Supporting Information for

Synthesis of Highly Functionalized Decalins via Metallacycle-Mediated Cross-Coupling

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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 tetrahydrofuran (THF) and toluene (PhMe) were obtained by distillation over sodium and benzophenone. Anhydrous dichloromethane (CH_2Cl_2) was purchased from Aldrich and was thoroughly degassed before use. Titanium isopropoxide ($Ti(O\textit{i}\text{-}Pr)_4$) was distilled before use. Solutions of *n*-BuLi were purchased from Aldrich and titrated against *N*-benzylbenzamide. Isopulegol was purchased from TCI America and oxidized to isopulegone[1], which was used as precursor for enyne **23**, **25**, **27**, **29**. These compounds were not optically pure, therefore optical rotations were not reported. 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. Thin layer chromatography (TLC) analyses were performed on EMD TLC Silica gel 60 F254 Glass Plates and the spots were visualized by UV-light (254 nm) or an aqueous solution of phosphomolybdic acid and anisaldehyde stain. ^1H NMR data were recorded on a Bruker Avance III 500 MHz spectrometer (TBI probe) and a Bruker Avance III 600 MHz spectrometer (BBFO probe) with calibration of spectra to $CDCl_3$ (7.26 ppm) or C_6D_6 (7.16 ppm). ^{13}C NMR data were recorded at 125 MHz on a Bruker Avance III 500 MHz spectrometer (TBI probe) and at 150 MHz on a Bruker Avance III 600 MHz spectrometer (BBFO probe) with calibration to the central line of $CDCl_3$ (77.16 ppm) or C_6D_6 (128.06 ppm). Two-dimensional NMR spectra, including COSY, HSQC, HMBC and NOESY were recorded on a Bruker Avance III 500 MHz spectrometer (TBI probe) and a Bruker Avance III 600 MHz spectrometer (BBFO probe). Infrared spectra were recorded on a JASCO FT/IRM4100 Fourier Transform Infrared Spectrometer. HRMS (ESI-TOF) analyses were performed at the Mass Spectrometry Laboratory of University of Illinois at Urbana-Champaign. X-ray crystallographic analysis was performed at the Center for Crystallographic Research of Michigan State University. All compounds purified by chromatography were sufficiently pure for use in further experiments, unless indicated otherwise.

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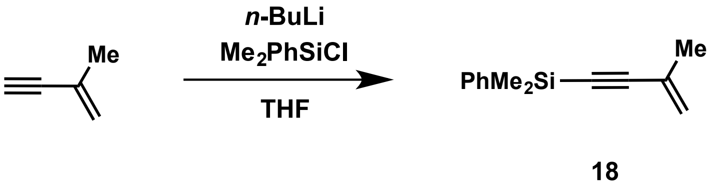
[1] Moreira, J. A.; Correa, A. G. *Tetrahedron Asymmetry*, **2003**, *14*, 3787-3795.

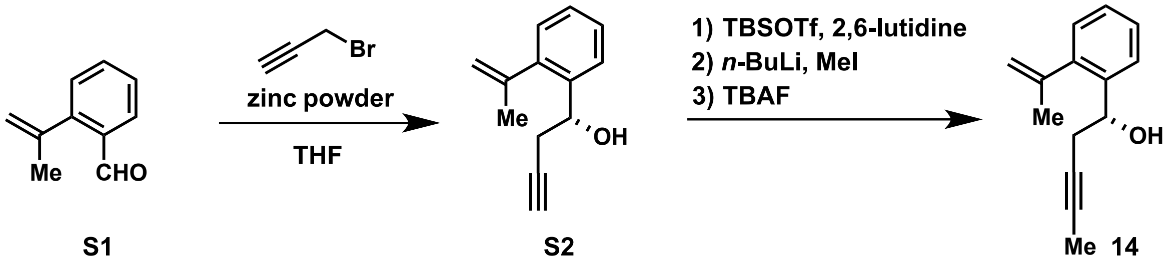
2. Experimental Procedures

A. Synthesis of alkyne 18 and enyne substrates 11, 14, 16, 23, 25, 27 29 and 36



Dimethyl(3-methylbut-3-en-1-yn-1-yl)(phenyl)silane (18) A solution of 2-methyl-3-buten-1-yne (2.38 mL, 25.0 mmol) in THF (25.0 mL) was cooled to –78 °C and *n*-BuLi (2.50 M, 9.5 mL, 23.8 mmol) was added dropwise over 5 min. After stirring for 1h, chloro(dimethyl)phenylsilane (4.18 mL, 25.0 mmol) was added dropwise. The solution was then allowed to warm slowly to rt overnight (12 h). After this period, the reaction was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **18** (4.82 g, quant.) as a colorless oil.

Spectral data for **18**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67-7.62 (2H, m), 7.41-7.36 (3H, m), 5.41 (1H, d, *J* = 0.7 Hz), 5.29 (1H, t, *J* = 1.5 Hz), 1.92 (3H, s), 0.44 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.25, 133.84, 129.51, 128.00, 126.91, 123.44, 108.21, 90.97, 23.42, -0.65; IR (thin film) 3069, 3051, 2960, 2922, 2153, 1955, 1818, 1609, 1429, 1275, 1251, 1118, 1042, 979, 901, 857, 835, 810, 781, 732, 700, 518, 471 cm^{-1}; HRMS (EI-TOF) calculated for $C_{13}H_{16}Si$ [M^+] 200.1021, found 200.1024.



(±)-1-(2-(prop-1-en-2-yl)phenyl)pent-3-yn-1-ol (14). To a mixture of aldehyde **S1**[2] (3.95 g, 27.0 mmol) and propargyl bromide (solution. 80 wt. % in toluene, 3.8 mL, 35.1 mmol) in anhydrous THF (135 mL) was added zinc powder (8.8 g, 135 mmol) and 1,2-dibromoethane (0.9 mL, 10.4 mmol) at room temperature. After stirring for 18.5 h, the reaction was quenched with saturated aqueous NH_4Cl and extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **S2** (2.98 g, 59%) as a colorless oil.

Spectral data for **S2**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (1H, dd, *J* = 7.7, 1.5 Hz), 7.34 (1H, td, *J* = 7.7, 1.5 Hz), 7.26 (1H, td, *J* = 7.7, 1.5 Hz), 7.12 (1H, dd, *J* = 7.7, 1.5 Hz), 5.25 (1H, quin, *J* = 1.5 Hz), 5.12 (1H, td, *J* = 6.6, 3.3 Hz), 4.86 (1H, m), 2.63 (2H, dd, *J* = 6.6, 2.6 Hz), 2.30 (1H, d, *J* = 3.3Hz), 2.08 (3H, s), 2.08-2.07 (1H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.74, 142.70, 138.99, 128.20, 127.83, 127.57, 125.62, 116.08, 81.25, 70.86, 68.93, 29.33, 25.81; IR (thin film) 3387, 3293, 3075, 3025, 2967, 2940, 2913, 2119, 1640, 1488, 1434, 1042, 1010, 904, 764, 641 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{13}H_{14}ONa$ [M+Na$^+$] 209.0937, found 209.0943.

To a solution of alcohol **S2** (233 mg, 1.25 mmol) in anhydrous CH_2Cl_2 (6.3 mL) was added 2,6-lutidine (260 µL, 2.25 mmol) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (375 µL, 1.63 mmol) at –78 °C. After stirring at –78 °C for 1 h, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with Et_2O. The combined organic extracts were washed with 1M aqueous HCl, saturated aqueous $NaHCO_3$, brine, and dried over Na_2SO_4. The solvent was removed *in vacuo* and the resulting crude mixture was used without purification for the next reaction.

A solution of crude silylether in anhydrous THF (7.0 mL) was cooled to –78 °C and *n*-BuLi (1.94 M in hexanes, 770 µL, 1.49 mmol) was added dropwise. After stirring at –78 °C for 1 h, the mixture was warmed up to rt and further stirred for 10 min. After cooling down to –78 °C, MeI (234 µL, 3.75 mmol) was added dropwise and the solution was allowed to warm slowly to rt overnight (18 h). After this period, the reaction was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, brine, and dried over Na_2SO_4. The solvent was removed *in vacuo* and the resulting crude mixture was used without purification for the next reaction. To a solution of this crude material in anhydrous THF (6.0 mL) was added TBAF (1.0 M in THF, 1.6 mL, 1.6 mmol) at 0 °C. After stirring for 1 h. The solution was warmed up to rt and stirred for an additional 4 h.

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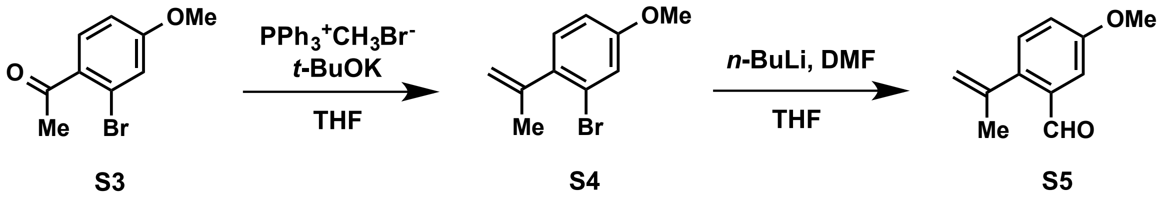
[2] Chaudhuri, R.; Das, A.; Liao, H.-Y. and Liu, R.-S. *Chem. Commun.* **2010**, *46*, 4601–4603.

The solvent was removed *in vacuo* and the resulting crude mixture was purified via flash chromatography to afford **14** (212 mg, 85% for 3 steps) as a colorless oil.

Spectral data for **14**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (1H, br-d, *J* = 7.3 Hz), 7.30 (1H, td, *J* = 7.3, 1.1 Hz), 7.24 (1H, td, *J* = 7.3, 1.1 Hz), 7.11 (1H, dd, *J* = 7.3, 1.1 Hz), 5.24 (1H, t, *J* = 1.7 Hz), 5.04 (1H, br-t, *J* = 6.6 Hz), 4.85 (1H, d, *J* = 1.1 Hz), 2.57-2.53 (2H, s), 2.44 (1H, br-s), 2.07 (3H, s), 1.82 (3H, t, *J* = 2.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.84, 142.65, 139.36, 128.09, 127.60, 127.47, 125.64, 115.90, 78.54, 75.80, 69.23, 29.94, 25.78, 3.71; IR (thin film) 3386, 3074, 3024, 2965, 2938, 2917, 1819, 1640, 1488, 1434, 1041, 1009, 903, 763 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{14}H_{16}ONa$ [M+Na$^+$] 223.1093, found 223.1103.



S3 S4 S5

(±)-1-(5-methoxy-2-(prop-1-en-2-yl)phenyl)pent-3-yn-1-ol (16). To a solution of methyltriphenylphosphonium bromide (12.4 g, 34.8 mmol) in anhydrous THF (90.0 mL) at 0 °C was added *t*-BuOK (3.90 g, 34.8 mmol) and the resulting solution was stirred at rt for 1h. The mixture was cooled to 0 °C and ketone **S3**[3] 6.64 g (29.0 mmol) was added. After stirring at rt for 20 h, the reaction was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic extracts were washed with brine, and dried over Na_2SO_4. The solvent was removed *in vacuo* and the resulting crude mixture was filtered through a SiO_2 pad and used for the next reaction without further purification.

A solution of crude aryl bromide **S4** in anhydrous THF (120 mL) was cooled to –78 °C and *n*-BuLi (2.38 M in hexanes, 15.8 mL, 37.7 mmol) was added dropwise. After stirring at –78 °C for 1.5 h, DMF (4.7 mL, 60.0 mmol) was added dropwise and the resulting solution was then allowed to warm to rt. After stirring at rt for 1 h, the reaction was quenched with saturated aqueous NH_4Cl at 0 °C and extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, brine, and dried over Na_2SO_4. The solvent was removed *in vacuo* and the resulting crude mixture was filtered through a SiO_2 pad and used without further purification for the next reaction.

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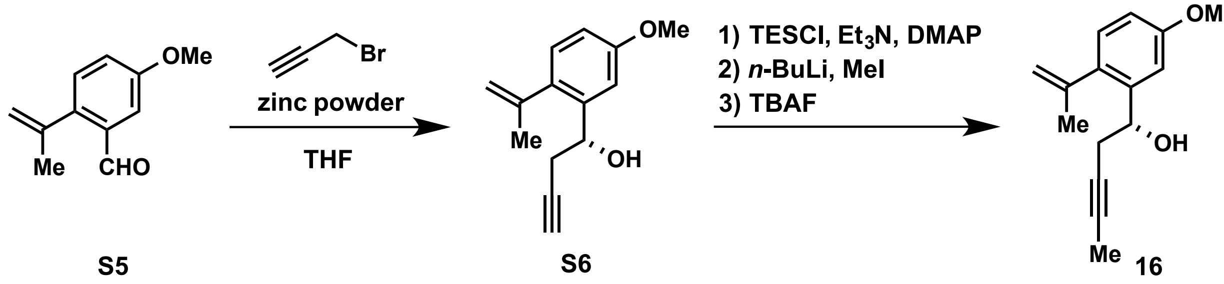
[3] Wang, F.; Zhang, Y. J.; Wei, H.; Zhang, J.; Zhang, W. *Tetrahedron Lett.*, **2007**, *48*, 4083-4086.



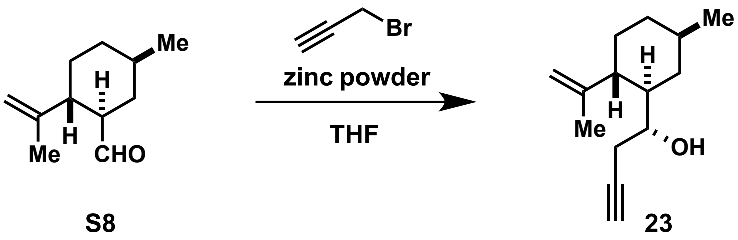
To a mixture of crude aldehyde **S5** and propargyl bromide (solution. 80 wt. % in toluene, 4.3 mL, 39.6 mmol) in anhydrous THF (140 mL) was added zinc powder (9.2 g, 142 mmol) and 1,2-dibromoethane (0.9 mL, 10.4 mmol) at room temperature. After stirring at the same temperature for 17 h, the reaction was quenched with saturated aqueous NH_4Cl and extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **S6** (4.35 g, 69% for 3 steps) as a colorless oil.

Spectral data for **S6**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (1H, d, J = 2.9 Hz), 7.04 (1H, d, J = 8.4 Hz), 6.81 (1H, dd, J = 8.4, 2.9 Hz), 5.23 (1H, s), 5.12-5.08 (1H, m), 4.83 (1H, s), 3.82 (3H, s), 2.63-2.59 (2H, m), 2.31 (1H, d, J = 3.3Hz), 2.09 (1H, t, J = 2.6 Hz), 2.05 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.97, 144.42, 140.45, 135.06, 129.37, 116.21, 113.75, 110.60, 81.20, 70.93, 68.96, 55.45, 29.41, 25.94; IR (thin film) 3431, 3291, 3077, 2963, 2938, 2914, 2837, 1608, 1498, 1290, 1230, 1036, 903, 640 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{14}H_{17}O_2$ [M+H$^+$] 217.1223, found 217.1220.

To a solution of alcohol **S6** (4.30 g, 19.9 mmol) in anhydrous CH_2Cl_2 (80.0 mL) at 0 °C was added triethylamine (4.2 mL, 30.0 mmol), chlorotriethylsilane (4.0 mL, 24.0 mmol) and a catalytic amount of DMAP (ca. 100 mg). After stirring at rt for 2.5 h, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with Et_2O. The combined organic extracts were washed with brine, and dried over Na_2SO_4. The solvent was removed *in vacuo* and the resulting crude mixture was used without purification for the next reaction.

A mixture of crude silylether in anhydrous THF (100 mL) was cooled to –78 °C and *n*-BuLi (2.30 M in hexanes, 11.3 mL, 26.0 mmol) was added dropwise. After stirring at –78 °C for 1 h, MeI (3.76 mL, 60.0 mmol) was added and the solution was allowed to warm slowly to rt overnight (12 h). After this period, the reaction was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, brine, and dried over Na_2SO_4. The solvent was removed *in vacuo* and the resulting crude mixture was used without purification for the next reaction. The crude mixture was dissolved in anhydrous THF (80.0 mL) and TBAF (1.0 M in THF, 25.0 mL, 25.0 mmol) was added at 0 °C. After stirring for 1 h, the solution was allowed to warm to rt and stirred for another 1 h. The solvent was removed *in vacuo* and the resulting crude mixture was purified via flash chromatography to afford **16** (4.28 g, 93% for 3 steps) as a colorless oil.

Spectral data for **16**: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.11 (1H, d, *J* = 2.9 Hz), 7.03 (1H, d, *J* = 8.4 Hz), 6.79 (1H, dd, *J* = 8.4, 2.9 Hz), 5.21 (1H, t, *J* = 1.8 Hz), 5.02 (1H, dd, *J* = 8.4, 4.4 Hz), 4.82 (1H, dd, *J* = 1.8, 0.7 Hz), 3.82 (3H, s), 2.58-2.48 (2H, m), 2.39 (1H, br-s), 2.04 (3H, s), 1.82 (3H, t, *J* = 2.6 Hz); ^{13}C NMR (150 MHz, CDCl$_3$) δ 158.94, 144.53, 140.82, 135.09, 129.29, 116.06, 113.65, 110.55, 78.68, 75.74, 69.27, 55.43, 30.03, 25.93, 3.76; IR (thin film) 3434, 3077, 2961, 2939, 2917, 2836, 1638, 1608, 1571, 1498, 1290, 1229, 1036, 902, 824 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{15}H_{19}O_2$ [M+H$^+$] 231.1380, found 231.1382.



1-((1*R*,2*R*,5*R*)-5-methyl-2-(prop-1-en-2-yl)cyclohexyl)but-3-yn-1-ol (23). To a mixture of aldehyde **S8**[4] (1.37 g, 8.24 mmol) and propargyl bromide (solution. 80 wt. % in toluene, 866 μL, 11.5 mmol) in anhydrous THF (41.0 mL) was added zinc powder (3.75 g, 57.7 mmol) and 1,2-dibromoethane (0.5 mL, 5.80 mmol) at room temperature. After stirring for 19.5 h, the reaction was quenched with saturated aqueous NH_4Cl and extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **23** (1.35 g, 79%) as 3:1 mixture of diastereomers. **23** was further purified to obtain a pure stereoisomer as a colorless oil before use in the annulation reaction.

Spectral data for **23**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.79 (1H, s), 4.78 (1H, s), 3.85 (1H, t, *J* = 7.0 Hz), 2.45 (1H, ddd, *J* = 16.5, 7.9, 1.5 Hz), 2.27 (1H, ddd, *J* = 16.5, 6.1, 1.8 Hz), 2.10 (1H, td, *J* = 11.6, 2.8 Hz), 2.01 (1H, s), 1.74-1.52 (5H, m), 1.67 (3H, s), 1.47-1.35 (2H, m), 1.01-0.87 (2H,

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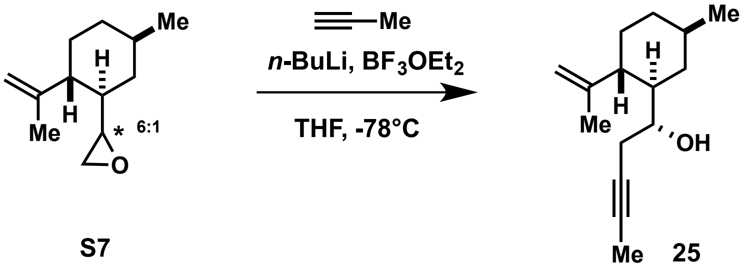
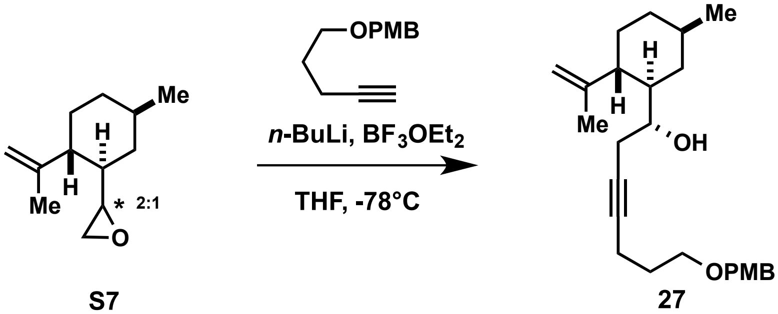
[4] Corey, E. J. and Staas, D. D. *J. Am. Chem. Soc.*, **1998**, *120*, 3526-3527.

m), 0.93 (3H, d, J = 6.4 Hz); ^{13}C NMR (125 MHz, CDCl$_3$) δ 148.76, 111.86, 81.91, 70.20, 70.10, 48.18, 42.52, 34.90, 32.54, 32.36, 32.15, 24.73, 23.01, 18.82; IR (thin film) 3421, 3309, 3071, 2947, 2922, 2868, 2854, 2118, 1644, 1455, 1376, 1024, 891, 636 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{14}H_{23}O$ [M+H$^+$] 207.1743, found 207.1746.



1-((1*R*,2*R*,5*R*)-5-methyl-2-(prop-1-en-2-yl)cyclohexyl)pent-3-yn-1-ol (25). A solution of *n*-BuLi (2.47 M in hexanes, 4.6 mL, 12.0 mmol) in anhydrous THF (20.0 mL) was cooled to -78 °C and propyne (gas, excess) was bubbled in to the mixture. After stirring for 1 h, BF_3•OEt_2 (1.26 mL, 10.0 mmol) was added dropwise and the resulting mixture was stirred for 15min. To this -78 °C mixture was added a solution of epoxide **S7**[3] (721 mg, 4.00 mmol) in anhydrous THF (10.0 mL) and the resulting solution was stirred for 1 h 20 min, after which time 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 was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 the pure diastereomer **25** (561 mg, 64%) as a colorless oil.

Spectral data for **25**: ^{1}H NMR (600 MHz, CDCl$_3$) δ 4.78 (1H, s), 4.76 (1H, s), 3.76 (1H, t, J = 7.0 Hz), 2.40-2.34 (1H, m), 2.19 (1H, ddd, J = 16.5, 5.9, 2.6 Hz), 2.10 (1H, td, J = 11.7, 2.9 Hz), 1.78 (3H, s), 1.71-1.58 (4H, m), 1.65 (3H, s), 1.51 (1H, br-t, J = 11.7 Hz), 1.44-1.34 (2H, m), 1.00-0.87 (2H, m), 0.92 (3H, d, J = 6.2 Hz); ^{13}C NMR (150 MHz, CDCl$_3$) δ 148.88, 111.73, 77.68, 76.43, 70.42, 48.16, 42.60, 34.92, 32.54, 32.47, 32.21, 25.19, 23.01, 18.83, 3.67; IR (thin film) 3409, 3071, 2947, 2921, 2854, 1644, 1447, 1376, 1101, 1023, 890 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{15}H_{25}O$ [M+H$^+$] 221.1900, found 221.1909.



7-((4-methoxybenzyl)oxy)-1-((1*R*,2*R*,5*R*)-5-methyl-2-(prop-1-en-2-yl)cyclohexyl)hept-3-yn-1-ol (27). A solution of alkyne[5] (615 mg, 3.01 mmol) in THF (10.0 ml) was cooled to -78 °C and *n*-BuLi (2.40 M in hexanes, 1.18 mL, 2.83 mmol) was added dropwise. After 40 min, BF_3•OEt_2 (378 μL, 3.01 mmol) was added dropwise and the resulting mixture was stirred for 20 min. To this -78 °C mixture was dropwise added a solution of epoxide **S7** (320 mg, 1.77 mmol) in anhydrous THF (4.0 mL) and the resulting solution was stirred for 1.5 h, after which time 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 was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 the pure diastereomer **27** (276 mg, 40%) and 1.6:1 mixture of diastereomers (295 mg, 43%) as a colorless oil.

Spectral data for **27**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (2H, d, *J* = 8.4 Hz), 6.88 (2H, d, *J* = 8.4 Hz), 4.79 (1H, s), 4.77 (1H, s), 4.43 (2H, s), 3.80 (3H, s), 3.76 (1H, br-s), 3.52 (2H, t, *J* = 6.2 Hz), 2.39 (1H, dd, *J* = 16.1, 7.7 Hz), 2.29-2.19 (3H, m), 2.10 (1H, td, *J* = 11.7, 3.3 Hz), 1.77 (2H, quin, *J* = 6.6 Hz), 1.72-1.59 (3H, m), 1.66 (3H, s), 1.57 (1H, s), 1.54 (1H, t, *J* = 11.7 Hz), 1.44-1.34 (2H, m), 0.99-0.89 (2H, m), 0.93 (3H, d, *J* = 6.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.28, 148.87, 130.72, 129.36, 113.91, 111.74, 81.83, 77.47, 72.77, 70.34, 68.84, 55.43, 48.15, 42.50, 34.93, 32.60, 32.49, 32.19, 29.30, 25.15, 23.03, 18.88, 15.85; IR (thin film) 3446, 3310, 3070, 2946, 2921, 2854, 1644, 1612, 1586, 1513, 1455, 1248, 1101, 1026, 890 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{25}H_{37}O_3$ [M+H$^+$] 385.2737, found 385.2740.

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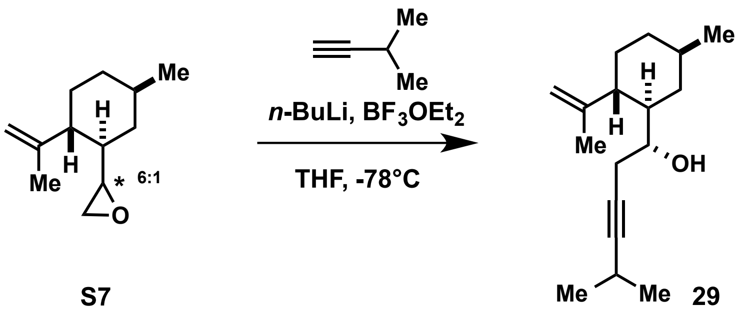
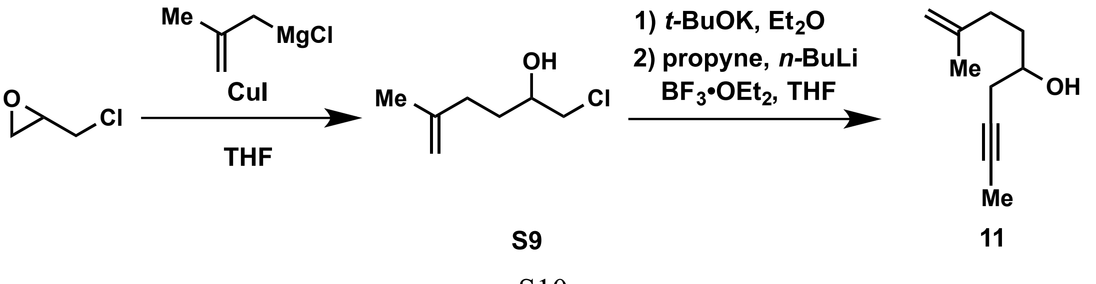
[5] Stivala, C. E.; Gu, Z.; Smith, L. L. and Zakarian, A. *Org. Lett.*, **2012**, *14*, 804-807.



5-methyl-1-((1*R*,2*R*,5*R*)-5-methyl-2-(prop-1-en-2-yl)cyclohexyl)hex-3-yn-1-ol (29). A solution of 3-methyl-1-butyne (750 μL, 7.33 mmol) in THF (17.0 ml) was cooled to -78 °C and *n*-BuLi (2.50 M in hexanes, 2.66 mL, 6.66 mmol) was added dropwise. After 1 h, BF_3•OEt_2 (817 μL, 6.50 mmol) was added dropwise and the resulting mixture was stirred for 15min. To this -78 °C mixture was dropwise added a solution of epoxide **S7** (600 mg, 3.33 mmol) in anhydrous THF (4.0 mL) and the resulting mixture was stirred at -78 °C for 1.5 h, after which time 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 was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 the pure diastereomer **29** (395 mg, 48%) as a colorless oil.

Spectral data for **29**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.79 (1H, s), 4.77 (1H, s), 3.76 (1H, t, *J* = 7.0,Hz), 2.56-2.48 (1H, m), 2.40 (1H, ddd, *J* = 16.5, 7.7, 1.8 Hz), 2.24 (1H, ddd, *J* = 16.1, 7.0, 1.8 Hz), 2.10 (1H, td, *J* = 11.7, 3.3 Hz), 1.72-1.52 (4H, m), 1.67 (3H, s), 1.56 (1H, t, *J* = 11.7 Hz), 1.45-1.35 (2H, m), 1.14 (6H, d, *J* = 1.0 Hz), 0.99-0.89 (2H, m), 0.93 (3H, d, *J* = 6.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.91, 111.72, 88.42, 76.23, 70.28, 48.17, 42.34, 34.96, 32.61, 32.52, 32.18, 25.07, 23.47, 23.04, 20.69, 18.82; IR (thin film) 3389, 3071, 2966, 2947, 2922, 2869, 2855, 1645, 1455, 1376, 1320, 1102, 1021, 890 cm^{-1}; LRMS (ESI-TOF) calculated for $C_{17}H_{28}ONa$ [M+Na$^+$] 271.2, found 271.2.

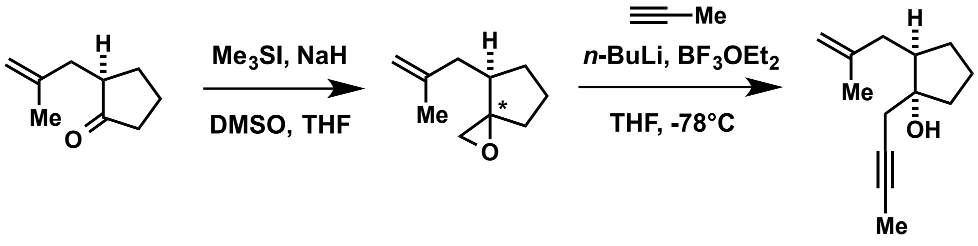


(±)-2-methylnon-1-en-7-yn-5-ol (11). A stirred mixture of *epi*-chlorohydrin (1.18 mL, 15.0 mmol) and CuI (428 mg, 2.25 mmol) in anhydrous THF (30.0 mL) was cooled to -78 °C and 2-methylallylmagnesium chloride (0.5 M in THF, 40 mL, 20.0 mmol) was added over 5 min. The reaction mixture was slowly wormed to 0 °C over 3.5 h and subsequently quenched by addition of saturated aqueous NH_4Cl. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, brine, and dried over Na_2SO_4. The solvent was removed *in vacuo* and the crude material was used without purification for the next reaction.

To a stirred solution of crude alcohol **S9** in Et_2O (150 mL) was added *t*-BuOK (1.68 g, 15.0 mmol) at 0 °C. After stirring for 35 min, the reaction was quenched with water. The organic layer was separated, and the aqueous layer was extracted with Et_2O. The combined organic extracts were washed with brine, and dried over Na_2SO_4. The solvent was removed *in vacuo* and the crude material was used without purification for the next reaction.

A solution of *n*-BuLi (2.40 M in hexanes, 9.4 mL, 22.5 mmol) in anhydrous THF (60.0 mL) was cooled to -78 °C and propyne (gas, excess) was bubbled in to the mixture. After stirring for 1 h, $BF_3 \bullet OEt_2$ (2.96 mL, 24.0 mmol) was added dropwise and the resulting mixture was stirred for 15min. To this -78 °C mixture was then dropwise added a solution of crude epoxide in anhydrous THF (15.0 mL) and the resulting solution was stirred for 30 min, after which time the reaction was quenched by the addition of saturated aqueous $NaHCO_3$. After warming up to rt, the organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **11** (975 mg, 43% over 3 steps) as a colorless oil.

Spectral data for **11**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.73 (1H, s), 4.72 (1H, s), 3.73-3.67 (1H, m), 2.39 (1H, dq, *J* = 16.5, 2.2 Hz), 2.31-2.24 (1H, m), 2.20-2.13 (1H, m), 2.12-2.05 (1H, m), 1.96 (1H, d, *J* = 4.8 Hz), 1.81 (3H, s), 1.74 (3H, s), 1.68-1.64 (2H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.65, 110.32, 78.63, 75.33, 70.10, 34.20, 34.05, 27.88, 22.60, 3.69; IR (thin film) 3364, 3074, 2920, 2857, 1650, 1444, 1375, 1077, 1031, 887 cm^{-1}; HRMS (EI-TOF) calculated for $C_{10}H_{16}O$ [M$^+$] 152.1201, found 152.1207.



S10 **S11** **36**

(±)-(1*R*,2*R*)-1-(but-2-yn-1-yl)-2-(2-methylallyl)cyclopentan-1-ol (36). Sodium hydride (60% dispersion in mineral oil, 768 mg, 19.2 mmol) was dissolved in DMSO (25.0 mL) and heated at 70 °C for 1 h. After cooling to rt, THF (30.0 mL) was added and cooled to 0 °C. To this solution was added a solution of trimethylsulfonium iodide (3.93 g, 19.2 mmol) in DMSO (15.0 mL) dropwise and stirred for 25 min. After warming up to rt, a solution of ketone **S10**[6] in THF (10.0 mL) was added dropwise and stirred for 3.5 h. The mixture was poured into ice cooled saturated aqueous $NaHCO_3$ and extracted with Et_2O. The combined organic extracts were washed with water, 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 epoxide **S11** (1.39 g) as a mixture of diastereomers. The mixture was used for the next reaction without further purification.

A solution of *n*-BuLi (2.49 M in hexanes, 9.4 mL, 23.4 mmol) in anhydrous THF (50.0 mL) was cooled to -78 °C and propyne (gas, excess) was bubbled in to the mixture. After stirring for 1 h, $BF_3•OEt_2$ (2.61 mL, 21.2 mmol) was added dropwise and the resulting mixture was stirred for 10 min. To this -78 °C mixture was added a solution of epoxide **S11** (1.39 g) in anhydrous THF (10.0 mL) and the resulting solution was stirred for 40 min, after which time 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 was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **36** (1.59 g, 65% for 2 step) as 1:1 mixture of diastereomers. **36** was further purified to obtain a pure stereoisomer as a colorless oil before use in the annulation reaction.

Spectral data for **36**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.74 (1H, s), 4.69 (1H, s), 2.39 (1H, ddd, *J* = 16.5, 4.8, 2.6 Hz), 2.30 (1H, ddd, *J* = 16.5, 5.1, 2.6 Hz), 2.22 (1H, dd, *J* = 13.6, 4.0 Hz), 2.10-2.04 (1H, m), 1.96-1.85 (1H, m), 1.82 (3H, t, *J* = 2.6 Hz), 1.83-1.78 (1H, m), 1.77-1.66 (3H, m), 1.72 (3H, s), 1.63-1.55 (1H, m), 1.34-1.27 (1H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.74, 111.59, 82.06, 78.55, 75.51, 46.55, 38.89, 38.00, 28.74, 27.20, 22.25, 20.80, 3.72; IR (thin film)

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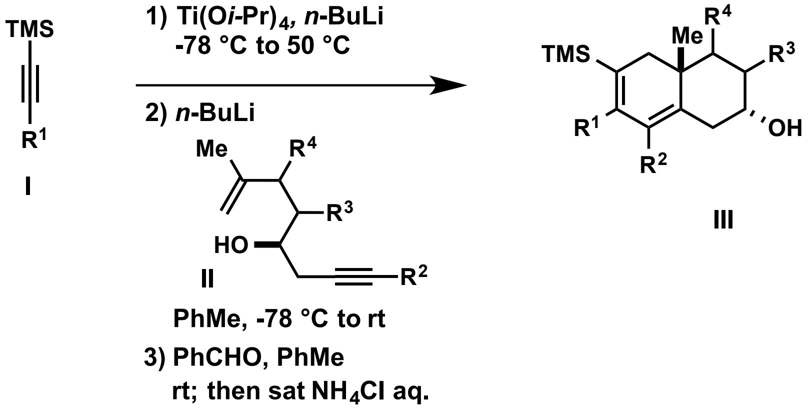
[6] Zhu, S.; Cohen, T. *Tetrahedron* **1997**, *53*, 17607–17624.

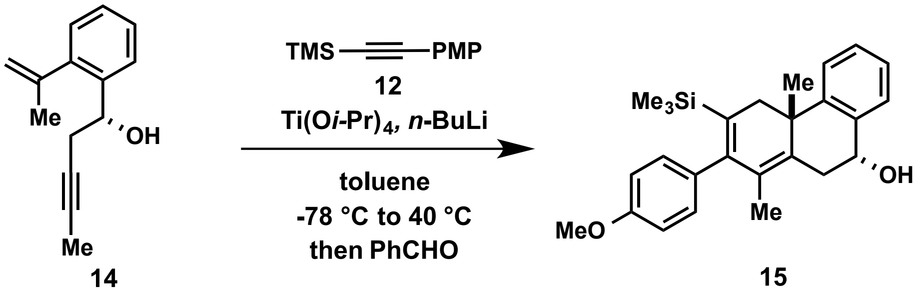
3445, 3072, 2961, 2920, 2873, 1649, 1446, 1374, 1276, 1054, 887 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{13}H_{21}O$ [M+H^{+}] 193.1587, found 193.1590.

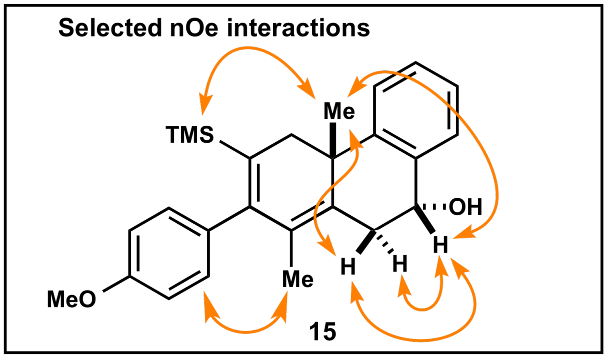
B. Synthesis of Functionalized Decalins via metallacycle mediated cross-coupling

General procedure I (benzaldehyde pre-quench)



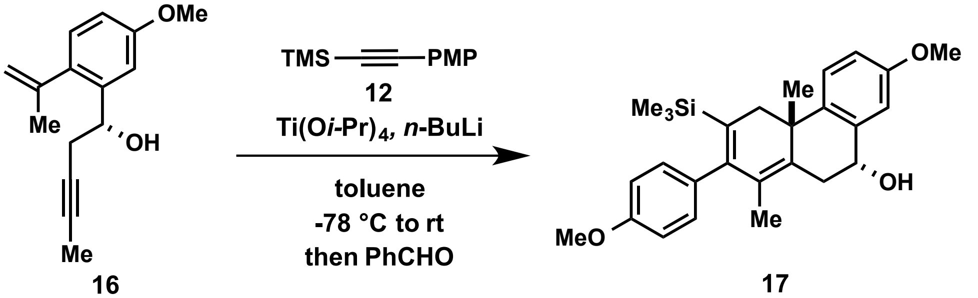
To a solution of alkyne **I** (1.00 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (1.00 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.50 M in hexanes, 0.80 mL, 2.00 mmol) was added dropwise (by syringe) over the course of 5 min. After this period, the flask was taken out of the cooling 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** (0.300 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (0.330 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 resulting reaction mixture was allowed to warm to rt overnight. To this mixture, a solution of benzaldehyde (150 µL, 1.47 mmol) in PhMe (5.0 mL) was added at rt and stirred for 1 h before the reaction was quenched with saturated aqueous NH$_4$Cl. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous NaHCO$_3$, brine, and dried over Na$_2$SO$_4$. The solvent was removed *in vacuo* and the resulting crude mixture was purified via flash chromatography to afford decalin **III**.





