Diastereoselective Oxidative α-Amination of Aliphatic Aldehyde Catalyzed by Iodine: Synthesis of *Syn*-γ-Hydroxy-α-Amino Acetals

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Supplementary Material

Supporting Information

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General Method

All reactions were carried out without exclusion of air or moisture unless otherwise stated. Copper salts and Indium salts. Commercial solvents and reagents were used without further purification. Allγ-protected hydroxyl aldehydes were synthesized as following description.

Reactions were monitored by thin layer chromatography [Merck 60 F_{254} precoated silica gel plate (0.2 mm thickness)]. Subsequent to elution, spots were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible using iodine vapor absorption as yellow stain. Flash chromatography was performed using Merck silica gel 60 with AR grade solvents.

Infrared spectra were recorded on a Shimadzu IR Prestige-21 FTIR. Liquid samples were examined as film between NaCl salt plates. HRMS spectra were recorded on a Waters Q–Tof Permier Spectrometer.

^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker Avance 400 MHz spectrometers ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.260, singlet). Multiplicities were given as: s (singlet); brs (broad singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); td (triplet of doublet); m (multiplets) and etc. Coupling constants are reported as a *J* value in Hz. ^{13}C NMR are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.00, triplet).

Mass spectral analyses were carried out on a VG 7035 micromass mass spectrophotometer at a source temperature of 200 ℃ and at an ion current of 70 eV. Mass spectral data were reported in units of mass to charge (m/z) and % intensity.

Preparation of Substrates

1. Allylation of Aldehydes

General Procedure for Aldehyde Allylation Reactions

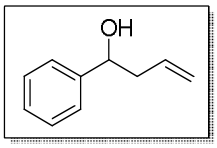
Representative procedure for allylation of aldehydes:

Preparation of 1-phenylhex-5-en-3-ol

3-Phenylpropanal (3.22 g, 24 mmol) and 3-bromoprop-1-ene (3.48 g, 29 mmol) in THF (30 mL) were added to zinc powder (3.14 g, 48 mmol) in saturated NH_4Cl solution (60 mL) at room temperature. The resulting mixture was stirred for one hour, diluted with water, extracted with dichloromethane (3 x 50 mL), washed with brine, dried over Na_2SO_4. Concentration of the organic phases *in vacuo* gave the crude reaction mixture which was purified *via* silica gel chromatography to afford the homoallylic alcohol as colorless oil (80% yield).[1]

Characterization of homoallylic alcohols:

1-Phenylbut-3-en-1-ol



Colorless oil (92% yield); R_f = 0.39 (3:1 hexane/ethyl acetate)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.36 (m, 5H), 5.76-5.86 (m, 1H), 5.13-5.18 (m, 2H), 4.73

[1] A. Durant, J. L. Delplancke, V. Libert and J. Reisse, *Eur. J. Org. Chem.* 1999, 2845.

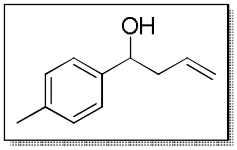
(dd, J_1 = 7.6, J_2 =5.6, 1H), 2.47-2.55 (m, 2H), 2.08 (brs., 1H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 134.4, 128.2, 127.4, 125.7, 118.0, 73.2, 43.6

FTIR (neat): 3404, 3062, 1641, 1492, 1265cm^{-1}

HRMS Calcd. for $C_{10}H_{13}O$ [M+H$^+$]: 149.0966. Found: 149.0969

1-(*p*-Tolyl)but-3-en-1-ol



Colorless oil (93% yield); R_f = 0.40 (3:1 hexane/ethyl acetate)

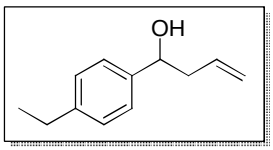
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.0, 2H), 7.15 (d, *J* = 8.0, 2H), 5.75-5.86 (m, 1H), 5.12-5.18 (m, 2H), 4.70 (brs., 1H), 2.48-2.52 (m, 2H), 2.34 (s, 3H), 1.99 (brs., 1H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0, 137.2, 134.6, 129.1, 125.8, 118.1, 73.2, 43.8, 21.1

FTIR (neat): 3447, 3050, 1265 cm^{-1}

HRMS Calcd. for $C_{11}H_{15}O$ [M+H$^+$]: 163.1123. Found: 163.1119

1-(4-Ethylphenyl)but-3-en-1-ol



Colorless oil (91% yield); R_f = 0.42 (3:1 hexane/ethyl acetate)

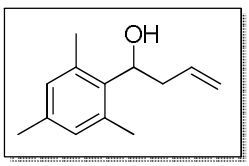
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.0, 2H), 7.18 (d, *J* = 8.0, 2H), 5.76-5.87 (m, 1H), 5.12-5.18 (m, 2H), 4.69-4.73 (m, 1H), 2.64 (q, *J* = 7.6, 2H), 2.45-2.56 (m, 2H), 1.98 (d, *J* = 3.2, 1H), 1.23 (t, *J* = 7.6, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 141.2, 134.6, 127.8, 125.8, 118.1, 73.2, 43.6, 28.5, 15.5

FTIR (neat): 3443, 3053, 1265 cm^{-1}

HRMS Calcd. for $C_{12}H_{17}O$ [M+H$^+$]: 177.1279. Found: 177.1270

1-Mesitylbut-3-en-1-ol



Colorless oil (92% yield); R_f = 0.43 (3:1 hexane/ethyl acetate)

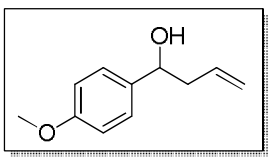
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 (s, 2H), 5.78-5.89 (m, 1H), 5.10-5.19 (m, 3H), 2.66-2.74 (m, 1H), 2.46-2.50 (m, 1H), 2.40 (s, 6H), 2.24 (s, 3H), 1.86 (brs., 1H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.6, 136.0, 135.9, 135.3, 130.1, 117.7, 70.7, 40.3, 20.73, 20.7

FTIR (neat): 3416 cm^{-1}

HRMS Calcd. for $C_{13}H_{19}O$ [M+H$^+$]: 191.1436. Found: 191.1440

1-(4-Methoxyphenyl)but-3-en-1-ol



Colorless oil (93% yield); R_f = 0.42 (3:1 hexane/ethyl acetate)

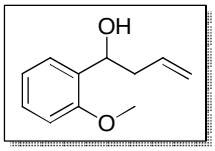
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.4, 2H), 6.88 (d, *J* = 8.8, 2H), 5.75-5.85 (m, 1H), 5.11-5.17 (m, 2H), 4.68 (td, J_1 = 6.4, J_2 = 3.2, 1H), 3.80 (s, 3H), 2.50 (t, *J* = 6.8, 1H), 1.99 (d, *J* = 2.4, 1H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 136.0, 134.5, 126.9, 117.6, 113.5, 72.8, 55.0, 43.4

FTIR (neat): 3446, 3074 cm^{-1}

HRMS Calcd. for $C_{11}H_{15}O_2$ [M+H$^+$]: 179.1072. Found: 179.1074

1-(2-Methoxyphenyl)but-3-en-1-ol



Colorless oil (90% yield); R_f = 0.40 (3:1 hexane/ethyl acetate)

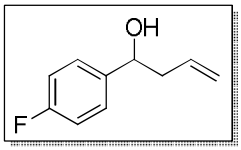
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.6, 1H), 7.23-7.27 (m, 1H), 6.94-6.98 (m, 1H), 6.88 (d, *J* = 8.4, 1H), 5.80-5.90 (m, 1H), 5.09-5.16 (m, 2H), 4.93-4.98 (m, 1H), 3.85 (s, 3H), 2.47-2.63 (m, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3, 135.2, 131.8, 128.2, 126.7, 120.6, 117.4, 110.4, 69.4, 55.2, 41.8

FTIR (neat): 3447, 3053, 1265 cm^{-1}

HRMS Calcd. for $C_{11}H_{15}O_2$ [M+Na$^+$]: 201.0891. Found: 201.0906

1-(4-Fluorophenyl)but-3-en-1-ol



Colorless oil (92% yield); R_f = 0.38 (3:1 hexane/ethyl acetate)

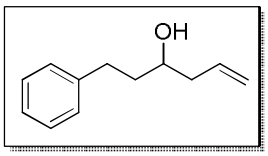
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dd, J_1 = 8.4, J_2 = 5.6, 2H), 7.02 (t, *J* = 8.8, 2H), 5.73-5.83 (m, 1H), 5.13-5.17 (m, 2H), 4.69-4.73 (m, 1H), 2.42-2.53 (m, 2H), 2.14 (brs., 1H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1 (d, *J* = 244.0), 139.5 (d, *J* = 3.0), 134.1, 127.4 (d, *J* = 8.0), 118.6, 115.2 (d, *J* = 21.0), 72.6, 43.9

FTIR (neat): 3420, 3079, 3055, 1605, 1510, 1265 cm^{-1}

HRMS Calcd. for $C_{10}H_{12}FO$ [M+H$^+$]: 167.0872. Found: 167.0870

1-Phenylhex-5-en-3-ol



Colorless oil (80% yield); R_f = 0.44 (3:1 hexane/ethyl acetate)

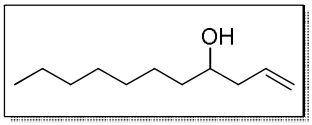
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16-7.29 (m, 5H), 5.76-5.86 (m, 1H), 5.11-5.15 (m, 2H), 3.63-3.69 (m, 1H), 2.76-2.84 (m, 1H), 2.64-2.71 (m, 1H), 2.28-2.34 (m, 1H), 2.14-2.21 (m, 1H), 1.71-1.83 (m, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 134.6, 128.4, 128.3, 125.8, 118.2, 69.9, 42.0, 38.4, 32.0

FTIR (neat): 3447, 3053, 1265 cm^{-1}

HRMS Calcd. for $C_{12}H_{17}O$ [M+H$^+$]: 177.1279. Found: 177.1272

Nndec-1-en-4-ol



Colorless oil (70% yield); R_f = 0.55 (3:1 hexane/ethyl acetate)

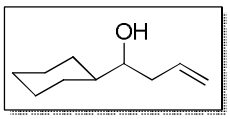
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.78-5.89 (m, 1H), 5.12-5.16 (m, 2H), 3.61-3.67 (m, 1H), 2.27-2.34 (m, 1H), 2.10-2.18 (m, 1H), 1.62 (brs., 1H), 1.29-1.48 (m, 12H), 0.88 (t, *J* = 6.4, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 134.9, 118.0, 70.7, 41.9, 36.8, 31.8, 29.6, 29.2, 25.6, 22.6, 14.1

FTIR (neat): 3441, 3053, 1265 cm^{-1}

HRMS Calcd. for $C_{11}H_{23}O$ [$M+H^+$]: 171.1749. Found: 171.1741

1-Cyclohexylbut-3-en-1-ol



Colorless oil (91% yield); R_f = 0.53 (3:1 hexane/ethyl acetate)

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.79-5.89 (m, 1H), 5.12-5.16 (m, 2H), 3.37-3.42 (m, 1H), 2.30-2.36 (m, 1H), 2.09-2.17 (m, 1H), 1.67-1.88 (m, 5H), 1.60 (brs., 1H), 0.97-1.41 (m, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 135.5, 117.9, 74.7, 43.0, 38.8, 29.1, 28.1, 26.5, 26.3, 26.1

FTIR (neat): 3451, 1265 cm^{-1}

HRMS Calcd. for $C_{10}H_{19}O$ [$M+H^+$]: 155.1436. Found: 155.1436

2. Protection of Homoallylic Alcohols

General Procedure for Protection Reactions of Homoallylic Alcohols

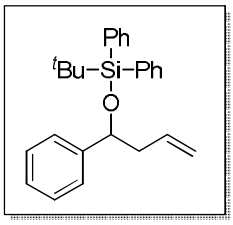
Representative procedure for protection reactions of homoallylic alcohols:

Preparation of *tert*-butyldiphenyl((1-phenylbut-3-en-1-yl)oxy)silane

The solution of 1-phenylhex-5-en-3-ol (2.24 g, 13 mmol), imidazole (1.78 g, 26 mmol) and DMAP (32 mg, 0.26 mmol) in anhydrous DMF (20 mL) was stirred for 10 min. *tert*-Butyldiphenylsilyl chloride (5.38 g, 20 mmol) was added and the reaction mixture was stirred for 12 h at room temperature. The reaction mixture was quenched with H_2O (45 mL) and extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified *via* silica gel chromatography to afford *tert*-butyldiphenyl((1-phenylbut-3-en-1-yl)oxy)- silane as colorless oil (88% yield).

Characterization of the protected homoallylic alcohols:

***tert*-Butyldiphenyl((1-phenylbut-3-en-1-yl)oxy)silane**



Colorless oil (87% yield); R_f = 0.76 (7:1 hexane/diethyl ether)

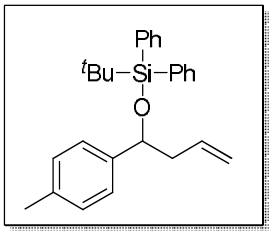
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.6, 2H), 7.31-7.46 (m, 6H), 7.18-7.24 (m, 7H), 5.48-5.58 (m, 1H), 4.78-4.87 (m, 2H), 4.70 (t, *J* = 6.4, 1H), 2.35-2.48 (m, 2H), 1.04 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 135.94, 135.91, 134.3, 134.2, 133.6, 129.6, 129.4, 127.8, 127.5, 127.3, 126.9, 126.3, 117.2, 75.5, 44.7, 27.0, 19.3

FTIR (neat): 3053, 1427, 1265 cm^{-1}

HRMS Calcd. for $C_{26}H_{31}OSi$ [M+H$^+$]: 387.2144. Found: 387.2148

***tert*-Butyldiphenyl((1-(p-tolyl)but-3-en-1-yl)oxy)silane**



Colorless oil (91% yield); R_f = 0.77 (7:1 hexane/diethyl ether)

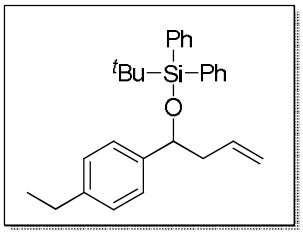
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.6, 2H), 7.46 (d, *J* = 7.6, 2H), 7.30-7.43 (m, 4H), 7.19-7.24 (m, 2H), 7.10 (d, *J* = 8.0, 2H), 7.04 (d, *J* = 8.0, 2H), 5.47-5.58 (m, 1H), 4.78-4.86 (m, 2H), 4.68 (t, *J* = 6.0, 1H), 2.33-2.46 (m, 2H), 2,30 (s, 3H), 1.04 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 136.4, 135.9, 134.4, 134.4, 133.7, 129.6, 129.4, 128.5, 127.5, 127.3, 126.2, 117.0, 75.4, 44.7, 27.0, 21.4, 19.4

FTIR (neat): 3051, 1427, 1265 cm^{-1}

HRMS Calcd. for $C_{27}H_{33}OSi$ [M+H$^+$]: 401.2301. Found: 401.2310

***tert*-Butyl((1-(4-ethylphenyl)but-3-en-1-yl)oxy)diphenylsilane**



Colorless oil (48% yield); R_f = 0.79 (7:1 hexane/diethyl ether)

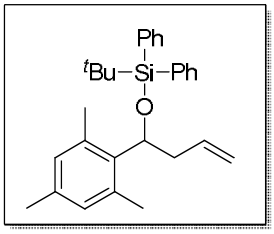
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 6.8, 2H), 7.30-7.45 (m, 6H), 7.20-7.24 (m, 2H), 7.11 (d, *J* = 8.0, 2H), 7.05 (d, *J* = 8.0, 2H), 5.49-5.60 (m, 1H), 4.80-4.87 (m, 2H), 4.67 (t, *J* = 6.0, 1H), 2.61 (q, *J* = 7.6, 2H), 2.34-2.48 (m, 2H), 1.22 (t, *J* = 7.6, 3H), 1.04 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 141.3, 136.0, 135.9, 134.5, 134.4, 133.8, 129.5, 129.3, 127.4, 127.3, 127.2, 126.3, 117.0, 75.4, 44.7, 28.5, 27.0, 19.4, 15.6

FTIR (neat): 3051, 1427, 1265 cm^{-1}

HRMS Calcd. for $C_{28}H_{35}OSi$ [M+H$^+$]: 415.2457. Found: 415.2469

***tert*-Butyl((1-mesitylbut-3-en-1-yl)oxy)diphenylsilane**



Colorless oil (42% yield); R_f = 0.78 (7:1 hexane/diethyl ether)

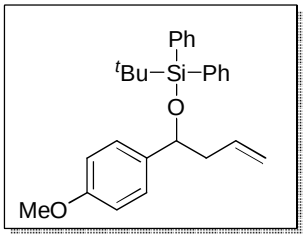
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 6.8, 2H), 7.30-7.44 (m, 6H), 7.18-7.21 (m, 2H), 6.82 (s, 1H), 6.60 (s, 1H), 5.32-5.40 (m, 1H), 5.01 (t, *J* = 7.2, 1H), 4.75-4.81 (m, 2H), 2.66 (s, 3H), 2.52-2.63 (m, 2H), 2.22 (s, 3H), 1.73 (s, 3H), 1.02 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1, 136.2, 136.05, 135.96, 135.89, 134.98, 134.94, 134.3, 133.6, 131.0, 129.6, 129.4, 128.4, 127.5, 127.2, 116.7, 72.2, 41.9, 27.0, 20.82, 20.79, 20.4, 19.3

FTIR (neat): 3051, 1636, 1427, 1265 cm^{-1}

HRMS Calcd. for $C_{29}H_{37}OSi$ [M+H$^+$]: 429.2614. Found: 429.2621

***tert*-Butyl((1-(4-methoxyphenyl)but-3-en-1-yl)oxy)diphenylsilane**



Colorless oil (69% yield); R_f = 0.74 (7:1 hexane/diethyl ether)

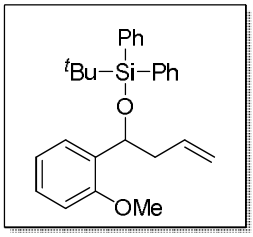
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 7.6, 2H), 7.32-7.46 (m, 6H), 7.21-7.25 (m, 2H), 7.11 (d, *J* = 8.4, 2H), 6.77 (d, *J* = 8.4, 2H), 5.48-5.58 (m, 1H), 4.79-4.87 (m, 2H), 4.65 (t, *J* = 6.4, 1H), 3.78 (s, 3H), 2.34-2.47 (m, 2H), 1.03 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 136.4, 135.93, 135.91, 134.4, 134.36, 133.7, 129.5, 129.4, 127.5, 127.3, 117.0, 113.2, 75.1, 55.2, 44.7, 27.0, 19.3

FTIR (neat): 3071, 3049, 1427 cm^{-1}

HRMS Calcd. for $C_{27}H_{33}O_2Si$ [M+H$^+$]: 417.2250. Found: 417.2270

***tert*-Butyl((1-(2-methoxyphenyl)but-3-en-1-yl)oxy)diphenylsilane**



Colorless oil (53% yield); R_f = 0.75 (7:1 hexane/diethyl ether)

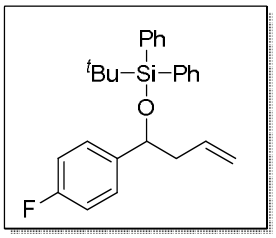
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.6, 2H), 7.58 (d, *J* = 7.6, 1H), 7.30-7.47 (m, 6H), 7.14-7.23 (m, 3H), 6.93 (t, *J* = 7.6, 1H), 6.68 (d, *J* = 8.4, 1H), 5.60-5.71 (m, 1H), 5.28 (t, *J* = 5.6, 1H), 4.81-4.88 (m, 2H), 3.57 (s, 3H), 2.33-2.46 (m, 2H), 1.05 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 134.0, 135.9, 134.7, 134.5, 134.0, 132.6, 129.4, 129.2, 127.6, 127.5, 127.4, 127.1, 120.2, 116.6, 109.8, 68.5, 55.0, 44.8, 27.0, 19.4

FTIR (neat): 3051, 1265 cm^{-1}

HRMS Calcd. for $C_{27}H_{33}O_2Si$ [M+H$^+$]: 417.2250. Found: 417.2253

***tert*-Butyl((1-(4-fluorophenyl)but-3-en-1-yl)oxy)diphenylsilane**



Colorless oil (83% yield); R_f = 0.71 (7:1 hexane/diethyl ether)

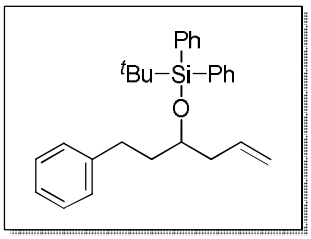
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.6, 2H), 7.31-7.45 (m, 6H), 7.23 (t, *J* = 7.6, 2H), 7.14 (dd, J_1 = 8.4, J_2 = 5.6, 2H), 6.90 (t, *J* = 8.8, 2H), 5.47-5.58 (m, 1H), 4.87 (d, *J* = 10, 1H), 4.81 (d, *J* = 17, 1H), 4.68 (t, *J* = 6.0, 1H), 2.33-2.47 (m, 2H), 1.04 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8 (d, *J* = 243.0), 139.8 (d, *J* = 3.0), 135.9, 135.8, 134.1, 133.9, 133.5, 129.7, 129.5, 127.8 (d, *J* = 8.0), 127.5, 127.4, 117.4, 114.6 (d, *J* = 22.0), 74.9, 44.7, 27.0, 19.3

FTIR (neat): 3053, 1636, 1265 cm^{-1}

HRMS Calcd. for $C_{26}H_{30}FOSi$ [M+H$^+$]: 405.2050. Found: 405.2048

***tert*-Butyldiphenyl((1-phenylhex-5-en-3-yl)oxy)silane**



Colorless oil (95% yield); R_f = 0.76 (7:1 hexane/diethyl ether)

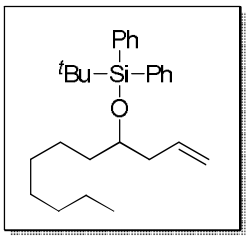
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.70 (m, 4H), 7.34-7.43 (m, 6H), 7.20 (t, *J* = 7.2, 2H), 7.12 (t, *J* = 7.2, 1H), 7.01 (d, *J* = 7.2, 2H), 5.69-5.80 (m, 1H), 4.93-5.00 (m, 2H), 3.81-3.87 (m, 1H), 2.52-2.61 (m, 2H), 2.24-2.30 (m, 2H), 1.72-1.77 (m, 2H), 1.08 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 135.96, 135.93, 134.7, 134.44, 134.37, 129.56, 129.53 128.27, 128.24, 127.53, 127.48, 125.5, 117.0, 72.4, 41.0, 37.8, 31.3, 27.1, 19.4

FTIR (neat): 3053, 1265 cm^{-1}

HRMS Calcd. for $C_{28}H_{35}OSi$ [M+H$^+$]: 415.2457. Found: 415.2455

***tert*-Butyldiphenyl(undec-1-en-4-yloxy)silane**



Colorless oil (84% yield); R_f = 0.78 (7:1 hexane/diethyl ether)

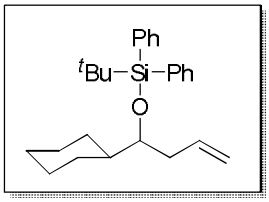
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.6, 4H), 7.33-7.42 (m, 6H), 5.69-5.79 (m, 1H), 4.90-4.96 (m, 2H), 3.73-3.79 (m, 1H), 2.12-2.26 (m, 2H), 1.36-1.46 (m, 2H), 1.10-1.26 (m, 11H), 1.06 (s, 9H), 0.86 (t, *J* = 6.4, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 135.96, 135.94, 135.1, 134.63, 134.60, 129.4, 127.4, 116.6, 72.8, 41.0, 36.0, 31.8, 29.6, 29.2, 27.1, 24.8, 22.6, 19.4, 14.1

FTIR (neat): 3051, 1639, 1263 cm^{-1}

HRMS Calcd. for $C_{27}H_{41}OSi$ [M+H$^+$]: 409.2927. Found: 409.2924

***tert*-Butyl((1-cyclohexylbut-3-en-1-yl)oxy)diphenylsilane**



Colorless oil (83% yield); R_f = 0.76 (7:1 hexane/diethyl ether)

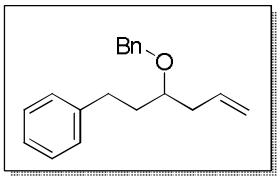
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.70 (m, 4H), 7.34-7.43 (m, 6H), 5.58-5.68 (m, 1H), 4.82-4.89 (m, 2H), 3.57 (dd, J_1 = 10.0, J_2 = 6.0, 1H), 2.08-2.24 (m, 2H), 1.56-1.69 (m, 5H), 1.08-1.37 (m, 6H), 1.06 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.1, 135.7, 134.8, 134.4, 129.44, 129.36, 127.4, 127.3, 116.3, 77.3, 42.4, 38.3, 29.1, 27.4, 27.2, 26.8, 26.51, 26.46, 19.6

FTIR (neat): 3071, 3049, 1471, 1449, 1427 cm^{-1}

HRMS Calcd. for $C_{26}H_{37}OSi$ [M+H$^+$]: 393.2614. Found: 393.2613

(3-(Benzyloxy)hex-5-en-1-yl)benzene



1-Phenylhex-5-en-3-ol (3.40 g, 19.3 mmol) was dissolved in DMF (100 mL) and cooled to 0℃. Sodium hydride (2.32 g, 57.9 mmol, 60%) was added in one portion and stirred for 30 minutes, followed by addition dropwise of benzyl bromide (2.97 g, 17.4 mmol). The solution was allowed to warm to room temperature and stirred over night under N_2. The reaction was quenched with a saturated ammonium chloride solution and diluted with ether. The organic phase was separated, washed three times with water then brine and dried over sodium sulfate. The solution was concentrated *in vacuo* and purified *via* silica gel chromatography to afford the desired compound.[2]

Colorless oil (71% yield); R_f = 0.72 (7:1 hexane/diethyl ether)

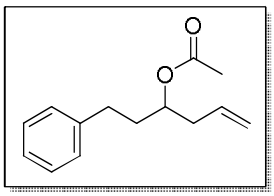
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.37 (m, 4H), 7.25-7.30 (m, 3H), 7.15-7.19 (m, 3H), 5.79-5.90 (m, 1H), 5.05-5.12 (m, 2H), 4.60 (d, J = 11.6, 1H), 4.48 (d, J = 11.6, 1H), 3.45-3.52 (m, 1H), 2.75-2.82 (m, 1H), 2.60-2.68 (m, 1H), 2.32-2.43 (m, 2H), 1.78-1.93 (m, 2H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3, 138.8, 134.7, 128.41, 128.36, 128.33, 127.8, 127.5, 125.7, 117.1, 77.8, 70.9, 38.2, 35.7, 31.7

FTIR (neat): 3053, 1636, 1265 cm^{-1}

HRMS Calcd. for $C_{19}H_{23}O$ [M+H$^+$]: 267.1749. Found: 267.1749

1-Phenylhex-5-en-3-yl acetate



1-Phenylhex-5-en-3-ol (2.90 g, 16.4 mmol) was dissolved in DCM (30 mL). Et_3N (2.49 g, 24.6

[2] K. M. McQuaid and D. Sames， *J. Am. Chem. Soc.* 2009, **131**, 402.

mmol) and DMAP (40 mg, 0.33 mmol) were added and stirred for 10 minutes, followed by addition dropwise of acetyl chloride (1.93 g, 24.6 mmol). The solution was stirred over night at room temperature under N_2. The reaction was quenched with a saturated sodium hydrogencarbonate solution. The organic phase was separated, washed three times with water then brine and dried over sodium sulfate. The solution was concentrated *in vacuo* and purified *via* silica gel chromatography to afford the desired compound.

Colorless oil (59% yield); R_f = 0.53 (7:1 hexane/diethyl ether)

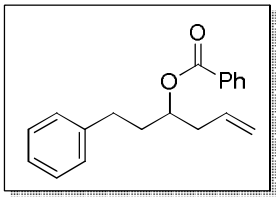
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15-7.29 (m, 5H), 5.70-5.80 (m, 1H), 5.05-5.10 (m, 2H), 4.94-5.00 (m, 1H), 2.58-2.71 (m, 2H), 2.34 (t, *J* = 6.4, 2H), 2.03 (s, 3H), 1.86-1.95 (m, 2H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 141.5, 133.5, 128.4, 128.3, 125.9, 117.8, 72.8, 38.7, 35.2, 31.7, 21.1

FTIR (neat): 1732 cm^{-1}

HRMS Calcd. for $C_{14}H_{19}O_2$ [M+H$^+$]: 219.1385. Found: 219.1394

1-Phenylhex-5-en-3-yl benzoate



1-Phenylhex-5-en-3-ol (2.99 g, 17.0 mmol) was dissolved in DCM (30 mL). Et_3N (2.58 g, 25.5 mmol) and DMAP (42 mg, 0.34 mmol) were added and stirred for 10 minutes, followed by addition dropwise of benzoyl chloride (3.58 g, 25.5 mmol). The solution was stirred over night at room temperature under N_2. The reaction was quenched with a saturated sodium hydrogencarbonate solution. The organic phase was separated, washed three times with water then brine and dried over sodium sulfate. The solution was concentrated *in vacuo* and purified *via* silica gel chromatography to afford the desired compound.

Colorless oil (71% yield); R_f = 0.57 (7:1 hexane/diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.6, 2H), 7.55 (t, *J* = 7.6, 1H), 7.44 (t, *J* = 7.6, 2H), 7.23-7.28 (m, 2H), 7.14-7.18 (m, 3H), 5.77-5.86 (m, 1H), 5.21-5.24 (m, 1H), 5.06-5.13 (m, 2H), 2.68-2.75 (m, 2H), 2.47 (t, *J* = 7.6, 2H), 1.98-2.07 (m, 2H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 141.5, 133.4, 132.8, 130.5, 129.5, 128.4, 128.3, 125.9, 118.0, 73.5, 38.7, 35.4, 31.7

FTIR (neat): 1713 cm^{-1}

HRMS Calcd. for $C_{19}H_{21}O_2$ [M+H$^+$]: 281.1542. Found: 281.1547

3. Preparation of Primary Alcohols *via* Brown Hydroboration Reaction

General Procedure for Primary Alcohols

Representative procedure for primary alcohols:

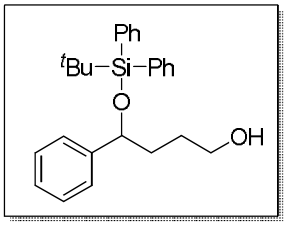
Preparation of 4-((*tert*-Butyldiphenylsilyl)oxy)-6-phenylhexan-1-ol

To a 0.5 M solution (78.6 mL, 39.3 mmol) of 9-BBN in THF was added dropwise a solution of *tert*-butyldiphenyl((1-phenylhex-5-en-3-yl)oxy)silane (5.43 g, 13.1 mmol) in THF (50 mL) over 10 min, and the mixture was heated under reflux for 2 h. After cooling, the reaction mixture was treated with EtOH (30 mL), 2N aqueous NaOH (15 mL), and 30% aqueous H_2O_2 (15 mL) at 50 °C for 1 h. The aqueous layer was saturated with K_2CO_3, separated from the organic layer, and

extracted with ether. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, and concentrated. Purification of the residue by silica gel chromatography provided the desired compound.[3]

Characterization of Primary Alcohols:

4-((*tert*-Butyldiphenylsilyl)oxy)-4-phenylbutan-1-ol



Colorless oil (71% yield); R_f = 0.26 (3:1 hexane/ethyl acetate)

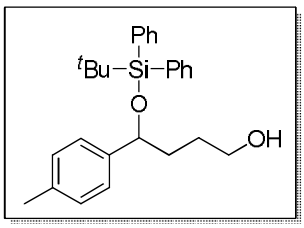
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, J_1 = 8.0, J_2 = 1.6, 2H), 7.31-7.46 (m, 6H), 7.17-7.26 (m, 7H), 4.72 (t, J = 6.0, 1H), 3.38 (dd, J_1 = 6.4, J_2 = 5.6, 2H), 1.62-1.77 (m, 2H), 1.30-1.38 (m, 2H), 1.23 (t, J = 5.6, 1H), 1.04 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 135.9, 135.8, 134.3, 133.5, 129.6, 129.4, 127.9, 127.5, 127.3, 126.9, 126.2, 75.3, 62.8, 36.1, 27.8, 27.0, 19.3

FTIR (neat): 3333 cm^{-1}

HRMS Calcd. for $C_{26}H_{33}O_2Si$ [M+H$^+$]: 405.2250. Found: 405.2245

4-((*tert*-Butyldiphenylsilyl)oxy)-4-(p-tolyl)butan-1-ol



Colorless oil (75% yield); R_f = 0.30 (3:1 hexane/ethyl acetate)

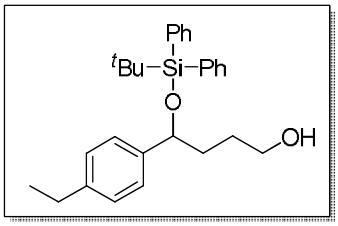
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69-7.71 (m, 2H), 7.32-7.47 (m, 6H), 7.21-7.25 (m, 2H), 7.11 (d, J = 8.0, 2H), 7.05 (d, J = 8.0, 2H), 4.69 (t, J = 6.0, 1H), 3.38 (t, J = 6.8, 2H), 2.31 (s, 3H), 1.60-1.72 (m, 2H), 1.29-1.37 (m, 2H), 1.31 (s, 1H), 1.03 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 136.4, 135.9, 135.8, 134.4, 133.6, 129.6, 129.4, 128.6, 127.5, 127.3, 126.1, 62.8, 36.1, 27.8, 27.0, 21.1, 19.3

FTIR (neat): 3354 cm^{-1}

HRMS Calcd. for $C_{27}H_{35}O_2Si$ [M+H$^+$]: 419.2406. Found: 419.2418

4-((*tert*-Butyldiphenylsilyl)oxy)-4-(4-ethylphenyl)butan-1-ol



[3] M. Ohba，N. Kawase and T. Fujii, *J. Am. Chem. Soc.* 1996, **118**, 8250.

Colorless oil (78% yield); R_f = 0.30 (3:1 hexane/ethyl acetate)

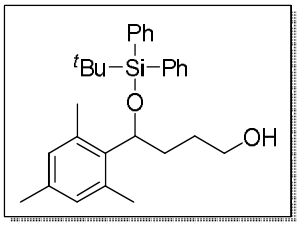
^{1}H NMR (400 MHz, $CDCl_3$): δ7.69 (dd, J_1 = 8.0, J_2 = 1.6, 2H), 7.31-7.45 (m, 6H), 7.22-7.24 (m, 2H), 7.12 (d, J = 8.0, 2H), 7.06 (d, J = 8.0, 2H), 4.70 (t, J = 6.0, 1H), 3.39 (brs., 2H), 2.61 (q, J = 7.6, 2H), 1.61-1.74 (m, 2H), 1.32-1.39 (m, 2H), 1.22 (t, J = 7.6, 3H), 1.15 (brs., 1H), 1.04 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 141.5, 135.91, 135.87, 134.4, 133.7, 129.6, 129.4, 127.5, 127.4, 127.3, 126.2, 62.9, 36.1, 27.8, 28.5, 27.9, 27.0, 19.3, 15.6

FTIR (neat): 3450 cm^{-1}

HRMS Calcd. for $C_{28}H_{37}O_2Si$ [M+H$^+$]: 433.2563. Found: 433.2568

4-((*tert*-Butyldiphenylsilyl)oxy)-4-mesitylbutan-1-ol



Colorless oil (77% yield); R_f = 0.28 (3:1 hexane/ethyl acetate)

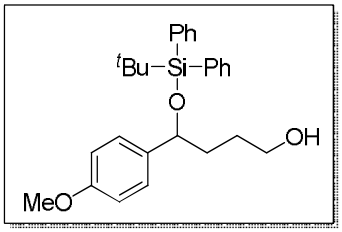
^{1}H NMR (400 MHz, $CDCl_3$): δ7.71 (dd, J_1 = 8.0, J_2 = 1.6, 2H), 7.32-7.46 (m, 6H), 7.21 (t, J = 7.6, 2H), 6.82 (s, 1H), 6.62 (s, 1H), 4.99 (t, J = 7.2, 1H), 3.33-3.37 (m, 2H), 2.65 (s, 3H), 2.23 (s, 3H), 1.80-1.95 (m, 2H), 1.78 (s, 3H), 1.31-1.42 (m, 1H), 1.06-1.16 (m, 1H), 1.00 (s, 9H), 0.95 (t, J = 5.6, 1H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1, 136.6, 136.0, 135.9, 134.8, 134.5, 133.6, 131.2, 129.6, 129.4, 128.5, 127.5, 127.3, 62.8, 33.4, 29.3, 27.0, 20.8, 20.75, 20.4, 19.3

FTIR (neat): 3450 cm^{-1}

HRMS Calcd. for $C_{29}H_{39}O_2Si$ [M+H$^+$]: 447.2719. Found: 447.2734

4-((*tert*-Butyldiphenylsilyl)oxy)-4-(4-methoxyphenyl)butan-1-ol



Colorless oil (69% yield); R_f = 0.23 (3:1 hexane/ethyl acetate)

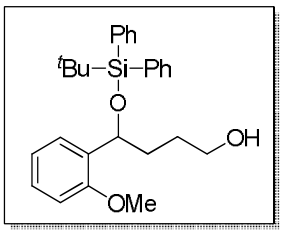
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.70 (m, 2H), 7.32-7.46 (m, 6H), 7.23 (t, J = 7.6 2H), 7.12 (d, J = 8.8, 2H), 6.78 (d, J = 8.8, 2H), 4.66 (t, J = 6.0, 1H), 3.78 (s, 3H), 3.40 (t, J = 6.8, 2H), 1.61-1.78 (m, 2H), 1.18-1.37 (m, 2H), 1.23 (br., 1H), 1.31 (s, 1H), 1.03 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 136.5, 135.9, 135.8, 134.4, 133.6, 129.6, 129.4, 127.5, 127.34, 127.29, 113.3, 75.0, 62.8, 55.2, 36.1, 27.9, 27.0, 19.3

FTIR (neat): 3445 cm^{-1}

HRMS Calcd. for $C_{27}H_{35}O_3Si$ [M+H$^+$]: 435.2355. Found: 435.2358

4-((*tert*-Butyldiphenylsilyl)oxy)-4-(2-methoxyphenyl)butan-1-ol



Colorless oil (77% yield); R_f = 0.26 (3:1 hexane/ethyl acetate)

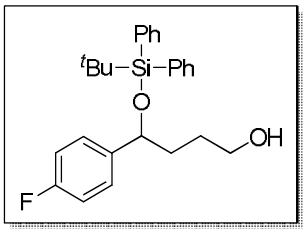
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.0, 2H), 7.61 (d, *J* = 7.6, 1H), 7.29-7.46 (m, 6H), 7.13-7.22 (m, 3H), 6.94 (t, *J* = 7.6, 1H), 6.67 (d, *J* = 8.0, 1H), 5.27 (t, *J* = 5.6, 1H), 3.55 (s, 3H), 3.40 (t, *J* = 6.8, 2H), 1.59-1.79 (m, 2H), 1.32-1.49 (m, 3H), 1.05 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 135.8, 134.4, 133.77, 133.75, 129.5, 129.2, 127.6, 127.41, 127.37, 127.1, 120.3, 109.9, 68.3, 63.0, 55.0, 34.5, 27.5, 27.0, 19.3

FTIR (neat): 3447 cm^{-1}

HRMS Calcd. for $C_{27}H_{35}O_3Si$ [M+H$^+$]: 435.2355. Found: 435.2355

4-((*tert*-Butyldiphenylsilyl)oxy)-4-(4-fluorophenyl)butan-1-ol



Colorless oil (66% yield); R_f = 0.23 (3:1 hexane/ethyl acetate)

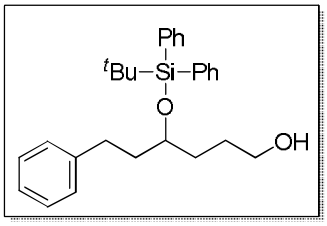
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (dd, J_1 = 8.0, J_2 = 1.2, 2H), 7.32-7.44 (m, 6H), 7.23 (t, *J* = 7.6, 2H), 7.14-7.17 (m, 2H), 6.89-6.93 (m, 2H), 4.69 (t, *J* = 6.0, 1H), 3.41 (t, *J* = 6.8, 2H), 1.62-1.79 (m, 2H), 1.30-1.38 (m, 2H), 1.24 (br., 1H), 1.04 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8 (d, *J* = 243.0), 140.1 (d, *J* = 3.0), 135.8, 134.1, 133.4, 129.7, 129.5, 127.8 (d, *J* = 8.0), 127.6, 127.4, 114.6 (d, *J* = 21.0), 74.8, 62.7, 36.2, 27.79, 27.97, 19.3

FTIR (neat): 3443 cm^{-1}

HRMS Calcd. for $C_{26}H_{32}FO_2Si$ [M+H$^+$]: 423.2156. Found: 423.2150

4-((*tert*-Butyldiphenylsilyl)oxy)-6-phenylhexan-1-ol



Colorless oil (68% yield); R_f = 0.25 (3:1 hexane/ethyl acetate)

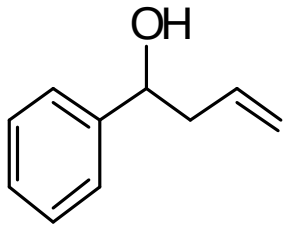
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.69 (m, 4H), 7.35-7.44 (m, 6H), 7.11-7.23 (m, 3H), 6.99 (d, *J* = 7.2, 2H), 3.83-3.85 (m, 1H), 3.48 (brs., 2H), 2.49-2.57 (m, 2H), 1.72-1.82 (m, 2H), 1.51-1.61 (m, 4H), 1.46 (brs., 1H), 1.07 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 135.9, 134.31, 134.28, 129.6, 128.24, 128.21, 127.5, 125.6, 72.5, 63.0, 37.8, 32.3, 31.4, 27.9, 27.1, 19.4

FTIR (neat): 3445 cm^{-1}

HRMS Calcd. for $C_{28}H_{37}O_2Si$ [M+H$^+$]: 433.2567. Found: 433.2567

4-((*tert*-Butyldiphenylsilyl)oxy)undecan-1-ol



Colorless oil (68% yield); R_f = 0.22 (3:1 hexane/ethyl acetate)

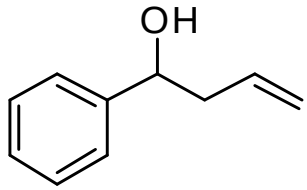
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.6, 4H), 7.35-7.44 (m, 6H), 3.75-3.79 (m, 1H), 3.49-3.51 (m, 2H), 1.36-1.56 (m, 7H), 1.09-1.29 (m, 10H), 1.06 (s, 9H), 0.86 (t, *J* = 7.2, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 135.9, 134.49, 134.46, 129.51, 129.49, 127.46, 127.43, 72.9, 63.1, 36.0, 32.3, 31.8, 29.5, 29.2, 27.8, 27.1, 25.0, 22.6, 19.4, 14.1

FTIR (neat): 3443 cm^{-1}

HRMS Calcd. for $C_{27}H_{43}O_2Si$ [M+H$^+$]: 427.3032. Found: 427.3032

4-((*tert*-Butyldiphenylsilyl)oxy)-4-cyclohexylbutan-1-ol



Colorless oil (68% yield); R_f = 0.21 (3:1 hexane/ethyl acetate)

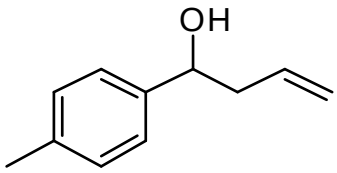
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.69 (m, 4H), 7.34-7.43 (m, 6H), 3.53-3.57 (m, 1H), 3.33-3.37 (m, 2H), 1.59-1.70 (m, 6H), 1.37-1.44 (m, 5H), 1.11 (brs., 5H), 1.06 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.04, 136.01, 134.9, 134.5, 129.46, 129.41, 127.39, 127.36, 77.4, 63.0, 42.8, 29.4, 28.7, 28.6, 28.2, 27.2, 26.7, 26.5, 19.6

FTIR (neat): 3443 cm^{-1}

HRMS Calcd. for $C_{26}H_{39}O_2Si$ [M+H$^+$]: 411.2719. Found: 411.2715

4-(Benzyloxy)-6-phenylhexan-1-ol



Colorless oil (68% yield); R_f = 0.20 (3:1 hexane/ethyl acetate)

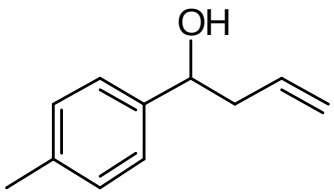
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16-7.35 (m, 10H), 4.52 (s, 2H), 3.59-3.49 (m, 2H), 3.45-3.49 (m, 1H), 2.62-2.77 (m, 2H), 1.79-1.99 (m, 3H), 1.63-1.72 (m, 4H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 138.5, 128.38, 128.35, 127.9, 127.6, 125.8, 70.8, 62.9, 35.4, 31.6, 30.1, 28.4

FTIR (neat): 3441 cm^{-1}

HRMS Calcd. for $C_{19}H_{25}O_2$ [M+H$^+$]: 285.1855. Found: 285.1856

6-Hydroxy-1-phenylhexan-3-yl acetate



Colorless oil (65% yield); R_f = 0.23 (3:1 hexane/ethyl acetate)

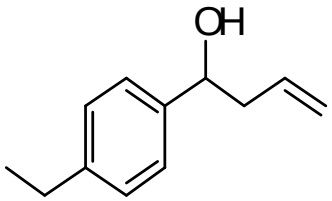
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16-7.30 (m, 5H), 4.93-4.99 (m, 1H), 3.63-3.66 (m, 2H), 2.57-2.71 (m, 2H), 2.04 (s, 3H), 1.81-1.96 (m, 2H), 1.65-1.70 (m, 2H), 1.54-1.60 (m, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0, 141.5, 128.4, 128.2, 125.8, 73.6, 62.4, 35.8, 31.7, 30.4, 28.3, 21.1

FTIR (neat): 3443, 1728 cm^{-1}

HRMS Calcd. for $C_{14}H_{21}O_3$ [M+H$^+$]: 237.1491. Found: 237.1487

6-Hydroxy-1-phenylhexan-3-yl benzoate



Colorless oil (60% yield); R_f = 0.27 (3:1 hexane/ethyl acetate)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.0, 2H), 7.54 (t, *J* = 7.6, 1H), 7.42 (t, *J* = 7.6, 2H), 7.13-7.27 (m, 5H), 5.18-5.24 (m, 1H), 3.63 (t, *J* = 6.4, 2H), 2.63-2.77 (m, 2H), 2.17 (br., 1H), 1.93-2.11 (m, 2H), 1.77-1.82 (m, 2H), 1.60-1.66 (m, 2H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 141.4, 132.8, 130.4, 129.5, 128.34, 128.29, 128.2, 125.8, 74.2, 62.3, 35.9, 31.7, 30.6, 28.3

FTIR (neat): 3447, 1713 cm^{-1}

HRMS Calcd. for $C_{19}H_{23}O_3$ [M+H$^+$]: 299.1647. Found: 299.1646

4. Preparation of γ-Protected Hydroxyl Aldehydes *via* Swern Oxidation

General Procedure for Swern Oxidation of Primary Alcohols

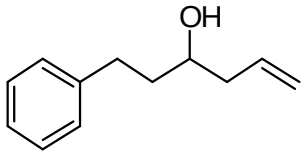
Representative procedure for Preparation of γ-protected hydroxyl aldehydes:

Preparation of 4-((tert-butyldiphenylsilyl)oxy)-6-phenylhexanal:

To a solution of oxalyl dichloride (0.74 mL, 8.5 mmol) in DCM (20 mL) cooled to -78℃ was added dropwise a solution of DMSO (0.65 mL, 9.2 mmol) in DCM (5.0 mL) and stirred for 10 min. A solution of 4-((*tert*-butyldiphenylsilyl)oxy)-6-phenylhexan-1-ol (3.06 g, 7.1 mmol) in DCM (5.0 mL) was added dropwise and stirred for 30 min at -78℃. Et_3N (4.95 mL, 35 mmol) was added in one portion and kept for 20 min then warmed to room temperature for 2h. The reaction mixture was washed with saturated NH_4Cl, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified *via* silica gel chromatography to afford the desired compound.

Characterization of the γ-protected hydroxyl aldehydes (materials for **1b**, **1c** and **1d**):

4-(Benzyloxy)-6-phenylhexanal



Colorless oil (71% yield); R_f = 0.33 (7:1 hexane/diethyl ether)

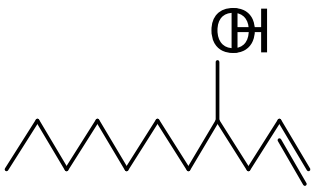
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (t, *J* = 1.6, 1H), 7.15-7.35 (m, 10H), 4.43-2.52 (m, 2H), 3.43-3.49 (m, 1H), 2.63-2.76 (m, 2H), 2.52 (td, J_1 = 7.2, J_2 = 1.6, 2H), 1.78-2.01 (m, 4H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 202.2, 142.0, 138.4, 128.40, 128.33, 127.9, 127.7, 125.9, 77.1, 70.9, 39.8, 35.5, 31.5, 26.1

FTIR (neat): 1722 cm^{-1}

HRMS Calcd. for $C_{19}H_{23}O_2$ [M+H$^+$]: 283.1698. Found: 283.1695

6-Oxo-1-phenylhexan-3-yl acetate



Colorless oil (82% yield); R_f = 0.32 (7:1 hexane/diethyl ether)

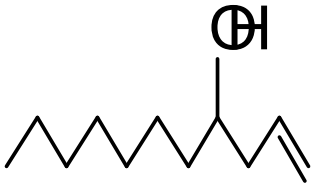
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (s, 1H), 7.15-7.30 (m, 5H), 4.93-4.97 (m, 1H), 2.57-2.70 (m, 2H), 2.48 (t, *J* = 7.6, 2H), 2.02 (s, 3H), 1.79-2.00 (m, 4H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 201.2, 170.8, 141.2, 128.5, 128.3, 126.0, 72.9, 39.9, 35.8, 31.7, 26.5, 21.1

FTIR (neat): 1730 cm^{-1}(br.)

