Supporting Information

Nickel/Photo-Cocatalyzed Three-Component Silylarylation of Electron-Deficient Alkenes

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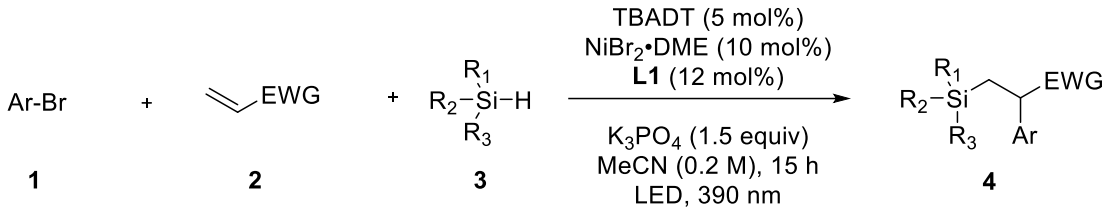
General Information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 400M NMR spectrometers at ambient temperature in $CDCl_3$ at 400 and 101 MHz. ^{19}F NMR were reported as ^{19}F exp. comp. pulse decoupling ($F^{19}CPD$) unless otherwise noted. The chemical shifts are given in ppm relative to tetramethylsilane [^{1}H: δ ($SiMe_4$) = 0.00 ppm] as an internal standard or relative to the resonance of the solvent [^{1}H: δ ($CDCl_3$) = 7.26, ^{13}C: δ ($CDCl_3$) = 77.16 ppm]. Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets), etc. Coupling constants are reported as *J* values in Hz. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. HPLC was performed on Thermo UltiMate 3000. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

Unless otherwise noted, all reagents and starting materials were purchased from Aldrich, Strem, Alfa Aesar Energy-chemical, or Adamas-beta and used without further purification. TBADT (tetrabutyl ammonium decatungstate) was synthesized according to the reported method (MacMillan, D. W. C. *Nature* **2018**, *560*, 70−75).

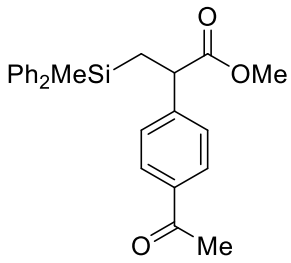
General Procedure for Nickel/Photo-Cocatalyzed Three-Component Silylarylation of Electron-Deficient Alkenes



In an N_2-filled glovebox, tetrabutylammonium decatungstate (TBADT) (33.2 mg, 0.01 mmol, 5 mol%), $NiBr_2$·DME (6.2 mg, 0.02 mmol, 10 mol%), dtbbpy **L1** (6.4 mg, 0.024 mmol, 12 mol%) K_3PO_4 (63.5 mg, 0.3 mmol, 1.5 equiv), the aryl bromides **1** (0.2 mmol, 1.0 equiv), the electron-deficient olefins **2** (0.6 mmol, 3.0 equiv), the hydrosilianes **3** (1 mmol, 5.0 equiv), and dry MeCN (1 mL) were placed in a tube equipped with a stir bar. Subsequently, the reaction mixture was stirred and irradiated using two 34 W 390 nm LED lamps (Kessil PR160-390, 5 cm away to keep the reaction below 40 °C) for 15 h. After exposing to air for 15 minutes, the reaction mixture was filtered through a pad of silica gel and concentrated under reduced pressure. The residue was purified through column chromatography (silica gel, petroleum ether/ethyl acetate) to afford the desired products **4**.

Characterization Data of Silylarylation Products 4

Methyl 2-(4-acetylphenyl)-3-(methyldiphenylsilyl)propanoate (4aaa)



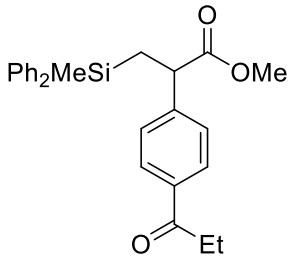
The title compound **4aaa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (52.3 mg, 65%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.83 (d, *J* = 8.4 Hz, 2H), 7.50 – 7.46 (m, 2H), 7.45 – 7.42 (m, 2H), 7.39 – 7.34 (m, 4H), 7.33 – 7.29 (m, 4H), 3.73 (dd, *J* = 8.2, 7.2 Hz, 1H), 3.46 (s, 3H), 2.57 (s, 3H), 2.05 (dd, *J* = 14.9, 8.2 Hz, 1H), 1.63 (dd, *J* = 14.9, 7.2 Hz, 1H), 0.37 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 197.8, 174.4, 146.3, 136.2 (2C), 135.8, 134.7 (2C), 134.5 (2C), 129.6, 129.5, 128.8 (2C), 128.2 (2C), 128.1 (2C), 128.0 (2C), 52.3, 47.2, 26.8, 19.2, –4.2 ppm.

HRMS (ESI) m/z calculated for $C_{25}H_{26}O_3Si$ $[M+Na]^+$: 425.1543, found: 425.1548.

Methyl 3-(methyldiphenylsilyl)-2-(4-propionylphenyl)propanoate (4baa)



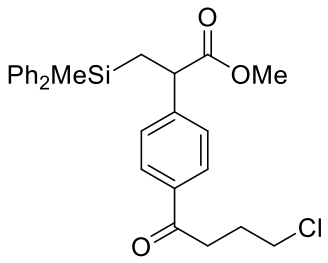
The title compound **4baa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (49.9 mg, 60%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.84 (d, *J* = 8.4 Hz, 2H), 7.50 – 7.46 (m, 2H), 7.46 – 7.43 (m, 2H), 7.40 – 7.34 (m, 4H), 7.33 – 7.29 (m, 4H), 3.73 (dd, *J* = 8.3, 7.2 Hz, 1H), 3.46 (s, 3H), 2.97 (q, *J* = 7.2 Hz, 2H), 2.06 (dd, *J* = 14.9, 8.2 Hz, 1H), 1.64 (dd, *J* = 14.9, 7.2 Hz, 1H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.38 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 200.4, 174.5, 146.0, 136.3, 136.0, 135.8, 134.7 (2C), 134.5 (2C), 129.6, 129.5, 128.4 (2C), 128.2 (2C), 128.1 (2C), 128.0 (2C), 52.2, 47.2, 31.9, 19.2, 8.4, –4.2 ppm.

HRMS (ESI) m/z calculated for $C_{26}H_{28}O_3Si$ $[M+Na]^+$: 439.1700, found: 439.1709.

Methyl 2-(4-(4-chlorobutanoyl)phenyl)-3-(methyldiphenylsilyl)propanoate (4caa)



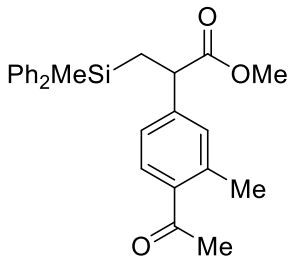
The title compound **4caa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (41.8 mg, 45%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.85 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.47 (m, 2H), 7.46 – 7.43 (m, 2H), 7.41 – 7.35 (m, 4H), 7.34 – 7.28 (m, 4H), 3.74 (t, *J* = 7.7 Hz, 1H), 3.68 (t, *J* = 6.2 Hz, 2H), 3.46 (s, 3H), 3.14 (t, *J* = 6.9 Hz, 2H), 2.28 – 2.17 (m, 2H), 2.06 (dd, *J* = 14.9, 8.2 Hz, 1H), 1.64 (dd, *J* = 15.5, 7.8 Hz, 1H), 0.38 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 198.5, 174.4, 146.4, 136.2, 135.8 (2C), 134.7 (2C), 134.5 (2C), 129.6, 129.5, 128.4 (2C), 128.3 (2C), 128.1 (2C), 128.0 (2C), 52.3, 47.2, 44.8, 35.4, 26.9, 19.2, –4.2 ppm.

HRMS (ESI) m/z calculated for $C_{27}H_{29}ClO_3Si$ $[M+Na]^+$: 487.1467, found: 487.1471.

Methyl 2-(4-acetyl-3-methylphenyl)-3-(methyldiphenylsilyl)propanoate (4daa)



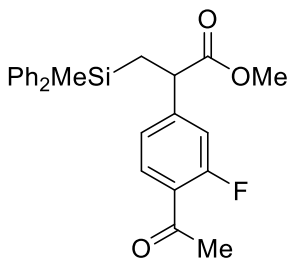
The title compound **4daa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (44.1 mg, 53%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.59 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.43 (m, 4H), 7.40 – 7.29 (m, 6H), 7.13 (d, *J* = 8.1 Hz, 1H), 7.05 (s, 1H), 3.68 (t, *J* = 7.7 Hz, 1H), 3.46 (s, 3H), 2.55 (s, 3H), 2.46 (s, 3H), 2.04 (dd, *J* = 14.9, 8.2 Hz, 1H), 1.63 (dd, *J* = 15.0, 7.1 Hz, 1H), 0.41 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 201.1, 174.5, 144.5, 139.2, 136.4, 136.3, 136.0, 134.7 (2C), 134.5 (2C), 131.8, 130.0, 129.6, 129.4, 128.0 (2C), 127.9 (2C), 125.2, 52.2, 47.0, 29.6, 21.9, 19.1, –4.2 ppm.

HRMS (ESI) m/z calculated for $C_{26}H_{28}O_3Si$ $[M+Na]^+$: 439.1700, found: 439.1709.

Methyl 2-(4-acetyl-3-fluorophenyl)-3-(methyldiphenylsilyl)propanoate (4eaa)



The title compound **4eaa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (42.1 mg, 50%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.75 (t, *J* = 7.9 Hz, 1H), 7.50 – 7.47 (m, 2H), 7.46 – 7.42 (m, 2H), 7.39 – 7.30 (m, 6H), 7.09 – 6.98 (m, 2H), 3.70 (t, *J* = 7.7 Hz, 1H), 3.46 (s, 3H),

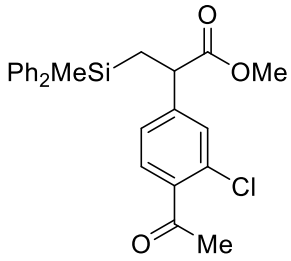
2.60 (d, J = 4.9 Hz, 3H), 2.03 (dd, J = 14.9, 8.3 Hz, 1H), 1.61 (dd, J = 15.0, 7.1 Hz, 1H), 0.43 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 195.5 (d, J_{C-F} = 3.6 Hz), 173.9, 162.3 (d, J_{C-F} = 255.6 Hz), 148.5 (d, J_{C-F} = 8.4 Hz), 135.8 (d, J_{C-F} = 30.8 Hz), 134.6 (2C), 134.5 (2C), 130.9 (d, J_{C-F} = 2.9 Hz), 129.7, 129.5, 128.1 (2C), 128.0 (2C), 124.5 (d, J_{C-F} = 13.0 Hz), 124.1 (d, J_{C-F} = 3.0 Hz), 116.3, 116.0, 52.4, 46.9 (d, J_{C-F} = 1.5 Hz), 31.5 (d, J_{C-F} = 7.4 Hz), 19.2, –4.2 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –108.72 (s, 1F).

HRMS (ESI) m/z calculated for $C_{25}H_{25}FO_3Si$ $[M+Na]^+$: 443.1449, found: 443.1458.

Methyl 2-(4-acetyl-3-chlorophenyl)-3-(methyldiphenylsilyl)propanoate (4faa)



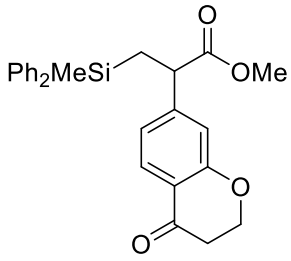
The title compound **4faa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (41.1 mg, 47%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.49 – 7.42 (m, 5H), 7.39 – 7.31 (m, 6H), 7.24 (d, J = 1.7 Hz, 1H), 7.17 (dd, J = 8.0, 1.7 Hz, 1H), 3.66 (t, J = 7.7 Hz, 1H), 3.46 (s, 3H), 2.61 (s, 3H), 2.01 (dd, J = 14.9, 8.3 Hz, 1H), 1.60 (dd, J = 14.9, 7.2 Hz, 1H), 0.44 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 199.9, 174.0, 145.5, 137.8, 135.9, 135.7, 134.6 (2C), 134.5 (2C), 131.7, 130.3, 129.9, 129.7, 129.6, 128.1 (2C), 128.0 (2C), 126.6, 52.4, 46.8, 30.8, 19.1, –4.2 ppm.

HRMS (ESI) m/z calculated for $C_{25}H_{25}ClO_3Si$ $[M+H]^+$: 437.1334, found: 437.1343.

Methyl 3-(methyldiphenylsilyl)-2-(4-oxochroman-8-yl)propanoate (4gaa)



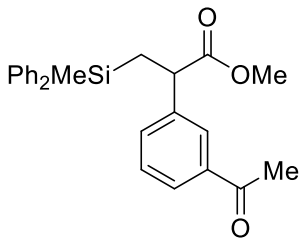
The title compound **4gaa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (35.3 mg, 41%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.76 (d, J = 8.1 Hz, 1H), 7.49 – 7.42 (m, 4H), 7.38 – 7.29 (m, 6H), 6.88 (dd, J = 8.1, 1.7 Hz, 1H), 6.83 (d, J = 1.7 Hz, 1H), 4.54 – 4.40 (m, 2H), 3.66 (dd, J = 8.4, 6.9 Hz, 1H), 3.46 (s, 3H), 2.85 – 2.66 (m, 2H)., 2.01 (dd, J = 14.9, 8.4 Hz, 1H), 1.60 (dd, J = 14.9, 6.9 Hz, 1H), 0.43 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 191.5, 174.0, 161.9, 149.6, 136.1, 135.8, 134.6 (2C), 134.5 (2C), 129.6, 129.4, 128.0 (4C), 127.6, 121.3, 120.4, 117.2, 67.2, 52.3, 47.3, 37.8, 19.0, –4.2 ppm.

HRMS (ESI) m/z calculated for $C_{26}H_{26}O_4Si$ $[M+Na]^+$: 453.1493, found: 453.1501.

Methyl 2-(3-acetylphenyl)-3-(methyldiphenylsilyl)propanoate (4haa)



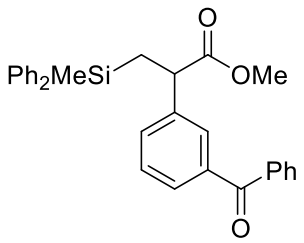
The title compound **4haa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (49.0 mg, 61%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.80 (d, *J* = 7.8 Hz, 1H), 7.75 (s, 1H), 7.50 – 7.41 (m, 5H), 7.40 – 7.29 (m, 7H), 3.75 (t, *J* = 7.8 Hz, 1H), 3.46 (s, 3H), 2.54 (s, 3H), 2.07 (dd, *J* = 14.9, 8.1 Hz, 1H), 1.67 (dd, *J* = 14.9, 7.5 Hz, 1H), 0.38 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 198.0, 174.7, 141.4, 137.4, 136.3, 135.8, 134.7 (2C), 134.5 (2C), 132.7, 129.6, 129.4, 128.9, 128.0 (5C), 127.4, 52.2, 47.0, 26.8, 19.2, –4.2 ppm.

HRMS (ESI) m/z calculated for $C_{25}H_{26}O_3Si$ $[M+Na]^+$: 425.1543, found: 425.1550.

Methyl 2-(3-benzoylphenyl)-3-(methyldiphenylsilyl)propanoate (4iaa)



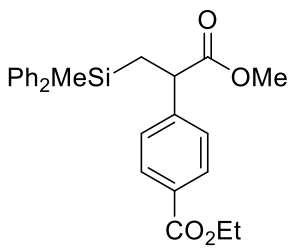
The title compound **4iaa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (48.3 mg, 52%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.75 (d, *J* = 7.4 Hz, 2H), 7.67 (s, 1H), 7.65 – 7.58 (m, 2H), 7.51 – 7.43 (m, 7H), 7.40 – 7.29 (m, 7H), 3.76 (t, *J* = 7.7 Hz, 1H), 3.46 (s, 3H), 2.06 (dd, *J* = 14.9, 8.2 Hz, 1H), 1.67 (dd, *J* = 14.9, 7.2 Hz, 1H), 0.42 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 196.5, 174.7, 141.3, 137.9, 137.6, 136.2, 135.9, 134.7 (2C), 134.5 (2C), 132.6, 132.0, 130.2 (2C), 129.7, 129.6, 129.5, 129.2, 128.6, 128.4 (2C), 128.0 (4C), 52.2, 47.0, 19.3, –4.1 ppm.

HRMS (ESI) m/z calculated for $C_{30}H_{28}O_3Si$ $[M+H]^+$: 465.1880, found: 465.1885.

Ethyl 4-(1-methoxy-3-(methyldiphenylsilyl)-1-oxopropan-2-yl)benzoate (4jaa)



The title compound **4jaa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (53.5.3 mg, 62%).

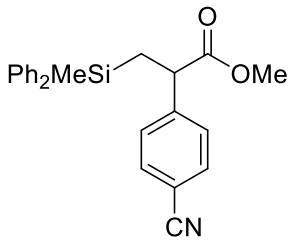
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.93 (d, *J* = 8.3 Hz, 2H), 7.51 – 7.48 (m, 2H), 7.46 – 7.44 (m, 2H), 7.40 – 7.34 (m, 4H), 7.33 – 7.27 (m, 4H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.72 (t, *J* =

7.7 Hz, 1H), 3.45 (s, 3H), 2.06 (dd, *J* = 14.9, 8.3 Hz, 1H), 1.64 (dd, *J* = 14.9, 7.2 Hz, 1H), 1.39 (t, *J* = 7.1 Hz, 3H), 0.36 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 174.5, 166.5, 145.9, 136.3, 135.8, 134.7 (2C), 134.5 (2C), 129.9 (2C), 129.6 (2C), 129.5, 128.1 (2C), 128.0 (4C), 61.1, 52.2, 47.2, 19.2, 14.5, –4.2 ppm.

HRMS (ESI) m/z calculated for $C_{26}H_{28}O_4Si$ $[M+Na]^+$: 455.1644, found: 455.1652.

Methyl 2-(4-acetylphenyl)-3-(methyldiphenylsilyl)propanoate (4kaa)



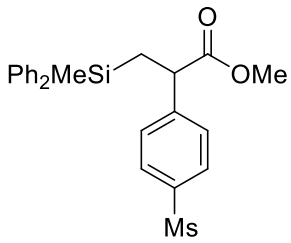
The title compound **4kaa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (33.1 mg, 43%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.51 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.45 (m, 2H), 7.43 – 7.41 (m, 2H), 7.39 – 7.34 (m, 4H), 7.34 – 7.28 (m, 4H), 3.72 (t, *J* = 7.7 Hz, 1H), 3.46 (s, 3H), 2.04 (dd, *J* = 14.9, 8.2 Hz, 1H), 1.62 (dd, *J* = 15.5, 7.2 Hz, 1H), 0.40 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 175.0, 147.1, 138.2, 136.9, 136.5, 135.6, 135.4, 135.1, 133.4 (2C), 131.0, 130.7, 130.6, 129.8, 129.1 (2C), 129.0 (2C), 119.8, 112.2, 53.4, 48.3, 20.3, –3.2 ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{23}NO_2Si$ $[M+Na]^+$: 408.1390, found: 408.1393.

Methyl 3-(methyldiphenylsilyl)-2-(4-(methylsulfonyl)phenyl)propanoate (4laa)



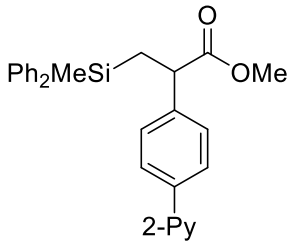
The title compound **4laa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 2:1) as a pale yellow oil (48.2 mg, 55%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.79 (d, *J* = 7.9 Hz, 2H), 7.50 – 7.29 (m, 12H), 3.77 (t, *J* = 7.7 Hz, 1H), 3.46 (s, 3H), 3.01 (s, 3H), 2.06 (dd, *J* = 14.9, 8.2 Hz, 1H), 1.63 (dd, *J* = 15.4, 6.8 Hz, 1H), 0.42 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 174.1, 147.1, 139.4, 135.8, 135.6, 134.6 (2C), 134.5 (2C), 129.7, 129.6, 129.0 (2C), 128.1 (2C), 128.0 (2C), 127.7 (2C), 52.4, 47.2, 44.6, 19.4, –4.2 ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{26}O_4SSi$ $[M+Na]^+$: 461.1213, found: 461.1216.

Methyl 3-(methyldiphenylsilyl)-2-(4-(pyridin-2-yl)phenyl)propanoate (4maa)



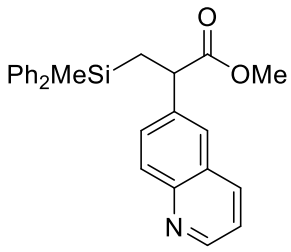
The title compound **4maa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (48.9 mg, 56%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.69 (d, *J* = 4.8 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.79 – 7.65 (m, 2H), 7.54 – 7.43 (m, 4H), 7.41 – 7.29 (m, 8H), 7.27 – 7.18 (m, 1H), 3.72 (t, *J* = 7.7 Hz, 1H), 3.46 (s, 3H), 2.07 (dd, *J* = 14.9, 8.2 Hz, 1H), 1.68 (dd, *J* = 14.9, 7.3 Hz, 1H), 0.37 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 175.0, 157.2, 149.8, 141.8, 138.5, 136.9, 136.6, 136.0, 134.7 (2C), 134.5 (2C), 129.5, 129.4, 128.4 (2C), 128.0 (4C), 127.2 (2C), 122.2, 120.6, 52.2, 46.9, 19.2, –4.1 ppm.

HRMS (ESI) m/z calculated for $C_{28}H_{27}NO_2Si$ $[M+H]^+$: 438.1884, found: 438.1889.

Methyl 3-(methyldiphenylsilyl)-2-(quinolin-6-yl)propanoate (4naa)



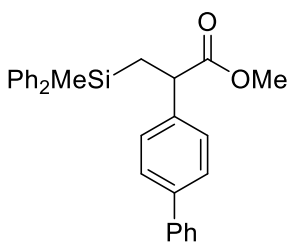
The title compound **4naa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (28.8 mg, 35%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.88 (d, *J* = 4.3 Hz, 1H), 8.07 – 7.94 (m, 2H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.57 (s, 1H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.41 – 7.33 (m, 4H), 7.31 – 7.27 (m, 4H), 3.88 (t, *J* = 7.7 Hz, 1H), 3.48 (s, 3H), 2.14 (dd, *J* = 14.9, 8.1 Hz, 1H), 1.75 (dd, *J* = 14.9, 7.3 Hz, 1H), 0.38 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 174.8, 150.4, 147.7, 139.1, 136.3, 136.1, 136.0, 134.7 (2C), 134.5 (2C), 129.9, 129.7, 129.6, 129.4, 128.2, 128.0 (2C), 127.9 (2C), 126.6, 121.4, 52.2, 47.1, 19.3, –4.2 ppm.

HRMS (ESI) m/z calculated for $C_{26}H_{25}NO_2Si$ $[M+H]^+$: 412.1727, found: 412.1736.

Methyl 2-([1,1'-biphenyl]-4-yl)-3-(methyldiphenylsilyl)propanoate (4oaa)



The title compound **4oaa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (37.5 mg, 43%).

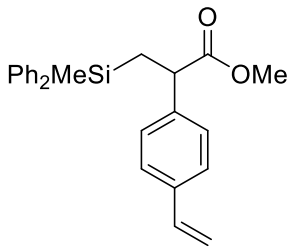
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.56 (d, *J* = 7.6 Hz, 2H), 7.53 – 7.43 (m, 8H), 7.40 – 7.27 (m, 9H), 3.73 (t, *J* = 7.7 Hz, 1H), 3.48 (s, 3H), 2.08 (dd, *J* = 14.9, 8.3 Hz, 1H), 1.69 (dd,

J = 14.9, 7.1 Hz, 1H), 0.41 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 175.1, 140.9, 140.3, 140.0, 136.5, 136.1 (2C), 134.7 (2C), 134.5 (2C), 129.5, 129.4, 128.9 (2C), 128.3 (2C), 128.0 (4C), 127.4 (2C), 127.2 (2C), 52.1, 46.8, 19.3, –4.2 ppm.

HRMS (ESI) m/z calculated for $C_{29}H_{28}O_2Si$ $[M+Na]^+$:459.1751, found: 459.1758.

Methyl 3-(methyldiphenylsilyl)-2-(4-vinylphenyl)propanoate (4paa)



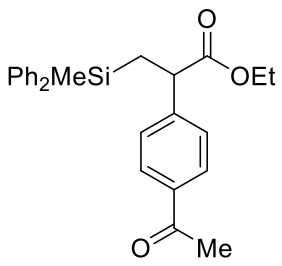
The title compound **4paa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (16.9 mg, 22%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.51 – 7.43 (m, 4H), 7.39 – 7.28 (m, 8H), 7.18 (d, *J* = 8.3 Hz, 2H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.71 (d, *J* = 17.6 Hz, 1H), 5.22 (d, *J* = 10.9 Hz, 1H), 3.65 (t, *J* = 7.7 Hz, 1H), 3.44 (s, 3H), 2.03 (dd, *J* = 14.9, 8.3 Hz, 1H), 1.63 (dd, *J* = 14.9, 7.1 Hz, 1H), 0.36 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 174.9, 140.5, 136.6, 136.5, 136.4, 136.0, 134.6 (2C), 134.4 (2C), 129.4, 129.3, 128.0 (2C), 127.9 (4C), 126.4 (2C), 113.8, 52.0, 46.7, 19.1, –4.3 ppm.

HRMS (ESI) m/z calculated for $C_{25}H_{26}O_2Si$ $[M+Na]^+$: 409.1594, found: 409.1604.

Ethyl 2-(4-acetylphenyl)-3-(methyldiphenylsilyl)propanoate (4aba)



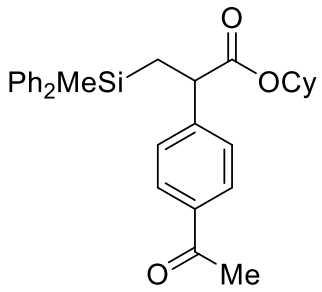
The title compound **4aba** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (46.6 mg, 56%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.83 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.44 (m, 4H), 7.40 – 7.28 (m, 8H), 3.91 (q, *J* = 7.1 Hz, 2H), 3.72 (t, *J* = 7.7 Hz, 1H), 2.58 (s, 3H), 2.06 (dd, *J* = 14.9, 8.3 Hz, 1H), 1.63 (dd, *J* = 14.7, 7.2 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.39 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 197.8, 174.0, 146.5, 136.3, 136.1, 135.9, 134.7 (2C), 134.5 (2C), 129.6, 129.4, 128.7 (2C), 128.2 (2C), 128.0 (4C), 61.2, 47.3, 26.7, 19.2, 14.1, –4.1 ppm.

HRMS (ESI) m/z calculated for $C_{26}H_{28}O_3Si$ $[M+H]^+$: 417.1880, found: 417.1883.

Cyclohexyl 2-(4-acetylphenyl)-3-(methyldiphenylsilyl)propanoate (4aca)



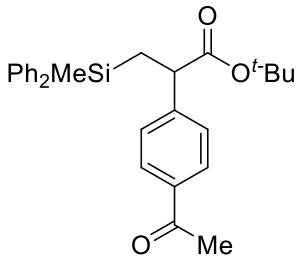
The title compound **4aca** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (34.8 mg, 37%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.81 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.41 (m, 4H), 7.37 – 7.28 (m, 8H), 4.65 – 4.55 (m, 1H), 3.69 (t, *J* = 7.6 Hz, 1H), 2.57 (s, 3H), 2.05 (dd, *J* = 14.9, 8.0 Hz, 1H), 1.71 – 1.53 (m, 5H), 1.35 – 1.14 (m, 6H), 0.38 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 197.9, 173.4, 146.8, 136.4, 136.1 (2C), 134.7 (2C), 134.5 (2C), 129.5, 129.4, 128.7 (2C), 128.2 (2C), 128.0 (4C), 73.4, 47.6, 31.4, 31.2, 26.7, 25.4, 23.7, 23.6, 18.8, –4.0 ppm.

HRMS (ESI) m/z calculated for $C_{30}H_{34}O_3Si$ $[M+Na]^+$: 493.2169, found: 493.2176.

***tert*-Butyl 2-(4-acetylphenyl)-3-(methyldiphenylsilyl)propanoate (4ada)**



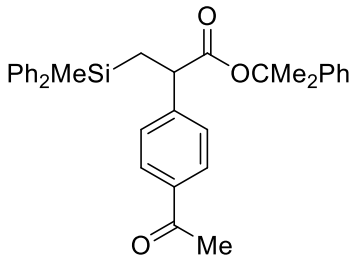
The title compound **4ada** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (39.9 mg, 45%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.76 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.36 (m, 4H), 7.32 – 7.19 (m, 8H), 3.56 (t, *J* = 7.5 Hz, 1H), 2.51 (s, 3H), 1.96 (dd, *J* = 15.0, 7.7 Hz, 1H), 1.53 (dd, *J* = 15.0, 7.4 Hz, 1H), 1.23 (s, 9H), 0.31 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 197.9, 173.2, 147.1, 136.5, 136.2, 135.9, 134.6 (2C), 134.5 (2C), 129.5, 129.4, 128.6 (2C), 128.1 (2C), 128.0 (4C), 81.1, 48.3, 27.9 (3C), 26.7, 18.7, –4.0 ppm.

HRMS (ESI) m/z calculated for $C_{28}H_{32}O_3Si$ $[M+Na]^+$: 467.2013, found: 467.2022.

2-Phenylpropan-2-yl 2-(4-acetylphenyl)-3-(methyldiphenylsilyl)propanoate (4aea)



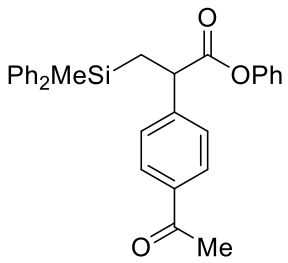
The title compound **4aea** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (46.5 mg, 46%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.75 (d, *J* = 7.9 Hz, 2H), 7.40 – 7.33 (m, 4H), 7.31 – 7.20 (m, 6H), 7.16 (d, *J* = 7.4 Hz, 2H), 7.11 – 7.05 (m, 3H), 6.98 – 6.88 (m, 2H), 3.63 (t, *J* = 7.6 Hz, 1H), 2.51 (s, 3H), 1.92 (dd, *J* = 15.0, 7.3 Hz, 1H), 1.58 (s, 3H), 1.51 (dd, *J* = 15.0, 7.0 Hz , 1H), 1.46 (s, 3H), 0.26 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 197.9, 172.2, 146.5, 145.4, 136.4, 136.2, 136.1, 134.6 (2C), 134.5 (2C), 129.5, 129.4, 128.6 (2C), 128.4 (2C), 128.2 (2C), 128.0 (4C), 127.1, 124.2 (2C), 82.2, 48.1, 29.2, 27.5, 26.8, 18.4, –4.0 ppm.

HRMS (ESI) m/z calculated for $C_{33}H_{34}O_3Si$ $[M+Na]^+$: 529.2169, found: 529.2181.

Methyl 2-(4-acetylphenyl)-3-(methyldiphenylsilyl)propanoate (4afa)



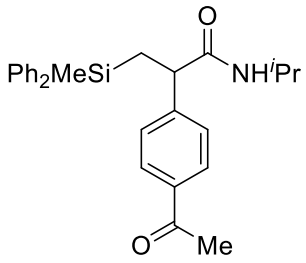
The title compound **4afa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (32.5 mg, 35%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.87 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.45 (m, 4H), 7.42 – 7.32 (m, 8H), 7.30 – 7.23 (m, 2H), 7.20 – 7.13 (m, 1H), 6.77 (d, *J* = 8.3 Hz, 2H), 3.96 (t, *J* = 7.6 Hz, 1H), 2.59 (s, 3H), 2.17 (dd, *J* = 15.0, 7.9 Hz, 1H), 1.74 (dd, *J* = 15.0, 7.3 Hz, 1H), 0.43 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 197.8, 172.6, 150.7, 145.8, 136.4, 136.1, 135.8, 134.7 (2C), 134.5 (2C), 129.7, 129.6, 129.4 (2C), 128.9 (2C), 128.3 (2C), 128.2 (2C), 128.1 (2C), 126.0, 121.3 (2C), 47.5, 26.8, 19.0, –3.9 ppm.

HRMS (ESI) m/z calculated for $C_{30}H_{28}O_3Si$ $[M+Na]^+$: 487.1700, found: 487.1707.

2-(4-Acetylphenyl)-N-isopropyl-3-(methyldiphenylsilyl)propanamide (4aga)



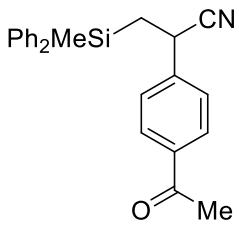
The title compound **4aga** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (38.6 mg, 45%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.35 (m, 4H), 7.30 – 7.17 (m, 8H), 4.99 (d, *J* = 7.8 Hz, 1H), 3.90 – 3.78 (m, 1H), 3.28 (t, *J* = 7.4 Hz, 1H), 2.49 (s, 3H), 2.05 (dd, *J* = 14.9, 7.3 Hz, 1H), 1.53 (dd, *J* = 15.0, 7.7 Hz, 1H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.87 (d, *J* = 6.5 Hz, 3H), 0.27 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 197.8, 172.1, 147.7, 136.5, 136.4, 136.0, 134.6 (2C), 134.5 (2C), 129.5, 129.4, 128.8 (2C), 128.0 (6C), 49.1, 41.7, 26.7, 22.6, 22.5, 19.0, –4.0 ppm.

HRMS (ESI) m/z calculated for $C_{27}H_{31}NO_2Si$ $[M+Na]^+$: 452.2016, found: 452.2023.

2-(4-Acetylphenyl)-3-(methyldiphenylsilyl)propanenitrile (4aha)



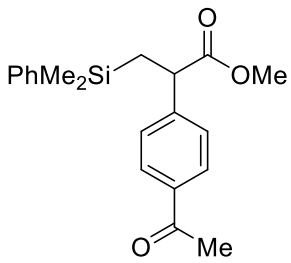
The title compound **4aha** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (29.5 mg, 40%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.87 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.44 (m, 4H), 7.43 – 7.34 (m, 6H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.77 (dd, *J* = 8.8, 6.8 Hz, 1H), 2.58 (s, 3H), 1.93 (dd, *J* = 15.0, 8.9 Hz, 1H), 1.73 (dd, *J* = 15.0, 6.8 Hz, 1H), 0.57 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 197.3, 143.2, 136.9, 134.9, 134.8, 134.5 (4C), 130.0 (2C), 129.2 (2C), 128.3 (4C), 127.5 (2C), 121.4, 32.8, 26.8, 22.5, –4.1 ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{23}NOSi$ $[M+H]^+$: 370.1622, found: 370.1629.

Methyl 2-(4-acetylphenyl)-3-(dimethyl(phenyl)silyl)propanoate (4aab)



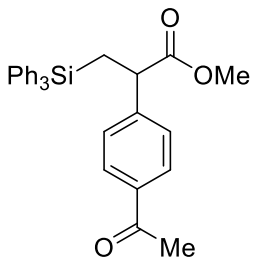
The title compound **4aab** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (32.6 mg, 48%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.85 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.41 (m, 2H), 7.38 – 7.32 (m, 5H), 3.67 (t, *J* = 7.8 Hz, 1H), 3.53 (s, 3H), 2.58 (s, 3H), 1.70 (dd, *J* = 14.8, 8.1 Hz, 1H), 1.34 (dd, *J* = 14.8, 7.6 Hz, 1H), 0.18 (s, 3H), 0.15 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 197.8, 174.6, 146.3, 137.9, 136.2, 133.7 (2C), 129.2, 128.7 (2C), 128.2 (2C), 127.9 (2C), 52.3, 47.3, 26.7, 20.8, –2.6, –2.9 ppm.

HRMS (ESI) m/z calculated for $C_{20}H_{24}O_3Si$ $[M+Na]^+$: 363.1387, found: 363.1390.

Methyl 2-(4-acetylphenyl)-3-(triphenylsilyl)propanoate (4aac)



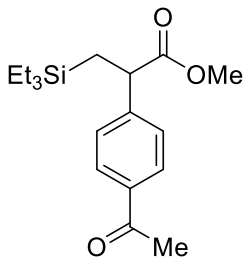
The title compound **4aac** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (33.4 mg, 36%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.82 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.49 (m, 6H), 7.44 – 7.31 (m, 11H), 3.91 (dd, *J* = 9.6, 5.2 Hz, 1H), 3.26 (s, 3H), 2.57 (s, 3H), 2.45 (dd, *J* = 15.0, 9.6 Hz, 1H), 1.87 (dd, *J* = 15.0, 5.1 Hz, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 197.8, 174.0, 146.7, 136.3, 136.1 (2C), 135.8 (6C), 134.0 (3C), 129.8 (3C), 128.8 (2C), 128.0 (6C), 52.1, 47.1, 26.8, 18.2 ppm.

HRMS (ESI) m/z calculated for $C_{30}H_{28}O_3Si$ $[M+H]^+$: 465.1880, found: 465.1887.

Methyl 2-(4-acetylphenyl)-3-(triethylsilyl)propanoate (4aad)



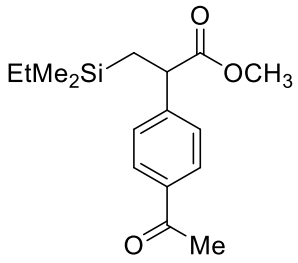
The title compound **4aad** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (16.1 mg, 25%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.90 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 3.71 (t, *J* = 7.8 Hz, 1H), 3.64 (s, 3H), 2.59 (s, 3H), 1.46 (dd, *J* = 14.8, 8.0 Hz, 1H), 1.12 (dd, *J* = 14.8, 7.6 Hz, 1H), 0.87 (t, *J* = 8.0 Hz, 9H), 0.50, – 0.33 (m, 6H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 197.8, 175.0, 147.0, 136.2, 128.8 (2C), 128.2 (2C), 52.4, 47.3, 26.8, 16.6, 7.4 (3C), 3.4 (3C) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{28}O_3Si$ $[M+H]^+$: 321.1880, found: 321.1886.

Methyl 2-(4-acetylphenyl)-3-(diethyl(methyl)silyl)propanoate (4aae)



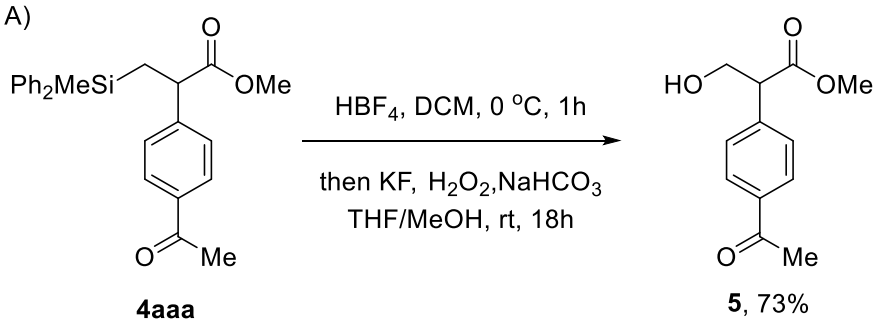
The title compound **4aae** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (13.4 mg, 23%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.90 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 3.71 (t, *J* = 7.9 Hz, 1H), 3.64 (s, 3H), 2.59 (s, 3H), 1.44 (dd, *J* = 14.7, 8.0 Hz, 1H), 1.12 (dd, *J* = 14.7, 7.8 Hz, 1H), 0.87 (t, *J* = 8.0 Hz, 3H), 0.44 – 0.34 (m, 2H), –0.12 (s, 3H), -0.16 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 197.8, 174.9, 146.7, 136.2, 128.8 (2C), 128.2 (2C), 52.3, 47.4, 26.8, 19.8, 7.3, 7.1, –3.6 (2C) ppm.

HRMS (ESI) m/z calculated for $C_{16}H_{24}O_3Si$ $[M+H]^+$: 293.1567, found: 293.1574.

Derivatization of the Silylarylation Products



4aaa **5**, 73%

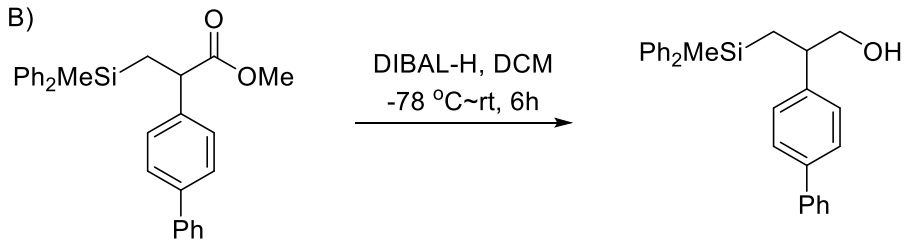
An oven-dried vial was charged with compound **4aaa** (40.2 mg, 0.1 mmol, 1.00 equiv)

and sealed with a rubber septum. After being evacuated and backfilled with N_2 for three times, dry CH_2Cl_2 (1 mL) was added via syringe. The solution was cooled to 0° C, and $HBF_4{\cdot}Et_2O$ (27 μL, 0.20 mmol, 2.0 equiv) was added dropwise. The resulting mixture was stirred at same temperature for 1 h before addition of saturated aqueous $NaHCO_3$ solution to quench the reaction. The mixture was extracted with Et_2O, and the organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated to afford a light yellow oil, which was used directly for the following oxidation without further purification. The crude fluorosilane was dissolved in mixed solvents of THF (1 mL) and MeOH (1 mL). Subsequently, KF (35 mg, 0.60 mmol, 6.0 equiv) and $NaHCO_3$ (50 mg, 0.60 mmol, 6.0 equiv) were added. After being cooled to 0 °C in an ice/water bath, 30% H_2O_2 solution was added dropwise, and the resulting mixture was stirred at room temperature for 18 h. The reaction was quenched by adding saturated aqueous $Na_2S_2O_3$ solution carefully in an ice/water bath. The reaction mixture was diluted with Et_2O, and the organic layer was separated, washed with brine, and dried over $MgSO_4$. Filtration and concentration followed by purification with flashcolumn chromatography (30% EtOAc in petroleum ether) provided the *methyl 2-(4-acetylphenyl)-3-hydroxypropanoate* (**5**) as a pale yellow oil (16.2 mg, 73% yield).

^{1}H NMR (400 MHz, Chloroform-d) δ = 7.93 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 4.14 (dd, *J* = 10.8, 8.1 Hz, 1H), 3.96 – 3.85 (m, 2H), 3.72 (s, 3H), 2.59 (s, 3H), 2.51– 2.40 (br s, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 197.7, 173.1, 141.0, 136.6, 129.0 (2C), 128.6 (2C), 64.4, 53.9, 52.6, 26.8 ppm.

HRMS (ESI) m/z calculated for $C_{12}H_{14}O_4$ $[M+H]^+$: 223.0695, found: 223.0702.



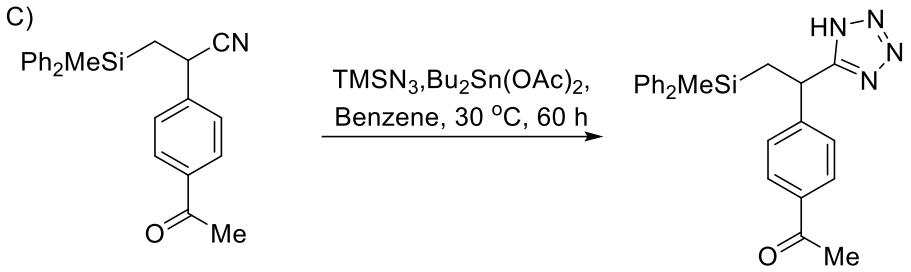
An oven-dried vial was charged with compound **4oaa** (43.6 mg, 0.1 mmol, 1.0 equiv) and sealed with a rubber septum. After being evacuated and backfilled with N_2 for three times, dry DCM (1 mL) was added via syringe under nitrogen. The vial was cooled down to –78 °C, and DIBAL-H (0.2 mmol, 2.0 equiv, 1.0 M in hexane) was added. The resulting solution was stirred at –78 °C for 30 min. Next, the reaction was warmed to room temperature within 6 h. The reaction was quenched by adding saturated aqreous NH_4Cl solution carefully in an ice/water bath. The organic phase was separated, extract with Et_2O, wash with brine, dried over $MgSO_4$, filtered, and concentrated. The crude

residue was purified by flash column chromatography (30% EtOAc in petroleum ether) to give the *2-([1,1'-biphenyl]-4-yl)-3-(methyldiphenylsilyl)propan-1-ol* (**6**) as a colorless oil (36.3 mg, 89% yield).