(±)-(4a*S*,9*R*)-2-(4-methoxyphenyl)-1,4a-dimethyl-3-(trimethylsilyl)-4,4a,9,10-tetrahydrophenanthren-9-ol (15). To a solution of alkyne **12** (213 μL, 1.00 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (300 μL, 1.01 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.50 M in hexanes, 0.80 mL, 2.00 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. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **14** (61.0 mg, 0.305 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (0.13 mL, 0.330 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (15.5 h). After this period, the cooling bath was removed and the mixture was stirred at 40 °C for an additional 3 h. To this mixture, a solution of benzaldehyde (150 μL, 1.47 mmol) in PhMe (5.0 mL) was added at rt and stirred for 1.5 h before the reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **15** (73.1 mg, 59%) as a colorless oil.

Spectral data for **15**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40-7.33 (3H, m), 7.23 (1H, td, *J* = 7.3, 1.5 Hz), 7.07 (1H, br-s), 6.94 (1H, br-s), 6.86 (2H, d, *J* = 8.4 Hz), 4.89 (1H, t, *J* = 3.3 Hz), 3.84 (3H, s), 3.13 (1H, dd, J = 13.9, 3.3 Hz), 2.65 (1H, d, J = 16.1 Hz), 2.43 (1H, d, J = 13.9 Hz), 2.18 (1H, d, J = 16.1 Hz), 1.89 (1H, br-s), 1.58 (3H, s), 1.30 (3H, s), -0.17 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.59, 148.67, 146.02, 137.42, 135.37, 134.15, 132.80, 131.45, 130.33, 130.15, 129.37, 128.77, 127.21, 126.17, 113.39, 112.97, 70.08, 55.36, 42.62, 37.34, 32.79, 22.22, 16.29, -0.52; IR (thin film) 3407, 3310, 3066, 3029, 2953, 2923, 1738, 1609, 1507, 1455, 1245, 1174, 1038, 861, 835, 759 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{26}H_{32}O_2SiNa$ [M+Na$^+$] 427.2064, found 427.2060.

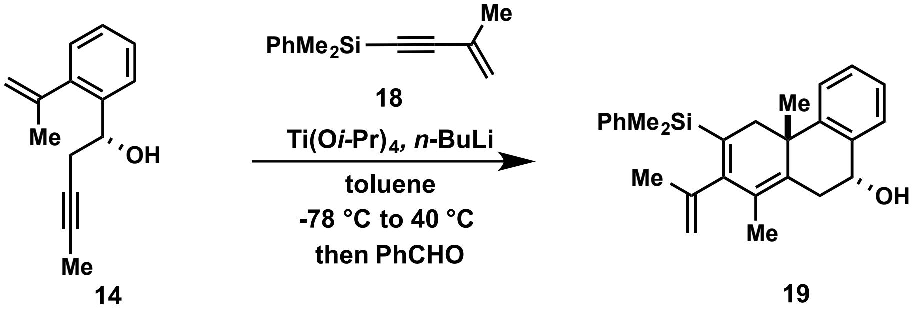


16

17

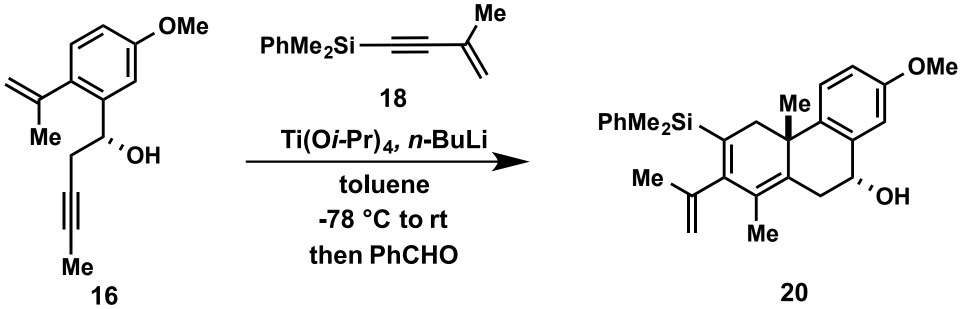
(±)-(4a*S*,9*R*)-7-methoxy-2-(4-methoxyphenyl)-1,4a-dimethyl-3-(trimethylsilyl)-4,4a,9,10-tetrahydrophenanthren-9-ol (17). To a solution of alkyne **12** (213 μL, 1.00 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (300 μL, 1.01 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.50 M in hexanes, 0.80 mL, 2.00 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. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **16** (70.0 mg, 0.304 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (0.13 mL, 0.330 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (17 h). To this mixture, a solution of benzaldehyde (150 μL, 1.47 mmol) in PhMe (5.0 mL) was added at rt and stirred for 1.5 h before the reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **17** (78.5 mg, 59%) as a colorless oil.

Spectral data for **17**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (1H, d, J = 8.8 Hz), 7.07 (1H, br-s), 6.93 (1H, br-s), 6.92 (1H, dd, J = 8.8, 2.6 Hz), 6.89 (1H, d, J = 2.6 Hz), 6.86 (2H, d, J = 8.4 Hz), 4.83 (1H, br-s), 3.83 (3H, s), 3.83 (3H, s), 3.10 (1H, dd, *J* = 14.3, 3.7 Hz), 2.62 (1H, d, *J* = 15.8 Hz), 2.44 (1H, br-d, *J* = 14.3 Hz), 2.15 (1H, d, *J* = 15.8 Hz) 1.89 (1H, br-s), 1.57 (3H, d, *J* = 1.1 Hz), 1.26 (3H, s), -0.18 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.56, 157.67, 148.60, 138.54, 138.05, 135.39, 134.18, 132.88, 131.46, 130.30, 130.13, 128.27, 115.55, 113.38, 113.12, 112.94, 70.23, 55.44, 42.72, 36.76, 32.91, 22.30, 16.30, -0.54; IR (thin film) 3389, 3030, 2997, 2954, 2835, 1609, 1507, 1454, 1285, 1245, 1173, 1033, 864, 834 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{27}H_{34}O_3SiNa$ [M+Na$^+$] 457.2169, found 457.2173.



(±)-(4a*S*,9*R*)-3-(dimethyl(phenyl)silyl)-1,4a-dimethyl-2-(prop-1-en-2-yl)-4,4a,9,10-tetrahydrophenanthren-9-ol (19). To a solution of alkyne **18** (200 mg, 1.00 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (300 μL, 1.01 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.50 M in hexanes, 0.80 mL, 2.00 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. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **14** (61.4 mg, 0.307 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (0.13 mL, 0.330 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (15 h). After this period, the cooling bath was removed and the mixture was stirred at 40 °C for an additional 3 h. To this mixture, a solution of benzaldehyde (150 μL, 1.47 mmol) in PhMe (5.0 mL) was added at rt and stirred for 1.5 h before the reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **19** (78.7 mg, 64%) as a pale yellow oil.

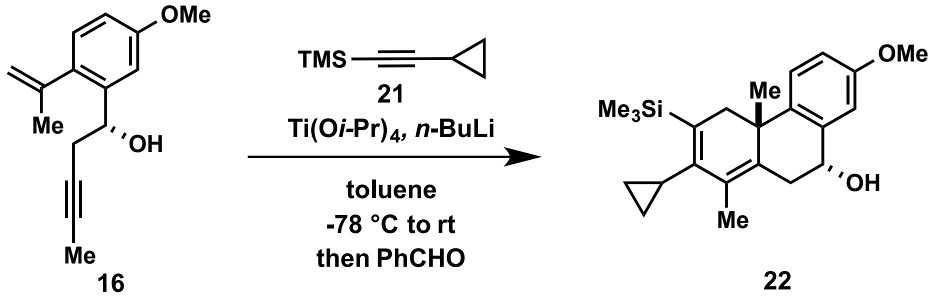
Spectral data for **19**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55-7.51 (2H, m), 7.36-7.31 (4H, m), 7.27 (1H, td, J = 7.7, 1.5 Hz), 7.18 (1H, td, J = 7.7, 0.7 Hz), 7.13 (1H, d, J = 7.7 Hz), 4.98 (1H, s), 4.86 (1H, t, J = 2.9 Hz), 4.78 (1H, s), 3.13 (1H, dd, J = 14.3, 3.7 Hz), 2.49 (1H, d, J = 15.4 Hz), 2.38 (1H, d, J = 14.3 Hz), 2.02 (1H, d, J = 15.4 Hz), 2.86 (3H, s), 1.71 (3H, br-s), 1.27 (1H, br-s), 1.10 (3H, s), 0.48 (3H, s), 0.45 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.63, 145.82, 137.22, 134.12, 129.26, 128.74, 127.73, 127.14, 126.09, 116.79, 70.09, 42.35, 37.32, 32.77, 29.86, 23.93, 21.85, 14.74, -0.47, -0.99; IR (thin film) 3310, 3068, 2958, 2923, 2857, 1642, 1553, 1453, 1427, 1247, 1110, 1035, 900, 830, 761, 735, 701 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{27}H_{32}OSiNa$ [M+Na$^+$] 423.2115, found 423.2111.



(±)-(4a*S*,9*R*)-3-(dimethyl(phenyl)silyl)-7-methoxy-1,4a-dimethyl-2-(prop-1-en-2-yl)-4,4a,9,10-tetrahydrophenanthren-9-ol (20). To a solution of alkyne **18** (200 mg, 1.00 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (300 μL, 1.01 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.50 M in hexanes, 0.80 mL, 2.00 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. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **16** (70.5 mg, 0.306 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (0.13 mL, 0.330 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (17 h). To this mixture, a solution of benzaldehyde (150 μL, 1.47 mmol) in PhMe (5.0 mL) was added at rt and stirred for 1.5 h before the reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, brine, and dried over

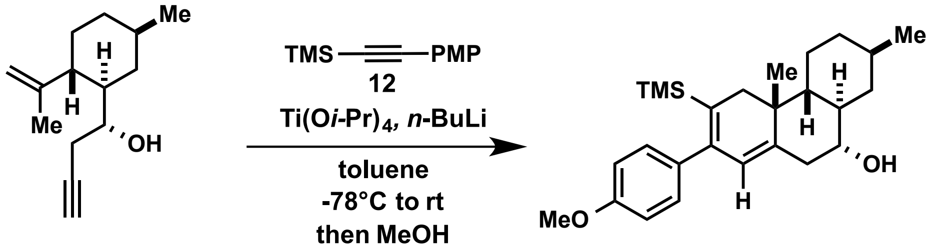
Na_2SO_4. The solvent was removed *in vacuo* and the resulting crude mixture was purified via flash chromatography to afford **20** (63.1 mg, 48%) as a pale yellow oil.

Spectral data for **20**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57-7.57 (2H, m), 7.39-7.34 (3H, m), 7.06 (1H, d, *J* = 8.4 Hz), 6.89-6.84 (2H, m), 5.00 (1H, s), 4.82 (1H, t, *J* = 2.9 Hz), 4.80 (1H, s), 3.81 (3H, s), 3.12 (1H, dd, *J* = 14.3, 3.7 Hz), 2.49 (1H, d, *J* = 15.4 Hz), 2.41 (1H, d, *J* = 14.3 Hz), 2.01 (1H, d, *J* = 15.4 Hz), 1.87 (3H, s), 1.92-1.80 (1H, br-s), 1.72 (3H, br-s), 1.09 (3H, s), 0.50 (3H, s), 0.47 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.61, 152.66, 146.63, 139.97, 138.35, 137.84, 136.23, 134.10, 128.72, 128.18, 127.70, 127.25, 116.73, 115.47, 113.04, 70.21, 55.38, 42.45, 36.74, 32.91, 24.02, 21.96, 14.74, -0.37, -1.00; IR (thin film) 3398, 3068, 3049, 2958, 2921, 2835, 1611, 1498, 1427, 1246, 1110, 1032, 897, 823, 772, 736, 702 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{28}H_{34}O_2SiNa$ [M+Na$^+$] 453.2220, found 453.2221.



(±)-(4a*S*,9*R*)-2-cyclopropyl-7-methoxy-1,4a-dimethyl-3-(trimethylsilyl)-4,4a,9,10-tetrahydrophenanthren-9-ol (22). To a solution of alkyne **21** (163 μL, 1.00 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (300 μL, 1.01 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.50 M in hexanes, 0.80 mL, 2.00 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. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **16** (71.6 mg, 0.311 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (0.13 mL, 0.330 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (22 h). To this mixture, a solution of benzaldehyde (150 μL, 1.47 mmol) in PhMe (5.0 mL) was added at rt and stirred for 1.5 h before the reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **22** (59.3 mg, 52%) as colorless oil.

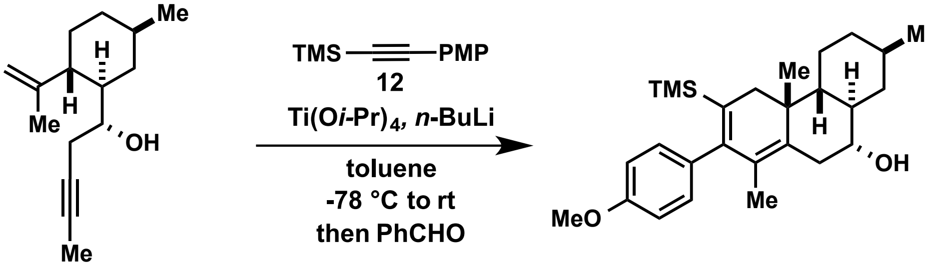
Spectral data for **22**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (1H, d, *J* = 8.4. Hz), 6.91-6.86 (2H, m), 4.79 (1H, s), 3.82 (3H, s), 3.08 (1H, dd, *J* = 14.3, 4.0 Hz), 2.38 (1H, br-d, *J* = 13.9 Hz), 2.37 (1H, d, *J* = 16.9 Hz), 2.04 (3H, s), 1.94 (1H, dd, *J* = 16.9, 4.0 Hz), 1.84 (1H, br-d, *J* = 8.4), 1.63-1.57 (1H, m), 1.01 (3H, s), 0.88-0.83 (1H, m), 0.80-0.74 (1H, m), 0.68 (1H, td, *J* = 6.5, 5.1 Hz), 0.22 (9H, s), 0.16-0.10 (1H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.63, 149.15, 138.67, 137.94, 134.14, 133.09, 132.12, 128.26, 115.39, 113.02, 69.97, 55.41, 44.24, 36.18, 32.57, 21.98, 15.23, 15.15, 11.11, 6.66, -0.34; IR (thin film) 3410, 2996, 2957, 2835, 1611, 1497, 1465, 1453, 1427, 1247, 1165, 1031, 908, 834, 738 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{23}H_{32}O_2SiNa$ [M+Na^{+}] 391.2064, found 391.2064.



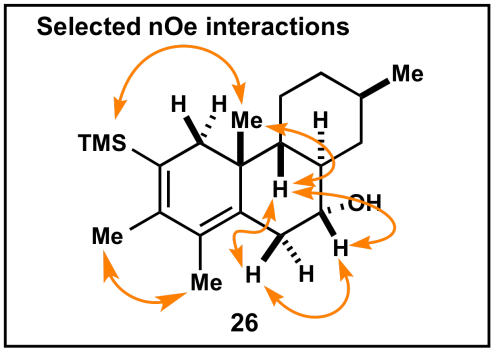
23 **24**

(4a*R*,4b*R*,7*R*,8a*R*,9*R*)-2-(4-methoxyphenyl)-4a,7-dimethyl-3-(trimethylsilyl)-4,4a,4b,5,6,7,8,8a,9,10-decahydrophenanthren-9-ol (24). To a solution of alkyne **12** (213 μL, 1.00 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (300 μL, 1.01 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.45 M in hexanes, 0.820 mL, 2.01 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. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **23** (61.9 mg, 0.300 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (0.135 mL, 0.331 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (17 h). The reaction mixture was then cooled to -78 °C and quenched with MeOH. After warming to rt, saturated aqueous NH_4Cl was added, and stirred vigorously until the color of the mixture turned pale yellow. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **24** (65.9 mg, 53%) as a pale yellow oil.

Spectral data for **24**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (2H, d, *J* = 8.2 Hz), 6.83 (2H, d, *J* = 8.2 Hz), 5.73 (1H, s), 3.81 (3H, s), 3.57 (1H, br-s), 2.64 (1H, dd, *J* = 14.0, 5.5 Hz), 2.22-2.12 (2H, m), 2.02-1.95 (2H, m), 1.78-1.67 (2H, m), 1.60 (1H, br-s), 1.40-1.29 (2H, m), 1.21-1.10 (2H, m), 0.96 (3H, s), 0.91 (3H, d, *J* = 6.4 Hz), 0.88-0.82 (1H, m), 0.78 (1H, q, *J* = 12.2 Hz), -0.12 (9H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.71, 145.47, 142.25, 136.74, 130.30, 129.47, 125.12, 113.38, 74.53, 55.39, 44.69, 44.39, 42.68, 37.51, 35.26, 35.11, 34.15, 32.64, 25.99, 22.64, 19.91, -0.40; IR (thin film) 3367, 2949, 2923, 3866, 2844, 1608, 1508, 1455, 1366, 1288, 1247, 1175, 1029, 834, 755, 739 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{26}H_{39}O_2Si$ [M+H$^+$] 411.2714, found 411.2708.



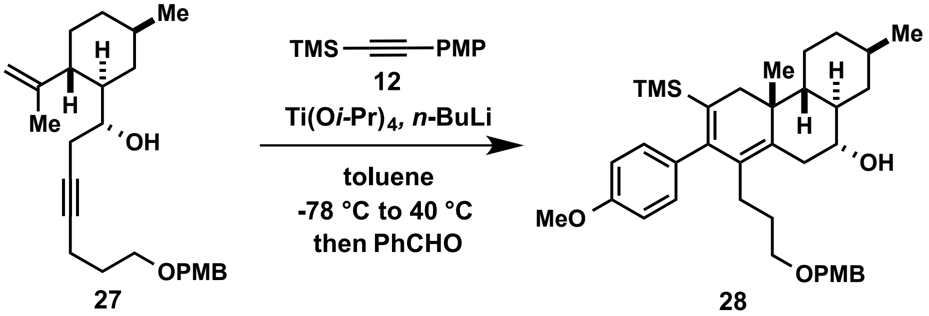
25 **26**


Selected nOe interactions

26

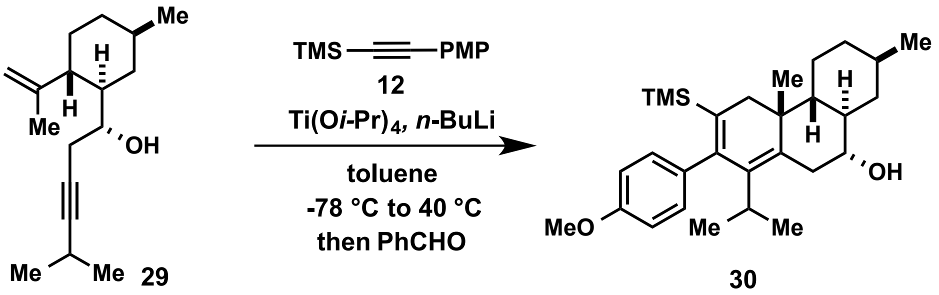
(4a*R*,4b*R*,7*R*,8a*R*,9*R*)-2-(4-methoxyphenyl)-1,4a,7-trimethyl-3-(trimethylsilyl)-4,4a,4b,5,6,7,8,8a,9,10-decahydrophenanthren-9-ol (26). To a solution of alkyne **12** (213 μL, 1.00 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (300 μL, 1.01 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.50 M in hexanes, 0.80 mL, 2.00 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. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **25** (66.5 mg, 0.302 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (0.13 mL, 0.330 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (17 h). To this mixture, a solution of benzaldehyde (150 μL, 1.47 mmol) in PhMe (5.0 mL) was added at rt and stirred for 1.5 h before the reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **26** (90.9 mg, 71%) as colorless oil.

Spectral data for **26**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.03 (1H, br-s), 6.87 (1H, br-s), 6.82 (2H, d, *J* = 7.7 Hz), 3.81 (3H, s), 3.63 (1H, t, *J* = 4.8 Hz), 2.54 (1H, d, *J* = 14.3 Hz), 2.32 (1H, dd, *J* = 14.3, 5.1 Hz), 2.18-2.13 (1H, m), 2.04 (2H, ABq, *J* = 16.1 Hz), 1.77-1.71 (1H, m), 1.70-1.66 (1H, m), 1.51 (1H, br-s), 1.45 (3H, s), 1.39-1.29 (2H, m), 1.20-1.13 (2H, m), 0.96 (3H, s), 0.90 (3H, d, *J* = 6.6 Hz), 0.89-0.81 (1H, m), 0.78 (1H, q, *J* = 12.1 Hz), -0.23 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.40, 148.14, 136.27, 135.69, 131.41, 130.85, 130.13, 127.52, 113.18, 112.86, 75.77, 55.32, 45.46, 44.16, 42.76, 35.87, 35.35, 33.00, 32.70, 32.26, 26.31, 22.65, 19.69, 16.02, -0.50; IR (thin film) 3335, 3030, 2949, 2924, 2865, 1609, 1572, 1507, 1455, 1363, 1284, 1173, 1066, 1038, 1012, 912, 865, 741 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{27}H_{41}O_2Si$ [M+H$^+$] 425.2870, found 425.2867.



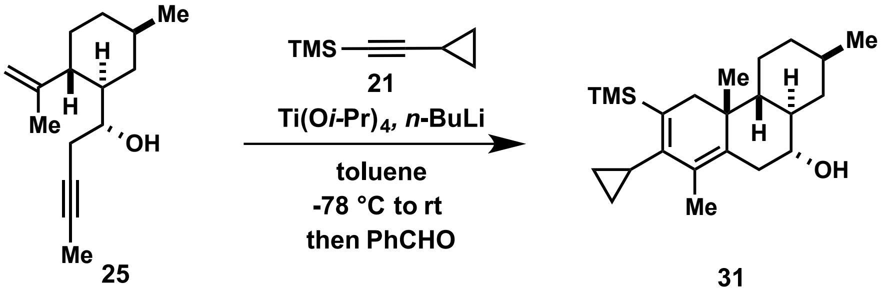
(4a*R*,4b*R*,7*R*,8a*R*,9*R*)-1-(3-((4-methoxybenzyl)oxy)propyl)-2-(4-methoxyphenyl)-4a,7-dimethyl-3-(trimethylsilyl)-4,4a,4b,5,6,7,8,8a,9,10-decahydrophenanthren-9-ol (28). To a solution of alkyne **12** (213 μL, 1.00 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (300 μL, 1.01 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.38 M in hexanes, 0.84 mL, 2.00 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. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **27** (103 mg, 0.268 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (125 μL, 0.295 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (16 h). After this period, the cooling bath was removed and the mixture was stirred at 40 °C for an additional 2.5 h. To this mixture, a solution of benzaldehyde (150 μL, 1.47 mmol) in PhMe (5.0 mL) was added at rt and stirred for 1.5 h before the reaction was quenched with saturated aqueous NH$_4$Cl. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous NaHCO$_3$, brine, and dried over Na$_2$SO$_4$. The solvent was removed *in vacuo* and the resulting crude mixture was purified via flash chromatography to afford **28** (95.9 mg, 61%) as colorless oil.

Spectral data for **28**: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.17 (2H, d, *J* = 8.4 Hz), 7.04 (1H, br-s), 6.88 (1H, br-s), 6.85 (2H, d, *J* = 8.4 Hz), 6.79 (2H, d, *J* = 8.8 Hz), 4.27 (2H, s), 3.79 (3H, s), 3.79 (3H, s), 3.57 (1H, t, *J* = 5.5 Hz), 3.20 (1H, dt, *J* = 9.5, 6.2 Hz), 3.14 (1H, dt, *J* = 9.5, 6.2 Hz), 2.53 (1H, d, *J* = 14.3 Hz), 2.31 (1H, dd, *J* = 14.3, 5.9 Hz), 2.18-2.12 (1H, m), 2.09 (1H, d, *J* = 15.8 Hz), 2.06-1.99 (1H, m), 1.94 (1H, d, *J* = 15.8 Hz), 1.94-1.88 (1H, m), 1.76-1.70 (1H, m), 1.69-1.63 (1H, m), 1.40-1.22 (4H, m), 1.16-1.10 (2H, m), 0.94 (3H, s), 0.90 (3H, d, *J* = 6.2 Hz), 0.87-0.79 (1H, m), 0.75 (1H, q, *J* = 12.1 Hz), -0.26 (9H, s); ^{13}C NMR (150 MHz, CDCl$_3$) δ 159.16, 158.42, 147.72, 137.53, 135.34, 132.03, 131.68, 131.45, 130.77, 130.62, 129.31, 113.77, 113.10, 112.77, 75.27, 72.09, 69.82, 55.38, 55.31, 45.15, 43.53, 42.76, 35.87, 35.33, 32.93, 32.60, 32.47, 30.20, 26.35, 25.01, 22.67, 19.75, -0.51; IR (thin film) 3421, 2949, 2924, 2858, 1609, 1509, 1456, 1363, 1246, 1173, 1100, 1037, 863, 835 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{37}H_{52}O_4SiNa$ [M+Na$^+$] 611.3527, found 611.3532.



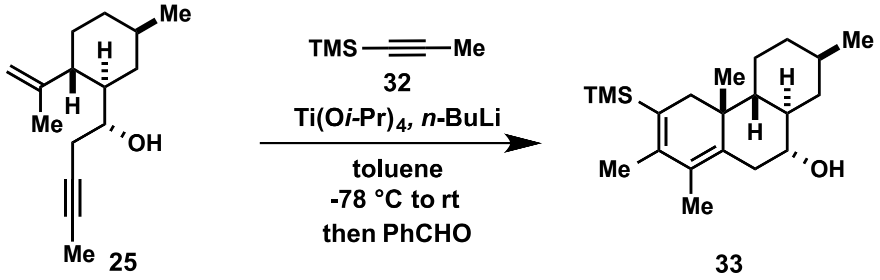
(4a*R*,4b*R*,7*R*,8a*R*,9*R*)-1-isopropyl-2-(4-methoxyphenyl)-4a,7-dimethyl-3-(trimethylsilyl)-4,4a,4b,5,6,7,8,8a,9,10-decahydrophenanthren-9-ol (30). To a solution of alkyne **12** (213 μL, 1.00 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (300 μL, 1.01 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.38 M in hexanes, 0.84 mL, 2.00 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. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **29** (74.5 mg, 0.300 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (140 μL, 0.333 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (16 h). After this period, the cooling bath was removed and the mixture was stirred at 40 °C for an additional 2.5 h. To this mixture, a solution of benzaldehyde (150 μL, 1.47 mmol) in PhMe (5.0 mL) was added at rt and stirred for 1.5 h before the reaction was quenched with saturated aqueous NH$_4$Cl. The organic layer was separated, and the aqueous was layer extracted with AcOEt. The combined organic extracts were washed with saturated aqueous NaHCO$_3$, brine, and dried over Na$_2$SO$_4$. The solvent was removed *in vacuo* and the resulting crude mixture was purified via flash chromatography to afford **30** (73.9 mg, 54%) as colorless oil.

Spectral data for **30**: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.03 (1H, br-d, *J* = 7.7 Hz), 6.87 (1H, br-d, *J* = 7.7 Hz), 6.81 (1H, br-d, *J* = 7.7 Hz), 6.87 (1H, br-d, *J* = 7.7 Hz), 3.81 (3H, s), 3.61 (1H, t, *J* = 5.5 Hz), 2.78 (1H, d, *J* = 14.7 Hz), 2.61-2.50 (1H, m), 2.33 (1H, dd, *J* = 14.7, 5.9 Hz), 2.18 (1H, br-d, *J* = 12.8 Hz), 2.12 (2H, ABq, *J* = 15.8 Hz), 1.73 (1H, br-d, *J* = 12.8 Hz), 1.68-1.64 (1H, m), 1.38-1.24 (3H, m), 1.20-1.10 (2H, m), 0.97 (3H, br-d, *J* = 7.0 Hz), 0.95 (3H, s), 0.90 (3H, d, *J* = 6.6 Hz), 0.86 (3H, d, *J* = 7.0 Hz), 0.87-0.80 (1H, m), 0.76 (1H, q, *J* = 12.1 Hz), -0.27 (9H, s); ^{13}C NMR (150 MHz, CDCl$_3$) δ 158.41, 148.69, 138.75, 137.75, 136.15, 132.07, 130.40, 112.97, 112.76, 75.58, 55.34, 45.04, 43.74, 42.76, 36.59, 35.35, 32.73, 32.62, 32.28, 28.54, 26.56, 23.43, 22.68, 22.16, 19.77, -0.35; IR (thin film) 3398, 2951, 2925, 2869, 1608, 1507, 1456, 1362, 1286, 1244, 1173, 1039, 869, 834 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{29}H_{45}O_2Si$ [M+H$^+$] 453.3183, found 453.3182.



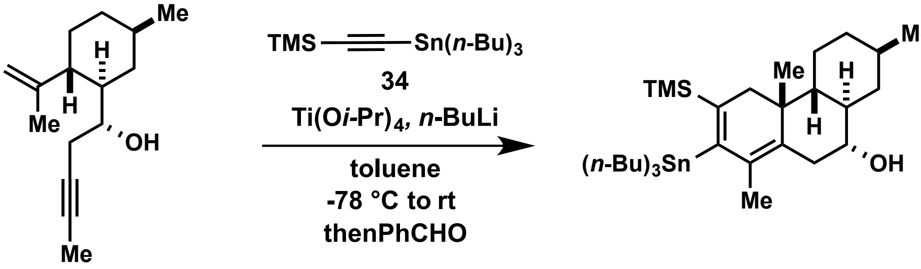
(4a*R*,4b*R*,7*R*,8a*R*,9*R*)-2-cyclopropyl-1,4a,7-trimethyl-3-(trimethylsilyl)-4,4a,4b,5,6,7,8,8a,9,10-decahydrophenanthren-9-ol (31). To a solution of alkyne **21** (163 μL, 1.00 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (300 μL, 1.01 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.50 M in hexanes, 0.80 mL, 2.00 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. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **25** (66.6 mg, 0.302 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (135 μL, 0.338 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (18 h). To this mixture, a solution of benzaldehyde (150 μL, 1.47 mmol) in PhMe (5.0 mL) was added at rt and stirred for 1.5 h before the reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **31** (76.9 mg, 71%) as colorless oil.

Spectral data for **31**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.57 (1H, t, *J* = 4.8 Hz), 2.54 (1H, dd, *J* = 14.3, 1.5 Hz), 2.24 (1H, dd, *J* = 14.3, 5.1 Hz), 2.11 (1H, ddd, *J* = 12.8, 6.2, 3.7 Hz), 1.92 (1H, dd, *J* = 16.5, 4.0 Hz), 1.92 (3H, s), 1.74 (1H, d, *J* = 16.5 Hz), 1.72-1.69 (1H, m), 1.67-1.62 (1H, m), 1.58-1.50 (2H, m), 1.38-1.29 (1H, m), 1.29-1.21 (1H, m), 1.13-1.04 (2H, m), 0.88 (3H, d, *J* = 6.2 Hz), 0.85-0.73 (3H, m), 0.73-0.66 (1H, m), 0.69 (3H, s), 1.59 (1H, ddd, *J* = 14.3, 5.1, 4.0 Hz), 0.18 (9H, s), 0.09-0.04 (1H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.58, 135.15, 131.69, 129.24, 75.46, 45.53, 44.19, 42.81, 35.39, 35.30, 34.26, 32.74, 31.58, 26.36, 22.62, 19.61, 15.05, 14.86, 10.93, 6.52, -0.33; IR (thin film) 3333, 3080, 2948, 2924, 2866, 1567, 1455, 1363, 1246, 1067, 1013, 911, 863, 834, 742 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{23}H_{39}OSi$ [M+H^{+}] 359.2765, found 359.2767.



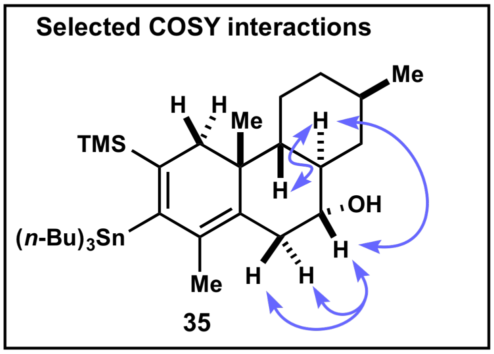
(4a*R*,4b*R*,7*R*,8a*R*,9*R*)-1,2,4a,7-tetramethyl-3-(trimethylsilyl)-4,4a,4b,5,6,7,8,8a,9,10-decahydrophenanthren-9-ol (33). To a solution of alkyne **32** (150 µL, 1.01 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (300 µL, 1.01 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.50 M in hexanes, 0.80 mL, 2.00 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. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **25** (66.1 mg, 0.300 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (135 µL, 0.338 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (23 h). To this mixture, a solution of benzaldehyde (150 µL, 1.47 mmol) in PhMe (5.0 mL) was added at rt and stirred for 1.25 h before the reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **33** (70.3 mg, 70%) as colorless oil.

Spectral data for **33**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.58 (1H, br-s), 2.55 (1H, dd, *J* = 14.3, 1.5 Hz), 2.27 (1H, dd, *J* = 14.3, 5.1 Hz), 2.14-2.09 (1H, m), 1.94 (1H, br-ddd, *J* = 15.9, 5.7, 3.3 Hz), 1.87 (3H, d, *J* = 2.6 Hz), 1.80 (1H, br-s), 1.77 (3H, d, *J* = 1.1 Hz), 1.73-1.67 (1H, m), 1.64-1.60 (1H, m), 1.36-1.27 (1H, m), 1.27-1.19 (2H, m), 1.13-1.04 (2H, m), 0.88 (3H, d, *J* = 6.2 Hz), 0.85-0.76 (1H, m), 0.80 (3H, s), 0.75 (1H, q, *J* = 12.1 Hz), 0.15 (9H, s); ^{13}C NMR (150 MHz, CDCl$_3$) δ 142.16, 136.07, 128.37, 127.18, 75.68, 45.44, 44.29, 42.77, 35.67, 35.38, 33.19, 32.71, 31.90, 26.17, 22.64, 20.10, 19.52, 14.58, 0.10; IR (thin film) 3330, 2948, 2924, 2864, 1570, 1455, 1363, 1247, 1092, 1065, 1011, 908, 872, 834, 750, 686, 637 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{21}H_{37}OSi$ [M+H$^+$] 333.2608, found 333.2616.

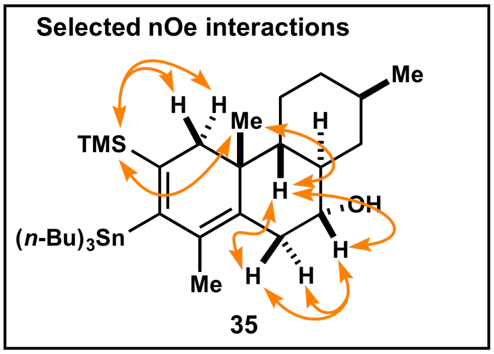


25

35


Selected COSY interactions

35

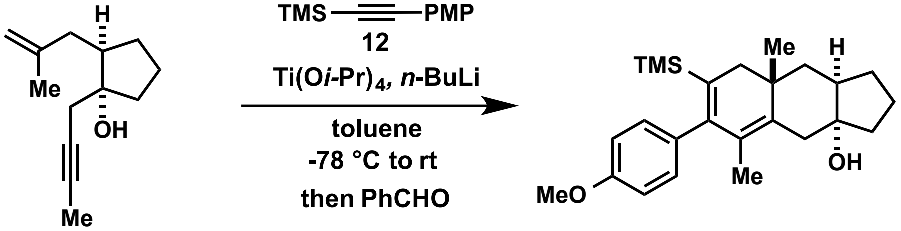

Selected nOe interactions

35

(4a*R*,4b*R*,7*R*,8a*R*,9*R*)-1,4a,7-trimethyl-2-(tributylstannyl)-3-(trimethylsilyl)-4,4a,4b,5,6,7,8,8a,9,10-decahydrophenanthren-9-ol (35). A solution of Ti(O*i*-Pr)$_4$ (300 μL, 1.01 mmol) in PhMe (6.0 mL) was cooled to -78 °C and *n*-BuLi (2.50 M in hexanes, 0.800 mL, 2.00 mmol) was added dropwise over the course of 5 min. After stirring at same temperature for 10 min, alkyne **34** was added and the flask was taken out of the cooling bath and allowed to warm to rt. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **25** (67.5 mg, 0.306 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (130 μL, 0.325 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (17 h). After this period, the cooling bath was removed and the mixture was stirred at 40 °C for an additional 2 h. To this mixture, a solution of benzaldehyde (150 μL, 1.47

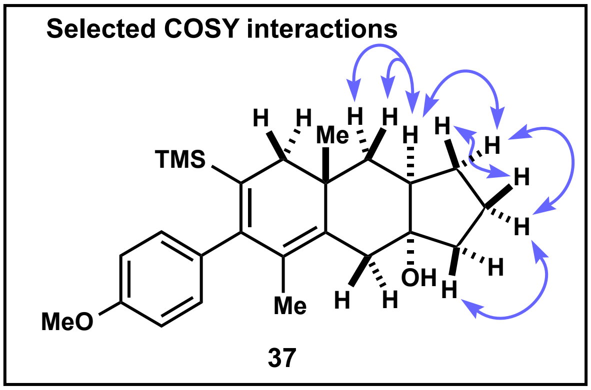
mmol) in PhMe (5.0 mL) was added at rt and stirred for 1.5 h before the reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, brine, and dried over Na_2SO_4. The solvent was removed *in vacuo* and the resulting crude mixture was purified via flash chromatography to afford **35** (104 mg, 56%) as colorless oil.

Spectral data for **35**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.61-3.55 (1H, m), 2.46 (1H, dd, *J* = 14.3, 1.1 Hz), 2.28 (1H, dd, *J* = 13.9, 4.8 Hz), 2.13-2.07 (1H, m), 1.87 (2H, ABq, *J* = 16.1 Hz), 1.82 (3H, d, *J* = 1.1 Hz), 1.72 (1H, dt, *J* = 12.5, 2.6 Hz), 1.68-1.64 (1H, m), 1.52-1.42 (6H, m), 1.37-1.28 (7H, m), 1.28-1.21 (1H, m), 1.14-1.04 (2H, m), 0.99-0.81 (20H, m), 0.78 (3H, s), 0.76 (1H, q, *J* = 12.1 Hz), 0.15 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.77, 147.44, 133.43, 131.78, 75.67, 45.54, 44.27, 42.83, 35.77, 35.45, 35.22, 32.79, 31.73, 29.32, 27.70, 26.67, 22.62, 19.92, 18.73, 13.83, 13.23, -0.27; IR (thin film) 3330, 2954, 2924, 2870, 2854, 1625, 1455, 1375, 1363, 1247, 1073, 1012, 908, 857, 835, 750, 698 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{32}H_{61}OSiSn$ [M+H$^+$] 609.3508, found 609.3514.

