*Supporting Information for:*

# Biphilic Organophosphorus Catalysis: Regioselective Reductive Transposition of Allylic Bromides via $P^{III}/P^{V}$ Redox Cycling

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## I. General Experimental

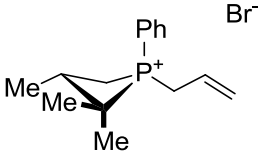
All reactions were carried out under an $N_2$ atmosphere using dry glassware and standard Schlenk techniques. Column chromatography was performed using 230-400 mesh silica gel purchased from Silicycle as the stationary phase. All NMR spectra were obtained in $CDCl_3$, $CD_2Cl_2$ or $C_6D_6$ using a Bruker DPX-300, AMX-360, DRX-400, or AVIII-HD500 spectrometer. $^1H$ spectra were referenced to an internal TMS standard, $^{13}C$ spectra to the internal solvent peak ($\delta$ 77.16 ppm for $CDCl_3$, $\delta$ 49.00 ppm for $CD_3OD$, $\delta$ 53.84 ppm for $CD_2Cl_2$) and $^{31}P$ spectra to an external sample of 85% $H_3PO_4$ ($\delta$ 0.0 ppm). High resolution EI and ESI mass spectra were obtained from the Mass Spectrometry Laboratory at the School of Chemical Sciences, University of Illinois at Urbana-Champaign.

All reagents were purchased through Sigma-Aldrich, Alfa Aesar, or Oakwood Chemical, and used as received unless otherwise noted. Dimethylphenylphosphine,[1] 1-phenylphospholane,[2] *P*-phenyl-5*H*-dibenzophosphole,[3] 1-ethyl-2,2,3-trimethylphosphetane[4], and their quaternization to allylic salts were prepared based on previous literature procedures.[3]

Gas chromatography was performed on a Shimadzu GC-2010 equipped with an FID detector, AOC-20i autoinjector, and Shimadzu SHRXI-5MS capillary column (30 m x 0.25 mm x 0.25 μm). Quantitative measurements were calibrated with samples of authentic analytes.

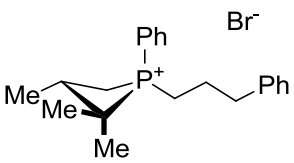
## II. Synthetic Procedures

### A. Representative Procedure for the Synthesis of Phosphetanium Bromide Salts (RP1)

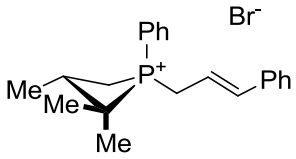



**1-allyl-2,2,3-trimethyl-1-phenylphosphetanium bromide (14·[Br]):** To a solution of 1-phenyl-2,2,3-trimethylphosphetane-1-oxide[5] (~5:1 trans:cis) (1.41 g, 6.8 mmol) in toluene (25 mL) was added triethylamine (1.0 mL, 7.0 mmol, 1.0 eq.) and trichlorosilane (0.7 mL, 6.9 mmol, 1.0 eq.) at ambient temperature. The resulting mixture was then stirred at 80 °C overnight. After cooling in an ice bath, the reaction was quenched with 10% w/w aqueous NaOH solution (40 mL), and the aqueous layer extracted with additional toluene. The combined organic layers were washed with saturated aqueous $NaHCO_3$ and NaCl solutions and dried over anhydrous $MgSO_4$. Filtration and removal of solvent yielded crude phosphetane as a mixture of diastereomers, which was immediately dissolved in allyl bromide (5 mL). Stirring overnight at ambient temperature yielded a thick precipitate, which was collected by filtration and washed with diethyl ether to afford the desired product as a white solid (1.52 g, 4.8 mmol, 72%). An approximately

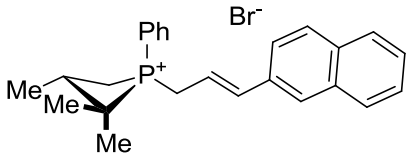
2.6:1 trans:cis diastereomeric mixture was used in all catalytic experiments. Recrystallization from methanol/diethyl ether can be used to provide a single diastereomer, which was unambiguously assigned as *trans* via x-ray crystallography. $^{1}$H NMR ($CD_3OD$, 400 MHz): δ = 1.14 (d, $J_{P\text{-}H}$ = 21 Hz, 3H, $CH_3$), 1.24 (d, $J$ = 6.7 Hz, 3H, $CH_3$), 1.66 (d, $J$ = 21 Hz, 3H, $CH_3$), 2.74-2.88 (m, 1H), 2.95-3.09 (m, 1H), 3.26-3.38 (m, 1H), 3.82 (dd, $J$ = 15, 7.4 Hz, 2H, $PCH_2$), 5.27-5.43 (m, 2H, $C{=}CH_2$), 5.53-5.67 (m, 1H, C=CH), 7.75-7.83 (m, 2H, Ar), 7.84-7.91 (m, 1H, Ar), 8.04-8.14 (m, 1H, Ar). **Minor (cis) diastereomer**: 1.19 (d, $J$ = 21 Hz, 3H, $CH_3$), 1.57 (d, $J$ = 21 Hz, 3H, $CH_3$), 3.90 (dd, $J$ = 15, 7.3 Hz, 2H, $PCH_2$), 5.68-5.78 (m, 1H, C=CH), 7.92-8.00 (m, 2H, Ar); $^{13}$C NMR ($CD_3OD$, 101 MHz): 15.5 (d, $J_{P\text{-}C}$ = 24 Hz), 17.5 (d, $J_{P\text{-}C}$ = 1.2 Hz), 23.3 (d, $J_{P\text{-}C}$ = 46 Hz), 24.1 (d, $J_{P\text{-}C}$ = 4.0 Hz), 28.4 (d, $J_{P\text{-}C}$ = 25 Hz), 40.9 (d, $J_{P\text{-}C}$ = 16 Hz), 47.8 (d, $J_{P\text{-}C}$ = 44 Hz), 117.1 (d, $J_{P\text{-}C}$ = 63 Hz), 124.5 (d, $J_{P\text{-}C}$ = 12 Hz), 125.1 (d, $J_{P\text{-}C}$ = 12 Hz), 131.3 (d, $J_{P\text{-}C}$ = 12 Hz), 134.2 (d, $J_{P\text{-}C}$ = 9.0 Hz), 136.0 (d, $J_{P\text{-}C}$ = 3.0 Hz). **Minor (cis) isomer:** 15.4 (d, $J_{P\text{-}C}$ = 24 Hz), 18.5 (d, $J_{P\text{-}C}$ = 2.5 Hz), 22.6 (2 unresolved resonances), 25.4 (d, $J_{P\text{-}C}$ = 32 Hz), 39.9 (d, $J_{P\text{-}C}$ = 16 Hz), 47.5 (d, $J_{P\text{-}C}$ = 45 Hz), 118.7 (d, $J_{P\text{-}C}$ = 56 Hz), 124.5 (d, $J_{P\text{-}C}$ = 11 Hz), 125.1 (d, $J_{P\text{-}C}$ = 12 Hz), 131.2 (d, $J_{P\text{-}C}$ = 12 Hz), 133.8 (d, $J_{P\text{-}C}$ = 9.7 Hz), 136.2 (d, $J_{P\text{-}C}$ = 3.2 Hz); $^{31}$P NMR ($CD_3OD$, 146 MHz): 46.8 (cis, minor), 48.9 (trans, major); HRMS (ESI) Calcd. For [$C_{15}H_{22}P^{+}$]: 233.1459, Found: 233.1454.




**2,2,3-trimethyl-1-phenyl-1-(3-phenylpropyl)phosphetanium bromide (18):** Prepared using **RP1** on a 36 mmol scale. The crude phosphetane was diluted with toluene (20 mL), then 1-bromo-3-phenylpropane (22 mL, 144 mmol) was added and heated to 90 °C for 8 h under a nitrogen atmosphere. Filtration afforded the desired product as a white solid (7.69 g, 55% yield over 2 steps). Recrystallization from methanol/ether at room temperature yielded a single diastereomer for characterization. $^{1}$H NMR ($CDCl_3$, 360 MHz): δ = 1.11-1.30 (m, 6H), 1.53-1.69 (m, 1H), 1.69 (d, $J$ = 21 Hz, 3H, $CH_3$), 1.77-1.93 (m, 1H), 2.65-2.87 (m, 3H), 3.25 (t, $J$ = 11 Hz, 3H), 3.45-3.62 (m, 1H), 7.07-7.25 (m, 5H, Ar), 7.66-7.82 (m, 3H, Ar), 8.13-8.26 (m, 2H, Ar); $^{13}$C NMR ($CDCl_3$, 101 MHz): 14.9 (d, $J_{P\text{-}C}$ = 8.7 Hz), 15.1 (d, $J_{P\text{-}C}$ = 9.3 Hz), 17.3, 22.2 (d, $J_{P\text{-}C}$ = 26 Hz), 23.1 (d, $J_{P\text{-}C}$ = 44 Hz), 23.7 (d, $J_{P\text{-}C}$ = 6.4 Hz), 35.5 (d, $J_{P\text{-}C}$ = 14 Hz), 39.8 (d, $J_{P\text{-}C}$ = 16 Hz), 46.1 (d, $J_{P\text{-}C}$ = 47 Hz), 115.2 (d, $J_{P\text{-}C}$ = 62 Hz), 126.1, 128.2, 130.0 (d, $J_{P\text{-}C}$ = 12 Hz), 132.8, 132.8 (d, $J_{P\text{-}C}$ = 20 Hz), 134.3, 139.7; $^{31}$P NMR ($CDCl_3$, 146 MHz): 52.5; HRMS (ESI) Calcd. For [$C_{21}H_{28}P^{+}$]: 311.1929, Found: 311.1923.

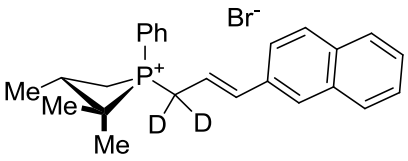


**2,2,3-trimethyl-1-phenyl-1-(3-phenylprop-2-enyl)phosphetanium bromide (12·[Br]):** Prepared using **RP1** on a 10 mmol scale. The crude phosphetane was diluted with toluene (5 mL), then 1-bromo-3-phenylprop-2-ene (2.0 g, 10 mmol) was added and heated to 90 °C for 8 h under a nitrogen atmosphere. Filtration afforded the desired product as a white solid (1.20 g, 31% yield over 2 steps). Recrystallization from methanol/ether at room temperature yielded a single diastereomer for characterization. $^{1}$H NMR ($CDCl_3$, 360 MHz): δ = 1.23 (d, $J$ = 6.7 Hz, 3H, $CH_3$), 1.30 (d, $J$ = 21 Hz, 3H, $CH_3$), 1.90 (d, $J$ = 21 Hz, 3H, $CH_3$), 2.58-2.75 (m, 1H), 3.08-3.24 (m, 1H), 3.44 (q, $J$ = 13 Hz, 1H), 4.36-4.50 (m, 1H), 4.55-4.71 (m, 1H), 5.77-5.92 (m, 1H, C=CH), 6.82 (dd, $J$ = 16, 5.8 Hz, 1H, C=CH), 7.18 (s, 5H, Ar), 7.64-7.78 (m, 3H, Ar), 8.26 (dd, $J$ = 12, 7.1 Hz, 2H, Ar); $^{13}$C NMR ($CDCl_3$, 101 MHz): 15.2 (d, $J_{P\text{-}C}$ =24 Hz), 17.6, 23.0 (d, $J_{P\text{-}C}$ = 46 Hz), 24.1 (d, $J_{P\text{-}C}$ = 3.8 Hz), 28.9 (d, $J_{P\text{-}C}$ = 23 Hz), 39.6 (d, $J_{P\text{-}C}$ = 15 Hz), 47.5 (d, $J_{P\text{-}C}$ = 43 Hz), 113.7 (d, $J_{P\text{-}C}$ = 13 Hz), 115.8 (d, $J_{P\text{-}C}$ = 62 Hz), 126.3 (d, $J_{P\text{-}C}$ = 1.9 Hz), 128.1, 128.4, 130.0 (d, $J_{P\text{-}C}$ = 12 Hz), 133.3 (d, $J_{P\text{-}C}$ = 8.9 Hz), 134.4 (d, $J_{P\text{-}C}$ = 2.9 Hz), 135.6 (d, $J_{P\text{-}C}$ = 4.2 Hz), 138.8 (d, $J_{P\text{-}C}$ = 13 Hz); $^{31}$P NMR ($CDCl_3$, 146 MHz): 48.5; HRMS (ESI) Calcd. For [$C_{21}H_{26}P^+$]: 309.1772, Found: 309.1777.



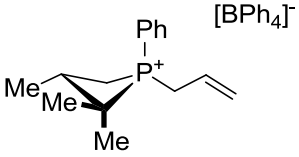
**2,2,3-trimethyl-1-phenyl-1- (3-naphthylprop-2-enyl-1-) phosphetanium bromide (15):** Prepared using **RP1** on a 10 mmol scale. The crude phosphetane was diluted with 5 mL toluene, then (*E*)-2-(3-bromoprop-1-en-1-yl)naphthalene (1.12 g, 4.5 mmol) was added and heated to 80 °C for 8 h under a nitrogen atmosphere. Filtration afforded the desired product as a white solid, (1.35 g, 68% yield). $^{1}$H NMR ($CDCl_3$, 360 MHz): δ = 1.23 (d, $J$ = 6.7 Hz, 3H, $CH_3$), 1.30 (d, $J$ = 21 Hz, 3H, $CH_3$), 1.80 (d, $J$ = 21 Hz, 3H, $CH_3$, minor isomer), 1.95 (d, $J$ = 21 Hz, 3H, $CH_3$), 2.56-2.70 (m, 1H), 3.00-3.14 (m, 1H), 3.39-3.56 (m, 1H), 4.50-4.64 (m, 1H), 4.66-4.80 (m, 1H), 5.84-5.99 (m, 1H, C=CH), 6.99 (dd, $J$ = 16, 5.0 Hz, 1H, C=CH), 7.25-7.31 (m, 1H, Ar), 7.35-7.42 (m, 2H, Ar), 7.52 (s, 1H, Ar), 7.54-7.77 (m, 6H, Ar), 8.17-8.27 (m, 2H, Ar); $^{13}$C NMR ($CDCl_3$, 75 MHz): 15.5 (d, $J_{P\text{-}C}$ = 24 Hz), 17.8, 23.1 (d, $J_{P\text{-}C}$ = 46 Hz), 24.3 (d, $J_{P\text{-}C}$ = 4.2 Hz), 29.2 (d, $J_{P\text{-}C}$ = 23 Hz), 39.8 (d, $J_{P\text{-}C}$ = 15 Hz), 47.8 (d, $J_{P\text{-}C}$ = 43 Hz), 114.0 (d, $J_{P\text{-}C}$ = 13 Hz), 116.1 (d, $J_{P\text{-}C}$ = 62 Hz), 123.0, 126.3, 126.4, 127.1 (d, $J_{P\text{-}C}$ = 3.3 Hz), 127.6, 128.1, 128.2, 130.2 (d, $J_{P\text{-}C}$ = 12 Hz), 133.1, 133.2, 133.3 (d, $J_{P\text{-}C}$ = 8.9 Hz), 134.5 (d, $J_{P\text{-}C}$ = 3.2 Hz), 139.1 (d, $J_{P\text{-}C}$ = 13 Hz) (1 resonance unresolved); $^{31}$P NMR ($CDCl_3$, 146

MHz): 48.3 (major), 47.2 (minor); HRMS (ESI) Calcd. For [$C_{25}H_{28}P^+$]: 359.1929, Found: 359.1932.



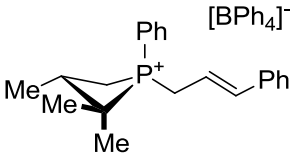

**2,2,3-trimethyl-1-phenyl-1- (3-naphthylprop-2-enyl-1-$d_2$) phosphetanium bromide (15-$d_2^a$):** Prepared using **RP1** on a 10 mmol scale. The crude phosphetane was diluted with toluene (5 mL), then **S26** (0.74 g, 3 mmol) was added and heated to 80 °C for 8 h under a nitrogen atmosphere. Filtration afforded the desired product as a white solid, which is a mixture of diastereomers (0.965 g, 73% yield). $^1$H NMR ($CDCl_3$, 360 MHz): δ = 1.23 (d, *J* = 6.7 Hz, 3H, $CH_3$), 1.30 (d, *J* = 21 Hz, 3H, $CH_3$), 1.80 (d, *J* = 21 Hz, 3H, $CH_3$, minor isomer), 1.95 (d, *J* = 21 Hz, 3H, $CH_3$), 2.56-2.70 (m, 1H), 3.00-3.14 (m, 1H), 3.39-3.56 (m, 1H), 5.92 (dd, *J* = 16, 5.6 Hz, 1H, C=CH), 7.00 (dd, *J* = 16, 5.9 Hz, 1H, C=CH), 7.25-7.31 (m, 1H, Ar), 7.33-7.42 (m, 2H, Ar), 7.52 (s, 1H, Ar), 7.54-7.77 (m, 6H, Ar), 8.17-8.27 (m, 2H, Ar); $^{13}$C NMR ($CDCl_3$, 101 MHz): 15.4 (d, $J_{P-C}$ = 24 Hz), 17.8, 23.1 (d, $J_{P-C}$ = 46 Hz), 24.3, 39.9 (d, $J_{P-C}$ = 15 Hz), 47.7 (d, $J_{P-C}$ = 43 Hz), 114.0 (d, $J_{P-C}$ = 13 Hz), 116.1 (d, $J_{P-C}$ = 62 Hz), 123.0, 126.2, 126.4, 127.0, 127.6, 128.1, 128.2, 130.2 (d, $J_{P-C}$ = 12 Hz), 133.1, 133.2, 133.4 (d, $J_{P-C}$ = 8.9 Hz), 134.6, 139.1 (d, $J_{P-C}$ = 13 Hz) (2 resonances unresolved); $^{31}$P NMR ($CDCl_3$, 146 MHz): 48.3 (major), 47.0 (minor); HRMS (ESI) Calcd. For [$C_{25}H_{26}D_2P^+$]: 361.2054, Found: 361.2049.

**B. Representative Procedure for the Synthesis of Phosphetanium Tetraphenylborate Salts (RP2)**

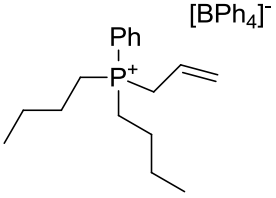



**1-allyl-2,2,3-trimethyl-1-phenylphosphetanium tetraphenylborate (14):** Phosphetanium salt **14·[Br]** (0.936 g, 3.0 mmol) was dissolved in water (30 mL), sodium tetraphenylborate (1.13 g, 3.3 mmol, 1.1 equiv) was added and the solution was stirred rapidly at ambient temperature for 30 minutes. White precipitate formed immediately and was filtered, washed with water (50 mL) and dried to give the product as a white powder (1.32 g, 80%). $^1$H NMR ($CD_2Cl_2$, 360 MHz): δ = 1.08 (d, *J* = 21 Hz, 3H, $CH_3$), 1.13 (d, *J* = 6.8 Hz, 3H, $CH_3$), 1.36 (d, *J* = 21 Hz, 3H, $CH_3$), 2.00-2.85 (m, 5H), 5.15-5.45 (m, 3H), 7.03 (t, *J* = 7.1 Hz, 4H, Ar), 7.17 (t, *J* = 7.3 Hz, 8H, Ar), 7.28-7.37 (m, 2H, Ar), 7.46-7.57 (m, 8H, Ar), 7.65-7.85 (m, 3H, Ar); $^{13}$C NMR ($CD_2Cl_2$, 125 MHz): major peaks: 15.3 (d, $J_{P-C}$ = 24 Hz), 18.5 (d, $J_{P-C}$ = 2.6 Hz), 22.2 (d, $J_{P-C}$ = 45 Hz),

22.6 (d, $J_{P\text{-}C}$ = 3.9 Hz), 25.0 (d, $J_{P\text{-}C}$ = 31 Hz), 39.2 (d, $J_{P\text{-}C}$ = 16 Hz), 46.4 (d, $J_{P\text{-}C}$ = 44 Hz), 116.4 (d, $J_{P\text{-}C}$ = 56 Hz), 122.2, 122.6 (d, $J_{P\text{-}C}$ = 11 Hz), 125.7 (d, $J_{P\text{-}C}$ = 7.9 Hz), 126.1, 130.7 (d, $J_{P\text{-}C}$ = 12 Hz), 131.9 (d, $J_{P\text{-}C}$ = 9.2 Hz), 135.7 (d, $J_{P\text{-}C}$ = 3.2 Hz), 136.3, 164.3 (q, $J_{B\text{-}C}$ = 49 Hz); $^{31}$P NMR ($CD_2Cl_2$, 146 MHz): 46.2 (minor), 44.8 (major).

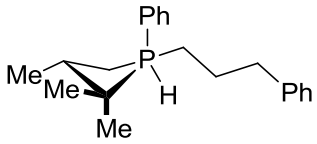



**2,2,3-trimethyl-1-phenyl-1-(3-phenylprop-2-enyl)phosphetanium tetraphenylborate (12):** Prepared using **RP2** from a single diastereomer of **12·[Br]** (0.33 g, 0.86 mmol). Product was isolated as a white solid (0.291 g, 54% yield). $^1$H NMR ($CD_2Cl_2$, 400 MHz): δ = 0.98-1.15 (m, 6H), 1.40 (d, *J* = 21 Hz, 3H, $CH_3$), 2.12 (q, *J* = 14 Hz, 1H), 2.43-2.64 (m, 2H), 2.80-3.00 (m, 2H), 5.47-5.62 (m, 1H, C=CH), 6.37 (dd, *J* = 16, 4.6 Hz, 1H, C=CH), 6.87-6.99 (m, 4H, Ar), 7.07 (t, *J* =7.0 Hz, 8H, Ar), 7.21-7.29 (m, 2H, Ar), 7.31-7.38 (m, 3H, Ar), 7.39-7.50 (m, 10 H, Ar), 7.62-7.71 (m, 2H, Ar), 7.75-7.88 (m, 1H, Ar); $^{13}$C NMR ($CD_2Cl_2$, 125 MHz): 15.5 (d, $J_{P\text{-}C}$ = 23 Hz), 17.9 (d, $J_{P\text{-}C}$ = 1.7 Hz), 23.0 (d, $J_{P\text{-}C}$ = 45 Hz), 24.1 (d, $J_{P\text{-}C}$ = 4.0 Hz), 27.7 (d, $J_{P\text{-}C}$ = 24 Hz), 40.0 (d, $J_{P\text{-}C}$ = 16 Hz), 47.0 (d, $J_{P\text{-}C}$ = 43 Hz), 112.2 (d, $J_{P\text{-}C}$ = 12 Hz), 114.8 (d, $J_{P\text{-}C}$ = 62 Hz), 122.3, 126.1 (q, $J_{B\text{-}C}$ = 2.5 Hz), 126.9 (d, $J_{P\text{-}C}$ = 1.9 Hz), 129.1, 129.3, 130.9 (d, $J_{P\text{-}C}$ = 12 Hz), 132.5 (d, $J_{P\text{-}C}$ = 8.5 Hz), 135.5 (d, $J_{P\text{-}C}$ = 4.2 Hz), 135.7 (d, $J_{P\text{-}C}$ = 2.9 Hz), 136.4, 140.0 (d, $J_{P\text{-}C}$ = 12 Hz), 164.4 (q, $J_{B\text{-}C}$ = 49 Hz); $^{31}$P NMR ($CD_2Cl_2$, 146 MHz): 45.8.

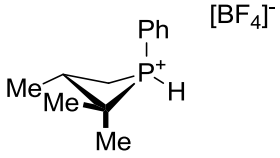



**allyldibutylphenylphosphonium tetraphenylborate (13):** Following literature precedent,[6] to dichlorophenylphosphine (2.0 mL, 15 mmol) in ether at -78 °C under a nitrogen atmosphere was added n-BuLi (12 mL, 2.5 M in hexanes, 30 mmol) dropwise. The reaction was stirred at room temperature overnight, then filtered under a nitrogen atmosphere and the filtrate concentrated to yield crude dibutylphenylphosphine as a colorless oil. To this oil was added neat allyl chloride (4 mL, 45 mmol) under a nitrogen atmosphere and stirred at room temperature overnight, then triturated with pentane to give the product **13·[Br]** as a white solid. **13·[Br]** (0.500 g, 1.7 mmol) was converted via **RP2** in 2% acetone/water (50 mL) to give desired product as a white solid (0.84 g, 85%). $^1$H NMR ($CD_2Cl_2$, 360 MHz): δ = 1.00 (t, *J* = 7.2 Hz, 6H), 1.23-1.40 (m, 4H), 1.40-1.54 (m, 4H), 1.81-1.98 (m, 4H), 2.52 (dd, *J* = 15, 6.4 Hz, 2H), 5.25-5.48 (m, 3H), 7.00 (t, *J* = 7.1 Hz, 4H, Ar), 7.14 (t, *J* = 7.2 Hz, 8H, Ar), 7.30-7.40 (m, 2H, Ar), 7.44-7.55 (m, 8H, Ar), 7.62-7.72 (m, 2H, Ar), 7.82 (t, *J* = 7.5 Hz, 1H, Ar); $^{13}$C NMR ($CD_2Cl_2$, 101 MHz): 13.5, 19.1 (d, $J_{P\text{-}C}$ = 49 Hz), 23.6, 24.0 (d, $J_{P\text{-}C}$ = 15 Hz), 25.1 (d, $J_{P\text{-}C}$ = 49 Hz), 116.1 (d, $J_{P\text{-}C}$ = 80 Hz), 122.3,

122.7 (d, $J_{P\text{-}C}$ = 12 Hz), 125.6 (d, $J_{P\text{-}C}$ = 12 Hz), 126.1, 130.9 (d, $J_{P\text{-}C}$ = 12 Hz), 131.7 (d, $J_{P\text{-}C}$ = 8.5 Hz), 135.5, 136.4, 164.5 (q, $J_{B\text{-}C}$ = 49 Hz); $^{31}$P NMR ($CD_2Cl_2$, 146 MHz): 26.6; HRMS (ESI) Calcd. For [$C_{17}H_{28}P^+$]: 263.1929, Found: 263.1934.



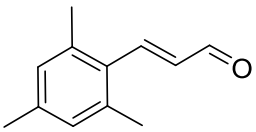

**2,2,3-trimethyl-1-hydrido-1-phenyl-1-(3-phenylpropyl)-λ$^5$-phosphetane (19):** To a suspension of phosphonium salt **18** (2.09 g, 5.34 mmol) in pentane (150 mL) and THF (1 mL) under a nitrogen atmosphere was added $LiAlH_4$ (0.244 g, 6.4 mmol) and the resulting mixture stirred for 0.5 h at ambient temperature. The salt dissolved, and the solution was filtered over a pad of celite under a nitrogen atmosphere, then concentrated. The concentrate was redissolved in pentane and again filtered over celite under a nitrogen atmosphere and concentrated to give a clear, tacky liquid which is a 1:4 mixture of diastereomers (0.588 g, 35% yield). $^1$H NMR ($CD_3CN$, 360 MHz): δ = 0.86-1.19 (m, 9H), 1.50-1.70 (m, 3H), 1.78-1.90 (m, 1H), 2.00-1.25 (m, 2H), 2.45-2.95 (m, 3H), 5.42 (1H, d, *J* = 248 Hz. 1H, major isomer), 5.48 (dd, *J* = 240, 3.1 Hz, 1H, minor isomer), 7.03 (d, *J* = 6.8 Hz, 2H, Ar), 7.13 (t, *J* = 7.3 Hz, 1H, Ar), 7.18-7.25 (m, 2H, Ar), 7.30-7.55 (m, 3H, Ar), 7.64-7.74 (m, 2H, major isomer, Ar), 7.83-7.92 (m, 2H, minor isomer, Ar); $^{13}$C NMR ($CD_3CN$, 101 MHz, predominantly major diastereomer): 15.4 (d, $J_{P\text{-}C}$ = 31 Hz), 17.6, 22.0, 27.9, 28.5, 32.4, 37.1 (d, $J_{P\text{-}C}$ = 13 Hz), 59.7 (d, $J_{P\text{-}C}$ = 6.6 Hz), 66.1 (d, $J_{P\text{-}C}$ = 62 Hz), 126.6, 128.9 (d, $J_{P\text{-}C}$ = 13 Hz), 129.1, 129.2, 131.1 (d, $J_{P\text{-}C}$ = 3.4 Hz), 133.5 (d, $J_{P\text{-}C}$ = 14 Hz), 134.5 (d, $J_{P\text{-}C}$ = 11 Hz), 143.1; $^{31}$P NMR ($C_6D_6$, 146 MHz): 76.3 (d, $J_{P\text{-}H}$ = 239 Hz, minor isomer), 80.4 (d, $J_{P\text{-}H}$ = 248 Hz, major isomer). HRMS (EI) Calcd. For $C_{21}H_{29}P$: 312.20069, Found: 312.20066.



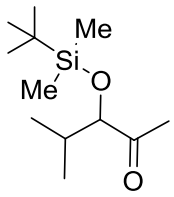

**2,2,3-trimethyl-1-phenylphosphetanium tetrafluoroborate (10·HBF$_4$):** To an ice-cold solution of 2,2,3-trimethyl-1-phenylphosphetane (0.361 g, 1.9 mmol) in ether (5 mL) was added tetrafluoroboric acid diethyl ether complex (0.25 mL, 1.9 mmol, 1.0 eq), and the mixture stirred for 0.5 h at ambient temperature to yield a white precipitate. Filtration and washing with diethyl ether afforded the desired product as a white solid (0.428 g, 1.5 mmol, 81%). $^1$H NMR ($CDCl_3$, 360 MHz): δ = 1.12-1.24 (m, 6H, $CH_3$), 1.60 (d, *J* = 23 Hz, 3H, $CH_3$), 2.90-3.07 (m, 2H), 3.08-3.28 (m, 1H), 7.57-7.68 (m, 2H, Ar), 7.69-7.80 (m, 1H, Ar), 7.94-8.06 (m, 2H, Ar), 7.72 (d, $J_{P\text{-}H}$ = 502 Hz, 1H, P-H); $^{13}$C NMR ($CDCl_3$, 91 MHz): 15.7 (d, $J_{P\text{-}C}$ = 21 Hz), 18.8 (d, $J_{P\text{-}C}$ = 1.2 Hz), 22.0 (d, $J_{P\text{-}C}$ = 46 Hz), 22.4 (d, $J_{P\text{-}C}$ = 3.6 Hz), 41.5 (d, $J_{P\text{-}C}$ = 18 Hz), 46.0 (d, $J_{P\text{-}C}$ =

48 Hz), 113.6 (d, $J_{P\text{-}C}$ = 65 Hz), 130.1 (d, $J_{P\text{-}C}$ = 13 Hz), 133.6 (d, $J_{P\text{-}C}$ = 10 Hz), 135.2 (d, $J_{P\text{-}C}$ = 3.5 Hz). $^{31}$P NMR ($CDCl_3$, 146 MHz): 30.7 (d, $J_{P\text{-}H}$ = 491 Hz).

**C. Synthesis of Substrates**

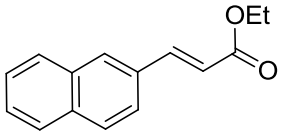


**(*E*)-3-mesitylacrylaldehyde (S1):** Following literature precedent,[7] activated $MnO_2$ (20.9 g, 240 mmol, 9 eq.) was added to a solution of **S17** (4.74 g, 27 mmol) in dichloromethane (40 mL) at ambient temperature. After stirring for 3.5 h, the mixture was filtered over celite and the filtrate adsorbed onto silica gel. Column chromatography (silica gel, 5:1 hexanes:EtOAc) afforded the desired aldehyde as a white solid (3.11 g, 18 mmol, 66%). $^1$H NMR ($CDCl_3$, 400 MHz): δ = 2.30 (s, 3H, $ArCH_3$), 2.36 (s, 6H, $ArCH_3$), 6.41 (dd, *J* = 16, 7.7 Hz, 1H, C=CH), 6.93 (s, 2H, Ar), 7.68 (d, *J* = 16 Hz, 1H, C=CH), 9.70 (d, *J* = 7.7 Hz, 1H, C(O)H); $^{13}$C NMR ($CDCl_3$, 101 MHz): 21.3, 21.4, 129.7, 130.3, 133.9, 137.3, 139.8, 151.7, 194.4; HRMS (EI) Calcd. For $C_{12}H_{14}O$: 174.1045, Found: 174.1049.

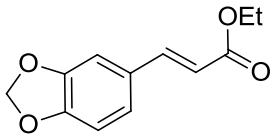



**3-((*tert*-butyldimethylsilyl)oxy)-4-methylpentan-2-one (S2):** Following a modified literature procedure,[8] a solution of 2-((*tert*-butyldimethylsilyl)oxy)-3-methylbutanenitrile (8.70 g, 41 mmol) in ether (100 mL) was treated with MeMgBr (3.0 M in ether, 27 mL, 2 eq.) and the mixture refluxed overnight. Upon complete conversion, the reaction was quenched with saturated aqueous $NH_4Cl$ solution, and the product extracted with ether. The combined organic layers were concentrated, and the residue dissolved in aqueous methanol and stirred until complete hydrolysis of the imine was observed (~2.5 days). Water and EtOAc were then added, and the organic layer was separated, washed with saturated aqueous NaCl solution, and dried over $Na_2SO_4$. Column chromatography (silica gel, 8:1 hexanes:EtOAc) afforded the desired product as a colorless oil. (5.76 g, 25 mmol, 61%). $^1$H NMR ($CDCl_3$, 400 MHz): δ = 0.02 (s, 3H, $SiCH_3$), 0.05 (s, 3H, $SiCH_3$), 0.89 (d, *J* = 7.0 Hz, 3H. $CH_3$), 0.91 (d, *J* = 6.8 Hz, 3H, $CH_3$), 0.94 (s, 9H, $Si^tBu$), 1.84-1.96 (m, 1H, ($Me_2CH$), 2.14 (s, 3H, $CH_3$), 3.68 (d, *J* = 5.8 Hz, 1H, OCH); $^{13}$C NMR ($CDCl_3$, 101 MHz): -5.0, -4.7, 17.6, 18.3, 18.9, 25.9 (2), 32.7, 84.0, 212.5; HRMS (EI) Calcd. For $C_{11}H_{23}O_2Si$ [M-$CH_3$]: 215.1467, Found: 215.1461.

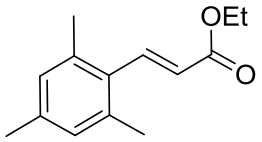
**C.1. Representative Procedure for the Synthesis of Allylic Esters (RP3)**



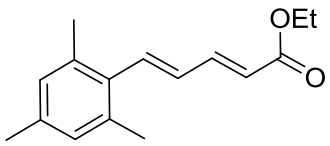
**ethyl (*E*)-3-(naphthalene-2-yl)acrylate (S3):** To an ice-cold suspension of NaH (60% dispersion in mineral oil, 1.23 g, 31 mmol, 1.2 eq.) in THF (30 mL) was added neat triethyl phosphonoacetate (6.1 mL, 31 mmol, 1.2 eq.) dropwise, and the mixture stirred for an additional 0.5 h at ambient temperature after all visible solid dissolved. A solution of 2-naphthaldehyde (3.91 g, 25 mmol) in THF (15 mL) was then added and the solution stirred at ambient temperature. Upon complete consumption of the starting material, the reaction was quenched with saturated aqueous $NH_4Cl$ solution (20 mL), and the aqueous layer extracted with EtOAc. The combined organic layers were washed with saturated aqueous NaCl solution, dried over anhydrous $Na_2SO_4$, and concentrated. Column chromatography (silica gel, hexanes to 5:1 hexanes:EtOAc) afforded the desired product as a white solid (4.26 g, 19 mmol, 75%). Spectral data agrees with previous literature characterization.[9] $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.36 (t, *J* = 7.1 Hz, 3H, $CH_3$), 4.29 (d, *J* = 7.1 Hz, 2H, $OCH_2$), 6.55 (d, *J* = 16 Hz, 1H, C=CH), 7.48-7.54 (m, 2H, Ar), 7.64-7.69 (m, 1H, Ar), 7.80-7.88 (m, 4H, Ar), 7.93 (s, 1H, Ar).



**ethyl (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)acrylate (S4):** Prepared analogously from piperonal (4.55 g, 30 mmol) using **RP3**. Isolated as a white solid (5.66 g, 26 mmol, 85%). Spectral data agrees with previous literature characterization.[10] $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.33 (t, *J* = 7.1 Hz, 3H, $CH_3$), 4.25 (q, *J* = 7.1 Hz, 2H, $OCH_2$), 6.00 (s, 2H, $O_2CH_2$), 6.26 (d, *J* = 16 Hz, 1H, C=CH), 6.81 (d, *J* = 8.0 Hz, 1H, Ar), 7.00 (d, *J* = 8.0 Hz, 1H, Ar), 7.03 (s, 1H, Ar), 7.59 (d, *J* = 16 Hz, 1H, C=CH).

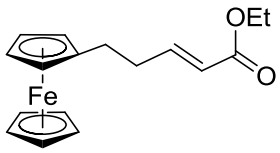


**ethyl (*E*)-3-mesitylacrylate (S5):** Prepared analogously from mesitaldehyde (3.73 g, 25 mmol) using **RP3**. Isolated as a white solid (5.14 g, 23 mmol, 93%). Spectral data agrees with previous literature characterization.[11] $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.34 (t, *J* = 7.1 Hz, 3H, $CH_3$), 2.28 (s, 3H, $ArCH_3$), 2.33 (s, 3H, $ArCH_3$), 4.27 (q, *J* = 7.1 Hz, 2H, $OCH_2$), 6.05 (d, *J* = 16 Hz, 1H, C=CH), 6.89 (s, 2H, Ar), 7.83 (d, *J* = 16 Hz, 1H, C=CH).

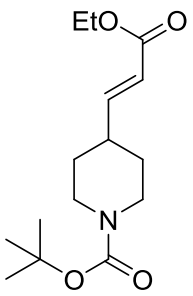


**ethyl (2*E*, 4*E*)-5-mesitylpenta-2,4-dienoate (S6):** Prepared analogously from **S1** (3.00 g, 17 mmol) using **RP3**. Isolated as a white solid (4.12 g, 17 mmol, 98%). $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.32 (t, *J* = 7.1 Hz, 3H, $CH_3$), 2.28 (s, 3H, $ArCH_3$), 2.30 (s, 6H,

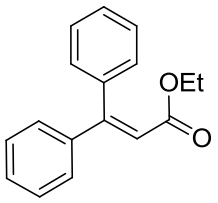
$ArCH_3$), 4.23 (q, *J* = 7.1 Hz, 2H, $OCH_2$), 5.92 (d, *J* = 15 Hz, 1H, $(CO_2Et)HC$=CH), 6.43 (dd, *J* = 16, 11 Hz, 1H, ArHC=C*H*), 6.88 (s, 2H, Ar), 6.98 (d, *J* = 16 Hz, 1H, Ar*H*C=CH), 7.47 (dd, *J* = 15, 11 Hz, 1H, $(CO_2Et)$HC=C*H*); $^{13}$C NMR ($CDCl_3$, 101 MHz): 14.5, 21.1, 21.2, 60.4, 120.8, 129.2, 131.6, 132.6, 136.4, 137.6, 139.2, 145.3, 167.3; HRMS (EI) Calcd. For $C_{16}H_{20}O_2$: 244.1463, Found: 244.1464.



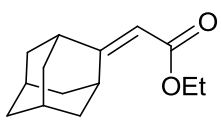

**ethyl (*E*)-5-(ferrocenyl)pent-2-enoate (S7):** Prepared analogously from 3-ferrocenylpropanal[12] (3.45 g, 14 mmol) using **RP3**. Isolated as an orange oil (3.87 g, 12 mmol, 87%). $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.29 (t, *J* = 7.1 Hz, 3H, $CH_3$), 2.38-2.46 (m, 2H), 2.46-2.53 (m, 2H), 4.06 (s, 4H, $C_5H_4$), 4.10 (s, 5H, $C_5H_5$), 4.19 (q, *J* = 7.1 Hz, 2H, $OCH_2$), 5.84 (d, *J* = 16 Hz, 1H, C=CH), 7.00 (dt, *J* = 16, 6.6 Hz); $^{13}$C NMR ($CDCl_3$, 101 MHz): 14.4, 28.3, 33.7, 60.3, 67.4, 68.1, 68.6, 87.9, 121.6, 148.6, 166.7; HRMS (ESI) Calcd. For $C_{17}H_{20}O_2Fe$: 312.0813, Found: 312.0817.




***tert*-butyl (*E*)-4-(3-ethoxy-3-oxoprop-1-en-1-yl)piperidine-1-carboxylate (S8):** Prepared analogously from *tert*-butyl 4-formylpiperidine-1-carboxylate[13] (6.51 g, 30 mmol) using **RP3**. Isolated as a colorless oil (4.22 g, 15 mmol, 49%). $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.29 (t, *J* = 7.1 Hz, 3H, $CH_3$), 1.27-1.41 (m, 2H), 1.46 (s, 9H, O$^t$Bu), 1.68-1.78 (m, 2H), 2.23-2.35 (m, 1H), 2.68-2.84 (m, 2H), 4.02-4.20 (br, 2H), 4.19 (q, *J* = 7.1 Hz, 2H, $OCH_2$), 5.80 (d, *J* = 16 Hz, 1H, C=CH), 6.90 (dd, *J* = 16, 6.6 Hz, 1H, C=CH); $^{13}$C NMR ($CDCl_3$, 101 MHz): 14.4, 28.6, 30.8, 38.7, 43.5 (br), 60.4, 79.6, 120.2, 151.8, 154.8, 166.8; HRMS (EI) Calcd. For $C_{15}H_{25}NO_4$: 283.1784, Found: 283.1784.

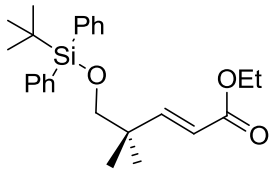



**ethyl 3,3-diphenylacrylate (S9):** Prepared analogously from benzophenone (5.60 g, 31 mmol) using **RP3**. Isolated as a colorless oil (7.21 g, 29 mmol, 93%). Spectral data agrees with previous literature characterization.[14] $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.11 (t, *J* = 7.1 Hz, 3H, $CH_3$), 4.05 (q, *J* = 7.1 Hz, 2H, $OCH_2$), 6.36 (s, 1H, C=CH), 7.17-7.23 (m, 2H, Ar), 7.27-7.40 (m, 8H, Ar).

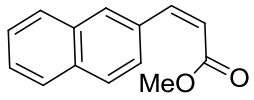



**ethyl 2-(adamantan-2-ylidene)acetate (S10):** Prepared analogously from 2-adamantanone (4.52 g, 30 mmol) using **RP3**. Isolated as a colorless oil (6.40

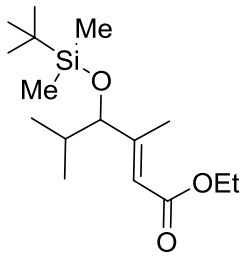
g, 29 mmol, 96%). Spectral data agrees with previous literature characterization.[15] $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.27 (t, *J* = 7.1 Hz, 3H, $CH_3$), 1.78-1.89 (m, 6H), 1.91-1.99 (m, 6H), 2.43 (br s, 1H), 4.07 (br s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H, $OCH_2$), 5.58 (s, 1H, C=CH).




**ethyl (*E*)-5-((tert-butyldiphenylsilyl)oxy)-4,4-dimethylpent-2-enoate (S11):** Prepared analogously from 3-((*tert*-butyldiphenylsilyl)oxy)-2,2-dimethylpropionaldehyde[16] (7.50 g, 22 mmol) using **RP3**. Isolated as a colorless oil (8.33 g, 20 mmol, 92%). $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.05 (s, 9H, Si$^t$Bu), 1.09 (s, 6H, $CH_3$), 1.29 (t, *J* = 7.1 Hz, 3H, $CH_3$), 3.42 (s, 2H, $SiOCH_2$), 4.20 (q, *J* = 7.1 Hz, 2H, $OCH_3$), 5.80 (d, *J* = 16, Hz, 1H, C=CH), 7.02 (d, *J* = 16 Hz, 1H, C=CH), 7.34-7.45 (m, 6H, Ar), 7.61-7.66 (m, 4H, Ar); $^{13}$C NMR ($CDCl_3$, 101 MHz): 14.4, 19.5, 23.5, 27.0, 39.6, 60.31, 71.8, 119.2, 127.8, 129.8, 133.6, 135.8, 155.9, 167.1; HRMS (ESI) Calcd. For $C_{25}H_{34}O_3SiNa$ [M+Na$^+$]: 433.2175, Found: 433.2175.



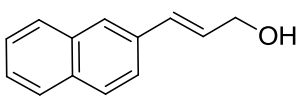

**methyl (*Z*)-3-(naphthalen-2-yl)acrylate (S12):** To a solution of methyl *P*,*P*-bis(2,2,2-trifluoroethyl)phosphonoacetate[17] (6.20 g, 19 mmol, 1.2 eq.) and 18-crown 6 (10.80 g, 2.5 eq.) in THF (100 mL) at -78 °C was added KHMDS (0.5 M in PhMe, 39 mL, 1.2 eq.), and the resulting mixture was stirred for 0.5 h before 2-naphthaldehyde (2.50 g, 16 mmol) in THF (15 mL) was added dropwise. After stirring for 8 h at -78 °C, the reaction was quenched with saturated aqueous $NH_4Cl$ solution (20 mL) and warmed to ambient temperature. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with saturated aqueous NaCl solution, dried over anhydrous $Na_2SO_4$, and concentrated. Column chromatography (silica gel, hexanes to 5:1 hexanes:EtOAc) afforded the desired product as a white solid (2.73 g, 13 mmol, 80%). $^1$H NMR ($CDCl_3$, 400 MHz): δ = 3.73 (s, 3H, $OCH_3$, 6.03 (d, *J* = 13 Hz, 1H, C=CH), 7.10 (d, *J* = 13 Hz, 1H, C=CH), 7.44-7.52 (m, 2H, Ar), 7.71-7.76 (m, 1H, Ar), 7.77-7.87 (m, 3H, Ar), 8.04 (s, 1H, Ar); $^{13}$C NMR ($CDCl_3$, 101 MHz): 51.6, 119.6, 126.4, 127.0, 127.1, 127.6, 127.7, 128.67, 130.1, 132.5, 133.1, 133.6, 143.5; HRMS (ESI) Calcd. For $C_{14}H_{13}O_2$ [M+H$^+$]: 213.0916, Found: 213.0916.



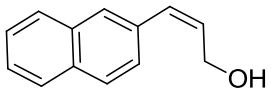

**ethyl (*E*)-4-((*tert*-butyldimethylsilyl)oxy)-3,5-dimethylhex-2-enoate (S13):** Prepared from **S2** (5.71 g, 25 mmol) with the following modifications to **RP3**: **S2** was treated with 1.5 equivalents of triethyl phosphonoacetate/NaH, and the reaction was stirred at 40 °C for 2.5 days. Identical work-up afforded the desired product as a colorless oil (5.69 g, 19

mmol, 76%). $^{1}$H NMR ($CDCl_3$, 400 MHz): δ = -0.03 (s, 3H, $SiCH_3$), 0.04 (s, 3H, $SiCH_3$), 0.83 (d, *J* = 6.8 Hz, 3H, $CH_3$), 0.87 (d, *J* = 6.8 Hz, 3H, $CH_3$), 0.91 (s, 9H, Si$^{t}$Bu), 1.29 (t, *J* = 7.1 Hz, 3H, $CH_3$), 1.72-1.84 (m, 1H, $Me_2CH$), 2.07 (s, 3H, $CH_3$), 3.67 (d, *J* = 6.0 Hz, 1H, OCH), 4.15 (q, *J* = 7.1 Hz, 2H, $OCH_2$), 5.78 (s, 1H, C=CH); $^{13}$C NMR ($CDCl_3$, 101 MHz): -5.0, -4.4, 14.4, 14.9, 17.7, 18.3, 19.9, 26.0, 32.2, 59.7, 83.0, 116.4, 160.3, 166.9, ; HRMS (EI) Calcd. For $C_{16}H_{32}O_3Si$: 300.2121, Found: 300.2122.

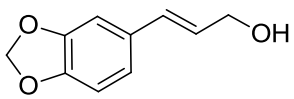
**C.2. Representative Procedure for the Reduction of Allylic Alcohols (RP4)**




**(*E*)-3-(naphthalen-2-yl)prop-2-en-1-ol (S14):** To a solution of **S3** (4.07 g, 20 mmol) in THF (80 mL) at -78 °C was added DIBAL-H (1.0 M in hexanes, 42 mL, 2.3 eq.) dropwise, and the solution stirred at this temperature for 2 h. The reaction was then stirred for an additional 0.5 h at 0 °C before quenching with saturated aqueous $NH_4Cl$ solution (30 mL) to yield a thick emulsion. Saturated aqueous Rochelle's salt (100 mL) and EtOAc (200 mL) were added and the mixture vigorously stirred until two layers were observed and separated. The aqueous layer was extracted with additional EtOAc, and the combined organic layers washed with saturated aqueous NaCl solution and dried over anhydrous $MgSO_4$. Filtration over a plug of silica gel followed by removal of solvent afforded the desired product as a white solid (3.12 g, 17 mmol, 94%). No further purification attempted. Spectral data agrees with previous literature characterization.[18] $^{1}$H NMR ($CDCl_3$, 400 MHz): δ = 2.07 (br, 1H, OH), 4.32 (d, *J*= 5.3 Hz, 2H, $OCH_2$), 6.43 (dt, *J* = 16, 5.4 Hz, 1H, C=CH), 6.71 (d, *J* = 16 Hz, 1H, C=CH), 7.38-7.46 (m, 2H, Ar), 7.54 (d, *J* = 8.6 Hz, 1H, Ar), 7.66 (s, 1H, Ar), 7.70-7.80 (m, 3H, Ar).

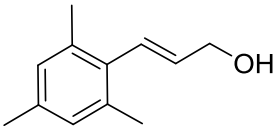



**(*Z*)-3-(naphthalen-2-yl)prop-2-en-1-ol (S15):** Prepared analogously from **S12** (2.50 g, 12 mmol) using **RP4**. Isolated as a white solid (1.98 g, 11 mmol, 91%). $^{1}$H NMR ($CDCl_3$, 400 MHz): δ = 1.69 (br s, 1H, OH), 4.52 (dd, *J* = 6.4, 1.5 Hz, 2H, $OCH_2$), 5.95 (dt, *J* = 12, 6.4 Hz. 1H, C=CH), 6.70 (d, *J* = 12 Hz, 1H, C=CH), 7.34 (d, *J* = 8.4 Hz 1H, Ar), 7.42-7.51 (m, 2H, Ar), 7.63 (s, 1H, Ar), 7.75-7.85 (m, 3H, Ar); $^{13}$C NMR ($CDCl_3$, 101 MHz): 59.95, 126.2, 126.4, 127.0, 127.7, 127.9, 128.0, 128.2, 131.2, 131.7, 132.6, 133.3, 134.2; HRMS (EI) Calcd. For $C_{13}H_{12}O$: 184.0888, Found: 184.0888.

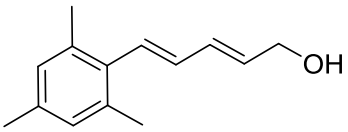



**(*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)prop-2-en-1-ol (S16):** Prepared analogously from **S4** (4.33 g, 20 mmol) using **RP4**. Isolated as a white

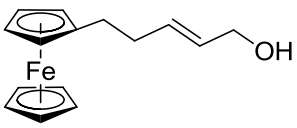
solid (3.30 g, 19 mmol, 94%). Spectral data agrees with previous literature characterization.[10] $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.45 (br, 1H, OH), 4.29 (t, *J* = 5.5 Hz, 2H, $OCH_2$), 5.96 (s, 2H, $O_2CH_2$), 6.20 (dt, *J* = 16, 6.0 Hz 1H, C=CH), 6.52 (d, *J* = 16 Hz, 1H, C=CH), 6.75 (d, *J* = 8.0 Hz, 1H, Ar), 6.81 (d, *J* = 8.0 Hz, 1H, Ar), 6.93 (s, 1H, Ar).



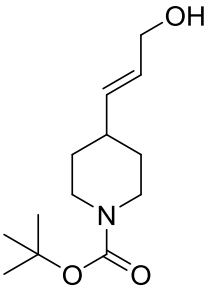

**(*E*)-3-mesitylprop-2-en-ol (S17):** Prepared analogously from **S5** (4.93 g, 22 mmol) using **RP4**. Isolated as a white solid (3.68 g, 21 mmol, 92%). Spectral data agrees with previous literature characterization.[11] $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.46 (t, *J* = 5.4 Hz, 1H, OH), 2.27 (s, 9H, $ArCH_3$), 4.34 (t, *J* = 5.0 Hz, 2H, $OCH_2$), 5.87 (dt, *J* = 16, 5.7 Hz. 1H, C=CH), 6.57 (d, *J* = 16 Hz, 1H, C=CH), 6.87 (s, 2H, Ar).




**(2*E*, 4*E*)-5-mesitylpenta-2,4-dien-1-ol (S18):** Prepared analogously from **S6** (3.99 g, 16 mmol) using **RP4**. Isolated as a white solid (3.30 g, 16 mmol, 100%). $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.44 (t, *J* = 5.8 Hz, 1H, OH), 2.26 (s, 3H, $ArCH_3$), 2.28 (s, 6H, $ArCH_3$), 4.25 (t, *J* = 5.6 Hz, 2H, $OCH_2$), 5.87 (dt, *J* = 15, 5.9 Hz, 1H, $(HOCH_2)$*H*C=CH), 6.28 (dd, *J* = 16, 10 Hz, 1H, ArHC=C*H*), 6.45 (dd, *J* = 15, 10 Hz, 1H, $(HOCH_2)$HC=C*H*), 6.57 (d, *J* = 16 Hz, 1H, Ar*H*C=CH), 6.86 (s, 2H, Ar); $^{13}$C NMR ($CDCl_3$, 101 MHz): 21.1, 21.2, 63.6, 128.9, 131.2, 131.5, 132.4, 133.3, 133.7, 136.1, 136.5; HRMS (EI) Calcd. For $C_{14}H_{18}O$: 202.1358, Found: 202.1359.

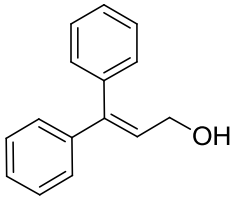



**(*E*)-5-(ferrocenyl)pent-2-en-1-ol (S19):** Prepared analogously from **S7** (3.87 g, 12 mmol) using **RP4**. Isolated as an orange oil (3.15 g, 12 mmol, 94%). $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.63 (br, 1H, OH), 2.21-2.30 (m, 2H), 2.37-2.44 (m, 2H), 4.02-4.07 (m, 6H, overlapping resonances) 4.09 (s, 5H, $C_5H_5$), 5.59-5.77 (m, 2H, HC=CH); $^{13}$C NMR ($CDCl_3$, 101 MHz): 29.4, 33.8, 63.7, 67.2, 68.1, 68.6, 88.6, 129.3, 132.7; HRMS (ESI) Calcd. For $C_{15}H_{18}OFe$: 270.0707, Found: 270.0705.

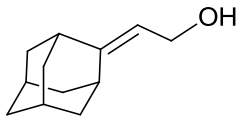



***tert*-butyl (*E*)-4-(3-hydroxyprop-1-en-1-yl)piperidine-1-carboxylate (S20):** Prepared analogously from **S8** (4.06 g, 14 mmol) using **RP4.** Isolated as a colorless oil (3.31 g, 14 mmol, 96%). $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.20-1.34 (m, 2H), 1.46 (s, 9H, O$^t$Bu), 1.62-1.72 (m, 3H), 2.07-2.18 (m, 1H), 2.65-2.82 (m, 2H), 4.00-4.18 (br, 4H, overlapping resonances), 5.61-5.66 (m, 2H, HC=CH); $^{13}$C NMR ($CDCl_3$, 101 MHz): 28.6, 31.8, 38.6, 43.7 (br), 63.7, 79.5,

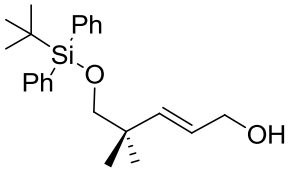
127.9, 136.5, 155.0; HRMS (ESI) Calcd. For $C_{13}H_{23}NO_3Na$ [M+$Na^+$]: 264.1576, Found: 264.1577.



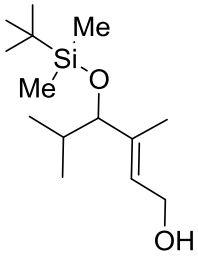

**3,3-diphenylprop-2-en-1-ol (S21):** Prepared analogously from **S9** (4.38 g, 17 mmol) using **RP4**. Isolated as a white solid (2.70 g, 13 mmol, 74%). Spectral data agrees with previous literature characterization.[19] $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.36 (t, *J* = 5.6 Hz, 1H, OH), 4.22 (t, *J* = 6.3 Hz, 2H, $OCH_2$), 6.25 (t, *J* = 6.9 Hz, 1H, C=CH), 7.14-7.20 (m, 2H, Ar), 7.22-7.31 (m, 5H, Ar), 7.32-7.41 (m, 3H, Ar).



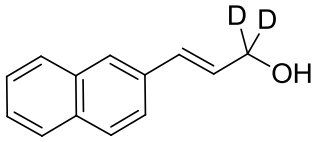

**2-(adamantan-2-ylidene)ethan-1-ol (S22):** Prepared analogously from **S10** (4.40 g, 20 mmol) using **RP4**. Isolated as a colorless oil (2.91 g, 16 mmol, 82%). Spectral data agrees with previous literature characterization.[15] $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.14 (br, 1H, OH), 1.68-1.76 (m, 2H), 1.75-1.85 (m, 4H), 1.85-1.93 (m, 4H), 1.93-1.99 (m, 2H), 2.38 (br s, 1H). 2.88 (br s, 1H), 4.13 (d, *J* = 7.1 Hz, 2H, $OCH_2$), 5.34 (t, *J* = 7.1 Hz, 1H, C=CH).




**(*E*)-5-((tert-butyldiphenylsilyl)oxy)-4,4-dimethylpent-2-en-1-ol (S23):** Prepared analogously from **S11** (8.33, 20 mmol) using **RP4**. Isolated as a colorless oil (7.26 g, 20 mmol, 97%). $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.04 (s, 6H, $CH_3$), 1.06 (s, 9H, Si$^t$Bu), 1.18 (t, *J* = 5.9 Hz, 1H, OH), 3.38 (s, 2H, $SiOCH_2$), 4.08 (t, *J* = 5.5 Hz, 2H, HOC$H_2$), 5.59 (dt, *J* = 16, 5.5 Hz, 1H, C=CH), 5.69 (d, *J* = 16 Hz, 1H, C=CH), 7.34-7.45 (m, 6H, Ar), 7.62-7.67 (m, 4H, Ar); $^{13}$C NMR ($CDCl_3$, 101 MHz): 19.6, 24.2, 27.0, 38.6, 64.3, 72.6, 126.4, 127.7, 129.7, 134.0, 135.9, 140.4; HRMS (ESI) Calcd. For $C_{23}H_{32}O_2NaSi$ [M+$Na^+$]: 391.2069, Found: 391.2068.

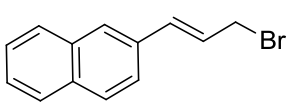



**(*E*)-4-((*tert*-butyldimethylsilyl)oxy)-3,5-dimethylhex-2-en-1-ol (S24):** Prepared analogously from **S13** (5.32 g, 18 mmol) using **RP4**. Isolated as a colorless oil after chromatography (silica gel, 8:1 hexanes:EtOAc) (3.62 g, 14 mmol, 79%). $^1$H NMR ($CDCl_3$, 400 MHz): δ = -0.03 (s, 3H, $SiCH_3$), 0.04 (s, 3H, $SiCH_3$), 0.75 (d, *J* = 6.8 Hz, 3H, $CH_3$), 0.89 (s, 9H, Si$^t$Bu), 0.90 (d, *J* = 6.8 Hz, 3H, $CH_3$), 1.17 (br, 1H, OH), 1.60 (s, 3H, $CH_3$), 1.65-1.79 (m, 1H, $Me_2CH$), 3.54 (d, *J* = 7.7 Hz, 1H, OCH), 4.19 (br, 2H, $OCH_2$), 5.50 (t, *J* = 6.5 Hz, 1H, C=CH); $^{13}$C NMR ($CDCl_3$, 101 MHz): -4.9, -4.3, 11.7, 18.4, 18.9, 19.6, 26.0, 32.1, 59.3, 84.1, 125.6, 140.6; HRMS (EI) Calcd. For $C_{14}H_{30}O_2Si$: 258.2015, Found: 258.2013.

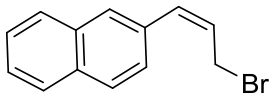



**(*E*)-3-(naphthalen-2-yl)prop-2-en-1-$d_2$-1-ol (S25):** Following literature precedent,[20] to a suspension of LiD (0.200 g, 22.2 mmol) in THF (5 mL) under a nitrogen atmosphere at ambient temperature is added dropwise dimethylaluminum chloride (0.9 M in heptane, 25 mL, 22.2 mmol). The solution was heated to 60 °C with reflux apparatus for 4 h, then cooled to room temperature. The resultant soluble solution was transferred via cannula slowly to a solution of **S3** (2.28 g, 10 mmol) in toluene (50 mL) at -78 °C. The solution was allowed to warm to ambient temperature and stirred for 8 h, then cooled to 0 °C and quenched slowly with aqueous saturated ammonium chloride. The resultant slurry is filtered over celite and rinsed with ethyl acetate (50 mL). The aqueous layer is extracted with ethyl acetate (20 mL), then the combined organic layers were dried over sodium sulfate, concentrated, and purified by column chromatography (silica gel, 10% to 25% EtOAc:hexanes) to give the desired product as a white solid (0.970 g, 52%). $^1$H NMR ($CDCl_3$, 400 MHz): 1.77 (s, 1H, OH), 6.45 (d, $J$ = 16 Hz, 1H, C=CH), 6.74 (d, $J$ = 16 Hz, 1H, C=CH), 7.40-7.48 (m, 2H, Ar), 7.56 (d, $J$ = 8.6 Hz, 1H, Ar), 7.69 (s, 1H, Ar), 7.73-7.81 (m, 3H, Ar); $^{13}$C NMR ($CDCl_3$, 101 MHz): 63.1 (pentet, $J_{C\text{-}D}$ = 22 Hz), 123.7, 126.0, 126.4, 126.6, 127.8, 128.1, 128.3, 128.9, 131.4, 133.1, 133.6, 134.2; HRMS (EI): Calcd. for $C_{13}H_{10}D_2O$: 186.10137, Found: 186.10333.

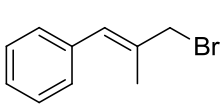
### C.3. Representative Procedure for the Synthesis of Allylic Bromides (RP5)



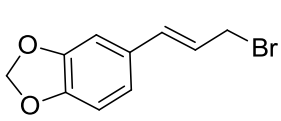

**(*E*)-2-(3-bromoprop-1-en-1-yl)naphthalene:** To an ice-cold solution of **S14** (1.71 g, 9 mmol) in diethyl ether (10 mL) was added neat $PBr_3$ (0.96 mL, 1.1 eq.) dropwise, and the mixture stirred at this temperature for 1 h. The reaction was then poured into ice cold saturated aqueous $NaHCO_3$ (20 mL), and the aqueous layer extracted with diethyl ether. The combined organic layers were washed with saturated aqueous $NaHCO_3$ and water, dried over anhydrous $MgSO_4$, and filtered. Removal of solvent afforded the desired product as a white solid (1.73 g, 7.0 mmol, 75%). No further purification attempted. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 4.21 (d, $J$ = 7.8 Hz, 2H, $BrCH_2$, 6.51 (dt, $J$ = 16, 7.8 Hz, 1H, C=CH), 6.79 (d, $J$ = 16 Hz, 1H, C=CH), 7.42-7.50 (m, 2H, Ar), 7.58 (dd, $J$ = 8.6, 1.2 Hz, 1H, Ar), 7.73 (s, 1H, Ar), 7.76-7.83 (m, 3H, Ar); $^{13}$C NMR ($CDCl_3$, 101 MHz): 33.7, 123.6, 125.7, 126.4, 126.6, 127.3, 127.8, 128.2, 128.5, 133.4, 133.5, 133.6, 134.8; HRMS (EI) Calcd. For $C_{13}H_{11}Br$: 246.0044, Found: 246.0046.



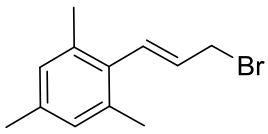
**(*Z*)-2-(3-bromoprop-1-en-1-yl)naphthalene:** Prepared analogously from **S15** (0.91 g, 5.0 mmol) using **RP5**. Isolated as a white solid (0.88 g, 3.6 mmol, 72%). $^{1}$H NMR indicated ~4:1 *Z*/*E* ratio. $^{1}$H NMR ($CDCl_3$, 400 MHz): δ = 4.22 (dd, *J* = 8.7, 0.7 Hz, 2H, $BrCH_2$), 6.05 (dt, *J* = 11, 8.7 Hz, 1H, C=CH), 6.73 (d, *J* = 11 Hz, 1H, C=CH), 7.40-7.52 (m, 3H, Ar), 7.74-7.87 (m, 4H, Ar); $^{13}$C NMR ($CDCl_3$, 101 MHz): 29.2, 126.5 (2), 126.7, 127.4, 127.8, 128.0, 128.3, 132.8, 133.2, 133.4, 133.7 (1 resonance unresolved); HRMS (EI) Calcd. For $C_{13}H_{11}Br$: 246.0044, Found: 246.0042.



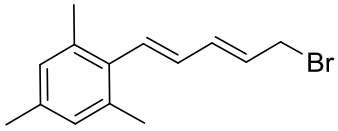
**(*E*)-(3-bromo-2-methylprop-1-en-1-yl)benzene:** Prepared analogously from (*E*)-2-methyl-3-phenyl-2-propen-1-ol (2.14 g, 14 mmol) using **RP5**. Isolated as a colorless oil (1.78g, 8.4 mmol, 58%). Spectral data agrees with previous literature characterization, although HRMS data was not given.[21] $^{1}$H NMR ($CDCl_3$, 400 MHz): δ = 2.02 (s, 3H, $CH_3$), 4.14 (s, 2H, $BrCH_2$), 6.64 (s, 1H, C=CH), 7.21-7.30 (m, 3H, Ar), 7.30-7.38 (m, 2H, Ar); HRMS (EI) Calcd. For $C_{10}H_{11}Br$: 210.0044, Found: 210.0054.



**(*E*)-5-(3-bromoprop-1-en-1-yl)benzo[*d*][1,3]dioxole:** Prepared analogously from **S16** (1.07 g, 6.0 mmol) using **RP5**. Isolated as a white solid (1.21 g, 5.0 mmol, 84%). $^{1}$H NMR ($CDCl_3$, 400 MHz): δ = 4.14 (d, *J* = 7.8 Hz, 2H, $BrCH_2$, 5.96 (s, 2H, $O_2CH_2$) 6.22 (dt, *J* = 16, 7.8 Hz, 1H, C=CH), 6.55 (d, *J* = 16 Hz, 1H, C=CH), 6.75 (d, *J* = 8.0 Hz, 1H, Ar), 6.81 (d, *J* = 8.0 Hz, 1H, Ar), 6.92 (s, 1H, Ar); $^{13}$C NMR ($CDCl_3$, 101 MHz): 33.9, 101.4, 106.0, 108.5, 121.9, 123.6, 130.4, 134.4, 148.0, 148.3; HRMS (EI) Calcd. For $C_{10}H_9O_2Br$: 239.9786, Found: 239.9786.

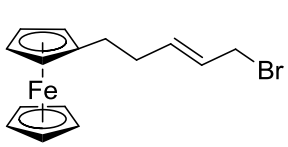


**(*E*)-2-(3-bromoprop-1-en-1-yl)-1,3,5-trimethylbenzene:** Prepared analogously from **S17** (0.881 g, 5.0 mmol) using **RP5**. Isolated as a colorless oil (0.79 g, 3.3 mmol, 66%). $^{1}$H NMR ($CDCl_3$, 400 MHz): δ = 2.26 (s, 9H, $ArCH_3$), 4.16 (d, *J* = 7.8 Hz, 2H, $BrCH_2$), 5.91 (dt, *J* = 16, 7.7 Hz, 1H, C=CH), 6.63 (d, *J* = 16 Hz, 1H, C=CH), 6.85 (s, 2H, Ar); $^{13}$C NMR ($CDCl_3$, 101 MHz): 20.8, 21.0, 33.6, 128.8, 130.5, 132.4, 132.5, 136.1, 136.8; HRMS (EI) Calcd. For $C_{12}H_{15}Br$: 238.0357, Found: 238.0360.

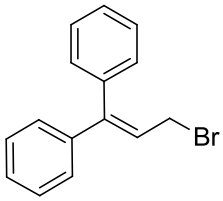


**2-((1*E*,3*E*)-5-bromopenta-1,3-dien-1-yl)-1,3,5-trimethylbenzene:** Prepared analogously from **S18** (0.951 g, 4.7 mmol) using **RP5**. Isolated as a white solid upon cooling (1.09 g, 4.1 mmol, 88%). $^{1}$H NMR ($CDCl_3$, 400 MHz): δ = 2.27 (s, 3H, $ArCH_3$), 2.28 (s, 6H, $ArCH_3$), 4.10 (d, *J* = 8.0 Hz, 2H,

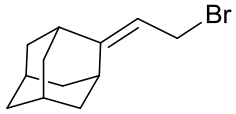
$BrCH_2$), 5.90 (dt, *J* = 15, 8.0 Hz, 1H, ($BrCH_2$)*H*C=CH), 6.27 (dd, *J* = 16, 10 Hz, 1H, ArHC=C*H*), 6.48 (dd, *J* = 15, 10 Hz, 1H, ($BrCH_2$)HC=C*H*), 6.63 (d, *J* = 16 Hz, 1H, Ar*H*C=CH), 6.86 (s, 2H, Ar); $^{13}$C NMR ($CDCl_3$, 101 MHz): 21.1, 21.2, 33.7, 128.1, 129.0, 132.5, 133.0, 133.3, 135.8, 136.2, 136.8; HRMS (EI) Calcd. For $C_{14}H_{17}Br$: 264.0514, Found: 264.0508.



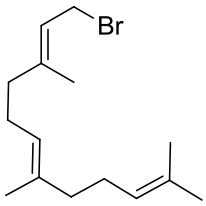

**(*E*)-(5-bromopent-3-en-1-yl)ferrocene:** Prepared analogously from **S19** (1.52 g, 5.6 mmol) using **RP5**. Isolated as an orange solid (1.26 g, 3.8 mmol, 67%). $^1$H NMR ($CDCl_3$, 400 MHz): δ = 2.23-2.32 (m, 2H), 2.38-2.45 (m, 2H), 3.95 (d, *J* = 7.4 Hz, 2H, $BrCH_2$), 4.05 (s, 4H, $C_5H_4$), 4.09 (s, 5H, $C_5H_5$), 5.71 (dt, *J* = 16, 7.4 Hz, 2H, HC=CH), 5.81 (dt, *J* = 16, 6.4 Hz, 2H, HC=CH); $^{13}$C NMR ($CDCl_3$, 101 MHz): 29.1, 33.5, 33.7, 67.3, 68.2, 68.6, 88.3, 126.7, 136.1; HRMS (ESI) Calcd. For $C_{15}H_{17}FeBr$: 331.9863, Found: 331.9864.



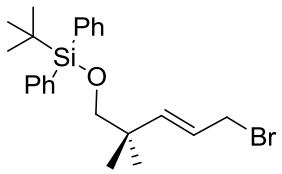

**(3-bromoprop-1-ene-1,1-diyl)dibenzene:** Prepared analogously from **S21** (0.88 g, 4.1 mmol) using **RP5**. Isolated as a white solid (1.03 g, 3.8 mmol, 90%). $^1$H NMR ($CDCl_3$, 400 MHz): δ = 4.05 (d, *J* = 8.5 Hz, 2H, $BrCH_2$), 6.33 (t, *J* = 8.5 Hz, 1H, C=CH), 7.20-7.32 (m, 7H, Ar), 7.33-7.45 (m, 3H, Ar); $^{13}$C NMR ($CDCl_3$, 101 MHz): 31.3, 123.9, 127.9, 128.0, 128.2, 128.4, 128.6, 129.6, 138.3, 141.3, 146.3; HRMS (EI) Calcd. For $C_{15}H_{13}Br$: 272.0201, Found: 272.0204.



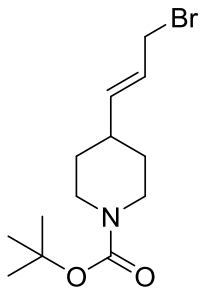

**2-(2-bromoethylidene)adamantane:** Prepared analogously from **S22** (1.03 g, 5.7 mmol) using **RP5**. Isolated as a colorless oil (0.98 g, 4.1 mmol, 70%). $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.72-2.01 (m, 12H), 2.38 (s, 1H), 2.94 (s, 1H), 4.05 (d, *J* = 8.5 Hz, 2H, $BrCH_2$), 5.46 (t, *J* = 8.5 Hz, 1H, C=CH); $^{13}$C NMR ($CDCl_3$, 101 MHz): 28.5, 29.1, 32.4, 37.1, 38.9, 39.8, 40.6, 112.9, 156.4; HRMS (ESI) Calcd. For $C_{12}H_{17}Br$: 240.0514, Found: 240.0511.



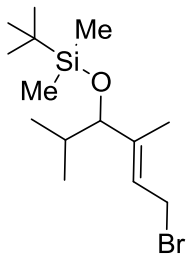

**(2*E*,6*E*)-1-bromo-3,7,11-trimethyldodeca-2,6,10-triene:** Prepared analogously from *trans,trans*-farnesol (1.14 g, 5.1 mmol) using **RP5**. Isolated as a colorless oil (1.24 g, 4.3 mmol, 85%). Spectral data agrees with previous literature characterization and commercially available material.[22] $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.60 (s, 6H, $CH_3$), 1.68 (s, 3H, $CH_3$), 1.73 (s, 3H $CH_3$), 1.95-2.01 (m, 2H), 2.02-2.15 (m, 6H), 4.02 (d, *J* = 8.4 Hz, 2H, $BrCH_2$), 5.05-5.13 (m, 2H, C=CH), 5.53 (t, *J* = 8.4 Hz, 1H, C=C*H*$CH_2$Br).



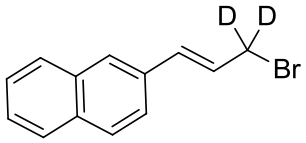
**(*E*)-((5-bromo-2,2-dimethylpent-3-en-1-yl)oxy)(tert-butyl)diphenylsilane:** Prepared analogously from **S23** (1.94 g, 5.3 mmol) using **RP5**. Isolated as a colorless oil (0.72 g, 1.7 mmol, 32%). $^{1}$H NMR ($CDCl_3$, 400 MHz): δ = 1.03 (s, 6H, $CH_3$), 1.06 (s, 9H, Si$^{t}$Bu), 3.36 (s, 2H, $SiOCH_2$), 3.95 (d, *J* = 7.4 Hz, 2H, $BrCH_2$), 5.66 (dt, *J* = 16, 7.4 Hz, 1H, C=CH), 5.79 (d, *J* = 16 Hz, 1H, C=CH), 7.34-7.46 (m, 6H, Ar), 7.61-7.68 (m, 4H, Ar); $^{13}$C NMR ($CDCl_3$, 101 MHz): 19.6, 24.0, 27.0, 34.0, 38.8, 72.4, 124.0, 127.8, 129.7, 133.8, 135.8, 143.5; HRMS (EI) Calcd. For $C_{23}H_{31}OSiBr$: 430.1328, Found: 430.1321.



***tert*-butyl (*E*)-4-(3-bromoprop-1-en-1-yl)piperidine-1-carboxylate:** To a solution of **S20** (1.12 g, 4.6 mmol) and triphenylphosphine (1.81 g, 6.9 mmol, 1.5 eq.) in THF (10 mL) was added $CBr_4$ (2.36 g, 7.1 mmol, 1.5 eq.) and the resulting orange solution stirred at ambient temperature for 1 h. Diethyl ether (50 mL) was added and the resulting mixture filtered over celite. Removal of solvent followed by chromatography of the residue (silica gel, hexanes to 5:1 hexanes:EtOAc) afforded the desired product as a colorless oil which solidified upon cooling (0.899 g, 2.9 mmol, 64%). Spectral data agrees with previous literature characterization.[23] $^{1}$H NMR ($CDCl_3$, 400 MHz): δ = 1.20-1.34 (m, 2H), 1.46 (s, 9H, O$^{t}$Bu), 1.62-1.73 (m, 2H), 2.09-2.21 (m, 1H), 2.64-2.82 (m, 2H), 3.94 (d, *J* = 6.1 Hz, 2H, $BrCH_2$), 3.99-4.21 (br, 2H), 5.63-5.76 (m, 2H, HC=CH); HRMS (ESI) Calcd. For $C_{13}H_{22}NO_2NaBr$ [M+Na$^{+}$]: 326.0732, Found: 326.0731.