HRMS Calcd. for $C_{14}H_{19}O_3$ [M+H$^+$]: 235.1334. Found: 235.1332

6-Oxo-1-phenylhexan-3-yl benzoate



Colorless oil (82% yield); R_f = 0.31 (7:1 hexane/diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (s, 1H), 8.03 (d, *J* = 7.6, 2H), 7.43-7.59 (m, 3H), 7.16-7.28 (m, 3H), 5.19-5.25 (m, 1H), 2.66-2.76 (m, 2H), 2.56 (t, *J* = 7.6, 2H), 1.94-2.15 (m, 4H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 166.2, 141.1, 133.0, 130.1, 129.6, 128.43, 128.39, 128.3, 126.0, 73.4, 39.8, 36.0, 31.7, 26.6

FTIR (neat): 1712 cm^{-1}(br.)

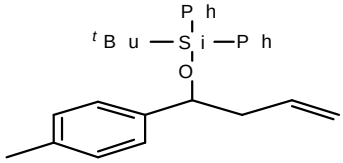
HRMS Calcd. for $C_{19}H_{21}O_3$ [M+H$^+$]: 297.1491. Found: 297.1498

Preparation of γ-Hydroxy(protected)-α-amino Acetals (**1b**, **1c** and **1d**):

Typical procedure for the diastereoselective synthese of γ-hydroxy-α-amino acetals *via* iodine-catalyzed oxidative rearrangement of tertiary amines (*N*, *N*-dibenzyl-4-((*tert*-butyldiphenylsilyl)oxy)-1,1-dimethoxy-6-phenylhexan-2-amine **1a** as an example): 4-((*tert*-Butyldiphenylsilyl)oxy)-6-phenylhexanal **1** (0.279 g, 0.65 mmol) was added to a mixture of $HNBn_2$ (0.153 g, 0.78 mmol) and I_2 (33 mg, 0.13 mmol) in methanol (0.5 mL, 19

equiv.)/dichloroethane (2.0 mL), following adition of $NaCO_3 \cdot 1.5H_2O_2$ (0.101g, 0.65 mmol). The mixture was stirred for 72 h at at room temperature. The resulting reaction mixture was mixed with a small amount of silica gel and concentrated. The crude product was purified by flash silica gel column chromatography (triethylamine/diethyl ether/hexane = 0.1:1:100, v/v/v) to afford the desired product **1aa** as a light yellowish oil and **1ab** as a colorless crystal (62% total yield). The d.r. (**1ab**(*syn*)/**1aa**(*anti*)) was detected by crude ^{1}H NMR before isolation. It is necessary to point out that most of the diastereoisomers were separated easily by silica gel column chromatography. The structure of compound **10ab** was conformed as *syn*-isomer according to its crystal structure (Figure 2) and the structures of other pairs of diastereoisomers were obtained by comparing their NMR date.

***N, N*-dibenzyl-4-(benzyloxy)-1,1-dimethoxy-6-phenylhexan-2-amine (1b)**



Light yellowish oil (46% total yield); R_f = 0.30 (7:1 hexane/diethyl ether)

Anti- **1b** (**1ba**) mixed with *syn*- **1b** (**1bb**):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07-7.34 (overlap), 4.40-4.47 (overlap), 4.18 (d, *J* = 11.2), 3.64-3.84 (overlap), 3.33 (s), 3.32 (s), 3.04-3.07 (m), 2.64-2.73 (overlap), 1.80-1.84 (m)

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5, 140.6, 139.3, 129.1-128.0 (overlap), 127.8, 127.5, 127.0, 125.6, 106.7, 76.0, 70.2, 54.4-54.8 (overlap), 53.3, 36.0, 32.5, 31.2

Syn- **1b** (**1bb**) mixed with *anti*- **1b** (**1ba**):

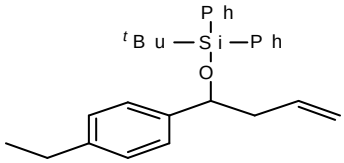
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07-7.34 (overlap), 4.40-4.47 (overlap), 3.64-3.84 (overlap), 3.36 (s, 3H), 3.26 (s, 3H), 2.86-2.89 (m, 1H), 2.64-2.73 (overlap), 2.44-2.52
(m, 1H), 1.92-1.99 (m, 1H), 1.64-1.70 (m, 1H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 140.4, 139.0, 129.1-128.0 (overlap), 127.6, 127.2, 126.8, 125.5, 107.7, 76.4, 70.5, 54.4-54.8 (overlap), 35.4, 31.3, 30.8

FTIR (neat): 3050, 1634, 1603, 1495, 1454, 1265, 1067 cm^{-1}

HRMS Calcd. for $C_{35}H_{42}NO_3$ [M+H$^+$]: 524.3165. Found: 524.3166

5-(Dibenzylamino)-6,6-dimethoxy-1-phenylhexan-3-yl acetate (1c)



Light yellowish oil (63% total yield); R_f = 0.25 (7:1 hexane/diethyl ether)

Anti- **1c** (**1ca**) mixed with *syn*- **1c** (**1cb**):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04-7.40 (overlap), 5.05-5.11 (m), 4.46 (d, *J* = 4.8), 3.83 (d, *J* = 13.6), 3.59-3.66 (overlap), 3.31-3.39 (overlap), 2.89-2.91 (m), 2.40-2.60 (overlap), 1.66-1.95 (overlap)

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 141.7, 140.1, 129.2-128.1 (overlap), 126.78, 125.74, 105.9, 71.7, 55.2, 54.6, 54.0, 53.9, 35.9, 31.2, 30.6, 21.15

Syn- **1c** (**1cb**) mixed with *anti*- **1c** (**1ca**):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04-7.40 (overlap), 5.13-5.20 (m, 1H), 4.41 (d, *J* = 4.8, 1H),

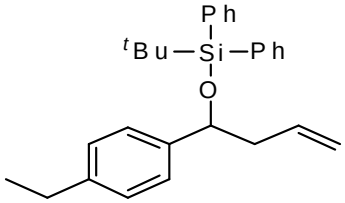
3.78 (d, *J* = 13.2, 2H), 3.59-3.66 (overlap), 3.31-3.39 (overlap), 2.76-2.80 (m, 1H), 2.40-2.60 (overlap), 1.66-1.95 (overlap), 1.43-1.53 (m, 2H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 141.9, 140.3, 129.2-128.1 (overlap), 126.85, 125.66, 107.0, 72.6, 55.0, 54.7, 54.4, 54.3, 35.0, 31.4, 31.0, 21.20

FTIR (neat): 3061, 1730, 1636, 1265, 1250 cm^{-1}

HRMS Calcd. for $C_{30}H_{38}NO_4$ [M+H$^+$]: 476.2801. Found: 476.2802

5-(Dibenzylamino)-6,6-dimethoxy-1-phenylhexan-3-yl benzoate (1d)



Light yellowish solid (74% total yield); R_f = 0.28 (7:1 hexane/diethyl ether)

Anti- **1d** (**1da**) mixed with *syn*- **1d** (**1db**):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.86 (m), 6.98-7.55 (overlap), 5.32-5.38 (m), 4.47 (d, *J* = 4.4), 3.79-3.85 (overlap), 3.62 (d, *J* = 13.6), 3.42 (s), 3.34 (s), 2.98-3.02 (m), 2.50-2.74 (overlap), 1.82-2.18 (overlap)

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 141.6, 140.0, 132.4, 130.8, 129.4, 128.8, 128.3-128.2 (overlap), 128.0, 126.7, 125.8, 106.1, 72.4, 55.2, 54.7, 54.3, 54.2, 36.1, 31.3, 30.7

Syn- **1d** (**1db**) mixed with *anti*- **1c** (**1da**):

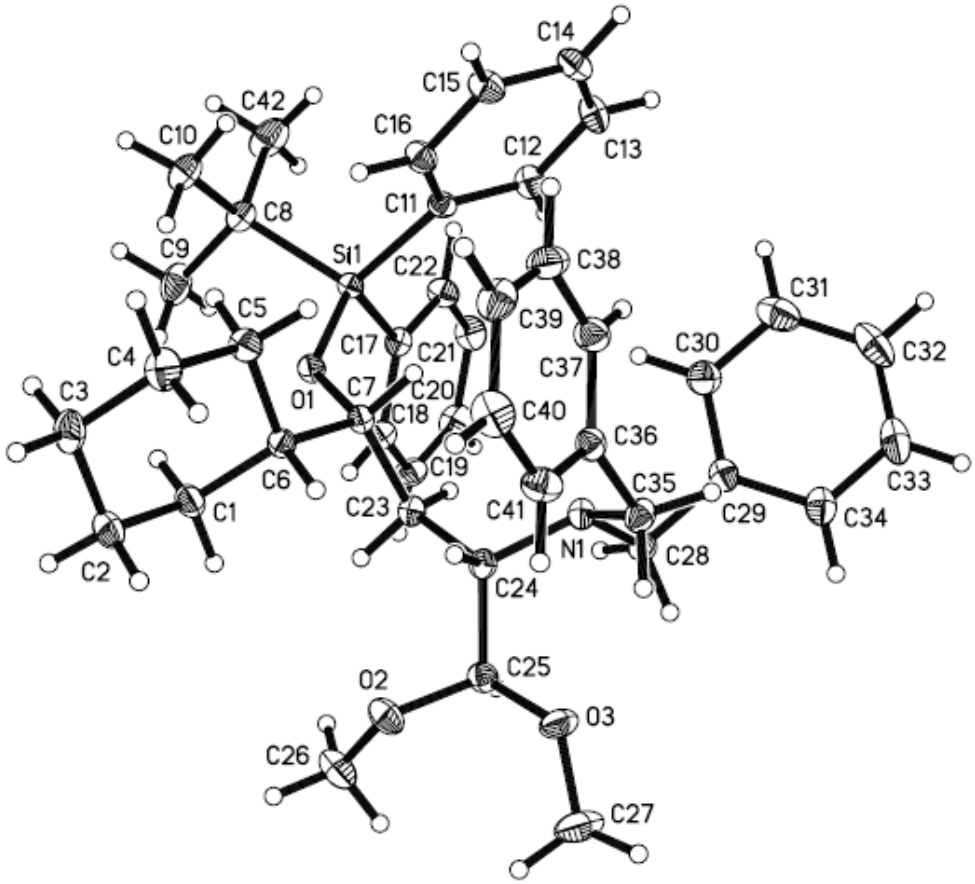
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.97 (m, 2H), 6.98-7.55 (overlap), 5.39-5.45 (m, 1H), 4.42 (d, *J* = 4.4, 1H), 3.79-3.85 (overlap), 3.66 (d, *J* = 13.6, 2H), 3.37 (s, 3H), 3.28 (s, 3H), 2.98-3.02 (m, 1H), 2.50-2.74 (overlap), 1.82-2.18 (overlap), 1.58-1.74 (m, 2H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 141.9, 140.3, 132.6, 130.85, 129.5, 129.2, 128.3-128.2 (overlap), 126.8, 125.7, 107.1, 73.2, 55.0, 54.8, 54.5, 54.4, 35.3, 31.4, 31.0

FTIR (neat): 3053, 1713, 1452, 1265 cm^{-1}

HRMS Calcd. for $C_{35}H_{40}NO_4$ [M+H$^+$]: 538.2957. Found: 538.2957

Crystal data and structure of *syn*-**10a (10ab)**



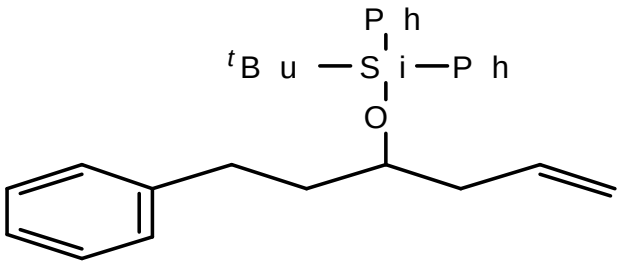


Table 1. Crystal data and structure refinement for ltp216s.

Identification code	ltp216s	
Empirical formula	C42 H55 N O3 Si	
Formula weight	649.96	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.7071(2) Å	□= 81.2230(10)°.

	b = 11.1189(2) Å □= 76.8780(10)°.
	c = 18.7507(3) Å □ =
72.9850(10)°.	
Volume	1876.61(6) $Å^3$
Z	2
Density (calculated)	1.150 Mg/m^3
Absorption coefficient	0.101 mm^{-1}
F(000)	704
Crystal size	0.40 x 0.40 x 0.36 mm^3
Theta range for data collection	2.13 to 28.33°.
Index ranges	-12<=h<=12, -14<=k<=12, -24<=l<=24
Reflections collected	27629
Independent reflections	9115 [R(int) = 0.0213]
Completeness to theta = 25.00°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9647 and 0.9608
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9115 / 0 / 429
Goodness-of-fit on F^2	1.071
Final R indices [I>2sigma(I)]	R1 = 0.0372, wR2 = 0.0990
R indices (all data)	R1 = 0.0461, wR2 = 0.1094
Largest diff. peak and hole	0.376 and -0.252 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ltp216s. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	8540(1)	7118(1)	1532(1)	20(1)
C(2)	8996(1)	5897(1)	1151(1)	24(1)
C(3)	8310(1)	6082(1)	474(1)	24(1)
C(4)	6645(1)	6582(1)	665(1)	24(1)
C(5)	6187(1)	7798(1)	1048(1)	18(1)
C(6)	6868(1)	7615(1)	1731(1)	14(1)
C(7)	6356(1)	8812(1)	2140(1)	13(1)
C(8)	7384(1)	11754(1)	632(1)	17(1)
C(9)	9041(1)	11381(2)	618(1)	30(1)
C(10)	7107(1)	11071(1)	48(1)	23(1)
C(11)	4384(1)	11768(1)	1670(1)	15(1)
C(12)	3426(1)	12704(1)	2105(1)	19(1)
C(13)	1929(1)	13097(1)	2096(1)	23(1)

C(14)	1344(1)	12547(1)	1664(1)	22(1)
C(15)	2263(1)	11595(1)	1242(1)	20(1)
C(16)	3757(1)	11214(1)	1245(1)	19(1)
C(17)	7014(1)	12027(1)	2268(1)	16(1)
C(18)	8091(1)	11301(1)	2664(1)	17(1)
C(19)	8604(1)	11836(1)	3143(1)	21(1)
C(20)	8045(1)	13114(1)	3240(1)	23(1)
C(21)	7000(1)	13860(1)	2845(1)	23(1)
C(22)	6503(1)	13324(1)	2362(1)	20(1)
C(23)	6730(1)	8588(1)	2908(1)	15(1)
C(24)	5851(1)	7770(1)	3448(1)	15(1)
C(25)	6774(1)	6952(1)	4000(1)	17(1)
C(26)	9380(1)	5998(1)	3692(1)	29(1)
C(27)	6492(2)	5694(2)	5136(1)	34(1)
C(28)	4415(1)	9214(1)	4389(1)	18(1)
C(29)	3038(1)	10279(1)	4546(1)	18(1)
C(30)	2651(1)	11242(1)	4002(1)	25(1)
C(31)	1359(2)	12197(1)	4143(1)	32(1)
C(32)	440(2)	12201(1)	4827(1)	33(1)
C(33)	820(1)	11255(1)	5372(1)	30(1)
C(34)	2112(1)	10297(1)	5233(1)	23(1)
C(35)	3224(1)	7924(1)	3928(1)	19(1)
C(36)	2848(1)	7682(1)	3233(1)	17(1)
C(37)	2167(1)	8692(1)	2780(1)	22(1)
C(38)	1778(1)	8482(1)	2149(1)	26(1)
C(39)	2090(1)	7261(1)	1956(1)	25(1)
C(40)	2788(1)	6254(1)	2393(1)	26(1)
C(41)	3154(1)	6464(1)	3031(1)	22(1)
C(42)	6852(2)	13186(1)	443(1)	32(1)
N(1)	4404(1)	8567(1)	3765(1)	15(1)
O(1)	7042(1)	9739(1)	1699(1)	15(1)
O(2)	7945(1)	6057(1)	3602(1)	22(1)
O(3)	5866(1)	6331(1)	4520(1)	23(1)
Si(1)	6432(1)	11282(1)	1590(1)	13(1)

Table 3. Bond lengths [Å] and angles [°] for ltp216s.

C(1)-C(6)	1.5309(15)
C(1)-C(2)	1.5322(16)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(3)	1.5252(18)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900

C(3)-C(4)	1.5238(18)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.5293(16)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.5310(15)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(7)	1.5347(15)
C(6)-H(6)	1.0000
C(7)-O(1)	1.4418(13)
C(7)-C(23)	1.5305(14)
C(7)-H(7)	1.0000
C(8)-C(9)	1.5340(17)
C(8)-C(10)	1.5351(15)
C(8)-C(42)	1.5352(18)
C(8)-Si(1)	1.8967(12)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-C(12)	1.4001(16)
C(11)-C(16)	1.4061(15)
C(11)-Si(1)	1.8774(11)
C(12)-C(13)	1.3925(17)
C(12)-H(12)	0.9500
C(13)-C(14)	1.3843(17)
C(13)-H(13)	0.9500
C(14)-C(15)	1.3866(17)
C(14)-H(14)	0.9500
C(15)-C(16)	1.3882(16)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(17)-C(18)	1.4046(16)
C(17)-C(22)	1.4051(16)
C(17)-Si(1)	1.8826(11)
C(18)-C(19)	1.3957(16)
C(18)-H(18)	0.9500
C(19)-C(20)	1.3885(18)
C(19)-H(19)	0.9500
C(20)-C(21)	1.3877(18)

C(20)-H(20)	0.9500
C(21)-C(22)	1.3929(16)
C(21)-H(21)	0.9500
C(22)-H(22)	0.9500
C(23)-C(24)	1.5370(15)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-N(1)	1.4710(14)
C(24)-C(25)	1.5363(15)
C(24)-H(24)	1.0000
C(25)-O(3)	1.4010(14)
C(25)-O(2)	1.4204(14)
C(25)-H(25)	1.0000
C(26)-O(2)	1.4219(15)
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-O(3)	1.4237(15)
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-N(1)	1.4680(14)
C(28)-C(29)	1.5096(16)
C(28)-H(28A)	0.9900
C(28)-H(28B)	0.9900
C(29)-C(30)	1.3908(17)
C(29)-C(34)	1.3924(17)
C(30)-C(31)	1.3881(18)
C(30)-H(30)	0.9500
C(31)-C(32)	1.387(2)
C(31)-H(31)	0.9500
C(32)-C(33)	1.379(2)
C(32)-H(32)	0.9500
C(33)-C(34)	1.3890(18)
C(33)-H(33)	0.9500
C(34)-H(34)	0.9500
C(35)-N(1)	1.4733(14)
C(35)-C(36)	1.5115(15)
C(35)-H(35A)	0.9900
C(35)-H(35B)	0.9900
C(36)-C(41)	1.3911(17)
C(36)-C(37)	1.3961(16)
C(37)-C(38)	1.3912(17)
C(37)-H(37)	0.9500

C(38)-C(39)	1.3871(19)
C(38)-H(38)	0.9500
C(39)-C(40)	1.3821(19)
C(39)-H(39)	0.9500
C(40)-C(41)	1.3932(17)
C(40)-H(40)	0.9500
C(41)-H(41)	0.9500
C(42)-H(42A)	0.9800
C(42)-H(42B)	0.9800
C(42)-H(42C)	0.9800
O(1)-Si(1)	1.6405(8)

C(6)-C(1)-C(2)	111.41(10)
C(6)-C(1)-H(1A)	109.3
C(2)-C(1)-H(1A)	109.3
C(6)-C(1)-H(1B)	109.3
C(2)-C(1)-H(1B)	109.3
H(1A)-C(1)-H(1B)	108.0
C(3)-C(2)-C(1)	111.21(10)
C(3)-C(2)-H(2A)	109.4
C(1)-C(2)-H(2A)	109.4
C(3)-C(2)-H(2B)	109.4
C(1)-C(2)-H(2B)	109.4
H(2A)-C(2)-H(2B)	108.0
C(4)-C(3)-C(2)	111.30(10)
C(4)-C(3)-H(3A)	109.4
C(2)-C(3)-H(3A)	109.4
C(4)-C(3)-H(3B)	109.4
C(2)-C(3)-H(3B)	109.4
H(3A)-C(3)-H(3B)	108.0
C(3)-C(4)-C(5)	111.43(10)
C(3)-C(4)-H(4A)	109.3
C(5)-C(4)-H(4A)	109.3
C(3)-C(4)-H(4B)	109.3
C(5)-C(4)-H(4B)	109.3
H(4A)-C(4)-H(4B)	108.0
C(4)-C(5)-C(6)	111.55(10)
C(4)-C(5)-H(5A)	109.3
C(6)-C(5)-H(5A)	109.3
C(4)-C(5)-H(5B)	109.3
C(6)-C(5)-H(5B)	109.3
H(5A)-C(5)-H(5B)	108.0
C(1)-C(6)-C(5)	110.53(9)
C(1)-C(6)-C(7)	113.36(9)

C(5)-C(6)-C(7)	111.88(9)
C(1)-C(6)-H(6)	106.9
C(5)-C(6)-H(6)	106.9
C(7)-C(6)-H(6)	106.9
O(1)-C(7)-C(23)	109.46(8)
O(1)-C(7)-C(6)	107.90(8)
C(23)-C(7)-C(6)	113.42(9)
O(1)-C(7)-H(7)	108.7
C(23)-C(7)-H(7)	108.7
C(6)-C(7)-H(7)	108.7
C(9)-C(8)-C(10)	108.33(10)
C(9)-C(8)-C(42)	109.35(11)
C(10)-C(8)-C(42)	109.03(10)
C(9)-C(8)-Si(1)	108.07(8)
C(10)-C(8)-Si(1)	111.62(8)
C(42)-C(8)-Si(1)	110.40(8)
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(12)-C(11)-C(16)	116.89(10)
C(12)-C(11)-Si(1)	124.10(9)
C(16)-C(11)-Si(1)	118.93(8)
C(13)-C(12)-C(11)	121.48(11)
C(13)-C(12)-H(12)	119.3
C(11)-C(12)-H(12)	119.3
C(14)-C(13)-C(12)	120.38(11)
C(14)-C(13)-H(13)	119.8
C(12)-C(13)-H(13)	119.8
C(13)-C(14)-C(15)	119.36(11)
C(13)-C(14)-H(14)	120.3
C(15)-C(14)-H(14)	120.3
C(14)-C(15)-C(16)	120.24(11)
C(14)-C(15)-H(15)	119.9
C(16)-C(15)-H(15)	119.9
C(15)-C(16)-C(11)	121.63(11)

C(15)-C(16)-H(16)	119.2
C(11)-C(16)-H(16)	119.2
C(18)-C(17)-C(22)	116.89(10)
C(18)-C(17)-Si(1)	119.99(9)
C(22)-C(17)-Si(1)	122.93(8)
C(19)-C(18)-C(17)	121.57(11)
C(19)-C(18)-H(18)	119.2
C(17)-C(18)-H(18)	119.2
C(20)-C(19)-C(18)	120.05(11)
C(20)-C(19)-H(19)	120.0
C(18)-C(19)-H(19)	120.0
C(21)-C(20)-C(19)	119.67(11)
C(21)-C(20)-H(20)	120.2
C(19)-C(20)-H(20)	120.2
C(20)-C(21)-C(22)	120.02(11)
C(20)-C(21)-H(21)	120.0
C(22)-C(21)-H(21)	120.0
C(21)-C(22)-C(17)	121.75(11)
C(21)-C(22)-H(22)	119.1
C(17)-C(22)-H(22)	119.1
C(7)-C(23)-C(24)	112.63(9)
C(7)-C(23)-H(23A)	109.1
C(24)-C(23)-H(23A)	109.1
C(7)-C(23)-H(23B)	109.1
C(24)-C(23)-H(23B)	109.1
H(23A)-C(23)-H(23B)	107.8
N(1)-C(24)-C(25)	116.09(9)
N(1)-C(24)-C(23)	109.71(9)
C(25)-C(24)-C(23)	110.36(9)
N(1)-C(24)-H(24)	106.7
C(25)-C(24)-H(24)	106.7
C(23)-C(24)-H(24)	106.7
O(3)-C(25)-O(2)	110.11(9)
O(3)-C(25)-C(24)	107.52(9)
O(2)-C(25)-C(24)	107.32(9)
O(3)-C(25)-H(25)	110.6
O(2)-C(25)-H(25)	110.6
C(24)-C(25)-H(25)	110.6
O(2)-C(26)-H(26A)	109.5
O(2)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
O(2)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5

O(3)-C(27)-H(27A)	109.5
O(3)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
O(3)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
N(1)-C(28)-C(29)	110.99(9)
N(1)-C(28)-H(28A)	109.4
C(29)-C(28)-H(28A)	109.4
N(1)-C(28)-H(28B)	109.4
C(29)-C(28)-H(28B)	109.4
H(28A)-C(28)-H(28B)	108.0
C(30)-C(29)-C(34)	118.86(11)
C(30)-C(29)-C(28)	120.61(11)
C(34)-C(29)-C(28)	120.52(11)
C(31)-C(30)-C(29)	120.31(12)
C(31)-C(30)-H(30)	119.8
C(29)-C(30)-H(30)	119.8
C(32)-C(31)-C(30)	120.35(13)
C(32)-C(31)-H(31)	119.8
C(30)-C(31)-H(31)	119.8
C(33)-C(32)-C(31)	119.73(13)
C(33)-C(32)-H(32)	120.1
C(31)-C(32)-H(32)	120.1
C(32)-C(33)-C(34)	120.12(13)
C(32)-C(33)-H(33)	119.9
C(34)-C(33)-H(33)	119.9
C(33)-C(34)-C(29)	120.64(13)
C(33)-C(34)-H(34)	119.7
C(29)-C(34)-H(34)	119.7
N(1)-C(35)-C(36)	111.64(9)
N(1)-C(35)-H(35A)	109.3
C(36)-C(35)-H(35A)	109.3
N(1)-C(35)-H(35B)	109.3
C(36)-C(35)-H(35B)	109.3
H(35A)-C(35)-H(35B)	108.0
C(41)-C(36)-C(37)	118.47(11)
C(41)-C(36)-C(35)	121.49(11)
C(37)-C(36)-C(35)	120.04(11)
C(38)-C(37)-C(36)	120.68(12)
C(38)-C(37)-H(37)	119.7
C(36)-C(37)-H(37)	119.7
C(39)-C(38)-C(37)	120.08(12)
C(39)-C(38)-H(38)	120.0

C(37)-C(38)-H(38)	120.0
C(40)-C(39)-C(38)	119.83(12)
C(40)-C(39)-H(39)	120.1
C(38)-C(39)-H(39)	120.1
C(39)-C(40)-C(41)	120.03(12)
C(39)-C(40)-H(40)	120.0
C(41)-C(40)-H(40)	120.0
C(36)-C(41)-C(40)	120.89(12)
C(36)-C(41)-H(41)	119.6
C(40)-C(41)-H(41)	119.6
C(8)-C(42)-H(42A)	109.5
C(8)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5
C(8)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
C(28)-N(1)-C(24)	113.98(9)
C(28)-N(1)-C(35)	111.95(9)
C(24)-N(1)-C(35)	113.89(9)
C(7)-O(1)-Si(1)	130.37(7)
C(25)-O(2)-C(26)	116.03(9)
C(25)-O(3)-C(27)	114.14(10)
O(1)-Si(1)-C(11)	110.45(5)
O(1)-Si(1)-C(17)	110.38(5)
C(11)-Si(1)-C(17)	111.69(5)
O(1)-Si(1)-C(8)	105.03(5)
C(11)-Si(1)-C(8)	111.05(5)
C(17)-Si(1)-C(8)	108.01(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for ltp216s. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	18(1)	20(1)	20(1)	-6(1)	-4(1)	0(1)
C(2)	24(1)	18(1)	25(1)	-6(1)	0(1)	2(1)
C(3)	28(1)	20(1)	23(1)	-9(1)	2(1)	-6(1)
C(4)	28(1)	21(1)	25(1)	-10(1)	-4(1)	-8(1)
C(5)	20(1)	17(1)	20(1)	-5(1)	-6(1)	-4(1)
C(6)	16(1)	11(1)	15(1)	-2(1)	-2(1)	-3(1)
C(7)	13(1)	12(1)	15(1)	-2(1)	-1(1)	-4(1)
C(8)	20(1)	17(1)	16(1)	-1(1)	-3(1)	-8(1)

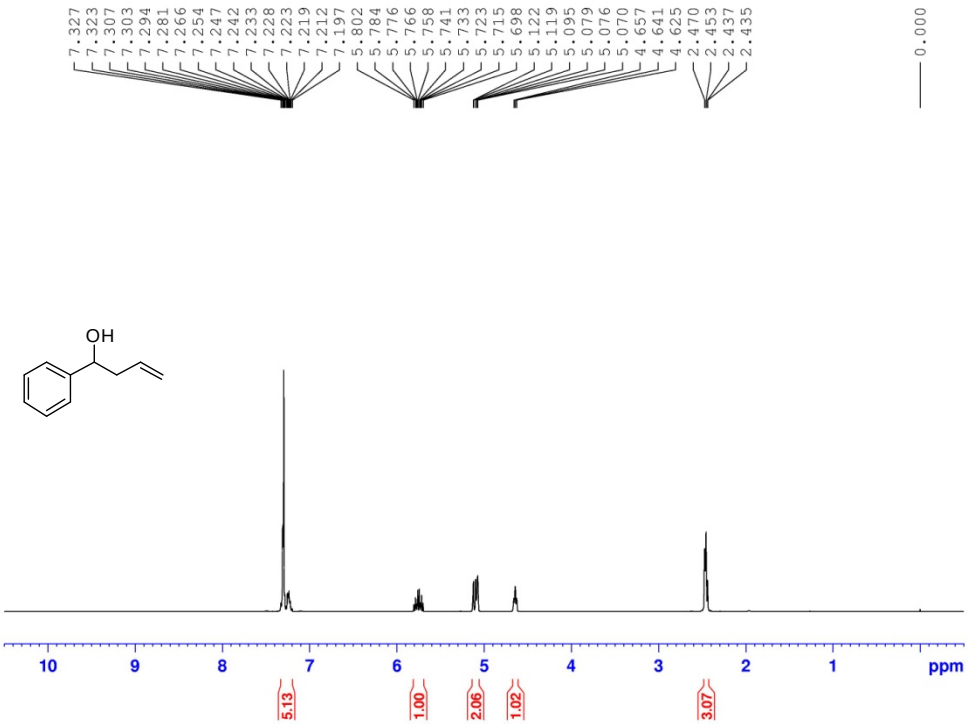
C(9)	21(1)	48(1)	23(1)	-7(1)	1(1)	-16(1)
C(10)	30(1)	26(1)	16(1)	-3(1)	-4(1)	-13(1)
C(11)	15(1)	12(1)	17(1)	1(1)	-4(1)	-4(1)
C(12)	19(1)	19(1)	21(1)	-5(1)	-3(1)	-6(1)
C(13)	18(1)	22(1)	28(1)	-9(1)	0(1)	-2(1)
C(14)	15(1)	21(1)	29(1)	-1(1)	-6(1)	-2(1)
C(15)	19(1)	20(1)	26(1)	-3(1)	-8(1)	-6(1)
C(16)	18(1)	16(1)	22(1)	-5(1)	-4(1)	-2(1)
C(17)	16(1)	16(1)	16(1)	-2(1)	-2(1)	-7(1)
C(18)	18(1)	16(1)	18(1)	-1(1)	-3(1)	-7(1)
C(19)	23(1)	25(1)	19(1)	1(1)	-8(1)	-10(1)
C(20)	28(1)	27(1)	21(1)	-7(1)	-6(1)	-13(1)
C(21)	26(1)	18(1)	27(1)	-8(1)	-4(1)	-7(1)
C(22)	21(1)	16(1)	23(1)	-3(1)	-6(1)	-5(1)
C(23)	16(1)	16(1)	15(1)	-3(1)	-2(1)	-6(1)
C(24)	15(1)	15(1)	15(1)	-3(1)	-2(1)	-5(1)
C(25)	18(1)	14(1)	19(1)	-2(1)	-3(1)	-4(1)
C(26)	20(1)	27(1)	38(1)	-9(1)	-6(1)	2(1)
C(27)	38(1)	35(1)	30(1)	16(1)	-15(1)	-14(1)
C(28)	18(1)	21(1)	15(1)	-4(1)	-4(1)	-4(1)
C(29)	17(1)	20(1)	19(1)	-6(1)	-4(1)	-4(1)
C(30)	26(1)	25(1)	23(1)	-4(1)	-5(1)	-3(1)
C(31)	32(1)	24(1)	38(1)	-5(1)	-14(1)	1(1)
C(32)	20(1)	31(1)	48(1)	-20(1)	-9(1)	3(1)
C(33)	19(1)	41(1)	31(1)	-17(1)	2(1)	-8(1)
C(34)	20(1)	28(1)	22(1)	-7(1)	-2(1)	-8(1)
C(35)	17(1)	24(1)	16(1)	0(1)	-2(1)	-9(1)
C(36)	14(1)	20(1)	18(1)	-1(1)	-2(1)	-6(1)
C(37)	22(1)	19(1)	23(1)	-2(1)	-5(1)	-4(1)
C(38)	27(1)	28(1)	22(1)	3(1)	-10(1)	-6(1)
C(39)	25(1)	34(1)	20(1)	-4(1)	-6(1)	-13(1)
C(40)	27(1)	23(1)	32(1)	-8(1)	-6(1)	-10(1)
C(41)	22(1)	20(1)	27(1)	1(1)	-8(1)	-7(1)
C(42)	52(1)	19(1)	24(1)	3(1)	-3(1)	-15(1)
N(1)	14(1)	18(1)	15(1)	-4(1)	-2(1)	-5(1)
O(1)	15(1)	11(1)	17(1)	-1(1)	-1(1)	-4(1)
O(2)	21(1)	17(1)	29(1)	-8(1)	-6(1)	-1(1)
O(3)	24(1)	23(1)	21(1)	7(1)	-7(1)	-9(1)
Si(1)	13(1)	11(1)	14(1)	-2(1)	-3(1)	-3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for ltp216s.

	x	y	z	U(eq)
H(1A)	8955	6956	1984	24
H(1B)	8947	7767	1202	24
H(2A)	10079	5629	1004	29
H(2B)	8684	5221	1501	29
H(3A)	8714	6685	100	28
H(3B)	8568	5266	259	28
H(4A)	6231	5934	992	28
H(4B)	6239	6749	210	28
H(5A)	5104	8066	1194	22
H(5B)	6501	8475	701	22
H(6)	6503	6944	2074	17
H(7)	5268	9146	2188	16
H(9A)	9378	10471	752	45
H(9B)	9245	11843	970	45
H(9C)	9559	11591	123	45
H(10A)	7666	11292	-434	34
H(10B)	6057	11329	33	34
H(10C)	7420	10156	172	34
H(12)	3805	13080	2412	23
H(13)	1306	13747	2388	28
H(14)	324	12818	1657	26
H(15)	1868	11203	950	25
H(16)	4372	10561	952	22
H(18)	8479	10425	2605	21
H(19)	9335	11326	3404	25
H(20)	8376	13475	3574	28
H(21)	6625	14737	2903	28
H(22)	5800	13848	2089	24
H(23A)	6527	9414	3104	18
H(23B)	7792	8170	2870	18
H(24)	5669	7177	3151	18
H(25)	7162	7486	4245	20
H(26A)	9600	6807	3503	44
H(26B)	10097	5323	3419	44
H(26C)	9432	5825	4215	44
H(27A)	7352	5003	4974	51

H(27B)	5765	5351	5495	51
H(27C)	6791	6289	5365	51
H(28A)	5284	9554	4278	21
H(28B)	4492	8601	4830	21
H(30)	3274	11246	3531	30
H(31)	1103	12853	3768	38
H(32)	-447	12852	4921	40
H(33)	197	11257	5842	36
H(34)	2367	9648	5611	27
H(35A)	2338	8451	4225	22
H(35B)	3539	7110	4223	22
H(37)	1966	9532	2904	26
H(38)	1299	9175	1850	31
H(39)	1825	7117	1526	30
H(40)	3019	5418	2257	31
H(41)	3620	5767	3333	27
H(42A)	7093	13628	793	47
H(42B)	5786	13431	474	47
H(42C)	7336	13413	-56	47

NMR Spectra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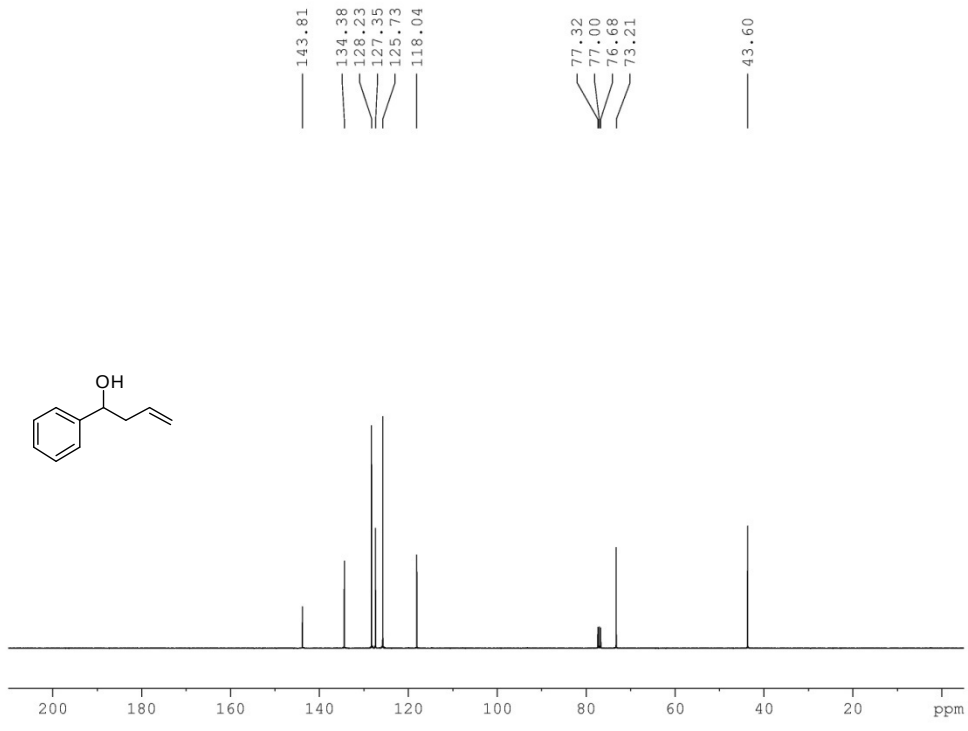
7.223
7.219
7.212
7.197
5.802
5.784
5.776
5.766
5.758
5.741
5.733
5.723
5.715
5.698
5.122
5.119
5.095
5.079
5.076
5.070
4.657
4.641
4.625
2.470
2.453
2.437
2.435
0.000
OH
10
9
8
7
6
5
4
3
2
1
ppm
5.13
1.00
2.06
1.02
3.07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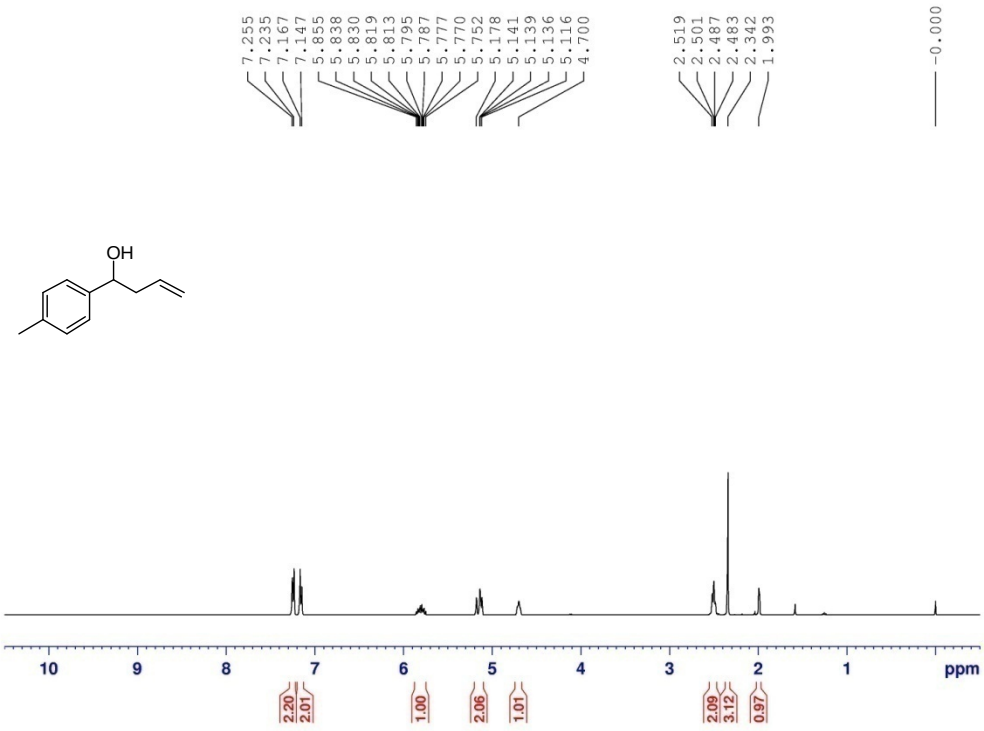
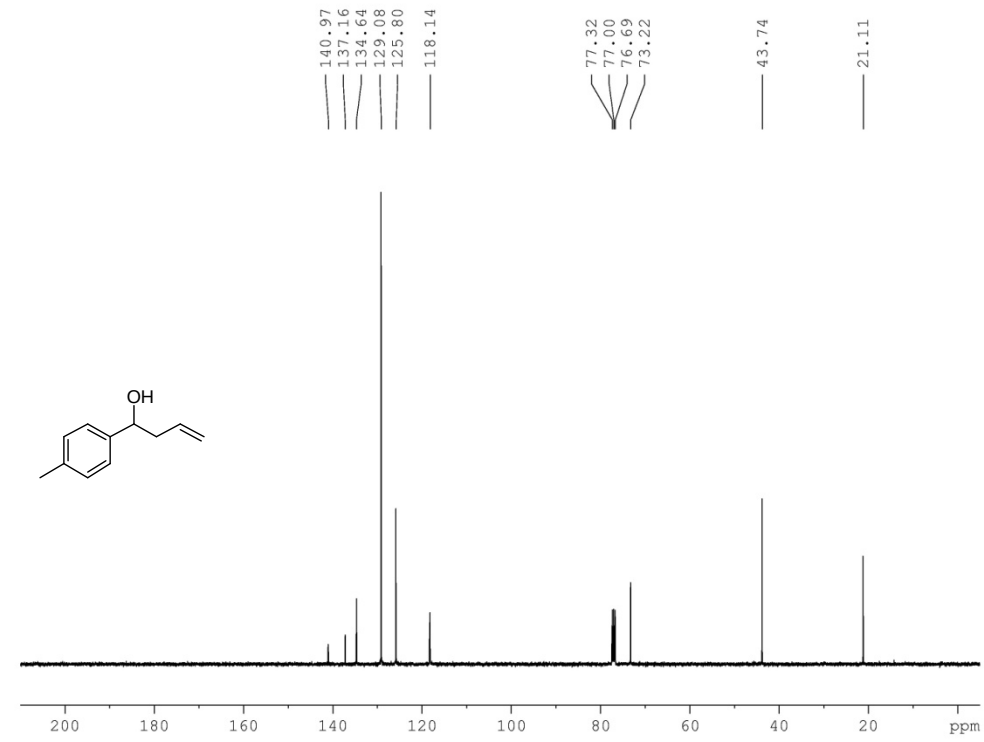
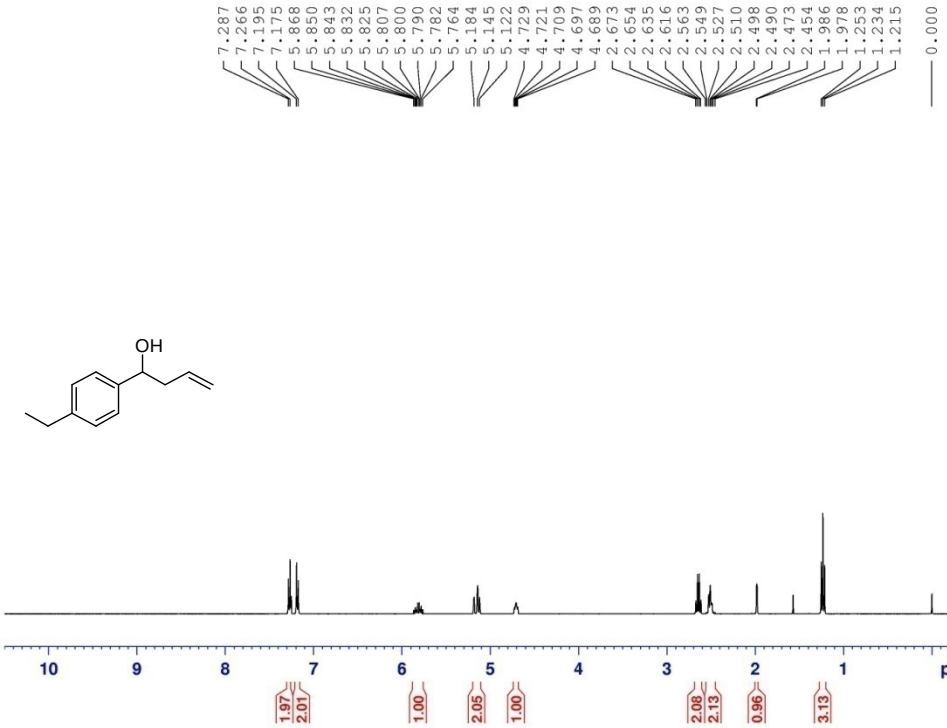
134.38
128.23
127.35
125.73
118.04
77.32
77.00
76.68
73.21
43.60
OH
200
180
160
140
120
100
80
60
40
20
ppm



