Electronic Supplementary Information

Zinc mediated allylations of chlorosilanes promoted by ultrasound: Synthesis of novel constrained sila amino acids

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General:

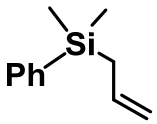
All reagents, starting materials, and solvents (including dry solvents) were obtained from commercial suppliers and used as such without further purification. Reactions were carried out in oven-dried glassware under a positive pressure of argon unless otherwise mentioned. Air sensitive reagents and solutions were transferred *via* syringe or cannula and were introduced to the apparatus *via* rubber septa. The sonication reactions were performed in a commercial ultrasound cleaning bath (37 KHz, 320 W). Reactions were monitored by thin layer chromatography (TLC) with 0.25 mm pre-coated silica gel plates (60 F254). Visualization was accomplished with either UV light, Iodine adsorbed on silica gel or by immersion in ethanolic solution of phosphomolybdic acid (PMA), *para*-anisaldehyde, 2,4-DNP, $KMnO_4$ or Ninhydrin solution followed by heating with a heat gun for ~15 sec. Column chromatography was performed on silica gel (100-200 mesh) or neutral alumina. Deuterated solvents for NMR spectroscopic analyses were used as received. All ^{1}H NMR and ^{13}C NMR spectra were obtained using a 200 MHz, 400 MHz or 500 MHz spectrometer. Coupling constants were measured in Hertz. All chemical shifts were quoted in ppm, relative to TMS, using the residual solvent peak as a reference standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. HRMS (ESI) were recorded on ORBITRAP mass analyser (Thermo Scientific, Q Exactive). Fourier transform infrared (FT-IR) spectra were taken on a Bruker Optics ALPHA-E spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory in the 600-4000 cm–1 region or using a Diamond ATR (Golden Gate). Chemical nomenclature was generated using Chem Bio Draw Ultra 13.0.

Experimental Procedures

General procedure for the synthesis of allylsilanes from monochlorosilanes.

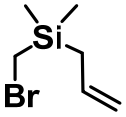
Allyl bromide (2 mmol), Zn dust (2 mmol) and monochlorosilane (1 mmol) were taken in dry THF (5 mL) and sonicated by placing in an ultrasound cleaning bath. After consumption of starting material (approx. 10 min.), the reaction mixture was cooled to 0 °C and saturated ammonium chloride was added till the excess Zn dissolved. Diethyl ether was added and the organic layer was separated. The aqueous layer was then extracted twice with diethyl ether, dried over Na_2SO_4 and the solvent was removed. The crude reaction mass was

then purified by column chromatography on silica gel (100-200) using pet ether to afford the pure compound.



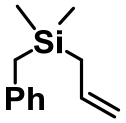
2

Allyldimethyl(phenyl)silane (2)[1]: 98% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.55 - 7.48 (m, 2H), 7.38 - 7.32 (m, 3H), 5.89 - 5.67 (dddd, *J* = 18.6 Hz, 10.8 Hz, 8.1 Hz, 8.1 Hz, 1H), 4.92 - 4.86 (m, 1H), 4.82 (m, 1H), 1.78 - 1.73 (m, 2H), 0.28 (s, 6H).



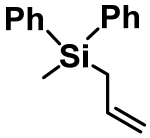
3

Allyl(bromomethyl)dimethylsilane (3)[2]: 71% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.83 – 5.72 (dddd, *J* = 18.3 Hz, 10.1 Hz, 8.7 Hz, 8.7 Hz, 1H), 4.94 – 4.87 (m, 2H), 2.48 (s, 2H), 1.67 (d, *J* = 8.2 Hz, 2H), 0.15 (s, 6H).



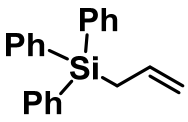
4

Allyl(benzyl)dimethylsilane (4)[3]: 95% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.26 – 7.18 (m, 2H), 7.11 - 6.99 (m, 3H), 5.88 - 5.66 (m, 1H), 4.93 - 4.89 (m, 1H), 4.84 (m, 1H), 2.11 (s, 2H), 1.53 (d, *J* = 8.1 Hz, 2H), 0.01 (s, 6H).



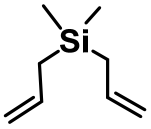
5

Allyl(methyl)diphenylsilane (5)[4]: 71% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.54 - 7.50 (m, 4H), 7.40 - 7.32 (m, 6H), 5.90 - 5.69 (dddd, *J* = 17.9 Hz, 9.9 Hz, 7.9 Hz, 7.9 Hz, 1H), 4.95 – 4.84 (m, 2H), 2.08 (d, *J* = 8.0 Hz, 2H), 0.56 (s, 3H).



6

Allyltriphenylsilane (6)[4]: 88% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 6H), 7.42 - 7.32 (m, 9H), 5.98 - 5.78 (m, 1H), 5.00– 4.85 (m, 2H), 2.42 – 2.37 (m, 2H).

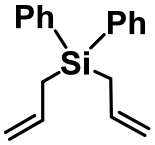


7

Diallyldimethylsilane (7)[1]: 22% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.88 – 5.66 (m, 2H), 4.91 - 4.86 (m, 2H), 4.81 (m, 2H), 1.56 - 1.52 (m, 4H), 0.06 (s, 6H).

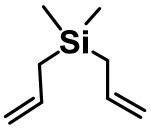
General procedure for the synthesis of diallylsilanes from dichlorosilanes.

Allyl bromide (4 mmol), Zn dust (4 mmol) and dichlorosilane (1 mmol) was taken in dry THF (10 mL) and the same procedure for monoallylation was followed.



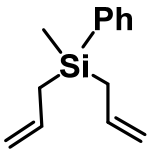
1

Diallyldiphenylsilane (1)[1]: 88% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.55 - 7.30 (m, 10H), 5.90 - 5.69 (dddd, *J* = 17.0 Hz, 10.1 Hz, 7.9 Hz, 7.9 Hz, 2H), 4.98 - 4.86 (m, 4H), 2.15 – 2.10 (m, 4H).



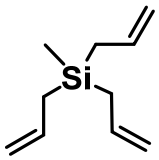
7

Diallyldimethylsilane (7)[1]: NMR spectrum matched with the compound prepared by monoallylation. The product was isolated with a yield of 40%.



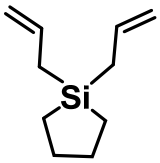
8

Diallyl(methyl)(phenyl)silane (8)[1]: 78% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.53 - 7.33 (m, 5H), 5.88 - 5.67 (m, 2H), 4.94 - 4.83 (m, 4H), 1.84 – 1.79 (m, 4H), 0.29 (s, 3H).



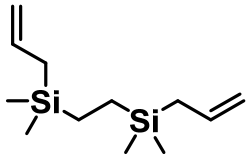
9

Triallyl(methyl)silane (9)[4]: 79% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.88 - 5.67 (m, 3H), 4.92 - 4.83 (m, 6H), 1.59 - 1.55 (m, 6H), 0.00 (s, 3H).



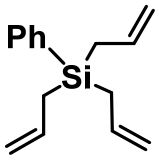
10

1,1-Diallylsilolane (10)[5]: 50% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.90 – 5.69 (m, 2H), 4.94 - 4.81 (m, 4H), 1.64 (td, *J* = 8.1 Hz, 1.1 Hz, 4H), 1.58 - 1.50 (m, 4H, merged with $CDCl_3$ moisture), 0.61 - 0.54 (m, 4H).



12

1,2-Bis(allyldimethylsilyl)ethane (12)[6]: 81% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.89 – 5.67 (dddd, *J* = 18.4 Hz, 10.5 Hz, 8.1 Hz, 8.1 Hz, 1H), 4.89 - 4.83 (m, 2H), 4.79 (m, 2H), 1.52 (m, 4H), 0.41 (s, 4H), -0.03 (s, 12H).

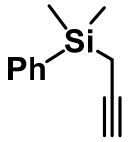


11

Triallyl(phenyl)silane (11)[4]: Allyl bromide (0.48 mL, 5.7 mmol), Zn dust (373 mg, 5.7 mmol) and phenyltrichlorosilane (0.16 mL, 0.95 mmol) was taken in dry THF (15 mL) and was sonicated for about 10 min. Work up was done as mentioned in the above procedure and the product was purified by silica gel column chromatography (pet ether) to afford **11** (130 mg, 60% yield). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.55 - 7.48 (m, 2H), 7.40 - 7.32 (m, 3H), 5.90 - 5.69 (dddd, *J* = 18.1 Hz, 10.1 Hz, 7.9 Hz, 7.9 Hz, 3H), 4.97 – 4.86 (m, 6H), 1.87 (d, *J* = 8.0 Hz, 6H).

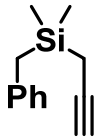
General procedure for the synthesis of monopropargylsilanes from monochlorosilanes.

Propargyl bromide (2 mmol), Zn dust (2 mmol) and monochlorosilane (1 mmol) was taken in dry THF (5 mL) and was sonicated for about 10 min. Work up was done as mentioned in the above procedure and the product was purified by column chromatography with silica gel (100-200) using pet ether.



13

Dimethyl(phenyl)(prop-2-yn-1-yl)silane (13)[7]: 98% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.59 - 7.53 (m, 2H), 7.41 - 7.36 (m, 3H), 1.86 (t, *J* = 2.9 Hz, 1H), 1.72 (d, *J* = 2.9 Hz, 2H), 0.40 (s, 6H).

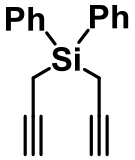


14

Benzyldimethyl(prop-2-yn-1-yl)silane (14): 82% yield; IR υ_{max}(film): cm^{-1} 3313, 3025, 2959, 2117, 1726, 1601, 1494, 1251, 1208; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.24 - 6.96 (m, 5H), 2.21 (s, 2 H), 1.88 (t, *J* = 3.0 Hz, 1H), 1.46 - 1.43 (m, 2H), 0.09 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.3, 128.3 (2C), 128.1 (2C), 124.2, 82.1, 67.3, 24.2, 4.9, -4.2 (2C); MS (70 eV) m/z 188.

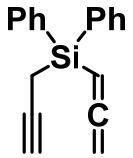
General procedure for the synthesis of dipropargylsilanes from dichlorosilanes.

Propargyl bromide (4 mmol), Zn dust (4 mmol) and Dichlorosilane (1 mmol) was taken in dry THF (10 mL) and the same procedure mentioned above was followed.



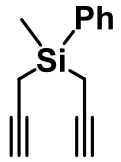
15a

Diphenyldi(prop-2-yn-1-yl)silane (15a)[8]: 45% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.68-7.63 (m, 4H), 7.49- 7.35 (m, 6H), 2.20 (d, *J* = 2.9 Hz, 4H), 1.90 (t, *J* = 2.9 Hz, 2H).



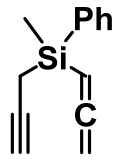
15b

Diphenyl(prop-2-yn-1-yl)(propa-1,2-dien-1-yl)silane (15b): 5% yield; IR υ_{max}(film): cm^{-1} 3256, 3070, 2951, 2252, 1930, 1653, 1557, 1428; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.67 - 7.59 (m, 4H), 7.44 - 7.33 (m, 6H), 5.33 (t, *J* = 7.1 Hz, 1H), 4.47 (d, *J* = 7.2 Hz, 2H), 2.14 (d, *J* = 3.0 Hz, 2H), 1.86 (t, *J* = 2.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.1, 135.0 (4C), 133.3 (2C), 130.0 (2C), 127.9 (4C), 80.9, 75.9, 68.7, 68.6, 4.3; MS (70 eV) m/z 260.



16a

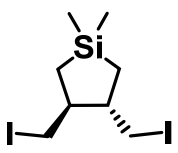
Methyl(phenyl)di(prop-2-yn-1-yl)silane (16a)[8]: 51% yield; ^{1}H NMR (200 MHz $CDCl_3$) δ 7.67 - 7.61 (m, 2H), 7.44 - 7.36 (m, 3H), 1.93 – 1.86 (m, 6H), 0.52 (s, 3H).



16b

Methyl(phenyl)(prop-2-yn-1-yl)(propa-1,2-dien-1-yl)silane (16b): 10% yield; IR υ_{max}(film): cm^{-1} 3295, 3071, 2924, 2182, 2104, 1931, 1429, 1216, 1115; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 - 7.58 (m, 2H), 7.43 - 7.35 (m, 3H), 5.14 (t, *J* = 7.1 Hz, 1H), 4.45 (d, *J* = 7.2 Hz, 2H), 1.86 - 1.84 (m, 3H), 0.51 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 214.2, 135.4, 134.0 (2C), 129.8, 127.9 (2C), 81.3, 77.1, 68.2, 67.9, 5.3, -4.9; MS (70 eV) m/z 197.

Synthesis of intermediate 17[9]

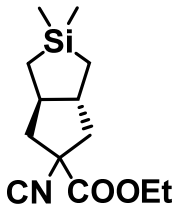


17

(**3S*,4S*)-3,4-bis(iodomethyl)-1,1-dimethylsilolane (17)**: A two neck RB was charged with dichlorozirconocene (3.2 g, 10.94 mmol) and flushed with Argon. Dry THF (15 mL) was

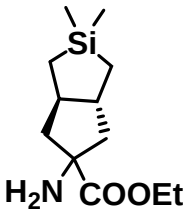
added, cooled to -78 °C and n-BuLi (16.4 mL, 1.6 M in hexanes, 26.3 mmol) was added dropwise so as to generate bis(cyclopentadienyl)zirconium. The yellow solution obtained was stirred at the same temperature for 1h. Then a solution of diallyldimethylsilane (2 mL, 10.94 mmol) in dry THF was added and the reaction was allowed to warm to rt and stirring was continued. After 10 h, the reaction mixture was cooled to -78 °C and a solution of Iodine (5.6 g, 21.88 mmol) in THF was added, warmed to rt and allowed to stir at rt for 1h. The reaction mixture was quenched with 1*N* H_2SO_4, diethyl ether was added and the organic layer was separated. This layer was then washed with aq. Sodium thiosulphate solution so as to remove excess iodine, dried over Na_2SO_4 and concentrated. The crude was then purified by column chromatography (silica gel 100-200, pet ether) to afford the compound as a light yellow liquid (2.2 g, 51%).

Synthesis of unnatural α- amino acid



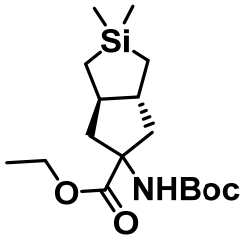
18

Ethyl (3aS*,6aS*)-5-isocyano-2,2-dimethyloctahydrocyclopenta[c]silole-5-carboxylate (18): Ethylisocyanoacetate (0.06 mL, 0.51 mmol) was taken in dry acetonitrile (5 mL), added K_2CO_3 (282 mg, 2.04 mmol), a pinch of 18-crown-6 and stirred for 5 min. Then a solution of **17** (200 mg, 0.51 mmol) in acetonitrile (5 mL) was added and refluxed overnight. The reaction mass was cooled to rt, added water and the organic layer was separated, washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was then purified by column chromatography (silica gel 100-200, 2% ethyl acetate- pet ether) to afford the compound as a light yellow liquid (95 mg, 74%). IR υ_{max}(film): cm^{-1} 2134, 1742, 1253, 1027; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.26 (q, *J* = 7.0 Hz, 2H), 2.65 - 2.61 (m, 1H), 2.36 - 2.32 (m, 1H), 1.97 - 1.81 (m, 2H), 1.75 - 1.65 (m, 2H), 1.33 (t, *J* = 7.0 Hz, 3H), 0.94 - 0.88 (m, 4H), 0.20 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 157.3, 69.0, 62.6, 50.3, 49.2, 47.0, 46.9, 16.9, 16.4, 14.0, -0.8 (2C); HRMS (ESI): m/z calculated for $C_{13}H_{21}NO_2NaSi$ $[M + Na]^+$ 274.1234, found 274.1228.



19

Ethyl (3aS*,6aS*)-5-amino-2,2-dimethyloctahydrocyclopenta[c]silole-5-carboxylate (19): To a solution of **18** (80 mg, 0.32 mmol) in ethanol (2 mL) was added a drop of con. HCl and stirred at rt for 30 min. Ethanol was removed and to the residue DCM and water were added and the aqueous layer was separated. It was then neutralised with *2N* NaOH, and the aqueous layer was extracted with DCM, dried over Na_2SO_4 and concentrated under vacuum to give the pure compound (70 mg, 91%). IR υ_{max}(film): cm^{-1} 3220, 2955, 2933, 1728, 1248, 1192, 1030, 840; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.17 (q, *J* = 7.0 Hz, 2H), 2.41 - 2.37 (m, 1H), 2.11 (m, 3H), 1.92 - 1.84 (m, 1H), 1.78 - 1.64 (m, 3H), 1.28 (t, *J* = 7.0 Hz, 3H), 0.90 - 0.84 (m, 4H), 0.16 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.0, 66.6, 61.2, 51.2, 49.0, 46.6, 45.9, 17.4, 17.0, 14.2, -0.7 (2C); HRMS (ESI): m/z calculated for $C_{12}H_{24}NO_2Si$ $[M + H]^+$ 242.1571, found 242.1568.

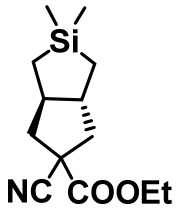


20

Ethyl (3aS*,6aS*)-5-((tert-butoxycarbonyl)amino)-2,2-dimethyloctahydrocyclopenta[c]silole-5-carboxylate (20): To a solution of **19** (20 mg, 0.083 mmol) in DCM (2 mL) was added triethylamine (17 μL, 0.124 mmol), Boc anhydride (28 μL, 0.124 mmol) and stirred at rt for 3h. To the reaction mixture, water was added and the organic layer was separated. The aqueous layer was extracted with DCM and the combined organic layer was dried over Na_2SO_4, concentrated under reduced pressure and purified by column chromatography (silica gel 100-200 mesh, 5% ethyl acetate - pet ether). The product was obtained as a yellow solid (23 mg, 82%). IR υ_{max}(film): cm^{-1} 3300, 2955, 1707, 1499, 1249, 1208, 839; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.03 (br s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.55 (m, 1H), 1.97 – 1.69 (m, 4H), 1.43 (s, 9H), 1.36 (m, 1H), 1.29 – 1.24 (m, 4H), 0.89 – 0.83 (m, 3H), 0.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 155.0, 79.5, 67.6,

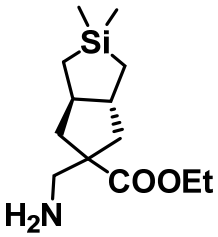
61.2, 50.1, 49.1, 45.5, 44.5, 28.3, 17.2, 17.0, 14.2, -0.71 (2C); HRMS (ESI): m/z calculated for $C_{17}H_{31}NO_4NaSi$ $[M + Na]^+$ 364.1915, found 364.1910.

Synthesis of unnatural β- amino acid



21

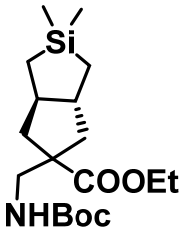
Ethyl (3aS*,6aS*)-5-cyano-2,2-dimethyloctahydrocyclopenta[c]silole-5-carboxylate (21): To a solution of ethylcyanoacetate (0.11 mL, 1.01 mmol) in dry acetonitrile (40 mL) was added K_2CO_3 (419 mg, 3.03 mmol), a pinch of 18-crown-6 and stirred for 5 min. Then a solution of **17** (400 mg, 1.01 mmol) in acetonitrile (20 mL) was added and refluxed overnight. The reaction mass was cooled to rt, added DCM (30 mL) and water (10 mL) and the organic layer was separated, washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude mass was then purified by column chromatography (silica gel 100-200 mesh, 2% ethyl acetate- pet ether) to afford the compound as a colorless liquid (220 mg, 87%). IR υ_{max}(film): cm^{-1} 2894, 2200, 1742, 1250, 1211, 1159, 882; ^1H NMR (400 MHz, $CDCl_3$) δ 4.25 (q, *J* = 7.3 Hz, 2H), 2.55 - 2.47 (m, 2H), 1.86 - 1.70 (m, 4H), 1.33 (t, *J* = 7.3 Hz, 3H), 0.94 - 0.88 (m, 4H), 0.19 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 122.2, 62.7, 50.4, 50.1, 48.1, 43.7, 43.1, 16.7, 16.4, 14.0, -0.71, -0.74; HRMS (ESI): m/z calculated for $C_{13}H_{22}NO_2Si$ $[M + H]^+$ 252.1414, found 252.1412.



22

Ethyl (3aS*,6aS*)-5-(aminomethyl)-2,2-dimethyloctahydrocyclopenta[c]silole-5-carboxylate (22): A solution of **21** (45 mg, 0.179 mmol) in ethanol (5 mL) was taken in a hydrogenation reaction bottle, Raney Ni in EtOH (cat. amount) was added and hydrogenated under a pressure of 60 psi in a parr hydrogenator for 4h. The reaction mass was filtered through celite, excess Ni was quenched with 1*N* HCl and the filtrate was concentrated under reduced pressure. The crude was purified by column chromatography (neutral alumina, 2%

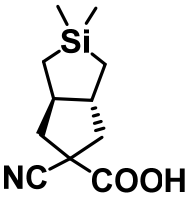
methanol- DCM) to afford the compound as a light yellow sticky solid (28 mg, 62%). IR υ_{max}(film): cm^{-1} 3300, 2933, 1722, 1248, 1157, 839; ^1H NMR (400 MHz, $CDCl_3$) δ 4.16 (q, *J* = 7.1 Hz, 2H), 2.91 - 2.78 (m, 2H), 2.30 - 2.25 (m, 1H), 1.81 - 1.76 (m, 1H), 1.71 - 1.41 (m, 4H, merged with $CDCl_3$ moisture), 1.27 (t, *J* = 7.1 Hz, 3H), 1.06 - 0.99 (m, 1H), 0.91- 0.81 (m, 3H), 0.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 60.4, 58.1, 50.8, 50.3, 49.5, 41.1, 40.2, 17.4, 17.2, 14.2, -0.69, -0.72; HRMS (ESI): m/z calculated for $C_{13}H_{26}NO_2Si$ $[M + H]^+$ 256.1727, found 256.1726.



23

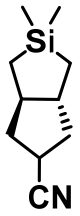
Ethyl (3aS*,6aS*)-5-(((tert-butoxycarbonyl)amino)methyl)-2,2-dimethyloctahydrocyclopenta[c]silole-5-carboxylate (23): To a solution of **21** (40 mg, 0.159 mmol) in ethanol (5 mL) was added Boc anhydride (55 μL, 0.238 mmol), Raney Ni in EtOH (catalytic) and hydrogenated under a pressure of 60 psi in a parr hydrogenator for 4h. The reaction mass was filtered through celite and the filtrate was concentrated under reduced pressure and purified by column chromatography (silica gel 100-200, 5% ethyl acetate- pet ether) to afford the compound as a light yellow liquid (40 mg, 71%). IR υ_{max}(film): cm^{-1} 3460, 3379, 1716, 1502, 1247, 1160; ^1H NMR (400 MHz, $CDCl_3$) δ 5.05 (br s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.35 - 3.22 (m, 2H), 2.11 (dd, *J* = 12.8, 6.2 Hz, 1H), 1.83 - 1.49 (m, 4H), 1.43 (s, 9H), 1.29 - 1.25 (m, 4H), 1.08 (t, *J* = 11.5 Hz, 1H), 0.95 - 0.78 (m, 3H), 0.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 156.3, 79.0, 60.7, 56.2, 50.5, 49.3, 47.5, 41.2, 39.9, 28.4 (3C), 17.3, 17.1, 14.1, -0.71, -0.68; HRMS (ESI): m/z calculated for $C_{18}H_{33}NO_4NaSi$ $[M + Na]^+$ 378.2071, found 378.2069.

Synthesis of new GABA analogue[10]



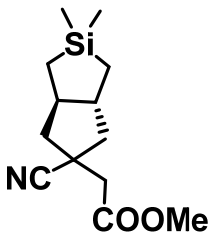
(3aS*,6aS*)-5-cyano-2,2-dimethyloctahydrocyclopenta[c]silole-5-carboxylic acid: To a solution of **21** (1.5 g, 5.97 mmol) in ethanol (20 mL) was added aq. KOH (670 mg, 11.94

mmol) and refluxed for 3h. The reaction mass was cooled to rt and the solvent was removed under reduced pressure. The solid obtained was dissolved in minimal amount of water and washed with diethyl ether. The aqueous layer was separated, neutralized with 1*N* HCl and the product was extracted with ethylacetate, dried over Na_2SO_4 and concentrated under vacuum to afford the compound as a light brown solid (1.35 g, 100%). IR υ_{max}(film): cm^{-1} 3100 (broad peak), 2953, 1718, 1250, 1161; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.61 - 2.52 (m, 2H), 1.91 - 1.72 (m, 4H), 1.07 - 0.89 (m, 4H), 0.20 (s, 3H), 0.19 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 121.4, 50.4, 50.2, 48.2, 43.7, 43.2, 16.7, 16.4, -0.72 (2C); HRMS (ESI): m/z calculated for $C_{11}H_{17}NO_2NaSi$ $[M + Na]^+$ 246.0921, found 246.0917.



