

SUPPORTING INFORMATION

NanoGold-Catalyzed *cis*-Silaboration of Alkynes with Abnormal Regioselectivity

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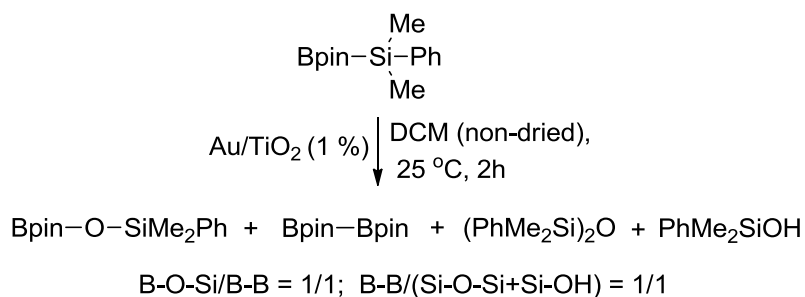
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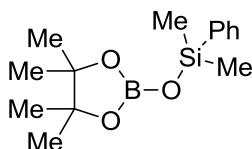
Starting materials

Alkynes **1-6**, **9**, and **11-19** are commercially available. Aryl propargyl ether **7**¹ and acetate **10**² were available from previous studies in our lab. Silyl ether **8**³ was prepared by reaction of propargyl alcohol with TBDPS-Cl under standard protection conditions, while **8-d** (95% D) from reaction of **8** with *n*-BuLi in THF at 0 °C followed by quench with D₂O. ¹H NMR of **8-d** (300 MHz, CDCl₃): 7.74-7.70 (m, 4H), 7.48-7.37 (m, 6H), 4.31 (s, 2H), 1.07 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): 135.6, 132.9, 129.8, 127.7, 81.6 (t, *J*_{C-D} = 7.0 Hz), 72.8 (t, *J*_{C-D} = 38.0 Hz), 52.4, 26.6, 19.1.

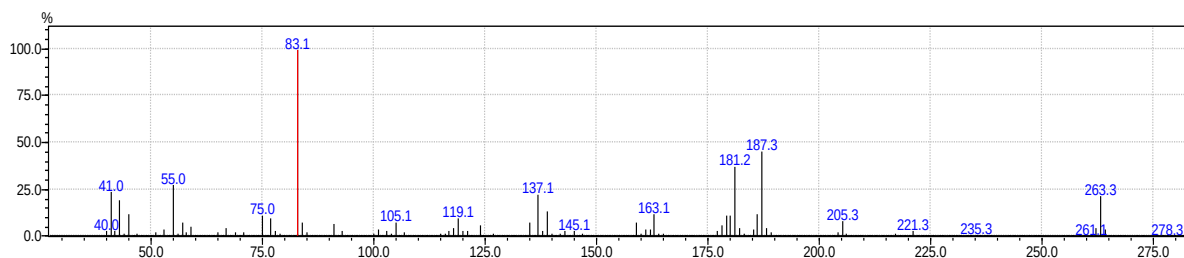
Au-catalyzed hydrolysis of pinB-SiMe₂Ph



Dimethyl(phenyl)((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane⁴

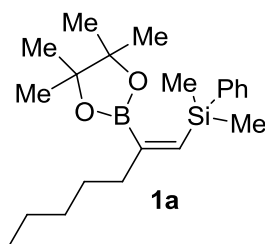


¹H NMR (300 MHz, C₆D₆): 7.68-7.63 (m, 2H), 7.26-7.16 (m, 3H), 1.02 (s, 9H), 0.45 (s, 6H). ¹³C NMR (75 MHz, C₆D₆): 138.6, 133.5, 129.8, 128.1, 82.2, 24.6, 0.0. MS (EI): 278 (M⁺, <1%), 263 (M⁺-Me, 22%), 187 (46%), 181 (34%), 83 (100%).



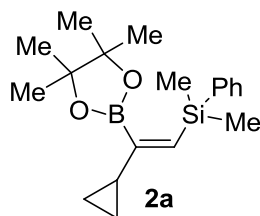
Spectroscopic data of products from the silaboration of alkynes

(*E*)-Dimethyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-1-en-1-yl)silane (1a)



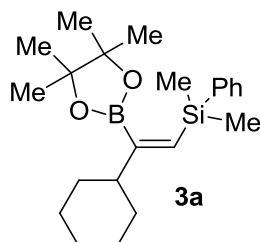
^1H NMR (300 MHz, CDCl_3): 7.57-7.53 (m, 2H), 7.34-7.29 (m, 3H), 6.41 (br s, 1H), 2.26 (t, $J = 7.5$ Hz, 2H), 1.48-1.38 (m, 2H), 1.35-1.25 (m, 4H), 1.12 (s, 12H), 0.89 (t, $J = 7.5$ Hz, 3H), 0.40 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): 143.8, 141.3, 133.8, 128.3, 127.4, 83.3, 41.3, 31.5, 29.2, 24.7, 22.6, 14.0, -0.7. ^{11}B NMR (160 MHz, CDCl_3): 29.3 relative to $\text{B}(\text{OMe})_3$. HRMS (ESI-Orbit trap) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{35}\text{BO}_2\text{Si}+\text{H}$, 359.2578; found 359.2575.

(*E*)-(2-Cyclopropyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dimethyl(phenyl)silane (2a)



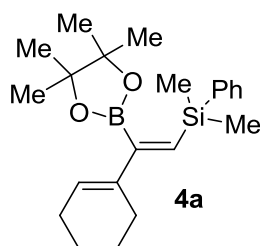
^1H NMR (300 MHz, CDCl_3): 7.56-7.51 (m, 2H), 7.33-7.29 (m, 3H), 6.24 (br s, 1H), 1.70-1.61 (m, 1H), 1.11 (s, 12H), 0.75-0.61 (m, 4H), 0.38 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): 141.2, 138.2, 133.8, 128.3, 127.5, 83.4, 24.8, 19.7, 8.3, -0.6. ^{11}B NMR (160 MHz, CDCl_3): 29.3 relative to $\text{B}(\text{OMe})_3$. HRMS (ESI-Orbit trap) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{29}\text{BO}_2\text{Si}+\text{H}$, 329.2108; found 329.2107.

(*E*)-(2-Cyclohexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dimethyl(phenyl)silane (3a)



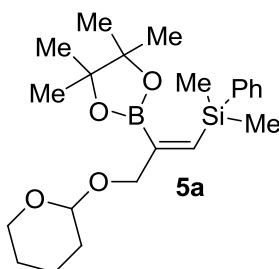
^1H NMR (300 MHz, CDCl_3): 7.57-7.51 (m, 2H), 7.34-7.29 (m, 3H), 6.34 (br s, 1H), 2.24-2.13 (m, 1H), 1.80-1.62 (m, 5H), 1.38-1.11 (m, 5H), 1.11 (s, 12H), 0.38 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): 141.3, 139.1, 133.8, 128.3, 127.4, 83.2, 47.8, 32.6, 26.8, 26.3, 24.9, -0.5. ^{11}B NMR (160 MHz, CDCl_3): 29.3 relative to $\text{B}(\text{OMe})_3$. HRMS (ESI-Orbit trap) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{35}\text{BO}_2\text{Si}+\text{H}$, 371.2578; found 371.2570.

(E)-(2-(Cyclohex-1-en-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dimethyl(phenyl)silane (4a)



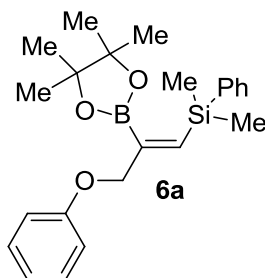
^1H NMR (300 MHz, CDCl_3): 7.57-7.52 (m, 2H), 7.34-7.29 (m, 3H), 6.40 (br s, 1H), 6.04 (br m, 1H), 2.25-2.15 (m, 4H), 1.72-1.66 (m, 2H), 1.62-1.54 (m, 2H), 1.14 (s, 12H), 0.42 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): 140.7, 140.4, 134.6, 134.1, 129.3, 128.6, 127.6, 83.7, 29.1, 26.3, 25.5, 22.8, 22.2, -0.4. ^{11}B NMR (160 MHz, CDCl_3): 30.3 relative to $\text{B}(\text{OMe})_3$. HRMS (ESI-Orbit trap) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{33}\text{BO}_2\text{Si}+\text{H}$, 369.2421; found 369.2414.

(E)-Dimethyl(phenyl)(3-((tetrahydro-2H-pyran-2-yl)oxy)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)silane (5a)



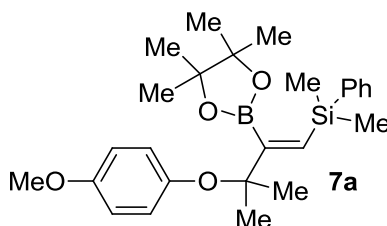
^1H NMR (300 MHz, CDCl_3): 7.57-7.52 (m, 2H), 7.33-7.29 (m, 3H), 6.76 (br s, 1H), 4.67 (m, 1H), 4.41 (dd, $J_1 = 13.0$ Hz, $J_2 = 1.5$ Hz, 1H), 4.13 (dd, $J_1 = 13.0$ Hz, $J_2 = 1.5$ Hz, 1H), 3.93-3.87 (m, 1H), 3.52-3.46 (m, 1H), 1.92-1.82 (m, 1H), 1.75-1.48 (m, 5H), 1.12 (s, 12H), 0.42 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): 143.1, 140.7, 133.9, 128.4, 127.5, 97.9, 83.4, 72.7, 61.9, 30.6, 25.5, 24.8, 24.7, 19.4, -0.8, -0.8. ^{11}B NMR (160 MHz, CDCl_3): 29.5 relative to $\text{B}(\text{OMe})_3$; HRMS: calcd for $\text{C}_{22}\text{H}_{35}\text{BO}_4\text{Si}+\text{H}$, 403.2476; found 403.2474.

(E)-Dimethyl(3-phenoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)(phenyl)silane (6a)



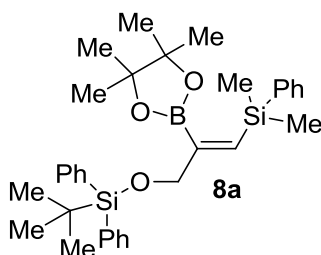
^1H NMR (300 MHz, CDCl_3): 7.56-7.50 (m, 2H), 7.35-7.23 (m, 6H), 6.97-6.90 (m, 3H), 6.89 (br t, $J = 1.5$ Hz, 1H), 4.68 (d, $J = 1.5$ Hz, 2H), 1.13 (s, 12H), 0.43 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): 158.8, 144.7, 140.4, 133.8, 129.3, 128.5, 127.5, 120.5, 115.1, 83.7, 73.1, 24.6, -0.9. ^{11}B NMR (160 MHz, CDCl_3): 29.4 relative to $\text{B}(\text{OMe})_3$. HRMS: calcd for $\text{C}_{23}\text{H}_{31}\text{BO}_3\text{Si}+\text{H}$, 395.2214; found 395.2208.

(E)-(3-(4-Methoxyphenoxy)-3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl)dimethyl(phenyl)silane (7a)



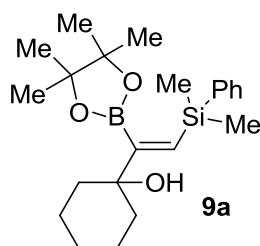
^1H NMR (300 MHz, CDCl_3): 7.56-7.51 (m, 2H), 7.35-7.31 (m, 3H), 6.92 (d, $J = 7.0$ Hz, 2H), 6.75 (d, $J = 7.0$ Hz, 2H), 6.42 (br s, 1H), 3.76 (s, 3H), 1.44 (s, 6H), 1.09 (s, 12H), 0.42 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): 154.8, 149.2, 140.2, 136.3, 133.9, 128.6, 127.6, 123.4, 113.6, 84.6, 83.5, 55.5, 27.1, 25.0, -0.7. ^{11}B NMR (160 MHz, CDCl_3): 29.4 relative to $\text{B}(\text{OMe})_3$. HRMS: calcd for $\text{C}_{26}\text{H}_{37}\text{BO}_4\text{Si}+\text{H}$, 453.2632; found 453.2627.

(E)-tert-Butyl((3-(dimethyl(phenyl)silyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)oxy)diphenylsilane (8a)



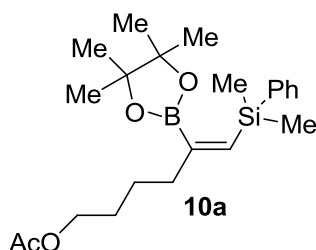
^1H NMR (300 MHz, CDCl_3): 7.73-7.69 (m, 4H), 7.57-7.52 (m, 2H), 7.42-7.30 (m, 9H), 7.05 (br t, $J = 1.5$ Hz, 1H), 4.42 (d, $J = 1.5$ Hz, 2H), 1.44 (s, 6H), 1.08 (s, 9H), 1.07 (s, 12H), 0.44 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): 141.6, 141.1, 135.6, 134.0, 133.8, 129.5, 128.3, 127.5, 127.4, 83.3, 68.2, 26.9, 24.6, 19.3, -0.8. ^{11}B NMR (160 MHz, CDCl_3): 29.7 relative to $\text{B}(\text{OMe})_3$. HRMS: calcd for $\text{C}_{33}\text{H}_{45}\text{BO}_3\text{Si}_2+\text{H}$, 557.3079; found 557.3074.

(E)-1-(2-(Dimethyl(phenyl)silyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)cyclohexanol (9a)



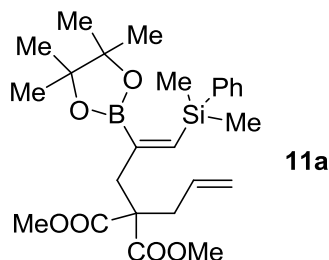
^1H NMR (300 MHz, CDCl_3): 7.54-7.50 (m, 2H), 7.33-7.29 (m, 3H), 6.53 (br s, 1H), 2.43 (br s, 1H, -OH), 1.76-1.52 (m, 10H), 1.11 (s, 12H), 0.40 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): 140.8, 138.2, 133.8, 128.4, 127.5, 83.7, 75.8, 36.7, 25.7, 24.8, 22.0, -0.5. ^{11}B NMR (160 MHz, CDCl_3): 29.5 relative to $\text{B}(\text{OMe})_3$. HRMS (ESI-Orbit trap) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{35}\text{BO}_3\text{Si}+\text{H}$, 387.2527; found 387.2521. $[\text{M}-\text{H}_2\text{O}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{33}\text{BO}_2\text{Si}+\text{H}$, 369.2421; found 369.2419.

(E)-6-(Dimethyl(phenyl)silyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-yl acetate (10a)



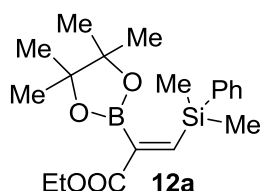
^1H NMR (300 MHz, CDCl_3): 7.56-7.51 (m, 2H), 7.34-7.29 (m, 3H), 6.43 (br s, 1H), 4.06 (t, $J = 6.5$ Hz, 2H), 2.28 (br t, $J = 7.5$ Hz, 2H), 2.04 (s, 3H), 1.69-1.58 (m, 2H), 1.54-1.43 (m, 2H), 1.11 (s, 12H), 0.39 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): 171.3, 144.9, 141.1, 133.8, 128.3, 127.5, 83.4, 64.6, 40.8, 28.2, 25.7, 24.7, 21.0, -0.7. ^{11}B NMR (160 MHz, CDCl_3): 29.4 relative to $\text{B}(\text{OMe})_3$. HRMS (ESI-Orbit trap) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{35}\text{BO}_4\text{Si}+\text{H}$, 403.2476; found 403.2473.

(E)-dimethyl-2-allyl-2-(3-(dimethyl(phenyl)silyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)malonate (11a)



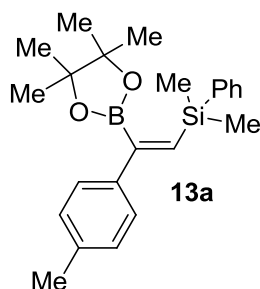
^1H NMR (300 MHz, CDCl_3): 7.53-7.49 (m, 2H), 7.32-7.28 (m, 3H), 6.50 (s, 1H), 5.92-5.83 (m, 1H), 5.05 (br d, $J = 16.0$ Hz, 1H), 5.03 (br d, $J = 11.0$ Hz, 1H), 3.64 (s, 6H), 2.90 (br s, 2H), 2.57 (d, $J = 6.0$ Hz, 2H), 1.08 (s, 12H), 0.38 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3): 171.3, 152.7, 140.8, 133.7, 133.5, 128.4, 127.5, 118.4, 83.6, 59.6, 52.0, 41.9, 36.9, 24.6, -0.8; HRMS (ESI-Orbit trap) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{38}\text{BO}_6\text{Si}+\text{H}$, 473.2531; found 473.2532.