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5.782
5.764
5.184
5.145
5.122
4.729
4.721
4.709
4.697
4.689
2.673
2.654
2.635
2.616
2.563
2.549
2.527
2.510
2.498
2.490
2.473
2.454
1.986
1.978
1.253
1.234
1.215
0.000
OH
10
9
8
7
6
5
4
3
2
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ppm
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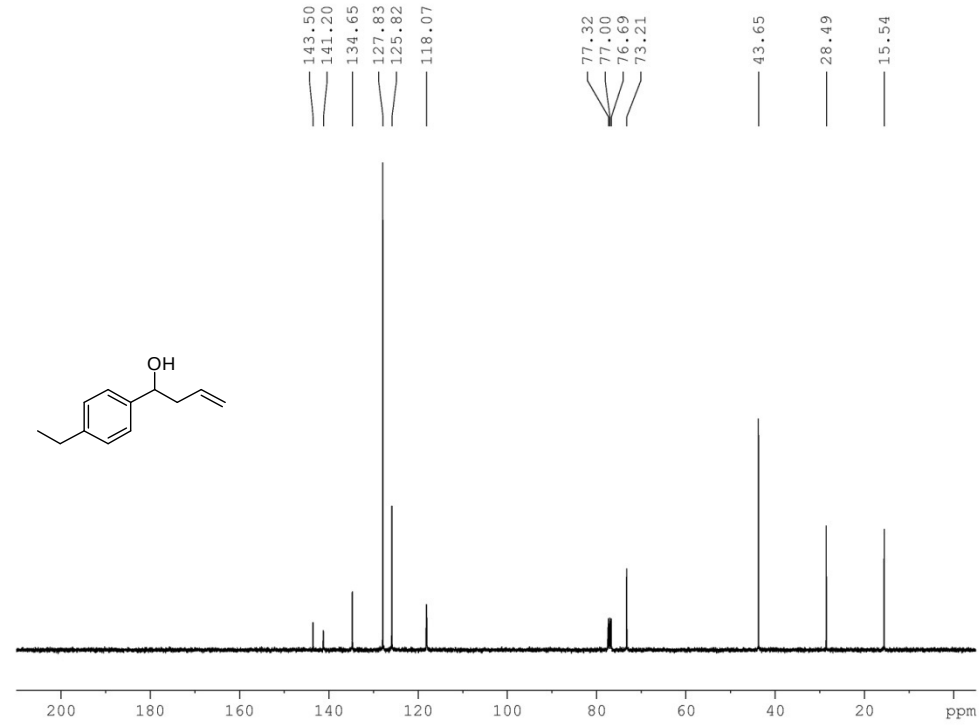
1.00
2.05
1.00
2.08
2.13
0.96
3.13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141.20
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125.82
118.07
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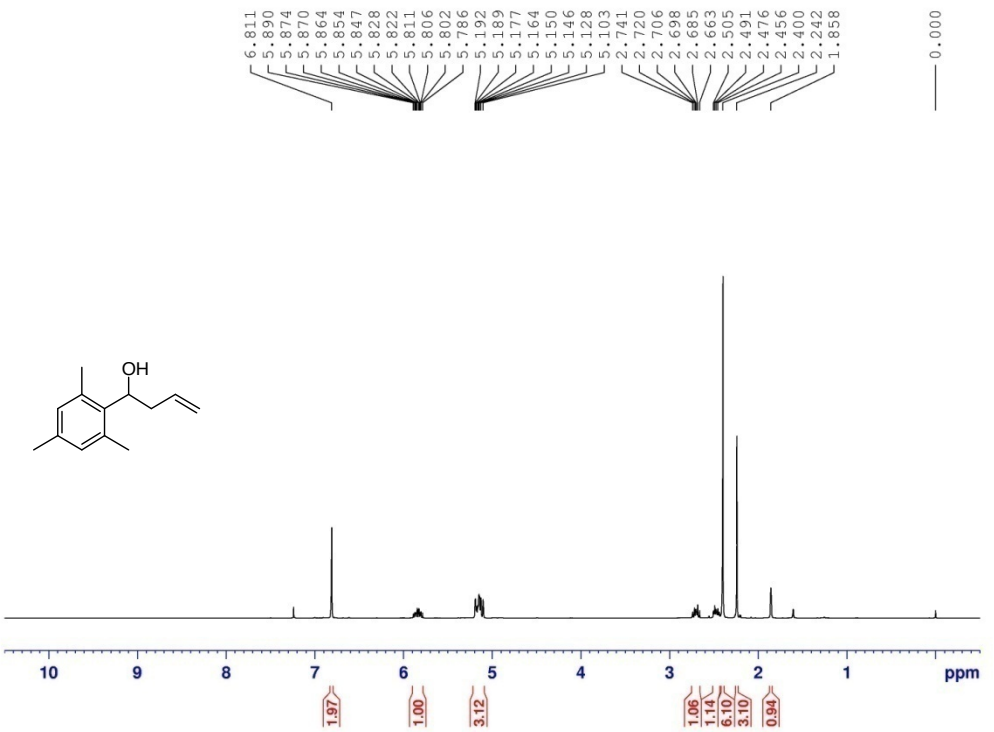
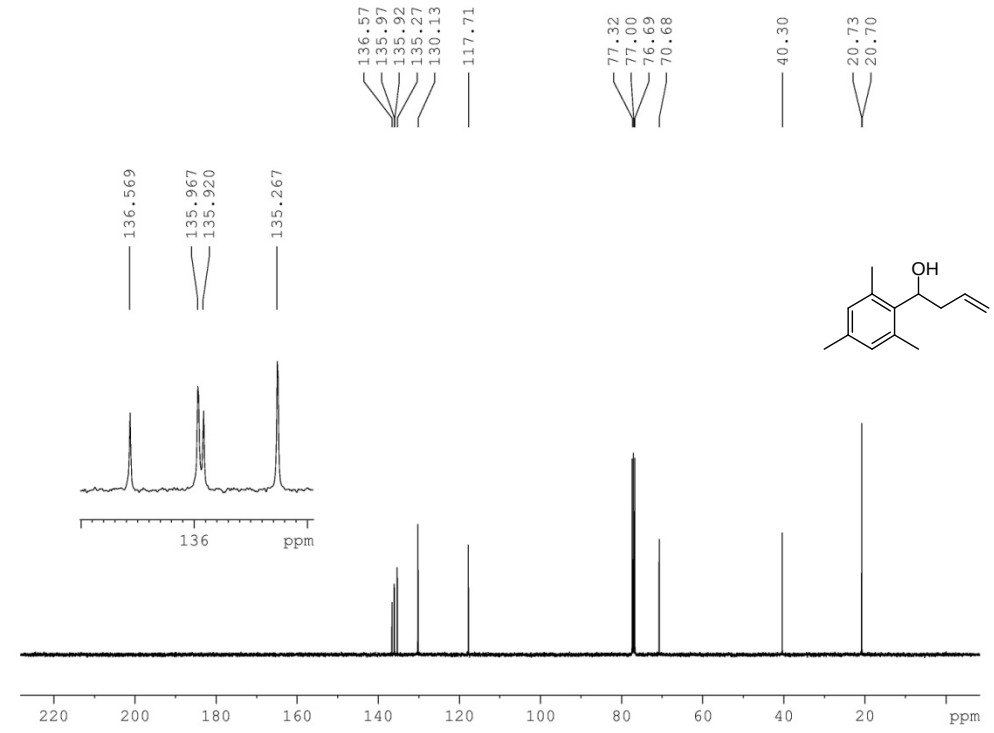
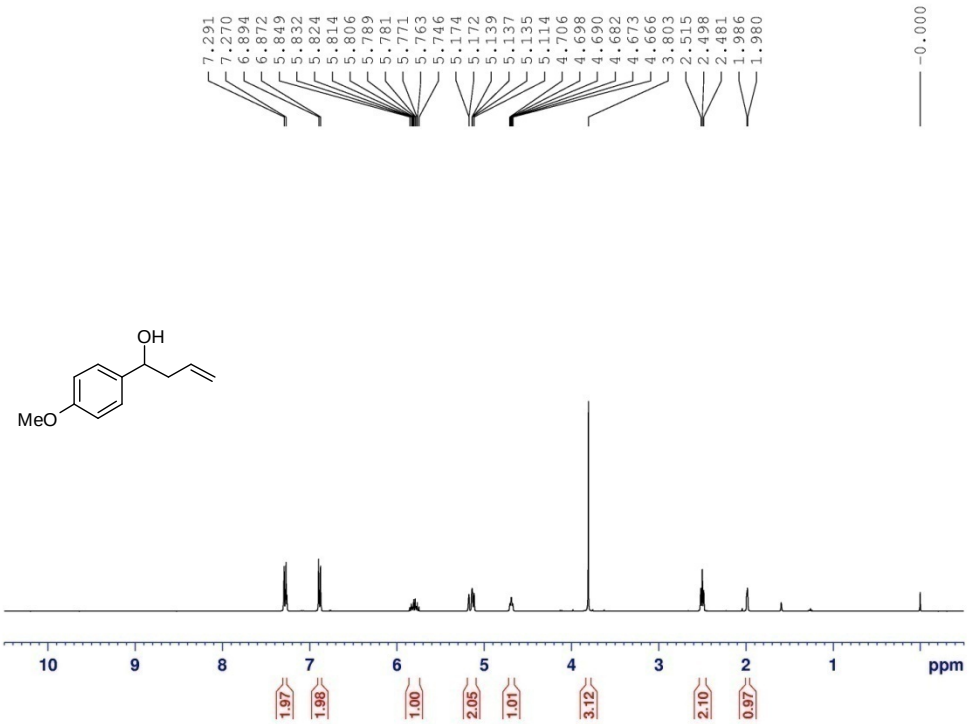
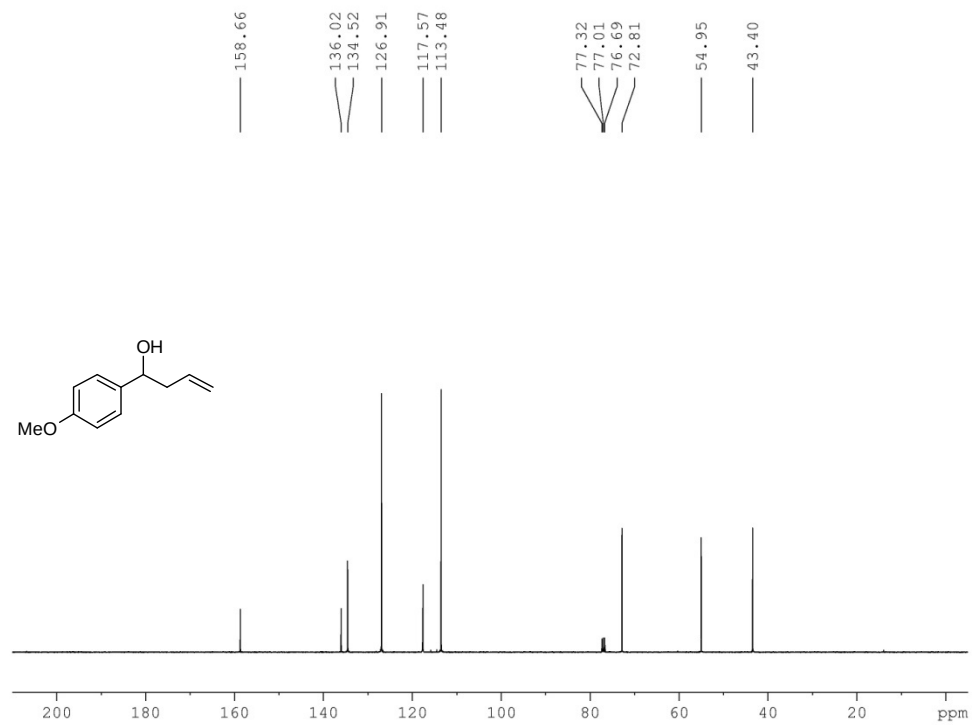
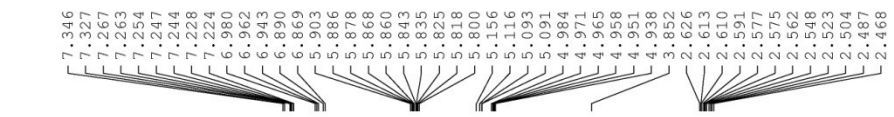
77.00
76.69
73.21
43.65
28.49
15.54
OH
200
180
160
140
120
100
80
60
40
20
ppm







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7.228
7.224
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6.890
6.869
5.903
5.886
5.878
5.868
5.860
5.843
5.835
5.825
5.818
5.800
5.156
5.116
5.093
5.091
4.984
4.971
4.965
4.958
4.951
4.938
3.852
2.626
2.613
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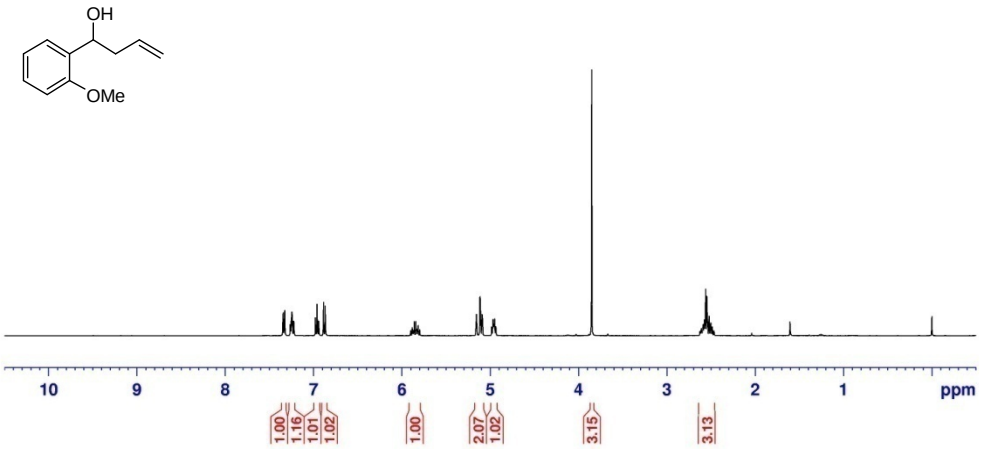
2.591
2.577
2.575
2.562
2.548
2.523
2.504
2.487
2.468


OH
OMe
10
9
8
7
6
5
4
3
2
1
ppm
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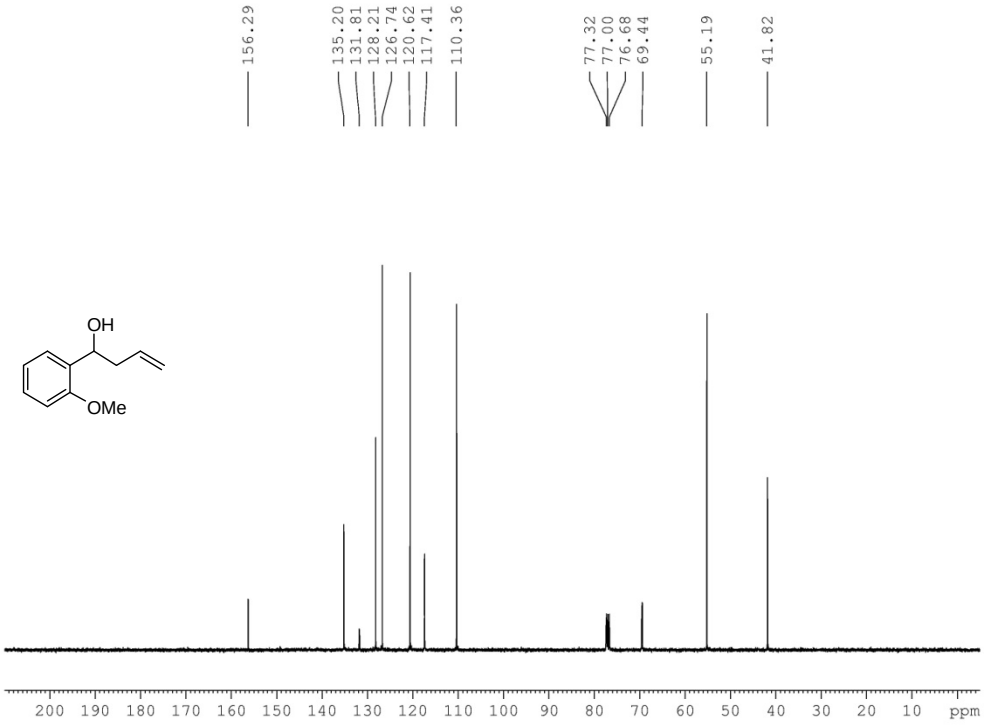
1.16
1.01
1.02
1.00
2.07
1.02
3.15
3.13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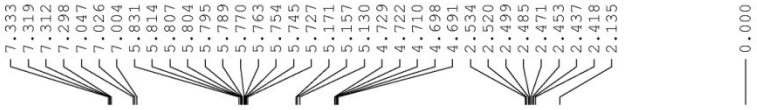
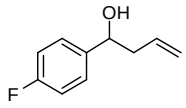
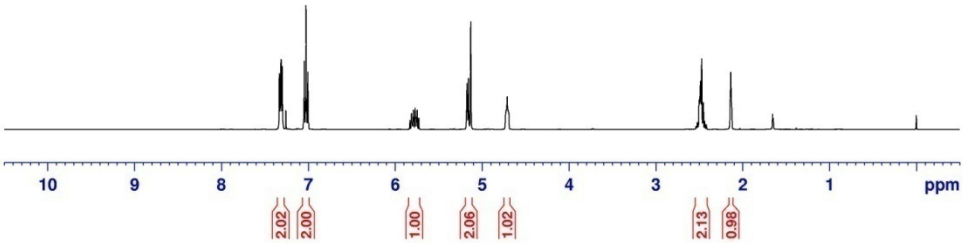
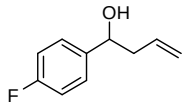
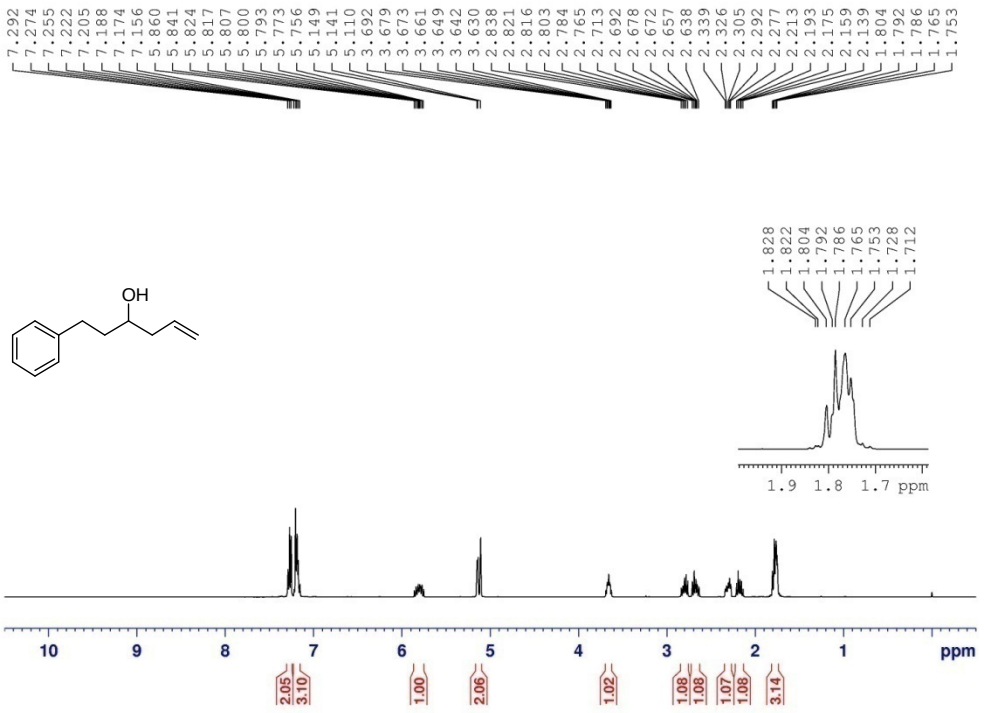
135.20
131.81
128.21
126.74
120.62
117.41
110.36
77.32
77.00
76.68
69.44
55.19
41.82
OH
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm







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5.824
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5.807
5.800
5.793
5.773
5.756
5.149
5.141
5.110
3.692
3.679
3.673
3.661
3.649
3.642
3.630
2.838
2.821
2.816
2.803
2.784
2.765
2.713
2.692
2.678
2.672
2.657
2.638
2.339
2.326
2.305
2.292
2.277
2.213
2.193
2.175
2.159
2.139
1.804
1.792
1.786
1.765
1.753
1.728
1.712
OH
1.828
1.822
1.804
1.792
1.786
1.765
1.753
1.728
1.712
1.9 1.8 1.7 ppm
10 9 8 7 6 5 4 3 2 1 ppm
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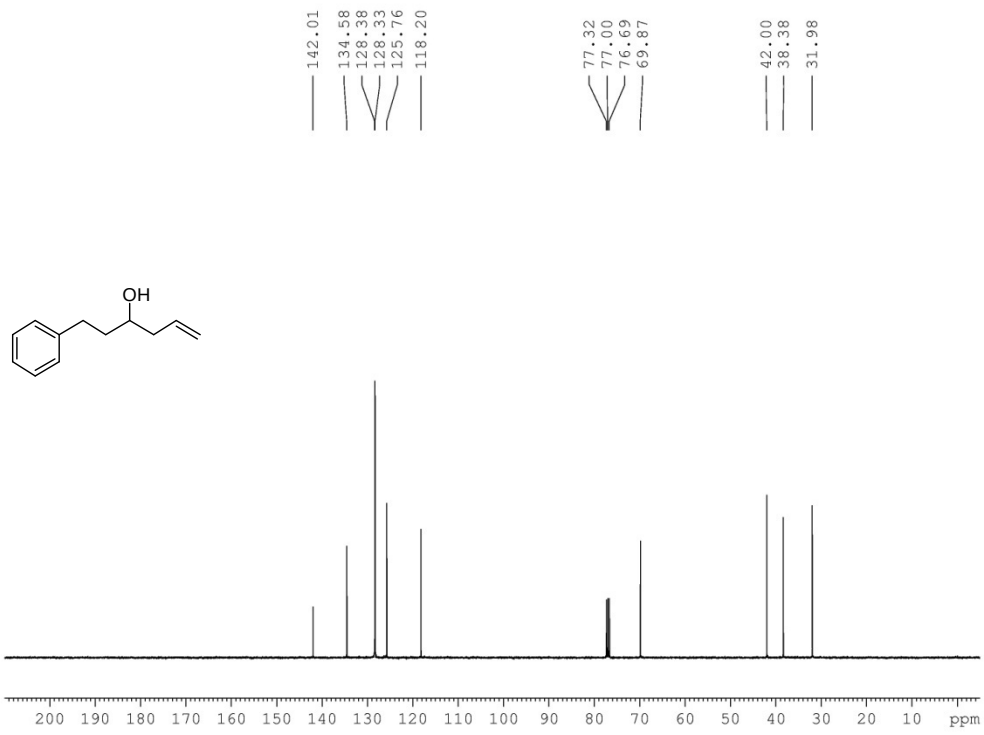
2.06
1.02
1.08
1.08
1.07
1.08
3.14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69.87
42.00
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31.98
OH
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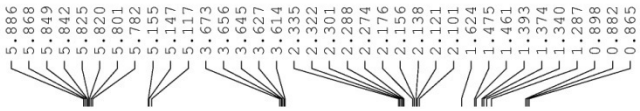

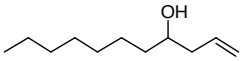

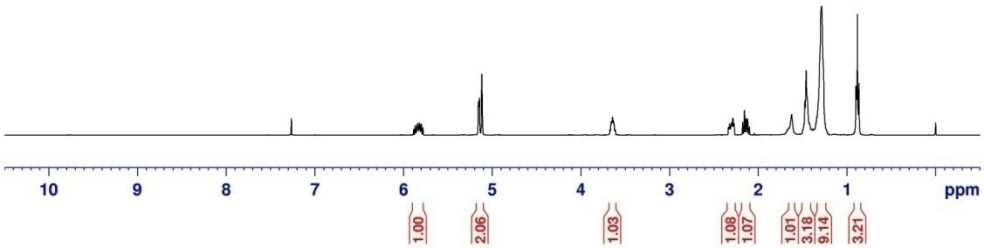

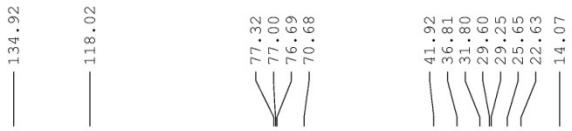

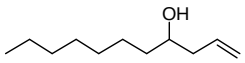

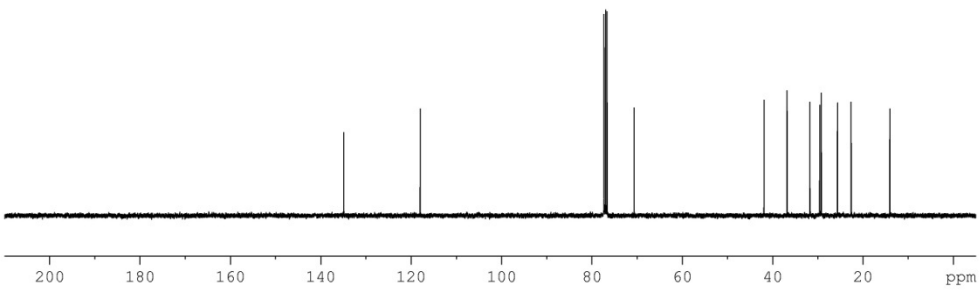

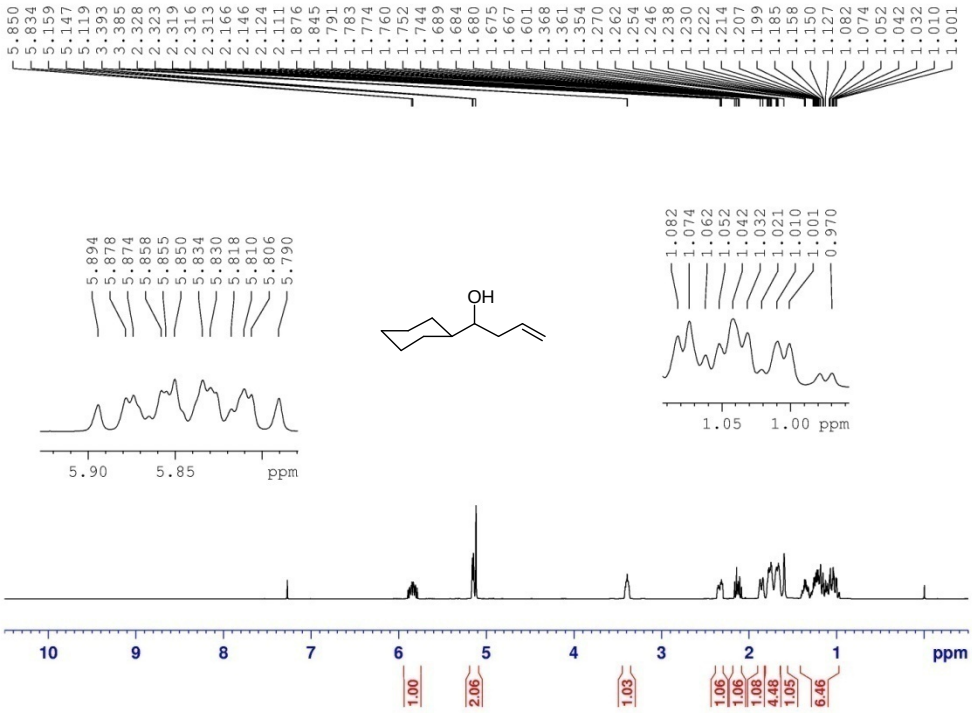
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2.146
2.124
2.111
1.876
1.845
1.791
1.783
1.774
1.760
1.752
1.744
1.689
1.684
1.680
1.675
1.667
1.601
1.368
1.361
1.354
1.270
1.262
1.254
1.246
1.238
1.230
1.222
1.214
1.207
1.199
1.185
1.158
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1.074
1.052
1.042
1.032
1.010
1.001
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5.874
5.858
5.855
5.850
5.834
5.830
5.818
5.810
5.806
5.790
5.90
5.85
ppm
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1.062
1.052
1.042
1.032
1.021
1.010
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0.970
1.05
1.00 ppm
10
9
8
7
6
5
4
3
2
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ppm
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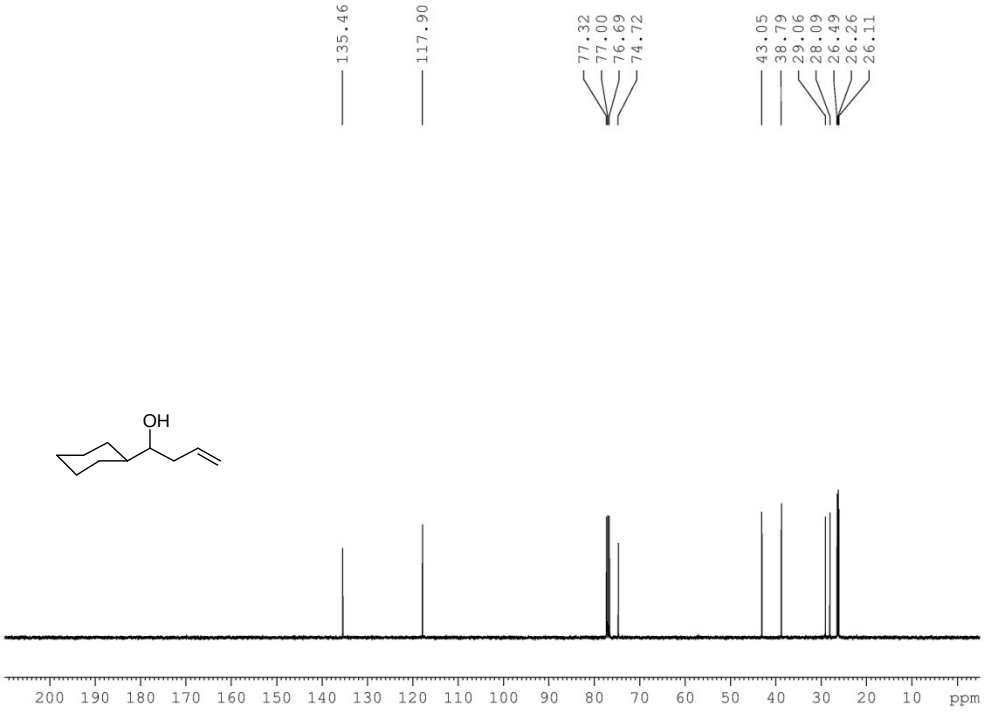
1.03
1.06
1.06
1.08
4.48
1.05
6.46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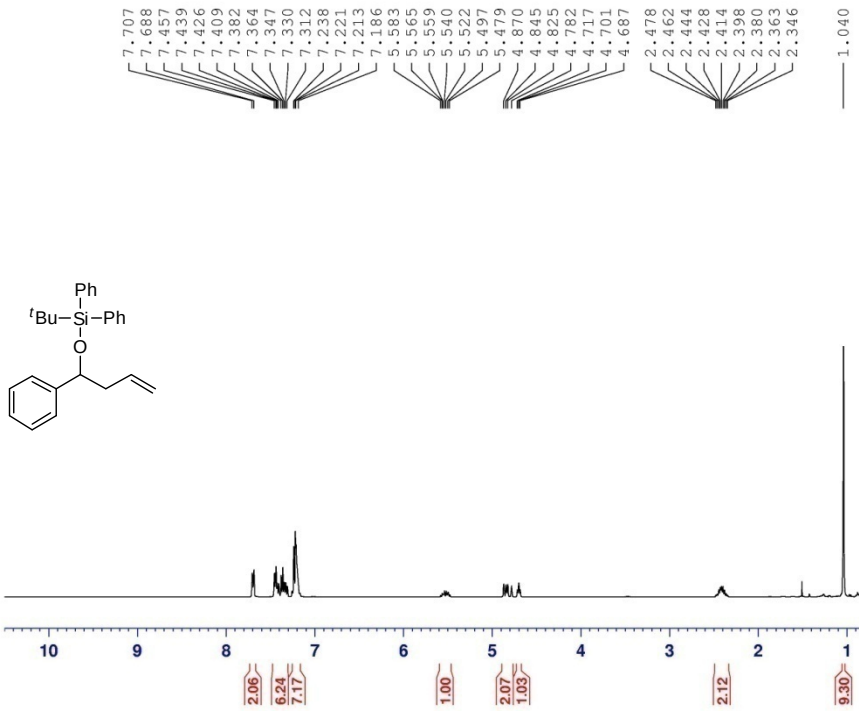
74.72
43.05
38.79
29.06
28.09
26.49
26.26
26.11
OH
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.688
7.457
7.439
7.426
7.409
7.382
7.364
7.347
7.330
7.312
7.238
7.221
7.213
7.186
5.583
5.565
5.559
5.540
5.522
5.497
5.479
4.870
4.845
4.825
4.782
4.717
4.701
4.687
2.478
2.462
2.444
2.428
2.414
2.398
2.380
2.363
2.346
1.040
Ph
tBu–Si–Ph
O
10
9
8
7
6
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ppm
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1.00
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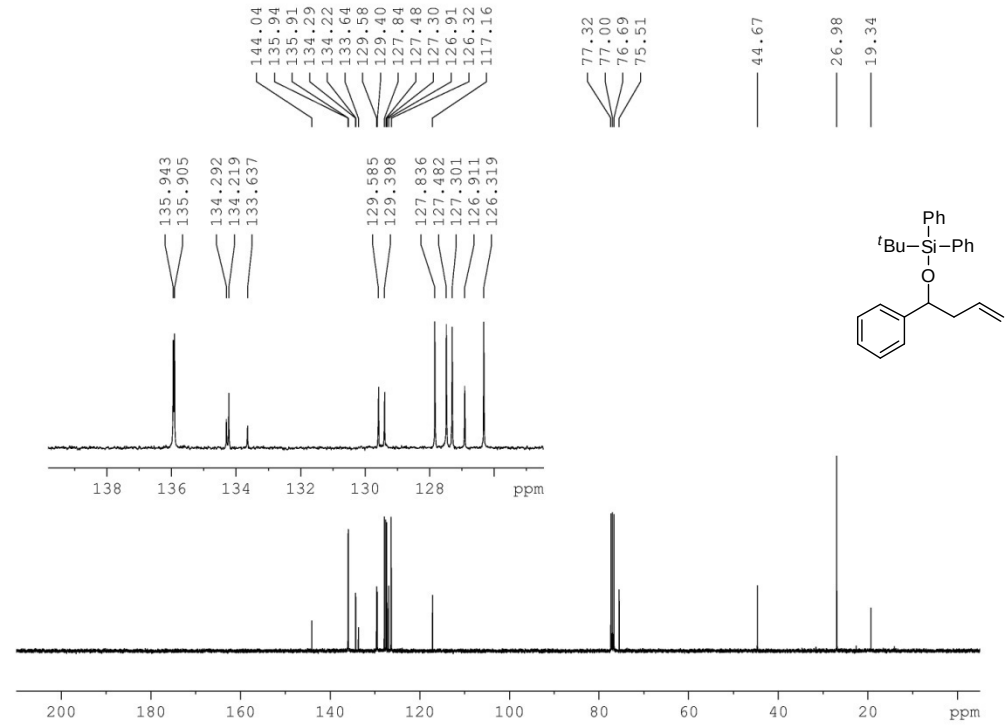
1.03
2.12
9.30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126.91
126.32
117.16
77.32
77.00
76.69
75.51
44.67
26.98
19.34
135.943
135.905
134.292
134.219
133.637
129.585
129.398
127.836
127.482
127.301
126.911
126.319
Ph
tBu–Si–Ph
O
138
136
134
132
130
128
ppm
200
180
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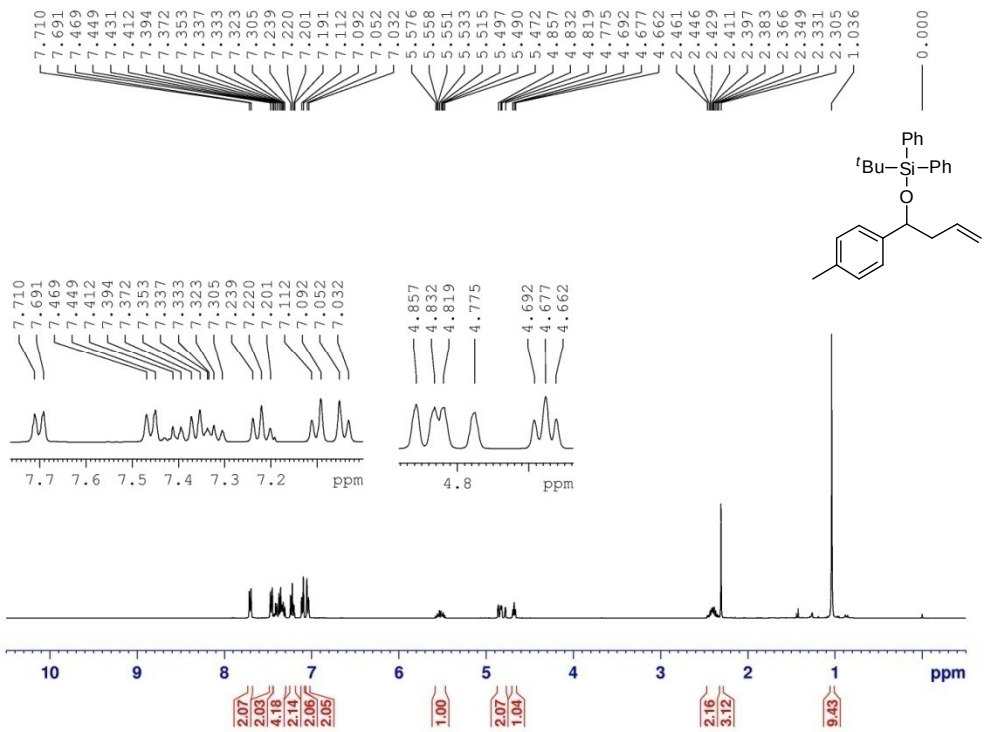
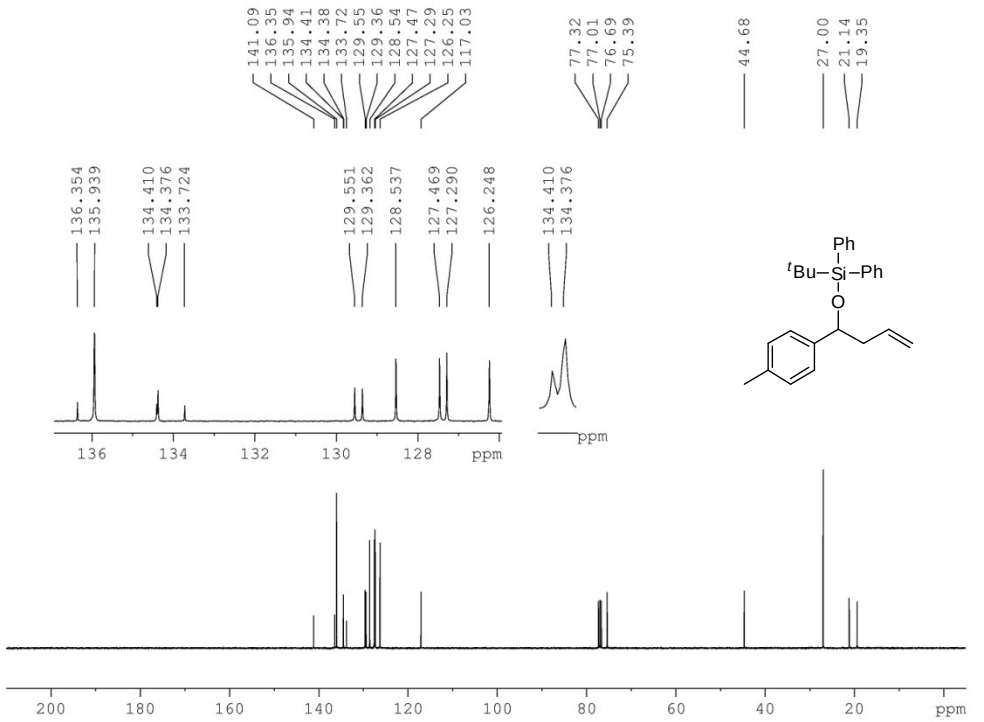
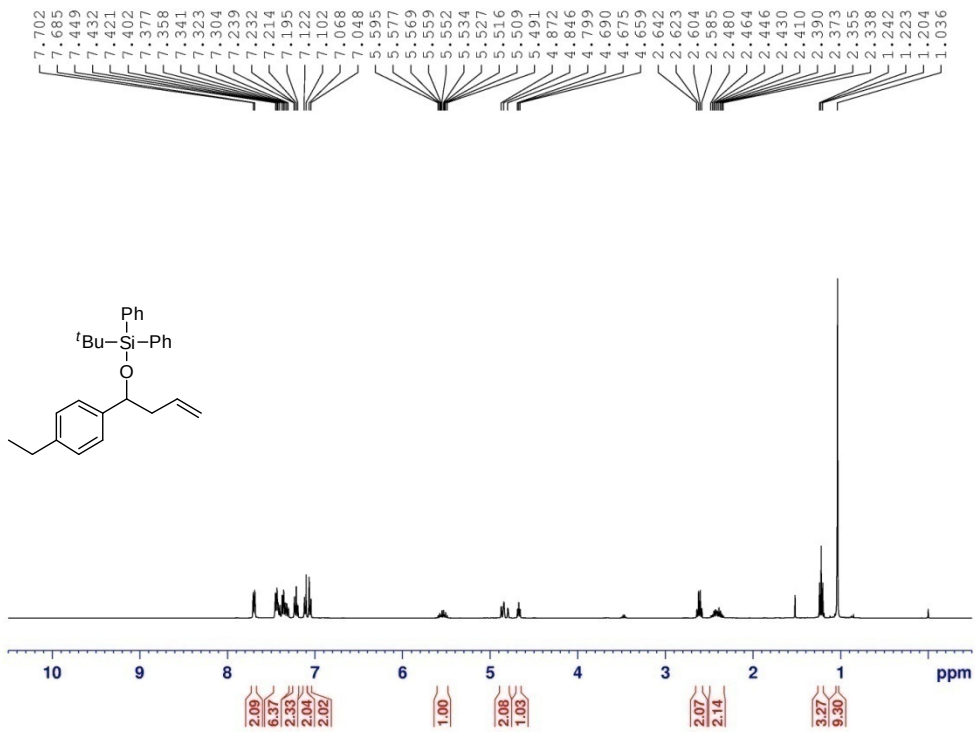
140
120
100
80
60
40
20
ppm



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7.232
7.214
7.195
7.122
7.102
7.068
7.048
5.595
5.577
5.569
5.559
5.552
5.534
5.527
5.516
5.509
5.491
4.872
4.846
4.799
4.690
4.675
4.659
2.642
2.623
2.604
2.585
2.480
2.464
2.446
2.430
2.410
2.390
2.373
2.355
2.338
1.242
1.223
1.204
1.036
Ph
tBu–Si–Ph
O
10
9
8
7
6
5
4
3
2
1
ppm
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1.00
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1.03
2.07
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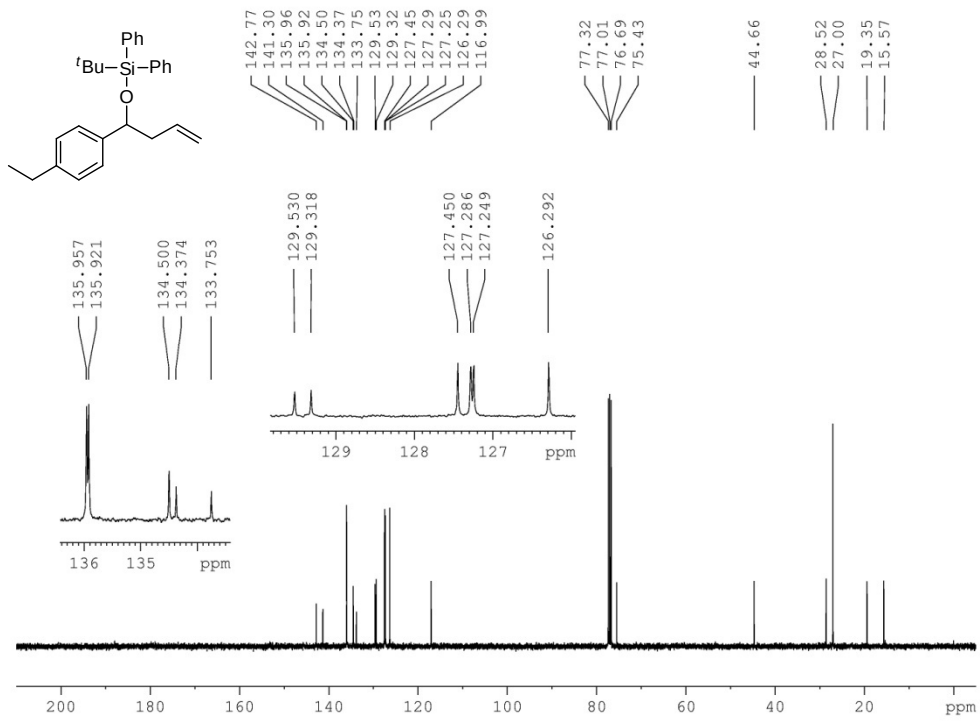
3.27
9.30


Ph
tBu–Si–Ph
O
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127.29
127.25
126.29
116.99
77.32
77.01
76.69
75.43
44.66
28.52
27.00
19.35
15.57
135.957
135.921
134.500
134.374
133.753
129.530
129.318
127.450
127.286
127.249
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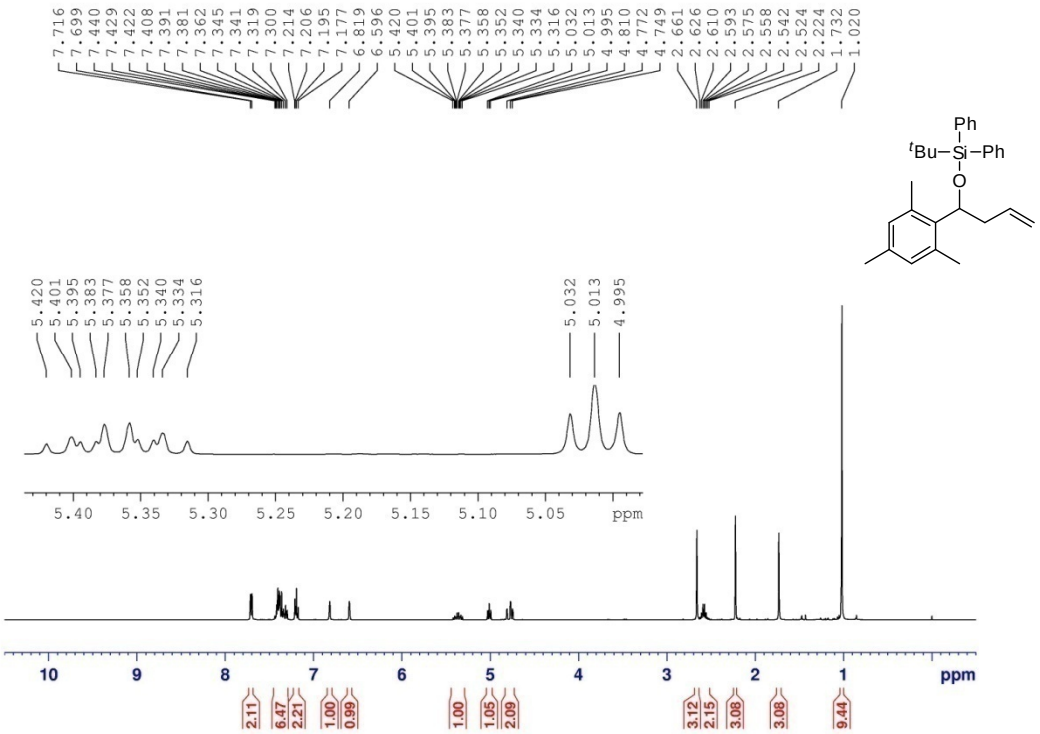
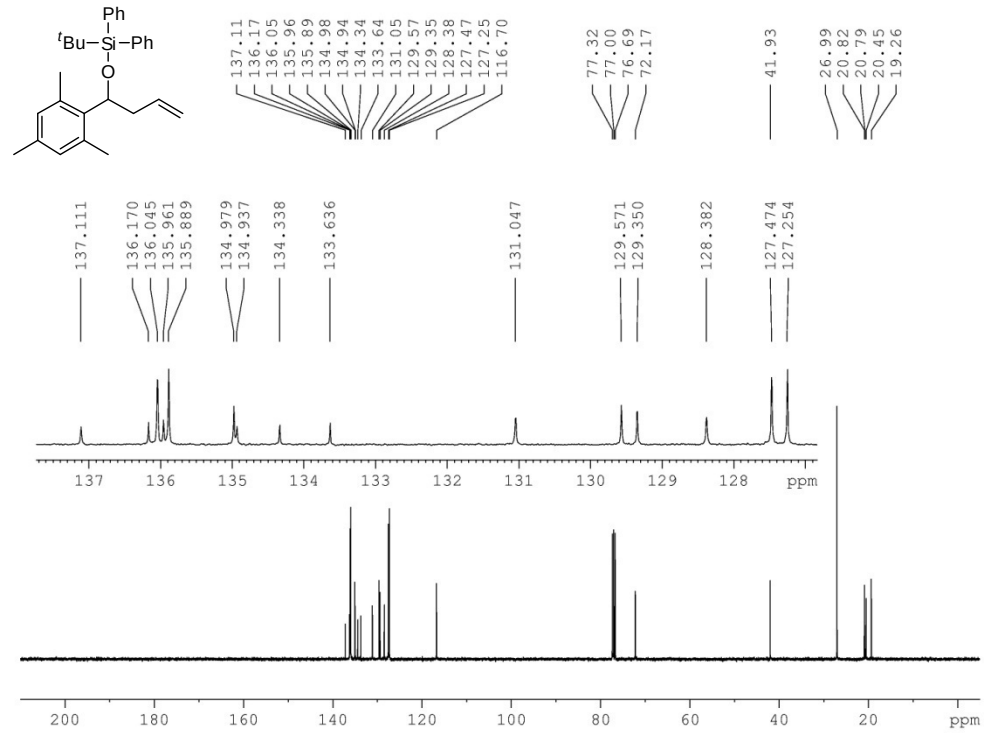
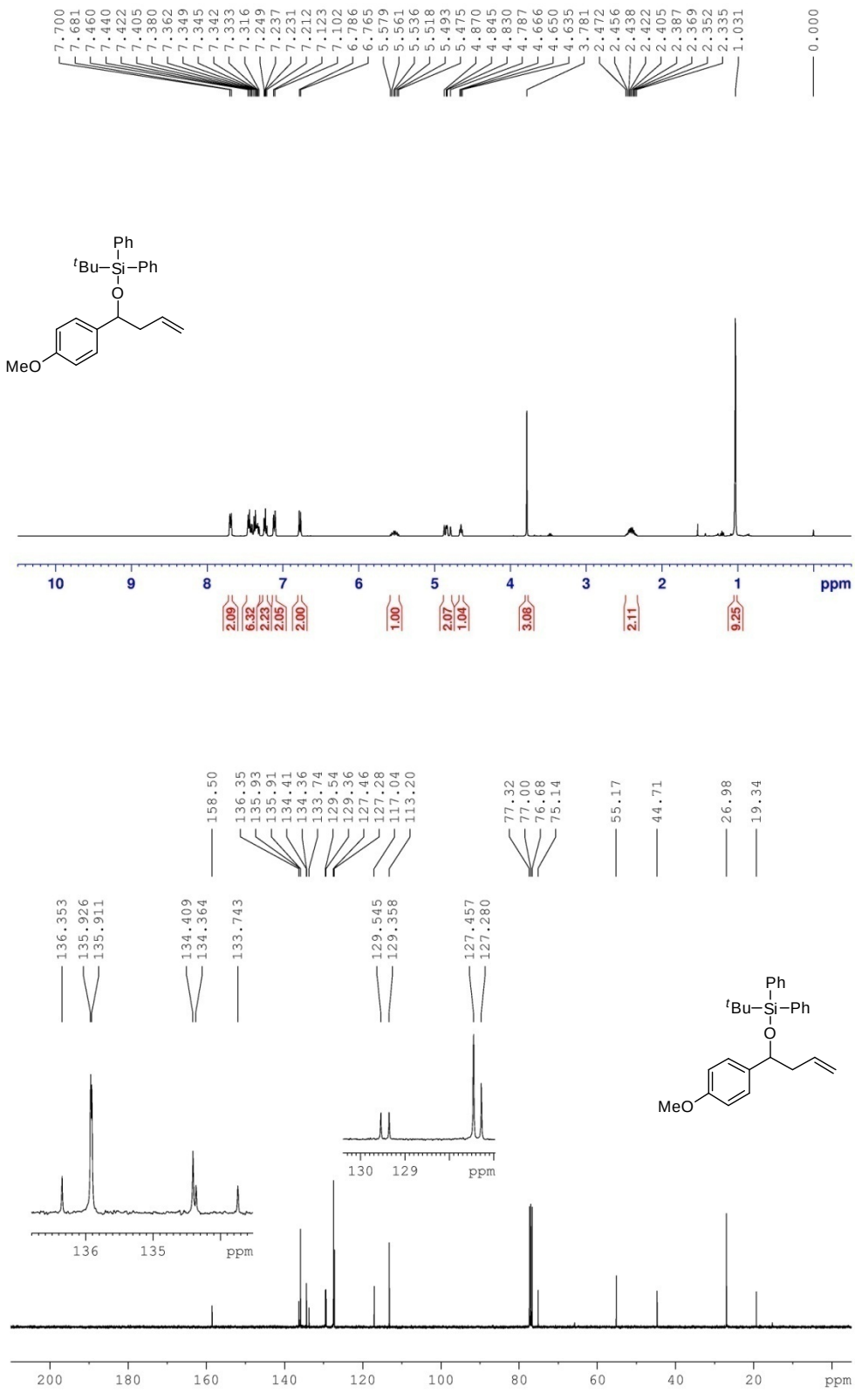
135
ppm
129
128
127
ppm
200
180
160
140
120
100
80
60
40
20
ppm