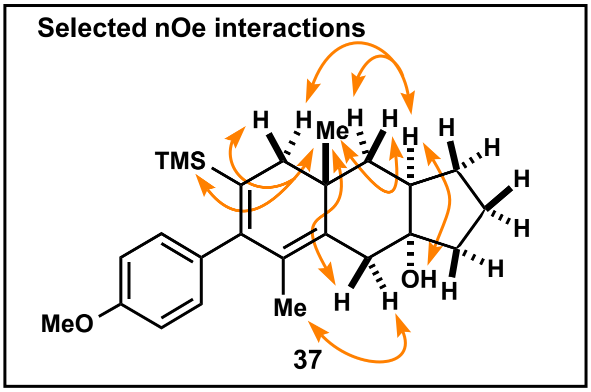


36

37


Selected COSY interactions

37


Selected nOe interactions

37

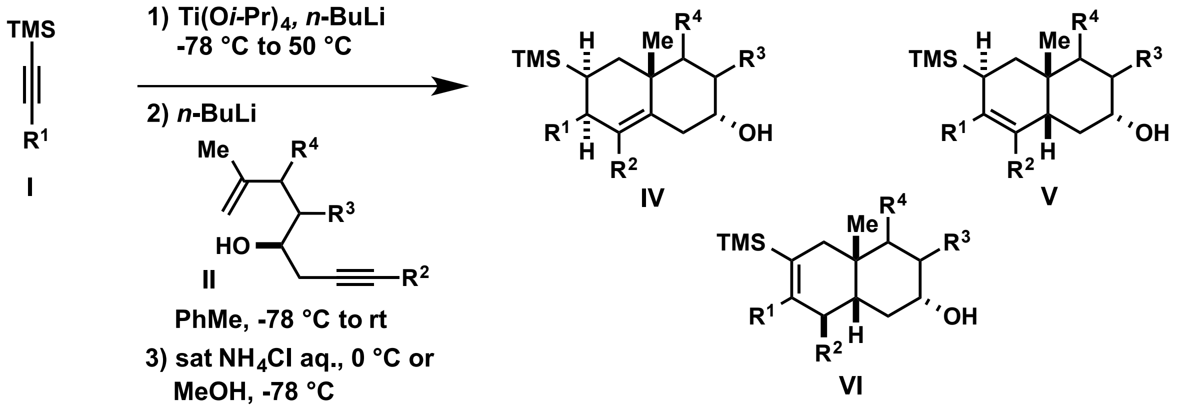
(±)-(3a*R*,8a*S*,9a*R*)-6-(4-methoxyphenyl)-5,8a-dimethyl-7-(trimethylsilyl)-1,2,3,4,8,8a,9,9a-octahydro-3a*H*-cyclopenta[*b*]naphthalen-3a-ol (37). To a solution of alkyne **12** (220 mL, 1.03

mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (300 mL, 1.01 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.49 M in hexanes, 0.80 mL, 2.00 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. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **36** (57.2 mg, 0.297 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (0.13 mL, 0.330 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (19.5 h). To this mixture, a solution of benzaldehyde (150 mL, 1.47 mmol) in PhMe (5.0 mL) was added at rt and stirred for 1 h before the reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **37** (67.4 mg, 57%) as a colorless oil.

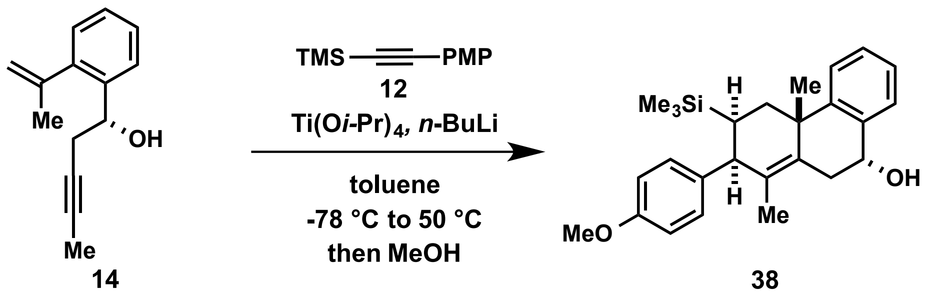
Spectral data for **37**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.03 (1H, br-s), 6.88 (1H, br-s), 6.82 (2H, d, *J* = 8.1 Hz), 3.81 (3H, s), 2.69 (1H, d, *J* = 13.6 Hz), 2.44 (1H, d, *J* = 16.1 Hz), 2.11 (1H, d, *J* = 13.6 Hz), 2.11-2.05 (1H, m), 1.96-1.86 (2H, m), 1.86 (1H, d, *J* = 16.1 Hz), 1.83-1.76 (1H, m), 1.71 (1H, br-s), 1.71-1.64 (1H, m), 1.57 (1H, ddd, *J* = 12.8, 9.9, 6.6 Hz), 1.45 (3H, d, *J* = 1.1 Hz), 1.40 (1H, dd, *J* = 13.9, 4.8 Hz), 1.25 (1H, t, *J* = 13.9 Hz), 1.18-1.10 (1H, m), 0.96 (3H, s), -0.24 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.43, 148.20, 137.28, 135.63, 132.02, 131.39, 130.27, 127.52, 113.18, 112.93, 82.97, 55.34, 46.02, 43.49, 40.76, 38.49, 37.43, 33.85, 32.59, 29.00, 25.13, 22.68, 15.82, -0.60

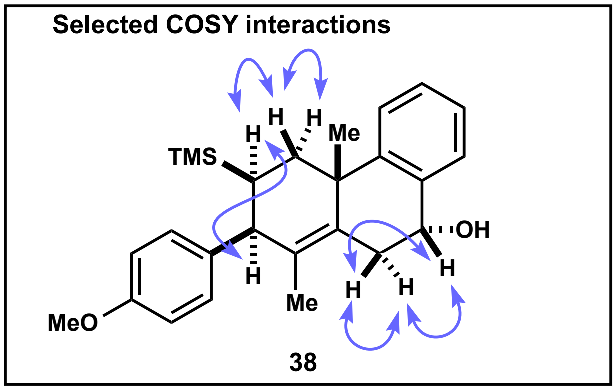
; IR (thin film) 3409, 2951, 2855, 1640, 1609, 1573, 1558, 1506, 1456, 1283, 1245, 1173, 1079, 1064, 1038, 912, 889, 857, 835, 757, 740 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{25}H_{37}O_2Si$ [M+H$^+$] 397.2557, found 397.2545.

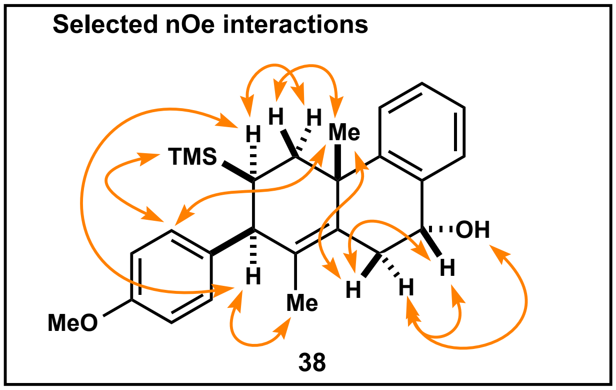
General procedure II (protic quench)



To a solution of alkyne **I** (1.00 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (1.00 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.50 M in hexanes, 0.80 mL, 2.00 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** (0.300 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (0.330 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 resulting reaction mixture was allowed to warm to rt overnight. The reaction mixture was then cooled to 0 °C (or -78 °C) and quenched with saturated aqueous NH$_4$Cl (or MeOH 3.0 mL). After warming to rt, the organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous NaHCO$_3$, brine, and dried over Na$_2$SO$_4$. The solvent was removed *in vacuo* and the resulting crude mixture was purified via flash chromatography to afford decalins **IV**, **V**, or **VI**.

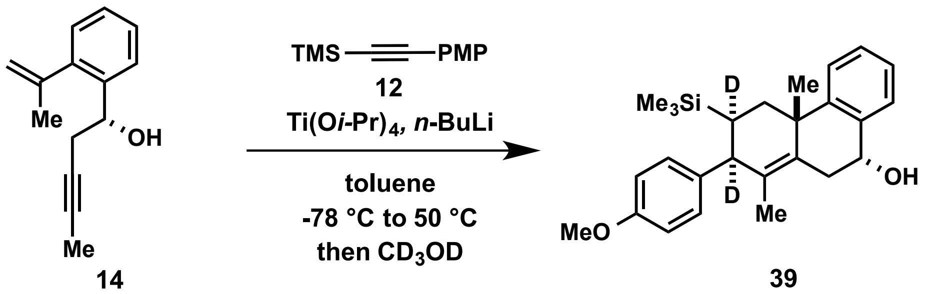






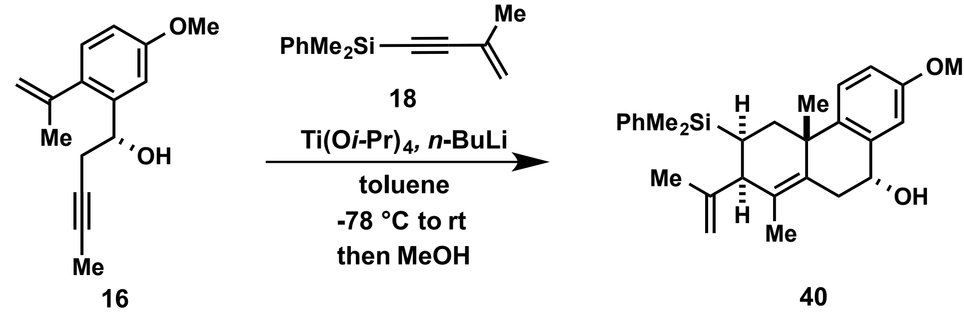
(±)-(2*R*,3*S*,4a*S*,9*R*)-2-(4-methoxyphenyl)-1,4a-dimethyl-3-(trimethylsilyl)-2,3,4,4a,9,10-hexahydrophenanthren-9-ol (38). To a solution of alkyne **12** (213 µL, 1.00 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (300 µL, 1.01 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.40 M in hexanes, 0.835 mL, 2.00 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. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **14** (60.1 mg, 0.300 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (135 µL, 0.324 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (12.5 h). After this period, the cooling bath was removed and the mixture was stirred at 50 °C for an additional 5 h. The reaction mixture was then cooled to -78 °C and quenched with MeOH. After warming to rt, saturated aqueous NH_4Cl was added, and stirred vigorously until the color of the mixture turned pale yellow. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **38** (66.4 mg, 54%) as a white solid.

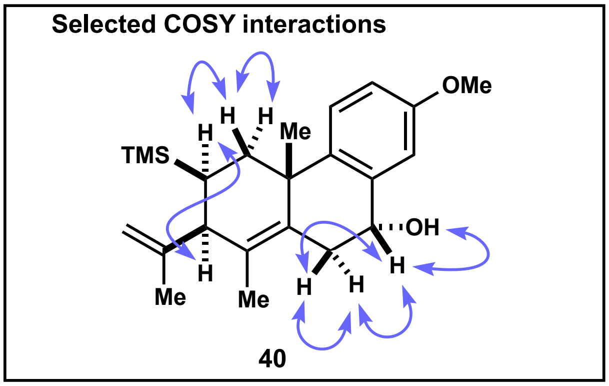
Spectral data for **38**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (1H, dd, J = 7.6, 0.9 Hz), 7.33 (1H, d, J = 7.6 Hz), 7.27 (1H, td, J = 7.6, 0.9 Hz), 7.22 (1H, td, J = 7.6, 0.9 Hz), 7.19 (2H, d, J = 8.5 Hz), 6.85 (2H, d, J = 8.5 Hz), 4.84 (1H, br-s), 3.81 (3H, s), 3.31 (1H, d, J = 4.6 Hz), 3.05 (1H, dd, J = 13.7, 2.1 Hz), 2.95 (1H, dd, J = 13.7, 4.0 Hz), 2.36 (1H, d, J = 14.3 Hz), 2.00 (1H, br-d, J = 8.9 Hz), 1.95 (1H, t, J = 14.3 Hz), 1.65 (3H, s), 1.43 (3H, s), 0.94 (1H, ddd, J = 14.3, 4.6, 1.2 Hz), -0.27 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.42, 146.15, 139.32, 134.64, 133.94, 131.62, 130.94, 130.84, 128.34, 126.45, 124.09, 113.44, 71.14, 55.35, 48.73, 40.63, 33.12, 32.62, 31.68, 26.54, 19.35, -2.59; IR (thin film) 3398, 3276, 3060, 2952, 2903, 2864, 2834, 1608, 1508, 1445, 1248, 1175, 1038, 865, 830, 760, 737 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{26}H_{34}O_2SiNa$ [M+Na$^+$] 429.2220, found 429.2235.

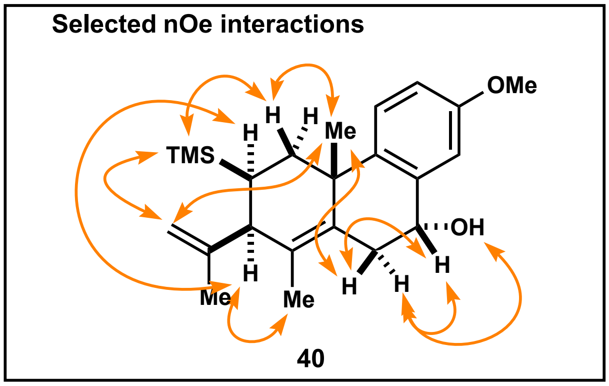


(±)-(2*R*,3*S*,4a*S*,9*R*)-2-(4-methoxyphenyl)-1,4a-dimethyl-3-(trimethylsilyl)-2,3,4,4a,9,10-hexahydrophenanthren-2,3-*d*$_2$-9-ol (39). To a solution of alkyne **12** (213 µL, 1.00 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (300 µL, 1.01 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.40 M in hexanes, 0.830 mL, 1.99 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. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **14** (61.2 mg, 0.305 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (140 µL, 0.336 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (12.5 h). After this period, the cooling bath was removed and the mixture was stirred at 50 °C for an additional 3 h. The reaction mixture was then cooled to -78 °C and quenched with CD_3OD. After warming to rt, saturated aqueous NH_4Cl was added, and stirred vigorously until the color of the mixture turned pale yellow. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **39** (59.5 mg, 48%) as a white solid.

Spectral data for **39**: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.37 (1H, dd, *J* = 7.6, 0.9 Hz), 7.33 (1H, d, *J* = 7.6 Hz), 7.27 (1H, td, *J* = 7.6, 0.9 Hz), 7.22 (1H, td, *J* = 7.6, 0.9 Hz), 7.19 (2H, d, *J* = 8.5 Hz), 6.85 (2H, d, *J* = 8.5 Hz), 4.84 (1H, br-s), 3.81 (3H, s), 3.05 (1H, dd, *J* = 13.7, 2.1 Hz), 2.95 (1H, dd, *J* = 13.7, 4.0 Hz), 2.34 (1H, d, *J* = 14.3 Hz), 1.98 (1H, d, *J* = 8.9 Hz), 1.94 (1H, d, *J* = 14.3 Hz), 1.64 (3H, s), 1.42 (3H, s), -0.28 (9H, s); HRMS (ESI-TOF) calculated for $C_{26}H_{32}D_2O_2SiNa$ [M+Na$^+$] 431.2346, found 431.2346.

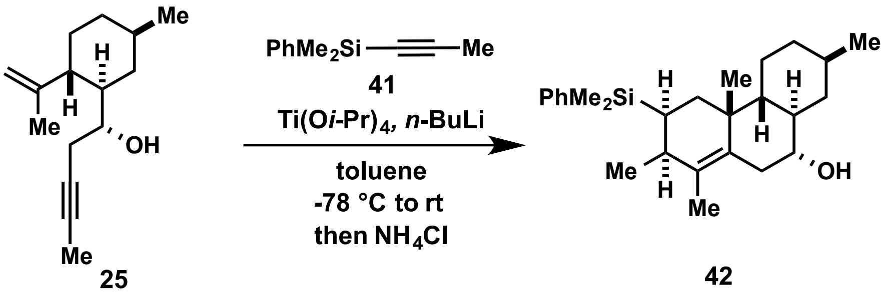


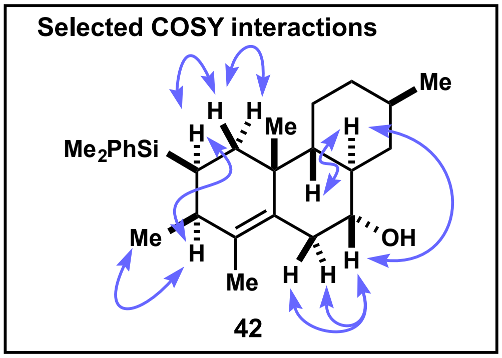

Selected COSY interactions

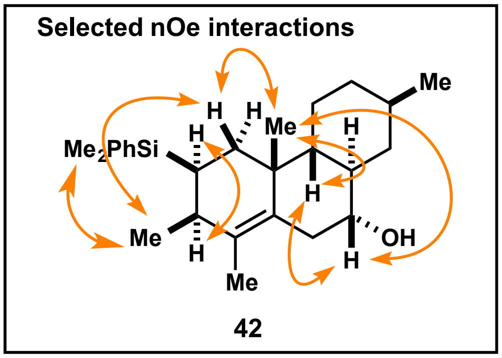

Selected nOe interactions

(±)-(2*R*,3*S*,4a*S*,9*R*)-3-(dimethyl(phenyl)silyl)-7-methoxy-1,4a-dimethyl-2-(prop-1-en-2-yl)-2,3,4,4a,9,10-hexahydrophenanthren-9-ol (40). To a solution of alkyne **18** (200 mg, 1.00 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (300 μL, 1.01 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.47 M in hexanes, 0.810 mL, 2.00 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. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **16** (69.1 mg, 0.300 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (135 μL, 0.333 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (17.5 h). The reaction mixture was then cooled to -78 °C and quenched with MeOH. After warming to rt, saturated aqueous NH_4Cl was added, and stirred vigorously until the color of the mixture turned pale yellow. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **40** (61.7 mg, 48%) as a white solid.

Spectral data for **40**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46-7.43 (2H, m), 7.39-7.35 (1H, m), 7.35-7.31 (2H, m), 6.86 (1H, d, *J* = 2.6 Hz), 6.65 (1H, d, *J* = 8.8 Hz), 6.59 (1H, dd, *J* = 8.8, 2.6 Hz), 4.91 (1H, s), 4.77 (1H, d, *J* = 2.2 Hz), 4.75 (1H, dd, *J* = 4.0, 2.6 Hz), 3.79 (3H, s), 2.99 (1H, dd, *J* = 13.9, 2.2 Hz), 2.89 (1H, dd, *J* = 13.9, 4.0 Hz), 2.76 (1H, d, *J* = 5.1 Hz), 2.30 (1H, d, *J* = 14.3 Hz), 1.94 (1H, d, *J* = 10.3 Hz), 1.90 (1H, t, *J* = 14.3 Hz), 1.69 (3H, s), 1.68 (3H, s), 1.21 (3H, s), 1.09 (1H, ddd, *J* = 13.9, 5.1, 1.5 Hz), 0.31 (3H, s), 0.30 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.85, 146.57, 140.35, 138.99, 137.81, 134.20, 132.46, 132.09, 128.81, 127.73, 125.24, 116.07, 114.78, 114.39, 71.32, 55.42, 50.76, 39.92, 32.93, 32.85, 32.83, 24.51, 23.10, 18.48, -3.67, -4.49; IR (thin film) 3330, 3068, 3049, 2952, 2908, 2861, 2834, 1634, 1608, 1575, 1496, 1463, 1427, 1370, 1305, 1291, 1247, 1229, 1113, 1040, 998, 898, 845, 815, 774, 736, 701 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{28}H_{36}O_2SiNa$ [M+Na$^+$] 455.2377, found 455.2379.




Selected COSY interactions


Selected nOe interactions

(2*R*,3*S*,4a*R*,4b*R*,7*R*,8a*R*,9*R*)-3-(dimethyl(phenyl)silyl)-1,2,4a,7-tetramethyl-2,3,4,4a,4b,5,6,7,8,8a,9,10-dodecahydrophenanthren-9-ol (42). To a solution of alkyne **41**[7] 6.64 (174 mg, 1.00 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (300 μL, 1.01 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.50 M in hexanes, 0.800 mL, 2.00 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. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **25** (67.5 mg, 0.306 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (130 μL, 0.325 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (20 h). The reaction mixture was then cooled to 0 °C and quenched with saturated aqueous NH$_4$Cl. The mixture was stirred vigorously until the color of the mixture turned pale yellow after which the organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous NaHCO$_3$, brine, and dried over Na$_2$SO$_4$. The solvent was removed *in vacuo* and the resulting crude mixture was purified via flash chromatography to afford **42** (74.2 mg, 61%) as a colorless oil.

Spectral data for **42**: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.55-7.52 (2H, m), 7.36-7.33 (3H, m), 3.61 (1H, td, *J* = 8.4, 4.0 Hz), 2.57 (1H, dd, *J* = 15.0, 7.3 Hz), 2.34 (1H, dd, *J* = 15.0, 4.0 Hz), 2.09-2.04 (1H, m), 1.99 (1H, ddd, *J* = 12.8, 5.5, 3.3 Hz), 1.83 (1H, d, *J* = 14.3 Hz), 1.67 (3H, s), 1.53-1.46 (1H, m), 1.40-1.35 (1H, m), 1.28 (1H, t, *J* = 14.3 Hz), 1.22-1.12 (1H, m), 1.10-1.05 (1H, m), 1.00-0.93 (1H, m), 0.98 (3H, s), 0.91 (3H, d, *J* = 7.0 Hz), 0.84 (3H, d, *J* = 6.6 Hz), 0.82-0.73 (2H, m), 0.68 (1H, qd, *J* = 12.1, 2.9 Hz), 0.55 (1H, q, J = 12.1 Hz), 0.31 (6H, s); ^{13}C NMR (150 MHz, CDCl$_3$) δ 139.28, 134.59, 134.06, 132.15, 128.82, 127.68, 74.94, 48.84, 47.33, 40.20, 38.15, 37.01, 36.21, 34.92, 33.92, 32.10, 30.02, 28.66, 26.22, 22.69, 18.94, 15.98, -3.87, -3.93; IR (thin film) 3331, 3068, 3048, 2952, 2920, 2865, 1454, 1427, 1369, 1249, 1190, 1113, 1069, 1057, 835, 817, 787, 733, 700 cm^{-1}; HRMS (ESI-TOF) calculated for C$_{18}$H$_{29}$ [(M-H$_2$O-Me$_2$PhSi+H)+H$^+$] 245.2264, found 245.2267.

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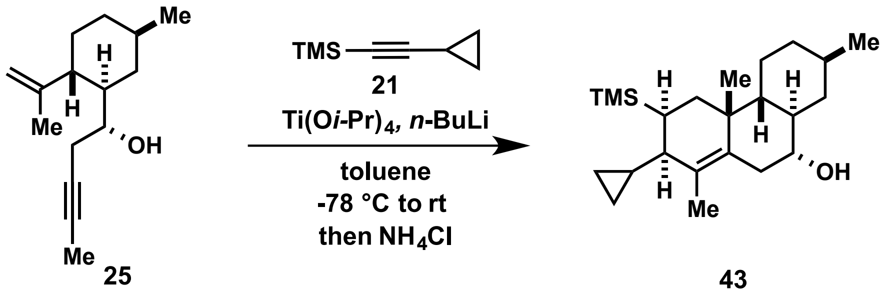
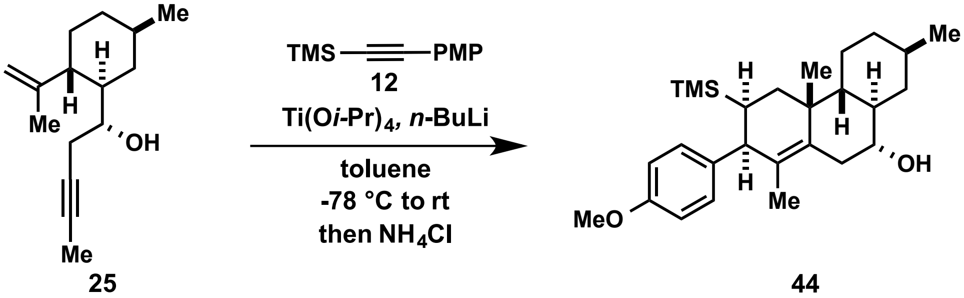
[7] Kubota, K.; Yamamoto, E.; Ito, H. *Adv. Synth. Catal.* **2013**, *355,* 3527-3531.



(2*R*,3*S*,4a*R*,4b*R*,7*R*,8a*R*,9*R*)-2-cyclopropyl-1,4a,7-trimethyl-3-(trimethylsilyl)-2,3,4,4a,4b,5,6,7,8,8a,9,10-dodecahydrophenanthren-9-ol (43). To a solution of alkyne **21** (165 μL, 1.01 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (300 μL, 1.01 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.50 M in hexanes, 0.800 mL, 2.00 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. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **25** (66.1 mg, 0.300 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (135 μL, 0.338 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (18 h). The reaction mixture was then cooled to 0 °C and quenched with saturated aqueous NH_4Cl. The mixture was stirred vigorously until the color of the mixture turned pale yellow after which the organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **43** (58.2 mg, 54%) as a colorless oil.

Spectral data for **43**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.61 (1H, ddd, *J* = 8.1, 7.7, 3.3 Hz), 2.51 (1H, dd, *J* = 15.0, 7.0 Hz), 2.44 (1H, dd, *J* = 15.0, 3.3 Hz), 2.03 (1H, ddd, *J* = 12.8, 5.9, 3.0 Hz), 1.96 (1H, d, *J* = 14.7 Hz), 1.79 (3H, s), 1.81-1.72 (2H, m), 1.56 (1H, dd, *J* = 8.8, 3.7 Hz), 1.46 (1H, t, *J* = 14.7 Hz), 1.29-1.21 (1H, m), 1.16 (1H, qd, *J* = 12.5, 2.9 Hz), 1.05 (3H, s), 1.02-0.96 (1H, m), 0.90-0.78 (3H, m), 0.87 (3H, d, *J* = 6.6 Hz), 0.71-0.65 (1H, m), 0.61 (1H, q, *J* = 12.1 Hz), 0.50-0.45 (1H, m), 0.42-0.37 (1H, m), 0.34-0.28 (1H, m), 0.16-0.12 (1H, m), 0.04 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 134.12, 132.90, 75.74, 48.79, 47.10, 46.27, 40.89, 38.42, 36.16, 34.30, 33.66, 32.26, 30.61, 29.23, 28.14, 22.62, 21.48, 13.18, 4.69, 4.51, -1.54; IR (thin film)

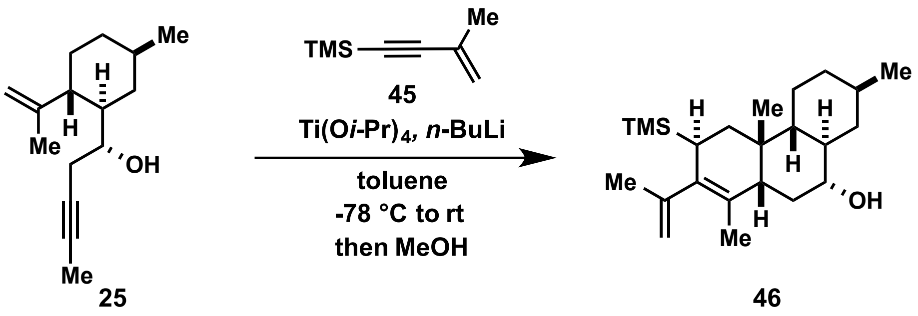
3369, 3082, 3006, 2949, 2923, 2865, 1455, 1374, 1247, 1070, 1049, 1020, 864, 835, 738 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{20}H_{31}$ [(M-H_2O-TMS+H)+H^+] 271.2420, found 271.2427.

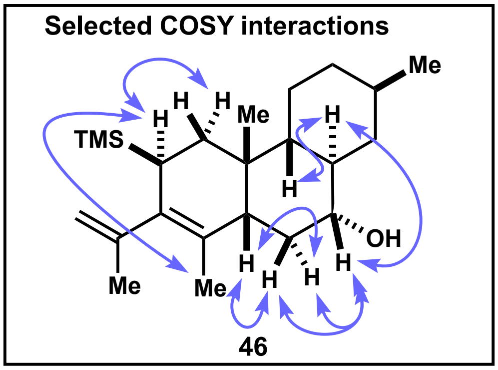


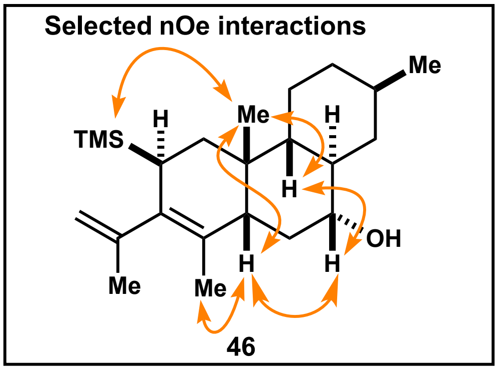
(2*R*,3*S*,4a*R*,4b*R*,7*R*,8a*R*,9*R*)-2-(4-methoxyphenyl)-1,4a,7-trimethyl-3-(trimethylsilyl)-2,3,4,4a,4b,5,6,7,8,8a,9,10-dodecahydrophenanthren-9-ol (44). To a solution of alkyne **12** (215 μL, 1.01 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (300 μL, 1.01 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.50 M in hexanes, 0.800 mL, 2.00 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. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **25** (67.8 mg, 0.308 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (135 μL, 0.338 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (22.5 h). The reaction mixture was then cooled to 0 °C and quenched with saturated aqueous NH_4Cl. The mixture was stirred vigorously until the color of the mixture turned pale yellow after which the organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **44** (89.4 mg, 68%) as a colorless oil.

Spectral data for **44**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10 (2H, d, *J* = 8.4 Hz), 6.78 (2H, d, *J* = 8.4 Hz), 3.78 (3H, s), 3.73 (1H, ddd, *J* = 9.2, 8.4, 4.4 Hz), 3.24 (1H, d, *J* = 4.8 Hz), 2.77 (1H, dd, *J* = 15.4, 8.4 Hz), 2.42 (1H, dd, *J* = 15.4, 4.4 Hz), 2.06 (1H, ddd, *J* = 12.8, 5.5, 3.3 Hz), 1.86-1.75 (3H, m), 1.52 (3H, s), 1.41 (1H, t, *J* = 14.7 Hz), 1.36-1.29 (1H, m), 1.24 (1H, qd, *J* = 12.5, 2.9

Hz), 1.19 (3H, s), 1.14-1.07 (2H, m), 0.95 (1H, td, J = 12.1, 3.7 Hz), 0.89 (3H, d, J = 6.2 Hz), 0.86 (1H, qd, J = 12.5, 2.9 Hz), 0.64 (1H, q, J = 12.1 Hz), -0.29 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.27, 135.19, 133.47, 131.85, 130.88, 113.30, 74.52, 55.34, 49.57, 48.43, 47.53, 39.91, 37.66, 36.40, 35.28, 33.98, 32.25, 30.29, 29.22, 27.32, 22.72, 19.20, -2.37; IR (thin film) 3339, 2948, 2923, 2865, 1608, 1580, 1501, 1456, 1374, 1300, 1250, 1038, 864, 842, 739 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{24}H_{32}O$ [(M-H_2O-TMS+H)+H$^+$] 337.2526, found 337.2525.

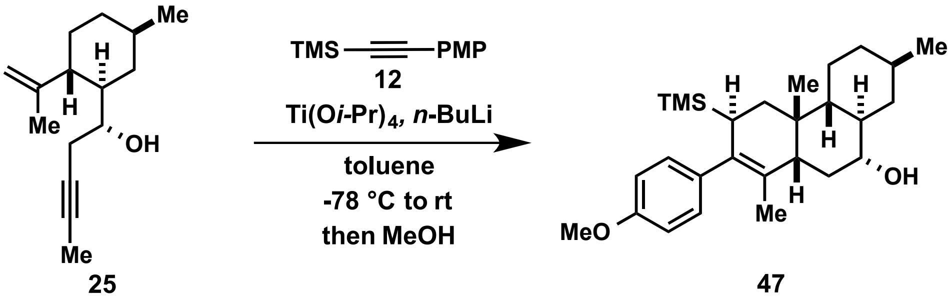


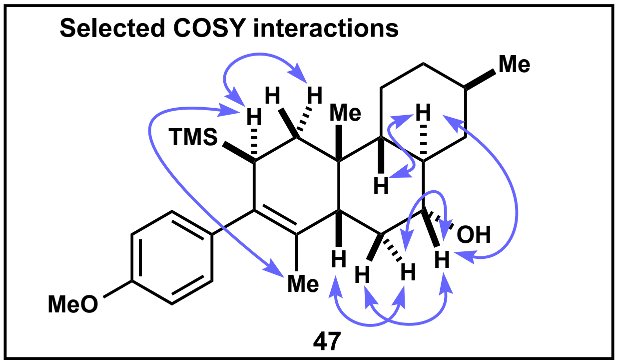


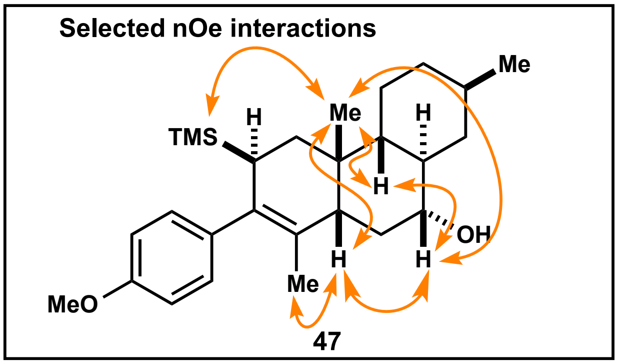


(3*S*,4a*R*,4b*R*,7*R*,8a*R*,9*R*,10a*S*)-1,4a,7-trimethyl-2-(prop-1-en-2-yl)-3-(trimethylsilyl)-3,4,4a,4b,5,6,7,8,8a,9,10,10a-dodecahydrophenanthren-9-ol (46). To a solution of alkyne **45** (180 μL, 1.02 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (300 μL, 1.01 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.47 M in hexanes, 0.810 mL, 2.00 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. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **25** (66.1 mg, 0.300 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (135 μL, 0.333 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (20.5 h). The reaction mixture was then cooled to -78 °C and quenched with MeOH. After warming to rt, saturated aqueous NH_4Cl was added, and stirred vigorously until the color of the mixture turned pale yellow. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **46** (58.6 mg, 54%) as a pale yellow oil.

Spectral data for **46**: ^{1}H NMR (600 MHz, C_6D_6) δ 5.00-4.98 (1H, m), 4.77 (1H, dd, *J* = 2.6, 0.7 Hz), 2.99 (1H, ddd, *J* = 11.4, 9.9, 4.4 Hz), 2.29 (1H, ddd, *J* = 12.8, 5.5, 3.3 Hz), 1.96 (1H, dt, *J* = 12.8, 4.0 Hz), 1.85-1.78 (2H, m), 1.74 (3H, s), 1.73 (3H, d, *J* = 1.8 Hz), 1.73-1.68 (2H, m), 1.44 (1H, ddd, *J* = 12.5, 3.7, 1.1 Hz), 1.40 (1H, dd, *J* = 12.5, 1.5 Hz), 1.31-1.22 (1H, m), 1.22-1.03 (3H, m), 0.97 (3H, d, *J* = 6.6 Hz), 0.94 (3H, s), 0.89-0.79 (1H, m), 1.70 (1H, td, *J* = 11.7, 2.9 Hz), 0.49 (1H, q, *J* = 12.1 Hz), 0.16 (9H, s); ^{13}C NMR (150 MHz, C_6D_6) δ 146.91, 134.10, 127.19, 114.48, 75.02, 51.10, 48.69, 44.45, 39.50, 38.37, 36.00, 34.21, 32.37, 26.62, 26.33, 26.15, 24.37, 23.37, 23.11, 19.81, 0.86; IR (thin film) 3339, 3075, 2945, 2867, 2844, 1648, 1454, 1375, 1247, 1049, 997, 898, 838, 741, 684 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{20}H_{31}$ [(M-H_2O-TMS+H)+H^+] 271.2420, found 271.2422.

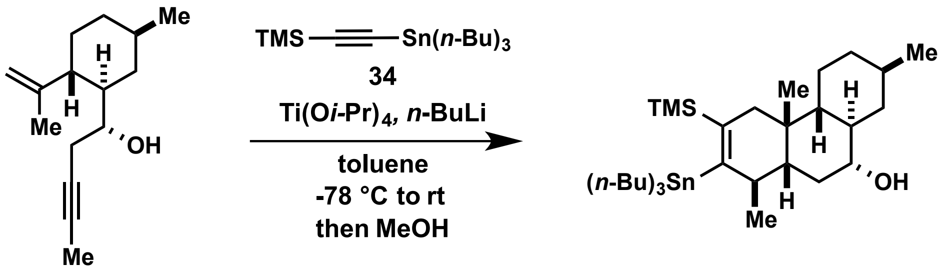



Selected COSY interactions

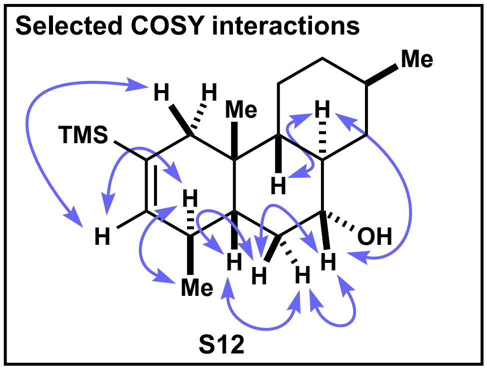

Selected nOe interactions

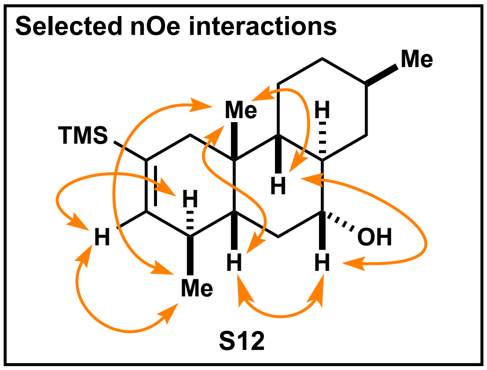
(3*S*,4a*R*,4b*R*,7*R*,8a*R*,9*R*,10a*S*)-2-(4-methoxyphenyl)-1,4a,7-trimethyl-3-(trimethylsilyl)-3,4,4a,4b,5,6,7,8,8a,9,10,10a-dodecahydrophenanthren-9-ol (47). To a solution of alkyne **12** (215 μL, 1.01 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (300 μL, 1.01 mmol) at rt. The mixture was cooled to -78 °C and *n*-BuLi (2.30 M in hexanes, 0.870 mL, 2.00 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. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **25** (68.0 mg, 0.309 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (140 μL, 0.322 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (18 h). The reaction mixture was then cooled to -78 °C and quenched with MeOH. After warming to rt, saturated aqueous NH$_4$Cl was added, and stirred vigorously until the color of the mixture turned pale yellow. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous NaHCO$_3$, brine, and dried over Na$_2$SO$_4$. The solvent was removed *in vacuo* and the resulting crude mixture was purified via flash chromatography to afford **47** (84.1 mg, 64%) as a pale yellow oil.

