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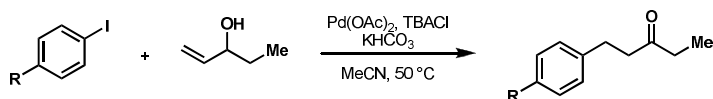
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Materials and Methods

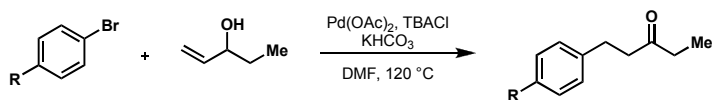
All silylation reactions were assembled in an N₂-filled glovebox using oven-dried glassware and were stirred with Teflon-coated magnetic stirring bars. [Ir(cod)OMe]₂ was obtained as a gift from Johnson Matthey and was used as received. Ru(PPh₃)₃Cl₂ was purchased from Strem and was used as received. 3,4,7,8-Tetramethyl-1,10-phenanthroline (Me₄phen) was purchased from Aldrich and was used as received. Diethylsilane (Et₂SiH₂) was purchased from Alfa Aesar and was used as received. Norbornene (nbe) was purchased from Aldrich and was used as received. Tetrahydrofuran (THF) was degassed by purging with nitrogen and then dried with a solvent purification system containing activated alumina. All other solvents and reagents were used as received, with the exception of dihydrolinalool, which was purified by bulb-to-bulb distillation. Half-saturated aq. solutions refer to a freshly prepared 1:1 v/v mixture of the corresponding saturated aq. solution and deionized water. Reaction temperatures above 23 °C refer to temperatures of an aluminum heating block, which were either controlled by an electronic temperature modulator, or controlled manually and monitored using a standard alcohol thermometer. Silica gel chromatography was performed using a Teledyne Isco CombiFlash[®] R_f system with RediSep R_f Gold[™] columns. Kugelrohr distillation was performed using a Büchi Glass Oven B-580. ¹H NMR spectra were recorded on Varian UI-500NB, U-500 and VXR-500 spectrometers. ¹³C NMR spectra were recorded on Varian U-500 and VXR-500 spectrometers with ¹³C operating frequencies of 125 MHz. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal (δ = 7.26 for ¹H NMR and δ = 77.16 for ¹³C NMR). ¹⁹F NMR spectra were recorded on a Varian U-500 spectrometer with a ¹⁹F operating frequency of 470 MHz. Data for ¹H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of hydrogens). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). GC-MS data were obtained on an Agilent 6890-N GC system containing an Alltech EC-1 capillary column and an Agilent 5973 mass selective detector. High-resolution mass spectral data were obtained from the University of Illinois SCS Mass Spectrometry Laboratory.

Experimental Procedures

Synthesis of Substrates: Substrates Prepared by Heck Coupling



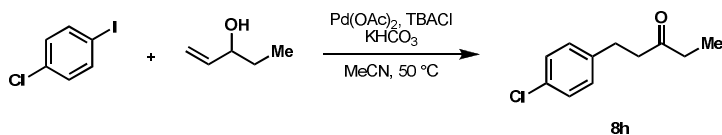
General procedure for Heck coupling of aryl iodides: The general conditions described by Jeffrey¹ were employed with slight modification. In an N₂-filled glovebox, a 20 mL screw-capped vial was charged with Pd(OAc)₂ (30 μmol, 1 mol %), KHCO₃ (7.5 mmol, 2.5 equiv), tetrabutylammonium chloride (3.0 mmol, 1.0 equiv), aryl iodide (3.0 mmol, 1.0 equiv), 1-penten-3-ol (6.0 mmol, 2.0 equiv) and MeCN (6.0 mL). A stir bar was added, and the vial was capped with a Teflon-lined screw cap and placed in a pre-heated aluminum block at 50 °C (CAUTION: CO₂ evolution!). Upon complete consumption of the aryl iodide (as determined by GC-MS analysis, generally 12-24 h), the stir bar was removed, and the reaction mixture was directly concentrated by rotary evaporation. The resulting residue was dissolved in a mixture of hexanes and EtOAc,² filtered through a short plug of SiO₂, and concentrated. The residue was adsorbed onto SiO₂ and purified by silica gel chromatography to provide the ketone product.



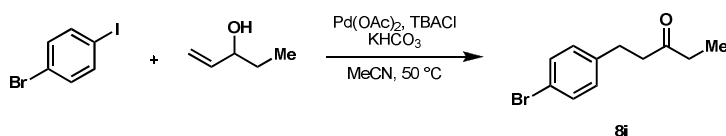
General procedure for Heck coupling of aryl bromides: In an N₂-filled glovebox, a 20 mL screw-capped vial was charged with Pd(OAc)₂ (30 μmol, 1 mol %), KHCO₃ (7.5 mmol, 2.5 equiv), tetrabutylammonium chloride (3.0 mmol, 1.0 equiv), aryl bromide (3.0 mmol, 1.0 equiv), 1-penten-3-ol (6.0 mmol, 2.0 equiv) and DMF (6.0 mL). A stir bar was added, and the vial was capped with a Teflon-lined screw cap and placed in a pre-heated aluminum block at 120 °C (CAUTION: CO₂ evolution!). Upon complete consumption of the aryl bromide (as determined by GC-MS analysis, generally 12-24 h), the reaction mixture was directly loaded onto a short plug of SiO₂. The product was eluted with 80:20 hexanes/EtOAc and concentrated. The residue was dissolved in Et₂O (75 mL). The resulting solution was washed (3 x 30 mL water, then 30 mL brine), dried (MgSO₄) and

concentrated. The crude product was then adsorbed onto SiO₂ and purified by silica gel chromatography.

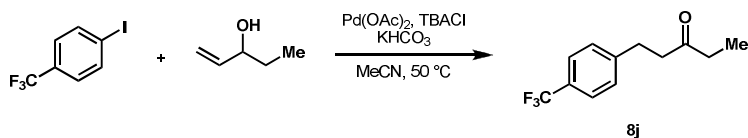
Spectral data and additional transformations for products of Heck coupling:



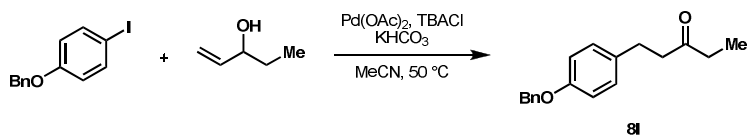
Ketone 8h¹: Following the general procedure, 1-chloro-4-iodobenzene (716 mg, 3.00 mmol) was coupled with 1-penten-3-ol in MeCN at 50 °C. After removal of the solvent, the residue was dissolved in an 80:20 mixture of hexanes and EtOAc, filtered through SiO₂, and concentrated. The crude product was purified by silica gel chromatography (40 g SiO₂ column, 100:0→85:15 hexanes/EtOAc) to give 417 mg (2.12 mmol, 71%) of ketone **8h**¹ as a light golden oil. ¹H NMR (500 MHz, CDCl₃) δ 7.22 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 2.86 (t, *J* = 7.5 Hz, 2H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.39 (q, *J* = 7.3 Hz, 2H), 1.03 (t, *J* = 7.3 Hz, 3H) (lit. ¹H NMR data not reported); ¹³C NMR (125 MHz, CDCl₃) δ 210.2, 139.8, 131.9, 129.8, 128.6, 43.7, 36.2, 29.2, 7.8 (lit. ¹³C NMR data not reported); HRMS (EI⁺) calcd for [C₁₁H₁₃ClO]⁺: *m/z* 196.0655, found 196.0661.



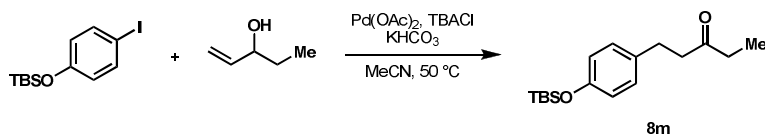
Ketone 8i: Following the general procedure, 1-bromo-4-iodobenzene (848 mg, 3.00 mmol) was coupled with 1-penten-3-ol in MeCN at 50 °C. After removal of the solvent, the residue dissolved in an 80:20 mixture of hexanes and EtOAc, filtered through SiO₂, and concentrated. The crude product was purified by silica gel chromatography (40 g SiO₂ column, 100:0→85:15 hexanes/EtOAc) to give 484 mg (2.01 mmol, 67%) of ketone **8i** as a pale yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 2.84 (t, *J* = 7.5 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 2.39 (q, *J* = 7.3 Hz, 2H), 1.03 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 210.2, 140.3, 131.6, 130.2, 119.9, 43.6, 36.2, 29.2, 7.8; HRMS (ESI⁺) calcd for [C₁₁H₁₃BrNaO]⁺ (M+Na)⁺: *m/z* 263.0047, found 263.0048.



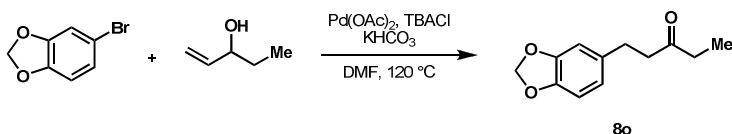
Ketone 8j: Following the general procedure, 4-iodobenzotrifluoride (817 mg, 3.00 mmol) was coupled with 1-penten-3-ol in MeCN at 50 °C. After removal of the solvent, the residue was dissolved in an 80:20 mixture of hexanes and EtOAc, filtered through SiO₂ and concentrated. The crude product was purified by silica gel chromatography (40 g SiO₂ column, 100:0→85:15 hexanes/EtOAc) to give 449 mg (1.95 mmol, 65%) of ketone **8j** as a light yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.95 (t, *J* = 7.5 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.04 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 210.0, 145.5, 128.8, 128.6 (q, *J* = 32 Hz), 125.5 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 272 Hz), 43.4, 36.2, 29.6, 7.8; ¹⁹F NMR (470 MHz, CDCl₃) δ -62.80; HRMS (EI⁺) calcd for [C₁₂H₁₃F₃O]⁺: *m/z* 230.0918, found 230.0926.



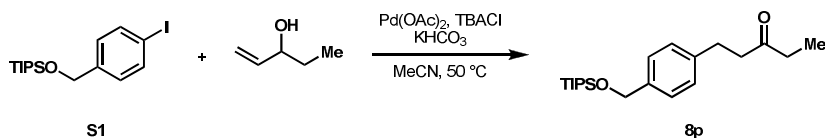
Ketone 8i: Following the general procedure, 4-iodobenzyl alcohol (925 mg, 2.98 mmol) was coupled with 1-penten-3-ol in MeCN at 50 °C. After removal of the solvent, the residue was dissolved in an 80:20 mixture of hexanes and EtOAc, filtered through SiO₂ and concentrated. The crude product was purified by silica gel chromatography (40 g SiO₂ column, 100:0→85:15 hexanes/EtOAc) to give 590 mg (2.20 mmol, 74%) of ketone **8i** as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 7.45 (d, *J* = 6.9 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 5.05 (s, 2H), 2.87 (t, *J* = 7.6 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.06 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 210.8, 157.2, 137.2, 133.6, 129.3, 128.6, 128.0, 127.5, 114.9, 70.1, 44.2, 36.2, 29.1, 7.8; HRMS (ESI⁺) calcd for [C₁₈H₂₀NaO₂]⁺ (M+Na)⁺: *m/z* 291.1361, found 291.1361.



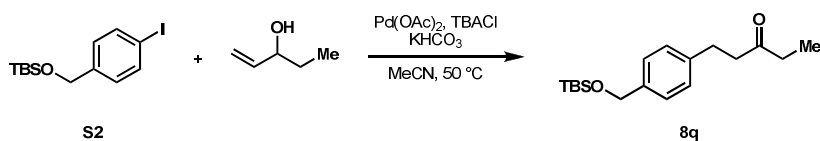
Ketone 8m: Following the general procedure, 1-iodo-4-[(*tert*-butyldimethylsilyl)oxy]benzene³ (1.34 g, 4.01 mmol) was coupled with 1-penten-3-ol in MeCN at 50 °C. After removal of the solvent, the residue was dissolved in an 80:20 mixture of hexanes and EtOAc, filtered through SiO₂ and concentrated. The crude product was purified by silica gel chromatography (40 g SiO₂ column, 100:0→85:15 hexanes/EtOAc) to give 365 mg (1.25 mmol, 31%) of ketone **8m** as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.02 (d, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.38 (q, *J* = 7.3 Hz, 2H), 1.03 (t, *J* = 7.3 Hz, 3H), 0.97 (s, 9H), 0.17 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 211.0, 154.0, 133.9, 129.3, 120.1, 44.3, 36.3, 29.3, 25.8, 18.3, 7.9, -4.3; HRMS (ESI⁺) calcd for [C₁₇H₁₈NaO₂Si]⁺ (M+Na)⁺: *m/z* 315.1756, found 315.1758.



Ketone 8o: Following the general procedure, 4-bromo-1,2-(methylenedioxy)benzene (613 mg, 3.05 mmol) was coupled with 1-penten-3-ol in DMF at 120 °C. Following workup, the crude product was purified by silica gel chromatography (40 g SiO₂ column, 100:0→85:15 hexanes/EtOAc) to give 456 mg (2.21 mmol, 73%) of ketone **8o** as a light yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 6.70 (d, *J* = 7.9 Hz, 1H), 6.65 (d, *J* = 1.5 Hz, 1H), 6.61 (dd, *J* = 8.0, 1.5 Hz, 1H), 5.89 (s, 2H), 2.80 (t, *J* = 7.5 Hz, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 2.38 (q, *J* = 7.3 Hz, 2H), 1.03 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 210.6, 147.7, 145.8, 135.0, 121.1, 108.8, 108.3, 100.9, 44.2, 36.2, 29.7, 7.8; HRMS (EI⁺) calcd for [C₁₂H₁₄O₃]⁺: *m/z* 206.0943, found 206.0941.

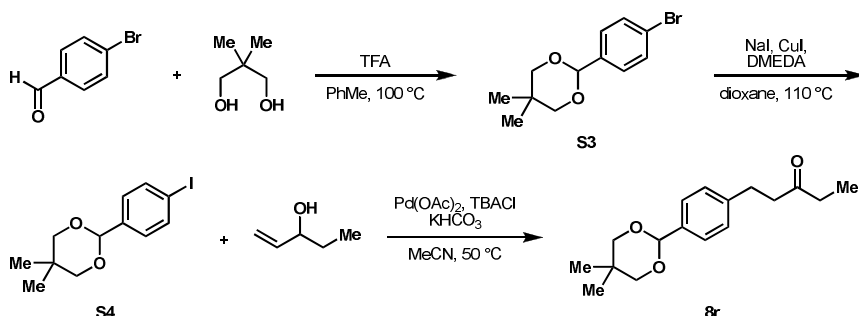


Ketone 8p: Following the general procedure, TIPS ether **S1**⁴ (819 mg, 2.10 mmol) was coupled with 1-penten-3-ol in MeCN at 50 °C. After removal of the solvent, the residue was dissolved in an 80:20 mixture of hexanes and EtOAc, filtered through SiO₂ and concentrated. The crude product was purified by silica gel chromatography (40 g SiO₂ column, 100:0→90:10 hexanes/EtOAc) to give 525 mg (1.51 mmol, 72%) of ketone **8p** as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 4.81 (s, 2H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.40 (q, *J* = 7.3 Hz, 2H), 1.24–1.14 (m, 3H), 1.10 (d, *J* = 6.7 Hz, 18H), 1.05 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 210.8, 139.7, 139.6, 128.2, 126.0, 65.0, 44.1, 36.2, 29.7, 18.2, 12.2, 7.9; HRMS (ESI⁺) calcd for [C₂₁H₃₆NaO₂Si]⁺ (M+Na)⁺: *m/z* 371.2382, found 371.2383.



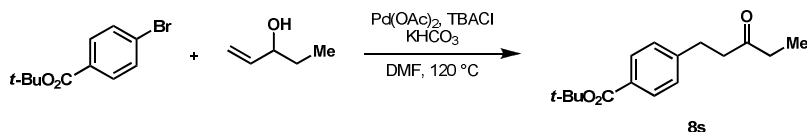
Ketone 8q: TBS ether **S2**⁵ was prepared from 4-iodobenzyl alcohol (706 mg, 3.02 mmol) using TBSCl (1.1 equiv) and imidazole (1.2 equiv) in CH₂Cl₂ (7.5 mL) at room temperature. After stirring overnight, the reaction mixture was diluted with EtOAc, filtered through SiO₂ and concentrated. The resulting residue was dissolved in a 90:10 mixture of hexanes and EtOAc, filtered through a short plug of SiO₂ and concentrated to provide crude TBS ether **S2**,⁵ which was used without further purification. Following the general procedure, crude **S2** was coupled with 1-penten-3-ol in MeCN at 50 °C. After removal of the solvent, the residue was dissolved in an 80:20 mixture of hexanes and EtOAc, filtered through SiO₂ and concentrated. The crude product was purified by silica gel chromatography (40 g SiO₂ column, 100:0→85:15 hexanes/EtOAc) to give 663 mg (2.16 mmol, 72% over 2 steps) of ketone **8q** as a light golden oil. ¹H NMR (500 MHz, CDCl₃) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 4.71 (s, 2H), 2.89 (t, *J* = 7.7 Hz, 2H), 2.72 (t, *J* = 7.7 Hz, 2H), 2.40 (q, *J* = 7.3 Hz, 2H), 1.04 (t, *J* = 7.3 Hz, 3H), 0.95 (s, 9H), 0.10 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 210.7, 139.9, 139.3, 128.2, 126.4,

64.9, 44.1, 36.2, 29.7, 26.2, 18.5, 7.9, -5.1; **HRMS** (ESI+) calcd for $[\text{C}_{18}\text{H}_{31}\text{O}_2\text{Si}]^+$ (M+H)⁺: m/z 307.2093, found 307.2086.

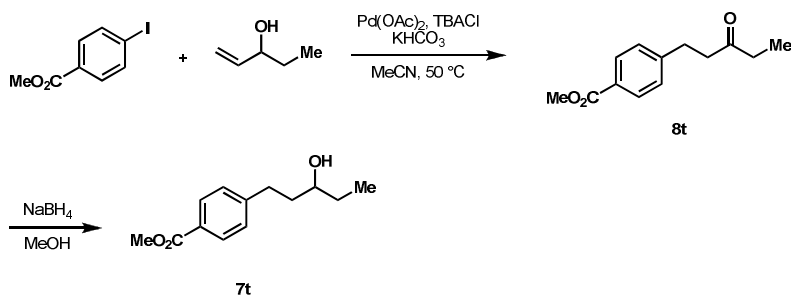


Ketone 8r: Following a literature procedure⁶ with slight modification, a solution of 4-bromobenzaldehyde (923 mg, 4.99 mmol) in PhMe (15 mL) was treated sequentially with neopentyl glycol (1.30 g, 12.5 mmol) and TFA (0.12 mL, 1.6 mmol). The resulting mixture was heated at 100 °C for 17 h. After cooling to room temperature, the reaction mixture was diluted with Et₂O (75 mL) and washed sequentially with sat. NaHCO₃ (30 mL), water (3 x 30 mL) and brine (30 mL). The organic layer was dried (MgSO₄), concentrated, and the resulting material was adsorbed onto SiO₂. Purification by silica gel chromatography (40 g SiO₂ column, 100:0→90:10 hexanes/EtOAc) gave 1.19 g (4.39 mmol, 88%) of bromide **S3** as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 5.35 (s, 1H), 3.76 (d, *J* = 11.2 Hz, 2H), 3.64 (d, *J* = 10.6 Hz, 2H), 1.27 (s, 3H), 0.80 (s, 3H). Following the general procedure for an aromatic Finkelstein reaction,⁷ a vial charged with bromide **S3** (1.19 g, 4.39 mmol), CuI (40.0 mg, 0.210 mmol), NaI (1.32 g, 8.81 mmol) and *N,N'*-dimethylethylenediamine (50 μL, 0.470 mmol) in dioxane (4.5 mL) was heated at 110 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc, filtered through SiO₂ and concentrated. The resulting residue was dissolved in an 80:20 mixture of hexanes and EtOAc, filtered through a short plug of SiO₂ and concentrated to give 1.37 g (4.31 mmol, 98%) of iodide **S4**⁸ as a light yellow solid, which was used without further purification. ¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 5.33 (s, 1H), 3.76 (d, *J* = 11.2 Hz, 2H), 3.63 (d, *J* = 10.7 Hz, 2H), 1.27 (s, 3H), 0.80 (s, 3H) (¹H NMR data were consistent with previously reported values⁸). Following the general procedure, iodide **S4** (1.37 g, 4.31 mmol) was coupled with 1-penten-3-ol in MeCN at 50

°C. After removal of the solvent, the residue was dissolved in an 80:20 mixture of hexanes and EtOAc, filtered through SiO₂ and concentrated. The crude product was purified by silica gel chromatography (40 g SiO₂ column, 100:0→75:25 hexanes/EtOAc) to give 899 mg (3.25 mmol, 76%) of ketone **8r** as colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.41 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 5.35 (s, 1H), 3.75 (d, *J* = 11.2 Hz, 2H), 3.63 (d, *J* = 10.8 Hz, 2H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.37 (q, *J* = 7.3 Hz, 2H), 1.28 (s, 3H), 1.02 (t, *J* = 7.3 Hz, 3H), 0.78 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 210.5, 142.0, 136.5, 128.3, 126.3, 101.7, 77.7, 43.9, 36.2, 30.3, 29.7, 23.1, 21.9, 7.8; HRMS (ESI+) calcd for [C₁₇H₂₅O₃]⁺ (M+H)⁺: *m/z* 277.1804, found 277.1802.

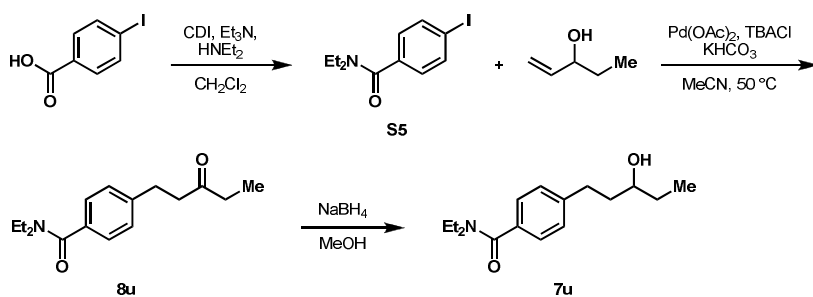


Ketone 8s: Following the general procedure, *tert*-butyl 4-bromobenzoate⁹ (839 mg, 3.26 mmol) was coupled with 1-penten-3-ol in DMF at 120 °C. Following workup, the crude product was purified by silica gel chromatography (40 g SiO₂ column, 100:0→85:15 hexanes/EtOAc) to give 661 mg (2.52 mmol, 77%) of ketone **8s** as a yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.71 (t, *J* = 7.5 Hz, 2H), 2.38 (q, *J* = 7.3 Hz, 2H), 1.56 (s, 9H), 1.02 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 210.1, 165.8, 146.2, 130.1, 129.7, 128.3, 80.8, 43.4, 36.2, 29.8, 28.3, 7.8; HRMS (ESI+) calcd for [C₁₆H₂₂NaO₃]⁺: *m/z* 285.1467, found 285.1462.



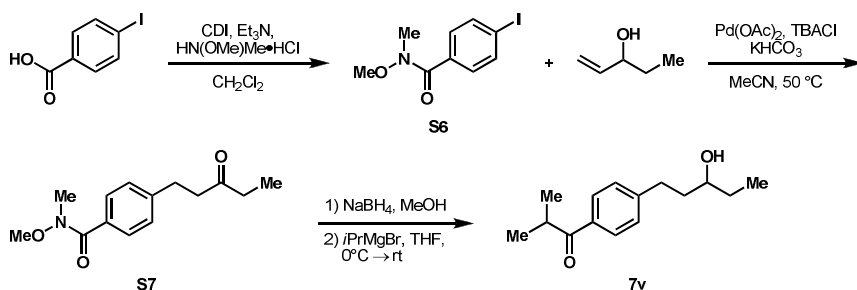
Alcohol 7t: Following the general procedure, methyl 4-iodobenzoate (1.05 g, 4.01 mmol) was coupled with 1-penten-3-ol in MeCN at 50 °C. After removal of the solvent, the

residue was dissolved in a 65:35 mixture of hexanes and EtOAc, filtered through SiO₂ and concentrated. The crude product was purified by silica gel chromatography (40 g SiO₂ column, 100:0→75:25 hexanes/EtOAc) to give 631 mg (2.86 mmol, 72%) of ketone **8t**¹⁰ as a light golden oil. ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H), 2.95 (t, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.04 (t, *J* = 7.3 Hz, 3H) (¹H NMR data were consistent with previously reported values¹⁰). A solution of ketone **8t** (631 mg, 2.86 mmol) in MeOH (8 mL) at 0 °C was treated with NaBH₄ (143 mg, 3.78 mmol). The resulting mixture was stirred for 2.5 h, during which time the cooling bath was allowed to gradually expire. The reaction mixture was then carefully poured onto half-sat. aq. NH₄Cl (30 mL) and extracted with EtOAc (30 mL, then 2 x 15 mL). The combined organic layers were washed (30 mL brine), dried (MgSO₄) and concentrated to provide 617 mg (2.78 mmol, 97%) of alcohol **7t** as a pale golden oil, which was used without purification. ¹H NMR (500 MHz, CDCl₃) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 3H), 3.59-3.50 (m, 1H), 2.92-2.81 (m, 1H), 2.73 (ddd, *J* = 13.8, 9.8, 6.8 Hz, 1H), 1.85 (s, 1H), 1.84-1.68 (m, 2H), 1.60-1.42 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 167.2, 148.0, 129.8, 128.5, 127.8, 72.5, 52.0, 38.2, 32.2, 30.4, 9.9; HRMS (ESI+) calcd for [C₁₃H₁₈NaO₃]⁺ (M+Na)⁺: *m/z* 245.1154, found 245.1153.



Alcohol 7u: To a solution of 4-iodobenzoic acid (1.25 g, 5.04 mmol) in CH₂Cl₂ (10 mL) was carefully added 1,1'-carbonyldiimidazole (891 mg, 5.50 mmol). The resulting mixture was stirred at room temperature for 1 h and then treated with HNEt₂ (1.2 mL, 12 mmol). After being stirred at room temperature for 12 h, the reaction mixture was diluted with EtOAc, filtered through SiO₂ and concentrated. The crude product was adsorbed onto SiO₂ and purified by silica gel chromatography (40 g SiO₂ column, 90:10→50:50 hexanes/EtOAc) to give 1.35 g (4.45 mmol, 88%) of iodide **S5**¹¹ as a light yellow oil. ¹H

NMR (500 MHz, CDCl₃) δ 7.74 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 3.52 (br s, 2H), 3.23 (br s, 2H), 1.23 (br s, 3H), 1.10 (br s, 3H). Following the general procedure, iodide **S5** (1.35 g, 4.45 mmol) was coupled with 1-penten-3-ol in MeCN at 50 °C. Following evaporation of the solvent, the residue was dissolved in an 50:50 mixture of hexanes and EtOAc, filtered through SiO₂ and concentrated. The crude product was purified by silica gel chromatography (40 g SiO₂ column, 85:15→35:65 hexanes/EtOAc) to give 772 mg (2.95 mmol, 66%) of ketone **8u** as a colorless oil. **¹H NMR** (500 MHz, CDCl₃) δ 7.28 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 3.53 (br s, 2H), 3.25 (br s, 2H), 2.91 (t, J = 7.6 Hz, 2H), 2.73 (t, J = 7.6 Hz, 2H), 2.41 (q, J = 7.3 Hz, 2H), 1.23 (br s, 3H), 1.11 (br s, 3H), 1.04 (t, J = 7.3 Hz, 3H). A solution of ketone **8u** (772 mg, 2.95 mmol) in MeOH (7 mL) at 0 °C was treated with NaBH₄ (131 mg, 3.46 mmol). The resulting mixture was stirred for 1.5 h, during which time the cooling bath was allowed to gradually expire. The reaction mixture was then carefully poured onto half-sat. aq. NH₄Cl (30 mL) and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed (30 mL brine), dried (MgSO₄) and concentrated to provide 759 mg (2.88 mmol, 98%) of alcohol **7u** as a colorless oil, which was used without purification. **¹H NMR** (500 MHz, CDCl₃) δ 7.29 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 3.65-3.40 (m, 3H), 3.27 (br s, 2H), 2.85-2.76 (m, 1H), 2.67 (ddd, J = 13.8, 9.7, 6.8 Hz, 1H), 1.84 (br s, 1H), 1.81-1.65 (m, 2H), 1.58-1.41 (m, 2H), 1.23 (br s, 3H), 1.11 (br s, 3H), 0.93 (t, J = 7.4 Hz, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 171.6, 143.6, 134.7, 128.5, 126.5, 72.4, 43.4, 39.3, 38.4, 31.9, 30.4, 14.3, 13.0, 10.0; **HRMS** (ESI+) calcd for [C₁₆H₂₆NO₂]⁺ (M+H)⁺: m/z 264.1964, found 264.1958.

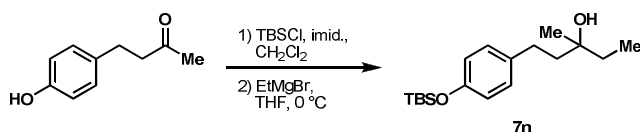


Alcohol 7v: To a solution of 4-iodobenzoic acid (997 mg, 4.02 mmol) in CH₂Cl₂ (8 mL) was carefully added 1,1'-carbonyldiimidazole (717 mg, 4.42 mmol) (CAUTION: CO₂ evolution!). The resulting mixture was stirred at room temperature for 1 h and then

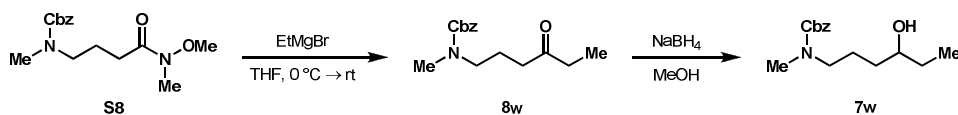
treated with Et₃N (0.61 mL, 4.4 mmol) and HN(OMe)Me•HCl (432 mg, 4.43 mmol). After being stirred at room temperature for 3 h, the reaction mixture was diluted with EtOAc, filtered through SiO₂ and concentrated. The crude product was adsorbed onto SiO₂ and purified by silica gel chromatography (40 g SiO₂ column, 100:0→50:50 hexanes/EtOAc) to give 1.17 g of iodide **S6** as a pale golden oil. ¹H NMR (500 MHz, CDCl₃) δ 7.75 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 3.53 (s, 3H), 3.35 (s, 3H). Following the general procedure, iodide **S6** (1.17 g) was coupled with 1-penten-3-ol in MeCN at 50 °C. After removal of the solvent, the residue was dissolved in a 50:50 mixture of hexanes and EtOAc, filtered through SiO₂ and concentrated. The crude product was purified by silica gel chromatography (40 g SiO₂ column, 85:15→35:65 hexanes/EtOAc) to give 696 mg (2.79 mmol, 69% over 2 steps) of ketone **S7** as colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 3.55 (s, 3H), 3.35 (s, 3H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.04 (t, *J* = 7.3 Hz, 3H). A solution of ketone **S7** (696 mg, 2.79 mmol) in MeOH (6 mL) at 0 °C was treated with NaBH₄ (125 mg, 3.30 mmol). After being stirred at 0 °C for 1 h, the reaction mixture was carefully poured onto half-sat. aq. NH₄Cl (30 mL) and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed (30 mL brine), dried (MgSO₄) and concentrated to provide the crude alcohol, which was used immediately without purification. The crude alcohol was dissolved in THF (6 mL) and cooled to 0 °C. A solution of *i*PrMgCl (2.0 M in Et₂O, 3.3 mL, 6.6 mmol) was added slowly over 5 min at 0 °C. Upon completion of the addition, the resulting mixture was allowed to warm to room temperature, and stirring was continued for 2 h. The reaction was quenched by careful addition of 1 N HCl (30 mL), and the resulting mixture was extracted with EtOAc (3 x 30 mL). The combined organic layers were washed (30 mL sat. NaHCO₃, then 30 mL brine), dried (MgSO₄) and concentrated. The crude product was adsorbed onto SiO₂ and purified by silica gel chromatography (40 g SiO₂ column, 85:15→50:50 hexanes/EtOAc) to give 324 mg (1.38 mmol, 50% over 2 steps) of alcohol **7v** as a pale yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 3.59-3.48 (m, 2H), 2.90-2.81 (m, 1H), 2.72 (ddd, *J* = 13.8, 9.8, 6.7 Hz, 1H), 1.84-1.67 (m, 3H), 1.59-1.42 (m, 2H), 1.20 (d, *J* = 6.8 Hz, 6H), 0.94 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 204.3, 148.0, 134.1, 128.8, 128.7, 72.6, 38.3, 35.3,

32.2, 30.5, 19.3, 10.0 (Note: A single peak at δ 19.3 is observed for the diastereotopic isopropyl methyl groups); **HRMS** (ESI+) calcd for $[\text{C}_{15}\text{H}_{22}\text{NaO}_2]^+$ ($\text{M}+\text{Na}$) $^+$: m/z 257.1517, found 257.1520.

Synthesis of Other Substrates



Alcohol 7n: To a solution of 4-(4-hydroxyphenyl)-2-butanone (497 mg, 3.03 mmol) and imidazole (251 mg, 3.69 mmol) in CH_2Cl_2 (7.5 mL) was added TBSCl (505 mg, 3.35 mmol). After being stirred at room temperature for 44 h, the reaction mixture was diluted with EtOAc, filtered through SiO_2 and concentrated to provide the crude TBS ether,¹² which was used directly without further purification. To a solution of the above prepared crude TBS ether in THF (6 mL) at 0 °C was added EtMgBr (1.0 M in THF, 3.6 mL, 3.6 mmol) over 3 min. The resulting mixture was stirred at 0 °C for 2 h and then carefully quenched with half-saturated aq. NH_4Cl (30 mL) and extracted with EtOAc (30 mL, then 2 x 15 mL). The combined organic layers were washed (30 mL brine), dried (MgSO_4) and concentrated. The resulting residue was adsorbed onto SiO_2 and purified by silica gel chromatography (40 g SiO_2 column, 100:0→80:20 hexanes/EtOAc) to give 465 mg (1.51 mmol, 50% over 2 steps) of alcohol **7n** as a colorless oil. **^1H NMR** (500 MHz, CDCl_3) δ 7.05 (d, $J = 8.4$ Hz, 2H), 6.76 (d, $J = 8.4$ Hz, 2H), 2.65–2.57 (m, 2H), 1.78–1.70 (m, 2H), 1.60–1.51 (m, 2H), 1.31 (br s, 1H), 1.22 (s, 3H), 0.99 (s, 9H), 0.94 (t, $J = 7.5$ Hz, 3H), 0.19 (s, 6H); **^{13}C NMR** (125 MHz, CDCl_3) δ 153.7, 135.3, 129.2, 120.0, 72.9, 43.5, 34.5, 29.6, 26.5, 25.8, 18.3, 8.4, -4.3; **HRMS** (ESI+) calcd for $[\text{C}_{18}\text{H}_{32}\text{NaO}_2\text{Si}]^+$ ($\text{M}+\text{Na}$) $^+$: m/z 331.2069, found 331.2070.



Alcohol 7w: To a solution of Weinreb amide **S8**¹³ (1.02 g, 3.47 mmol) in THF (8 mL) at 0 °C was added EtMgBr (1.0 M in THF, 4.2 mL, 4.2 mmol) over 5 min. The resulting

mixture was stirred at 0 °C for 15 min and then allowed to warm to room temperature. After being stirred for an additional 3.5 h, the reaction was carefully quenched with half-saturated aq. NH₄Cl (30 mL) and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed (30 mL brine), dried (MgSO₄) and concentrated. The resulting residue was adsorbed onto SiO₂ and purified by silica gel chromatography (40 g SiO₂ column, 100:0→60:40 hexanes/EtOAc) to give 826 mg (3.14 mmol, 91%) of ketone **8w** as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.40-7.28 (m, 5H), 5.12 (s, 2H), 3.29 (br s, 2H), 2.90 (s, 3H), 2.47-2.25 (m, 4H), 1.88-1.74 (m, 2H), 1.09-0.92 (m, 3H). A solution of ketone **8w** (826 mg, 3.14 mmol) in MeOH (10 mL) at 0 °C was treated with NaBH₄ (145 mg, 3.83 mmol) After being stirred at 0 °C for 2 h, the reaction mixture was carefully poured onto half-sat. aq. NH₄Cl (30 mL) and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed (30 mL brine), dried (MgSO₄) and concentrated. The resulting residue was adsorbed onto SiO₂ and purified by silica gel chromatography (40 g SiO₂ column, 85:15→45:55 hexanes/EtOAc) to give 777 mg (2.93 mmol, 93%) of the alcohol **7w** as a colorless oil. ¹H NMR (500 MHz, CDCl₃, 50 °C) δ 7.38-7.24 (m, 5H), 5.12 (s, 2H), 3.51 (br s, 1H), 3.38-3.23 (m, 2H), 2.91 (s, 3H), 1.90 (br s, 1H), 1.75-1.64 (m, 1H), 1.64-1.52 (m, 1H), 1.52-1.28 (m, 4H), 0.91 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃, 20 °C) δ 156.5, 137.0, 128.5, 128.0, 127.8, 72.8, 67.0, 49.0*, 48.7*, 34.6*, 34.0*, 33.7*, 33.5*, 30.4, 24.2*, 23.7*, 10.0 (Note: At 20 °C, a mixture of rotamers are observed; signals that correspond to the individual rotamers, and which coalesce at 50 °C, are indicated with a *); ¹³C NMR (125 MHz, CDCl₃, 50 °C) δ 156.5, 137.2, 128.5, 128.0, 127.9, 73.0, 67.1, 49.0, 34.3*, 33.8, 30.4, 24.1, 9.9 (Note: At 50 °C, the N-Me group appears as a broad, low-intensity signal between δ 35-34; the mid-point of this signal is estimated and is indicated with a *); HRMS (ESI+) calcd for [C₁₅H₂₃NNaO₃]⁺ (M+Na)⁺: *m/z* 288.1576, found 288.1572.

General Procedures

General procedure for Ir-catalyzed silylation of alcohols or ketones: In an N₂-filled glovebox, ca. 1.0 mmol of the alcohol or ketone substrate was weighed into a one-dram screw-capped vial. A stir bar was added, and the substrate was dissolved in THF (0.50

mL). The resulting solution was treated first with a freshly prepared stock solution of $[\text{Ir}(\text{cod})\text{OMe}]_2$ (0.5 μmol , 0.05 mol %, unless otherwise specified) in THF (0.50 mL) and then neat Et_2SiH_2 (1.20 mmol). The vial was capped with a Teflon-lined screw cap, and the resulting solution was stirred in the glovebox at room temperature (unless otherwise specified) until complete conversion to the corresponding diethyl(hydrido)silyl ether was observed, as determined by GC, GC-MS or ^1H NMR analysis (generally 5-12 h) (CAUTION: H_2 evolution in the case of alcohol substrates!).

General procedure for Ru-catalyzed silylation of alcohols: In an N_2 -filled glovebox, ca. 1.0 mmol of the alcohol substrate was weighed into a one-dram screw-capped vial. A stir bar was added, and the substrate was dissolved in a freshly prepared stock solution of $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ (2.0 μmol , 0.2 mol %) in PhH or PhMe (1.0 mL). The resulting solution was treated with neat Et_2SiH_2 (1.20 mmol), and the vial was capped with a Teflon-lined screw cap. The vial was then removed from the glovebox, placed in a pre-heated aluminum heating block at 50 $^\circ\text{C}$ and stirred until complete conversion to the corresponding diethyl(hydrido)silyl ether was observed, as determined by GC or GC-MS analysis (generally overnight) (CAUTION: H_2 evolution!).

General procedure for Ir-catalyzed intramolecular aliphatic silylation: In an N_2 -filled glovebox, the crude reaction mixture containing the diethyl(hydrido)silyl ether (ca. 1.0 mmol) and solvent was placed under high-vacuum for 1 h (the stir bar was temporarily removed during this operation to prevent bumping). The stir bar was replaced, and the concentrated diethyl(hydrido)silyl ether was then sequentially treated with freshly prepared stock solutions of norbornene (1.20 mmol) in THF (1.0 mL) and $[\text{Ir}(\text{cod})\text{OMe}]_2$ (5.0 μmol , 0.5 mol %) in THF (0.50 mL), and then with a slurry of Me_4phen (12.5 μmol , 1.25 mol %) in THF (0.50 mL). The Teflon-lined screw cap was replaced, and the resulting solution was stirred in the glovebox for 1 h (to ensure complete formation of the active Ir species). The vial was then removed from the glovebox, placed in a pre-heated aluminum block at the specified temperature and stirred for the indicated period of time.

General procedure for Tamao-Fleming oxidation of oxasilolanes: On the bench top, the crude reaction mixture containing the oxasilolane (ca. 1.0 mmol) in THF (2.0 mL) was transferred to a 20 mL screw-capped vial via pipette and sequentially treated with MeOH (2.0 mL), KHCO_3 (2.5 mmol) and H_2O_2 (30% solution in H_2O , 10 mmol). The vial was sealed with a Teflon-lined screw cap, and the resulting mixture was stirred overnight at 50 °C (unless otherwise specified) (CAUTION: CO_2 evolution!). The reaction was carefully quenched with aq. NaHSO_3 (30 mL) (CAUTION: further CO_2 evolution!), and the resulting mixture was extracted with EtOAc (30 mL, then 2 x 15 mL). The combined organic layers were washed (30 mL 1 N HCl, then 30 mL sat. NaHCO_3), dried (MgSO_4), filtered through Celite, and concentrated to provide the crude diol.

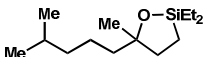
General procedure for Tamao-Fleming oxidation of oxasilolanes with added KF: On the bench top, the crude reaction mixture containing the oxasilolane (ca. 1.0 mmol) in THF (2.0 mL) was transferred to a 20 mL screw-capped vial via pipette and sequentially treated with KHCO_3 (2.5 mmol), a solution of KF (2.5 mmol) in MeOH (2.0 mL) and H_2O_2 (30% solution in H_2O , 10 mmol). The vial was sealed with a Teflon-lined screw cap, and the resulting mixture was stirred overnight at 50 °C (CAUTION: CO_2 evolution!). The reaction was carefully quenched with aq. Na_2SO_3 (20 mL), and the resulting mixture was extracted with EtOAc (3 x 30 mL, then 2 x 15 mL). The combined organic layers were dried (MgSO_4), filtered through Celite, and concentrated to provide the crude diol.

General procedure for diacylation of diol intermediates:

The crude diol was dissolved in 4:1 $\text{CH}_2\text{Cl}_2/\text{Et}_3\text{N}$ (ca. 0.3 M), and the resulting solution was treated with DMAP (0.05 equiv) and Ac_2O (3.0 equiv). After being stirred at room temperature overnight, the reaction mixture was filtered through SiO_2 (rinsing with EtOAc) and concentrated. The resulting residue was adsorbed onto SiO_2 and purified by silica gel chromatography to provide the diacetate product.

General procedure for monoacylation of diol intermediates:

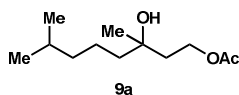
The crude diol was dissolved in 5:1 CH₂Cl₂/Et₃N (ca. 0.3 M), and the resulting solution was treated with Ac₂O (1.5 equiv). After being stirred at room temperature overnight, the reaction mixture was filtered through SiO₂ (rinsing with EtOAc) and concentrated. The resulting residue was adsorbed onto SiO₂ and purified by silica gel chromatography to provide the monoacetate product.



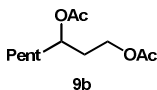
Oxasilolane 6: In an N₂-filled glovebox, tetrahydrolinalool (792 mg, 5.00 mmol) was weighed into a 20 mL screw-capped vial. A stir bar was added, followed by THF (3.0 mL). The resulting solution was treated first with a freshly prepared solution of [Ir(cod)OMe]₂ (1.3 mg, 2.0 μmol, 0.04 mol %) in THF (2.0 mL) and then neat Et₂SiH₂ (496 mg, 5.62 mmol). The vial was capped with a Teflon-lined screw cap, and the resulting solution was stirred in the glovebox at room temperature for 15 h, at which point GC-MS analysis indicated full conversion to diethyl(hydrido)silyl ether **5**. **GC/MS:** *m/z* 243.1 (0.1%, [M-H]⁺), 229.2 (6.4%, [M-Me]⁺), 215.2 (59.4%, [M-Et]⁺), 159.1 (100.0%, [M-C₆H₁₃]⁺). The volatile materials were removed by placing the reaction mixture directly under high vacuum for 4 h (the stir bar was temporarily removed during this operation to prevent bumping). The stir bar was replaced, and the concentrated diethyl(hydrido)silyl ether was then sequentially treated with freshly prepared solutions of norbornene (565 mg, 6.00 mmol) in THF (6.0 mL) and [Ir(cod)OMe]₂ (7.3 mg, 11 μmol, 0.22 mol %) in THF (2.0 mL), and then with a slurry of Me₄phen (8.3 mg, 35 μmol, 0.70 mol %) in THF (2.0 mL). The Teflon-lined screw cap was replaced, and the resulting solution was stirred in the glovebox for 3 h (to ensure complete formation of the active Ir species). The vial was then removed from the glovebox, placed in a pre-heated aluminum block at 80 °C, and the reaction was stirred for 43 h. The reaction mixture was then allowed to cool to room temperature, and the solvent was removed by rotary evaporation. The resulting residue was purified by Kugelrohr distillation (55 mTorr, 70 °C) to give 1.10 g (91%) of oxasilolane **6** as a colorless oil. **¹H NMR** (500 MHz, CDCl₃) δ 1.80-1.71 (m, 1H), 1.69-1.60 (m, 1H), 1.58-1.48 (m, 1H), 1.48-1.26 (m, 4H), 1.19-1.11 (m, 2H), 1.16 (s, 3H), 1.00-0.92 (m, 6H), 0.86 (d, *J* = 6.7 Hz, 6H), 0.82-0.73 (m, 2H),

0.71-0.52 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 81.6, 43.0, 39.8, 36.1, 28.1, 27.5, 22.8, 22.7, 22.4, 7.03, 7.01, 6.99, 6.9 (Note: Due to overlap of the signals for two of the C–Si carbons, only 13 carbon signals were observed); GC/MS: m/z 242.4 (0.2%, $[\text{M}]^+$), 227.1 (6.4%, $[\text{M}-\text{Me}]^+$), 213.2 (1.9%, $[\text{M}-\text{Et}]^+$), 157.1 (100.0%, $[\text{M}-\text{C}_6\text{H}_{13}]^+$); HRMS (EI+) calcd for $[\text{C}_{14}\text{H}_{30}\text{OSi}]^+$: m/z 242.2066, found 242.2059.