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7.362
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7.345
7.342
7.333
7.316
7.249
7.237
7.231
7.212
7.123
7.102
6.786
6.765
5.579
5.561
5.536
5.518
5.493
5.475
4.870
4.845
4.830
4.787
4.666
4.650
4.635
3.781
2.472
2.456
2.438
2.422
2.405
2.387
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2.352
2.335
1.031
0.000
Ph
tBu–Si–Ph
O
MeO
10
9
8
7
6
5
4
3
2
1
ppm
2.09
6.32
2.23
2.05
2.00
1.00
2.07
1.04
3.08
2.11
9.25
158.50
136.35
135.93
135.91
134.41
134.36
133.74
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129.36
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127.28
117.04
113.20
77.32
77.00
76.68
75.14
55.17
44.71
26.98
19.34
136.353
135.926
135.911
134.409
134.364
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129.358
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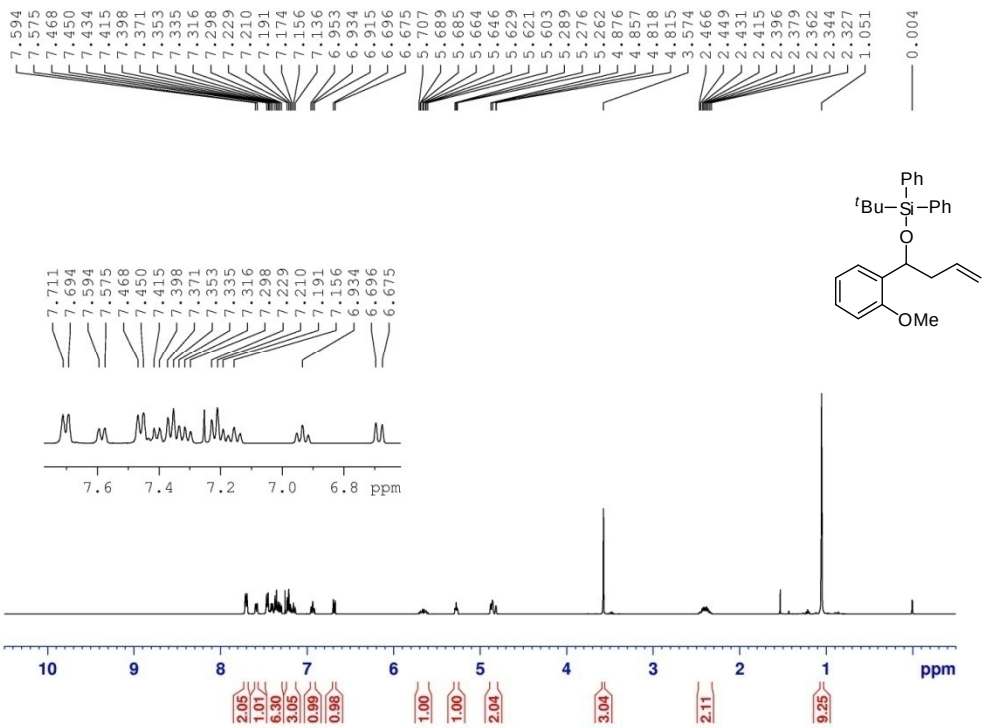
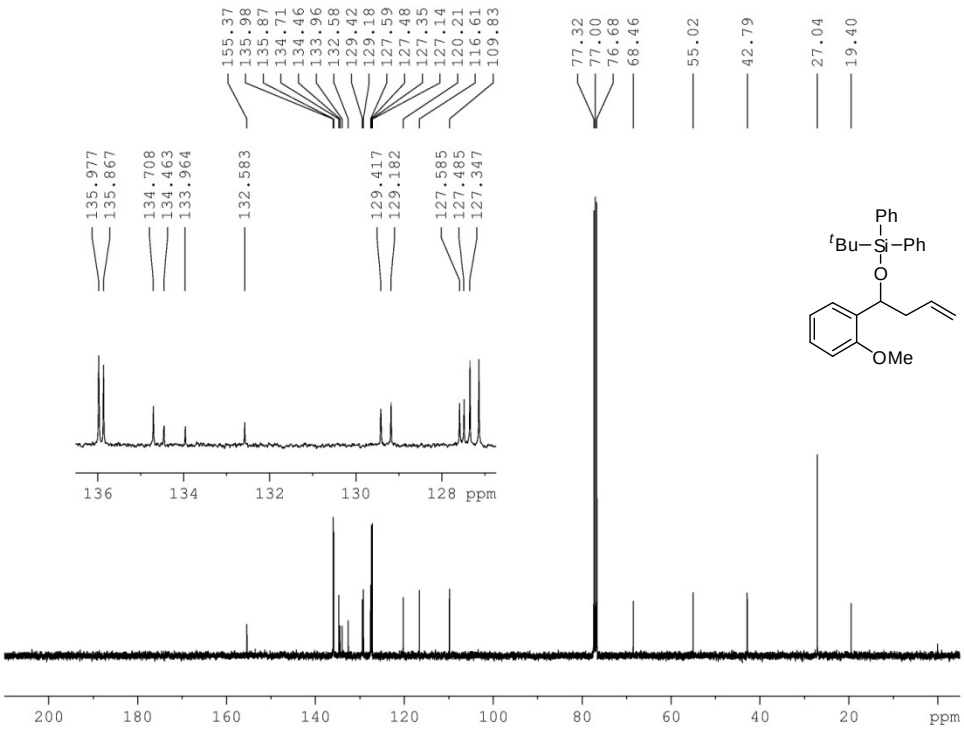
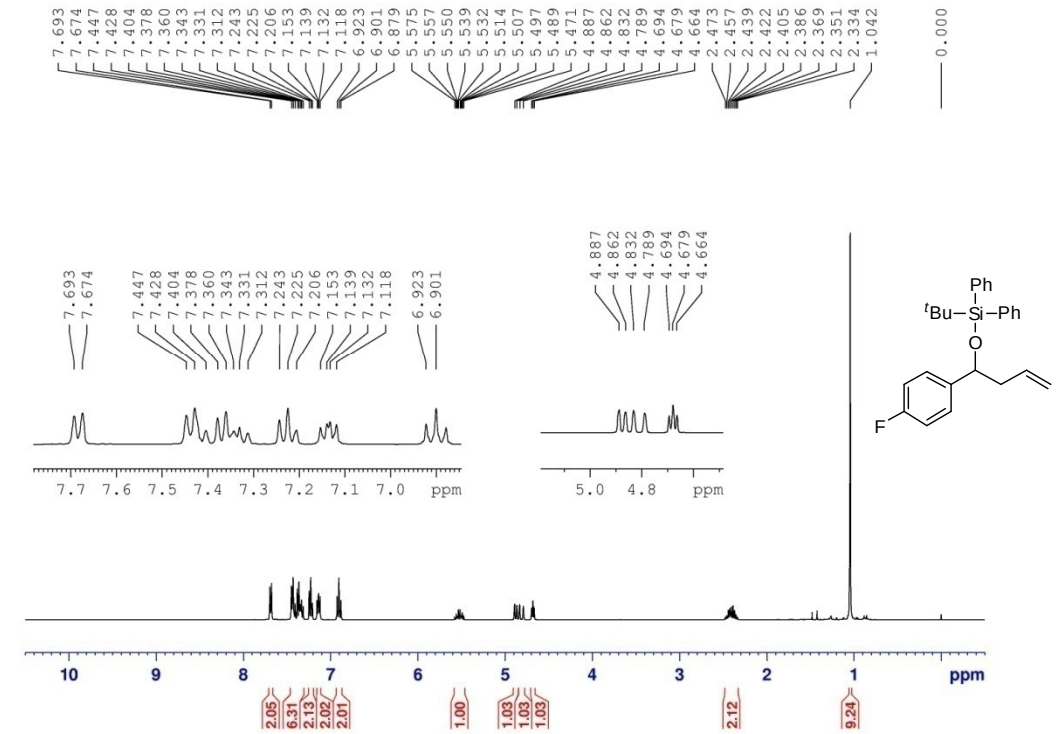
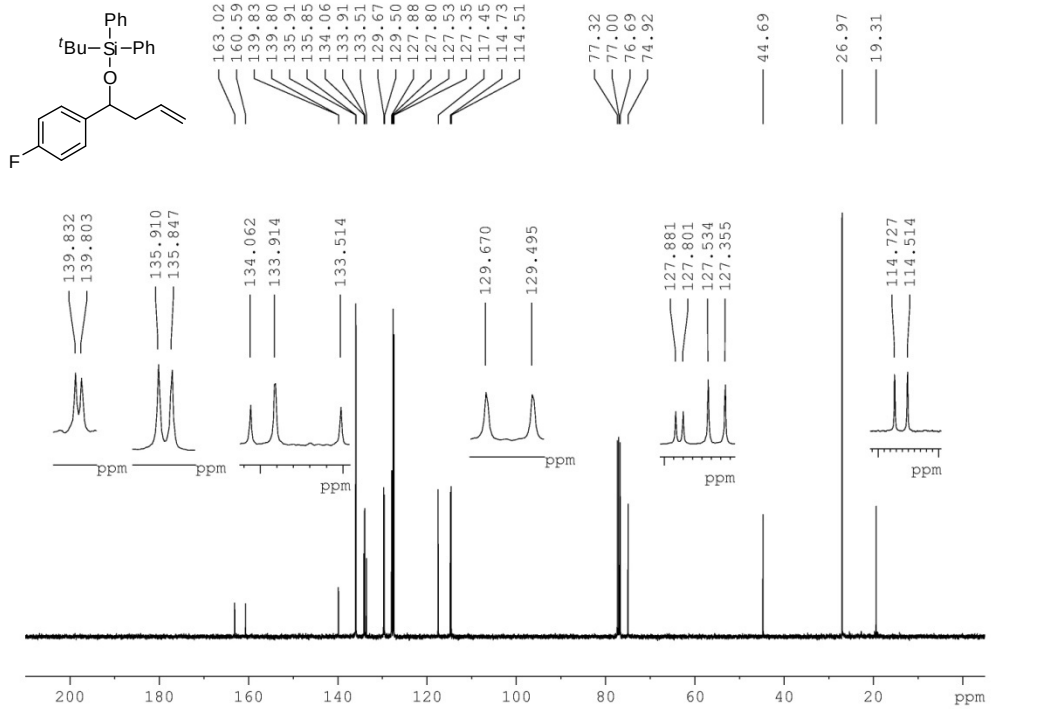
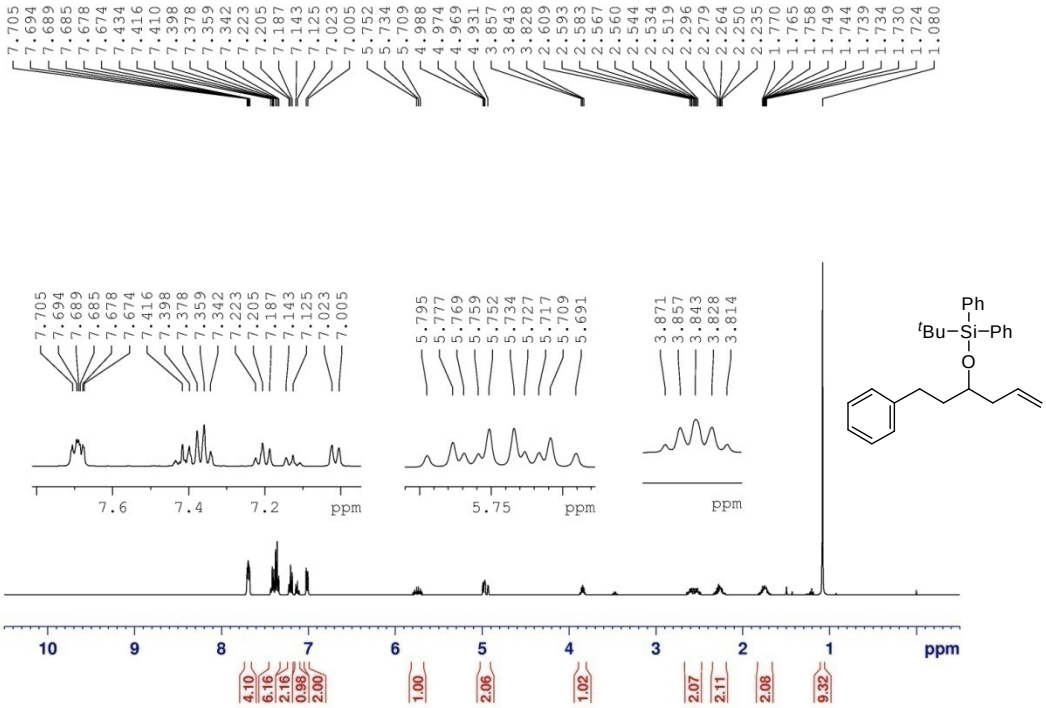
ppm
130
129
ppm
200
180
160
140
120
100
80
60
40
20
ppm

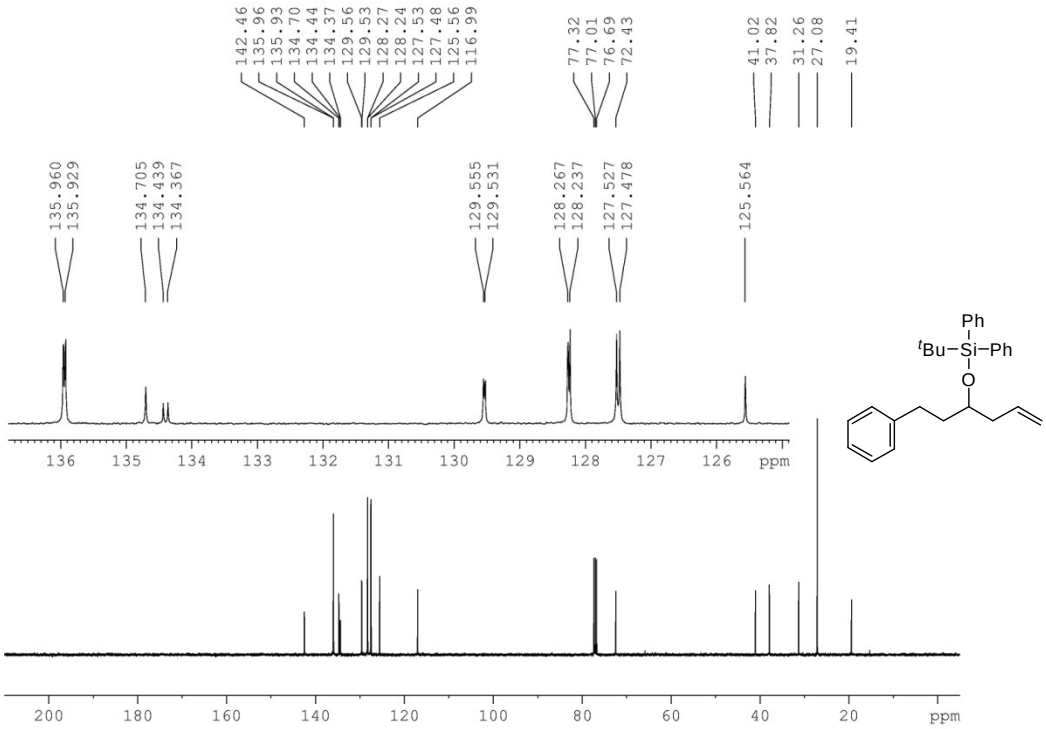









7.705 7.694 7.689 7.685 7.678 7.674 7.434 7.416 7.410 7.398 7.378 7.359 7.342 7.223 7.205 7.187 7.143 7.125 7.023 7.005 5.752 5.734 5.709 4.988 4.974 4.969 4.931 3.857 3.843 3.828 2.609 2.593 2.583 2.567 2.560 2.544 2.534 2.519 2.296 2.279 2.264 2.250 2.235 1.770 1.765 1.758 1.749 1.744 1.739 1.734 1.730 1.724 1.080
Ph
tBu–Si–Ph
O
ppm
4.10 6.16 2.16 0.98 2.00 1.00 2.06 1.02 2.07 2.11 2.08 9.32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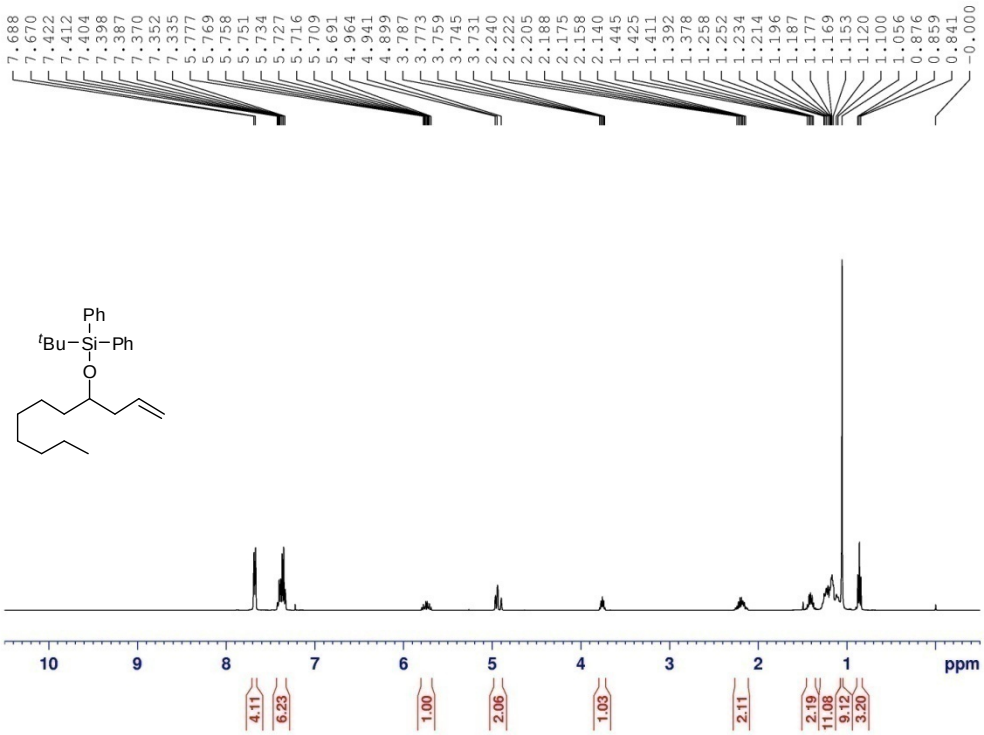
77.32 77.01 76.69 72.43
41.02 37.82 31.26 27.08 19.41
135.960 135.929 134.705 134.439 134.367 129.555 129.531 128.267 128.237 127.527 127.478 125.564
Ph
tBu–Si–Ph
O
ppm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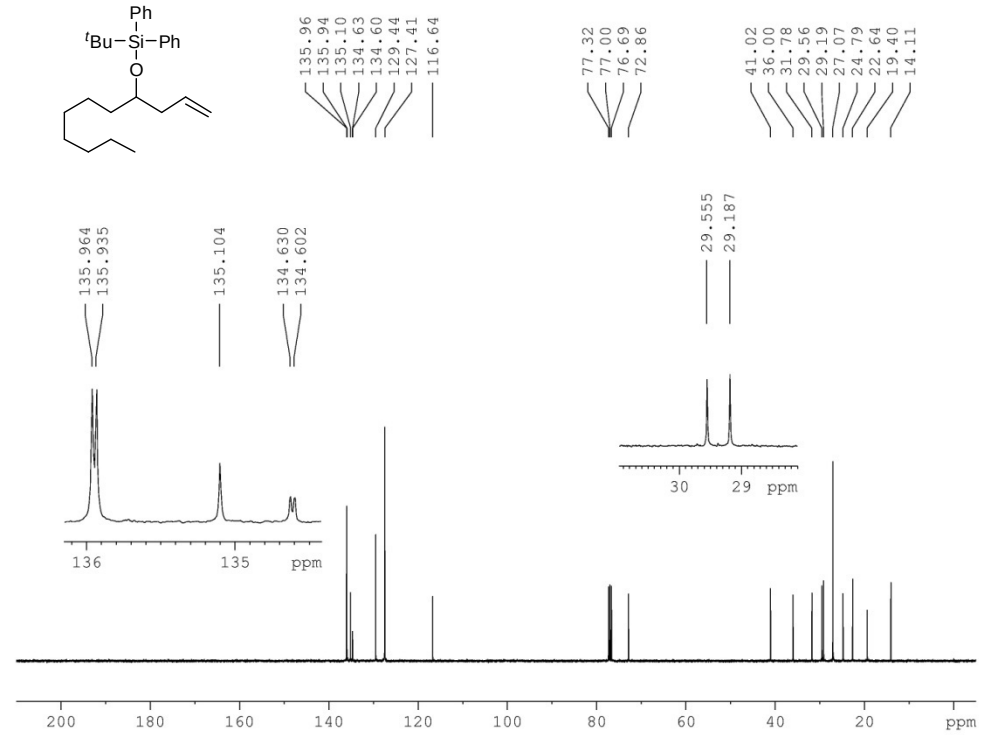
5.758
5.751
5.734
5.727
5.716
5.709
5.691
4.964
4.941
4.899
3.787
3.773
3.759
3.745
3.731
2.240
2.222
2.205
2.188
2.175
2.158
2.140
1.445
1.425
1.411
1.392
1.378
1.258
1.252
1.234
1.214
1.196
1.187
1.177
1.169
1.153
1.120
1.100
1.056
0.876
0.859
0.841
-0.000
Ph
tBu−Si−Ph
O
10
9
8
7
6
5
4
3
2
1
ppm
4.11
6.23
1.00
2.06
1.03
2.11
2.19
11.08
9.12
3.20


Ph
tBu−Si−Ph
O
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135.94
135.10
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134.60
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127.41
116.64
77.32
77.00
76.69
72.86
41.02
36.00
31.78
29.56
29.19
27.07
24.79
22.64
19.40
14.11
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135
ppm
30
29
ppm
200
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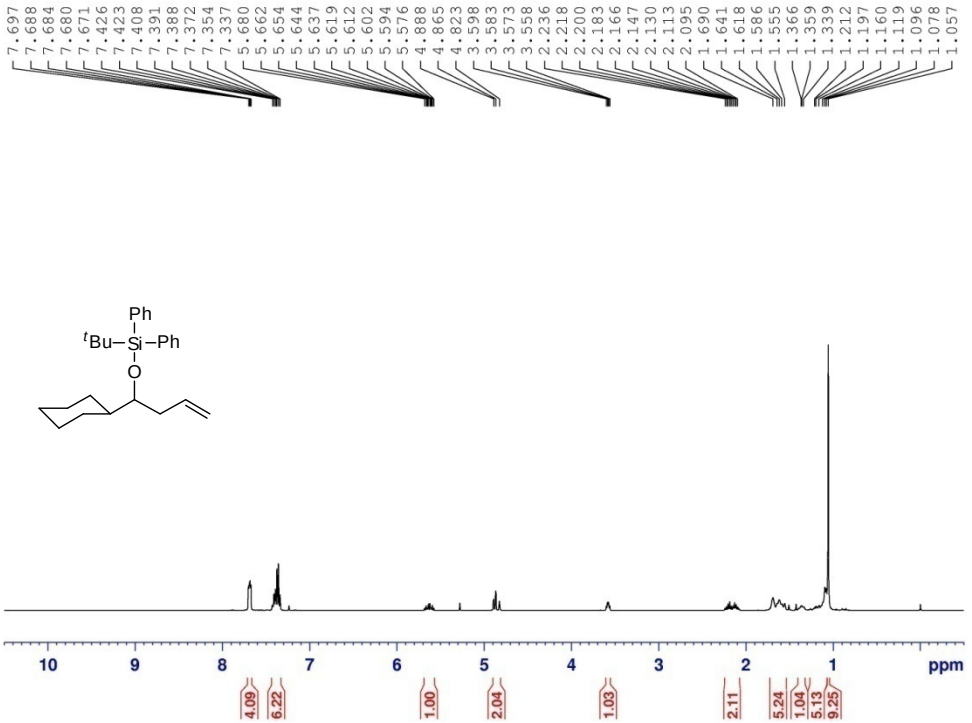
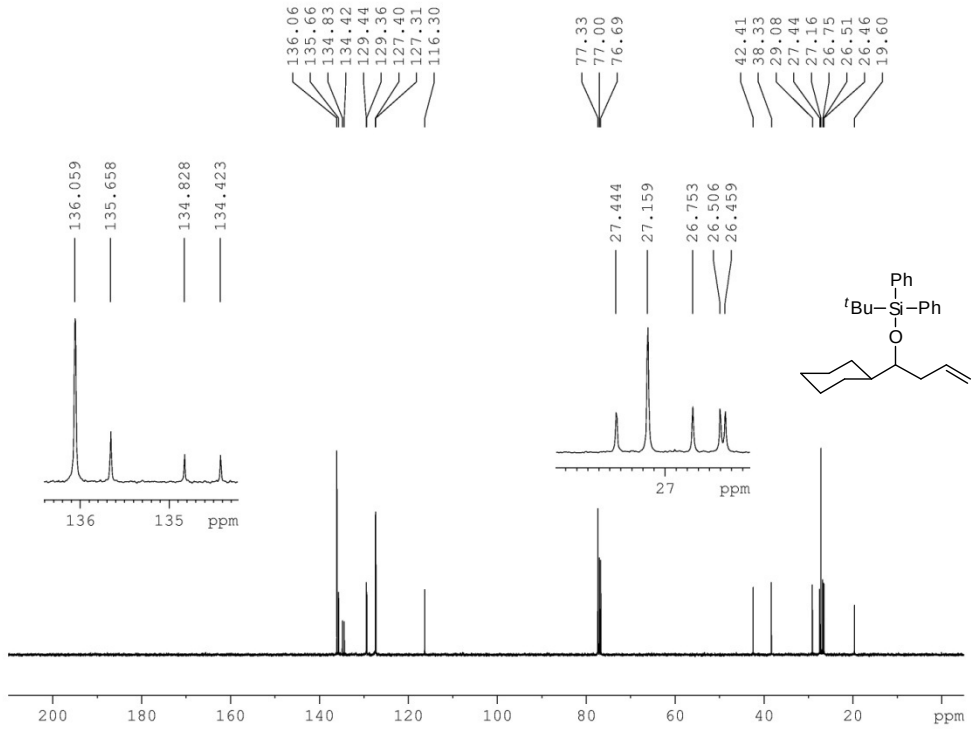
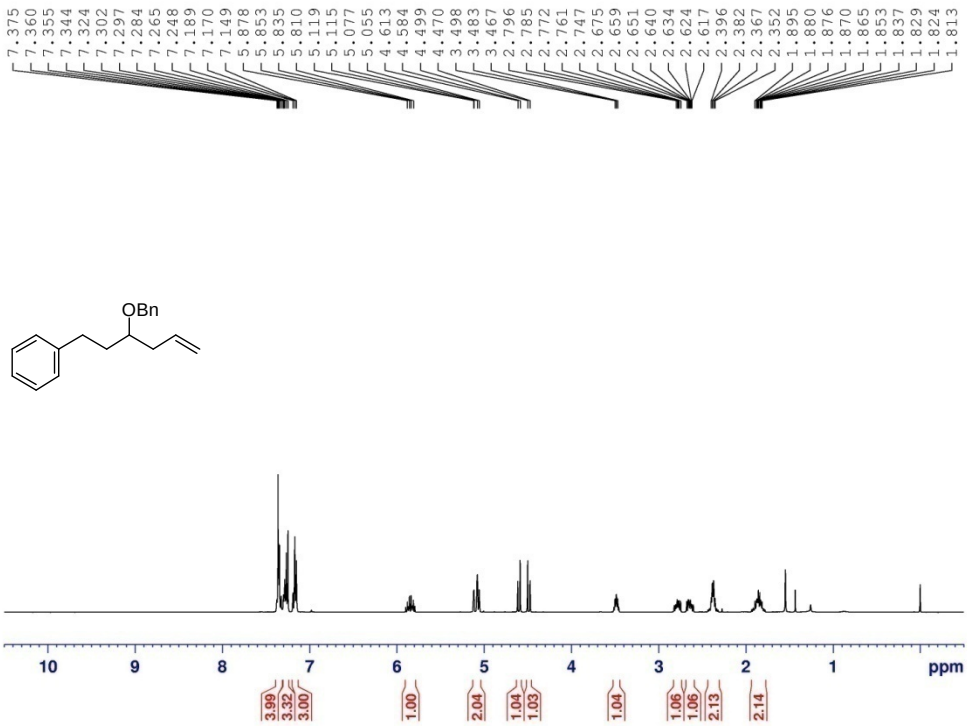
140
120
100
80
60
40
20
ppm



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7.149
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5.835
5.810
5.119
5.115
5.077
5.055
4.613
4.584
4.499
4.470
3.498
3.483
3.467
2.796
2.785
2.772
2.761
2.747
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2.352
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1.853
1.837
1.829
1.824
1.813
OBn
10
9
8
7
6
5
4
3
2
1
ppm
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1.04
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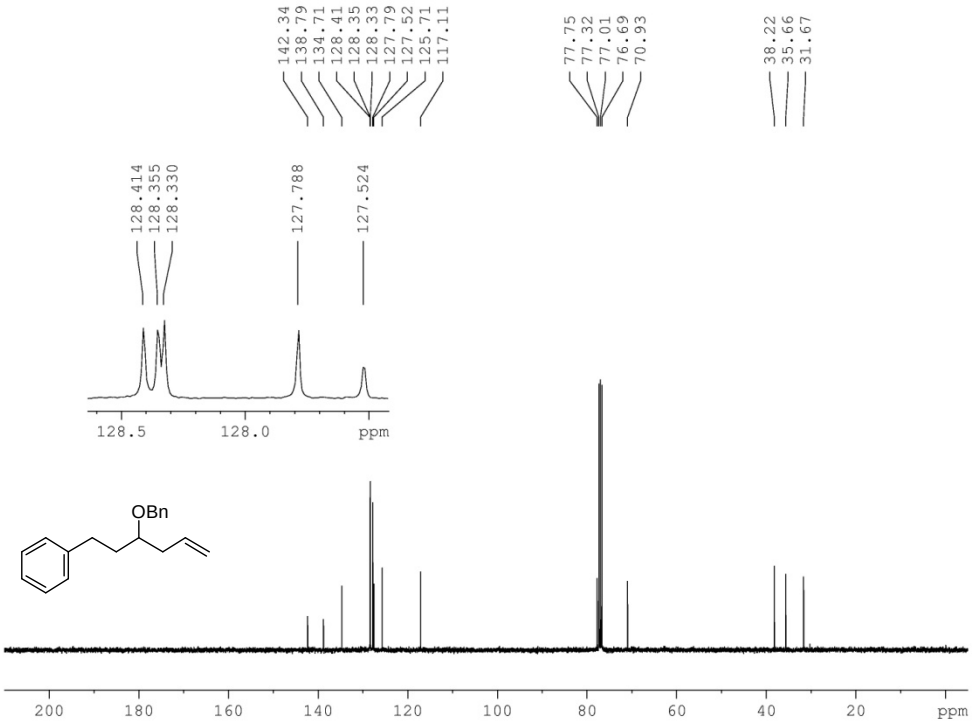
1.06
2.13
2.14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125.71
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77.01
76.69
70.93
38.22
35.66
31.67
128.414
128.355
128.330
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128.0
ppm
OBn
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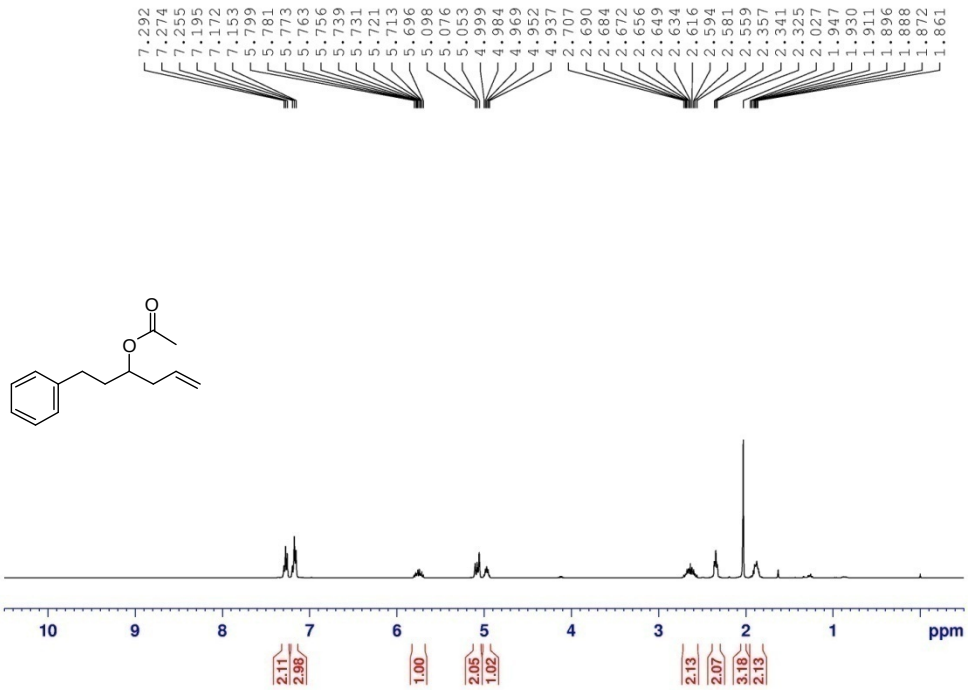
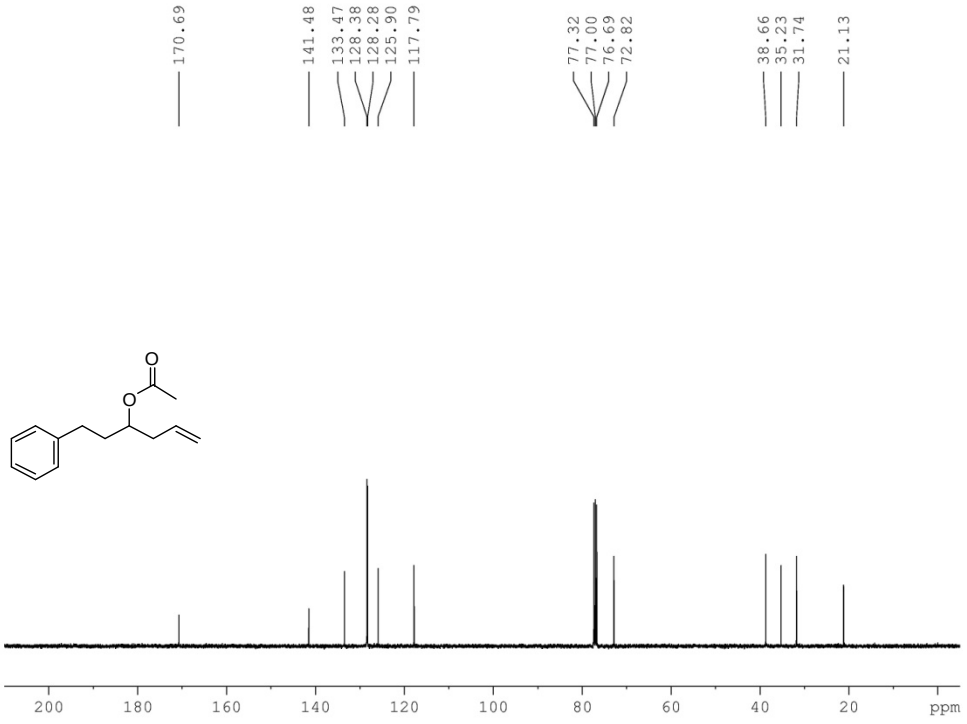
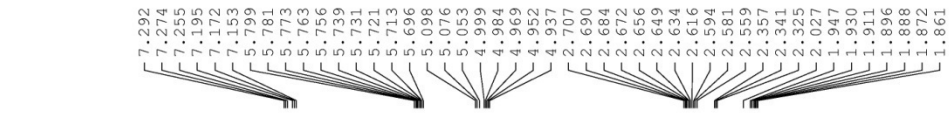
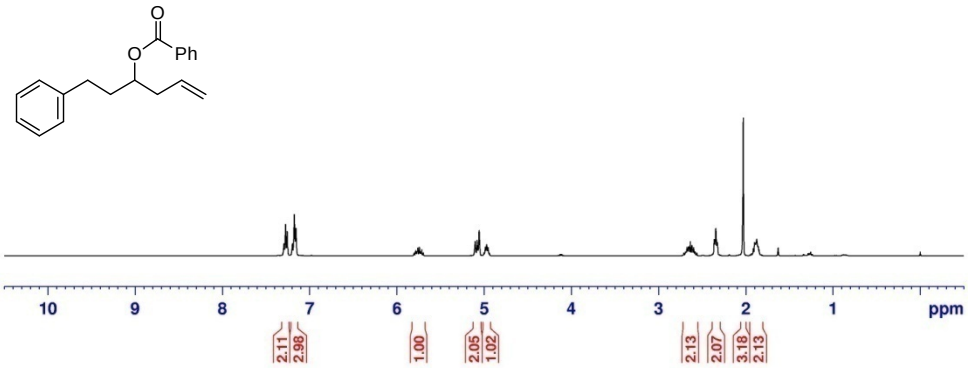
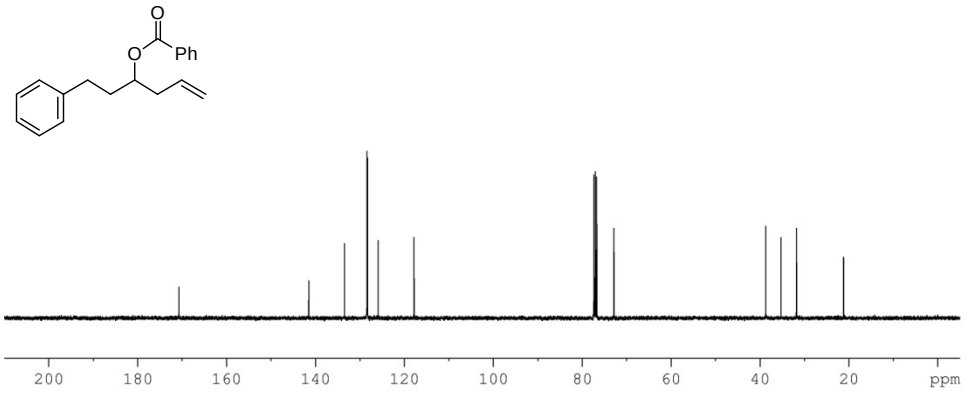
160
140
120
100
80
60
40
20
ppm

