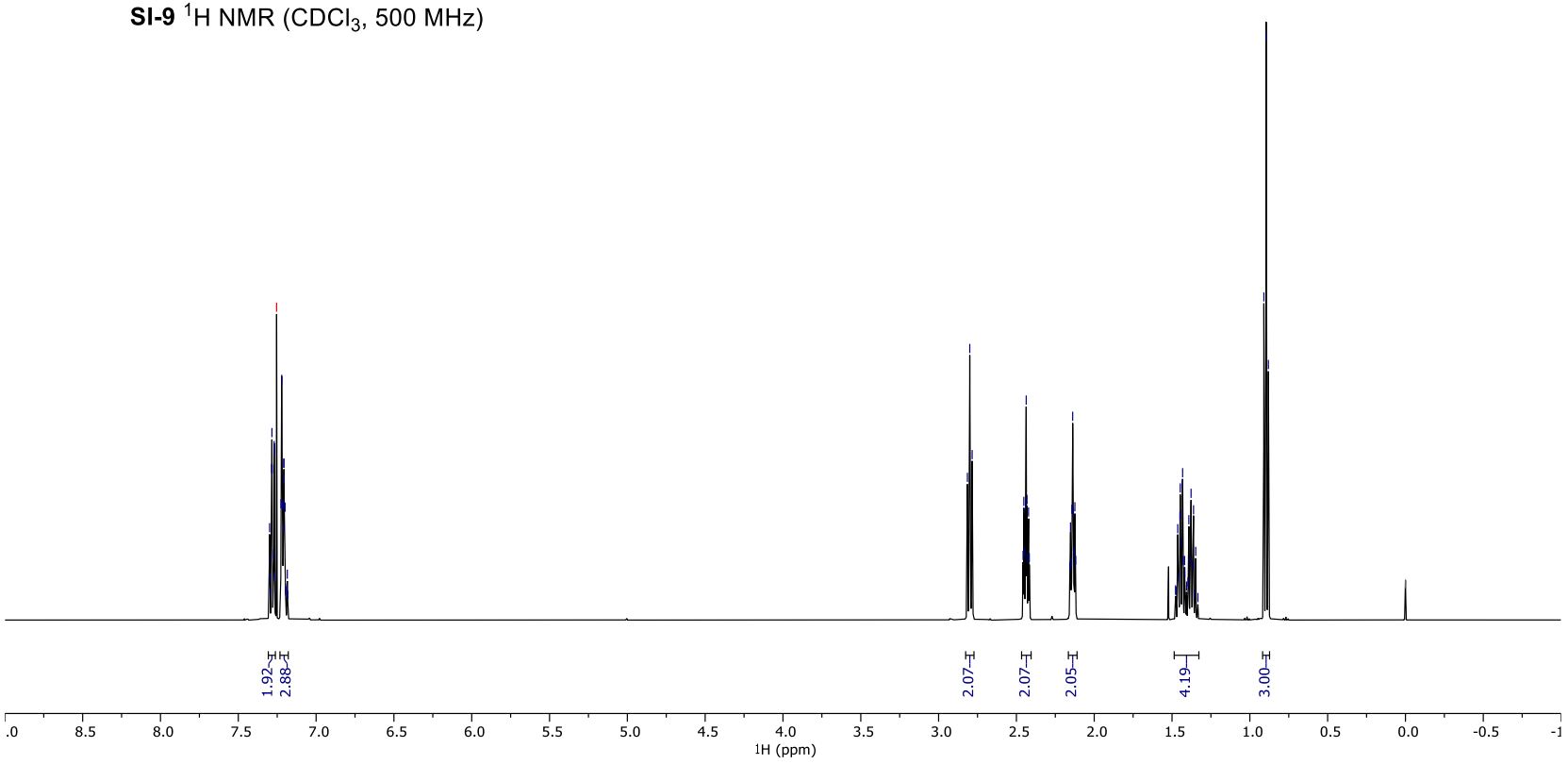

140.8
130.5
128.4
128.4
128.3
128.3
126.3
126.1
123.9
80.9
79.0
77.3 cdcl3
77.0 cdcl3
76.8 cdcl3
35.3
33.0
32.8
32.5
32.3
21.4
21.4
21.4
21.4
20.8
17.9
-0.0
Ph
CF3
7 13C NMR (CDCl3, 126 MHz)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C (ppm)

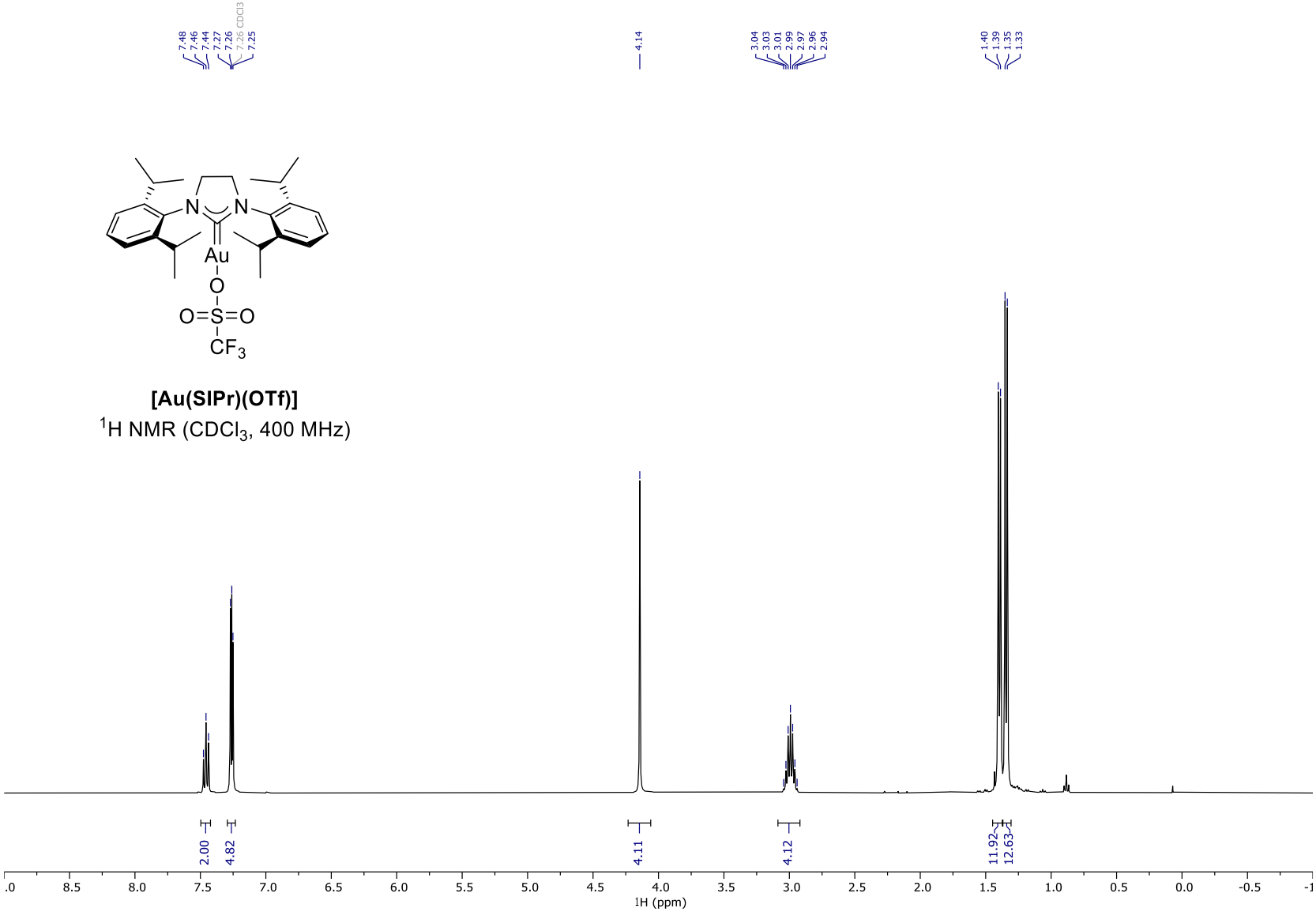


7 ^{19}F NMR ($CDCl_3$, 470 MHz)



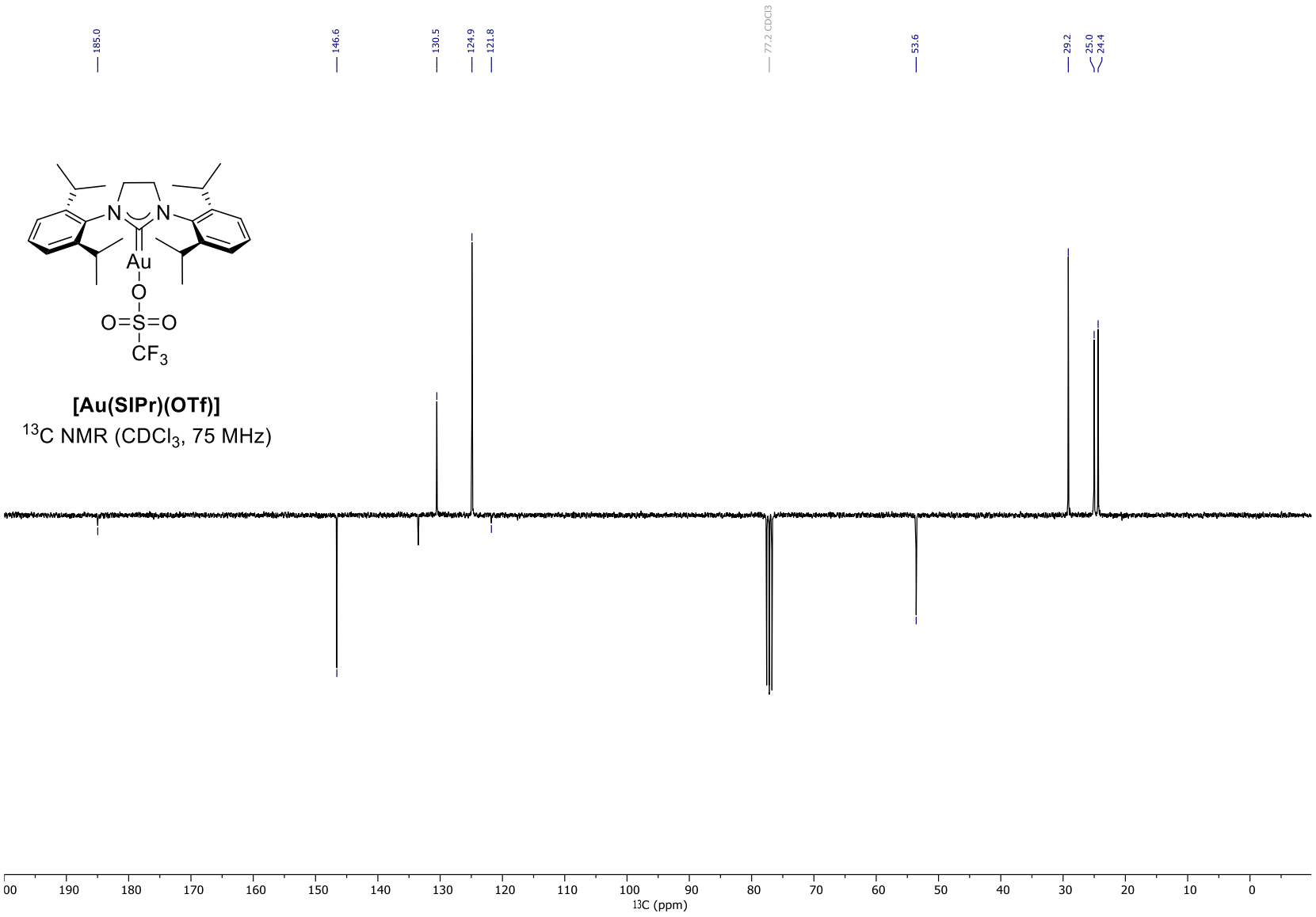
SI-9 ^{1}H NMR ($CDCl_3$, 500 MHz)

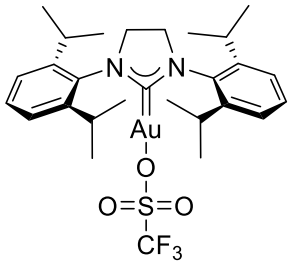




[Au(SIPr)(OTf)]

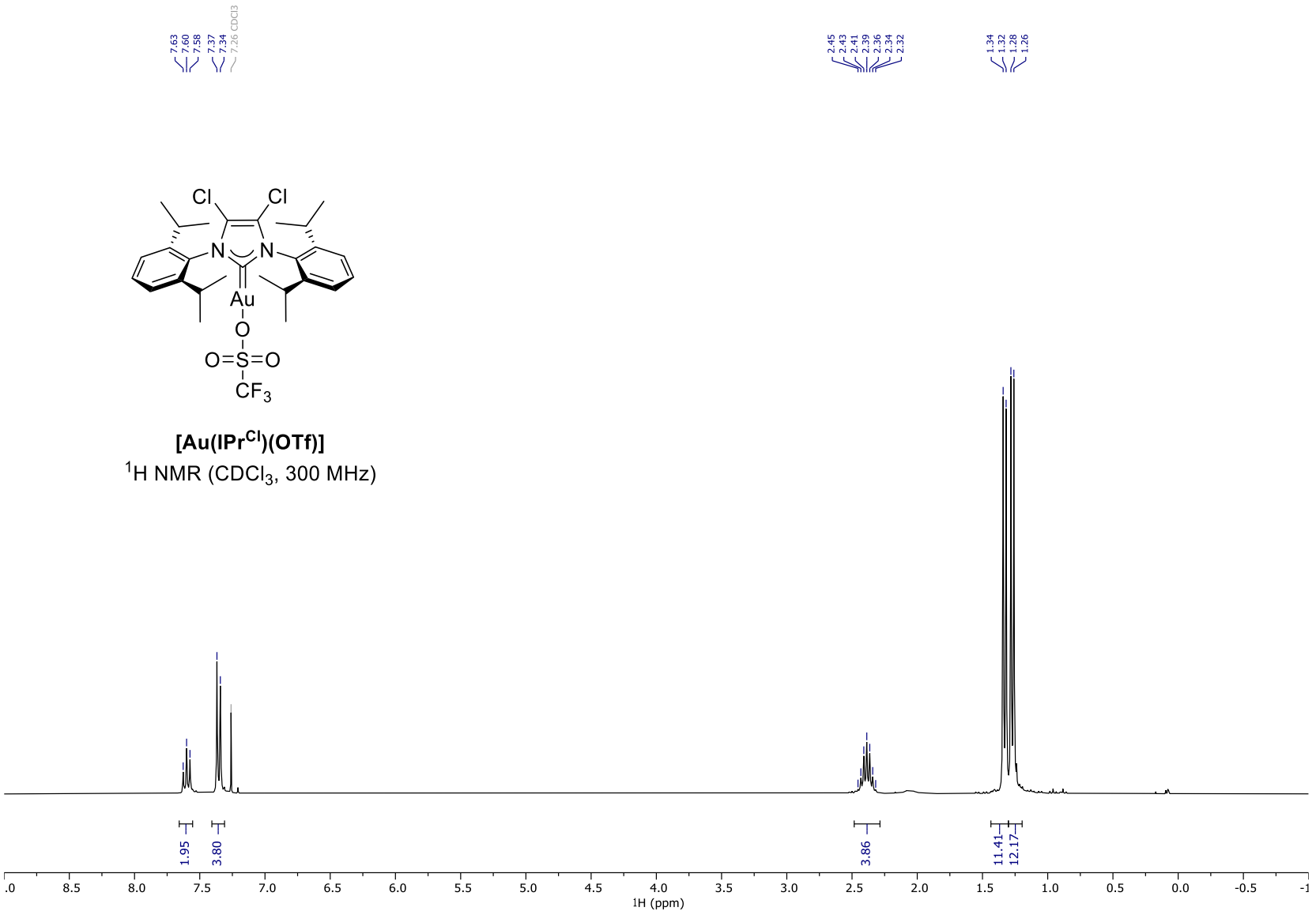
^{1}H NMR ($CDCl_3$, 400 MHz)

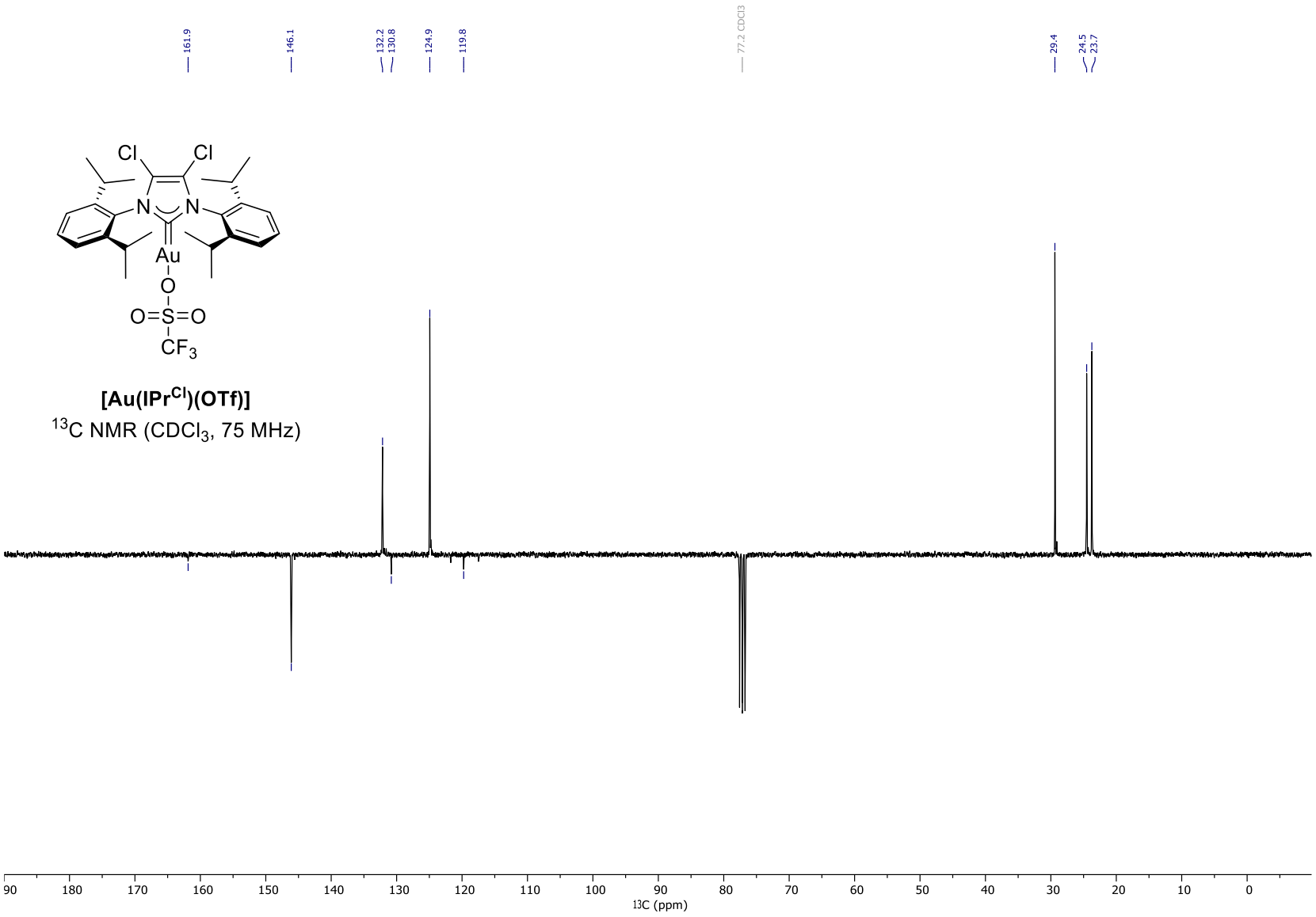

185.0
146.6
130.5
124.9
121.8
77.2 CDCl3
53.6
29.2
25.0
24.4
N
N
Au
O
O=S=O
CF3
[Au(SIPr)(OTf)]
13C NMR (CDCl3, 75 MHz)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C (ppm)

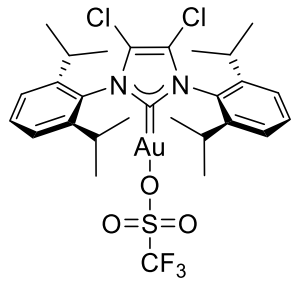


[Au(SIPr)(OTf)]

^{19}F NMR ($CDCl_3$, 377 MHz)

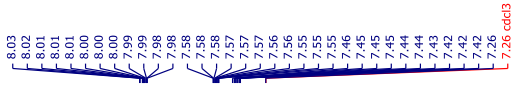

7.63
7.60
7.58
7.37
7.34
7.26 CDCl3
2.45
2.43
2.41
2.39
2.36
2.34
2.32
1.34
1.32
1.28
1.26
Cl
Cl
N
N
Au
O
O=S=O
CF3
[Au(IPrCl)(OTf)]
1H NMR (CDCl3, 300 MHz)
1.95
3.80
3.86
11.41
12.17
1H (ppm)

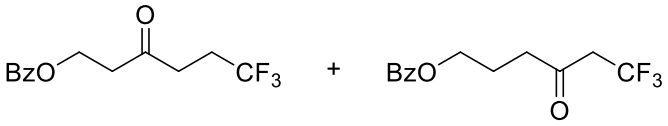

161.9
146.1
132.2
130.8
124.9
119.8
77.2 CDCl3
29.4
24.5
23.7
Cl
Cl
N
N
Au
O
O=S=O
CF3
[Au(IPrCl)(OTf)]
13C NMR (CDCl3, 75 MHz)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C (ppm)



