Supporting Information for

Synthesis of Angularly Substituted *Trans*-fused Hydroindanes by Convergent Coupling of Acyclic Precursors

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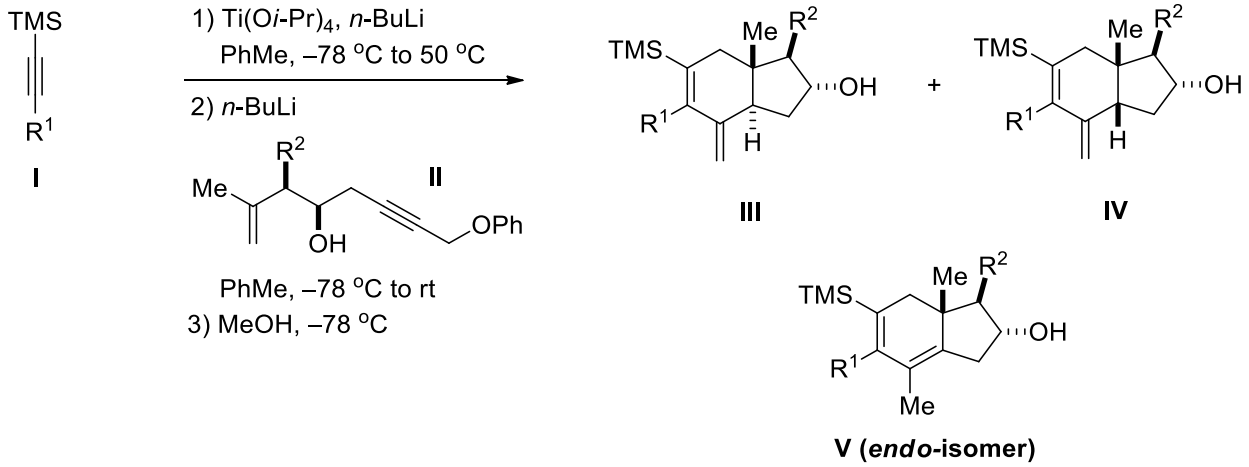
1. Materials and Methods:

All reactions were conducted in flame-dried glassware under a nitrogen atmosphere with dry solvents, unless otherwise noted. All reagents and starting materials were purchased from commercial sources and used as supplied, unless otherwise indicated. Anhydrous diethyl ether (Et_2O), tetrahydrofuran (THF), and toluene (PhMe) were obtained by distillation over sodium and benzophenone. Anhydrous *t*-butanol (*t*-BuOH), dichloromethane (CH_2Cl_2), methanol (MeOH), isopropanol (*i*-PrOH), and trifluoroethanol (CF_3CH_2OH) were purchased from Aldrich and were thoroughly degassed before use. Titanium isopropoxide ($Ti(O\textit{i}\text{-}Pr)_4$) was distilled before use. Solutions of *n*-BuLi and *c*-C_5H_9MgCl were purchased from Aldrich and titrated against *N*-benzylbenzamide and salicylaldehyde phenylhydrazone, respectively. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Flash column chromatography was performed on the Biotage® Automated Liquid Chromatography System Isolera One® using Biotage® SNAP KP-Sil 10-100 g silica gel cartridges. Preparative thin layer chromatography (PTLC) and TLC analyses were performed on EMD TLC Silica gel 60 F_{254} Glass Plates and the spots were visualized by UV-light (254 nm) or an aqueous solution of phosphomolybdic acid, ceric sulfate, and sulfuric acid. ^{1}H NMR data were recorded on Varian Unity Plus 300 and 500 MHz NMR spectrometers and Bruker Avance III 500 MHz spectrometer (TBI probe) with calibration of spectra to residual $CHCl_3$ (7.26 ppm). ^{13}C NMR data were recorded at 75 MHz and 125 MHz on on Varian Unity Plus 300 and 500 MHz NMR spectrometers and Bruker Avance III 500 MHz spectrometer (TBI probe) with calibration to the central line of $CDCl_3$ (77.00 ppm). Infrared spectra were recorded on a JASCO FT/IR-4100 Fourier Transform Infrared Spectrometer. HRMS (ESI-TOF) analyses were performed at the Mass Spectrometry Laboratory of University of Illinois at Urbana-Champaign. All compounds purified by chromatography were sufficiently pure for use in further experiments, unless indicated otherwise.

Note: While the parent compound numbers for the hydroindane products reported in this supporting information remain the same as the numbers employed in the manuscript, distinction between *trans*- and *cis*-fused isomers here has been accomplished by a subclassification in the style of "**compound #a**" for the *trans*-isomer and "**compound #b**" for the *cis*-isomer.

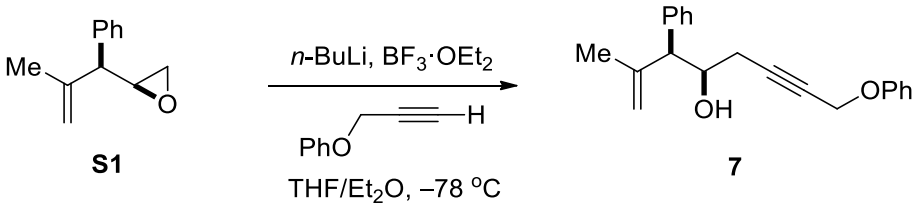
2. Experimental Procedures:

A: General Procedure for the Ti(O*i*-Pr)$_4$/*n*-BuLi-mediated Coupling Process.

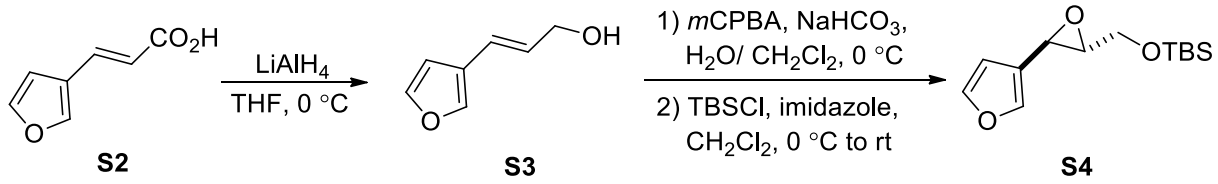


To a solution of alkyne **I** (1.0 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (1.0 mmol) at rt. The mixture was cooled to –78 °C and *n*-BuLi (2.49 M in hexanes, 0.80 mL, 2.0 mmol) was added dropwise (by syringe) over the course of 5 min. After this period, the flask was taken out of the cooling bath and allowed to warm to rt (approx. 20 min). The reaction mixture was then heated to 50 °C (no reflux condenser required) for 1 h and allowed to cool to rt before it was placed into a –78 °C cooling bath. In the meantime, enyne **II** (0.30 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (0.33 mmol) at –78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise (by syringe) to the above black Ti-alkyne complex solution at –78 °C. The reaction mixture was then allowed to warm to rt overnight (approx. 15 h). After this period, the cooling bath was removed and the mixture was stirred at rt for an additional 2 h. The reaction mixture was then drawn into a syringe and added dropwise to vigorously stirring, freshly degassed anhydrous MeOH (60 mL) at –78 °C (under N_2 atmosphere). The flask was then allowed to warm to rt, water (20 mL) was added, and the organic solvents were removed *in vacuo*. (*Note:* The evaporation of methanol prior to the aqueous workup minimizes the loss of organic material that can be caused by its increased partitioning into the aqueous phase.) The crude residue from evaporation was diluted with copious amounts of saturated aqueous NH_4Cl and extracted with Et_2O (three times). The combined organic extracts were vigorously stirred with 10% aqueous KOH for 5 minutes (to remove PhOH from the mixture), the organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting crude mixture was subjected to flash chromatography purification to afford hydroindanes **III** (*trans*-fused isomer), **IV** (*cis*-fused isomer), and a small amount of **V** (*endo*-isomer).

B: Synthesis of Enynes 7, 14, 16, and 18.



(+/–)-(3*S*,4*R*)-2-methyl-8-phenoxy-3-phenyloct-1-en-6-yn-4-ol (7): A solution of phenyl propargyl ether (2.09 g, 15.8 mmol) in THF (35.0 ml) was cooled to –78 °C and *n*-BuLi (2.33 M in hexanes, 4.06 mL, 9.46 mmol) was added dropwise. After 30 min, BF_3•OEt_2 (1.71 mL, 13.9 mmol) was added dropwise and the resulting mixture was stirred at the same temperature for 30 min. A solution of epoxide **S1**[1] (1.10 g, 6.31 mmol) in Et_2O (5.0 ml) was added and the resulting mixture was stirred at –78 °C for an additional hour after which the reaction was quenched by the addition of saturated aqueous $NaHCO_3$. The flask was allowed to warm to rt, the organic layer was separated, and the aqueous layer extracted with Et_2O (three times). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ and brine, and dried over $MgSO_4$. The solvent was removed *in vacuo* and the resulting crude mixture was purified via flash chromatography to afford **7** (1.85 g, 96%) as a colorless oil. Spectral data for **7**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.36 (m, 4H), 7.29 – 7.24 (m, 3H), 7.05 – 6.98 (m, 3H), 4.97 (s, 1H), 4.89 (t, *J* = 1.7 Hz, 1H), 4.75 (d, *J* = 2.0 Hz, 1H), 4.74 (d, *J* = 2.0 Hz, 1H), 4.35 – 4.28 (m, 1H), 3.40 (d, *J* = 8.3 Hz, 1H), 2.60 (ddt, *J* = 16.7, 4.7, 2.0 Hz, 1H), 2.49 (ddt, *J* = 16.7, 6.3, 2.0 Hz, 1H), 1.73 (d, *J* = 4.7 Hz, 1H), 1.61 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6, 145.2, 139.0, 129.4, 128.8, 128.5, 127.0, 121.3, 114.9, 112.6, 84.3, 77.7, 69.7, 57.9, 56.2, 25.7, 21.5; IR (thin film): 3553, 3455, 3061, 3028, 2968, 2914, 2289, 2229, 1644, 1598, 1495, 1452, 1374, 1215, 753, 701 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{21}H_{23}O_2$ [M+H$^+$] 307.1693, found 307.1694.

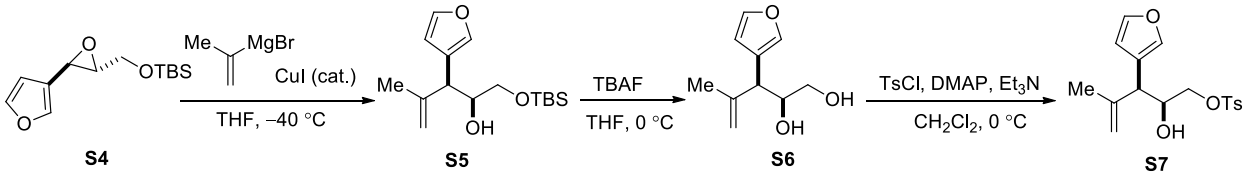


(+/–)-*Tert*-butyl(((2*R*,3*R*)-3-(furan-3-yl)oxiran-2-yl)methoxy)dimethylsilane (S4): To a stirred suspension of $LiAlH_4$ (2.06 g, 54.3 mmol) in anhydrous THF (40 mL) at 0 °C was added dropwise a solution of *trans*-3-furanacrylic acid **S2** (5.00 g, 36.2 mmol) in anhydrous THF (40 mL). The reaction mixture was allowed to warm to rt and stirred for 1.5 h. Upon cooling back to 0 °C, the excess $LiAlH_4$ was quenched by careful addition of water (dropwise). After hydrogen evolution ceased, the reaction mixture was diluted with Et_2O and water, followed by a 20% aqueous solution of Rochelle salt. After stirring for 30 min, the organic layer was separated and the aqueous layer was extracted with Et_2O (three times). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo* to give the crude alcohol

[1] Greszler, S., Reichard, H. A., Micalizio, G. C. *J. Am. Chem. Soc*. **2012**, *134*, 2766-2774.

S3 (4.58 g) as a colorless oil which was used in the next step immediately without purification. The spectral data of alcohol **S3** were identical to those reported in the literature.[2]

The crude alcohol **S3** was dissolved in CH_2Cl_2 (180 mL) and saturated $NaHCO_3$ (180 mL) was added. This mixture was cooled to 0 °C and *m*CPBA (≤ 77%, 12.2 g, 54.3 mmol) was added in small portions. The resulting heterogeneous mixture was stirred vigorously at the same temperature for 1 h. After this period, it was transferred to a separatory funnel (while still cold) and the layers were separated. The organic layer was washed with saturated aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$, and brine and dried over Na_2SO_4. Removal of the solvent *in vacuo* affored a crude oil which was dissolved in dry CH_2Cl_2 (47 mL) and cooled to 0 °C immediately. To this solution was added imidazole (1.58 g, 23.3 mmol), followed by TBSCl (3.51 g, 23.3 mmol). The resulting mixture was warmed to rt and stirred for 2 h. After this period, it was partitioned between CH_2Cl_2 and saturated aqueous $NaHCO_3$, and the aqueous layer was extracted with CH_2Cl_2 (twice). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude residue by flash chromatography (silica gel, 94:6:1 hexanes:EtOAc:Et_3N) afforded the *tert*-butyl dimethylsilyl ether **S4** (1.63 g, 23% over three steps) as a colorless oil. Spectral data for **S4**: ^{1}H NMR (500 MHz, $CDCl_3$) 7.51 – 7.50 (m, 1H), 7.38 – 7.37 (m, 1H), 6.29 – 6.28 (m, 1H), 3.93 (dd, *J* = 12.0, 3.1 Hz, 1H), 3.80 (dd, *J* = 12.0, 4.3 Hz, 1H), 3.74 (d, *J* = 2.2 Hz, 1H), 3.22 (ddd, *J* = 4.3, 3.1, 2.2 Hz, 1H), 0.91 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 141.5, 122.8, 108.4, 63.0, 61.2, 49.6, 26.1 (3C), 18.6, –5.1 (2C); IR (thin film): 2958, 2926, 2896, 2857, 1505, 1466, 1362,1254, 1104, 1024, 936, 877, 839, 780, 731, 665, 595 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{13}H_{22}O_3NaSi$ [M+Na^+] 277.1236, found 277.1230.



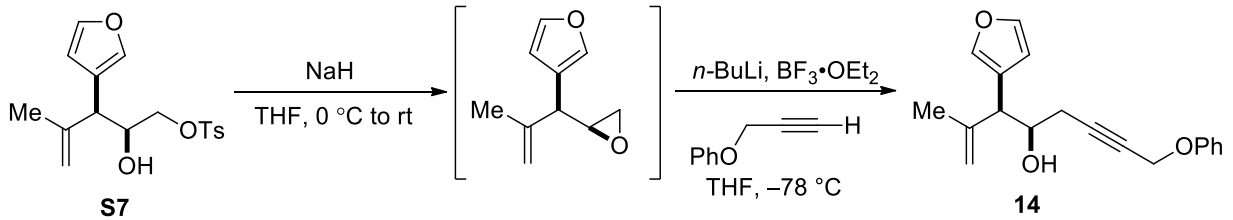
(+/–)-(2*S*,3*S*)-3-(furan-3-yl)-2-hydroxy-4-methylpent-4-en-1-yl 4-methylbenzenesulfonate (S7): To a stirred suspension of CuI (0.36 g, 1.89 mmol) in anhydrous THF (10 mL) at –60 °C was added isopropenylmagnesium bromide (0.50 M in THF, 50.3 mL, 25.2 mmol) over 5 min. The resulting yellow mixture was allowed to warm to –40 °C (over the course of 30 min) and a solution of epoxide **S4** (1.60 g, 6.29 mmol) in THF (10 mL) was added via syringe. The reaction mixture was stirred at –40 °C for 1.5 h and subsequently quenched by addition of saturated aqueous NH_4Cl. After further dilution with water and Et_2O, the layers were separated and the aqueous layer was extracted with Et_2O (four times). The combined organic extracts were dried over Na_2SO_4 and concentrated *in vacuo* to give the crude alcohol **S5** (1.88 g) as a pale yellow oil. This alcohol was sufficiently pure to be used in the next step without purification. An analytical sample was obtained as a colorless oil by purification of 20 mg of the crude product by flash chromatography (silica gel, gradient 98:2 to 80:20 hexanes: EtOAc). Spectral data for **S5**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.39 (m, 1H), 7.37 – 7.36 (m, 1H), 6.36 – 6.35 (m, 1H), 4.91 – 4.90 (m, 1H), 4.88 – 4.86 (m, 1H), 4.00 – 3.96 (m, 1H), 3.65 (dd, *J* = 10.2, 3.6 Hz, 1H), 3.50 (dd, *J* = 10.0, 6.8 Hz, 1H), 3.34 (d, *J* = 7.9 Hz, 1H), 2.45 (d, *J* = 4.0 Hz, 1H), 1.68 (app. dd, *J* = 1.4, 0.8 Hz, 3H), 0.91 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (125

[2] Menon, R. S., Banwell, M. G. *Org*. *Biomol*. *Chem*. **2010**, *8*, 5483–5485.

MHz, $CDCl_3$) δ 145.0, 142.7, 140.5, 124.1, 113.4, 111.3, 71.9, 65.5, 47.1, 26.1 (3C), 20.7, 18.5, –5.1, –5.2; IR (thin film) 3568, 3153, 2961, 2930, 2885, 2853, 1505, 1469, 1389, 1257, 1160, 1111, 1027, 936, 874, 843, 783, 728, 665, 594 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{16}H_{28}O_3SiNa$ [M+Na^+] 319.1705, found 319.1705.

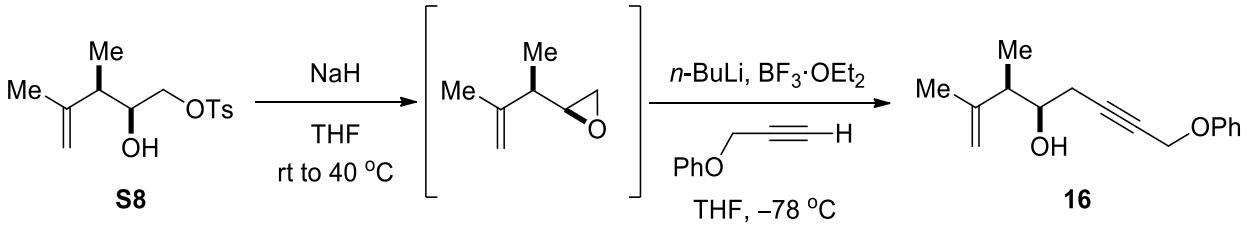
To a solution of the above crude alcohol **S5** (1.88 g) in anhydrous THF (21 mL) at 0 °C was added TBAF (1.0 M in THF, 6.9 mL, 6.9 mmol). The solution was stirred at 0 °C for 1 h after which time water was added. The layers were separated and the aqueous layer extracted with Et_2O (five times). The combined organic extracts were dried over Na_2SO_4 and the solvent was removed *in vacuo*. The resulting crude diol **S6** (1.46 g) was used directly in the next step without purification. A pure sample of the diol was obtained as a colorless oil by purification of 30 mg of the crude product by flash chromatography (silica gel, 50:50:2.3 hexanes:EtOAc:MeOH). Spectral data for diol **S6**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 2H), 6.35 – 6.34 (m, 1H), 4.91 – 4.90 (m, 1H), 4.89 – 4.87 (m, 1H), 4.04 – 3.99 (m, 1H), 3.70 (ddd, *J* = 11.3, 5.4, 3.4 Hz, 1H), 3.52 (ddd, *J* = 11.2, 6.8, 3.2 Hz, 1H), 3.32 (d, *J* = 8.5 Hz, 1H), 2.38 – 2.34 (m, 1H), 2.30 (d, *J* = 3.2 Hz, 1H), 1.69 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 143.3, 140.5, 123.6, 113.4, 110.9, 72.3, 65.1, 47.3, 21.1; IR (thin film) 3390, 3077, 2969, 2920, 2885, 1644, 1501, 1439, 1376, 1195, 1150, 1100, 1024, 895, 874, 776, 731, 661, 599 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{10}H_{14}O_3Na$ [M+Na^+] 205.0841, found 205.0837.

The crude diol **S6** from the above step was dissolved in dry CH_2Cl_2 (20 mL) and cooled to 0 °C. Et_3N (2.64 mL, 18.84 mmol) was added, followed by TsCl (1.44 g, 7.54 mmol) and DMAP (153 mg, 1.26 mmol). The reaction mixture was stirred at 0 °C for 3 h. After this period, saturated aqueous $NaHCO_3$ was added, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (four times). The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by flash chromatography (silica gel, gradient 80:20:1 to 70:30:1 hexanes:EtOAc:Et_3N) to yield tosylate **S7** (1.17 g, 55% over three steps) as a yellow oil. Spectral data for **S7** : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 2H), 7.37 – 7.32 (m, 4H), 6.30 – 6.29 (m, 1H), 4.89 – 4.88 (m, 1H), 4.87 – 4.86 (m, 1H), 4.22 – 4.17 (m, 1H), 4.11 (dd, *J* = 10.3, 3.5 Hz, 1H), 3.97 (dd, *J* = 10.3, 6.6 Hz, 1H), 3.33 (d, *J* = 7.5 Hz, 1H), 2.45 (s, 3H), 2.01 – 1.99 (m, 1H), 1.67 (app. dd, *J* = 1.4, 0.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2, 144.0, 143.1, 140.7, 132.8, 130.0 (2C), 128.1 (2C), 122.4, 114.0, 111.0, 72.3, 69.7, 46.5, 21.8, 21.1; IR (thin film) 3533, 3146, 3069, 2972, 2951, 2920, 1769, 1644, 1596, 1501, 1445, 1362, 1173, 1097, 1024, 975, 815, 665, 599, 550 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{17}H_{20}O_5NaS$ [M+Na^+] 359.0929, found 359.0932.



(+/–)-(3*S*,4*R*)-3-(furan-3-yl)-2-methyl-8-phenoxyoct-1-en-6-yn-4-ol (14): To a solution of tosylate **S7** (390 mg, 1.16 mmol) in THF (5.0 mL) was added NaH (140 mg, 60% dispersion in mineral oil, 3.48 mmol) at 0 °C and the resulting heterogeneous mixture was stirred at rt for 5 h (or until TLC indicated complete consumption of the starting material). In the meantime, phenyl propargyl ether (1.80 mL, 2.32 mmol) was

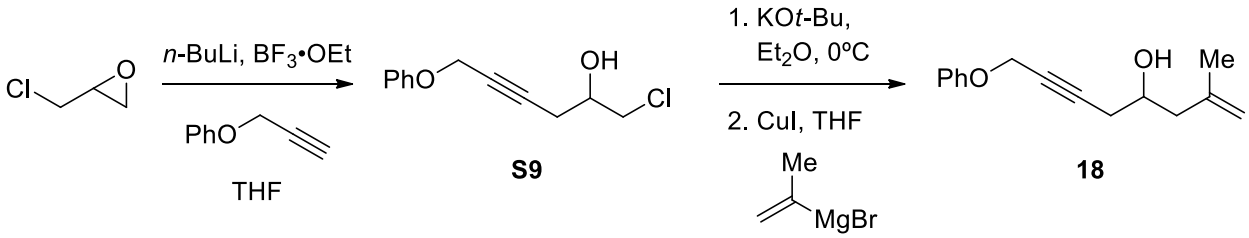
dissolved in THF (5.0 mL), treated with *n*-BuLi (0.93 mL, 2.5 M in hexanes, 2.32 mmol) at –78 °C, and stirred at this temperature for 15 min before it was allowed to warm to a temperature between 0 °C and rt (approx. 15 min). The resulting lithium acetylide solution was added dropwise (by syringe) to the above epoxide solution at –78 °C, followed by BF_3•OEt_2 (0.26 mL, 2.09 mmol). After 45 min at –78 °C, TLC indicated full consumption of the epoxide intermediate and the reaction was quenched with saturated NH_4Cl, followed by dilution with water. After the layers were separated, the aqueous layer was extracted with Et_2O (three times). The combined organic extracts were washed with brine and dried over Na_2SO_4. The solvent was removed *in vacuo* and the resulting crude product was purified by flash chromatography (silica gel, 80:20:1 hexanes:EtOAc:Et_3N) to afford the title compound as a colorless oil (253 mg, 74%). Spectral data for **14**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.37 (m, 1H), 7.32 – 7.28 (m, 3H), 7.00 – 6.97 (m, 3H), 6.32 – 6.31 (m, 1H), 4.89 – 4.88 (m, 1H), 4.88 – 4.86 (m, 1H), 4.72 (t, *J* = 2.1 Hz, 2H), 4.10 – 4.05 (m, 1H), 3.33 (d, *J* = 7.2 Hz, 1H), 2.52 – 2.41 (m, 2H), 1.86 (d, *J* = 4.3 Hz, 1H), 1.67 (dd, *J* = 1.3, 0.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.8, 144.9, 143.1, 140.7, 129.6 (2C), 122.9, 121.6, 115.2 (2C), 113.7, 111.2, 84.4, 77.9, 70.2, 56.4, 49.1, 25.7, 21.3; IR (neat) 3547, 3142, 3073, 2969, 2913, 1644, 1603, 1495, 1452,1372, 1303, 1261, 1216, 1177, 1156. 1080, 1027, 899, 871, 787, 756, 689, 599 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{19}H_{20}O_3Na$ [M+Na$^+$] 319.1310, found 319.1311.



(+/–)-(3*R*,4*R*)-2,3-dimethyl-8-phenoxyoct-1-en-6-yn-4-ol (16): To a solution of tosylate **S8**[3] (2.00 g, 7.03 mmol) in THF (35.0 mL) was added NaH (60% dispersion in mineral oil, 562 mg, 14.2 mmol) at 0 °C and the resulting suspension was stirred at rt for 4 h. Additional NaH (60% dispersion in mineral oil, 250 mg, 6.25 mmol) was then added and the mixture was stirred for 1 h at rt. After this period, the reaction mixture was heated to 40 °C for 1 h to drive the formation of the epoxide to completion. In the meantime, phenyl propargyl ether (1.80 mL, 14.1 mmol) was dissolved in THF (25 mL), treated with *n*-BuLi (2.39 M in hexanes, 5.00 mL, 12.0 mmol) at –78 °C, and stirred at this temperature for 40 min. The resulting lithium acetylide solution was added dropwise to the above epoxide solution at –78 °C. After 15 min, neat BF_3•OEt_2 (1.56 mL, 12.7 mmol) was added dropwise at –78 °C. After 35 min, the reaction was quenched by the addition of saturated aqueous $NaHCO_3$.[4] The flask was allowed to warm to rt, the organic layer was separated, and the aqueous layer extracted with Et_2O (three times). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ and brine, and dried over $MgSO_4$. The solvent was removed *in vacuo* and the resulting crude mixture was purified via flash chromatography to afford **16** (1.52 g, 89%) as a colorless oil. Spectral data for **16**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.01 – 6.95 (m, 3H), 4.81 (t, *J* = 1.7 Hz, 1H), 4.75 (s, 1H), 4.70 (d, *J* = 2.0 Hz, 1H), 4.71 (d, *J* = 2.0 Hz, 1H), 3.69 – 3.63 (m, 1H), 2.46 (ddt, *J* = 16.7, 7.0, 2.0 Hz, 1H), 2.39 (ddt, *J* = 16.7, 7.0, 2.0 Hz, 1H), 2.26 (quin, *J* = 7.0 Hz, 1H), 1.78 (d, *J* = 4.7 Hz, 1H), 1.67

[3] Greszler, S., Reichard, H. A., Micalizio, G. C. *J. Am. Chem. Soc*. **2012**, *134*, 2766-2774.
[4] Woo, S. K., Lee, E. *J. Am. Chem. Soc.* **2010**, *132*, 4564-4565.

(s, 3H), 1.07 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6, 147.2, 129.4, 121.4, 115.0, 112.0, 84.6, 77.5, 71.2, 56.2, 45.7, 25.5, 20.4, 14.2; IR (thin film): 3545, 3449, 3071, 3049, 2967, 2936, 2914, 2291, 2230, 1644, 1598, 1495, 1374, 1216, 1031, 1011, 894, 753, 690 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{16}H_{21}O_2$ [M+H$^+$] 245.1536, found 245.1540.

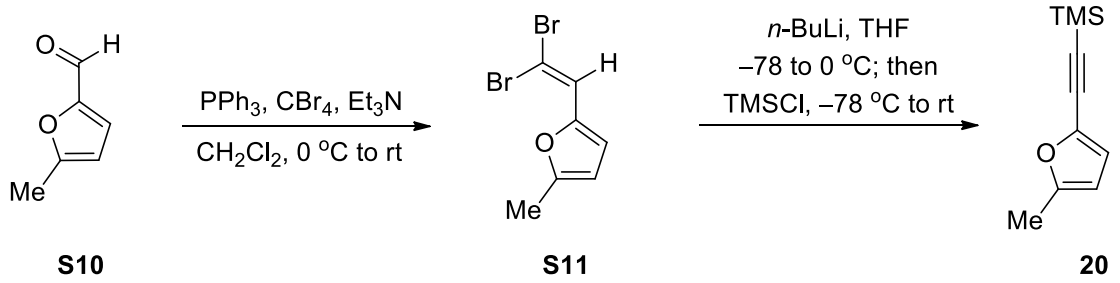


1-chloro-6-phenoxyhex-4-yn-2-ol (S9): To a –78˚C solution of phenyl propargyl ether (10.0 g, 75.7 mmol) in THF (300 mL) was added *n*-BuLi (29.0 mL, 2.5 M in hexanes, 72.5 mmol) dropwise. The reaction was stirred at –78˚C for 15 minutes, then BF_3•OEt_2 (13.1 ml, 106.5 mmol) was added dropwise. The solution was stirred at –78˚C for an additional 5 minutes after which time (+/–)-epichlorohydrin (3.80 ml, 48.5 mmol) was added dropwise via syringe. The reaction mixture was stirred at –78 ˚C for an additional 30 minutes and subsequently quenched by the addition of saturated aqueous $NaHCO_3$ (at –78˚C). The resulting suspension was allowed to warm to rt, the layers were separated, and the aqueous layer was extracted with Et_2O (three times). The combined organic extracts were washed with brine and dried over Na_2SO_4. Concentration *in vacuo* gave a crude yellow oil that was purified via flash chromatography to provide chlorohydrin **S9** (15.2 g, 89%) as a colorless oil. Spectral data for **S9**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.02 – 6.95 (m, 3H), 4.70 (s, 2H), 3.99 – 3.93 (m, 1H), 3.65 (dd, *J* = 11.2, 4.4 Hz, 1H), 3.57 (dd, *J* = 11.2, 4.4 Hz, 1H), 2.63 – 2.53 (m, 2H), 2.30 (br. s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6, 129.6, 121.6, 115.1, 82.8, 78.3, 69.7, 56.2, 48.4, 24.8; IR (thin film): 3419, 3040, 2915, 2359, 1598, 1495, 1374, 1214, 1174, 1030, 754, 691 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{12}H_{13}ClO_2Na^+$ [M+Na$^+$] 247.0502, found 247.0504.

2-methyl-8-phenoxyoct-1-en-6-yn-4-ol (18): To a 0˚C solution of chlorohydrin **S9** (2.0 g, 8.9 mmol) in Et_2O (200 mL) was added KO*t*-Bu (0.90 g, 8.0 mmol). The reaction mixture was allowed to stir at 0˚C for 25 minutes, at which point TLC analysis indicated complete consumption of the starting material. The suspension was decanted into a separatory funnel and washed with saturated $NaHCO_3$, then dried over Na_2SO_4, and concentrated. The resulting oil was used in the next step without further purification. The intermediate epoxide was dissolved in THF (45 mL), CuI (0.34 g, 1.8 mmol) was added, and the reaction mixture was cooled to –78 ˚C. Isopropenylmagnesium bromide (0.50 M in Et_2O, 25.8 mL, 12.9 mmol) was added by syringe and the mixture was allowed to warm to rt. After stirring at rt for 1 hour, the reaction mixture was quenched with saturated aqueous NH_4Cl. The layers were separated and the aqueous layer was extracted with Et_2O (three times). The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude oil which was purified via flash chromatography to provide enyne **18** (1.29 g, 63% over 2 steps). Spectral data for **18**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.00 – 6.96 (m, 3H), 4.87 (s, 1H), 4.77 (s, 1H), 4.72 (app. t, *J* = 2.1 Hz, 2H), 3.93 – 3.83 (m, 1H), 2.47 – 2.43 (m, 2H), 2.30 – 2.13 (m, 2H), 1.90 (d, *J* = 6.45 Hz, 1H), 1.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 129.7, 121.7, 115.1, 73.9, 69.8, 56.3, 48.5, 24.9, 21.7; IR (thin film): 3427, 3073, 2934, 1647, 1599, 1495,

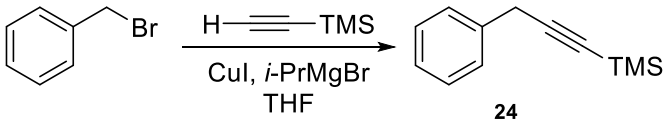
1375, 1216, 1174, 1031, 893, 754, 691 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{15}H_{19}O_2$ [M+H^+] 231.1385, found 231.1385.

C: Synthesis of Alkynes 20, 24, and 29.



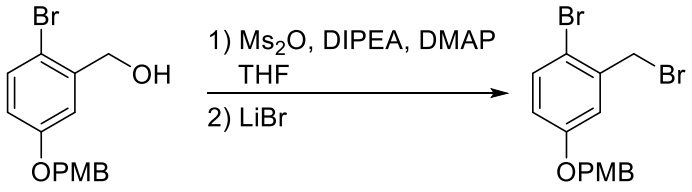
S10 **S11** **20**

Trimethyl((5-methylfuran-2-yl)ethynyl)silane (20): To a solution of PPh_3 (31.5 g, 120 mmol) in CH_2Cl_2 (120 mL) was added CBr_4 (19.9 g, 60.0 mmol) at 0 °C. After 10 min, Et_3N (18.0 mL, 129 mmol) was added and the reaction mixture was stirred for an additional 10 min at the same temperature. To this solution, 5-methyl-2-furaldehyde **S10** (2.98 mL, 30.0 mmol) was added dropwise and the resulting mixture was stirred at rt for 2 h. After this period, the reaction was quenched by the addition of saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$, and the resulting mixture was extracted with EtOAc. The combined organic extracts were washed with saturated aqueous $NaHCO_3$ and brine, and dried over Na_2SO_4. The solvent was removed *in vacuo* and the resulting crude mixture was purified via flash chromatography to afford dibromoalkene **S11** (5.89 g, 22.2 mmol). A solution of dibromoalkene **S11** in THF (88.0 ml) was cooled to –78 °C and treated dropwise with *n*-BuLi (2.50 M in hexanes, 26.4 mL, 66.0 mmol). After 1 h, the mixture was warmed to 0 °C and stirred for an additional 2h 45 min at the same temperature. The mixture was then cooled to –78 °C and treated with TMSCl (5.58 ml, 44.0 mmol). After stirring for 50 min, the mixture was warmed to 0 °C and stirred for an additional 1h 20 min at the same temperature. The reaction was quenched by saturated aqueous NH_4Cl at 0 °C, the organic layer was separated, and the aqueous layer extracted with EtOAc. The combined organic extracts were washed with saturated aqueous $NaHCO_3$ and brine, and dried over Na_2SO_4. The solvent was removed *in vacuo*, and the resulting crude mixture was purified via flash chromatography to afford **20** (2.93 g, 55% for 2 steps) as a colorless oil. Spectral data for **20**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.50 (d, *J* = 3.3 Hz, 1H), 5.96 – 5.94 (m, 1H), 2.29 (dd, *J* = 0.95, 0.5 Hz, 3H), 0.241 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.7, 135.3, 117.0, 106.9, 99.0, 94.6, 13.8, –0.2; IR (neat): 2960, 2925, 2899, 2153, 1595, 1527, 1251, 1021, 946, 859, 845 cm^{-1}; HRMS (EI) Calculated for $C_{10}H_{14}OSi$ [M^+] 178.0808, found 178.0816.



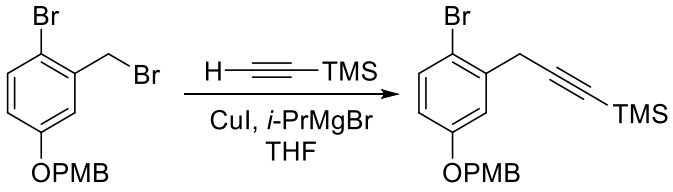
24

Benzyltrimethylsilane (24): To a flask charged with ethynyltrimethylsilane (5.80 mL, 41.0 mmol) and THF (40 mL) was added isopropylmagnesium bromide (2.0 M in Et_2O, 20 mL, 40 mmol) dropwise at 0°C. After the addition was complete, the ice bath was removed and the reaction mixture was stirred at rt for 45 min before CuI (0.80 g, 4.2 mmol) was added in one portion. After 5 min, benzyl bromide (1.20 mL, 10.2 mmol) was added, the reaction vessel was equipped with a reflux condenser, and refluxed overnight. After completion of the reaction, the heating bath was removed and the mixture was allowed to cool to rt. Subsequently, the reaction vessel was placed into an ice bath and saturated aqueous NH_4Cl was added. The resulting heterogeneous mixture was then diluted with EtOAc, washed with brine, filtered through $MgSO_4$, and concentrated *in vacuo*. The crude residue from evaporation was purified via flash chromatography to afford **24** (1.82 g, 95%) as a colorless oil. All characterization data for **24** matched the previously reported literature values.[5]



S12 **S13**

1-bromo-2-(bromomethyl)-4-((4-methoxybenzyl)oxy)benzene (S13): To a 0 °C solution of **S12**[6] (2.0 g, 6.18 mmol) in THF (10.0 mL) were added DIPEA (3.2 mL, 18.54 mmol) and DMAP (73 mg, 0.6 mmol). Methanesulfonic anhydride (2.15 g, 12.36 mmol) dissolved in THF (10 mL) was then added dropwise and the reaction mixture was stirred at rt for 3 h. After this period, LiBr (2.15 g, 24.72 mmol) dissolved in THF (15.0 mL) was added and the reaction mixture was stirred overnight at rt. Subsequently $NaHCO_3$ (25 mL, aq. sat.) was added and the resulting heterogeneous mixture was then diluted with EtOAc (100 mL), washed with brine, filtered through $MgSO_4$, and concentrated *in vacuo* to give the crude bromide **S13** (4.5 g) as a white solid which was used in the next step without further purification.



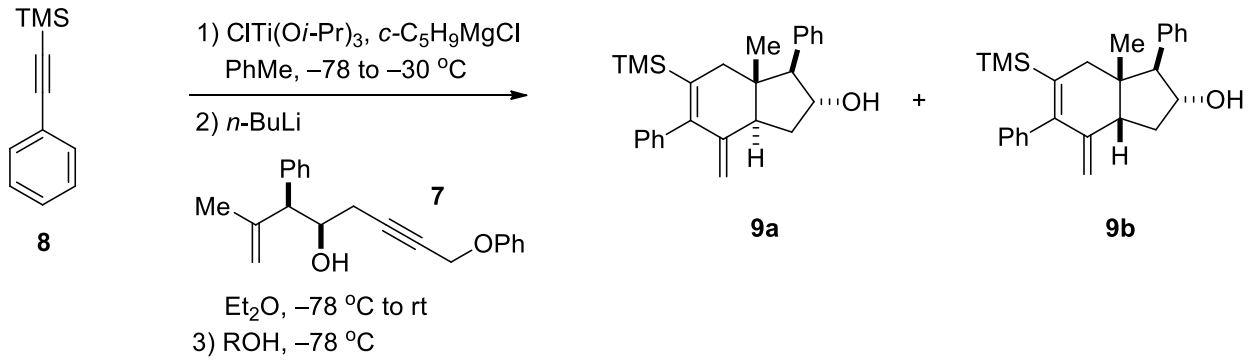
S13 **29**

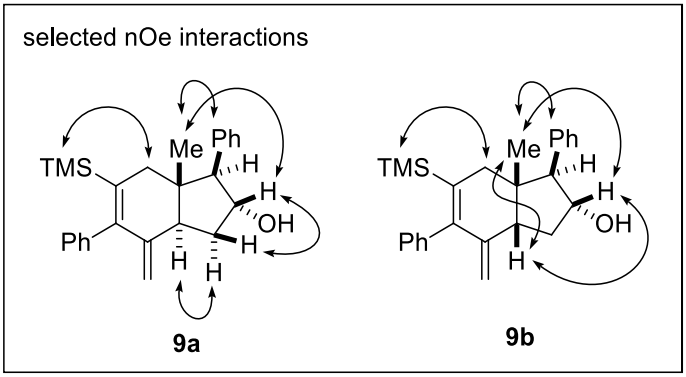
[5] Wender, P. A., Lesser, A. B. and Sirois, L. E. *Angew. Chem. Int. Ed*. **2012**, *51*, 2736-2740; Das, M., O'Shea, D. F. *Tetrahedron* **2013**, *69*, 6448-6460.