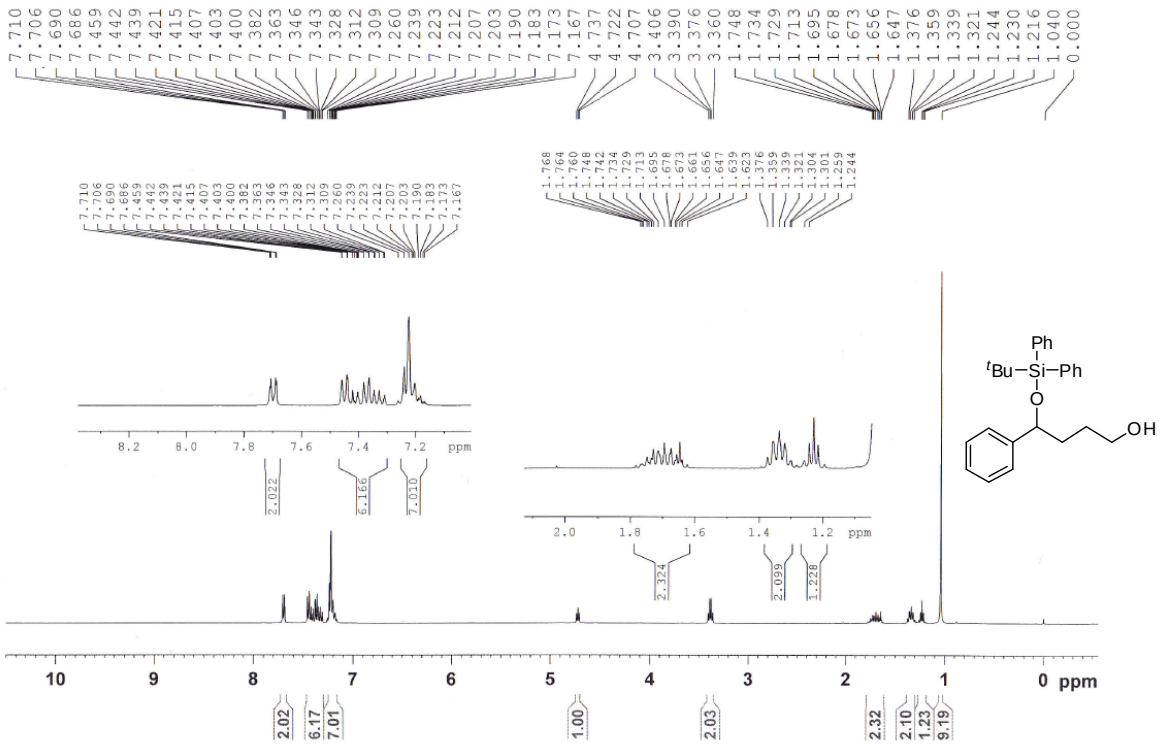


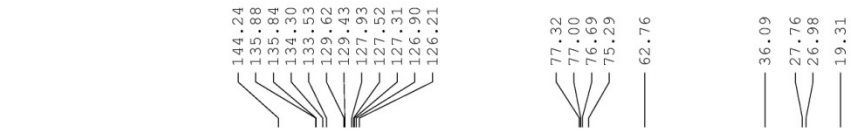


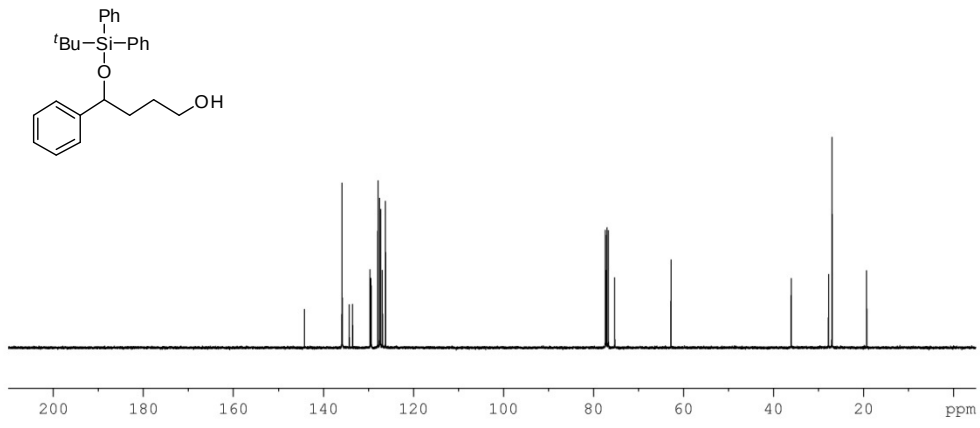


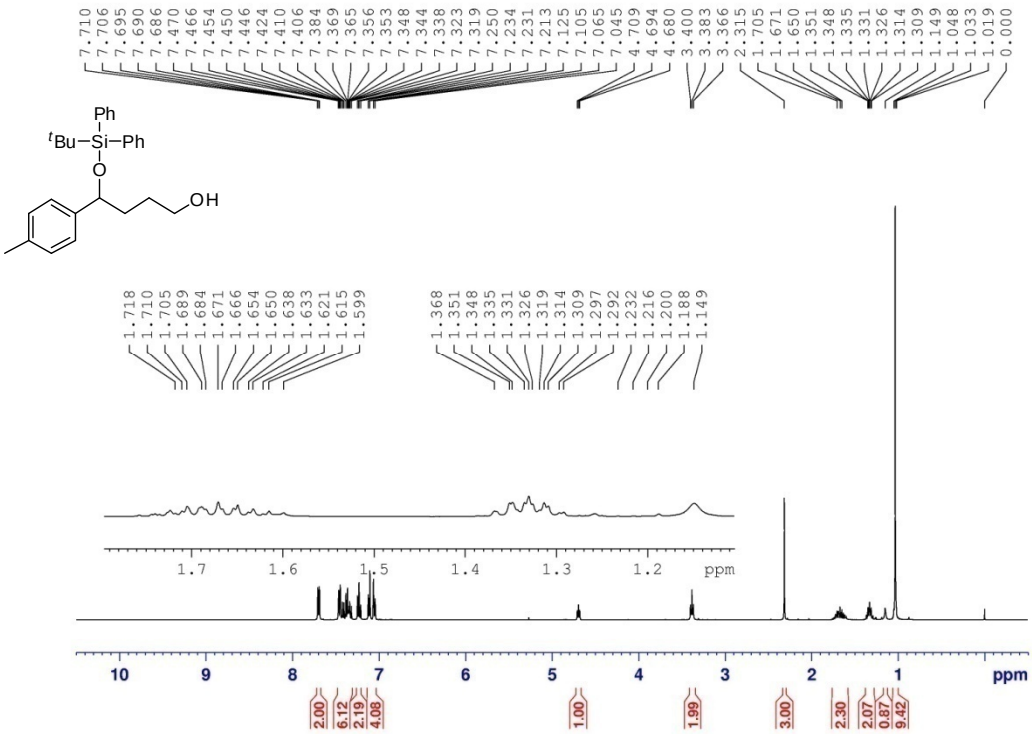


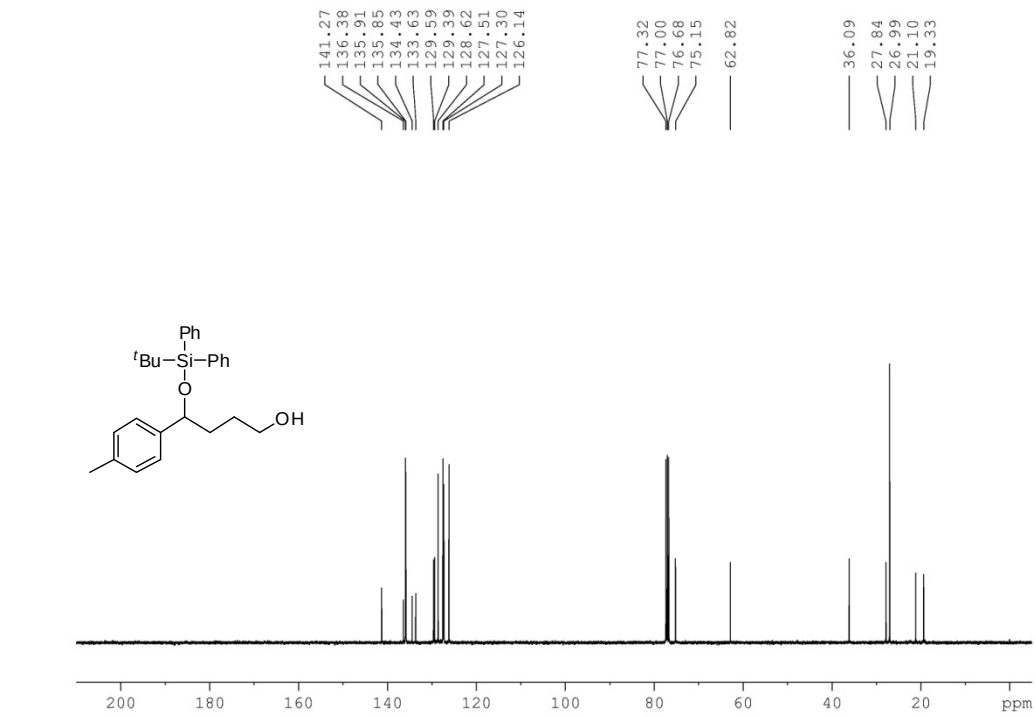


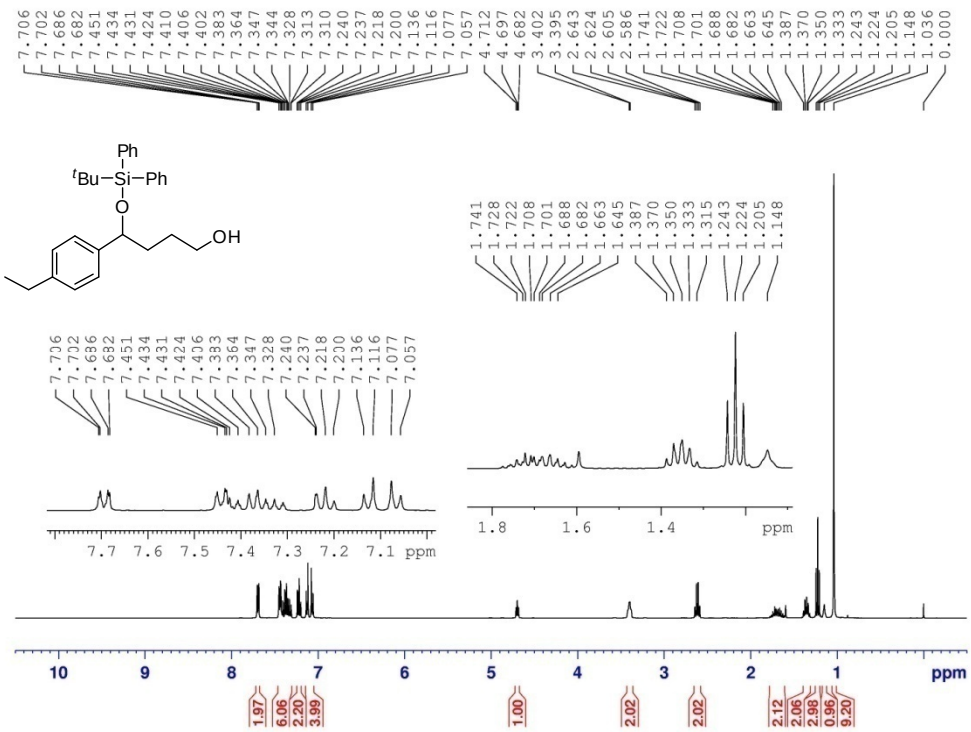








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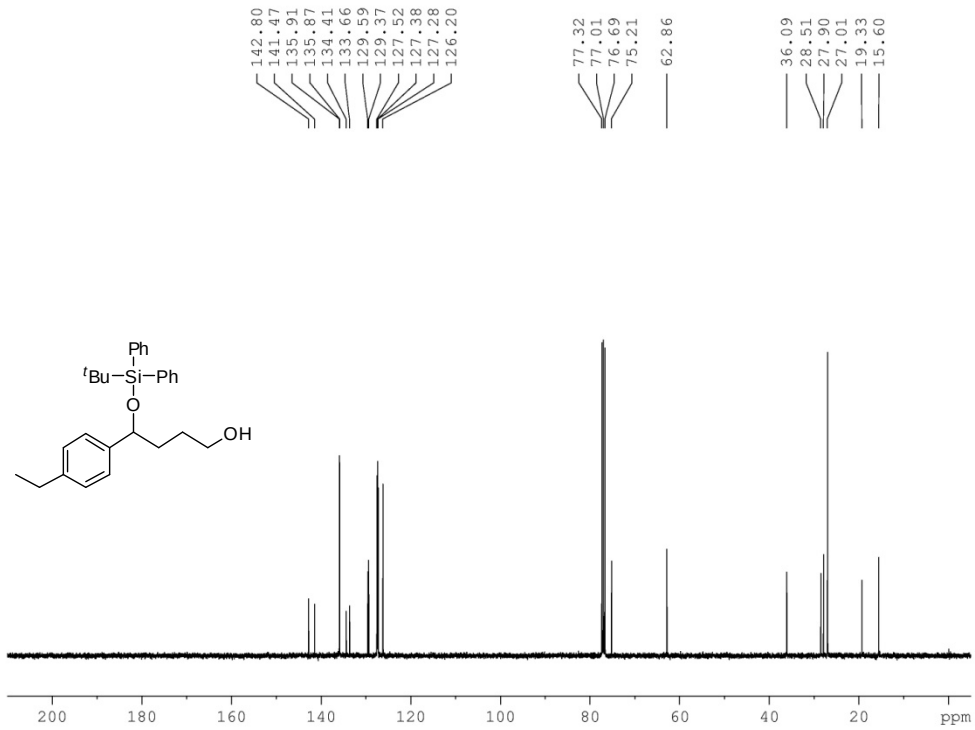
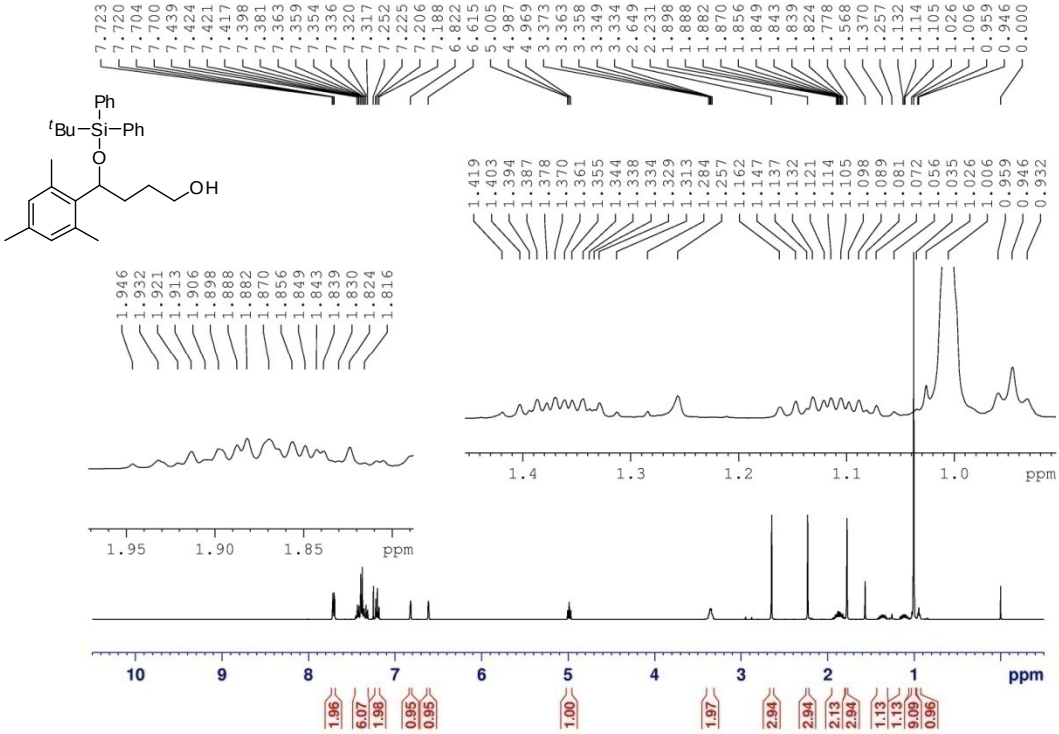
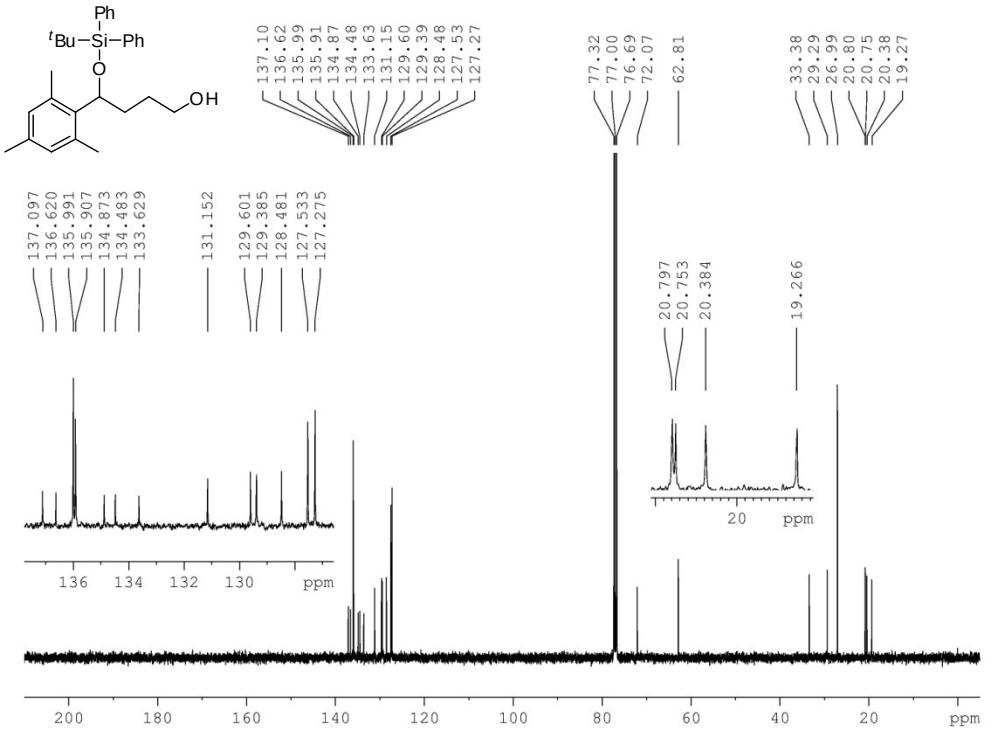
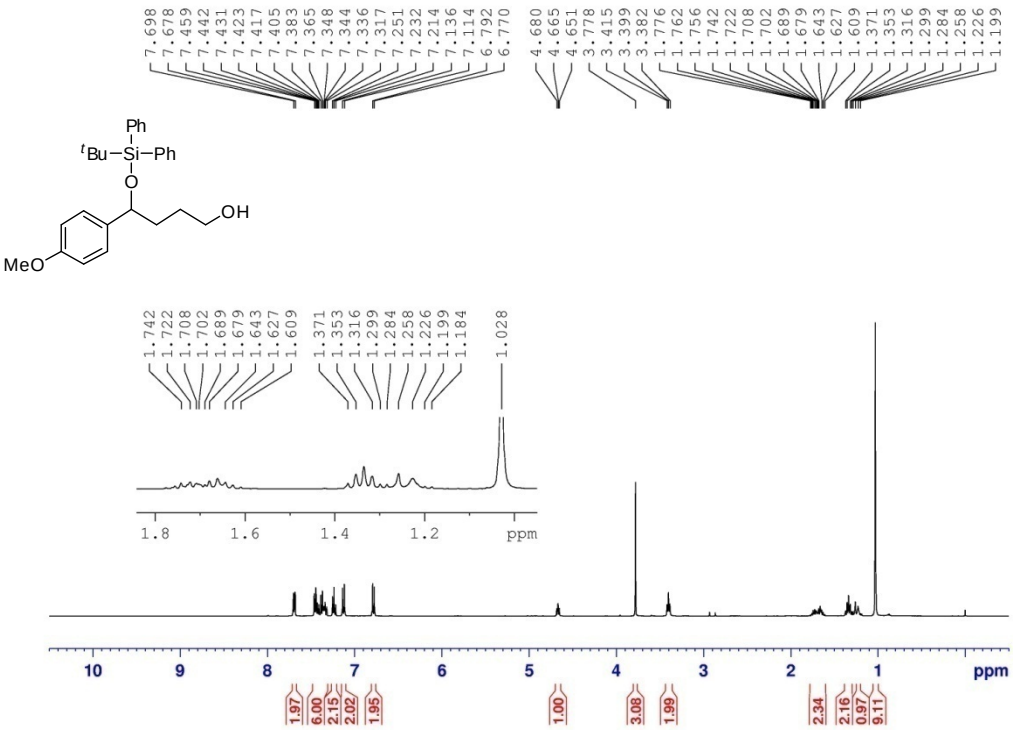
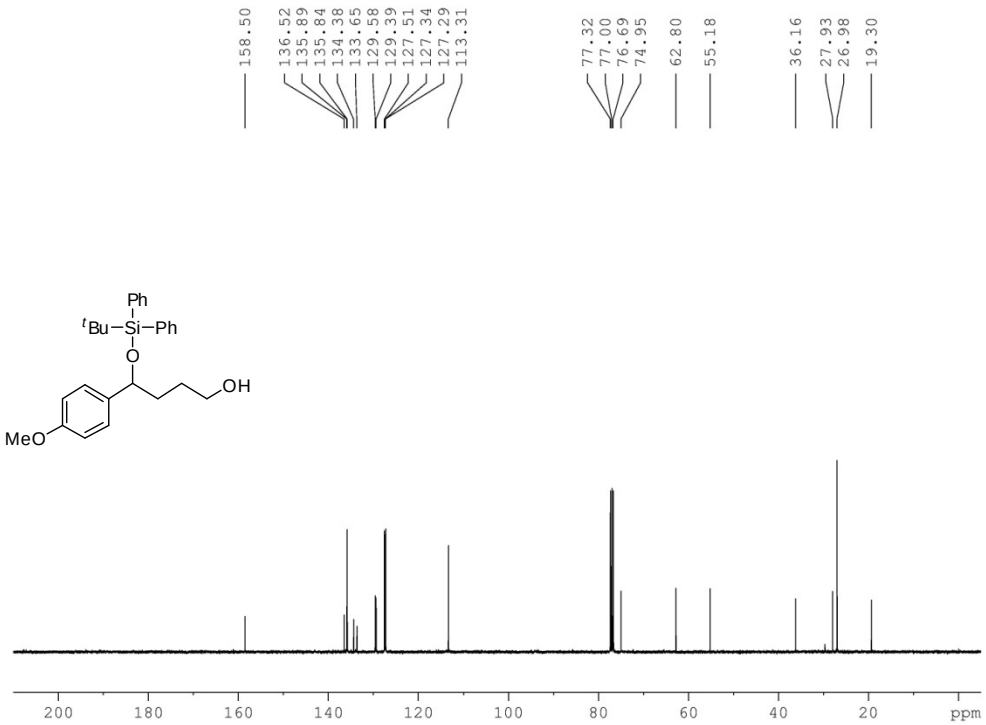
tBu–Si–Ph
O
OH
ppm

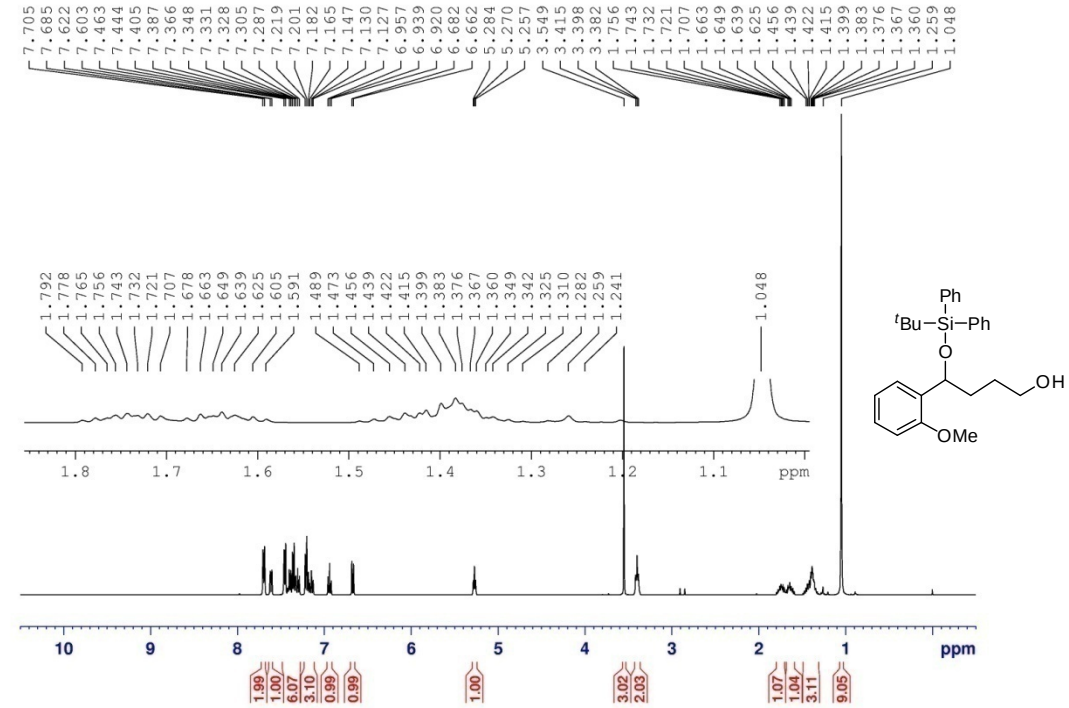

Ph
tBu–Si–Ph
O
OH
ppm

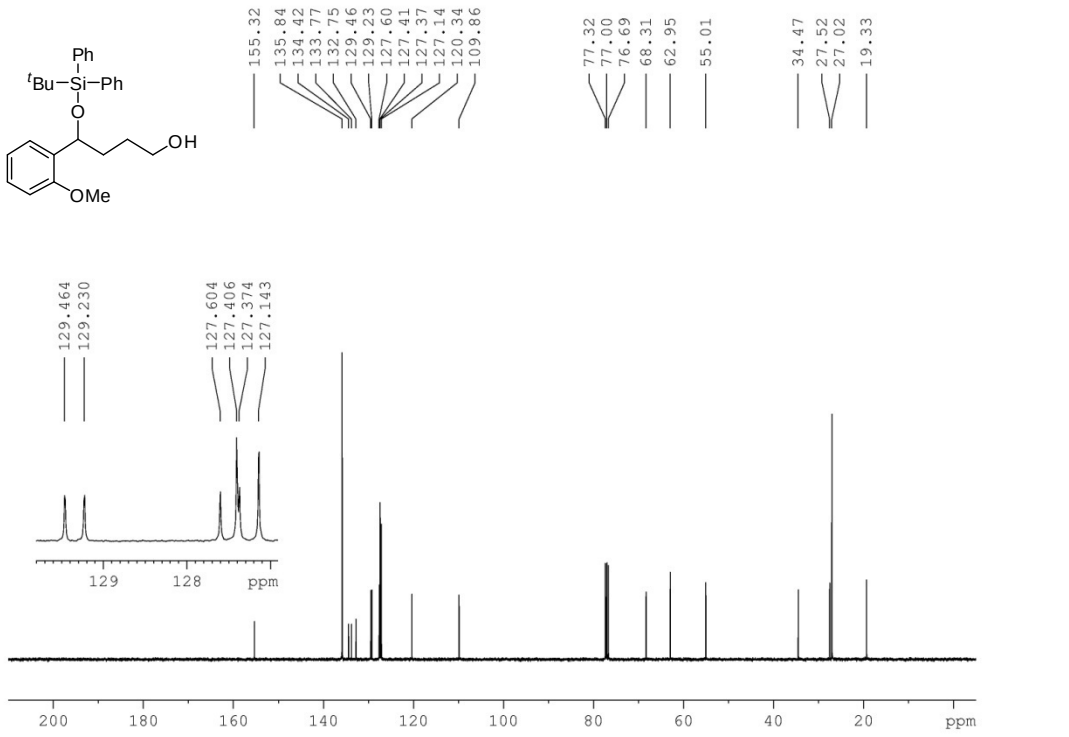

Ph
tBu–Si–Ph
O
OH
ppm

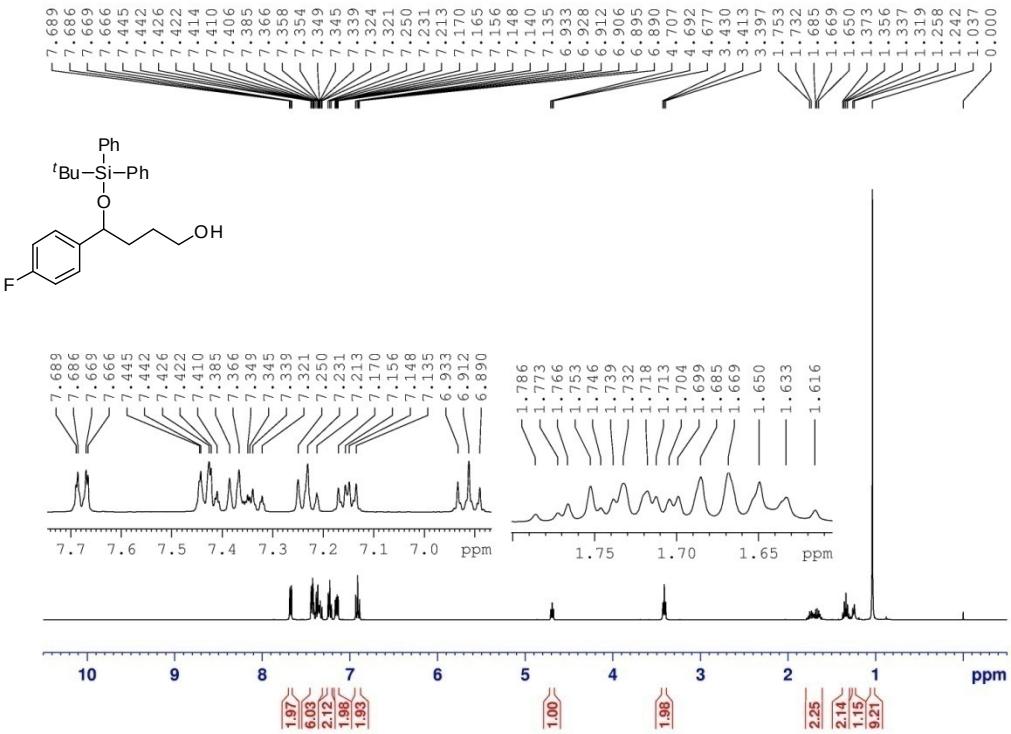

Ph
tBu–Si–Ph
O
OH
ppm

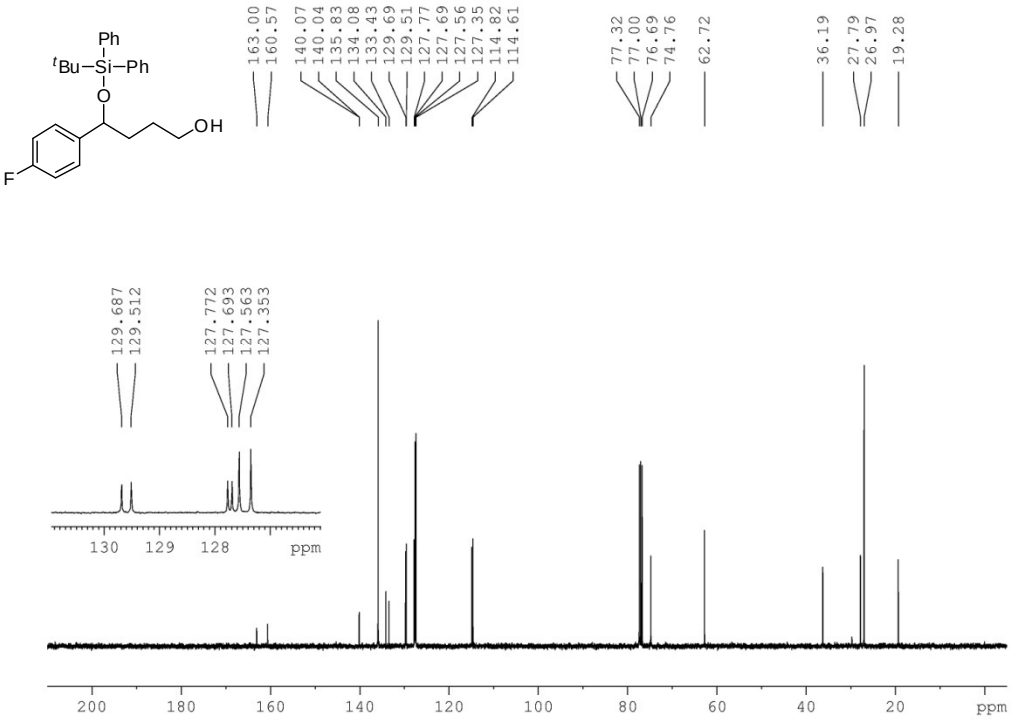


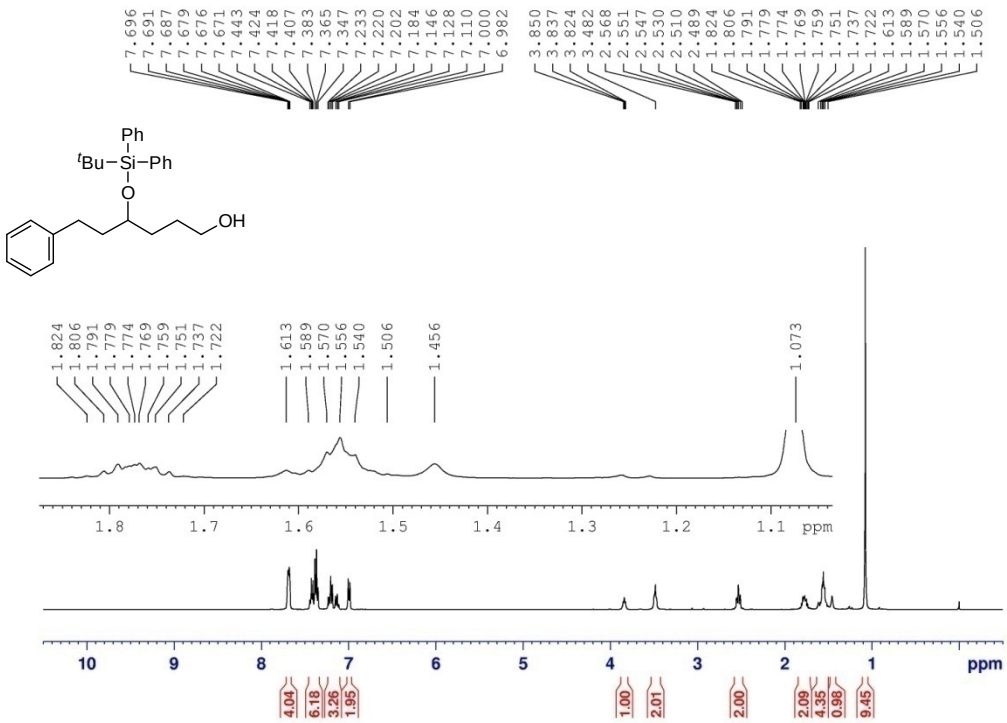








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1.506
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tBu–Si–Ph
O
OH
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1.7
1.6
1.5
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1.2
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ppm
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8
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6
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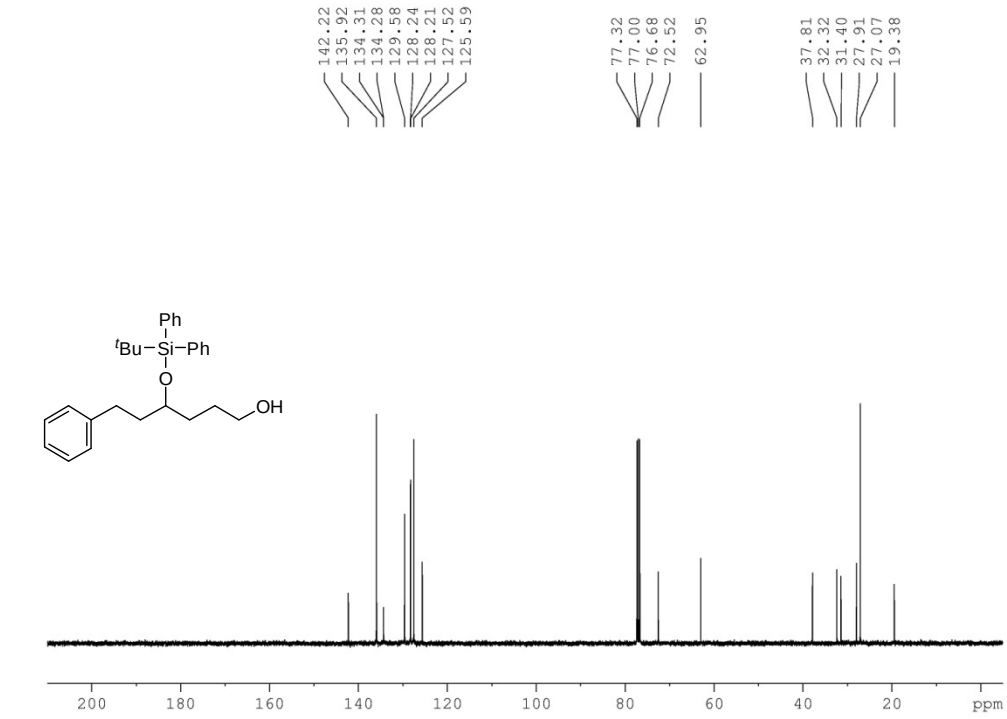
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27.91
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tBu–Si–Ph
O
OH
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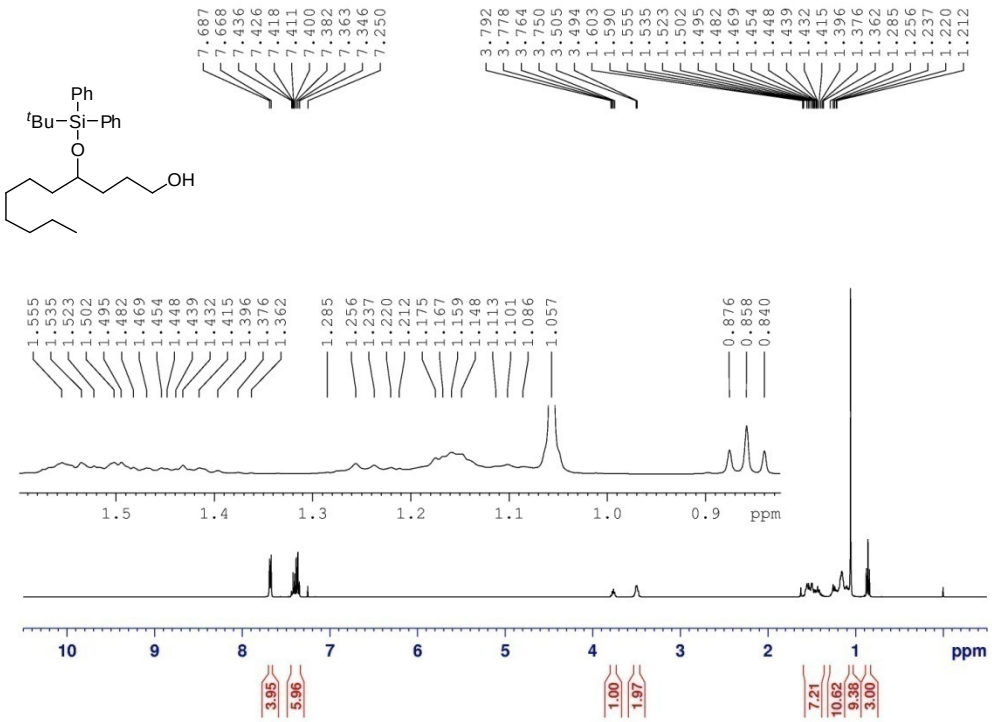
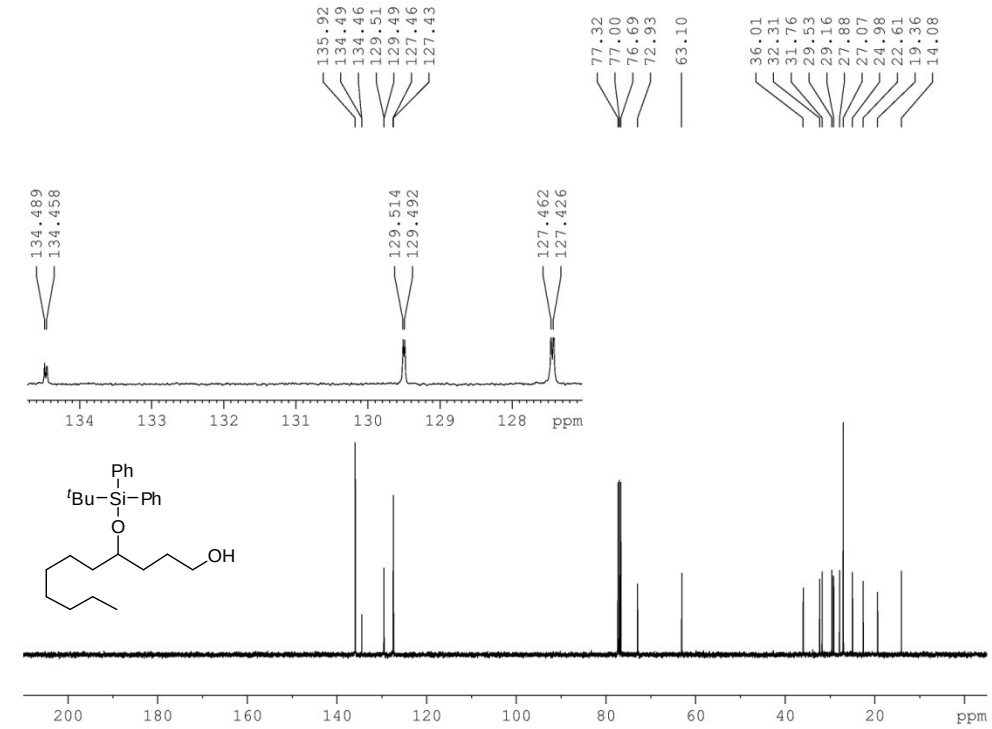
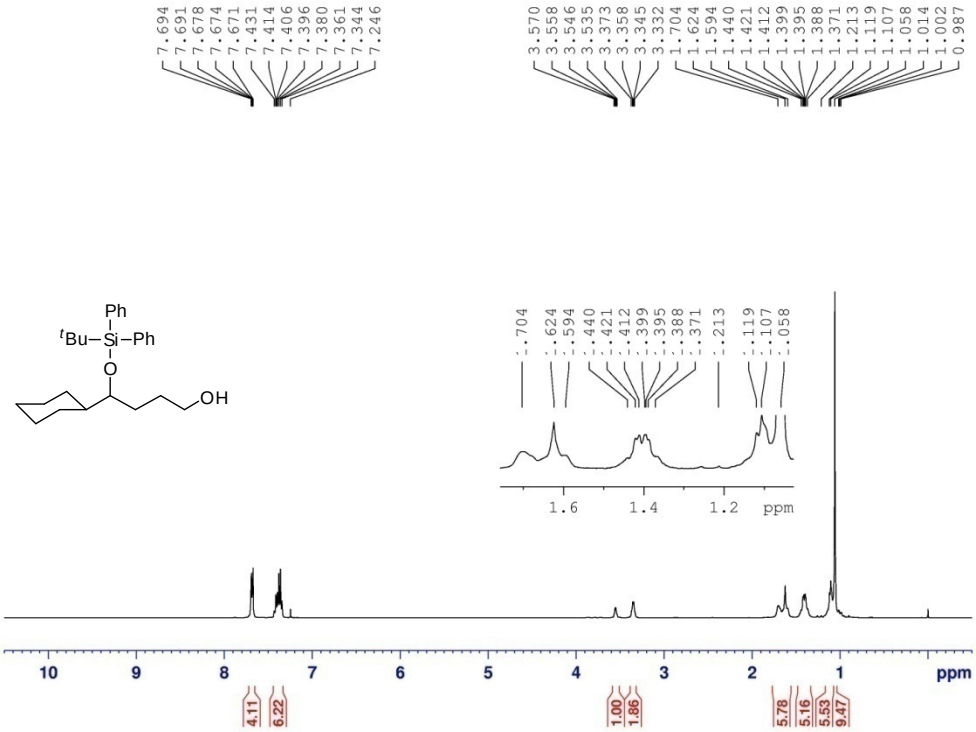
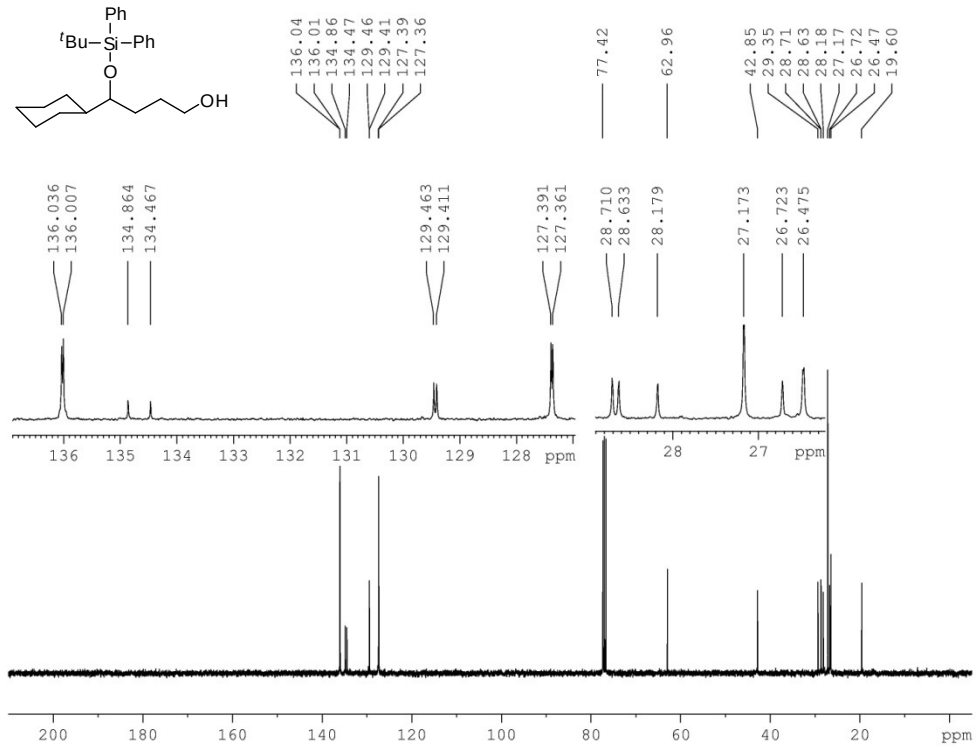
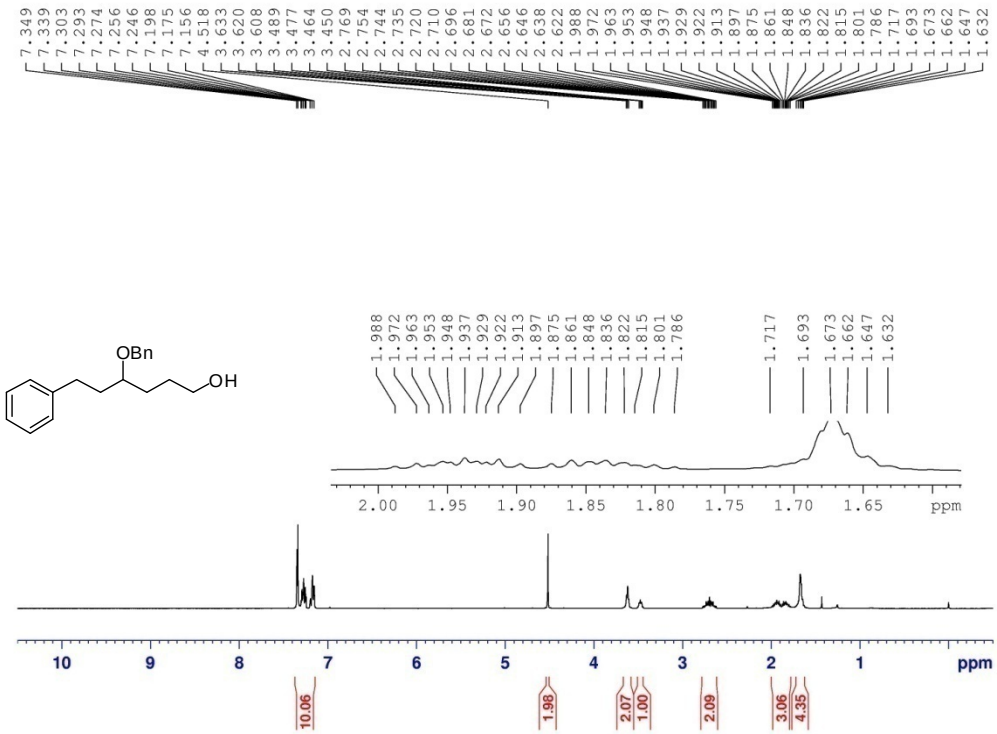
ppm







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2.656
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2.622
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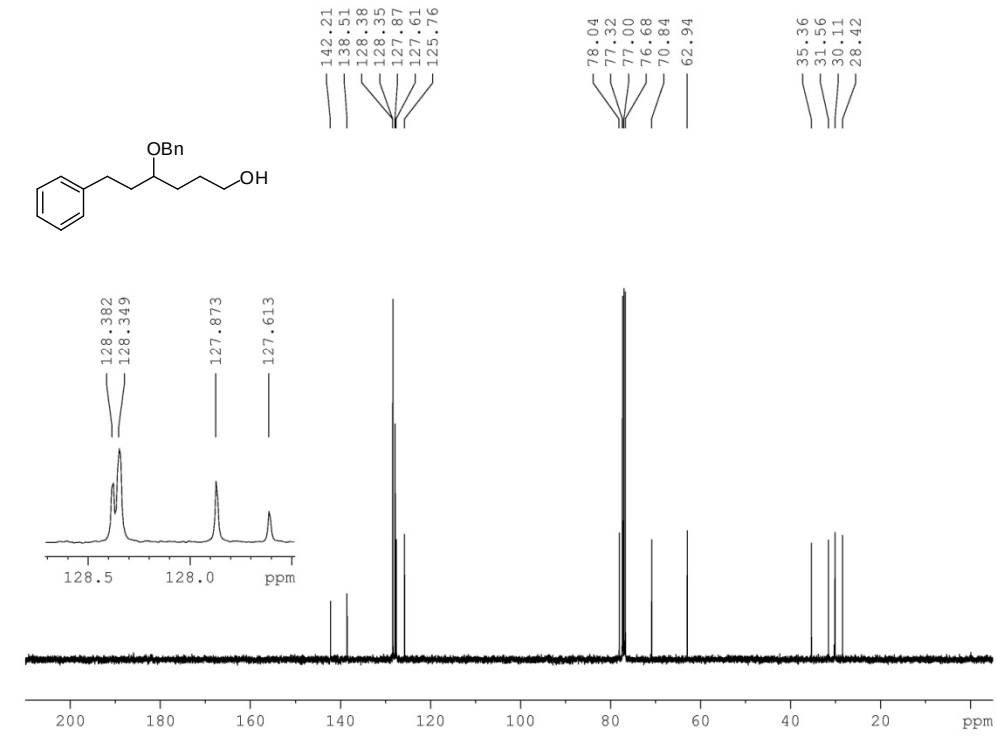
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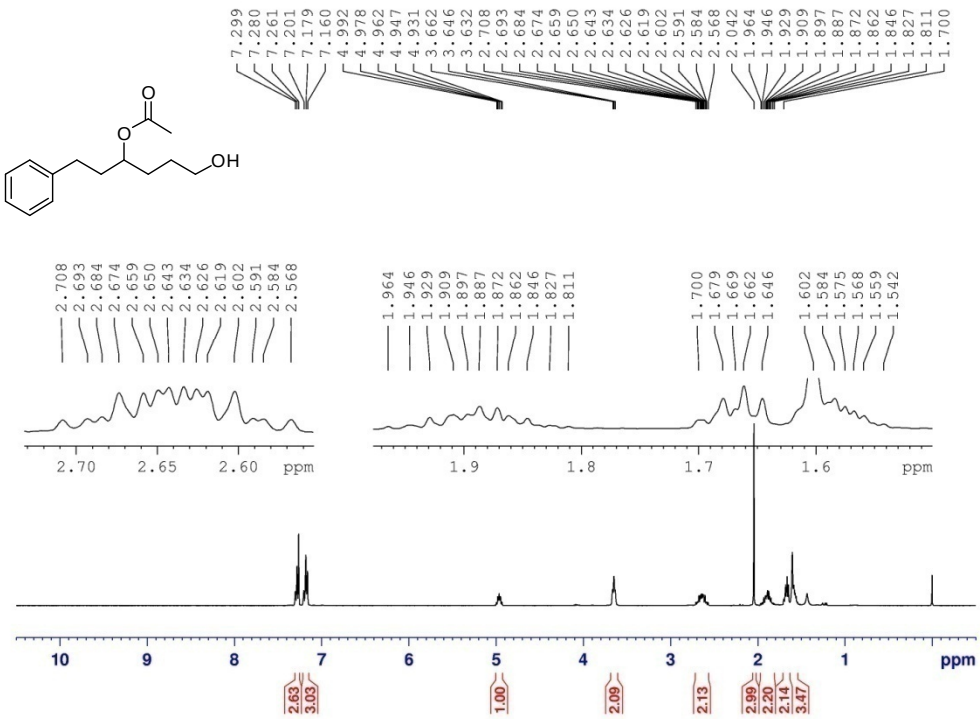
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3.632
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2.619
2.602
2.591
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1.872
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1.811
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O
OH
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1.7
1.6
ppm
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7
6
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ppm
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2.14
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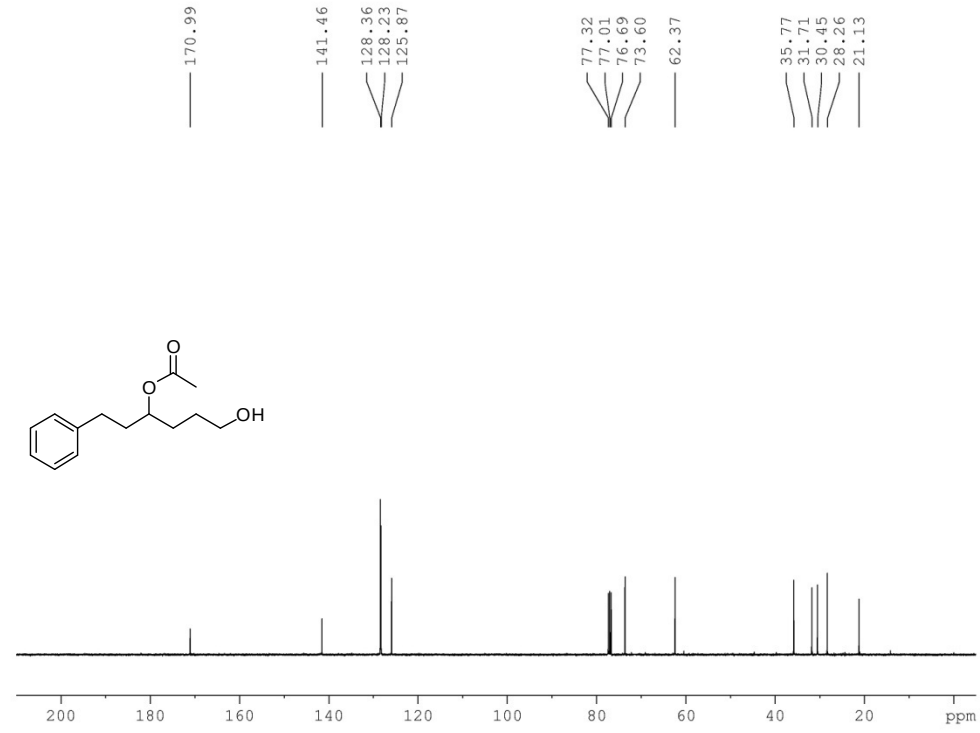
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O
OH
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60
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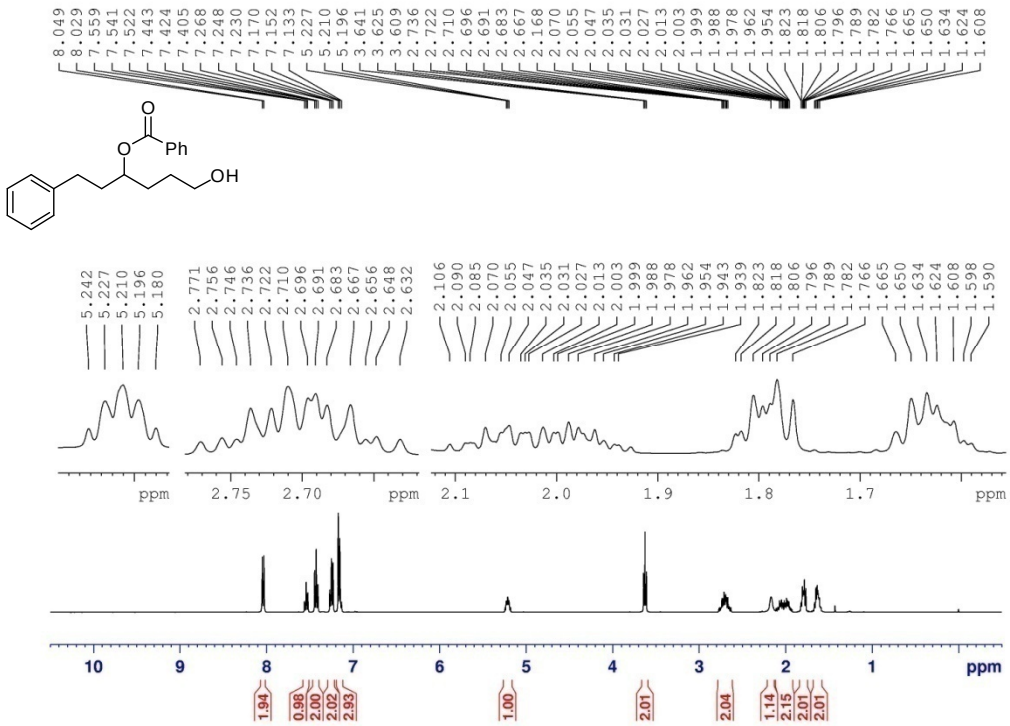
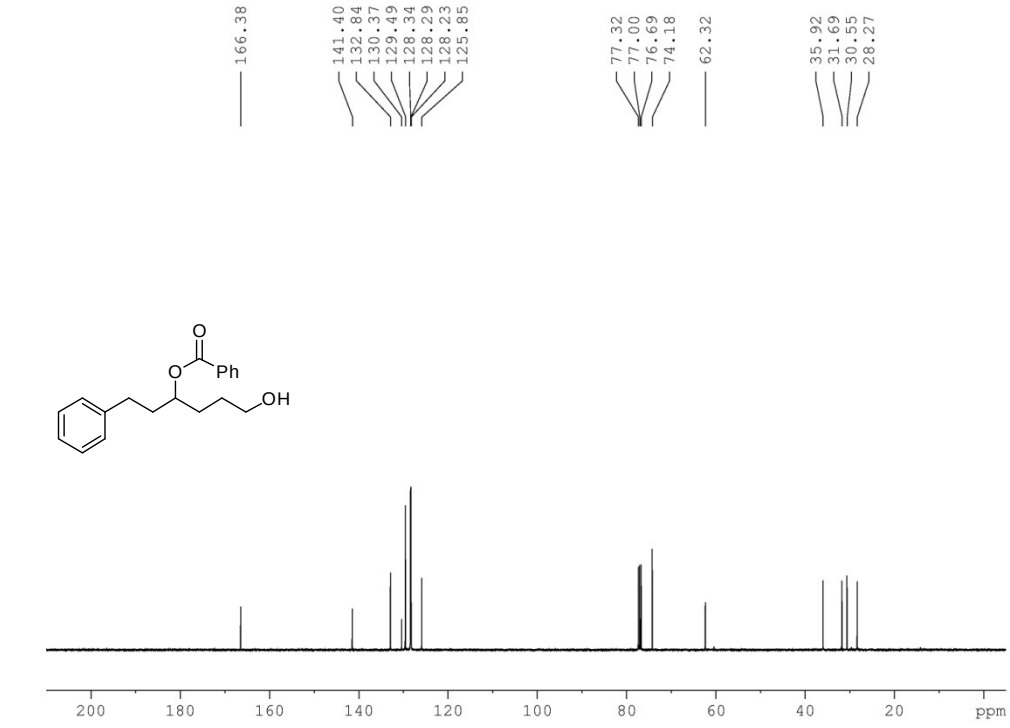
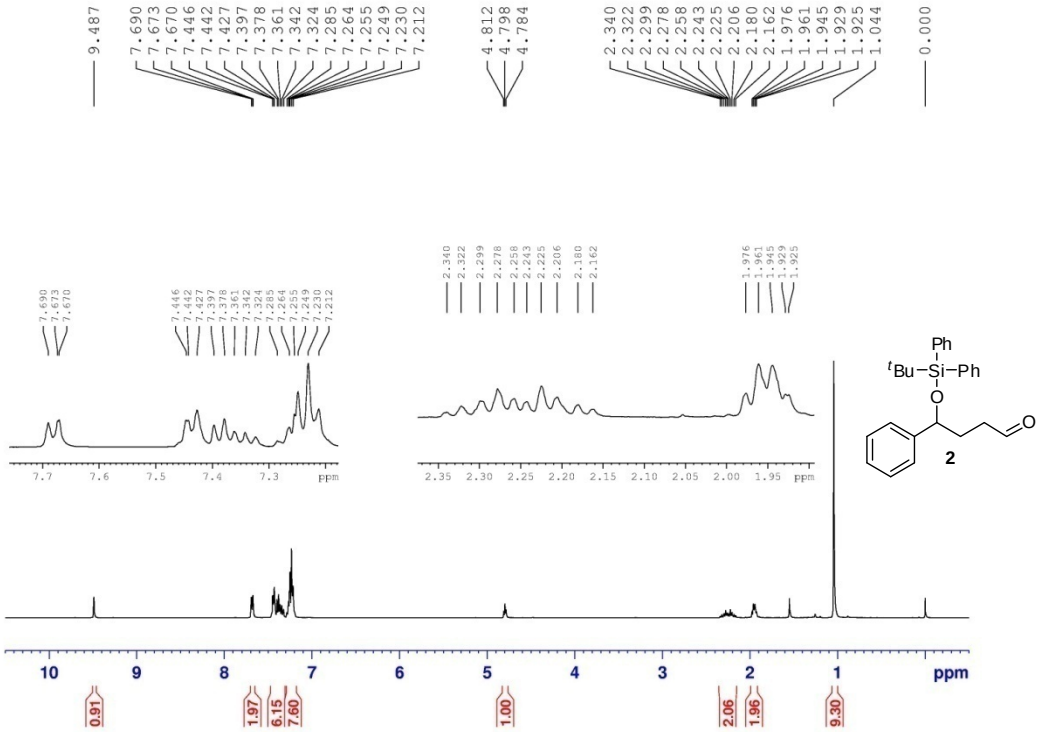
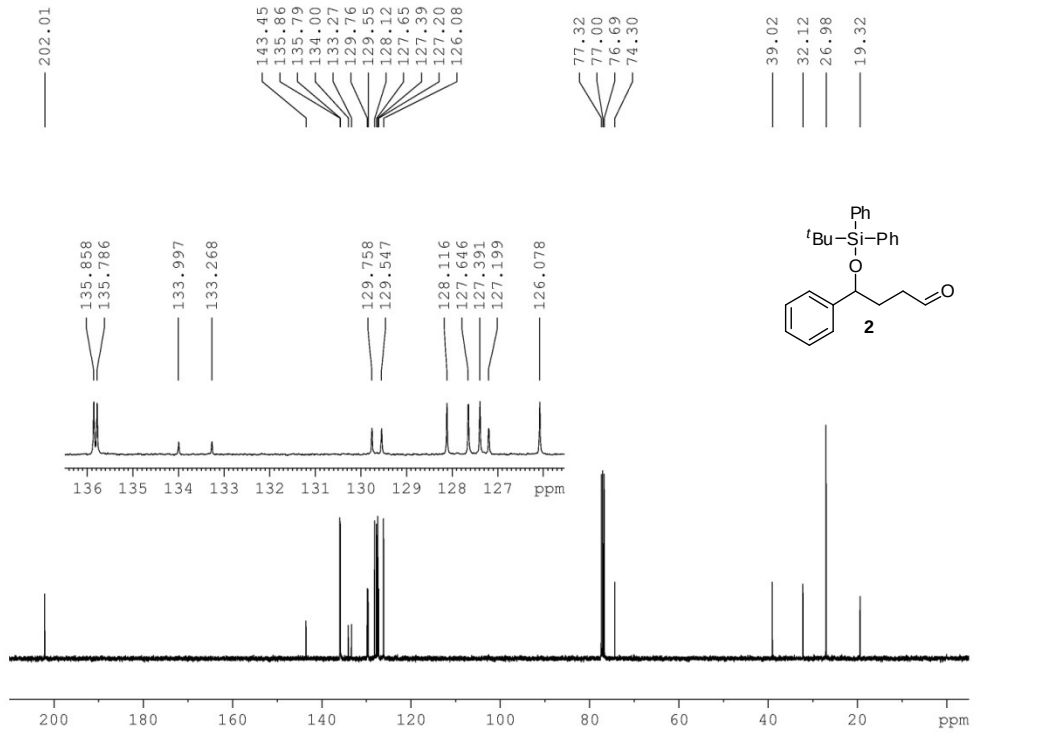
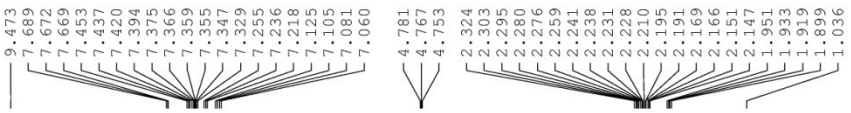
20
ppm