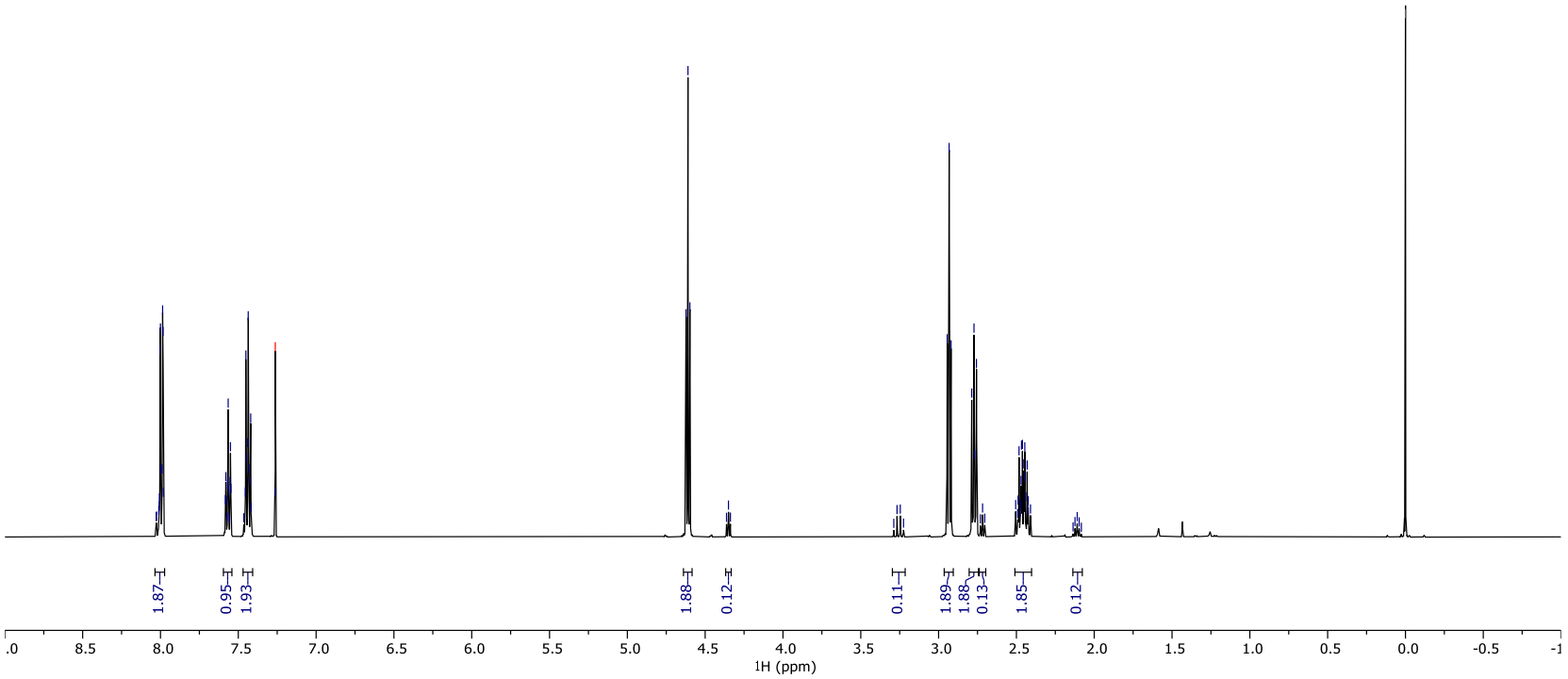
[Au(IPr^{Cl})(OTf)]

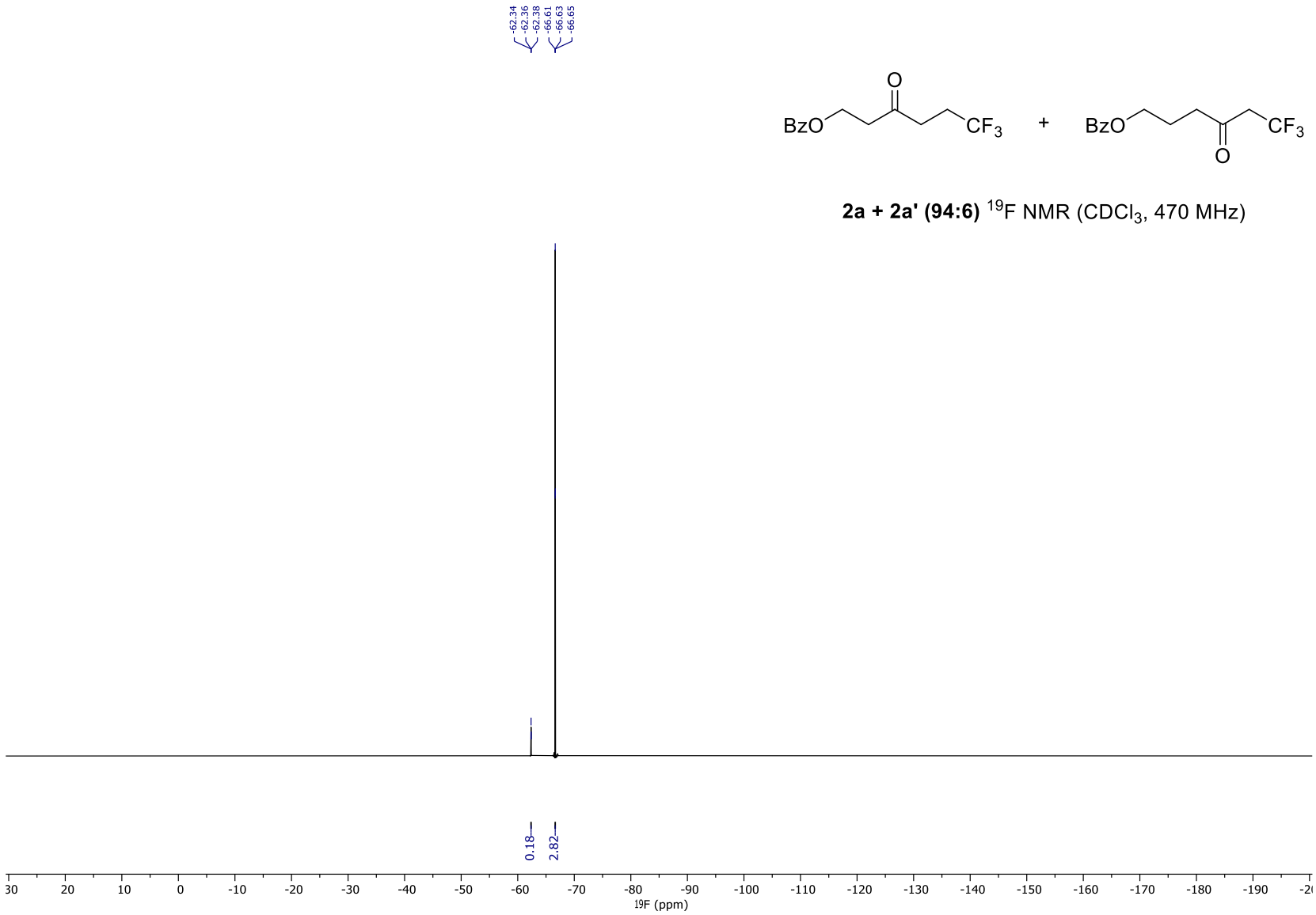
^{19}F NMR ($CDCl_3$, 377 MHz)

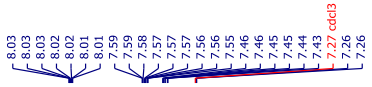


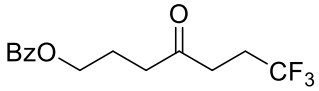


2a + 2a' (94:6) ^{1}H NMR ($CDCl_3$, 500 MHz)

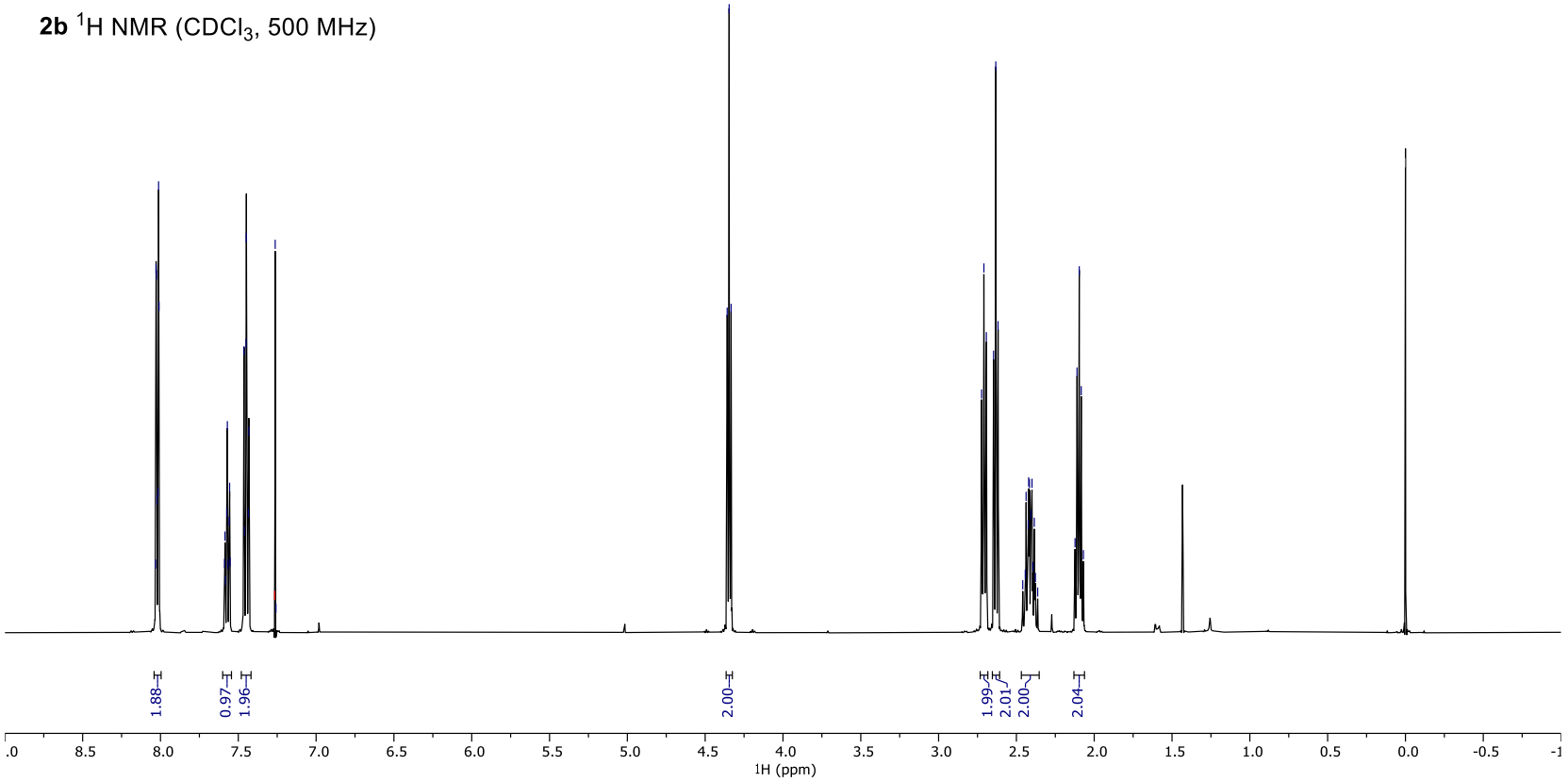


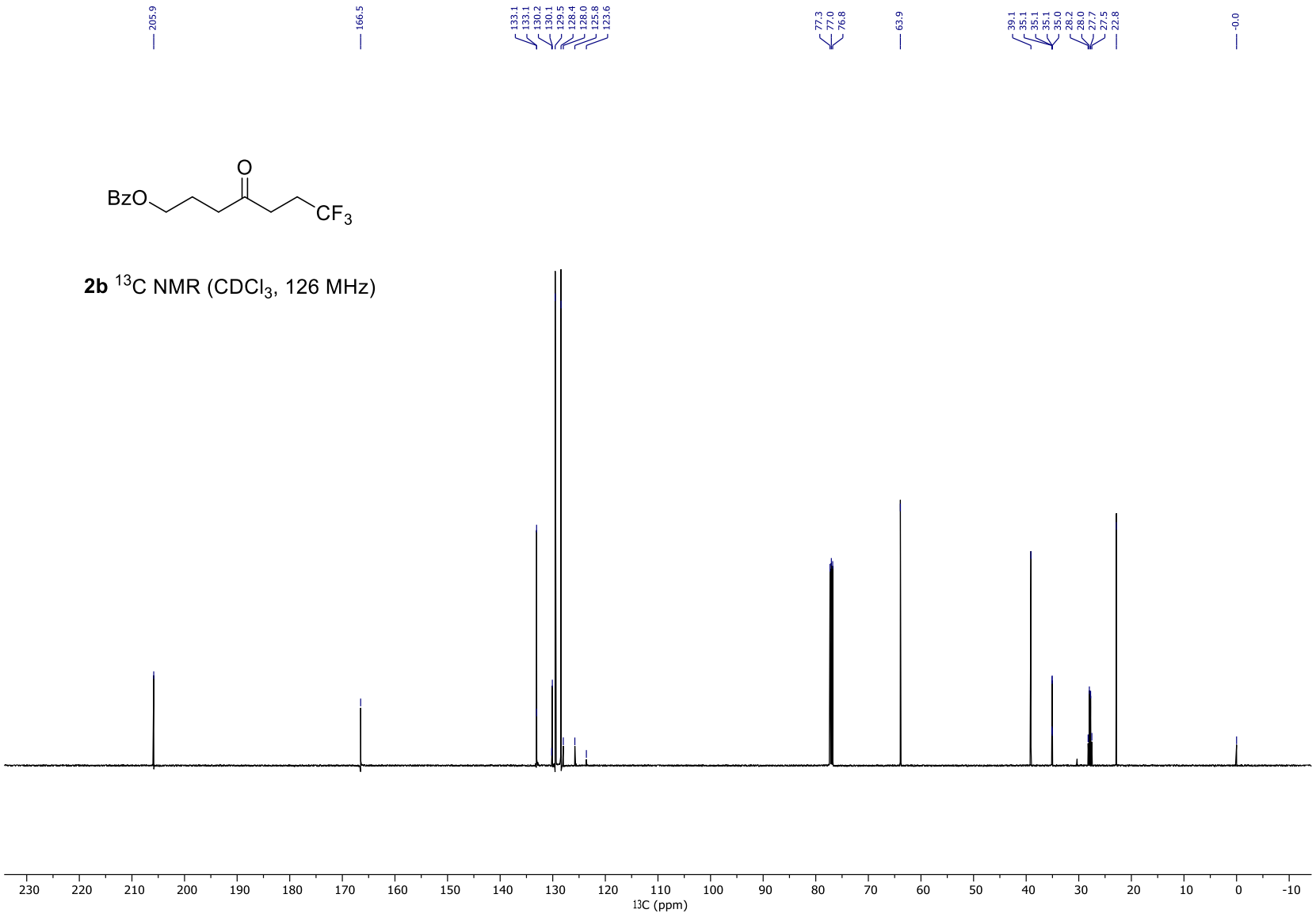

-62.34
-62.36
-62.38
-66.61
-66.63
-66.65
BzO
CF3
+
BzO
CF3
O
O
2a + 2a' (94:6) 19F NMR (CDCl3, 470 MHz)
0.18
2.82
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
19F (ppm)

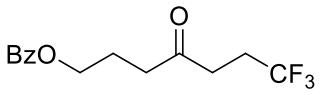




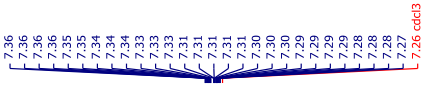
2b ^{1}H NMR ($CDCl_3$, 500 MHz)

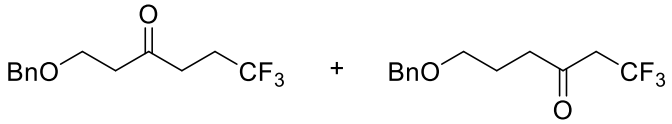



205.9
166.5
133.1
133.1
130.2
130.1
129.5
128.4
128.0
125.8
123.6
77.3
77.0
76.8
63.9
39.1
35.1
35.1
35.1
35.0
28.2
28.0
27.7
27.5
22.8
-0.0
BzO
O
CF3
2b 13C NMR (CDCl3, 126 MHz)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)

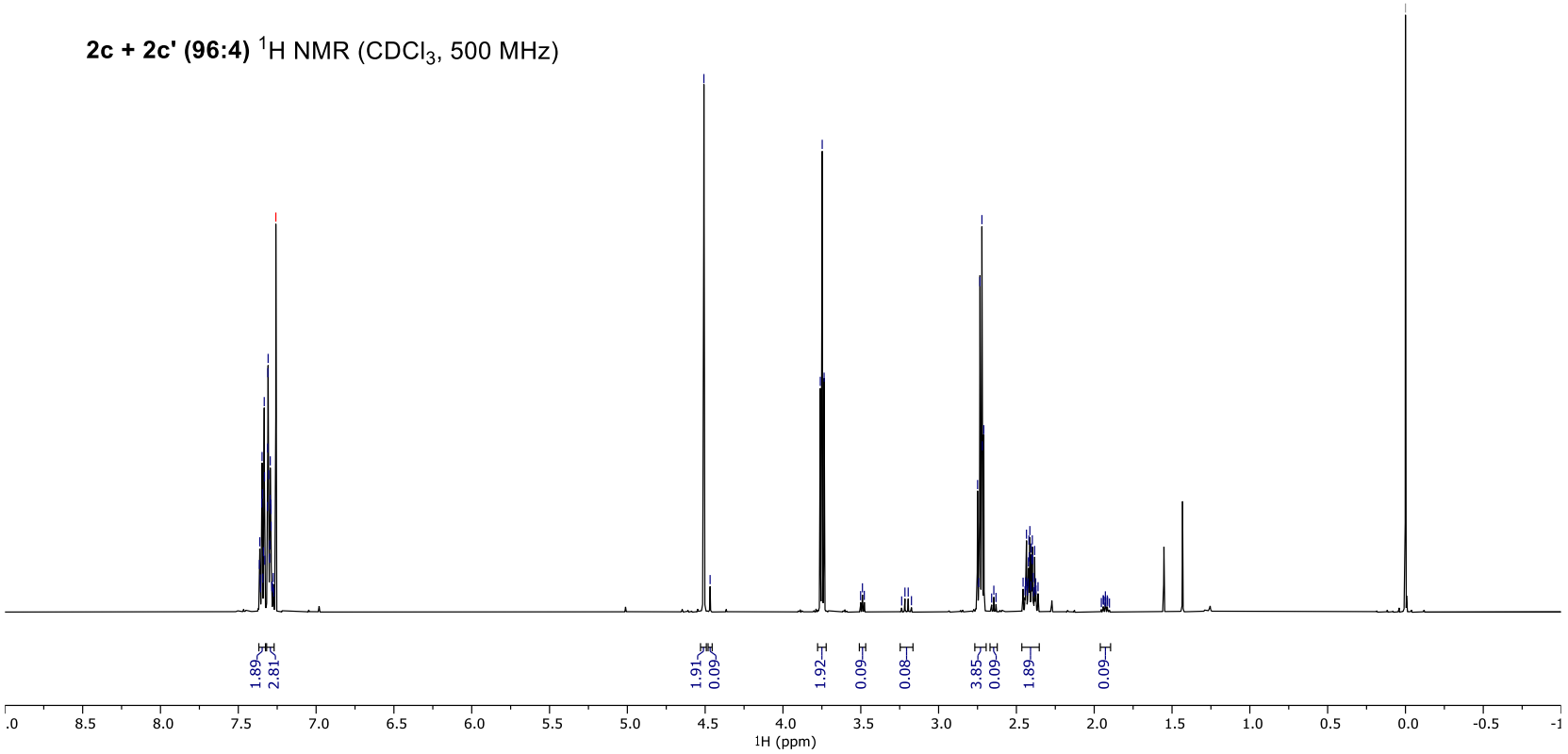


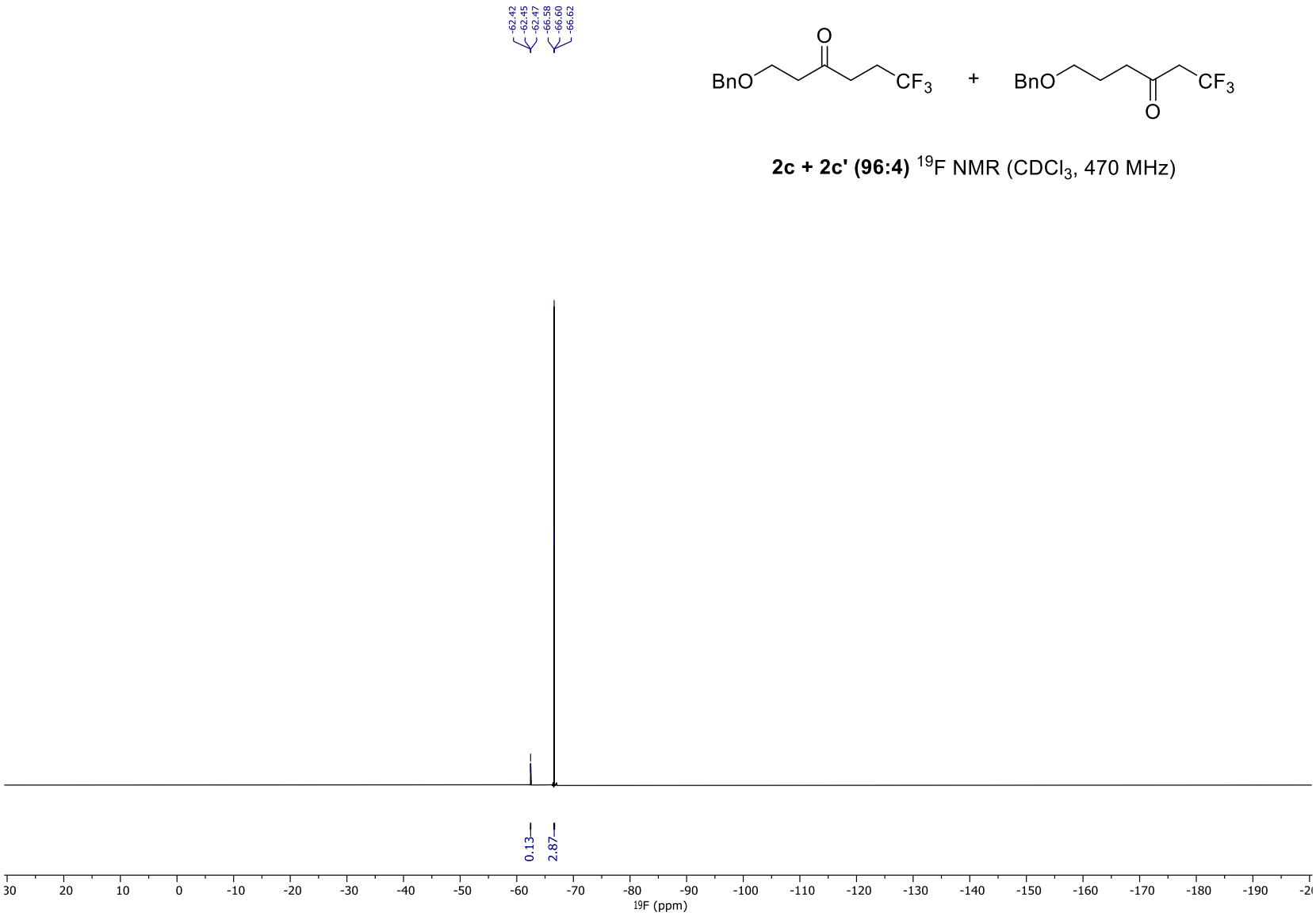
2b ^{19}F NMR ($CDCl_3$, 470 MHz)



