Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Gold-catalyzed cycloisomerization of trifluoromethylated allenols: sustainability and mechanistic studies

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Supplementary Information

Contents

1. General Information

All reactions were carried out under argon atmosphere in dried glassware. For air and moisture sensitive liquids syringes and septa were used. Solids were added in argon reverse flow. All reactions were performed in dry solvents, which were dried with the *MB-SPS-800* solvent system from *M. Braun*.

Chemicals were purchased from *ABCR*, *Acros Organics*, *Sigma Aldrich*, *Fluorochem* and *TCI*. They were directly used, if not otherwise noted. Ionic liquids and gold catalysts were obtained from the following suppliers:

[BMIM][PF_6]: *Acros Organics*;

[BMIM][BF_4], [BMIM][HSO_4], [EMIM][HSO_4]: *Sigma Aldrich*;

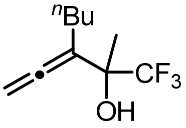
[EMIM][BF_4], [EMIM][$(PO_2)OEt_2$]: *Alfa Aesar*;

JohnPhosAu(MeCN)SbF_6, JohnPhosAuCl, Ph_3PAuCl, $Ph_3PAuNTf_2$, **C**, **D**: *Sigma Aldrich*;

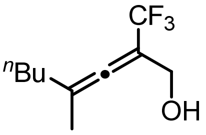
$AuCl_3$, $AuBr_3$: *Alfa Aesar*; $AgSbF_6$: *Fluorochem;* AgOTf: *TCI.*

Synthesis of $(4\text{-}MeOC_6H_4)_3PAuCl$, $(4\text{-}MeC_6H_4)_3PAuCl$, $(4\text{-}CF_3C_6H_4)_3PAuCl$, $[2,4,6\text{-}(MeO)_3C_6H_2)_3PAuCl$, and $(2\text{-}MeOC_6H_4)_3PAuCl$ were performed according to the known procedure.[SI1]

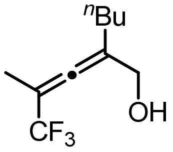
2. Allenes used in this work



1a

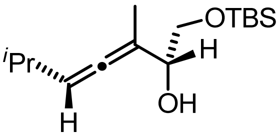


1b

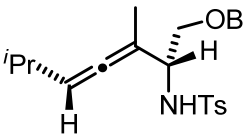


1c

The synthesis of **1a**, **b** and **c** is described in sections 4 to 6.



3a



3b

The synthesis of **3a** and **b** was performed according to a known procedure.[SI2]

[SI1] C. Nieto-Oberhuber, S. Lopez and A. M. Echavarren, *J. Am. Chem. Soc.,* 2005, **127**, 6178.

[SI2] For **3a** see: B. Gockel and N. Krause, *Eur. J. Org. Chem.,* 2010, 311. For **3b** see: N. Morita and N. Krause, *Org. Lett.,* 2004, **6**, 4121–4123.

3. Additional Results

A mixture of allene **1a** and [BMIM][PF_6] was treated in an ultrasonic bath. Under a light microscope, small droplets of the allene in the IL are detected.

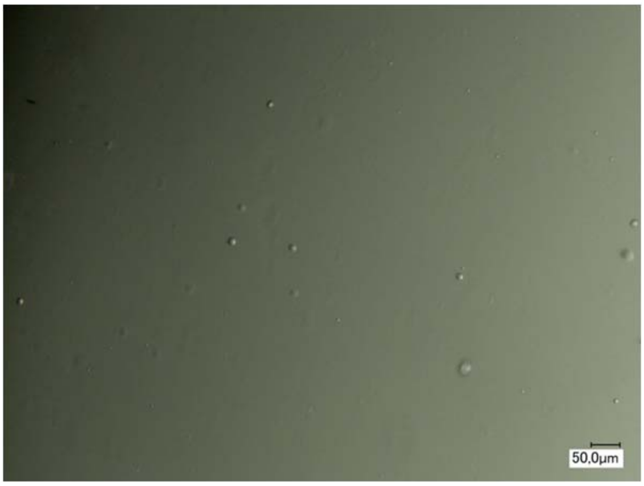


Figure SI1: Formation of allene droplets in [BMIM][PF_6].

To investigate the influence of the droplet size on the reaction time, the reaction was performed in an ultrasonic bath. [BMIM][PF_6] and allene **1a** were used. To ensure a uniform distribution of the allene in the IL, the mixture was stirred for 2 min before it was put into the ultrasonic bath. This approach was necessary because without stirring in the beginning, the allene stays on top of the IL.

Table SI1: Influence of ultrasonic sound to the cycloisomerization of allene **1a** in [BMIM][PF_6].[a]

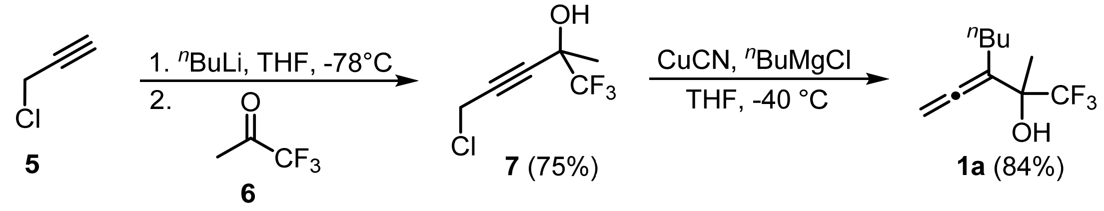
Entry	x mol% [Au]	Time with Ultrasound[b]	Time without Ultrasound
1	5 mol% $AuCl_3$	2 h	4 h
2	2 mol% **A**	10 min	15 min
3	2 mol% $Ph_3PAuNTf_2$	40 min	1.5 h

[a] Time required for complete consumption of the starting material, determined by GC-FID.
[b] Reaction mixture was stirred for 2 min before the ultrasonic bath was used.

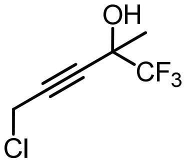
General procedure:

The gold catalyst was dissolved in [BMIM][PF_6] (0.4 mL, 4 mL/mmol). Then the allene (0.10 mmol) was added. The mixture was stirred for 2 min before it was put into the ultrasonic bath. The progress of the reaction was determined by GC-FID. Small samples were taken and washed with Et_2O; the extract was filtered and the conversion determined until no more starting material was detected.

4. Synthesis of allene 1a



5-Chloro-1,1,1-trifluoro-2-methylpent-3-yn-2-ol (7)



27.7 mL ^{n}BuLi (69.19 mmol, 2.5 M in hexane) were slowly added to a stirred solution of 5 mL (69.19 mmol) propargyl chloride **5** in 200 mL THF at –78 °C. After 30 min 5.2 mL (58.10 mmol) 1,1,1-trifluoroacetone **6** was dropped into the reaction mixture and stirred for 1 h. Then the mixture was hydrolyzed and washed three times with sat. aq. NH_4Cl. The combined aqueous layers were extracted with EtOAc. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified via silica gel column chromatography (SiO_2, pentane/Et_2O, 4:1). 8.14 g (43.10 mmol, 75%) of the product **7** were isolated as solution in pentane/Et_2O (70%).

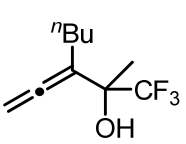
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.16 (s, 2 H, CH_2), 2.65 (s, 1 H, OH), 1.64 (s, 1 H, CH_3).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 123.8 (q, J_{CF} = 284.2 Hz), 81.9, 81.4, 68.7 (q, J_{CF} = 33.1 Hz), 29.3, 22.8.

^{19}F-NMR (282 MHz, $CDCl_3$): δ (ppm) = –82.0.

IR: ν (cm^{-1}) = 3320 (br, OH), 2961 (s, C–H), 2933 (s, C–H), 2861 (s, C–H), 2249 (m, C≡C).

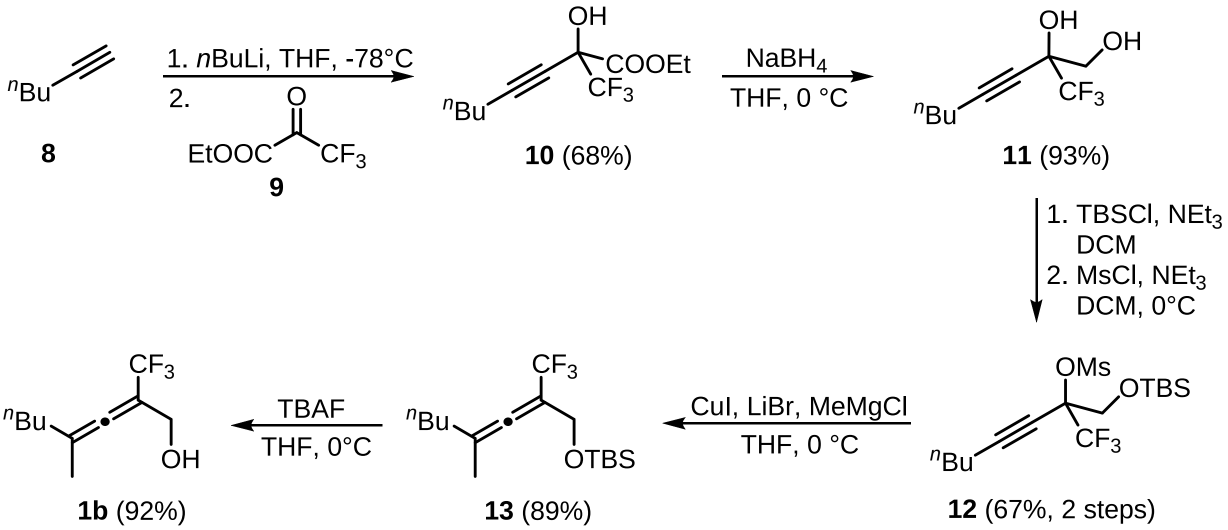
1,1,1-Trifluoro-2-methyl-3-vinylidenheptane-2-ol (1a)



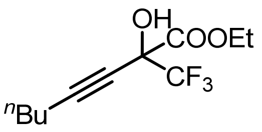
A suspension of 4.62 g CuCN (51.6 mmol) in 250 mL THF was cooled to – 40°C before 51.6 mL (103.2 mmol, 2 M in THF) ^{n}BuMgCl was added. The mixture was stirred for 30 min at the same temperature. Then 8.02 g (43.00 mmol) of alkyne **7** was dissolved in a small amount of THF and dropped into the cuprate-mixture. After 2 h sat. aq. NH_4Cl (0.5 mL/mmol) was added and the mixture warmed up to room temperature. The solid was filtered over celite. The filtrate was dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified via silica gel column chromatography (SiO_2, pentane/Et_2O, 6:1 to 4:1). 7.52 g (36.12 mmol, 84%) of the product **1a** were isolated as colorless oil.

^{1}H-NMR (300 MHz, CDCl$_3$): δ (ppm) = 5.09 (m, 2 H, CH$_2$=C), 2.48 (br s, 1 H, OH), 2.05 (m, 2 H, CH$_2$), 1.50 (s, 3 H, CH$_3$), 1.46-1.30 (m, 4 H, CH$_2$), 0.91 (t, J = 7.1 Hz, 3 H, CH$_3$).
^{13}C-NMR (76 MHz, CDCl$_3$): δ (ppm) = 204.9, 125.7 (q, J$_{CF}$ = 286.4 Hz), 105.9, 81.9, 72.8 (q, J$_{CF}$ = 28.9 Hz), 30.1, 26.2 (q, J$_{CF}$ = 1.4 Hz), 22.3, 20.7, 13.9.
^{19}F-NMR (282 MHz, CDCl$_3$): δ (ppm) = –79.8.
IR: ν (cm^{-1}) = 3458 (br, OH), 2959 (m, C–H), 2933 (m, C–H), 2863 (m, C–H), 1956 (m, C=C=C).

5. Synthesis of allene 1b



Ethyl 2-hydroxy-2-(trifluoromethyl)oct-3-ynoate (10)



7.0 mL ^{n}BuLi (17.62 mmol, 2.5 M in hexane) were slowly added to a stirred solution of 1.4 mL (12.54 mmol) 1-hexyne **8** in 17 mL THF at –78 °C. After 30 min 2.0 mL (14.68 mmol) of ethyl 3,3,3-trifluoropyruvate **9** were dropped into the reaction mixture and stirred for 30 min. Then the mixture was hydrolyzed and washed three times with sat. aq. NH$_4$Cl. The combined aqueous layers were extracted with EtOAc. The combined organic layers were dried over MgSO$_4$ and concentrated *in vacuo*. The crude product was purified via silica gel column chromatography (SiO$_2$, pentane/Et$_2$O, 4:1). 2.15 g (8.53 mmol, 68%) of the product **10** were isolated as light yellow oil.

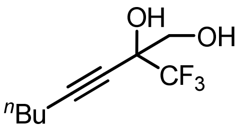
^{1}H-NMR (300 MHz, CDCl$_3$): δ (ppm) = 4.41 (m, 2 H, CH$_2$-COOEt), 4.11 (br s, 1 H, OH), 2.26 (t, J = 7.0 Hz, 2 H, CH$_2$), 1.58-1.47 (m, 2 H, CH$_2$), 1.45-1.35 (m, 2 H, CH$_2$), 1.37 (t, J = 7.1 Hz, 3 H, CH$_3$-COOEt), 0.91 (t, J = 7.3 Hz, 3 H, CH$_3$).

^{13}C-NMR (76 MHz, CDCl$_3$): δ (ppm) = 166.8, 121.7 (q, J$_{CF}$ = 286.1 Hz), 89.1, 71.5, 71.4, 64.7, 29.8, 21.7, 18.3, 13.8, 13.5.

^{19}F-NMR (282 MHz, CDCl$_3$): δ (ppm) = –77.9.

Known compound.[SI3]

2-(Trifluoromethyl)oct-3-yne-1,2-diol (11)



Ester **10** (1.71 g, 6.79 mmol) was dissolved in 67 mL THF and 14 mL MeOH and cooled to 0 °C. Then NaBH$_4$ (1.03 g, 27.14 mmol) was slowly added and the mixture stirred for 3 h before the mixture was given into ice cooled sat. aq. NH$_4$Cl. The phases were separated and the aqueous layer was extracted with Et$_2$O. The combined organic layers were dried over MgSO$_4$ and concentrated *in vacuo*. The crude product was purified via silica gel column chromatography (SiO$_2$, Cy/EtOAc, 8:1 to 2:1). 1.27 g (6.32 mmol, 93%) of the product **11** were isolated as white solid.

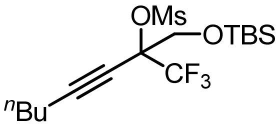
^{1}H-NMR (300 MHz, CDCl$_3$): δ (ppm) = 3.90-3.71 (m, 2 H, CH$_2$), 3.70 (br s, 1 H, OH), 2.72 (br s, 1 H, OH), 2.24 (t, J = 7.1 Hz, 2 H, CH$_2$), 1.56-1.46 (m, 2 H, CH$_2$), 1.45-1.33 (m, 2 H, CH$_2$), 0.90 (t, J = 7.26 Hz, 3 H, CH$_3$).

^{13}C-NMR (76 MHz, CDCl$_3$): δ (ppm) = 123.4 (q, J$_{CF}$ = 285.3 Hz), 89.8, 73.2, 71.5 (q, J$_{CF}$ = 30.6 Hz), 64.6, 30.0, 21.8, 18.2, 13.4.