24

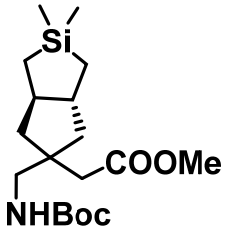
(3aS*,6aS*)-2,2-dimethyloctahydrocyclopenta[c]silole-5-carbonitrile (24): (3aS*****,6aS*****)-5-cyano-2,2-dimethyloctahydrocyclopenta[c]silole-5-carboxylic acid (150 mg, 0.671 mmol) obtained in the previous step was dissolved in DMSO (2 mL) and heated at 150 °C for 6h. The reaction mass was cooled to rt, added diethyl ether and the organic layer was separated. The aqueous layer was again extracted with ether, dried over Na_2SO_4 and the solvent was removed. The crude mass was then purified by column chromatography (silica gel 100-200, 20% DCM- pentane) to afford the compound as a colorless liquid (84 mg, 70%). IR υ_{max}(film): cm^{-1} 2260, 1259; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.07- 3.00 (m, 1H), 2.30 - 2.23 (m, 1H), 2.15 - 2.10 (m, 1H), 1.75 - 1.63 (m, 1H), 1.56 - 1.37 (m, 3H), 1.03 - 0.86 (m, 4H), 0.17 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.5, 50.8, 50.0, 37.0, 36.3, 27.9, 16.8 (2C), -0.75 (2C); MS (70 eV) m/z 179.



25

Methyl 2-((3aS*,6aS*)-5-cyano-2,2-dimethyloctahydrocyclopenta[c]silol-5-yl)acetate (25)[11]: A solution of **24** (70 mg, 0.39 mmol) in dry THF (2 mL) was cooled to -78 °C, NaHMDS in THF (0.6 mL, 1M in THF, 0.59 mmol) was added and stirred for 5 min. Then a

solution of 3,3-dimethylallylbromide (54 μL, 0.47 mmol) in THF (1 mL) was added at the same temperature, the reaction mass was allowed to warm to 0 °C and then quenched by drop wise addition of sat. NH_4Cl. Diethyl ether was added, the organic layer was separated and the aqueous layer was extracted again with diethyl ether, dried over Na_2SO_4 and concentrated. The crude mass was then subjected to purification by column chromatography (silica gel 100-200 mesh, 1% ethyl acetate- pet ether) to afford the compound as a mixture along with a very close spot (40 mg, 0.162 mmol). This mixture was dissolved in DCM (10 mL), added 2.5 *M* methanolic NaOH (0.32 mL, 0.808 mmol) cooled to -78 °C and a stream of ozone was passed till the initial yellow precipitate disappeared and the characteristic blue color of ozone was attained (10 - 15 min). The reaction mass was warmed to rt, water was added and the organic layer was separated. The aqueous layer was re-extracted with DCM, the combined organic layers were dried over Na_2SO_4 and concentrated. The crude was then purified by column chromatography (silica gel 100-200, 5% ethylacetate- pet ether) to give the product as a colorless liquid (25 mg, 26% over two steps starting from **24**). IR υ_{max}(film): cm^{-1} 2233, 1740, 1437, 1248, 1196, 840; ^1H NMR (400 MHz, $CDCl_3$) δ 3.74 (s, 3H), 2.68 (AB quartet, 2H), 2.51 - 2.47 (m, 1H), 2.13 - 2.08 (m, 1H), 1.87 - 1.73 (m, 2H), 1.57 - 1.47 (m, 1H), 1.33 - 1.25 (m, 2H), 0.93 - 0.85 (m, 3H), 0.18 (s, 3H), 0.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 125.7, 52.0, 50.1, 49.2, 45.1, 43.99, 43.97, 39.9, 17.0, 16.8, -0.77 (2C); HRMS (ESI): m/z calculated for $C_{13}H_{21}NO_2NaSi$ $[M + Na]^+$ 274.1234, found 274.1232.



26

Methyl 2-((3aS*,6aS*)-5-((((l1-methyl)(l1-oxidanyl)boranyl)amino)methyl)-2,2-dimethyloctahydrocyclopenta[c]silol-5-yl)acetate (26): To a solution of **25** (20 mg, 0.08 mmol) in methanol (5 mL) was added Boc anhydride (28 μL, 0.119 mmol), Raney Ni in MeOH (catalytic) and hydrogenated under a pressure of 60 psi in a parr hydrogenator for 4h. The reaction mass was filtered through celite and the filtrate was concentrated under reduced pressure and purified by column chromatography (silica gel 100-200, 5% ethyl acetate- pet ether) to afford the compound as a light yellow liquid (22 mg, 78%). IR υ_{max}(film): cm^{-1} 3376, 2950, 1717, 1509, 1247, 1166; ^1H NMR (500 MHz, $CDCl_3$) δ 4.97 (br s, 1H), 3.67 (s, 3H), 3.23 (dd, *J* = 13.7, 7.3 Hz, 1H), 3.00 (dd, *J* = 13.7, 5.5 Hz, 1H), 2.36 (AB quartet, 2H),

1.83 - 1.78 (m, 2H), 1.56 – 1.28 (m, 13H), 1.01– 0.97 (m, 2H), 0.88 - 0.80 (m, 2H), 0.13 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.8, 156.4, 79.0, 51.4, 49.6, 49.4, 49.2, 48.1, 44.0, 42.6, 42.2, 28.4 (3C), 17.60, 17.57, -0.70, -0.74; HRMS (ESI): m/z calculated for $C_{18}H_{33}NO_4NaSi$ $[M + Na]^+$ 378.2071, found 378.2068.

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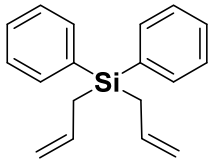
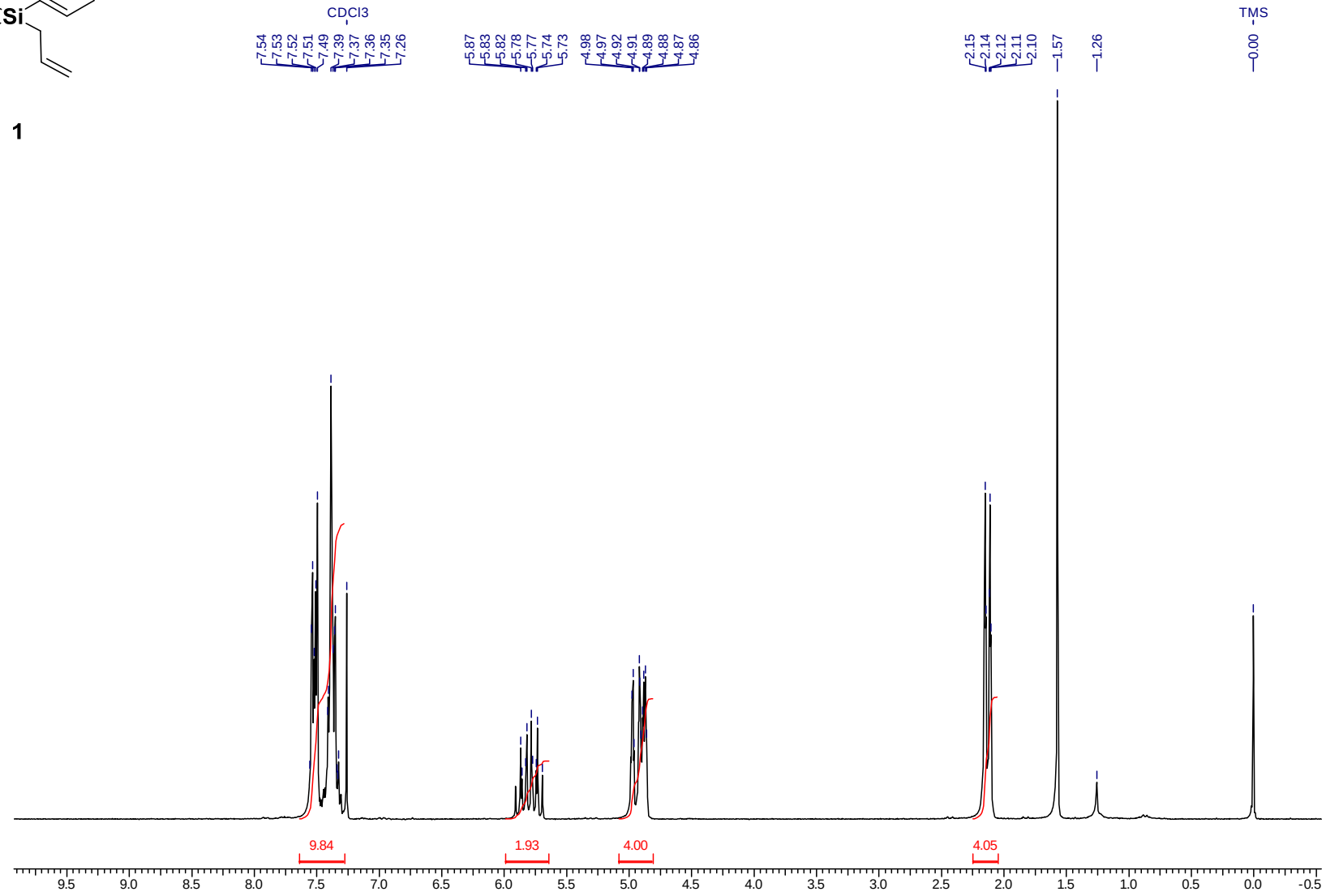

Si

1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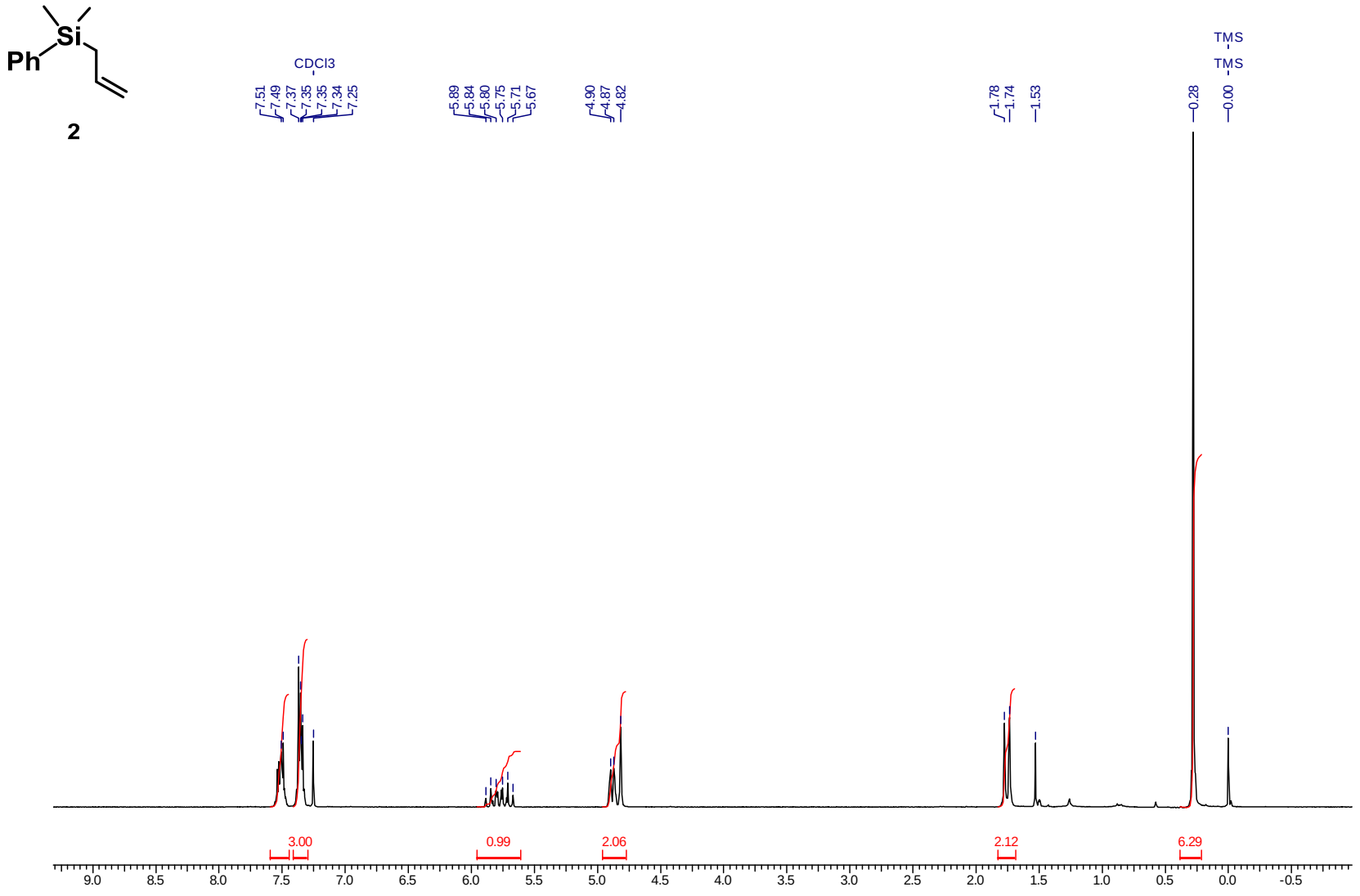
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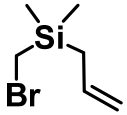
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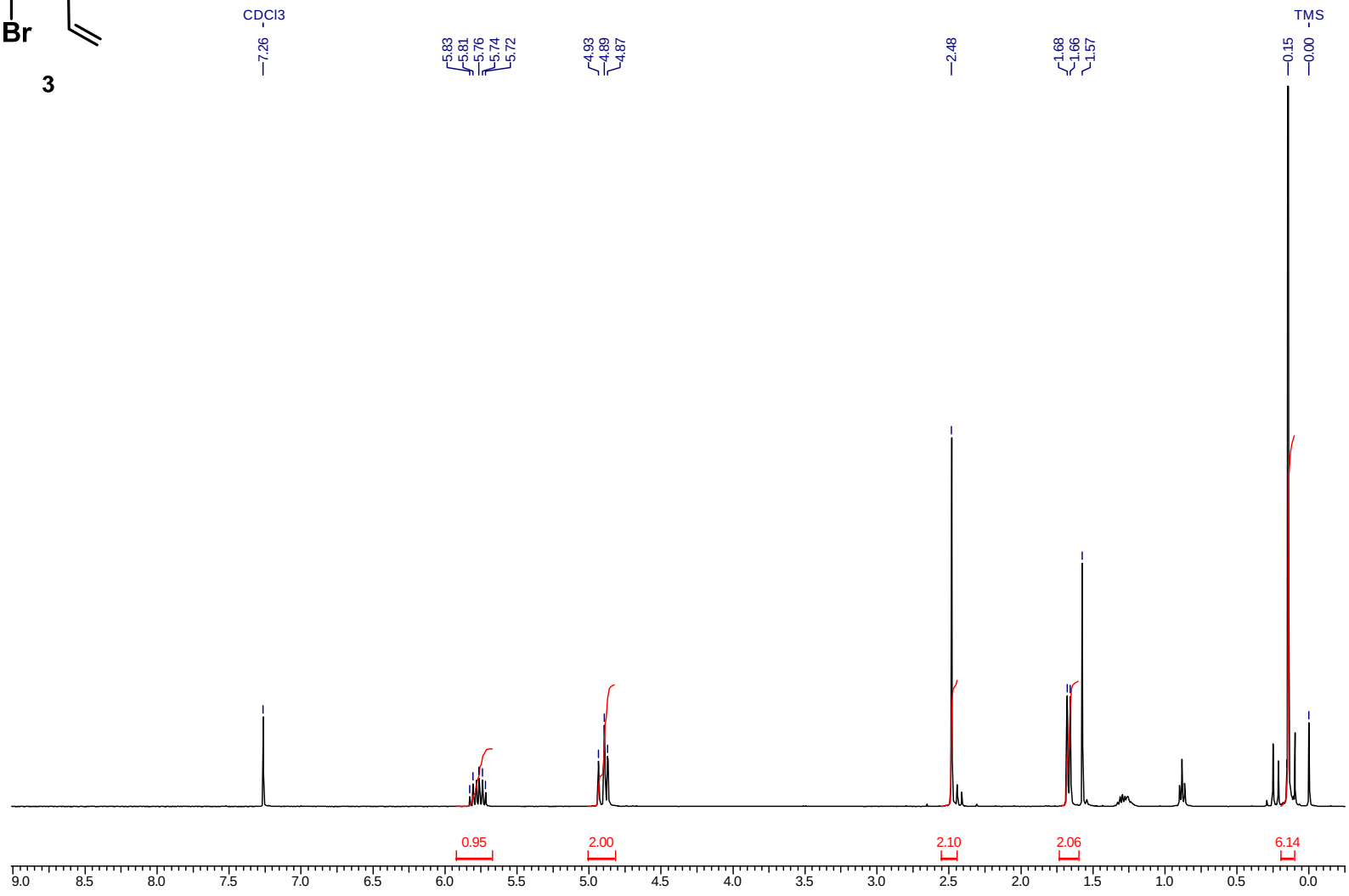
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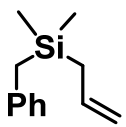
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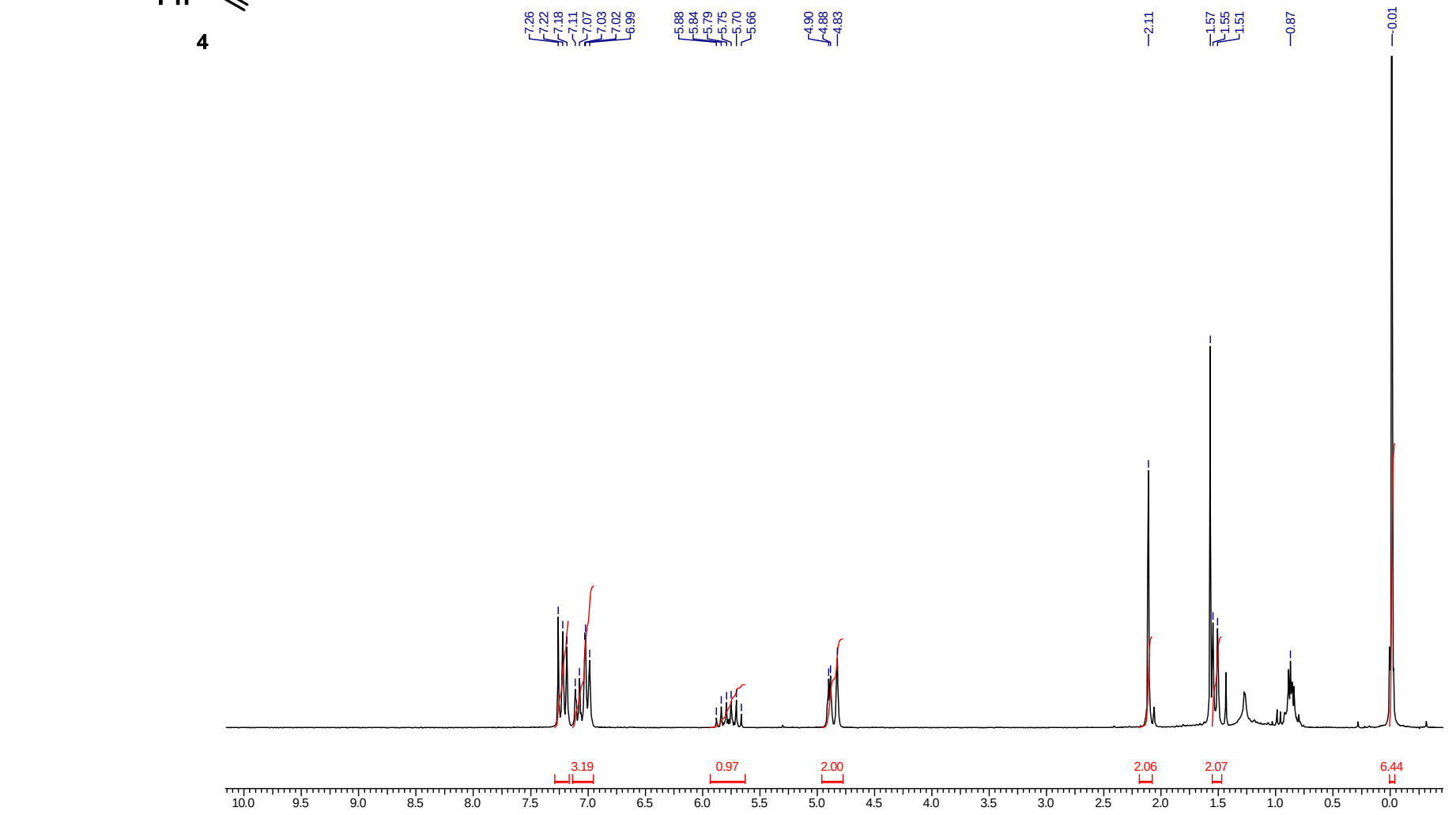
Ph

4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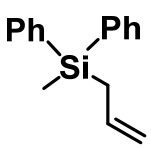
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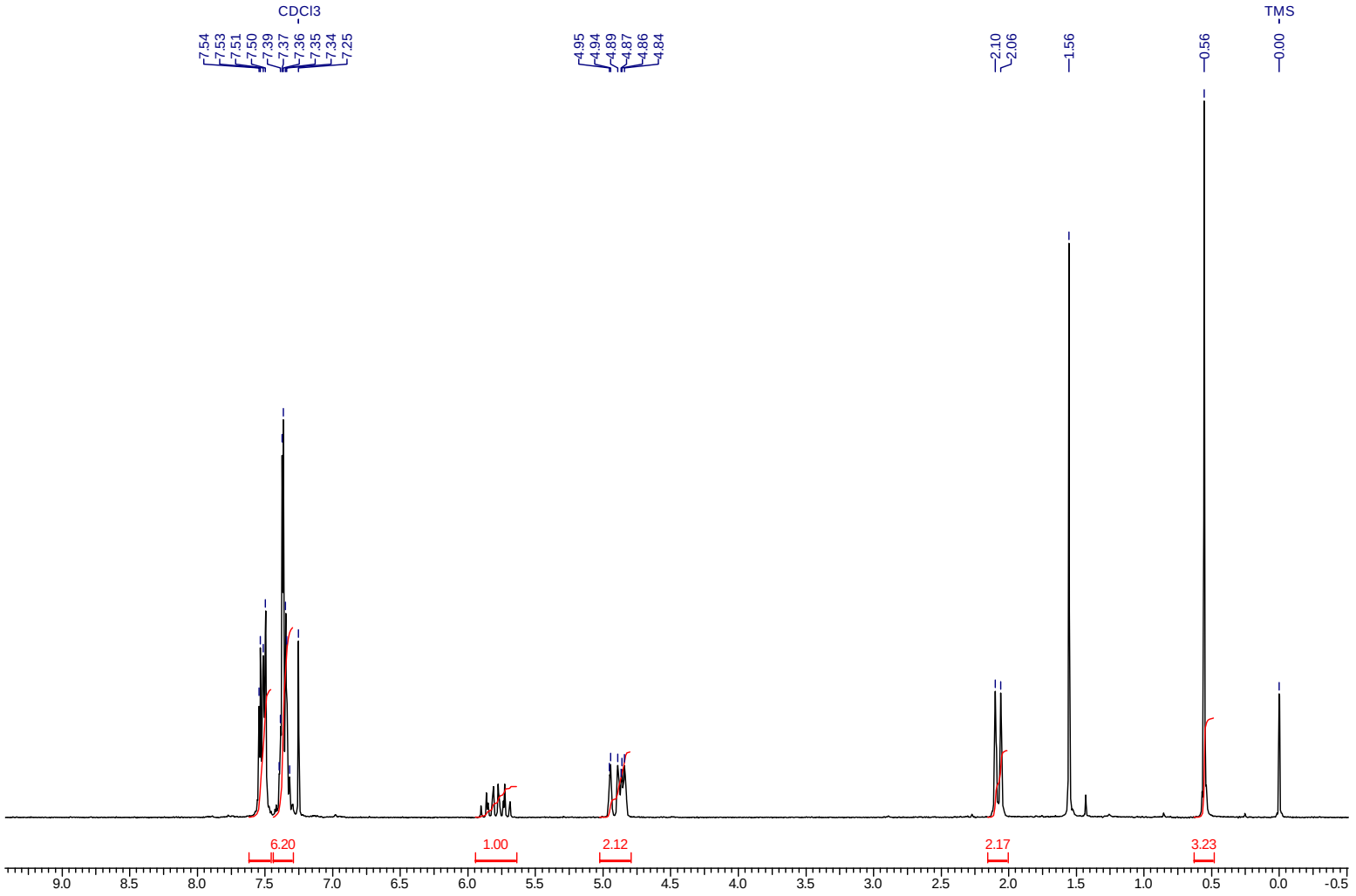
Ph
Si