(E)-Ethyl 3-(dimethyl(phenyl)silyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (12a)



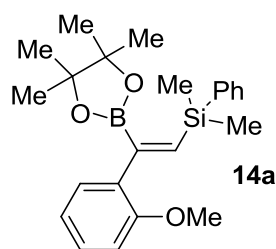
^1H NMR (500 MHz, CDCl_3): 7.75 (br s, 1H), 7.56-7.51 (m, 2H), 7.36-7.30 (m, 3H), 4.21 (q, $J = 7.0$ Hz, 2H), 1.29 (t, $J = 7.0$ Hz, 3H), 1.18 (s, 12H), 0.45 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3): 168.1, 157.0, 137.7, 134.1, 129.2, 127.8, 84.2, 60.8, 24.9, 14.2, -1.5. ^{11}B NMR (160 MHz, CDCl_3): 29.3 relative to $\text{B}(\text{OMe})_3$. HRMS (ESI-Orbit trap) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{29}\text{BO}_4\text{Si}+\text{H}$, 361.2006; found 361.2002.

(E)-Dimethyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(p-tolyl) vinyl) silane (13a)



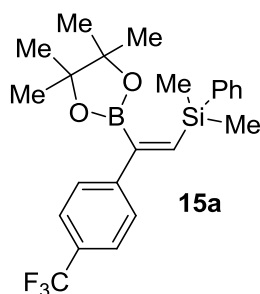
^1H NMR (300 MHz, CDCl_3): 7.66-7.61 (m, 2H), 7.42-7.34 (m, 5H), 7.16 (d, $J = 8.0$ Hz, 2H), 6.89 (br s, 1H), 2.38 (s, 3H), 1.20 (s, 12H), 0.53 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): 146.3, 142.4, 140.7, 136.6, 133.9, 128.7, 128.5, 127.6, 126.9, 83.8, 24.8, 21.1, -0.6. ^{11}B NMR (160 MHz, CDCl_3): 29.8 relative to $\text{B}(\text{OMe})_3$. HRMS (ESI-Orbit trap) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{31}\text{BO}_2\text{Si}+\text{H}$, 379.2265; found 379.2261.

(E)-(2-(2-Methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dimethyl(phenyl)silane (14a)



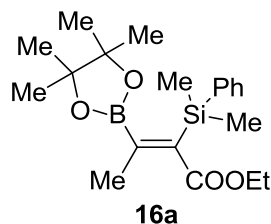
^1H NMR (300 MHz, CDCl_3): 7.65-7.61 (m, 2H), 7.38-7.20 (m, 5H), 6.95 (dt, $J_1 = 7.5$ Hz, $J_2 = 1.0$ Hz, 1H), 6.82 (dd, $J_1 = 7.5$ Hz, $J_2 = 1.0$ Hz, 1H), 6.71 (br s, 1H), 3.81 (s, 3H), 1.14 (s, 12H), 0.52 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): 155.9, 146.3, 140.7, 136.2, 133.9, 128.9, 128.5, 128.4, 127.6, 121.2, 110.1, 83.3, 55.2, 25.0, -0.5. ^{11}B NMR (160 MHz, CDCl_3): 29.9 relative to $\text{B}(\text{OMe})_3$. HRMS (ESI-Orbit trap) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{31}\text{BO}_3\text{Si}+\text{H}$, 395.2214; found 395.2207.

(E)-Dimethyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-(trifluoromethyl)phenyl)vinyl)silane (15a)



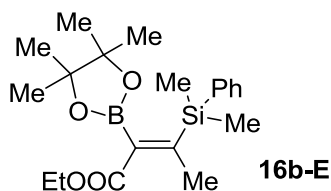
^1H NMR (300 MHz, CDCl_3): 7.60-7.49 (m, 6H), 7.38-7.33 (m, 3H), 6.93 (br s, 1H), 1.16 (s, 12H), 0.50 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): 151.1, 148.9 (q, $J_{\text{C-F}} = 1.5$ Hz), 140.1, 133.8, 128.7, 128.7 (q, $J_{\text{C-F}} = 32.0$ Hz), 127.7, 127.3, 124.4 (q, $J_{\text{C-F}} = 270.0$ Hz), 124.9 (q, $J_{\text{C-F}} = 4.0$ Hz), 84.1, 24.8, -0.7. ^{11}B NMR (160 MHz, CDCl_3): 29.7 relative to $\text{B}(\text{OMe})_3$. MS (EI): 432 (M^+ , 1%), 417 (M^+-Me , 3%), 278 (11%), 135 (32%), 84 (43%), 40 (100%).

(E)-Ethyl 2-(dimethyl(phenyl)silyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-enoate (16a)



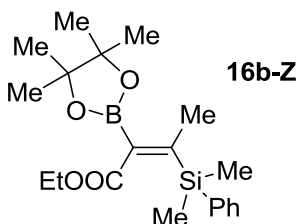
^1H NMR (500 MHz, CDCl_3): 7.57-7.53 (m, 2H), 7.32-7.27 (m, 3H), 4.05 (q, $J = 7.0$ Hz, 2H), 1.90 (s, 3H), 1.22 (t, $J = 7.0$ Hz, 3H), 1.03 (s, 12H), 0.45 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3): 172.8, 150.4, 139.3, 134.0, 128.6, 127.4, 83.8, 60.1, 24.5, 21.0, 14.3, -1.1. ^{11}B NMR (160 MHz, CDCl_3): 29.5 relative to $\text{B}(\text{OMe})_3$. MS (EI): 374 (M^+ , 1%), 359 ($\text{M}^+ - \text{Me}$, 5%), 277 (9%), 199 (14%), 159 (18%), 135 (21%), 83 (100%). HRMS (ESI-Orbit trap) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{31}\text{BO}_4\text{Si} + \text{H}$, 375.2163; found 375.2156.

(E)-Ethyl 3-(dimethyl(phenyl)silyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-enoate (16b-E)



^1H NMR (500 MHz, CDCl_3): 7.55-7.50 (m, 2H), 7.34-7.29 (m, 3H), 4.24 (q, $J = 7.0$ Hz, 2H), 1.96 (s, 3H), 1.30 (t, $J = 7.0$ Hz, 3H), 1.10 (s, 12H), 0.46 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3): 170.6, 160.3, 138.8, 134.0, 128.8, 127.7, 83.9, 60.2, 24.7, 23.3, 14.4, -1.3. ^{11}B NMR (160 MHz, CDCl_3): 28.7 relative to $\text{B}(\text{OMe})_3$. MS (EI): 374 (M^+ , <1%), 359 ($\text{M}^+ - \text{Me}$, 13%), 296 (78%), 249 (23%), 231 (25%), 186 (28%), 159 (53%), 135 (100%), 83 (95%). HRMS (ESI-Orbit trap) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{31}\text{BO}_4\text{Si} + \text{H}$, 375.2163; found 375.2156.

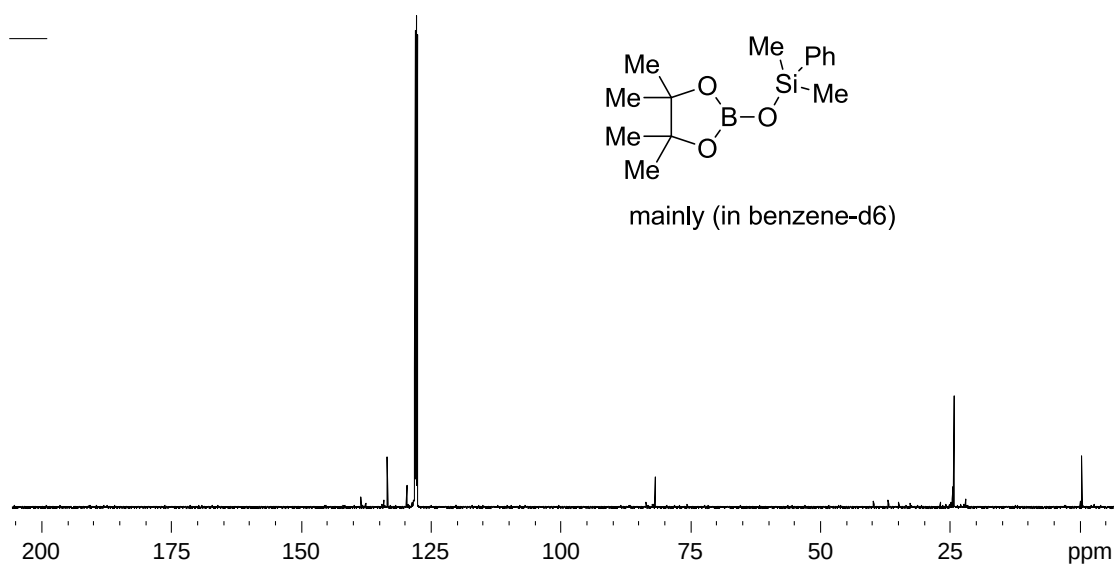
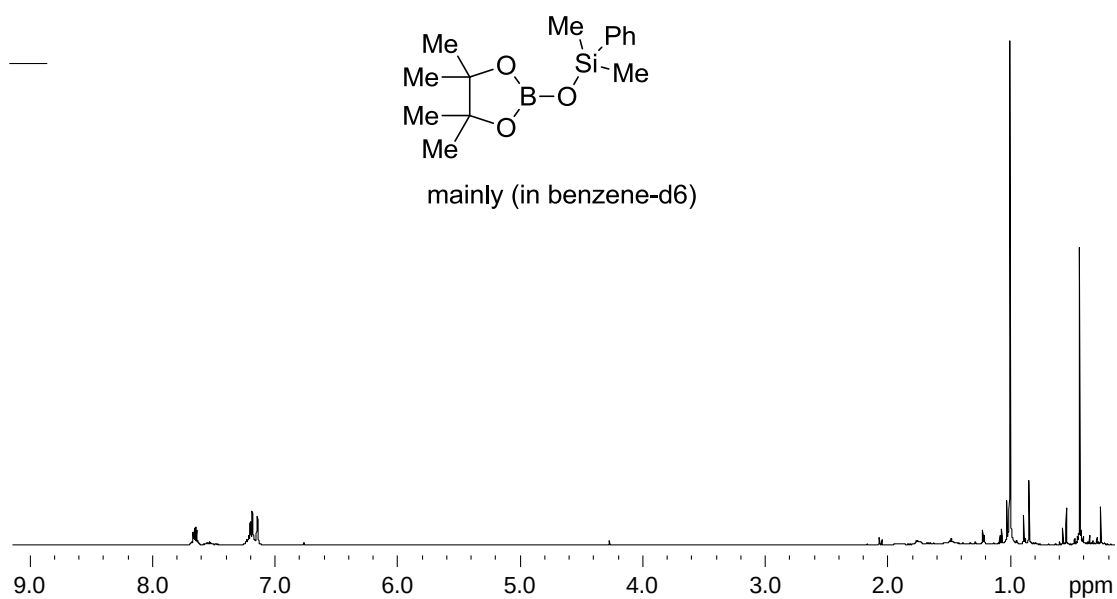
(Z)-Ethyl 3-(dimethyl(phenyl)silyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-enoate (16b-Z)

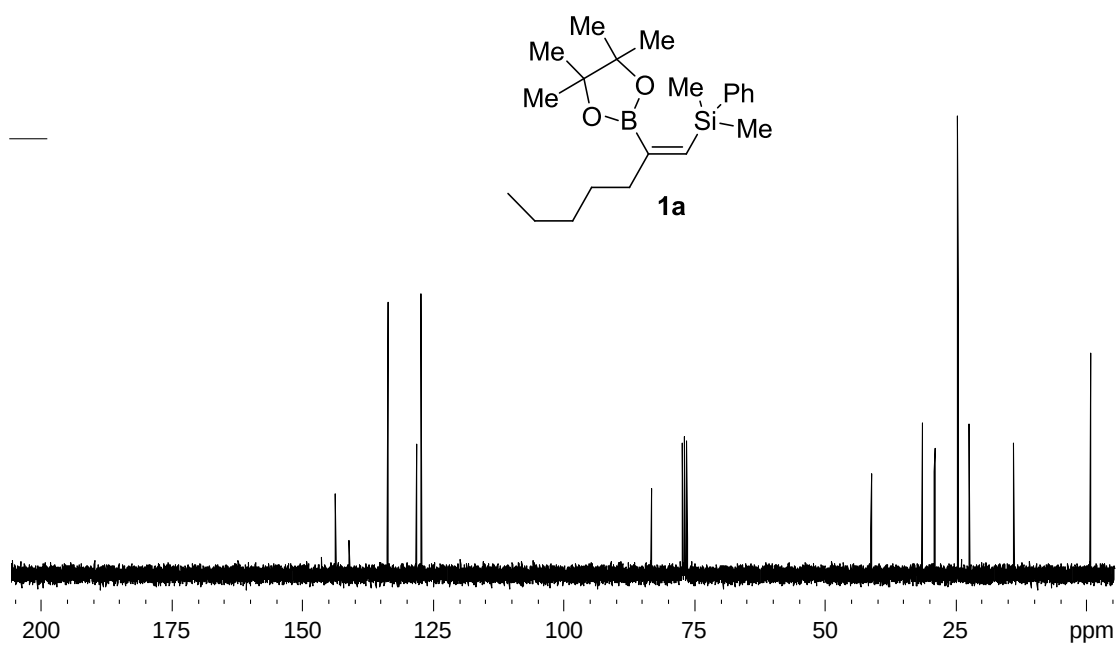
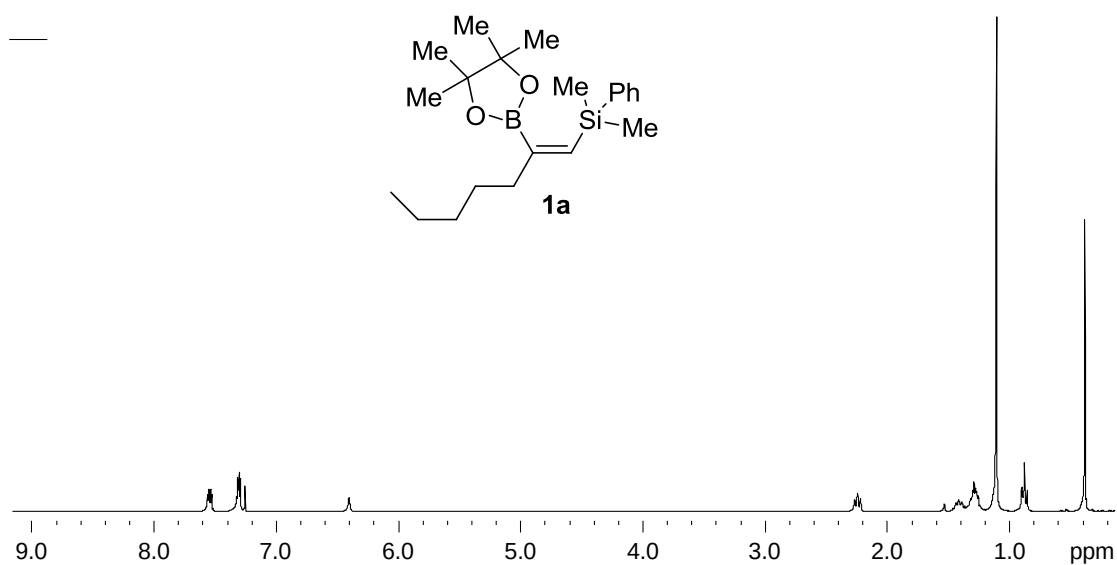