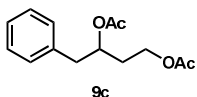
Spectral data for acetate products:



Compound 9a: Following the general procedure, tetrahydrolinalool (159 mg, 1.01 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $[\text{Ir}(\text{cod})\text{OMe}]_2$ (0.05 mol %) as catalyst at room temperature. GC/MS: m/z 243.1 (0.1%, $[\text{M}-\text{H}]^+$), 229.2 (6.4%, $[\text{M}-\text{Me}]^+$), 215.2 (59.4%, $[\text{M}-\text{Et}]^+$), 159.1 (100.0%, $[\text{M}-\text{C}_6\text{H}_{13}]^+$). The subsequent cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (1.0 mol %) at 80 °C for 12 h to provide the intermediate oxasilolane. GC/MS: m/z 242.4 (0.2%, $[\text{M}]^+$), 227.1 (6.4%, $[\text{M}-\text{Me}]^+$), 213.2 (1.9%, $[\text{M}-\text{Et}]^+$), 157.1 (100.0%, $[\text{M}-\text{C}_6\text{H}_{13}]^+$). Tamao-Fleming oxidation, followed by monoacylation and purification by silica gel chromatography (12 g SiO_2 column, 100:0→65:35 hexanes/EtOAc) gave 165 mg (76% overall yield) of **9a**¹⁴ as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 4.19 (t, $J = 7.1$ Hz, 2H), 2.01 (s, 3H), 1.88 (br s, 1H), 1.83-1.72 (m, 2H), 1.51 (septet, $J = 6.7$ Hz, 1H), 1.44-1.38 (m, 2H), 1.34-1.25 (m, 2H), 1.17 (s, 3H), 1.17-1.10 (m, 2H), 0.84 (d, $J = 6.6$ Hz, 6H) (^1H NMR data were consistent with previously reported values¹⁴); ^{13}C NMR (125 MHz, CDCl_3) δ 171.2, 71.9, 61.4, 42.8, 39.7, 39.5, 28.0, 27.1, 22.7*, 21.8, 21.1 (Note: The signals for the two diastereotopic methyl groups that are part of the isopropyl moiety appear as a single overlapping peak, which is indicated with a *). ^{13}C NMR data were consistent with previously reported values¹⁴); HRMS (ESI+) calcd for $[\text{C}_{12}\text{H}_{24}\text{NaO}_3]^+$ ($\text{M}+\text{Na}$)⁺: m/z 239.1623, found 239.1625.

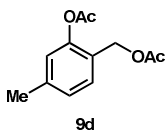


Compound 9b: Following the general procedure, 3-octanone (130 mg, 1.01 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $[\text{Ir}(\text{cod})\text{OMe}]_2$ (0.05 mol %) as catalyst at room temperature. **GC/MS:** m/z 215.2 (1.5%, $[\text{M}-\text{H}]^+$), 187.2 (100.0%, $[\text{M}-\text{Et}]^+$), 145.1 (87.9%, $[\text{M}-\text{C}_5\text{H}_{11}]^+$). The subsequent cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (1.0 mol %) at 100 °C for 18 h to provide the intermediate oxasilolane. **GC/MS:** m/z 213.3 (0.5%, $[\text{M}-\text{H}]^+$), 185.2 (52.2%, $[\text{M}-\text{Et}]^+$), 143.1 (100.0%, $[\text{M}-\text{C}_5\text{H}_{11}]^+$). Tamao-Fleming oxidation, followed by diacylation and purification by silica gel chromatography (12 g SiO_2 column, 100:0→75:25 hexanes/EtOAc) gave 155 mg (66% overall yield) of **9b**¹⁵ as a colorless oil. **^1H NMR** (500 MHz, CDCl_3) δ 4.94 (tt, $J = 7.8, 5.2$ Hz, 1H), 4.05 (t, $J = 6.6$ Hz, 2H), 2.01 (s, 6H), 1.92-1.76 (m, 2H), 1.60-1.43 (m, 2H), 1.33-1.17 (m, 6H), 0.84 (t, $J = 6.8$ Hz, 3H) (^1H NMR data were consistent with previously reported values¹⁵); **^{13}C NMR** (125 MHz, CDCl_3) δ 171.1, 170.7, 71.2, 61.0, 34.3, 33.0, 31.7, 24.9, 22.6, 21.2, 21.0, 14.0 (lit. ^{13}C NMR data not reported); **HRMS** (ESI+) calcd for $[\text{C}_{12}\text{H}_{22}\text{NaO}_4]^+$ ($\text{M}+\text{Na}$)⁺: m/z 253.1416, found 253.1415.

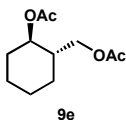


Compound 9c: Following the general procedure, 1-phenyl-2-butanol (149 mg, 0.992 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $[\text{Ir}(\text{cod})\text{OMe}]_2$ (0.05 mol %) as catalyst at room temperature. **GC/MS:** m/z 235.1 (1.3%, $[\text{M}-\text{H}]^+$), 207.0 (37.2%, $[\text{M}-\text{Et}]^+$), 145.1 (100.0%, $[\text{M}-\text{Bn}]^+$). The subsequent cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (1.0 mol %) at 100 °C for 12 h to provide the intermediate oxasilolane. **GC/MS:** m/z 205.3 (4.4%, $[\text{M}-\text{Et}]^+$), 143.2 (100.0%, $[\text{M}-\text{Bn}]^+$). Tamao-Fleming oxidation, followed by diacylation and purification by silica gel chromatography (12 g SiO_2 column, 100:0→75:25 hexanes/EtOAc) gave 132 mg (53% overall yield) of **9c** as a colorless oil. **^1H NMR** (500 MHz, CDCl_3) δ 7.31-7.26 (m, 2H), 7.25-7.16 (m, 3H), 5.21-5.14 (m, 1H), 4.13-4.03 (m, 2H), 2.92 (dd, $J = 13.7, 6.5$ Hz, 1H), 2.83 (dd, $J = 13.7, 6.5$ Hz, 1H), 2.02 (s, 3H), 2.00 (s, 3H), 1.95-1.79 (m, 2H); **^{13}C NMR** (125 MHz, CDCl_3) δ 171.0, 170.5, 137.0, 129.5, 128.5, 126.7, 71.6, 60.8, 40.7, 32.4,

21.2, 21.0; **HRMS** (ESI+) calcd for $[\text{C}_{14}\text{H}_{22}\text{NaO}_4]^+$ ($\text{M}+\text{Na}$) $^+$: m/z 273.1103, found 273.1105.

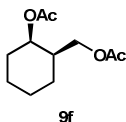


Compound 9d: Following the general procedure, 2,5-dimethylphenol (121 mg, 0.991 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $[\text{Ir}(\text{cod})\text{OMe}]_2$ (0.05 mol %) as catalyst at room temperature. **GC/MS**: m/z 208.1 (100.0%, $[\text{M}]^+$), 193.0 (4.1%, $[\text{M}-\text{Me}]^+$), 179.1 (66.4%, $[\text{M}-\text{Et}]^+$). The subsequent cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (1.0 mol %) at 80 °C for 13 h to provide the intermediate oxasilolane. **GC/MS**: m/z 206.1 (78.8%, $[\text{M}]^+$), 177.1 (100.0%, $[\text{M}-\text{Et}]^+$). Tamao-Fleming oxidation (at 40 °C), followed by diacylation and purification by silica gel chromatography (12 g SiO_2 column, 100:0→80:20 hexanes/EtOAc) gave 151 mg (69% overall yield) of **9d** as a colorless oil. **^1H NMR** (500 MHz, CDCl_3) δ 7.31 (d, $J = 7.8$ Hz, 1H), 7.05 (d, $J = 7.8$ Hz, 1H), 6.91 (s, 1H), 5.04 (s, 2H), 2.35 (s, 3H), 2.31 (s, 3H), 2.05 (s, 3H); **^{13}C NMR** (125 MHz, CDCl_3) δ 170.7, 169.5, 149.1, 140.2, 130.5, 127.0, 125.0, 1233, 61.4, 21.2, 20.94, 20.92; **HRMS** (ESI+) calcd for $[\text{C}_{12}\text{H}_{14}\text{NaO}_4]^+$ ($\text{M}+\text{Na}$) $^+$: m/z 245.0790, found 245.0790.

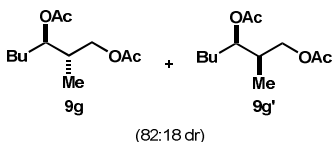


Compound 9e: Following the general procedure, *trans*-2-methylcyclohexanol (117 mg, 1.03 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $[\text{Ir}(\text{cod})\text{OMe}]_2$ (0.05 mol %) as catalyst at room temperature. **GC/MS**: m/z 200.0 (21.6%, $[\text{M}]^+$), 171.2 (100.0%, $[\text{M}-\text{Et}]^+$). The subsequent cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (1.0 mol %) at 100 °C for 15 h to provide the intermediate oxasilolane. **GC/MS**: m/z 198.1 (12.0%, $[\text{M}]^+$), 169.1 (100.0%, $[\text{M}-\text{Et}]^+$). Tamao-Fleming oxidation (with added KF), followed by diacylation and purification by silica gel chromatography (12 g SiO_2 column, 100:0→75:25 hexanes/EtOAc) gave 148 mg (68% overall yield) of **9e** as a pale yellow oil. **^1H NMR** (500 MHz, CDCl_3) δ 4.62 (td, $J = 10.3$,

4.5 Hz, 1H), 4.05-3.96 (m, 2H), 2.07-1.98 (m, 1H), 2.03 (s, 3H), 2.02 (s, 3H), 1.88-1.64 (m, 4H), 1.37-1.17 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.2, 170.6, 73.3, 65.4, 41.7, 31.8, 28.3, 24.9, 24.4, 21.3, 21.0; HRMS (ESI+) calcd for $[\text{C}_{11}\text{H}_{18}\text{NaO}_4]^+$ ($\text{M}+\text{Na}$) $^+$: m/z 237.1103, found 237.1104.

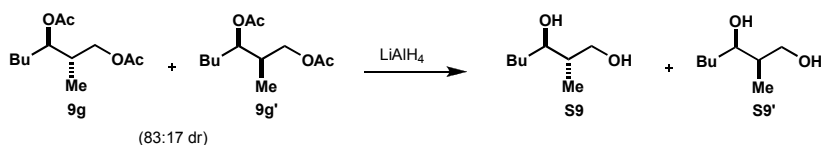


Compound 9f: Following the general procedure, *cis*-2-methylcyclohexanol (116 mg, 1.02 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $[\text{Ir}(\text{cod})\text{OMe}]_2$ (0.05 mol %) as catalyst at room temperature. GC/MS: m/z 200.1 (29.0%, $[\text{M}]^+$), 171.1 (100.0%, $[\text{M}-\text{Et}]^+$). The subsequent cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (1.0 mol %) at 100 °C for 12 h to provide the intermediate oxasilolane. GC/MS: m/z 197.8 (20.0%, $[\text{M}]^+$), 169.2 (100.0%, $[\text{M}-\text{Et}]^+$). Tamao-Fleming oxidation (with added KF), followed by diacylation and purification by silica gel chromatography (12 g SiO_2 column, 100:0→70:30 hexanes/EtOAc) gave 153 mg (70% overall yield) of **9f** as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 5.06-5.02 (m, 1H), 3.93 (dd, $J = 10.9, 8.4$ Hz, 1H), 3.84 (dd, $J = 10.9, 6.5$ Hz, 1H), 2.01 (s, 3H), 1.99 (s, 3H), 1.92-1.82 (m, 2H), 1.73-1.66 (m, 1H), 1.52-1.31 (m, 5H), 1.31-1.22 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.1, 170.5, 69.3, 65.1, 39.3, 29.5, 24.6, 23.9, 21.2, 20.9, 20.6; HRMS (ESI+) calcd for $[\text{C}_{11}\text{H}_{18}\text{NaO}_4]^+$ ($\text{M}+\text{Na}$) $^+$: m/z 237.1103, found 237.1104.

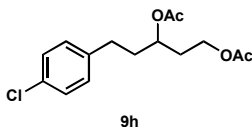


Compounds 9g and 9g': Following the general procedure, 2-methyl-3-heptanone (129 mg, 1.01 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $[\text{Ir}(\text{cod})\text{OMe}]_2$ (0.25 mol %) as catalyst at 50 °C. GC/MS: m/z 215.4 (0.9%, $[\text{M}-\text{H}]^+$), 187.3 (5.5%, $[\text{M}-\text{Et}]^+$), 173.1 (100.0%, $[\text{M}-i\text{Pr}]^+$), 159.2 (24.1%, $[\text{M}-\text{Bu}]^+$). The subsequent cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (1.0 mol %) at 100 °C for 17 h to provide the intermediate oxasilolane (80:20 dr, as determined by GC analysis). GC/MS (major, 1st eluting): m/z 214.1 (0.2%, $[\text{M}]^+$), 185.1 (37.8%, $[\text{M}-\text{Et}]^+$),

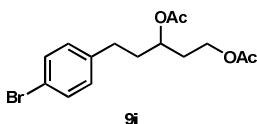
157.2 (100.0%, [M-Bu]⁺); (*minor*, 2nd eluting): *m/z* 214.1 (2.2%, [M]⁺), 185.1 (35.9%, [M-Et]⁺), 157.2 (100.0%, [M-Bu]⁺). Tamao-Fleming oxidation, followed by diacylation and purification by silica gel chromatography (12 g SiO₂ column, 100:0→75:25 hexanes/EtOAc) gave 140 mg (60% overall yield) of an 82:18 mixture (as determined by ¹H NMR analysis) of **9g** and **9g'** as a colorless oil. (Note: This purified material contained ca. 2%, as determined by GC analysis, of an unidentified by-product, which is co-polar with **9g** and **9g'** on silica gel.) ¹H NMR (500 MHz, CDCl₃) δ 4.96-4.90 (m, 1H, *minor*), 4.85 (dd, *J* = 12.6, 6.0 Hz, 1H, *major*), 3.99 (dd, *J* = 11.0, 5.3 Hz, 1H, *major*), 3.96-3.89 (m, 1H, *overlapping*), 3.84 (dd, *J* = 11.0, 6.5 Hz, 1H, *minor*), 2.08-1.95 (m, 7H, *overlapping*), 1.60-1.41 (m, 2H, *overlapping*), 1.34-1.14 (m, 4H, *overlapping*), 0.96-0.88 (m, 3H, *overlapping*), 0.85 (t, *J* = 7.0 Hz, 3H, *overlapping*); ¹³C NMR (125 MHz, CDCl₃) δ 171.2 (*major*), 171.1 (*minor*), 170.8 (*minor*), 170.7 (*major*), 75.0 (*major*), 73.8 (*minor*), 66.1 (*minor*), 65.8 (*major*), 36.0 (*major*), 35.7 (*minor*), 31.1 (*minor*), 31.0 (*major*), 27.8 (*minor*), 27.5 (*major*), 22.63 (*major*), 22.60 (*minor*), 21.1 (*overlapping*), 21.0 (*overlapping*), 14.0 (*major* or *overlapping*), 13.7 (*major* or *overlapping*), 11.4 (*minor*); HRMS (ESI+) calcd for [C₁₂H₂₂NaO₄]⁺ (M+Na)⁺: *m/z* 253.1416, found 253.1420.



Determination of relative configurations of **9g and **9g'**:** The relative configurations of **9g** and **9g'** were determined by treatment of an 83:17 mixture of **9g** and **9g'** (prepared in a experiment separate from that described above, but under otherwise identical conditions) with LiAlH₄ to give a mixture of diol products. The major diol product gave ¹H NMR data consistent with that previously reported for **S9**,¹⁶ while the minor diol product gave ¹H and ¹³C NMR data consistent with that previously reported for **S9'**.¹⁷

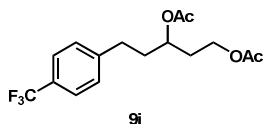


Compound 9h: Following the general procedure, ketone **8h** (202 mg, 1.03 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $[\text{Ir}(\text{cod})\text{OMe}]_2$ (0.05 mol %) as catalyst at room temperature. **GC/MS:** m/z 284.0 (2.7%, $[\text{M}]^+$), 255.1 (34.1%, $[\text{M-Et}]^+$), 125.1 (100.0%, $[\text{C}_7\text{H}_6\text{Cl}]^+$). The subsequent cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (1.0 mol %) at 100 °C for 14 h to provide the intermediate oxasilolane. **GC/MS:** m/z 282.0 (4.8%, $[\text{M}]^+$), 253.1 (45.9%, $[\text{M-Et}]^+$), 143.1 (35.9%, $[\text{M-C}_8\text{H}_8\text{Cl}]^+$), 125.1 (100.0%, $[\text{C}_7\text{H}_6\text{Cl}]^+$). Tamao-Fleming oxidation, followed by diacylation and purification by silica gel chromatography (12 g SiO_2 column, 100:0→65:35 hexanes/EtOAc) gave 221 mg (72% overall yield) of **9h** as a colorless oil. **$^1\text{H NMR}$** (500 MHz, CDCl_3) δ 7.22 (d, $J = 8.3$ Hz, 2H), 7.08 (d, $J = 8.3$ Hz, 2H), 5.00 (tt, $J = 7.6, 4.9$ Hz, 1H), 4.08 (t, $J = 6.5$ Hz, 2H), 2.66-2.51 (m, 2H), 2.02 (s, 3H), 2.01 (s, 3H), 1.96-1.77 (m, 4H); **$^{13}\text{C NMR}$** (125 MHz, CDCl_3) δ 171.0, 170.6, 139.7, 131.8, 129.7, 128.6, 70.6, 60.7, 35.8, 33.1, 31.1, 21.1, 20.9; **HRMS** (ESI+) calcd for $[\text{C}_{15}\text{H}_{19}\text{ClNaO}_4]^+$ ($\text{M}+\text{Na}$) $^+$: m/z 321.0870, found 321.0864.

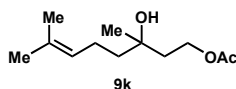


Compound 9i: Following the general procedure, ketone **8i** (246 mg, 1.02 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $[\text{Ir}(\text{cod})\text{OMe}]_2$ (0.05 mol %) as catalyst at room temperature. **GC/MS:** m/z 329.1 (4.6%, $[\text{M}(^{81}\text{Br})\text{-H}]^+$), 328.2 (4.3%, $[\text{M}(^{79}\text{Br})]^+$), 301.1 (55.7%, $[\text{M}(^{81}\text{Br})\text{-Et}]^+$), 299.1 (39.5%, $[\text{M}(^{79}\text{Br})\text{-Et}]^+$), 226.0 (80.0%, $[\text{M}(^{81}\text{Br})\text{-HOSi}(\text{H})\text{Et}_2]^+$), 224.1 (100.0%, $[\text{M}(^{79}\text{Br})\text{-HOSi}(\text{H})\text{Et}_2]^+$), 171.0 (98.5%, $[\text{C}_7\text{H}_6^{81}\text{Br}]^+$), 169.1 (93.3%, $[\text{C}_7\text{H}_6^{79}\text{Br}]^+$). The subsequent cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (1.0 mol %) at 100 °C for 14 h to provide the intermediate oxasilolane. **GC/MS:** m/z 328.1 (4.7%, $[\text{M}(^{81}\text{Br})]^+$), 326.1 (9.0%, $[\text{M}(^{79}\text{Br})]^+$), 299.2 (30.7%, $[\text{M}(^{81}\text{Br})\text{-Et}]^+$), 297.1 (46.8%, $[\text{M}(^{79}\text{Br})\text{-Et}]^+$), 171.0 (78.1%, $[\text{C}_7\text{H}_6^{81}\text{Br}]^+$), 168.9 (67.8%, $[\text{C}_7\text{H}_6^{79}\text{Br}]^+$), 143.0 (21.7%, $[\text{M-C}_8\text{H}_8\text{Br}]^+$), 115.1 (100.0%). Tamao-Fleming oxidation, followed by diacylation and purification by silica gel

chromatography (12 g SiO₂ column, 100:0→70:30 hexanes/EtOAc) gave 251 mg (72% overall yield) of **9i** as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 5.01 (tt, *J* = 7.6, 4.9 Hz, 1H), 4.08 (t, *J* = 6.5 Hz, 2H), 2.65-2.51 (m, 2H), 2.023 (s, 3H), 2.018 (s, 3H), 1.95-1.78 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 171.0, 170.7, 140.3, 131.6, 130.1, 119.8, 70.6, 60.7, 35.8, 33.1, 31.1, 21.2, 21.0; HRMS (ESI+) calcd for [C₁₅H₁₉BrNaO₄]⁺ (M+Na)⁺: *m/z* 365.0364, found 365.0362.

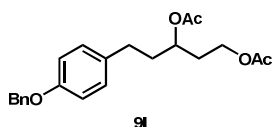


Compound 9j: Following the general procedure, ketone **8j** (232 mg, 1.01 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with [Ir(cod)OMe]₂ (0.05 mol %) as catalyst at room temperature. GC/MS: *m/z* 317.2 (1.6%, [M-H]⁺), 289.1 (55.9%, [M-Et]⁺), 195.2 (100.0%). The subsequent cyclization was conducted with [Ir(cod)OMe]₂/Me₄phen (1.0 mol %) at 100 °C for 14 h to provide the intermediate oxasilolane. GC/MS: *m/z* 315.0 (2.3%, [M-H]⁺), 287.2 (29.1%, [M-Et]⁺), 153.1 (100.0%), 143.1 (49.8%, [M-C₉H₈F₃]⁺). Tamao-Fleming oxidation, followed by diacylation and purification by silica gel chromatography (12 g SiO₂ column, 100:0→65:35 hexanes/EtOAc) gave 221 mg (72% overall yield) of **9j** as a pale yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 5.03 (tt, *J* = 7.6, 5.0 Hz, 1H), 4.09 (t, *J* = 6.5 Hz, 2H), 2.76-2.61 (m, 2H), 2.019 (s, 3H), 2.016 (s, 3H), 2.00-1.82 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 171.0, 170.7, 145.5, 128.7, 128.5 (q, *J* = 32 Hz), 125.5 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 272 Hz), 70.6, 60.7, 35.6, 33.2, 31.6, 21.1, 20.9; ¹⁹F NMR (470 MHz, CDCl₃) δ -62.80; HRMS (ESI+) calcd for [C₁₆H₁₉F₃NaO₄]⁺ (M+Na)⁺: *m/z* 355.1133, found 355.1131.

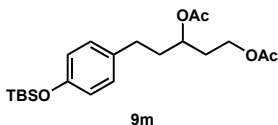


Compound 9k: Following the general procedure, dihydrolinalool (153 mg, 0.979 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with [Ir(cod)OMe]₂ (0.05 mol %) as catalyst at room temperature. GC/MS: *m/z* 227.1 (3.1%, [M-Me]⁺), 213.2 (53.1%, [M-Et]⁺), 159.1 (47.7%, [M-C₆H₁₁]⁺), 109.2 (100.0%). The subsequent

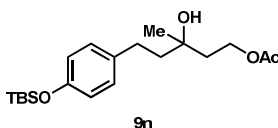
cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (1.0 mol %) at 100 °C for 43 h to provide the intermediate oxasilolane. **GC/MS**: m/z 240.2 (3.1%, $[\text{M}]^+$), 225.4 (5.2%, $[\text{M}-\text{Me}]^+$), 157.2 (100.0%, $[\text{M}-\text{C}_6\text{H}_{11}]^+$). Tamao-Fleming oxidation, followed by monoacylation and purification by silica gel chromatography (12 g SiO_2 column, 100:0→65:35 hexanes/EtOAc) gave 126 mg (60% overall yield) of **9k**¹⁸ as a colorless oil. **¹H NMR** (500 MHz, CDCl_3) δ 5.11-5.05 (m, 1H), 4.20 (t, $J = 7.1$ Hz, 2H), 2.06-1.99 (m, 2H), 2.02 (s, 3H), 1.86 (br s, 1H), 1.85-1.75 (m, 2H), 1.66 (s, 3H), 1.59 (s, 3H), 1.51-1.46 (m, 2H), 1.19 (s, 3H) (¹H NMR data were consistent with previously reported values¹⁸); **¹³C NMR** (125 MHz, CDCl_3) δ 171.2, 132.0, 124.2, 71.9, 61.4, 42.3, 39.8, 27.0, 25.8, 22.7, 21.2, 17.8 (¹³C NMR data were consistent with previously reported values¹⁸); **HRMS** (ESI+) calcd for $[\text{C}_{12}\text{H}_{22}\text{NaO}_3]^+$ ($\text{M}+\text{Na}$)⁺: m/z 237.1467, found 237.1472.



Compound 9l: Following the general procedure, ketone **8l** (263 mg, 0.980 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $[\text{Ir}(\text{cod})\text{OMe}]_2$ (0.05 mol %) as catalyst at room temperature. **GC/MS**: m/z 356.3 (5.9%, $[\text{M}]^+$), 327.1 (7.9%, $[\text{M}-\text{Et}]^+$), 265.1 (2.5%, $[\text{M}-\text{Bn}]^+$), 91.1 (100.0%, $[\text{C}_7\text{H}_7]^+$). The subsequent cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (1.0 mol %) at 100 °C for 14 h to provide the intermediate oxasilolane. **GC/MS**: m/z 354.4 (72.5%, $[\text{M}]^+$), 325.1 (11.5%, $[\text{M}-\text{Et}]^+$), 263.2 (4.7%, $[\text{M}-\text{Bn}]^+$), 91.1 (100.0%, $[\text{C}_7\text{H}_7]^+$). Tamao-Fleming oxidation, followed by diacylation and purification by silica gel chromatography (12 g SiO_2 column, 100:0→65:35 hexanes/EtOAc) gave 270 mg (75% overall yield) of **9l** as a colorless oil. **¹H NMR** (500 MHz, CDCl_3) δ 7.43 (d, $J = 7.1$ Hz, 2H), 7.38 (t, $J = 7.4$ Hz, 2H), 7.32 (t, $J = 7.2$ Hz, 1H), 7.09 (d, $J = 8.6$ Hz, 2H), 6.91 (d, $J = 8.6$ Hz, 2H), 5.11-4.99 (m, 1H), 5.04 (s, 2H), 4.11 (t, $J = 6.5$ Hz, 2H), 2.67-2.53 (m, 2H), 2.05 (s, 3H), 2.04 (s, 3H), 1.99-1.79 (m, 4H); **¹³C NMR** (125 MHz, CDCl_3) δ 171.0, 170.7, 157.2, 137.2, 133.7, 129.3, 128.6, 128.0, 127.5, 114.9, 70.8, 70.1, 60.8, 36.2, 33.1, 30.8, 21.2, 21.0; **HRMS** (ESI+) calcd for $[\text{C}_{22}\text{H}_{26}\text{NaO}_5]^+$ ($\text{M}+\text{Na}$)⁺: m/z 393.1678, found 393.1675.

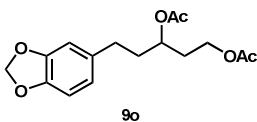


Compound 9m: Following the general procedure, ketone **8m** (292 mg, 0.998 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $[\text{Ir}(\text{cod})\text{OMe}]_2$ (0.05 mol %) as catalyst at room temperature. The subsequent cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (1.0 mol %) at 100 °C for 15 h to provide the intermediate oxasilolane. Tamao-Fleming oxidation, followed by diacylation and purification by silica gel chromatography (12 g SiO_2 column, 100:0→75:25 hexanes/EtOAc) gave 267 mg (68% overall yield) of **9m** as a colorless oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.00 (d, $J = 8.5$ Hz, 2H), 6.74 (d, $J = 8.4$ Hz, 2H), 5.02 (tt, $J = 7.6, 4.9$ Hz, 1H), 4.09 (t, $J = 6.5$ Hz, 2H), 2.63-2.49 (m, 2H), 2.031 (s, 3H), 2.027 (s, 3H), 1.97-1.77 (m, 4H), 0.97 (s, 9H), 0.17 (s, 6H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 171.1, 170.7, 153.9, 134.0, 129.2, 120.1, 70.9, 60.9, 36.2, 33.1, 30.9, 25.8, 21.2, 21.0, 18.3, -4.3; **HRMS** (ESI+) calcd for $[\text{C}_{21}\text{H}_{34}\text{NaO}_5\text{Si}]^+$ ($\text{M}+\text{Na}$) $^+$: m/z 417.2073, found 417.2079.

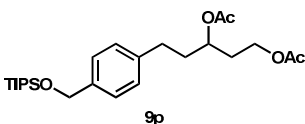


Compound 9n: Following the general procedure, alcohol **7n** (305 mg, 0.989 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $[\text{Ir}(\text{cod})\text{OMe}]_2$ (0.05 mol %) as catalyst at room temperature. **GC/MS:** m/z 394.4 (2.5%, $[\text{M}]^+$), 365.4 (3.0%, $[\text{M}-\text{Et}]^+$), 290.3 (69.1%, $[\text{M}-\text{HOSi}(\text{H})\text{Et}_2]^+$), 261.2 (100.0%). The subsequent cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (1.0 mol %) at 100 °C for 15 h to provide the intermediate oxasilolane. **GC/MS:** m/z 392.3 (27.7%, $[\text{M}]^+$), 363.3 (1.3%, $[\text{M}-\text{Et}]^+$), 261.2 (100.0%). Tamao-Fleming oxidation, followed by monoacylation and purification by silica gel chromatography (12 g SiO_2 column, 100:0→65:35 hexanes/EtOAc) gave 231 mg (64% overall yield) of **9n** as a colorless oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.03 (d, $J = 8.4$ Hz, 2H), 6.75 (d, $J = 8.4$ Hz, 2H), 4.25 (t, $J = 7.0$ Hz, 2H), 2.66-2.57 (m, 2H), 2.04 (s, 3H), 1.95-1.81 (m, 3H), 1.80-1.72 (m, 2H), 1.27 (s, 3H), 0.97 (s, 9H), 0.18 (s, 6H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 171.2, 153.8, 134.9, 129.2, 120.1, 71.8, 61.3, 44.5,

39.9, 29.5, 27.1, 25.8, 21.2, 18.3, -4.3; **HRMS** (ESI+) calcd for $[\text{C}_{20}\text{H}_{34}\text{NaO}_4\text{Si}]^+$ ($\text{M}+\text{Na}$) $^+$: m/z 389.2124, found 389.2124.

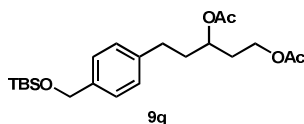


Compound 9o: Following the general procedure, ketone **8o** (211 mg, 1.02 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $[\text{Ir}(\text{cod})\text{OMe}]_2$ (0.05 mol %) as catalyst at room temperature. **GC/MS:** m/z 294.2 (23.5%, $[\text{M}]^+$), 265.2 (12.6%, $[\text{M}-\text{Et}]^+$), 190.1 (84.1%, $[\text{M}-\text{HOSi}(\text{H})\text{Et}_2]^+$), 135.1 (100.0%, $[\text{C}_8\text{H}_7\text{O}_2]^+$). The subsequent cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (1.0 mol %) at 100 °C for 18 h to provide the intermediate oxasilolane. **GC/MS:** m/z 292.2 (91.5%, $[\text{M}]^+$), 263.2 (34.2%, $[\text{M}-\text{Et}]^+$), 135.1 (100.0%, $[\text{C}_8\text{H}_7\text{O}_2]^+$). Tamao-Fleming oxidation, followed by diacylation and purification by silica gel chromatography (12 g SiO_2 column, 100:0→70:30 hexanes/EtOAc) gave 211 mg (67% overall yield) of **9o** as a faint golden oil. **^1H NMR** (500 MHz, CDCl_3) δ 6.70 (d, $J = 7.9$ Hz, 1H), 6.64 (d, $J = 1.6$ Hz, 1H), 6.59 (dd, $J = 7.9$, 1.6 Hz, 1H), 5.89 (s, 2H), 5.00 (tt, $J = 7.7$, 4.8 Hz, 1H), 4.08 (t, $J = 6.5$ Hz, 2H), 2.60–2.47 (m, 2H), 2.03 (s, 3H), 2.02 (s, 3H), 1.95–1.75 (m, 4H); **^{13}C NMR** (125 MHz, CDCl_3) δ 171.0, 170.7, 147.7, 145.8, 135.1, 121.1, 108.8, 108.3, 100.9, 70.7, 60.8, 36.3, 33.1, 31.4, 21.2, 21.0; **HRMS** (ESI+) calcd for $[\text{C}_{16}\text{H}_{20}\text{NaO}_6]^+$ ($\text{M}+\text{Na}$) $^+$: m/z 331.1158, found 331.1158.

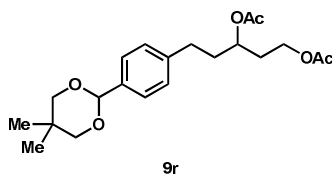


Compound 9p: Following the general procedure, ketone **8p** (344 mg, 0.987 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $[\text{Ir}(\text{cod})\text{OMe}]_2$ (0.05 mol %) as catalyst at room temperature. The subsequent cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (1.0 mol %) at 100 °C for 21 h to provide the intermediate oxasilolane. Tamao-Fleming oxidation, followed by diacylation and purification by silica gel chromatography (12 g SiO_2 column, 100:0→75:25 hexanes/EtOAc) gave 325 mg (73% overall yield) of **9p** as a colorless oil. **^1H NMR** (500 MHz, CDCl_3) δ 7.29 (d, $J =$

8.3 Hz, 2H), 7.15 (d, $J = 8.0$ Hz, 2H), 5.07 (tt, $J = 7.7, 4.9$ Hz, 1H), 4.82 (s, 2H), 4.12 (t, $J = 6.5$ Hz, 2H), 2.72-2.58 (m, 2H), 2.06 (s, 6H), 2.00-1.83 (m, 4H), 1.26-1.15 (m, 3H), 1.11 (d, $J = 6.8$ Hz, 18H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.1, 170.7, 139.8, 139.5, 128.2, 126.0, 70.9, 65.0, 60.9, 36.1, 33.2, 31.4, 21.2, 21.0, 18.2, 12.2; HRMS (ESI+) calcd for $[\text{C}_{25}\text{H}_{42}\text{NaO}_5\text{Si}]^+$ ($\text{M}+\text{Na}$) $^+$: m/z 473.2699, found 473.2696.

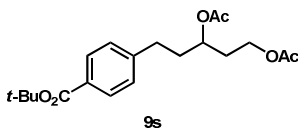


Compound 9q: Following the general procedure, ketone **8q** (310 mg, 1.01 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $[\text{Ir}(\text{cod})\text{OMe}]_2$ (0.05 mol %) as catalyst at room temperature. GC/MS: m/z 394.3 (3.2%, $[\text{M}]^+$), 290.2 (3.4%, $[\text{M}-\text{HOSi}(\text{H})\text{Et}_2]^+$), 177.1 (100.0%), 159.2 (74.5%, $[\text{M}-\text{C}_{14}\text{H}_{23}\text{OSi}]^+$), 117.1 (97.2%). The subsequent cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (1.0 mol %) at 100 °C for 14 h to provide the intermediate oxasilolane. GC/MS: m/z 391.1 (0.9%, $[\text{M}-\text{H}]^+$), 335.2 (9.5%, $[\text{M}-t\text{-Bu}]^+$), 177.1 (62.3%), 117.1 (100.0%). Tamao-Fleming oxidation, followed by diacylation and purification by silica gel chromatography (12 g SiO_2 column, 100:0→75:25 hexanes/EtOAc) gave 228 mg (55% overall yield) of **9q** as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.24 (d, $J = 8.0$ Hz, 2H), 7.13 (d, $J = 8.0$ Hz, 2H), 5.04 (tt, $J = 7.7, 4.9$ Hz, 1H), 4.70 (s, 2H), 4.10 (t, $J = 6.5$ Hz, 2H), 2.70-2.55 (m, 2H), 2.04 (s, 3H), 2.03 (s, 3H), 1.98-1.81 (m, 4H), 0.94 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.0, 170.7, 140.0, 139.2, 128.2, 126.4, 70.9, 64.9, 60.9, 36.1, 33.2, 31.4, 26.1, 21.2, 21.0, 18.5, -5.1; HRMS (ESI+) calcd for $[\text{C}_{22}\text{H}_{36}\text{NaO}_5\text{Si}]^+$ ($\text{M}+\text{Na}$) $^+$: m/z 431.2230, found 431.2231.

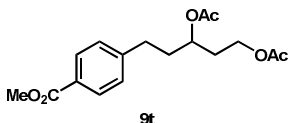


Compound 9r: Following the general procedure, ketone **8r** (272 mg, 0.984 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $[\text{Ir}(\text{cod})\text{OMe}]_2$ (0.05 mol %) as catalyst at room temperature. The subsequent cyclization was conducted with

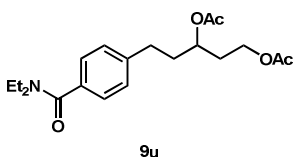
[Ir(cod)OMe]₂/Me₄phen (1.0 mol %) at 100 °C for 15 h to provide the intermediate oxasilolane. Tamao-Fleming oxidation, followed by diacylation and purification by silica gel chromatography (12 g SiO₂ column, 100:0→70:30 hexanes/EtOAc) gave 277 mg (74% overall yield) of **9r** as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.41 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 5.35 (s, 1H), 5.02 (tt, *J* = 7.7, 4.8 Hz, 1H), 4.08 (t, *J* = 6.5 Hz, 2H), 3.74 (d, *J* = 11.2 Hz, 2H), 3.63 (d, *J* = 10.8 Hz, 2H), 2.69-2.54 (m, 2H), 2.03 (s, 3H), 2.02 (s, 3H), 1.96-1.77 (m, 4H), 1.28 (s, 3H), 0.78 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.0, 170.7, 142.0, 136.5, 128.3, 126.3, 101.7, 77.7, 70.8, 60.8, 36.0, 33.1, 31.5, 30.3, 23.1, 22.0, 21.2, 21.0; HRMS (ESI+) calcd for [C₂₁H₃₀NaO₆]⁺ (M+Na)⁺: *m/z* 401.1940, found 401.1942.



Compound 9s: Following the general procedure, ketone **8s** (267 mg, 1.02 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with [Ir(cod)OMe]₂ (0.05 mol %) as catalyst at room temperature. GC/MS: *m/z* 294.0 (16.4%, [M-C₄H₈]⁺), 265.1 (100.0%), 145.1 (34.6%, [M-C₁₃H₁₇O₂]⁺). The subsequent cyclization was conducted with [Ir(cod)OMe]₂/Me₄phen (1.0 mol %) at 120 °C for 18 h to provide the intermediate oxasilolane. GC/MS: *m/z* 292.5 (5.8%, [M-C₄H₈]⁺), 263.1 (100.0%), 143.2 (48.7%, [M-C₁₃H₁₇O₂]⁺). Tamao-Fleming oxidation, followed by diacylation and purification by silica gel chromatography (12 g SiO₂ column, 100:0→75:25 hexanes/EtOAc) gave 262 mg (71% overall yield) of **9s** as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 5.01 (tt, *J* = 7.6, 4.9 Hz, 1H), 4.07 (t, *J* = 6.5 Hz, 2H), 2.74-2.58 (m, 2H), 2.02 (s, 3H), 2.01 (s, 3H), 1.97-1.80 (m, 4H), 1.56 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 171.0, 170.7, 165.7, 146.2, 130.0, 129.7, 128.2, 80.8, 70.6, 60.7, 35.6, 33.1, 31.7, 28.3, 21.1, 21.0; HRMS (ESI+) calcd for [C₂₀H₂₈NaO₆]⁺ (M+Na)⁺: *m/z* 387.1784, found 387.1786.

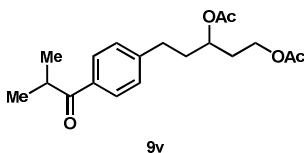


Compound 9t: Following the general procedure, alcohol **7t** (220 mg, 0.990 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with Ru(PPh₃)₃Cl₂ (0.2 mol %) as catalyst in PhH at 50 °C. The subsequent cyclization was conducted with [Ir(cod)OMe]₂/Me₄phen (1.0 mol %) at 120 °C for 20 h to provide the intermediate oxasilolane. Tamao-Fleming oxidation, followed by diacylation and purification by silica gel chromatography (12 g SiO₂ column, 100:0→65:35 hexanes/EtOAc) gave 227 mg (71% overall yield) of **9t** as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 5.01 (tt, *J* = 7.6, 4.9 Hz, 1H), 4.07 (t, *J* = 6.5 Hz, 2H), 3.87 (s, 3H), 2.73-2.60 (m, 2H), 2.004 (s, 3H), 2.002 (s, 3H), 1.97-1.81 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 171.0, 170.6, 167.0, 146.8, 129.9, 128.4, 128.1, 70.6, 60.7, 52.0, 35.5, 33.1, 31.7, 21.1, 20.9; HRMS (ESI+) calcd for [C₁₇H₂₂NaO₆]⁺ (M+Na)⁺: *m/z* 345.1314, found 345.1314.

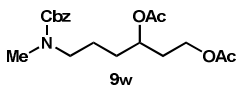


Compound 9u: Following the general procedure, alcohol **7u** (261 mg, 0.991 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with Ru(PPh₃)₃Cl₂ (0.2 mol %) as catalyst in PhH at 50 °C. The subsequent cyclization was conducted with [Ir(cod)OMe]₂/Me₄phen (2.0 mol %) at 120 °C for 23 h to provide the intermediate oxasilolane. Tamao-Fleming oxidation (with added KF), followed by diacylation and purification by silica gel chromatography (12 g SiO₂ column, 85:15→50:50 hexanes/EtOAc) gave 186 mg (52% overall yield) of **9u** as a golden oil. ¹H NMR (500 MHz, CDCl₃) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.03 (tt, *J* = 7.6, 4.9 Hz, 1H), 4.09 (t, *J* = 6.5 Hz, 2H), 3.52 (br s, 2H), 3.25 (br s, 2H), 2.71-2.56 (m, 2H), 2.03 (s, 3H), 2.02 (s, 3H), 1.97-1.79 (m, 4H), 1.21 (br s, 3H), 1.10 (br s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.3, 171.0, 170.7, 142.5, 135.0, 128.3, 126.6, 70.7, 60.7, 43.3, 39.3,

35.8, 33.1, 31.5, 21.1, 21.0, 14.3, 12.9; **HRMS** (ESI+) calcd for $[\text{C}_{20}\text{H}_{30}\text{NO}_5]^+$ ($\text{M}+\text{H}$) $^+$: m/z 364.2124, found 364.2127.

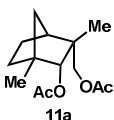


Compound 9v: Following the general procedure, alcohol **7v** (228 mg, 0.973 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ (0.2 mol %) as catalyst in PhH at 50 °C. The subsequent cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (1.0 mol %) at 120 °C for 19 h to provide the intermediate oxasilolane. Tamao-Fleming oxidation, followed by diacylation and purification by silica gel chromatography (12 g SiO_2 column, 100:0→70:30 hexanes/EtOAc) gave 226 mg (69% overall yield) of **9v** as a colorless oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.83 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 4.99 (tt, J = 7.6, 4.9 Hz, 1H), 4.05 (t, J = 6.5 Hz, 2H), 3.48 (septet, J = 6.8 Hz, 1H), 2.72-2.58 (m, 2H), 1.98 (s, 3H), 1.98 (s, 3H), 1.94-1.80 (m, 4H), 1.15 (d, J = 6.8 Hz, 6H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 204.0, 170.9, 170.6, 146.7, 134.2, 128.6, 128.5, 70.5, 60.6, 35.4, 35.2, 33.0, 31.6, 21.0, 20.9, 19.17, 19.16; **HRMS** (ESI+) calcd for $[\text{C}_{19}\text{H}_{26}\text{NaO}_5]^+$ ($\text{M}+\text{Na}$) $^+$: m/z 357.1678, found 357.1678.