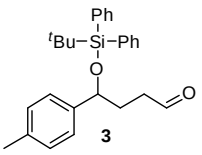


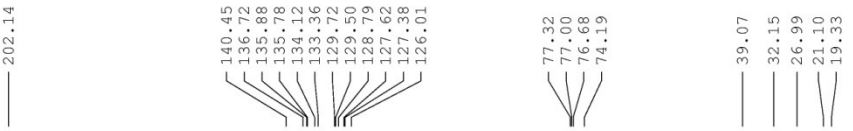


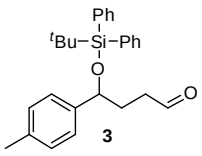


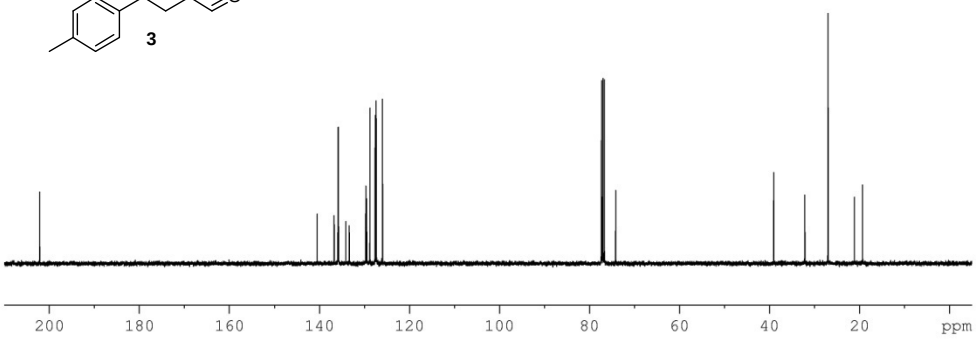


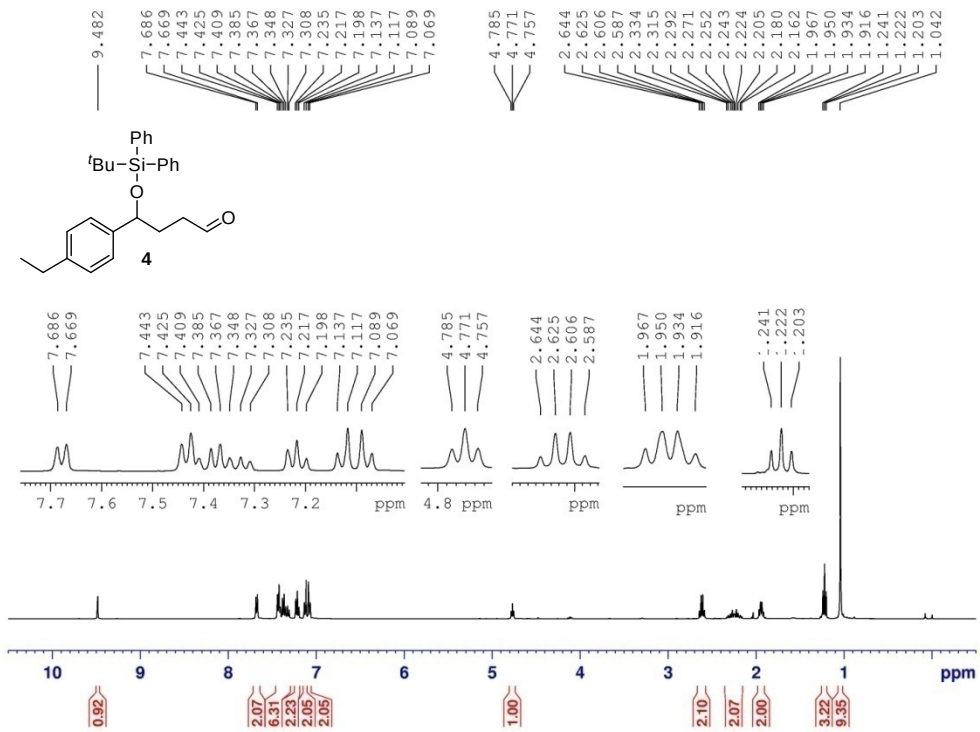








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O
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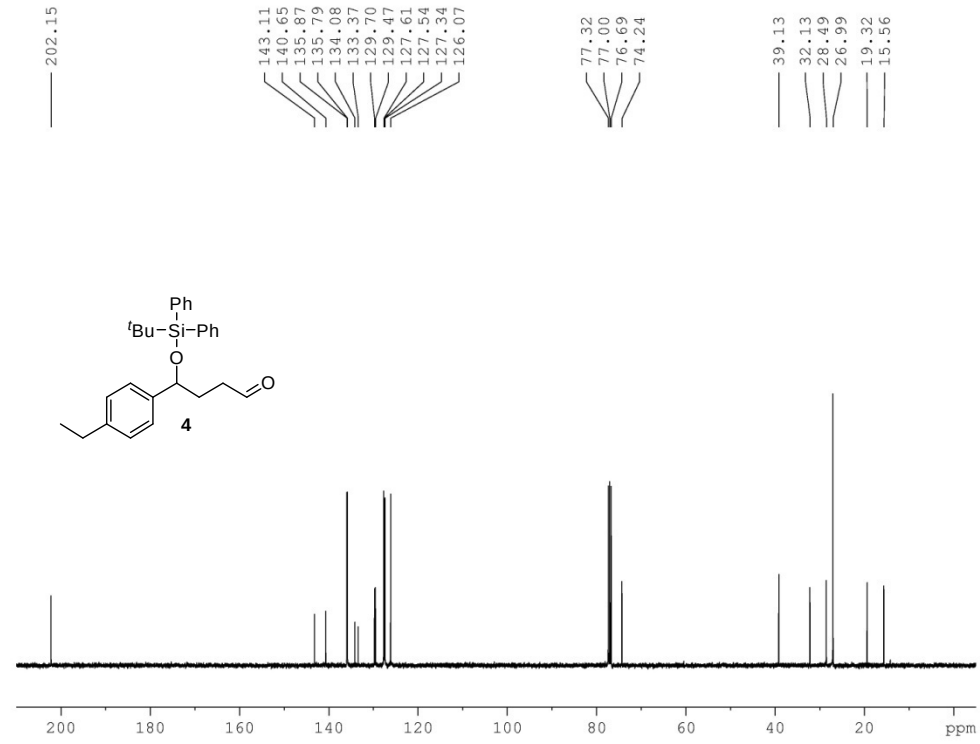
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77.00
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32.13
28.49
26.99
19.32
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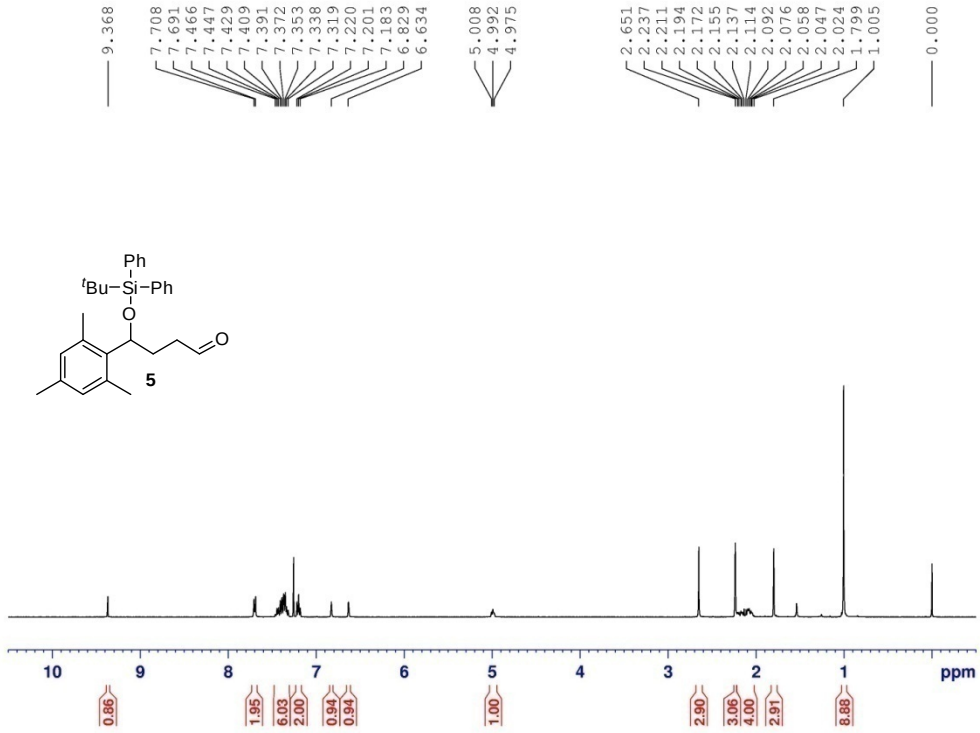
Ph
tBu–Si–Ph
O
O
4
ppm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2.024
1.799
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tBu–Si–Ph
O
O
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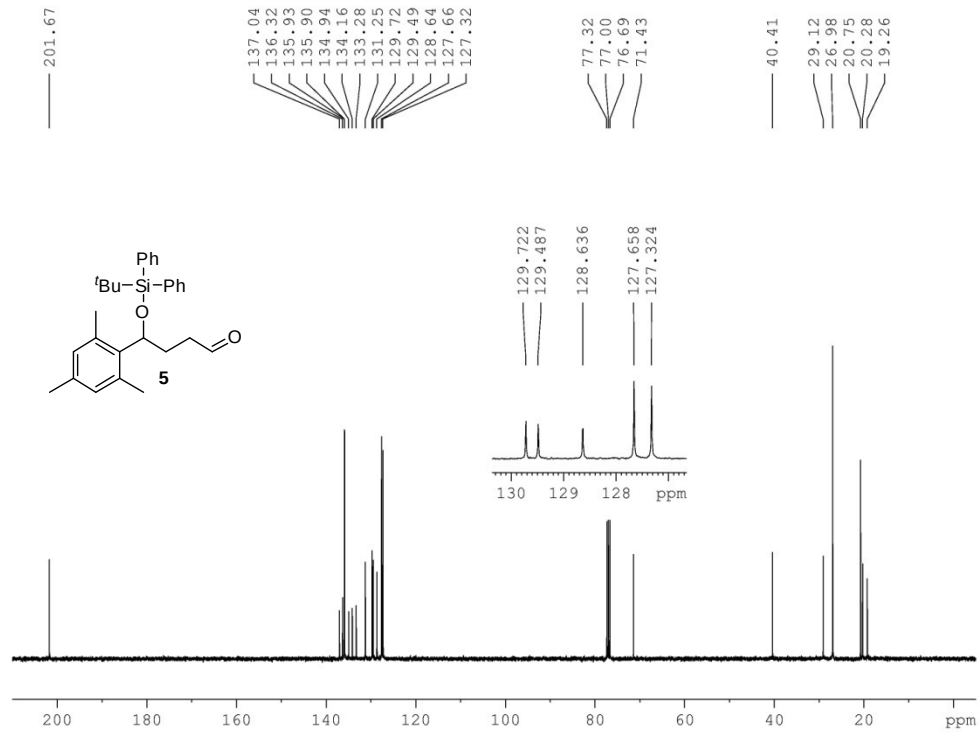
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26.98
20.75
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Ph
tBu–Si–Ph
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ppm
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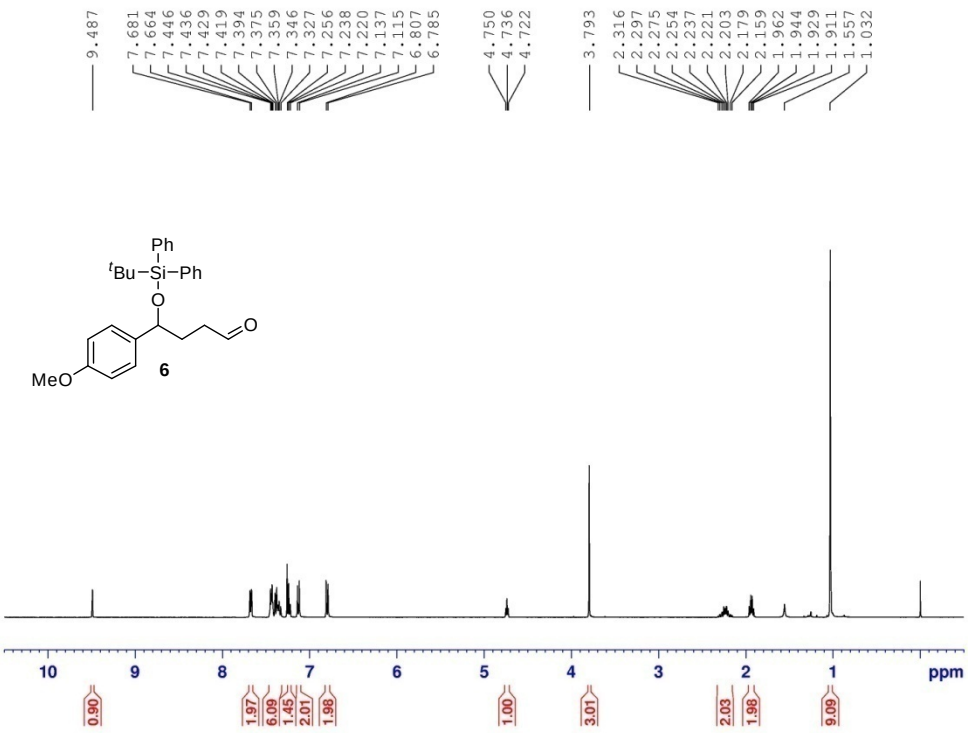

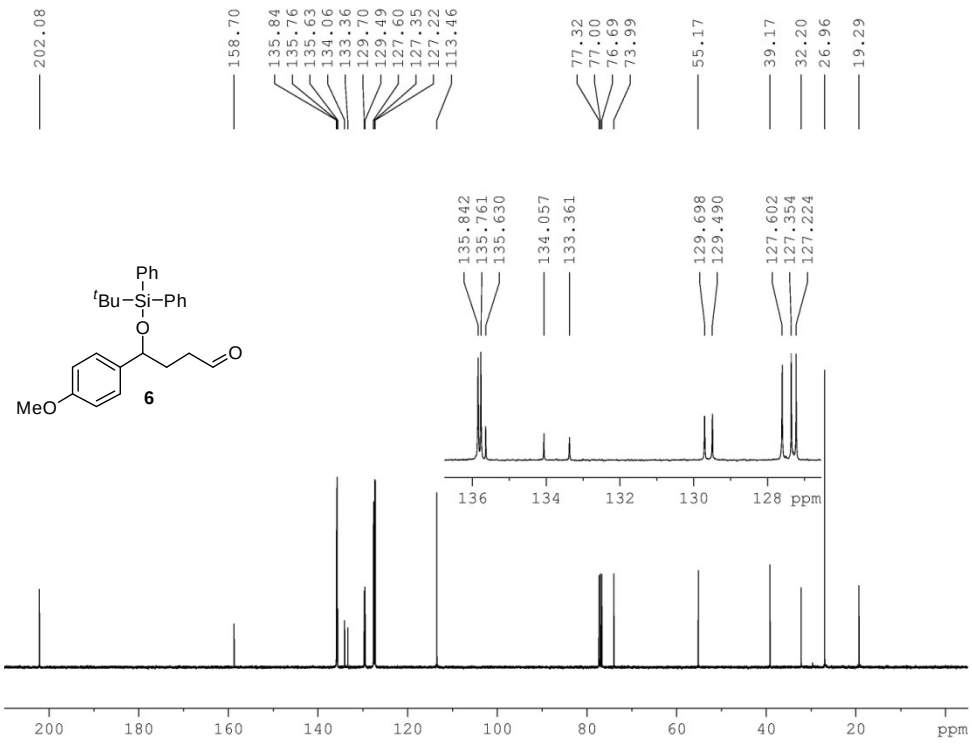

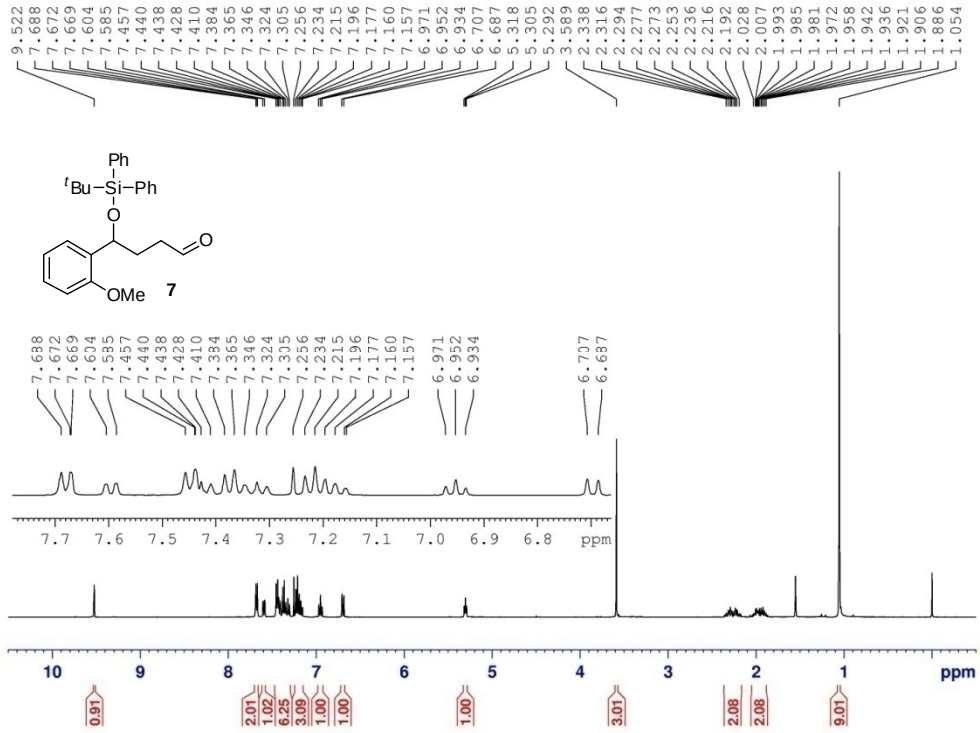
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Ph
tBu–Si–Ph
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OMe
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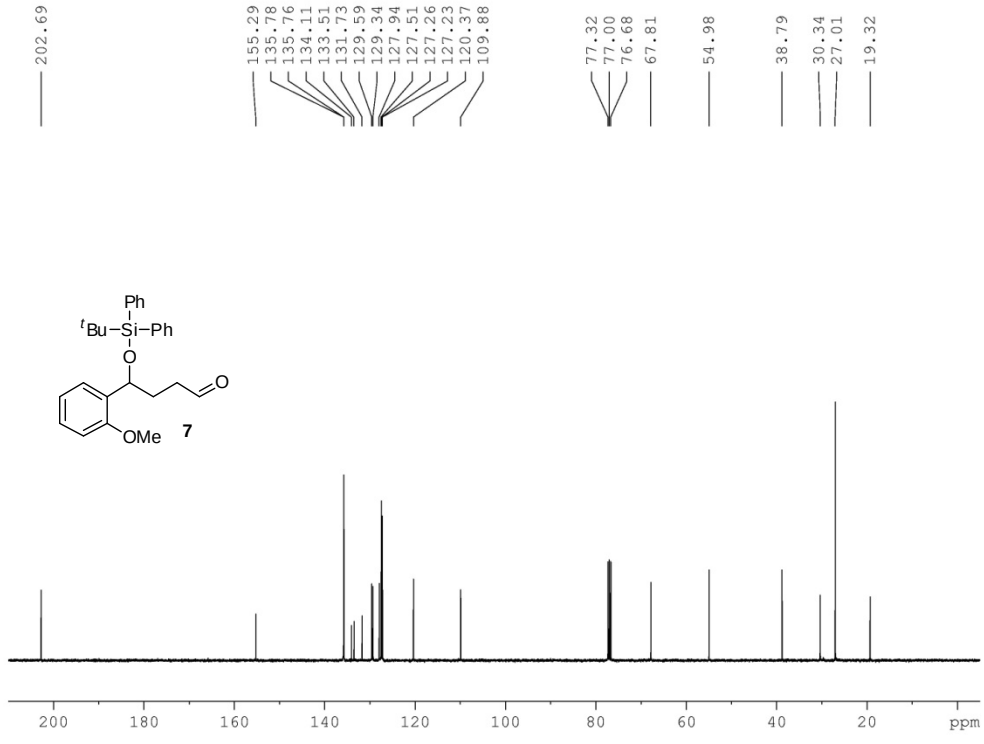
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77.00
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tBu–Si–Ph
O
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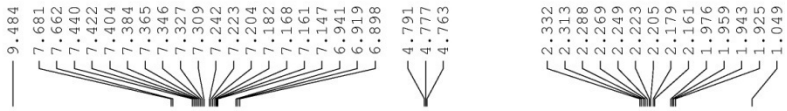
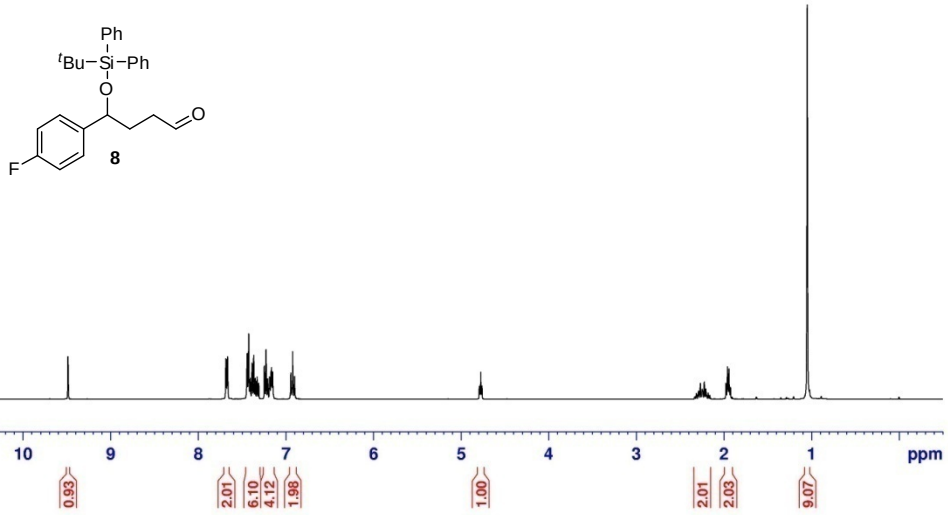
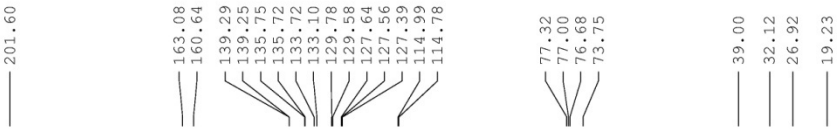
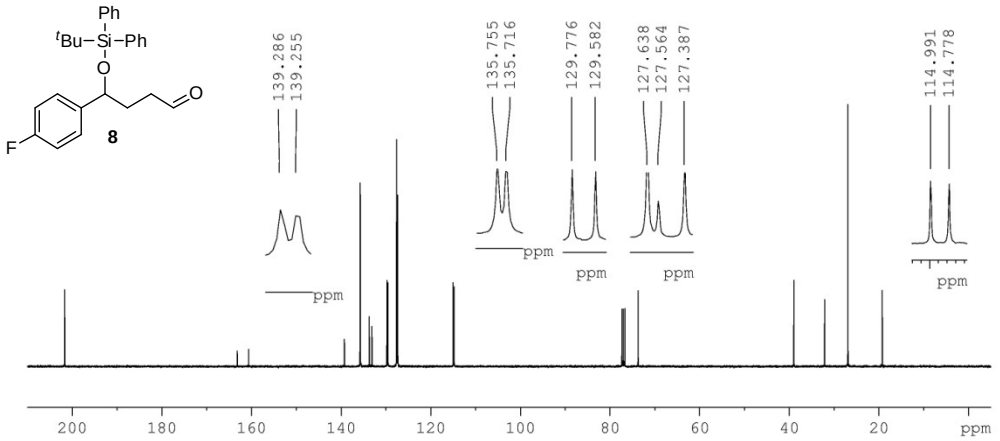
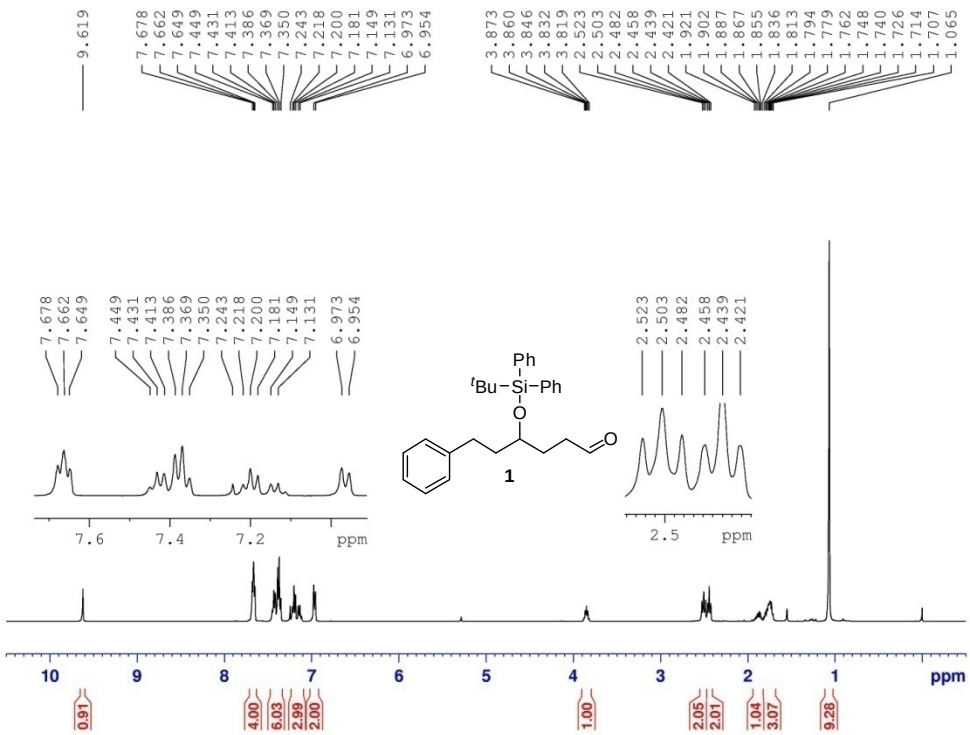
OMe
7
ppm

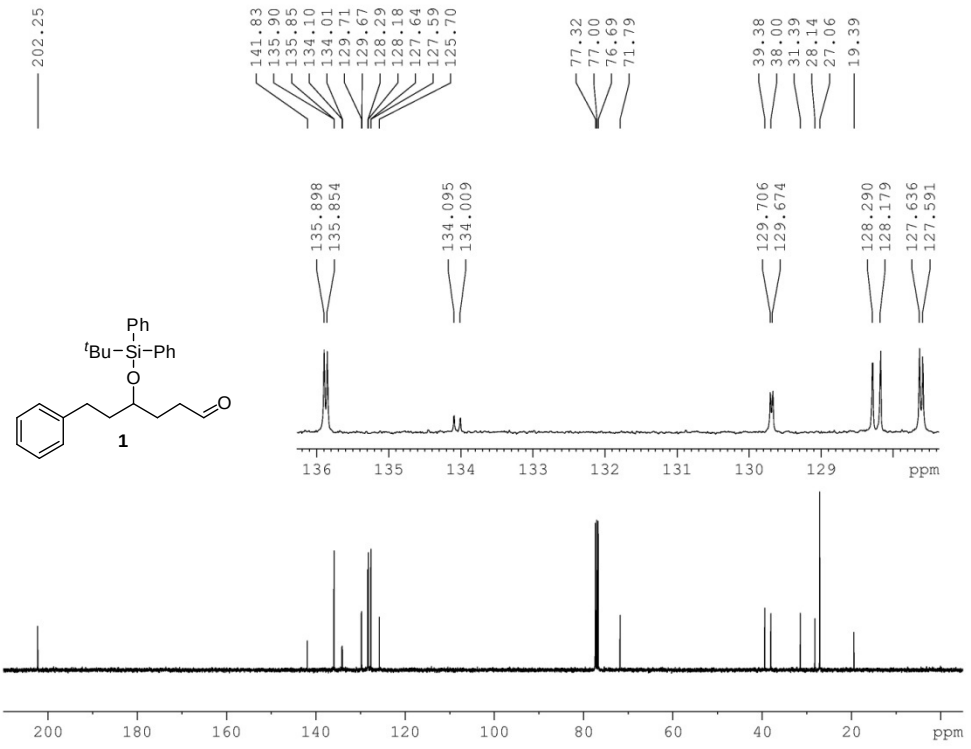


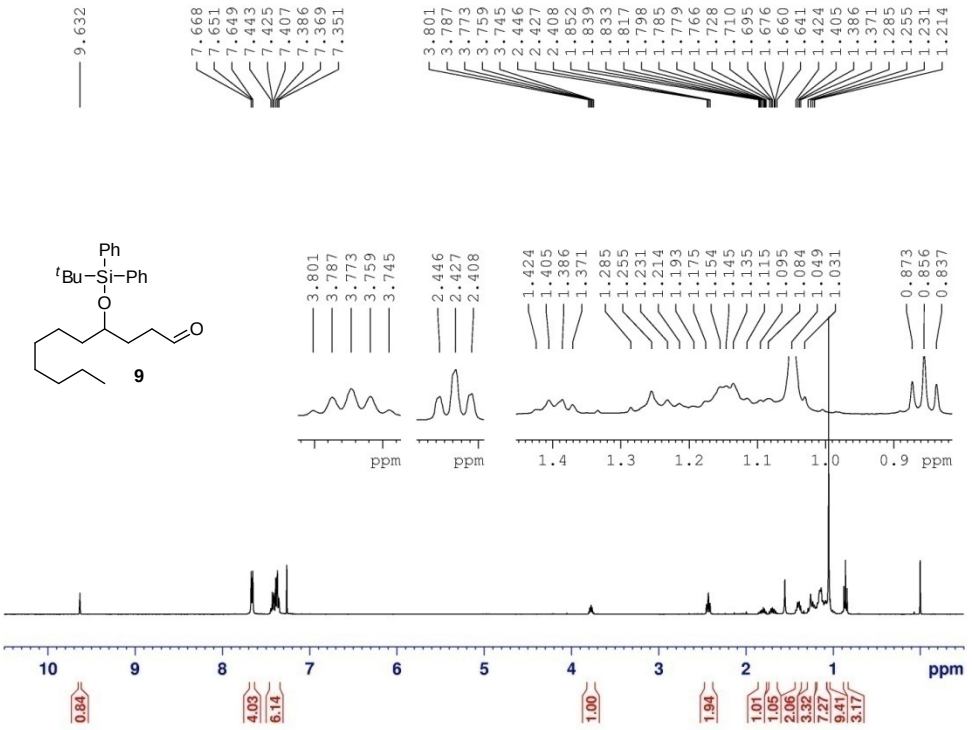








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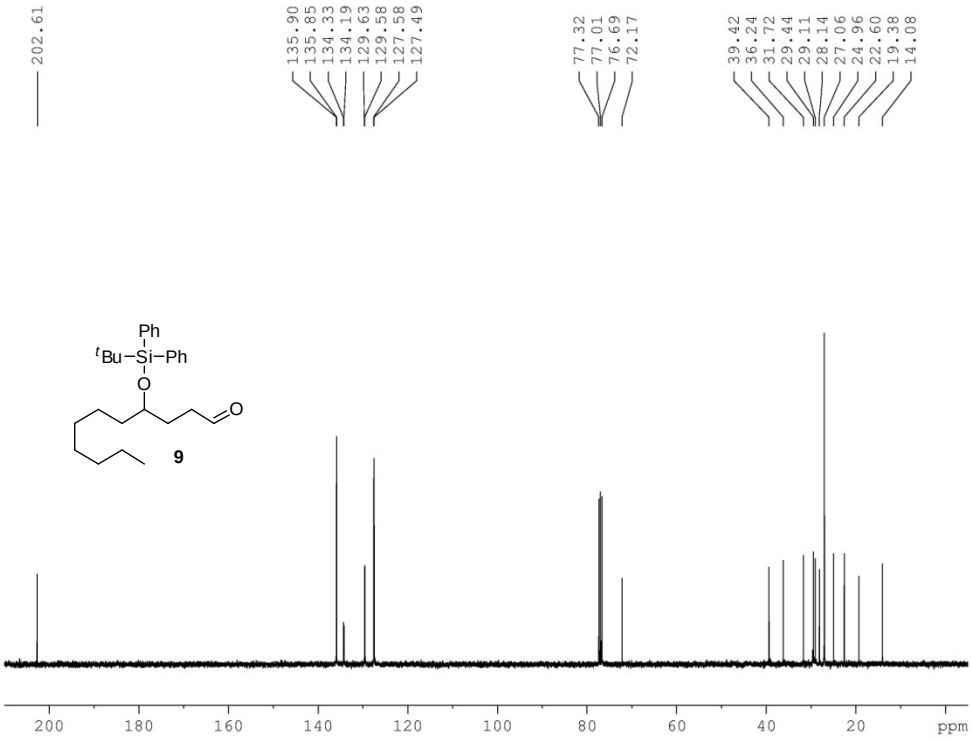
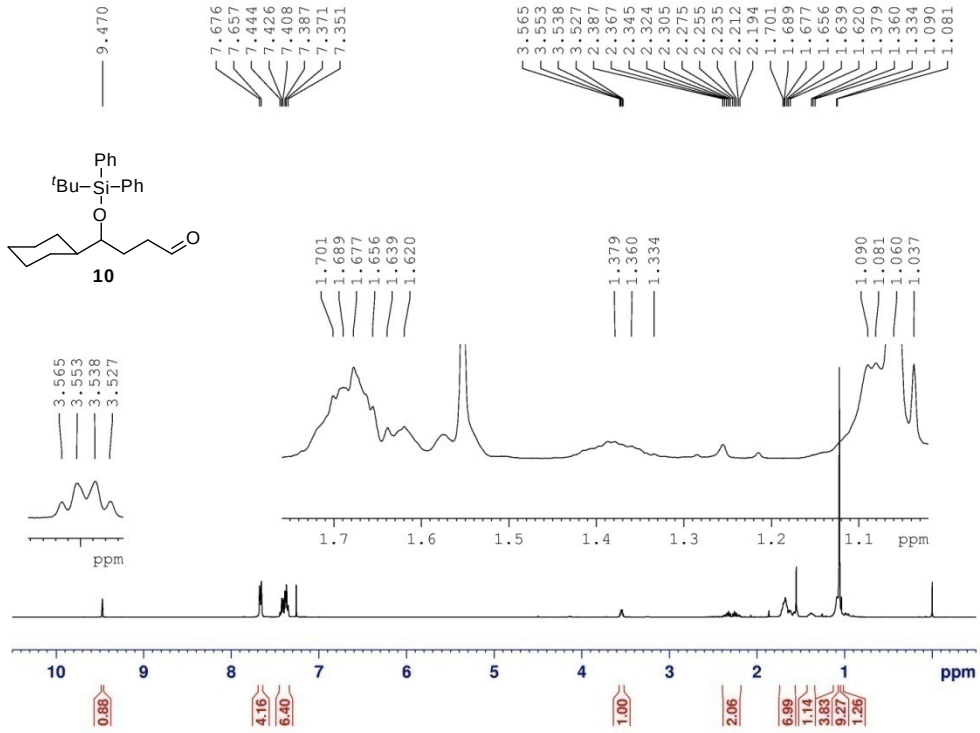
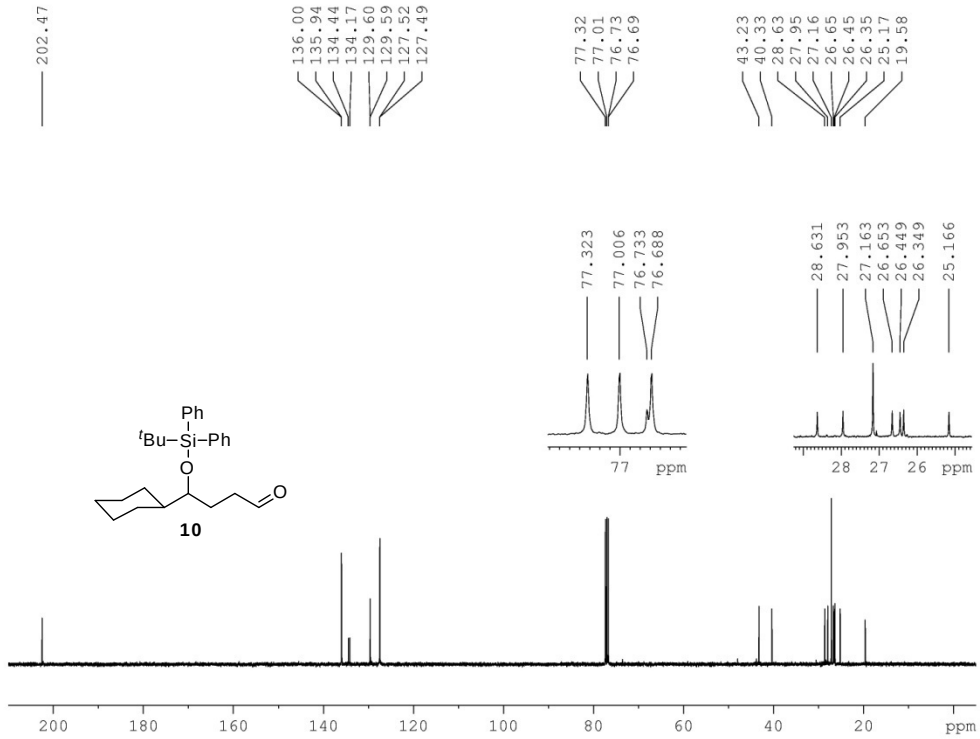
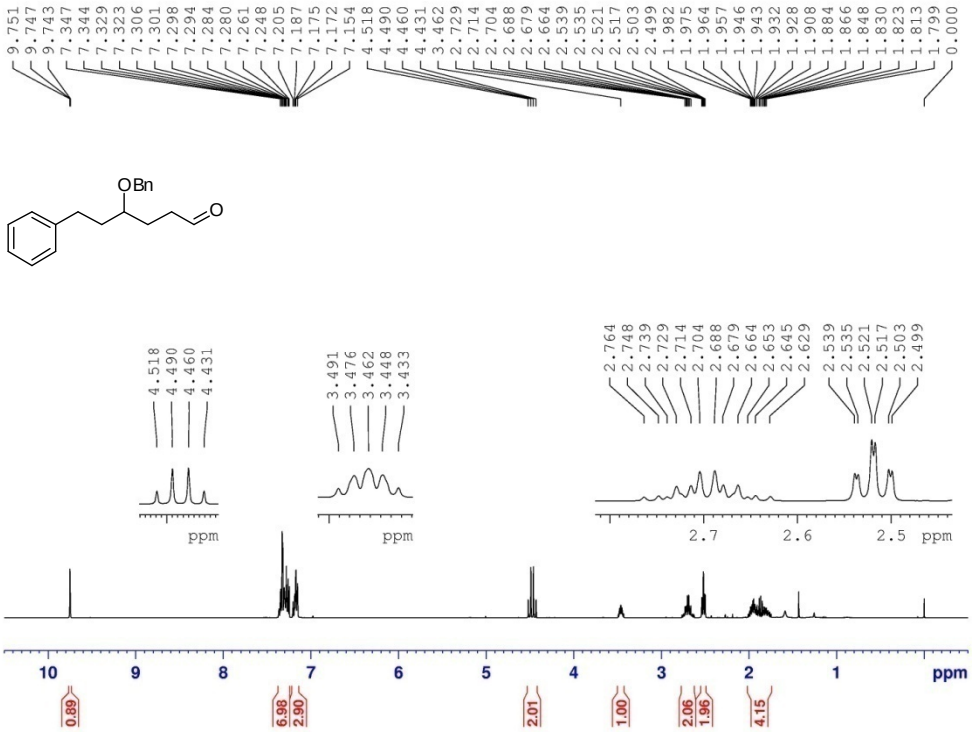
1.798
1.785
1.779
1.766
1.728
1.710
1.695
1.676
1.660
1.641
1.424
1.405
1.386
1.371
1.285
1.255
1.231
1.214
1.193
1.175
1.154
1.145
1.135
1.115
1.095
1.084
1.049
1.031
0.873
0.856
0.837
Ph
tBu–Si–Ph
O
O
9
ppm
ppm
1.4
1.3
1.2
1.1
1.0
0.9 ppm
10
9
8
7
6
5
4
3
2
1
ppm
0.84
4.03
6.14
1.00
1.94
1.01
1.05
2.06
3.32
7.27
9.41
3.17


202.61
135.90
135.85
134.33
134.19
129.63
129.58
127.58
127.49
77.32
77.01
76.69
72.17
39.42
36.24
31.72
29.44
29.11
28.14
27.06
24.96
22.60
19.38
14.08
Ph
tBu–Si–Ph
O
O
9
200
180
160
140
120
100
80
60
40
20
ppm