**(*E*)-((6-bromo-2,4-dimethylhex-4-en-3-yl)oxy)(*tert*-butyl)dimethylsilane:** Prepared in a similar fashion as *tert*-butyl (*E*)-4-(3-bromoprop-1-en-1-yl)piperidine-1-carboxylate from **S24** (1.34 g, 5.2 mmol). Isolated as a colorless oil after chromatography (silica gel, hexanes to 10:1 hexanes:ether) (1.03 g, 3.2 mmol, 61%). $^{1}$H NMR ($CDCl_3$, 400 MHz): δ = -0.02 (s, 3H, $SiCH_3$), 0.03 (s, 3H, $SiCH_3$), 0.75 (d, *J* = 6.8 Hz, 3H, $CH_3$), 0.89 (s, 9H, Si$^{t}$Bu), ~0.89 (unresolved, 3H, $CH_3$), 1.66 (s, 3H, $CH_3$), 1.66-1.73 (m, 1H, $Me_2CH$), 3.55 (d, *J* = 7.4 Hz, 1H, OCH), 4.19 (d, *J* = 8.4 Hz, 2H, $BrCH_2$), 5.64 (t, *J* = 8.4 Hz, 1H, C=CH); $^{13}$C NMR ($CDCl_3$, 101 MHz): -4.9, -4.2, 11.6, 18.3, 18.7, 19.5, 26.0, 28.7, 32.4, 83.5, 121.9, 144.8; HRMS (EI) Calcd. For $C_{14}H_{29}OSiBr$: 320.1171, Found: 320.1174.



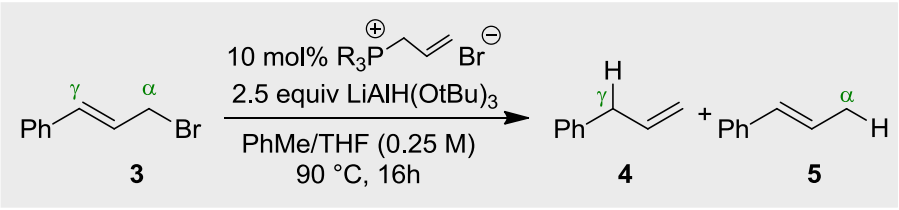

**(*E*)-2-(3-bromo-3-$d_2$-prop-1-en-1-yl)naphthalene (S26):** Prepared analogously from **S25** (0.90 g, 4.8 mmol) using **RP5**. Isolated as a white solid (0.87 g, 3.5 mmol, 72%). $^1$H NMR ($CDCl_3$, 360 MHz): δ = 6.50 (d, *J* = 16 Hz, 1H, C=CH), 6.79 (d, *J* = 16 Hz, 1H, C=CH), 7.42-7.51 (m, 2H, Ar), 7.57 (dd, *J* = 8.6, 1.8 Hz, 1H, Ar), 7.71-7.84 (m, 4H, Ar); $^{13}$C NMR ($CDCl_3$, 125 MHz): 33.3 (pentet, $J_{C\text{-}D}$ = 23 Hz), 123.6, 125.5, 126.4, 126.6, 127.3, 127.8, 128.2, 128.5, 133.4 (2), 133.6, 134.9; HRMS (EI) Calcd. For $C_{13}H_9D_2Br$: 248.01696, Found: 248.01595.

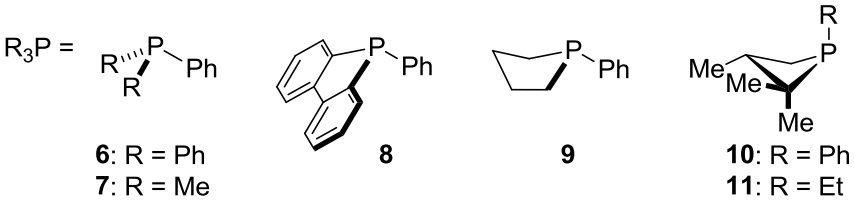
## III. Optimization and Procedure for Catalytic Allylic Reduction

### A. General Procedure for the Screening of Organophosphorus Catalyst

A solution of $LiHAl(O^tBu)_3$ (2.5 mmol, 2.5 eq.) in THF (6 mL) was added dropwise over 15 h via syringe pump to a 90 °C mixture of distilled cinnamyl bromide (1.0 mmol), organophosphonium catalyst (0.1 mmol, 0.1 eq.), and dodecane (1.0 mmol, 1.0 eq.) in PhMe (4 mL). After complete addition, the reaction mixture was stirred for an additional 1 h before cooling to ambient temperature. A 1.0 mL aliquot was removed and filtered over a small pad of silica gel, which was rinsed with dichloromethane (6 mL). The combined filtrate was then diluted to 12 mL with additional dichloromethane and analyzed directly by GC (Instrument settings: 0.1 μL injection volume, 280 °C injection temperature, 3.0 mL/min column flow, 8.0 mL/min total flow. Oven temperature settings: Hold at initial 50 °C for 3 minutes, then increase at 5 °C/min to 130 °C followed by 10 °C/min to 250 °C). **Retention times**: 8.6 min (allylbenzene **(4)**), 11.3 min (*trans*-β-methylstyrene **(5)**), 16.6 min (dodecane).

**Table 1 (from text).** Effect of Organophosphorus Catalyst on Regioselectivity of Transpositive Allylic Reduction



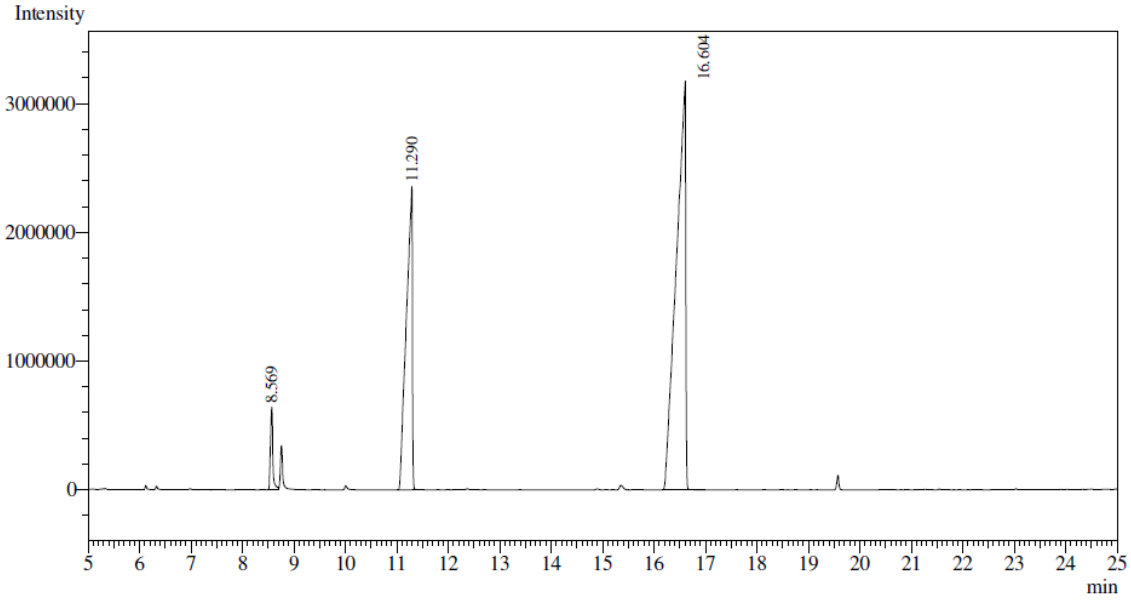




| Entry | $R_3P$ | Yield | Ratio (**4**:**5**) |
|---|---|---|---|
| 1 | none | 80 | 9 : 91 |
| 2 | **6** | 78 | 18 : 82 |
| 3 | **7** | 85 | 11 : 89 |
| 4 | **8** | 95 | 19 : 81 |
| 5 | **9** | 95 | 54 : 46 |
| 6 | **10** | 96 | 94 : 6 |
| 7 | **10**[a] | 100 | 98:2 |
| 8 | **10**[b] | 81 | 88:12 |
| 9 | **11** | 96 | 91 : 9 |

[a] Free **10** as catalyst. [b] **10**·$HBF_4$ salt as precatalyst.

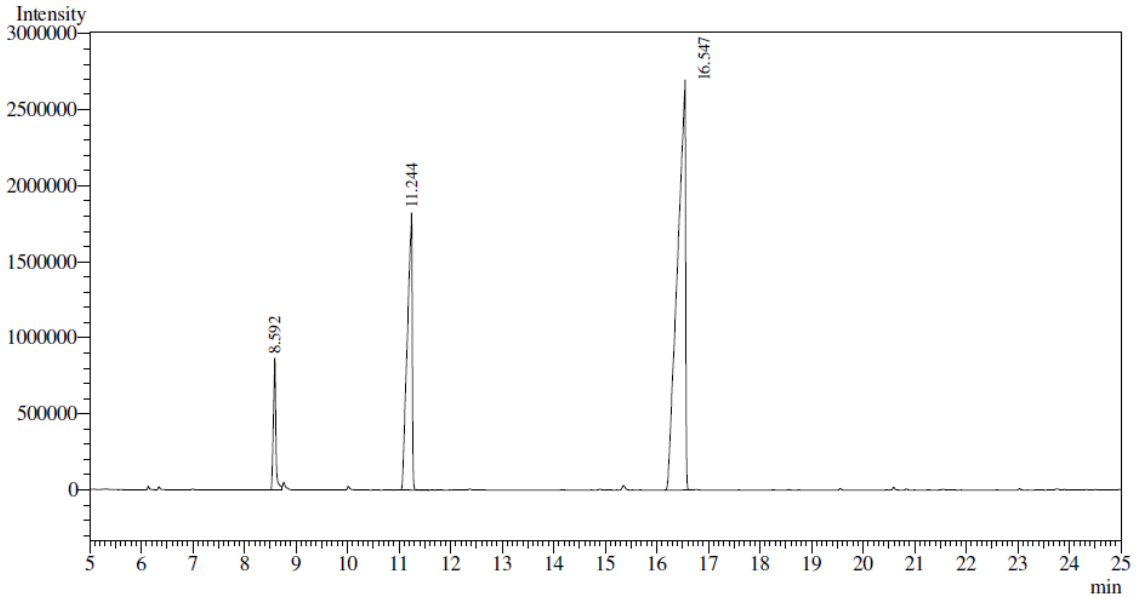
*Chromatograms for data tabulated in Table 1.*

**Table 1, Entry 1**



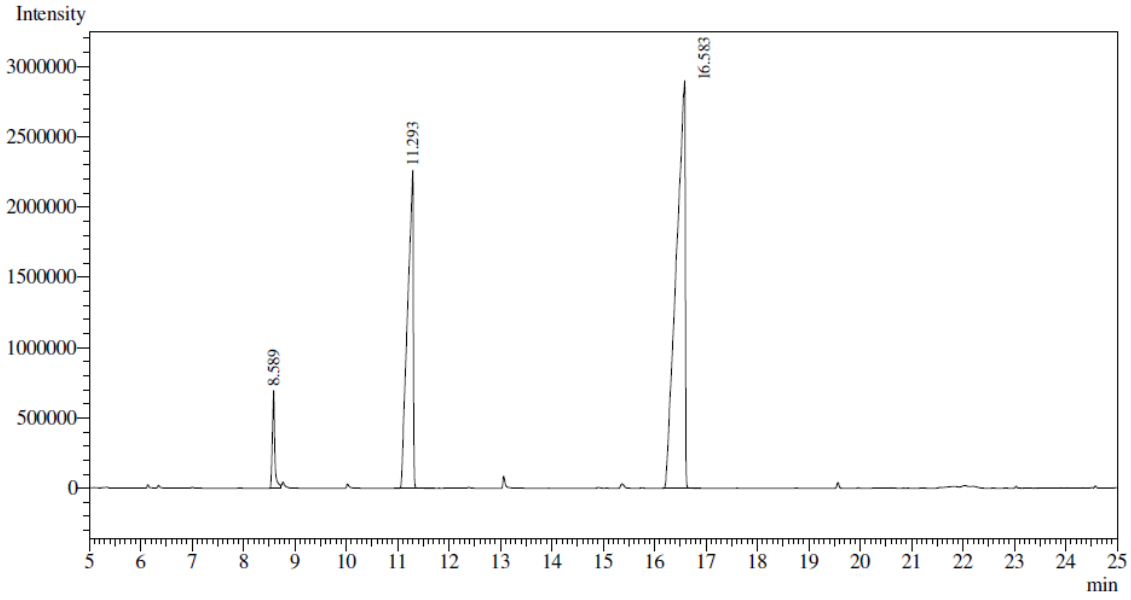

| Peak# | Ret.Time | Area | Height |
|---|---|---|---|
| 1 | 8.569 | 2085212 | 637576 |
| 2 | 11.290 | 19037853 | 2336852 |
| 3 | 16.604 | 40314118 | 3165524 |

**Table 1, Entry 2**



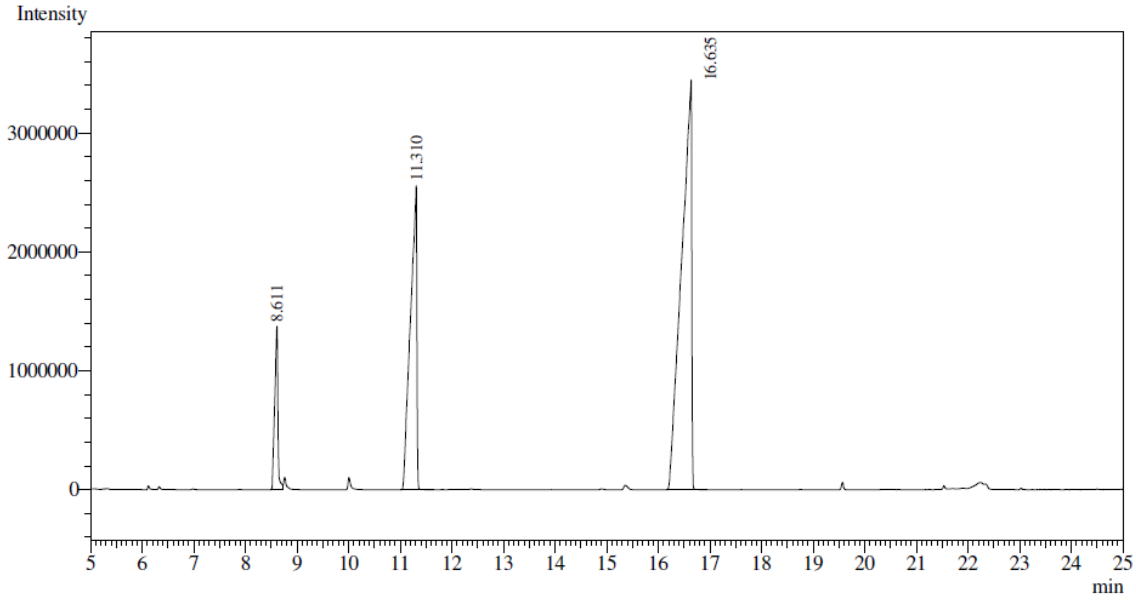

| Peak# | Ret.Time | Area | Height |
|---|---|---|---|
| 1 | 8.592 | 2935962 | 861343 |
| 2 | 11.244 | 12068251 | 1808292 |
| 3 | 16.547 | 29583159 | 2686787 |

**Table 1, Entry 3**



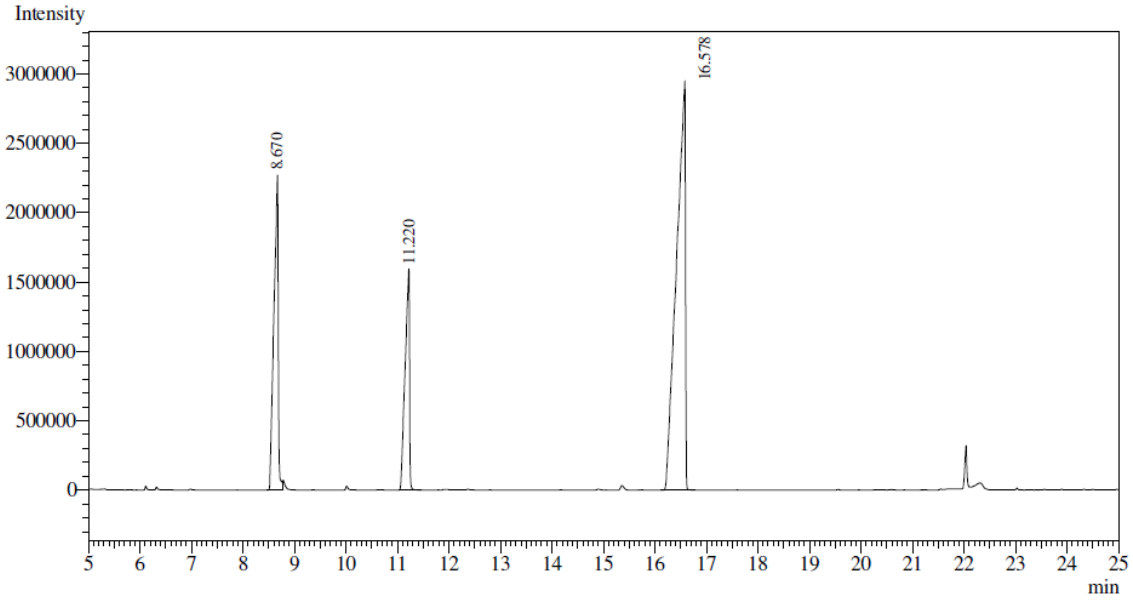

| Peak# | Ret.Time | Area | Height |
|---|---|---|---|
| 1 | 8.589 | 2322924 | 686840 |
| 2 | 11.293 | 17472424 | 2256865 |
| 3 | 16.583 | 34638210 | 2894003 |

**Table 1, Entry 4**



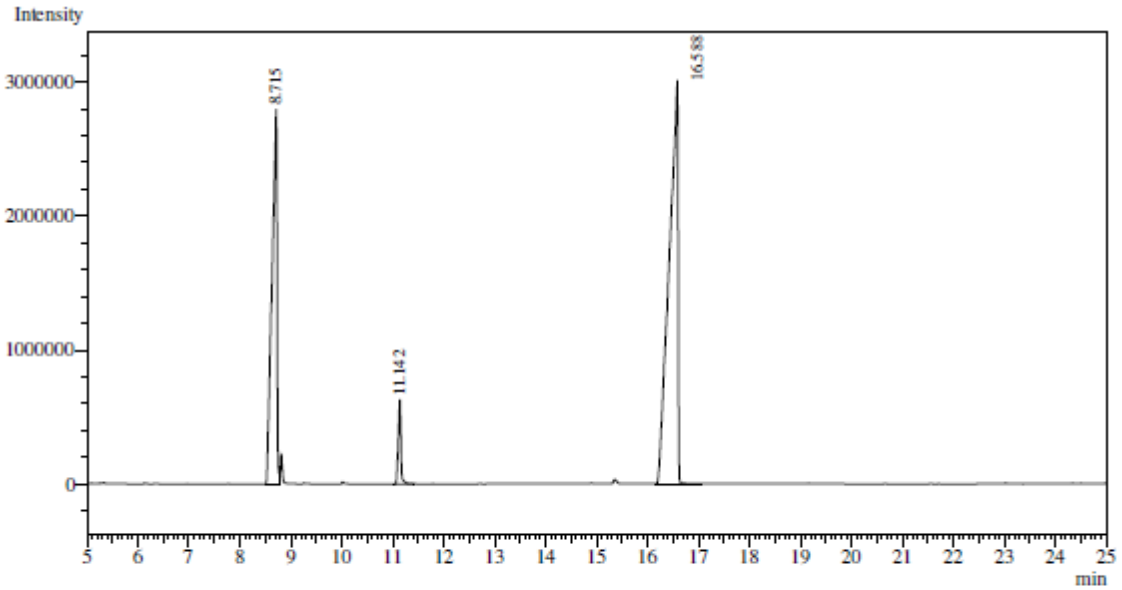

| Peak# | Ret.Time | Area | Height |
|---|---|---|---|
| 1 | 8.611 | 5807670 | 1365964 |
| 2 | 11.310 | 22050939 | 2537034 |
| 3 | 16.635 | 46593809 | 3440326 |

**Table 1, Entry 5**



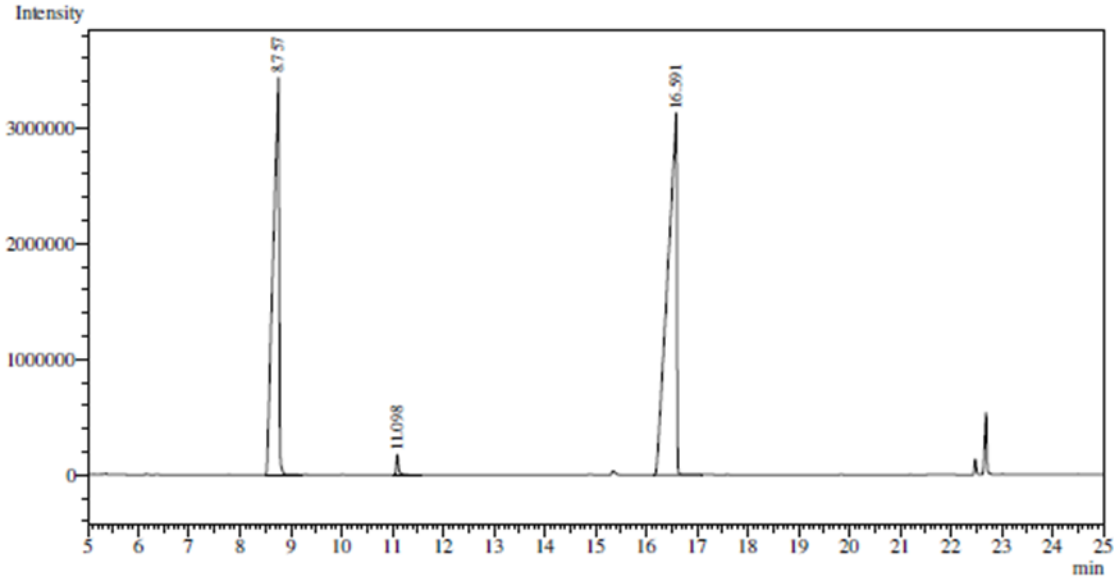

| Peak# | Ret.Time | Area | Height |
|---|---|---|---|
| 1 | 8.670 | 13093213 | 2262349 |
| 2 | 11.220 | 9330337 | 1586359 |
| 3 | 16.578 | 34980629 | 2921293 |

**Table 1, Entry 6**



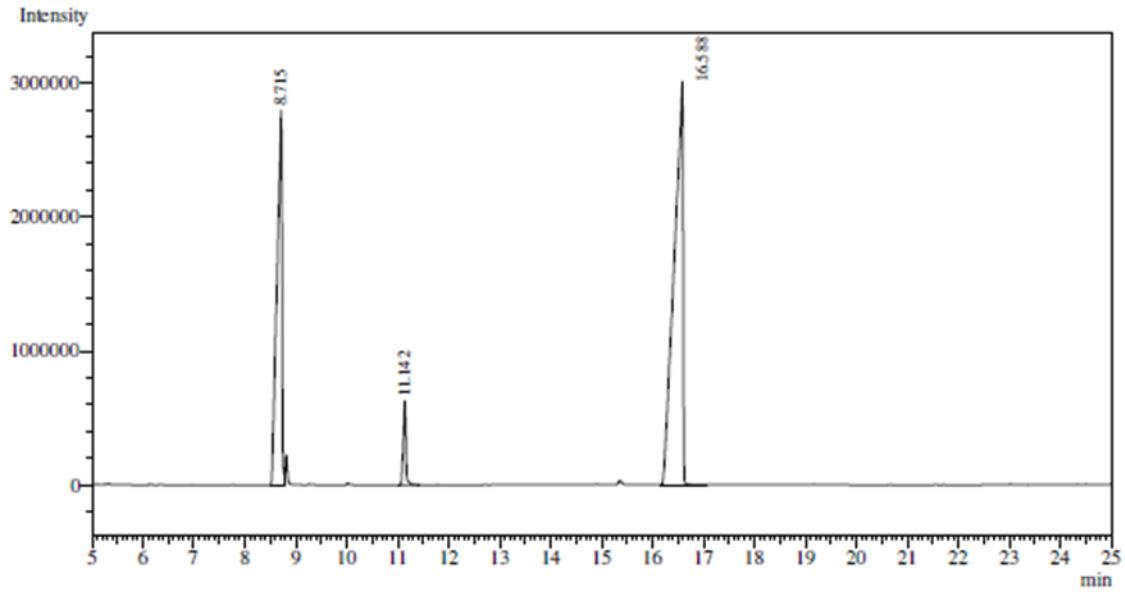

| Peak# | Ret.Time | Area | Height |
|---|---|---|---|
| 1 | 8.715 | 18880190 | 2769205 |
| 2 | 11.142 | 2257562 | 623515 |
| 3 | 16.588 | 35915435 | 2984925 |

**Table 1, Entry 7**



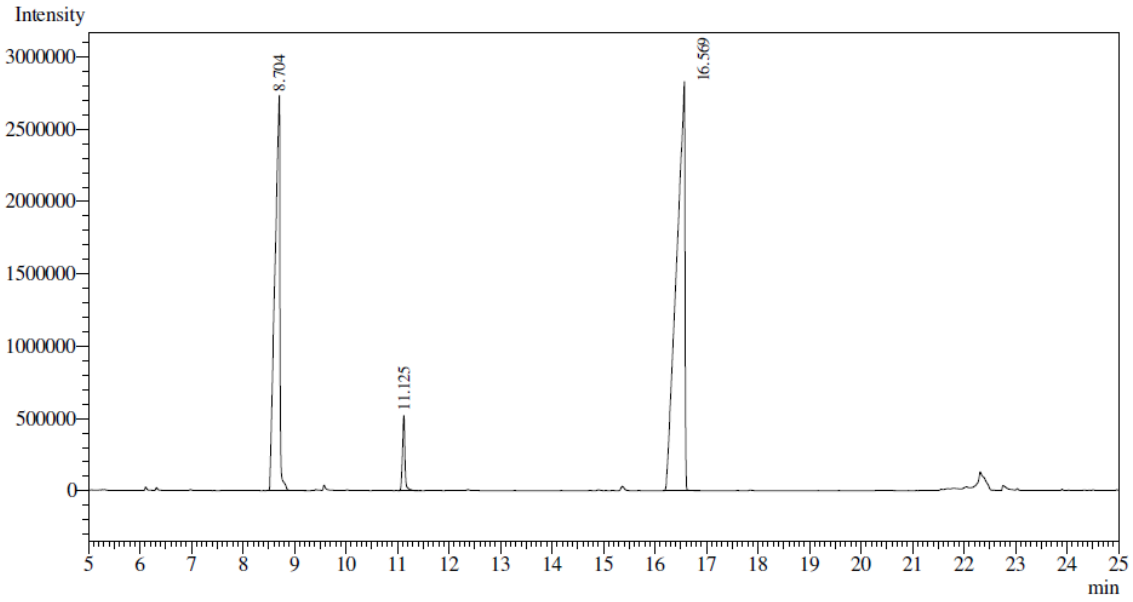

| Peak# | Ret.Time | Area | Height |
|---|---|---|---|
| 1 | 8.757 | 27667631 | 3423395 |
| 2 | 11.098 | 555467 | 173887 |
| 3 | 16.591 | 38903417 | 3108870 |

**Table 1, Entry 8**




| Peak# | Ret.Time | Area | Height |
|---|---|---|---|
| 1 | 8.715 | 18880190 | 2769205 |
| 2 | 11.142 | 2257562 | 623515 |
| 3 | 16.588 | 35915435 | 2984925 |

**Table 1, Entry 9**




| Peak# | Ret.Time | Area | Height |
|---|---|---|---|
| 1 | 8.704 | 18598475 | 2717497 |
| 2 | 11.125 | 1717144 | 518327 |
| 3 | 16.569 | 31866757 | 2824996 |

**B. Reductant Screening and Data**

To probe the effect of various hydride sources on the allylic transposition, the procedure outlined in Section III. A was followed, and the results are summarized below (Table S1).

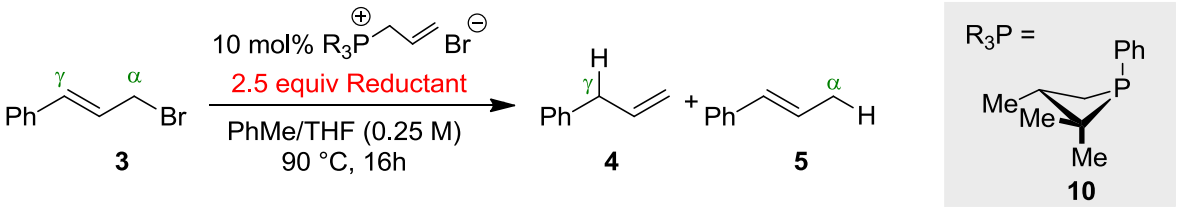



**Table S1.** Effect of Hydride Source on Regioselectivity

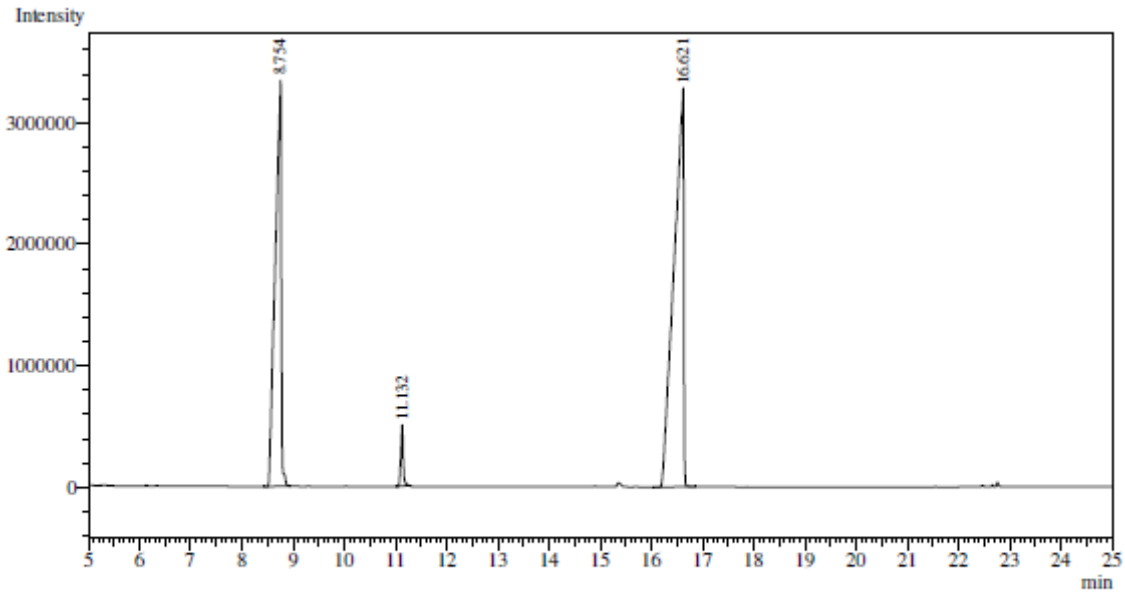
| Entry | Reductant | Yield (%)[a,b] | 4:5[a] |
|---|---|---|---|
| 1 | $LiAlH_4$ | 95 | 94:6 |
| 2 | $LiAlH(OtBu)_3$ | 96 | 94:6 |
| 3 | DIBAL-H | 42[c] | 30:70 |
| 4 | $[NBu_4][BH_4]$ | trace[d] | - |
| 5 | $PhSiH_3$ | -[e] | - |
| 6 | $PhSi_2H_2$ | -[e] | - |
| 7 | $Et_3SiH$ | -[e] | - |

[a] Determined by GC analysis. [b] Combined Yield. [c] propylbenzene observed in 4% yield. [d] Complex mixture [e] Reduction of allylphosphetanium not observed.

$LiAlH_4$ (entry 1) was found to be equally effective as $LiAlH(OtBu)_3$ (entry 2) in promoting the transposition, however the neutral aluminium hydride DIBAL-H resulted in reduced **4**:**5** ratios and propylbenzene byproduct in 4% yield (entry 3). Although $[BH_4]^-$ was capable of reducing allylphosphetanium salts in stoichiometric experiments in MeOH, applying this reductant to our catalytic conditions resulted in a complex mixture with trace **4**/**5** formation (entry 4). We attribute this to potential catalyst inhibition from $BH_3$ produced *in situ*. Several silanes were incapable of reducing allylphosphetanium salts in stoichiometric experiments (entries 5-7), prompting us to choose $LiAlH(OtBu)_3$ as our model reductant over $LiAlH_4$ due to increased safety and milder hydricity.

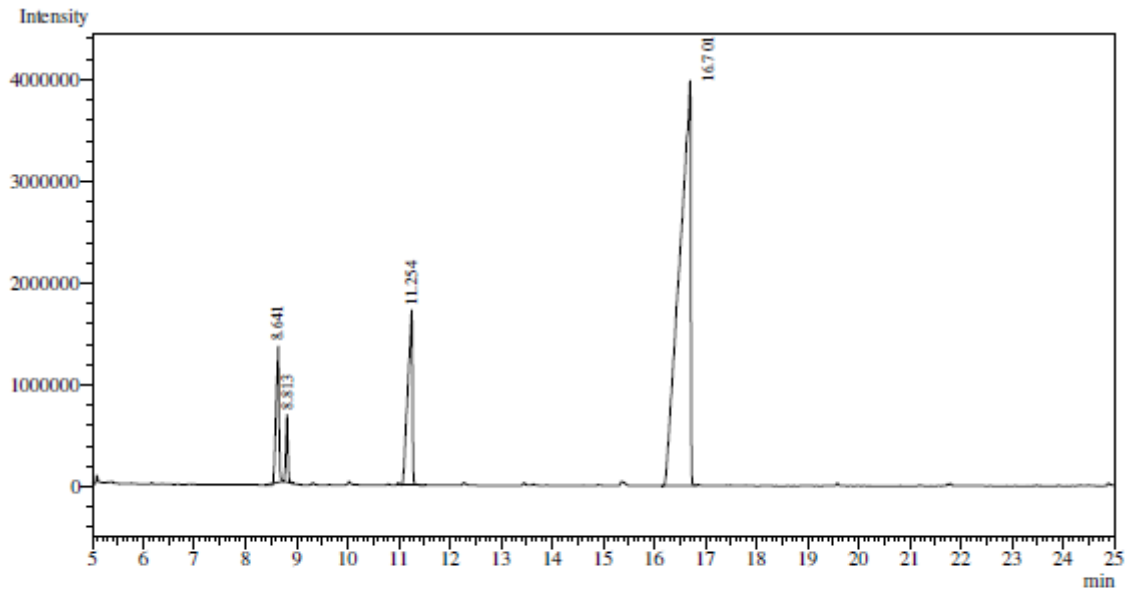
*Chromatograms for data tabulated in Table S1.*

**Table S1, Entry 1**




| Peak# | Ret.Time | Area | Height |
|---|---|---|---|
| 1 | 8.754 | 26881966 | 3323810 |
| 2 | 11.132 | 1645069 | 495428 |
| 3 | 16.621 | 43117050 | 3275632 |

**Table S1, Entry 3**




| Peak# | Ret.Time | Area | Height |
|---|---|---|---|
| 1 | 8.641 | 5362231 | 1331941 |
| 2 | 8.813 | 1840689 | 658698 |
| 3 | 11.254 | 10713304 | 1707735 |
| 4 | 16.701 | 59603604 | 3960960 |

## C. Effect of Leaving Group and Data

The effect of various leaving groups on the allylic transposition has been examined using the procedure outlined in Section III A, and the results are summarized below in Table S2.

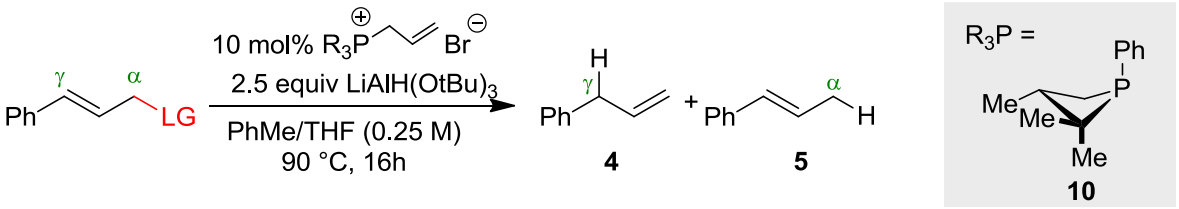



**Table S2.** Effect of Leaving Group on Regioselectivity

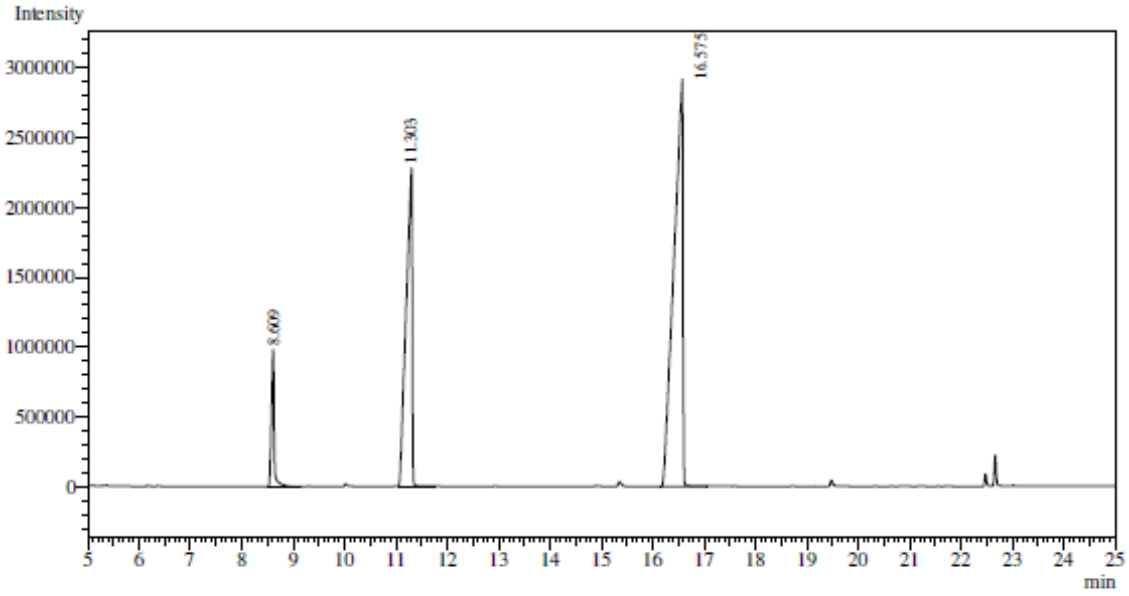
| Entry | Leaving Group | Yield (%)[a,b] | 4:5[a] |
|---|---|---|---|
| 1 | Cl | 98 | 15:85 |
| 2 | Br | 96 | 94:6 |
| 3 | I | 90 | 84:16 |
| 4 | $CO_2CF_3$ | trace[c] | - |

[a] Determined by GC analysis. [b] Combined Yield. [c] Cinnamyl alcohol major product as determined by $^1$H NMR.

Allylic chlorides were found to be poor substrates for our conditions, providing linear **5** as the major product (entry 1). We attribute this reversal in selectivity to sluggish displacement of chloride by **10**, allowing direct reduction to outcompete catalytic transposition by **10**. Alkylation of **10** in neat allyl chloride was significantly slower in comparison to allyl bromide, furthering this notion. Allylic iodides also provide **4** selectively (entry 3), albeit with slightly diminished regioisomeric ratios in comparison to allylic bromides (entry 2). Reduction to the corresponding allylic alcohol was observed when a trifluoroacetate leaving group was employed (entry 4), indicating preferential reduction of the electron-deficient ester moiety. From these results, allylic bromides were chosen as the optimal substrate for our allylic transposition conditions.

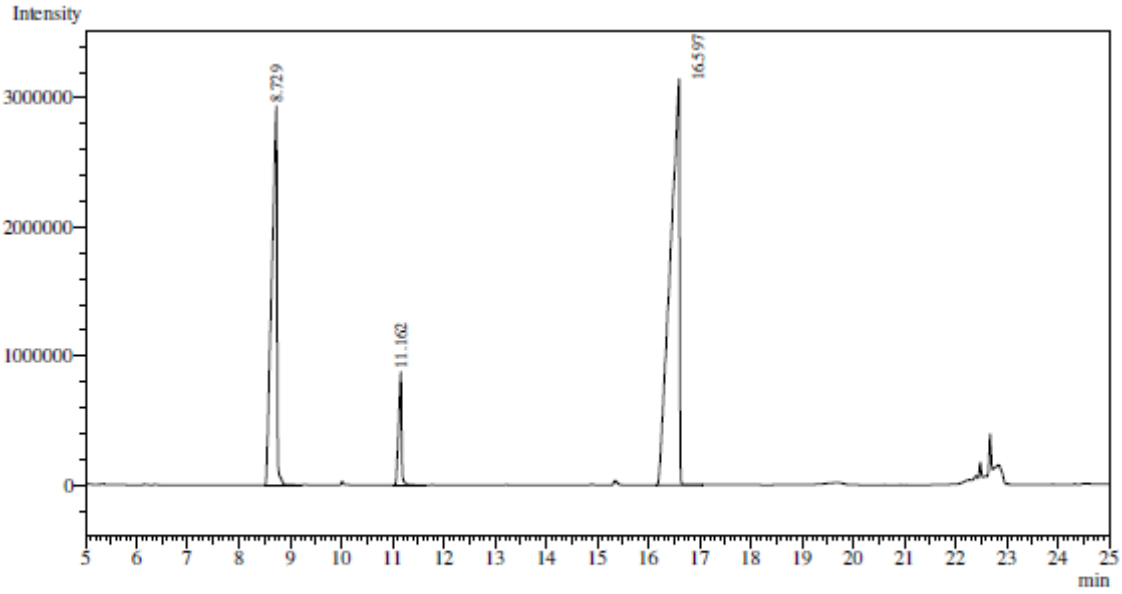
*Chromatograms for data tabulated in Table S2.*

**Table S2, Entry 1**




| Peak# | Ret.Time | Area | Height |
|---|---|---|---|
| 1 | 8.609 | 3618268 | 977597 |
| 2 | 11.303 | 18263104 | 2270113 |
| 3 | 16.575 | 34930472 | 2910429 |

**Table S2, Entry 3**

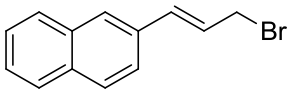
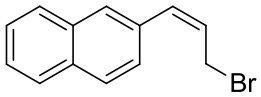
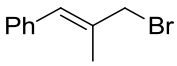
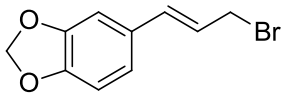
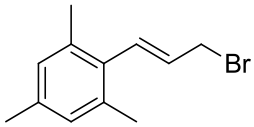
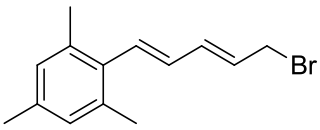


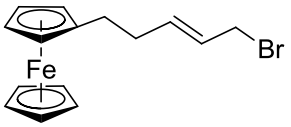
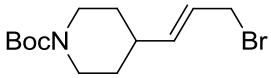
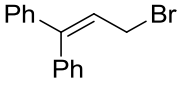
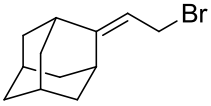
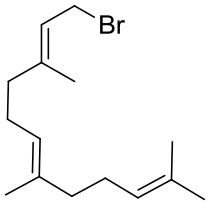
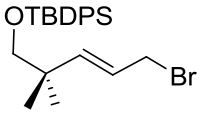
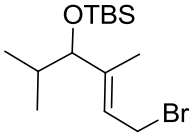

| Peak# | Ret.Time | Area | Height |
|---|---|---|---|
| 1 | 8.729 | 20788412 | 2926652 |
| 2 | 11.162 | 3586178 | 874669 |
| 3 | 16.597 | 39417142 | 3135754 |

**D.General Procedure for the Phosphetane-Catalyzed Reduction of Allylic Bromides**

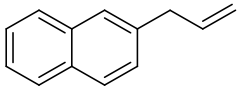
A solution of $LiHAl(O^tBu)_3$ (2.5 mmol, 2.5 eq.) in THF (6 mL) was added dropwise over 15 h via syringe pump to a 90 °C mixture of allylic bromide (1.0 mmol) and **14·[Br]** (0.1 mmol, 0.1 eq.) in PhMe (4 mL). After complete addition, the reaction mixture was stirred for an additional 1 h before cooling to ambient temperature and quenching with saturated aqueous $NH_4Cl$ solution (2 mL). The aqueous layer was extracted with diethyl ether, and the combined organic layers washed with saturated aqueous NaCl solution and dried over $Na_2SO_4$. Removal of solvent followed by column chromatography (silica gel) afforded the desired product as a mixture of isomers. Ratios of γ to α reduction products determined by $^1H$ NMR analysis of clearly distinguishable peaks (generally allylic methylene of γ product, allylic methyl of α product) unless otherwise stated.

**Table S3.** Phosphetane-Catalyzed Allylic Reduction

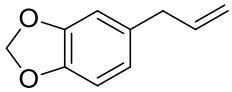
| Entry | Substrate | Substrate Mass (g) | Catalyst Mass (g) | Reductant Mass (g) | Eluting Solvent | Product Mass (g) (% yield)[a] | γ:α[b] |
|---|---|---|---|---|---|---|---|
| 1 |  | 0.249 | 0.033 | 0.646 | hexanes | 0.145 (86) | 94:6 |
| 2 |  | 0.251 | 0.033 | 0.636 | hexanes | 0.125 (73) | >95:5 |
| 3 |  | 0.212 | 0.032 | 0.642 | - | - (91)[c] | 97:3[c] |
| 4 |  | 0.249 | 0.034 | 0.657 | 4:1 hexanes: DCM | 0.127 (76) | 88:12 |
| 5[d] |  | 0.239 | 0.031 | 0.636 | - | - (97)[c] | 87:13[c] |
| 6 |  | 0.265 | 0.032 | 0.647 | hexanes | 0.110 (59)[e] | 92:8 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 7 |  | 0.343 | 0.039 | 0.670 | pentane | 0.230 (88) | 95:5 |
| 8 |  | 0.306 | 0.033 | 0.646 | 7:1 hexanes: EtOAc | 0.176 (78) | 95:5 |
| 9 |  | 0.280 | 0.032 | 0.645 | hexanes | 0.168 (84) | 92:8 |
| 10 |  | 0.245 | 0.034 | 0.649 | pentane | 0.145 (88) | 94:6 |
| 11 |  | 0.290 | 0.033 | 0.656 | pentane | 0.185 (88) | 93:7[c] |
| 12[f] |  | 0.431 | 0.032 | 0.646 | hexanes | 0.298 (84) | 89:11 |
| 13[g] |  | 0.321 | 0.032 | 0.645 | hexanes | 0.195 (80)[h] 1.4:1 *dr* | 90:10 |

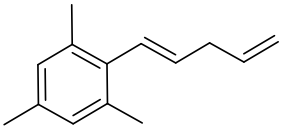
[a] Isolated yields are reported unless otherwise stated. [b] Ratios (γ:α) determined by $^1$H NMR integration unless otherwise stated. [c] Determined by GC analysis. [d] Mes = mesityl. [e] Reaction time 10 h due to thermal instability of substrate. [f] TBDPS = *tert*-butyldiphenylsilyl. [g] TBS = *tert*-butyldimethylsilyl. [h] *d.r.* and relative stereochemistry of major isomer determined after TBS deprotection.



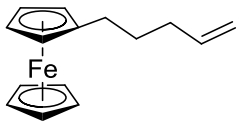
**2-allylnaphthalene:**[24] Colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ = 3.53 (d, *J* = 6.6 Hz, 2H, $CH_2$), 5.07-5.17 (m, 2H, C=$CH_2$), 5.97-6.10 (m, 1H, C=CH), 7.31 (d, *J* = 8.4 Hz, 1H, Ar), 7.37-7.46 (m, 2H, Ar), 7.60 (s, 1H, Ar), 7.72-7.81 (m, 3H, Ar). **Minor Isomer**: 1.91 (d, *J* = 6.5 Hz, 3H) 6.34 (dq, *J* = 16, 6.5 Hz), 6.54 (d, *J* = 16 Hz); HRMS (EI) Calcd. For $C_{13}H_{12}$: 168.0939, Found: 168.0932.



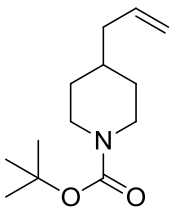
**5-allylbenzo[*d*][1,3]dioxole:**[25] Colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ = 3.29 (d, *J* = 6.7 Hz, 2H, $CH_2$), 5.01-5.09 (m, 2H, C=$CH_2$), 5.90 (s, 2H, $O_2CH_2$), 5.92 (ddt, *J* = 17, 10, 6.7 Hz, 1H, C=CH), 6.63 (d, *J* = 7.8 Hz, 1H, Ar), 6.67 (s, 1H, Ar), 6.73 (d, *J* =7.8 Hz, 1H, Ar). **Minor isomer:**[26] 1.84 (d, *J* = 6.6 Hz, 3H, $CH_3$), 6.05 (dq, *J* = 16, 6.6 H, 1H, C=CH), 6.30 (d, *J* = 16 Hz, 1H, C=CH), 6.87 (s, 1H, Ar); HRMS (EI) Calcd. For $C_{10}H_{10}O_2$: 162.0681, Found: 162.0683.



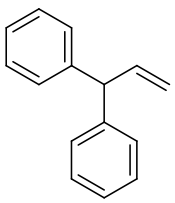
**(*E*)-1,3,5-trimethyl-2-(penta-1,4-dien-1-yl)benzene:** Colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ = 2.26 (s, 9H, $ArCH_3$), 2.98 (m, 2H, $(C=CH)_2C\mathit{H}_2$), 5.05 (d, *J* = 10 Hz, 1H, C=CH*H*), 5.12 (d, *J* = 17 Hz, 1H, C=CH*H*), 5.66 (dt, *J* = 16, 6.8 Hz, 1H, ArCH=C*H*), 5.87-5.99 (m, 1H, C*H*=$CH_2$), 6.32 (d, *J* = 16 Hz, 1H, ArC*H*=CH), 6.85 (s, 2H, Ar). **Minor isomer**: 1.81 (d, *J* = 6.6 Hz, 3H, $CH_3$); $^{13}$C NMR ($CDCl_3$, 101 MHz): 21.0 (2), 37.6, 115.5, 128.5, 128.6, 132.8, 134.6, 135.9, 136.0, 137.1; HRMS (EI) Calcd. For $C_{14}H_{18}$: 186.1409, Found: 186.1404.




**pent-4-en-1-ylferrocene:** Orange oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.60 (quintet, *J* = 7.6 Hz, 2H, $CH_2$), 2.08 (q, *J* = 7.1 Hz, 2H, $CH_2$), 2.33 (t, *J* = 7.8 Hz, 2H, $CH_2$), 4.03 (br s, 2H, $C_5H_4$), 4.05 (br s, 2H, $C_5H_4$), 4.08 (s, 5H, $C_5H_5$), 4.97 (d, *J* = 10 Hz, 1H, C=CH*H*), 5.02 (d, *J* = 17 Hz, 1H, C=CH*H*), 5.82 (ddt, *J* = 17, 10, 6.7 Hz). **Minor Isomer**: 5.42-5.49 (m, 2H, HC=CH); $^{13}$C NMR ($CDCl_3$, 101 MHz): 29.1, 30.4, 33.8, 67.2, 68.2, 68.6, 89.2, 114.7, 138.9; HRMS (ESI) Calcd. For $C_{15}H_{18}Fe$: 254.0758, Found: 254.0756.

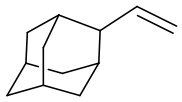



***tert*-butyl 4-allylpiperidine-1-carboxylate:** Colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.02-1.16 (m, 2H), 1.45 (s, 9H, O$^t$Bu), ~1.47 ppm (m, 1H), 1.60-1.70 (m, 2H), 1.98-2.02 (m, 2H), 2.57-2.78 (m, 2H), 3.95-4.22 (br, 2H), 4.96-5.05 (m, 2H, C=$CH_2$), 5.69-5.83 (m, 1H, C=CH). **Minor isomer:** 5.32-5.48 (m, 2H, HC=CH); $^{13}$C NMR ($CDCl_3$, 101 MHz): 28.6, 32.0, 36.1, 41.0, 44.1 (br), 79.3, 116.2, 136.6, 155.0; HRMS (EI) Calcd. For $C_{13}H_{23}NO_2$: 225.1729, Found: 225.1727.

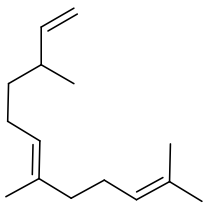


**prop-2-ene-1,1-diyldibenzene:**[27] Colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ = 4.72 (d, *J* = 7.2 Hz, 1H, $Ph_2CH$), 4.94-5.03 (m, 1H, C=CH*H*), 5.18-5.25 (m, 1H, C=C*H*H), 6.30 (ddd, *J* = 17, 10, 7.2 Hz, 1H, C=CH), 7.15-7.22 (m, 6H, Ar), 7.25-7.32 (m, 4H, Ar); **Minor Isomer:**[28] 1.75 (d, *J* = 7.0 Hz, 3H, $CH_3$), 6.17 (q, *J* =

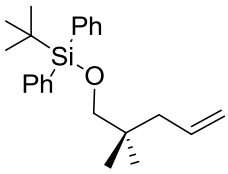
7.0 Hz, 1H, C=CH); HRMS (EI) Calcd. For $C_{15}H_{14}$: 194.1096, Found: 194.1091.



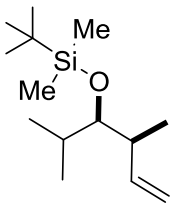
**2-vinyladamantane:** Colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.48-1.56 (m, 2H), 1.69-1.98 (m, 12H), 2.39 (s, 1H), 4.99-5.07 (m, 2H, C=CH), 6.04 (m, 1H, C=CH). **Minor isomer**: 2.32 (s, 1H), 2.84 (s, 1H); $^{13}$C NMR ($CDCl_3$, 101 MHz): 28.1, 28.3, 32.2, 32.8, 38.3, 38.9, 48.0, 113.6, 143.2; HRMS (EI) Calcd. For $C_{12}H_{18}$: 162.1409, Found: 162.1407.



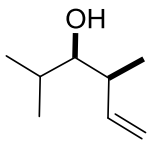
**(*E*)-3,7,11-trimethyldodeca-1,6,10-triene:**[29] Colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ = 0.98 (d, *J* = 6.7 Hz, 3H, $CH_3$), 1.28-1.36 (m, 2H), 1.59 (s, 3H, $CH_3$), 1.60 (s, 3H, $CH_3$), 1.68 (s, 3H, $CH_3$), 1.93-2.02 (m, 4H), 2.02-2.16 (m, 3H), 4.88-4.99 (m, 2H, C=$CH_2$), 5.05-5.14 (m, 2H), 5.70 (ddd, *J* = 17, 10, 7.6 Hz, 1H, C=CH); HRMS (EI) Calcd. For $C_{15}H_{26}$: 206.2035, Found: 206.2039.




**tert-butyl((2,2-dimethylpent-4-en-1-yl)oxy)diphenylsilane:** Colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ = 0.88 (s, 6H, $CH_3$), 1.07 (s, 9H, Si$^t$Bu), 2.07 (d, *J* = 7.4 Hz, 2H, $CH_2$), 3.31 (s, 2H, $SiOCH_2$), 4.97-5.05 (m, 2H, C=$CH_2$), 5.79 (m, 1H, C=CH), 7.33-7.45 (m, 6H, Ar), 7.63-7.70 (m, 4H, Ar). **Minor isomer**: 1.02 (s, 6H, $CH_3$), 1.65 (d, *J* = 4.9 Hz, 3H, $CH_3$), 3.33 (s, 2H, $SiOCH_2$), 5.34-5.48 (m, 2H, HC=CH); $^{13}$C NMR ($CDCl_3$, 101 MHz): 19.6, 24.2, 27.1, 36.1, 43.4, 72.2, 116.7, 127.7, 129.7, 134.1, 135.7, 135.9; HRMS (EI) Calcd. For $C_{23}H_{31}OSi$ [M-H$^+$]: 351.2144, Found: 351.2144.

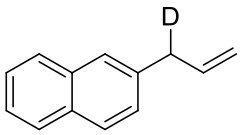



***tert*-butyl((2,4-dimethylhex-5-en-3-yl)oxy)dimethylsilane:**[30] Colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ = 0.05 (s, 6H, $SiCH_3$), 0.88-0.92 (unresolved doublets, 6H, $CH_3$), 0.92 (s, 9H, Si$^t$Bu), 0.97-1.01 (unresolved doublets, 3H, $CH_3$), 1.71-1.83 (m, 1H, CH), 2.28-2.42 (m, 1H), 3.26-3.32 (m, 1H, OCH), 4.91-5.02 (m, 2H, C=$CH_2$), 5.82 (ddd, *J* = 17, 10, 7.7 Hz, 1H, C=CH, major isomer), 5.90 (ddd, *J* = 17, 10, 8.0 Hz, 1H, C=CH, minor isomer). **Minor Isomer:** 0.72 (d, *J* = 6.8 Hz, 3H, $CH_3$), 1.59 (d, *J* = 6.7 Hz, 3H, $CH_3$), 3.47 (d, *J* = 8.2 Hz, 1H, OCH), 5.32 (q, *J* = 6.7 Hz, 1 H, C=CH); HRMS (EI) Calcd. For $C_{14}H_{29}OSi$ [M-H$^+$]: 241.1988, Found: 241.1984.

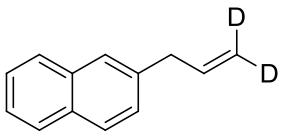



**2,4-dimethylhex-5-en-3-ol:** A solution of *tert*-butyl((2,4-dimethylhex-5-en-3-yl)oxy)dimethylsilane in $CD_3OD$ was treated with two drops of TMSCl in a standard NMR tube, and essentially complete deprotection was observed after 1 h. $^1$H NMR indicates a 1.4:1 dr in favor of the syn product based on previous

literature characterization.[30] $^1$H NMR ($CD_3OD$), 400 MHz): δ = 1.03 (d, *J* = 6.6 Hz, 3H, $CH_3$), 1.63-1.82 (m, 1H), 2.23-2.42 (m, 1H), 2.99-3.05 (m, 1H, minor isomer, OCH), 3.06-3.12 (m, 1H, major isomer, OCH), 4.90-5.04 (m, 2H, C=CH), 5.75 (ddd, *J* = 17, 10, 8.3 Hz, 1H, C=CH, major isomer), 5.86 (ddd, *J* = 17, 10, 8.5 Hz, 1H, minor isomer).



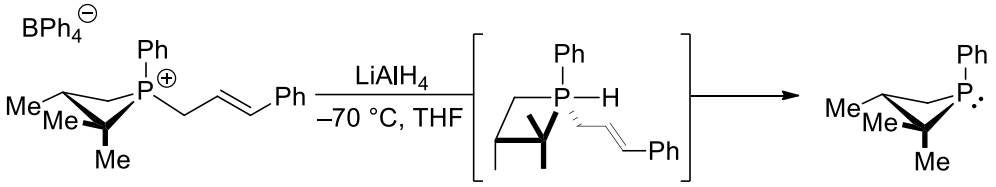

**2-(1-*d*-allyl)naphthalene (16-*d*$_\gamma$):** To a suspension of napthyl phosphetanium salt **S15** (0.438 g, 1 mmol) in THF (10 mL) was added $LiAlD_4$ (0.046 g, 1.1 mmol) and the reaction was stirred at ambient temperature for 30 min, then quenched with concentrated aqueous ammonium chloride solution (5 mL). The reaction was diluted with ether (20 mL), and combined organics washed with brine (2 x 10 mL), dried over sodium sulfate and concentrated to give a clear liquid, which was purified by column chromatography (silica gel, hexanes) to give the desired product as a colorless oil (0.093 mg, 55%). No other isomers or products were observed in this reaction. $^1$H NMR ($CDCl_3$, 400 MHz): δ = 3.51 (br s, 1H, ArCHD), 5.07-5.16 (m, 2H C=$CH_2$), 6.03 (ddd, *J* = 17, 10, 7.0 Hz, 1H, C=CH), 7.31 (d, *J* = 7.9 Hz, 1H, Ar), 7.37-7.46 (m, 2H Ar), 7.61 (s, 1H, Ar), 7.72-7.81 (m, 3H, Ar); $^{13}$C NMR ($CDCl_3$, 101 MHz): 40.5 (t, $J_{C-D}$ = 19 Hz), 116.5, 125.7, 126.4, 127.1, 127.8, 127.9, 128.1, 128.4, 132.6, 134.1, 137.7, 138.0; HRMS (EI) Calcd. For $C_{13}H_{11}D$: 169.1002, Found: 169.1001.




**2-(3-$d_2$-allyl)naphthalene (16-$d_2^\alpha$):** To a suspension of napthyl phosphetanium salt **15-$d_2^\alpha$** (0.441 g, 1 mmol) in THF (10 mL) was added $LiAlH(O^tBu)_3$ (0.305 g, 1.2 mmol) and the reaction was stirred at ambient temperature for 3 h, then quenched with concentrated aqueous ammonium chloride solution (5 mL). The reaction was diluted with ether (20 mL), and combined organics washed with brine (2 x 10 mL), dried over sodium sulfate and concentrated to give a clear liquid, which was purified by column chromatography (silica gel, hexanes) to give the desired product as a colorless oil (0.128 g, 75%). No other isomers or products were observed in this reaction. $^1$H NMR ($CDCl_3$, 360 MHz): δ = 3.54 (d, *J* = 6.6 Hz, 2H), 6.03 (br s, 1H, C=CH), 7.32 (dd, *J* = 8.4, 1.8 Hz, 1H, Ar), 7.39-7.48 (m, 2H, Ar), 7.63 (s, 1H, Ar), 7.75-7.84 (m, 3H, Ar); $^{13}$C NMR ($CDCl_3$, 101 MHz): 40.4, 115.7 (pentet, *J* = 24 Hz), 125.4, 126.1, 126.8, 127.5, 127.6, 127.8, 128.1, 132.3, 133.8, 137.2, 137.7; HRMS (EI) Calcd. For $C_{13}H_{10}D_2$: 170.10645, Found: 170.10652.

## IV. VT-NMR EXPERIMENTS

### A. Observation of Hydridophosphorane Intermediate




**12** δ +48.5 ppm

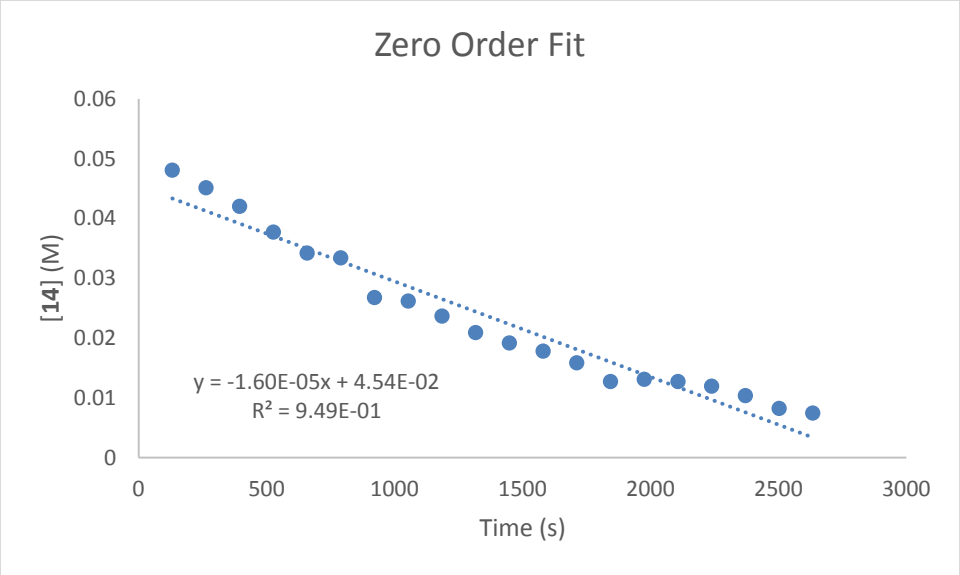
**17** δ –75.4 ppm (d, *J* = 258 Hz)

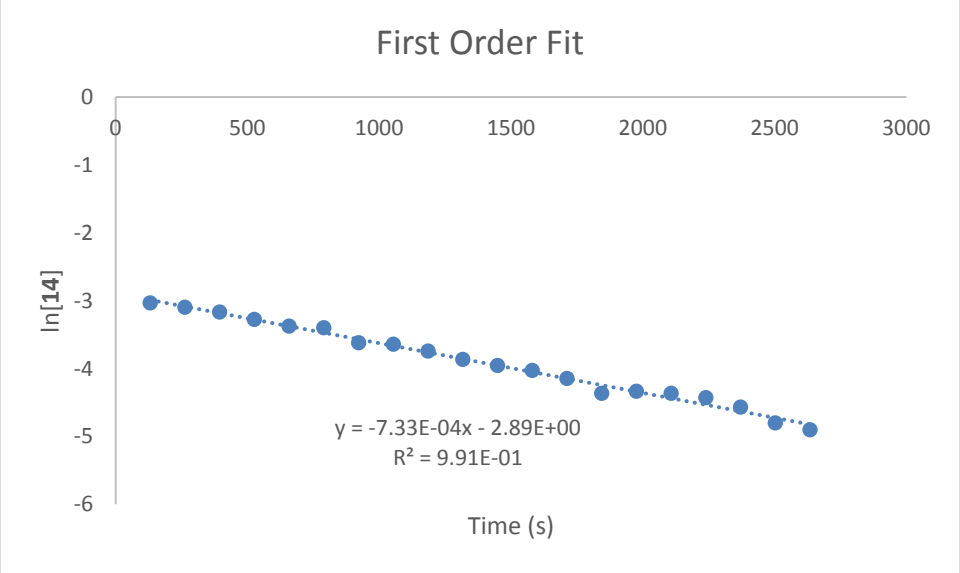
**10** δ +25.1 ppm

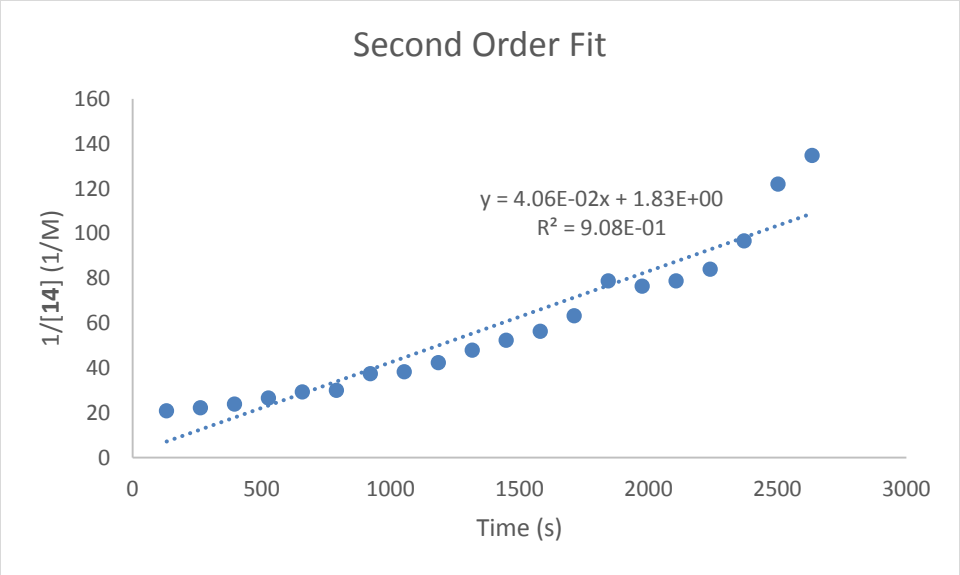
To cinammyl phosphetanium **12** (single diastereomer, 0.047 g, 0.075 mmol) dissolved in THF (0.5 mL) in a J. Young NMR tube sealed under a nitrogen atmosphere and cooled in a dry ice/acetone bath was added a solution of $LiAlH_4$ (0.014 g, 0.375 mmol) in THF (0.5 mL) via a septum. The NMR tube was resealed and removed from the cooling bath, shaken twice to mix the reagents and placed in an NMR probe thermostatted at -80 °C. The reaction course was monitored via $^{31}P$ NMR, with spectra obtained sequentially at increasing 20 °C intervals.

### B. Order in Phosphorus

To **14** (6:1 trans:cis mix of diastereomers, 0.0414 g, 0.075 mmol) and triphenylphosphine (0.005 g, 0.02 mmol) dissolved in THF (0.5 mL) in a J. Young NMR tube sealed under a nitrogen atmosphere and cooled in a dry ice/acetone bath was added a solution of $LiAlH_4$ (0.014 g, 0.375 mmol) in THF (0.5 mL) via a septum. The NMR tube was resealed and removed from the cooling bath, shaken twice to mix the reagents and placed in an NMR probe thermostatted at -55 °C. The reaction course was monitored by $^{31}P$ NMR ($D_1$=5 sec), only the major diastereomer was integrated. The decay of **14** has a linear fit for ln[**14**] over time, indicating the reaction is first order in **14**.


Zero Order Fit
0.06
0.05
0.04
0.03
0.02
0.01
0
[14] (M)
y = -1.60E-05x + 4.54E-02
R² = 9.49E-01
0
500
1000
1500
2000
2500
3000
Time (s)


First Order Fit
0
-1
-2
-3
-4
-5
-6
ln[14]
0
500
1000
1500
2000
2500
3000
y = -7.33E-04x - 2.89E+00
R² = 9.91E-01
Time (s)

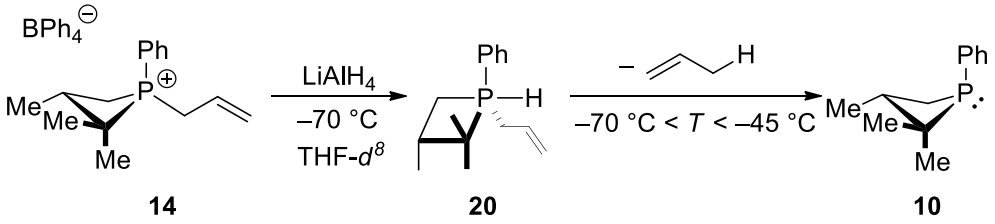



**C. Order in Reductant**

To **14** (6:1 trans:cis mix of diastereomers, 0.0207 g, 0.038 mmol) and triphenylphosphine (0.005 g, 0.02 mmol) dissolved in THF (0.5 mL) in a J. Young NMR tube sealed under a nitrogen atmosphere and cooled in a dry ice/acetone bath was added a solution of $LiAlH_4$ (2.5-20 equiv) in THF (0.5 mL) via a septum. The NMR tube was resealed and removed from the cooling bath, shaken twice to mix the reagents and placed in an NMR probe thermostatted at -55 °C. The reaction course was monitored by $^{31}P$ NMR ($D_1$=5 sec), only the major diastereomer was integrated. The rate does not depend on the concentration of the reductant.

| Equivalents of LAH | Rate ($s^{-1}$) |
|---|---|
| 2.5 | 8.85E-04 |
| 5 | 3.61E-04 |
| 10 | 9.34E-04 |
| 10 | 9.53E-04 |
| 10 | 1.40E-03 |
| 15 | 2.62E-04 |
| 20 | 1.22E-03 |

## D. Eyring Kinetic Experiments




**14** **20** **10**

To **14** (6:1 trans:cis mix of diastereomers, 0.0414 g, 0.075 mmol) and triphenylphosphine (0.005 g, 0.02 mmol) dissolved in THF (0.5 mL) in a J. Young NMR tube sealed under a nitrogen atmosphere and cooled in a dry ice/acetone bath was added a solution of $LiAlH_4$ (0.014 g, 0.375 mmol) in THF (0.5 mL) via a septum. The NMR tube was resealed and removed from the cooling bath, shaken twice to mix the reagents and placed in an NMR probe thermostatted at the desired temperature. The reaction course was monitored by $^{31}P$ NMR ($D_1$=5 sec), only the major diastereomer was integrated.

| Temp (K) | k ($s^{-1}$) | 1/T (1/ K) | ln(k/T) |
|---|---|---|---|
| 228 | 4.09E-03 | 4.39E-03 | -1.09E+01 |
| 223 | 1.05E-03 | 4.48E-03 | -1.23E+01 |
| 218 | 7.33E-04 | 4.59E-03 | -1.26E+01 |
| 213 | 1.75E-04 | 4.69E-03 | -1.40E+01 |
| 208 | 1.19E-04 | 4.81E-03 | -1.44E+01 |
| 203 | 5.22E-05 | 4.93E-03 | -1.52E+01 |

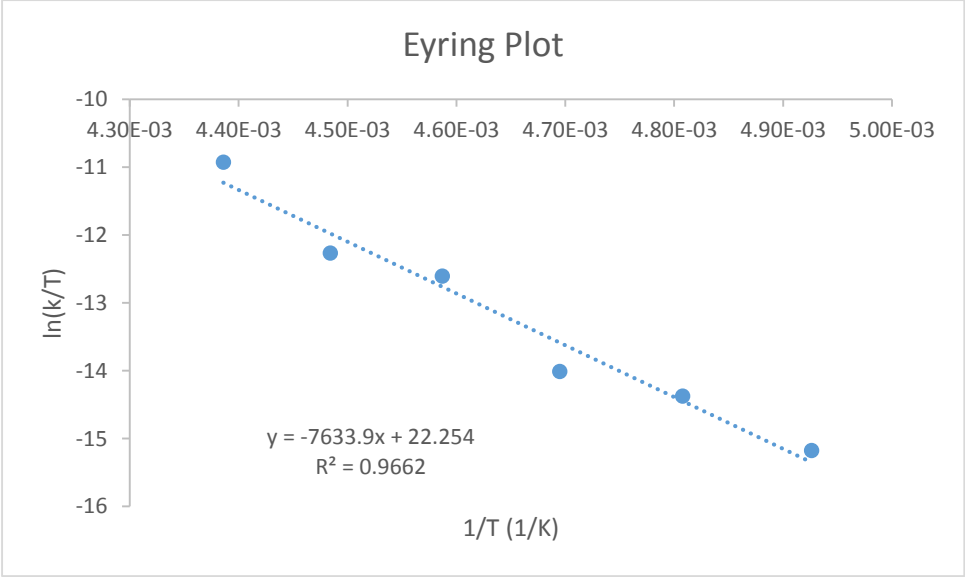



**Figure S1**: Eyring plot of the conversion of **20** to **10** from –70 to –45 °C.

## V. COMPUTATIONAL DATA

### A. General Computational Information

Geometries were optimized in Gaussian 09[31] using the M06-2X[32] density functional with 6-311++G(2d,2p) basis set. Geometry optimizations were performed in the gas phase without symmetry constraint. Stationary points were characterized by frequency calculations to confirm their identity as either local minima (zero imaginary frequencies) or first-order saddle points (one imaginary frequency). For transition structure **TS**, an intrinsic reaction coordinate (IRC) calculation was conducted to ensure connection along the potential energy surface to **21** and products.