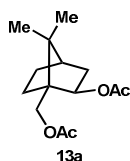


Compound 9w: Following the general procedure, alcohol **7w** (267 mg, 1.01 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ (0.2 mol %) as catalyst in PhMe at 50 °C. The subsequent cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (1.0 mol %) at 120 °C for 49 h to provide the intermediate oxasilolane. Tamao-Fleming oxidation, followed by diacylation and purification by silica gel chromatography (12 g SiO_2 column, 85:15→50:50 hexanes/EtOAc) gave 255 mg (70% overall yield) of **9w** as a colorless oil. $^1\text{H NMR}$ (500 MHz, CDCl_3 , 50 °C) δ 7.36-7.24 (m, 5H), 5.11 (s, 2H), 4.97 (br s, 1H), 4.11-4.00 (m, 2H), 3.34-3.20 (m, 2H), 2.89 (s, 3H), 2.00 (s, 6H), 1.83 (br s, 2H), 1.54 (br s, 4H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3 , 20 °C) δ 171.1, 170.8, 156.4, 137.0, 128.6, 128.0, 127.9, 70.8*, 70.6*, 67.1, 60.8, 48.9*, 48.4*,

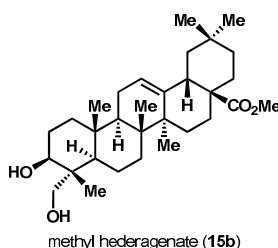
34.7*, 34.0*, 33.1, 31.4, 23.8*, 23.4*, 21.2, 21.0 (Note: At 20 °C, a mixture of rotamers are observed; signals that correspond to the individual rotamers, and which coalesce at 50 °C, are indicated with a *); ^{13}C NMR (125 MHz, CDCl_3 , 50 °C) δ 170.8, 170.5, 156.4, 137.2, 128.5, 128.0, 127.9, 70.9, 67.1, 60.8, 48.8, 34.4*, 33.3, 31.5, 23.7, 21.1, 20.9 (Note: At 50 °C, the N–Me group appears as a broad, low-intensity signal between δ 35–34; the mid-point of this signal is estimated and is indicated with a *); HRMS (ESI+) calcd for $[\text{C}_{19}\text{H}_{27}\text{NNaO}_6]^+$ (M+Na) $^+$: m/z 388.1736, found 388.1737.



Compound 11a: Following the general procedure, (+)-fenchol (**10**, 156 mg, 1.01 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $[\text{Ir}(\text{cod})\text{OMe}]_2$ (0.05 mol %) as catalyst at room temperature. GC/MS: m/z 240.1 (0.7%, $[\text{M}]^+$), 224.9 (2.6%, $[\text{M}-\text{Me}]^+$), 211.2 (93.9%, $[\text{M}-\text{Et}]^+$), 121.1 (100.0%). The subsequent cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (1.0 mol %) at 100 °C for 12 h to provide the intermediate oxasilolane. GC/MS: m/z 238.2 (13.7%, $[\text{M}]^+$), 223.1 (5.4%, $[\text{M}-\text{Me}]$), 209.1 (38.3%, $[\text{M}-\text{Et}]^+$), 157.1 (100.0%). Tamao-Fleming oxidation, followed by diacylation and purification by silica gel chromatography (12 g SiO_2 column, 100:0→80:20 hexanes/EtOAc) gave 169 mg (66% overall yield) of **11a**¹⁹ as a colorless oil. On standing in the freezer, this material crystallized as a colorless solid. ^1H NMR (500 MHz, CDCl_3) δ 4.52 (d, $J = 1.9$ Hz, 1H), 4.00 (d, $J = 11.0$ Hz, 1H), 3.78 (d, $J = 11.0$ Hz, 1H), 2.02 (s, 3H), 1.99 (s, 3H), 1.89–1.85 (m, 1H), 1.77–1.69 (m, 1H), 1.60–1.52 (m, 2H), 1.51–1.42 (m, 1H), 1.21 (d, $J = 10.3$ Hz, 1H), 1.15–1.07 (m, 1H), 1.11 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.4, 171.2, 84.8, 66.8, 48.4, 45.8, 42.0, 41.4, 26.6, 25.6, 24.7, 21.04, 21.02, 18.9; HRMS (ESI+) calcd for $[\text{C}_{14}\text{H}_{22}\text{NaO}_4]^+$ (M+Na) $^+$: m/z 277.1416, found 277.1419.

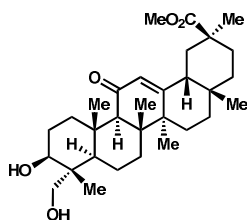


Compound 13a: Following the general procedure, (+)-camphor (**12**, 153 mg, 1.01 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $[\text{Ir}(\text{coe})_2\text{Cl}]_2$ (0.05 mol %) as catalyst in PhH at room temperature. **GC/MS:** m/z 240.0 (3.1%, $[\text{M}]^+$), 225.2 (7.2%, $[\text{M}-\text{Me}]^+$), 211.2 (100.0%, $[\text{M}-\text{Et}]^+$). The subsequent cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (1.0 mol %) at 120 °C for 20 h to provide the intermediate oxasilolane. **GC/MS:** m/z 238.2 (100.0%, $[\text{M}]^+$), 223.3 (16.7%, $[\text{M}-\text{Me}]^+$), 209.2 (83.2%, $[\text{M}-\text{Et}]^+$). Tamao-Fleming oxidation, followed by diacylation and purification by silica gel chromatography (12 g SiO_2 column, 100:0→75:25 hexanes/EtOAc) gave 147 mg (57% overall yield) of **13a** as a colorless oil. **^1H NMR** (500 MHz, CDCl_3) δ 4.80 (dd, $J = 8.1, 3.1$ Hz, 1H), 4.27 (d, $J = 11.1$ Hz, 1H), 3.94 (d, $J = 11.1$ Hz, 1H), 1.98 (s, 3H), 1.97 (s, 3H), 1.87-1.80 (m, 1H), 1.77-1.63 (m, 4H), 1.33-1.26 (m, 1H), 1.13-1.07 (m, 1H), 1.04 (s, 3H), 0.90 (s, 3H); **^{13}C NMR** (125 MHz, CDCl_3) δ 171.3, 170.3, 77.9, 63.0, 51.2, 47.4, 45.9, 39.0, 29.8, 26.8, 21.3, 20.9, 20.8, 20.3; **HRMS** (ESI+) calcd for $[\text{C}_{14}\text{H}_{22}\text{NaO}_4]^+$ ($\text{M}+\text{Na}$) $^+$: m/z 277.1416, found 277.1414.



Methyl hederagenate (15b): Following the general procedure, methyl oleanate (**14b**, 232 mg, 0.493 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with $[\text{Ir}(\text{cod})\text{OMe}]_2$ (0.1 mol %) as catalyst in THF (1.0 mL) at room temperature. **^1H NMR** (500 MHz, CDCl_3) δ 5.28 (t, $J = 3.5$ Hz, 1H), 4.43 (pentet, $J = 2.3$ Hz, 1H), 3.62 (s, 3H), 3.21 (dd, $J = 11.5, 4.4$ Hz, 1H), 2.86 (dd, $J = 13.7, 4.3$ Hz, 1H), 1.12 (s, 3H), 0.923 (s, 3H), 0.918 (s, 3H), 0.899 (s, 3H), 0.897 (s, 3H), 0.75 (s, 3H), 0.71 (s, 3H). The subsequent cyclization was conducted with $[\text{Ir}(\text{cod})\text{OMe}]_2/\text{Me}_4\text{phen}$ (2.0 mol %) in THF (2.0 mL) at 120 °C for 34 h to provide the intermediate oxasilolane. **^1H NMR** (500 MHz,

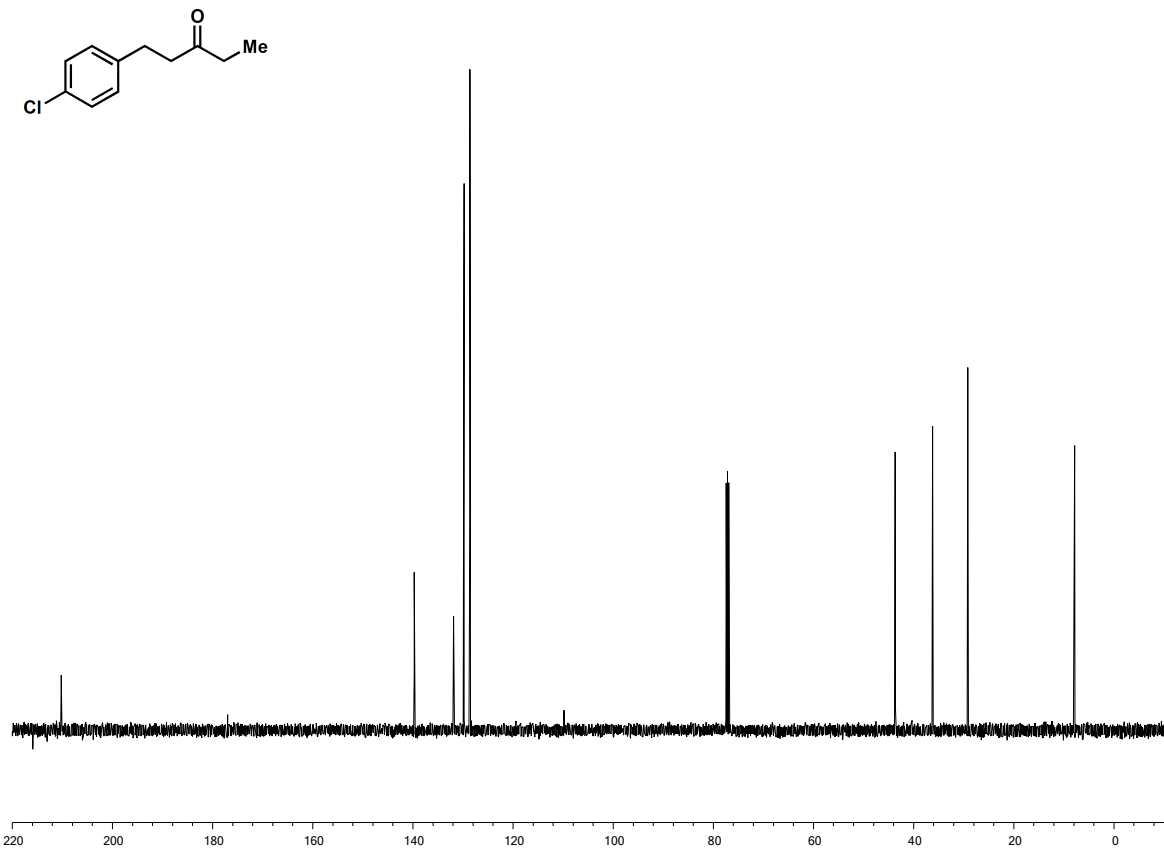
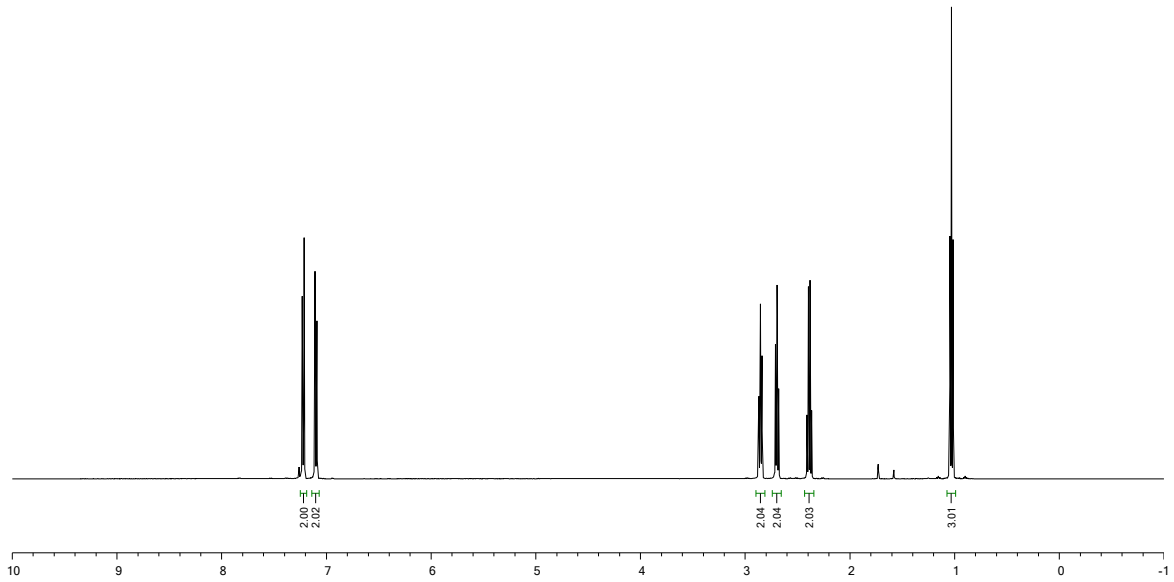
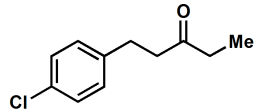
CDCl₃) δ 5.28 (t, J = 3.4 Hz, 1H), 3.62 (s, 3H), 3.22 (dd, J = 11.5, 4.2 Hz, 1H), 2.89-2.82 (m, 1H), 1.15 (s, 3H), 0.93 (s, 3H), 0.92 (s, 3H), 0.90 (s, 3H), 0.79 (s, 3H), 0.71 (s, 3H). Tamao-Fleming oxidation (2.0 mL MeOH added), followed by purification by silica gel chromatography (12 g SiO₂ column, 85:15→0:100 hexanes/EtOAc) gave 147 mg (61% overall yield) of **15b** as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 5.26 (t, J = 3.5 Hz, 1H), 3.69 (d, J = 10.4 Hz, 1H), 3.65-3.56 (m, 1H), 3.61 (s, 3H), 3.40 (d, J = 10.4 Hz, 1H), 3.10-2.56 (br m, 2H), 2.84 (dd, J = 13.7, 4.2 Hz, 1H), 2.01-1.90 (m, 1H), 1.91-1.80 (m, 2H), 1.11 (s, 3H), 0.93 (s, 3H), 0.91 (s, 3H), 0.88 (s, 3H), 0.87 (s, 3H), 0.70 (s, 3H) (¹H NMR data were consistent with previously reported values²⁰); ¹³C NMR (125 MHz, CDCl₃) δ 178.5, 143.9, 122.4, 77.0, 72.3, 51.7, 49.9, 47.7, 46.8, 46.0, 41.9, 41.8, 41.4, 39.4, 38.2, 37.0, 34.0, 33.2, 32.54, 32.49, 30.8, 27.8, 26.8, 26.1, 23.8, 23.5, 23.2, 18.6, 17.0, 15.8, 11.5 (¹³C NMR data were consistent with previously reported values²⁰⁻²¹); HRMS (ESI+) calcd for [C₃₁H₅₁O₄]⁺ (M+H)⁺: m/z 487.3787, found 487.3786.

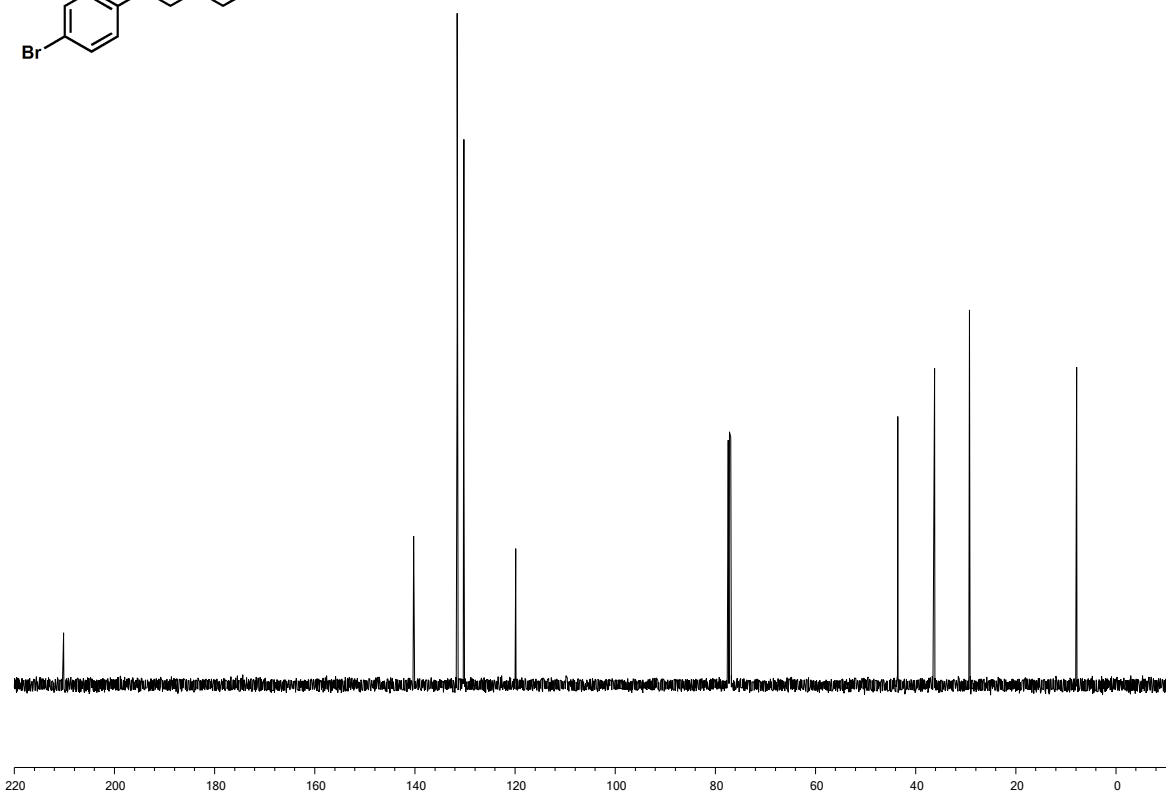
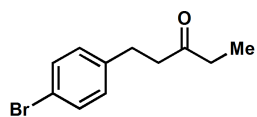
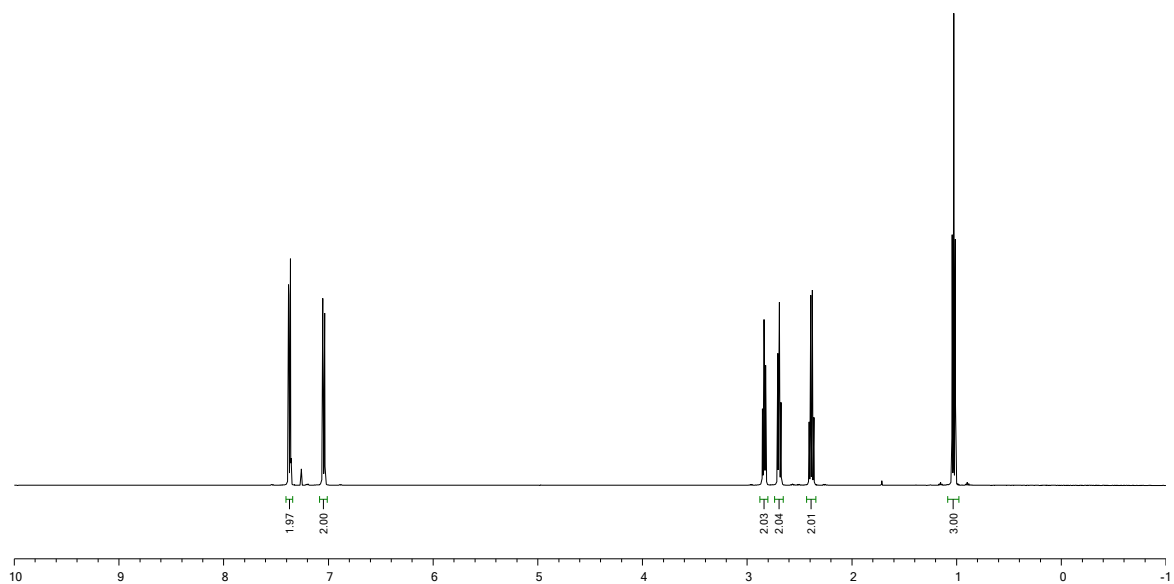
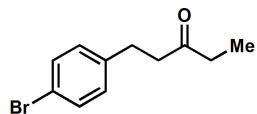


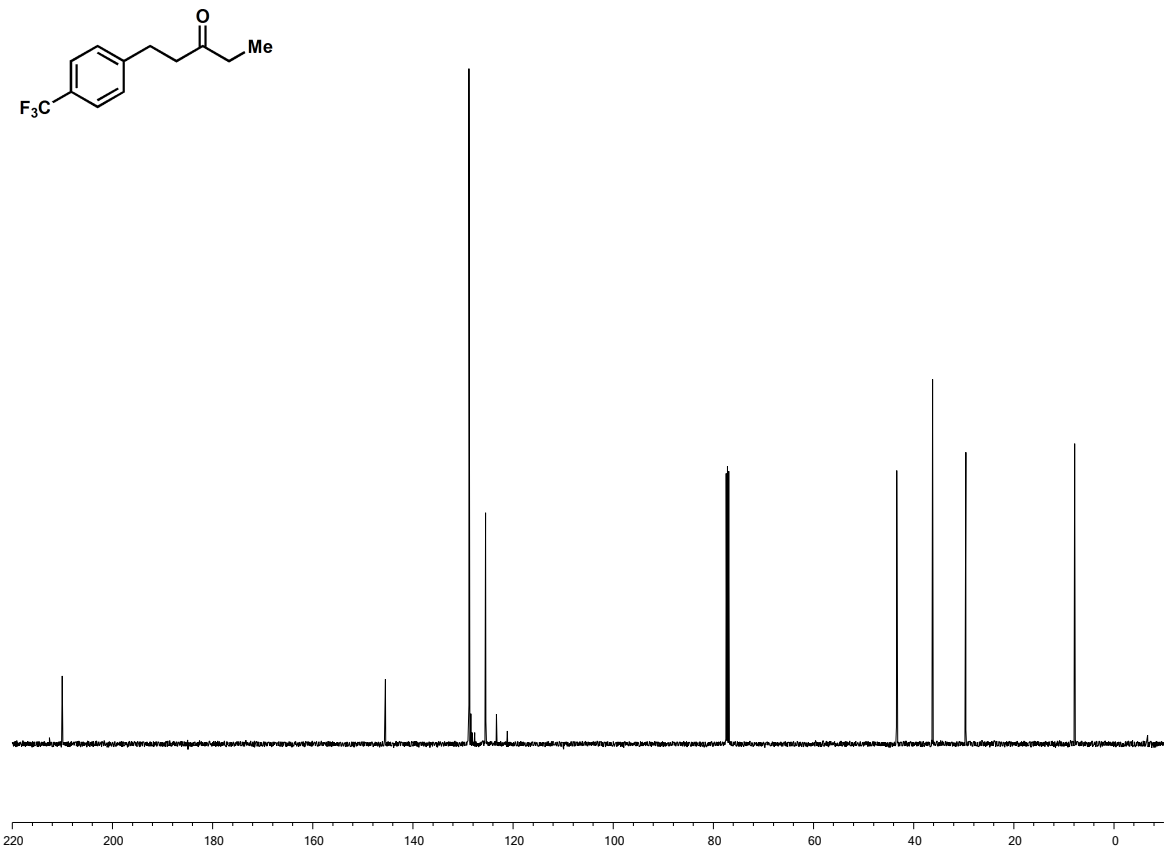
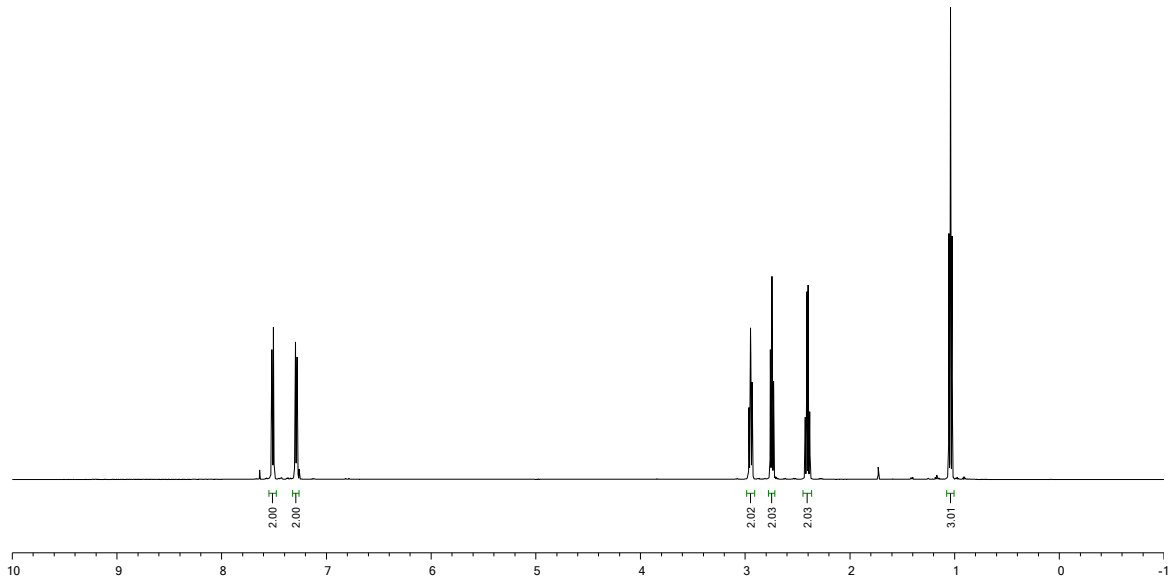
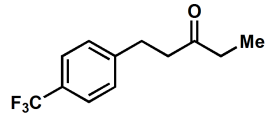
methyl 23-hydroxyglycyrrhetinate (**17a**)

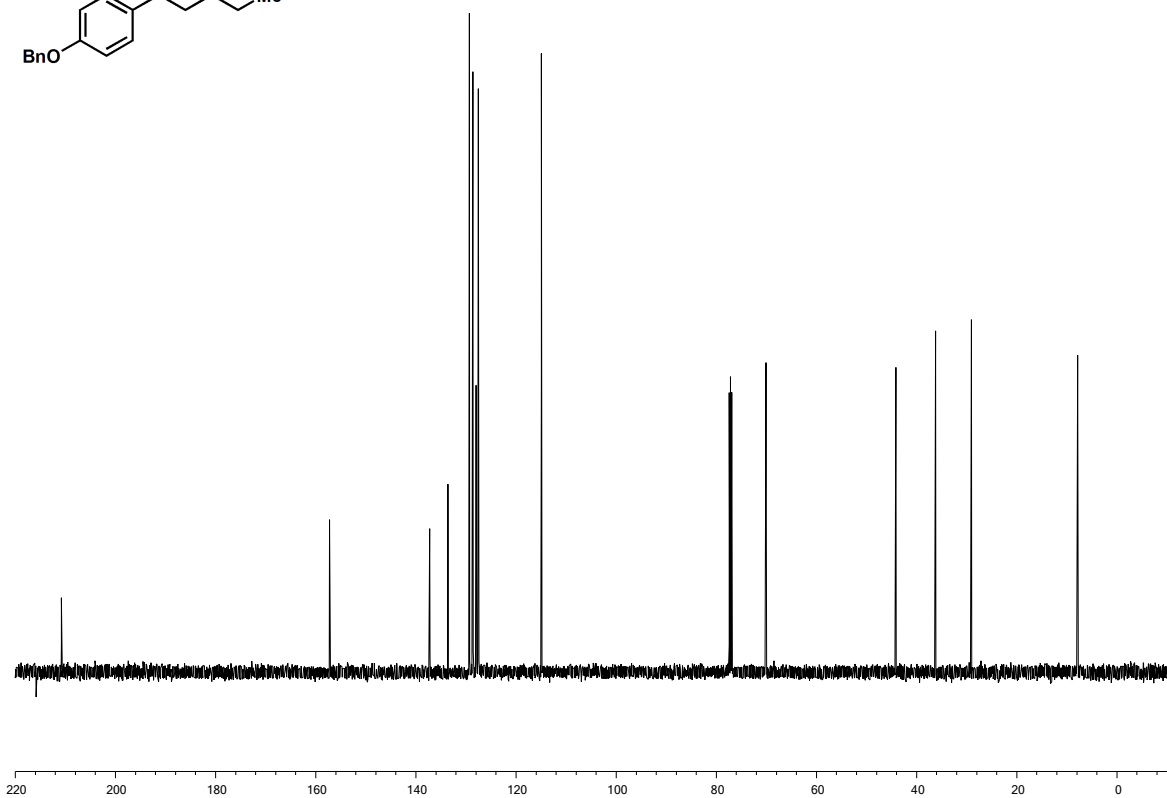
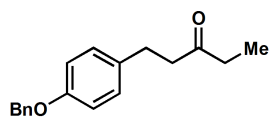
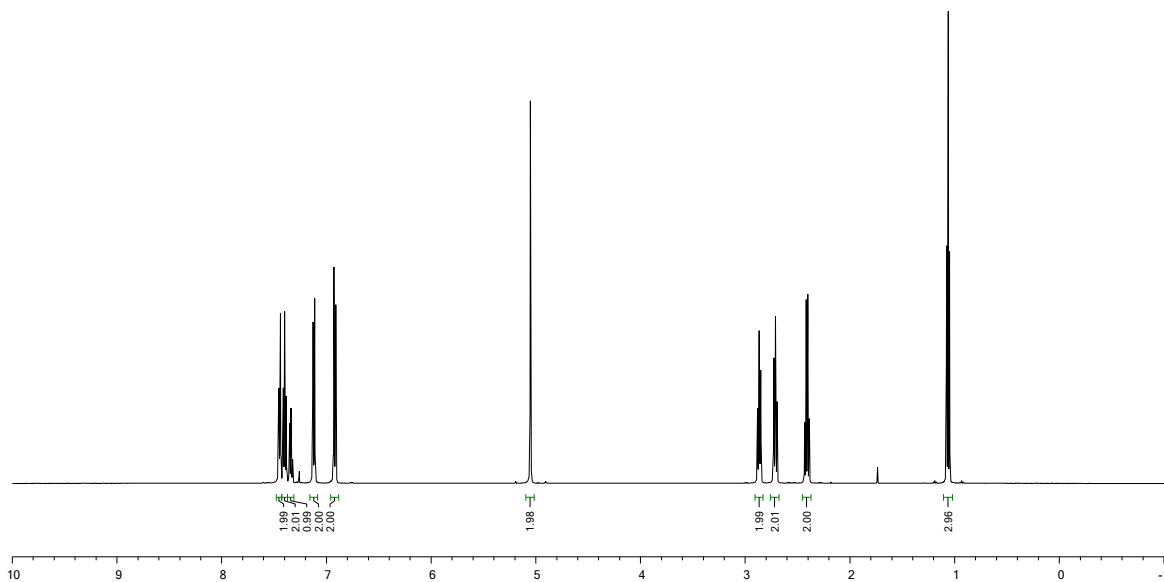
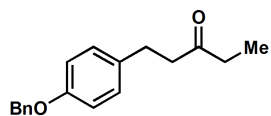
Methyl 23-hydroxyglycyrrhetinate (17a): Following the general procedure, methyl glycyrrhetinate (**16**, 242 mg, 0.499 mmol) was converted to the corresponding diethyl(hydrido)silyl ether with Ru(PPh₃)₃Cl₂ (0.2 mol %) as catalyst in PhH (4.0 mL) at 50 °C. (Note: **16** was not fully soluble in PhH at room temperature.) ¹H NMR (500 MHz, CDCl₃) δ 5.66 (s, 1H), 4.46-4.42 (m, 1H), 3.69 (s, 3H), 3.23 (dd, J = 11.6, 4.5 Hz, 1H), 2.80-2.72 (m, 1H), 2.33 (s, 1H), 1.36 (s, 3H), 1.15 (s, 3H), 1.13 (s, 3H), 1.12 (s, 3H), 0.94 (s, 3H), 0.80 (s, 3H), 0.78 (s, 3H). The subsequent cyclization was conducted with [Ir(cod)OMe]₂/Me₄phen (2.0 mol %) in THF (2.0 mL) at 120 °C for 26 h to provide the intermediate oxasilolane. ¹H NMR (500 MHz, CDCl₃) δ 5.67 (s, 1H), 3.69 (s, 3H), 3.26-3.21 (m, 1H), 2.92-2.86 (m, 1H), 2.37 (s, 1H), 1.38 (s, 3H), 1.15 (s, 3H), 1.14 (s, 3H), 1.12 (s, 3H), 0.81 (s, 3H), 0.80 (s, 3H). Tamao-Fleming oxidation (2.0 mL MeOH added), followed by purification by silica gel chromatography (12 g SiO₂ column,

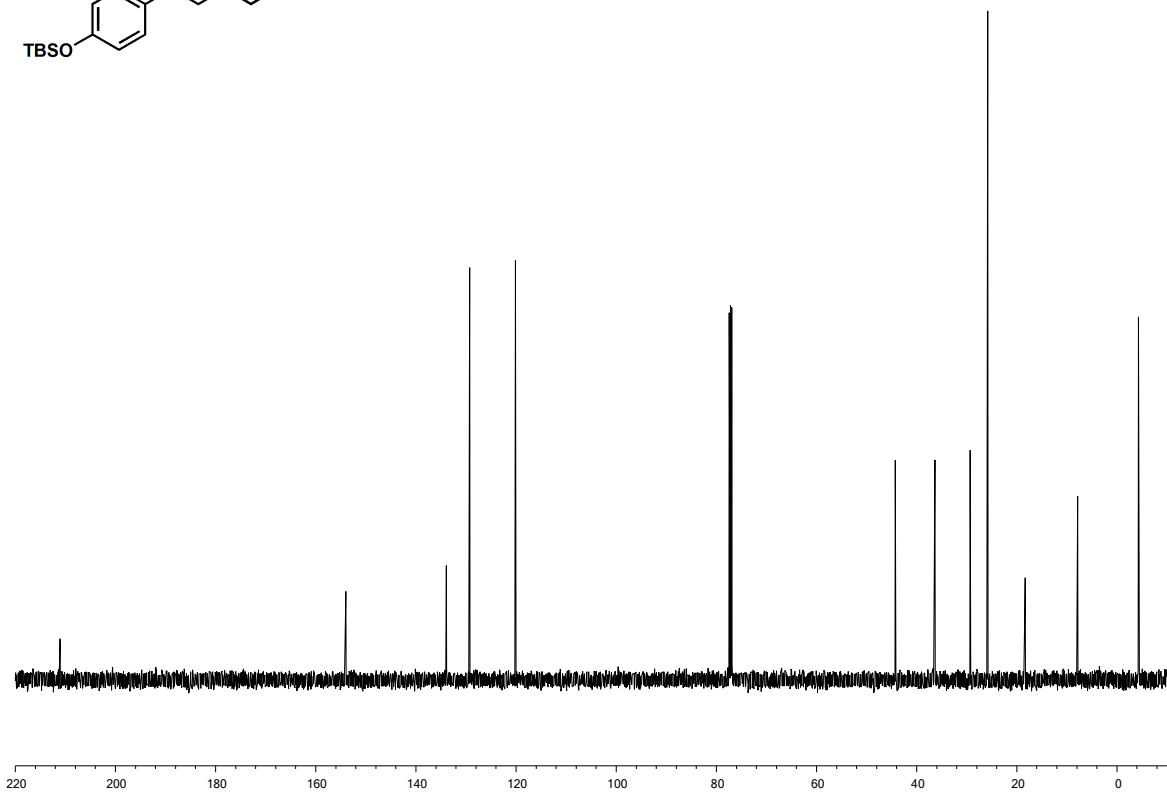
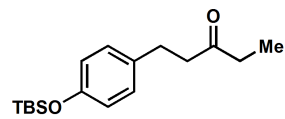
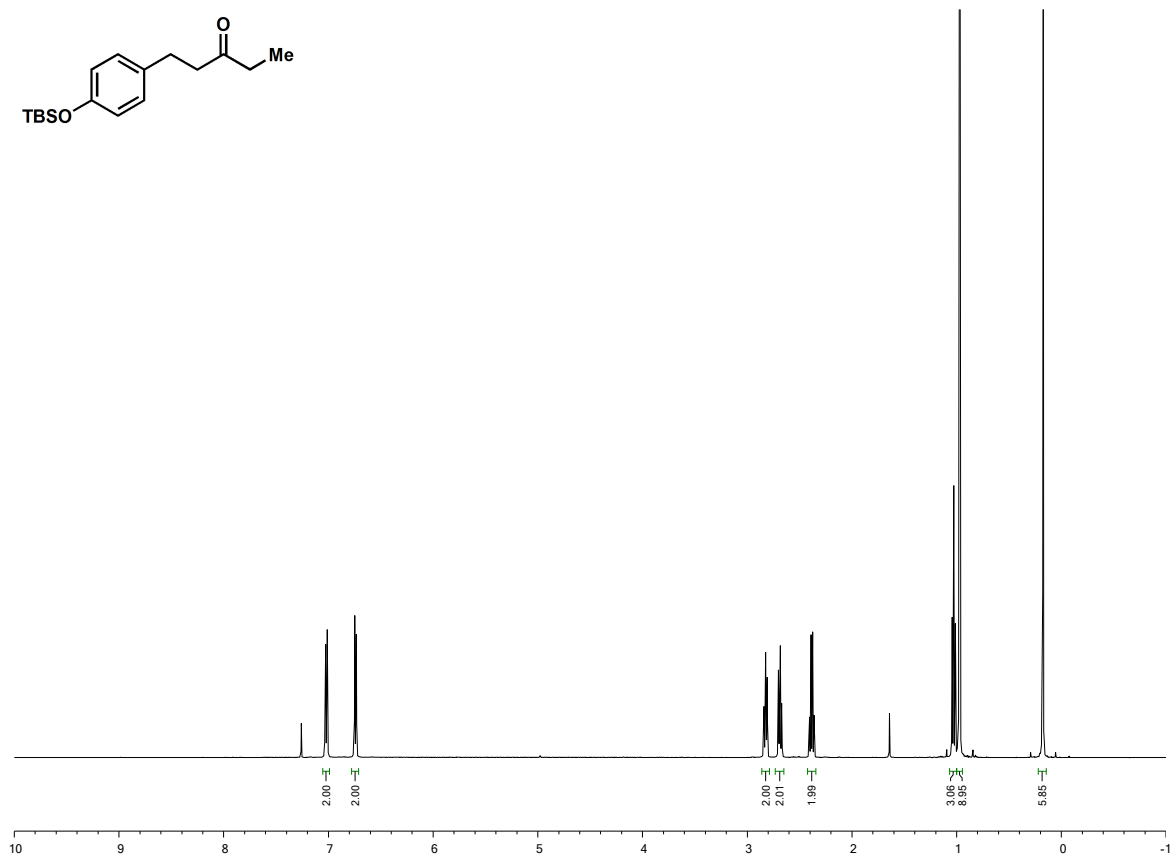
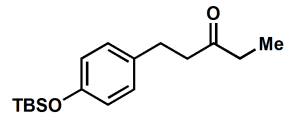
85:15→0:100 hexanes/EtOAc) gave 128 mg (51% overall yield) of **17a** as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 5.64 (s, 1H), 3.674 (d, *J* = 10.5 Hz, 1H), 3.671 (s, 3H), 3.64 (dd, *J* = 11.6, 4.7 Hz), 3.39 (d, *J* = 10.5 Hz, 1H), 2.77 (dt, *J* = 13.3, 3.3 Hz, 1H), 2.35 (s, 1H), 1.79 (td, *J* = 13.6, 4.4 Hz, 1H), 1.34 (s, 3H), 1.16 (s, 3H), 1.13 (s, 3H), 1.10 (s, 3H), 0.85 (s, 3H), 0.78 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 200.3, 177.1, 169.6, 128.6, 75.8, 70.6, 61.8, 51.9, 49.1, 48.5, 45.5, 44.2, 43.4, 42.4, 41.2, 38.9, 37.9, 37.1, 32.6, 32.0, 31.2, 28.6, 28.4, 26.9, 26.6, 26.5, 23.5, 18.8, 17.6, 16.8, 11.7; HRMS (ESI+) calcd for [C₃₁H₄₉O₅]⁺ (M+H)⁺: *m/z* 501.3580, found 501.3582.

