Supporting Information

$B(C_6F_5)_3$-Catalyzed Allylation of Propargyl Acetates with Allylsilanes

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NMR spectra were recorded on Bruker Avance DPX-400 (400 MHz) and DRX-500 (500 MHz) instruments. GC/MS analyses were performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). The same GC system with FID (30 m x 0.25 mm capillary column, HP-5) was used for capillary GLC analyses. HR EI MS analysis was performed on a JEOL GCmate II mass spectrometer. Elemental analyses were made by Midwest Microlab, Indiana.

All manipulations were conducted under an argon atmosphere using a combination of glovebox and standard Schlenk techniques. Anhydrous ether, THF, dichloromethane, triethylamine, and pyridine were purchased from Aldrich and stored over calcium hydride. $B(C_3F_5)_3$ is commercially available, but for our purpose it was prepared according to the known procedure.[1] Compounds **1a**,[2] **1c**,[3] **4a**,[4] were prepared according to the known procedures. Preparation of other substrates is provided below.

The spectral data for new compounds **1d-s, 2c-m, 4b, 5b** are provided below, as well as for known compound **2a**,[5] **2b**,[6] **4a**,[4] **5a**[7] for which spectral data presented in literature are incomplete. (+) and (-) represent positive and negative intensities of signals in ^{13}C DEPT-135 experiment.

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(1) (a) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245. (b) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1966**, 5, 218.
(2) Spee, M. P. R.; Boersma, J.; Meijer, M. D.; Slagt, M. Q.; van Koten, G.; Geus, J. W. *J. Org. Chem.* **2001**, *66*, 1647.
(3) Fleming, I.; Higgins, D.; Lawrence, N. J.; Thomas, A. P. *J. Chem. Soc. Perkin Trans. 1* **1992**, 3331.
(4) Mahrwald, R.; Quint, S. *Tetrahedron* **2000**, *56*, 7463.
(5) Luzung, M. R.; Toste, F. D. *J. Am. Chem. Soc.* **2003**, *125*, 15760.
(6) Ma, S.-M.; Wang, L.-S. *Chin. J. Chem.* **1999**, *17*, 531.
(7) Renard, D.; Rezaei, H.; Zard, S. Z. *Syn. Lett.* **2002**, 1257.

1d: To a stirred solution of 4-phenylbut-3-yn-2-ol (**1a**) (731 mg, 5.0 mmol), pyridine (15.0 mmol, 1.2 mL), and DMAP (15 mg) in anhydrous CH_2Cl_2 (10 mL) at 0°C was slowly added pivaloyl chloride (10 mmol, 1.2 mL). The mixture was warmed to room temperature, and stirred overnight, quenched with 2M aqueous HCl, and extracted with ether. The combined etheral phases were washed (saturated aqueous $NaHCO_3$, brine), dried ($MgSO_4$), and concentrated in vacuum. The residue was purified by preparative column chromatography on Silica gel, eluent hexane-EtOAc (30:1). Yield 1.15 g (5.0 mmol, 100%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.30-7.27 (m, 3H), 5.67 (q, J = 6.4 Hz, 1H), 1.56 (d, J = 6.4 Hz, 3H), 1.23 (s, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 177.4, 131.8 (+), 128.5 (+, 2C), 128.3 (+, 2C), 122.5, 87.7, 84.3, 60.6 (+), 38.7, 27.1 (+, 3C), 21.4 (+); GC/MS *m/z* 230 (M^+, 4.8%), 174 (M^+- C_4H_8), 128 (M^+-$(CH_3)_3CCOOH$, 100%).

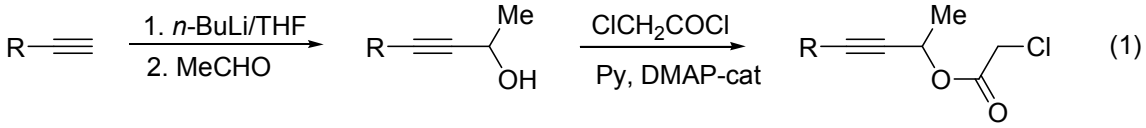
1e: To a stirred solution of **1a** (1.46 g, 10.0 mmol), triethylamine (16.0 mmol, 2.2 mL), and DMAP (15 mg) in anhydrous hexane (15 mL) at 0°C was slowly added trifluoroacetic anhydride (15.0 mmol, 2.1 mL). The mixture was warmed up to room temperature and quenched with ice-cold water and extracted with CH_2Cl_2. The combined organic phases were (with ice-cold water, brine), dried ($MgSO_4$), filtered, and concentrated in vacuum. The residue was purified by distillation in vacuum, bp 62°C (1 mm Hg). Yield 1.40 g (5.78 mmol, 58%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.48-7.46 (m, 2H), 7.37-7.32 (m, 3H), 5.83 (q, J = 6.6 Hz, 1H), 1.73 (d, J = 6.6 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 157.0 (q, $^2J_{CF}$ = 42.6 Hz), 132.4 (+, 2C), 129.6 (+), 128.8 (+, 2C), 121.9, 114.8 (q, $^1J_{CF}$ = 284.9 Hz), 87.3, 85.0, 66.0 (+), 21.6 (+); GC/MS *m/z* 242 (M^+, 18%), 173 (M^+-CF_3, 8.6%), 128 (M^+-F_3CCOOH, 100%).

1f: To a stirred solution of **1a** (1.46 g, 10.0 mmol), pyridine (30.0 mmol, 2.4 mL), and DMAP (15 mg) in anhydrous CH_2Cl_2 (15 mL) at 0°C was slowly added trichloroacetic anhydride (15.0 mmol, 2.1 mL). The mixture was warmed to room temperature, and stirred overnight, quenched with diluted aqueous HCl, and extracted with CH_2Cl_2. Combined organic phases were washed (10% aq. Na_2CO_3, brine), dried ($MgSO_4$), filtered and concentrated in vacuum. The residue was purified by preparative column chromatography on Silica gel, eluent hexane-EtOAc (50:1). Yield 2.19 g (7.50 mmol, 75%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.50-7.47 (m, 2H), 7.37-7.31 (m, 3H), 5.80 (q, J = 7.0 Hz, 1H), 1.75 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 160.9, 132.0 (+), 129.1 (+, 2C), 128.4 (+, 2C), 121.7, 89.8, 86.8, 85.0, 66.7 (+), 21.1 (+); GC/MS *m/z* 290 (M^+, 1.4%), 255 (M^+-Cl, 19%), 128 (M^+-Cl_3CCOOH, 100%).

1g: To a stirred solution of **1a** (2.92 g, 20.0 mmol), pyridine (28.0 mmol, 2.3 mL), and DMAP (10 mg) in anhydrous CH_2Cl_2 (20 mL) at 0°C was slowly added chloroacetyl chloride (24.0 mmol, 1.9 mL). The mixture was warmed to room temperature, and stirred overnight, quenched with 2M aqueous HCl, and extracted with ether. The combined etheral phases were washed (saturated aqueous $NaHCO_3$, brine), dried ($MgSO_4$), and concentrated in vacuum. The residue was purified by preparative column chromatography on Silica gel, eluent hexane-EtOAc (30:1). Yield 3.44 g (15.4 mmol, 77%). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.46-7.43 (m, 2H), 7.33-7.28 (m, 3H), 5.75 (q, J = 6.7 Hz, 1H), 4.10 (s, 2H), 1.62 (d, J = 6.7 Hz, 3H); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ

166.3, 131.9 (+, 2C), 128.9 (+), 128.3 (+, 2C), 121.9, 86.4, 85.5, 62.9 (+), 41.0 (-), 21.4 (+); GC/MS *m/z* 222 (M^+, 5%), 187 (M^+-Cl, 45%), 128 (M^+-$ClCH_2COOH$, 100%).

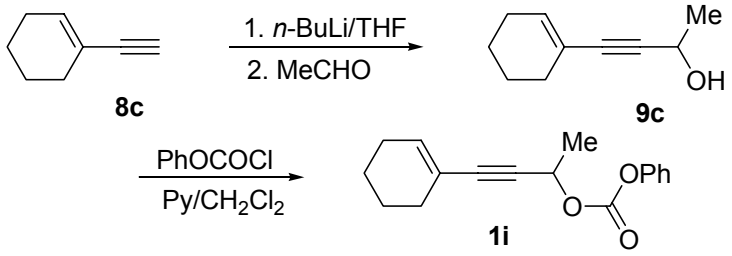
1h: To a stirred solution of **1a** (731 mg, 5.0 mmol) and pyridine (10.0 mmol, 0.81 mL) in anhydrous CH_2Cl_2 (15 mL) at 0°C was slowly added phenyl chloroformate (10.0 mmol, 1.3 mL). Standard aqueous work-up (see procedure for preparation of **1g**), and purification by preparative column chromatography on Silica gel (eluent hexane-EtOAc 20:1) gave 1.26 g (4.73 mmol, 95%) of **1h**. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.43-7.38 (m, 2H), 7.35-7.30 (m, 2H), 7.29-7.26 (m, 1H), 7.25-7.21 (m, 2H), 5.67 (q, *J* = 6.6 Hz, 1H), 1.73 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 153.2, 151.5, 132.4 (+, 2C), 129.9 (+, 2C), 129.3 (+), 128.7 (+, 2C), 126.5 (+), 122.4, 121.5 (+, 2C), 86.6, 86.4, 66.2 (+), 22.0 (+);



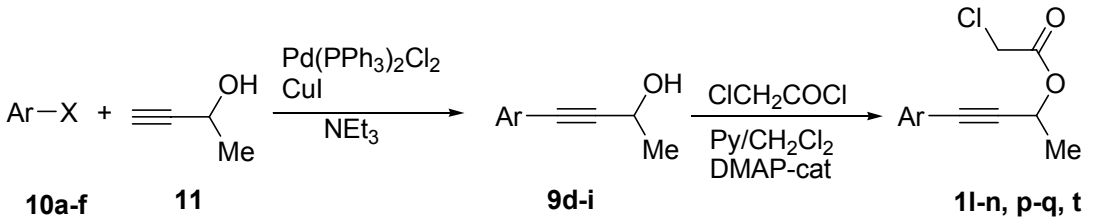
8a: R = $(CH_2)_3Cl$ **9a**: R = $(CH_2)_3Cl$ **1j**: R = $(CH_2)_3Cl$
8b: R = TIPS **9b**: R = TIPS **1k**: R = TIPS

1j: To a stirred solution of 5-chloropentyne **8a** (524 μL, 5.0 mmol) in anhydrous THF (10 mL) at -78°C was added n-BuLi (2.5M in hexane, 2.2 mL, 5.5 mmol). The mixture was stirred for 30 min at -78°C and quenched with ethanal (600 μL, 10.6 mmol). Saturated aqueous NH_4Cl was added, and the mixture was extracted (ether), washed (water, brine), dried ($MgSO_4$), filtered, and concentrated in vacuum. The obtained crude propargylic alcohol **9a** was converted into chloroacetate **1j** according to procedure described above for the preparation of **1g**. Yield 981 mg (4.4 mmol, 88%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 5.49 (qt, *J* = 6.6 Hz, 1.5 Hz, 1H), 4.06 (s, 2H), 3.62 (t, *J* = 6.3 Hz, 2H), 2.40 (td, *J* = 6.9 Hz, 1.5 Hz, 2H), 1.95 (ps-quintet, *J* = 6.6 Hz, 2H), 1.50 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 166.7, 84.9, 79.2, 63.2 (+), 43.9 (-), 41.3 (-), 31.4 (-), 22.0 (+), 16.5 (-); GC/MS *m/z* 187 (M^+-Cl, 45%), 100 (75%), 77 (100%).

1k: Similar procedure starting from triisopropylsilylacetylene **8b** gave chloroacetate **1k**. Yield 1.29 g (4.26 mmol, 85%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 5.54 (q, *J* = 6.6 Hz, 1H); 4.07 (m, 2H), 1.54 (d, *J* = 6.6 Hz, 3H), 1.07-1.03 (m, 21H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 166.2, 104.5, 87.0, 62.8 (+), 40.9 (-), 21.5 (+), 18.5 (+, 6C), 11.0 (+, 3C); GC/MS *m/z* 259 (M^+-$(CH_3)_2CH$, 11%), 207 (11%), 165 (18%), 123 (35%), 109 (47%), 95 (100%).



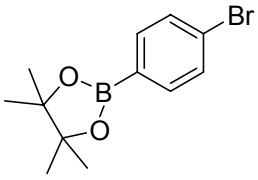
1i: To a stirred solution of 1-ethynylcyclohexene **8c** (0.6 mL, 5 mmol) in anhydrous THF (10 mL) at -78°C was added n-BuLi (2.5M in hexane, 2.2 mL, 5.5 mmol). The mixture was stirred for 30 min at -78°C and quenched with ethanal (0.55 mL, 10 mmol). Saturated aqueous NH_4Cl was added, and the mixture was extracted (ether), washed (water, brine), dried ($MgSO_4$), filtered, and concentrated in vacuum. The obtained crude alcohol **9c** was transformed into phenylcarbonate **1i** according to procedure described above for the preparation of **1h**. Yield 1.314 g (4.86 mmol, 97%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.40-7.37 (m, 2H), 7.26-7.23 (m, 1H), 7.21-7.19 (m, 2H), 6.17 (tt, *J* = 4.0 Hz, 1.8 Hz, 1H), 5.55 (q, *J* = 6.6 Hz, 1H), 2.14-2.07 (m, 4H), 1.63 (d, *J* = 6.6 Hz, 3H), 1.65-1.61 (m, 2H), 1.61-1.55 (m, 2H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 153.2, 151.5, 136.9 (+), 129.9 (+, 2C), 126.4 (+), 121.3 (+, 2C), 120.1, 88.2, 83.9, 66.4 (+), 29.3 (-), 26.0 (-), 22.6 (-), 22.1 (+), 21.8 (-); GC/MS *m/z* 270 (M^+, 2%), 226 (M^+-CO_2, 5%), 133 (M^+-$PhOCO_2$, 100%).



10a-f **11** **9d-i** **1l-n, p-q, t**

10a, **9d**, **1l**: Ar = *p*-PB-C_6H_4; **10a**: X = Br
10b, **9e**, **1m**: Ar = *p*-$CF_3C_6H_4$; **10b**: X = Br
10c, **9f**, **1n**: Ar = *o*-FC_6H_4; **10c**: X = I
10d, **9g**, **1p**: Ar = *p*-$EtOCOC_6H_4$; **10d**: X = Br
10e, **9h**, **1q**: Ar = *p*-$O_2NC_6H_4$; **10e**: X = Br
10f, **9i**, **1t**: Ar = *p*-MeC_6H_4; **10f**: X = I

1l: Ar = *p*-PB-C_6H_4



1l: $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol), CuI (38mg, 0.2 mmol), and **10a**[8] (1.42 g, 5 mmol) were dissolved in dry Et_3N (10 mL) and **11** (590 μL, 7.5 mmol) was added to the solution. The reaction was heated to 80°C and stirred overnight. When **10a** had been consumed, the reaction was cooled to room temperature and quenched with 2M aqueous HCl. The mixture was extracted (CH_2Cl_2), washed (sat. $NaHCO_3$, brine), dried ($MgSO_4$), filtered, and concentrated in vacuum. The crude alcohol **9d** was converted to the chloroacetate **1l** according to procedure described above for the preparation of **1g**. Yield 0.872 g (2.5 mmol, 50%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 7.7 Hz, 2H), 5.76 (q, *J* = 6.7 Hz, 1H), 4.12 (s, 2H), 1.63 (d, *J* = 6.7 Hz, 3H), 1.34 (s, 12H); ^{13}C NMR (125.76 MHz, $CDCl_3$)[9] δ 166.7, 134.9 (+, 2C), 131.4 (+, 2C), 124.9, 87.9, 86.0, 84.4 (2C), 63.3 (+), 41.4 (-), 25.3 (+, 4C), 21.8 (+); ^{11}B NMR (160.46

(8) Koolmeister, T.; Sodergren, M.; Scobie, M. *Tetrahedron Lett.* **2002**, *43*, 5965.
(9) Signal of the aromatic quaternary carbon next to boron atom cannot be observed in the spectrum recorded at room temperature due to extreme broadening, caused by quick relaxation of the ^{13}C nuclei *via* the ^{13}C/^{11}B dipole/quadrupole interaction.

MHz, $CDCl_3$) δ 30.6; GC/MS *m/z* 348 (M^+, <1%), 313 (M^+-Cl, 7%), 254 (M^+-$ClCH_2COOH$, 45%), 168 (50%), 154 (100%).

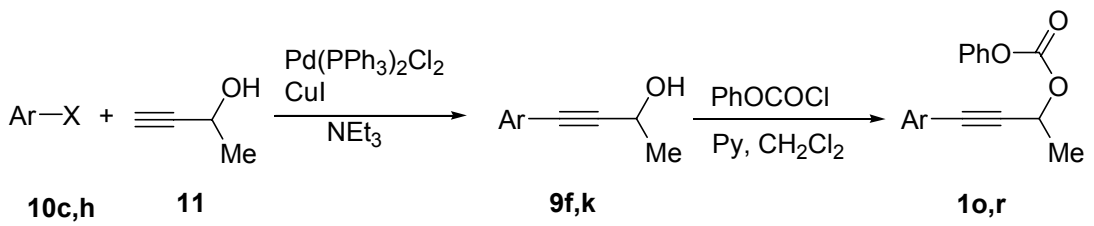
1m: Similar procedure starting from **10b** gave chloroacetate **1m**. Yield 1.15 g (3.95 mmol, 79%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 5.75 (q, *J* = 6.6 Hz, 1H), 4.12 (s, 2H), 1.64 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 166.3, 132.1 (+, 2C), 130.4, 125.7, 125.2 (+, q, $^3J_{CF}$ = 3.7 Hz), 123.8 (q, $^1J_{CF}$ = 271.9 Hz), 88.7, 84.0, 62.6 (+), 40.8 (-), 21.2 (+); ^{19}F NMR (470.59 MHz, $CDCl_3$) δ -64.5; GC/MS *m/z* 290 (M^+, 8%), 271 (M^+-F, 4%), 255 (M^+-Cl), 241 (M^+-CH_2Cl), 196 (M^+-$ClCH_2COOH$, 100%), 177 (61%), 145 ($F_3CC_6H_4^+$, 40%), 128 (70%).

1n: Similar procedure starting from **10c** gave chloroacetate **1n**. Yield 0.999 g (4.15 mmol, 83%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.43 (td, *J* = 7.7 Hz, 1.5 Hz, 1H), 7.34-7.29 (m, 1H), 7.09 (t, *J* = 7.7 Hz, 1H), 7.06 (t, *J* = 8.5 Hz, 1H), 5.78 (q, *J* = 6.6 Hz, 1H), 4.12 (s, 2H), 1.64 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 166.7, 163.4 (d, $^1J_{CF}$ = 251.5 Hz), 134.2 (+), 131.1 (+, d, $^3J_{CF}$ = 7.4 Hz), 124.4 (+, d, $^3J_{CF}$ = 3.7 Hz), 115.9 (+, d, $^2J_{CF}$ = 22.2 Hz), 110.9 (d, $^2J_{CF}$ = 14.8 Hz), 91.8 (d, $^3J_{CF}$ = 2.8 Hz), 79.4, 63.3 (+), 41.3 (-), 21.7 (+); ^{19}F NMR (470.59 MHz, $CDCl_3$) δ -111.2; GC/MS *m/z* 240 (M^+, 7%), 205 (M^+-Cl, 40%), 146 (M^+-$ClCH_2COOH$, 100%).

1p: Similar procedure starting from **10d** gave chloroacetate **1p**. Yield 1.40 g (4.75 mmol, 95%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 5.75 (q, *J* = 6.6 Hz, 1H), 4.36 (q, *J* = 7.0 Hz, 2H), 4.11 (br. s, 4H), 1.63 (d, *J* = 6.6 Hz, 3H), 1.38 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 166.3, 165.9, 131.7 (+, 2C), 130.4, 129.4, 129.3 (+, 2C), 126.4, 89.0, 84.6, 62.7 (+), 61.2 (-), 40.8 (-), 21.2 (+), 14.2 (+); GC/MS *m/z* 294 (M^+, 3%), 259 (M^+-Cl, 81%), 249 (M^+-CH_2Cl, 11%), 200 (M^+-$ClCH_2COOH$, 46%), 155 (100%), 127 (50%).

1q: Similar procedure starting from **10e** gave chloroacetate **1q**. Yield 0.843 g (3.15 mmol, 63%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 5.75 (q, *J* = 6.6 Hz, 1H), 4.13 (s, 2H), 1.65 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 166.3, 147.4, 132.6 (+, 2C), 128.7, 123.5 (+, 2C), 91.4, 83.4, 62.4 (+), 40.8 (-), 21.0 (+); GC/MS *m/z* 267 (M^+, 7%), 232 (M^+-Cl, 100%), 173 (M^+-$ClCH_2COOH$, 80%).

1t: Similar procedure starting from **10f** gave chloroacetate **1t**. Yield 1.152 g (4.86 mmol, 97%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 5.76 (q, *J* = 6.6 Hz, 1H), 4.12 (d, J = 15.0 Hz, 1H), 4.10 (d, J = 15.0 Hz, 1H), 2.35 (s, 3H), 1.62 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 166.3, 139.0, 131.8 (+, 2C), 129.0 (+, 2C), 118.8, 85.6, 63.0, 40.9 (-), 21.4 (+); GC/MS *m/z* 236 (M^+, 3%), 201 (M^+-Cl, 33%), 142 (M^+-$ClCH_2COOH$, 100%), 115 (63%).

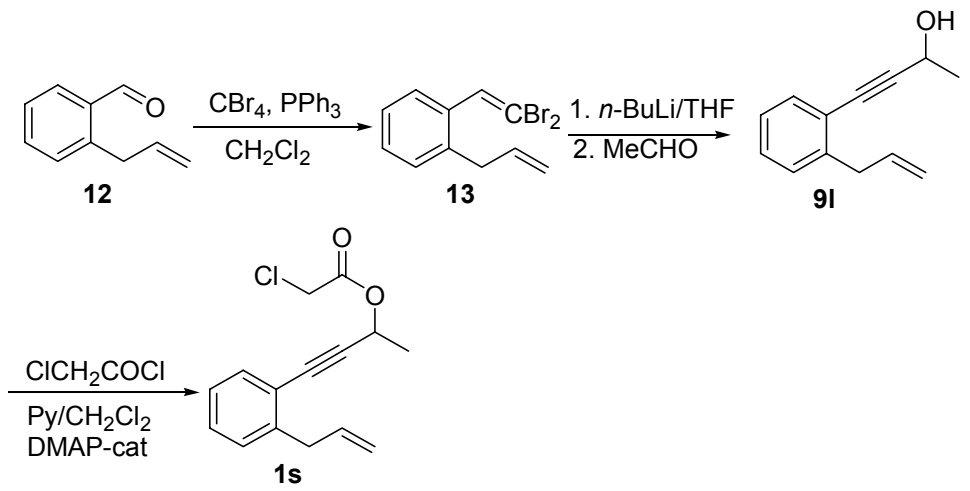


10c,h **11** **9f,k** **1o,r**

10c, **9f**, **1o**: Ar = *o*-FC_6H_4; **10c**: X = I
10h, **9k**, **1r**, Ar = 2-napthyl ; **10h**: X = Br

1o: $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol), CuI (38mg, 0.2 mmol), and **10c** (g, mmol) were dissolved in dry Et_3N (10 mL) and **11** (590 μL, 7.5 mmol) was added to the solution. The reaction was heated to 60°C and stirred overnight. When **10ca** had been consumed, the reaction was cooled to room temperature and quenched with 2M aqueous HCl. The mixture was extracted (CH_2Cl_2), washed (sat. $NaHCO_3$, brine), dried ($MgSO_4$), filtered, and concentrated in vacuum. The crude alcohol **9f** was converted to the phenylcarbonate **1o** according to procedure described above for the preparation of **1h**. Yield 1.42 g (5 mmol, 100%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.47 (td, J = 7.3 Hz, 1.8 Hz, 1H), 7.40 (m, 2H), 7.35-7.31 (m, 1H), 7.26 (t, J = 7.3 Hz, 1H), 7.23 (m, 2H), 7.11 (td, J = 7.7 Hz, 0.7 Hz, 1H), 7.09 (ps-t, J = 8.4 Hz, 1H), 5.70 (q, J = 6.6 Hz, 1H), 1.75 (d, J = 6.6 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 162.8 (d, $^1J_{CF}$ = 251.5 Hz), 152.7, 151.0, 133.7 (+), 130.6 (+, d, $^2J_{CF}$ = 7.4 Hz), 129.4 (+, 2C), 126.1 (+), 123.9 (+, d, $^3J_{CF}$ = 3.7 Hz), 121.0 (+, 2C), 115.5 (+, d, $^2J_{CF}$ = 22.2 Hz), 110.5, 91.2 (d, $^3J_{CF}$ = 3.7 Hz), 79.3, 65.6 (+), 21.3 (+); ^{19}F NMR (470.59 MHz, $CDCl_3$) δ -111.1; GC/MS *m/z* 240 (M^+-CO_2, <1%), 147 (M^+-CO_3Ph, 100%), 127 (12%), 120 (16%), 94 (24%).

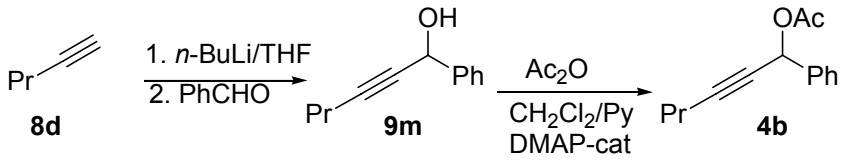
1r: Similar procedure starting from **10h** gave phenylcarbonate **1r**. Yield 1.49 g (4.7 mmol, 94%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.83-7.79 (m, 3H), 7.52-7.50 (m, 3H), 7.43-7.39 (m, 2H), 7.30-7.24 (m, 3H), 5.72 (q, J = 6.6 Hz, 1H), 1.77 (d, J = 6.6 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 152.8, 151.1, 133.0, 132.8, 132.1 (+), 129.5 (+, 2C), 128.4 (+), 128.0 (+), 127.82 (+), 127.76 (+), 126.9 (+), 126.6 (+), 126.1 (+), 121.0 (+, 2C), 119.3, 86.5, 86.3, 65.8 (+), 21.6 (+); GC/MS *m/z* 316 (M^+, 3%), 179 (M^+-CO_3Ph, 100%), 152 (32%).



1s: To a stirred solution of PPh_3 (5.25 g, 20 mmol) in dry CH_2Cl_2 (40 mL) at 0°C was added a solution of CBr_4 (3.28 g, 10 mmol) in dry CH_2Cl_2 (20 mL) *via* cannula. The subsequent yellow solution was stirred for 10 minutes, followed by the addition of **12**[10] in dry CH_2Cl_2 (40 mL). The solution was stirred for 1 hour at 0°C. The reaction was quenched with brine, extracted (CH_2Cl_2), washed (H_2O), dried ($MgSO_4$), and concentrated. The crude product was diluted (hexanes) and filtered (Silica gel). The dibromide **13** was dissolved in THF (25 mL) and cooled to -78°C. To the reaction was added *n*-BuLi (2.5 M in hexane, 5 mL, 12.5 mmol) and the solution was stirred for 20 minutes before being quenched with ethanal (0.6 mL, 10 mmol). The solution was warmed to 0°C and 2M aqueous HCl was added and the mixture was extracted (ether), washed (water, brine), dried ($MgSO_4$), filtered, and concentrated in vacuum. The crude alcohol **9l** was converted to the chloroacetate **1s** in a manner described for **1g**. Yield 2.57 g (9.8 mmol, 98%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.43 (d, J = 7.7 Hz, 1H), 7.29 (td, J = 7.5 Hz, 1.5 Hz, 1H), 7.21 (d, J = 7.7 Hz, 1H), 7.17 (td, J = 7.5 Hz, 1.1 Hz, 1H), 5.96 (ddt, J = 16.5 Hz, 10.6 Hz, 6.6 Hz, 1H), 5.78 (q, J = 6.6 Hz, 1H), 5.09 (m, J = 16.5 Hz, 1H), 5.08 (m, J = 10.6 Hz, 1H), 4.10 (s, 2H), 3.54 (d, J = 6.6 Hz, 2H), 1.64 (d, J = 6.6 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 166.3, 142.4, 136.3 (+), 132.5 (+), 131.9, 129.1 (+), 128.8 (+), 128.3, 126.1 (+), 121.4, 116.1 (-), 90.2, 84.1, 63.0 (+), 40.9 (-), 38.6 (-), 21.4 (+); GC/MS *m/z* 262 (M^+, <1%), 227 (M^+-Cl, <1%), 213 (M^+-CH_2Cl, 3.8%), 167 (76%), 153 (100%).

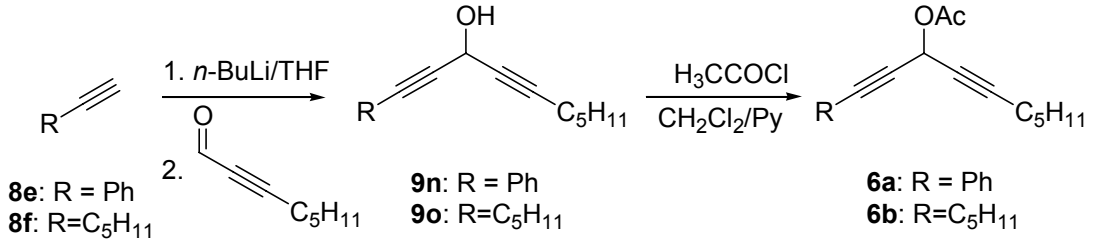
4a: Was prepared by method reported in literature[4]. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.67-7.63 (m, 2H), 7.53-7.50 (m, 2H), 7.45-7.40 (m, 3H), 7.35-7.31 (m, 3H), 6.75 (s, 1H), 2.15 (s, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 170.3, 137.6, 132.4 (+, 2C), 129.4 (+), 129.3 (+), 129.2 (+, 2C), 129.0 (+, 2C), 128.8 (+, 2C), 128.3 (+, 2C), 122.5, 87.5, 86.1, 66.5 (+), 21.6 (+); GC/MS *m/z* 250 (M^+, 45%), 208 (M^+-CH_2CO, 85%), 191 (M^+-CH_3CO_2, 93%), 189 (100%).

(10) Ashby, E. C.; Coleman, D.; Gamasa, M. *J. Org. Chem.* **1987**, *52*, 4079.



4b: To a solution of **8d** (0.99 mL, 10 mmol) in anhydrous THF (10 mL) at -78°C was added *n*-BuLi (2.5M in hexane, 4.4 mL, 11 mmol). The solution was stirred for 30 minutes, warmed to 0°C for 1 hour, and cooled back to -78°C. After 10 minutes, the reaction was quenched with benzaldehyde (1.2 mL, 12 mmol). Upon warmup to room temperature, 2M aqueous HCl was added and the mixture was extracted with ether. Etheral layers were combined and washed (sat. $NaHCO_3$, brine), brine ($MgSO_4$), and concentrated in vacuum to give **9m** of reasonably high purity. Yield 2.16 g (10 mmol, 100%). To a solution of **9m** (0.865 g, 4 mmol) and DMAP (10 mg, 0.08 mmol) in dry CH_2Cl_2 (10 mL) at 0°C was added pyridine (0.45mL, 5.6 mmol). After stirring for several minutes, acetic anhydride (0.5 mL, 4.8 mmol) was added slowly. Reaction was stirred overnight, quenched (2M aqueous HCl), extracted (CH_2Cl_2), washed (brine), dried ($MgSO_4$), and concentrated in vacuum. The crude oil was purified by preparative column chromatography (eluent hexane-EtOAc-CH_2Cl_2 30:1:3) to give **4b**. Yield 0.631 g (2.9 mmol, 73%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.55-7.52 (m, 2H), 7.40-7.32 (m, 3H), 6.47 (s, 1H), 2.27-2.24 (m, 2H), 2.09 (s, 3H), 1.58 (ps-sextet, J = 7.4 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 170.3, 138.1, 129.2 (+), 129.0 (+, 2C), 128.1 (+, 2C), 88.6, 77.3, 66.5 (+), 22.3 (-), 21.6 (+), 21.2 (-), 13.9 (+); GC/MS *m/z* 216 (M^+, 20%), 174 (M^+-CH_2CO, 45%), 173 (M^+-C_3H_7, 45%), 156 (M^+-CH_3CO_2H, 40%), 141 (90%), 128 (80%), 115 (100%).

4c: This compound was prepared from commercially available 1-phenyl-2-propyn-1-ol *via* standard procedure described previously for **1g**. Yield 0.58 g (2.78 mmol, 56%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.57-7.55 (m, 2H), 7.44-7.41 (m, 3H), 6.52 (d, J = 1.8 Hz, 1H), 4.12 (d, J = 15.0 Hz, 1H), 4.08 (d, J = 15.0 Hz, 1H), 2.73 (d, J = 1.8 Hz, 1H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 166.1, 135.5, 129.5 (+), 128.8 (+, 2C), 127.8 (+, 2C), 79.2, 76.4 (+), 67.1 (+), 40.8 (-); GC/MS *m/z* 208 (M^+, 4%), 173 (M^+-Cl, 19%), 131 (M^+-Ph, 32%), 114 (M^+-$ClCH_2COOH$, 100%).



6a: To a stirred at -78°C solution of **8e** (1.1 mL, 10 mmol) in anhydrous THF (15 mL) was added *n*-BuLi (2.5M in hexane, 4.8 mL, 12 mmol). The solution was stirred for 20 minutes, followed by the addition of 2-octynal (1.6 mL, 11 mmol). Solution was warmed to room temperature and 2M aqueous HCl was added. The mixture was extracted (ether), washed (sat. $NaHCO_3$, brine), dried ($MgSO_4$), and concentrated in vacuum. The crude

alcohol **9n** was dissolved in anhydrous CH_2Cl_2 (15 mL) and cooled to 0°C. Pyridine (1.6 mL, 19.8 mmol) was added, followed by acetyl chloride (0.9 mL, 12.7 mmol). The reaction was warmed to room temperature and stirred for one hour. When reaction had completed, 2M aqueous HCl was added and mixture was extracted with ether, washed (sat. $NaHCO_3$, brine), dried ($MgSO_4$), and concentrated in vacuum. The crude oil was purified by preparative column chromatography on Silica gel (eluent hexane-EtOAc-CH_2Cl_2 30:1:3) Yield 2.50 g (9.3 mmol, 93%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.34-7.29 (m, 3H), 6.27 (t, *J* = 2.2 Hz, 1H), 2.25 (td, *J* = 7.3 Hz, 2.2 Hz, 2H), 2.15 (s, 3H), 1.55 (ps-quintet, *J* = 7.3 Hz, 2H), 1.40-1.30 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 169.3, 132.0 (+, 2C), 128.9 (+), 128.2 (+, 2C), 121.7, 86.9, 84.5, 83.4, 74.1, 54.0 (+), 31.0 (-), 27.8 (-), 22.1 (-), 20.9 (+), 18.7 (-), 13.9 (+); GC/MS *m/z* 267 (M^+-H, 6%), 211 (M^+-Bu, 30%), 178 (46%), 165 (77%), 152 (100%).

6b: Similar procedure starting from **8f** gave acetate **6b**. Yield 2.62 g (10 mmol, 100%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 6.01 (m, 1H), 2.22 (td, J = 7.2 Hz, 2.2 Hz, 4H), 2.11 (s, 3H), 1.52 (ps-quintet, *J* = 7.3 Hz, 4H), 1.38-1.28 (m, 8H), 0.89 (t, *J* = 7.0 H, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 169.4, 86.1 (2C), 74.7 (2C), 54.0 (-), 31.0 (-, 2C), 27.9 (-, 2C), 22.1 (-, 2C), 21.0 (+), 18.7 (-, 2C), 13.9 (+, 2C); GC/MS *m/z* 262 (M^+, 11%), 219 (M^+-CH_3CO, 27%), 202 (M^+-CH_3COOH, 25%), 91 (100%).

Procedure for $B(C_6F_5)_3$-Catalyzed Allylation of 2a is representative

2a: To a solution of **1g** (223 mg, 1.0 mmol) and allyltrimethylsilane (240μL, 1.5 mmol) in anhydrous CH_2Cl_2 (0.5 mL) was added a solution of $B(C_6F_5)_3$ (26mg, 0.05 mmol) in anhydrous CH_2Cl_2 (0.5 mL). The reaction was stirred at room temperature for several hours. Upon consumption of **1g**, the reaction was filtered through Silica gel and concentrated. The crude product was purified by preparative column chromatography using Silica gel (eluent hexanes). Yield 162 mg (0.95 mmol, 95%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.43-7.41 (m, 2H), 7.32-7.27 (m, 3H), 5.96 (ddt, *J* = 17.2 Hz, 10.3 Hz, 7.3 Hz, 1H), 5.16 (ddt, *J* = 17.2 Hz, 2.2 Hz, 1.5 Hz, 1H), 5.12 (ddt, *J* = 10.3 Hz, 1.8 Hz, 1.1 Hz, 1H), 2.75 (ps-sextet, *J* = 6.8 Hz, 1H), 2.37-2.27 (m, 2H), 1.28 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 136.5 (+), 132.0 (+, 2C), 128.6 (+, 2C), 128.0 (+), 124.4, 117.1 (-), 94.5, 81.5, 41.6 (-), 26.9 (+), 20.9 (+); GC/MS *m/z* 170 (M^+, 10%), 155 (M^+-Me, 20%), 129 (M^+-C_3H_5, 100%).

2b: ^{1}H NMR (500.13 MHz, C_6D_6) δ 7.40-7.38 (m, 2H), 7.30-7.27 (m, 3H), 4.84 (br. s 1H), 4.82 (br. s 1H), 2.84 (app. sextet, *J* = 7.0 Hz, 1H), 2.34 (dd, *J* = 13.7 Hz, 7.7 Hz, 1H), 2.20 (dd, *J* = 13.7 Hz, 7.2 Hz, 1H), 1.79 (br. s, 3H), 1.25 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 143.2, 131.6 (+, 2C), 128.1 (+, 2C), 127.5 (+), 124.0, 112.5 (-), 94.5, 80.8, 45.3 (-), 24.9 (+), 22.3 (+), 20.7 (+); GC/MS *m/z* 184 (M^+, 9%), 169 (M^+-CH_3, 54%), 128 (M^+-C_4H_8, 100%). HRMS Calcd for $C_{14}H_{16}$ 184.1252. Found 184.1262.

2c: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 6.01 (tt, *J* = 4.0 Hz, 1.8 Hz, 1H), 5.87 (ddt, *J* = 17.2, 10.3, 7.0 Hz, 1H), 5.07 (m, 1H), 5.05 (m, 1H), 2.64 (ps-sextet, *J* = 6.6 Hz, 1 H),

2.21 (m, 2 H), 2.08 (m, 4 H), 1.59 (m, 4 H), 1.17 (d, J = 6.97 Hz, 3 H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 136.6 (+), 133.8 (+), 121.3, 116.9 (-), 91.6, 83.2, 41.7 (-), 30.1 (-), 26.7 (+), 26.0 (-), 22.8 (-), 22.0 (-), 21.1 (+); GC/MS *m/z* 174 (M^+, 10%), 159 (M^+-Me, 10%), 133 (M^+-C_3H_5, 95%), 105 ($C_6H_9C{\equiv}C^+$, 100%). HRMS Calcd for $C_{13}H_{18}$ 174.1409. Found 174.1403.

2d: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 5.85 (ddt, J = 17.2 Hz, 10.3 Hz, 7.0 Hz, 1H), 5.07 (m, J = 17.2 Hz, 1H), 5.04 (m, J = 10.3 Hz, 1H), 3.65 (t, J = 6.2 Hz, 2H), 2.47 (m, J = 7.0 Hz, 2.2 Hz, 1H), 2.35 (td, J = 6.8 Hz, 2.2 Hz, 2H), 2.16 (ps-tq, J = 7.0 Hz, 1.5 Hz, 2H), 1.92 (ps-quintet, J = 6.6 Hz, 2H), 1.13 (d, J = 6.6 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 136.6 (+), 116.8 (-), 85.8, 79.0, 44.2 (-), 41.8 (-), 32.2 (-), 26.3 (+), 21.3 (+), 16.6 (-); GC/MS *m/z* 170 (M^+, <1%), 155 (M^+-Me, 1%), 135 (M^+-Cl, 7%), 129 (M^+-C_3H_5, 10%), 107 (M^+-$(CH_2)_2$Cl, 20%), 93 (M^+-$(CH_2)_3$Cl, 100%), 77 ($^+(CH_2)_3$Cl, 70%). HRMS Calcd for $C_{10}H_{16}Cl$ 171.0941. Found 171.0938.