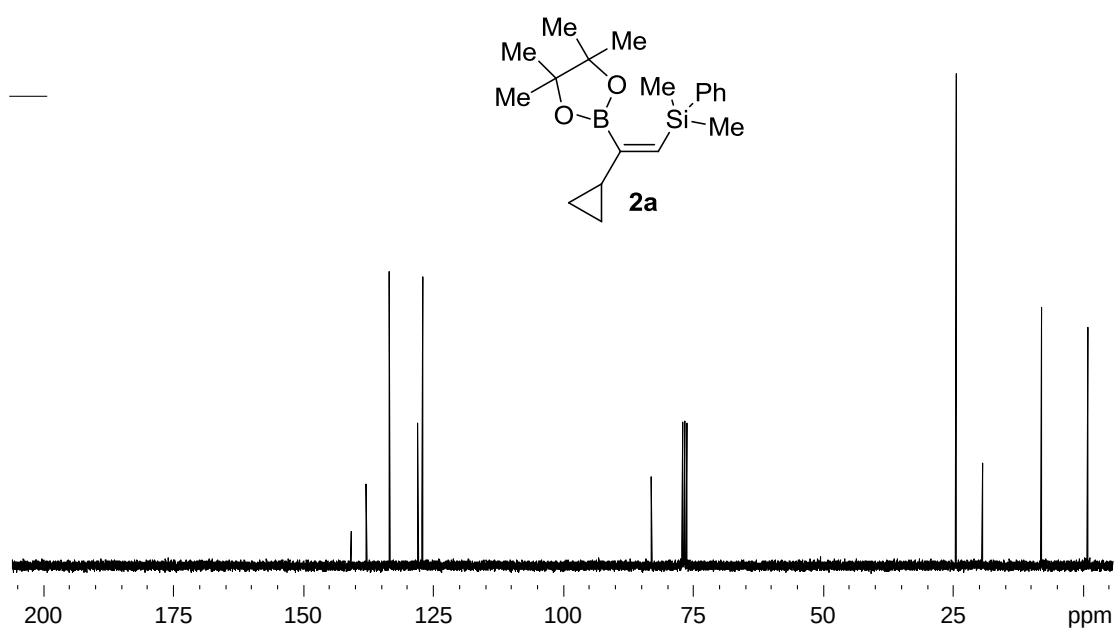
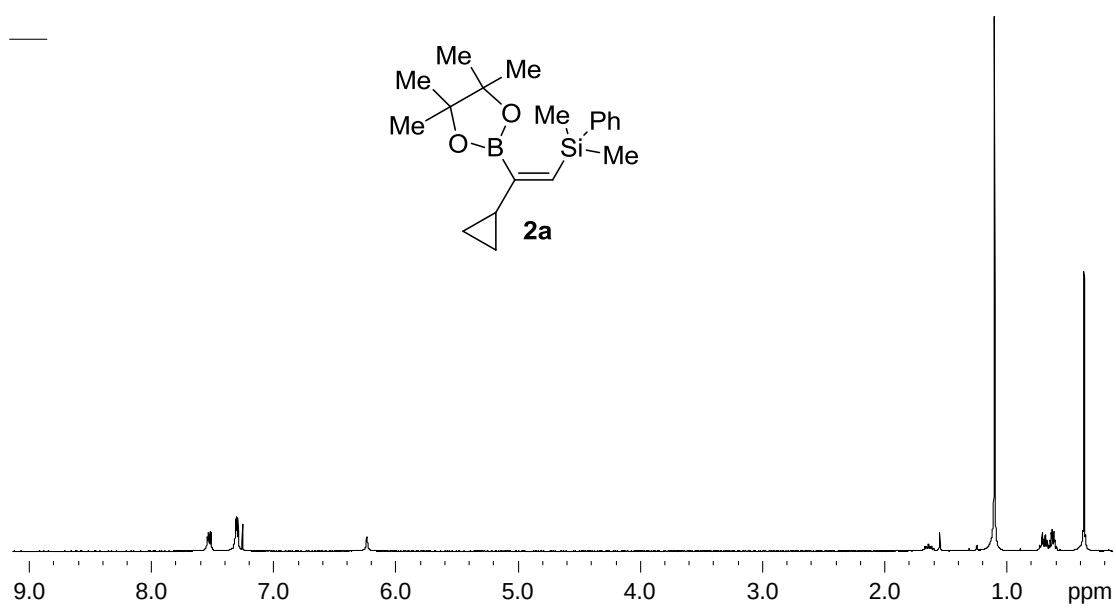
^1H NMR (500 MHz, CDCl_3): 7.59-7.55 (m, 2H), 7.41-7.36 (m, 3H), 3.97 (q, $J = 7.0$ Hz, 2H), 1.99 (s, 3H), 1.31 (s, 12H), 1.16 (t, $J = 7.0$ Hz, 3H), 0.43 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3): 168.5, 167.2, 139.0, 133.8, 128.5, 127.5, 84.0, 60.2, 25.2, 24.7, 14.0, -1.9. MS (EI): 359 ($\text{M}^+ - \text{Me}$, 59%), 297 (25%), 249 (58%), 231 (42%), 187 (36%), 135 (57%), 83 (67%), 43 (100%).

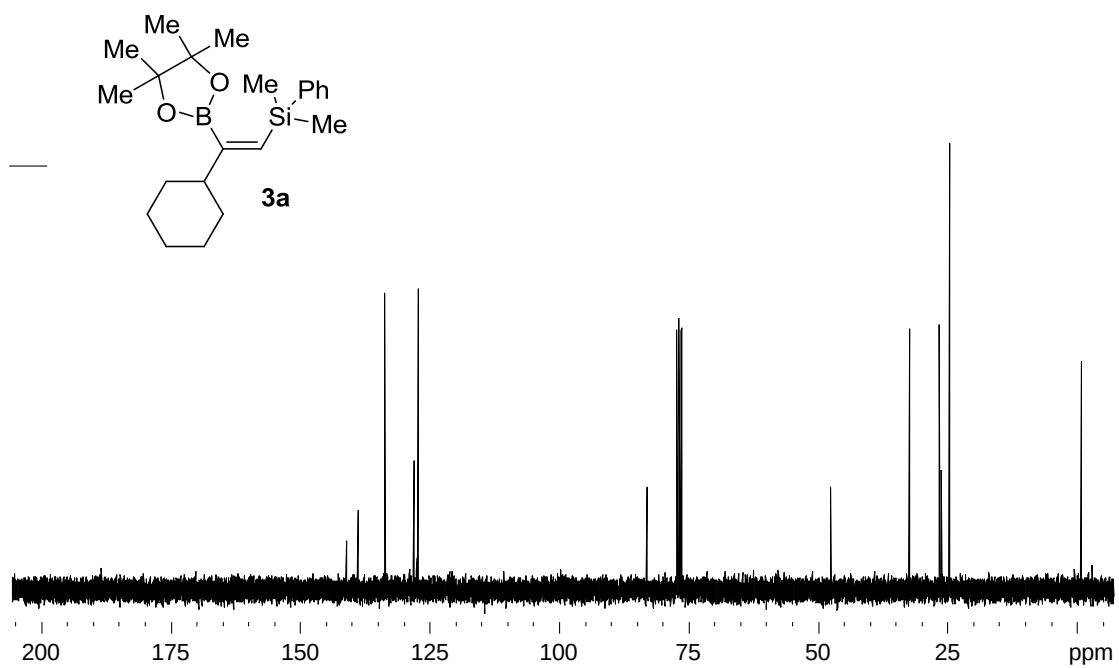
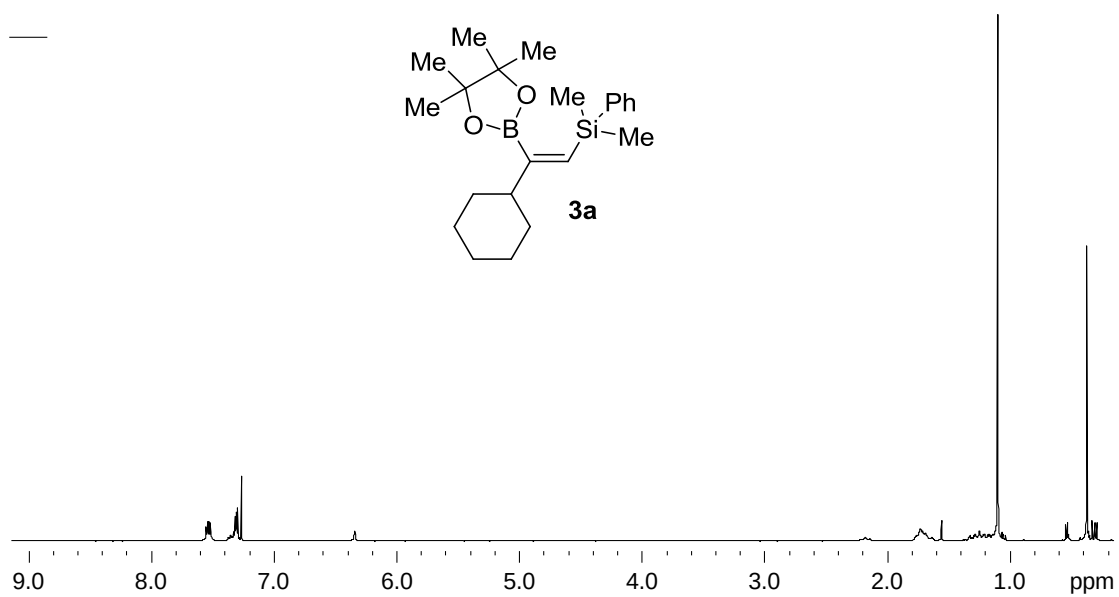
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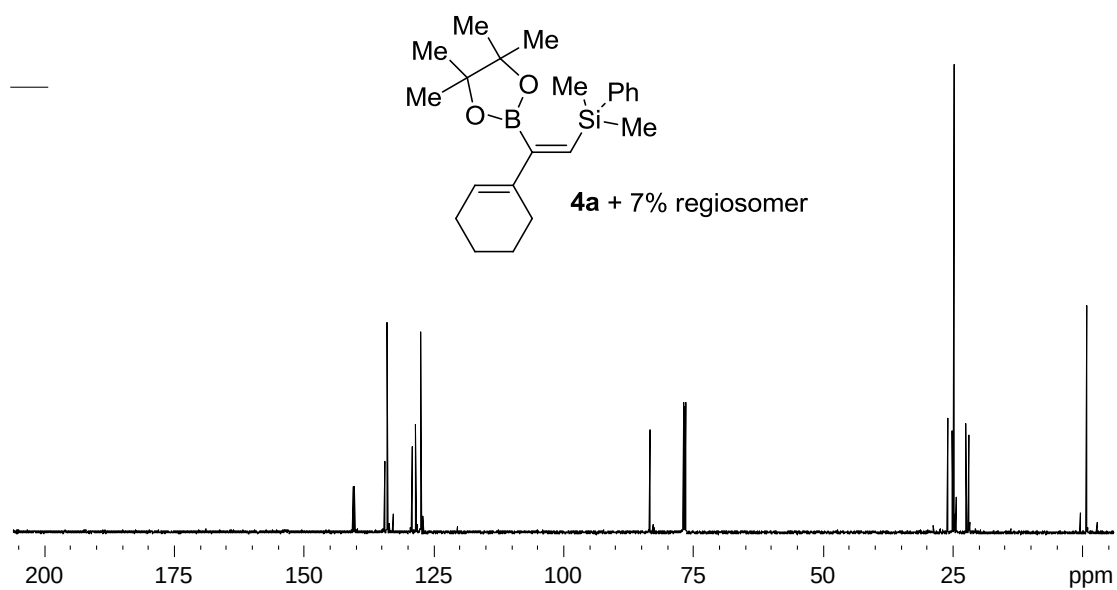
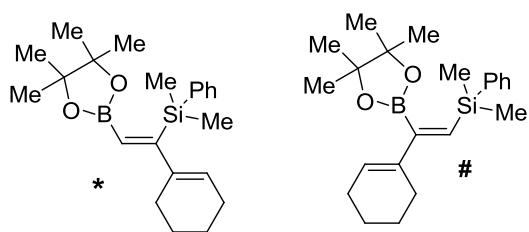
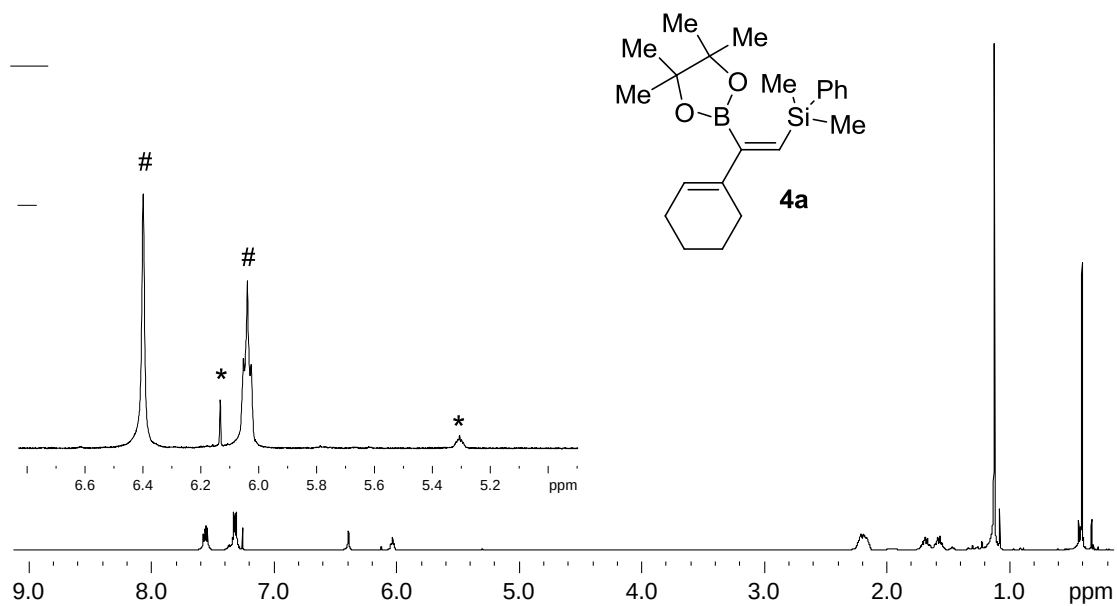
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2. Lykakis, I. N.; Psyllaki, A.; Stratakis, M. *J. Am. Chem. Soc.* **2011**, 133, 10426.
3. Tokiwano, T.; Watanabe, H.; Seo, T.; Oikawa, H. *Chem. Commun.* **2008**, 6016.
4. Kleeberg, C.; Cheung, M. S.; Lin, Z.; Marder, T. B. *J. Am. Chem. Soc.* **2011**, 133, 19060.

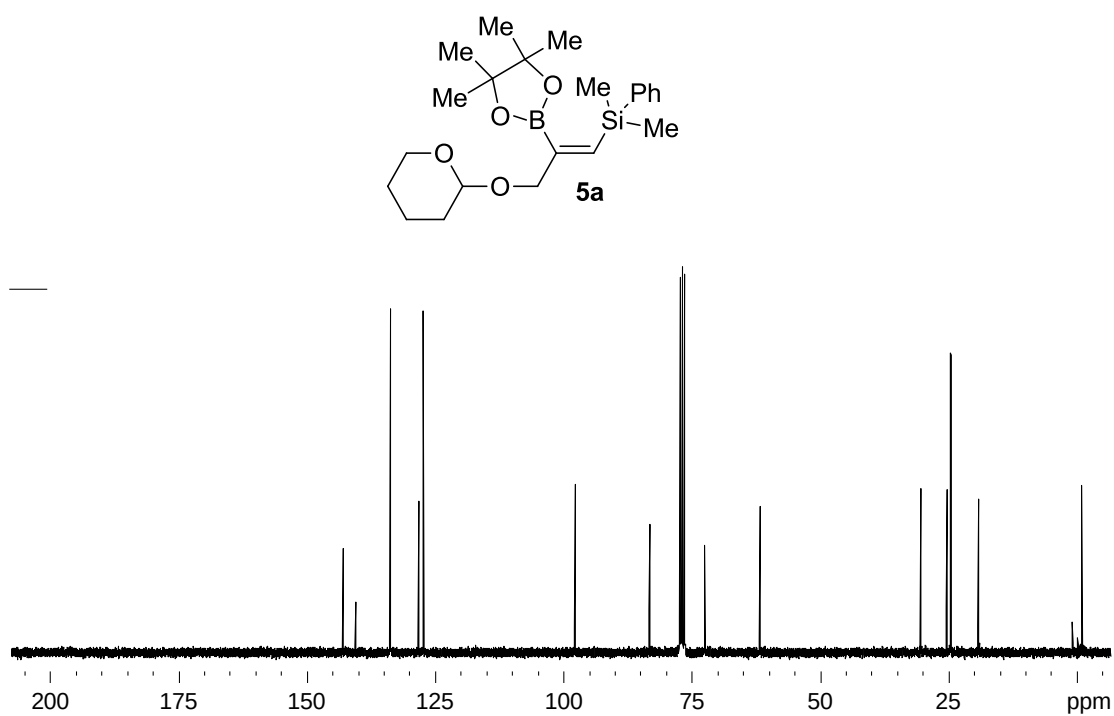
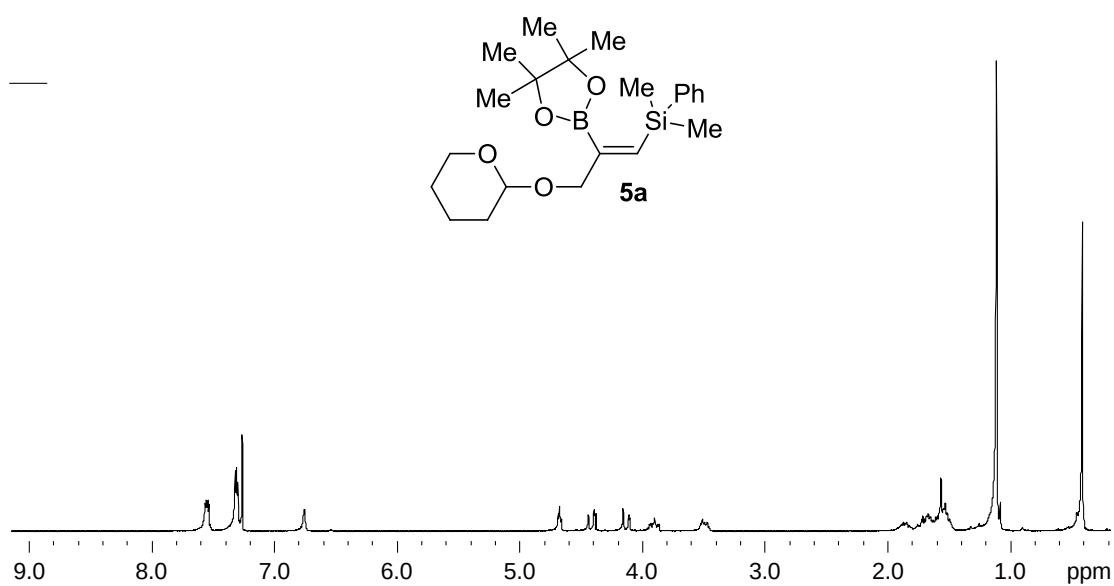
^1H and ^{13}C NMR spectra