^{19}F-NMR (282 MHz, CDCl$_3$): δ (ppm) = –78.9.

Known compound.[SI3]

2-((*t*-Butyldimethylsilyloxy)methyl)-1,1,1-trifluorooct-3-yn-2-yl-methanesulfonat (12)



1.17 g (4.65 mmol) of diol **11** were dissolved in 20 mL DCM and 876 mg (5.81 mmol) TBSCl, 1.2 mL (8.66 mmol) Et$_3$N and 56 mg (0.47 mmol) DMAP added successively. After 29 h 720 µl (9.31 mmol) MsCl and another 2 mL (14.4 mmol) Et$_3$N were added at 0 °C. The mixture was stirred for further 16 h, while warming up to room temperature was allowed. Then it was hydrolyzed and washed three times with sat. aq. NH$_4$Cl. The combined aqueous layers were extracted with DCM. The combined organic layers were dried over MgSO$_4$ and concentrated

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[SI3] I. K. Ivanov, I. D. Parushev and V. C. Christov, *Heteroatom Chem.*, 2013, **24**, 322.

in vacuo. The crude product was purified via silica gel column chromatography (SiO_2, Cy/Et_2O, 30:1). 1.25 g (3.10 mmol, 67%) of the product **12** were isolated as colorless oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 4.16 (d, J = 11.2 Hz, 1H, CH_2), 4.06 (d, J = 11.1 Hz, 1 H, CH_2), 3.21 (s, 3 H, CH_3-Ms), 2.33 (t, J = 7.07 Hz, 2 H, CH_2), 1.61-1.51 (m, 2 H, CH_2), 1.49-1.37 (m, 2 H, CH_2), 0.92 (t, J = 7.3 Hz, 3 H, CH_3), 0.90 (s, 9 H, *t*-Bu), 0.10 (2 s, 6 H, CH_3).

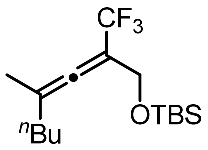
^{13}C-NMR (76 MHz, $CDCl_3$): δ (ppm) = 121.7 (q, J_{CF} = 285.3 Hz), 95.3, 80.5, 69.0, 65.0, 40.4, 29.7, 25.6, 21.8, 18.5, 18.2, 13.4, –5.6.

^{19}F-NMR (282 MHz, $CDCl_3$): δ (ppm) = –76.0.

HR-MS (ESI): $C_{16}H_{29}F_3O_4SSi$ (402.54), calculated: 403.15807 $[M+H]^+$, found: 403.15768.

IR: ν (cm^{-1}) = 2957 (m, C–H), 2933 (m, C–H), 2860 (m, C–H), 2248 (m, C≡C), 1472.

t-Butyldimethyl-(4-methyl-2-(trifluoromethyl)octa-2,3-dienyloxy)silane (13)



A suspension of 2.46 g (12.91 mmol) CuI and 1.15 g (12.91 mmol) LiBr in 25 mL THF was cooled to 0 °C, before 4.3 mL (12.91 mmol, 3 M in THF) MeMgCl were added. The mixture was stirred for 30 min at the same temperature. Then 1.30 g (3.23 mmol) of alkyne **12** was dissolved in a small amount of THF and dropped into the cuprate-mixture. After 1 h sat. aq. NH_4Cl was added and the mixture warmed up to room temperature. When necessary, the solid was filtered over celite. The organic layer was washed with sat. aq. $NaHCO_3$ for several times. The combined aqueous phases were extracted with Et_2O and the combined organic layers dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified via silica gel column chromatography (SiO_2, pentane/Et_2O, 20:1). 929 mg (2.88 mmol, 89%) of the product **13** were isolated as colorless oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 4.25 (s, 2 H, CH_2), 2.05 (m, 2 H, CH_2), 1.77 (s, 3 H, CH_3), 1.45-1.30 (m, 4 H, CH_2), 0.90 (t, J = 7.5 Hz, 3 H, CH_3), 0.89 (s, 9 H, *t*-Bu), 0.07 (s, 6 H, CH_3).

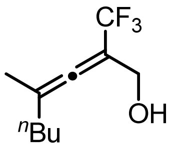
^{13}C-NMR (76 MHz, $CDCl_3$): δ (ppm) = 200.1 (q, J_{CF} = 4.1 Hz), 123.6 (q, J_{CF} = 273.9 Hz), 108.4, 98.1 (q, J_{CF} = 32.5 Hz), 59.5, 33.2, 29.2, 25.7, 22.1, 18.2, 18.2, 13.8, –5.5.

^{19}F-NMR (282 MHz, $CDCl_3$): δ (ppm) = –61.5.

HR-MS (ESI): $C_{16}H_{29}F_3OSi$ (322.48), calculated: 323.20125 $[M+H]^+$, found: 323.20063.

IR: ν (cm^{-1}) = 2957 (m, C–H), 2930 (m, C–H), 2859 (m, C–H), 1981 (w, C=C=C), 1735.

4-Methyl-2-(trifluoromethyl)octa-2,3-diene-1-ol (1b)



929 mg (2.88 mmol) of allene **13** were dissolved in 29 mL THF and 5.8 mL (5.76 mmol, 1 M in THF) TBAF added at 0 °C. After complete consumption of the starting material, the mixture was hydrolyzed and washed with sat. aq. NH_4Cl for three times. The combined aqueous layers were extracted with Et_2O. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified via silica gel column chromatography (SiO_2, pentane/Et_2O, 10:1 to 4:1). 552 mg (2.65 mmol, 92%) of the product **1b** were isolated as colorless oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 4.23 (s, 2 H, CH_2), 2.05 (t, J = 7.9 Hz, 2 H, CH_2), 1.80 (s, 3 H, CH_3), 1.65 (br s, 1 H, OH), 1.46-1.30 (m, 4 H, CH_2), 0.90, (t, J = 7.0 Hz, Hz, 3 H, CH_3).

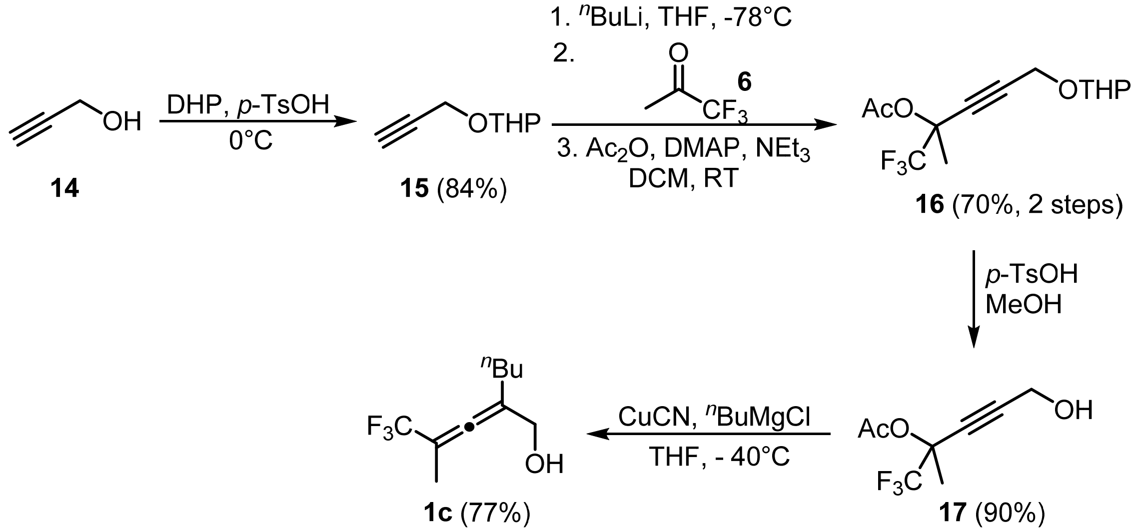
^{13}C-NMR (76 MHz, $CDCl_3$): δ (ppm) = 199.8 (q, J_{CF} = 4.1 Hz), 123.5 (q, J_{CF} = 273.9 Hz), 109.9, 98.2 (q, J_{CF} = 34.0 Hz), 59.2, 33.2, 29.2, 22.1, 18.4, 13.8.

^{19}F-NMR (282 MHz, $CDCl_3$): δ (ppm) = –61.7.

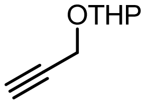
HR-MS (ESI): $C_{10}H_{15}O_1F_3$ (208.22), berechnet: 208.10695 $[M]^+$, gefunden: 208.10695.

IR: ν (cm^{-1}) = 3352 (br, OH), 2959 (m, C–H), 2931 (m, C–H), 2875 (w, C–H), 1977 (w, C=C=C), 1718.

6. Synthesis of allene 1c



2-(2-Propynyloxy)-tetrahydro-*2H*-pyran (15)



A mixture of 6.0 mL (103.82 mmol) freshly distilled propargyl alcohol **14**, 12.1 mL (134.96 mmol) DHP and 215 mg (1.04 mmol, 1 mol%) p-TsOH·H_2O

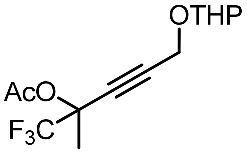
were stirred for 1 h at 0 °C. The reaction mixture was directly purified by silica gel column chromatography (pentane:Et_2O, 30:1) to give 12.16 g (86.76 mmol, 84%) of the product **15** as colorless clear oil (97% in Et_2O /pentane).

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 4.81 (t, J = 3.4 Hz, 1H, CH-THP), 4.25 (ddd, J = 27.4, 15.7, 2.4 Hz, 2 H, CH_2), 3.83 (m, 1 H, CH_2-THP), 3.54 (m, 1 H, CH_2-THP), 2.40 (t, *J* = 2.4 Hz, 1 H, CH), 1.87-1.79 (m, 2H, CH_2-THP), 1.63-1.52 (m,4 H, CH_2-THP).

^{13}C-NMR (76 MHz, $CDCl_3$): δ (ppm) = 96.8, 79.7, 74.0, 61.9, 53.9, 30.2, 25.3, 19.0.

Known compound.[SI4]

1,1,1-Trifluoro-2-methyl-5-(tetrahydro-*2H*-pyran-2-yloxy)pent-3-yn-2-yl-acetate (16)



At –78 °C 14.3 mL (35.67 mmol, 2.5 M in hexane) *n*-BuLi were slowly added to a stirred solution of 5 g (35.67 mmol) of alkyne **15** in 46 mL THF. After 30 min 2.9 mL (32.40 mmol) 1,1,1-trifluoraceton **6** were dropped into the reaction mixture and stirred for 3 h. Then the mixture was hydrolyzed and washed three times with sat. aq. NH_4Cl. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was directly used in the acetylation reaction. Therefore it was dissolved in 100 mL DCM and 6.7 mL (71.34 mmol) Ac_2O, 14.8 mL (107.01 mmol) Et_3N und 436 mg (3.57 mmol) DMAP added at room temperature. After 20 h the reaction mixture was washed with sat. aq. NH_4Cl and sat. aq. $NaHCO_3$ successively. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified via silica gel column chromatography (SiO_2, cy/Et_2O, 10:1). 6.57 g (22.33 mmol, 70%) of the product **16** were isolated as light yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$): *δ* (ppm) = 4.79 (t, J = 2.9 Hz, 1 H, CH-THP), 4.30 (m, 2 H, CH_2), 3.81 (m, 1 H, CH_2-THP), 3.51 (m, 1 H, CH_2-THP), 2.09 (s, 3 H, CH_3-Ac), 1.84 (m, 3 H, CH_3), 1.80-1.68 (m, 2H, CH_2-THP), 1.63-1.50 (m, 4H, CH_2-THP).

^{13}C-NMR (76 MHz, $CDCl_3$): *δ* (ppm) = 167.6/167.6*, 122.8 (q, J_{CF} = 283.0 Hz), 96.7/96.7*, 84.4/84.4*, 78.2/78.1*, 73.4 (q, J_{CF} = 32.6 Hz), 62.0/61.9*, 53.8/53.7*, 30.1/30.1*, 25.3, 21.4, 20.4, 18.9/18.9*.

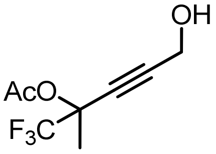
^{19}F-NMR (282 MHz, $CDCl_3$): *δ* (ppm) = –80.7/–80.8*.

HR-MS (ESI): $C_{11}H_{15}O_3F_3$ (294.27), calculated: 295.11517 $[M+H]^+$, found: 294.11470.

IR: ν (cm^{-1}) = 2945 (m, C–H), 2872 (w, C–H), 1761 (s, C=O).

[SI4] A. Córdova, S. Lin and A. Tseggai, *Adv. Synth. Catal.*, 2012, **354**, 1363.

1,1,1-Trifluoro-5-hydroxy-2-methylpent-3-yn-2-yl-acetate (17)



6.57 g (22.33 mmol) of alkyne **16** were dissolved in 26 mL MeOH and 212 mg (1.12 mmol) *p*-TsOH·H_2O added. The solution was stirred for 3 h and washed with sat. aq. $NaHCO_3$. The combined aqueous layers were extracted with Et_2O and the combined organic layers dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified via silica gel column chromatography (SiO_2, cy/EtOAc, 6:1 to 3:1). 4.23 g (20.13 mmol, 90%) of the product **17** were isolated as light yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 4.30 (s, 2 H, CH_2), 2.56 (br s, 1 H, OH), 2.11 (s, 3 H, CH_3), 1.85 (d, J = 0.8 Hz, 3 H, CH_3).

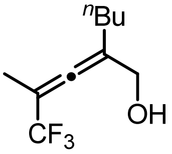
^{13}C-NMR (76 MHz, $CDCl_3$): δ (ppm) = 168.1, 122.7 (q, J_{CF} = 283.0 Hz), 86.6, 77.6, 73.5 (q, J_{CF} = 32.8 Hz), 50.7, 21.5, 20.4.

^{19}F-NMR (282 MHz, $CDCl_3$): δ (ppm) = –80.7.

HR-MS (ESI): $C_{18}H_{18}O_4F_3$ (210.15), calculated: 211.05766 $[M+H]^+$, found: 211.05765.

IR: ν (cm^{-1}) = 3400 (br, OH), 2923 (w, C–H), 1760 (s, C=O).

2-(3,3,3-Trifluoro-2-methylprop-1-enylidene)hexan-1-ol (1c)



A suspension of 256 mg (2.86 mmol) CuCN and 7 mL THF was cooled to –40 °C before 3.3 mL (5.72 mmol, 20 ωt in THF) *n*-BuMgCl were added. The mixture was stirred for 30 min at the same temperature. Then 500 mg (2.38 mmol) of acetate **17** was dissolved in a small amount of THF and dropped into the cuprate-mixture. After 1 h 1.2 mL sat. aq. NH_4Cl (0.5 mL/mmol) were added and the mixture warmed up to room temperature. The solid was filtered over celite. The filtrate was dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified via silica gel column chromatography (SiO_2, pentane/Et_2O, 10:1 to 3:1). 381 mg (1.83 mmol, 77%) of the product **1c** were isolated as colorless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.11 (m, 2 H, CH_2), 2.08 (t, J = 7.1 Hz, 2 H, CH_2), 1.86 (s, 3 H, CH_3), 1.54 (br s, 1 H, OH), 1.46-1.39 (m, 2 H, CH_2), 1.39-1.31 (m, 2 H, CH_2), 0.91 (t, J = 7.3 Hz, 3 H CH_3).