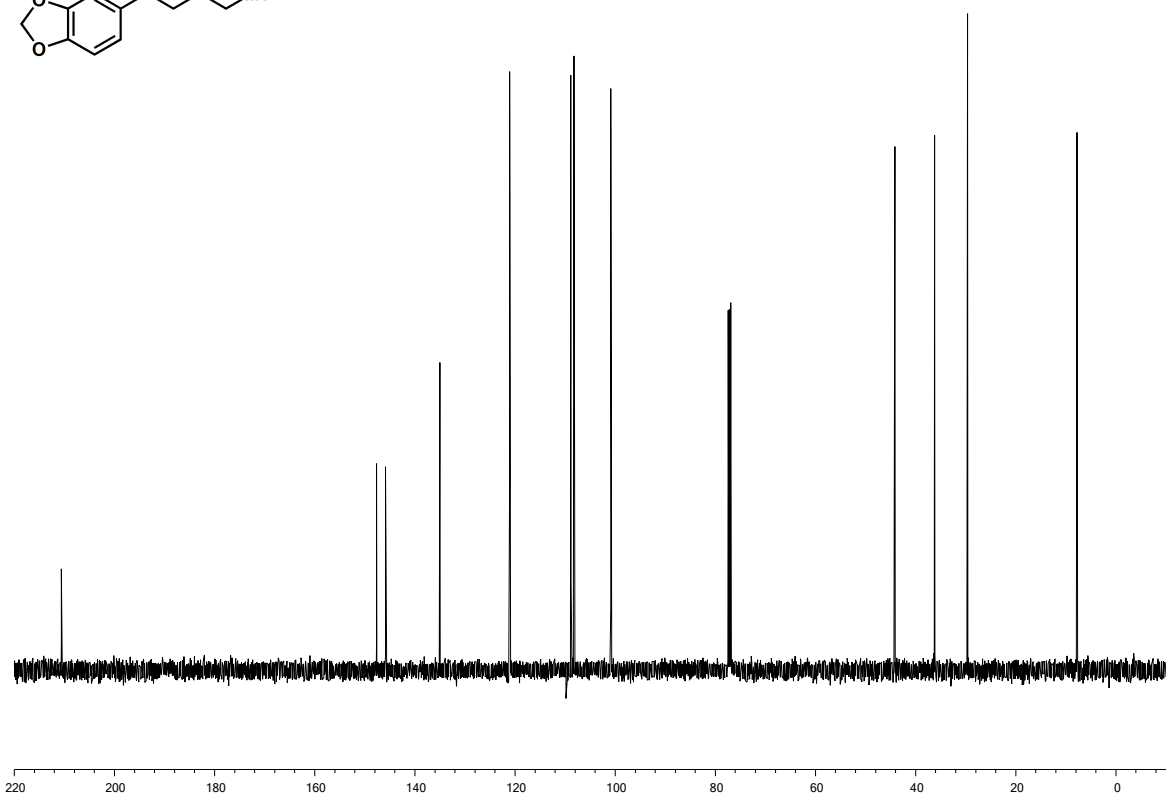
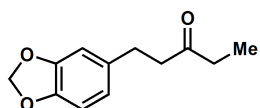
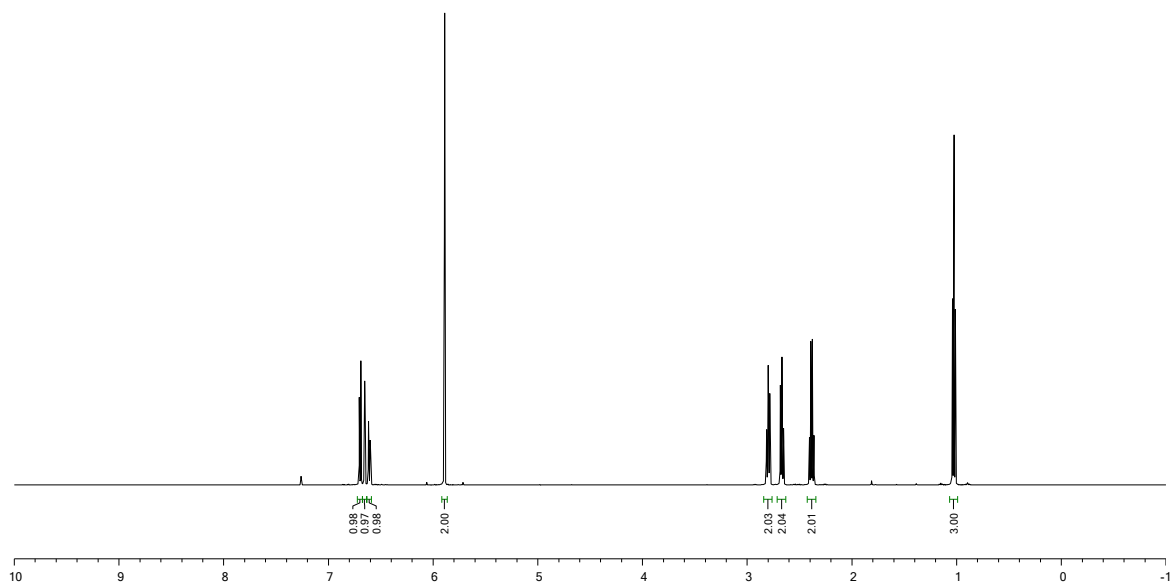
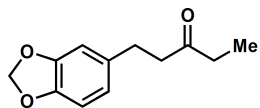


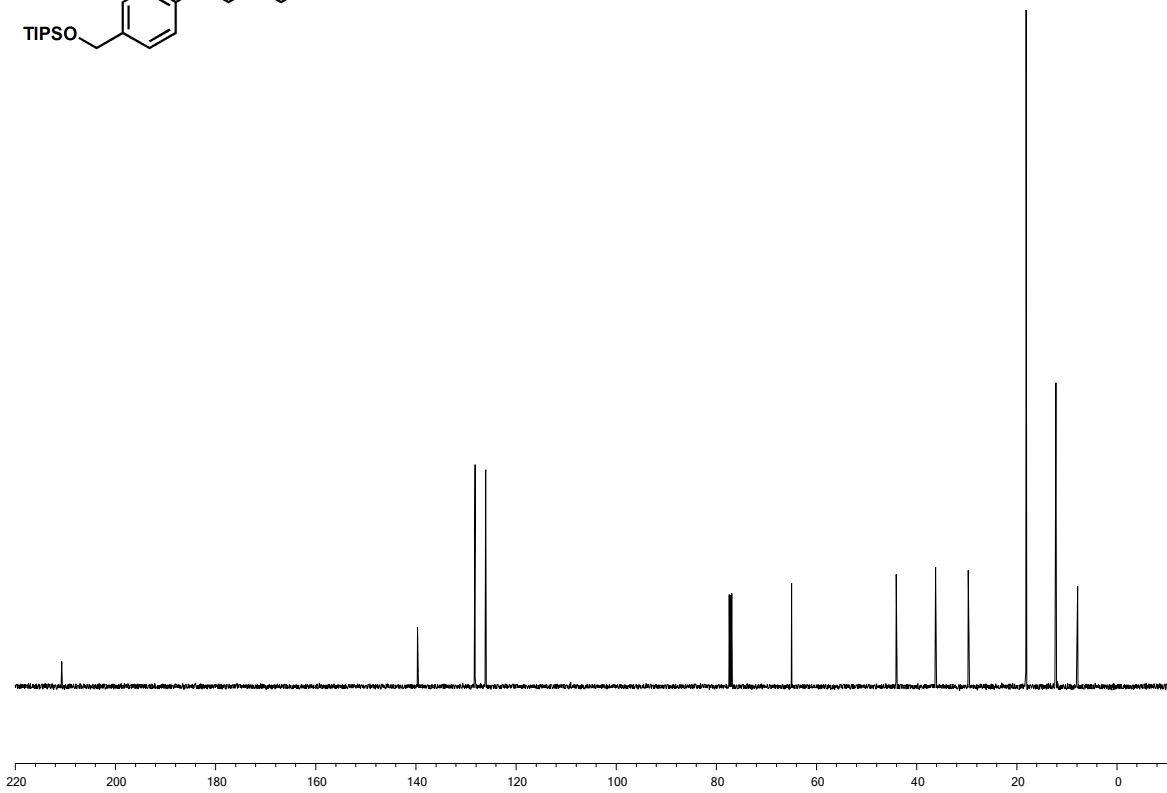
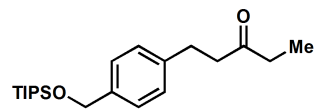
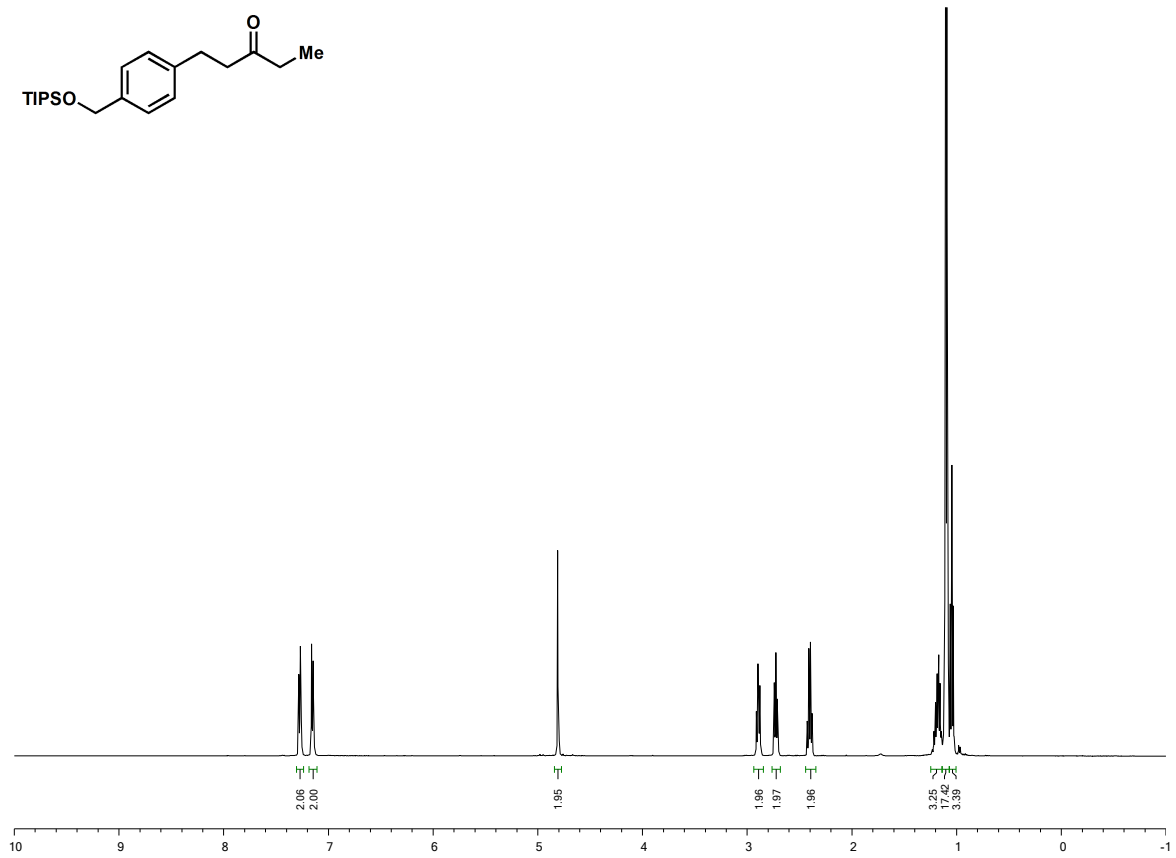
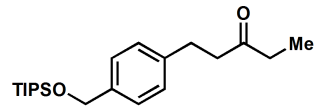


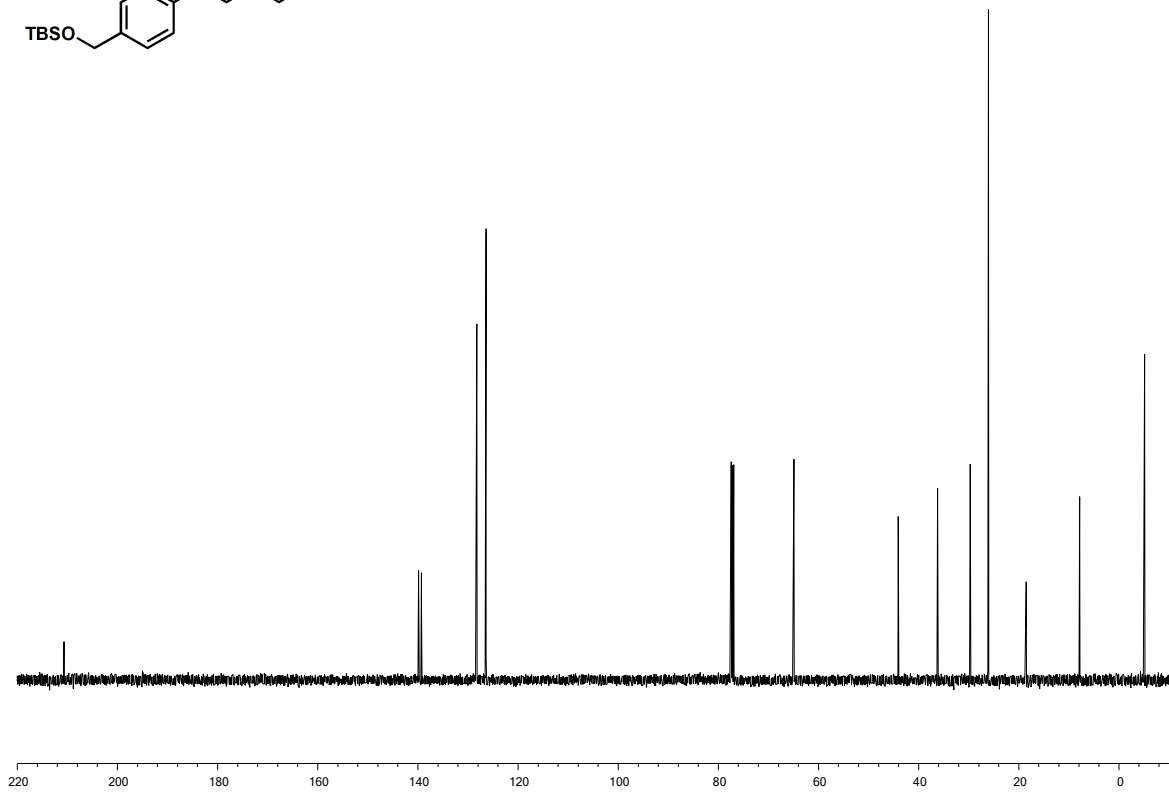
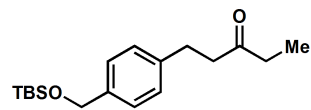
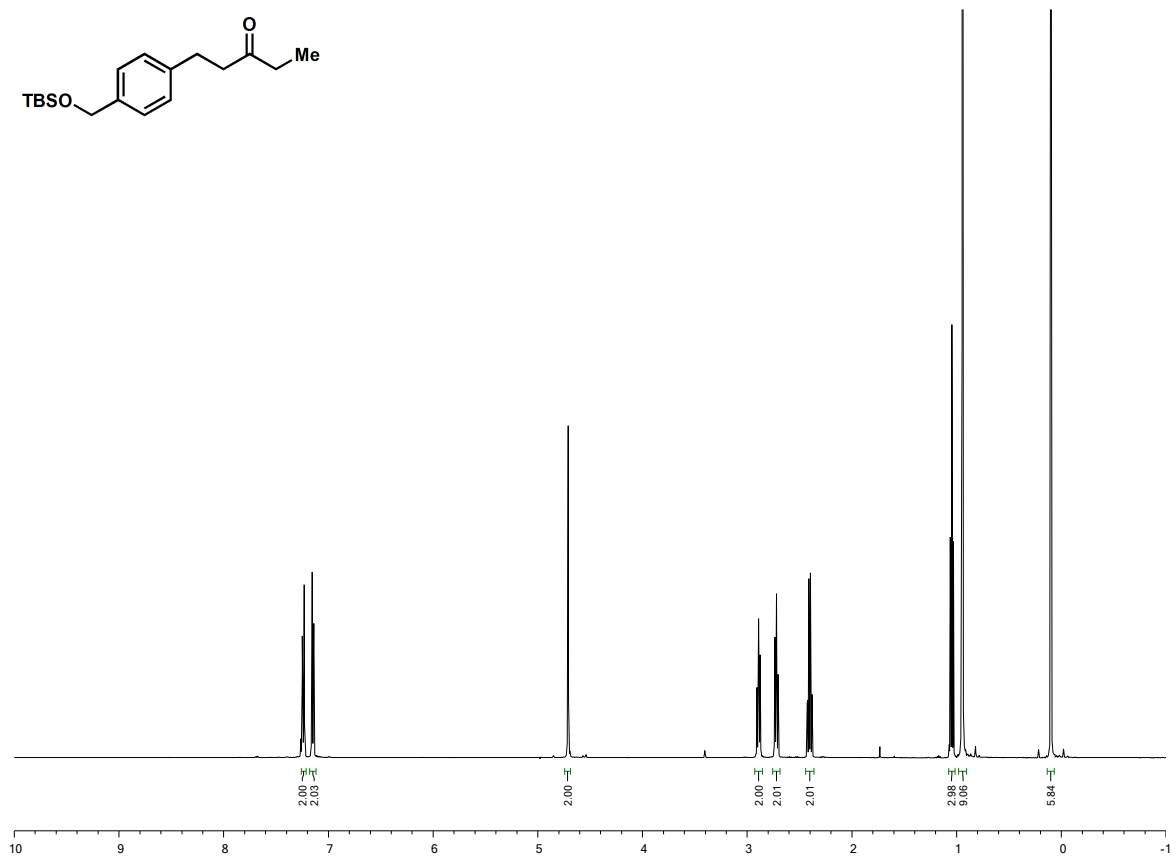
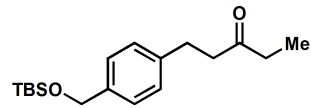


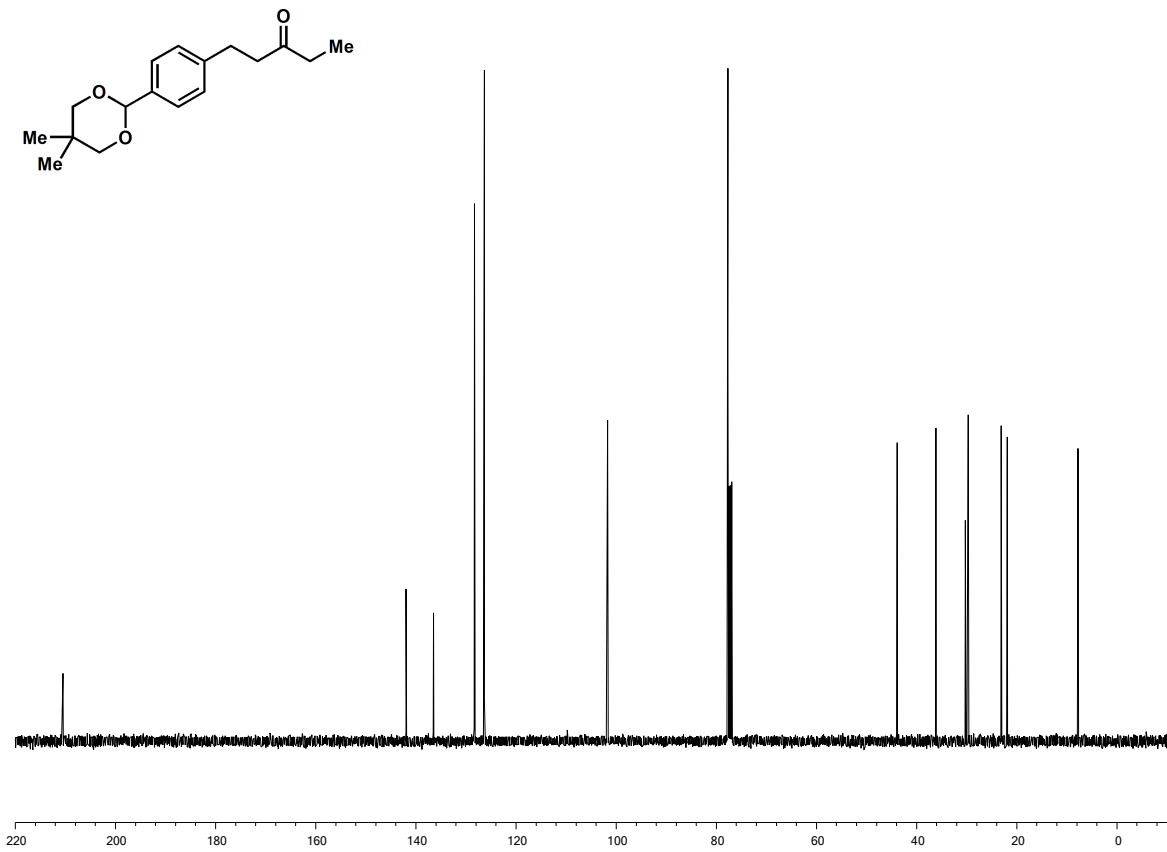
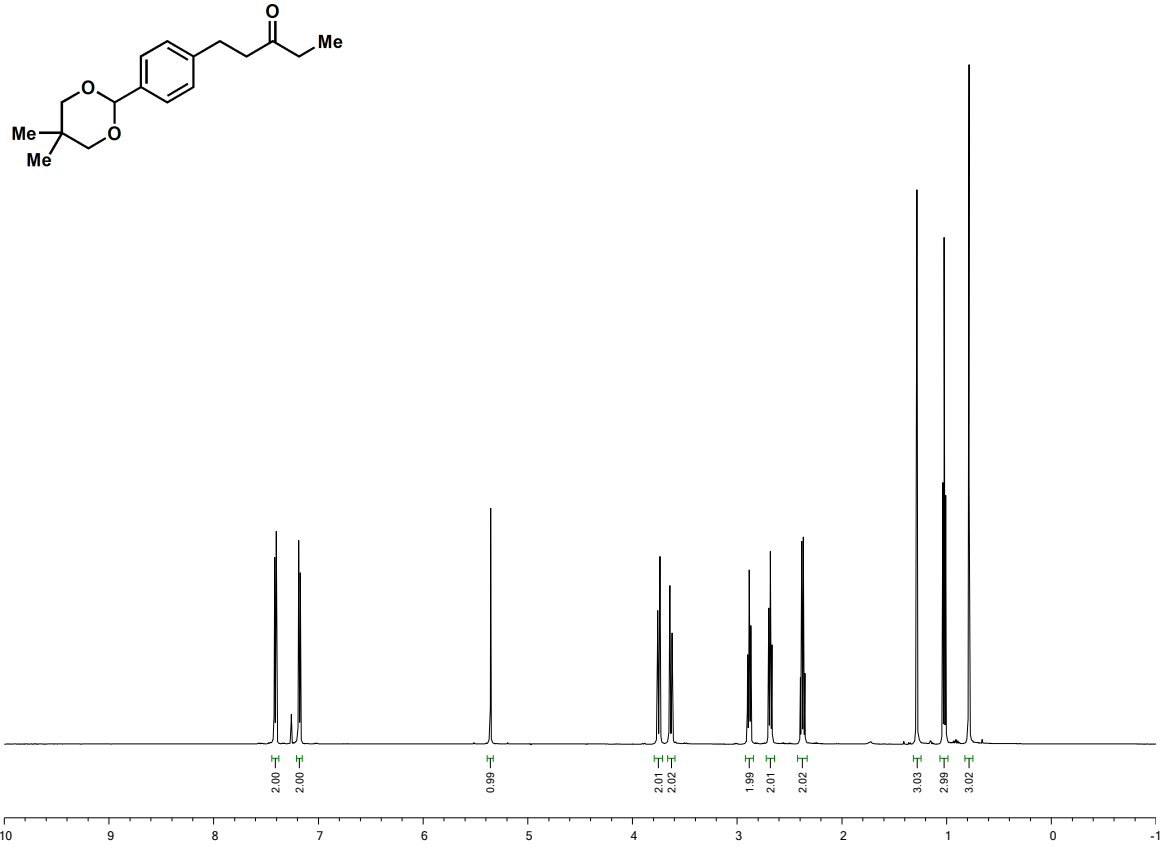


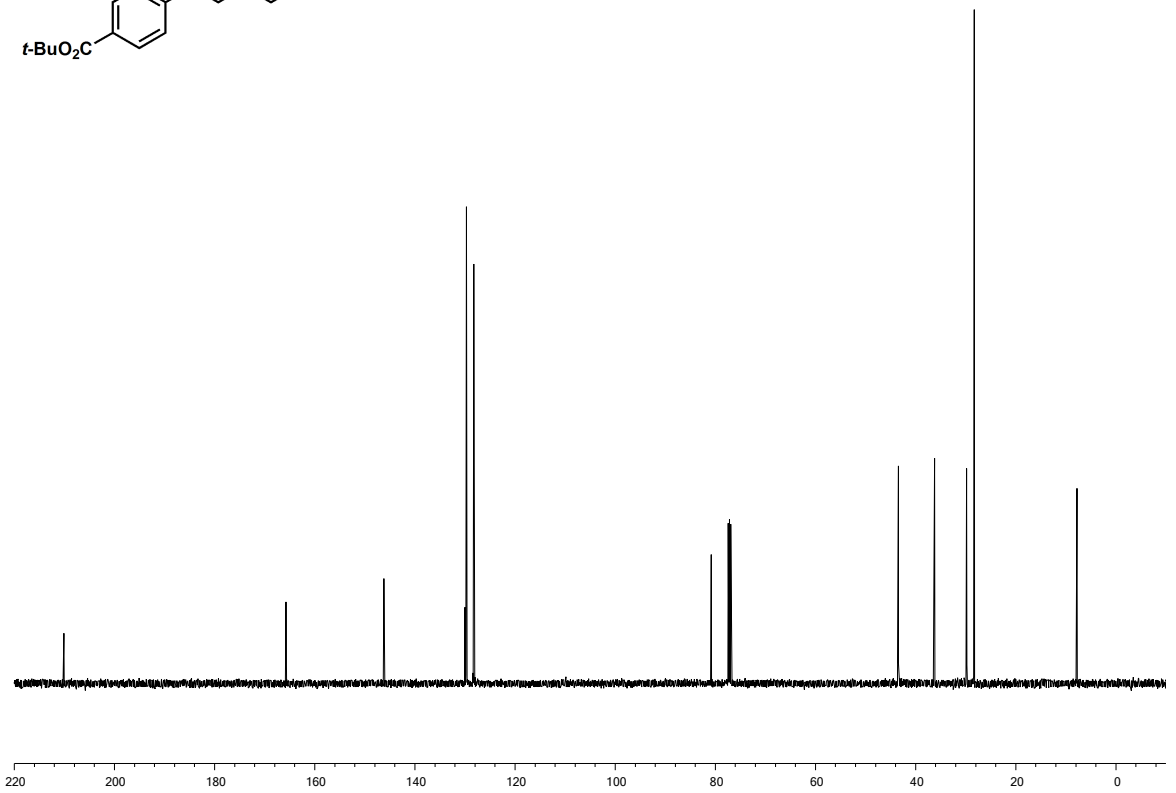
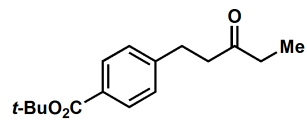
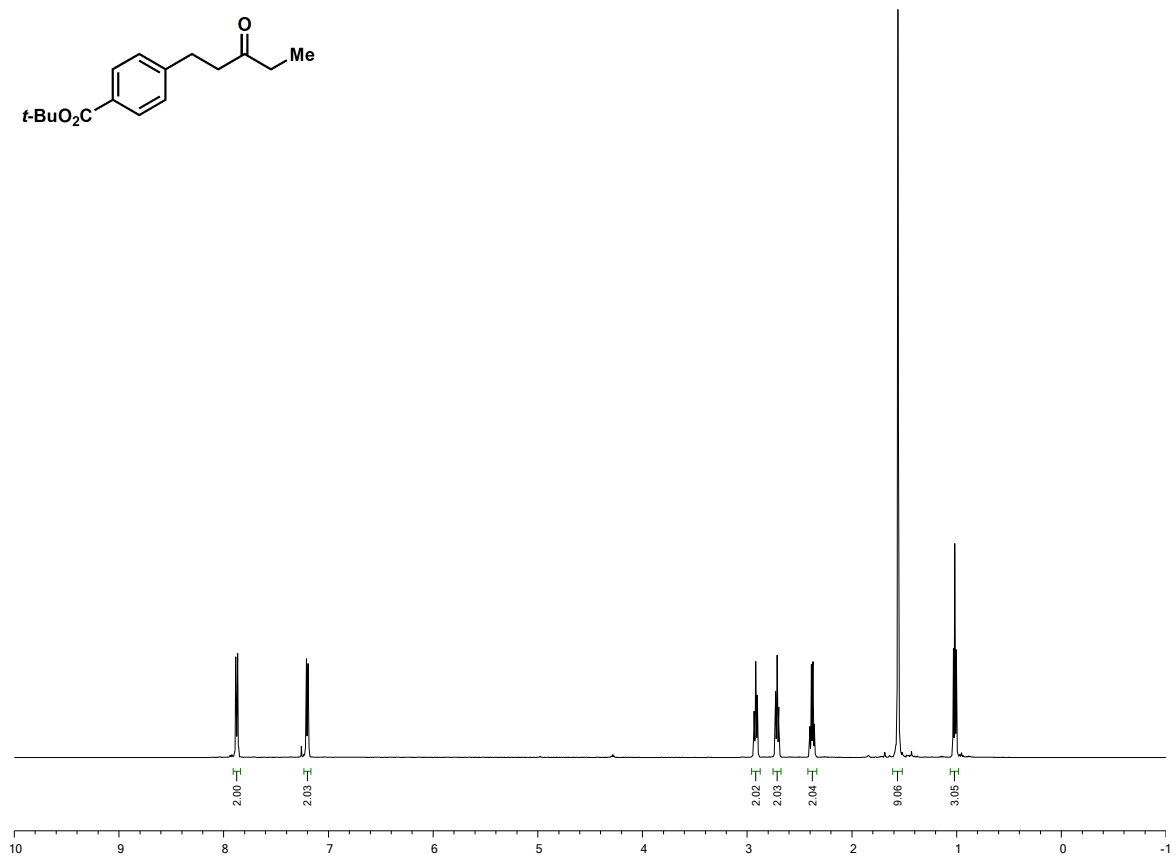
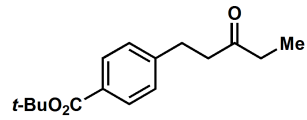


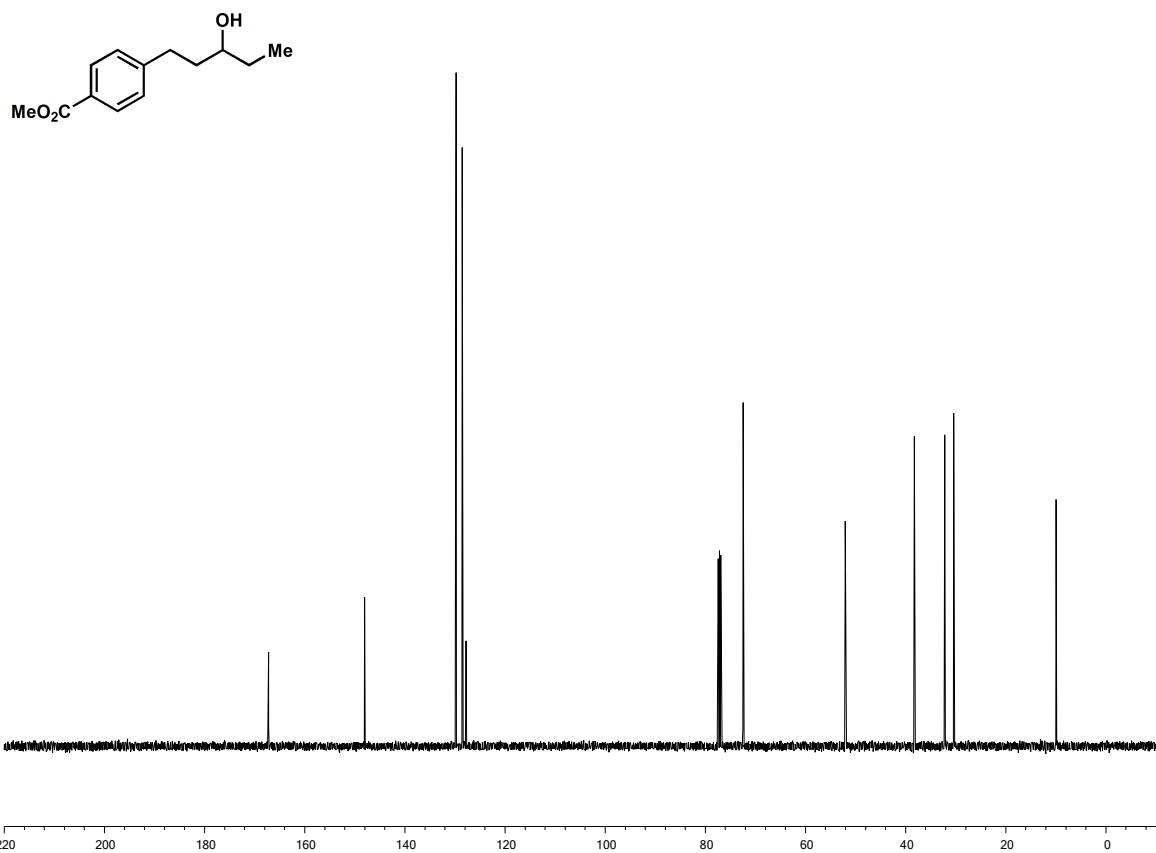
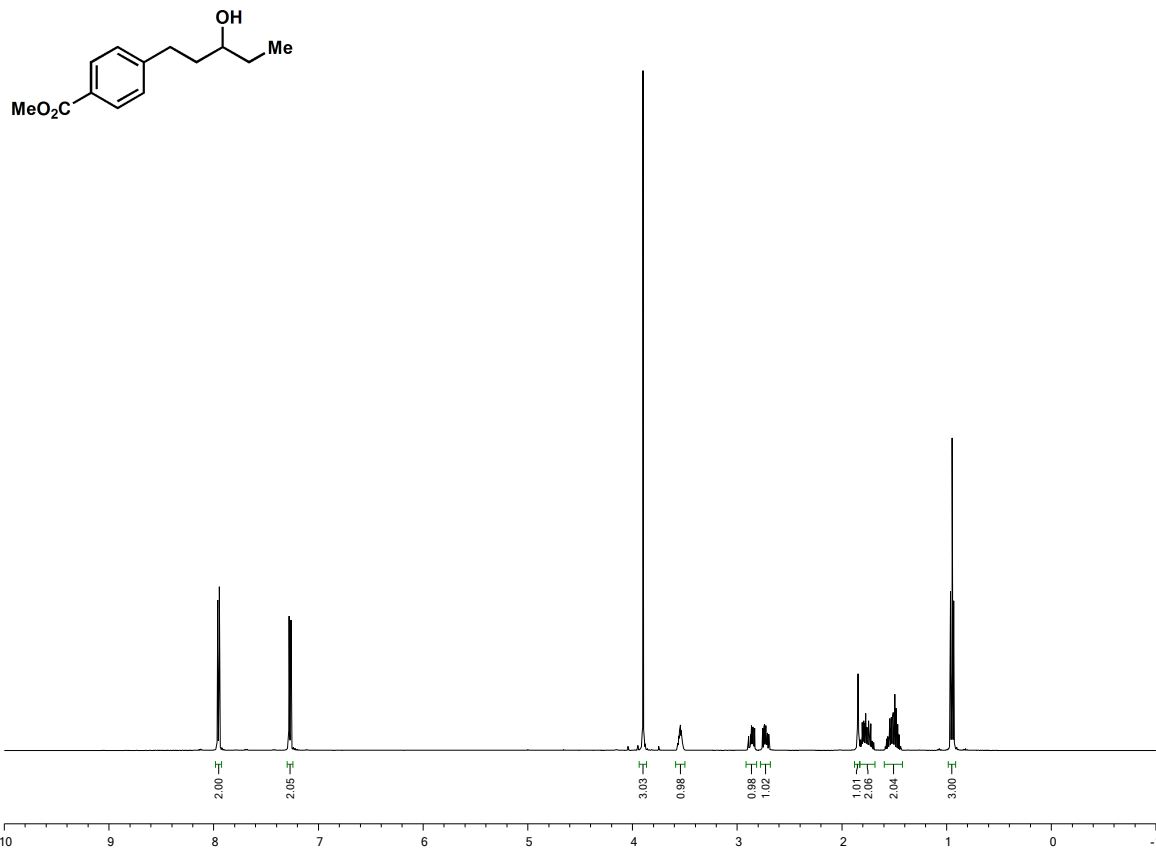


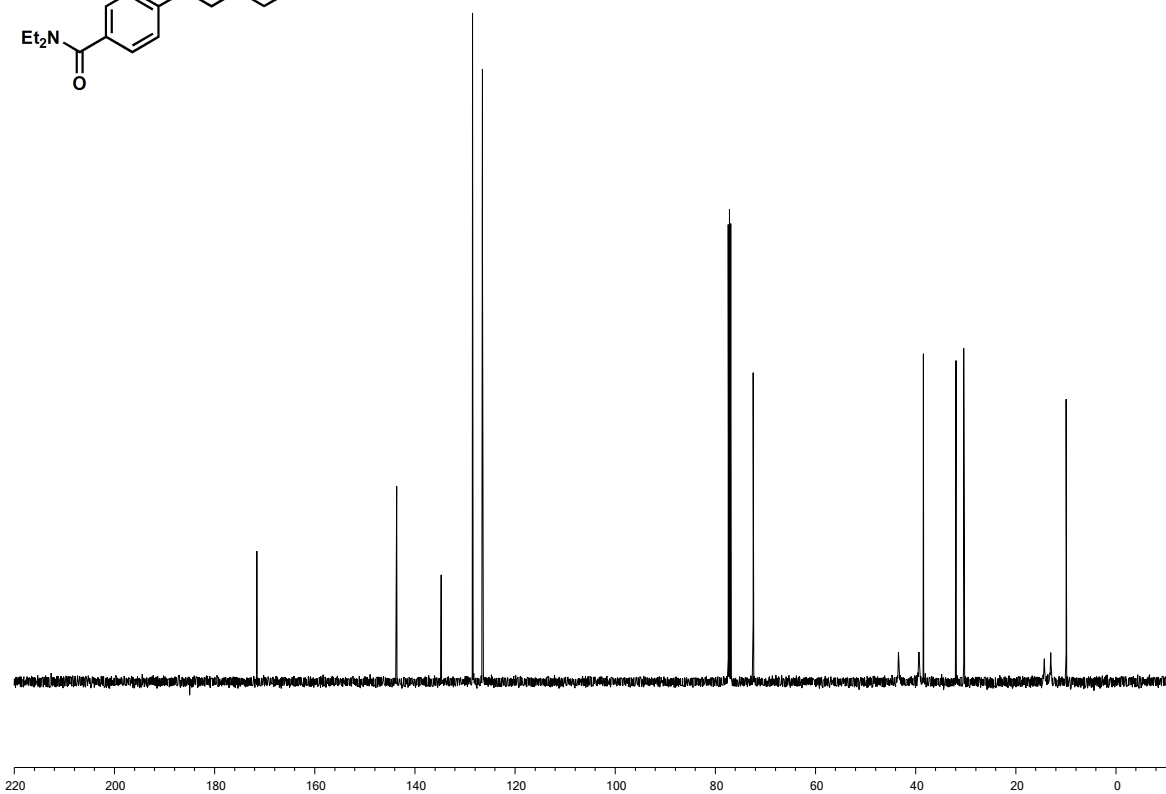
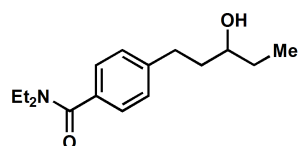
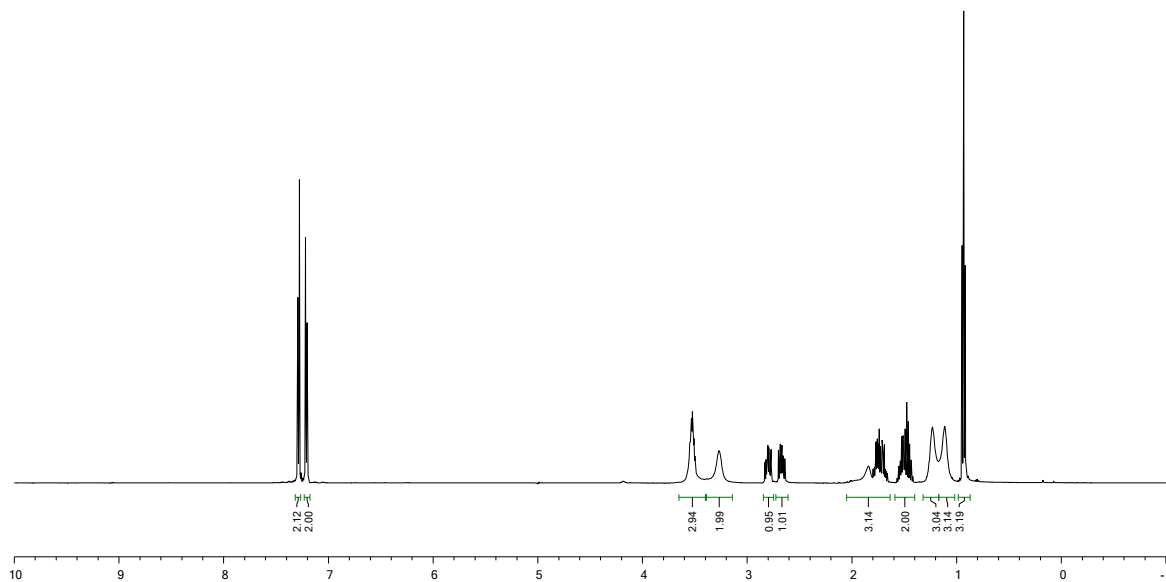
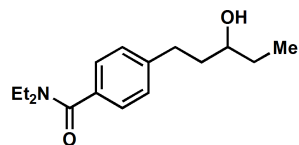


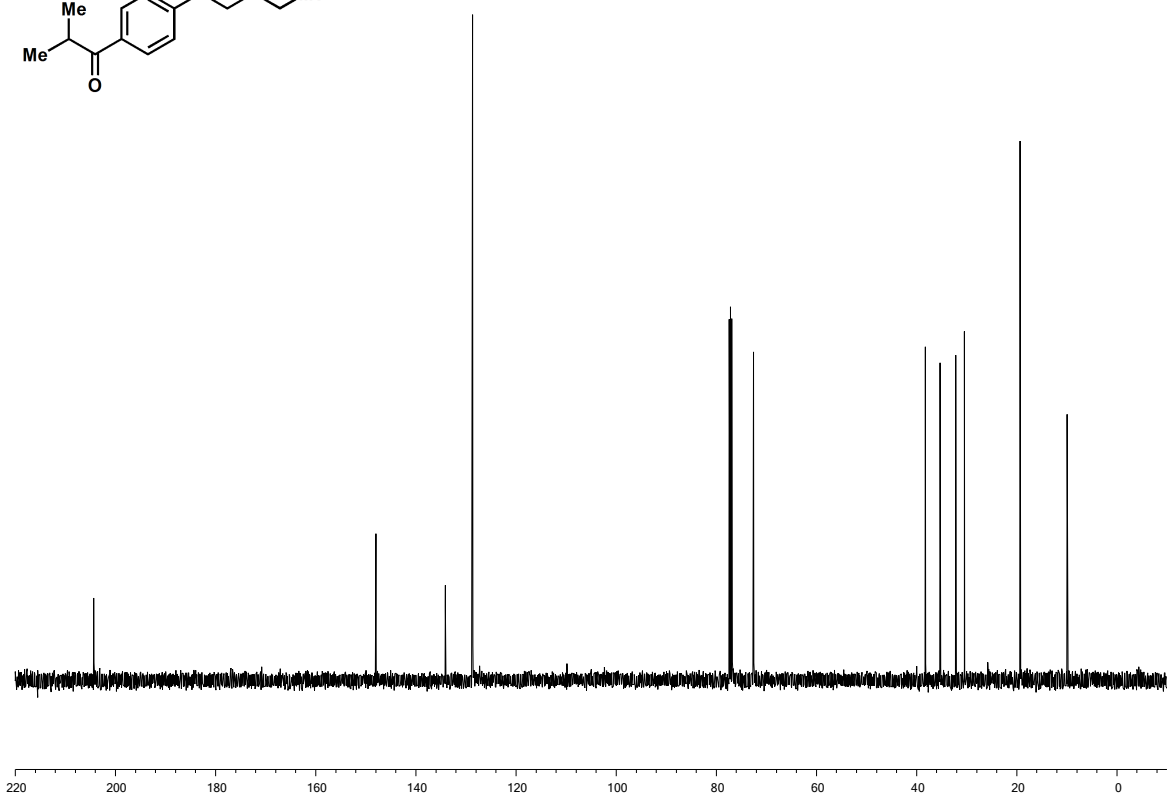
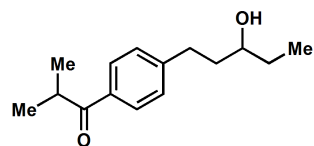
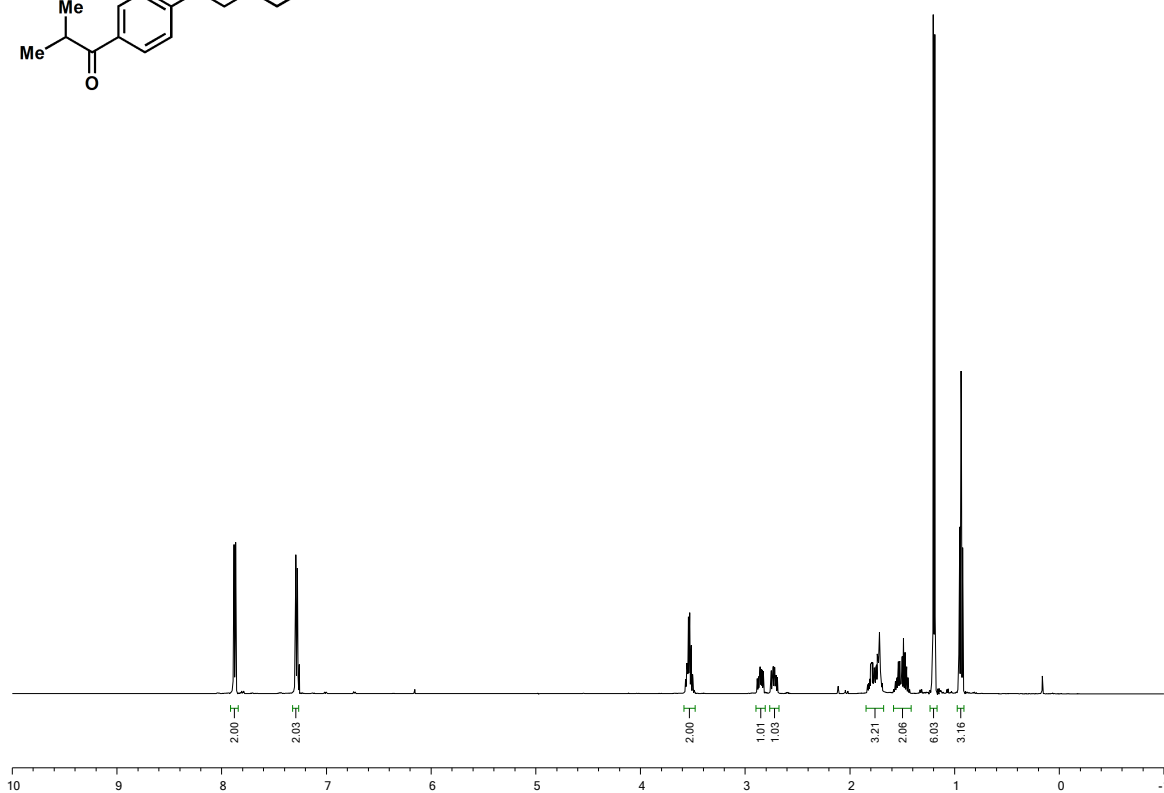
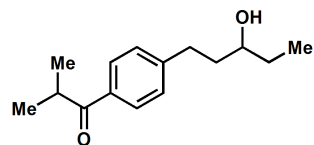