2e: ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 5.88 (ddt, J = 17.0 Hz, 9.9 Hz, 7.0 Hz, 1H), 5.07 (m, J = 17.0 Hz, 1H), 5.04 (m, J = 9.9 Hz, 1H), 2.54 (ps-sextet, J = 7.0 Hz, 1H), 2.21 (ps-tq, J = 7.0 Hz, 1.1 Hz, 2H), 1.17 (d, J = 7.0 Hz, 3H), 1.06 (m, 3H), 1.05 (m, 18H); ^{13}C NMR (100.61 MHz, $CDCl_3$) δ 136.0 (+), 116.5 (-), 113.1, 80.1, 41.3 (-), 26.9 (+), 20.8 (+), 18.6 (+, 6C), 11.2 (+, 3C); GC/MS *m/z* 250 (M^+, <1%), 207 (M^+-$(CH_3)_2$CH, 100%), 137 (53%), 123 (59%), 109 (54%), 59 (62%). HRMS Calcd for $C_{16}H_{30}Si$ 250.2117. Found 250.2133.

2f: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 5.93 (ddt, J = 16.9 Hz, 9.9 Hz, 7.0 Hz, 1H), 5.12 (m, J = 16.9 Hz, 1H), 5.09 (m, J = 9.9 Hz, 1H), 2.73 (ps-sextet, J = 7.0 Hz, 1H), 2.35-2.24 (m, 2H), 1.34 (s, 12H), 1.25 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$)[9] δ 136.4 (+), 134.9 (+, 2C), 131.2 (+, 2C), 127.1, 117.2 (-), 95.9, 84.3 (2C), 81.7, 41.5 (-), 26.9 (+), 25.3 (+, 4C), 20.9 (+); ^{11}B NMR (160.46 MHz, $CDCl_3$) δ 30.9; GC/MS *m/z* 296 (M^+, 7%), 255 (M^+-C_3H_5, 100%). HRMS Calcd for $C_{19}H_{25}O_2B$ 296.1948. Found 296.1939.

2g: ^{1}H NMR (500.13 MHz, C_6D_6) δ 7.54 (d, J = 8.4 Hz, 2H), 7.49 (d, J =8.4 Hz, 2H), 5.92 (ddt, J = 17.2 Hz, 10.3 Hz, 7.3 Hz, 1H), 5.15 (m, J = 17.2 Hz, 1H), 5.11 (m, J = 10.3 Hz, 1H), 2.75 (app. sextet, J = 6.6 Hz, 1H), 2.33 (dd, J = 13.9 Hz, 7.0 Hz, 1H), 2.29 (dd, J = 13.9 Hz, 7.0 Hz, 1H), 1.28 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 135.7 (+), 131.8 (+, 2C), 129.3 (q, $^2J_{CF}$ = 33.3 Hz), 127.8, 125.1 (+, 2C), 123.7 (q, $^1J_{CF}$ = 271.9 Hz), 116.9 (-), 96.8, 80.0, 40.9 (-), 26.5 (+), 20.3 (+); ^{19}F NMR (470.59 MHz, $CDCl_3$) δ -64.3; GC/MS *m/z* 238 (M^+, 8.6%), 197 (M^+-allyl, 100%), 177 (77%). HRMS Calcd for $C_{14}H_{13}F_3$ 238.0969. Found 238.0961.

2h: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.39 (td, J = 7.7 Hz, 1.8 Hz, 1H), 7.24 (m, 1H), 7.08-7.02 (m, 2H), 5.95 (ddt, J = 17.2 Hz, 10.3 Hz, 7.3 Hz, 1H), 5.14 (ddt, J = 17.2 Hz, 1.7 Hz, 1.5 Hz, 1H), 5.10 (ddt, J = 10.3 Hz, 2.2 Hz, 1.1 Hz, 1H), 2.78 (ps-sextet, J = 6.6 Hz, 1H), 2.38-2.27 (m, 2H), 1.28 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 163.2 (d, $^1J_{CF}$ = 251.6 Hz), 136.2 (+), 134.0 (+), 129.6 (+, d, $^3J_{CF}$ = 7.4 Hz), 124.2 (+, d, $^3J_{CF}$ = 3.7 Hz), 117.2 (-), 115.7 (+, d, $^2J_{CF}$ = 20.3 Hz), 112.8 (d, $^2J_{CF}$ = 16.6 Hz), 99.9 (d,

$^3J_{CF}$ = 3.7 Hz), 74.8, 41.4 (-), 27.1 (+), 20.8 (+); ^{19}F NMR (470.59 MHz, $CDCl_3$) δ -112.4; GC/MS *m/z* 188 (M^+, 7%), 173 (M^+-Me, 20%), 147 (M^+-C_3H_5, 100%). HRMS Calcd for $C_{13}H_{13}F$ 188.1001. Found 188.0985.

2i: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 5.92 (ddt, *J* = 17.2 Hz, 9.9 Hz, 7.0 Hz, 1H), 5.13 (m, *J* = 17.2 Hz, 1H), 5.10 (m, *J* = 9.9 Hz, 1H), 4.36 (q, *J* = 7.3 Hz, 2H), 2.75 (ps-sextet, *J* = 7.0 Hz, 1H), 2.35-2.25 (m, 2H), 1.39 (t, *J* = 7.3 Hz, 3H), 1.26 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 166.2, 135.7 (+), 131.4 (+, 2C), 129.3 (+, 2C), 129.2, 128.6, 116.9 (-), 97.3, 80.6, 61.0 (-), 40.9 (-), 26.5 (+), 20.3 (+), 14.3 (+); GC/MS *m/z* 242 (M^+, 5%), 201 (M^+-allyl, 100%), 169 (18%), 128 (45%). HRMS Calcd for $C_{16}H_{18}O_2$ 242.1307. Found 242.1296.

2j: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 5.90 (ddt, *J* = 16.9 Hz, 9.9 Hz, 7.0 Hz, 1H), 5.14 (m, *J* = 16.9 Hz, 1H), 5.11 (m, *J* = 9.9 Hz, 1H), 2.77 (ps-sextet, *J* = 7.0 Hz, 1H), 2.36-2.27 (m, 2H), 1.28 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 146.6, 135.5 (+), 132.3 (+, 2C), 131.0, 123.5 (+, 2C), 117.1 (-), 100.1, 79.8, 40.7 (-), 26.6 (+), 20.1 (+); GC/MS *m/z* 215 (M^+, 7%), 174 (M^+-allyl, 100%), 128 (M^+-allyl-NO_2, 78%), 115 (53%). HRMS Calcd for $C_{13}H_{13}NO_2$ 215.0946. Found 215.0936.

2k: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.82-7.76 (m, 3H), 7.50-7.45 (m, 3H), 6.00 (ddt, *J* = 17.2 Hz, 10.3 Hz, 7.0 Hz, 1H), 5.19 (m, *J* = 17.2 Hz, 1H), 5.15 (m, J = 10.3 Hz, 1H), 2.81 (ps-sextet, *J* = 6.6 Hz, 1H), 2.42-2.31 (m, 2H), 1.33 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 136.0 (+), 133.1, 132.5, 131.1 (+), 128.8 (+), 127.8 (+), 127.7 (+), 127.6 (+), 126.3 (+), 126.2 (+), 121.3, 116.7 (-), 94.5, 81.5, 41.2 (-), 26.6 (+), 20.5 (+); GC/MS *m/z* 220 (M^+, 17%), 179 (M^+-allyl, 100%), 152 (17%). EA Calcd for $C_{17}H_{16}$: C 92.68, H 7.32. Found C 92.68, H 7.30.

2l: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.3 Hz, 1H), 7.22 (td, *J* = 7.3 Hz, 1Hz, 1H), 7.19 (d, J = 7.3 Hz, 1H), 7.14 (td, *J* = 7.3 Hz, 1.8 Hz, 1H), 6.00 (ddt, *J* = 16.9 Hz, 9.9 Hz, 6.6 Hz, 1H), 5.10 (m, *J* = 16.9 Hz, 1H), 5.07 (m, *J* = 9.9 Hz, 1H), 4.85 (br. s. 1H), 4.83 (br. s. 1H), 3.56 (d, *J* = 6.6 Hz, 2H), 2.90 (sextet, *J* = 7.3 Hz, 1H), 2.36 (dd, *J* = 13.6 Hz, 7.7 Hz, 1H), 2.22 (dd, *J* = 13.6 Hz, 6.6 Hz, 1H), 1.80 (s, 3H), 1.29 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 143.1, 141.8, 136.9 (+), 132.2 (+), 128.6 (+), 127.7 (+), 125.9 (+), 123.4, 115.7 (-), 112.5 (-), 98.3, 79.4, 45.4 (-), 38.8 (-), 25.1 (+), 22.3 (+), 20.9 (+); GC/MS *m/z* 224 (M^+, 4%), 209 (M^+-CH_3, 33%), 153 (M^+-C_5H_{11}, 96%), 141 (100%). HRMS Calcd for $C_{17}H_{20}$ 224.1565. Found 224.1552.

2m: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.9 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 1H), 5.94 (ddt, *J* = 16.9 Hz, 9.9 Hz, 7.0 Hz, 1H), 5.13 (m, *J* = 16.9 Hz, 1H), 5.09 (m, *J* = 9.9 Hz, 1H), 2.72 (ps-sextet, *J* = 7.0 Hz, 1H), 2.34 (s, 3H), 2.32-2.27 (m, 2H), 1.26 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 137.5, 136.1, 131.4 (+, 2C), 128.9 (+, 2C), 120.8, 116.6 (-), 93.2, 81.0, 41.2 (-), 26.4 (+), 21.4 (+), 20.5 (+); GC/MS *m/z* 184 (M^+, 12%), 169 (M^+-CH_3, 10%), 143 (M^+-allyl, 100%), 128 (M^+-allyl-CH_3, 55%). HRMS Calcd for $C_{14}H_{16}$ 184.1252. Found 184.1247.

5a: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.48-7.42 (m, 4H), 7.37-7.34 (m, 2H), 7.32-7.29 (m, 3H), 7.29-7.25 (m, 1H), 5.93 (ddt, *J* = 17.2 Hz, 10.3 Hz, 7.3 Hz, 1H), 5.13 (m, 1H), 5.09 (m, 1H), 3.93 (t, *J* = 7.0 Hz, 1H), 2.61 (ps-t, *J* = 7.0 Hz, 2H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 141.8, 135.9 (+), 132.1 (+, 2C), 128.9 (+, 2C), 128.6 (+, 2C), 128.2 (+), 128.0 (+, 2C), 127.2 (+), 124.1, 117.5 (-), 91.4, 84.2, 43.2 (-), 39.0 (+); GC/MS *m/z* 232 (M^+, <1%), 191 (M^+-C_3H_5, 100%).

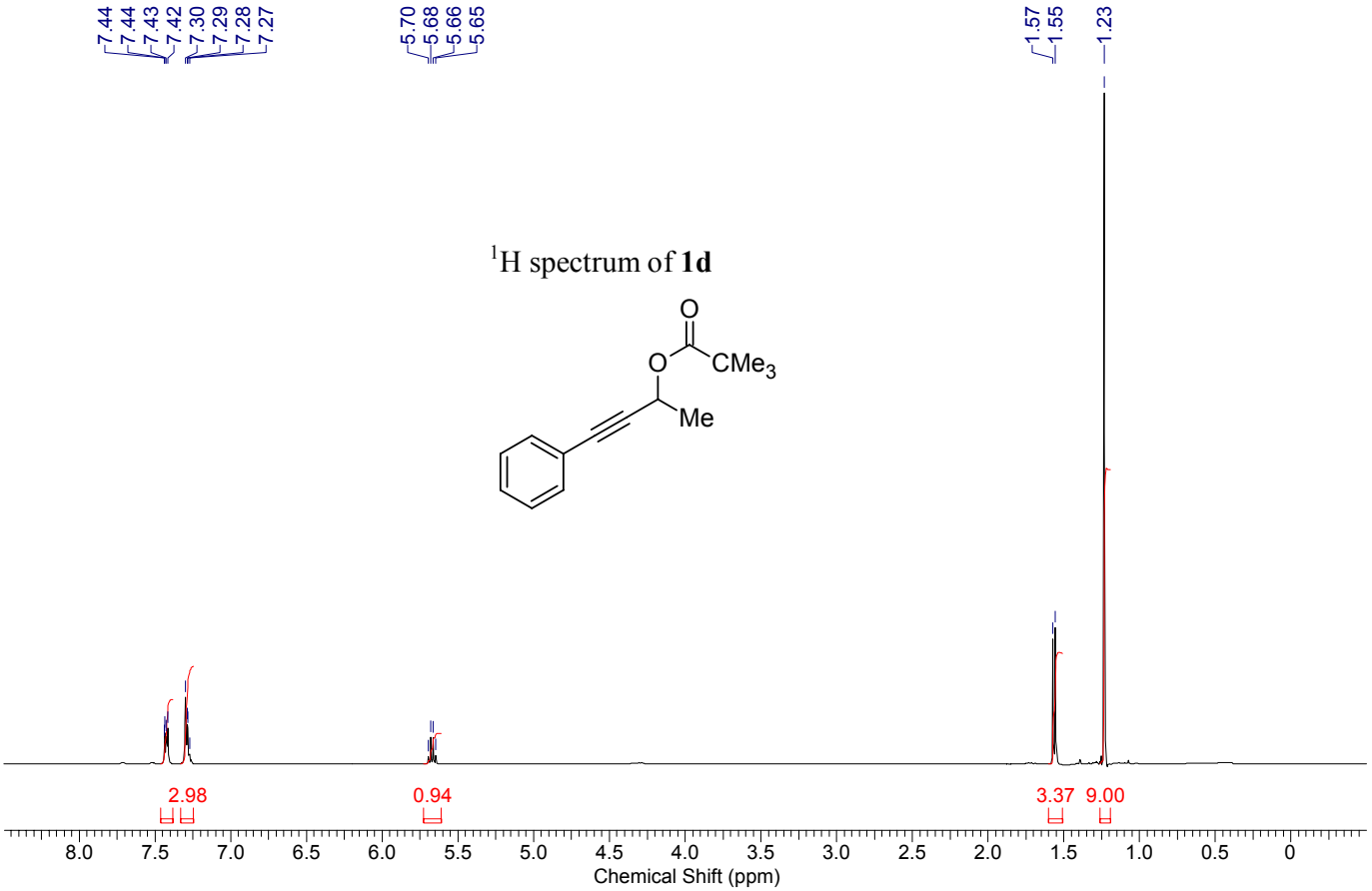
5b: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.38-7.36 (m, 2H), 7.34-7.30 (m, 2H), 7.26-7.21 (m, 1H), 5.87 (ddt, *J* = 17.2, 10.3, 7.0 Hz, 1H), 5.08-5.02 (m, 2H), 3.68 (m, *J* = 7.3 Hz, 2.2 Hz, 1H), 2.48 (t, *J* = 7.2 Hz, 2H), 2.22 (m, 2H), 1.56 (ps-sextet, *J* = 7.3 Hz, 2H), 1.01 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 142.6, 136.3 (+), 128.7 (+, 2C), 127.9 (+, 2C), 127.0 (+), 117.1 (-), 84.0, 81.7, 43.5 (-), 38.5 (+), 22.9 (-), 21.3 (-), 13.9 (+); GC/MS *m/z* 198 (M^+, <1%), 157 (M^+-C_3H_5, 100%). HRMS Calcd for $C_{15}H_{18}$ 198.1409. Found 198.1413.

5c: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.35 (app. t, 2H), 7.26 (app. t, 1H), 5.87 (ddt, *J* = 17.2 Hz, 10.3 Hz, 7.0 Hz, 1H), 5.09 (m, *J* = 17.2 Hz, 1H), 5.08 (m, *J* = 10.3 Hz, 1H), 3.72 (td, *J* = 7.2 Hz, 2.2 Hz, 1H), 2.54 (ps-t, *J* = 7.0-7.2 Hz, 2H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 140.7, 135.1, 128.5 (+, 2C), 127.4 (+, 2C), 126.9 (+), 117.2 (-), 85.3, 71.4 (+), 42.4 (-), 37.7 (+); GC/MS *m/z* 156 (M^+, 2%), 155 (M^+-H, 6%), 141 (7%), 128 (7%), 115 (100%). HRMS Calcd for $C_{12}H_{12}$ 156.0939. Found 156.0934.

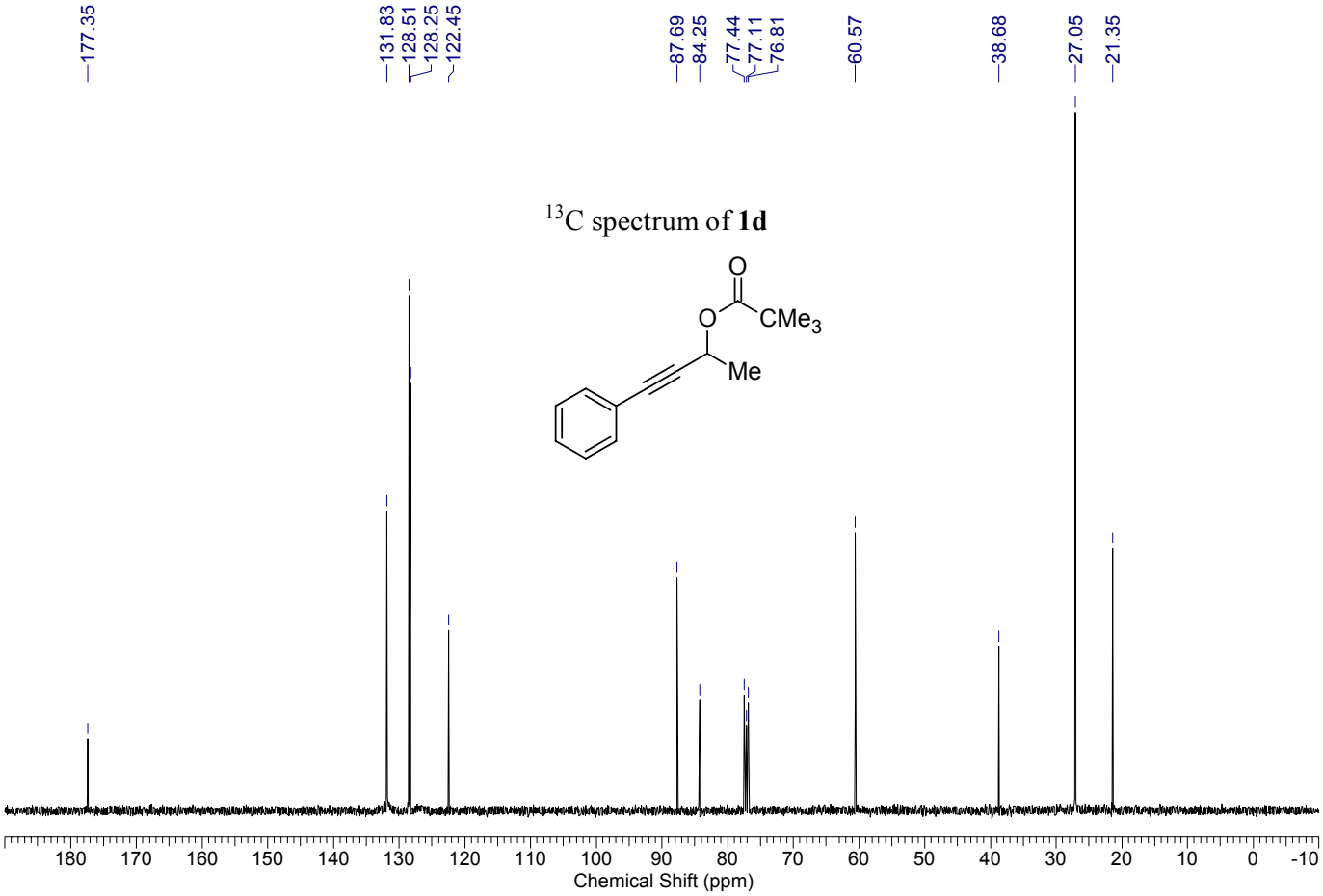
Procedure for isolation of acid-sensitive endiynes

7a: Allylation was performed similarly as for **2a**. Reaction mixture was filtered through basic alumina and concentrated in vacuum. The crude oil was purified by preparative column chromatography using basic alumina (eluent pentane). Yield 198 mg (0.79 mmol, 79%). ^{1}H NMR (500.13 MHz, C_6D_6) δ 7.43-7.41 (m, 2H), 6.95-6.93 (m, 3H), 6.03 (ddt, *J* = 17.2 Hz, 10.3 Hz, 7.0 Hz, 1H), 5.12 (m, *J* = 17.2 Hz, 1H), 5.09 (m, *J* = 10.3 Hz, 1H), 3.62 (tt, *J* = 6.6 Hz, 2.2 Hz, 1H), 2.52 (app. t, *J* = 7.0 Hz, 2H), 2.04 (td, *J* = 7.3 Hz, 2.2 Hz, 2H), 1.37 (app. quintet, *J* = 7.7 Hz, 2H), 1.28-1.22 (m, 2H), 1.16 (app. sextet, *J* = 7.3-7.7 Hz, 2H), 0.81 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125.76 MHz, C_6D_6) δ 135.1 (+), 132.0 (+, 2C), 128.4 (+, 2C), 128.1 (+), 123.9, 117.6 (-), 88.8, 82.2, 81.9, 78.3, 40.9 (-), 31.3 (-), 28.8 (-), 24.8 (+), 22.5 (-), 19.0 (-), 14.1 (+); GC/MS *m/z* 244 (M^+, 2%), 203 (M^+-allyl, 2%), 105 (65%), 91 (100%). HRMS Calcd for $C_{19}H_{21}$ 249.1643. Found 249.1628.

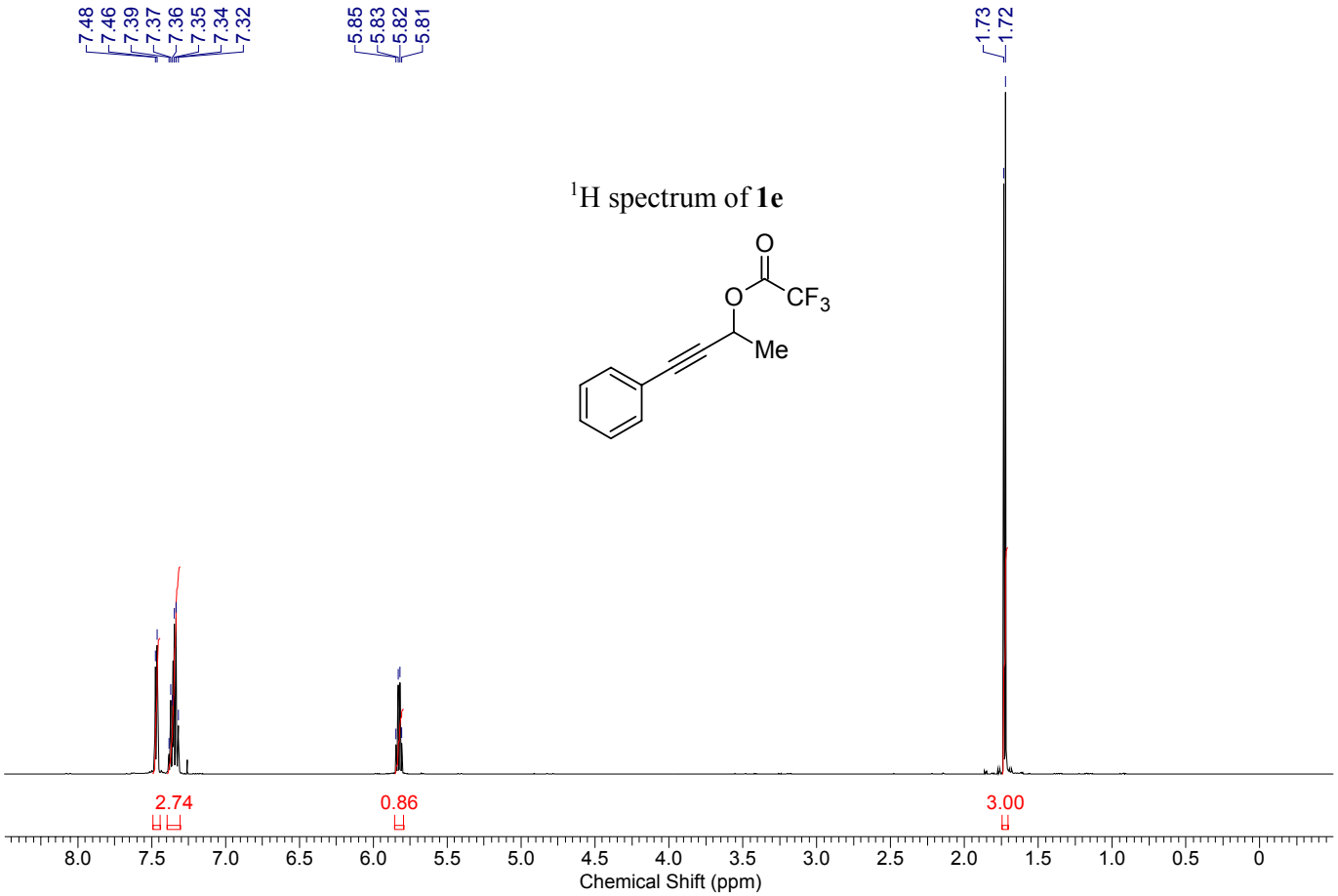
7b: ^{1}H NMR (500.13 MHz, C_6D_6) δ 6.05 (dddt, *J* = 17.2 Hz, 10.3 Hz, 7.0 Hz, 1.5 Hz, 1H), 5.11 (m, *J* = 17.2 Hz, 1H), 5.09 (m, *J* = 10.3 Hz, 1H), 3.48 (triplet of quintets, *J* = 8.9 Hz, 2.2 Hz, 1H), 2.52-2.48 (m, 2H), 2.04 (td, *J* = 7.0 Hz, 2.2 Hz, 4H), 1.37 (app. quintet, *J* = 7.0 Hz, 4H), 1.28-1.22 (m, 4H), 1.16 (sextet, *J* = 7.3 Hz, 4H), 0.81 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (125.76 MHz, C_6D_6) δ 135.5 (+), 117.2 (-), 81.5 (2C), 79.2 (2C), 41.3 (-), 31.3 (-, 2C), 28.8 (-, 2C), 24.3 (+), 22.5 (-, 2C), 19.0 (-, 2C), 14.1 (+, 2C); GC/MS *m/z* 250 (M^+, 4%), 209 (M^+-allyl, 49%), 165 (100%), 152 (91%).