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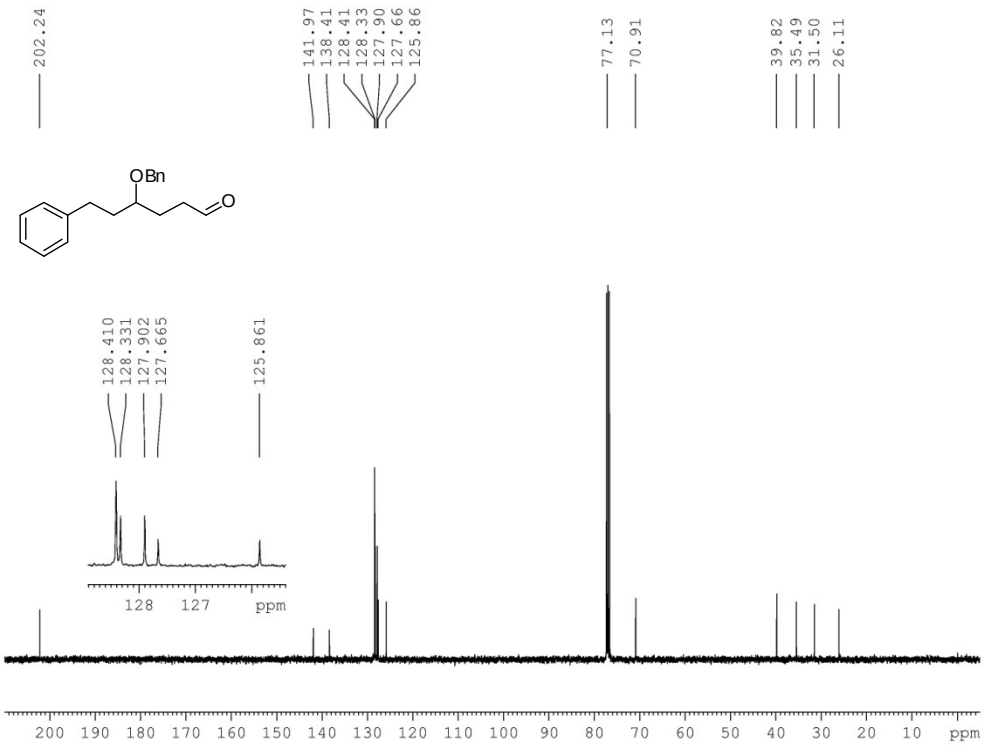
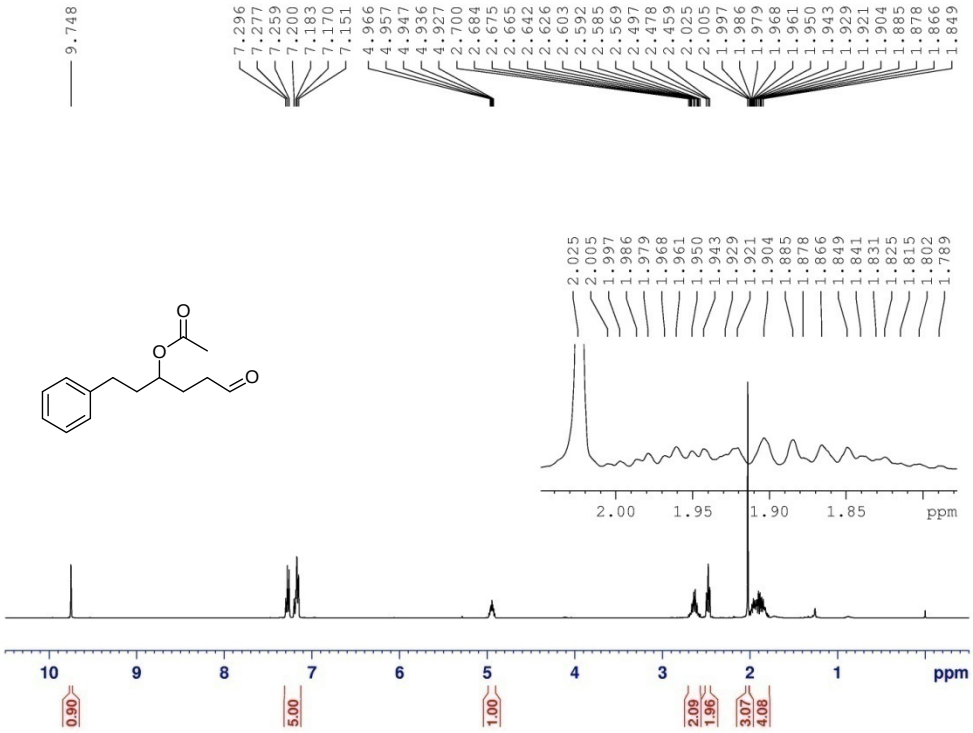
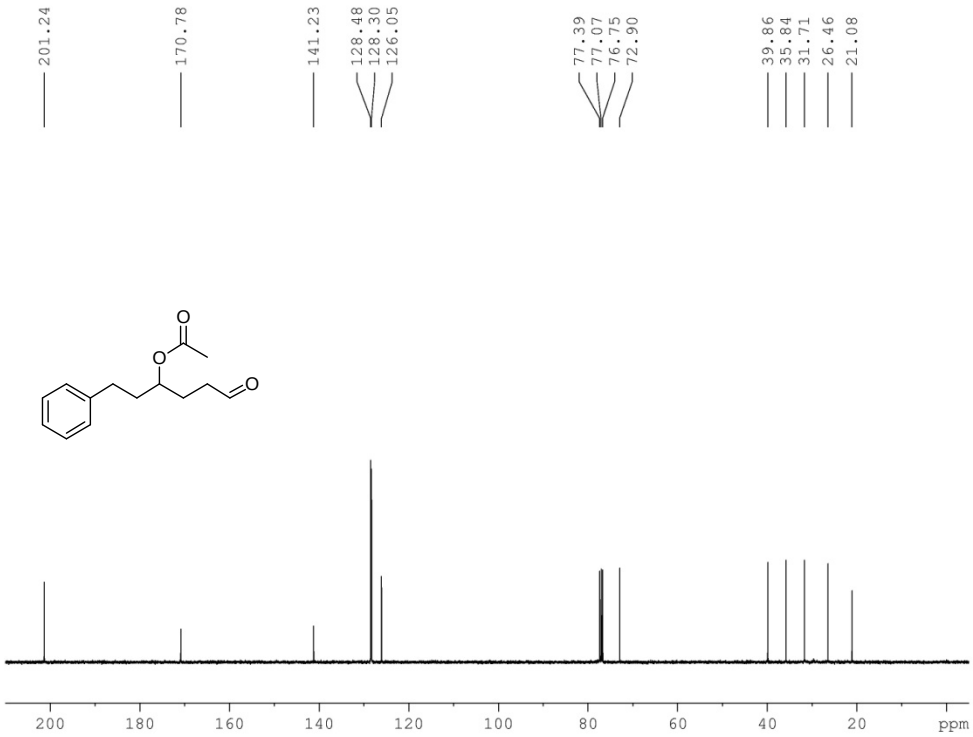
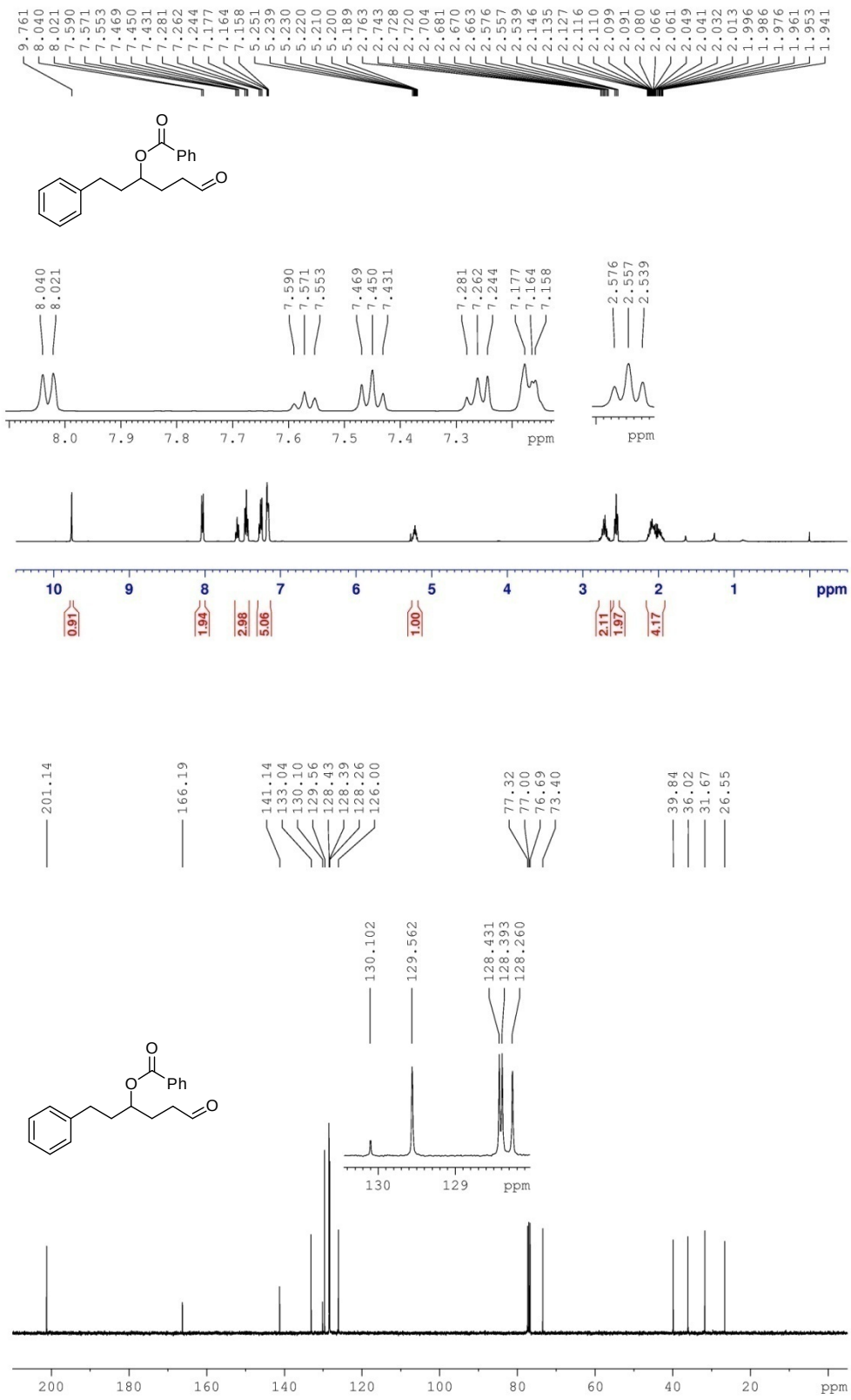
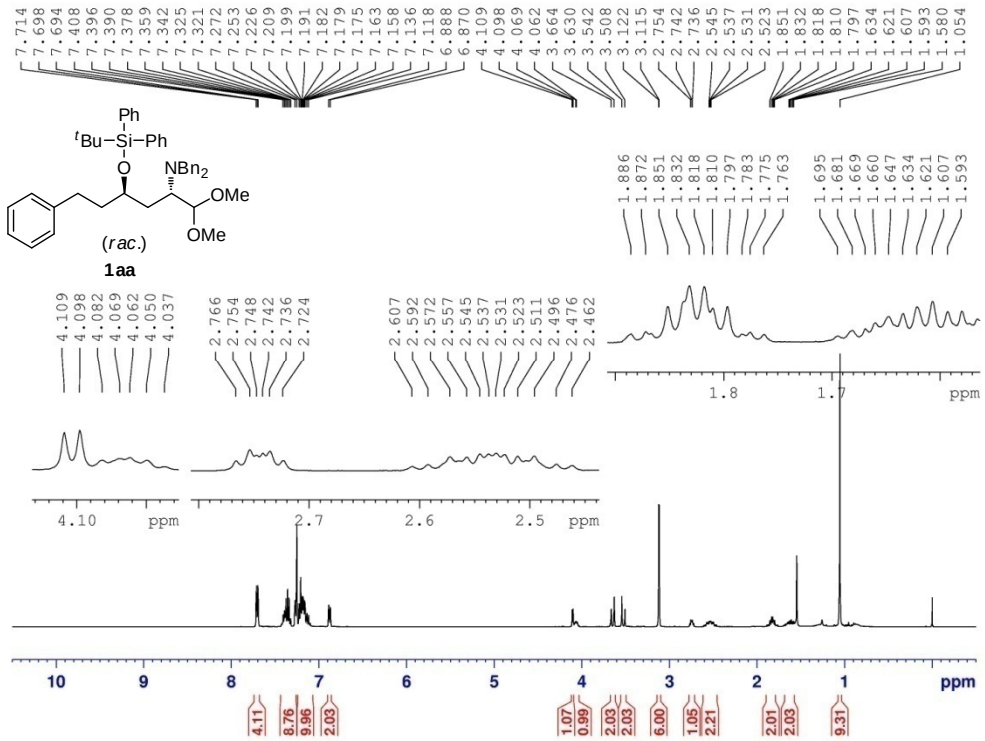
9.747
9.743
7.347
7.344
7.329
7.323
7.306
7.301
7.298
7.294
7.284
7.280
7.261
7.248
7.205
7.187
7.175
7.172
7.154
4.518
4.490
4.460
4.431
3.462
2.729
2.714
2.704
2.688
2.679
2.664
2.539
2.535
2.521
2.517
2.503
2.499
1.982
1.975
1.964
1.957
1.946
1.943
1.932
1.928
1.908
1.884
1.866
1.848
1.830
1.823
1.813
1.799
0.000
OBn
O
4.518
4.490
4.460
4.431
ppm
3.491
3.476
3.462
3.448
3.433
ppm
2.764
2.748
2.739
2.729
2.714
2.704
2.688
2.679
2.664
2.653
2.645
2.629
2.539
2.535
2.521
2.517
2.503
2.499
2.7
2.6
2.5
ppm
10
9
8
7
6
5
4
3
2
1
ppm
0.89
6.98
2.90
2.01
1.00
2.06
1.96
4.15

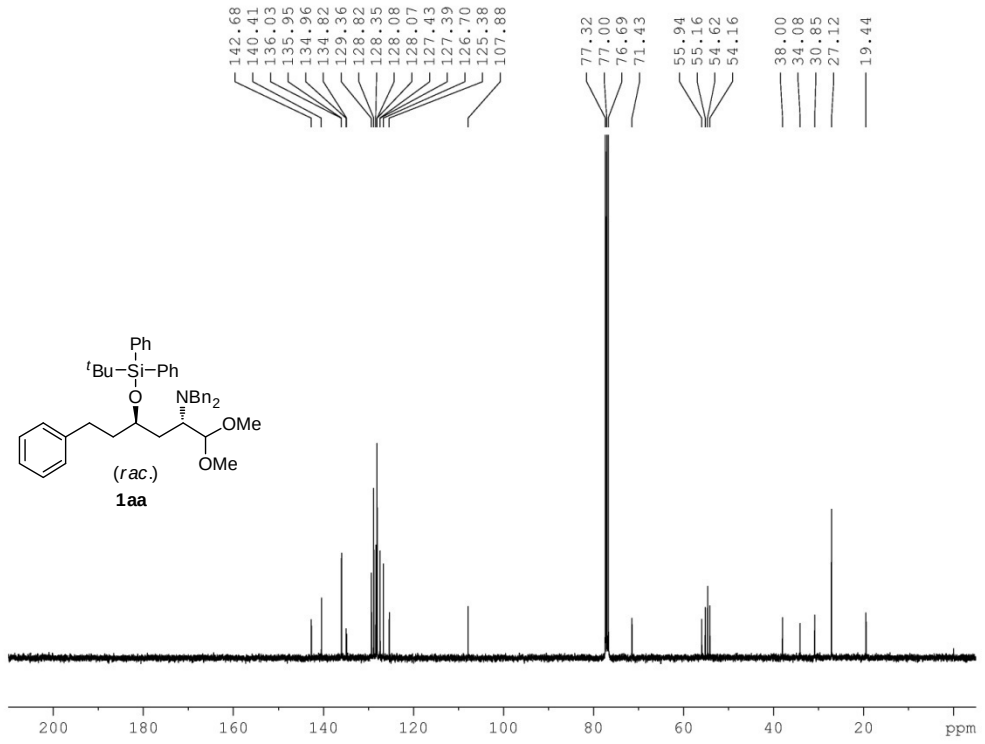

202.24
141.97
138.41
128.41
128.33
127.90
127.66
125.86
77.13
70.91
39.82
35.49
31.50
26.11
OBn
O
128.410
128.331
127.902
127.665
125.861
128
127
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

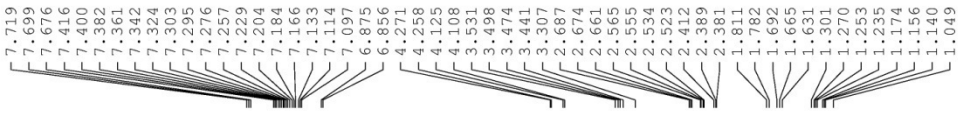





9.761
8.040
8.021
7.590
7.571
7.553
7.469
7.450
7.431
7.281
7.262
7.244
7.177
7.164
7.158
5.251
5.239
5.230
5.220
5.210
5.200
5.189
2.763
2.743
2.728
2.720
2.704
2.681
2.670
2.663
2.576
2.557
2.539
2.146
2.135
2.127
2.116
2.110
2.099
2.091
2.080
2.066
2.061
2.049
2.041
2.032
2.013
1.996
1.986
1.976
1.961
1.953
1.941
O
O
Ph
O
8.040
8.021
7.590
7.571
7.553
7.469
7.450
7.431
7.281
7.262
7.244
7.177
7.164
7.158
2.576
2.557
2.539
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
ppm
ppm
10
9
8
7
6
5
4
3
2
1
ppm
0.91
1.94
2.98
5.06
1.00
2.11
1.97
4.17
201.14
166.19
141.14
133.04
130.10
129.56
128.43
128.39
128.26
126.00
77.32
77.00
76.69
73.40
39.84
36.02
31.67
26.55
130.102
129.562
128.431
128.393
128.260
O
O
Ph
O
130
129
ppm
200
180
160
140
120
100
80
60
40
20
ppm






7.719
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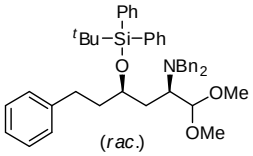
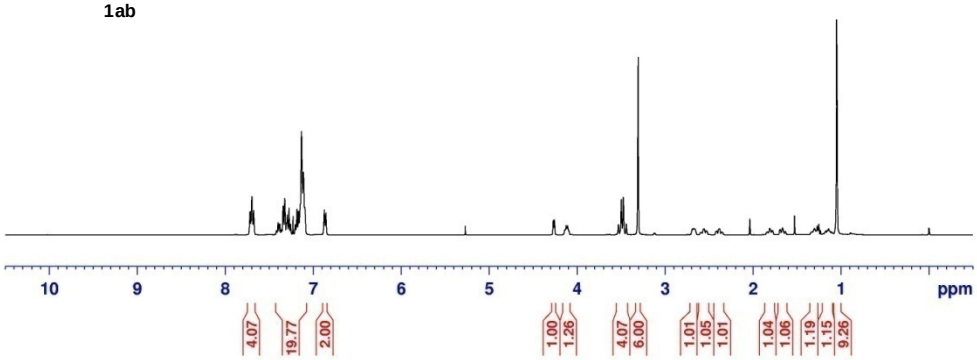
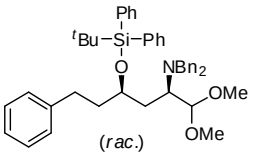
7.676
7.416
7.400
7.382
7.361
7.342
7.324
7.303
7.295
7.276
7.257
7.229
7.204
7.184
7.166
7.133
7.114
7.097
6.875
6.856
4.271
4.258
4.125
4.108
3.531
3.498
3.474
3.441
3.307
2.687
2.674
2.661
2.565
2.555
2.534
2.523
2.412
2.389
2.381
1.811
1.782
1.692
1.665
1.631
1.301
1.270
1.253
1.235
1.174
1.156
1.140
1.049


Ph
tBu–Si–Ph
O
NBn2
OMe
OMe
(rac.)

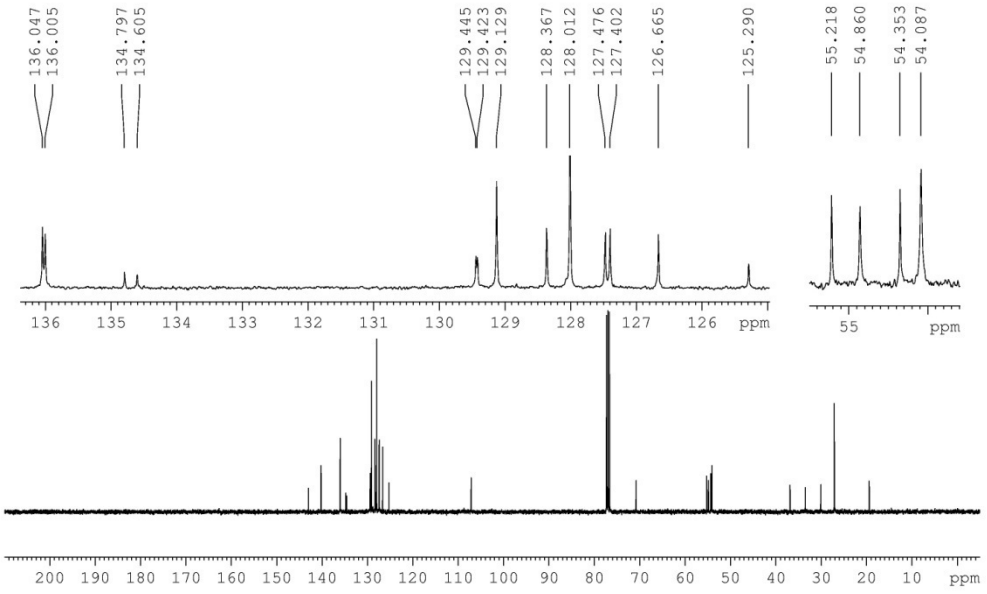
1ab

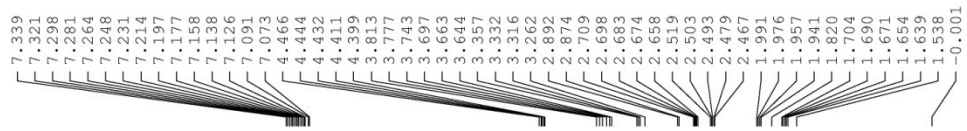

10
9
8
7
6
5
4
3
2
1
ppm
4.07
19.77
2.00
1.00
1.26
4.07
6.00
1.01
1.05
1.01
1.04
1.06
1.19
1.15
9.26

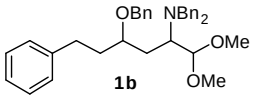

Ph
tBu–Si–Ph
O
NBn2
OMe
OMe
(rac.)

1ab


143.03
140.26
136.05
136.01
134.80
134.60
129.45
129.42
129.13
128.37
128.01
127.48
127.40
126.67
125.29
107.17
70.79
55.22
54.86
54.35
54.09
36.88
33.51
30.08
27.10
19.38

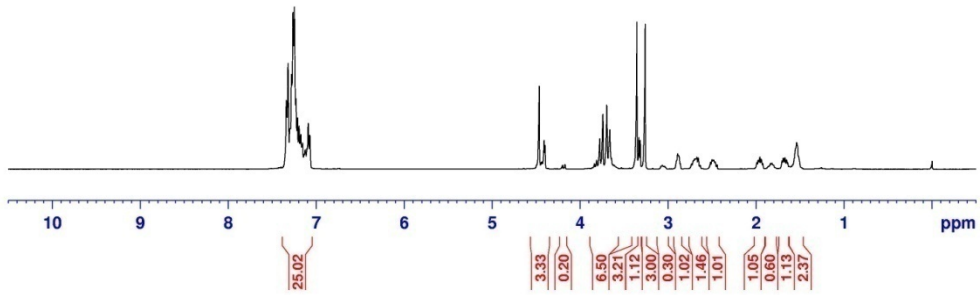

136.047
136.005
134.797
134.605
129.445
129.423
129.129
128.367
128.012
127.476
127.402
126.665
125.290
55.218
54.860
54.353
54.087
136
135
134
133
132
131
130
129
128
127
126
ppm
55
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

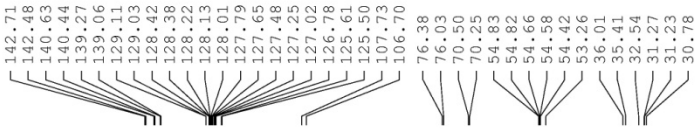


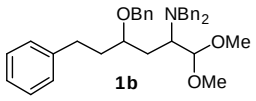


1b

dr 82:18 (*syn*/*anti*)

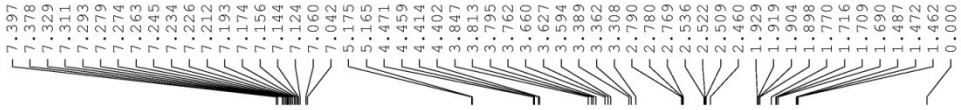


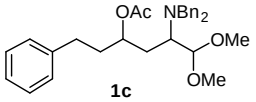




1b

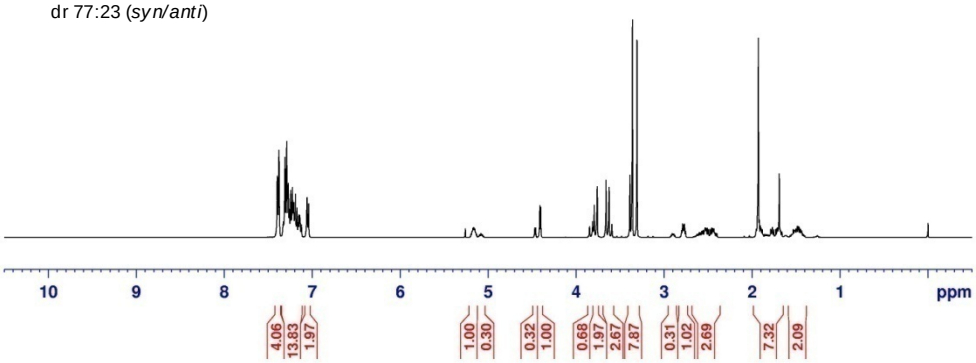
dr 82:18 (*syn*/*anti*)

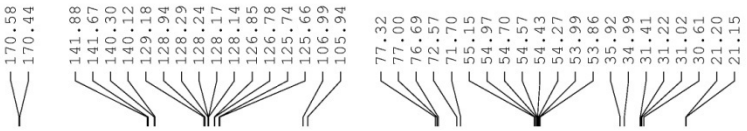


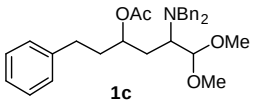


1c

dr 77:23 (*syn*/*anti*)

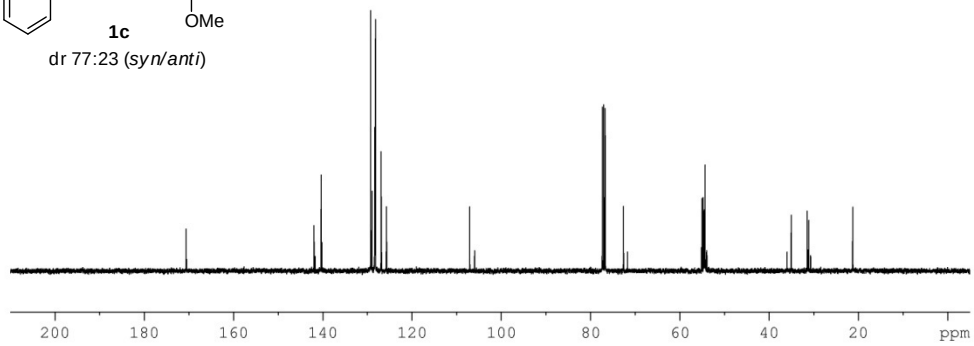


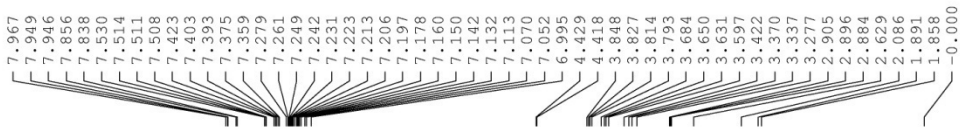


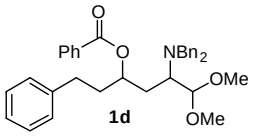


1c

dr 77:23 (*syn*/*anti*)

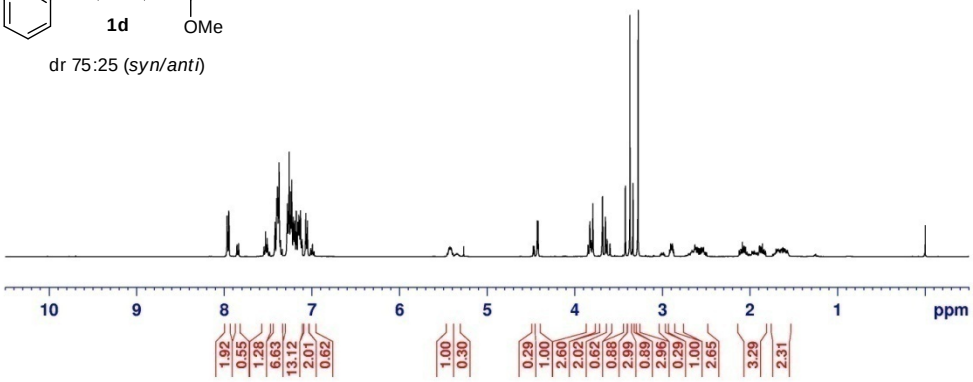


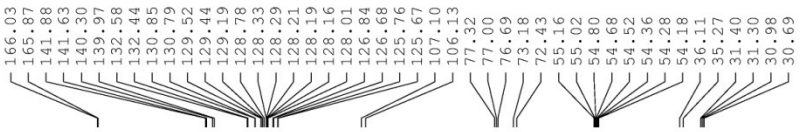


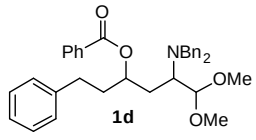


1d

dr 75:25 (*syn*/*anti*)

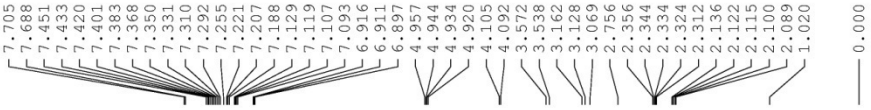


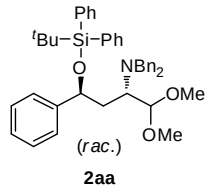




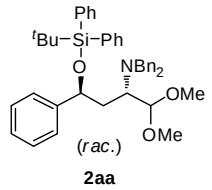
1d

dr 75:25 (*syn*/*anti*)

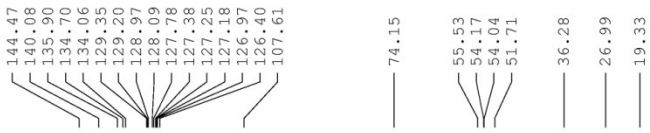


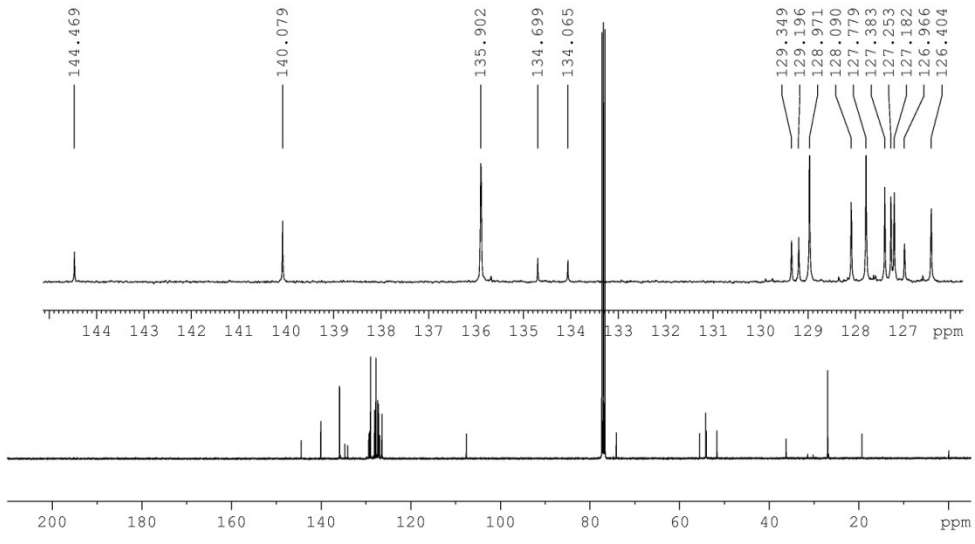


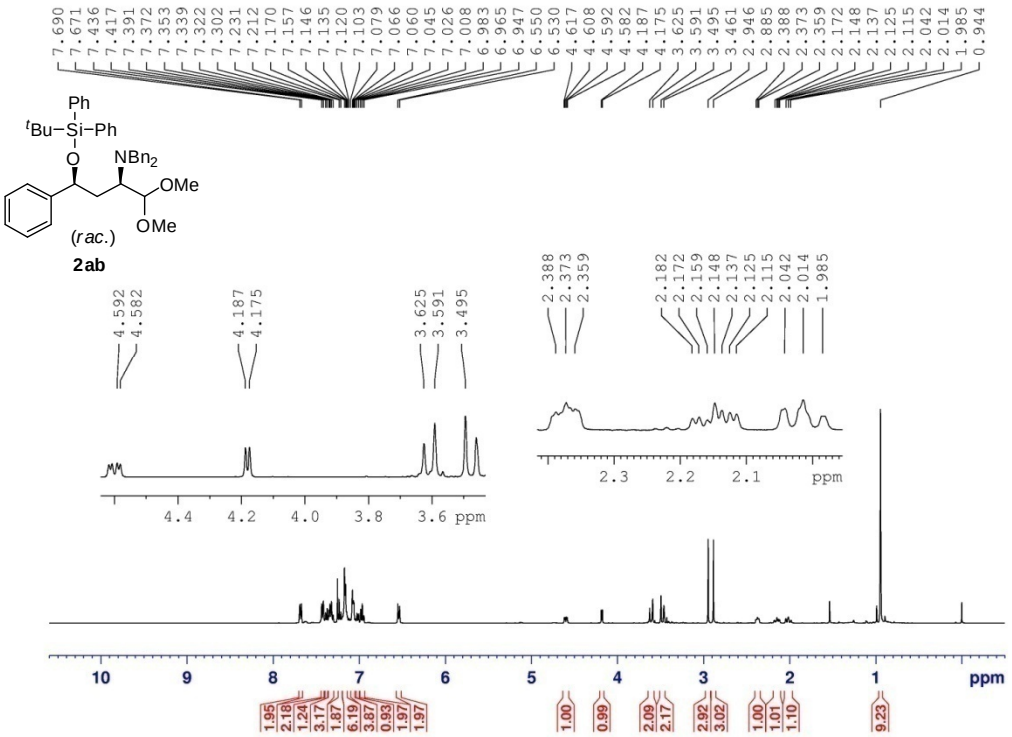
2aa

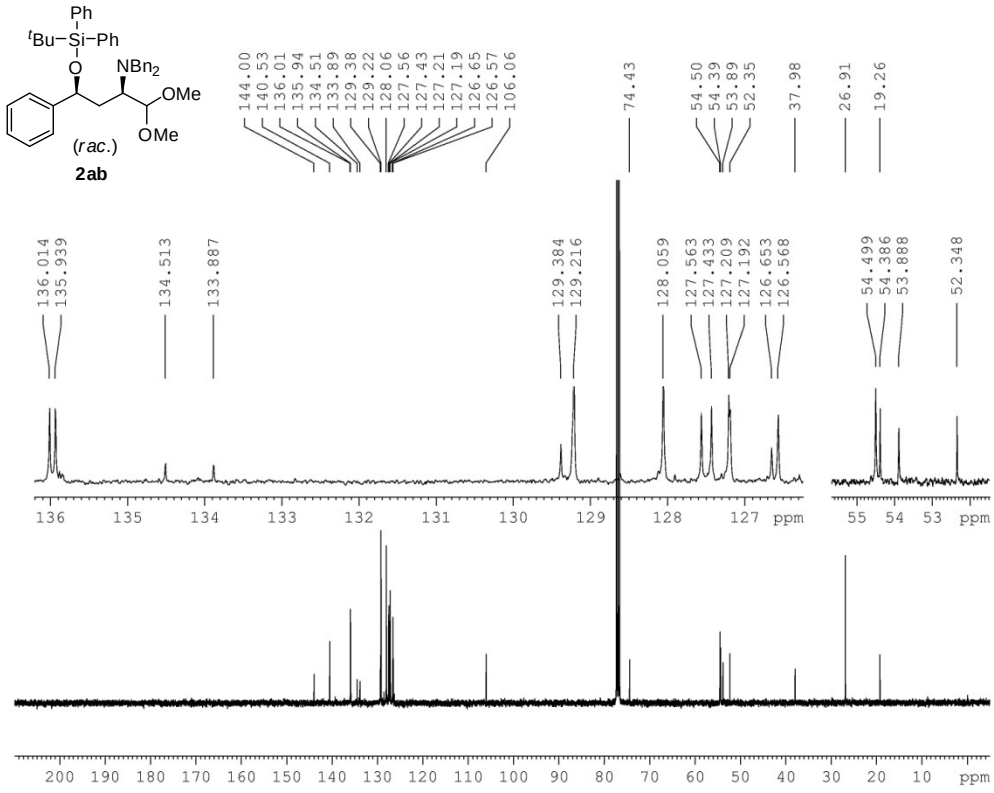


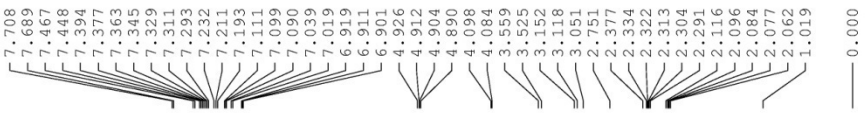
2aa

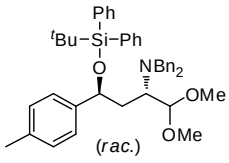




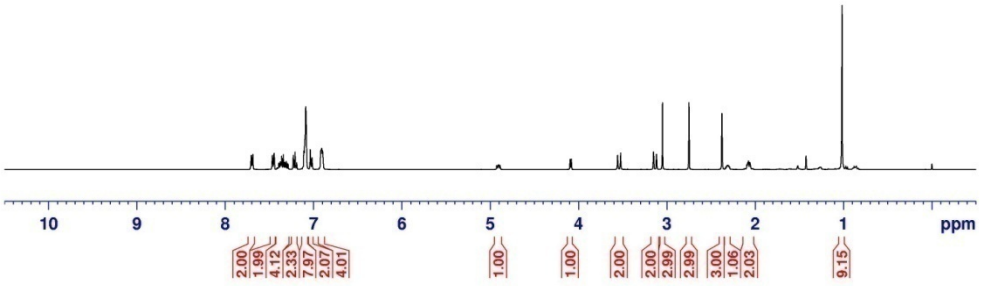

Ph
tBu–Si–Ph
O
NBn2
OMe
OMe
(rac.)
2ab
ppm

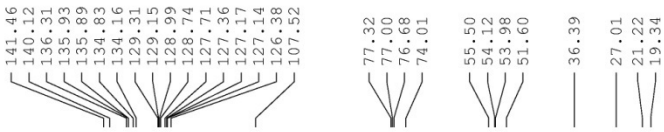

Ph
tBu–Si–Ph
O
NBn2
OMe
OMe
(rac.)
2ab
ppm

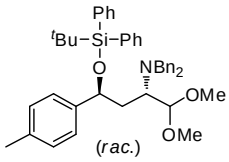




3aa







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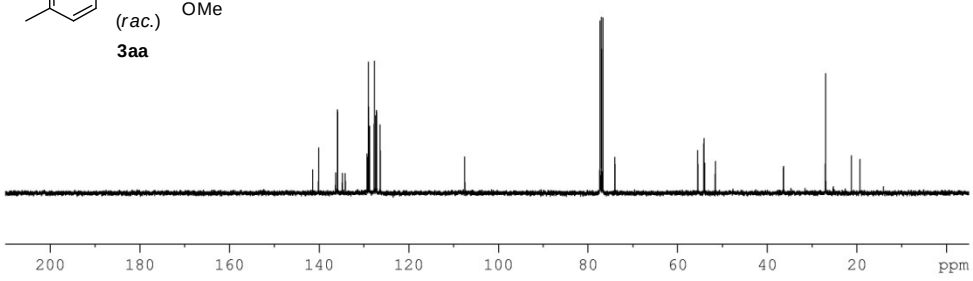

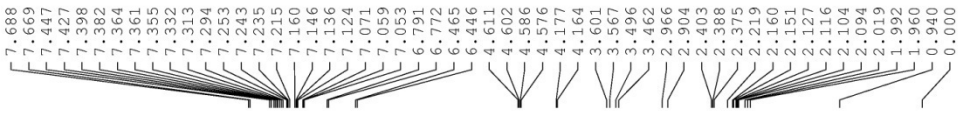

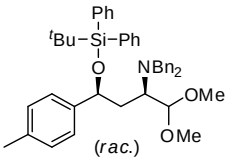

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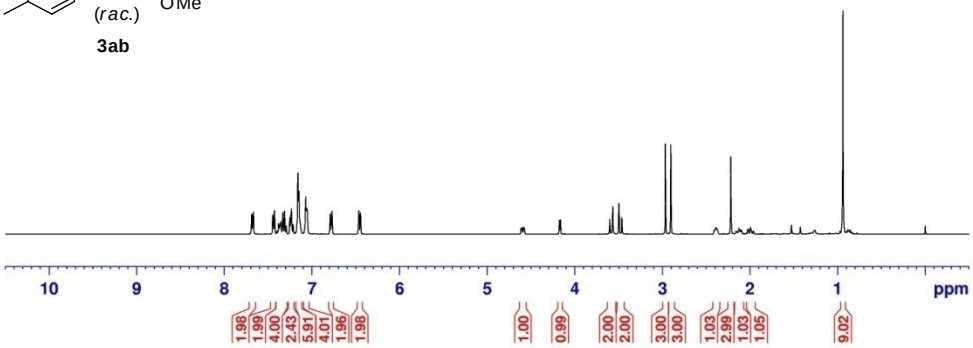

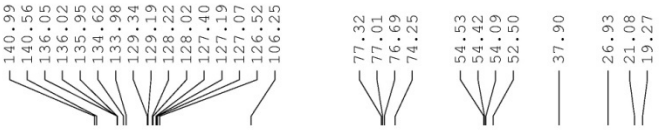

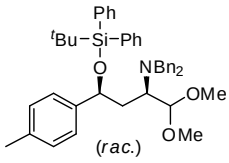

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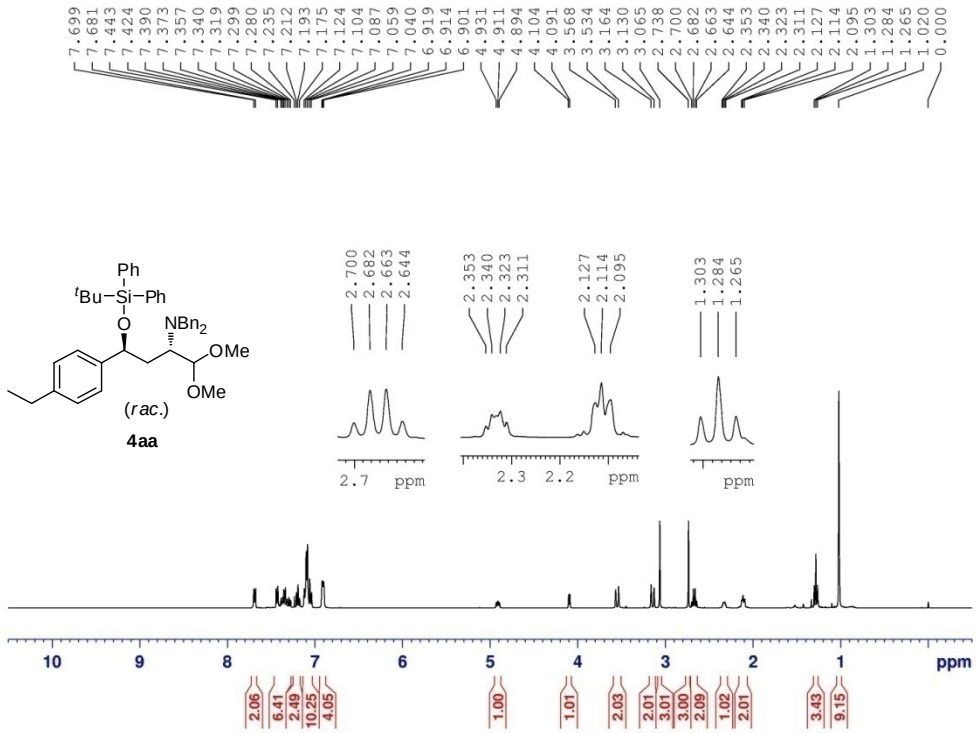
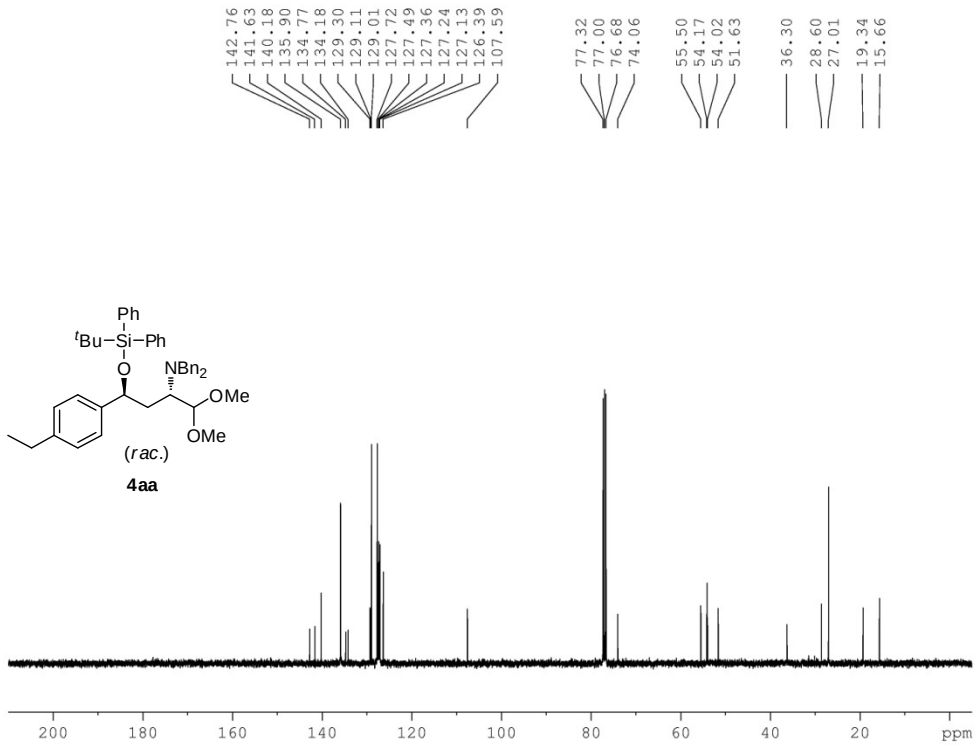
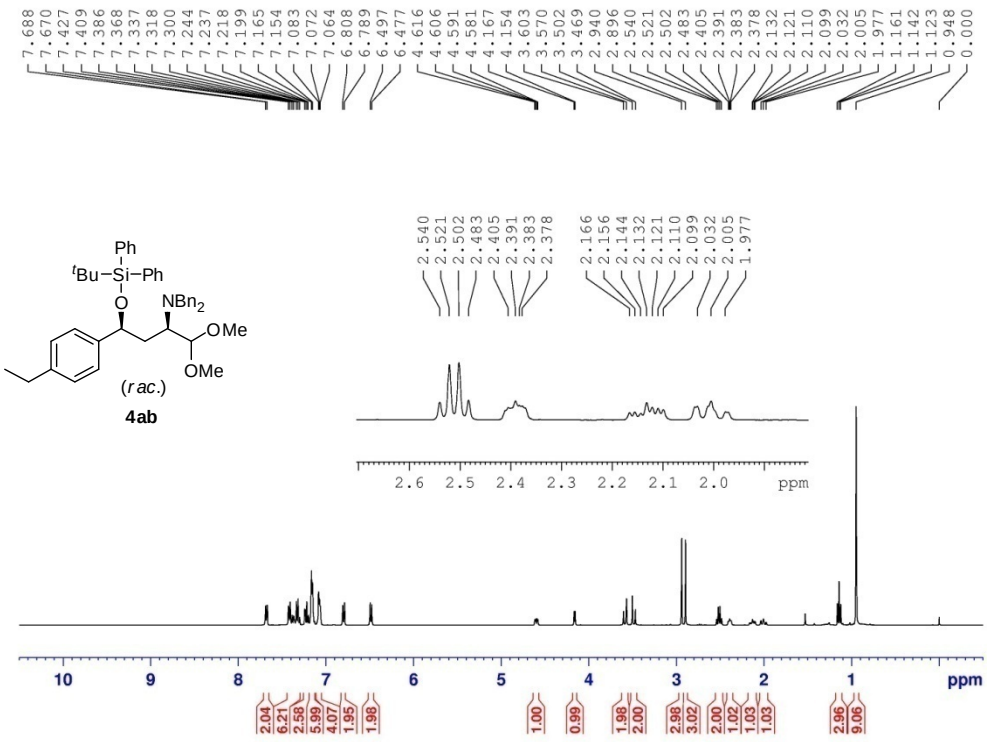
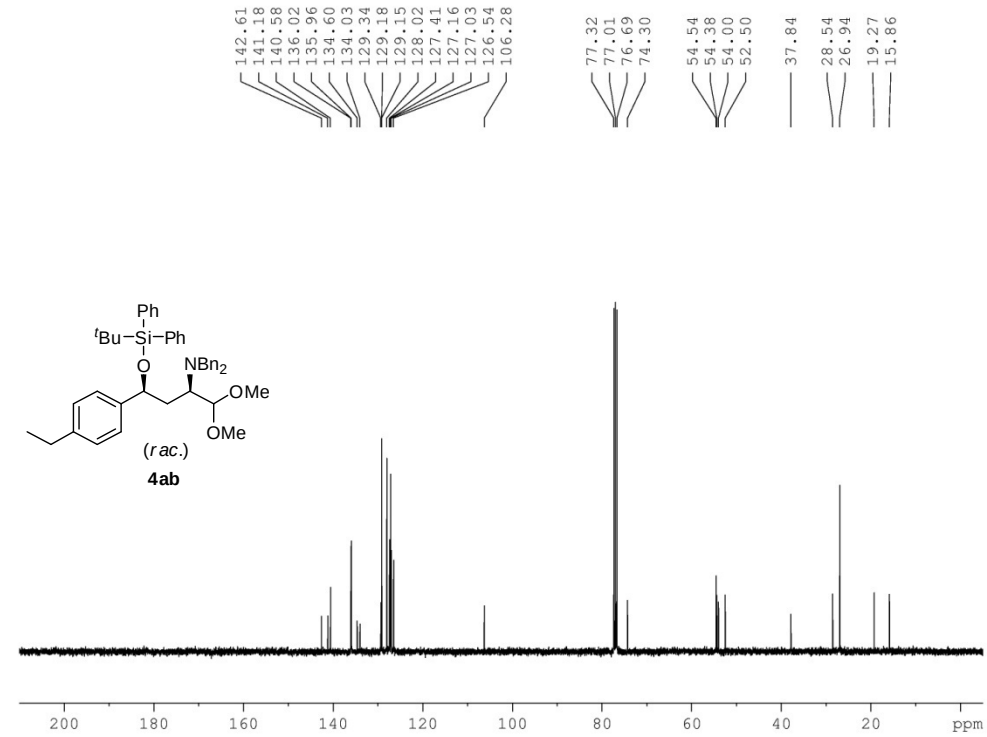
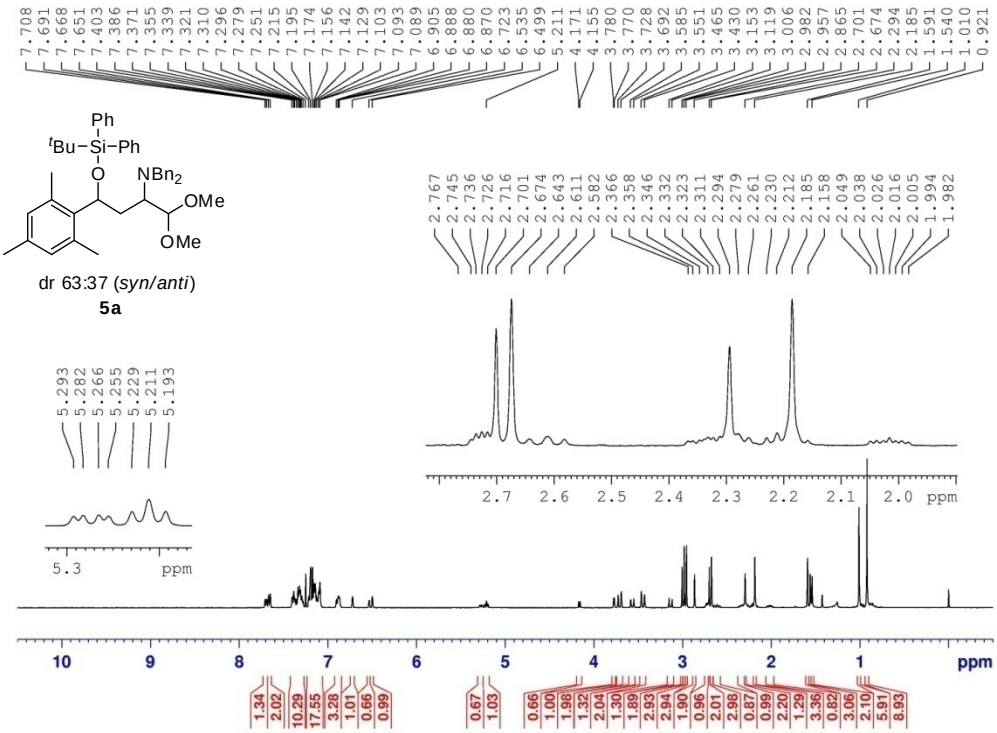