^{13}C-NMR (76 MHz, $CDCl_3$): δ (ppm) = 198.3 (q, J_{CF} = 4.1 Hz), 123.8 (q, J_{CF} = 273.2 Hz), 112.2, 96.8 (q, J_{CF} = 34.9 Hz), 62.6, 29.3, 28.6, 22.2, 13.8, 13.2.

^{19}F-NMR (282 MHz, $CDCl_3$): δ (ppm) = –64.9.

HR-MS (ESI): $C_{10}H_{25}O_1F_3$ (208.22), calculated: 208.10695 $[M]^+$, found: 208.10646.

IR: ν (cm^{-1}) = 3329 (br, OH), 2960 (m, C–H), 2931 (m, C–H), 2869 (m, C–H), 1981 (w, C=C=C), 1722.

7. Cycloisomerization and recycling in ILs

General procedure:

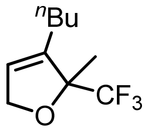
The gold catalyst and the silver additive (when necessary) were dissolved in the respective ionic liquid (0.4 mL, 4 mL/mmol). Then the allene (0.10 mmol) was added. The reaction progress was determined by GC-FID. Small samples were taken and washed with Et$_2$O; the extract was filtered and the conversion determined.

Isolated yields and recycling:

Under optimized conditions the products were isolated with pentane to determine isolated yields. 3 mL pentane were added and the mixture was stirred throughly. The extraction process was repeated four times. The organic phases were combined, the solvent removed *in vacuo* and the crude product purified via silica gel column chromatography (SiO$_2$, pentane/Et$_2$O, 10:1).

Residual solvent in the IL was removed *in vacuo* and the IL (containing the catalyst) was reused by adding another trifluoromethylated allene.

3-Butyl-2-methyl-2-(trifluoromethyl)-2,5-dihydrofuran (2a)



3.7 mg (1.00 µmol) of catalyst **A** were dissolved in 2 mL [BMIM][PF$_6$] and 100 mg (0.48 mmol) of allene **1a** were added. After 15 min the product was isolated and purified following the general procedure. 88 mg (0.42 mmol, 88%) of the product **2a** were isolated as colorless oil. The IL was reused.

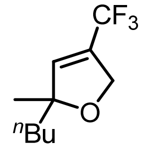
^{1}H-NMR (400 MHz, CDCl$_3$): δ (ppm) = 5.73 (s, 1 H, CH), 4.64 (m, 2 H, CH$_2$), 2.11-1.94 (m, 2 H, CH$_2$), 1.62-1.48 (m, 2 H, CH$_2$), 1.44 (s, 3 H, CH$_3$), 1.41-1.37 (m, 2 H, CH$_2$), 0.94 (t, 3 H, J = 7.3 Hz, CH$_3$).

^{13}C-NMR (101 MHz, CDCl$_3$): δ (ppm) = 139.8, 125.6 (q, J$_{CF}$ = 287.3 Hz), 123.7, 89.2 (q, J$_{CF}$ = 28.9 Hz), 74.9, 29.8, 25.7, 22.5, 19.1, 13.9.

^{19}F-NMR (282 MHz, CDCl$_3$): δ (ppm) = –79.0.

IR: ν (cm^{-1}) = 2960 (m, C–H), 2933 (m, C–H), 2866 (m, C–H), 1700 (w).

2-Butyl-2-methyl-4-(trifluoromethyl)-2,5-dihydrofuran (2b)



3.7 mg (1.00 µmol) of catalyst **A** were dissolved in 2 mL [BMIM][PF_6] and 100 mg (0.48 mmol) of allene **1b** were added. After 6 h the product was isolated and purified following the general procedure. 91 mg (0.44 mmol, 91%) of the product **2b** were isolated as colorless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 6.22 (m, 1 H, CH), 4.74 (m, 2 H, CH_2), 1.66-1.55 (m, 2 H, CH_2), 1.34-1.20 (m, 4 H, 2xCH_2), 1.32 (s, 3 H, CH_3), 0.90 (t, J = 7.2 Hz, 3 H, CH_3).

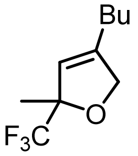
^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 137.9 (q, J_{CF} = 4.4 Hz), 129.3 (q, J_{CF} = 34.7 Hz), 121.4 (q, J_{CF} = 268.8 Hz), 91.5, 71.5, 40.2, 26.3, 25.6, 23.0, 14.0.

^{19}F-NMR (282 MHz, $CDCl_3$): δ (ppm) = –64.0.

HR-MS (ESI): $C_{10}H_{15}O_1F_3$ (208.22), calculated: 208.10695 $[M]^+$, found: 208.10694.

IR: ν (cm^{-1}) = 2960 (m, C–H), 2933 (s, C–H), 2863 (m, C–H), 1681 (w).

4-Butyl-2-methyl-2-(trifluoromethyl)-2,5-dihydrofuran (2c)



3.7 mg (1.00 µmol) of catalyst **A** were dissolved in 2 mL [BMIM][PF_6] and 100 mg (0.48 mmol) of allene **1c** were added. After 2 h the product was isolated and purified following the general procedure. 90 mg (0.44 mmol, 90%) of the product **2c** were isolated as colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.33 (m, 1 H, CH), 4.61 (m, 2 H, CH_2), 2.12 (t, J = 7.4 Hz, 2 H, CH_2), 1.51-1.44 (m, 2 H, CH_2), 1.43 (q, J = 1.0 Hz, 3 H, CH_3), 1.39-1.32 (m, 2 H, CH_2), 0.92 (t, J = 7.3 Hz, 3 H, CH_3).

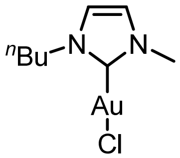
^{13}C-NMR (107 MHz, $CDCl_3$): δ (ppm) = 146.3, 125.6 (q, J_{CF} = 285.7 Hz), 119.0, 89.1 (q, J_{CF} = 30.0 Hz), 78.1, 29.5, 26.6, 22.3, 20.4, 13.8.

^{19}F-NMR (377 MHz, $CDCl_3$): δ (ppm) = –81.6.

IR: ν (cm^{-1}) = 2960 (m, C–H), 2934 (m, C–H), 2864 (m, C–H), 1789, 1730, 1666.

8. Synthesis of NHC-gold(I) complexes

NHC-gold(I) complex E



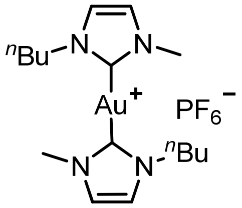
30 mg (0.17 mmol) [BMIM][Cl] were dissolved in 4 mL DCM and 22 mg (95 µmol) Ag_2O added. The reaction mixture was stirred for 24 h in darkness. Then 51 mg (0.17 mmol) AuCl·SMe_2 were added and the mixture stirred for further 3.5 h. Then it was filtered over celite and the solvent removed *in vacuo*. The crude product was dissolved in a small amount of DCM and given into n-pentane. At –20 °C the product separated as oily layer. The solvent was decanted and the catalyst dried *in vacuo* to achieve 63 mg (0.17mmol, 99%) of complex **E** as white solid.

^{1}H-NMR (500 MHz, $CO(CD_3)_2$): δ (ppm) = 7.38 (d, J = 1.9 Hz, 1 H, CH), 7.34 (d, J = 1.9 Hz, 1 H, CH), 4.20 (t, J = 7.2 Hz, 2 H, CH_2), 3.84 (s, 3 H, CH_3), 1.86 (q, J = Hz, 2 H, CH_2), 1.86 (pqi, J = 7.4 Hz, 2 H, CH_2), 1.34 (psx, J = 7.6 Hz, 2 H, CH_2), 0.94 (t, J = 7.4 Hz, 3 H, CH_3).

^{13}C-NMR (126 MHz, $CO(CD_3)_2$): δ (ppm) = 171.3, 123.1, 121.7, 51.3, 38.3, 33.7, 20.1, 13.8.

Known compound.[SI5]

NHC-gold(I) complex F



37 mg (0.21 mmol) [BMIM][Cl] were dissolved in 0.5 mL DMF before 40 mg (0.22 mmol) LiHMDS were added at room temperature. The mixture was stirred for 30 min and 15 mg (0.05 mmol) AuCl·SMe_2 dissolved in 0.25 mL DMF were dropped into. After 4 h the solvent was removed *in vacuo*, the crude product washed with Et_2O and dissolved in 0.5 mL H_2O. The product was precipitated by adding a sat. aq. KPF_6-solution. The solid was washed with H_2O and dried *in vacuo*. 15 mg (25 µmol, 50%) of complex **F** were isolated as white solid.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.50 (d, J = 1.4 Hz, 1 H, CH), 7.44 (d, J = 1.4 Hz, 1 H, CH), 4.34 (t, J = 7.2 Hz, 2 H, CH_2), 4.00 (s, 3 H, CH_3), 1.94 (pquint, J = 7.3 Hz, 2 H, CH_2), 1.41 (ph, J = 7.6 Hz, 2 H, CH_2), 0.96 (t, J = 7.4 Hz, 3 H, CH_3).

^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 184.8, 124.0, 122.6, 51.4, 38.2, 34.3, 20.3, 13.9.

Known compound.[SI5]

[SI5] L. Messori, L. Marchetti, L. Massai, F. Scaletti, A. Guerri, I. Landini, S. Nobili, G. Perrone, E. Mini, P. Leoni, M. Pasquali and C. Gabbiani, *Inorg. Chem.*, 2014, **53**, 2396.

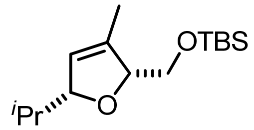
9. Kinetic studies in organic solvents

General procedure:

The gold catalyst and AgOTf were dissolved in the appropriate solvent and stirred for 5 minutes at room temperature, before the allene was added to the mixture. The reaction progress was observed via TLC. Additionally, small samples were taken in defined intervals and Et_3N was added to stop the reaction. Then the catalyst was removed by filtration. The solvent was removed *in vacuo* and the conversion determined by GC-FID.

The additives pyridine-N-oxide and Bu_4NOTf were used in the appropriate reactions with 5 mol% loading.

***tert*-Butyl((-5-isopropyl-3-methyl-2,5-dihydrofuran-2-yl)methoxy)dimethylsilan (4a)**



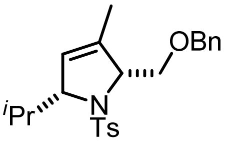
Following the general procedure 70 mg (0.26 mmol) allene **3a** was added to a solution of 4 mol% gold catalyst and 4 mol% AgOTf in 7 mL DMF and the conversion was determined via GC-FID until no more starting material was detected.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.45 (s, 1 H, CH), 4.55 (s, 1 H, CH), 4.41-4.39 (m, 1 H, CH), 3.67-3.66 (m, 2 H, CH_2), 1.73 (s, 1 H, CH), 0.92-0.84 (m, 15 H, 5 x CH_3), 0.06-0.05 (m, 6 H, 2 x CH_3).

^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 137.7, 123.8, 90.8, 88.1, 66.0, 33.9, 27.0, 26.0, 21.2, -5.3.

Known compound.[SI2]

2-((Benzyloxy)methyl)-5-isopropyl-3-methyl-1-tosyl-2,5-dihydro-1*H*-pyrrol (4b)



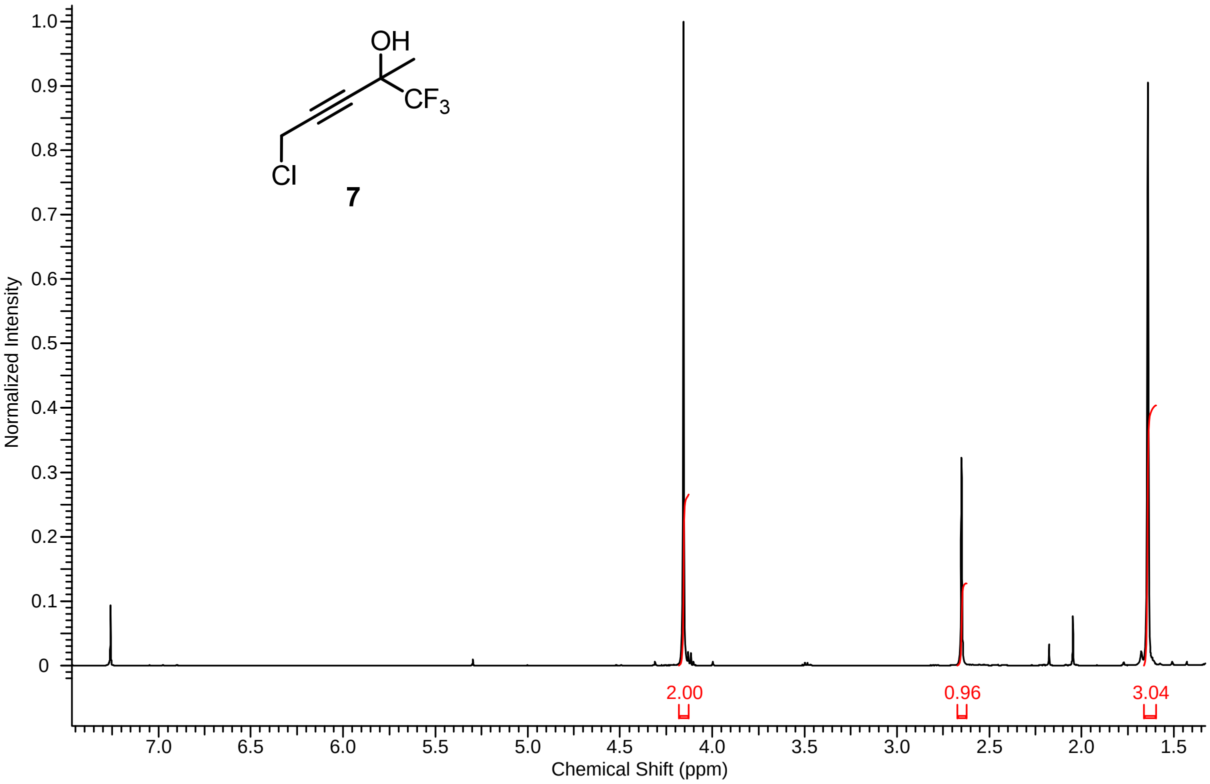
Following the general procedure 80 mg (0.20 mmol) allene **3b** was added to a solution of 2 mol% gold catalyst and 2 mol% AgOTf in 8 mL THF and the conversion was determined via GC-FID until no more starting material was detected.