^{1}H NMR (400 MHz, Chloroform-d) δ = 7.56 (d, *J* = 7.2 Hz, 2H), 7.50 – 7.42 (m, 6H), 7.40 – 7.31 (m, 6H), 7.29 – 7.23 (m, 3H), 7.15 (d, *J* = 8.2 Hz, 2H), 3.67 (d, *J* = 7.4 Hz, 2H), 3.02 – 2.92 (m, 1H), 1.57 (dd, *J* = 14.9, 5.1 Hz, 1H), 1.43 (dd, *J* = 14.8, 9.8 Hz, 1H), 1.34 – 1.25 (m, 1H), 0.30 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 142.5, 141.0, 139.8, 137.4, 136.8, 134.6 (2C), 134.4 (2C), 129.4, 129.1, 128.9 (2C), 128.6 (2C), 128.0 (2C), 127.9 (2C), 127.4 (2C), 127.3, 127.1 (2C), 69.9, 44.1, 17.8, –3.9 ppm.

HRMS (ESI) m/z calculated for $C_{28}H_{28}OSi$ $[M+Na]^+$: 431.1802, found: 431.1809.



4aha **7**, 76%

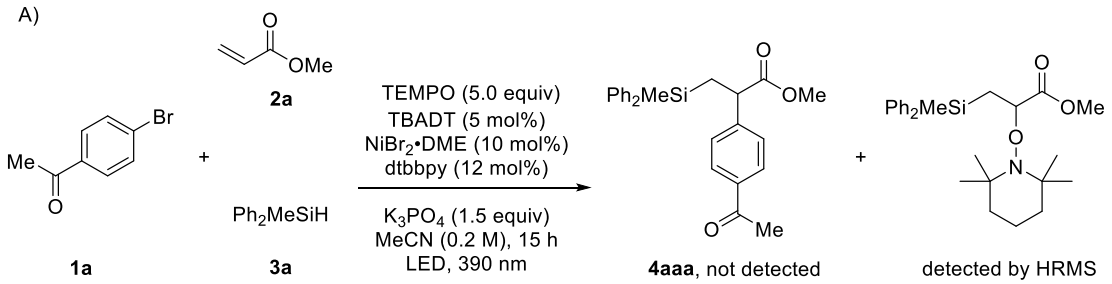
To a microwave tube (5 mL) were added compound **4aha** (46.9 mg, 0.1 mmol, 1 equiv), benzene (1 mL), $TMSN_3$ (40 μL, 0.2 mmol, 3 equiv), and $Bu_2Sn(OAc)_2$ (26.5 μL, 0.1 mmol, 1 equiv) sequentially under nitrogen. The tube was sealed, and the reaction was stirred at 30 °C for 60 h. The crude product was purified by flash column chromatography on silica gel (EA : MeOH = 2:1) to provide the *1-(4-(2-(methyldiphenylsilyl)-1-(1H-tetrazol-5-yl)ethyl)phenyl)ethan-1-one* (**7**) as a white solid (31.3 mg, 76% yield).

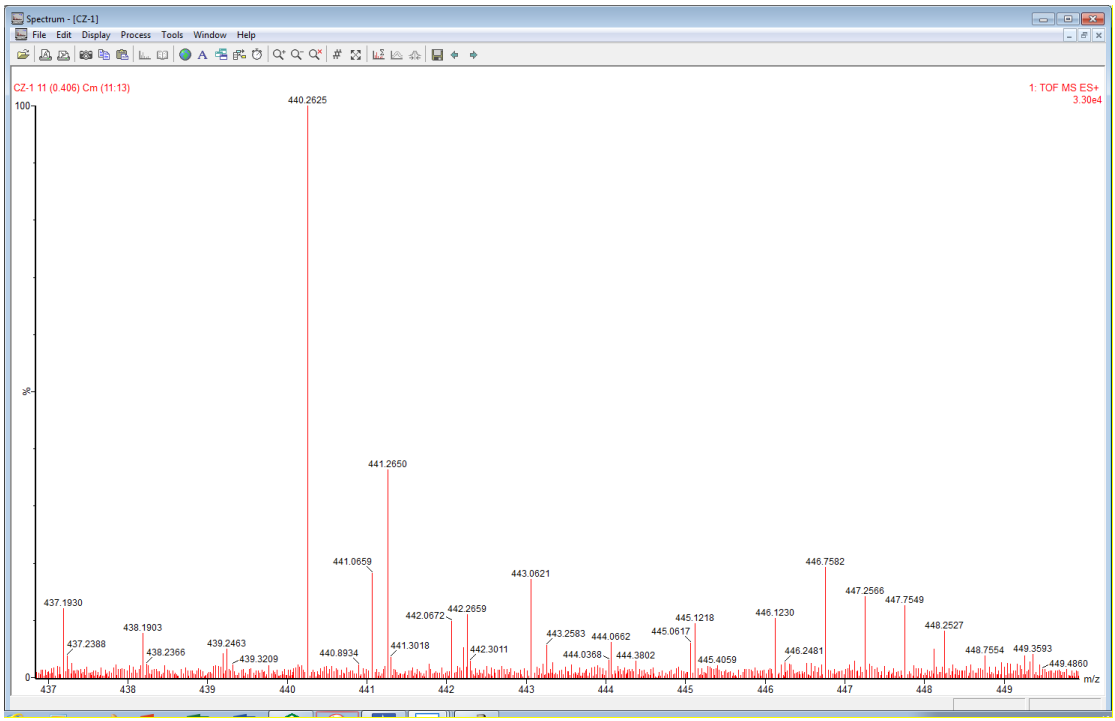
^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.67 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.31 (m, 4H), 7.29 – 7.22 (m, 8H), 4.24 (dd, *J* = 8.8, 6.5 Hz, 1H), 2.45 – 2.41 (m, 1H), 2.41 (s, 3H), 2.06 (dd, *J* = 14.6, 8.8 Hz, 1H), 1.75 (dd, *J* = 15.3, 6.5 Hz, 1H), –0.12 (s, 3H) ppm.

^{13}C NMR (101 MHz, DMSO-d_6) δ = 197.9, 164.4, 153.1, 137.7, 137.4, 134.9, 134.5 (4C), 129.5 (2C), 128.5 (2C), 128.3 (6C), 39.0, 27.1, 22.7, –4.6 ppm.

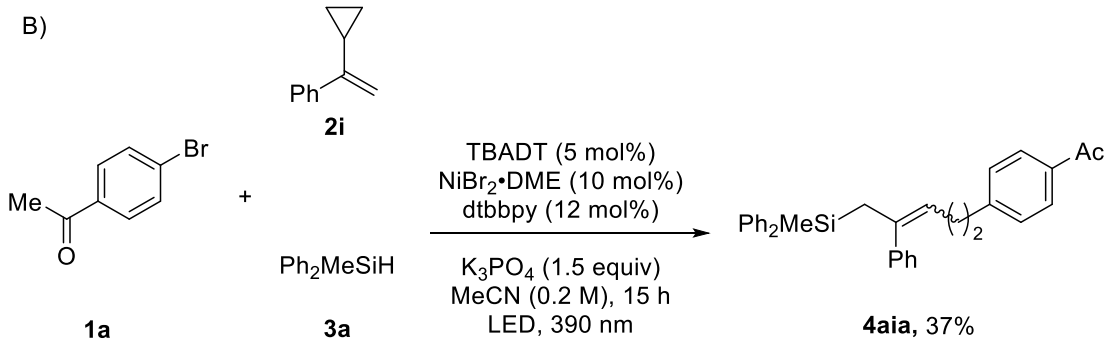
HRMS (ESI) m/z calculated for $C_{24}H_{24}N_4OSi$ $[M+Na]^+$: 435.1612, found: 435.1617.

Mechanistic Studies





HRMS (ESI) m/z calculated for $C_{26}H_{37}NO_3Si$ $[M+H]^+$: 440.2615, found: 440.2625.



In an N_2-filled glovebox, tetrabutylammonium decatungstate (TBADT) (33.2 mg, 0.01 mmol, 5 mol%), $NiBr_2$·DME (6.2 mg, 0.02 mmol, 10 mol%), dtbbpy **L1** (6.4 mg, 0.024 mmol, 12 mol%) K_3PO_4 (63.5 mg, 0.3 mmol, 1.5 equiv), 1-(4-bromophenyl)ethan-1-one **1a** (39.8 mg, 0.2 mmol, 1.0 equiv), (1-cyclopropylvinyl)benzene **2i** (86.4mg, 0.6 mmol, 3.0 equiv), diphenylmethylsilane **3a** (198mg, 1 mmol, 5.0 equiv), and dry MeCN (1 mL) were placed in a tube equipped with a stir bar. Subsequently, the reaction

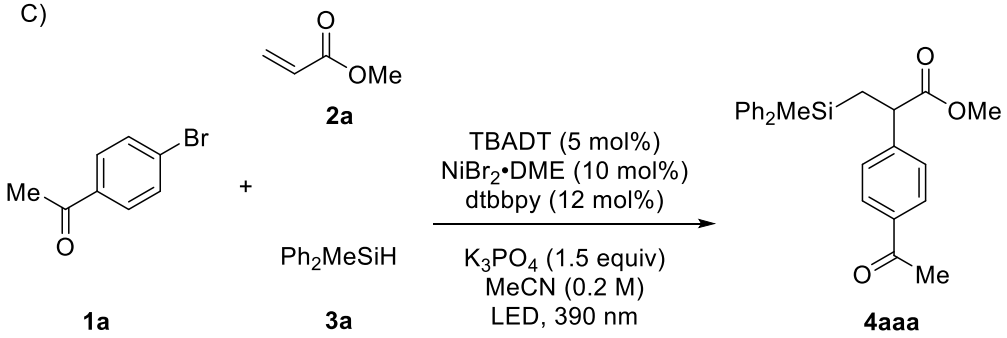
mixture was stirred and irradiated using two 34 W 390 nm LED lamps (Kessil PR160-390, 5 cm away to keep the reaction below 40 °C) for 15 h. After exposing to air for 15 minutes, the reaction mixture was filtered through a pad of silica gel and concentrated under reduced pressure. The residue was purified through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) to afford the desired products **4aia** as a pale yellow oil (33.0 mg, 37%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 7.85 (d, *J* = 8.3 Hz, 2H), 7.46 – 7.40 (m, 4H), 7.37 – 7.26 (m, 6H), 7.27 – 7.16 (m, 5H), 7.11 (d, *J* = 8.3 Hz, 2H), 5.46 (t, *J* = 6.9 Hz, 1H), 2.59 (s, 3H), 2.54 – 2.50 (m, 2H), 2.49 (s, 2H), 2.17 – 2.08 (m, 2H), 0.22 (s, 3H) ppm.

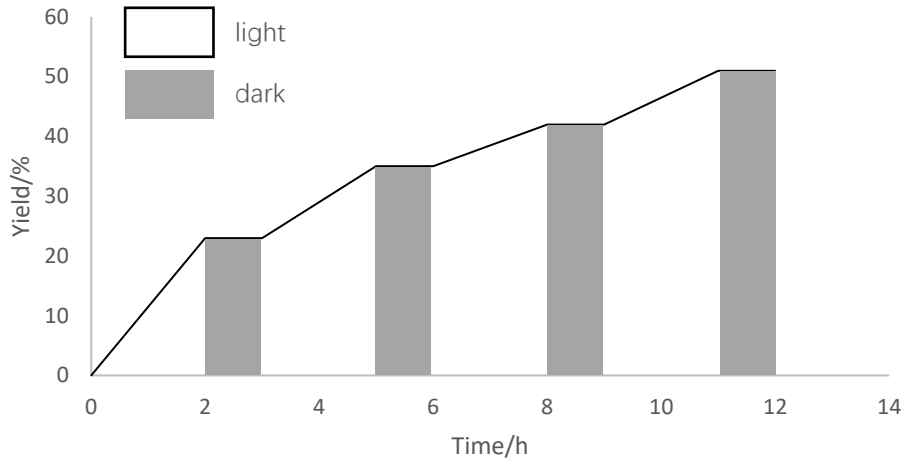
^{13}C NMR (101 MHz, Chloroform-d) δ = 198.1, 148.1, 144.4, 137.7, 136.9, 135.1, 134.7 (4C), 129.4 (2C), 128.7 (2C), 128.5 (2C), 128.2 (2C), 127.8 (5C), 126.8 (2C), 125.9 (2C), 35.7, 30.6, 26.7, 19.3, –3.8 ppm.

HRMS (ESI) m/z calculated for $C_{32}H_{32}OSi$ $[M+Na]^+$: 483.2115, found: 483.2124.

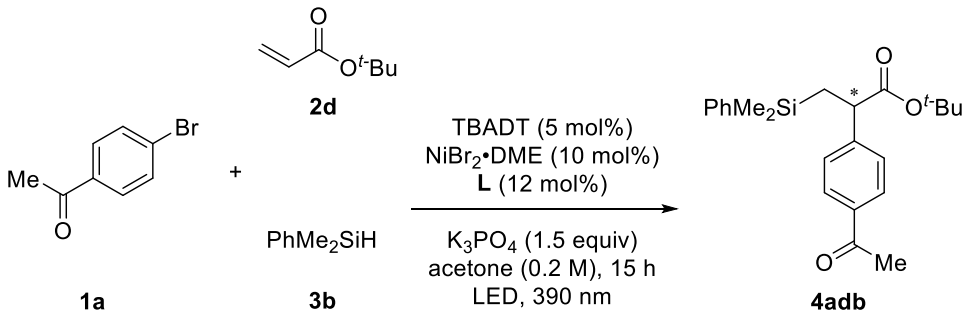
C)

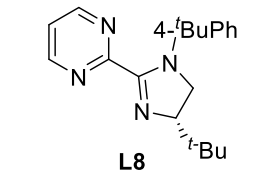


Eight parallel reactions were performed between **1a**, **2a** and **3a** according to the General Procedure. The NMR yields of the desired products **4aaa** with mesitylene as an internal standard. The white area indicates the light irradiation, while the grey area indicates time in the dark.



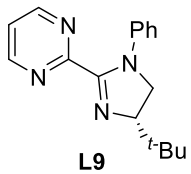
Studies of the Stereochemical Course





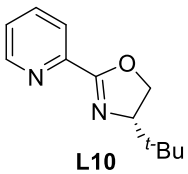
L8

54%, 69% *ee*



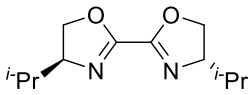
L9

57%, 60% *ee*



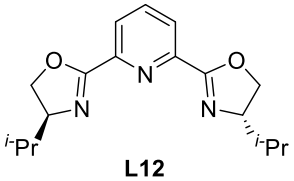
L10

14%, 31% *ee*



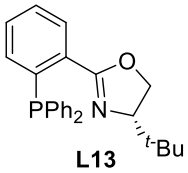
L11

traces



L12

traces



L13

traces

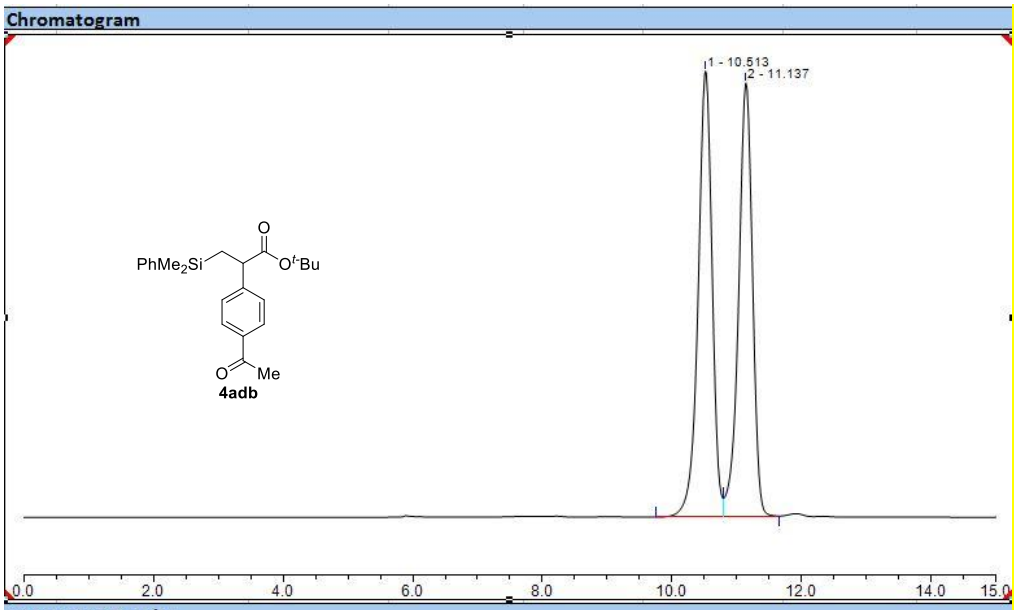
In an N_2-filled glovebox, tetrabutylammonium decatungstate (TBADT) (33.2 mg, 0.01 mmol, 5 mol%), $NiBr_2$·DME (6.2 mg, 0.02 mmol, 10 mol%), **L8** – **L13** (0.024 mmol, 12 mol%) K_3PO_4 (63.5 mg, 0.3 mmol, 1.5 equiv), the 4-bromoacetophenone **1a** (0.2 mmol, 1.0 equiv, 39.8 mg), olefins **2e** (0.6 mmol, 3.0 equiv, 114.0 mg), Ph_2MeSiH **3a** (1 mmol, 5.0 equiv, 198.3 mg), and acetone (1 mL) were placed in a tube equipped with a stir bar. Subsequently, the reaction mixture was stirred and irradiated using two 34 W 390 nm LED lamps (Kessil PR160-390, 5 cm away to keep the reaction below 40 °C) for 15 h. After exposing to air for 15 minutes, the reaction mixture was filtered through a pad of silica gel and concentrated under reduced pressure. The residue was purified through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) to afford the *tert-butyl 2-(4-acetylphenyl)-3-(dimethyl(phenyl)silyl)propanoate* **4adb** as a pale yellow oil (41.3 mg, 54% yield, 69% ee).

^{1}H NMR (400 MHz, Chloroform-d) δ = 7.84 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.40 (m, 2H), 7.36 – 7.29 (m, 5H), 3.56 (t, *J* = 7.7 Hz, 1H), 2.58 (s, 3H), 1.65 (dd, *J* = 14.8, 7.7 Hz,

1H), 1.32 (s, 9H), 1.29 (dd, J = 14.2, 7.1 Hz, 1H), 0.17 (s, 3H), 0.15 (s, 3H) ppm.

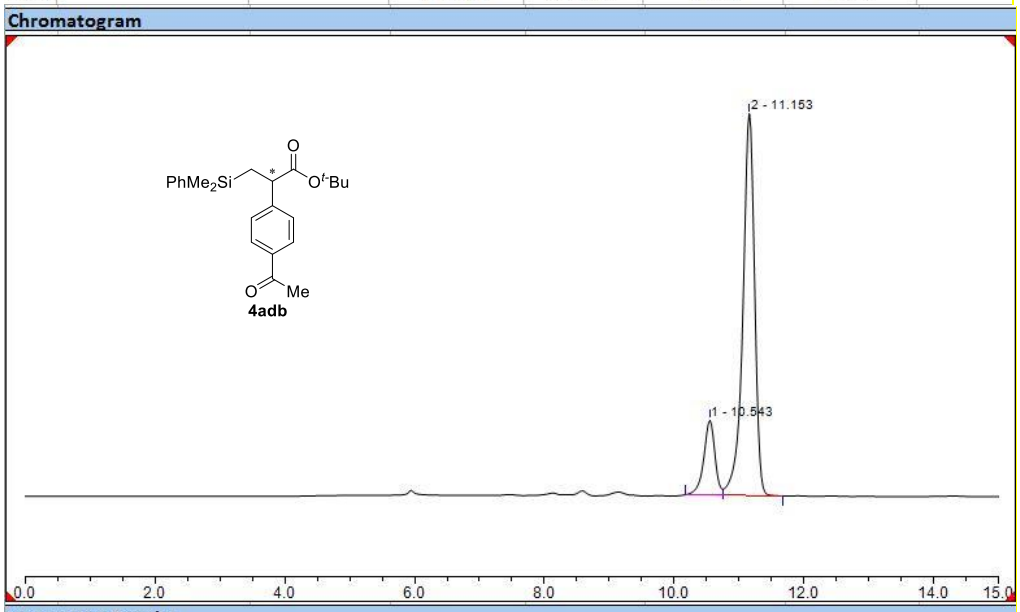
^{13}C NMR (101 MHz, Chloroform-d) δ = 198.0 , 173.3 , 147.1 , 138.3 , 135.9 , 133.7 (2C), 129.1 , 128.6 (2C), 128.1 (2C), 127.9 (2C), 81.0 , 48.5 , 27.9 (3C), 26.8 , 20.3 , –2.6 (2C) ppm.

HRMS (ESI) m/z calculated for $C_{23}H_{30}O_3Si$ $[M+Na]^+$: 405.1856, found: 405.1868.



Integration Results

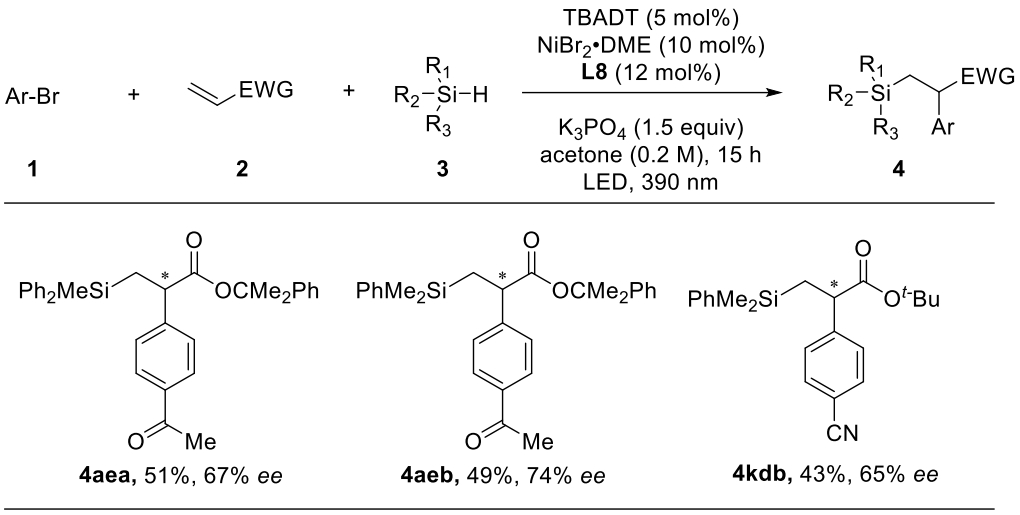
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.513	208.658	835.500	50.88	50.69	n.a.
2		11.137	201.461	812.611	49.12	49.31	n.a.
Total:			**410.119**	**1648.111**	**100.00**	**100.00**	



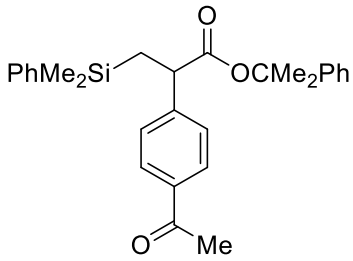
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.543	9.722	48.914	15.65	16.35	n.a.
2		11.153	52.402	250.243	84.35	83.65	n.a.
Total:			**62.124**	**299.156**	**100.00**	**100.00**	

HPLC (Chiralpak IA): t_R=10.5 min (minor), 11.1 min (major), Condition: 95:5, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 ºC, 254 nm.



2-Phenylpropan-2-yl 2-(4-acetylphenyl)-3-(dimethyl(phenyl)silyl)propanoate (4aeb)



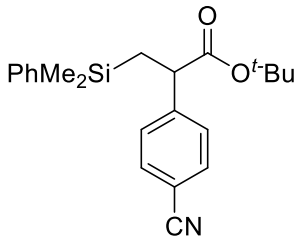
The title compound **4aeb** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (43.5 mg, 49% yield, 74% ee).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.86 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.40 (m, 2H), 7.36 – 7.27 (m, 5H), 7.18 – 7.15 (m, 3H), 7.05 – 7.00 (m, 2H), 3.65 (t, *J* = 7.7 Hz, 1H), 2.61 (s, 3H), 1.70 (s, 3H), 1.63 (dd, *J* = 14.9, 7.4 Hz, 1H), 1.58 (s, 3H), 1.28 (dd, *J* = 14.9, 8.0 Hz, 1H), 0.15 (s, 3H), 0.12 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 198.0 , 172.3 , 146.6 , 145.4 , 138.3 , 136.0 , 133.7 (2C), 129.2 , 128.6 (2C), 128.4 (2C), 128.2 (2C), 127.9 (2C), 127.1 , 124.2 (2C), 82.1 , 48.3 , 29.1 , 27.7 , 26.8 , 20.0 , –2.5 (2C) ppm.

HRMS (ESI) m/z calculated for $C_{28}H_{32}O_3Si$ $[M+Na]^+$: 467.2013, found: 467.2021.

***tert*-Butyl 2-(4-cyanophenyl)-3-(dimethyl(phenyl)silyl)propanoate (4kdb)**



The title compound **4kdb** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow oil (23.2 mg, 43%, 65% ee).

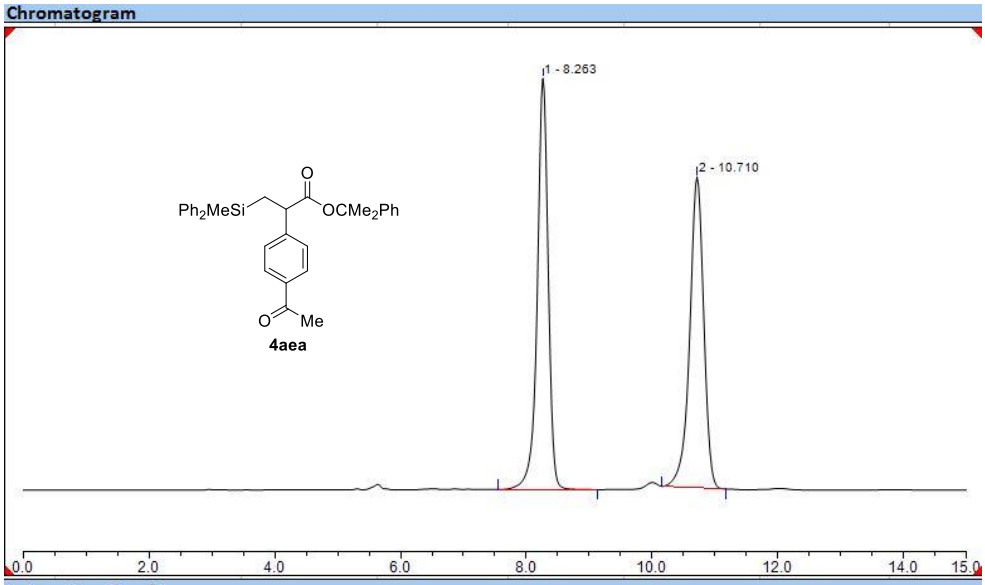
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.52 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.38 (m, 2H), 7.36 – 7.28 (m, 5H), 3.54 (s, 1H), 1.64 (dd, *J* = 14.8, 7.7 Hz, 1H), 1.32 (s, 9H), 1.25 (dd, *J* = 14.8, 7.8 Hz, 1H), 0.19 (s, 3H), 0.16 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 172.9 , 147.0 , 138.0 , 133.6 (2C), 132.3 (2C), 129.3 , 128.7 (2C), 128.0 (2C), 119.0 , 110.9 , 81.3 , 48.6 , 27.9 (3C), 20.4 , –2.6 (2C) ppm.

HRMS (ESI) m/z calculated for $C_{22}H_{27}NO_2Si$ $[M+Na]^+$: 388.1703, found: 388.1709.

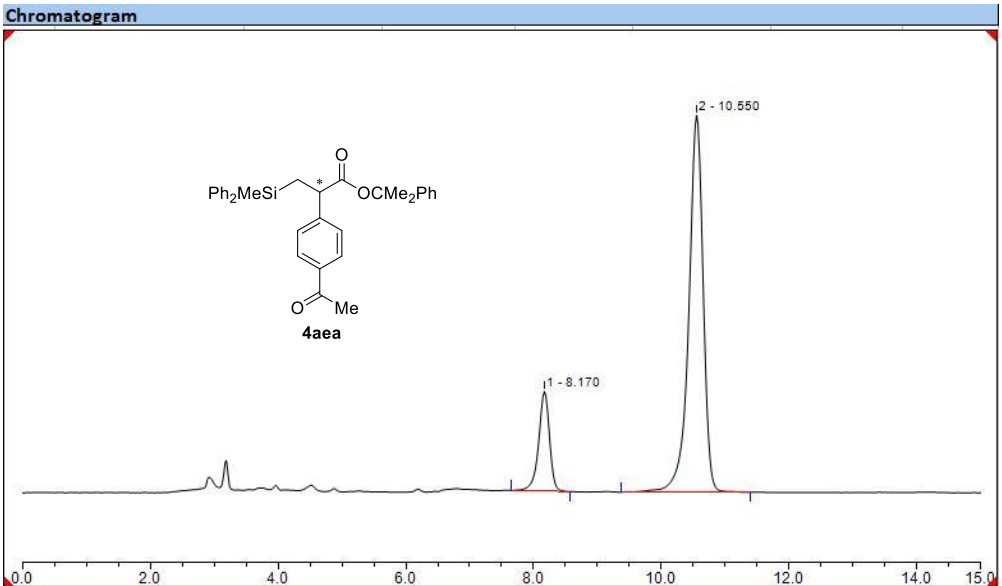
^{13}C NMR (101 MHz, Chloroform-d) δ = 197.8, 174.9, 146.7, 136.2, 128.8 (2C), 128.2 (2C), 52.3, 47.4, 26.8, 19.8, 7.3, 7.1, –3.6 (2C) ppm.

HRMS (ESI) m/z calculated for $C_{16}H_{24}O_3Si$ $[M+H]^+$: 293.1567, found: 293.1574.



Integration Results

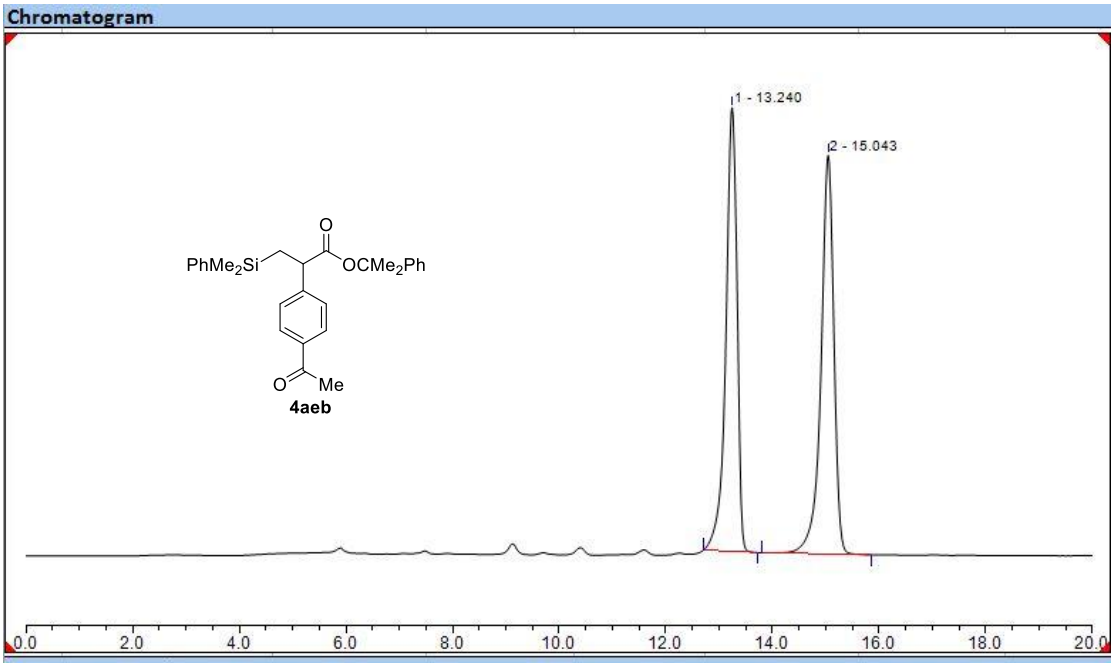
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.263	144.240	715.602	50.84	56.95	n.a.
2		10.710	139.472	540.980	49.16	43.05	n.a.
Total:			**283.712**	**1256.582**	**100.00**	**100.00**	



Integration Results

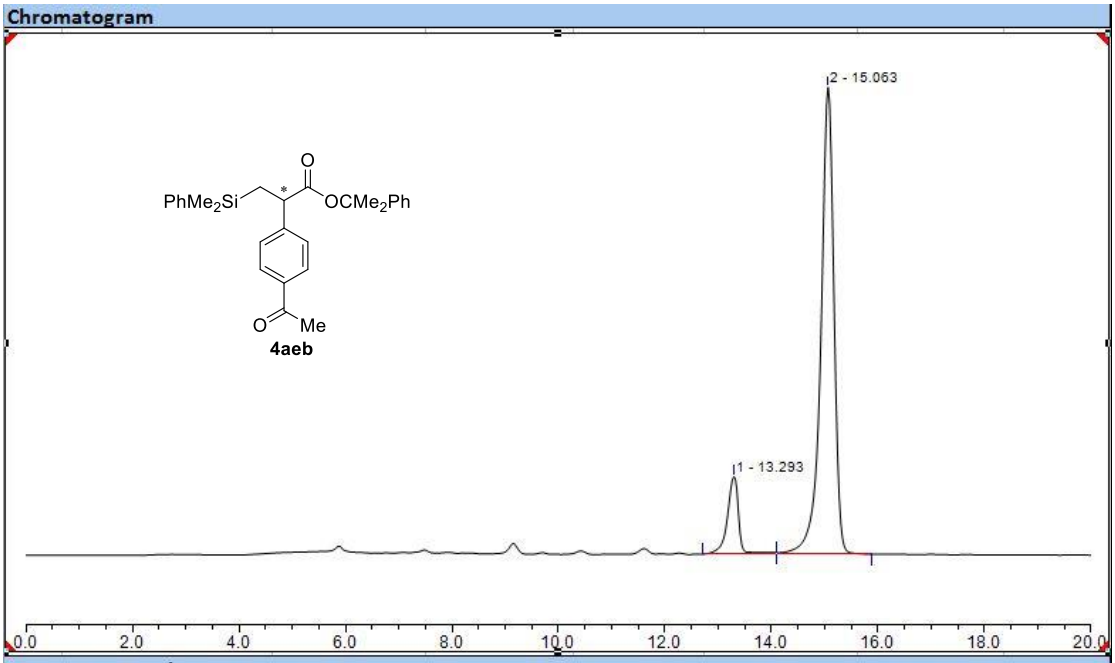
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.170	1.500	7.606	16.65	20.94	n.a.
2		10.550	7.506	28.720	83.35	79.06	n.a.
Total:			**9.006**	**36.326**	**100.00**	**100.00**	

HPLC (Chiralpak IA): t_R=8.2 min (minor), 10.5 min (major), Condition: 95:5, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 ºC, 254 nm.



Integration Results

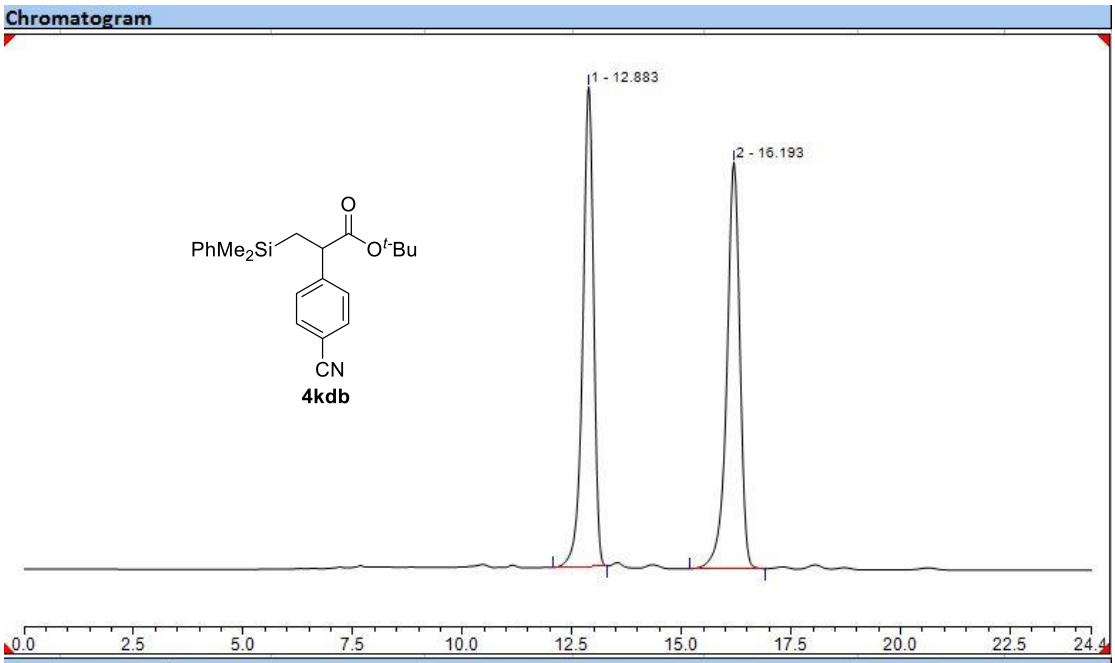
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.240	16.621	68.310	49.22	52.67	n.a.
2		15.043	17.146	61.394	50.78	47.33	n.a.
Total:			**33.767**	**129.705**	**100.00**	**100.00**	



Integration Results

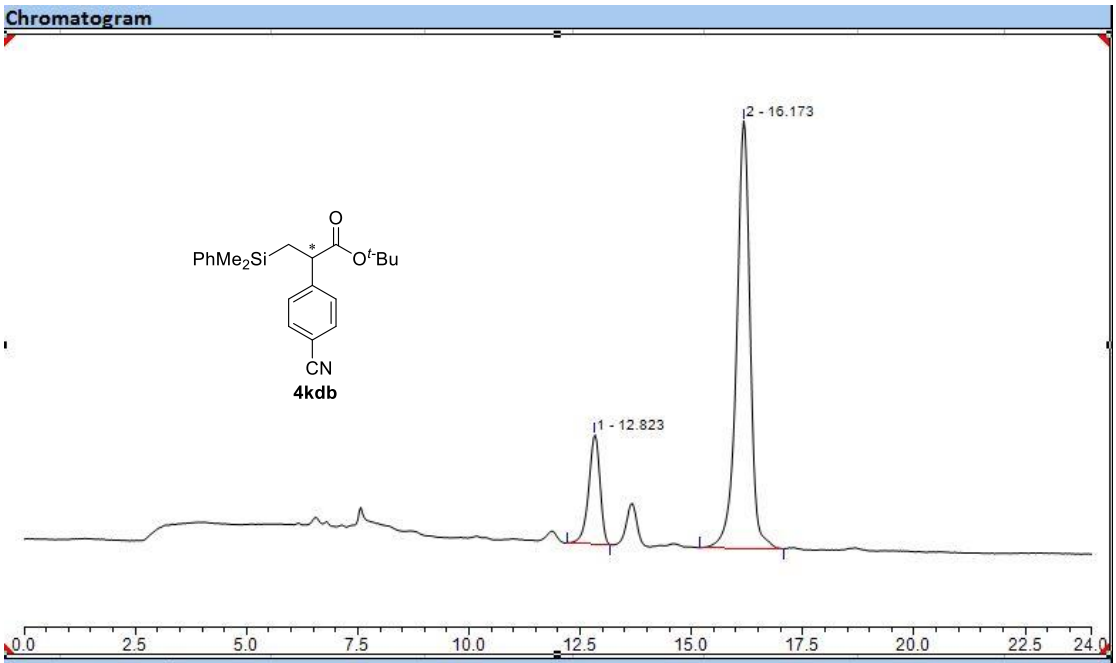
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.293	2.987	11.974	12.71	14.26	n.a.
2		15.063	20.515	71.967	87.29	85.74	n.a.
Total:			**23.501**	**83.940**	**100.00**	**100.00**	

HPLC (Chiralpak IA): t_R=13.2 min (minor), 15.0 min (major), Condition: 95:5, *n*-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 ºC, 254 nm.