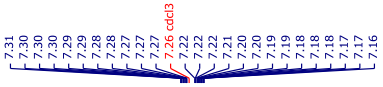


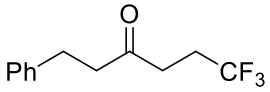
2c + 2c' (96:4) ^{1}H NMR ($CDCl_3$, 500 MHz)



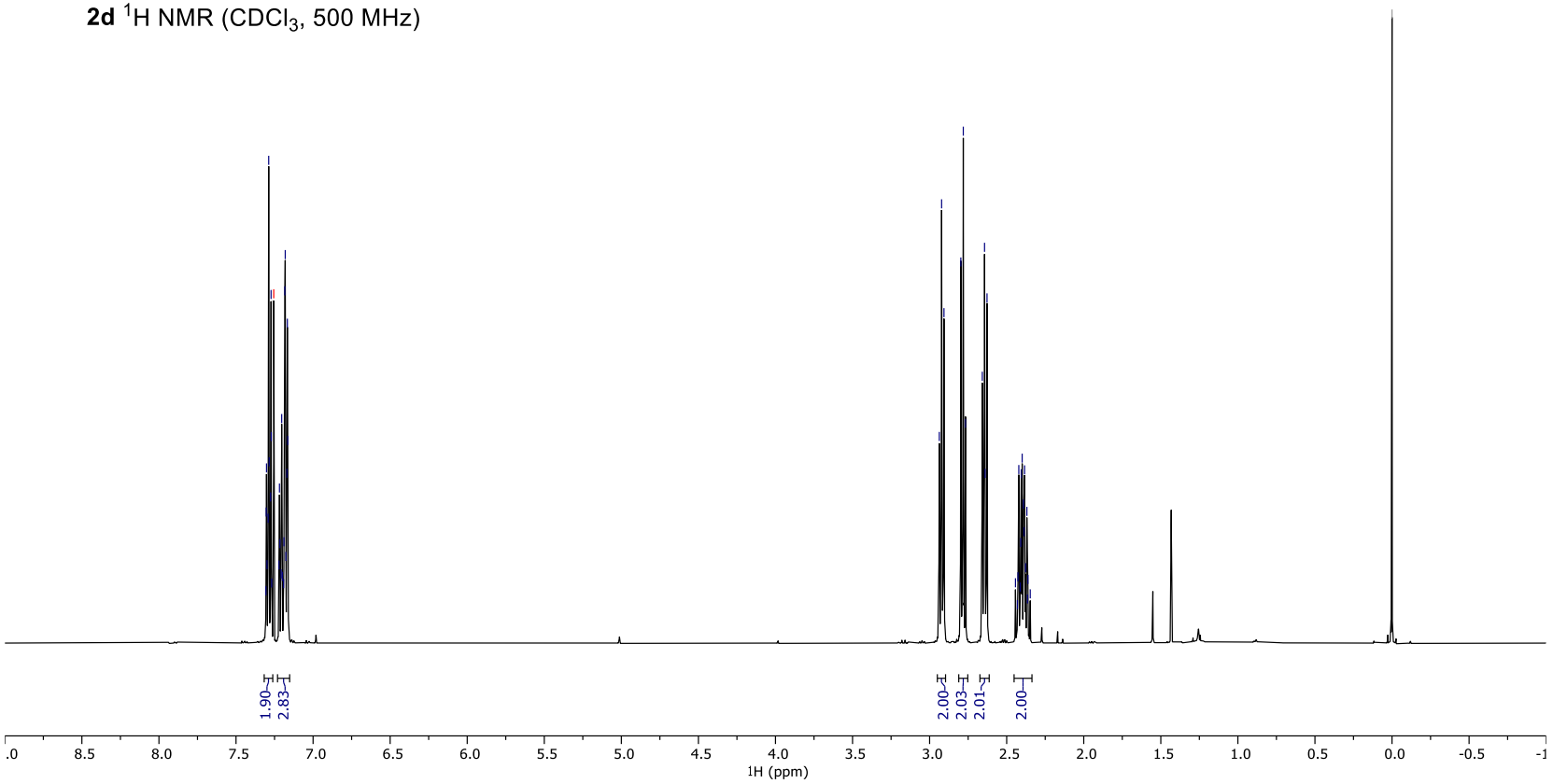


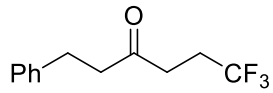
2c + 2c' (96:4) ^{19}F NMR ($CDCl_3$, 470 MHz)



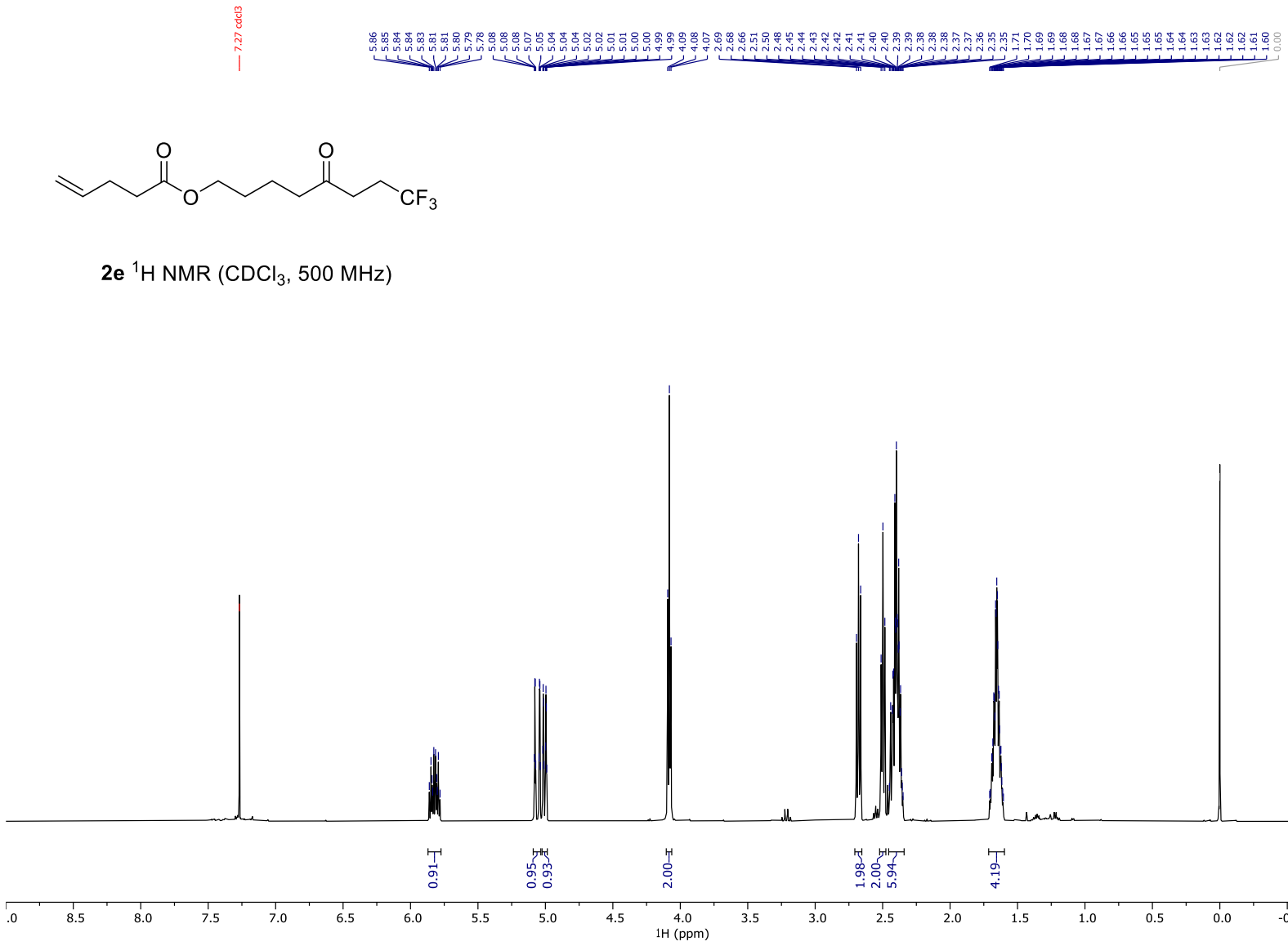


2d ^{1}H NMR ($CDCl_3$, 500 MHz)

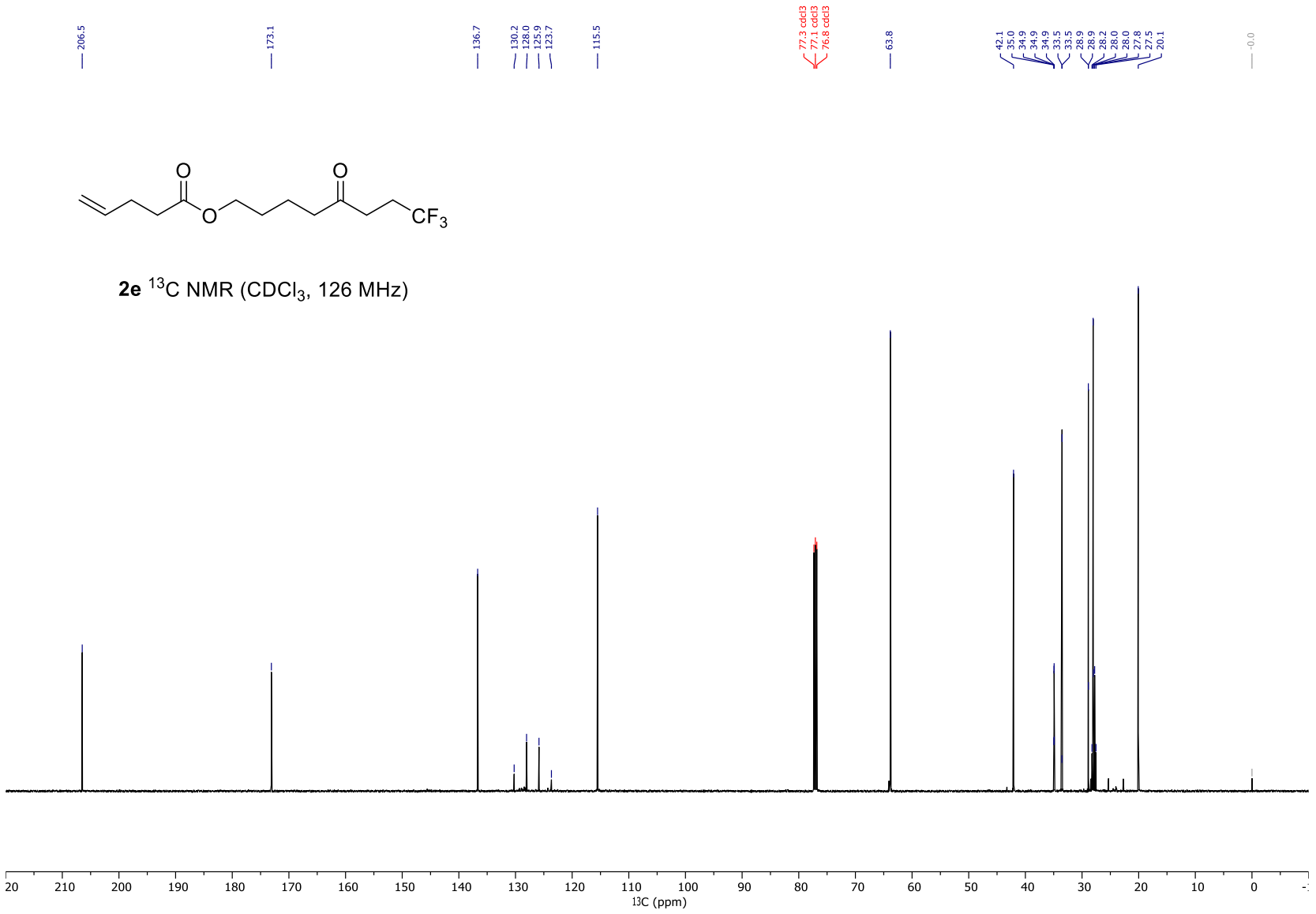


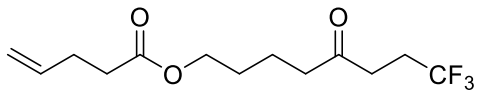


2d ^{19}F NMR ($CDCl_3$, 470 MHz)

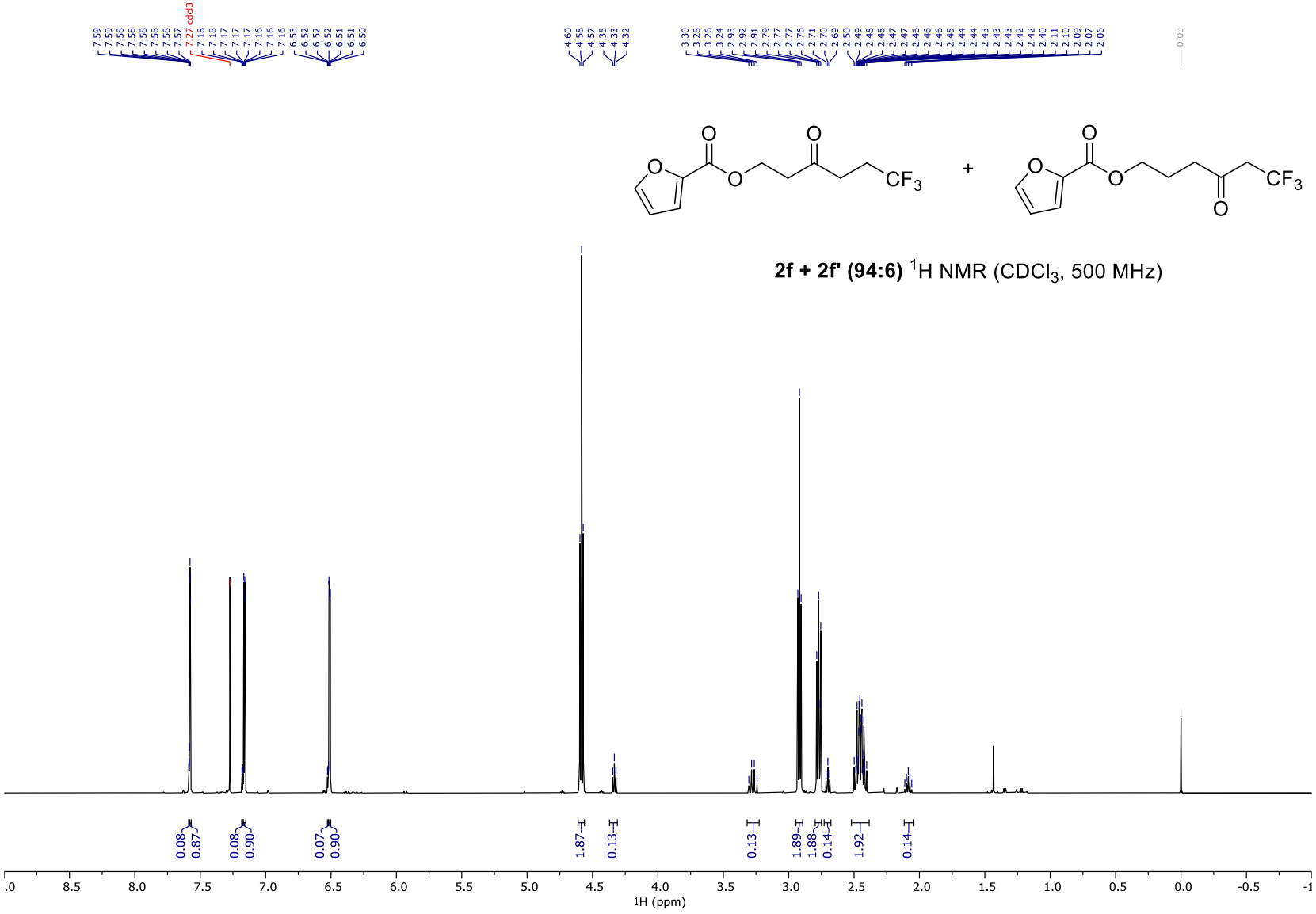


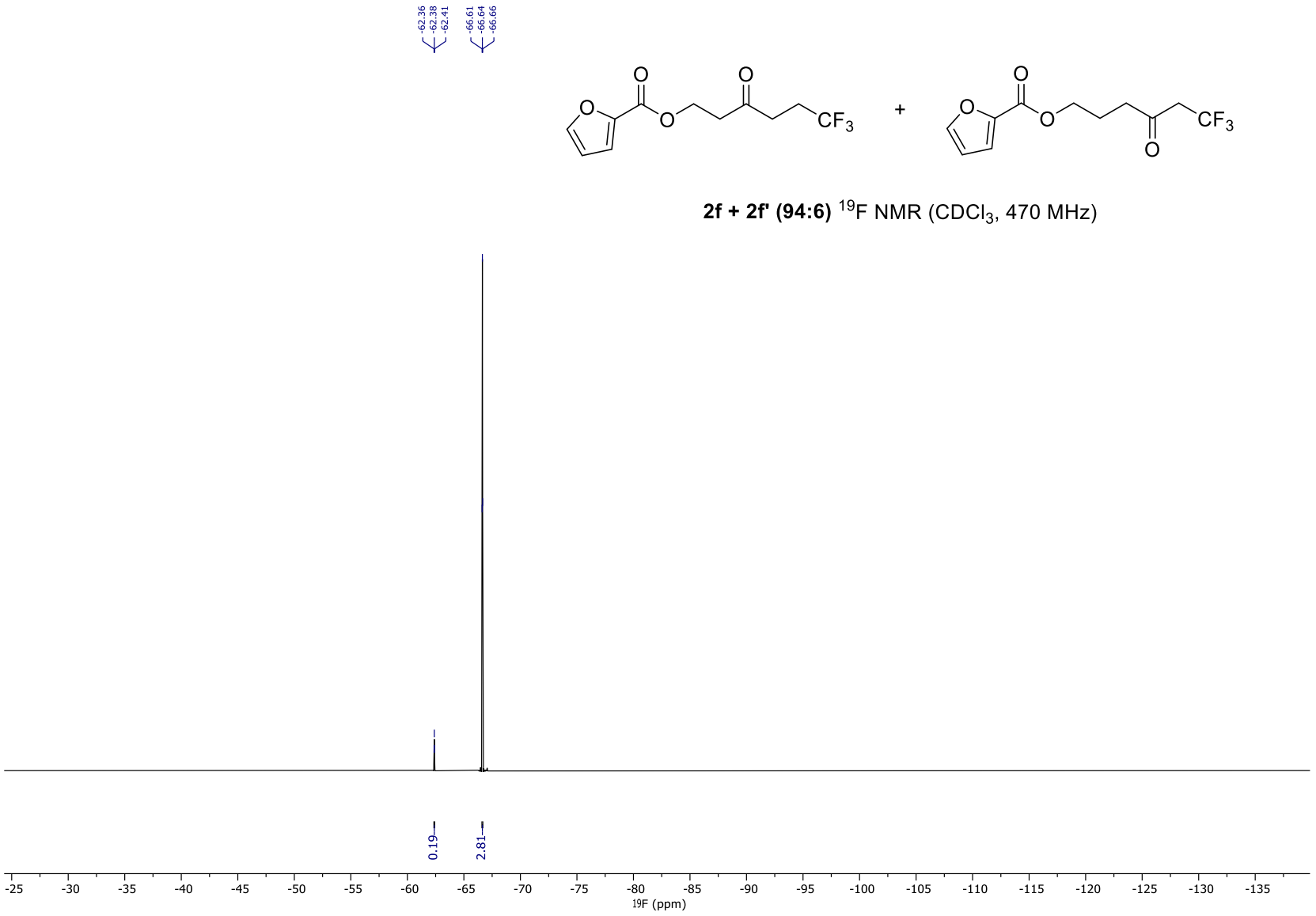
2e ^{1}H NMR ($CDCl_3$, 500 MHz)