[6] Sharma, R., Akerman, M., Cardozo, M.G., Houze, J.B., Li, A.R., Liu, J., Liu, J., Ma, Z., Medina, J., Schmitt, M.J, Sun, Y., Wang, Z., Zhu, L., Bicyclic carboxylic acid derivatives useful for treating metabolic disorders. WO 2007/106469 A2, September 20, 2007.

(3-(2-bromo-5-((4-methoxybenzyl)oxy)phenyl)prop-1-yn-1-yl)trimethylsilane (29): To a flask charged with ethynyltrimethylsilane (3.0 mL, 20.8 mmol) and THF (20 mL) was added isopropylmagnesium bromide (2.0 M in Et_2O, 10 mL, 20.4 mmol) dropwise at 0°C. After the addition was complete, the ice bath was removed and the reaction mixture was stirred at rt for 45 min before CuI (0.40 g, 2.0 mmol) was added in one portion. After 5 min, a solution of benzyl bromide **S13** (2.0 g, 5.2 mmol) in THF (20 mL) was added, the reaction vessel was equipped with a reflux condenser, and refluxed overnight. After completion of the reaction, the heating bath was removed and the mixture was allowed to cool to rt. Subsequently, the reaction vessel was placed into an ice bath and saturated aqueous NH_4Cl was added. The resulting heterogeneous mixture was then diluted with EtOAc, washed with brine, filtered through $MgSO_4$, and concentrated *in vacuo*. The crude residue from evaporation was purified via flash chromatography to afford **29** (1.8 g, 90%) as a white solid. Spectral data for **29**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.7 Hz, 1H), 4.35 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 3.0 Hz, 1H), 6.94 – 6.90 (m, 2H), 6.74 (dd, *J* = 8.7, 3.0 Hz, 1H), 4.99 (s, 2H), 3.82 (s, 3H), 3.68 (s, 2H), 0.21 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 158.2, 136.6, 132.9, 129.2, 128.5, 115.9, 115.2, 114.2, 114.0, 102.9, 88.4, 69.9, 55.3, 27.3, 0.1; IR (thin film): 2957, 2898, 2834, 2178, 1613, 1591, 1573, 1515, 1465, 1250, 1173, 1036, 1016, 845 cm^{-1}; HRMS (EI-TOF) Calculated for $C_{20}H_{24}BrO_2Si$ [M^+] 402.0651, found 402.0652.

D: Representative Procedure for the ClTi(O*i*-Pr)$_3$/*c*-C$_5$H$_9$MgCl-mediated Coupling Process.



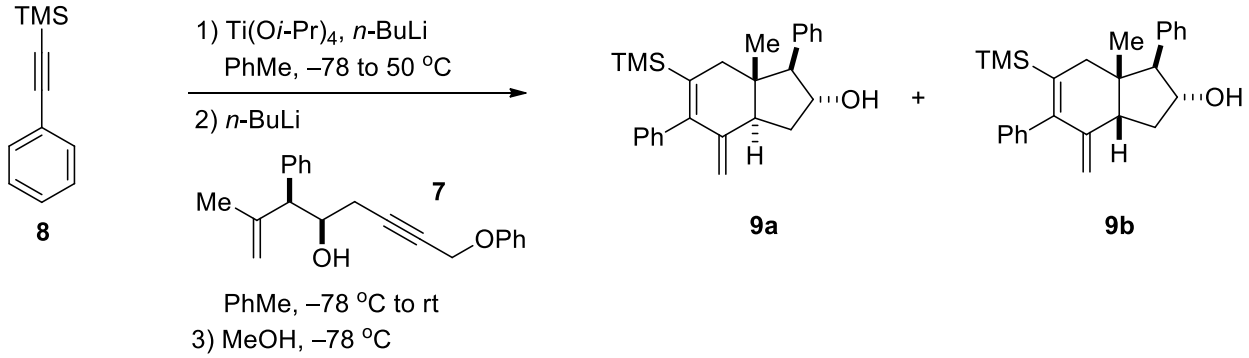


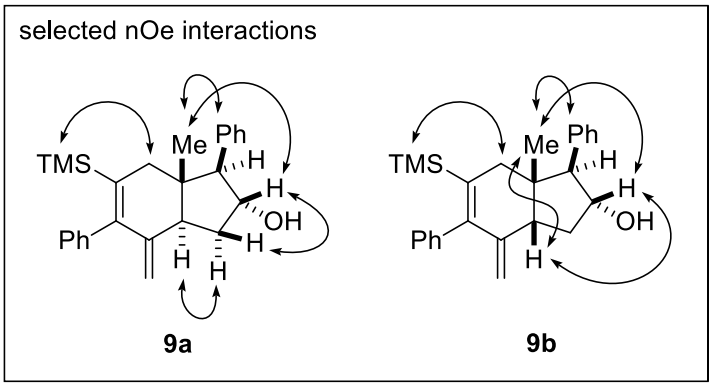
(+/–)-(1*S*,2*R*,3a*R*,7a*S*)-7a-methyl-4-methylene-1,5-diphenyl-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (9a) and **(+/–)-(1*S*,2*R*,3a*S*,7a*S*)-7a-methyl-4-methylene-1,5-diphenyl-6-(trimethylsilyl)-**

2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (9b): To a solution of alkyne **8** (174 mg, 1.0 mmol) and ClTi(O*i*-Pr)$_3$ (1.0 M in hexanes, 1.0 mL, 1.0 mmol) in PhMe (10.0 mL) was added *c*-C_5H_9MgCl (1.93 M in ether, 1.05 mL, 2.0 mmol) dropwise at –78 °C. After the addition, the reaction mixture was allowed to warm to –30 °C and stirred at this temperature for an additional 2 h. In the meantime, in a separate flask, a solution of enyne **7** (93 mg, 0.30 mmol) in Et_2O (4.0 mL) was treated with *n*-BuLi (2.33 M in hexanes, 0.140 mL, 0.333 mmol) at –78 °C and the resulting mixture was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at –78 °C. The resulting mixture was allowed to warm to –30 °C and stirred at this temperature for 15 h in a cryostatic bath. After this period, the reaction mixture was allowed to warm to rt over the course 3 h after which it was slowly added (by syringe) to vigorously stirring, freshly degassed anhydrous MeOH[7] (60 mL) at –78 °C (under N_2 atmosphere). The flask was then allowed to warm to rt, water (20 mL) was added, and the organic solvents were evaporated *in vacuo*. (*Note:* The evaporation of methanol prior to the aqueous workup minimizes the loss of organic material that can be caused by its increased partitioning into the aqueous phase.) The crude residue after evaporation was diluted with saturated aqueous NH_4Cl and extracted with Et_2O (three times). The combined organic extracts were stirred vigorously with a 10% aqueous solution of KOH (to remove PhOH from the mixture), the organic layer was separated, dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue after evaporation was purified by flash chromatography to afford **9a** (63 mg, 54%) as a while solid and **9b** (11 mg, 10%) as a colorless oil. Spectral data for **9a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.0, 6.9 Hz, 2H), 7.32 – 7.26 (m, 6H), 7.12 (ddt, *J* = 7.4, 2.4, 1.2 Hz, 1H), 7.04 – 7.01 (m, 1H), 4.90 (ddd, *J* = 9.5, 7.7, 2.3 Hz, 1H), 4.82 (s, 1H), 4.42 (s, 1H), 2.95 (ddt, *J* = 12.2, 8.0, 2.4 Hz, 1H), 2.90 (d, *J* = 7.6 Hz, 1H), 2.41 (app. d, *J* = 17.3 Hz, 1H), 2.27 (ddd, *J* = 13.9, 11.6, 9.2 Hz, 1H), 2.11 (app. d, *J* = 17.3 Hz, 1H), 1.95 (ddd, *J* = 13.9, 8.0, 2.3 Hz, 1H), 0.52 (s, 3H), -0.30 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.2, 148.2, 142.2, 138.8, 137.3, 130.6, 130.6, 128.9, 128.5, 127.8, 127.6, 126.9, 126.9, 112.2, 75.8, 68.0, 49.7, 45.4, 44.3, 34.6, 13.5, –0.7; IR (thin film) 3326, 2959, 2360, 1246, 1048, 834, 700 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{26}H_{33}NOSi$ [M+H$^+$] 389.2301, found 389.2303. Spectral data for **9b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 6H), 7.21 – 7.19 (m, 2H), 7.11 – 7.09 (m, 2H), 4.95 (s, 1H), 4.69 (td, *J* = 7.6, 5.4 Hz, 1H), 4.47 (d, *J* = 1.5 Hz, 1H), 2.83 (d, *J* = 5.4 Hz, 1H), 2.67 (dd, *J* = 11.4, 7.3 Hz, 1H), 2.61 (app. d, *J* = 17.3 Hz, 1H), 2.51 (dt, *J* = 12.9, 7.4 Hz, 1H), 2.12 (app. d, *J* = 17.4 Hz, 1H), 1.94 – 1.88 (m, 1H), 0.59 (s, 3H), –0.22 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.0, 147.0, 142.5, 141.9, 137.1, 130.4, 129.2, 128.4, 127.7, 126.8, 126.6, 115.5, 78.1, 65.2, 49.8, 43.7, 41.9, 40.7, 24.0, –0.4; IR (thin film) 3400, 2953, 1600, 1491, 1453, 1246, 1052, 835, 701 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{26}H_{33}NOSi$ [M+H$^+$] 389.2301, found 389.2296.

[7] Other alcohols (*i*-PrOH, etc.) can be used in an analogous fashion, provided their melting points are above –78 °C, otherwise a 1:1 mixture of THF and the corresponding alcohol (*t*-BuOH, CF_3CH_2OH, etc.) was used instead.

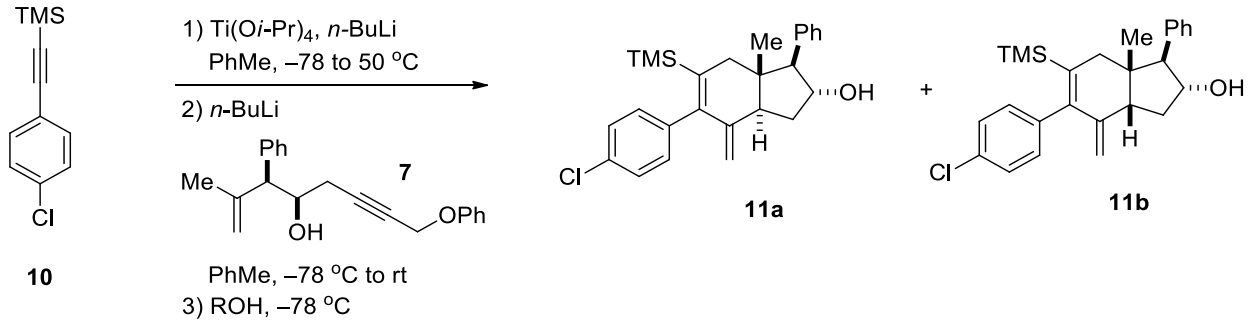
E: Synthesis of Hydroindanes 9, 11, 13, 15, 17, 19, 21, 23, 25, 26, 28 and 30 via the Ti(O*i*-Pr)$_4$/*n*-BuLi-mediated Coupling Process.

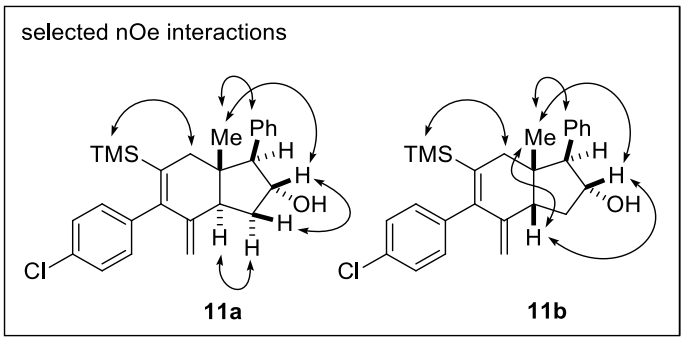




(+/–)-(1*S*,2*R*,3a*R*,7a*S*)-7a-methyl-4-methylene-1,5-diphenyl-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (9a) and **(+/–)-(1*S*,2*R*,3a*S*,7a*S*)-7a-methyl-4-methylene-1,5-diphenyl-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (9b):** To a solution of alkyne **8** (174 mg, 1.0 mmol) in PhMe (6.0 mL) was added Ti(O*i*Pr)$_4$ (0.30 mL, 1.0 mmol) at rt. The mixture was cooled to –78 °C and *n*-BuLi (2.49 M in hexanes, 0.80 mL, 2.0 mmol) was added dropwise (by syringe) over the course of 5 min. After this period, the flask was taken out of the cooling bath and allowed to warm to rt (approx. 20 min). The reaction mixture was then heated to 50 °C (no reflux condenser required) for 1 h and allowed to cool to rt before it was placed into a –78 °C cooling bath. In the meantime, enyne **7** (93 mg, 0.30 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (2.49 M in hexanes, 0.135 mL, 0.333 mmol) at –78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise (by syringe) to the above black Ti-alkyne complex solution at –78 °C. The reaction mixture was then allowed to warm to rt overnight (approx. 15 h). After this period, the cooling bath was removed and the mixture was stirred at rt for an additional 2 h. The reaction mixture was then drawn into a syringe and added dropwise to vigorously stirring, freshly degassed anhydrous MeOH (60 mL) at –78 °C (under N_2 atmosphere). The flask was then allowed to warm to rt, water (20 mL) was added, and the organic solvents were removed *in vacuo*. (*Note:* The evaporation of methanol prior to the aqueous workup minimizes the loss of organic material that can be caused by its increased partitioning into the aqueous phase.) The crude residue from evaporation was diluted with copious amounts of saturated aqueous NH_4Cl and extracted with Et_2O (three times). The combined organic extracts were vigorously stirred with 10% aqueous KOH for 5 minutes, the

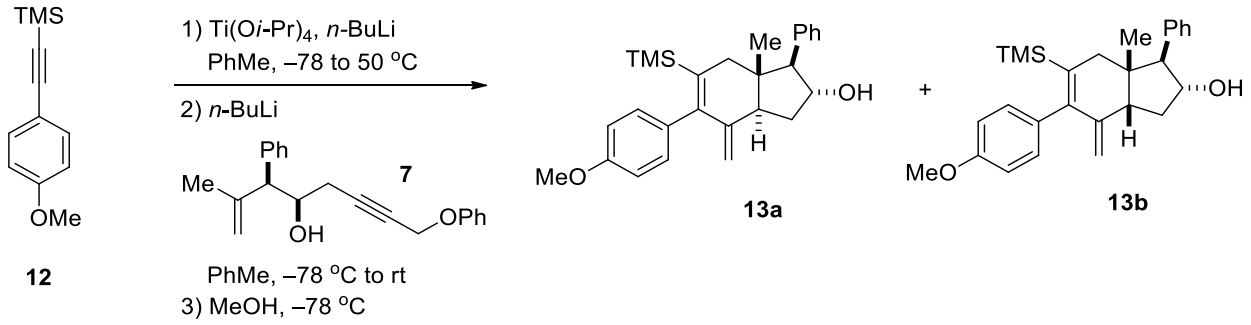
organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude mixture by flash chromatography afforded hydroindanes **9a** (white solid) and **9b** (colorless oil) (78 mg, 67%, ds = 10:1, determined by NMR analysis of the crude reaction mixture) as well as a small amount of the *endo*-isomer (20 mg, 17%, white solid). Spectral data for **9a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.0, 6.9 Hz, 2H), 7.32 – 7.26 (m, 6H), 7.12 (ddt, *J* = 7.4, 2.4, 1.2 Hz, 1H), 7.04 – 7.01 (m, 1H), 4.90 (ddd, *J* = 9.5, 7.7, 2.3 Hz, 1H), 4.82 (s, 1H), 4.42 (s, 1H), 2.95 (ddt, *J* = 12.2, 8.0, 2.4 Hz, 1H), 2.90 (d, *J* = 7.6 Hz, 1H), 2.41 (app. d, *J* = 17.3 Hz, 1H), 2.27 (ddd, *J* = 13.9, 11.6, 9.2 Hz, 1H), 2.11 (app. d, *J* = 17.3 Hz, 1H), 1.95 (ddd, *J* = 13.9, 8.0, 2.3 Hz, 1H), 0.52 (s, 3H), –0.30 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.2, 148.2, 142.2, 138.8, 137.3, 130.6, 130.6, 128.9, 128.5, 127.8, 127.6, 126.9, 126.9, 112.2, 75.8, 68.0, 49.7, 45.4, 44.3, 34.6, 13.5, –0.7; IR (thin film) 3326, 2959, 2360, 1246, 1048, 834, 700 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{26}H_{33}NOSi$ [M+H$^+$] 389.2301, found 389.2303. Spectral data for **9b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 6H), 7.21 – 7.19 (m, 2H), 7.11 – 7.09 (m, 2H), 4.95 (s, 1H), 4.69 (td, *J* = 7.6, 5.4 Hz, 1H), 4.47 (d, *J* = 1.5 Hz, 1H), 2.83 (d, *J* = 5.4 Hz, 1H), 2.67 (dd, *J* = 11.4, 7.3 Hz, 1H), 2.61 (app. d, *J* = 17.3 Hz, 1H), 2.51 (dt, *J* = 12.9, 7.4 Hz, 1H), 2.12 (app. d, *J* = 17.4, 1H), 1.94 – 1.88 (m, 1H), 0.59 (s, 3H), –0.22 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.0, 147.0, 142.5, 141.9, 137.1, 130.4, 129.2, 128.4, 127.7, 126.8, 126.6, 115.5, 78.1, 65.2, 49.8, 43.7, 41.9, 40.7, 24.0, –0.4; IR (thin film) 3400, 2953, 1600, 1491, 1453, 1246, 1052, 835, 701 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{26}H_{33}NOSi$ [M+H$^+$] 389.2301, found 389.2296.

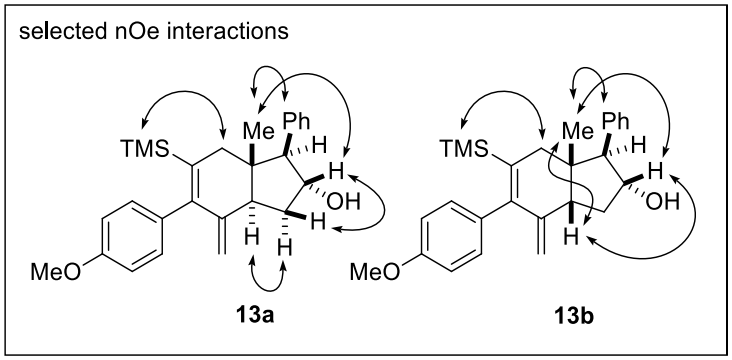




(+/–)-(1*S*,2*R*,3a*R*,7a*S*)-5-(4-chlorophenyl)-7a-methyl-4-methylene-1-phenyl-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (11a) and **(+/–)-(1*S*,2*R*,3a*S*,7a*S*)-5-(4-chlorophenyl)-7a-methyl-4-methylene-1-phenyl-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (11b):** To a solution of alkyne **10** (215 mg, 1.0 mmol) in PhMe (6.0 mL) was added Ti(O*i*Pr)$_4$ (0.30 mL, 1.0 mmol) at rt. The mixture was cooled to –78 °C and *n*-BuLi (2.49 M in hexanes, 0.80 mL, 2.0 mmol) was added dropwise (by syringe) over the course of 5 min. After this period, the flask was taken out of the cooling bath and allowed to

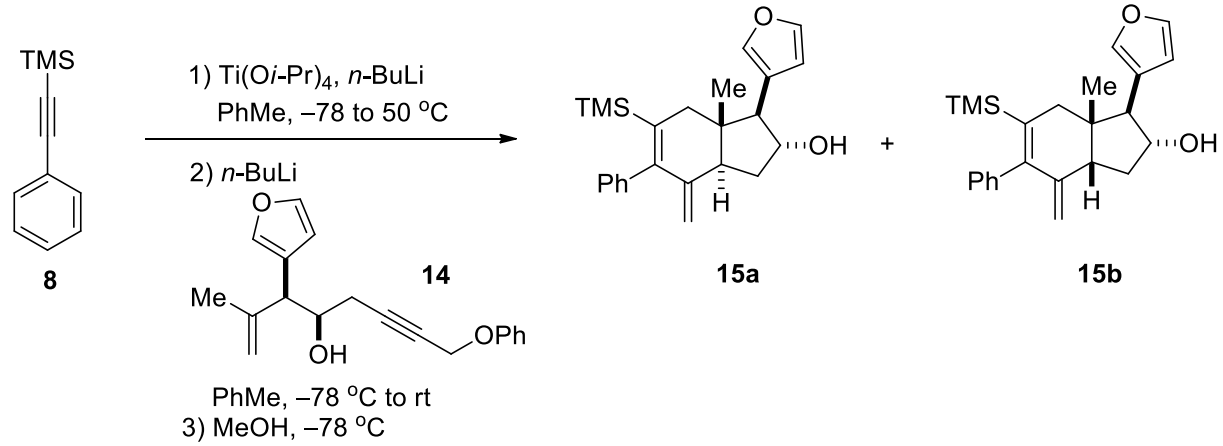
warm to rt (approx. 20 min). The reaction mixture was then heated to 50 °C (no reflux condenser required) for 1 h and allowed to cool to rt before it was placed into a –78 °C cooling bath. In the meantime, enyne **7** (93 mg, 0.30 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (2.49 M in hexanes, 0.135 mL, 0.333 mmol) at –78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise (by syringe) to the above black Ti-alkyne complex solution at –78 °C. The reaction mixture was then allowed to warm to rt overnight (approx. 15 h). After this period, the cooling bath was removed and the mixture was stirred at rt for an additional 2 h. The reaction mixture was then drawn into a syringe and added dropwise to vigorously stirring, freshly degassed anhydrous MeOH (60 mL) at –78 °C (under N_2 atmosphere). The flask was then allowed to warm to rt, water (20 mL) was added, and the organic solvents were removed *in vacuo*. (*Note:* The evaporation of methanol prior to the aqueous workup minimizes the loss of organic material that can be caused by its increased partitioning into the aqueous phase.) The crude residue from evaporation was diluted with copious amounts of saturated aqueous NH_4Cl and extracted with Et_2O (three times). The combined organic extracts were vigorously stirred with 10% aqueous KOH for 5 minutes, the organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude mixture by flash chromatography afforded hydroindanes **11a** and **11b** (both as colorless oils) (77 mg, 61%, ds = 15:1, determined by NMR analysis of the crude reaction mixture) as well as a small amount of the *endo*-isomer (15 mg, 12%, white solid). Spectral data for **11a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.31 – 7.25 (m, 5H), 7.06 (ddd, *J* = 8.3, 2.1, 0.6 Hz, 1H), 6.96 (ddd, *J* = 8.0, 2.2, 0.5 Hz, 1H), 4.89 (ddd, *J* = 9.4, 7.6, 2.3 Hz, 1H), 4.82 (s, 1H), 4.39 (dt, *J* = 2.2, 1.0 Hz, 1H), 2.93 (ddt, *J* = 9.5, 6.4, 3.1 Hz, 1H), 2.89 (d, *J* = 7.7 Hz, 1H), 2.40 (app. d, *J* = 17.4 Hz, 1H), 2.26 (ddd, *J* = 13.9, 11.6, 9.2 Hz, 1H), 2.10 (app. d, *J* = 17.4 Hz, 1H), 1.94 (ddd, *J* = 13.9, 8.0, 2.2 Hz, 1H), 0.49 (s, 3H), –0.28 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 147.0, 140.7, 138.6, 138.2, 132.8, 132.0, 131.9, 128.9, 128.5, 128.1, 127.8, 126.9, 112.3, 75.7, 68.0, 49.6, 45.3, 44.4, 34.5, 13.5, –0.6; IR (thin film) 3331, 2960, 1485, 1247, 1089, 889, 835, 733, 701 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{26}H_{32}ClOSi$ [M+H$^+$] 423.1911, found 423.1907. Spectral data for **11b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.30 – 7.24 (m, 3H), 7.19 – 7.17 (m, 2H), 7.05 – 7.02 (m, 2H), 4.95 (s, 1H), 4.68 (td, *J* = 7.5, 5.3 Hz, 1H), 4.42 (s, 1H), 2.82 (d, *J* = 5.3 Hz, 1H), 2.66 (dd, *J* = 11.5, 7.4 Hz, 1H), 2.61 (app. d, *J* = 17.4 Hz, 1H), 2.50 (dt, *J* = 13.0, 7.4 Hz, 1H), 2.12 (app. d, *J* = 17.3 Hz, 1H), 1.88 (ddd, *J* = 12.9, 11.5, 7.7 Hz, 1H), 0.57 (s, 3H), –0.20 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.0, 145.7, 141.9, 141.0, 138.0, 132.8, 131.8, 129.1, 128.4, 128.0, 126.6, 115.6, 78.1, 65.3, 49.7, 43.7, 41.9, 40.8, 23.9, –0.3; IR (thin film) 3403, 2953, 2360, 2341, 1486, 1247, 1088, 836, 701 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{26}H_{32}ClOSi$ [M+H$^+$] 423.1911, found 423.1902.

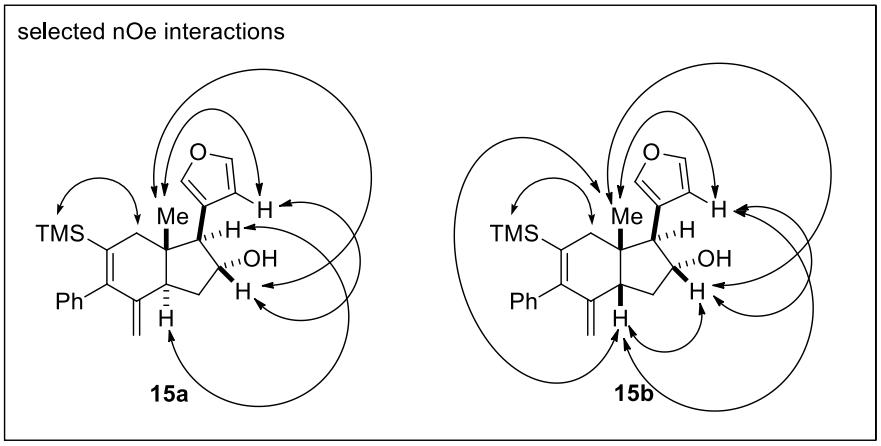




(+/–)-(1*S*,2*R*,3a*R*,7a*S*)-5-(4-methoxyphenyl)-7a-methyl-4-methylene-1-phenyl-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (13a) and **(1*S*,2*R*,3a*S*,7a*S*)-5-(4-methoxyphenyl)-7a-methyl-4-methylene-1-phenyl-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (13b):** To a solution of alkyne **12** (220 µL, 1.00 mmol) in PhMe (6.0 mL) was added Ti(O*i*Pr)$_4$ (0.30 mL, 1.0 mmol) at rt. The mixture was cooled to –78 °C and *n*-BuLi (2.49 M in hexanes, 0.80 mL, 2.0 mmol) was added dropwise (by syringe) over the course of 5 min. After this period, the flask was taken out of the cooling bath and allowed to warm to rt (approx. 20 min). The reaction mixture was then heated to 50 °C (no reflux condenser required) for 1 h and allowed to cool to rt before it was placed into a –78 °C cooling bath. In the meantime, enyne **7** (93 mg, 0.30 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (2.49 M in hexanes, 0.135 mL, 0.333 mmol) at –78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise (by syringe) to the above black Ti-alkyne complex solution at –78 °C. The reaction mixture was then allowed to warm to rt overnight (approx. 15 h). After this period, the cooling bath was removed and the mixture was stirred at rt for an additional 2 h. The reaction mixture was then drawn into a syringe and added dropwise to vigorously stirring, freshly degassed anhydrous MeOH (60 mL) at –78 °C (under N_2 atmosphere). The flask was then allowed to warm to rt, water (20 mL) was added, and the organic solvents were removed *in vacuo*. (*Note:* The evaporation of methanol prior to the aqueous workup minimizes the loss of organic material that can be caused by its increased partitioning into the aqueous phase.) The crude residue from evaporation was diluted with copious amounts of saturated aqueous NH_4Cl and extracted with Et_2O (three times). The combined organic extracts were vigorously stirred with 10% aqueous KOH for 5 minutes, the organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude mixture by flash chromatography afforded hydroindanes **13a** and **13b** (both as colorless oils) (97 mg, 76%, ds = 12:1, determined by NMR analysis of the crude reaction mixture) as well as a small amount of the *endo*-isomer (15 mg, 12%, white solid). Spectral data for **13a:** ^{1}H NMR (500 MHz,$CDCl_3$) δ 7.39 – 7.36 (m, 2H), 7.30 – 7.26 (m, 3H), 7.02 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.93 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.86 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.80 (dd, *J* = 8.3, 2.7 Hz, 1H), 4.90 (ddd, *J* = 9.5, 7.6, 2.2 Hz, 1H), 4.81 (s, 1H), 4.45 (s, 1H), 3.82 (d, *J* = 0.8 Hz, 3H), 2.96 – 2.91 (m, 1H), 2.89 (d, *J* = 7.6 Hz, 1H), 2.40 (app. d, *J* = 17.3 Hz, 1H), 2.27 (ddd, *J* = 13.7, 11.6, 9.2 Hz, 1H), 2.09 (app. d, *J* = 17.3 Hz, 1H), 1.94 (ddd, *J* = 14.0, 8.0, 2.2 Hz, 1H), 0.50 (s, 3H), –0.28 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 148.5, 147.8, 138.8, 137.4, 134.6, 131.6, 131.6, 128.9, 128.5, 126.9, 113.5, 112.6, 112.0, 75.8, 68.0, 55.4, 49.7, 45.4, 44.4, 34.6, 13.5, –0.6; IR (thin film) 3341, 2954, 1608, 1506, 1245, 1173, 1035, 834, 704 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{27}H_{35}O_2Si$ [M+H$^+$] 419.2406, found 419.2403. Spectral data for **13b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 3H), 7.28 – 7.23 (m, 1H), 7.21 – 7.17 (m, 1H), 7.01 – 6.99 (m, 2H), 6.85 – 6.83 (m, 2H), 4.93 (s, 1H), 4.68 (td, *J* = 7.6, 5.6 Hz, 1H), 4.49 (s, 1H), 3.83 (s, 3H), 2.82 (d, *J* = 5.6 Hz, 1H), 2.66 (dd, *J* = 11.4, 7.3 Hz, 1H), 2.58 (app. d, *J* = 17.3 Hz, 1H), 2.49 (dt, *J* = 12.9, 7.3 Hz, 1H), 2.10 (app. d, *J* = 17.2 Hz, 1H), 1.89 (ddd, *J* =

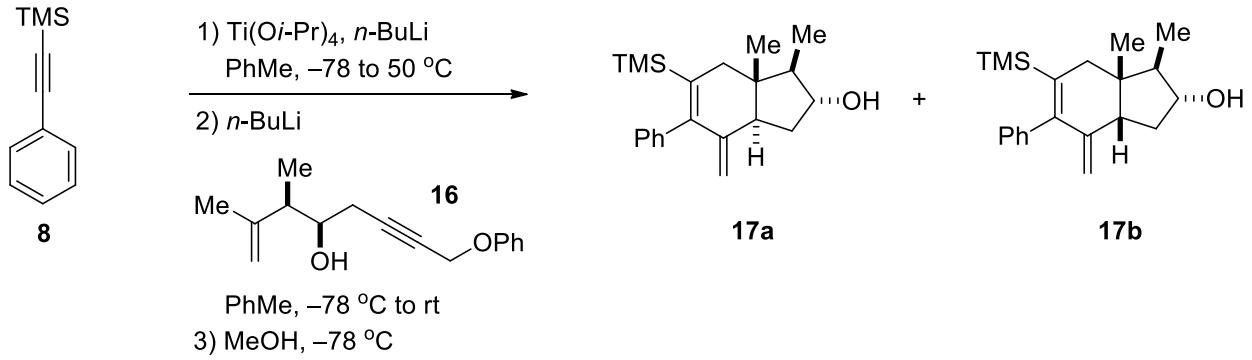
12.9, 11.4, 7.8 Hz, 1H), 0.58 (s, 3H), –0.20 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 147.4, 146.7, 141.9, 137.3, 135.0, 131.4, 129.2, 128.3, 126.6, 115.2, 113.1, 78.1, 65.2, 55.4, 49.8, 43.7, 41.9, 40.8, 24.0, –0.2; IR (thin film) 2954, 2924, 1608, 1507, 1245, 1174, 1036, 835, 701 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{27}H_{35}O_2Si$ [M+H$^+$] 419.2406, found 419.2401.

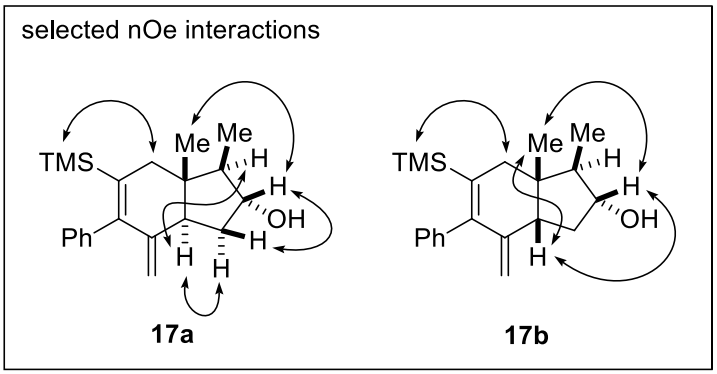




(+/–)-(1*S*,2*R*,3a*R*,7a*S*)-1-(furan-3-yl)-7a-methyl-4-methylene-5-phenyl-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (15a) and **(+/–)-(1*S*,2*R*,3a*S*,7a*S*)-1-(furan-3-yl)-7a-methyl-4-methylene-5-phenyl-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (15b):** To a solution of alkyne **8** (145 mg, 0.83 mmol) in PhMe (4.5 mL) was added Ti(O*i*Pr)$_4$ (0.25 mL, 0.83 mmol) at rt. The mixture was cooled to –78 °C and *n*-BuLi (2.37 M in hexanes, 0.70 mL, 1.66 mmol) was added dropwise (by syringe) over the course of 5 min. After this period, the flask was taken out of the cooling bath and allowed to warm to rt (approx. 20 min). The reaction mixture was then heated to 50 °C (no reflux condenser required) for 1 h and allowed to cool to rt before it was placed into a –78 °C cooling bath. In the meantime, enyne **14** (74 mg, 0.25 mmol) was dissolved in PhMe (3.0 mL), treated with *n*-BuLi (2.37 M in hexanes, 0.11 mL, 0.26 mmol) at –78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise (by syringe) to the above Ti-alkyne complex solution at –78 °C. The reaction mixture was then allowed to warm to rt overnight (approx. 15 h). After this period, the cooling bath was removed and the mixture was stirred at rt for an additional 3 h. The reaction mixture was then drawn into a syringe and added dropwise to vigorously stirring, freshly degassed anhydrous MeOH (50 mL) at –78 °C (under N_2 atmosphere). The flask was then allowed to warm to rt, water (20 mL) was added, and the organic solvents

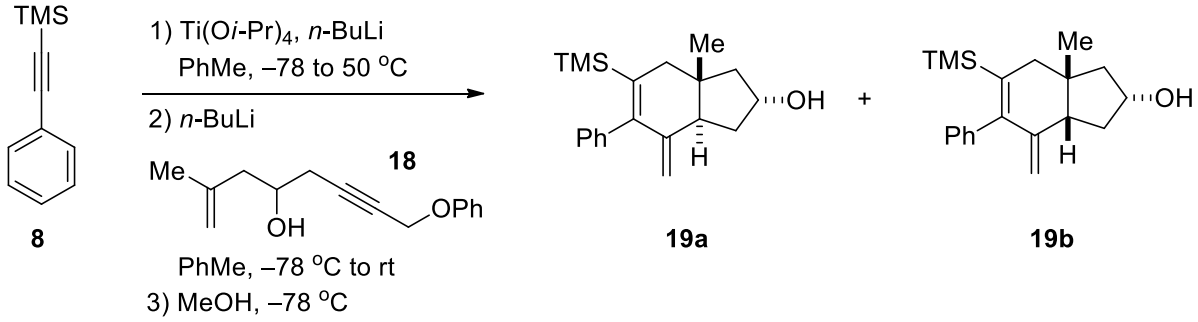
were removed *in vacuo*. (*Note:* The evaporation of methanol prior to the aqueous workup minimizes the loss of organic material that can be caused by its increased partitioning into the aqueous phase.) The crude residue from evaporation was diluted with copious amounts of saturated aqueous NH_4Cl and extracted with Et_2O (three times). The combined organic extracts were vigorously stirred with 10% aqueous KOH for 5 minutes, the organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude mixture by flash chromatography (silica gel, gradient 95:5:1 to 75:25:1 hexanes:EtOAc:Et_3N) afforded hydroindanes **15a** (white solid) and **15b** (colorless oil) (61 mg, 64%, ds = 10:1, determined by NMR analysis of the crude reaction mixture) as well as a small amount of the *endo*-isomer (14 mg, 15%, colorless oil). Spectral data for **15a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (app. t, *J* = 1.6 Hz, 1H), 7.39 – 7.38 (m, 1H), 7.31 – 7.26 (m, 3H), 7.11 – 7.09 (m, 1H), 7.04 – 7.02 (m, 1H), 6.38 (dd, *J* = 1.7, 0.8 Hz, 1H), 4.80 (s, 1H), 4.57 (ddd, *J* = 9.0, 7.8, 2.3 Hz, 1H), 4.42 – 4.40 (m, 1H), 2.88 – 2.82 (m, 1H), 2.71 (d, *J* = 7.6 Hz, 1H), 2.32 (app. d, *J* = 17.3 Hz, 1H), 2.23 (app. d, *J* = 17.3 Hz, 1H), 2.26 – 2.18 (m, 1H), 1.90 (ddd, *J* = 13.9, 8.1, 2.3 Hz, 1H), 1.78 (bs, 1H), 0.55 (s, 3H), –0.29 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.2, 148.9, 143.3, 142.3, 139.9, 137.3, 130.64, 130.63, 127.8, 127.7, 127.0, 123.1, 112.4, 111.0, 76.8, 58.6, 49.1, 44.6, 44.4, 34.7, 13.9, –0.6 (3C). IR (thin film) 3362, 3080, 3056, 3024, 2954, 1735, 1560, 1501, 1442, 1254, 1061, 1051, 884, 832, 763, 700, 634, 599 cm^{-1}. HRMS (ESI-TOF) Calculated for $C_{24}H_{31}O_2Si$ [M+H$^+$] 379.2093, found 379.2083. Spectral data for **15b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.42 (m, 1H), 7.31–7.27 (m, 4H), 7.11–7.09 (m, 2H), 6.33–6.32 (m, 1H), 4.92 (s, 1H), 4.47–4.45 (m, 1H), 4.37 (dd, *J* = 14.8, 7.0 Hz, 1H), 2.69 (d, *J* = 6.5 Hz, 1H), 2.59 (dd, *J* = 10.8, 7.6 Hz, 1H), 2.50 (app. d, *J* = 17.0 Hz, 1H), 2.48–2.42 (m, 1H), 1.98 (app. d, *J* = 16.8 Hz, 1H), 1.79 (ddd, *J* = 12.7, 10.9, 8.3 Hz, 1H), 1.76 (bs, 1H), 0.76 (s, 3H), –0.22 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 147.9, 143.2, 142.7, 140.2, 137.1, 130.4 (2C), 127.8 (2C), 126.9, 124.5, 115.0, 111.2, 77.5, 54.7, 49.6, 42.9, 42.0, 39.9, 25.1, –0.3 (3C). IR (thin film) 3414, 3077, 3056, 3021, 2954, 2926, 2892, 1728, 1683, 1564, 1495, 1452, 1376, 1247, 1065, 1027, 867, 832, 755, 702, 599 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{24}H_{30}NO_2NaSi$ [M+Na$^+$] 401.1913, found 401.1913.