5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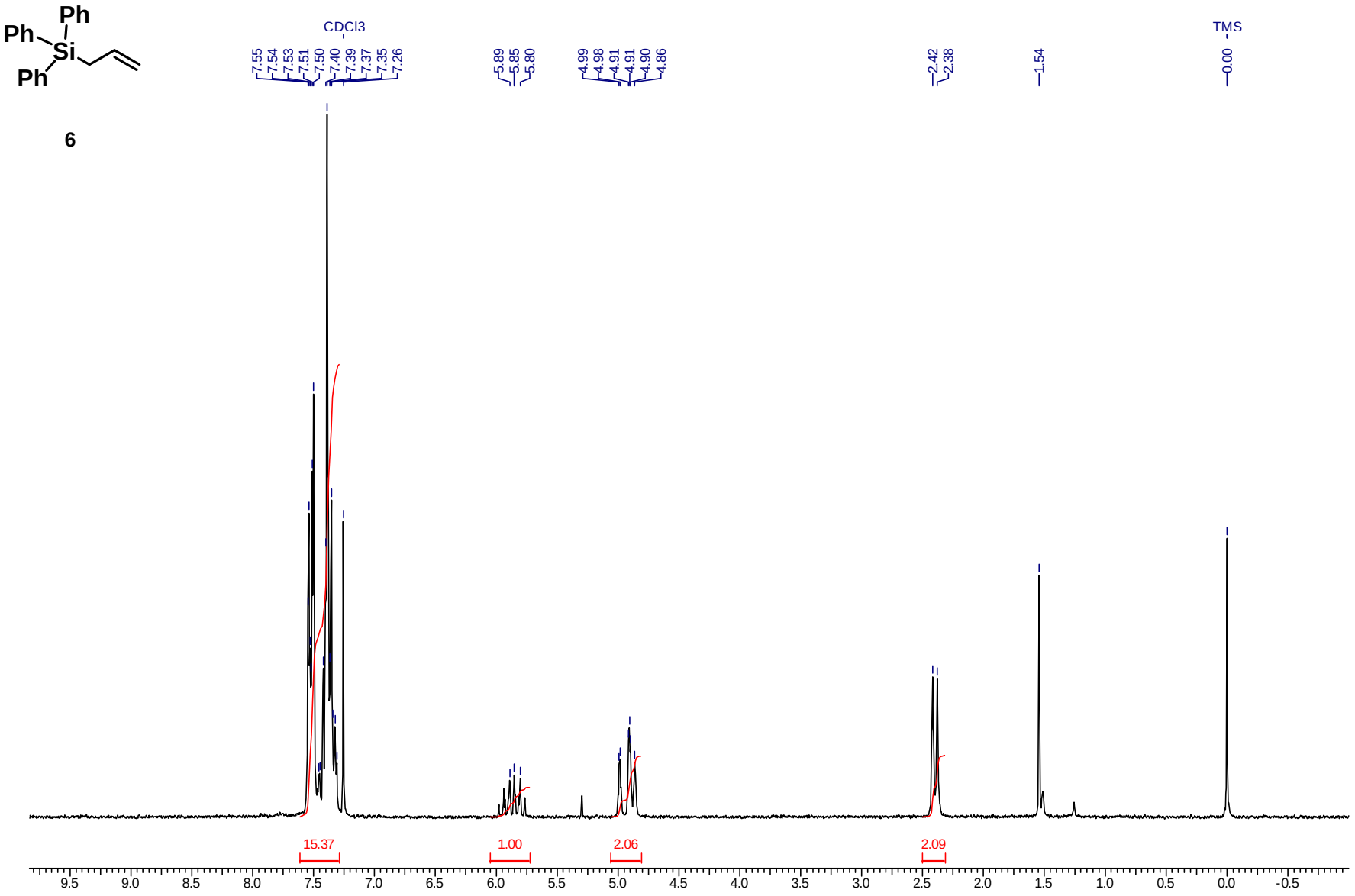
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4.98
4.91
4.91
4.90
4.86
2.42
2.38
1.54
0.00
15.37
1.00
2.06
2.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
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1.5
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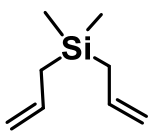
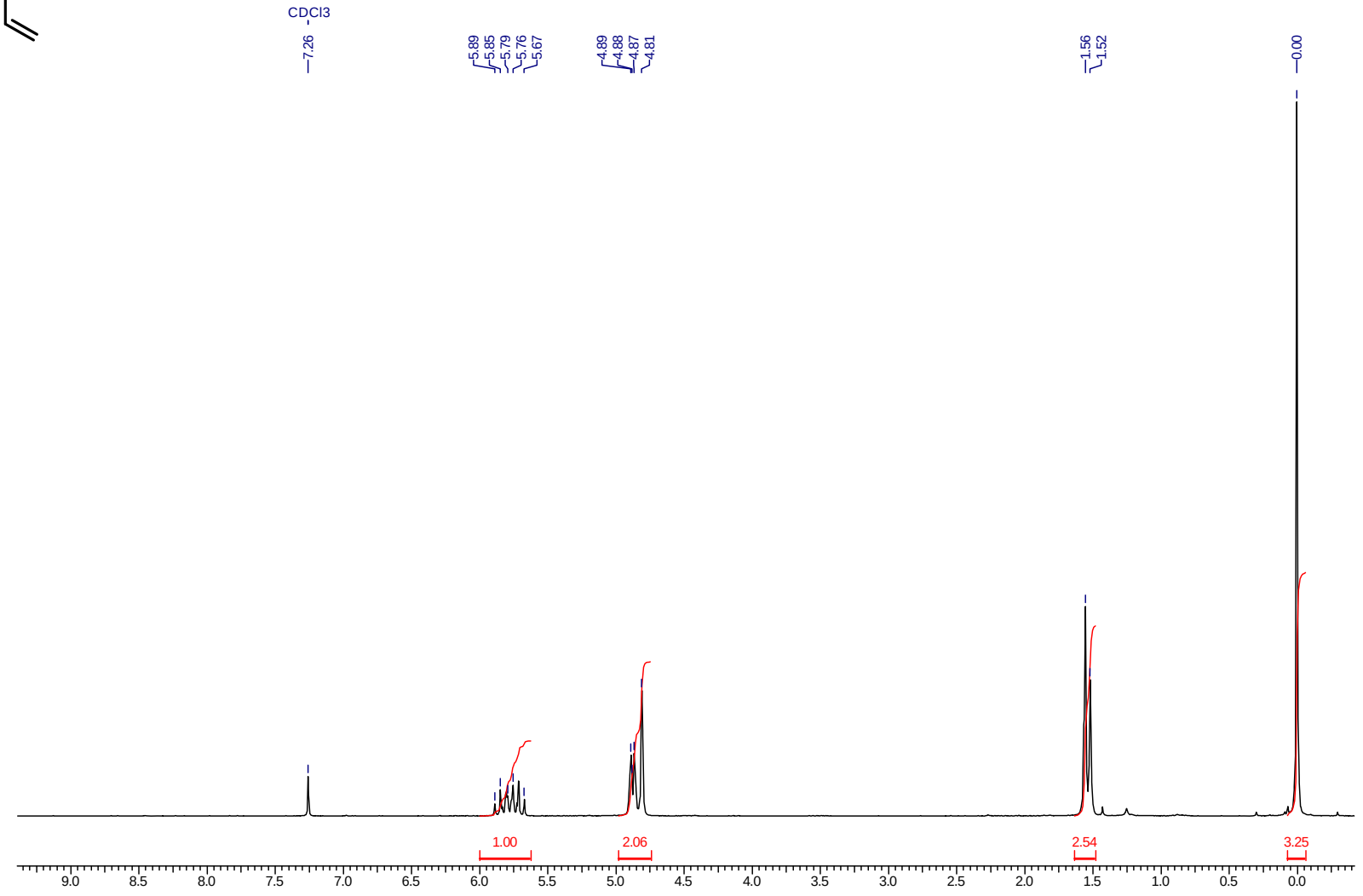
0.0
-0.5


Si

7


CDCl3
7.26
5.89
5.85
5.79
5.76
5.67
4.89
4.88
4.87
4.81
1.56
1.52
0.00
1.00
2.06
2.54
3.25
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
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1.0
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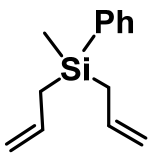
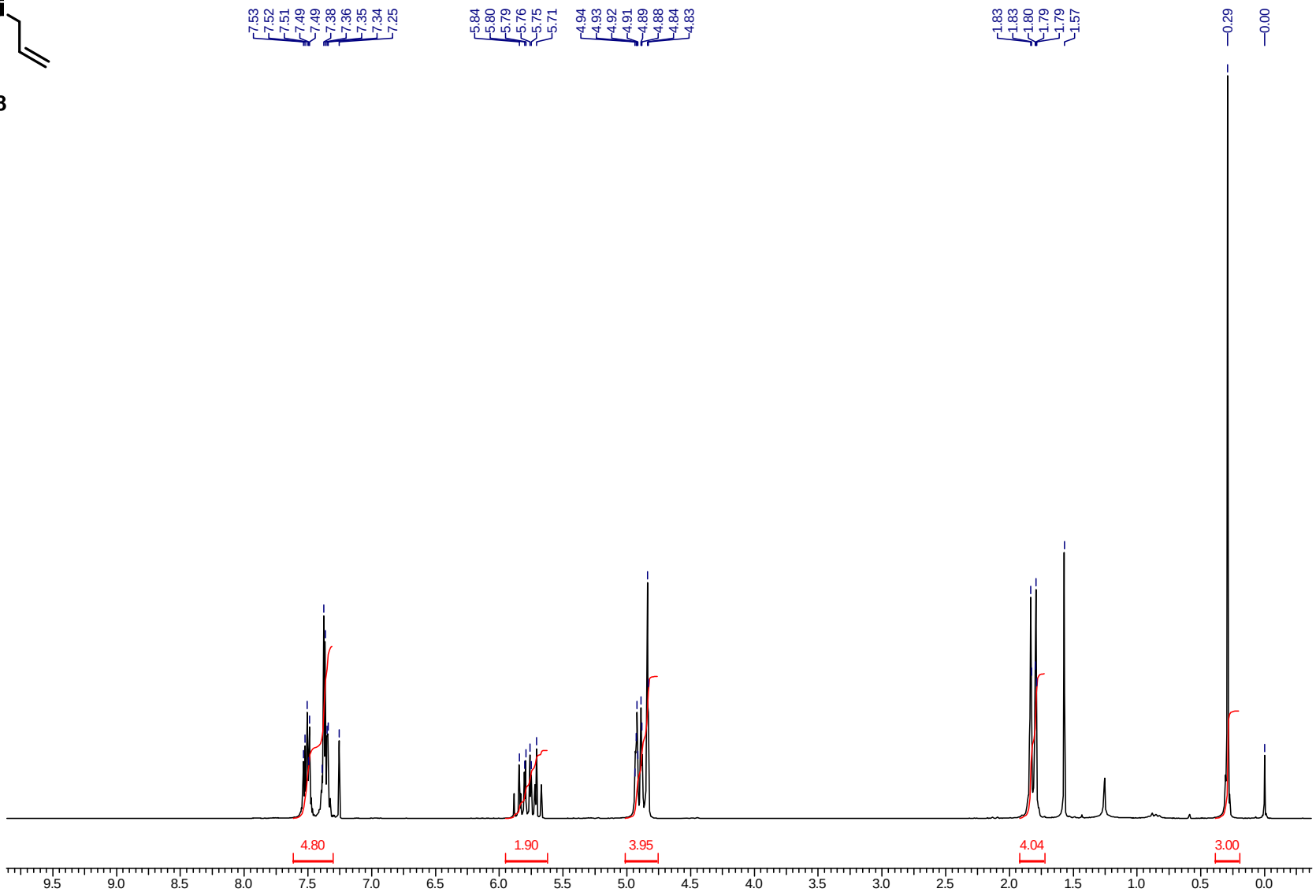
0.0


Ph
Si

8


7.53
7.52
7.51
7.49
7.49
7.38
7.36
7.35
7.34
7.25
5.84
5.80
5.79
5.76
5.75
5.71
4.94
4.93
4.92
4.91
4.89
4.88
4.84
4.83
1.83
1.83
1.80
1.79
1.79
1.57
0.29
0.00
4.80
1.90
3.95
4.04
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
4.0
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3.0
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2.0
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1.0
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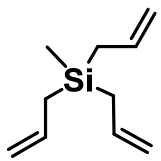
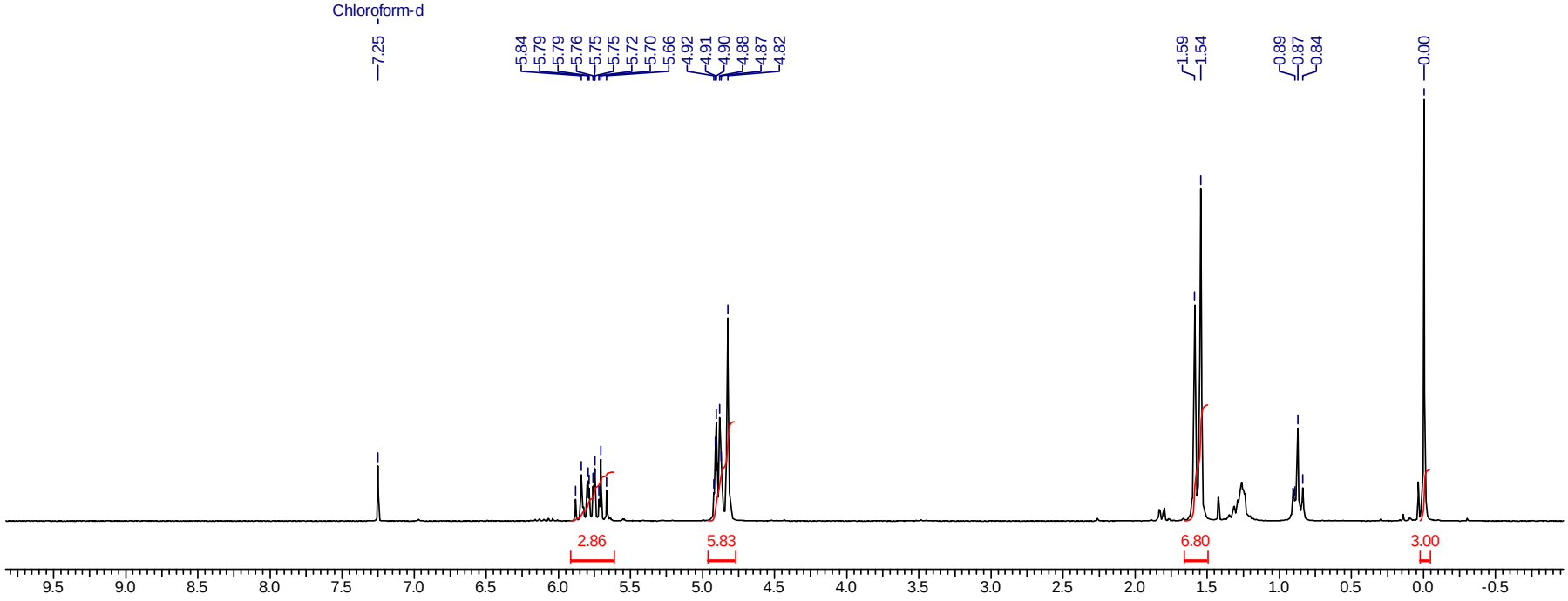
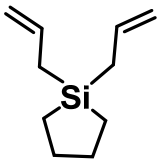
0.0

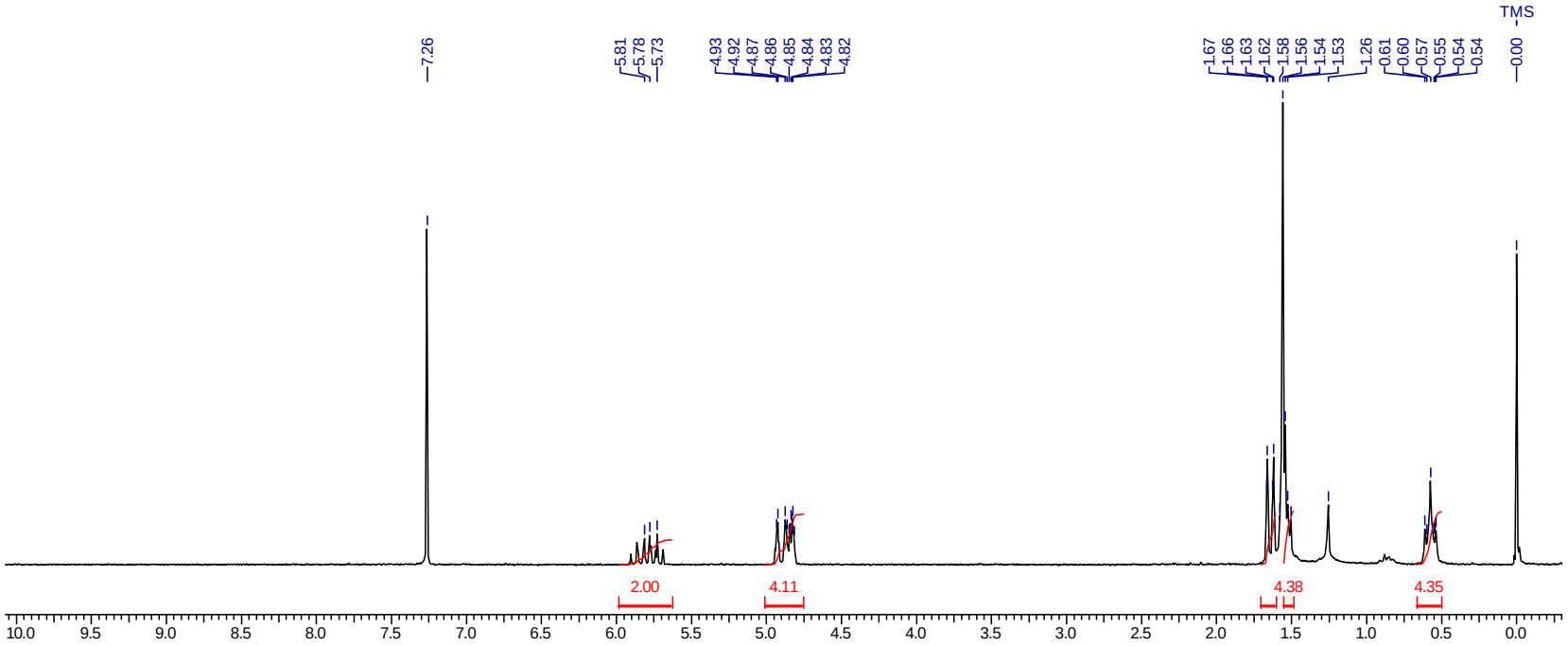

Si

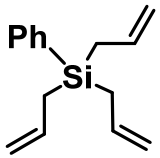
9


Chloroform-d
7.25
5.84
5.79
5.79
5.76
5.75
5.75
5.72
5.70
5.66
4.92
4.91
4.90
4.88
4.87
4.82
1.59
1.54
0.89
0.87
0.84
0.00
2.86
5.83
6.80
3.00
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

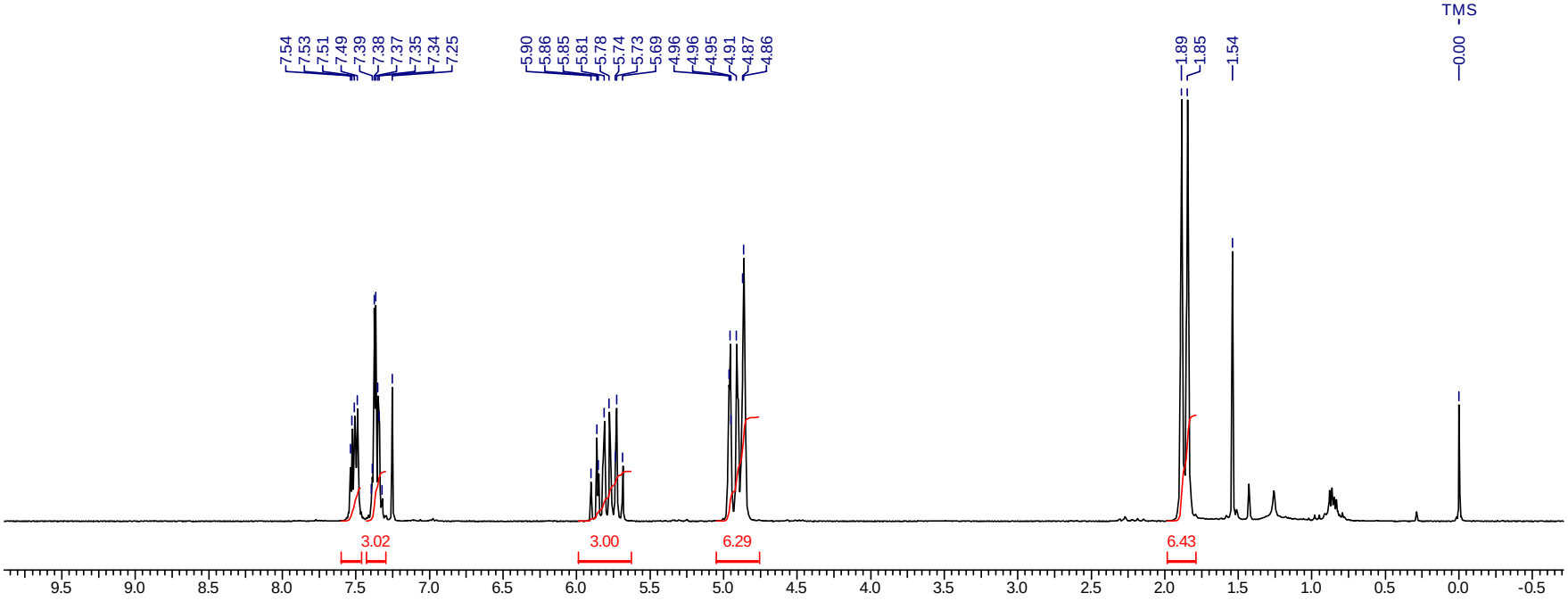

Si

10


TMS
7.26
5.81
5.78
5.73
4.93
4.92
4.87
4.86
4.85
4.84
4.83
4.82
1.67
1.66
1.63
1.62
1.58
1.56
1.54
1.53
1.26
0.61
0.60
0.57
0.55
0.54
0.54
0.00
2.00
4.11
4.38
4.35
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