206.5
173.1
136.7
130.2
128.0
125.9
123.7
115.5
77.3 cdcl3
77.1 cdcl3
76.8 cdcl3
63.8
42.1
35.0
34.9
34.9
34.9
33.5
33.5
28.9
28.9
28.2
28.0
28.0
27.8
27.5
20.1
-0.0
O
O
O
CF3
2e 13C NMR (CDCl3, 126 MHz)
13C (ppm)

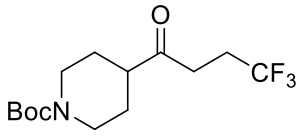


2e ^{19}F NMR ($CDCl_3$, 470 MHz)

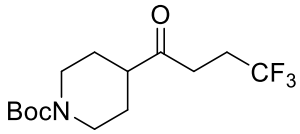

7.59 7.59 7.58 7.58 7.58 7.58 7.58 7.57 7.27 cdcl3 7.18 7.18 7.17 7.17 7.17 7.16 7.16 7.16 6.53 6.52 6.52 6.52 6.51 6.51 6.50
4.60 4.58 4.57 4.35 4.33 4.32
3.30 3.28 3.26 3.24 2.93 2.92 2.91 2.79 2.77 2.77 2.76 2.71 2.70 2.69 2.50 2.49 2.48 2.48 2.47 2.47 2.46 2.46 2.45 2.44 2.44 2.43 2.43 2.42 2.42 2.40 2.11 2.10 2.09 2.07 2.06
0.00
O
O
O
O
CF3
+
O
O
O
O
CF3
2f + 2f' (94:6) 1H NMR (CDCl3, 500 MHz)
0.08 0.87 0.08 0.90 0.07 0.90 1.87 0.13 0.13 1.89 1.88 0.14 1.92 0.14
.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 -1
1H (ppm)



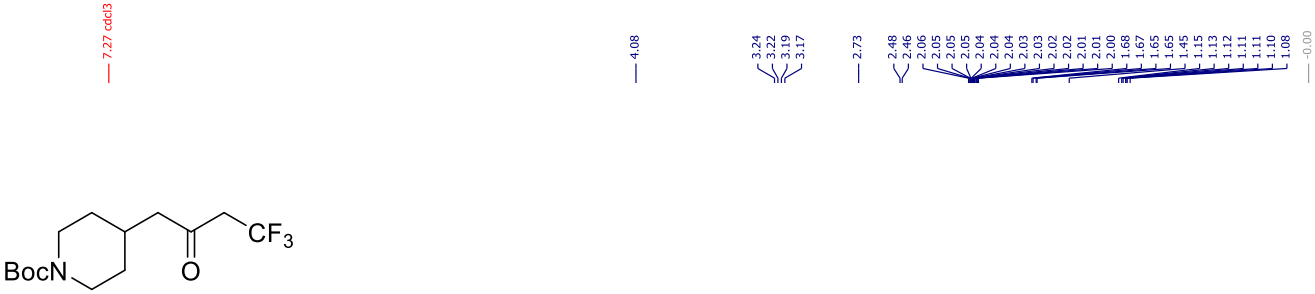
2f + 2f' (94:6) ^{19}F NMR ($CDCl_3$, 470 MHz)



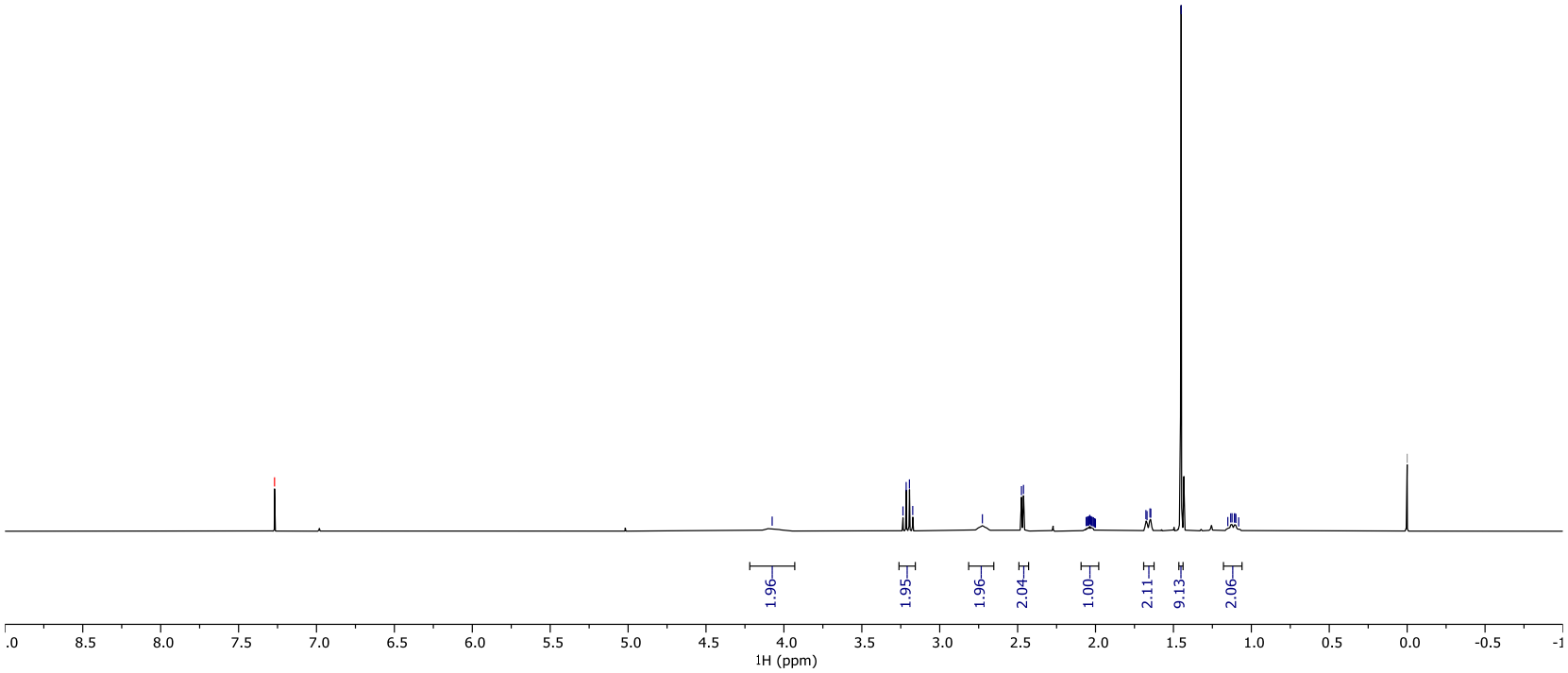
2g ^{1}H NMR ($CDCl_3$, 500 MHz)

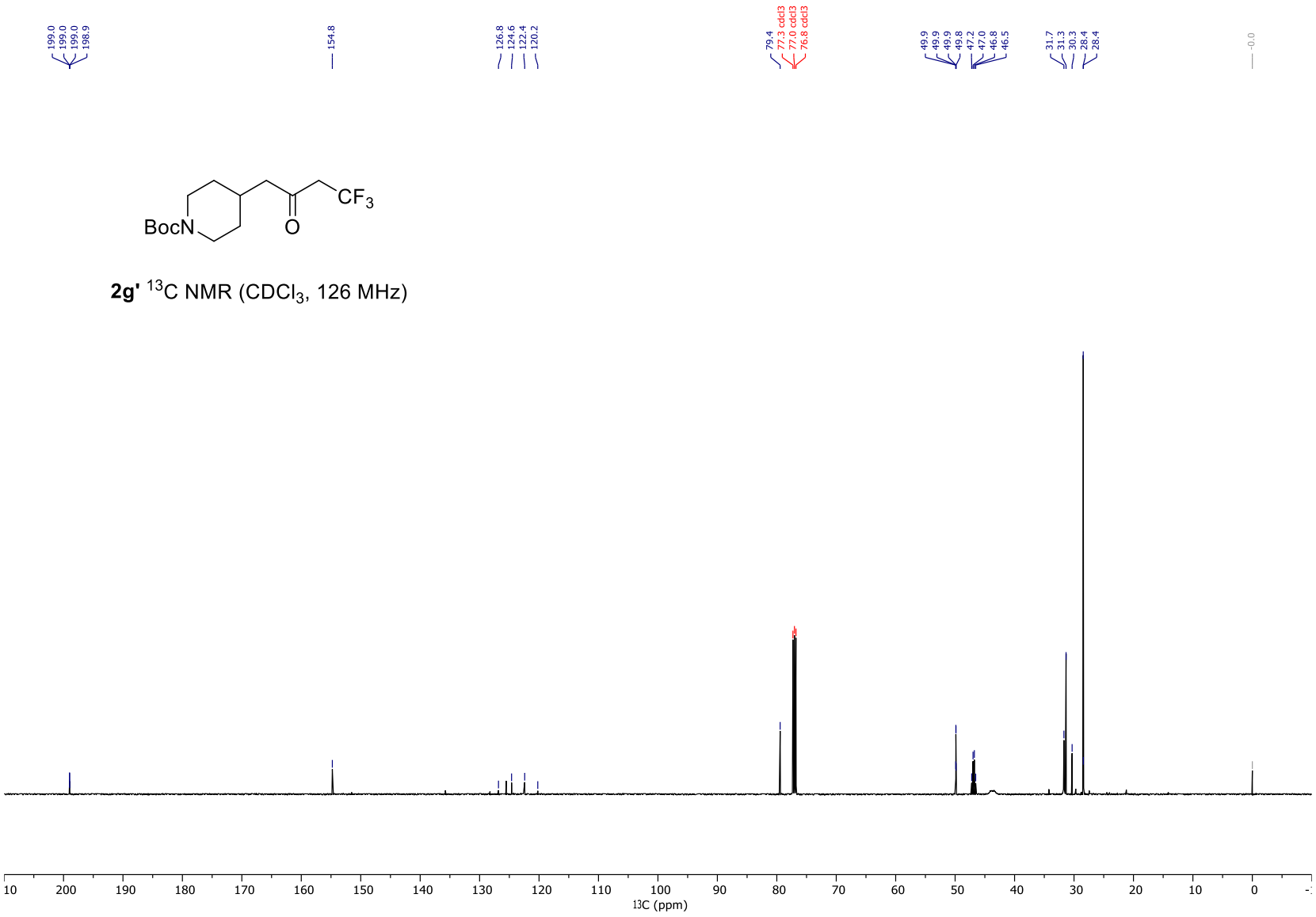


2g ^{19}F NMR ($CDCl_3$, 470 MHz)

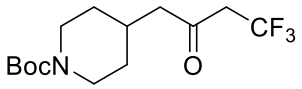


2g' ^{1}H NMR ($CDCl_3$, 500 MHz)

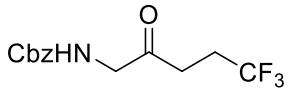




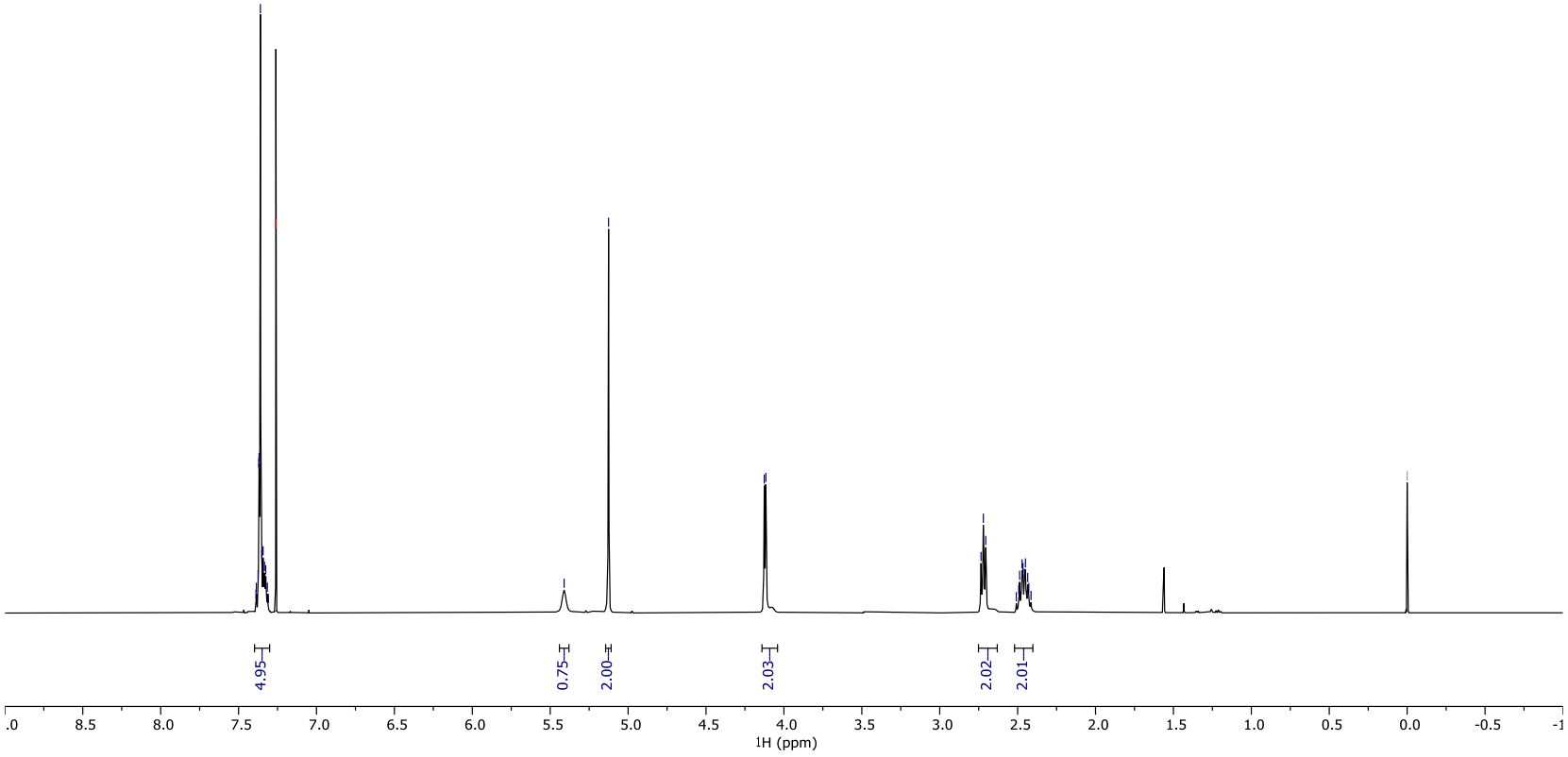
2g' ^{13}C NMR ($CDCl_3$, 126 MHz)

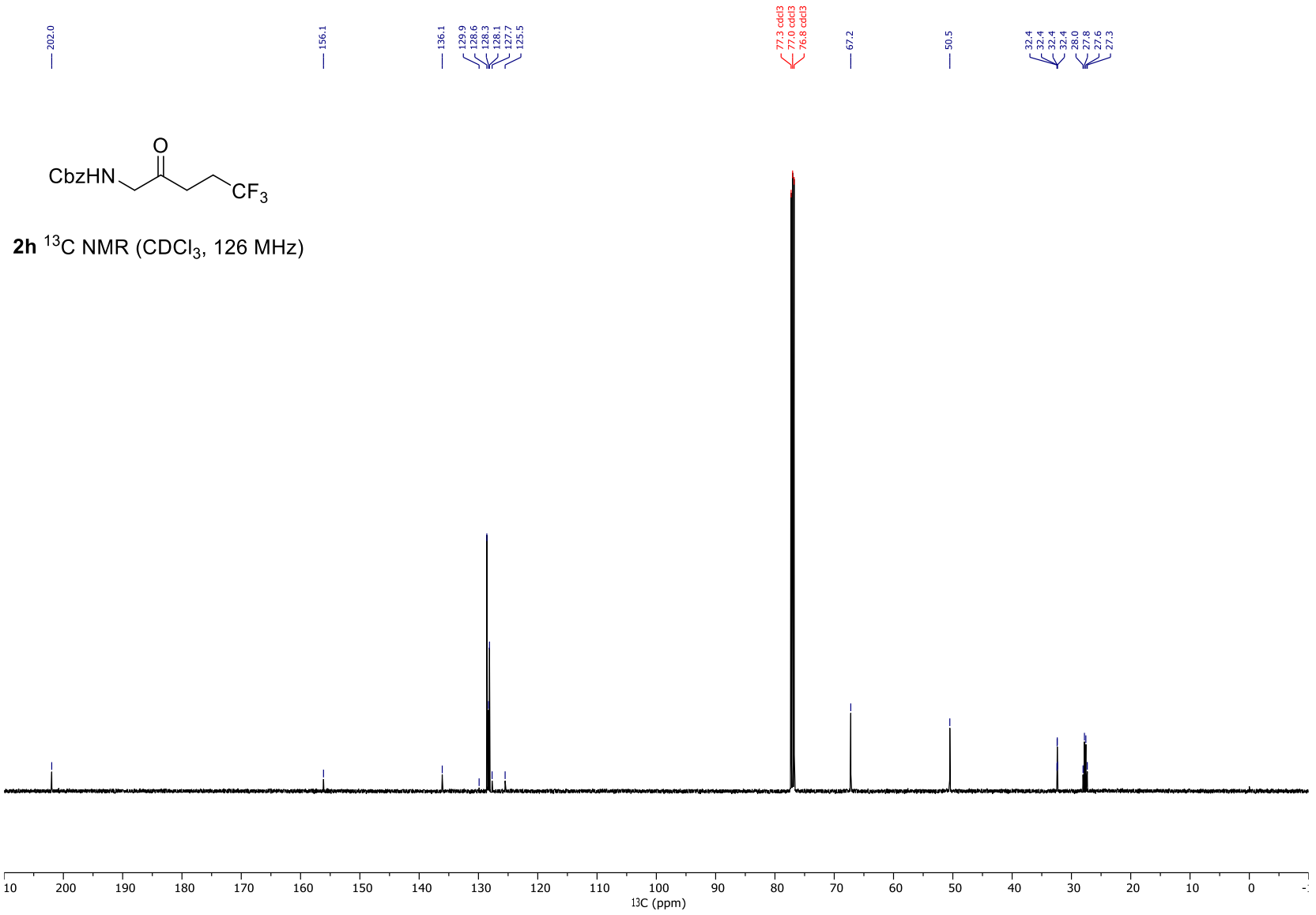


2g' ^{19}F NMR ($CDCl_3$, 470 MHz)

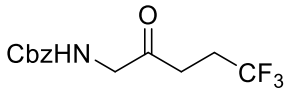


2h ^{1}H NMR ($CDCl_3$, 500 MHz)