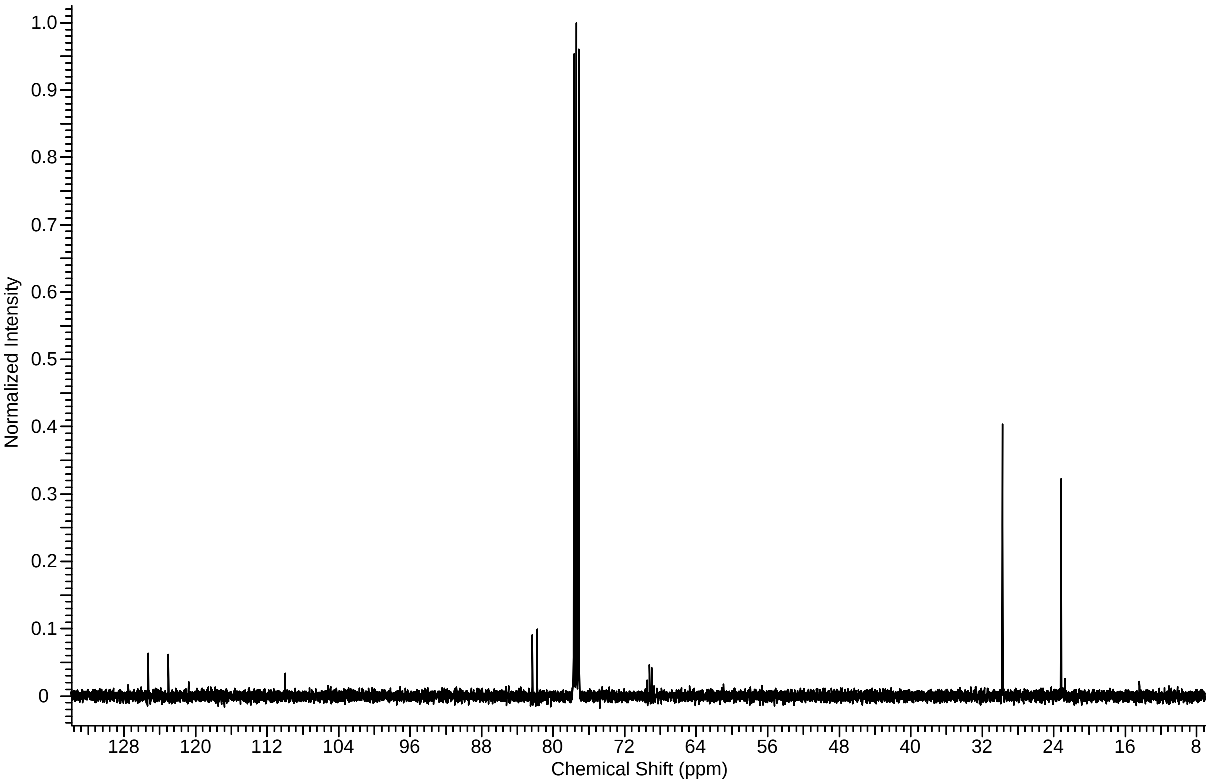
^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.75 (d, J = 8.3 Hz, 2 H), 7.35-7.10 (m, 7 H), 5.37 (d, J = 1.5 Hz, 1 H), 4.52-4.49 (m, 1 H), 4.48-4.44 (m, 1 H), 4.17 (q, J = 12.0 Hz, 2 H), 4.01 (dd, J = 10.6, 2.8 Hz, 1 H), 3.55 (dd, J = 10.6, 2.0 Hz, 1 H), 2.73- 2.67 (m, 1 H), 2.33 (s, 3 H), 1.66 (s, 3 H), 0.90 (d, J = 7.0 Hz, 3 H), 0.64 (d, J = 6.5 Hz, 3 H).

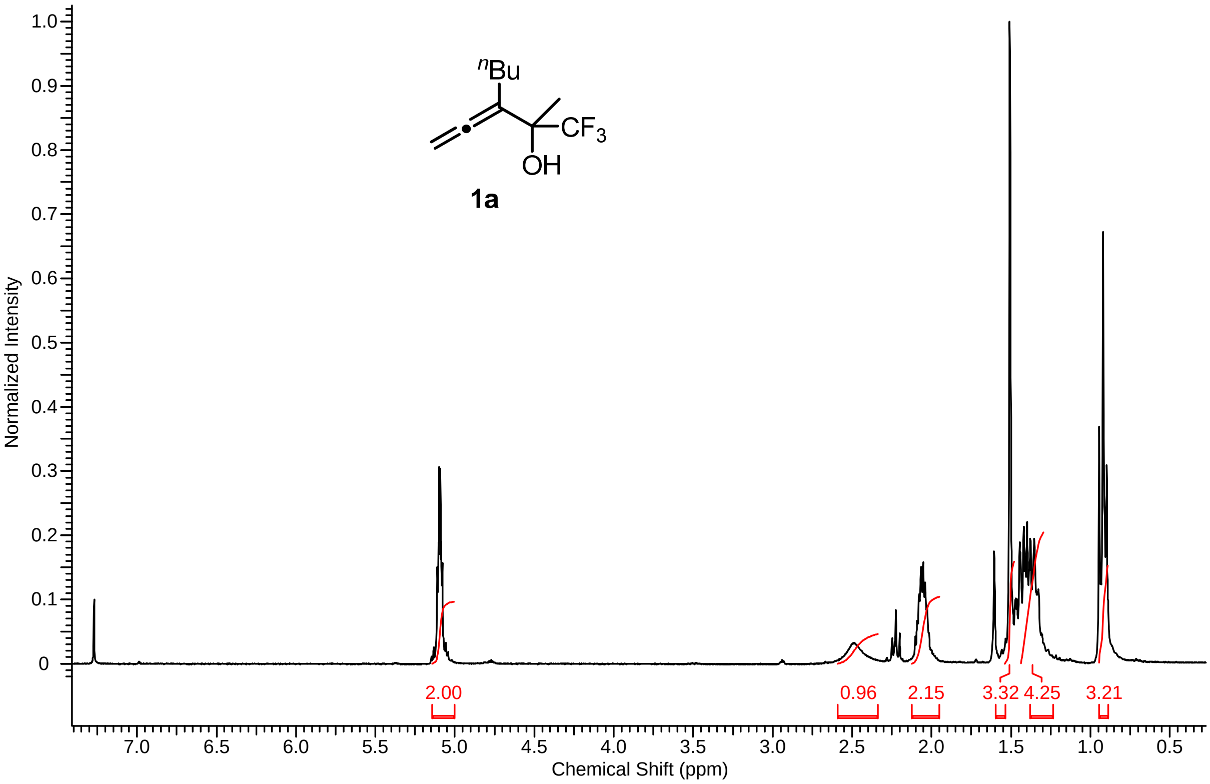
^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 142.6, 139.4, 138.2, 136.5, 129.3, 128.3, 127.6, 127.5, 126.8, 120.9, 72.8, 72.6, 70.4, 67.4, 30.7, 21.5, 19.6, 15.2, 13.8.

Known compound.[SI2]

10. NMR-Spectra







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0.1
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2.00
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3.32
4.25
3.21
7.0
6.5
6.0
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1.5
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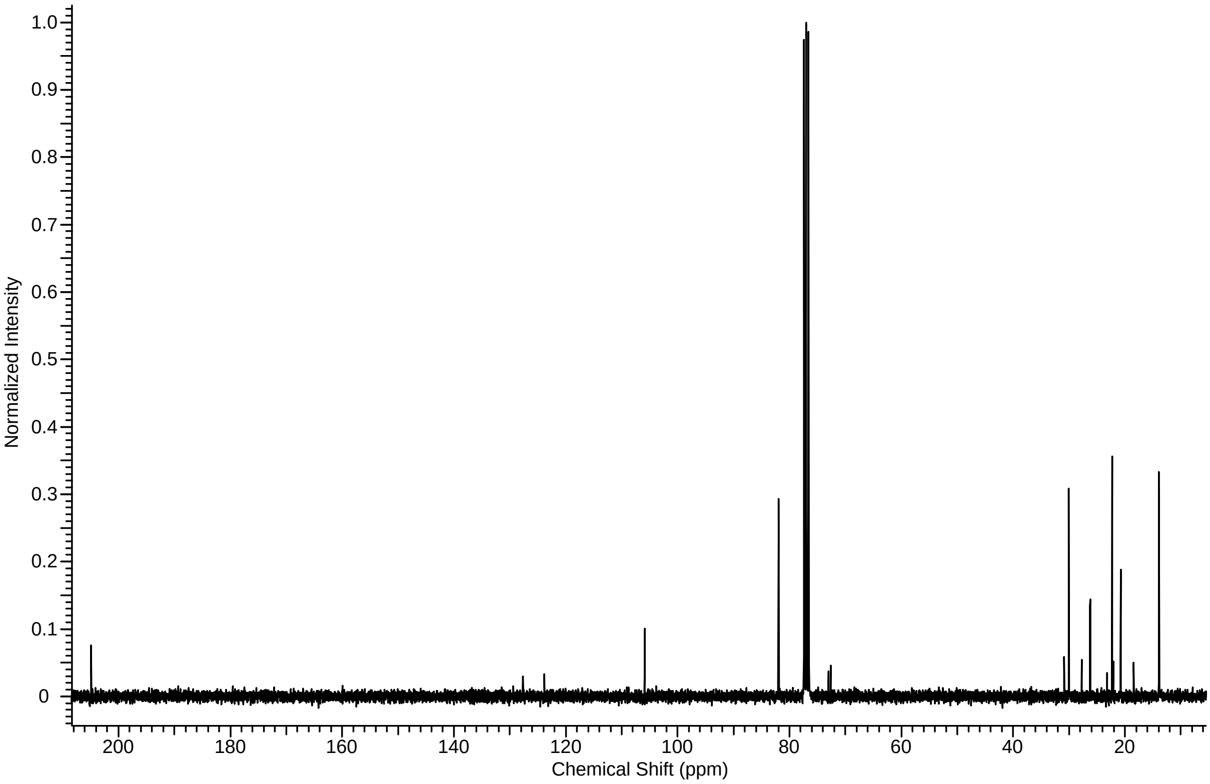
Chemical Shift (ppm)



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120
100
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60
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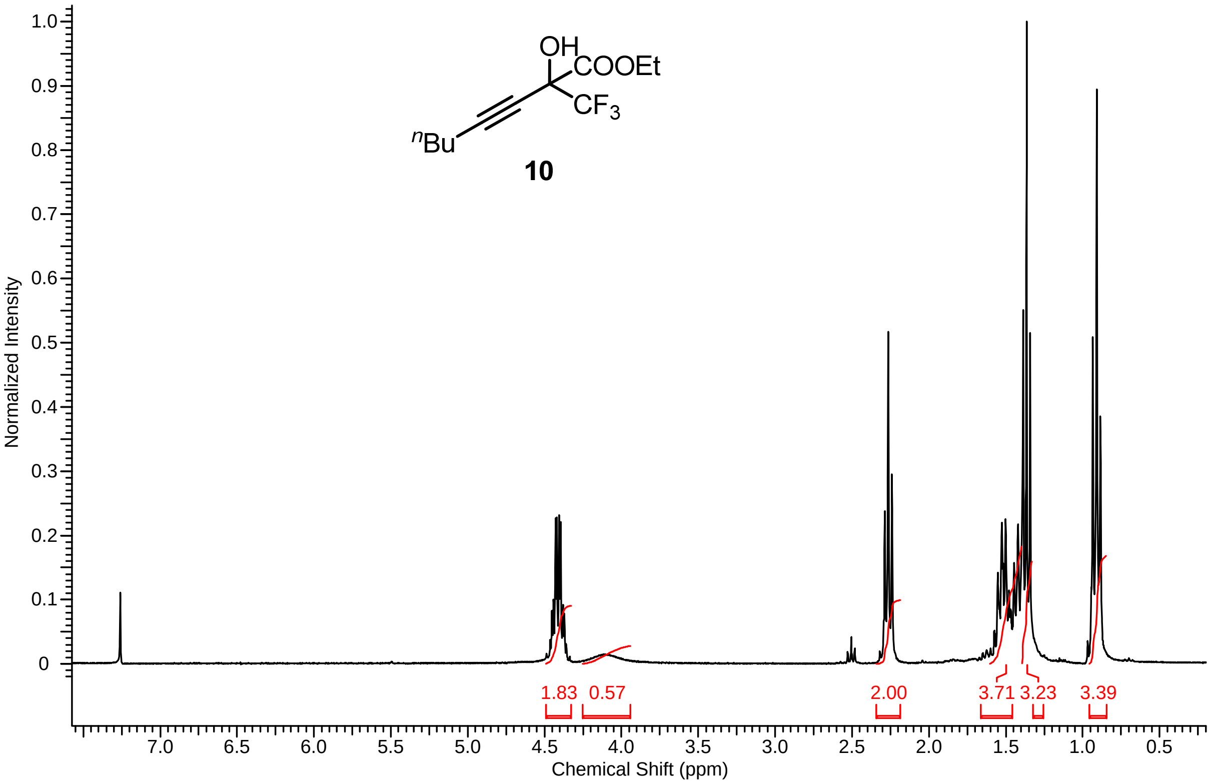
20
Chemical Shift (ppm)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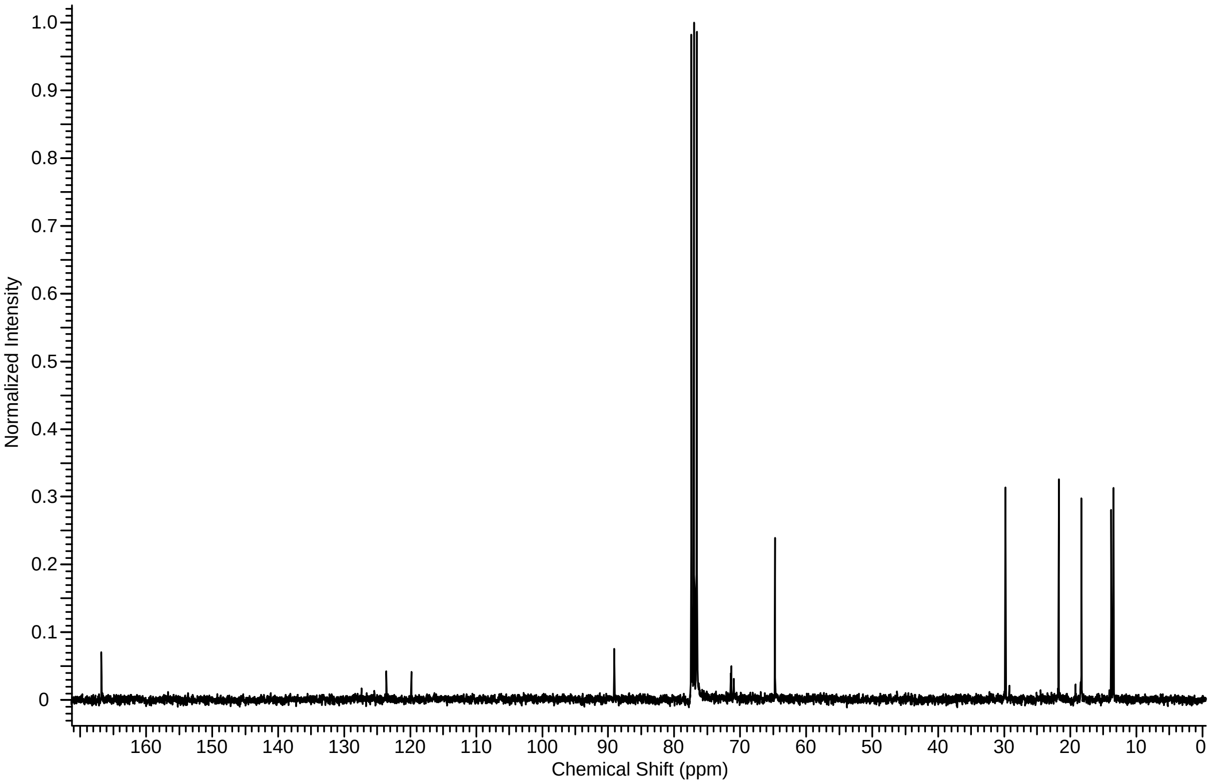
Chemical Shift (ppm)