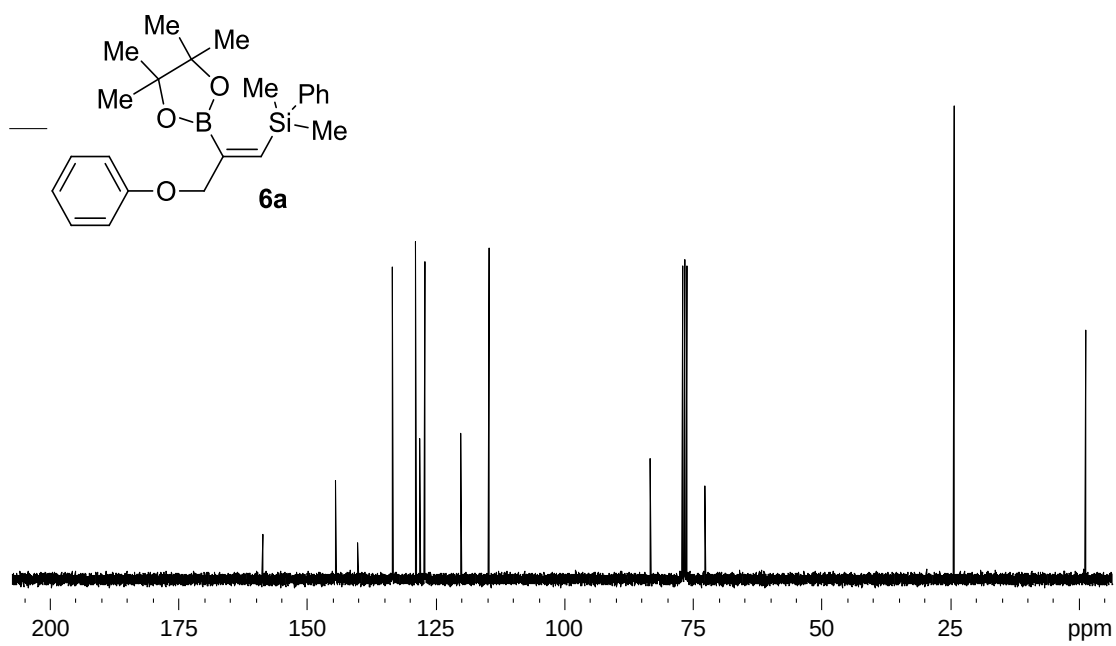


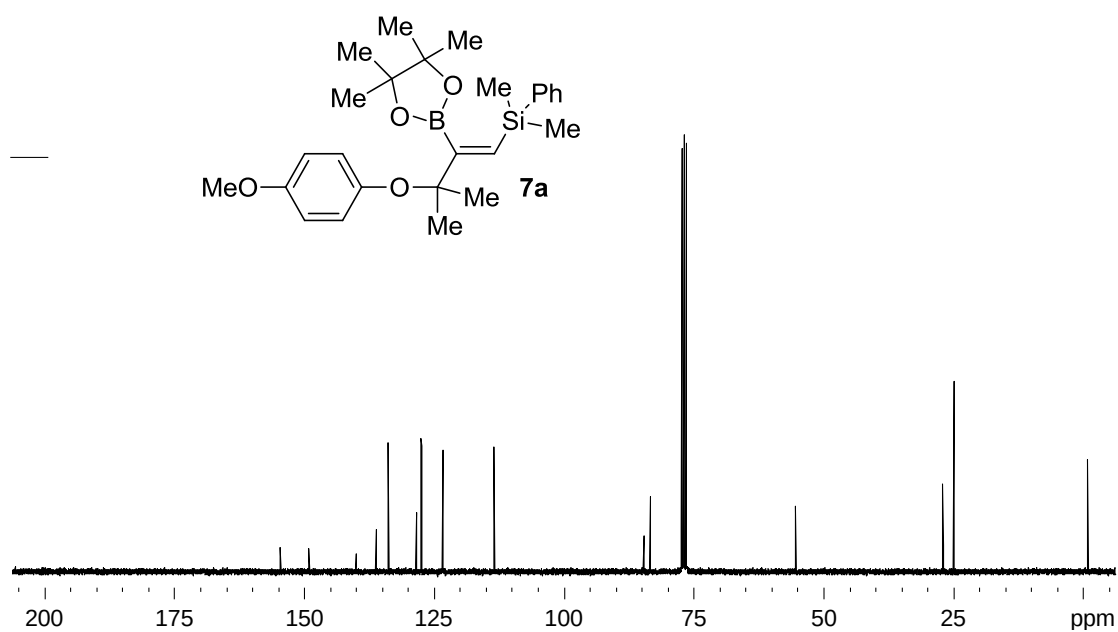
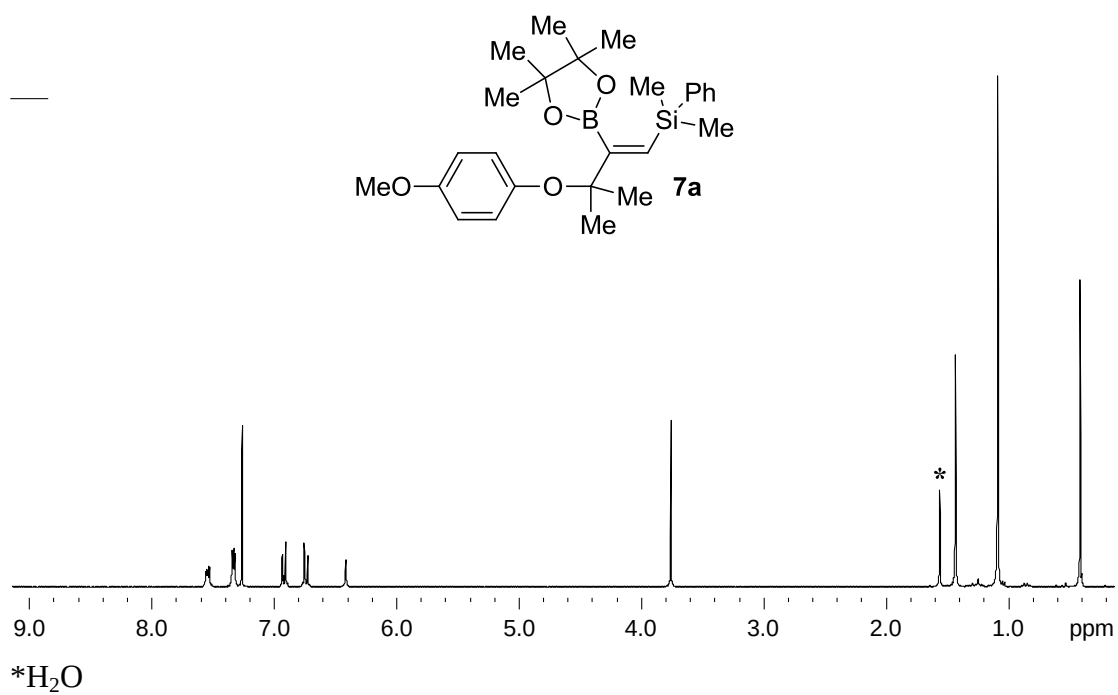


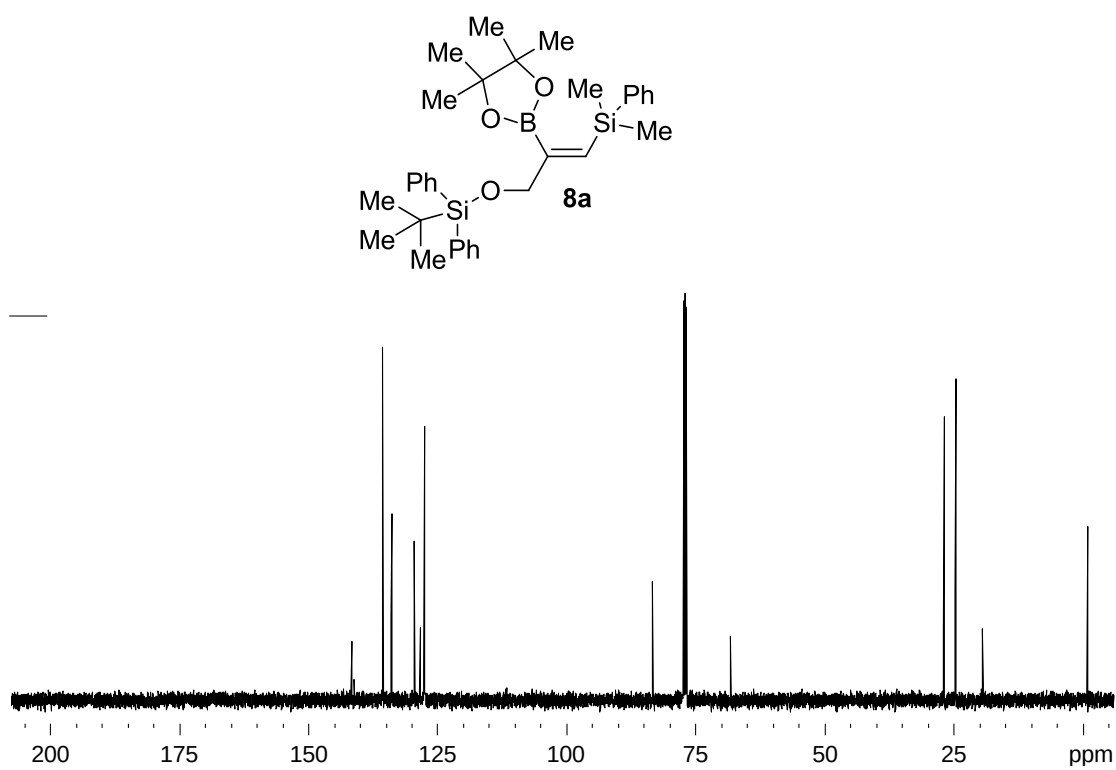
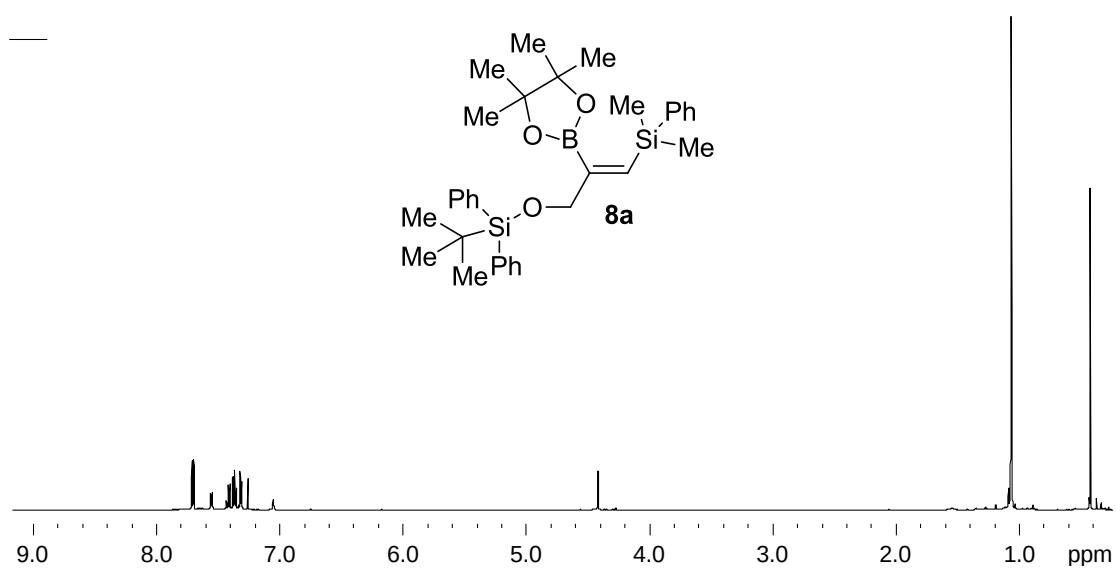


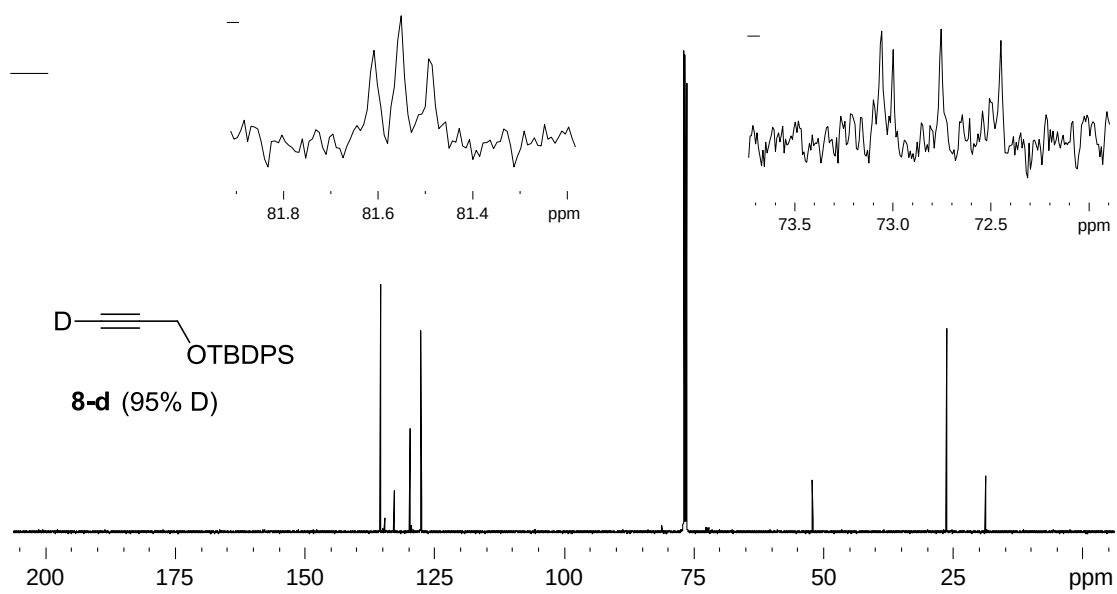
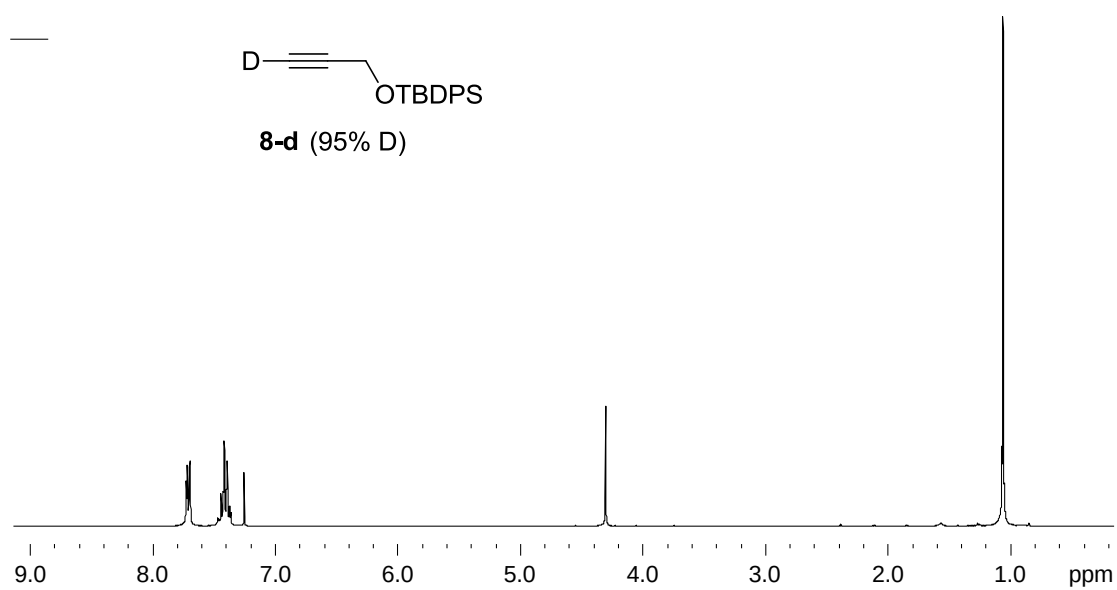