Ph
Si

11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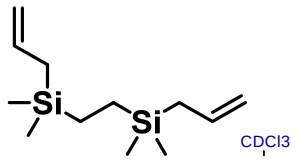
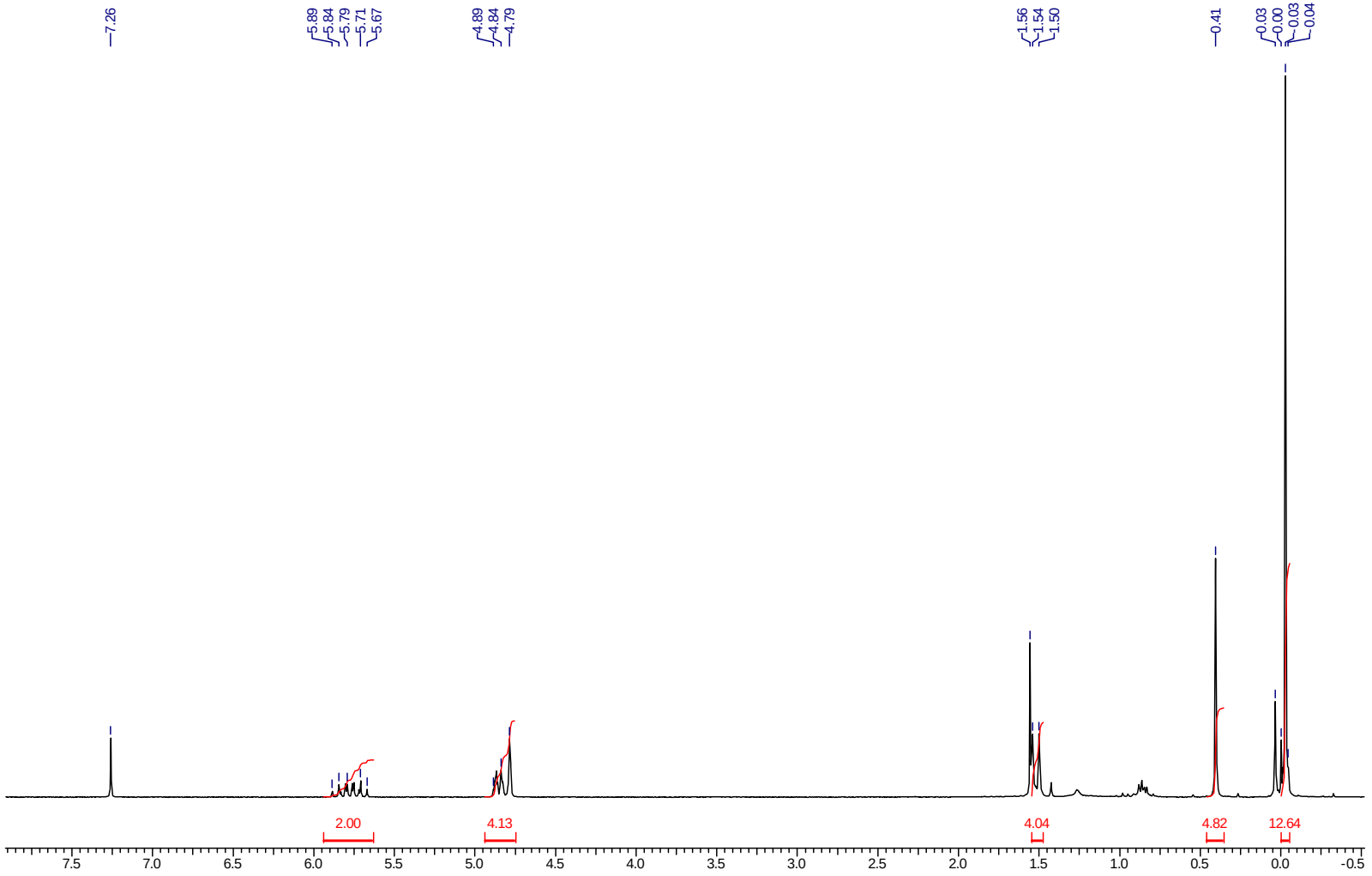
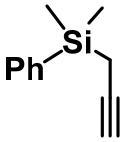
7.53
7.51
7.49
7.39
7.38
7.37
7.35
7.34
7.25
5.90
5.86
5.85
5.81
5.78
5.74
5.73
5.69
4.96
4.96
4.95
4.91
4.87
4.86
1.89
1.85
1.54
TMS
0.00
3.02
3.00
6.29
6.43
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

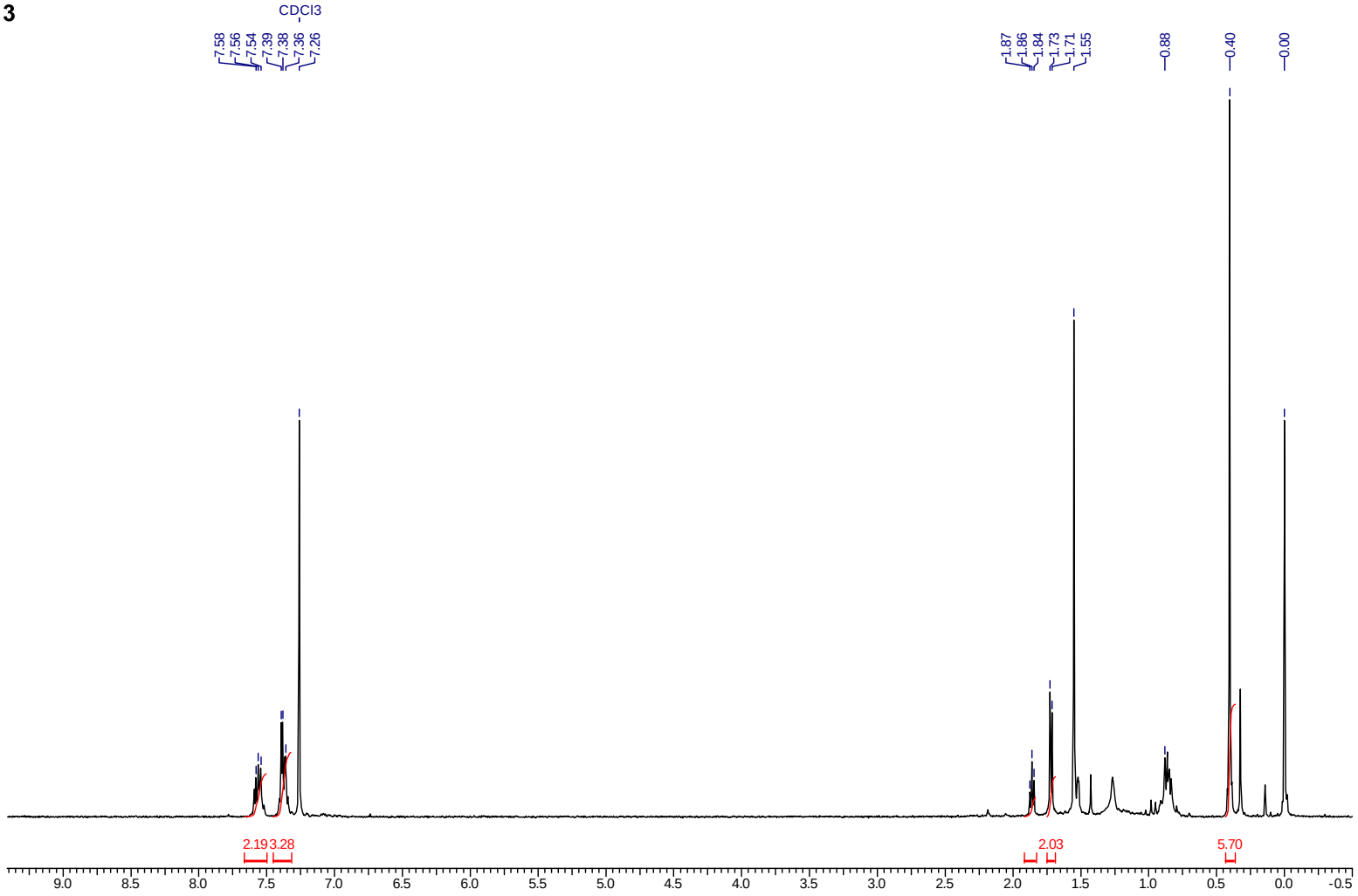

Si
Si

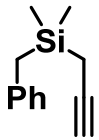
12


CDCl3
7.26
5.89
5.84
5.79
5.71
5.67
4.89
4.84
4.79
1.56
1.54
1.50
0.41
0.03
0.00
0.03
0.04
2.00
4.13
4.04
4.82
12.64
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

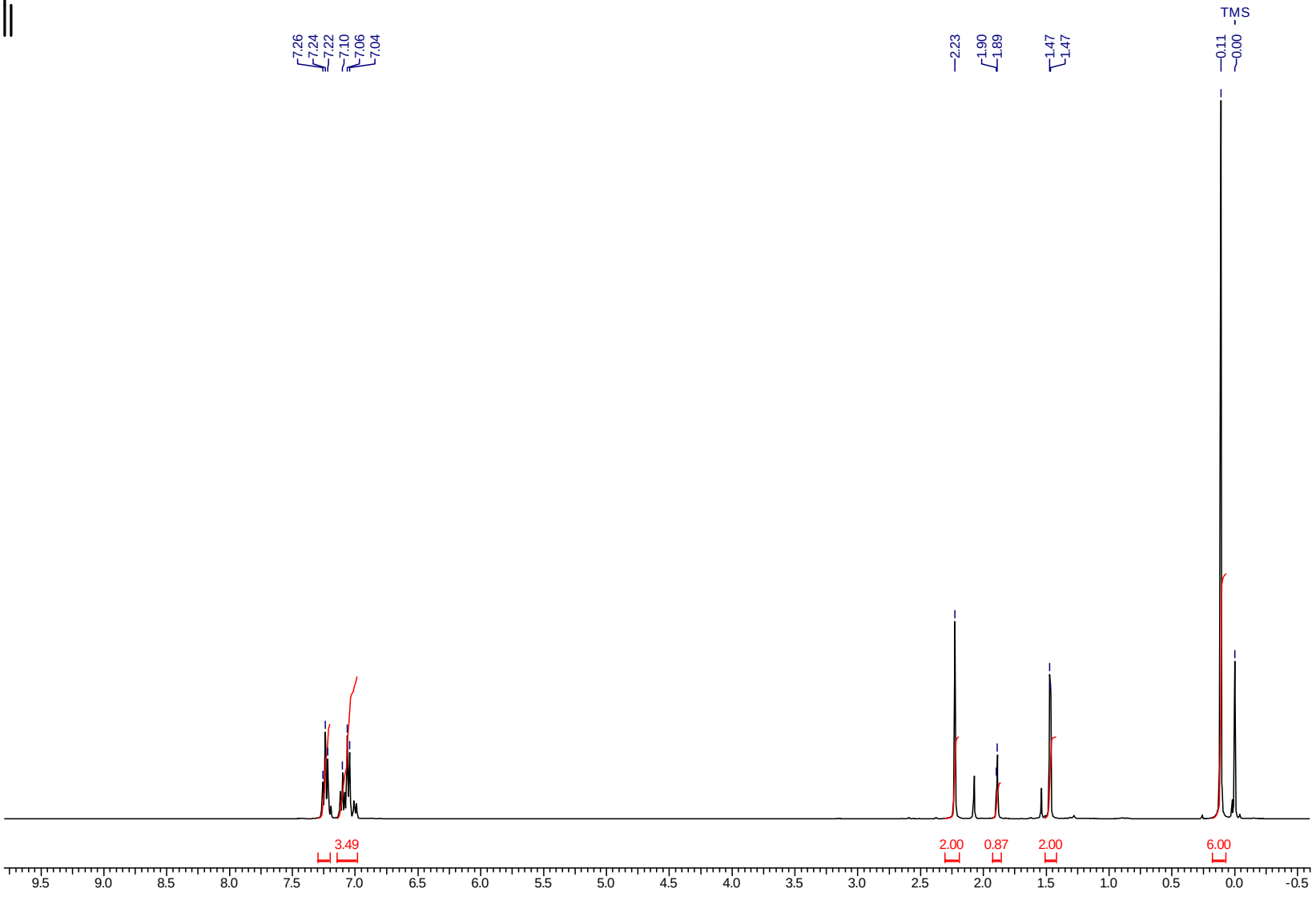

Si
Ph

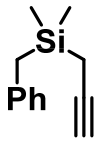
13


CDCl3
7.58
7.56
7.54
7.39
7.38
7.36
7.26
1.87
1.86
1.84
1.73
1.71
1.55
0.88
0.40
0.00
2.19
3.28
2.03
5.70
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

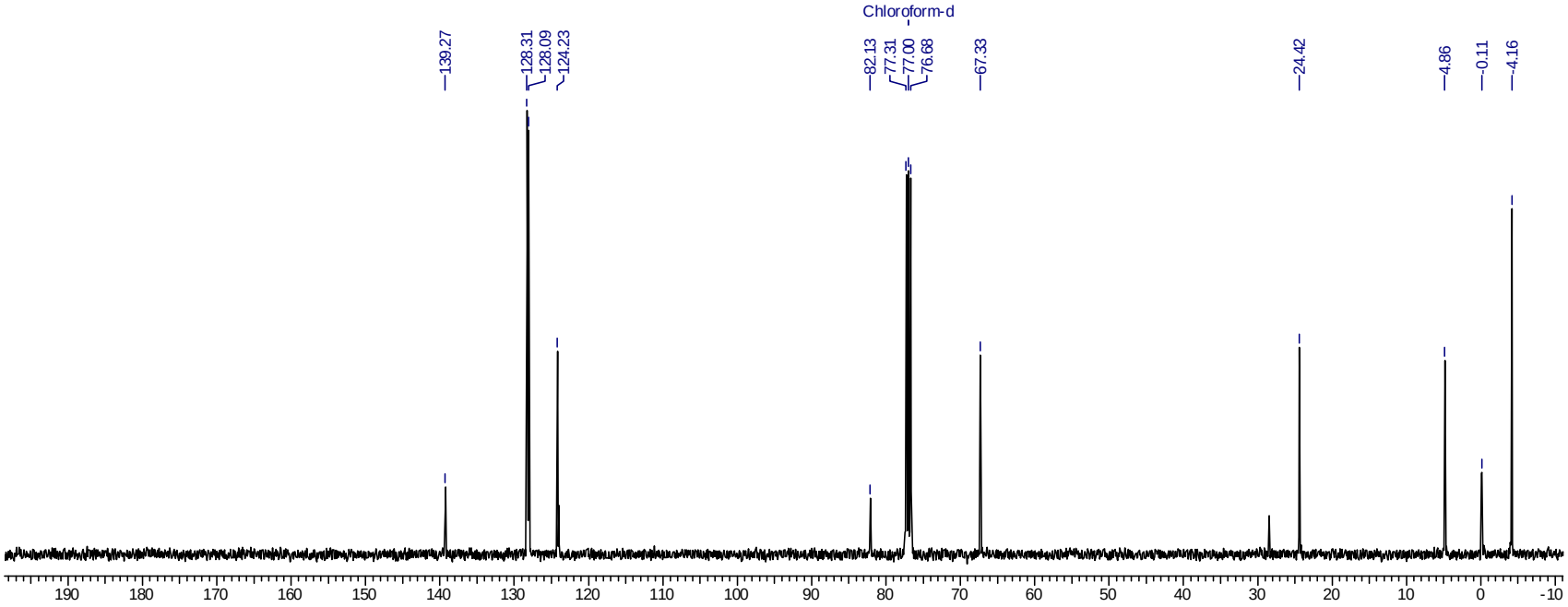

Si
Ph

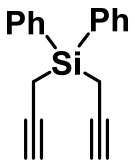
14


7.26
7.24
7.22
7.10
7.06
7.04
2.23
1.90
1.89
1.47
1.47
TMS
0.11
0.00
3.49
2.00
0.87
2.00
6.00
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

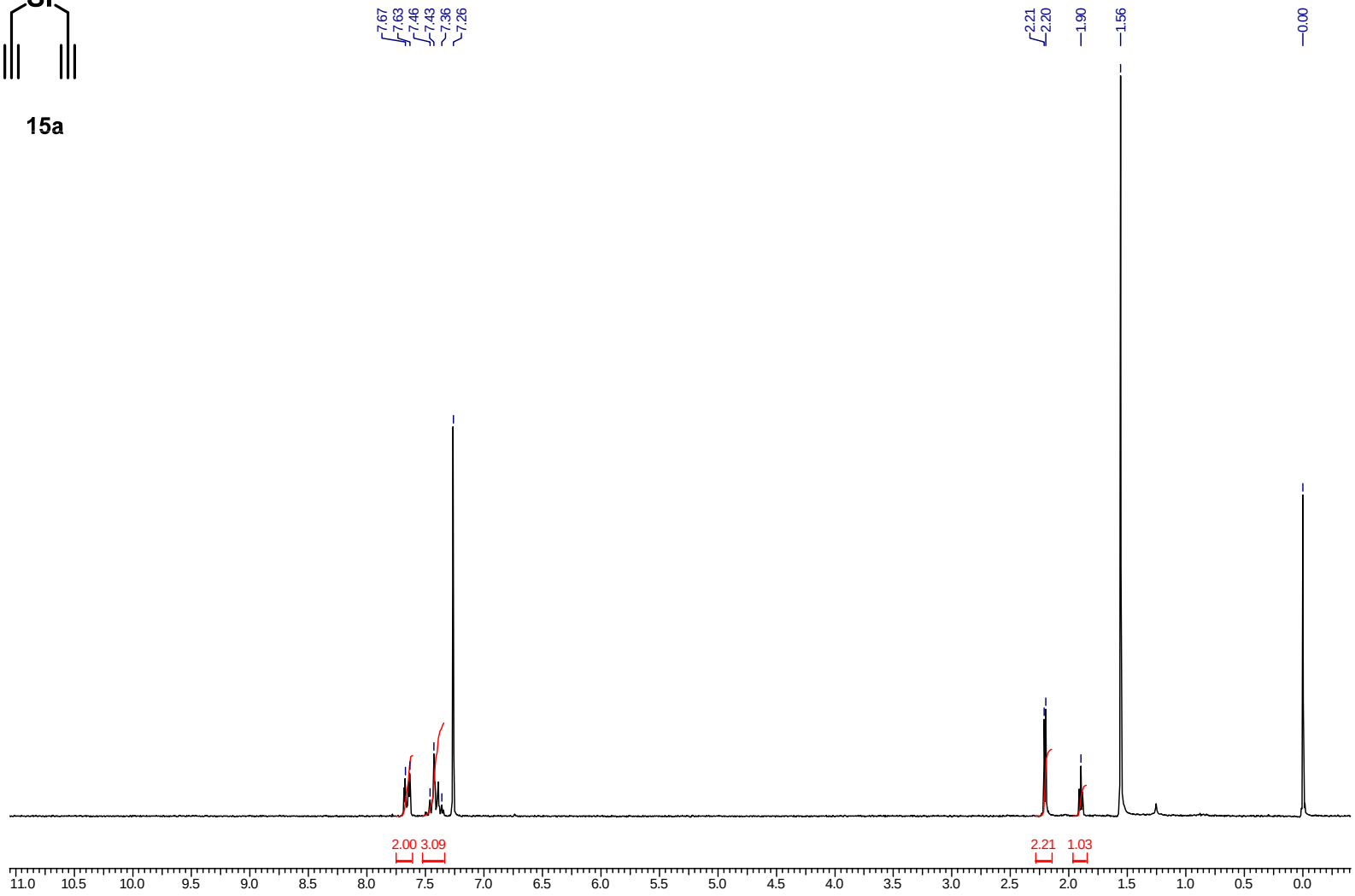

Si
Ph

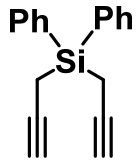
14


Chloroform-d
139.27
128.31
128.09
124.23
82.13
77.31
77.00
76.68
67.33
24.42
4.86
-0.11
-4.16
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

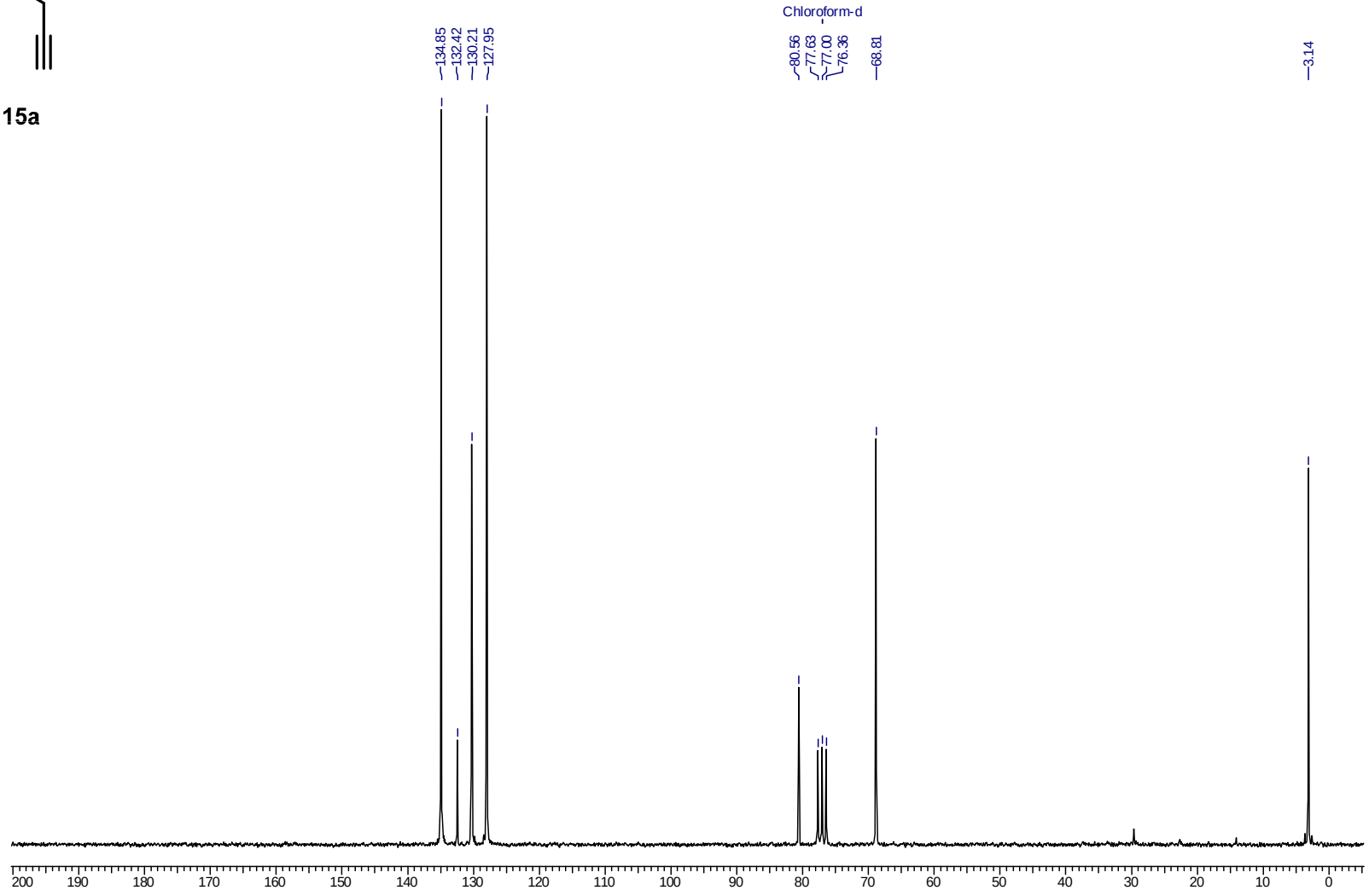

Ph
Ph
Si

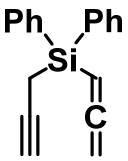
15a


7.67
7.63
7.46
7.43
7.36
7.26
2.21
2.20
1.90
1.56
0.00
2.00
3.09
2.21
1.03
11.0
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