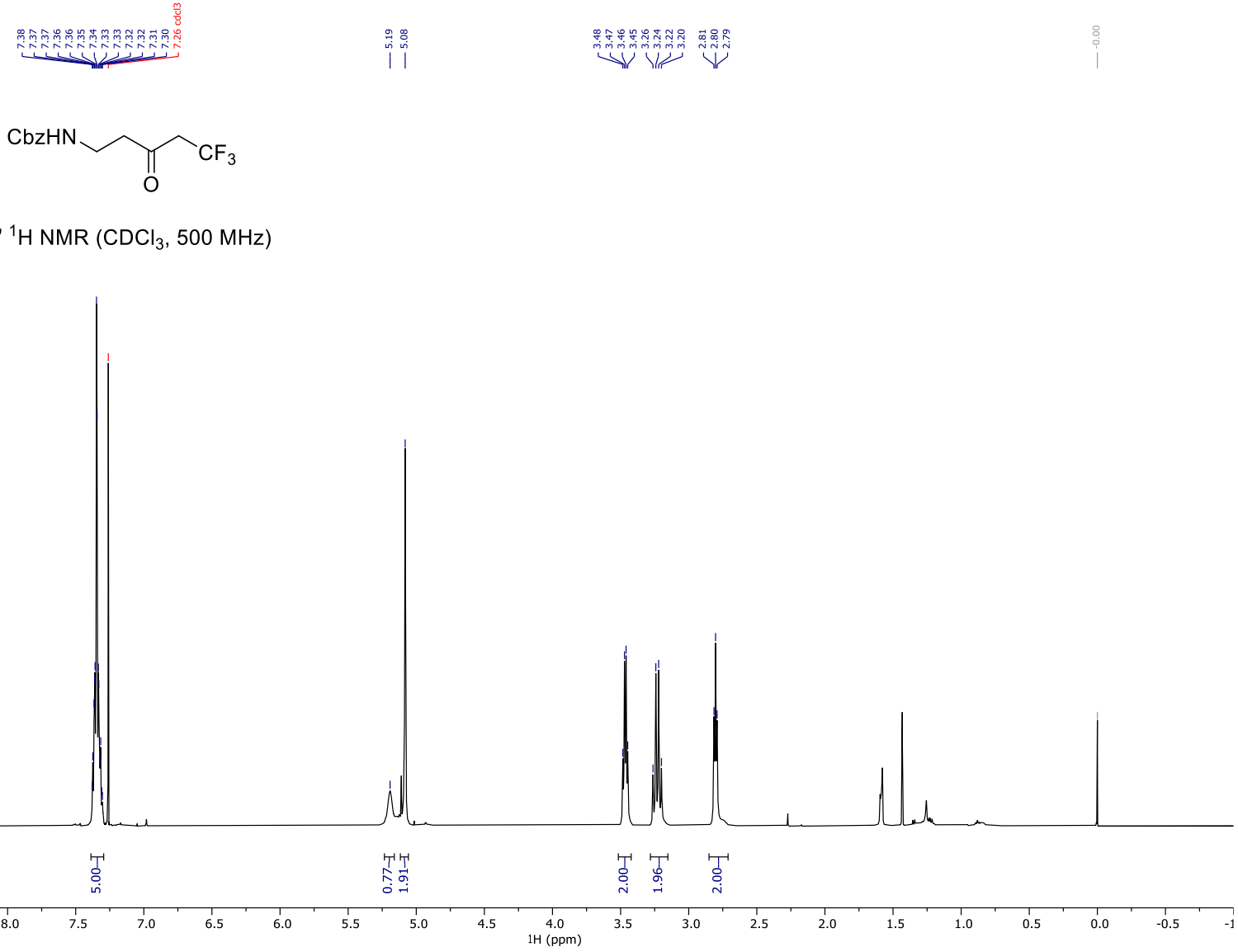




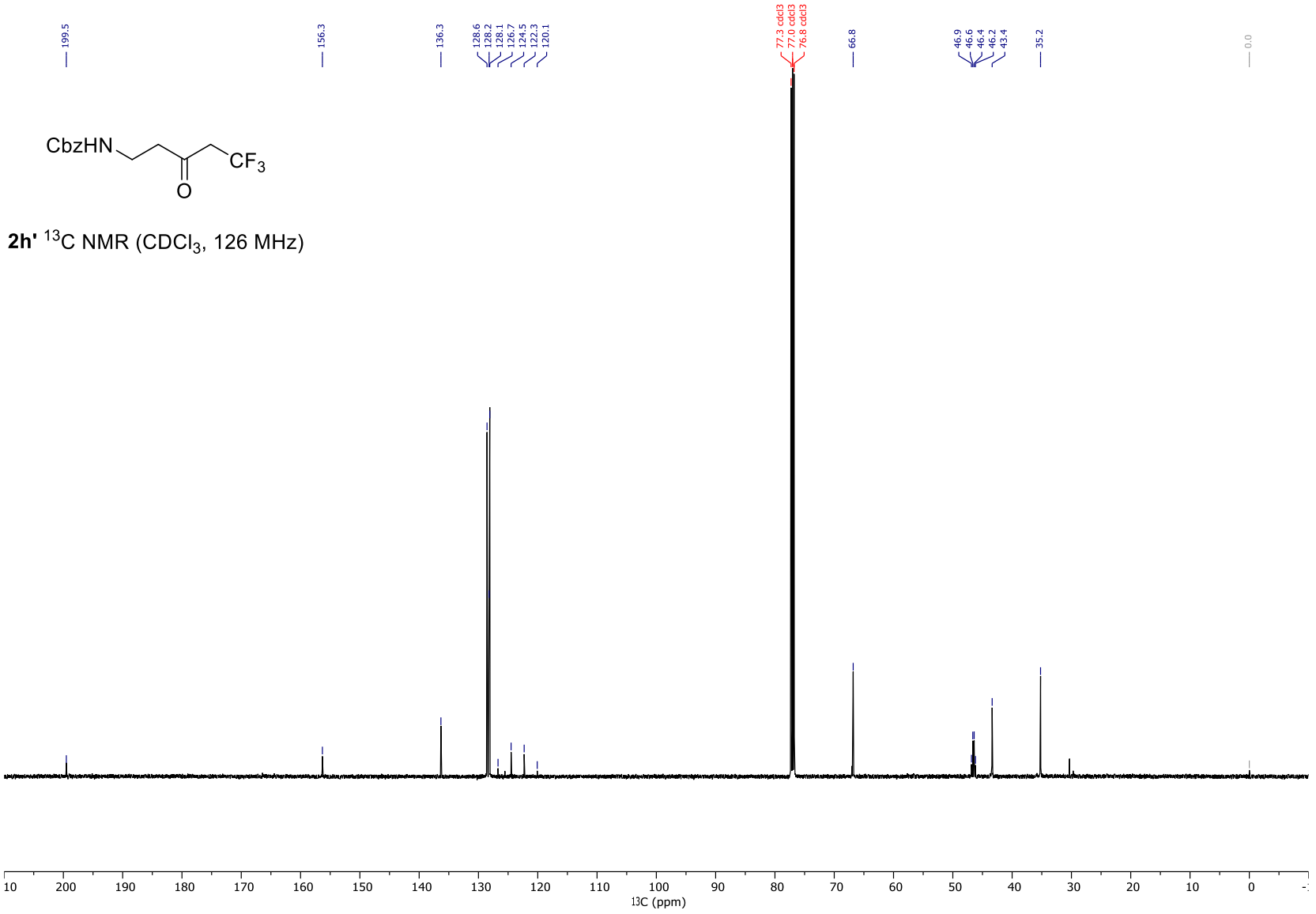
2h ^{13}C NMR ($CDCl_3$, 126 MHz)



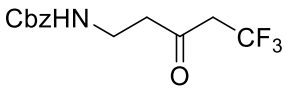
2h ^{19}F NMR ($CDCl_3$, 470 MHz)



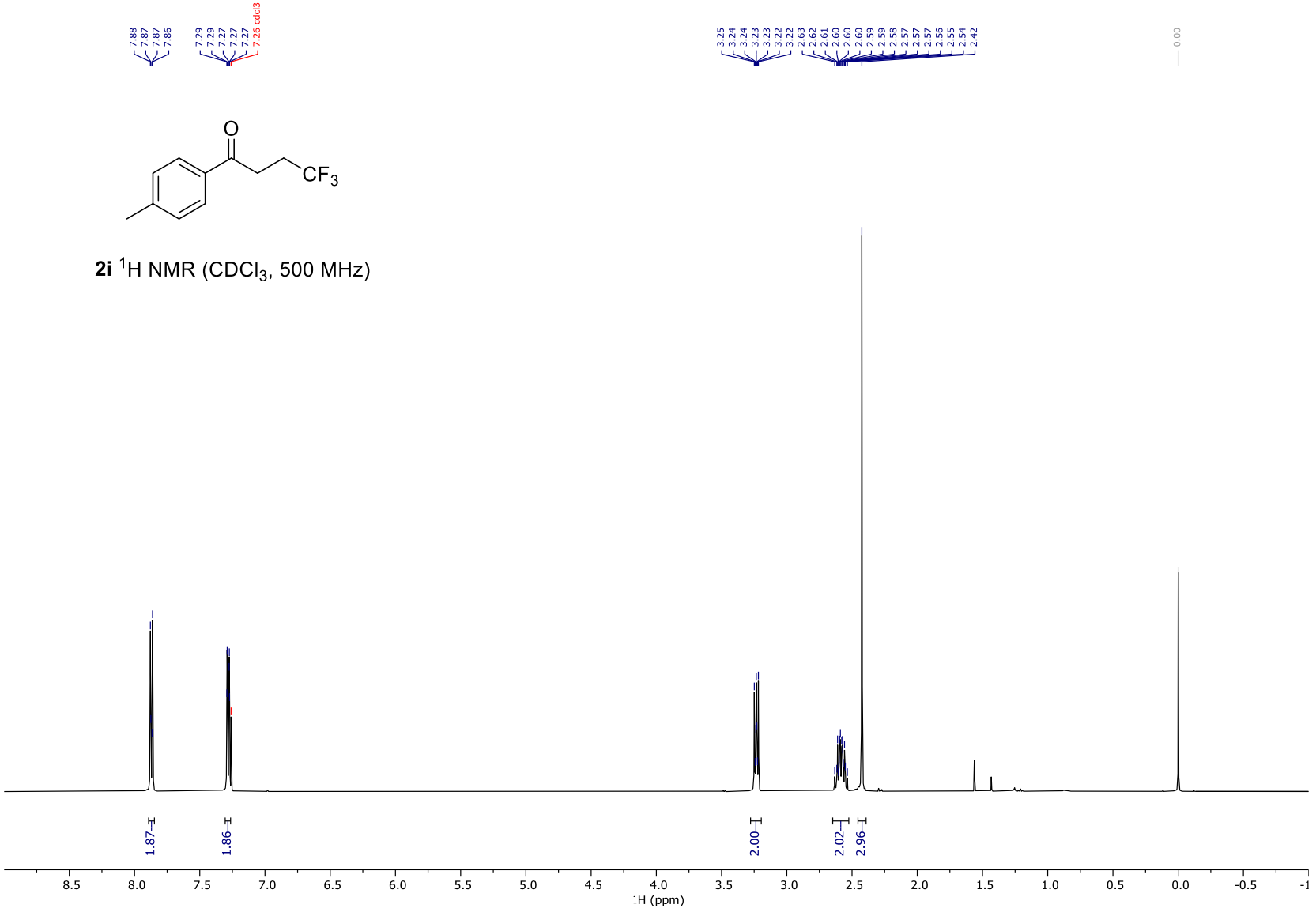
2h' ^{1}H NMR ($CDCl_3$, 500 MHz)

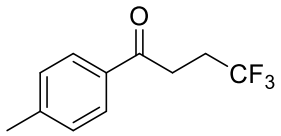


2h' ^{13}C NMR ($CDCl_3$, 126 MHz)

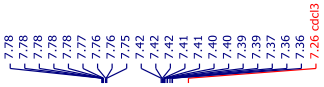


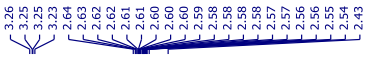
2h' ^{19}F NMR ($CDCl_3$, 470 MHz)

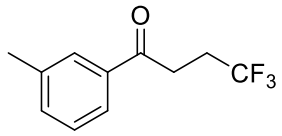

7.88
7.87
7.87
7.86
7.29
7.29
7.27
7.27
7.27
7.26 cdcl3
3.25
3.24
3.24
3.23
3.23
3.22
3.22
2.63
2.62
2.61
2.60
2.60
2.60
2.59
2.59
2.58
2.57
2.57
2.57
2.56
2.55
2.54
2.42
0.00
O
CF3
2i 1H NMR (CDCl3, 500 MHz)
1.87
1.86
2.00
2.02
2.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1H (ppm)



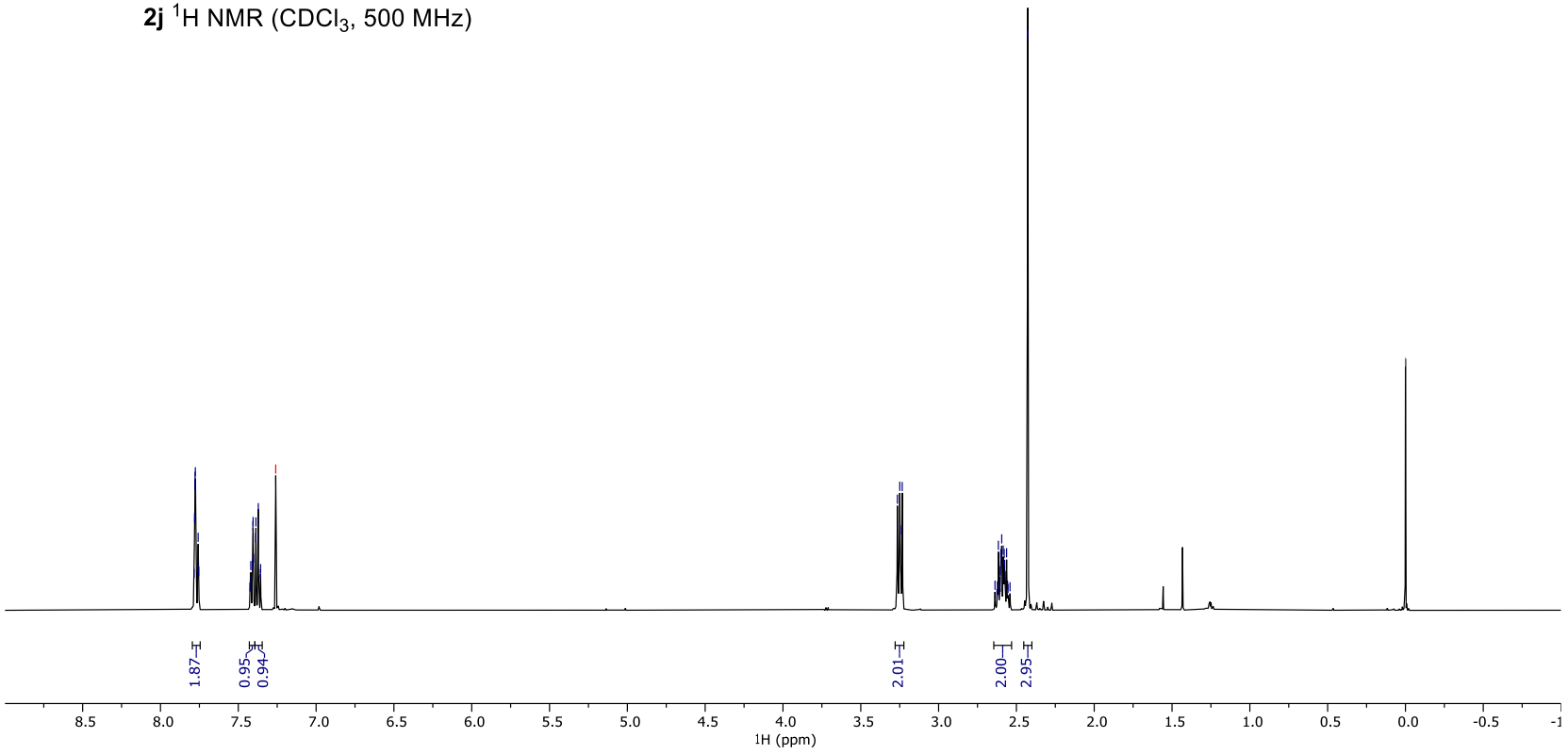
2i ^{19}F NMR ($CDCl_3$, 470 MHz)

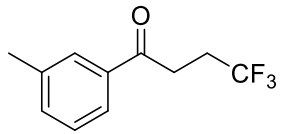




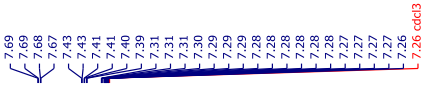


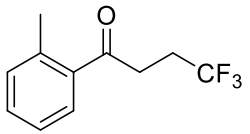
2j ^{1}H NMR ($CDCl_3$, 500 MHz)



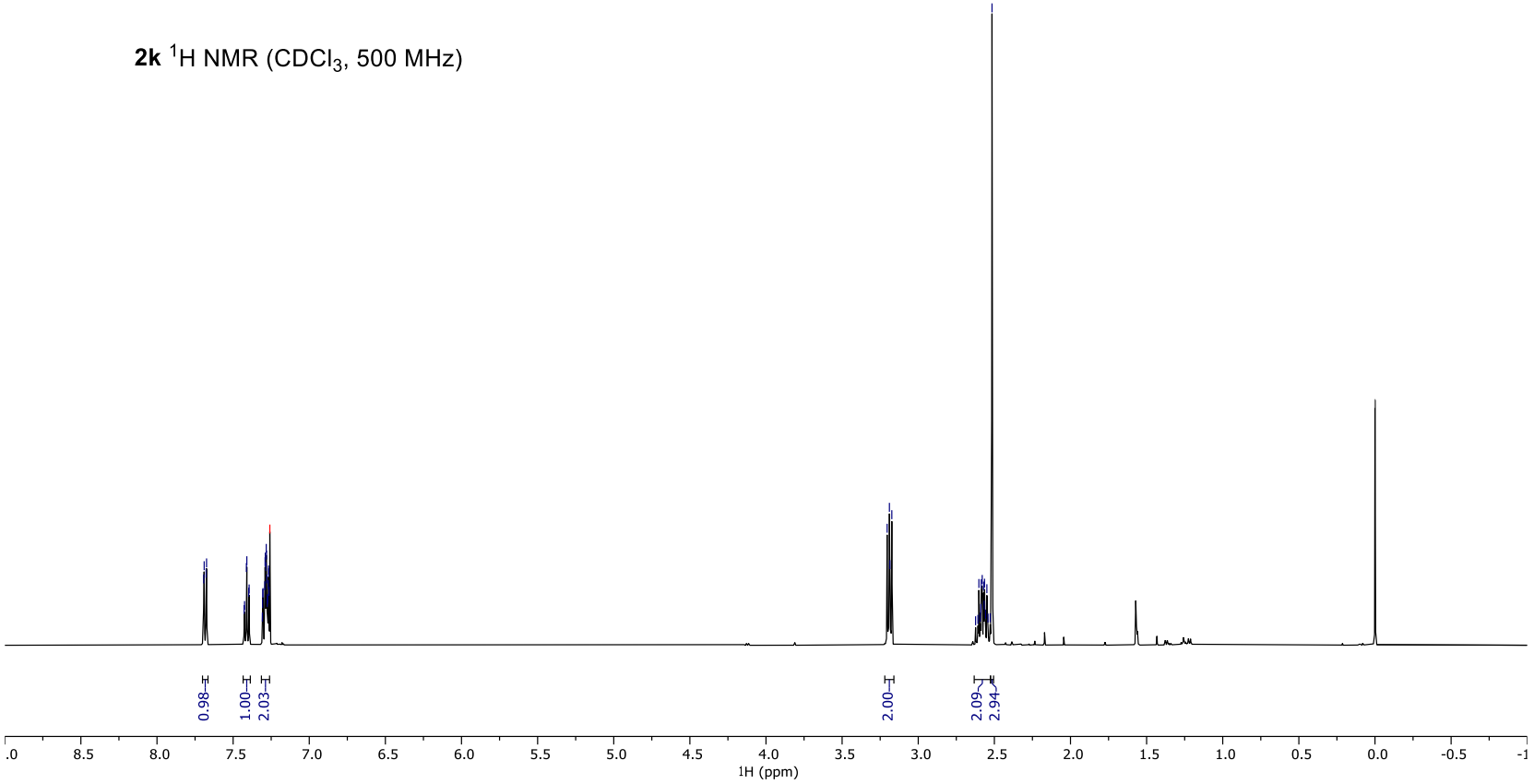


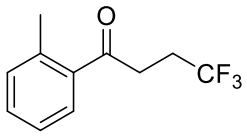
2j ^{19}F NMR ($CDCl_3$, 470 MHz)



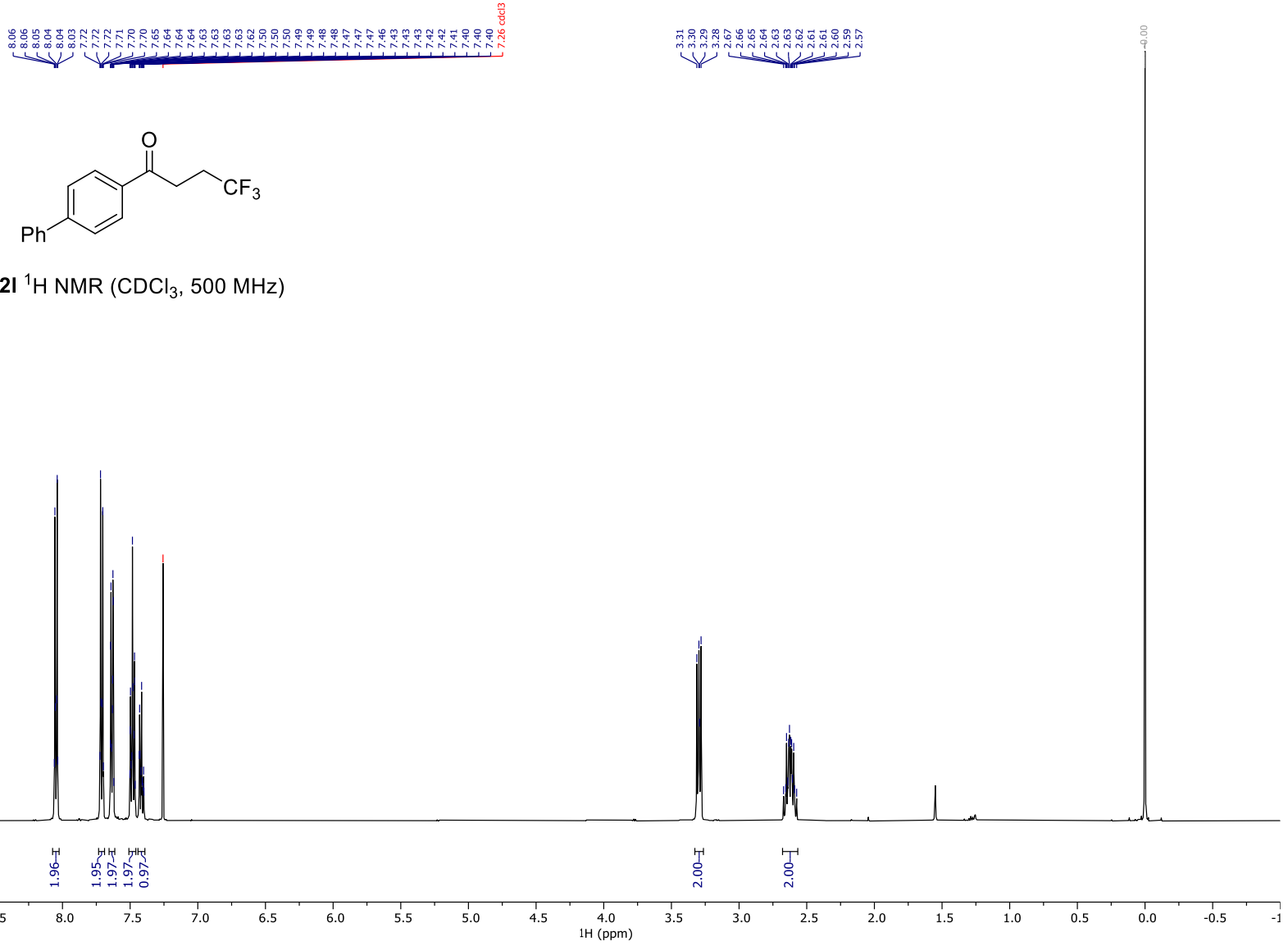


2k ^{1}H NMR ($CDCl_3$, 500 MHz)