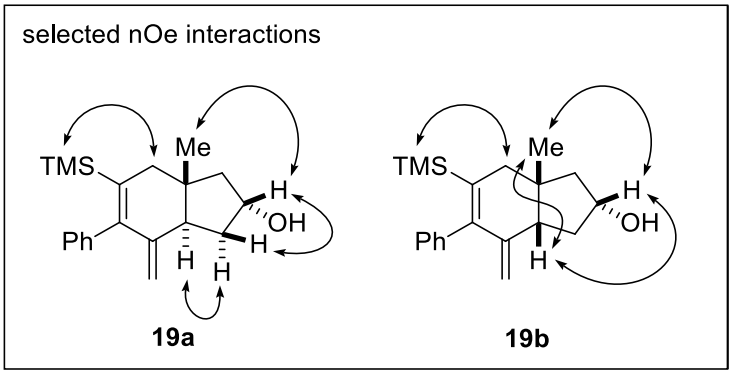




(+/–)-(1*R*,2*R*,3a*R*,7a*S*)-1,7a-dimethyl-4-methylene-5-phenyl-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (17a) and **(1*R*,2*R*,3a*S*,7a*S*)-1,7a-dimethyl-4-methylene-5-phenyl-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (17b) :** To a solution of alkyne **8** (0.200 mL, 1.00 mmol) in PhMe (6.0 mL) was added Ti(O*i*Pr)$_4$ (0.30 mL, 1.0 mmol) at rt. The mixture was cooled to –78 °C and *n*-BuLi (2.49 M in hexanes, 0.80 mL, 2.0 mmol) was added dropwise (by syringe) over the course of 5 min. After this period, the flask was taken out of the cooling bath and allowed to warm to rt (approx. 20 min). The reaction mixture was then heated to 50 °C (no reflux condenser required) for 1 h and allowed to cool to rt before it was placed into a –78 °C cooling bath. In the meantime, enyne **16** (73 mg, 0.30 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (2.49 M in hexanes, 0.135 mL, 0.333 mmol) at –78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise (by syringe) to the above Ti-alkyne complex solution at –78 °C. The reaction mixture was then allowed to warm to rt overnight (approx. 15 h). After this period, the cooling bath was removed and the mixture was stirred at rt for an additional 2h. The reaction mixture was then drawn into a syringe and added dropwise to vigorously stirring, freshly degassed anhydrous MeOH (60 mL) at –78 °C (under N_2 atmosphere). The flask was then allowed to warm to rt, water (20 mL) was added, and the organic solvents were removed *in vacuo*. (*Note:* The evaporation of methanol prior to the aqueous workup minimizes the loss of organic material that can be caused by its increased partitioning into the aqueous phase.) The crude residue from evaporation was diluted with copious amounts of saturated aqueous NH_4Cl and extracted with Et_2O (three times). The combined organic extracts were vigorously stirred with 10% aqueous KOH for 5 minutes, the organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude mixture by flash chromatography afforded hydroindanes **17a** (white solid) and **17b** (colorless oil) (65 mg, 66%, ds = 11:1, determined by NMR analysis of the crude reaction mixture) as well as a small amount of the *endo*-isomer (11 mg, 11%, colorless oil). Spectral data for **17a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 3H), 7.10 – 7.01 (m, 2H), 4.74 (s, 1H), 4.37 (s, 1H), 3.99 (ddd, *J* = 9.0, 7.0, 2.0 Hz, 1H), 2.67 (ddt, *J* = 11.7, 8.0, 2.3 Hz, 1H), 2.28 (app. d, *J* = 17.4 Hz, 1H), 2.15 (app. d, *J* = 17.4 Hz, 1H), 2.07 (ddd, *J* = 14.0, 11.7, 9.0 Hz, 1H), 1.76 (ddd, *J* = 14.0, 8.0, 2.0 Hz, 1H), 1.63 – 1.56 (m, 2H), 1.09 (d, *J* = 7.0 Hz, 3H), 0.55 (s, 3H), –0.27 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 147.8, 142.2, 137.2, 130.4, 127.6, 127.5, 126.7, 111.9, 79.3, 55.8, 48.8, 44.0, 43.0, 35.3, 12.5, 12.0, –0.8; IR (neat): 3349, 3078, 3057, 3024, 2957, 2893, 1724, 1682, 1442, 1248, 1063, 877, 835, 754, 702 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{21}H_{31}OSi$ [M+H$^+$] 327.2139, found 327.2136. Spectral data for **17b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 3H), 7.10 – 7.07 (m, 2H), 4.86 (s, 1H), 4.40 (d, *J* = 1.7 Hz, 1H), 3.86 (td, *J* = 7.3, 6.0 Hz, 1H), 2.45 (dd, *J* = 10.7, 7.3 Hz, 1H), 2.42 (app. d, *J* = 16.7 Hz, 1H), 2.34 (dt, *J* = 12.7, 7.3 Hz, 1H), 1.92 (app. d, *J* = 16.7 Hz, 1H), 1.65 – 1.56 (m, 2H), 1.54 (br-s, 1H), 0.99 (d, *J* = 7.3 Hz, 3H), 0.88 (s, 3H) , –0.25 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.1, 147.3,

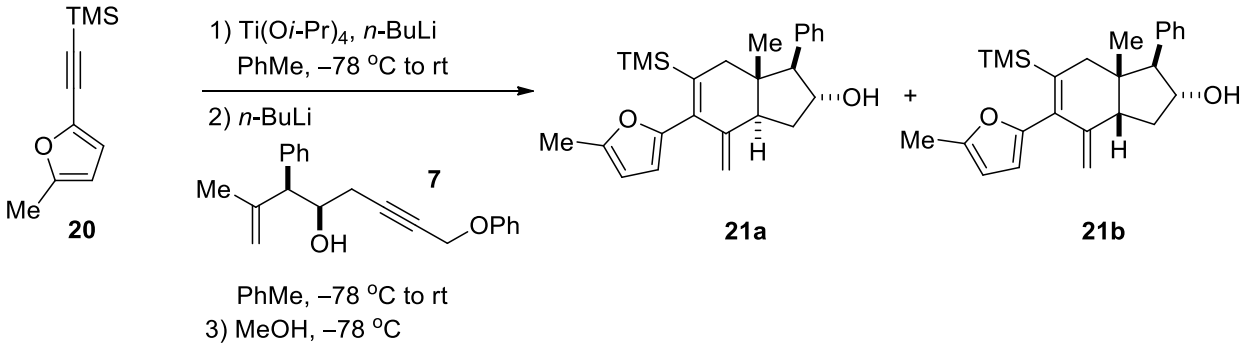
142.7, 137.3, 130.2, 127.5, 126.6, 114.5, 79.1, 50.9, 48.9, 42.4, 41.5, 39.5, 22.9, 13.9, –0.7; IR (neat): 3316, 3079, 3057, 3024, 2955, 2894, 1565, 1247, 835, 760, 701; HRMS (ESI-TOF) Calculated for $C_{21}H_{31}OSi$ [M+H$^+$] 327.2139, found 327.2145.

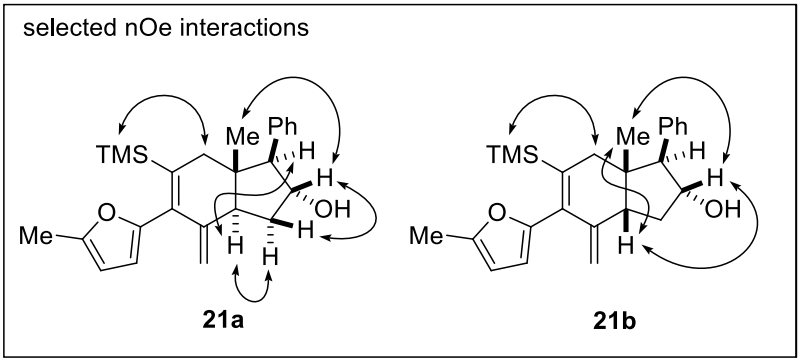




(+/–)-(2*R*,3a*S*,7a*R*)-3a-methyl-7-methylene-6-phenyl-5-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (19a) and **(2*R*,3a*S*,7a*S*)-3a-methyl-7-methylene-6-phenyl-5-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (19b) :** To a solution of alkyne **8** (0.20 mL, 1.0 mmol) in PhMe (6.0 mL) was added Ti(O*i*Pr)$_4$ (0.20 mL, 1.0 mmol) at rt. The mixture was cooled to –78 °C and *n*-BuLi (2.49 M in hexanes, 0.80 mL, 2.0 mmol) was added dropwise over the course of 5 min. After this period, the flask was taken out of the cooling bath and allowed to warm to rt (approx. 20 min). The reaction mixture was then heated to 50 °C (no reflux condenser required) for 1 h and allowed to cool to rt before it was placed into a –78 °C cooling bath. In the meantime, enyne **18** (0.069 g, 0.30 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (1.89 M in hexanes, 0.175 mL, 0.333 mmol) at –78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise (by syringe) to the above black Ti-alkyne complex solution at –78 °C. The reaction mixture was then allowed to warm to rt overnight (approx. 15 h). After this period, the cooling bath was removed and the mixture was stirred at rt for an additional 2h. The reaction mixture was then drawn into a syringe and added dropwise to vigorously stirring, freshly degassed anhydrous MeOH (60 mL) at –78 °C (under N_2 atmosphere). The flask was then allowed to warm to rt, water (20 mL) was added, and the organic solvents were removed *in vacuo*. (*Note:* The evaporation of methanol prior to the aqueous workup minimizes the loss of organic material that can be caused by its increased partitioning into the aqueous phase.) The crude residue from evaporation was diluted with

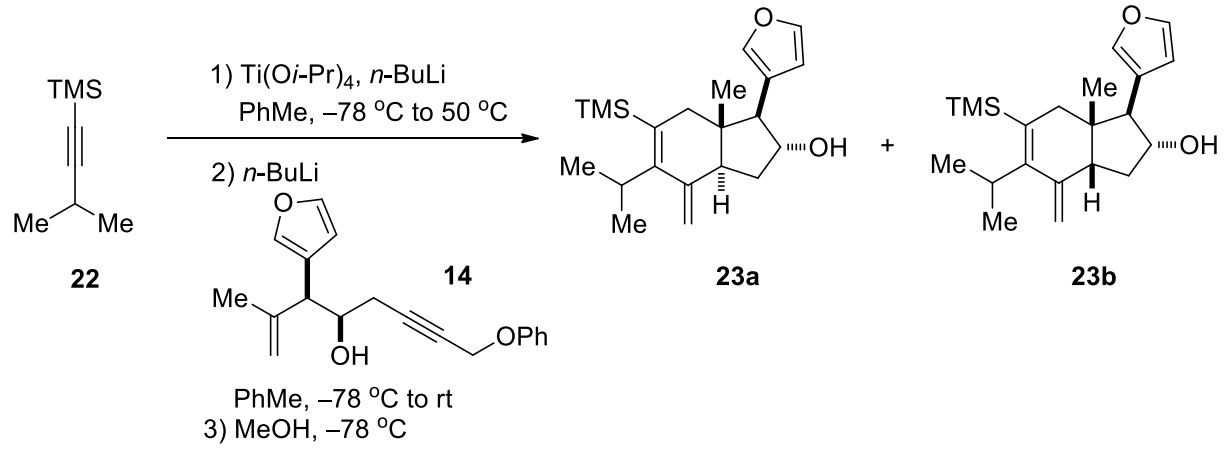
copious amounts of saturated aqueous NH_4Cl and extracted with Et_2O (three times). The combined organic extracts were vigorously stirred with 10% aqueous KOH for 5 minutes, the organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude mixture by flash chromatography afforded hydroindanes **19a** and **19b** (both as colorless oils) (48 mg, 52%, dr = 5:1) as well as a small amount of the *endo*-isomer **19c** (10 mg, 11 %, yellow oil). Spectral data for **19a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 3H), 7.10 – 7.08 (m, 1H), 7.05 – 7.03 (m, 1H), 4.76 (s, 1H), 4.58 – 4.53 (m, 1H), 4.36 (s, 1H), 2.72 – 2.68 (m, 1H), 2.40 – 2.28 (m, 3H), 2.05 – 1.99 (m, 1H), 1.81 (dd, *J* = 13.7, 7.2 Hz, 1H), 1.54 (br. s, 1H), 1.43 (dd, *J* = 12.9, 5.6 Hz, 1H), 0.68 (s, 3H), –0.27 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6, 148.1, 142.5, 138.0, 130.7, 127.8, 126.9, 51.9, 48.2, 45.6, 41.7, 36.9, 29.9, 18.6, –0.1; IR (thin film): 3398, 2953, 2359, 1614, 1441, 1248, 1041, 834, 755, 701 cm^{-1}; HRMS (EI-TOF) Calculated for $C_{20}H_{28}OSi$ [M^+] 312.1909, found 312.1909. Spectral data for **19b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 3H), 7.08 – 7.06 (m, 2H), 4.85 (s, 1H), 4.49 – 4.44 (m, 1H), 4.38 (s, 1H), 2.60, 2.07 (ABq, *J* = 17.8 Hz, 2H), 2.39 – 2.30 (m, 2H), 1.87 (dd, J = 16.3, 8.6, 1H), 1.77 – 1.71 (m, 1H), 1.63 (dd, *J* = 13.9, 2.5 Hz, 1H), 1.55 (br. s, 1H), 0.97 (s, 3H), –0.26 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 145.7, 142.6, 137.29, 130.6, 129.8, 127.7, 126.8, 115.5, 114.9, 71.8, 51.5, 50.7, 43.9, 40.0, 39.1, 25.7, 4.0, 0.49; IR (thin film): 3389, 2952, 2359, 1442, 1613, 1248, 1071, 835, 755, 702 cm^{-1}; HRMS (EI-TOF) Calculated for $C_{20}H_{28}OSi$ [M^+] 312.1909, found 312.1906.

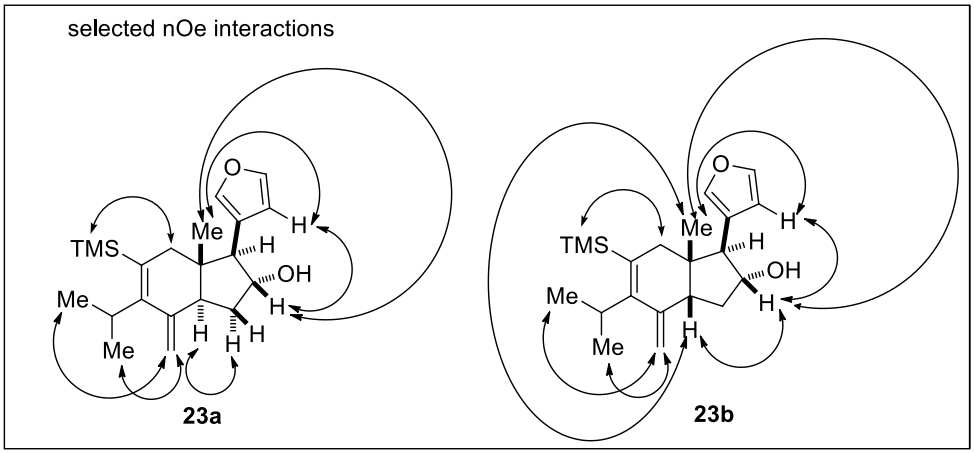




(+/–)-(1*S*,2*R*,3a*R*,7a*S*)-7a-methyl-4-methylene-5-(5-methylfuran-2-yl)-1-phenyl-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (21a) and **(1*S*,2*R*,3a*S*,7a*S*)-7a-methyl-4-methylene-5-(5-**

methylfuran-2-yl)-1-phenyl-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (21b): To a solution of alkyne **20** (178 mg, 1.00 mmol) in PhMe (6.0 mL) was added $Ti(O\textit{i}Pr)_4$ (0.30 mL, 1.0 mmol) at rt. The mixture was cooled to –78 °C and *n*-BuLi (2.49 M in hexanes, 0.80 mL, 2.0 mmol) was added dropwise (by syringe) over the course of 5 min. After the addition was finished, the flask was taken out of the cooling bath and allowed to warm to rt (approx. 20 min) and stirred for an additional 9 h at the same temperature. After this period, the flask was placed into a –78 °C cooling bath. In the meantime, enyne **7** (91 mg, 0.30 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (2.49 M in hexanes, 0.135 mL, 0.333 mmol) at –78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise (by syringe) to the above black Ti-alkyne complex solution at –78 °C. The reaction mixture was then allowed to warm to rt overnight (approx. 18 h). After this period, the cooling bath was removed and the mixture was stirred at rt for an additional 7 h. The reaction mixture was then drawn into a syringe and added dropwise to vigorously stirring, freshly degassed anhydrous MeOH (60 mL) at – 78 °C (under N_2 atmosphere). The flask was then allowed to warm to rt, water (20 mL) was added, and the organic solvents were removed *in vacuo*. (*Note:* The evaporation of methanol prior to the aqueous workup minimizes the loss of organic material that can be caused by its increased partitioning into the aqueous phase.) The crude residue from evaporation was diluted with copious amounts of saturated aqueous NH_4Cl and extracted with Et_2O (three times). The combined organic extracts were vigorously stirred with 10% aqueous KOH for 5 minutes, the organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude mixture by flash chromatography afforded hydroindanes **21a** and **21b** (both as pale yellow oils) (52 mg, 44%, dr = 4:1) as well as a small amount of the *endo*-isomer (13 mg, 11%, pale yellow oil). Spectral data for **21a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.31 – 7.26 (m, 3H), 6.03 (d, *J* = 3.0 Hz, 1H), 5.98 – 5.96 (m, 1H), 4.91 – 4.84 (m, 3H), 2.92 – 2.86 (m, 1H), 2.87 (d, *J* = 7.7 Hz, 1H), 2.41 (app. d, *J* = 18.0 Hz, 1H), 2.30 (s, 3H), 2.32 – 2.27 (m, 1H), 2.10 (app. d, *J* = 18.0, 1H), 1.92 (ddd, *J* = 13.7, 8.0, 2.3 Hz, 1H), 1.71 (br-s, 1H), 0.46 (s, 3H),–0.15 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0, 150.4, 146.3, 142.9, 138.5, 137.8, 128.7, 128.3, 126.7, 110.6, 106.5, 75.6, 67.7, 49.3, 45.1, 44.5, 34.1, 13.5, 13.5, –1.2; IR (neat): 3315, 3087, 3060, 3029, 2958, 2894, 1498, 1453, 1248, 1089, 1049, 878, 836, 704 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{25}H_{33}O_2Si$ $[M+H^+]$ 393.2244, found 393.2246. Spectral data for **21b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.28 – 7.23 (m, 1H), 7.22 – 7.18 (m, 2H), 6.10 (d, *J* = 3.0 Hz, 1H), 5.99 – 5.98 (m, 1H), 4.99 (s, 1H), 4.95 (d, *J* = 1.3 Hz, 1H), 4.61 (dt, *J* = 8.7, 7.3 Hz, 1H), 2.75 (d, *J* = 7.3 Hz, 1H), 2.58 (dd, *J* = 11.0, 7.7 Hz, 1H), 2.46 (app. d, *J* = 16.4 Hz, 1H), 2.47-2.42 (m, 1H), 2.33 (s, 3H), 2.01 (app. d, *J* = 16.4, 1H), 1.74 (ddd, *J* = 12.7, 11.0, 8.7 Hz, 1H), 1.66 (br-s, 1H), 0.59 (s, 3H), 0.03 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2, 150.8, 146.6, 140.4, 140.2, 138.4, 129.1, 128.2, 126.6, 112.9, 110.3, 106.9, 76.0, 63.8, 49.8, 43.9, 40.6, 30.3, 25.3, 13.6, –0.3; IR (neat): 3335, 3085, 3060, 3028, 2953, 2923, 2897, 1497, 1452, 1247, 1083, 1021, 865, 837, 702 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{25}H_{33}O_2Si$ $[M+H^+]$ 393.2244, found 393.2249.

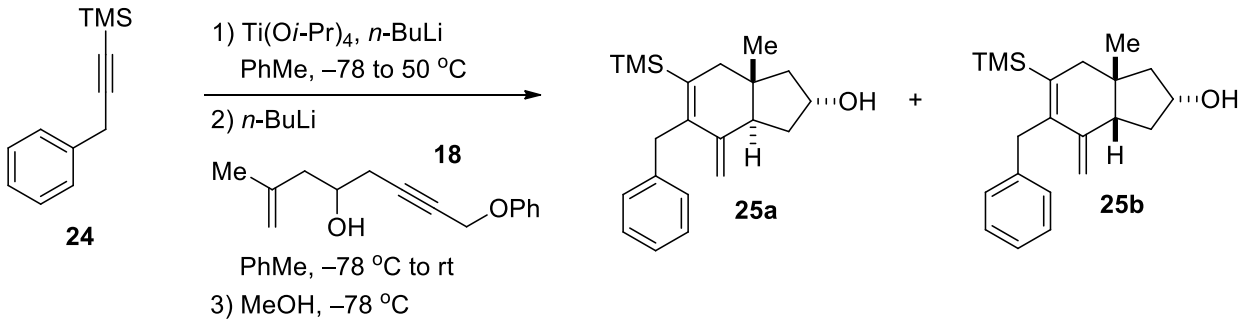


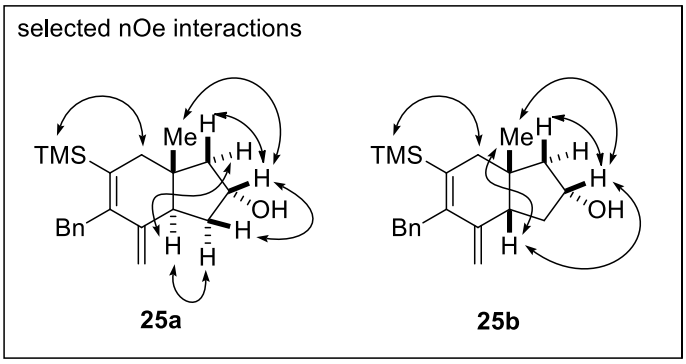


(+/–)-(1*S*,2*R*,3a*R*,7a*S*)-1-(furan-3-yl)-5-isopropyl-7a-methyl-4-methylene-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (23a) and **(+/–)-(1*S*,2*R*,3a*S*,7a*S*)-1-(furan-3-yl)-5-isopropyl-7a-methyl-4-methylene-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (23b):** To a solution of alkyne **22**[8] (147 mg, 1.05 mmol) in PhMe (6.3 mL) was added Ti(O*i*Pr)$_4$ (0.31 mL, 1.05 mmol) at rt. The mixture was cooled to –78 °C and *n*-BuLi (2.60 M in hexanes, 0.81 mL, 2.10 mmol) was added dropwise (by syringe) over the course of 5 min. After this period, the flask was taken out of the cooling bath and allowed to warm to rt (approx. 20 min). The reaction mixture was then heated to 50 °C (no reflux condenser required) for 1 h and allowed to cool to rt before it was placed into a –78 °C cooling bath. In the meantime, enyne **14** (89 mg, 0.30 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (2.60 M in hexanes, 0.121 mL, 0.31 mmol) at –78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise (by syringe) to the above black Ti-alkyne complex solution at –78 °C. The reaction mixture was then allowed to warm to rt overnight (approx. 15 h). After this period, the cooling bath was removed and the mixture was stirred at rt for an additional 3 h. The reaction mixture was then drawn into a syringe and added dropwise to vigorously stirring, freshly degassed anhydrous MeOH (60 mL) at –78 °C (under N_2 atmosphere). The flask was then allowed to warm to rt, water (20 mL)

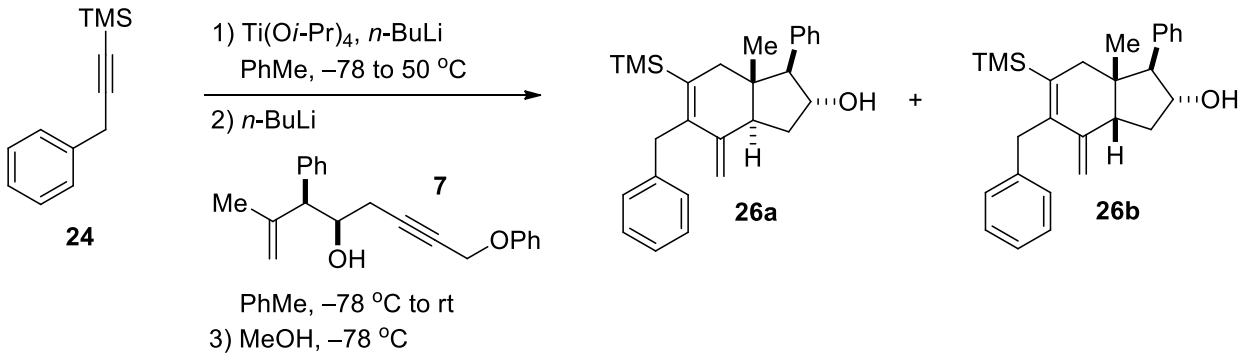
[8] Haddaway, K., Somekawa, K., Fleming, P., Tossell, J. A., Mariano, P. S. *J. Org. Chem.* **1987**, *52*, 4239–4253.

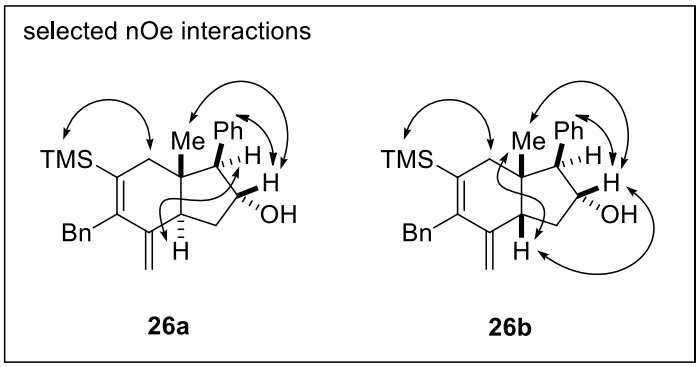
was added, and the organic solvents were removed *in vacuo*. (*Note:* The evaporation of methanol prior to the aqueous workup minimizes the loss of organic material that can be caused by its increased partitioning into the aqueous phase.) The crude residue from evaporation was diluted with copious amounts of saturated aqueous NH_4Cl and extracted with Et_2O (three times). The combined organic extracts were vigorously stirred with 10% aqueous KOH for 5 minutes, the organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude mixture by flash chromatography (silica gel, gradient 95:5 to 60:40 hexanes:EtOAc) afforded hydroindanes **23a** (white solid) and **23b** (colorless oil) (46 mg, 46%, ds = 11:1, determined by NMR analysis of the crude reaction mixture) as well as a small amount of the *endo*-isomer (4 mg, 4%, colorless oil). Spectral data for **23a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.40 (m, 1H), 7.33 – 7.32 (m, 1H), 6.32 – 6.30 (m, 1H), 5.29 – 5.27 (m, 1H), 4.85 (s, 1H), 4.50 (ddd, *J* = 9.0, 7.9, 2.3 Hz, 1H), 2.98 (sep, *J* = 7.2 Hz, 1H), 2.62 – 2.57 (m, 2H), 2.23 – 2.15 (m, 2H), 2.08 (app. d, *J* = 17.6 Hz, 1H), 1.90 (bs, 1H), 1.78 (ddd, *J* = 13.8, 7.9, 2.3 Hz, 1H), 1.28 (d, *J* = 7.3 Hz, 3H), 1.24 (d, *J* = 7.1 Hz, 3H), 0.40 (s, 3H), 0.26 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.9, 143.1, 142.8, 139.7, 134.6, 123.2, 110.9, 110.1, 76.7, 58.7, 50.1, 45.2, 44.2, 35.8, 34.6, 23.5, 20.8, 13.8, 0.4 (3C); IR (thin film) 3349, 2958, 2898, 2874, 1743, 1613, 1542, 1502, 1458, 1363, 1335, 1249, 1161, 1027, 931, 891, 873, 835, 766, 727, 684, 630, 600 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{21}H_{33}O_2Si$ [M+H$^+$] 345.2250, found 345.2242. Spectral data for **23b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.42 (m, 1H), 7.31 – 7.30 (m, 1H), 6.34 – 6.33 (m, 1H), 4.93 (d, *J* = 1.7 Hz, 1H), 4.85 – 4.84 (m, 1H), 4.15 (ddd, *J* = 10.5, 10.5, 6.0 Hz, 1H), 2.97 (sep, *J* = 7.0 Hz, 1H), 2.38 (d, *J* = 10.5 Hz, 1H), 2.35–2.30 (m, 1H), 2.24 (ddd, *J* = 11.9, 7.9, 6.0 Hz, 1H), 2.07 (app. d, *J* = 14.7 Hz, 1H), 1.59 (bs, 1H), 1.51 (app.d, *J* = 14.7 Hz, 1H), 1.38 (ddd, *J* = 11.9, 10.6, 10.6 Hz, 1H), 1.22 (d, *J* = 7.1 Hz, 3H), 1.11 (d, *J* = 6.8 Hz, 3H), 0.74 (s, 3H), 0.20 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.6, 147.5, 143.3, 140.6, 134.5, 122.7, 111.1, 109.1, 74.4, 53.2, 53.0, 43.6, 40.4, 39.6, 34.6, 27.8, 23.9, 21.5, 0.9 (3C); IR (thin film) 3413, 2957, 2929, 2871, 1769, 1561, 1499, 1455, 1378, 1249, 1163, 1100, 1065, 1028, 1100, 1065, 1028, 891, 873, 856, 836, 754, 688, 601 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{21}H_{33}O_2Si$ [M+H$^+$] 345.2250, found 345.2241.





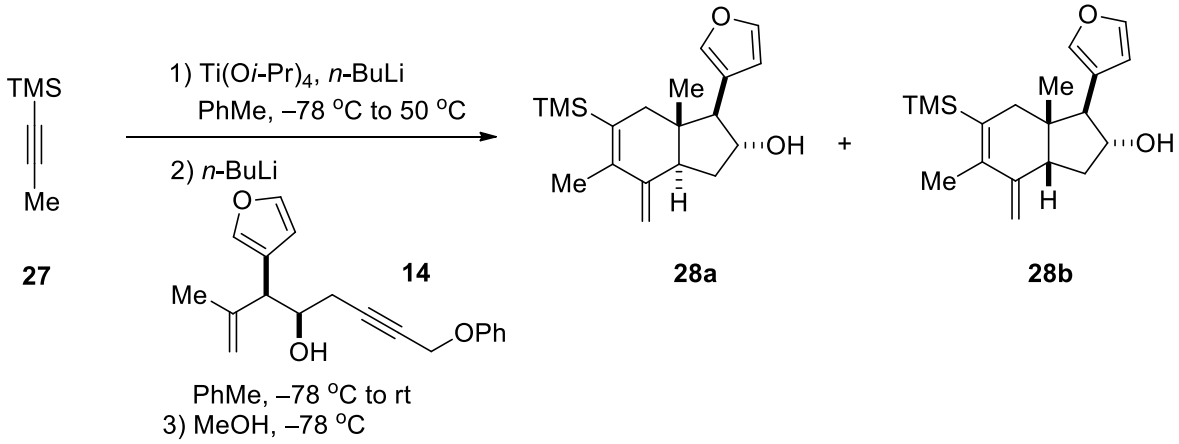
(+/–)-(2*R*,3a*S*,7a*R*)-6-benzyl-3a-methyl-7-methylene-5-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (**25a)** and **(2*R*,3a*S*,7a*S*)-6-benzyl-3a-methyl-7-methylene-5-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (25b):** To a solution of alkyne **24** (565 mg, 3.0 mmol) in PhMe (18.0 mL) was added Ti(O*i*Pr)$_4$ (0.9 mL, 3.0 mmol) at rt. The mixture was cooled to –78 °C and *n*-BuLi (2.49 M in hexanes, 2.40 mL, 6.0 mmol) was added dropwise (by syringe) over the course of 5 min. After this period, the flask was taken out of the cooling bath and allowed to warm to rt (approx. 20 min). The reaction mixture was then heated to 50 °C (no reflux condenser required) for 1 h and allowed to cool to rt before it was placed into a –78 °C cooling bath. In the meantime, enyne **18** (230 mg, 1.0 mmol) was dissolved in PhMe (12.0 mL), treated with *n*-BuLi (2.49 M in hexanes, 0.44 mL, 1.1 mmol) at –78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise (by syringe) to the above black Ti-alkyne complex solution at –78 °C. The reaction mixture was then allowed to warm to rt overnight (approx. 15 h). After this period, the cooling bath was removed and the mixture was stirred at rt for an additional 2 h. The reaction mixture was then drawn into a syringe and added dropwise to vigorously stirring, freshly degassed anhydrous MeOH (180 mL) at –78 °C (under N_2 atmosphere). The flask was then allowed to warm to rt, water (20 mL) was added, and the organic solvents were removed *in vacuo*. (*Note:* The evaporation of methanol prior to the aqueous workup minimizes the loss of organic material that can be caused by its increased partitioning into the aqueous phase.) The crude residue from evaporation was diluted with copious amounts of saturated aqueous NH_4Cl and extracted with Et_2O (three times). The combined organic extracts were vigorously stirred with 10% aqueous KOH for 5 minutes, the organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude mixture by flash chromatography afforded hydroindanes **25a** and **25b** (both as colorless oils) (166 mg, 51%, dr = 1:3) as well as a small amount of the *endo*-isomer (32 mg, 10%, colorless oil). Spectral data for **25a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 2H), 7.14 – 7.12 (m, 3H), 4.88 (s, 1H), 4.63 (s, 1H), 4.54 – 4.49 (m, 1H), 3.90, 3.75 (ABq, *J* = 16.8 Hz, 2H), 2.59 – 2.55 (m, 1H),2.38, 2.33 (ABq, *J* = 17.6 Hz, 2H), 2.26 (dd, *J* = 12.9, 7.4 Hz, 1H), 1.99 – 1.92 (m, 1H), 1.71 (dd, *J* = 13.8, 7.0 Hz, 1H), 1.55 (br. s, 1H), 1.40 (dd, *J* = 12.9, 5.5 Hz, 1H), 0.63 (s, 3H), 0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 142.2, 141.6 138.9, 128.4, 128.3, 128.0, 125.8, 109.2, 72.0, 52.0, 48.5, 46.3, 41.6, 38.8, 36.8, 29.9, 19.0, 0.3; IR (thin film) 3336, 2950, 2854, 1555, 1493, 1249, 1042, 854, 835, 695 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{21}H_{30}OSiH^+$ [M+H$^+$] 327.2144, found 327.2138. Spectral data for **25b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 2H), 7.15 – 7.13 (m, 3H), 4.90 (s, 1H), 4.74 (s, 1H), 4.44 – 4.38 (m, 1H), 3.86, 3.78 (ABq, *J* = 16.3 Hz, 2H), 2.58, 2.08 (ABq, *J* = 18.0 Hz, 2H), 2.26 – 2.16 (m, 2H), 1.82 (dd, J = 13.7, 8.6 Hz, 1H), 1.62 – 1.55 (m, 3H), 0.94 (s, 3H), 0.13 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 141.5, 140.3, 138.5, 128.4, 128.2, 128.1, 125.8, 112.7, 71.7, 52.0, 50.7, 43.6, 40.0, 39.9, 38.9, 26.2, 0.4; IR (thin film) 3349, 2950, 1718, 1493, 1453, 1248, 1055, 835, 695 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{21}H_{30}OSiH^+$ [M+H$^+$] 327.2144, found 327.2138.

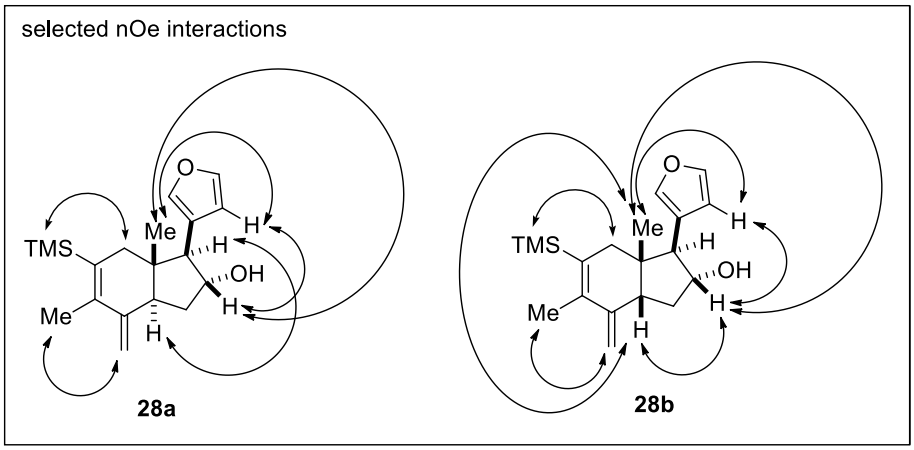




(+/–)-(1*S*,2*R*,3a*R*,7a*S*)-5-benzyl-7a-methyl-4-methylene-1-phenyl-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (26a) and **(1S,2R,3aS,7aS)-5-benzyl-7a-methyl-4-methylene-1-phenyl-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (26b):** To a solution of alkyne **24** (463 mg, 2.46 mmol) in PhMe (18.0 mL) was added Ti(O*i*Pr)$_4$ (0.73 mL, 2.46 mmol) at rt. The mixture was cooled to –78 °C and *n*-BuLi (2.49 M in hexanes, 2.0 mL, 4.92 mmol) was added dropwise (by syringe) over the course of 5 min. After this period, the flask was taken out of the cooling bath and allowed to warm to rt (approx. 20 min). The reaction mixture was then heated to 50 °C (no reflux condenser required) for 1 h and allowed to cool to rt before it was placed into a –78 °C cooling bath. In the meantime, enyne **7** (250 mg, 0.82 mmol) was dissolved in PhMe (12.0 mL), treated with *n*-BuLi (2.49 M in hexanes, 0.36 mL, 0.90 mmol) at –78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise (by syringe) to the above black Ti-alkyne complex solution at –78 °C. The reaction mixture was then allowed to warm to rt overnight (approx. 15 h). After this period, the cooling bath was removed and the mixture was stirred at rt for an additional 2 h. The reaction mixture was then drawn into a syringe and added dropwise to vigorously stirring, freshly degassed anhydrous MeOH (180 mL) at –78 °C (under N_2 atmosphere). The flask was then allowed to warm to rt, water (20 mL) was added, and the organic solvents were removed *in vacuo*. (*Note:* The evaporation of methanol prior to the aqueous workup minimizes the loss of organic material that can be caused by its increased partitioning into the aqueous phase.) The crude residue from evaporation was diluted with copious amounts of saturated aqueous NH_4Cl and extracted with Et_2O (three times). The combined organic extracts were vigorously stirred with 10% aqueous KOH for 5 minutes, the organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude mixture by flash chromatography afforded hydroindanes **26a** and **26b** (both as colorless oils) (175 mg, 53%, ds = 1:3, determined by NMR analysis of the crude reaction mixture) as well as a small amount of the *endo*-isomer (33 mg, 10 %, colorless oil). Spectral data for **26a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.35

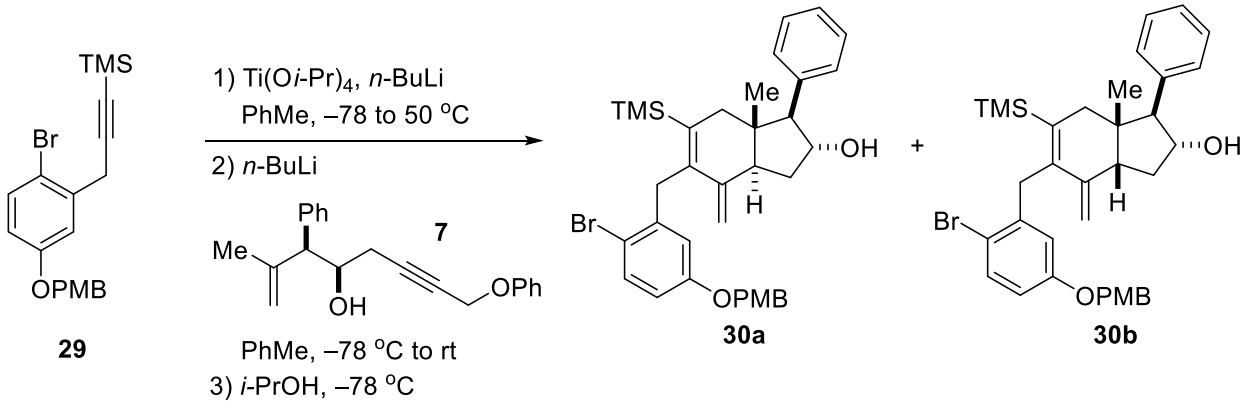
(m, 2H), 7.29 – 7.22 (m, 5H), 7.16 – 7.12 (m, 3H), 4.94 (s, 1H), 4.88 – 4.85 (m, 1H), 4.69 (s, 1H), 3.90, 3.75 (ABq, *J* = 16.6 Hz, 2H), 2.88 (d, *J* = 7.5 Hz, 1H), 2.84 – 2.80 (m, 1H), 2.43, 2.12 (ABq *J* = 17.6 Hz, 2H), 2.25 – 2,17 (m, 1H), 1.88 – 1.83 (m, 1H), 1.66 (br. s, 1H) 0.46 (s, 3H), 0.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.7, 142.4, 141.5, 138.9, 138.3, 128.9, 128.5, 128.4, 128.3, 128.0, 126.9, 125.8, 109.5, 75.8, 68.1, 50.0, 45.1, 38.8, 34.7, 14.0, 0.2; IR (thin film) 3476, 2925, 1719, 1494, 1453, 1249, 836, 699 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{27}H_{35}OSiH^+$ [M+H$^+$] 403.2457, found 403.2459. Spectral data for **26b**; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 2H), 7.27 – 7.23 (m, 4H), 7.18 – 7.13 (m, 4H), 4.93 (s, 1H), 4.80 (s, 1H), 4.60 – 4.56 (m, 1H), 3.86, 3.82 (ABq, *J* = 16.3 Hz, 2H), 2.76 (d, *J* = 6.8 Hz, 1H), 2.46 – 2.44 (m, 2H) 2.33 – 2.28 (m, 1H), 2.04 (app. d, *J* = 16.8 Hz, 1H), 1.62 – 1.54 (m, 2H), 0.57 (s, 3H), 0.19 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6, 143.4, 141.2, 141.1, 137.8, 130.2, 129.4, 129.3, 128.5, 128.4, 128.3, 126.7, 125.9, 111.7, 72.4, 66.0, 64.5, 50.2, 43.6, 41.1, 39.5, 24.9, 0.6; IR (thin film) 3476, 2924, 2853, 1722, 1494, 1249, 1028, 838, 699 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{27}H_{35}OSiH^+$ [M+H$^+$] 403.2457, found 403.2459.