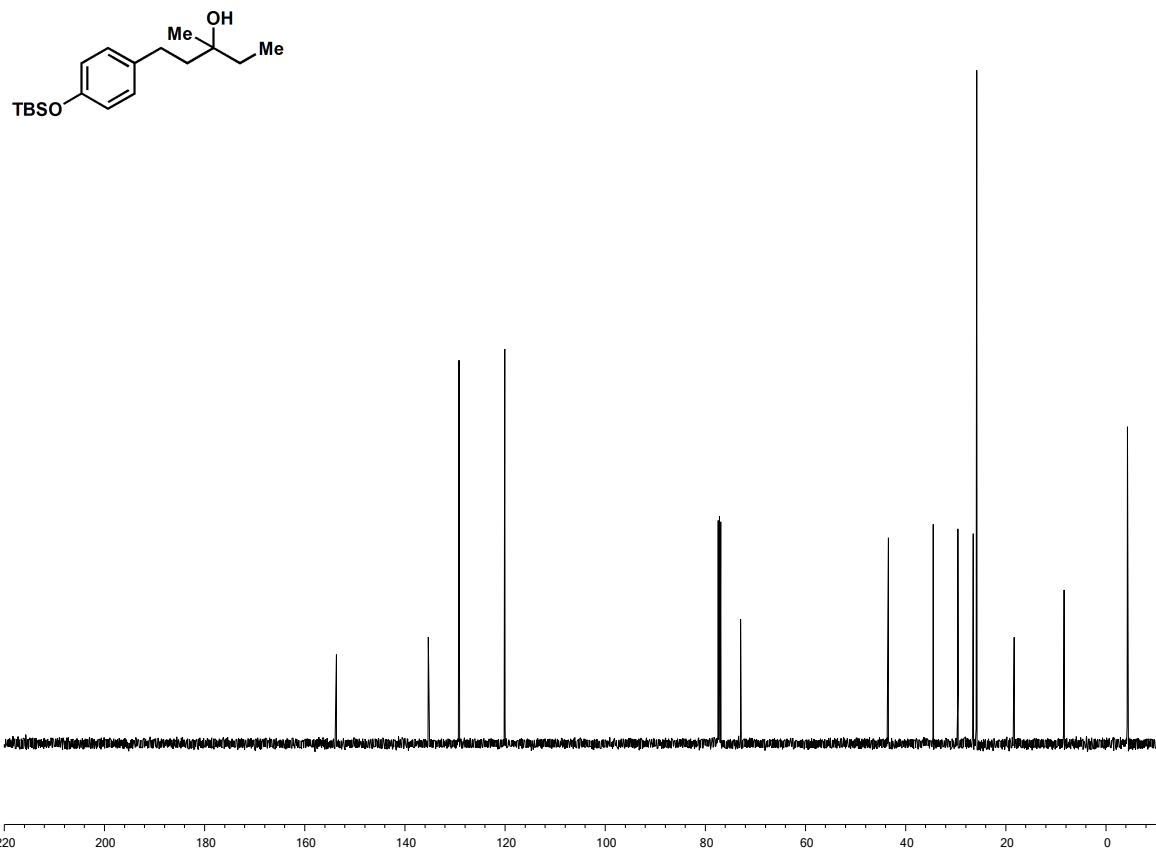
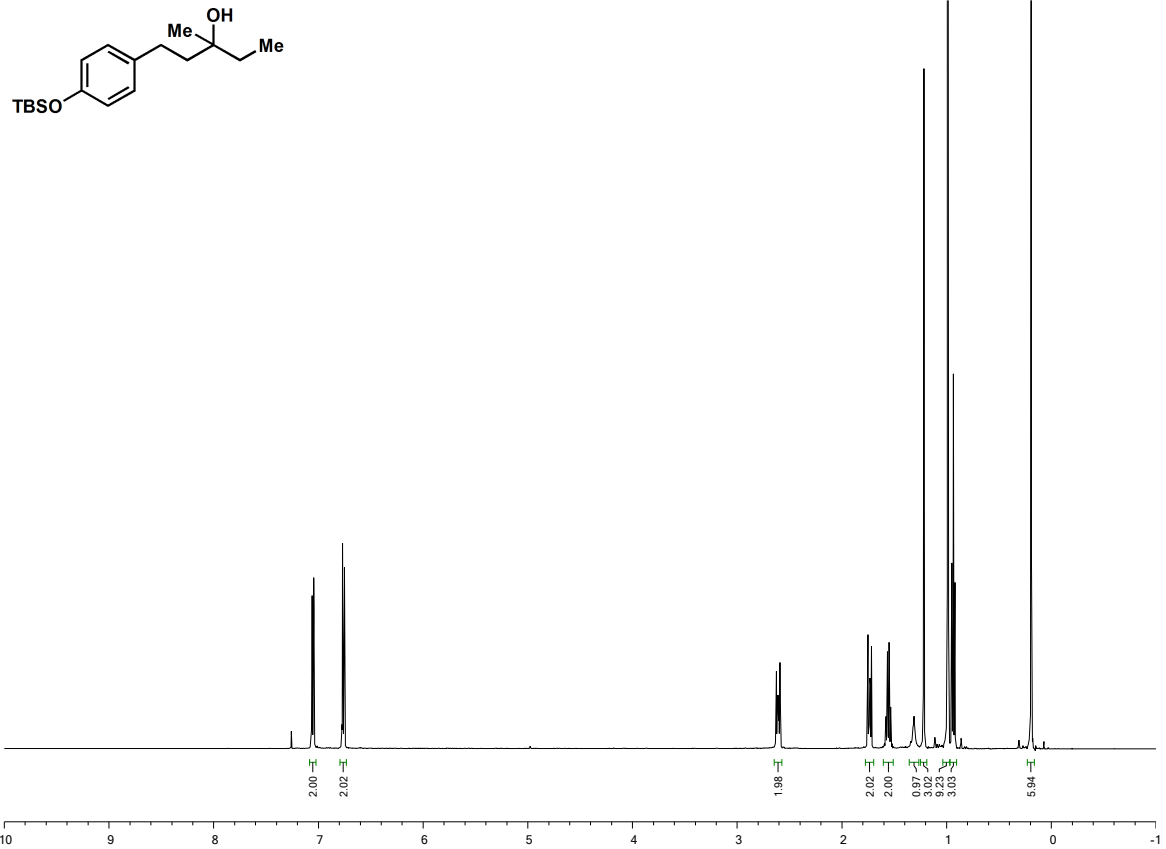


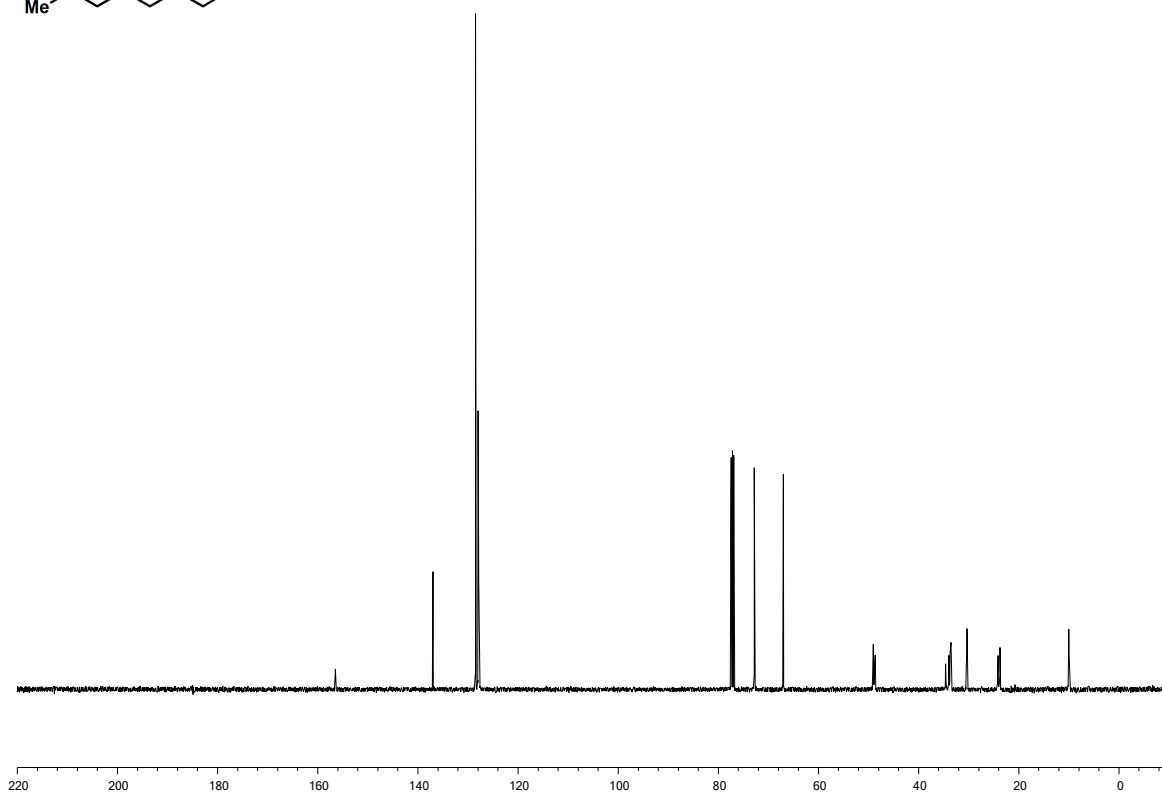
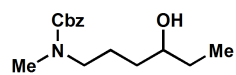
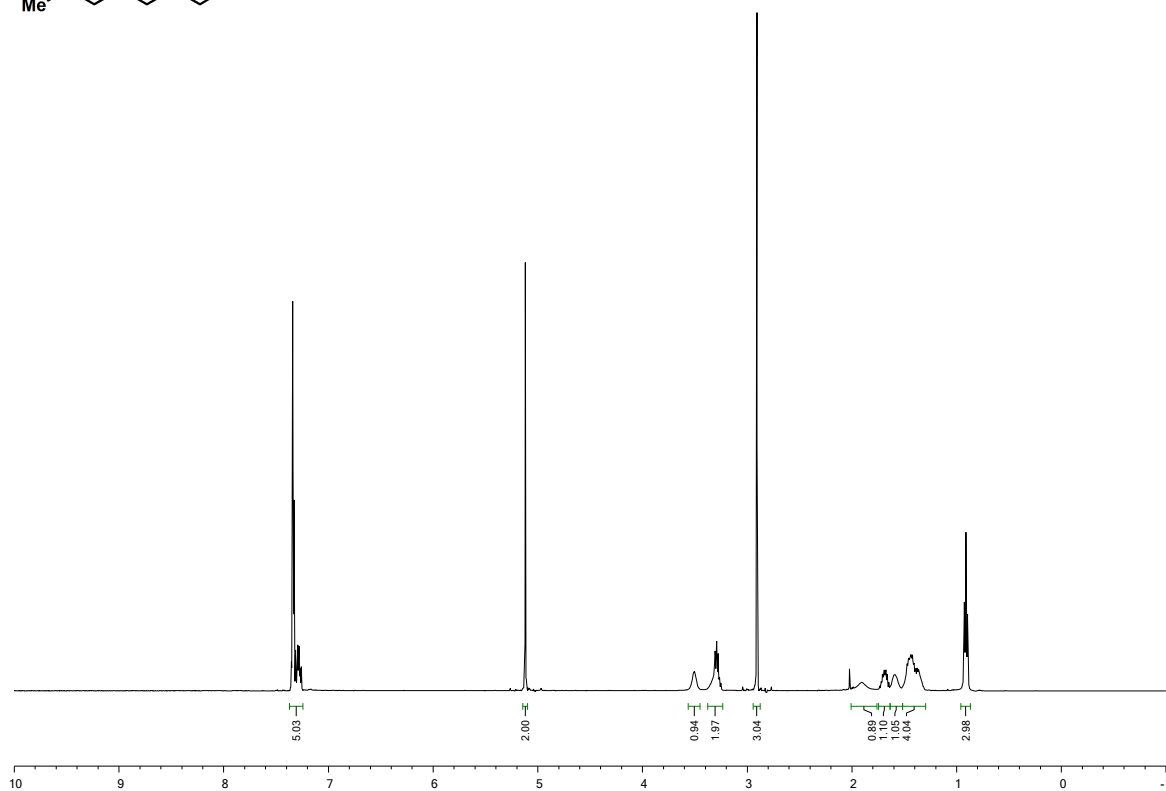
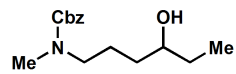


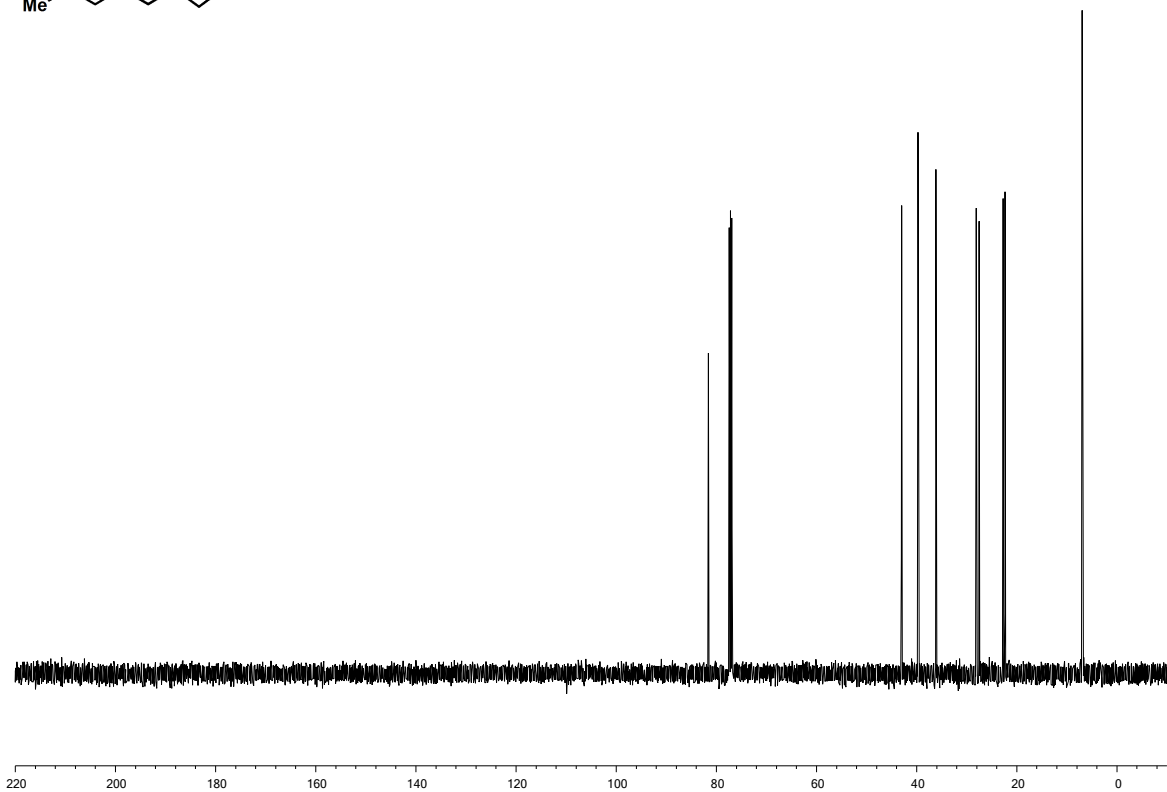
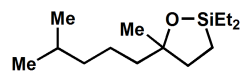
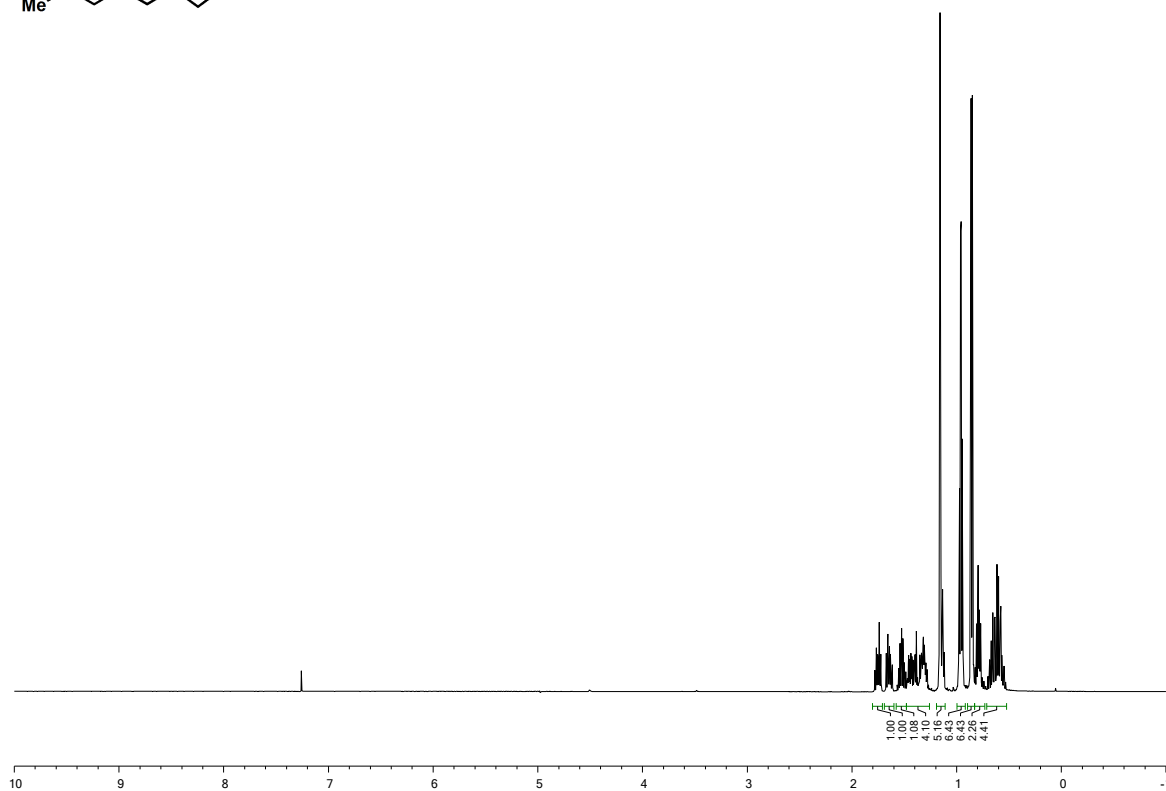
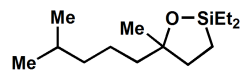


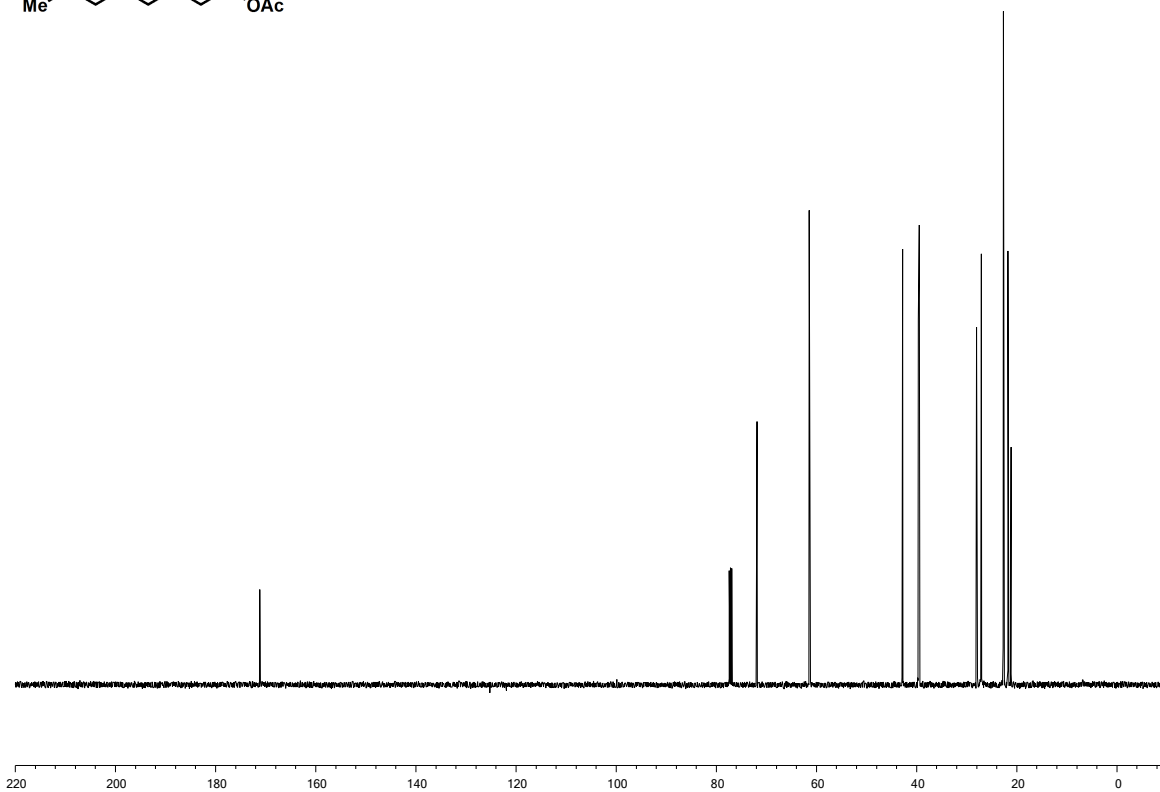
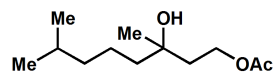
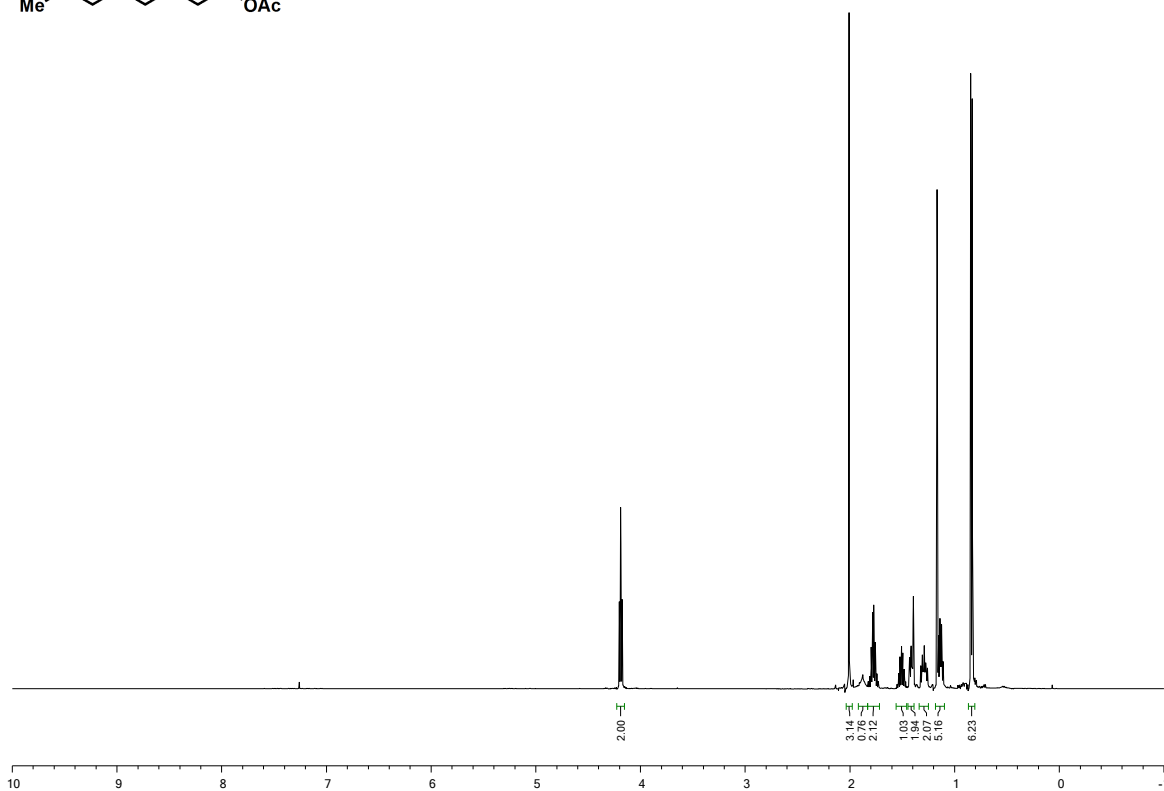
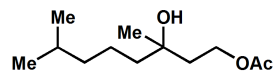


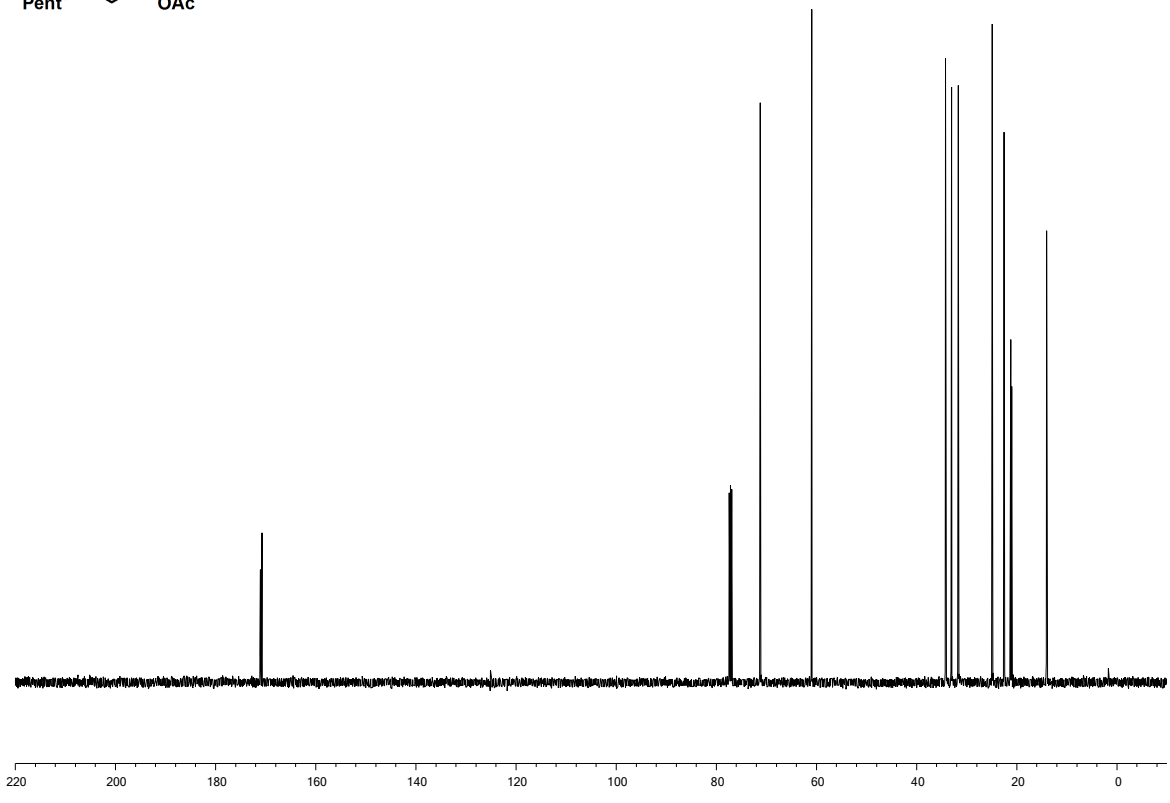
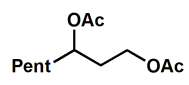
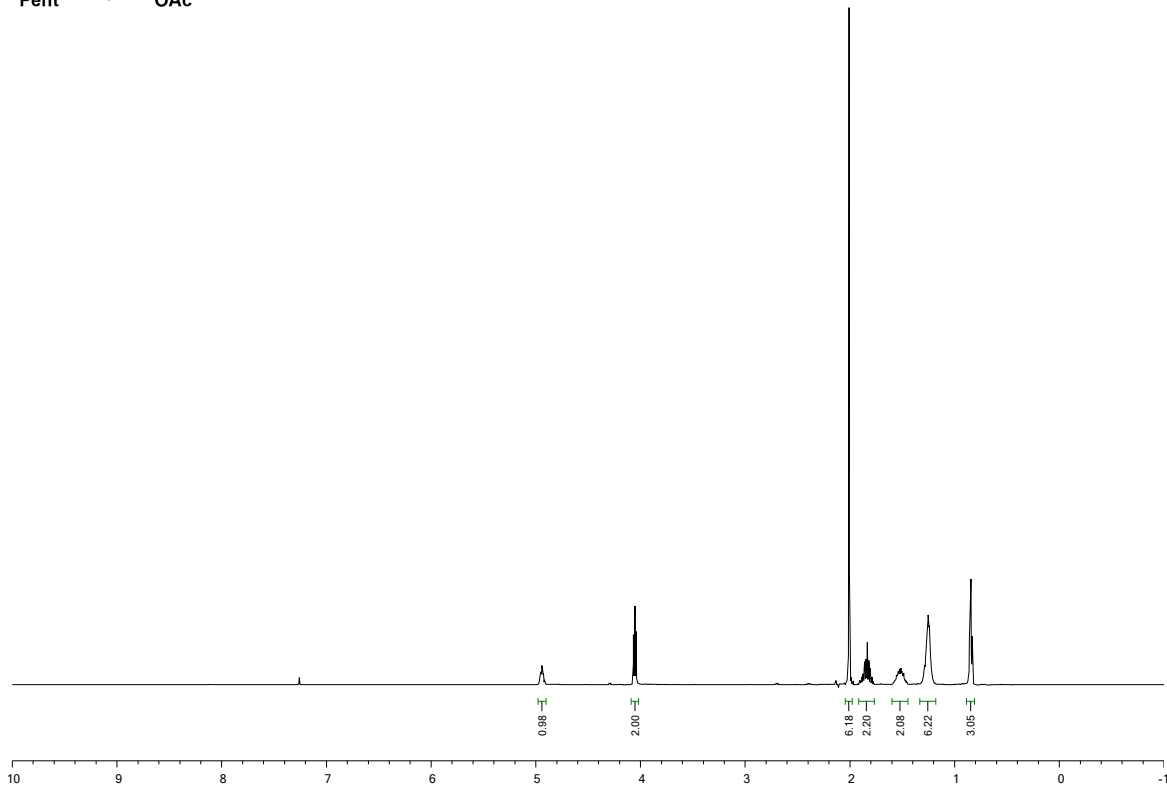
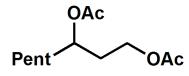


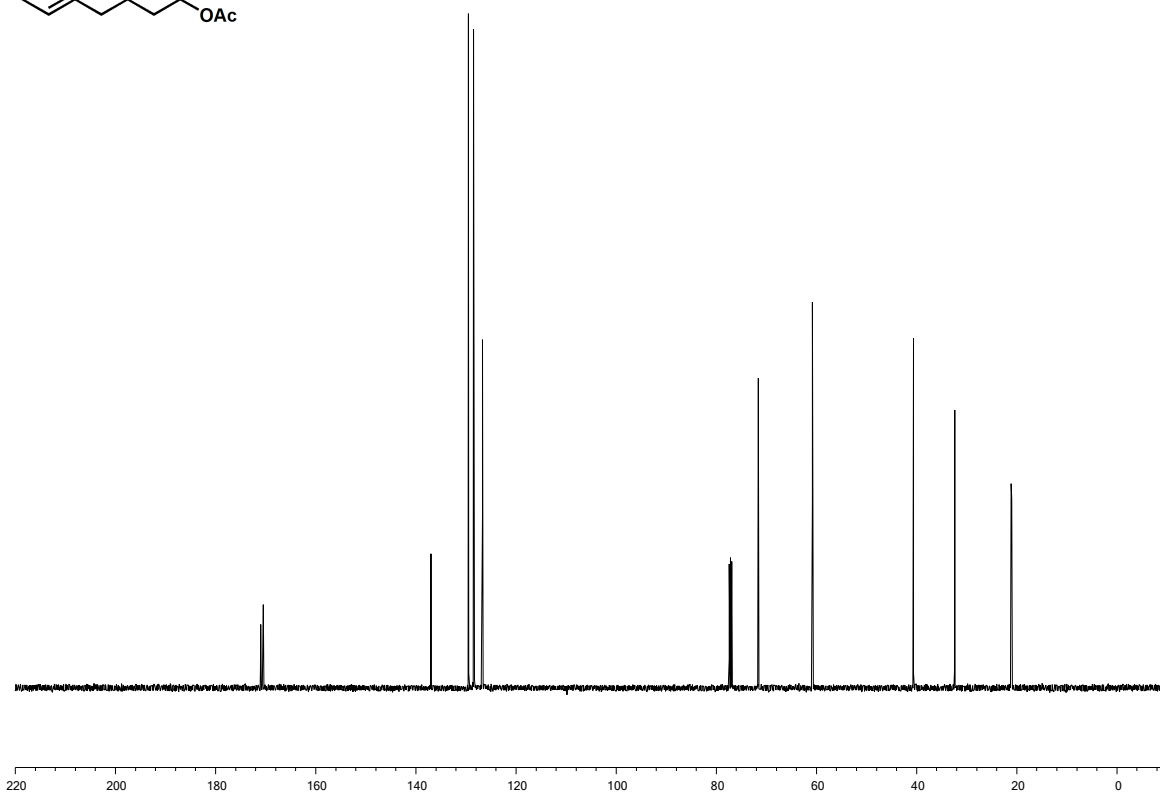
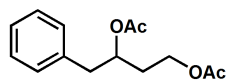
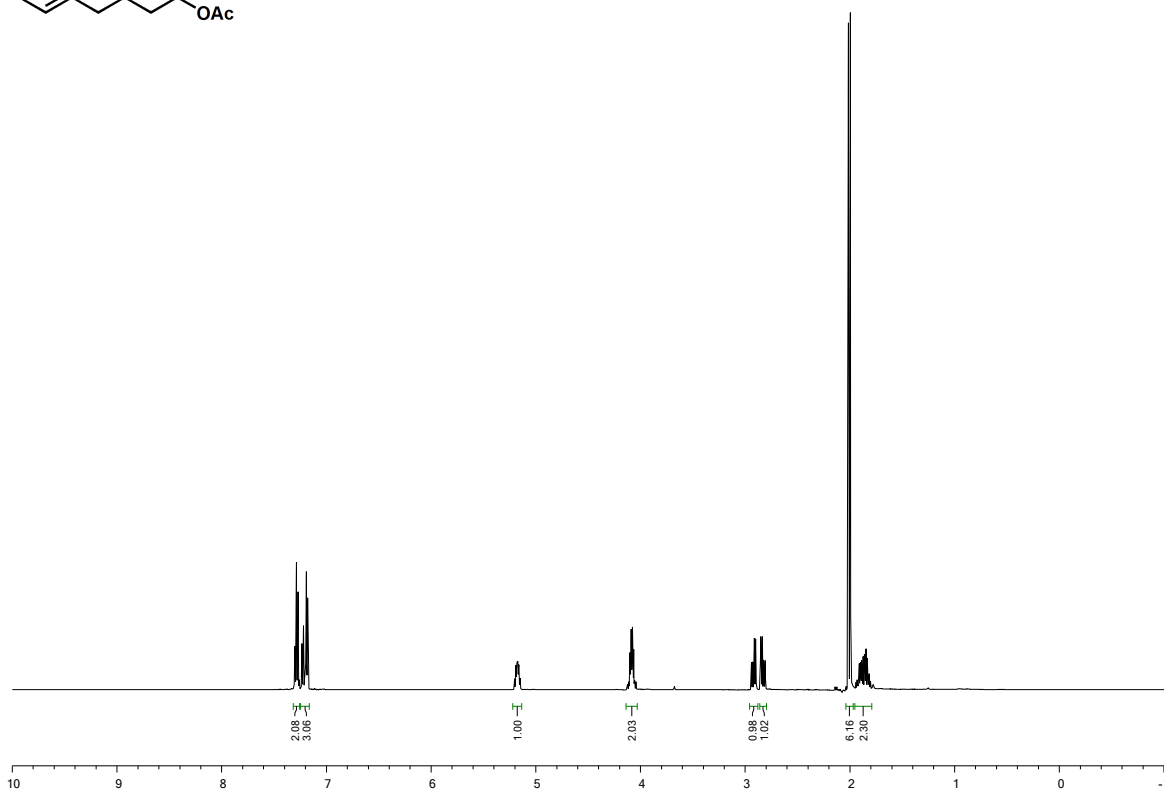
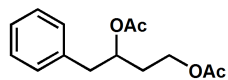


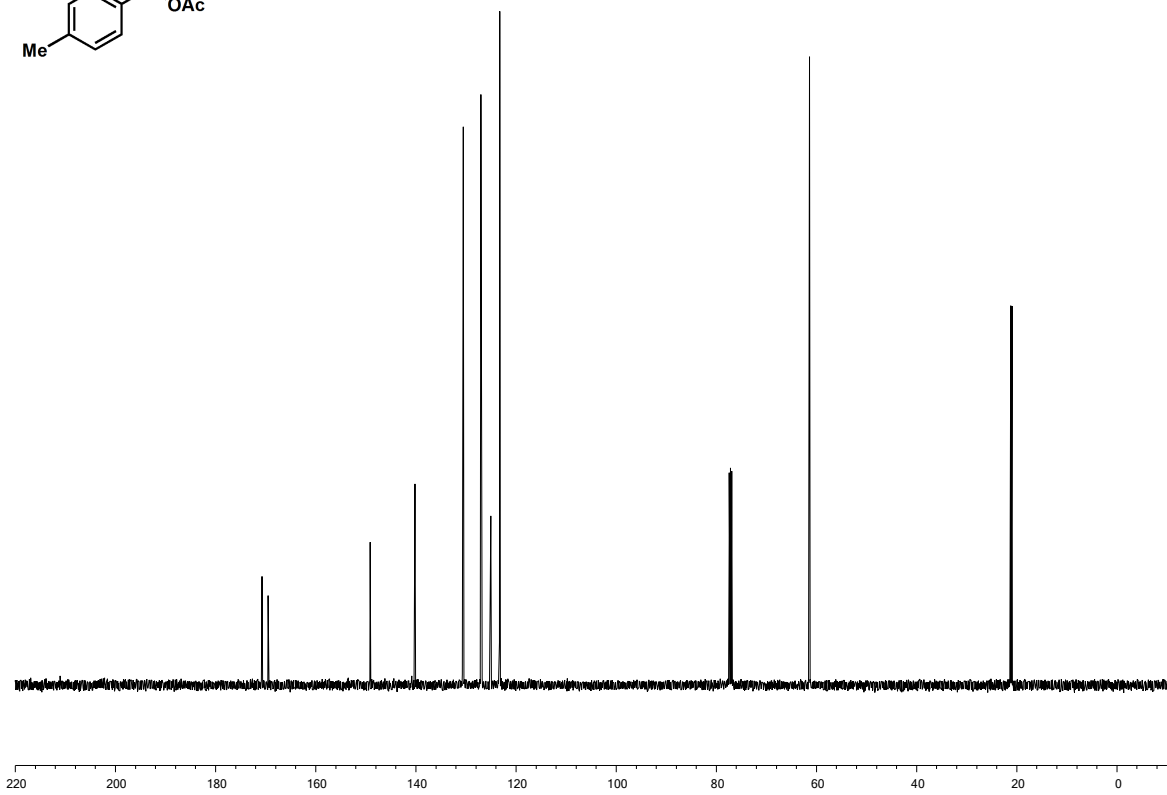
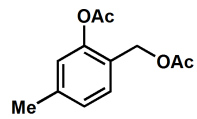
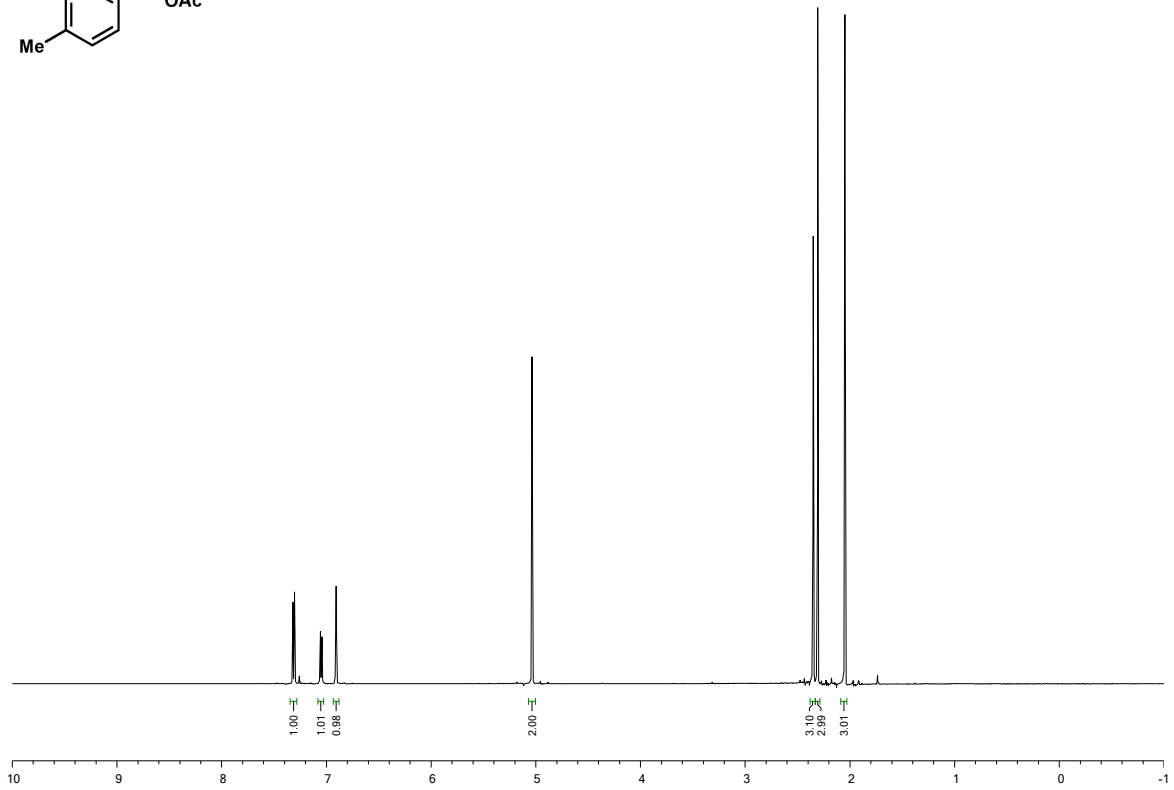
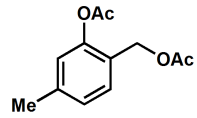


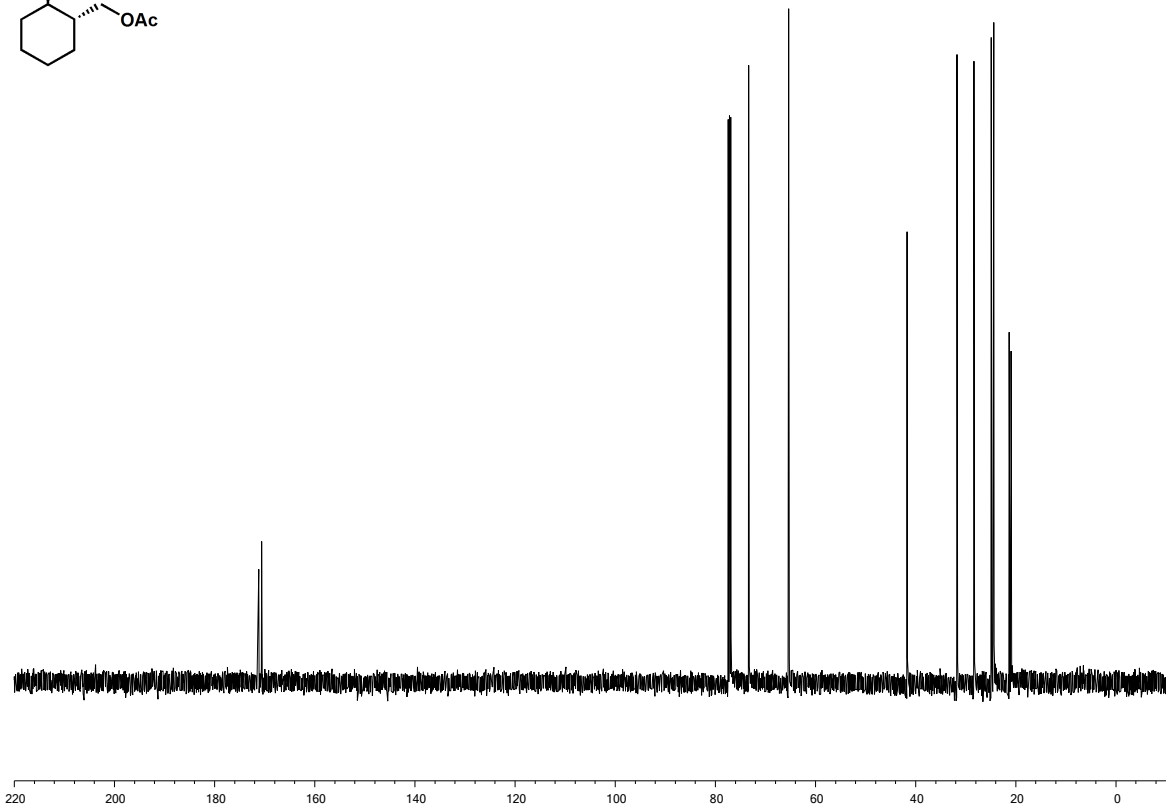
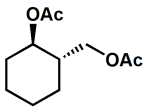
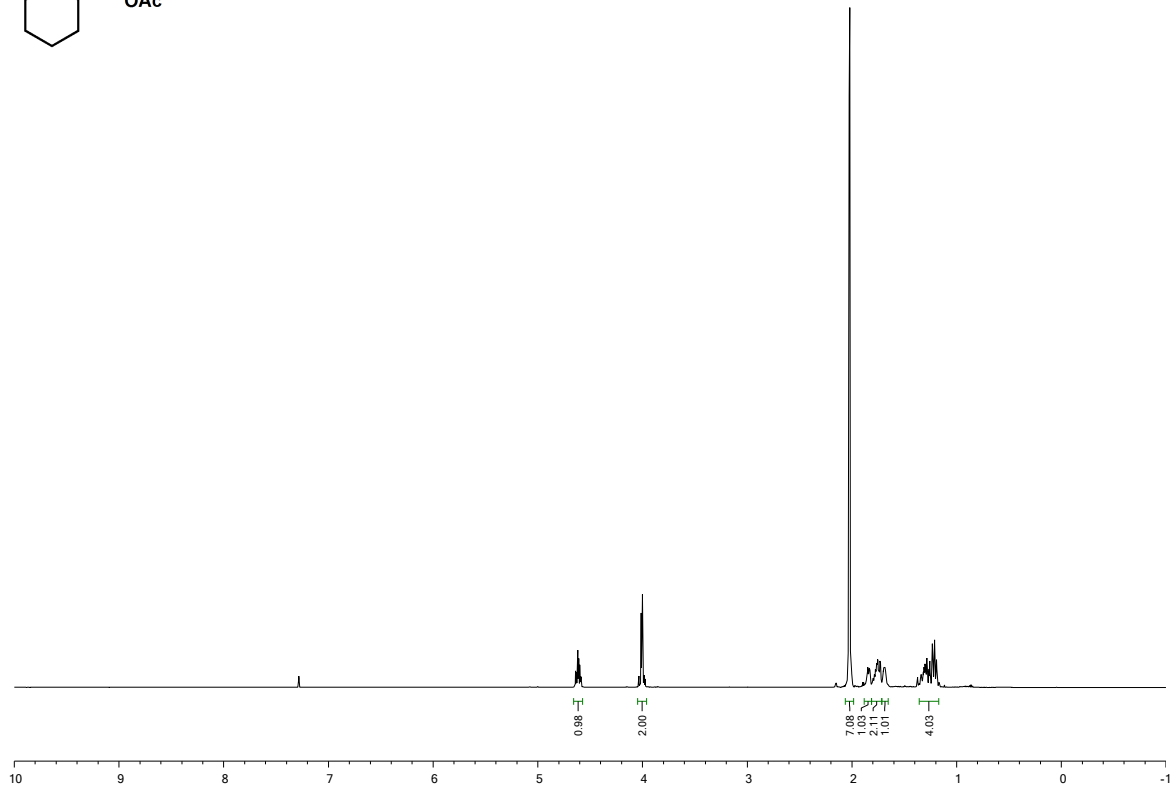
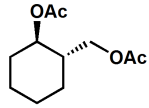