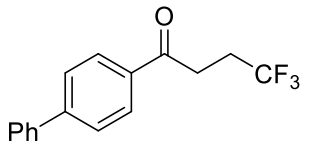




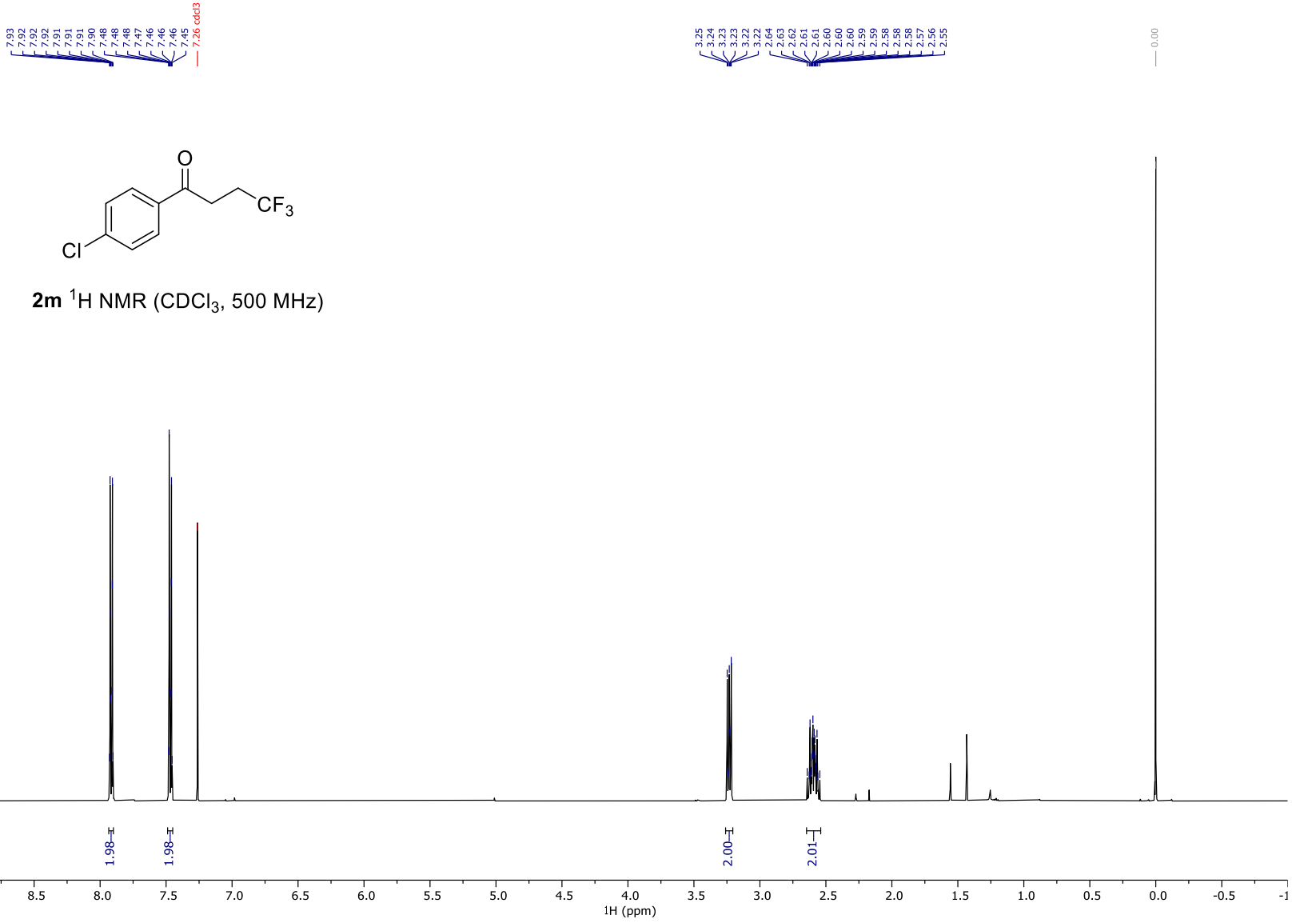
2k ^{19}F NMR ($CDCl_3$, 470 MHz)



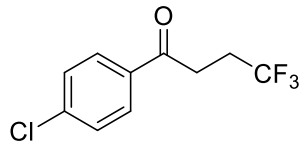
2l ^{1}H NMR ($CDCl_3$, 500 MHz)



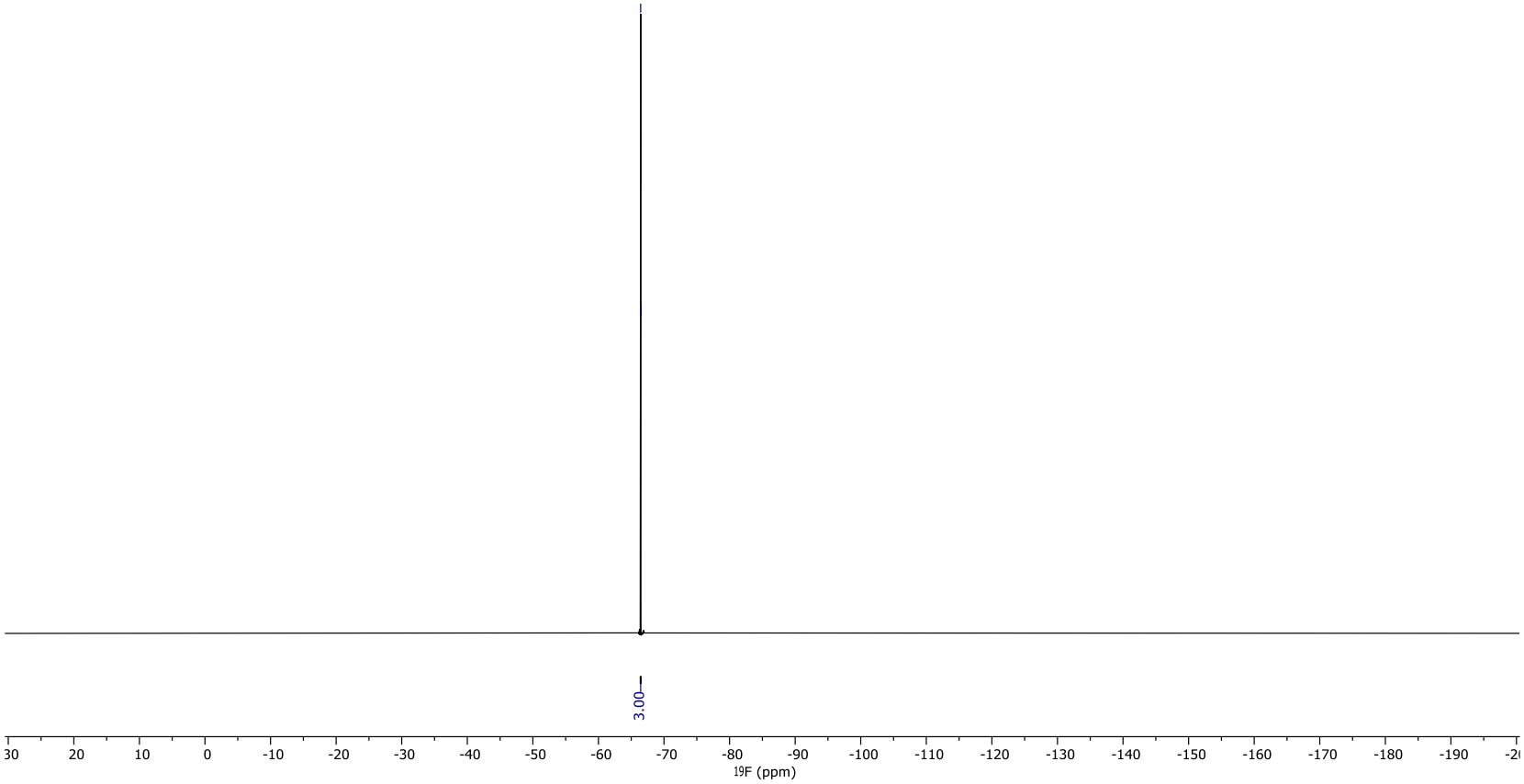
2l ^{19}F NMR ($CDCl_3$, 470 MHz)

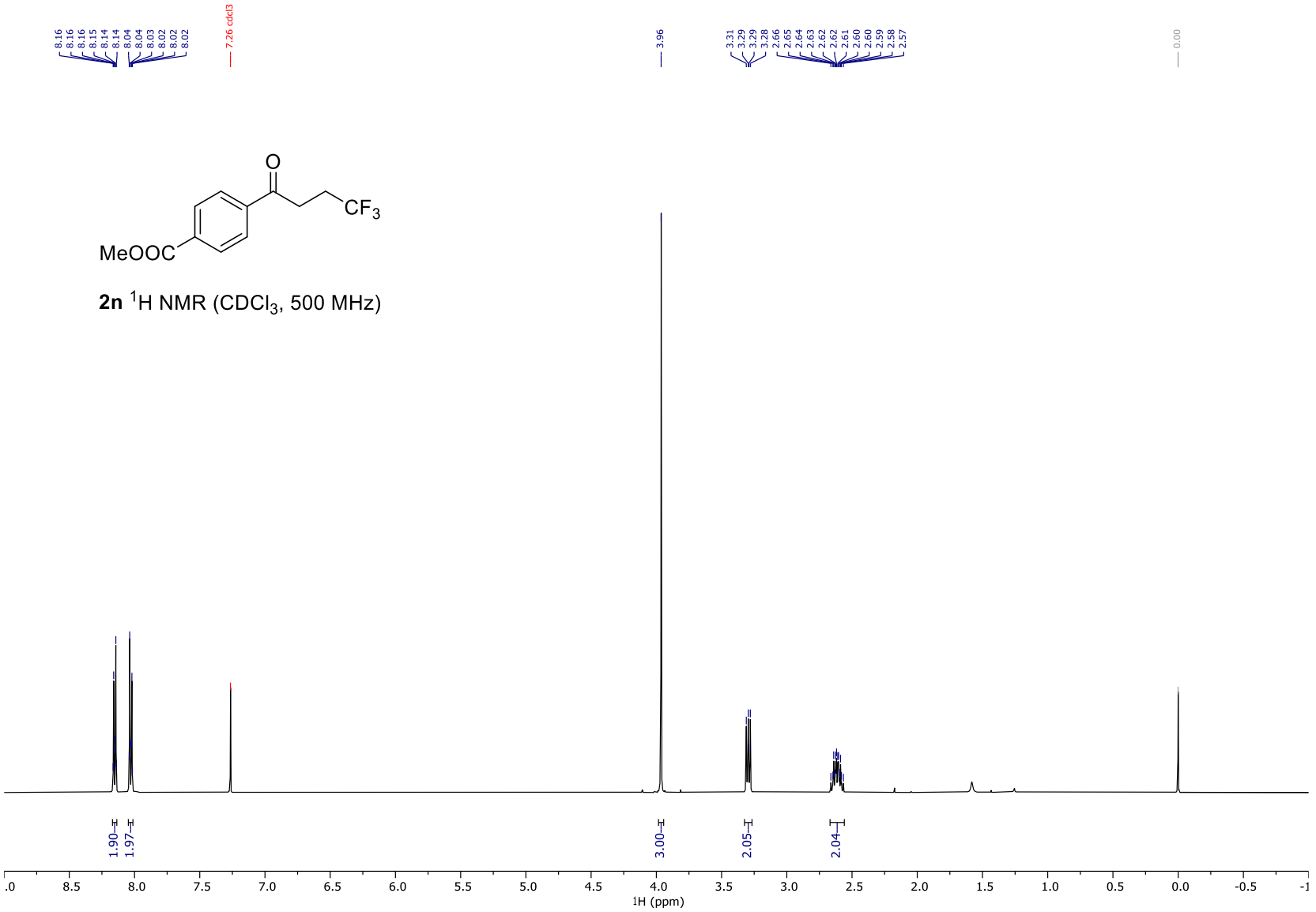


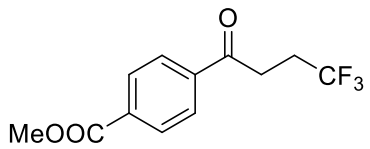
2m ^{1}H NMR ($CDCl_3$, 500 MHz)



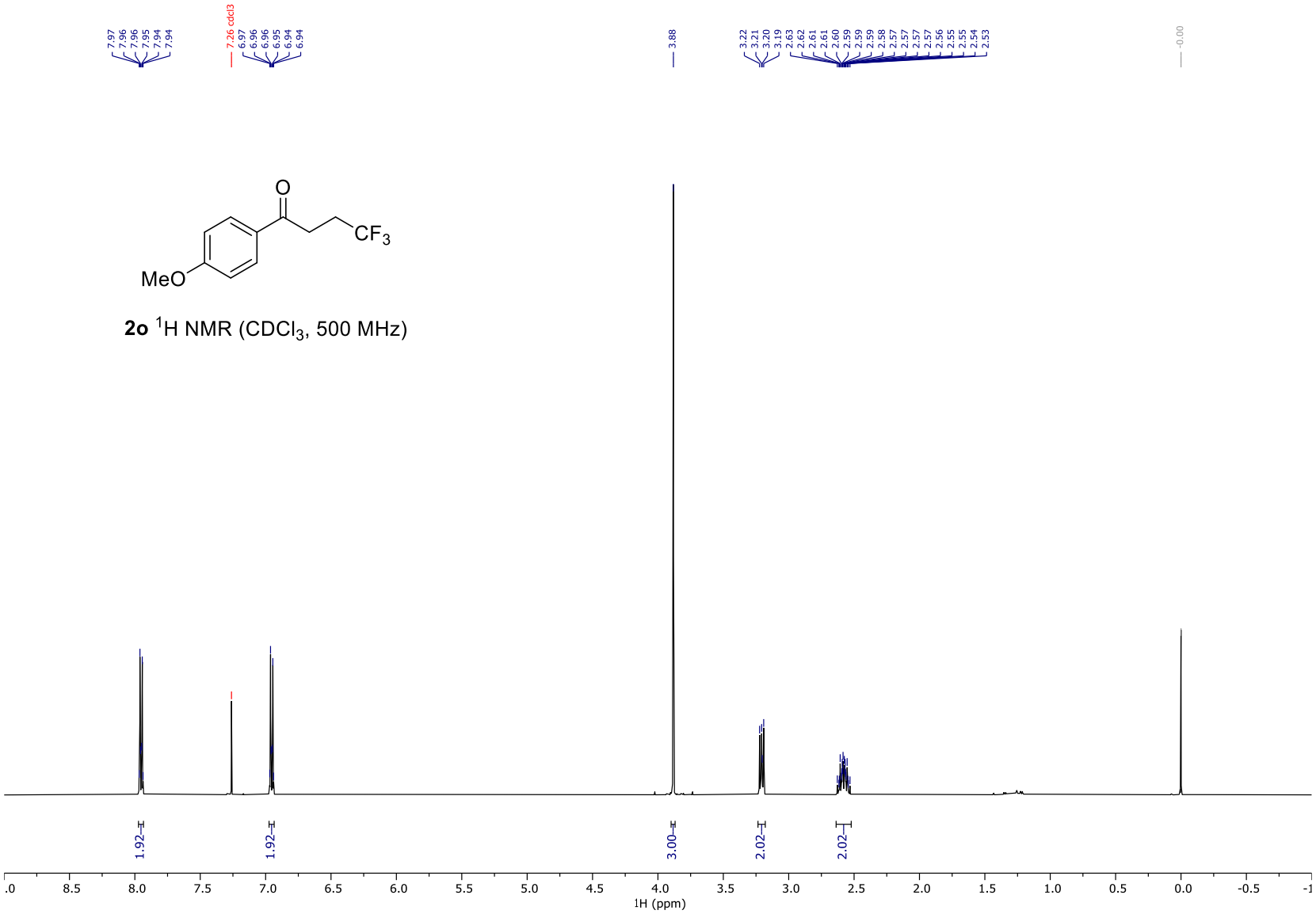
2m ^{19}F NMR ($CDCl_3$, 470 MHz)



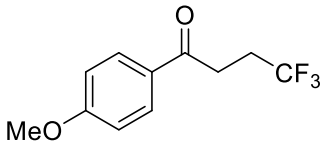

8.16
8.16
8.16
8.15
8.14
8.14
8.04
8.04
8.03
8.02
8.02
8.02
7.26 cdcl3
3.96
3.31
3.29
3.29
3.28
2.66
2.65
2.64
2.63
2.62
2.62
2.61
2.60
2.60
2.59
2.58
2.57
0.00
O
CF3
MeOOC
2n 1H NMR (CDCl3, 500 MHz)
1.90
1.97
3.00
2.05
2.04
1H (ppm)



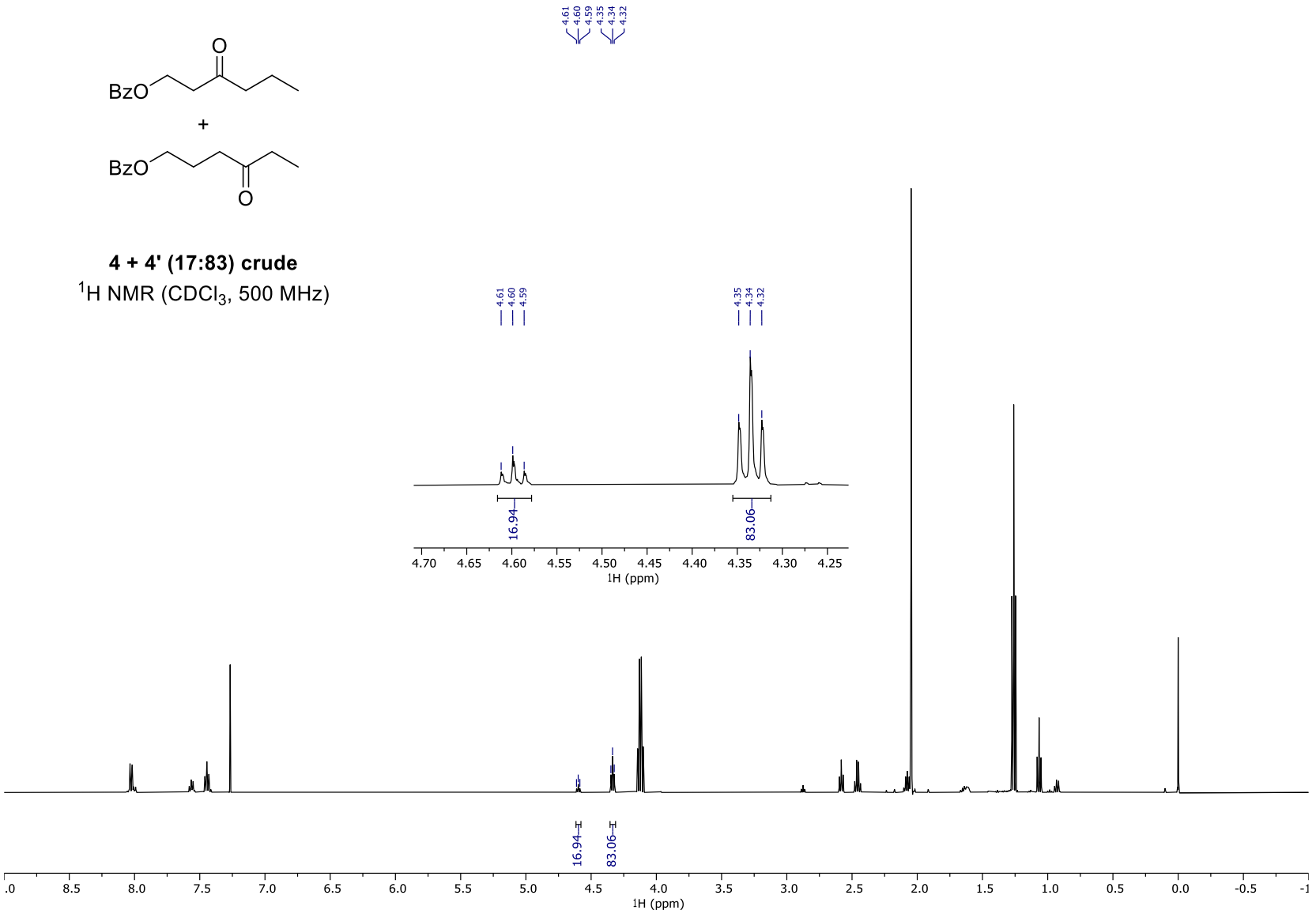
2n ^{19}F NMR ($CDCl_3$, 470 MHz)



2o ^{1}H NMR ($CDCl_3$, 500 MHz)

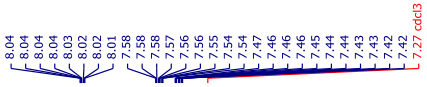


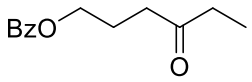
2o ^{19}F NMR ($CDCl_3$, 470 MHz)