10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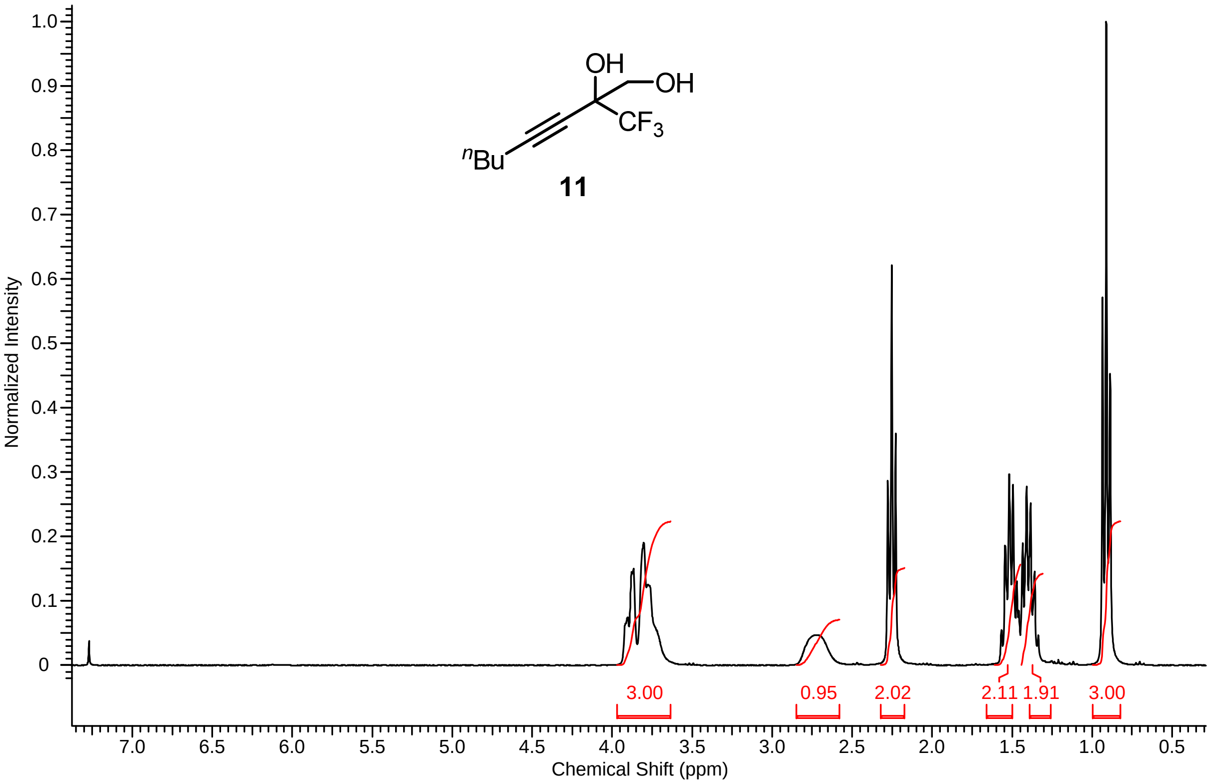
Chemical Shift (ppm)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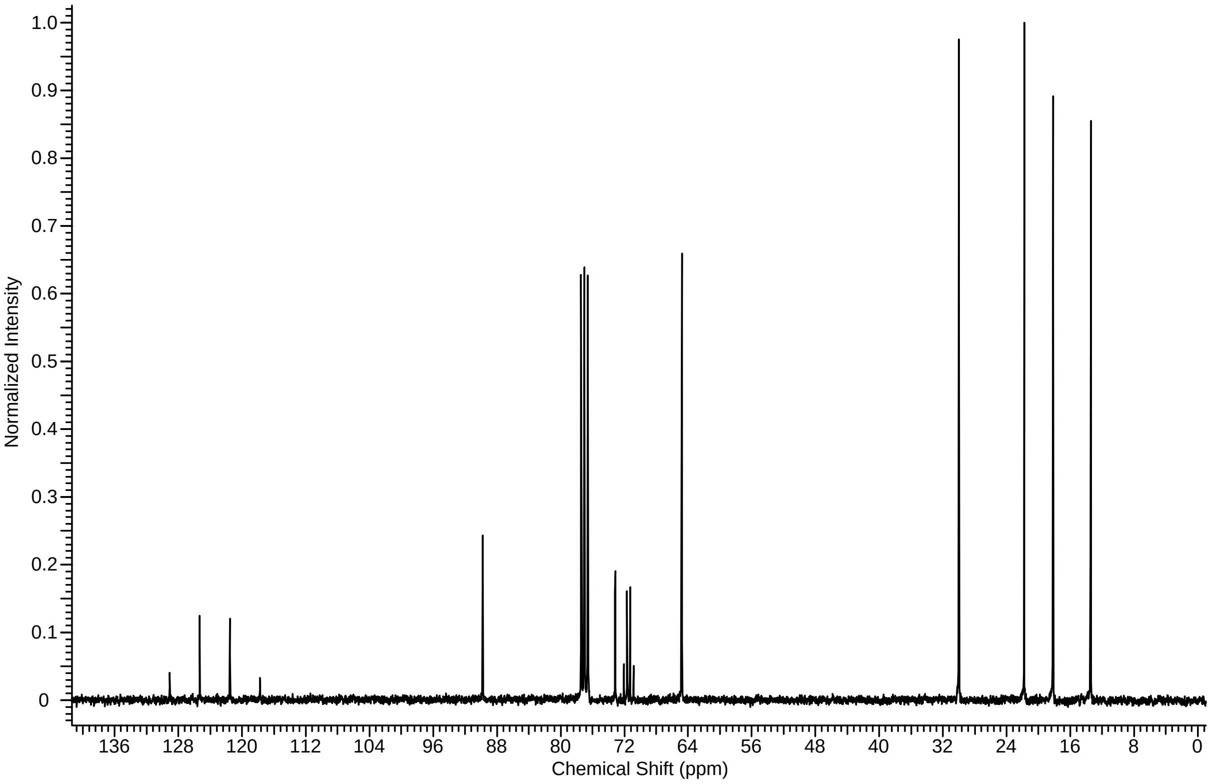
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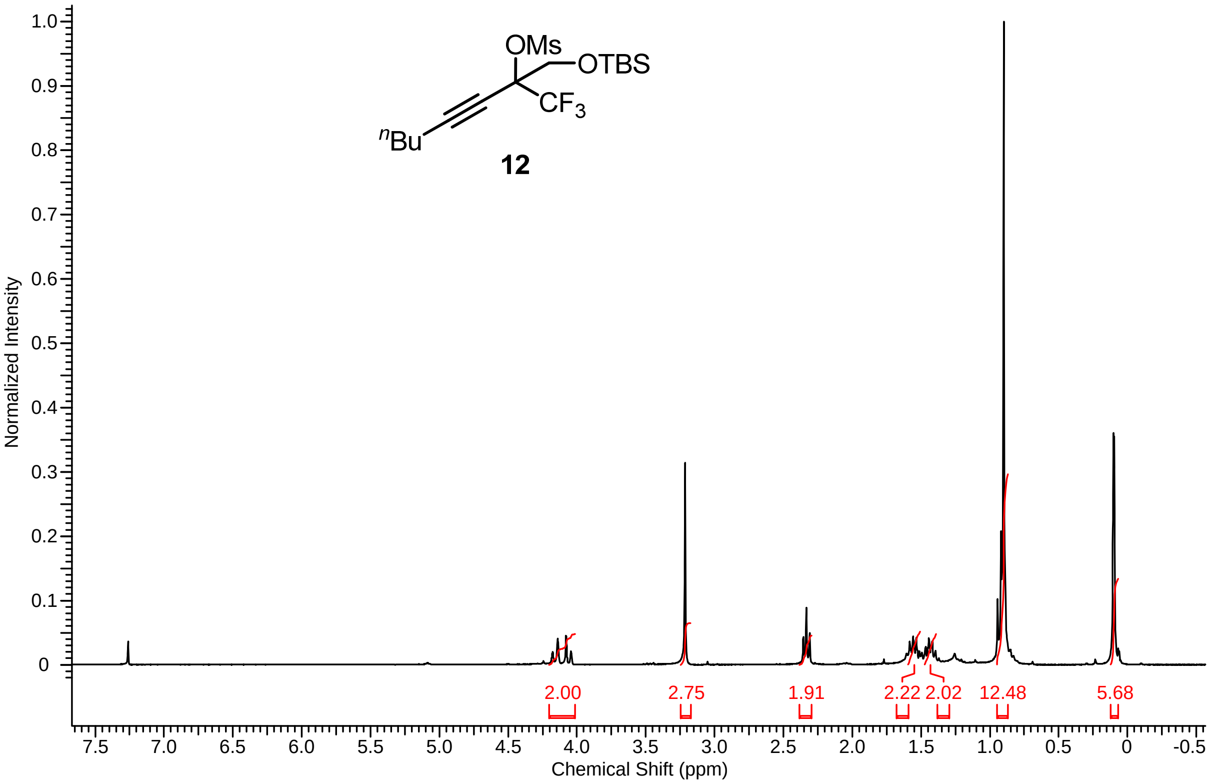
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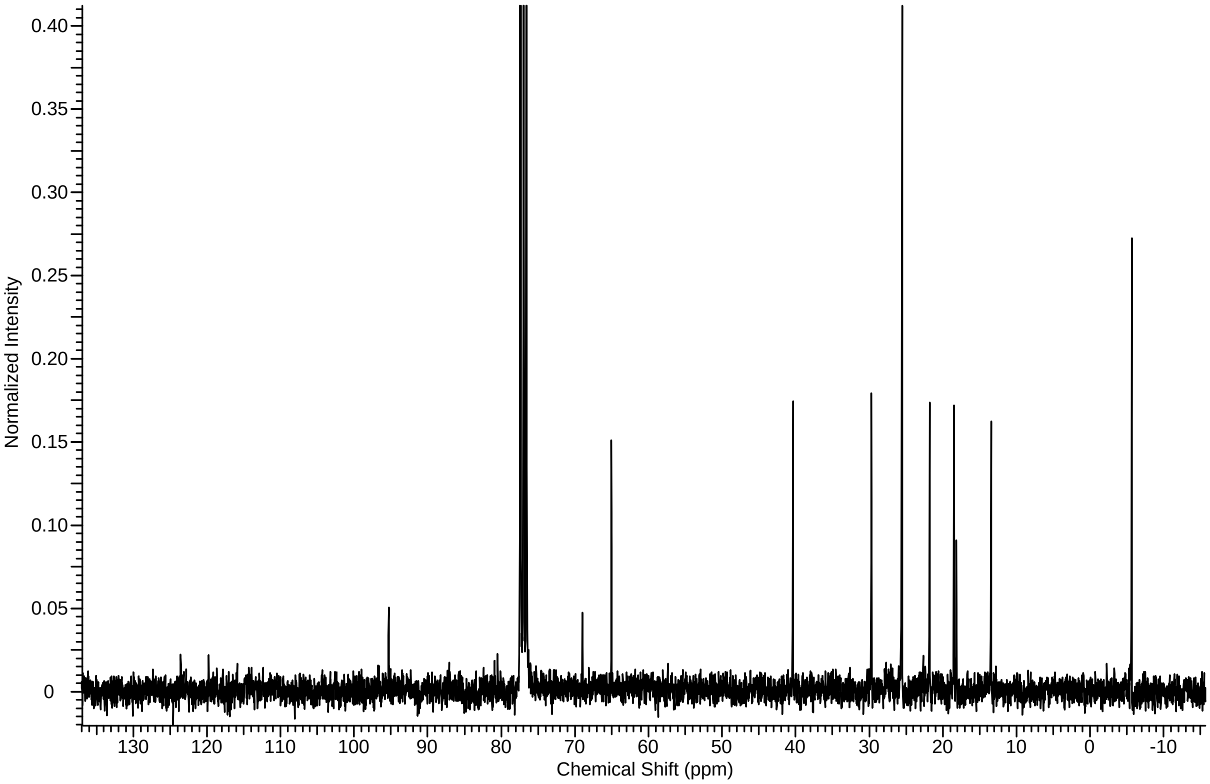
Chemical Shift (ppm)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30
20
10
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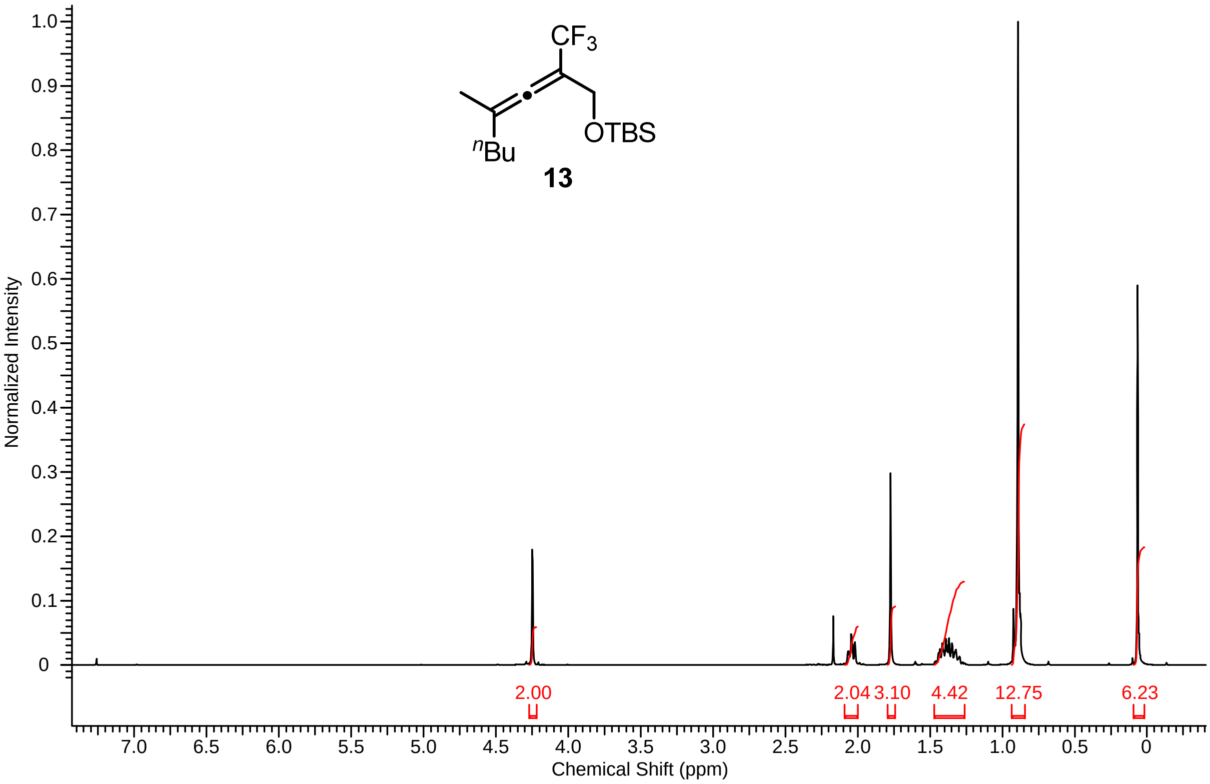
-10
Chemical Shift (ppm)


