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Supporting Information

Phosphine-free cobalt pincer complex catalyzed *Z*-selective semi-hydrogenation of unbiased alkynes

Vinod G. Landge,[1] Jayaraman Pitchaimani,[2] Siba P. Midya,[1] Murugan Subaramanian,[1]Vedichi Madhu,[2,*] and Ekambaram Balaraman[1,*]

[1]Catalysis Division, Dr. HomiBhabha Road, CSIR-National Chemical Laboratory (CSIR-NCL), Pune - 411008, INDIA.

[2] Department of Chemistry, Karunya University, Coimbatore - 641 114, INDIA.

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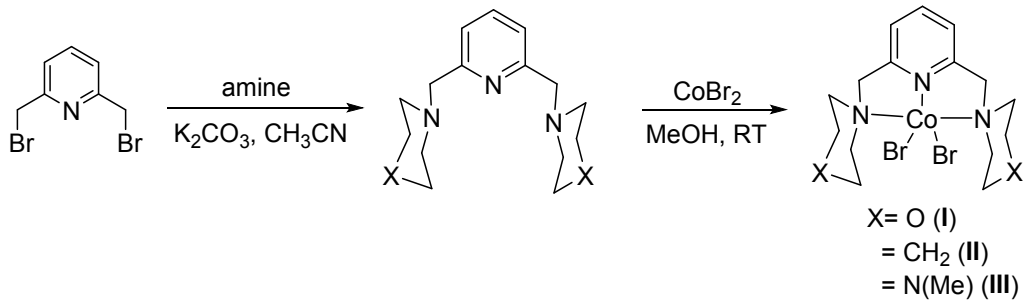
1. General Information

All catalytic experiments were carried out using standard Schlenk techniques. All solvents were reagent grade or better. Deuterated solvents were used as received. Toluene was refluxed over sodium/benzophenoneketyl and distilled under argon atmosphere and stored over sodium. Metal complexes and other chemicals used in catalysis reactions were used without additional purification. Most of the chemicals used in the catalytic reactions (alkynes, alkenes) were purified according to standard procedure.[S1] Thin layer chromatography (TLC) was performed using silica gel precoated glass plates, which were visualized with visualized with UV light at 254 nm or under iodine. Column chromatography was performed with SiO_2 (SilicycleSiliaflash F60 (230-400 mesh). ^{1}H NMR (400 or 500 MHz), ^{13}C{^{1}H} NMR (100 MHz) spectra were recorded on the NMR spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent [δ 7.26 for ^{1}H (chloroform-d), δ 77.2 for 13C{^{1}H} (chloroform-d). Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. GC analysis was carried out using a HP-5 column (30 m, 0.25 mm, 0.25μ). Mass spectra were obtained on a GCMS-QP 5000 instruments with ionization voltages of 70 eV. High resolution mass spectra (HRMS) were obtained on a High-resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique (magnetic sector-electric sector double focusing mass analyzer).

2. Experimental Section

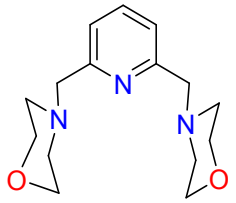
2.1 Synthesis of ligands and Cobalt-complexes



Scheme 1. Synthesis of cobalt complexes (**I-III**)

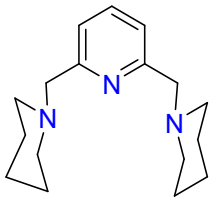
2.1.1 Synthesis of Ligands

a) 2,6-bis(morpholinomethyl)pyridine(NNN-L1)



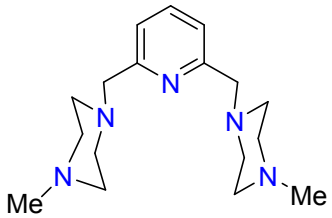
A solution of 2,6-bis(bromomethyl)pyridine (0.3 g, 1.13 mmol) in acetonitrile (30 mL) was added dropwise to solution of morpholine (0.197g, 2.26 mmol) and K_2CO_3 (0.468 g, 3.39 mmol) in CH_3CN (15 mL), the resulting reaction mixture was allowed to stir for 14 h at 80 °C, then cooled to room temperature. The solvent was evaporated under reduced pressure and the reaction mixture was extracted with chloroform. The organic layer was collected and dried over anhyd.Na_2SO_4, then evaporated in vacuum under the reduced pressure afforded **NNN-L1**. Yield (0.282 g, 90%). IR (KBr): ν = 2800 (m), 1575 (m), 1454 (m), 1298 (m), 1111 (s), 906 (m). ^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 7.65 - 7.52 (m, 1H), 7.31 (d, *J* = 7.6 Hz, 2H), 3.84 - 3.69 (m, 8H), 3.66 (s, 4H), 2.51 (s, 8H). ^{13}C NMR (126 MHz, CHLOROFORM-d) δ = 157.7, 136.7, 121.4, 77.3, 76.7, 66.9, 64.8, 53.7. HRMS (EI): *m/z* Calcd for $C_{15}H_{24}O_2N_3$: 278.1869; Found: 278.1863.

b) 2,6-bis(piperidin-1-ylmethyl)pyridine (NNN-L2)



A solution of 2,6-bis(bromomethyl)pyridine (152 mg, 0.55 mmol) in acetonitrile (5 mL) was added dropwise to solution of piperidine (1.1 mmol) and K_2CO_3 (331 mg, 2.42 mmol) in CH_3CN (10 mL), the resulting reaction mixture was allowed to stir for 14 h at 80 °C, then cooled to room temperature. The solvent was evaporated under reduced pressure and the reaction mixture was extracted with chloroform. The organic layer was collected and dried over anhyd. Na_2SO_4, then evaporated in vacuum under the reduced pressure afforded **NNN-L2**.Yield (131mg, 88%).^{1}H NMR (500 MHz,CHLOROFORM-d) δ = 7.70 - 7.54 (m, 1 H), 7.30 (d, *J* = 7.6 Hz, 2 H), 3.62 (s, 4 H), 2.44 (br. s., 8 H), 1.65 - 1.55 (m, 8 H), 1.50 - 1.41 (m, 4 H). ^{13}C NMR (126 MHz,CHLOROFORM-d) δ = 158.4, 136.4, 121.0, 77.3, 76.7, 65.3, 54.7, 25.9, 24.2. HRMS (EI): *m/z* Calcd for $C_{17}H_{28}N_3$: 274.2283; Found: 274.2278.

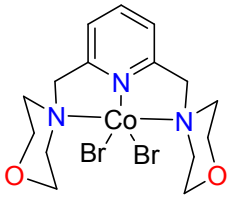
c) 2,6-bis((4-methylpiperazin-1-yl)methyl)pyridine (NNN-L3)



A solution of 2,6-bis(bromomethyl)pyridine (0.8 g, 3.0 mmol) in acetonitrile (45 mL) was added dropwise to solution of 1-methylpiperazine (0.669 g, 6.0 mmol) and K_2CO_3 (1.249 g, 9.0 mmol) in CH_3CN (20 mL), the resulting reaction mixture was allowed to stir for 14 h at 80 °C, then cooled to room temperature.The solvent was evaporated under reduced pressure and the reaction mixture was extracted with chloroform. The organic layer was collected and dried over anhyd.Na_2SO_4, then evaporated in vacuum under the reduced pressure afforded **NNN-L3**. Yield (0.82 g; 89%). IR (KBr): ν = 2945 (s), 2520 (m), 2042 (m), 1452 (s), 1029 (s), 651 (m). ^{1}H NMR

(500 MHz, CHLOROFORM-d) δ = 7.59 (s, 1H), 7.28 (s, 2H), 3.66 (s, 4H), 2.54 (s, 8H), 2.46 (s, 8H), 2.28 (s, 6 H). ^{13}C NMR (126 MHz, CHLOROFORM-d) δ = 158.0, 136.6, 121.3, 77.3, 76.7, 64.4, 55.1, 53.2, 46.1. HRMS (EI): *m/z* Calcd for $C_{17}H_{30}N_5$: 304.2501; Found: 304.2496.

2.1.2 Synthesis of Cobalt-complexes



I

Anhydrous $CoBr_2$ (200 mg, 1 equiv.) in methanol (5 mL) was added dropwise to solution of **NNN-L1** (1 equiv) in MeOH (2 mL) with stirring. The resulting reaction mixture was allowed to stir for 3 h at room temperature. The resulting solution was evaporated under vacuum afforded the blue color solid; the solid was washed with diethyl ether and dried at air. Yield (136 mg, 82%); IR (KBr): 2962, 2844, 2360, 1611, 1575, 1454, 1441, 1358, 1287, 1112, 1001, 871, 815, 787, 636 cm^{-1}. HRMS (EI): *m/z* Calcd for $C_{15}H_{24}O_2N_3Br_2Co$: 494.9567; Found: 494.9562. The crystal suitable for a single-crystal X-ray diffraction was obtained from MeOH : diethyl ether (by diffusion method) at room temperature after one day.

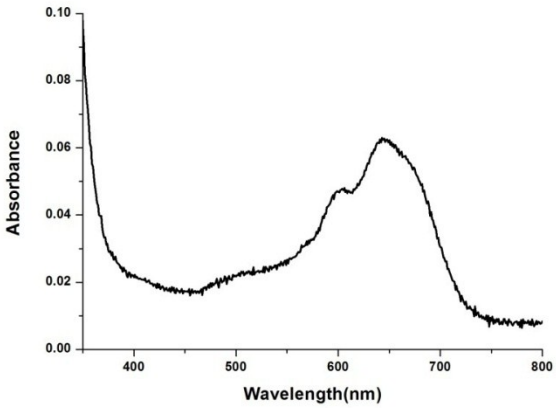
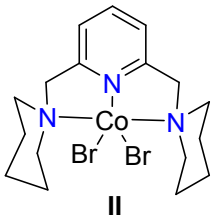


Figure S1. UV spectra of **I**.



II

Anhydrous $CoBr_2$ (200 mg, 1 equiv.) in methanol (5 mL) was added dropwise to solution of **NNN-L2** (1 equiv) in MeOH (2 mL) with stirring. The resulting reaction mixture was allowed to stir for 3 h at room temperature. The resulting solution was evaporated under vacuum afforded the blue color solid; the solid was washed with diethyl ether and dried at air. Yield (151 mg, 91%). IR (KBr): 2934, 2853, 2703, 2360, 1610, 1455, 1356, 1263, 1165, 1084, 985, 858, 769, 619cm^{-1}. HRMS (EI): *m/z* Calcd for $C_{17}H_{28}N_3Br_2Co$: 403.9982; Found: 490.9976.

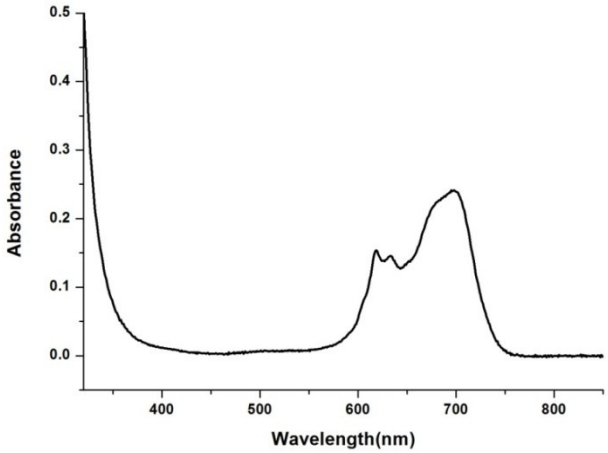
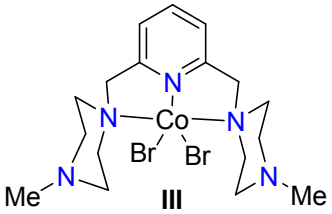


Figure S2. UV spectra of **II**.



III

Anhydrous $CoBr_2$ (200 mg, 1 equiv.) in methanol (5 mL) was added dropwise to solution of **NNN-L3** (1 equiv) in MeOH (2 mL) with stirring. The resulting reaction mixture was allowed to

stir for 3 h at room temperature. The resulting solution was evaporated under vacuum afforded the blue color solid; the solid was washed with diethyl ether and dried at air. Yield (103 mg, 62%). IR (KBr): 2962, 2844, 2360, 1611, 1575, 1454, 1441, 1358, 1287, 1112, 1001, 871, 815, 787, 636 cm^{-1}. HRMS (EI): *m/z* Calcd for $C_{17}H_{30}N_5Br_2Co$: 521.0194; Found: 521.0200.

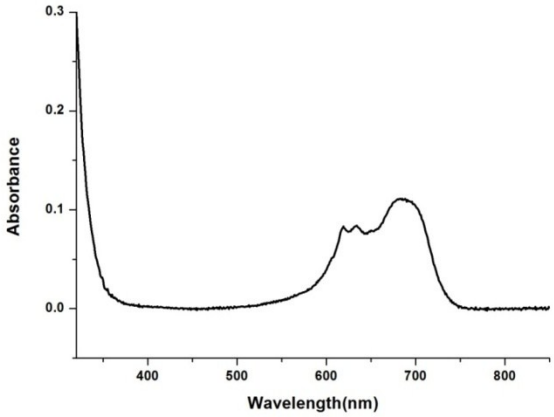
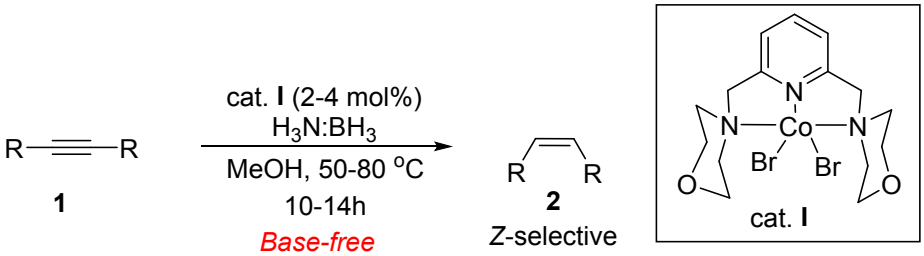


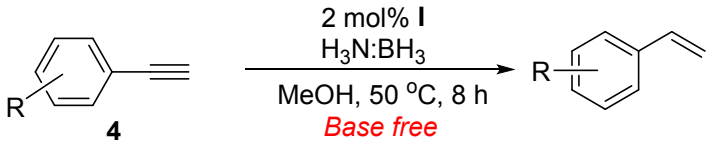
Figure S3. UV spectra of **III**.

2.2 General Procedure for *Z* selective semi-hydrogenation of internal alkynes



To an oven-dried 10 mL screw-capped vial, alkyne **1** (0.5mmol), ammonia-borane (0.6 mmol), Co-complex **I** (2-4 mol%) and methanol (1 mL) were added under a gentle stream of argon. The mixture was stirred for 10-14 h at 50-80 °C (bath temperature) followed by cooling to room temperature. The mixture was filtered through a celite pad with several washings (3 x 3 mL dichloromethane) and concentrated *in vacuo*. The yield of alkene was determined by GC. The crude ^{1}H NMR has been recorded and the compound data was in good accordance with the literature.

2.3 General Procedure for semi-hydrogenation of terminal alkynes



To an oven-dried 10 mL screw-capped vial, terminal alkyne **4** (0.5mmol), ammonia-borane (0.6mmol), Co-complex **I** (2 mol%) and methanol (1 mL) were added under a gentle stream of argon. The mixture was stirred for 8 h at 50 °C (bath temperature) followed by cooling to room temperature. The mixture was filtered through a celite pad with several washings (3 x 3 mL dichloromethane) and concentrated *in vacuo*. The yield of alkene was determined by GC.

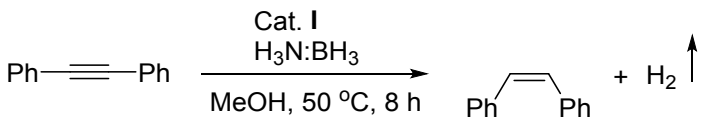
2.4 General Procedure for hydrogenation of terminal alkenes

To an oven-dried 10 mL screw-capped vial, alkene **5** (0.5mmol), ammonia-borane (0.6 mmol), catalyst **I** (4 mol%) and methanol (1 mL) were added under a gentle stream of argon. The mixture was stirred for 14 h at 80 °C (bath temperature) followed by cooling to room temperature. The mixture was filtered through a celite pad with several washings (3 x 3 mL dichloromethane) and concentrated *in vacuo*. The yield of alkene was determined by GC.

3. Mechanistic Investigation

3.1 H_2 detection

To an oven-dried 10 mL screw-capped vial, alkyne **1a** (0.1 mmol), ammonia-borane (0.15 mmol), Co complex **I** (4 mol%) and methanol (1 mL) were added under a gentle stream of argon. The mixture was stirred for 8 h at 50 °C (bath temperature) followed by cooling to room temperature.



Area % Report

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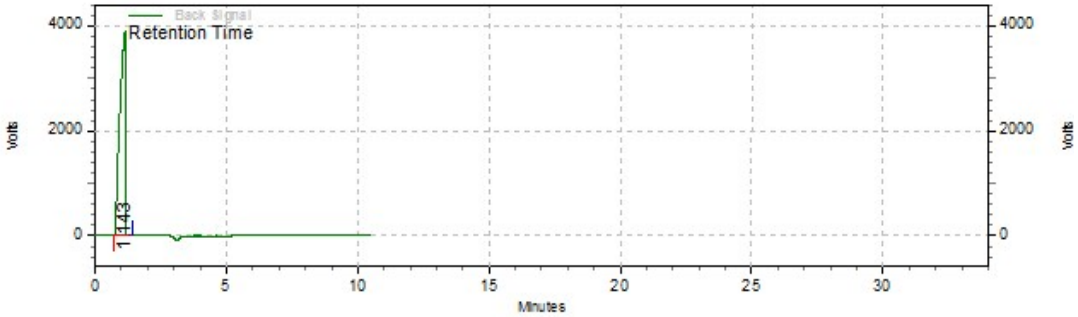
Printed: 8/12/2016 10:50:14 AM



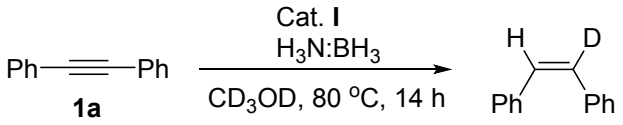
Back Signal
Results

Retention Time	Area	Area %	Height	Height %
1.143	435946301	100.00	30011049	100.00
Totals	435946301	100.00	30011049	100.00

Figure S4.GC of gaseous sample.

3.2 Labeling experiment

To an oven-dried 10 mL screw-capped vial, alkyne **1a** (0.1 mmol), ammonia-borane (0.15 mmol), **I** (4 mol%) and CD_3OD (2 mL) were added under a gentle stream of argon. The mixture was stirred for 14 h at 80 °C (bath temperature) followed by cooling to room temperature. The mixture was filtered through a celite pad with several washings (3 x 3 mL dichloromethane) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (eluent: pet ether) to afford the desired product **2a** (90% yield).