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.883	51.627	180.505	49.49	54.13	n.a.
2		16.193	52.685	152.946	50.51	45.87	n.a.
Total:			**104.312**	**333.451**	**100.00**	**100.00**	

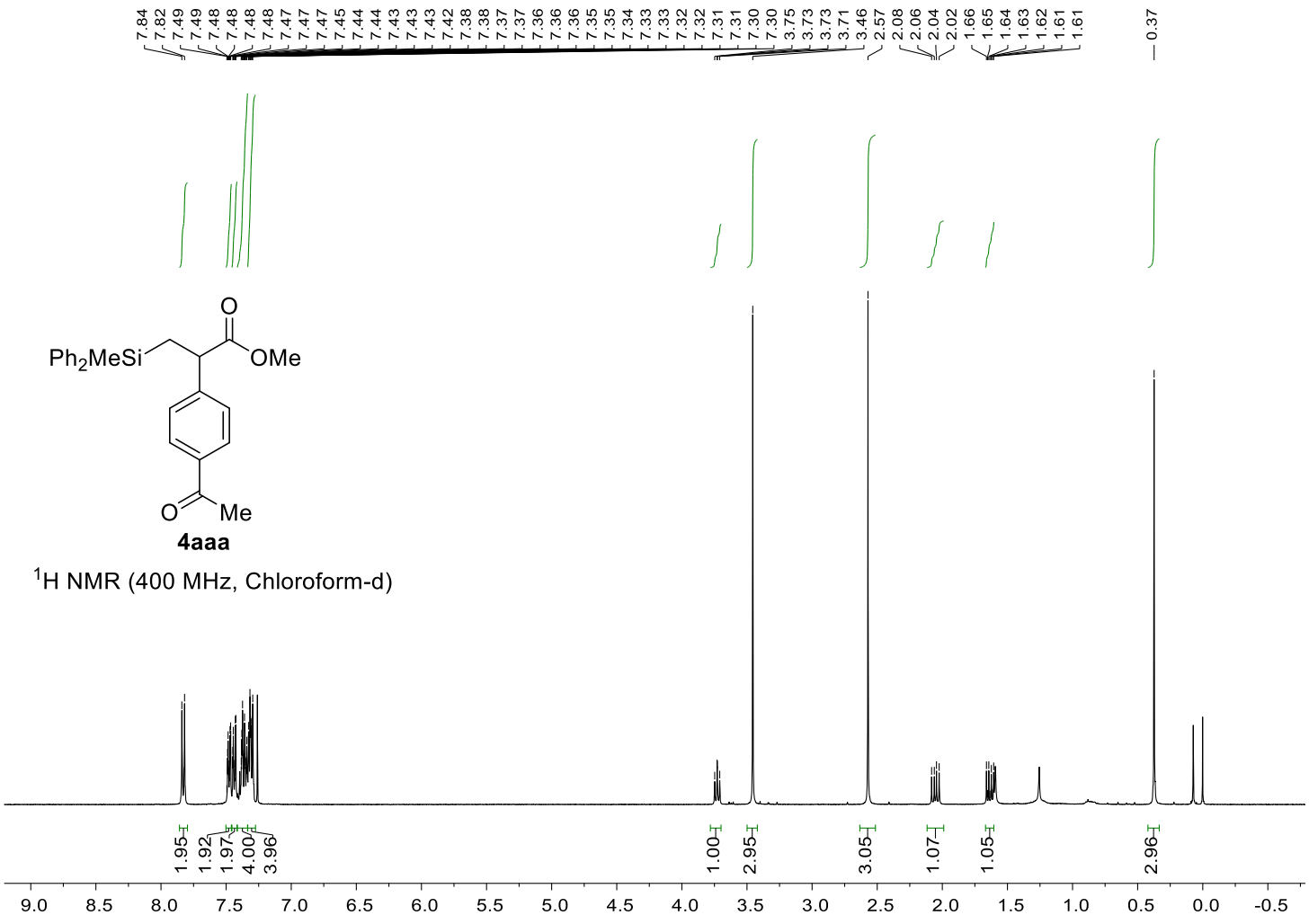


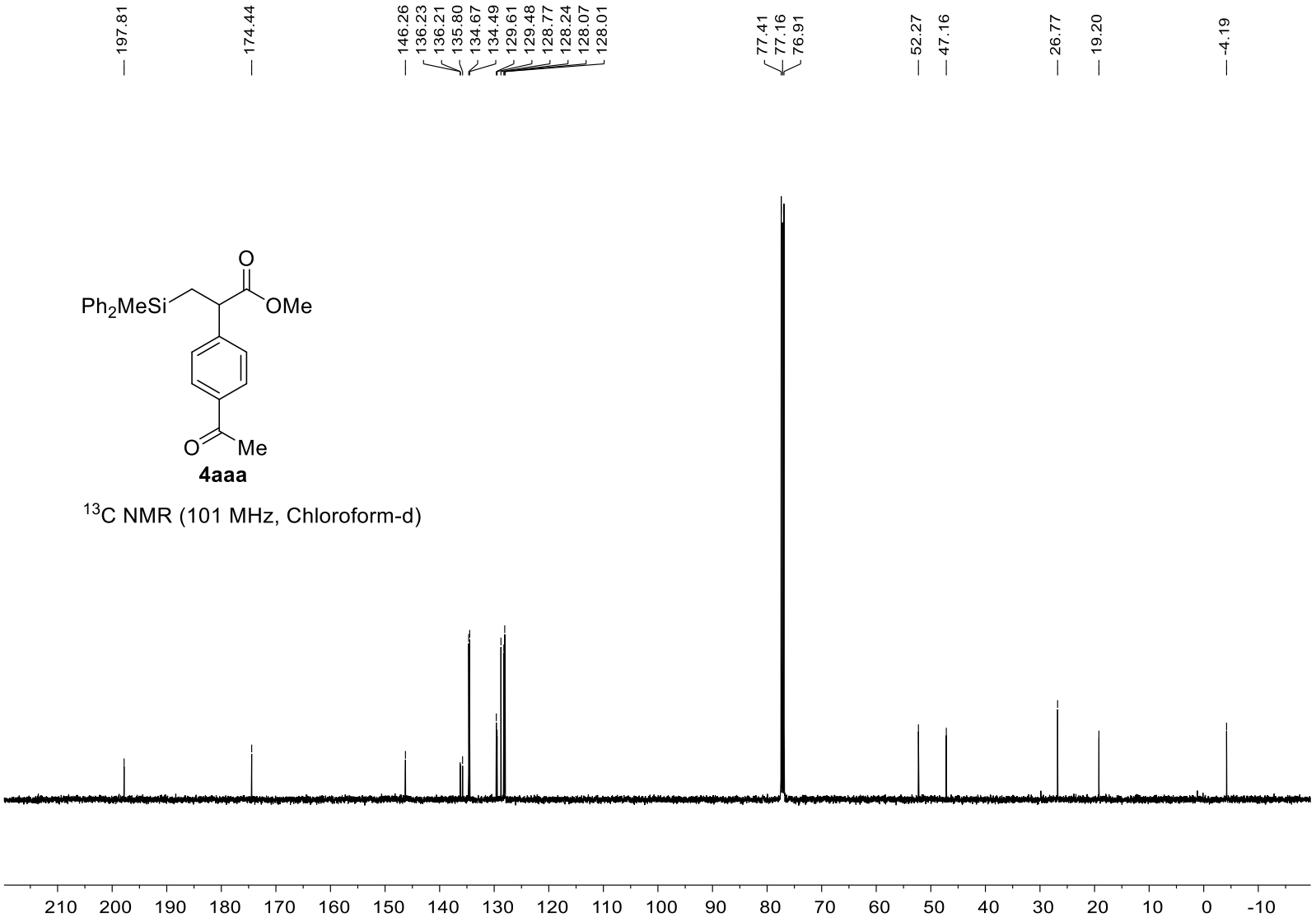
Integration Results

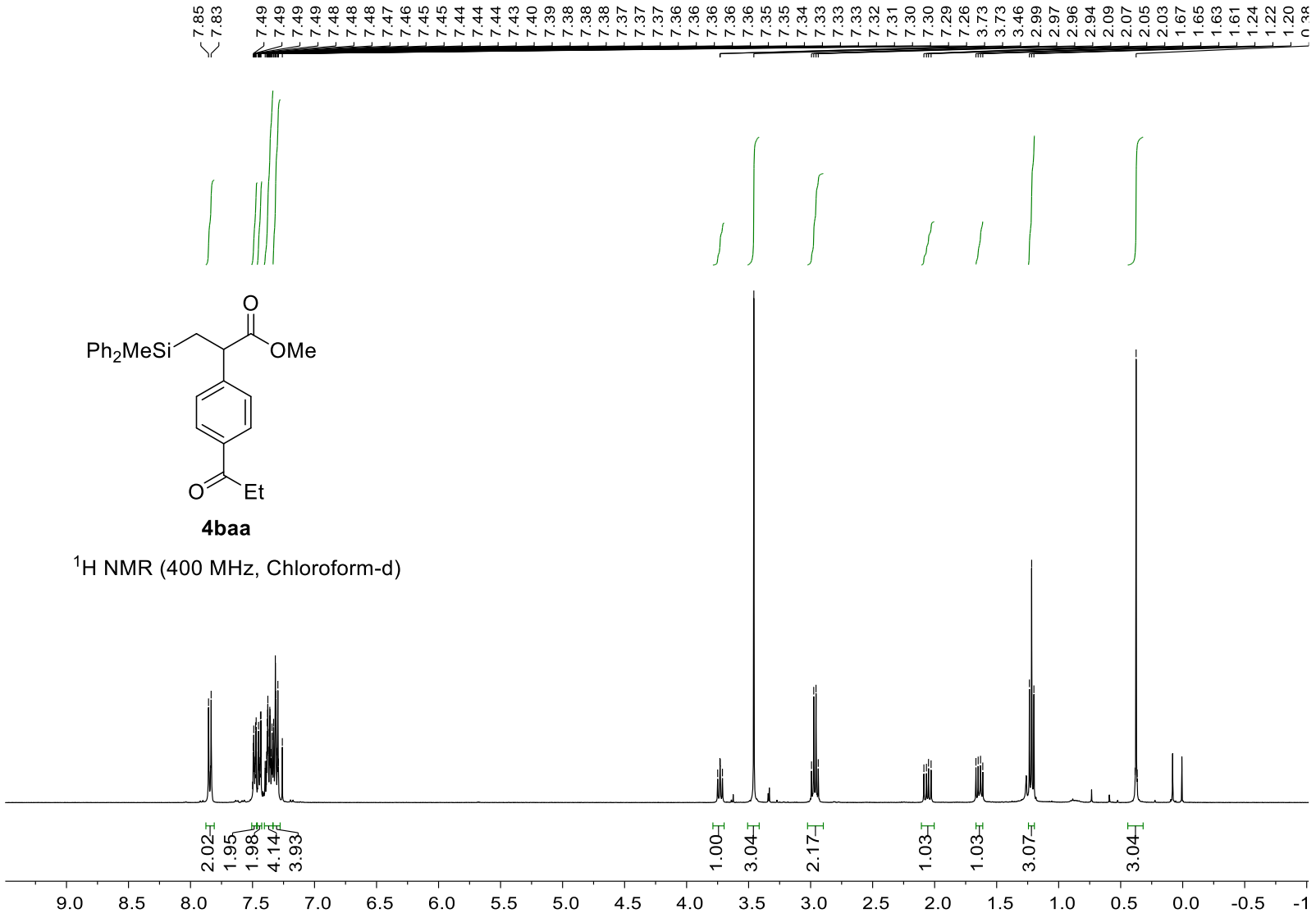
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.823	0.772	2.623	17.63	20.41	n.a.
2		16.173	3.605	10.227	82.37	79.59	n.a.
Total:			**4.377**	**12.850**	**100.00**	**100.00**	

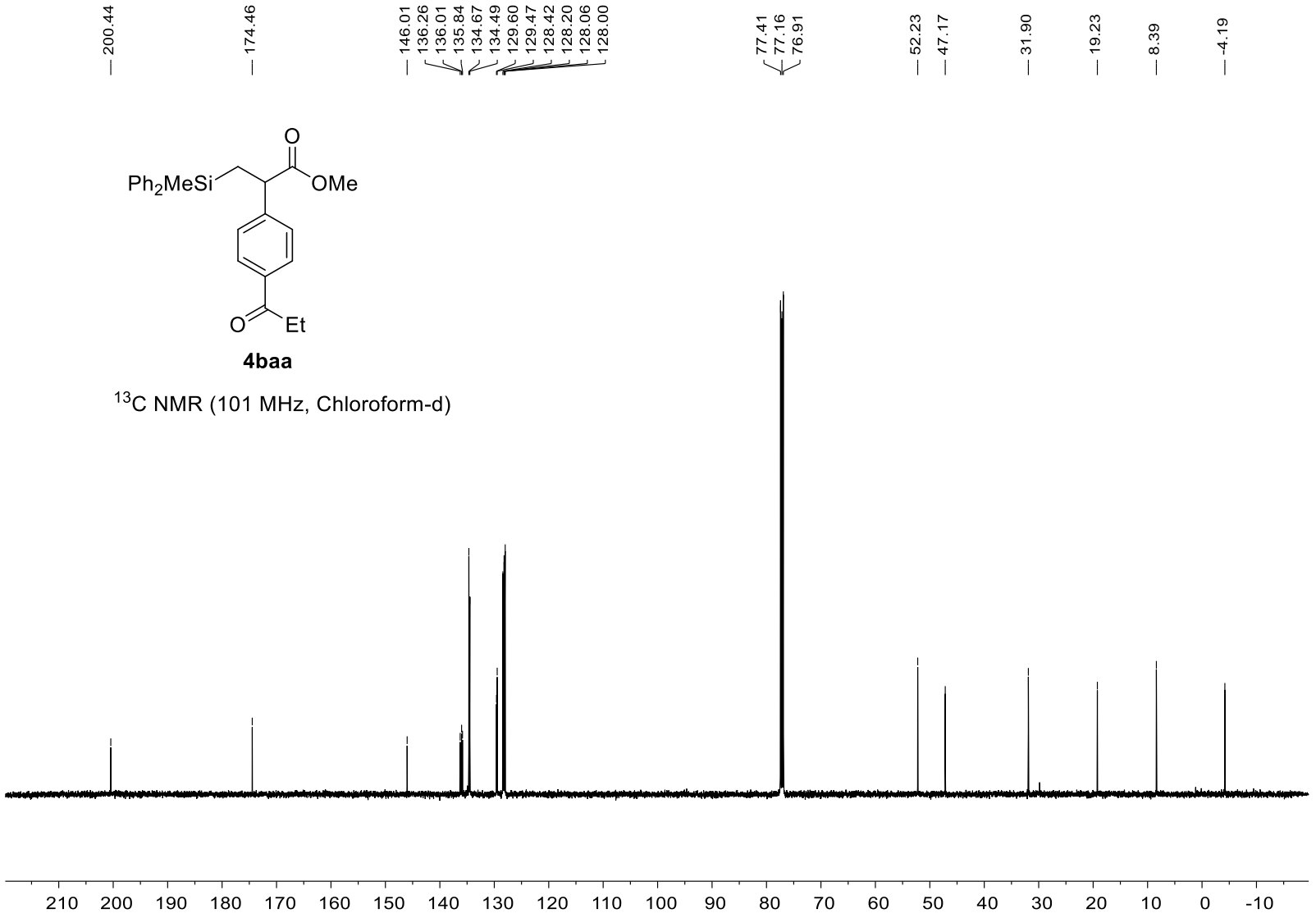
HPLC (Chiralpak IA): t_R=12.8 min (minor), 16.2 min (major), Condition: 95:5, *n*-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 ºC, 254 nm.

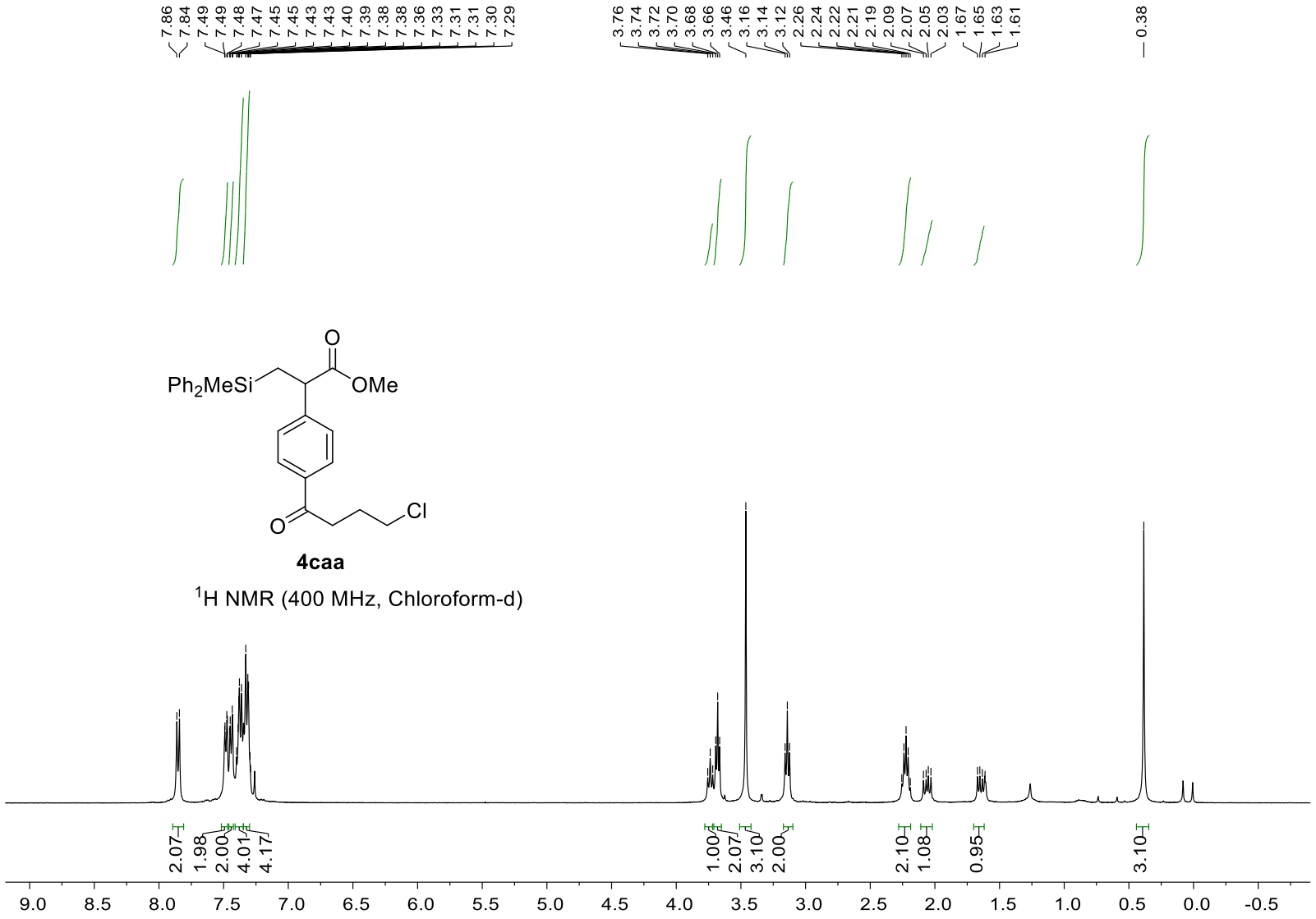
^{1}H, ^{13}C and ^{19}F-NMR Spectra

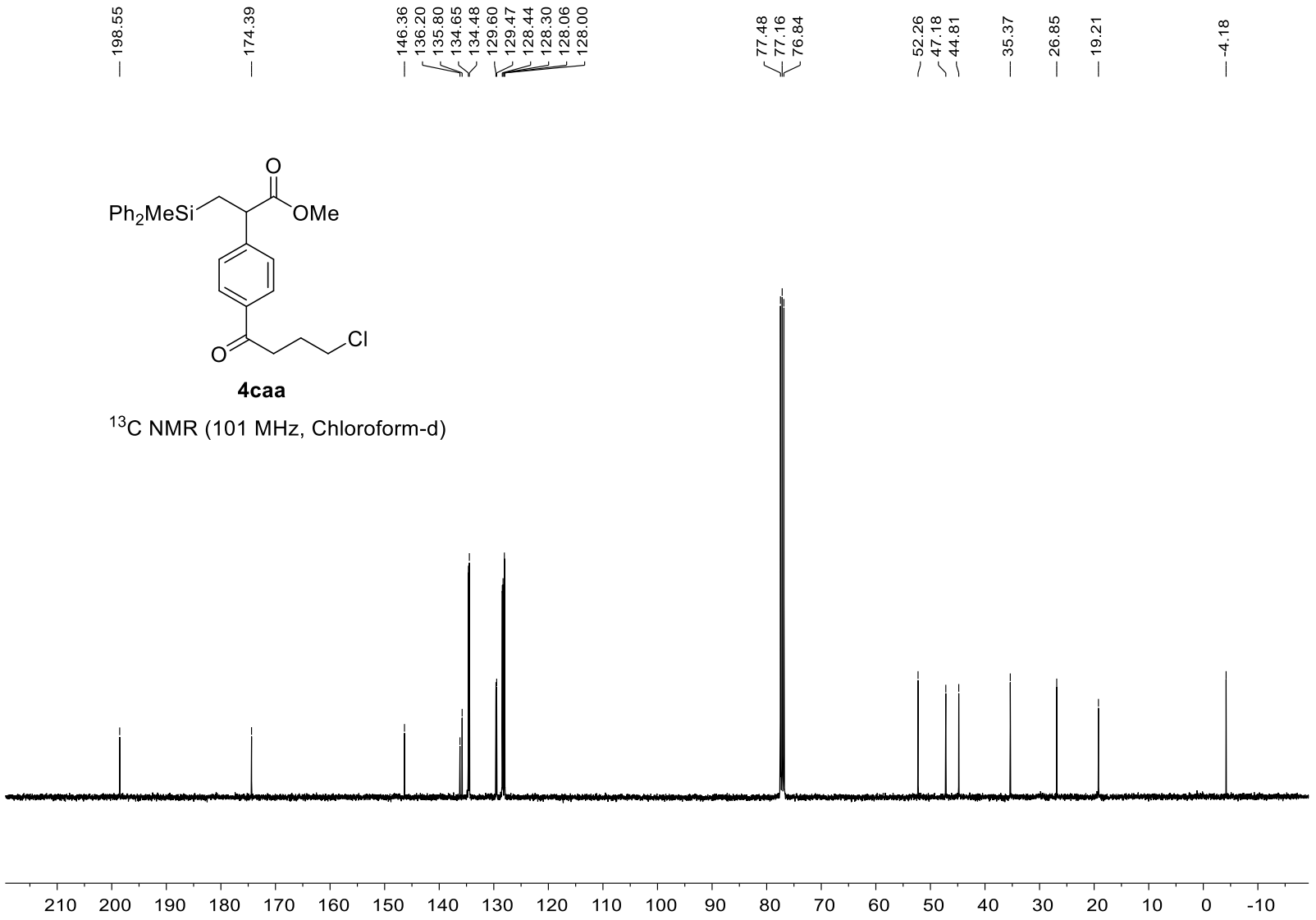


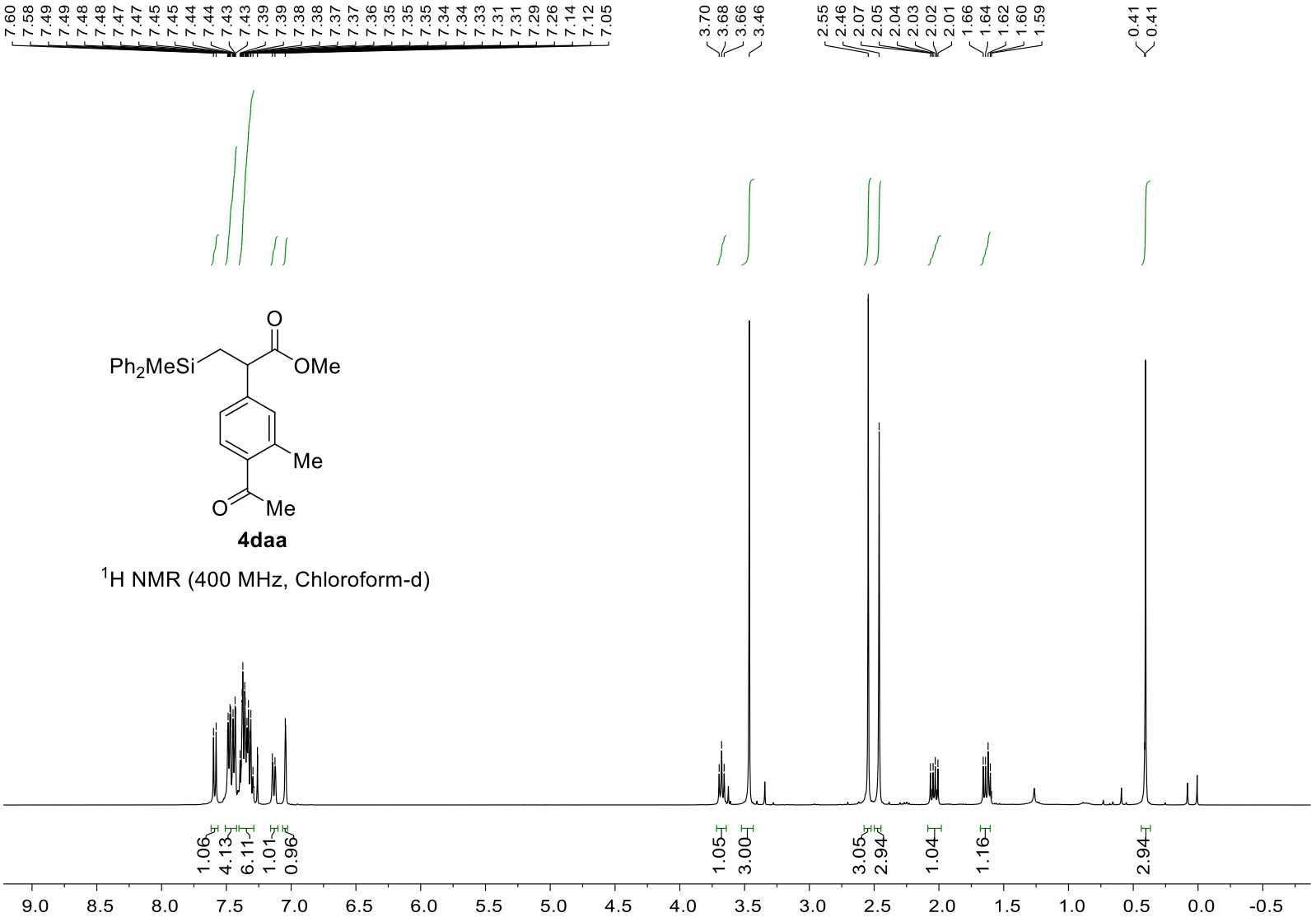

197.81
174.44
146.26
136.23
136.21
135.80
134.67
134.49
129.61
129.48
128.77
128.24
128.07
128.01
77.41
77.16
76.91
52.27
47.16
26.77
19.20
-4.19
Ph2MeSi
OMe
O
O
Me
4aaa
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

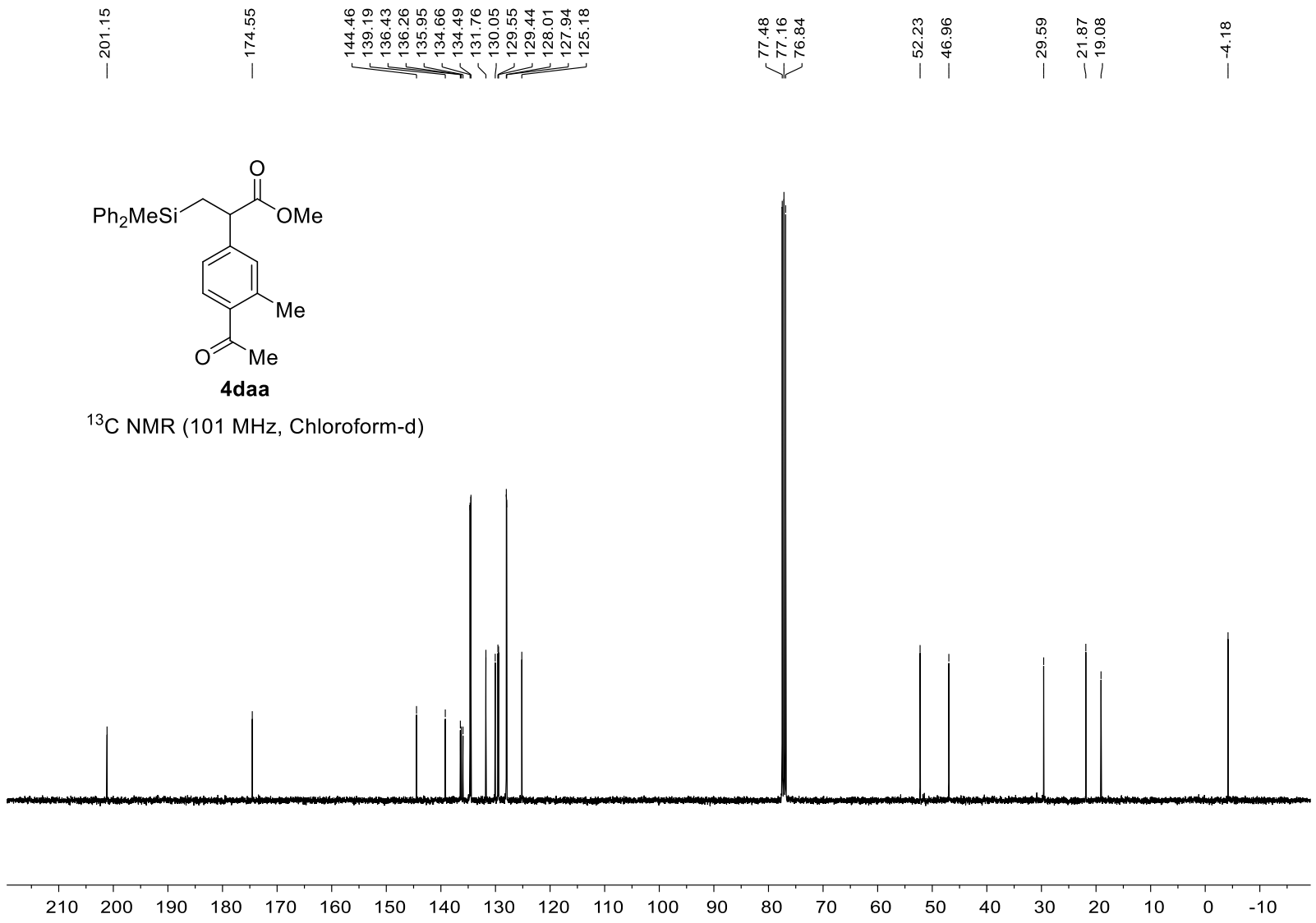

7.85 7.83 7.49 7.49 7.49 7.49 7.48 7.48 7.47 7.46 7.45 7.45 7.44 7.44 7.44 7.43 7.40 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.36 7.36 7.35 7.35 7.34 7.33 7.33 7.33 7.32 7.31 7.30 7.30 7.29 7.26 3.73 3.73 3.46 2.99 2.97 2.96 2.94 2.09 2.07 2.05 2.03 1.67 1.65 1.63 1.61 1.24 1.22 1.20
O
Ph2MeSi
OMe
O
Et
4baa
1H NMR (400 MHz, Chloroform-d)
2.02 1.95 1.98 4.14 3.93 1.00 3.04 2.17 1.03 1.03 3.07 3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1

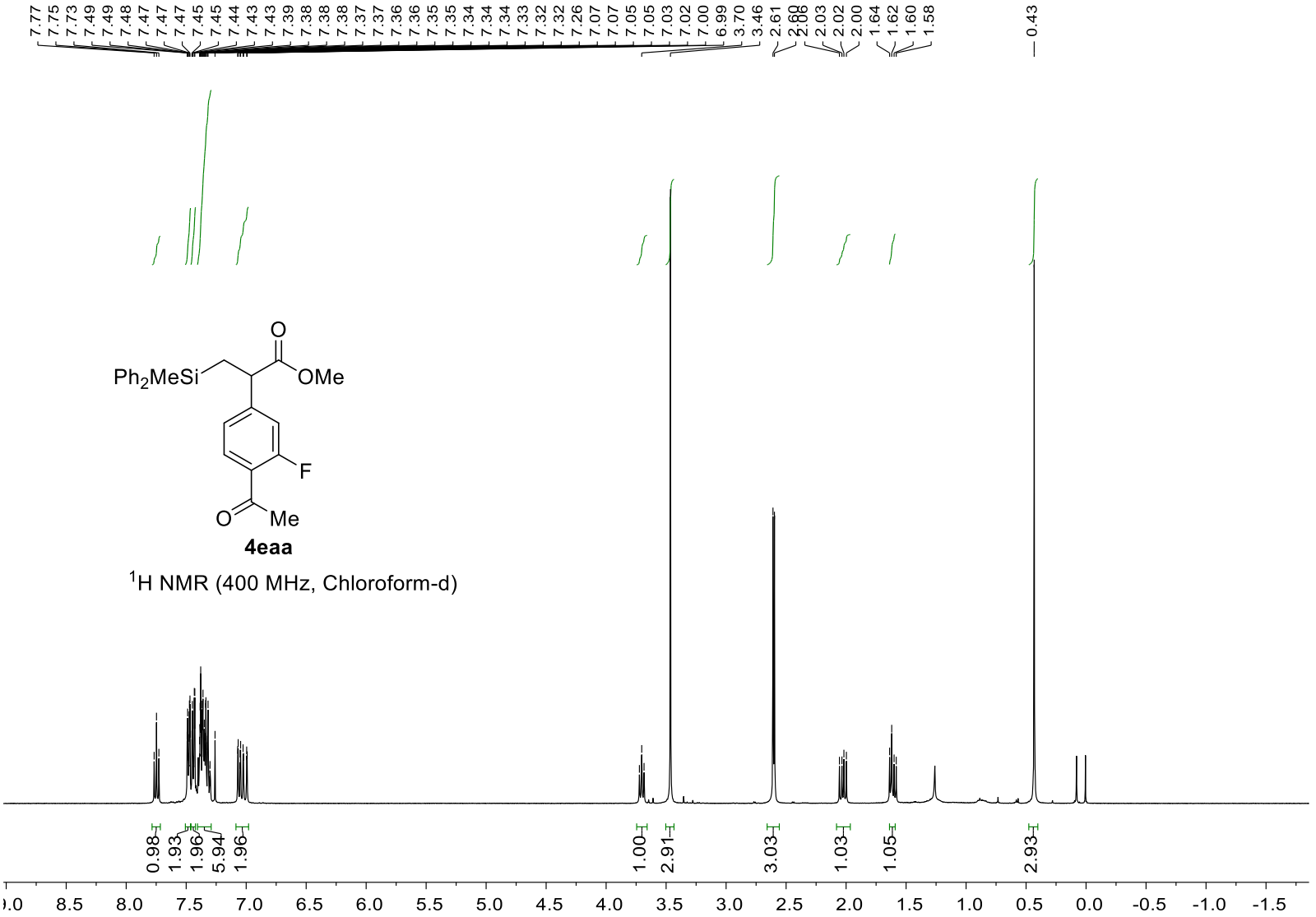

200.44
174.46
146.01
136.26
136.01
135.84
134.67
134.49
129.60
129.47
128.42
128.20
128.06
128.00
77.41
77.16
76.91
52.23
47.17
31.90
19.23
8.39
-4.19
Ph2MeSi
OMe
O
O
Et
4baa
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

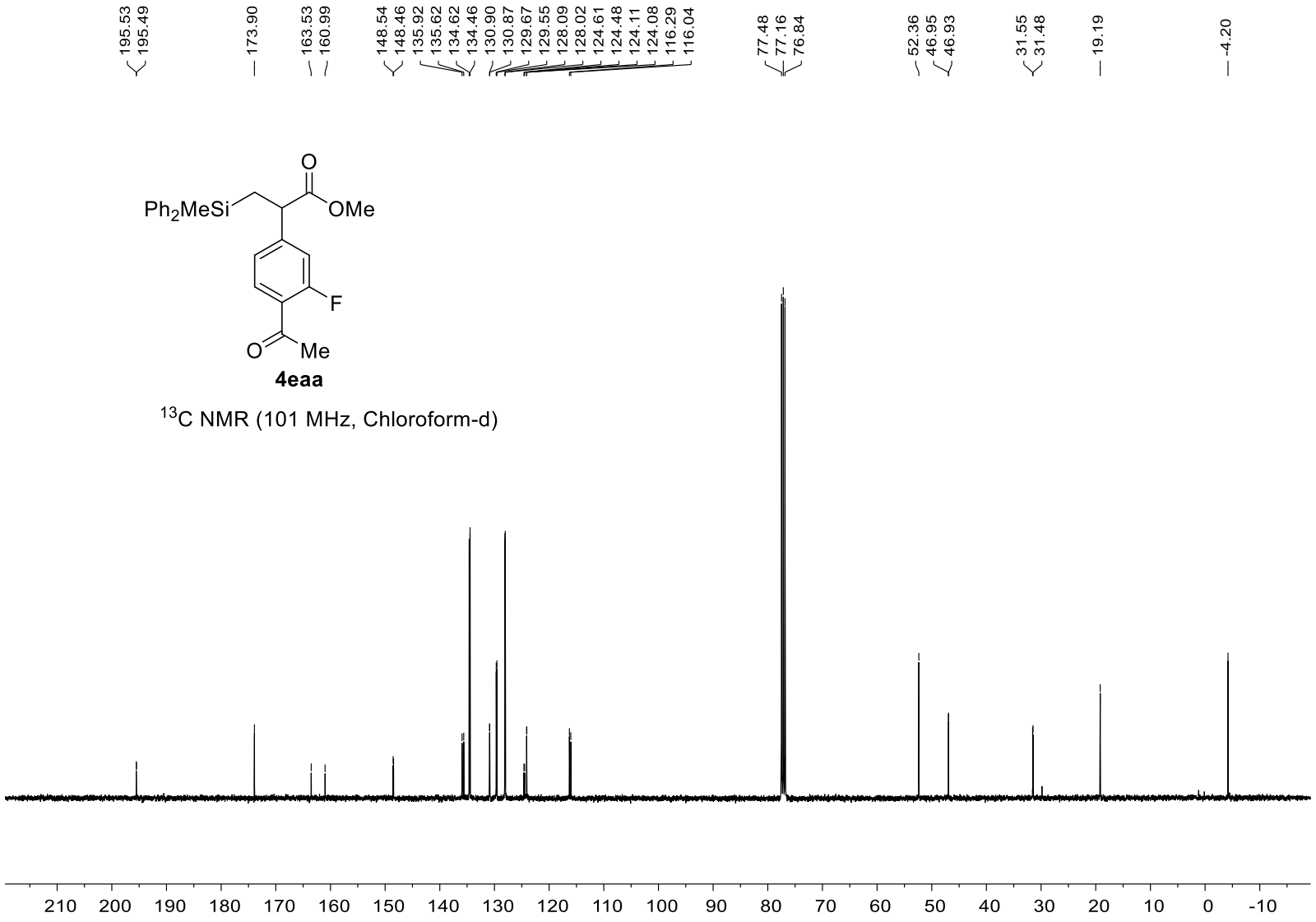

7.86
7.84
7.49
7.49
7.48
7.47
7.45
7.45
7.43
7.43
7.40
7.39
7.38
7.38
7.36
7.33
7.31
7.31
7.30
7.29
3.76
3.74
3.72
3.70
3.68
3.66
3.46
3.16
3.14
3.12
2.26
2.24
2.22
2.21
2.19
2.09
2.07
2.05
2.03
1.67
1.65
1.63
1.61
0.38
Ph2MeSi
O
OMe
O
Cl
4caa
1H NMR (400 MHz, Chloroform-d)
2.07
1.98
2.00
4.01
4.17
1.00
2.07
3.10
2.00
2.10
1.08
0.95
3.10
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

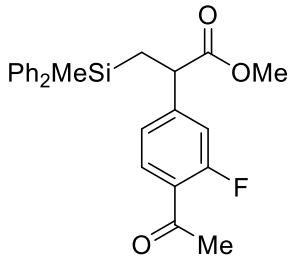

198.55
174.39
146.36
136.20
135.80
134.65
134.48
129.60
129.47
128.44
128.30
128.06
128.00
77.48
77.16
76.84
52.26
47.18
44.81
35.37
26.85
19.21
-4.18
Ph2MeSi
OMe
O
O
Cl
4caa
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


7.60 7.58 7.49 7.49 7.48 7.48 7.47 7.47 7.45 7.45 7.44 7.44 7.43 7.43 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.31 7.31 7.29 7.26 7.14 7.12 7.05
3.70 3.68 3.66 3.46
2.55 2.46 2.07 2.05 2.04 2.03 2.02 2.01
1.66 1.64 1.62 1.60 1.59
0.41 0.41
Ph2MeSi
O
OMe
Me
O
Me
4daa
1H NMR (400 MHz, Chloroform-d)
1.06 4.13 6.11 1.01 0.96
1.05 3.00
3.05 2.94
1.04
1.16
2.94
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


201.15
174.55
144.46
139.19
136.43
136.26
135.95
134.66
134.49
131.76
130.05
129.55
129.44
128.01
127.94
125.18
77.48
77.16
76.84
52.23
46.96
29.59
21.87
19.08
-4.18
Ph2MeSi
OMe
Me
O
Me
4daa
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

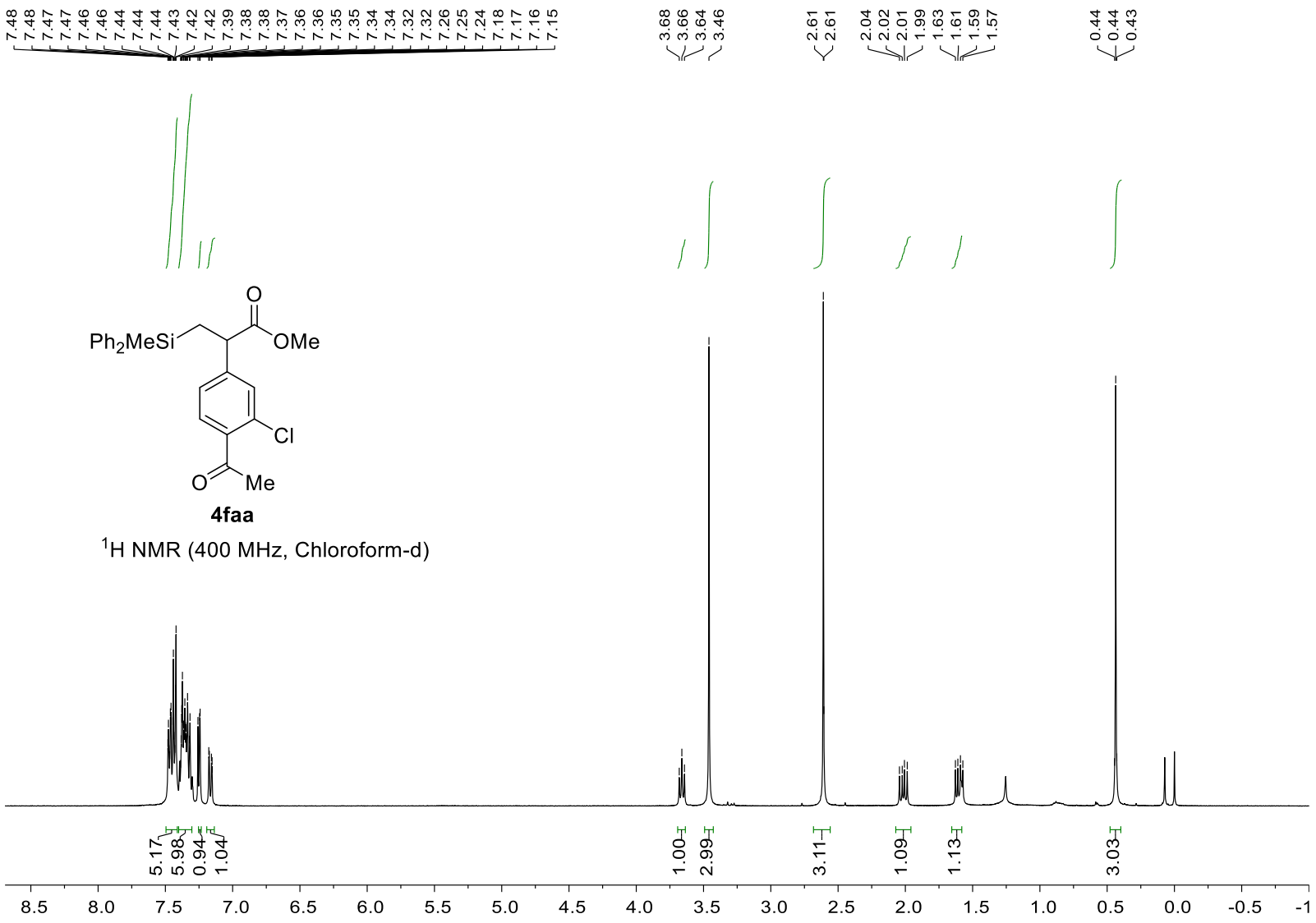

7.77 7.75 7.73 7.49 7.49 7.48 7.47 7.47 7.47 7.45 7.45 7.44 7.43 7.43 7.39 7.38 7.38 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.32 7.32 7.26 7.07 7.07 7.05 7.05 7.03 7.02 7.00 6.99 3.70 3.46 2.61 2.60 2.08 2.03 2.02 2.00 1.64 1.62 1.60 1.58 0.43
Ph2MeSi
OMe
O
F
O
Me
4eaa
1H NMR (400 MHz, Chloroform-d)
0.98 1.93 1.96 5.94 1.96 1.00 2.91 3.03 1.03 1.05 2.93
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5

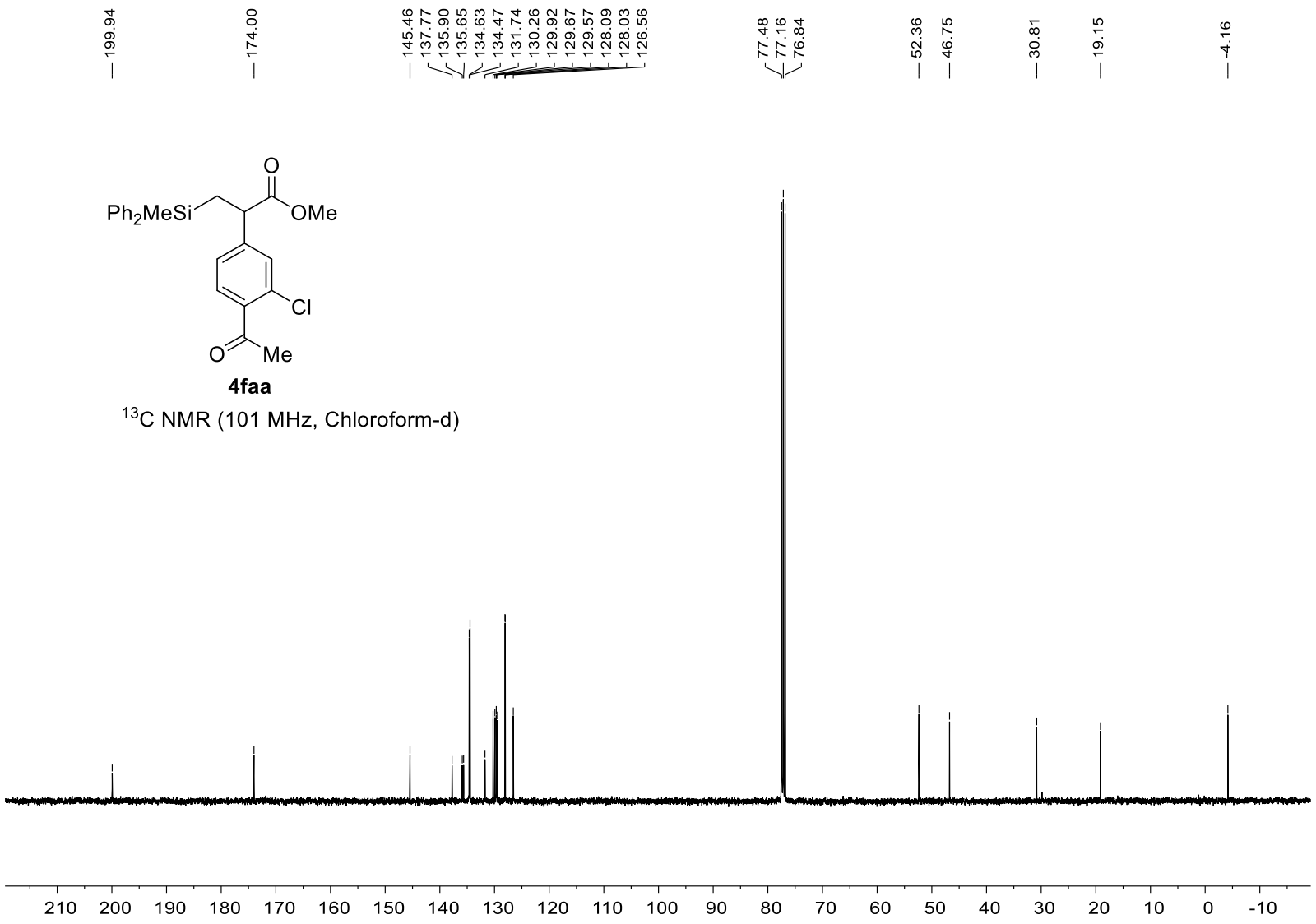

195.53
195.49
173.90
163.53
160.99
148.54
148.46
135.92
135.62
134.62
134.46
130.90
130.87
129.67
129.55
128.09
128.02
124.61
124.48
124.11
124.08
116.29
116.04
77.48
77.16
76.84
52.36
46.95
46.93
31.55
31.48
19.19
-4.20
Ph2MeSi
OMe
O
F
O
Me
4eaa
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