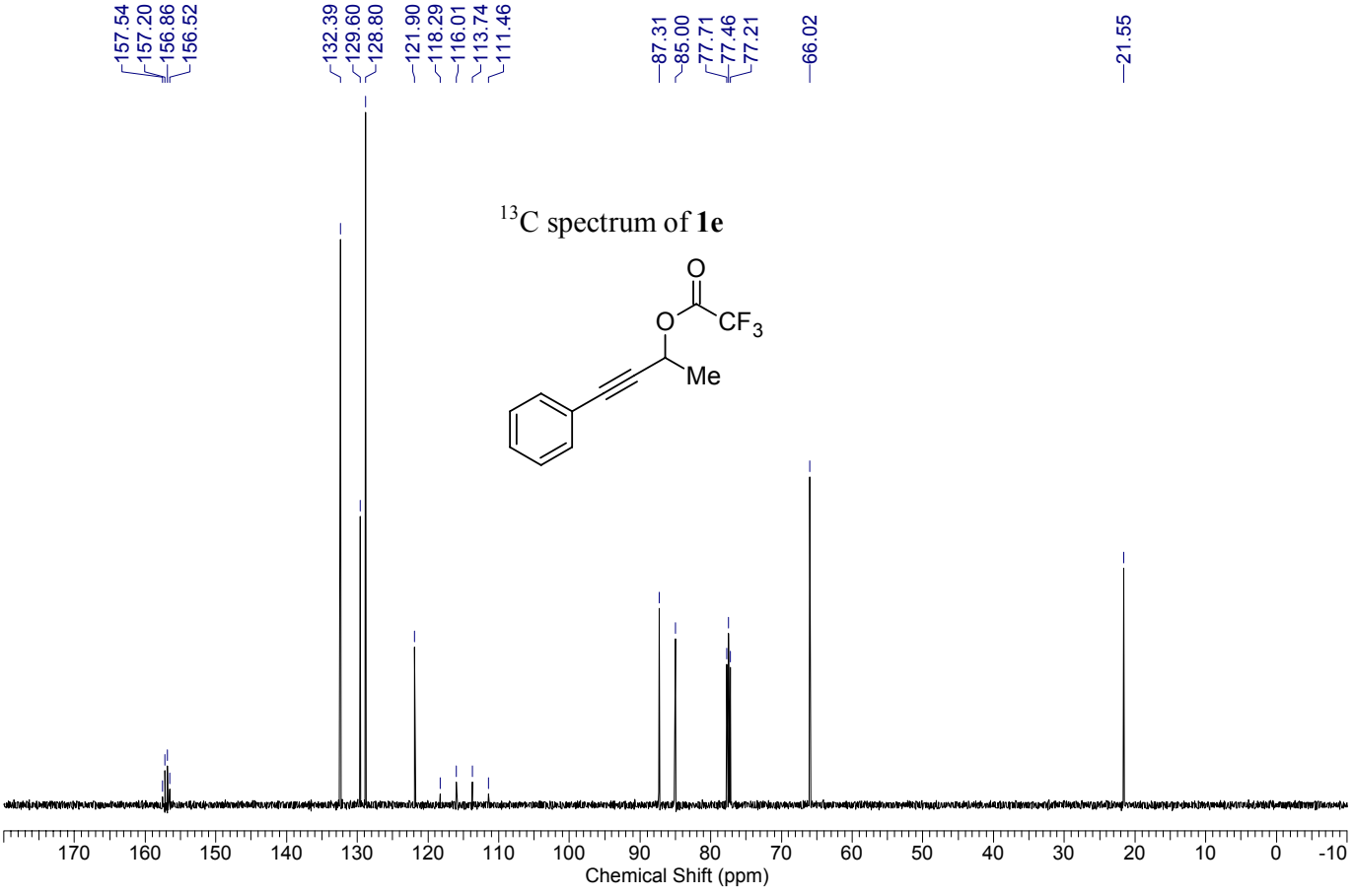
^{1}H spectrum of **1d**



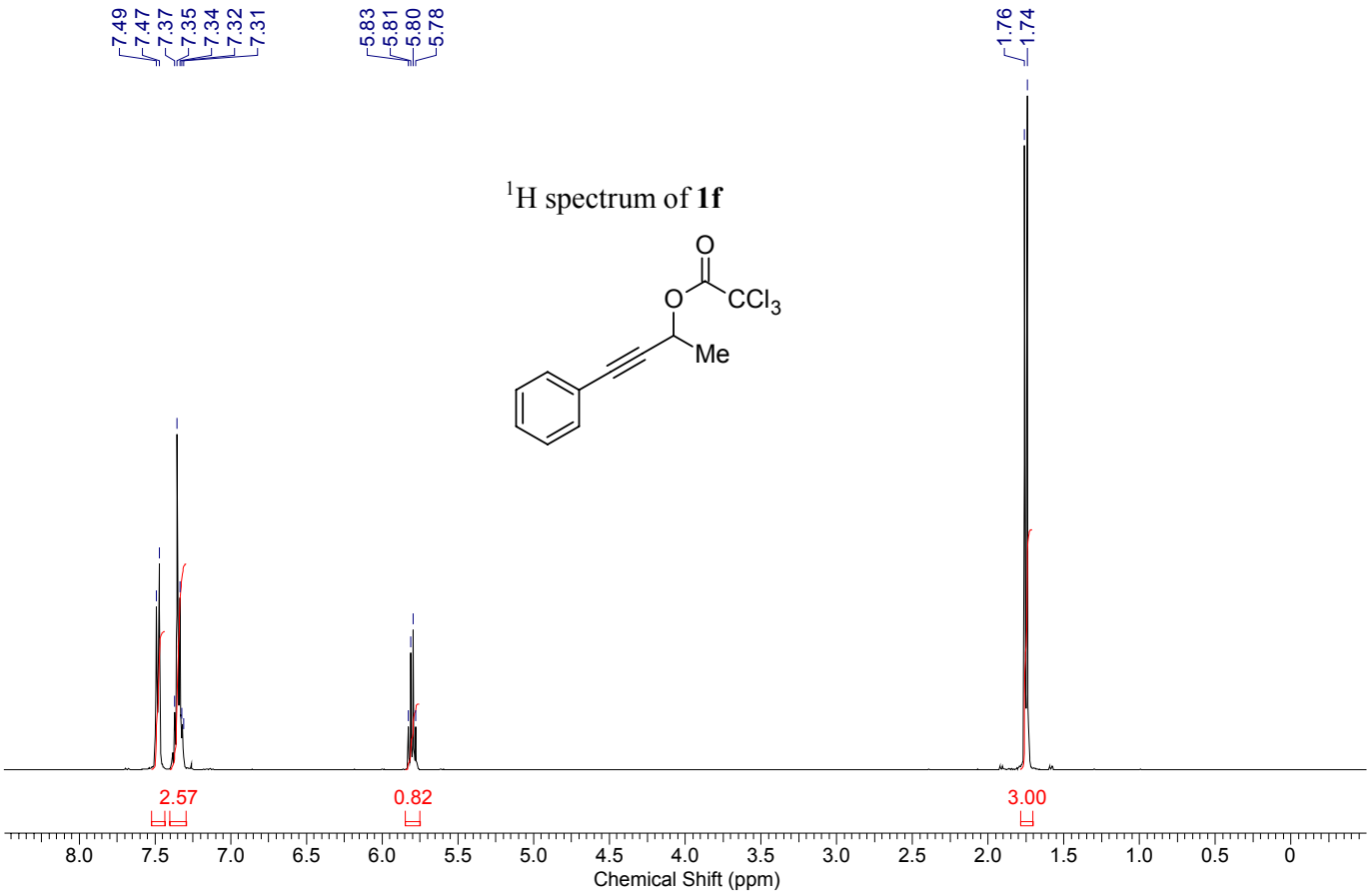
^{13}C spectrum of **1d**



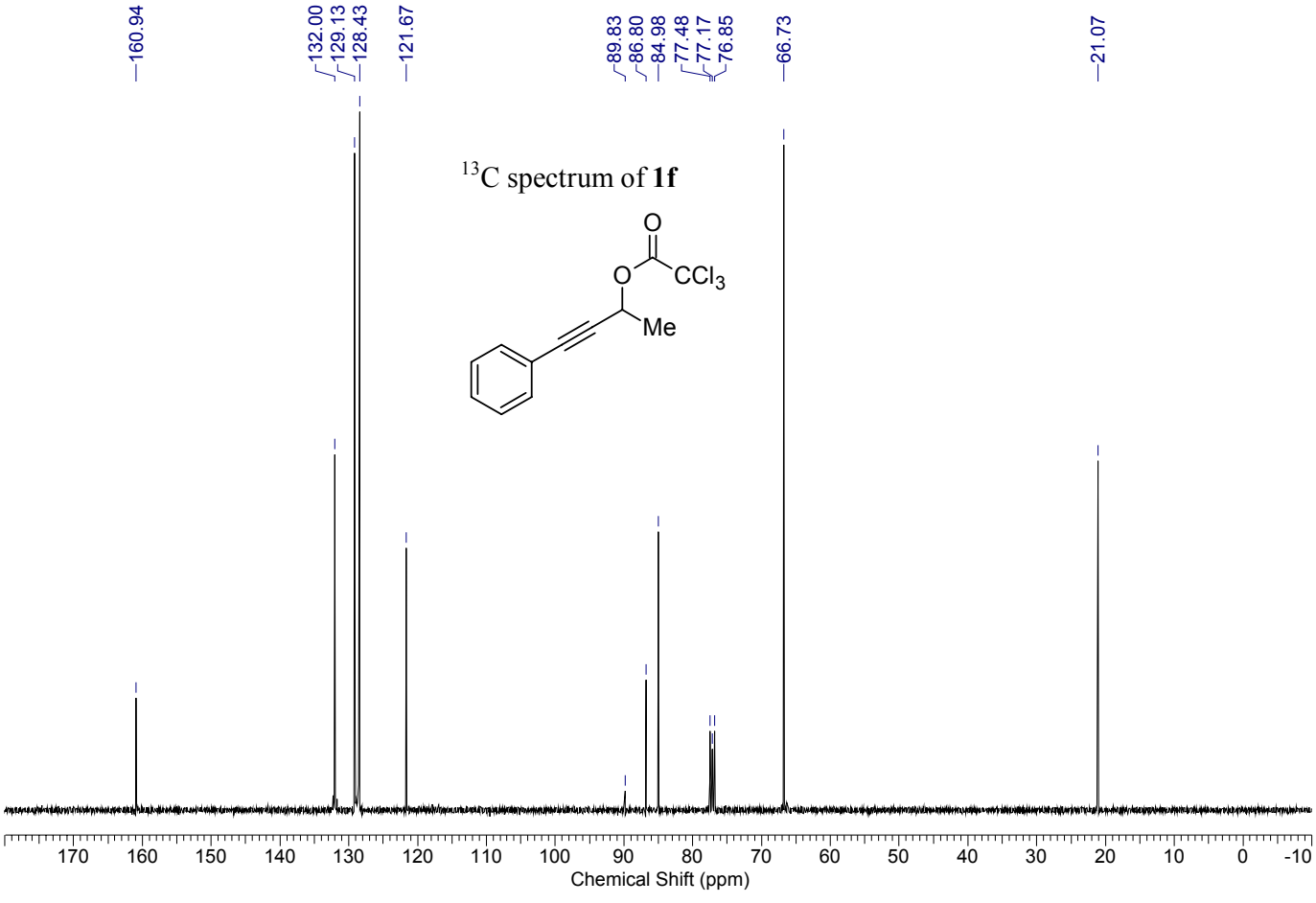
^{1}H spectrum of **1e**



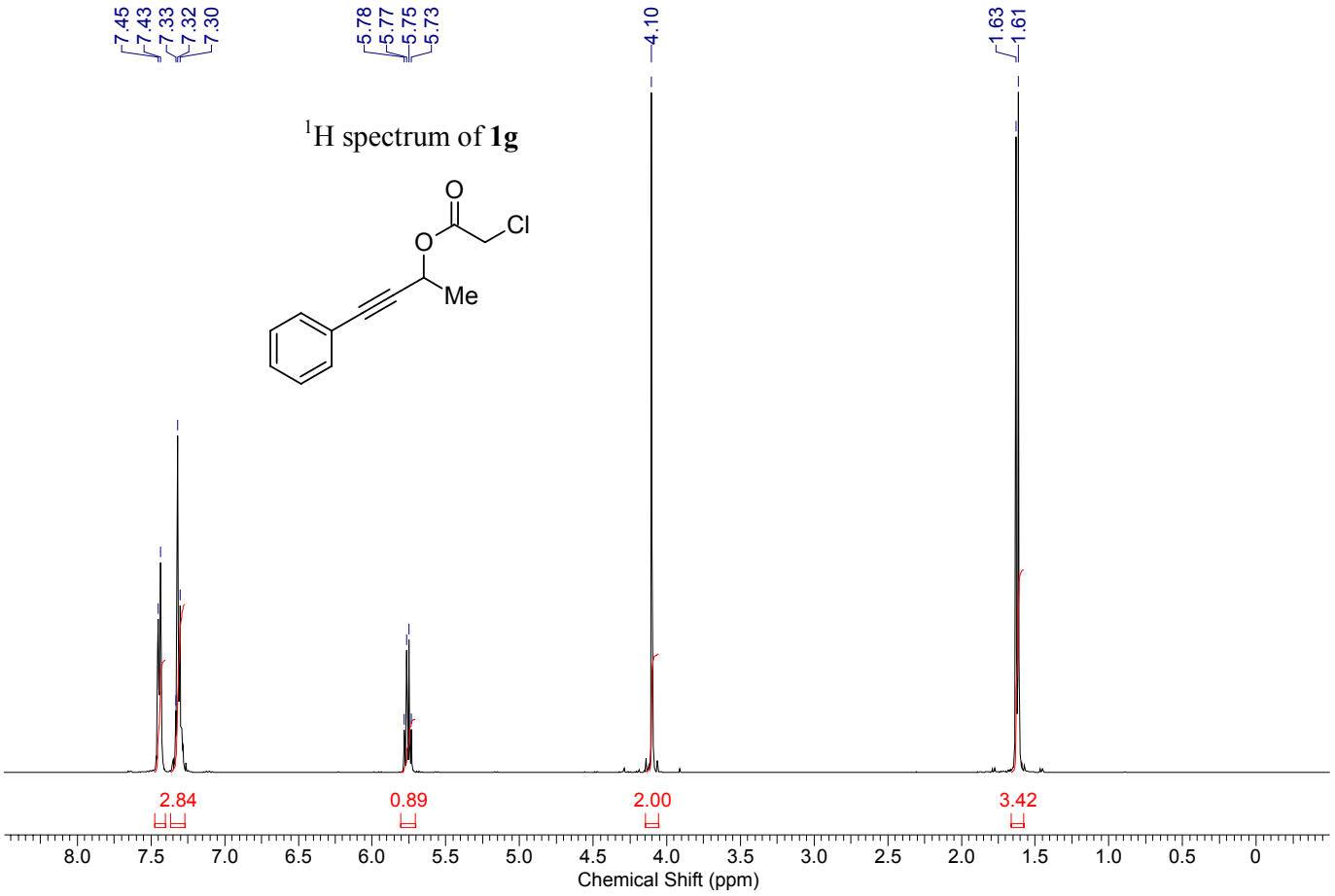
^{13}C spectrum of **1e**



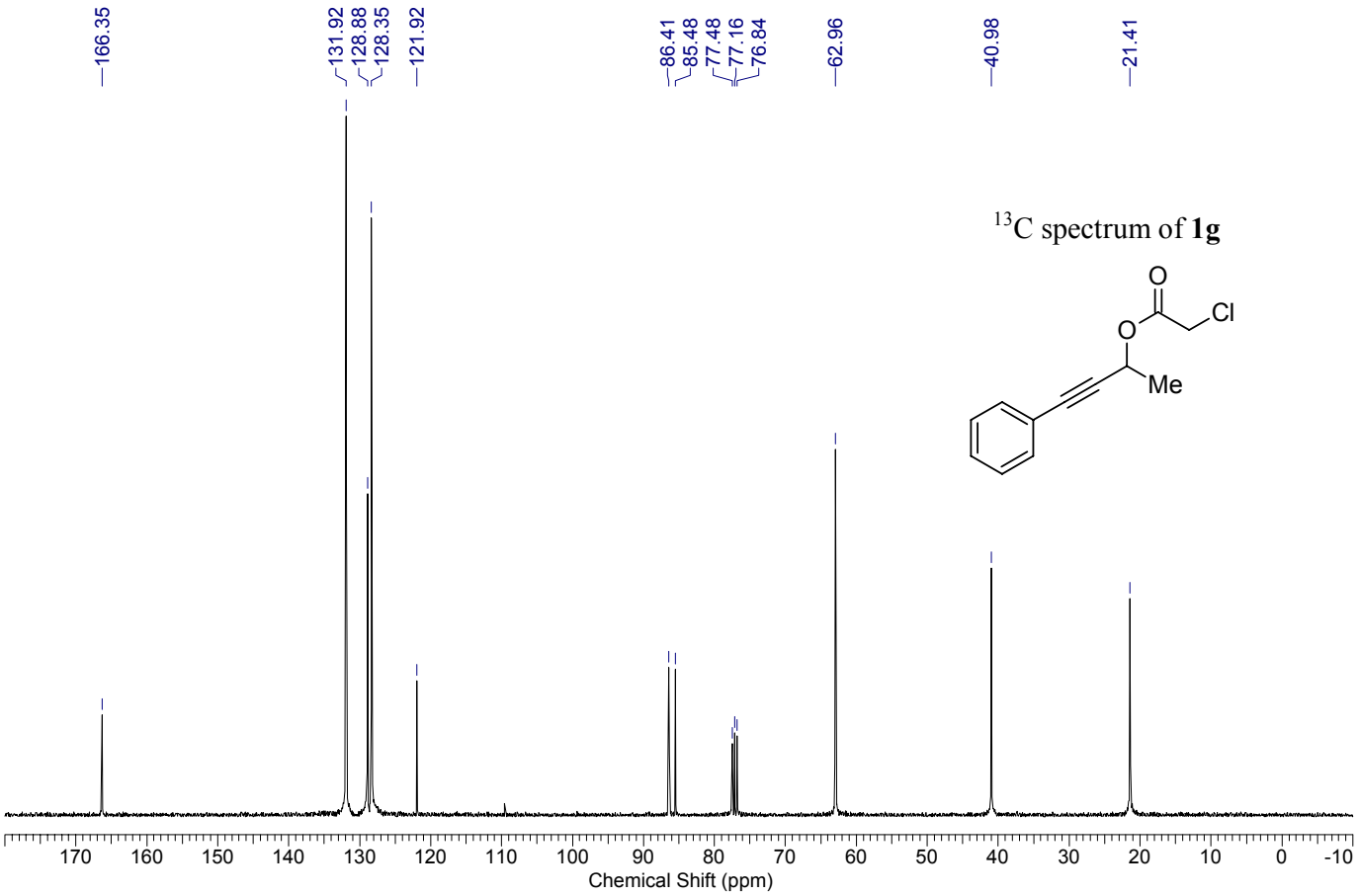
^{1}H spectrum of **1f**



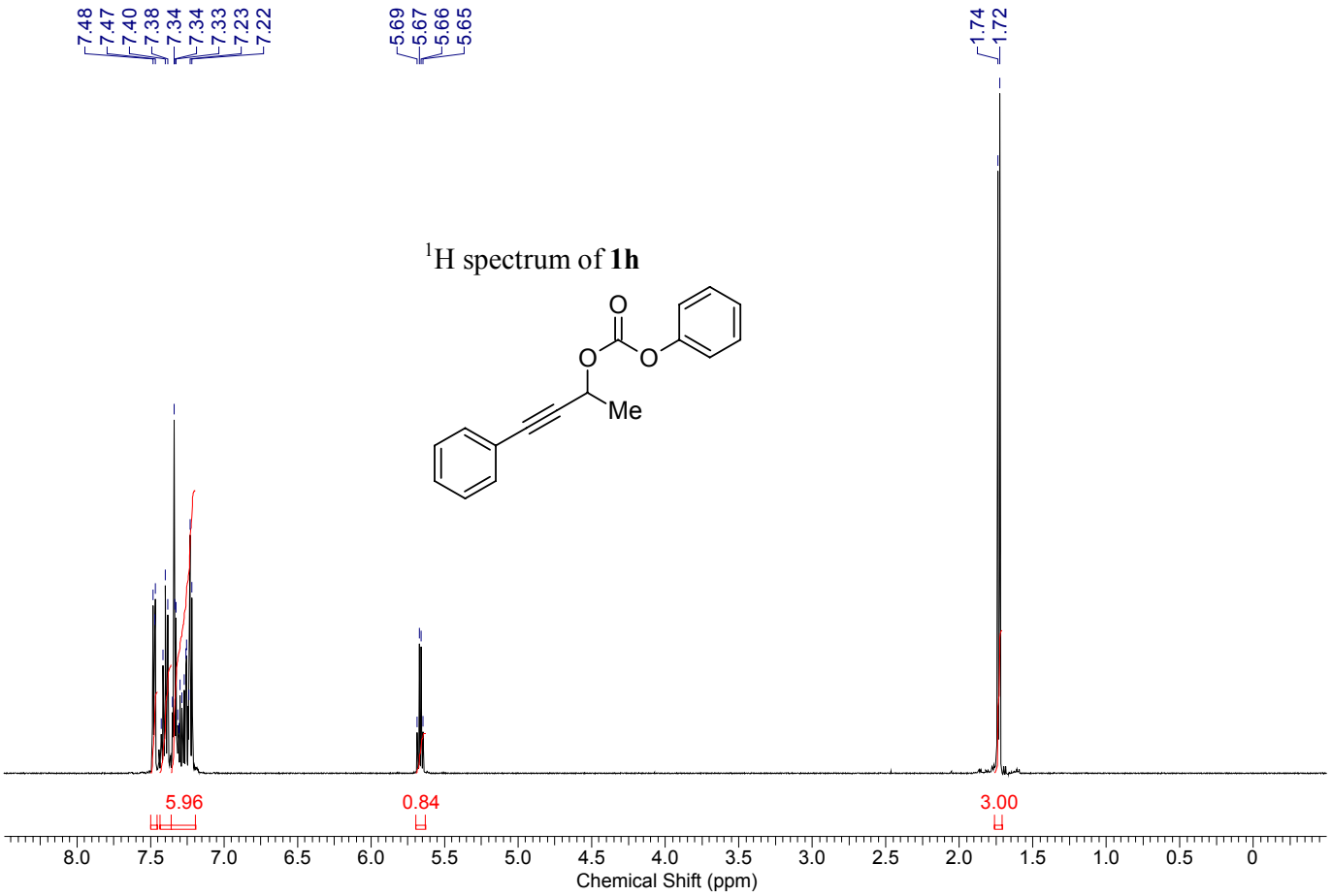
^{13}C spectrum of **1f**



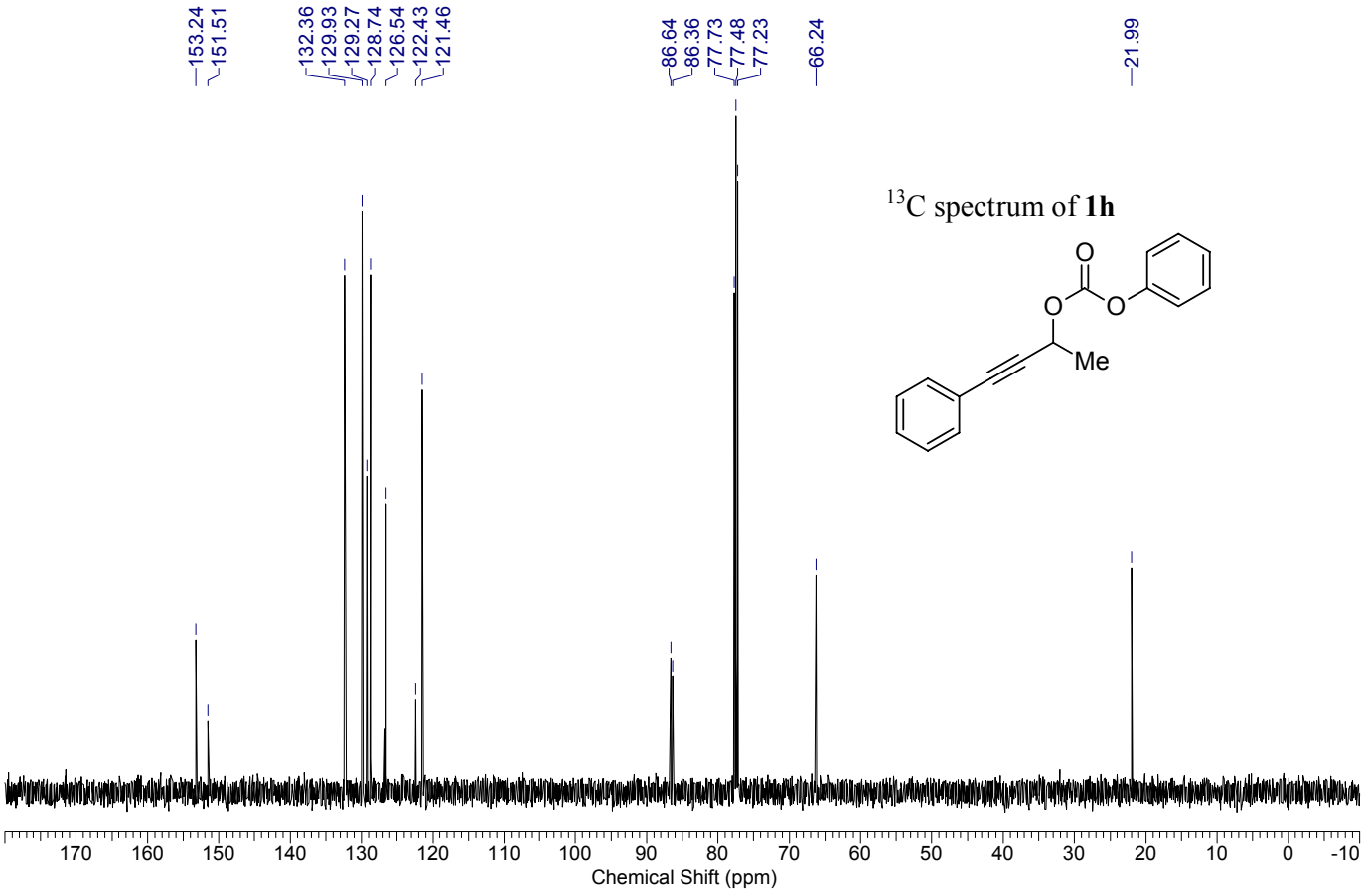
^{1}H spectrum of **1g**



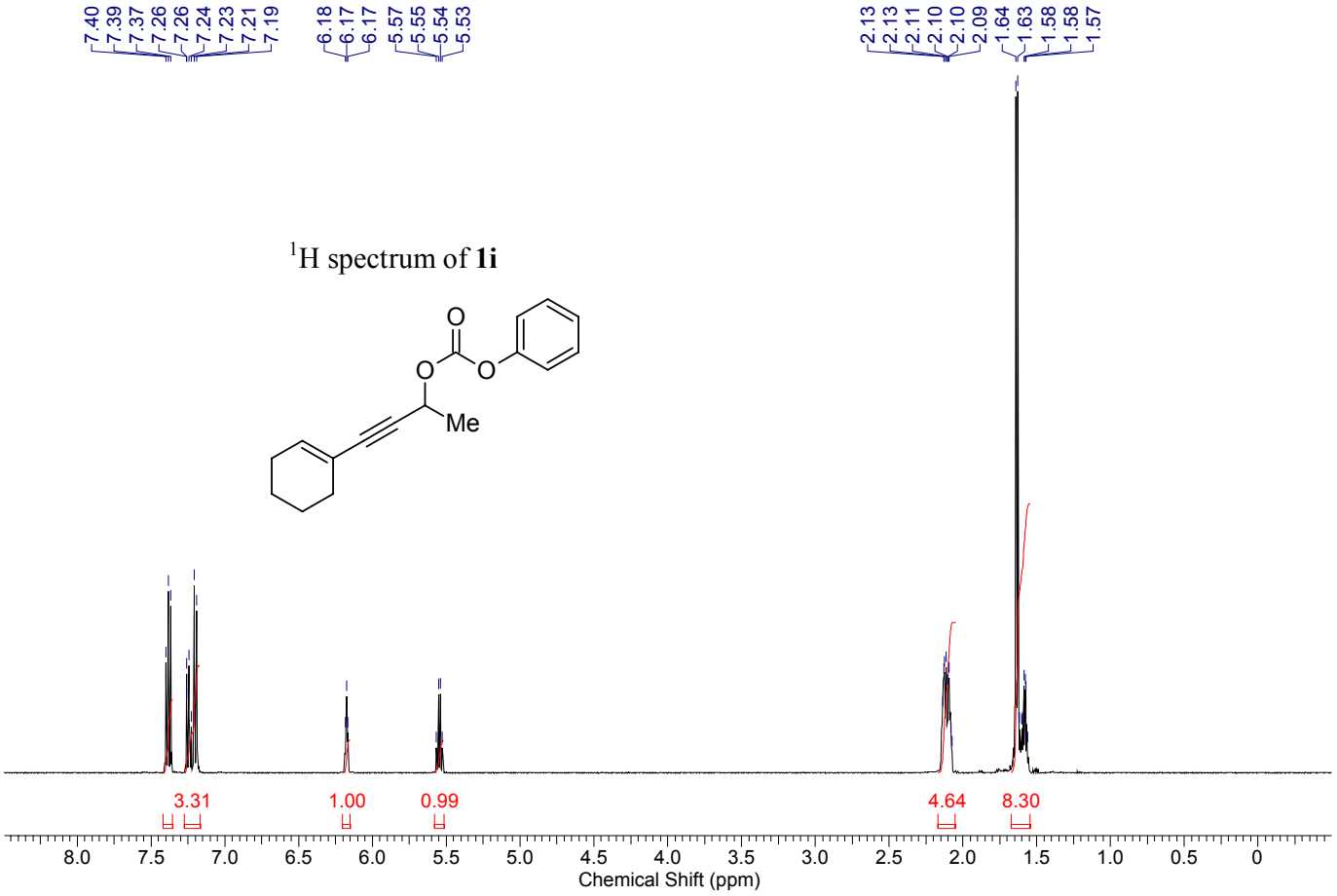
^{13}C spectrum of **1g**



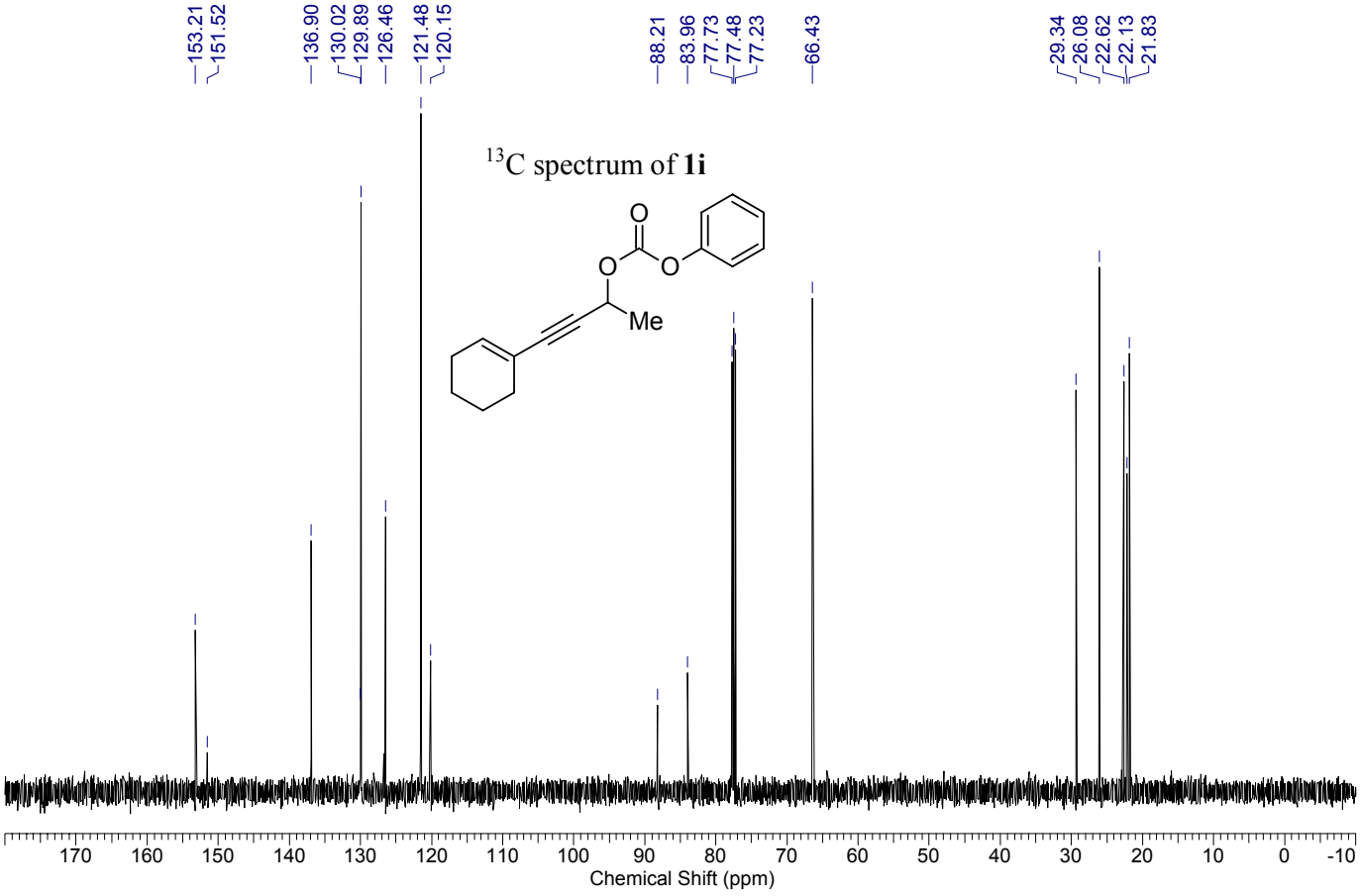
^{1}H spectrum of **1h**



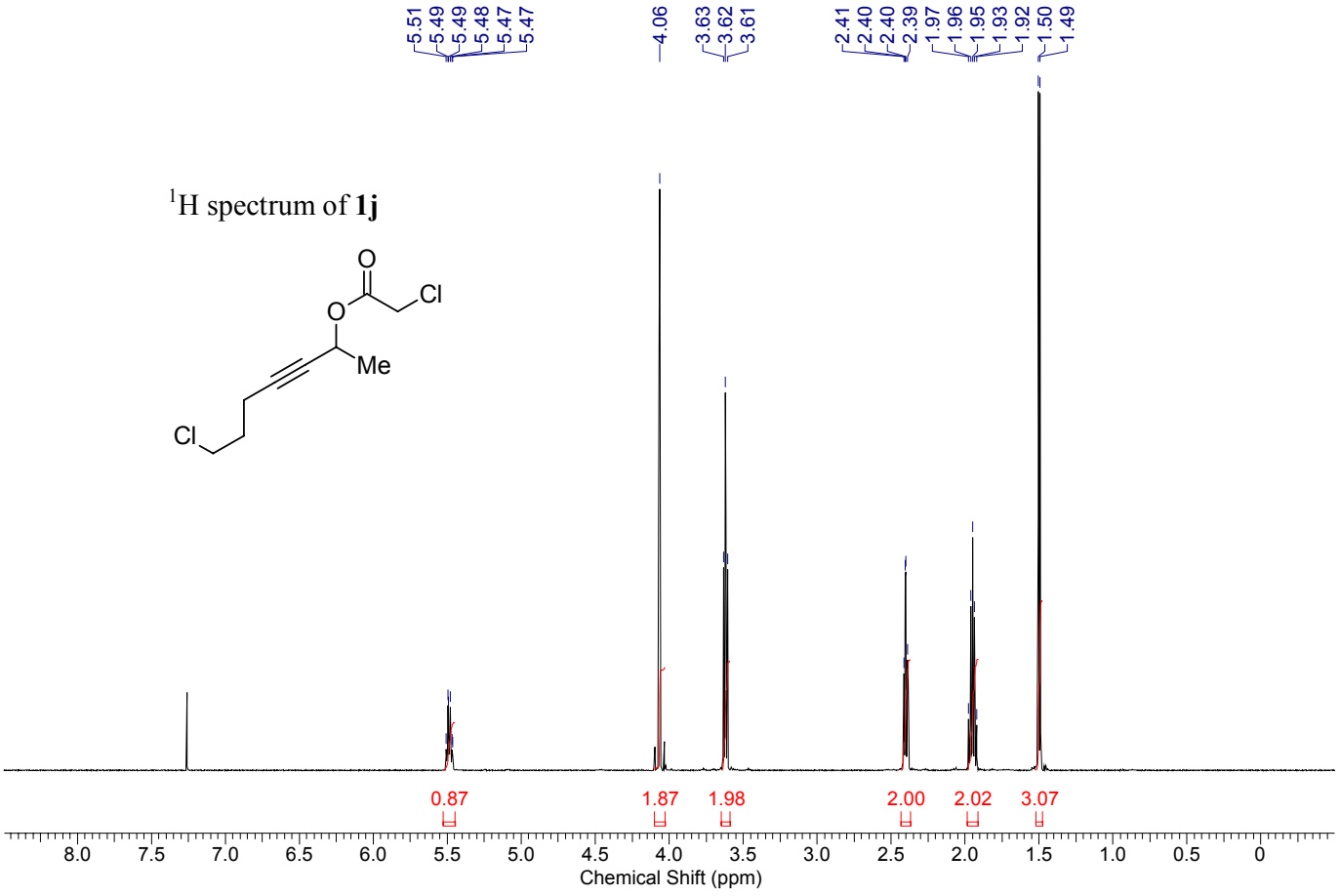
^{13}C spectrum of **1h**



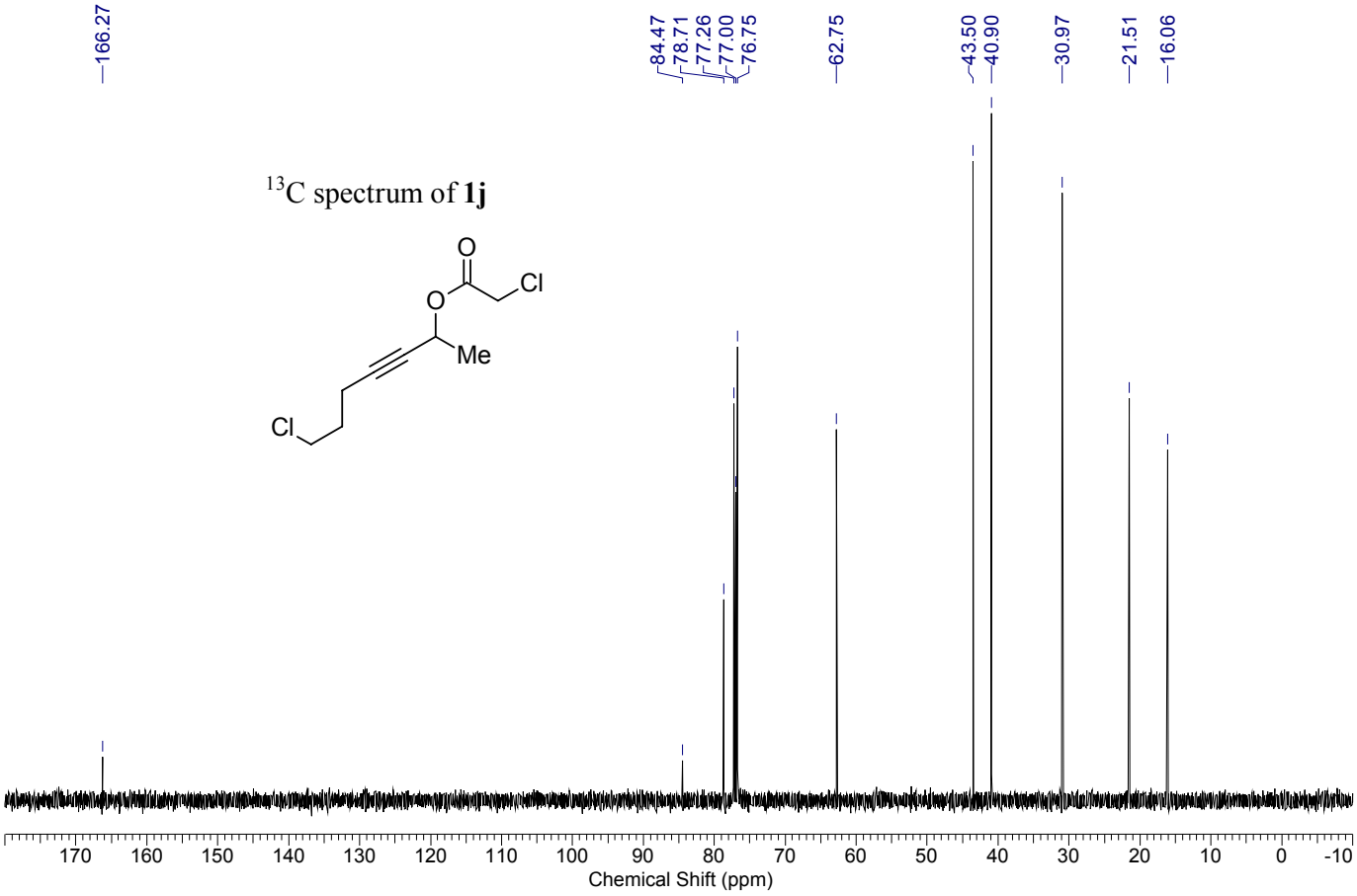
^{1}H spectrum of **1i**



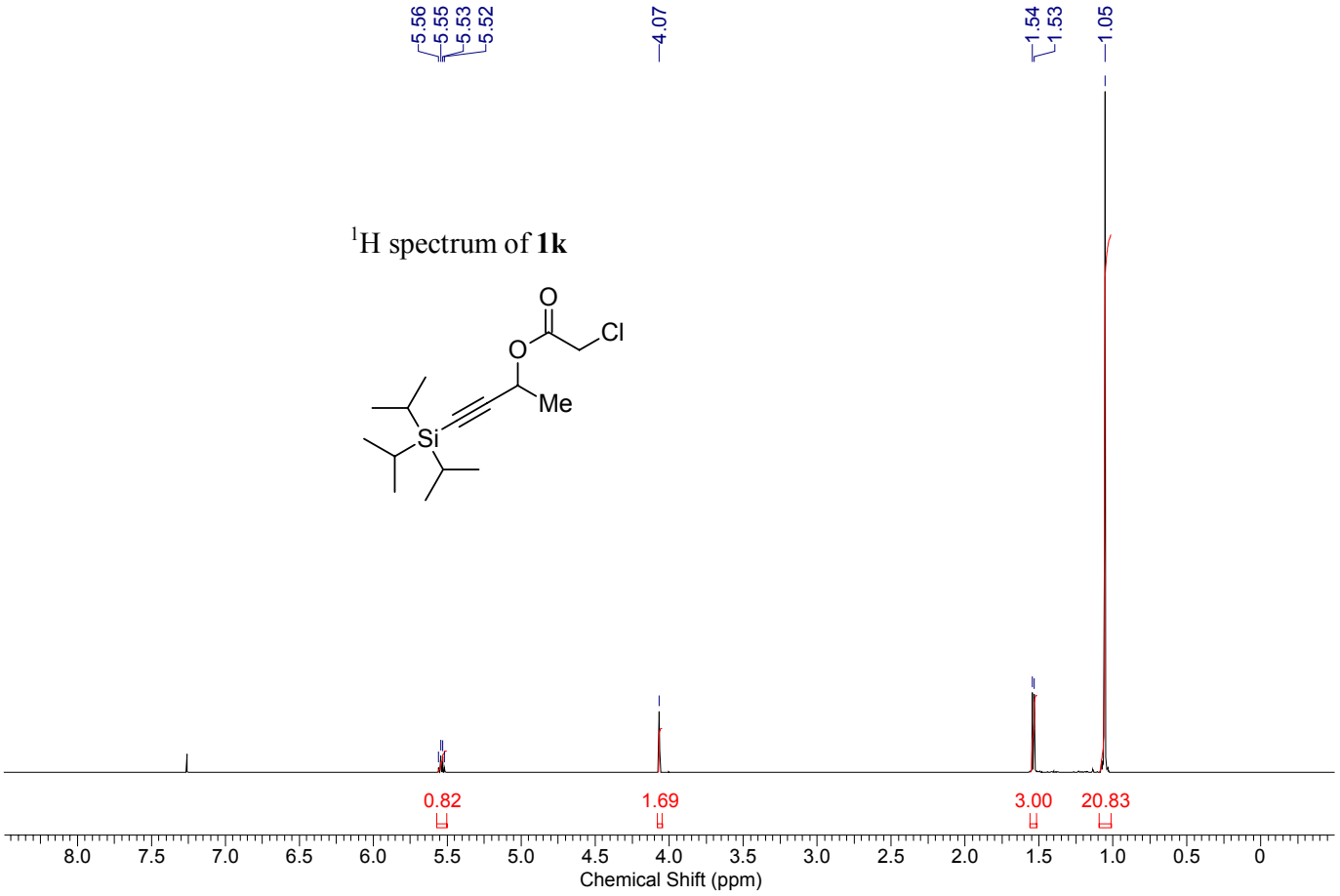
^{13}C spectrum of **1i**



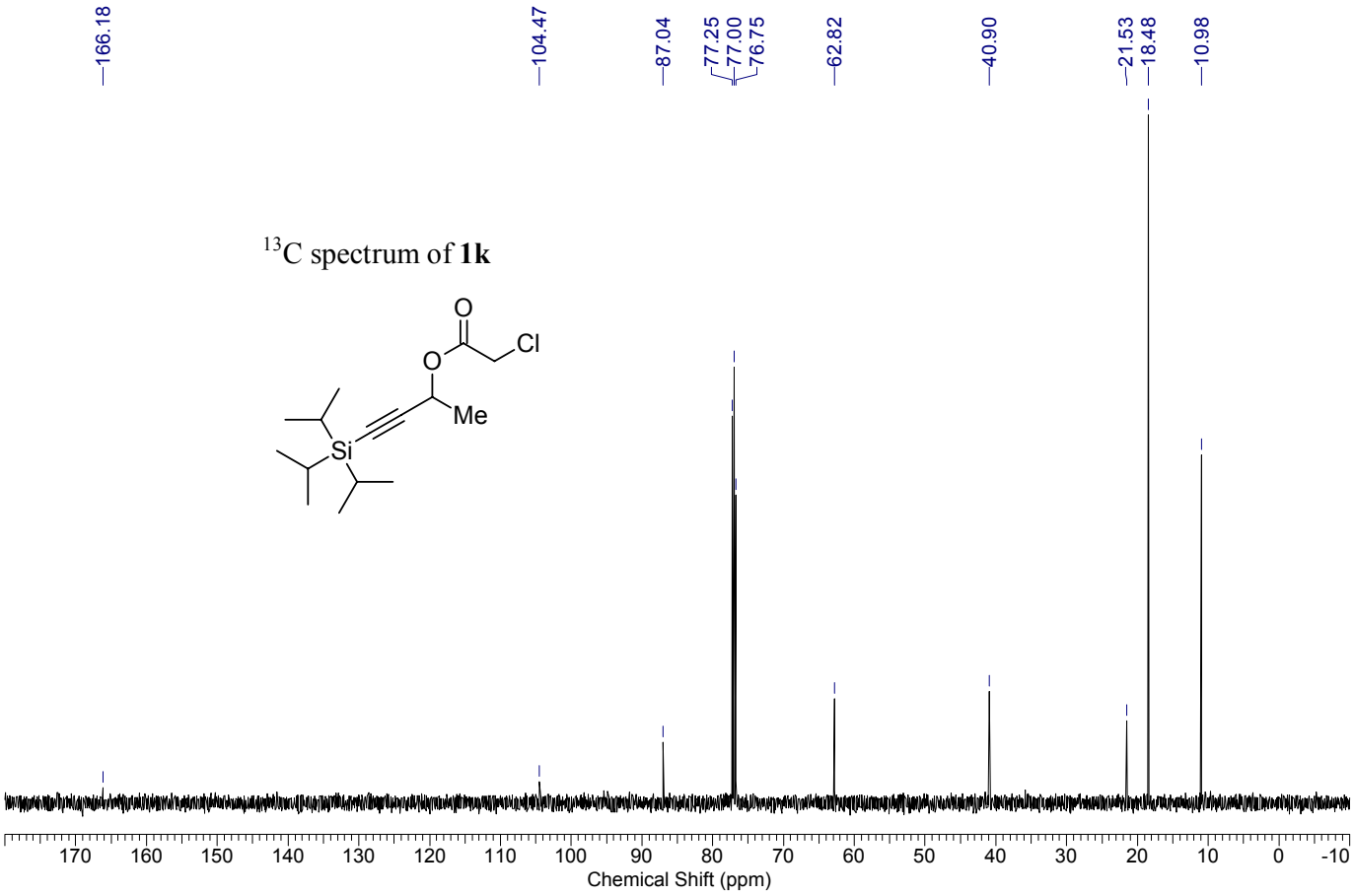
^{1}H spectrum of **1j**



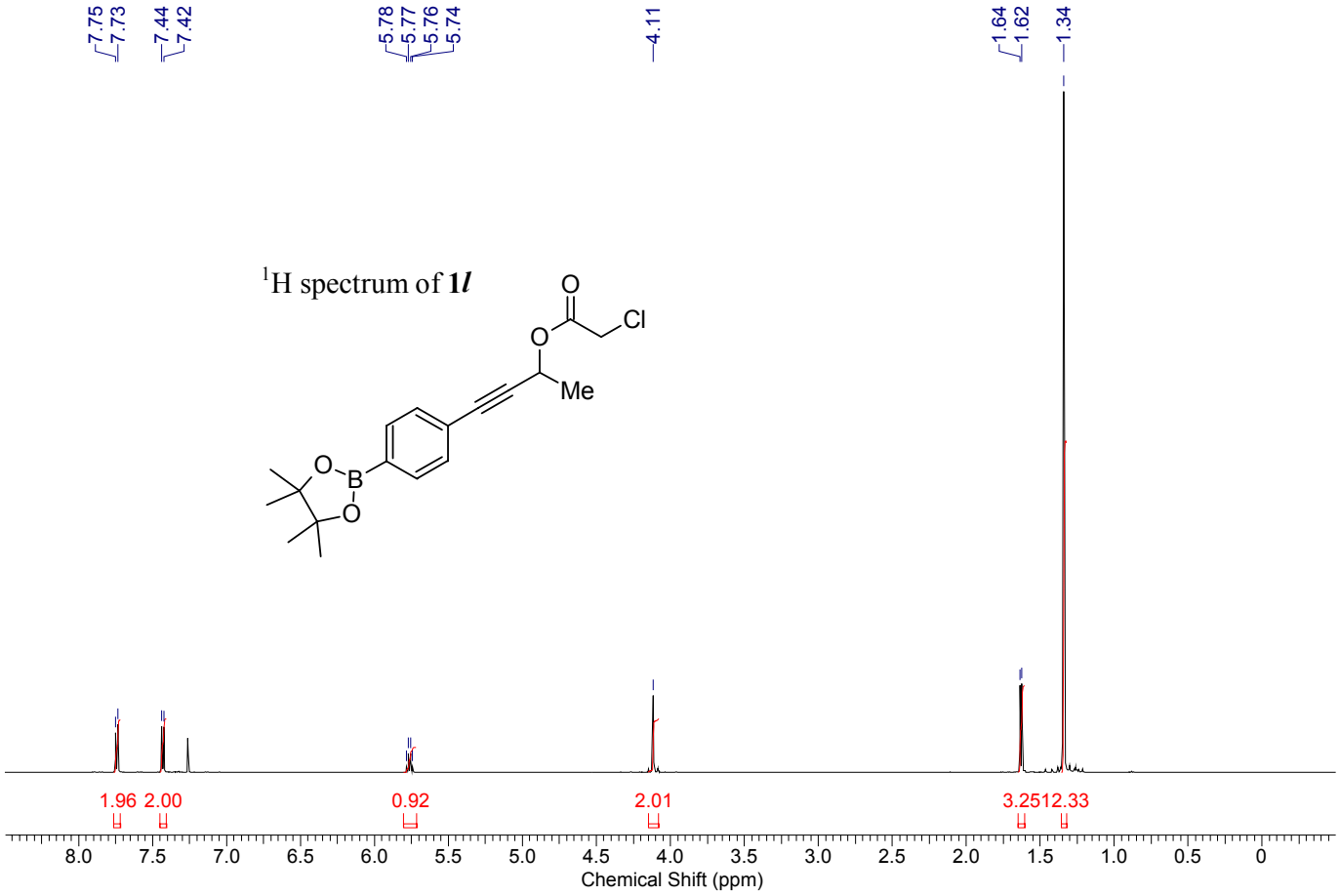
^{13}C spectrum of **1j**