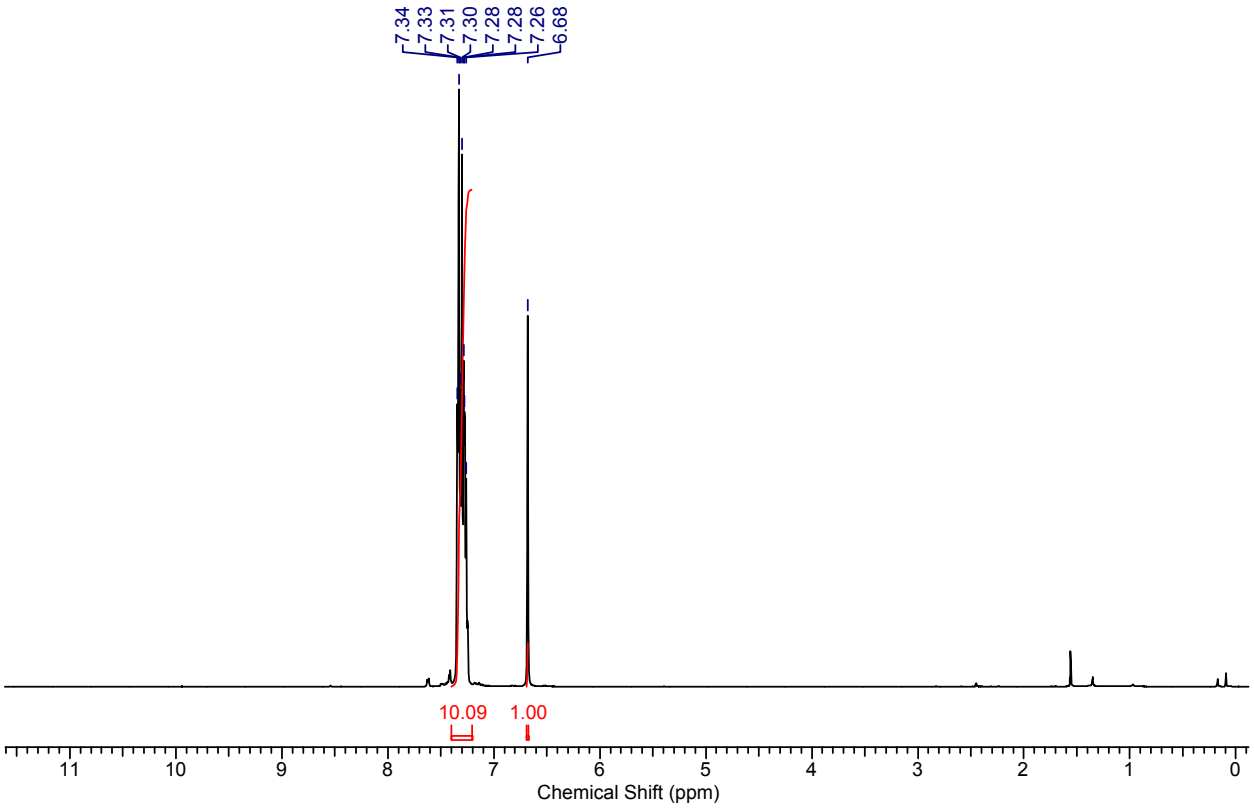
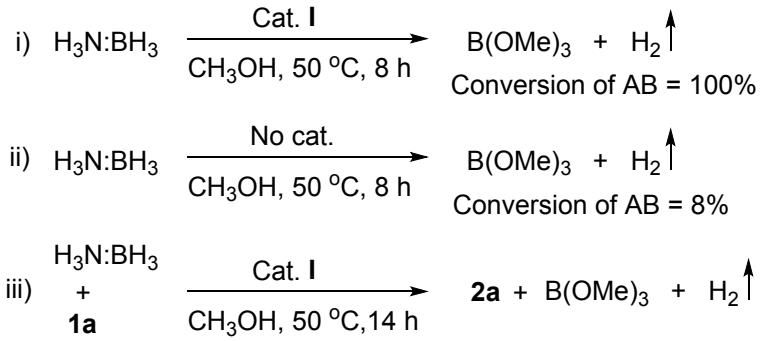


Figure S5.1H NMR of **[D]-2a**.

3.3 Determination of the dehydrogenation product of ammonia-borane



3.3.1 Dehydrogenation of ammonia-borane

To an oven-dried J Young NMR tube, ammonia-borane(0.15 mmol), Co-complex **I** (2 mol%), methanol (0.2 *m*L) in D_8-THF (0.3 *m*L) were added under a gentle stream of argon. The mixture was stirred for 8 h at 50 °C (bath temperature) followed by cooling to room temperature. Then submitted for ^{11}B NMR which show that complete conversion of AB into $B(OMe)_3$ (also confirmed by GC-MC) and the formation of dihydrogen was detected on GC.

The above experiment was carried out under identical conditions in the absence of **I** and only 8% of $B(OMe)_3$ was observed.

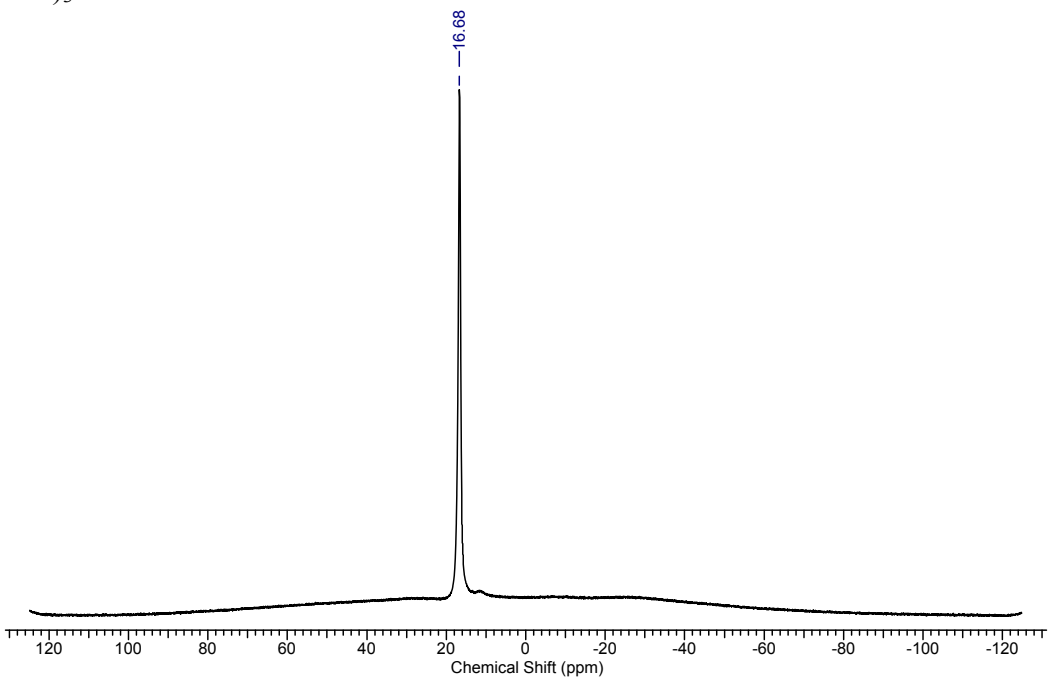


Figure S6. ^{11}B NMR of Reaction mixture.

3.3.2 Dehydrogenation of ammonia-boranein presence (AB) of 1a

To an oven-dried J Young NMR tube, alkyne **1a** (0.1 mmol), ammonia-borane (0.15 mmol), Co-complex **I** (4 mol%), methanol (0.2 mL) in D_8-THF (0.3 mL) were added under a gentle stream of argon. The mixture was stirred for 8 h at 50 °C (bath temperature) followed by cooling to room temperature. Then submitted for ^{11}B NMR which show that complete conversion of AB into $B(OMe)_3$ (also confirmed by GC-MC).

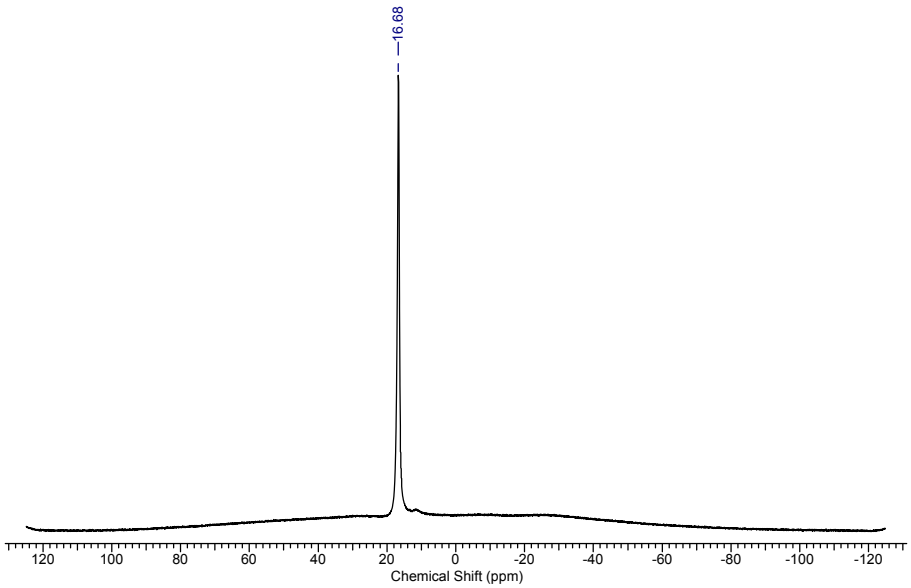


Figure S7. ^{11}B NMR of Reaction mixture.

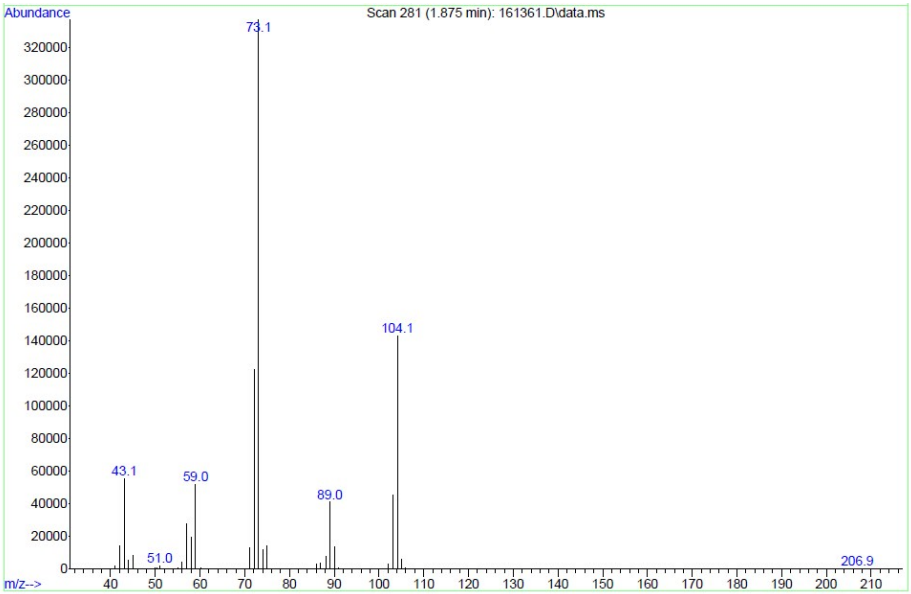
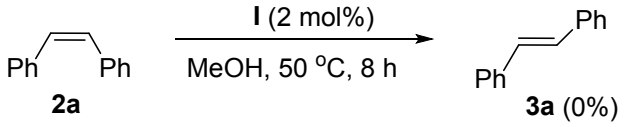


Figure S8. GC-MC of Reaction mixture.

3.4 Isomerisation experiment

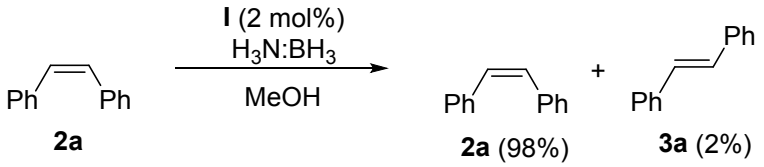


3.4.1 In absence of ammonia-borane(AB)

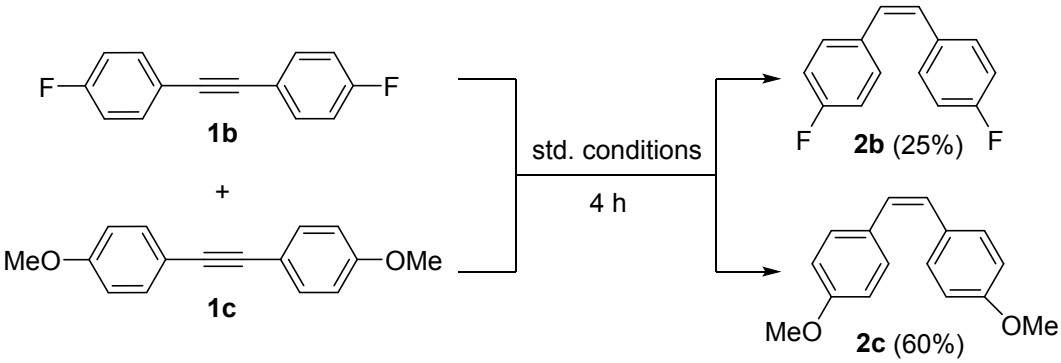
To an oven-dried 10 mL screw-capped vial, alkyne **1a** (0.1 mmol), Co-complex **I** (2 mol%) and methanol (1 mL) were added under a gentle stream of argon. The mixture was stirred for 8 h at 50 °C (bath temperature) followed by cooling to room temperature. The mixture was filtered through a celite pad with several washings (3 x 3 mL dichloromethane) and concentrated *in vacuo*.

3.4.2 In presence of ammonia-borane(AB)

To an oven-dried 10 mL screw-capped vial, alkyne **1a** (0.1 mmol), ammonia-borane (0.15 mmol), Co-complex **I** (2 mol%) and methanol (1 mL) were added under a gentle stream of argon. The mixture was stirred for 8 h at 50 °C (bath temperature) followed by cooling to room temperature. The mixture was filtered through a celite pad with several washings (3 x 3 mL dichloromethane) and concentrated *in vacuo*. The yield of alkene was determined by GC.

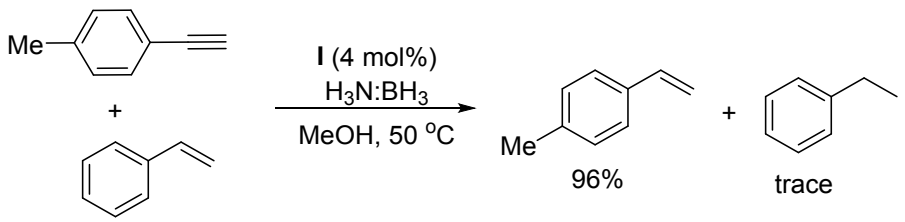


3.5 Intermolecular competitive experiment



To an oven-dried 10 mL screw-capped vial, **1b** and **1c** (each 0.5mmol), ammonia-borane (0.6 mmol), Co-complex **I** (4 mol%) and methanol (1 mL) were added under a gentle stream of argon. The mixture was stirred for 4 h at 80 °C (bath temperature) followed by cooling to room temperature. The mixture was filtered through a celite pad with several washings (3 x 3 mL dichloromethane) and concentrated *in vacuo*. The yields of alkenes (**2b** and **2c**) were determined by GC with diphenyl as the internal standard.

3.6 Competitive experiment (Alkyne *vs* Alkene)



To an oven-dried 10 mL screw-capped vial, all eleven parallel reaction kept using 4-methyl phenyl acetylene (0.1 mmol), styrene (0.1 mmol), ammonia-borane **2** (0.2 mmol), **I** (4 mol%), n-decane (0.1 mmol), and MeOH (2 mL) were added under a gentle stream of argon. The mixture was stirred at 50 °C (bath temperature). At regular time intervals, the reaction mixture was analyzed on GC.

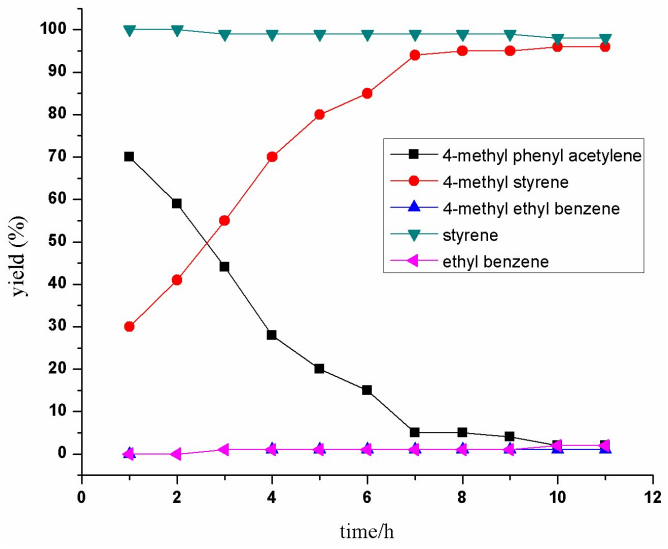
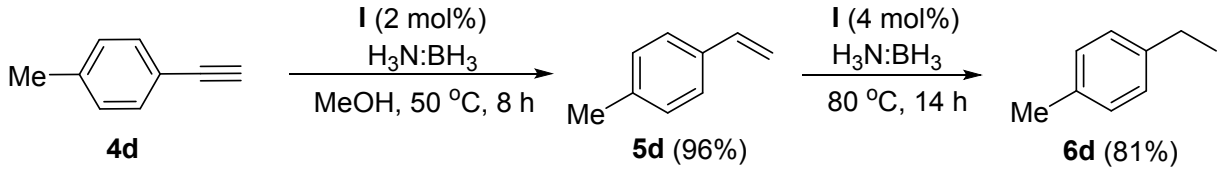


Figure S9. Kinetic profile.

3.7 Temperature-switch Chemoselectivity

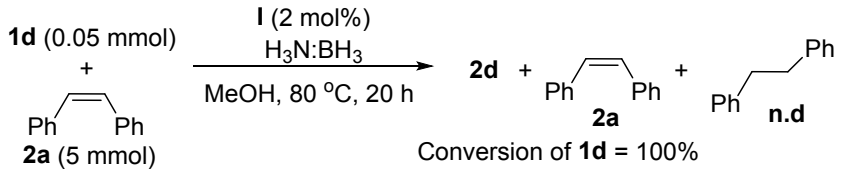


To an oven-dried 10 mL screw-capped vial, 4-methyl phenyl acetylene (0.1 mmol), ammonia-borane **2** (0.2 mmol), **I** (4mol%), n-decane (0.1 mmol), and MeOH (2 mL) were added under a gentle stream of argon. The mixture was stirred at 50 °C (bath temperature) for about 8 h and the reaction mixture analyzed on GC (**5d** is 96%). To that, an additional catalyst **I** (4 mol%) and ammonia-borane (0.2 mmol) was added and continued the heating at 80 °C for 14 h.

3.7 Homogenous test

To an oven-dried 10 mL screw-capped vial, **1a** (0.5mmol), ammonia-borane (0.6mmol), **I** (4 mol%), 10 equiv. of mercury and methanol (1 mL) were added under a gentle stream of argon. The mixture was stirred for 12 h at 50 °C (bath temperature) followed by cooling to room temperature. The mixture was filtered through a celite pad with several washings (3 x 3 mL dichloromethane) and concentrated *in vacuo*. The yield of alkene was determined by GC.

3.8 Purification of alkenes from alkyne impurities

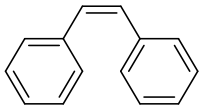


To an oven-dried 10 mL screw-capped vial, **1d** (0.05 mmol), **2a** (5 mmol), ammonia-borane (5.1 mmol), **I** (2 mol%), and methanol (2 mL) were added under a gentle stream of argon. The mixture was stirred for 20 h at 80 °C (bath temperature) followed by cooling to room temperature. The mixture was filtered through a celite pad with several washings (3 x 3 mL

dichloromethane) and concentrated *in vacuo*. The conversion alkyne and the yield of alkene were determined by GC.

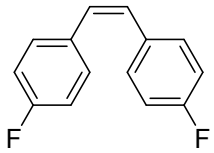
4. Characterization Data

(*Z*)-1,2-diphenylethene (2a)[S4]



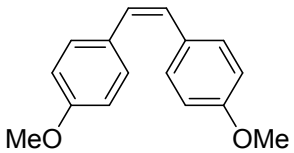
^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.30 (d, *J* = 9.2 Hz, 10 H), 6.67 (s, 2 H).

(*Z*)-1,2-bis(4-fluorophenyl)ethane (2b)



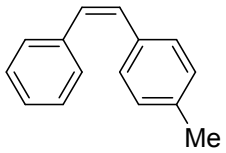
^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 7.24 - 7.15 (m, 4 H), 6.93 (t, *J* = 8.8 Hz, 4 H), 6.55 (s, 2 H).^{13}C NMR (126 MHz, $CDCl_3$) δ = 162.8, 160.9, 133.0, 133.0, 130.5, 130.4, 129.1, 115.3, 115.2.