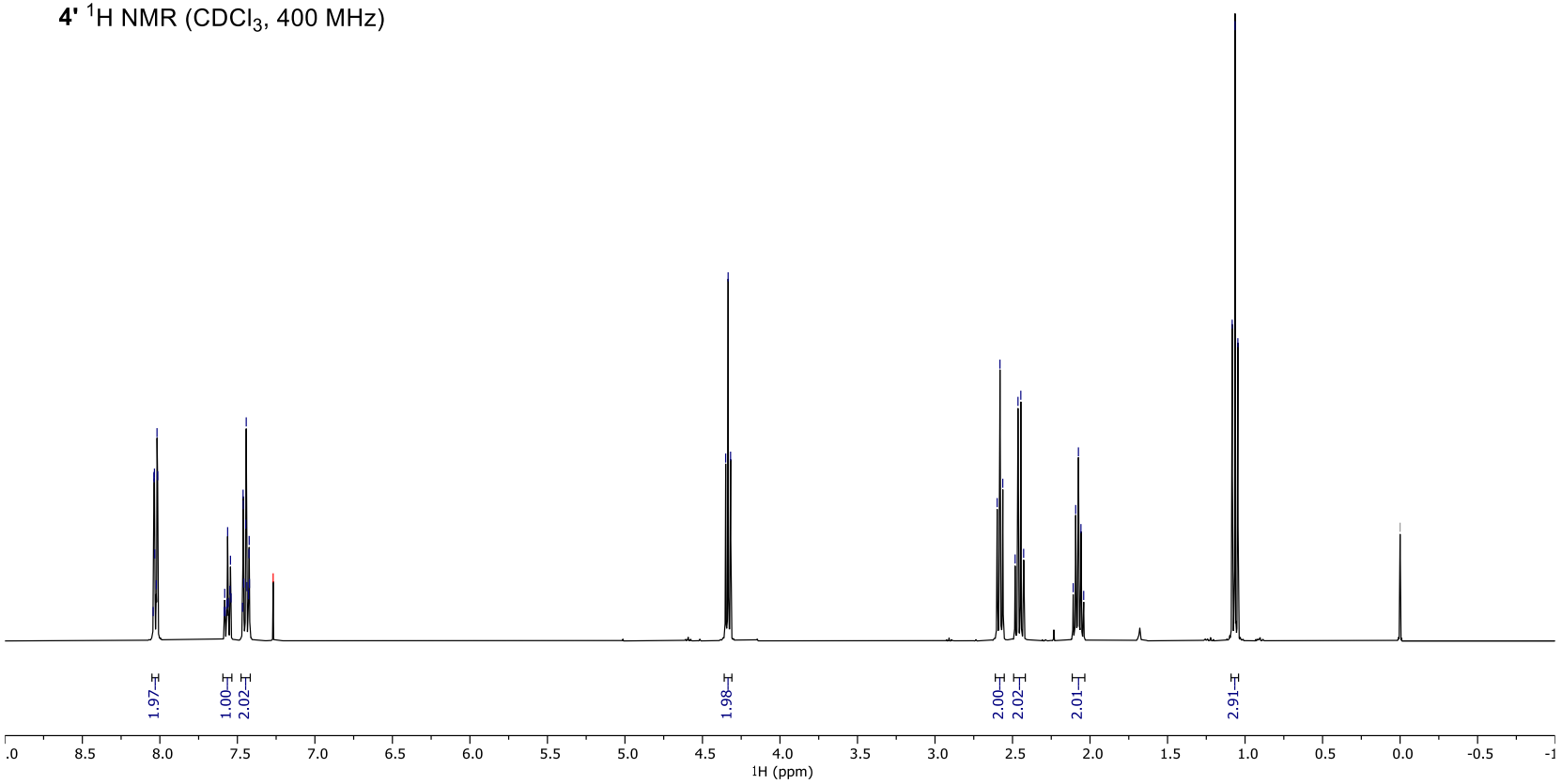
4 + 4' (17:83) crude

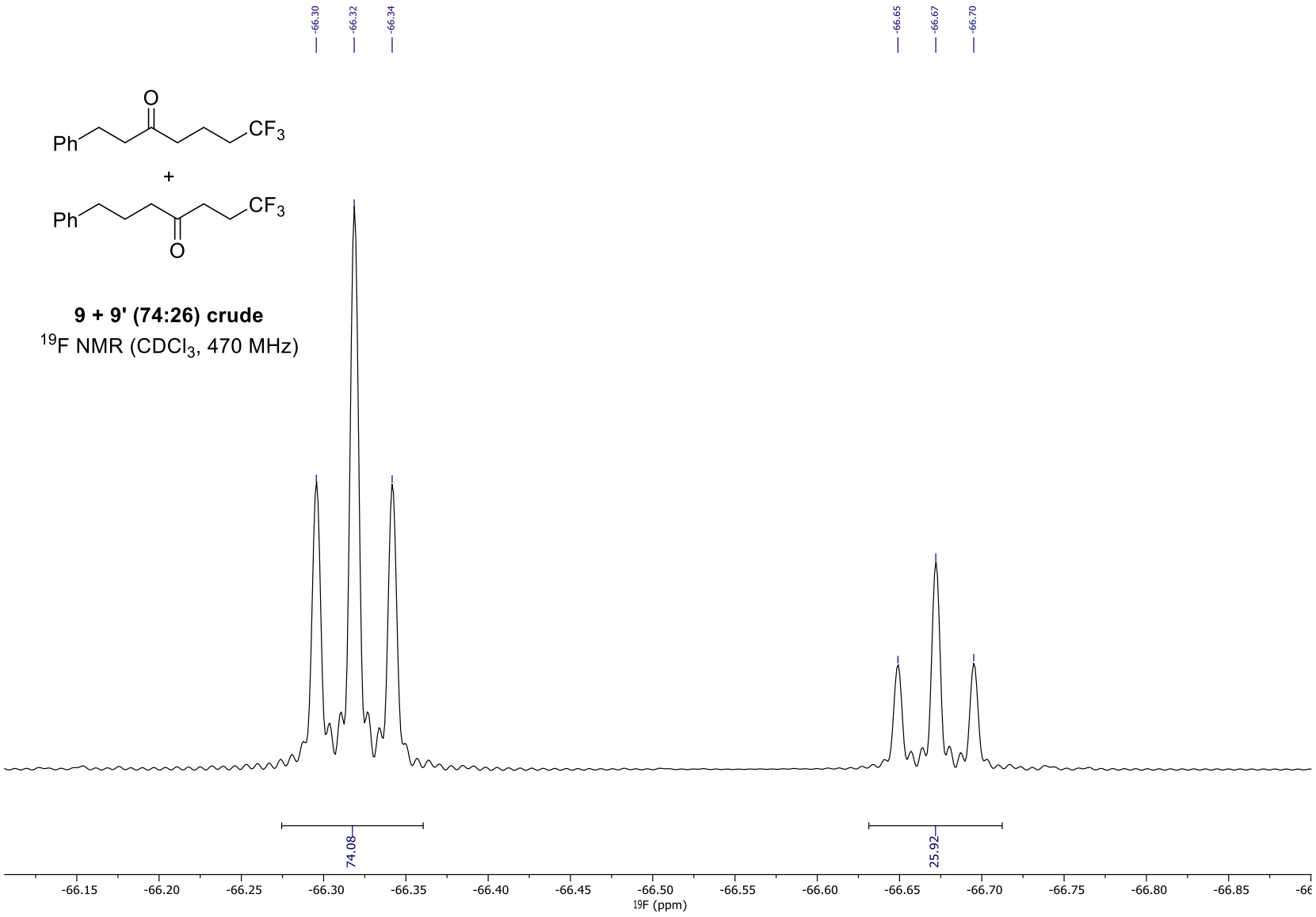
^{1}H NMR ($CDCl_3$, 500 MHz)

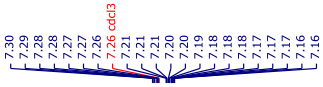


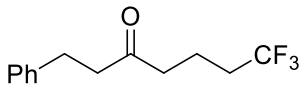


4' ^{1}H NMR ($CDCl_3$, 400 MHz)

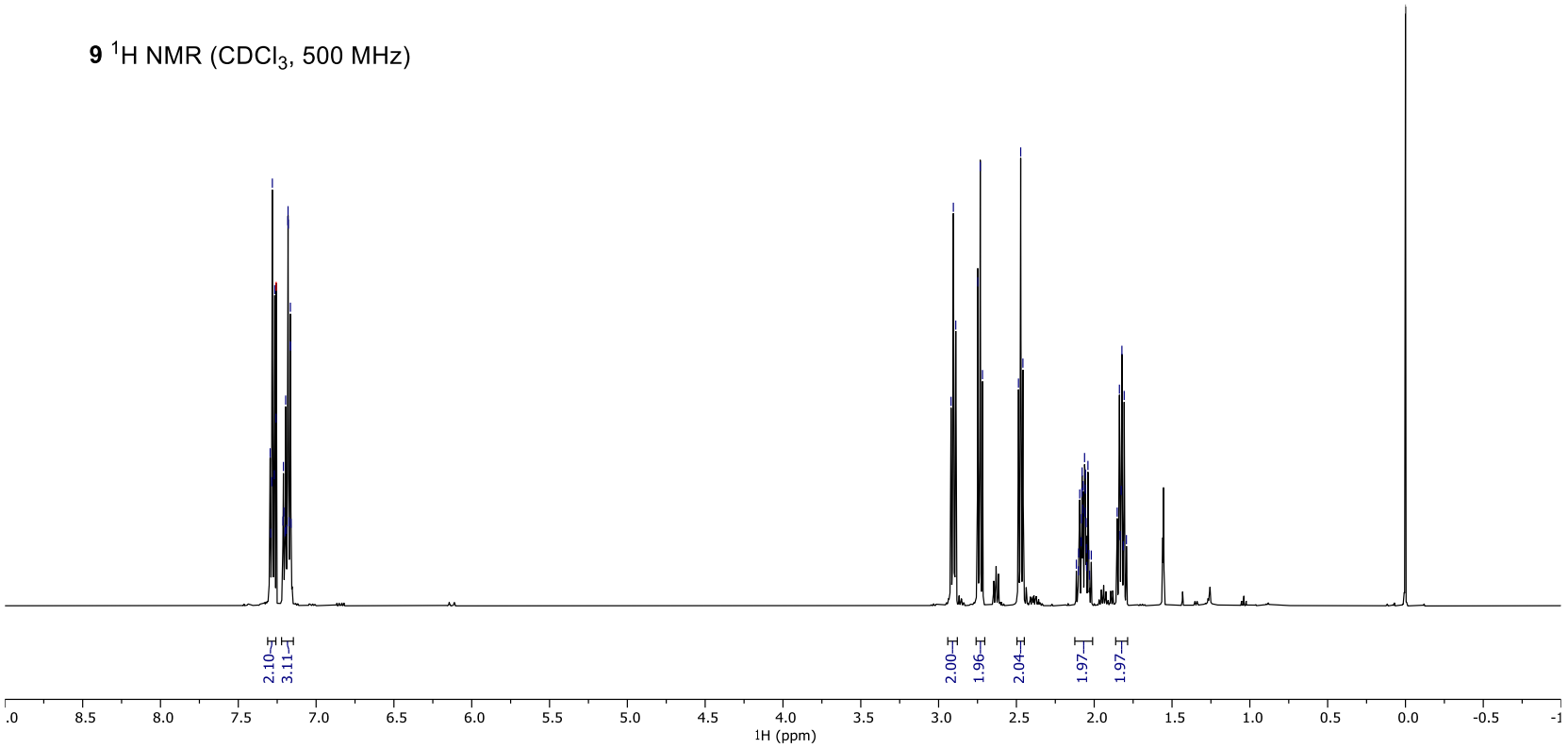


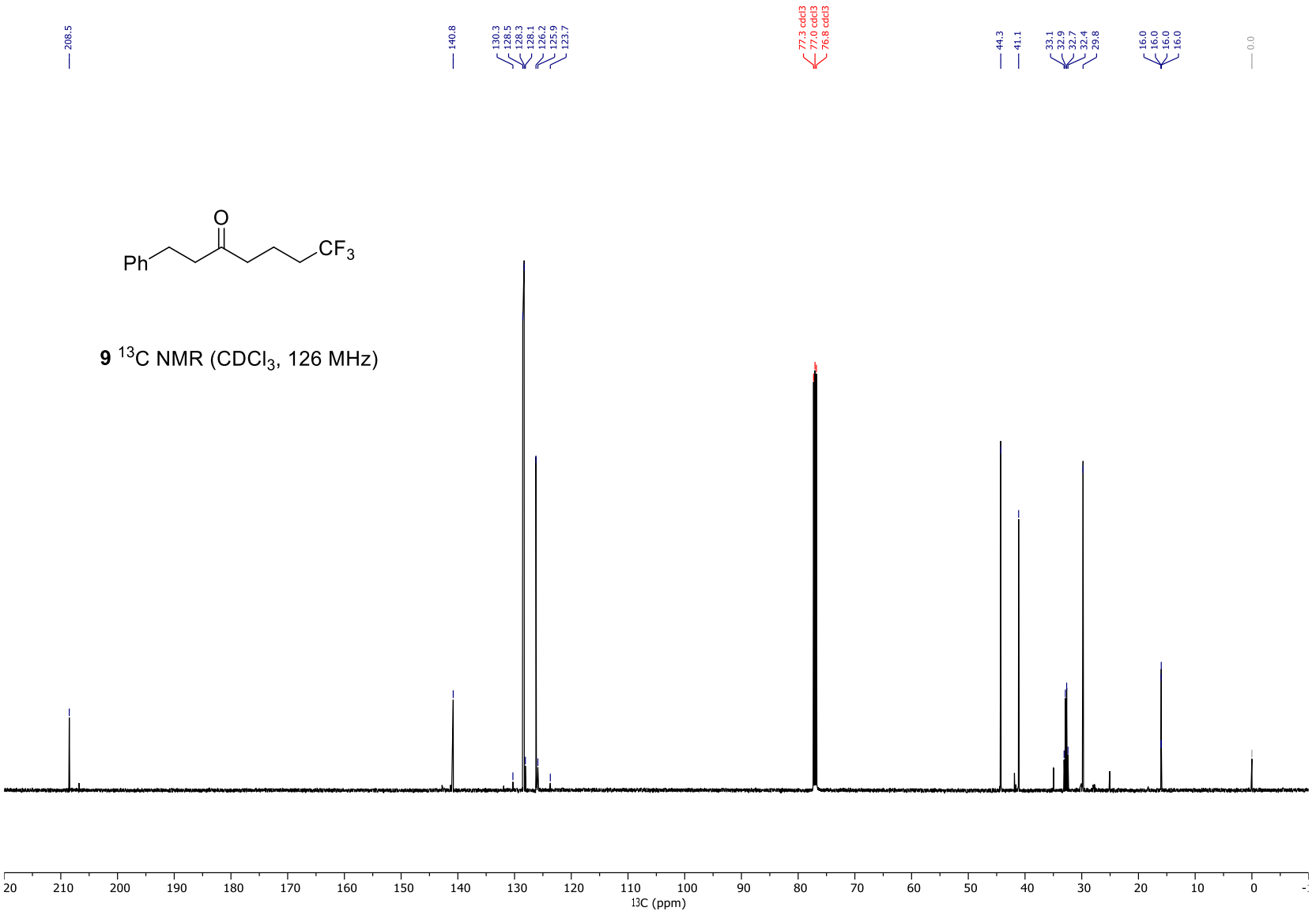

-66.30
-66.32
-66.34
-66.65
-66.67
-66.70
O
Ph
CF3
+
Ph
CF3
O
9 + 9' (74:26) crude
19F NMR (CDCl3, 470 MHz)
74.08
25.92
-66.15
-66.20
-66.25
-66.30
-66.35
-66.40
-66.45
-66.50
-66.55
-66.60
-66.65
-66.70
-66.75
-66.80
-66.85
19F (ppm)

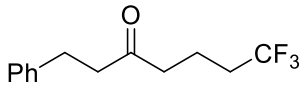




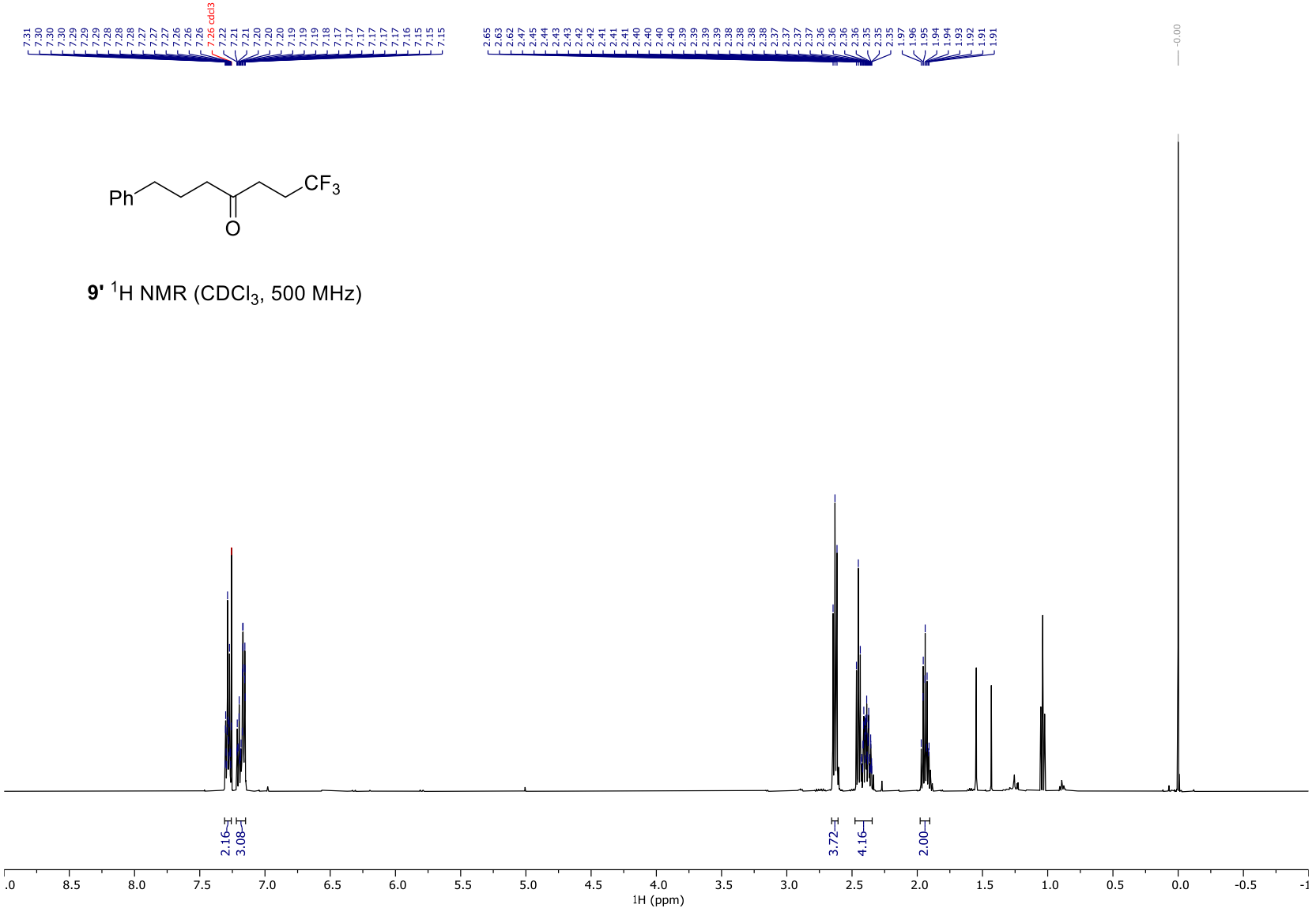
9 ^{1}H NMR ($CDCl_3$, 500 MHz)



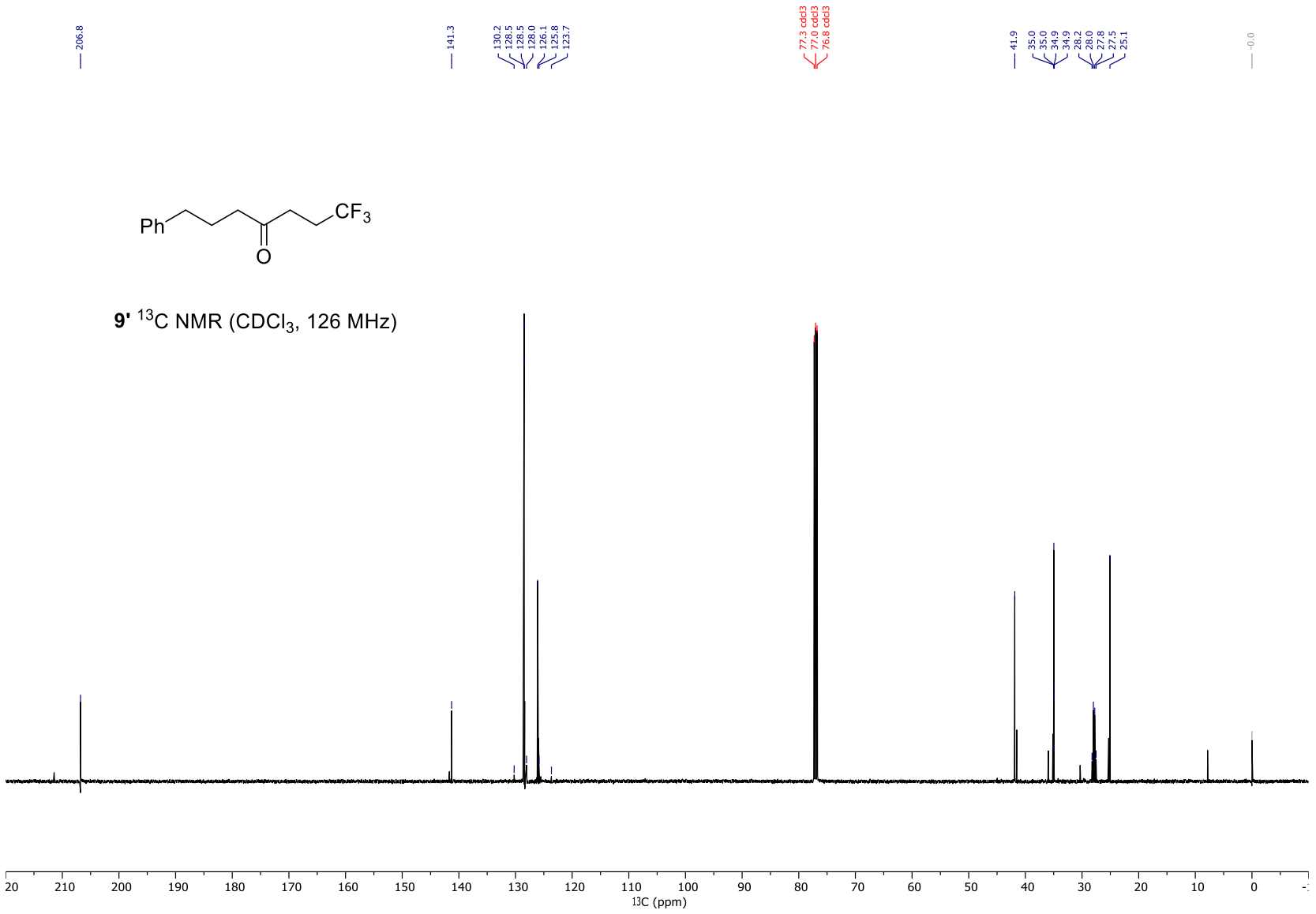

208.5
140.8
130.3
128.5
128.3
128.1
126.2
125.9
123.7
77.3 cdcl3
77.0 cdcl3
76.8 cdcl3
44.3
41.1
33.1
32.9
32.7
32.4
29.8
16.0
16.0
16.0
16.0
0.0
O
Ph
CF3
9 13C NMR (CDCl3, 126 MHz)
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C (ppm)