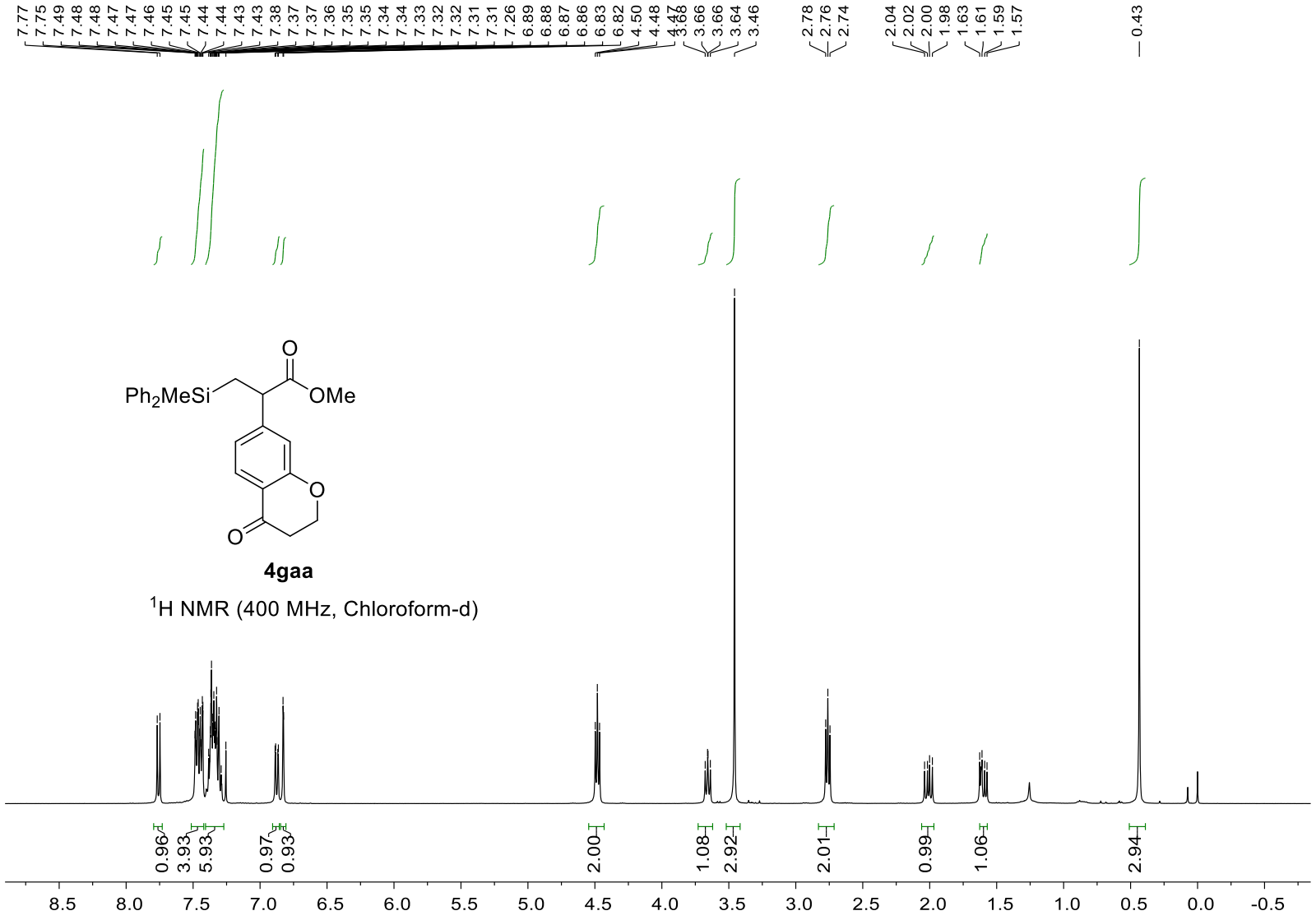


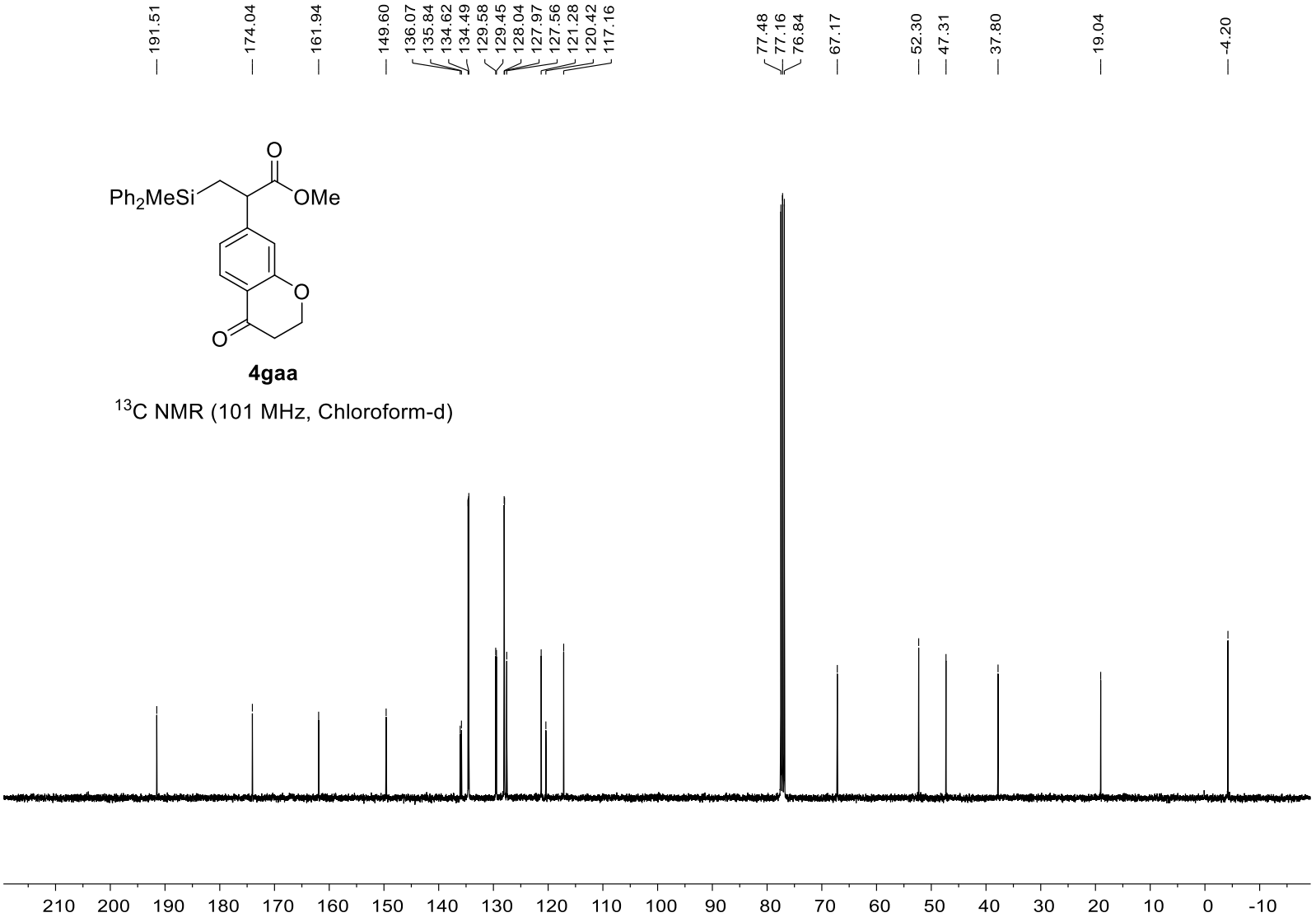
4eaa

^{19}F NMR (376 MHz, Chloroform-d)


7.48 7.48 7.47 7.47 7.46 7.46 7.44 7.44 7.44 7.43 7.42 7.42 7.39 7.38 7.38 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.32 7.32 7.26 7.25 7.24 7.18 7.17 7.16 7.15
3.68 3.66 3.64 3.46
2.61 2.61
2.04 2.02 2.01 1.99 1.63 1.61 1.59 1.57
0.44 0.44 0.43
O
Ph2MeSi
OMe
Cl
O
Me
4faa
1H NMR (400 MHz, Chloroform-d)
5.17 5.98 0.94 1.04 1.00 2.99 3.11 1.09 1.13 3.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1

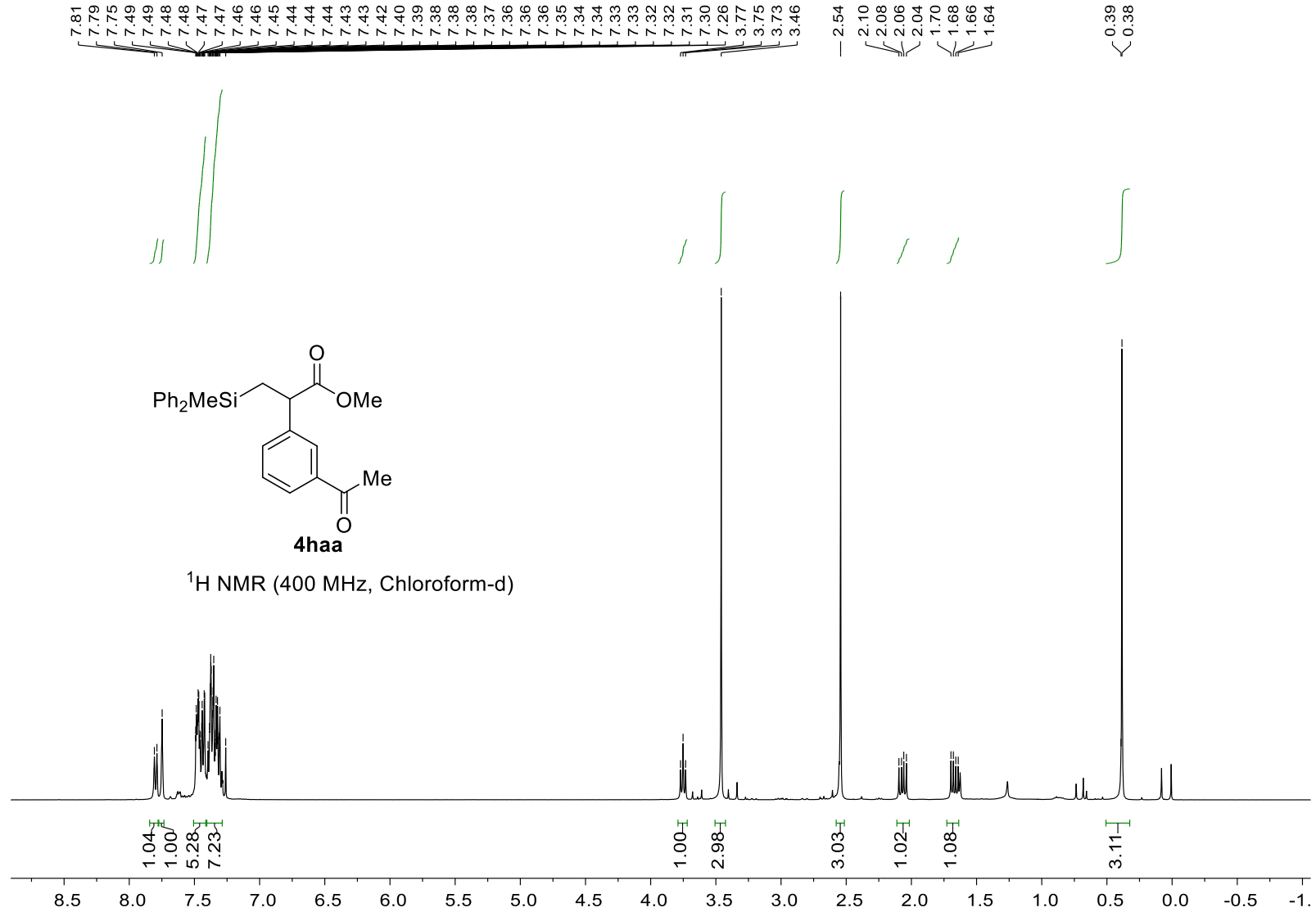

199.94
174.00
145.46
137.77
135.90
135.65
134.63
134.47
131.74
130.26
129.92
129.67
129.57
128.09
128.03
126.56
77.48
77.16
76.84
52.36
46.75
30.81
19.15
-4.16
O
Ph2MeSi
OMe
Cl
O
Me
4faa
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

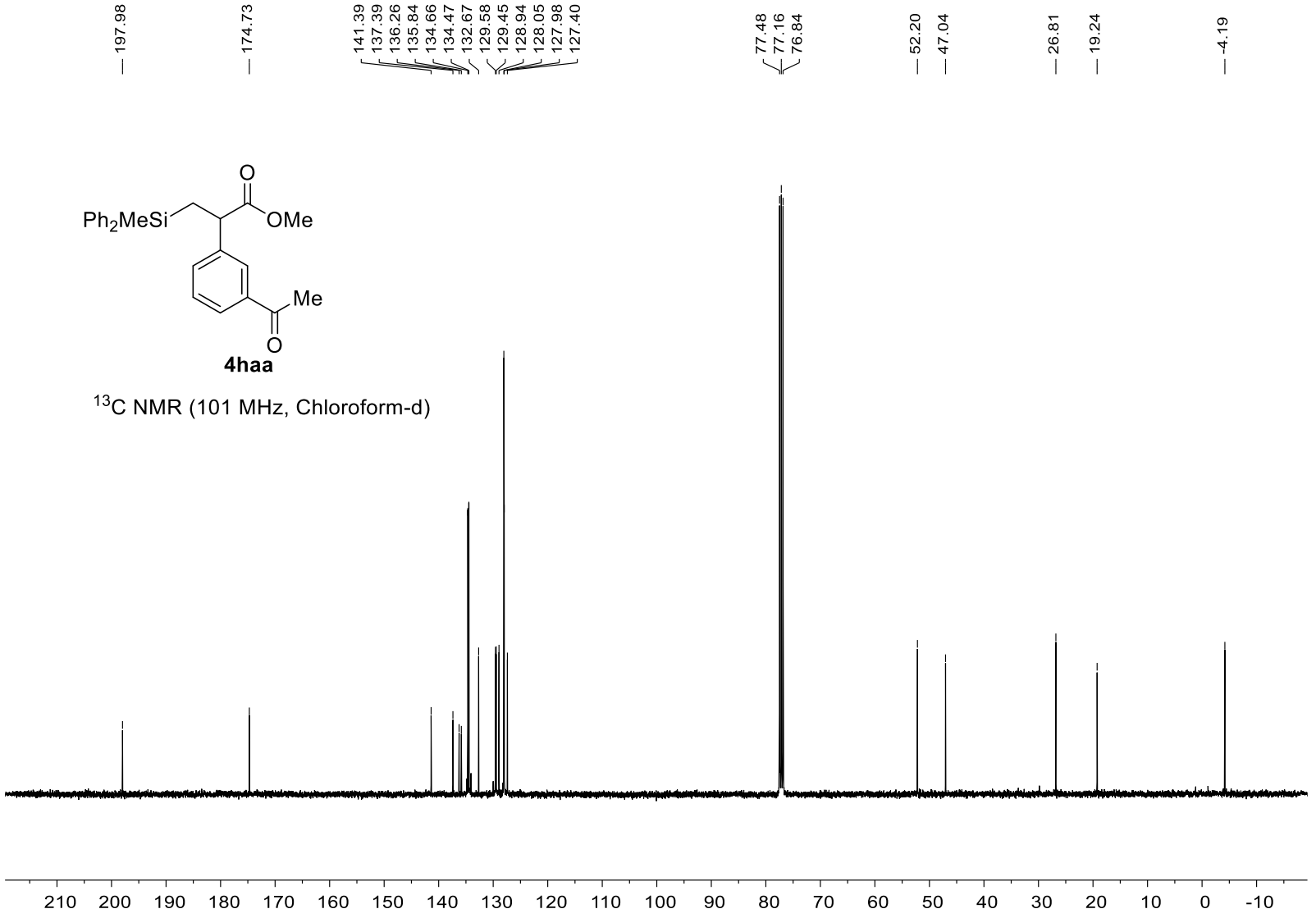

7.77 7.75 7.49 7.48 7.48 7.47 7.47 7.46 7.45 7.45 7.44 7.44 7.43 7.43 7.38 7.37 7.37 7.36 7.35 7.35 7.34 7.34 7.33 7.32 7.32 7.31 7.31 7.26 6.89 6.88 6.87 6.86 6.83 6.82 4.50 4.48 3.68 3.66 3.66 3.64 3.46
2.78 2.76 2.74
2.04 2.02 2.00 1.98 1.63 1.61 1.59 1.57
0.43
Ph2MeSi
OMe
O
O
O
4gaa
1H NMR (400 MHz, Chloroform-d)
0.96 3.93 5.93 0.97 0.93 2.00 1.08 2.92 2.01 0.99 1.06 2.94
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

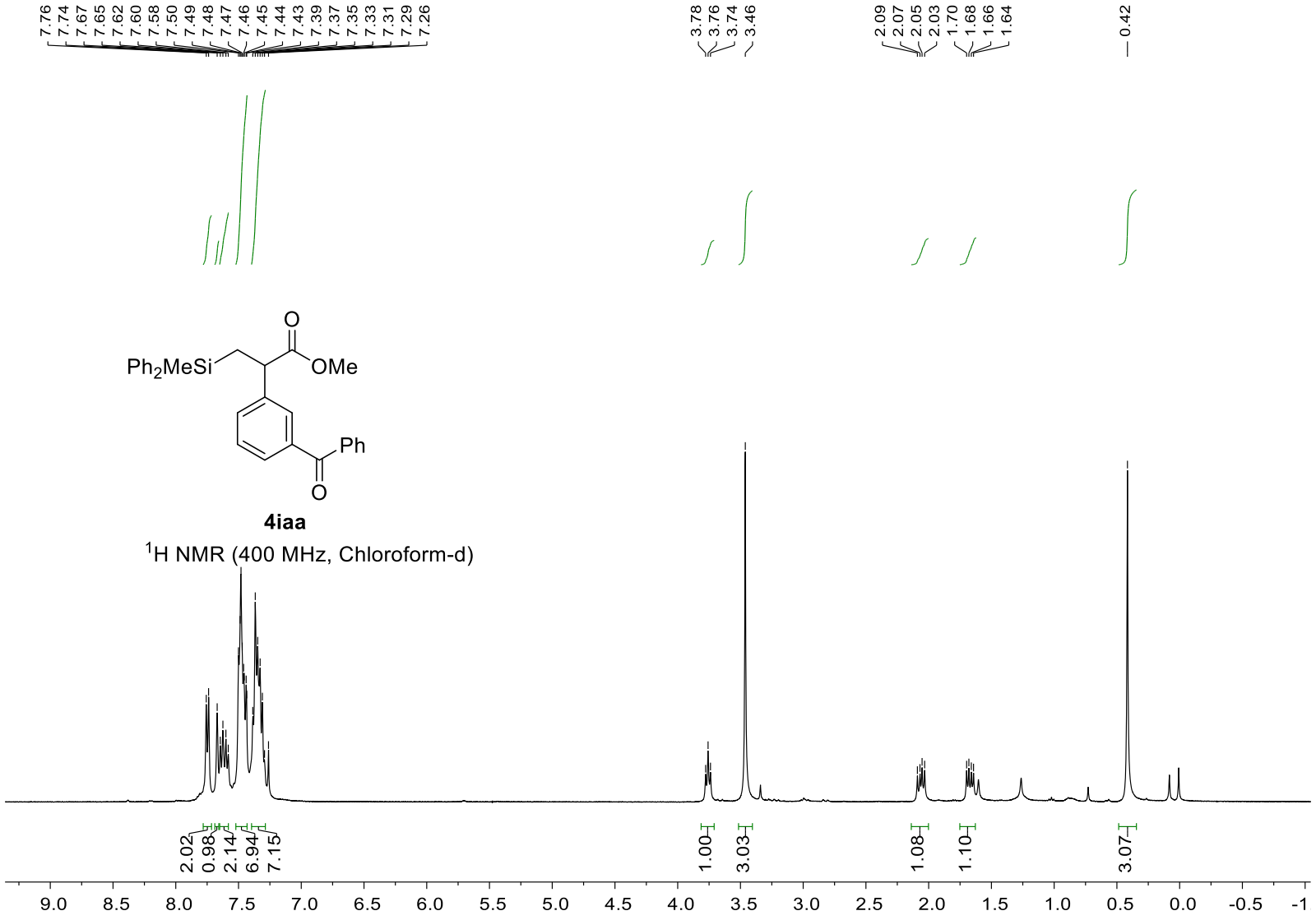


4gaa

^{13}C NMR (101 MHz, Chloroform-d)

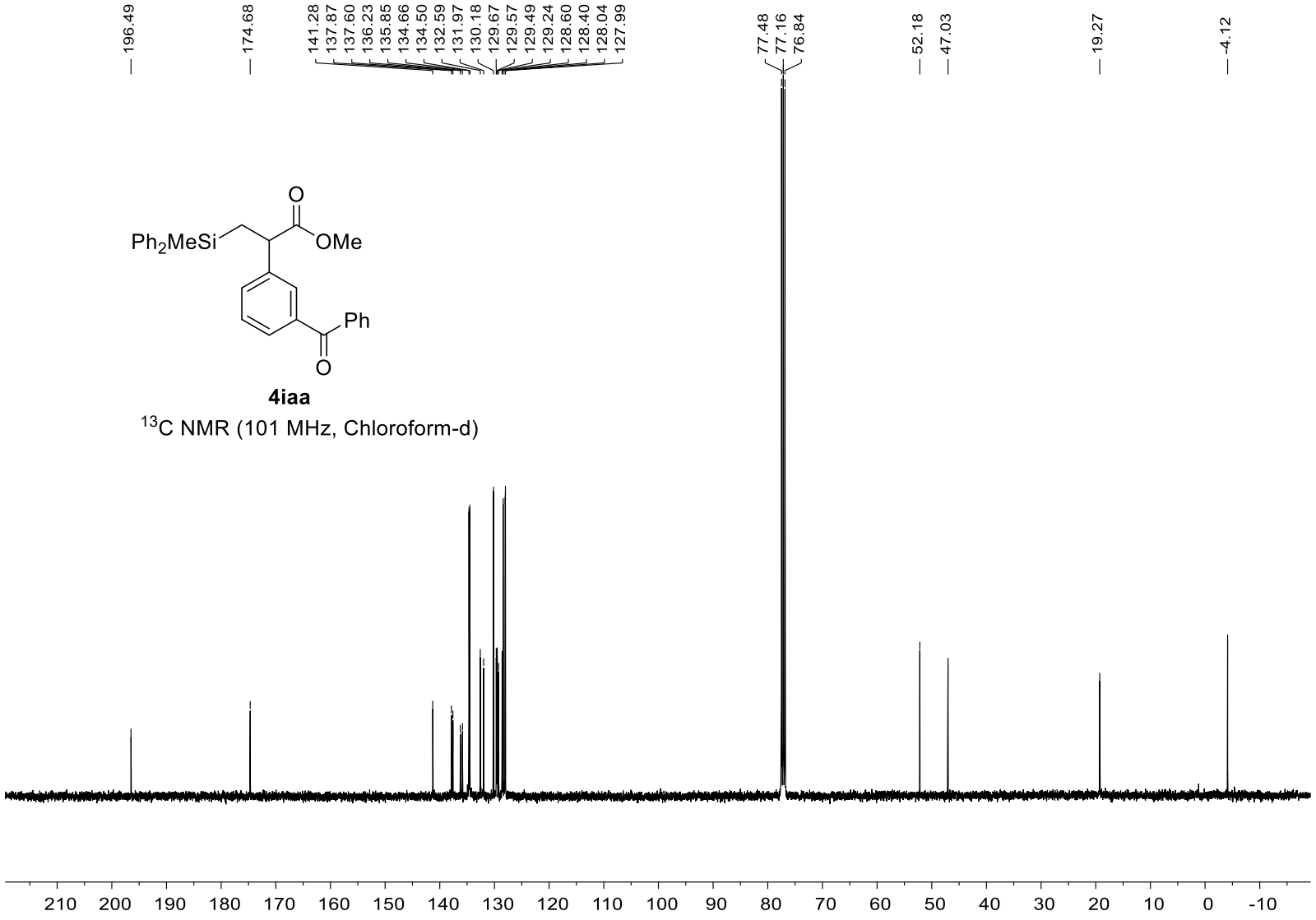

7.81 7.79 7.75 7.49 7.49 7.48 7.48 7.47 7.47 7.46 7.46 7.45 7.44 7.44 7.44 7.43 7.43 7.42 7.40 7.39 7.38 7.38 7.38 7.37 7.36 7.36 7.36 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.30 7.26 3.77 3.75 3.73 3.46
2.54 2.10 2.08 2.06 2.04 1.70 1.68 1.66 1.64
0.39 0.38
Ph2MeSi
OMe
Me
O
O
4haa
1H NMR (400 MHz, Chloroform-d)
1.04 1.00 5.28 7.23 1.00 2.98 3.03 1.02 1.08 3.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.

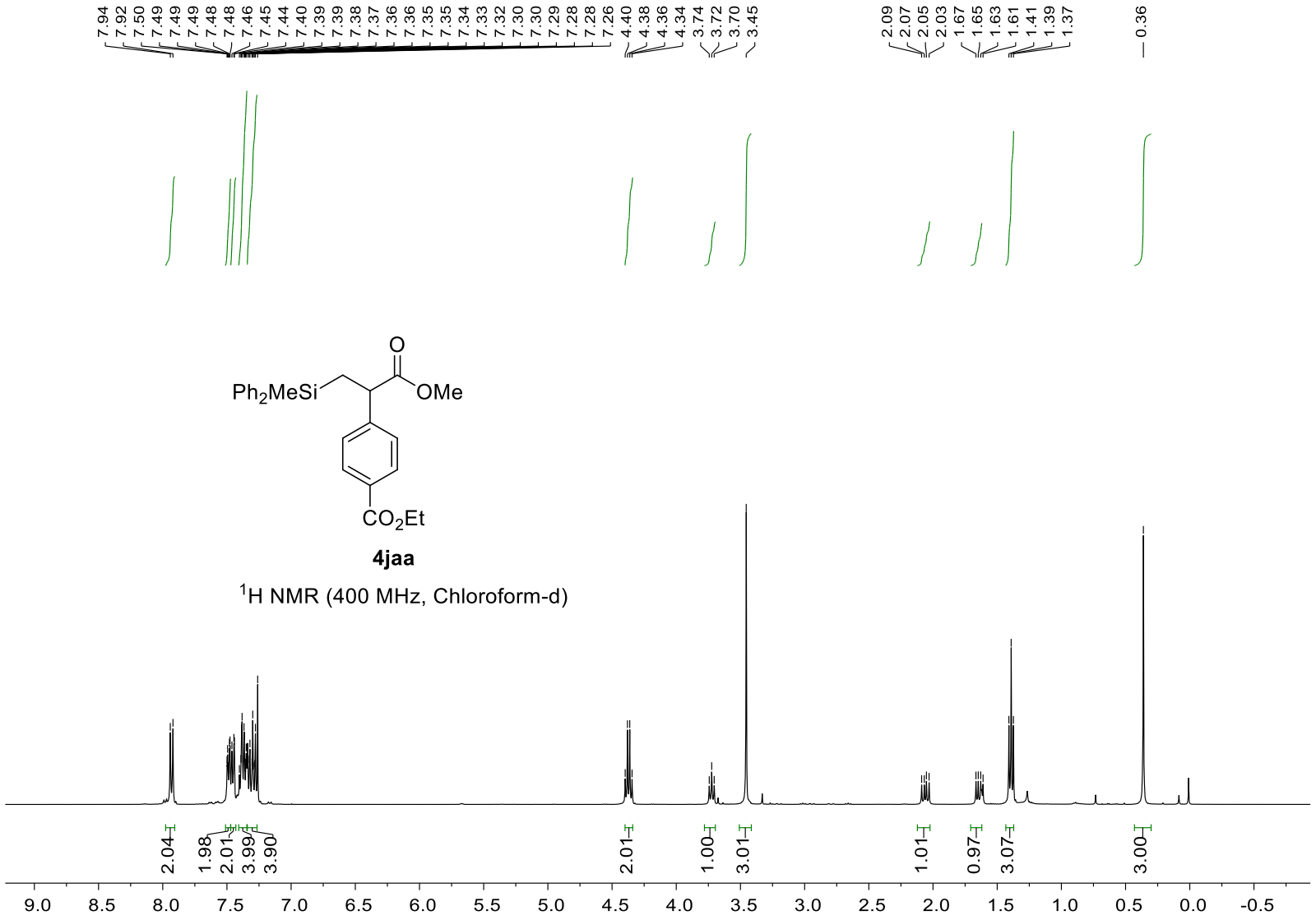

197.98
174.73
141.39
137.39
136.26
135.84
134.66
134.47
132.67
129.58
129.45
128.94
128.05
127.98
127.40
77.48
77.16
76.84
52.20
47.04
26.81
19.24
-4.19
Ph2MeSi
OMe
Me
O
O
4haa
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



4iaa

^{1}H NMR (400 MHz, Chloroform-d)


196.49
174.68
141.28
137.87
137.60
136.23
135.85
134.66
134.50
132.59
131.97
130.18
129.67
129.57
129.49
129.24
128.60
128.40
128.04
127.99
77.48
77.16
76.84
52.18
47.03
19.27
-4.12
Ph2MeSi
OMe
Ph
O
O
4iaa
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


7.94
7.92
7.50
7.49
7.49
7.49
7.48
7.48
7.46
7.45
7.44
7.40
7.39
7.39
7.38
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.32
7.30
7.30
7.29
7.28
7.28
7.26
4.40
4.38
4.36
4.34
3.74
3.72
3.70
3.45
2.09
2.07
2.05
2.03
1.67
1.65
1.63
1.61
1.41
1.39
1.37
0.36
O
Ph2MeSi
OMe
CO2Et
4jaa
1H NMR (400 MHz, Chloroform-d)
2.04
1.98
2.01
3.99
3.90
2.01
1.00
3.01
1.01
0.97
3.07
3.00
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
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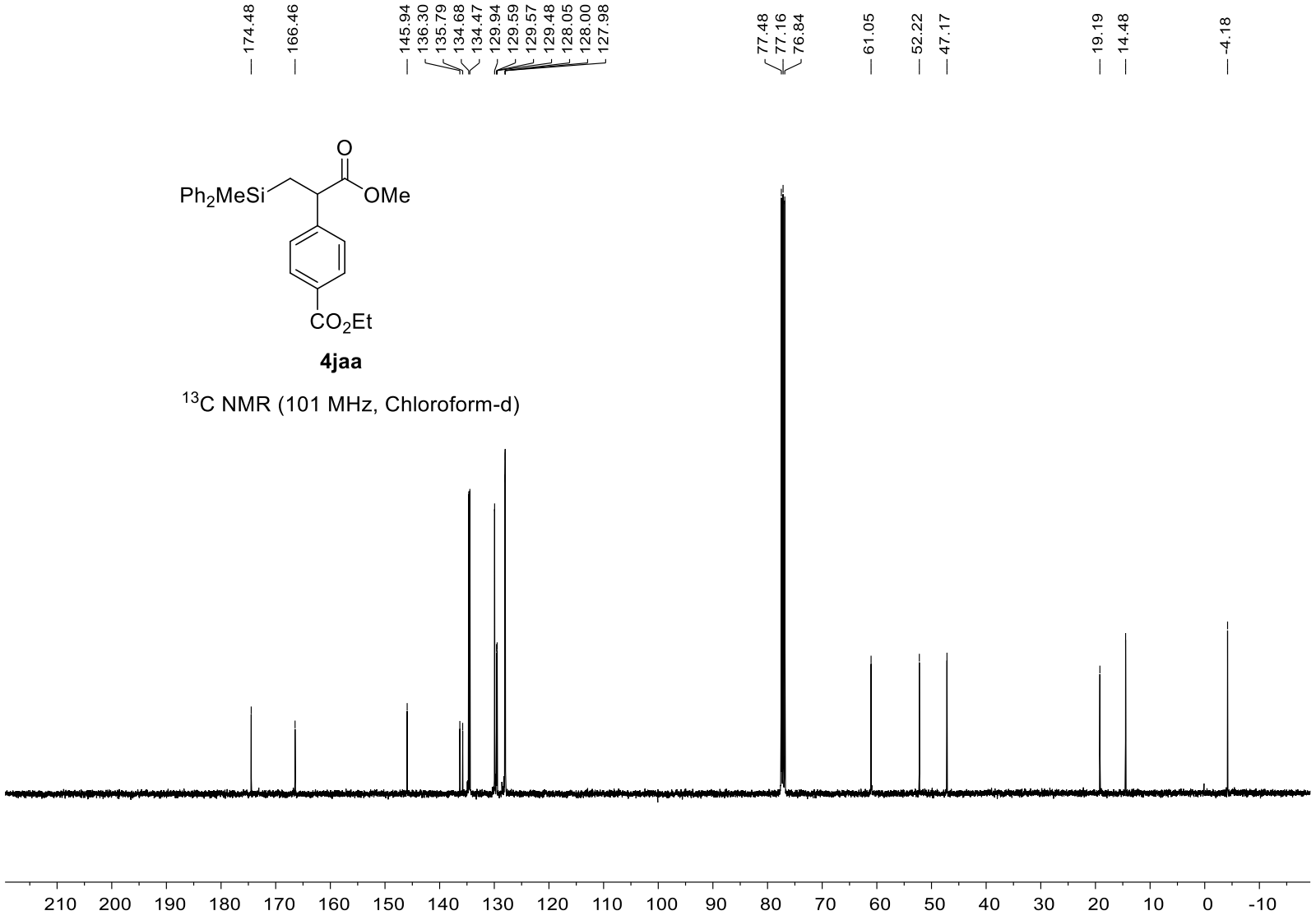
0.0
-0.5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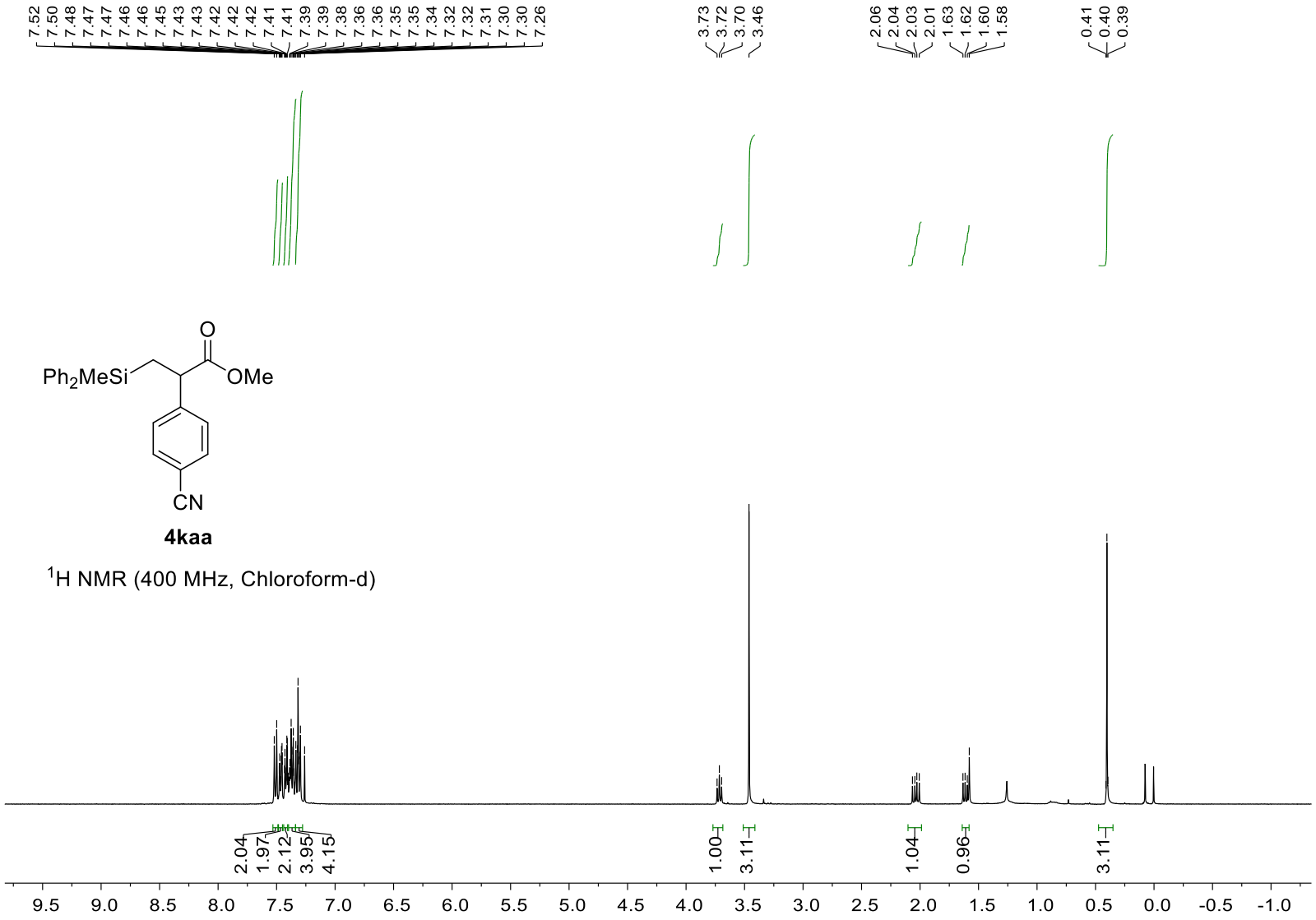
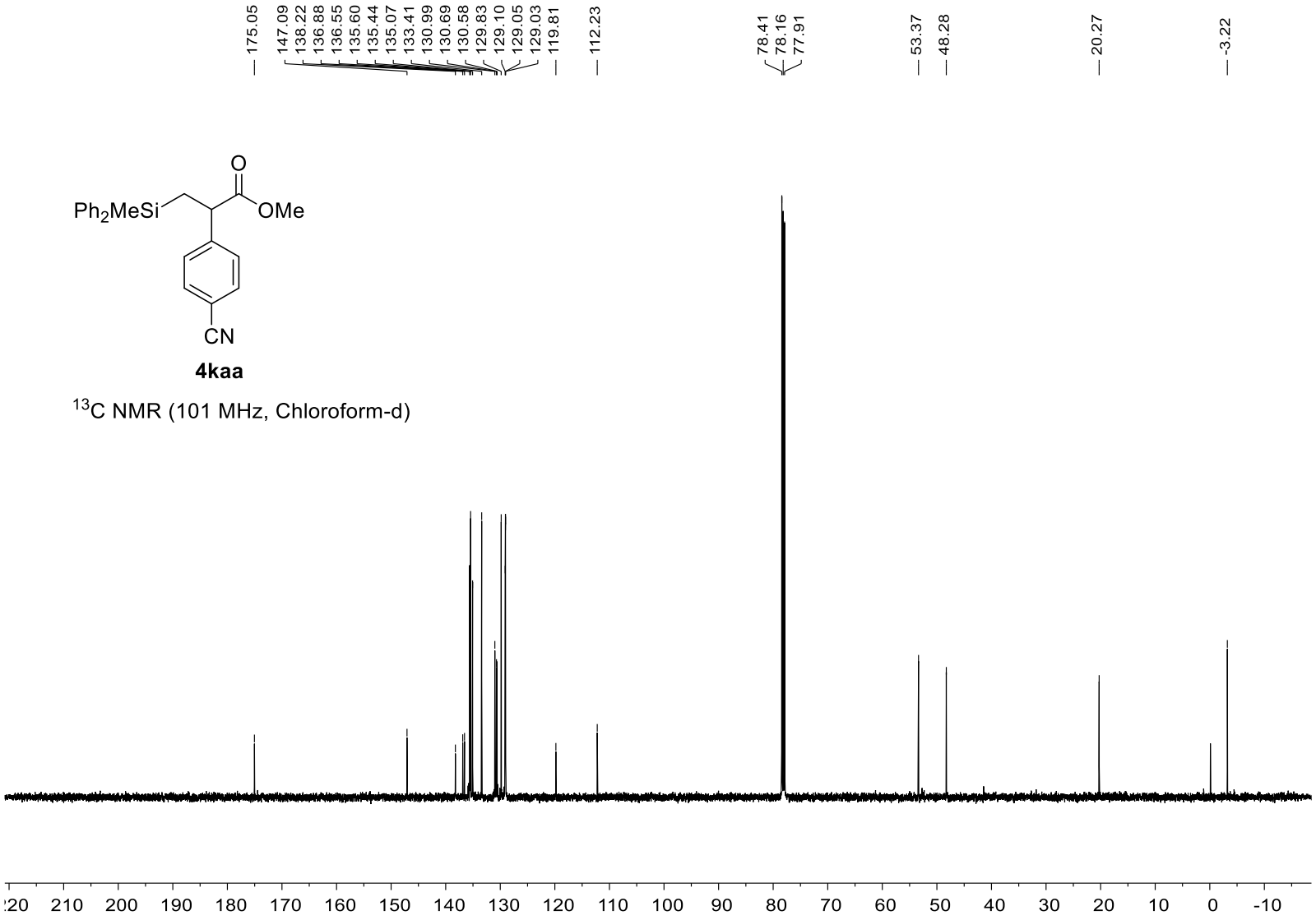
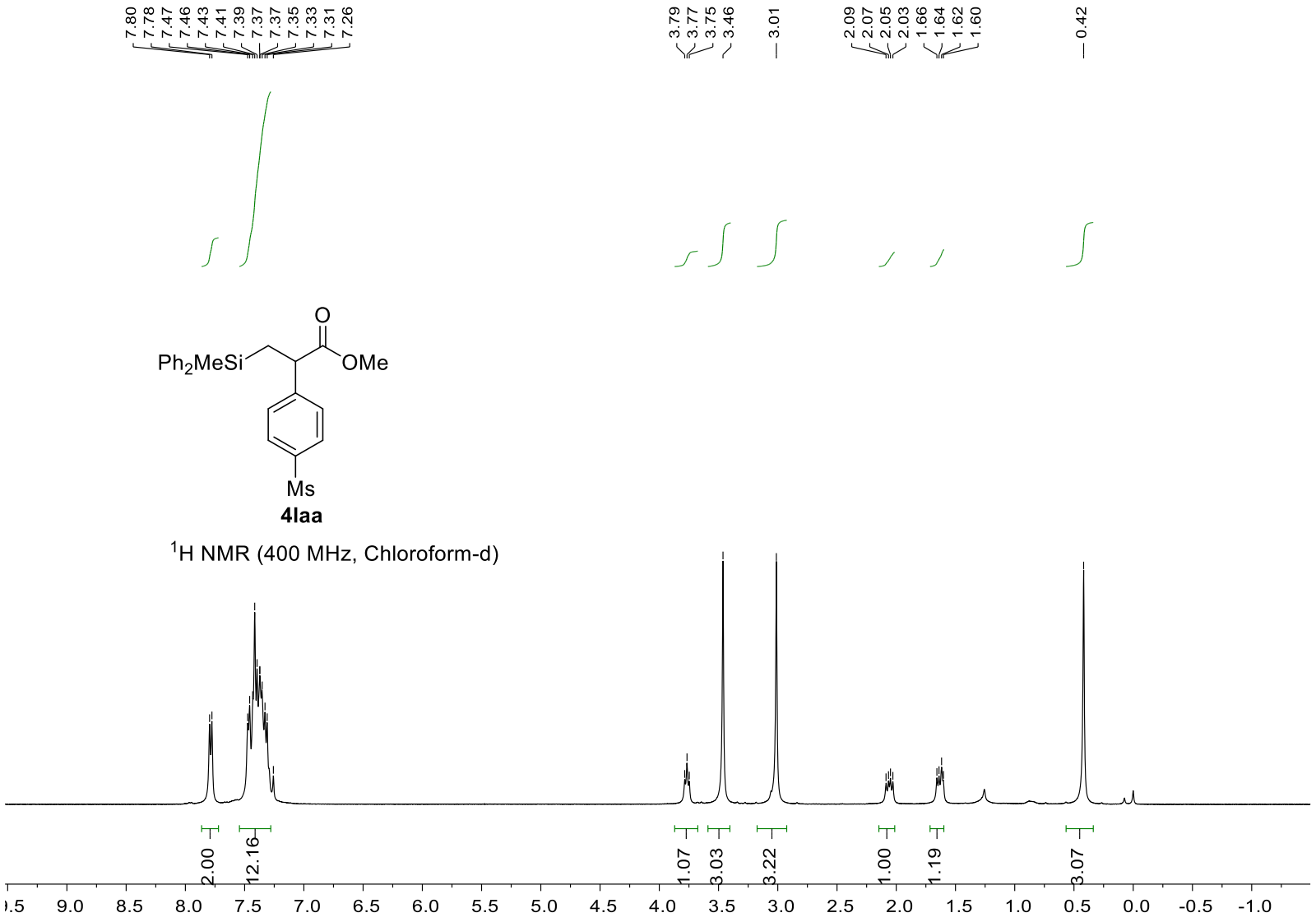
166.46
145.94
136.30
135.79
134.68
134.47
129.94
129.59
129.57
129.48
128.05
128.00
127.98
77.48
77.16
76.84
61.05
52.22
47.17
19.19
14.48
-4.18
O
Ph2MeSi
OMe
CO2Et
4jaa
13C NMR (101 MHz, Chloroform-d)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



4kaa

^{1}H NMR (400 MHz, Chloroform-d)