(*Z*)-1,2-bis(4-methoxyphenyl)ethane (2c)[S5]



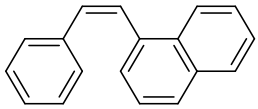
^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 7.23 (d, *J* = 8.8 Hz, 4 H), 6.80 (d, *J* = 8.8 Hz, 4 H), 6.47 (s, 2 H), 3.81 (s, 7 H).^{13}C NMR (126MHz, CHLOROFORM-d) δ = 158.5, 130.0, 129.3, 128.4, 113.7, 113.6, 55.1

(*Z*)-1-methyl-4-styrylbenzene (2d)[S4]



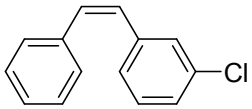
^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.40 - 7.35 (m, 2 H), 7.35 - 7.21 (m, 5 H), 7.12 (d, *J* = 7.9 Hz, 2 H), 6.65 (s, 2 H), 2.40 (s, 3 H).^{13}C NMR (101MHz, CHLOROFORM-d) δ = 137.5, 136.8, 134.3, 130.2, 129.5, 128.9, 128.8, 128.8, 128.2, 126.9, 21.2.

(*Z*)-1-styrylnaphthalene (2e)[S6]



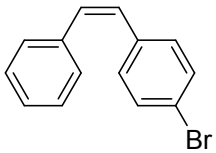
^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 8.14 - 8.03 (m, 1 H), 7.94 - 7.88 (m, 1 H), 7.79 (d, *J* = 7.3 Hz, 1 H), 7.57 - 7.48 (m, 3 H), 7.45 - 7.32 (m, 3 H), 7.11 - 7.05 (m, 5 H), 6.86 (d, *J* = 12.2 Hz, 1 H).

(*Z*)-1-chloro-3-styrylbenzene (2f)[S4]



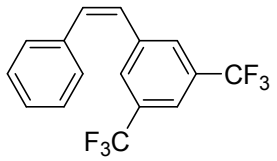
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.32 - 7.23 (m, 6 H), 7.23 - 7.13 (m, 3 H), 6.70 (d, *J* = 12.2 Hz, 1 H), 6.57 (d, *J* = 12.2 Hz, 1 H).

(*Z*)-1-bromo-4-styrylbenzene (2g)[S4]



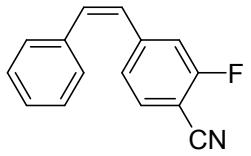
^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.38 (d, *J* = 8.5 Hz, 2 H), 7.29 (br. s., 5 H), 7.15 (d, *J* = 8.5 Hz, 2 H), 6.68 (d, *J* = 12.2 Hz, 1 H), 6.55 (d, *J* = 12.2 Hz, 1 H).

(*Z*)-1-styryl-3,5-bis(trifluoromethyl)benzene (2h)



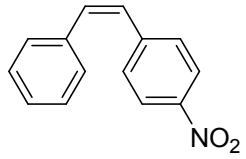
^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.75 - 7.59 (m, 3 H), 7.58 - 7.51 (m, 1 H), 7.32 - 7.09 (m, 5 H), 6.83 (d, *J* = 12.1 Hz, 1 H), 6.57 (d, *J* = 12.1 Hz, 1 H).

(*Z*)-2-fluoro-4-styrylbenzonitrile (2j)



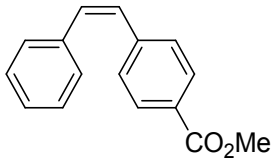
^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 7.30 (br. s., 4 H), 7.22 (br. s., 2 H), 7.17 - 7.01 (m, 3 H), 6.85 (d, *J* = 12.2 Hz, 1 H), 6.55 (d, *J* = 12.2 Hz, 1 H).

(*Z*)-1-nitro-4-styrylbenzene (2k)



^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 8.06 (d, *J* = 8.8 Hz, 1 H), 7.58 - 7.48 (m, 3 H), 7.32 - 7.12 (m, 5 H), 6.81 (d, *J* = 12.3 Hz, 1 H), 6.60 (d, *J* = 12.3 Hz, 1 H).

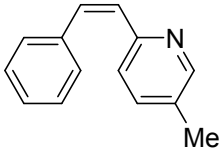
(*Z*)-methyl 4-styrylbenzoate (2l)[S4]



^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 7.92 (d, *J* = 8.4 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.28 - 7.21 (m, 5 H), 6.74 (d, *J* = 12.2 Hz, 1 H), 6.64 (d, *J* = 12.6 Hz, 1 H), 3.95 - 3.87 (m, 3 H).

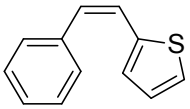
^{13}C NMR (126 MHz, CHLOROFORM-d) δ = 166.9, 142.1, 136.6, 132.2, 129.5, 129.2, 128.8, 128.3, 127.5, 52.0. HRMS (EI): *m/z* Calcd for $C_{16}H_{15}O_2$: 239.1072; Found: 239.1067.

(*Z*)-5-methyl-2-styrylpyridine (2m)



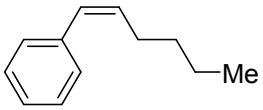
^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 8.46 - 8.39 (m, 1 H), 7.29 - 7.23 (m, 6 H), 7.09 (d, *J* = 8.0 Hz, 1 H), 6.81 (d, *J* = 12.2 Hz, 1 H), 6.69 (d, *J* = 12.2 Hz, 1 H).

(*Z*)-2-styrylthiophene (2n)[S4]



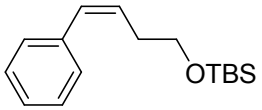
^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 7.42 - 7.35 (m, 5 H), 7.12 (d, *J* = 5.0 Hz, 1 H), 7.00 (d, *J* = 3.4 Hz, 1 H), 6.92 (dd, *J* = 3.8, 5.0 Hz, 1 H), 6.73 (d, *J* = 11.8 Hz, 1 H), 6.61 (d, *J* = 12.2 Hz, 1 H).

(*Z*)-hex-1-enylbenzene (2o)[S4]



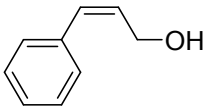
^{1}H NMR (500 MHz ,CHLOROFORM-d) δ = 7.40 - 7.31 (m, 5 H), 7.29 - 7.22 (m, 1 H), 6.46 (d, *J* = 11.8 Hz, 1 H), 5.72 (td, *J* = 7.4, 11.5 Hz, 1 H), 2.39 (dd, *J* = 1.3, 7.4 Hz, 2 H), 1.52 - 1.46 (m, 2 H), 1.45 - 1.38 (m, 2 H), 0.95 (t, *J* = 7.2 Hz, 3 H).

(*Z*)-tert-butyldimethyl(4-phenylbut-3-enyloxy)silane (2p)



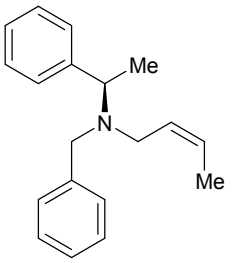
^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 7.43 - 7.30 (m, 4 H), 7.24 (dt, *J* = 2.9, 5.8 Hz, 1 H), 6.53 (d, *J* = 11.8 Hz, 1 H), 5.73 (td, *J* = 7.4, 11.5 Hz, 1 H), 3.74 (t, *J* = 6.7 Hz, 2 H), 2.64 - 2.54 (m, 2 H), 0.95 - 0.90 (m, 10 H), 0.19 - 0.03 (m, 7 H). ^{13}C NMR (126 MHz, CHLOROFORM-d) δ = 137.5, 130.4, 129.0, 128.7, 128.1, 126.6, 62.9, 32.2, 25.9, 18.4. HRMS (EI): *m/z*Calcd for $C_{16}H_{17}OSi$: 263.1831; Found: 263.1826.

(*Z*)-3-phenylprop-2-en-1-ol (2q)[S4]



^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.39 - 7.10 (m, 6 H), 6.54 (d, *J* = 11.7 Hz, 1 H), 5.85 (td, *J* = 6.4, 11.8 Hz, 1 H), 4.41 (d, *J* = 6.2 Hz, 3 H), 2.22 (br. s., 1 H)**.**

(*R*,*Z*)-*N*-benzyl-*N*-(1-phenylethyl)but-2-en-1-amine (2u)



^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 7.49 (d, *J* = 7.2 Hz, 2 H), 7.45 - 7.22 (m, 8 H), 5.63 (br. s., 2 H), 4.01 (d, *J* = 6.9 Hz, 1 H), 3.66 (d, *J* = 14.1 Hz, 1 H), 3.56 (d, *J* = 13.7 Hz, 1 H), 3.26 (br. s., 1 H), 3.05 (d, *J* = 13.4 Hz, 1 H), 1.75 - 1.52 (m, 3 H), 1.47 (d, *J* = 6.9 Hz, 3 H).^{13}C NMR (126 MHz, CHLOROFORM-d) δ = 144.0, 140.8, 128.6, 128.3, 128.1, 128.0, 127.8, 126.6, 126.5, 126.3, 57.8, 53.8, 45.7, 15.8, 13.1. HRMS (EI): *m/z* Calcd for $C_{19}H_{24}N$: 239.1909; Found: 266.1903.

5. X-ray Crystal Structure Determination of I

X-ray intensity data measurements of complex **I** was carried out on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (MoKα= 0.71073 Å) radiation between 150(2) - 296 (2) K. The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of

cell constants and an orientation matrix were calculated from three sets of 12 frames (total 36 frames). Data were collected with ω scan width of 0.5° at eight different settings of ϕ and 2θ with a frame time of 10 sec keeping the sample-to-detector distance fixed at 5.00 cm for all the compounds. The X-ray data collection was monitored by APEX2 program (Bruker, 2006).[S2] All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2006). SHELX-97 was used for structure solution and full matrix least-squares refinement on F^2.[S3] Hydrogen atoms were placed in geometrically idealized position and constrained to ride on their parent atoms.

Complex I: $C_{15}H_{23}Br_2CoN_3O_2$, Blue, block, 0.16 ×0.16 × 0.12 mm^3, monoclinic, *P2(1)/n*, a = 10.2514(4) Å, b = 14.6308(6) Å, c = 12.6552(5) Å, β = 92.105(4) deg., V = 1896.84(13) Å3, Z = 4, fw = 496.11, Dc = 1.737 Mg/m^3, μ = 5.129 mm^{-1}. Full matrix least-squares of refinement based on F^2gave an agreement factor R = 0.0477 for data with $I > 2\sigma(I)$ and R = 0.0762 for all data (2949 reflections) with a goodness-of-fit of 1.104. Idealized hydrogen atoms were placed and refined in the riding mode.

6. References

S1. Armarego, W. L. F.;Perrin, D. D. Purification of Laboratory Chemicals(Pergamon Press, Oxford, 1988) ed 3.

S2. APEX2, SAINT and SADABS.Bruker AXS Inc., Madison, Wisconsin, USA, 2006.

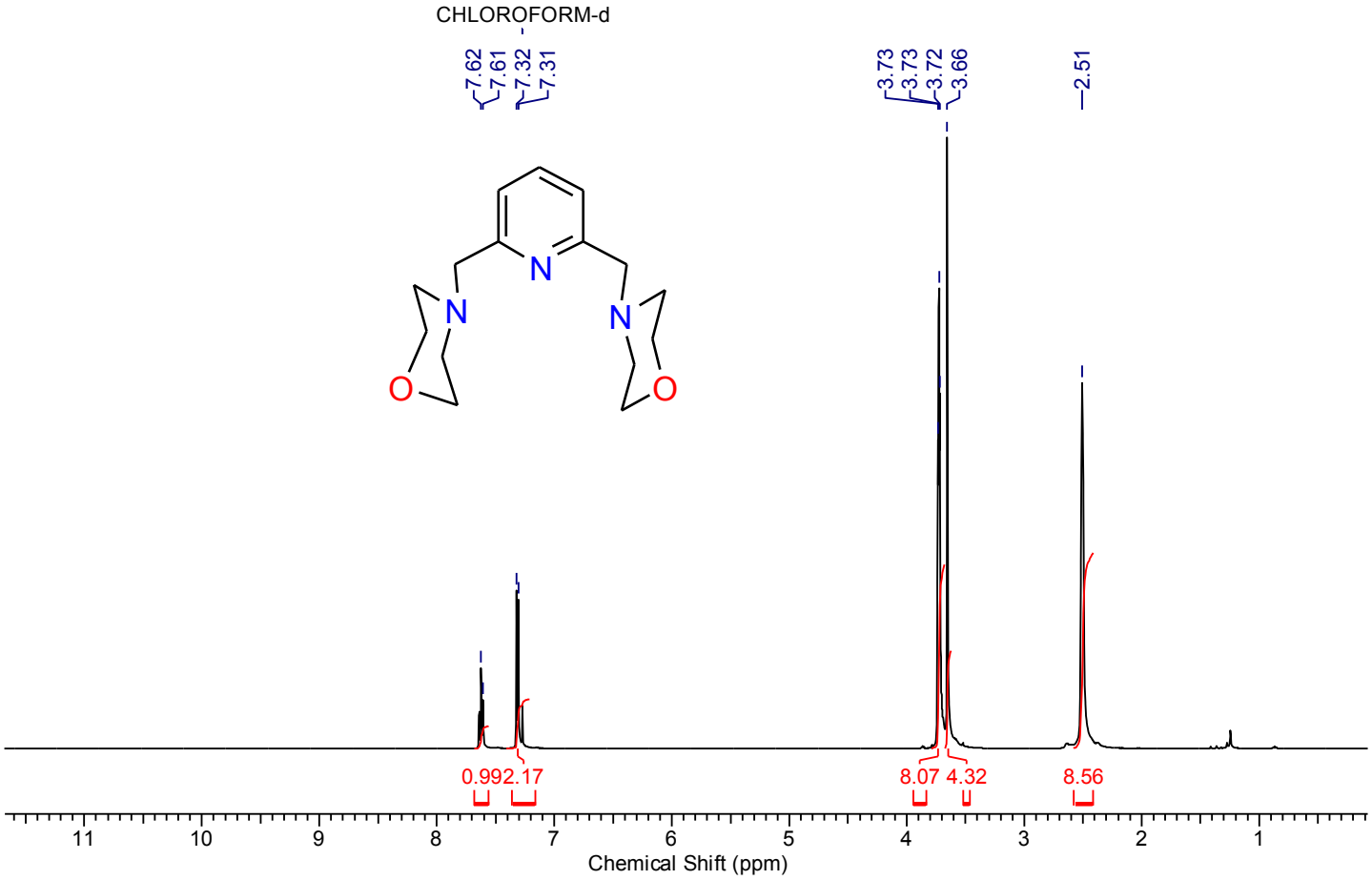
S3. Sheldrick, G. M. *ActaCrystallogr*. **2008**, *A64*, 112-122.

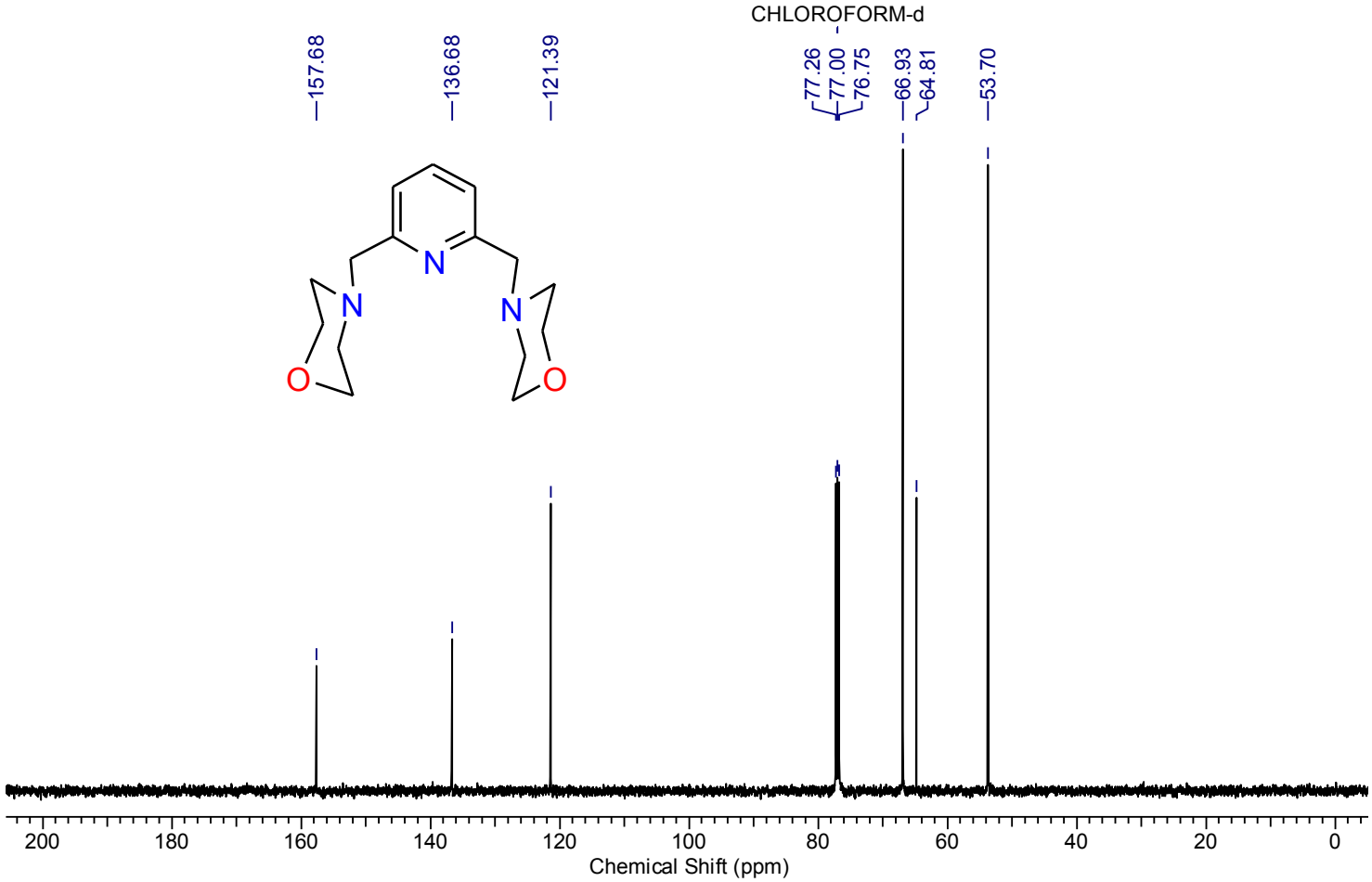
S4. Fu, S.; Chen, N. Y.; Liu, X.; Shao, Z.; LuoS. P.; Liu, Q.*J. Am. Chem. Soc.*, **2016**, 138, 8588-8594.

S5. Chen, Y.-J.; Chen, C. *Tetrahedron: Asymmetry* **2007**, 18, 1313-1319.

S6. Ilies, L.; Yoshida, T.; Nakamura, E. *J. Am. Chem. Soc.* **2012**, 134, 16951-16954.