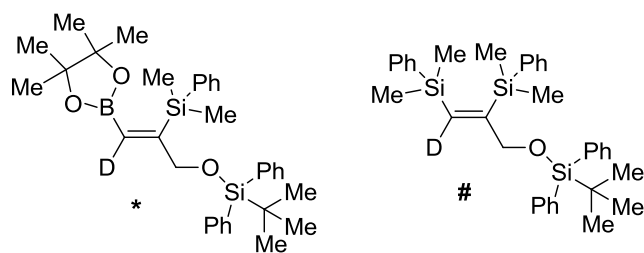
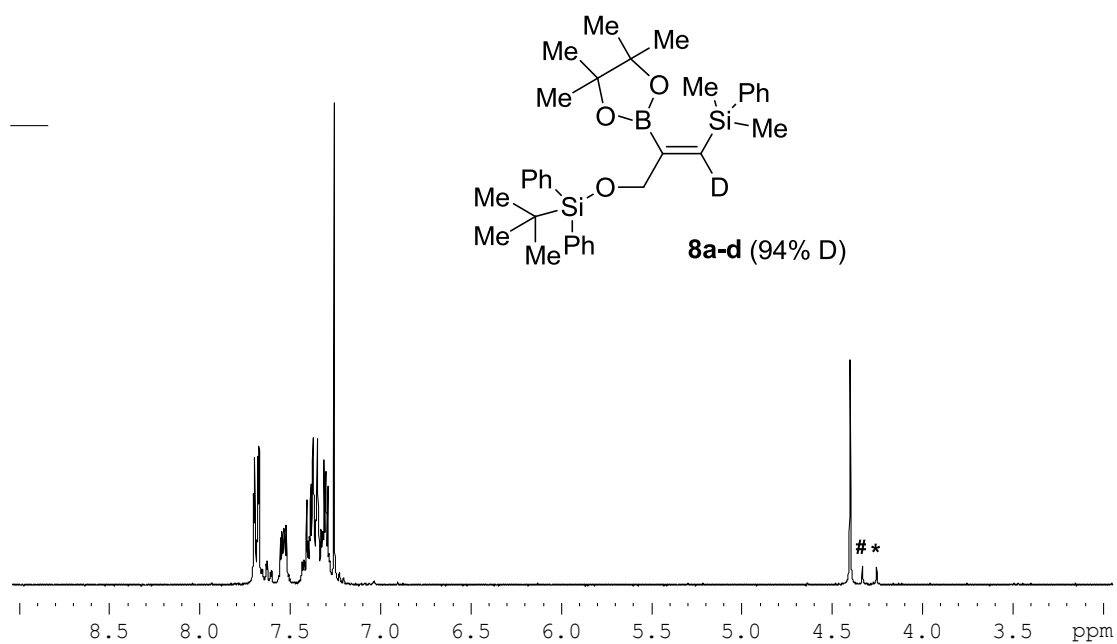


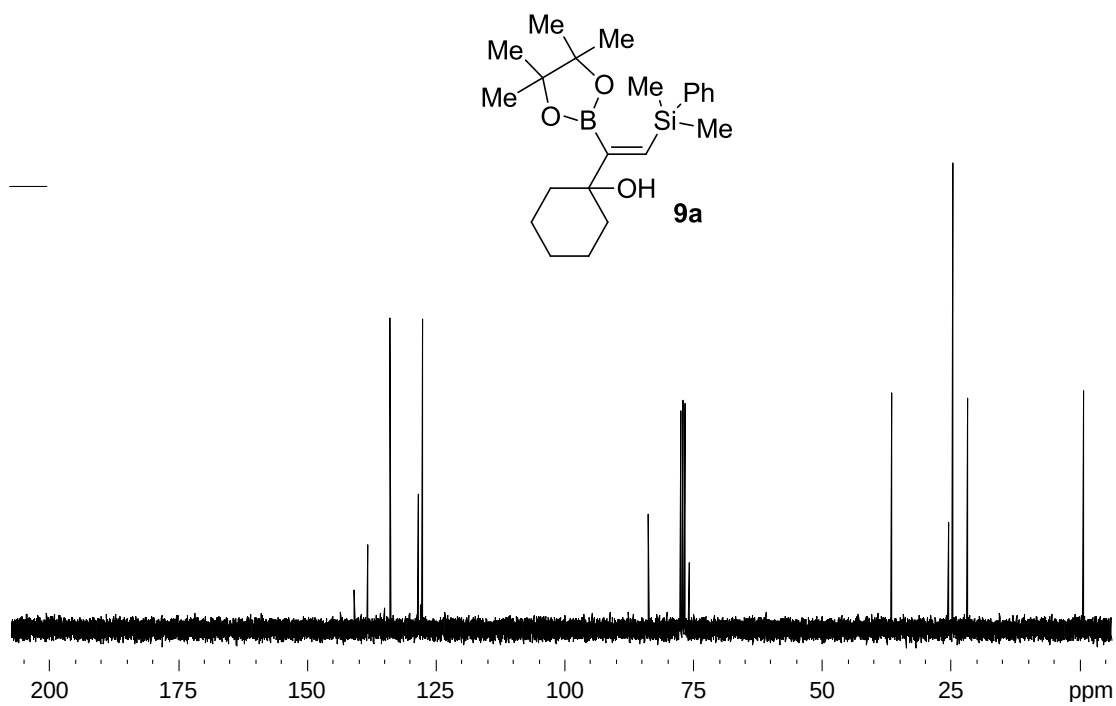
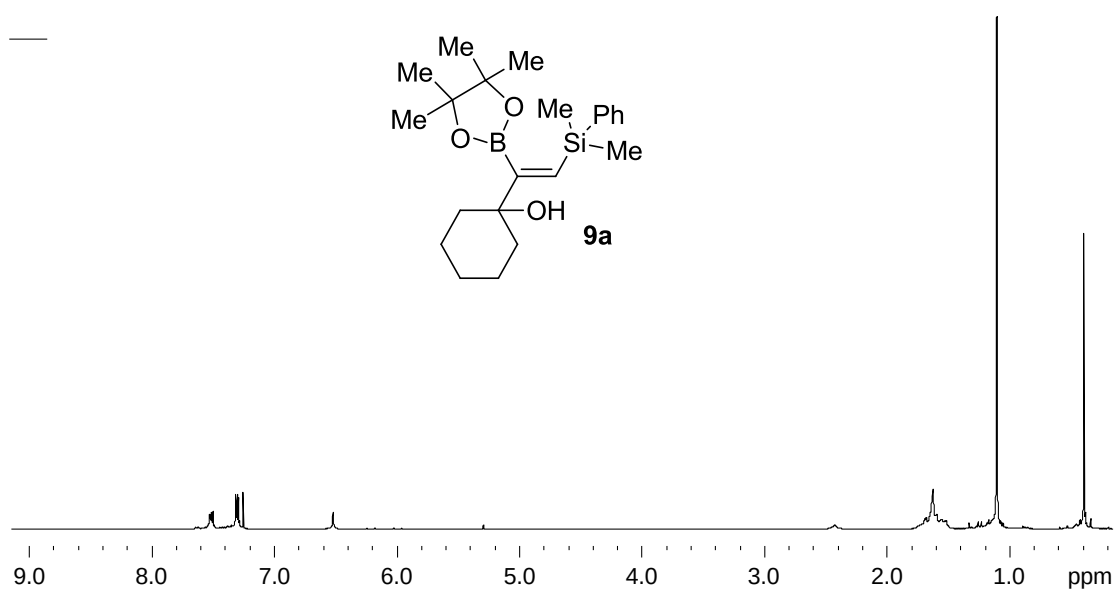


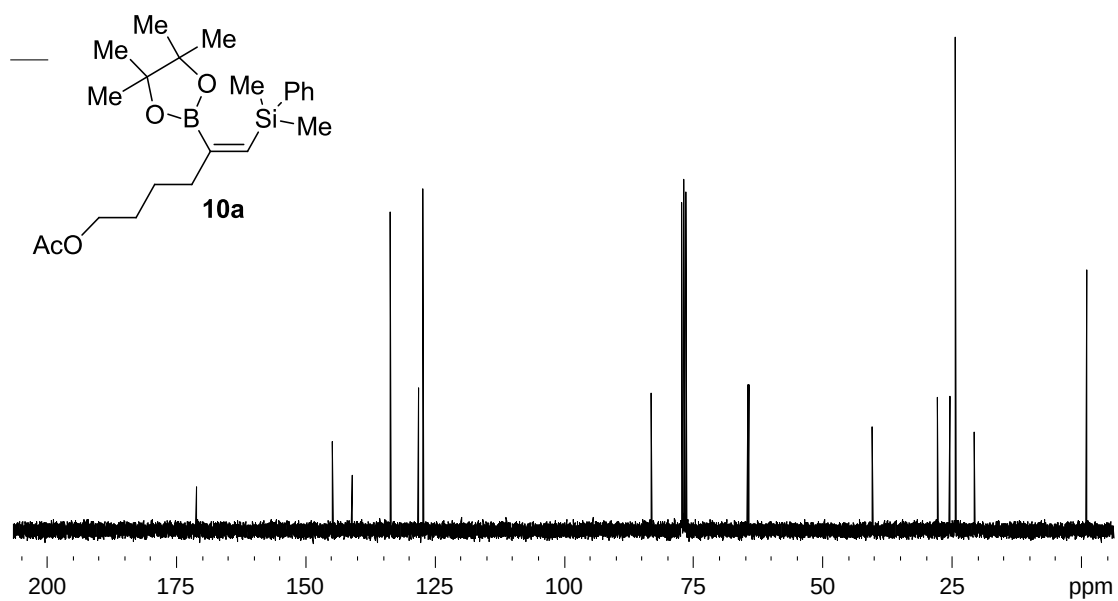
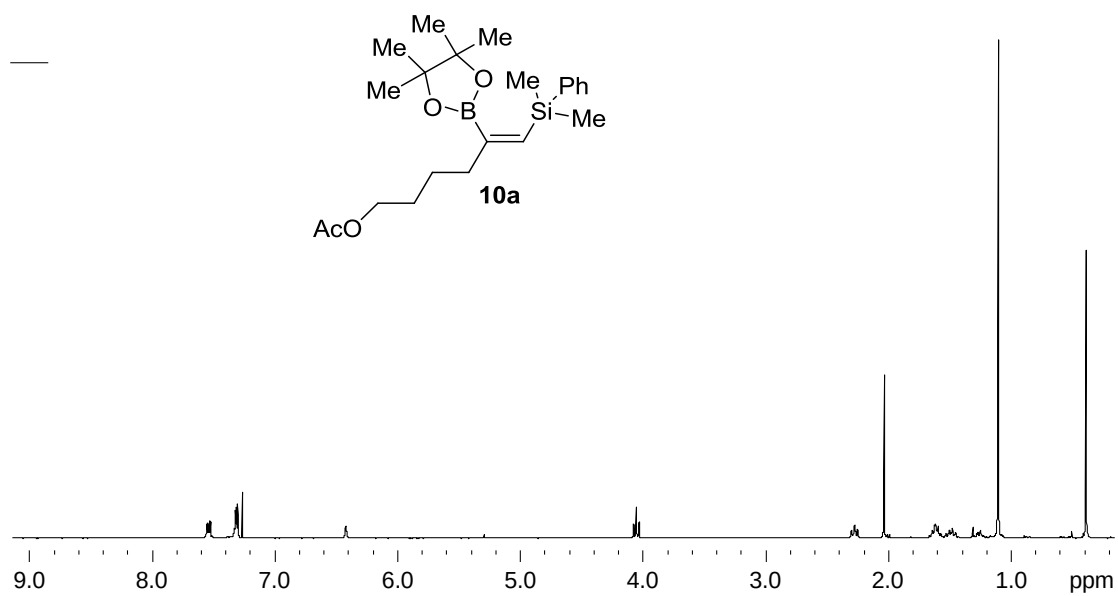


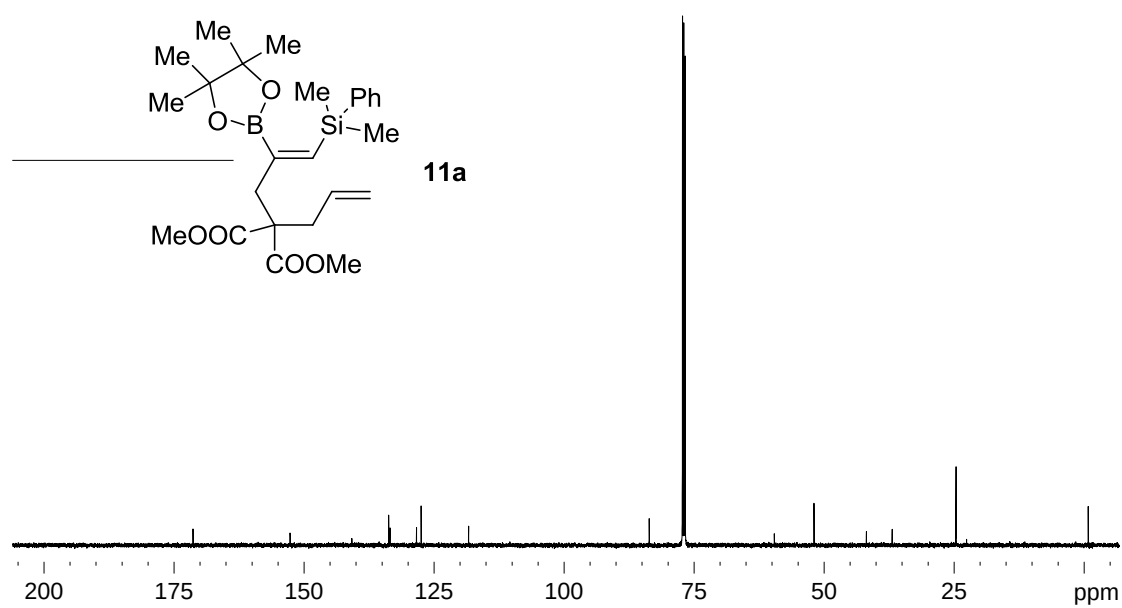
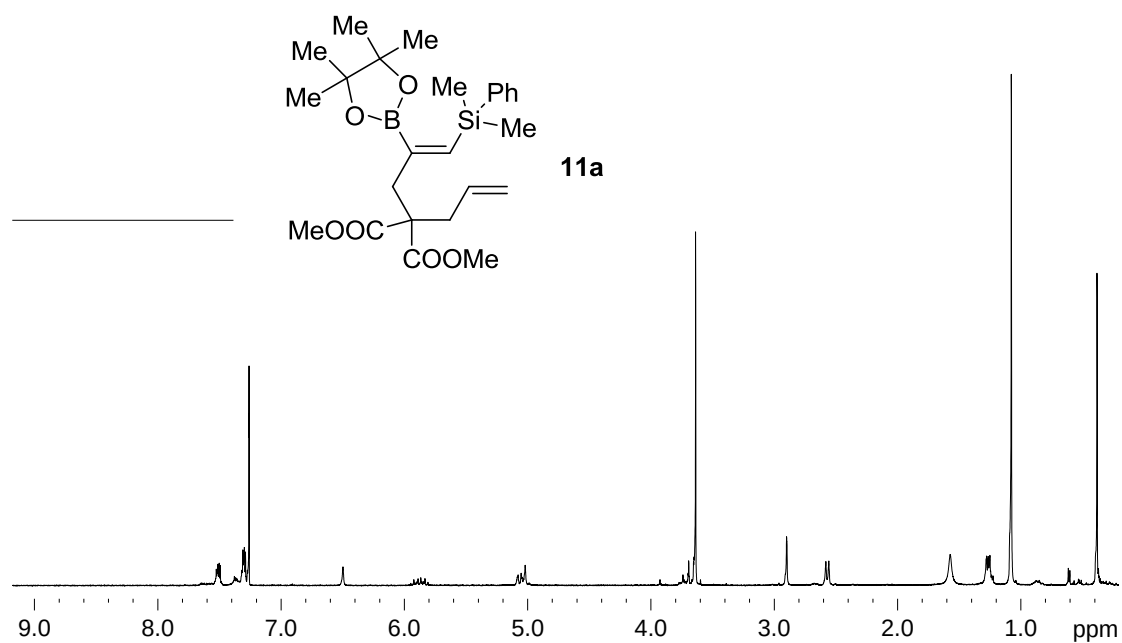