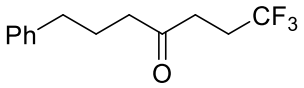


9 ^{19}F NMR ($CDCl_3$, 470 MHz)

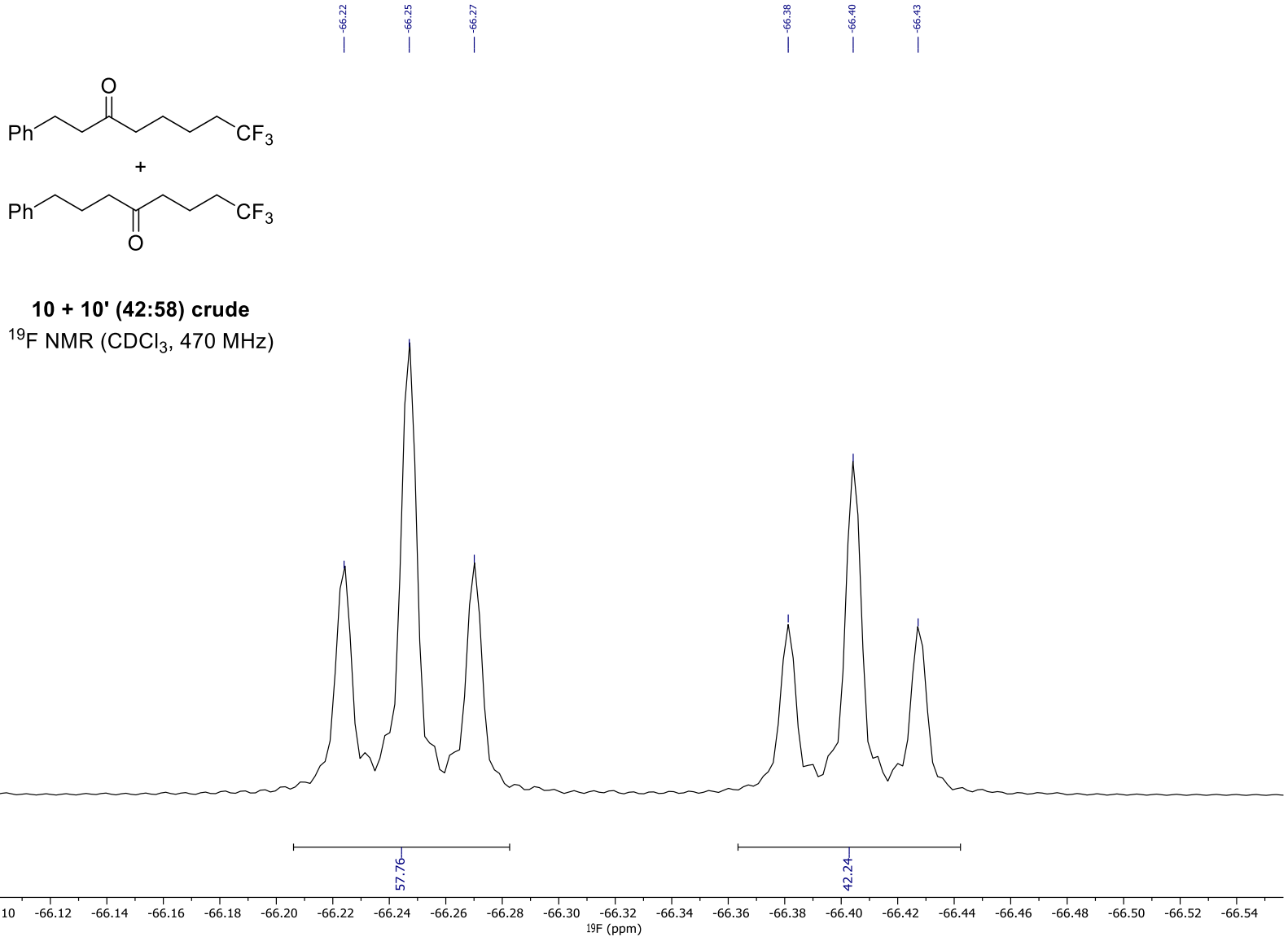


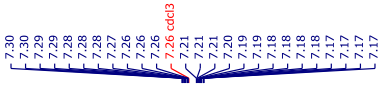
9' ^{1}H NMR ($CDCl_3$, 500 MHz)

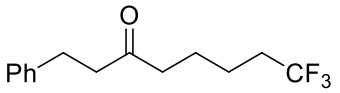

206.8
141.3
130.2
128.5
128.5
128.0
126.1
125.8
123.7
77.3 cdcl3
77.0 cdcl3
76.8 cdcl3
41.9
35.0
35.0
34.9
34.9
28.2
28.0
27.8
27.5
25.1
-0.0
Ph
CF3
O
9' 13C NMR (CDCl3, 126 MHz)
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C (ppm)



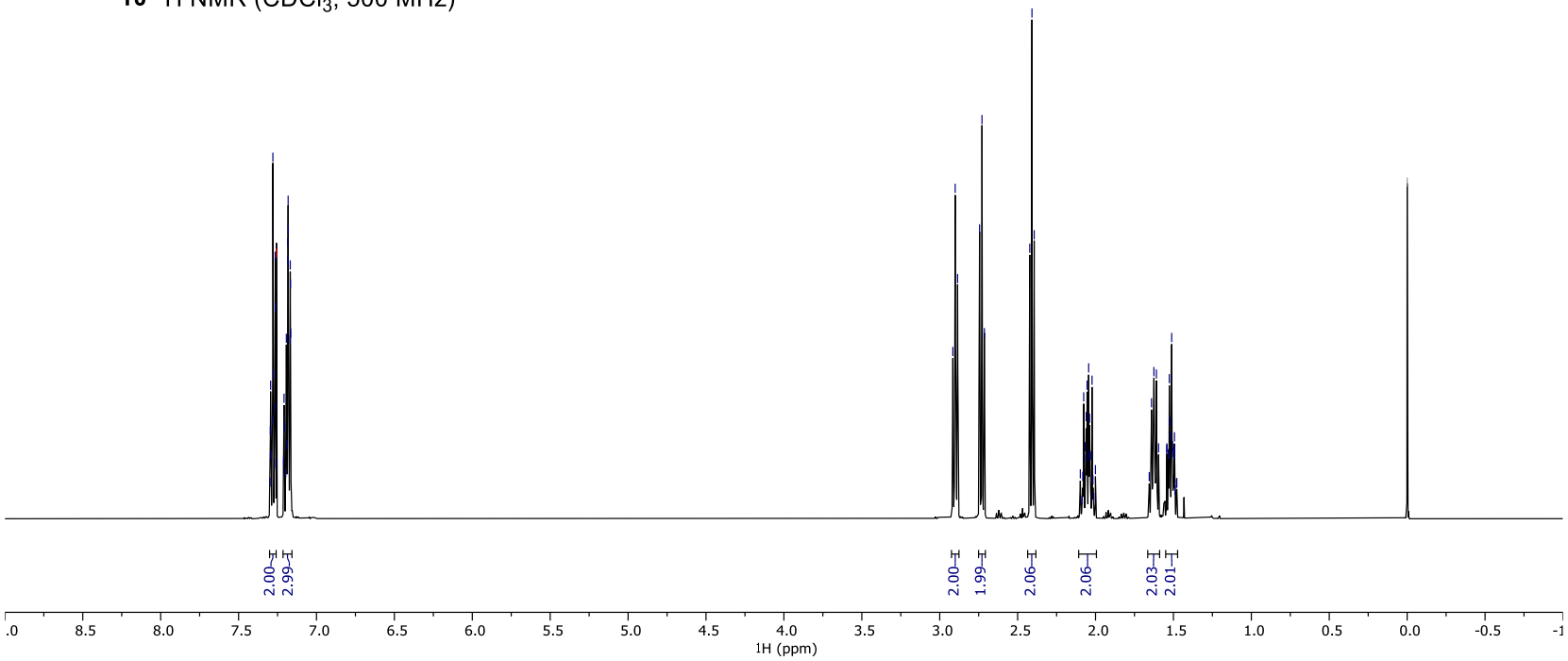
9' ^{19}F NMR ($CDCl_3$, 470 MHz)

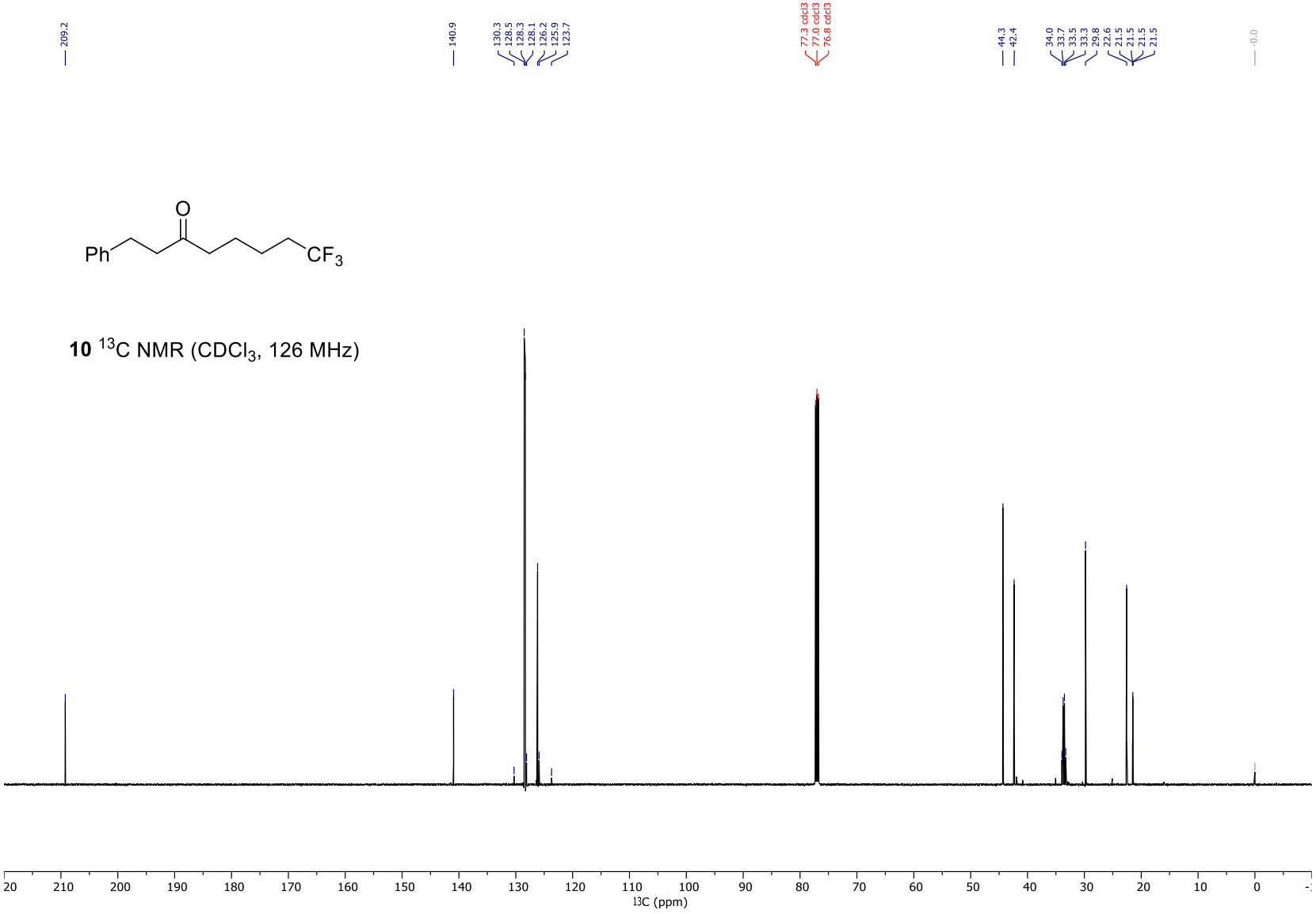

-66.22
-66.25
-66.27
-66.38
-66.40
-66.43
Ph
CF3
+
Ph
CF3
O
10 + 10' (42:58) crude
19F NMR (CDCl3, 470 MHz)
57.76
42.24
-66.10 -66.12 -66.14 -66.16 -66.18 -66.20 -66.22 -66.24 -66.26 -66.28 -66.30 -66.32 -66.34 -66.36 -66.38 -66.40 -66.42 -66.44 -66.46 -66.48 -66.50 -66.52 -66.54
19F (ppm)

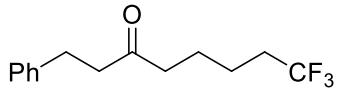




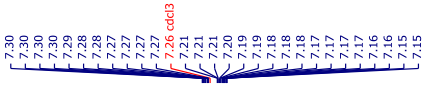
10 ^{1}H NMR ($CDCl_3$, 500 MHz)

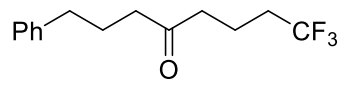



209.2
140.9
130.3
128.5
128.3
128.1
126.2
125.9
123.7
77.3 cdcl3
77.0 cdcl3
76.8 cdcl3
44.3
42.4
34.0
33.7
33.5
33.3
29.8
22.6
21.5
21.5
21.5
21.5
-0.0
O
Ph
CF3
10 13C NMR (CDCl3, 126 MHz)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
13C (ppm)

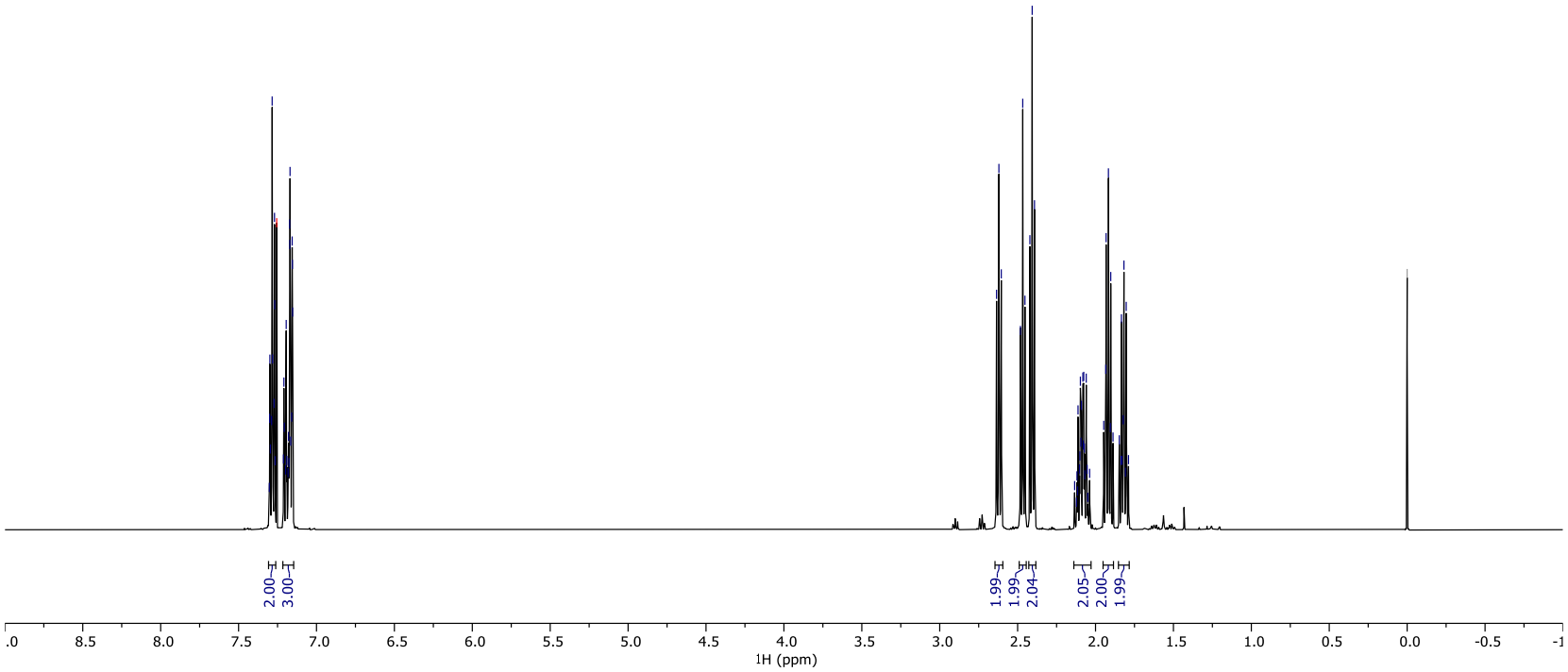


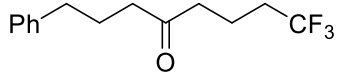
10 ^{19}F NMR ($CDCl_3$, 470 MHz)



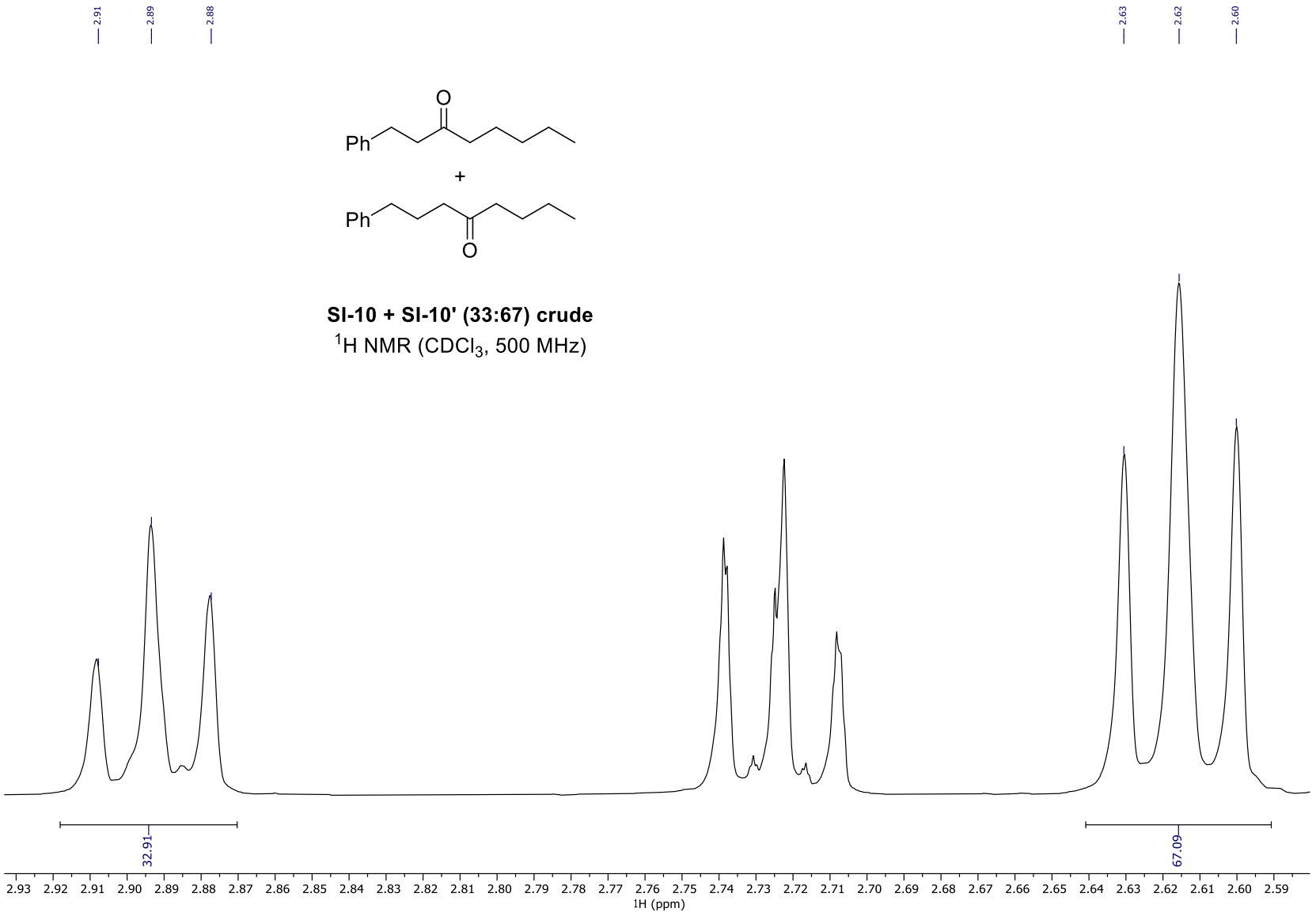


10' ^{1}H NMR ($CDCl_3$, 500 MHz)





10' ^{19}F NMR ($CDCl_3$, 470 MHz)


2.91
2.89
2.88
2.63
2.62
2.60
O
Ph
+
Ph
O
SI-10 + SI-10' (33:67) crude
1H NMR (CDCl3, 500 MHz)
32.91
67.09
2.93 2.92 2.91 2.90 2.89 2.88 2.87 2.86 2.85 2.84 2.83 2.82 2.81 2.80 2.79 2.78 2.77 2.76 2.75 2.74 2.73 2.72 2.71 2.70 2.69 2.68 2.67 2.66 2.65 2.64 2.63 2.62 2.61 2.60 2.59
1H (ppm)