7. Copy of Spectra




CHLOROFORM-d
157.68
136.68
121.39
77.26
77.00
76.75
66.93
64.81
53.70
N
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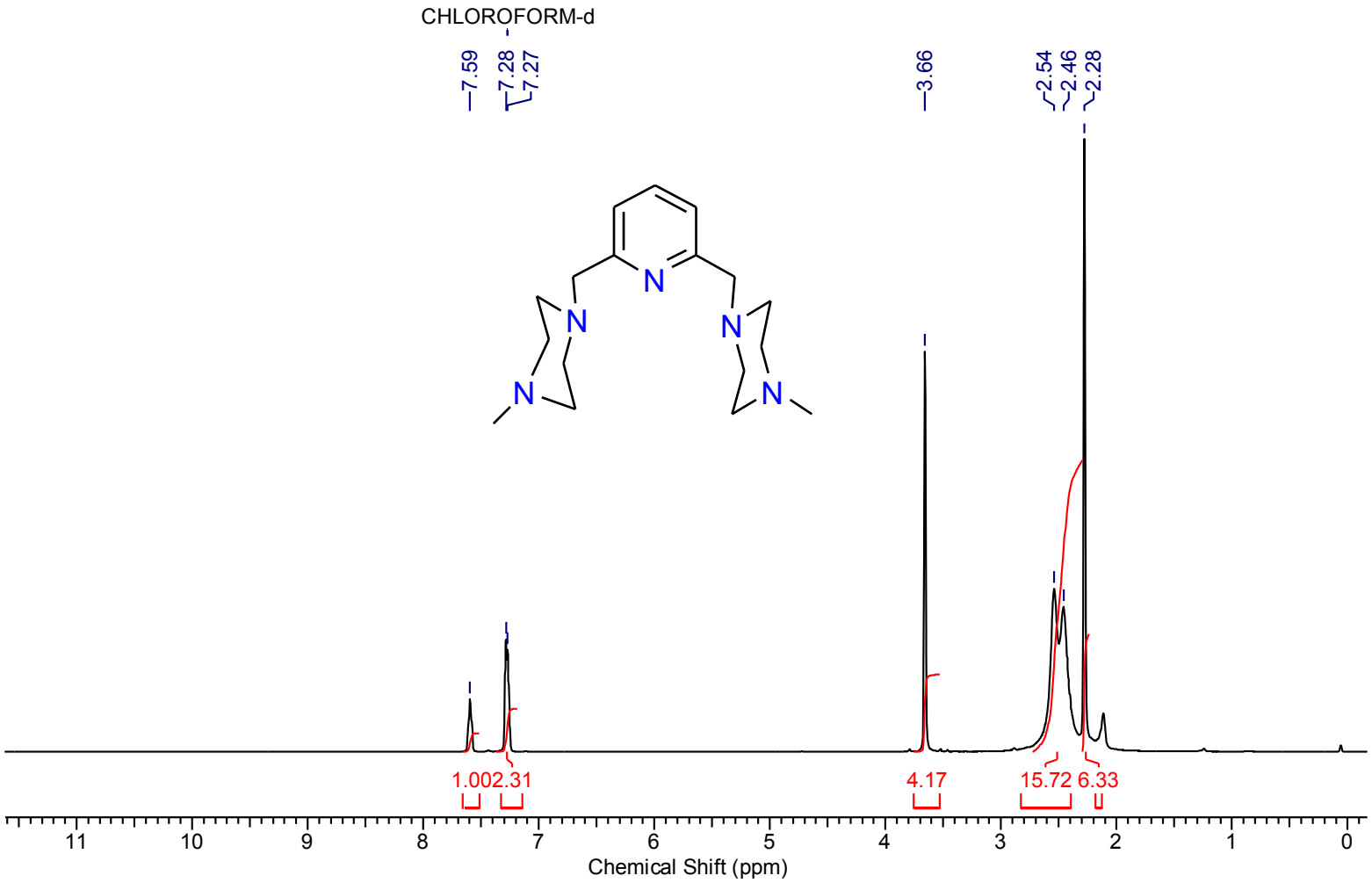
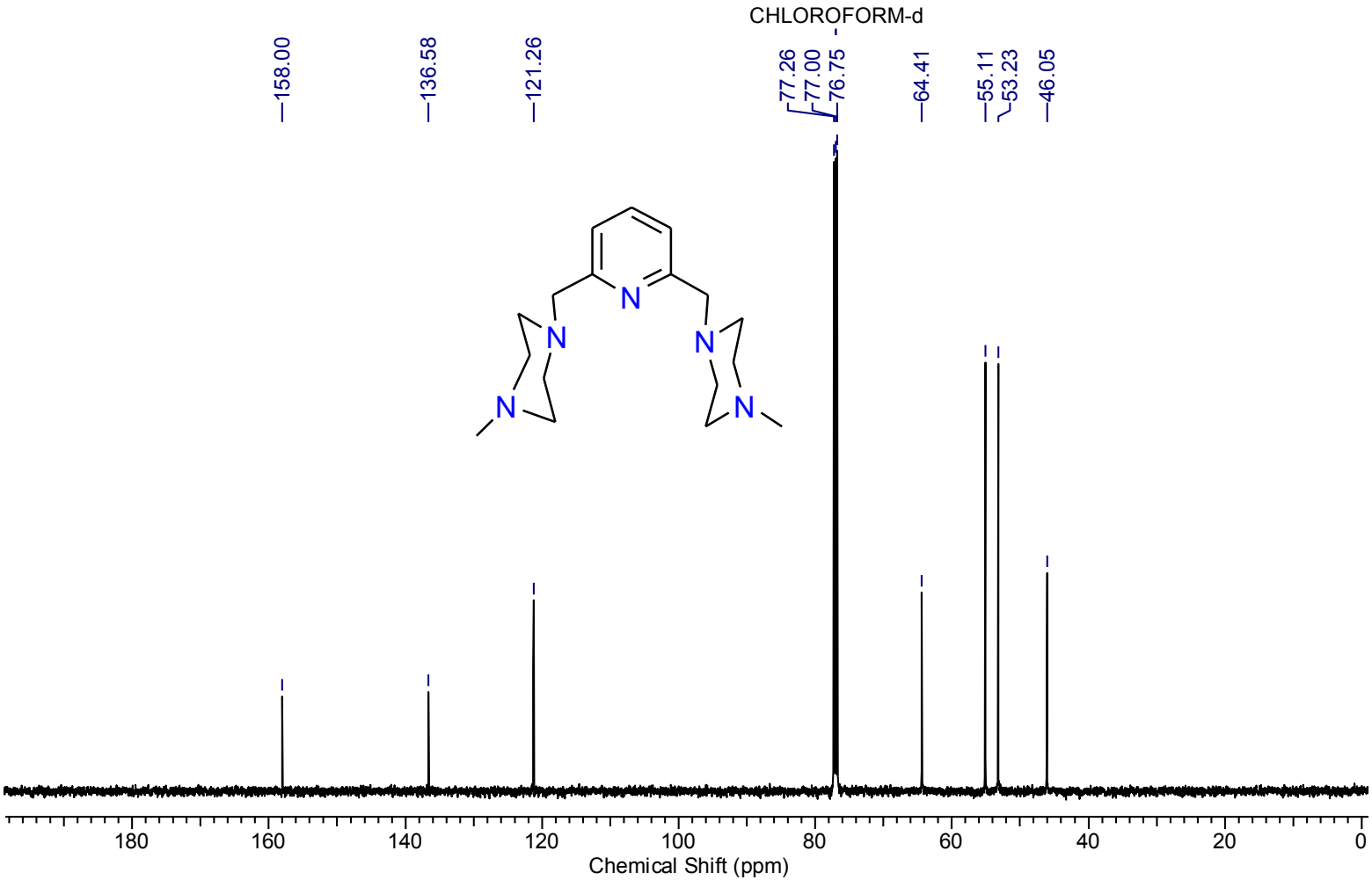
N
O
O
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


CHLOROFORM-d
7.59
7.28
7.27
3.66
2.54
2.46
2.28
N
N
N
N
N
1.00
2.31
4.17
15.72
6.33
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


CHLOROFORM-d
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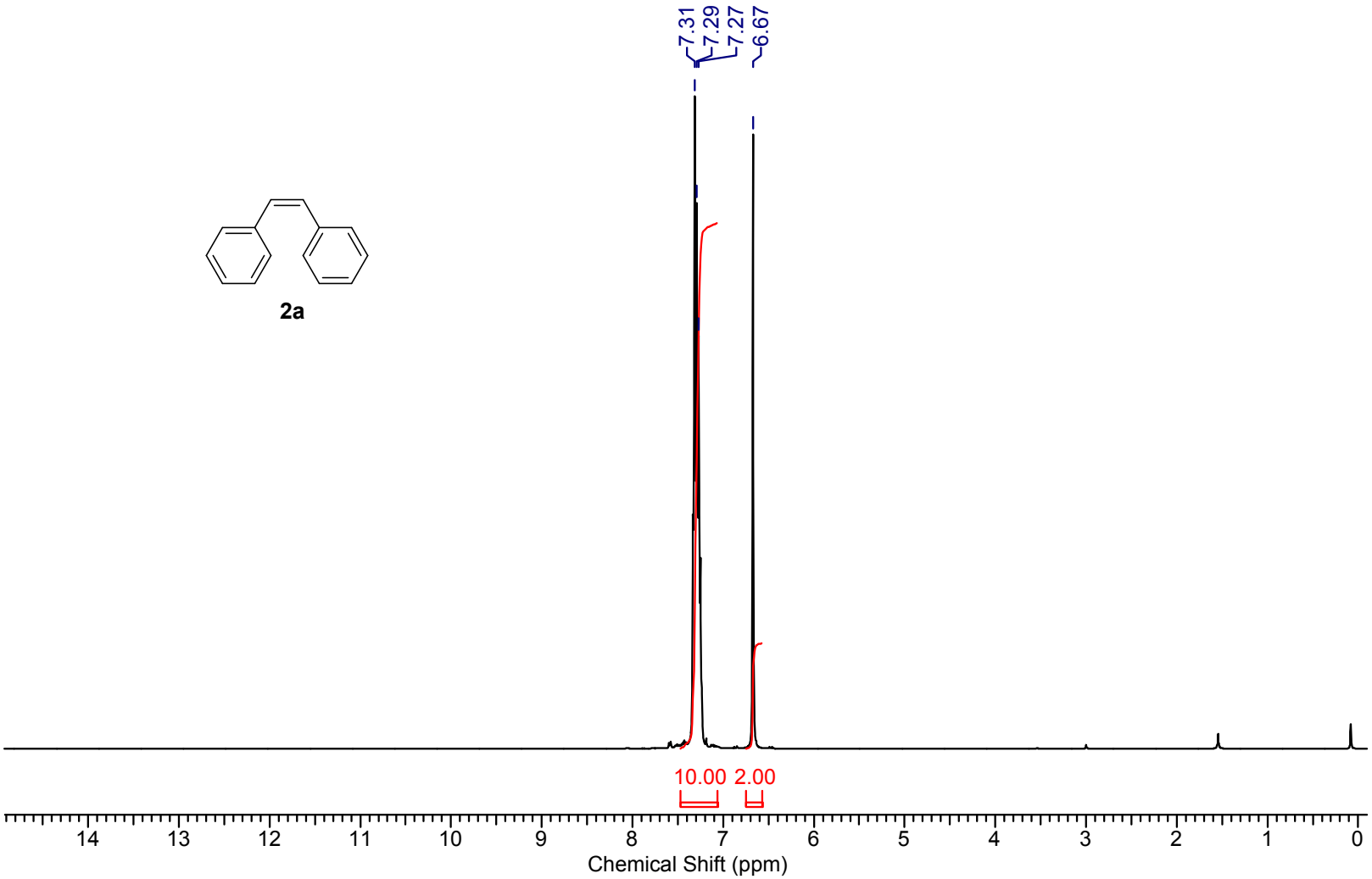
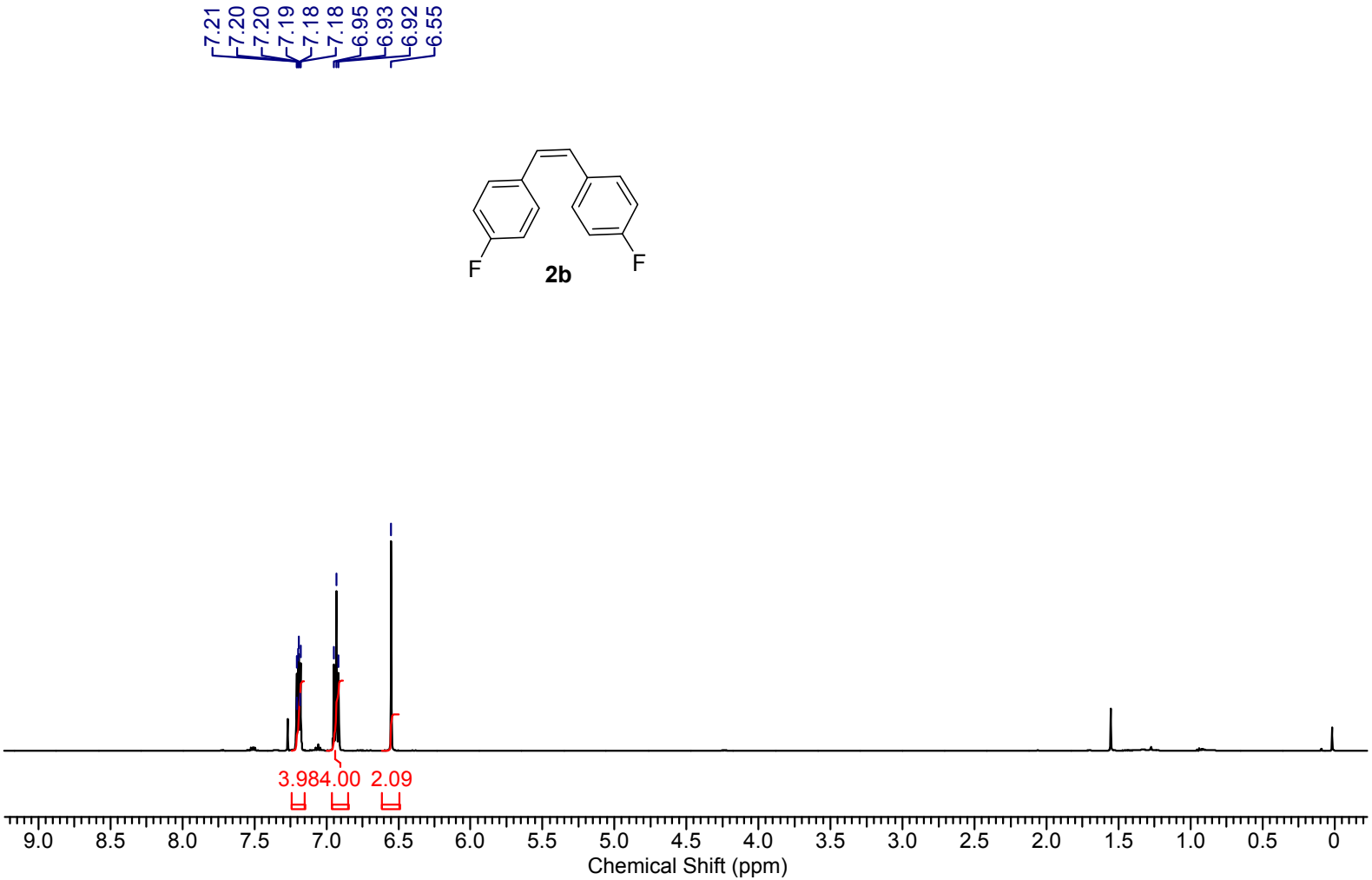
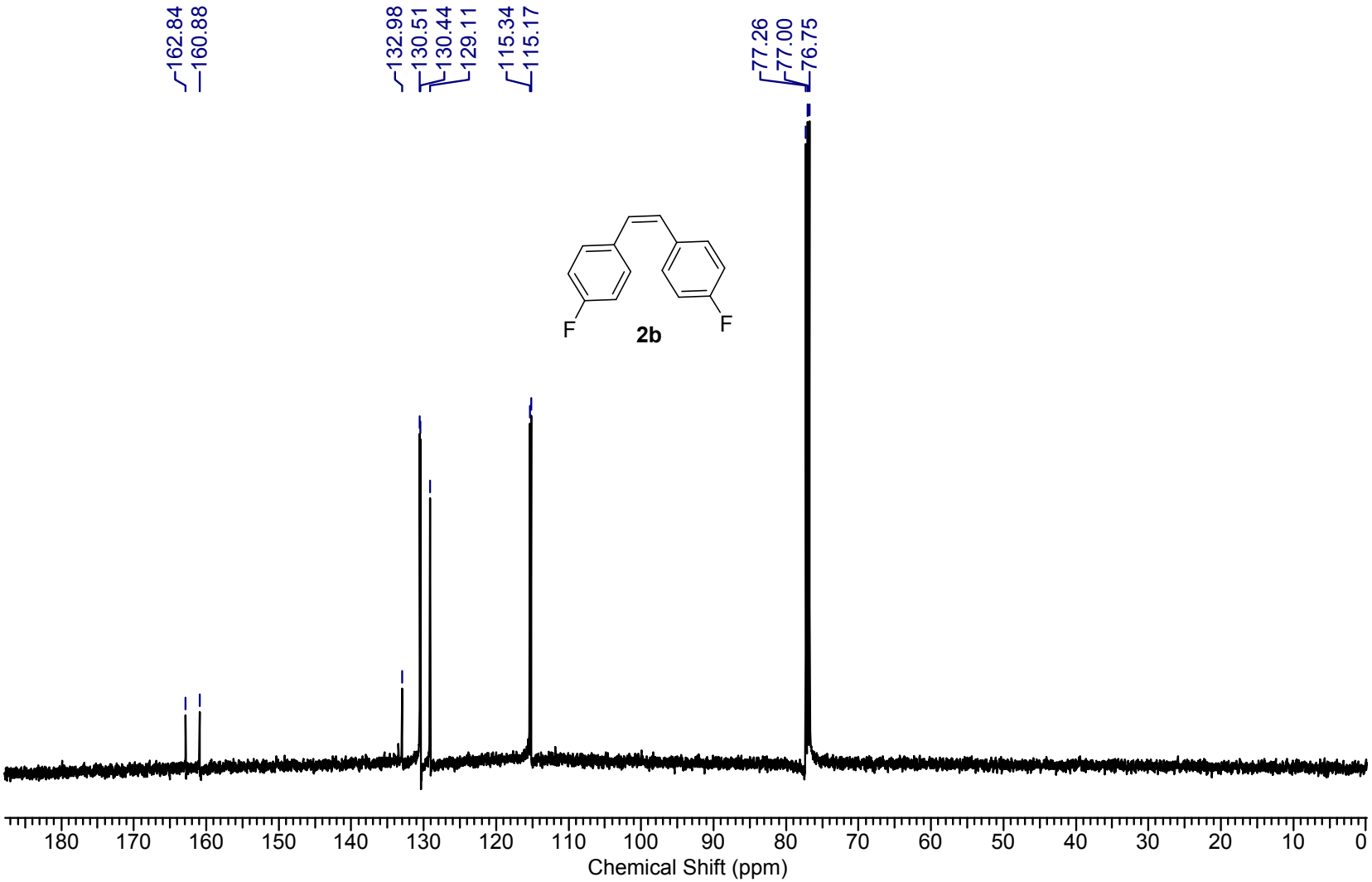
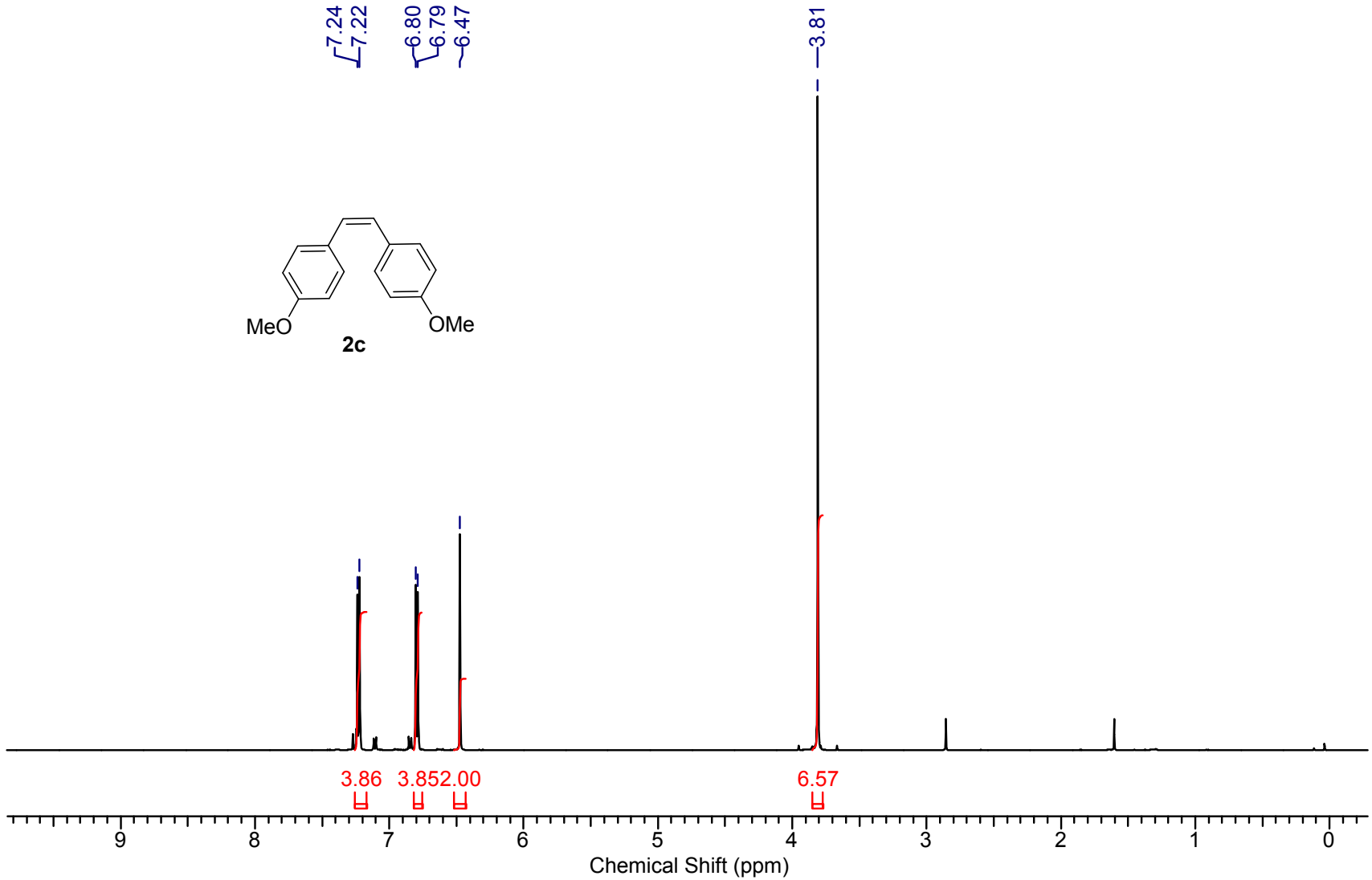
136.58
121.26
77.26
77.00
76.75
64.41
55.11
53.23
46.05
N
N
N
N
N
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