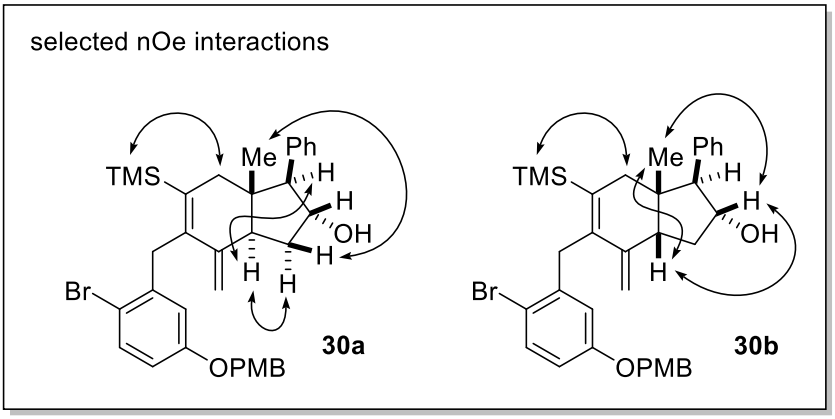




(+/–)-(1*S*,2*R*,3a*R*,7a*S*)-1-(furan-3-yl)-5,7a-dimethyl-4-methylene-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (28a) and **(+/–)-(1S,2R,3aS,7aS)-1-(furan-3-yl)-5,7a-dimethyl-4-methylene-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (28b):** To a solution of alkyne **27** (102 mg, 0.91

mmol) in PhMe (5.5 mL) was added Ti(O*i*Pr)$_4$ (0.27 mL, 0.91 mmol) at rt. The mixture was cooled to –78 °C and *n*-BuLi (2.37 M in hexanes, 0.77 mL, 1.82 mmol) was added dropwise (by syringe) over the course of 5 min. After this period, the flask was taken out of the cooling bath and allowed to warm to rt (approx. 20 min). The reaction mixture was then heated to 50 °C (no reflux condenser required) for 1 h and allowed to cool to rt before it was placed into a –78 °C cooling bath. In the meantime, enyne **14** (81 mg, 0.27 mmol) was dissolved in PhMe (3.6 mL), treated with *n*-BuLi (2.36 M in hexanes, 0.121 mL, 0.29 mmol) at –78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise (by syringe) to the above black Ti-alkyne complex solution at –78 °C. The reaction mixture was then allowed to warm to rt overnight (approx. 15 h). After this period, the cooling bath was removed and the mixture was stirred at rt for an additional 3 h. The reaction mixture was then drawn into a syringe and added dropwise to vigorously stirring, freshly degassed anhydrous MeOH (56 mL) at –78 °C (under N_2 atmosphere). The flask was then allowed to warm to rt, water (20 mL) was added, and the organic solvents were removed *in vacuo*. (*Note:* The evaporation of methanol prior to the aqueous workup minimizes the loss of organic material that can be caused by its increased partitioning into the aqueous phase.) The crude residue from evaporation was diluted with copious amounts of saturated aqueous NH_4Cl and extracted with Et_2O (three times). The combined organic extracts were vigorously stirred with 10% aqueous KOH for 5 minutes, the organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude mixture by flash chromatography (silica gel, gradient 95:5:1 to 75:25:1 hexanes:EtOAc:Et_3N) afforded hydroindanes **28a** (white solid) and **28b** (colorless oil) (46 mg, 52%, ds = 1:1, determined by NMR analysis of the crude reaction mixture) as well as a small amount of the *endo*-isomer (6 mg, 7%, colorless oil). Spectral data for **28a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (app. t, *J* = 1.8 Hz, 1H), 7.35 – 7.33 (m, 1H), 6.33 (dd, *J* = 1.6, 0.6 Hz, 1H), 5.12 (m, 1H), 4.73 – 4.71 (m, 1H), 4.56 – 4.51 (ddd, *J* = 7.7, 7.3, 2.2 Hz, 1H), 2.70 – 2.64 (m, 1H), 2.64 (d, *J* = 7.6 Hz, 1H), 2.24 – 2.17 (m, 2H), 2.11 (app. dd, *J* = 17.3, 0.9 Hz, 1H), 1.96 (app. dd, *J* = 2.1, 1.3 Hz, 3H), 1.85 (ddd, *J* = 13.8, 8.0, 2.3 Hz, 1H), 1.75 (bs, 1H), 0.41 (s, 3H), 0.14 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6, 143.2, 140.6, 139.8, 134.7, 123.1, 111.0, 107.3, 76.8, 58.6, 49.2, 44.7, 44.6, 34.8, 19.1, 13.9, 0.26 (3C); IR (thin film) 3276, 3195, 3088, 2961, 2926, 1724, 1564, 1497, 1445, 1376, 1243, 1201, 1156, 1063, 1024, 888, 873, 832, 752, 683, 599 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{19}H_{29}O_2Si$ [M+H$^+$] 317.1937, found 317.1930. Spectral data for **28b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.40 (m, 1H), 7.27 – 7.26 (m, 1H), 6.29 (dd, *J* = 1.8, 0.9 Hz, 1H), 5.02 (s, 1H), 4.84 (s, 1H), 4.27 (ddd, *J* = 7.8, 7.8, 7.8 Hz, 1H), 2.56 (d, *J* = 7.7 Hz, 1H), 2.48 (dd, *J* = 9.9, 8.0 Hz, 1H), 2.38 (ddd, *J* = 12.6, 7.0, 7.0 Hz, 1H), 2.25 (app. dd, *J* = 16.5, 1.1 Hz, 1H), 2.01 (app. t, *J* = 1.6 Hz, 3H), 1.75 (app. dd, *J* = 16.5, 1.8 Hz, 1H), 1.65 (bs, 1H), 1.52 (ddd, *J* = 12.7, 10.1, 8.6 Hz, 1H), 0.69 (s, 3H), 0.19 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.9, 143.2, 142.1, 140.2, 134.4, 124.0, 111.2, 109.5, 76.6, 53.8, 50.0, 42.7, 41.9, 39.9, 25.7, 20.7, 0.5 (3C); IR (thin film) 3370, 3080, 2954, 2930, 2898, 1766, 1672, 1571, 1501, 1452, 1375, 1250, 1162, 1058, 1026, 877, 856, 836, 752, 686, 602 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{19}H_{29}O_2Si$ [M+H$^+$] 317.1937, found 317.1931.





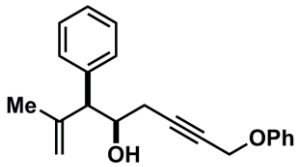
(+/–)-(1*S*,2*R*,3a*R*,7a*S*)-5-(2-bromo-5-((4-methoxybenzyl)oxy)benzyl)-7a-methyl-4-methylene-1-phenyl-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (30b) and **(+/–)-(1*S*,2*R*,3a*S*,7a*S*)-5-(2-bromo-5-((4-methoxybenzyl)oxy)benzyl)-7a-methyl-4-methylene-1-phenyl-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-inden-2-ol (30b):** To a –78 °C solution of Ti(OiPr)$_4$ (0.3 mL, 1.0 mmol) in PhMe (2 mL), *n*-BuLi (2.49 M in hexanes, 0.80 mL, 2.0 mmol) was added dropwise (by syringe) over the course of 5 min. After additional stirring for 10 min at –78 °C, a solution of alkyne **29** (400 mg, 1.0 mmol) in PhMe (6 mL) was added dropwise. (*Note*: The order of addition was modified in order to avoid potential metal-halogen exchange between *n*-Buli and alkyne **29**.) After this period, the flask was taken out of the cooling bath and allowed to warm to rt (approx. 20 min). The reaction mixture was then heated to 50 °C (no reflux condenser required) for 1 h and allowed to cool to rt before it was placed into a –78 °C cooling bath. In the meantime, enyne **7** (100 mg, 0.3 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (2.49 M in hexanes, 0.12 mL, 0.3 mmol) at –78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise (by syringe) to the above black Ti-alkyne complex solution at –78 °C. The reaction mixture was then allowed to warm to rt overnight (approx. 15 h). After this period, the cooling bath was removed and the mixture was stirred at rt for an additional 2 h. The reaction mixture was then drawn into a syringe and added dropwise to vigorously stirring *i*-PrOH (80 mL) at –78 °C (under N_2 atmosphere). The flask was then allowed to warm to rt, water (20 mL) was added, and the organic solvents were removed *in vacuo*. (*Note:* The evaporation of isopropanol prior to the aqueous workup minimizes

the loss of organic material that can be caused by its increased partitioning into the aqueous phase.) The crude residue from evaporation was diluted with copious amounts of saturated aqueous NH_4Cl and extracted with Et_2O (three times). The combined organic extracts were vigorously stirred with 10% aqueous KOH for 5 minutes, the organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude mixture by flash chromatography afforded hydroindanes **30a** and **30b** (both as colorless oils) (107 mg, 58%, ds = 3:1)[9] as well as a small amount of the *endo*-isomer (20 mg, 12%, colorless oil). Spectral data for **30a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.5 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.30 – 7.26 (m, 5H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.68 (dd, *J* = 8.5, 3.1 Hz, 1H), 6.62 (d, *J* = 3.1 Hz, 1H), 4.91 – 4.84 (m, 3H), 4.85 (s, 1H), 4.67 (s, 1H), 3.91, 3.59 (ABq, *J* = 17.4 Hz, 2H), 3.82 (s, 3H), 2.86 (d, *J* = 7.6 Hz, 1H), 2.68 (br-dd, *J* = 10.4, 9.2 Hz, 1H), 2.36 (d, *J* = 17.4 Hz, 1H), 2.23 (ddd, *J* = 14.0, 11.6, 9.2 Hz, 1H), 2.09 (d, *J* = 17.4 Hz, 1H), 1.84 (ddd, *J* = 14.0, 7.9, 2.1 Hz, 1H), 1.78 (br-s, 1H), 0.45 (s, 3H), 0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 158.0, 145.1, 141.7, 141.4, 139.1, 138.5, 132.7, 128.9, 128.9, 128.6, 128.3, 126.7, 115.7, 115.2, 114.5, 114.1, 109.0, 75.5, 69.8, 67.8, 55.4, 49.6, 45.1, 44.8, 38.7, 34.4, 13.7, -0.2 ; IR (thin film): 3364, 3086, 3060, 3028, 2955, 1945, 1878, 1724, 1613, 1589, 1515, 1463, 1283, 1250, 1038, 1011, 867, 836 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{35}H_{42}BrO_3Si$ [M+H$^+$] 617.2081, found 617.2081. Spectral data for **30b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.5 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.24 (m, 3H), 7.17 (dd, *J* = 8.2, 1.2 Hz, 2H), 6.89 – 6.85 (m, 2H), 6.73 (d, *J* = 3.1 Hz, 1H), 6.68 (dd, *J* = 8.5, 3.1 Hz, 1H), 4.91 – 4.87 (m, 3H), 4.84 (s, 1H), 4.64 (br-dd, *J* = 17.3, 7.3 Hz, 1H), 3.87, 3.75 (ABq, *J* = 17.4 Hz, 2H), 3.79 (s, 3H), 2.81 (d, *J* = 5.8 Hz, 1H), 2.59 – 2.53 (m, 1H), 2.54 (d, *J* = 17.1 Hz, 1H), 2.43 (ddd, *J* = 12.8, 7.6, 7.3 Hz, 1H), 2.11 (d, *J* = 17.1 Hz, 1H), 1.81 (br-s, 1H), 1.76 (ddd, *J* = 12.8, 11.3, 7.9 Hz, 1H), 0.59 (s, 3H), 0.12 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 158.0, 144.6, 141.4, 141.3, 141.3, 139.4, 132.8, 129.0, 128.7, 128.2, 126.5, 115.5, 115.2, 114.8, 113.9, 112.2, 77.4, 69.8, 64.7, 55.3, 49.8, 43.4, 41.4, 41.1, 39.4, 24.2, 0.0; IR (thin film): 3422, 3083, 3060, 3028, 2953, 2898, 2835, 1945, 1879, 1778, 1613, 1589, 1569, 1515, 1464, 1286, 1250, 1036, 1016, 860, 834 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{35}H_{42}BrO_3Si$ [M+H$^+$] 617.2081, found 617.2087.

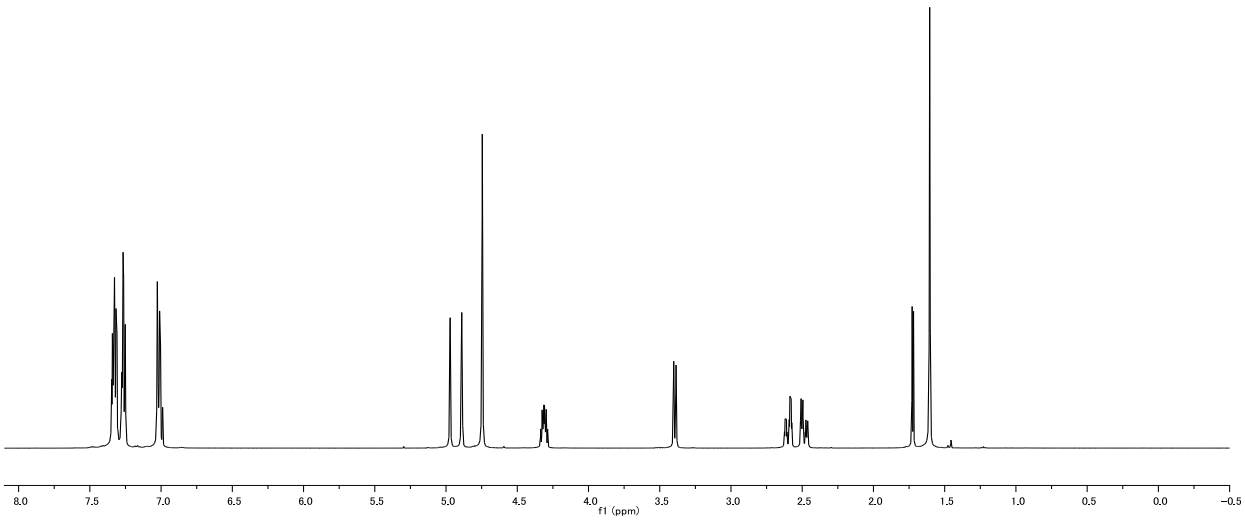
[9] The selectivity observed in this example varied significantly as a function of the *i*-PrOH used to quench the reaction. Freshly degassed anhydrous *i*-PrOH gave a 2:1:6 mixture of *trans:cis:endo* isomers, whereas reagent grade ("wet") *i*-PrOH delivered the *trans* isomer as the major product, along with a minor quantity of *cis*- and *endo*-isomers (3.6:1.2:1). Interestingly, quenching with freshly degassed anhydrous MeOH gave a 1:1:1 mixture of these isomers, and quenching with water at rt generated the *endo* isomer almost exclusively. A mechanistic rationale in support of these observations is currently lacking.

3. Spectral Data

***Figure S1*:** ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **7**.



7



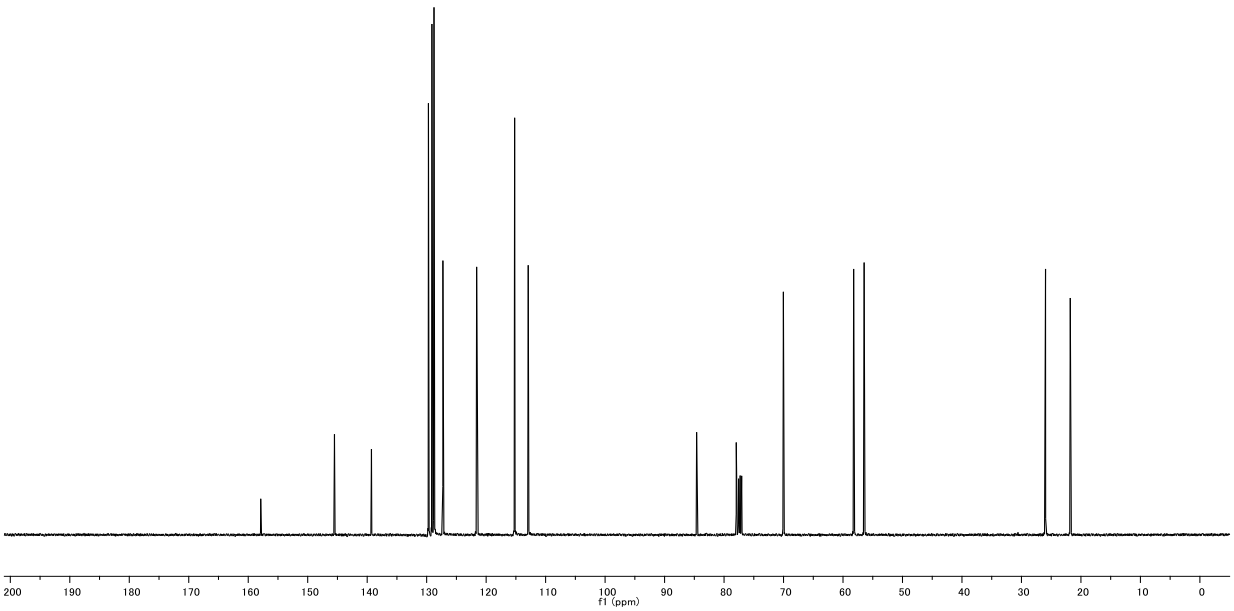
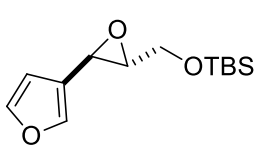


Figure S2: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **S4.**



S4

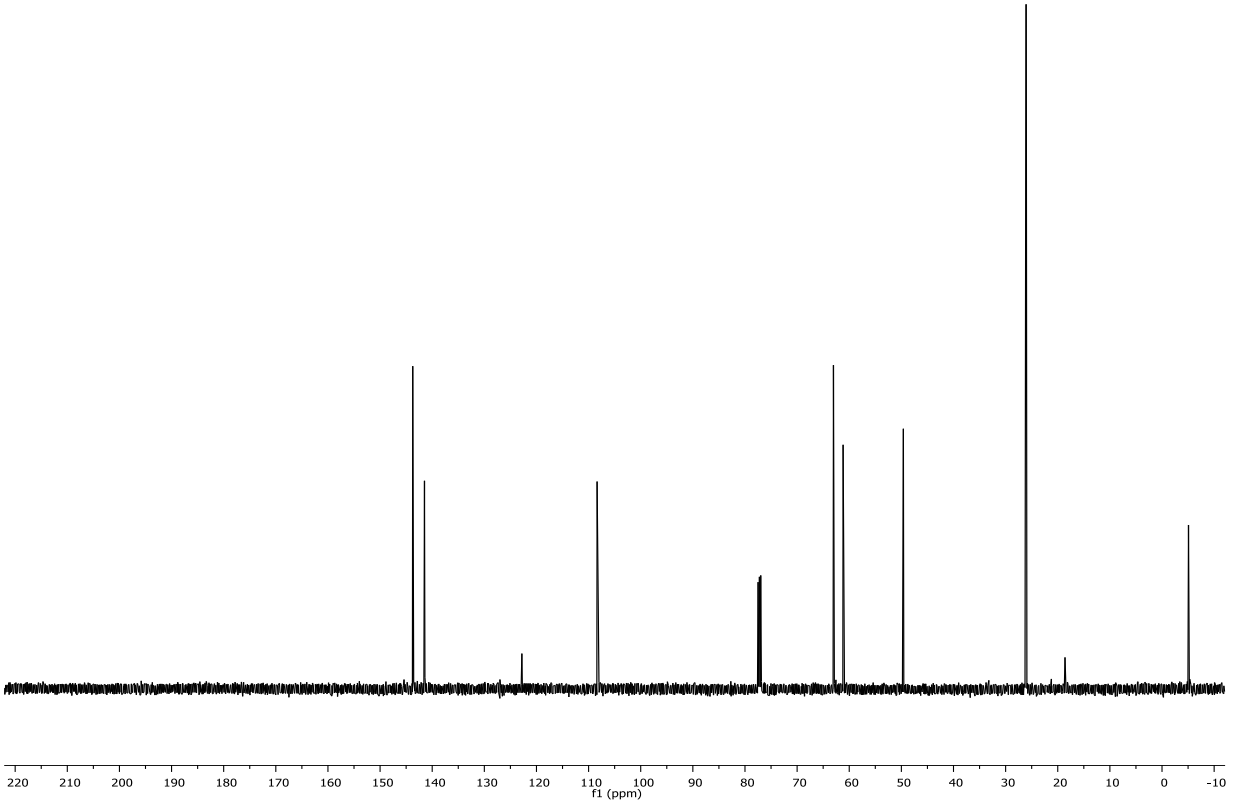
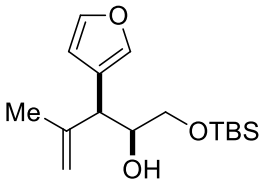


Figure S3: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **S5.**



S5

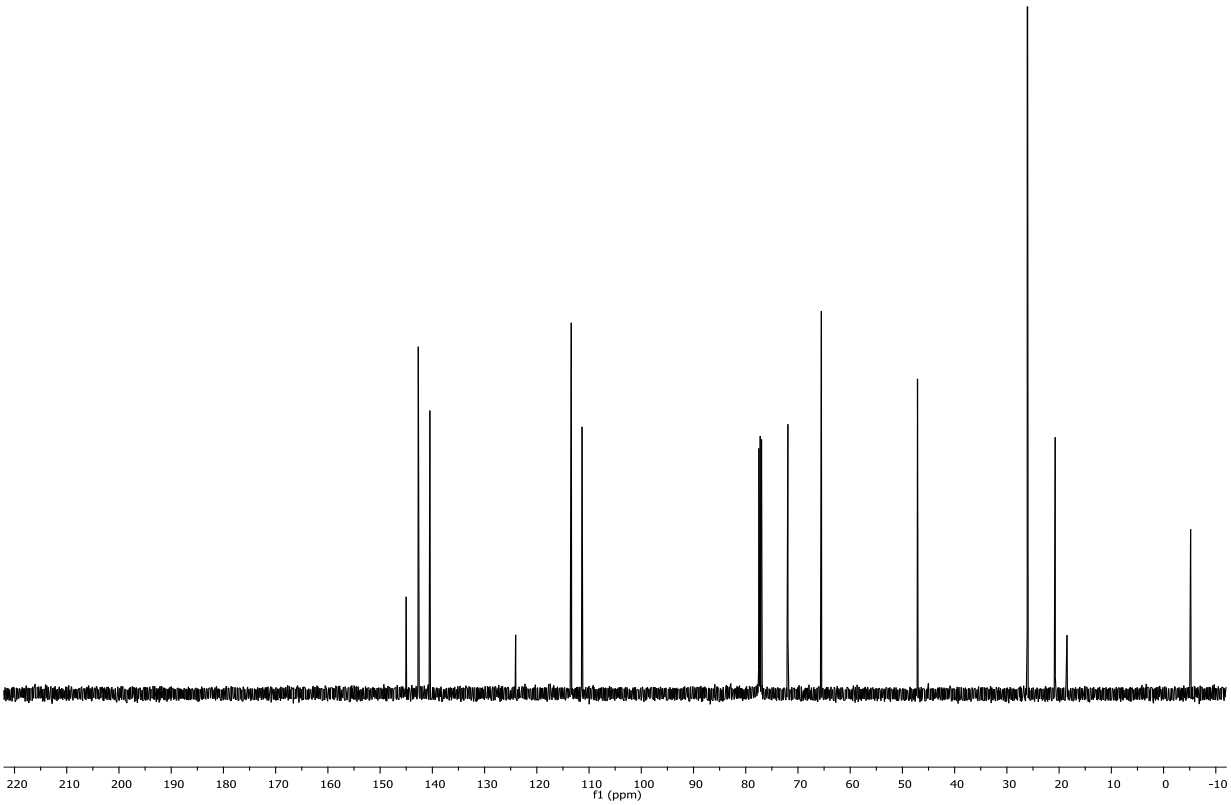
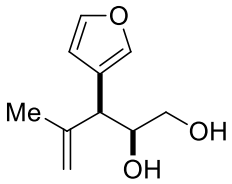
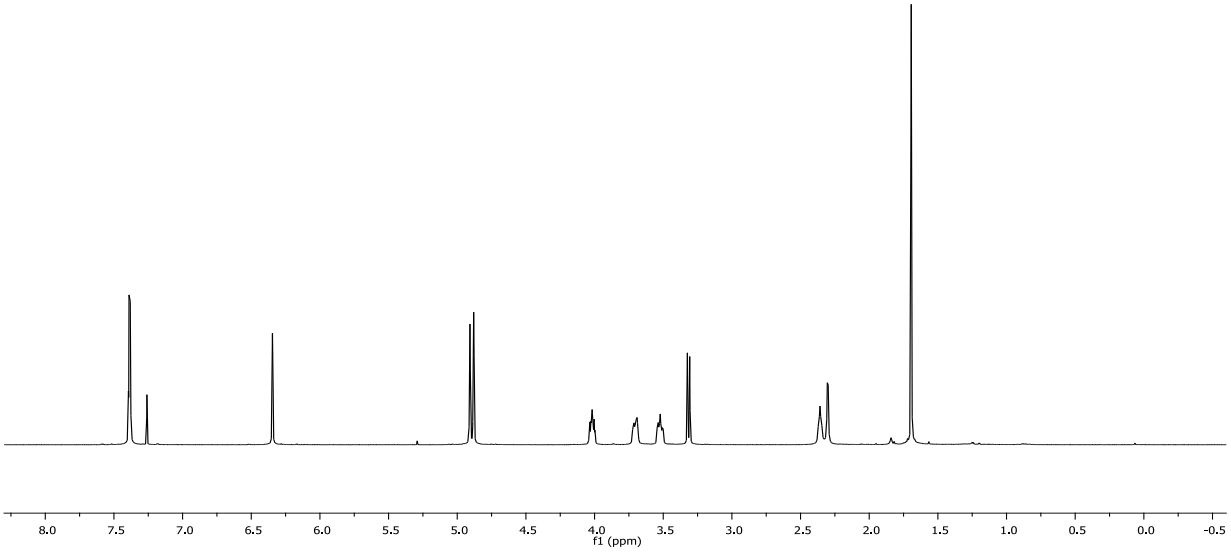


Figure S4: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **S6.**



S6



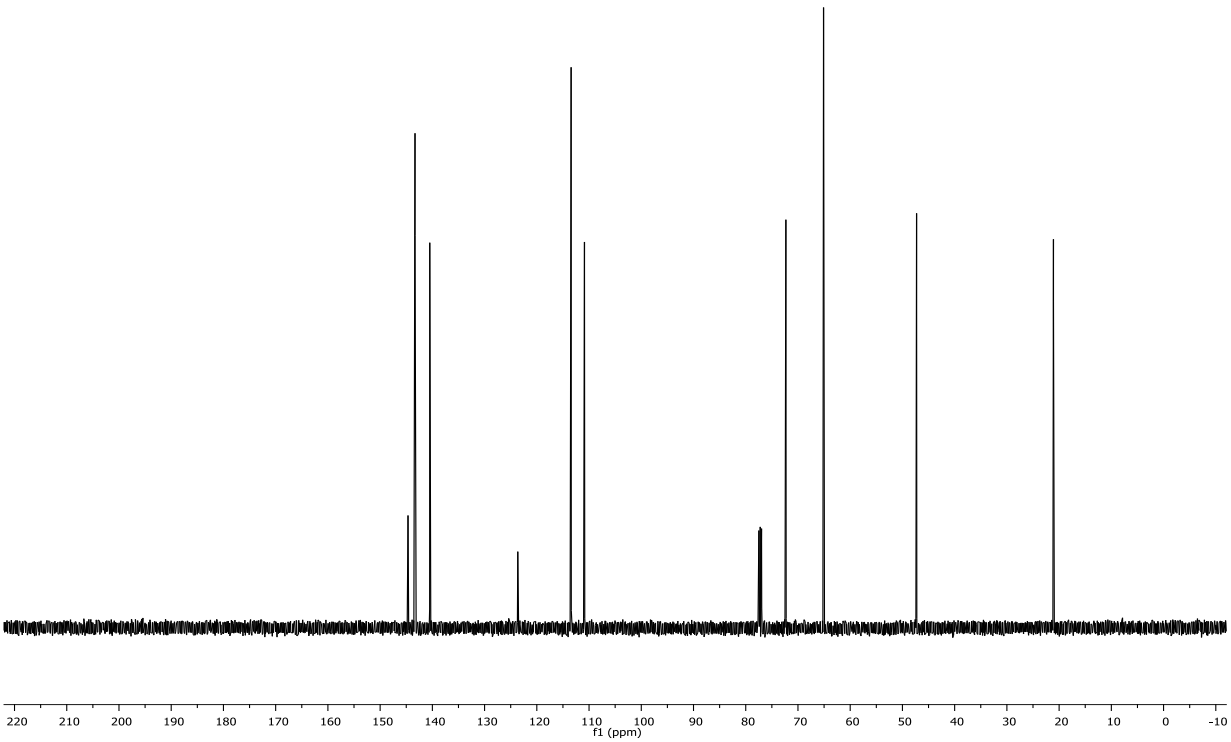
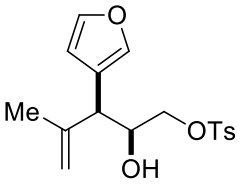
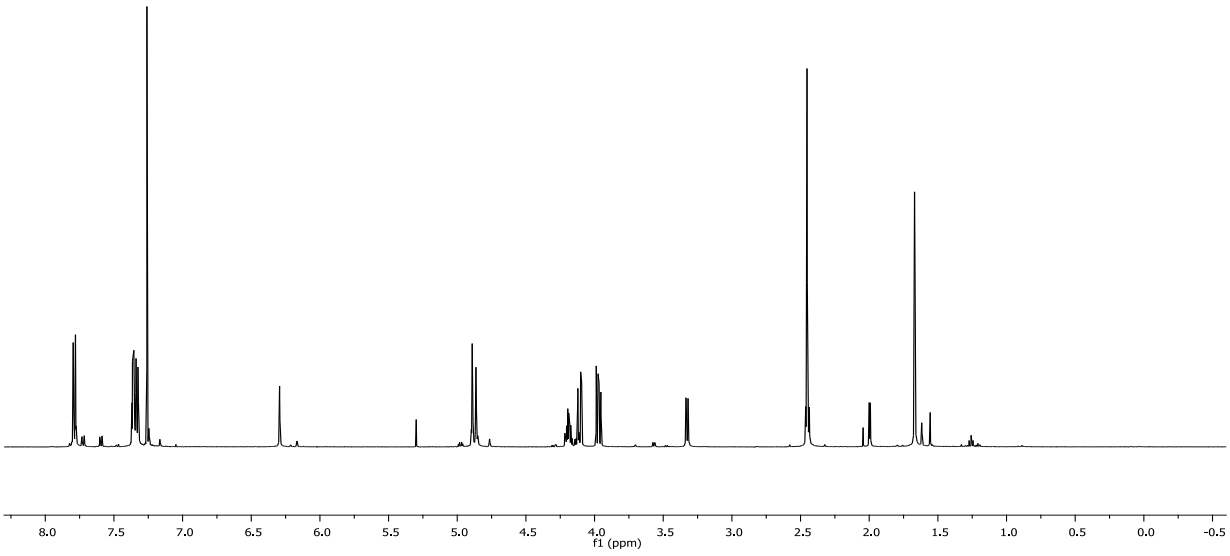


Figure S5: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **S7.**



S7



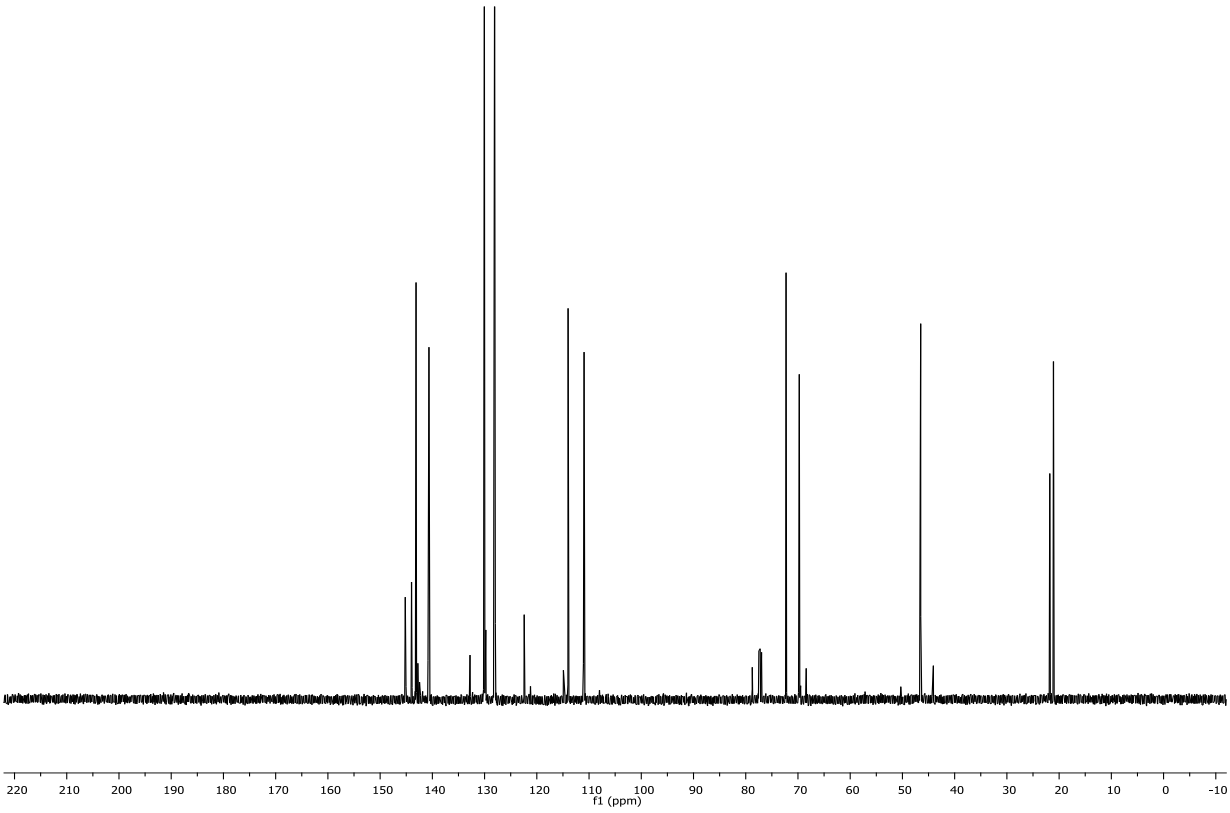
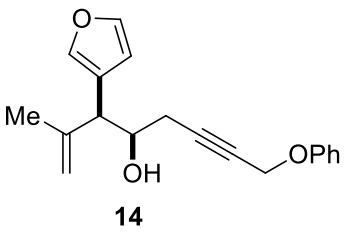
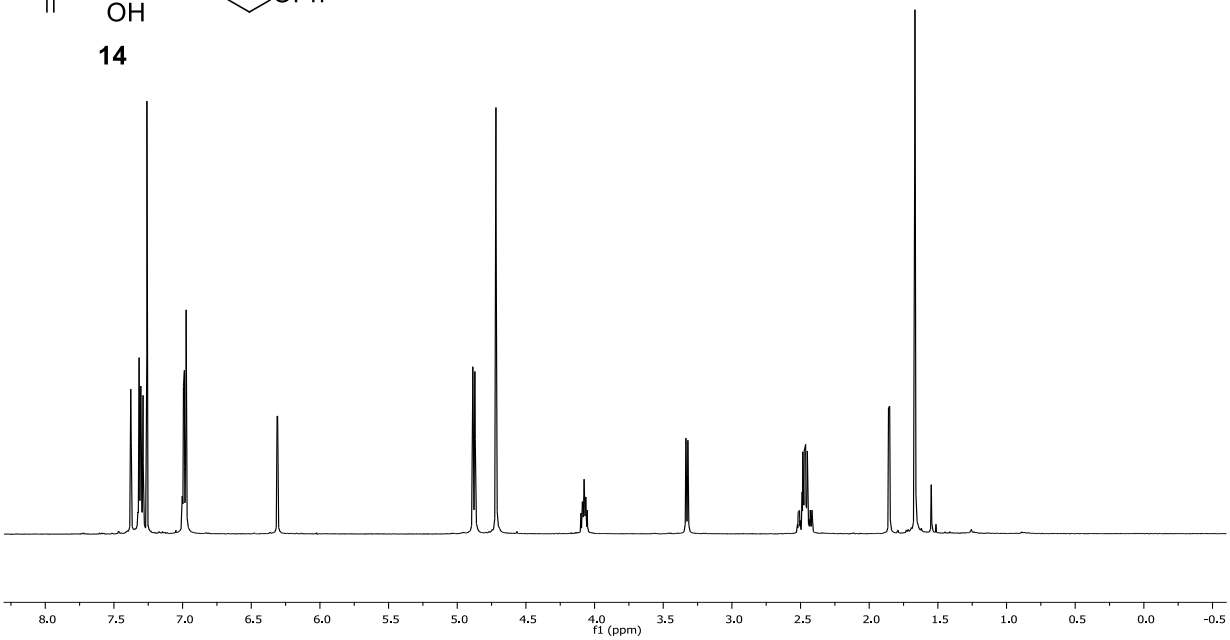