### B. Relative Energies of Polytopal Isomers of 21

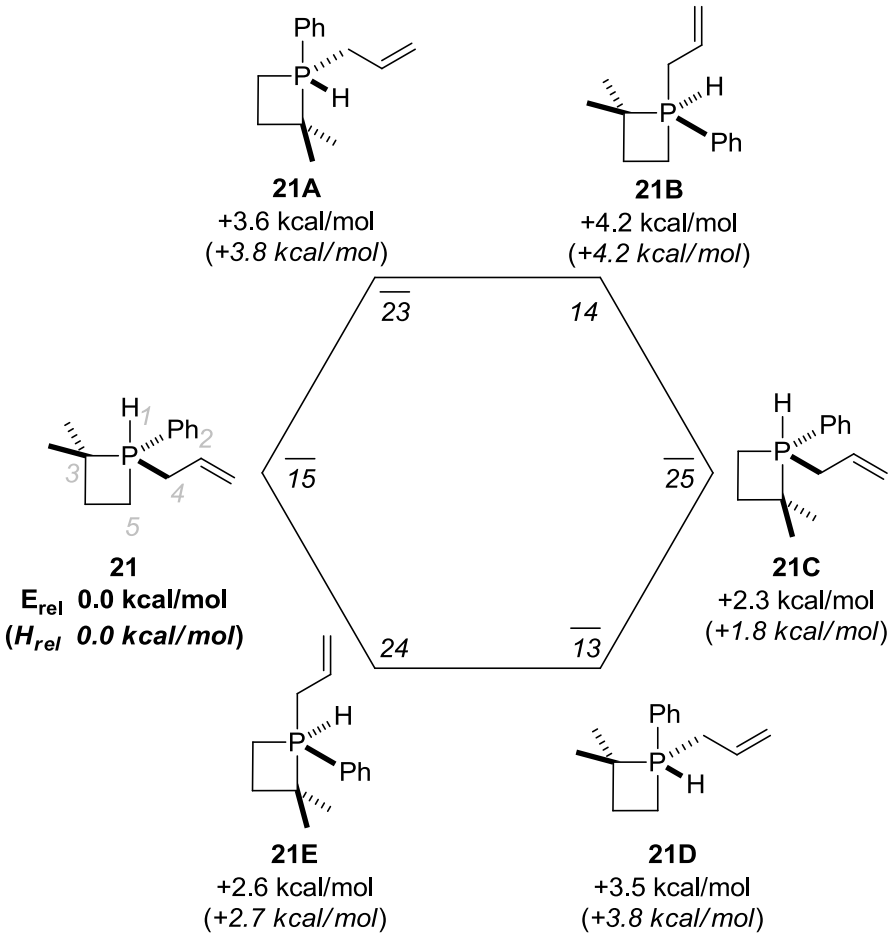
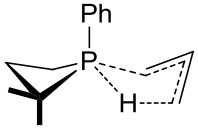
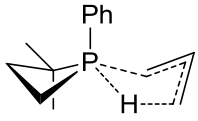



**Figure S2.** Graphical representation and computed relative energies for the polytopal rearrangement of **21**. All geometries optimized at M06-2X/6-311++G(2d,2p). Energies (*enthalpies*) reported in kcal/mol.

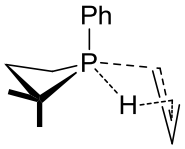
## C. Transition structures for concerted group transfer



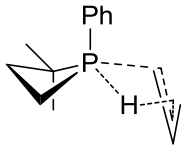

**TS**
**$E_{rel}$ 12.1 kcal/mol**
**(*$H_{rel}$ 11.9 kcal/mol*)**




**TS-*anti***
$E_{rel}$ 13.1 kcal/mol
($H_{rel}$ *12.8 kcal/mol*)




**TS-*exo***
$E_{rel}$ 14.8 kcal/mol
($H_{rel}$ *14.7 kcal/mol*)




**TS-*anti-exo***
$E_{rel}$ 15.1 kcal/mol
($H_{rel}$ *15.0 kcal/mol*)

**Figure S3.** Computed relative energies for concerted group transfer rearrangements. All geometries optimized at M06-2X/6-311++G(2d,2p). Energies (*enthalpies*) reported in kcal/mol relative to **21**.

**D. Cartesian coordinates**

M06-2X/6-311++G(2d,2p) stationary points in Å units and the absolute thermochemical data in Hartrees.

**21** — $E_{rel}$ = 0.0 kcal.mol

Temperature = 298.15 K
Pressure = 1.000 atm
Electronic and zero-point energies = -886.986744
Enthalpy = -886.969658

| | | | |
|---|---|---|---|
| 15 | -0.379547 | -0.044457 | -0.194206 |
| 6 | -1.513539 | 1.437892 | 0.060838 |
| 6 | -0.695943 | 0.054730 | 1.759533 |
| 6 | -1.892366 | 0.977213 | 1.479472 |
| 1 | -0.915347 | -0.847731 | 2.332074 |
| 1 | 0.106707 | 0.590560 | 2.266838 |
| 1 | -2.831480 | 0.424534 | 1.451483 |
| 1 | -2.008812 | 1.802477 | 2.184169 |
| 6 | -1.064527 | -1.760803 | -0.411401 |
| 1 | -0.946813 | -2.032485 | -1.458893 |
| 1 | -0.408153 | -2.389093 | 0.194680 |
| 6 | -2.483548 | -1.934266 | 0.025080 |
| 1 | -2.677154 | -1.847043 | 1.088476 |
| 6 | -3.491449 | -2.194710 | -0.797176 |
| 1 | -4.500052 | -2.315633 | -0.427832 |
| 1 | -3.335168 | -2.296722 | -1.863965 |
| 1 | -0.307669 | 0.193319 | -1.645192 |
| 6 | 1.464910 | -0.136936 | -0.143466 |
| 6 | 2.218770 | 0.371815 | -1.195974 |
| 6 | 2.122020 | -0.740963 | 0.927460 |
| 6 | 3.606272 | 0.293941 | -1.175881 |
| 1 | 1.714031 | 0.828360 | -2.037786 |
| 6 | 3.504847 | -0.849518 | 0.935932 |
| 1 | 1.547947 | -1.133173 | 1.756562 |
| 6 | 4.250222 | -0.322753 | -0.112608 |
| 1 | 4.181565 | 0.707219 | -1.992891 |
| 1 | 4.002588 | -1.336630 | 1.763264 |
| 1 | 5.329093 | -0.394081 | -0.099344 |
| 6 | -2.628503 | 1.591602 | -0.956412 |
| 1 | -3.287061 | 0.723174 | -0.965997 |
| 1 | -3.228678 | 2.475824 | -0.727579 |
| 1 | -2.217214 | 1.721271 | -1.959420 |
| 6 | -0.618649 | 2.678487 | 0.075660 |
| 1 | -0.151270 | 2.833325 | -0.899588 |
| 1 | -1.217478 | 3.563324 | 0.304542 |
| 1 | 0.172519 | 2.601664 | 0.823145 |

**21A** — $E_{rel}$ = +3.6 kcal.mol

Temperature = 298.15 K
Pressure = 1.000 atm
Electronic and zero-point energies = -886.980982
Enthalpy = -886.963533

| | | | |
|---|---|---|---|
| 6 | -2.630982 | -0.292641 | 0.181851 |
| 6 | -2.414838 | -1.785454 | 0.493268 |
| 6 | -1.039547 | -1.954791 | -0.168285 |
| 1 | -3.191169 | -2.445976 | 0.104784 |
| 1 | -2.332093 | -1.953111 | 1.568308 |
| 15 | -0.656007 | -0.142246 | 0.098987 |
| 1 | -0.619365 | 0.199044 | 1.470248 |
| 6 | -0.531891 | 1.366609 | -1.023360 |
| 6 | 1.247887 | -0.355295 | 0.092135 |
| 6 | 1.913912 | -0.834570 | -1.036064 |
| 6 | 2.002788 | -0.066225 | 1.222471 |
| 6 | 3.290331 | -1.016454 | -1.037430 |
| 1 | 1.352695 | -1.073964 | -1.934853 |
| 6 | 3.383585 | -0.241430 | 1.233281 |
| 1 | 1.509938 | 0.313317 | 2.111703 |
| 6 | 4.030247 | -0.716862 | 0.101579 |
| 1 | 3.787117 | -1.392022 | -1.922081 |
| 1 | 3.952693 | -0.002291 | 2.121822 |
| 1 | 5.102572 | -0.855184 | 0.104537 |
| 1 | -1.499689 | 1.545620 | -1.481862 |
| 1 | 0.204544 | 1.157189 | -1.796075 |
| 6 | -0.104914 | 2.535935 | -0.194173 |
| 1 | -0.872941 | 2.986326 | 0.426771 |
| 6 | 1.133336 | 3.010527 | -0.146881 |
| 1 | 1.925029 | 2.571383 | -0.741662 |
| 1 | 1.391977 | 3.842576 | 0.492751 |
| 6 | -3.330456 | -0.133538 | -1.164148 |
| 1 | -4.312802 | -0.615346 | -1.146053 |
| 1 | -3.495767 | 0.916337 | -1.410438 |
| 1 | -2.764316 | -0.581274 | -1.985831 |
| 6 | -3.333876 | 0.509923 | 1.257882 |
| 1 | -3.349677 | 1.573119 | 1.002694 |
| 1 | -4.373357 | 0.193621 | 1.392220 |
| 1 | -2.832881 | 0.405672 | 2.223328 |
| 1 | -0.320156 | -2.637583 | 0.276715 |
| 1 | -1.115732 | -2.168158 | -1.234575 |

**21B** — $E_{rel}$ = +4.2 kcal.mol

Temperature = 298.15 K
Pressure = 1.000 atm
Electronic and zero-point energies = -886.979973
Enthalpy = -886.963016

| | | | |
|---|---|---|---|
| 6 | -0.394348 | -1.682836 | -1.476249 |
| 6 | -1.748531 | -2.075254 | -0.879665 |
| 6 | -1.710139 | -1.194556 | 0.384366 |
| 1 | 0.406697 | -2.338252 | -1.135902 |
| 1 | -0.360122 | -1.620350 | -2.563378 |
| 1 | -1.883478 | -3.136663 | -0.662802 |
| 1 | -2.571283 | -1.755188 | -1.521506 |
| 15 | -0.502395 | -0.005540 | -0.454013 |
| 1 | -0.948587 | 0.710093 | -1.587200 |
| 6 | -0.910447 | 1.613091 | 0.623769 |
| 6 | -2.151299 | 2.272690 | 0.148125 |
| 1 | -0.055698 | 2.271333 | 0.466931 |
| 1 | -0.968139 | 1.370987 | 1.686566 |
| 6 | -2.222199 | 3.042314 | -0.937211 |
| 1 | -3.069029 | 2.073470 | 0.689543 |
| 1 | -1.336907 | 3.287632 | -1.512426 |
| 6 | -0.959673 | -1.883990 | 1.526679 |
| 1 | -0.757730 | -1.187452 | 2.343044 |
| 1 | -1.575848 | -2.693995 | 1.924174 |
| 1 | -0.010263 | -2.308844 | 1.199725 |
| 6 | -3.051162 | -0.678108 | 0.870532 |
| 1 | -3.660346 | -1.527660 | 1.190766 |
| 1 | -2.944281 | -0.010731 | 1.726351 |
| 1 | -3.590910 | -0.151761 | 0.084292 |
| 6 | 1.311081 | 0.110597 | -0.116276 |
| 6 | 2.198360 | -0.164989 | -1.154931 |
| 6 | 1.821678 | 0.441265 | 1.136196 |
| 6 | 3.568449 | -0.077590 | -0.956451 |
| 1 | 1.812372 | -0.452334 | -2.124238 |
| 6 | 3.194350 | 0.485097 | 1.348299 |
| 1 | 1.153248 | 0.665572 | 1.955600 |
| 6 | 4.069613 | 0.238381 | 0.300197 |
| 1 | 4.245011 | -0.269203 | -1.777823 |
| 1 | 3.578003 | 0.722713 | 2.330863 |
| 1 | 5.137386 | 0.288603 | 0.461862 |
| 1 | -3.158563 | 3.468455 | -1.268520 |

**21C** — $E_{rel}$ = +2.3 kcal.mol

Temperature = 298.15 K
Pressure = 1.000 atm
Electronic and zero-point energies = -886.983130
Enthalpy = -886.966816

| | | | |
|---|---|---|---|
| 15 | 0.559376 | -0.360286 | 0.381840 |
| 6 | 1.684501 | 0.293378 | 1.715253 |
| 6 | 0.863844 | 1.602939 | -0.036905 |
| 6 | 2.082456 | 1.525123 | 0.900735 |
| 1 | 2.994716 | 1.323174 | 0.337434 |
| 1 | 2.246242 | 2.428863 | 1.490061 |
| 6 | 1.410655 | -1.110473 | -1.089151 |
| 1 | 0.843293 | -2.014725 | -1.304969 |
| 1 | 1.336057 | -0.432169 | -1.935405 |
| 6 | 2.829516 | -1.444805 | -0.763505 |
| 1 | 3.551481 | -0.638755 | -0.844398 |
| 6 | 3.233621 | -2.637446 | -0.344922 |
| 1 | 4.266729 | -2.823633 | -0.087456 |
| 1 | 2.538701 | -3.462774 | -0.253234 |
| 1 | 0.469277 | -1.679076 | 1.014279 |
| 6 | -1.269156 | -0.397611 | 0.136348 |
| 6 | -2.082701 | -1.049481 | 1.055936 |
| 6 | -1.845307 | 0.178854 | -0.992415 |
| 6 | -3.458369 | -1.102343 | 0.867141 |
| 1 | -1.633667 | -1.526197 | 1.918829 |
| 6 | -3.213745 | 0.092734 | -1.205545 |
| 1 | -1.219271 | 0.692351 | -1.710022 |
| 6 | -4.023650 | -0.538110 | -0.268326 |
| 1 | -4.085555 | -1.594469 | 1.597622 |
| 1 | -3.649673 | 0.522185 | -2.097071 |
| 1 | -5.091890 | -0.592526 | -0.426153 |
| 1 | 2.456004 | -0.426023 | 1.986262 |
| 1 | 1.091137 | 0.528871 | 2.599320 |
| 6 | -0.221691 | 2.462051 | 0.609779 |
| 1 | 0.134864 | 3.489131 | 0.737668 |
| 1 | -1.126111 | 2.497132 | 0.002423 |
| 1 | -0.512323 | 2.090406 | 1.595762 |
| 6 | 1.198053 | 2.144590 | -1.419391 |
| 1 | 1.512355 | 3.192387 | -1.353503 |
| 1 | 2.017150 | 1.596914 | -1.889090 |
| 1 | 0.341697 | 2.116823 | -2.096147 |

**21D —** $E_{rel}$ = +3.5 kcal.mol

Temperature = 298.15 K
Pressure = 1.000 atm
Electronic and zero-point energies = -886.981106
Enthalpy = -886.963822

| | | | |
|---|---|---|---|
| 6 | 2.833297 | 0.828178 | -0.420794 |
| 6 | 3.009455 | -0.665057 | -0.708564 |
| 6 | 1.750587 | -1.194674 | 0.011116 |
| 1 | 3.304018 | 1.114206 | 0.520241 |
| 1 | 3.163316 | 1.513951 | -1.200343 |
| 1 | 3.933530 | -1.115255 | -0.341266 |
| 1 | 2.934668 | -0.872234 | -1.777572 |
| 15 | 0.912148 | 0.488514 | -0.236256 |
| 1 | 0.704156 | 0.740889 | -1.605150 |
| 6 | 2.021022 | -1.436502 | 1.497020 |
| 1 | 1.100454 | -1.670553 | 2.032371 |
| 1 | 2.693143 | -2.291556 | 1.605898 |
| 1 | 2.494393 | -0.579517 | 1.978584 |
| 6 | 1.081385 | -2.406205 | -0.614439 |
| 1 | 1.764728 | -3.258499 | -0.567402 |
| 1 | 0.166054 | -2.677215 | -0.088268 |
| 1 | 0.830388 | -2.229599 | -1.660894 |
| 6 | 0.528502 | 1.969597 | 0.862358 |
| 6 | -0.899557 | -0.155761 | -0.090970 |
| 6 | -1.469179 | -0.541827 | 1.123892 |
| 6 | -1.656920 | -0.334483 | -1.243870 |
| 6 | -2.743339 | -1.092126 | 1.183560 |
| 1 | -0.918115 | -0.414300 | 2.049830 |
| 6 | -2.936976 | -0.877001 | -1.197810 |
| 1 | -1.245160 | -0.039609 | -2.203953 |
| 6 | -3.482792 | -1.260726 | 0.018773 |
| 1 | -3.161450 | -1.387178 | 2.136884 |
| 1 | -3.506913 | -0.996941 | -2.109549 |
| 1 | -4.476877 | -1.683695 | 0.062262 |
| 1 | 1.467581 | 2.338109 | 1.267395 |
| 1 | -0.127562 | 1.659212 | 1.671387 |
| 6 | -0.139144 | 3.002497 | 0.010975 |
| 1 | 0.510135 | 3.567375 | -0.650496 |
| 6 | -1.447946 | 3.220461 | -0.016763 |
| 1 | -2.123485 | 2.662042 | 0.619570 |
| 1 | -1.879589 | 3.954424 | -0.682600 |

**21E —** $E_{rel}$ = +2.6 kcal.mol

Temperature = 298.15 K
Pressure = 1.000 atm
Electronic and zero-point energies = -886.982563
Enthalpy = -886.965301

| | | | |
|---|---|---|---|
| 6 | -0.603346 | 1.908906 | 0.088995 |
| 6 | -1.898939 | 1.958844 | -0.744527 |
| 6 | -1.796968 | 0.574343 | -1.399176 |
| 1 | -1.953062 | 2.793638 | -1.444467 |
| 1 | -2.777992 | 1.994760 | -0.098793 |
| 15 | -0.756503 | -0.070606 | 0.001005 |
| 1 | -1.392653 | -0.101603 | 1.265507 |
| 6 | -1.194562 | -1.966129 | -0.222224 |
| 6 | -2.651726 | -2.176391 | -0.051475 |
| 1 | -0.628626 | -2.482561 | 0.555038 |
| 1 | -0.843441 | -2.316781 | -1.193493 |
| 6 | -3.260231 | -2.311950 | 1.125222 |
| 1 | -3.267331 | -2.147523 | -0.945488 |
| 1 | -2.692353 | -2.359693 | 2.047072 |
| 6 | 1.047317 | -0.424502 | 0.029378 |
| 6 | 1.785876 | -0.102144 | 1.166000 |
| 6 | 1.697996 | -0.964082 | -1.075035 |
| 6 | 3.153780 | -0.335664 | 1.202961 |
| 1 | 1.292017 | 0.336400 | 2.023968 |
| 6 | 3.072182 | -1.169490 | -1.049201 |
| 1 | 1.137257 | -1.222249 | -1.965018 |
| 6 | 3.800480 | -0.863091 | 0.092006 |
| 1 | 3.715945 | -0.097371 | 2.095477 |
| 1 | 3.571311 | -1.574959 | -1.918446 |
| 1 | 4.867615 | -1.033596 | 0.116005 |
| 1 | -4.334560 | -2.402012 | 1.201772 |
| 6 | -0.700892 | 2.562876 | 1.453635 |
| 1 | 0.248077 | 2.502077 | 1.991168 |
| 1 | -0.957017 | 3.624155 | 1.371910 |
| 1 | -1.470182 | 2.088799 | 2.069411 |
| 6 | 0.567691 | 2.472228 | -0.707579 |
| 1 | 0.442216 | 3.547814 | -0.866829 |
| 1 | 1.514302 | 2.318549 | -0.187458 |
| 1 | 0.661670 | 2.004856 | -1.691205 |
| 1 | -2.711807 | 0.020918 | -1.591757 |
| 1 | -1.185777 | 0.582942 | -2.303334 |

**TS —** $E_{rel}$ = +12.1 kcal.mol

Lowest Frequency Vibration = -1118.2422 cm^-1
Temperature = 298.15 K
Pressure = 1.000 atm
Electronic and zero-point energies = -886.967477
Enthalpy = -886.950676

| | | | |
|---|---|---|---|
| 6 | 1.510070 | -0.334339 | 1.792549 |
| 6 | 1.835657 | -1.649146 | 1.064172 |
| 6 | 1.852882 | -1.086513 | -0.373668 |
| 1 | 1.013062 | -2.356003 | 1.178924 |
| 1 | 2.760194 | -2.140401 | 1.374890 |
| 15 | 0.810344 | 0.399024 | 0.213833 |
| 6 | 0.330339 | 2.469430 | 1.061524 |
| 6 | -0.397592 | 2.894368 | -0.053990 |
| 1 | 1.366450 | 2.780537 | 1.148865 |
| 1 | -0.172168 | 2.330616 | 2.012073 |
| 6 | 0.226628 | 2.936570 | -1.288454 |
| 1 | -1.477796 | 2.800556 | -0.025429 |
| 1 | -0.348102 | 3.088894 | -2.191998 |
| 1 | 1.268289 | 3.232310 | -1.348977 |
| 1 | 0.751766 | 1.425717 | -1.064515 |
| 6 | -0.903710 | -0.206720 | 0.109434 |
| 6 | -1.500617 | -0.291429 | -1.149253 |
| 6 | -1.666878 | -0.508774 | 1.235084 |
| 6 | -2.825970 | -0.683778 | -1.279067 |
| 1 | -0.925219 | -0.046342 | -2.032305 |
| 6 | -2.992198 | -0.902568 | 1.106213 |
| 1 | -1.233433 | -0.430315 | 2.222746 |
| 6 | -3.574687 | -0.991267 | -0.151043 |
| 1 | -3.273459 | -0.746991 | -2.261381 |
| 1 | -3.569975 | -1.137932 | 1.989432 |
| 1 | -4.607031 | -1.296291 | -0.250690 |
| 1 | 0.856430 | -0.375983 | 2.659809 |
| 1 | 2.402331 | 0.228063 | 2.066347 |
| 6 | 1.320531 | -1.993435 | -1.465285 |
| 1 | 0.355293 | -2.422699 | -1.199159 |
| 1 | 1.202700 | -1.446031 | -2.403737 |
| 1 | 2.020498 | -2.812844 | -1.651967 |
| 6 | 3.233461 | -0.552562 | -0.752445 |
| 1 | 3.930639 | -1.379329 | -0.909942 |
| 1 | 3.181368 | 0.027178 | -1.675923 |
| 1 | 3.655499 | 0.092909 | 0.020815 |

**TS-*anti* —** $E_{rel}$ = +13.1 kcal.mol

Lowest Frequency Vibration = -1109.1299 cm^-1
Temperature = 298.15 K
Pressure = 1.000 atm
Electronic and zero-point energies = -886.965880
Enthalpy = -886.949256

| | | | |
|---|---|---|---|
| 6 | 1.876813 | -0.973693 | 0.354897 |
| 6 | 1.651006 | -1.947778 | -0.819306 |
| 6 | 1.234201 | -0.911592 | -1.873047 |
| 1 | 0.814772 | -2.610277 | -0.592886 |
| 1 | 2.520550 | -2.559205 | -1.070633 |
| 1 | 0.481864 | -1.214218 | -2.596070 |
| 1 | 2.088570 | -0.506056 | -2.414707 |
| 15 | 0.745157 | 0.301915 | -0.514204 |
| 6 | 0.951126 | 2.019269 | 1.048968 |
| 6 | -0.073282 | 2.786833 | 0.486752 |
| 1 | 1.972817 | 2.258350 | 0.774038 |
| 1 | 0.846800 | 1.632957 | 2.056040 |
| 6 | 0.040019 | 3.214421 | -0.823378 |
| 1 | -1.062780 | 2.726203 | 0.926378 |
| 1 | -0.804533 | 3.655455 | -1.334434 |
| 1 | 1.014049 | 3.487080 | -1.213769 |
| 1 | 0.397523 | 1.686342 | -1.264872 |
| 6 | -0.977341 | -0.194315 | -0.154253 |
| 6 | -1.853906 | -0.459200 | -1.205408 |
| 6 | -1.472874 | -0.220092 | 1.149269 |
| 6 | -3.184702 | -0.770510 | -0.961020 |
| 1 | -1.501240 | -0.411770 | -2.226613 |
| 6 | -2.800440 | -0.541183 | 1.396894 |
| 1 | -0.821157 | 0.018571 | 1.977767 |
| 6 | -3.659419 | -0.820323 | 0.342287 |
| 1 | -3.849985 | -0.971194 | -1.789353 |
| 1 | -3.165501 | -0.563797 | 2.414410 |
| 1 | -4.694759 | -1.064998 | 0.535250 |
| 6 | 1.514677 | -1.490022 | 1.732970 |
| 1 | 1.527309 | -0.687486 | 2.473388 |
| 1 | 0.531721 | -1.958155 | 1.743592 |
| 1 | 2.248077 | -2.236873 | 2.050462 |
| 6 | 3.299788 | -0.417761 | 0.354573 |
| 1 | 3.413233 | 0.368027 | 1.101743 |
| 1 | 4.005231 | -1.216374 | 0.597094 |
| 1 | 3.586092 | -0.005625 | -0.614967 |

**TS-*exo*** — $E_{rel}$ = +14.8 kcal.mol

Lowest Frequency Vibration = -1059.6060 cm^-1
Temperature = 298.15 K
Pressure = 1.000 atm
Electronic and zero-point energies = -886.963144
Enthalpy = -886.946209

| | | | |
|---|---|---|---|
| 6 | 1.304243 | -0.715257 | 1.771365 |
| 6 | 1.262359 | -2.056256 | 1.020369 |
| 6 | 1.421947 | -1.492425 | -0.408805 |
| 1 | 0.282676 | -2.522305 | 1.131263 |
| 1 | 2.025406 | -2.780638 | 1.312856 |
| 15 | 0.803984 | 0.201648 | 0.214814 |
| 6 | 0.875411 | 2.368984 | 1.122323 |
| 6 | 1.523331 | 2.994653 | 0.055336 |
| 1 | 1.335803 | 2.373603 | 2.102659 |
| 1 | -0.210160 | 2.367407 | 1.139208 |
| 6 | 1.038923 | 2.859998 | -1.231414 |
| 1 | 2.566974 | 3.264637 | 0.180240 |
| 1 | 1.611515 | 3.214647 | -2.077281 |
| 1 | -0.030415 | 2.774857 | -1.393712 |
| 1 | 1.118632 | 1.222267 | -1.012410 |
| 6 | -1.007993 | 0.018746 | 0.111639 |
| 6 | -1.615290 | 0.209621 | -1.131883 |
| 6 | -1.811972 | -0.263350 | 1.213550 |
| 6 | -2.991980 | 0.107086 | -1.269937 |
| 1 | -1.005296 | 0.437573 | -1.996941 |
| 6 | -3.190490 | -0.364085 | 1.075934 |
| 1 | -1.368527 | -0.404458 | 2.189493 |
| 6 | -3.783697 | -0.180687 | -0.165378 |
| 1 | -3.446704 | 0.254476 | -2.239926 |
| 1 | -3.799959 | -0.587105 | 1.940870 |
| 1 | -4.856755 | -0.258494 | -0.271826 |
| 1 | 0.679829 | -0.591989 | 2.652367 |
| 1 | 2.317748 | -0.409162 | 2.027316 |
| 6 | 0.662520 | -2.204396 | -1.510321 |
| 1 | -0.379612 | -2.372193 | -1.240666 |
| 1 | 0.685443 | -1.624967 | -2.436526 |
| 1 | 1.121903 | -3.174307 | -1.720945 |
| 6 | 2.893062 | -1.334404 | -0.790630 |
| 1 | 3.346267 | -2.314682 | -0.958095 |
| 1 | 2.992305 | -0.753614 | -1.709257 |
| 1 | 3.470928 | -0.829653 | -0.013776 |

**TS-*exo-anti*** — $E_{rel}$ = +15.1 kcal.mol

Lowest Frequency Vibration = -1087.2903 cm^-1
Temperature = 298.15 K
Pressure = 1.000 atm
Electronic and zero-point energies = -886.962613
Enthalpy = -886.945725

| | | | |
|---|---|---|---|
| 6 | 1.421144 | -1.372300 | 0.369440 |
| 6 | 0.970703 | -2.285638 | -0.791514 |
| 6 | 0.775032 | -1.193903 | -1.855877 |
| 1 | 0.013633 | -2.747500 | -0.546202 |
| 1 | 1.681785 | -3.074864 | -1.043917 |
| 1 | -0.040600 | -1.336857 | -2.558046 |
| 1 | 1.686870 | -0.997508 | -2.419433 |
| 15 | 0.623293 | 0.108772 | -0.500819 |
| 6 | 1.177439 | 1.785707 | 1.173581 |
| 6 | 2.118682 | 2.433940 | 0.375075 |
| 1 | 1.484528 | 1.364133 | 2.123304 |
| 1 | 0.155625 | 2.148092 | 1.148408 |
| 6 | 1.780079 | 2.929389 | -0.870940 |
| 1 | 3.170965 | 2.264674 | 0.584294 |
| 1 | 2.539871 | 3.312492 | -1.537708 |
| 1 | 0.776089 | 3.300809 | -1.043899 |
| 1 | 1.211386 | 1.411854 | -1.213079 |
| 6 | -1.174839 | 0.082497 | -0.171671 |
| 6 | -2.087495 | 0.035690 | -1.225342 |
| 6 | -1.663808 | 0.191625 | 1.132208 |
| 6 | -3.454197 | 0.079261 | -0.982602 |
| 1 | -1.734701 | -0.026620 | -2.245462 |
| 6 | -3.029310 | 0.214694 | 1.375634 |
| 1 | -0.974435 | 0.262959 | 1.962003 |
| 6 | -3.928929 | 0.159501 | 0.318725 |
| 1 | -4.146428 | 0.048147 | -1.812535 |
| 1 | -3.390801 | 0.285859 | 2.392125 |
| 1 | -4.992768 | 0.186044 | 0.508659 |
| 6 | 0.951275 | -1.771264 | 1.753123 |
| 1 | 1.159926 | -0.988651 | 2.484413 |
| 1 | -0.114742 | -1.992855 | 1.769623 |
| 1 | 1.487824 | -2.669272 | 2.071147 |
| 6 | 2.931672 | -1.141361 | 0.363542 |
| 1 | 3.204642 | -0.359575 | 1.072968 |
| 1 | 3.442771 | -2.061856 | 0.654876 |
| 1 | 3.304488 | -0.848112 | -0.619540 |

## VI. CRYSTALLOGRAPHIC DATA

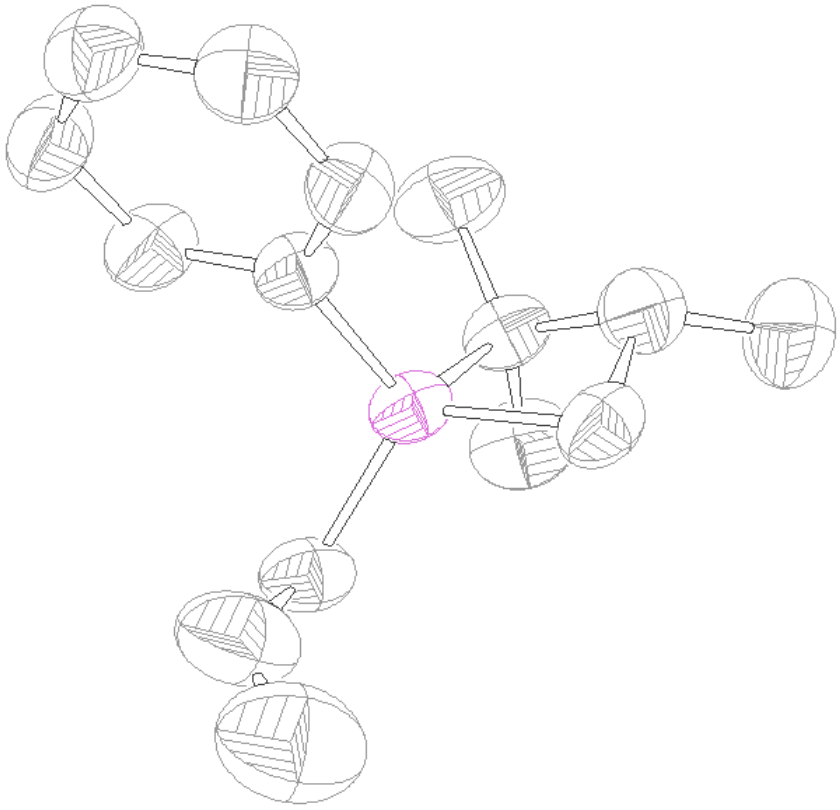


**Figure S4.** Thermal ellipsoid plot (50%) of 1-allyl-2,2,3-trimethyl-1-phenylphosphetanium bromide. Hydrogen atoms and $Br^-$ counterion omitted for clarity.

A colorless block shaped crystal with approximate dimensions 0.19 x 0.25 x 0.29 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 298(2) K, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoKα fine-focus sealed tube (λ = 0.71073Å) operated at 1600 watts power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal. A total of 1850 frames were collected with a scan width of 0.3º in ω and an exposure time of 10 seconds/frame. The total data collection time was about 8 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Orthorhombic unit cell yielded a total of 14351 reflections to a maximum θ angle of 28.30 ° (0.90 Å resolution), of which 3679 were independent, completeness = 99.8%, $R_{int}$ = 0.0264, $R_{sig}$ = 0.0292 and 3070 were greater than 2σ(I). The final cell constants: a = 13.3991(15)Å, b = 13.9186(15)Å, c = 8.4200(9)Å, α = 90°, β = 90°, γ = 90°, volume = 1570.3(3)$Å^3$, are based upon the refinement of the XYZ-centroids of 5656 reflections above 20σ(I) with 2.826° <θ <26.884°. Analysis of the data showed negligible decay during data

collection. Data were corrected for absorption effects using the multiscan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.6060. The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group Pna2(1), with Z = 4 for the formula unit, C15 H22 Br P. Hydrogen atoms were placed geometrically, except for one on C8, and rode the parent atom. The hydrogen atom on C8 was located in difference Fourier map and refined isotropically. The final anisotropic full-matrix least-squares refinement on $F^2$ with 161 variables converged at R1 = 3.35%, for the observed data and wR2 = 8.72% for all data. The goodness-of-fit was 0.998. The largest peak on the final difference map was 0.521 $e^-/Å^3$ and the largest hole was -0.217 $e^-/Å^3$. Based on the final model, the calculated density of the crystal is 1.325 $g/cm^3$ and F(000) amounts to 648 electrons.

**Table S4. Sample and crystal data for 1-allyl-2,2,3-trimethyl-1-phenylphosphetanium bromide**.

| | | |
|---|---|---|
| Crystallization solvents | Methanol/diethyl ether | |
| Crystallization method | slow diffusion | |
| | | |
| Empirical formula | C15 H22 Br P | |
| Formula weight | 313.21 | |
| Temperature | 298(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.29 x 0.25 x 0.19 mm | |
| Crystal habit | colorless block | |
| Crystal system | Orthorhombic | |
| Space group | Pna2(1) | |
| Unit cell dimensions | a = 13.3991(15) Å | α= 90° |
| | b = 13.9186(15) Å | β= 90° |
| | c = 8.4200(9) Å | γ = 90° |
| Volume | 1570.3(3) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.325 $g/cm^3$ | |
| Absorption coefficient | 2.699 $mm^{-1}$ | |
| F(000) | 648 | |

**Table S5. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for 1-allyl-2,2,3-trimethyl-1-phenylphosphetanium bromide.**

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Br1 | 0.079487(19) | 0.315045(17) | 0.51175(7) | 0.06052(11) |
| C1 | 0.1721(2) | 0.0231(2) | 0.7307(4) | 0.0500(6) |
| C2 | 0.0808(2) | 0.0525(2) | 0.6715(5) | 0.0639(9) |
| C3 | -0.0014(2) | -0.0069(3) | 0.6852(5) | 0.0710(9) |
| C4 | 0.0077(3) | -0.0950(2) | 0.7587(4) | 0.0672(9) |
| C5 | 0.0968(2) | -0.1223(2) | 0.8198(5) | 0.0670(9) |
| C6 | 0.1808(2) | -0.0648(2) | 0.8055(4) | 0.0585(7) |
| C7 | 0.3904(2) | 0.0540(2) | 0.7919(4) | 0.0601(8) |
| C8 | 0.3673(3) | 0.1157(3) | 0.9393(4) | 0.0692(9) |
| C9 | 0.2952(3) | 0.1906(2) | 0.8598(4) | 0.0596(8) |
| C10 | 0.3467(3) | 0.2788(3) | 0.7916(5) | 0.0838(12) |
| C11 | 0.2035(3) | 0.2194(3) | 0.9578(6) | 0.0932(14) |
| C12 | 0.4577(3) | 0.1551(4) | 1.0295(8) | 0.1008(13) |
| C13 | 0.2855(2) | 0.1361(2) | 0.4998(4) | 0.0614(7) |
| C14 | 0.2798(4) | 0.0468(4) | 0.3921(5) | 0.0980(14) |
| C15 | 0.3479(5) | 0.0086(4) | 0.3344(8) | 0.131(2) |
| P1 | 0.27813(5) | 0.09993(5) | 0.70392(9) | 0.04843(17) |

*Note: The small molecule crystallographic facility was established using funds from an NSF Chemistry Research Instrumentation and Facilities grant CHE-0131112.*

## VII. REFERENCES


[1] Mika, L. T.; Orha, L.; Farkas, N.; Horvath, I. T. *Organometallics* **2009**, *28*, 1593.

[2] Sun, X.-M.; Manabe, K.; Lam, W. W.-L.; Shiraishi, N.; Kobayashi, J.; Shiro, M.; Utsumi, H.; Kobayashi, S. *Chem. Eur. J.* **2005**, *11*, 361.

[3] Byrne, P. A.; Gilheany, D. G. *J. Am. Chem. Soc.* **2012**, *134*, 9225.

[4] Wetzel, R. B.; Kenyon, G. L. *J. Am. Chem. Soc.* **1974**, *96*, 5189.

[5] Cremer, S. E.; Chorvat, R. J. *J. Org. Chem.* **1967**, *32*, 4066.

[6] Owen, J.S.; Chan, E.M; Liu, H.; Alivisatos, A.P. *J. Am. Chem. Soc.* **2010**, *132*, 18206.

[7] Patil, N. T.; Singh, V. *Chem. Commun.* **2011**, *47*, 11116.

[8] Brussee, J.; Roos, E. C.; Van Der Gen, A. *Tetrahedron Lett.* **1988**, *29*, 4485.

[9] Zeitler, K. *Org. Lett.* **2006**, *8*, 637.

[10] Leung, P.; Teng, Y.; Toy, P. H. *Org. Lett.* **2010**, *12*, 4996.

[11] Bouziane, A.; Helou, M.; Carboni, B.; Carreaux, F.; Demerseman, B.; Bruneau, C.; Renaud, J.-L. *Chem. Eur. J.* **2008**, *14*, 5630.

[12] Granzhan, A.; Teulade-Fichou, M.-P. *Tetrahedron* **2009**, *65*, 1349.

[13] Maether, M.-P.; Bernat, V.; Maturano, M.; Andre-Barres, C.; Ladeira, S.; Valentin, A.; Vial, H.; Payrastre, C. *Org. Biomol.Chem.* **2011**, *9*, 7400.

[14] Kobayashi, K.; Ueno, M.; Knodo, Y. *Chem. Comm.* **2006**, 3128.

[15] Giraud, L.; Huber, V.; Jenny, T. *Tetrahedron* **1998**, *54*, 11899.

[16] DeLuca, R. J.; Sigman, M. S. *Org. Lett.* **2013**, *15*, 92.

[17] Still, W. C.; Gennari, C. *Tetrahedron Lett.* **1983**, *24*, 4405.

[18] Charette, A. B.; Molinaro, C.; Brochu, C. *J. Am. Chem. Soc.* **2001**, *123*, 12168.

[19] Zheng, H.; Lejkowski, M.; Hall, D. G. *Chem. Sci.* **2011**, *2*, 1305.

[20] Whitesides, G.M.; San Filippo, J. *J. Am. Chem. Soc.* **1970**, *92*, 6611.

[21] Frenking, G.; Hülskämper, L.; Weyerstahl, P. *Chem. Ber.* **1982**, *115*, 2826.

[22] Feld, B. K.; Weiss, G. A. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 1665.

[23] Katcher, M. H.; Sha, A.; Doyle, A. G. *J. Am Chem. Soc.* **2011**, *133*, 15902.

[24] Seomoon, D.; Lee, P. H. *J. Org. Chem.* **2008**, *73*, 1165.

[25] Datta, S.; Chang, C.-L.; Yeh, K.-L.; Liu, R.-S. *J. Am. Chem. Soc.* **2003**, *125*, 9294.

[26] Gauthier, D.; Lindhardt, A. T.; Olsen, E. P. K.; Overgaard, J.; Skrydstrup, T. *J. Am. Chem. Soc.* **2010**, *132*, 7998.

[27] Araki, S.; Shimizu, T.; Johar, P. S.; Jin, S.-J.; Butsugan, Y. *J. Org. Chem.* **1991**, *56*, 2538.

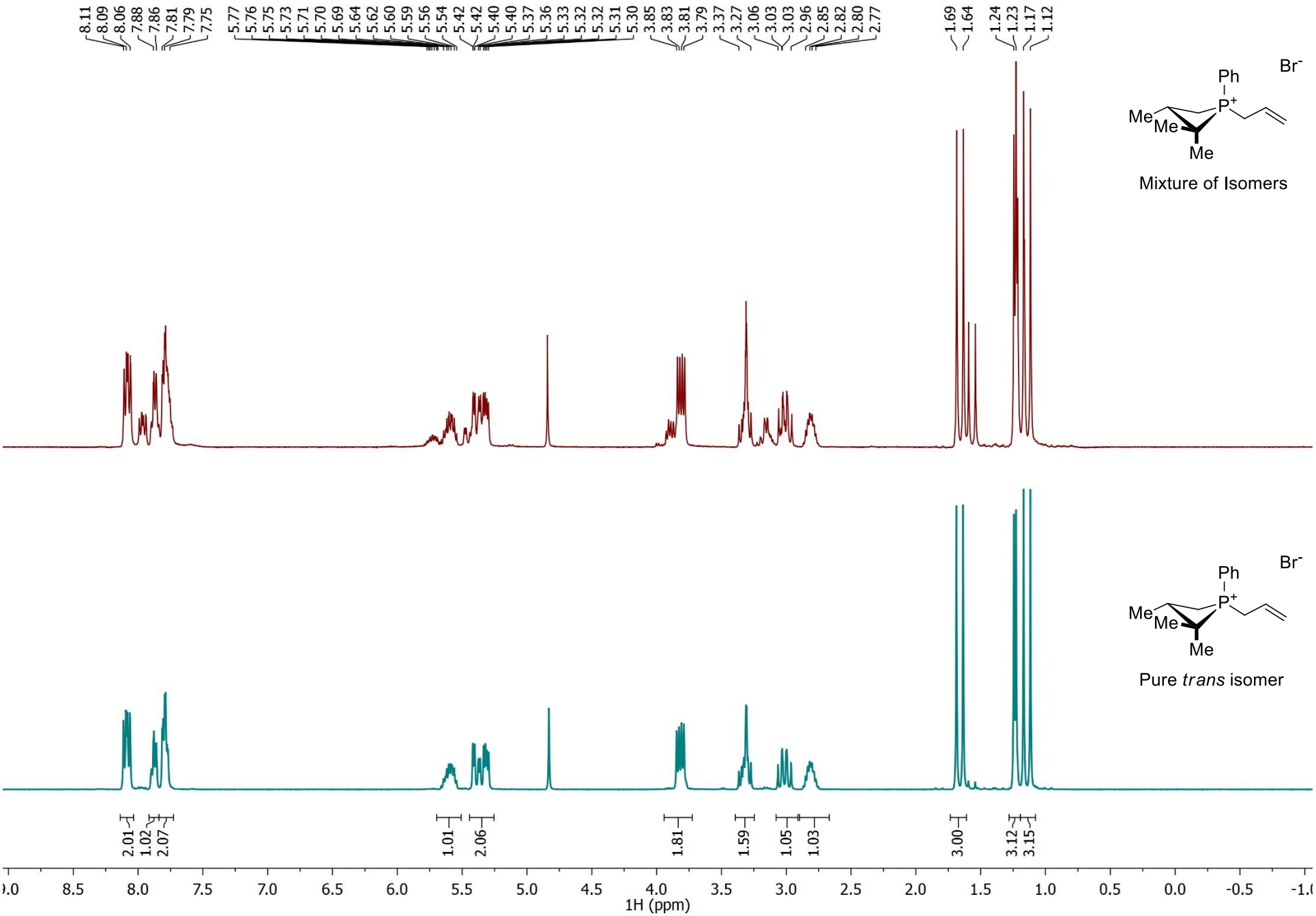
[28] Zhao, X.; Wu, G.; Yan, C.; Lu, K.; Li, Hui.; Zhang, Y.; Wang, J. *Org. Lett.* **2010**, *12*, 5580.

[29] Dieguez, H. R.; Lopez, A.; Domingo, V.; Arteaga, J. F.; Dobado, J. A.; Herrador, M, M.; Quilez del Moral, J. F.; Barrero, A. F. *J. Am. Chem. Soc.* **2010**, *132*, 254.

[30] Steel. P. G.; Thomas, E. J. *J. Chem. Soc., Perkin Trans. 1*. **1997**, 371.

[31] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O¨.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision B.01; Gaussian, Inc.: Wallingford, CT, 2009.