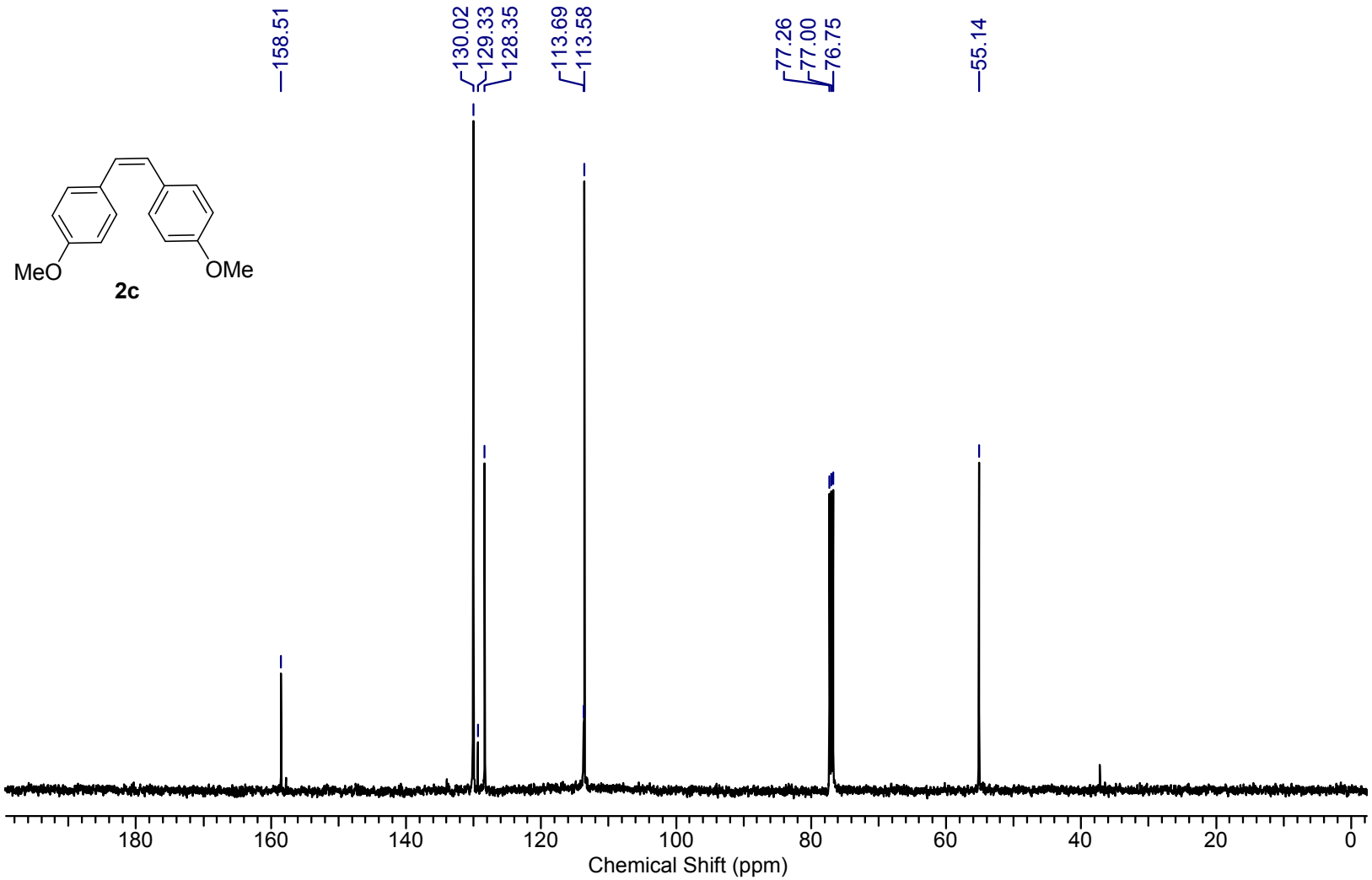
2a

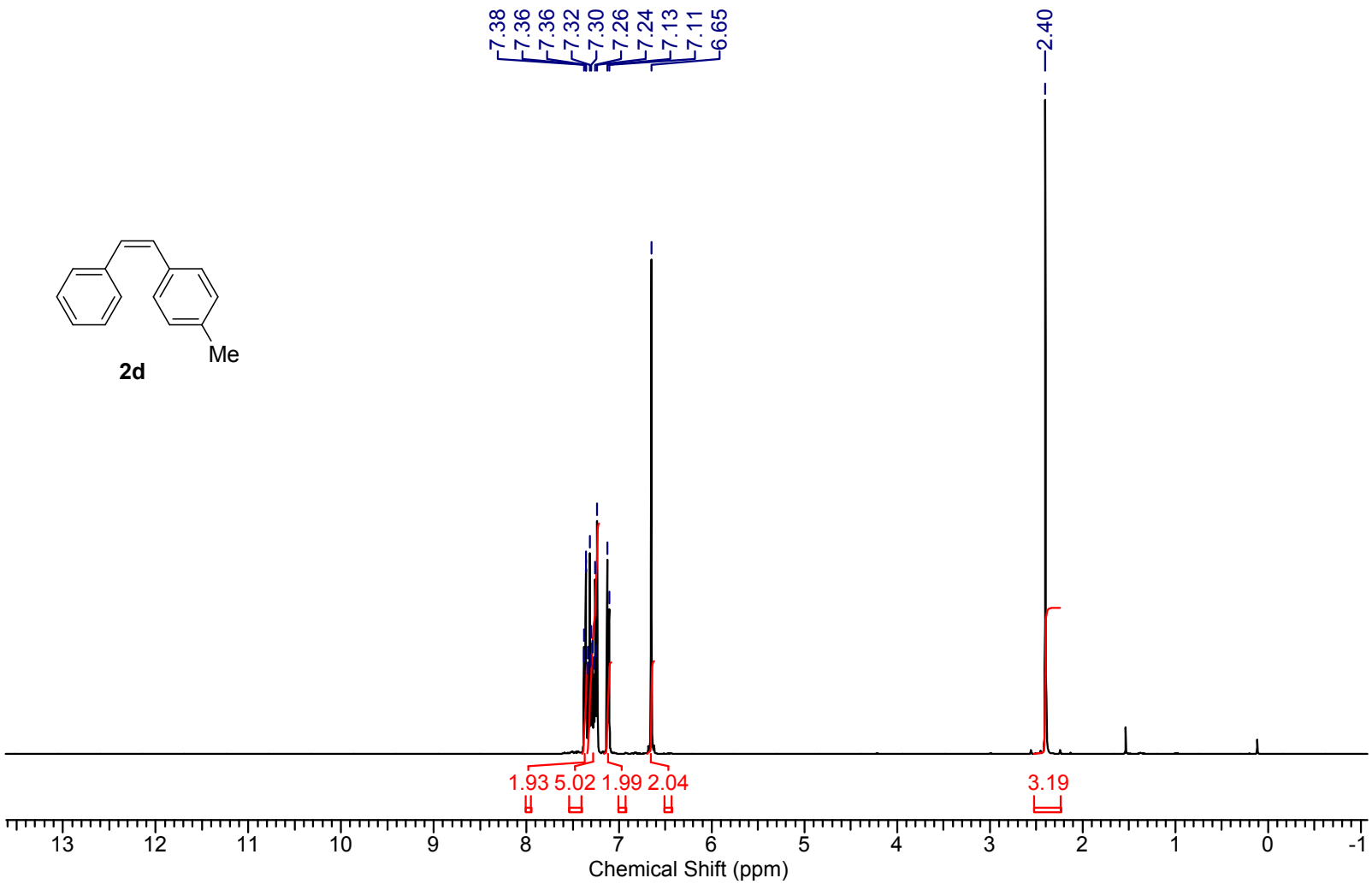

7.31
7.29
7.27
6.67
10.00
2.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

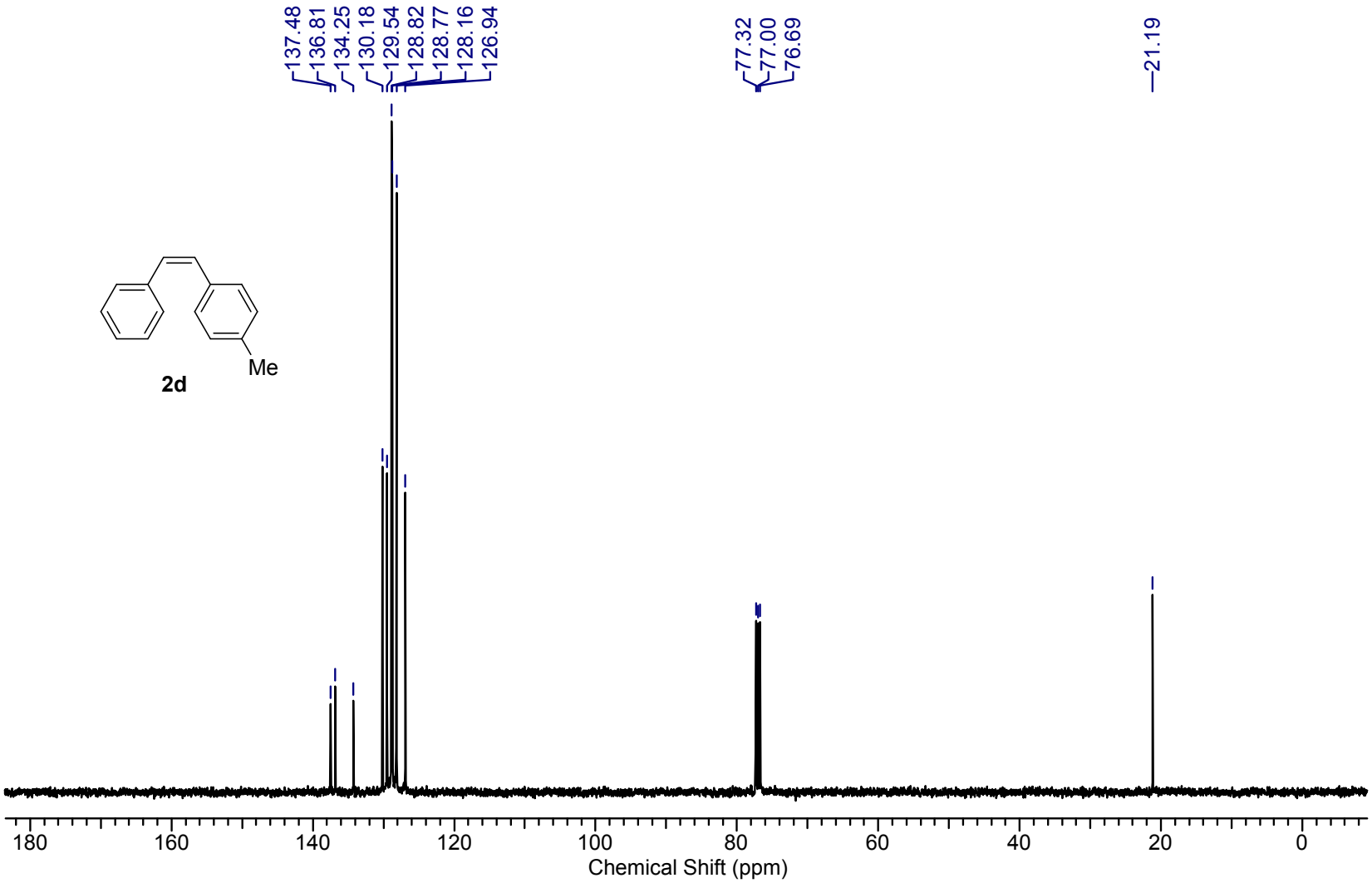

7.21
7.20
7.20
7.19
7.18
7.18
6.95
6.93
6.92
6.55
F
F
2b
3.98
4.00
2.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

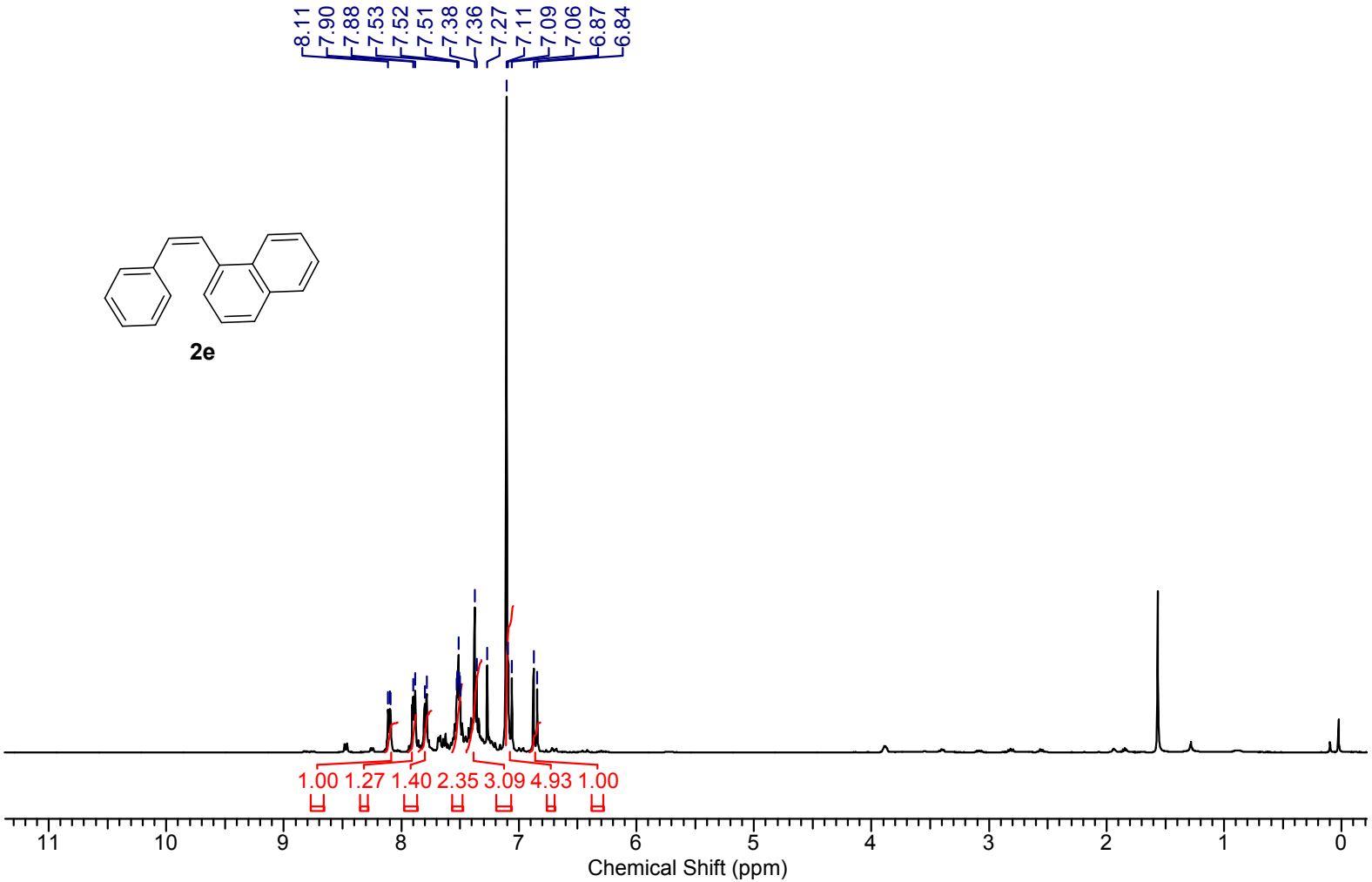

162.84
160.88
132.98
130.51
130.44
129.11
115.34
115.17
77.26
77.00
76.75
F
2b
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