Spectral data for **47**: ^{1}H NMR (600 MHz, C$_6$D$_6$) δ 7.02 (2H, d, *J* = 8.8 Hz), 6.82 (2H, d, *J* = 8.8 Hz), 3.34 (3H, s), 3.04 (1H, ddd, *J* = 11.4, 9.9, 4.4 Hz), 2.33 (1H, ddd, *J* = 12.8, 5.5, 3.7 Hz), 2.07 (1H, dd, *J* = 9.5, 2.2 Hz), 2.02-1.96 (1H, m), 1.78-1.71 (2H, m), 1.62 (3H, d, *J* = 2.6 Hz), 1.55 (1H, dd, *J* = 12.5, 3.3 Hz), 1.51 (1H, d, *J* = 13.6 Hz), 1.35 (1H, td, *J* = 12.5, 11.4 Hz), 1.33-1.22 (2H, m), 1.14 (1H, qd, *J* = 12.5, 3.3 Hz), 1.05 (3H, s), 0.98 (3H, d, *J* = 6.6 Hz), 0.91-0.83 (1H, m), 0.76 (1H, td, *J* = 11.7, 2.6 Hz), 0.52 (1H, q, *J* = 12.1 Hz), -0.11 (9H, s); ^{13}C NMR (150 MHz, C$_6$D$_6$) δ 158.70, 136.23, 132.19, 130.96, 129.58, 113.66, 75.06, 54.76, 51.11, 48.98, 44.48, 39.54, 38.58, 36.04, 34.24, 32.39, 30.67, 26.67, 26.26, 24.83, 23.12, 20.14, 0.73; IR (thin film) 3348, 2945, 2866, 2841, 1607, 1509, 1455, 1286, 1247, 1174, 1036, 837, 740 cm^{-1}; HRMS (ESI-TOF) calculated for C$_{24}$H$_{33}$O [(M-H$_2$O-TMS+H)+H$^+$] 337.2526, found 337.2526.



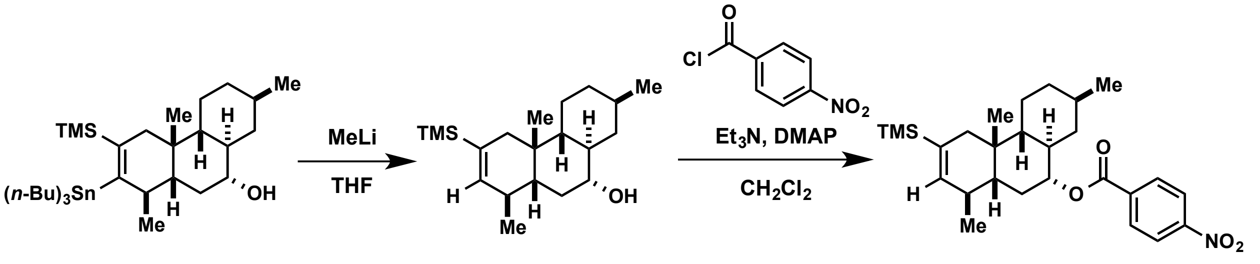
25 **48**



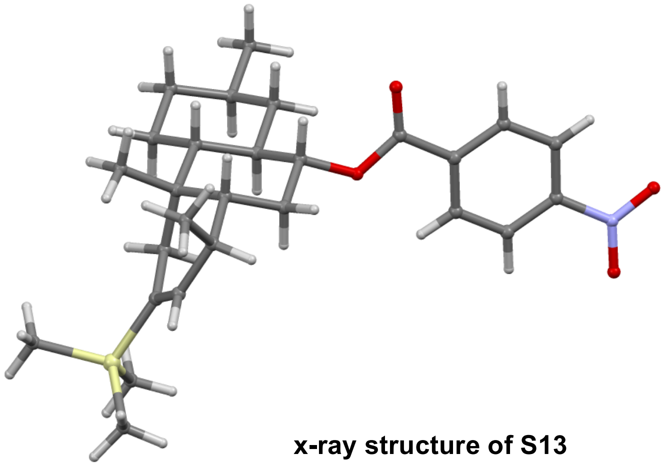


(1*R*,4a*R*,4b*R*,7*R*,8a*R*,9*R*,10a*R*)-1,4a,7-trimethyl-2-(tributylstannyl)-3-(trimethylsilyl)-1,4,4a,4b,5,6,7,8,8a,9,10,10a-dodecahydrophenanthren-9-ol (48). A solution of Ti(O*i*-Pr)$_4$ (300 µL, 1.01 mmol) in PhMe (6.0 mL) was cooled to -78 °C and *n*-BuLi (2.47 M in hexanes, 0.800 mL, 2.00 mmol) was added dropwise over the course of 5 min. After stirring at same temperature for 10 min, alkyne **34** was added and the flask was taken out of the cooling bath and allowed to warm to rt. The reaction mixture was then heated to 50 °C for 1 h and allowed to cool to rt before it was placed into a -78 °C cooling bath. In the meantime, enyne **25** (64.0 mg, 0.290 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (135 µL, 0.325 mmol) at -78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise to the above black Ti-alkyne complex solution at -78 °C. The resulting reaction mixture was allowed to warm to rt overnight (16.5 h). The reaction mixture was then cooled to -78 °C and quenched with MeOH. After warming to rt, saturated aqueous NaHCO$_3$ was added, and stirred vigorously until the color of the mixture turned pale yellow. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous NaHCO$_3$, brine, and dried over Na$_2$SO$_4$. The solvent was removed *in vacuo* and the resulting crude mixture was purified via flash chromatography to afford **48** (76.9 mg, 43%) as a pale yellow oil.

Spectral data for **48**: ^{1}H NMR (600 MHz, CDCl$_3$) δ 3.17 (1H, td, *J* = 10.3, 4.4 Hz), 2.15 (1H, ddd, *J* = 12.5, 5.1, 2.9 Hz), 2.11-2.05 (1H, m), 2.02 (1H, d, *J* = 16.9 Hz), 1.84 (1H, ddd, *J* = 12.8, 6.2, 2.9 Hz), 1.80 (1H, d, *J* = 16.9 Hz), 1.78-1.73 (1H, m), 1.60 (1H, ddd, *J* = 12.1, 4.0, 3.7 Hz), 1.49-1.40 (6H, m), 1.38-1.23 (9H, m), 1.23-1.13 (1H, m), 1.18 (3H, d, *J* = 7.3 Hz), 1.06-0.97 (1H, m), 0.93-0.81 (23H, m), 0.73 (1H, td, *J* = 11.4, 2.6 Hz), 0.56 (1H, q, *J* = 11.8 Hz), 0.11 (9H, s); ^{13}C NMR (150 MHz, CDCl$_3$) δ 154.25, 144.00, 75.13, 50.32, 46.25, 46.10, 44.56, 41.22, 39.08, 35.75, 33.82, 33.63, 32.15, 29.41, 27.68, 25.70, 25.26, 23.91, 22.77, 13.83, 12.88, 0.65; IR (thin film) 3332, 2953, 2920, 2869, 2854, 1455, 1376, 1247, 1059, 1047, 1033, 998, 859, 835, 754, 666 cm^{-1}; Reasonable HRMS (ESI-TOF) was not observed due to a fragmentation under conditions.



48 **S12** **S13**



x-ray structure of S13

(1*R*,4a*S*,4b*R*,7*R*,8a*R*,9*R*,10a*R*)-1,4a,7-trimethyl-3-(trimethylsilyl)-1,4,4a,4b,5,6,7,8,8a,9,10,10a-dodecahydrophenanthren-9-yl 4-nitrobenzoate (S13). To a solution of tricycle **48** (70.0 mg, 0.115 mmol) in THF (5.0 mL) was added MeLi (1.60 M in Et$_2$O, 0.200 mL, 0.320 mmol) at -78 °C. The mixture was then warmed to -30 °C over 1 h and an additional 0.480 mmol of MeLi was added (1.60 M in Et$_2$O, 0.300 mL). The resulting solution was warmed to rt, and stirred for 3 h prior to being quenched with saturated aqueous NH$_4$Cl. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous NaHCO$_3$, brine, and dried over Na$_2$SO$_4$. The solvent was removed *in vacuo* and the resulting crude mixture was purified via flash chromatography to afford **S12** (29.3 mg) with small amount of impurity. This mixture was used for the next reaction without further purification. To a solution of **S12** in CH_2Cl_2 at 0 °C was added triethylamine (77 μL, 0.548 mmol), 4-nitrobenzoyl chloride (50.9 mg, 0.274 mmol) and a catalytic amount of DMAP (a spatula tip). After stirring at rt for 14.5 h, the reaction mixture was diluted with AcOEt and quenched with saturated aqueous $NaHCO_3$. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, 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 **S13** (34.4 mg, 64% over 2 steps) as a colorless oil. **S13** was recrystallized from MeOH to give colorless cubic crystals.

Spectral data for **S12**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.81-5.78 (1H, m), 3.20 (1H, td, *J* = 10.4, 4.6 Hz), 2.19-2.13 (1H, m), 1.98 (1H, dt, *J* = 17.1, 2.8 Hz), 1.91-1.81 (2H, m), 1.79-1.73 (1H, m), 1.64 (1H, ddd, *J* = 12.3, 4.5, 3.7 Hz), 1.57 (1H, d, *J* = 17.1 Hz), 1.44 (1H, br-s), 1.40-1.27 (2H, m), 1.26-1.16 (2H, m), 1.14 (3H, d, *J* = 7.9 Hz), 1.05 (1H, qd, *J* = 12.5, 3.1 Hz), 0.90 (3H, d, *J* = 6.4 Hz), 0.87 (3H, s), 0.86-0.75 (2H, m), 0.57 (1H, q, *J* = 11.9 Hz), 0.03 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.60, 133.50, 75.31, 50.13, 45.52, 44.44, 41.14, 39.30, 39.17, 35.73, 34.79, 32.11, 28.59, 25.52, 24.88, 22.79, 22.27, -2.10; IR (thin film) 3324, 2949, 2920, 2867, 1622, 1452, 1376, 1246, 1044, 865, 830, 744 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{20}H_{35}Si$ [$M-H_2O+H^+$] 303.2503, found 303.2502.

Spectral data for **S13**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (2H, d, *J* = 8.8 Hz), 8.21 (2H, d, *J* = 8.8 Hz), 5.80 (1H, s), 4.76 (1H, td, *J* = 11.0, 4.4 Hz), 2.04 (1H, dt, *J* = 17.2, 2.6 Hz), 1.93-1.86 (3H, m), 1.83 (1H, dt, *J* = 12.5, 4.0 Hz), 1.81-1.76 (1H, m), 1.64 (1H, d, *J* = 17.2 Hz), 1.65-1.59 (1H, m), 1.48 (1H, dt, *J* = 12.8, 12.1 Hz), 1.38 (1H, dd, *J* = 13.9, 2.9 Hz), 1.39-1.32 (1H, m), 1.16 (3H, d, *J* = 7.7 Hz), 1.12 (1H, qd, *J* = 12.5, 3.3 Hz), 0.97 (1H, td, *J* = 11.4, 2.6 Hz), 0.92 (3H, s), 0.92-0.86 (1H, m), 0.85 (3H, d, *J* = 6.6 Hz), 0.64 (1H, q, *J* = 12.1 Hz), 0.05 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.65, 150.57, 138.60, 136.35, 133.42, 130.80, 123.61, 79.52, 50.27, 45.29, 41.38, 39.15, 38.98, 37.02, 35.55, 34.72, 31.98, 28.50, 25.53, 24.79, 22.64, 22.19, -2.08; IR (thin film) 2949, 2923, 2869, 1721, 1607, 1529, 1454, 1348, 1276, 1247, 1121, 1102, 1030, 1016, 867, 832, 741, 720 cm^{-1}; HRMS (EI-TOF) calculated for $C_{27}H_{39}NO_4Si$ [M^+] 469.2648, found 469.2657.

3. Spectral Data

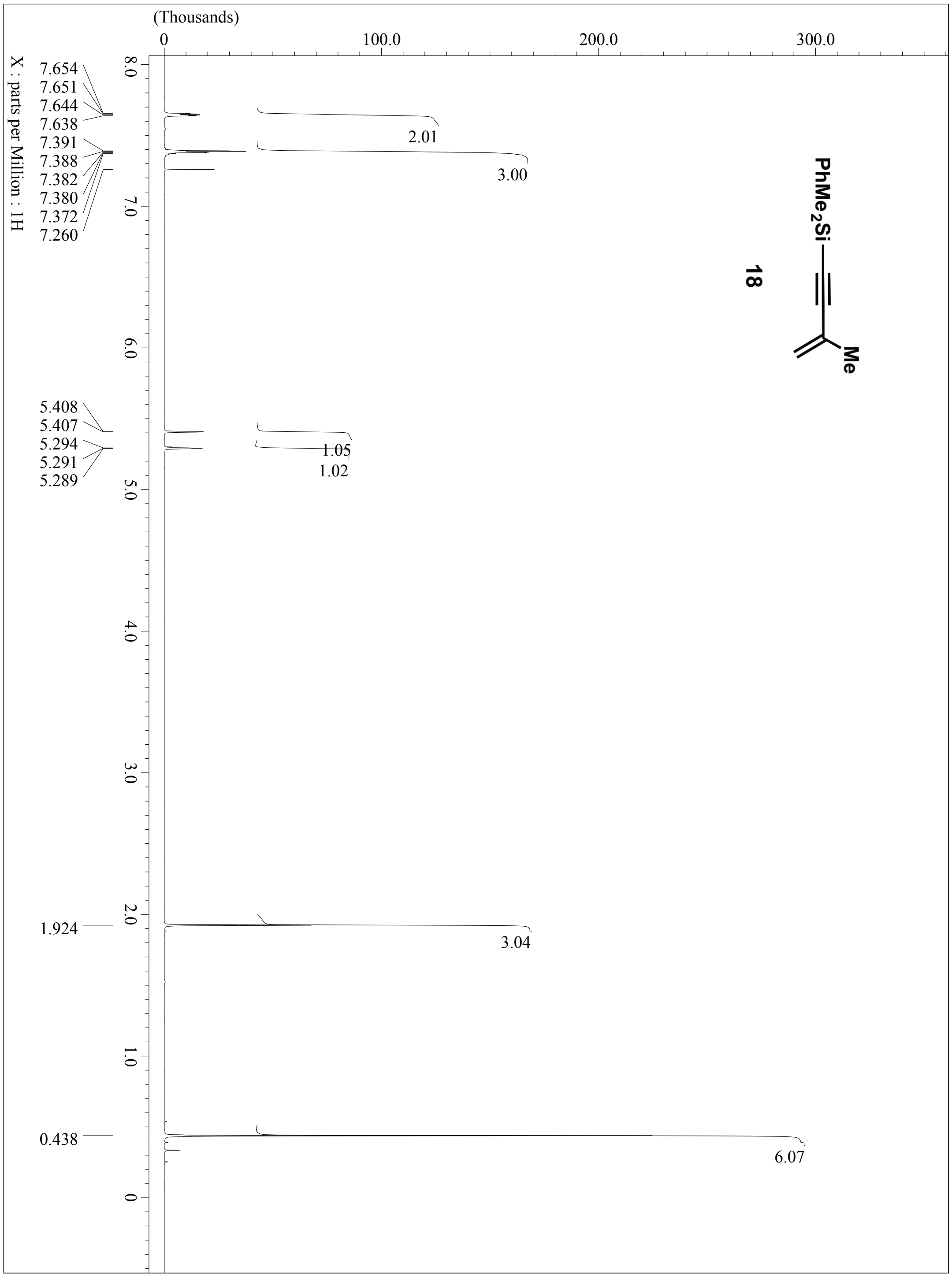


Figure S1: ^{1}H NMR (600 MHz, CDCl$_3$) of **18**.

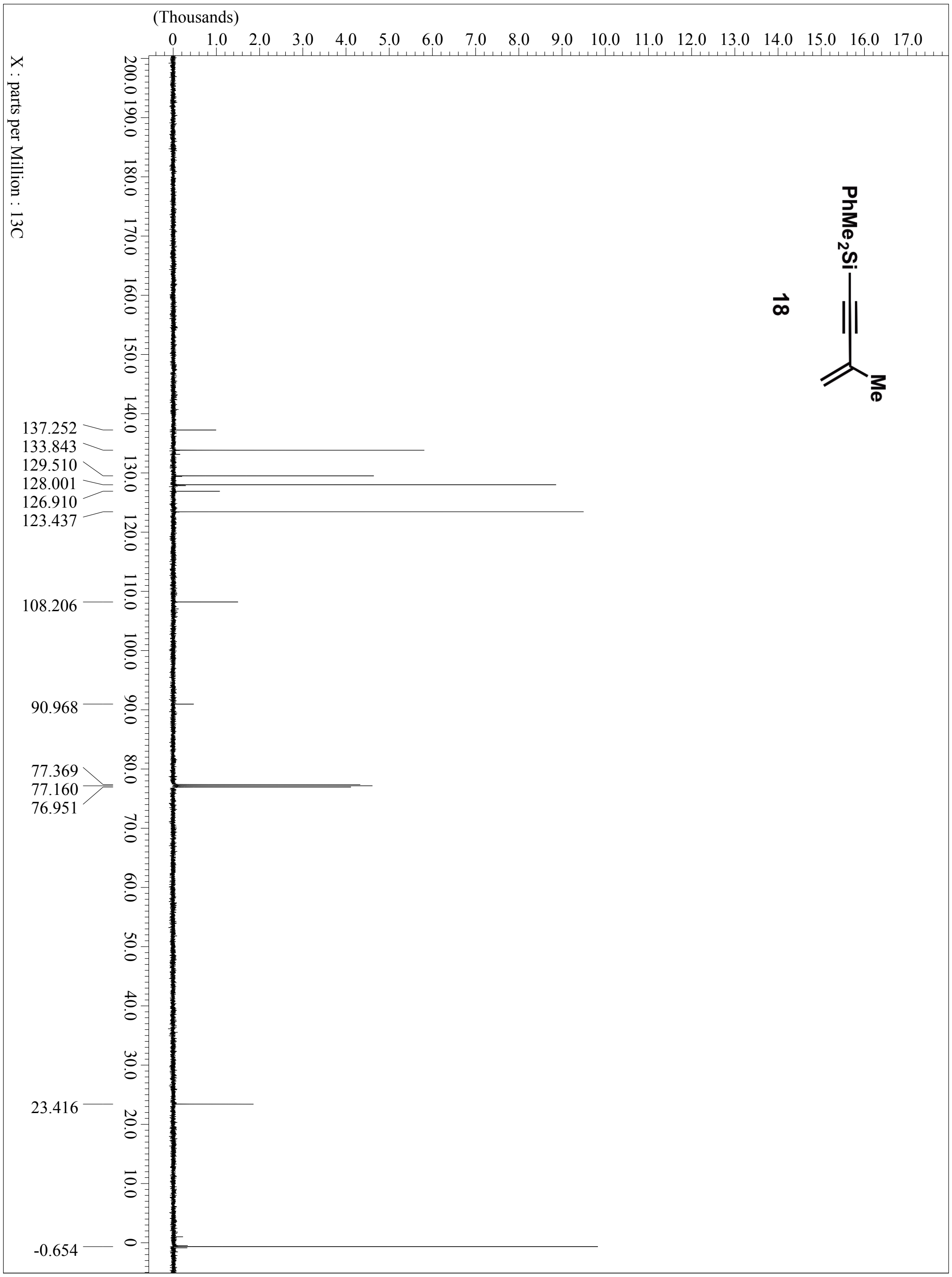


Figure S2: ^{13}C NMR (150 MHz, CDCl$_3$) of **18**.

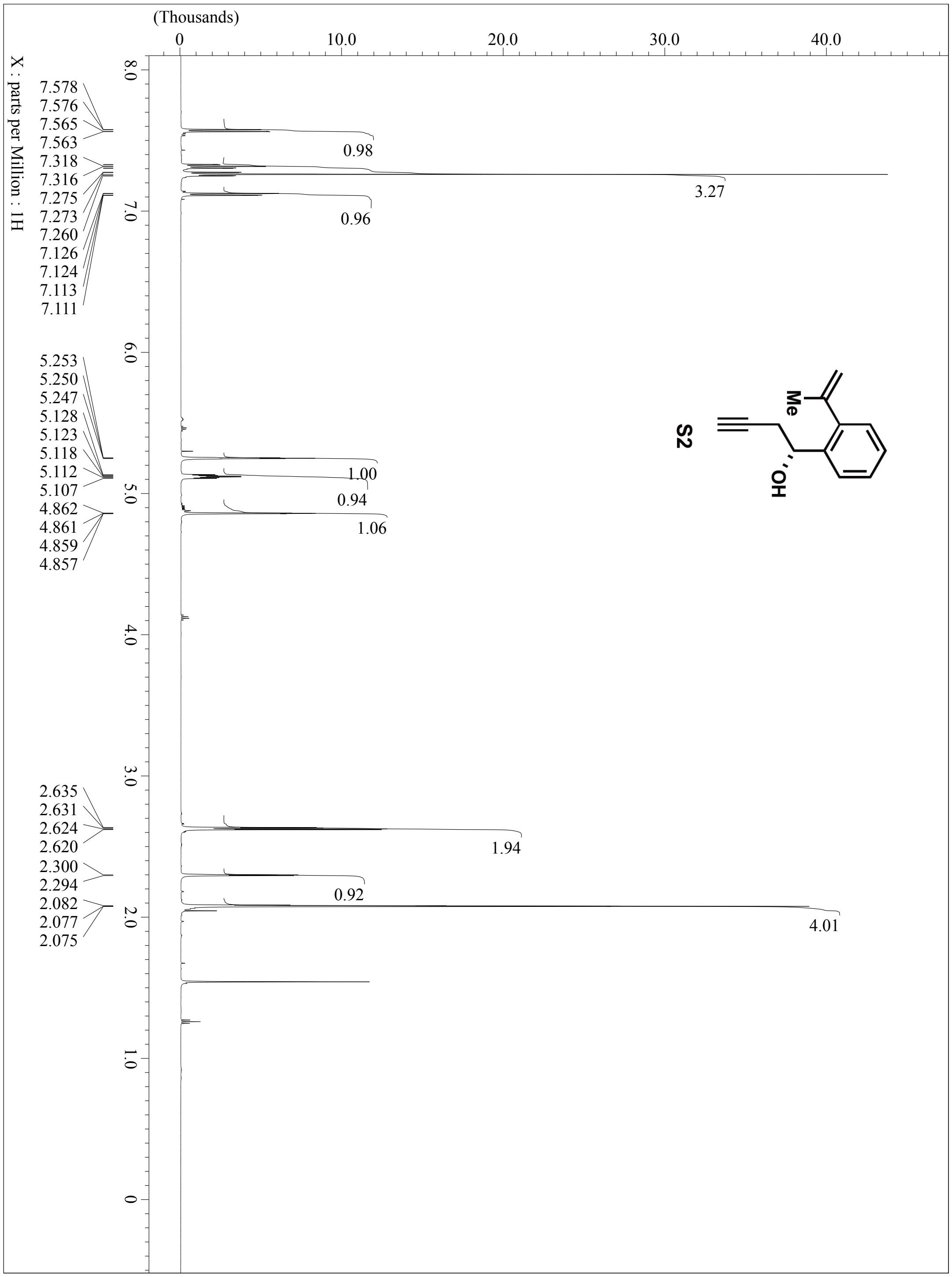


Figure S3: ^{1}H NMR (600 MHz, $CDCl_3$) of **S2**.

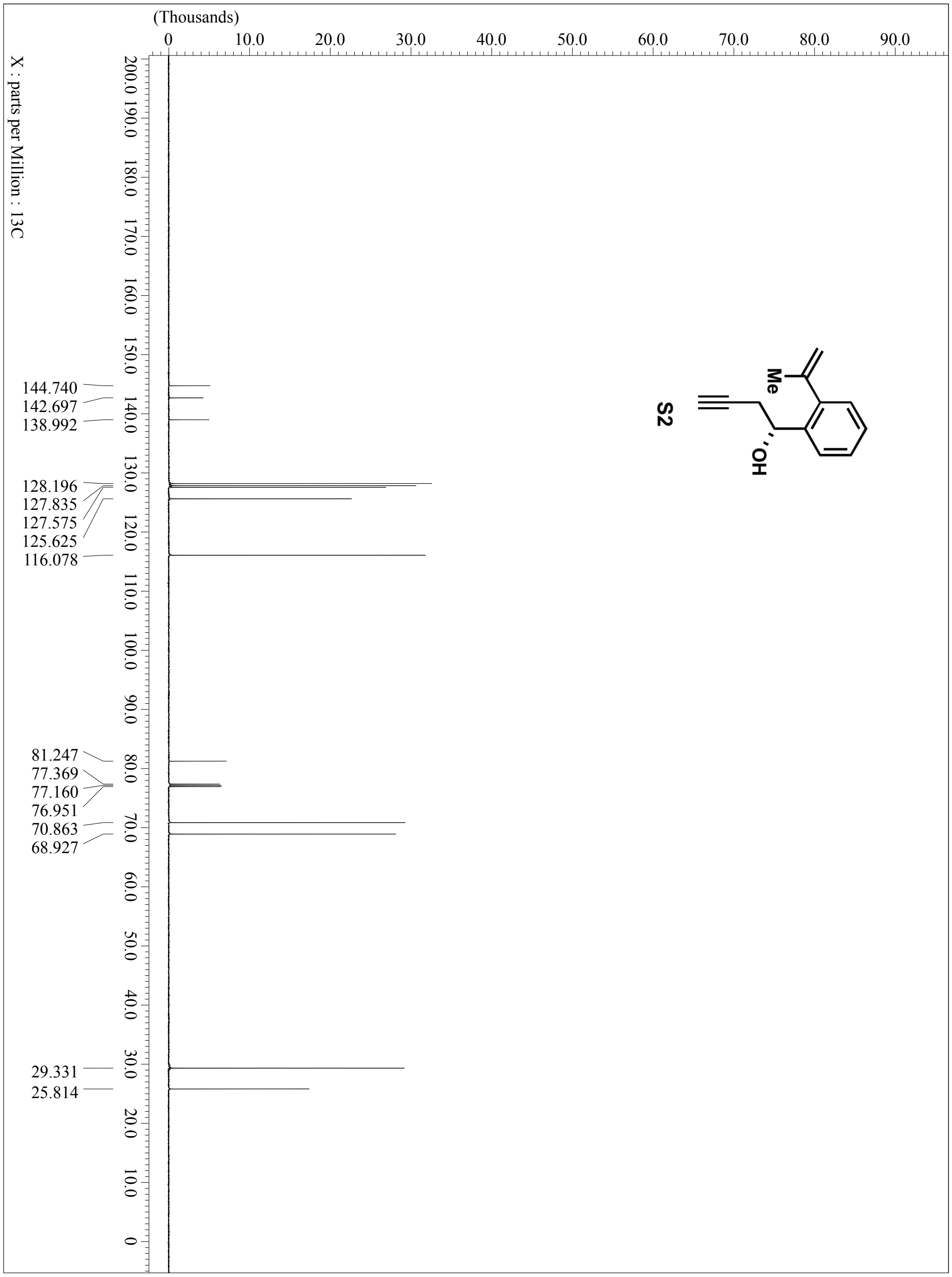


Figure S4: ^{13}C NMR (150 MHz, CDCl$_3$) of **S2**.

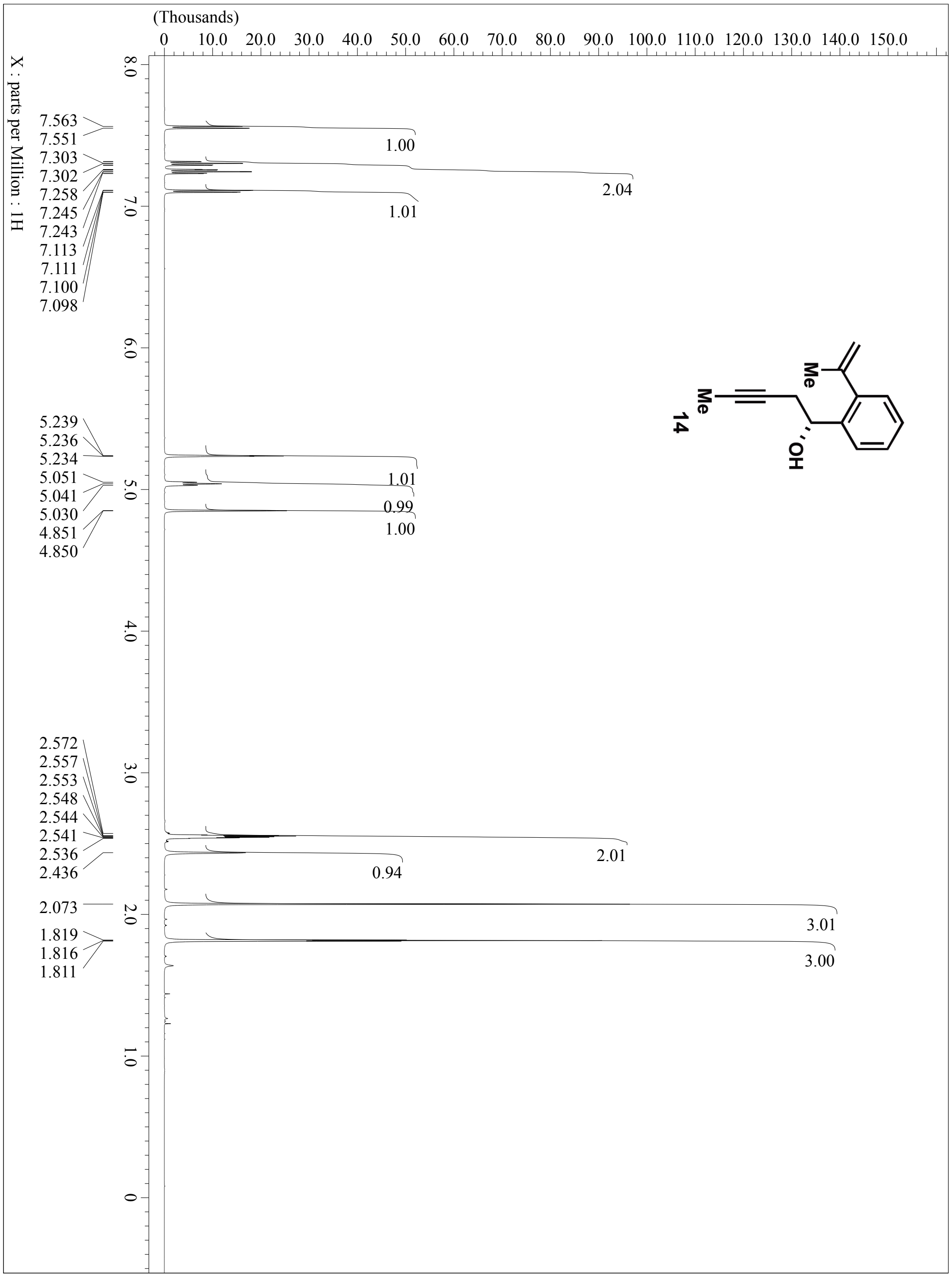


Figure S5: ^{1}H NMR (600 MHz, CDCl$_3$) of **14**.

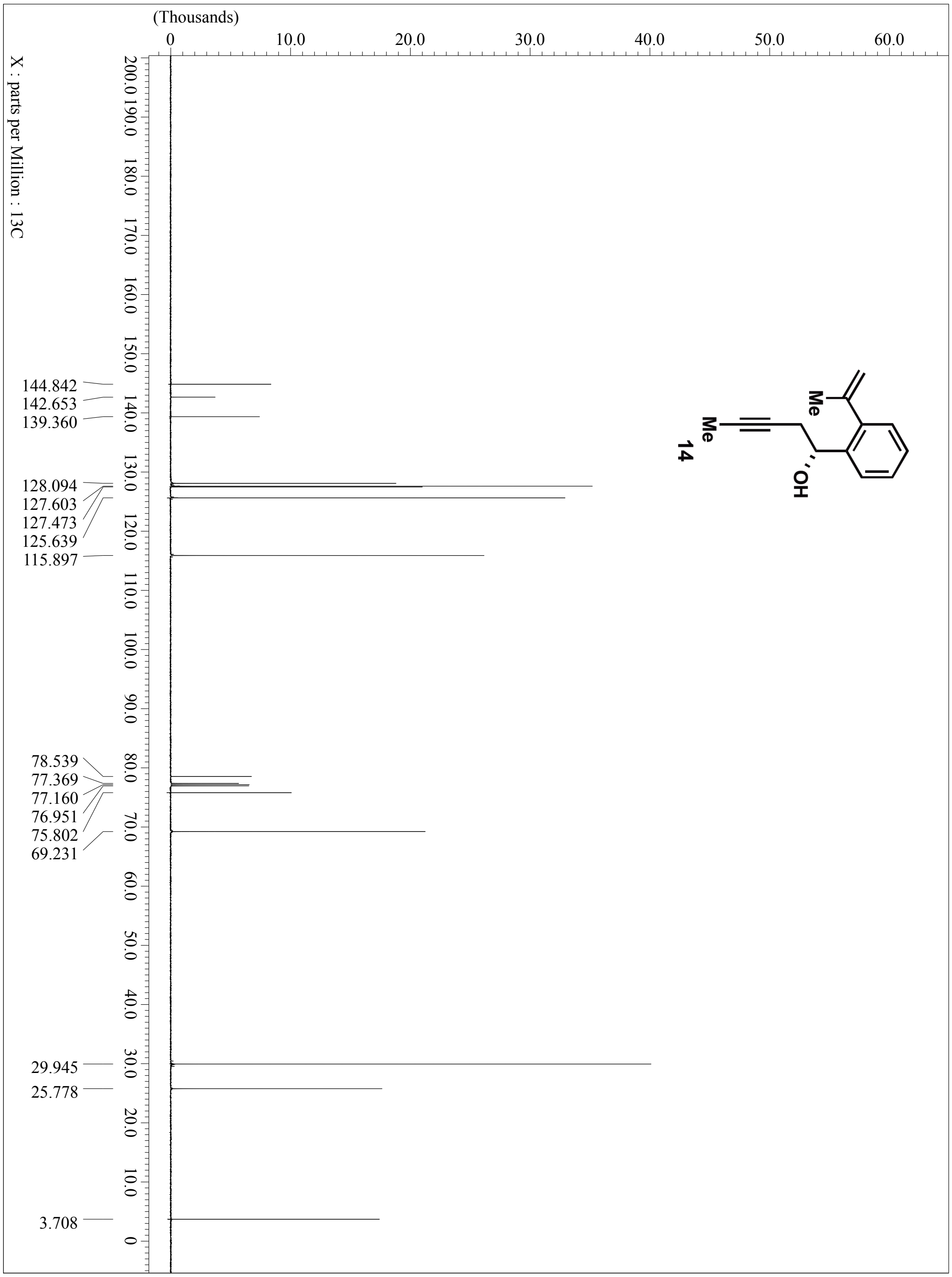


Figure S6: ^{13}C NMR (150 MHz, CDCl$_3$) of **14**.

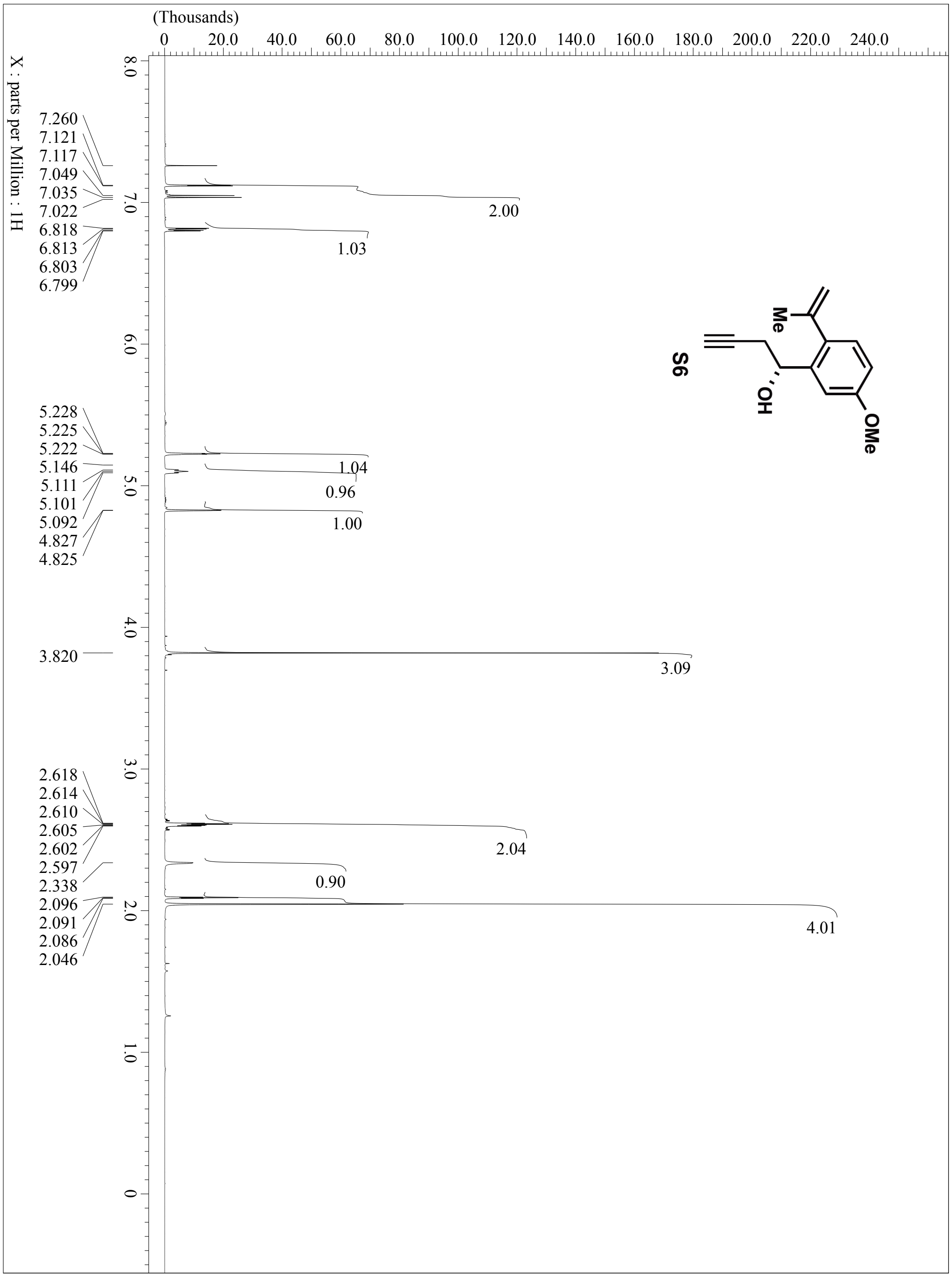


Figure S7: ^{1}H NMR (600 MHz, $CDCl_3$) of **S6**.