175.05
147.09
138.22
136.88
136.55
135.60
135.44
135.07
133.41
130.99
130.69
130.58
129.83
129.10
129.05
129.03
119.81
112.23
78.41
78.16
77.91
53.37
48.28
20.27
-3.22
O
Ph2MeSi
OMe
CN
4kaa
13C NMR (101 MHz, Chloroform-d)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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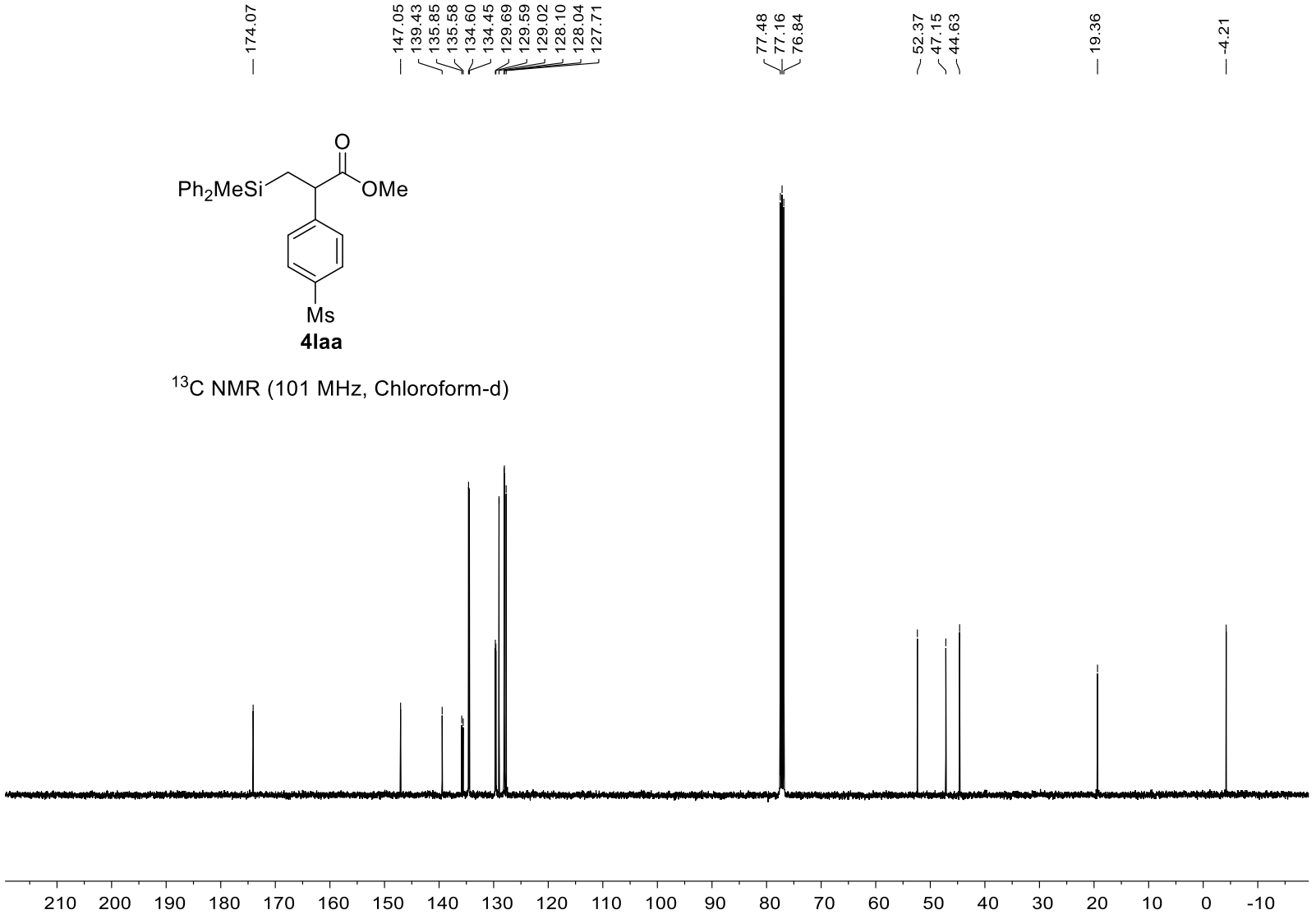
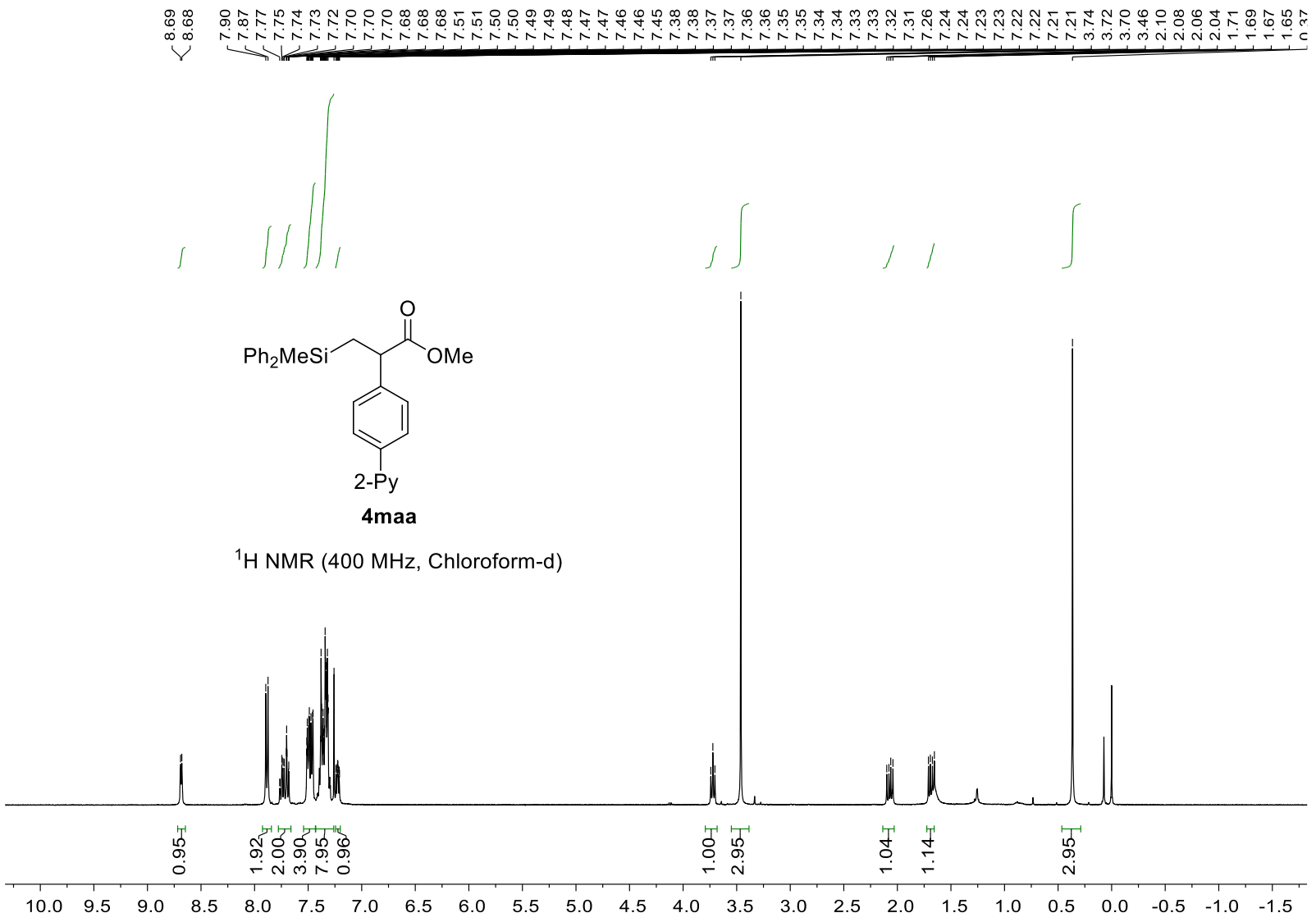
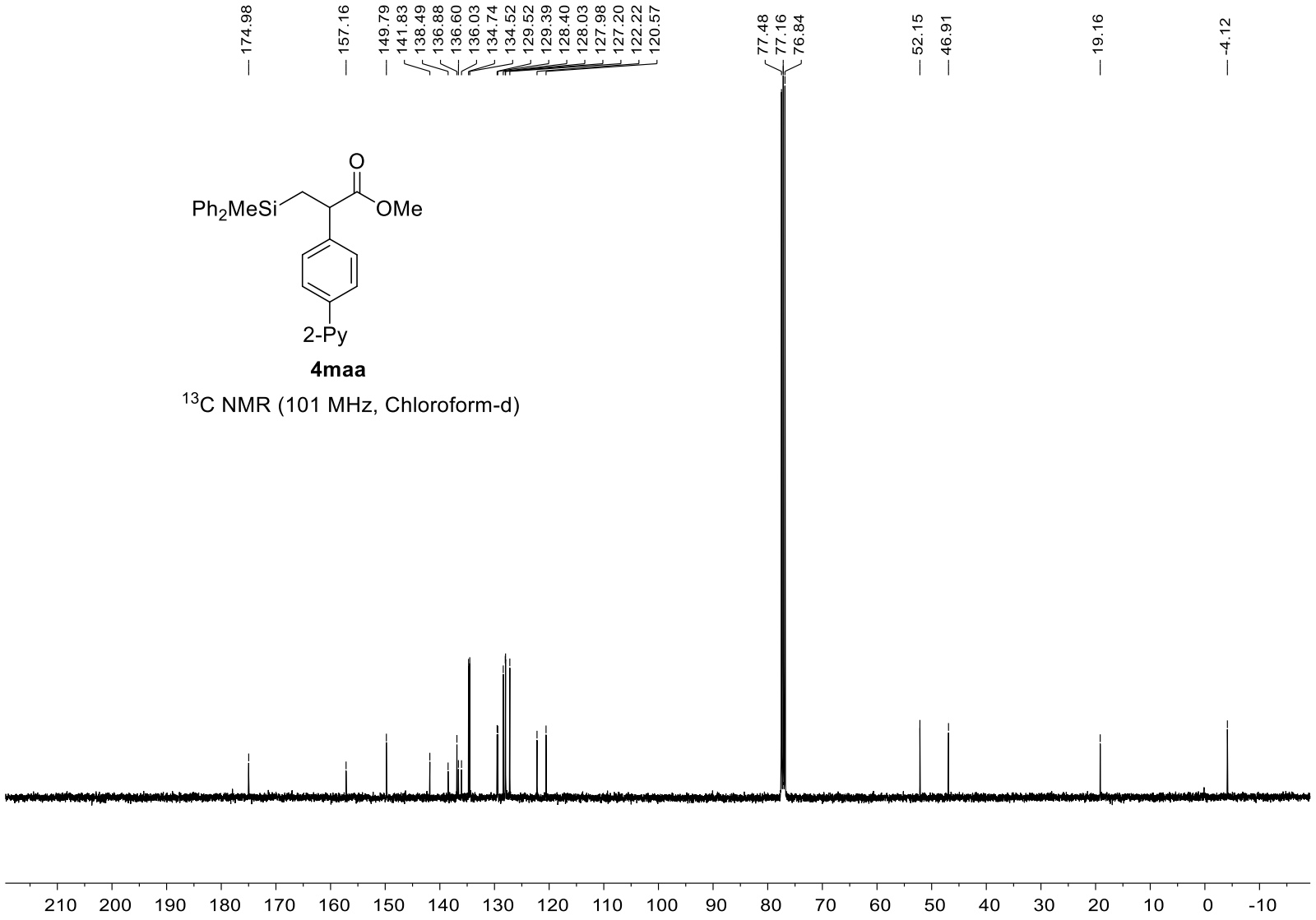
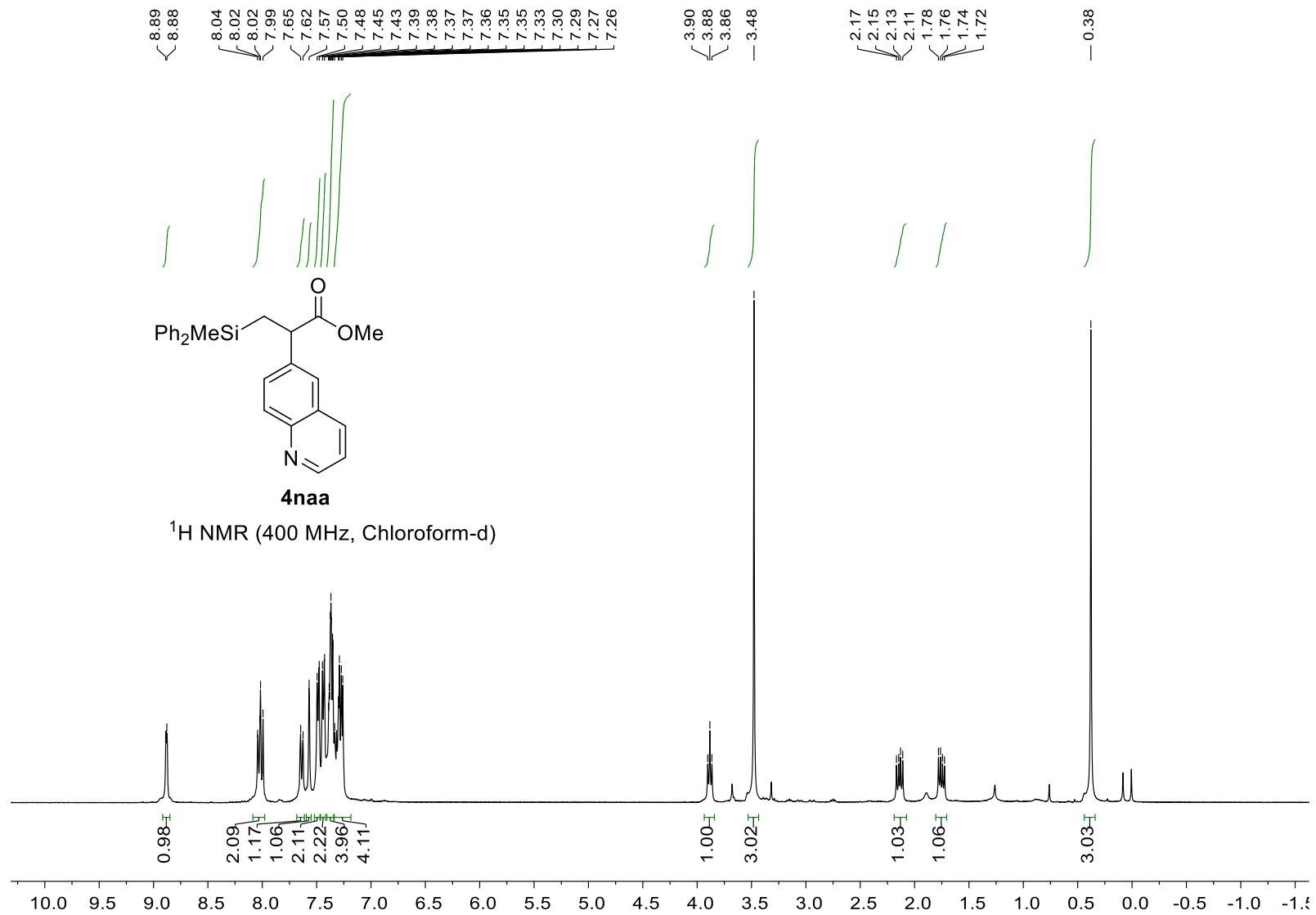
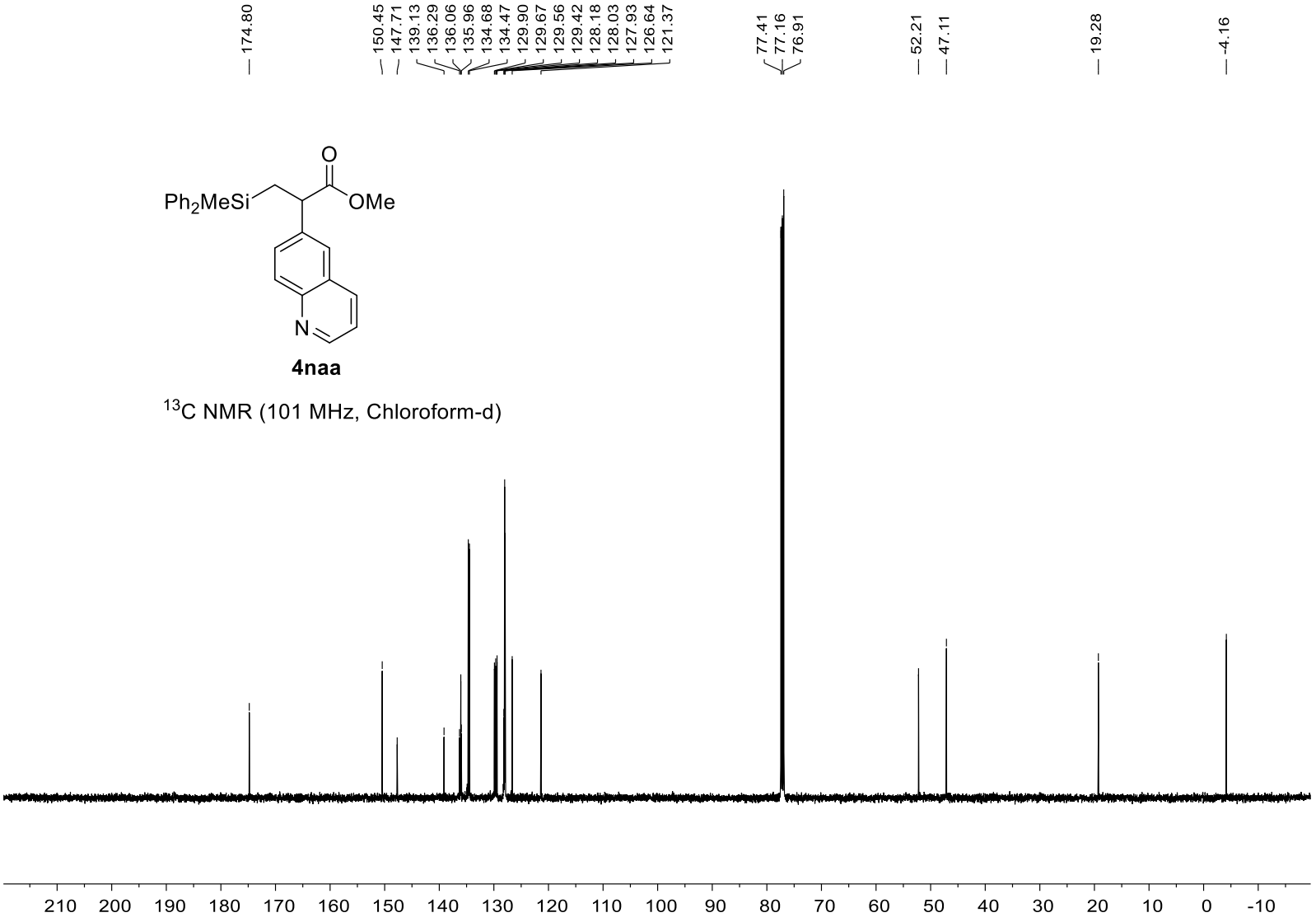
7.78
7.47
7.46
7.43
7.41
7.39
7.37
7.37
7.35
7.33
7.31
7.26
3.79
3.77
3.75
3.46
3.01
2.09
2.07
2.05
2.03
1.66
1.64
1.62
1.60
0.42
O
Ph2MeSi
OMe
Ms
4laa
1H NMR (400 MHz, Chloroform-d)
2.00
12.16
1.07
3.03
3.22
1.00
1.19
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0


174.07
147.05
139.43
135.85
135.58
134.60
134.45
129.69
129.59
129.02
128.10
128.04
127.71
77.48
77.16
76.84
52.37
47.15
44.63
19.36
-4.21
O
Ph2MeSi
OMe
Ms
4laa
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


8.69
8.68
7.90
7.87
7.77
7.75
7.74
7.73
7.72
7.70
7.70
7.70
7.68
7.68
7.68
7.51
7.51
7.50
7.50
7.49
7.49
7.48
7.47
7.47
7.46
7.46
7.45
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.26
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.21
3.74
3.72
3.70
3.46
2.10
2.08
2.06
2.04
1.71
1.69
1.67
1.65
O
Ph2MeSi
OMe
2-Py
4maa
1H NMR (400 MHz, Chloroform-d)
0.95
1.92
2.00
3.90
7.95
0.96
1.00
2.95
1.04
1.14
2.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5

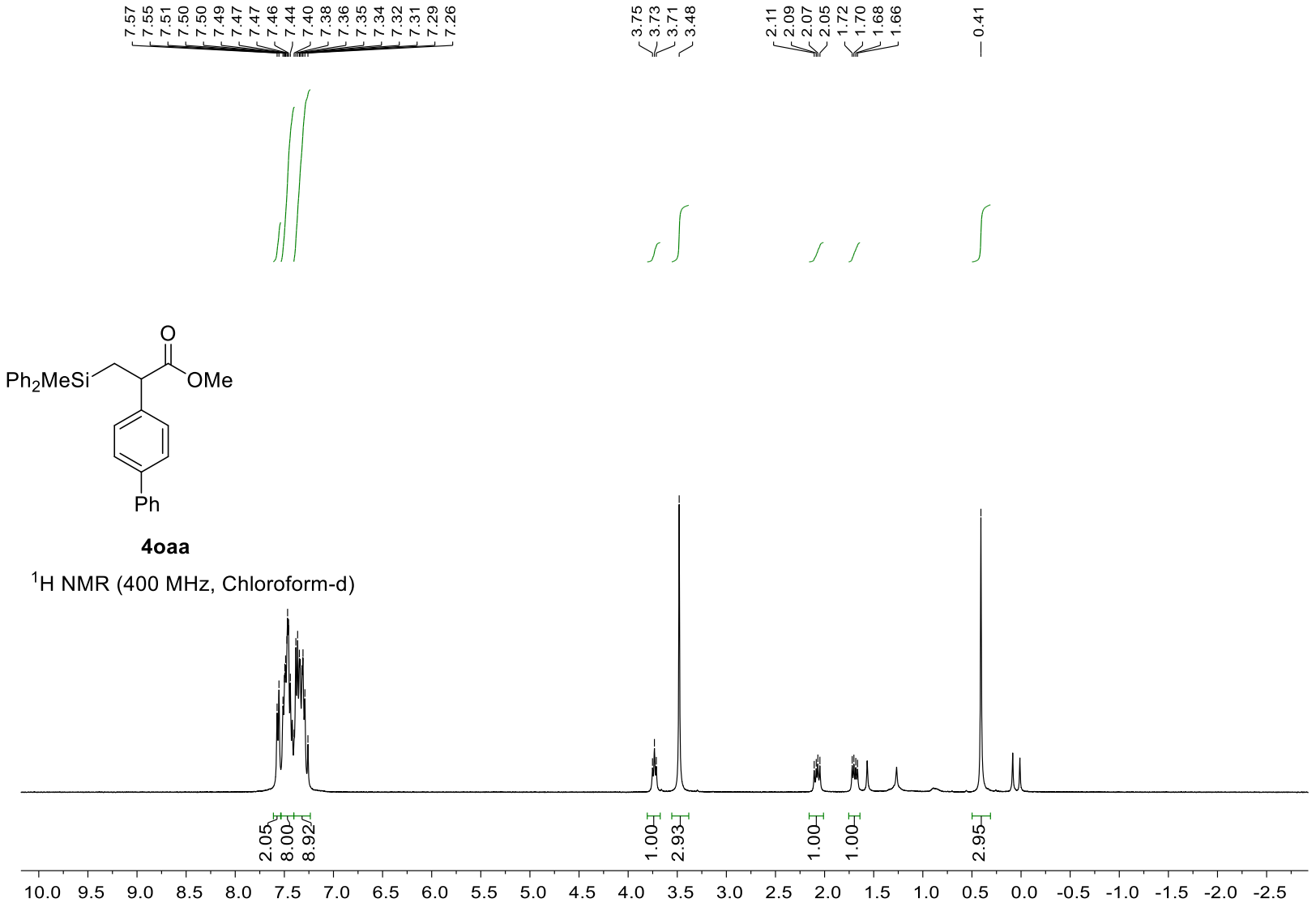

174.98
157.16
149.79
141.83
138.49
136.88
136.60
136.03
134.74
134.52
129.52
129.39
128.40
128.03
127.98
127.20
122.22
120.57
77.48
77.16
76.84
52.15
46.91
19.16
-4.12
O
Ph2MeSi
OMe
2-Py
4maa
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


8.89
8.88
8.04
8.02
8.02
7.99
7.65
7.62
7.57
7.50
7.48
7.45
7.43
7.39
7.38
7.37
7.37
7.36
7.35
7.35
7.33
7.30
7.29
7.27
7.26
3.90
3.88
3.86
3.48
2.17
2.15
2.13
2.11
1.78
1.76
1.74
1.72
0.38
O
Ph2MeSi
OMe
N
4naa
1H NMR (400 MHz, Chloroform-d)
0.98
2.09
1.17
1.06
2.11
2.22
3.96
4.11
1.00
3.02
1.03
1.06
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0



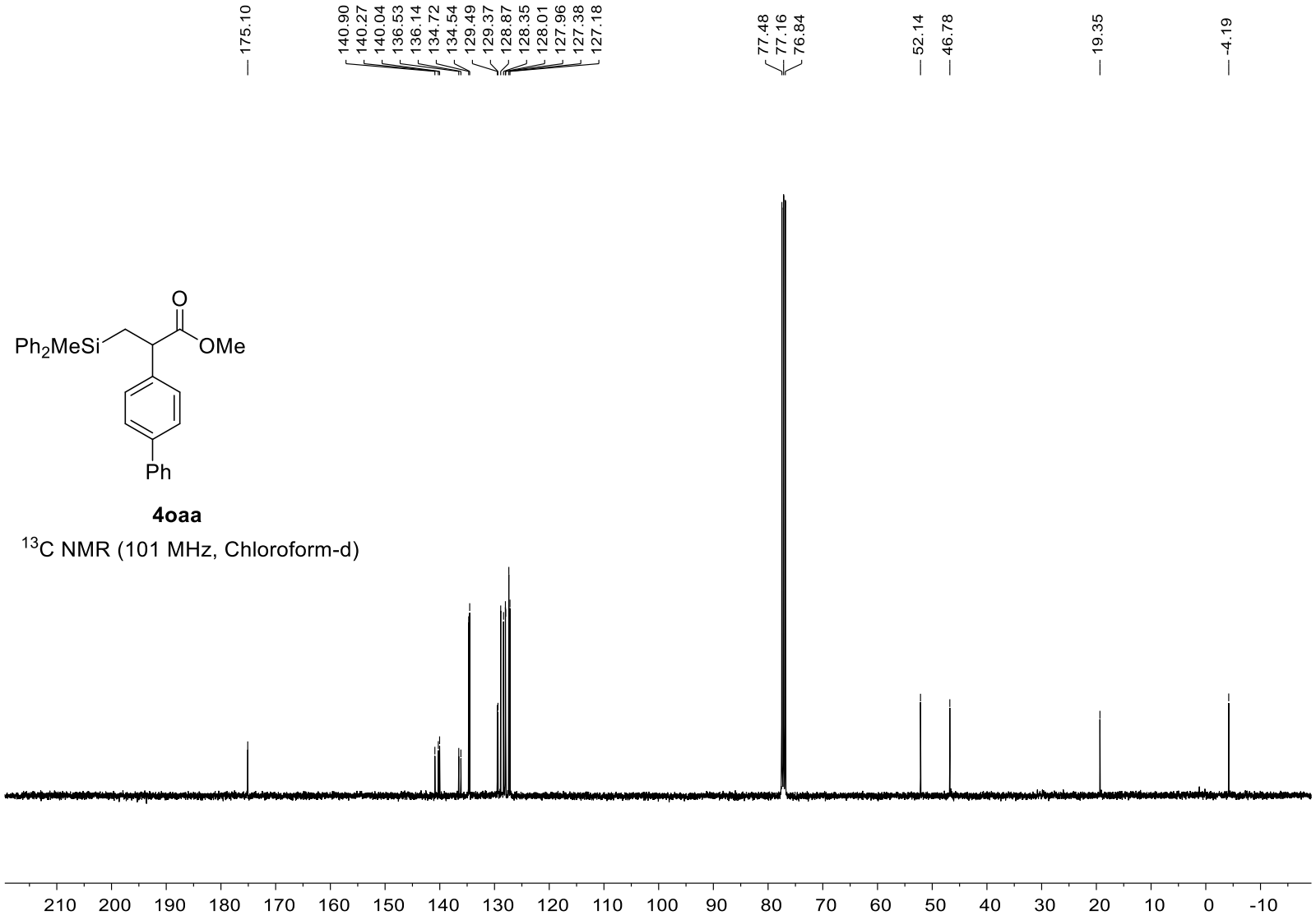
4naa

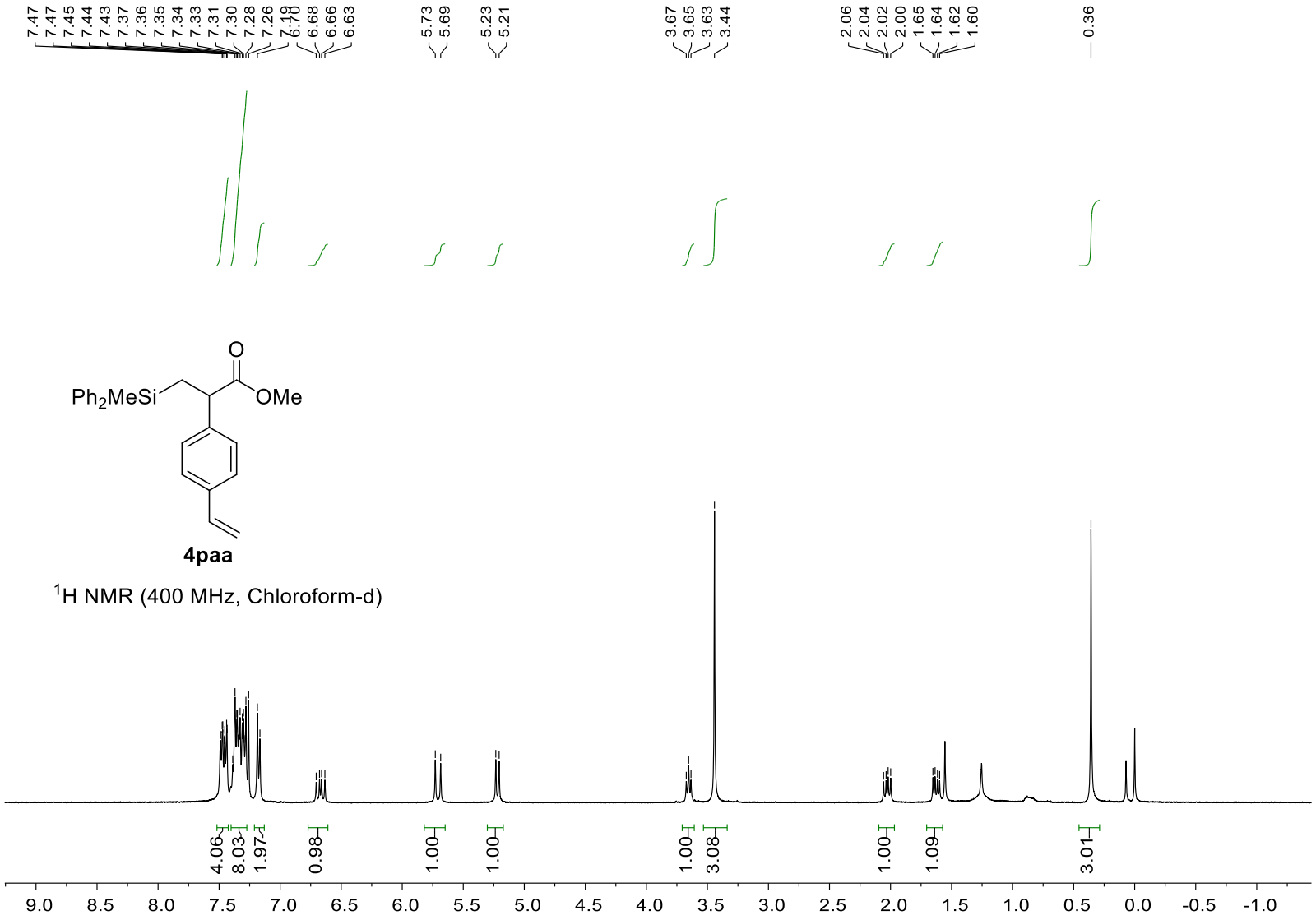
^{13}C NMR (101 MHz, Chloroform-d)

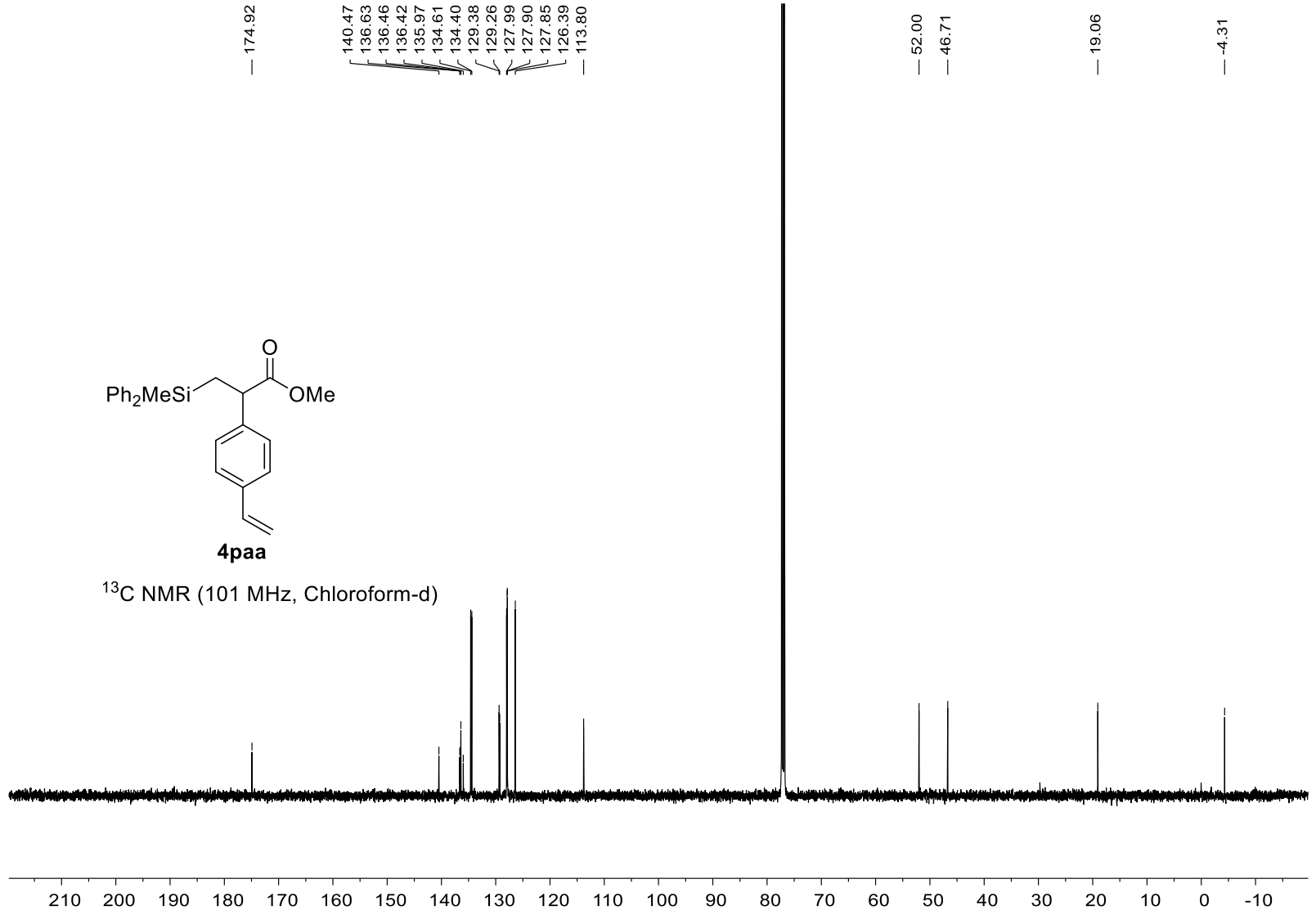


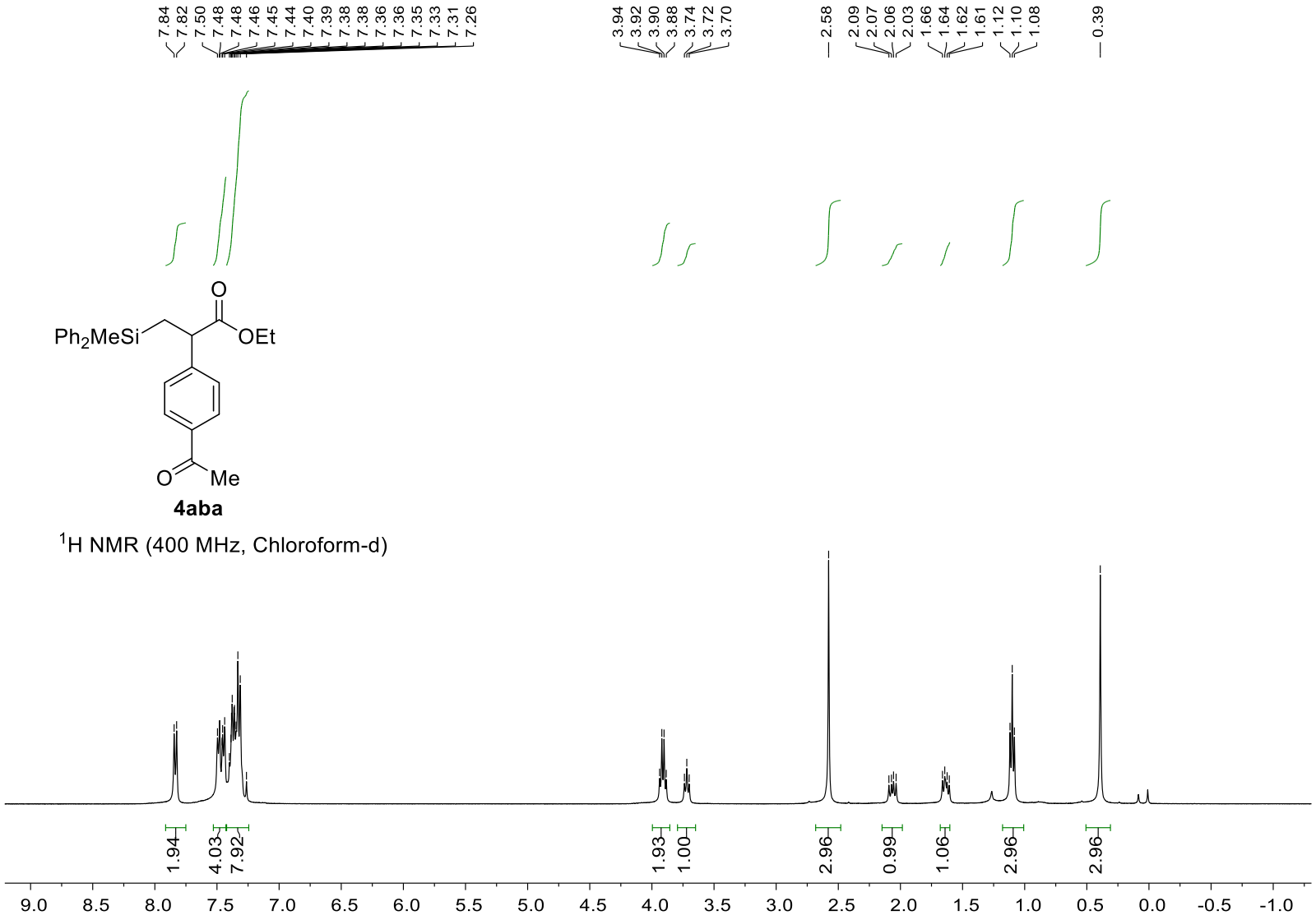
4oaa

^{1}H NMR (400 MHz, Chloroform-d)


175.10
140.90
140.27
140.04
136.53
136.14
134.72
134.54
129.49
129.37
128.87
128.35
128.01
127.96
127.38
127.18
77.48
77.16
76.84
52.14
46.78
19.35
-4.19
O
Ph2MeSi
OMe
Ph
4oaa
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

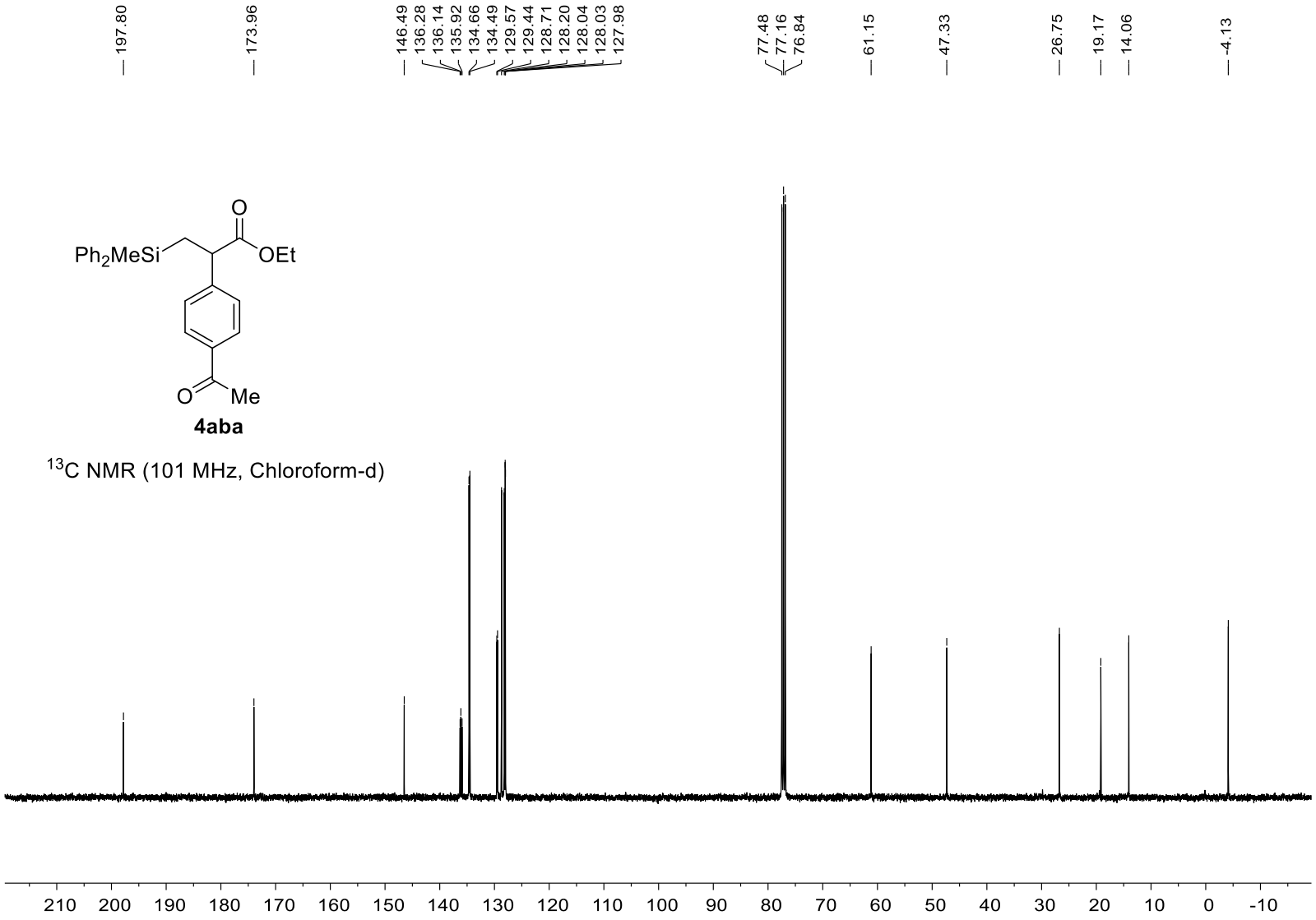

7.47
7.47
7.45
7.44
7.43
7.37
7.36
7.35
7.34
7.33
7.31
7.30
7.28
7.26
7.19
6.70
6.68
6.66
6.63
5.73
5.69
5.23
5.21
3.67
3.65
3.63
3.44
2.06
2.04
2.02
2.00
1.65
1.64
1.62
1.60
0.36
O
Ph2MeSi
OMe
4paa
1H NMR (400 MHz, Chloroform-d)
4.06
8.03
1.97
0.98
1.00
1.00
1.00
3.08
1.00
1.09
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

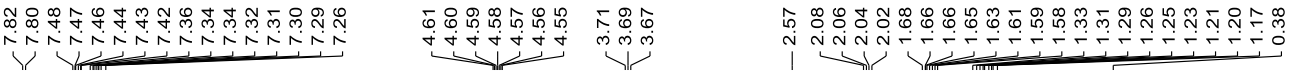

174.92
140.47
136.63
136.46
136.42
135.97
134.61
134.40
129.38
129.26
127.99
127.90
127.85
126.39
113.80
52.00
46.71
19.06
-4.31
O
Ph2MeSi
OMe
4paa
13C NMR (101 MHz, Chloroform-d)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