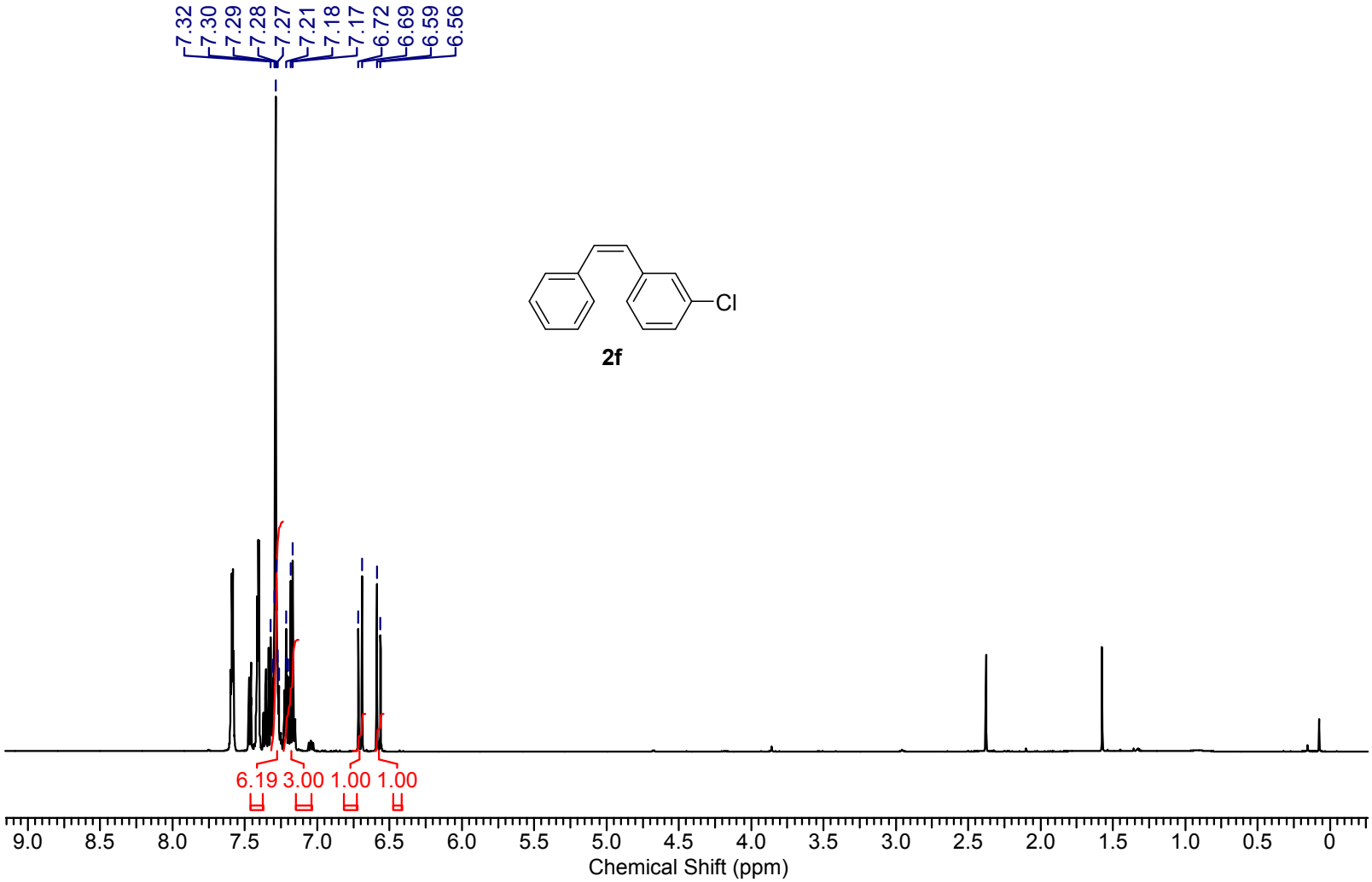

7.24
7.22
6.80
6.79
6.47
3.81
MeO
OMe
2c
3.86
3.85
2.00
6.57
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

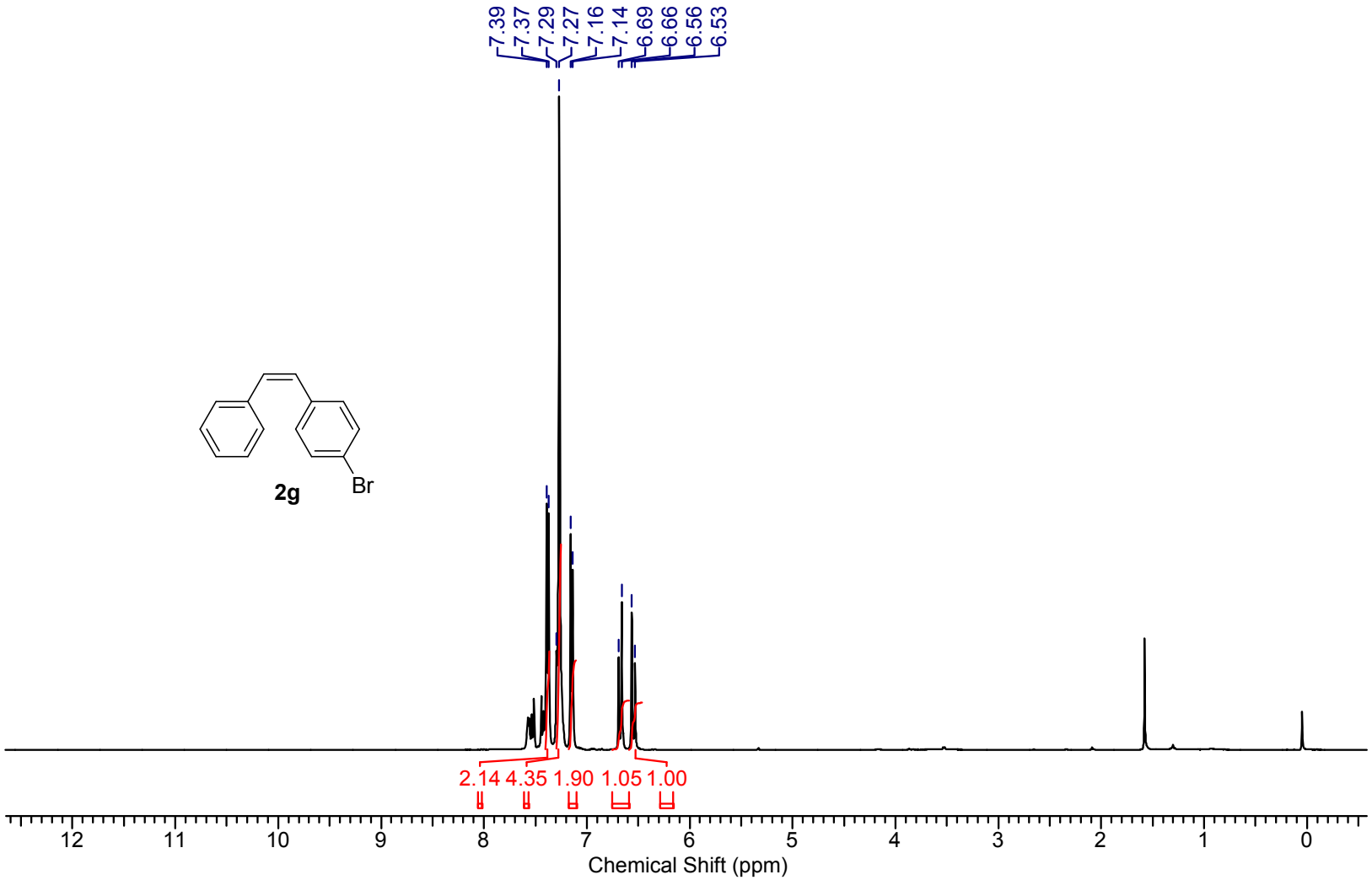

158.51
130.02
129.33
128.35
113.69
113.58
77.26
77.00
76.75
55.14
MeO
OMe
2c
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

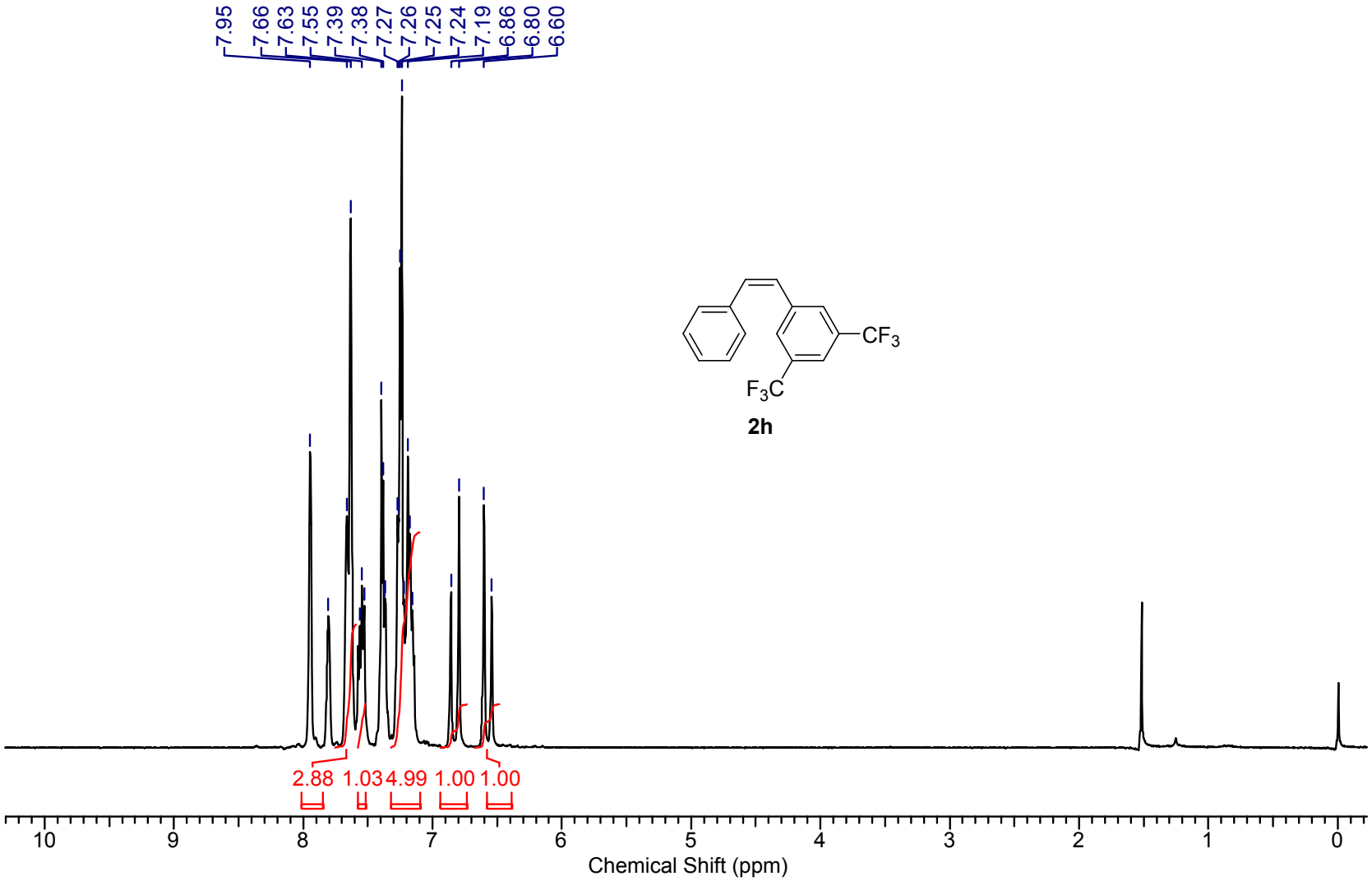

7.38
7.36
7.36
7.32
7.30
7.26
7.24
7.13
7.11
6.65
2.40
Me
2d
1.93 5.02 1.99 2.04
3.19
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
Chemical Shift (ppm)

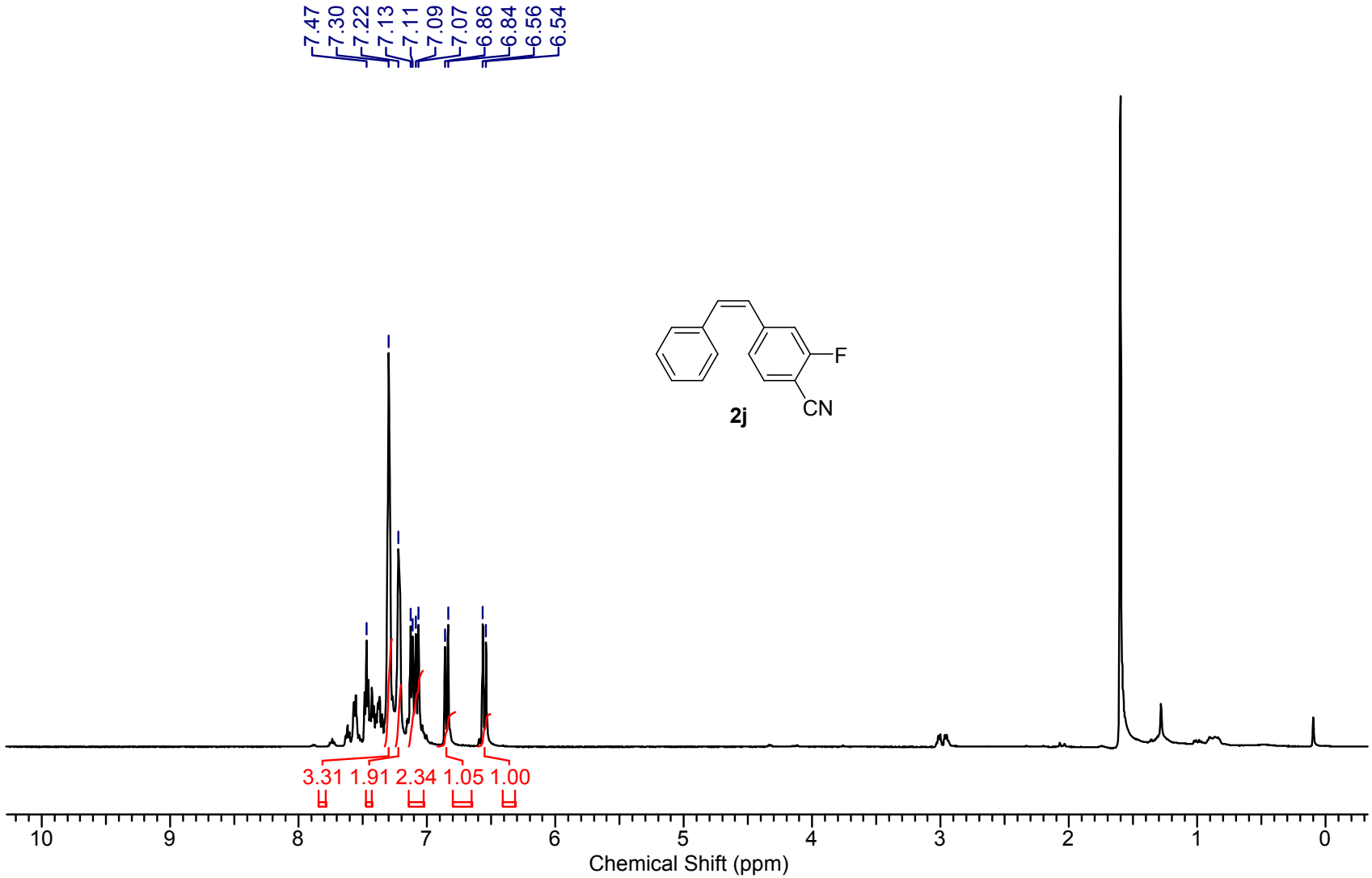

137.48
136.81
134.25
130.18
129.54
128.82
128.77
128.16
126.94
77.32
77.00
76.69
21.19
Me
2d
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

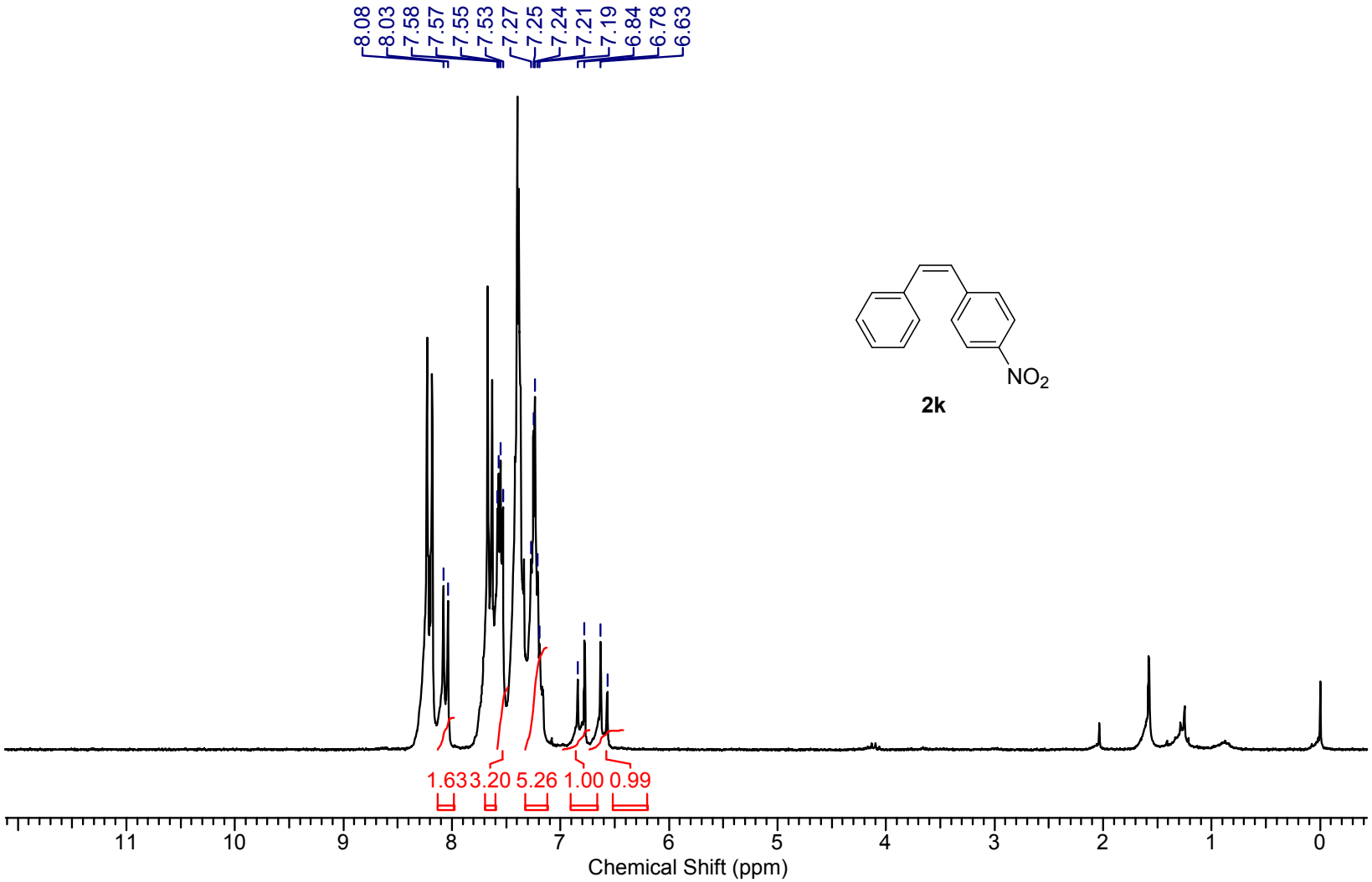

8.11
7.90
7.88
7.53
7.52
7.51
7.38
7.36
7.27
7.11
7.09
7.06
6.87
6.84
2e
1.00 1.27 1.40 2.35 3.09 4.93 1.00
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