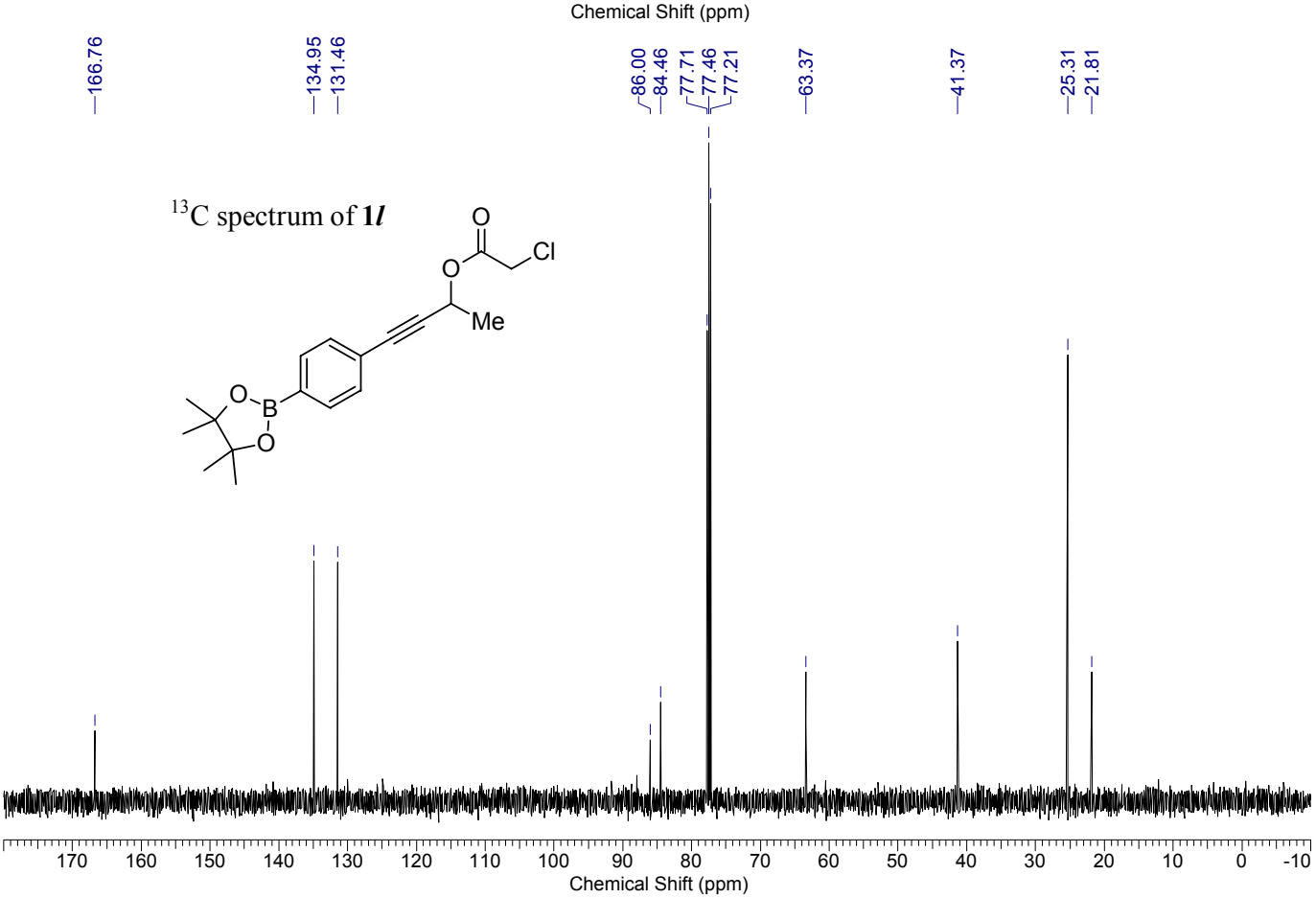
^{1}H spectrum of **1k**



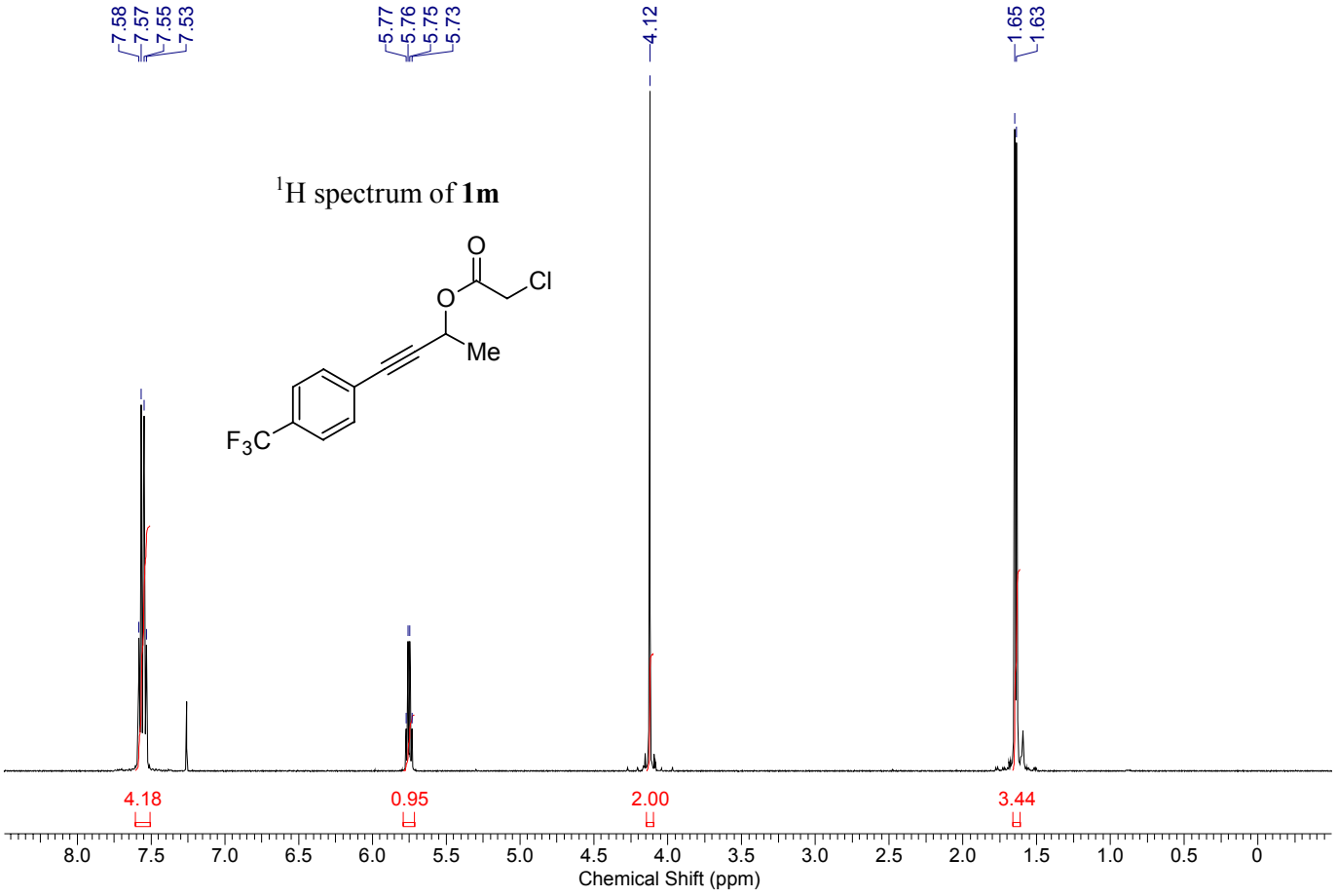
^{13}C spectrum of **1k**



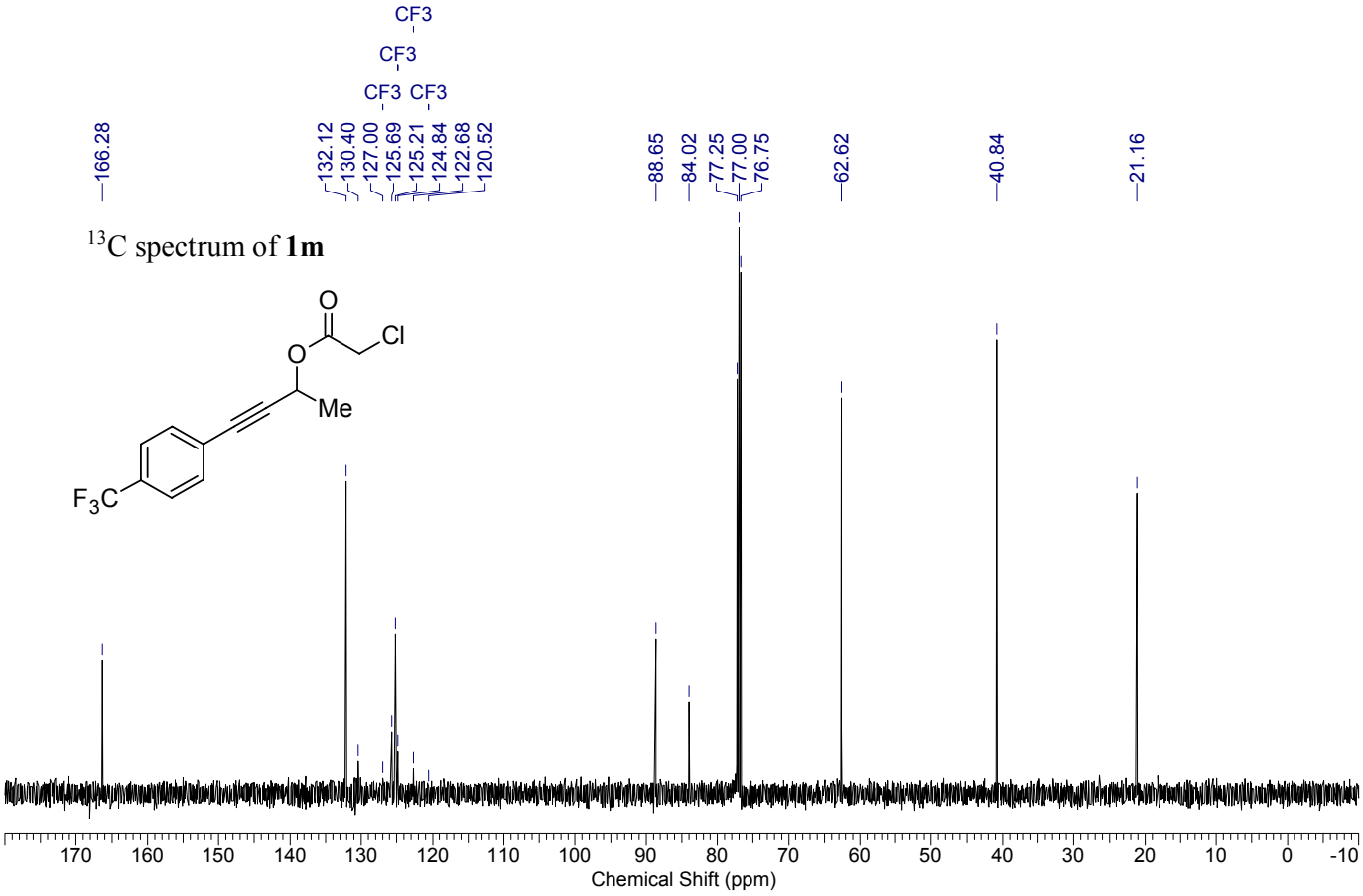
^{1}H spectrum of ***1l***



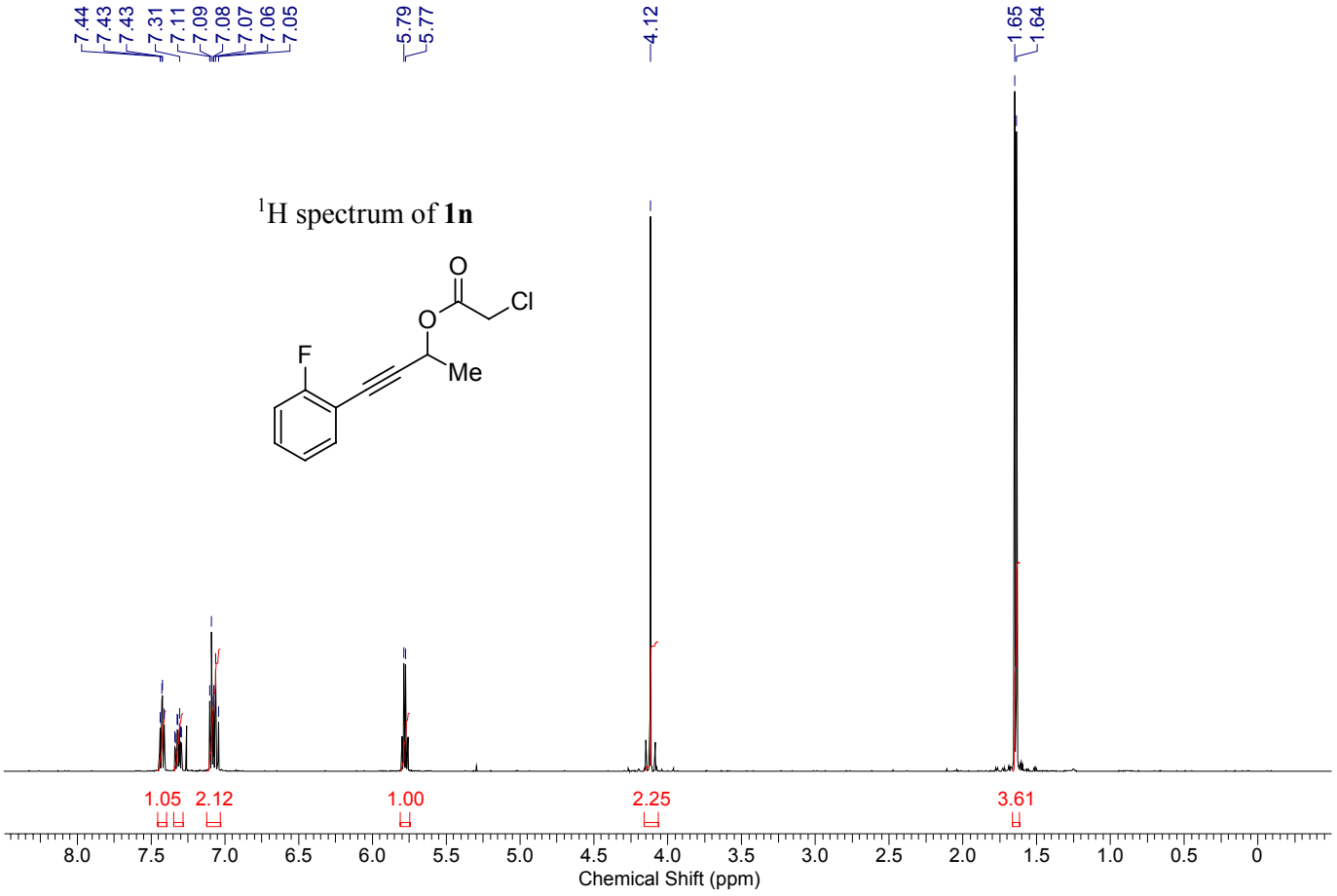
^{13}C spectrum of ***1l***



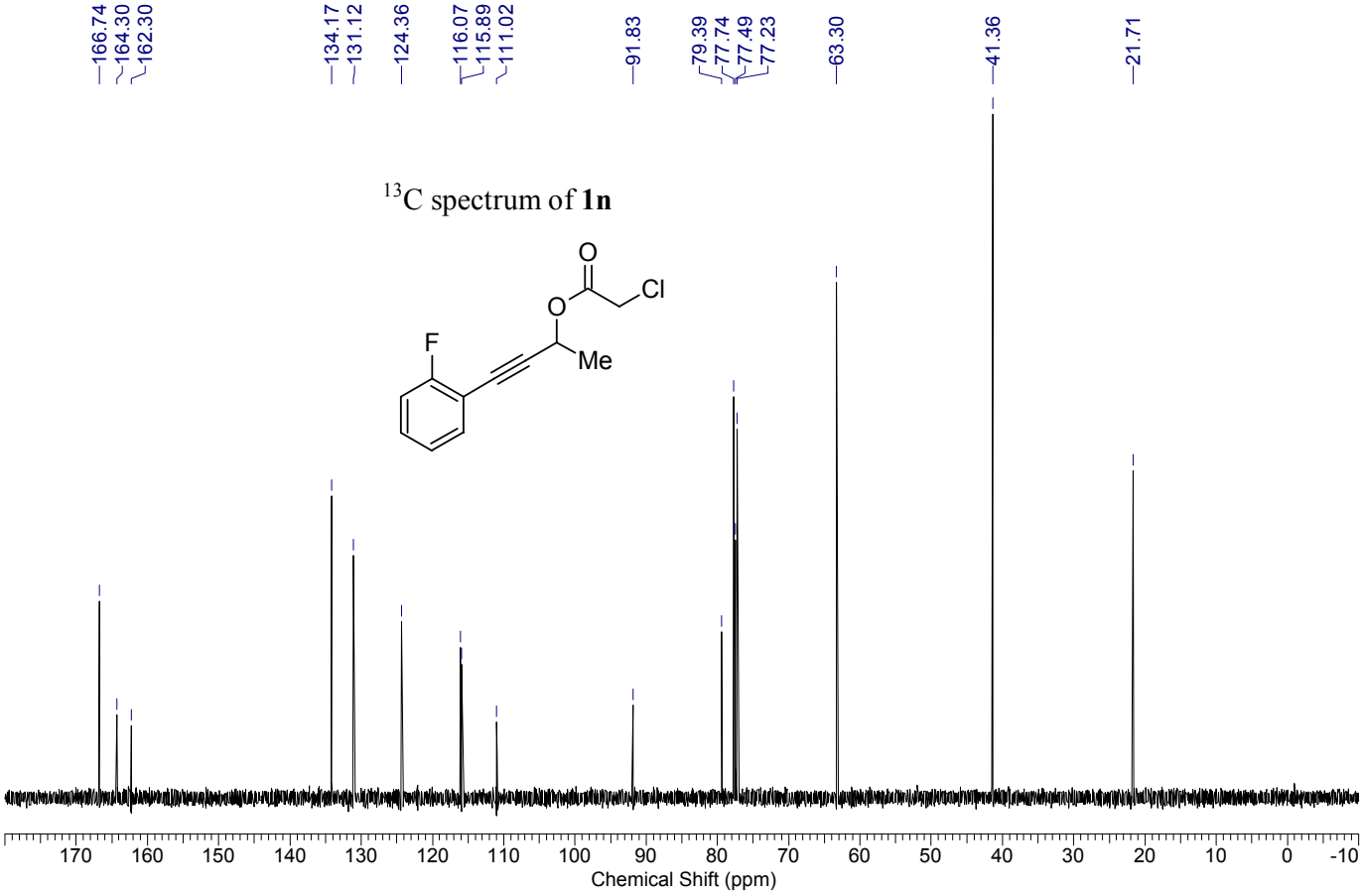
^{1}H spectrum of **1m**



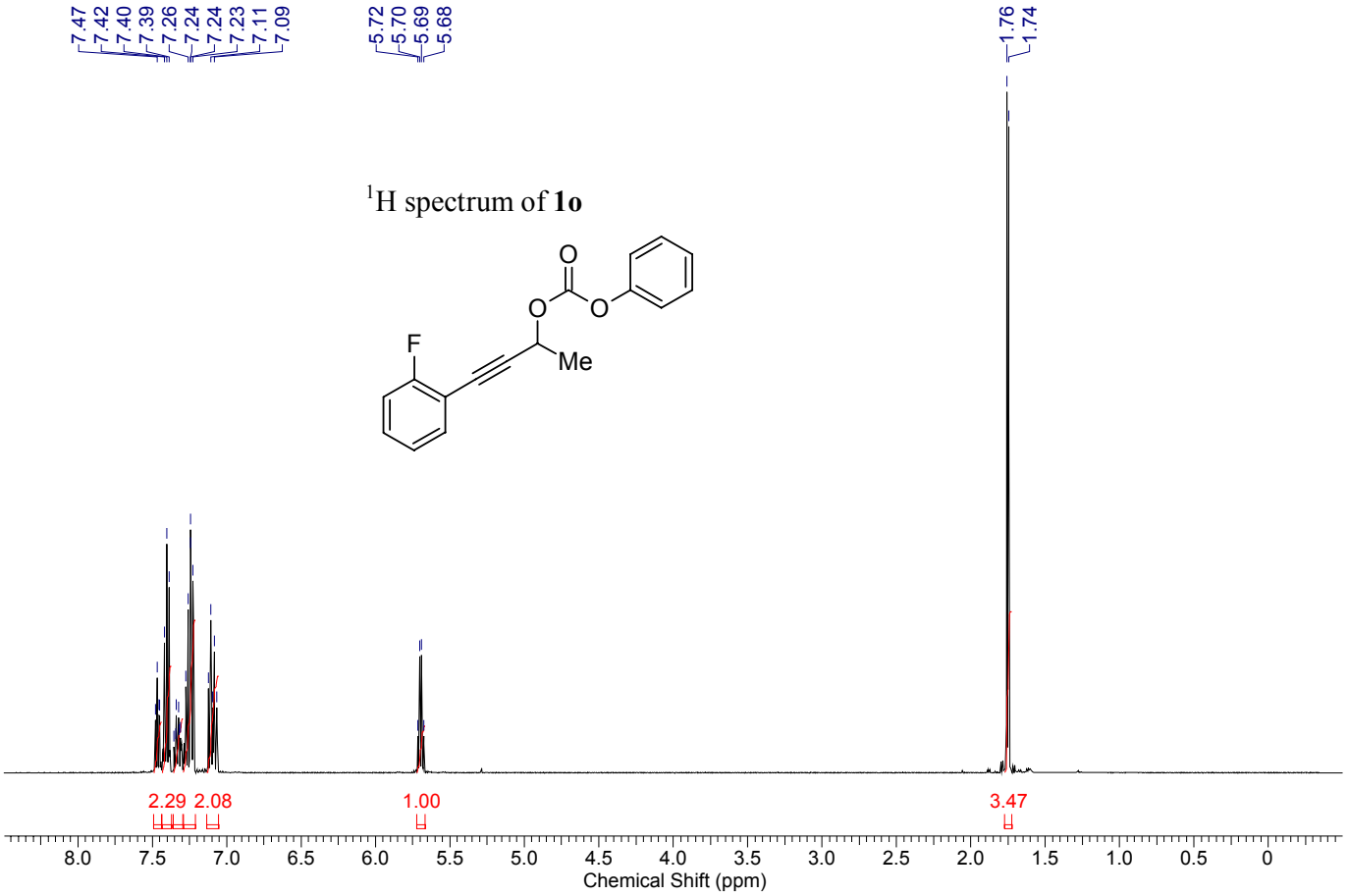
^{13}C spectrum of **1m**



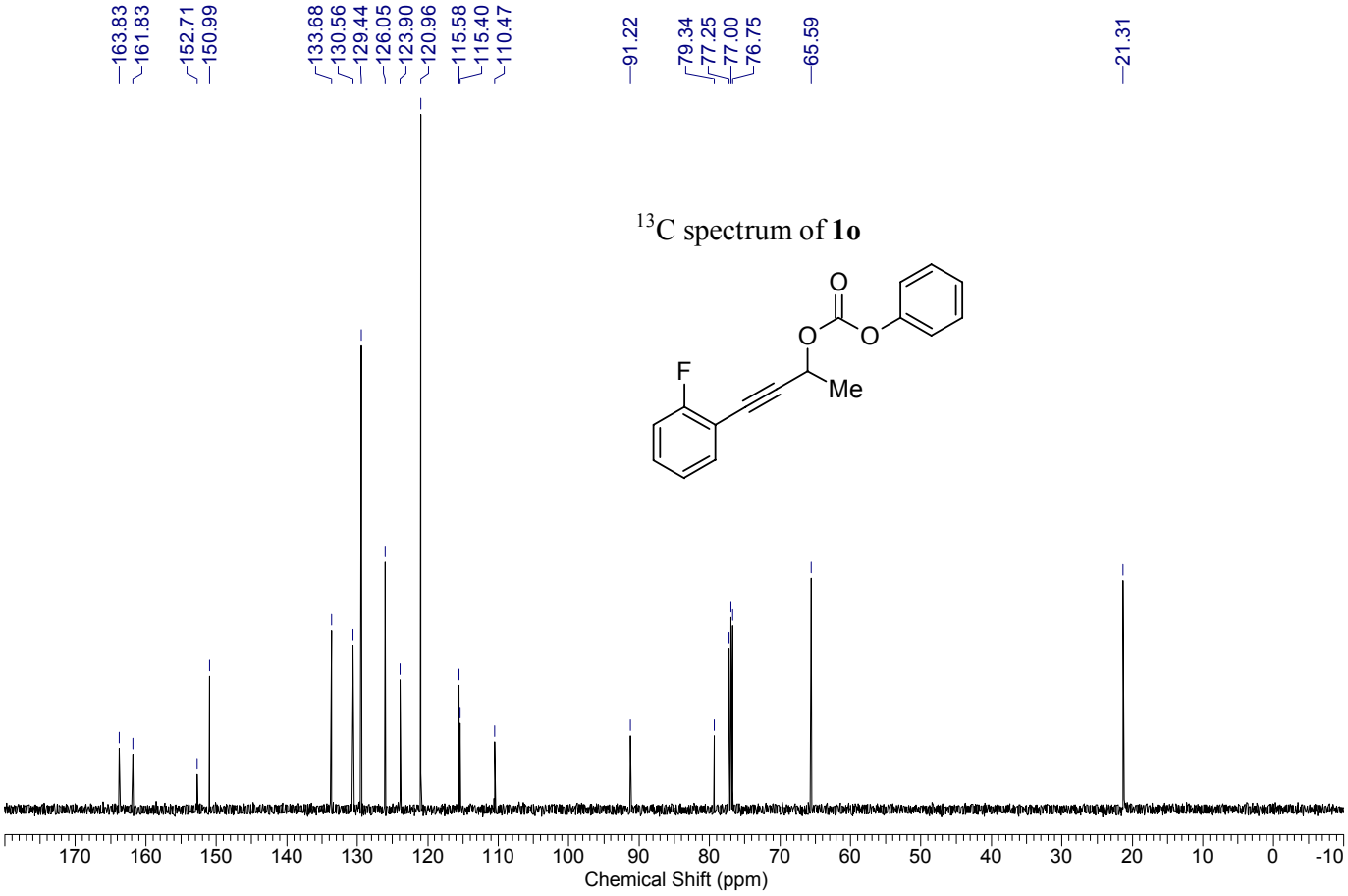
^{1}H spectrum of **1n**



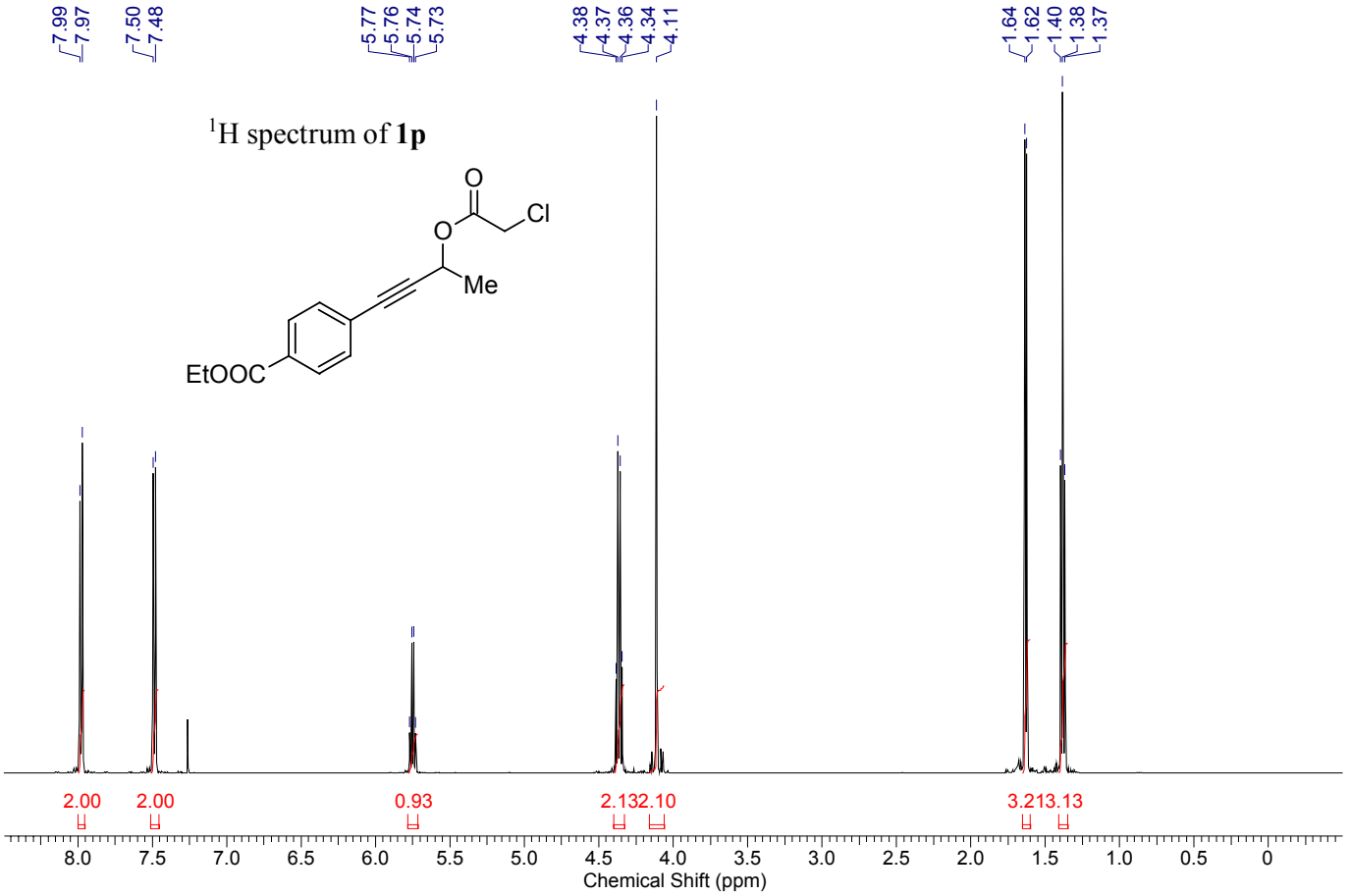
^{13}C spectrum of **1n**

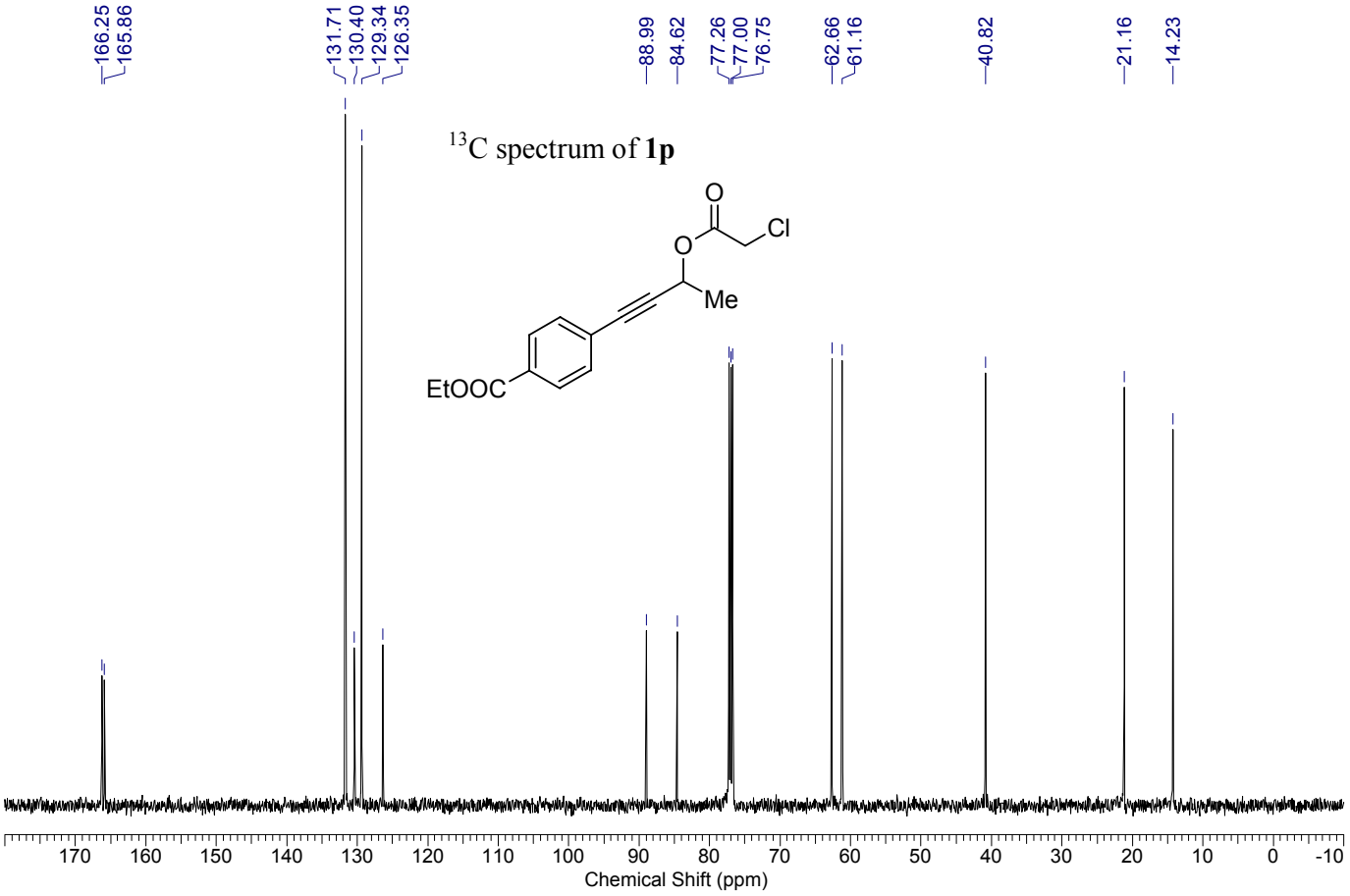


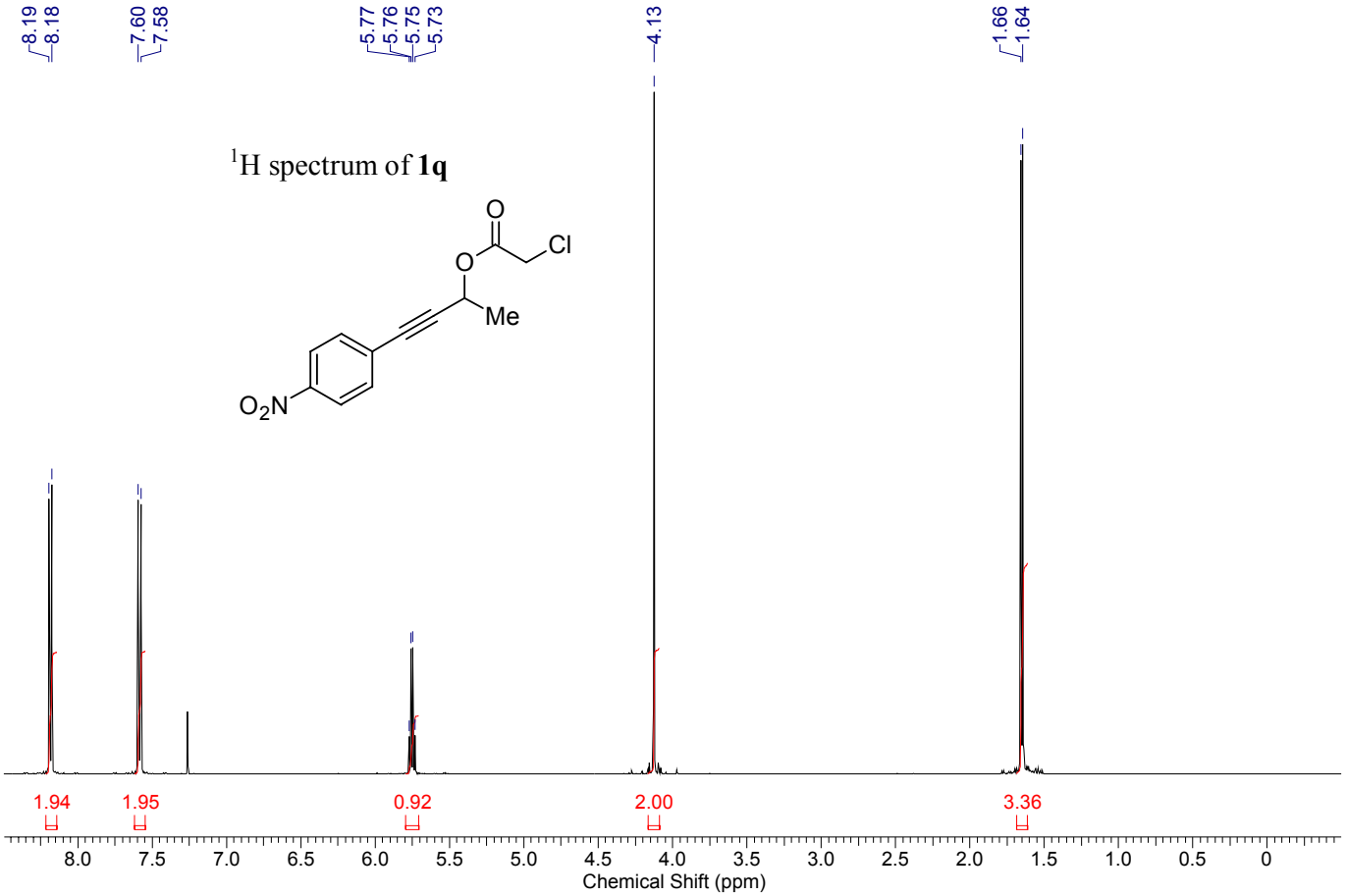
^{1}H spectrum of **1o**

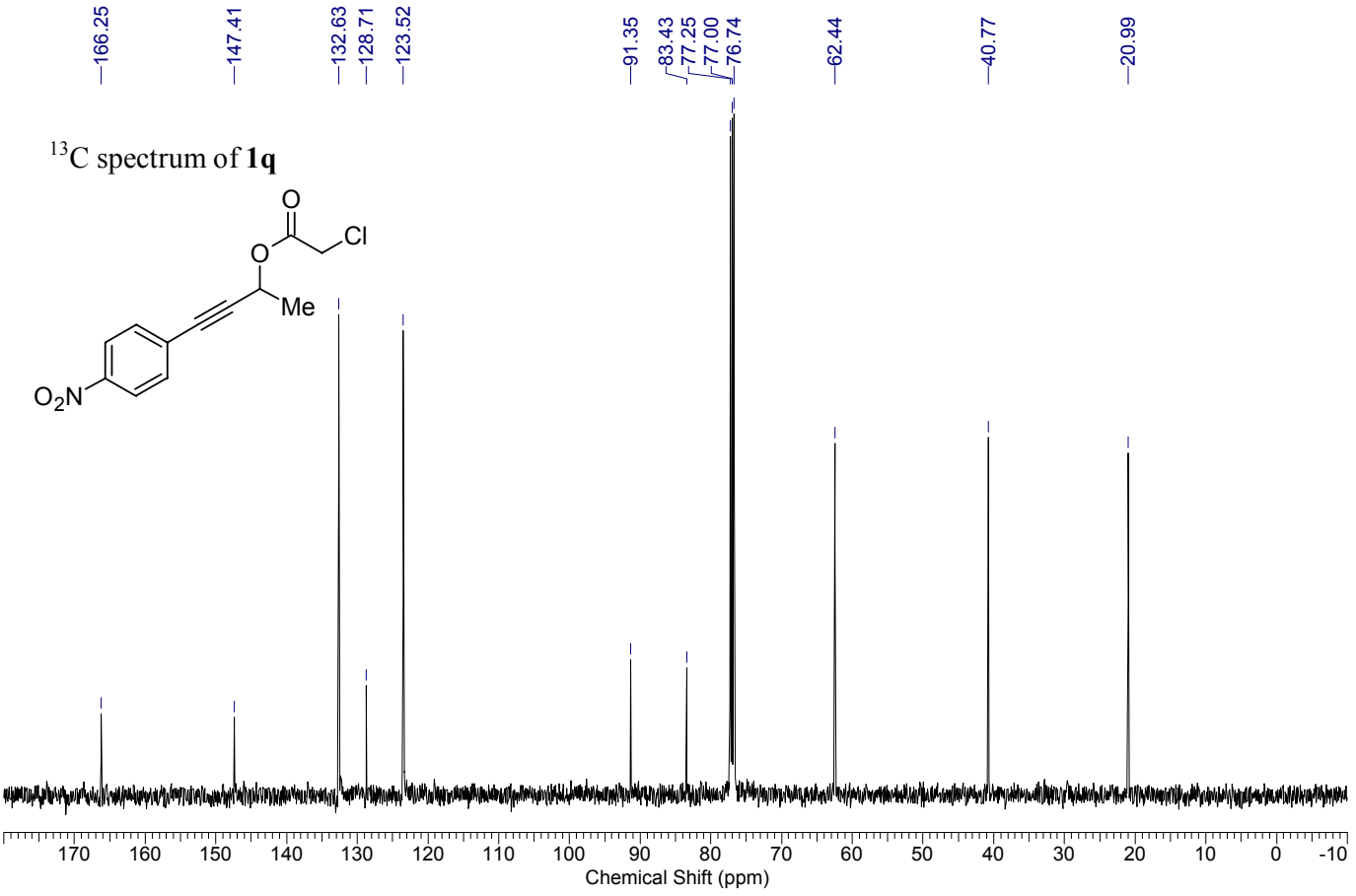


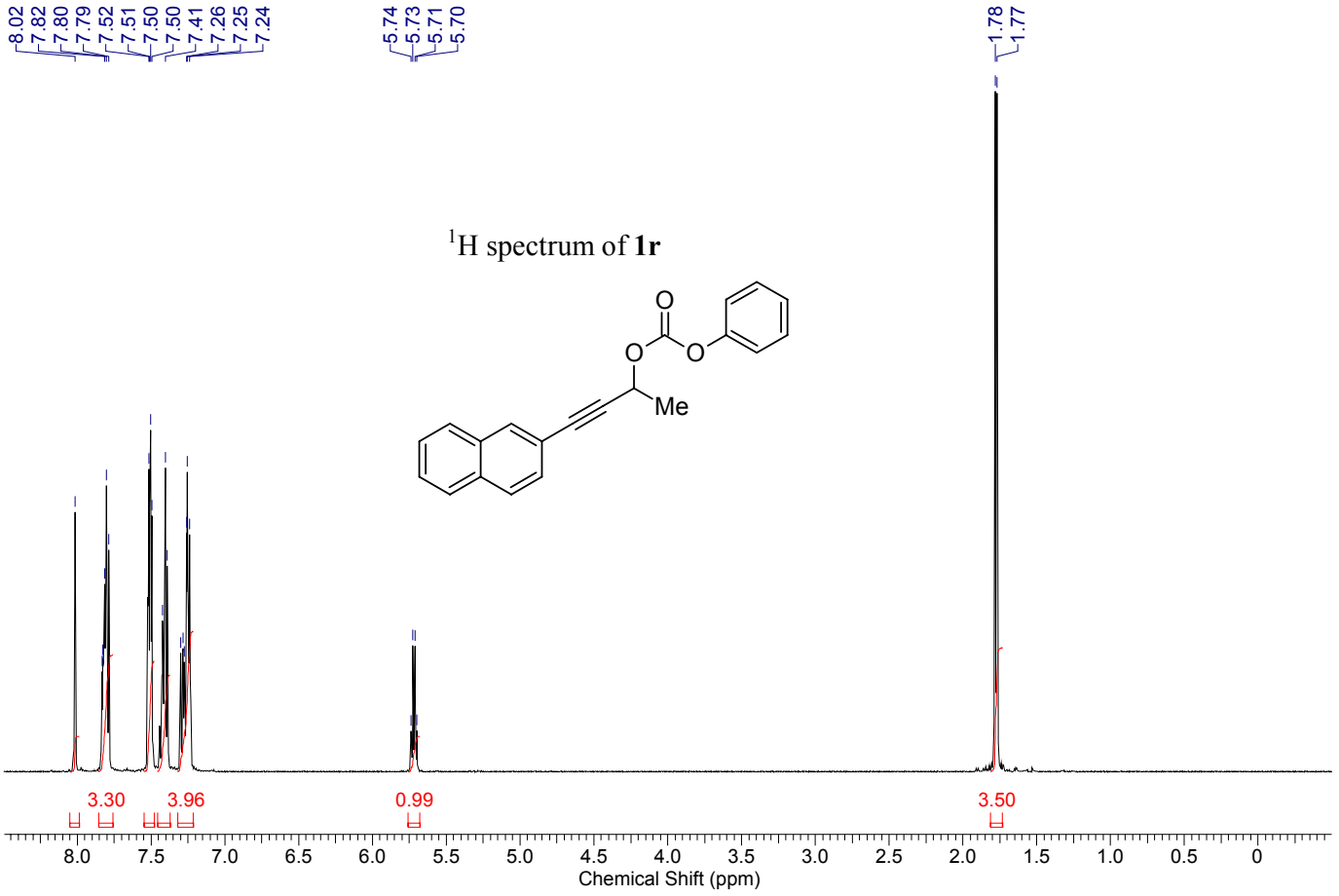
^{13}C spectrum of **1o**


7.99
7.97
7.50
7.48
5.77
5.76
5.74
5.73
4.38
4.37
4.36
4.34
4.11
1.64
1.62
1.40
1.38
1.37
^{1}H spectrum of **1p**
O
O
Cl
Me
EtOOC
2.00
2.00
0.93
2.13
2.10
3.21
3.13
Chemical Shift (ppm)