[32] (a) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215. (b) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157.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5.70
5.69
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5.62
5.60
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5.40
5.37
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5.32
5.32
5.31
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3.85
3.83
3.81
3.79
3.37
3.27
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3.03
3.03
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2.85
2.82
2.80
2.77
1.69
1.64
1.24
1.23
1.17
1.12
Br-
Ph
P+
Me
Me
Me
Mixture of Isomers
Br-
Ph
P+
Me
Me
Me
Pure trans isomer
2.01
1.02
2.07
1.01
2.06
1.81
1.59
1.05
1.03
3.00
3.12
3.15
8.5
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7.0
6.5
6.0
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5.0
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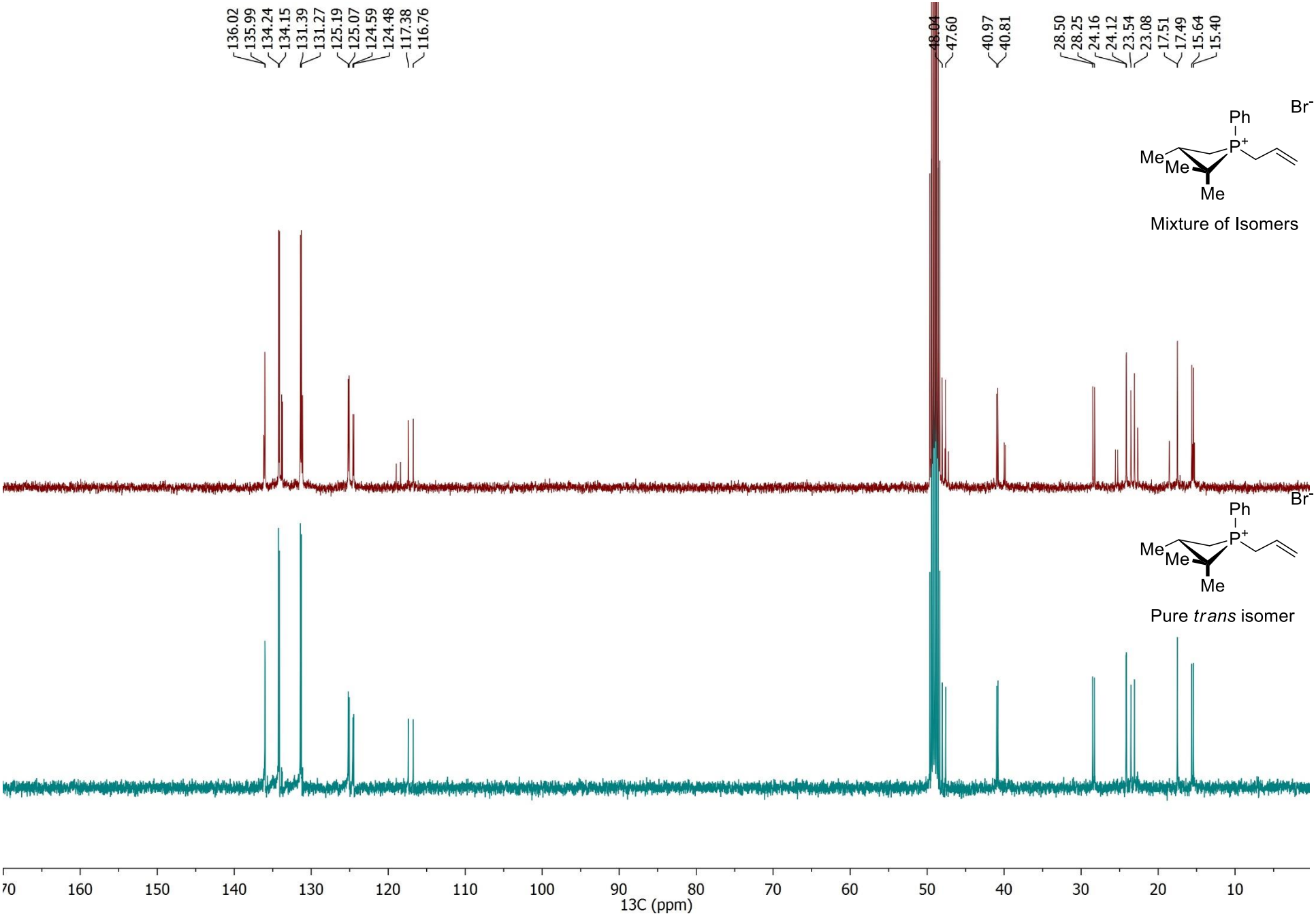
1H (ppm)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48.04
47.60
40.97
40.81
28.50
28.25
24.16
24.12
23.54
23.08
17.51
17.49
15.64
15.40
Br-
Ph
P+
Me
Me
Me
Mixture of Isomers
Br-
Ph
P+
Me
Me
Me
Pure trans isomer
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140
130
120
110
100
90
80
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60
50
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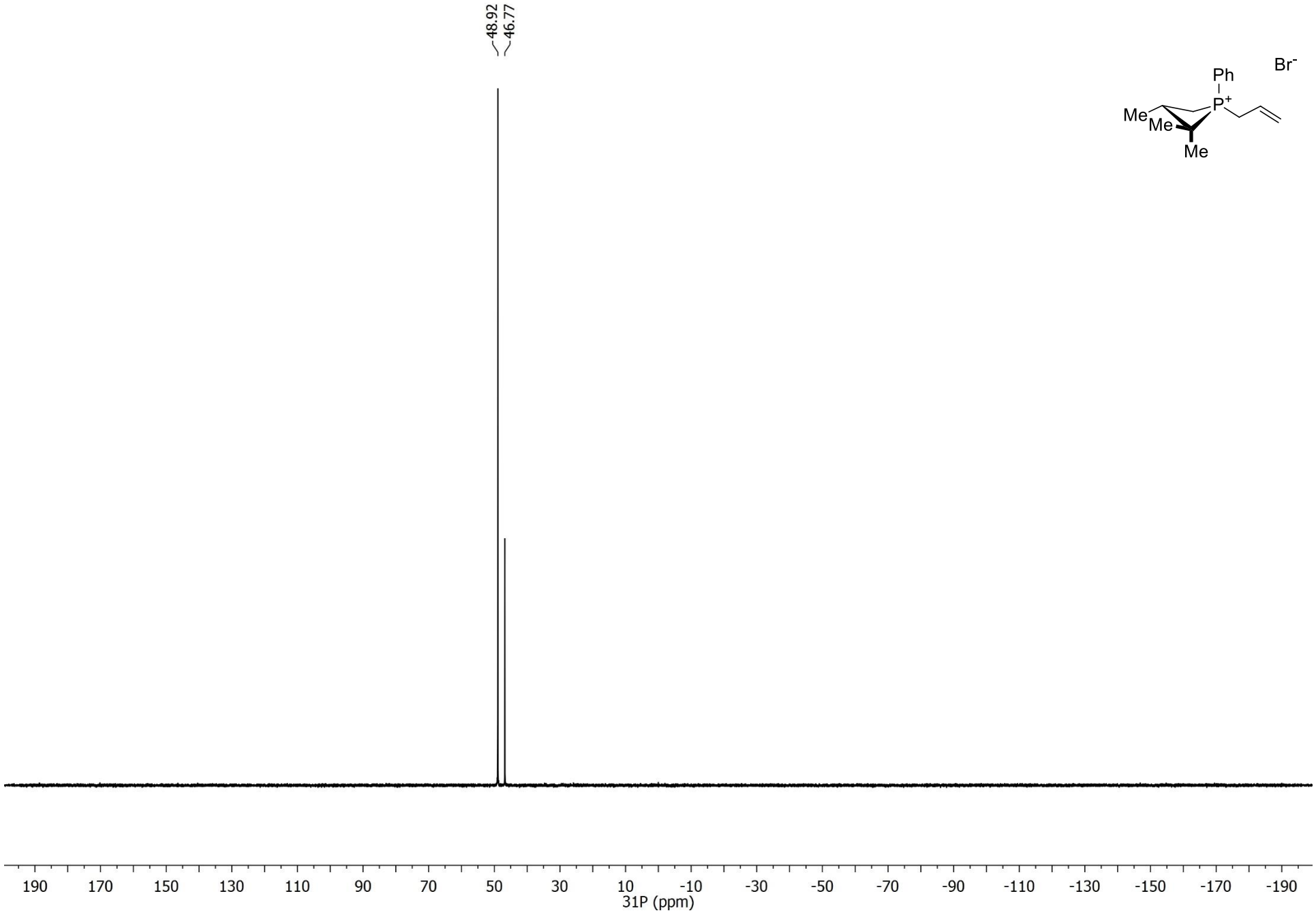
20
10
13C (ppm)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Me
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150
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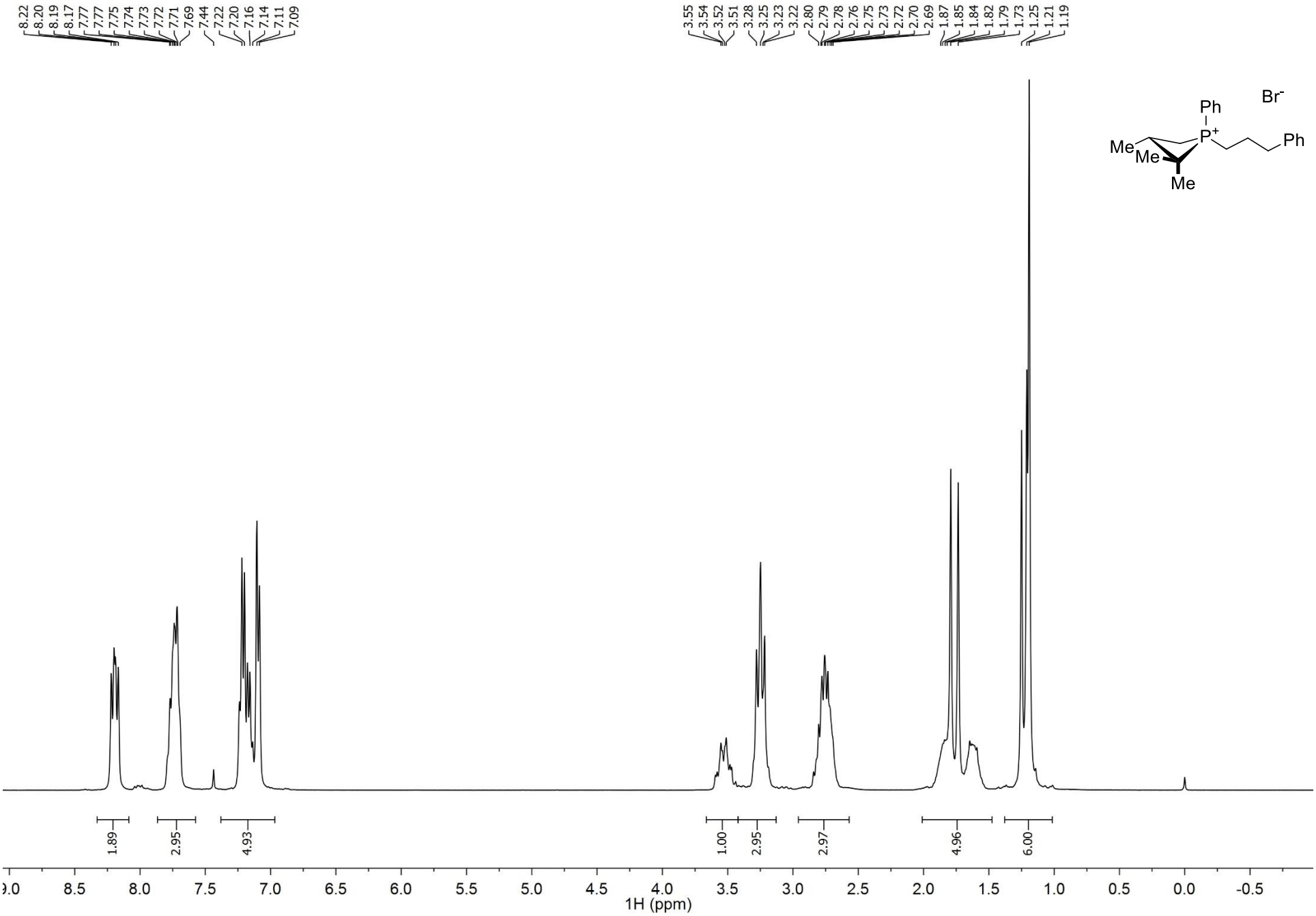
-110
-130
-150
-170
-190
31P (ppm)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7.77
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7.72
7.71
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7.44
7.22
7.20
7.16
7.14
7.11
7.09
3.55
3.54
3.52
3.51
3.28
3.25
3.23
3.22
2.80
2.79
2.78
2.76
2.75
2.73
2.72
2.70
2.69
1.87
1.85
1.84
1.82
1.79
1.73
1.25
1.21
1.19
Ph
Br-
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Me
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Me
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2.97
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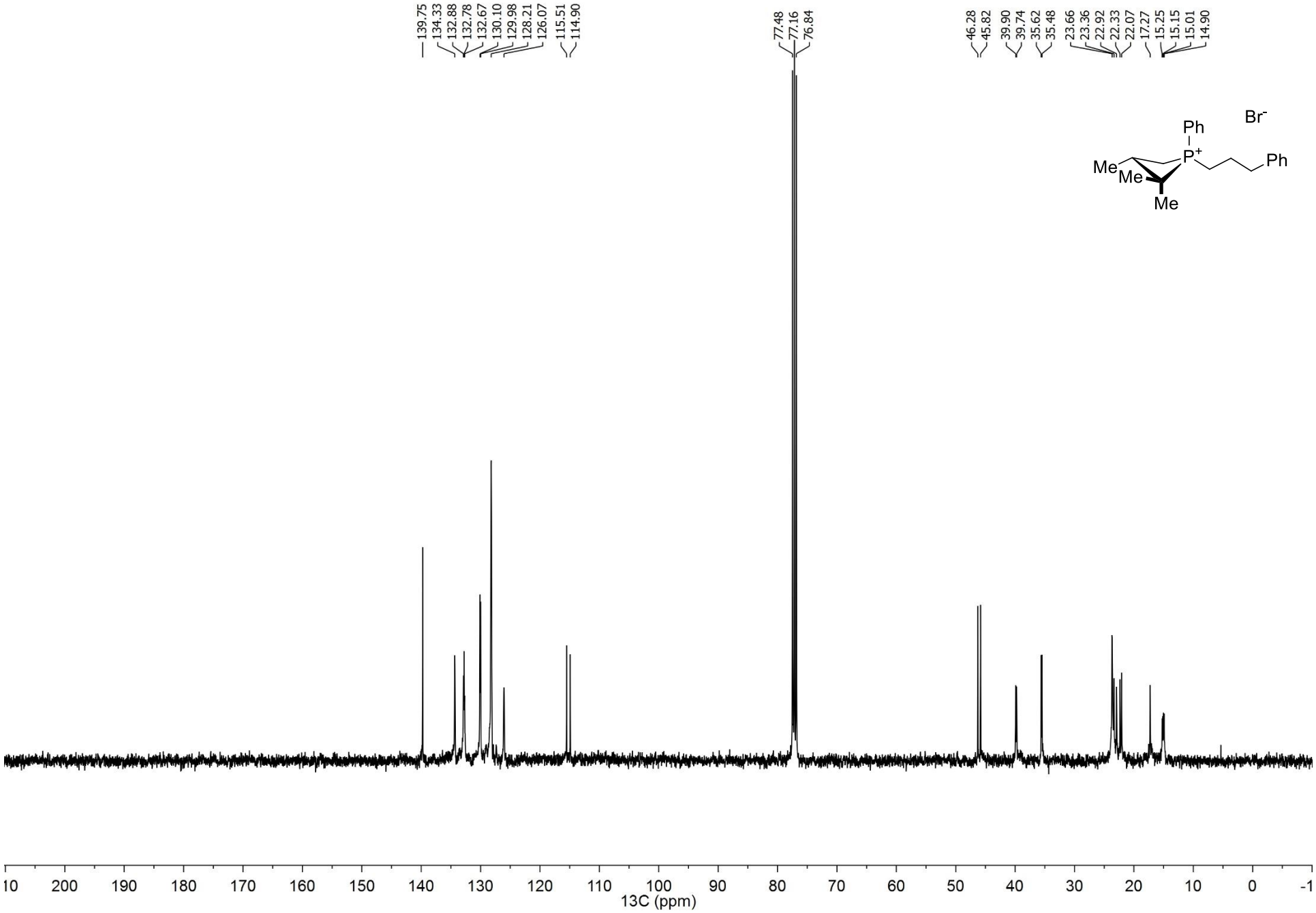
6.00
1H (ppm)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128.21
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115.51
114.90
77.48
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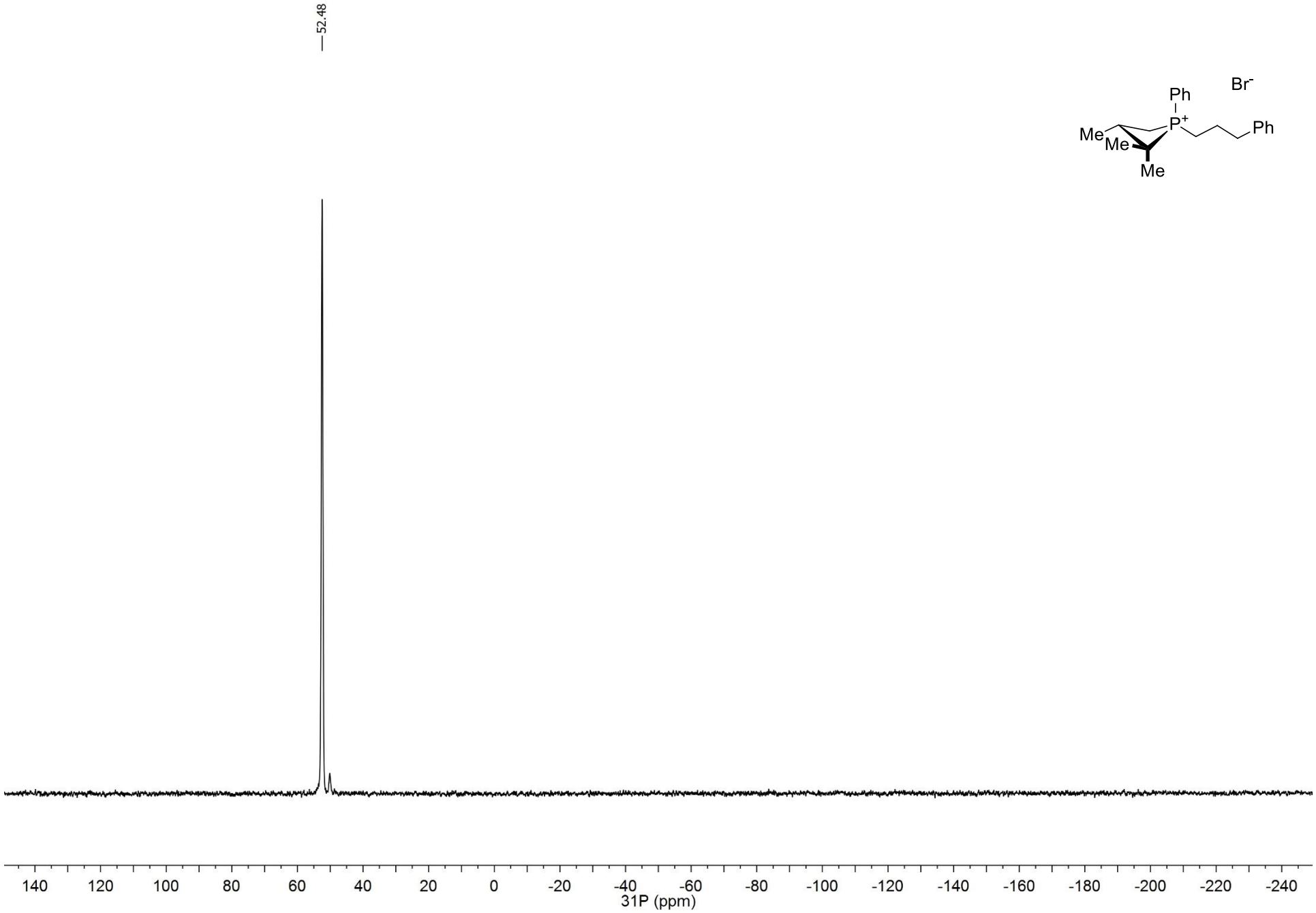
76.84
46.28
45.82
39.90
39.74
35.62
35.48
23.66
23.36
22.92
22.33
22.07
17.27
15.25
15.15
15.01
14.90
Br-
Ph
P+
Ph
Me
Me
Me
13C (ppm)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P+
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80
60
40
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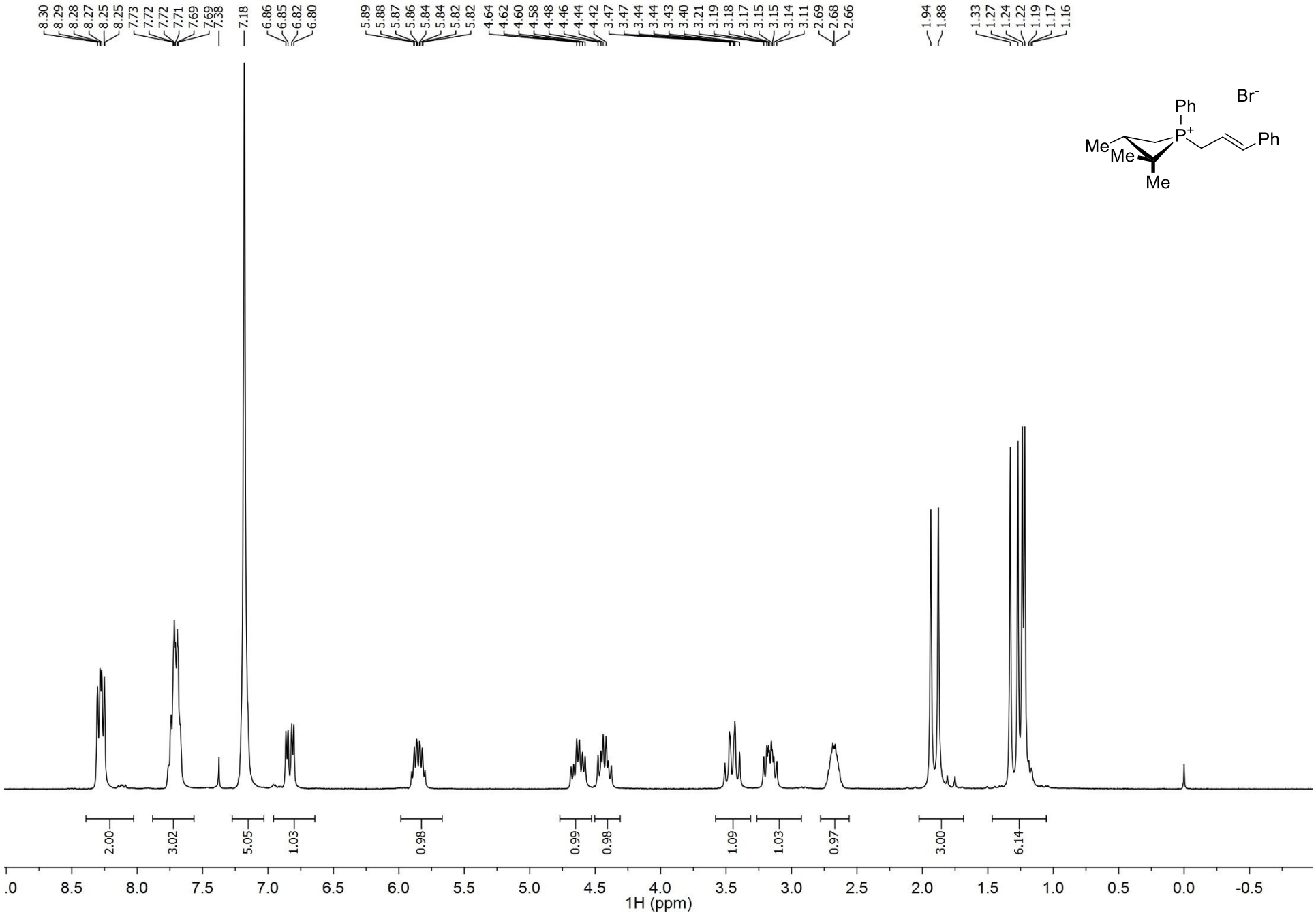
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
31P (ppm)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7.71
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7.69
7.38
7.18
6.86
6.85
6.82
6.80
5.89
5.88
5.87
5.86
5.84
5.84
5.82
5.82
4.64
4.62
4.60
4.58
4.48
4.46
4.44
4.42
3.47
3.47
3.44
3.44
3.43
3.40
3.21
3.19
3.18
3.17
3.15
3.15
3.14
3.11
2.69
2.68
2.66
1.94
1.88
1.33
1.27
1.24
1.22
1.19
1.17
1.16
Br-
Ph
P+
Ph
Me
Me
Me
2.00
3.02
5.05
1.03
0.98
0.99
0.98
1.09
1.03
0.97
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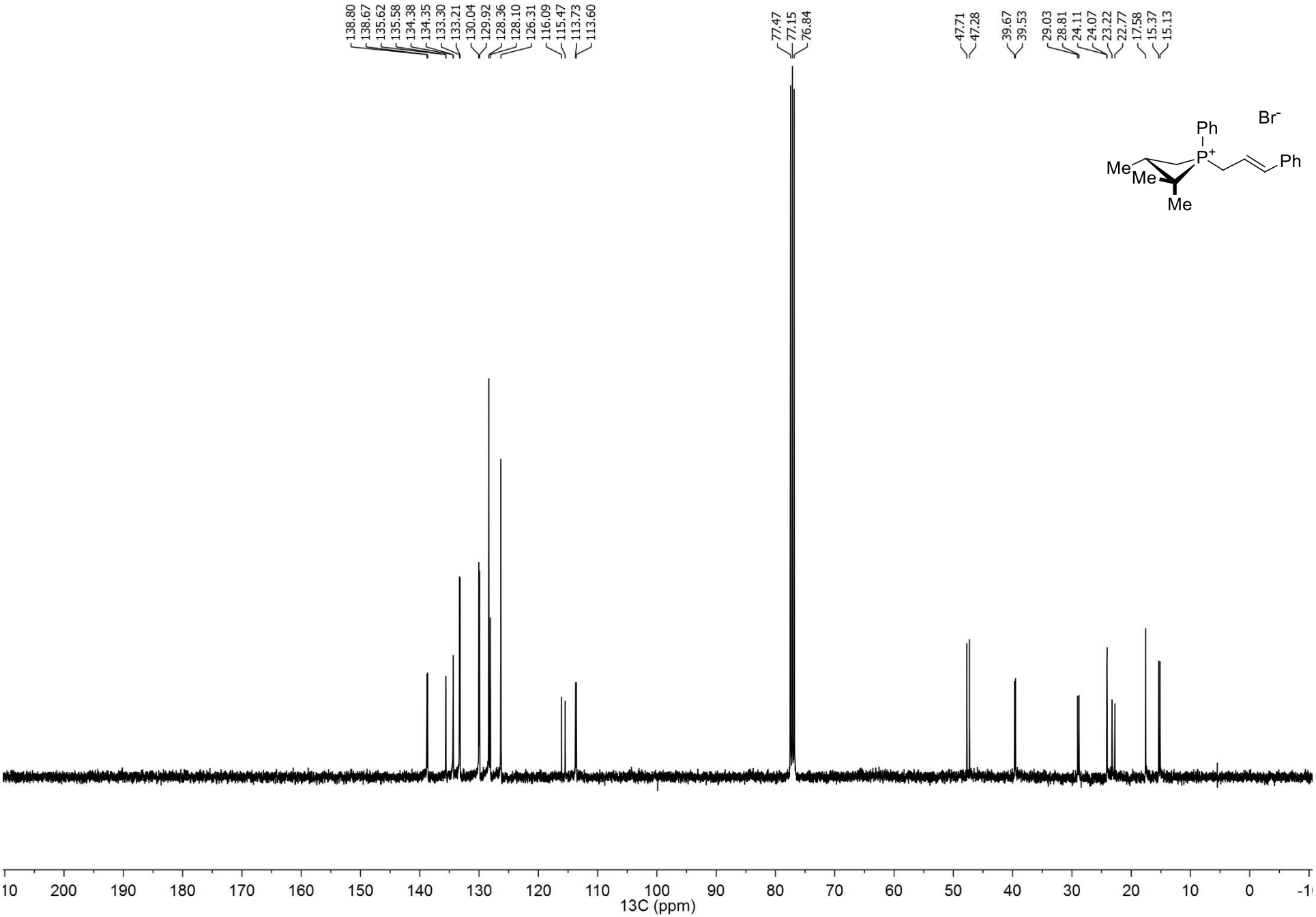
6.14
1H (ppm)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129.92
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116.09
115.47
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113.60
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77.15
76.84
47.71
47.28
39.67
39.53
29.03
28.81
24.11
24.07
23.22
22.77
17.58
15.37
15.13
Br-
Ph
P+
Ph
Me
Me
Me
10
200
190
180
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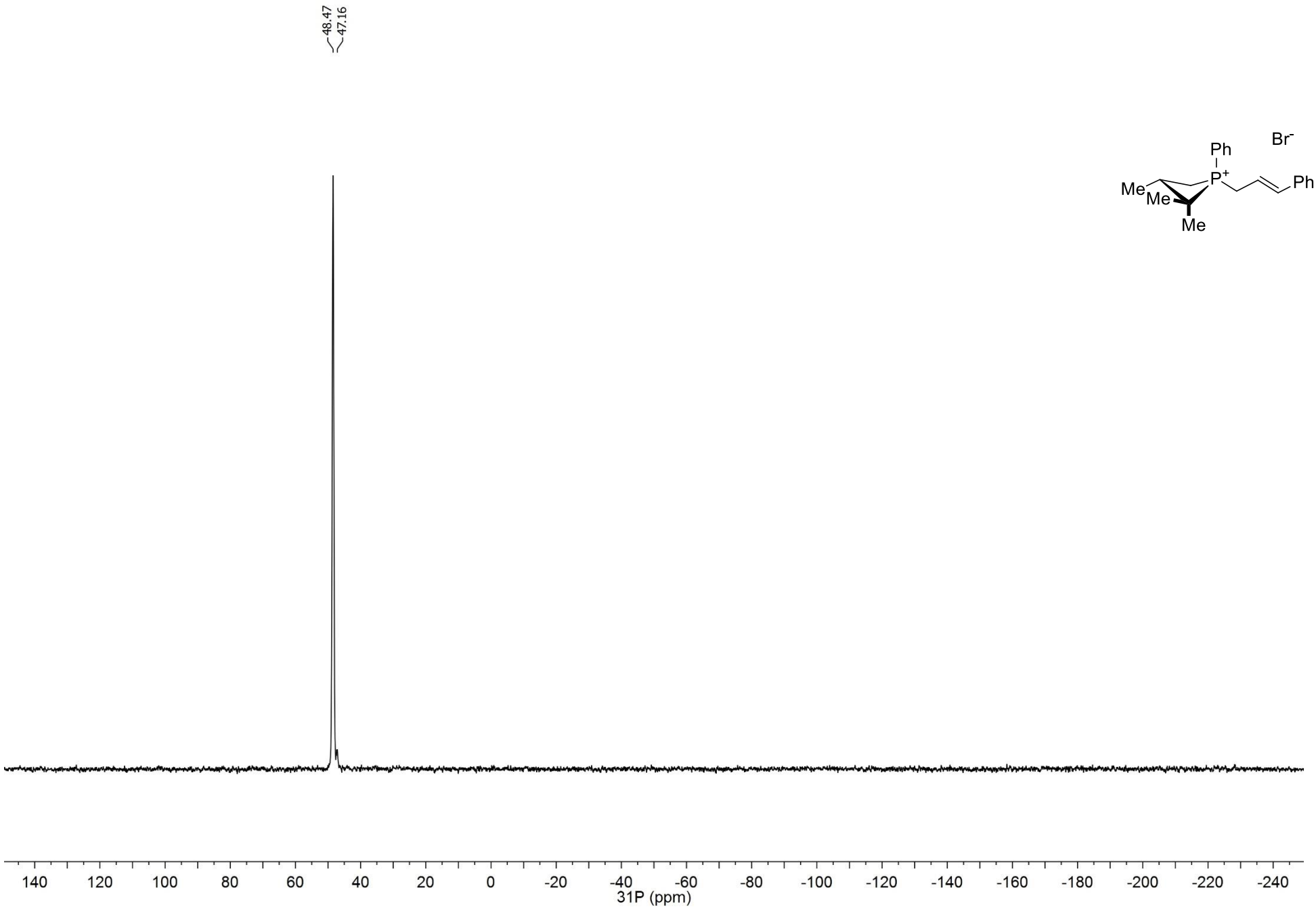
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C (ppm)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Ph
P+
Me
Me
Me
Ph
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120
100
80
60
40
20
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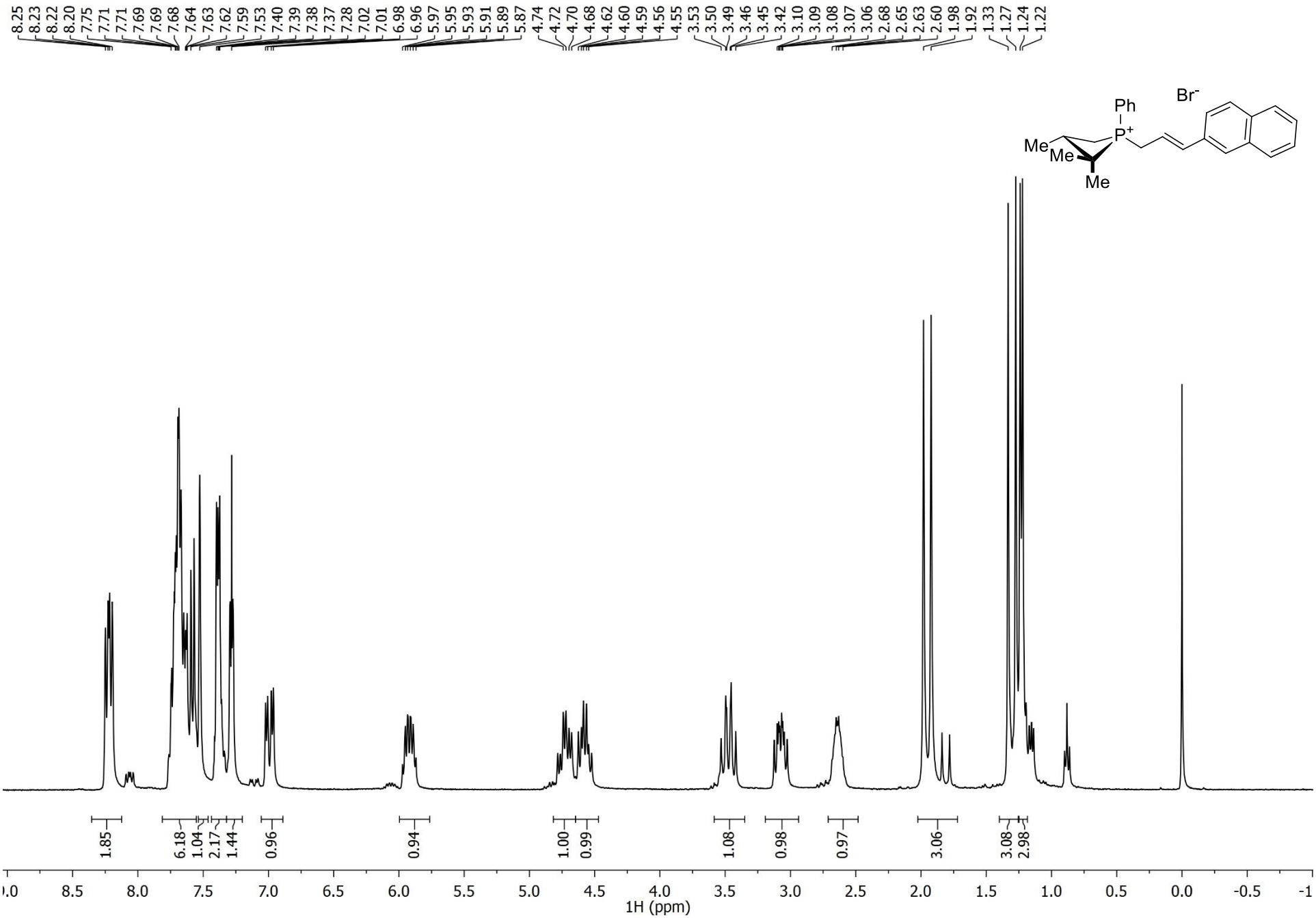
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
31P (ppm)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Ph
Br-
P+
Me
Me
Me
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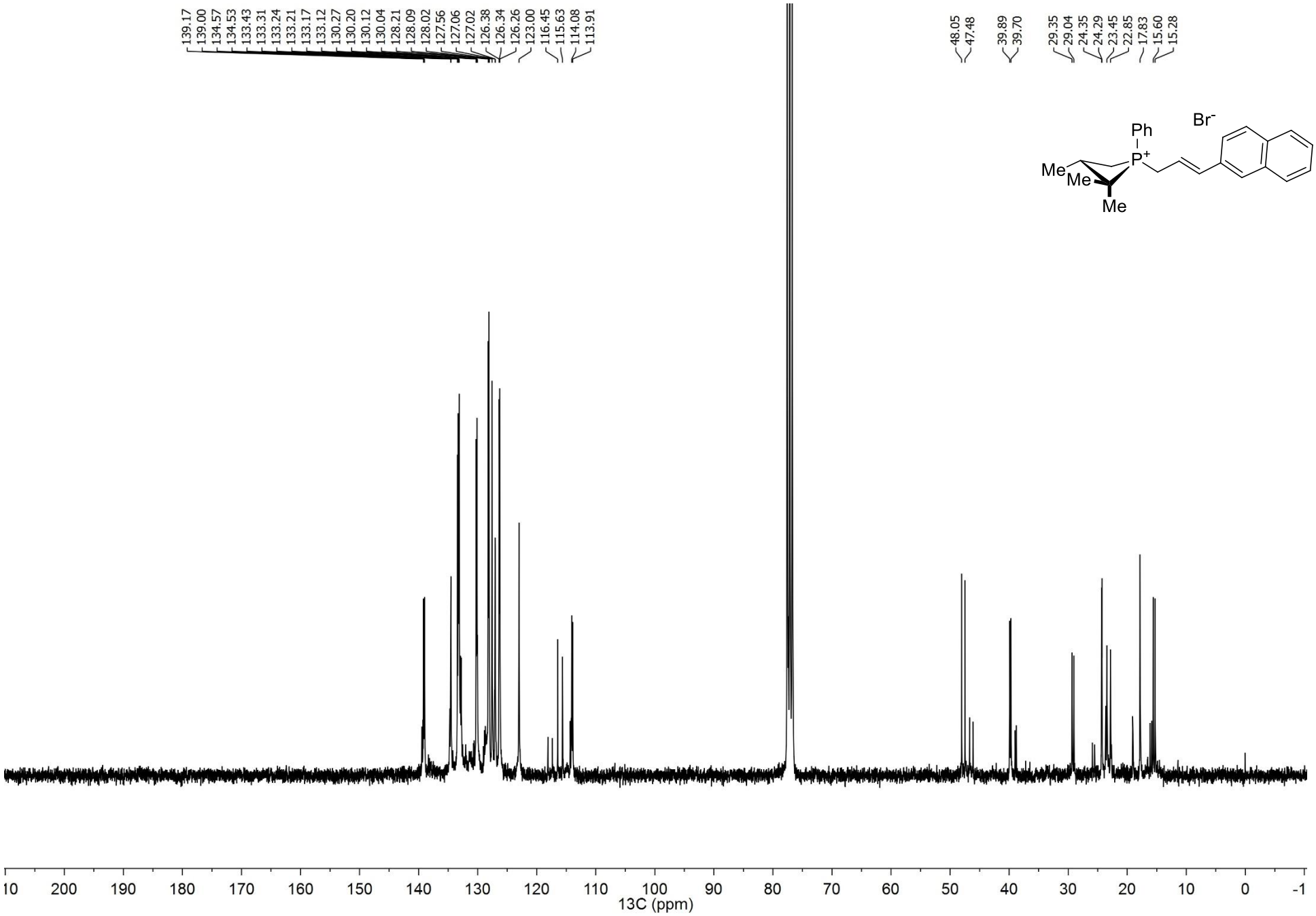
1H (ppm)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130.12
130.04
128.21
128.09
128.02
127.56
127.06
127.02
126.38
126.34
126.26
123.00
116.45
115.63
114.08
113.91
48.05
47.48
39.89
39.70
29.35
29.04
24.35
24.29
23.45
22.85
17.83
15.60
15.28
Ph
P+
Br-
Me
Me
Me
10
200
190
180
170
160
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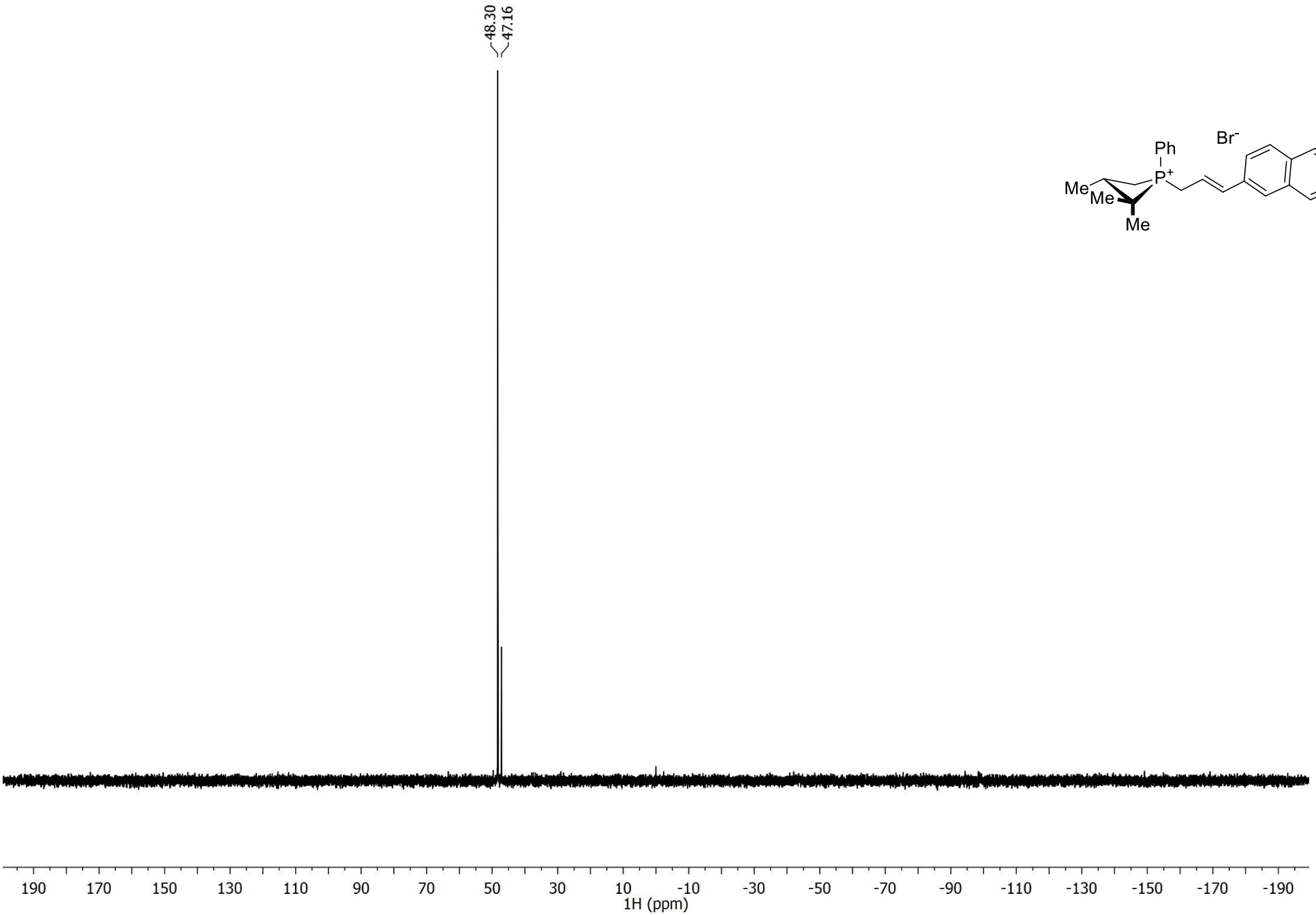
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
13C (ppm)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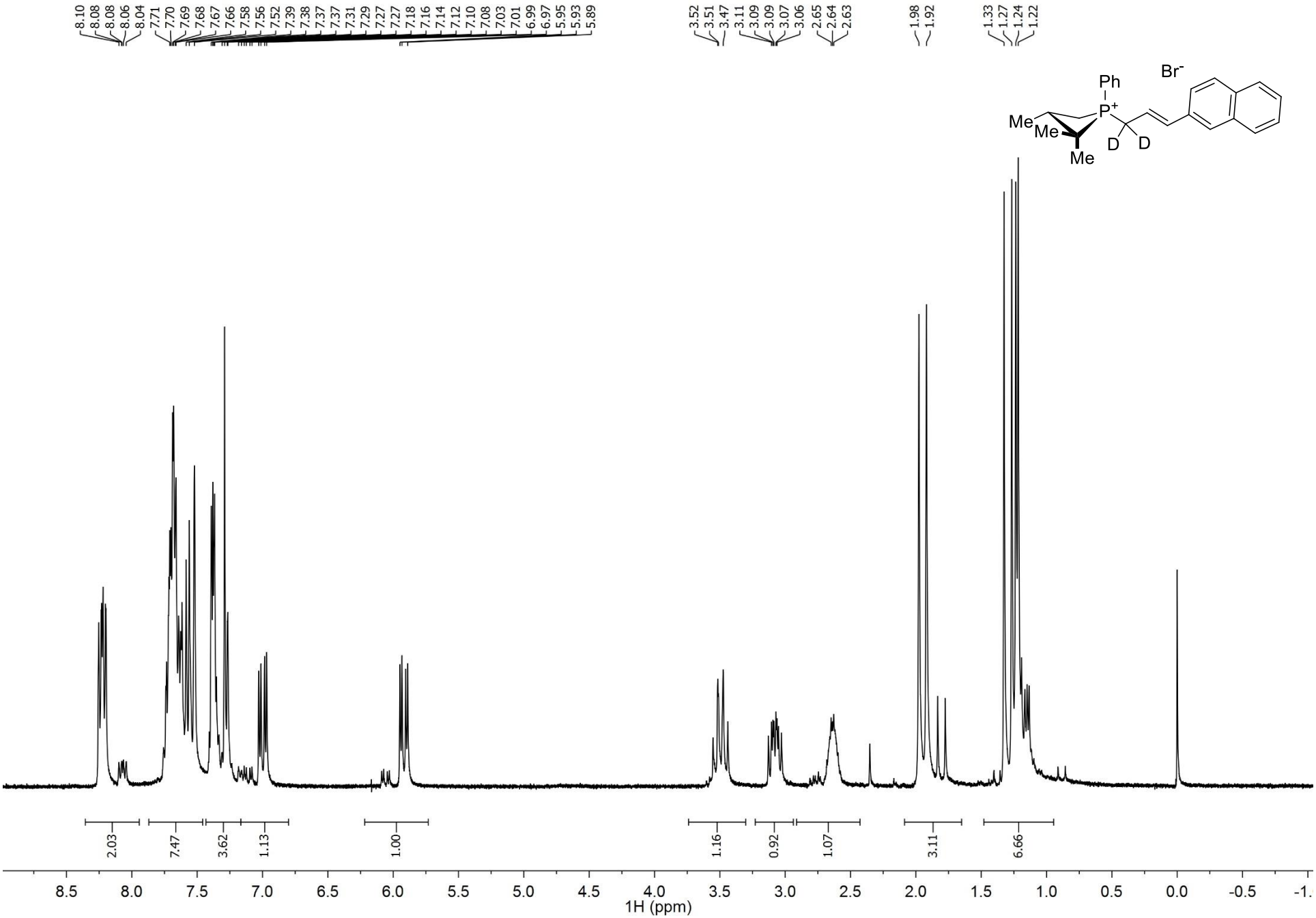
-110
-130
-150
-170
-190
1H (ppm)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7.67
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7.08
7.03
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6.97
5.95
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2.65
2.64
2.63
1.98
1.92
1.33
1.27
1.24
1.22
Ph
Br⁻
P⁺
Me
Me
Me
D
D
2.03
7.47
3.62
1.13
1.00
1.16
0.92
1.07
3.11
6.66
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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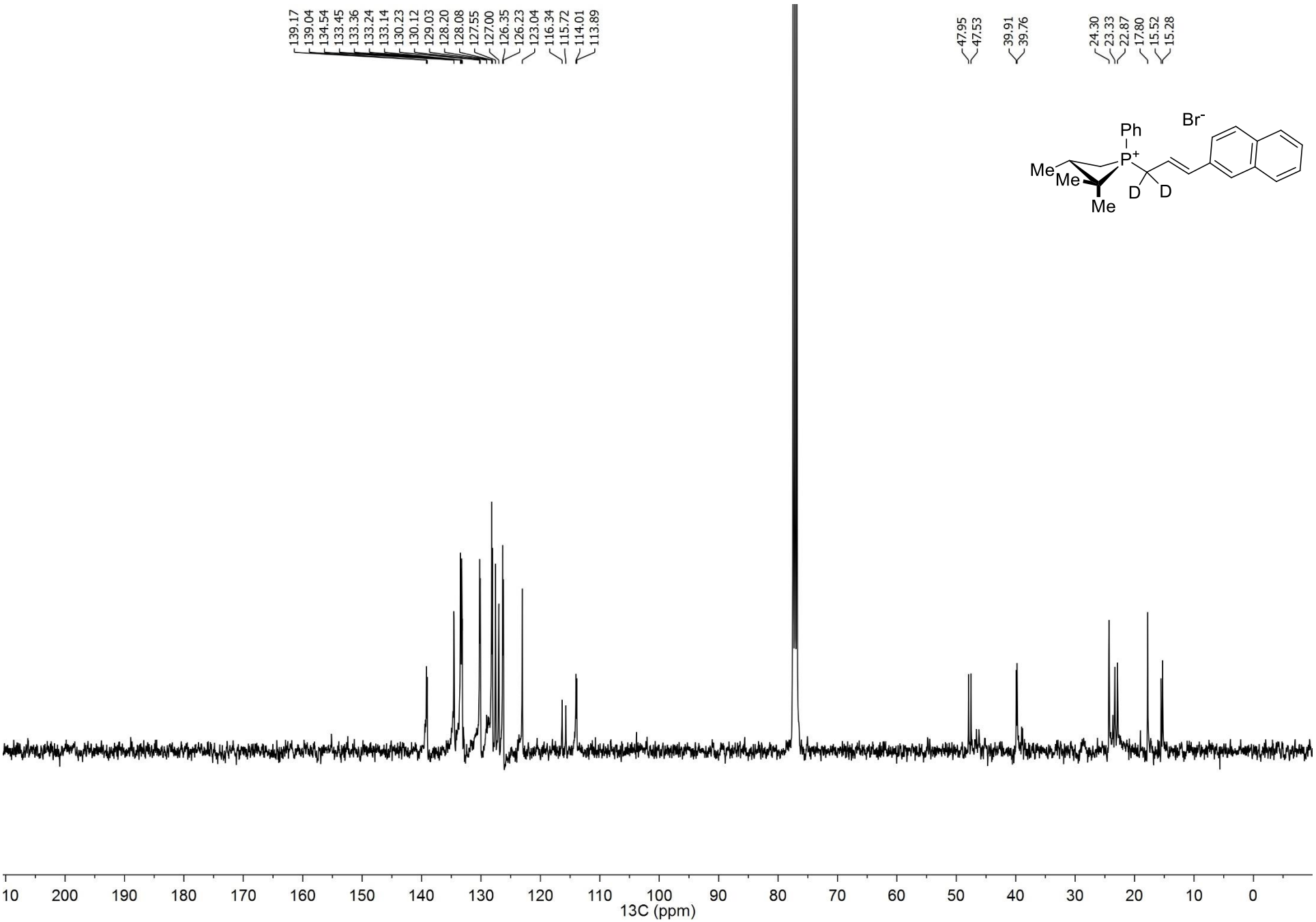
-1.
1H (ppm)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22.87
17.80
15.52
15.28
Br-
Ph
P+
Me
Me
Me
D
D
10
200
190
180
170
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130
120
110
100
90
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70
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50
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10
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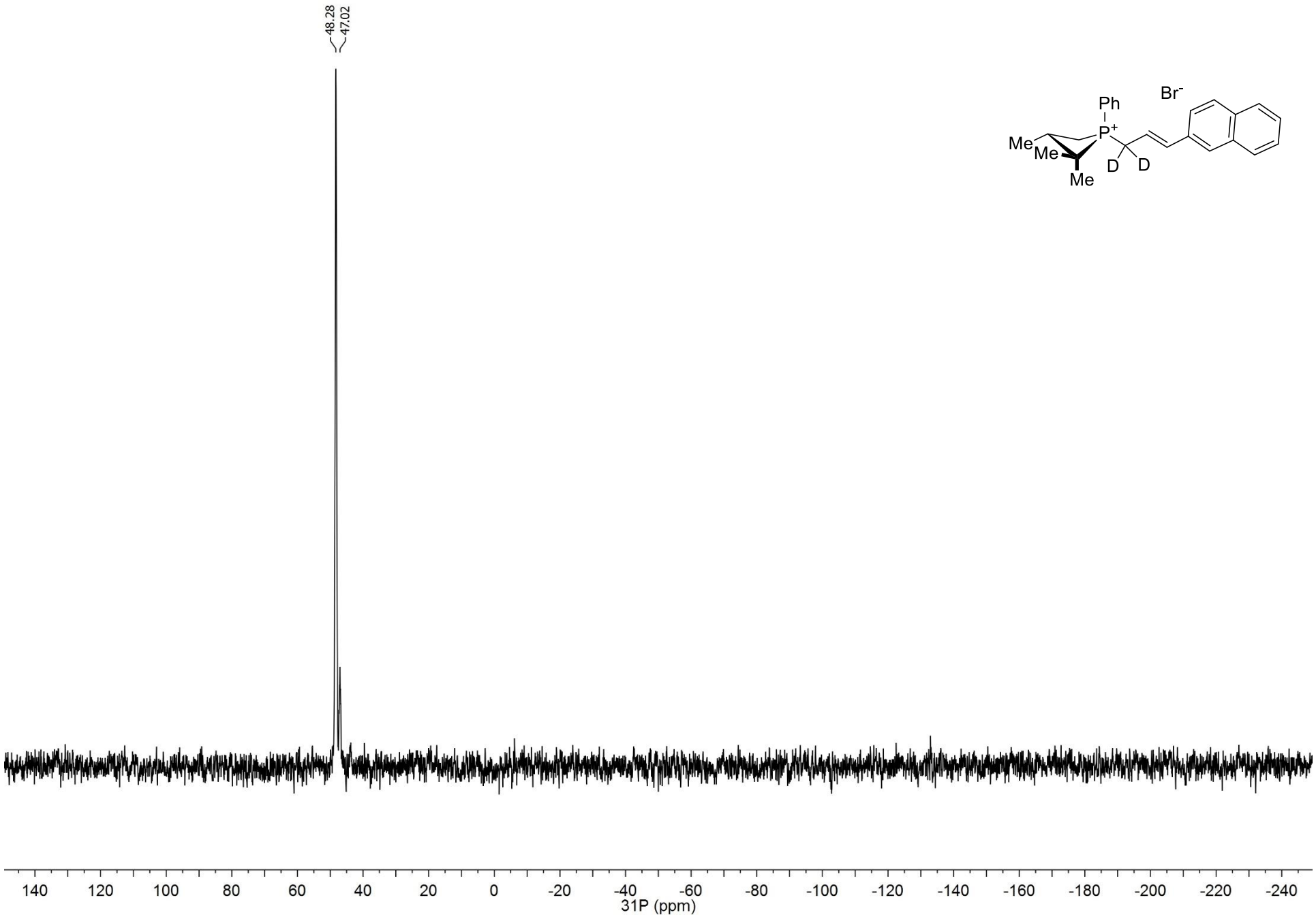
13C (ppm)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-80
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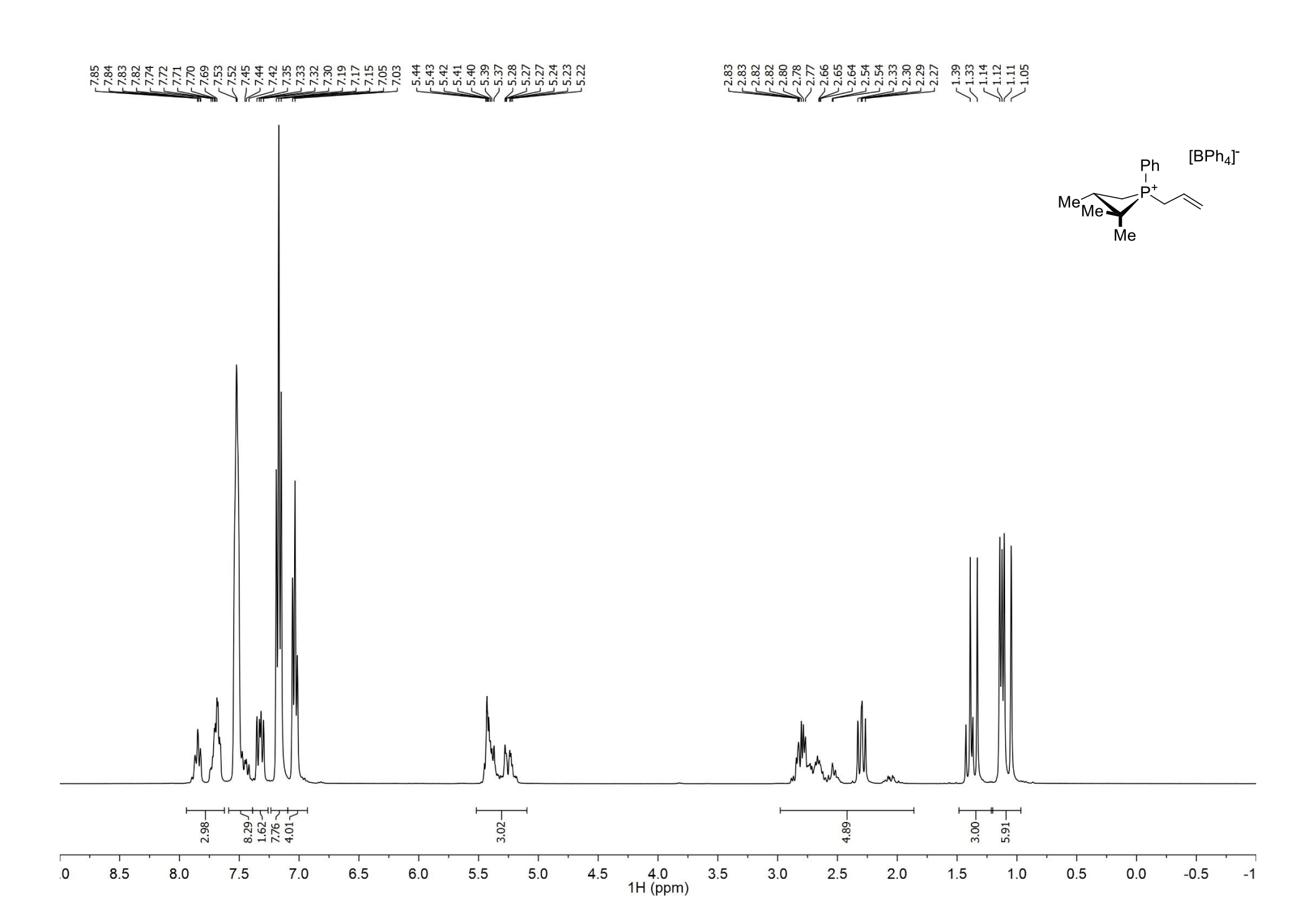
-220
-240
31P (ppm)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1.33
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1.11
1.05
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P+
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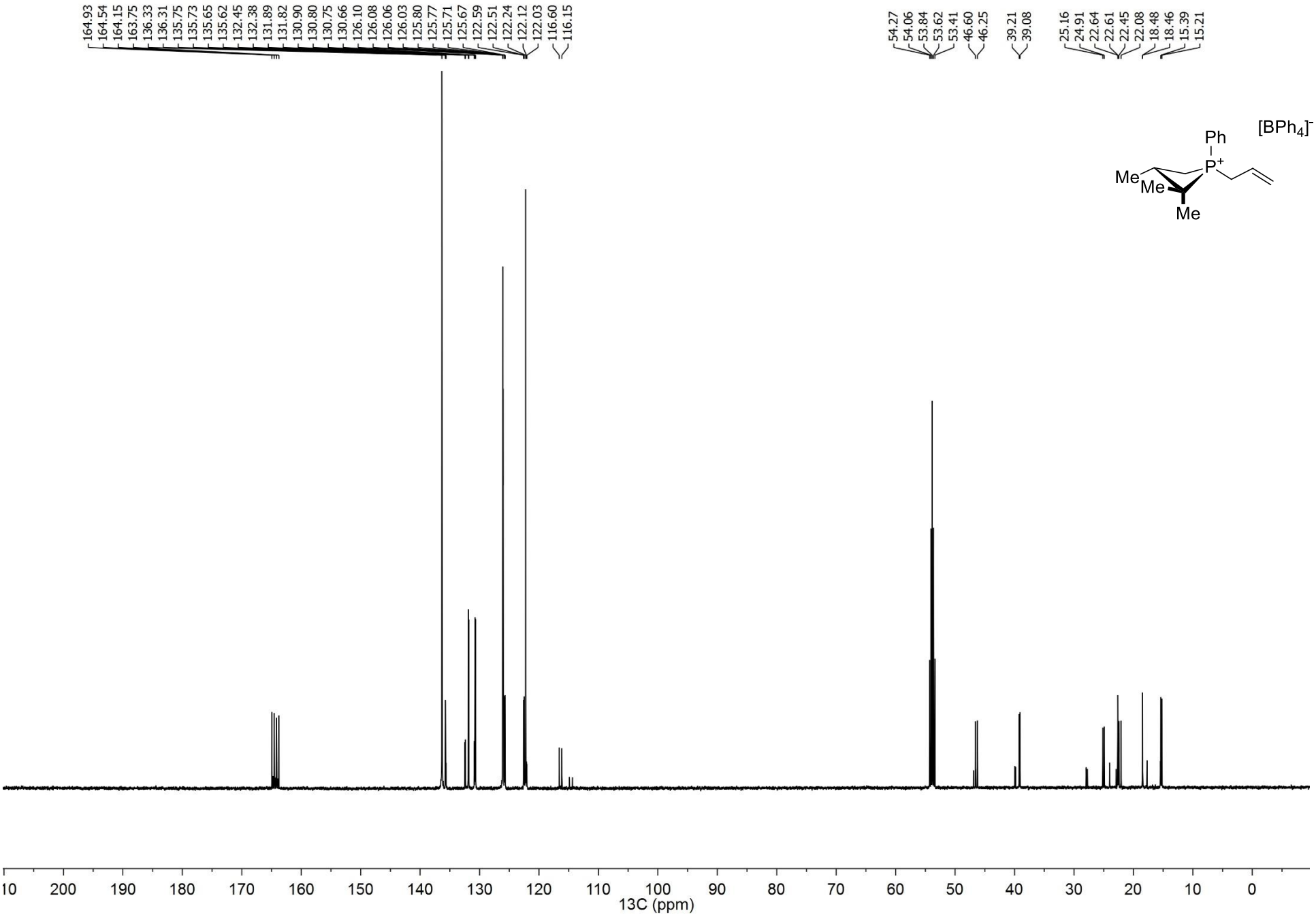
5.91
1H (ppm)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125.67
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122.12
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Ph
P+
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Me
Me
10
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190
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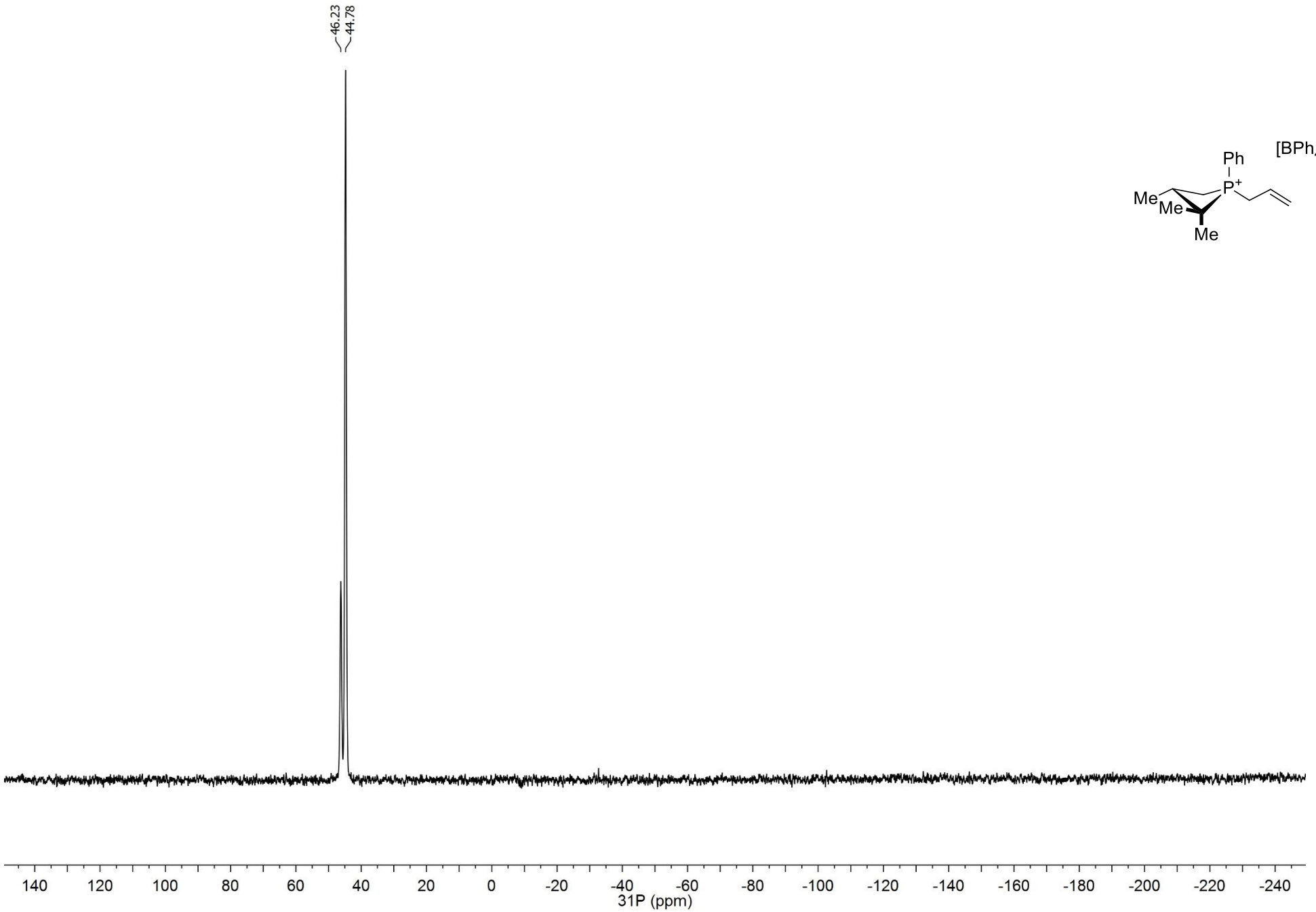
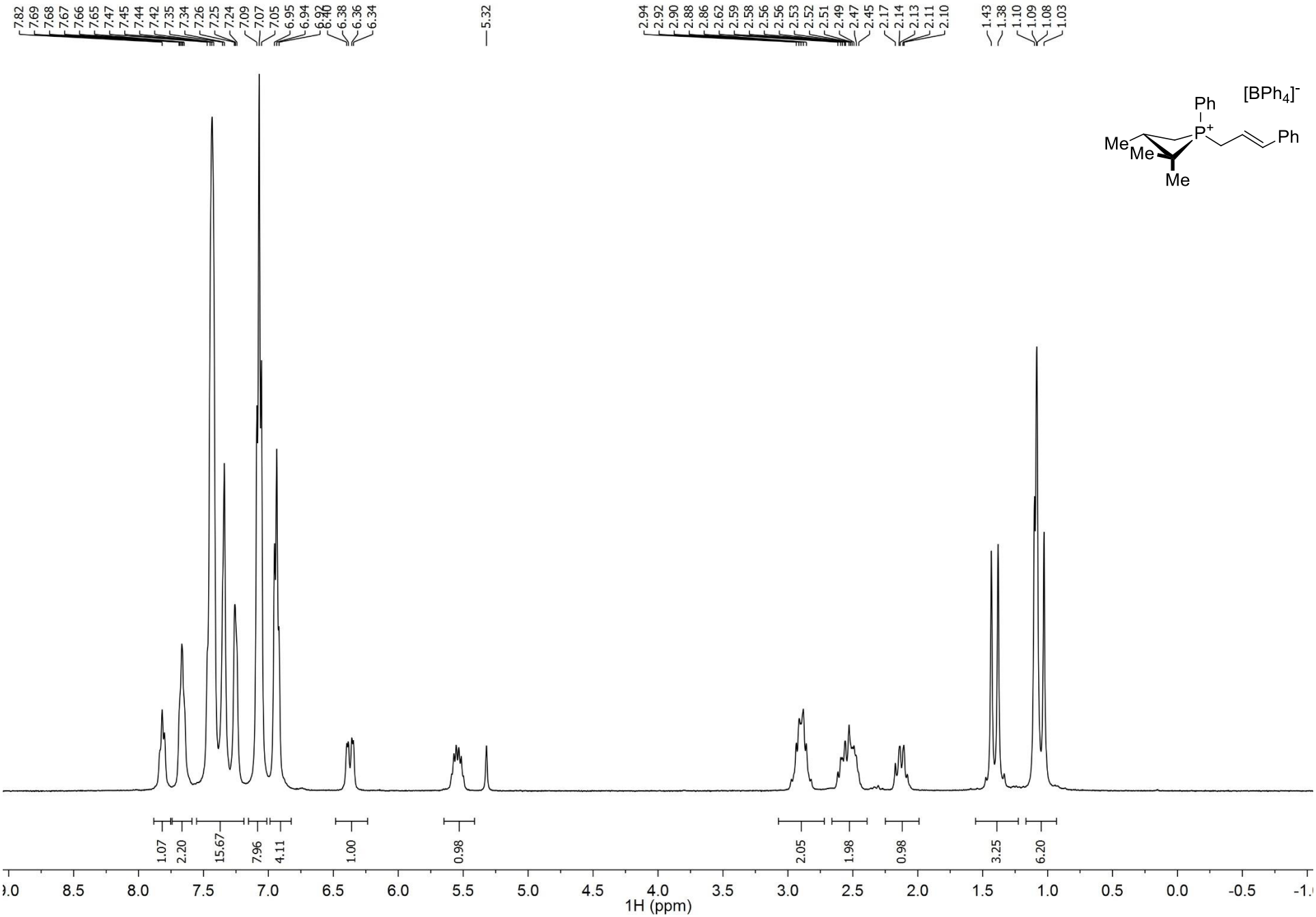
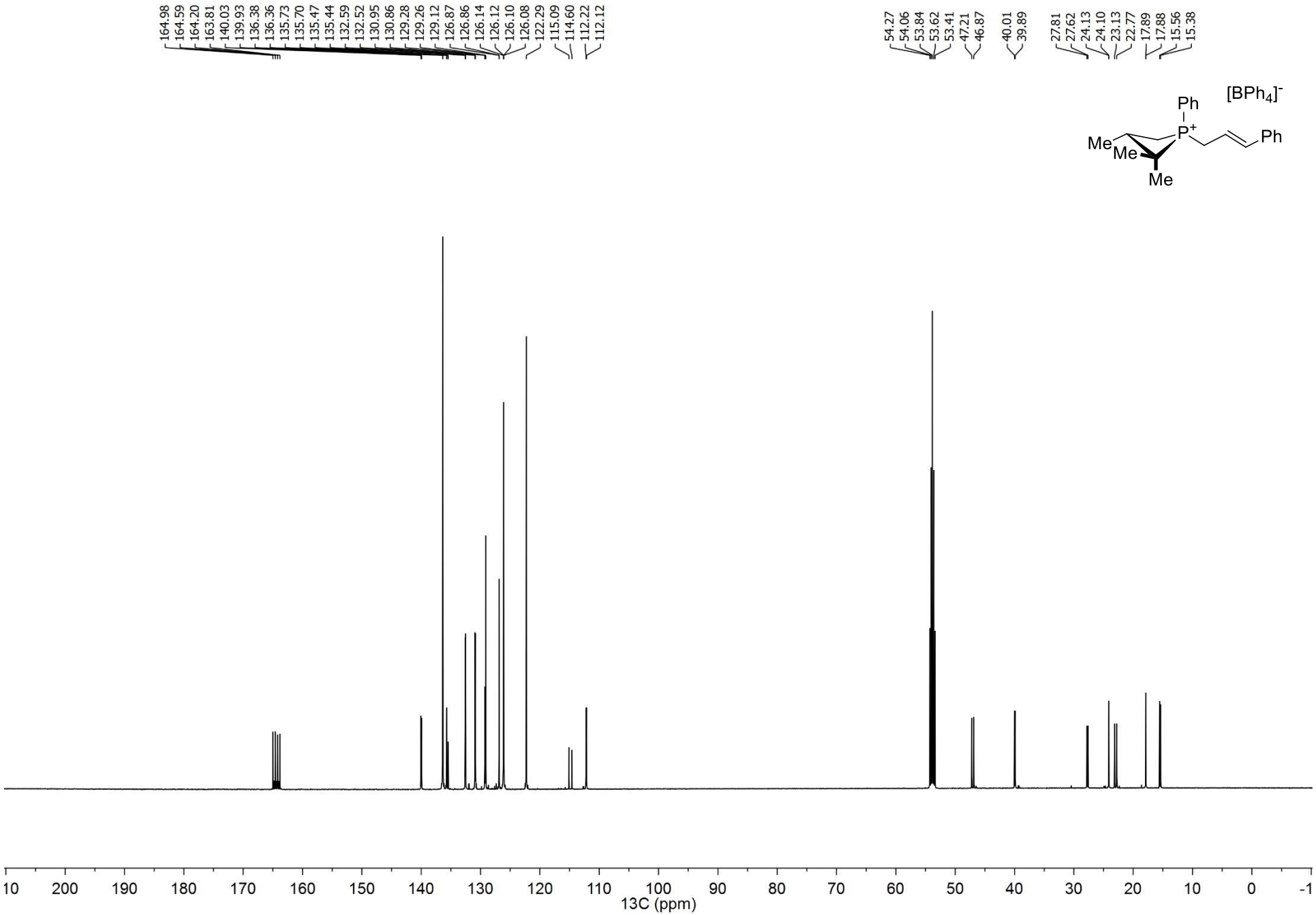
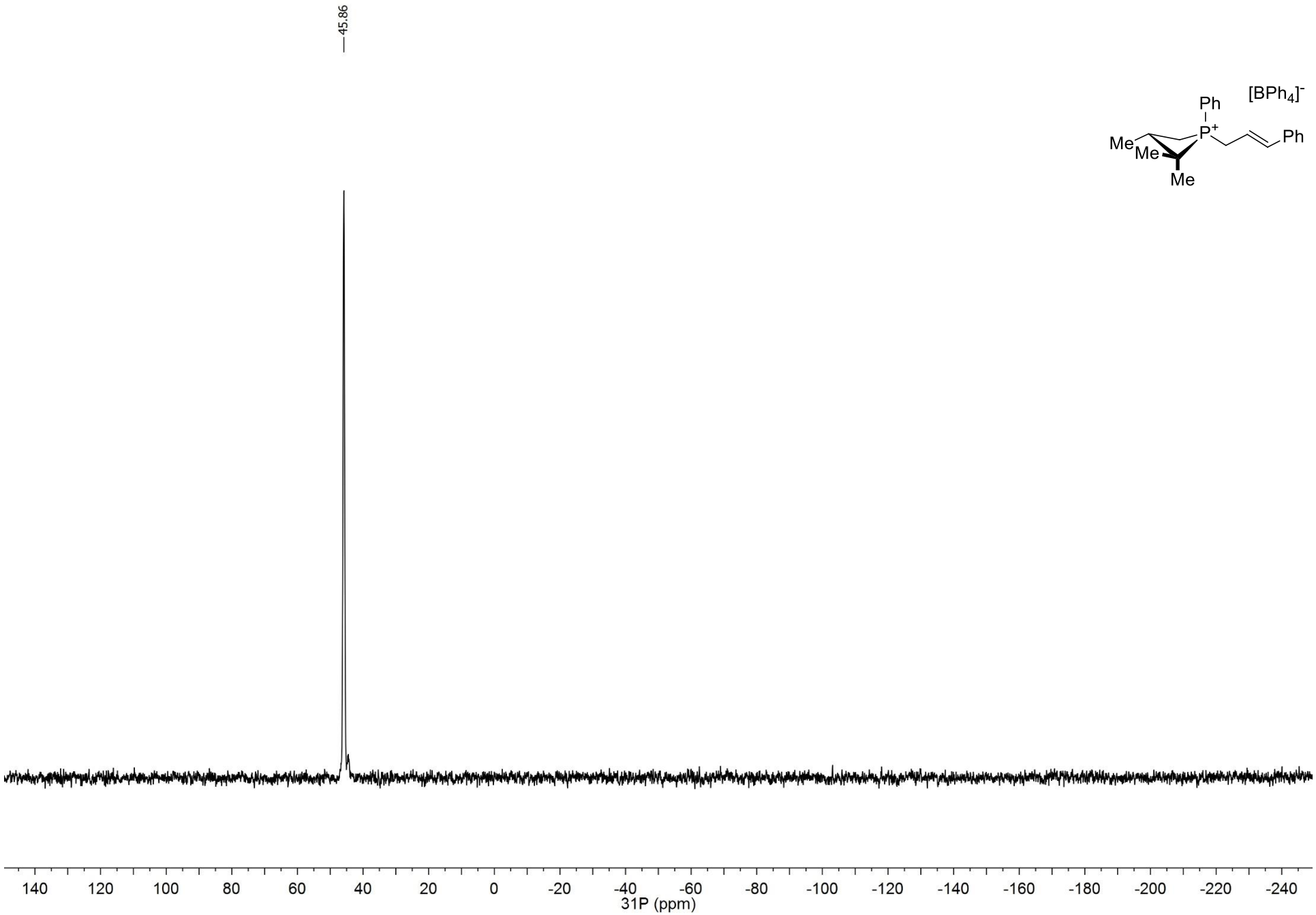
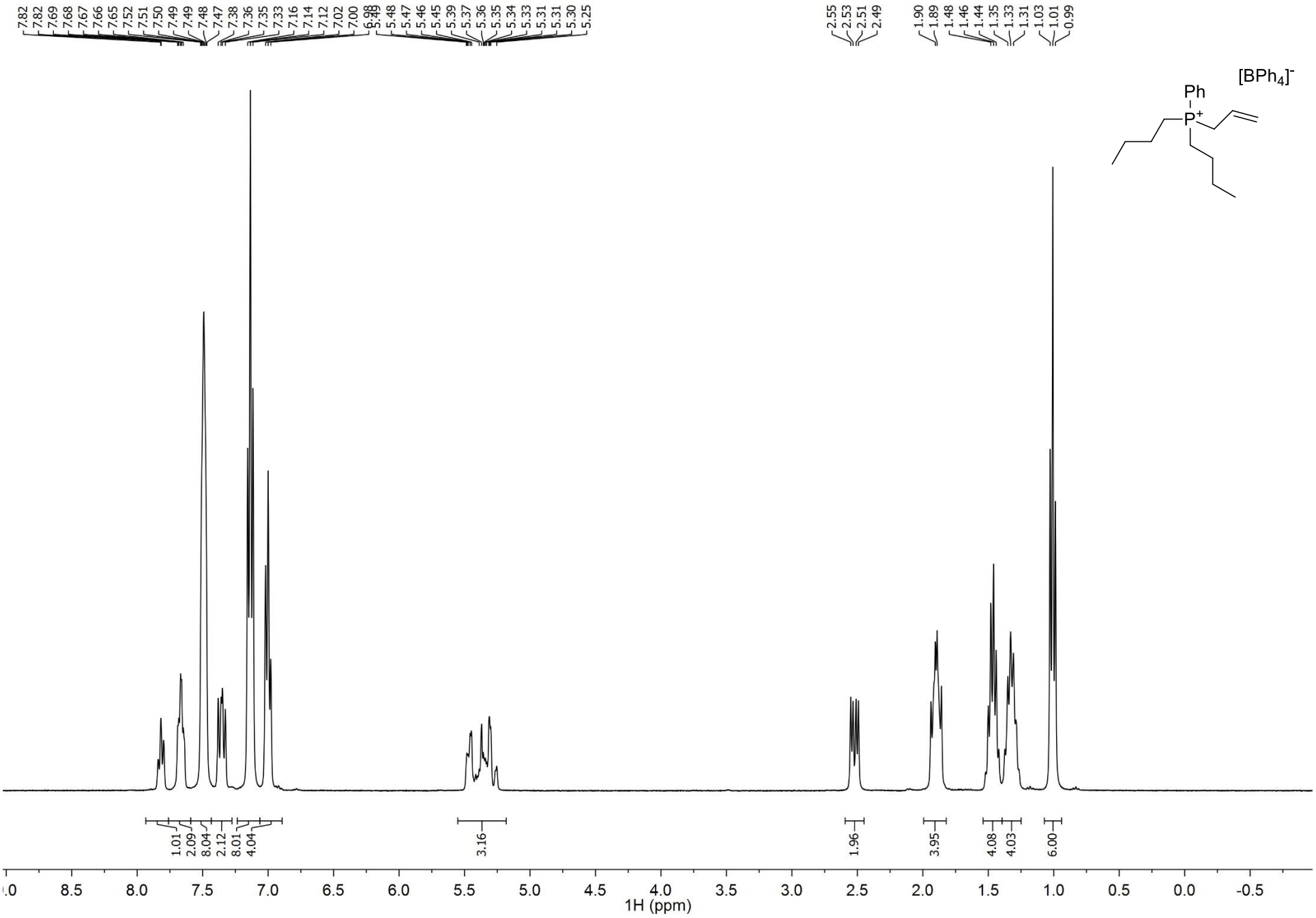
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C (ppm)

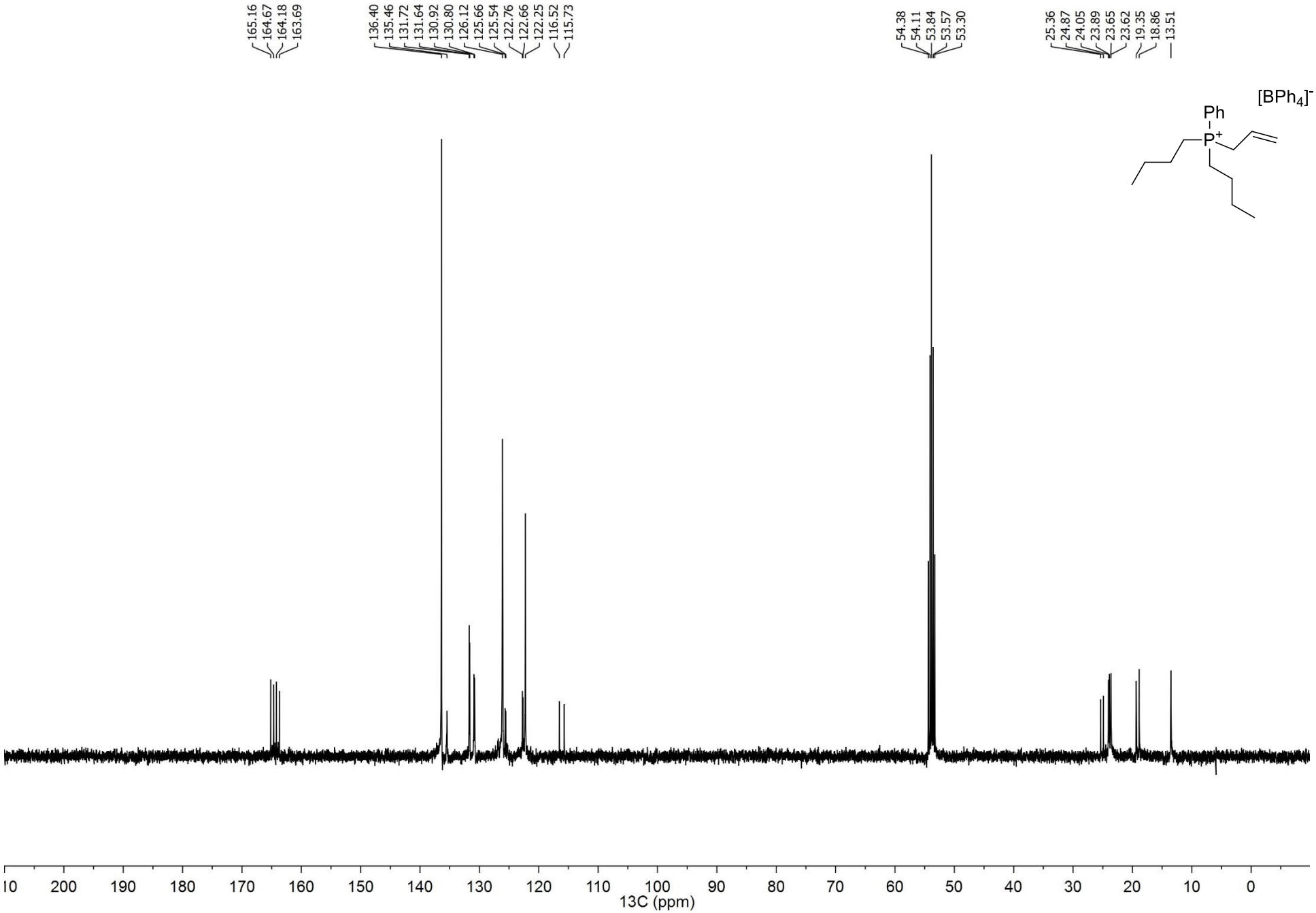

46.23
44.78
[BPh4]-
Ph
P+
Me
Me
Me
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
31P (ppm)

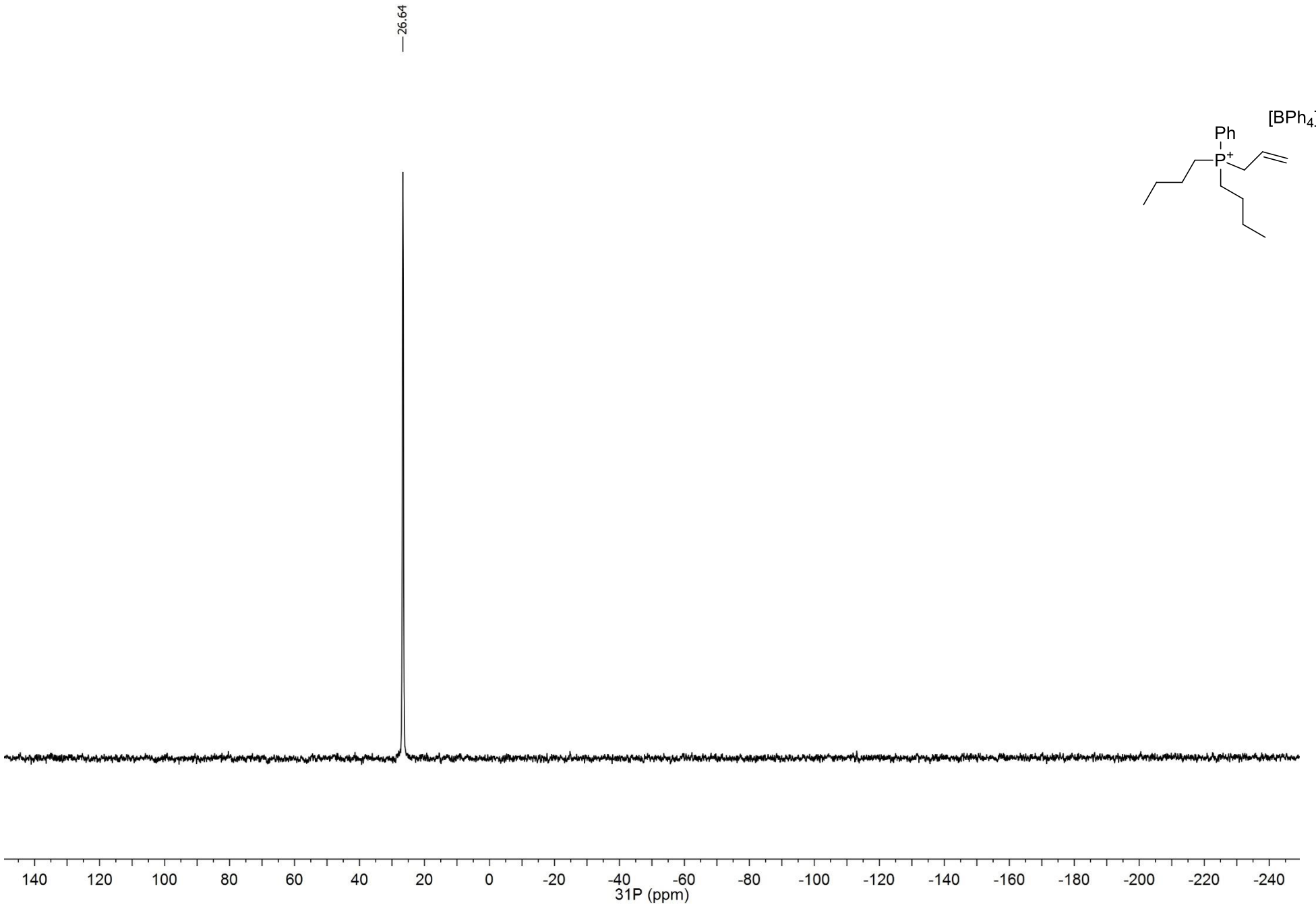

7.82
7.69
7.68
7.67
7.66
7.65
7.47
7.45
7.44
7.42
7.35
7.34
7.26
7.25
7.24
7.09
7.07
7.05
6.95
6.94
6.38
6.36
6.34
5.32
2.94
2.92
2.90
2.88
2.86
2.62
2.59
2.58
2.56
2.56
2.53
2.52
2.51
2.49
2.47
2.45
2.17
2.14
2.13
2.11
2.10
1.43
1.38
1.10
1.09
1.08
1.03
[BPh4]-
Ph
P+
Me
Me
Me
Ph
1.07
2.20
15.67
7.96
4.11
1.00
0.98
2.05
1.98
0.98
3.25
6.20
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1H (ppm)

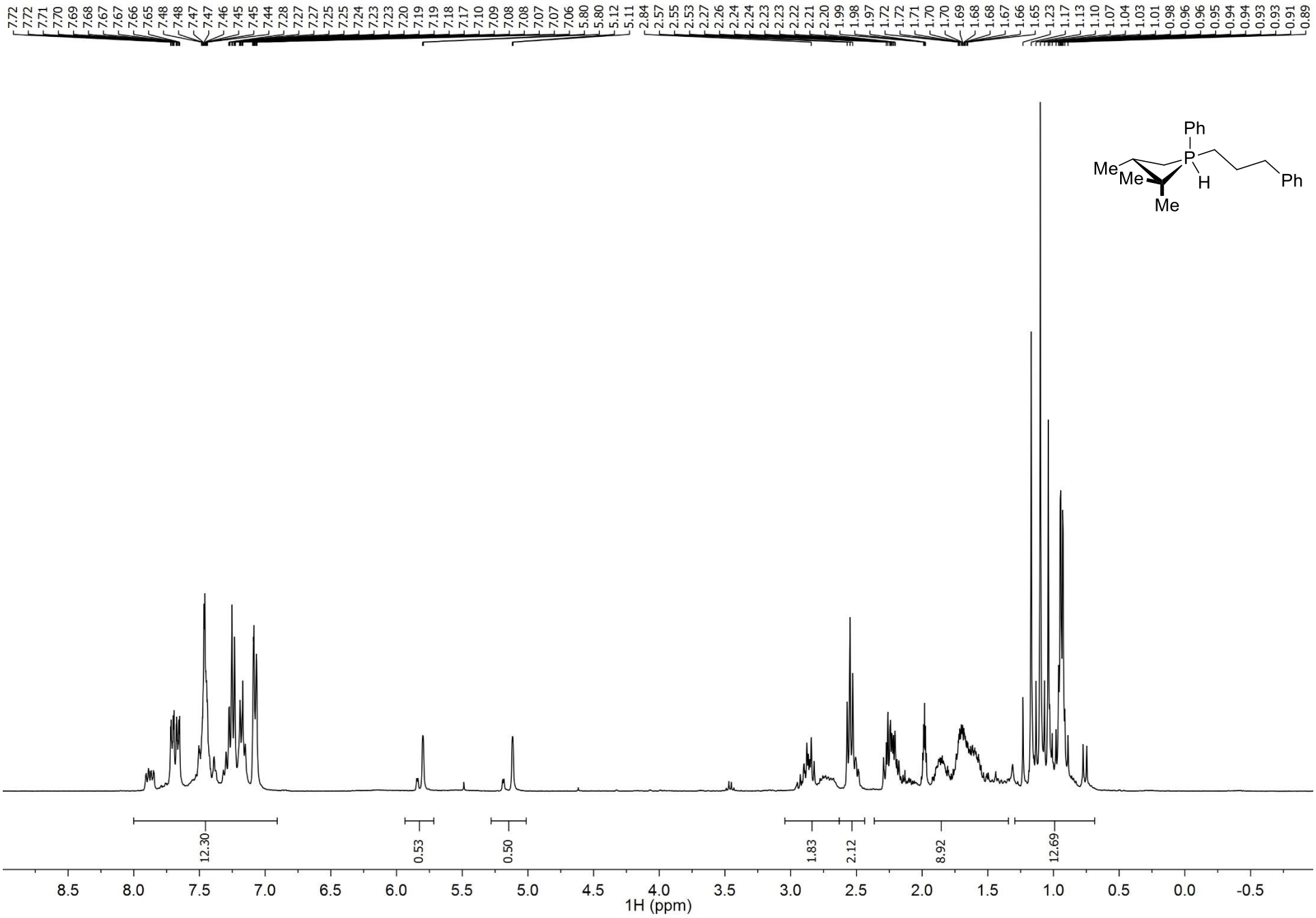

164.98
164.59
164.20
163.81
140.03
139.93
136.38
136.36
135.73
135.70
135.47
135.44
132.59
132.52
130.95
130.86
129.28
129.26
129.12
126.87
126.86
126.14
126.12
126.10
126.08
122.29
115.09
114.60
112.22
112.12
54.27
54.06
53.84
53.62
53.41
47.21
46.87
40.01
39.89
27.81
27.62
24.13
24.10
23.13
22.77
17.89
17.88
15.56
15.38
[BPh4]-
Ph
P+
Ph
Me
Me
Me
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
13C (ppm)

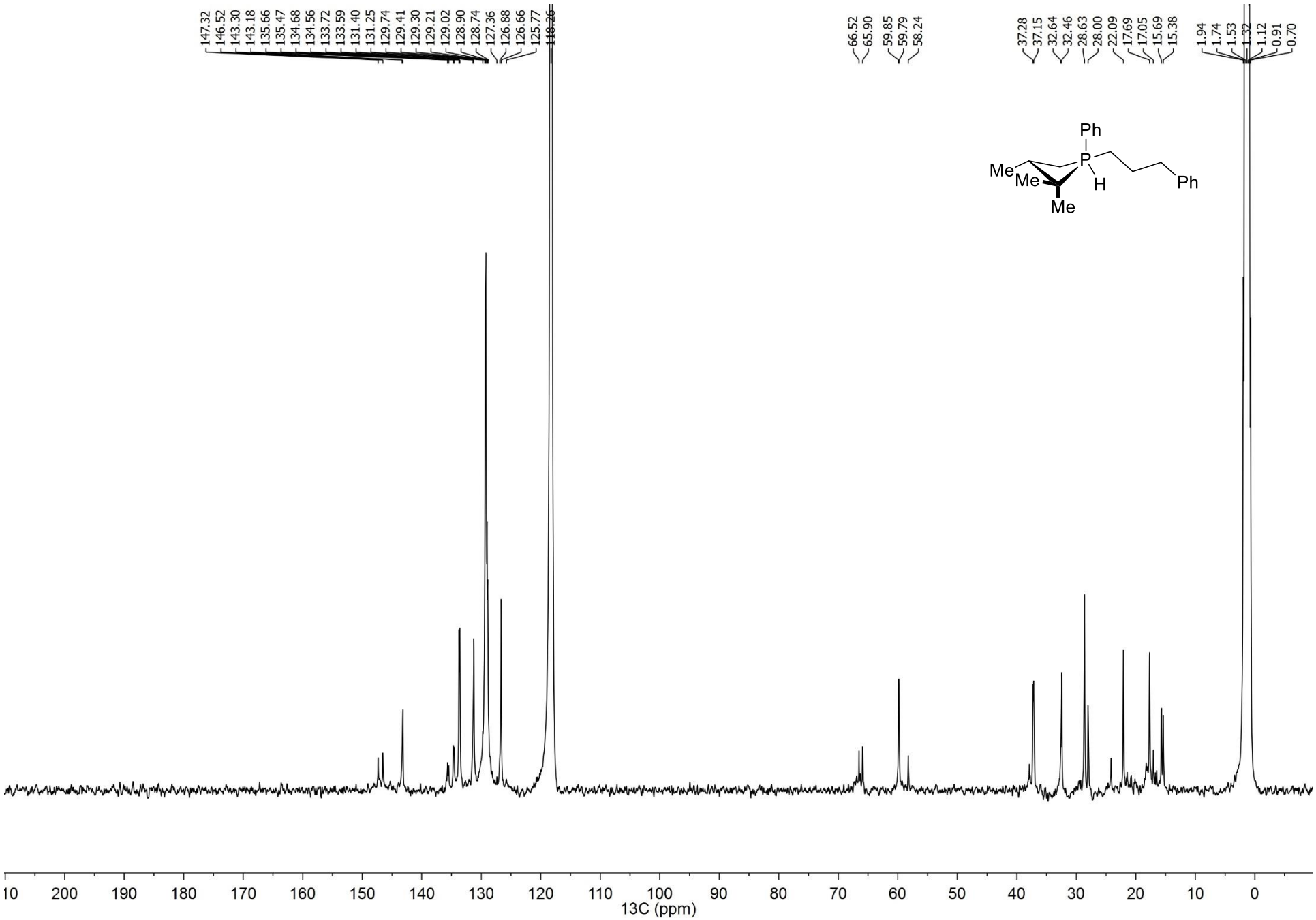

45.86
[BPh4]-
Ph
P+
Me
Me
Me
Ph
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
31P (ppm)

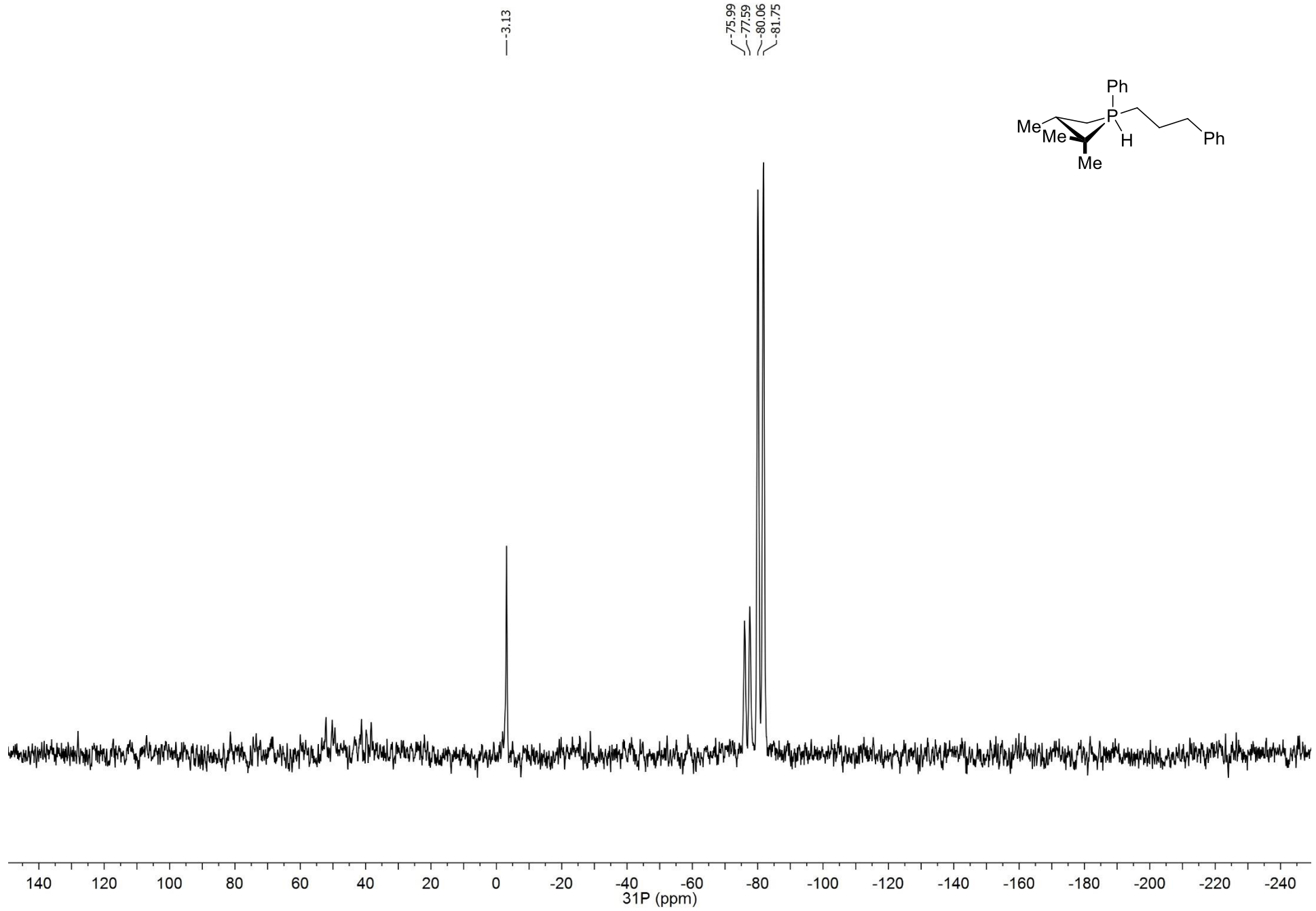

7.82
7.82
7.69
7.68
7.67
7.66
7.65
7.52
7.51
7.50
7.49
7.49
7.48
7.47
7.38
7.36
7.35
7.33
7.16
7.14
7.12
7.02
7.00
6.98
6.98
5.48
5.47
5.46
5.45
5.39
5.37
5.36
5.35
5.34
5.33
5.31
5.31
5.30
5.25
2.55
2.53
2.51
2.49
1.90
1.89
1.48
1.46
1.44
1.35
1.33
1.31
1.03
1.01
0.99
[BPh4]-
Ph
P+
1.01
2.09
8.04
2.12
8.01
4.04
3.16
1.96
3.95
4.08
4.03
6.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1H (ppm)

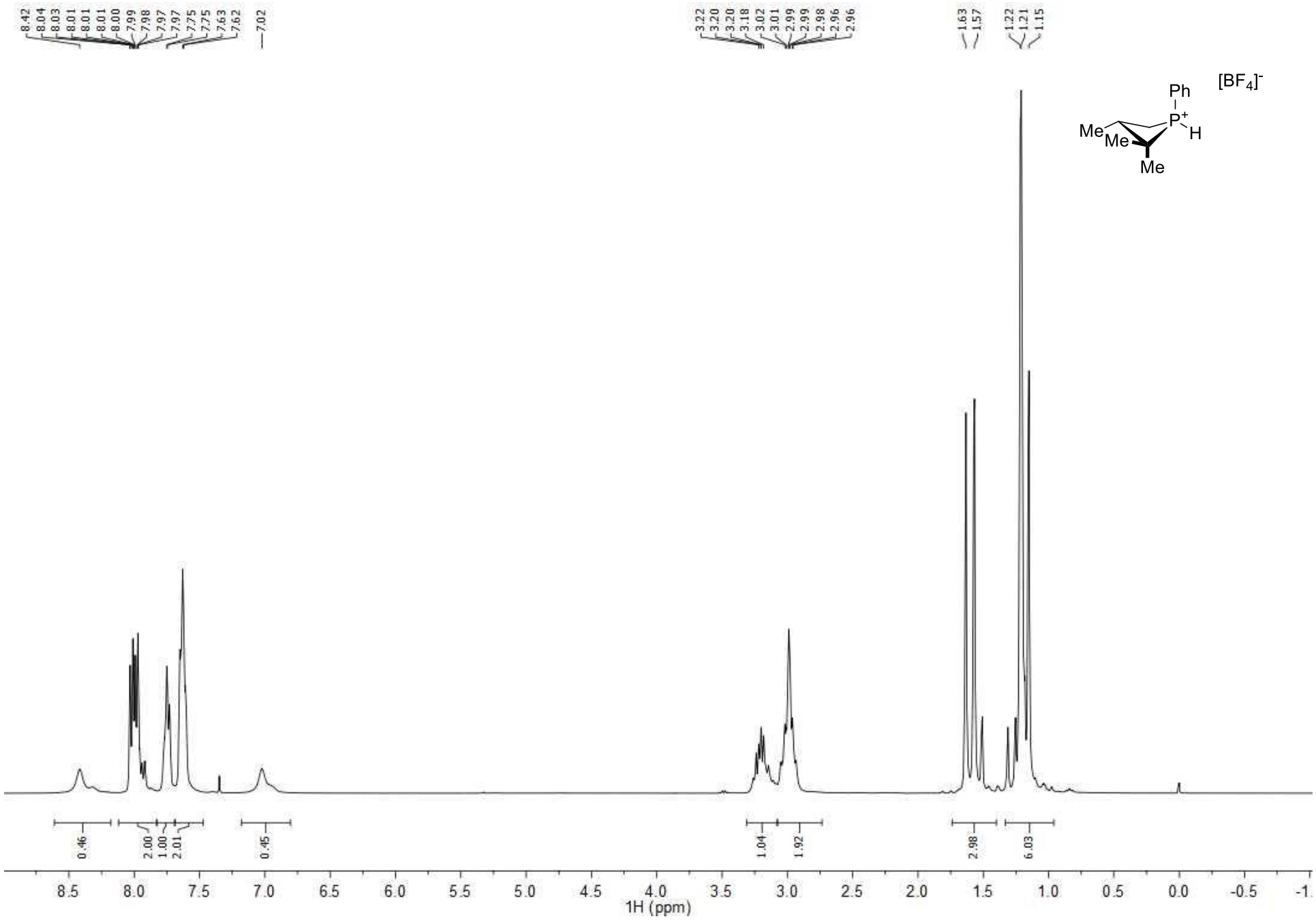

165.16
164.67
164.18
163.69
136.40
135.46
131.72
131.64
130.92
130.80
126.12
125.66
125.54
122.76
122.66
122.25
116.52
115.73
54.38
54.11
53.84
53.57
53.30
25.36
24.87
24.05
23.89
23.65
23.62
19.35
18.86
13.51
[BPh4]-
Ph
P+
13C (ppm)