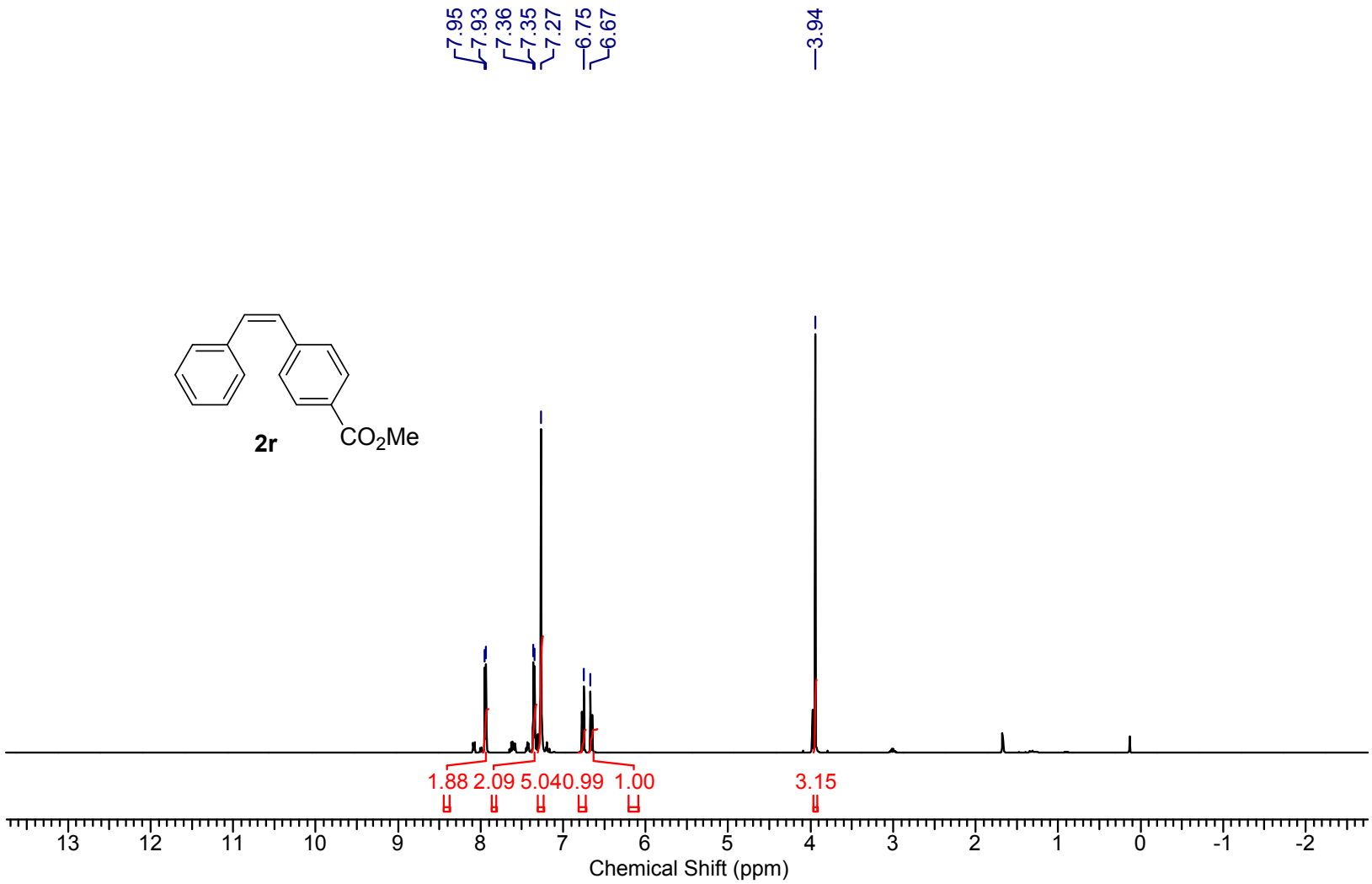

7.32
7.30
7.29
7.28
7.27
7.21
7.18
7.17
6.72
6.69
6.59
6.56
Cl
2f
6.19 3.00 1.00 1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

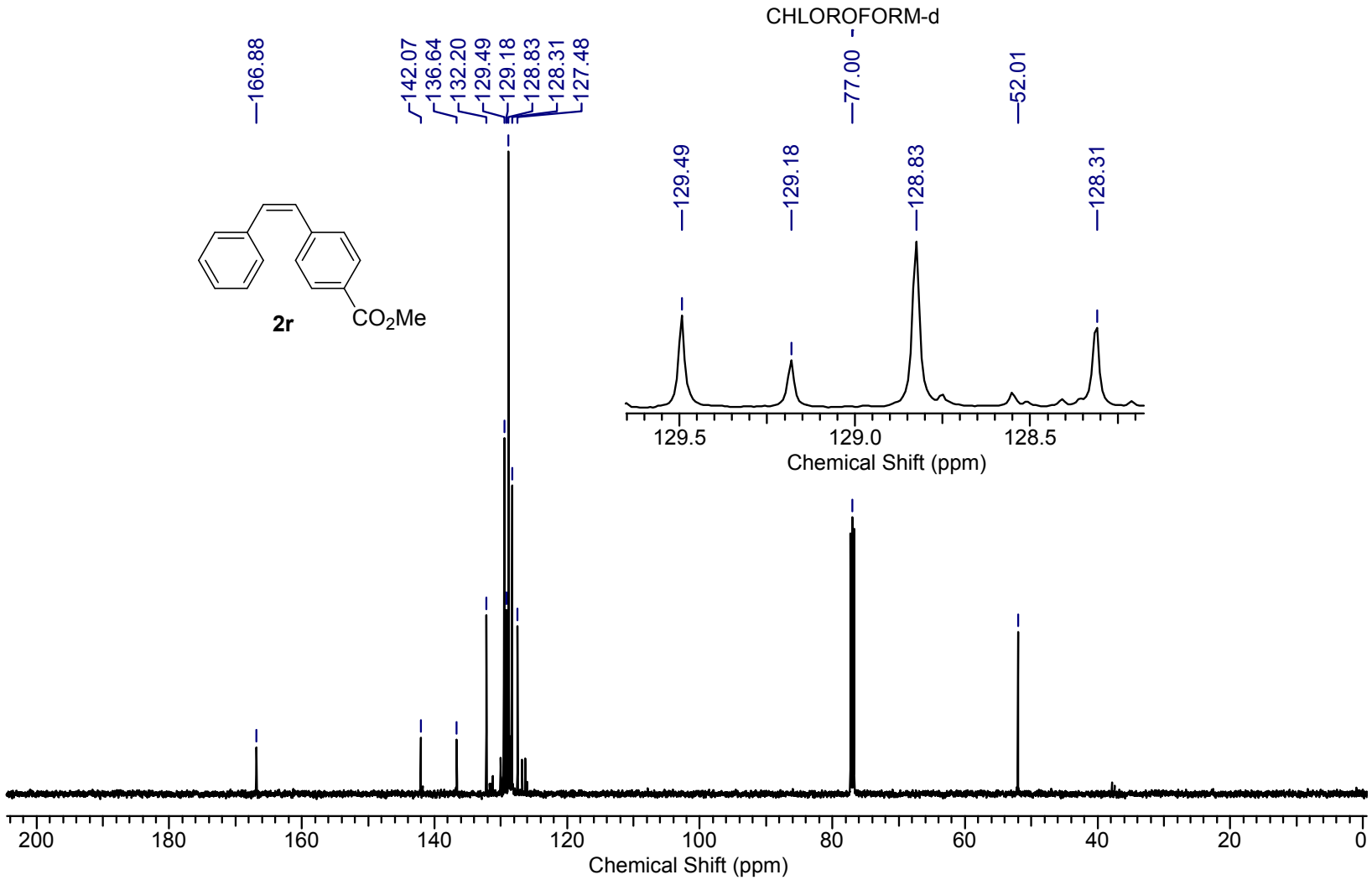

7.39
7.37
7.29
7.27
7.16
7.14
6.69
6.66
6.56
6.53
Br
2g
2.14 4.35 1.90 1.05 1.00
12 11 10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

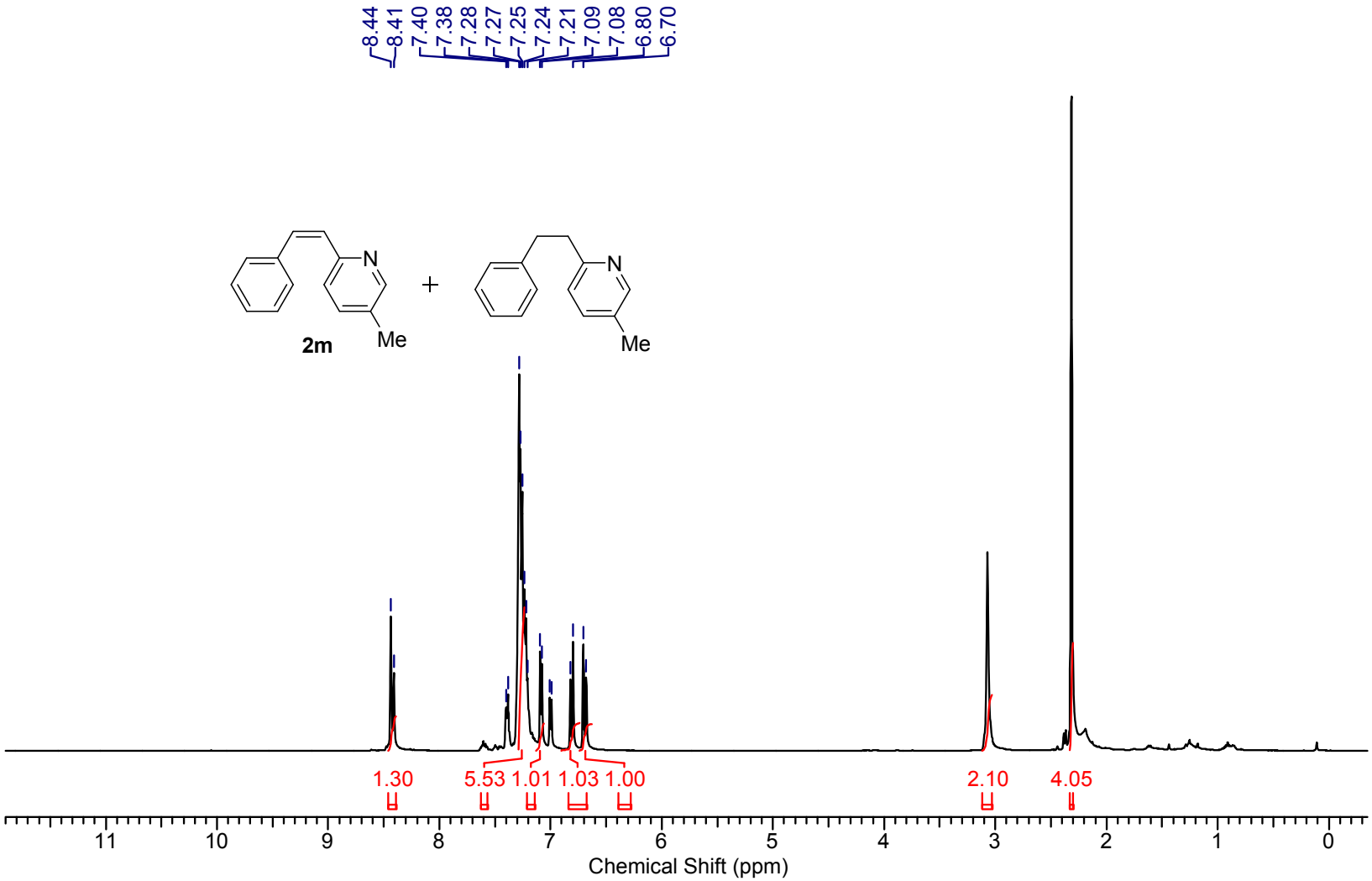

7.95
7.66
7.63
7.55
7.39
7.38
7.27
7.26
7.25
7.24
7.19
6.86
6.80
6.60
CF3
F3C
2h
2.88
1.03
4.99
1.00
1.00
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

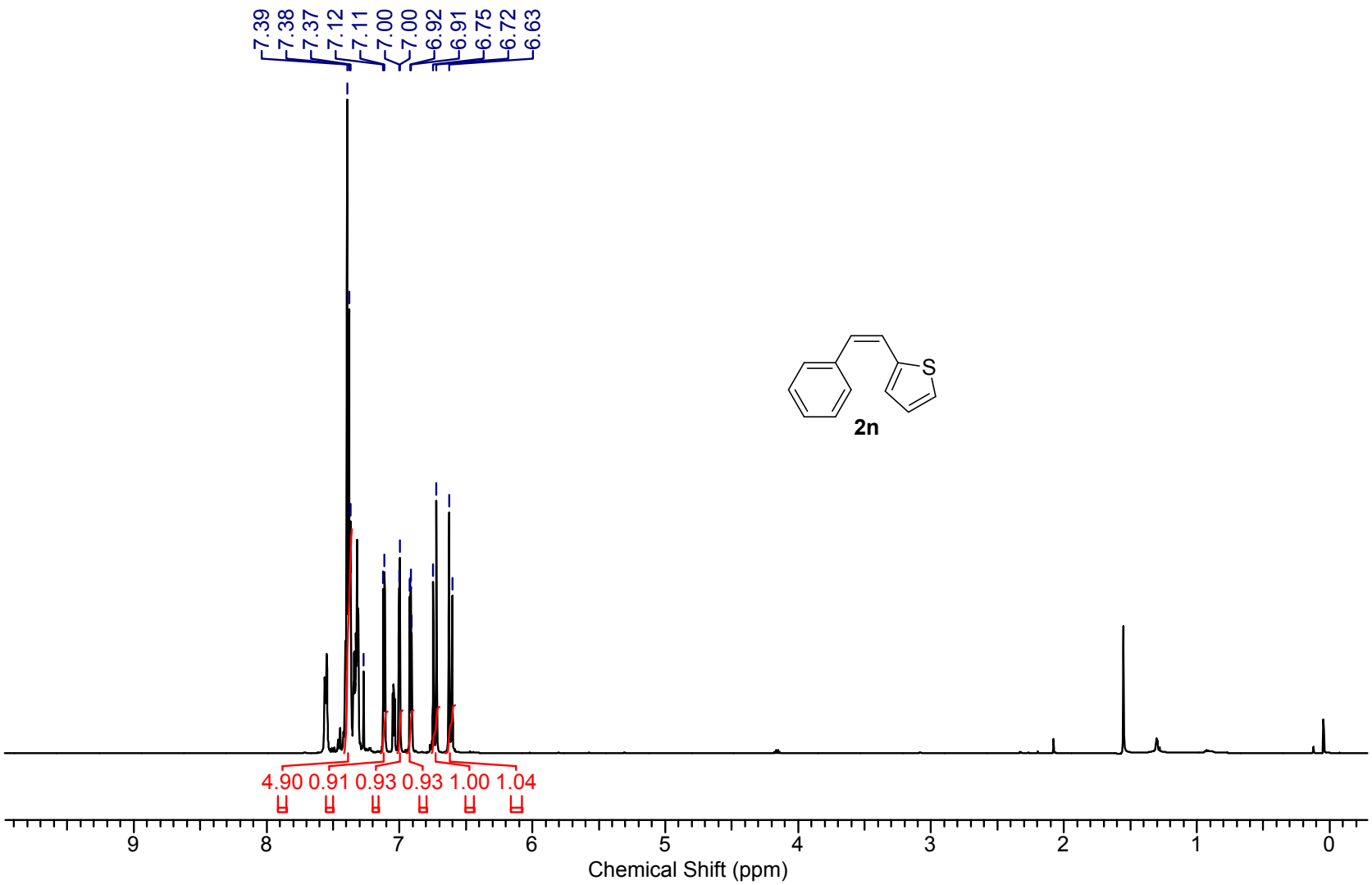

7.47
7.30
7.22
7.13
7.11
7.09
7.07
6.86
6.84
6.56
6.54
F
CN
2j
3.31 1.91 2.34 1.05 1.00
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

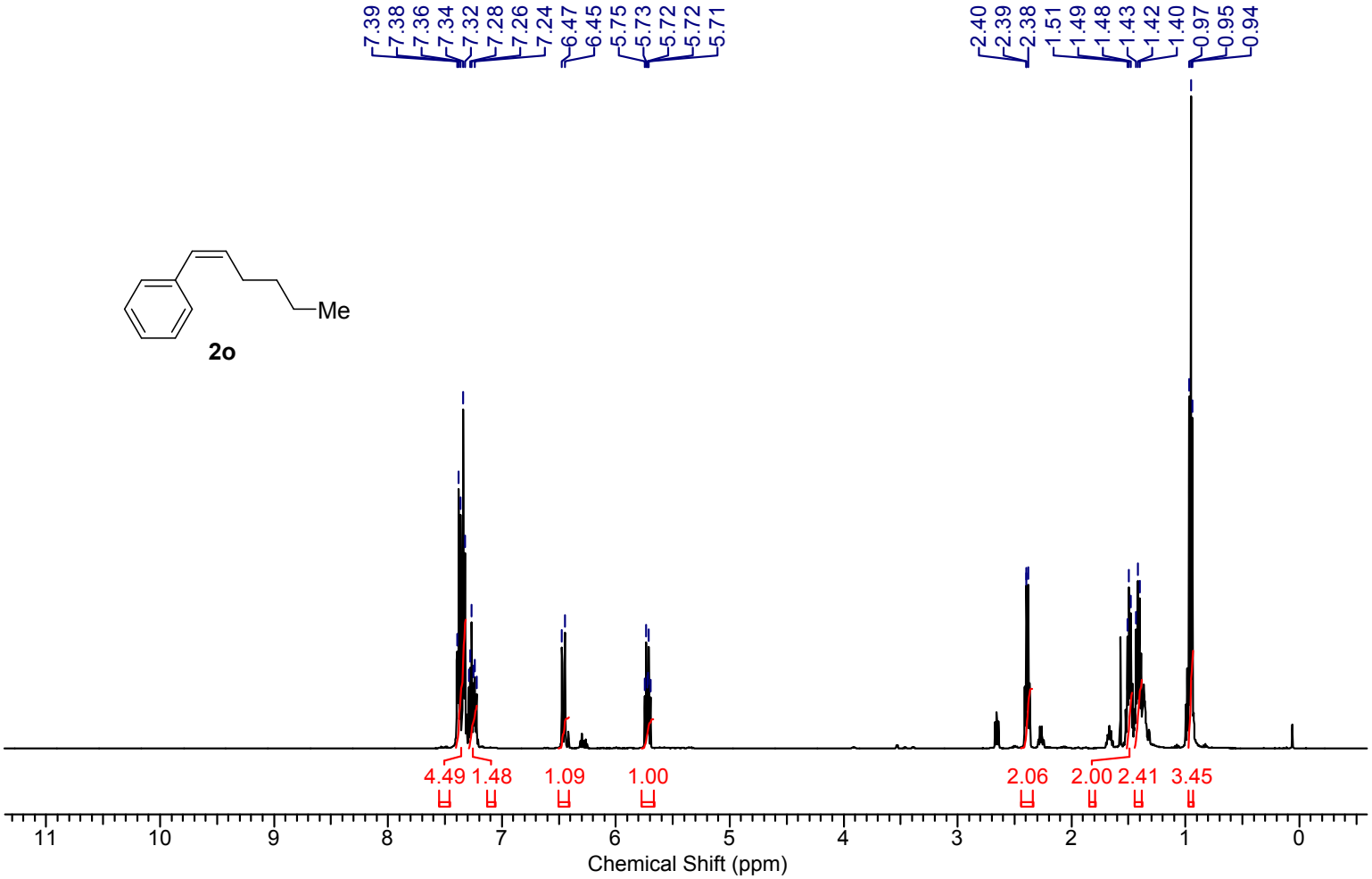

8.08
8.03
7.58
7.57
7.55
7.53
7.27
7.25
7.24
7.21
7.19
6.84
6.78
6.63
1.63
3.20
5.26
1.00
0.99
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)
NO2
2k