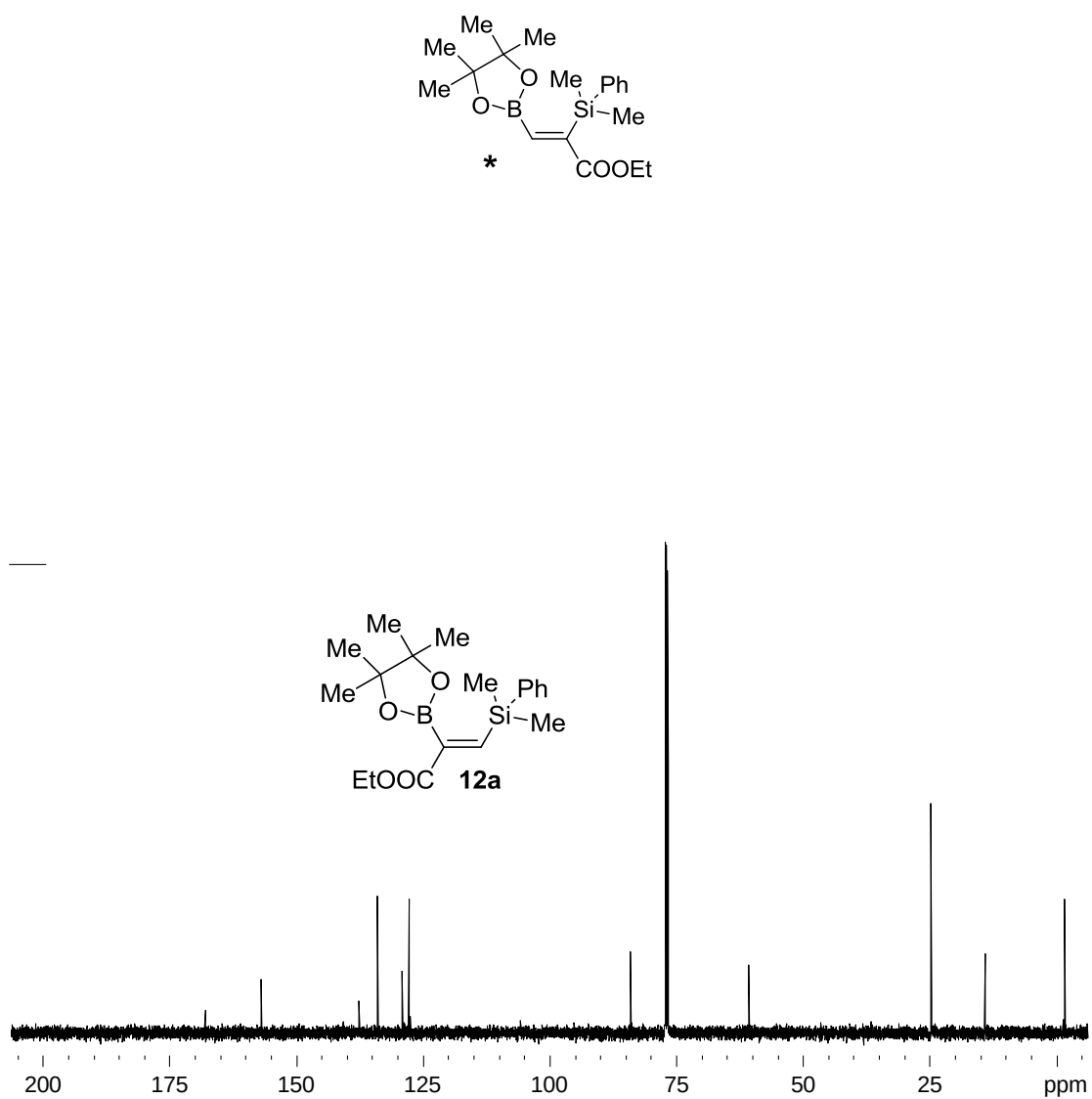
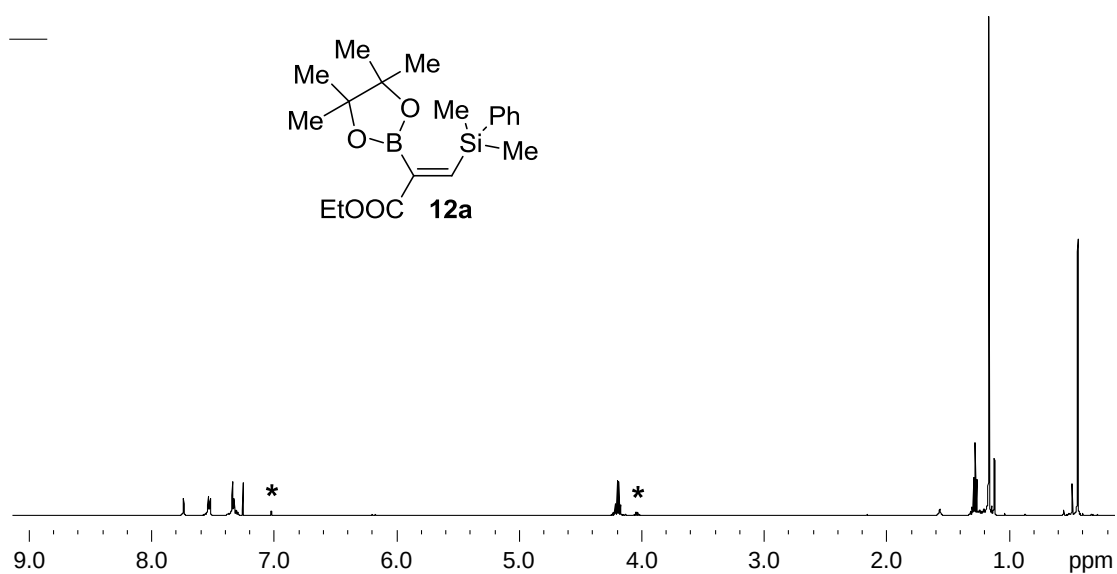


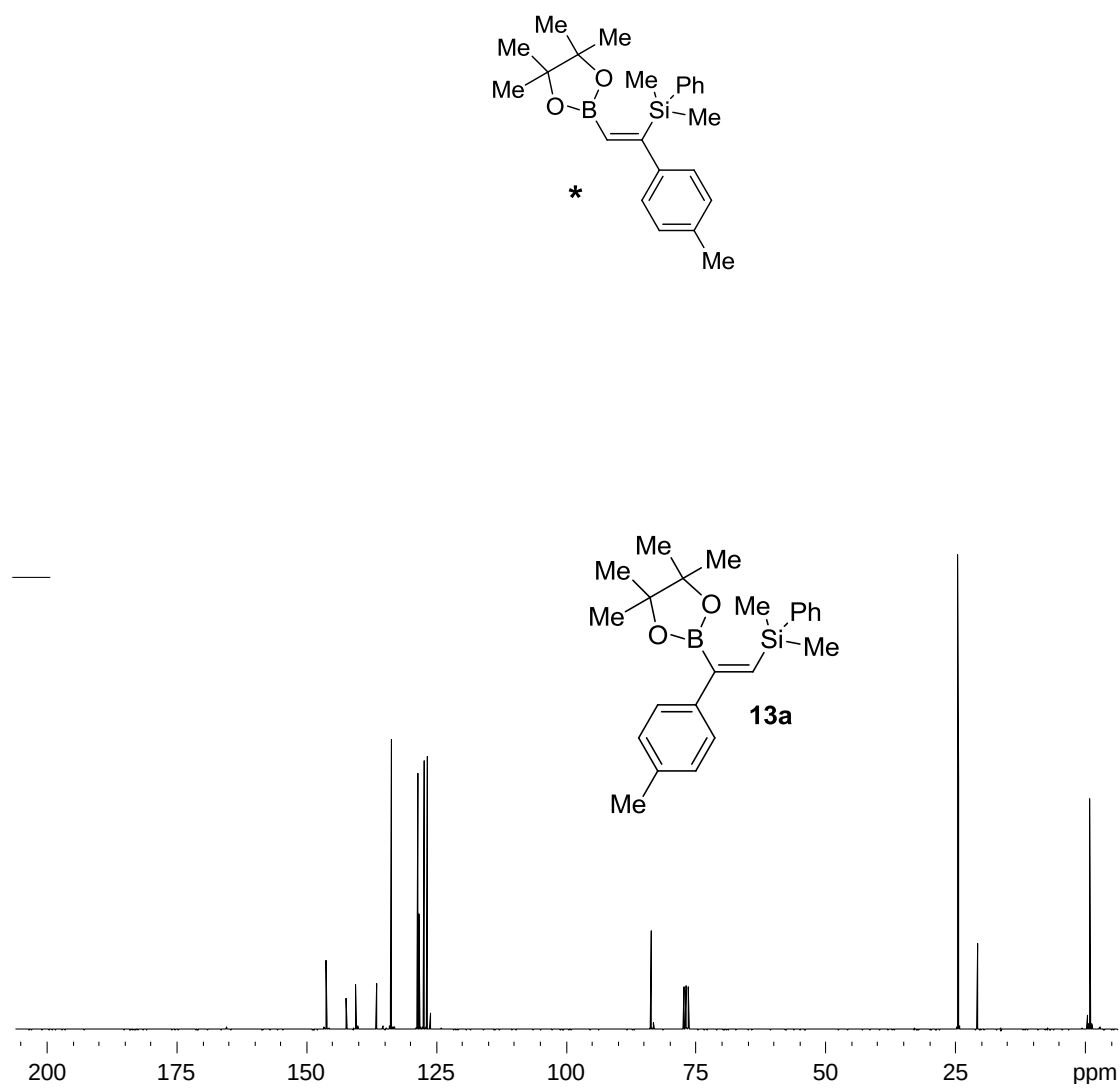
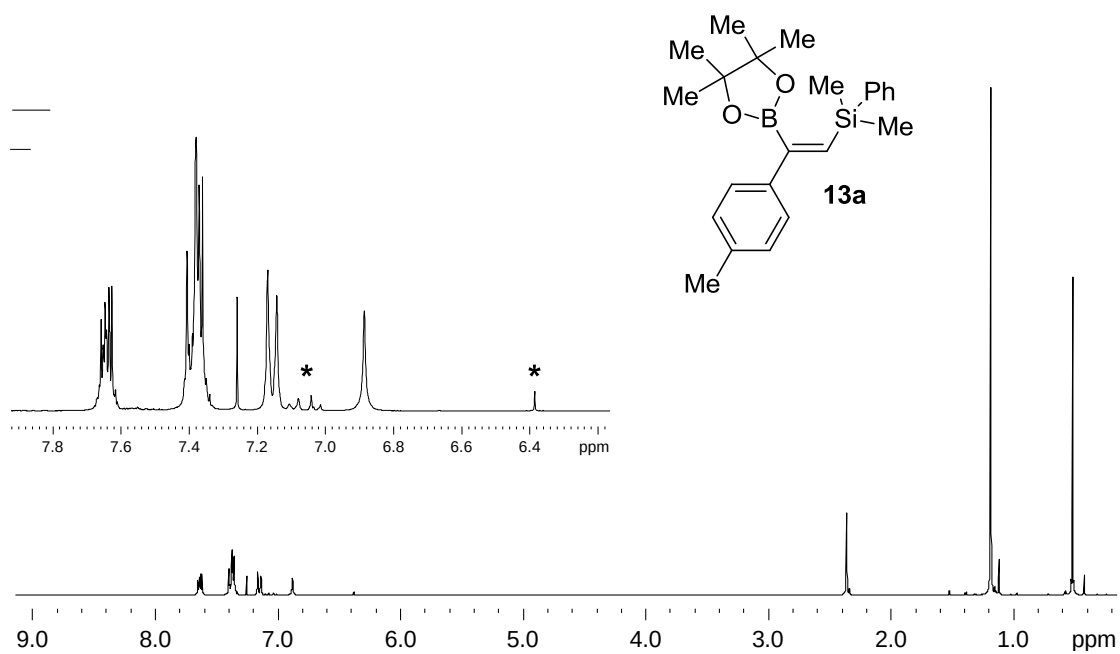


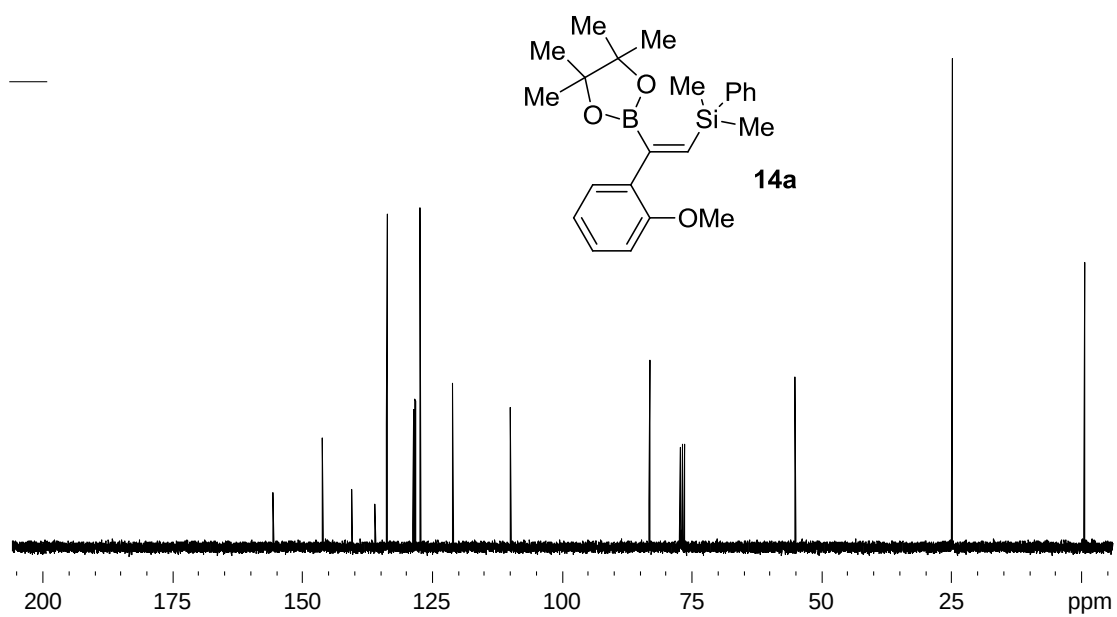
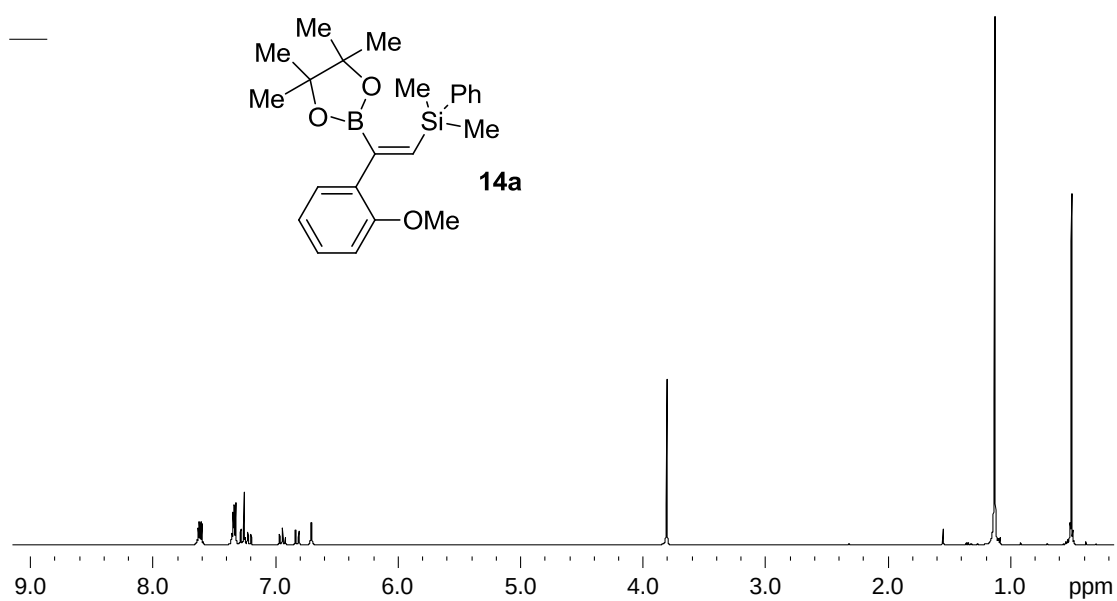