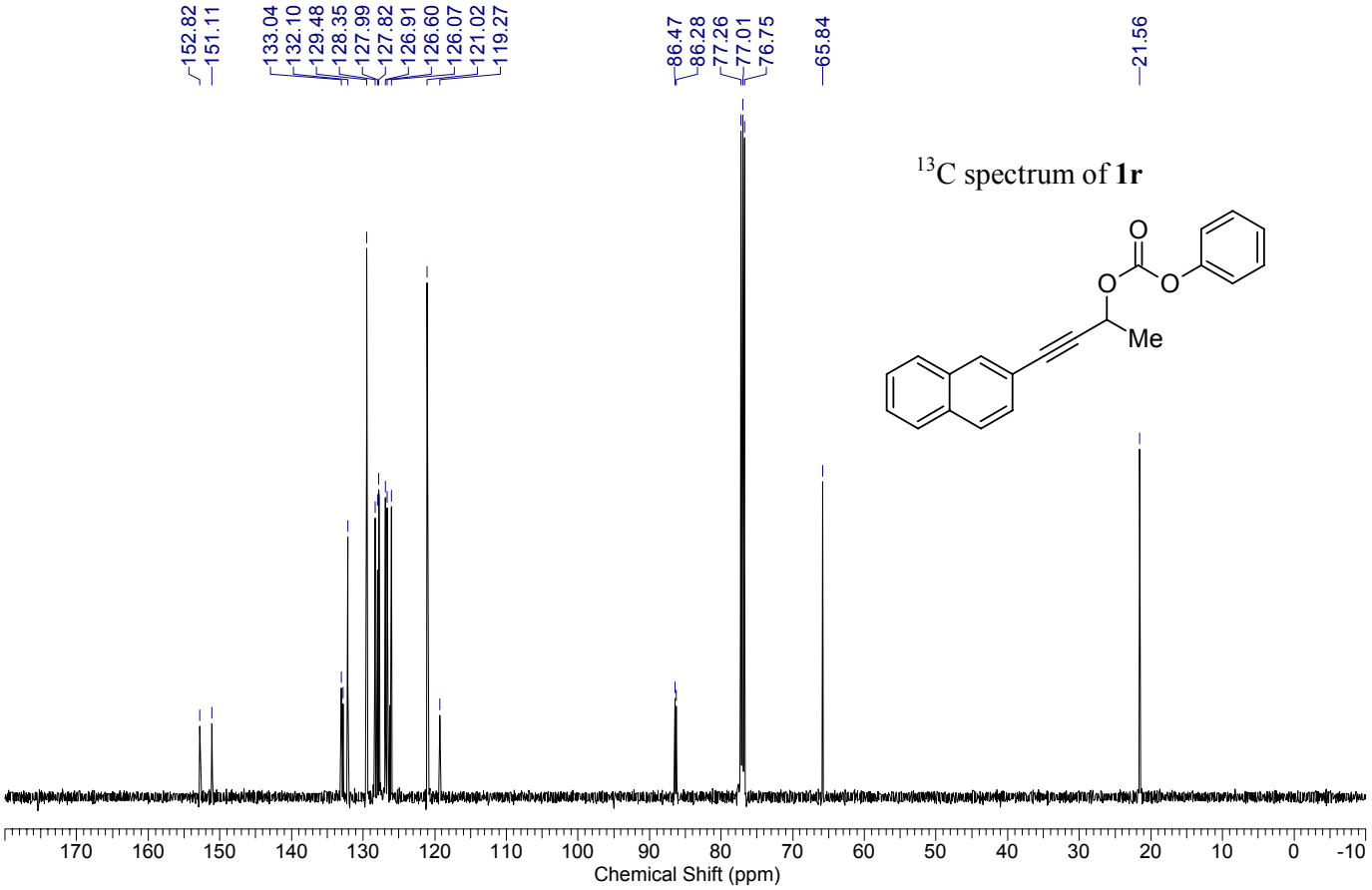

166.25
165.86
131.71
130.40
129.34
126.35
88.99
84.62
77.26
77.00
76.75
62.66
61.16
40.82
21.16
14.23
^{13}C spectrum of **1p**
O
O
Cl
Me
EtOOC
Chemical Shift (ppm)


8.19
8.18
7.60
7.58
5.77
5.76
5.75
5.73
4.13
1.66
1.64
^{1}H spectrum of **1q**
O
Cl
O
Me
O_2N
1.94
1.95
0.92
2.00
3.36
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
Chemical Shift (ppm)

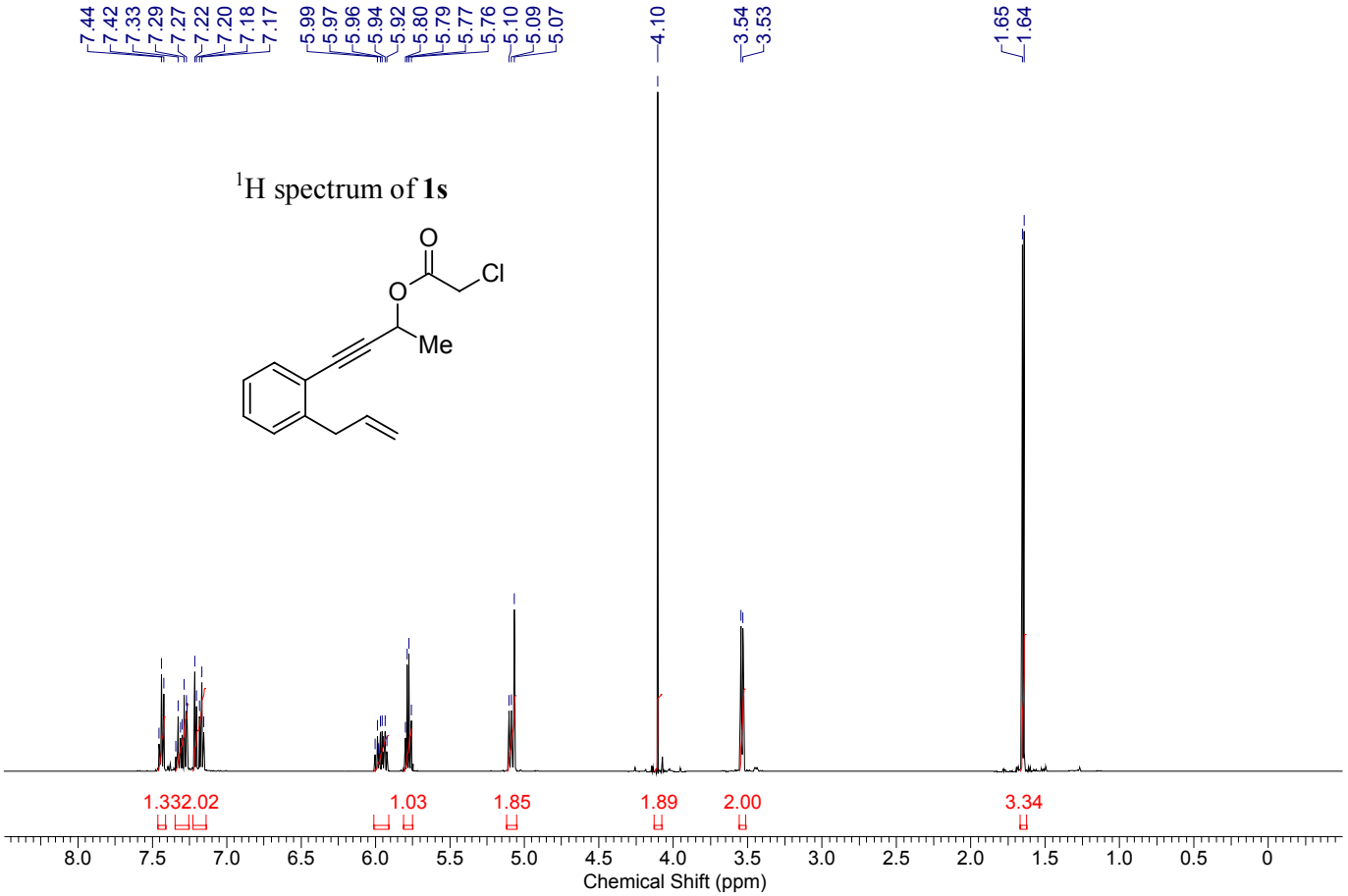

166.25
147.41
132.63
128.71
123.52
91.35
83.43
77.25
77.00
76.74
62.44
40.77
20.99
^{13}C spectrum of **1q**
O
Cl
O
Me
O_2N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Chemical Shift (ppm)

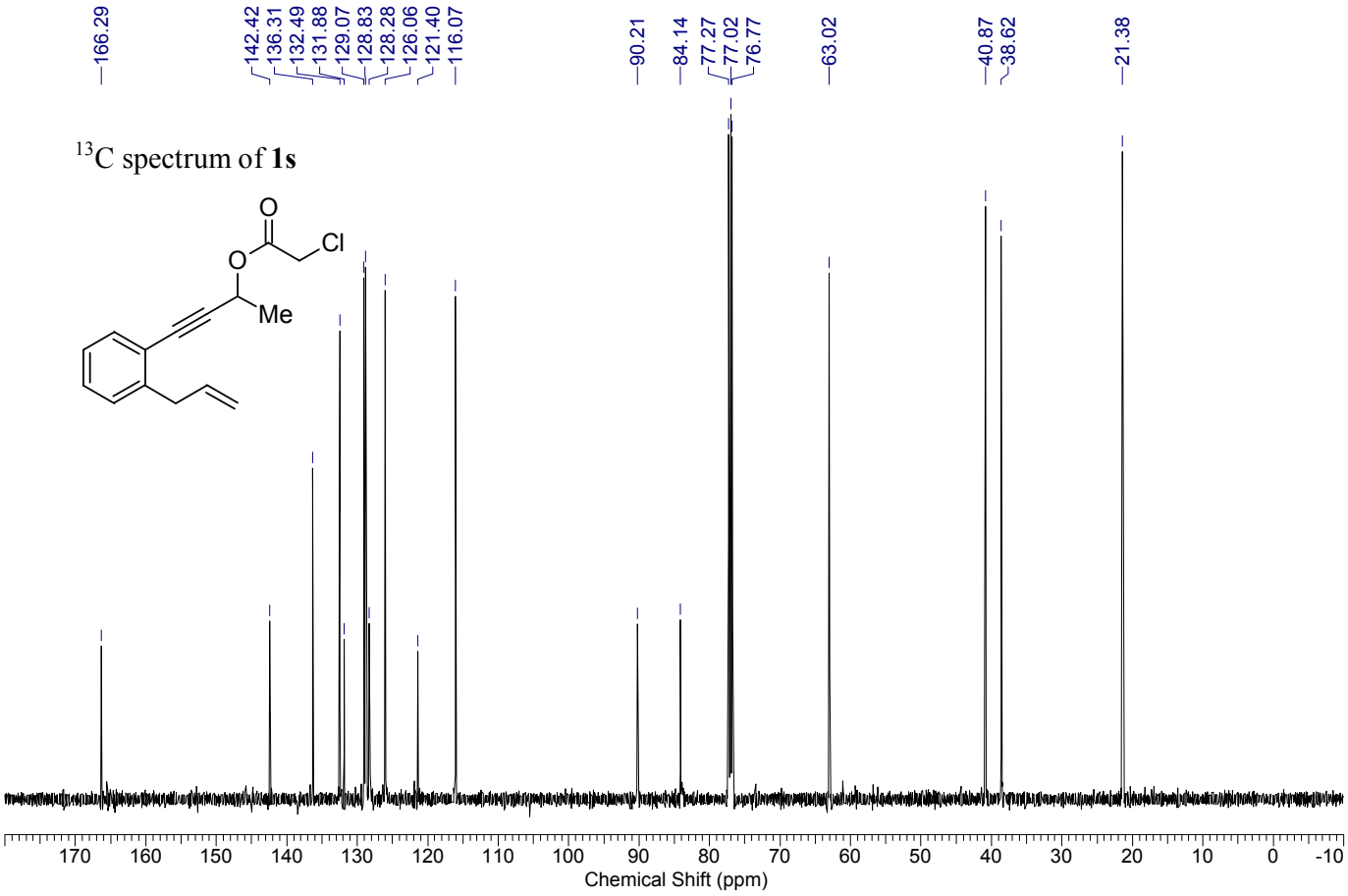


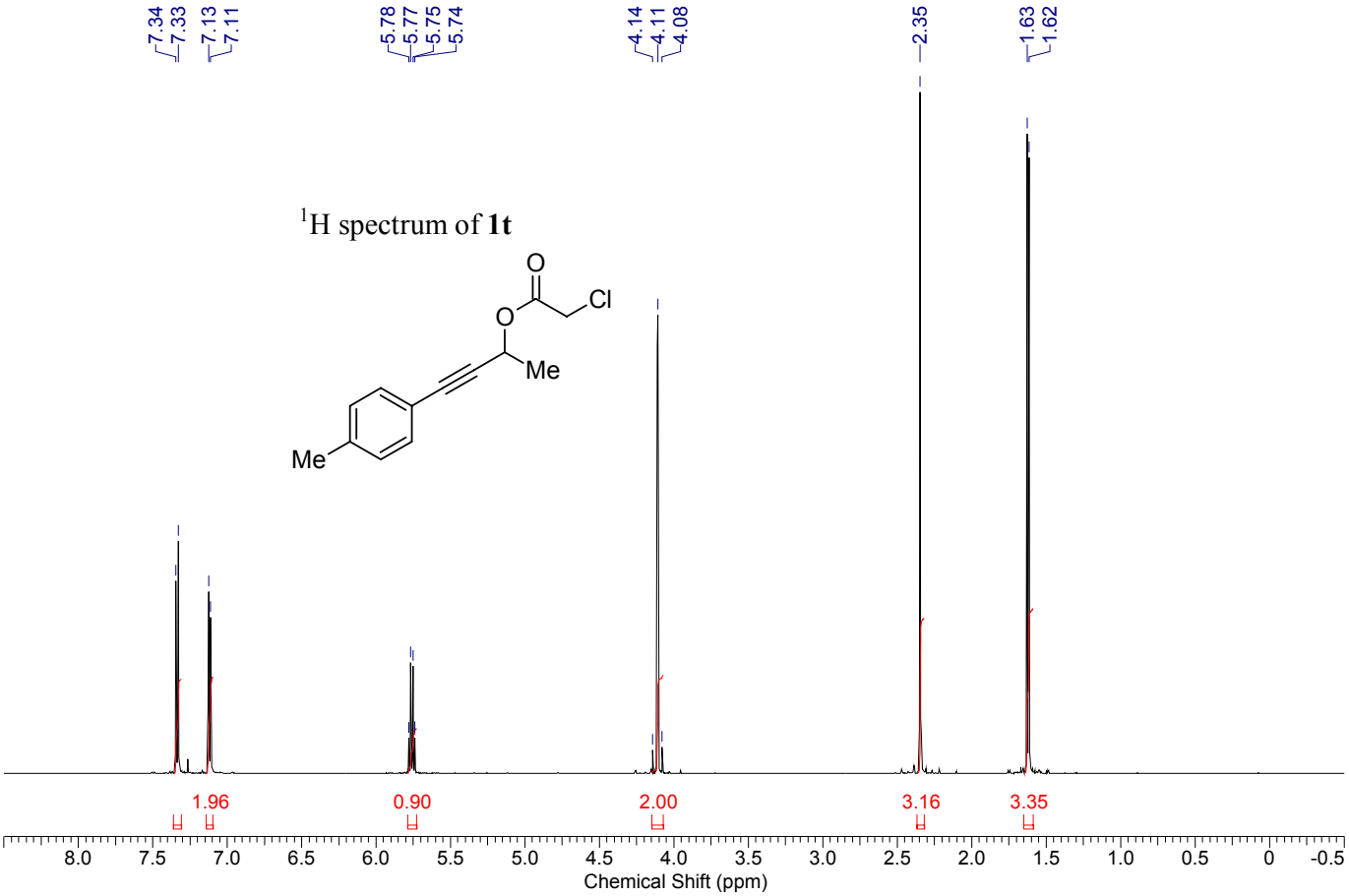
^{1}H spectrum of **1r**



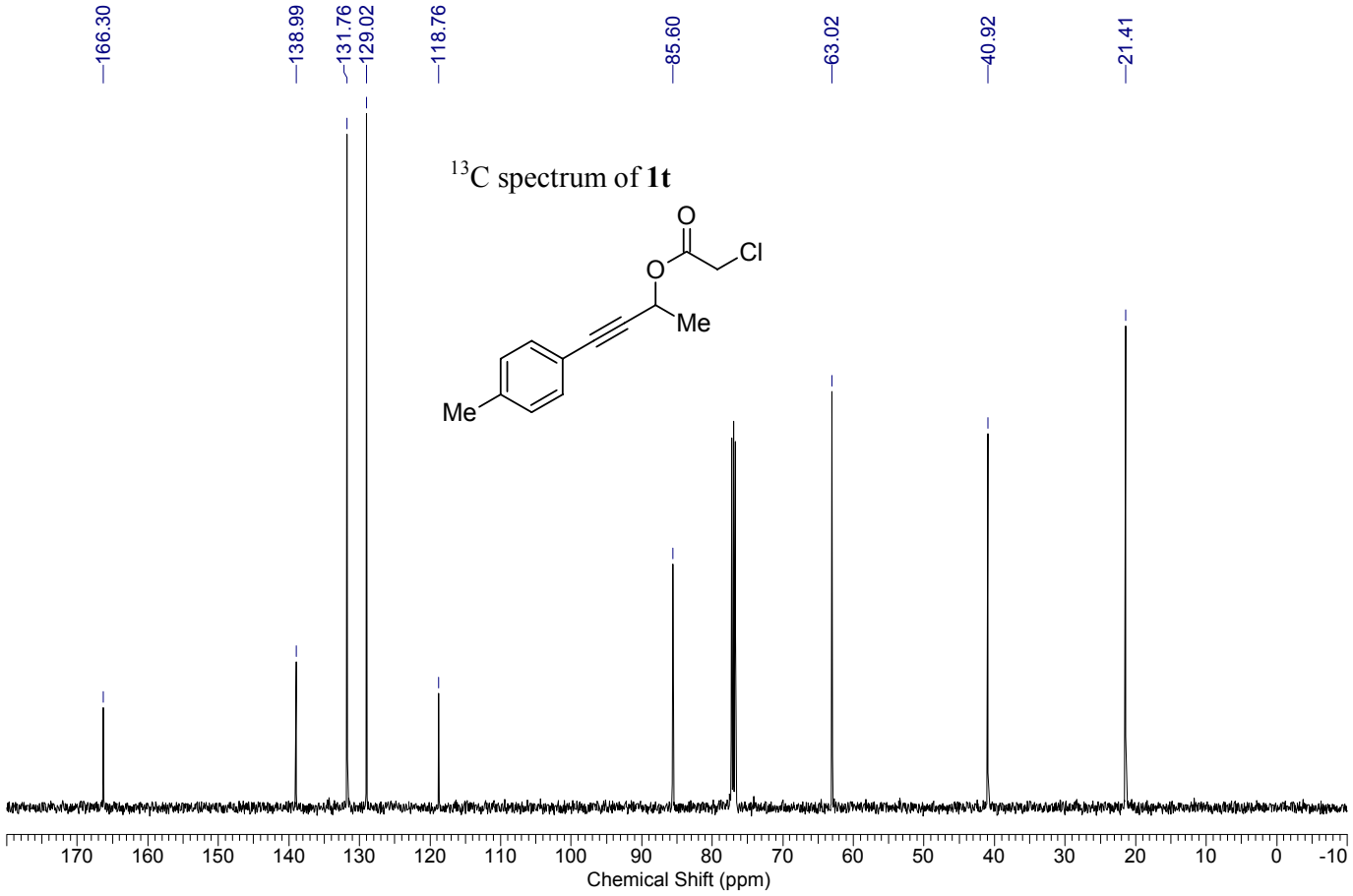
^{13}C spectrum of **1r**


7.44
7.42
7.33
7.29
7.27
7.22
7.20
7.18
7.17
5.99
5.97
5.96
5.94
5.92
5.80
5.79
5.77
5.76
5.10
5.09
5.07
4.10
3.54
3.53
1.65
1.64
1H spectrum of 1s
O
Cl
O
Me
1.33
2.02
1.03
1.85
1.89
2.00
3.34
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
Chemical Shift (ppm)

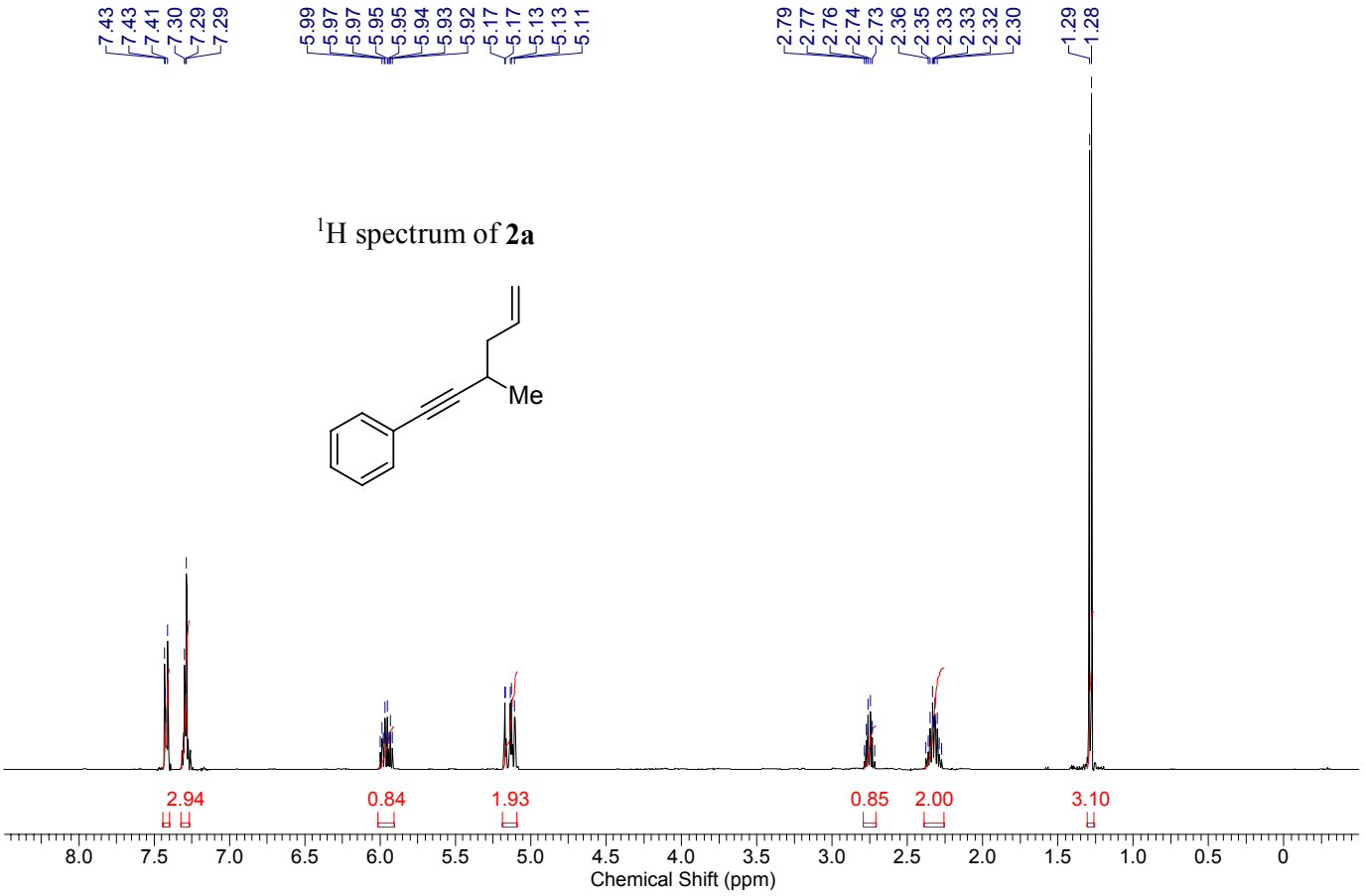

166.29
142.42
136.31
132.49
131.88
129.07
128.83
128.28
126.06
121.40
116.07
90.21
84.14
77.27
77.02
76.77
63.02
40.87
38.62
21.38
13C spectrum of 1s
O
Cl
O
Me
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Chemical Shift (ppm)