Figure S6: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **14.**



14



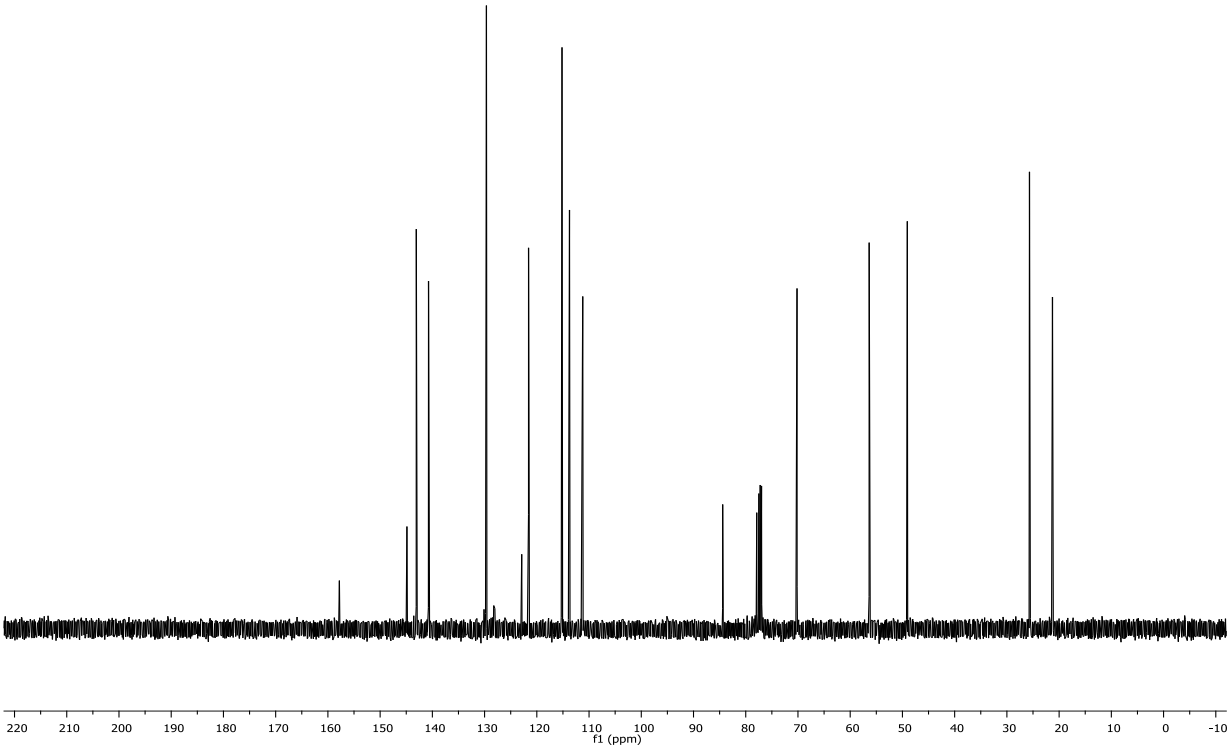
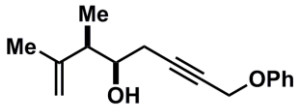
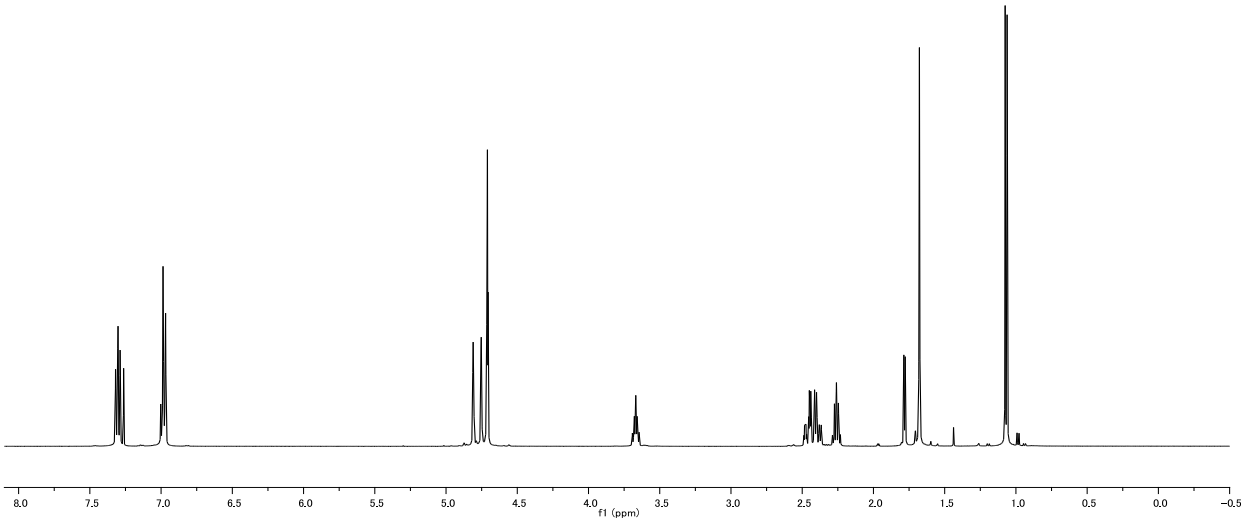


***Figure S7*:** ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **16.**



16



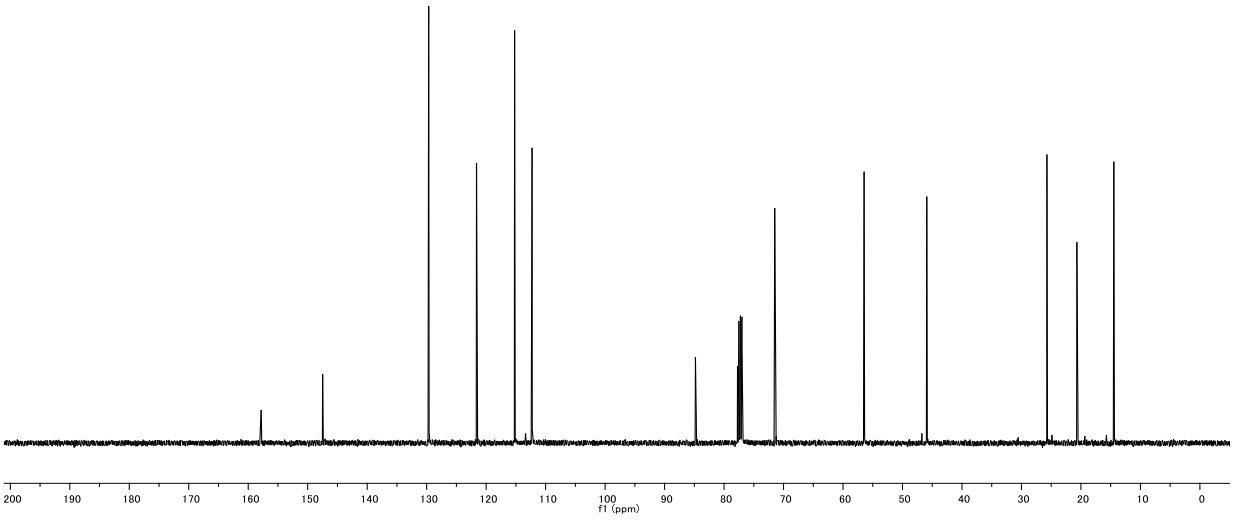
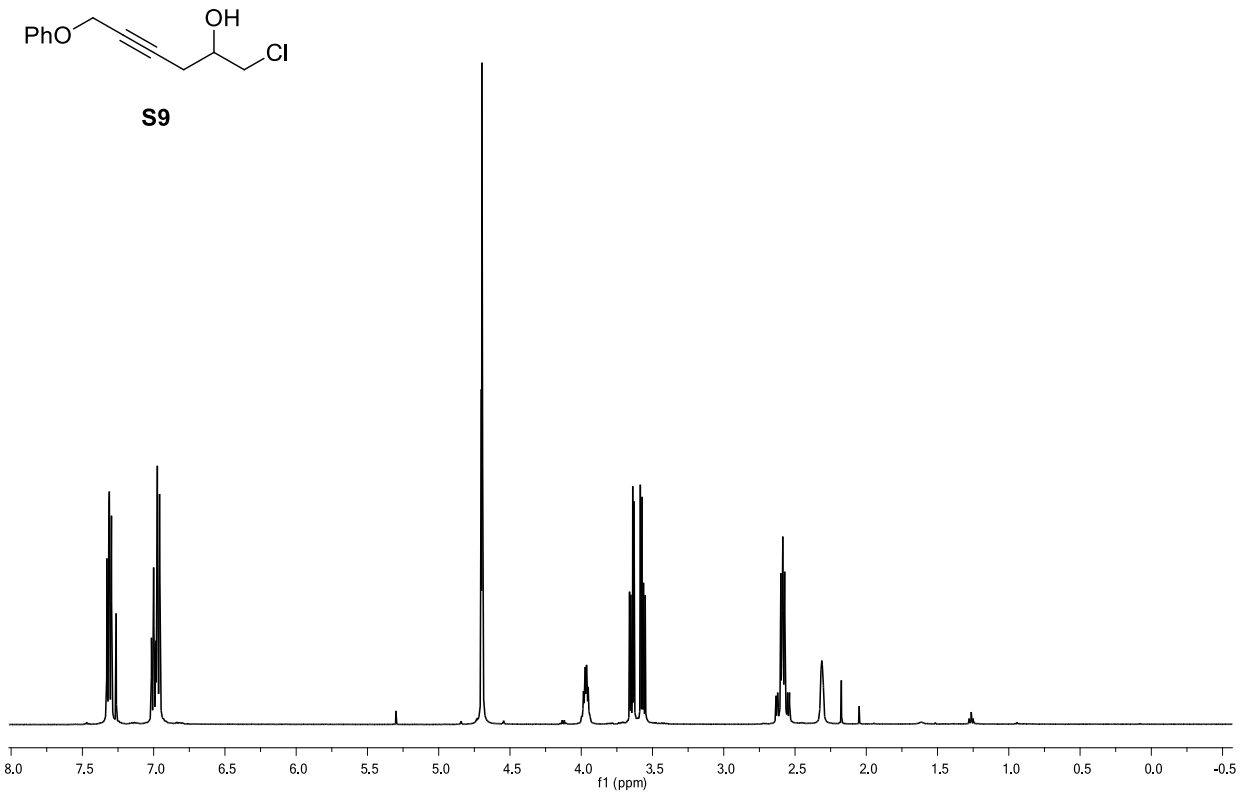


Figure S8: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **S9**.



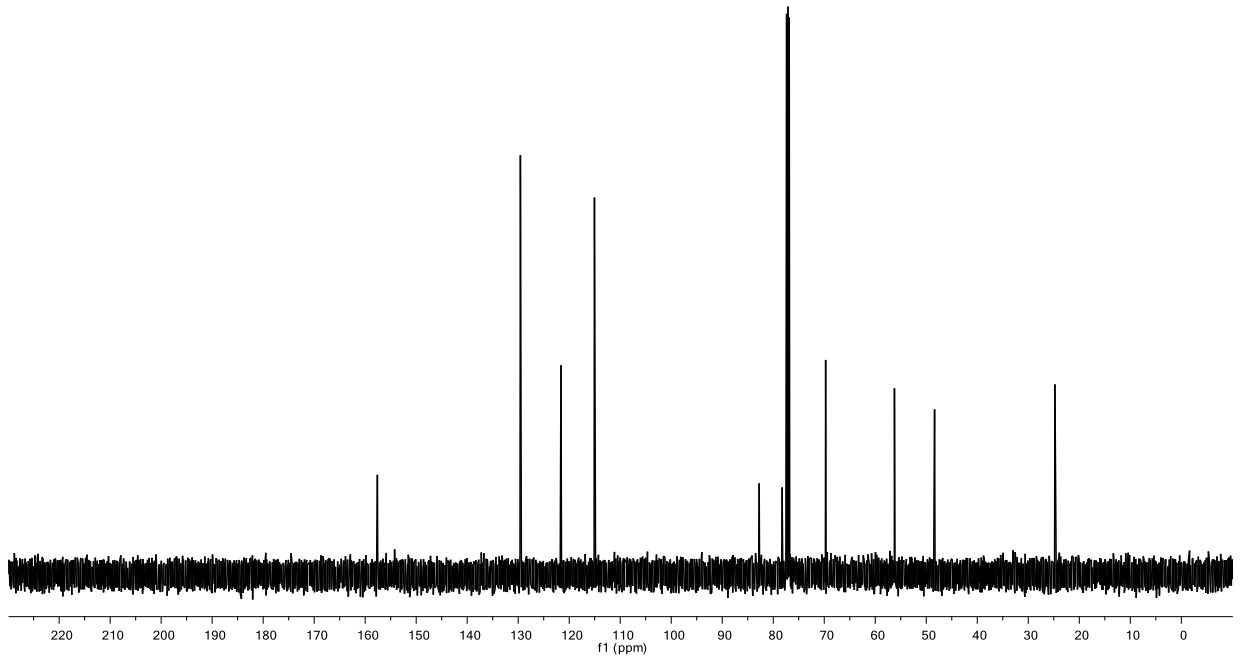
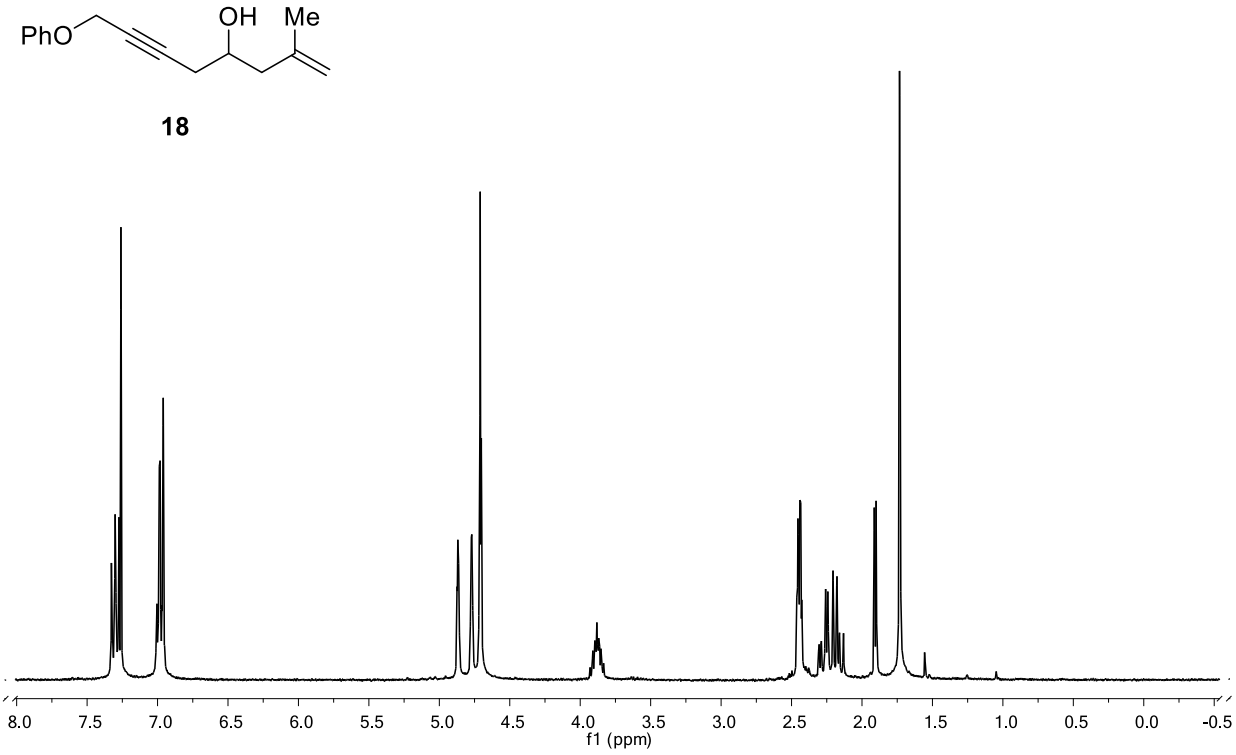


Figure S9: ^{1}H NMR (500 MHz, CDCl3) and ^{13}C NMR (125 MHz, CDCl3) of **18**.



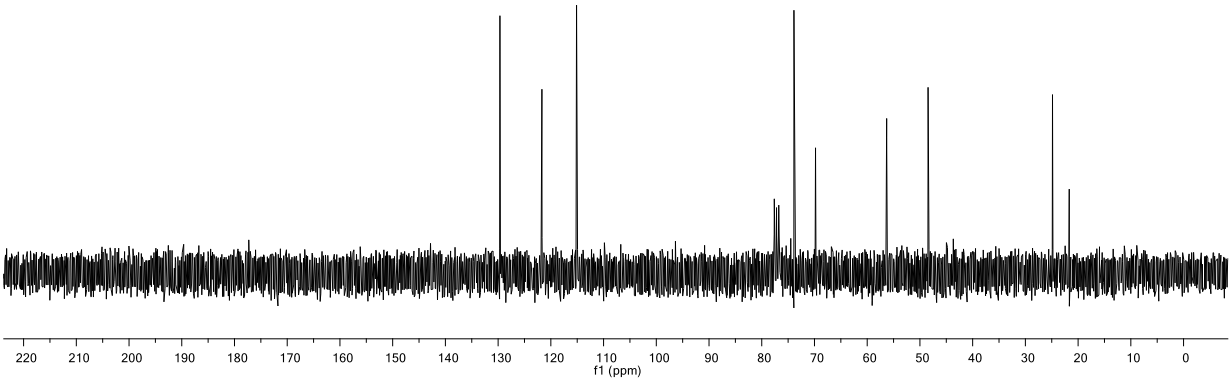
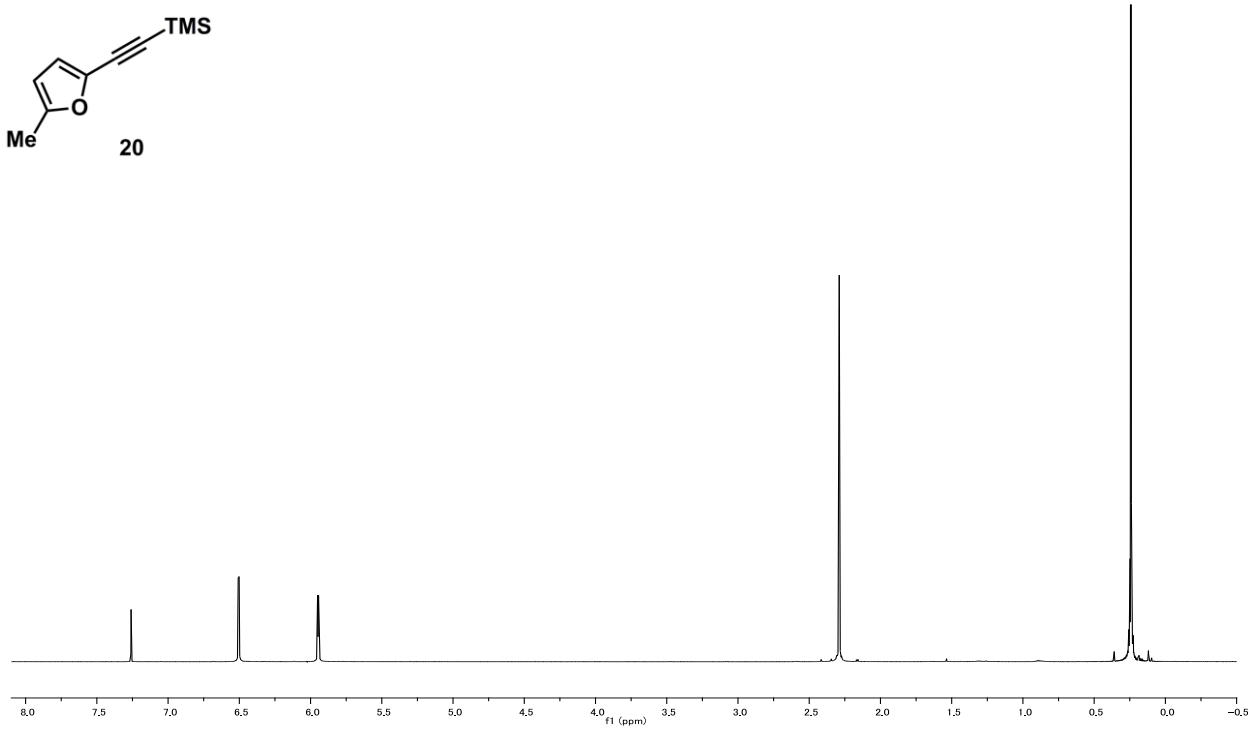


***Figure S10*:** ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **20**.



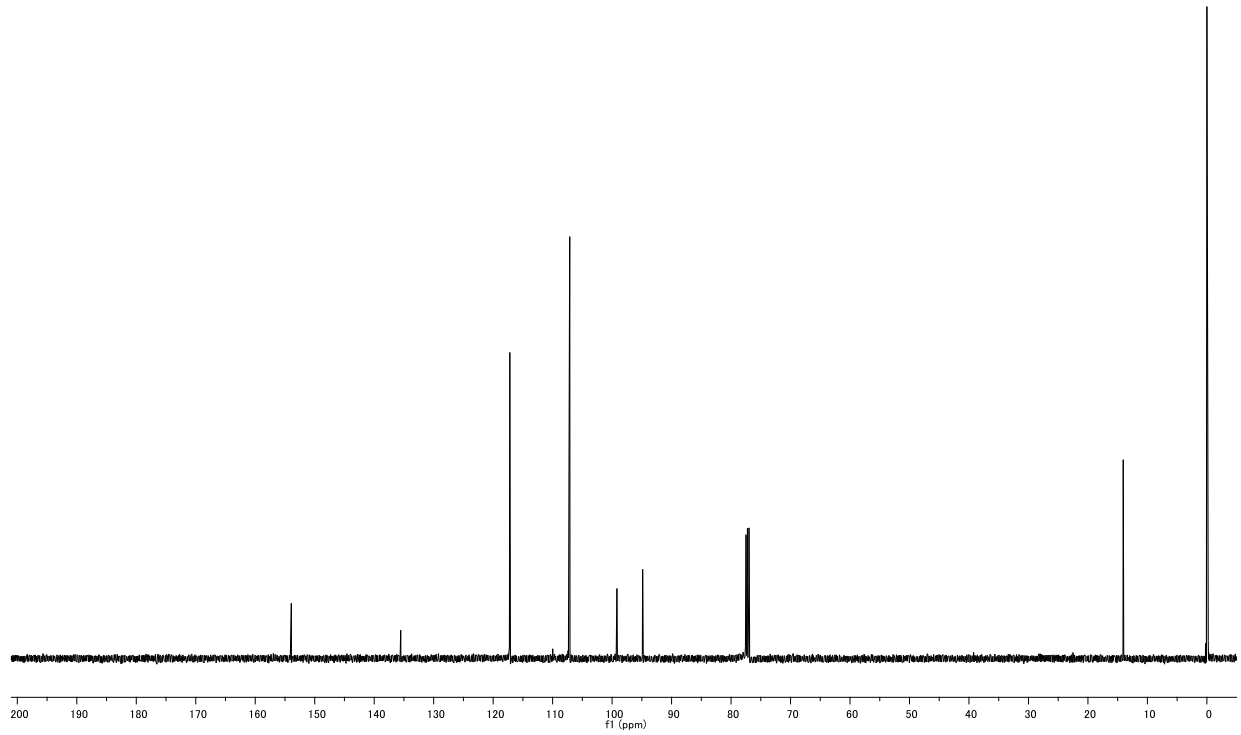
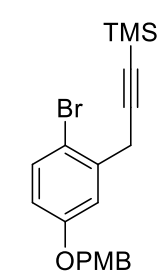


Figure S11: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **29**.



29

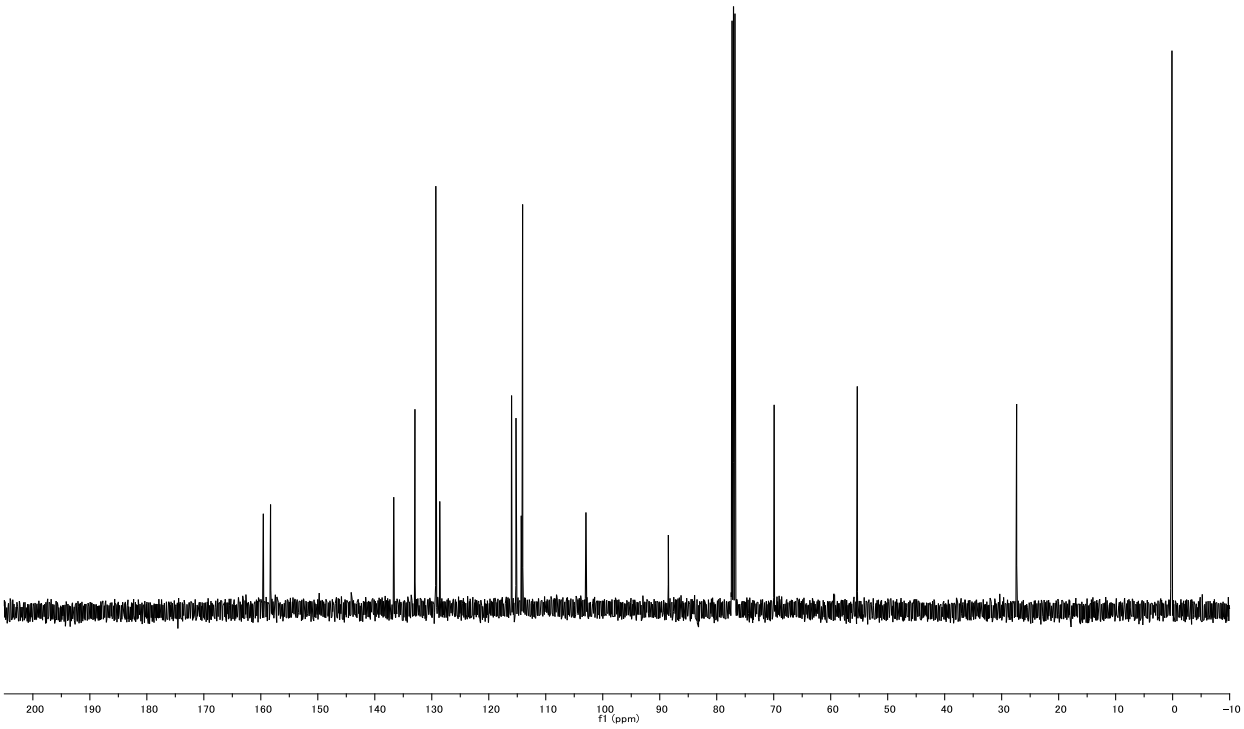
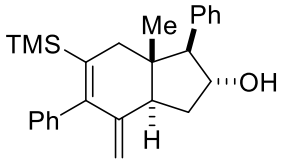


Figure S12: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **9a.**



9a

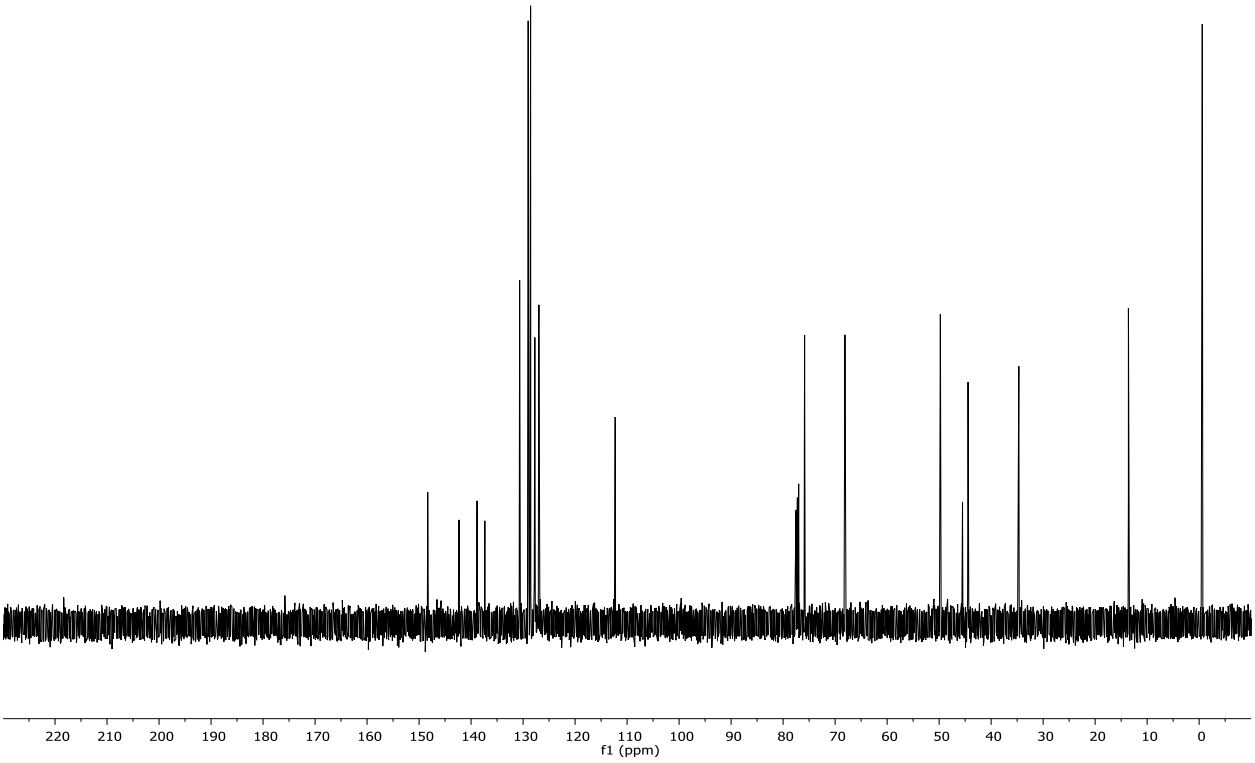
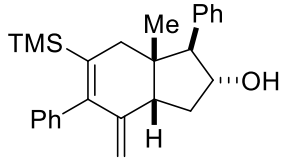


Figure S13: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **9b.**



9b

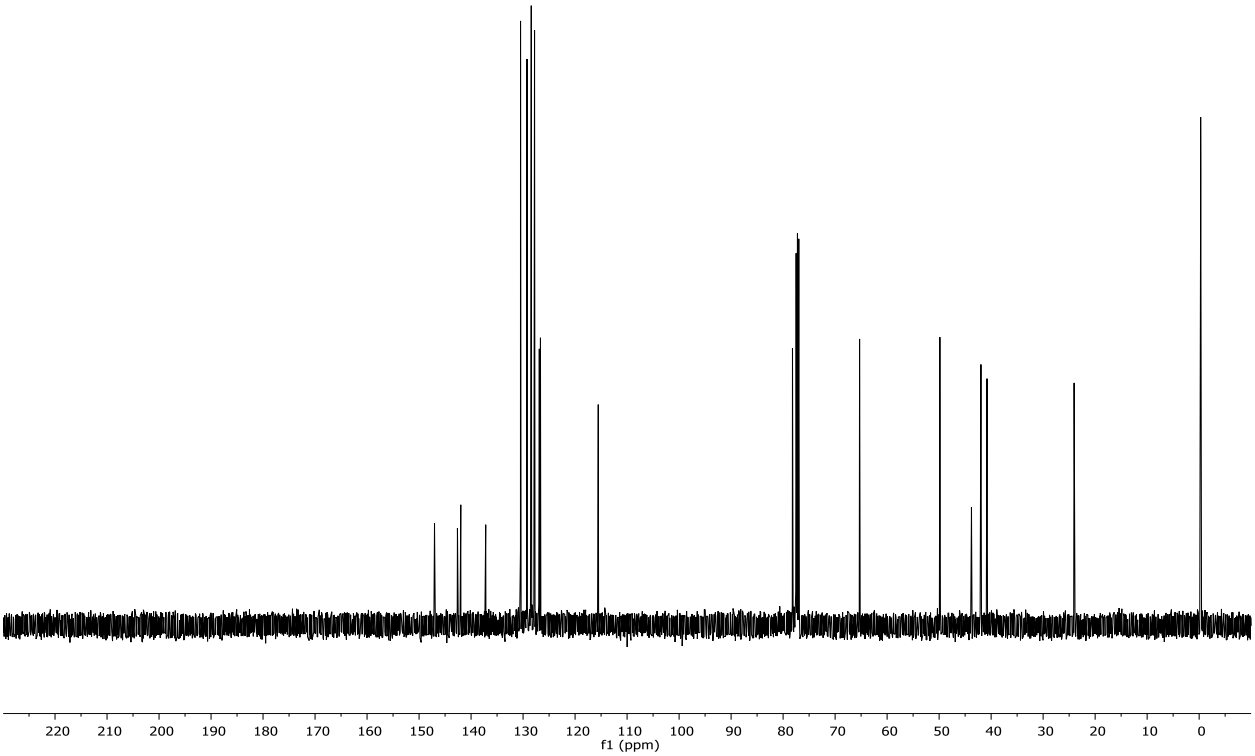
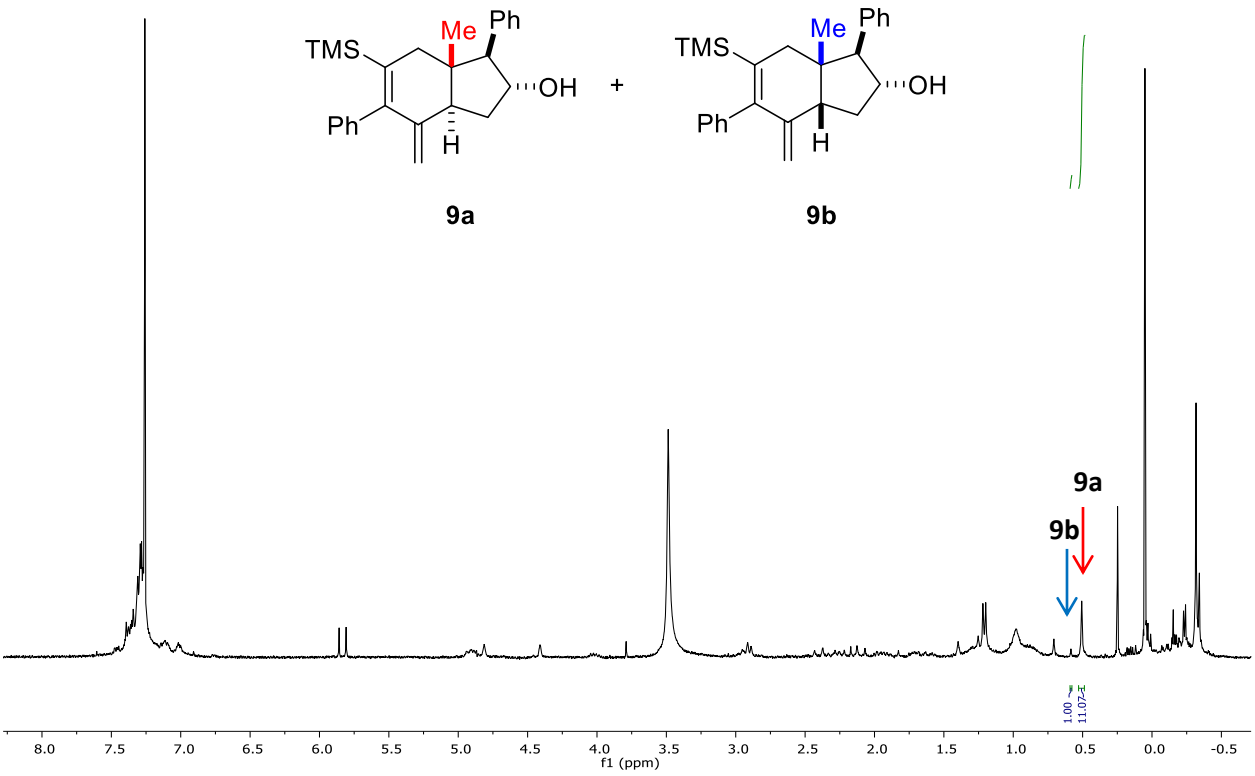


Figure S14: ^{1}H NMR (500 MHz, $CDCl_3$) of the crude mixture of **9a** and **9b.**



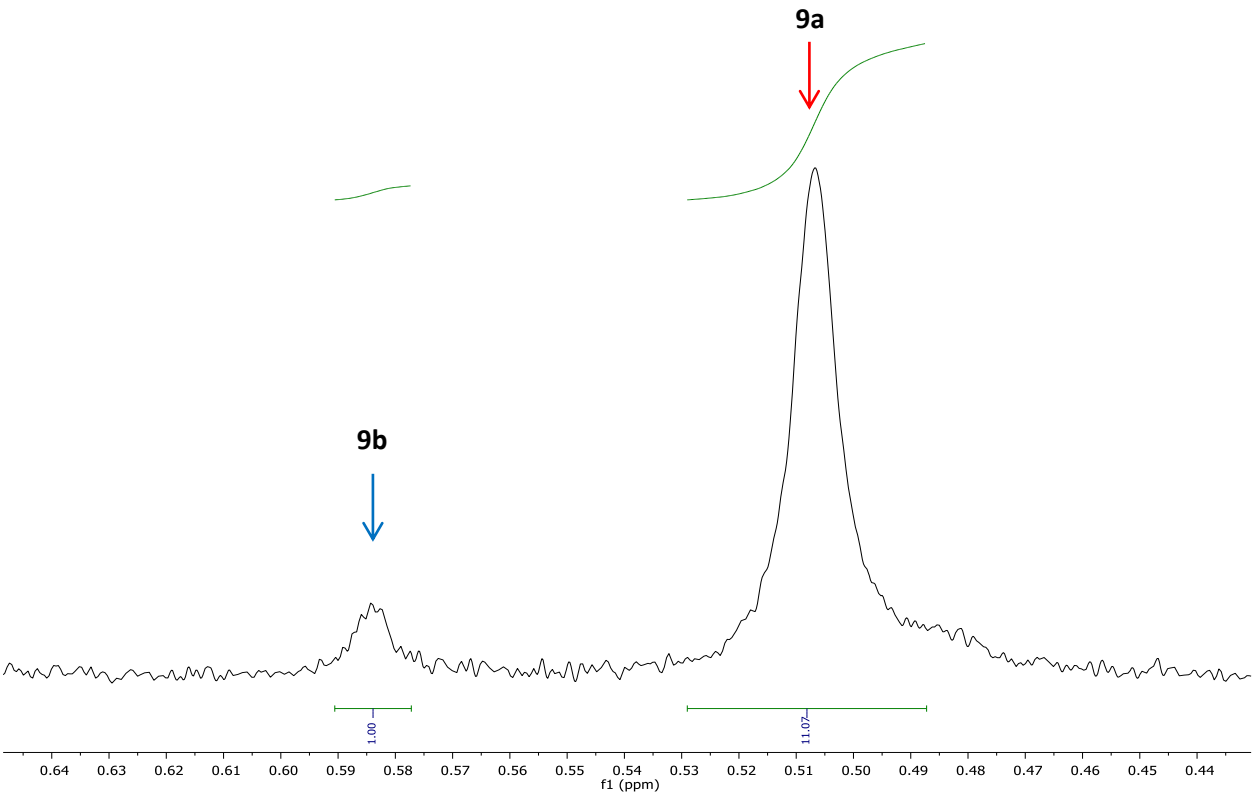
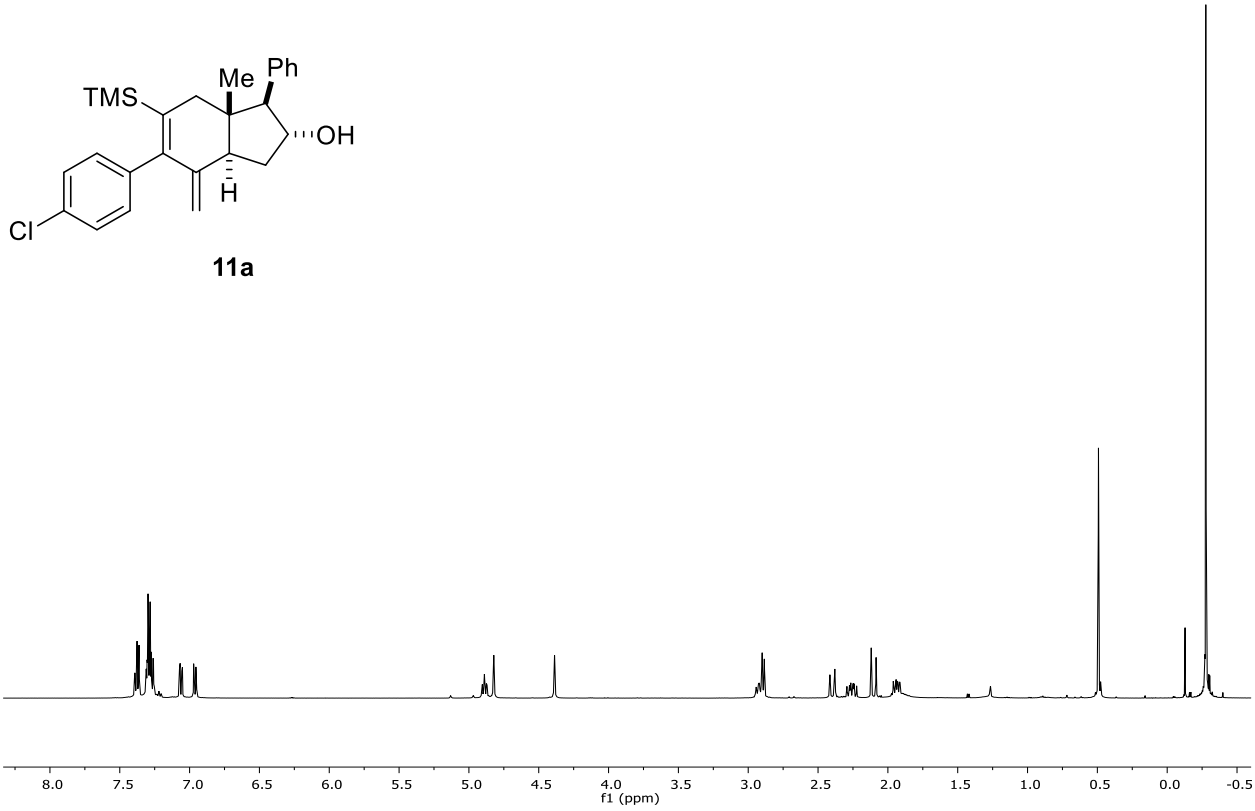