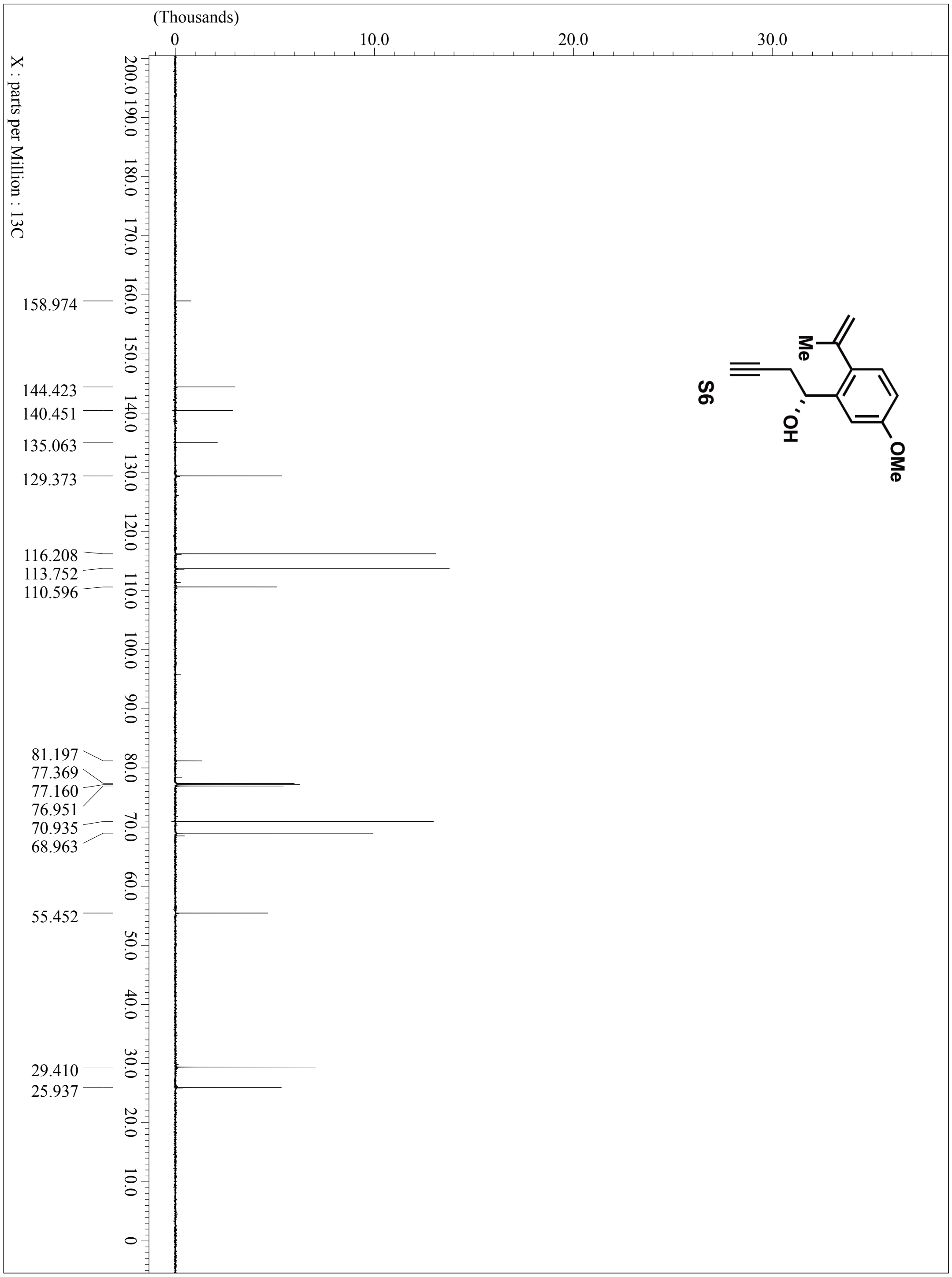


Figure S8: ^{13}C NMR (150 MHz, CDCl$_3$) of **S6**.

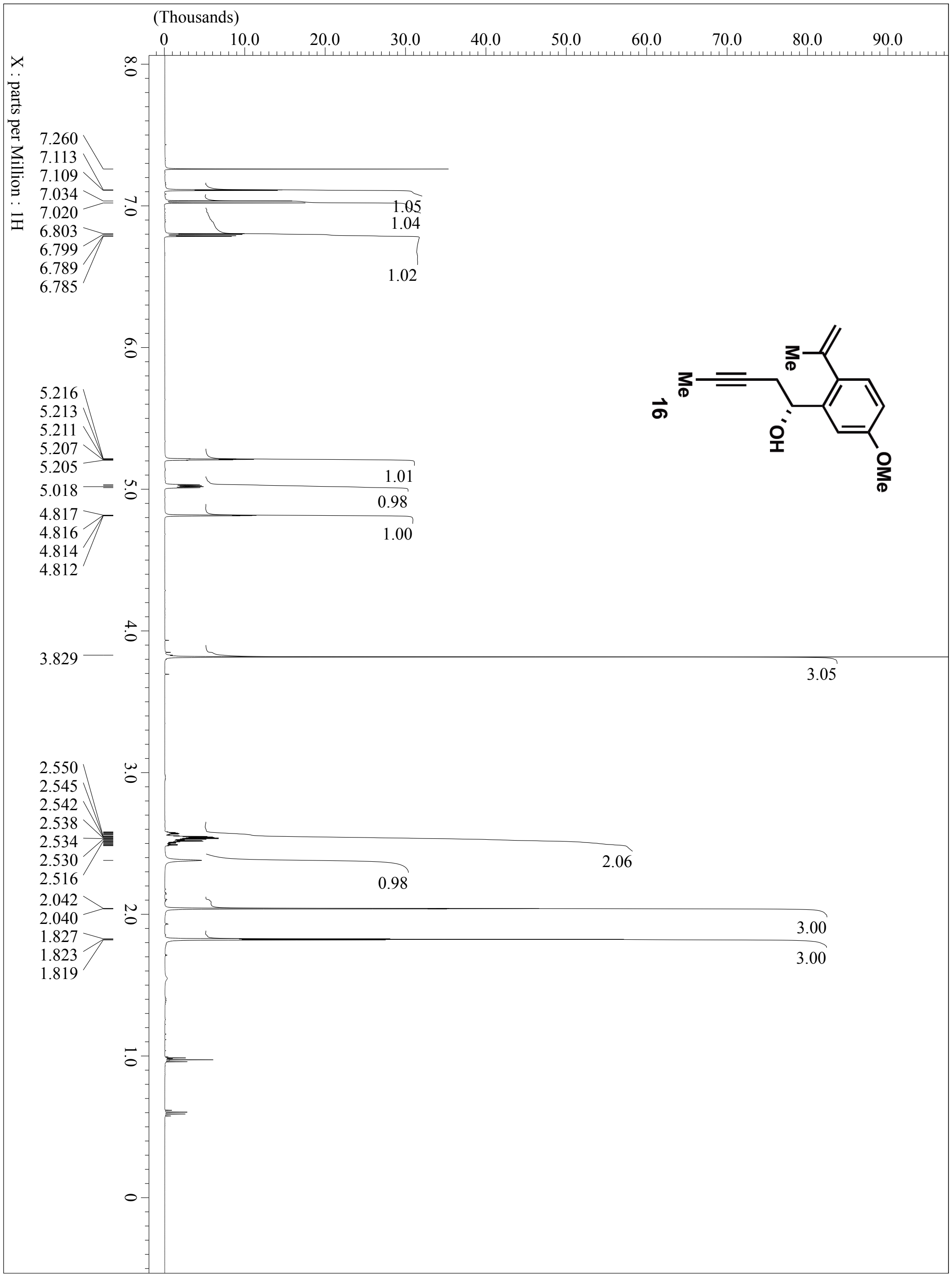


Figure S9: ^{1}H NMR (600 MHz, $CDCl_3$) of **16**.

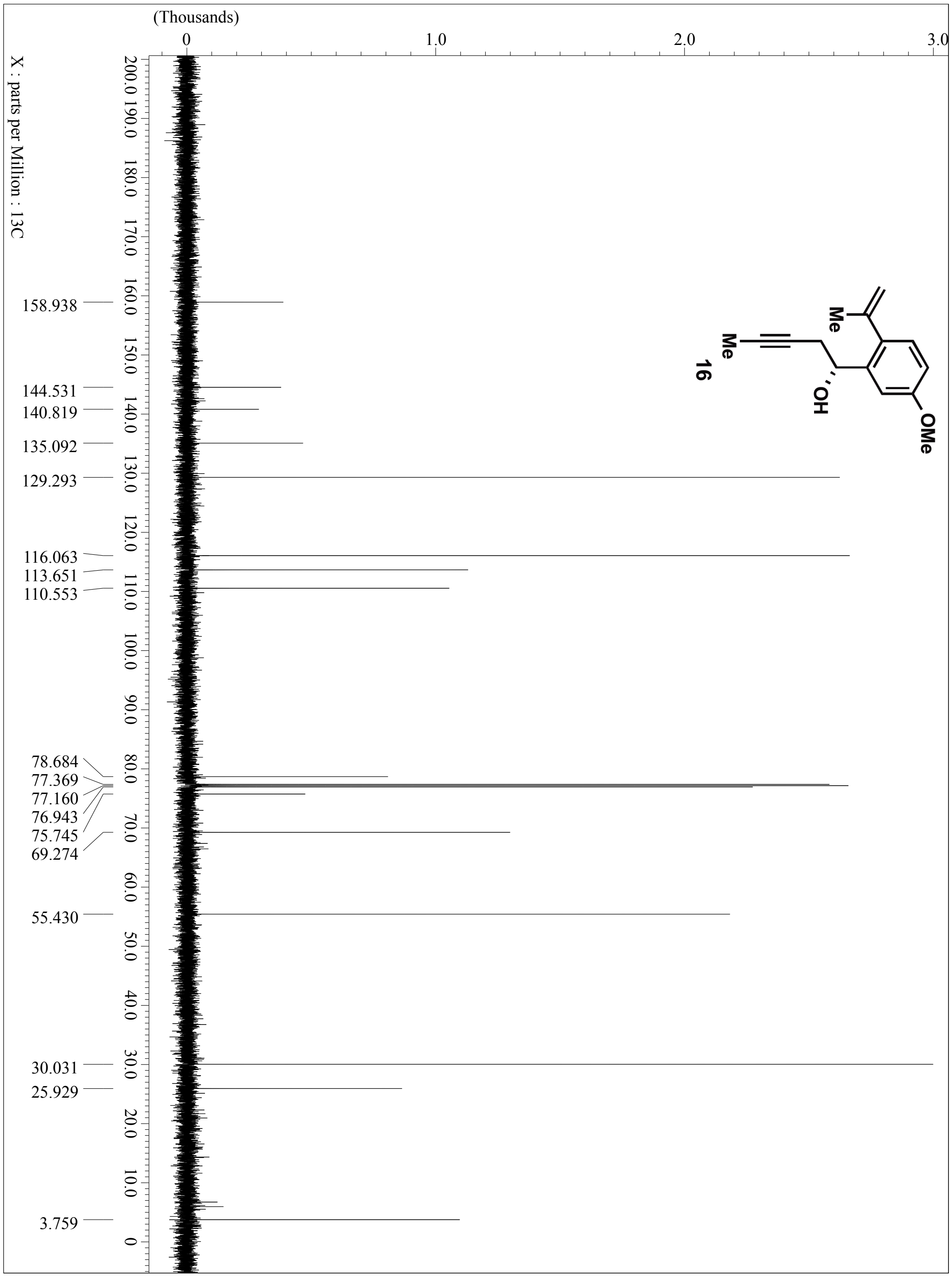


Figure S10: ^{13}C NMR (150 MHz, CDCl$_3$) of **16**.

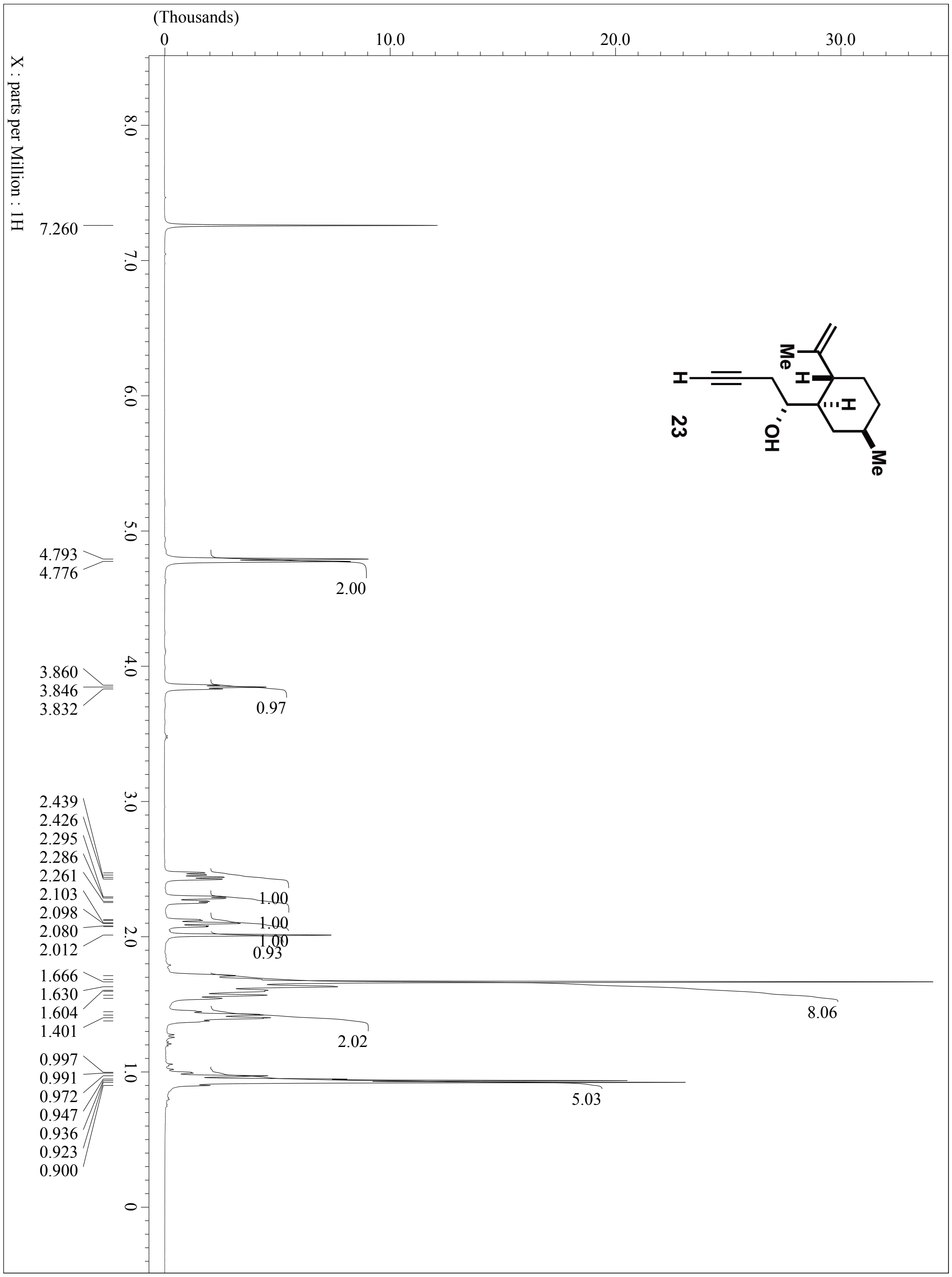


Figure S11: ^{1}H NMR (500 MHz, CDCl$_3$) of **23**.

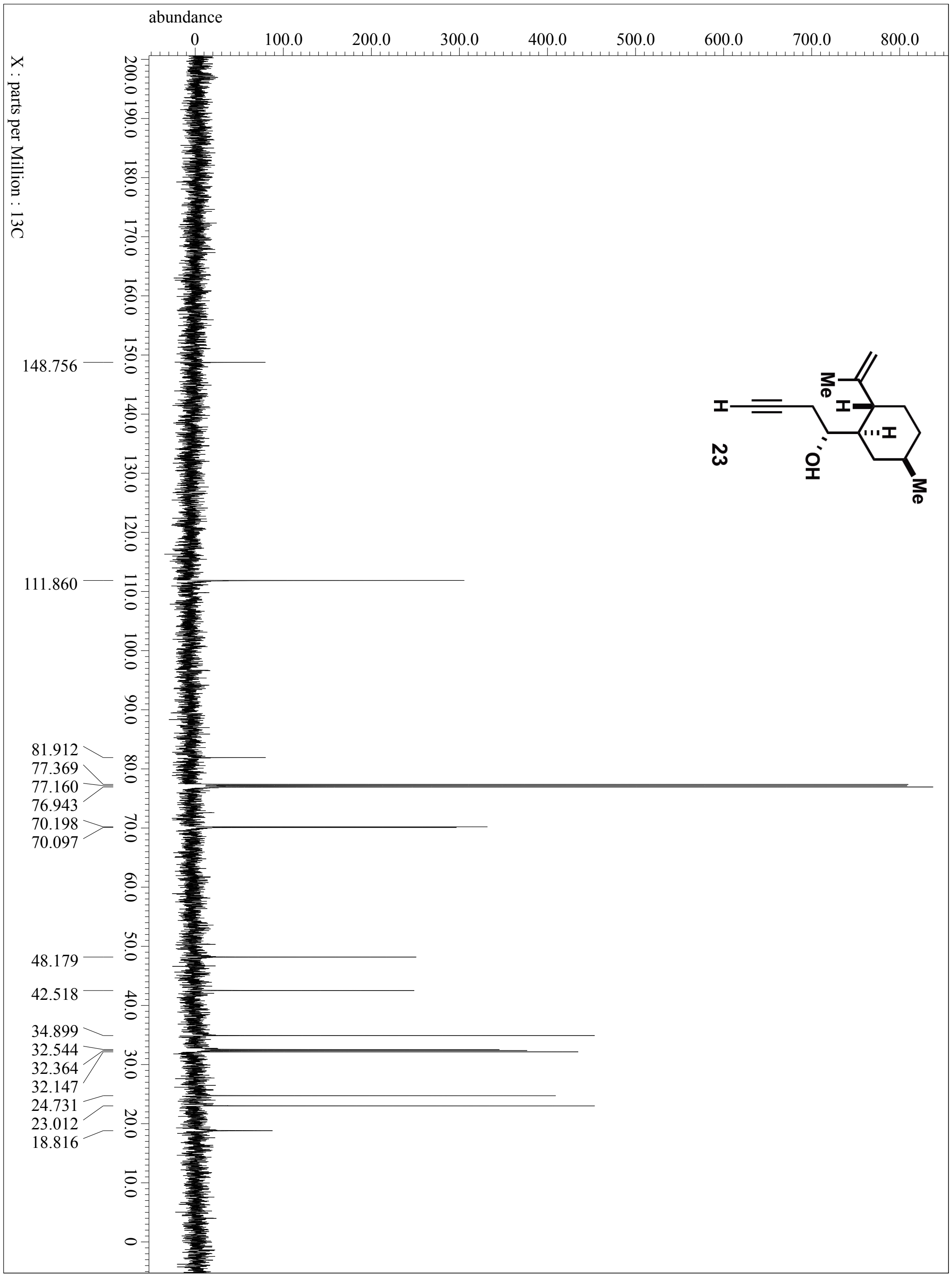


Figure S12: ^{13}C NMR (125 MHz, CDCl$_3$) of **23**.

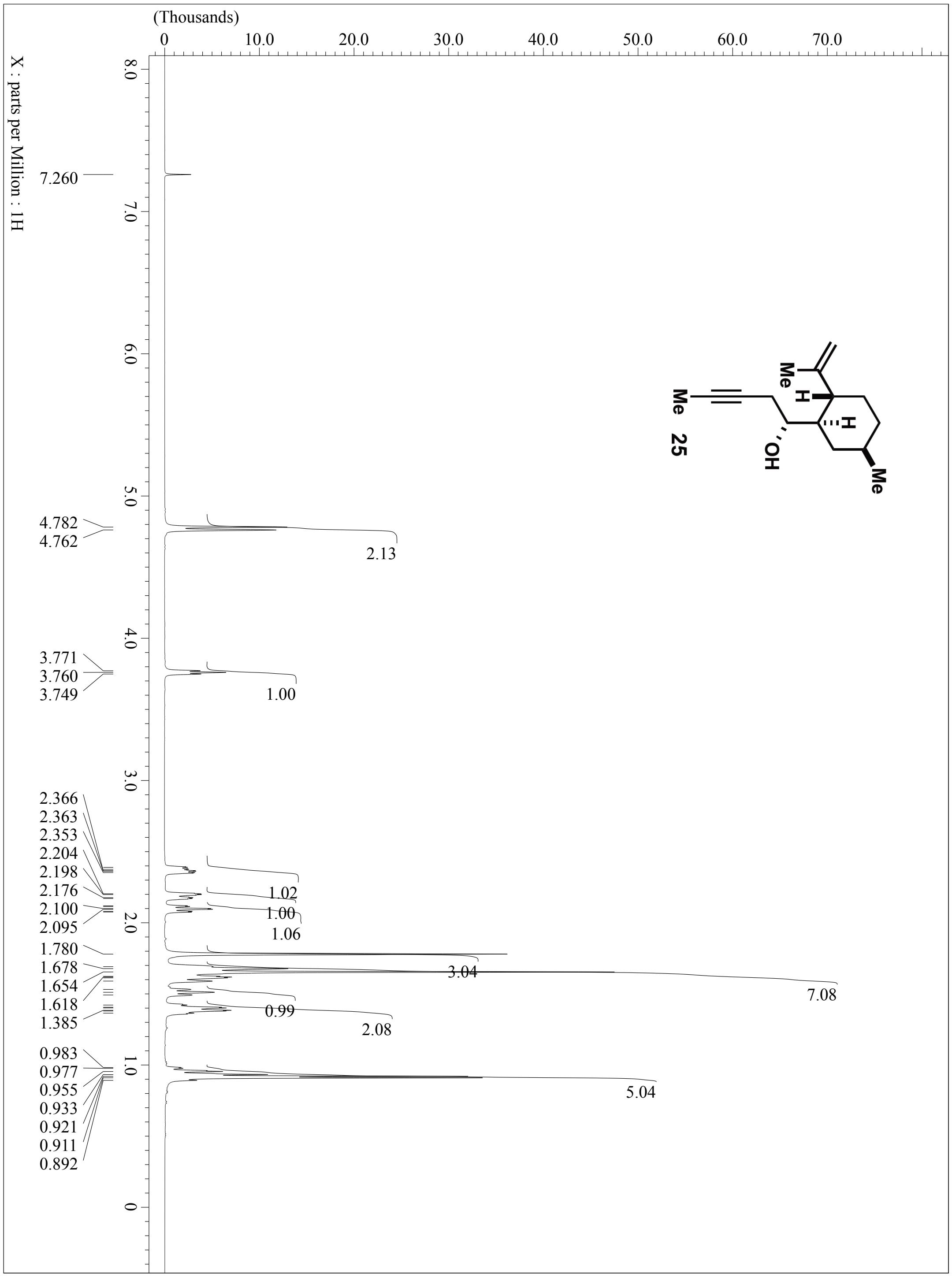


Figure S13: ^{1}H NMR (600 MHz, CDCl$_3$) of **25**.

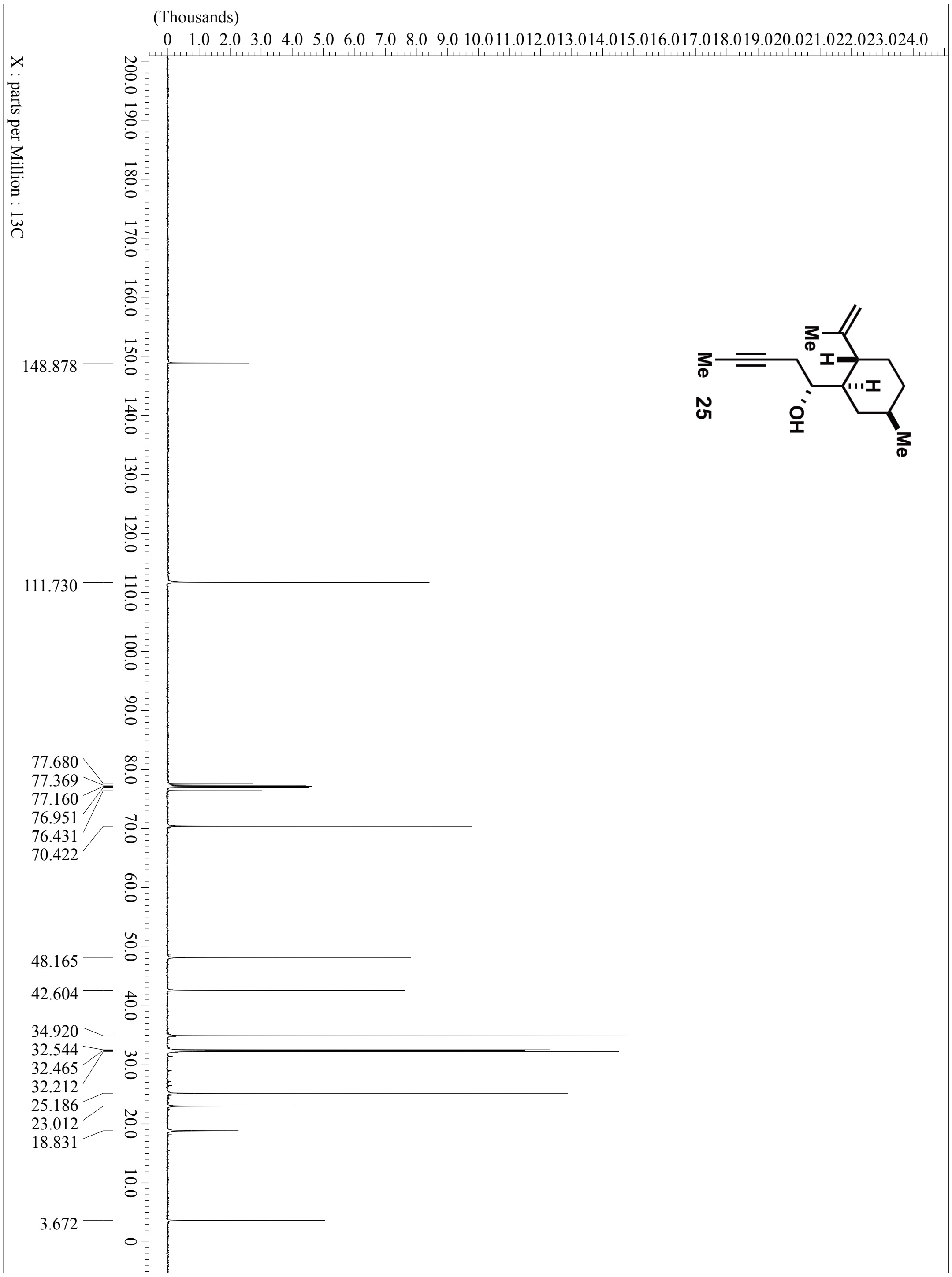


Figure S14: ^{13}C NMR (150 MHz, $CDCl_3$) of **25**.

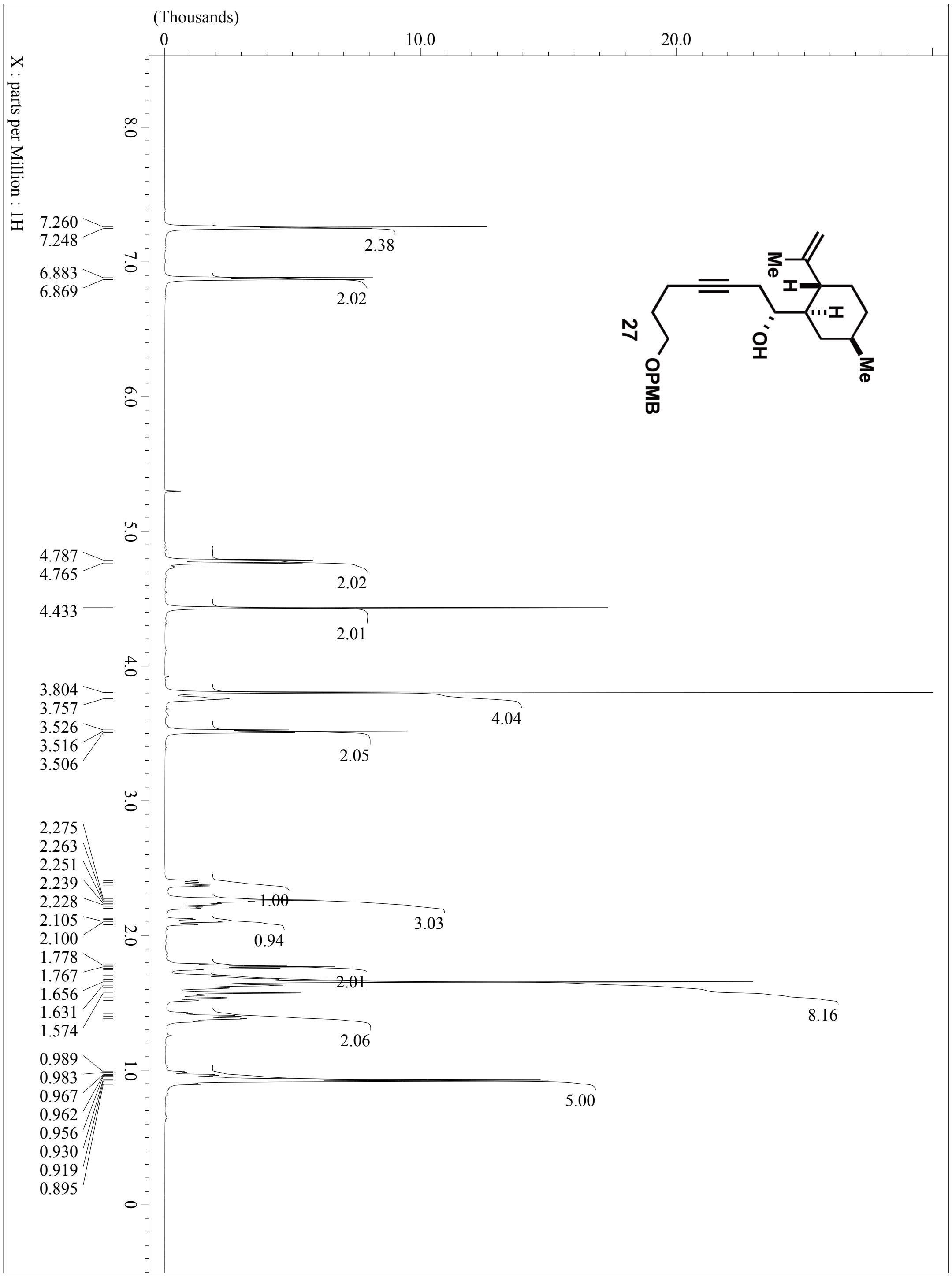


Figure S15: ^{1}H NMR (600 MHz, CDCl$_3$) of **27**.

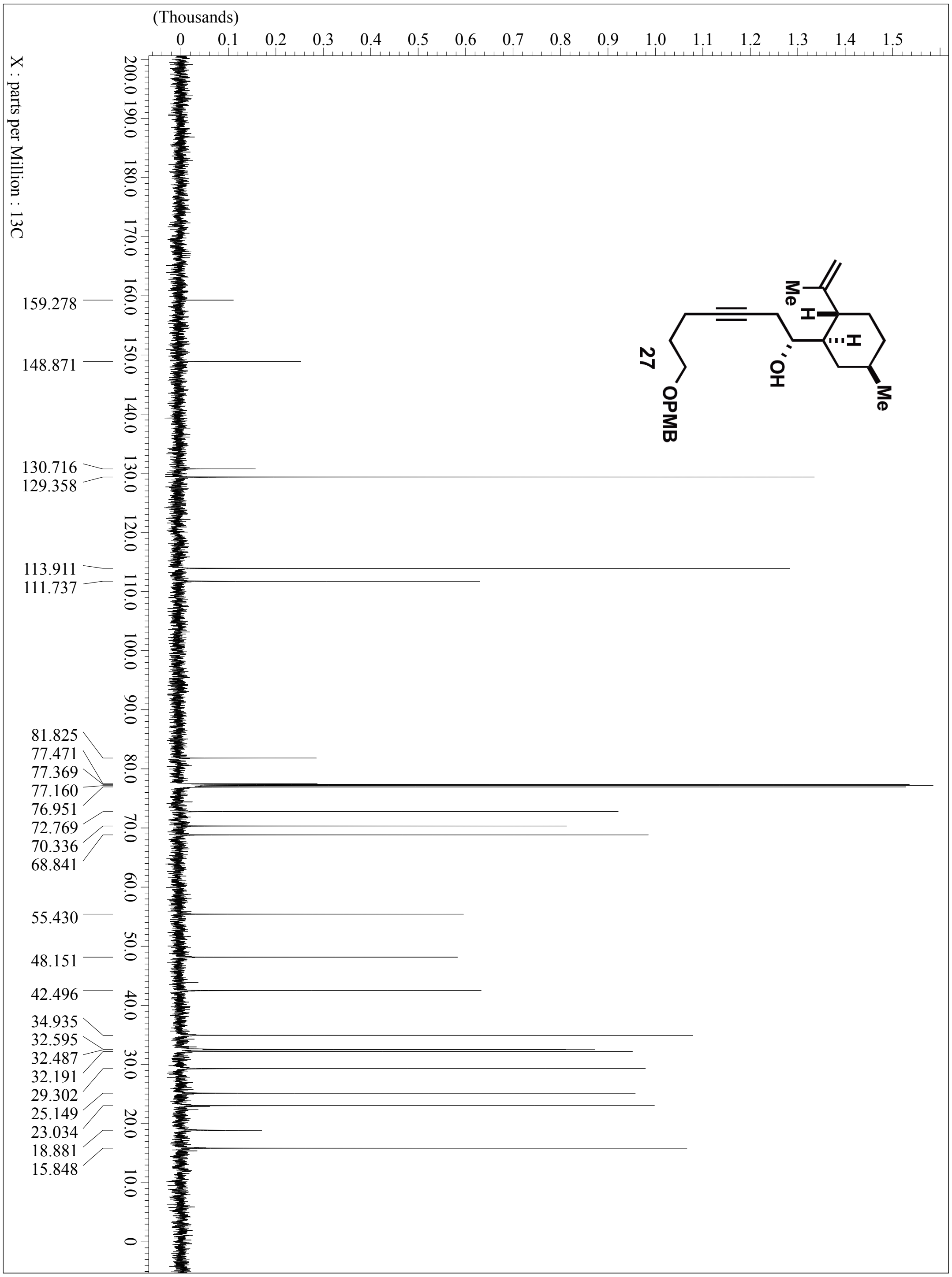


Figure S16: ^{13}C NMR (150 MHz, CDCl$_3$) of **27**.

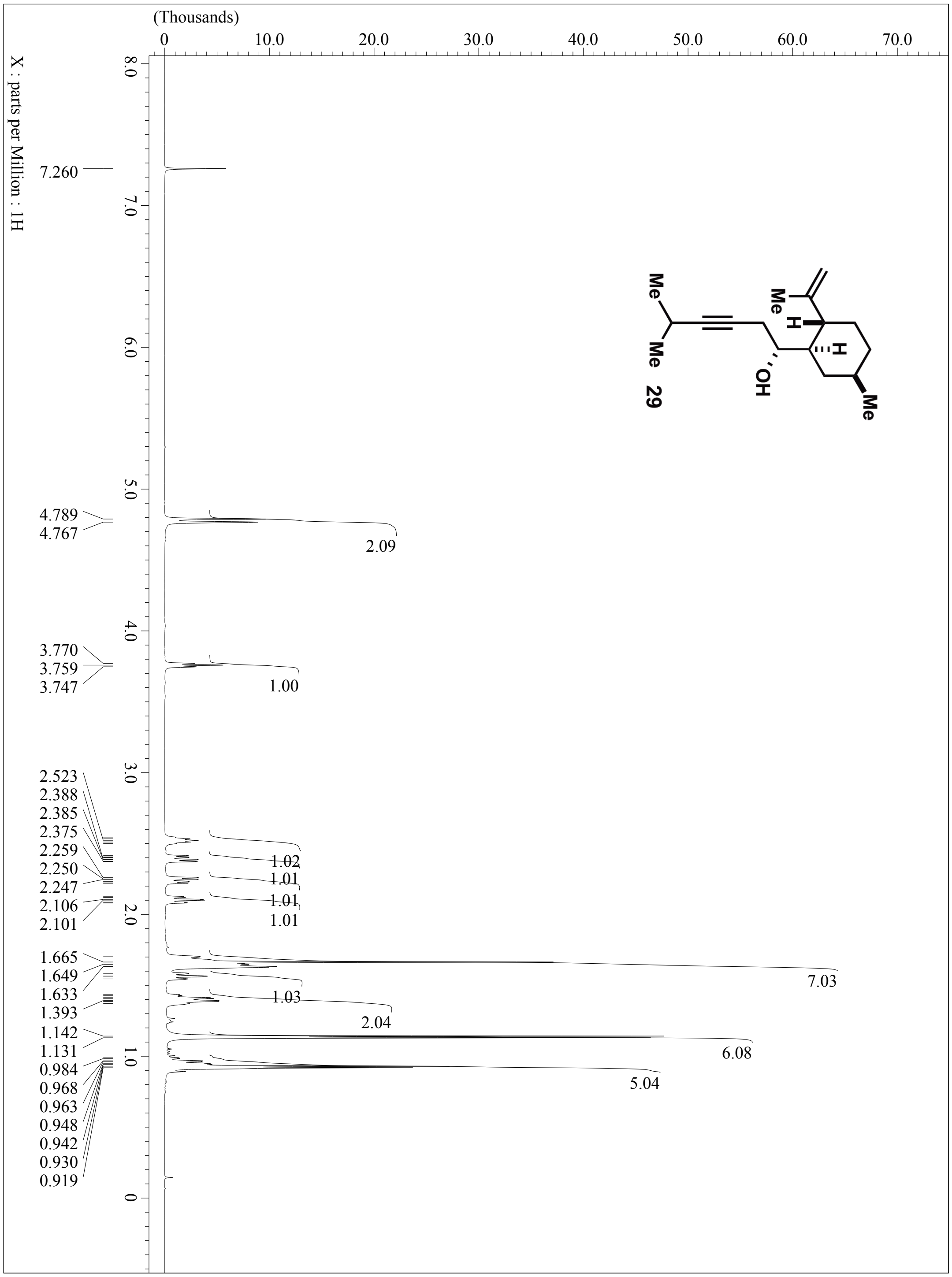


Figure S17: ^{1}H NMR (600 MHz, $CDCl_3$) of **29**.