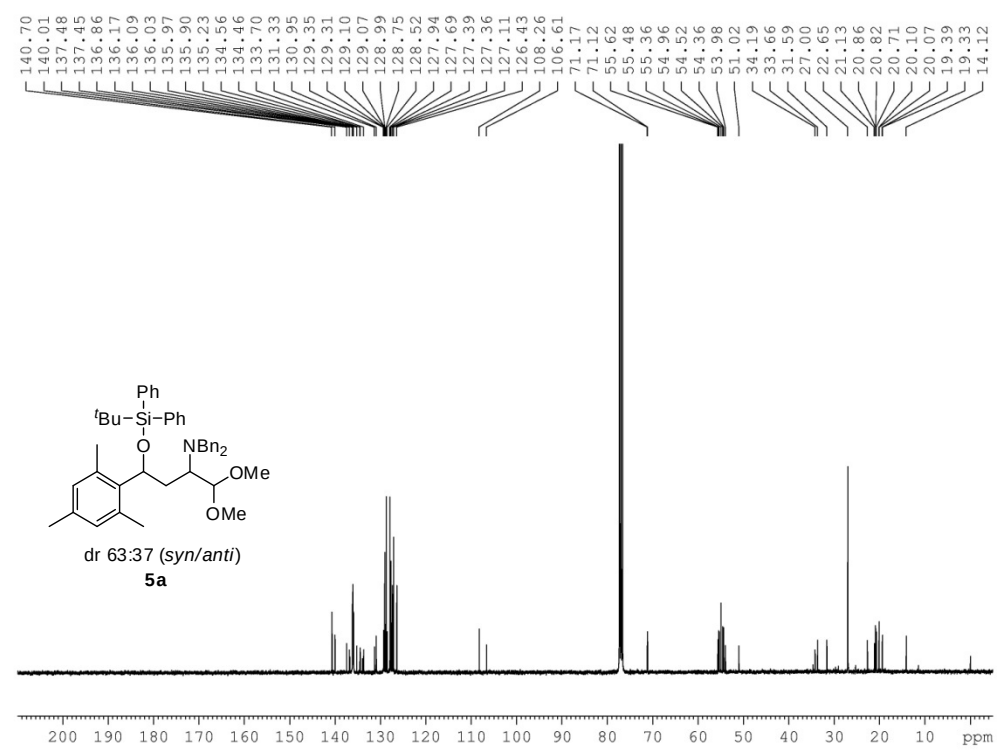






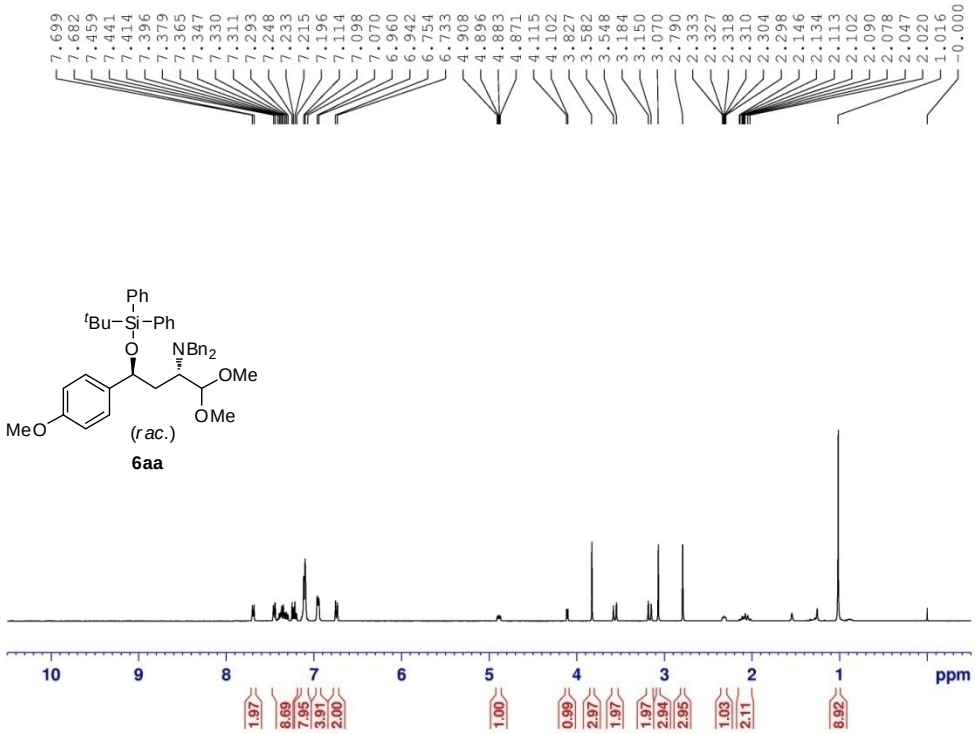
dr 63:37 (*syn/anti*)

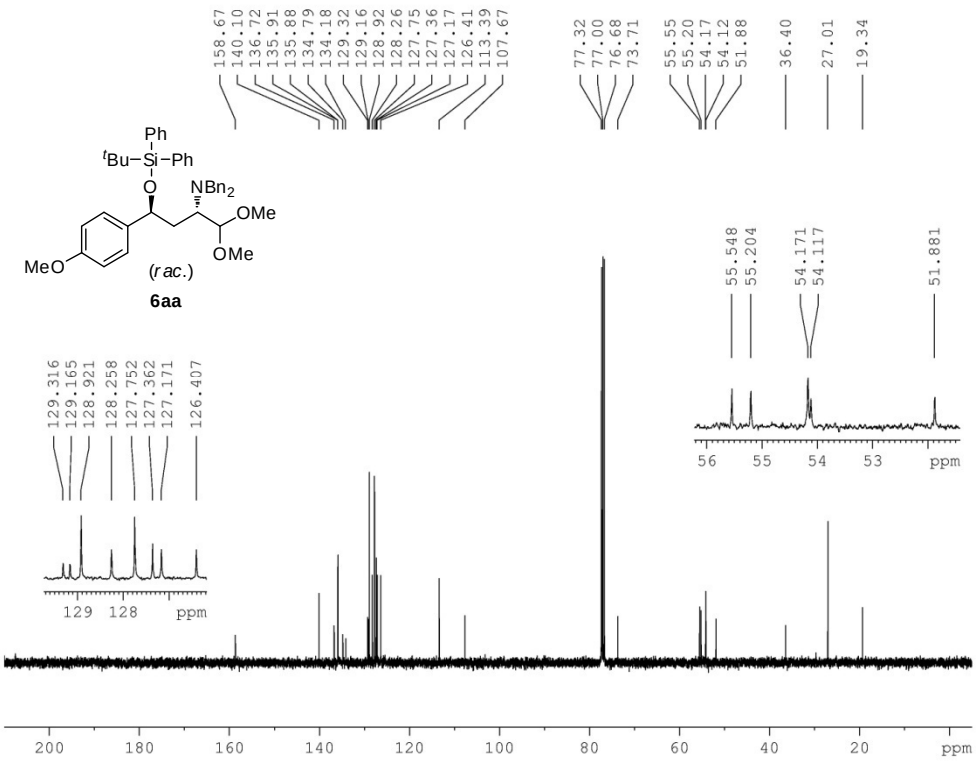
5a

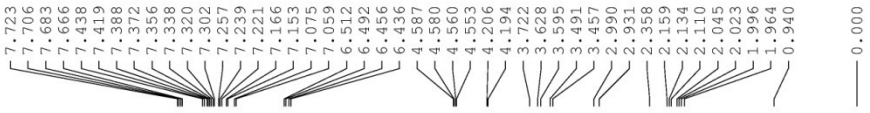


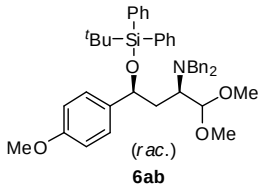
dr 63:37 (*syn/anti*)

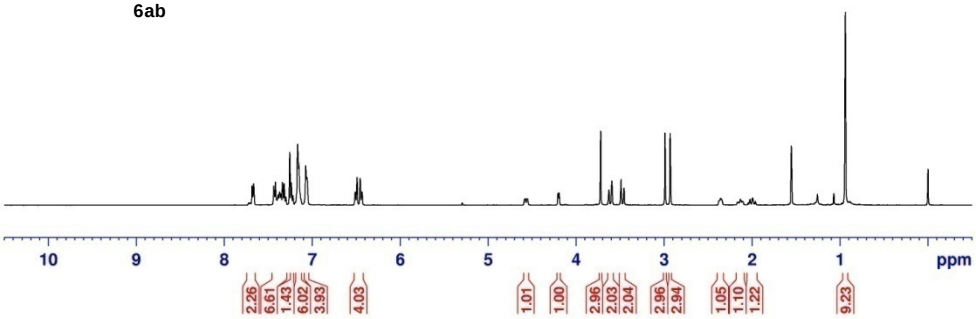
5a

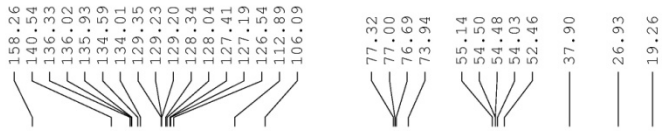


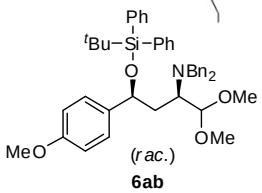


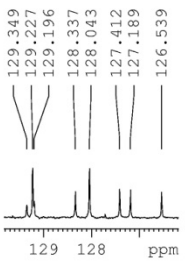


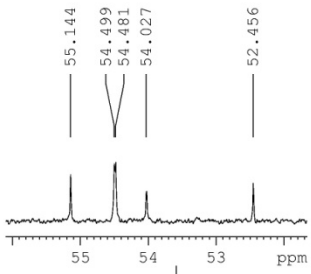


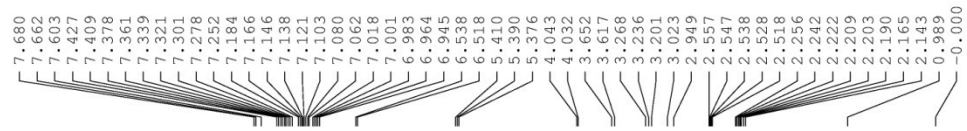


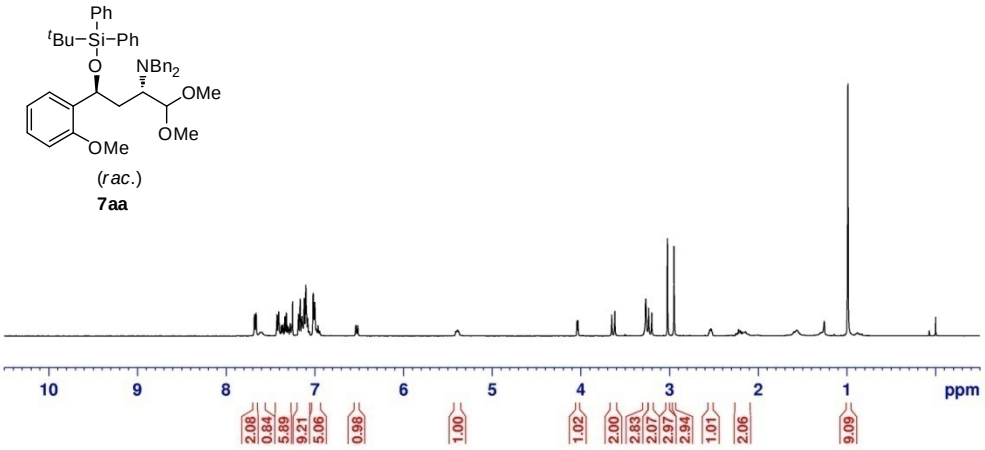


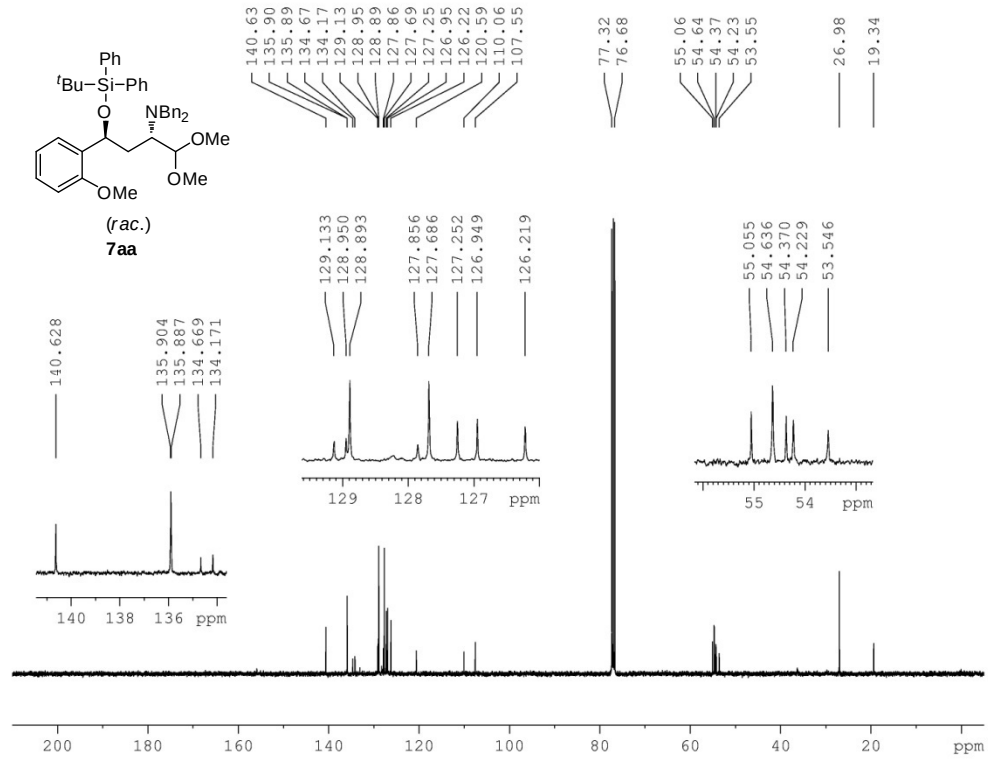


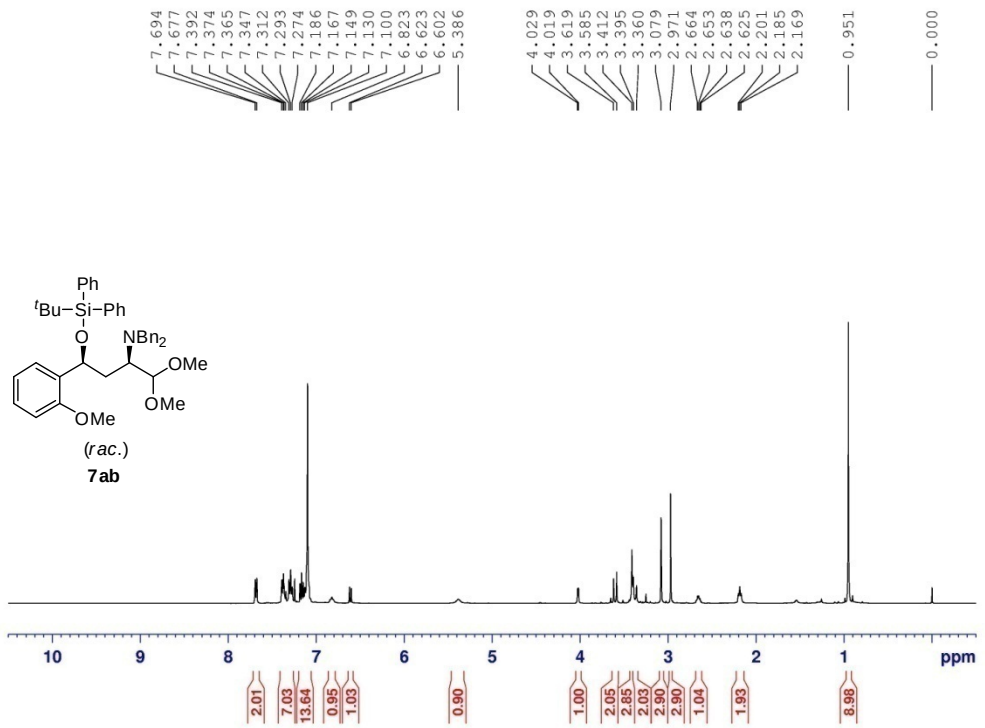


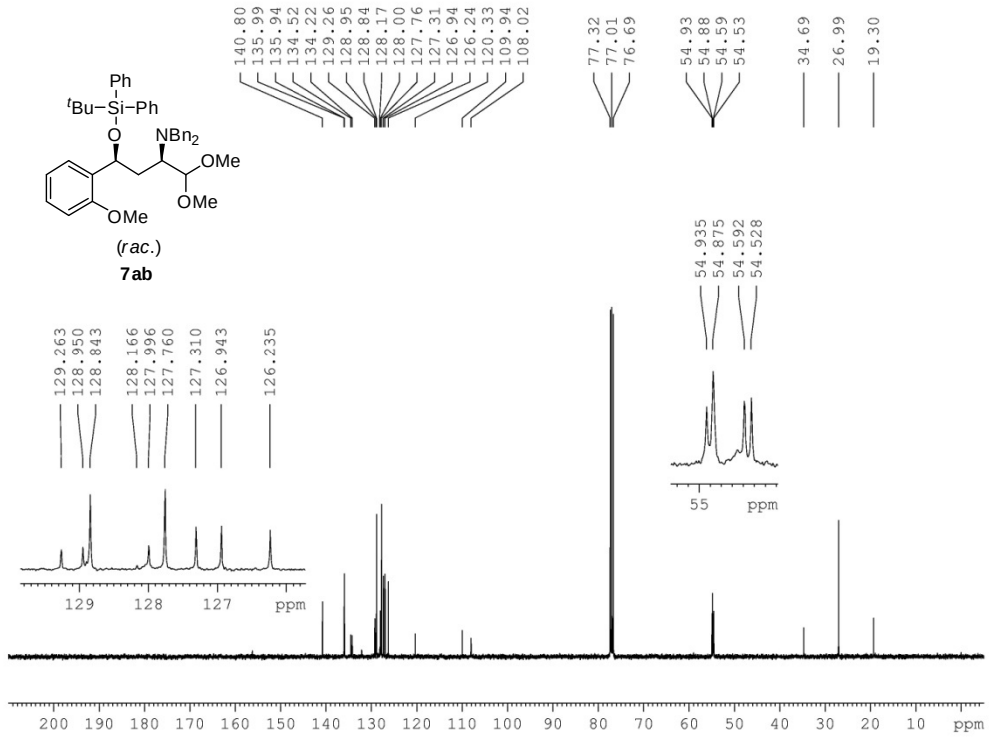


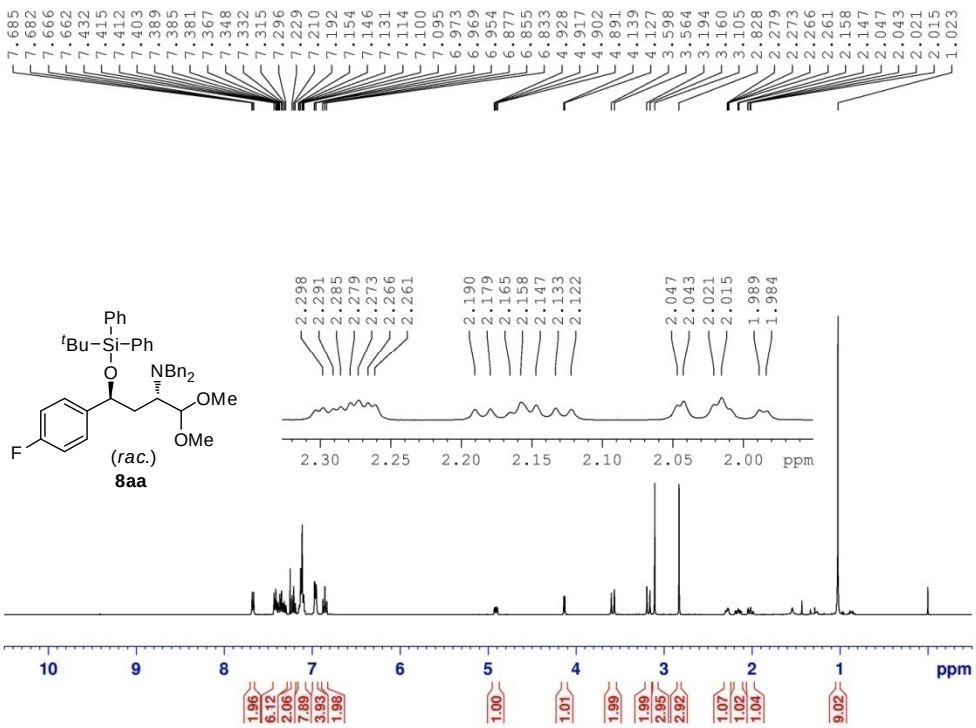


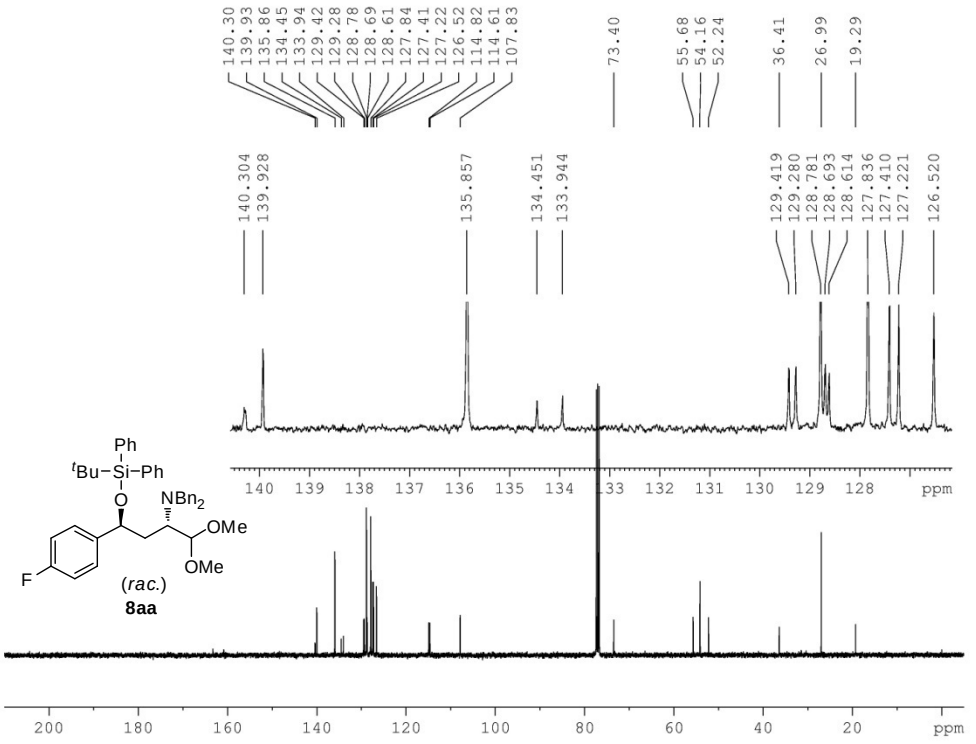


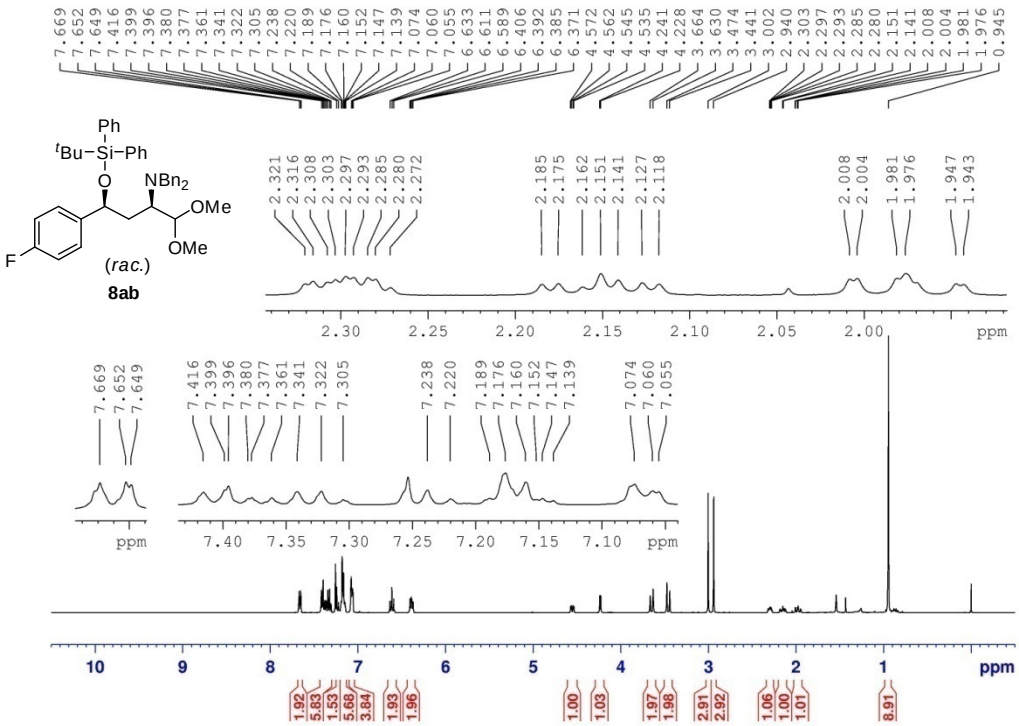


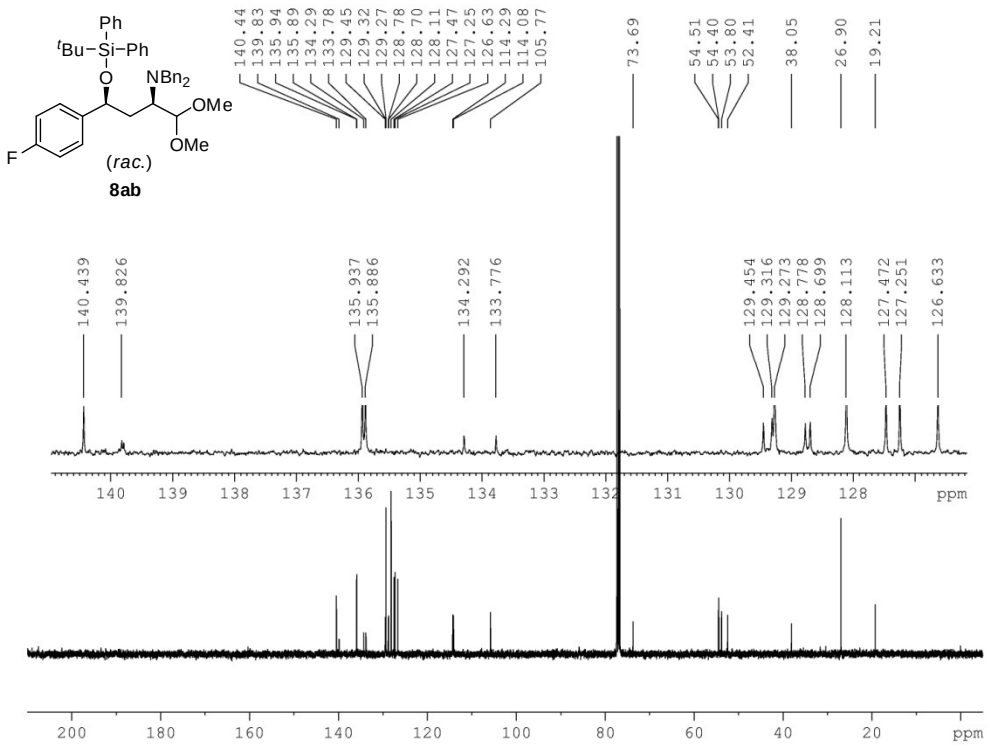


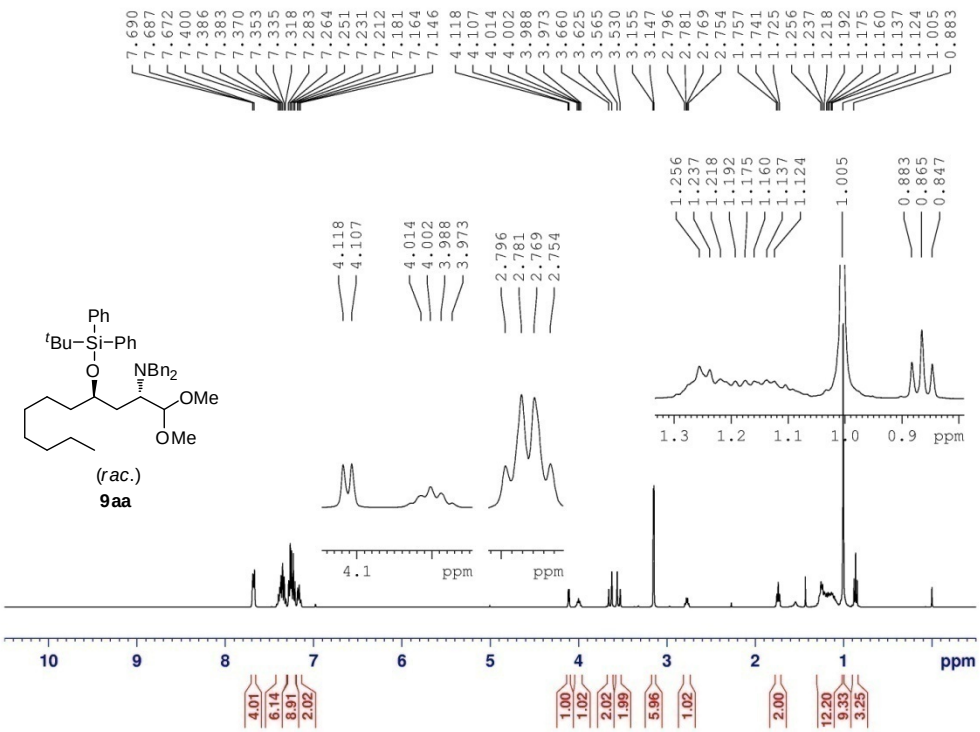


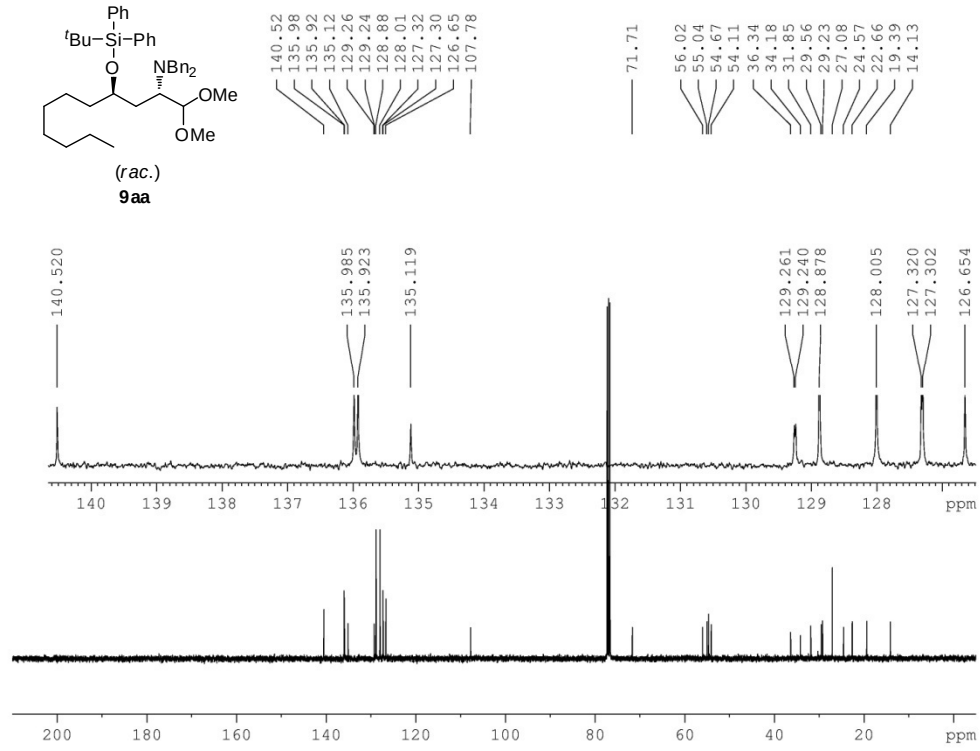


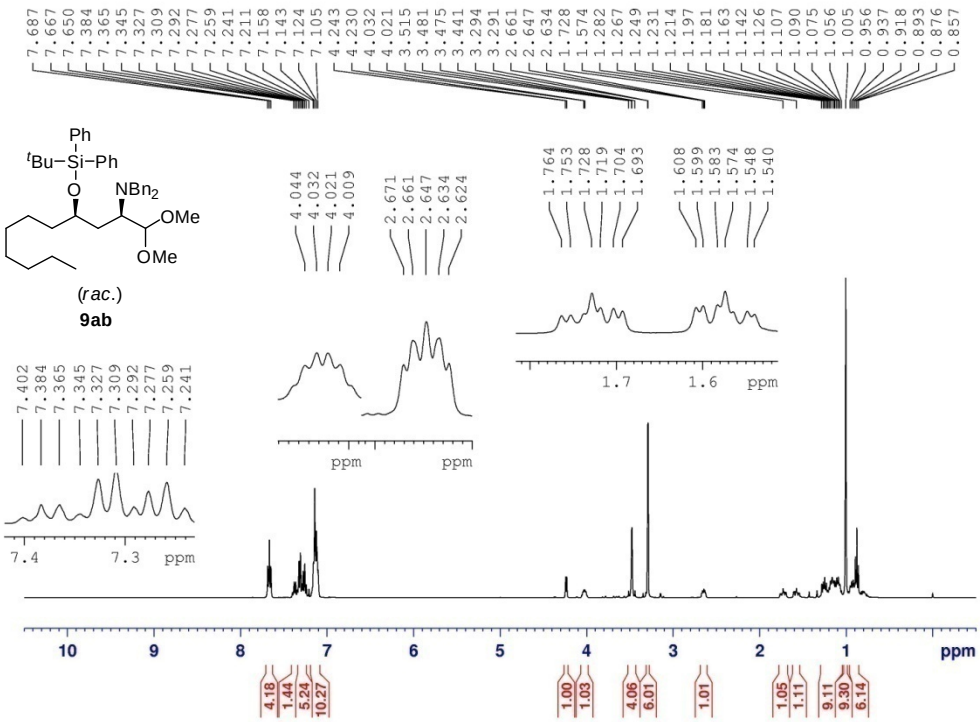


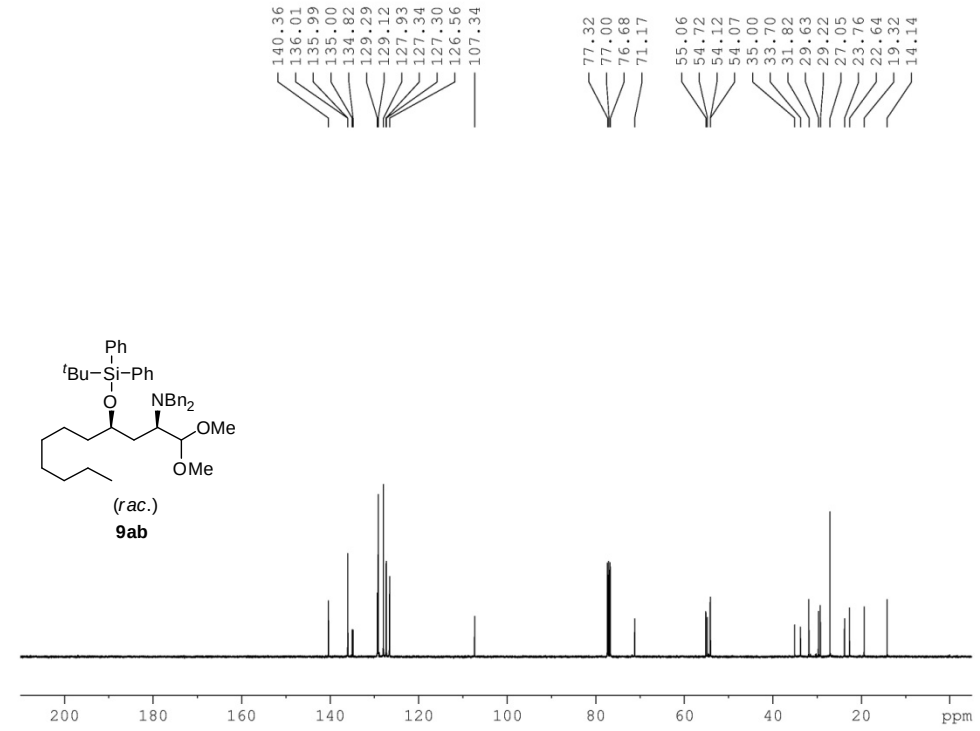


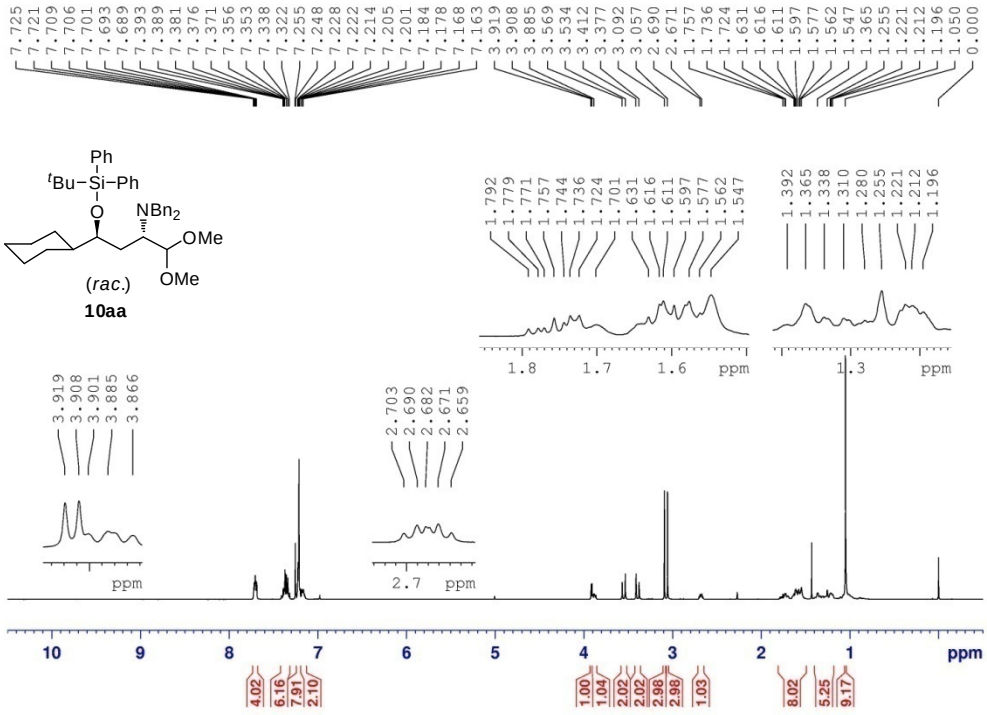


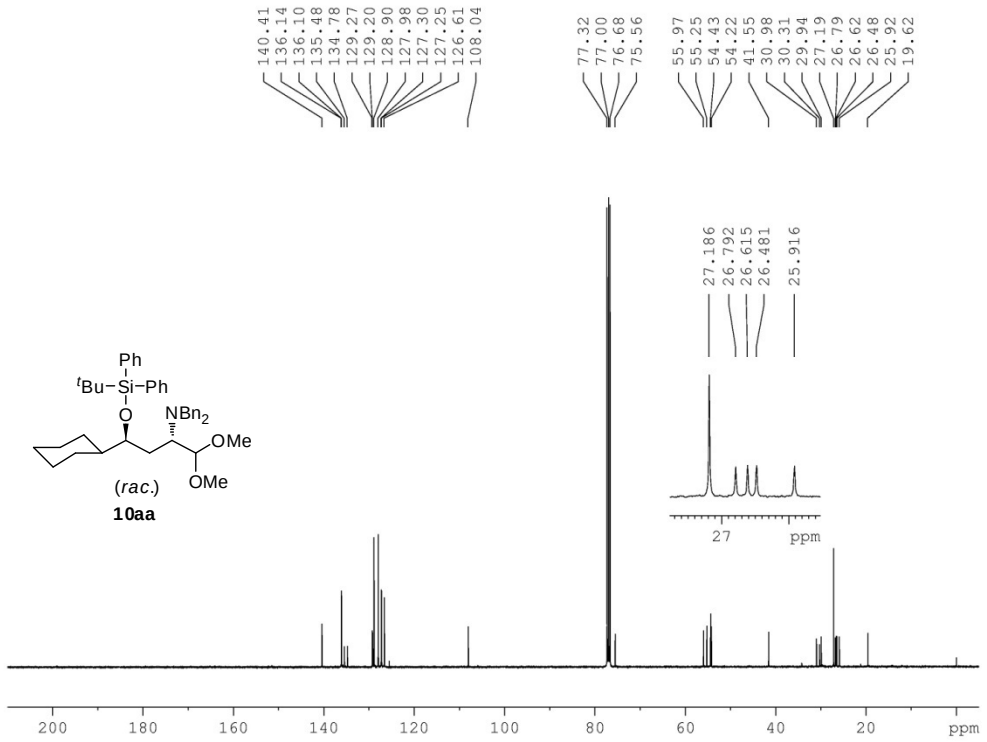


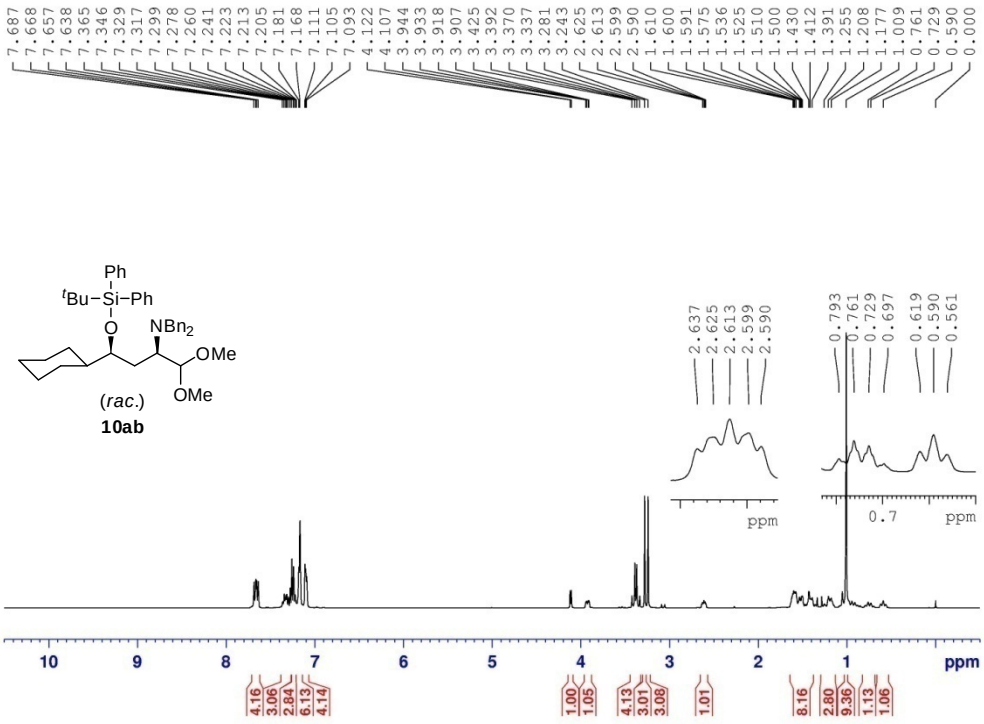



Ph
tBu–Si–Ph
O
NBn2
OMe
OMe
(rac.)
9ab
ppm
10
9
8
7
6
5
4
3
2
1
4.18
1.44
5.24
10.27
1.00
1.03
4.06
6.01
1.01
1.05
1.11
9.11
9.30
6.14


Ph
tBu–Si–Ph
O
NBn2
OMe
OMe
(rac.)
9ab
200
180
160
140
120
100
80
60
40
20
ppm



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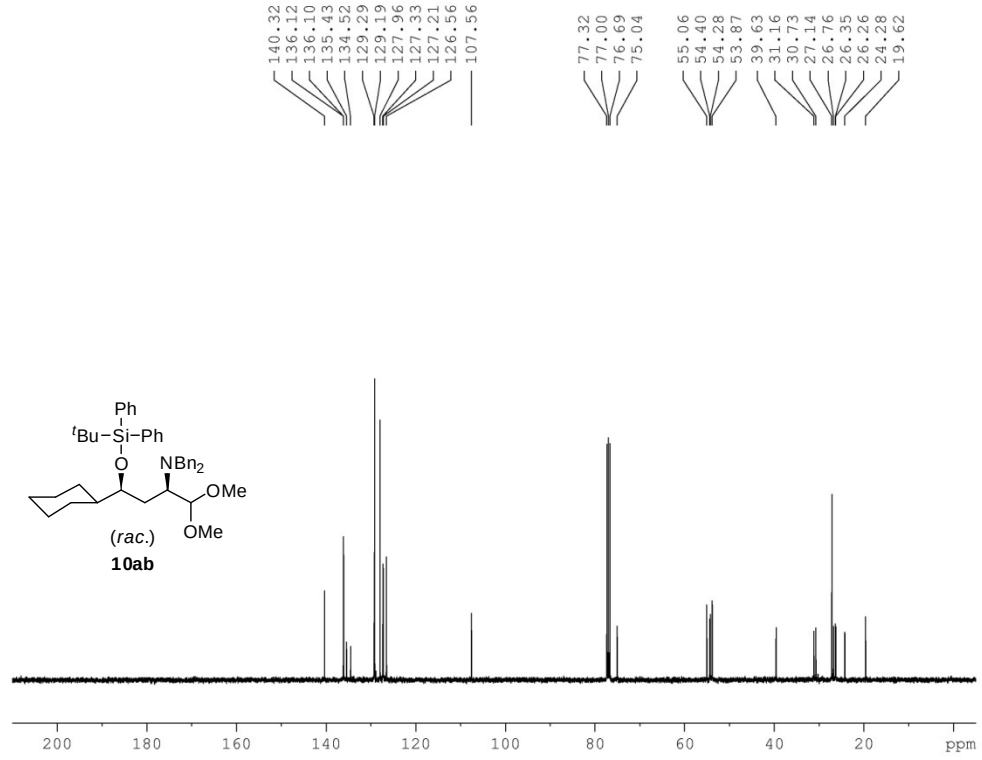
Ph
tBu–Si–Ph
O
NBn2
OMe
OMe
(rac.)
10ab
2.637 2.625 2.613 2.599 2.590
0.793 0.761 0.729 0.697 0.619 0.590 0.561
ppm
0.7 ppm
10 9 8 7 6 5 4 3 2 1 ppm
4.16 3.06 2.84 6.13 4.14 1.00 1.05 4.13 3.01 3.08 1.01 8.16 2.80 9.36 1.13 1.06


140.32 136.12 136.10 135.43 134.52 129.29 129.19 127.96 127.33 127.21 126.56 107.56
77.32 77.00 76.69 75.04
55.06 54.40 54.28 53.87 39.63 31.16 30.73 27.14 26.76 26.35 26.26 24.28 19.62
Ph
tBu–Si–Ph
O
NBn2
OMe
OMe
(rac.)
10ab
200 180 160 140 120 100 80 60 40 20 ppm