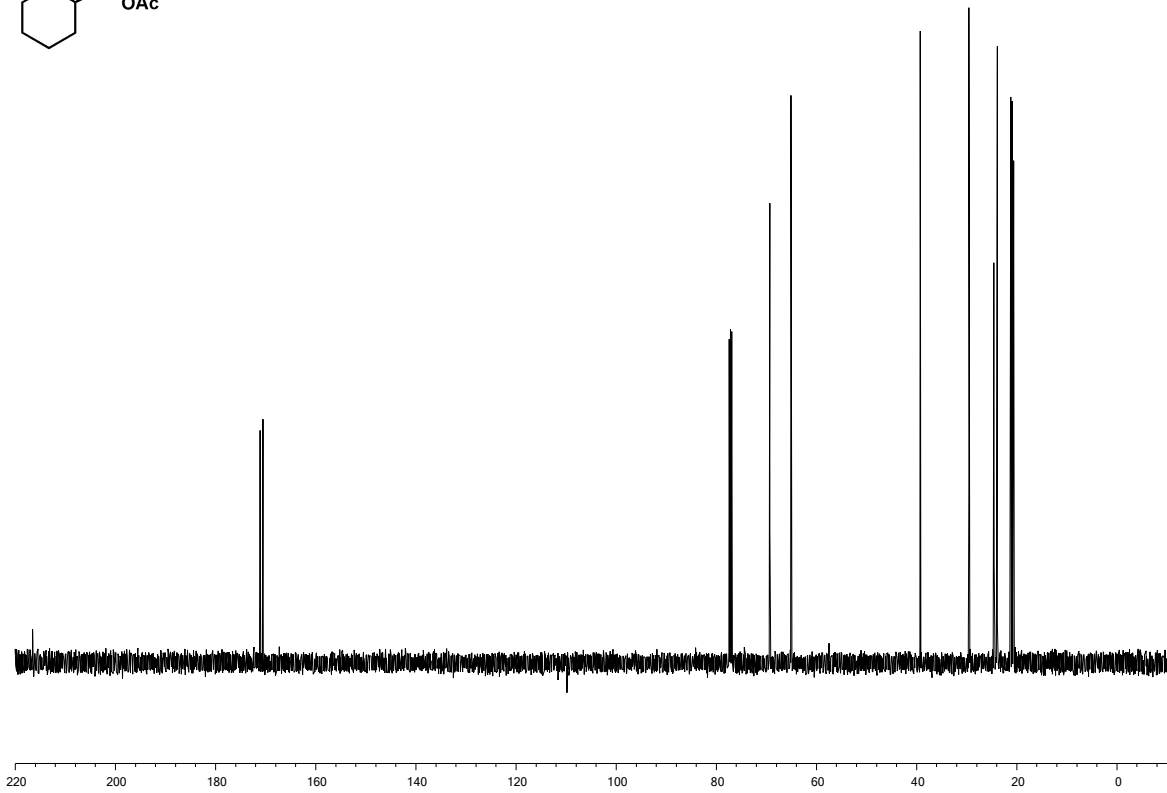
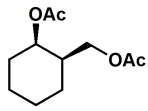
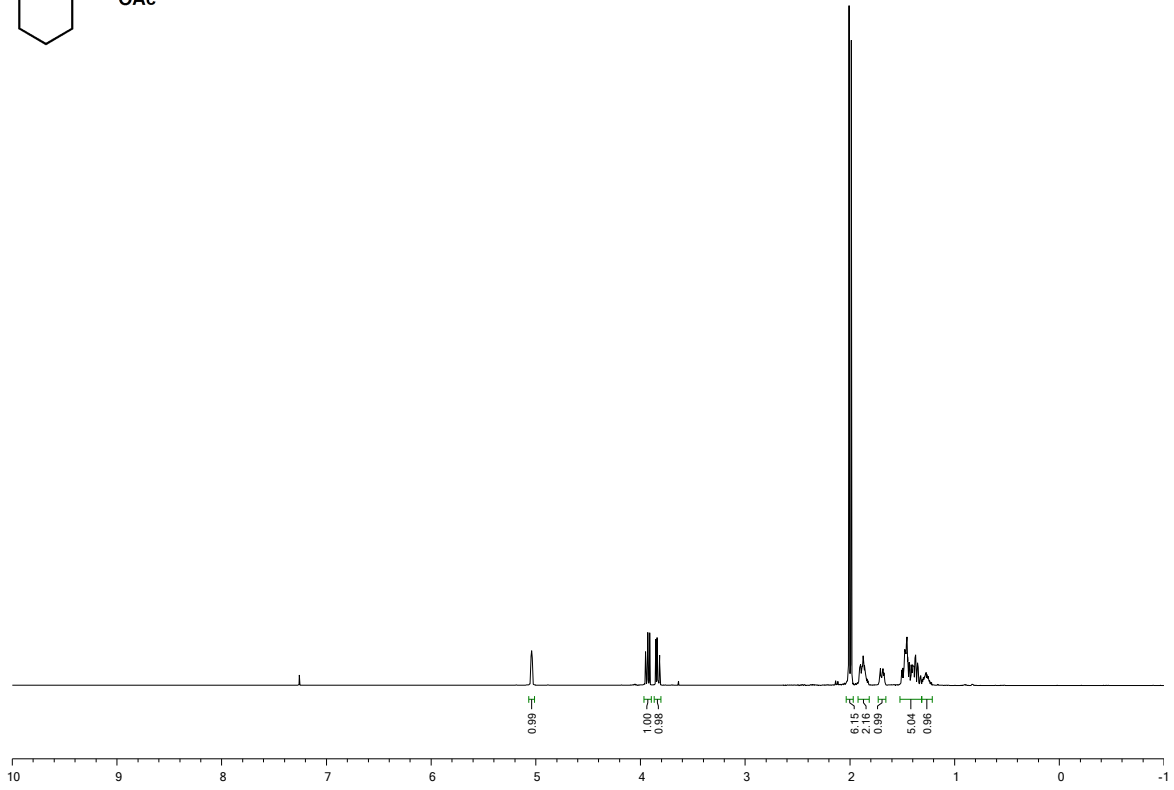
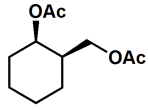


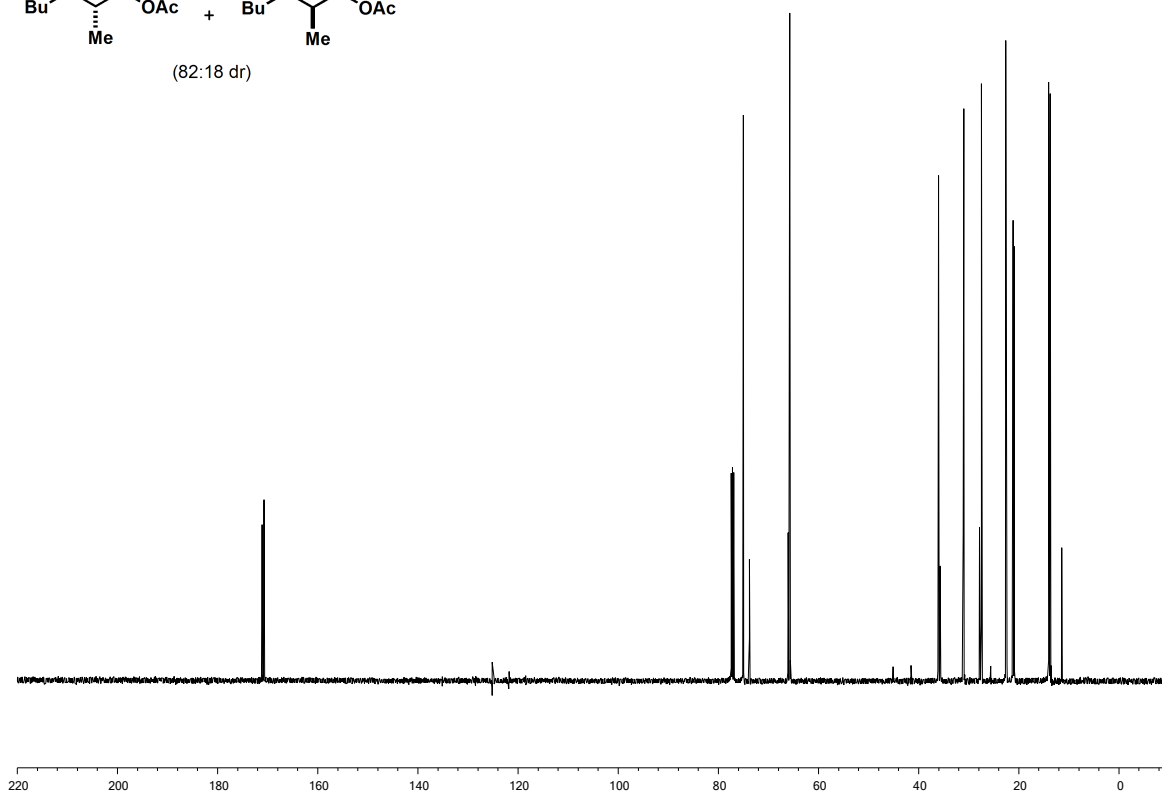
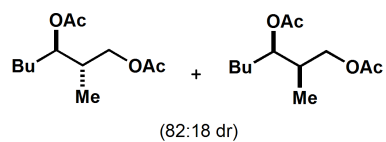
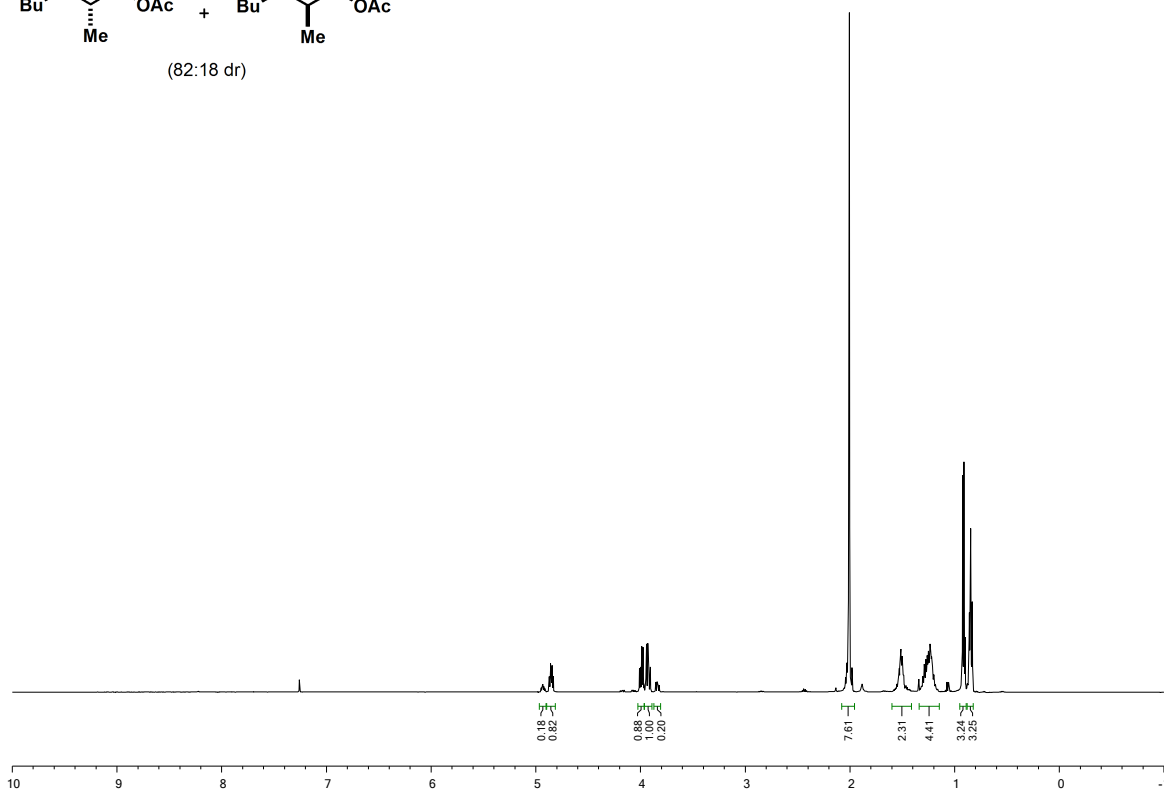
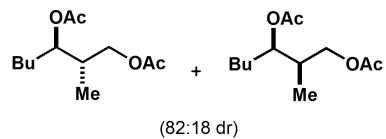


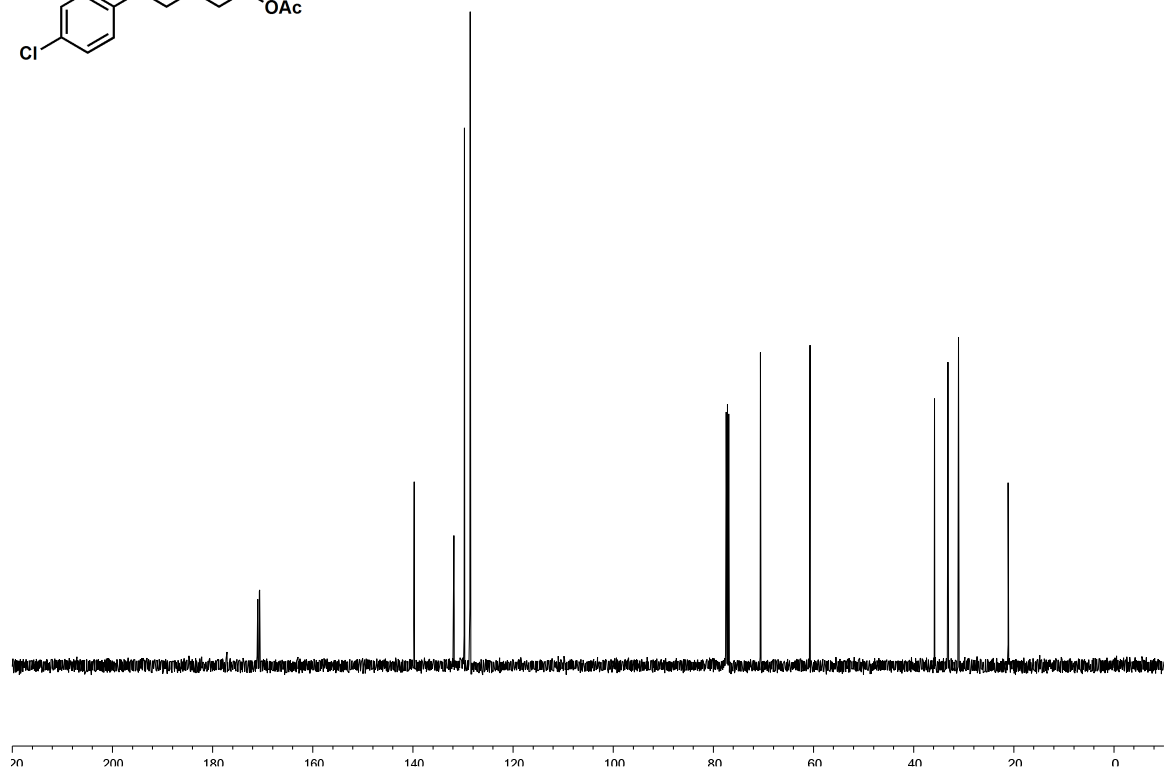
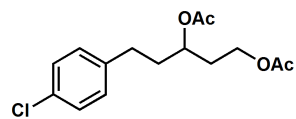
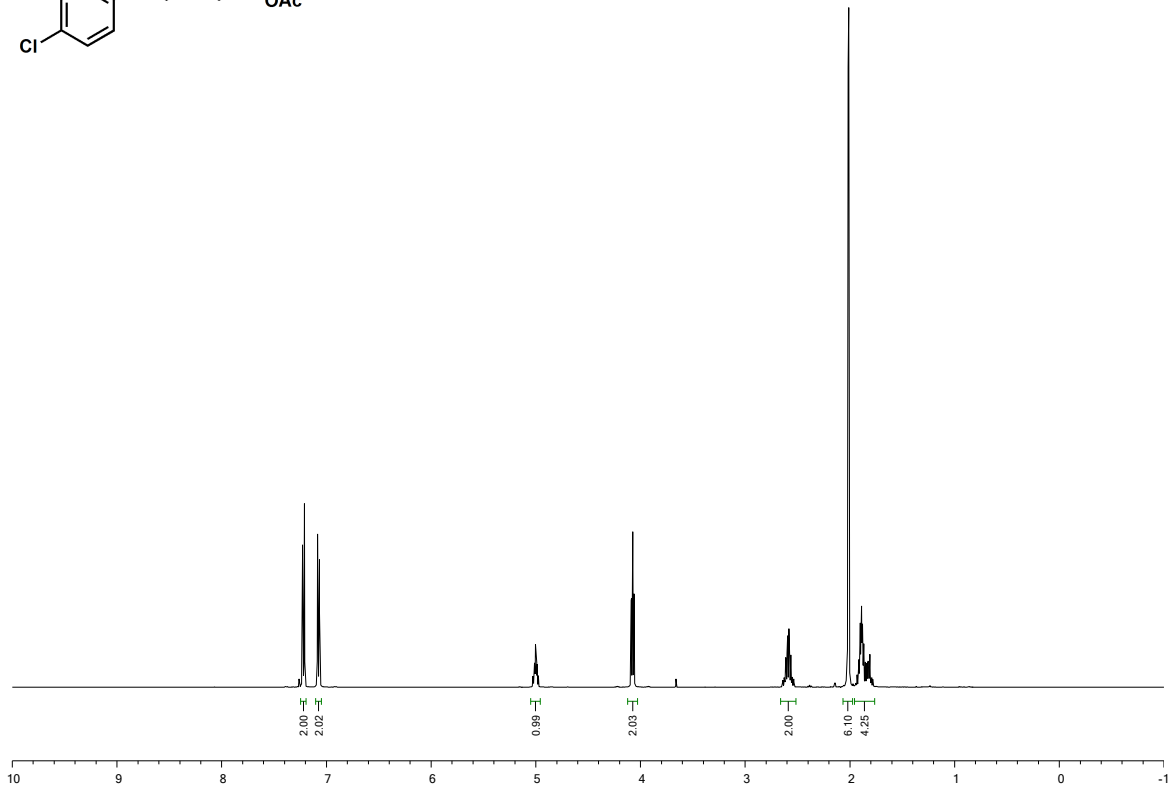
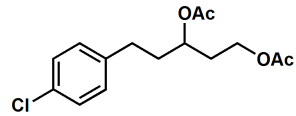


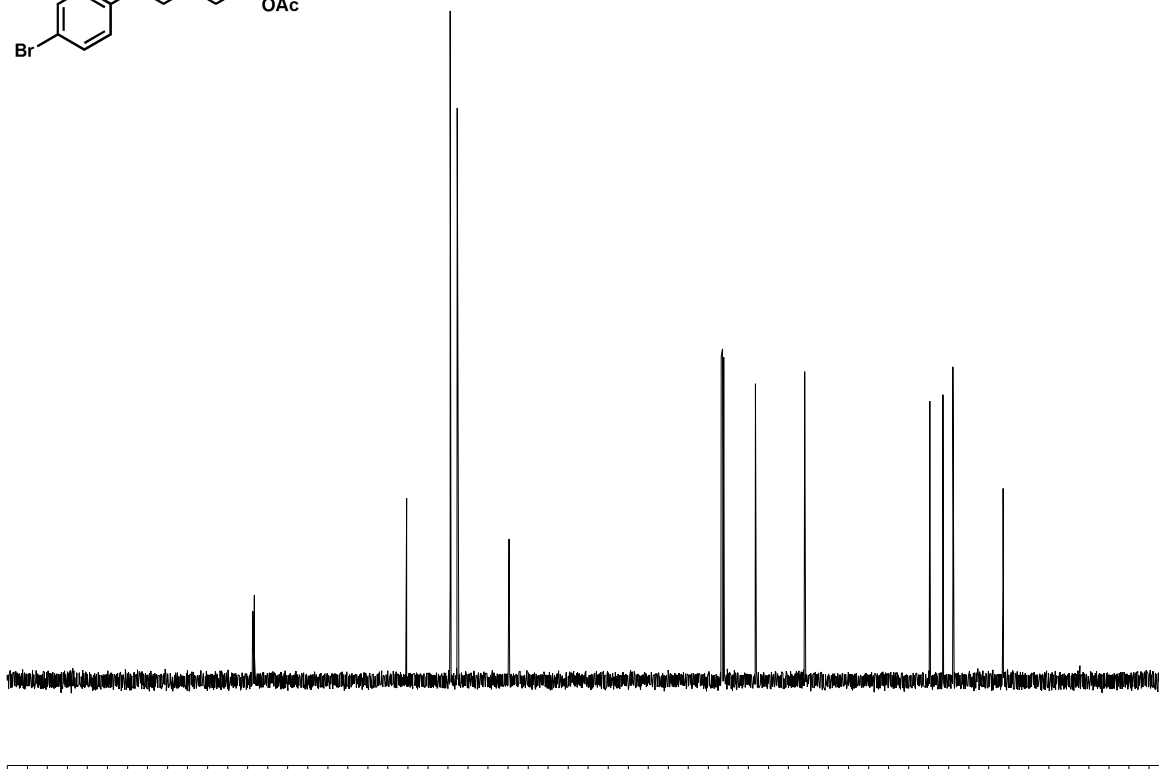
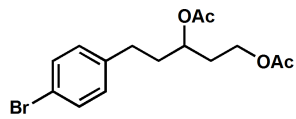
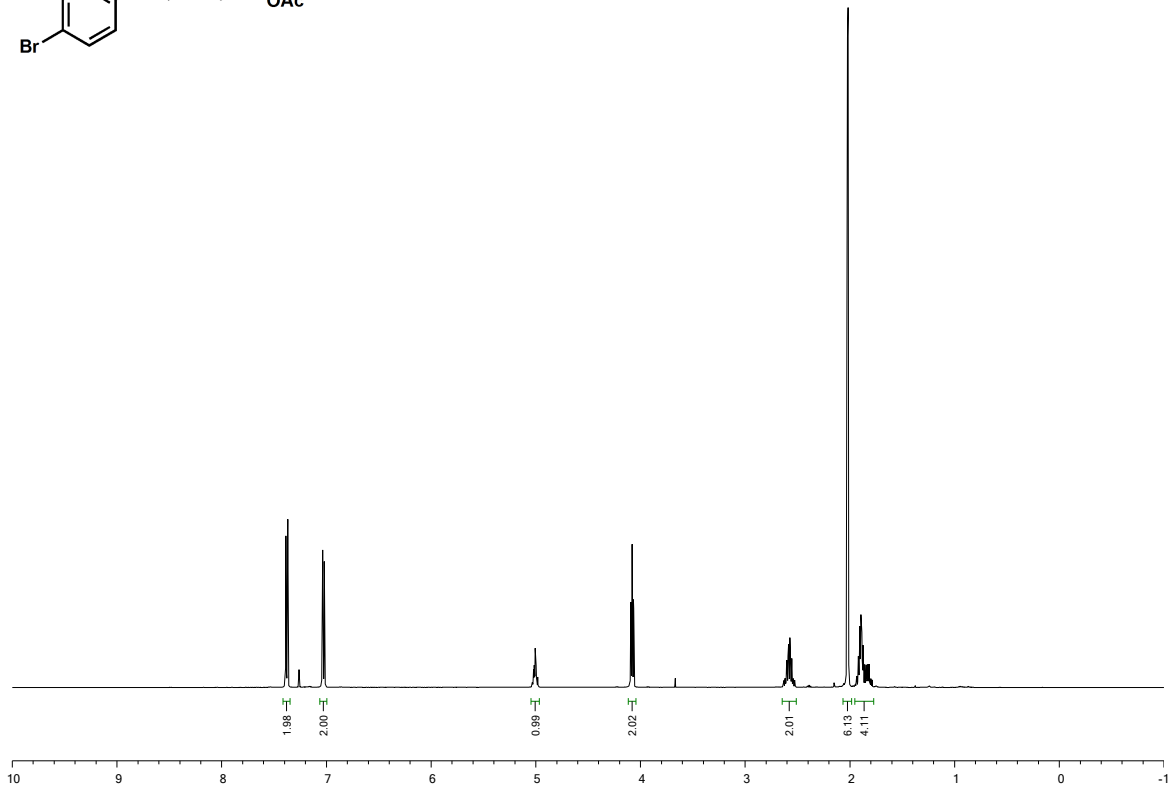
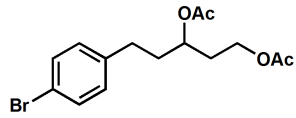


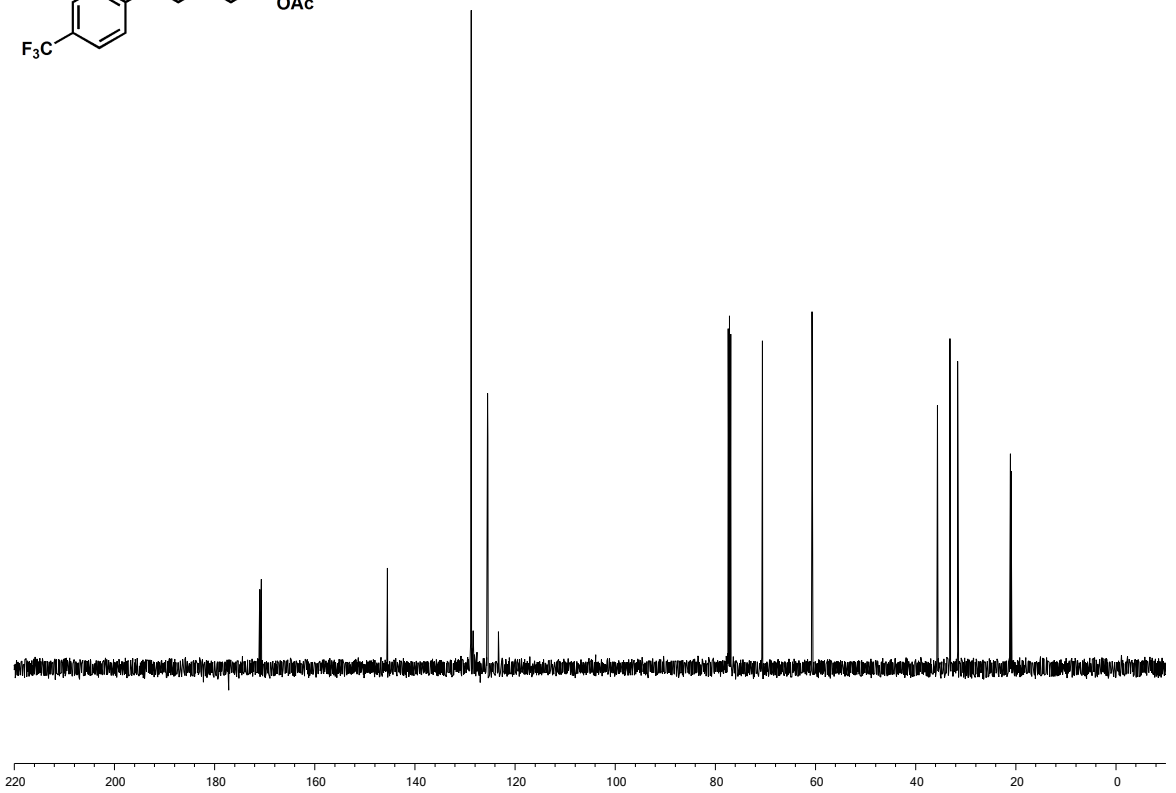
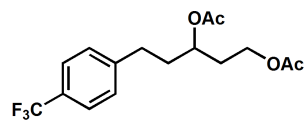
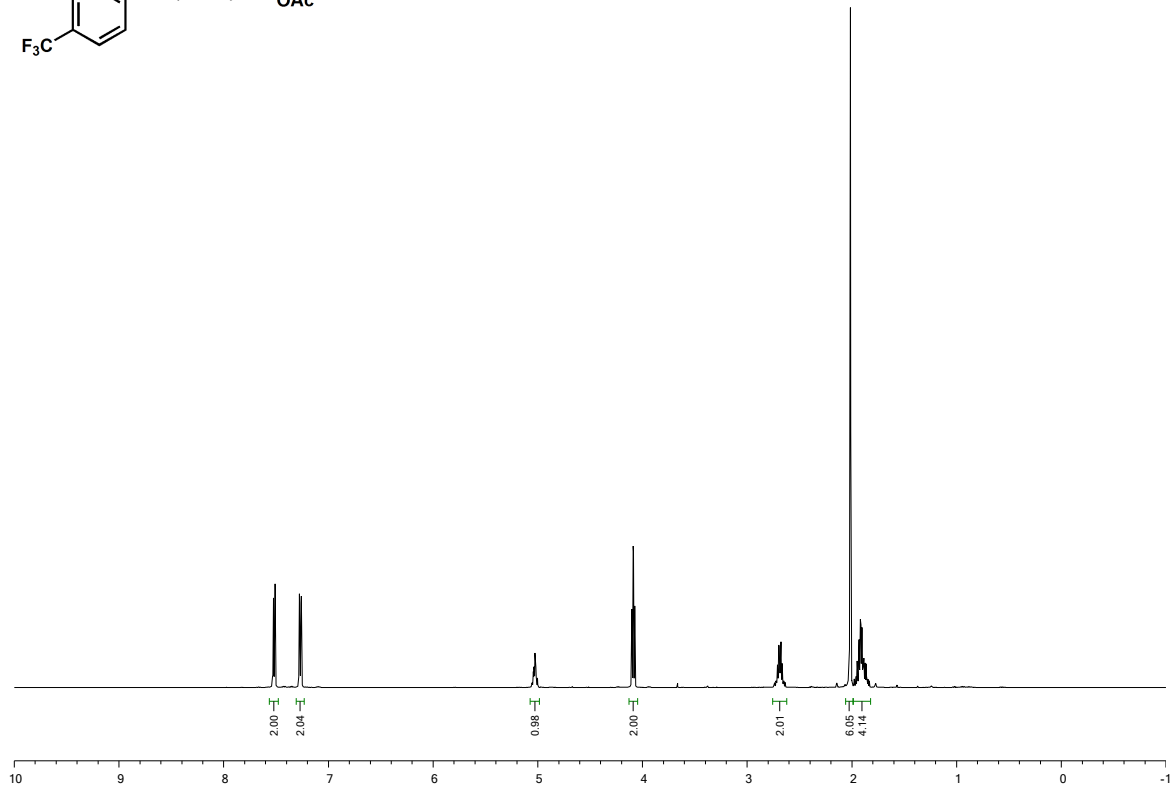
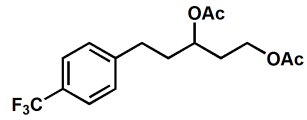


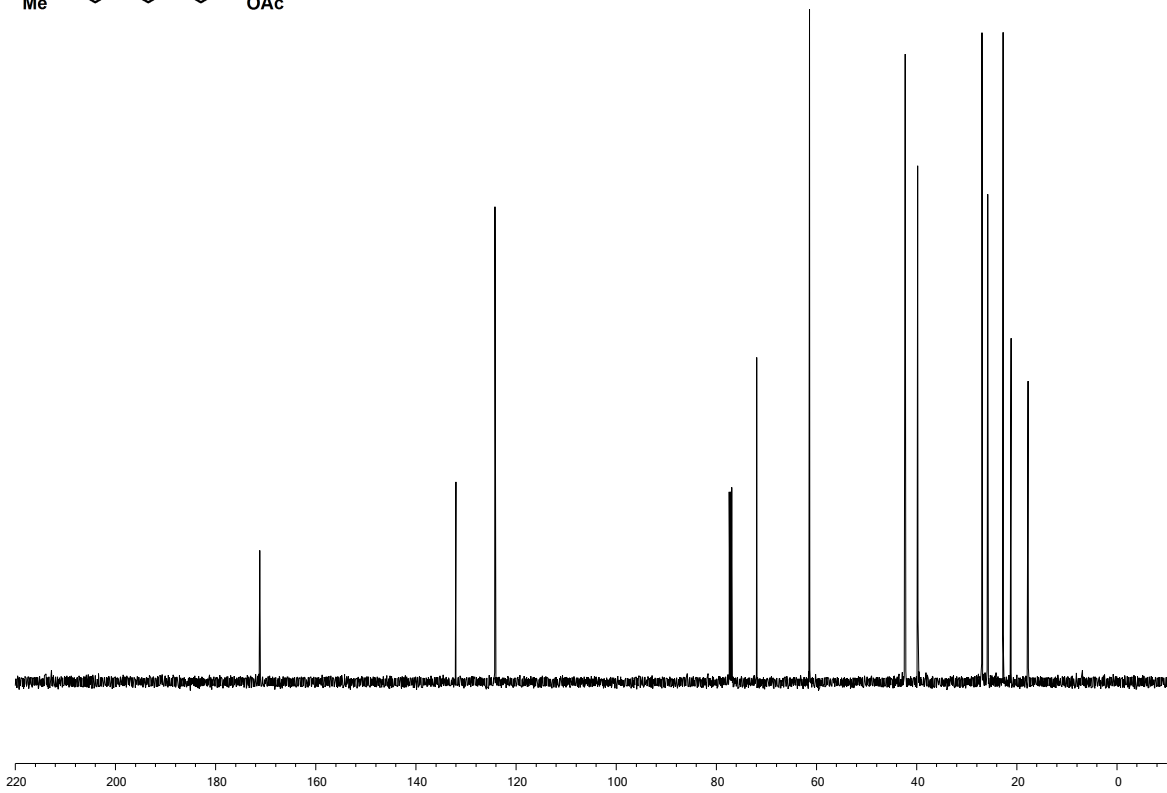
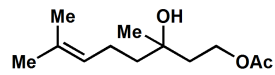
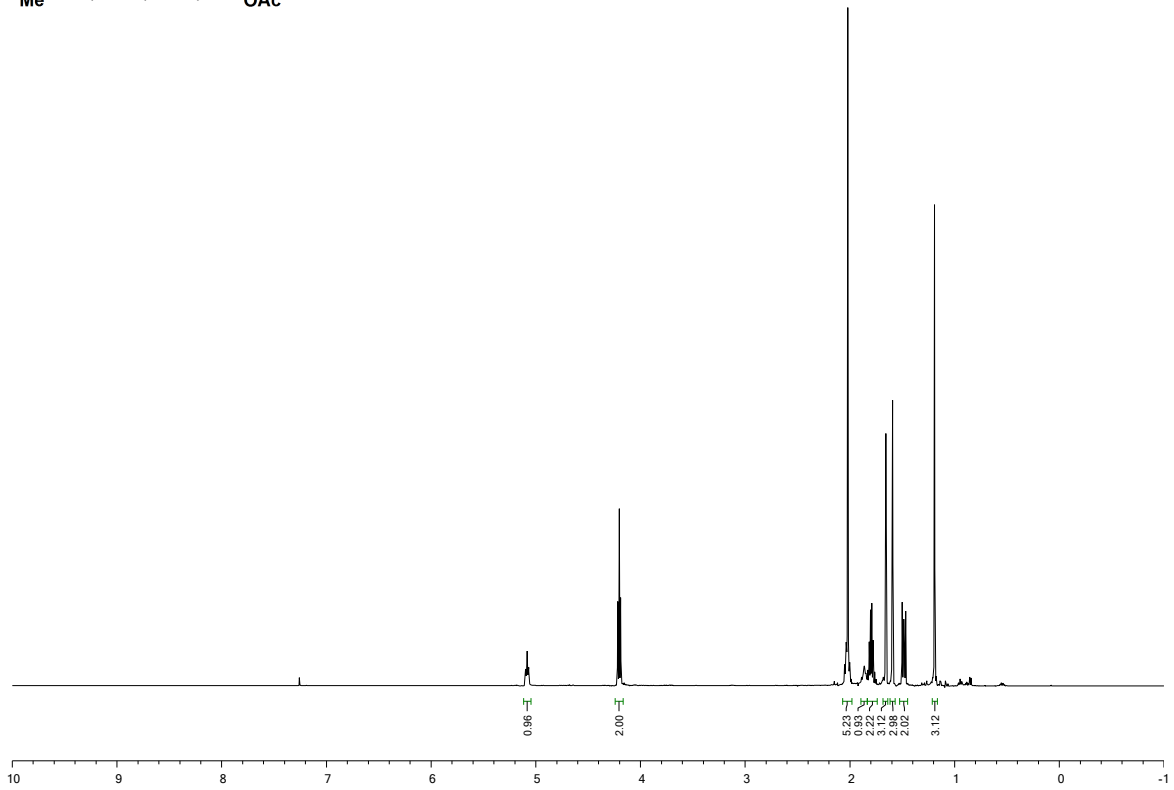
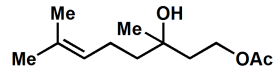


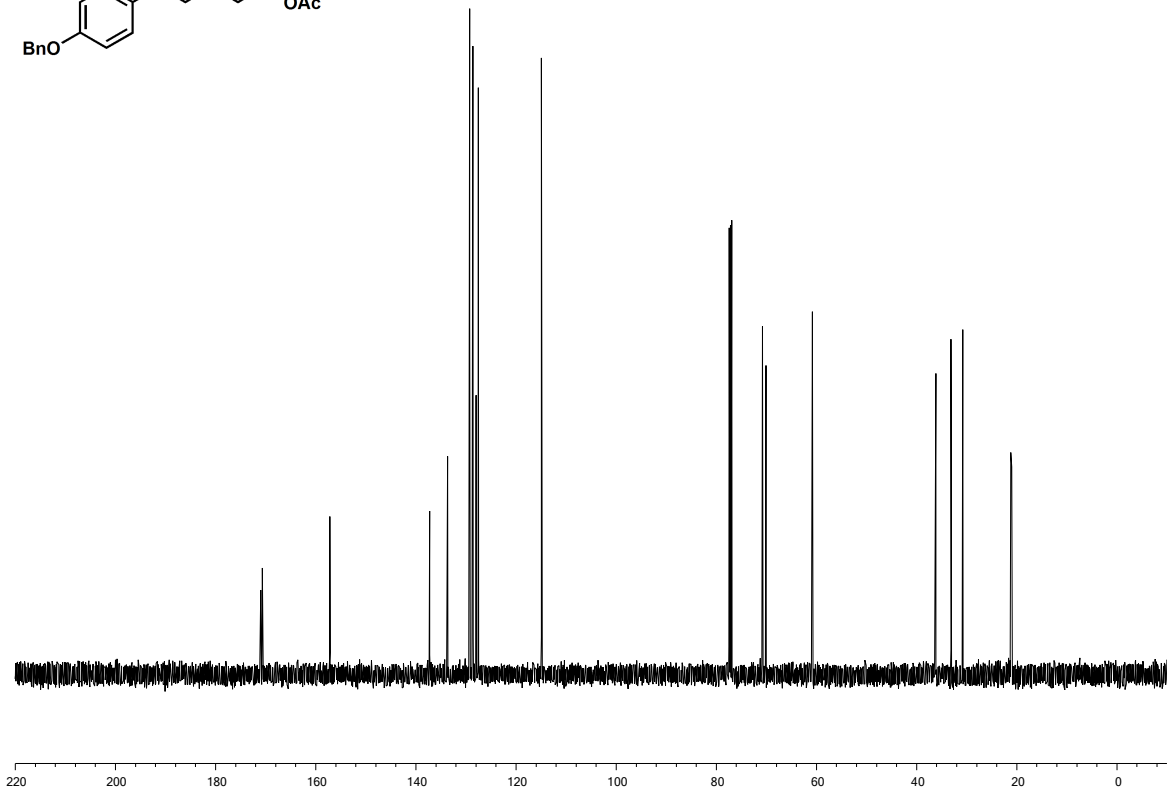
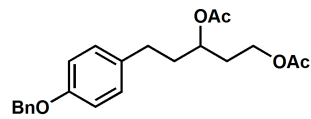
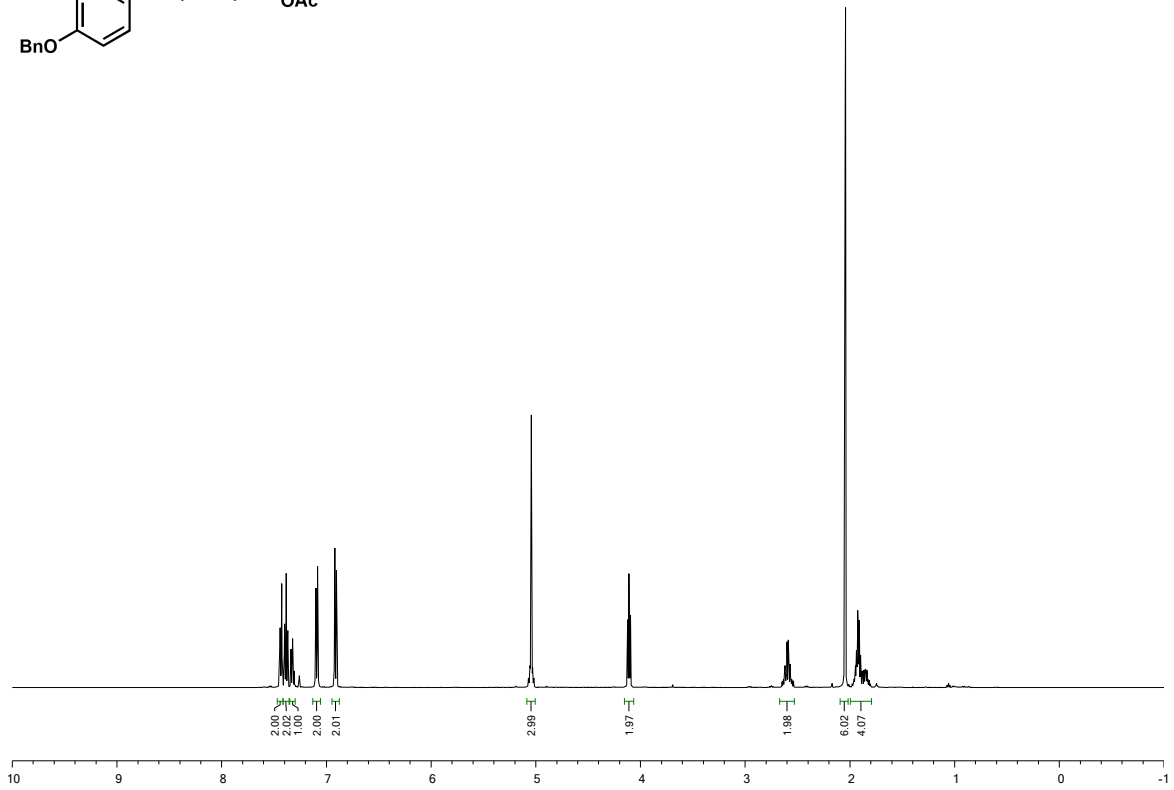
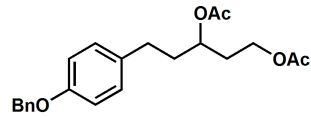