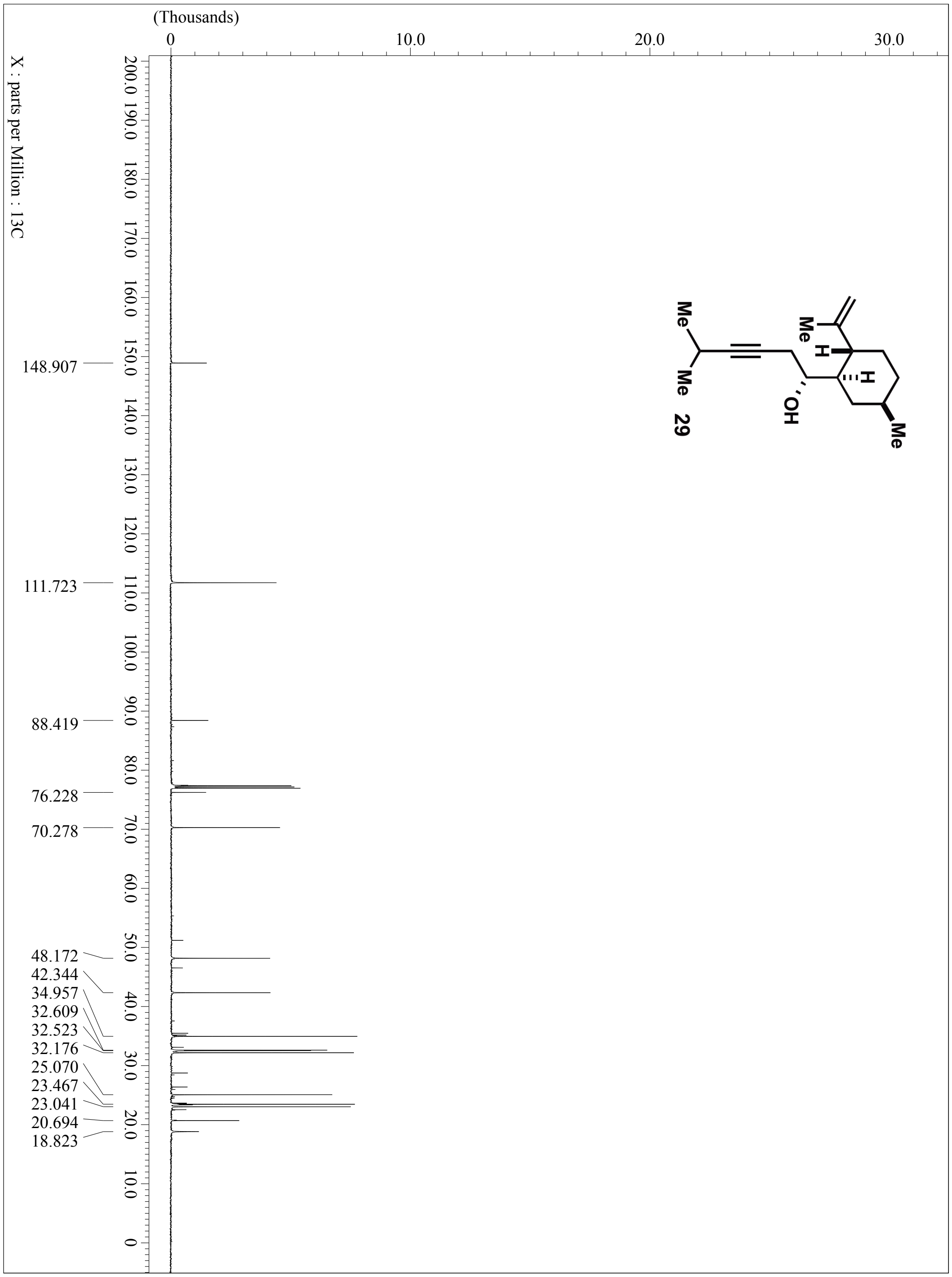


Figure S18: ^{13}C NMR (150 MHz, CDCl$_3$) of **29**.

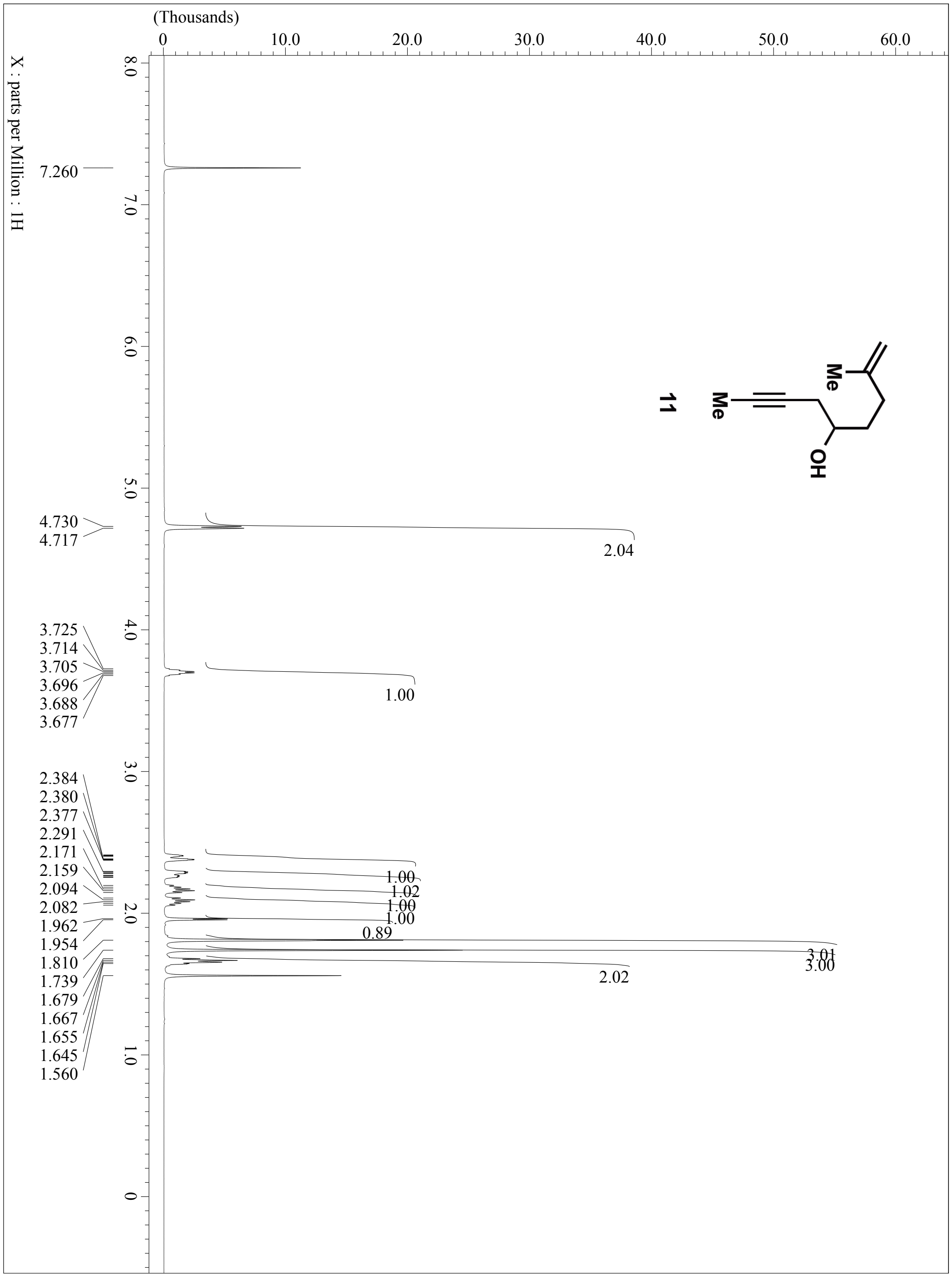


Figure S19: ^{13}C NMR (150 MHz, CDCl$_3$) of **11**.

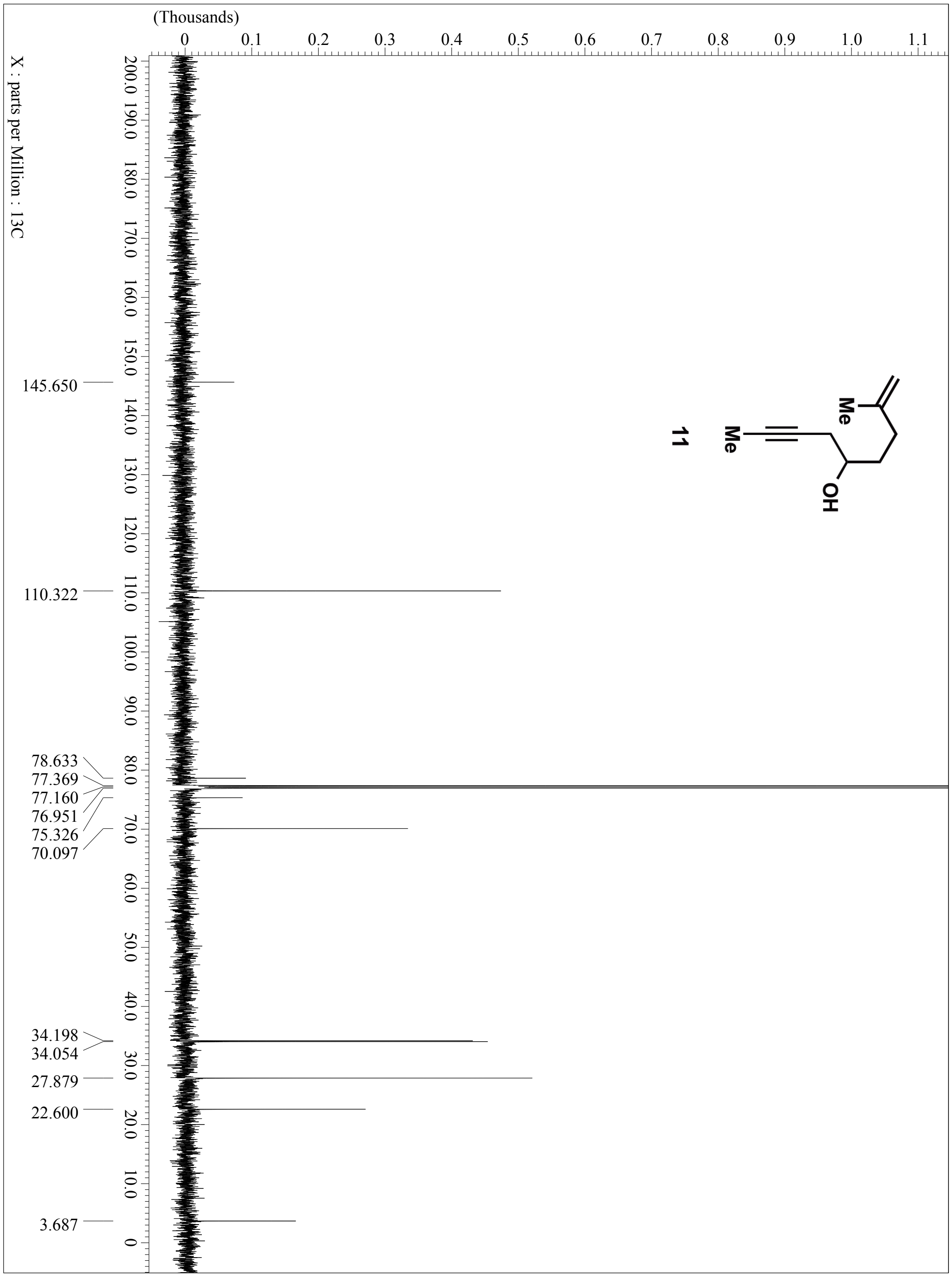


Figure S20: ^{13}C NMR (150 MHz, CDCl$_3$) of **11**.

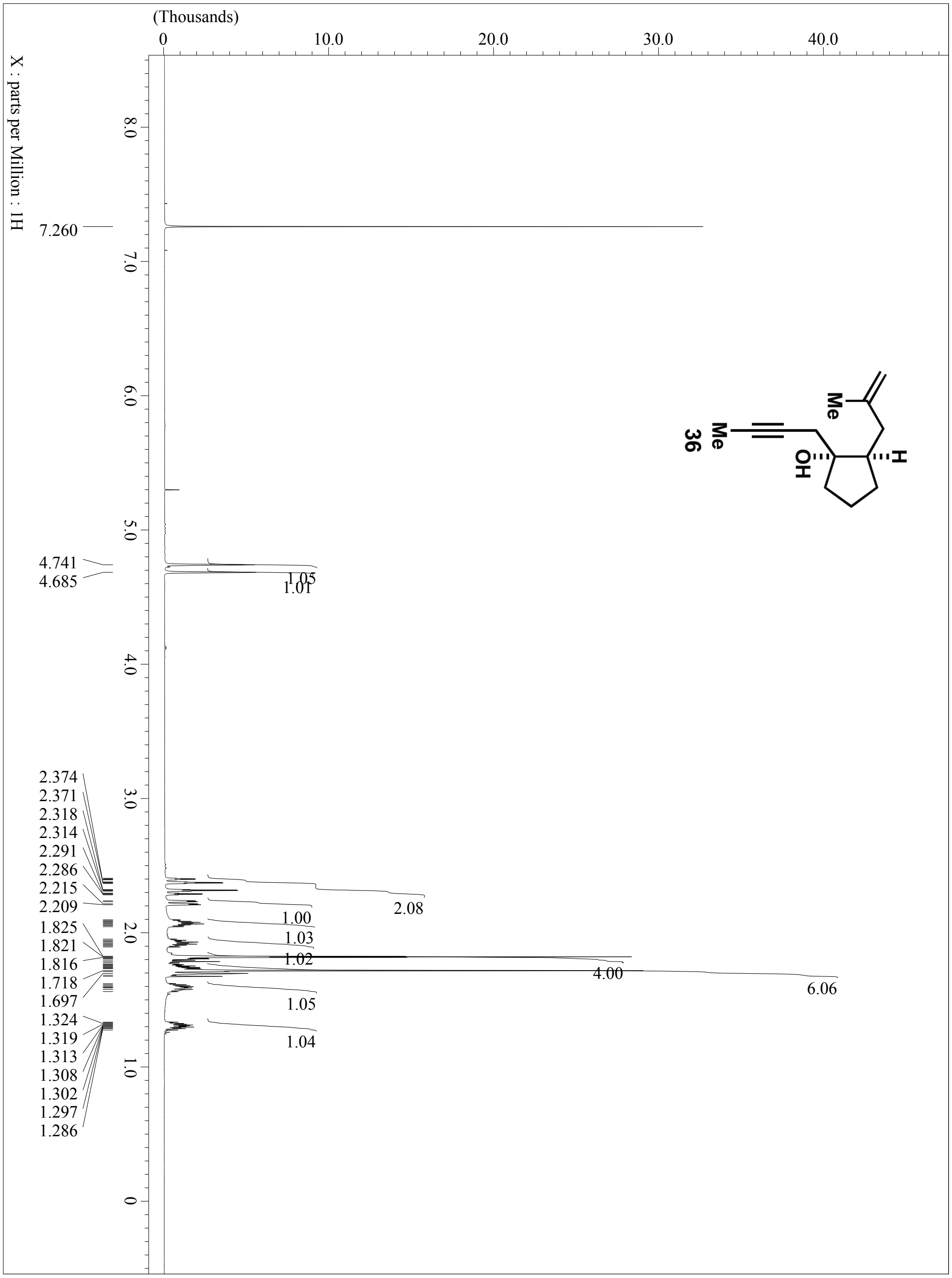


Figure S21: ^{1}H NMR (600 MHz, $CDCl_3$) of **36**.

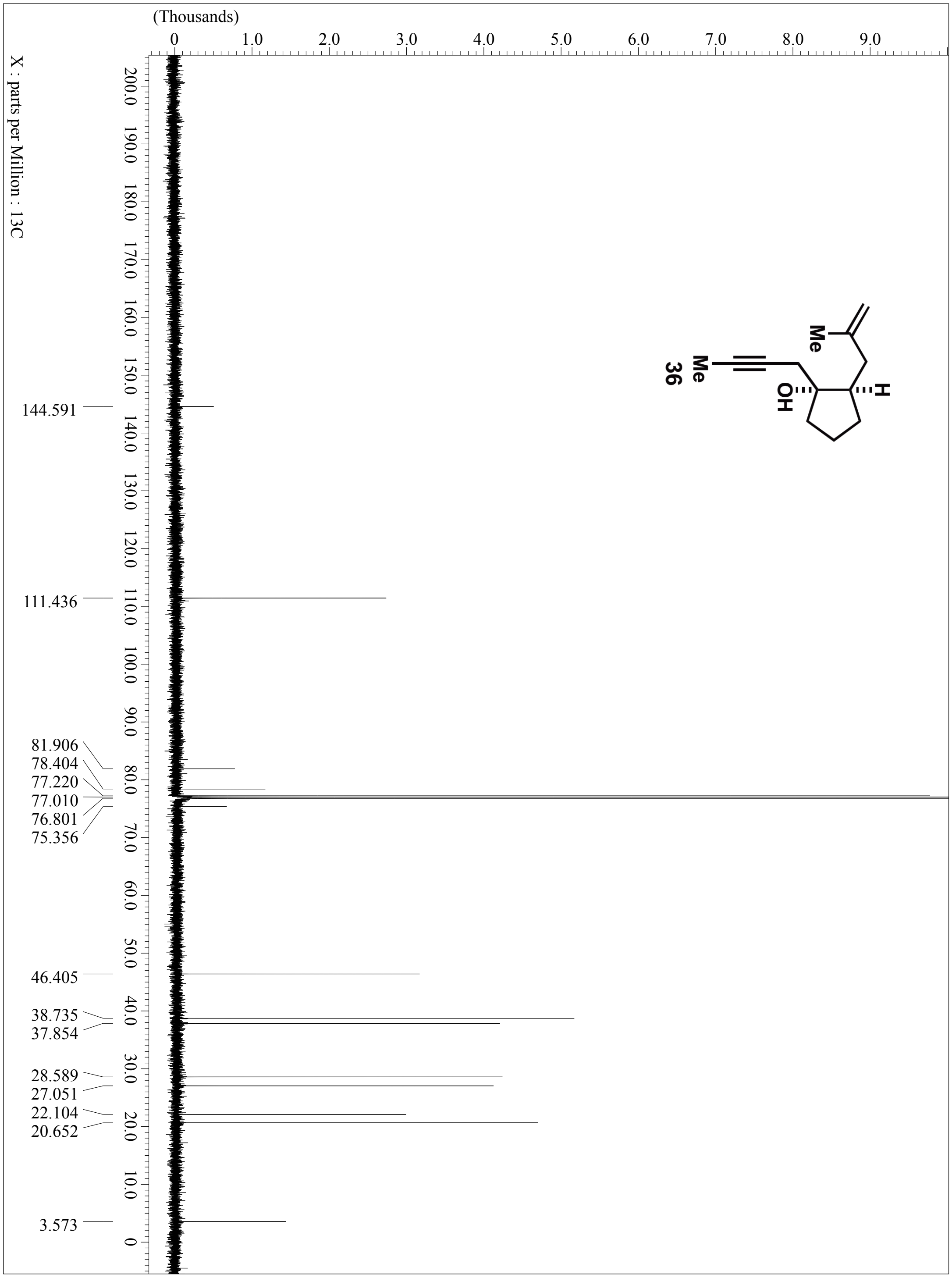


Figure S22: ^{13}C NMR (600 MHz, CDCl$_3$) of **36**.

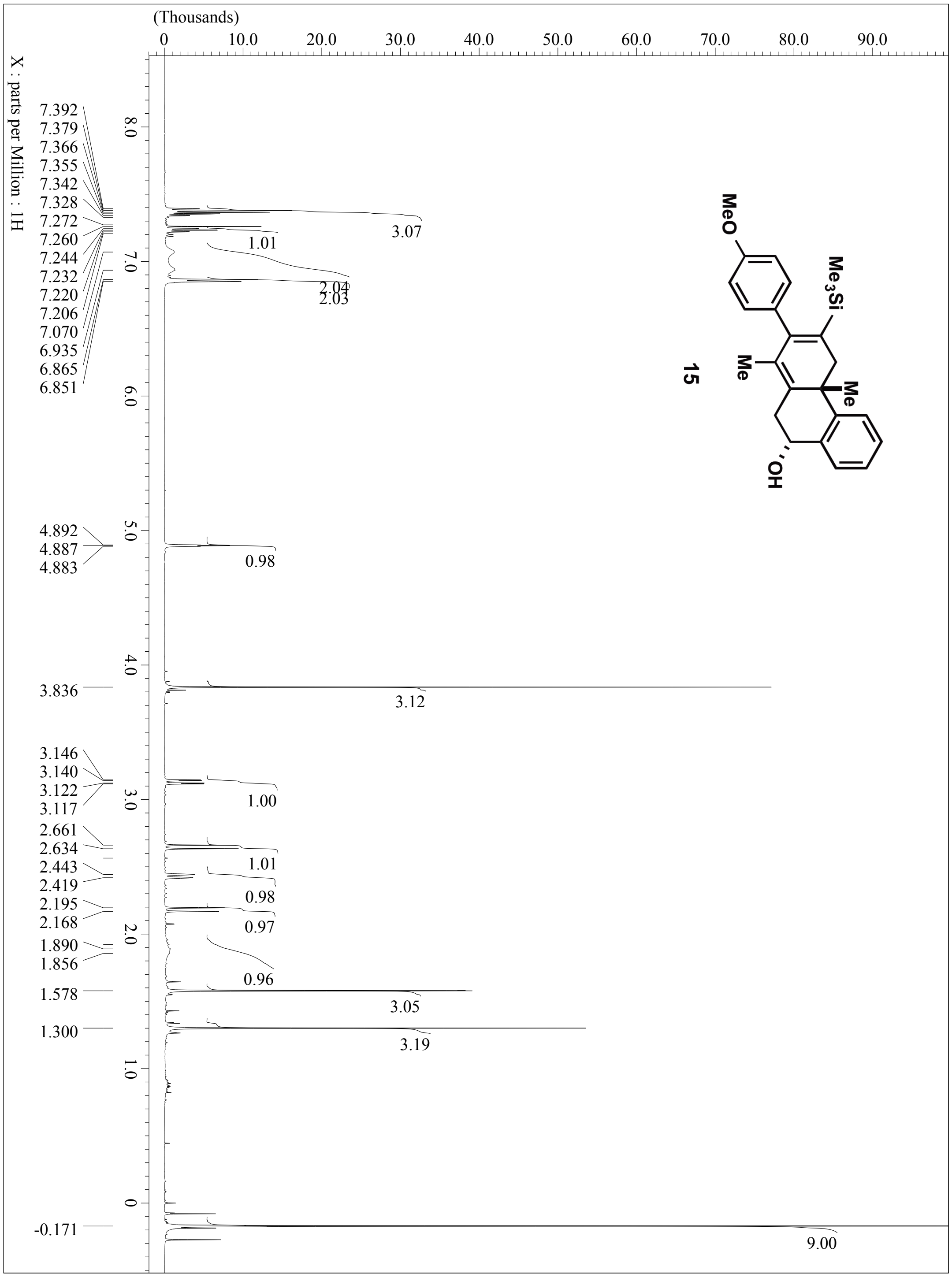


Figure S23: ^{1}H NMR (600 MHz, CDCl$_3$) of **15**.

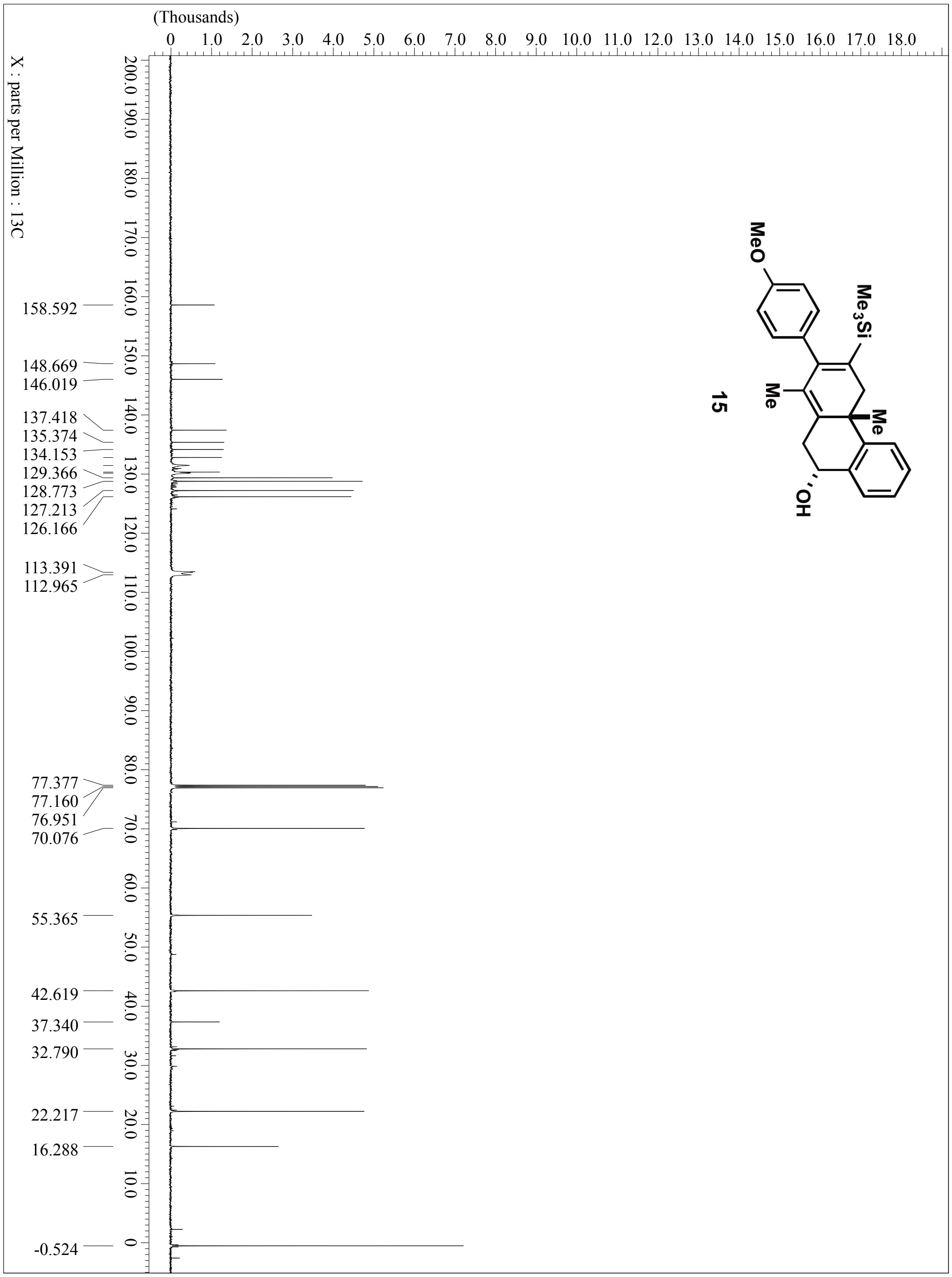


Figure S24: ^{13}C NMR (150 MHz, CDCl$_3$) of **15**.

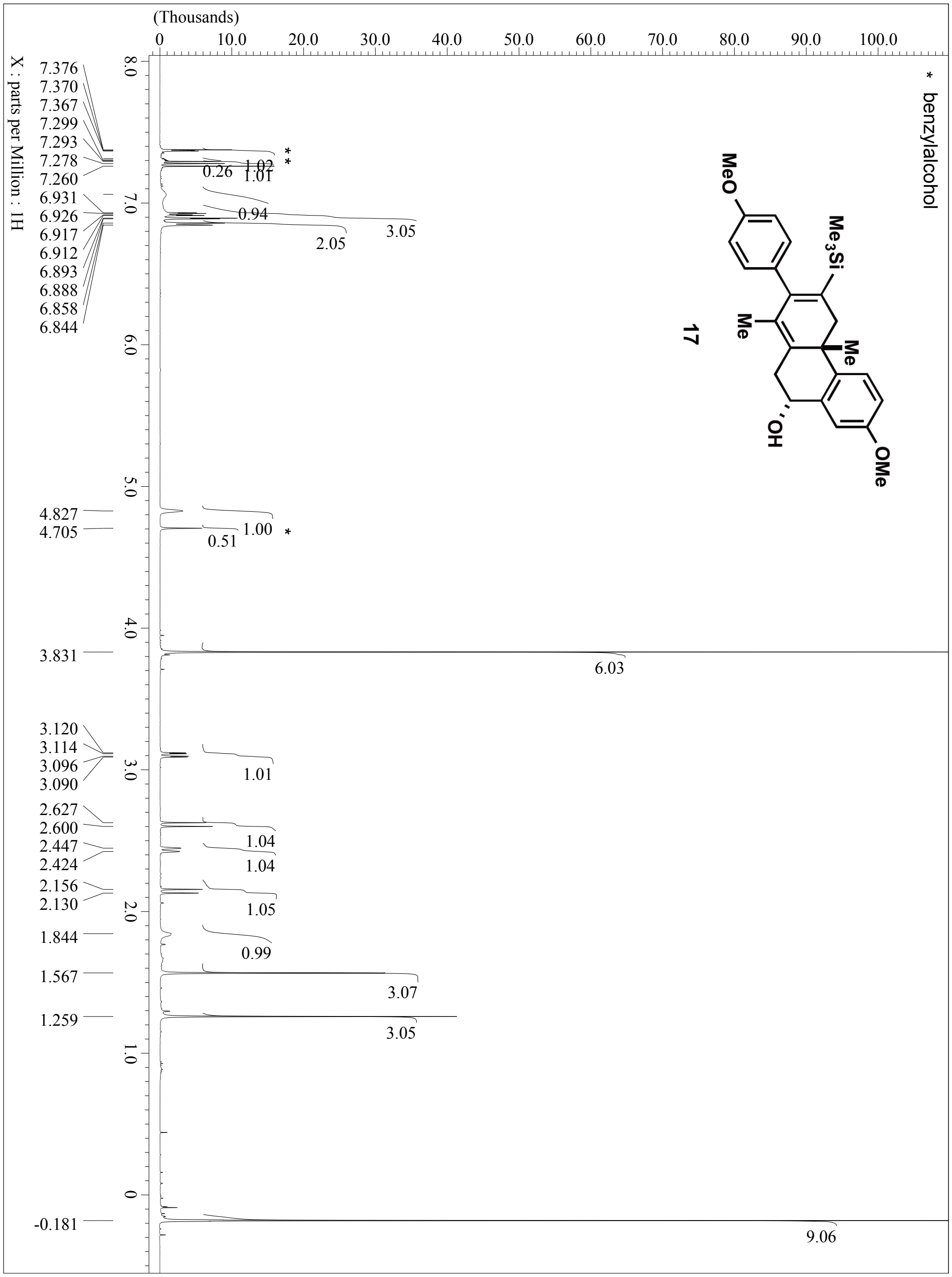


Figure S25: ^{1}H NMR (600 MHz, CDCl$_3$) of **17**.

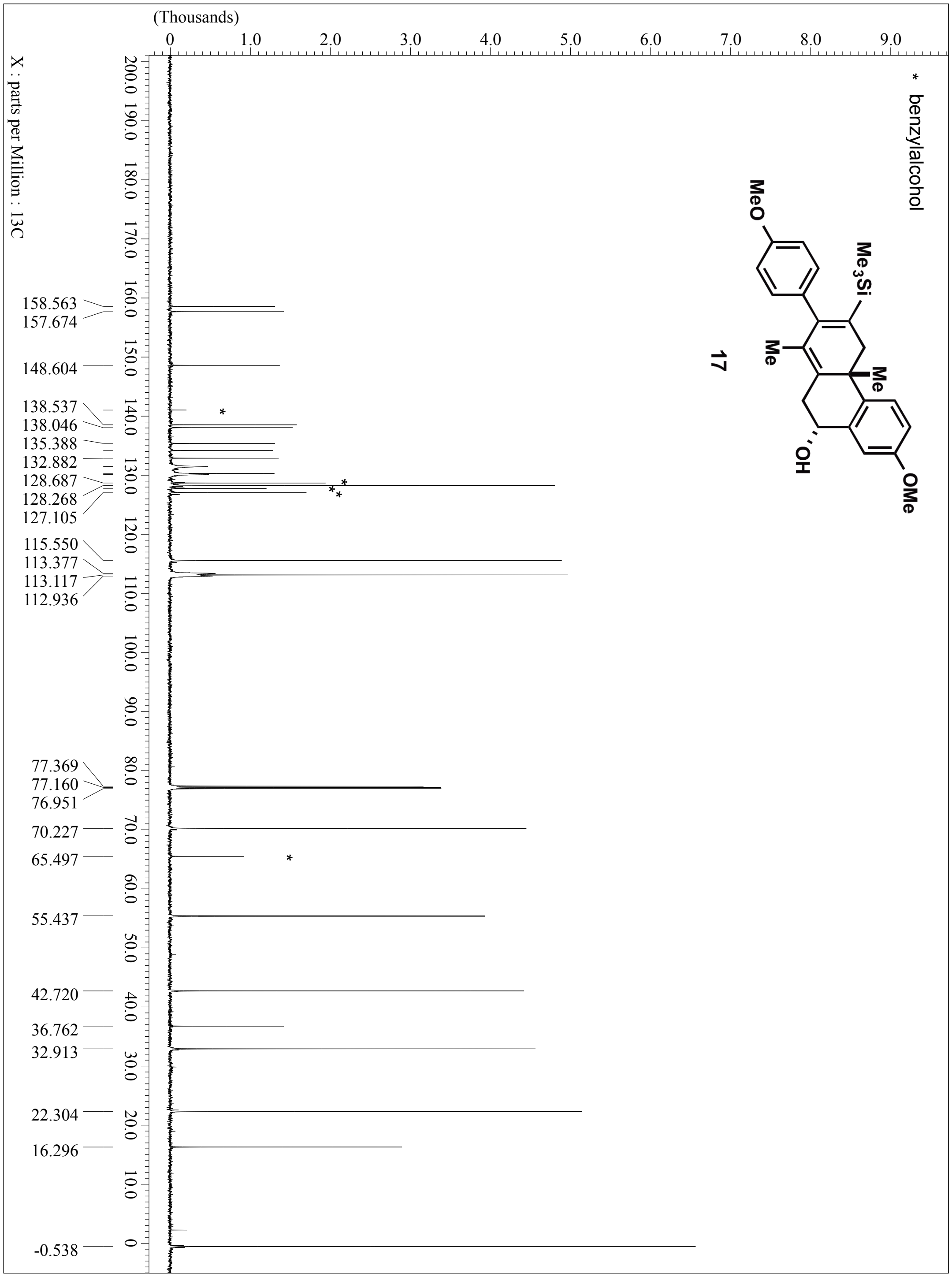


Figure S26: ^{13}C NMR (150 MHz, CDCl$_3$) of **17**.

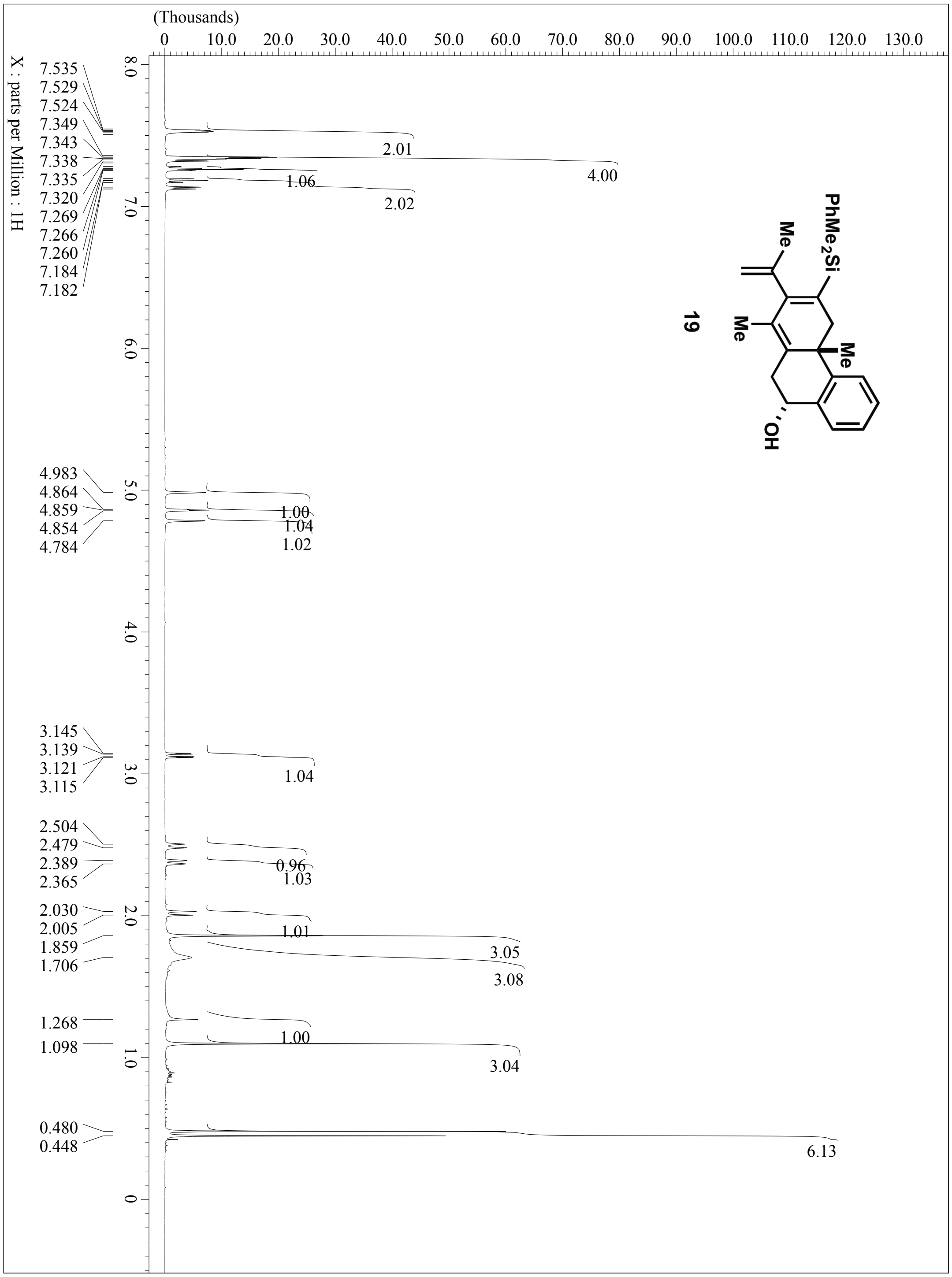


Figure S27: ^{1}H NMR (600 MHz, $CDCl_3$) of **19**.

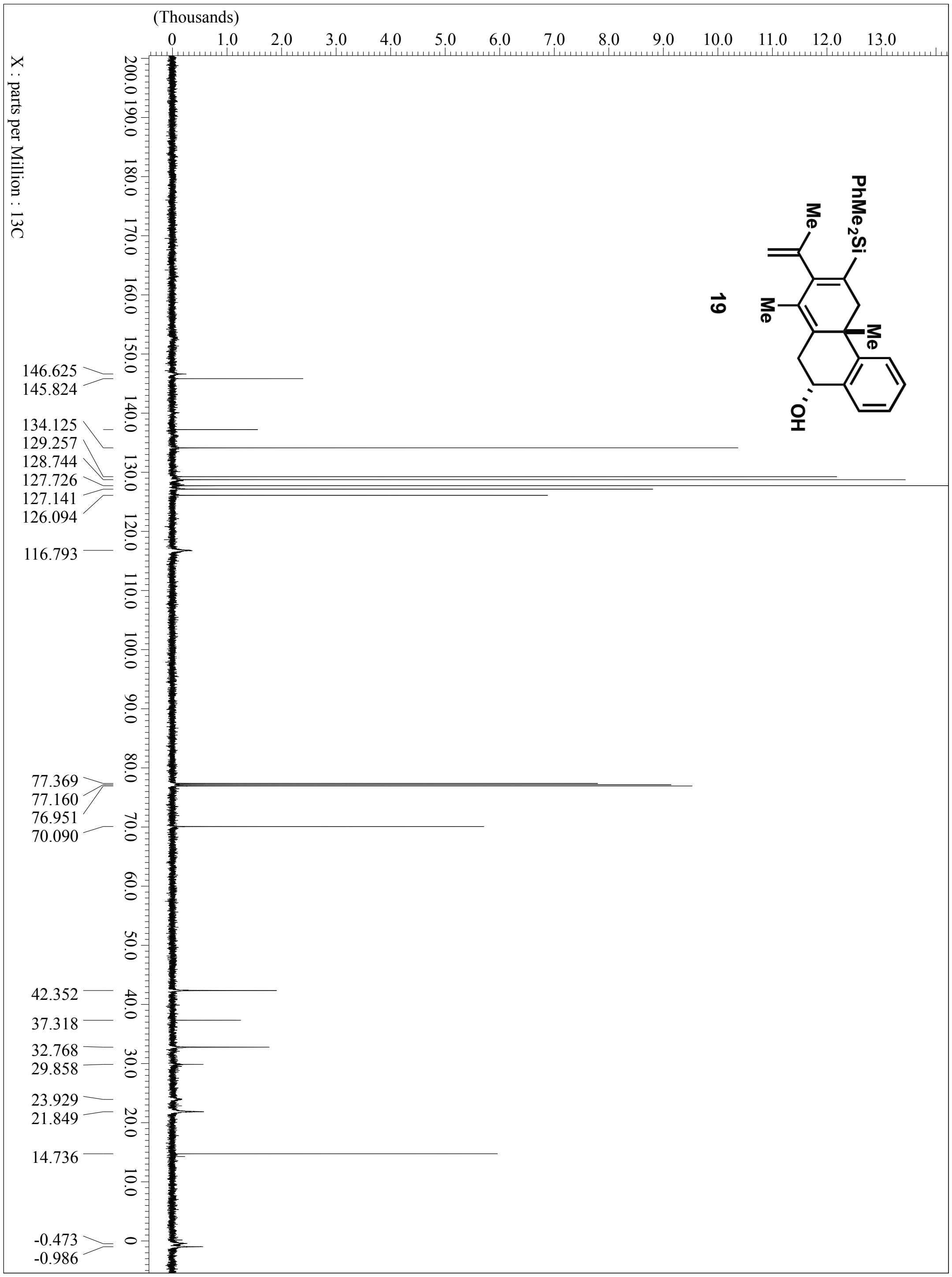


Figure S28: ^{13}C NMR (150 MHz, CDCl$_3$) of **19**.