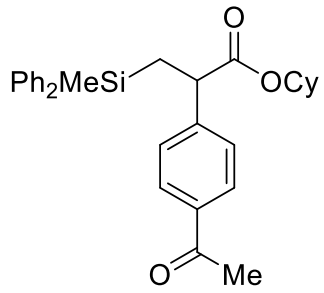


4aba

^{1}H NMR (400 MHz, Chloroform-d)

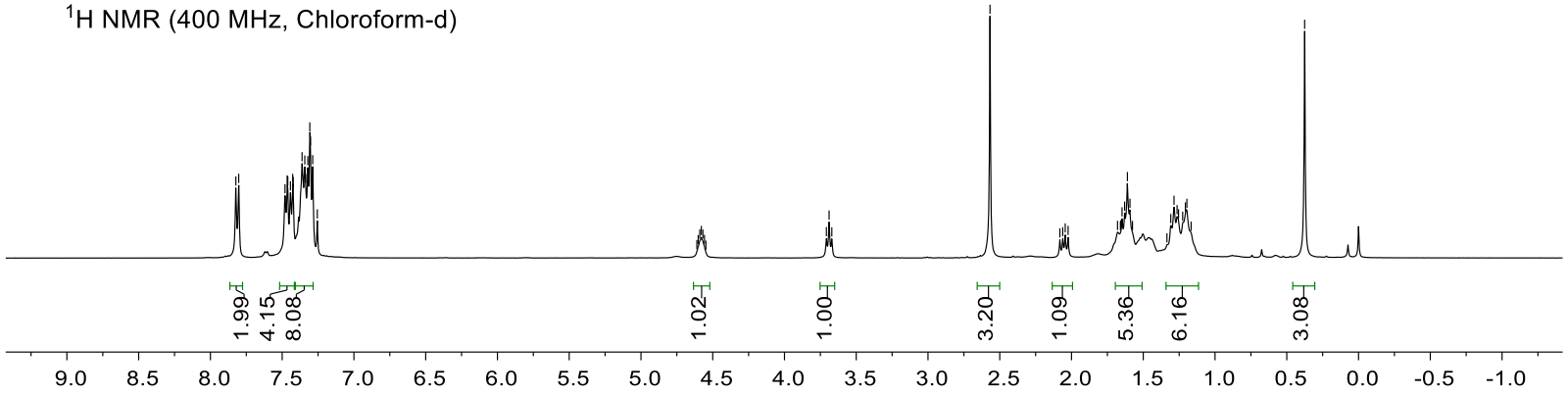

197.80
173.96
146.49
136.28
136.14
135.92
134.66
134.49
129.57
129.44
128.71
128.20
128.04
128.03
127.98
77.48
77.16
76.84
61.15
47.33
26.75
19.17
14.06
-4.13
Ph2MeSi
O
OEt
O
Me
4aba
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

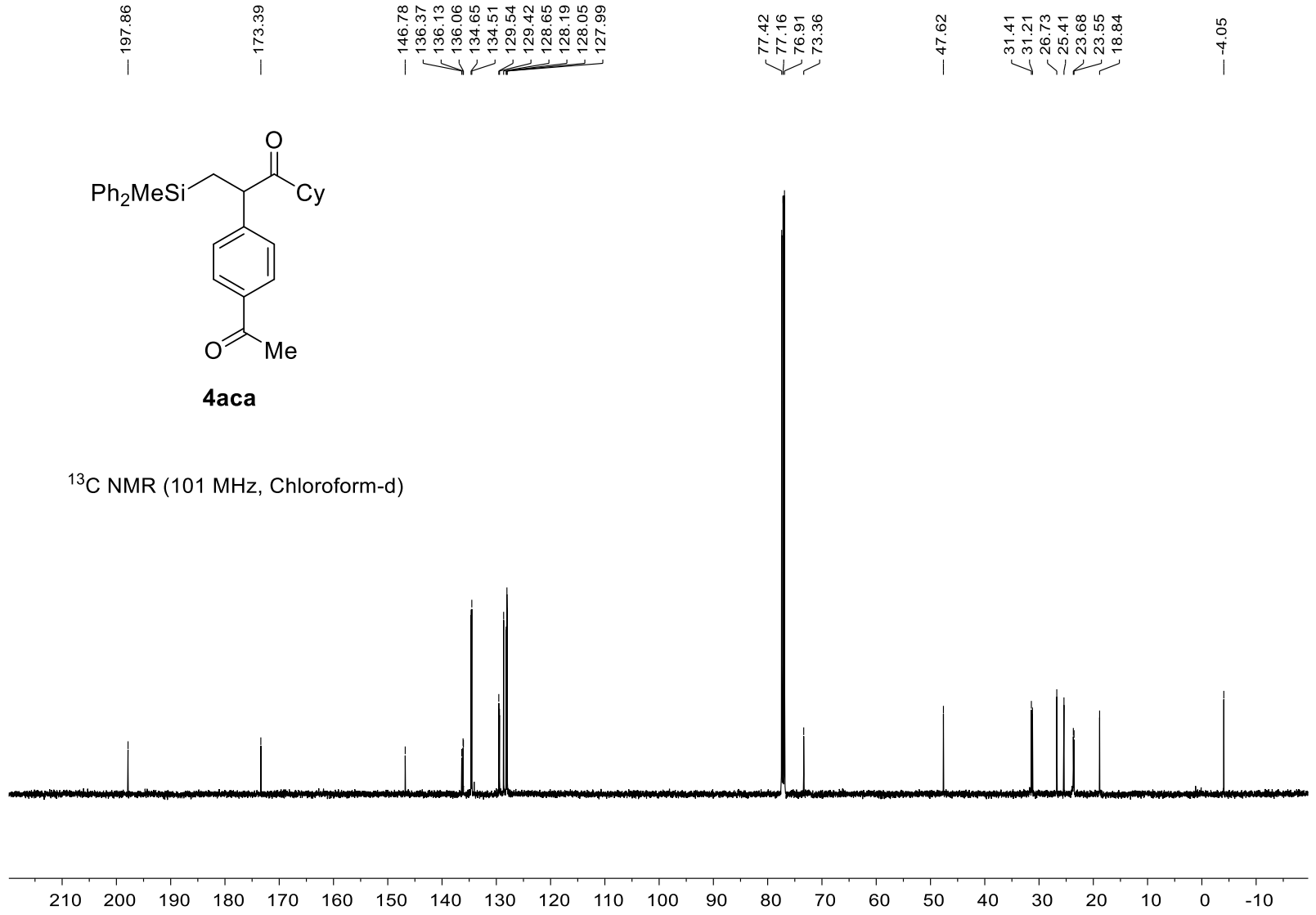




4aca

^{1}H NMR (400 MHz, Chloroform-d)

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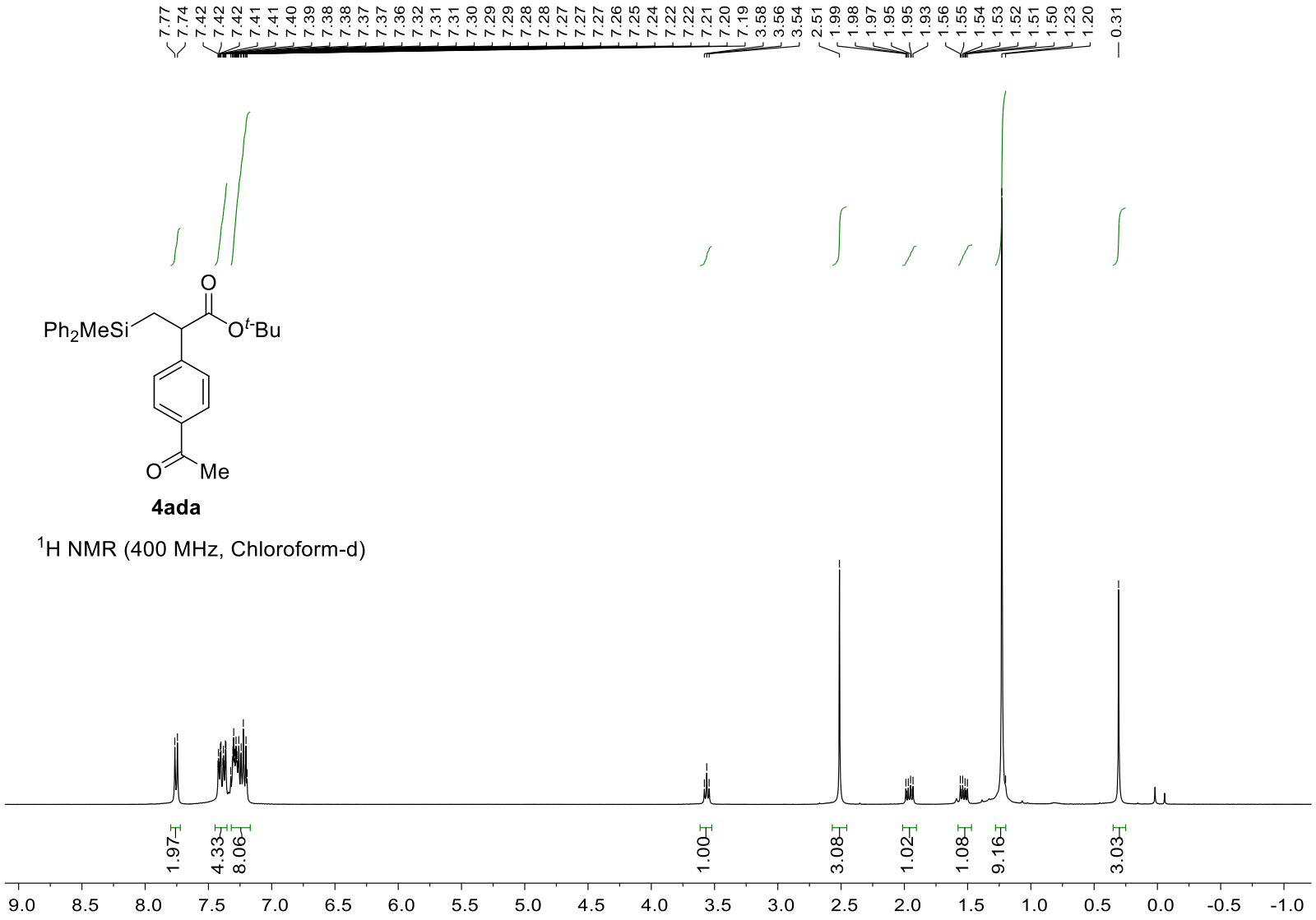
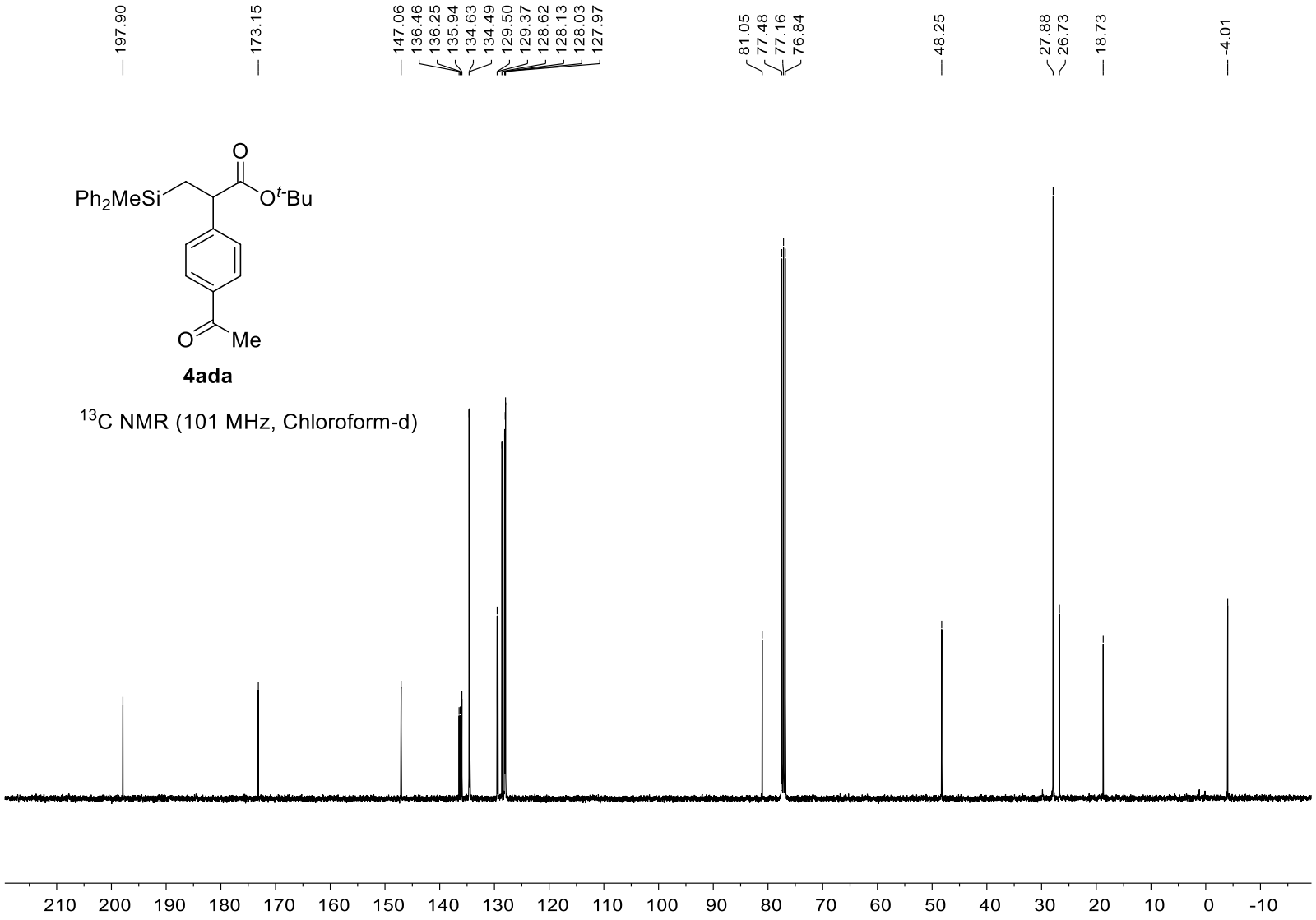
173.39
146.78
136.37
136.13
136.06
134.65
134.51
129.54
129.42
128.65
128.19
128.05
127.99
77.42
77.16
76.91
73.36
47.62
31.41
31.21
26.73
25.41
23.68
23.55
18.84
-4.05
O
Ph2MeSi
Cy
O
Me
4aca
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


7.77
7.74
7.42
7.42
7.42
7.41
7.41
7.40
7.39
7.38
7.38
7.37
7.37
7.36
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.27
7.26
7.25
7.24
7.22
7.22
7.21
7.20
7.19
3.58
3.56
3.54
2.51
1.99
1.98
1.97
1.95
1.95
1.93
1.56
1.55
1.54
1.53
1.52
1.51
1.50
1.23
1.20
0.31
O
Ph2MeSi
O
tBu
O
Me
4ada
1H NMR (400 MHz, Chloroform-d)
1.97
4.33
8.06
1.00
3.08
1.02
1.08
9.16
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0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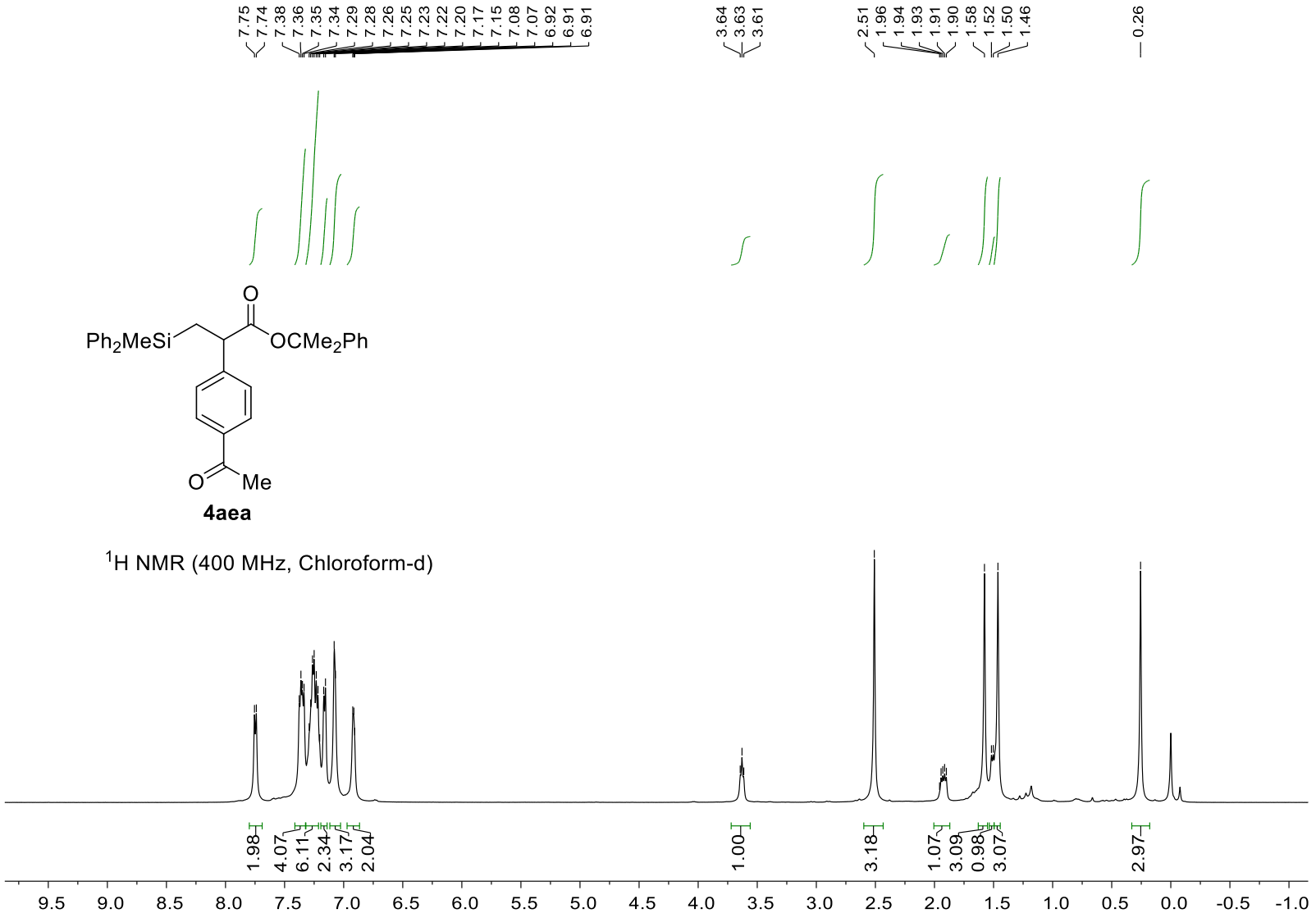
173.15
147.06
136.46
136.25
135.94
134.63
134.49
129.50
129.37
128.62
128.13
128.03
127.97
81.05
77.48
77.16
76.84
48.25
27.88
26.73
18.73
-4.01
Ph2MeSi
O
Ot-Bu
O
Me
4ada
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10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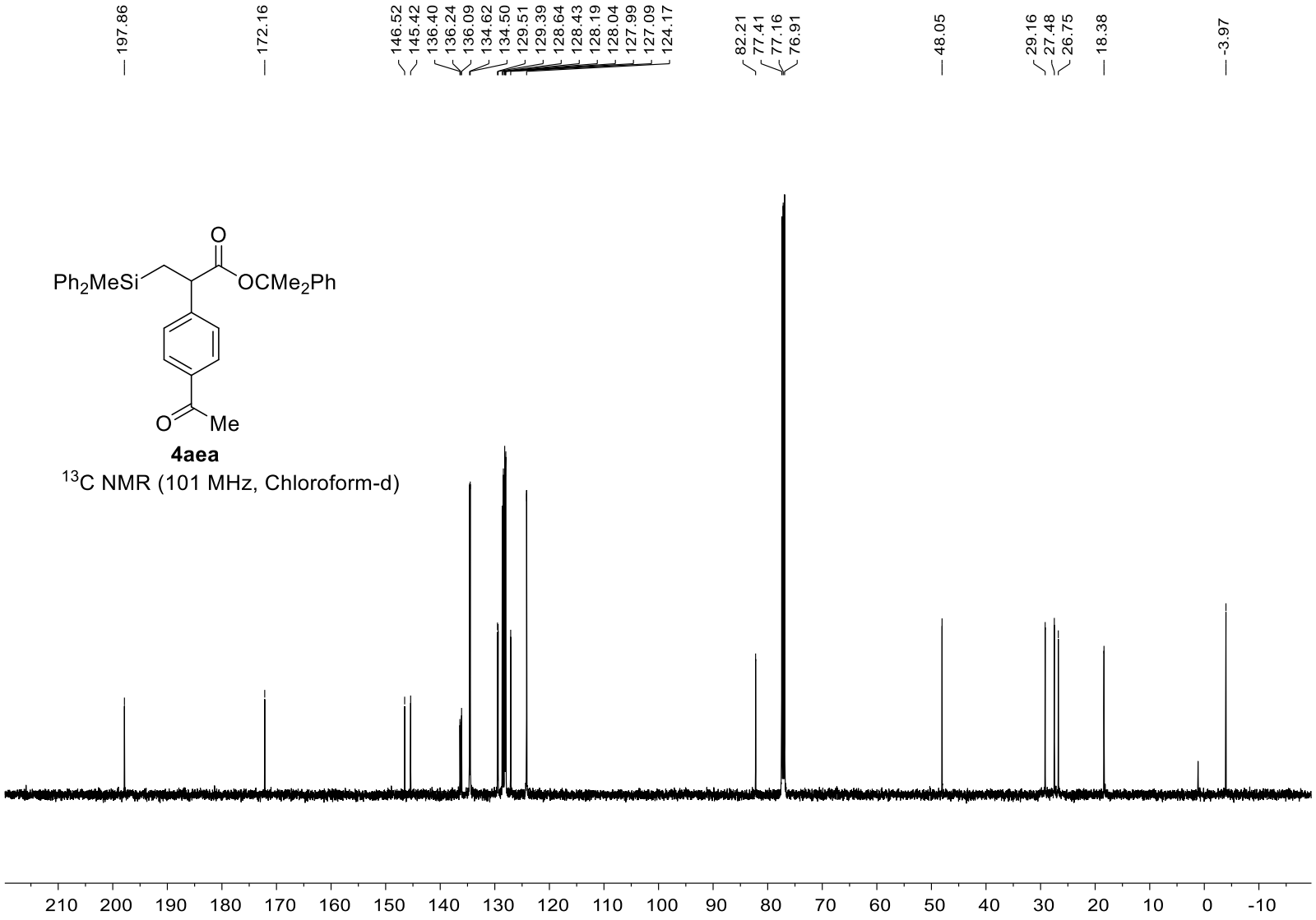
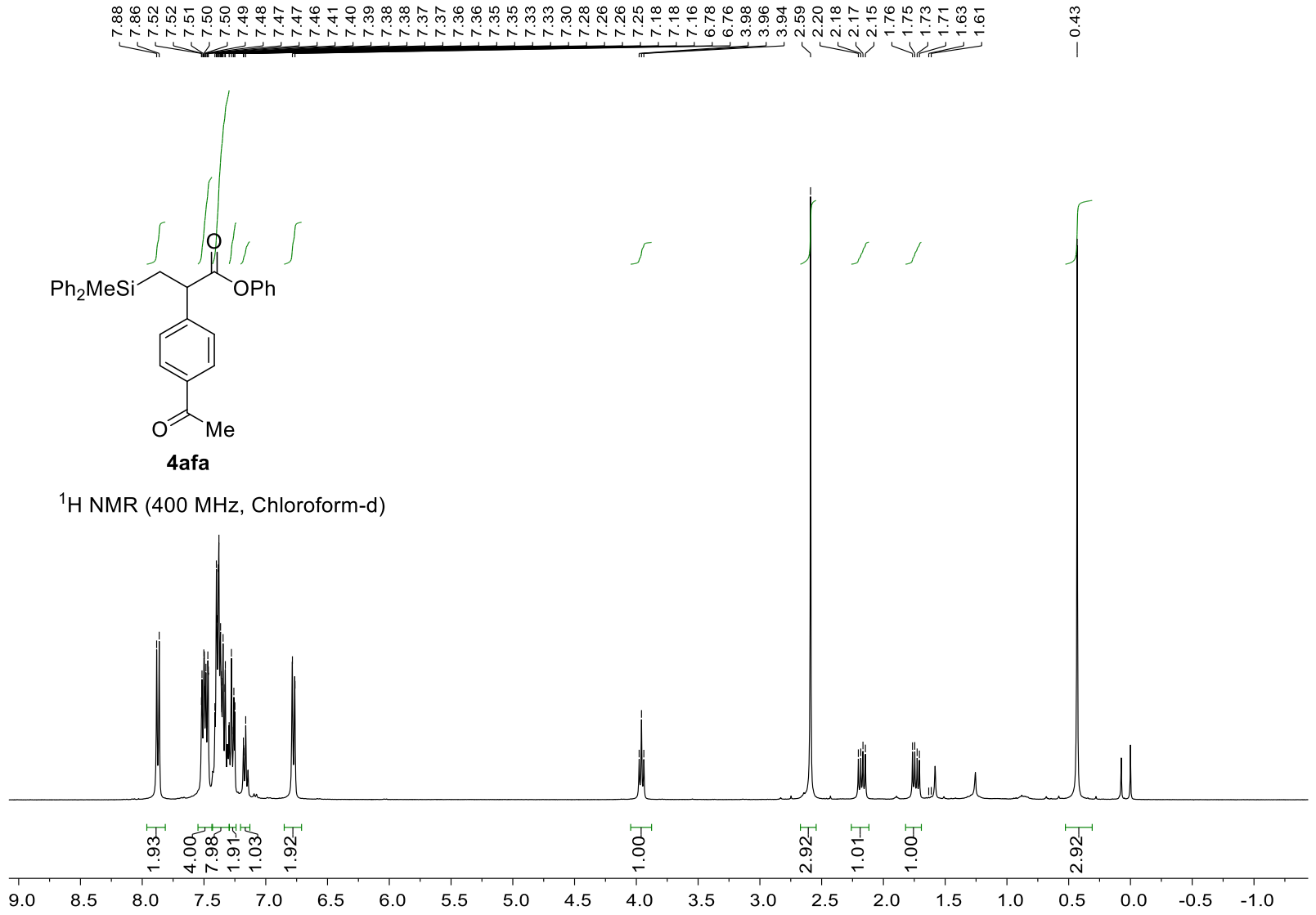
7.74
7.38
7.36
7.35
7.34
7.29
7.28
7.26
7.25
7.23
7.22
7.20
7.17
7.15
7.08
7.07
6.92
6.91
6.91
3.64
3.63
3.61
2.51
1.96
1.94
1.93
1.91
1.90
1.58
1.52
1.50
1.46
0.26
Ph2MeSi
O
OCMe2Ph
O
Me
4aea
1H NMR (400 MHz, Chloroform-d)
1.98
4.07
6.11
2.34
3.17
2.04
1.00
3.18
1.07
3.09
0.98
3.07
2.97
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0


197.86
172.16
146.52
145.42
136.40
136.24
136.09
134.62
134.50
129.51
129.39
128.64
128.43
128.19
128.04
127.99
127.09
124.17
82.21
77.41
77.16
76.91
48.05
29.16
27.48
26.75
18.38
-3.97
Ph2MeSi
O
OCMe2Ph
O
Me
4aea
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10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7.51
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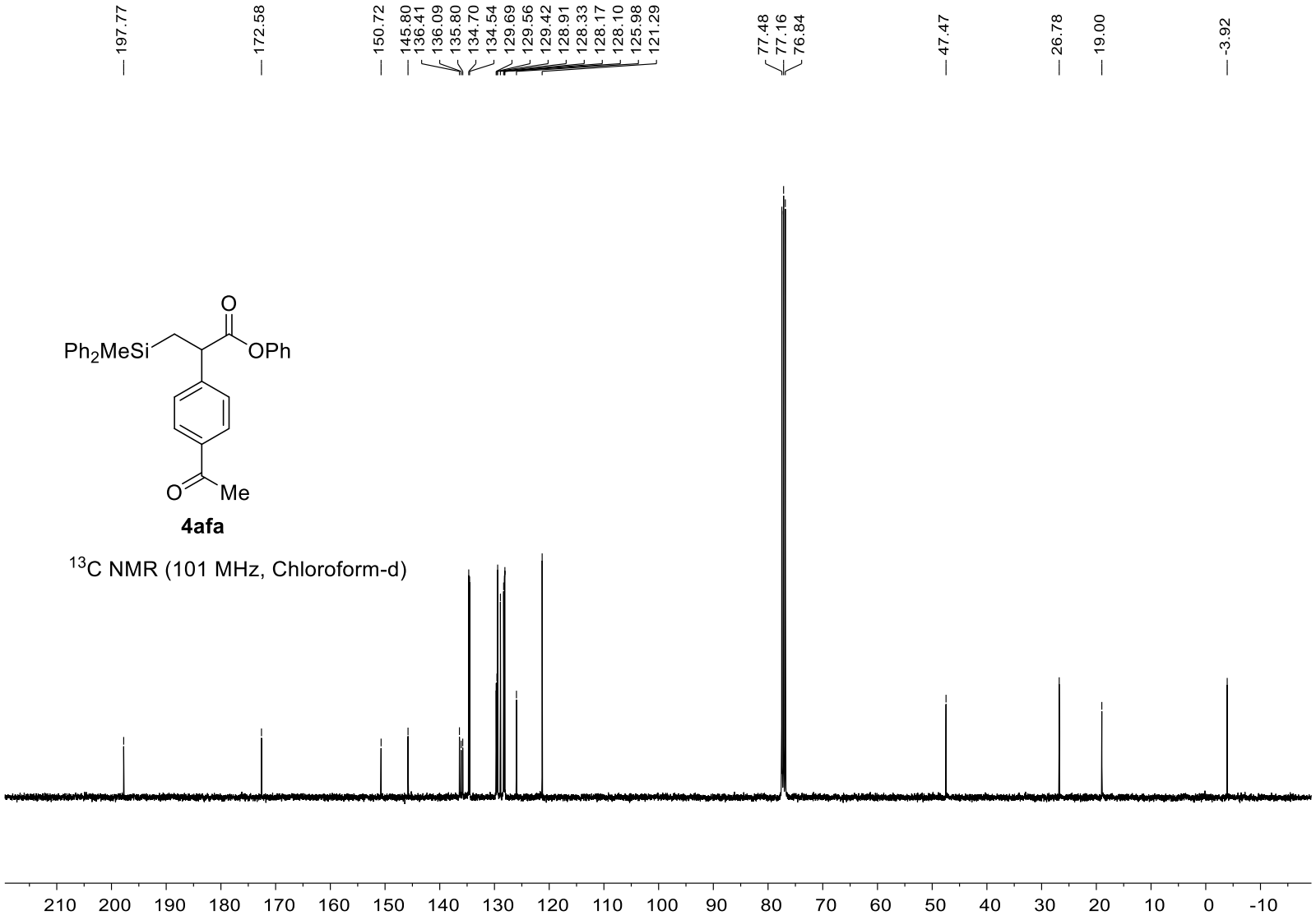
7.50
7.49
7.48
7.47
7.47
7.46
7.41
7.40
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.33
7.33
7.30
7.28
7.26
7.26
7.25
7.18
7.18
7.16
6.78
6.76
3.98
3.96
3.94
2.59
2.20
2.18
2.17
2.15
1.76
1.75
1.73
1.71
1.63
1.61
0.43
Ph2MeSi
O
OPh
O
Me
4afa
1H NMR (400 MHz, Chloroform-d)
1.93
4.00
7.98
1.91
1.03
1.92
1.00
2.92
1.01
1.00
2.92
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0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172.58
150.72
145.80
136.41
136.09
135.80
134.70
134.54
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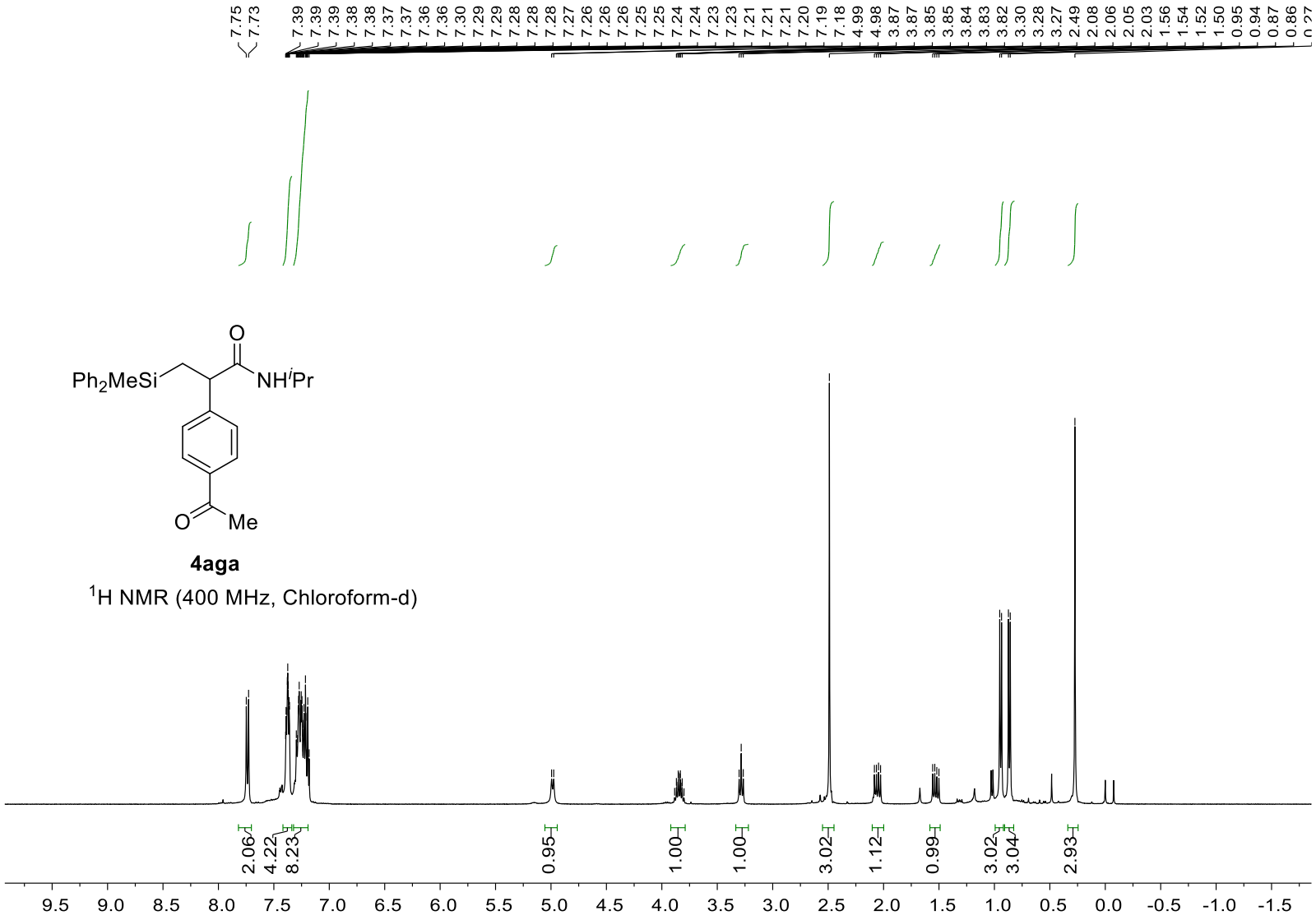
129.42
128.91
128.33
128.17
128.10
125.98
121.29
77.48
77.16
76.84
47.47
26.78
19.00
-3.92
Ph2MeSi
O
OPh
O
Me
4afa
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10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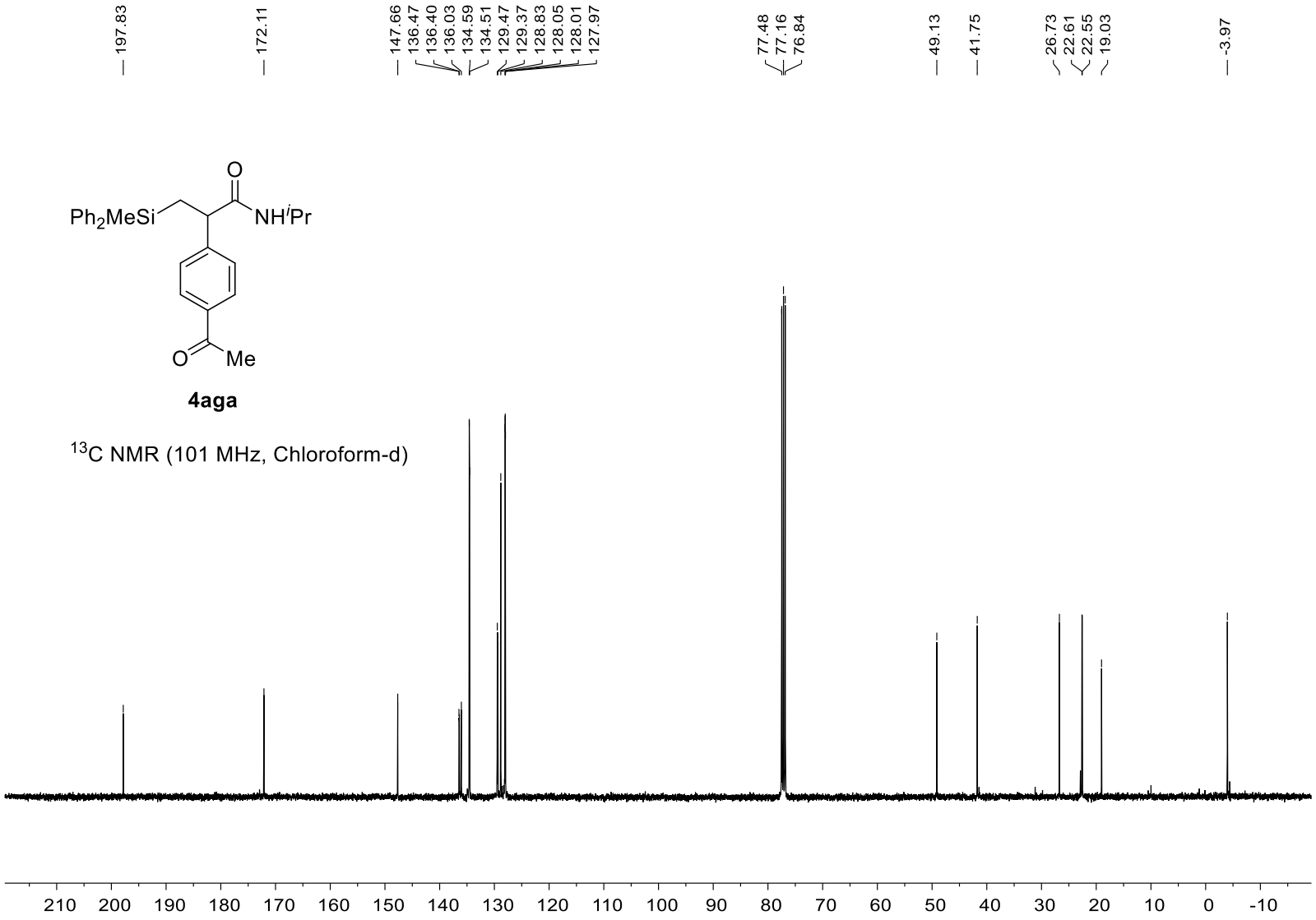
O
Ph2MeSi
NHiPr
O
Me
4aga
1H NMR (400 MHz, Chloroform-d)
2.06 4.22 8.23 0.95 1.00 1.00 3.02 1.12 0.99 3.02 3.04 2.93
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5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172.11
147.66
136.47
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134.59
134.51
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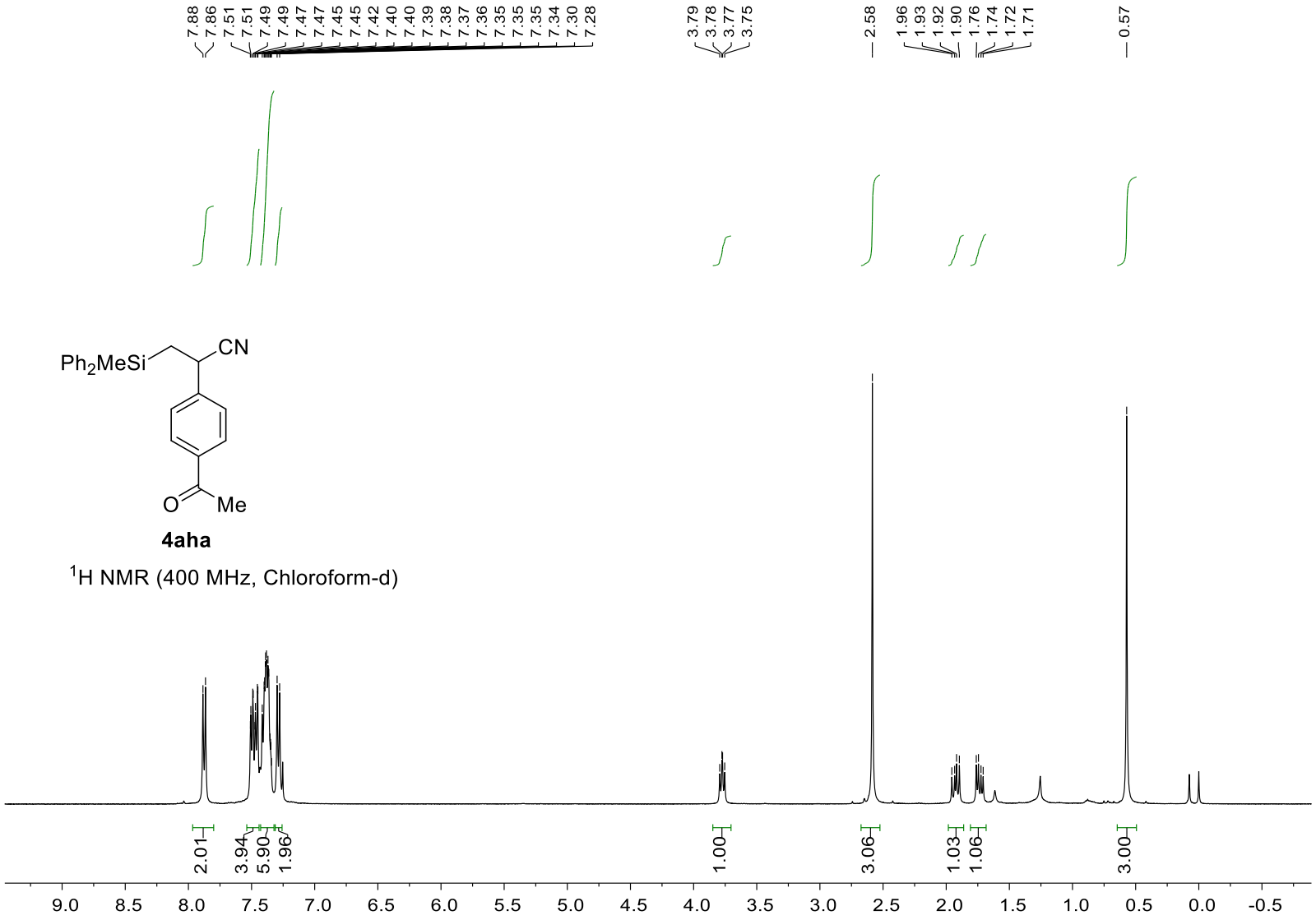
128.05
128.01
127.97
77.48
77.16
76.84
49.13
41.75
26.73
22.61
22.55
19.03
-3.97
Ph2MeSi
NHiPr
O
O
Me
4aga
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10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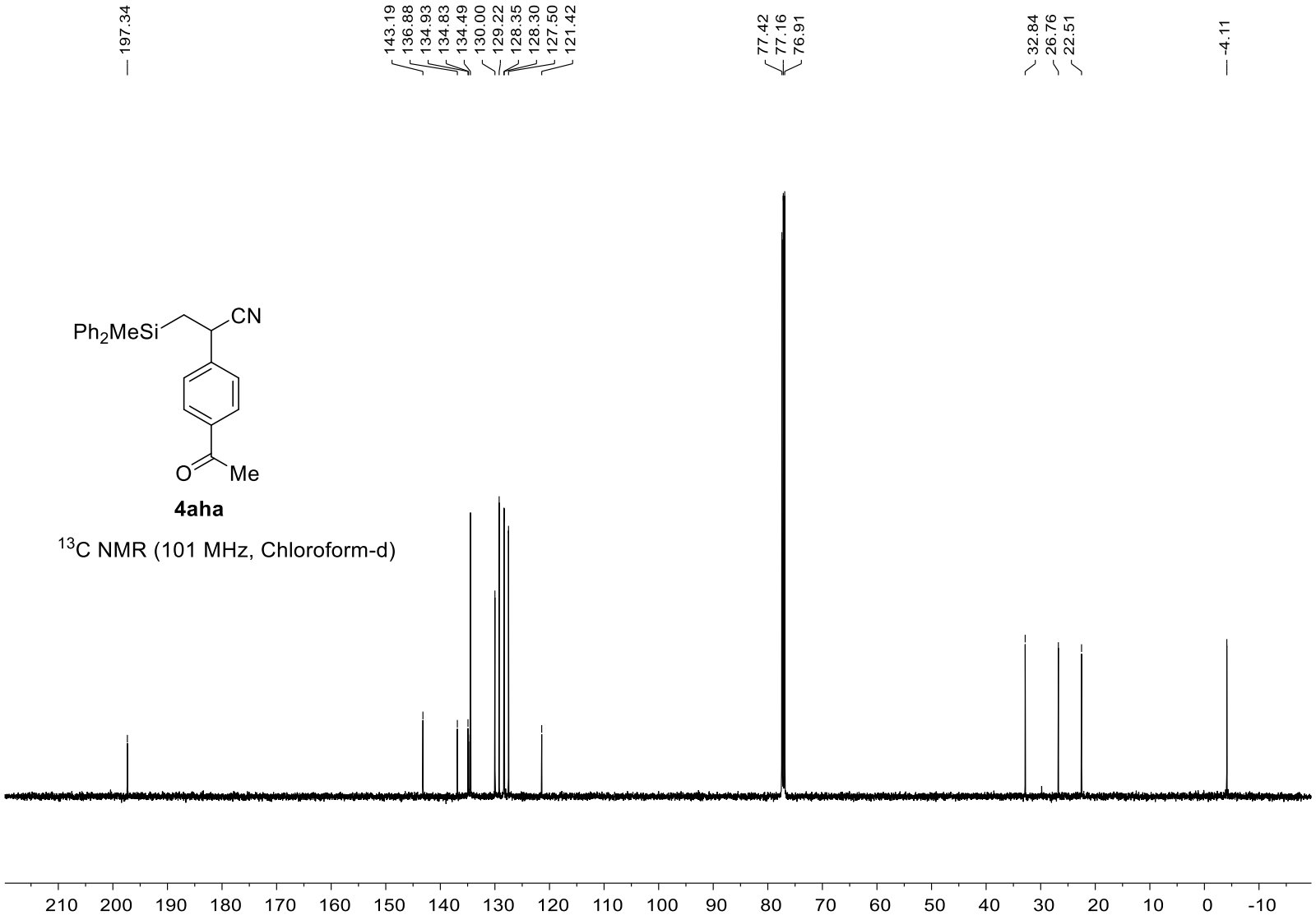
7.86
7.51
7.51
7.49
7.49
7.47
7.47
7.45
7.45
7.42
7.40
7.40
7.39
7.38
7.37
7.36
7.35
7.35
7.34
7.30
7.28
3.79
3.78
3.77
3.75
2.58
1.96
1.93
1.92
1.90
1.76
1.74
1.72
1.71
0.57
Ph2MeSi
CN
O
Me
4aha
1H NMR (400 MHz, Chloroform-d)
2.01
3.94
5.90
1.96
1.00
3.06
1.03
1.06
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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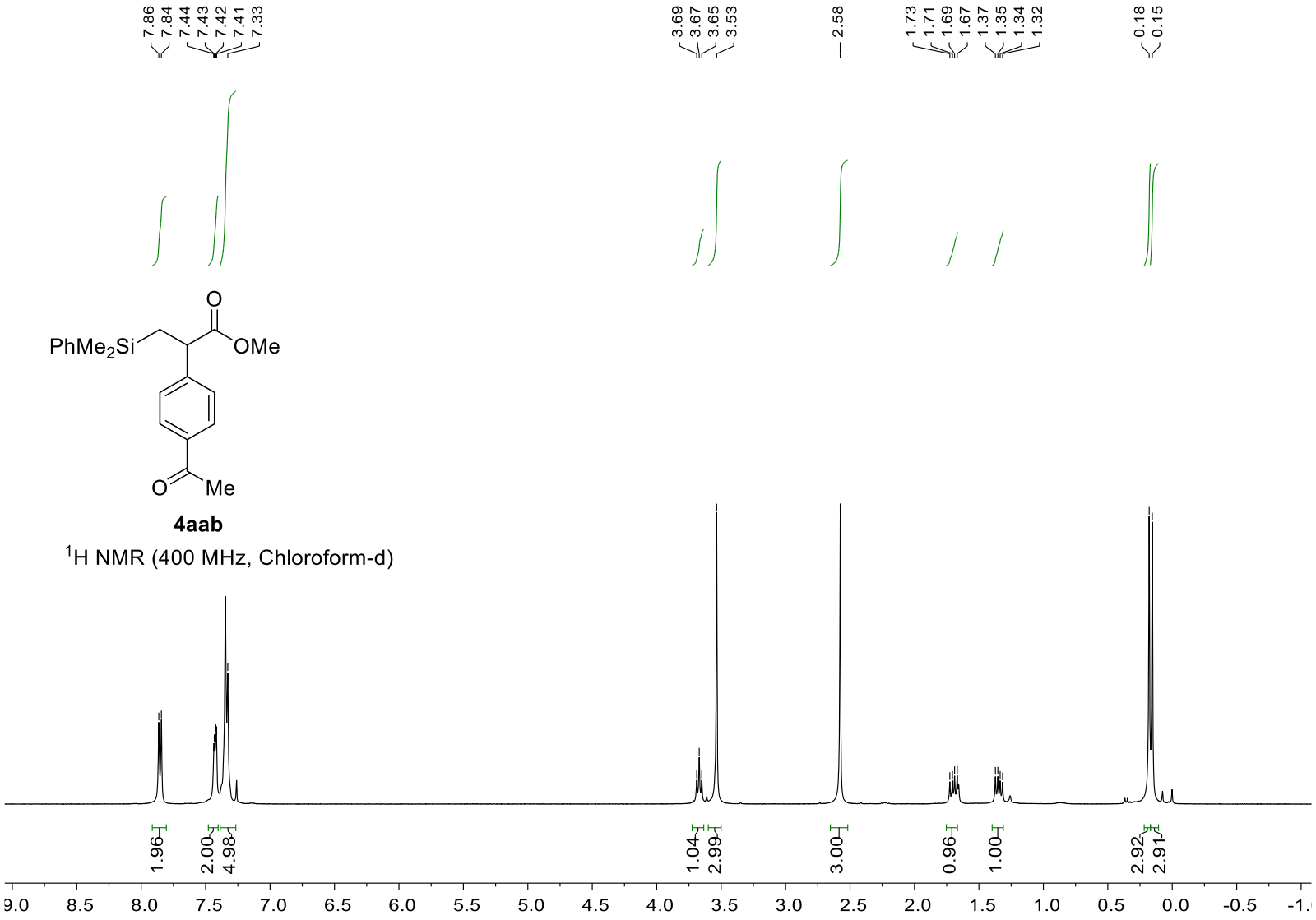
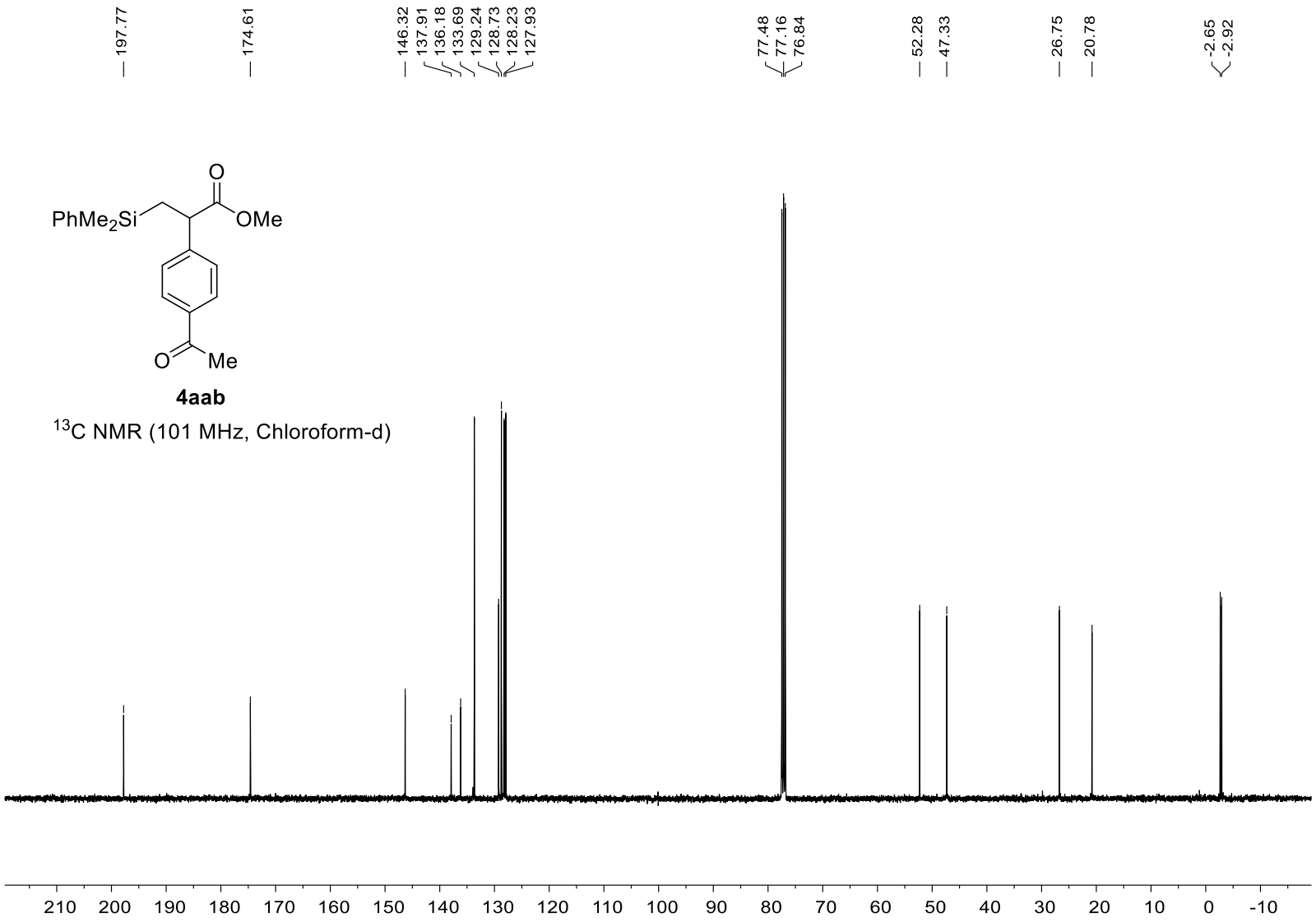
143.19
136.88
134.93
134.83
134.49
130.00
129.22
128.35
128.30
127.50
121.42
77.42
77.16
76.91
32.84
26.76
22.51
-4.11
Ph2MeSi
CN
O
Me
4aha
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