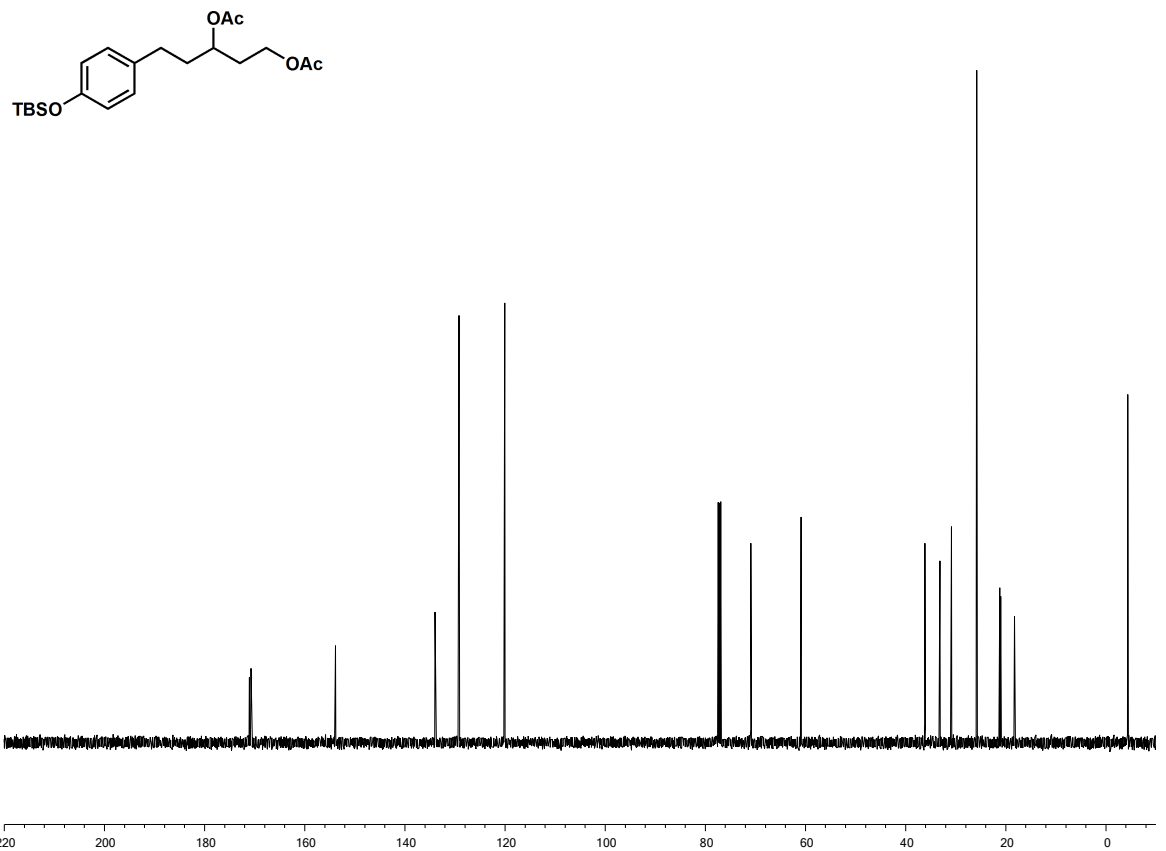
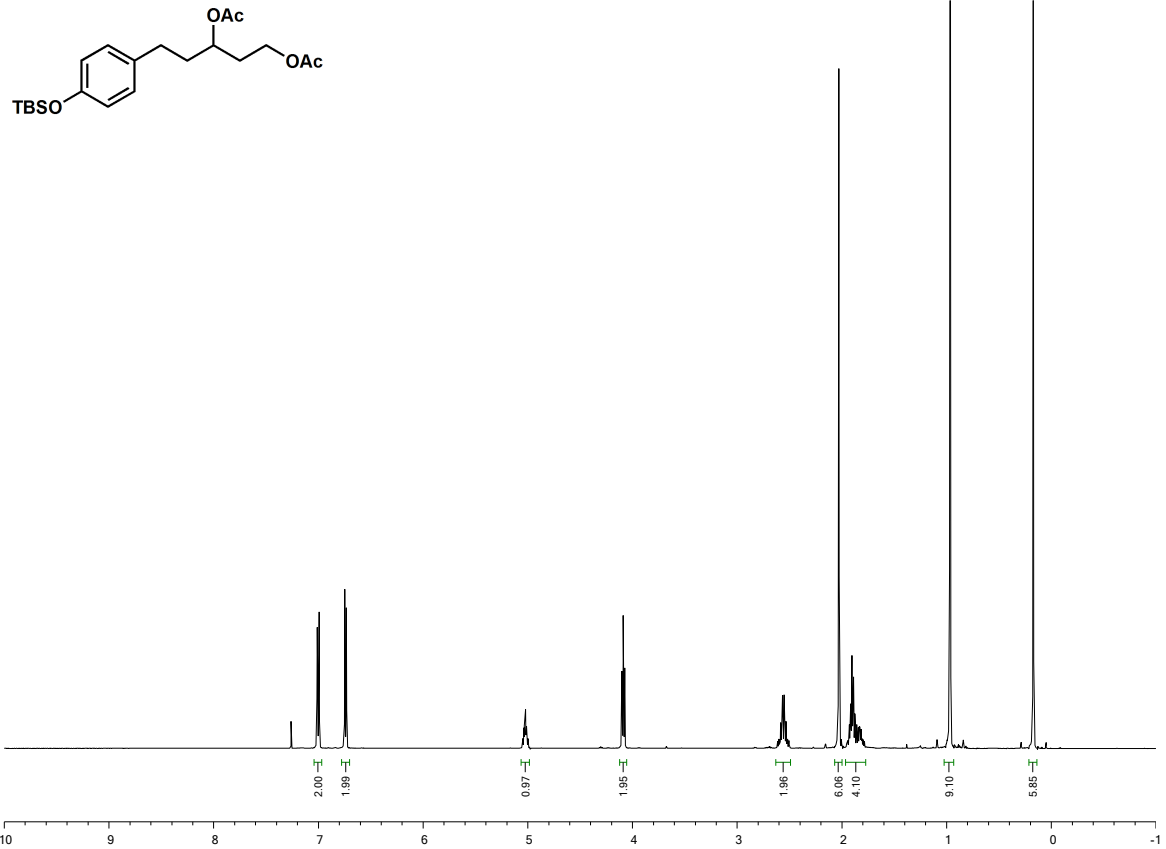


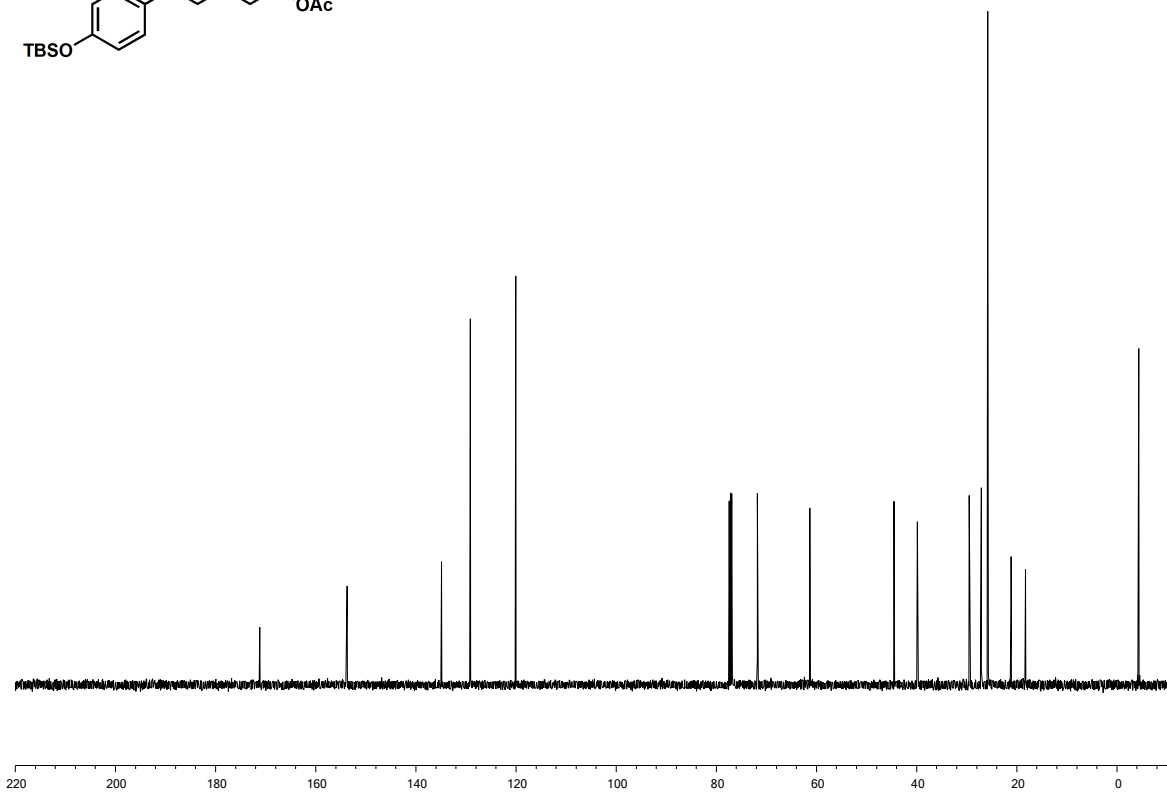
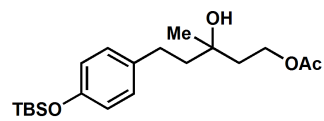
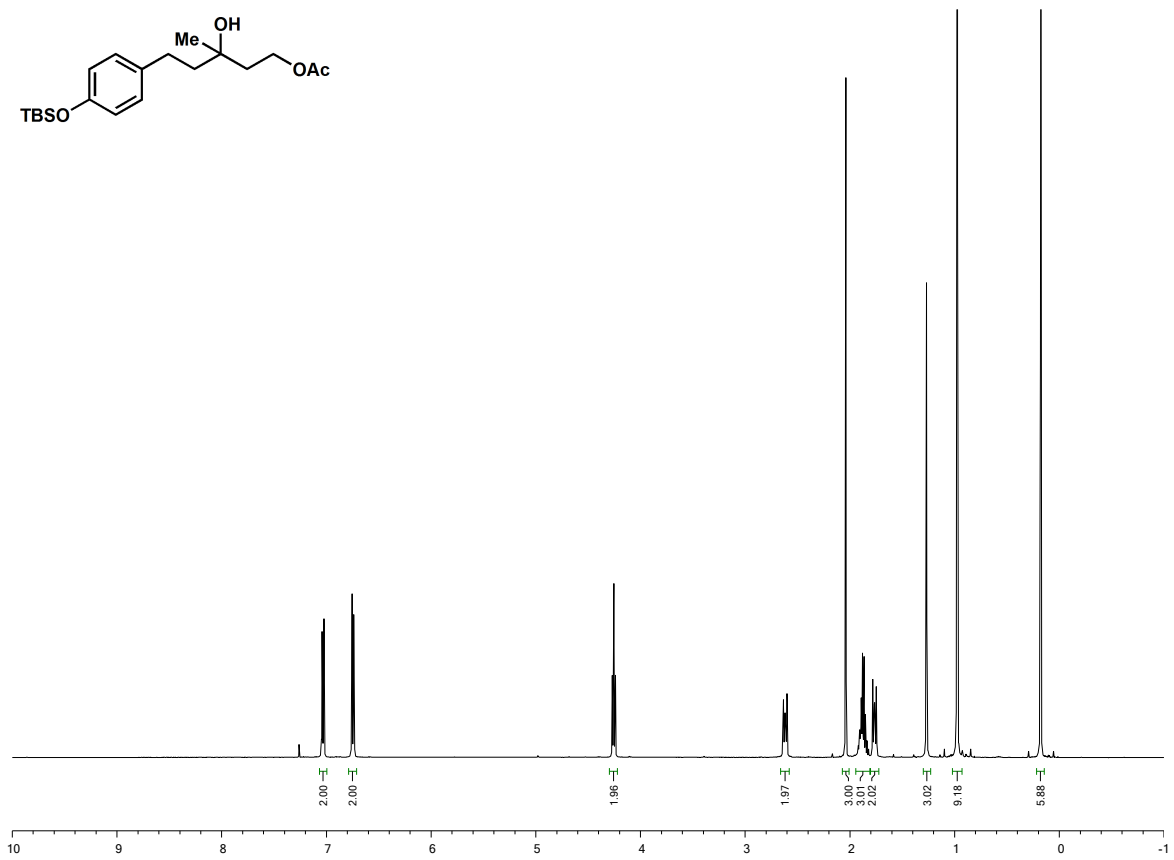
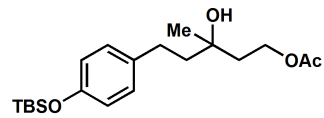


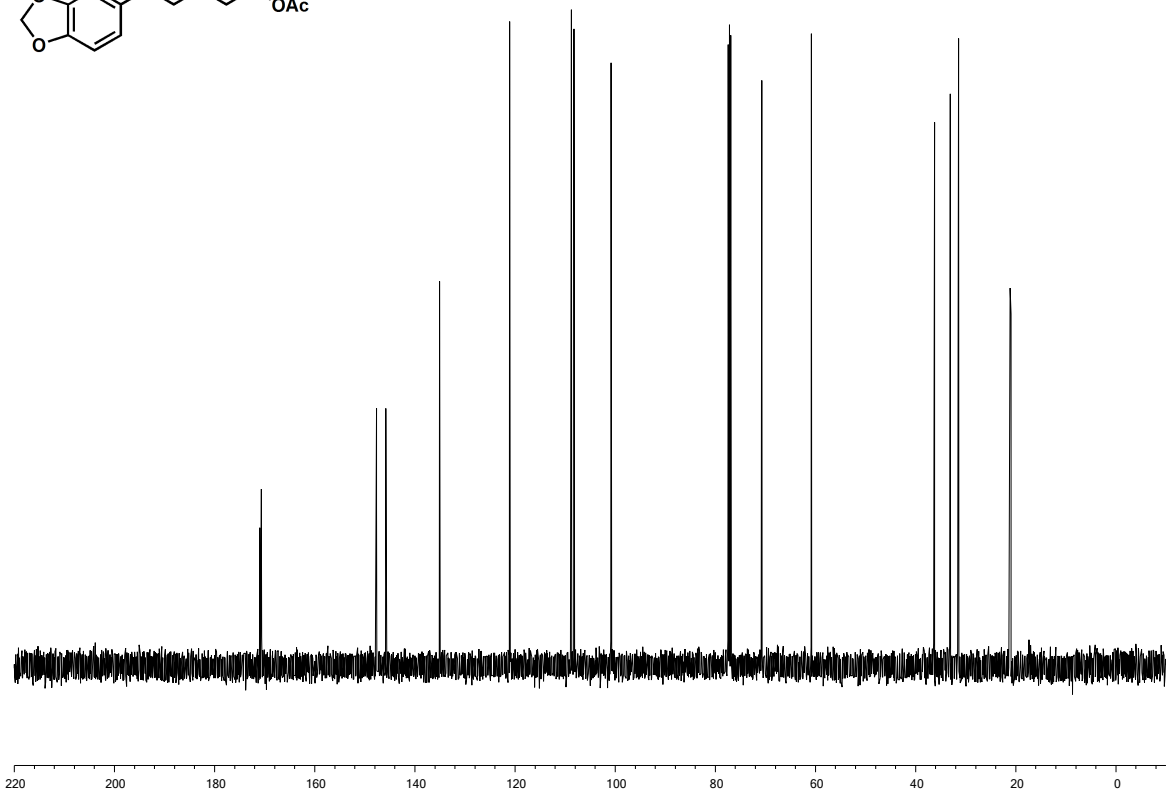
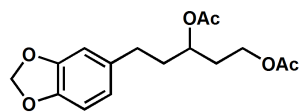
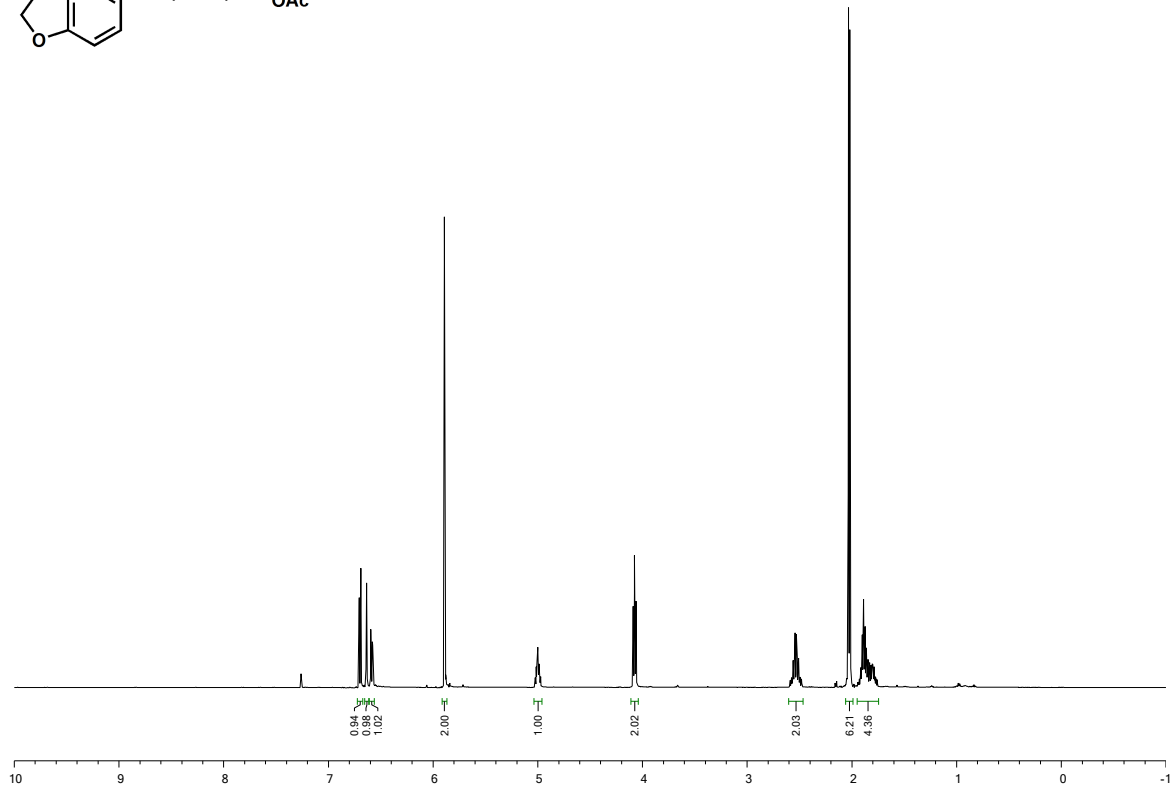
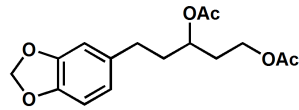


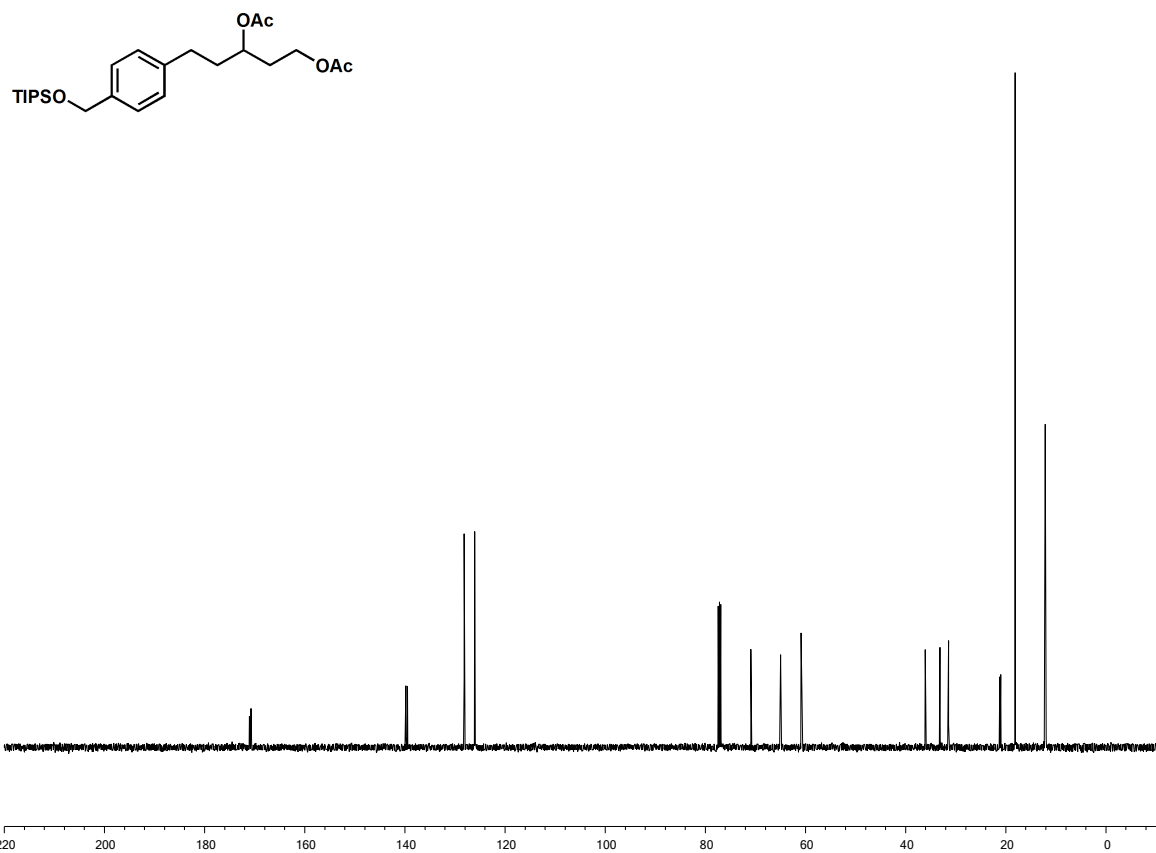
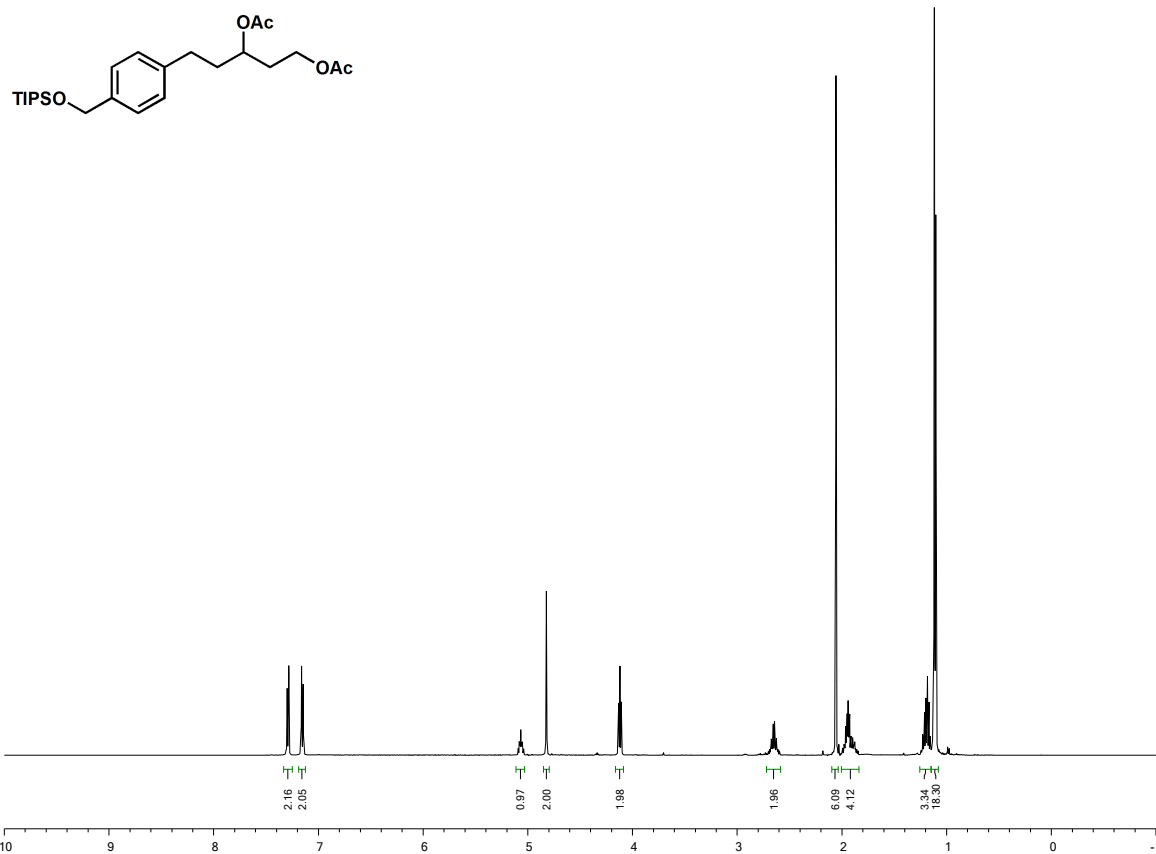


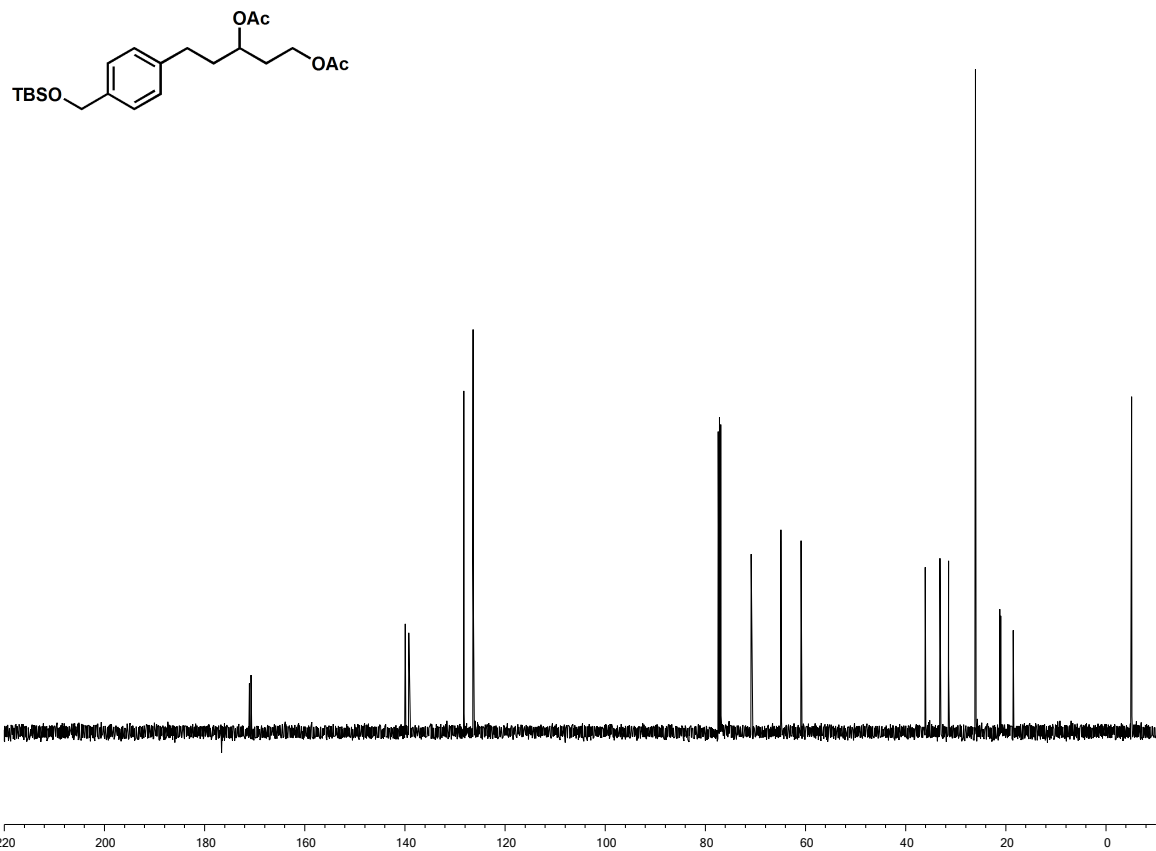
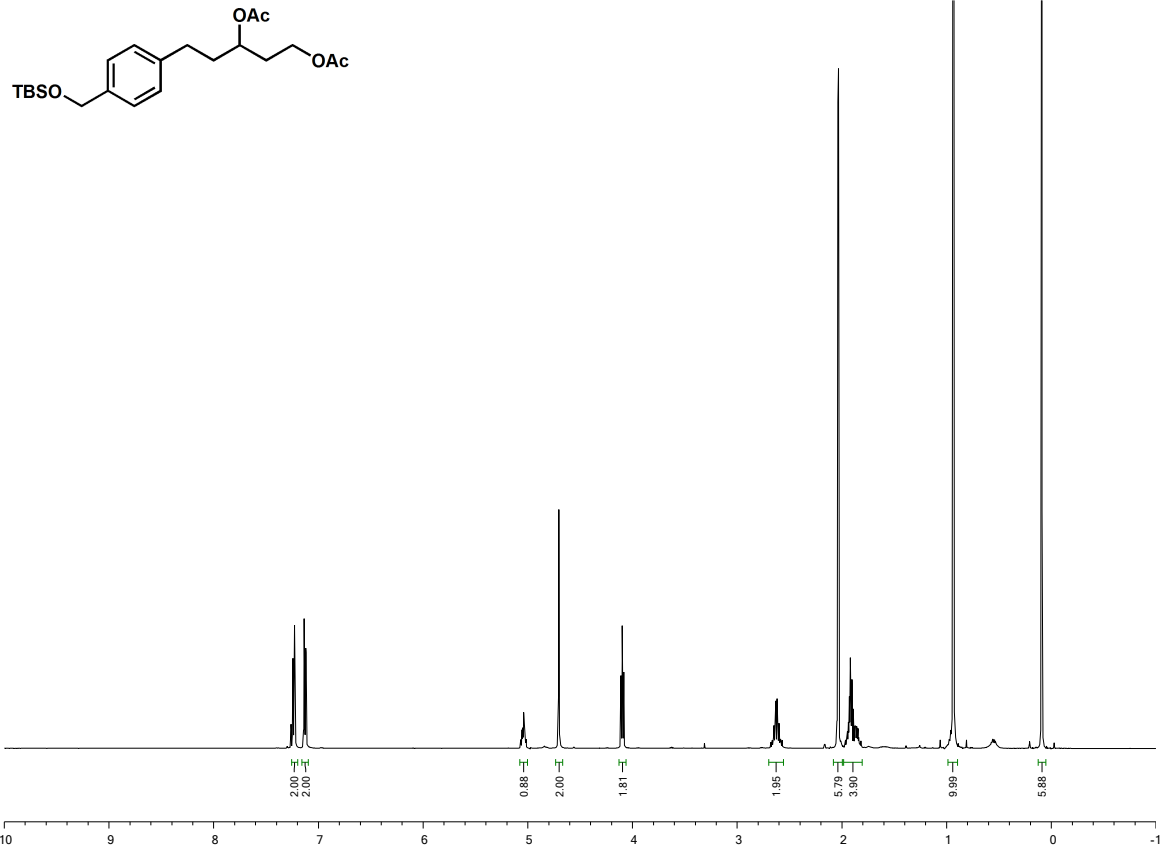


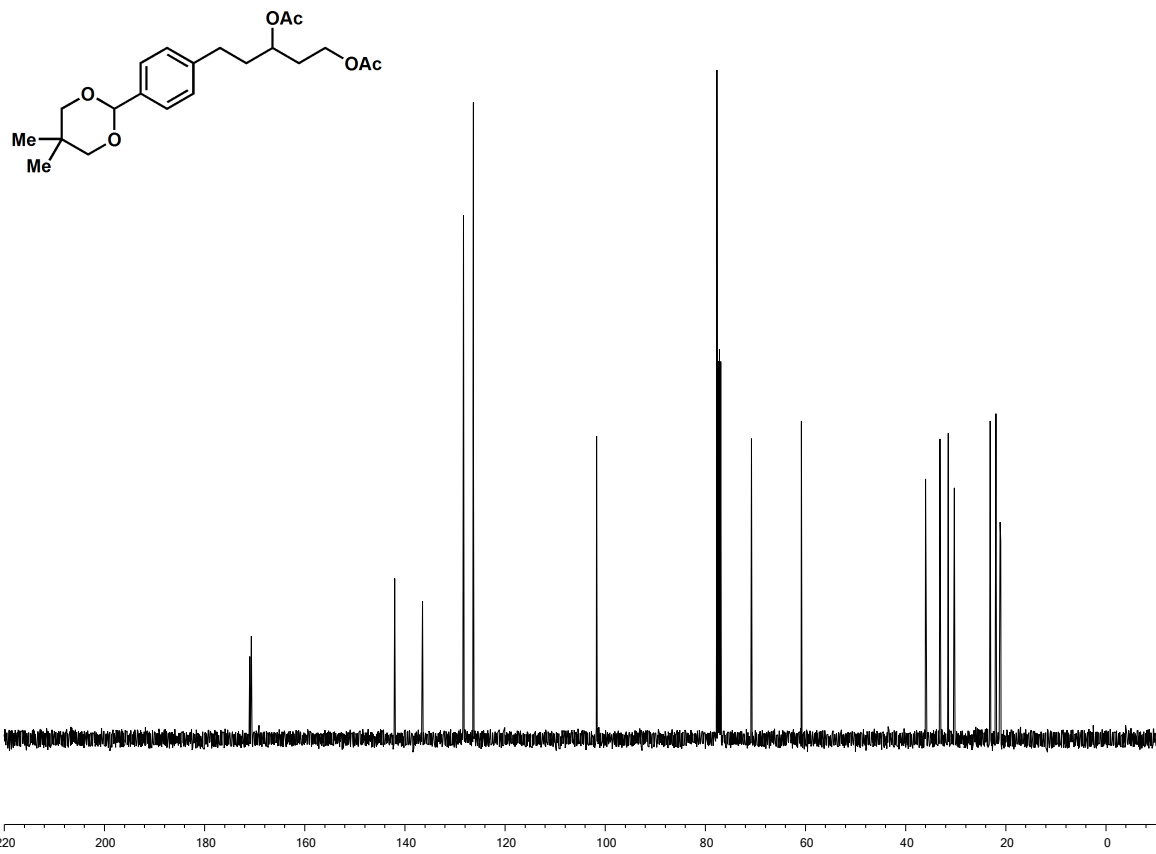
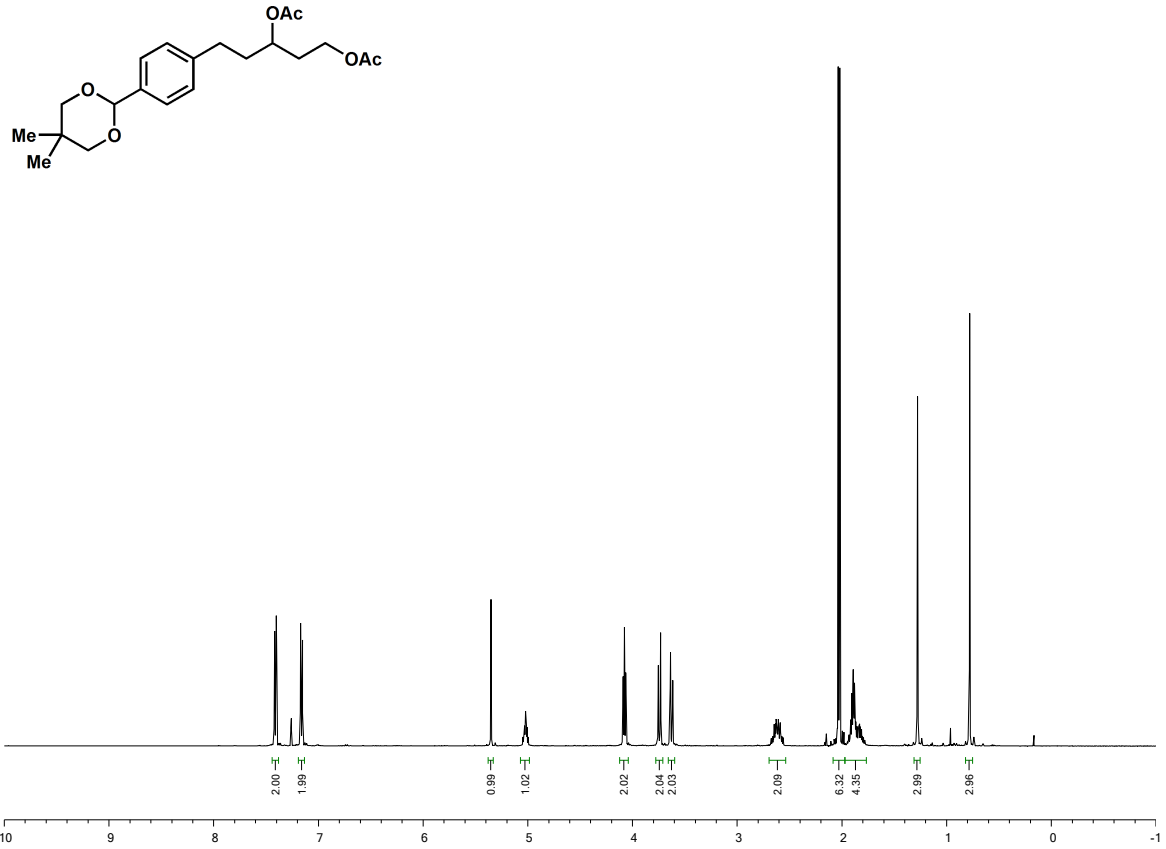


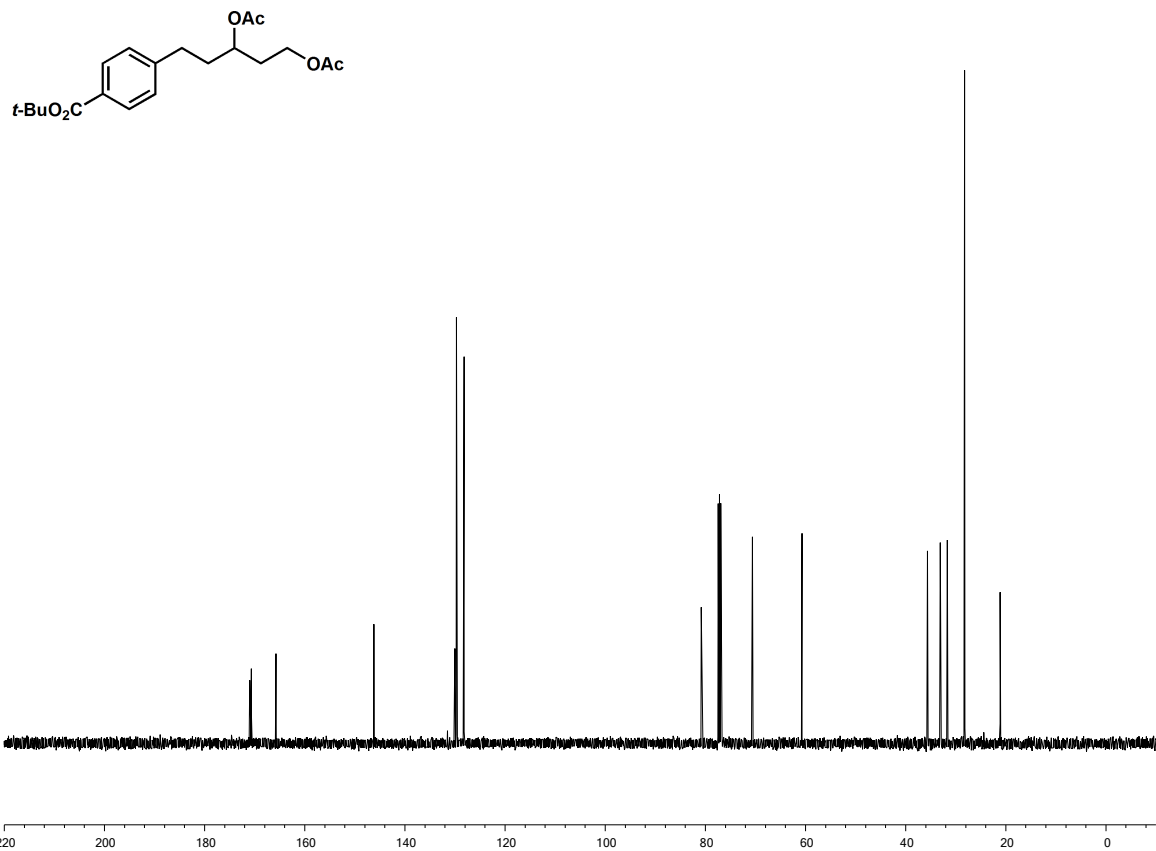
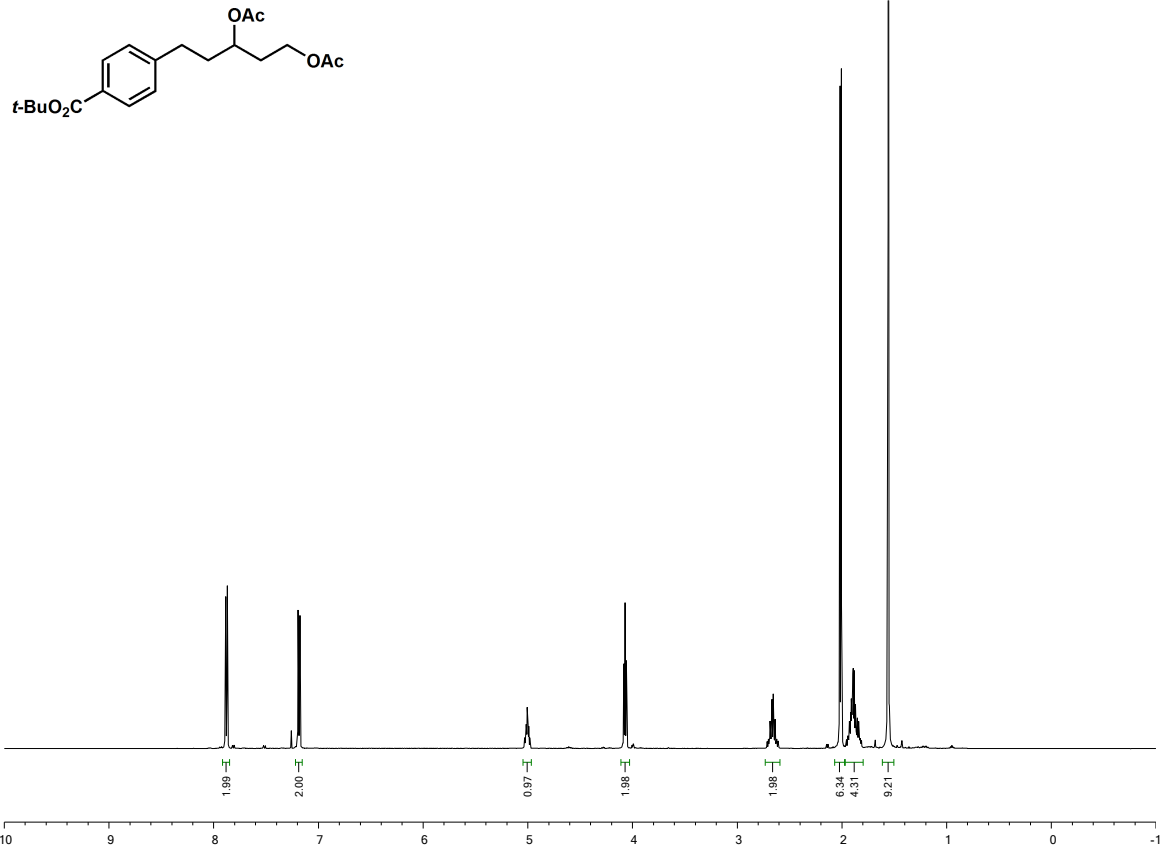


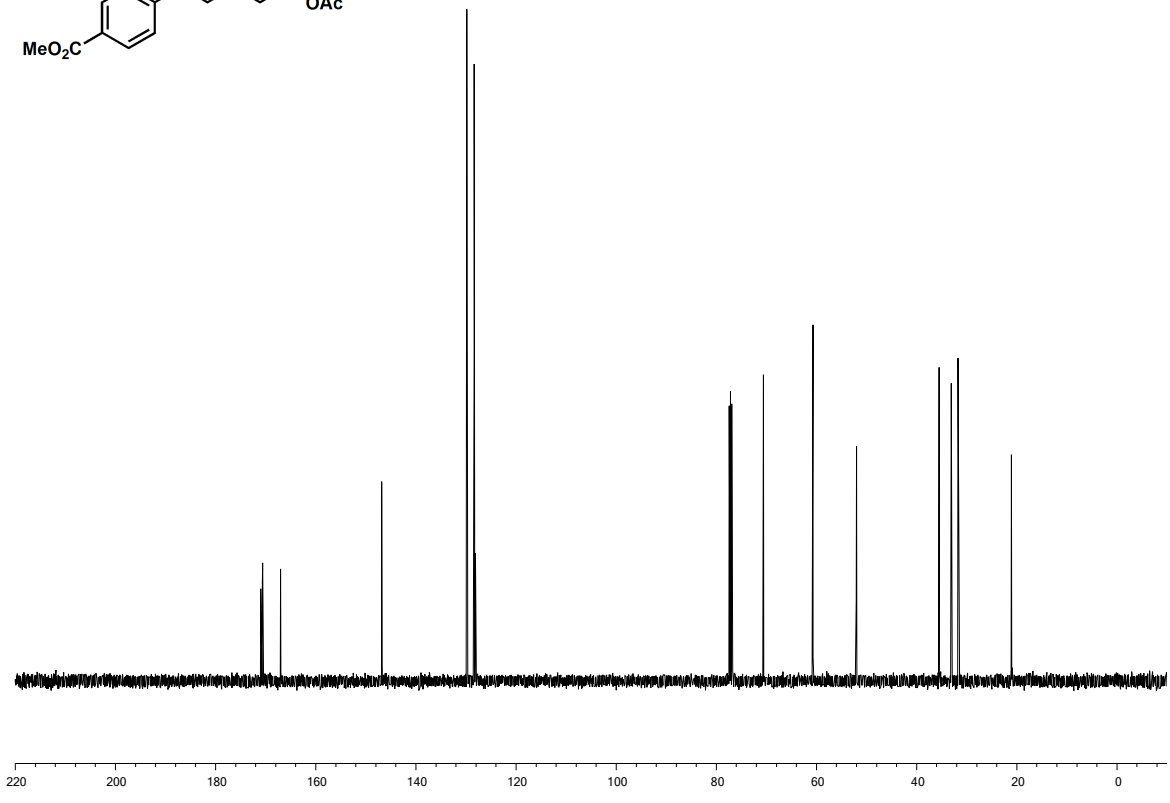
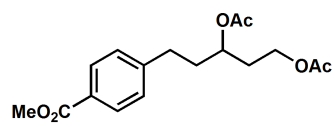
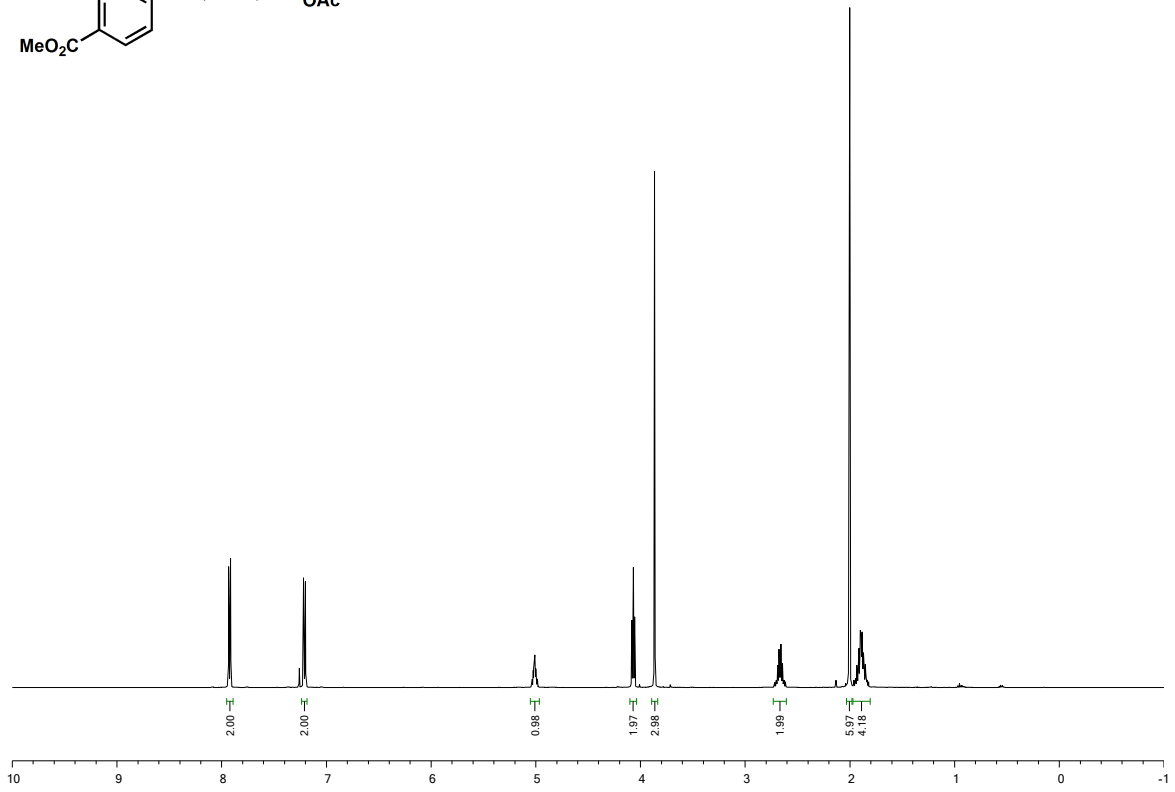
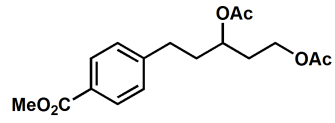