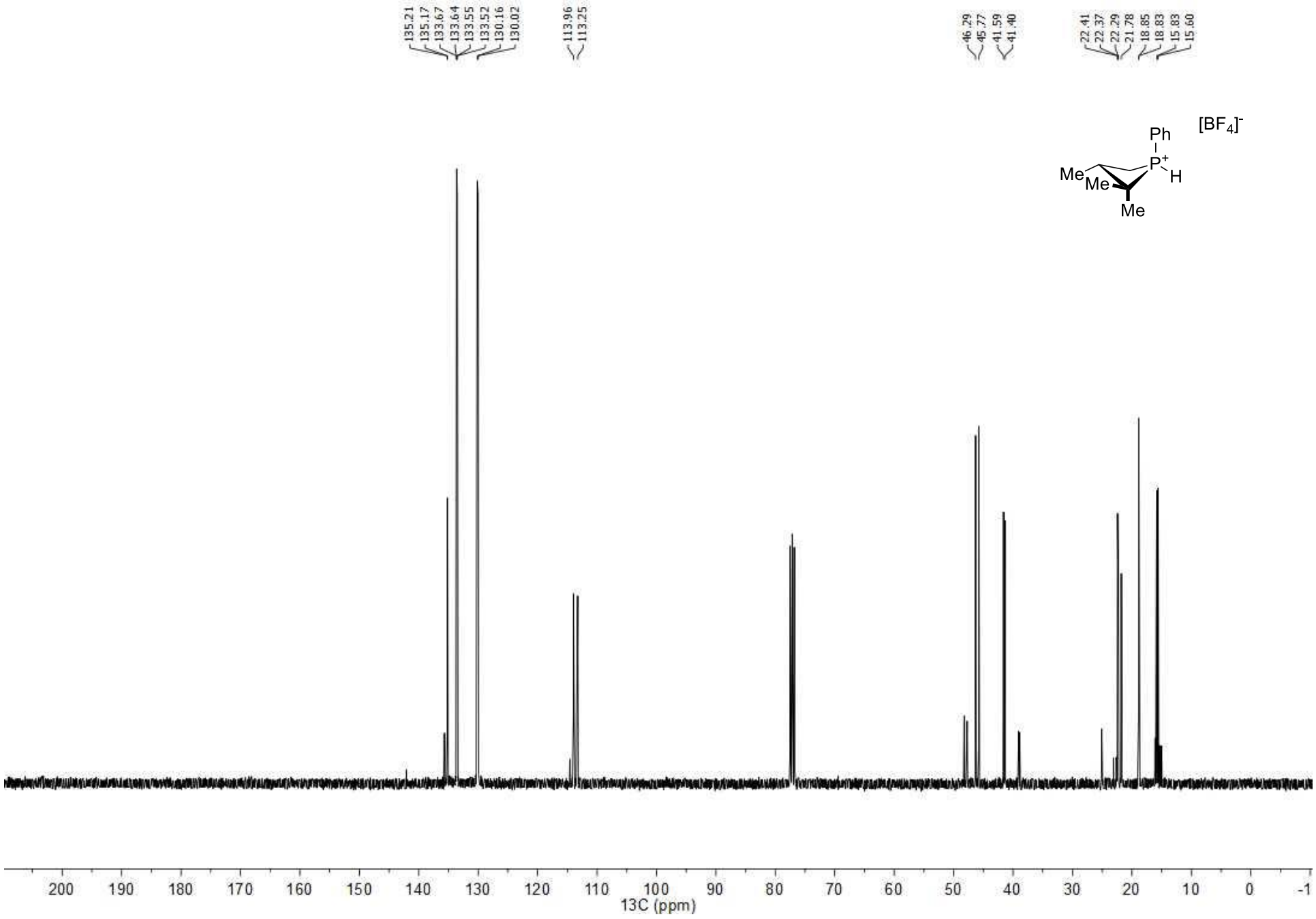

26.64
[BPh4]-
Ph
P+
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
31P (ppm)

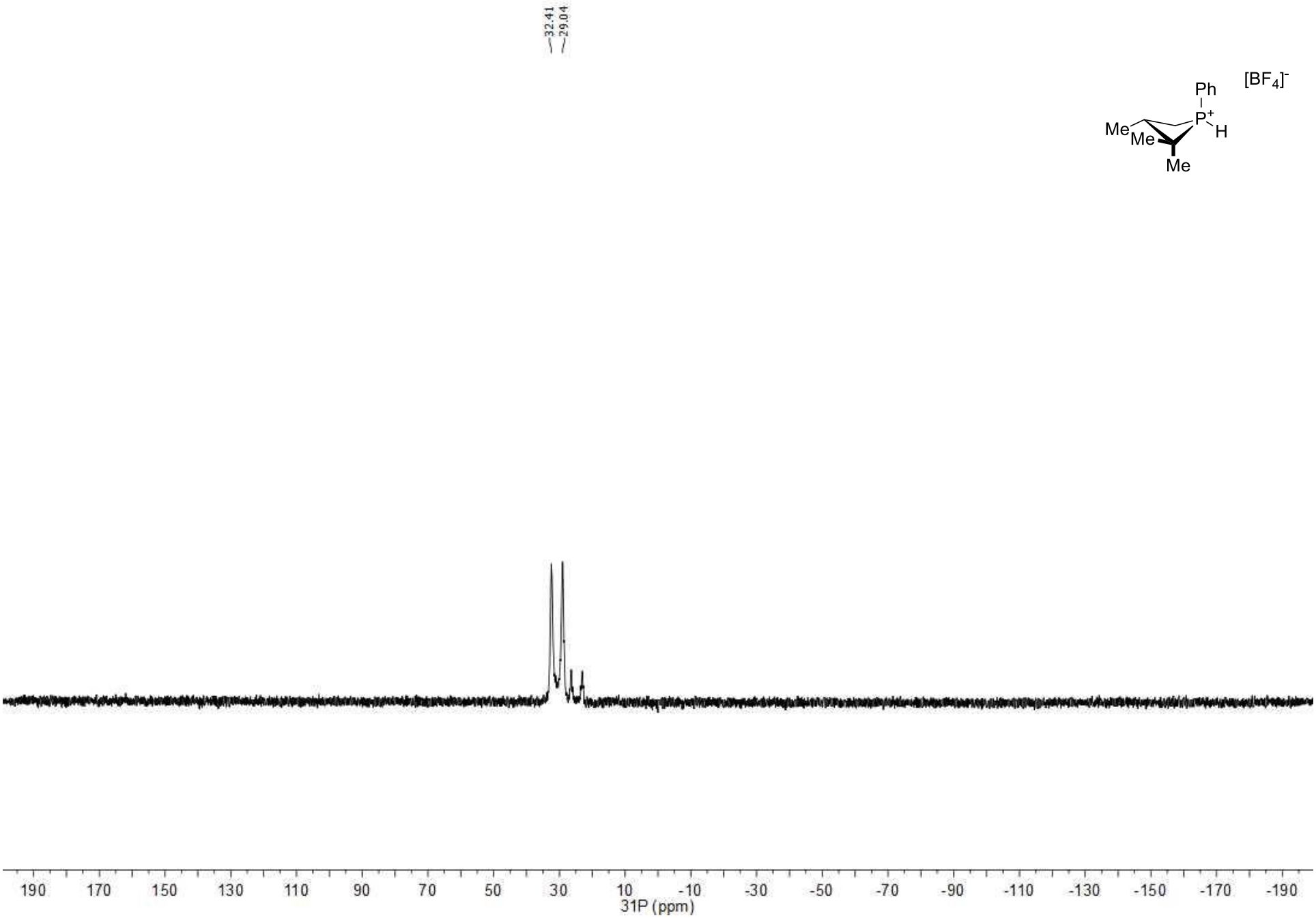

7.72 7.72 7.71 7.70 7.69 7.68 7.67 7.67 7.66 7.65 7.48 7.48 7.47 7.47 7.46 7.45 7.45 7.44 7.28 7.27 7.27 7.25 7.25 7.24 7.23 7.23 7.20 7.19 7.19 7.18 7.17 7.10 7.09 7.08 7.08 7.07 7.07 7.06 5.80 5.80 5.12 5.11
2.84 2.57 2.55 2.53 2.27 2.26 2.24 2.24 2.23 2.23 2.22 2.21 2.20 1.99 1.98 1.97 1.72 1.72 1.71 1.70 1.70 1.69 1.68 1.68 1.67 1.66 1.65 1.23 1.17 1.13 1.10 1.07 1.04 1.03 1.01 0.98 0.96 0.96 0.95 0.94 0.94 0.93 0.93 0.91 0.89
Ph
P
H
Ph
Me
Me
Me
12.30
0.53
0.50
1.83
2.12
8.92
12.69
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
1H (ppm)


147.32
146.52
143.30
143.18
135.66
135.47
134.68
134.56
133.72
133.59
131.40
131.25
129.74
129.41
129.30
129.21
129.02
128.90
128.74
127.36
126.88
126.66
125.77
118.26
66.52
65.90
59.85
59.79
58.24
37.28
37.15
32.64
32.46
28.63
28.00
22.09
17.69
17.05
15.69
15.38
1.94
1.74
1.53
1.32
1.12
0.91
0.70
Ph
P
H
Ph
Me
Me
Me
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C (ppm)


-3.13
-75.99
-77.59
-80.06
-81.75
Ph
P
H
Ph
Me
Me
Me
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
31P (ppm)


8.42
8.04
8.03
8.01
8.01
8.01
8.00
7.99
7.98
7.97
7.97
7.75
7.75
7.63
7.62
7.02
3.22
3.20
3.20
3.18
3.02
3.01
2.99
2.99
2.98
2.96
2.96
1.63
1.57
1.22
1.21
1.15
[BF4]-
Ph
P+
H
Me
Me
Me
0.46
2.00
1.00
2.01
0.45
1.04
1.92
2.98
6.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1H (ppm)


135.21
135.17
133.67
133.64
133.55
133.52
130.16
130.02
113.96
113.25
46.29
45.77
41.59
41.40
22.41
22.37
22.29
21.78
18.85
18.83
15.83
15.60
[BF4]-
Ph
P+
H
Me
Me
Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
13C (ppm)


32.41
29.04
[BF4]-
Ph
P+
H
Me
Me
Me
190
170
150
130
110
90
70
50
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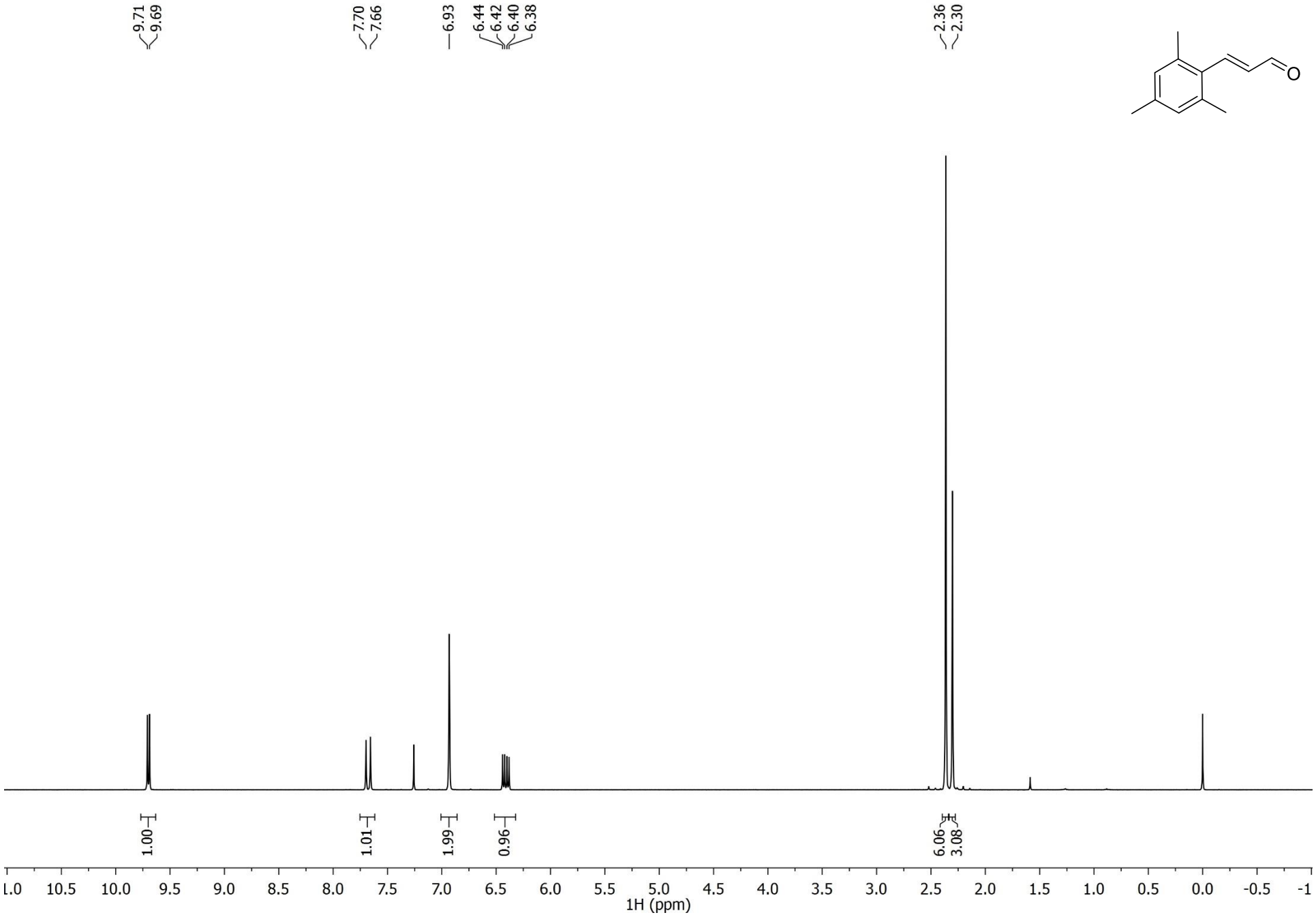
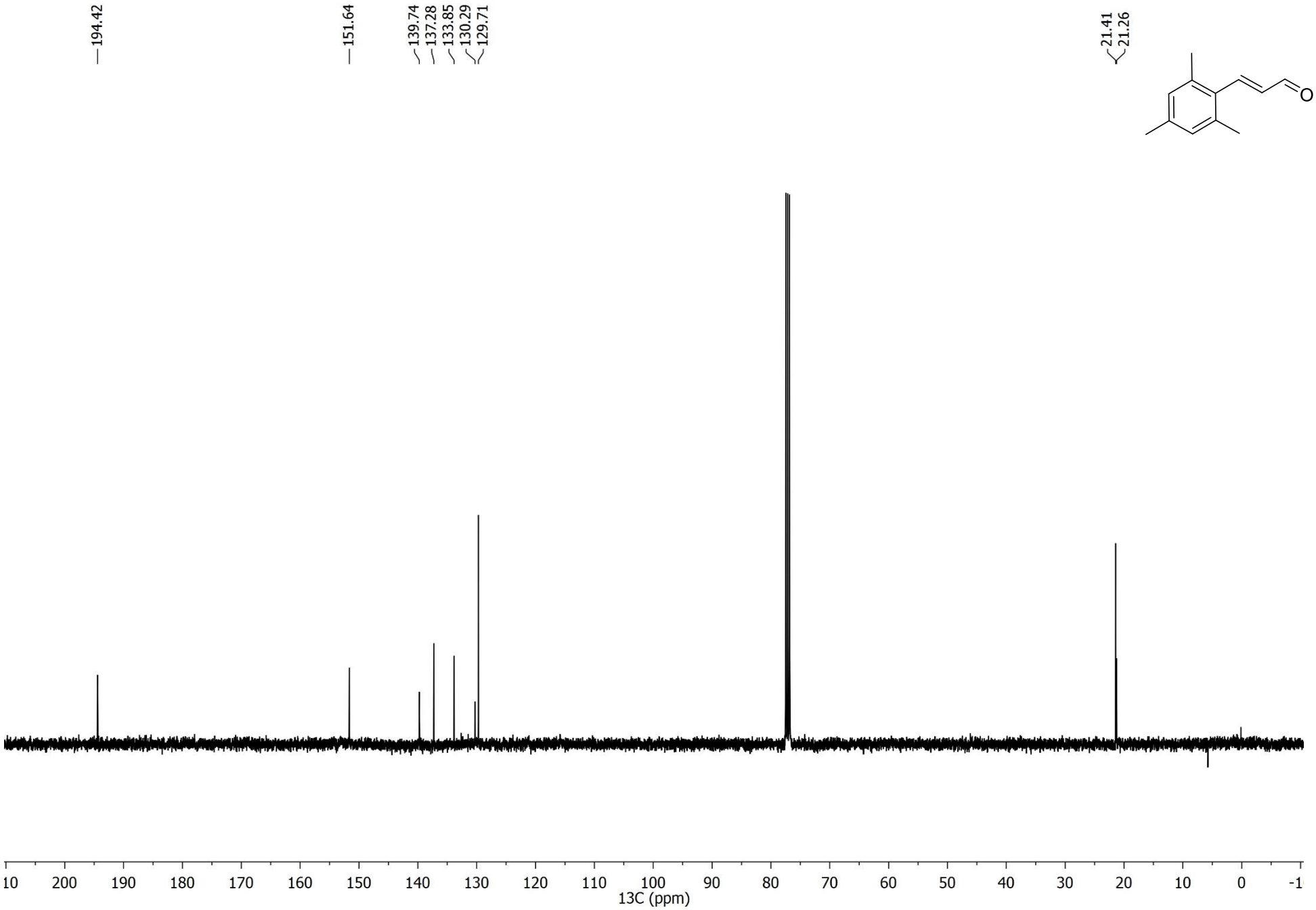
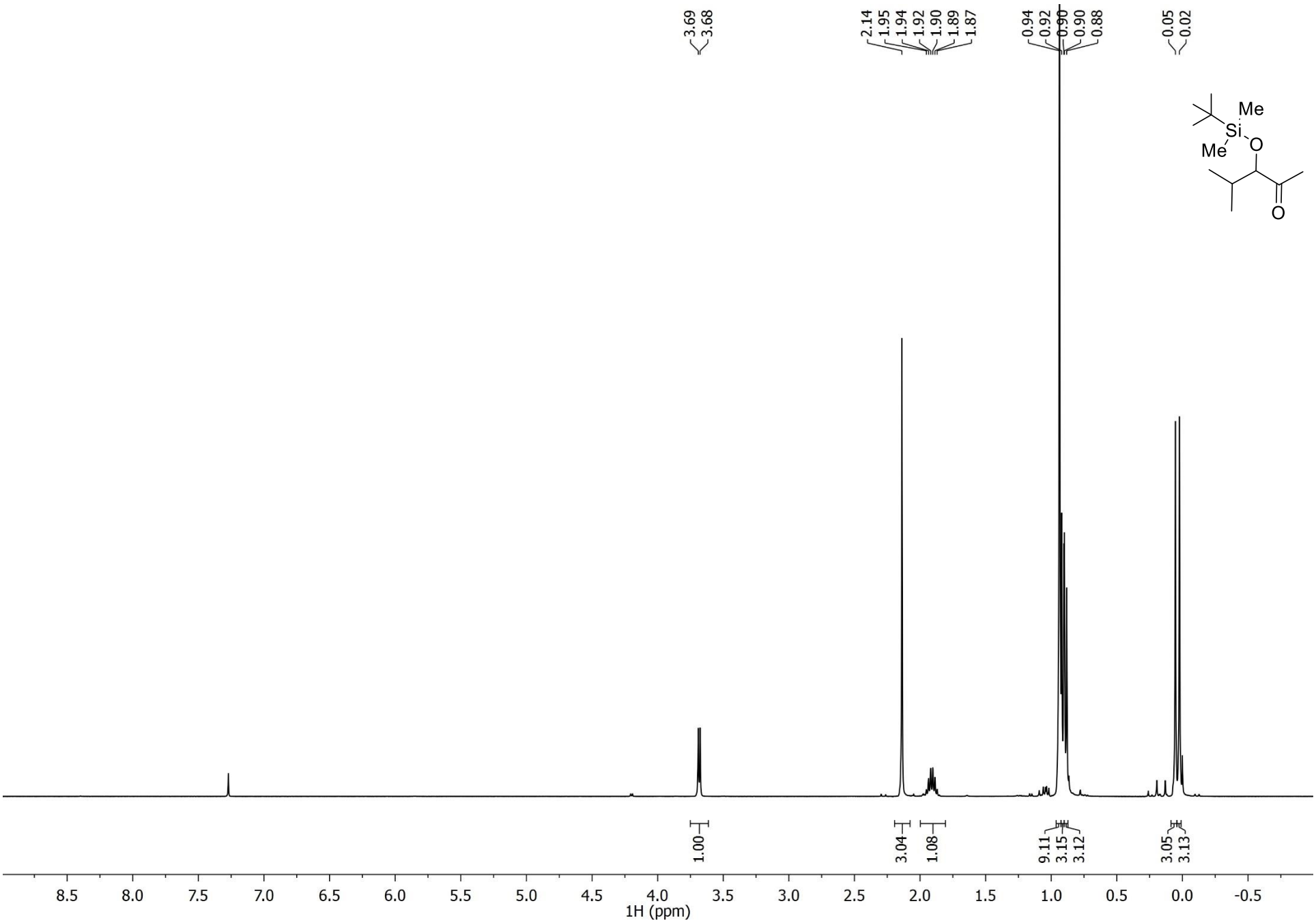
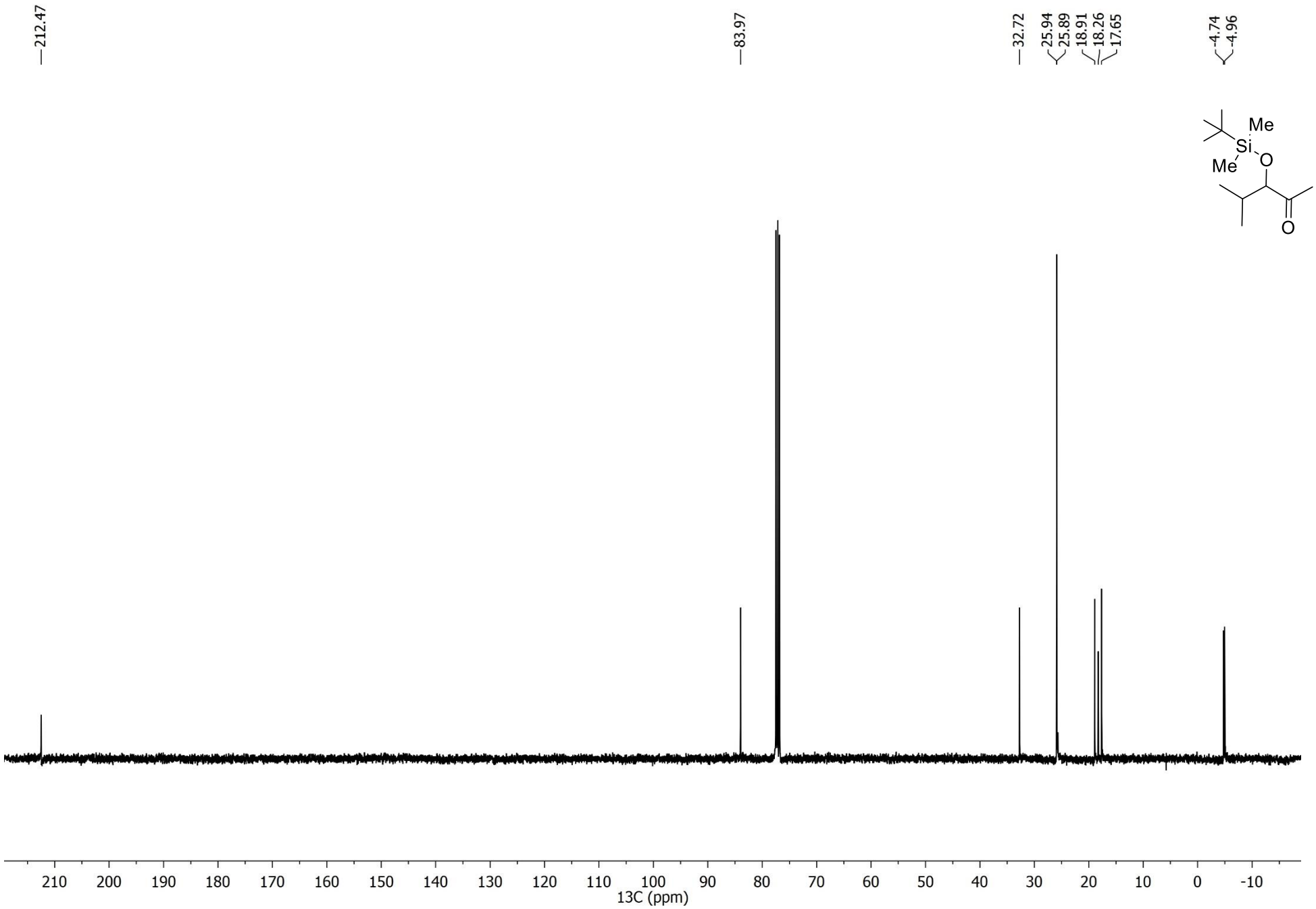
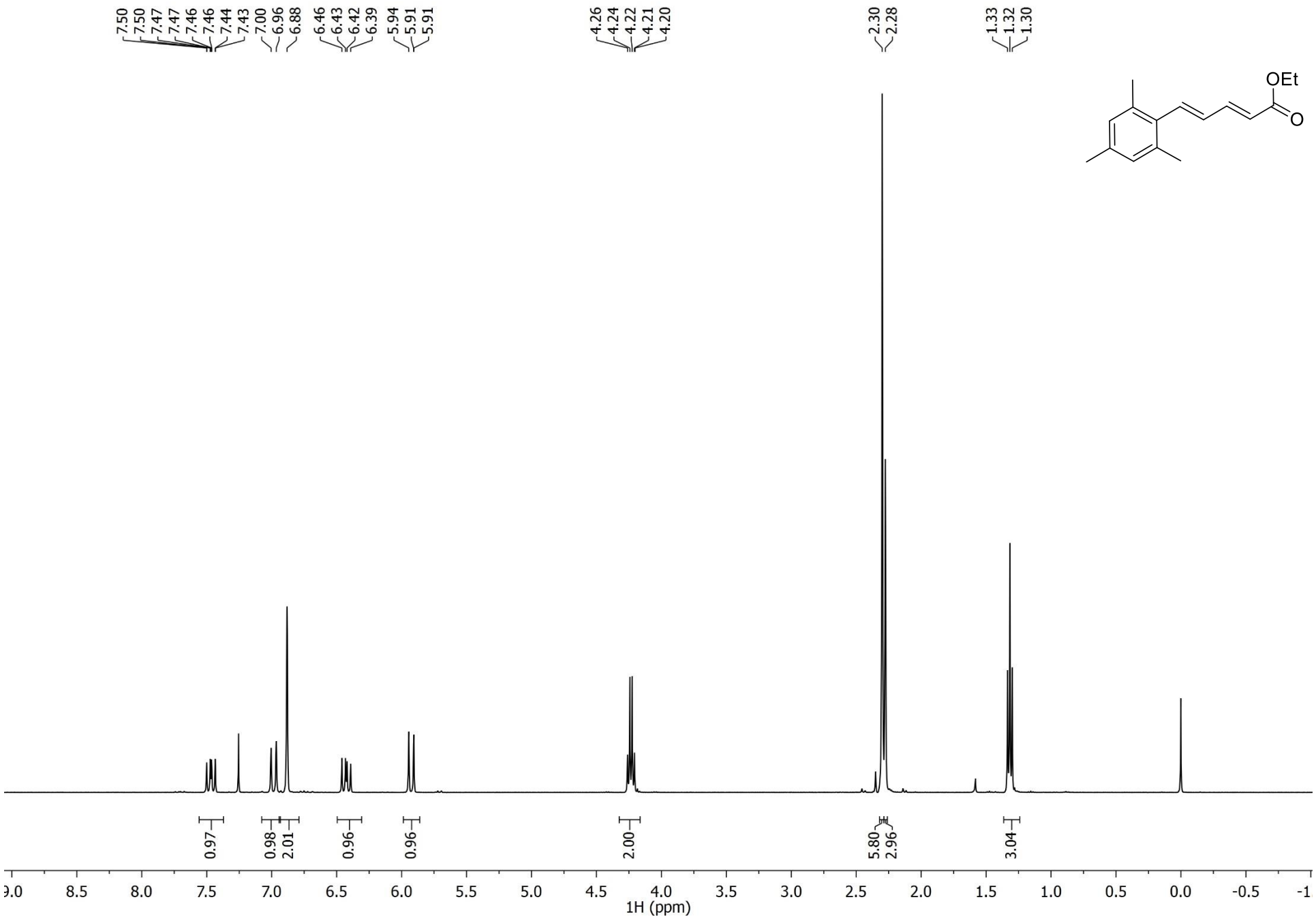
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
31P (ppm)

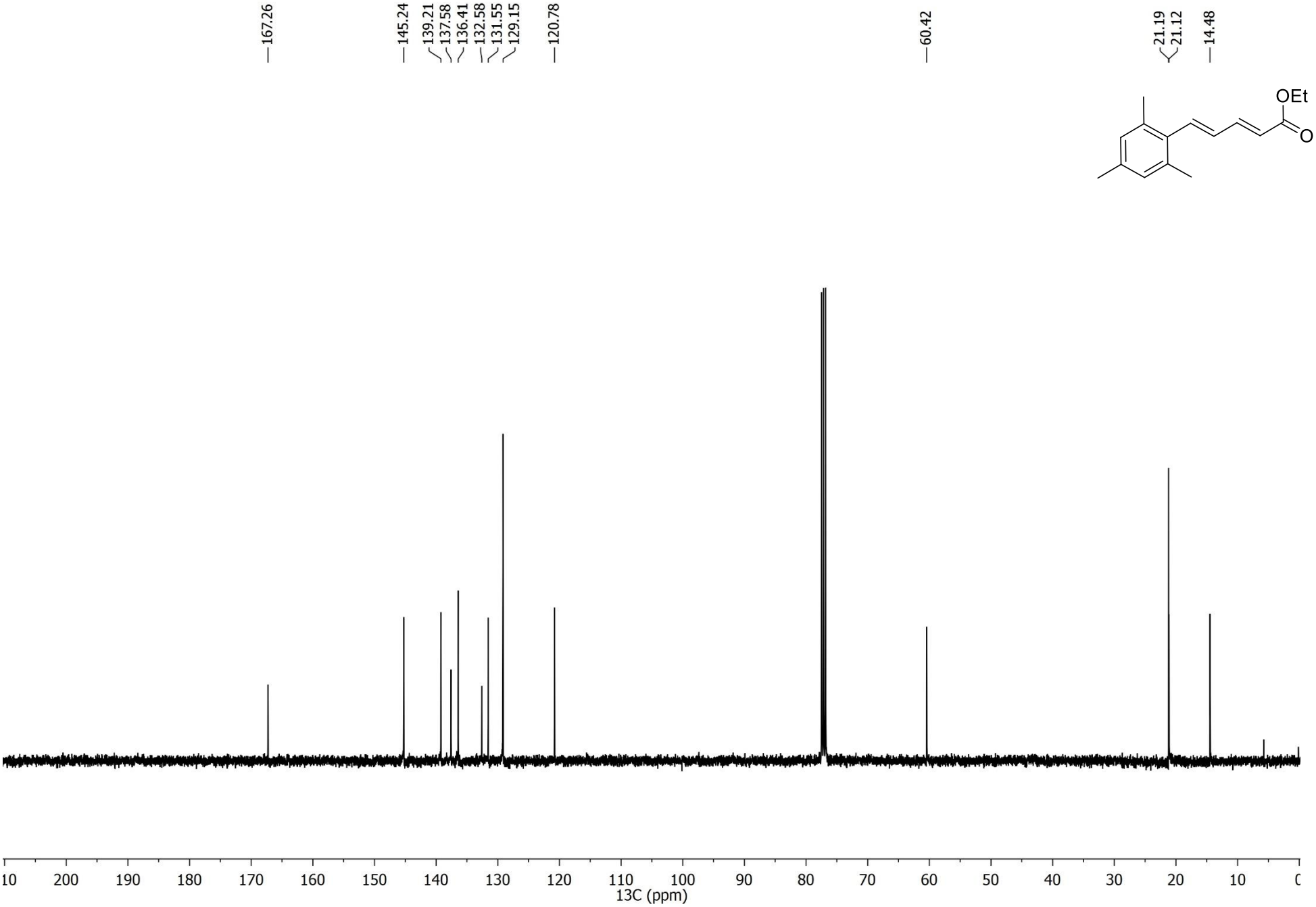

9.71
9.69
7.70
7.66
6.93
6.44
6.42
6.40
6.38
2.36
2.30
O
1.00
1.01
1.99
0.96
6.06
3.08
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
1H (ppm)

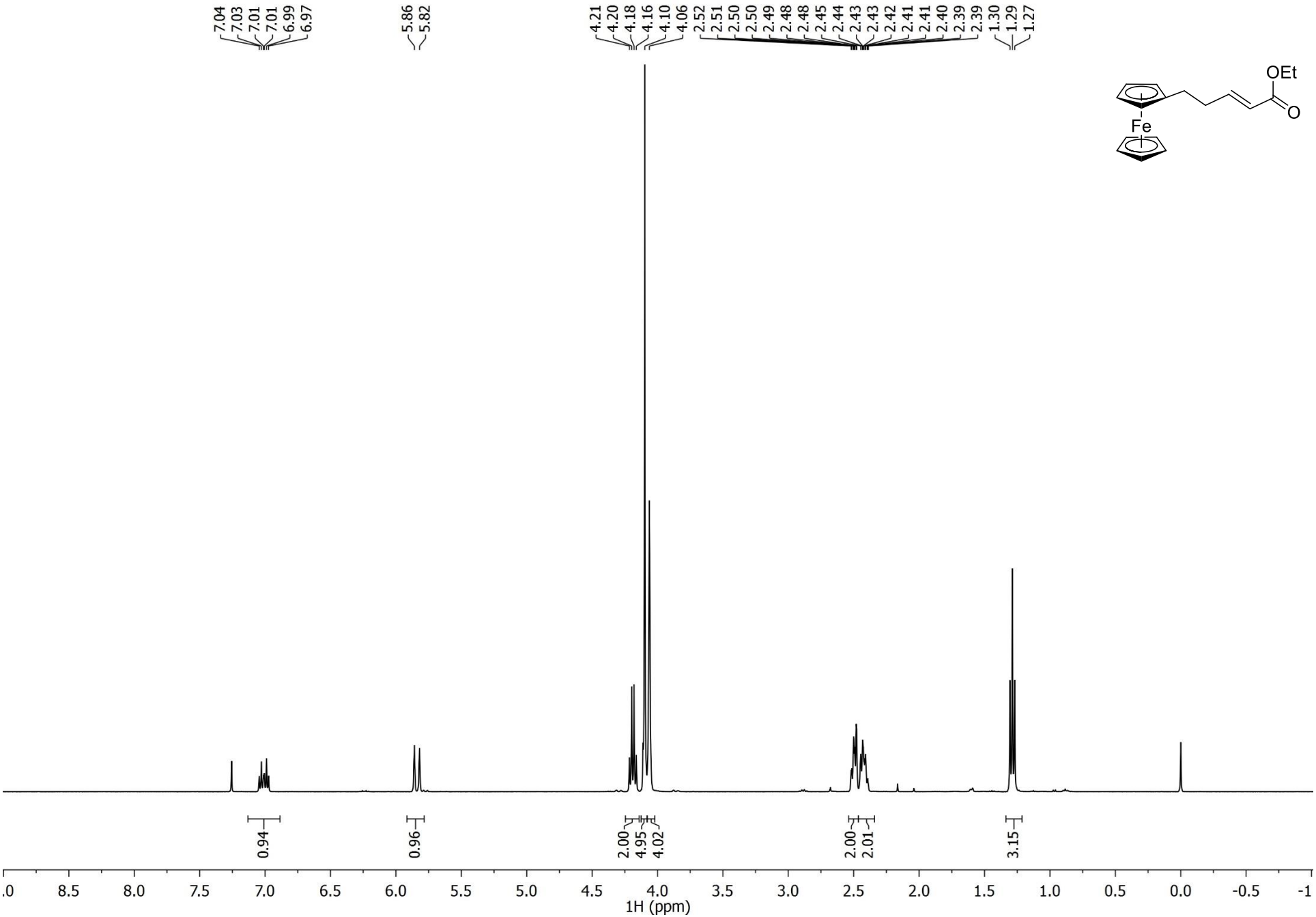

194.42
151.64
139.74
137.28
133.85
130.29
129.71
21.41
21.26
O
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
13C (ppm)

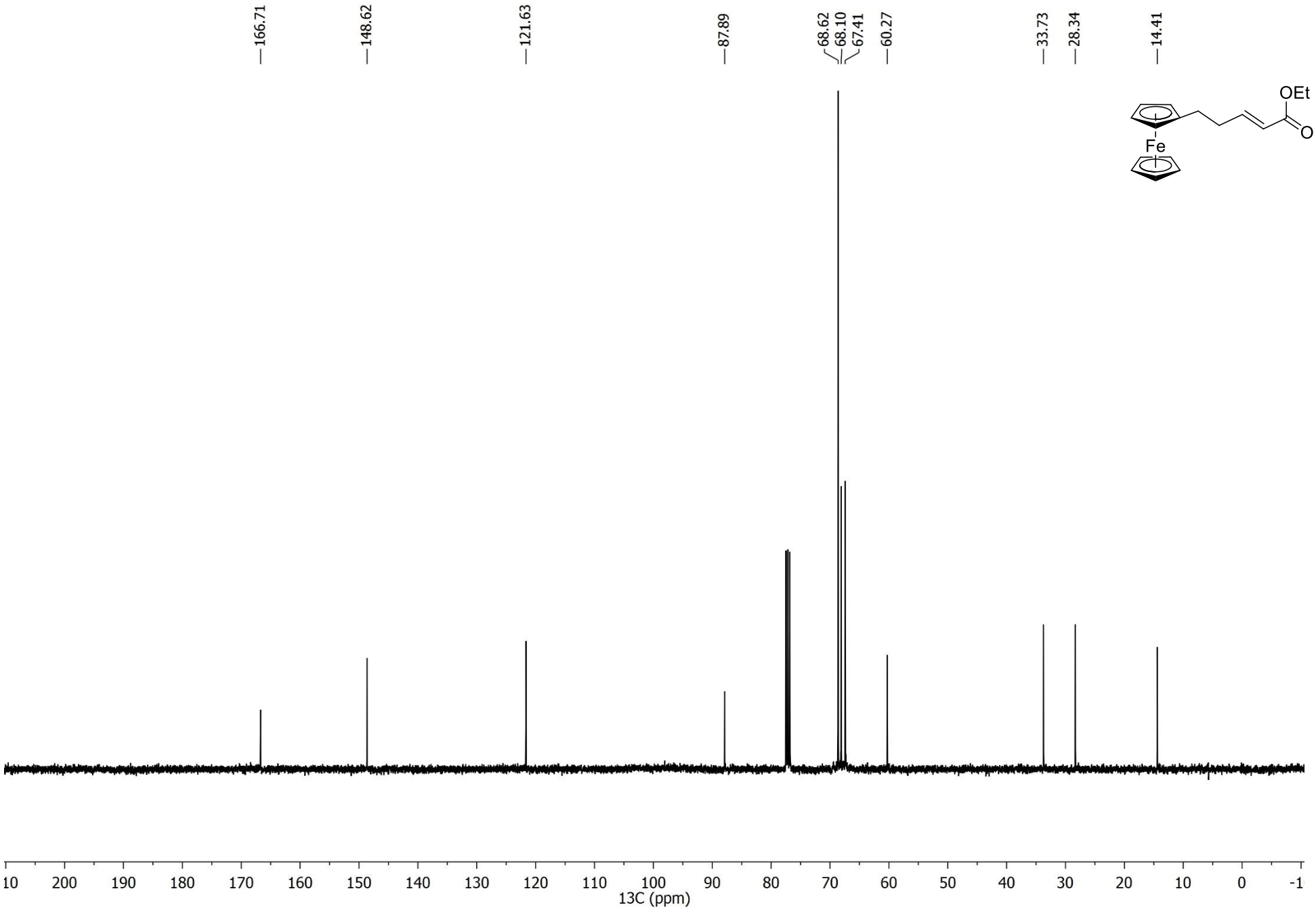

3.69
3.68
2.14
1.95
1.94
1.92
1.90
1.89
1.87
0.94
0.92
0.90
0.90
0.88
0.05
0.02
Me
Si
Me
O
O
1.00
3.04
1.08
9.11
3.15
3.12
3.05
3.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1H (ppm)

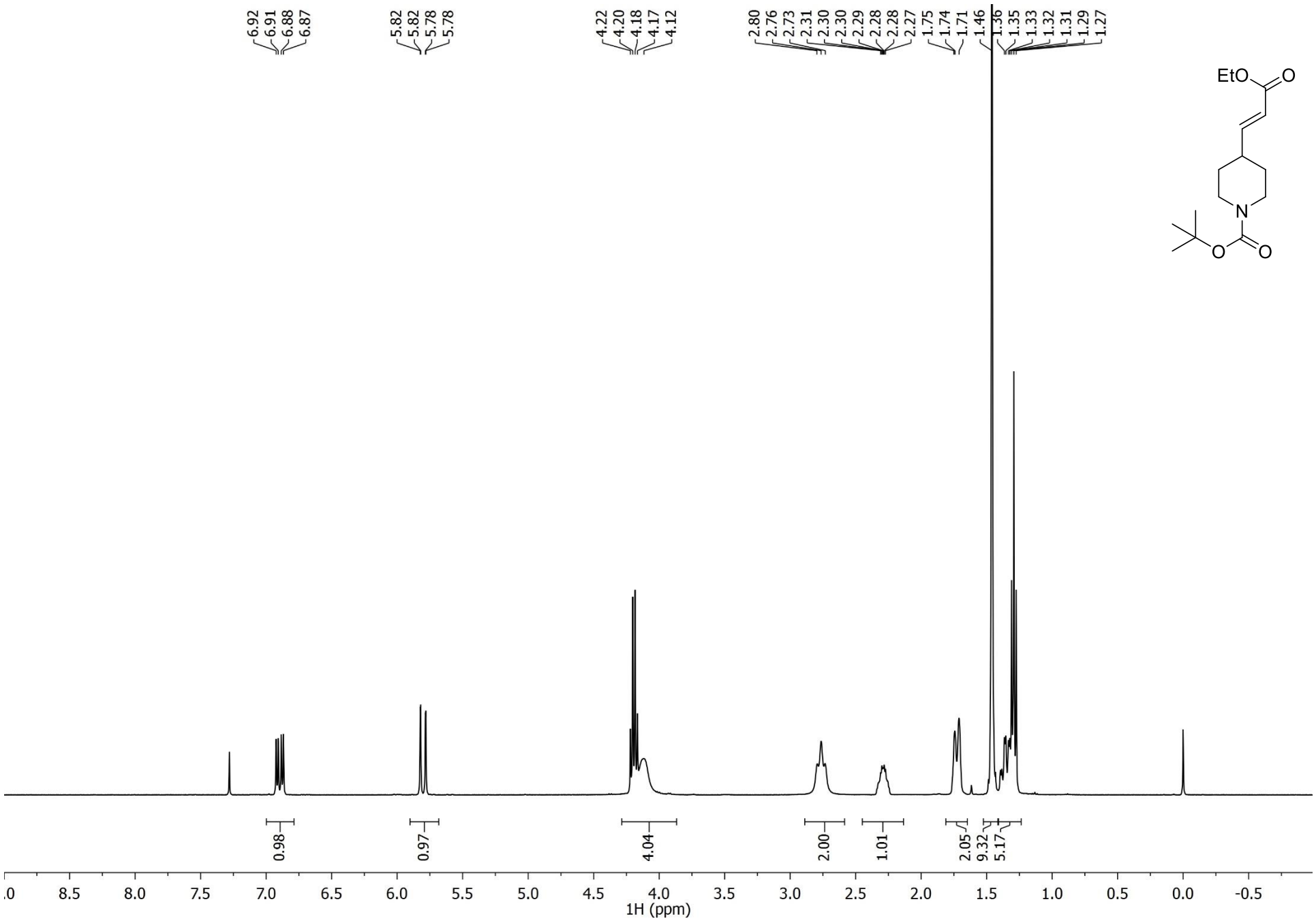

212.47
83.97
32.72
25.94
25.89
18.91
18.26
17.65
-4.74
-4.96
Me
Si
Me
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
13C (ppm)

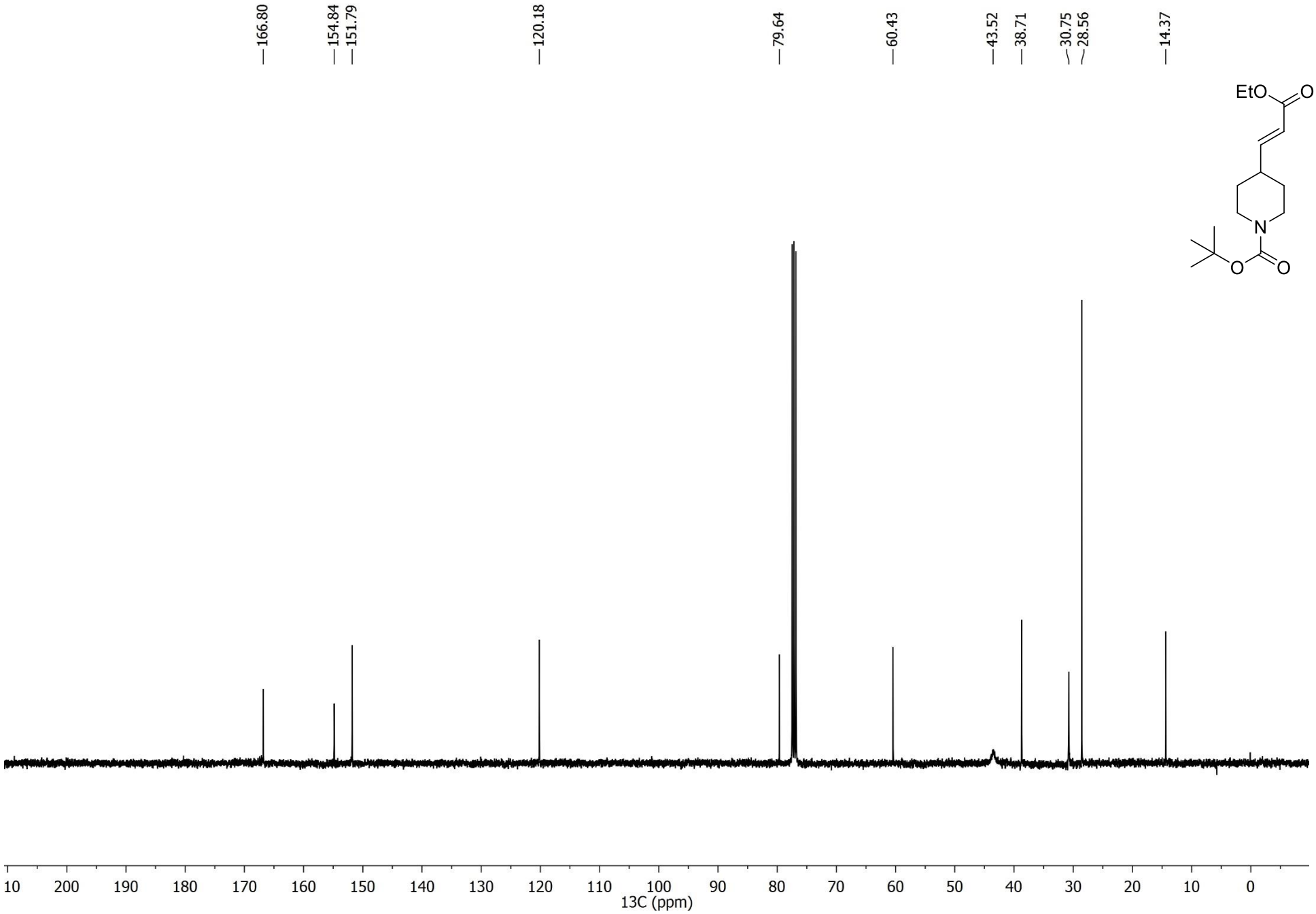

7.50
7.50
7.47
7.47
7.46
7.46
7.44
7.43
7.00
6.96
6.88
6.46
6.43
6.42
6.39
5.94
5.91
5.91
4.26
4.24
4.22
4.21
4.20
2.30
2.28
1.33
1.32
1.30
OEt
O
0.97
0.98
2.01
0.96
0.96
2.00
5.80
2.96
3.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
1H (ppm)

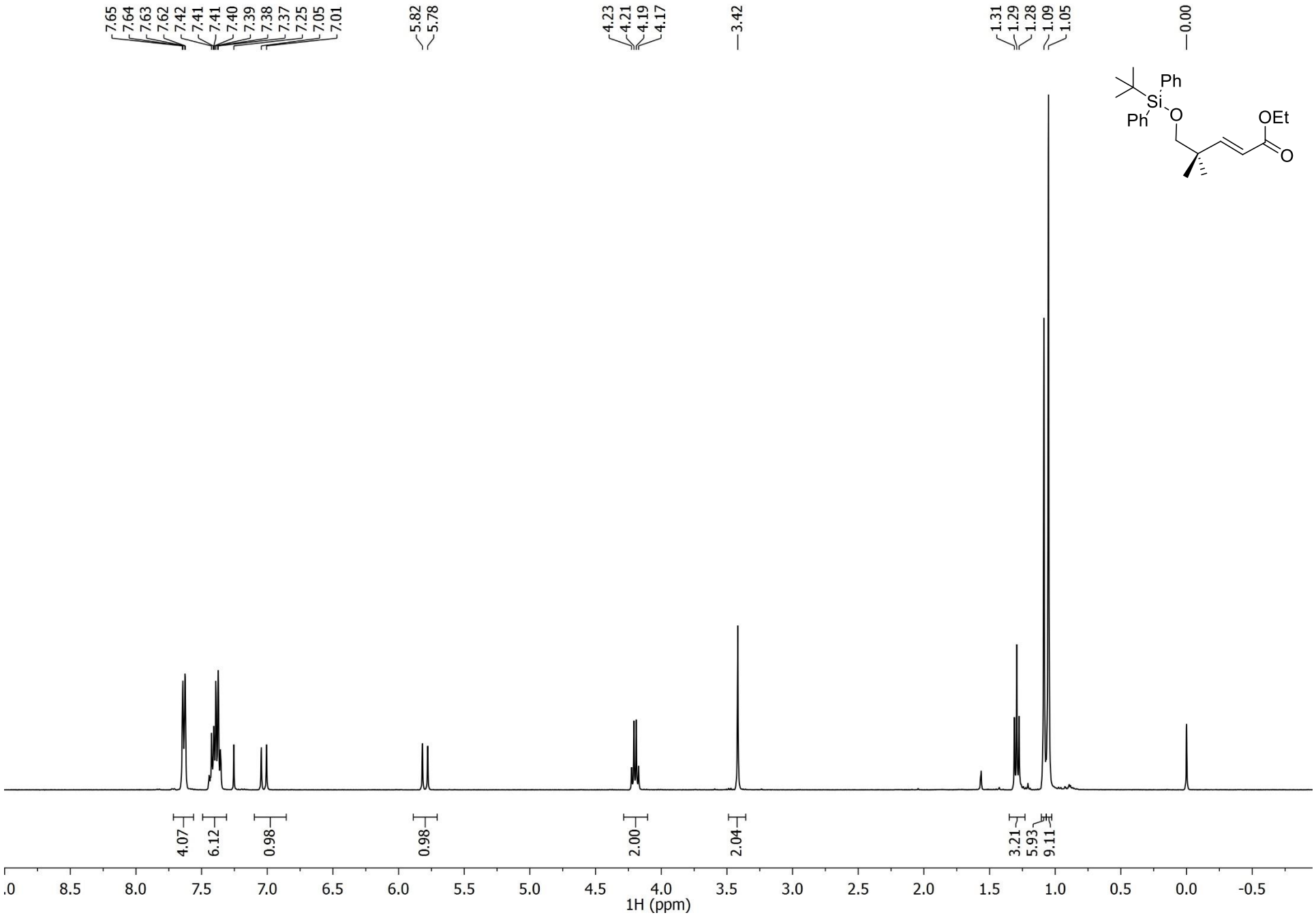

167.26
145.24
139.21
137.58
136.41
132.58
131.55
129.15
120.78
60.42
21.19
21.12
14.48
OEt
O
13C (ppm)


7.04
7.03
7.01
7.01
6.99
6.97
5.86
5.82
4.21
4.20
4.18
4.16
4.10
4.06
2.52
2.51
2.50
2.50
2.49
2.48
2.48
2.45
2.44
2.43
2.43
2.42
2.41
2.41
2.40
2.39
2.39
1.30
1.29
1.27
OEt
O
Fe
0.94
0.96
2.00
4.95
4.02
2.00
2.01
3.15
1H (ppm)


166.71
148.62
121.63
87.89
68.62
68.10
67.41
60.27
33.73
28.34
14.41
OEt
O
Fe
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
13C (ppm)


6.92
6.91
6.88
6.87
5.82
5.82
5.78
5.78
4.22
4.20
4.18
4.17
4.12
2.80
2.76
2.73
2.31
2.30
2.30
2.29
2.28
2.28
2.27
1.75
1.74
1.71
1.46
1.36
1.35
1.33
1.32
1.31
1.29
1.27
EtO
O
N
O
O
0.98
0.97
4.04
2.00
1.01
2.05
9.32
5.17
1H (ppm)


166.80
154.84
151.79
120.18
79.64
60.43
43.52
38.71
30.75
28.56
14.37
EtO
O
N
O
O
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C (ppm)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7.64
7.63
7.62
7.42
7.41
7.41
7.40
7.39
7.38
7.37
7.25
7.05
7.01
5.82
5.78
4.23
4.21
4.19
4.17
3.42
1.31
1.29
1.28
1.09
1.05
0.00
Ph
Si
Ph
O
OEt
O
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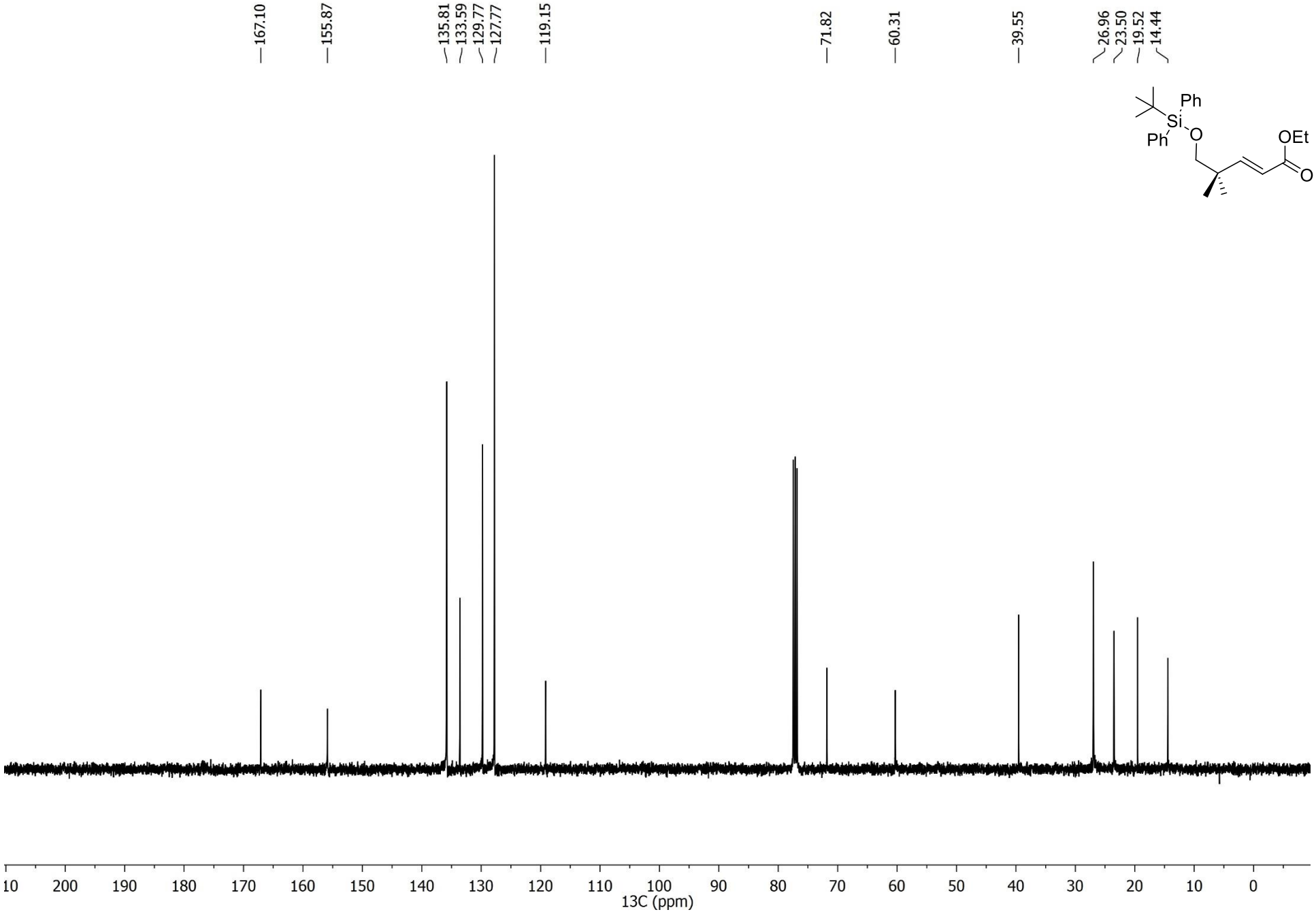
6.12
0.98
0.98
2.00
2.04
3.21
5.93
9.11
1H (ppm)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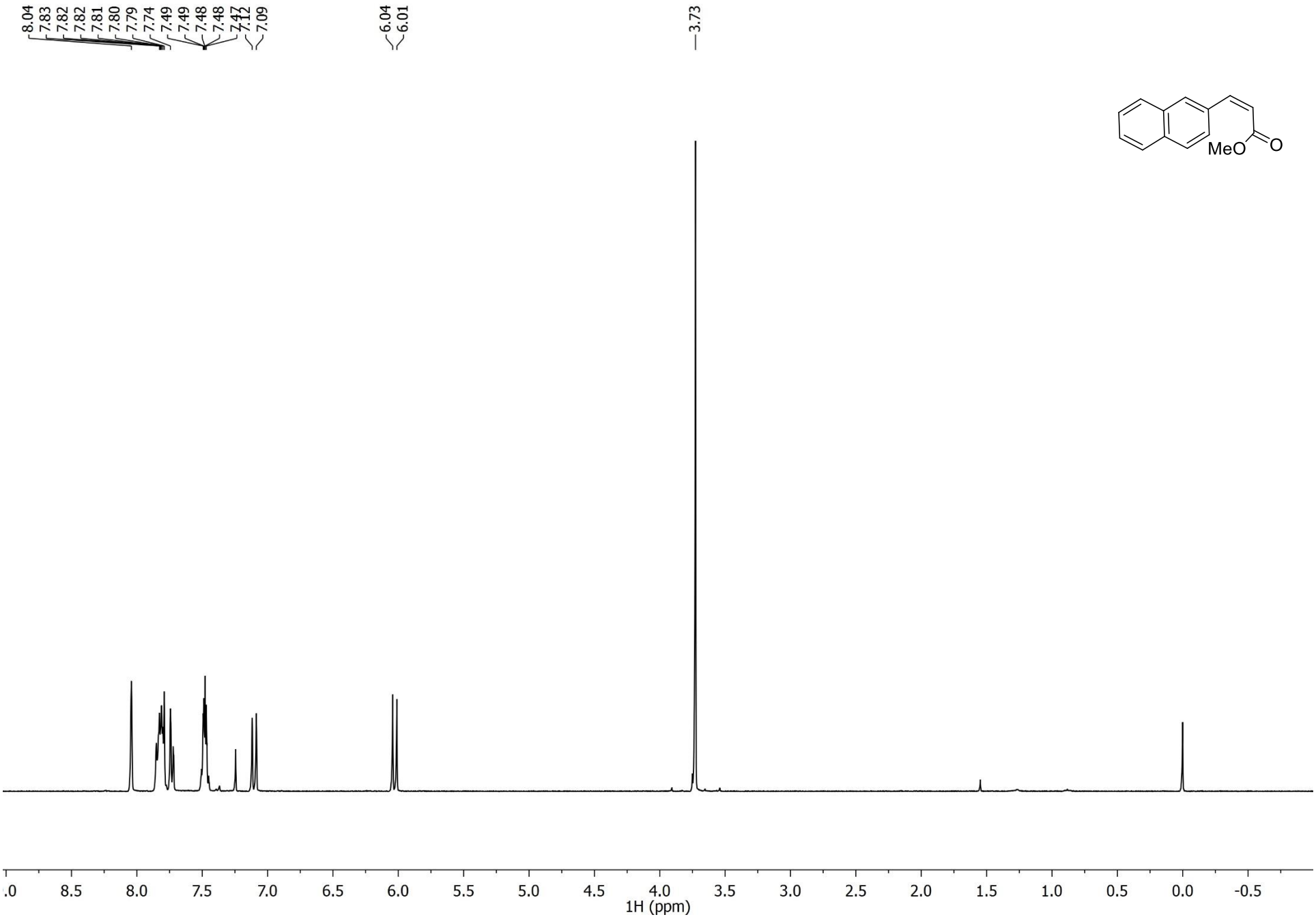
155.87
135.81
133.59
129.77
127.77
119.15
71.82
60.31
39.55
26.96
23.50
19.52
14.44
Ph
Si
Ph
O
OEt
O
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C (ppm)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7.83
7.82
7.82
7.81
7.80
7.79
7.74
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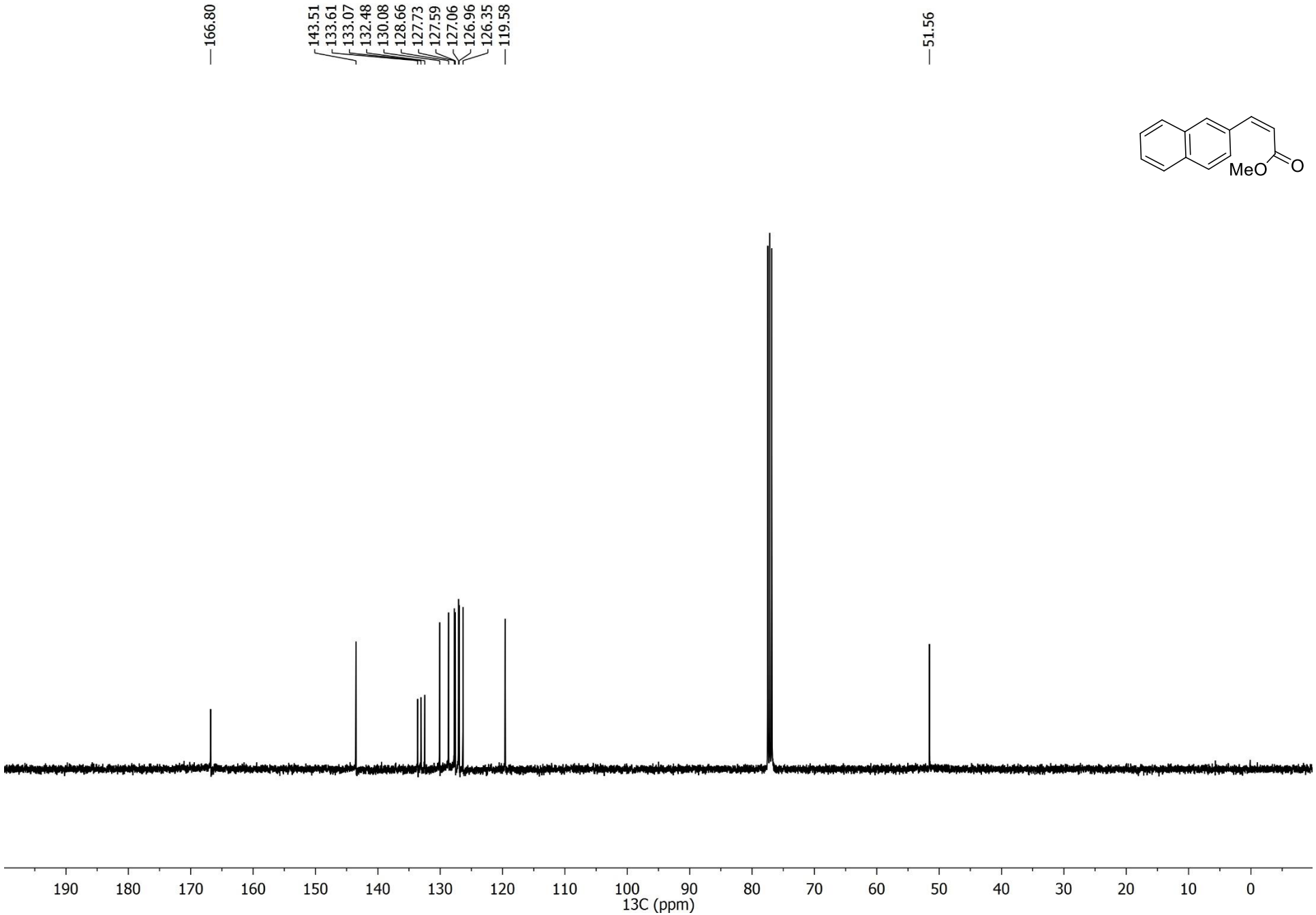
7.48
7.48
7.12
7.09
6.04
6.01
3.73
MeO
O
1H (ppm)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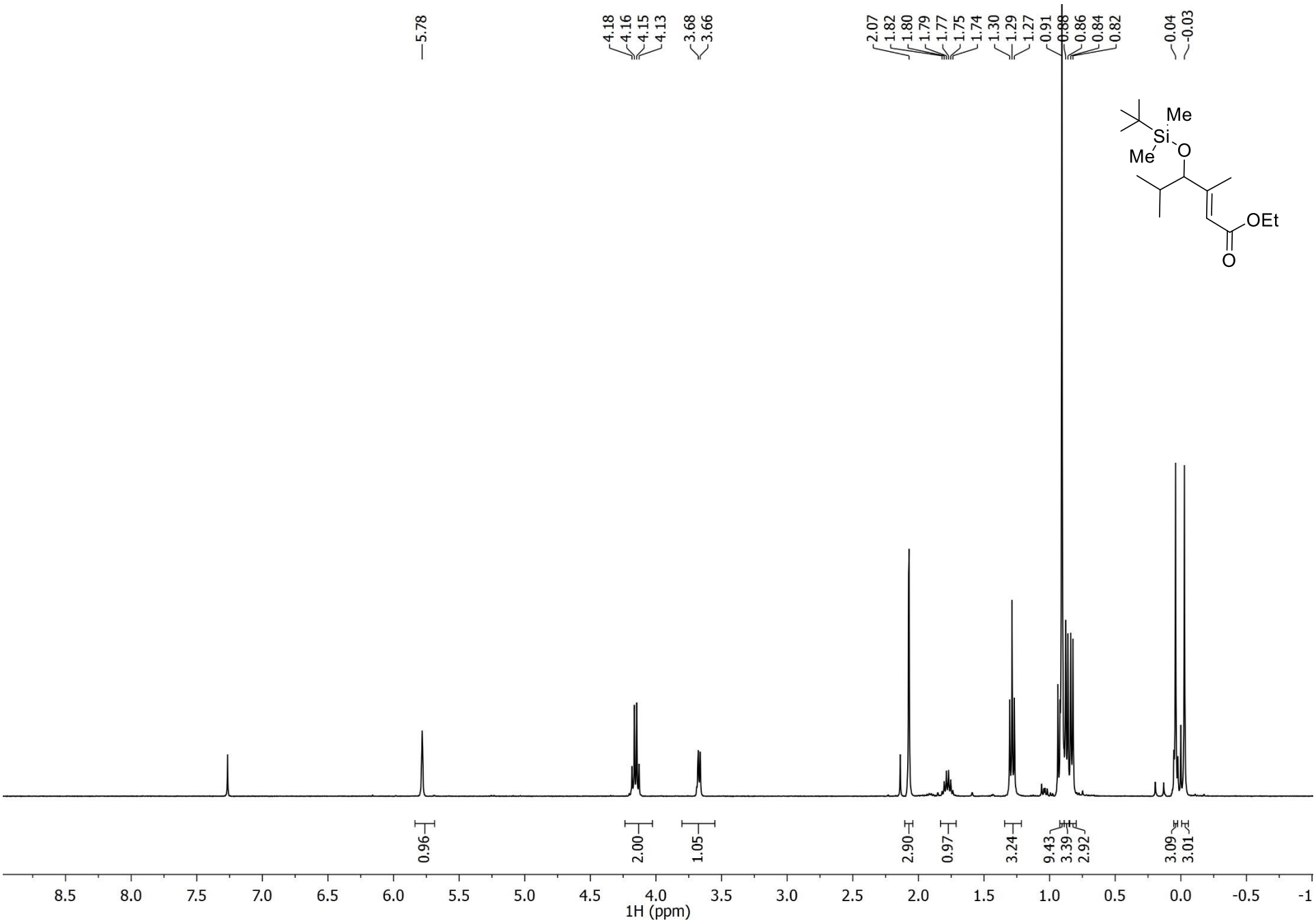
133.61
133.07
132.48
130.08
128.66
127.73
127.59
127.06
126.96
126.35
119.58
51.56
MeO
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C (ppm)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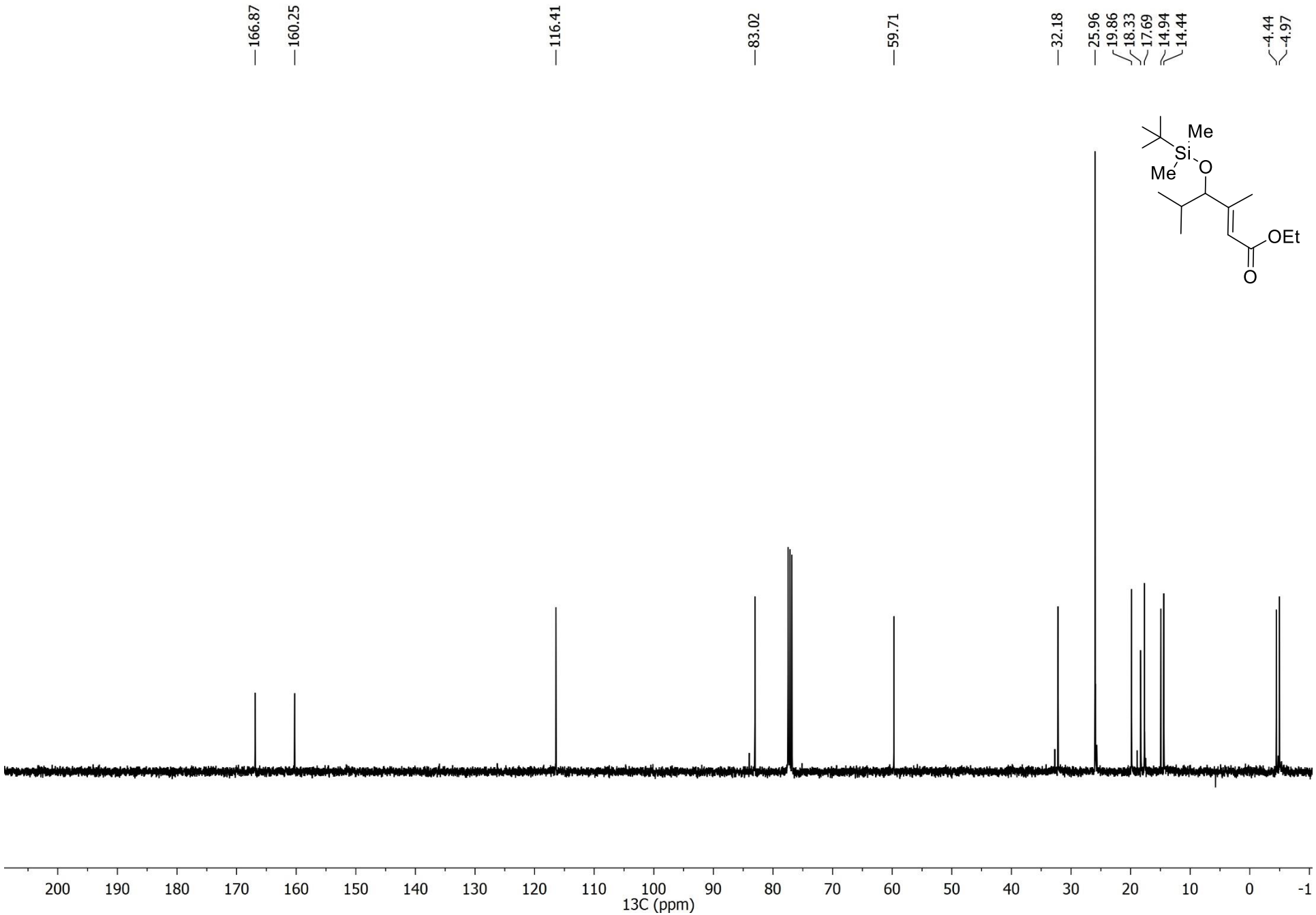
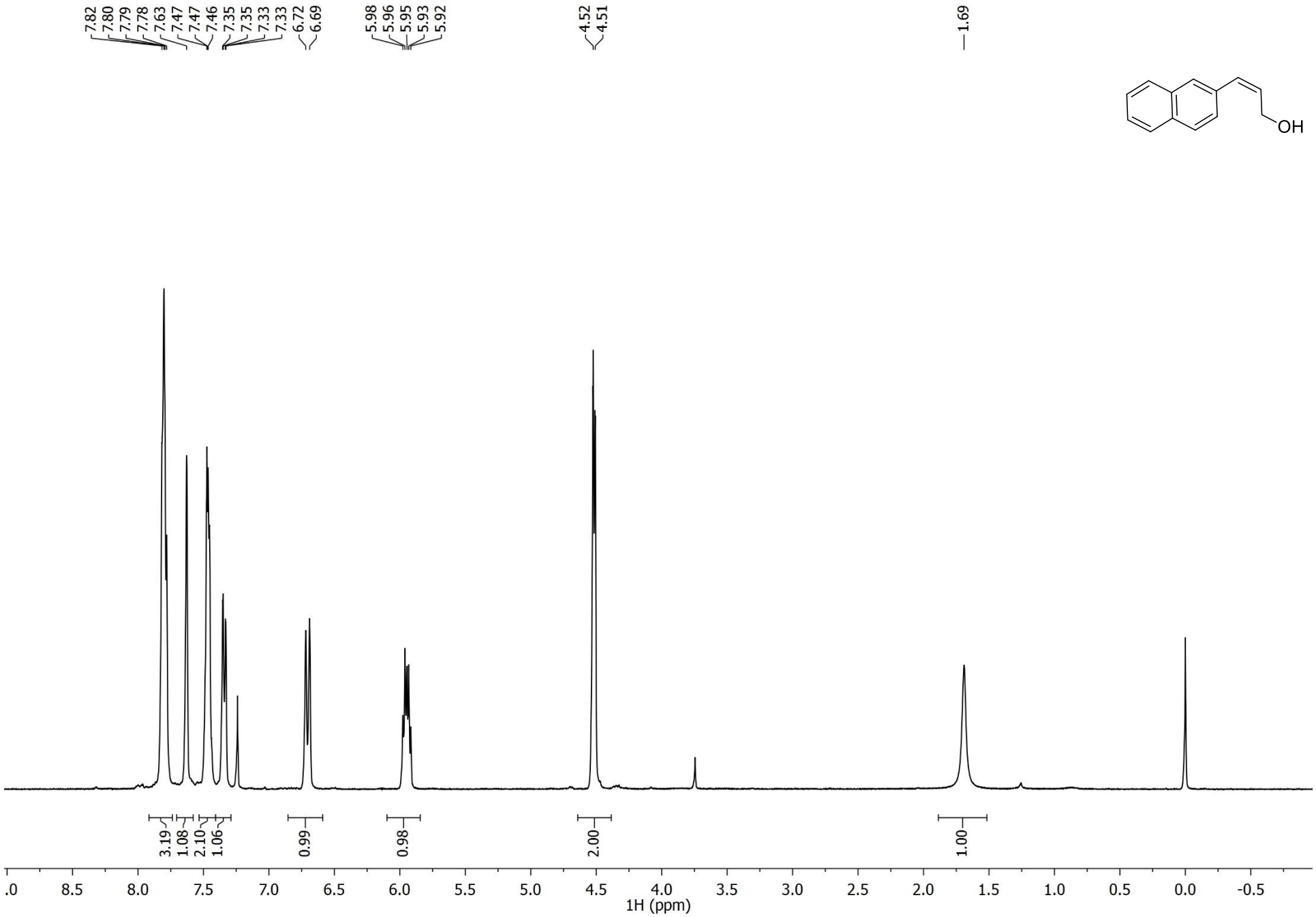
4.18
4.16
4.15
4.13
3.68
3.66
2.07
1.82
1.80
1.79
1.77
1.75
1.74
1.30
1.29
1.27
0.91
0.88
0.86
0.84
0.82
0.04
-0.03
Me
Si
Me
O
OEt
O
0.96
2.00
1.05
2.90
0.97
3.24
9.43
3.39
2.92
3.09
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
1H (ppm)