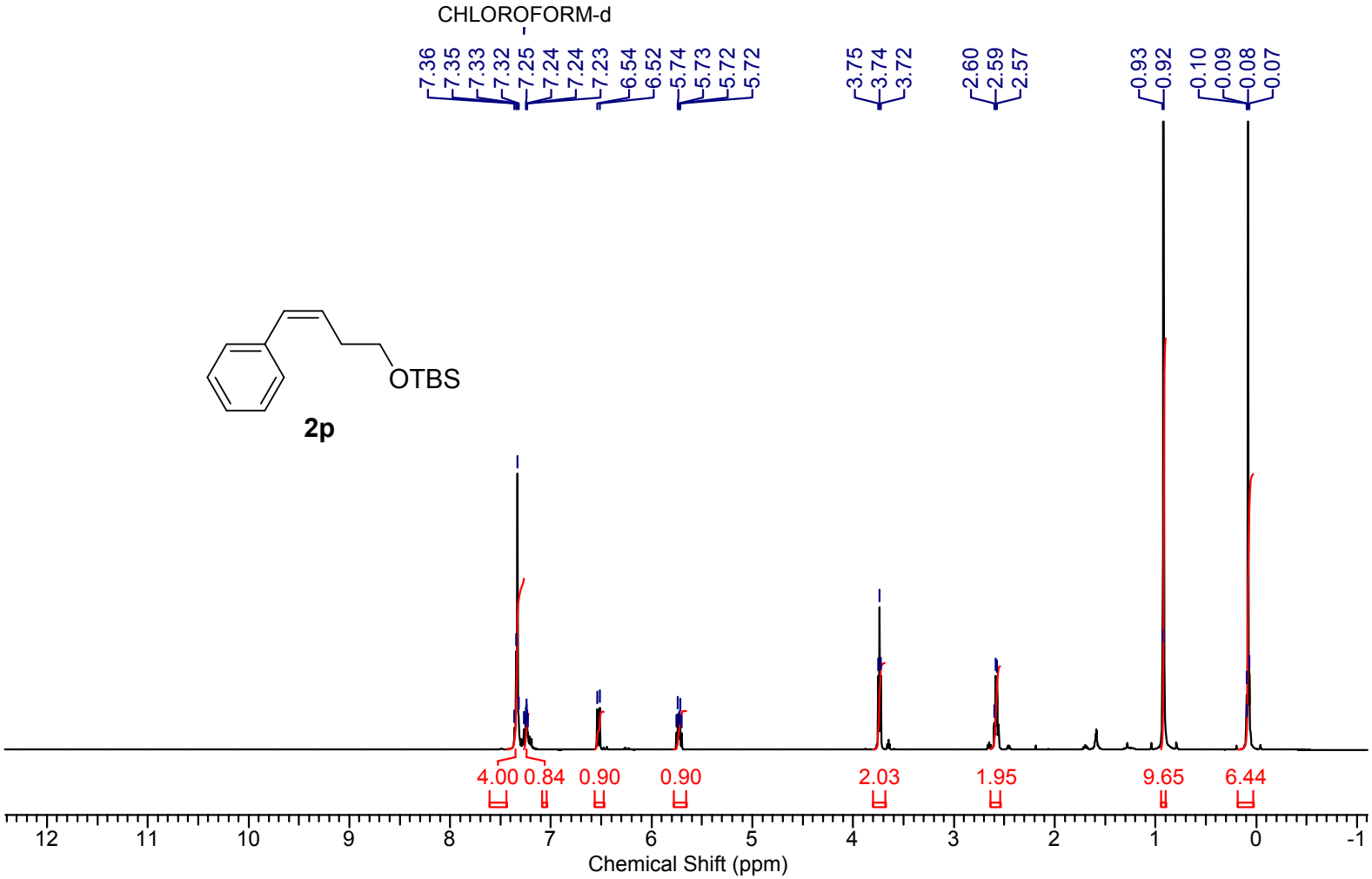

7.95
7.93
7.36
7.35
7.27
6.75
6.67
3.94
2r
CO2Me
1.88 2.09 5.04 0.99 1.00
3.15
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
Chemical Shift (ppm)

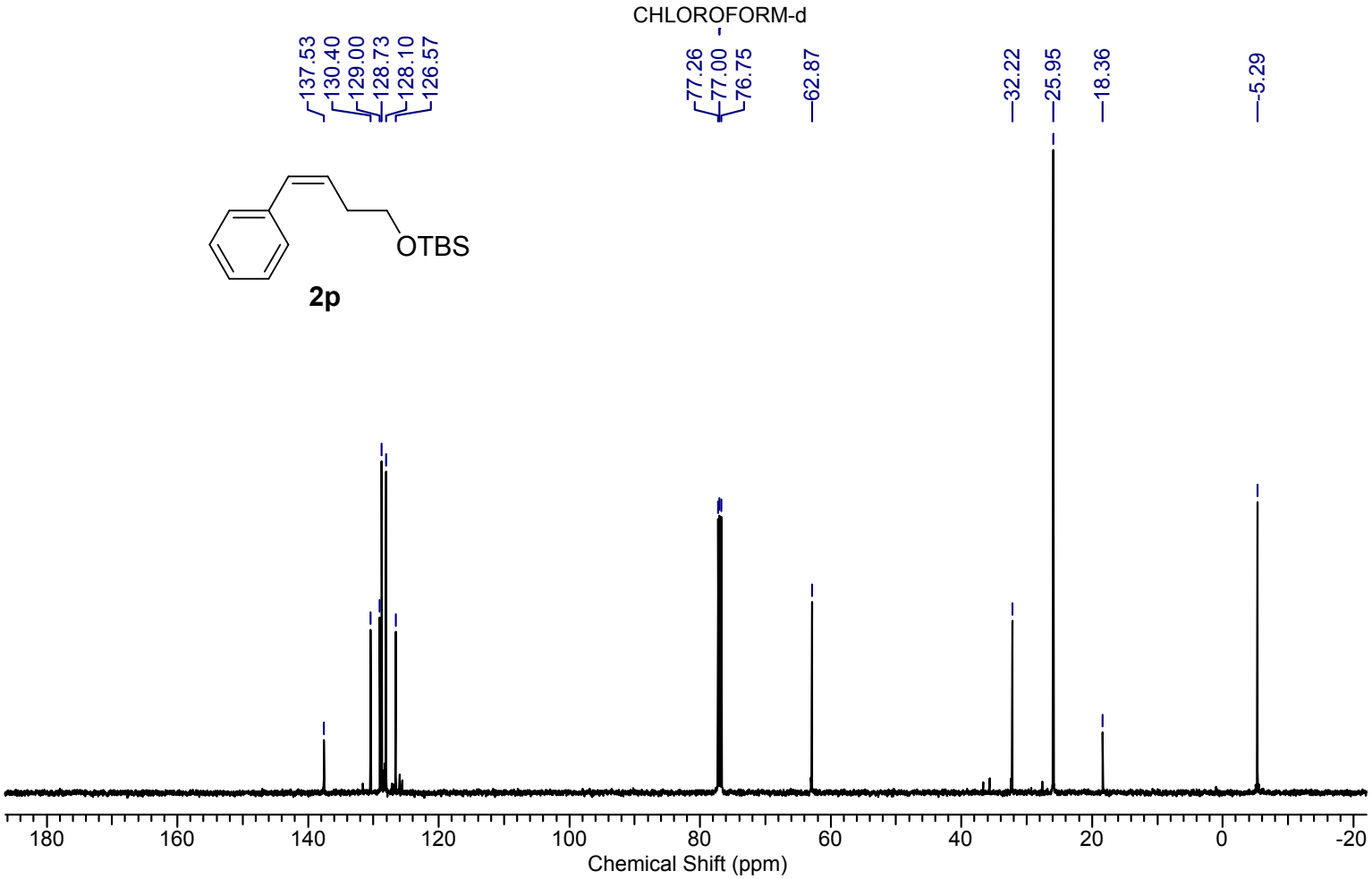

CHLOROFORM-d
166.88
142.07
136.64
132.20
129.49
129.18
128.83
128.31
127.48
77.00
52.01
2r
CO2Me
129.49
129.18
128.83
128.31
129.5
129.0
128.5
Chemical Shift (ppm)
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

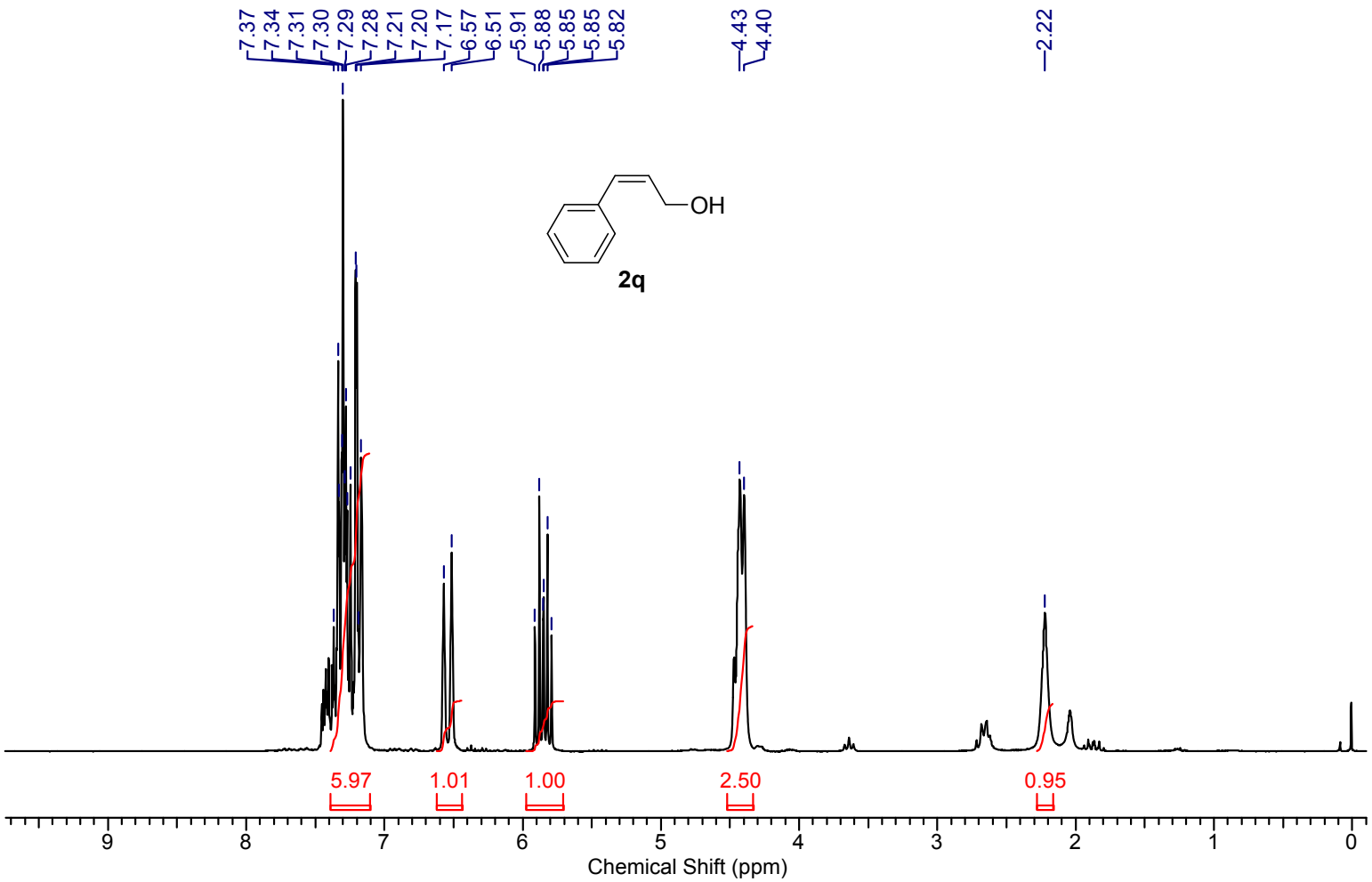

8.44
8.41
7.40
7.38
7.28
7.27
7.25
7.24
7.21
7.09
7.08
6.80
6.70
N
Me
2m
+
N
Me
1.30
5.53
1.01
1.03
1.00
2.10
4.05
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

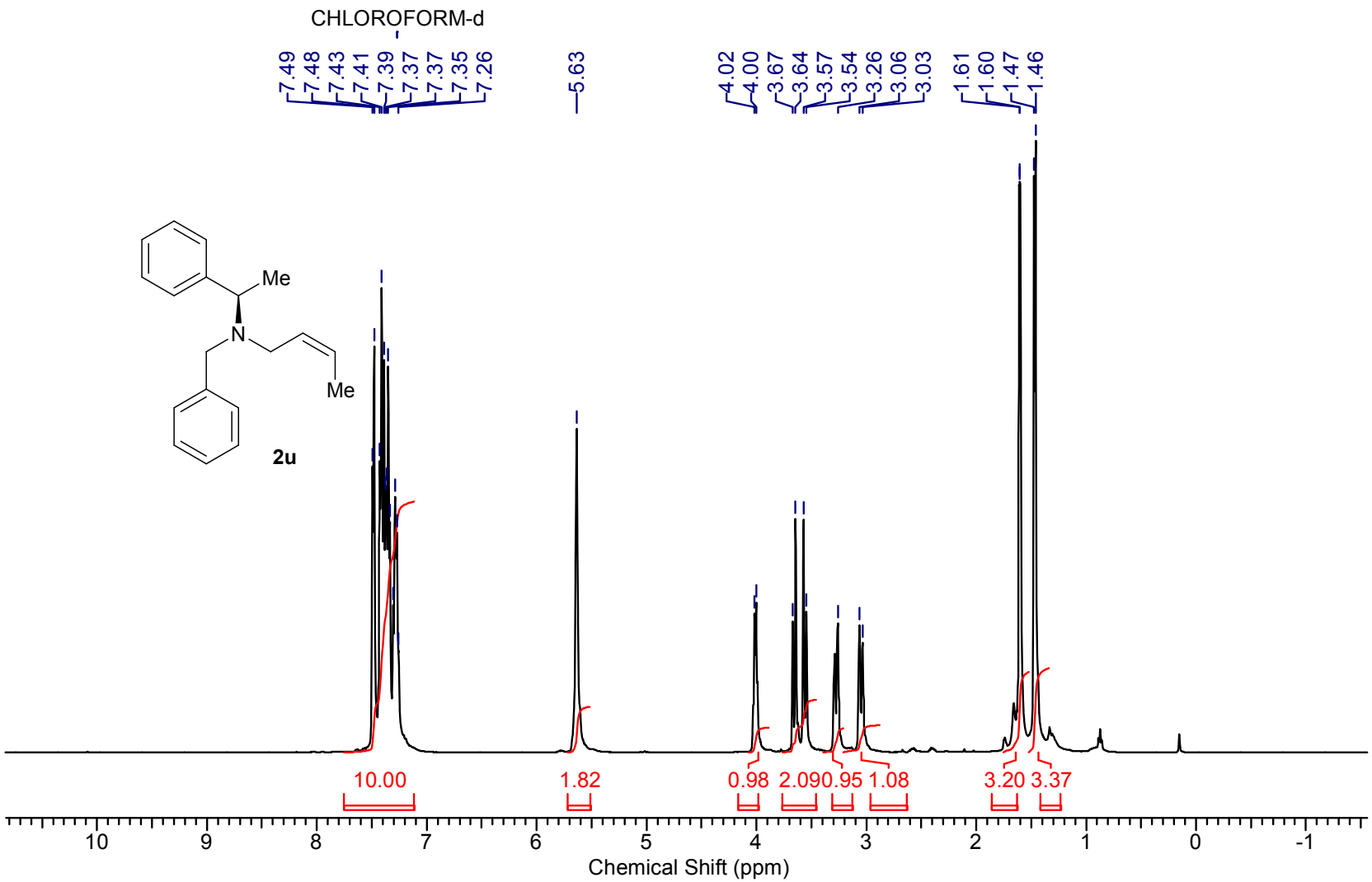

7.39
7.38
7.37
7.12
7.11
7.00
7.00
6.92
6.91
6.75
6.72
6.63
S
2n
4.90 0.91 0.93 0.93 1.00 1.04
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

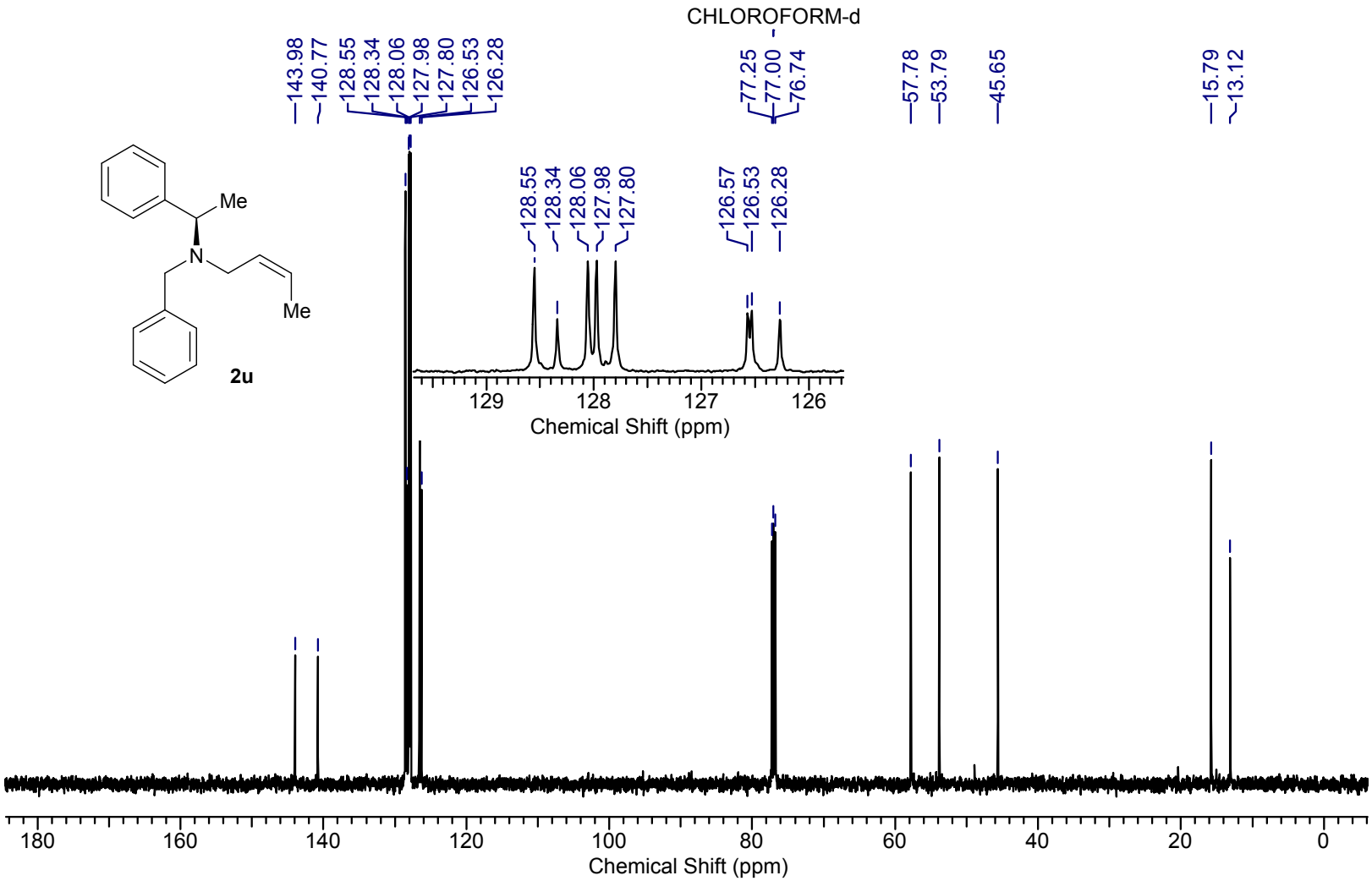

7.39
7.38
7.36
7.34
7.32
7.28
7.26
7.24
6.47
6.45
5.75
5.73
5.72
5.72
5.71
2.40
2.39
2.38
1.51
1.49
1.48
1.43
1.42
1.40
0.97
0.95
0.94
Me
2o
4.49
1.48
1.09
1.00
2.06
2.00
2.41
3.45
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


CHLOROFORM-d
7.36
7.35
7.33
7.32
7.25
7.24
7.24
7.23
6.54
6.52
5.74
5.73
5.72
5.72
3.75
3.74
3.72
2.60
2.59
2.57
0.93
0.92
0.10
0.09
0.08
0.07
OTBS
2p
4.00
0.84
0.90
0.90
2.03
1.95
9.65
6.44
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


CHLOROFORM-d
137.53
130.40
129.00
128.73
128.10
126.57
77.26
77.00
76.75
62.87
32.22
25.95
18.36
-5.29
OTBS
2p
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


7.37
7.34
7.31
7.30
7.29
7.28
7.21
7.20
7.17
6.57
6.51
5.91
5.88
5.85
5.85
5.82
4.43
4.40
2.22
OH
2q
5.97
1.01
1.00
2.50
0.95
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


CHLOROFORM-d
7.49
7.48
7.43
7.41
7.39
7.37
7.37
7.35
7.26
5.63
4.02
4.00
3.67
3.64
3.57
3.54
3.26
3.06
3.03
1.61
1.60
1.47
1.46
Me
N
Me
2u
10.00
1.82
0.98
2.09
0.95
1.08
3.20
3.37
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


CHLOROFORM-d
143.98
140.77
128.55
128.34
128.06
127.98
127.80
126.53
126.28
77.25
77.00
76.74
57.78
53.79
45.65
15.79
13.12
Me
N
Me
2u
126.57
Chemical Shift (ppm)
Chemical Shift (ppm)