4aab

^{1}H NMR (400 MHz, Chloroform-d)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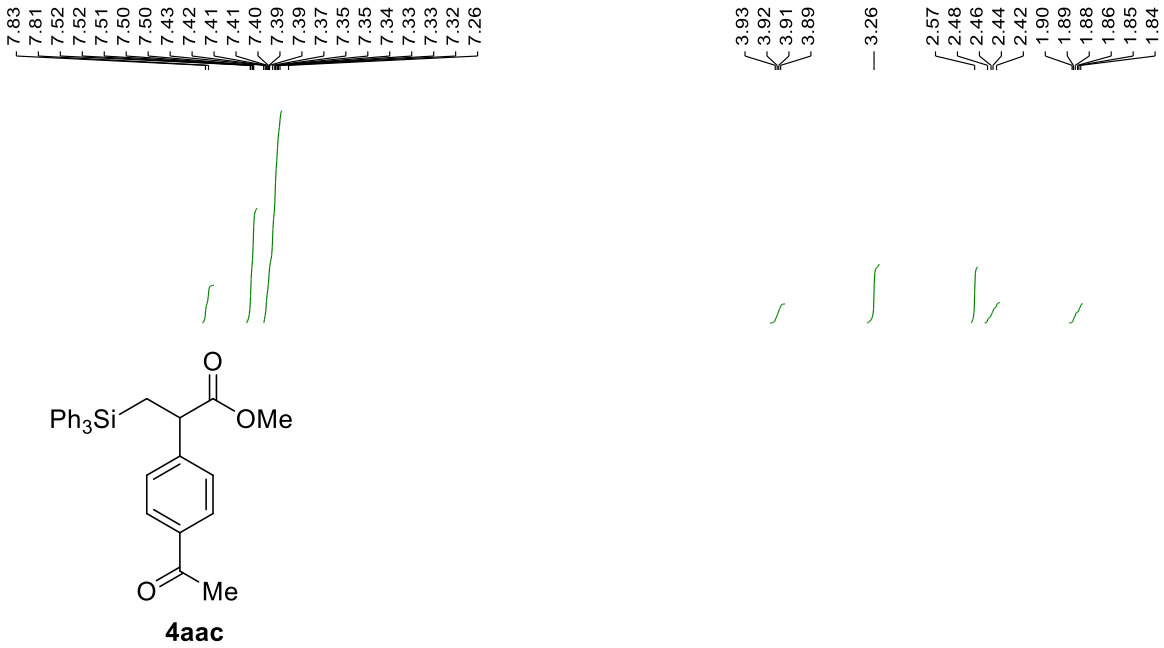
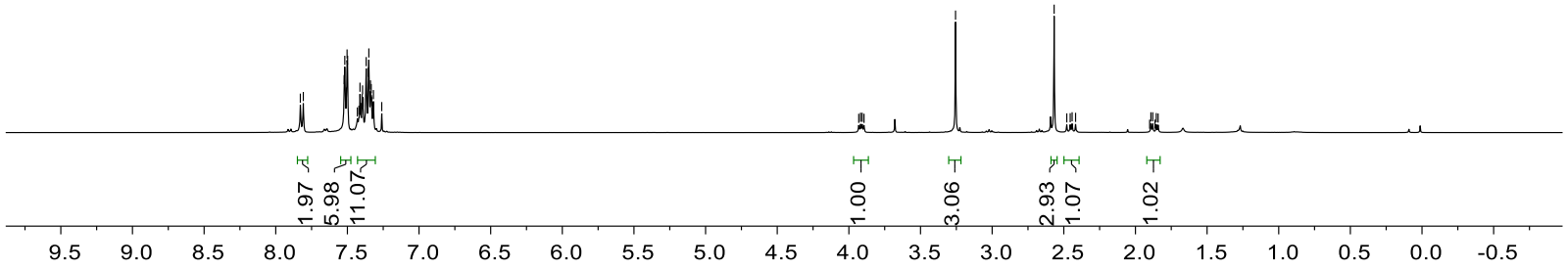
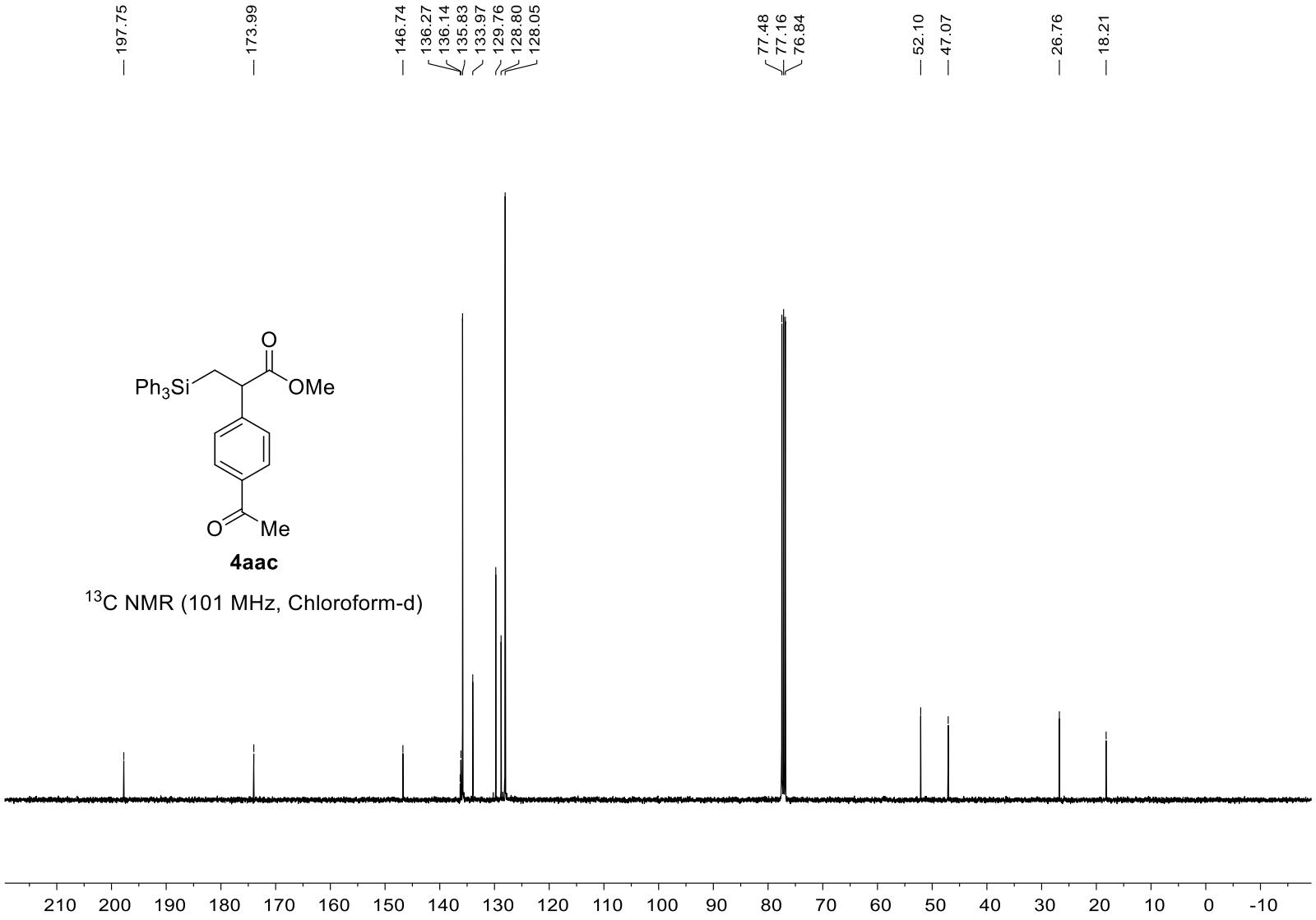
174.61
146.32
137.91
136.18
133.69
129.24
128.73
128.23
127.93
77.48
77.16
76.84
52.28
47.33
26.75
20.78
-2.65
-2.92
PhMe2Si
OMe
O
O
Me
4aab
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



4aac

^{1}H NMR (400 MHz, Chloroform-d)

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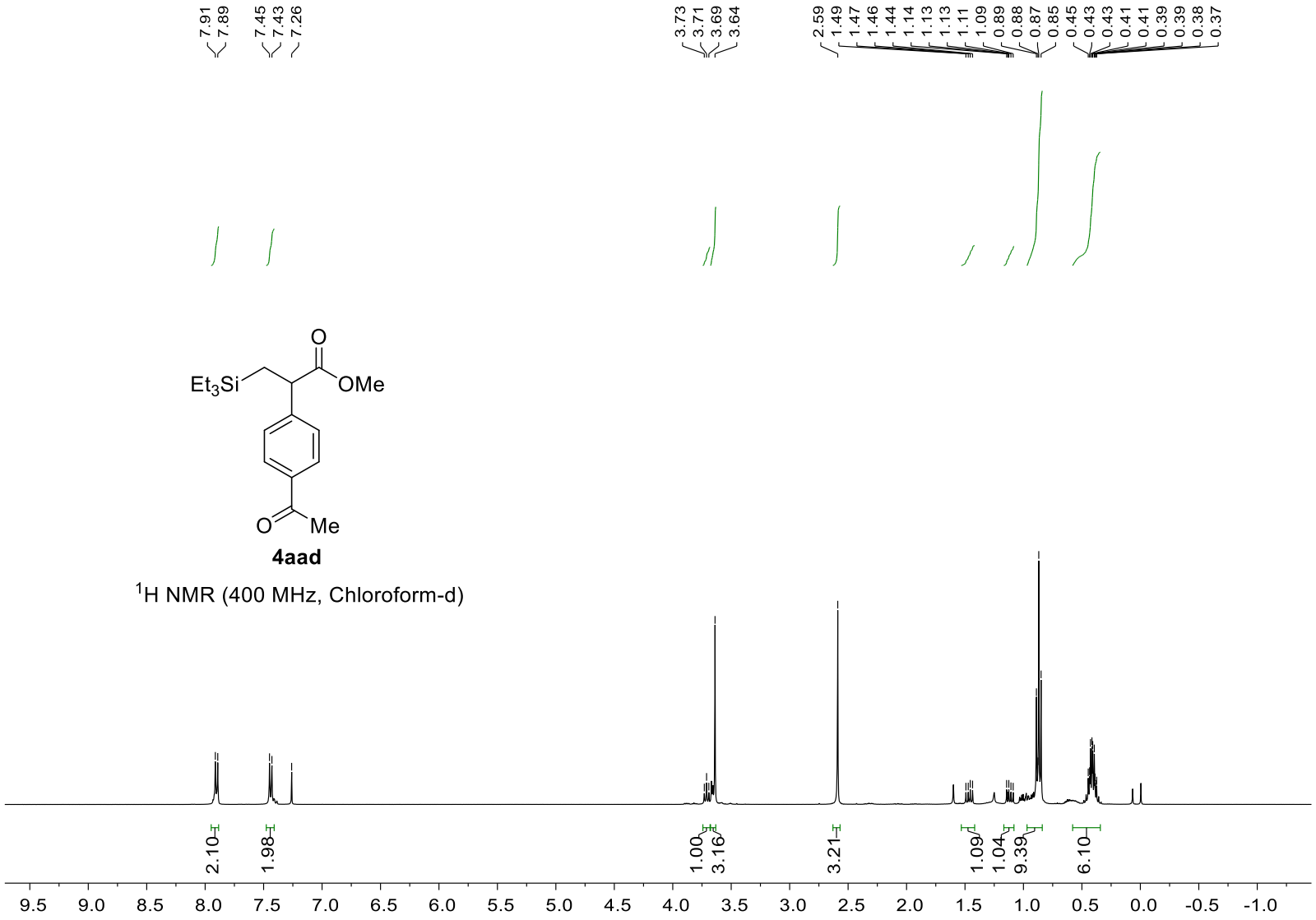
173.99
146.74
136.27
136.14
135.83
133.97
129.76
128.80
128.05
77.48
77.16
76.84
52.10
47.07
26.76
18.21
Ph3Si
O
OMe
O
Me
4aac
13C NMR (101 MHz, Chloroform-d)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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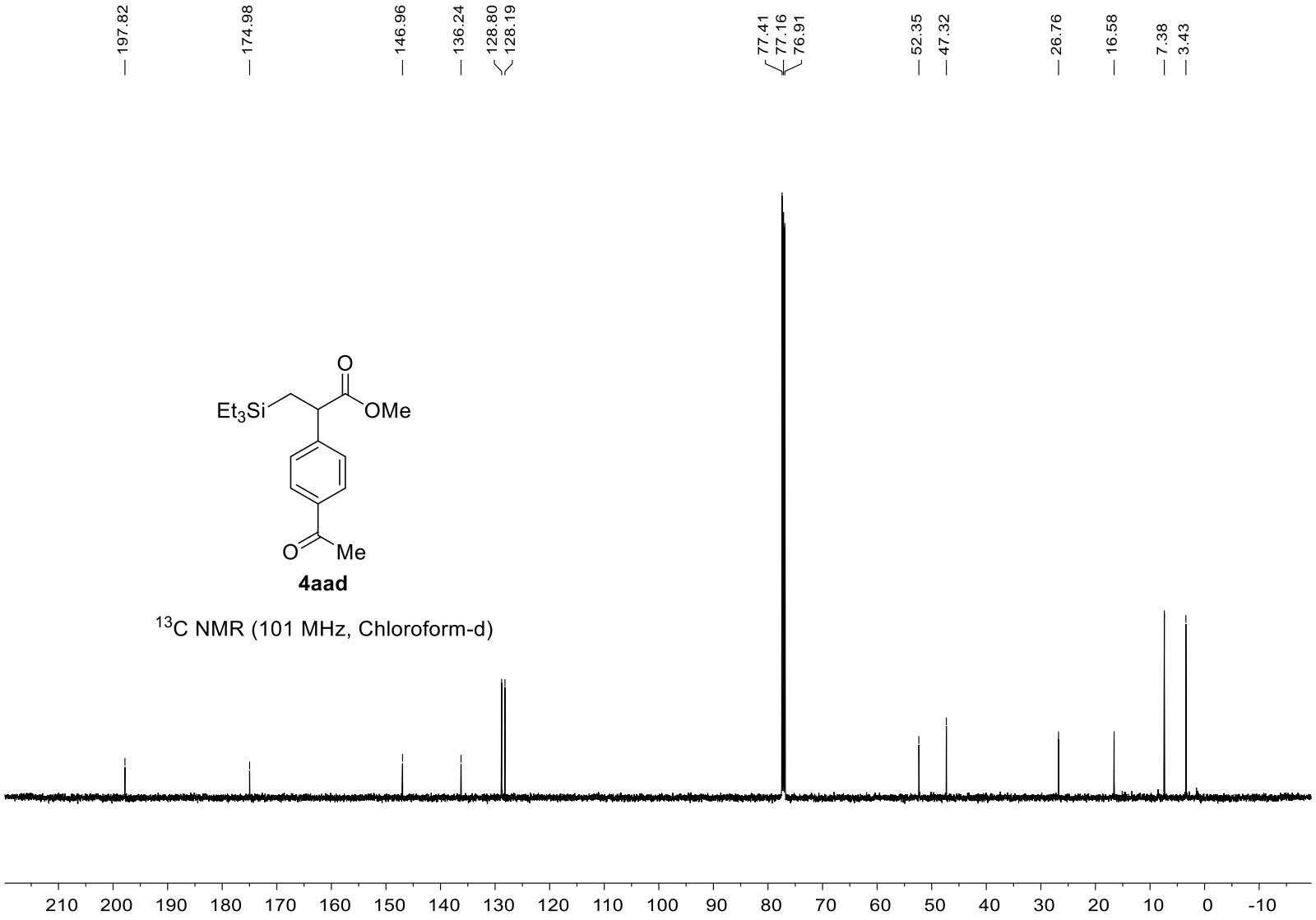
7.89
7.45
7.43
7.26
3.73
3.71
3.69
3.64
2.59
1.49
1.47
1.46
1.44
1.14
1.13
1.13
1.11
1.09
0.89
0.88
0.87
0.85
0.45
0.43
0.43
0.41
0.41
0.39
0.39
0.38
0.37
Et3Si
O
OMe
O
Me
4aad
1H NMR (400 MHz, Chloroform-d)
2.10
1.98
1.00
3.16
3.21
1.09
1.04
9.39
6.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0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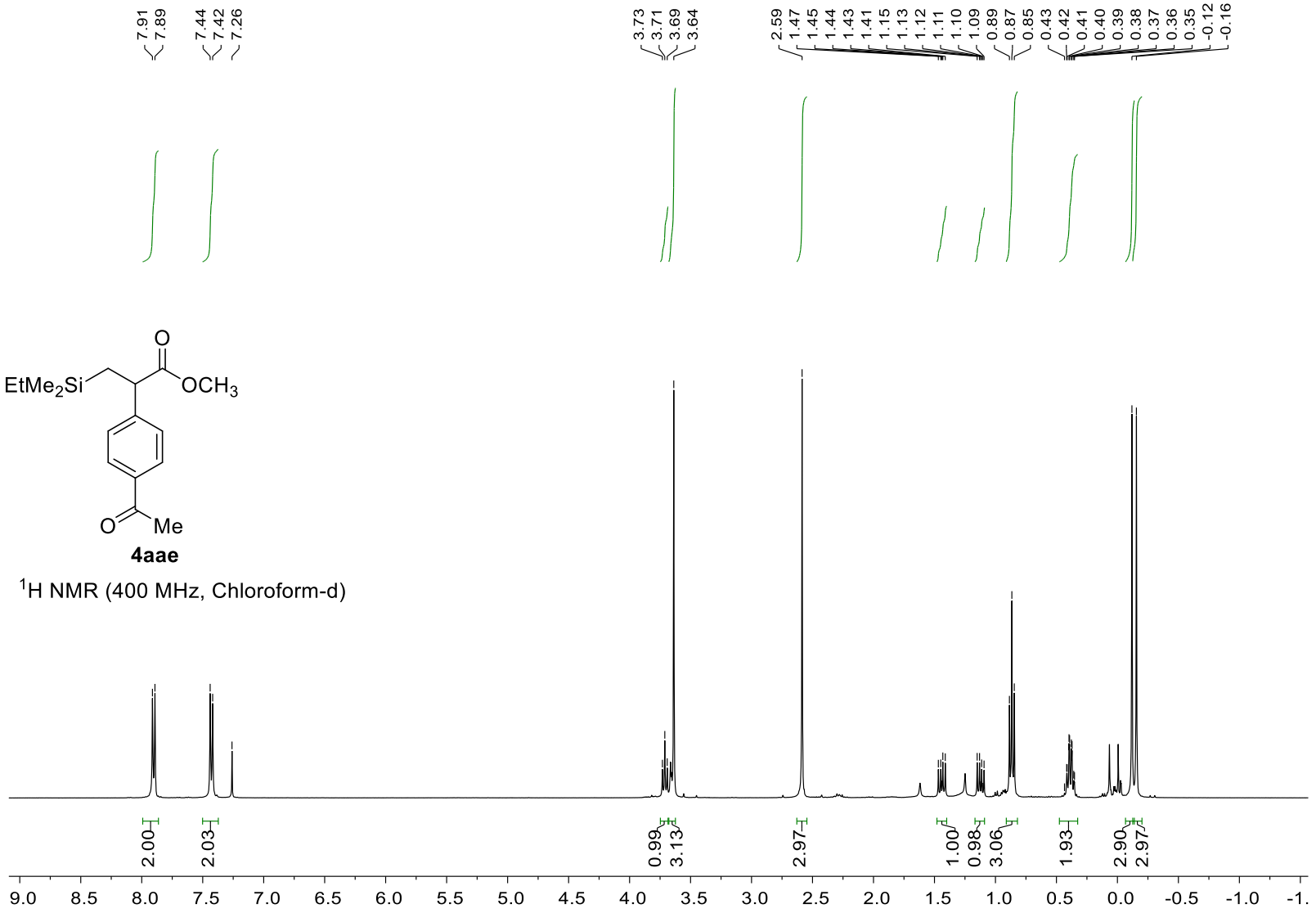
146.96
136.24
128.80
128.19
77.41
77.16
76.91
52.35
47.32
26.76
16.58
7.38
3.43
Et3Si
O
OMe
O
Me
4aad
13C NMR (101 MHz, Chloroform-d)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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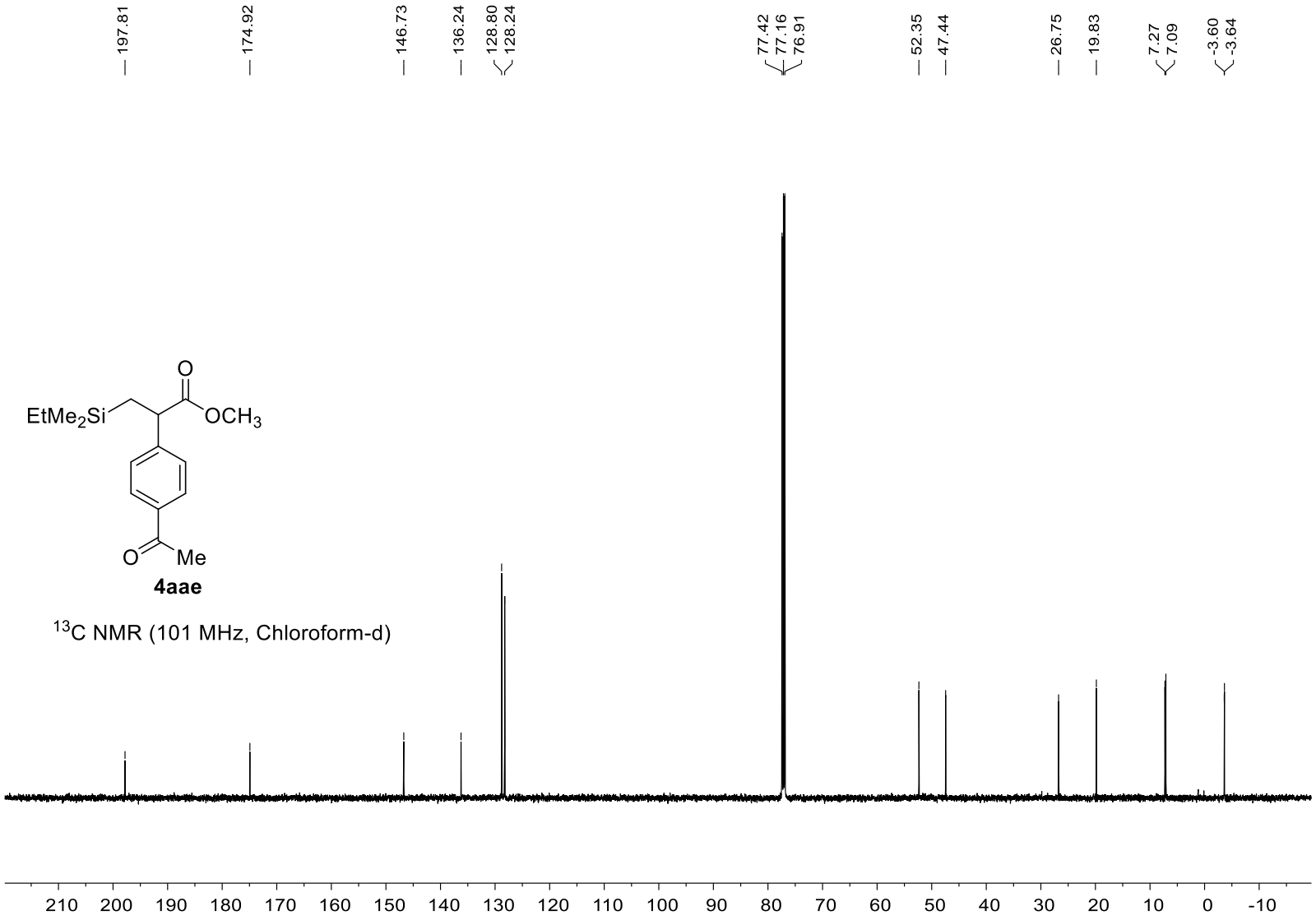
7.89
7.44
7.42
7.26
3.73
3.71
3.69
3.64
2.59
1.47
1.45
1.44
1.43
1.41
1.15
1.13
1.12
1.11
1.10
1.09
0.89
0.87
0.85
0.43
0.42
0.41
0.40
0.39
0.38
0.37
0.36
0.35
-0.12
-0.16
EtMe2Si
O
OCH3
O
Me
4aae
1H NMR (400 MHz, Chloroform-d)
2.00
2.03
0.99
3.13
2.97
1.00
0.98
3.06
1.93
2.90
2.97
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0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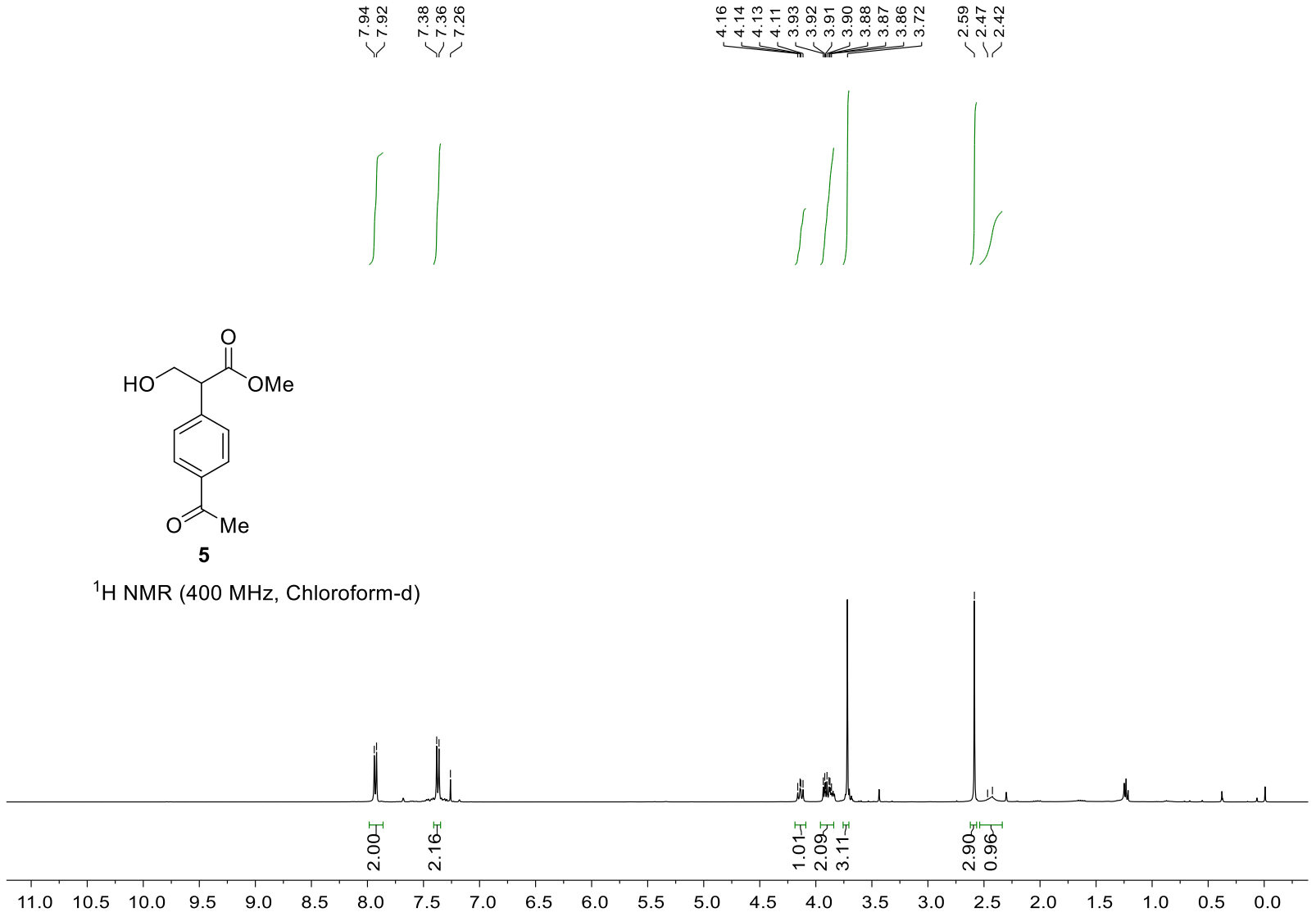
174.92
146.73
136.24
128.80
128.24
77.42
77.16
76.91
52.35
47.44
26.75
19.83
7.27
7.09
-3.60
-3.64
EtMe2Si
OCH3
O
O
Me
4aae
13C NMR (101 MHz, Chloroform-d)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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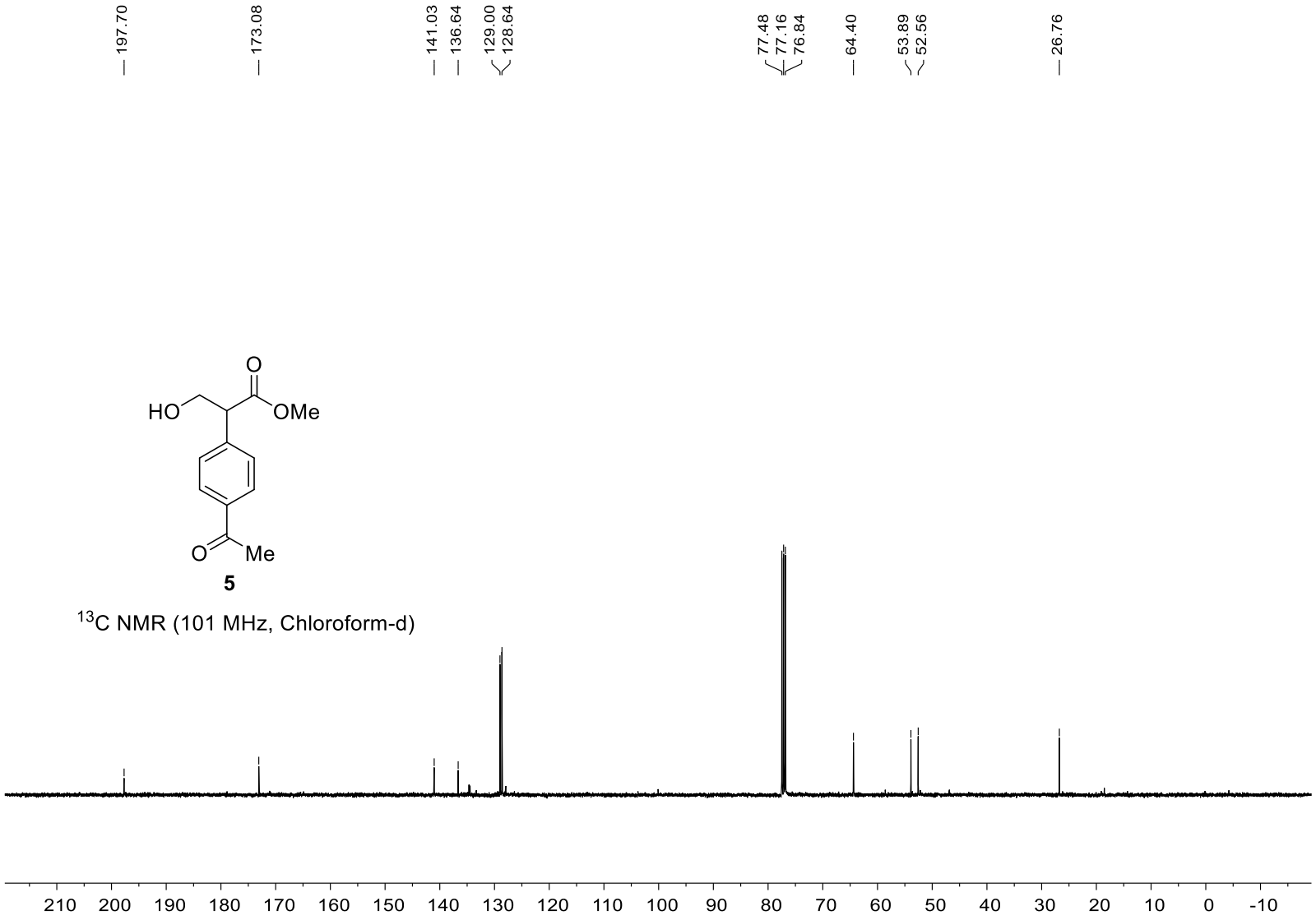
7.92
7.38
7.36
7.26
4.16
4.14
4.13
4.11
3.93
3.92
3.91
3.90
3.88
3.87
3.86
3.72
2.59
2.47
2.42
HO
O
OMe
O
Me
5
1H NMR (400 MHz, Chloroform-d)
2.00
2.16
1.01
2.09
3.11
2.90
0.96
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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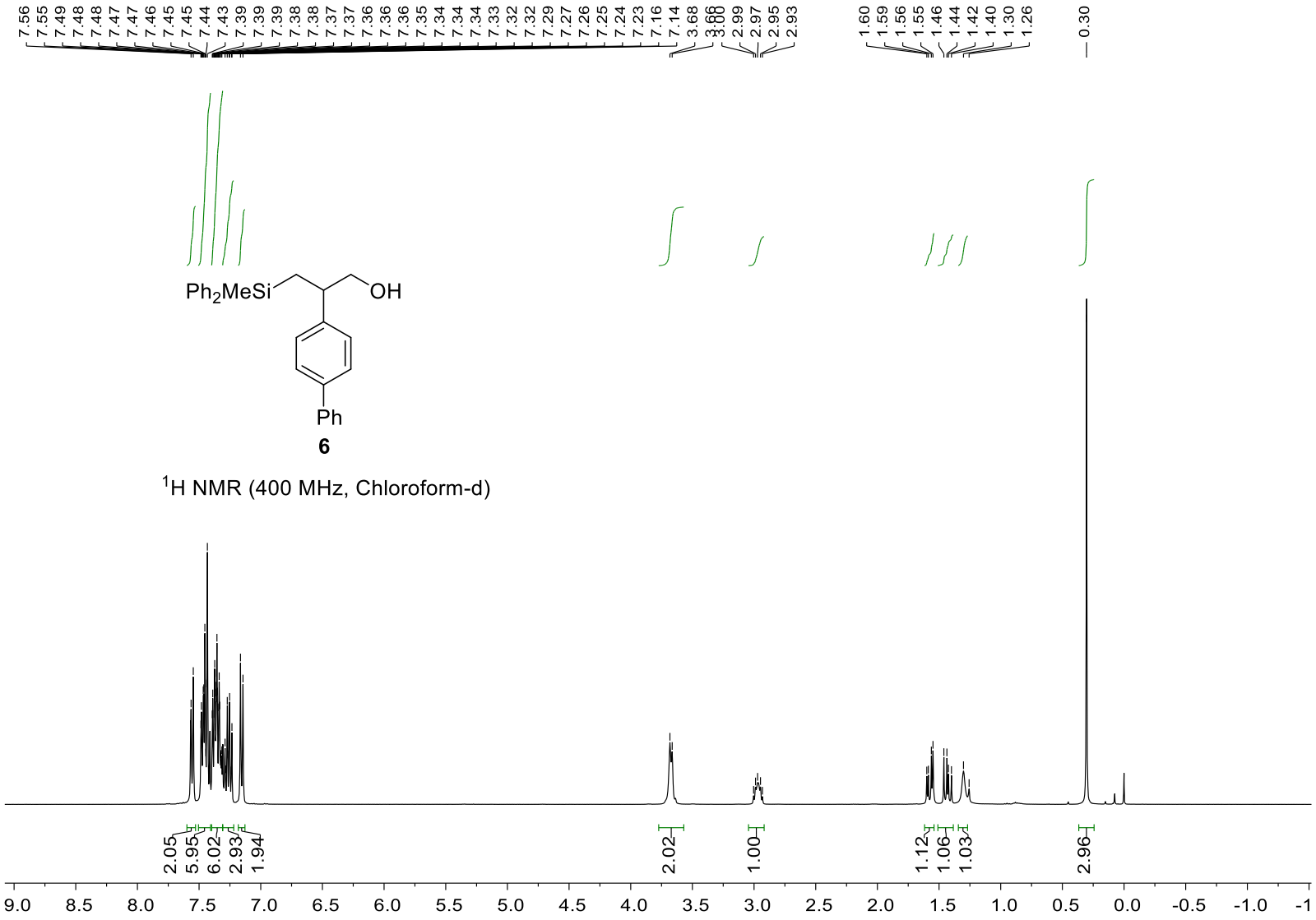
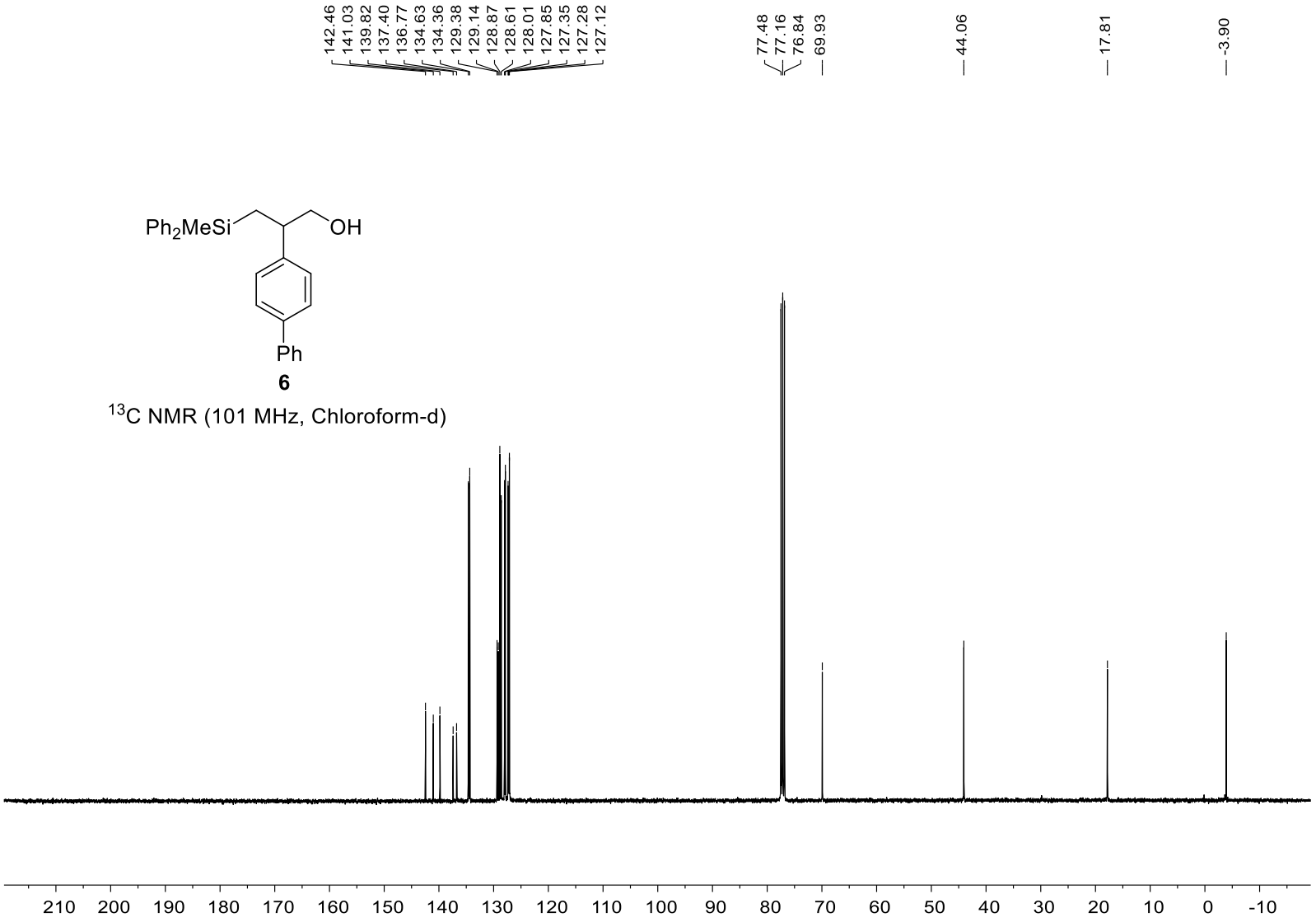
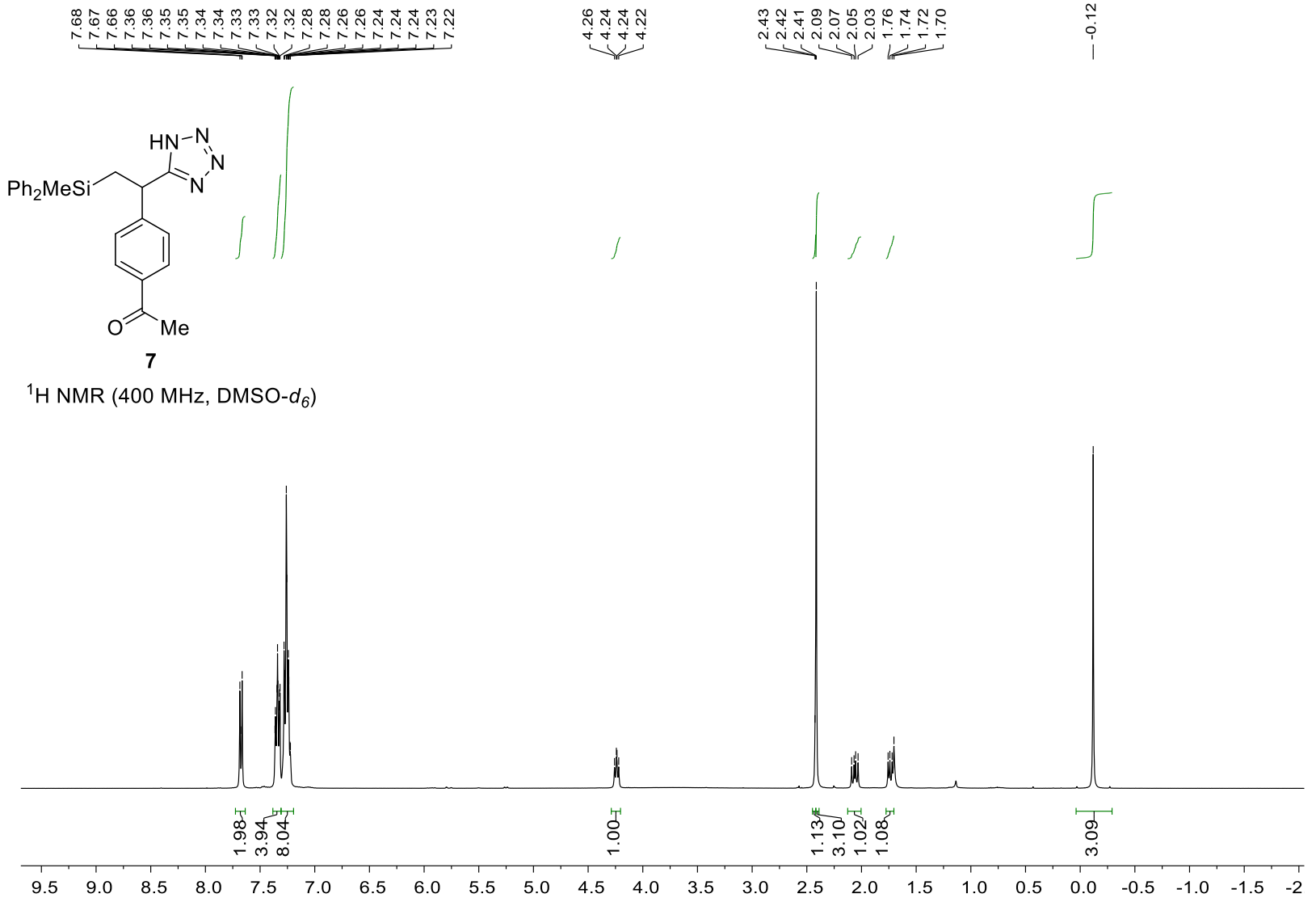
173.08
141.03
136.64
129.00
128.64
77.48
77.16
76.84
64.40
53.89
52.56
26.76
HO
OMe
O
O
Me
5
13C NMR (101 MHz, Chloroform-d)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