166.87
160.25
116.41
83.02
59.71
32.18
25.96
19.86
18.33
17.69
14.94
14.44
-4.44
-4.97
Me
Si
Me
O
OEt
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
13C (ppm)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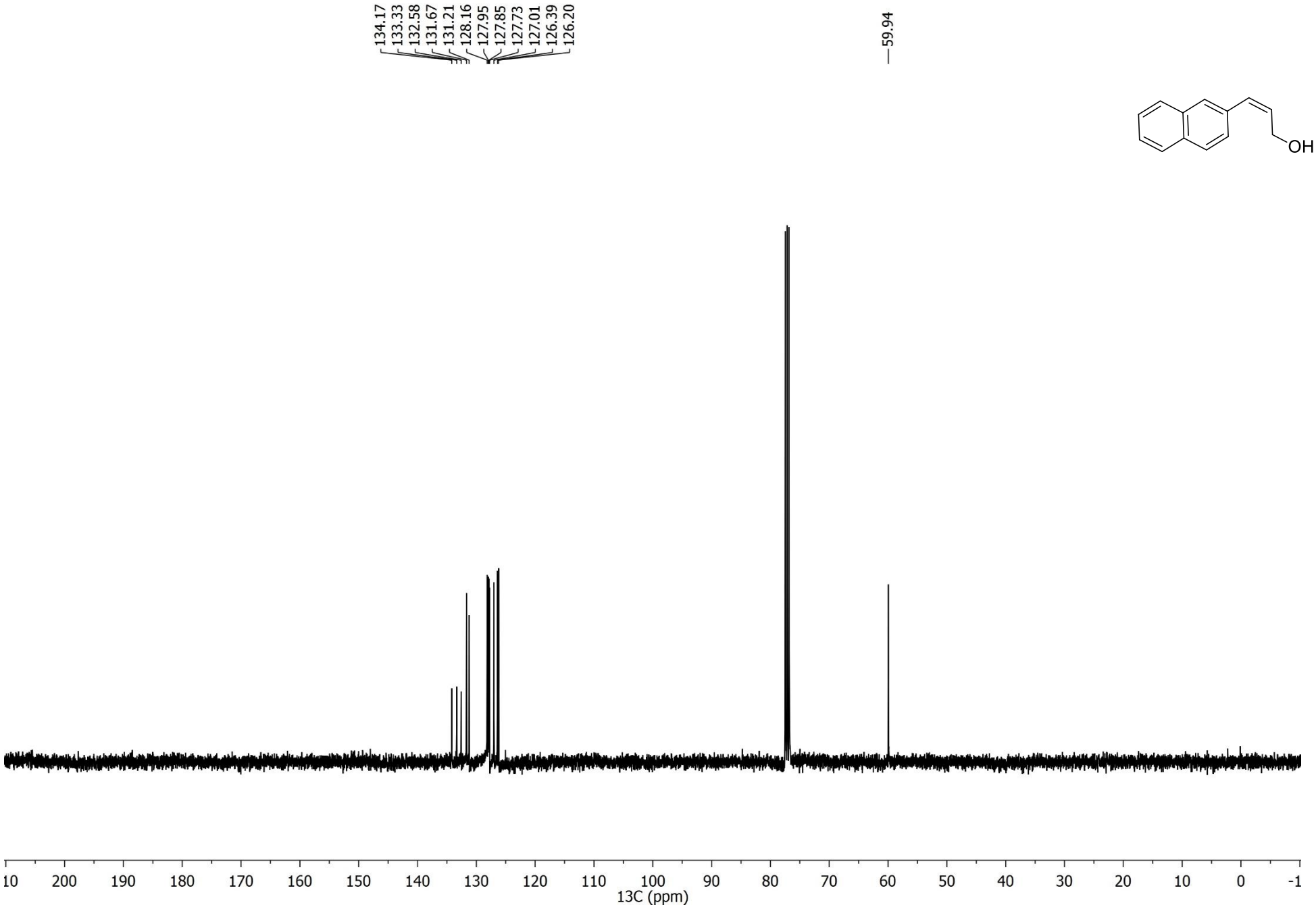
7.47
7.46
7.35
7.35
7.33
7.33
6.72
6.69
5.98
5.96
5.95
5.93
5.92
4.52
4.51
1.69
OH
3.19
1.08
2.10
1.06
0.99
0.98
2.00
1.00
1H (ppm)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127.73
127.01
126.39
126.20
59.94
OH
10
200
190
180
170
160
150
140
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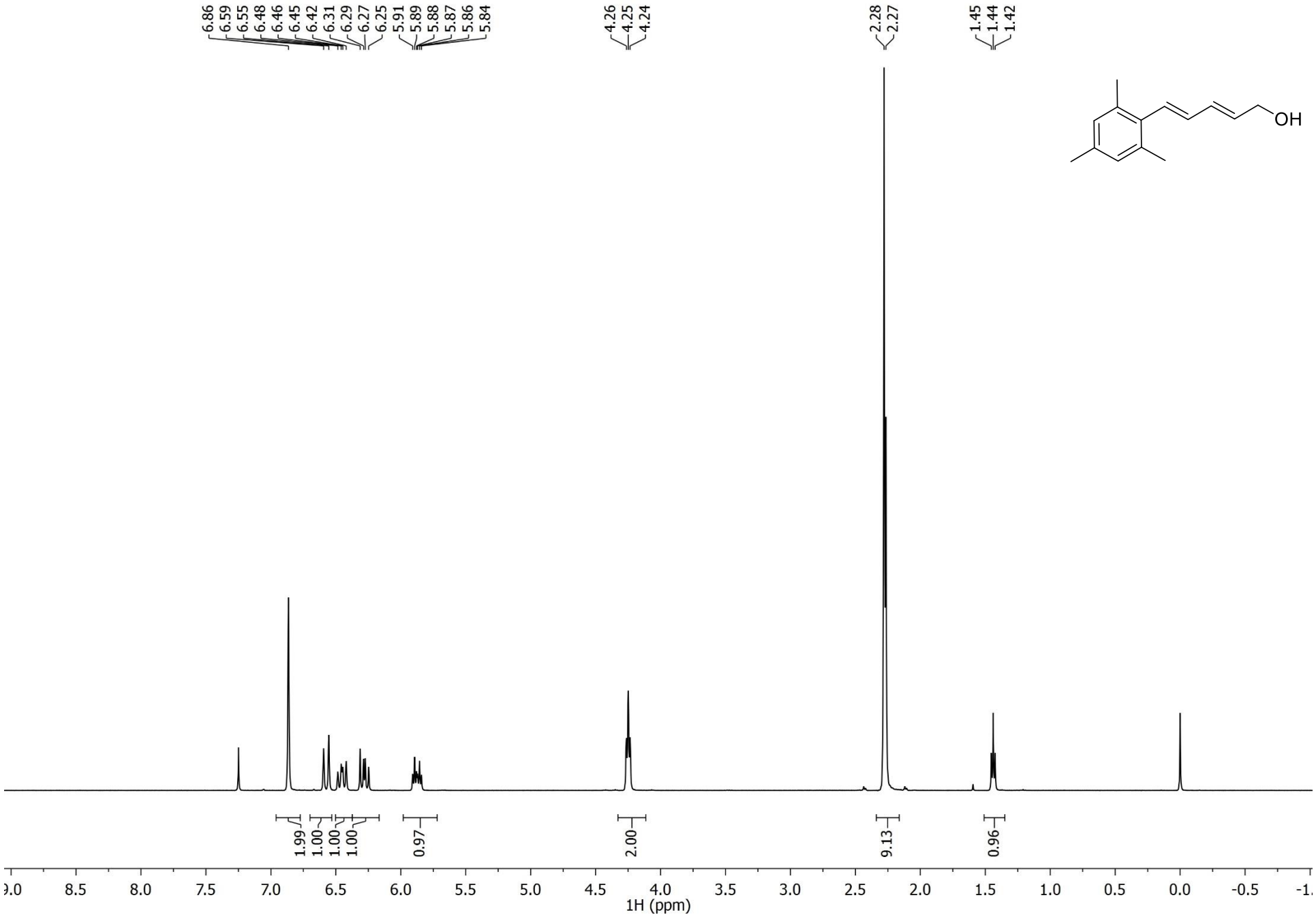
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
13C (ppm)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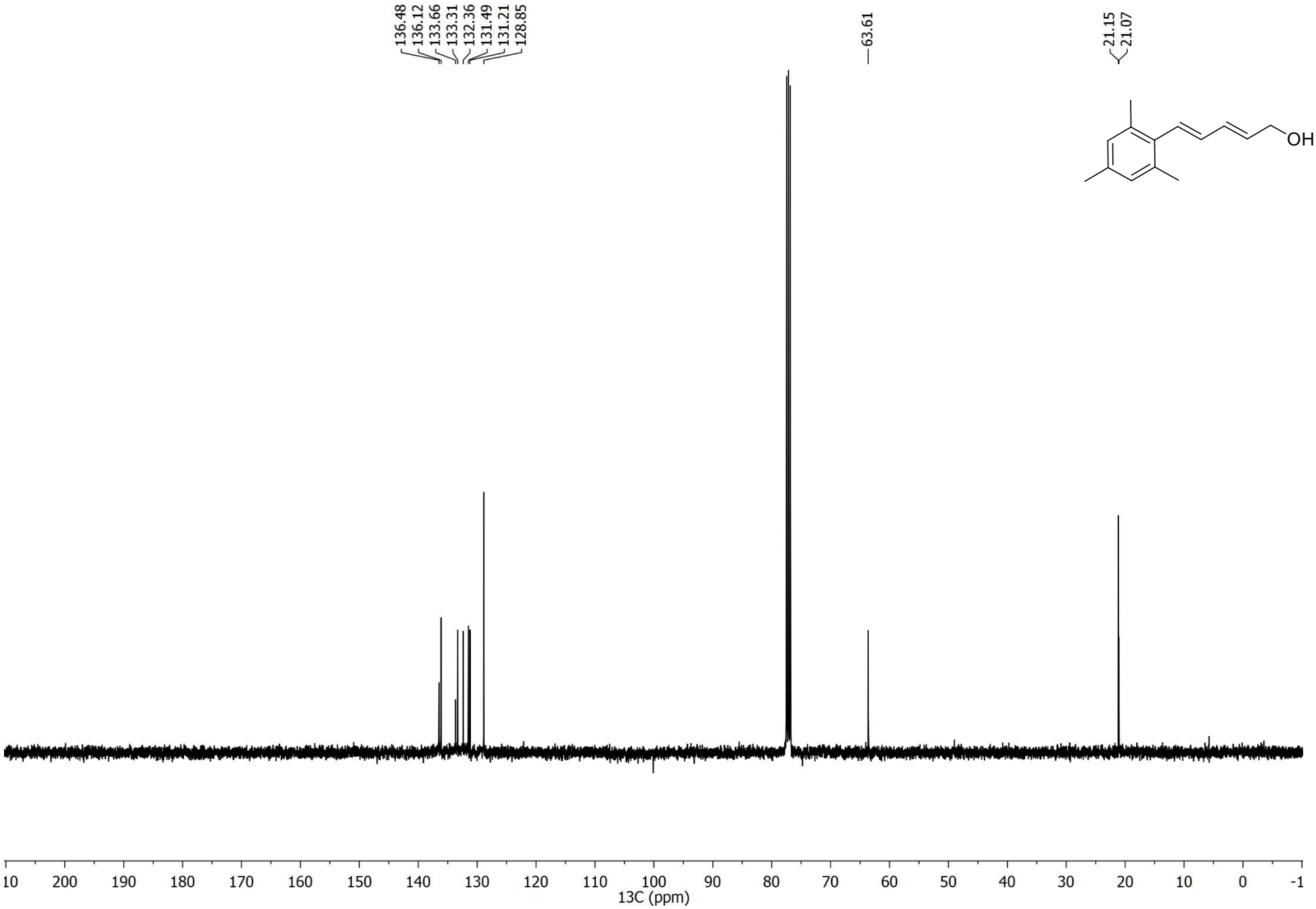
6.45
6.42
6.31
6.29
6.27
6.25
5.91
5.89
5.88
5.87
5.86
5.84
4.26
4.25
4.24
2.28
2.27
1.45
1.44
1.42
OH
1.99
1.00
1.00
1.00
0.97
2.00
9.13
0.96
1H (ppm)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136.12
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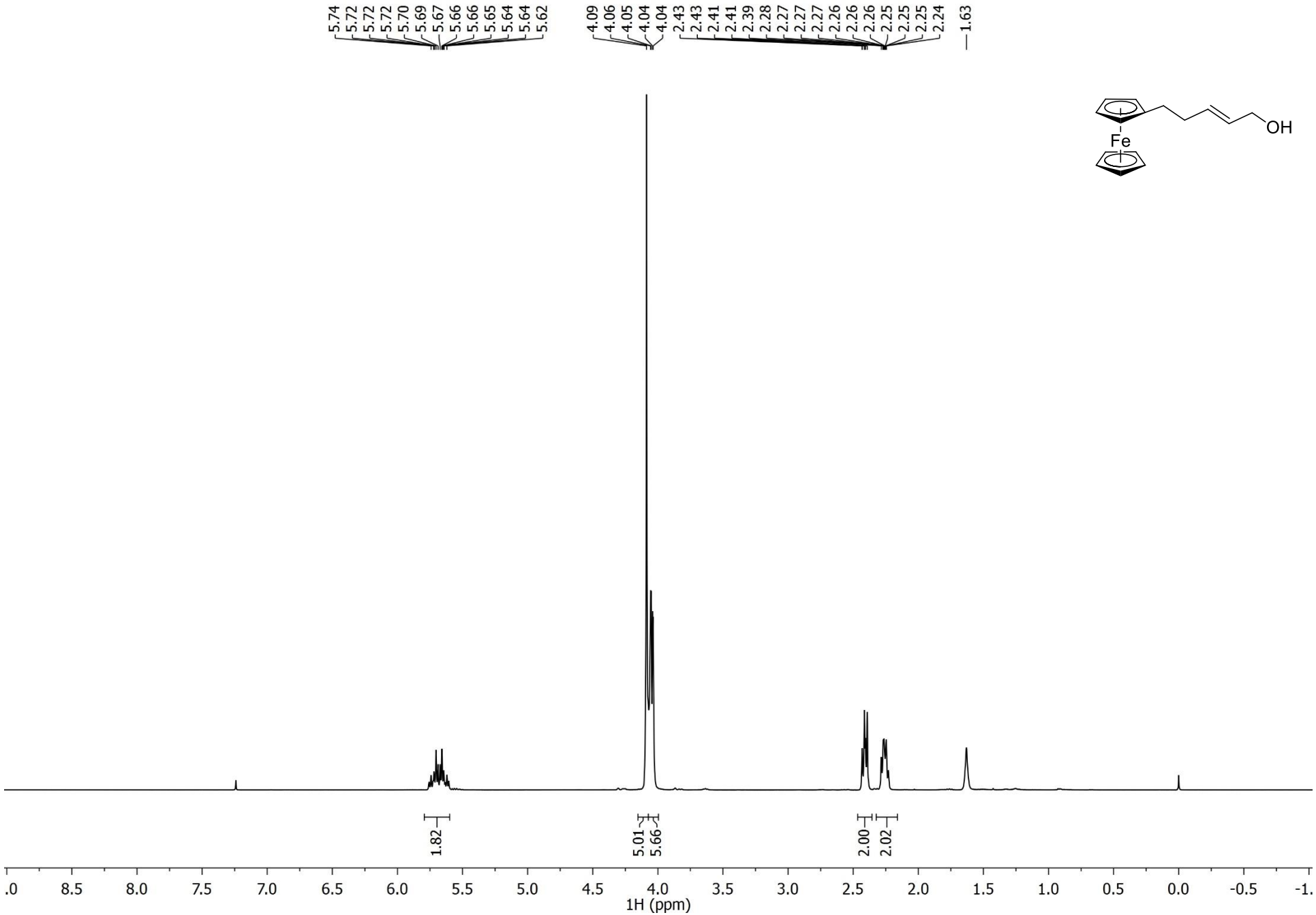
133.31
132.36
131.49
131.21
128.85
63.61
21.15
21.07
OH
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
13C (ppm)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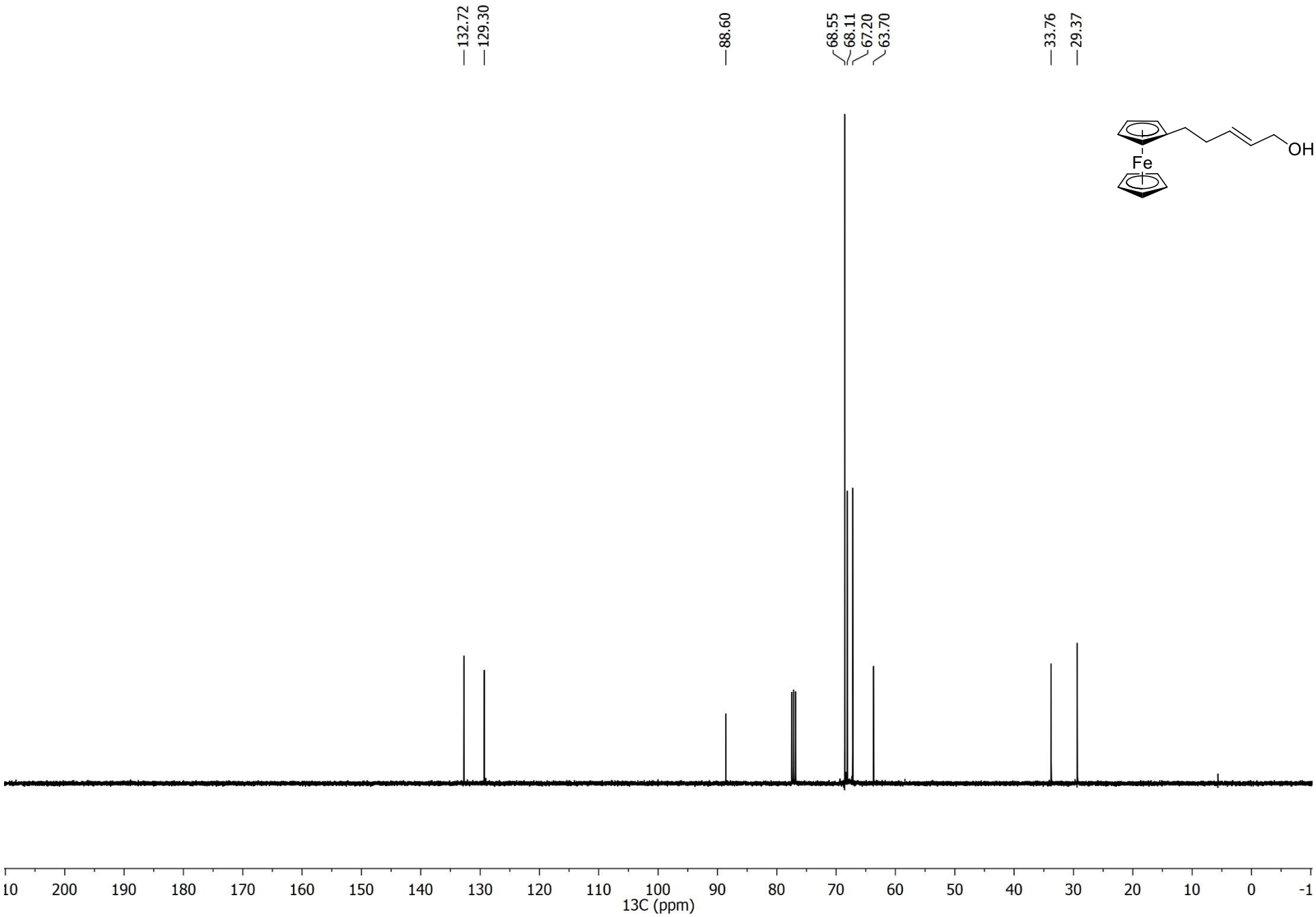
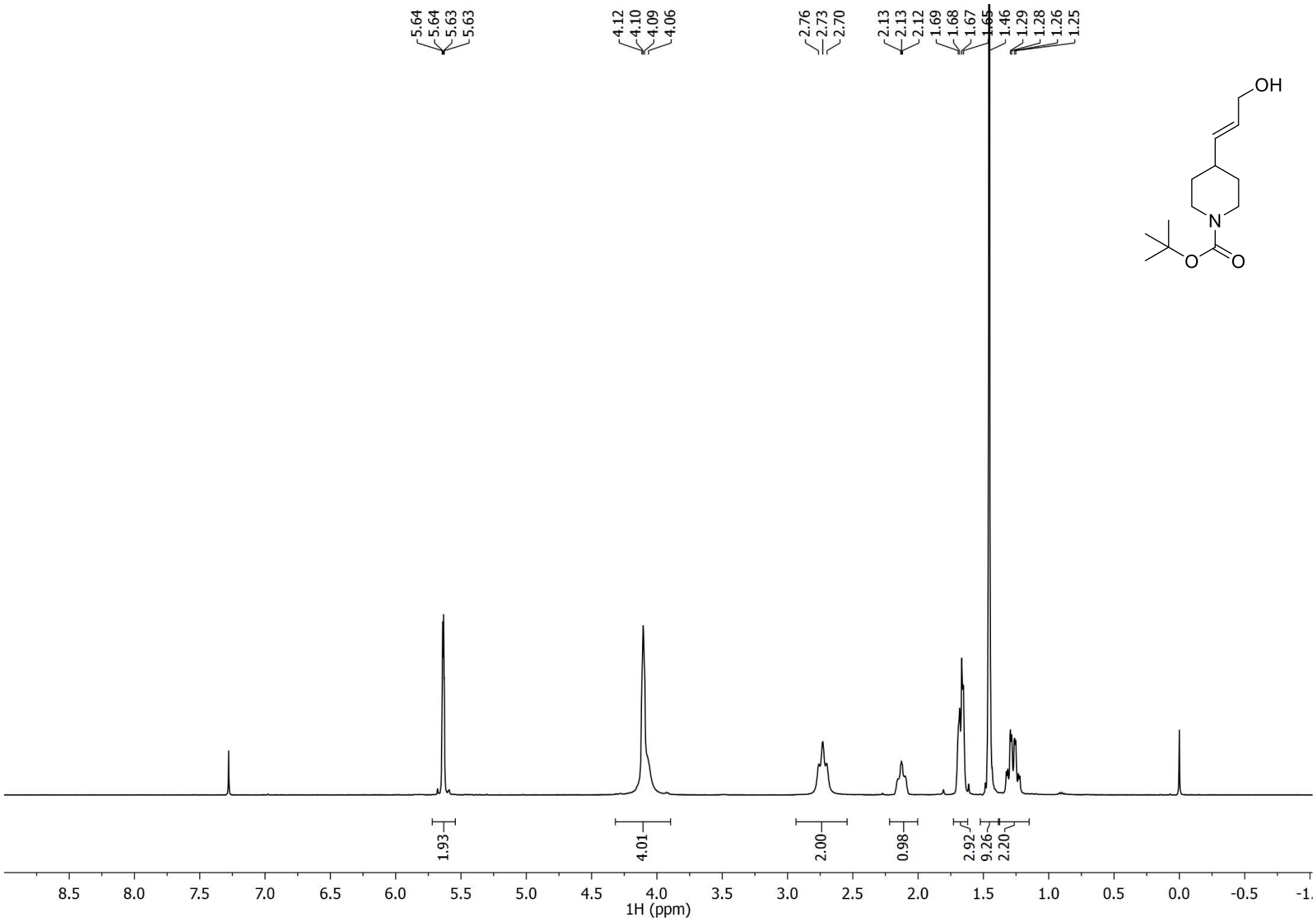
5.72
5.72
5.72
5.70
5.69
5.67
5.66
5.66
5.65
5.64
5.64
5.62
4.09
4.06
4.05
4.04
4.04
2.43
2.43
2.41
2.41
2.39
2.28
2.27
2.27
2.27
2.26
2.26
2.26
2.25
2.25
2.25
2.24
1.63
Fe
OH
1.82
5.01
5.66
2.00
2.02
1H (ppm)


132.72
129.30
88.60
68.55
68.11
67.20
63.70
33.76
29.37
Fe
OH
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
13C (ppm)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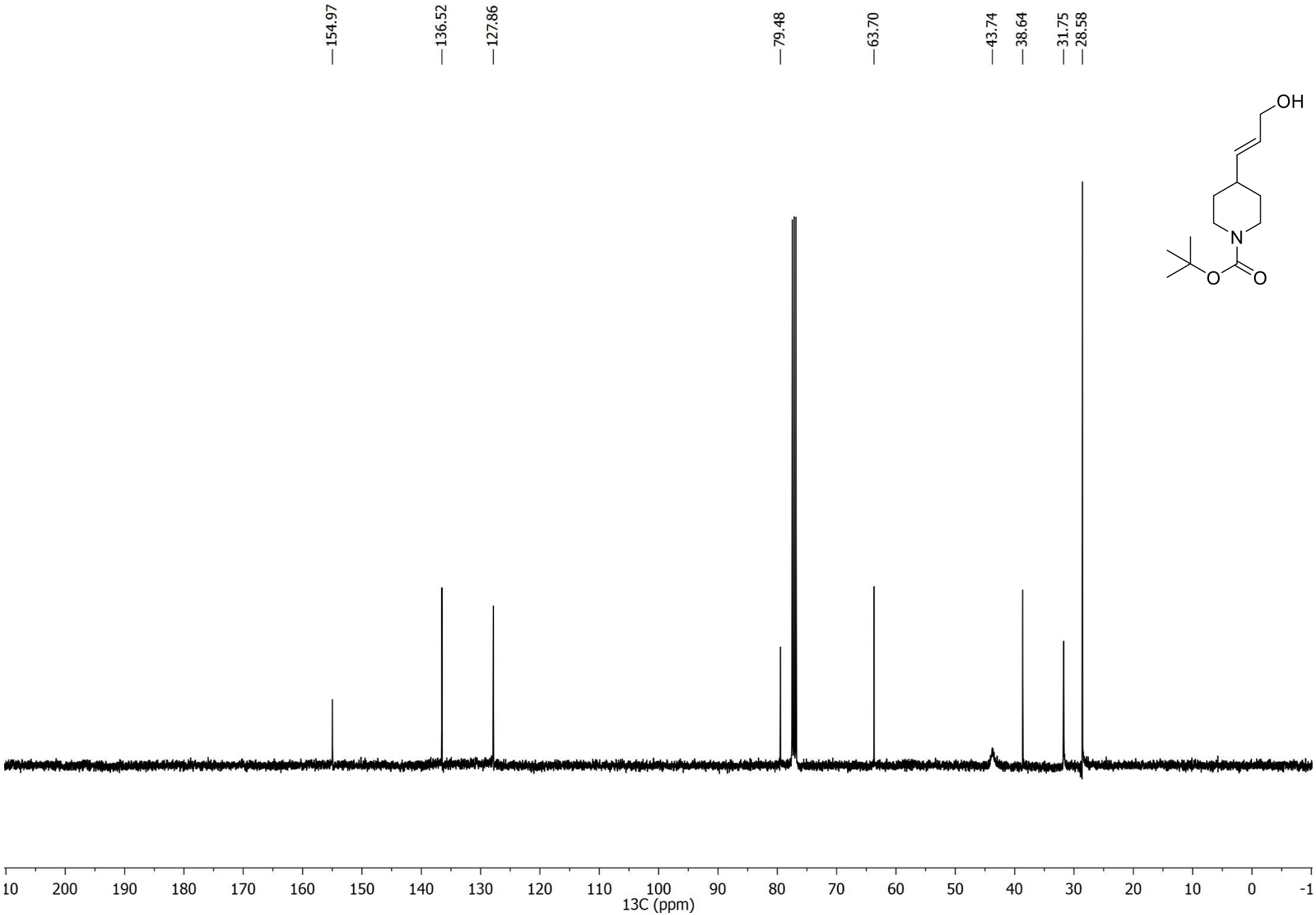
5.64
5.63
5.63
4.12
4.10
4.09
4.06
2.76
2.73
2.70
2.13
2.13
2.12
1.69
1.68
1.67
1.65
1.46
1.29
1.28
1.26
1.25
OH
N
O
O
1.93
4.01
2.00
0.98
2.92
9.26
2.20
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1H (ppm)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136.52
127.86
79.48
63.70
43.74
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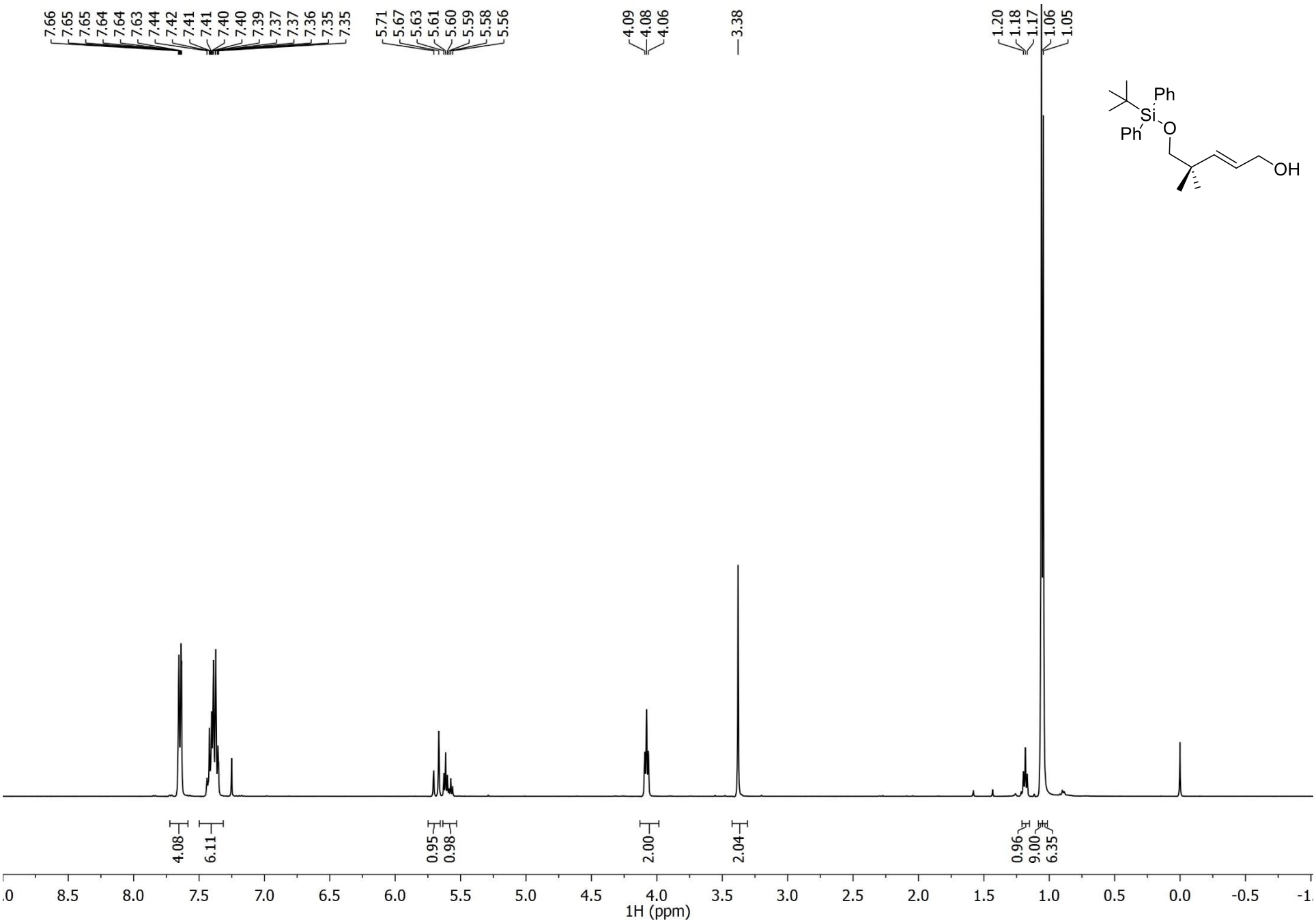
31.75
28.58
OH
N
O
O
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
13C (ppm)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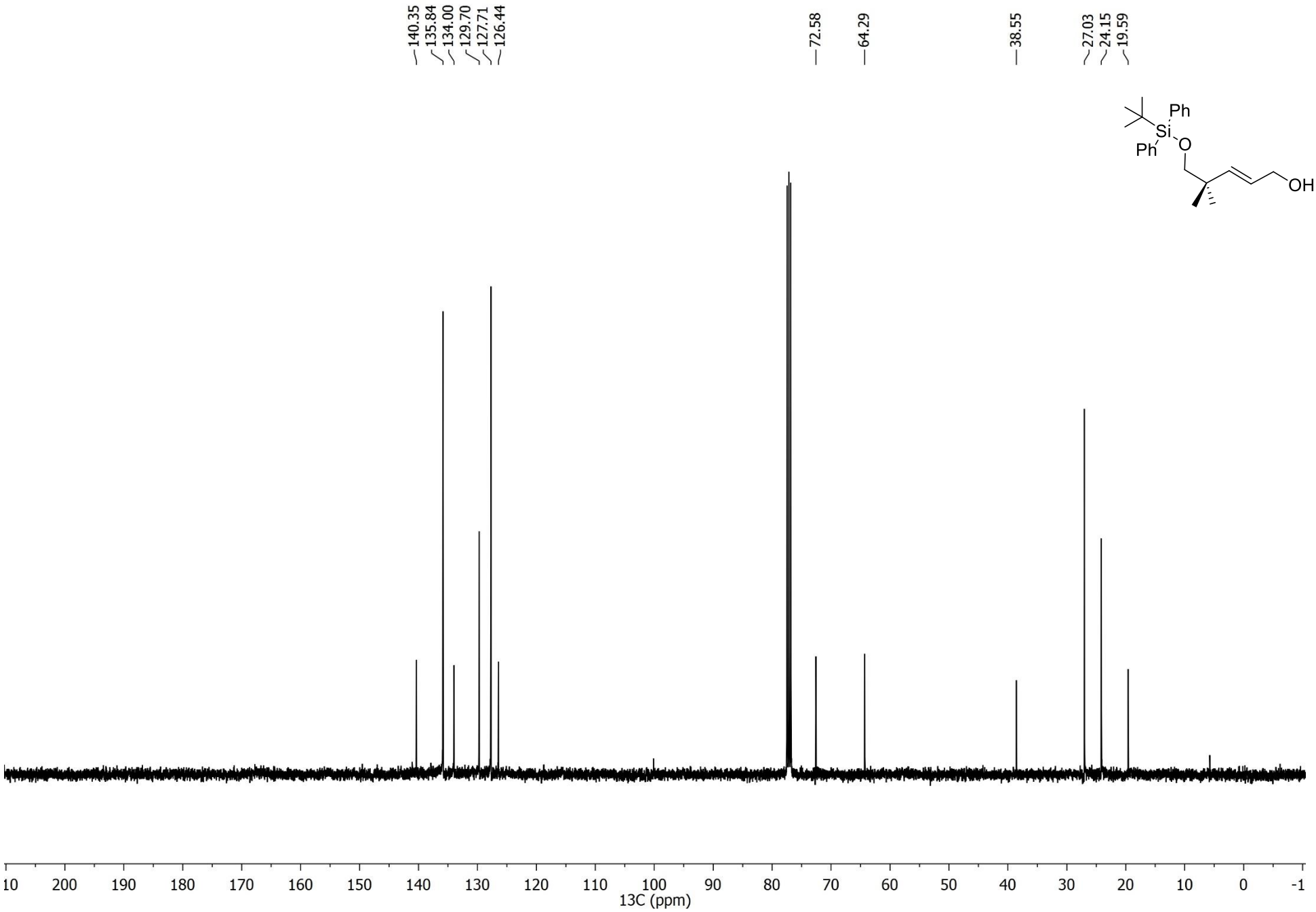
7.65
7.64
7.64
7.63
7.44
7.42
7.41
7.41
7.40
7.40
7.39
7.37
7.37
7.36
7.35
7.35
5.71
5.67
5.63
5.61
5.60
5.59
5.58
5.56
4.09
4.08
4.06
3.38
1.20
1.18
1.17
1.06
1.05
Ph
Si
Ph
O
OH
4.08
6.11
0.95
0.98
2.00
2.04
0.96
9.00
6.35
1H (ppm)


140.35
135.84
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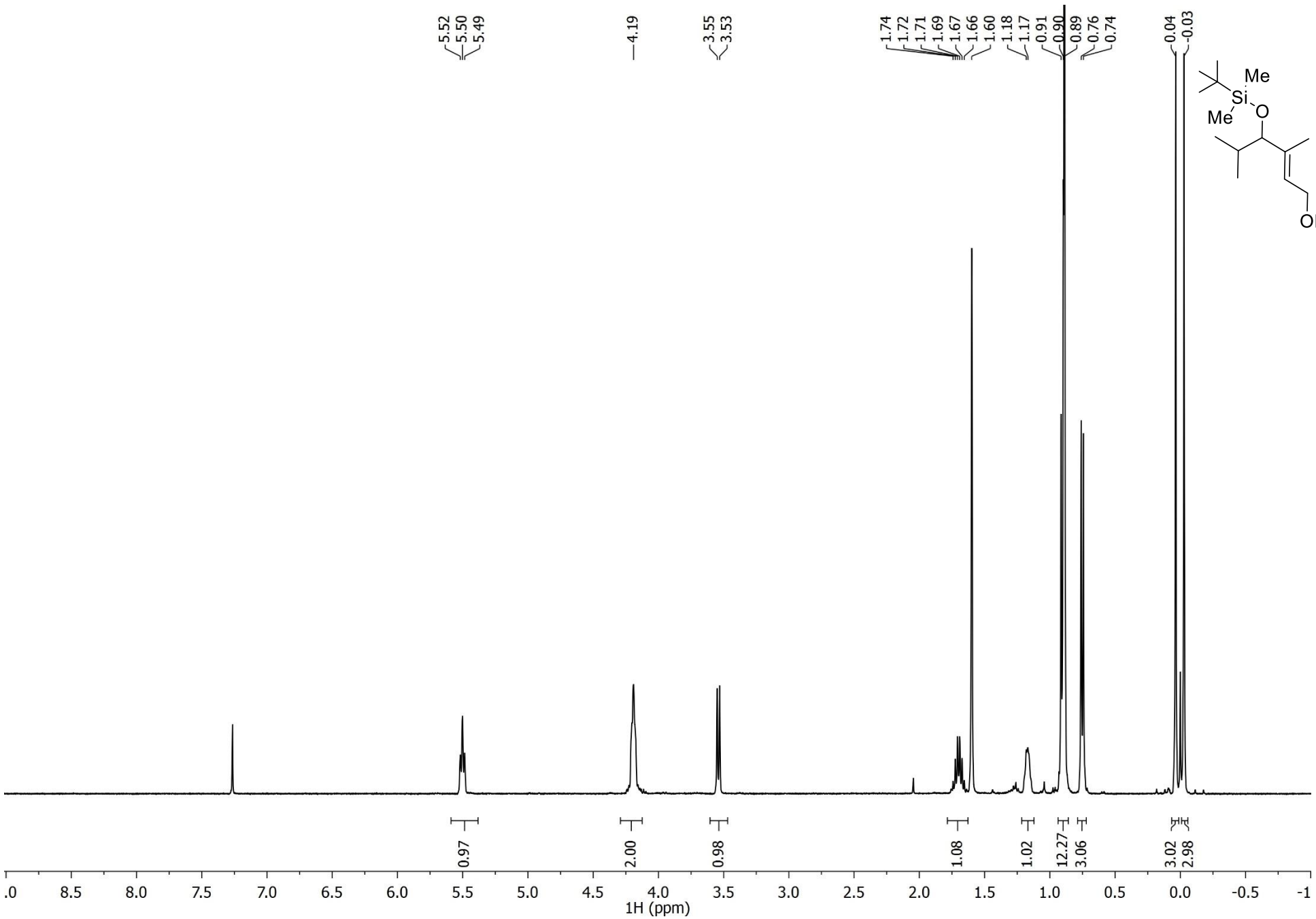
129.70
127.71
126.44
72.58
64.29
38.55
27.03
24.15
19.59
Ph
Si
Ph
O
OH
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
13C (ppm)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5.50
5.49
4.19
3.55
3.53
1.74
1.72
1.71
1.69
1.67
1.66
1.60
1.18
1.17
0.91
0.90
0.89
0.76
0.74
0.04
-0.03
Me
Si
Me
O
OH
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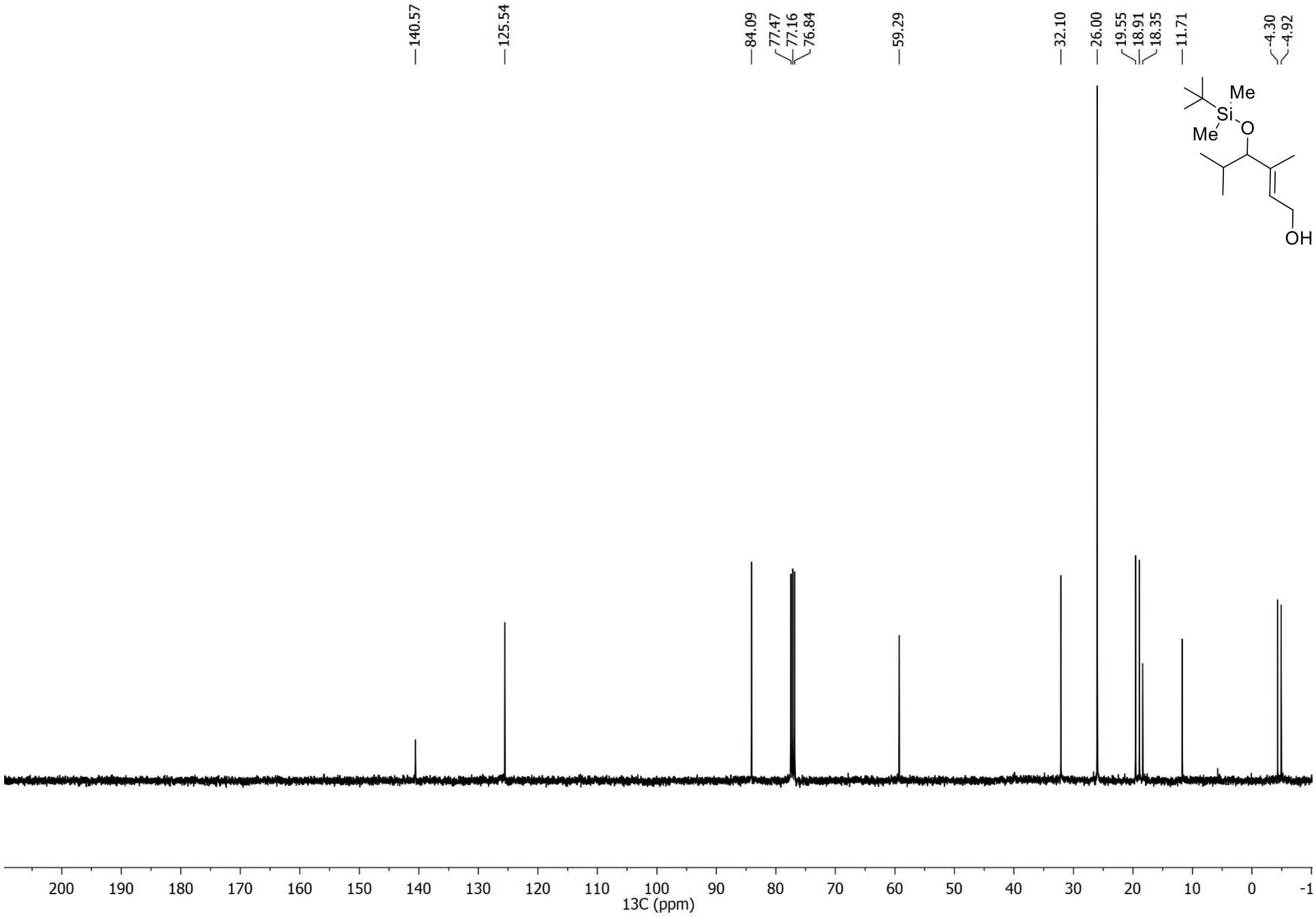
2.00
0.98
1.08
1.02
12.27
3.06
3.02
2.98
1H (ppm)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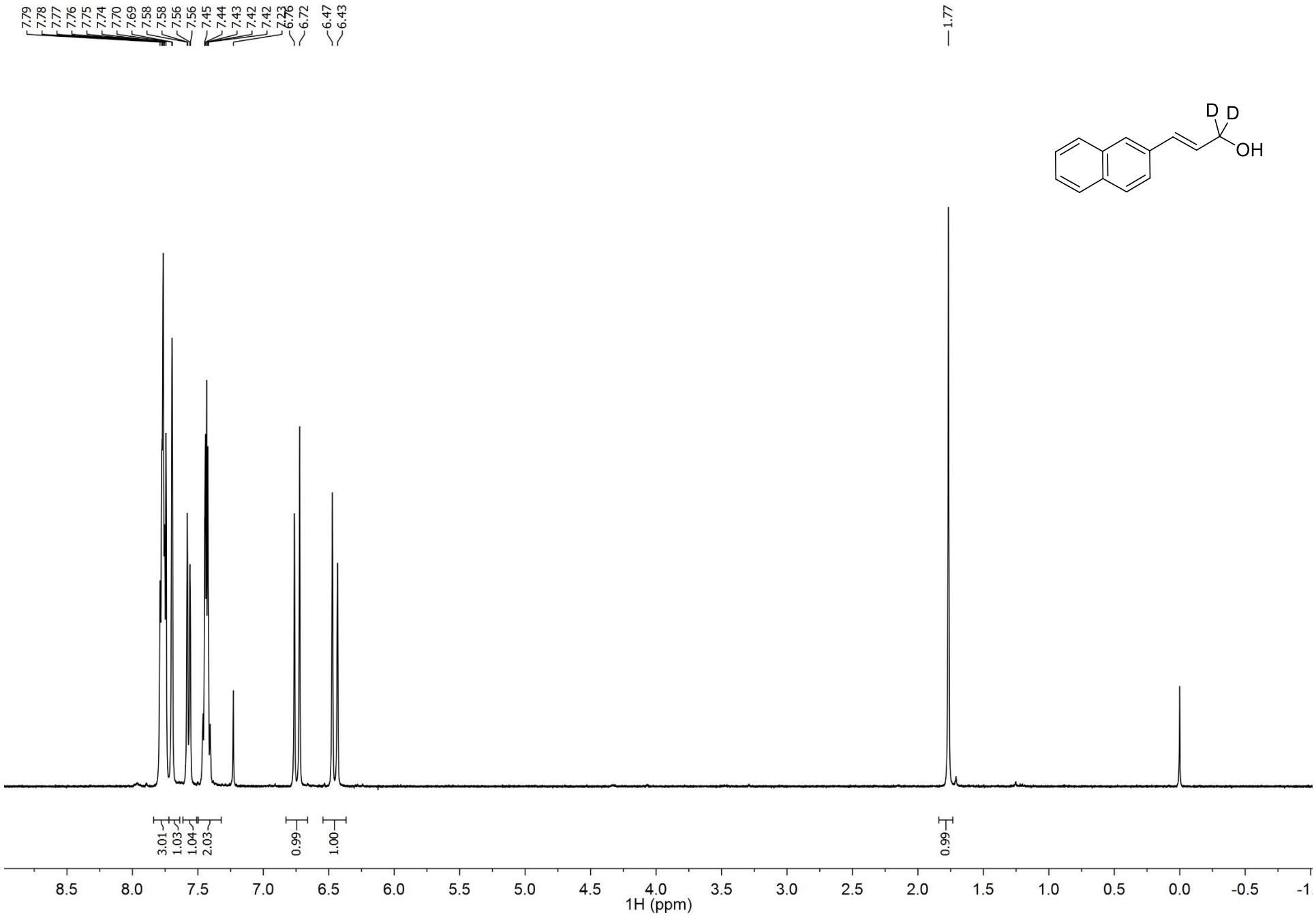
125.54
84.09
77.47
77.16
76.84
59.29
32.10
26.00
19.55
18.91
18.35
11.71
-4.30
-4.92
Me
Si
Me
O
OH
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
13C (ppm)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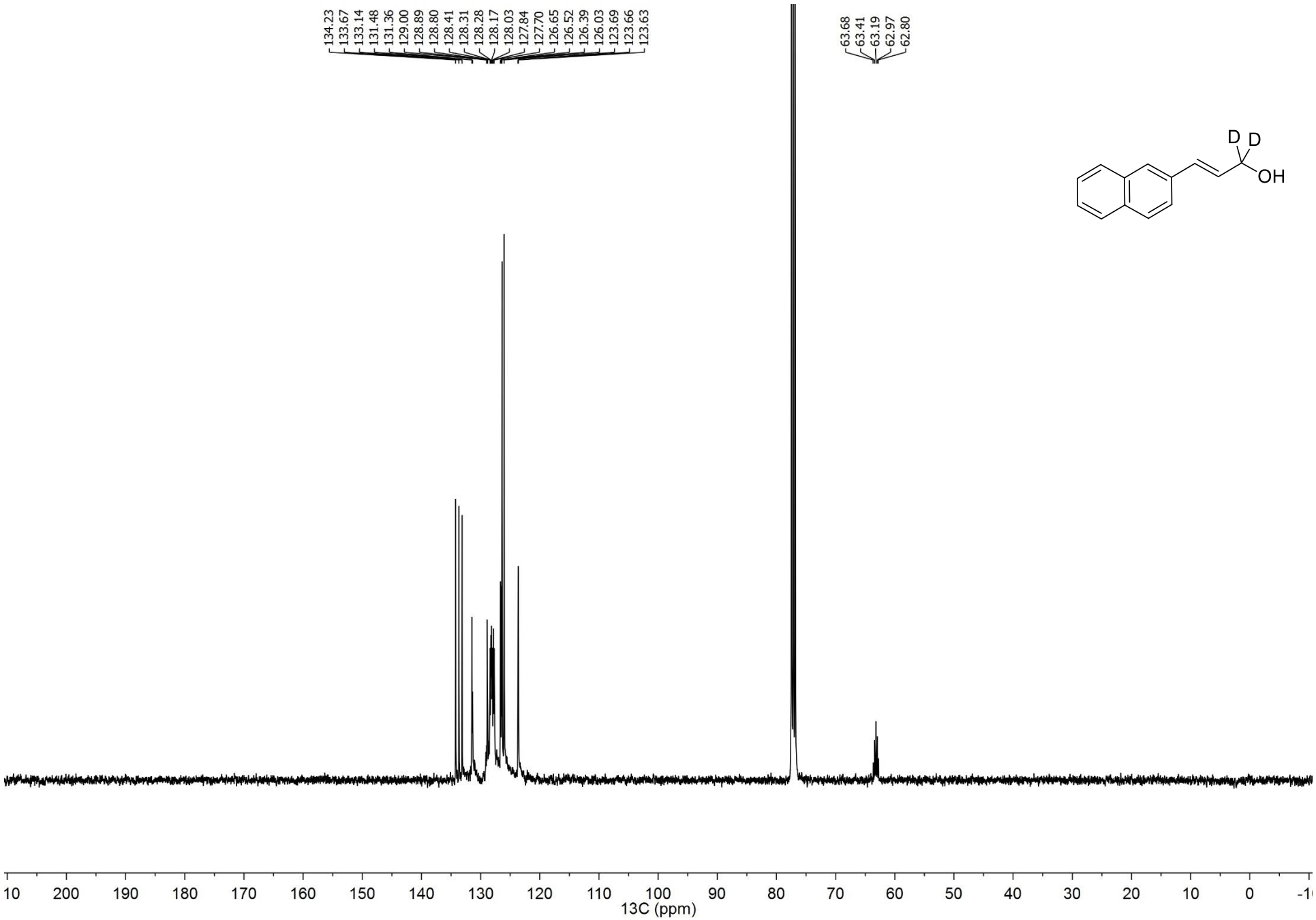
7.74
7.70
7.69
7.58
7.58
7.56
7.56
7.45
7.44
7.43
7.42
7.42
7.23
6.76
6.72
6.47
6.43
1.77
D D
OH
3.01
1.03
1.04
2.03
0.99
1.00
0.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
1H (ppm)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128.80
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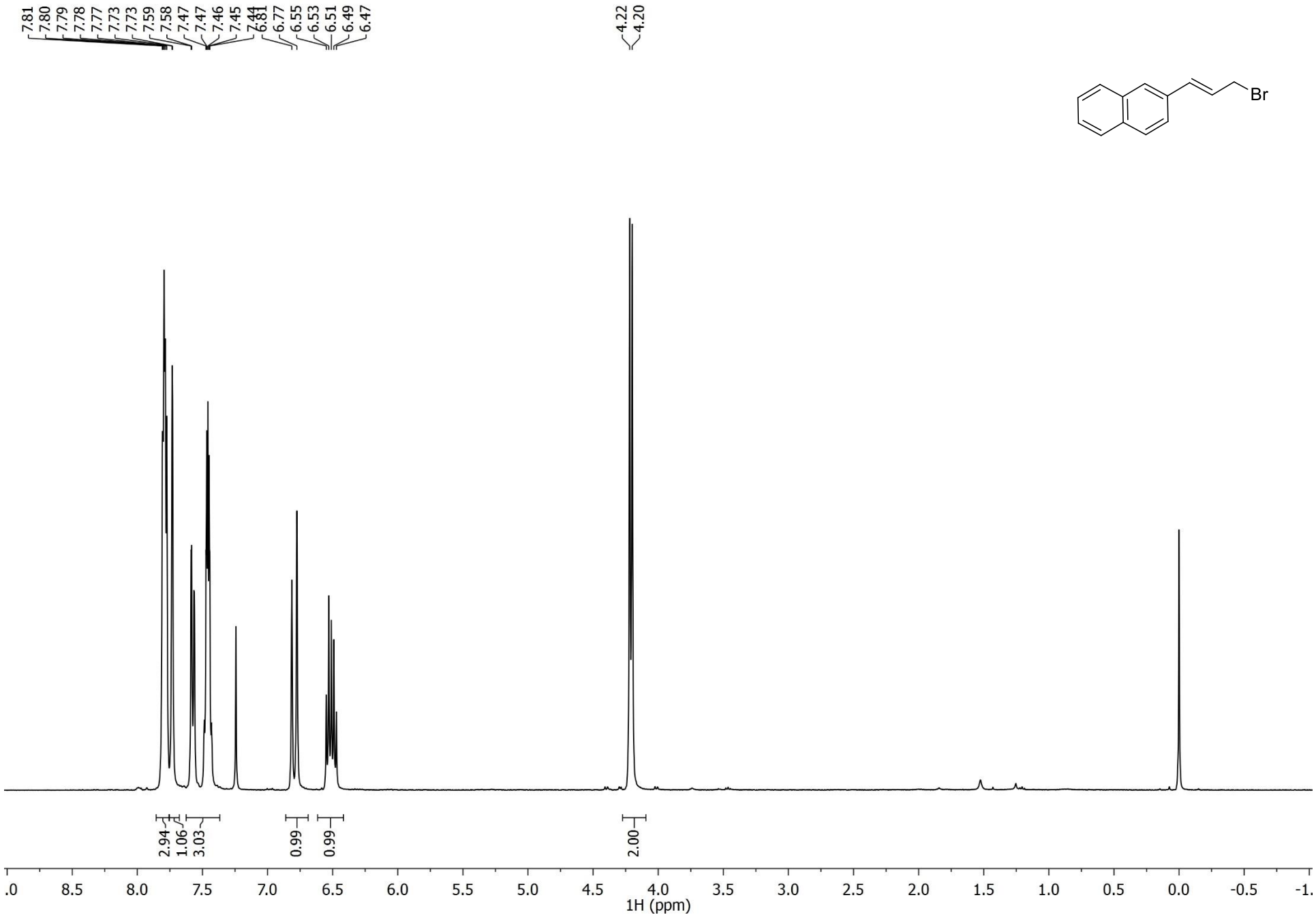
128.28
128.17
128.03
127.84
127.70
126.65
126.52
126.39
126.03
123.69
123.66
123.63
63.68
63.41
63.19
62.97
62.80
D D
OH
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
13C (ppm)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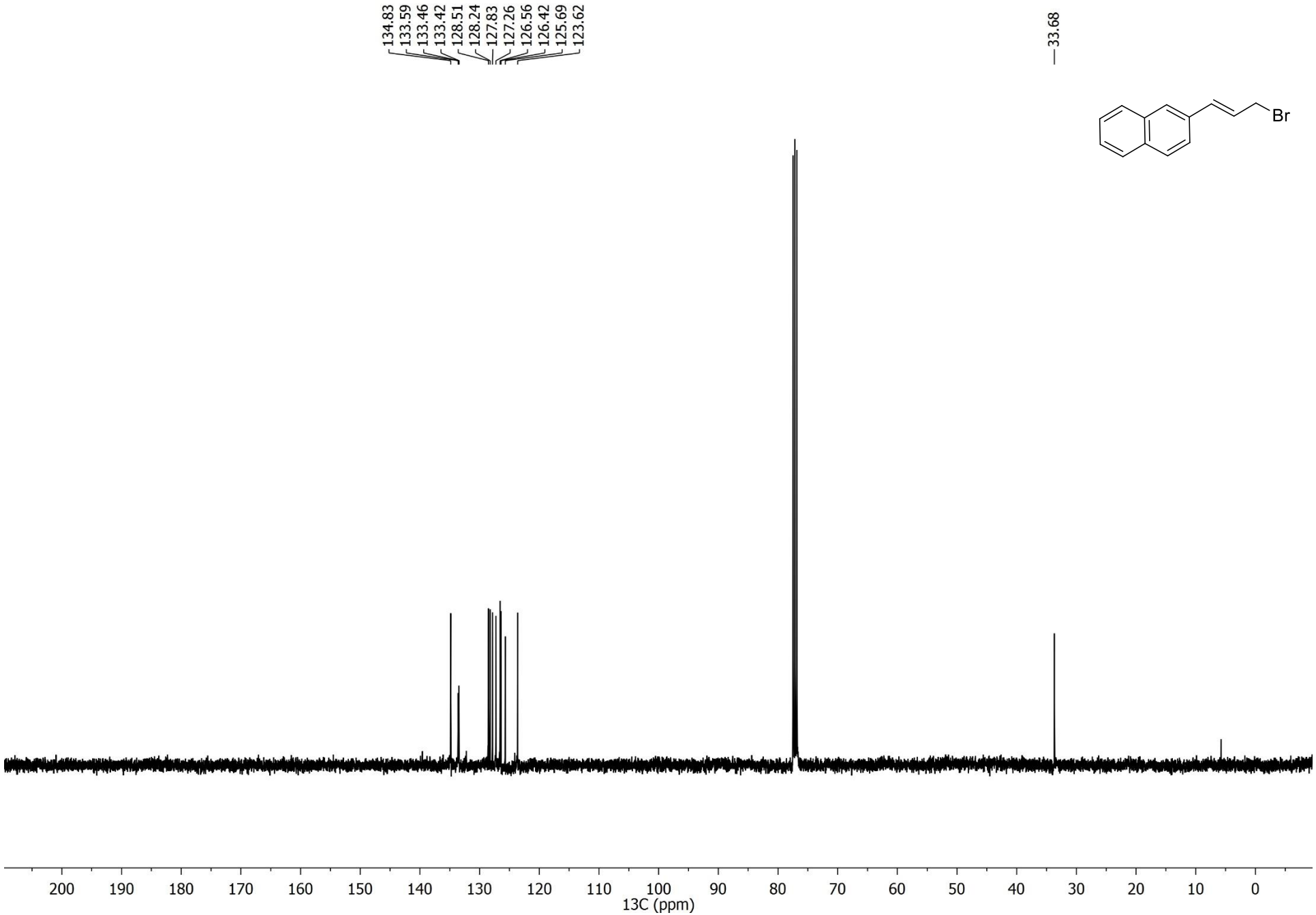
7.73
7.73
7.59
7.58
7.47
7.47
7.46
7.45
7.44
6.81
6.77
6.55
6.53
6.51
6.49
6.47
4.22
4.20
Br
2.94
1.06
3.03
0.99
0.99
2.00
1H (ppm)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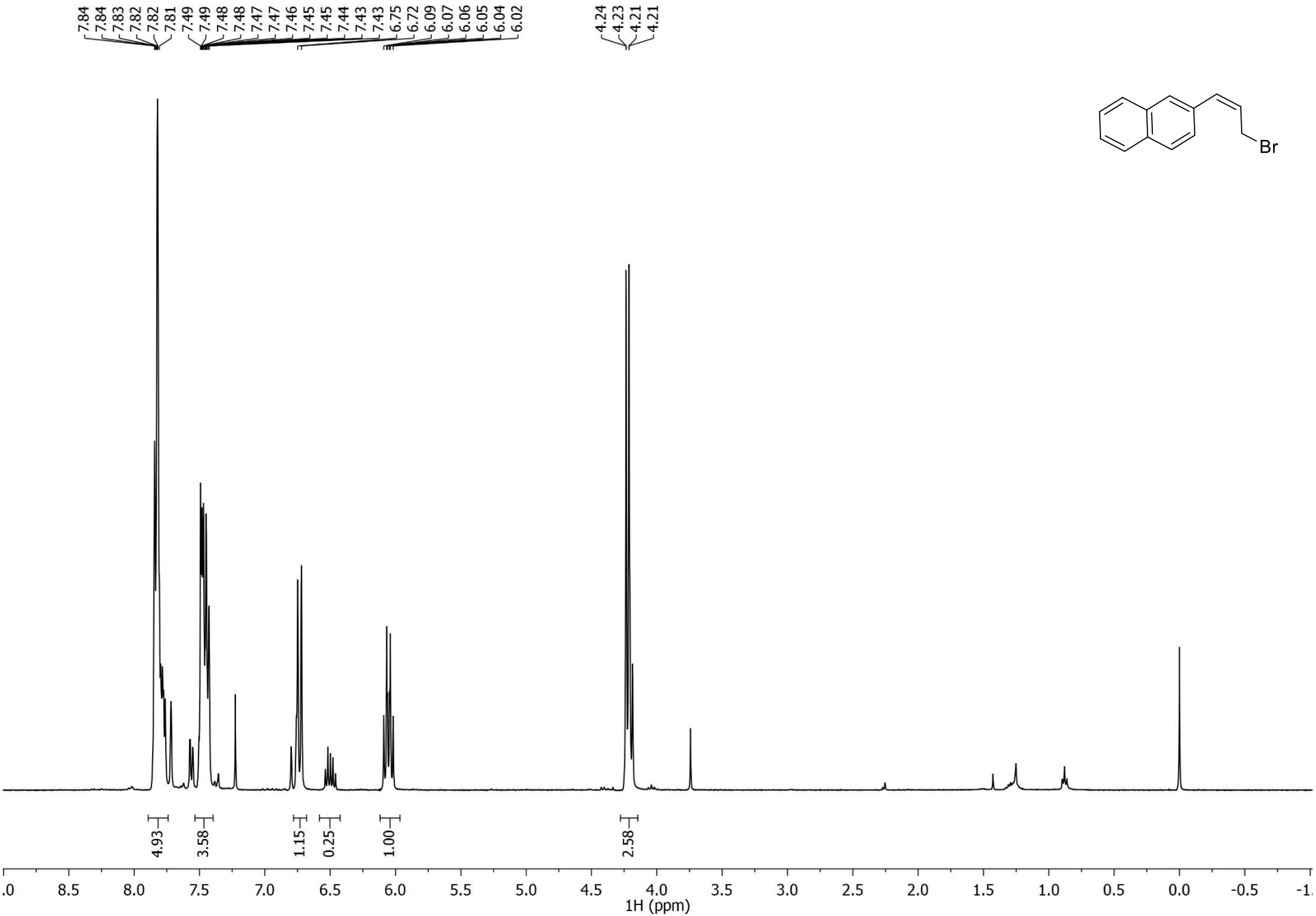
133.59
133.46
133.42
128.51
128.24
127.83
127.26
126.56
126.42
125.69
123.62
33.68
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C (ppm)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7.84
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7.82
7.81
7.49
7.49
7.48
7.48
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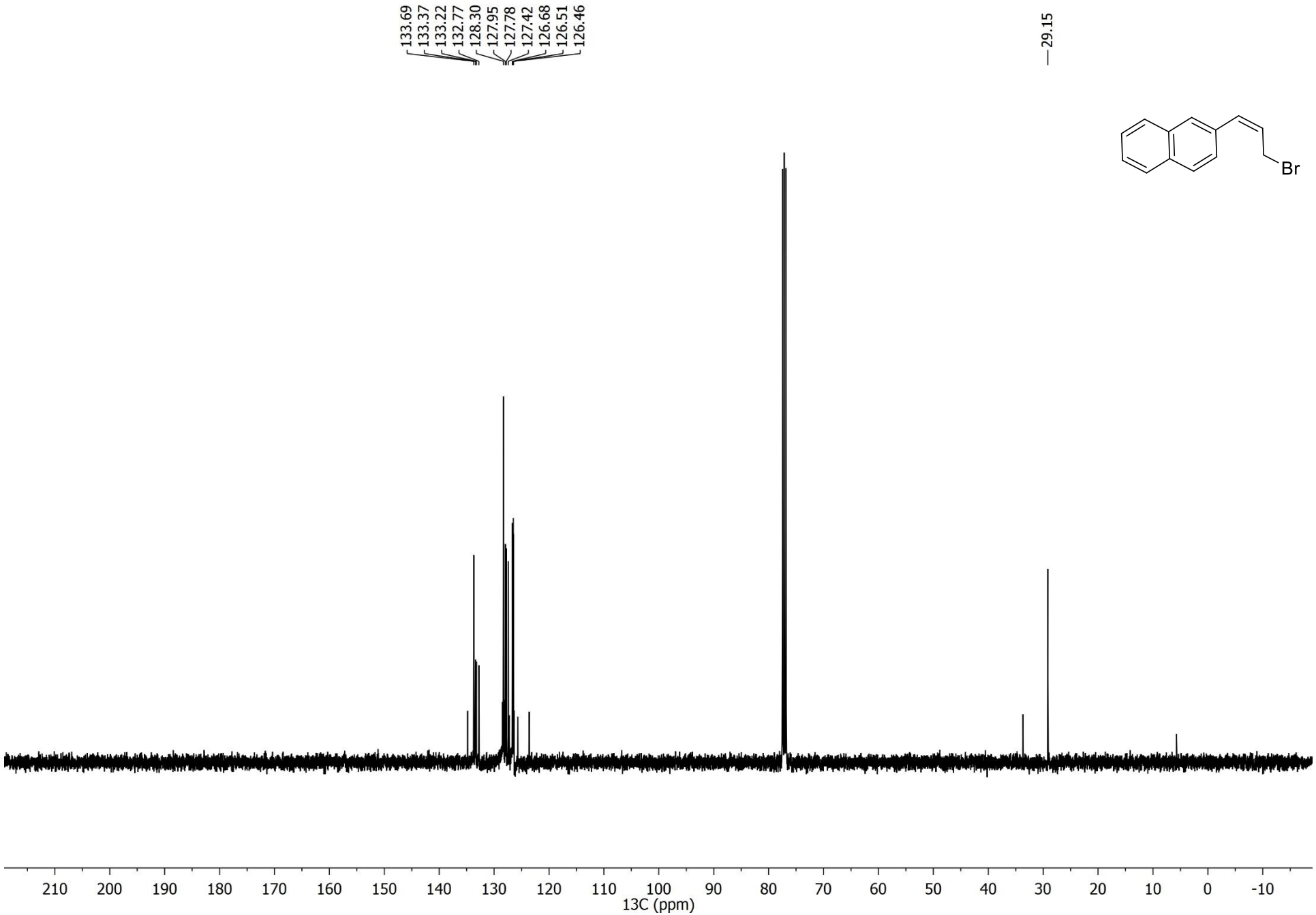
7.47
7.46
7.45
7.45
7.44
7.43
7.43
6.75
6.72
6.09
6.07
6.06
6.05
6.04
6.02
4.24
4.23
4.21
4.21
Br
4.93
3.58
1.15
0.25
1.00
2.58
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1H (ppm)


133.69
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132.77
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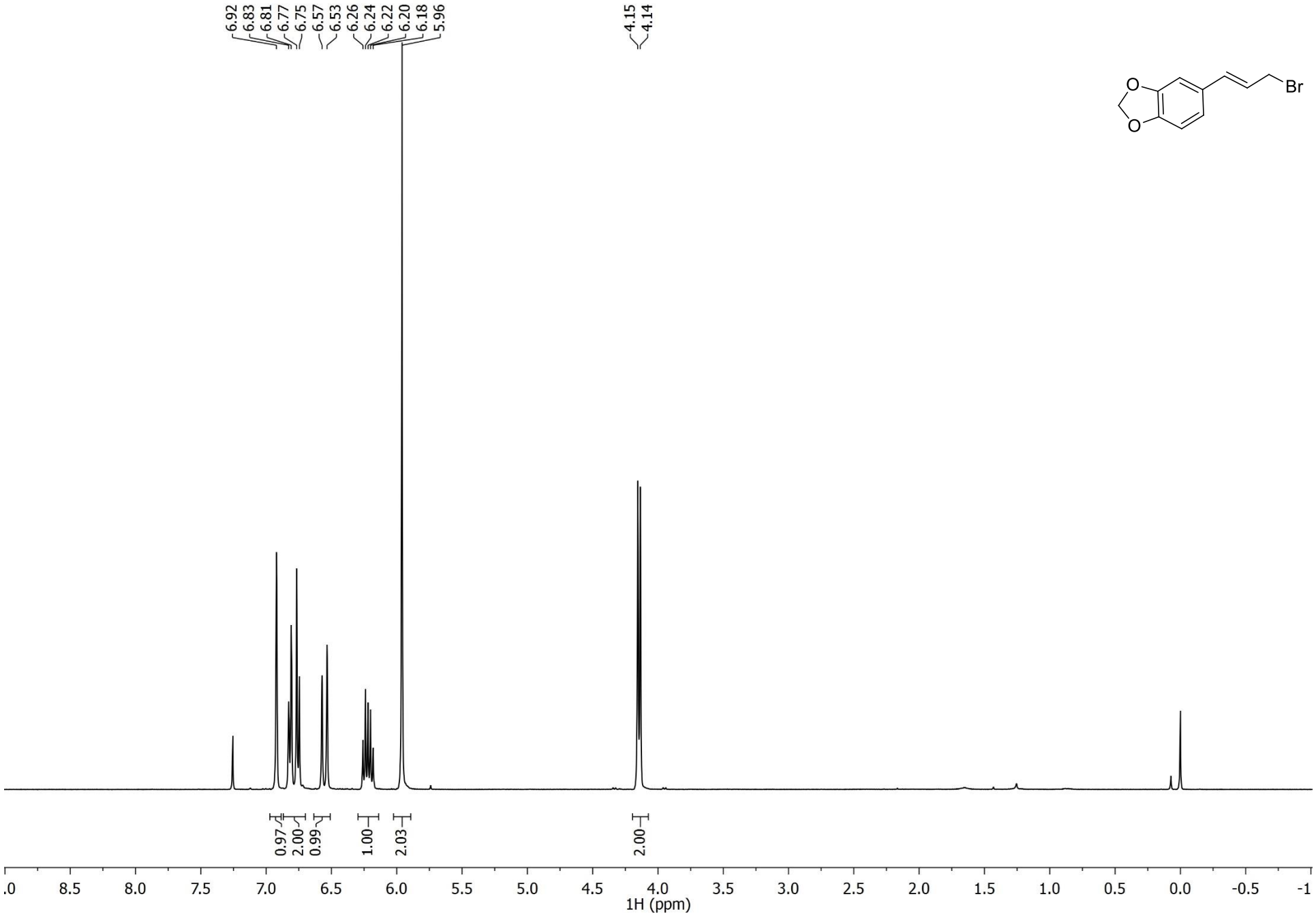
127.95
127.78
127.42
126.68
126.51
126.46
29.15
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
13C (ppm)


6.92
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6.77
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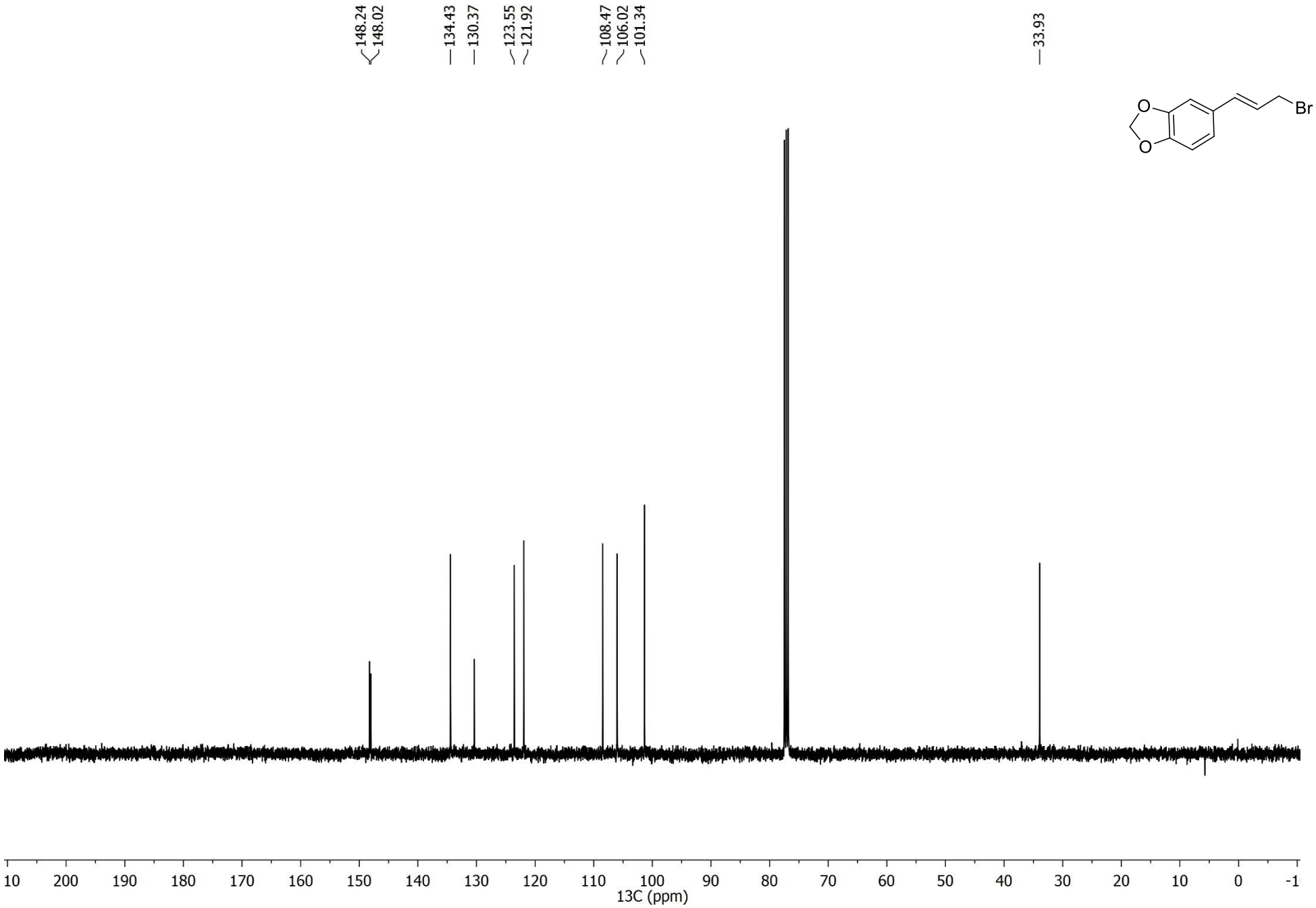
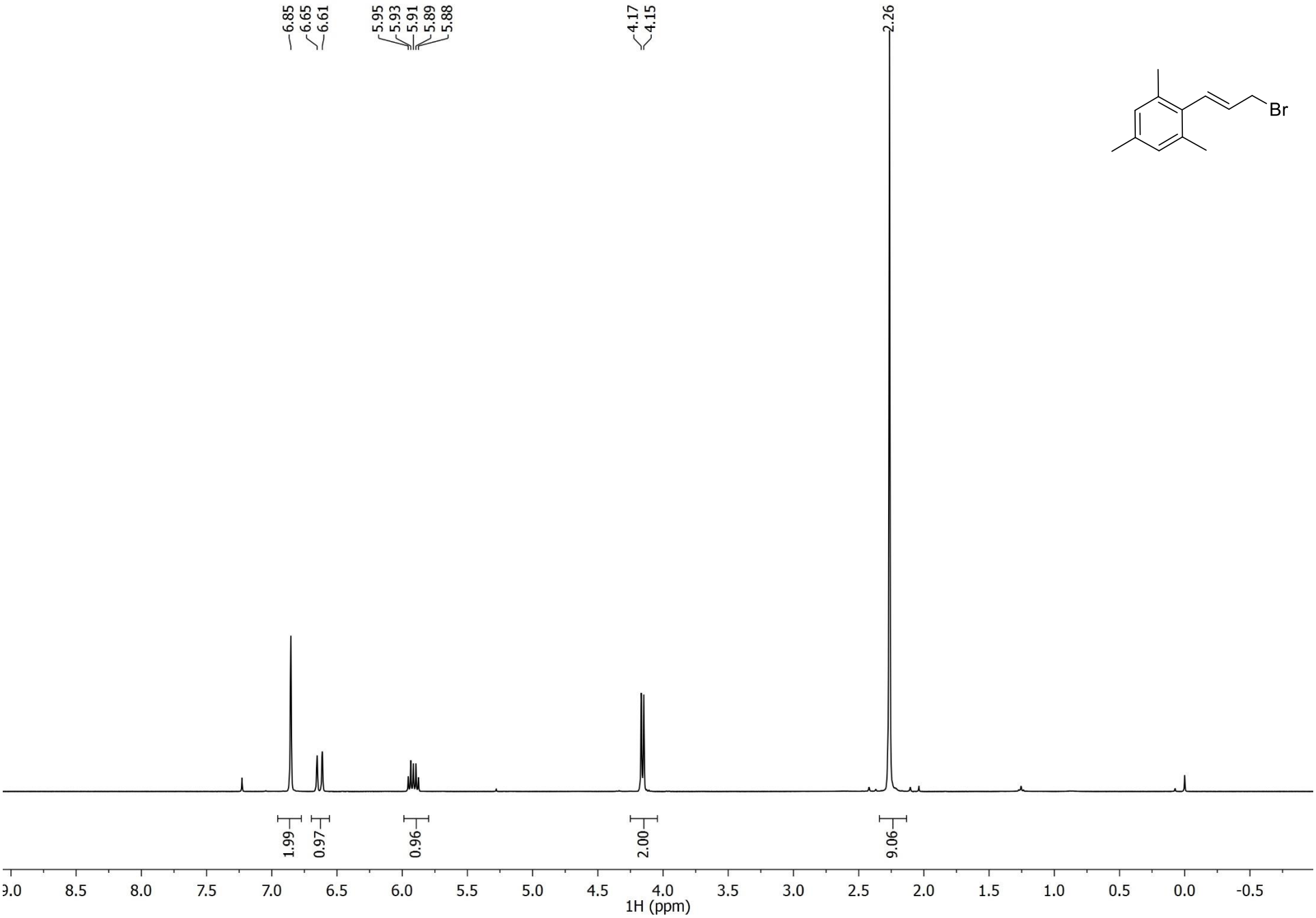
6.57
6.53
6.26
6.24
6.22
6.20
6.18
5.96
4.15
4.14
O
O
Br
0.97
2.00
0.99
1.00
2.03
2.00
1H (ppm)