Figure S15: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **11a.**



11a

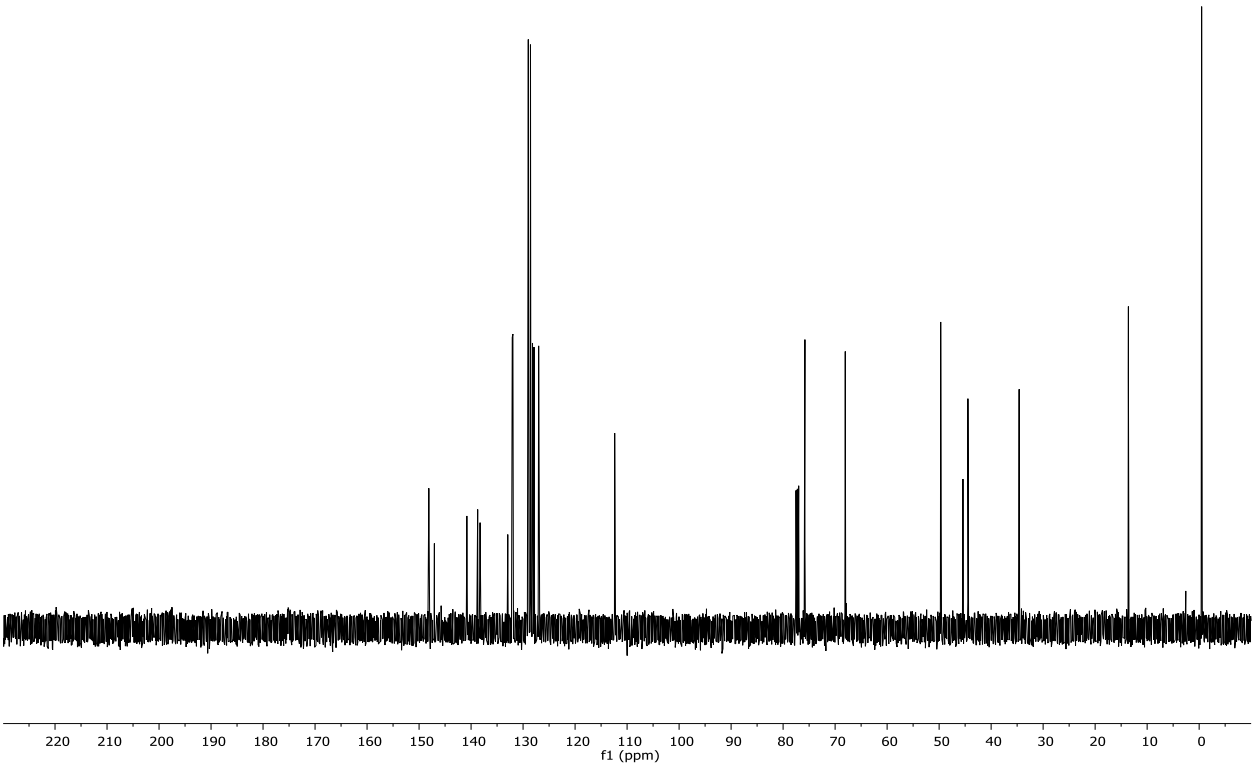


Figure S16: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **11b.**

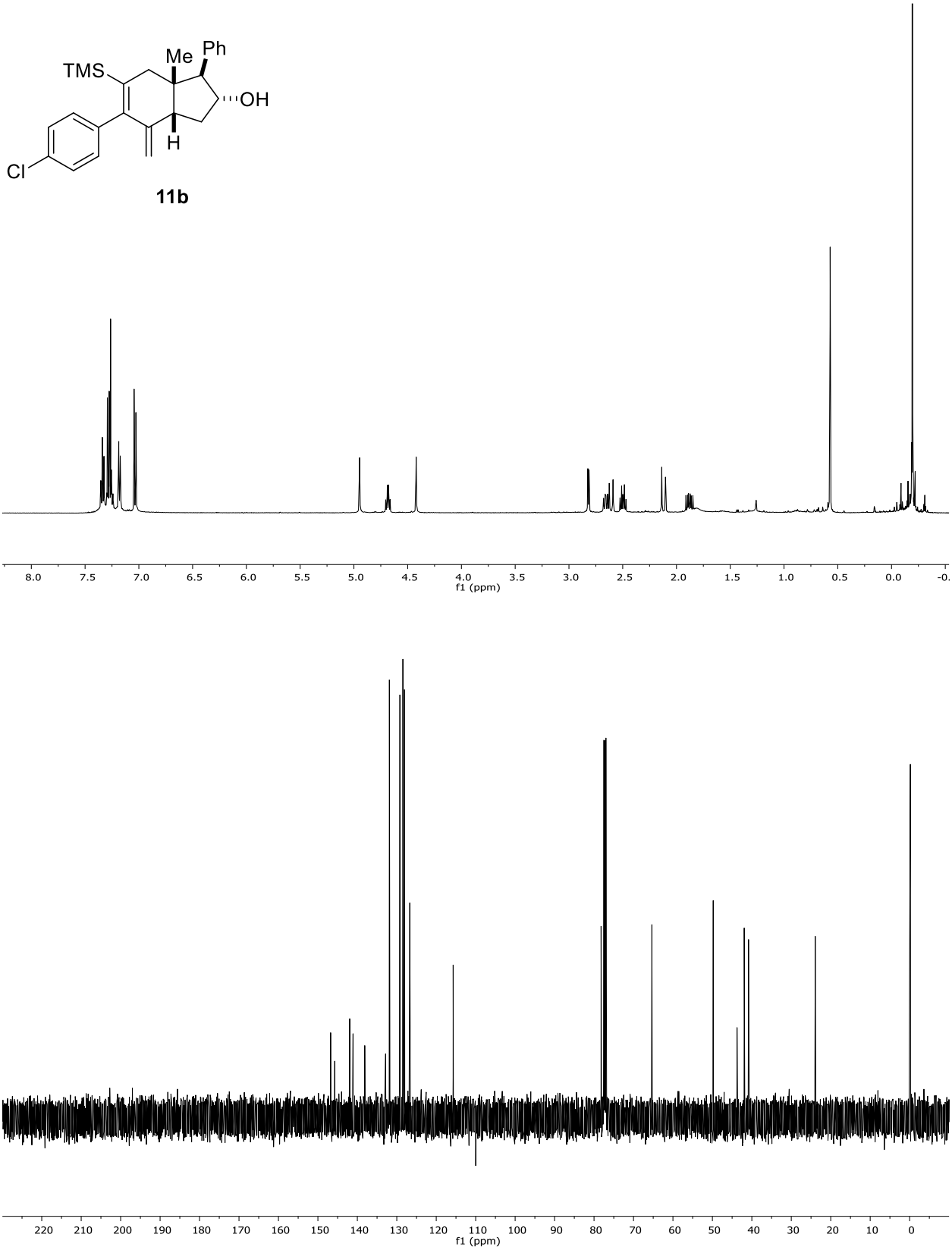


Figure S17: ^{1}H NMR (500 MHz, $CDCl_3$) of the crude mixture of **11a** and **11b.**

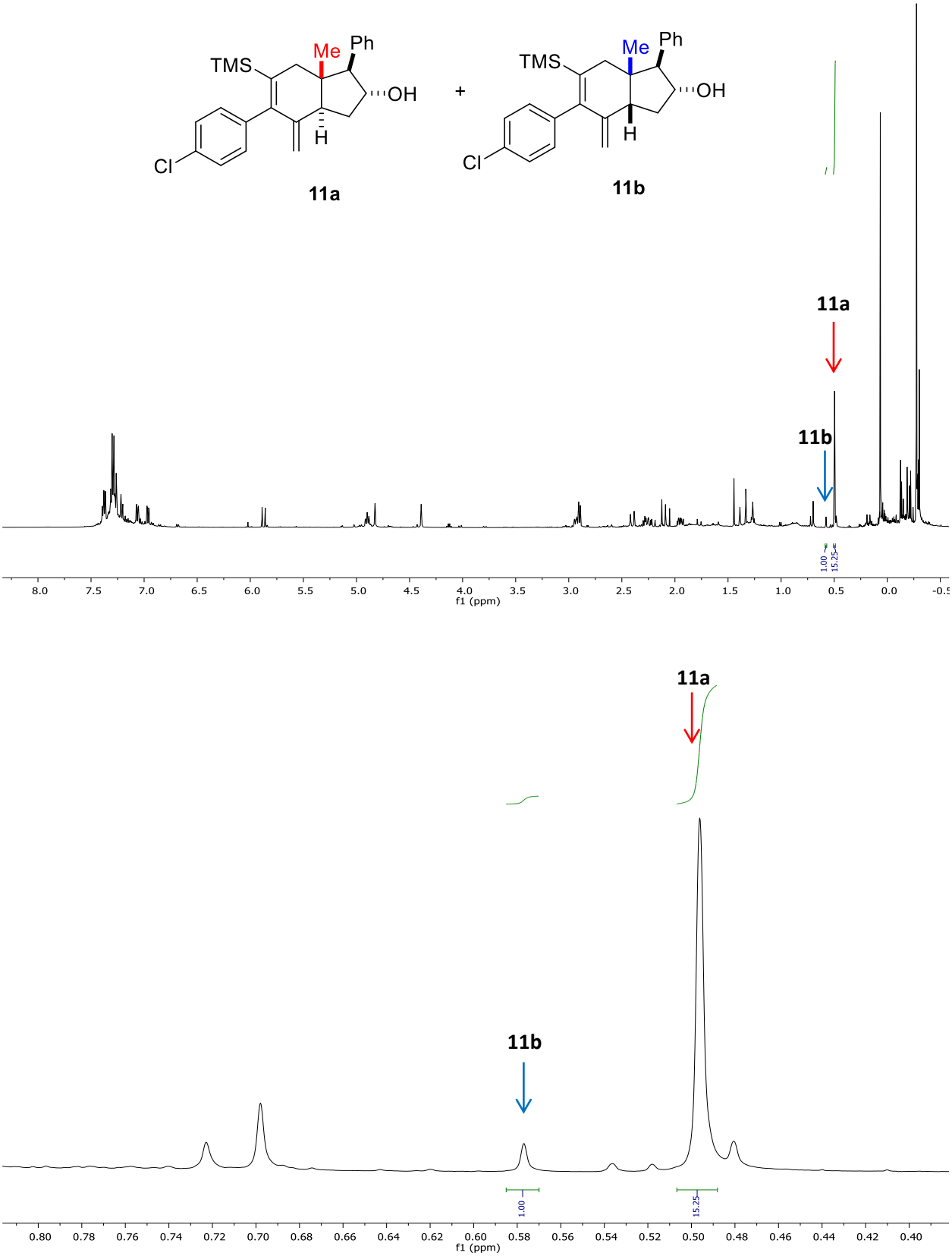
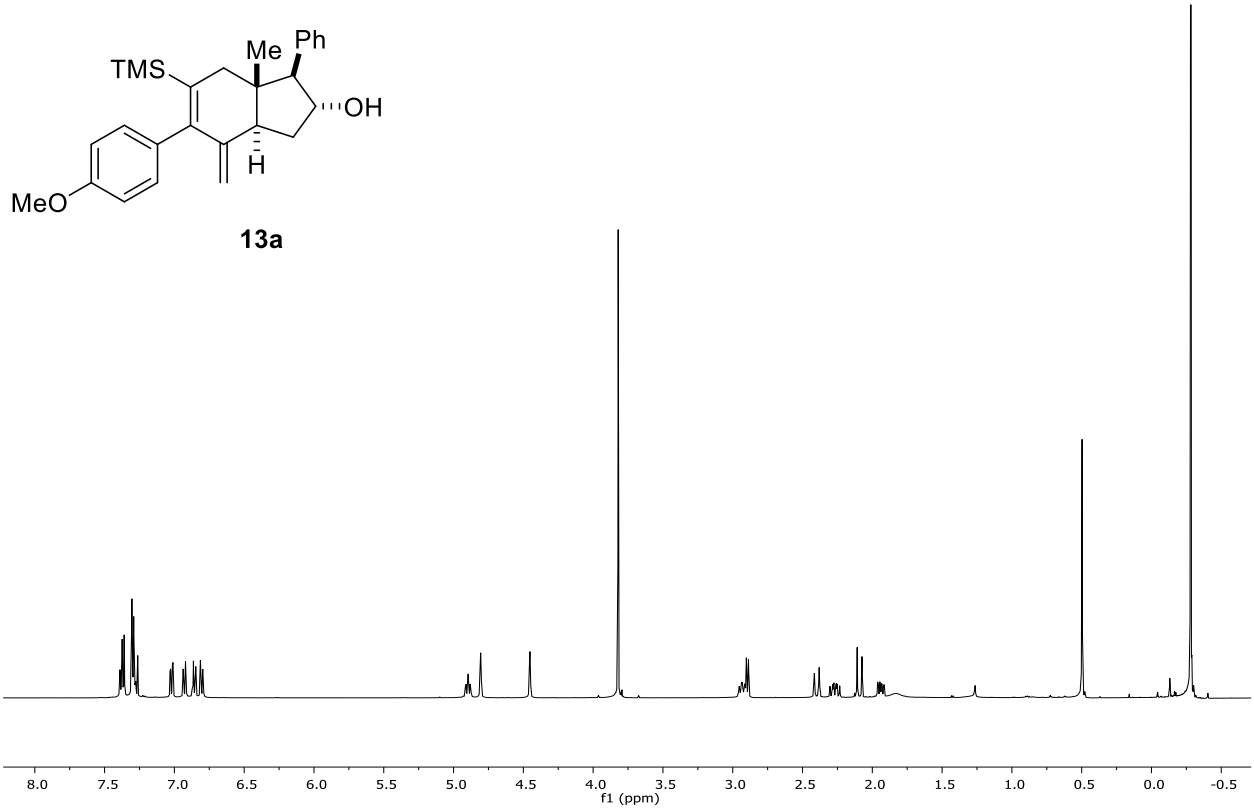


Figure S18: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **13a.**



13a

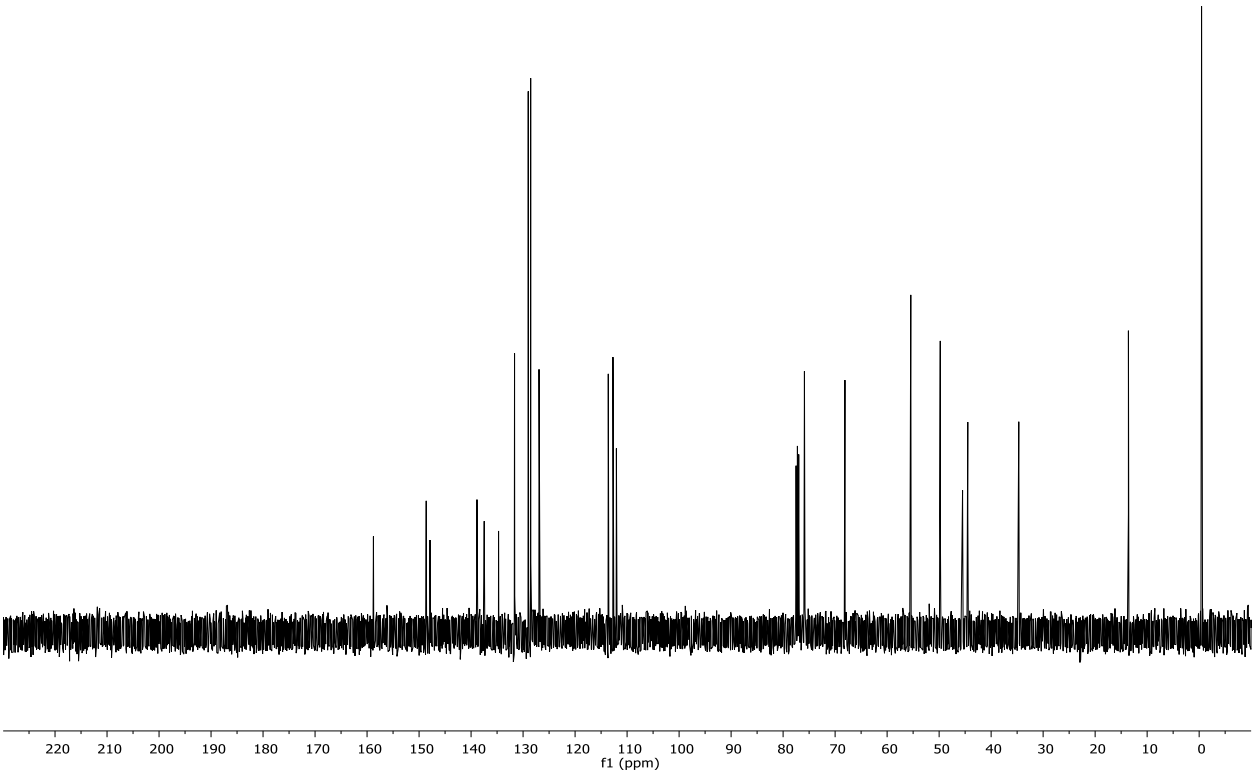


Figure S19: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **13b.**

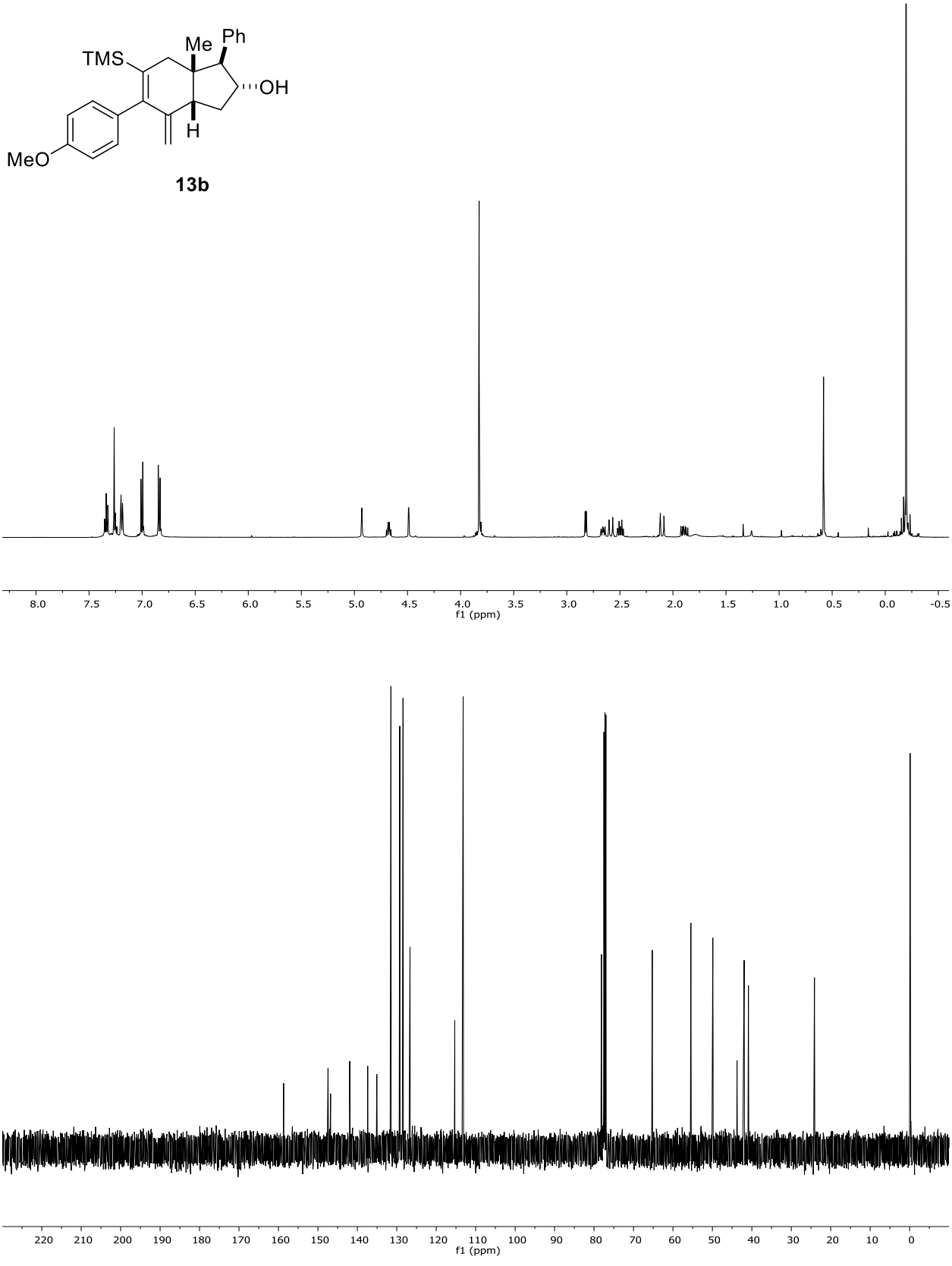
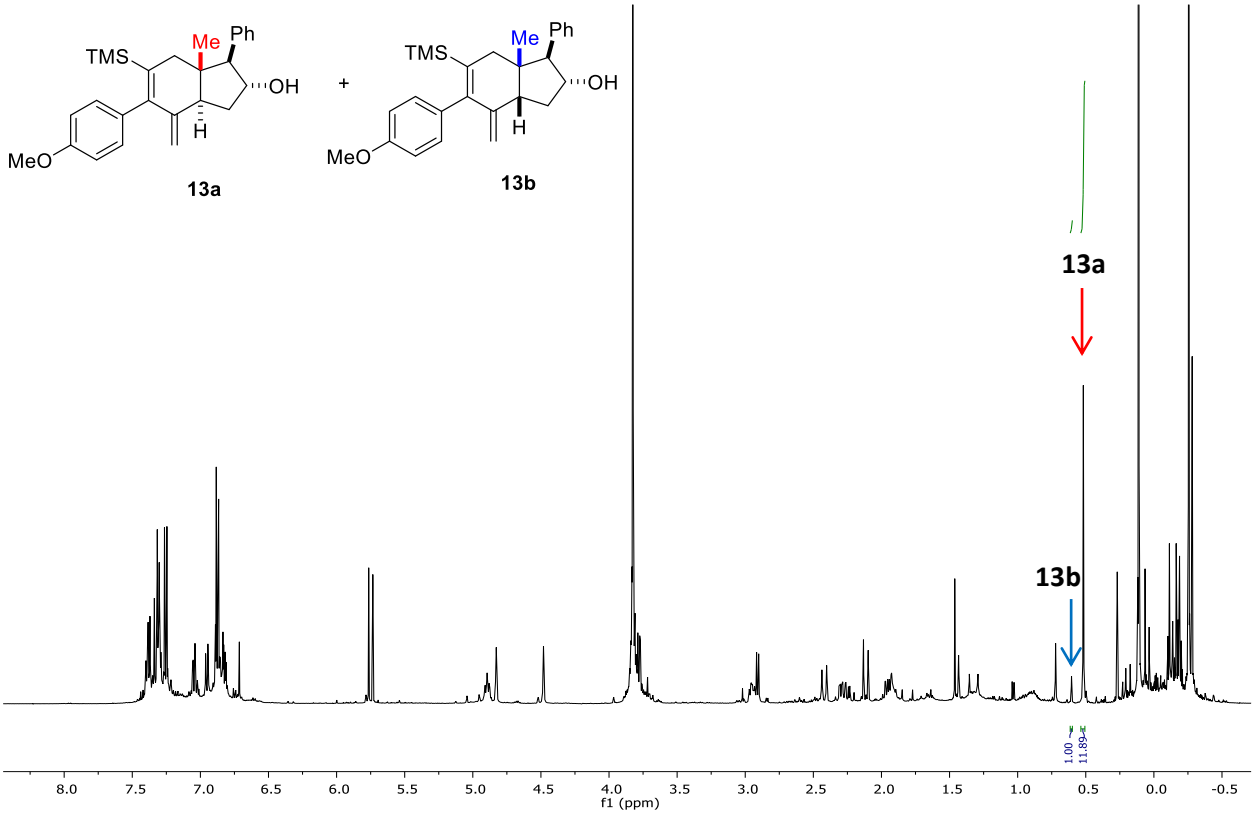


Figure S20: ^{1}H NMR (500 MHz, $CDCl_3$) of the crude mixture of **13a** and **13b.**



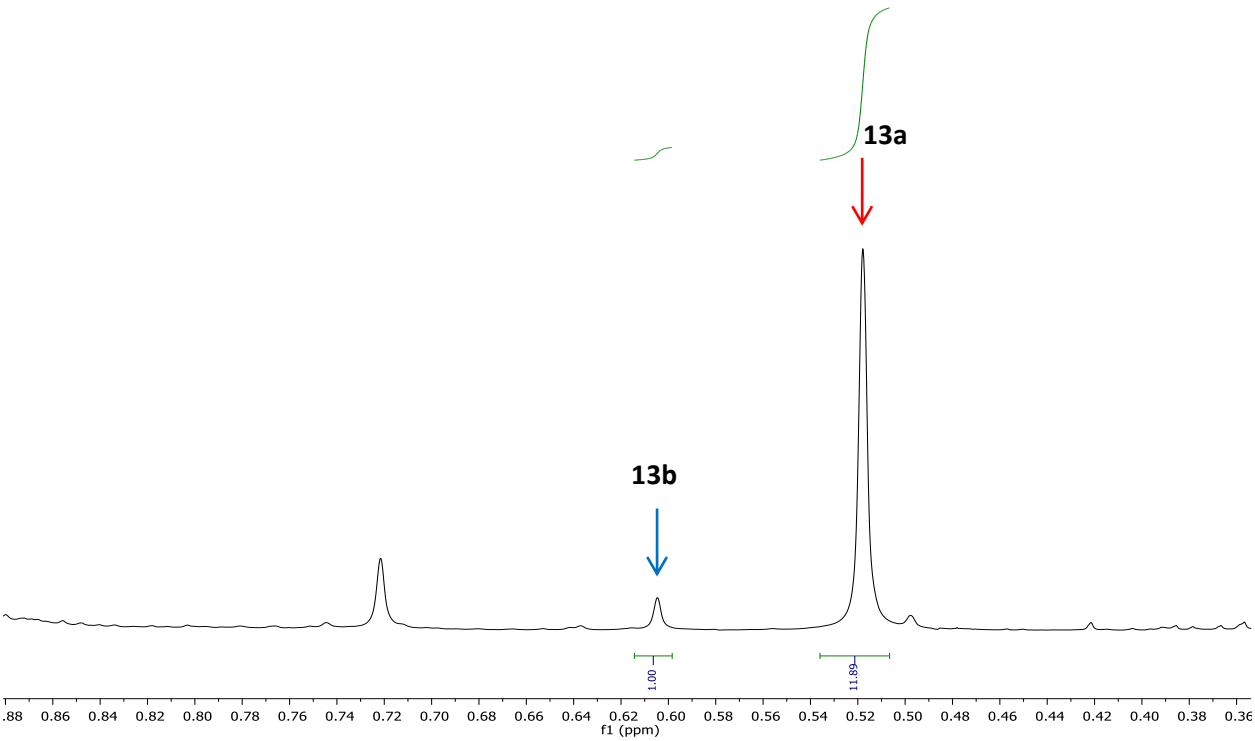
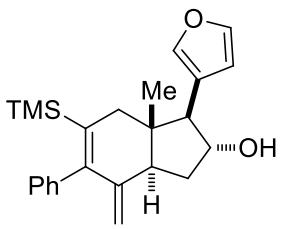


Figure S21: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **15a.**



15a

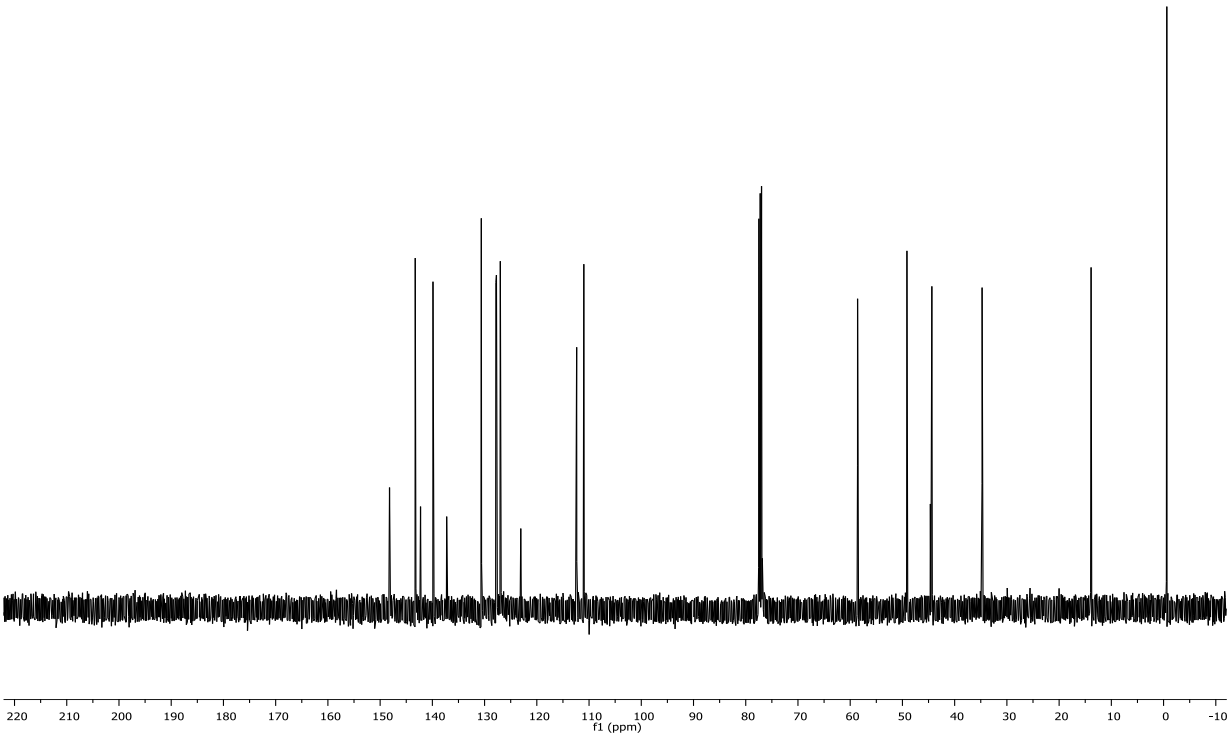
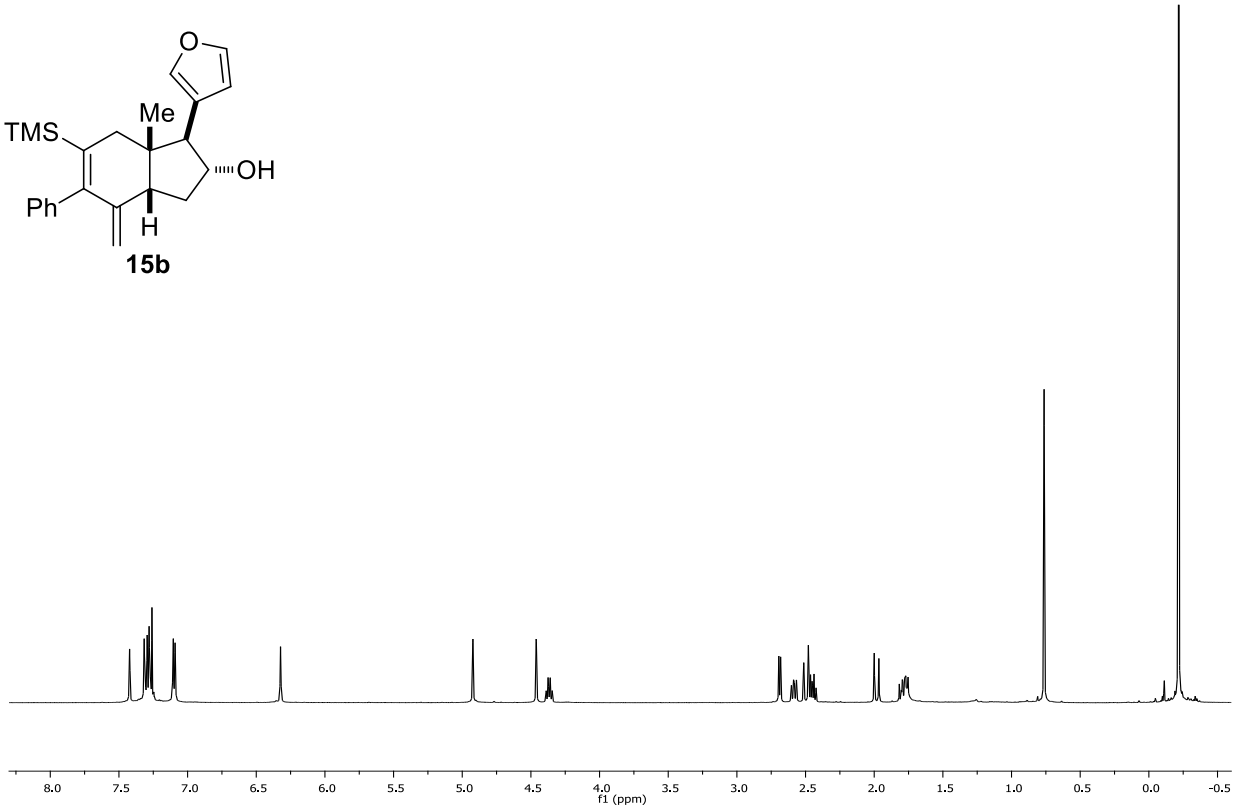


Figure S22: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **15b.**



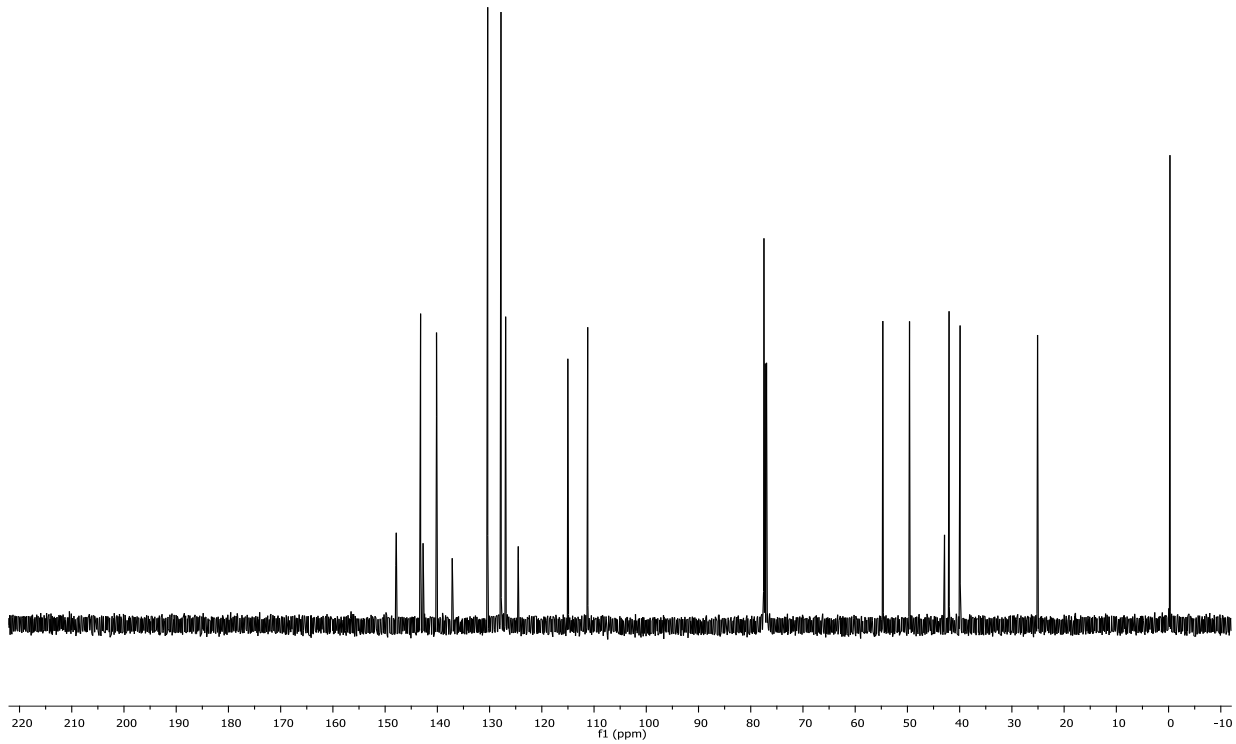


Figure S23: ^{1}H NMR (500 MHz, $CDCl_3$) of the crude mixture of **15a** and **15b.**

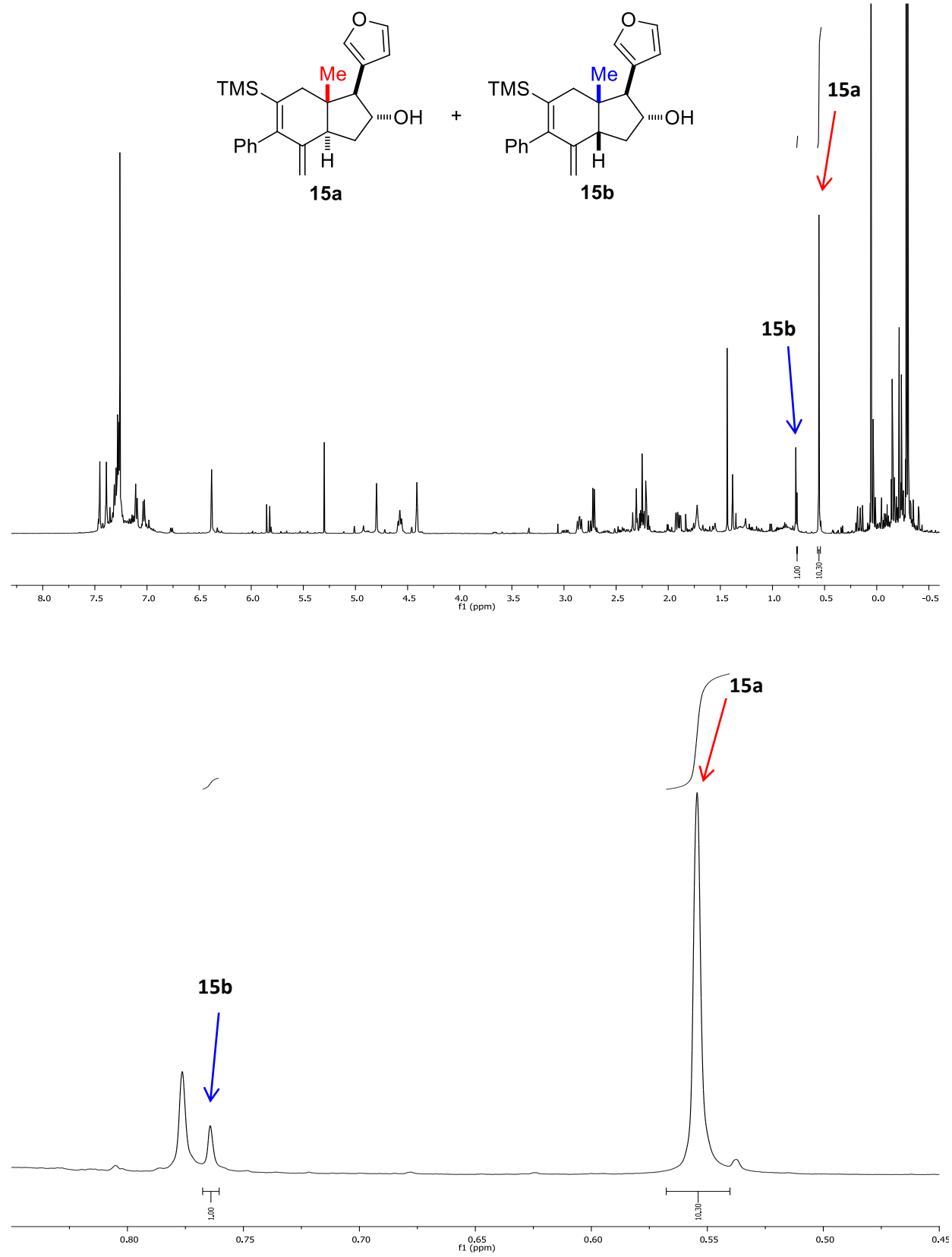
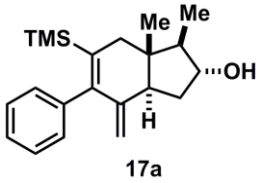