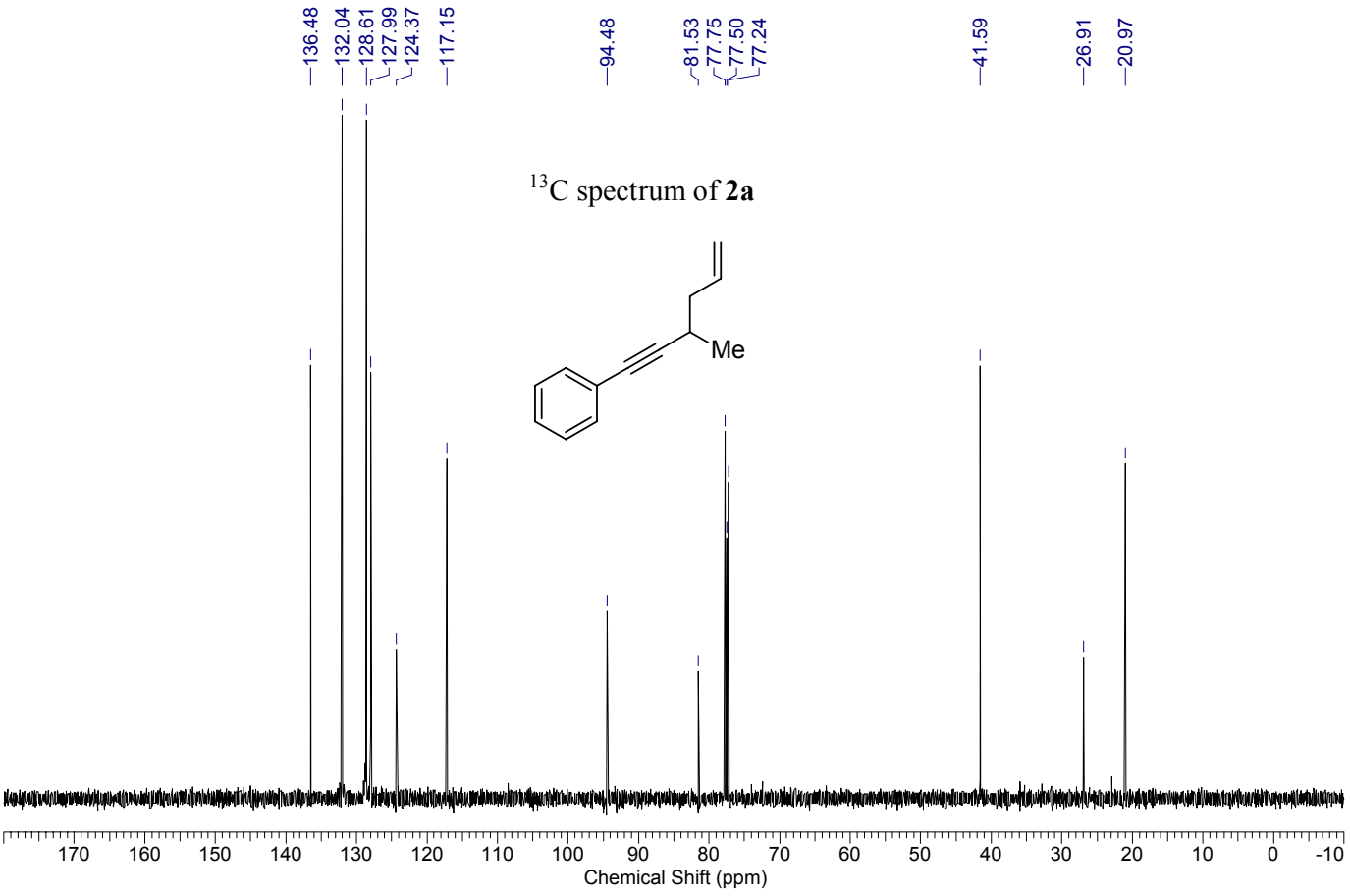
^{1}H spectrum of **1t**



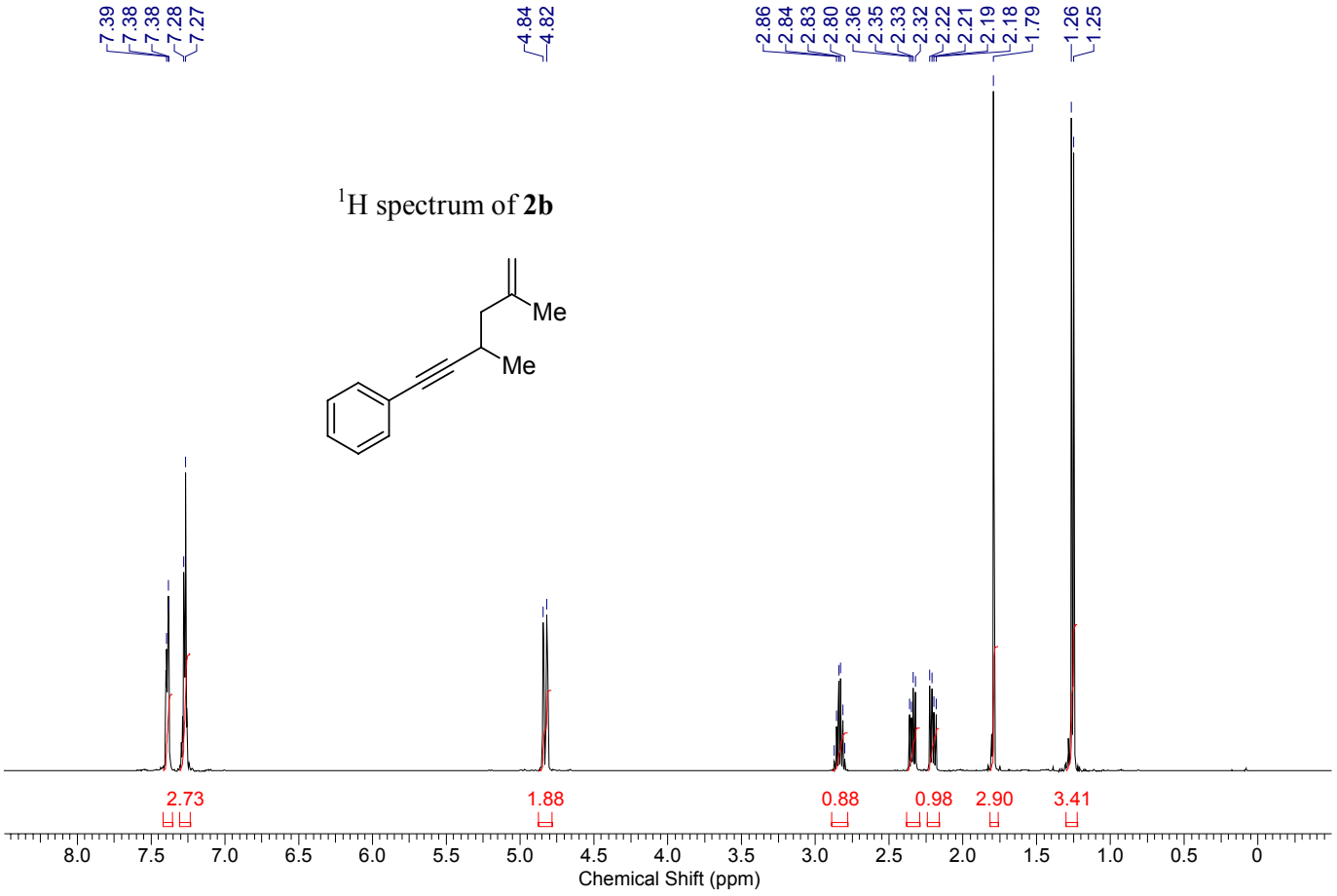
^{13}C spectrum of **1t**



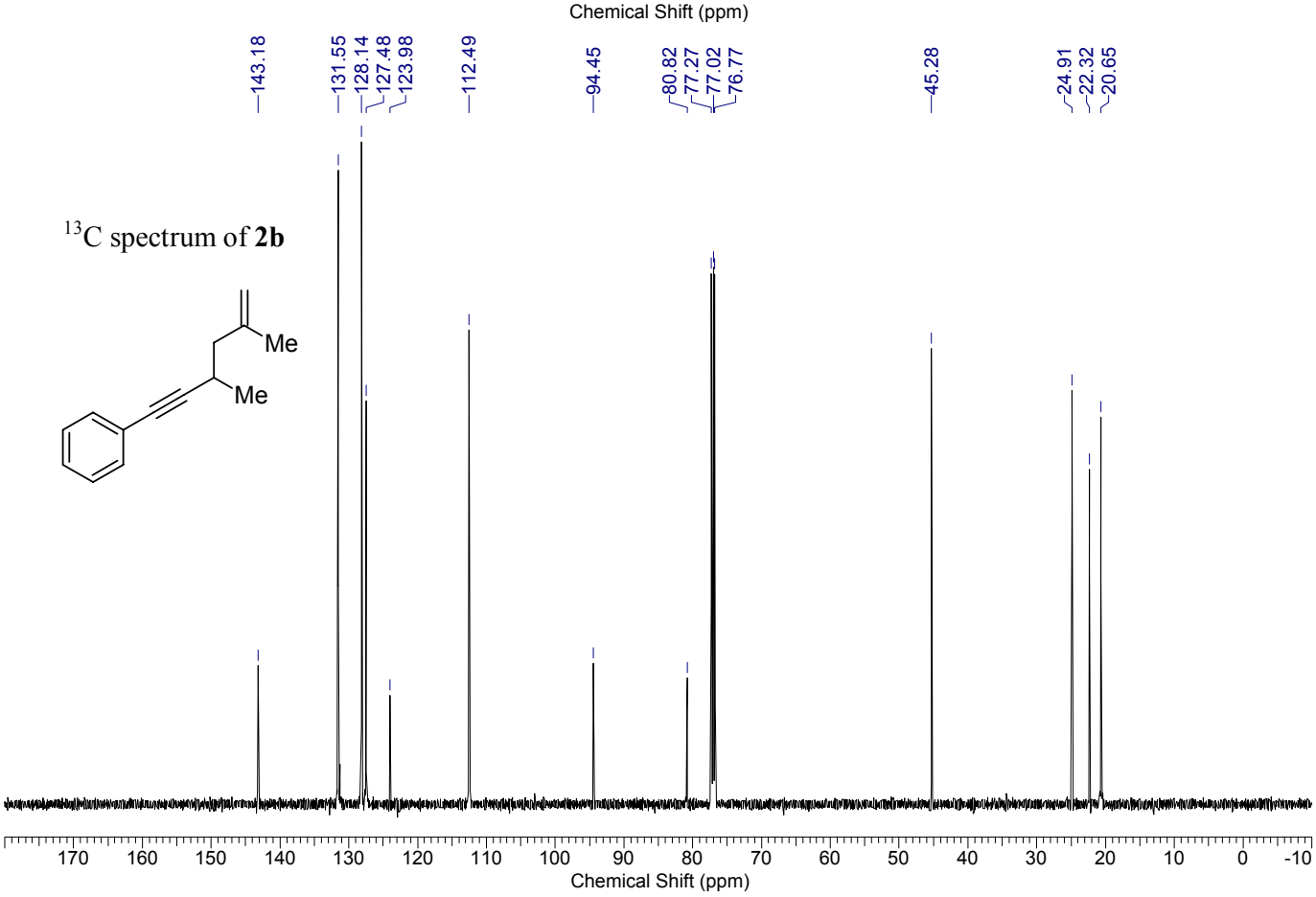
^{1}H spectrum of **2a**



^{13}C spectrum of **2a**

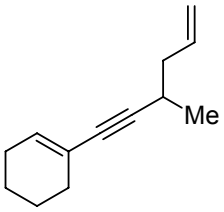


^{1}H spectrum of **2b**

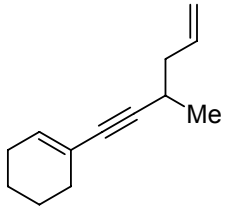


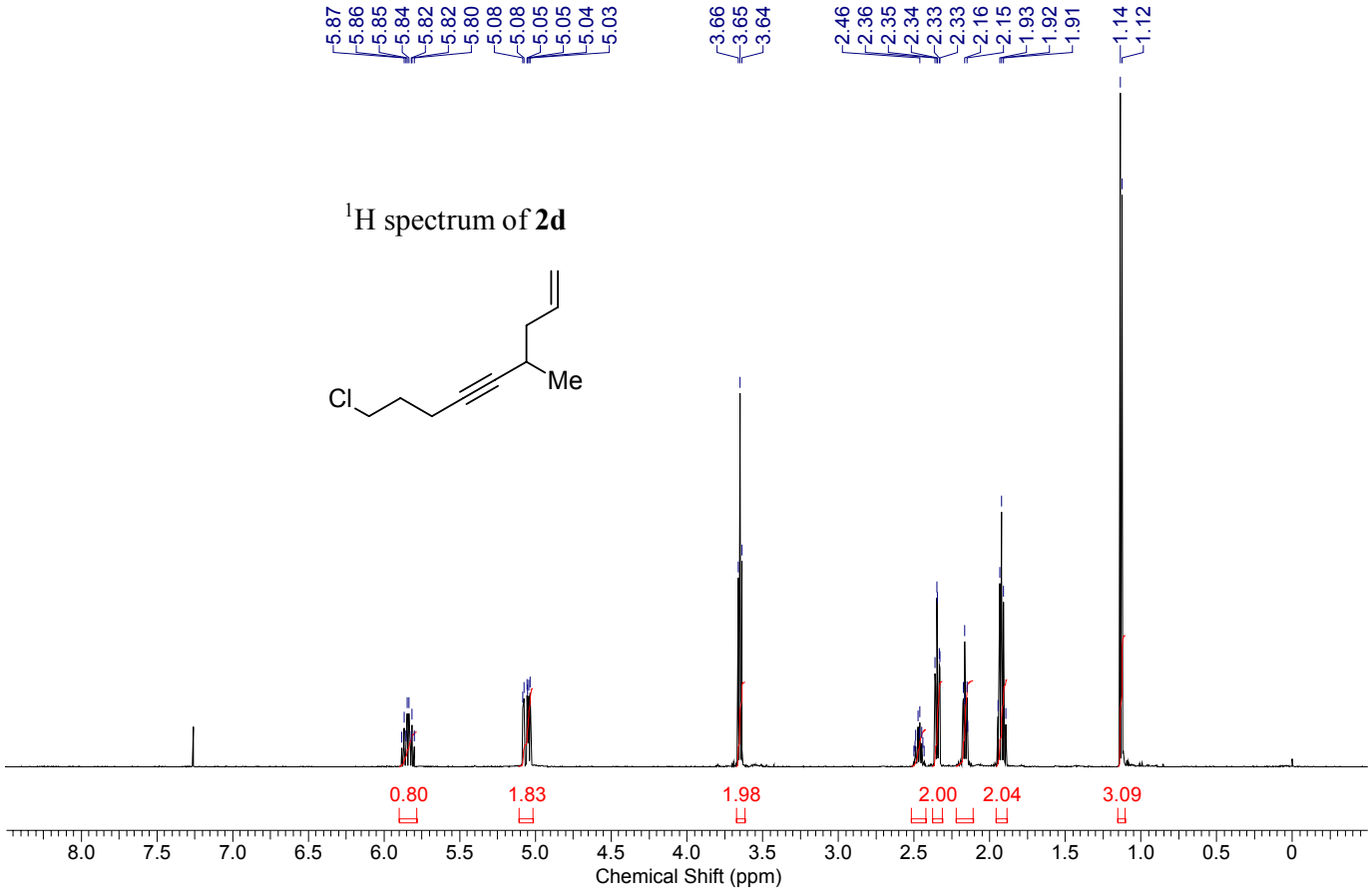
^{13}C spectrum of **2b**

^{1}H spectrum of **2c**

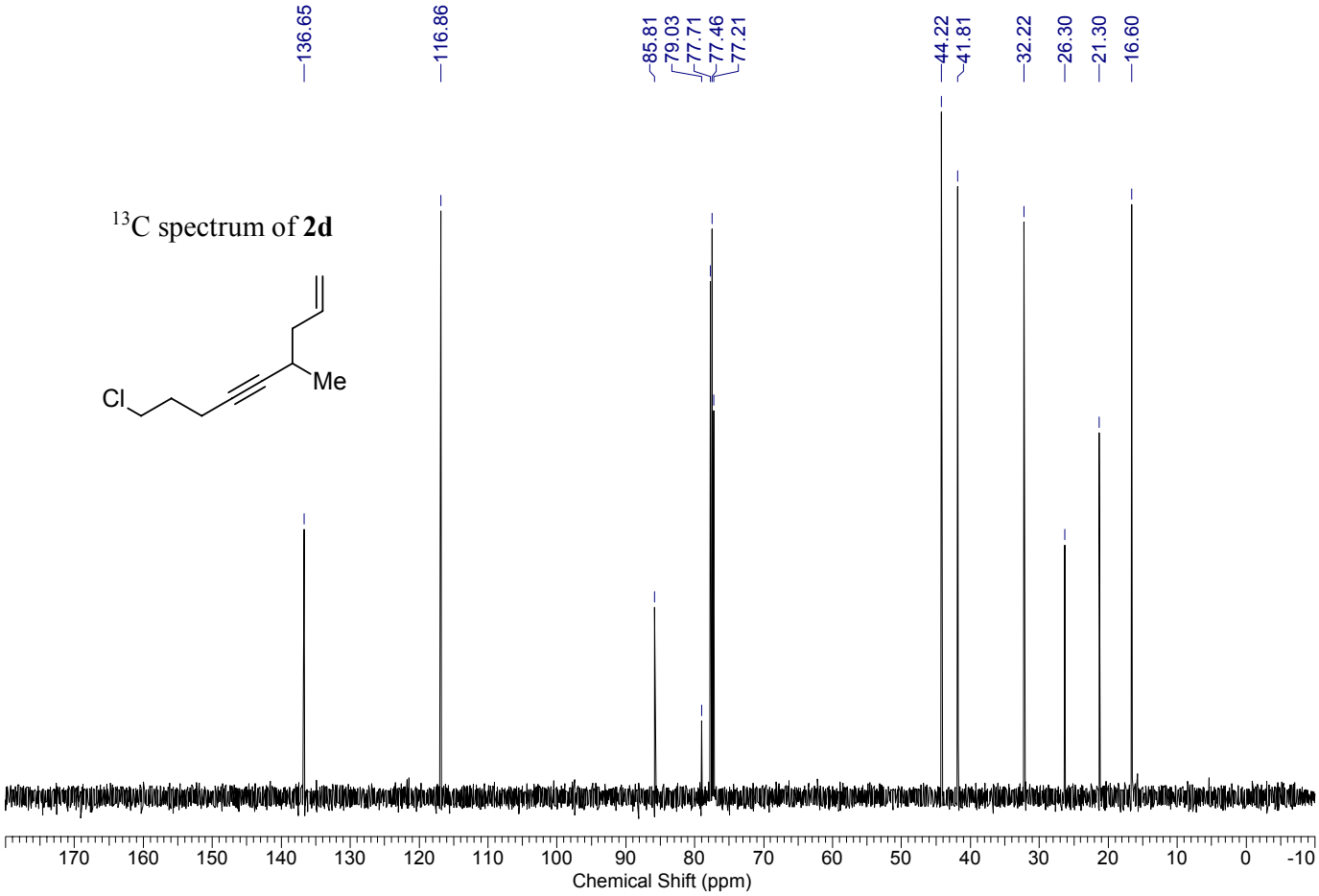


^{13}C spectrum of **2c**



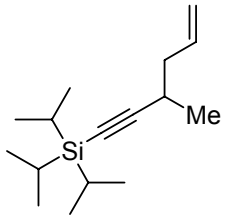


^{1}H spectrum of **2d**

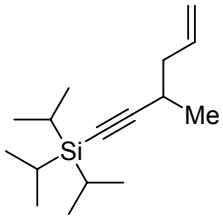


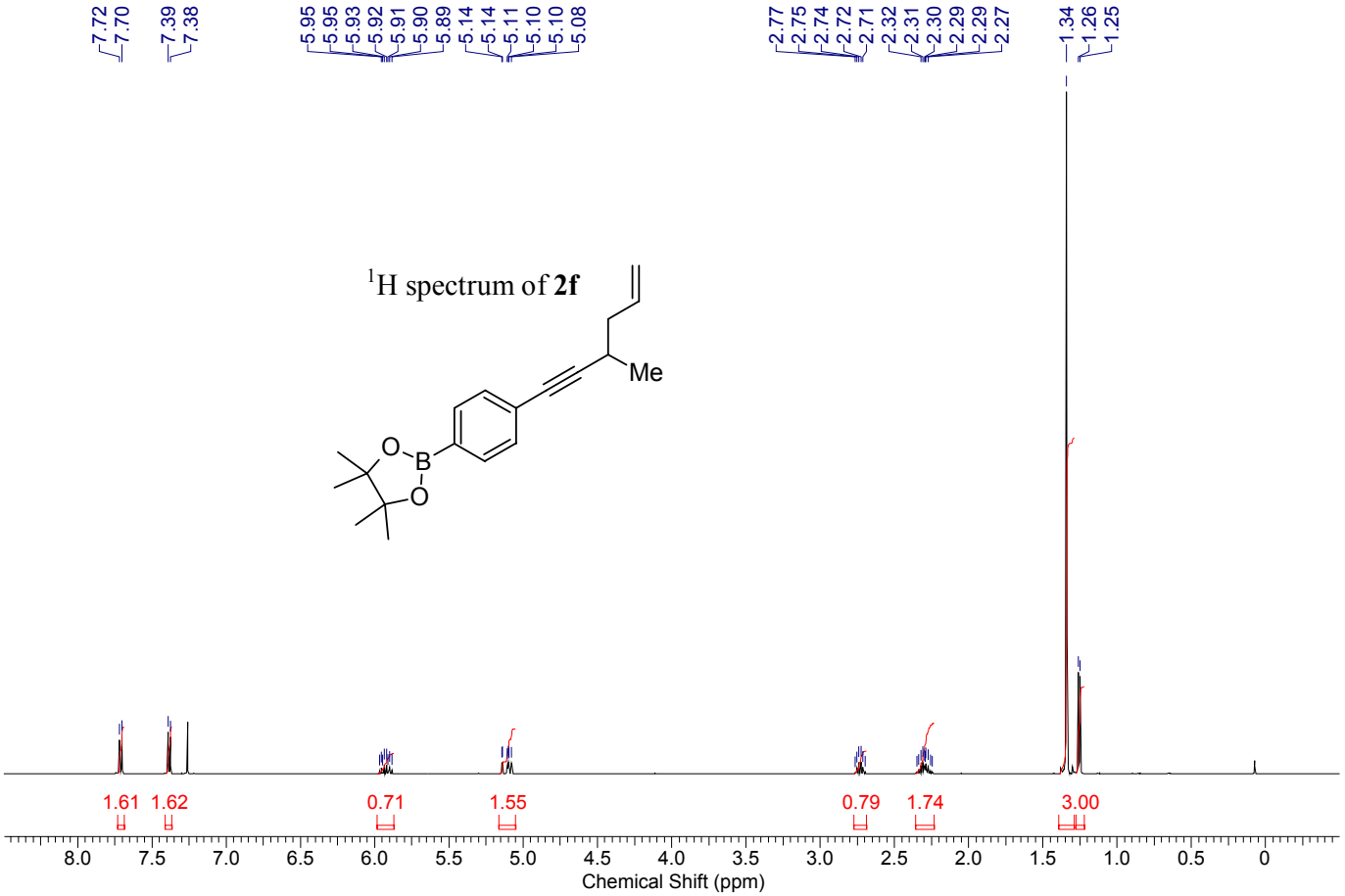
^{13}C spectrum of **2d**

^{1}H spectrum of **2e**

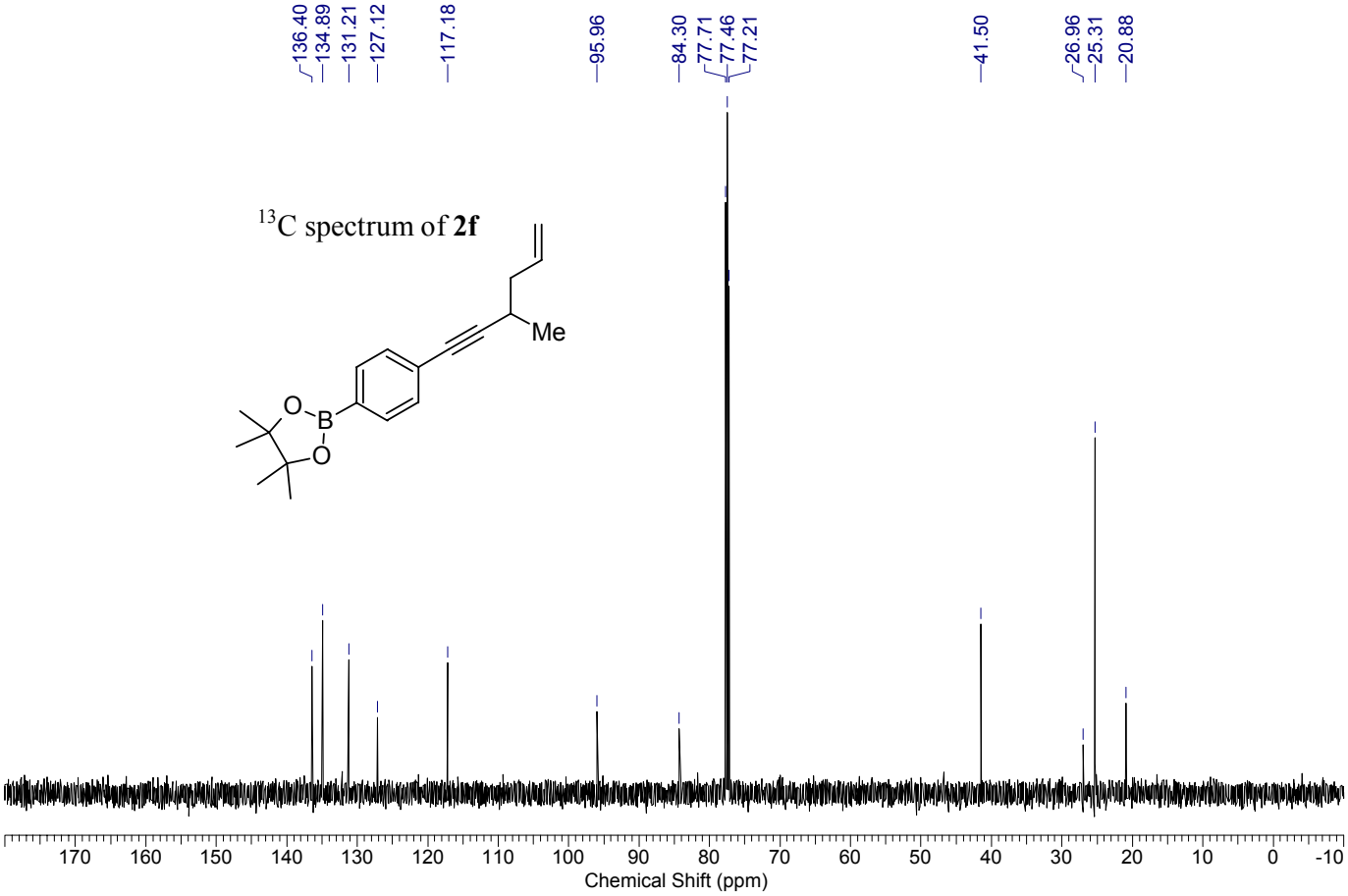


^{13}C spectrum of **2e**

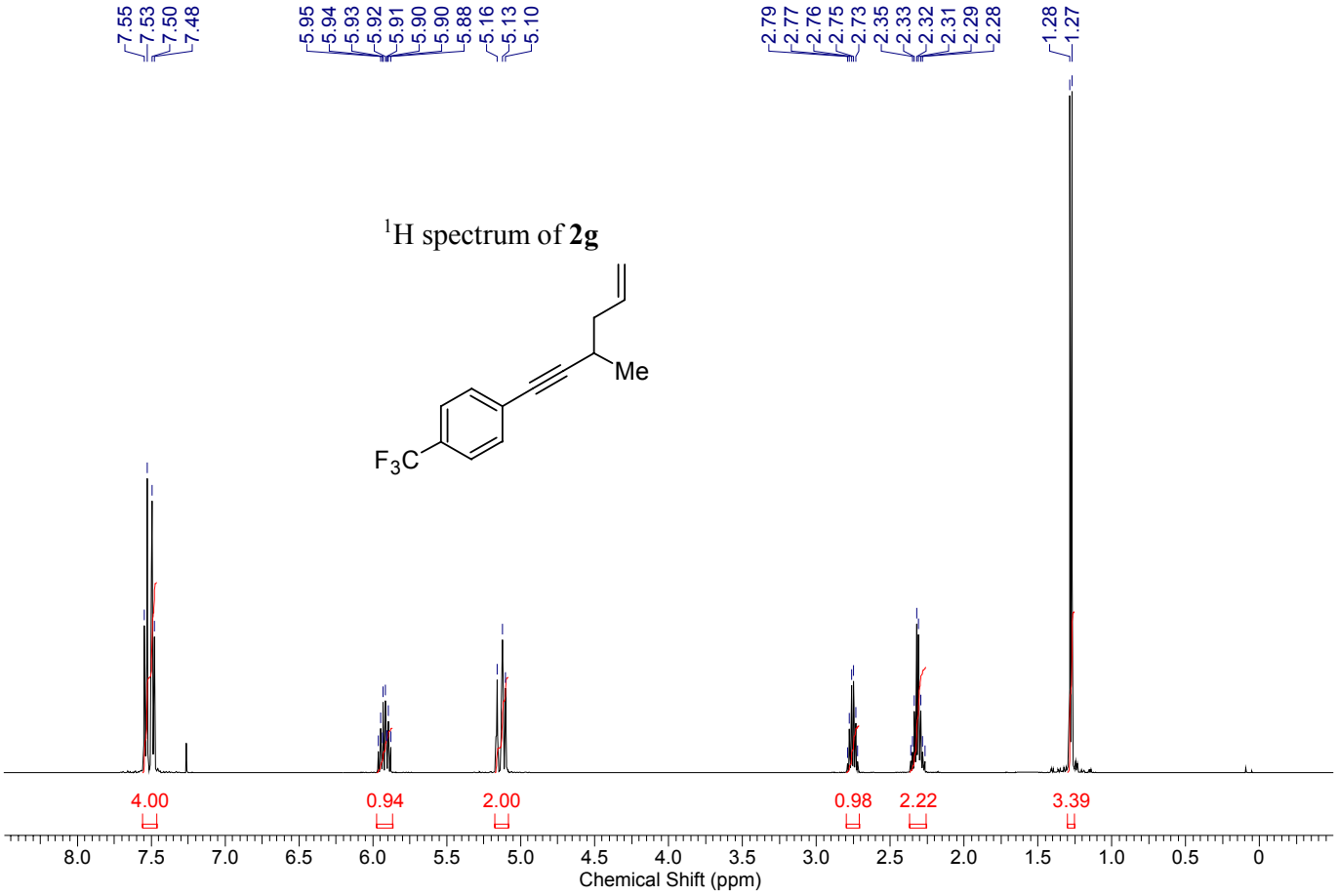




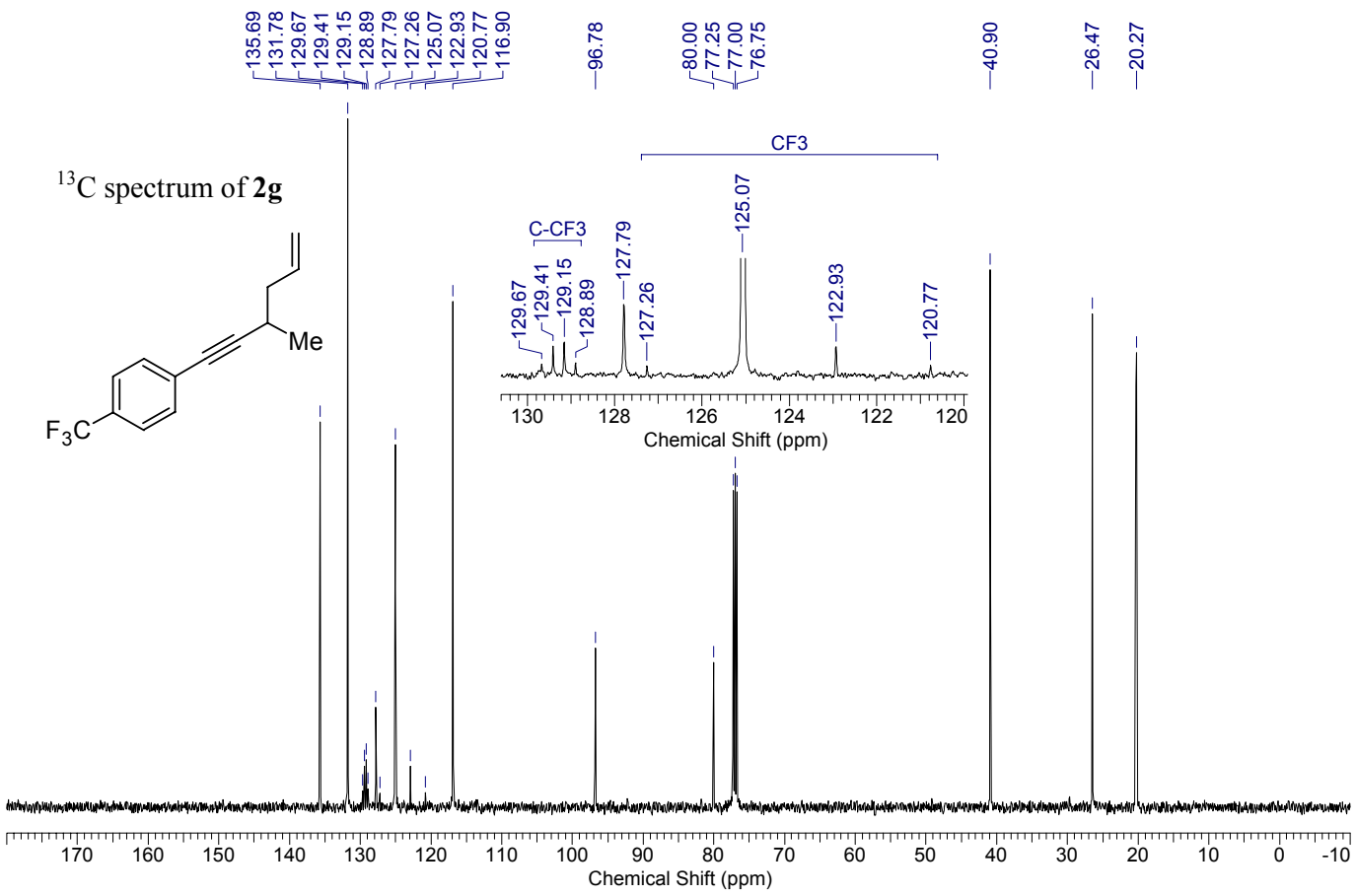
^{1}H spectrum of **2f**



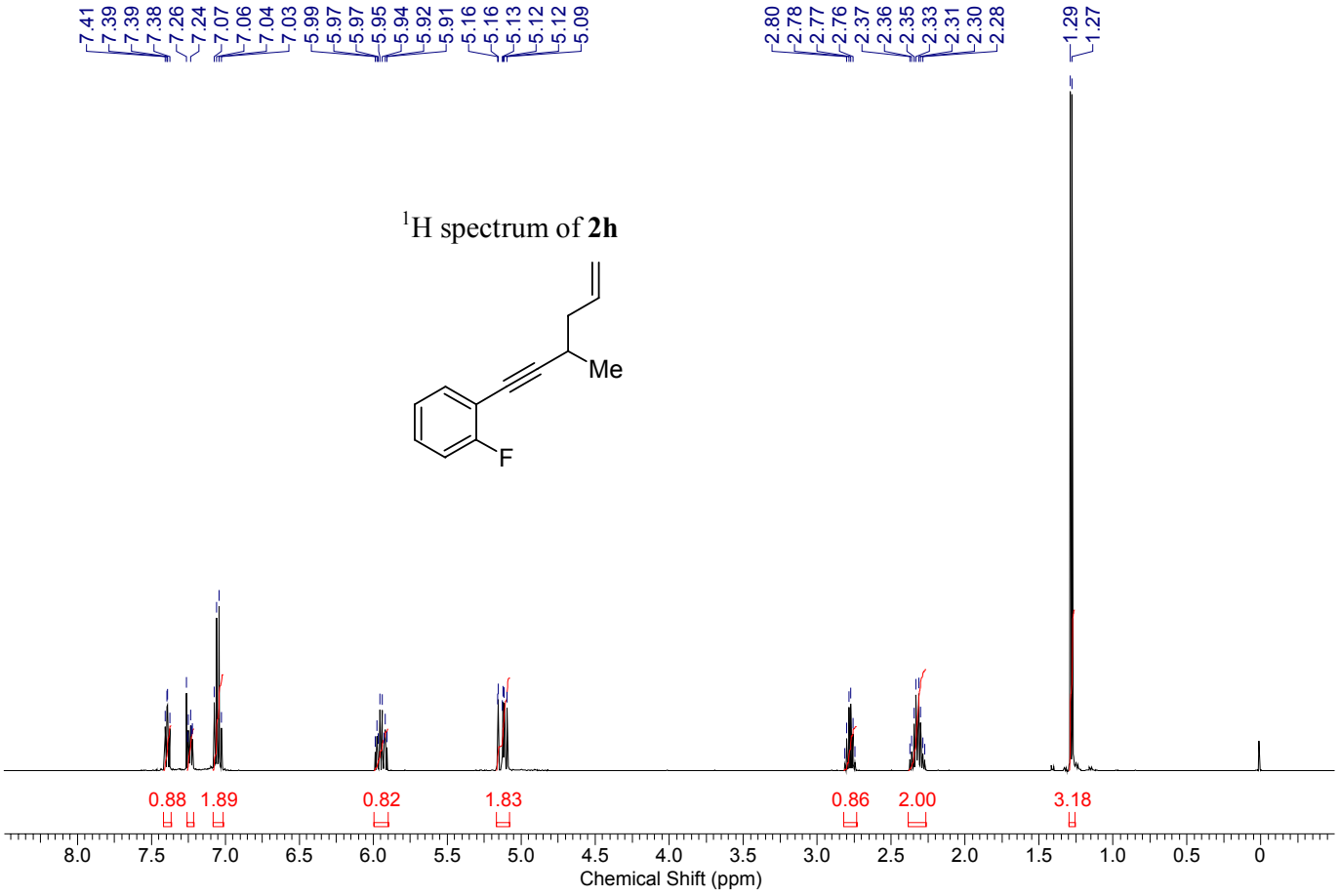
^{13}C spectrum of **2f**



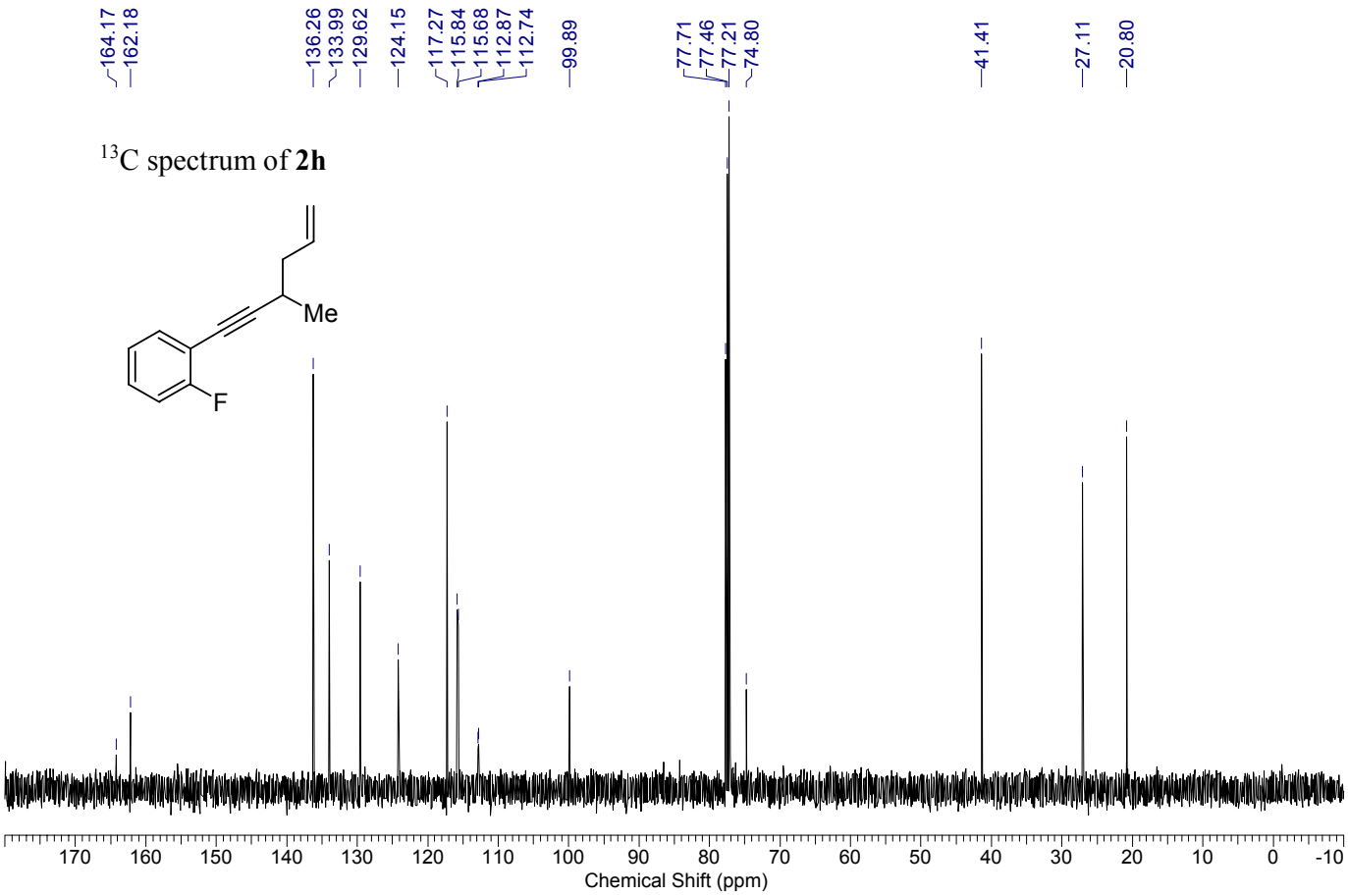
^{1}H spectrum of **2g**