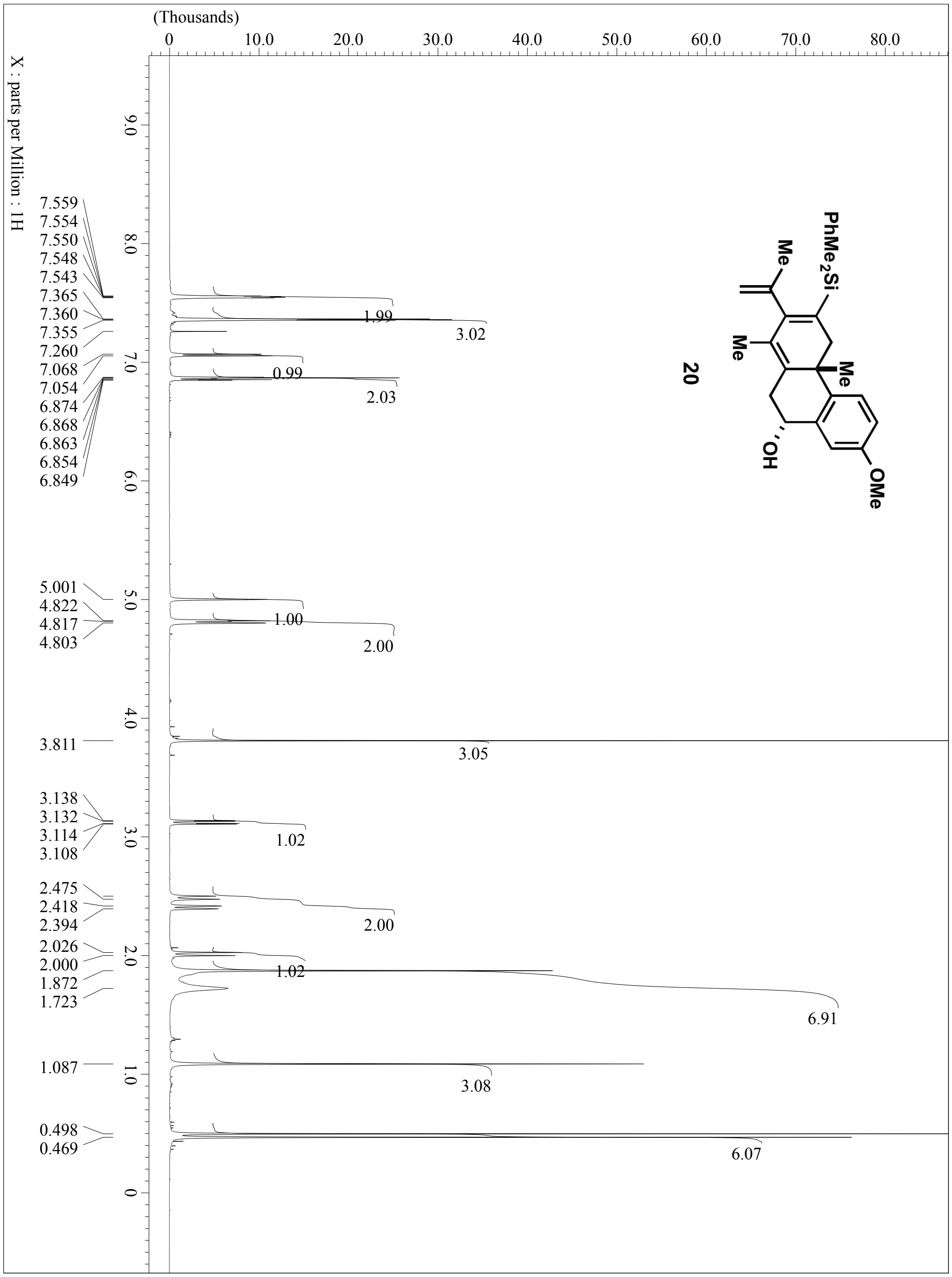


Figure S29: ^{1}H NMR (600 MHz, $CDCl_3$) of **20**.

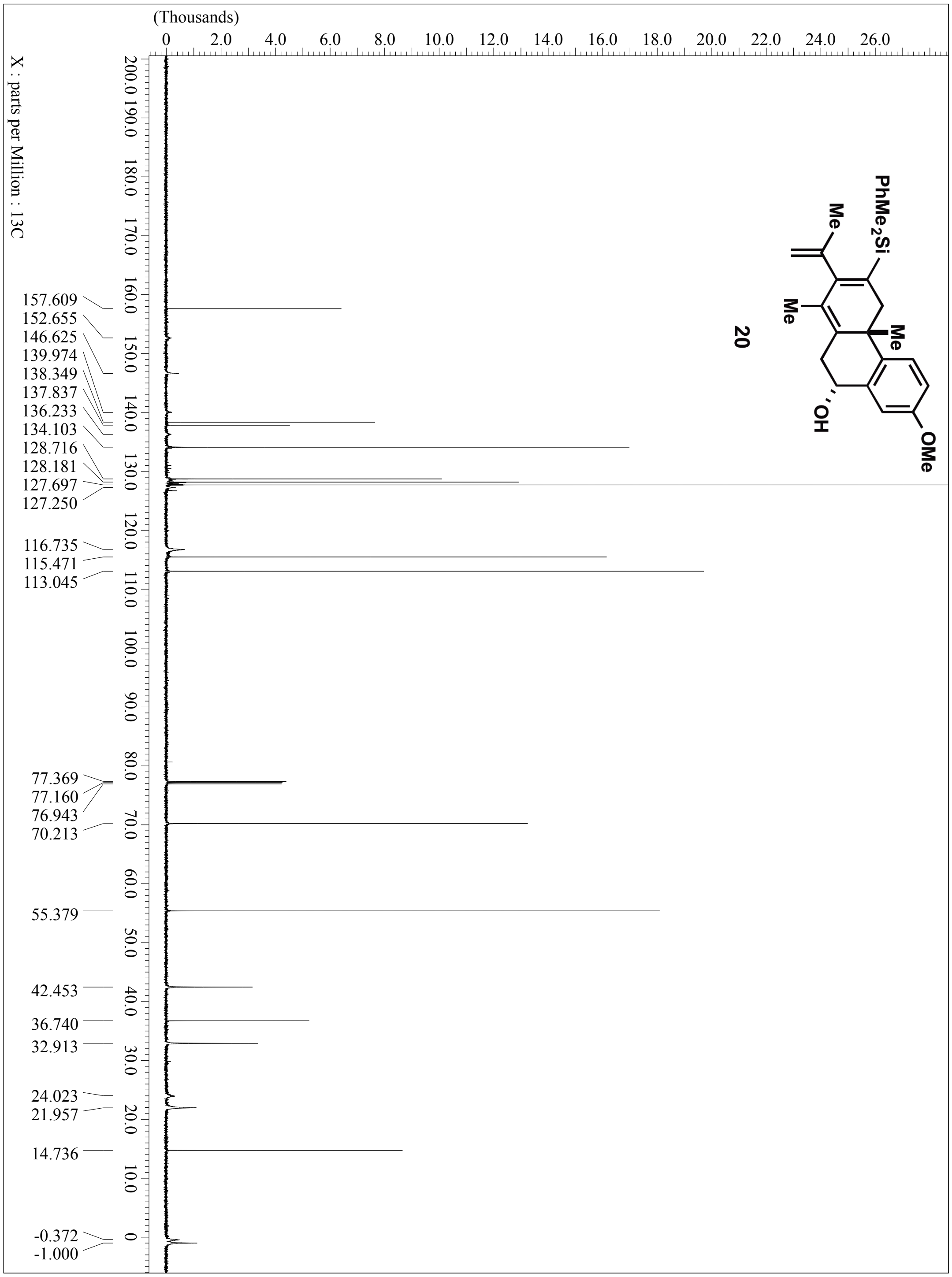


Figure S30: ^{13}C NMR (150 MHz, CDCl$_3$) of **20**.

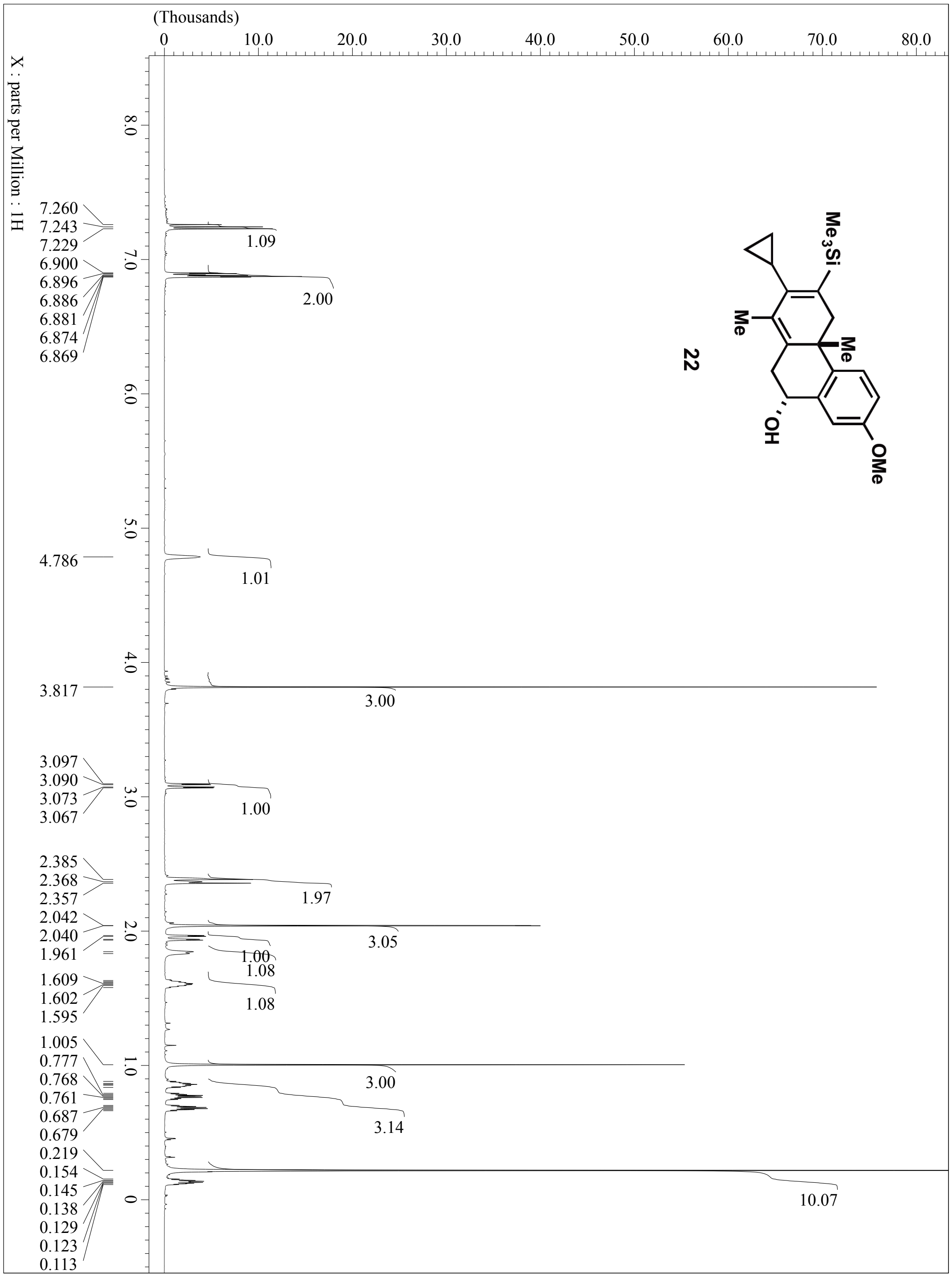


Figure S31: ^{1}H NMR (600 MHz, CDCl$_3$) of **22**.

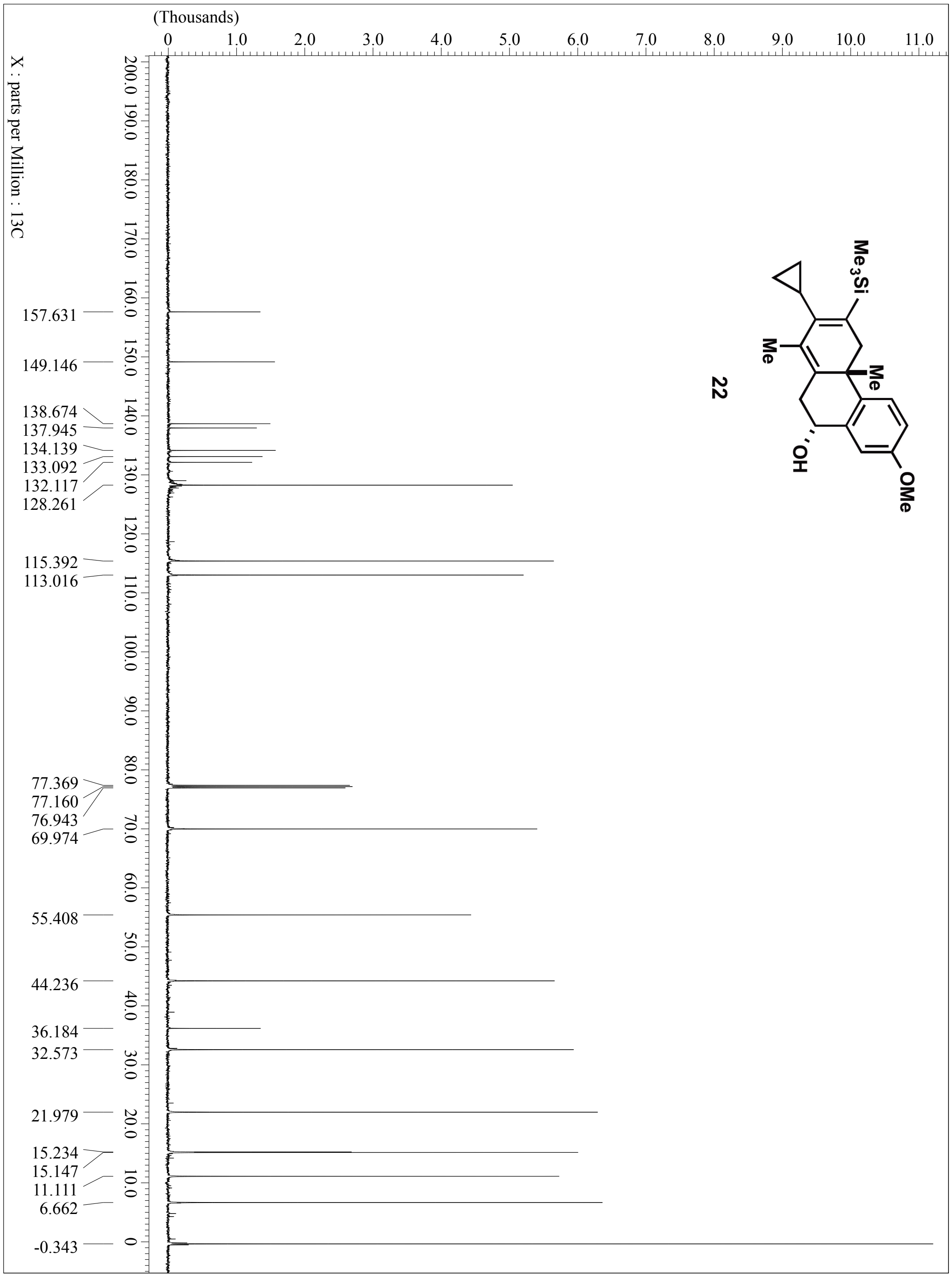


Figure S32: ^{13}C NMR (150 MHz, CDCl$_3$) of **22**.

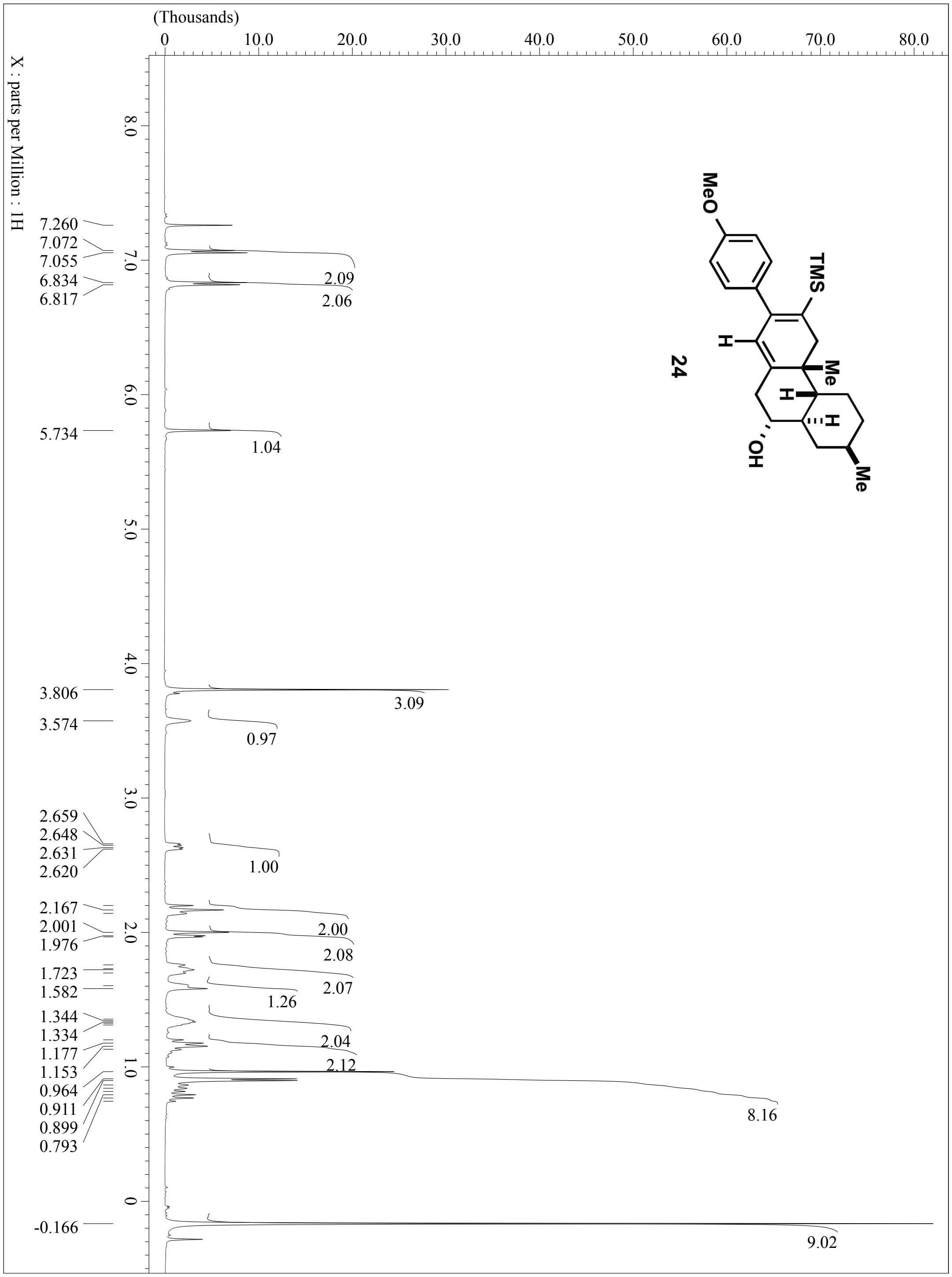


Figure S33: ^{1}H NMR (500 MHz, CDCl$_3$) of **24**.

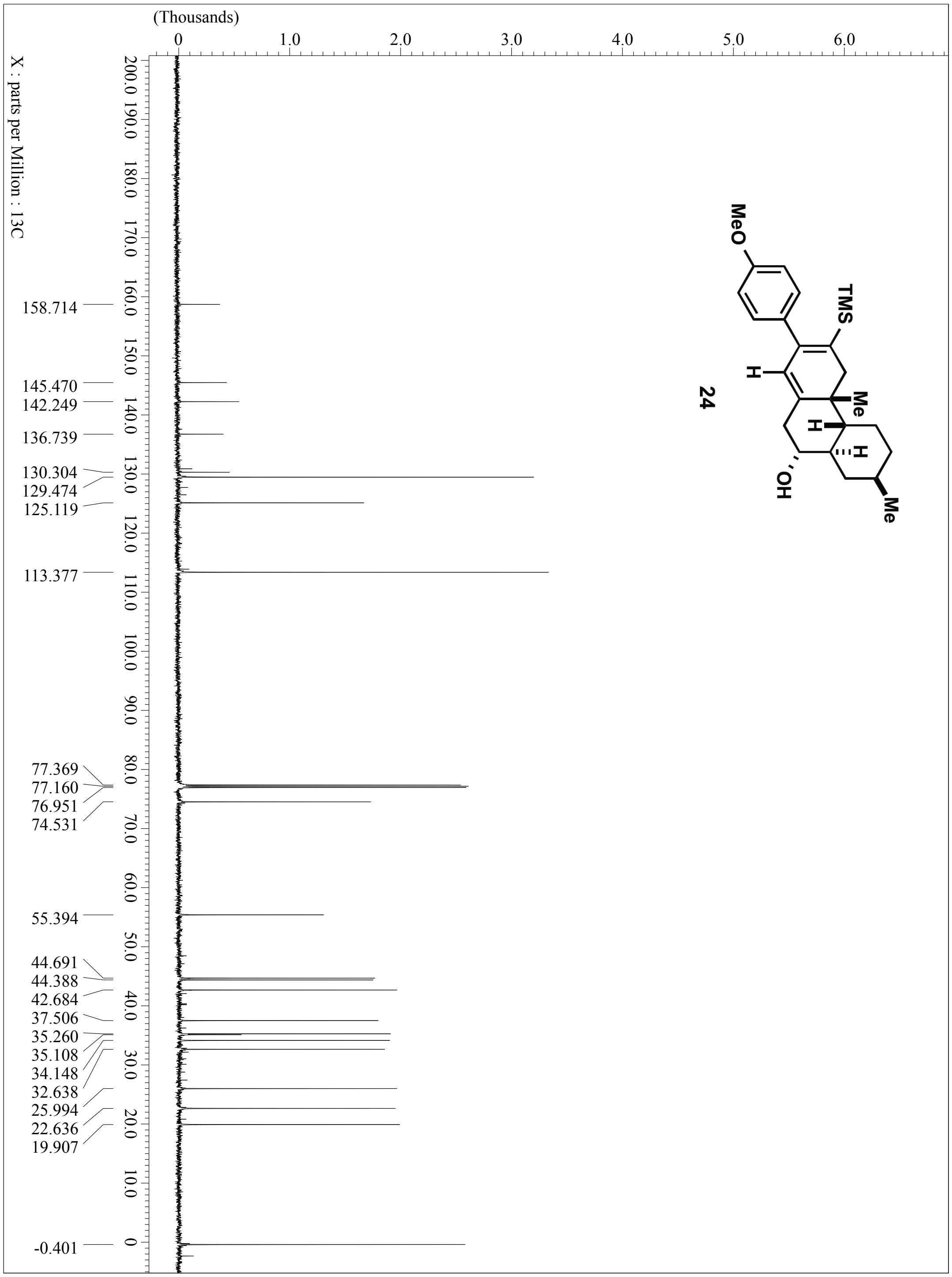


Figure S34: ^{13}C NMR (125 MHz, CDCl$_3$) of **24**.

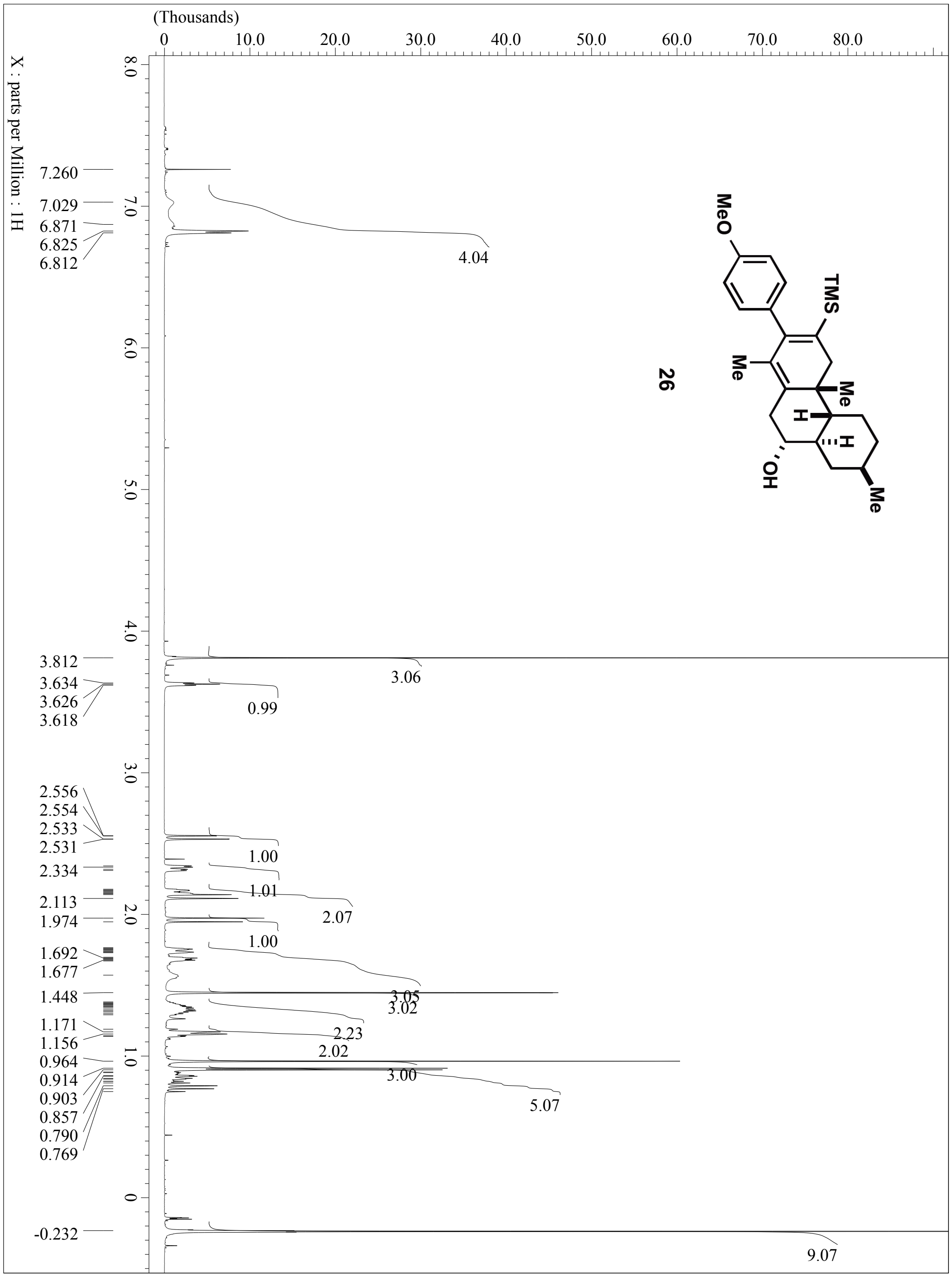


Figure S35: ^{1}H NMR (600 MHz, $CDCl_3$) of **26**.

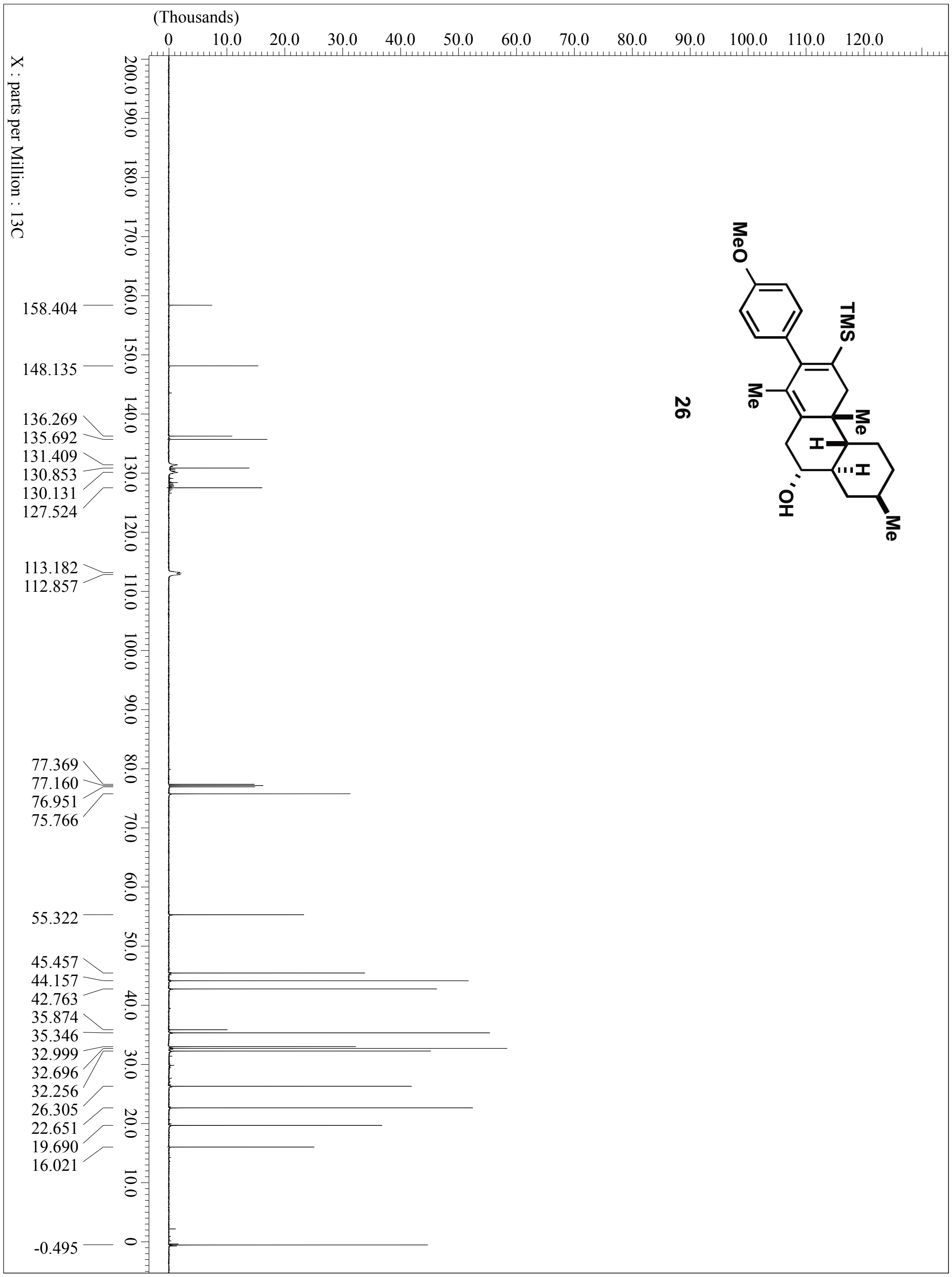


Figure S36: ^{13}C NMR (150 MHz, CDCl$_3$) of **26**.

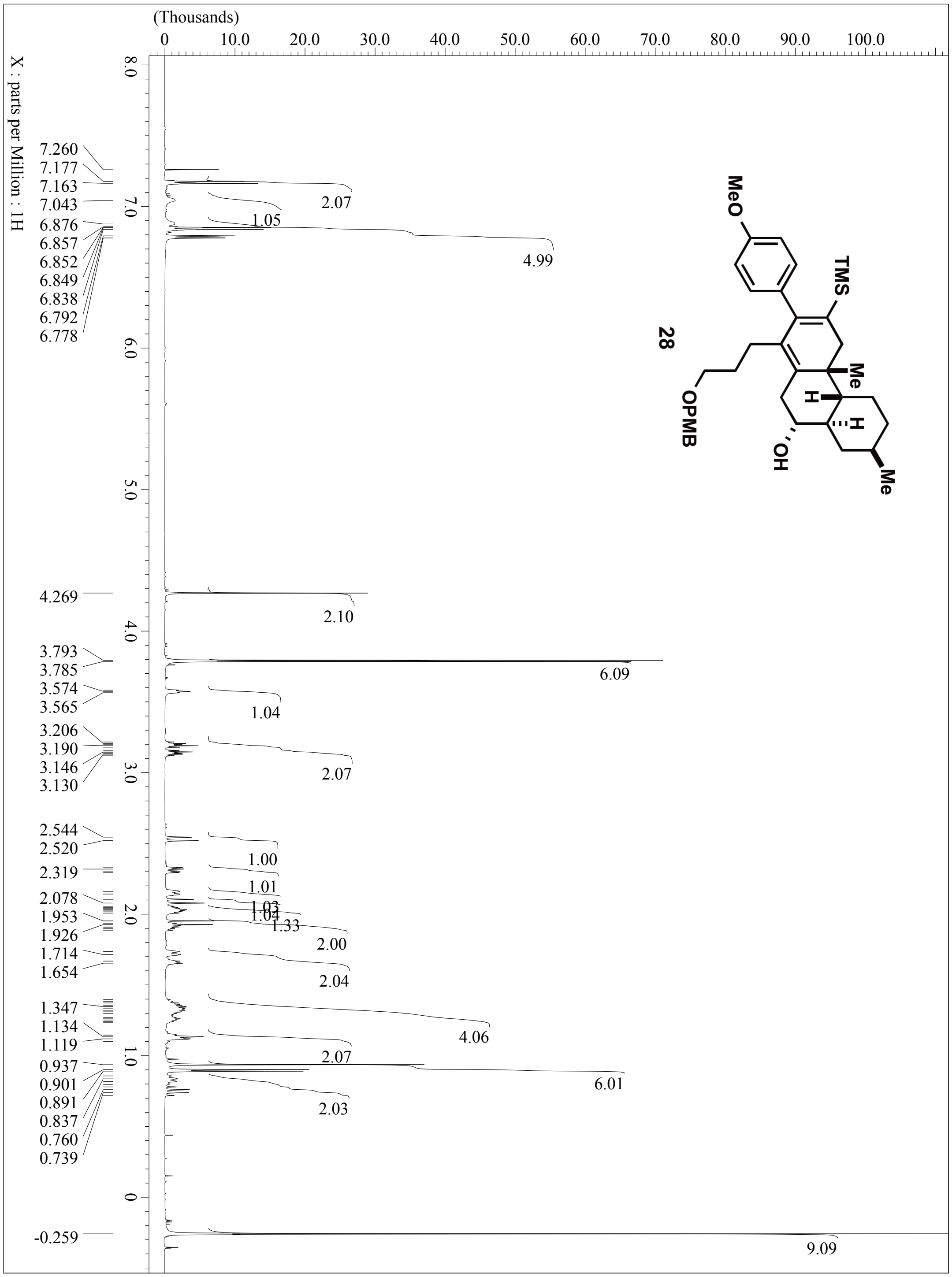


Figure S37: ^{1}H NMR (600 MHz, CDCl$_3$) of **28**.

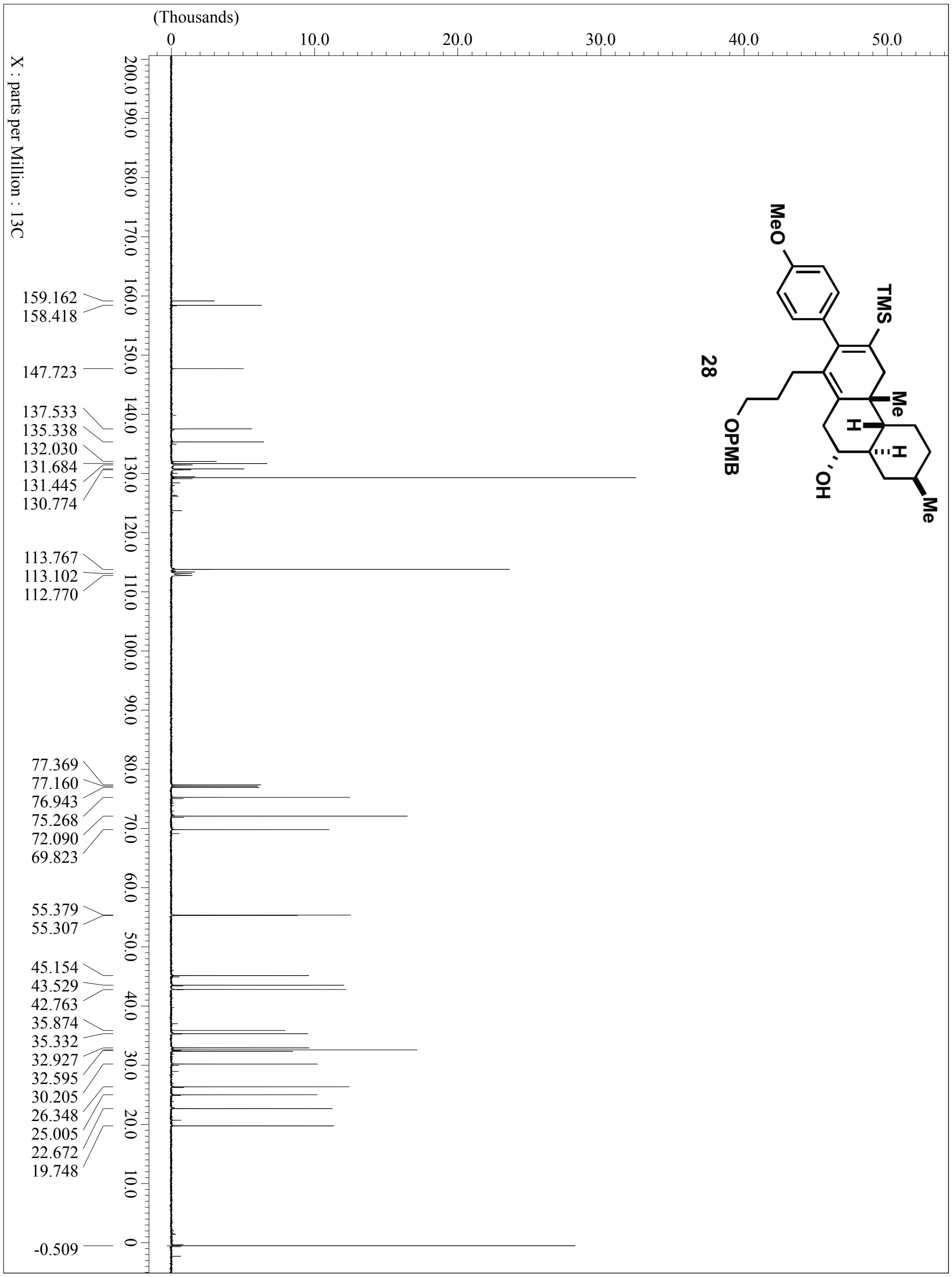


Figure S38: ^{13}C NMR (150 MHz, CDCl$_3$) of **28**.