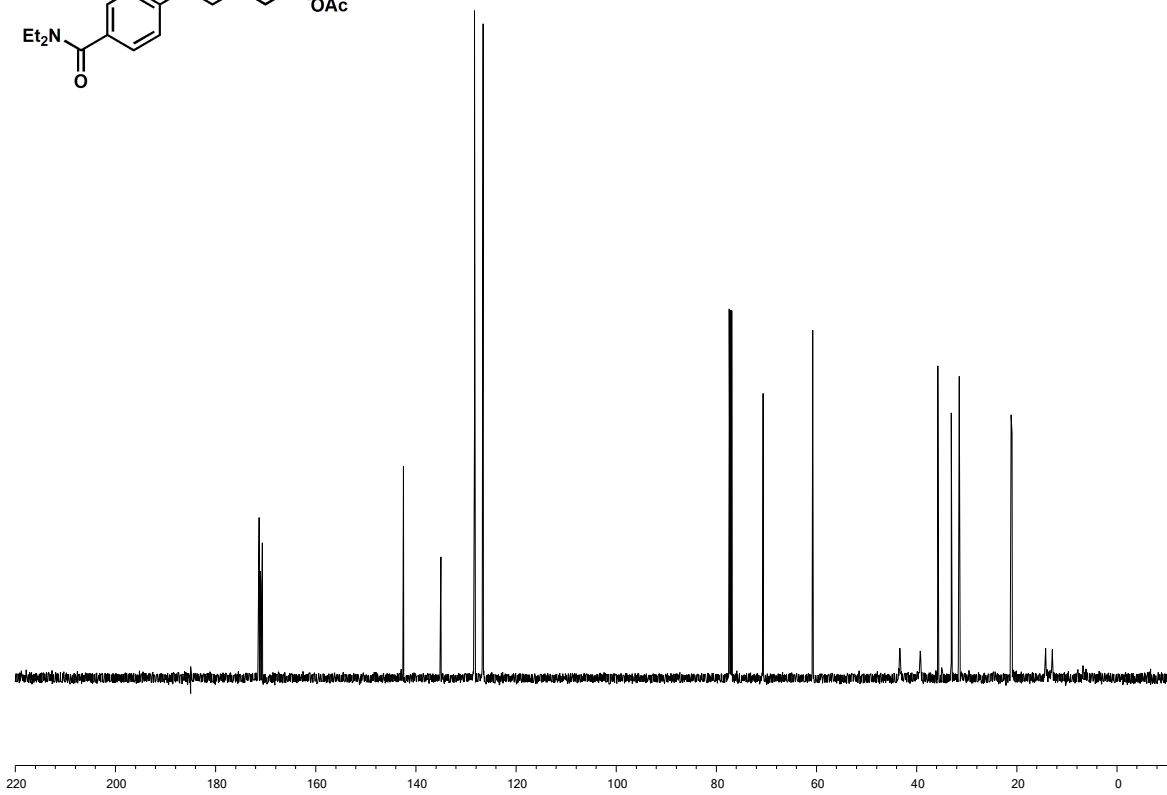
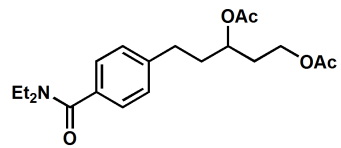
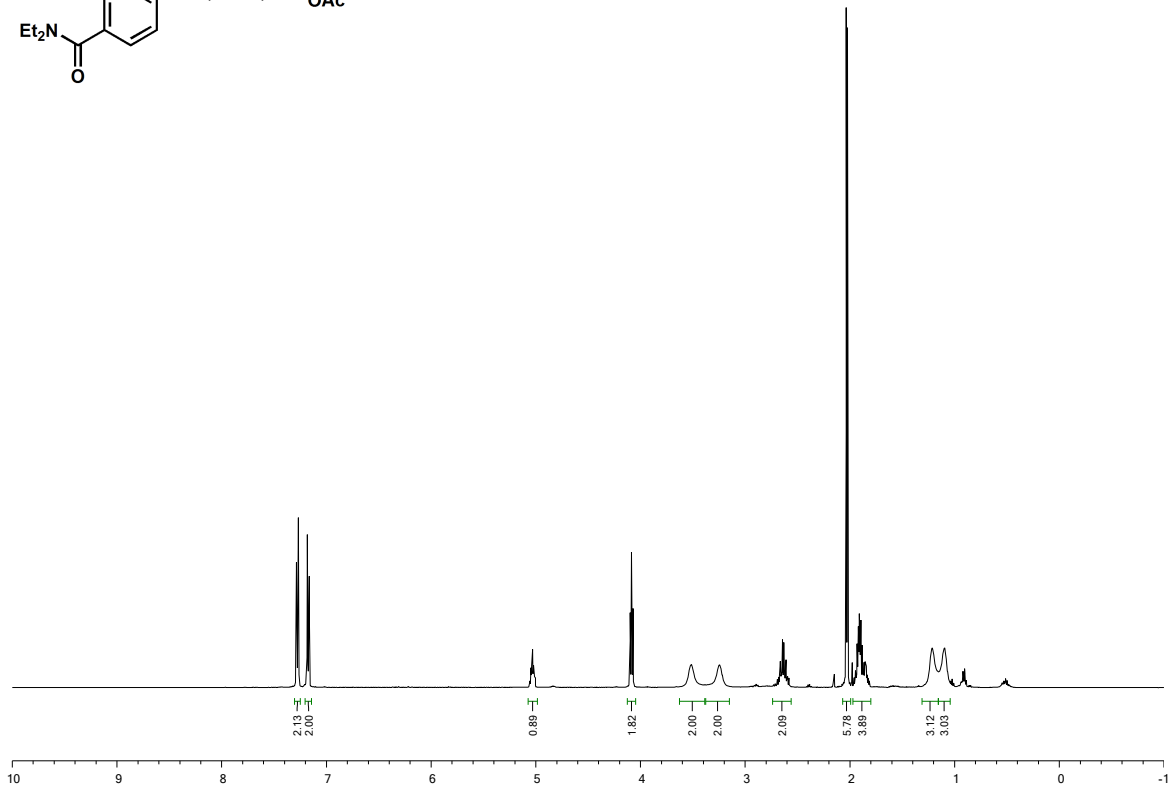
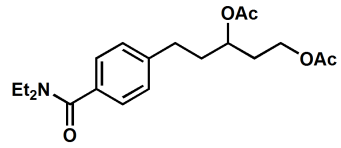


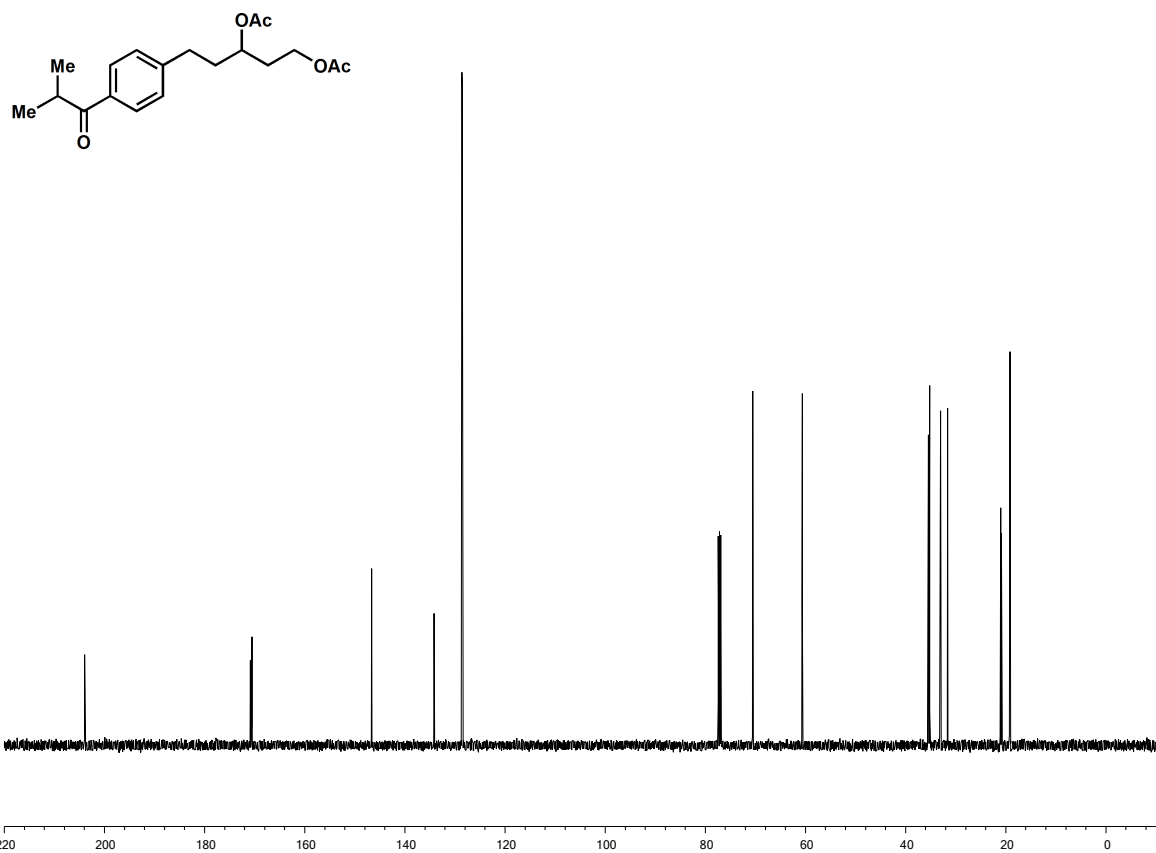
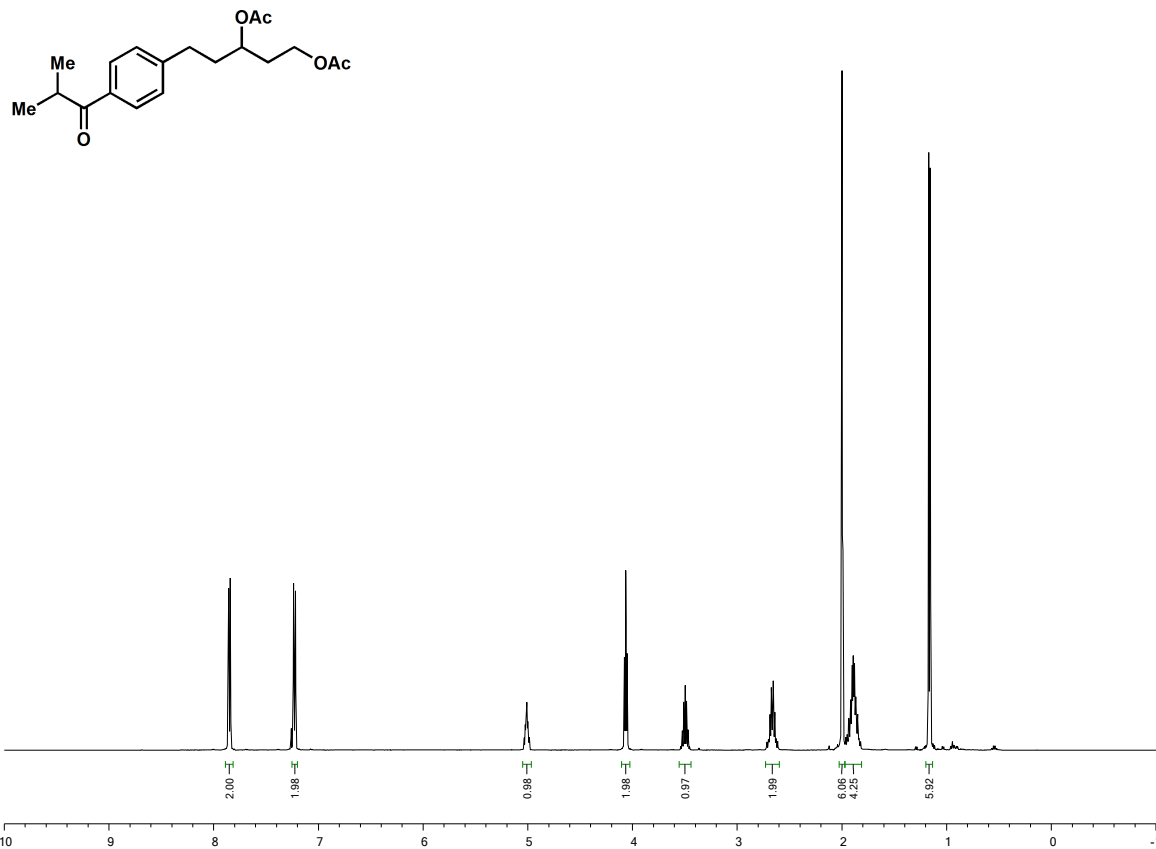


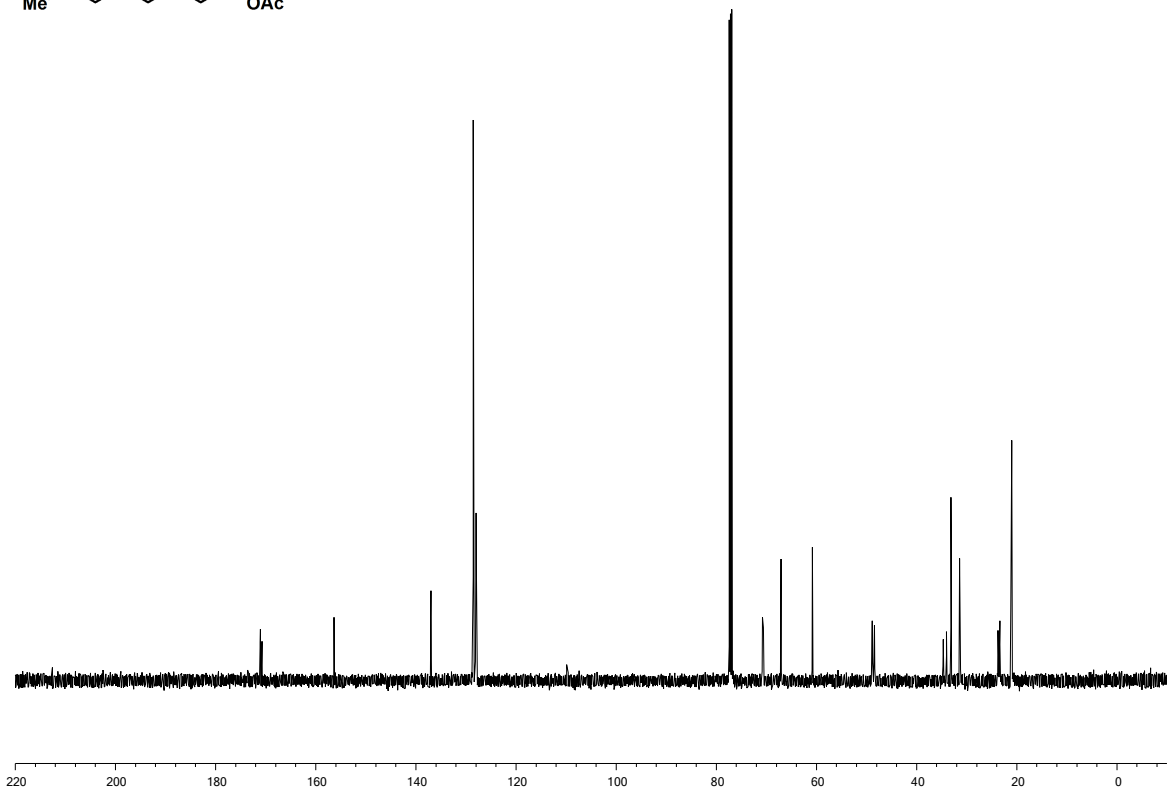
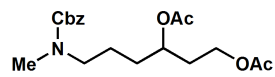
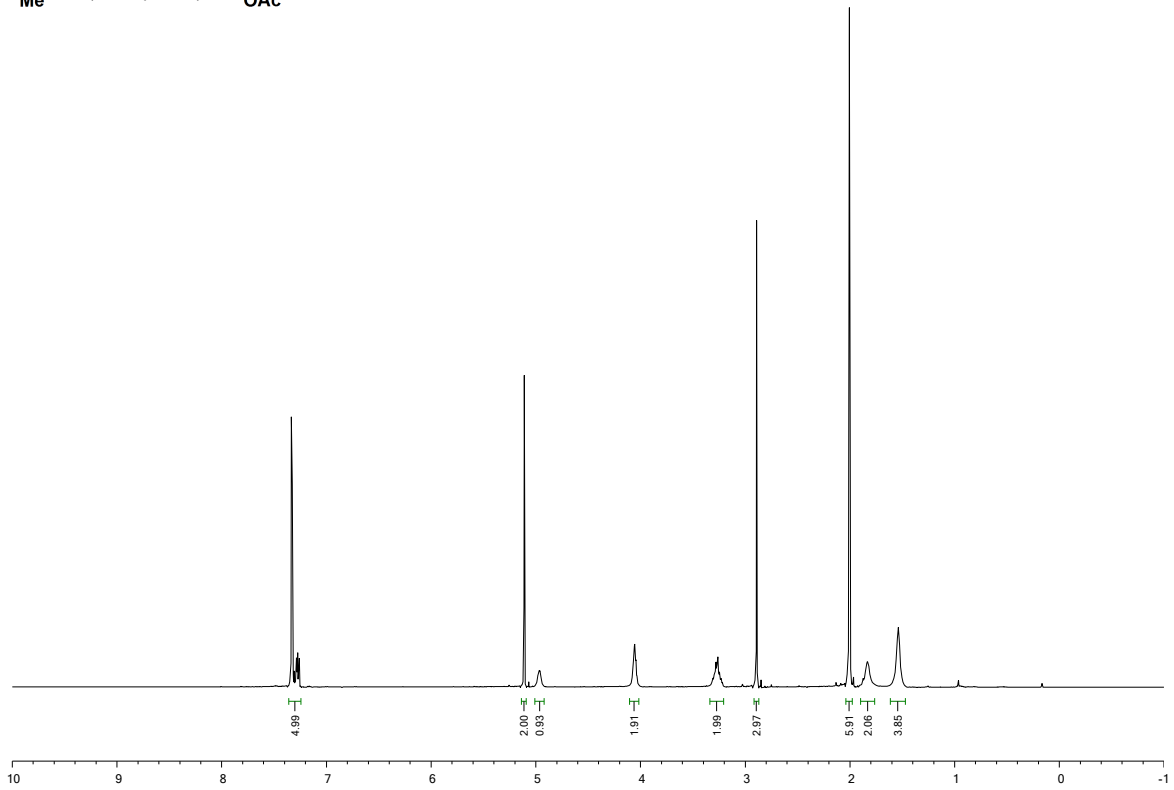
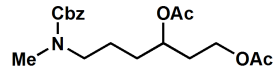


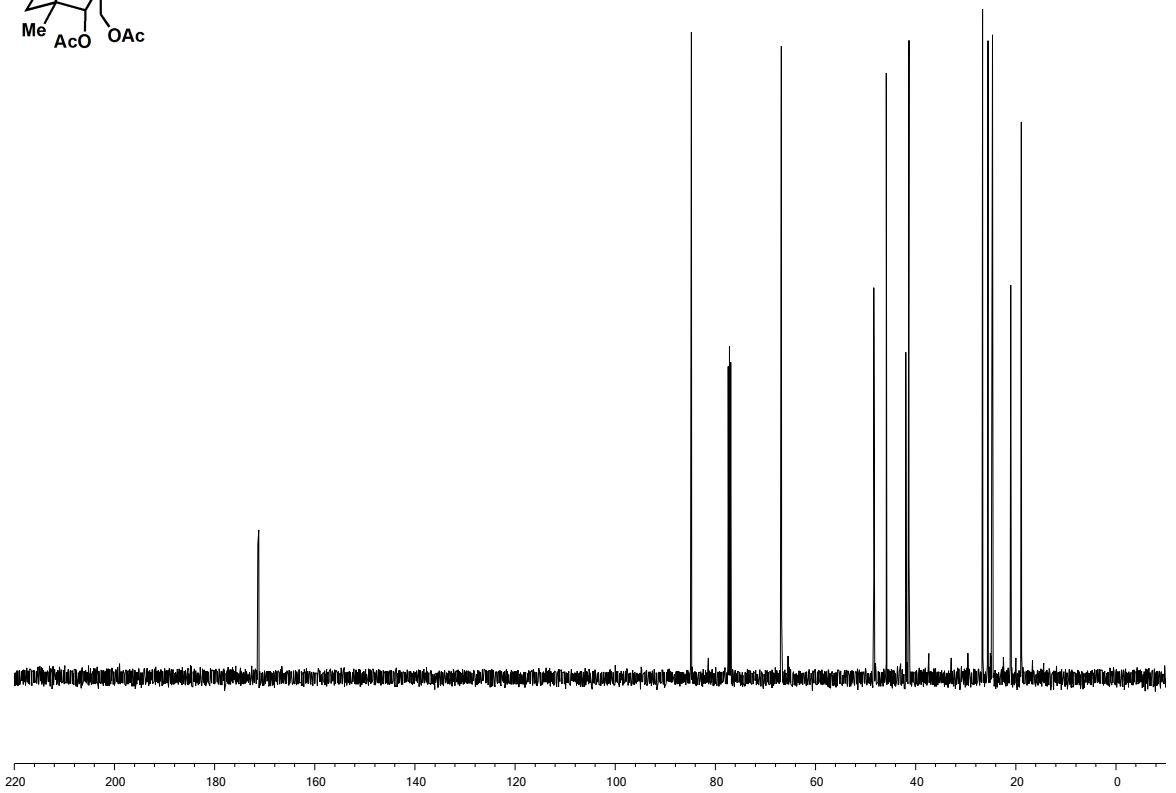
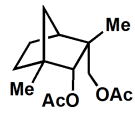
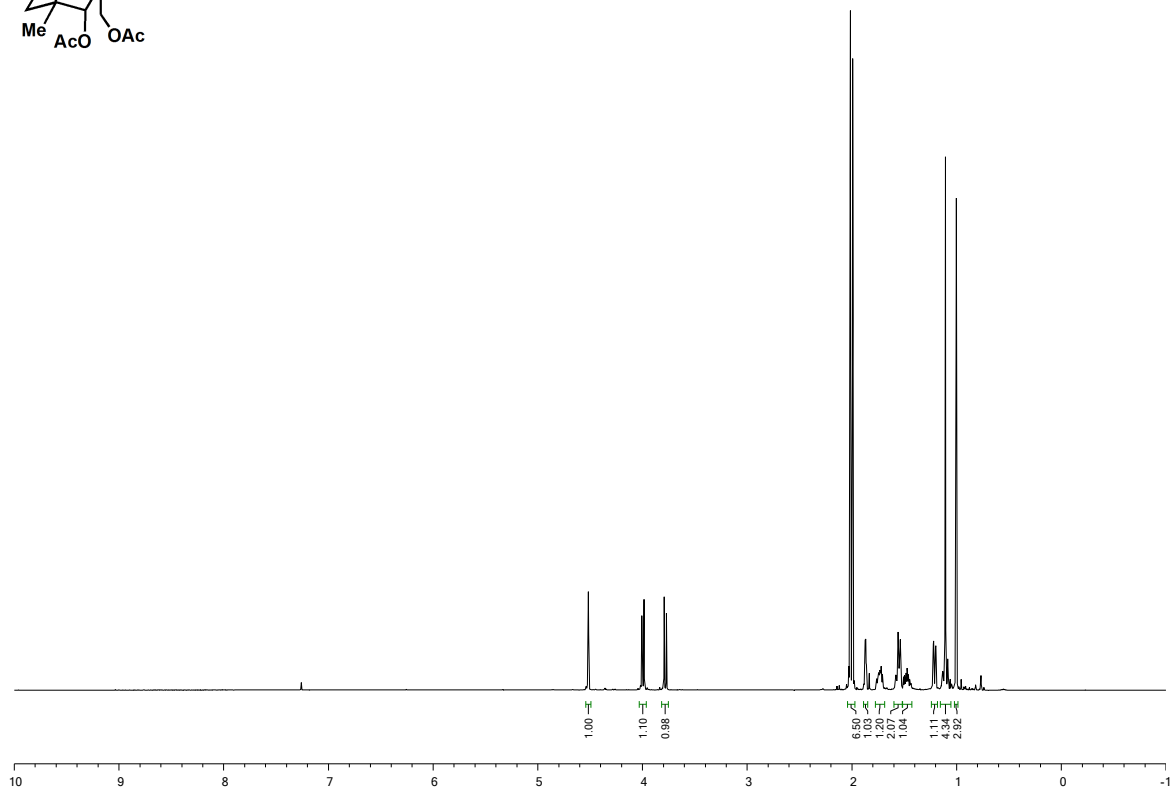
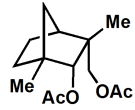


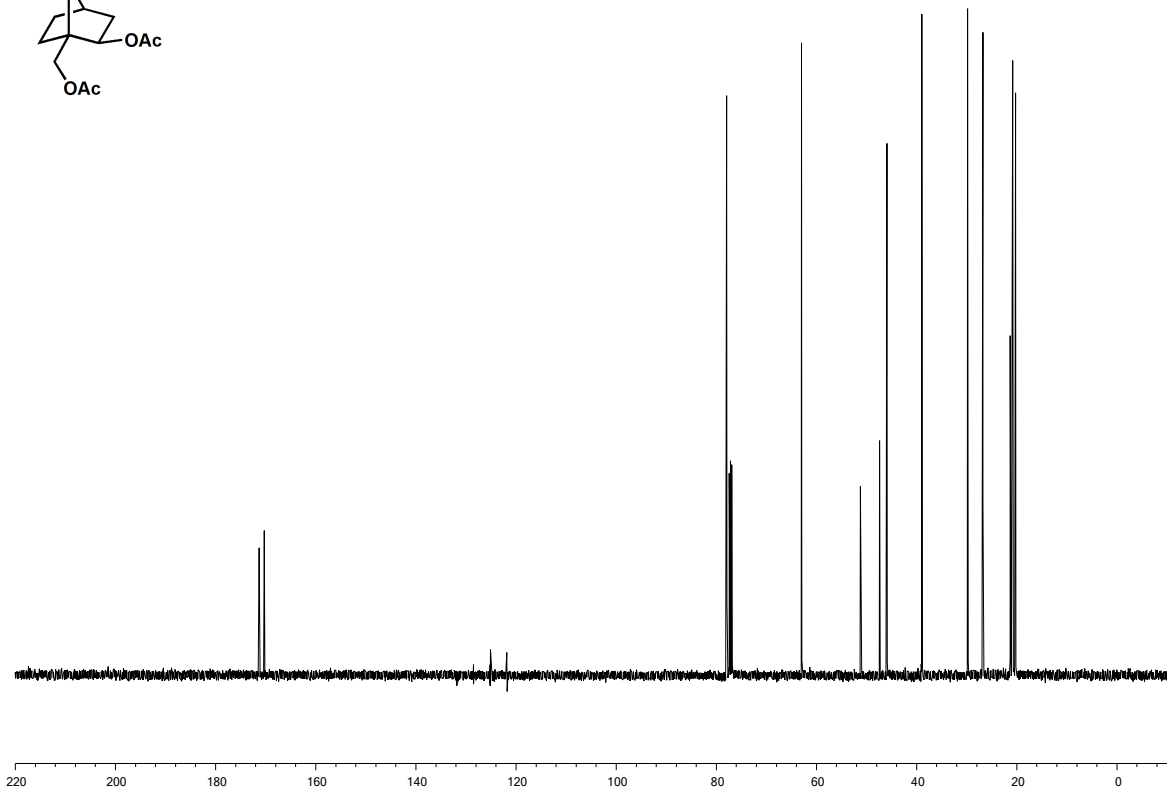
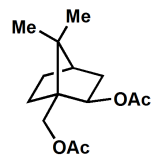
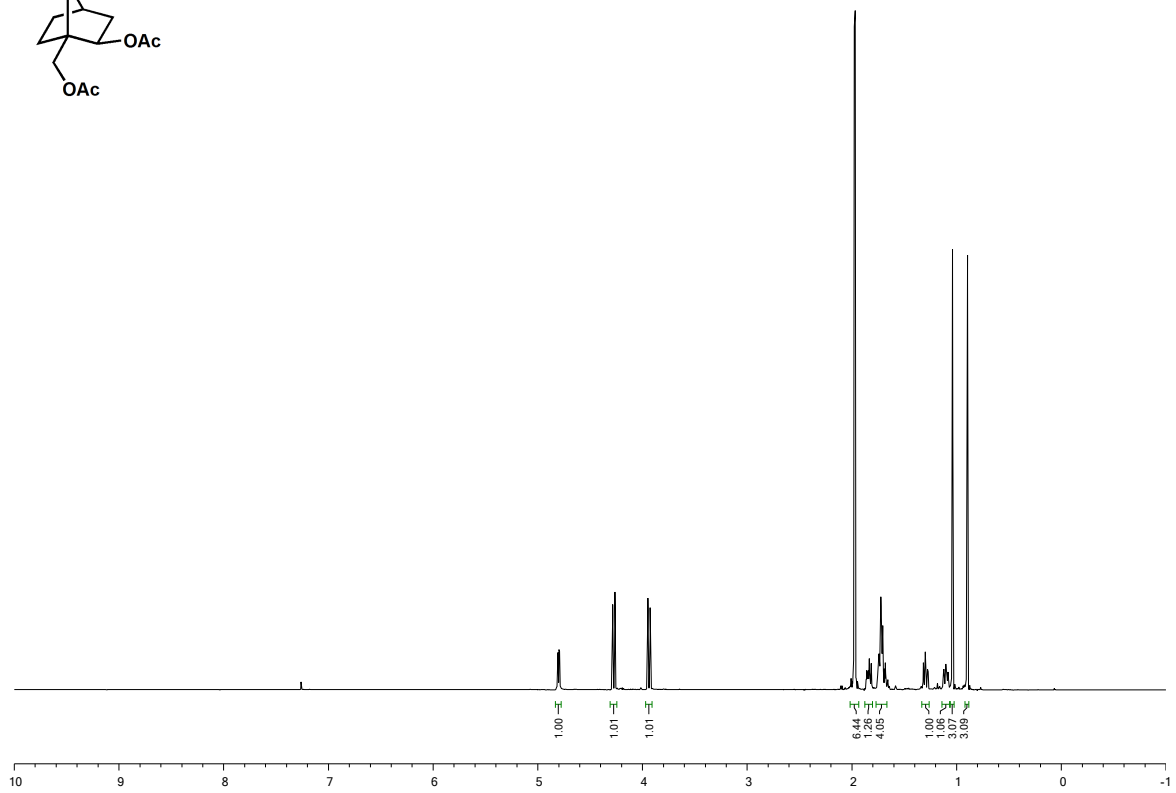
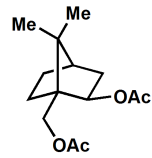


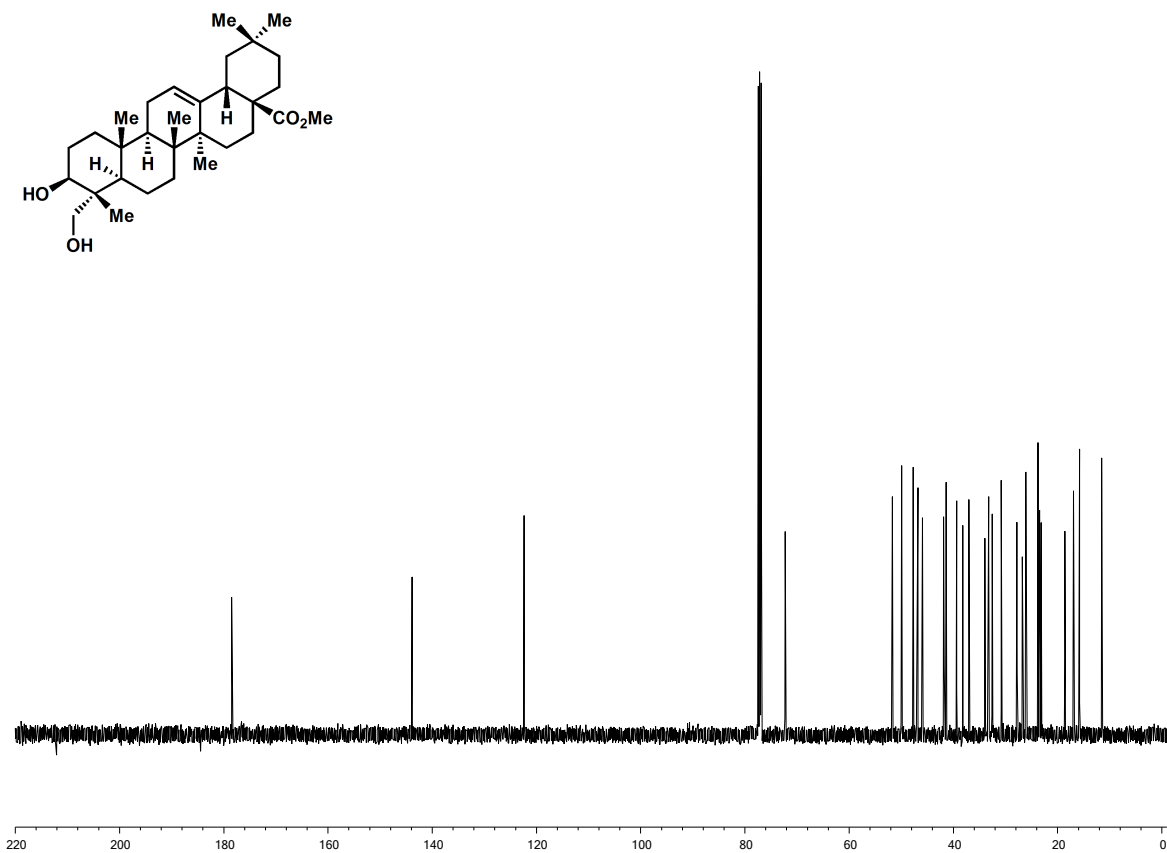
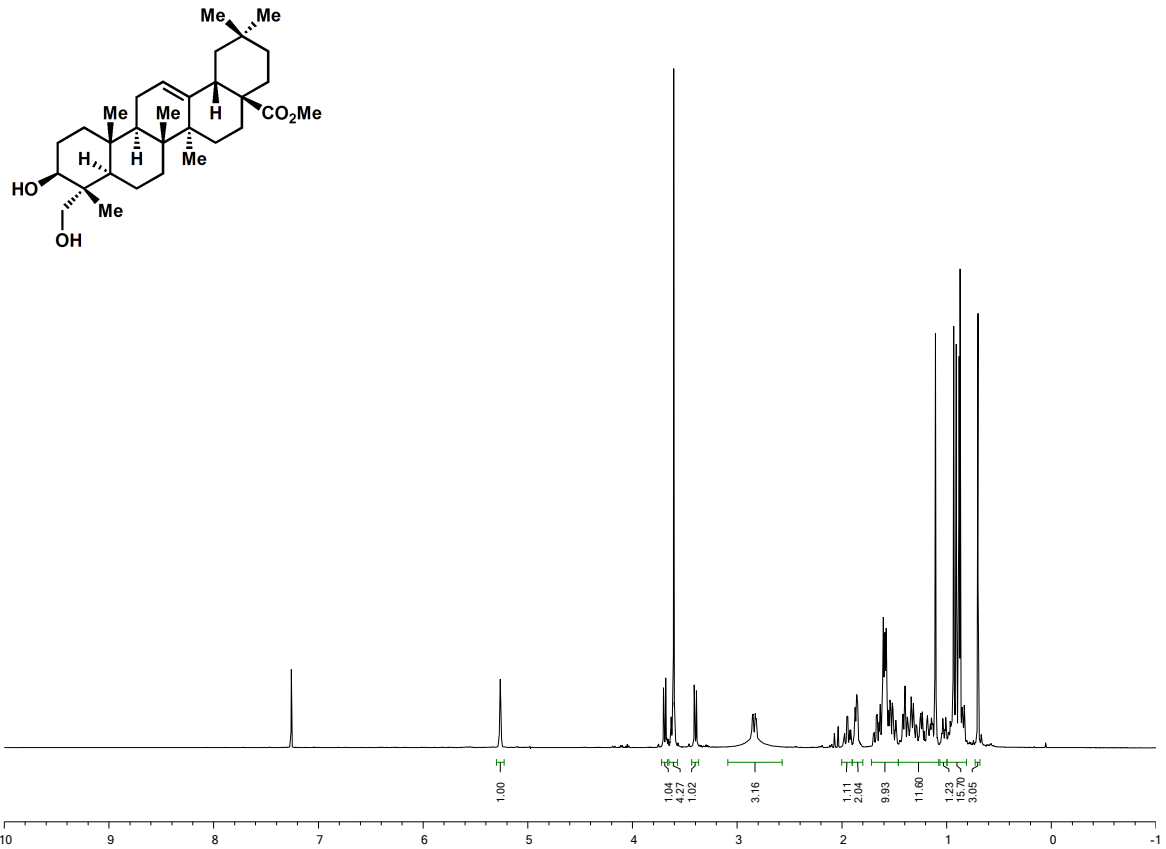


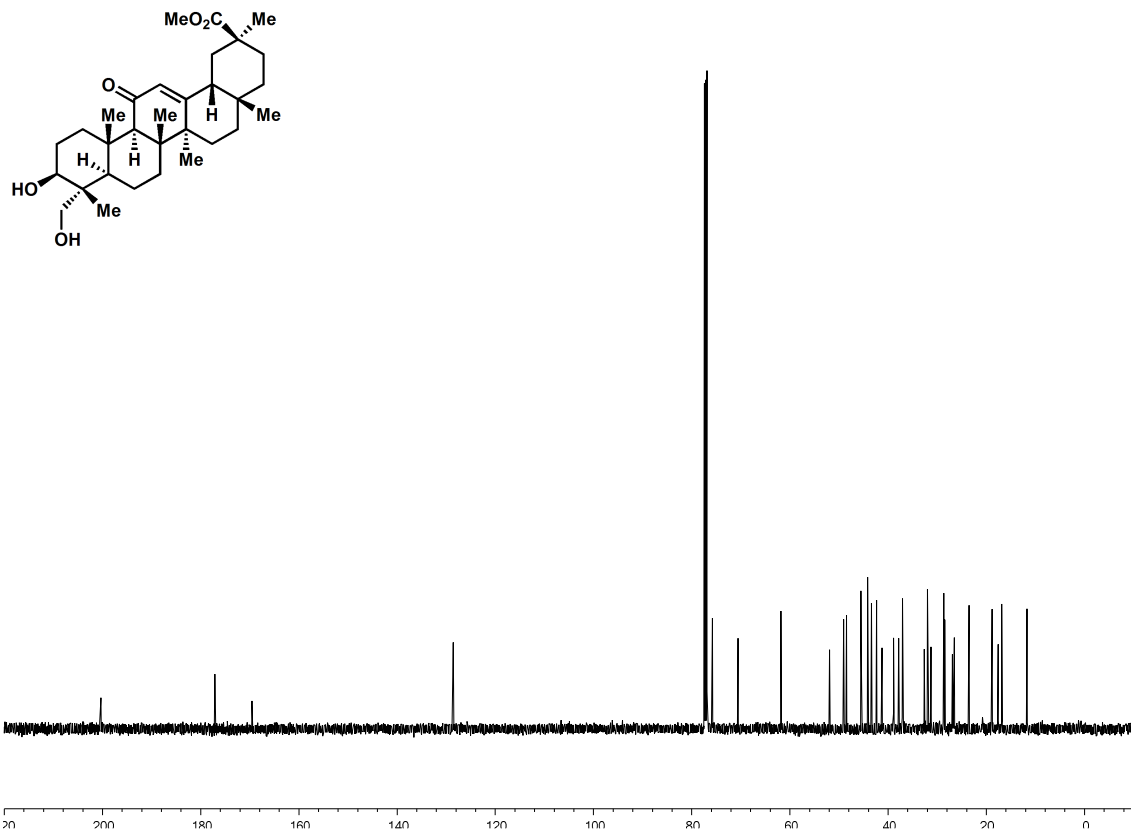
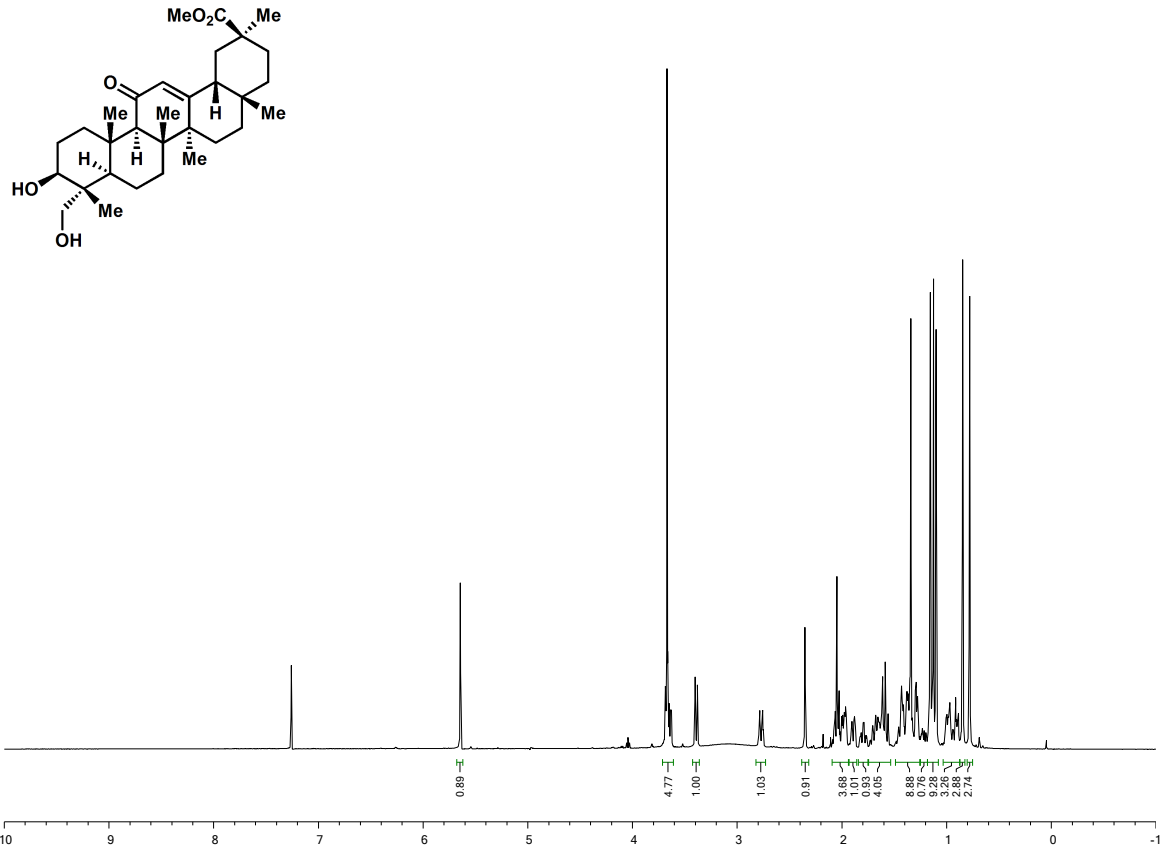












References

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