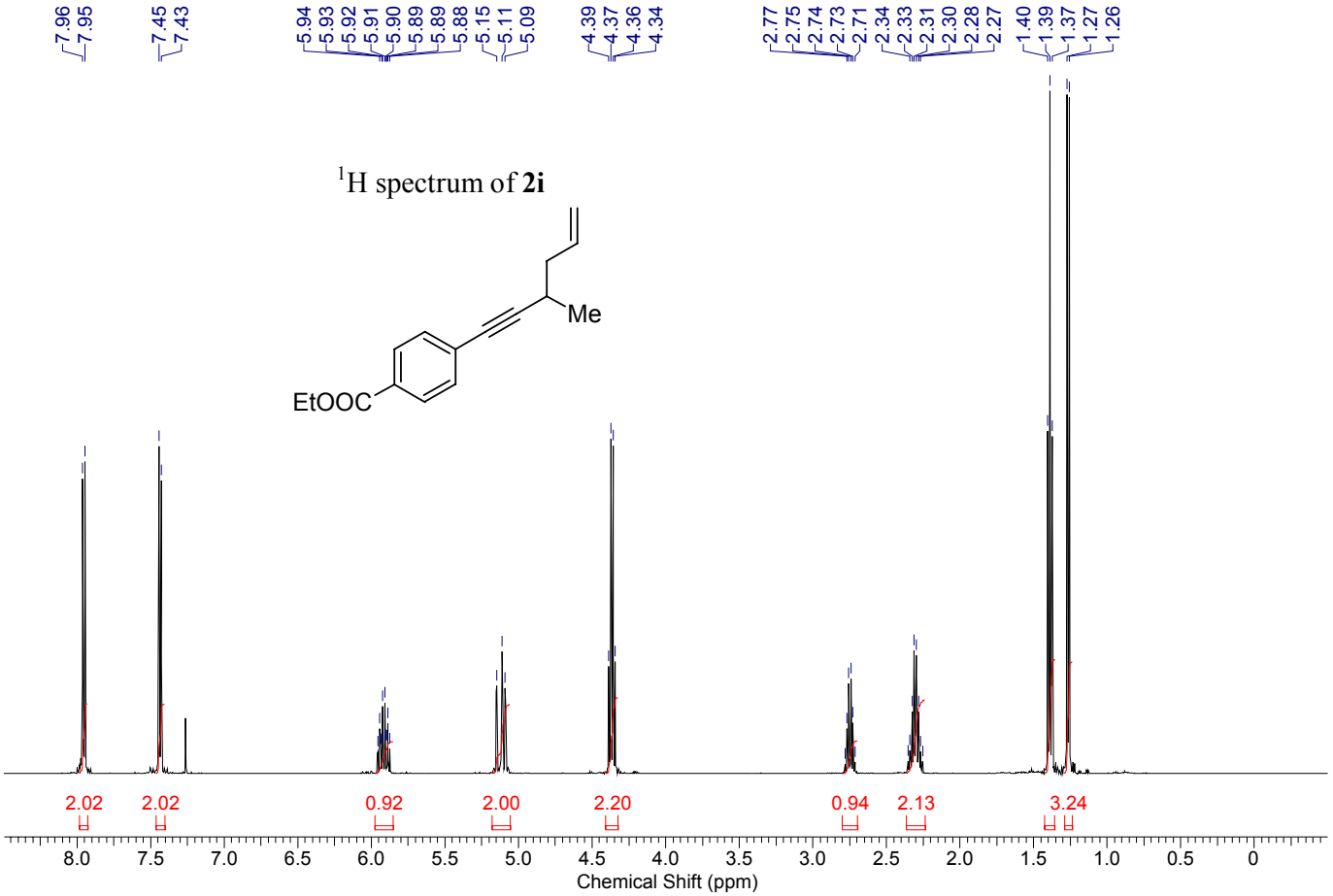
^{13}C spectrum of **2g**



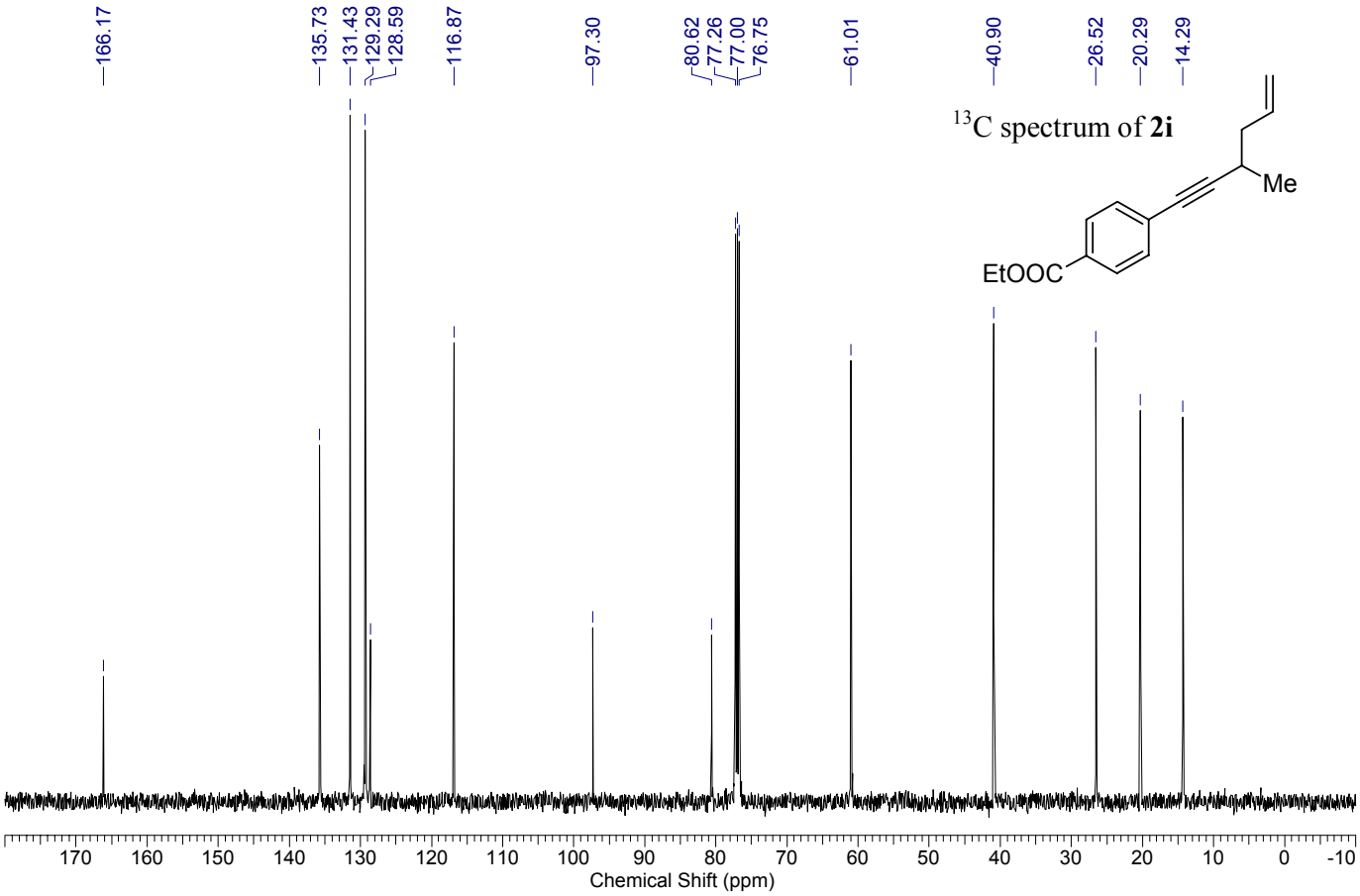
^{1}H spectrum of **2h**



^{13}C spectrum of **2h**

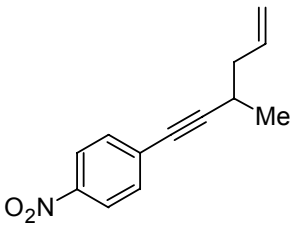


^{1}H spectrum of **2i**

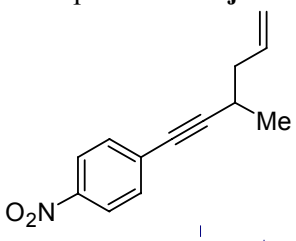


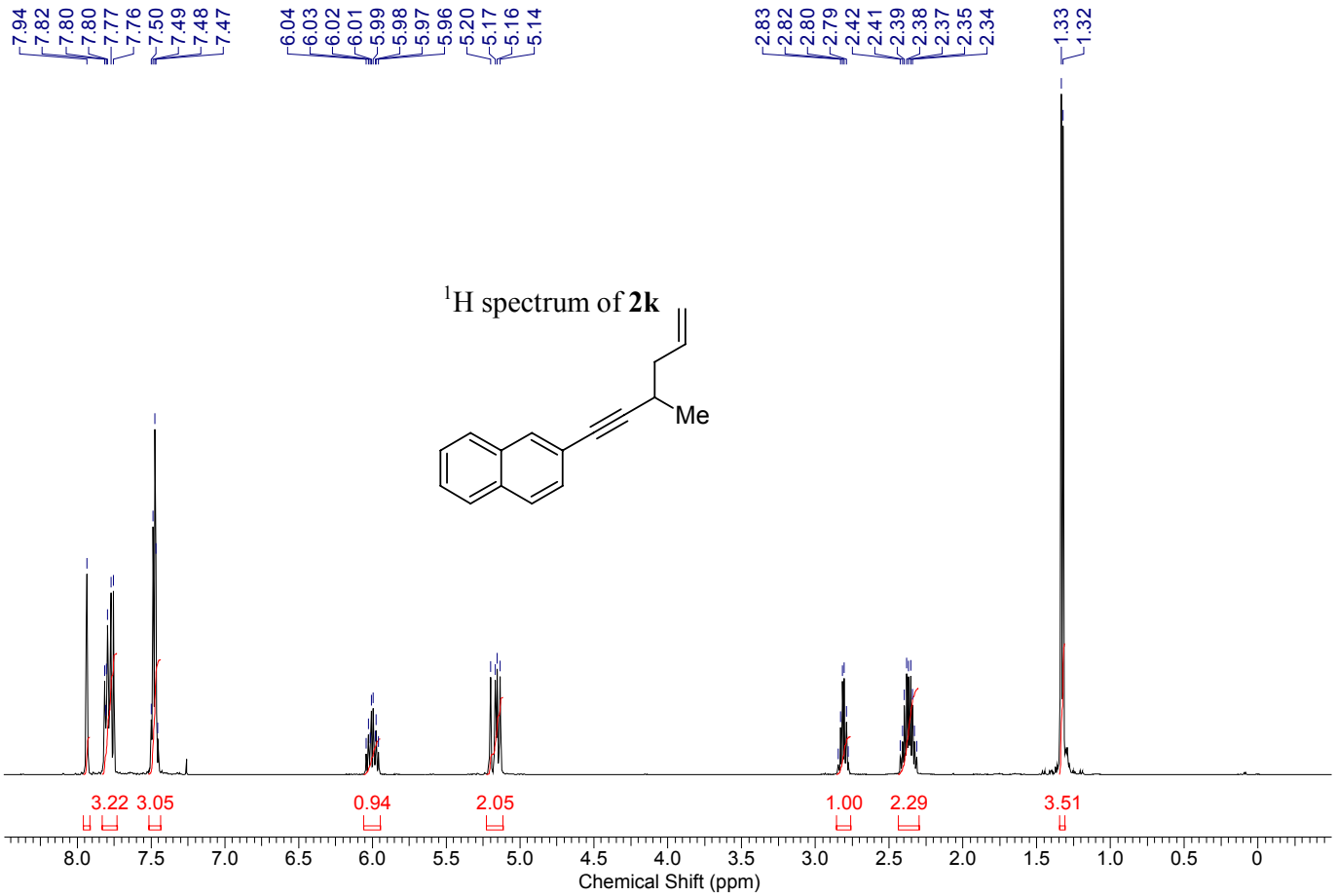
^{13}C spectrum of **2i**

^{1}H spectrum of **2j**

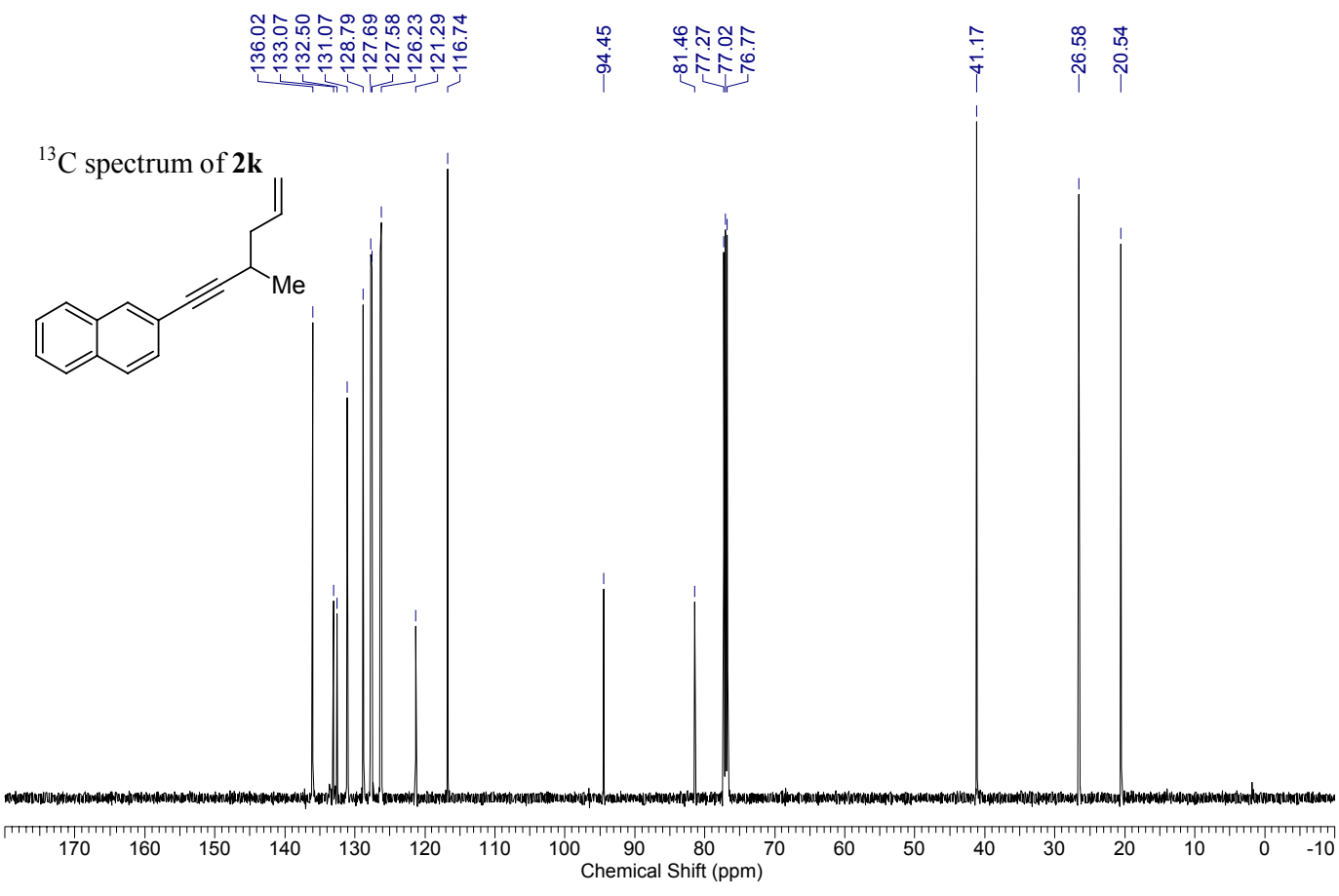


^{13}C spectrum of **2j**

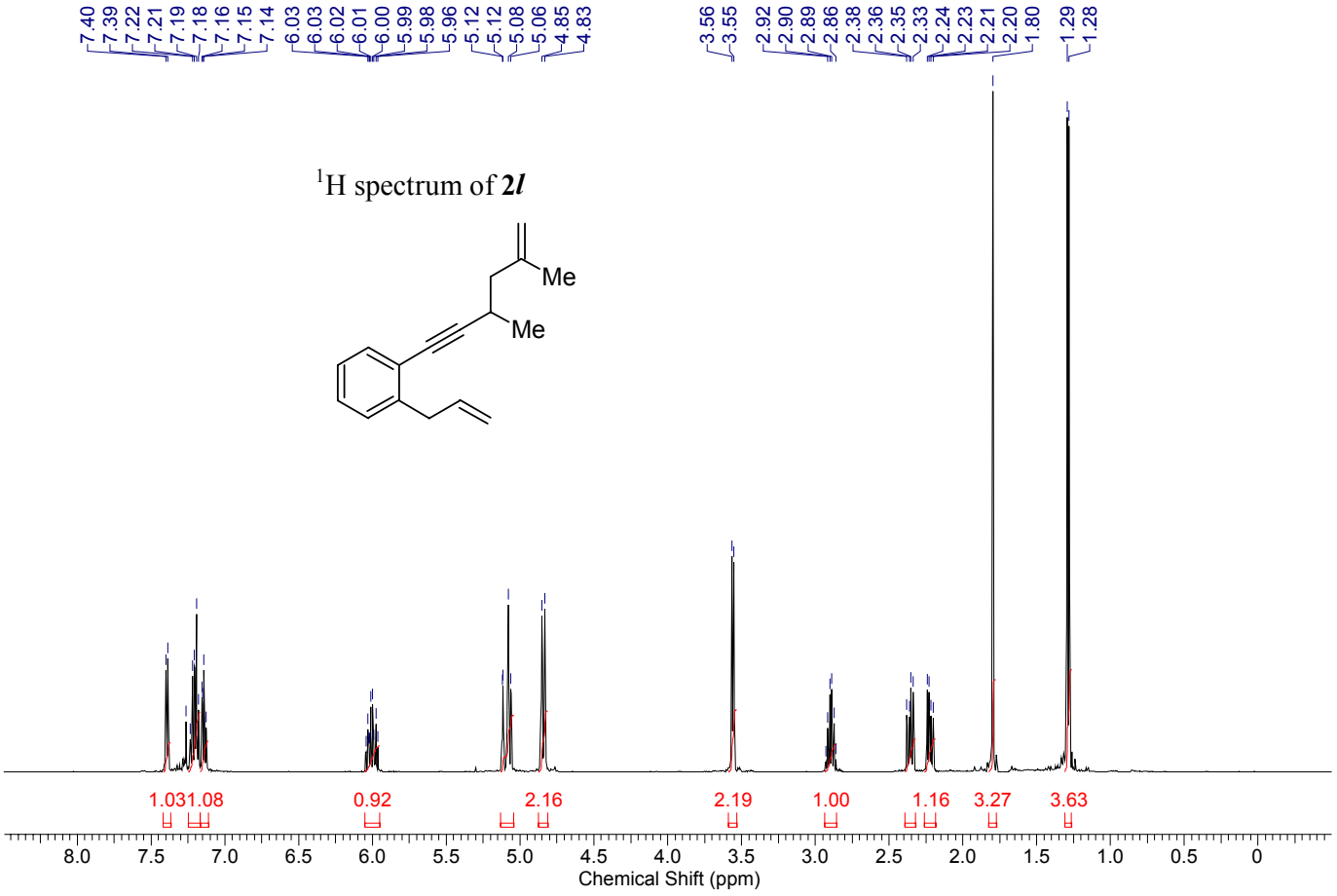




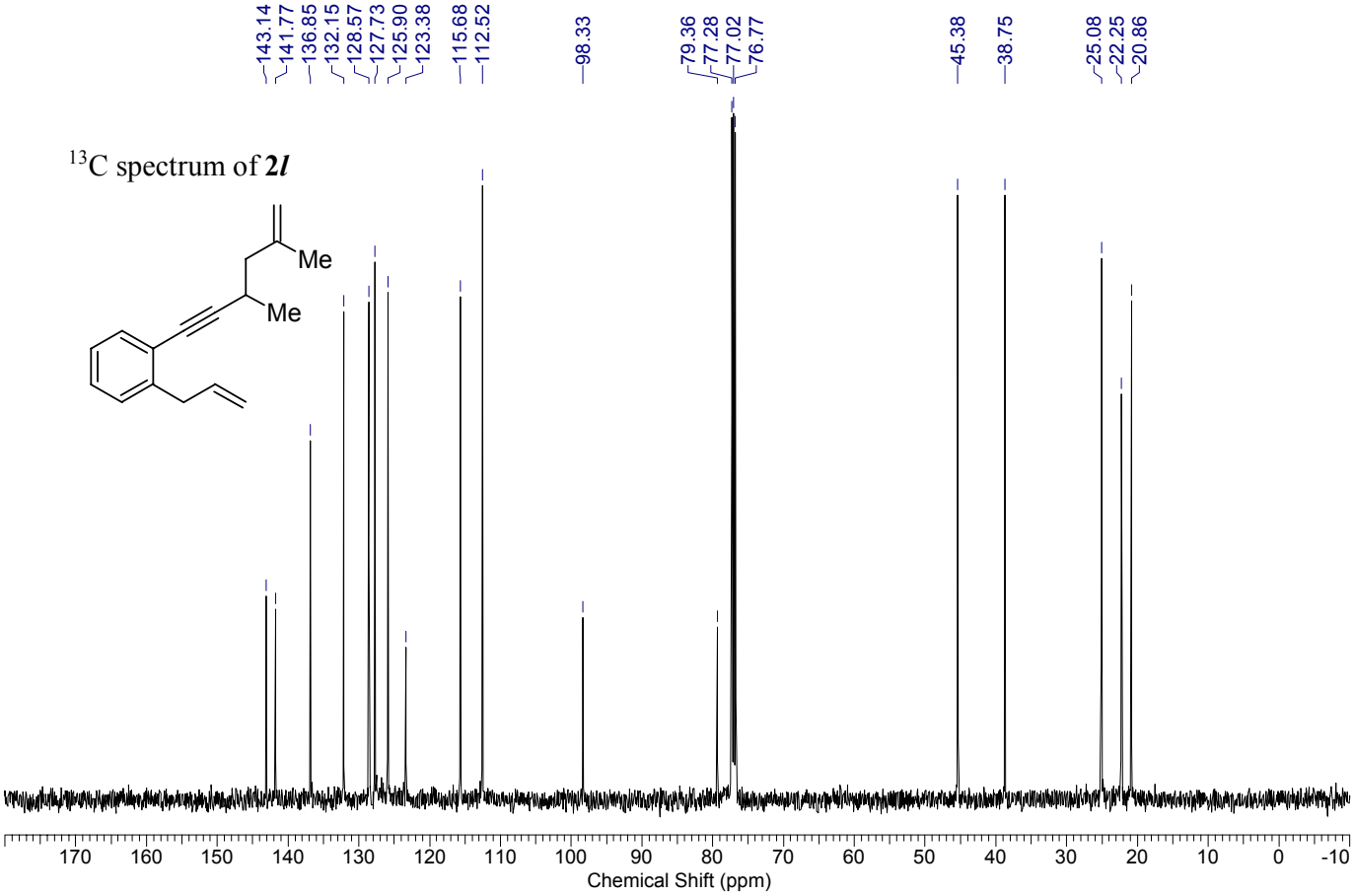
^{1}H spectrum of **2k**



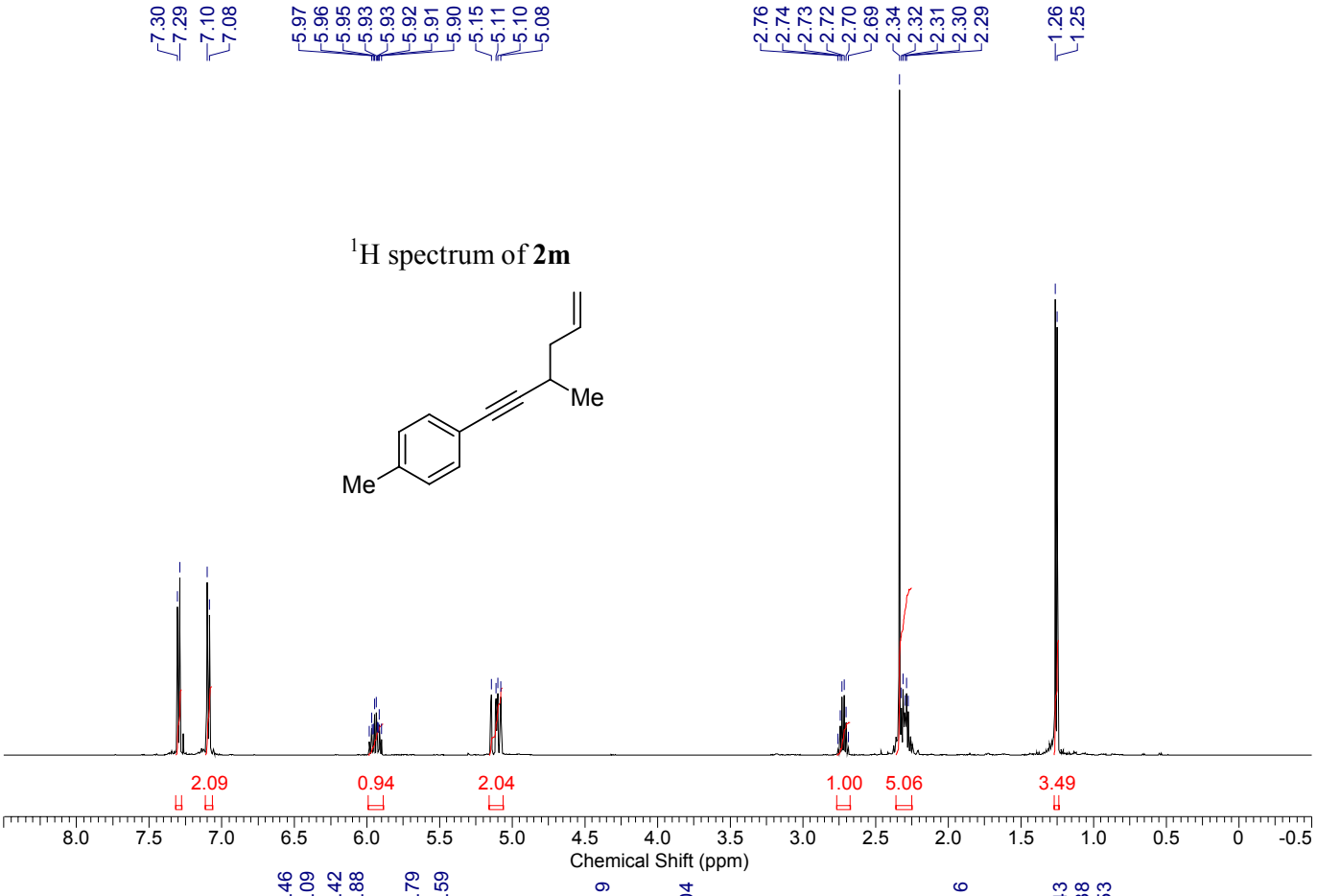
^{13}C spectrum of **2k**



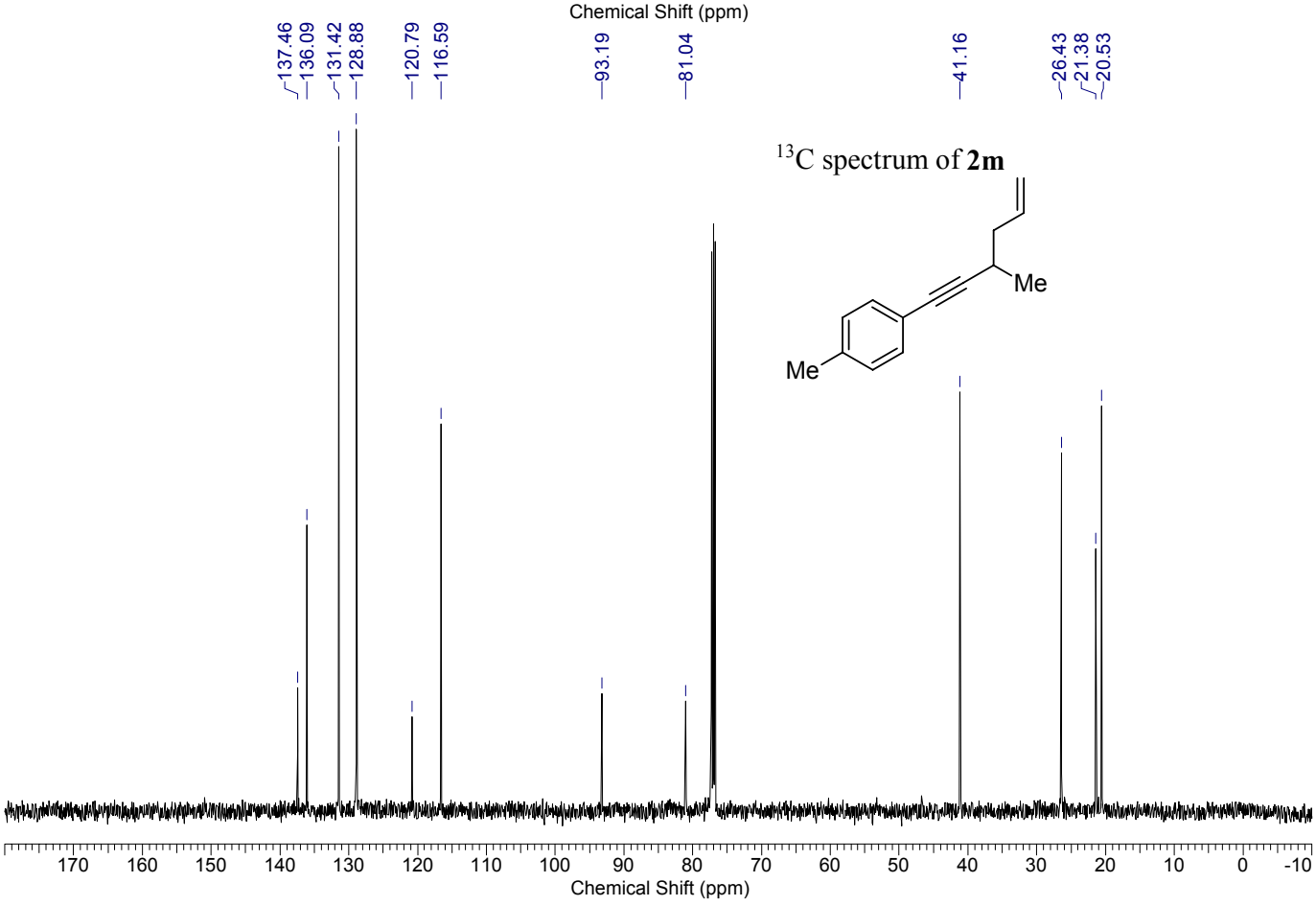
^{1}H spectrum of ***2l***



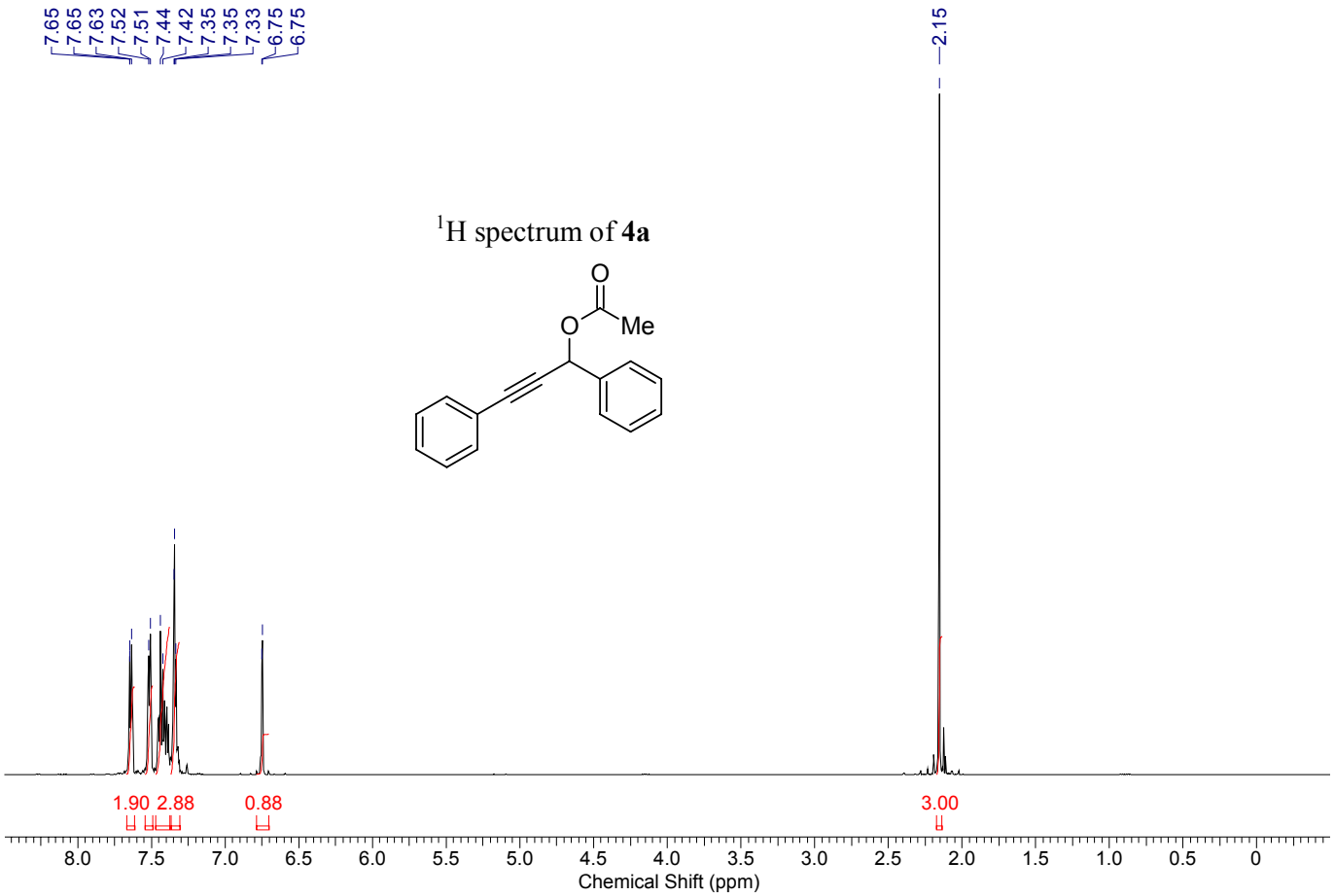
^{13}C spectrum of ***2l***



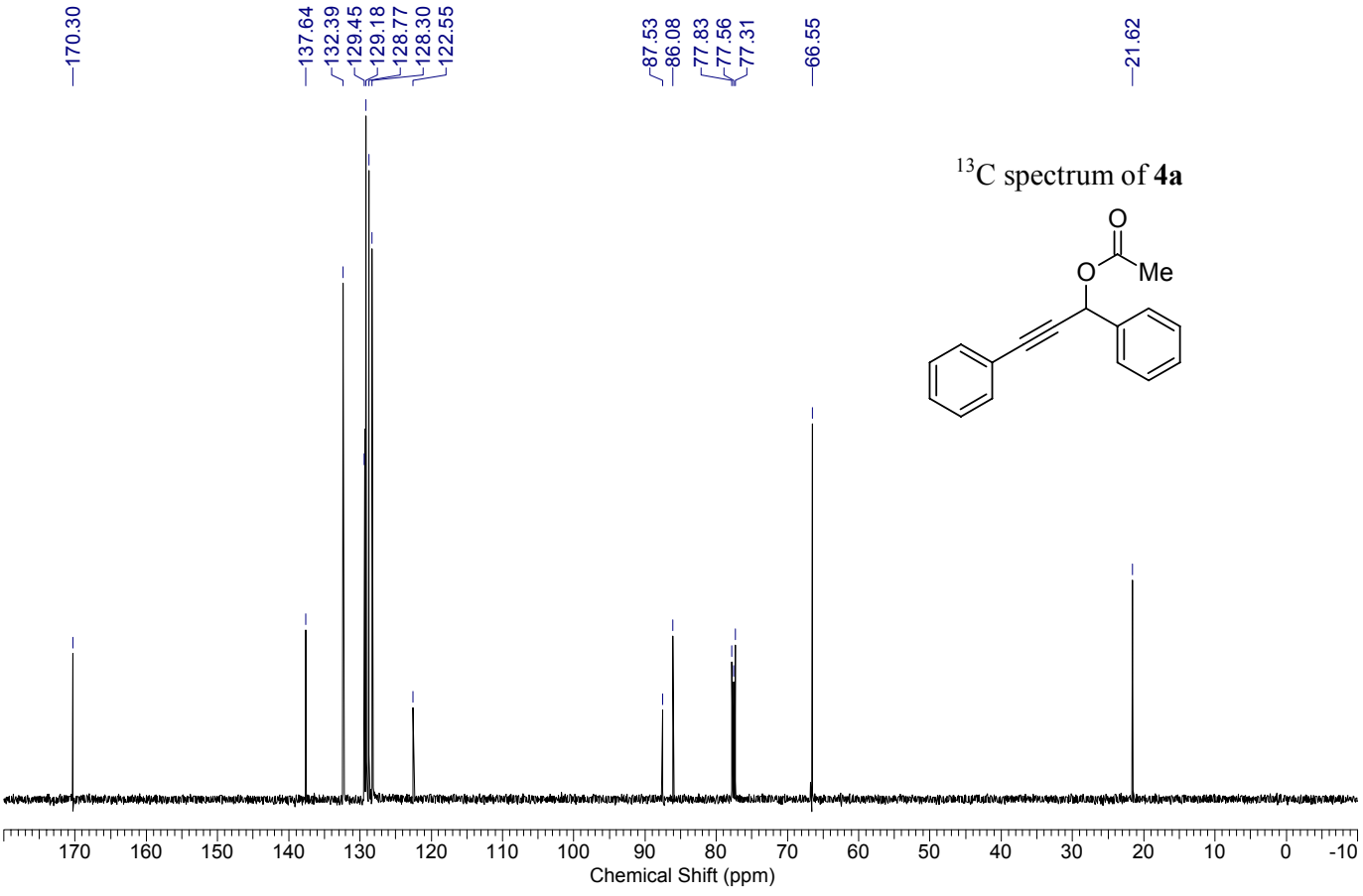
^{1}H spectrum of **2m**



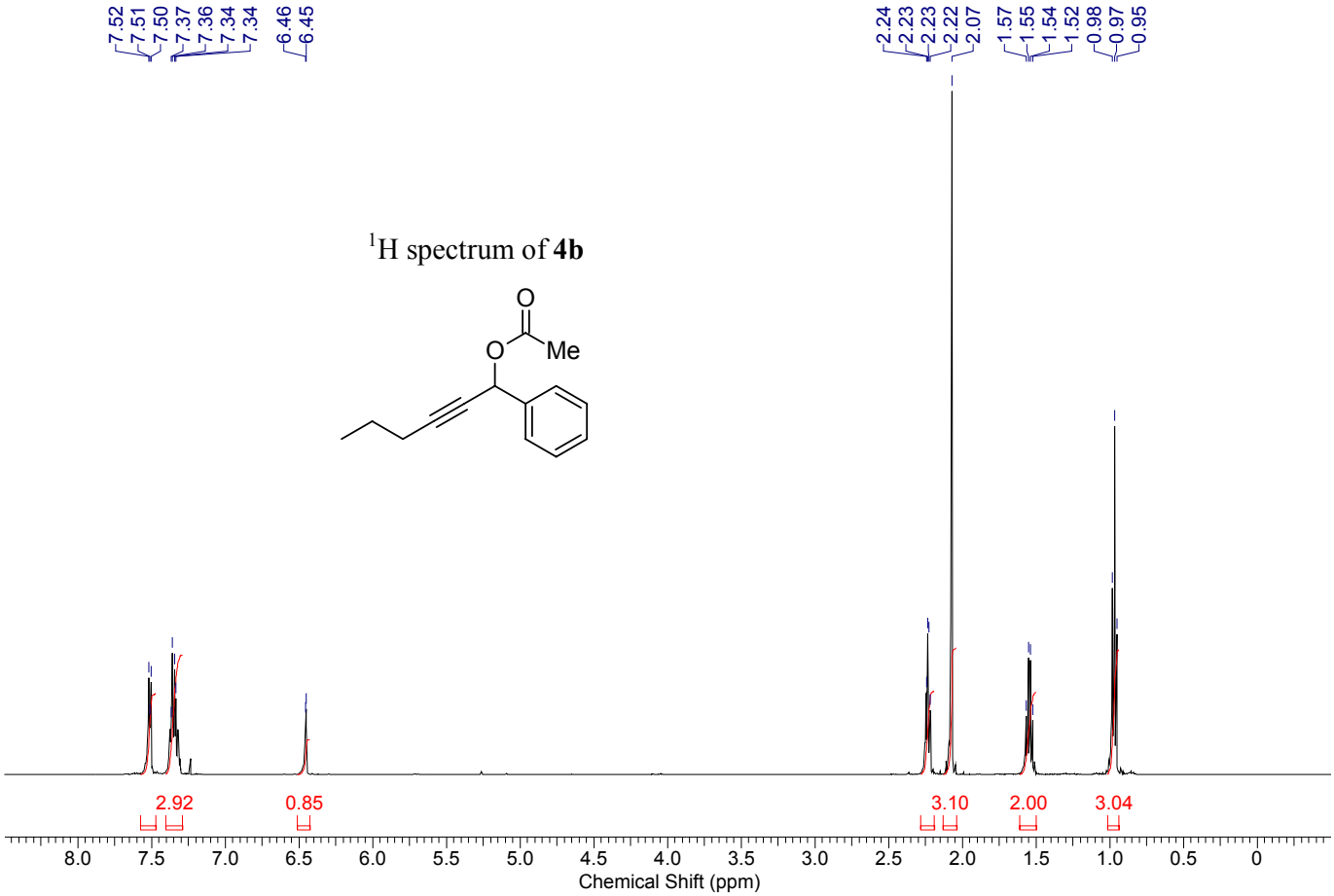
^{13}C spectrum of **2m**



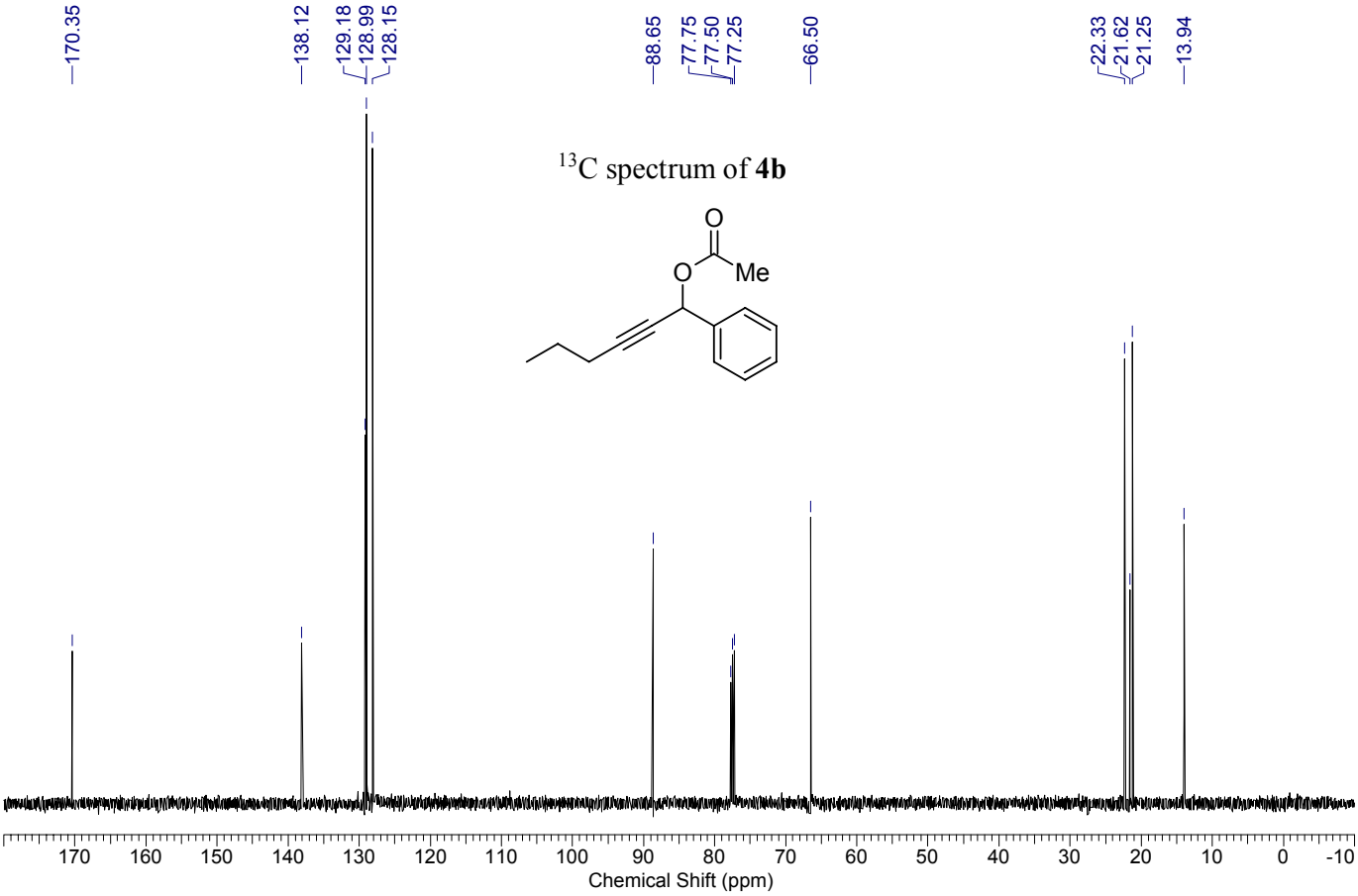
^{1}H spectrum of **4a**



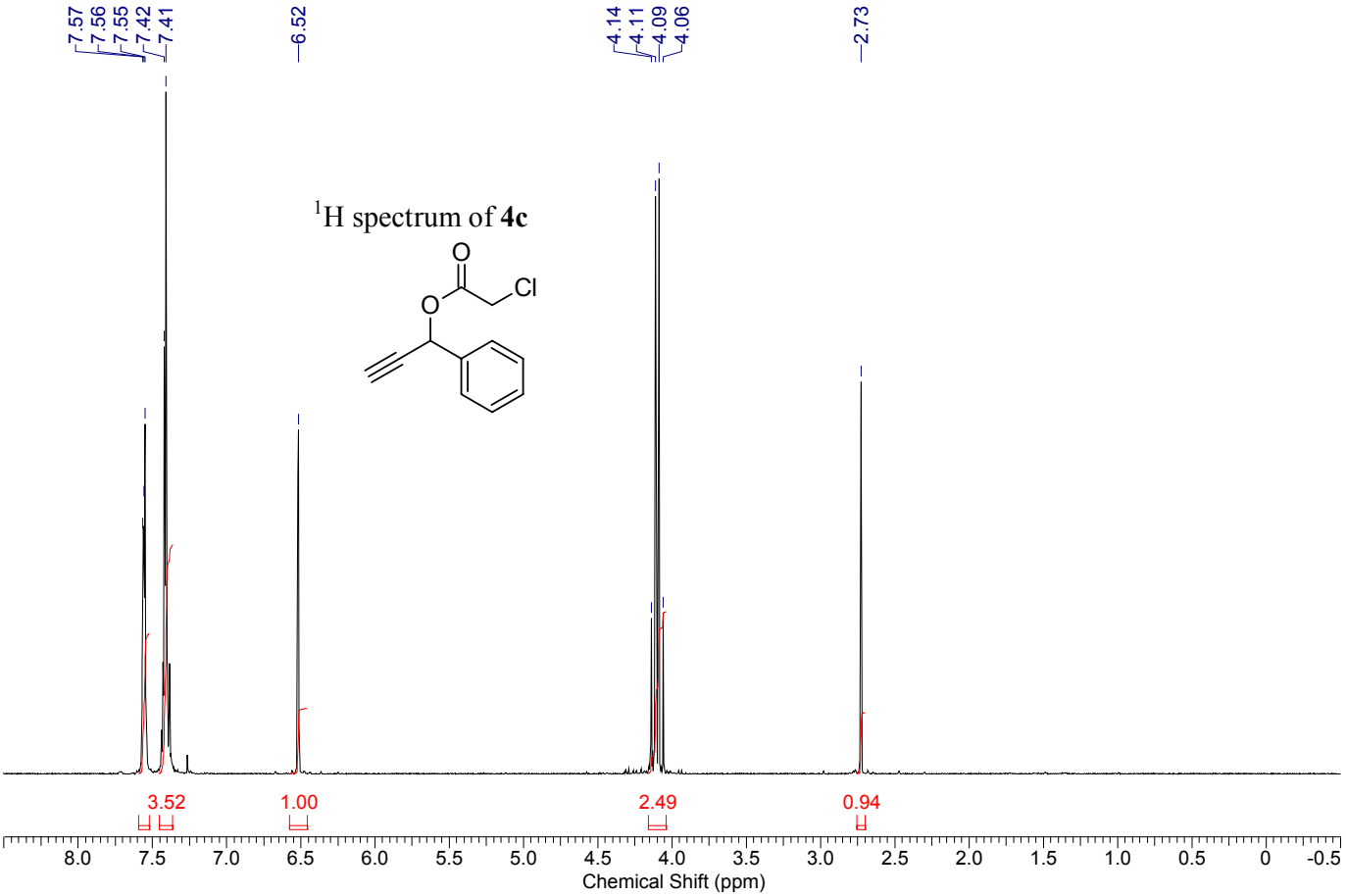
^{13}C spectrum of **4a**



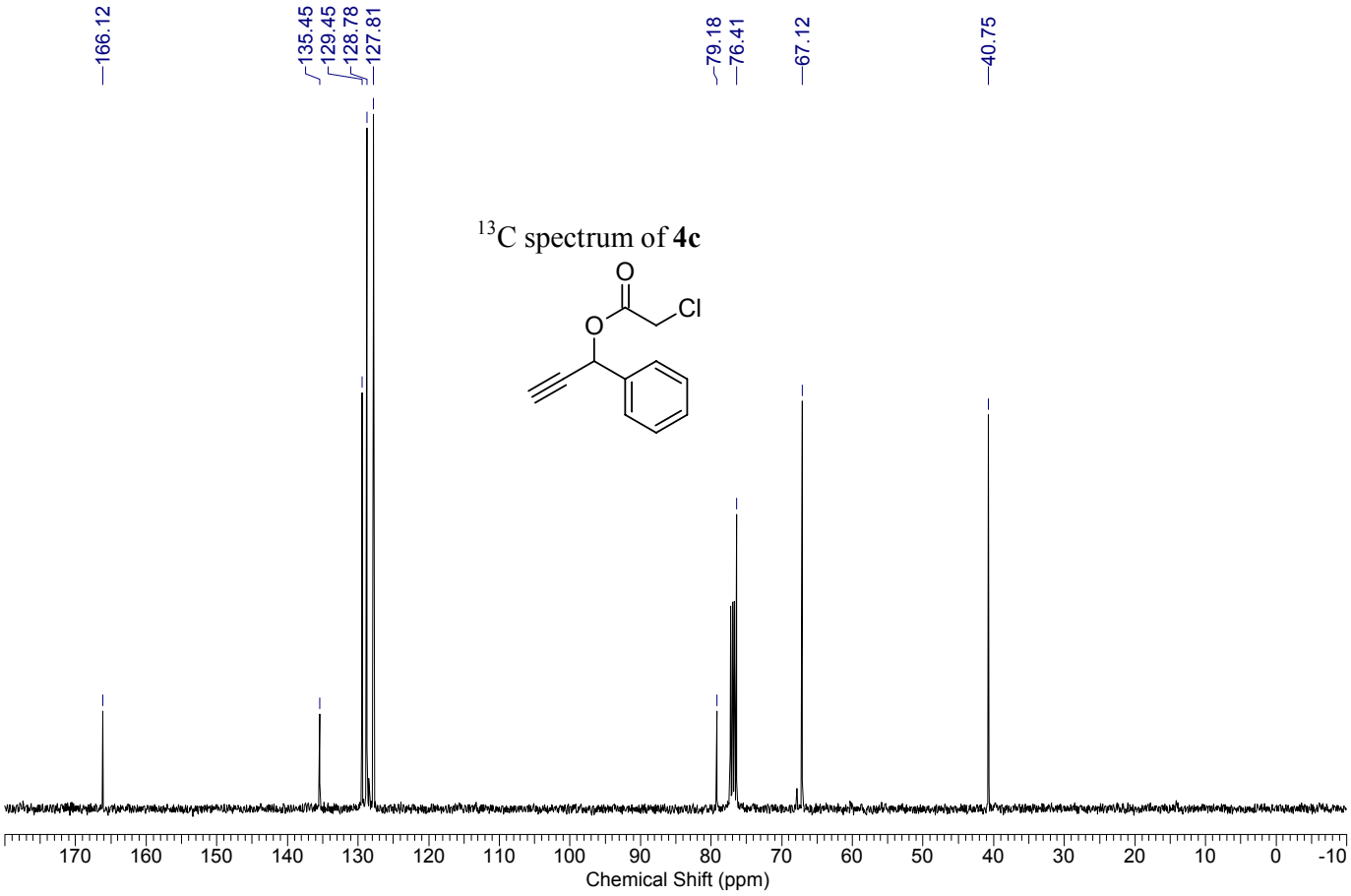