CF3
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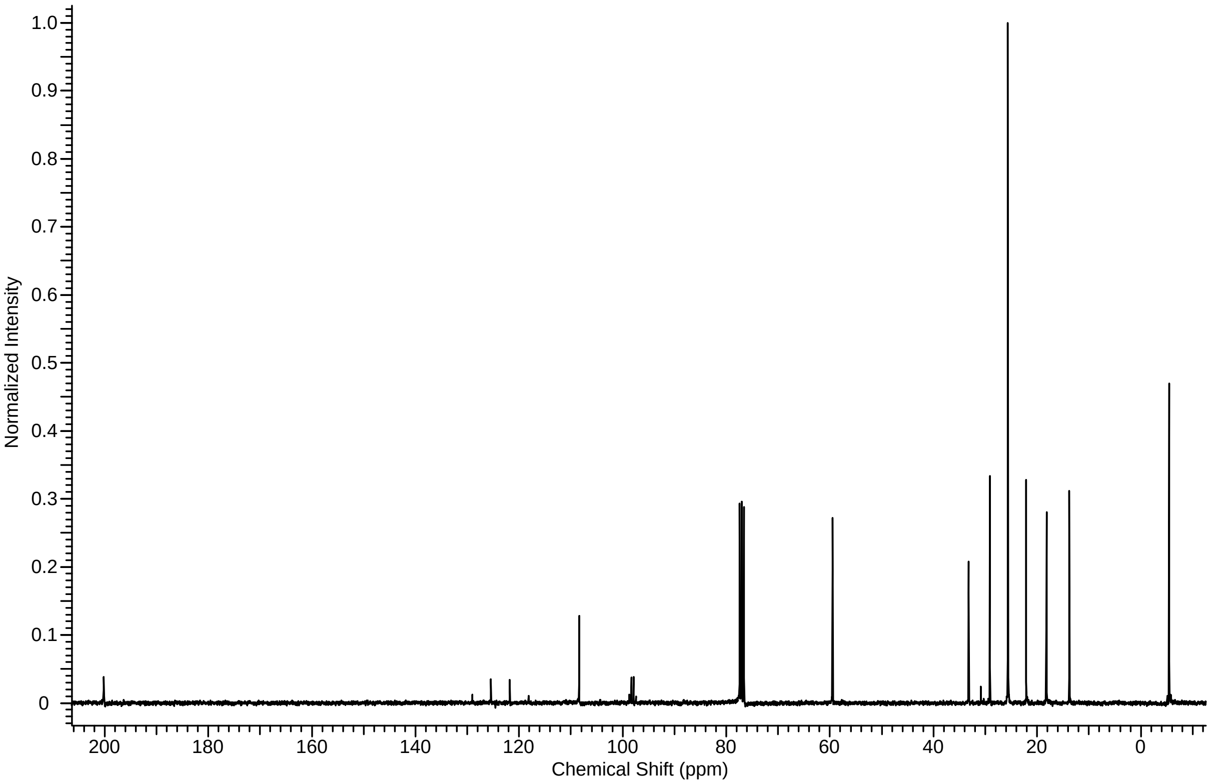
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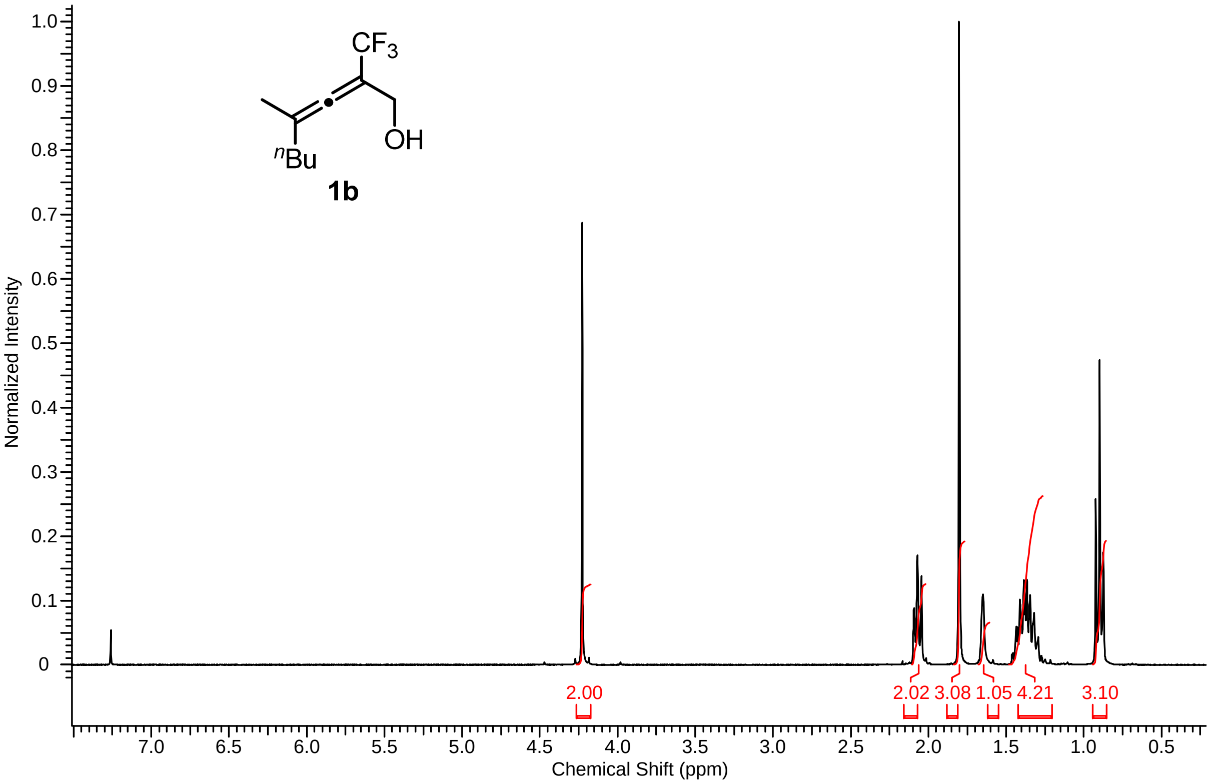
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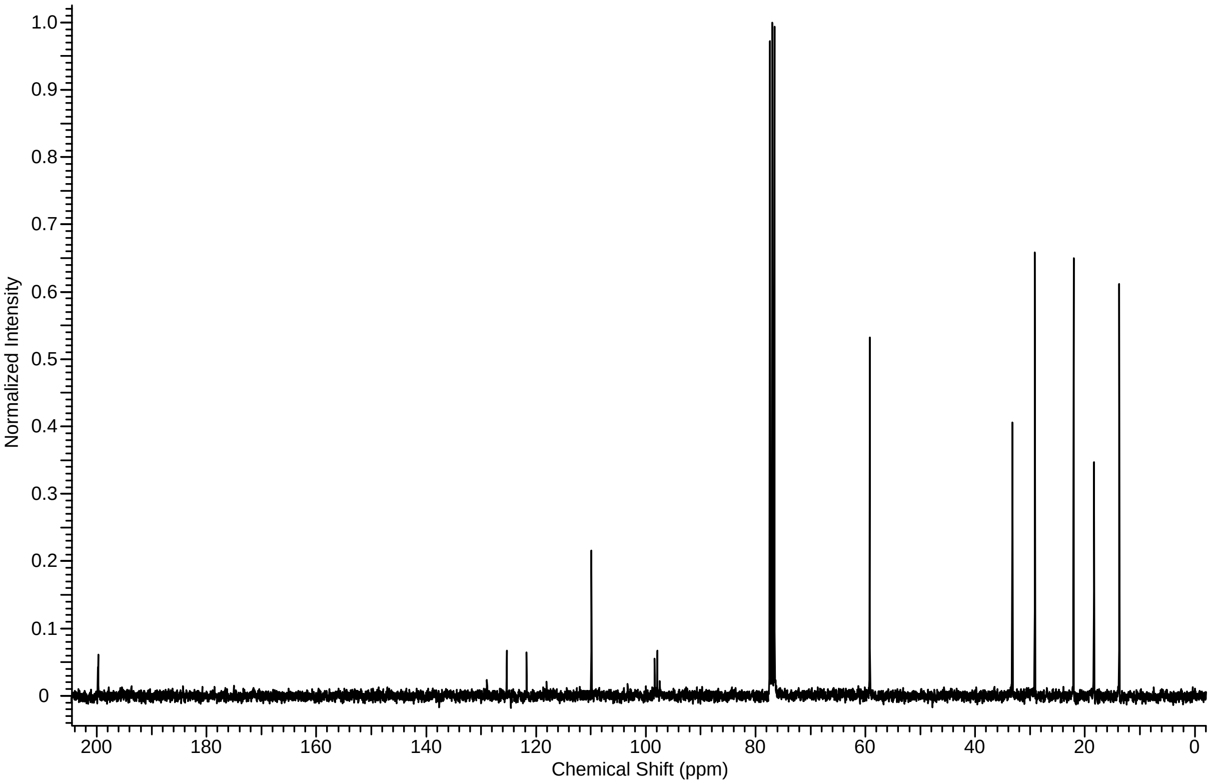
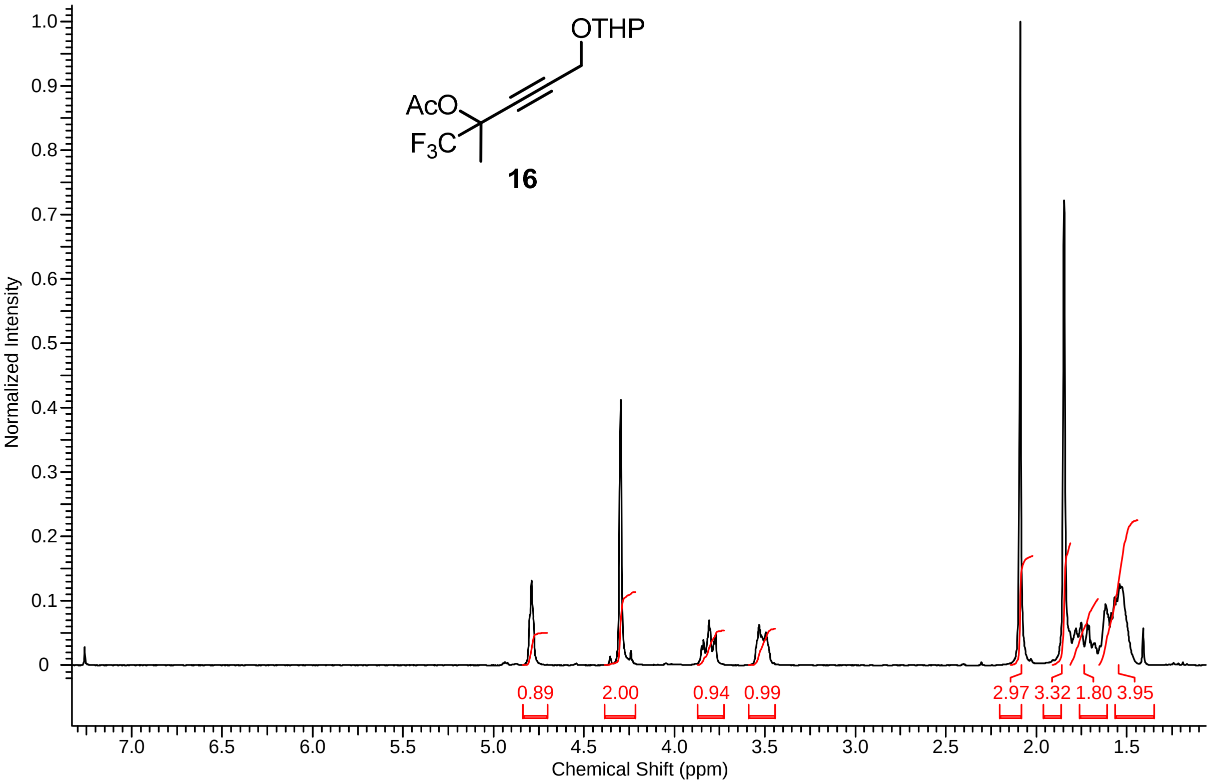
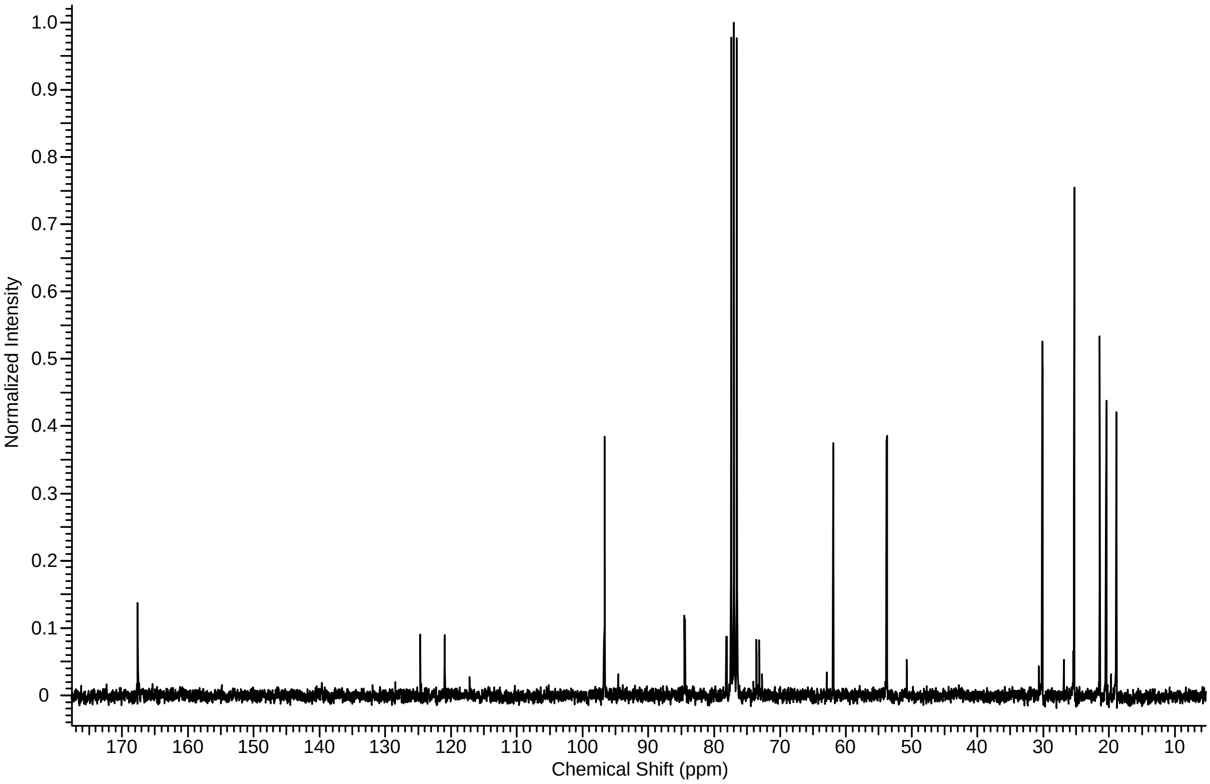
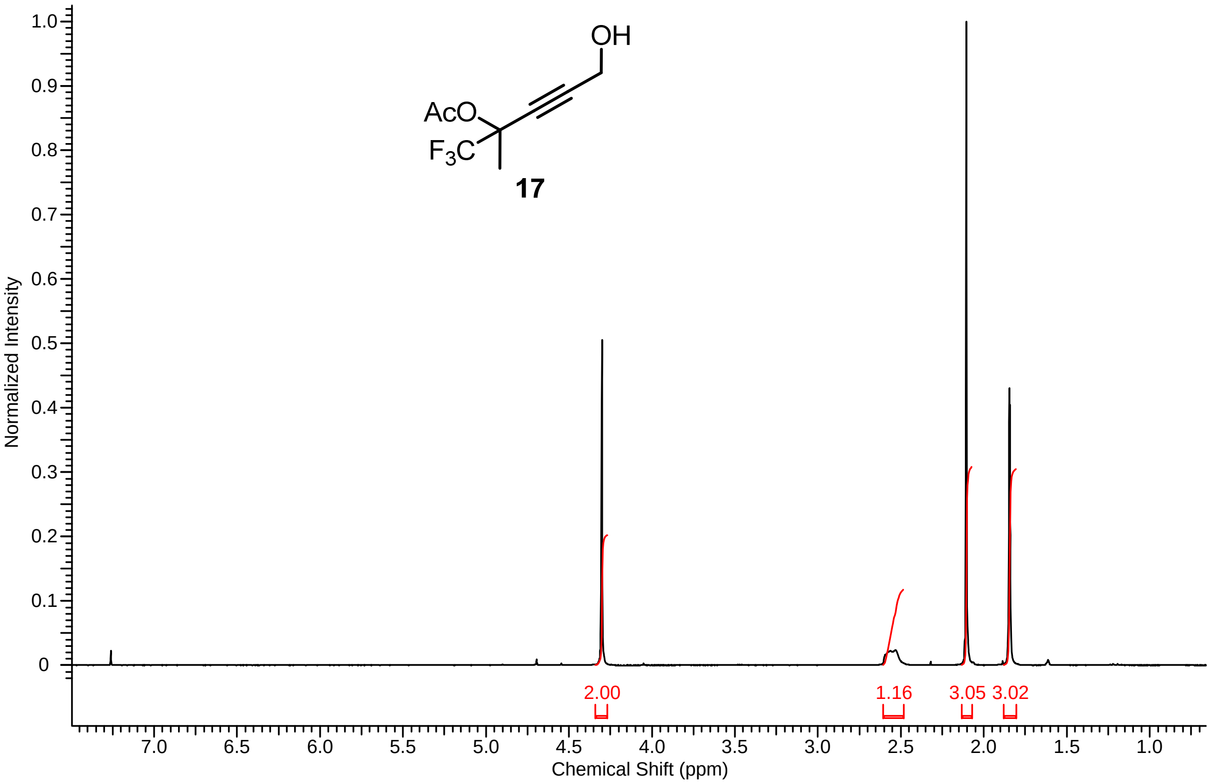
nBu
1b
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
2.00
2.02
3.08
1.05
4.21
3.10
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)


Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

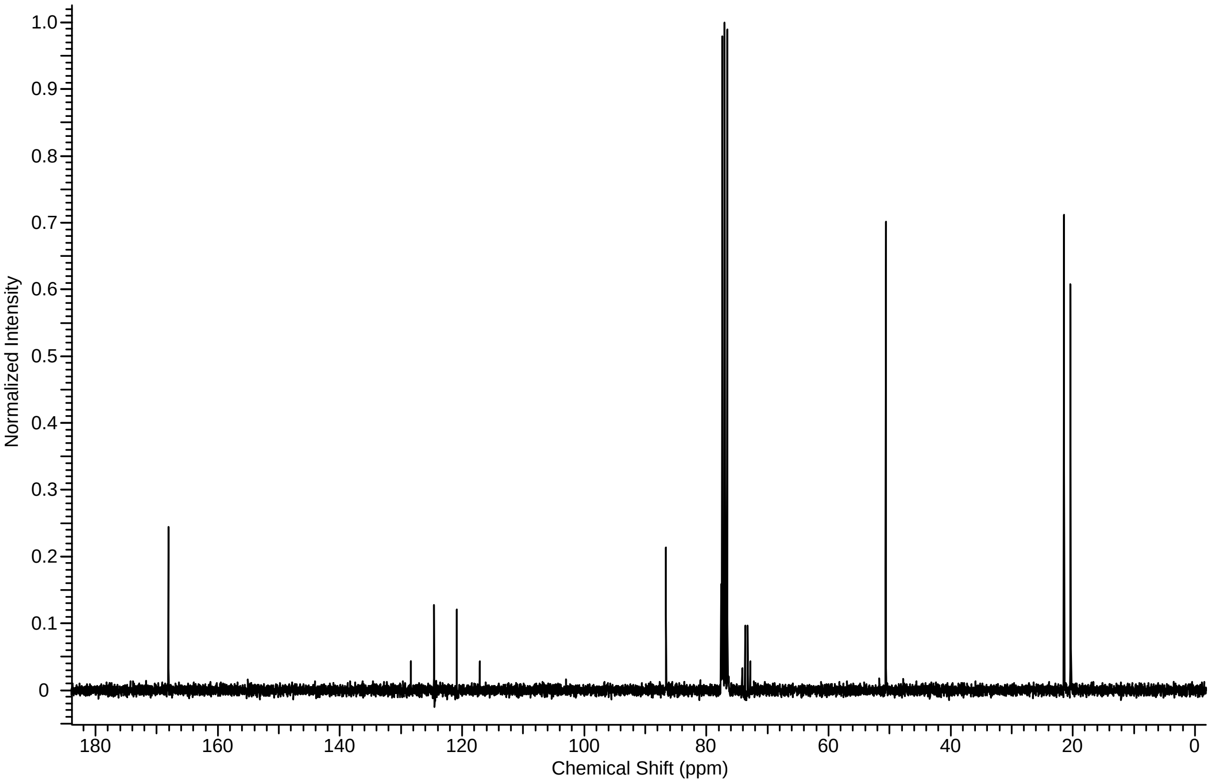

OTHP
AcO
F3C
16
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.89
2.00
0.94
0.99
2.97
3.32
1.80
3.95
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
Chemical Shift (ppm)


Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)

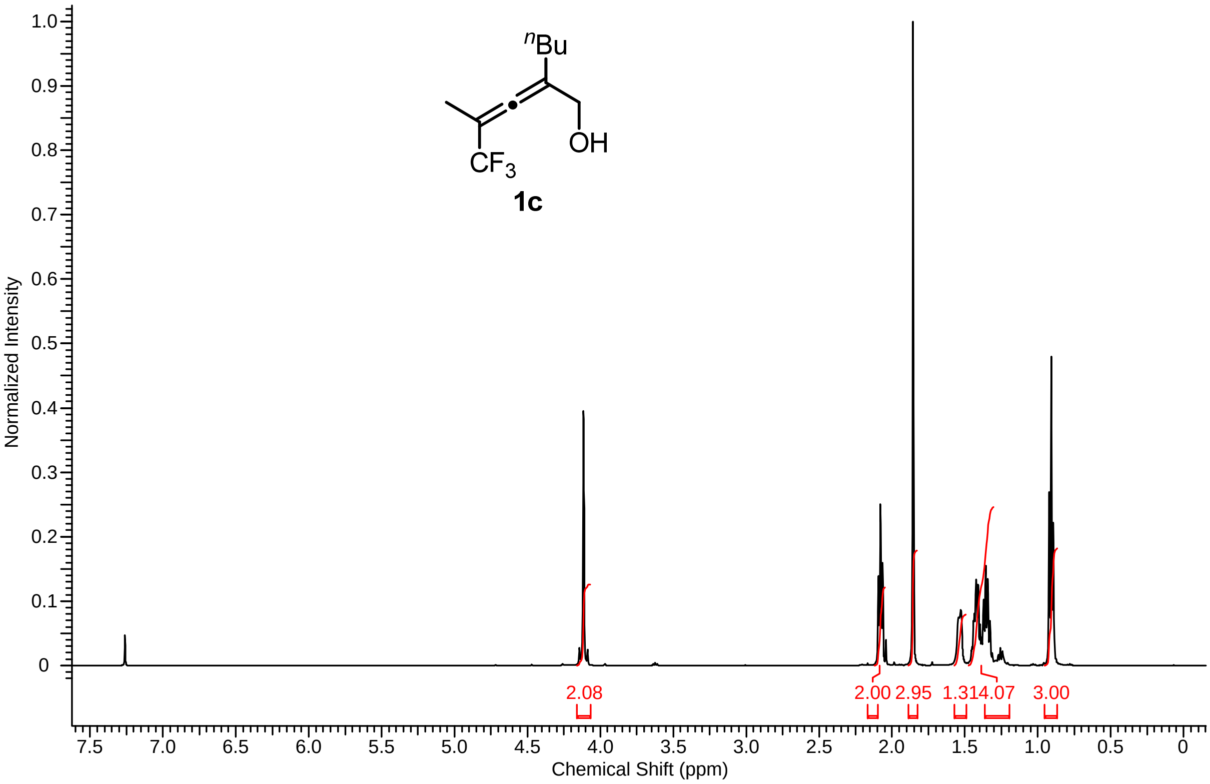


17

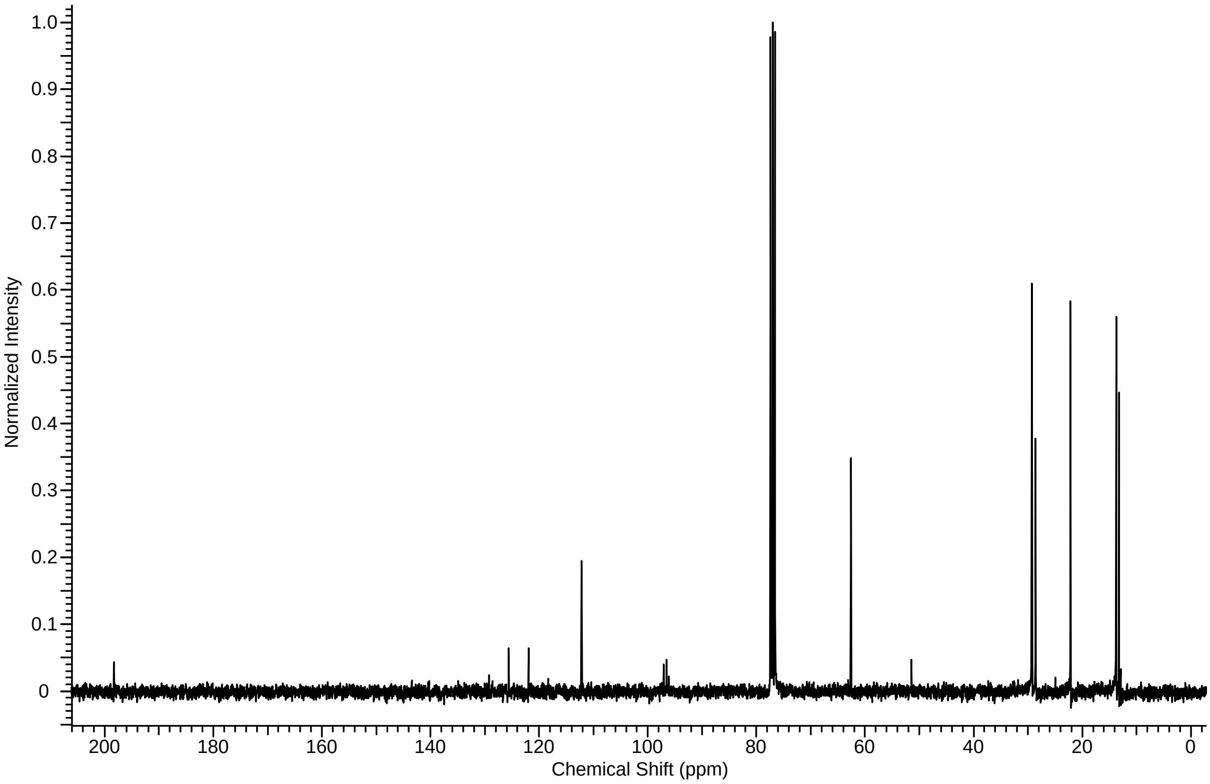
OH
AcO
F3C
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
2.00
1.16
3.05
3.02
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)



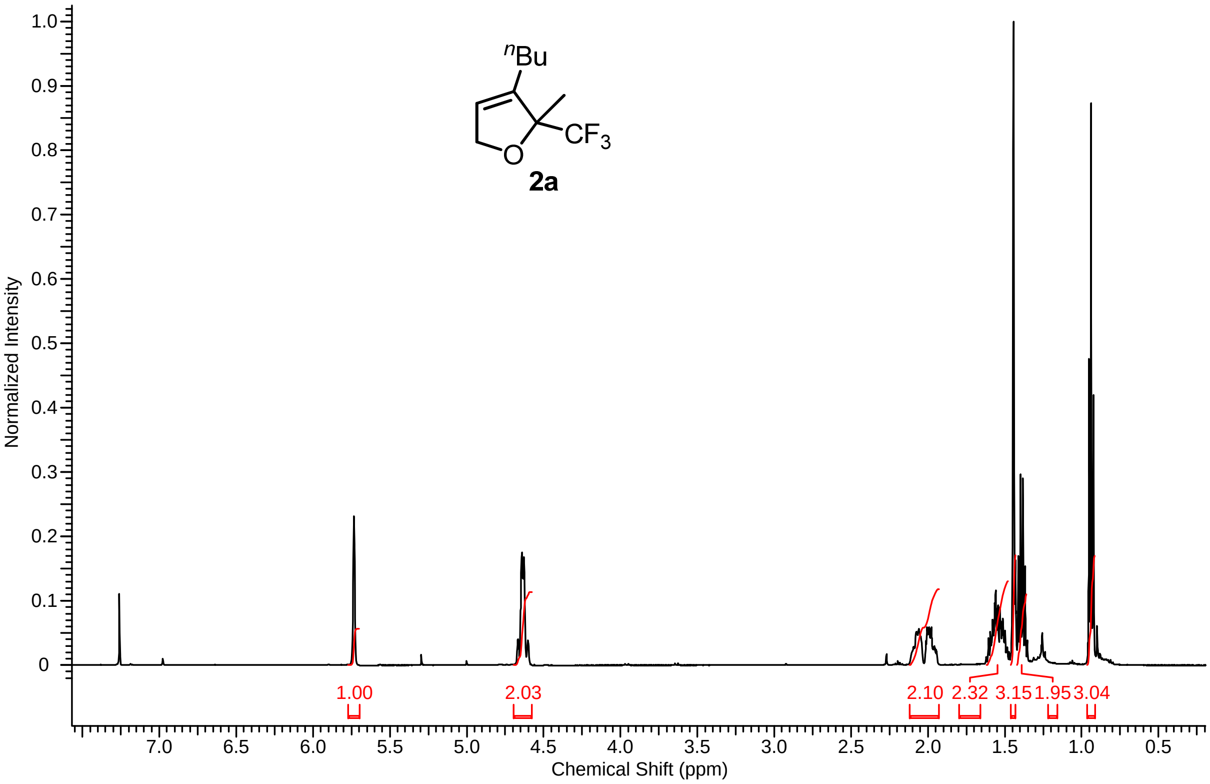
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