148.24
148.02
134.43
130.37
123.55
121.92
108.47
106.02
101.34
33.93
O
O
Br
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
13C (ppm)


6.85
6.65
6.61
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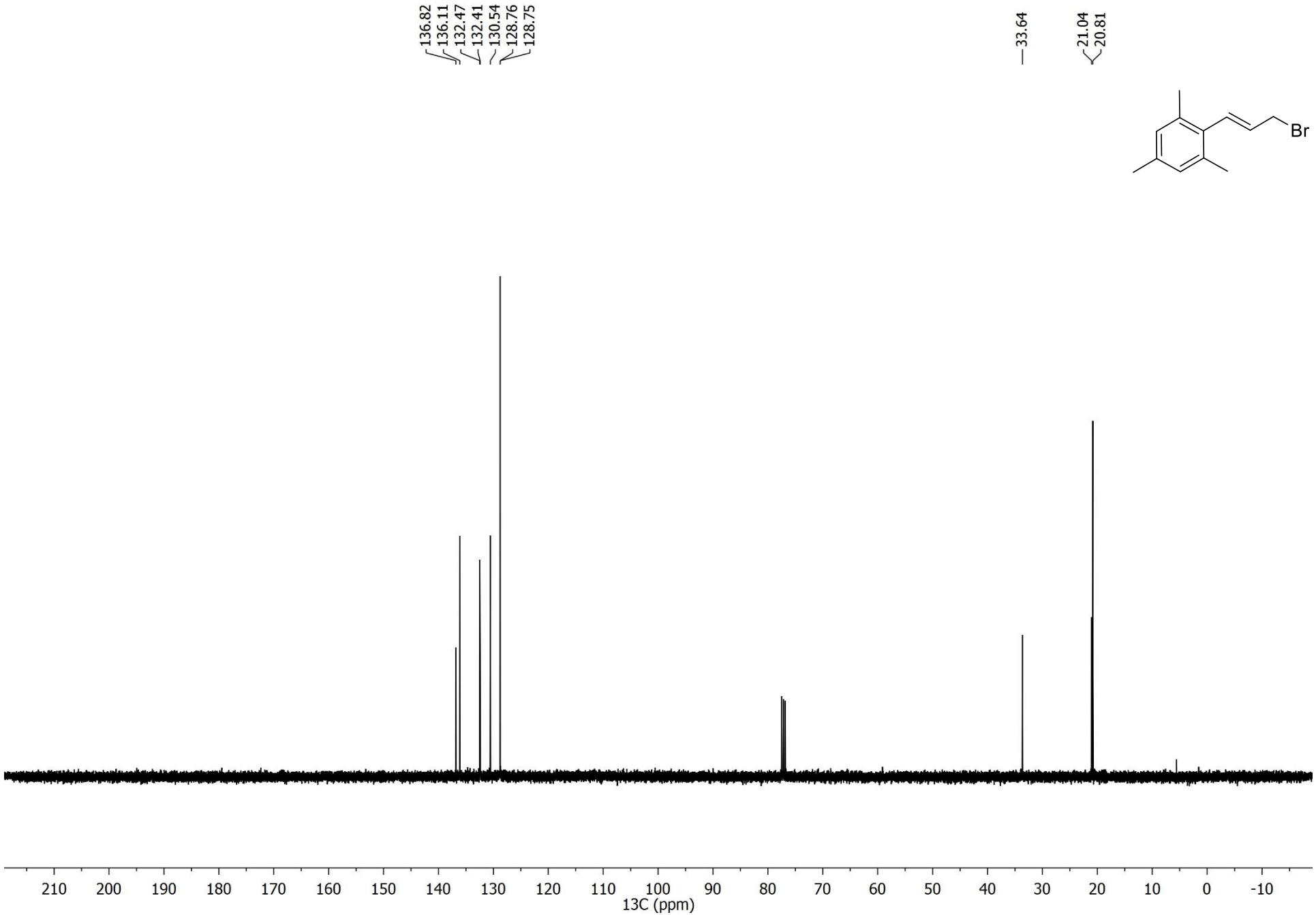
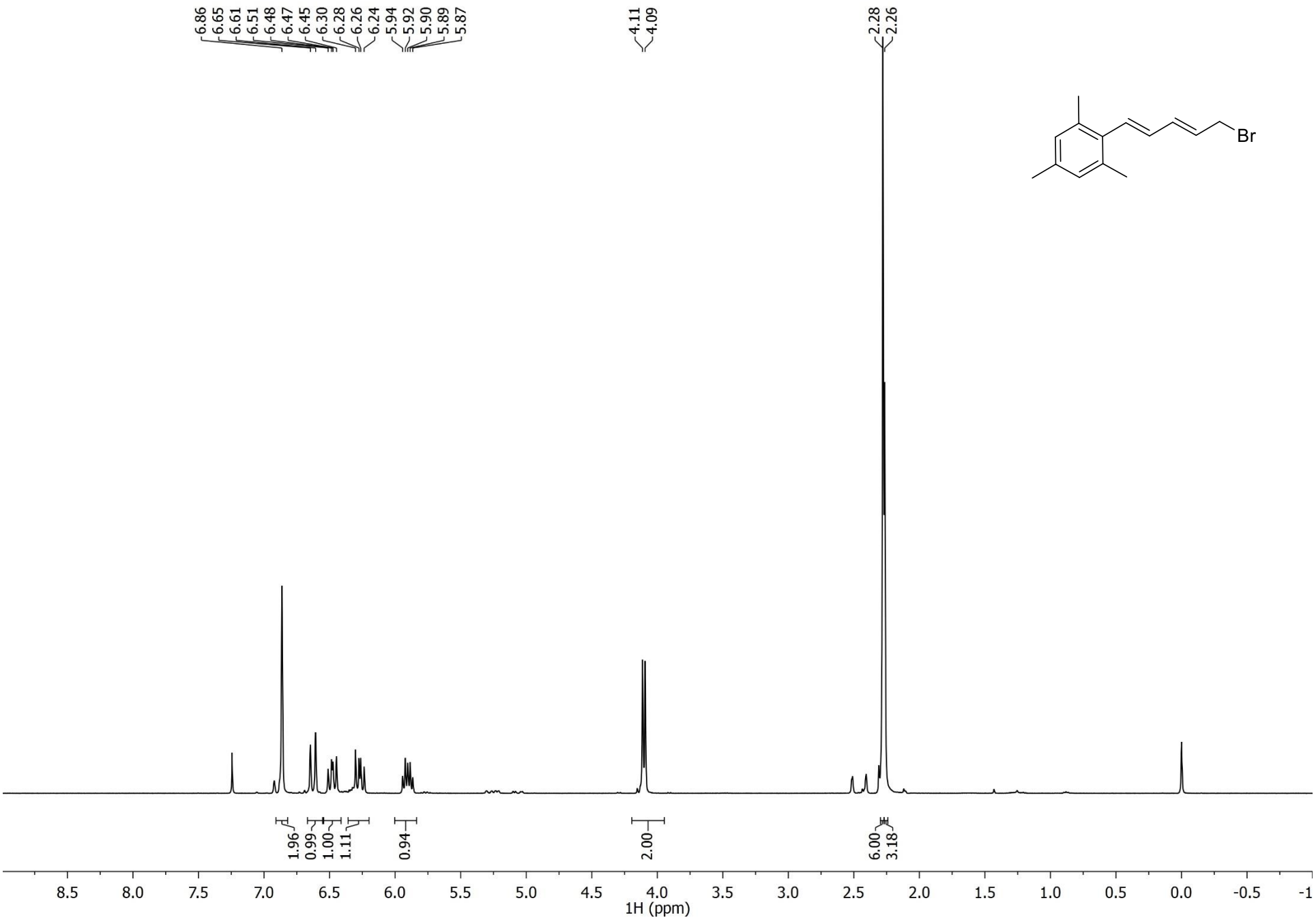
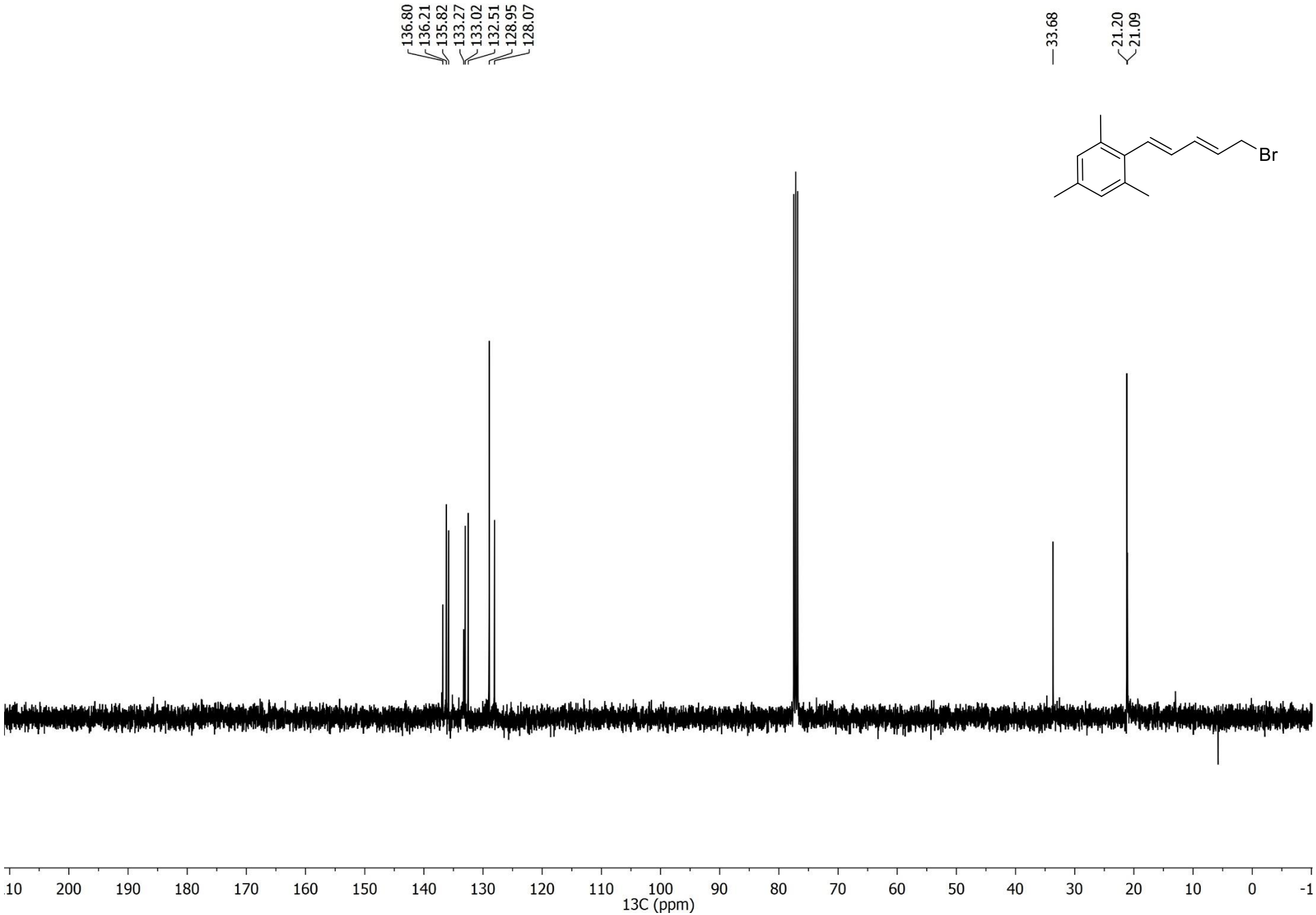
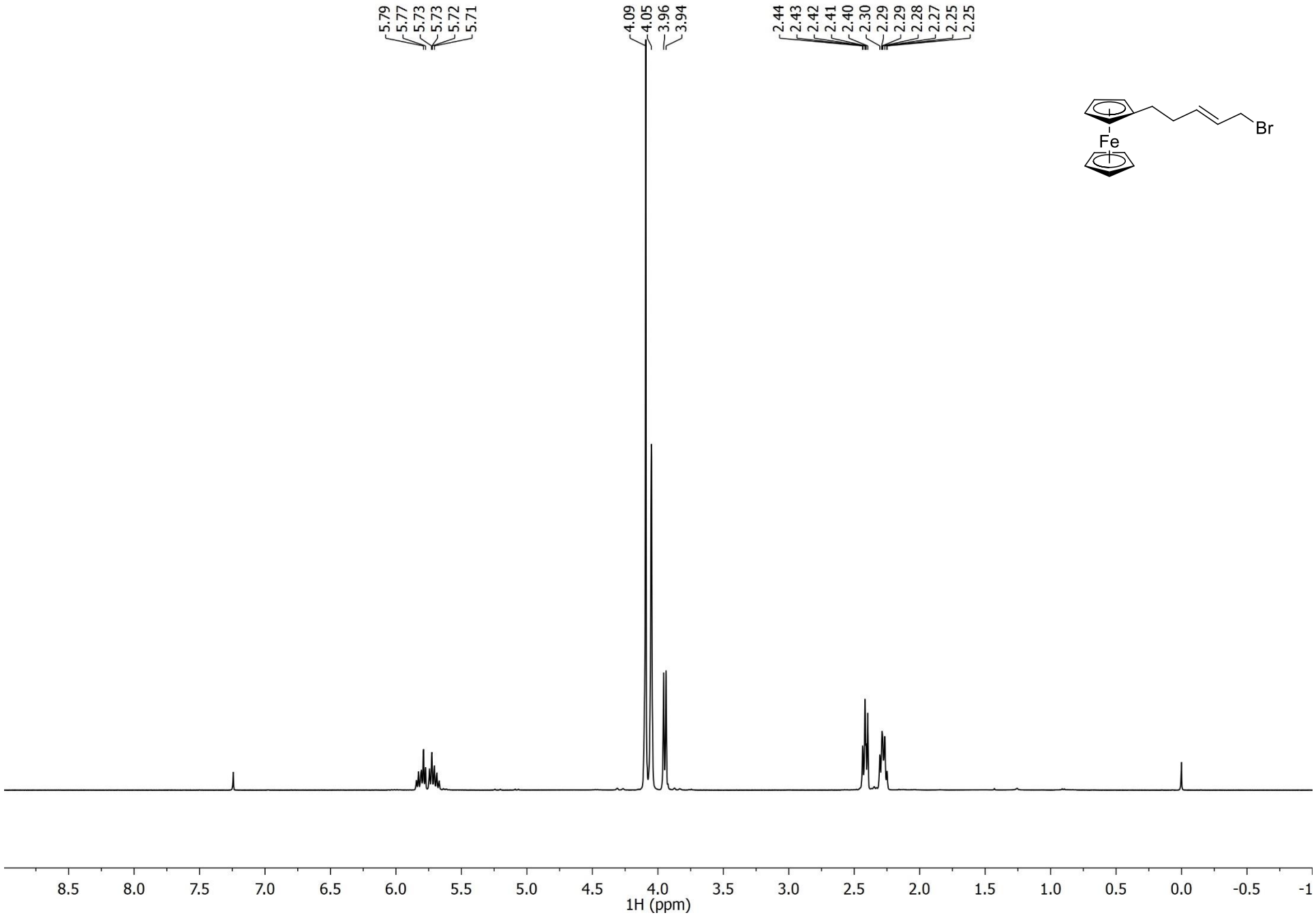
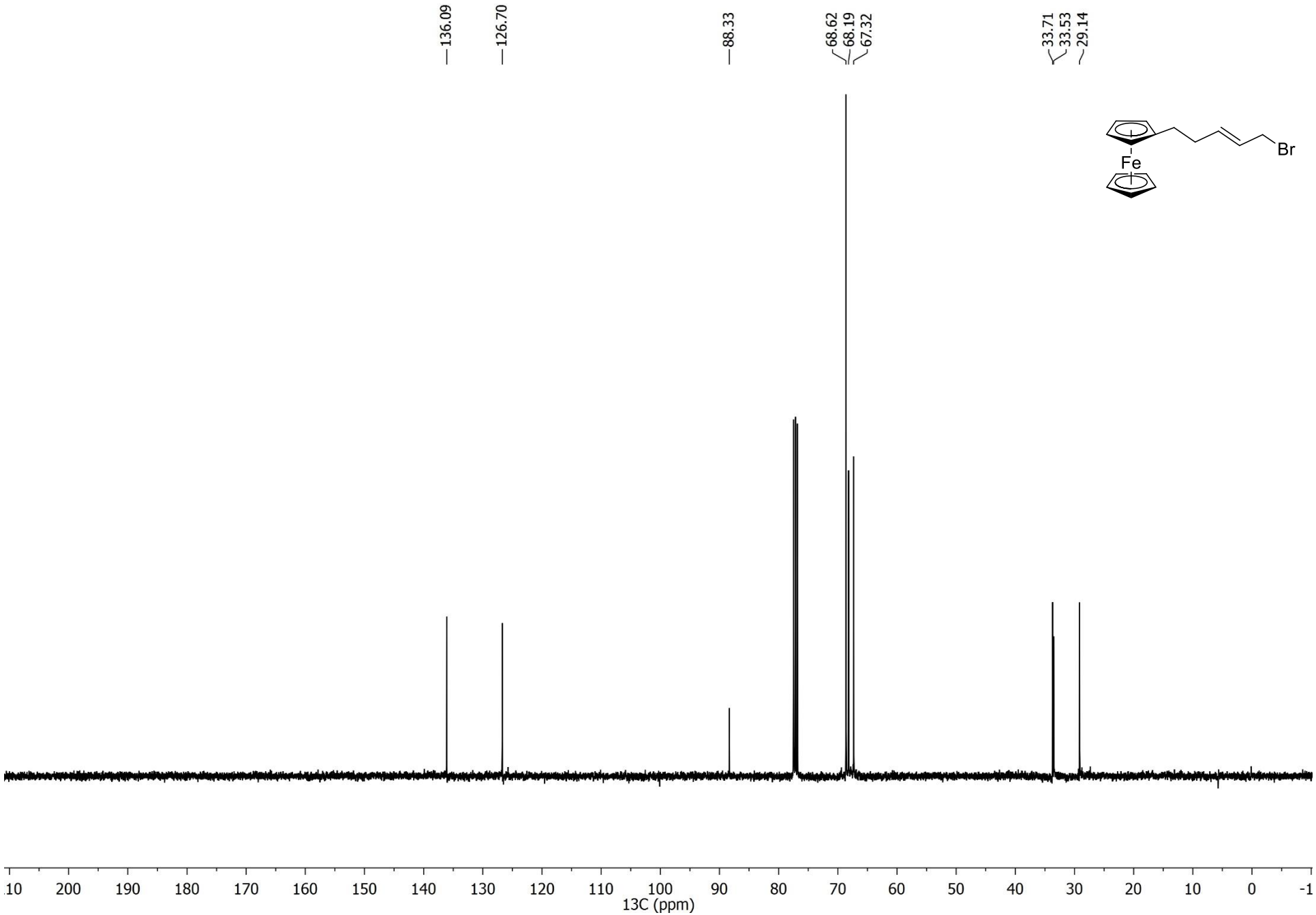
5.93
5.91
5.89
5.88
4.17
4.15
2.26
Br
1.99
0.97
0.96
2.00
9.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1H (ppm)

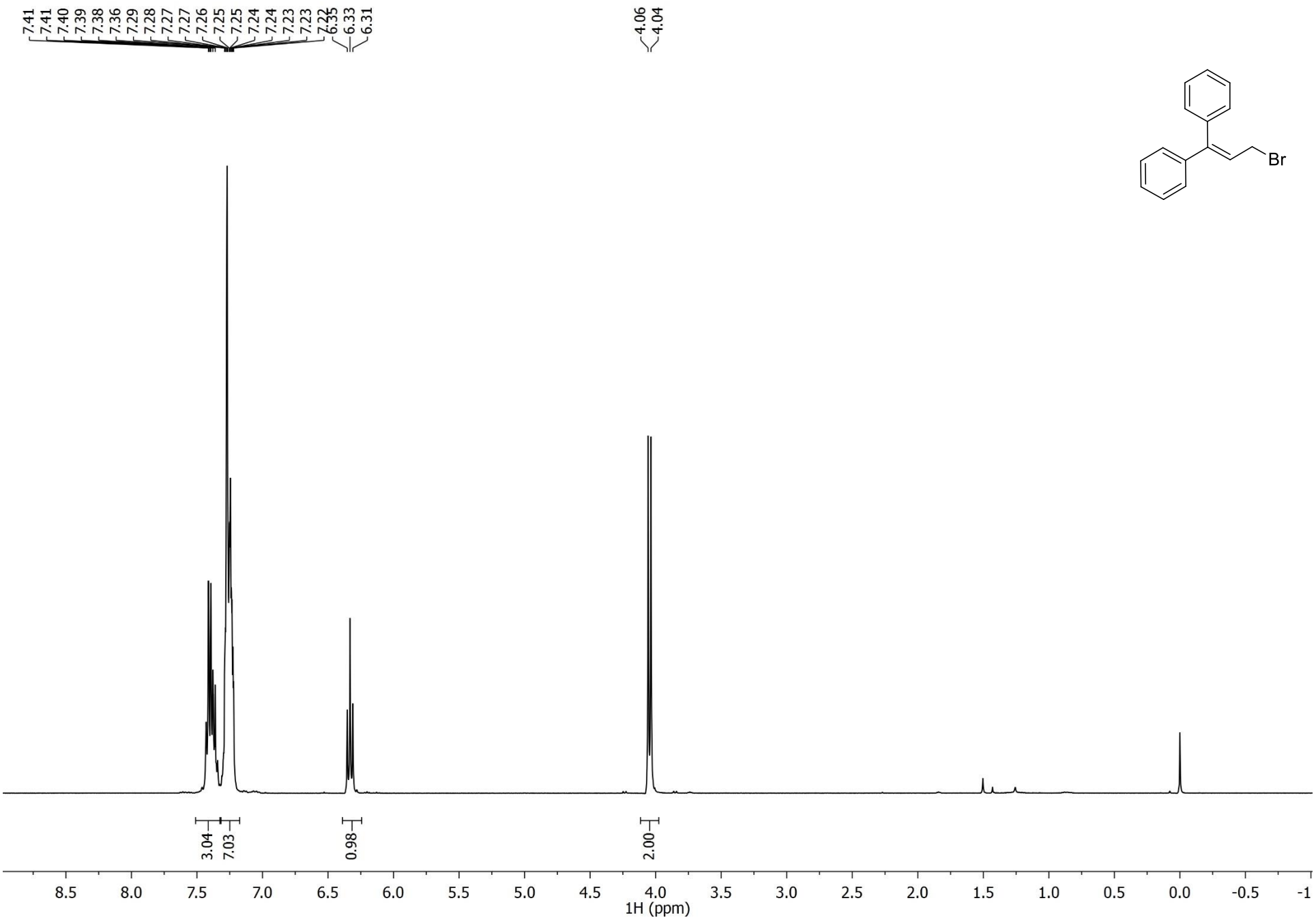

136.82
136.11
132.47
132.41
130.54
128.76
128.75
33.64
21.04
20.81
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
13C (ppm)

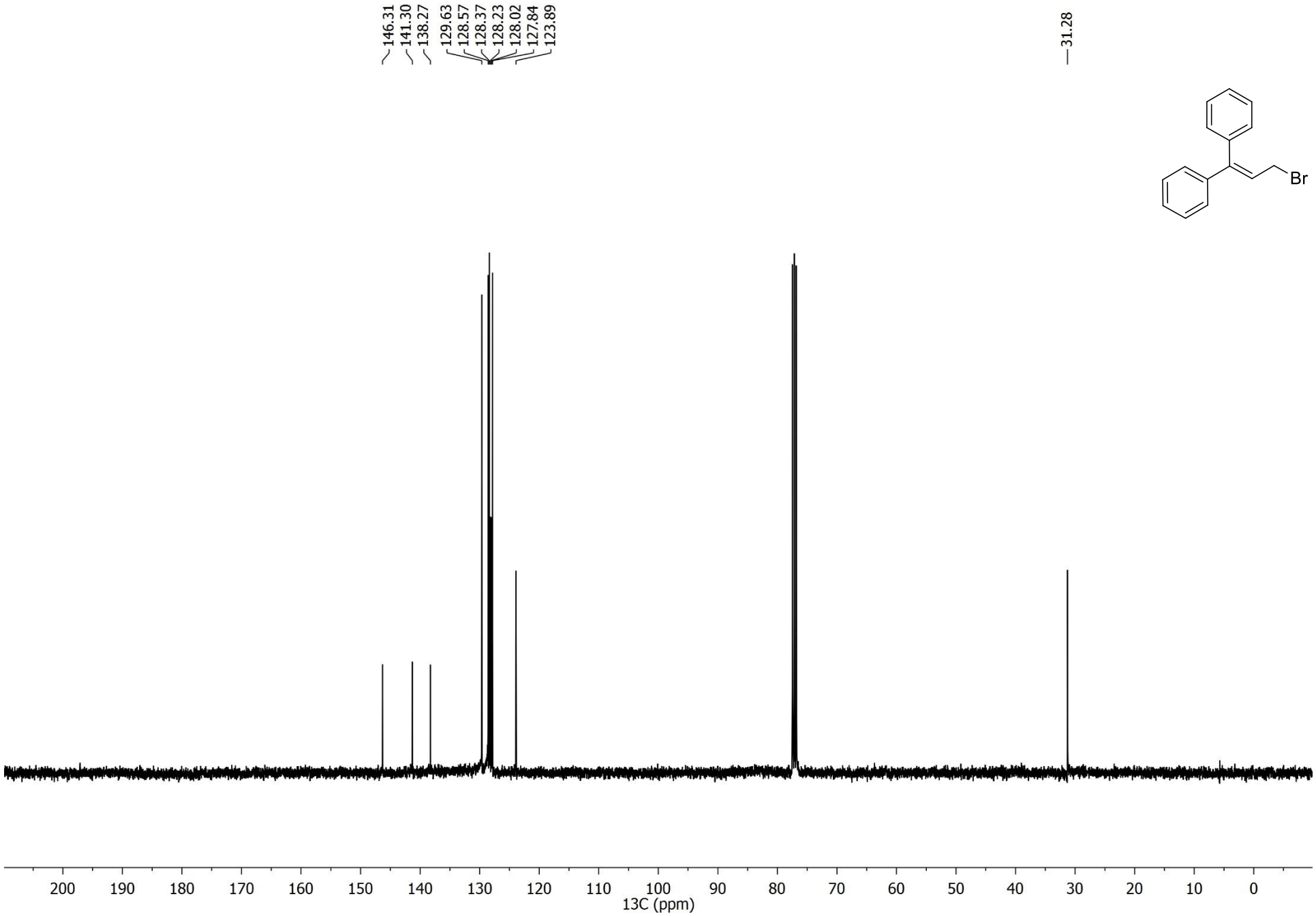

6.86
6.65
6.61
6.51
6.48
6.47
6.45
6.30
6.28
6.26
6.24
5.94
5.92
5.90
5.89
5.87
4.11
4.09
2.28
2.26
Br
1.96
0.99
1.00
1.11
0.94
2.00
6.00
3.18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
1H (ppm)

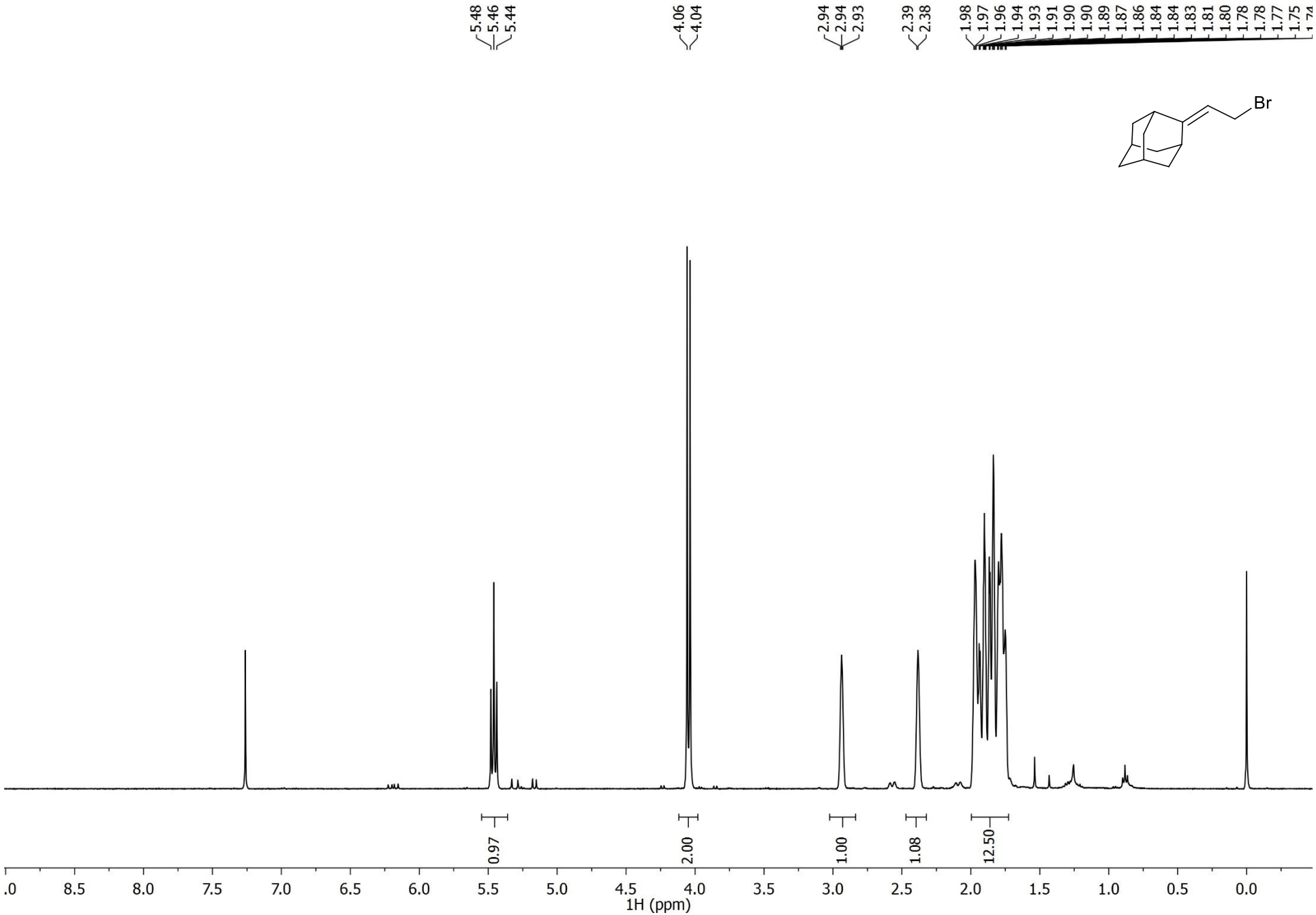

136.80
136.21
135.82
133.27
133.02
132.51
128.95
128.07
33.68
21.20
21.09
Br
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
13C (ppm)

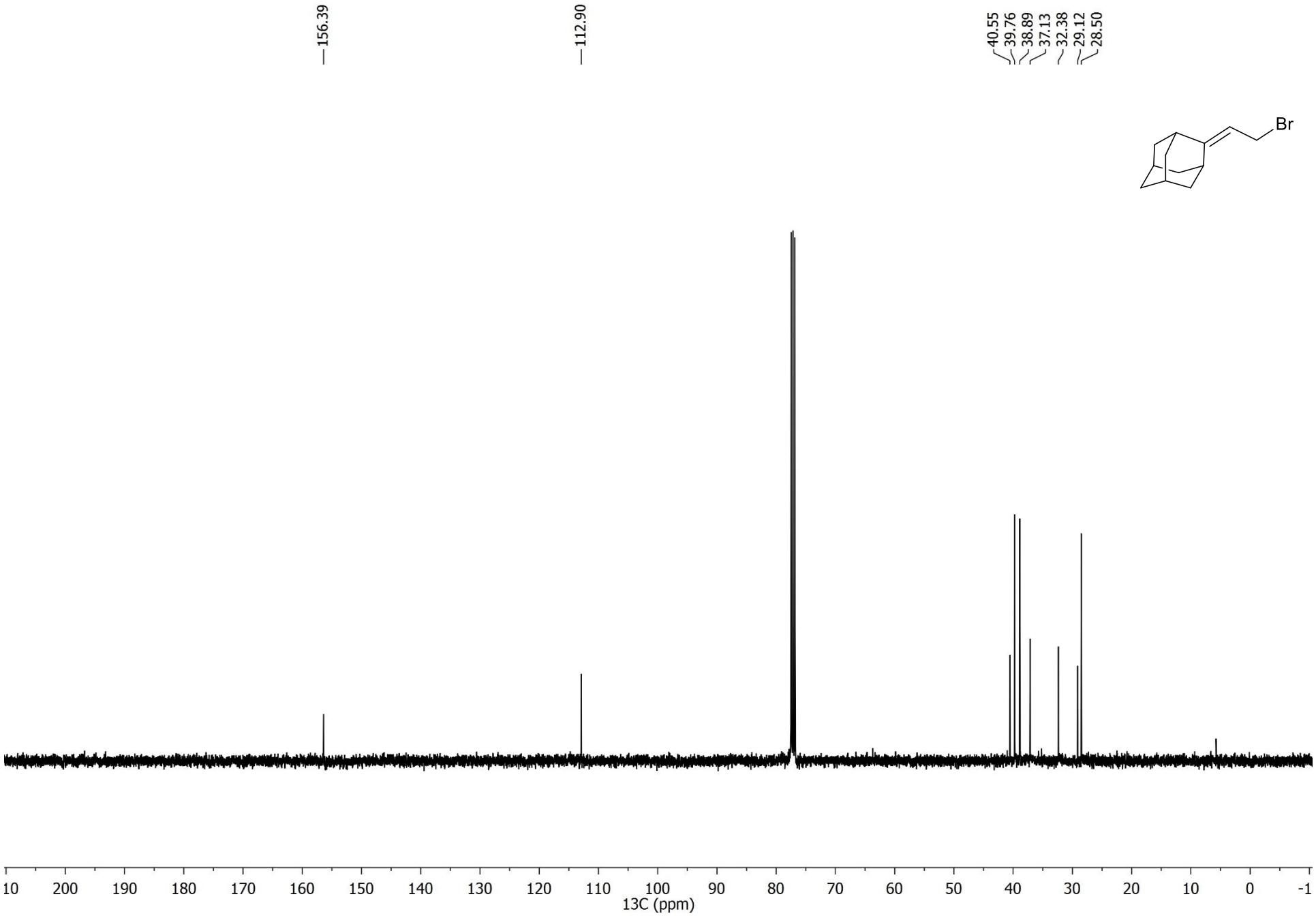

5.79
5.77
5.73
5.73
5.72
5.71
4.09
4.05
3.96
3.94
2.44
2.43
2.42
2.41
2.40
2.30
2.29
2.29
2.28
2.27
2.25
2.25
Fe
Br
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
1H (ppm)

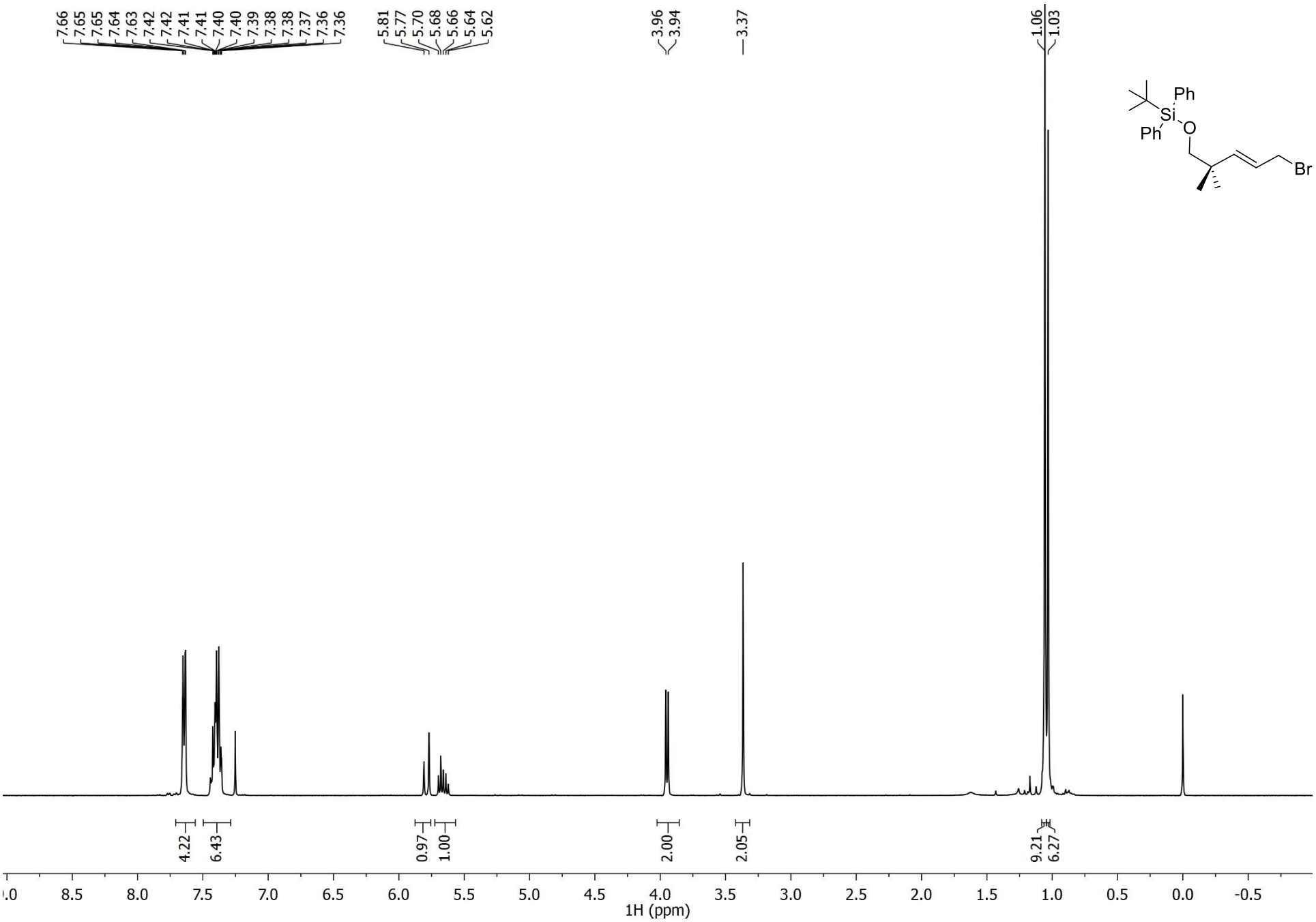

136.09
126.70
88.33
68.62
68.19
67.32
33.71
33.53
29.14
Fe
Br
13C (ppm)

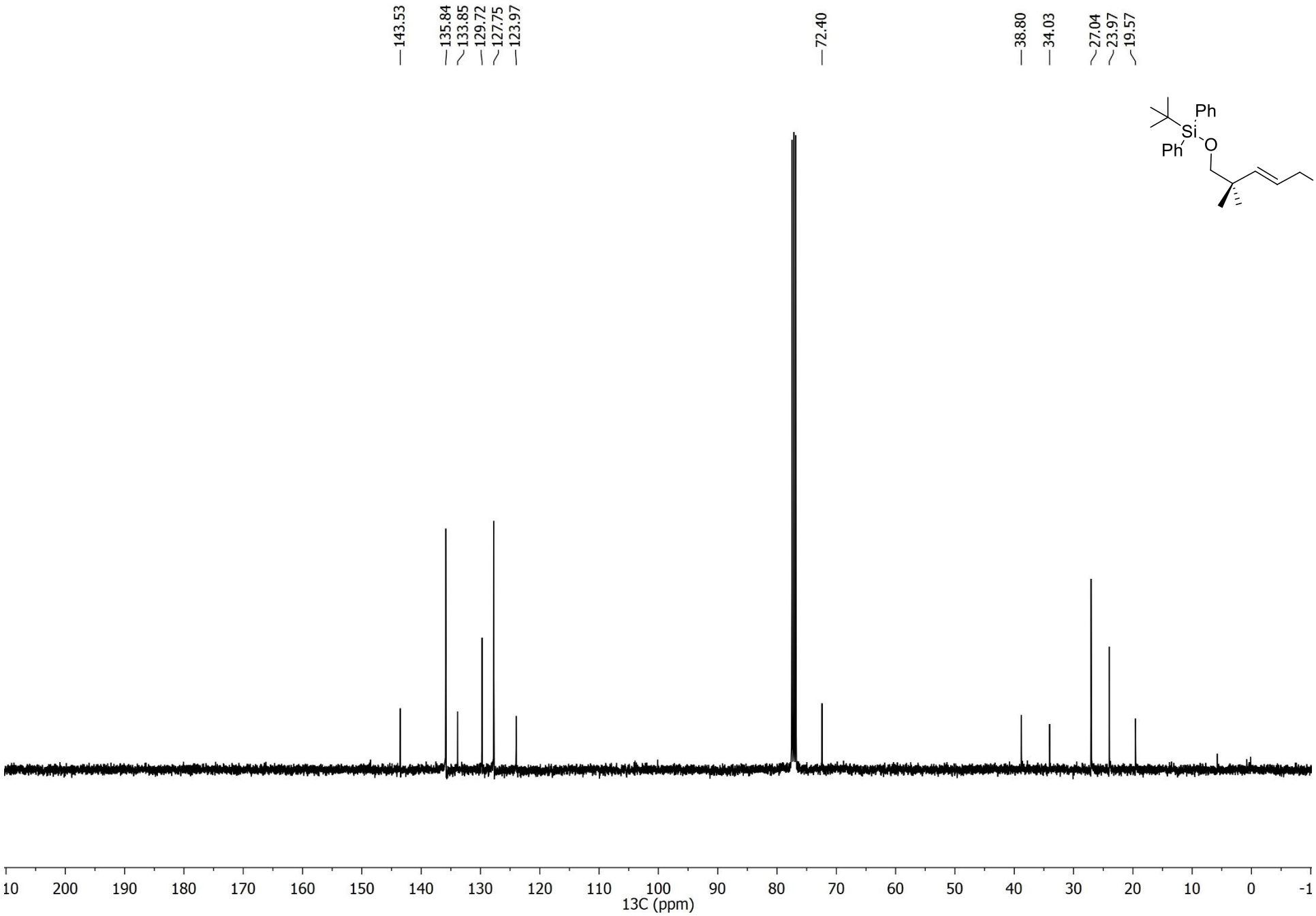

7.41
7.41
7.40
7.39
7.38
7.36
7.29
7.28
7.27
7.27
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.22
6.35
6.33
6.31
4.06
4.04
Br
3.04
7.03
0.98
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
1H (ppm)

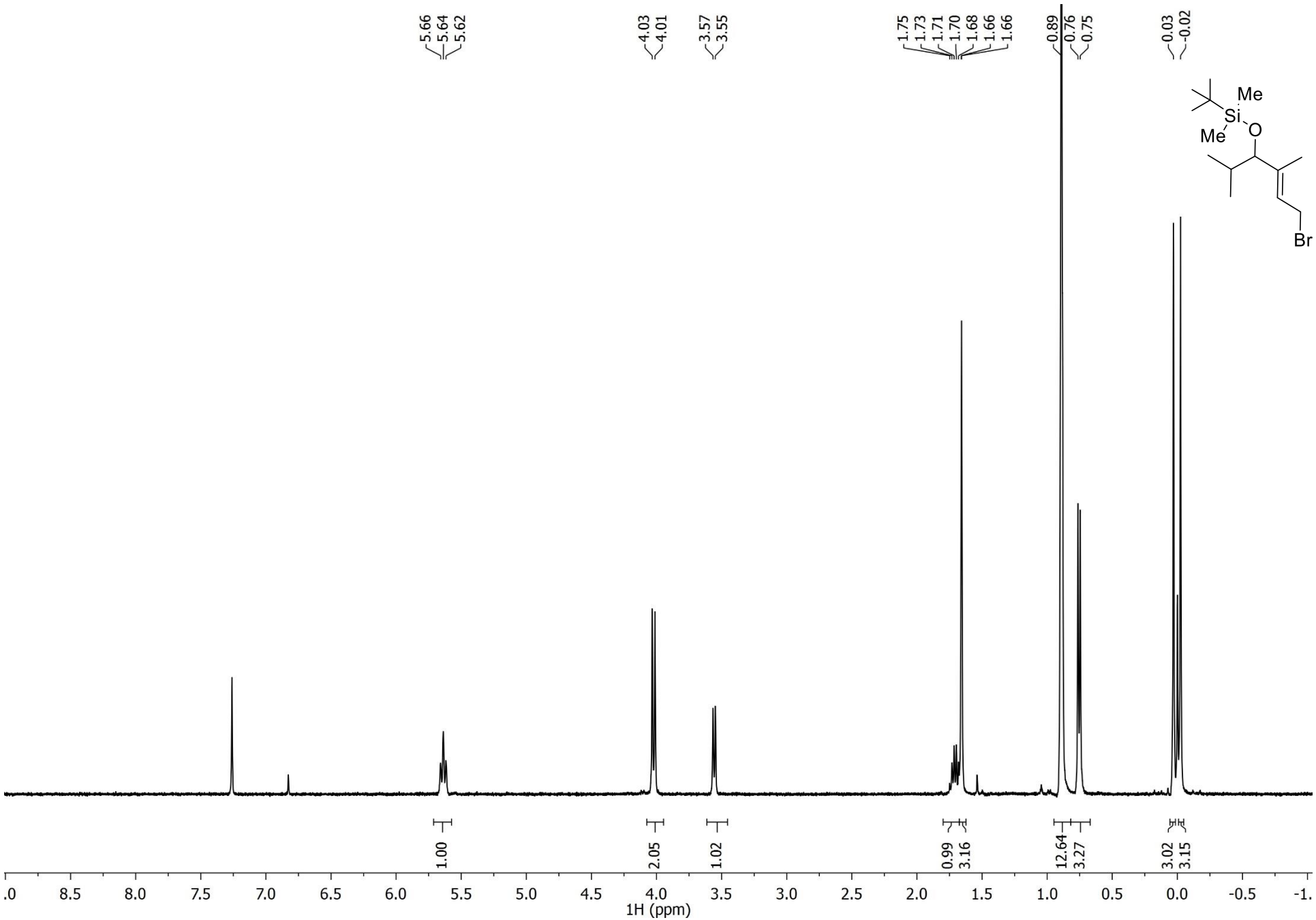

146.31
141.30
138.27
129.63
128.57
128.37
128.23
128.02
127.84
123.89
31.28
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C (ppm)

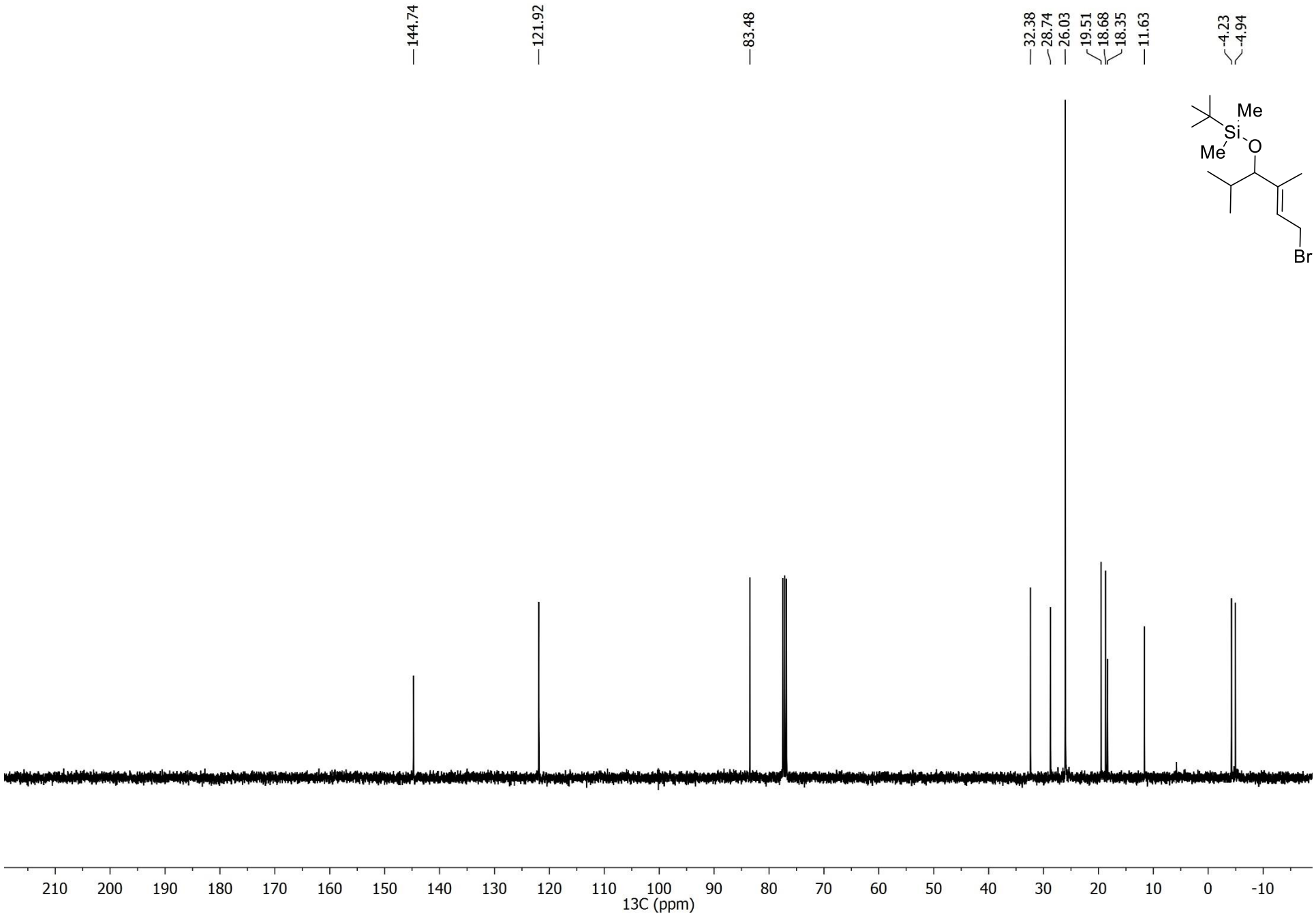

5.48
5.46
5.44
4.06
4.04
2.94
2.94
2.93
2.39
2.38
1.98
1.97
1.96
1.94
1.93
1.91
1.90
1.90
1.89
1.87
1.86
1.84
1.84
1.83
1.81
1.80
1.78
1.78
1.77
1.75
Br
0.97
2.00
1.00
1.08
12.50
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H (ppm)

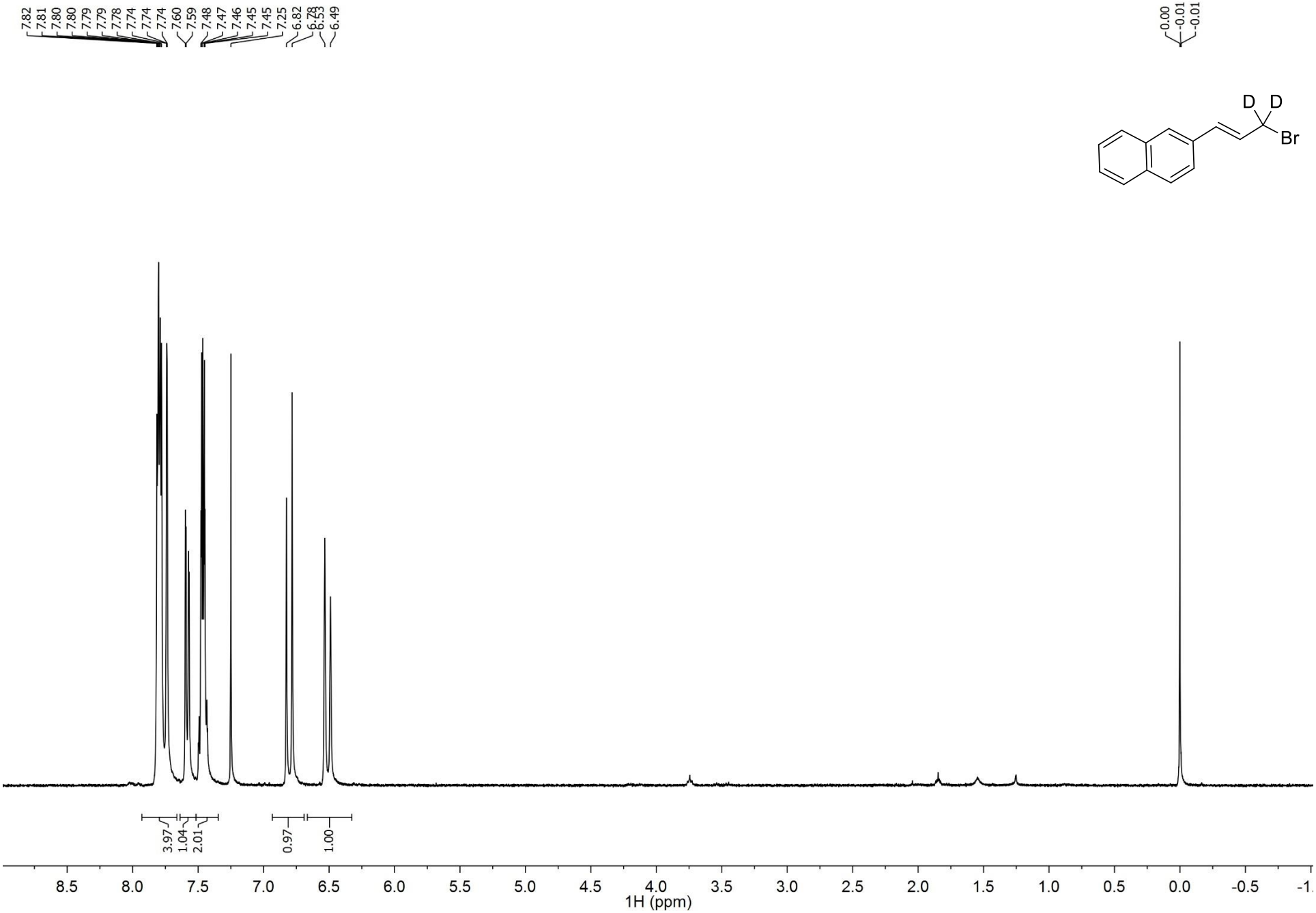

156.39
112.90
40.55
39.76
38.89
37.13
32.38
29.12
28.50
Br
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
13C (ppm)

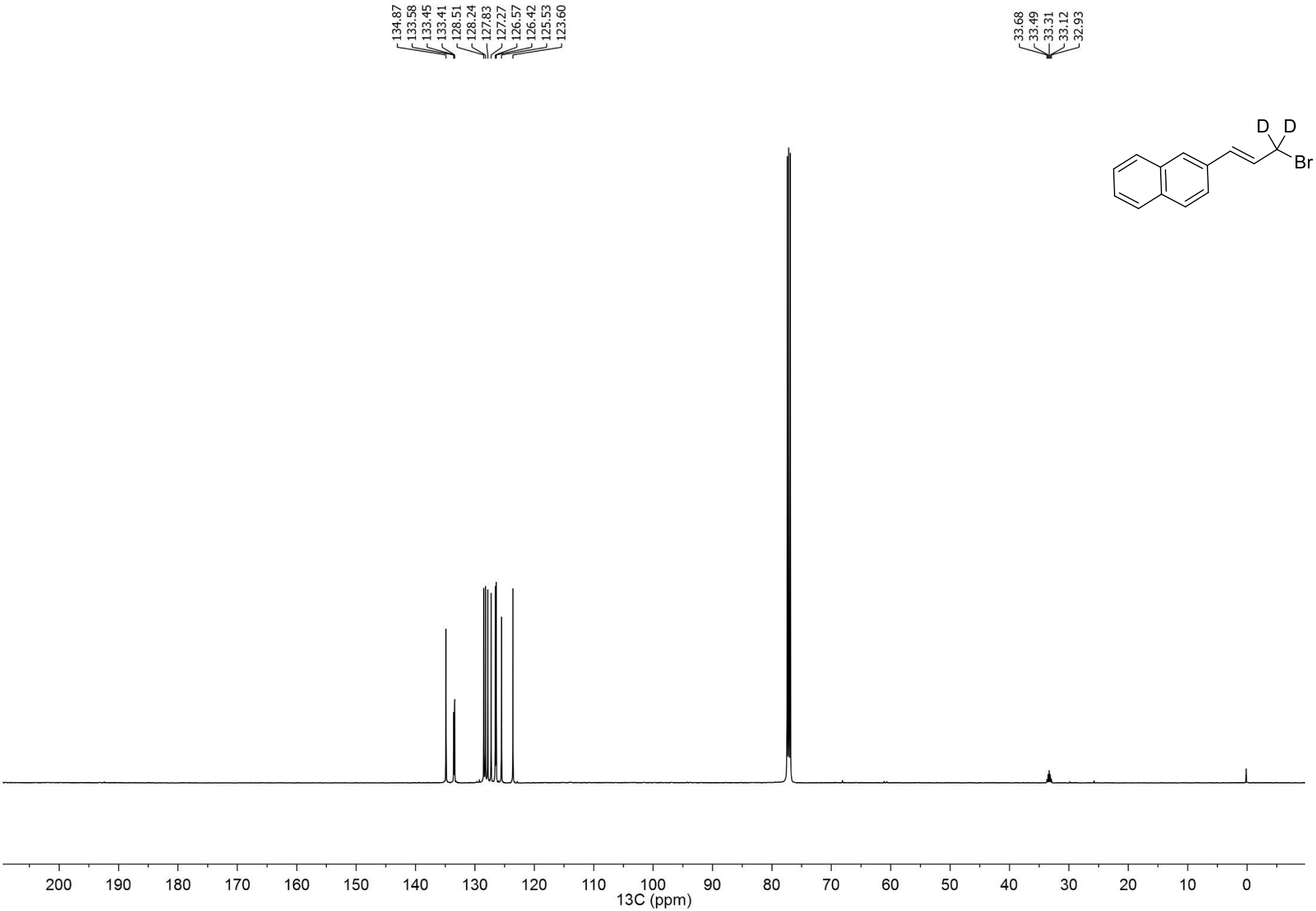

7.66
7.65
7.65
7.64
7.63
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.36
5.81
5.77
5.70
5.68
5.66
5.64
5.62
3.96
3.94
3.37
1.06
1.03
Ph
Si
O
Ph
Br
4.22
6.43
0.97
1.00
2.00
2.05
9.21
6.27
1H (ppm)

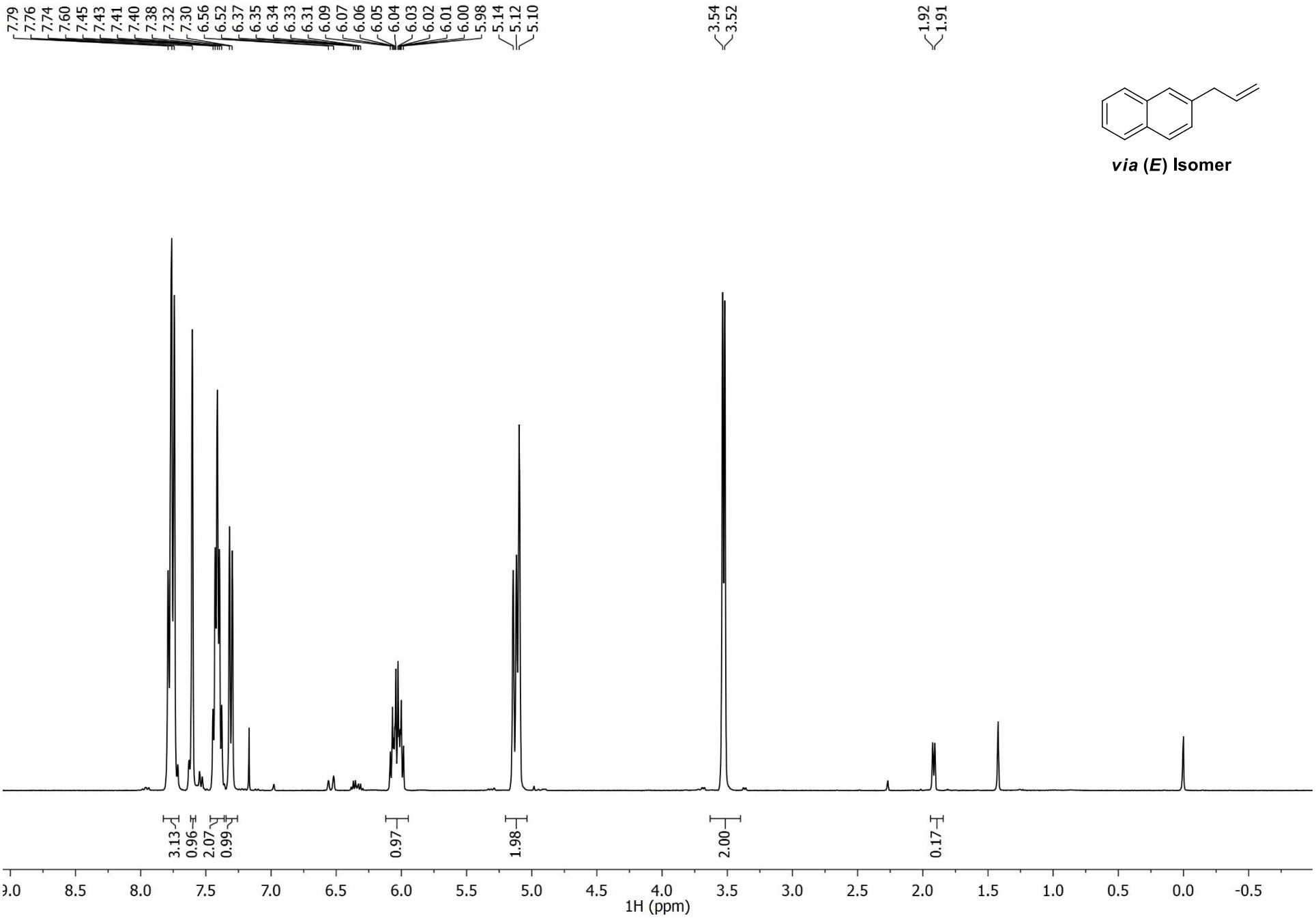

143.53
135.84
133.85
129.72
127.75
123.97
72.40
38.80
34.03
27.04
23.97
19.57
Ph
Si
O
Ph
Br
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
13C (ppm)


5.66
5.64
5.62
4.03
4.01
3.57
3.55
1.75
1.73
1.71
1.70
1.68
1.66
1.66
0.89
0.76
0.75
0.03
-0.02
Me
Si
Me
O
Br
1.00
2.05
1.02
0.99
3.16
12.64
3.27
3.02
3.15
1H (ppm)


144.74
121.92
83.48
32.38
28.74
26.03
19.51
18.68
18.35
11.63
-4.23
-4.94
Me
Si
Me
O
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)


7.82
7.81
7.80
7.80
7.79
7.79
7.78
7.74
7.74
7.74
7.60
7.59
7.48
7.47
7.46
7.45
7.45
7.25
6.82
6.78
6.53
6.49
0.00
-0.01
-0.01
D
D
Br
3.97
1.04
2.01
0.97
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1H (ppm)


134.87
133.58
133.45
133.41
128.51
128.24
127.83
127.27
126.57
126.42
125.53
123.60
33.68
33.49
33.31
33.12
32.93
D
D
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C (ppm)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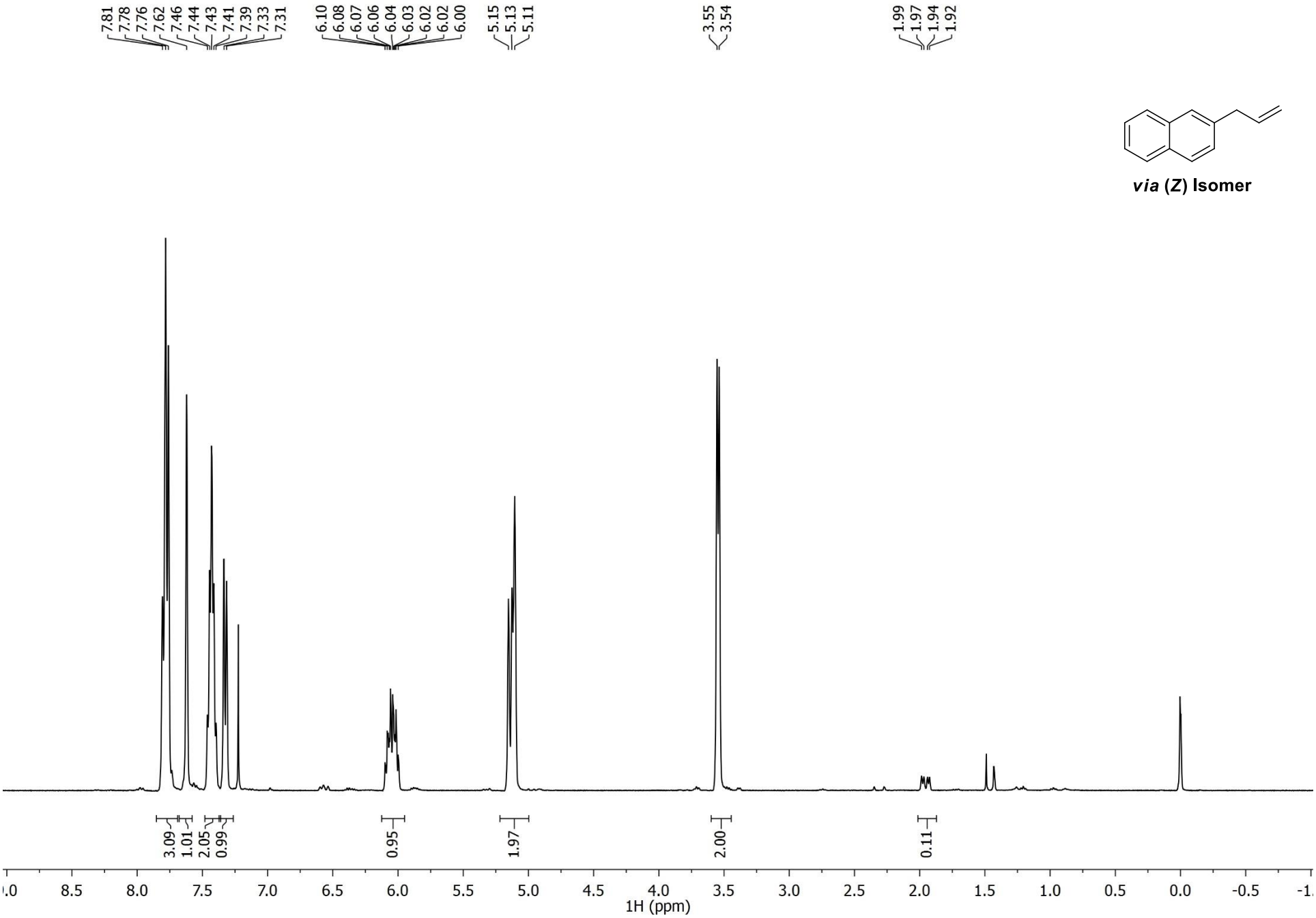
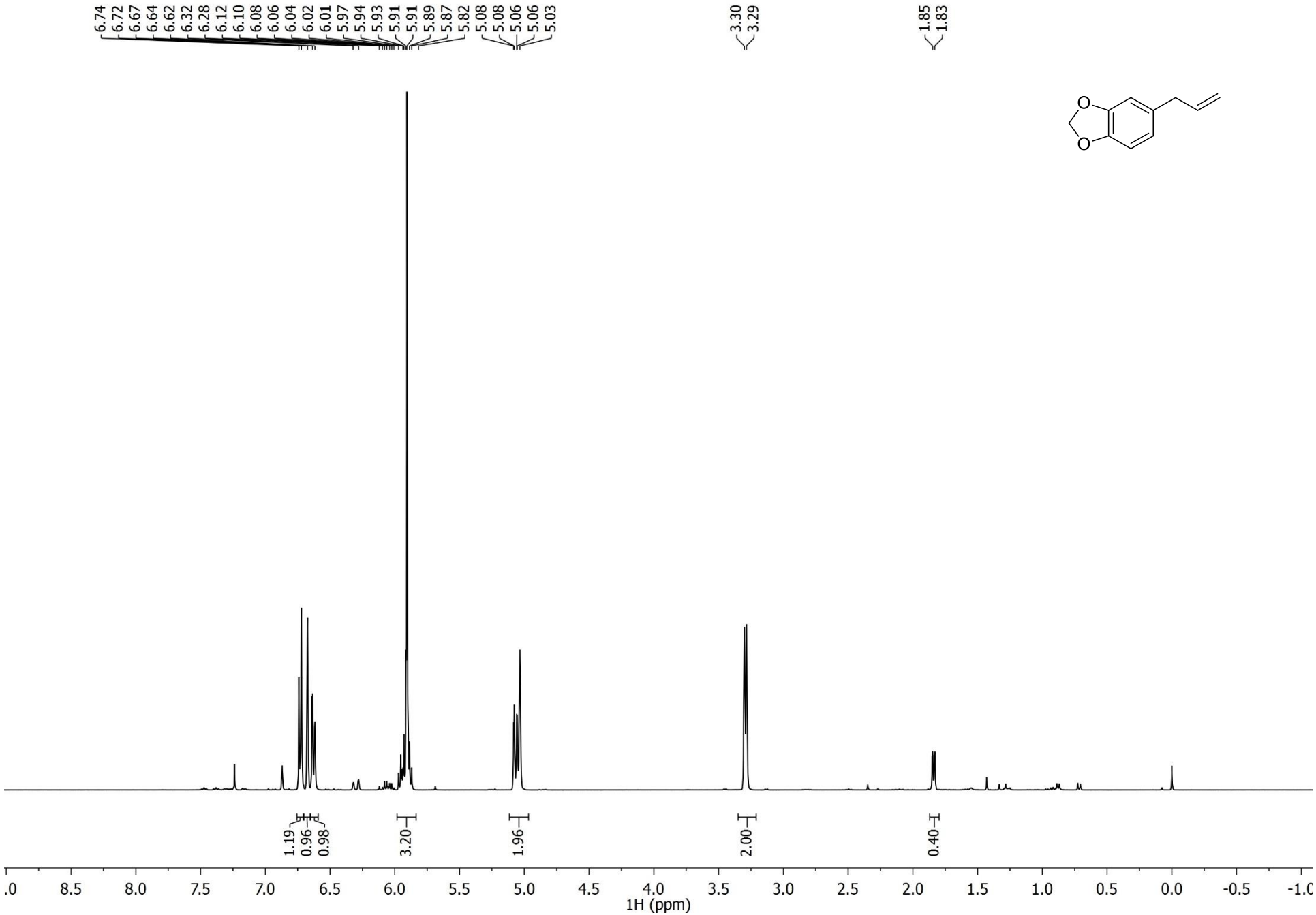
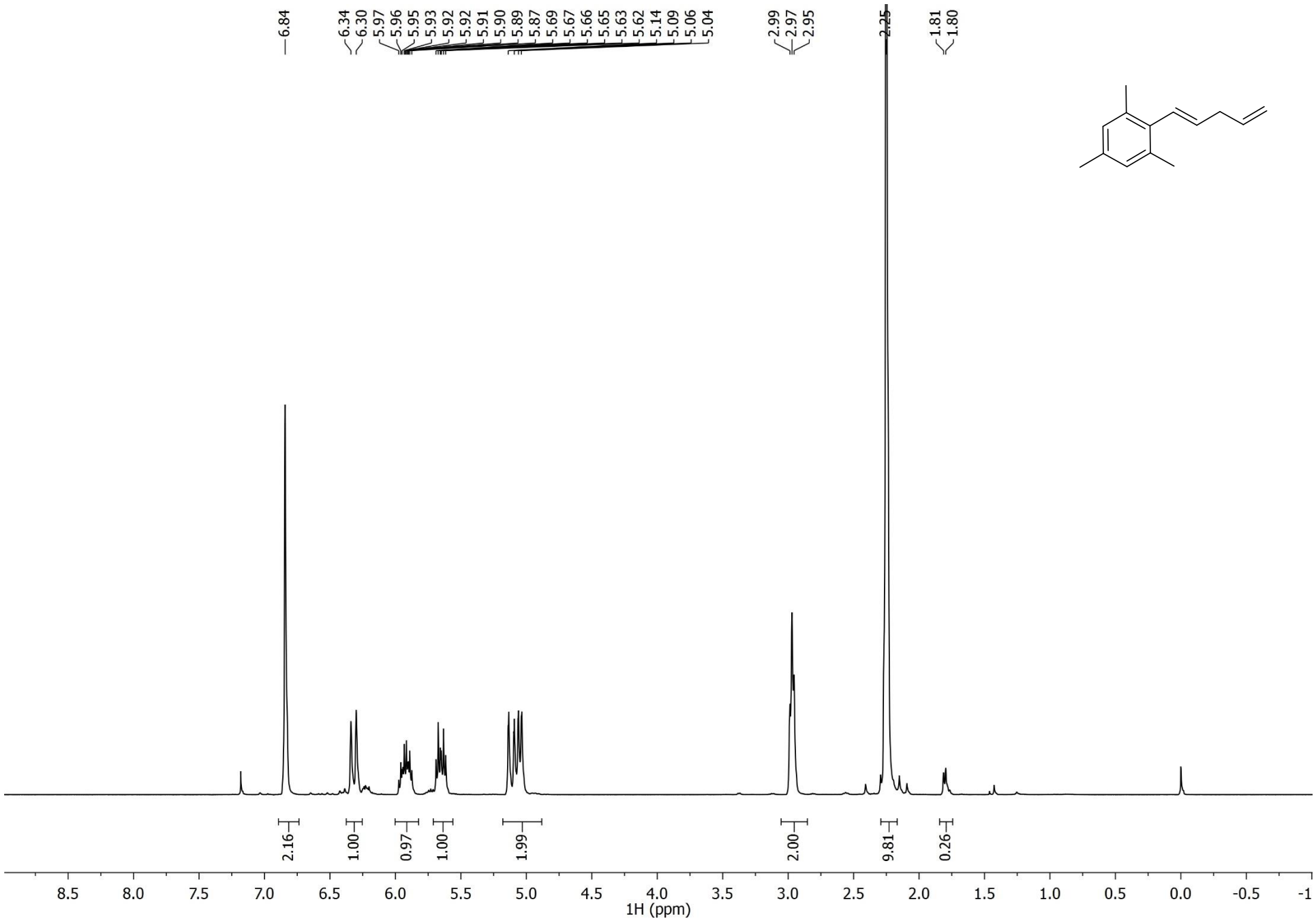
7.76
7.74
7.60
7.45
7.43
7.41
7.40
7.38
7.32
7.30
6.56
6.52
6.37
6.35
6.34
6.33
6.31
6.09
6.07
6.06
6.05
6.04
6.03
6.02
6.01
6.00
5.98
5.14
5.12
5.10
3.54
3.52
1.92
1.91
via (E) Isomer
3.13
0.96
2.07
0.99
0.97
1.98
2.00
0.17
1H (ppm)


7.81
7.78
7.76
7.62
7.46
7.44
7.43
7.41
7.39
7.33
7.31
6.10
6.08
6.07
6.06
6.04
6.03
6.02
6.02
6.00
5.15
5.13
5.11
3.55
3.54
1.99
1.97
1.94
1.92
via (Z) Isomer
3.09
1.01
2.05
0.99
0.95
1.97
2.00
0.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1H (ppm)