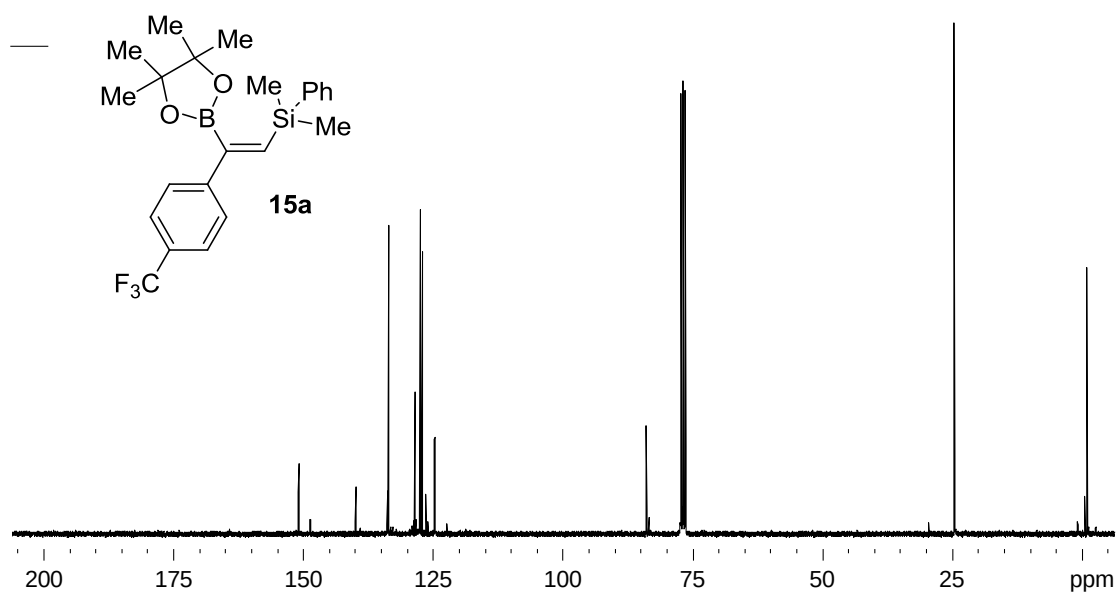
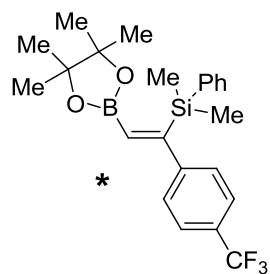
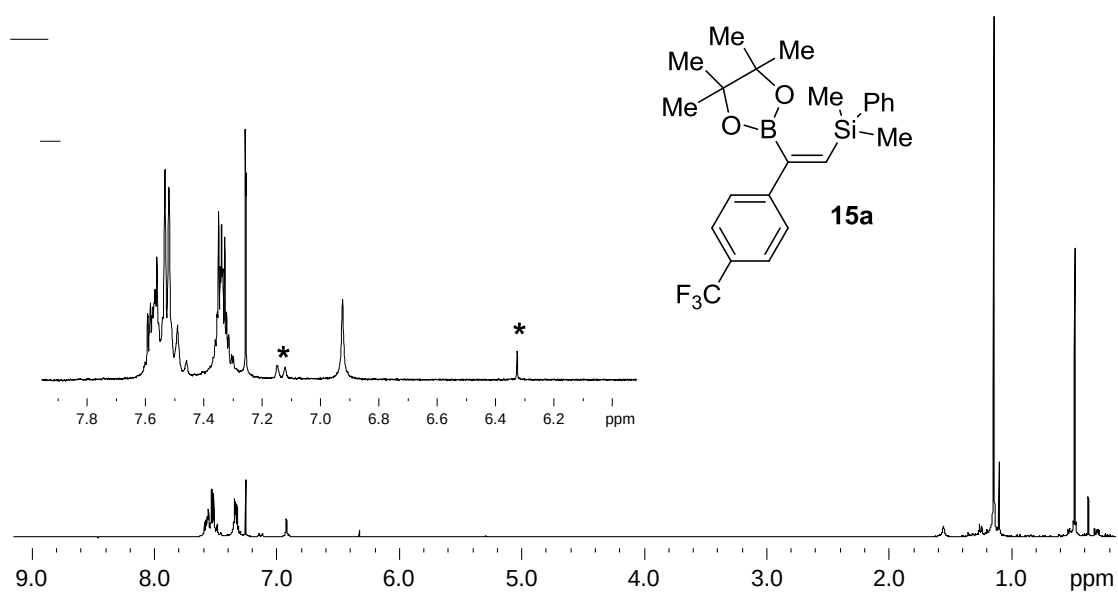


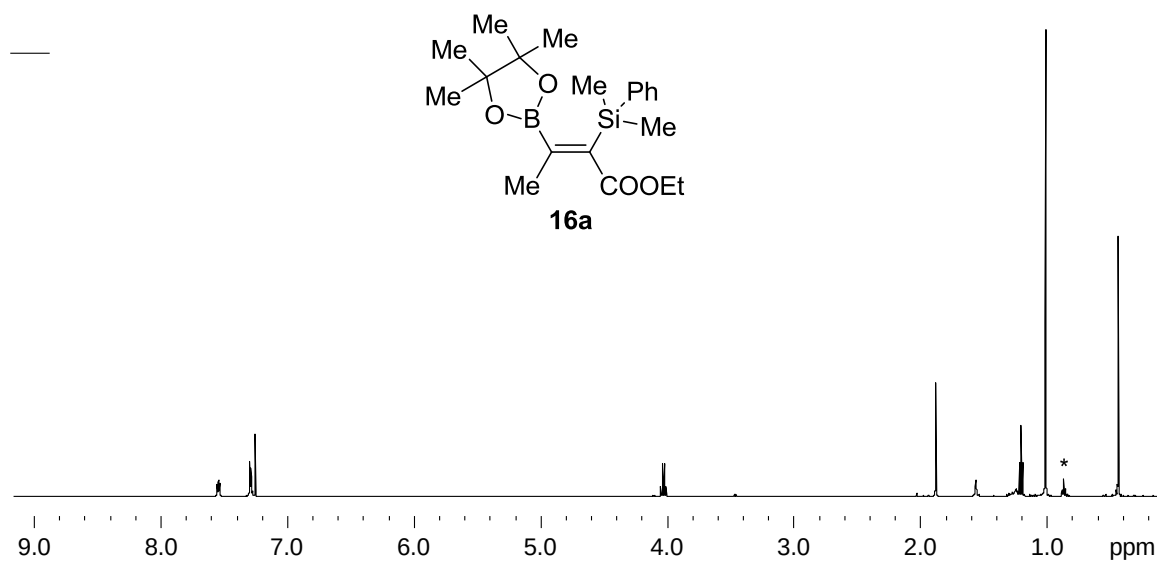




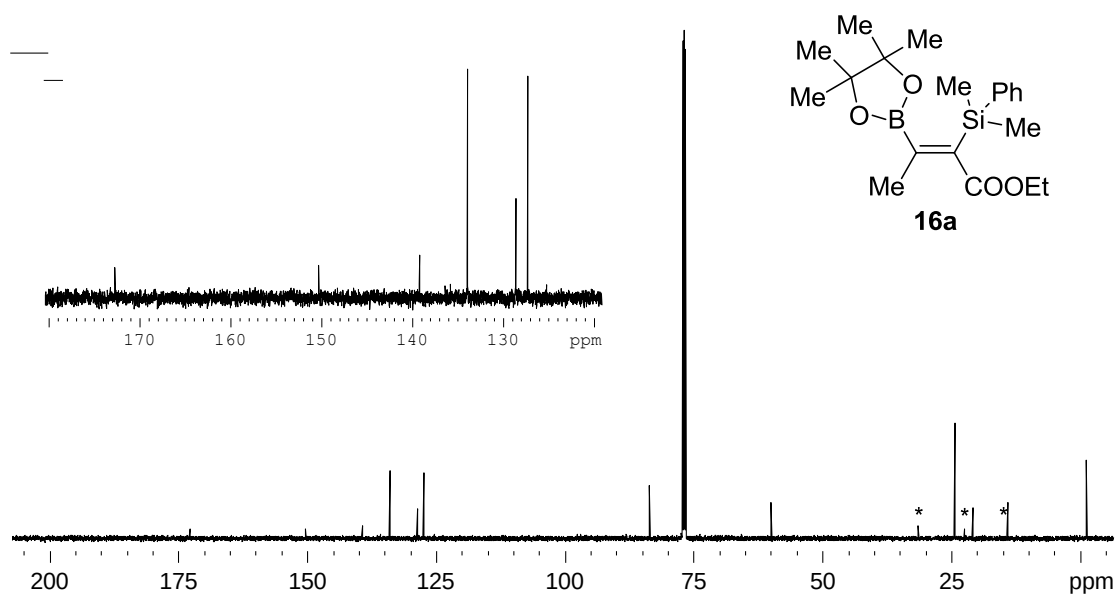




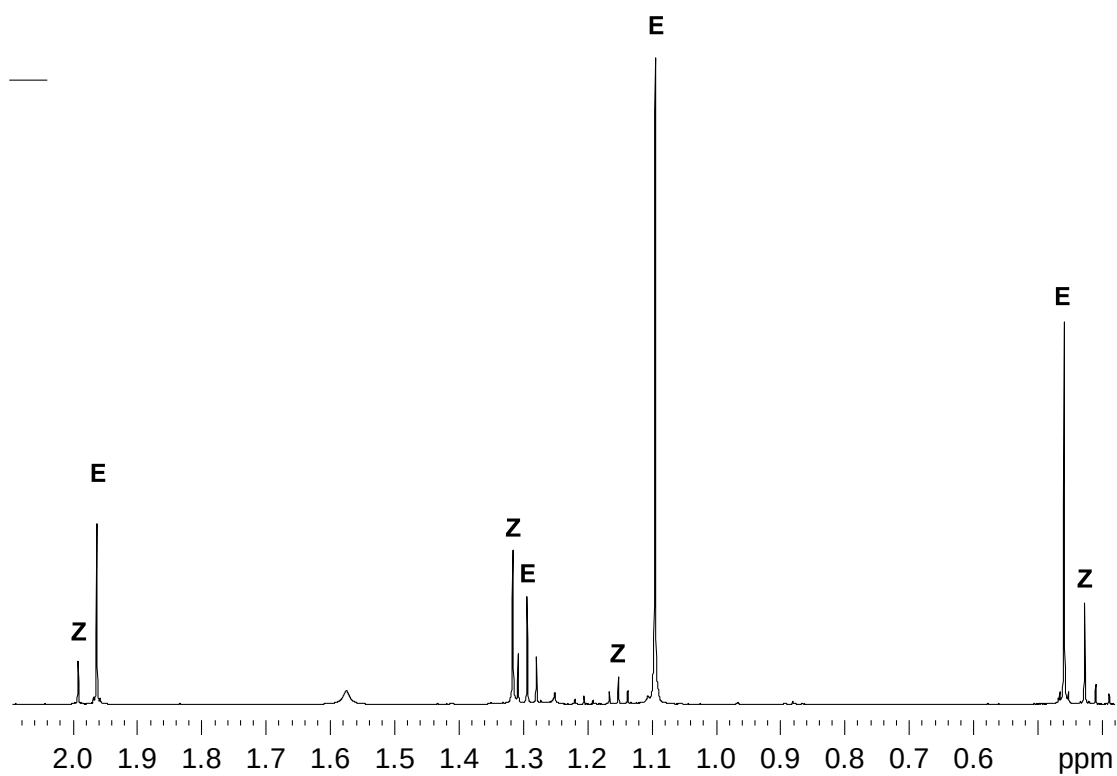
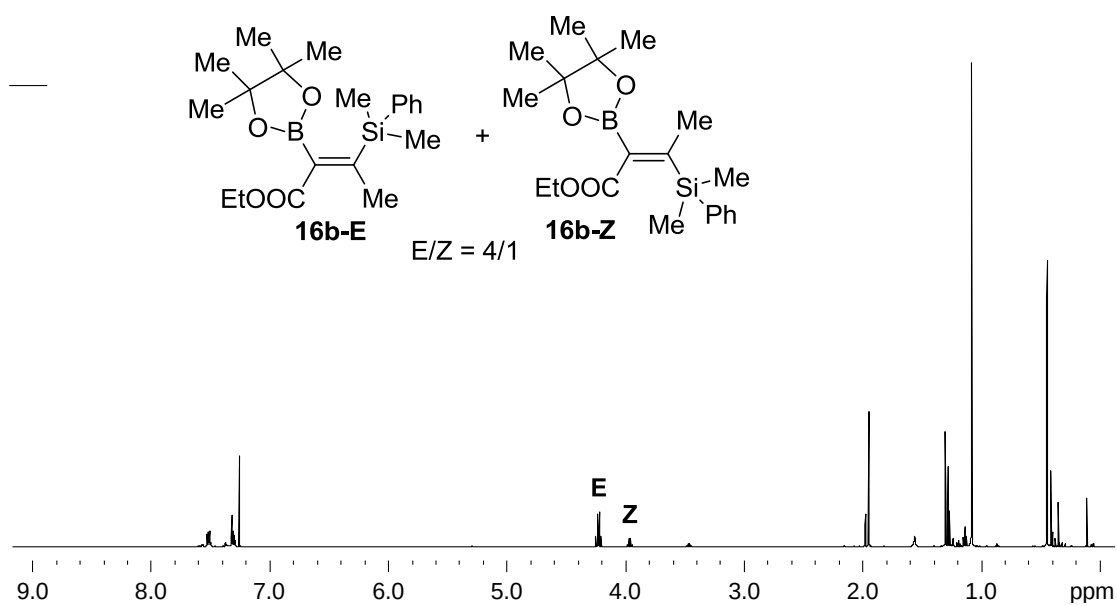


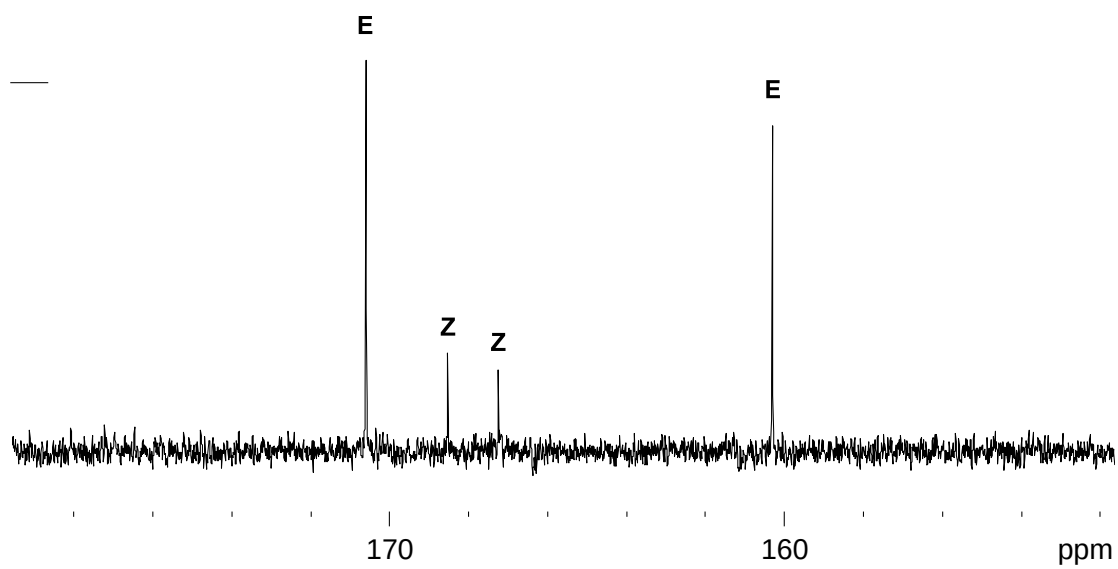
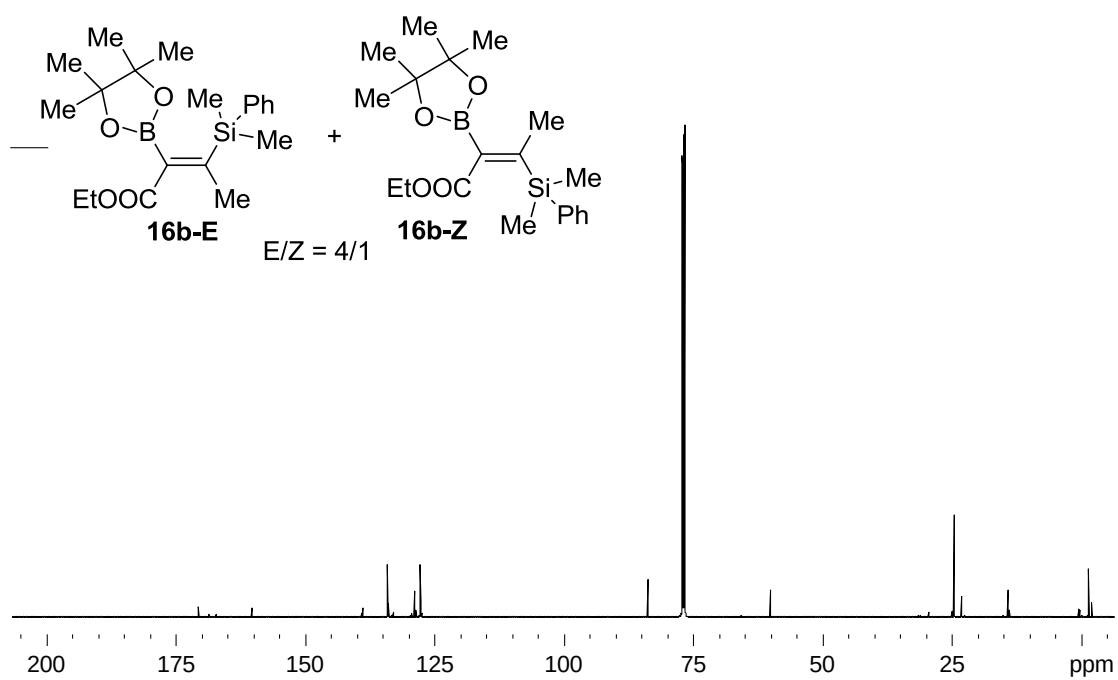