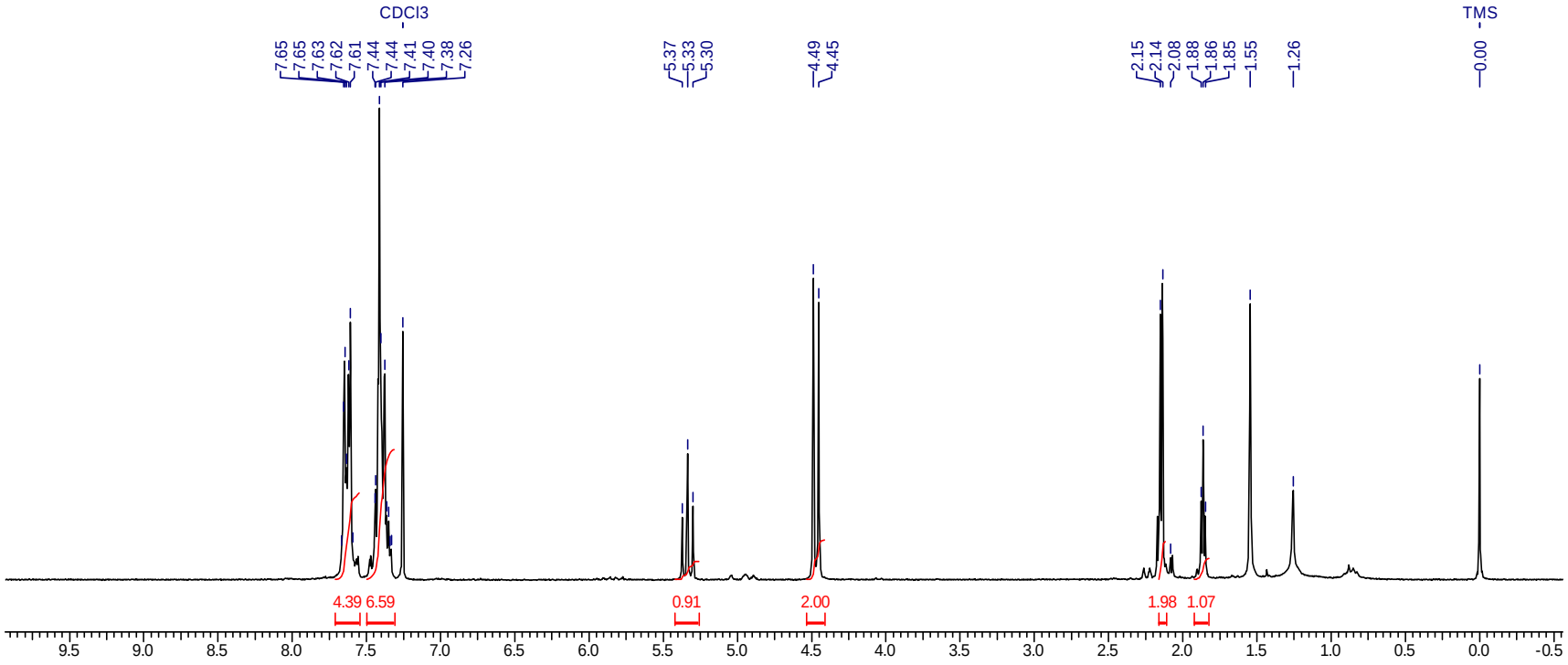

Ph
Ph
Si

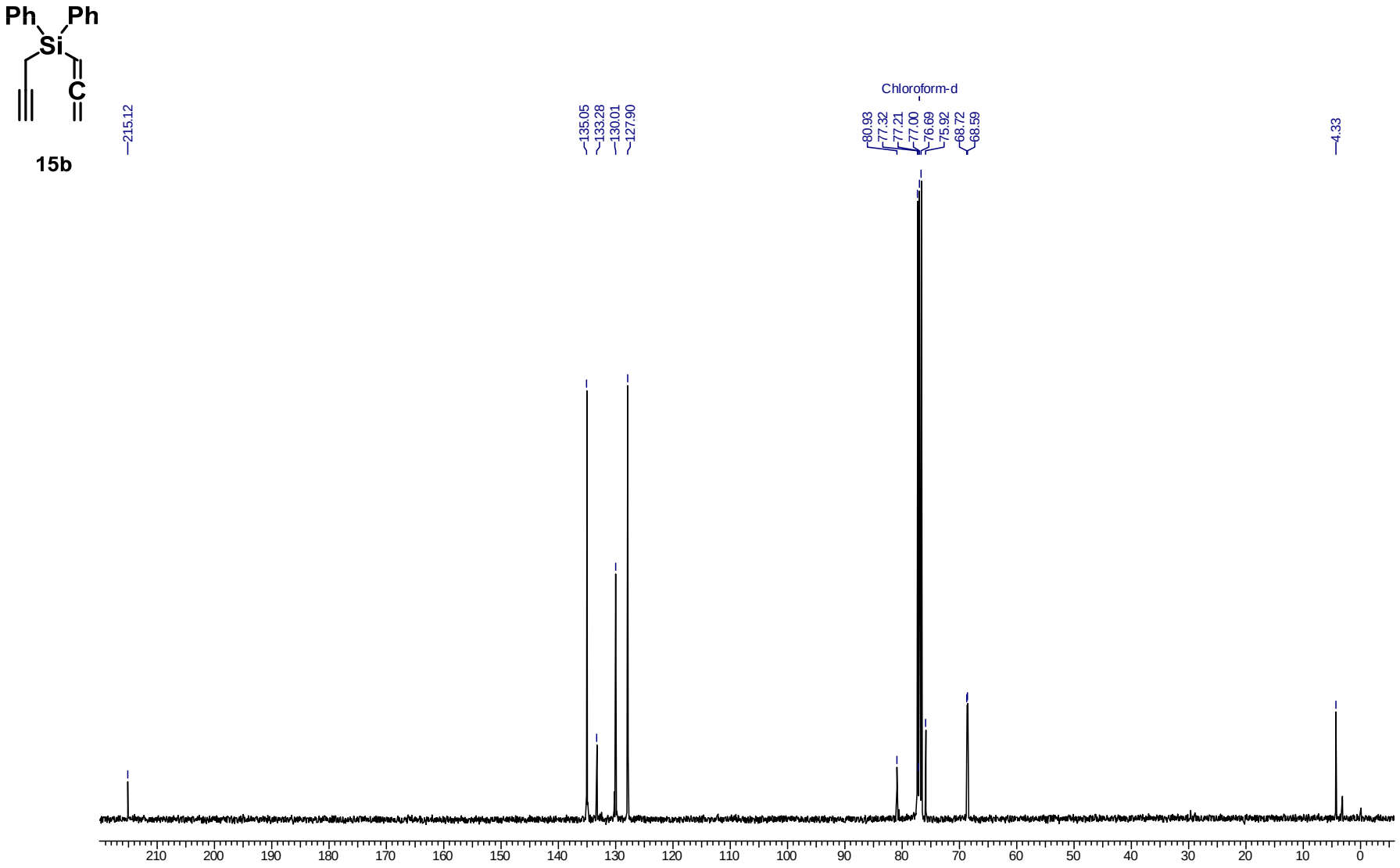
15a

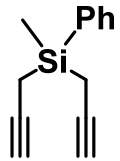

134.85
132.42
130.21
127.95
Chloroform-d
80.56
77.63
77.00
76.36
68.81
3.14
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Ph
Ph
Si
C

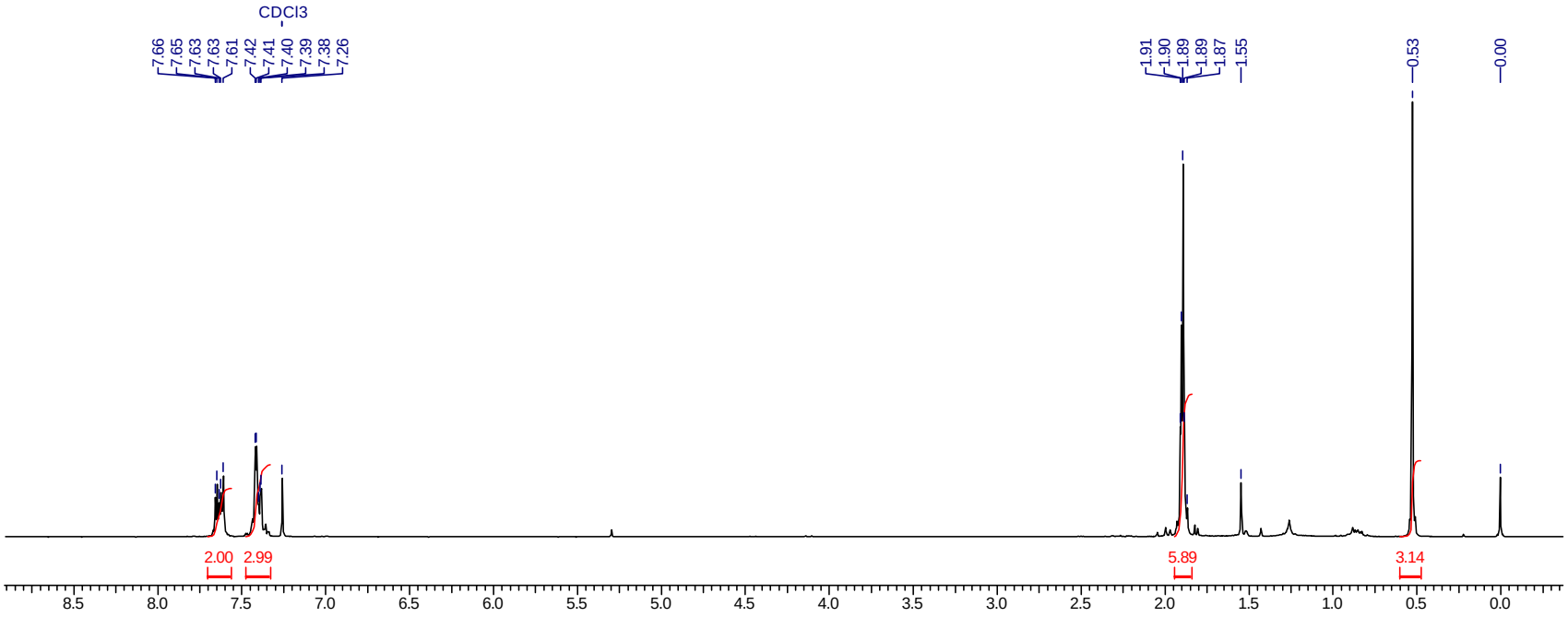
15b

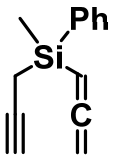

CDCl3
TMS
7.65
7.65
7.63
7.62
7.61
7.44
7.44
7.41
7.40
7.38
7.26
5.37
5.33
5.30
4.49
4.45
2.15
2.14
2.08
1.88
1.86
1.85
1.55
1.26
0.00
4.39
6.59
0.91
2.00
1.98
1.07


Ph
Ph
Si
C
15b
215.12
135.05
133.28
130.01
127.90
Chloroform-d
80.93
77.32
77.21
77.00
76.69
75.92
68.72
68.59
4.33
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

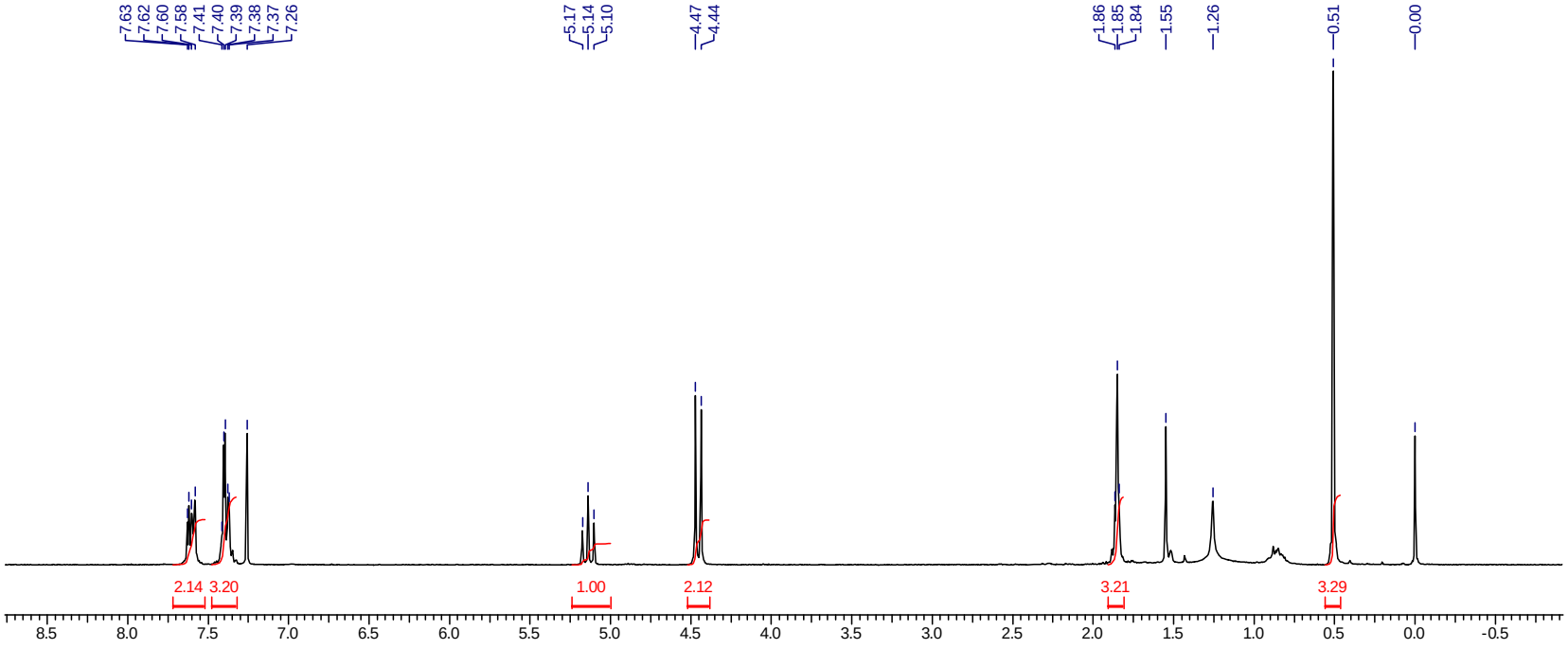

Ph
Si

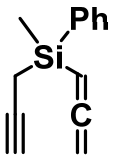
16a


CDCl3
7.66
7.65
7.63
7.63
7.61
7.42
7.41
7.40
7.39
7.38
7.26
1.91
1.90
1.89
1.89
1.87
1.55
0.53
0.00
2.00
2.99
5.89
3.14
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

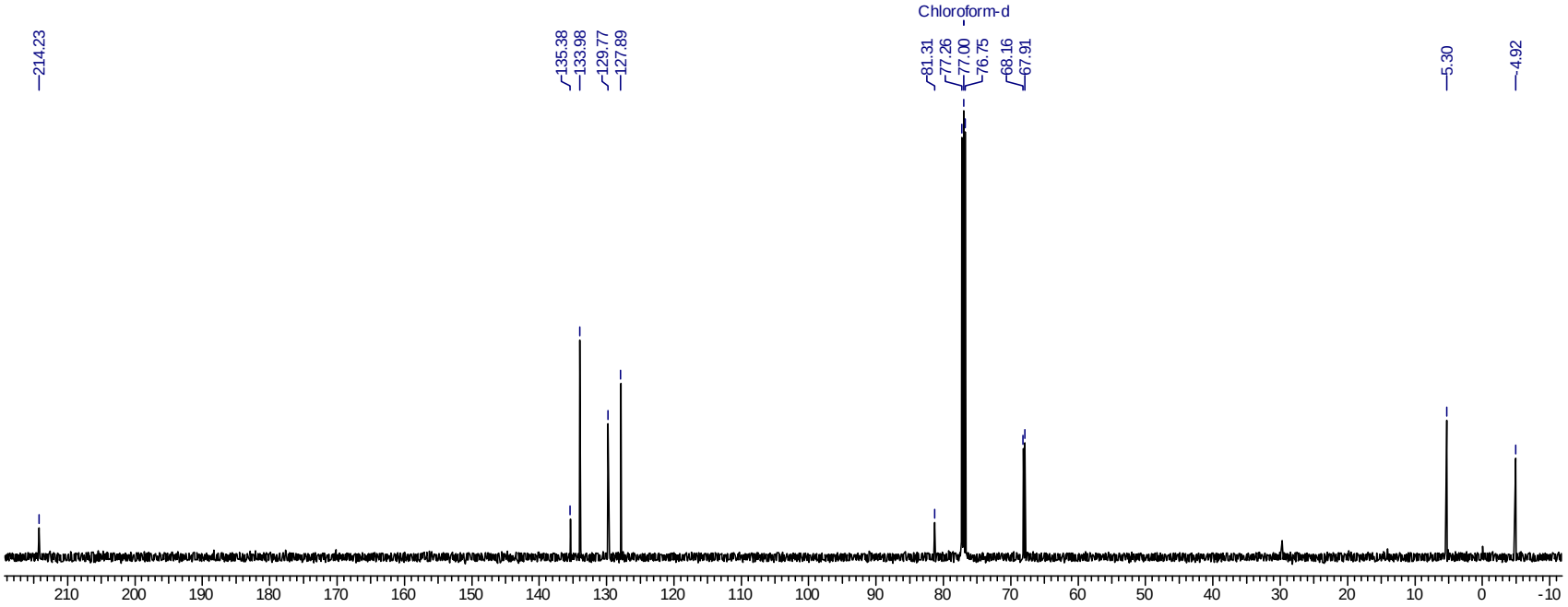

Ph
Si
C

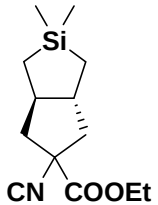
16b


7.63
7.62
7.60
7.58
7.41
7.40
7.39
7.38
7.37
7.26
5.17
5.14
5.10
4.47
4.44
1.86
1.85
1.84
1.55
1.26
0.51
0.00
2.14
3.20
1.00
2.12
3.21
3.29
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

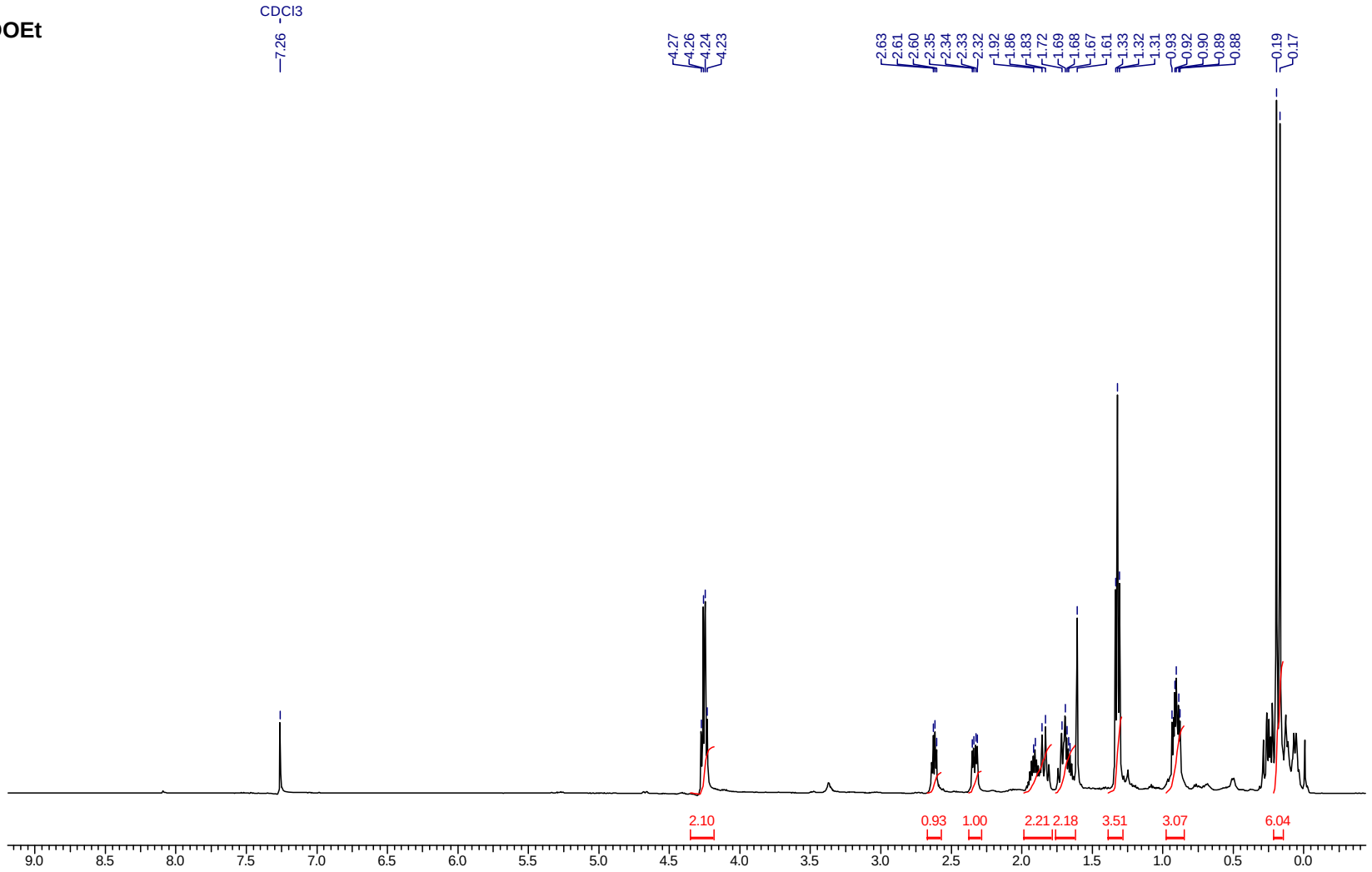

Ph
Si
C

16b


214.23
135.38
133.98
129.77
127.89
Chloroform-d
81.31
77.26
77.00
76.75
68.16
67.91
5.30
4.92
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

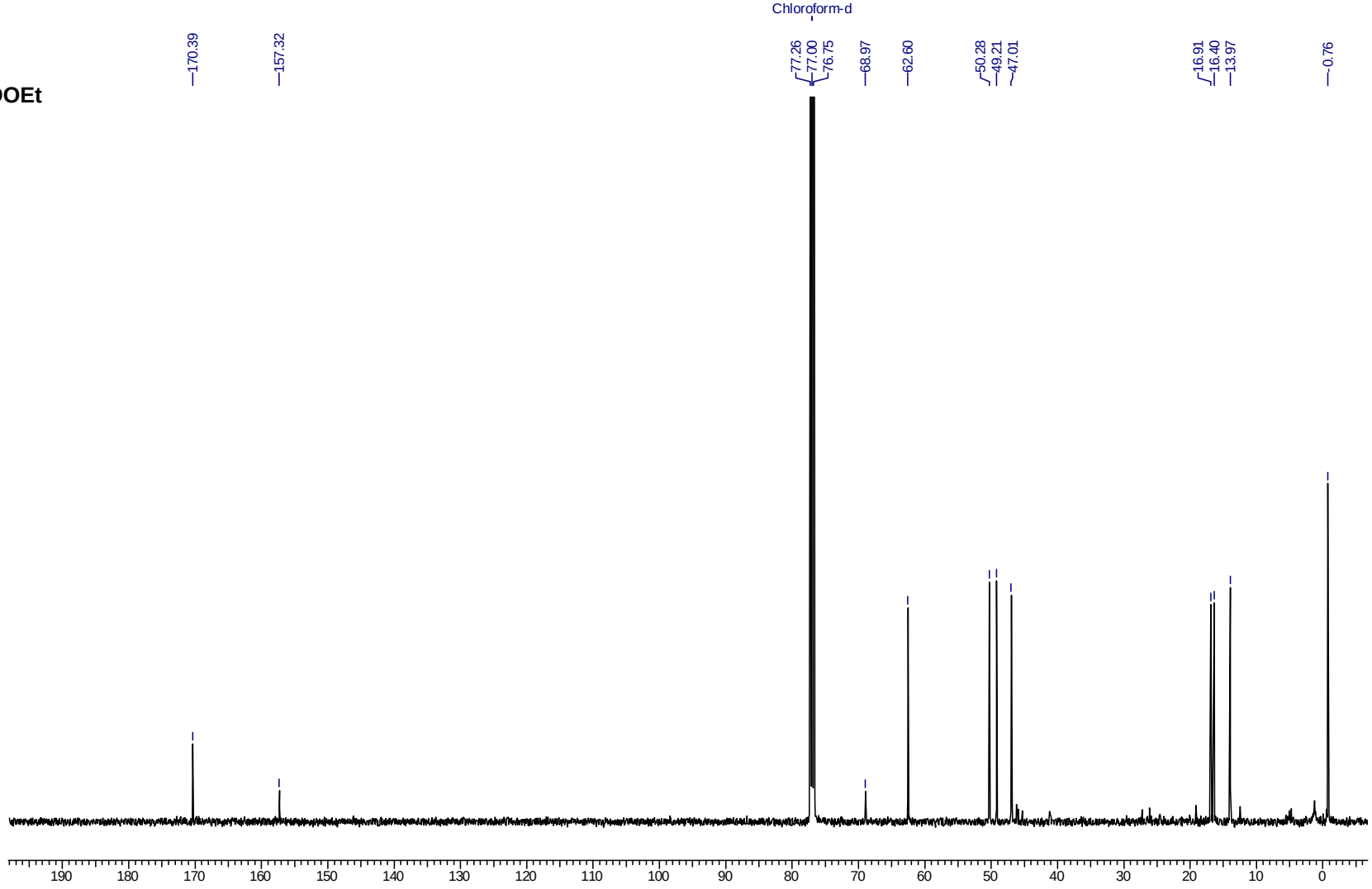

Si
CN
COOEt

18


CDCl3
7.26
4.27
4.26
4.24
4.23
2.63
2.61
2.60
2.35
2.34
2.33
2.32
1.92
1.86
1.83
1.72
1.69
1.68
1.67
1.61
1.33
1.32
1.31
0.93
0.92
0.90
0.89
0.88
0.19
0.17
2.10
0.93
1.00
2.21
2.18
3.51
3.07
6.04
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