6.74
6.72
6.67
6.64
6.62
6.32
6.28
6.12
6.10
6.08
6.06
6.04
6.02
6.01
5.97
5.94
5.93
5.91
5.91
5.89
5.87
5.82
5.08
5.08
5.06
5.06
5.03
3.30
3.29
1.85
1.83
O
O
1.19
0.96
0.98
3.20
1.96
2.00
0.40
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1H (ppm)


6.84
6.34
6.30
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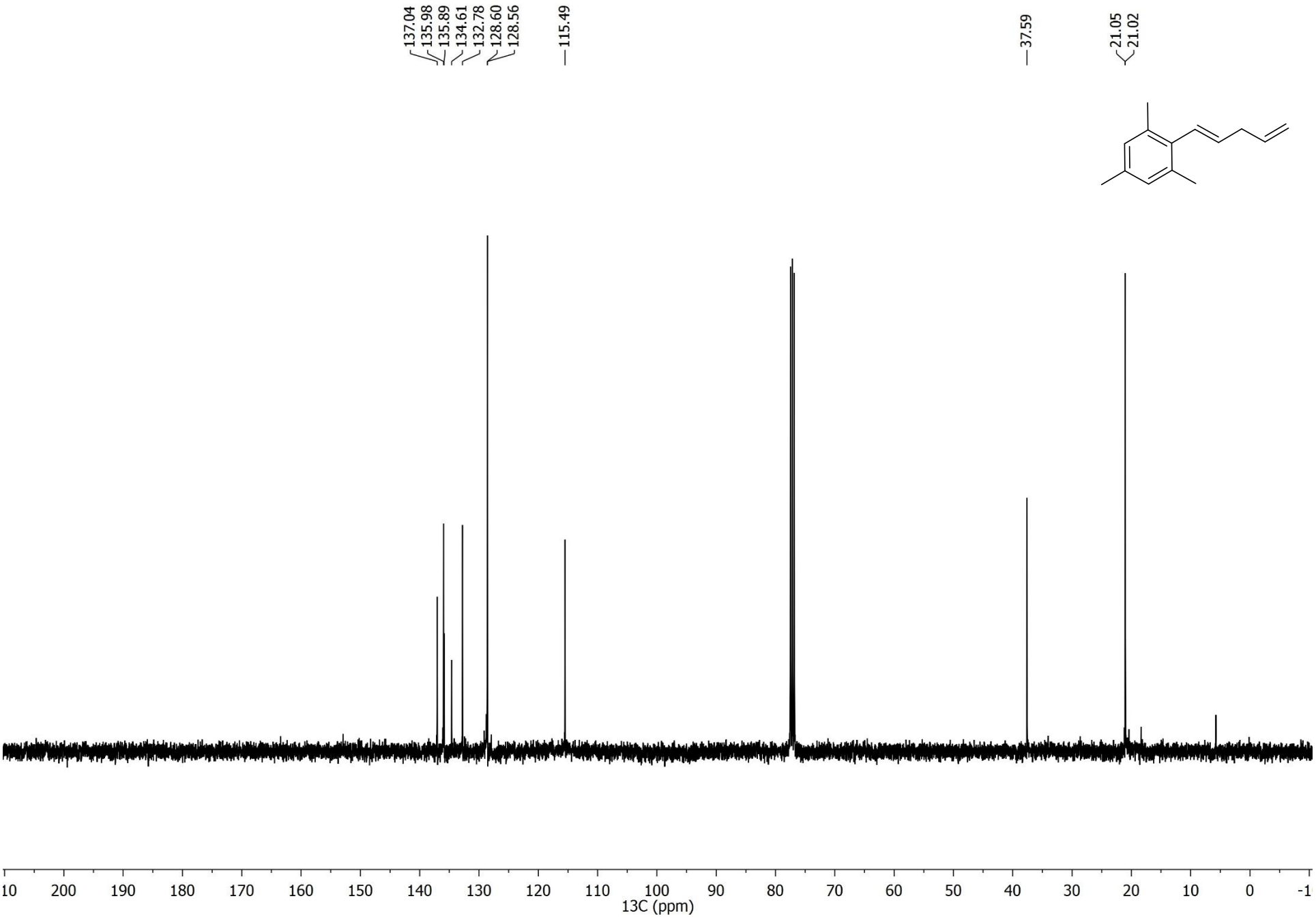
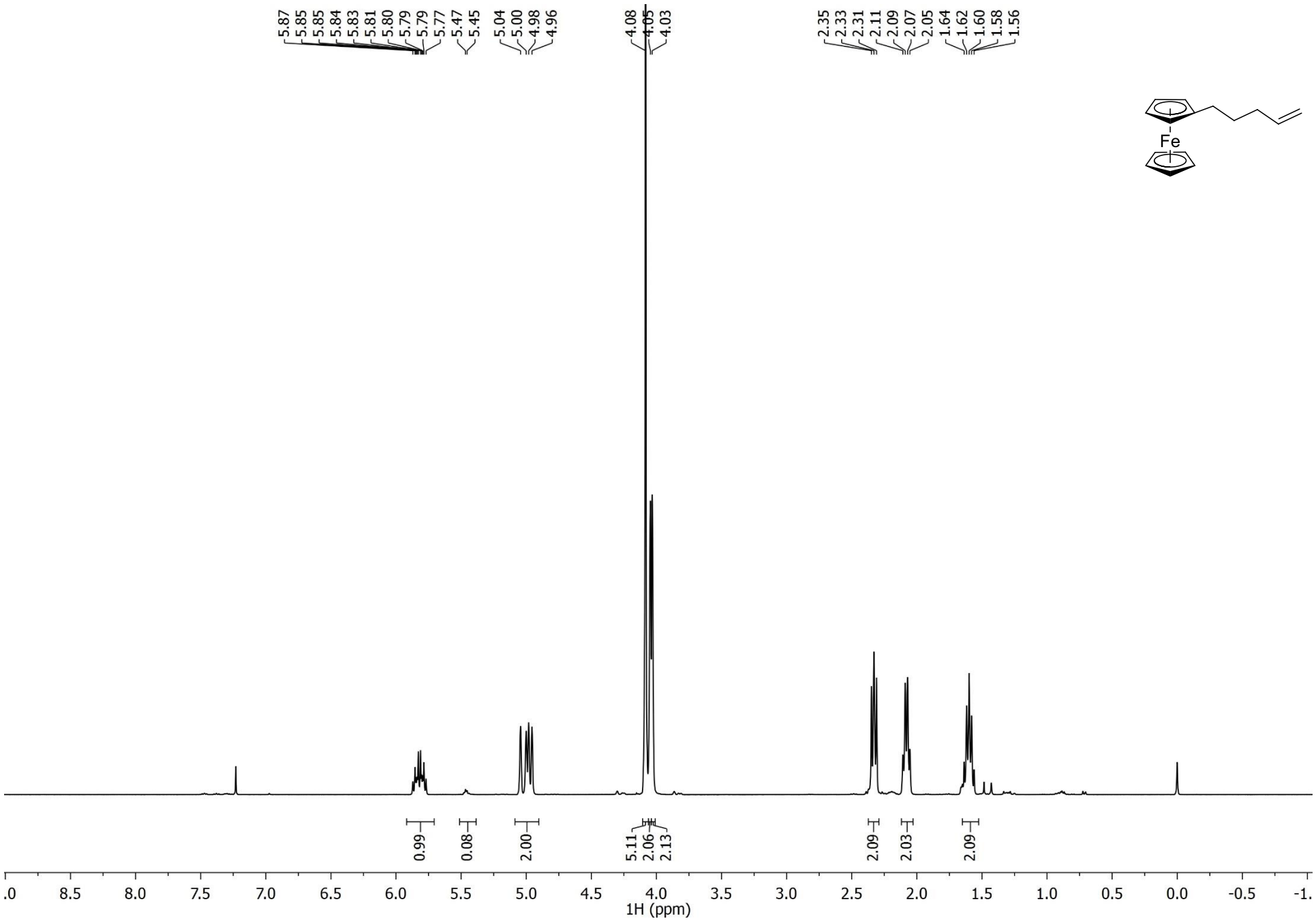
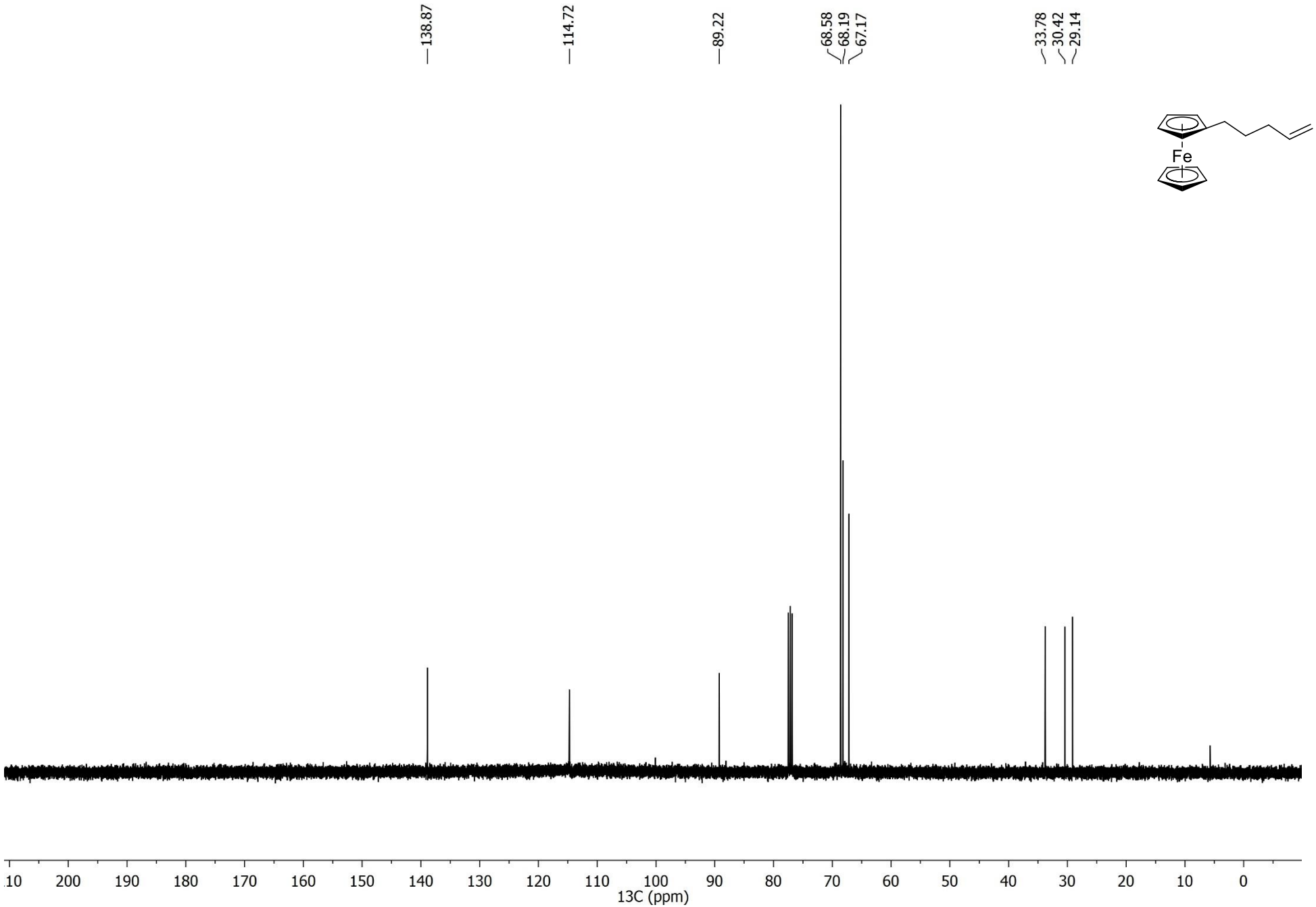
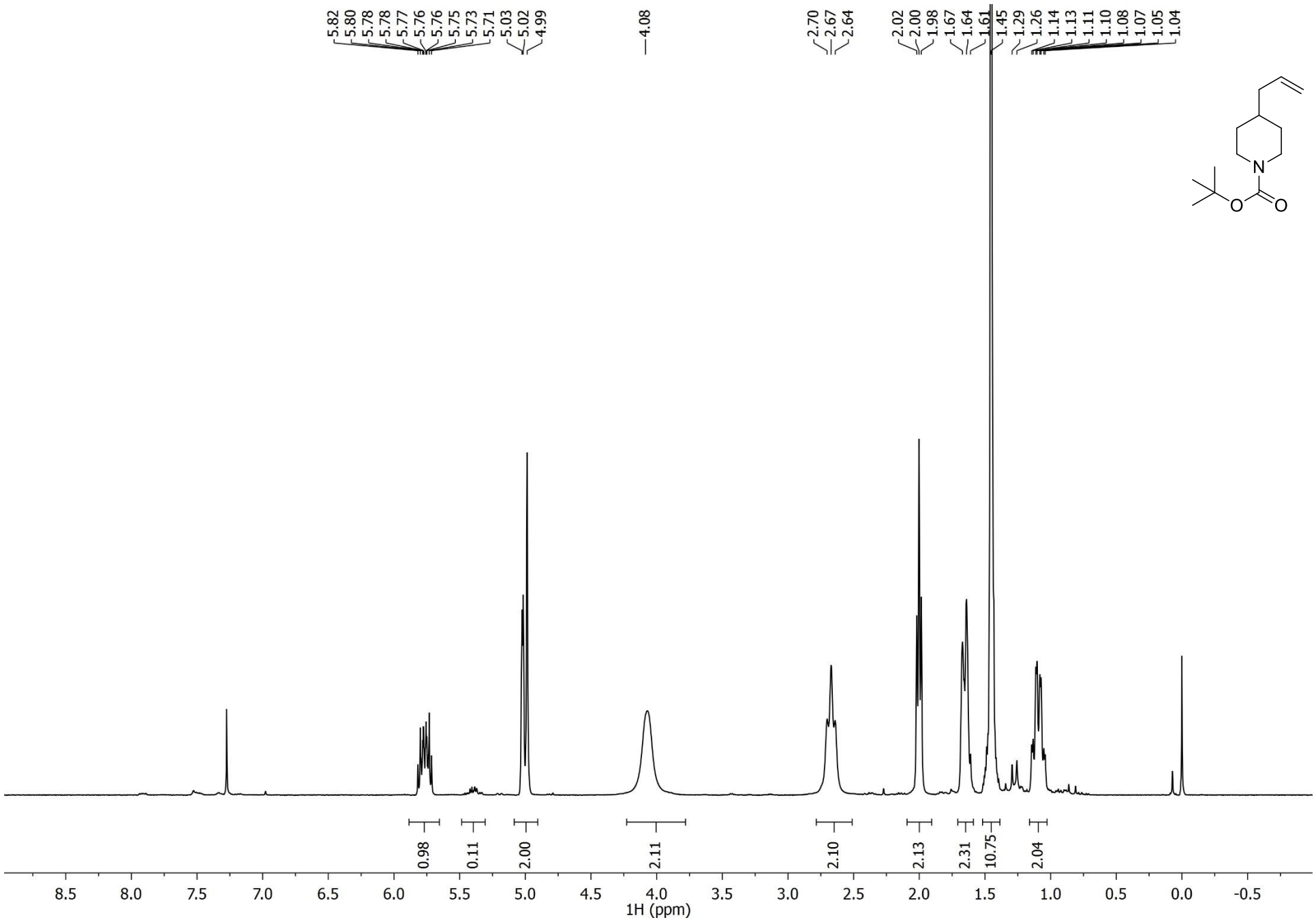
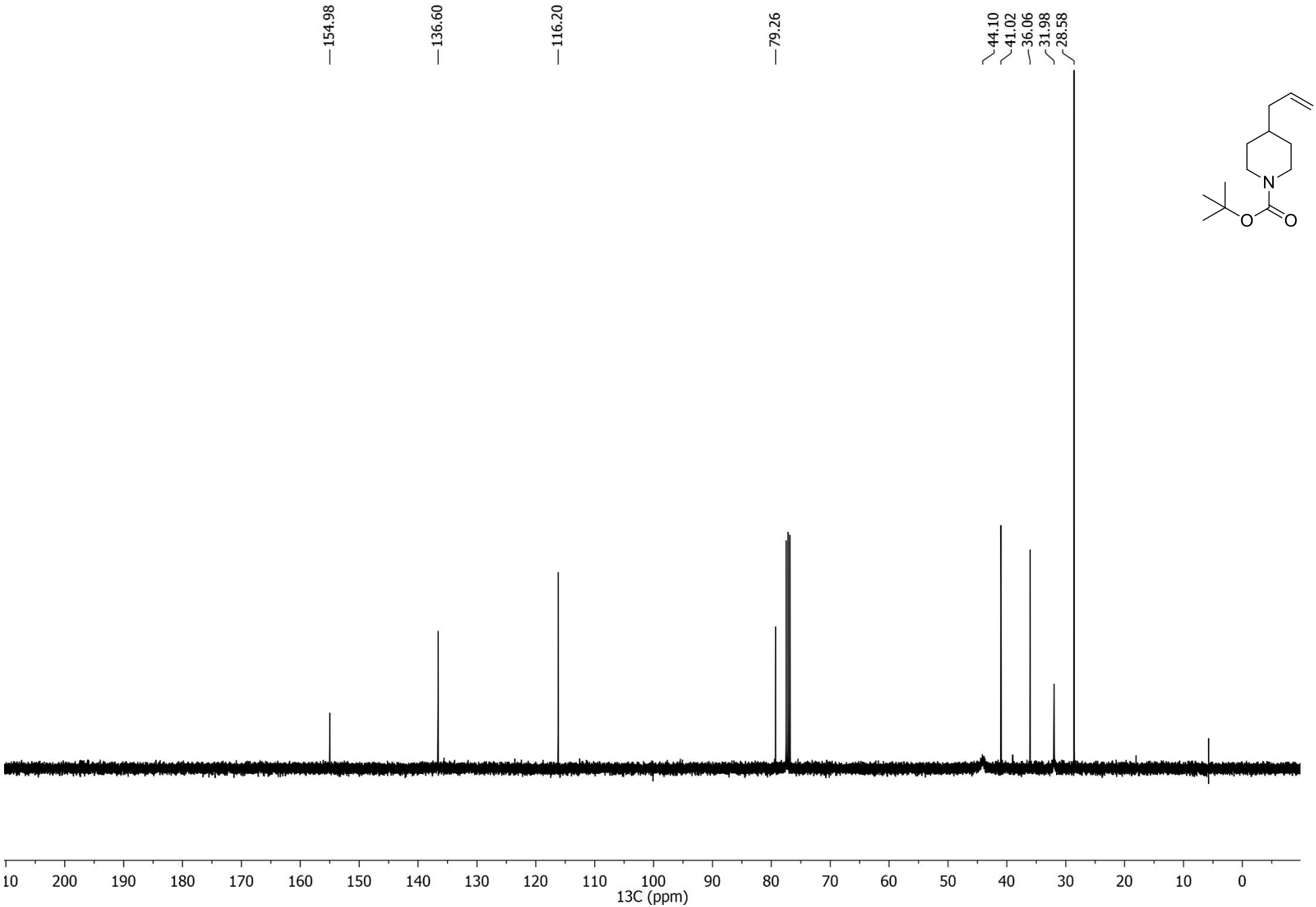
5.96
5.95
5.93
5.92
5.92
5.91
5.90
5.89
5.87
5.69
5.67
5.66
5.65
5.63
5.62
5.14
5.09
5.06
5.04
2.99
2.97
2.95
2.25
1.81
1.80
2.16
1.00
0.97
1.00
1.99
2.00
9.81
0.26
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
1H (ppm)

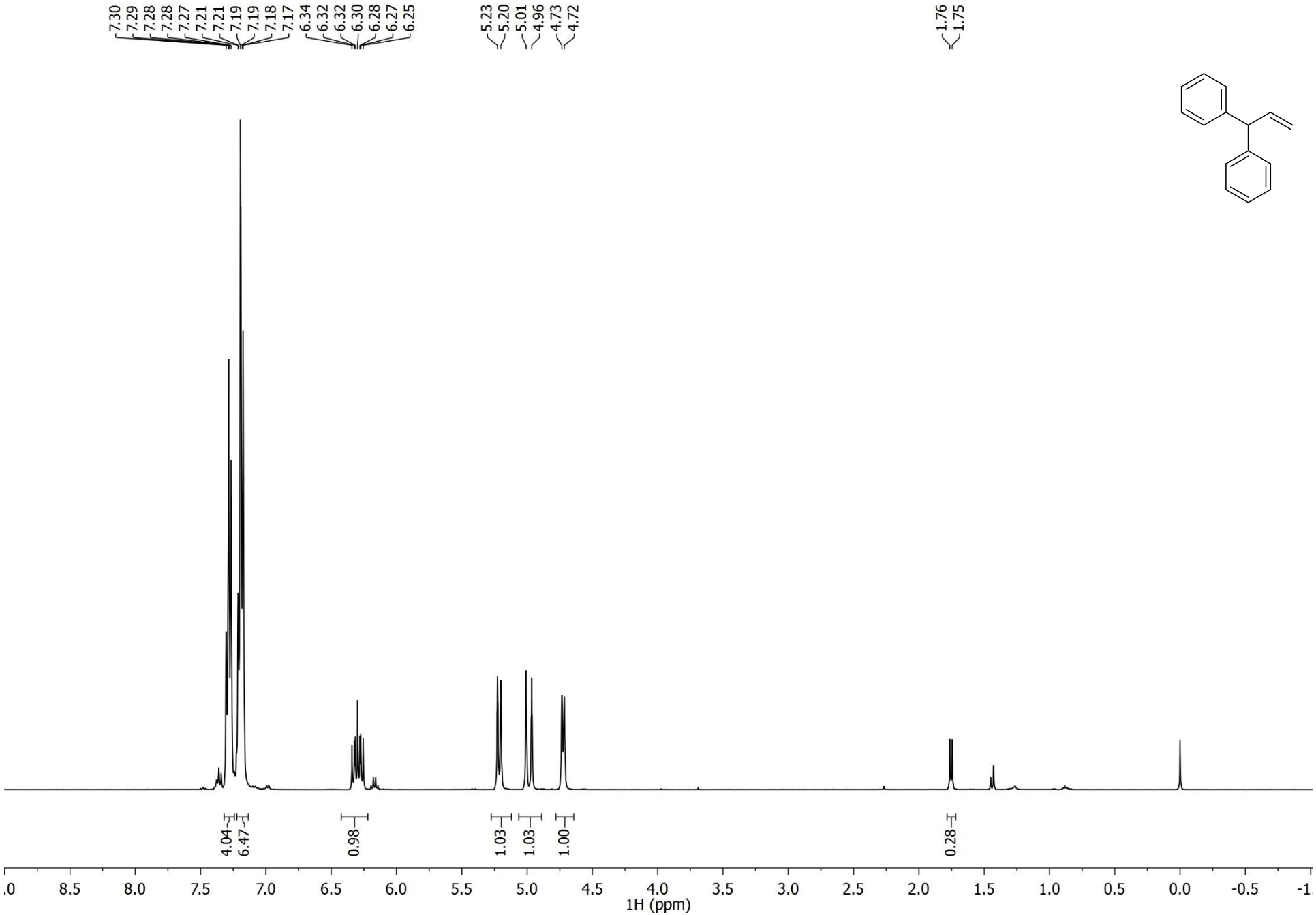

137.04
135.98
135.89
134.61
132.78
128.60
128.56
115.49
37.59
21.05
21.02
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
13C (ppm)

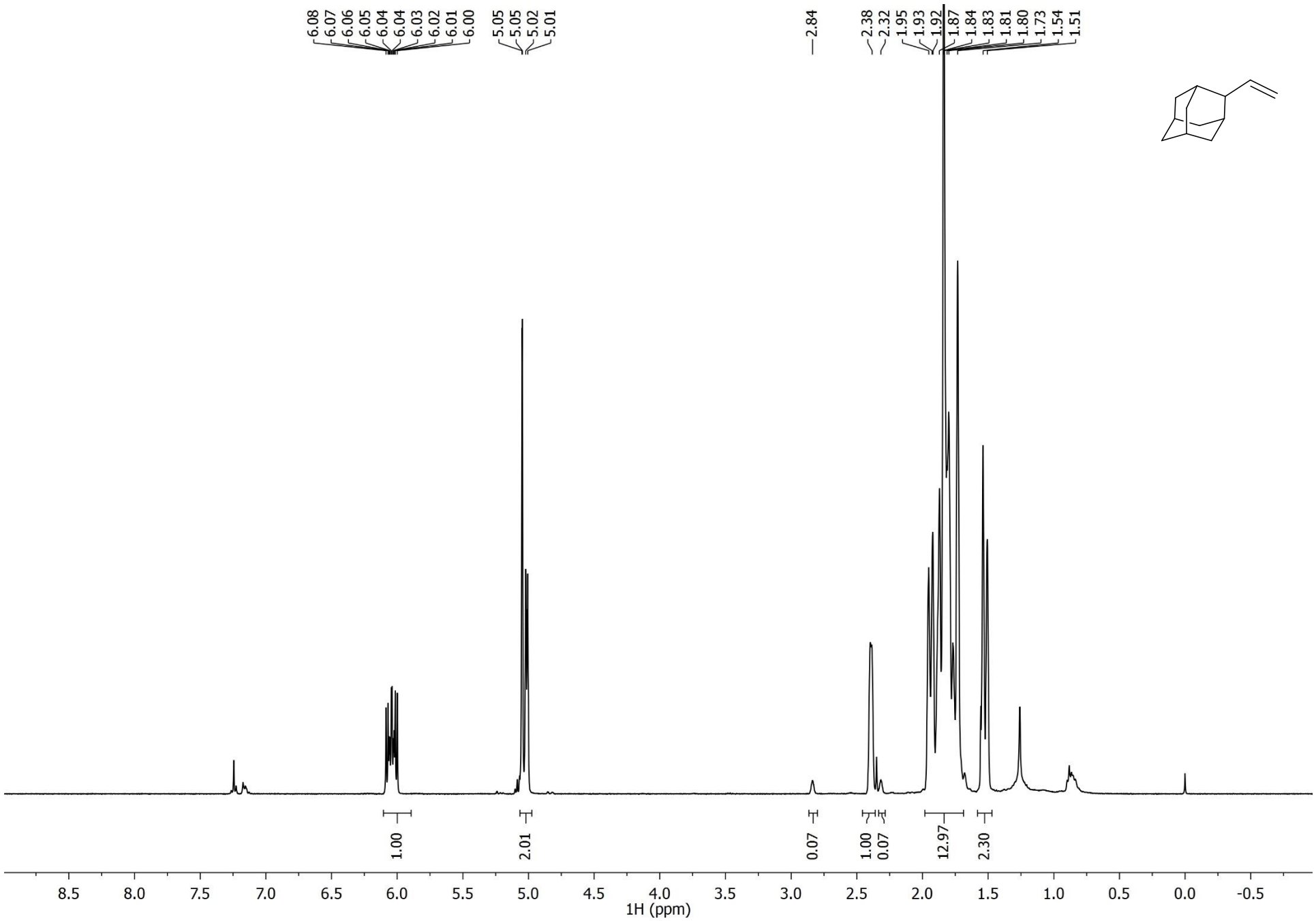

5.87
5.85
5.85
5.84
5.83
5.81
5.80
5.79
5.79
5.77
5.47
5.45
5.04
5.00
4.98
4.96
4.08
4.05
4.03
2.35
2.33
2.31
2.11
2.09
2.07
2.05
1.64
1.62
1.60
1.58
1.56
Fe
0.99
0.08
2.00
5.11
2.06
2.13
2.09
2.03
2.09
1H (ppm)

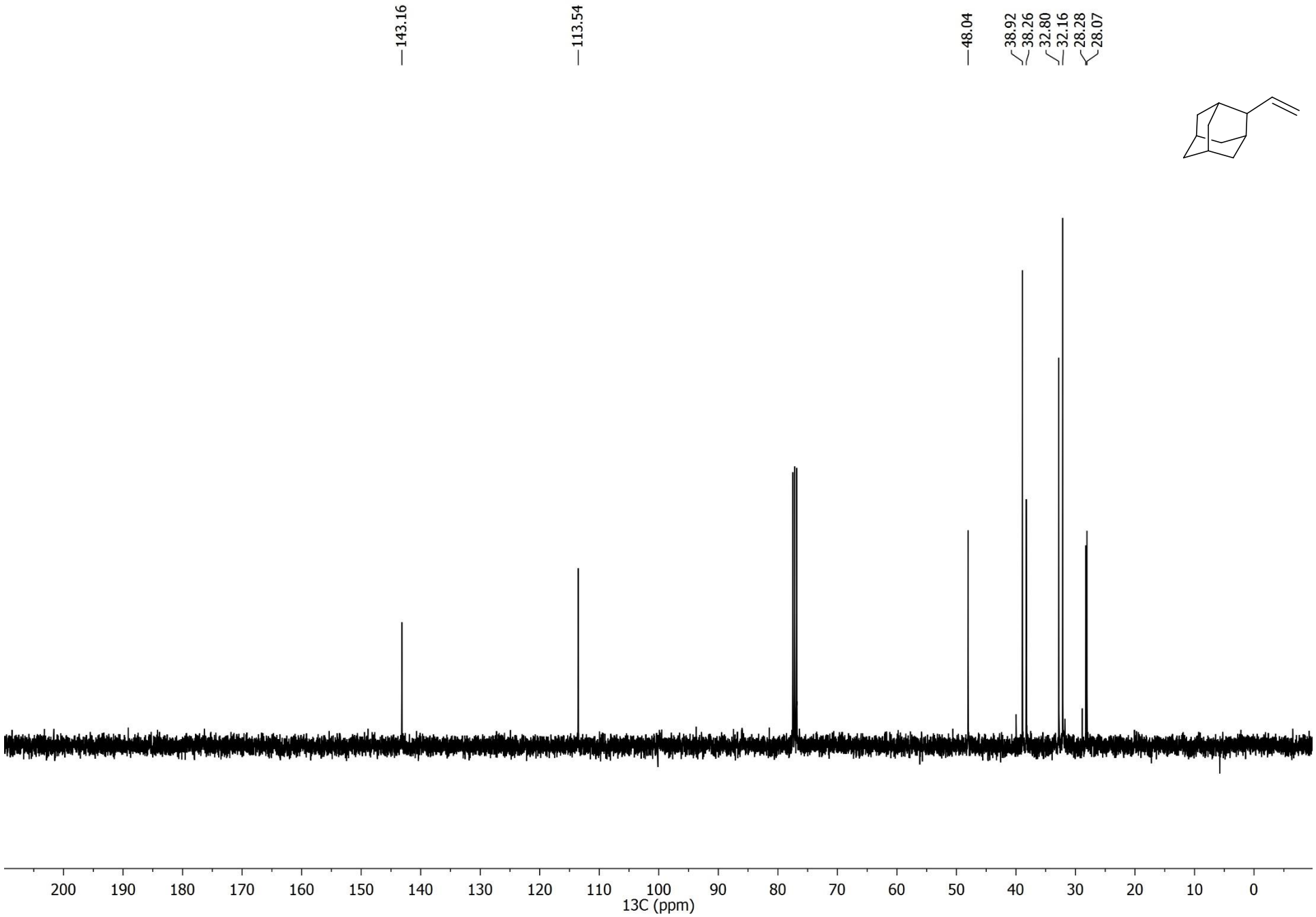

138.87
114.72
89.22
68.58
68.19
67.17
33.78
30.42
29.14
Fe
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C (ppm)

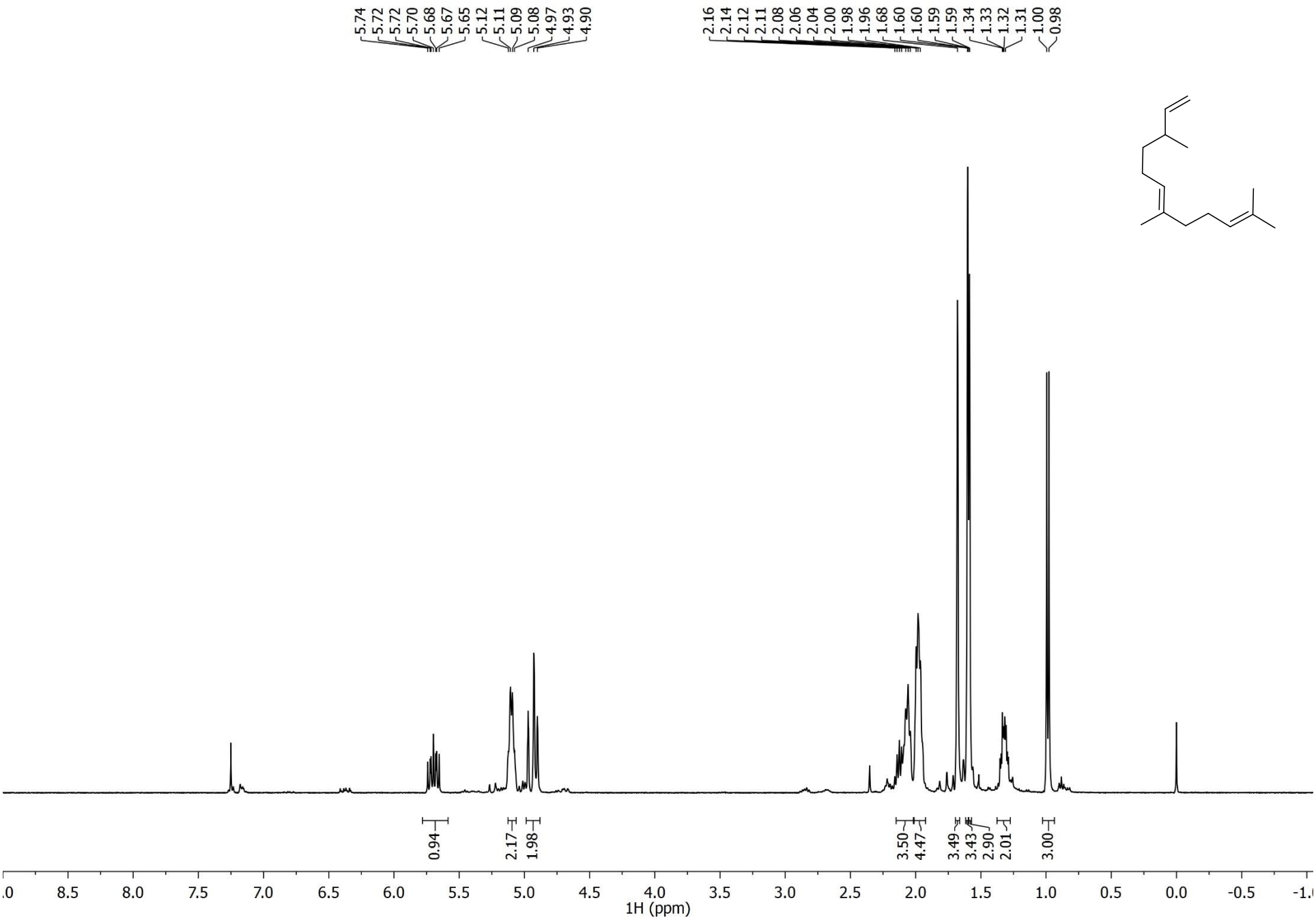

5.82
5.80
5.78
5.78
5.77
5.76
5.76
5.75
5.73
5.71
5.03
5.02
4.99
4.08
2.70
2.67
2.64
2.02
2.00
1.98
1.67
1.64
1.61
1.45
1.29
1.26
1.14
1.13
1.11
1.10
1.08
1.07
1.05
1.04
N
O
O
0.98
0.11
2.00
2.11
2.10
2.13
2.31
10.75
2.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1H (ppm)

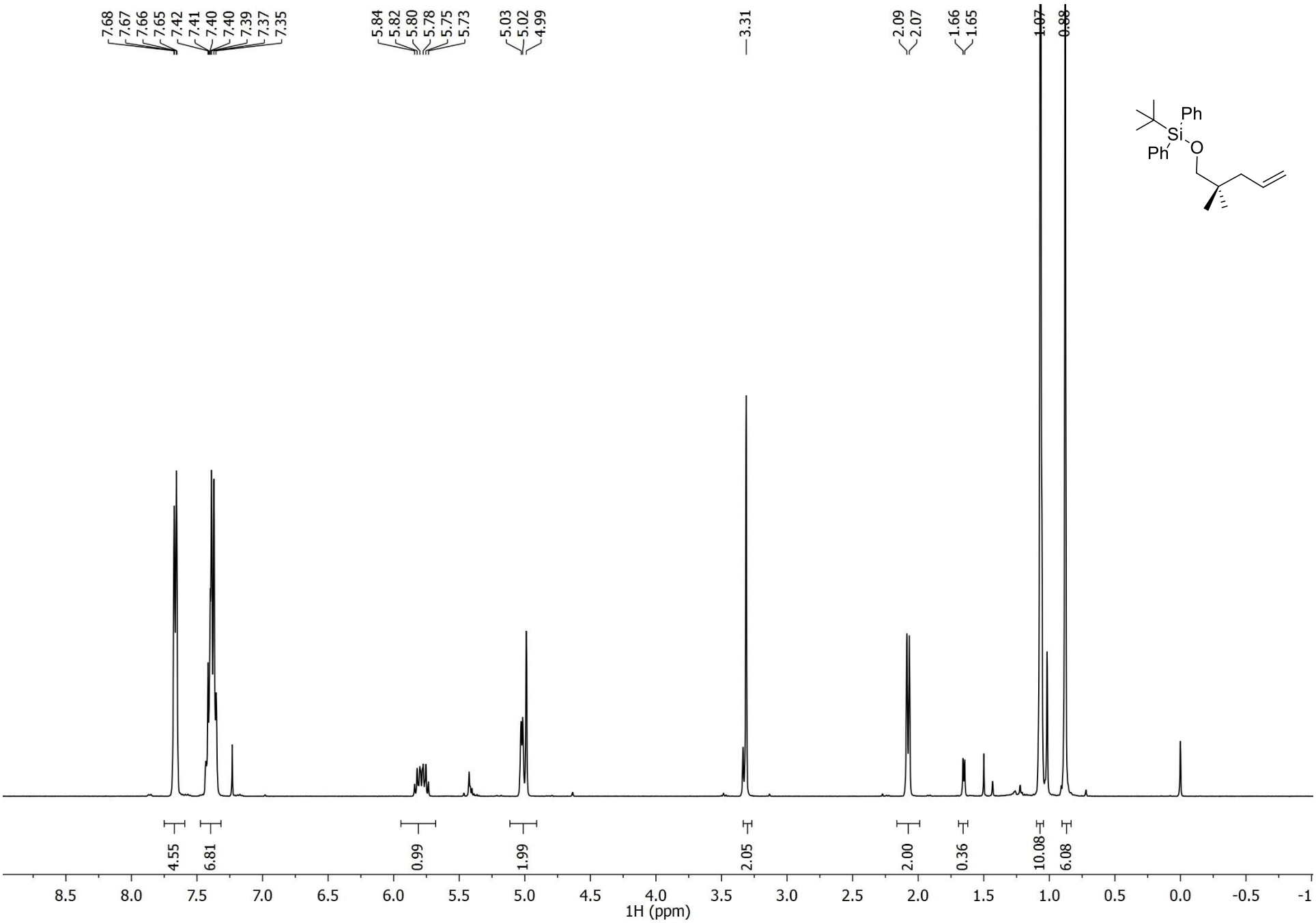

154.98
136.60
116.20
79.26
44.10
41.02
36.06
31.98
28.58
N
O
O
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C (ppm)


7.30
7.29
7.28
7.28
7.27
7.21
7.21
7.19
7.19
7.18
7.17
6.34
6.32
6.32
6.30
6.28
6.27
6.25
5.23
5.20
5.01
4.96
4.73
4.72
1.76
1.75
4.04
6.47
0.98
1.03
1.03
1.00
0.28
1H (ppm)


6.08
6.07
6.06
6.05
6.04
6.04
6.03
6.02
6.01
6.00
5.05
5.05
5.02
5.01
2.84
2.38
2.32
1.95
1.93
1.92
1.87
1.84
1.83
1.81
1.80
1.73
1.54
1.51
1.00
2.01
0.07
1.00
0.07
12.97
2.30
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1H (ppm)


143.16
113.54
48.04
38.92
38.26
32.80
32.16
28.28
28.07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C (ppm)


5.74
5.72
5.72
5.70
5.68
5.67
5.65
5.12
5.11
5.09
5.08
4.97
4.93
4.90
2.16
2.14
2.12
2.11
2.08
2.06
2.04
2.00
1.98
1.96
1.68
1.60
1.60
1.59
1.59
1.34
1.33
1.32
1.31
1.00
0.98
0.94
2.17
1.98
3.50
4.47
3.49
3.43
2.90
2.01
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1H (ppm)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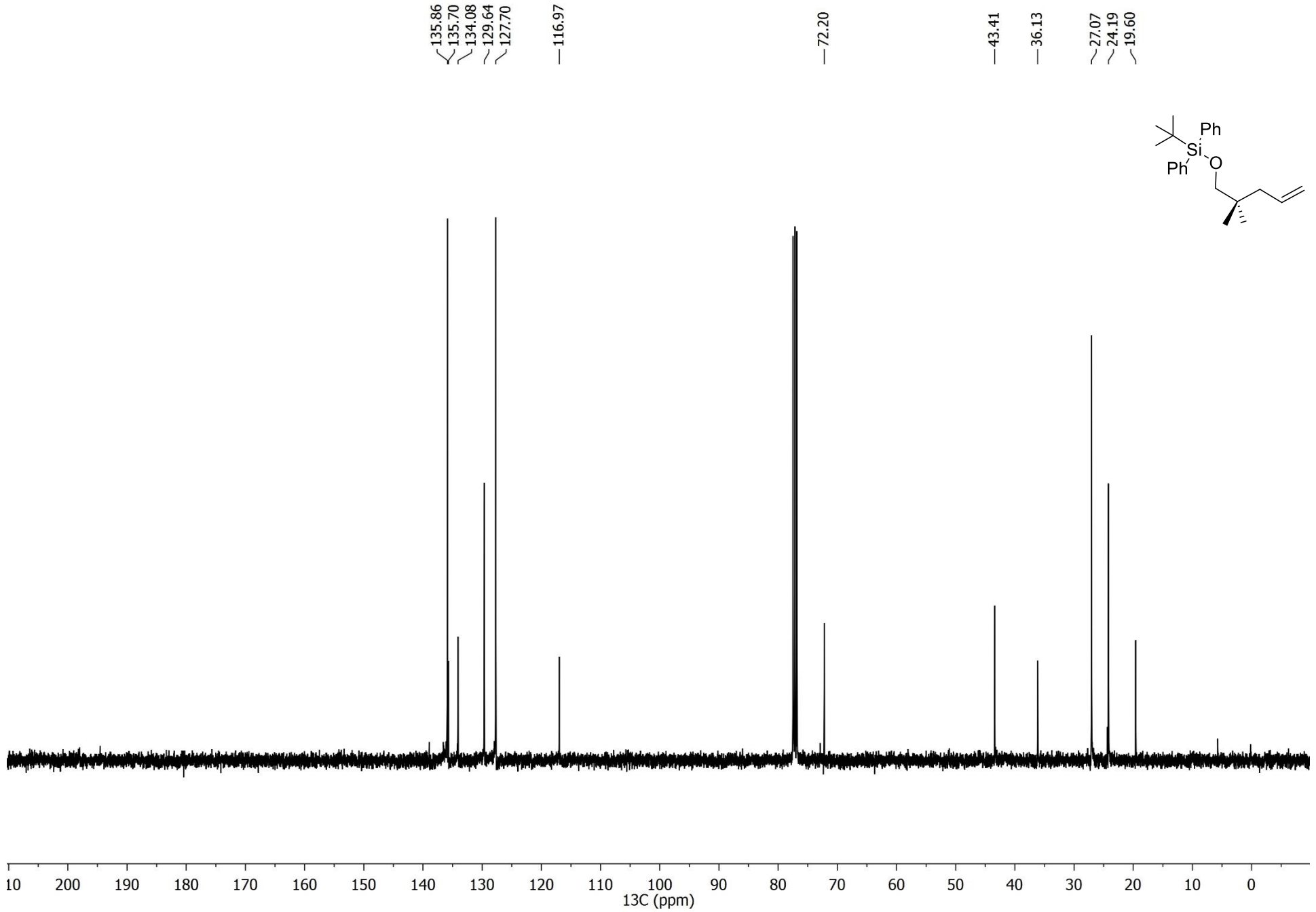
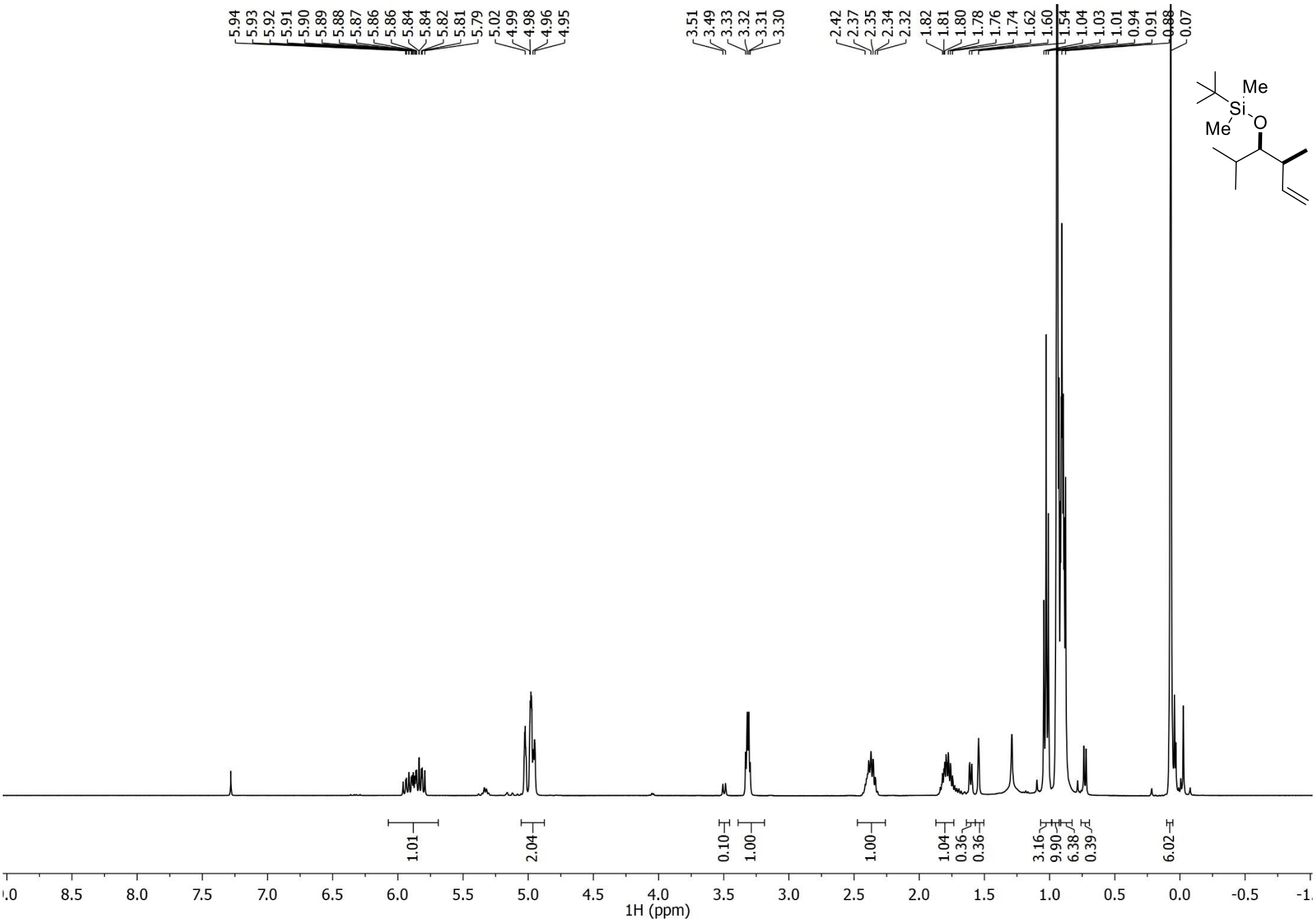
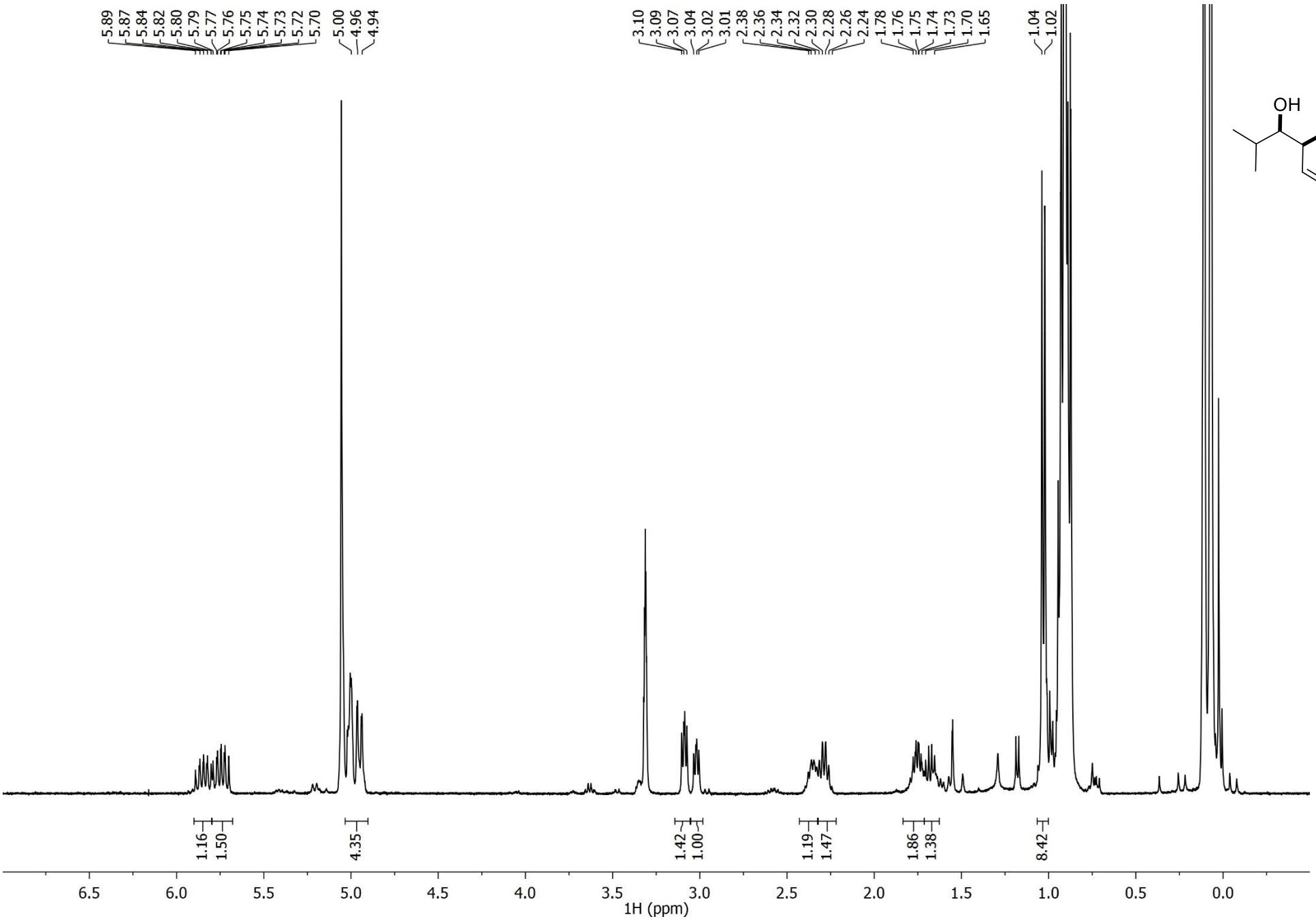
7.67
7.66
7.65
7.42
7.41
7.40
7.40
7.39
7.37
7.35
5.84
5.82
5.80
5.78
5.75
5.73
5.03
5.02
4.99
3.31
2.09
2.07
1.66
1.65
1.07
0.88
Ph
Si
Ph
O
4.55
6.81
0.99
1.99
2.05
2.00
0.36
10.08
6.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
1H (ppm)


135.86
135.70
134.08
129.64
127.70
116.97
72.20
43.41
36.13
27.07
24.19
19.60
Ph
Si
Ph
O
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C (ppm)


5.94
5.93
5.92
5.91
5.90
5.89
5.88
5.87
5.86
5.86
5.84
5.84
5.82
5.81
5.79
5.02
4.99
4.98
4.96
4.95
3.51
3.49
3.33
3.32
3.31
3.30
2.42
2.37
2.35
2.34
2.32
1.82
1.81
1.80
1.78
1.76
1.74
1.62
1.60
1.54
1.04
1.03
1.01
0.94
0.91
0.88
0.07
Me
Si
Me
O
1.01
2.04
0.10
1.00
1.00
1.04
0.36
0.36
3.16
9.90
6.38
0.39
6.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1H (ppm)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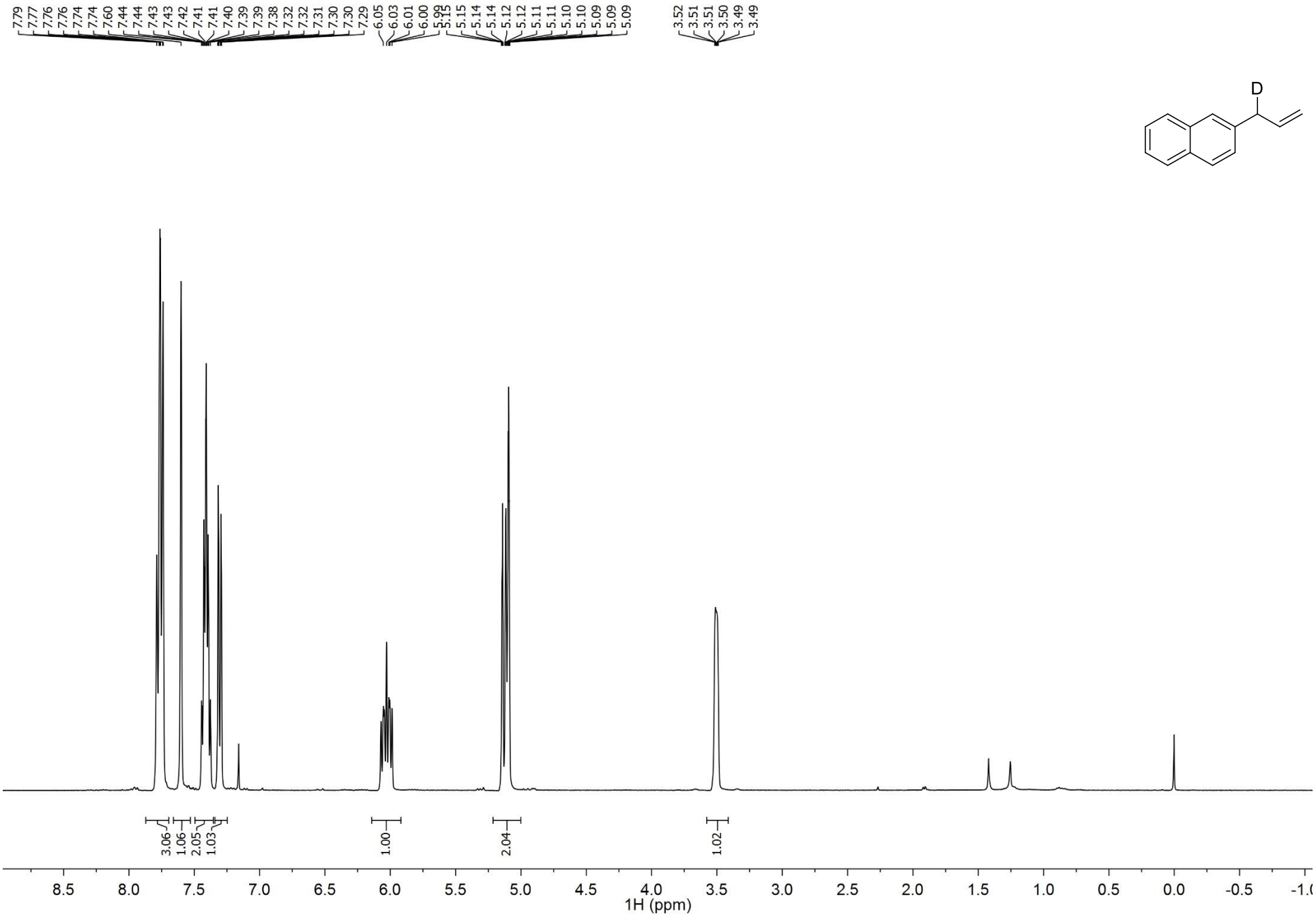
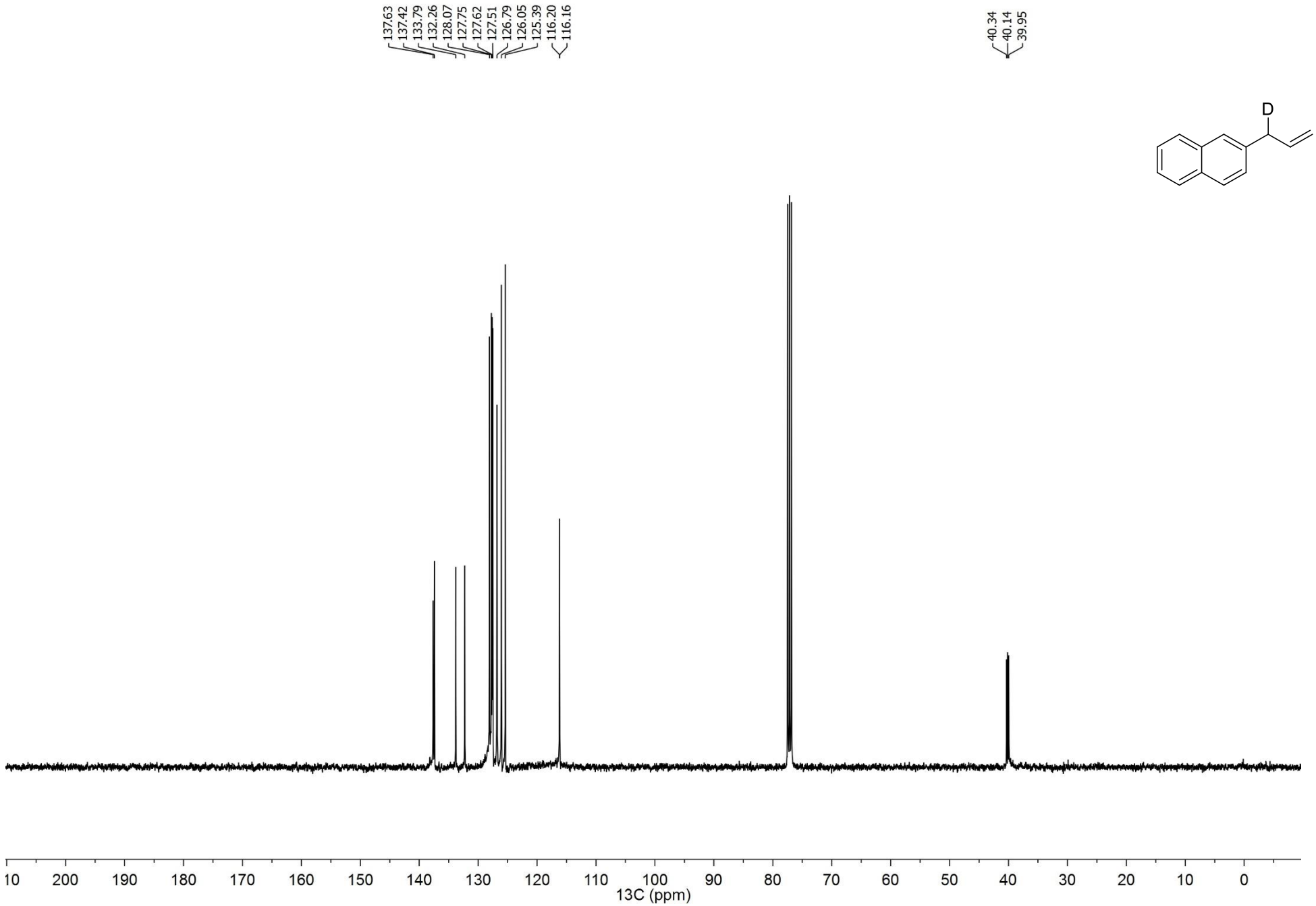
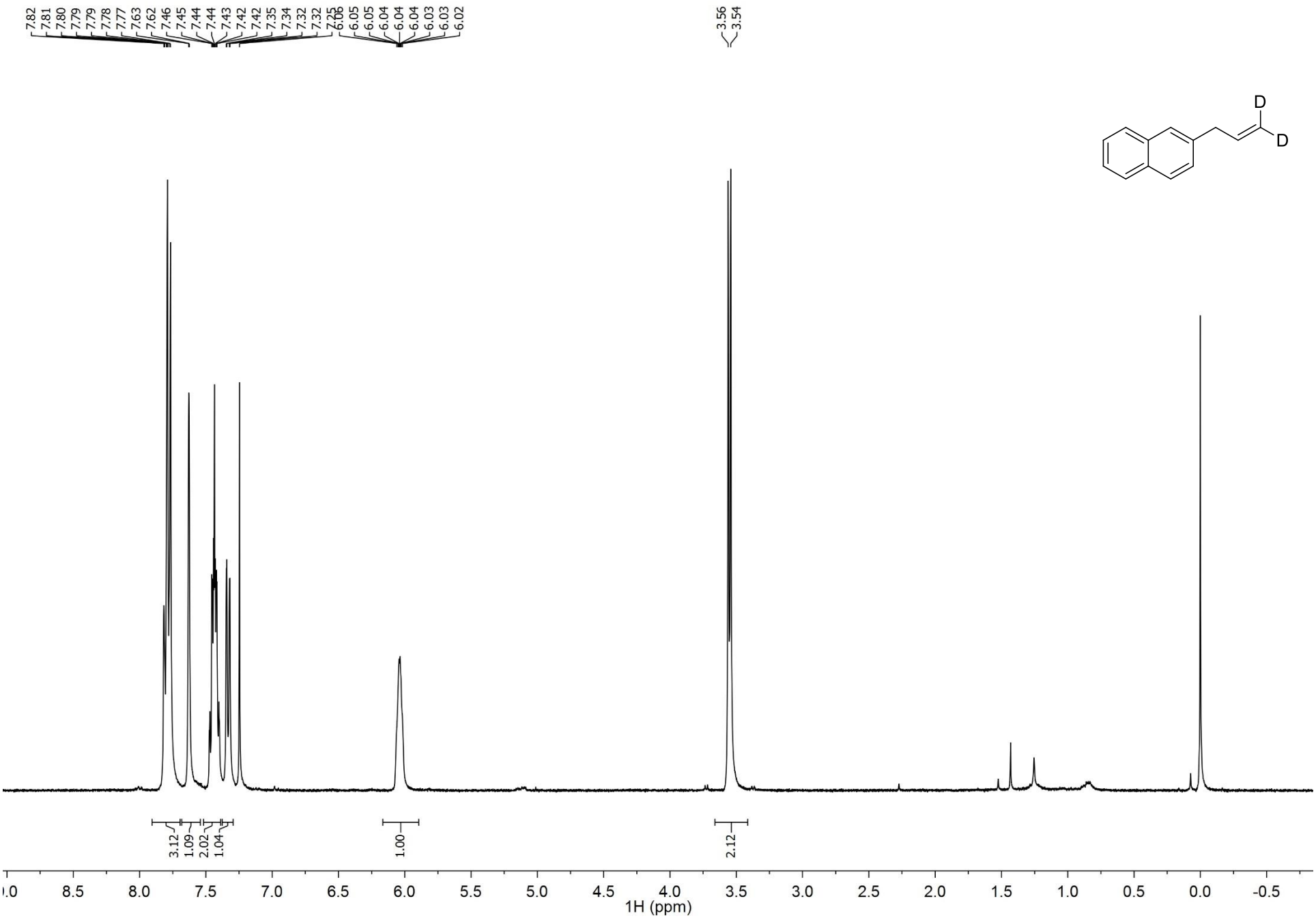
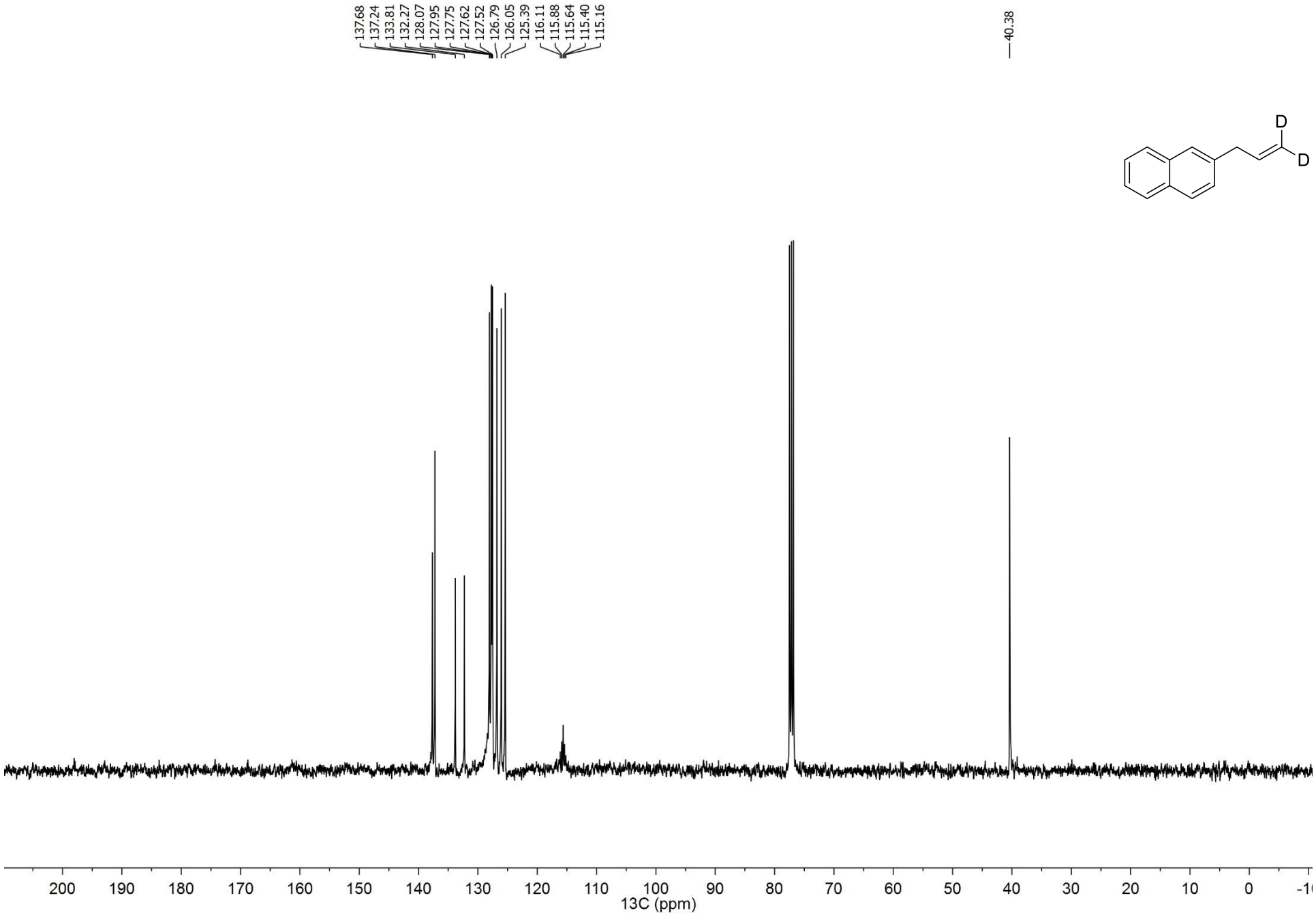
5.87
5.84
5.82
5.80
5.79
5.77
5.76
5.75
5.74
5.73
5.72
5.70
5.00
4.96
4.94
3.10
3.09
3.07
3.04
3.02
3.01
2.38
2.36
2.34
2.32
2.30
2.28
2.26
2.24
1.78
1.76
1.75
1.74
1.73
1.70
1.65
1.04
1.02
OH
1.16
1.50
4.35
1.42
1.00
1.19
1.47
1.86
1.38
8.42
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H (ppm)


7.79
7.77
7.76
7.76
7.74
7.74
7.60
7.44
7.44
7.43
7.43
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.32
7.32
7.31
7.30
7.30
7.29
6.05
6.03
6.01
6.00
5.15
5.15
5.14
5.14
5.12
5.12
5.11
5.11
5.10
5.10
5.09
5.09
5.09
3.52
3.51
3.51
3.50
3.49
3.49
D
3.06
1.06
2.05
1.03
1.00
2.04
1.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1H (ppm)

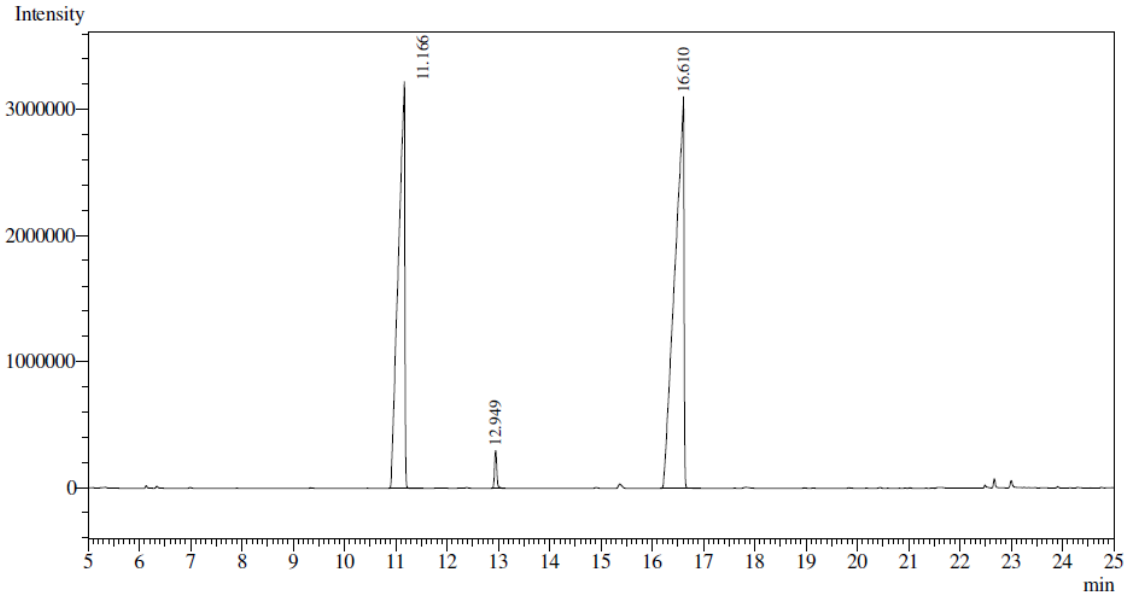

137.63
137.42
133.79
132.26
128.07
127.75
127.62
127.51
126.79
126.05
125.39
116.20
116.16
40.34
40.14
39.95
D
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
13C (ppm)


7.82
7.81
7.80
7.79
7.79
7.78
7.77
7.63
7.62
7.46
7.45
7.44
7.44
7.43
7.42
7.42
7.35
7.34
7.32
7.32
7.25
6.06
6.05
6.05
6.04
6.04
6.04
6.03
6.03
6.02
3.56
3.54
D
D
3.12
1.09
2.02
1.04
1.00
2.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1H (ppm)


137.68
137.24
133.81
132.27
128.07
127.95
127.75
127.62
127.52
126.79
126.05
125.39
116.11
115.88
115.64
115.40
115.16
40.38
D
D
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C (ppm)

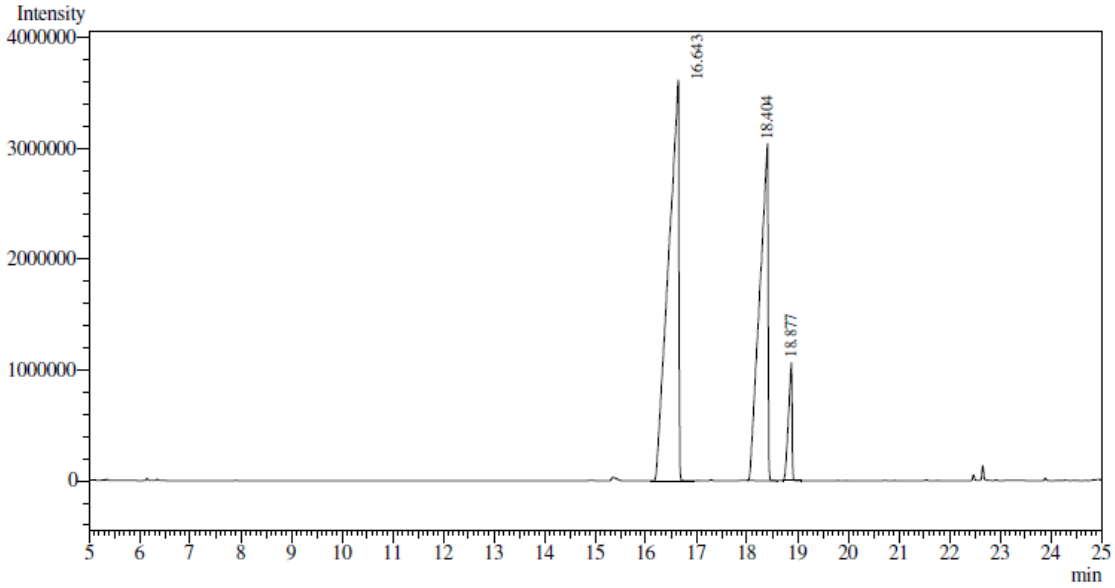
*Chromatograms for the determination of γ/α ratios in Table S3.*

**Table S3, Entry 3**



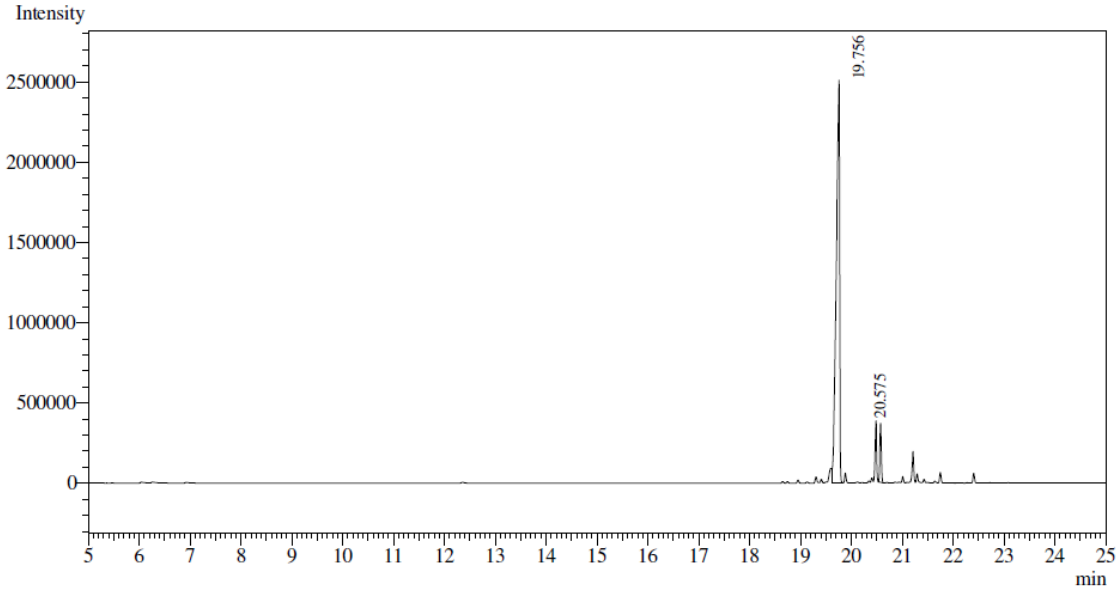

| Peak# | Ret.Time | Area | Height |
|---|---|---|---|
| 1 | 11.166 | 28320980 | 3215371 |
| 2 | 12.949 | 894558 | 298690 |
| 3 | 16.610 | 38369483 | 3078742 |

**Table S3, Entry 5**




| Peak# | Ret.Time | Area | Height |
|---|---|---|---|
| 1 | 16.643 | 50607484 | 3609758 |
| 2 | 18.404 | 34800244 | 3031960 |
| 3 | 18.877 | 5185580 | 1056176 |

**Table S3, Entry 11**




| Peak# | Ret.Time | Area | Height |
|---|---|---|---|
| 1 | 19.756 | 11352745 | 2491869 |
| 2 | 20.575 | 729368 | 364944 |