*Hexane



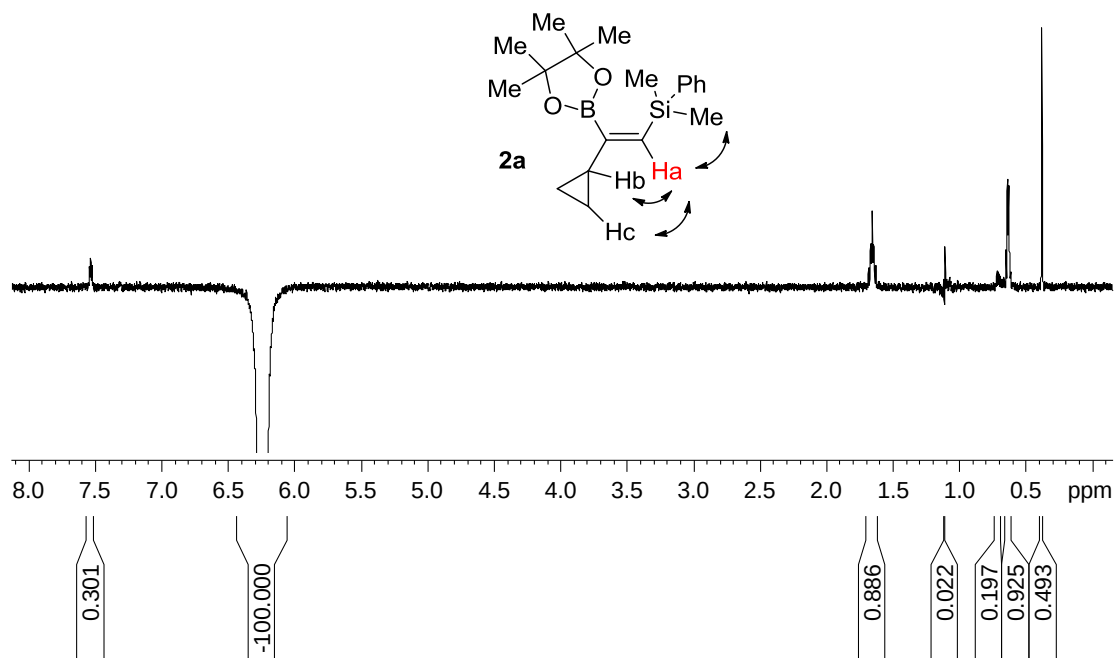
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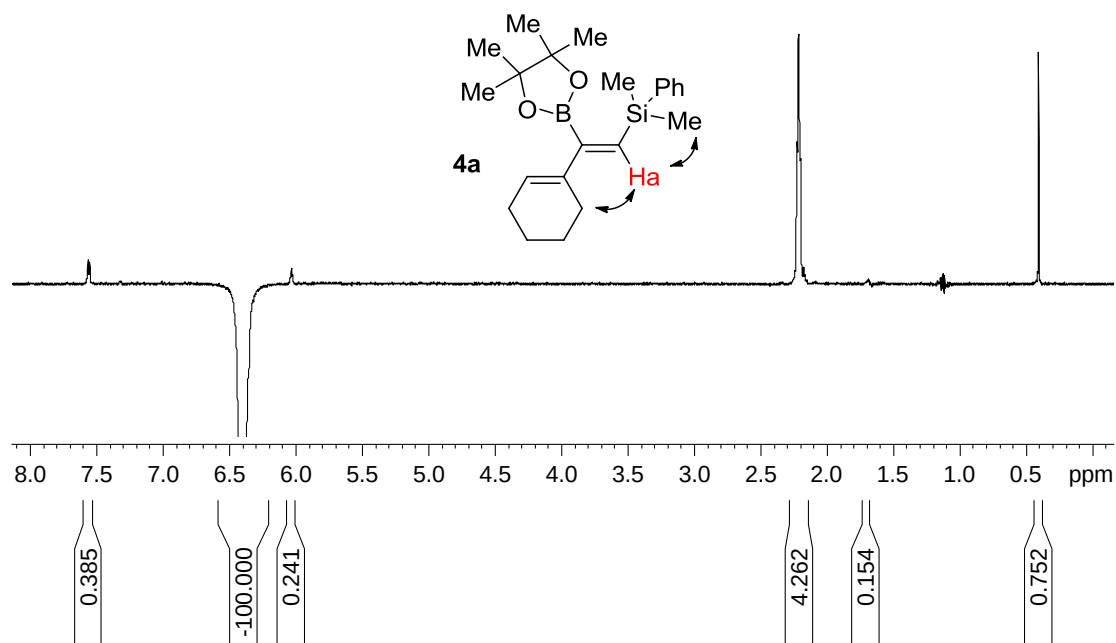


Representative nOe experiments for structure elucidation

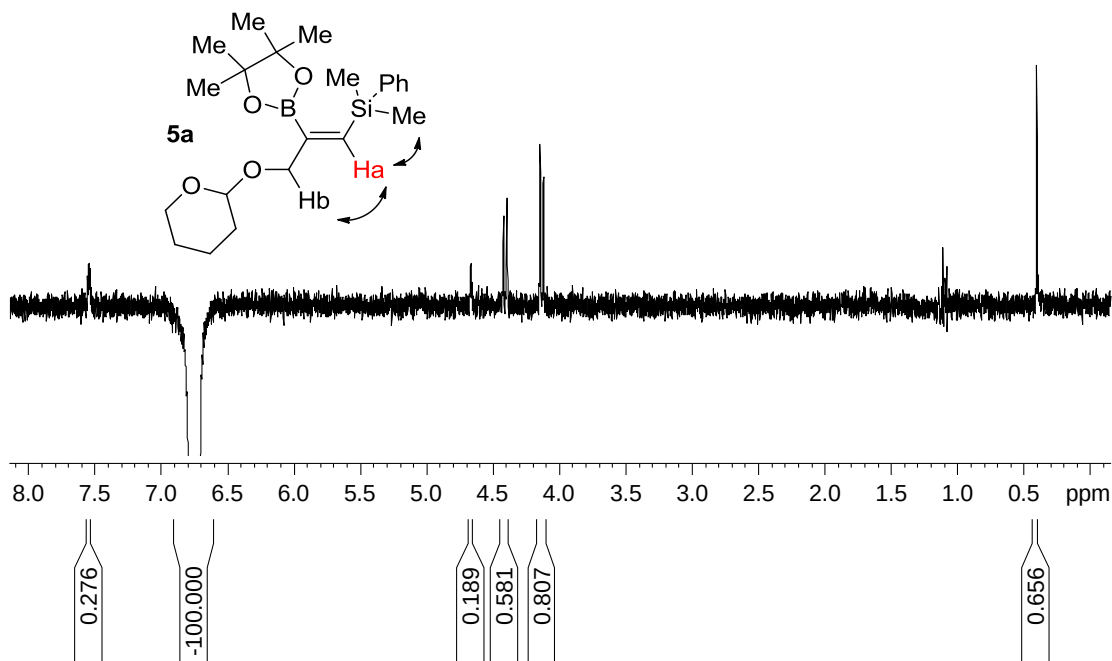
Irradiation of the olefinic H_a proton of **2a** resonating at 6.24 ppm results to signal enhancement of the allylic H_b (~0.9%) at ~1.65 ppm, the diastereotopic cyclopropyl H_c (~0.9%) at ~0.65 ppm, and the *gem*-methyls on silicon (0.5%) at 0.38 ppm.



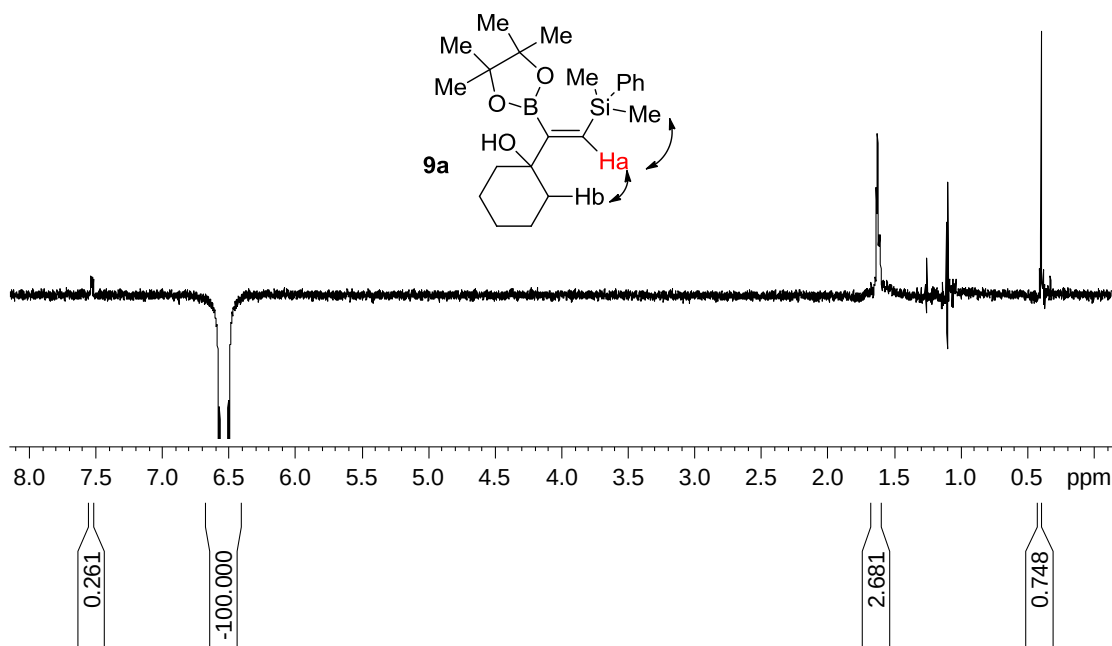
Irradiation of the H_a olefinic proton of **4a** resonating at 6.40 ppm results to signal enhancement of allylic H_b at ~2.20 ppm (4.3%), the olefinic proton of the cyclohexenyl ring (0.2%) at 6.04 ppm, and the *gem*-methyls on silicon (0.8%) at 0.42 ppm.



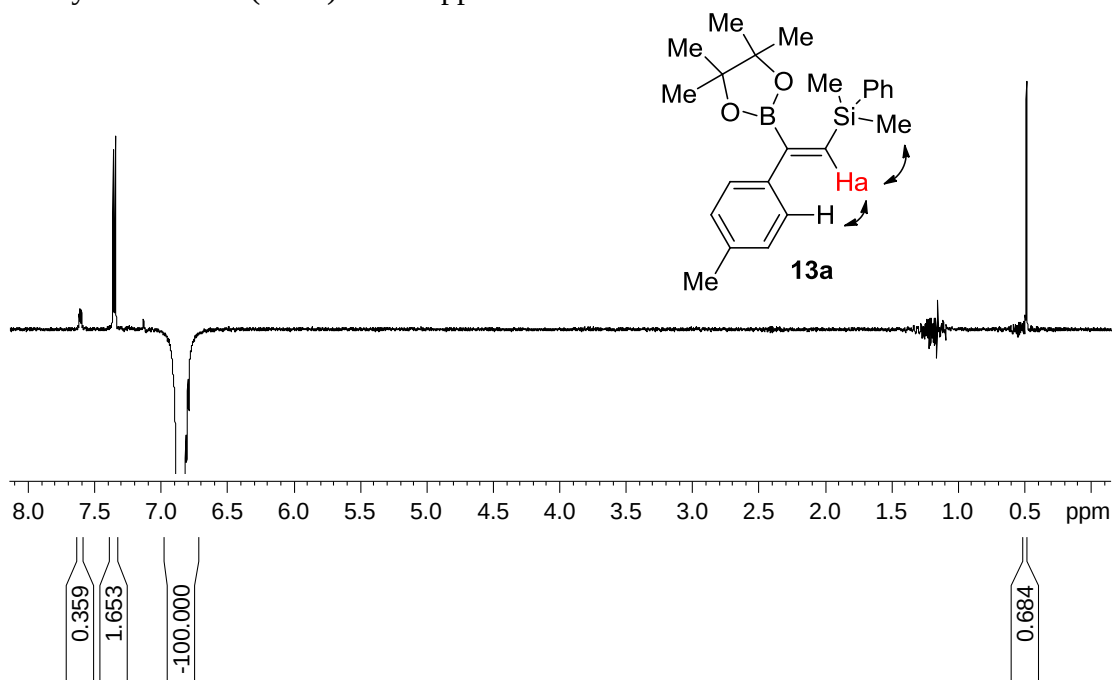
Irradiation of the olefinic H_a of **5a** resonating at 6.76 ppm, results to signal enhancement of the diastereotopic allylic H_b (0.6% and 0.8%, respectively) at 4.41 ppm and 4.13 ppm, and the *gem*-methyls on silicon (0.7%) at 0.42 ppm.



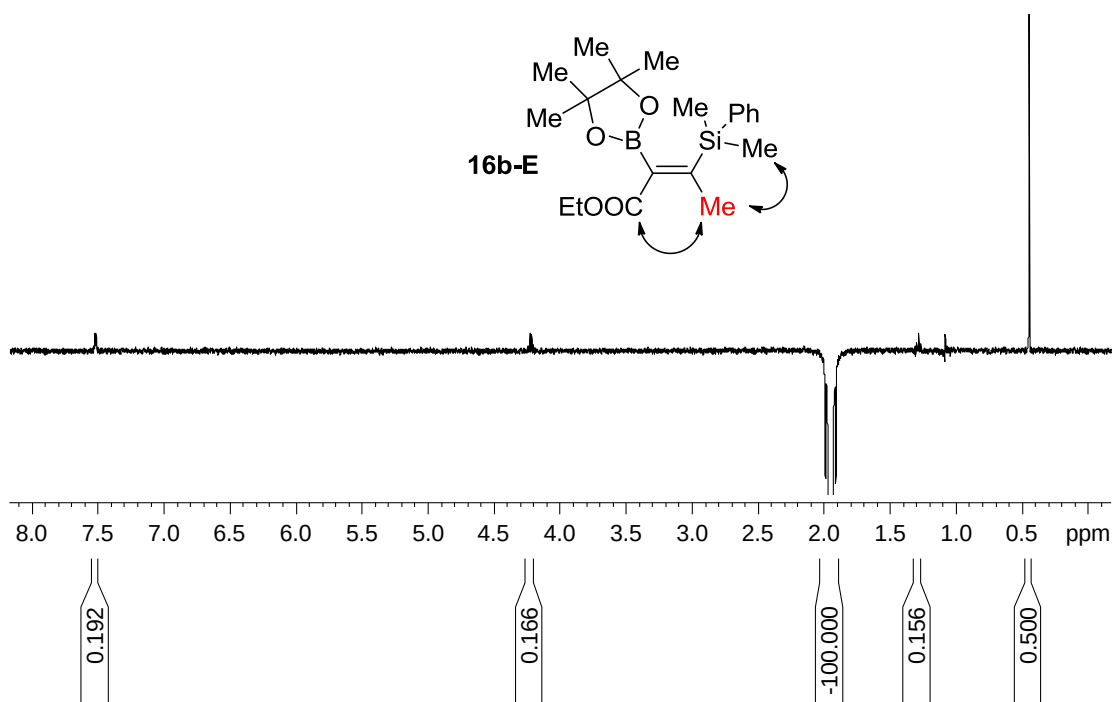
Irradiation of the olefinic H_a of **9a** resonating at 6.53 ppm, results to signal enhancement of the diastereotopic cyclohexyl protons H_b (2.7%) at ~1.65 ppm, and the *gem*-methyls on silicon (0.7%) at 0.40 ppm.



Irradiation of the olefinic H_a proton of **13a** resonating at 6.89 ppm, results to signal enhancement of the *ortho*-proton H_b of tolyl group (1.7%) at 7.39 ppm, and the *gem*-methyls on silicon (0.7%) at 0.53 ppm.



Irradiation of the allylic methyl group of **16b-E** resonating at 1.96 ppm, results to a small signal enhancement of the ethyl moiety of COOEt (~0.2%), and the *gem*-methyls on silicon (0.5%) at 0.46 ppm.



Irradiation of the allylic methyl group of **16b-Z** resonating at 1.99 ppm, results to signal enhancement of the *gem*-methyls on silicon (0.4%) at 0.43 ppm, and the methyl group of pinacolato moiety (~0.3%) at 1.16 ppm.