Si
CN
COOEt

18


Chloroform-d
170.39
157.32
77.26
77.00
76.75
68.97
62.60
50.28
49.21
47.01
16.91
16.40
13.97
0.76
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150
140
130
120
110
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90
80
70
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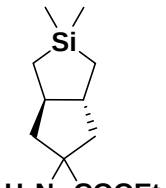
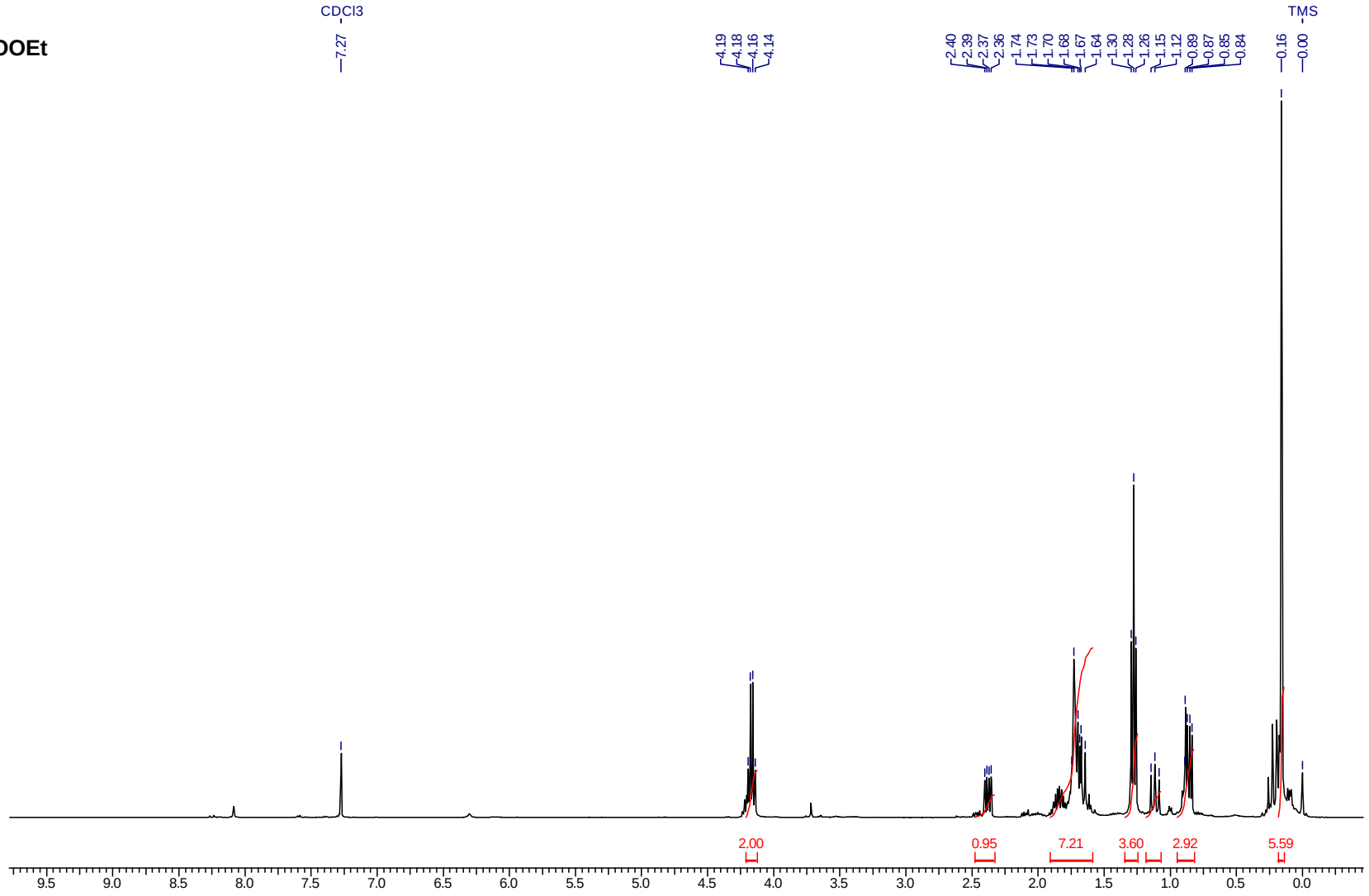
30
20
10
0


Si
H2N
COOEt

19


CDCl3
7.27
4.19
4.18
4.16
4.14
2.40
2.39
2.37
2.36
1.74
1.73
1.70
1.68
1.67
1.64
1.30
1.28
1.26
1.15
1.12
0.89
0.87
0.85
0.84
TMS
0.16
0.00
2.00
0.95
7.21
3.60
2.92
5.59
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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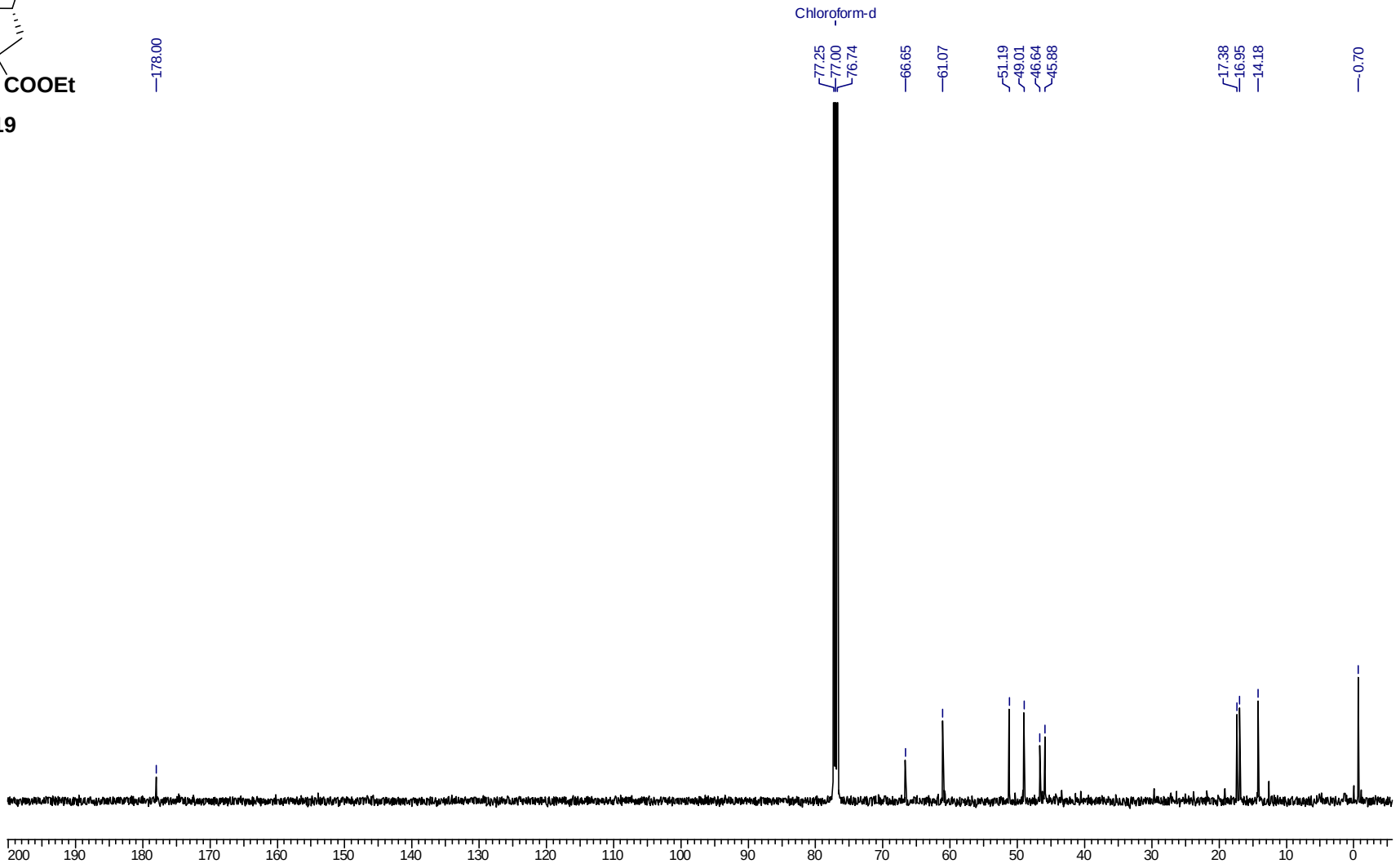
2.5
2.0
1.5
1.0
0.5
0.0

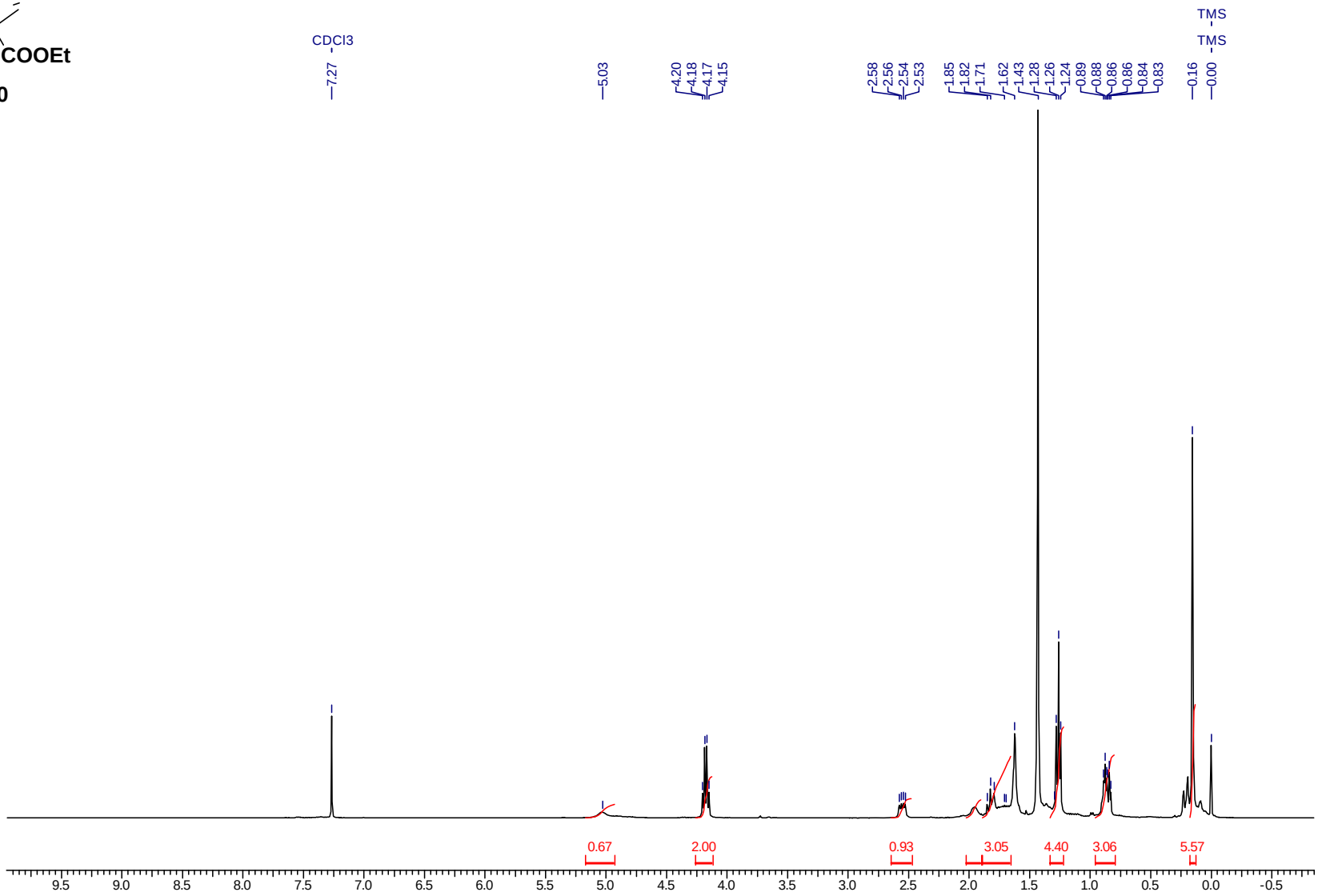

Si
H2N
COOEt

19


Chloroform-d
178.00
77.25
77.00
76.74
66.65
61.07
51.19
49.01
46.64
45.88
17.38
16.95
14.18
0.70
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Si
BocHN
COOEt

20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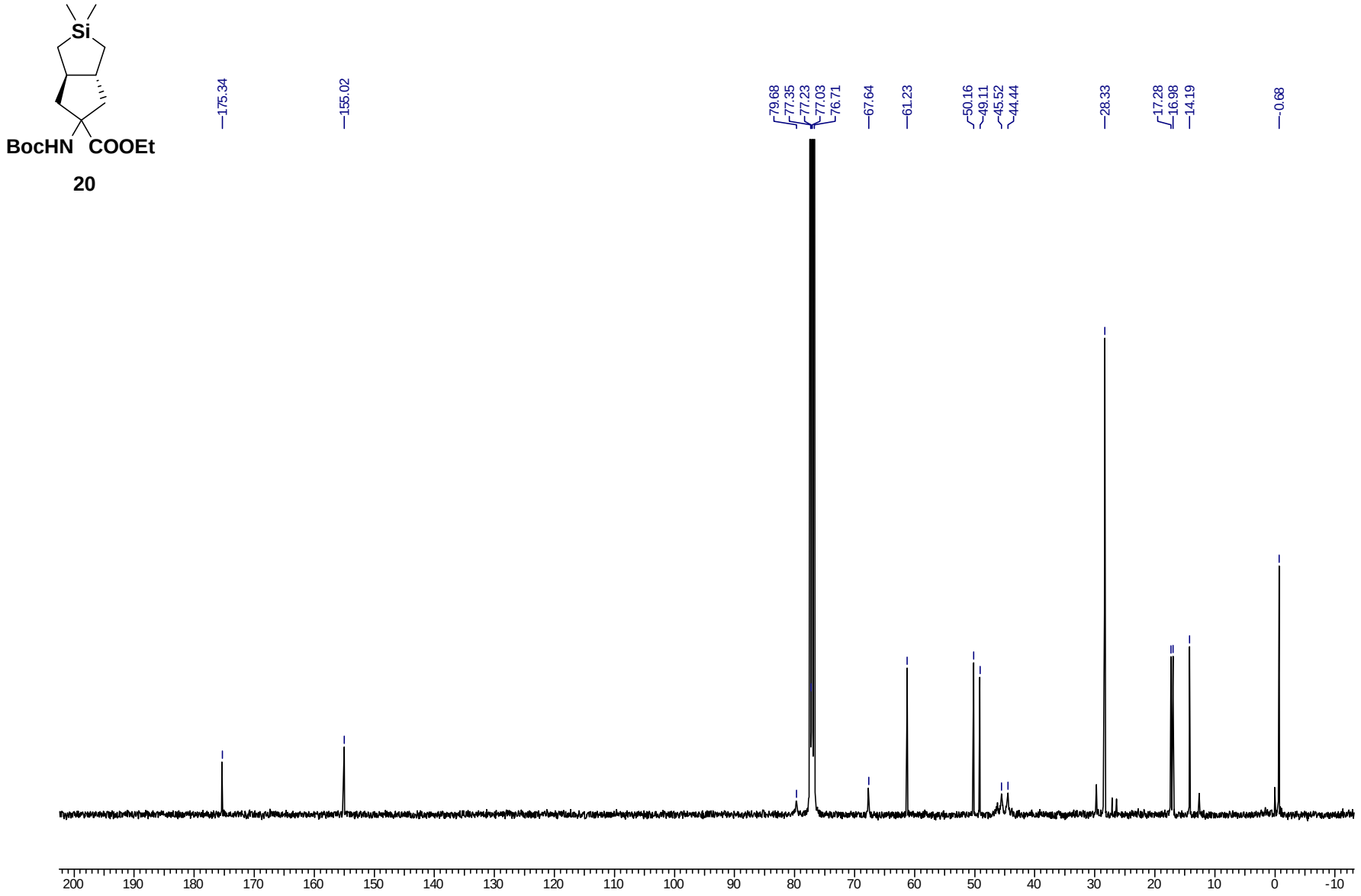
7.27
5.03
4.20
4.18
4.17
4.15
2.58
2.56
2.54
2.53
1.85
1.82
1.71
1.62
1.43
1.28
1.26
1.24
0.89
0.88
0.86
0.86
0.84
0.83
TMS
0.16
TMS
0.00
0.67
2.00
0.93
3.05
4.40
3.06
5.57
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


Si
BocHN COOEt
20
175.34
155.02
79.68
77.35
77.23
77.03
76.71
67.64
61.23
50.16
49.11
45.52
44.44
28.33
17.28
16.98
14.19
-0.68
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
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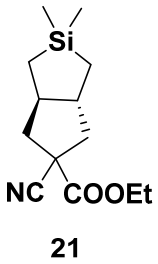
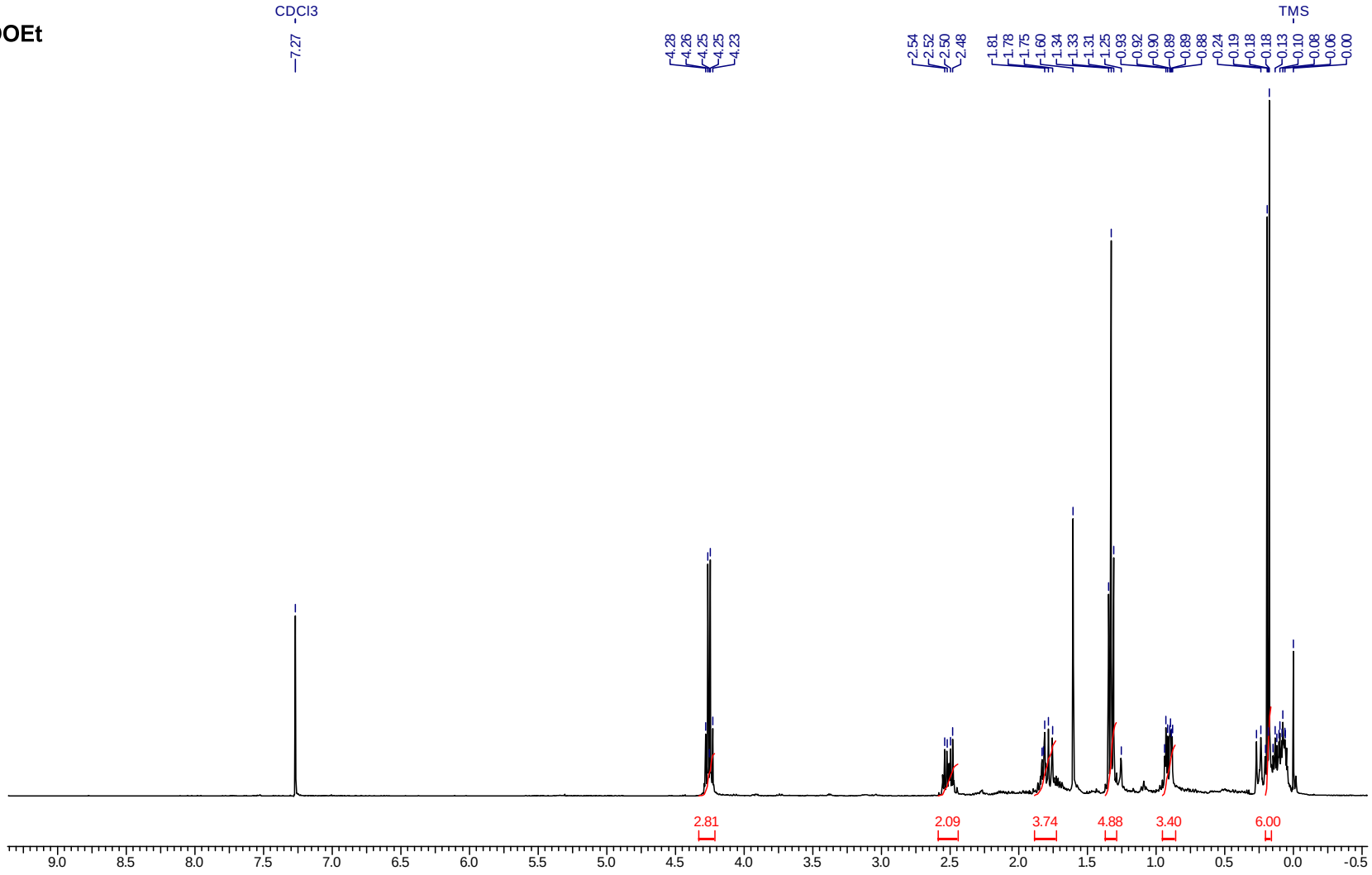
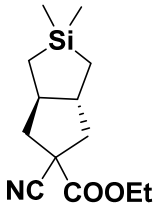
20
10
0
-10

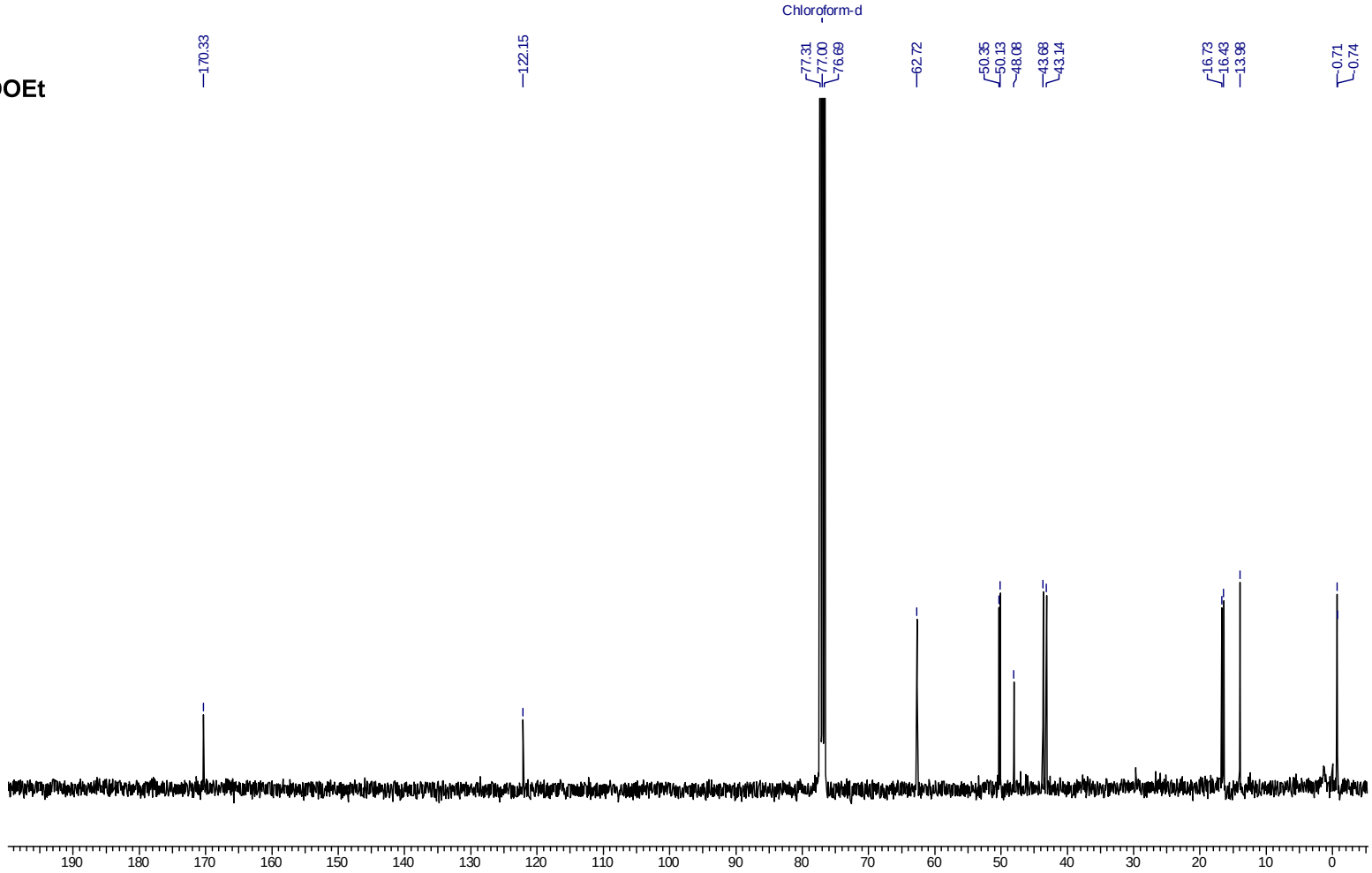

Si
NC
COOEt

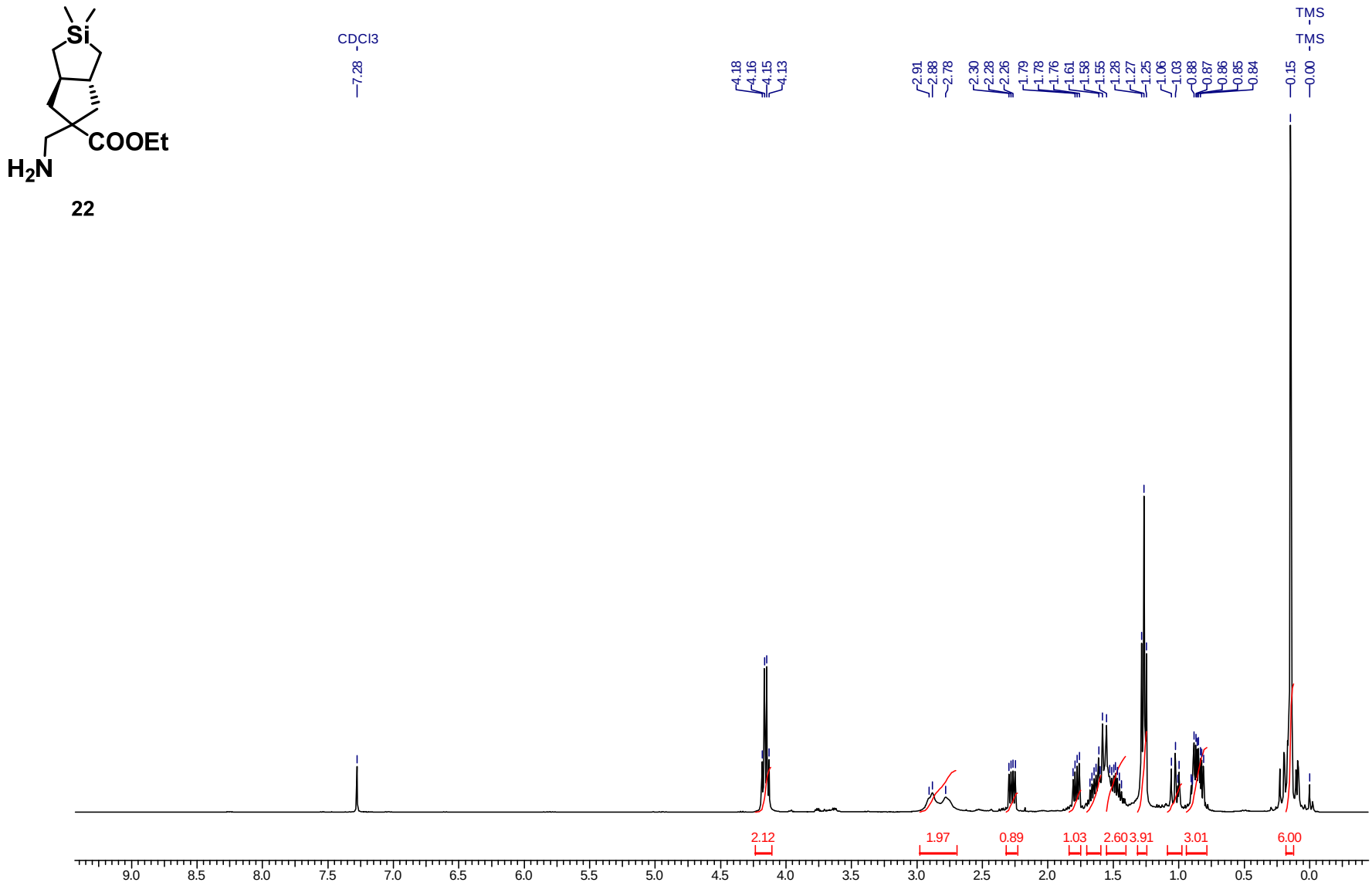
21

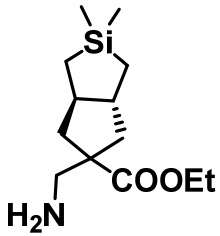

CDCl3
7.27
4.28
4.26
4.25
4.25
4.23
2.54
2.52
2.50
2.48
1.81
1.78
1.75
1.60
1.34
1.33
1.31
1.25
0.93
0.92
0.90
0.89
0.89
0.88
0.24
0.19
0.18
0.18
0.13
0.10
0.08
0.06
0.00
TMS
2.81
2.09
3.74
4.88
3.40
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