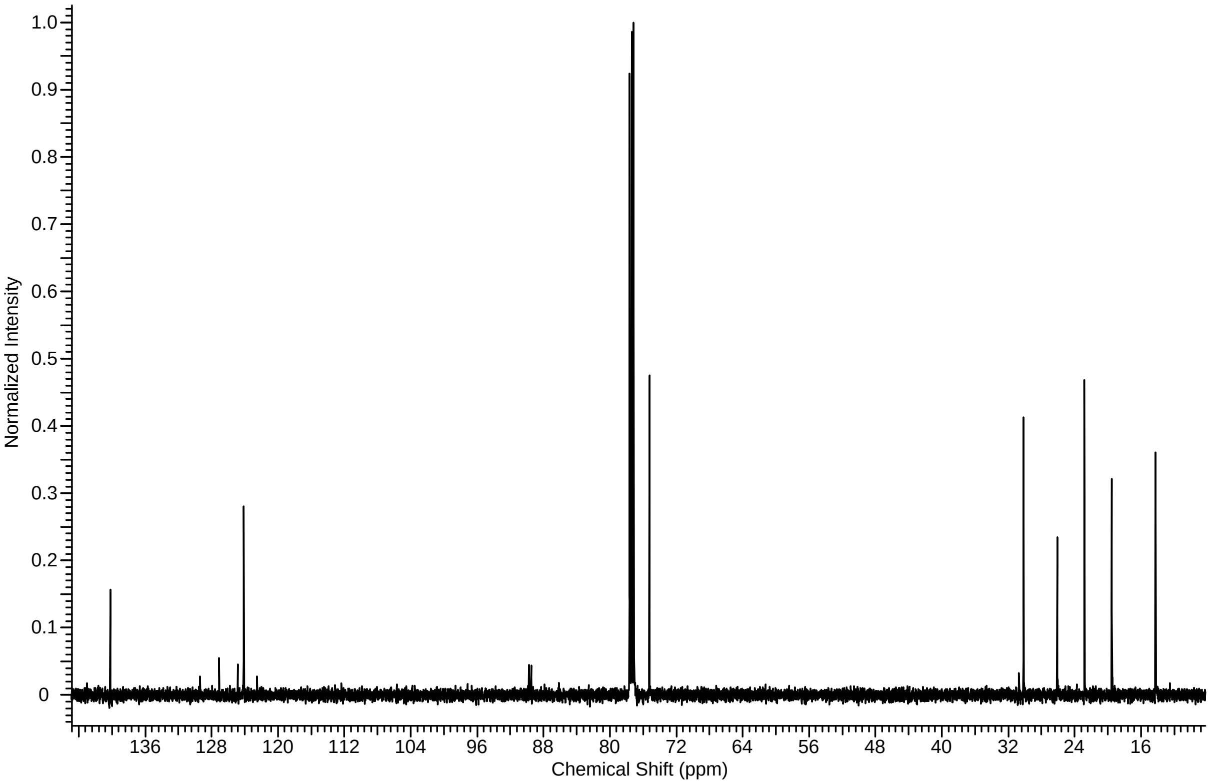
^{n}Bu
OH
CF$_3$
1c
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
2.08
2.00
2.95
1.31
4.07
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)



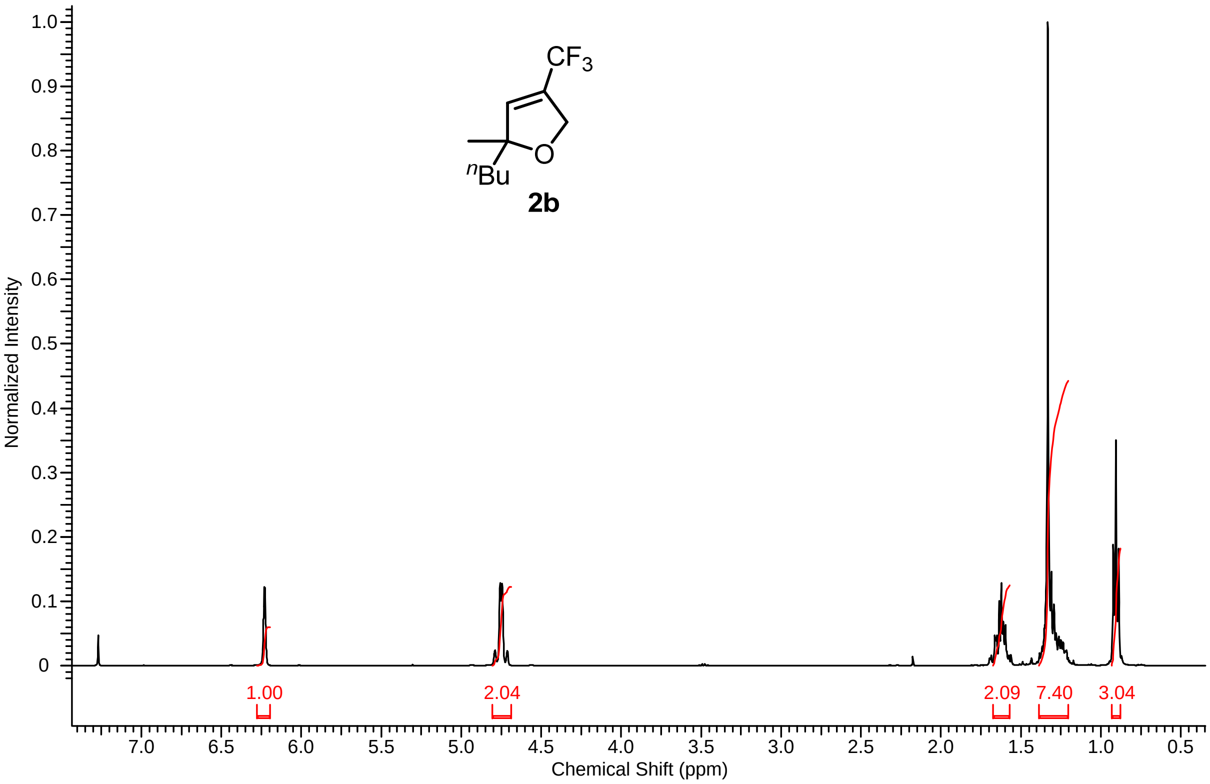
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

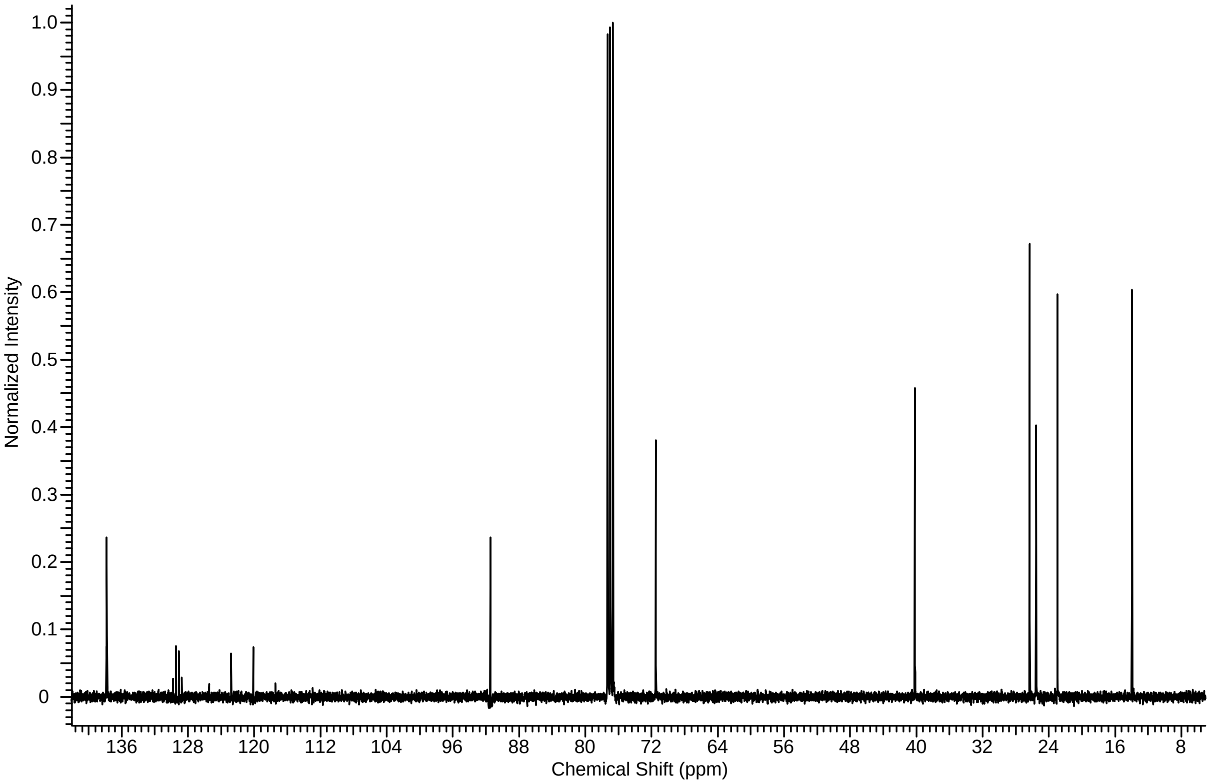


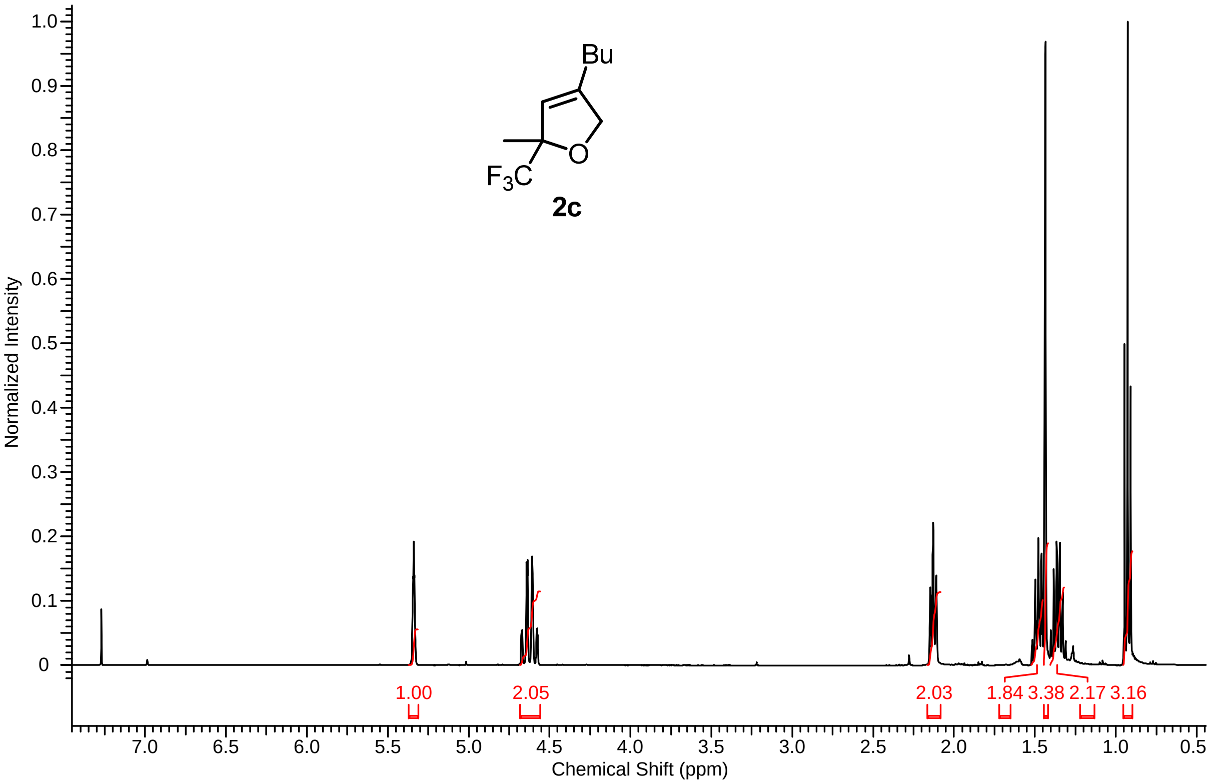
^{n}Bu
CF$_3$
O
2a
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1.00
2.03
2.10
2.32
3.15
1.95
3.04
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

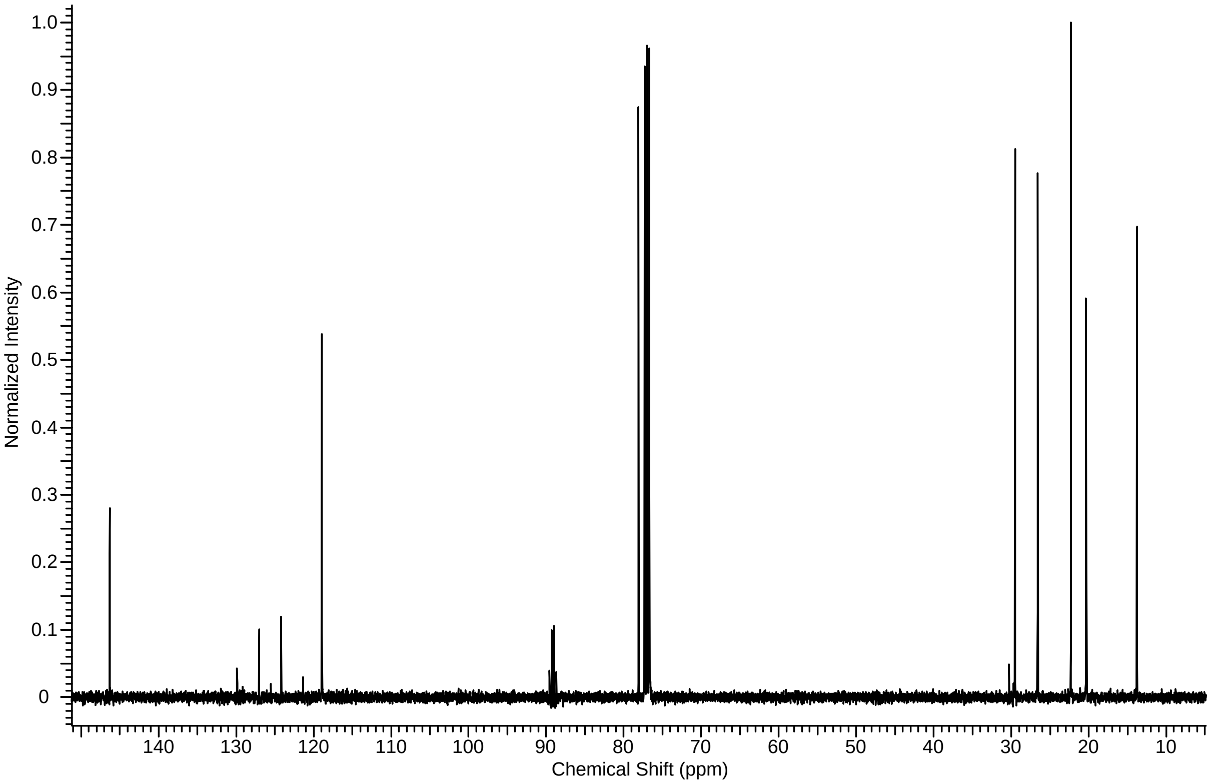


Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)


CF3
nBu
O
2b
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1.00
2.04
2.09
7.40
3.04
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
Chemical Shift (ppm)


Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


Bu
O
F3C
2c
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1.00
2.05
2.03
1.84
3.38
2.17
3.16
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
Chemical Shift (ppm)


Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)