***Figure S24*:** ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **17a**.



17a

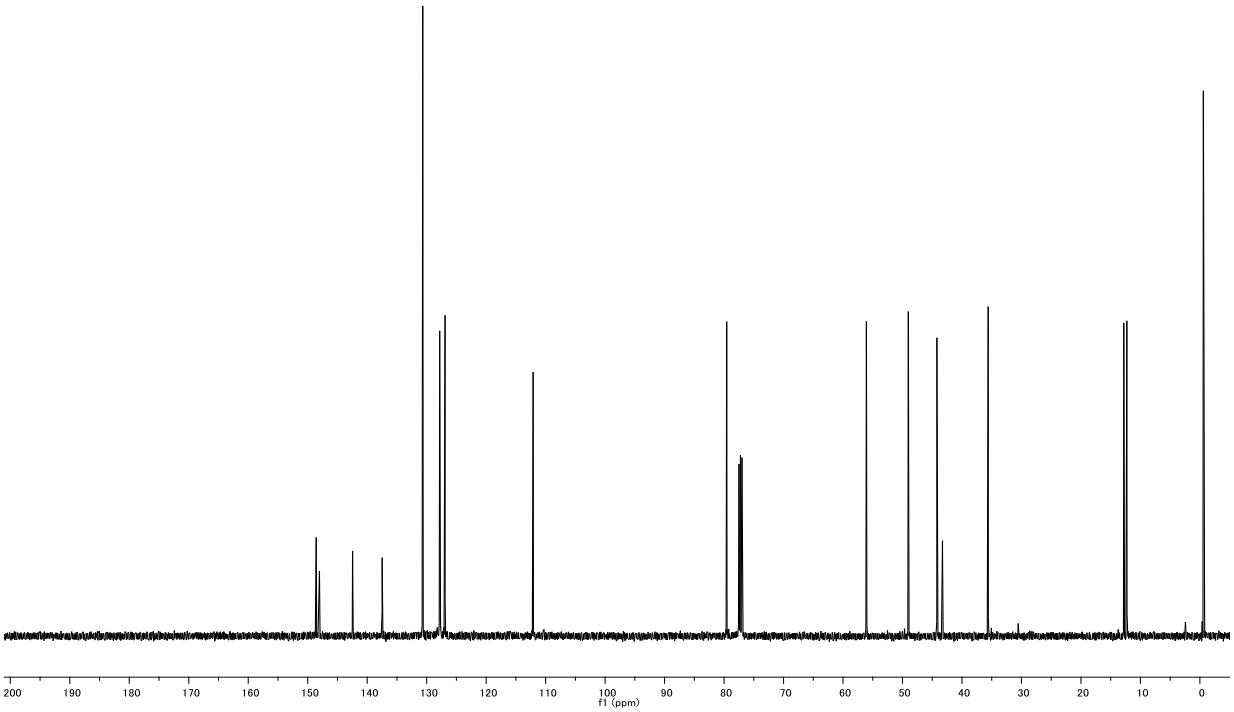
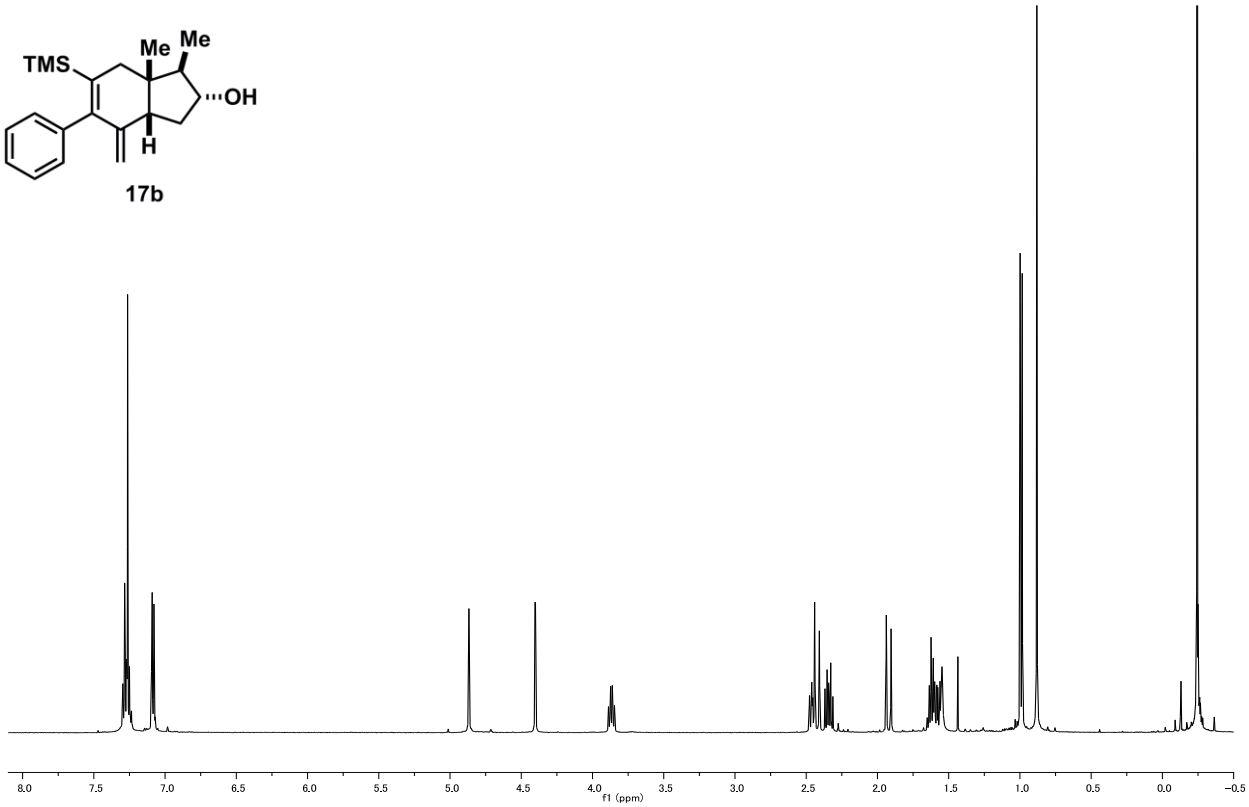


***Figure S25*:** ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **17b**.



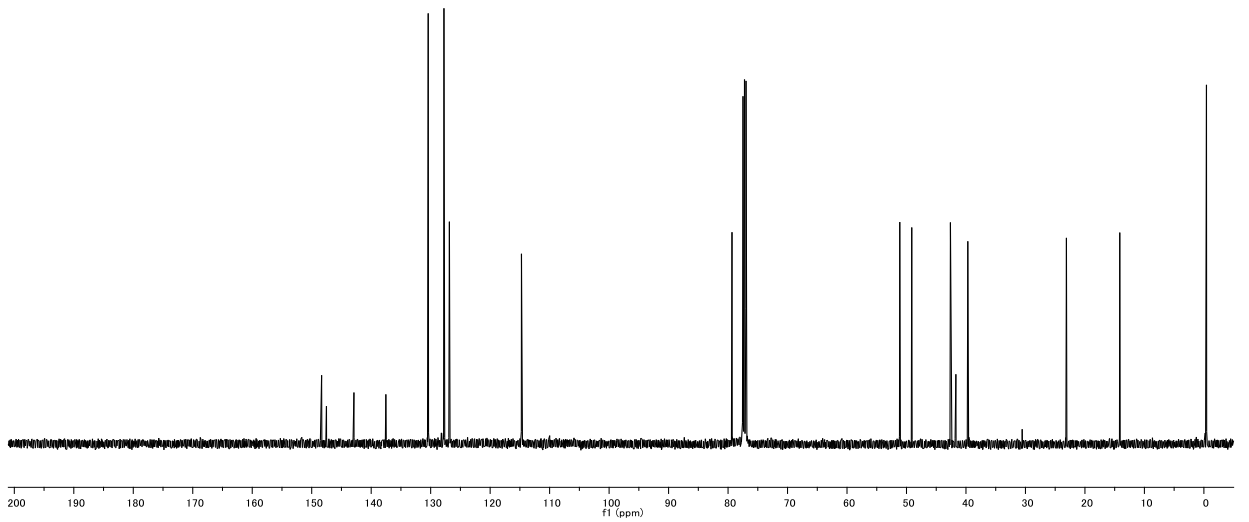
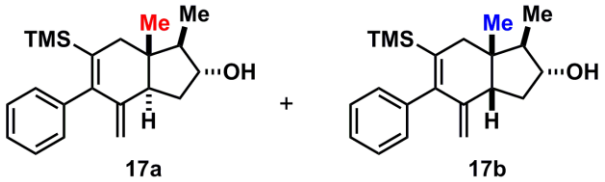


Figure S26: ^{1}H NMR (500 MHz, $CDCl_3$) of the crude mixture of **17a** and **17b.**



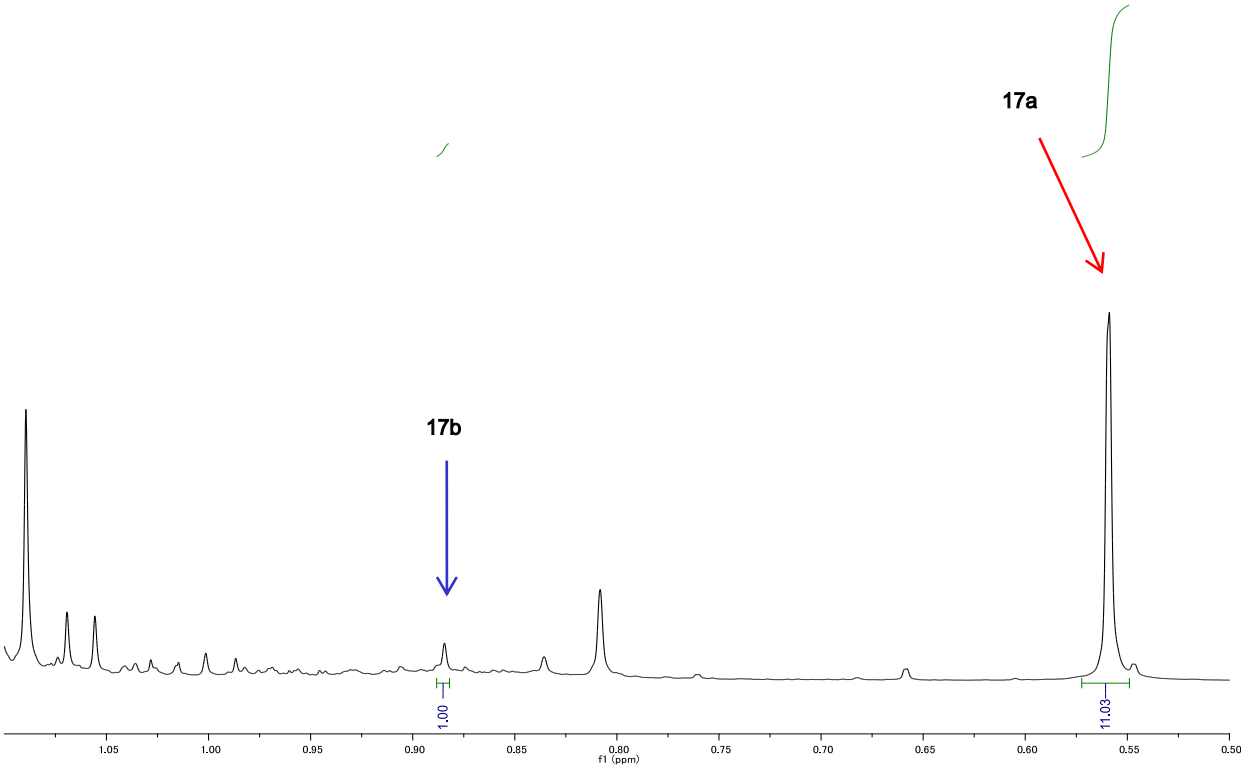
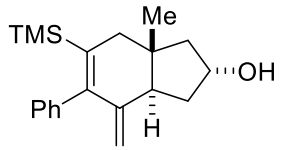


***Figure S27*:** ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **19a**.



19a

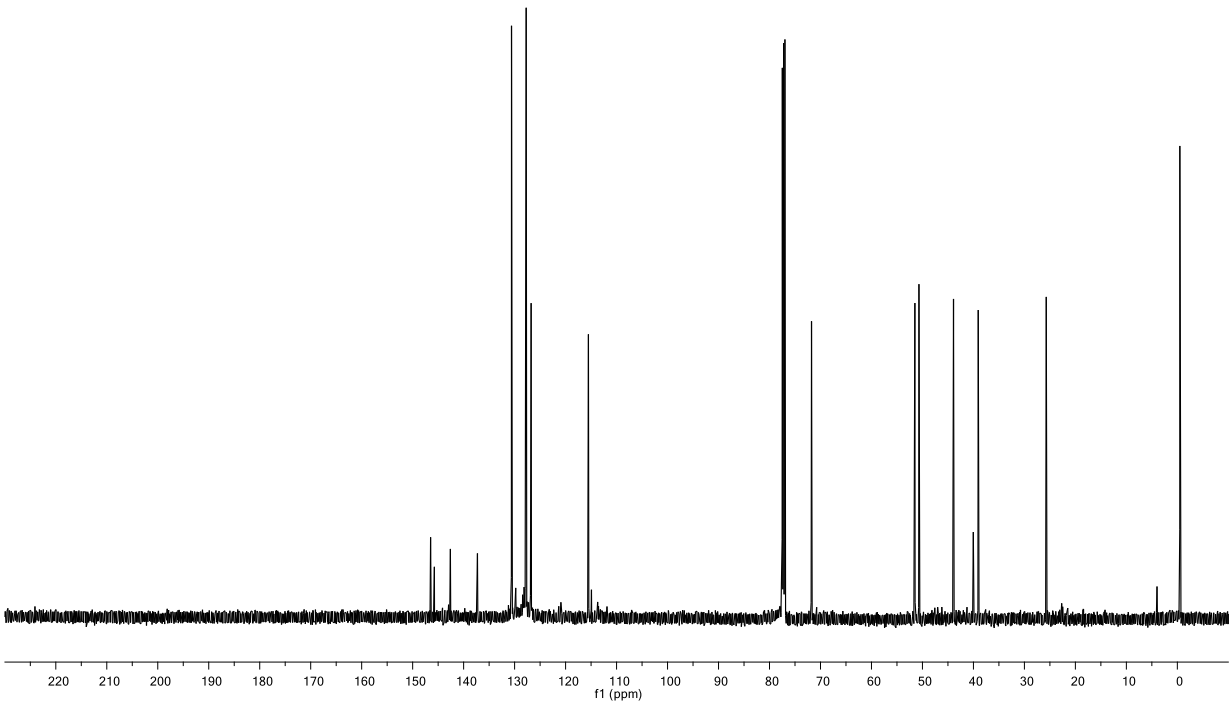
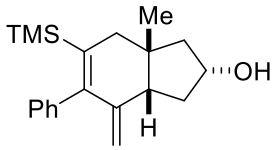


Figure S28: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **19b.**



19b

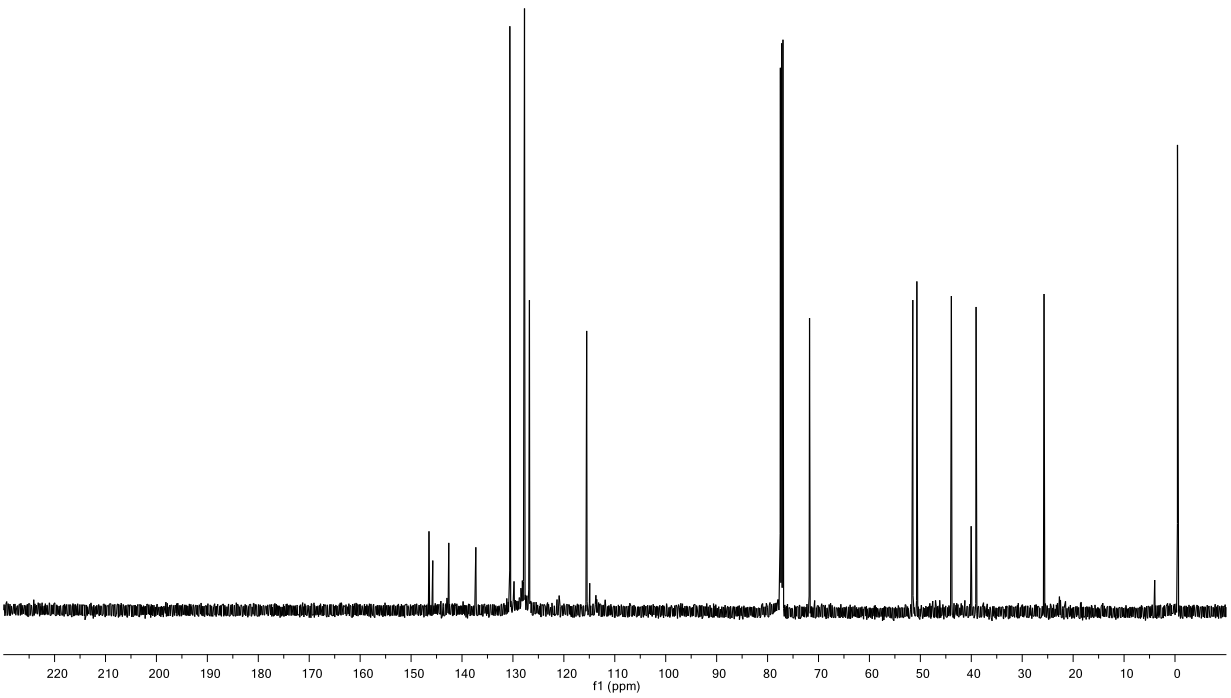
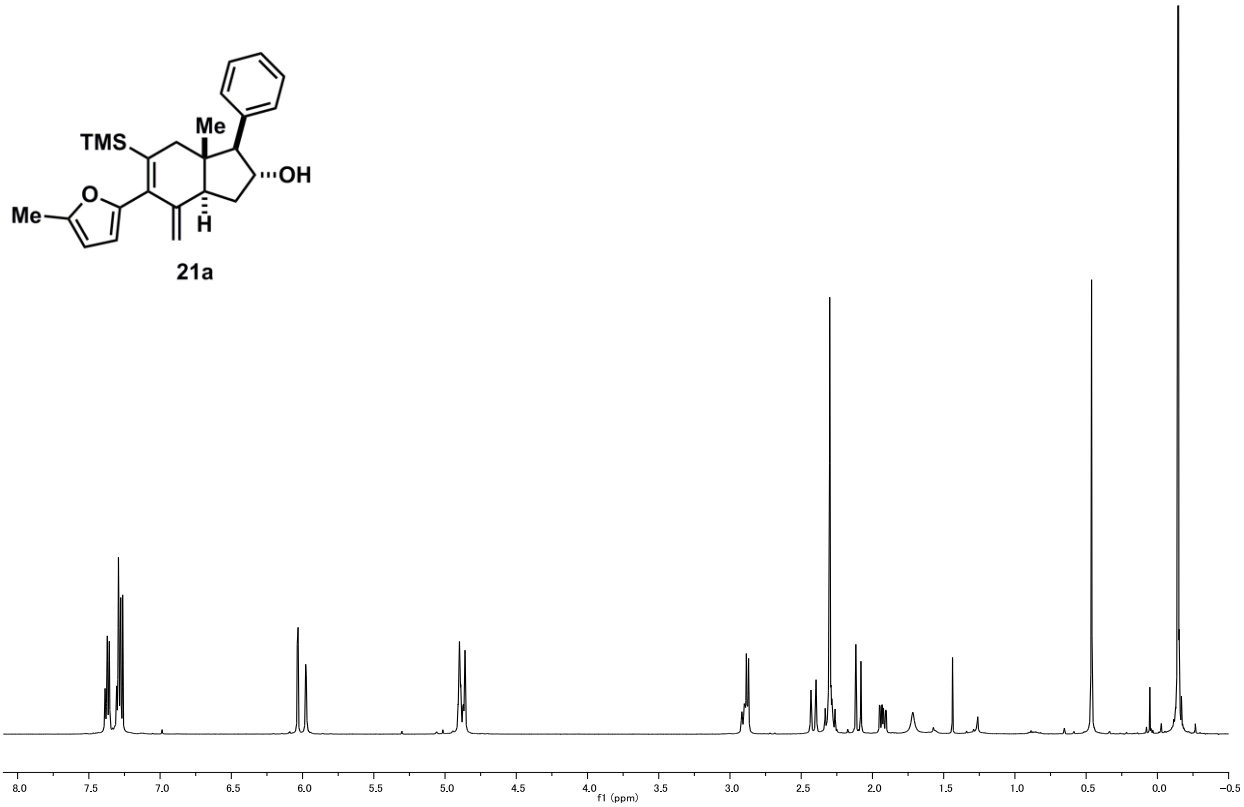


***Figure S29*:** ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **21a**.



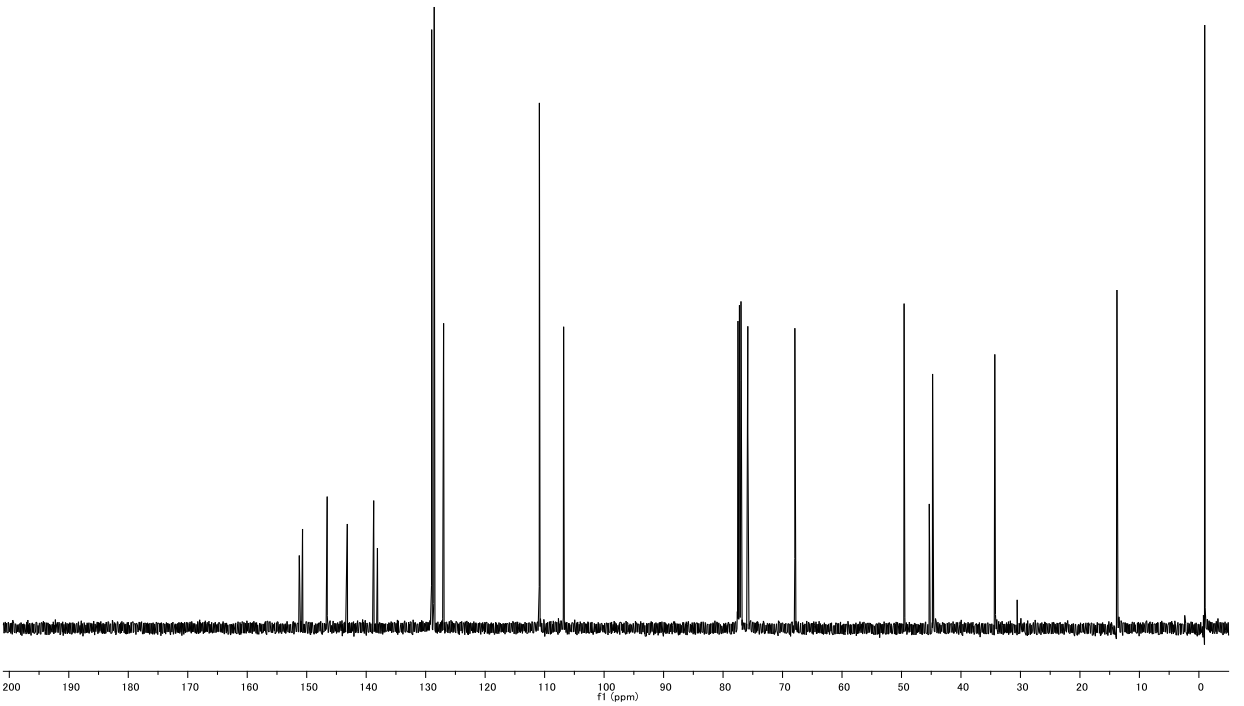
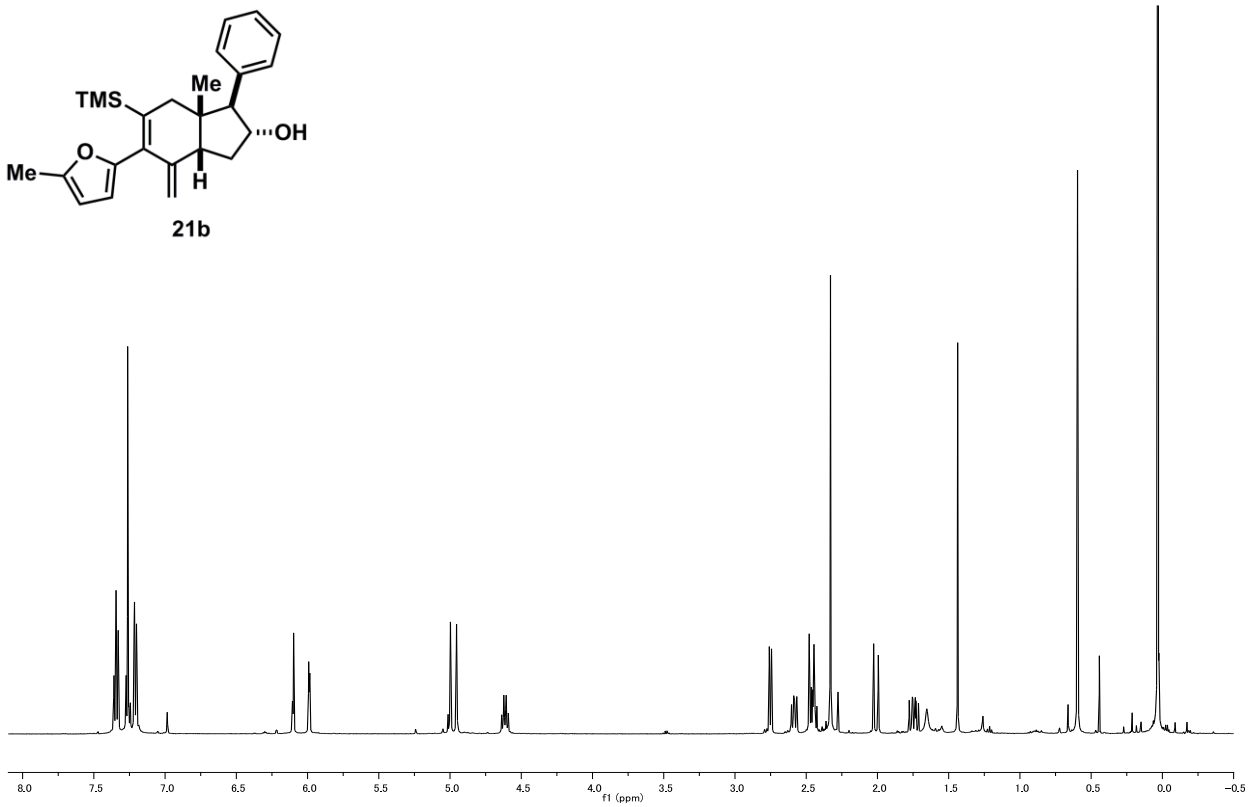


Figure S30: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **21b**.



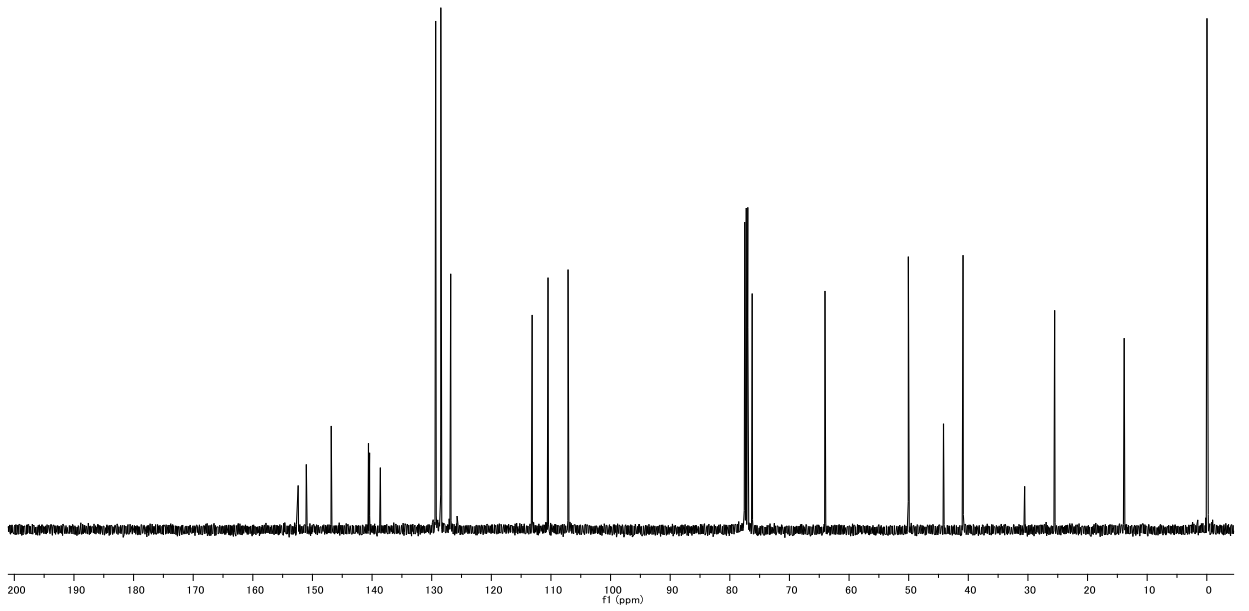
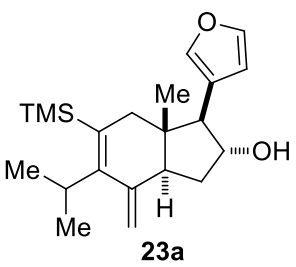


Figure S31: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **23a.**



23a

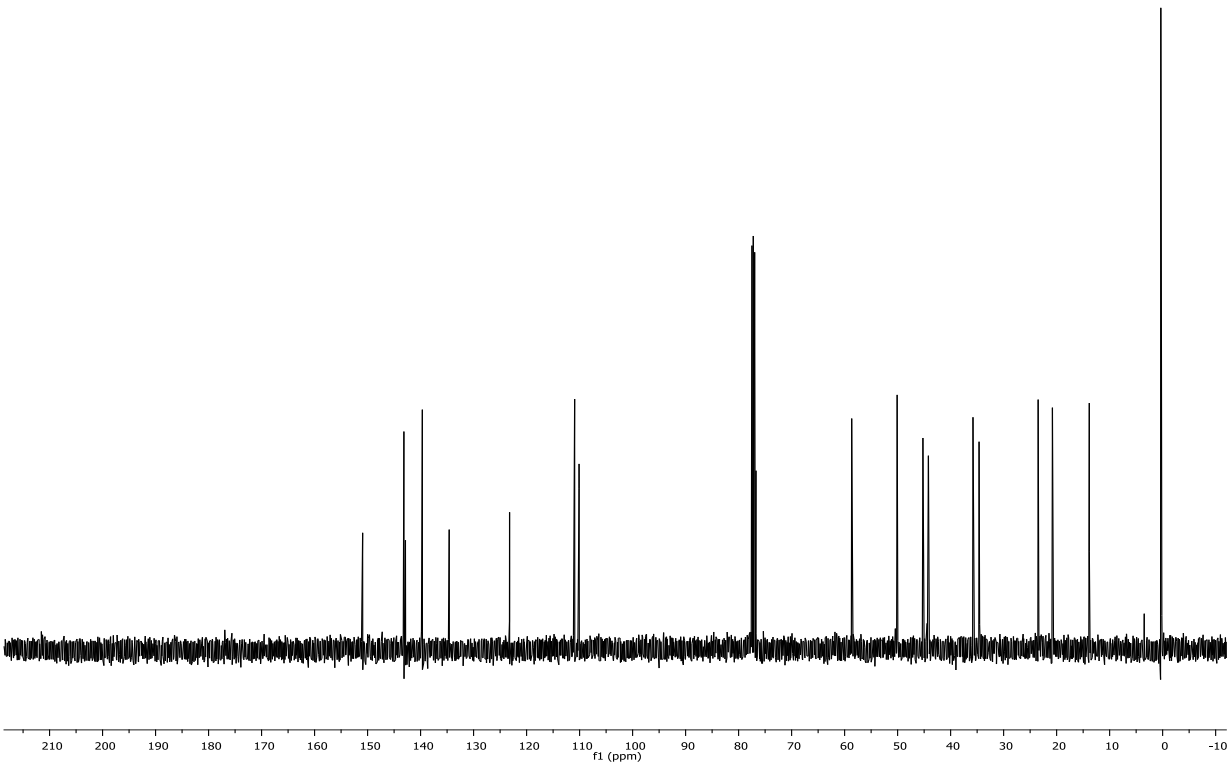


Figure S32: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **23b.**

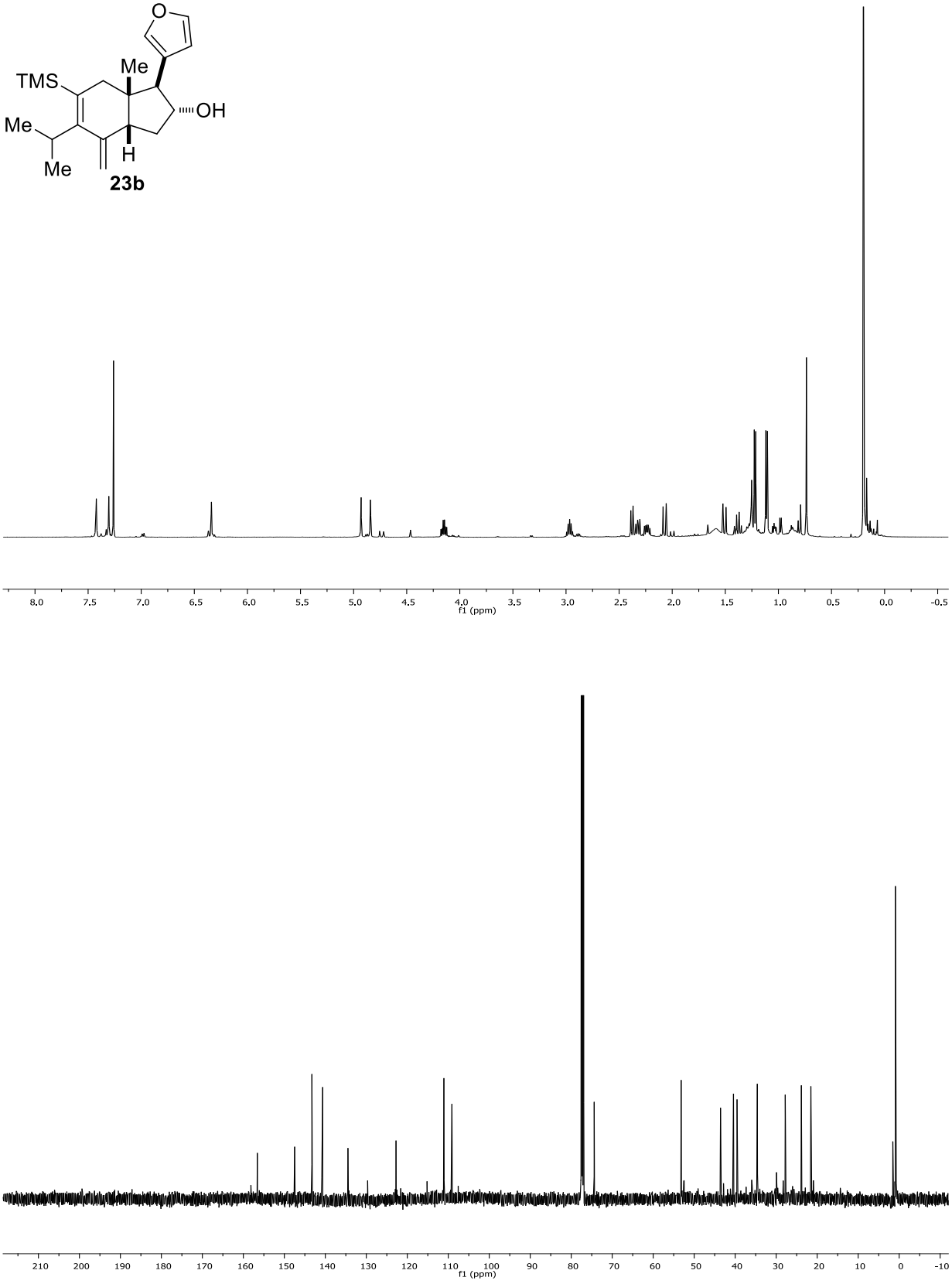
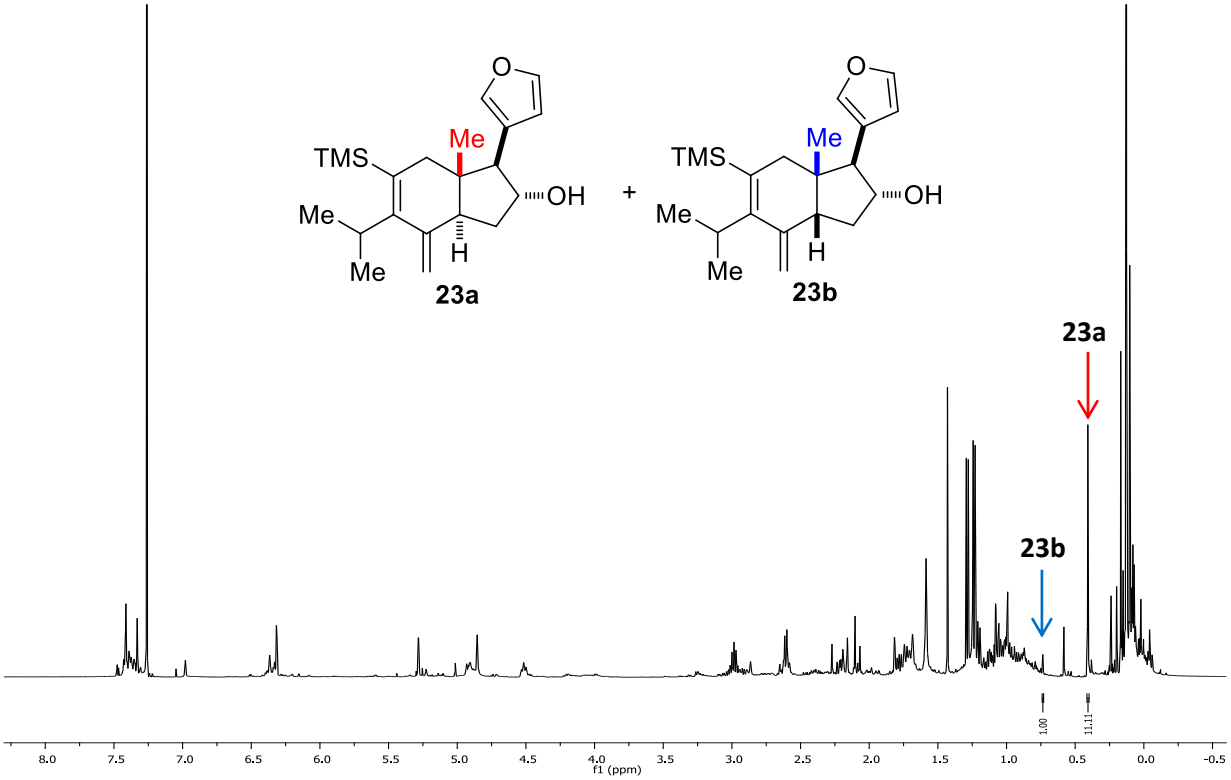


Figure S33: ^{1}H NMR (500 MHz, $CDCl_3$) of the crude mixture of **23a** and **23b.**



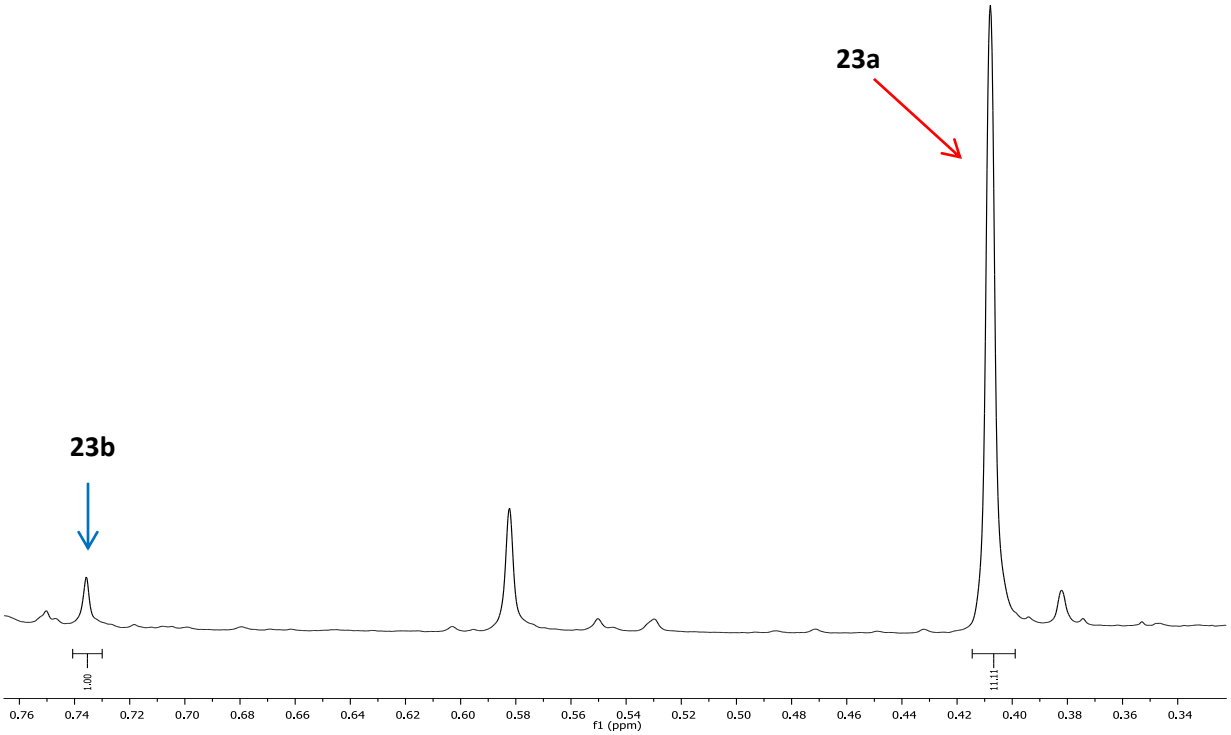
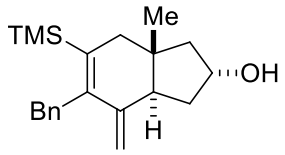


Figure S34: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **25a**.