Si
NC
COOEt

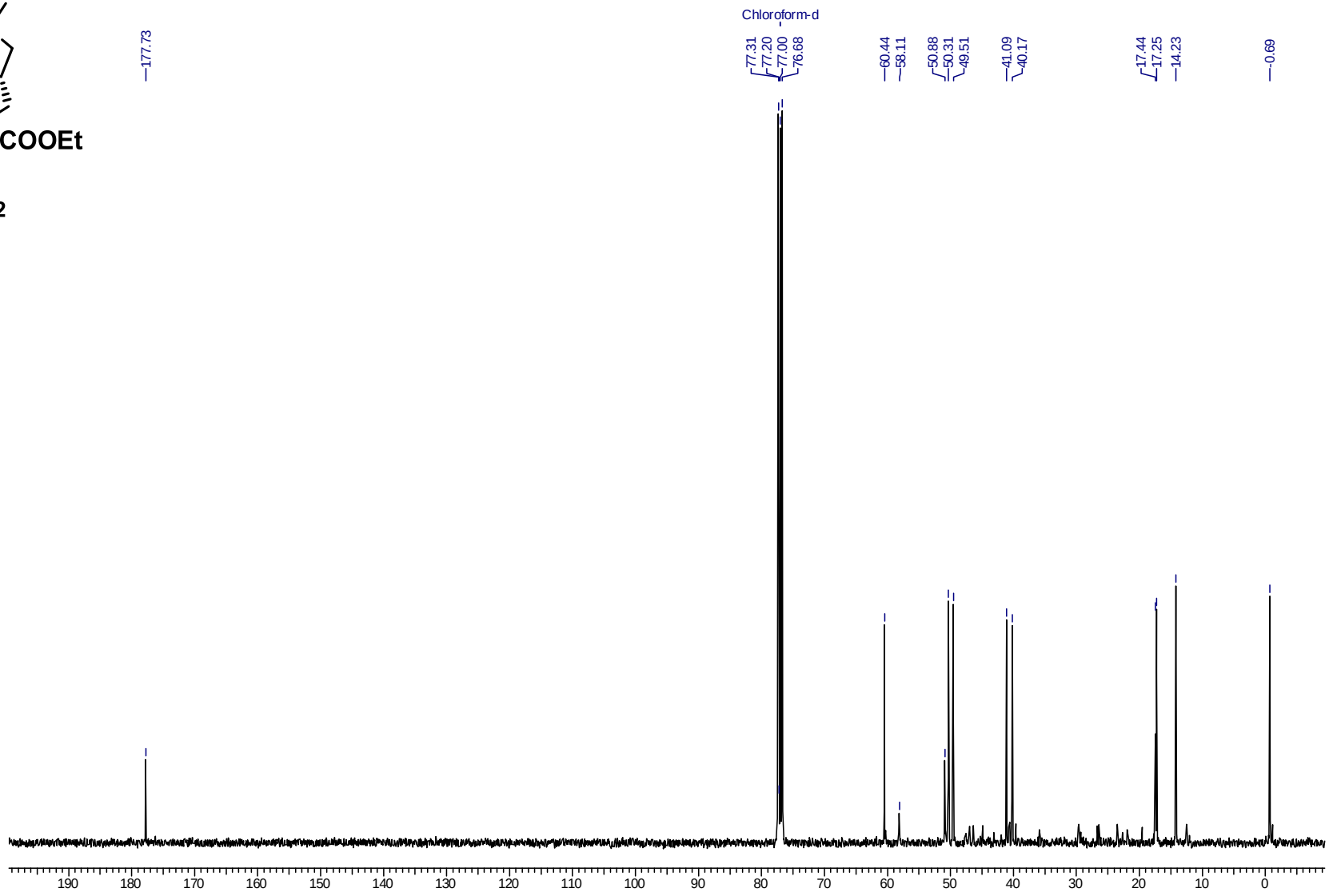
21


Chloroform-d
170.33
122.15
77.31
77.00
76.69
62.72
50.35
50.13
48.06
43.68
43.14
16.73
16.43
13.98
0.71
-0.74
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Si
COOEt
H2N
22
CDCl3
7.28
4.18
4.16
4.15
4.13
2.91
2.88
2.78
2.30
2.28
2.26
1.79
1.78
1.76
1.61
1.58
1.55
1.28
1.27
1.25
1.06
1.03
0.88
0.87
0.86
0.85
0.84
TMS
0.15
0.00
2.12
1.97
0.89
1.03
2.60
3.91
3.01
6.00
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
0.0


Si
COOEt
H2N

22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Chloroform-d
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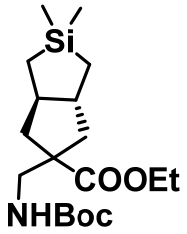
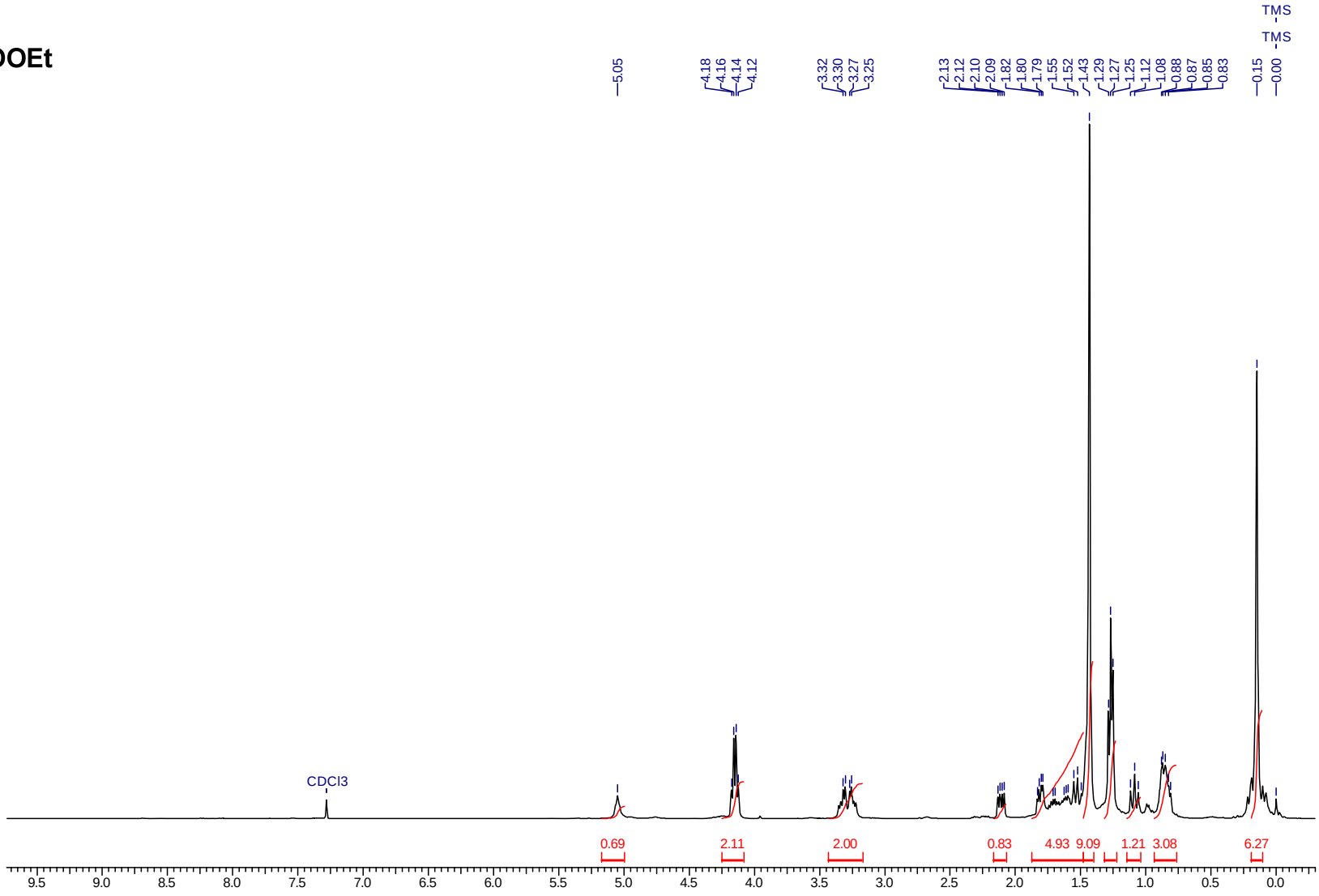
77.20
77.00
76.68
60.44
58.11
50.88
50.31
49.51
41.09
40.17
17.44
17.25
14.23
0.69
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Si
COOEt
NHBoc

23


TMS
TMS
5.05
4.18
4.16
4.14
4.12
3.32
3.30
3.27
3.25
2.13
2.12
2.10
2.09
1.82
1.80
1.79
1.55
1.52
1.43
1.29
1.27
1.25
1.12
1.08
0.88
0.87
0.85
0.83
0.15
0.00
CDCl3
0.69
2.11
2.00
0.83
4.93
9.09
1.21
3.08
6.27
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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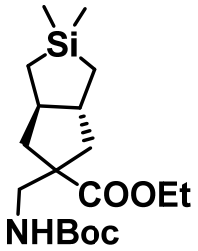
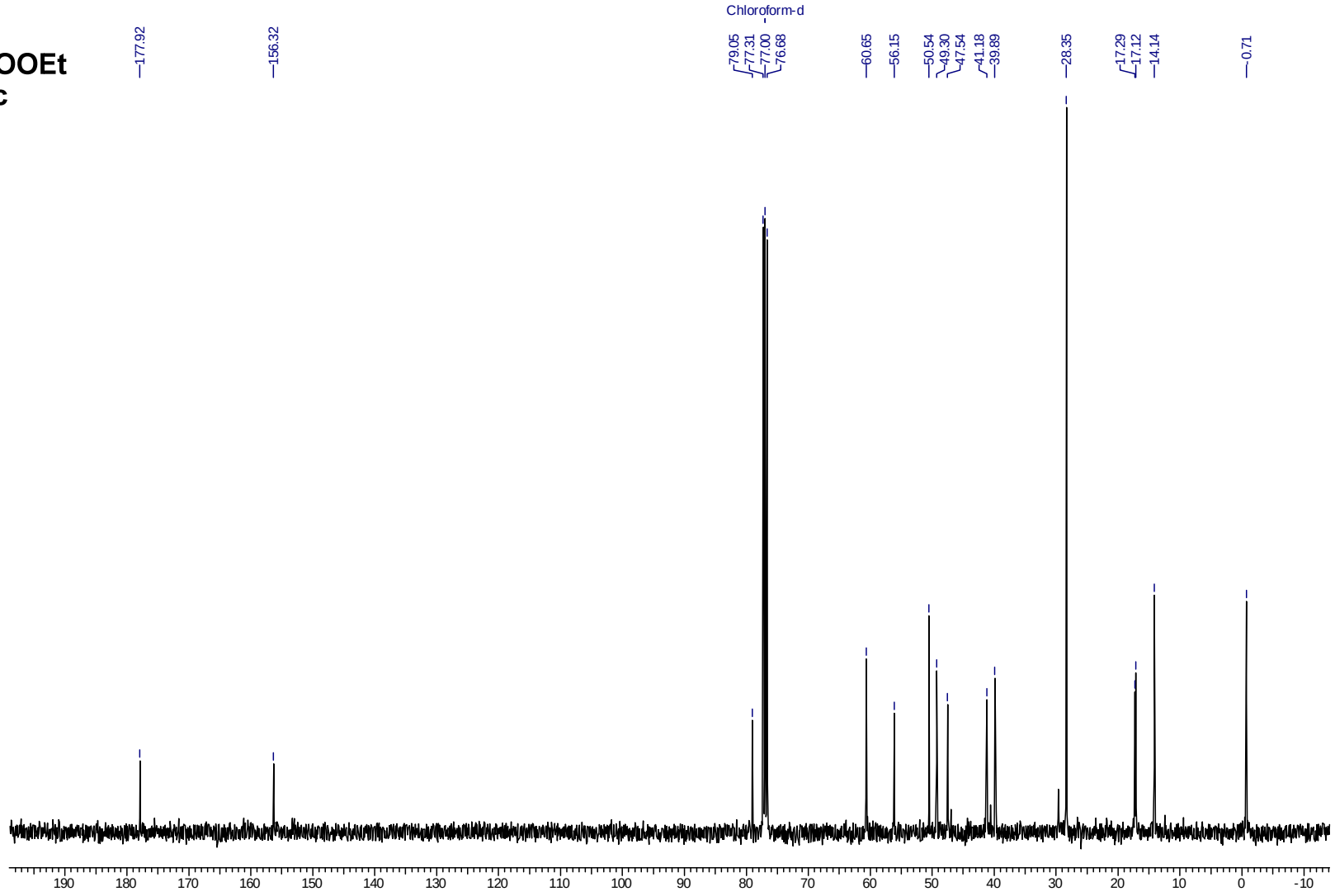
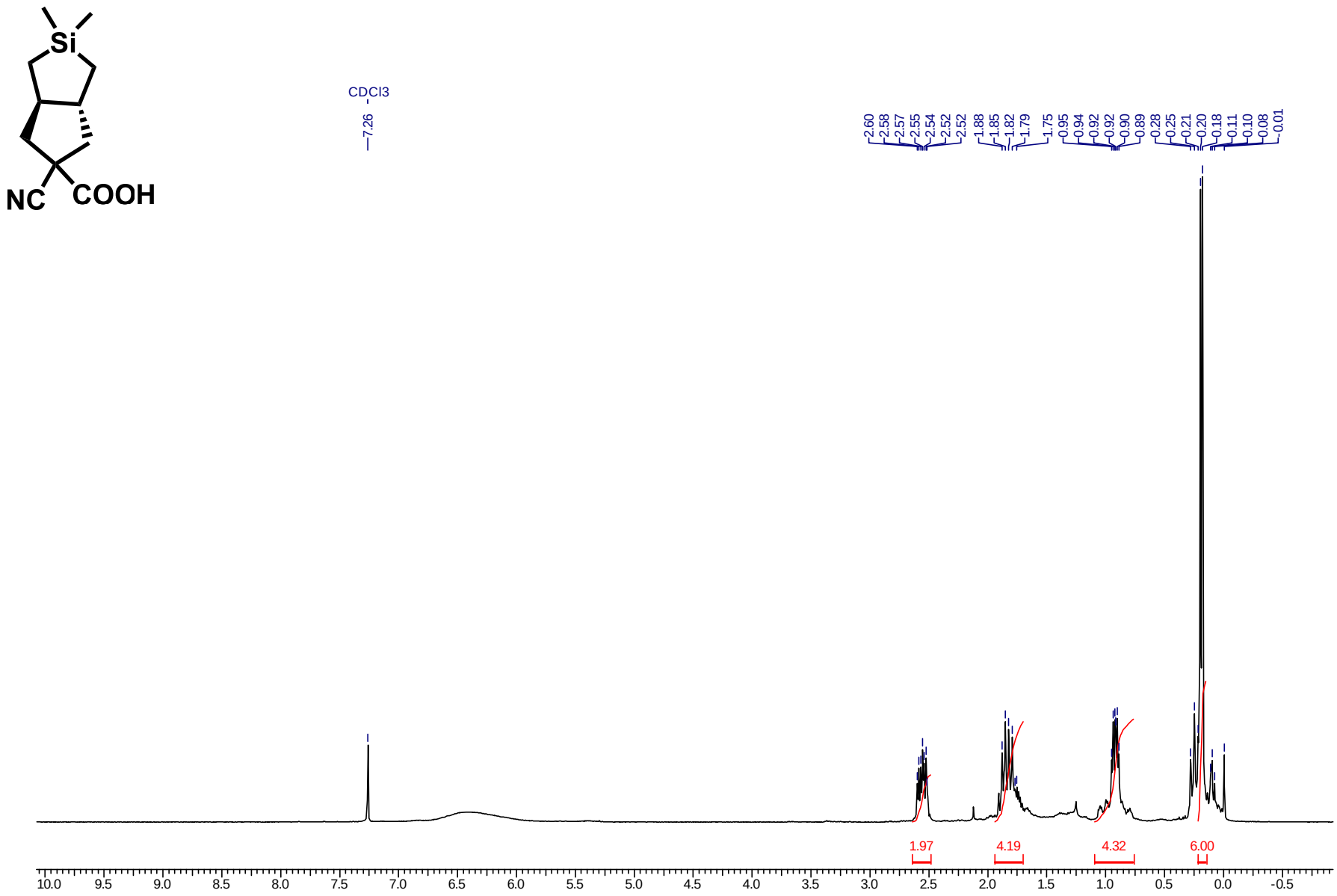
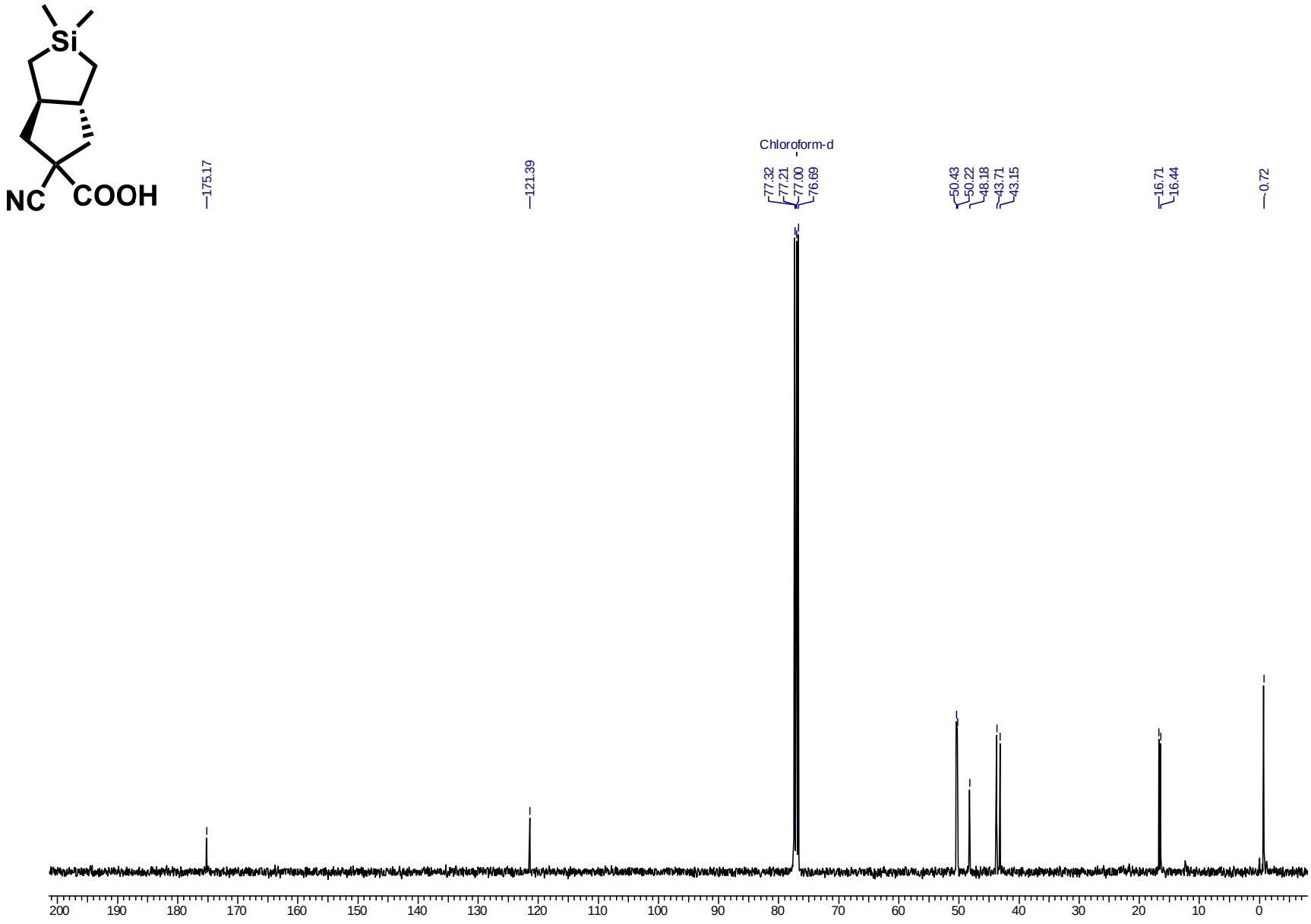
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


Si
COOEt
NHBoc

23


177.92
156.32
Chloroform-d
79.05
77.31
77.00
76.68
60.65
56.15
50.54
49.30
47.54
41.18
39.89
28.35
17.29
17.12
14.14
0.71
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