^{1}H spectrum of **4b**



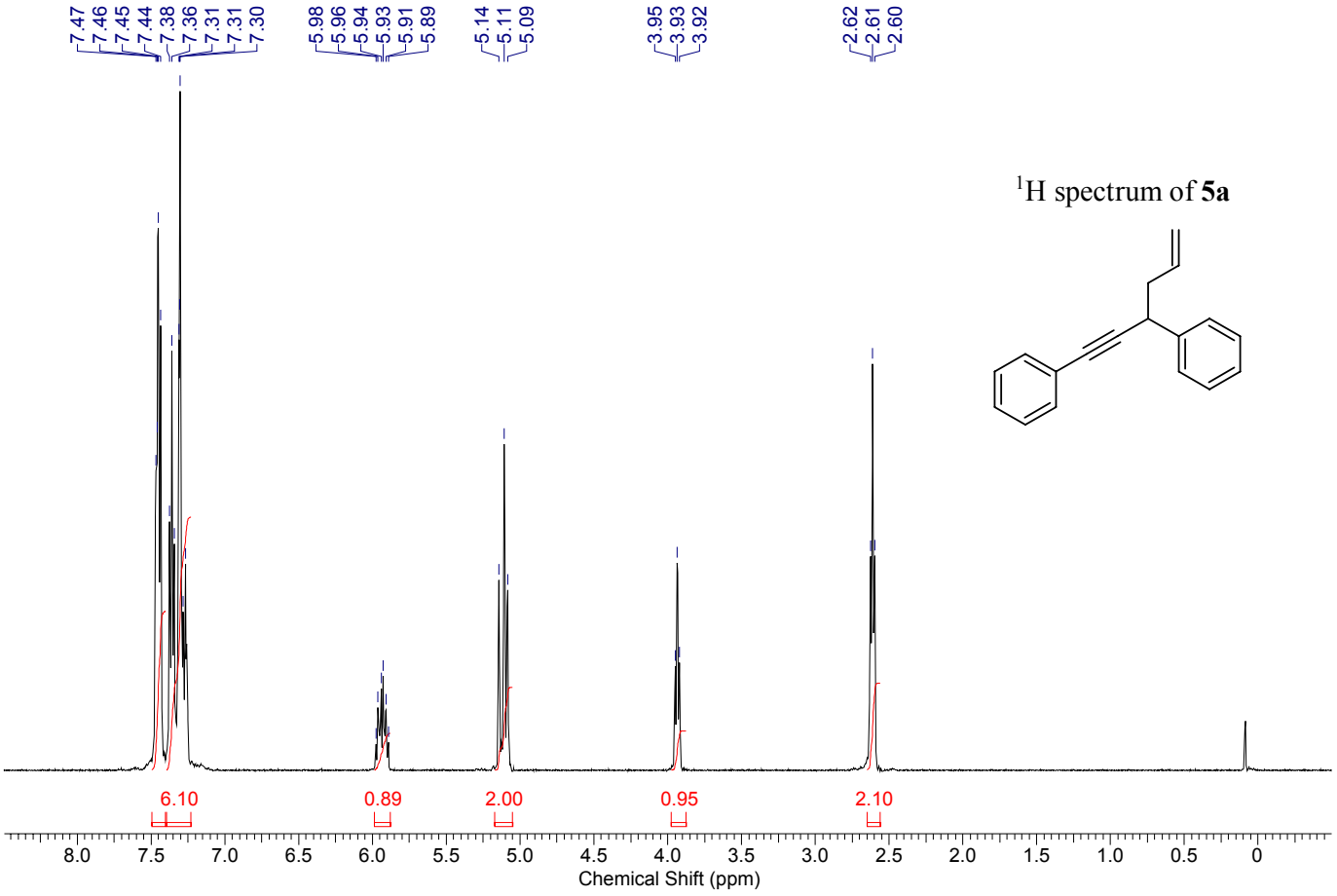
^{13}C spectrum of **4b**



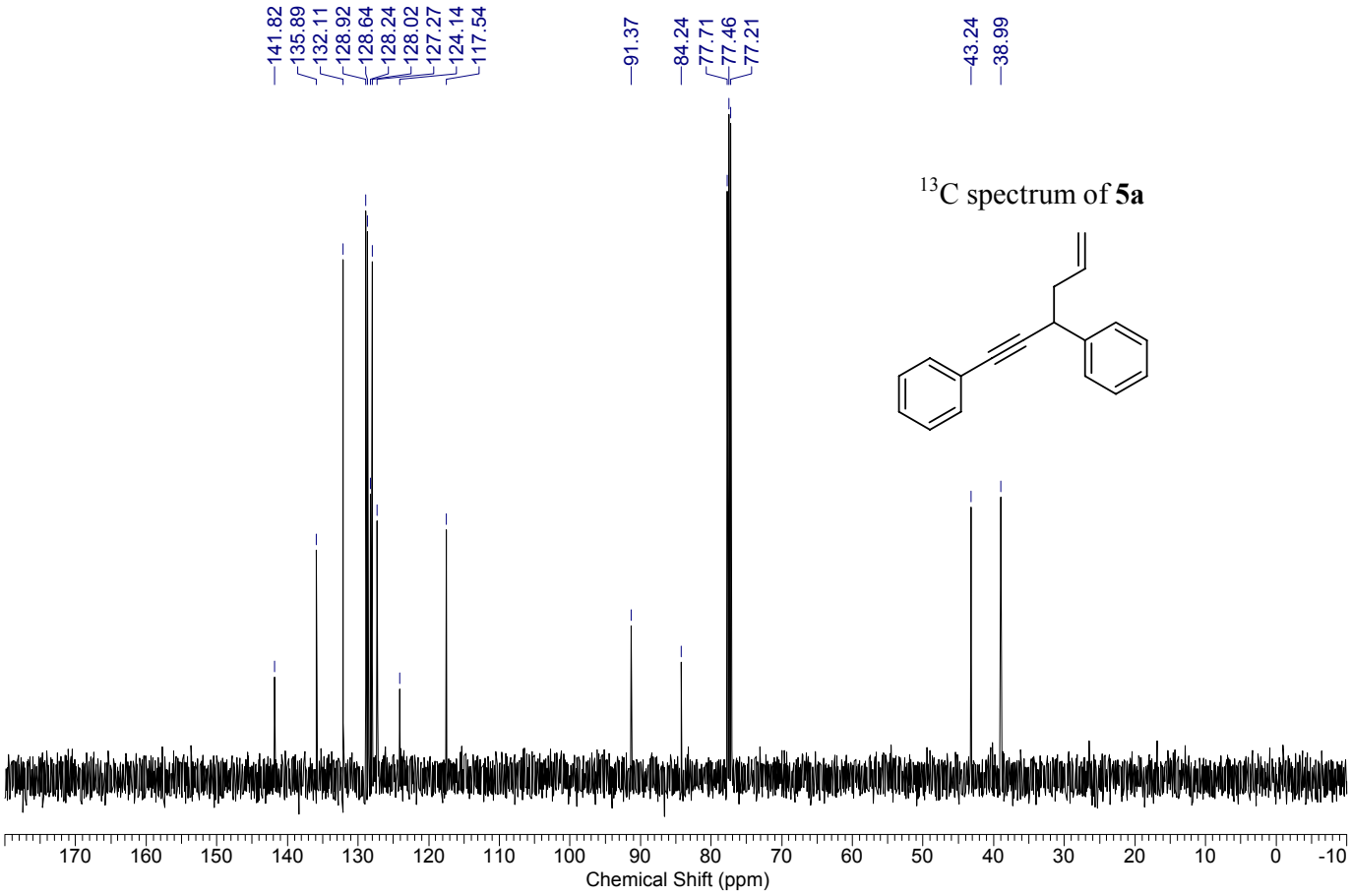
^{1}H spectrum of **4c**



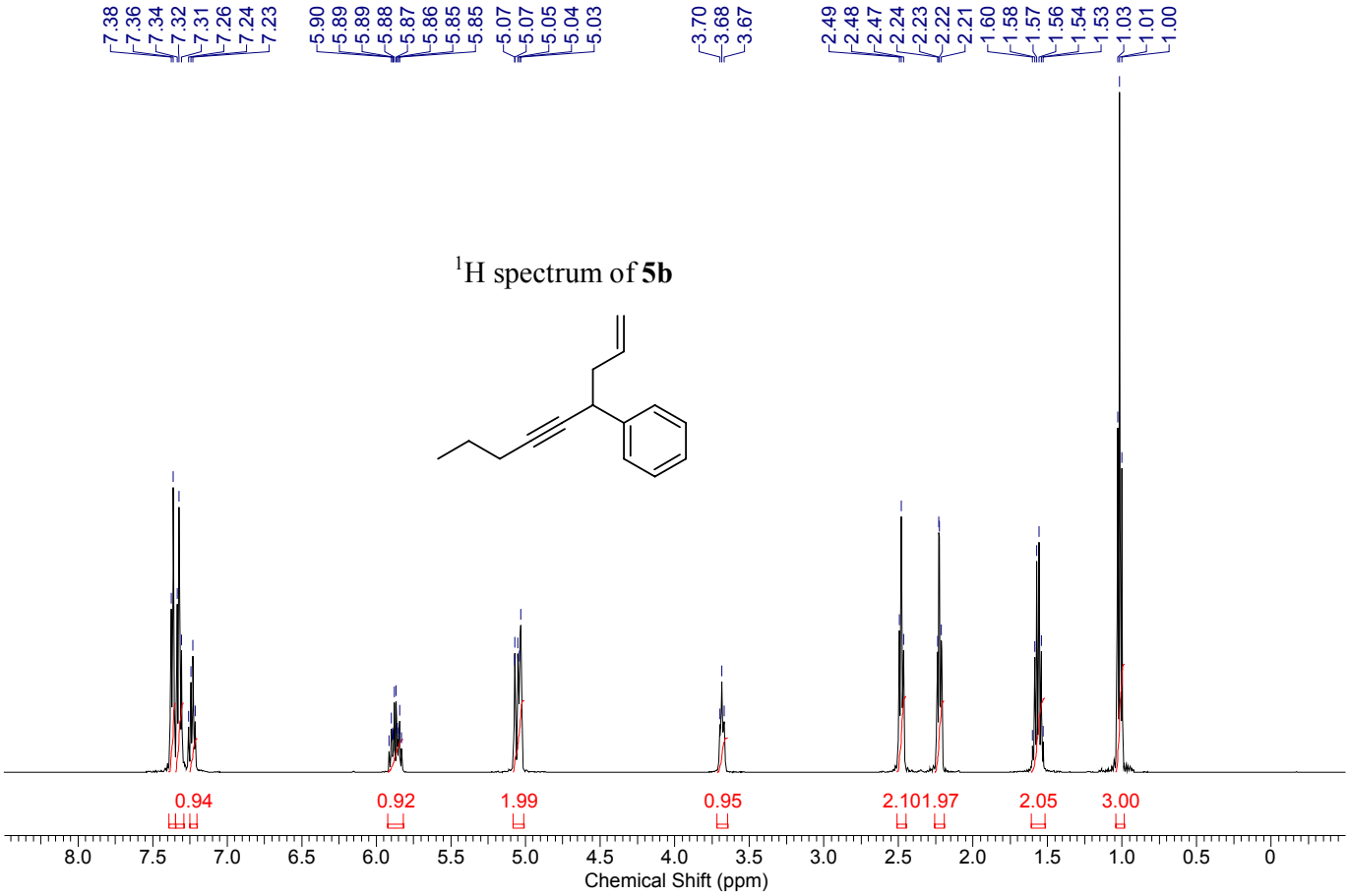
^{13}C spectrum of **4c**



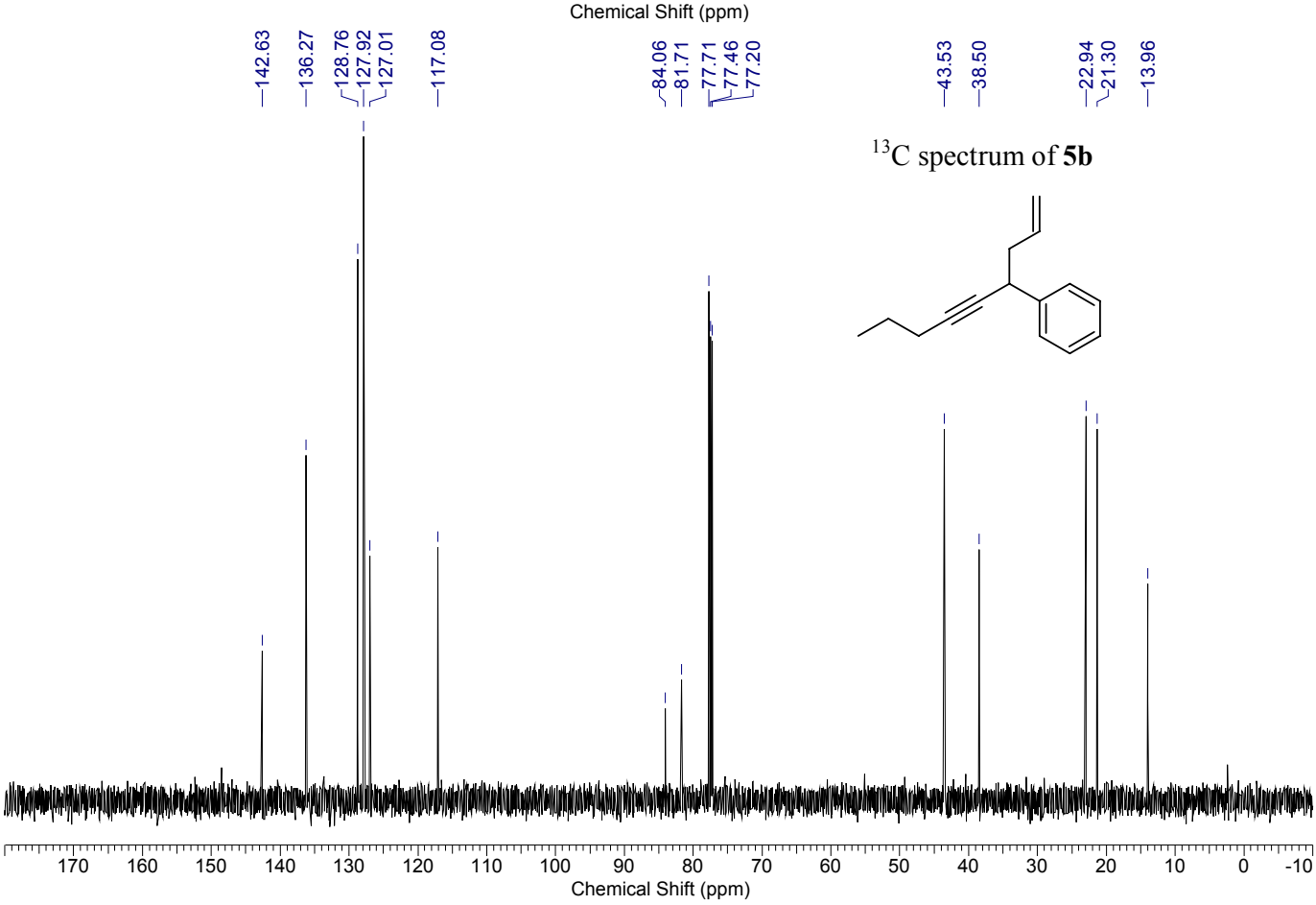
^{1}H spectrum of **5a**



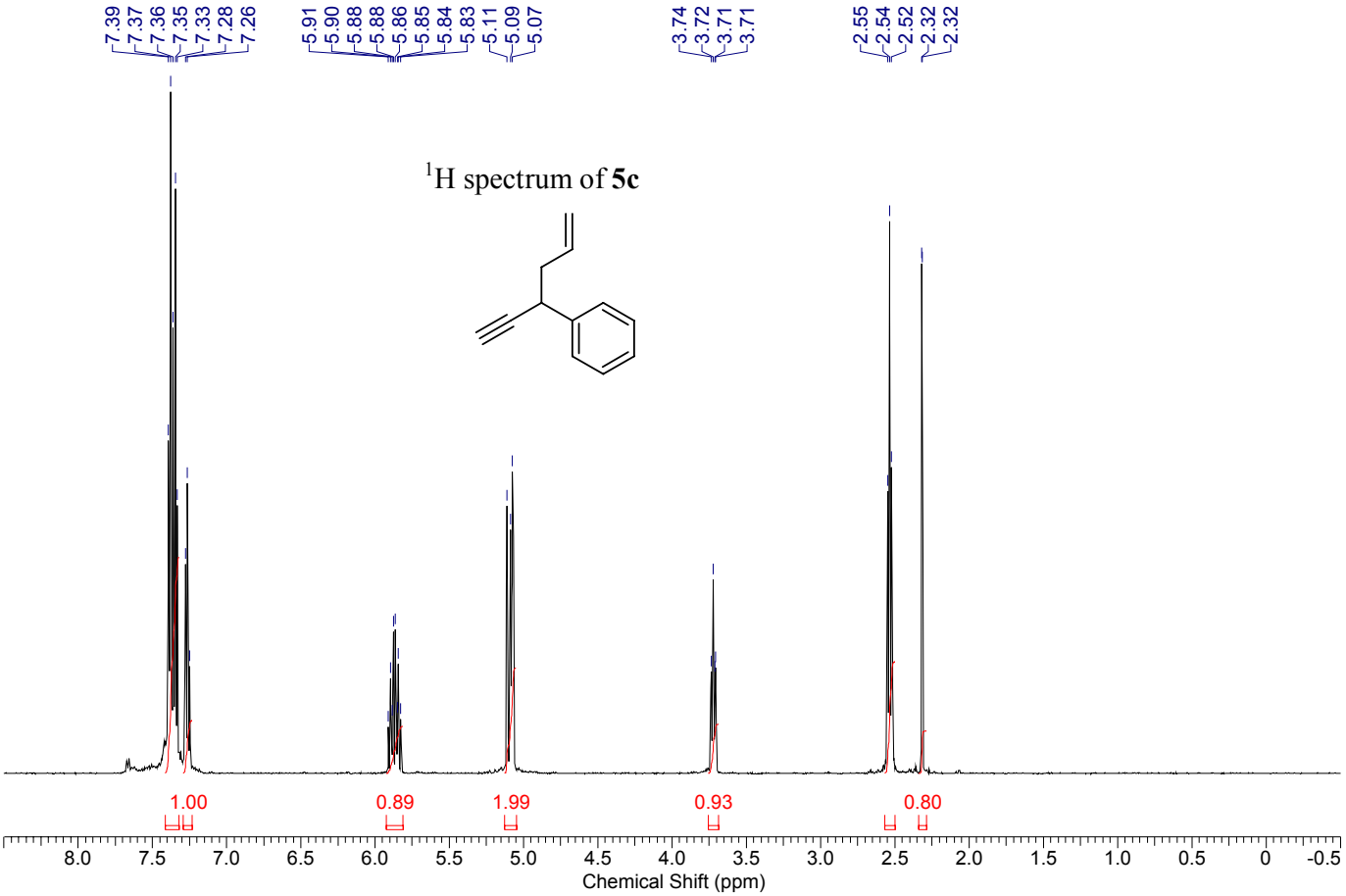
^{13}C spectrum of **5a**



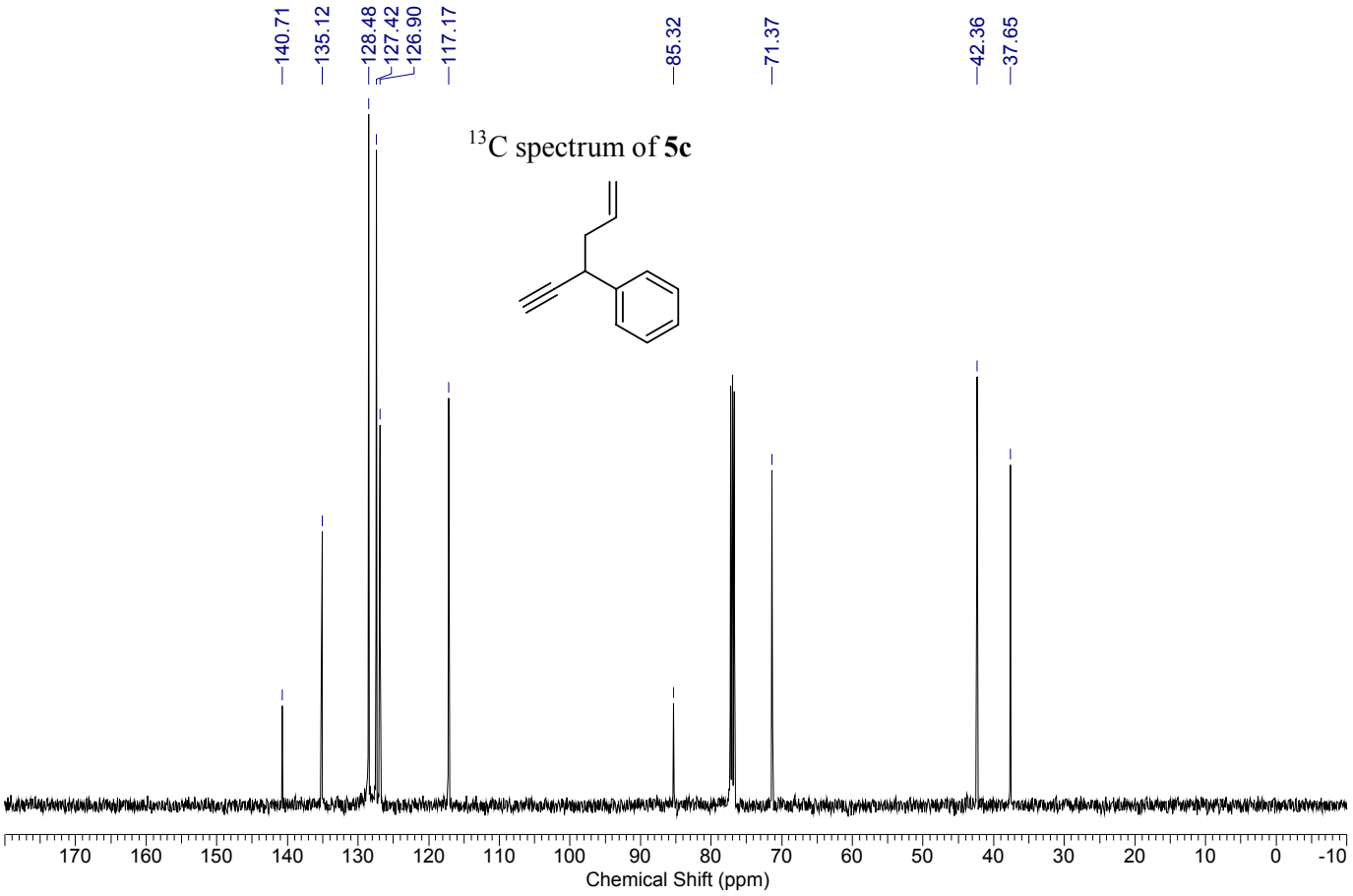
^{1}H spectrum of **5b**



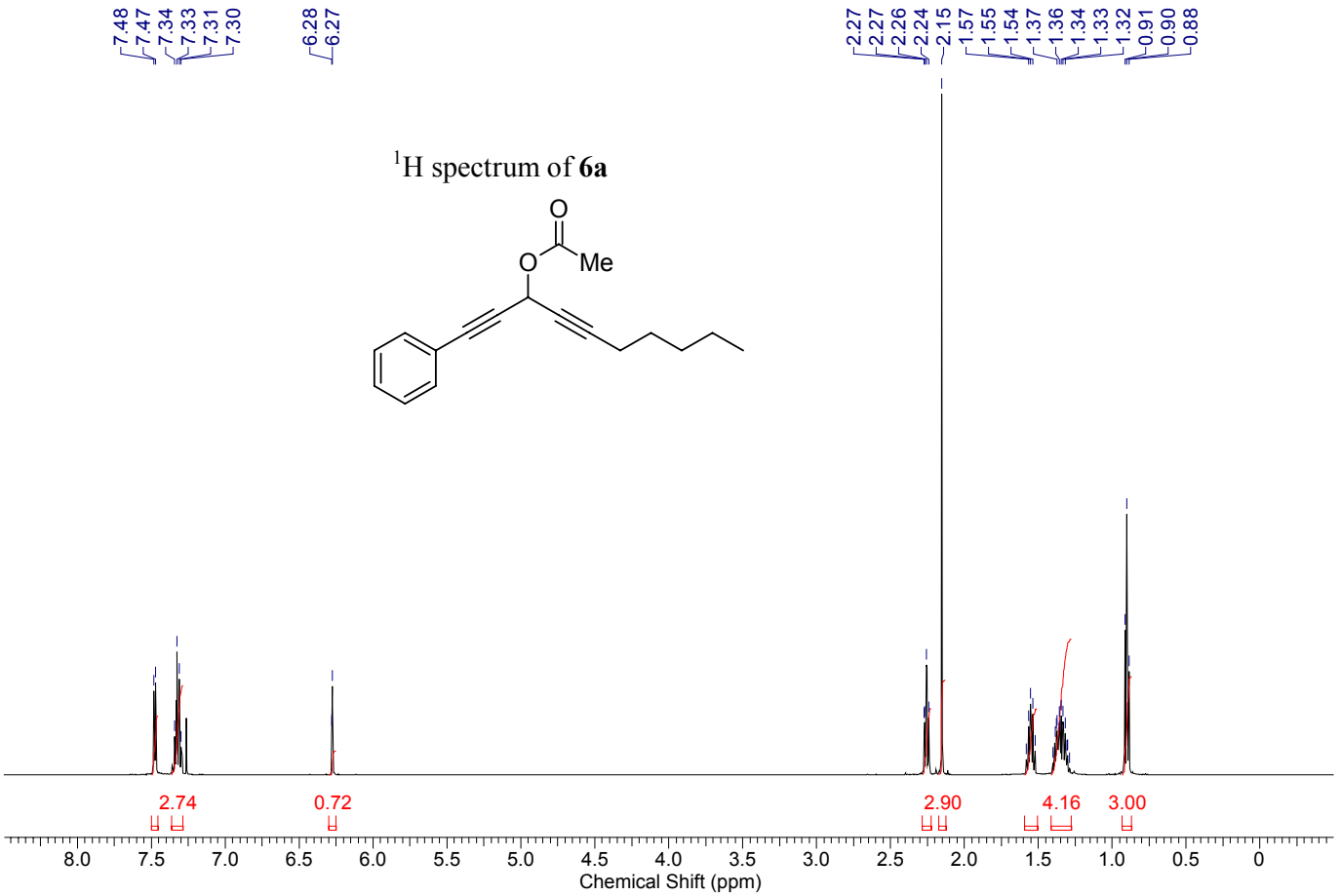
^{13}C spectrum of **5b**



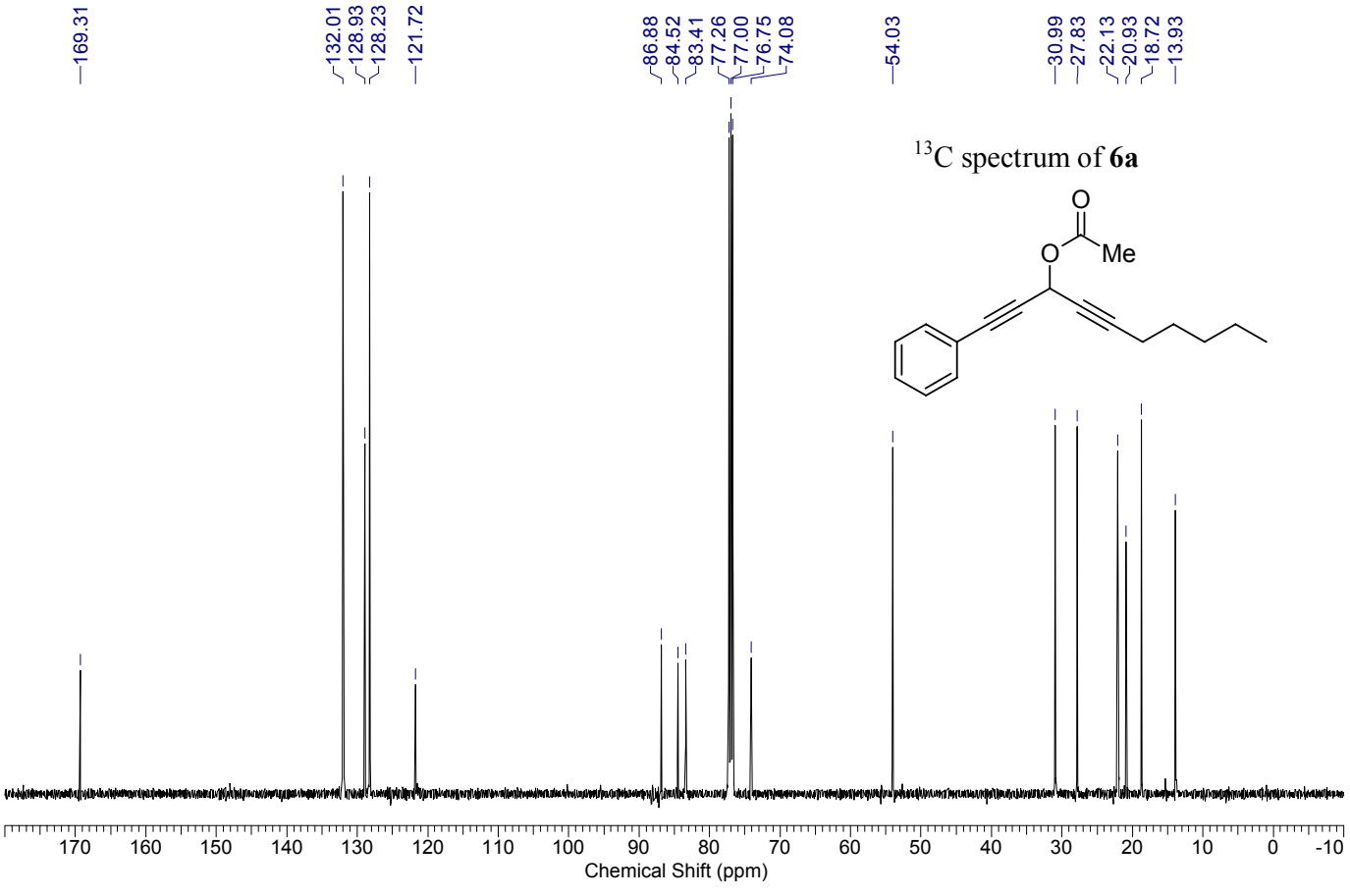
^{1}H spectrum of **5c**



^{13}C spectrum of **5c**

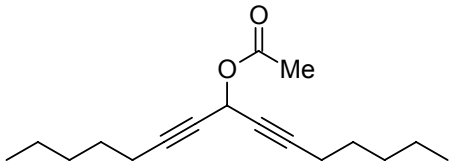


^{1}H spectrum of **6a**

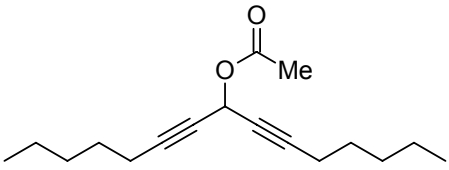


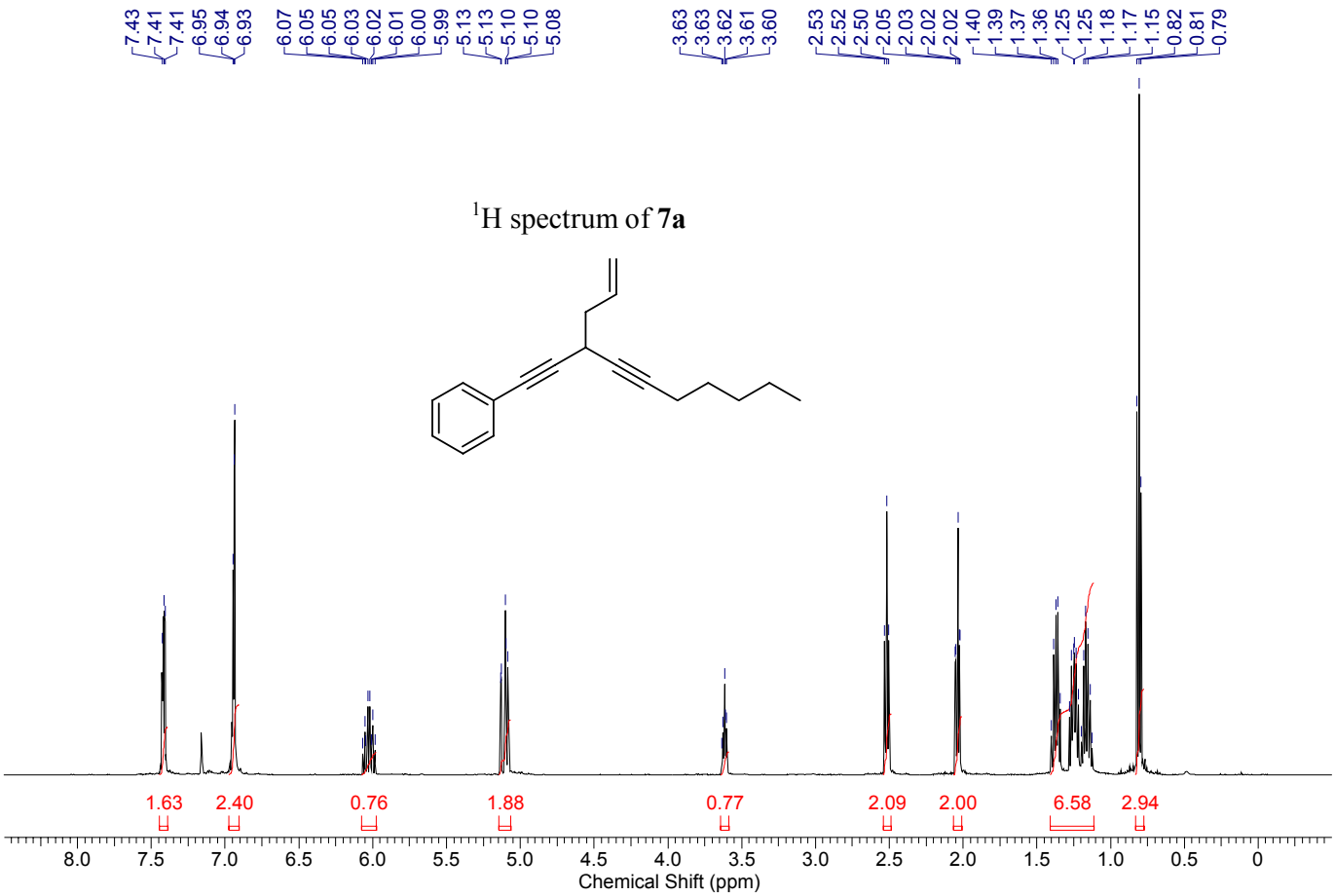
^{13}C spectrum of **6a**

^{1}H spectrum of **6b**

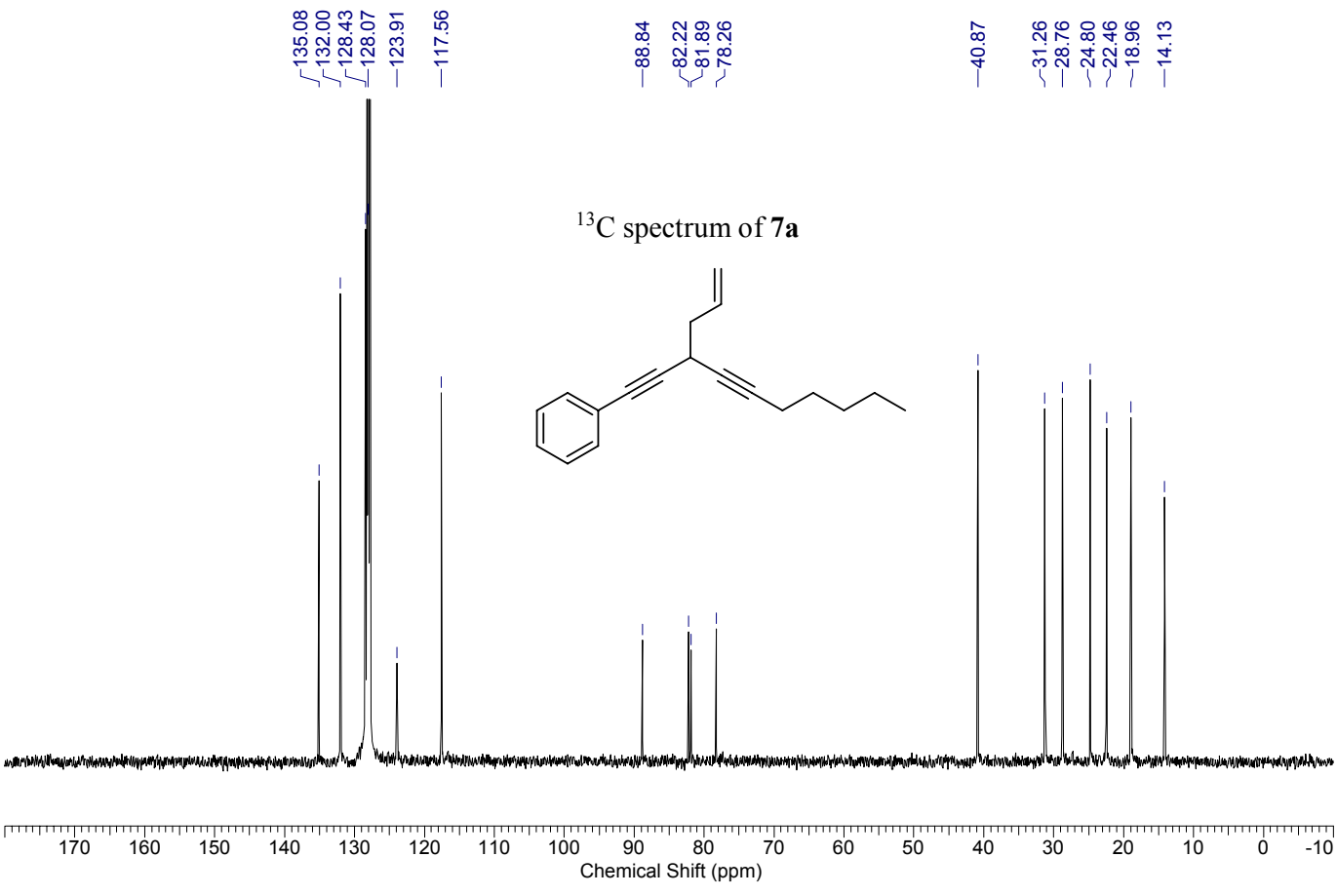


^{13}C spectrum of **6b**



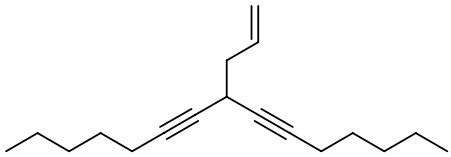


^{1}H spectrum of **7a**



^{13}C spectrum of **7a**

^{1}H spectrum of **7b**



^{13}C spectrum of **7b**