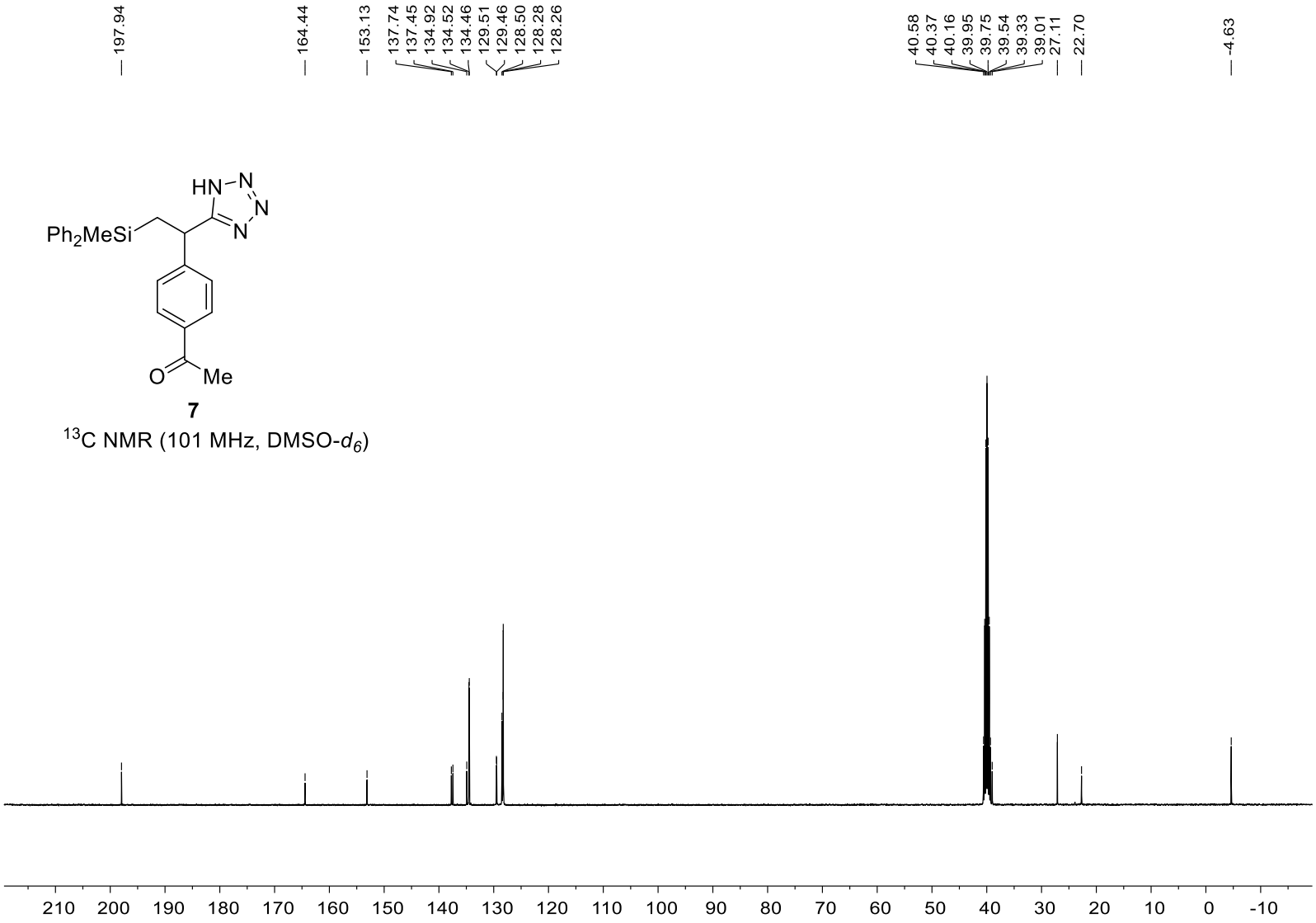

7.56 7.55 7.49 7.48 7.48 7.47 7.47 7.46 7.45 7.45 7.44 7.43 7.39 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.36 7.36 7.35 7.34 7.34 7.34 7.33 7.32 7.32 7.29 7.27 7.26 7.25 7.24 7.23 7.16 7.14 3.68 3.66 3.00 2.99 2.97 2.95 2.93
1.60 1.59 1.56 1.55 1.46 1.44 1.42 1.40 1.30 1.26
0.30
Ph2MeSi
OH
Ph
6
1H NMR (400 MHz, Chloroform-d)
2.05 5.95 6.02 2.93 1.94 2.02 1.00 1.12 1.06 1.03 2.96
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1


142.46
141.03
139.82
137.40
136.77
134.63
134.36
129.38
129.14
128.87
128.61
128.01
127.85
127.35
127.28
127.12
77.48
77.16
76.84
69.93
44.06
17.81
-3.90
Ph2MeSi
OH
Ph
6
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



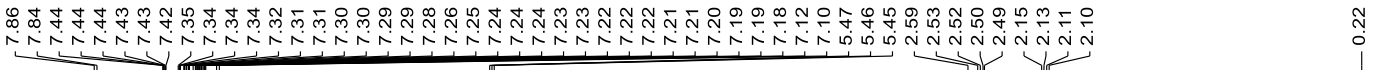
7

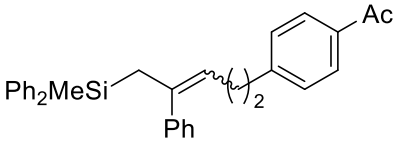
^{1}H NMR (400 MHz, DMSO-d_6)



7

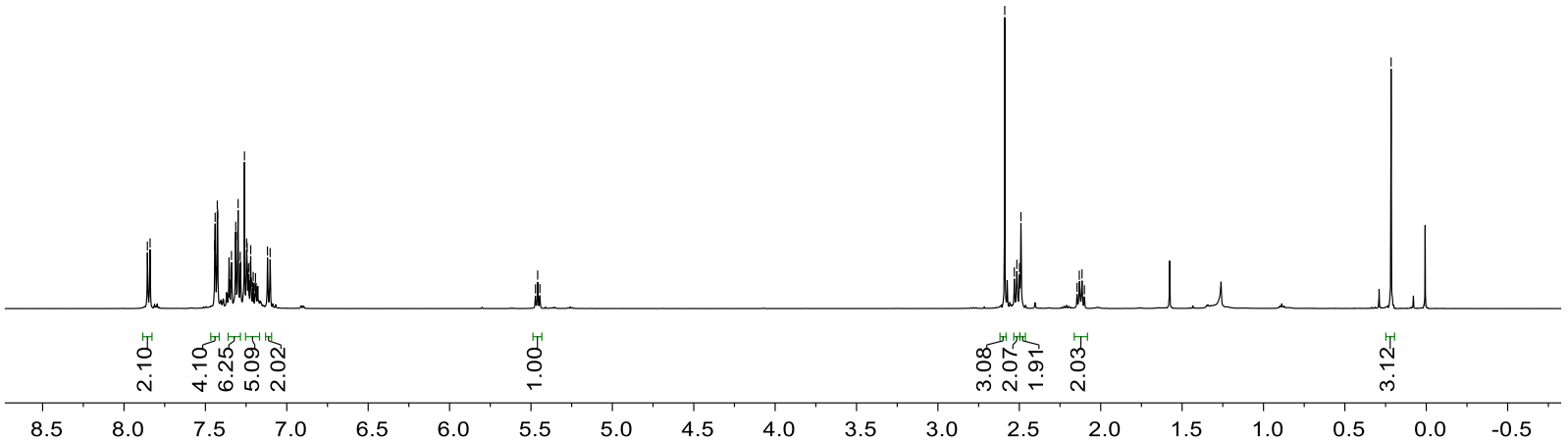
^{13}C NMR (101 MHz, DMSO-d_6)

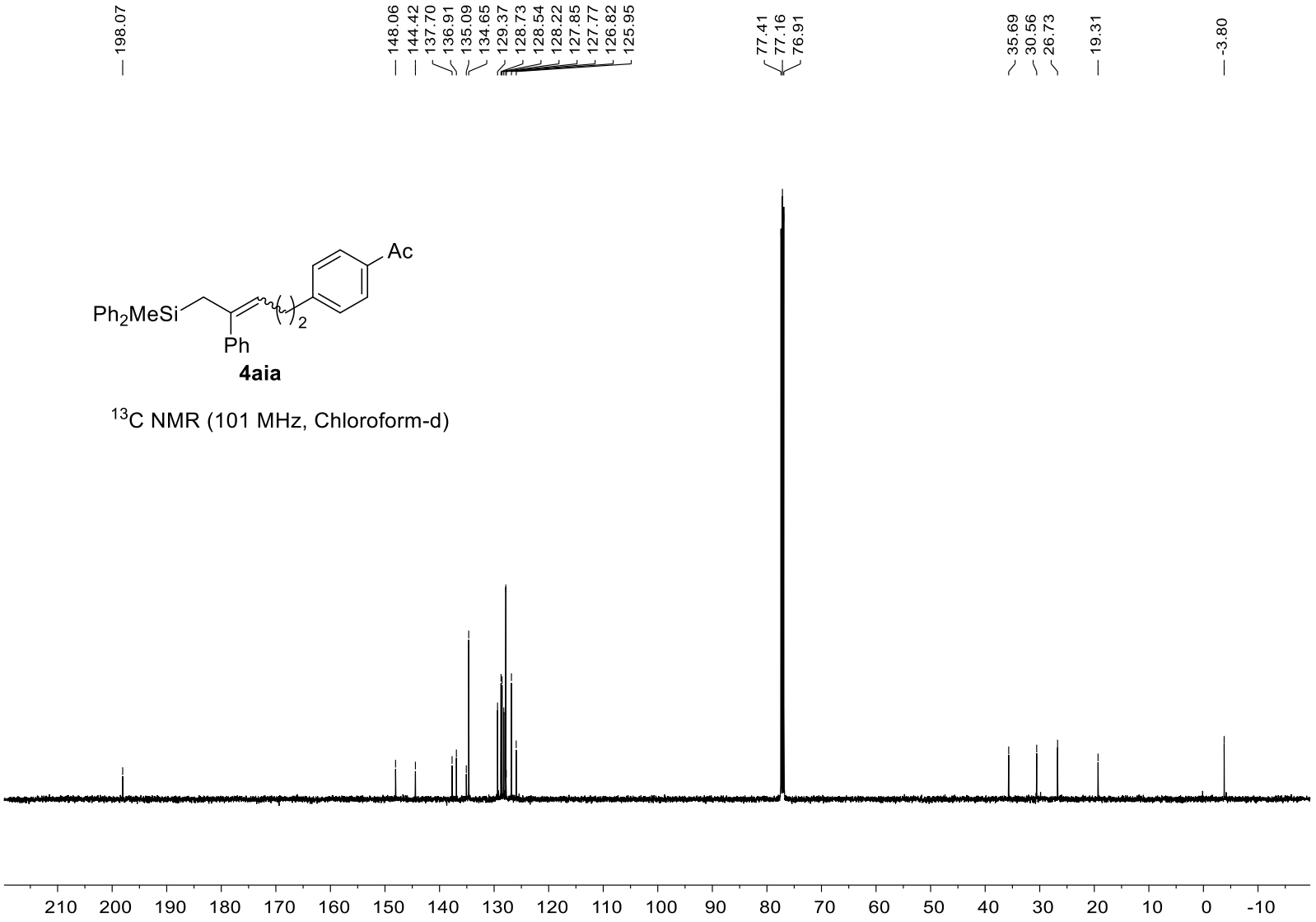




4aia

^{1}H NMR (400 MHz, Chloroform-d)

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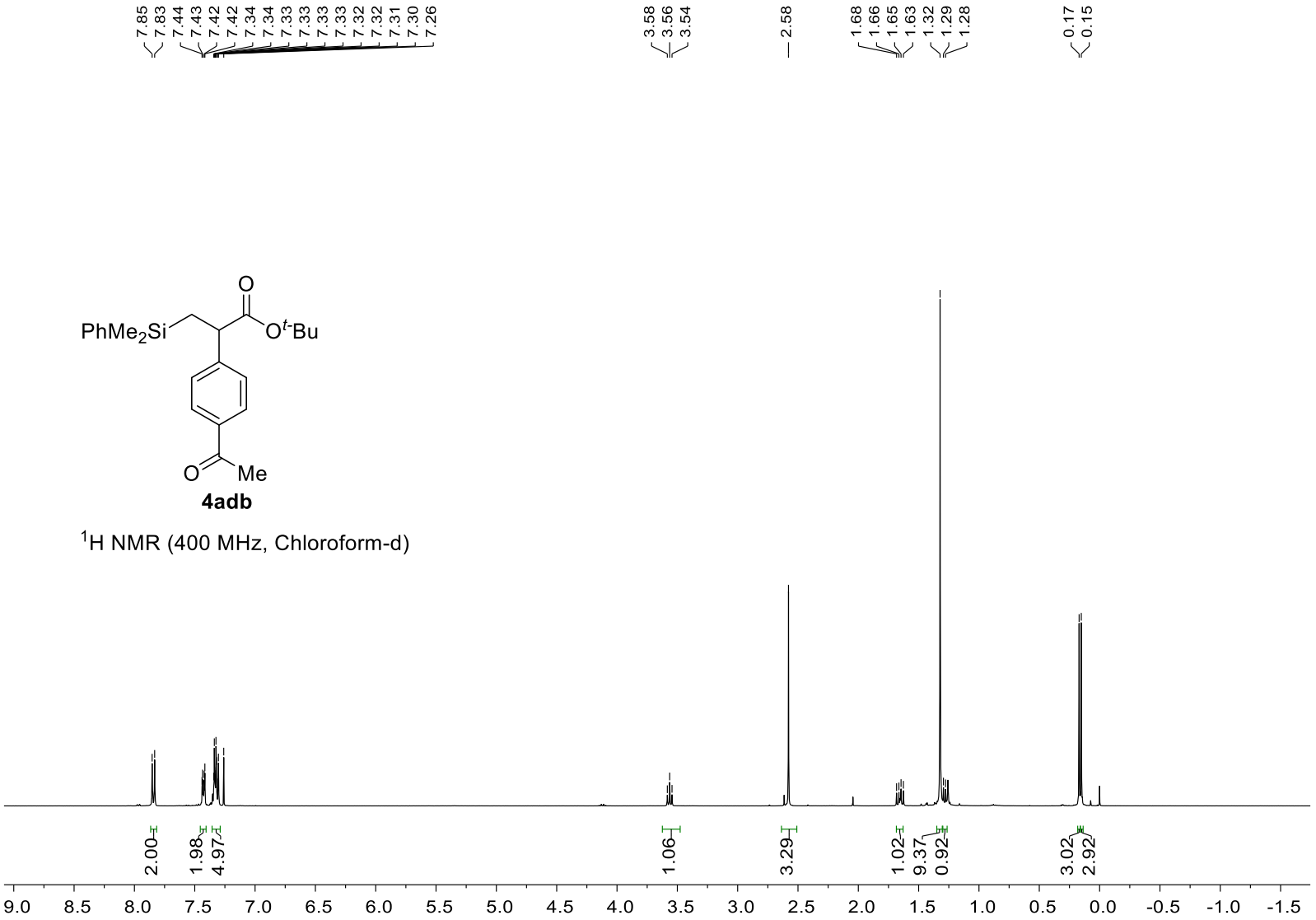
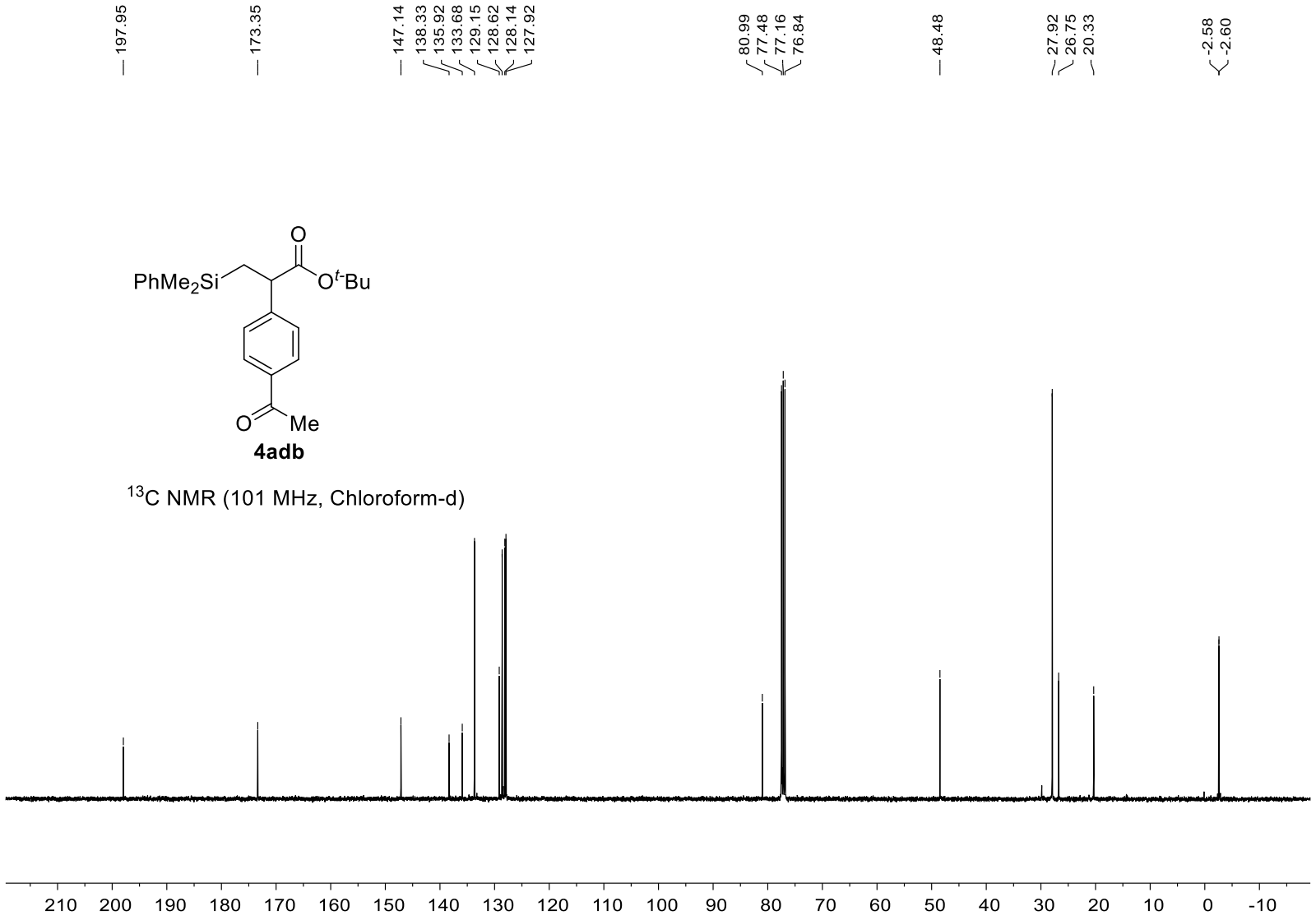
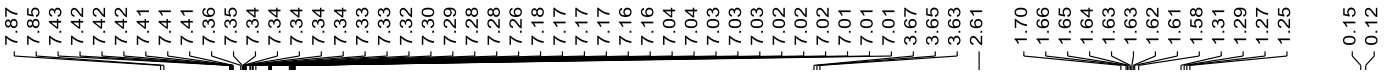
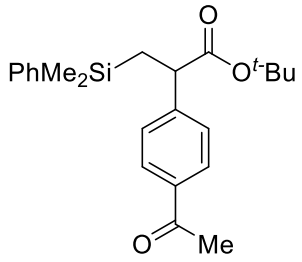
148.06
144.42
137.70
136.91
135.09
134.65
129.37
128.73
128.54
128.22
127.85
127.77
126.82
125.95
77.41
77.16
76.91
35.69
30.56
26.73
19.31
-3.80
Ac
Ph2MeSi
2
Ph
4aia
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


7.85
7.83
7.44
7.43
7.42
7.42
7.34
7.34
7.33
7.33
7.33
7.33
7.32
7.32
7.31
7.30
7.26
3.58
3.56
3.54
2.58
1.68
1.66
1.65
1.63
1.32
1.29
1.28
0.17
0.15
PhMe2Si
O
Ot-Bu
O
Me
4adb
1H NMR (400 MHz, Chloroform-d)
2.00
1.98
4.97
1.06
3.29
1.02
9.37
0.92
3.02
2.92
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5

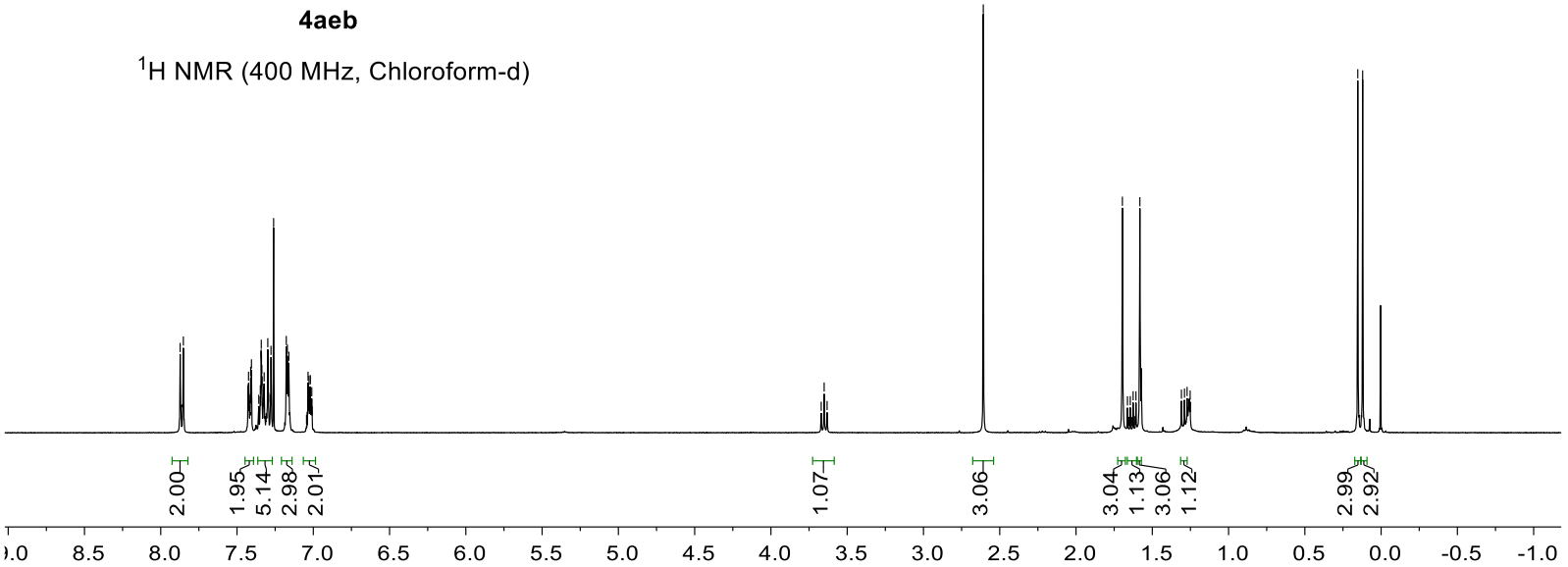

197.95
173.35
147.14
138.33
135.92
133.68
129.15
128.62
128.14
127.92
80.99
77.48
77.16
76.84
48.48
27.92
26.75
20.33
-2.58
-2.60
PhMe2Si
O
Ot-Bu
O
Me
4adb
13C NMR (101 MHz, Chloroform-d)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

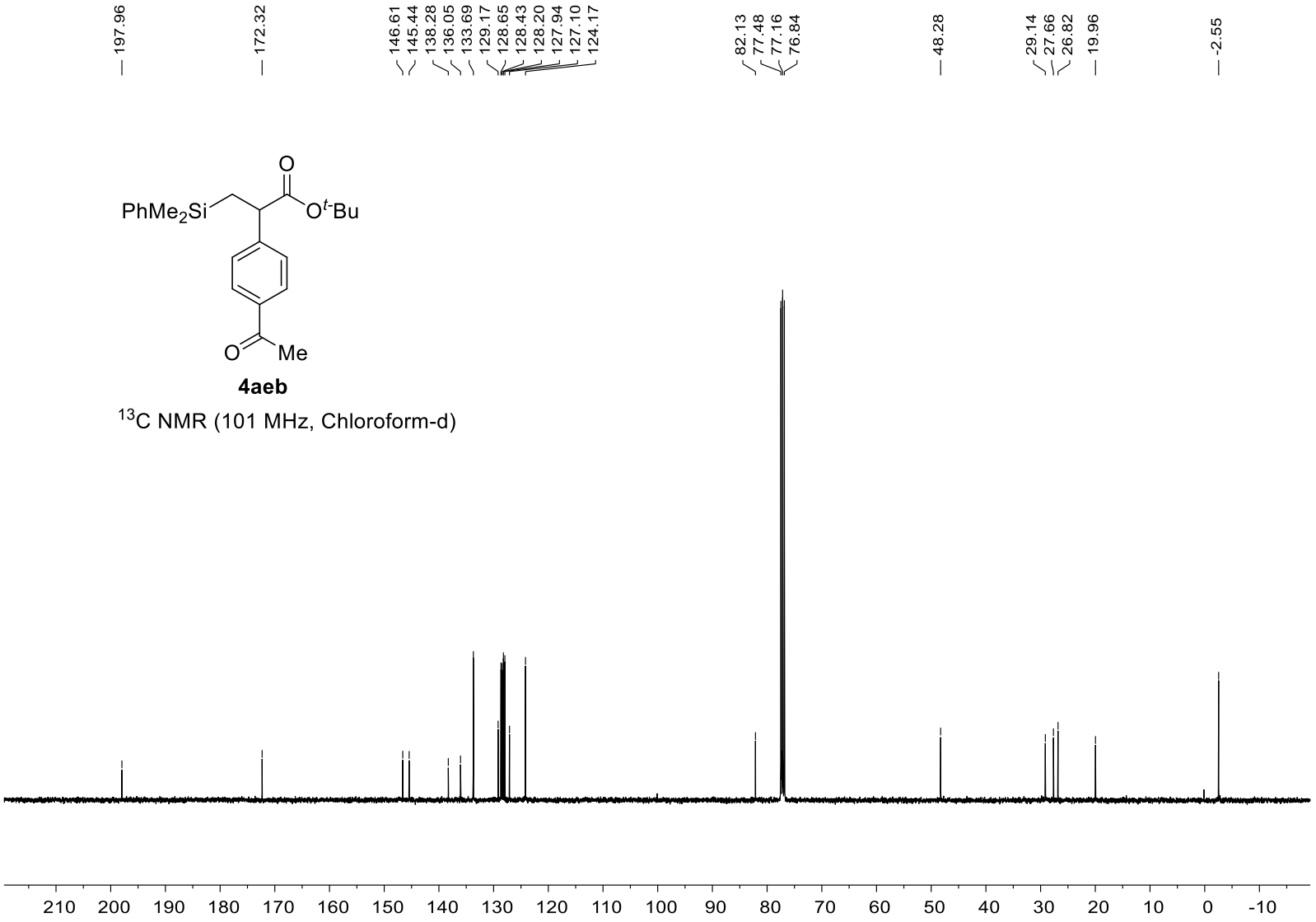


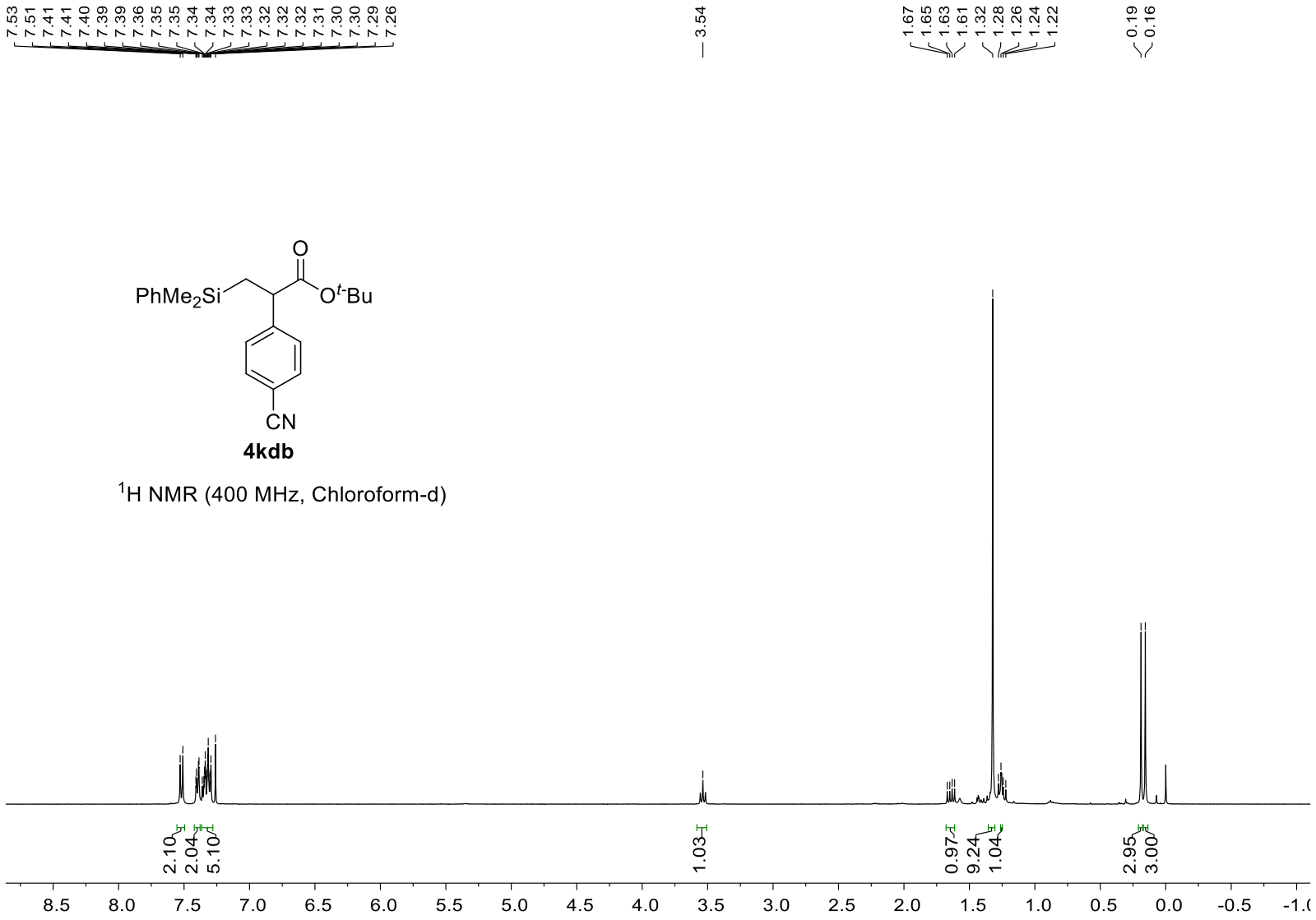


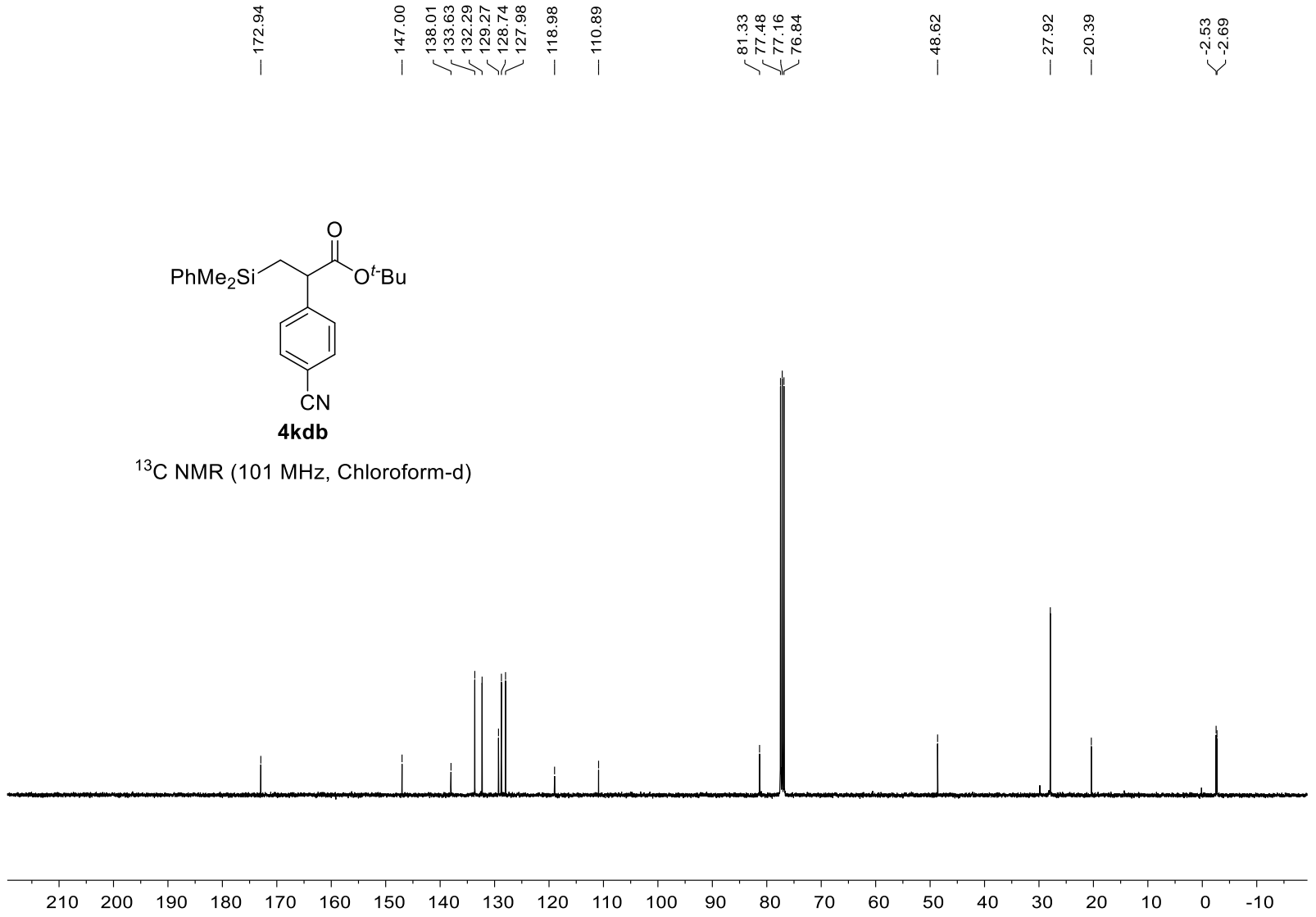
4aeb

^{1}H NMR (400 MHz, Chloroform-d)




197.96
172.32
146.61
145.44
138.28
136.05
133.69
129.17
128.65
128.43
128.20
127.94
127.10
124.17
82.13
77.48
77.16
76.84
48.28
29.14
27.66
26.82
19.96
-2.55
PhMe2Si
O
O
tBu
O
Me
4aeb
13C NMR (101 MHz, Chloroform-d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


7.53
7.51
7.41
7.41
7.40
7.39
7.39
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.32
7.31
7.30
7.30
7.29
7.26
3.54
1.67
1.65
1.63
1.61
1.32
1.28
1.26
1.24
1.22
0.19
0.16
PhMe2Si
O
Ot-Bu
CN
4kdb
1H NMR (400 MHz, Chloroform-d)
2.10
2.04
5.10
1.03
0.97
9.24
1.04
2.95
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


172.94
147.00
138.01
133.63
132.29
129.27
128.74
127.98
118.98
110.89
81.33
77.48
77.16
76.84
48.62
27.92
20.39
-2.53
-2.69
O
PhMe2Si
Ot-Bu
CN
4kdb
13C NMR (101 MHz, Chloroform-d)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10