25a

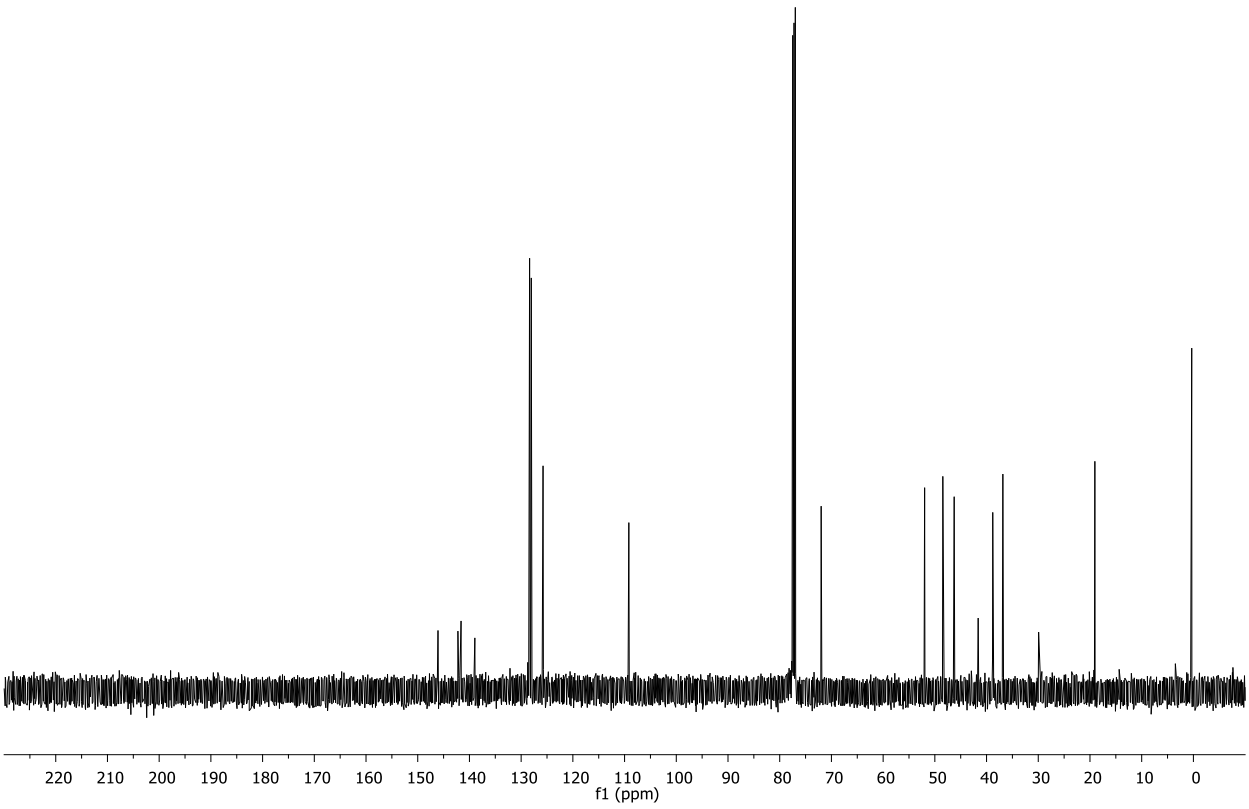
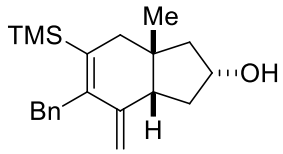


Figure S35: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **25b**.



25b

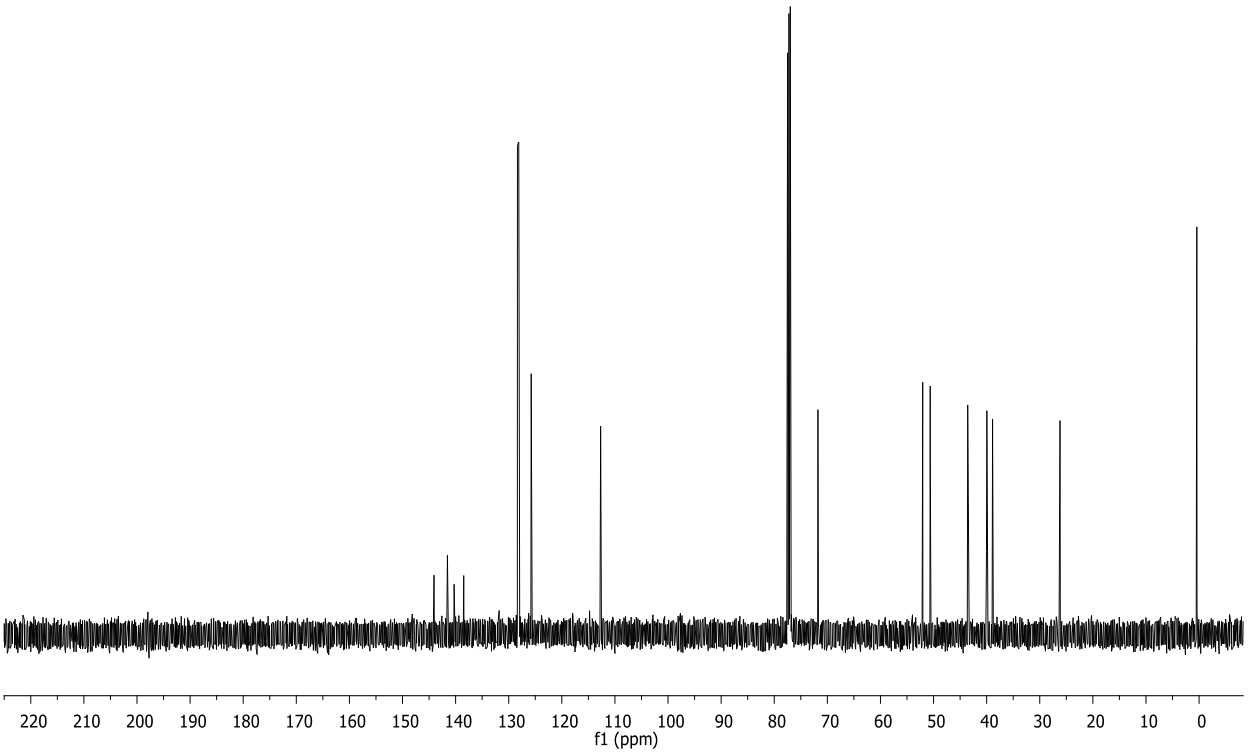
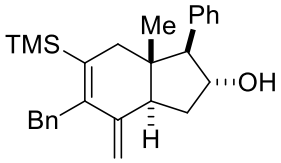


Figure S36: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **26a**.



26a

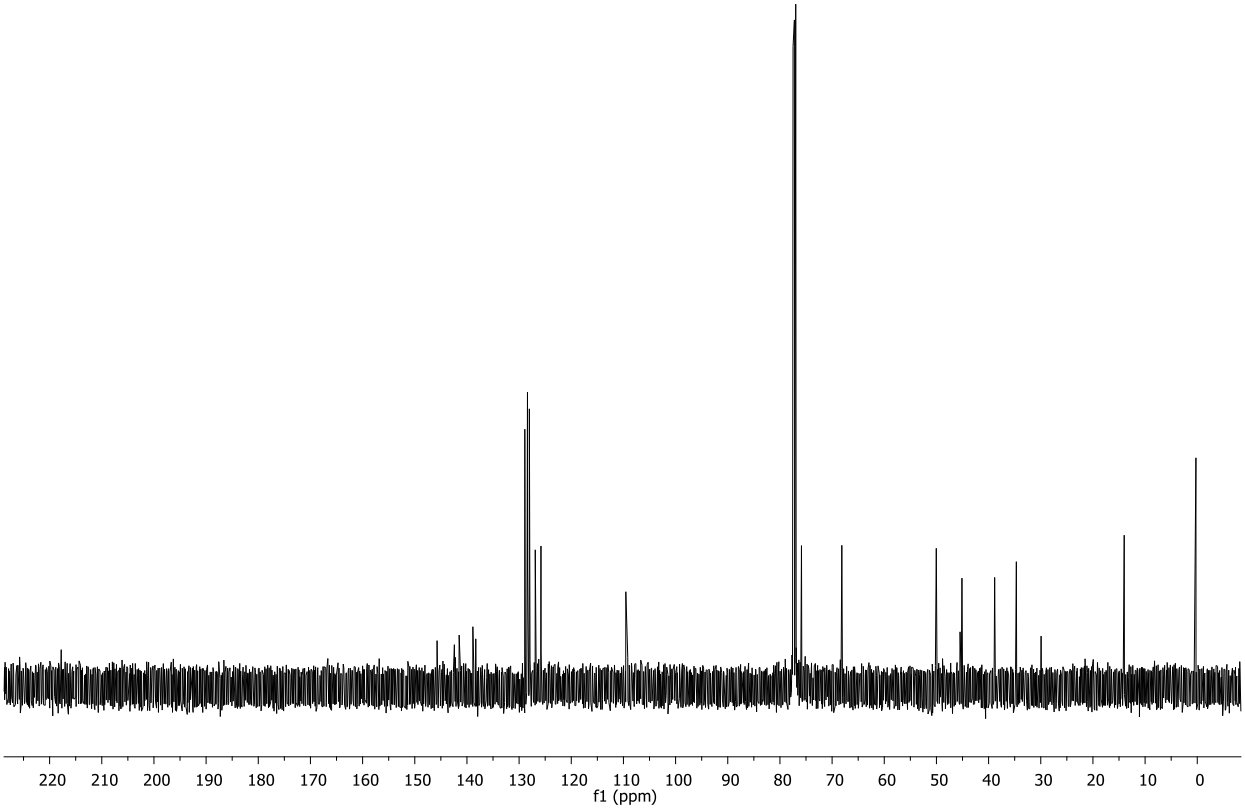
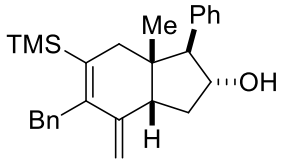


Figure S37: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **26b**.



26b

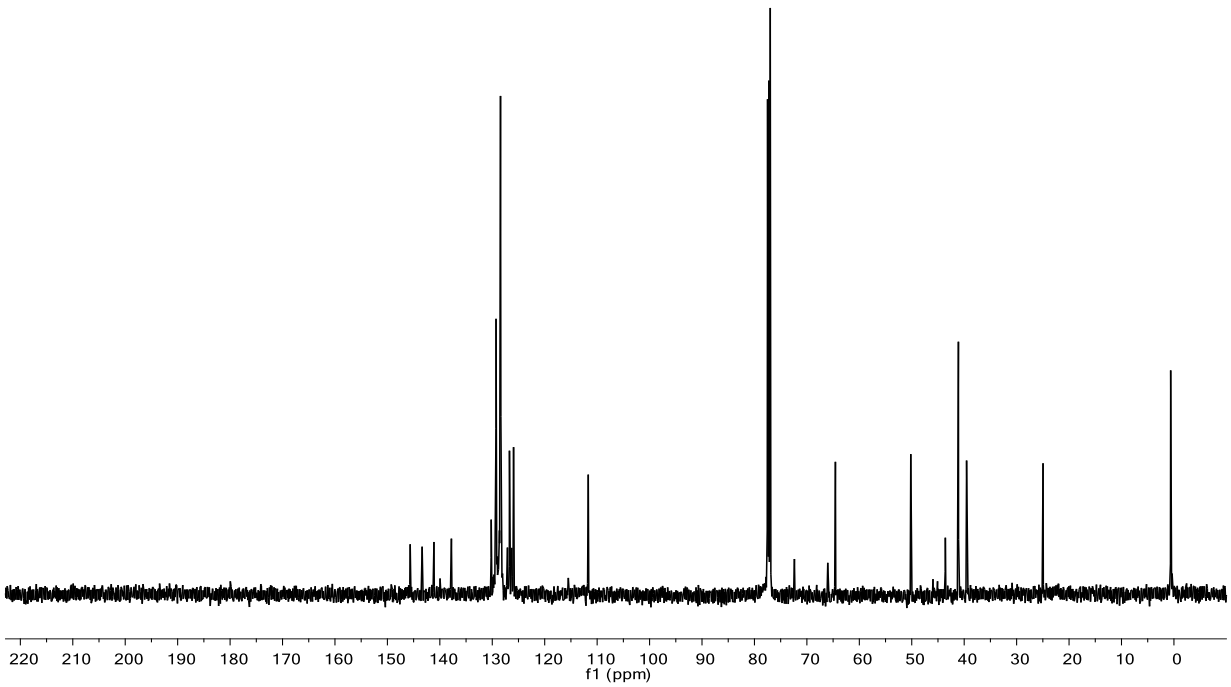


Figure S38: ^{1}H NMR (500 MHz, $CDCl_3$) of the crude mixture of **26a** and **26b**.

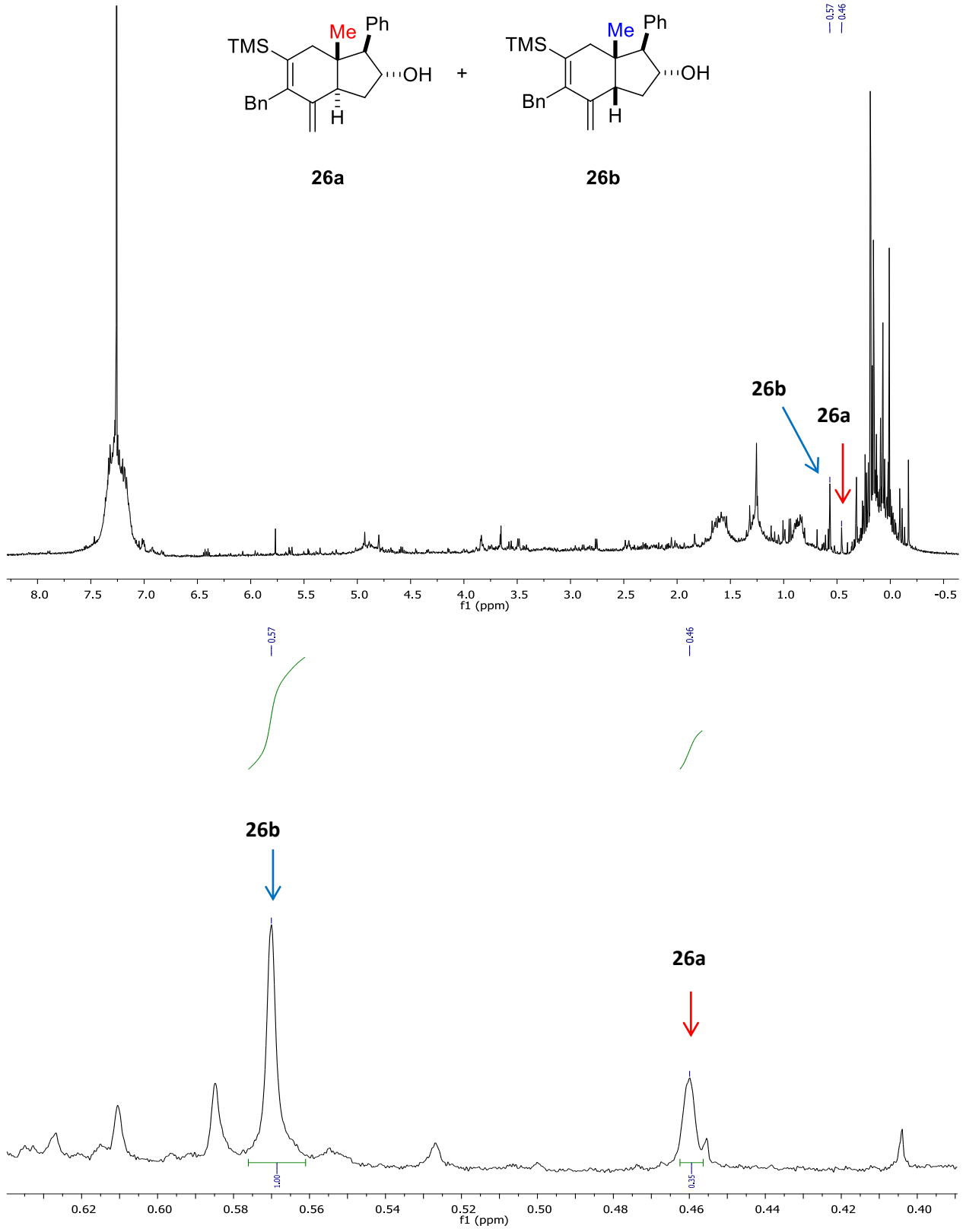
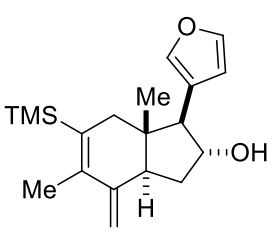


Figure S39: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **28a.**



28a

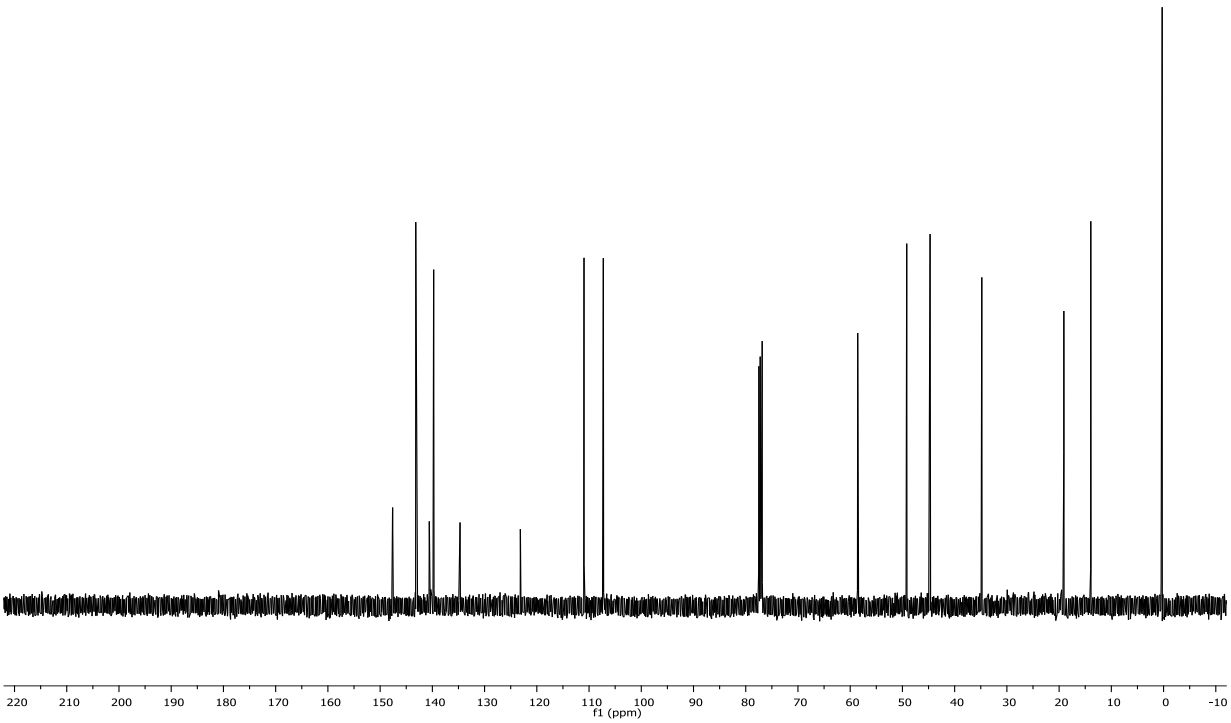


Figure S40: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **28b.**

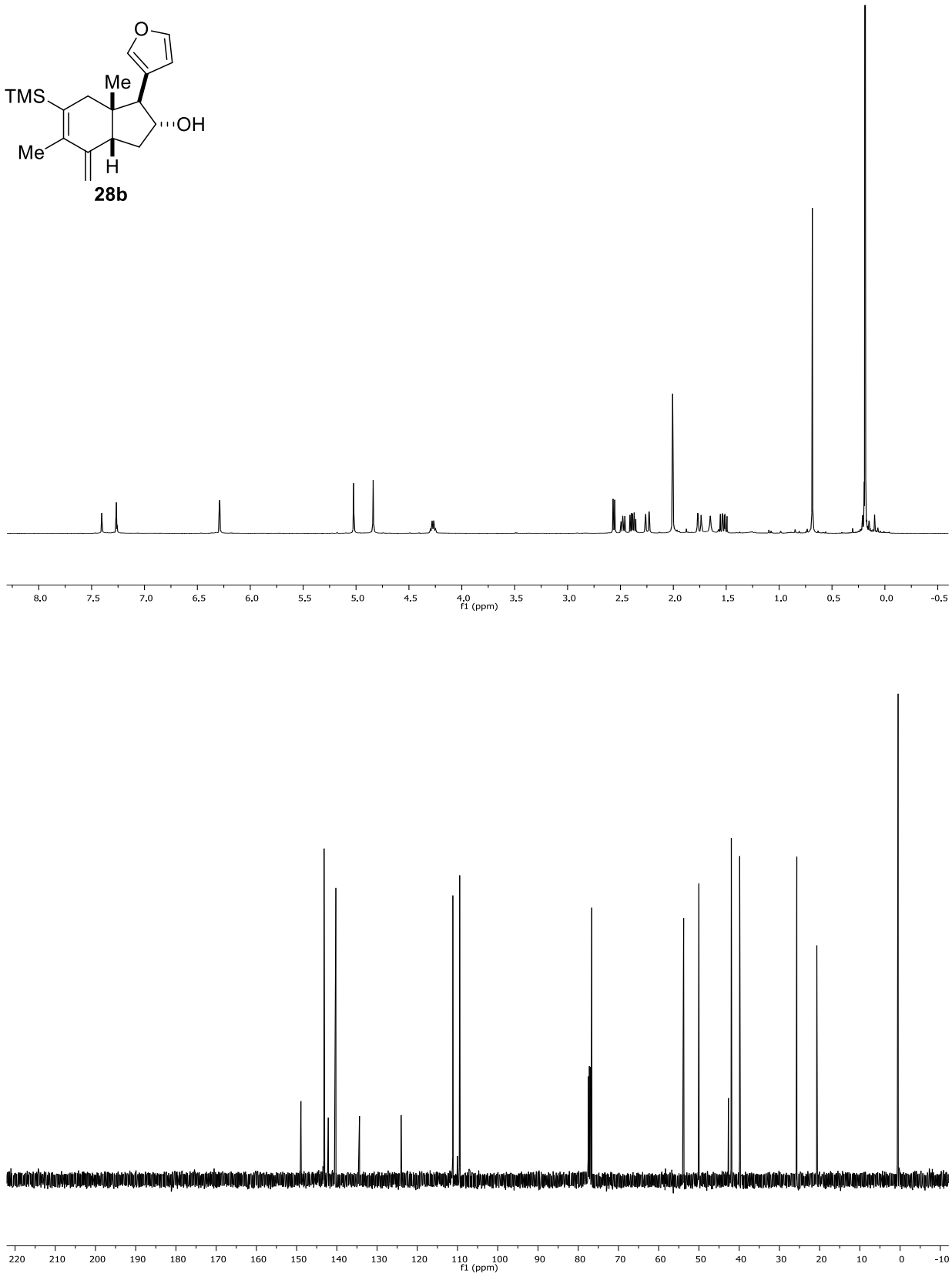


Figure S41: ^{1}H NMR (500 MHz, $CDCl_3$) of the crude mixture of **28a** and **28b.**

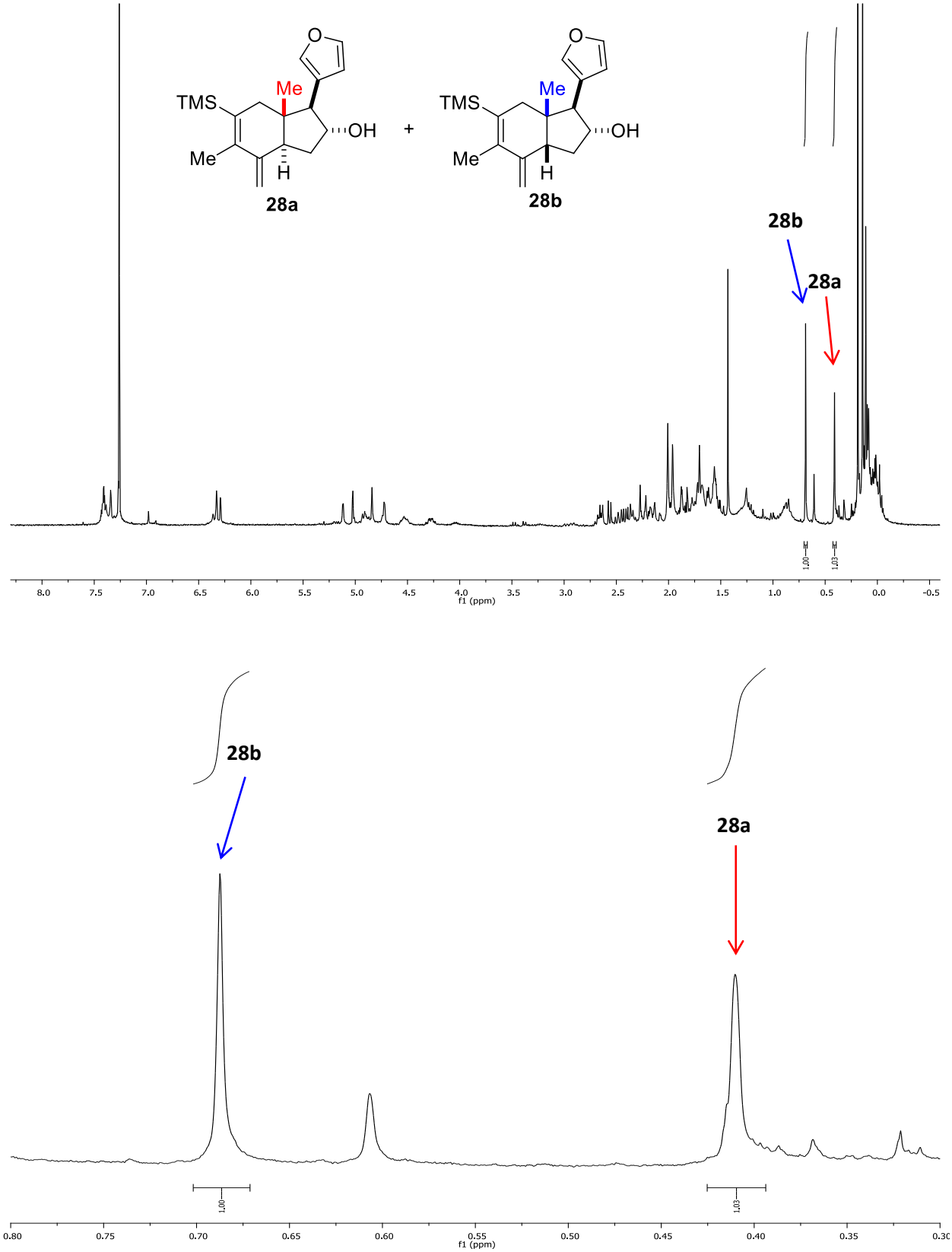
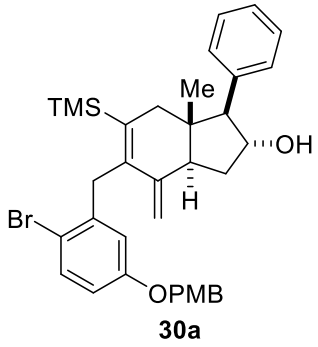


Figure S42: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **30a**.



30a

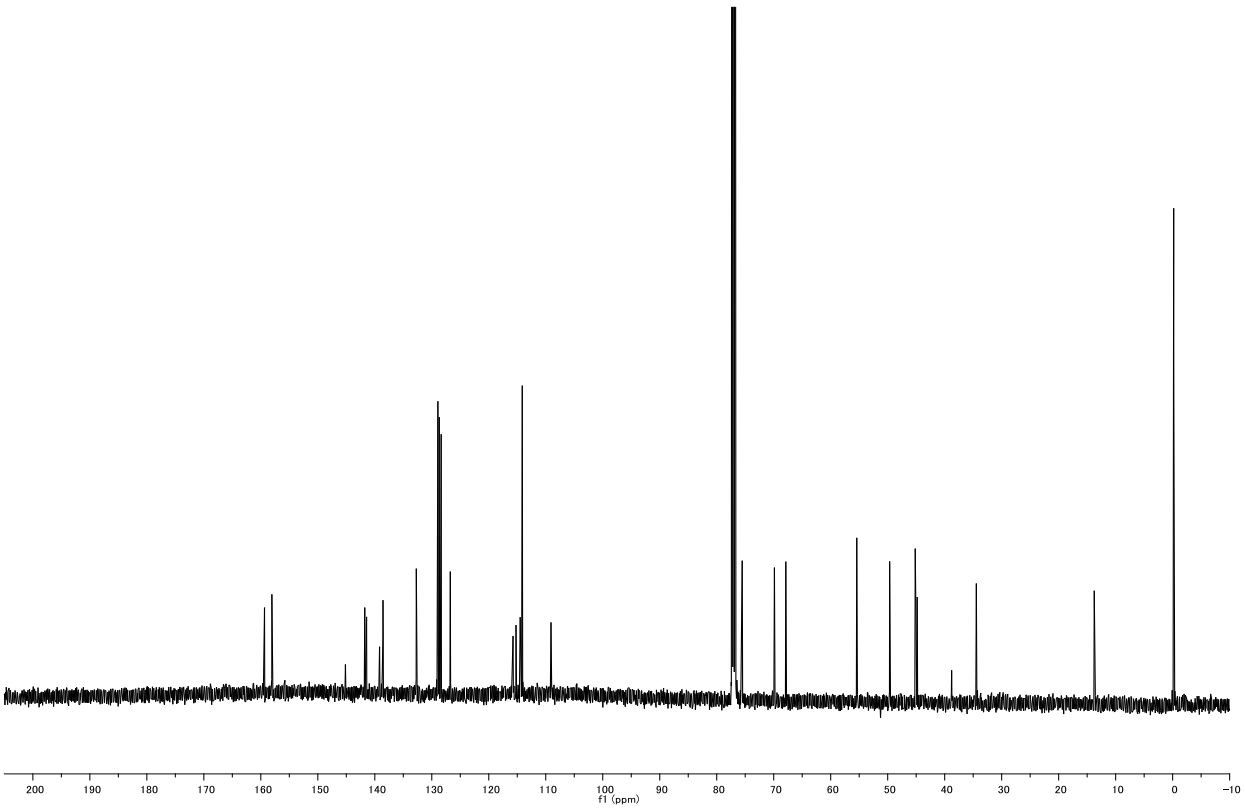
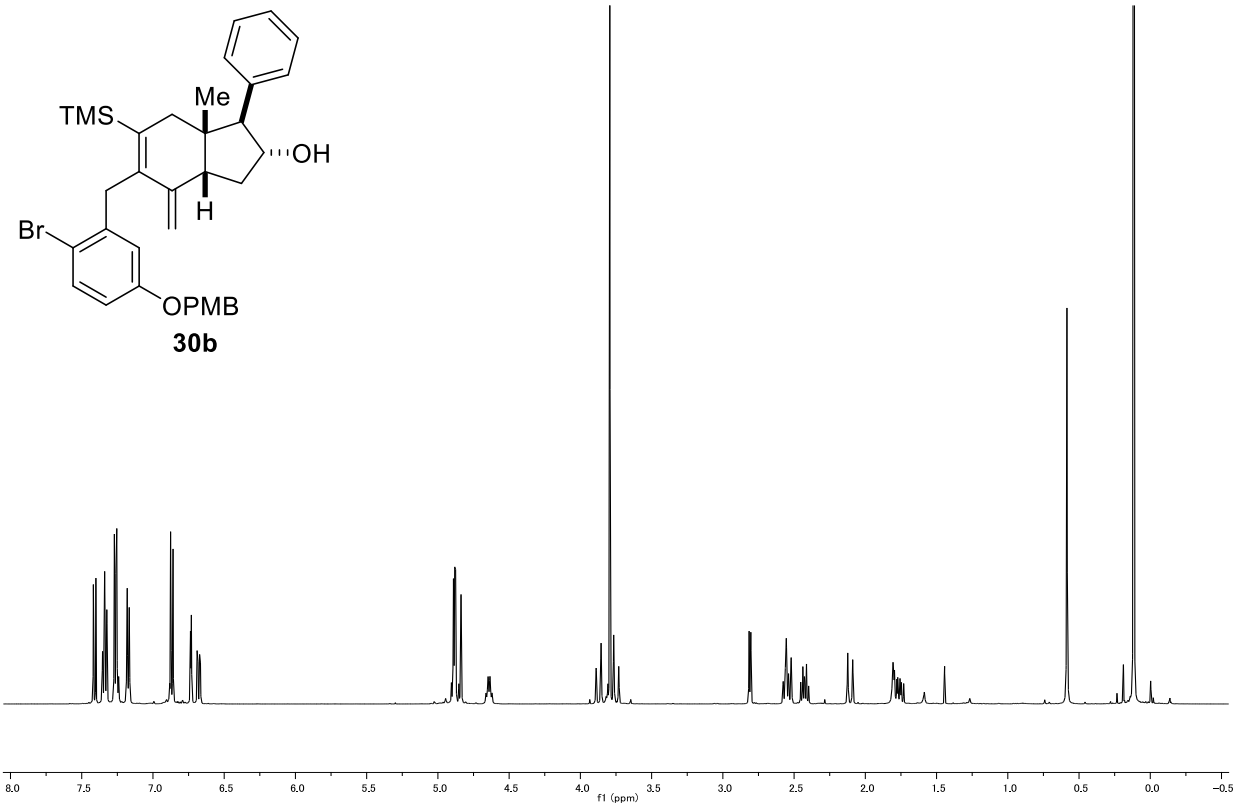


Figure S43: ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **30b**.



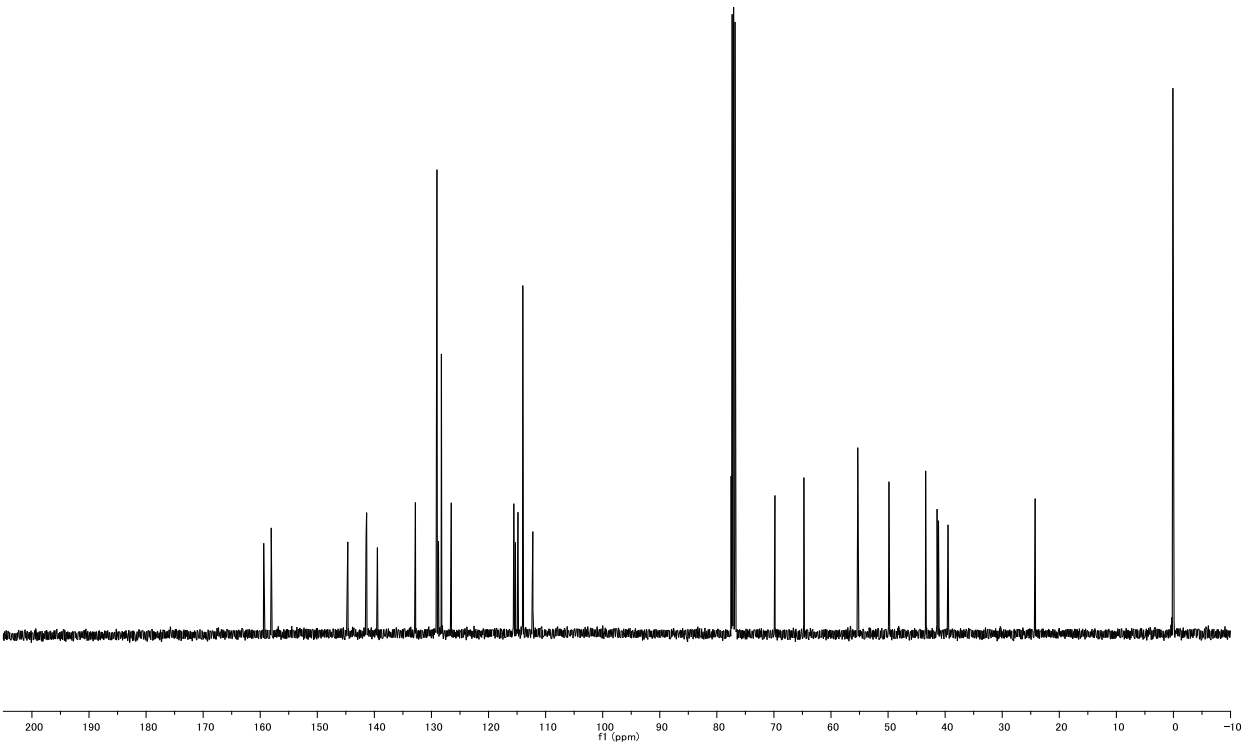


Figure S44: ^{1}H NMR (500 MHz, $CDCl_3$) of the crude mixture of **30a** and **30b**.