Si
NC
COOH
CDCl3
7.26
2.60
2.58
2.57
2.55
2.54
2.52
2.52
1.88
1.85
1.82
1.79
1.75
0.95
0.94
0.92
0.92
0.90
0.89
0.28
0.25
0.21
0.20
0.18
0.11
0.10
0.08
0.01
1.97
4.19
4.32
6.00
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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NC
COOH
175.17
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Chloroform-d
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77.21
77.00
76.69
50.43
50.22
48.18
43.71
43.15
16.71
16.44
0.72
200
190
180
170
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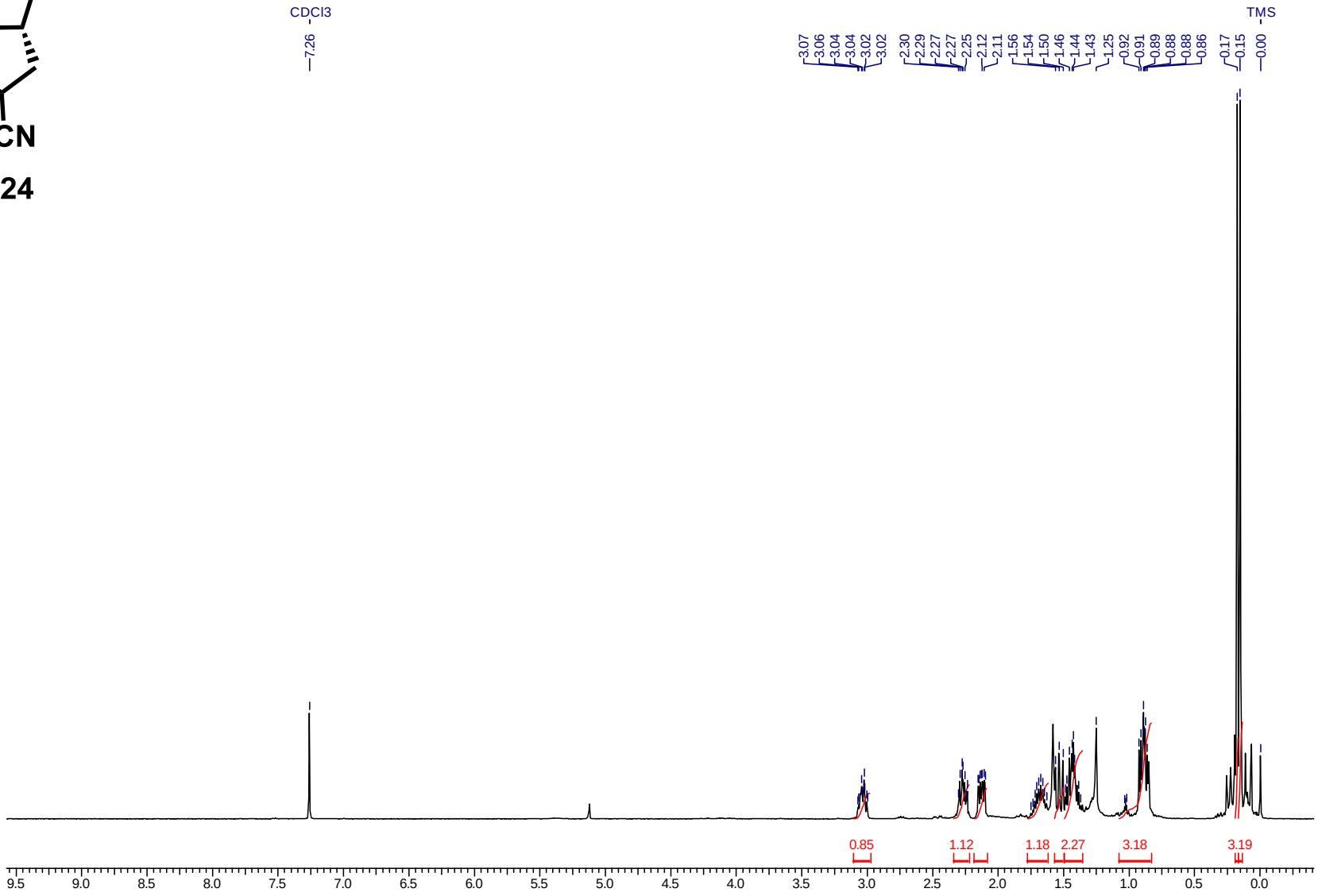
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Si
CN

24


CDCl3
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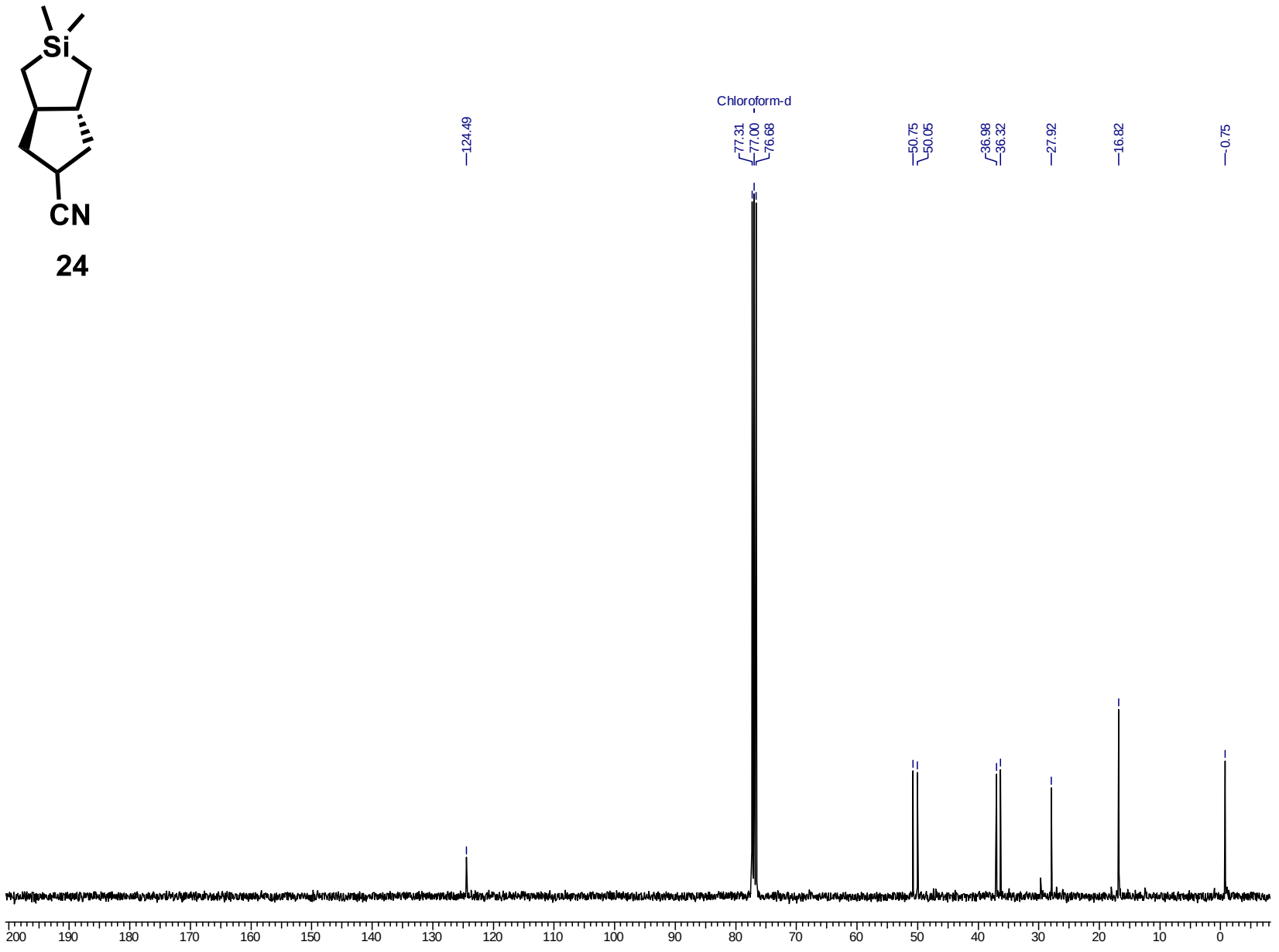
TMS
0.00
3.07
3.06
3.04
3.04
3.02
3.02
2.30
2.29
2.27
2.27
2.25
2.12
2.11
1.56
1.54
1.50
1.46
1.44
1.43
1.25
0.92
0.91
0.89
0.88
0.88
0.86
0.17
0.15
0.85
1.12
1.18
2.27
3.18
3.19
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


Si
CN
24
Chloroform-d
124.49
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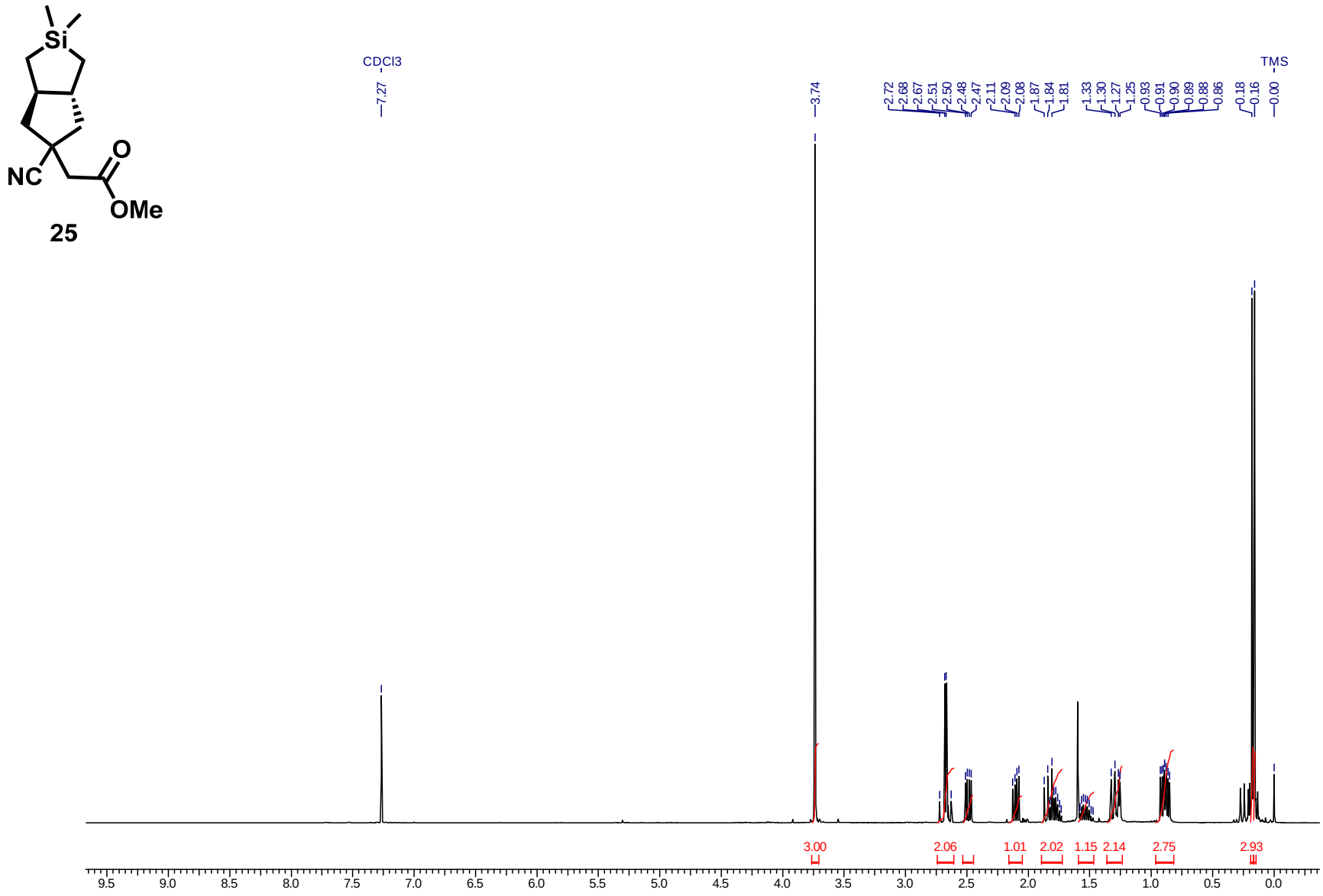
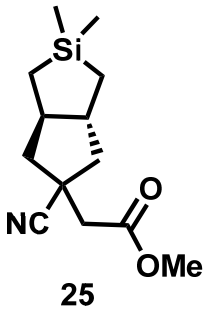
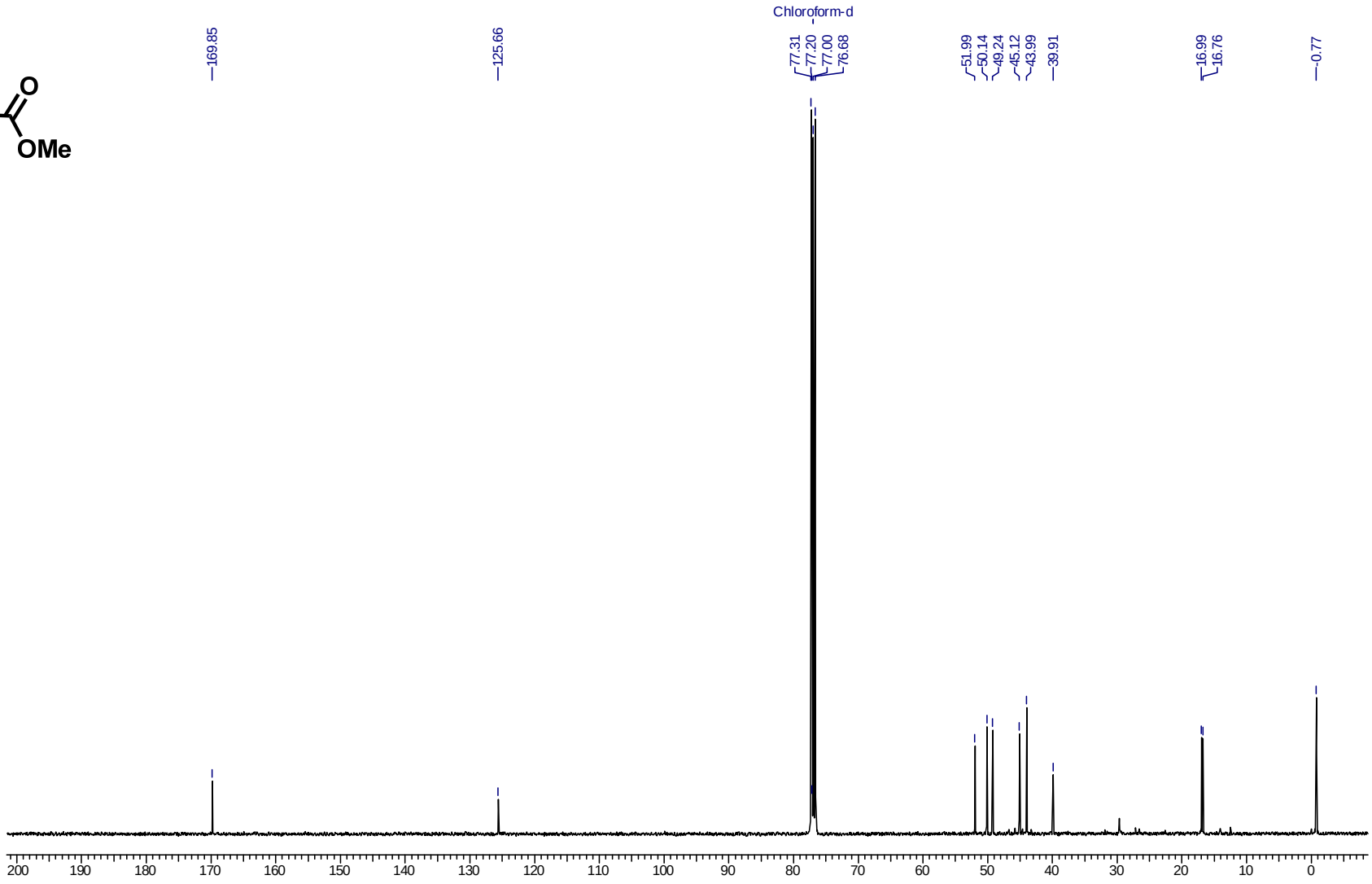
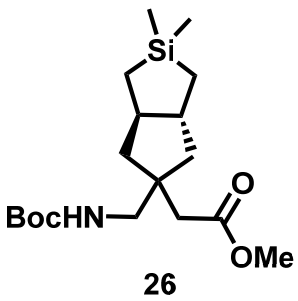
77.00
76.68
50.75
50.05
36.98
36.32
27.92
16.82
0.75
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Si
NC
O
OMe
25
CDCl3
7.27
3.74
2.72
2.68
2.67
2.51
2.50
2.48
2.47
2.11
2.09
2.08
1.87
1.84
1.81
1.33
1.30
1.27
1.25
0.93
0.91
0.90
0.89
0.88
0.86
0.18
0.16
TMS
0.00
3.00
2.06
1.01
2.02
1.15
2.14
2.75
2.93
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

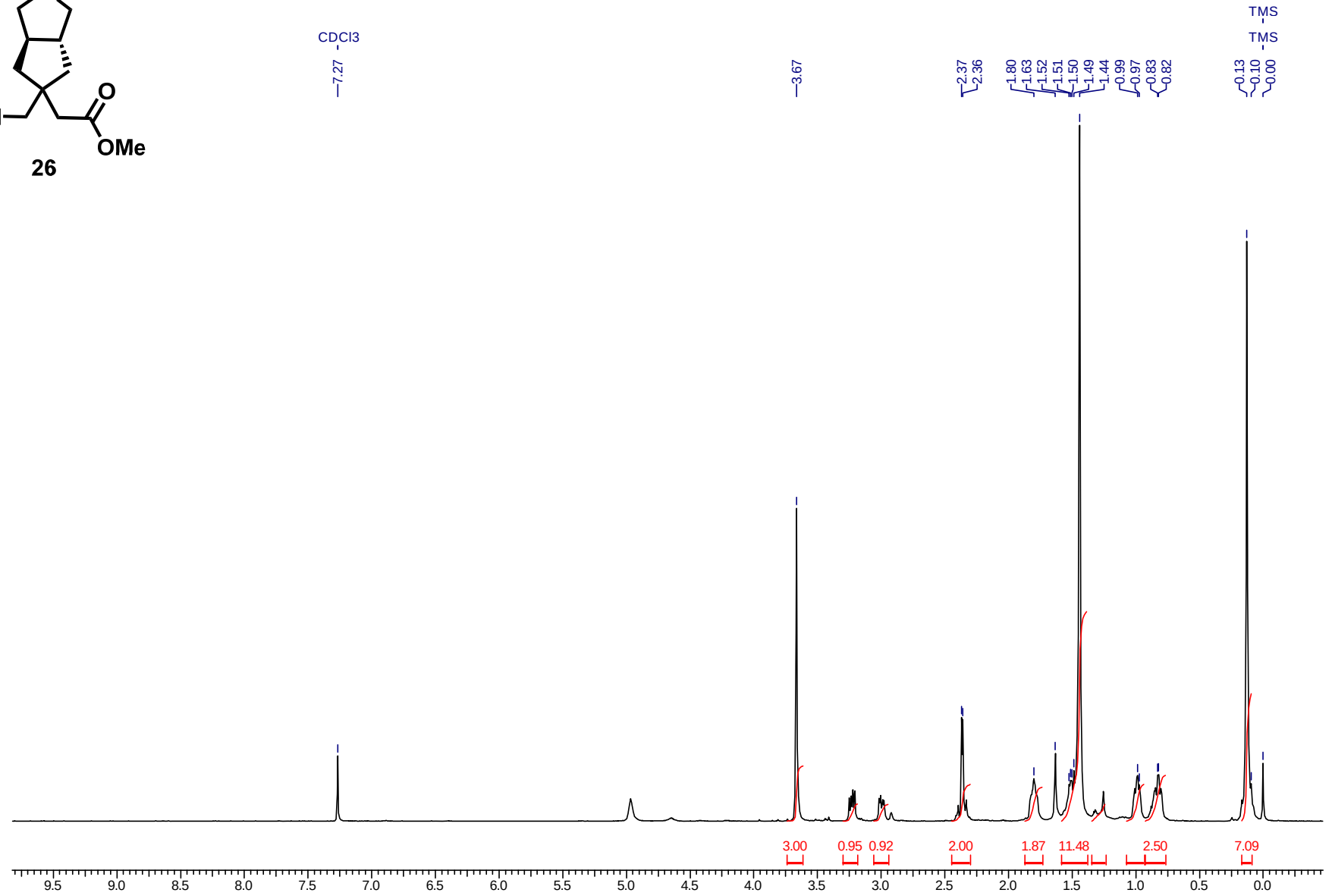

Si
NC
O
OMe

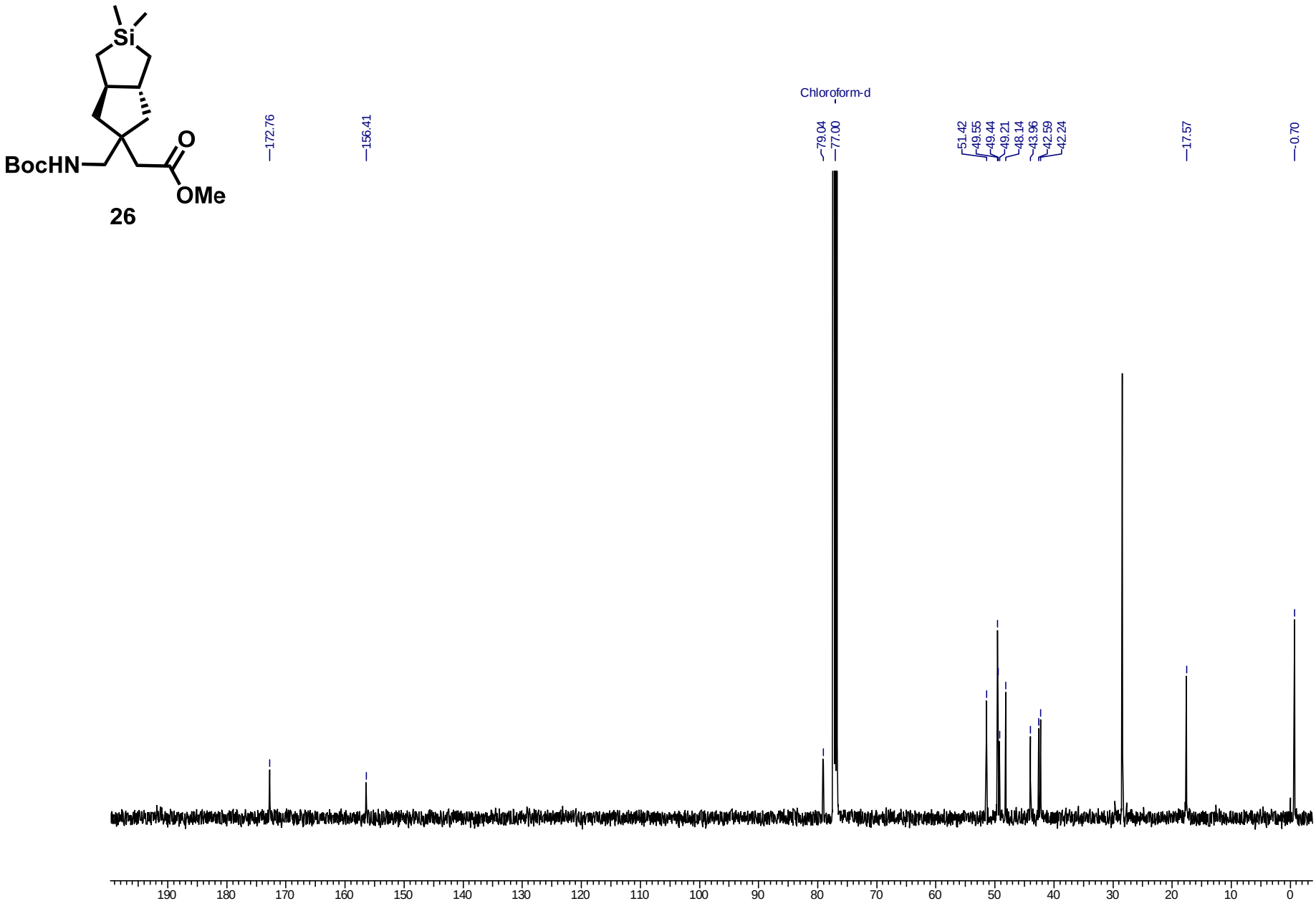
25


169.85
125.66
Chloroform-d
77.31
77.20
77.00
76.68
51.99
50.14
49.24
45.12
43.99
39.91
16.99
16.76
-0.77
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Si
BocHN
O
OMe

26


CDCl3
7.27
3.67
2.37
2.36
1.80
1.63
1.52
1.51
1.50
1.49
1.44
0.99
0.97
0.83
0.82
TMS
TMS
0.13
0.10
0.00
3.00
0.95
0.92
2.00
1.87
11.48
2.50
7.09
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


Si
BocHN
O
OMe
26
172.76
156.41
Chloroform-d
79.04
77.00
51.42
49.55
49.44
49.21
48.14
43.96
42.59
42.24
17.57
0.70
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0