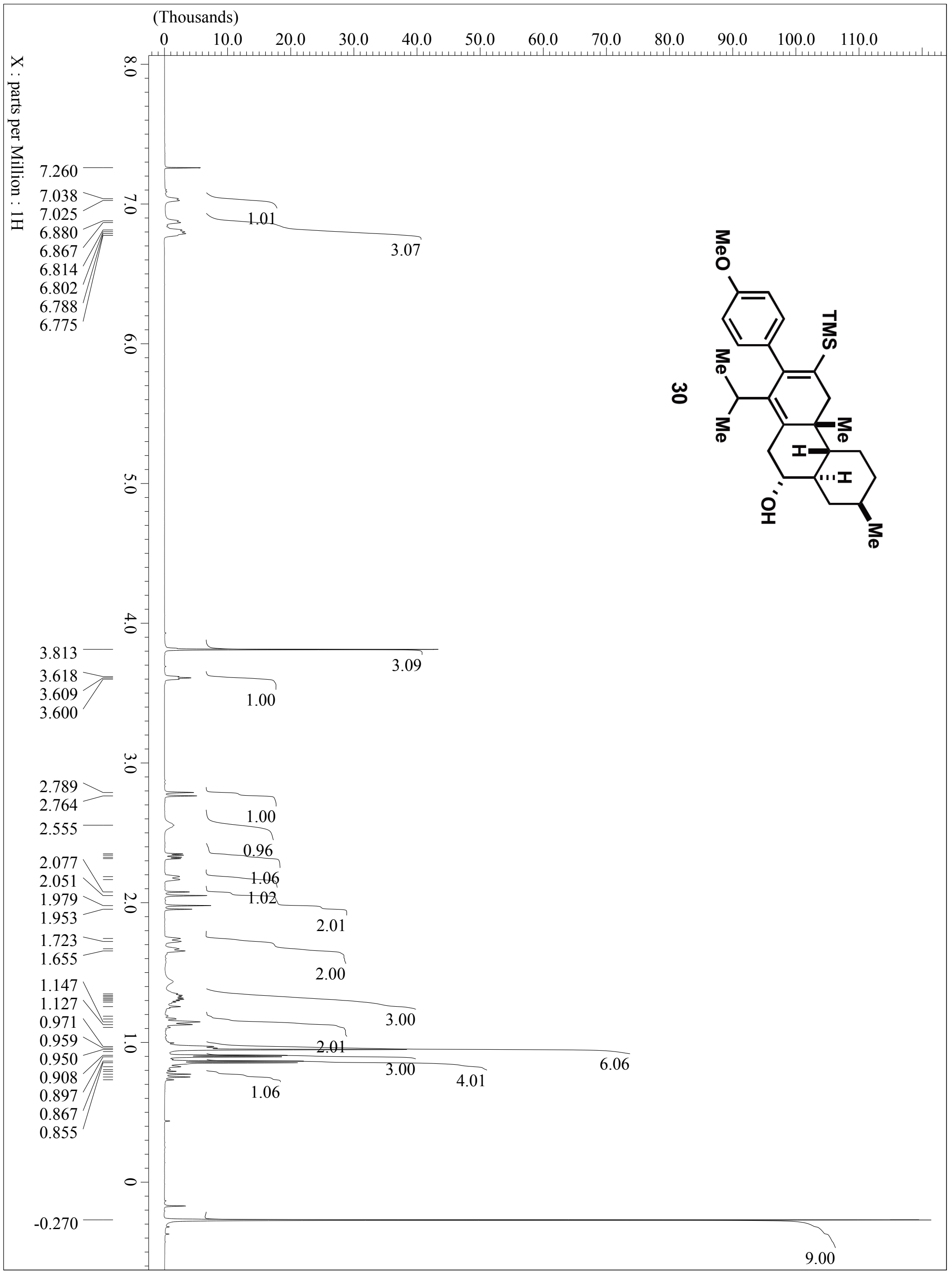


Figure S39: ^{1}H NMR (600 MHz, CDCl$_3$) of **30**.

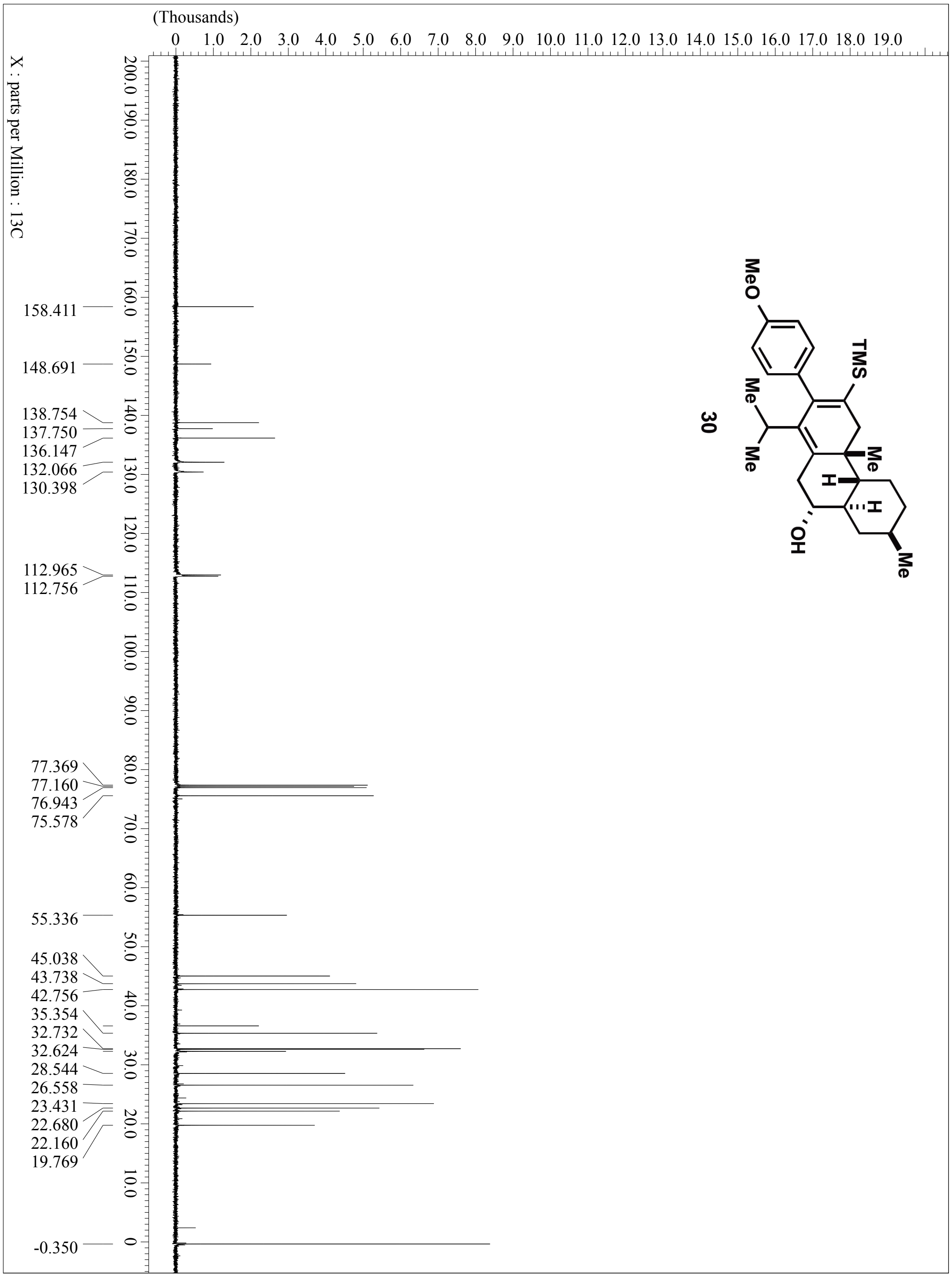


Figure S40: ^{13}C NMR (150 MHz, CDCl$_3$) of **30**.

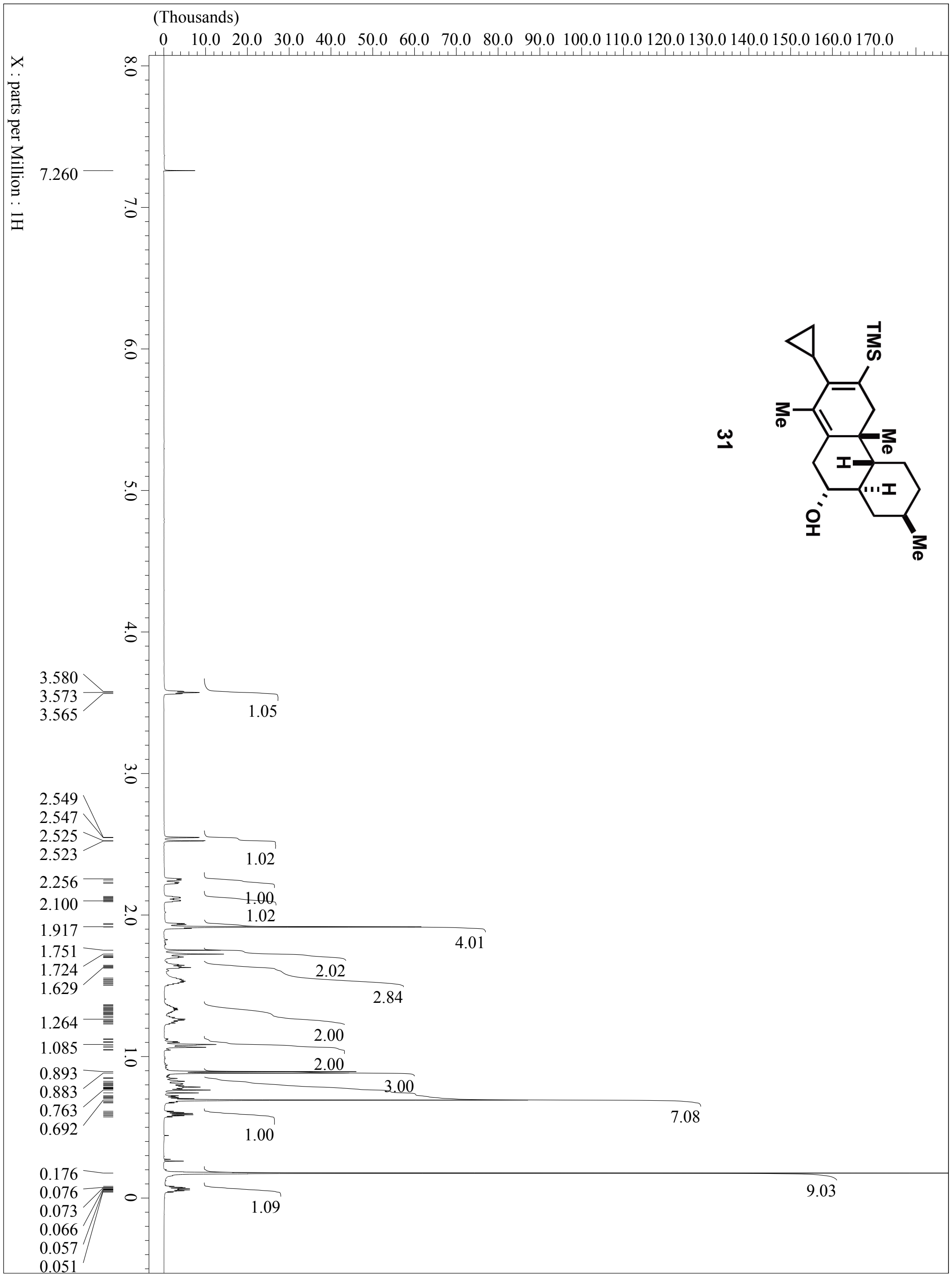


Figure S41: ^{1}H NMR (600 MHz, CDCl$_3$) of **31**.

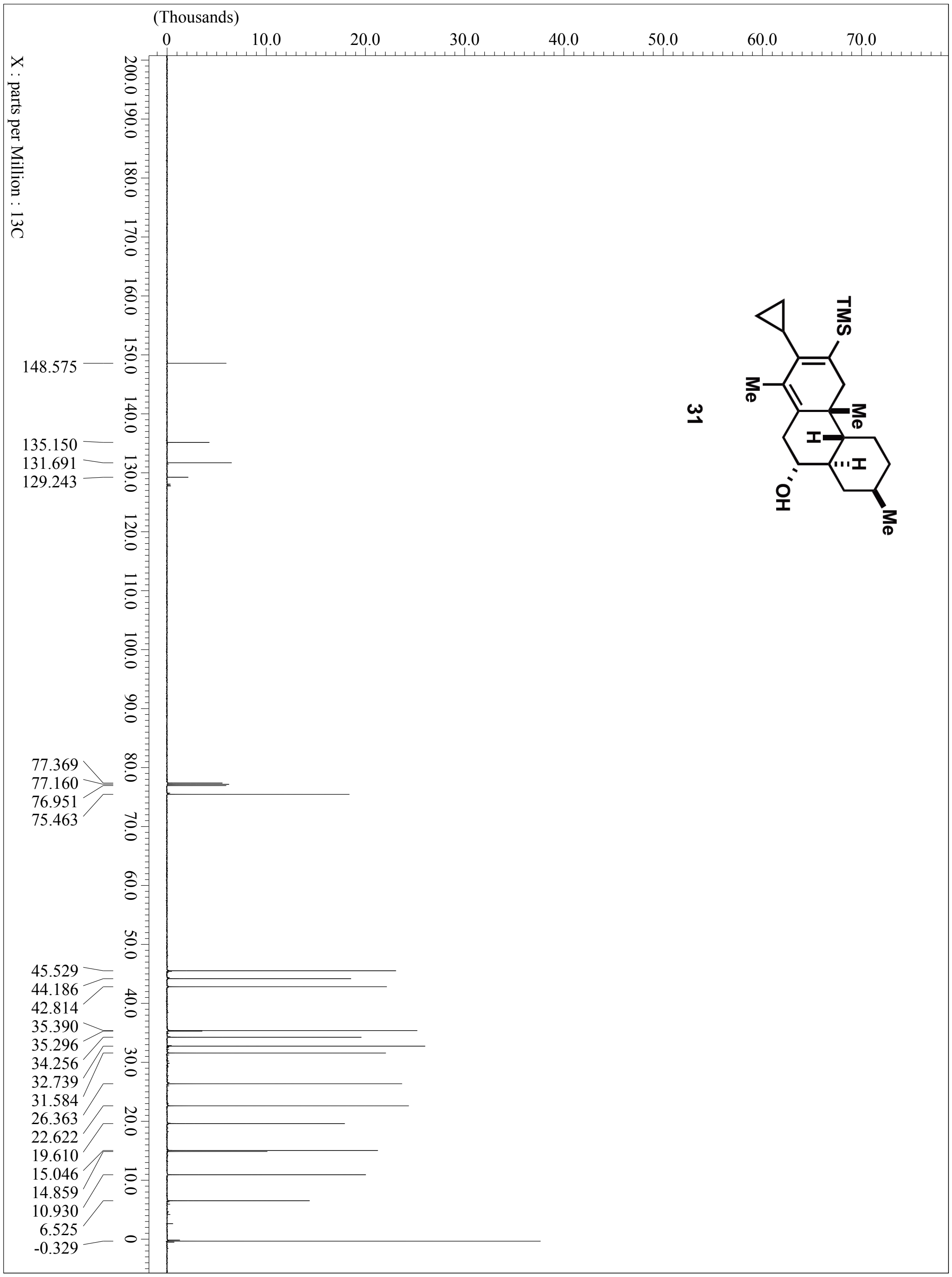


Figure S42: ^{13}C NMR (150 MHz, CDCl$_3$) of **31**.

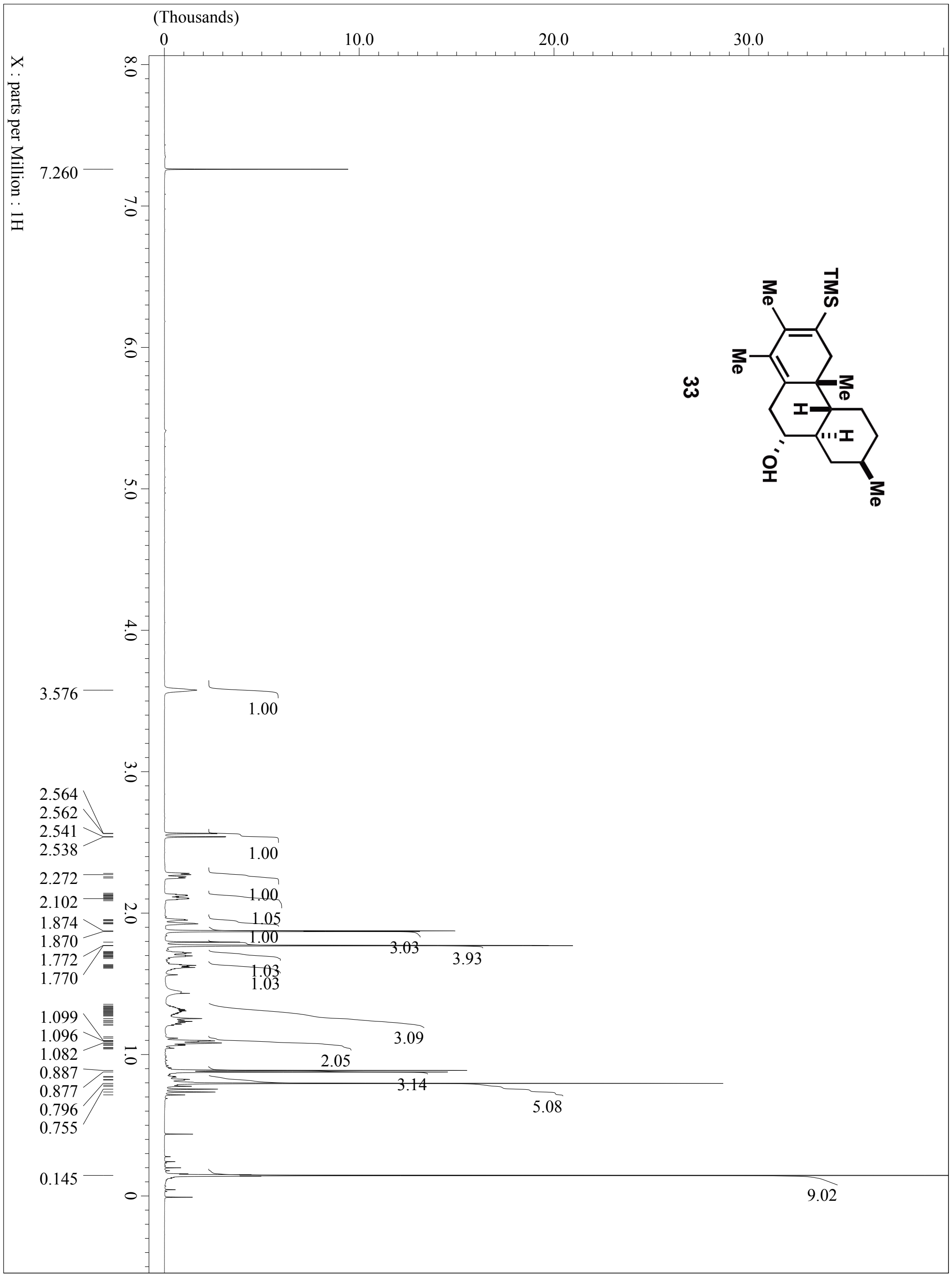


Figure S43: ^{1}H NMR (600 MHz, CDCl$_3$) of **33**.

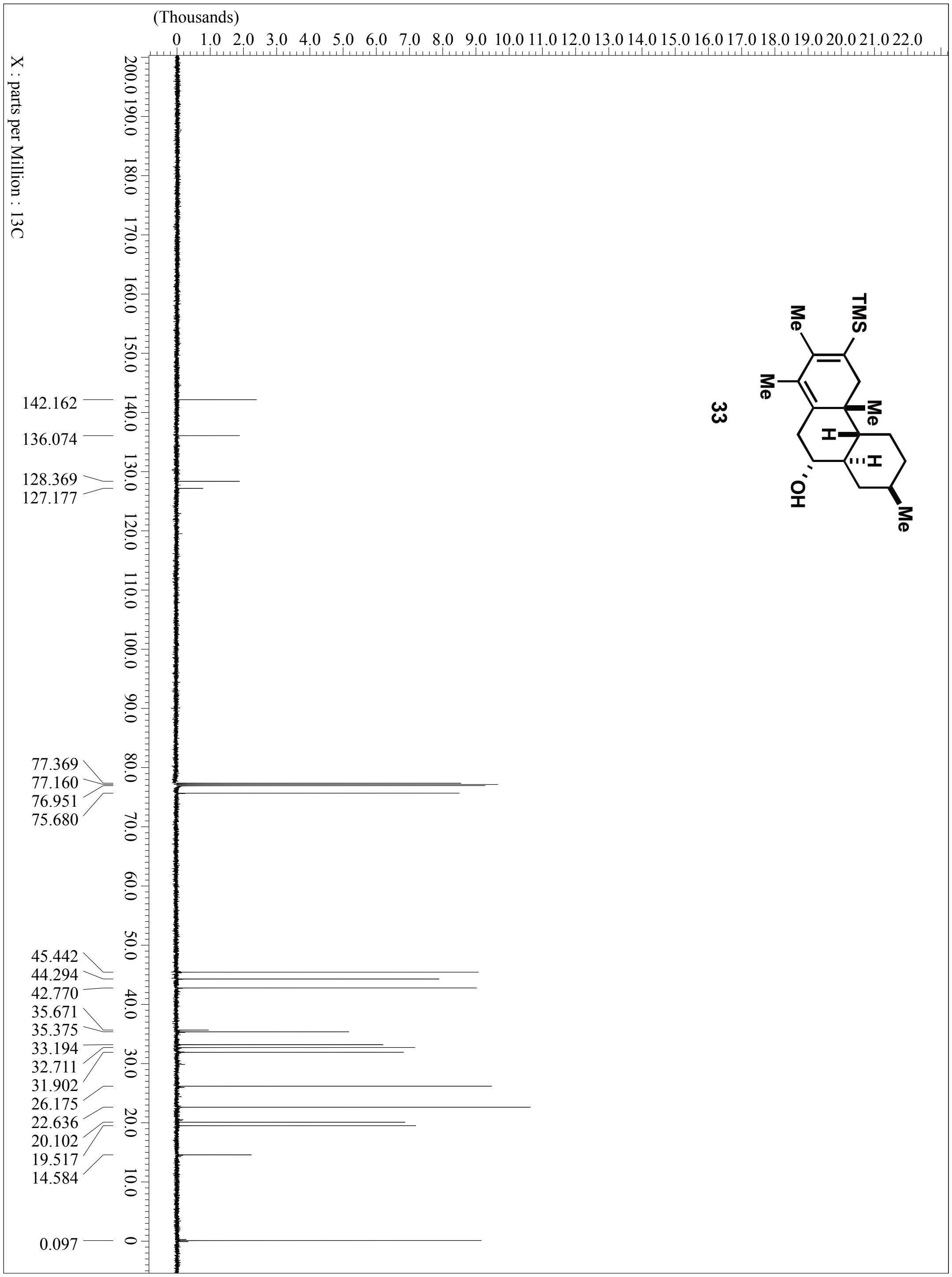


Figure S44: ^{13}C NMR (150 MHz, CDCl$_3$) of **33**.

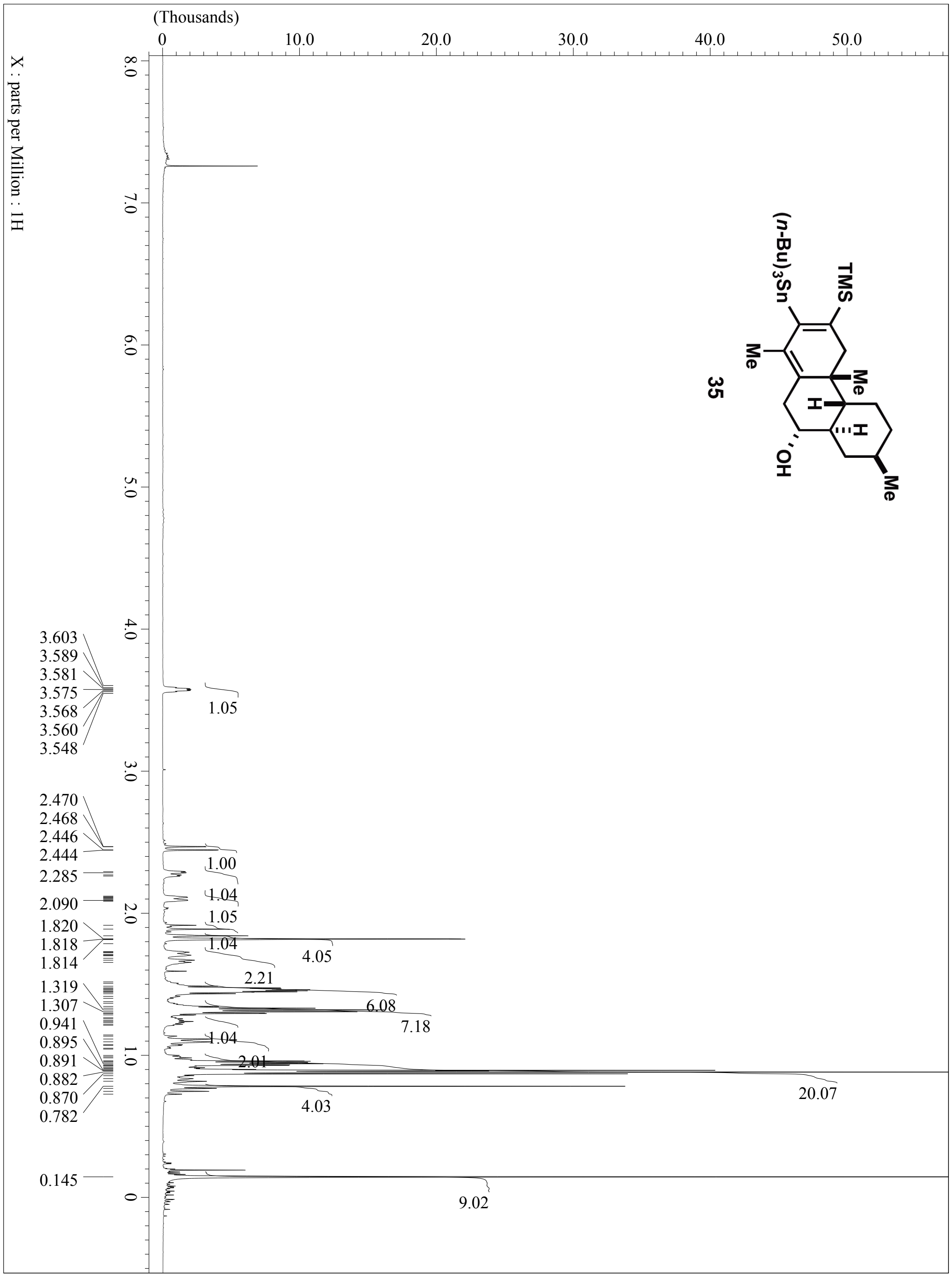


Figure S45: ^{1}H NMR (600 MHz, CDCl$_3$) of **35**.

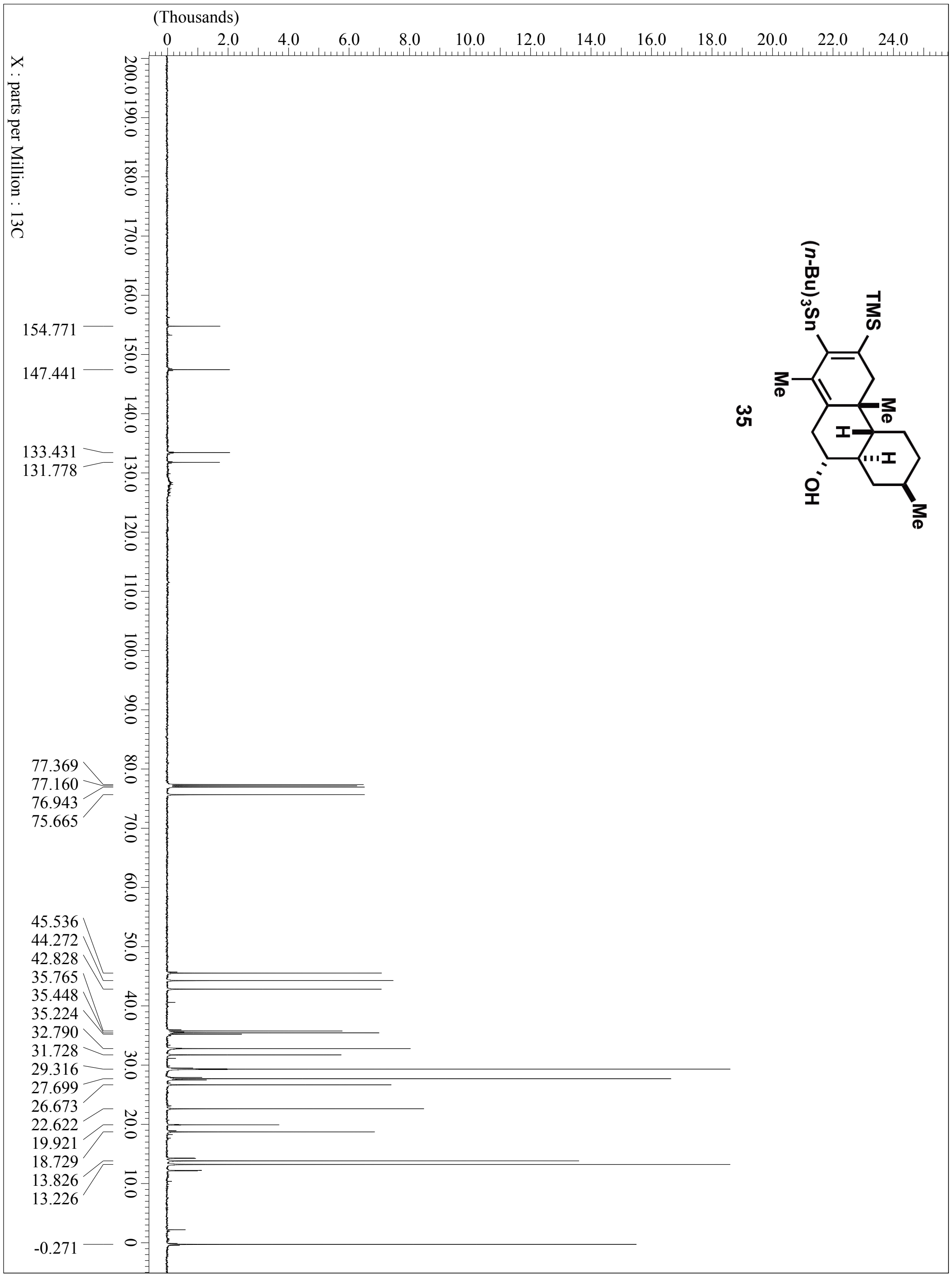


Figure S46: ^{13}C NMR (150 MHz, CDCl$_3$) of **35**.

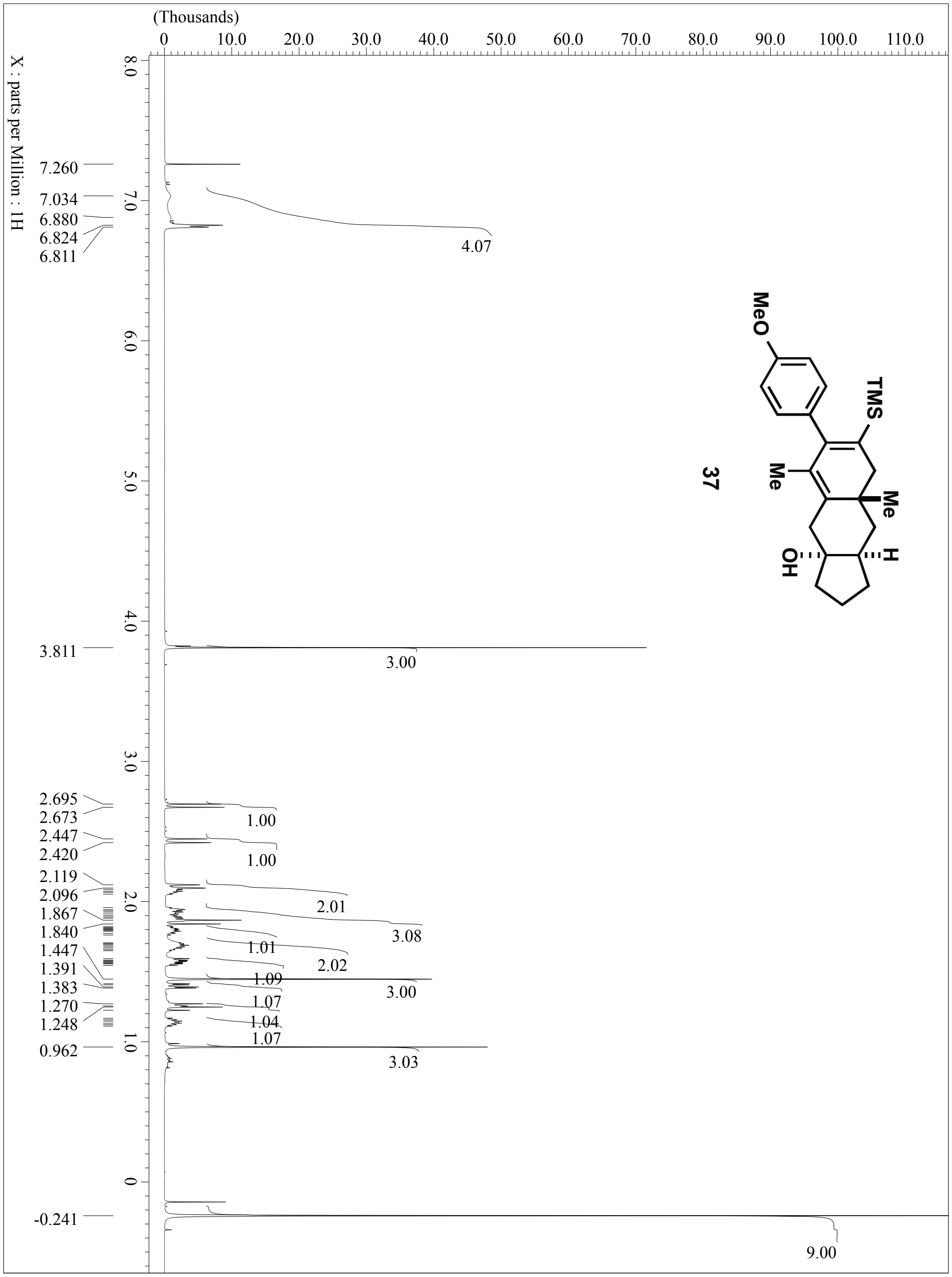


Figure S47: ^{1}H NMR (600 MHz, $CDCl_3$) of **37**.

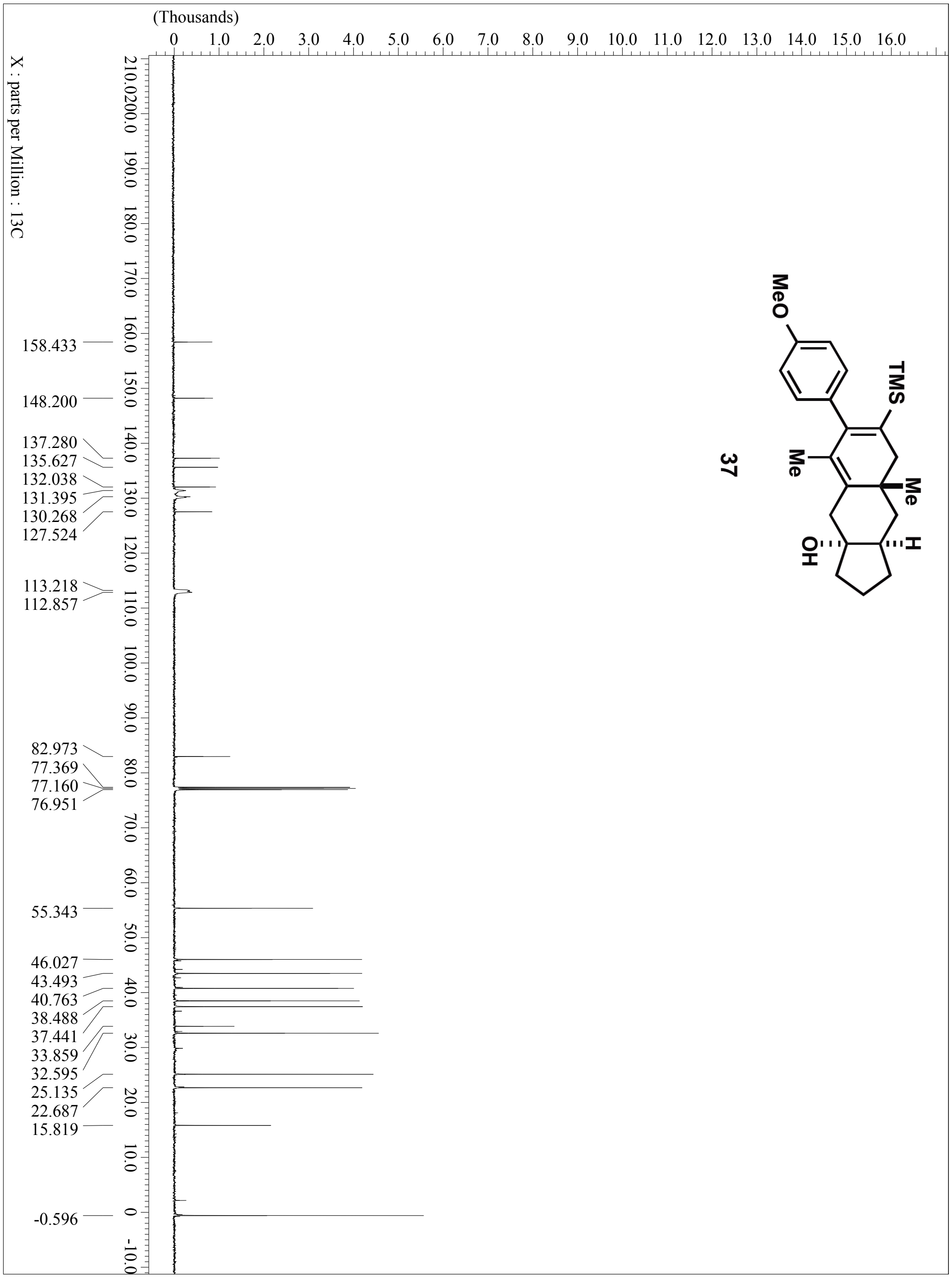
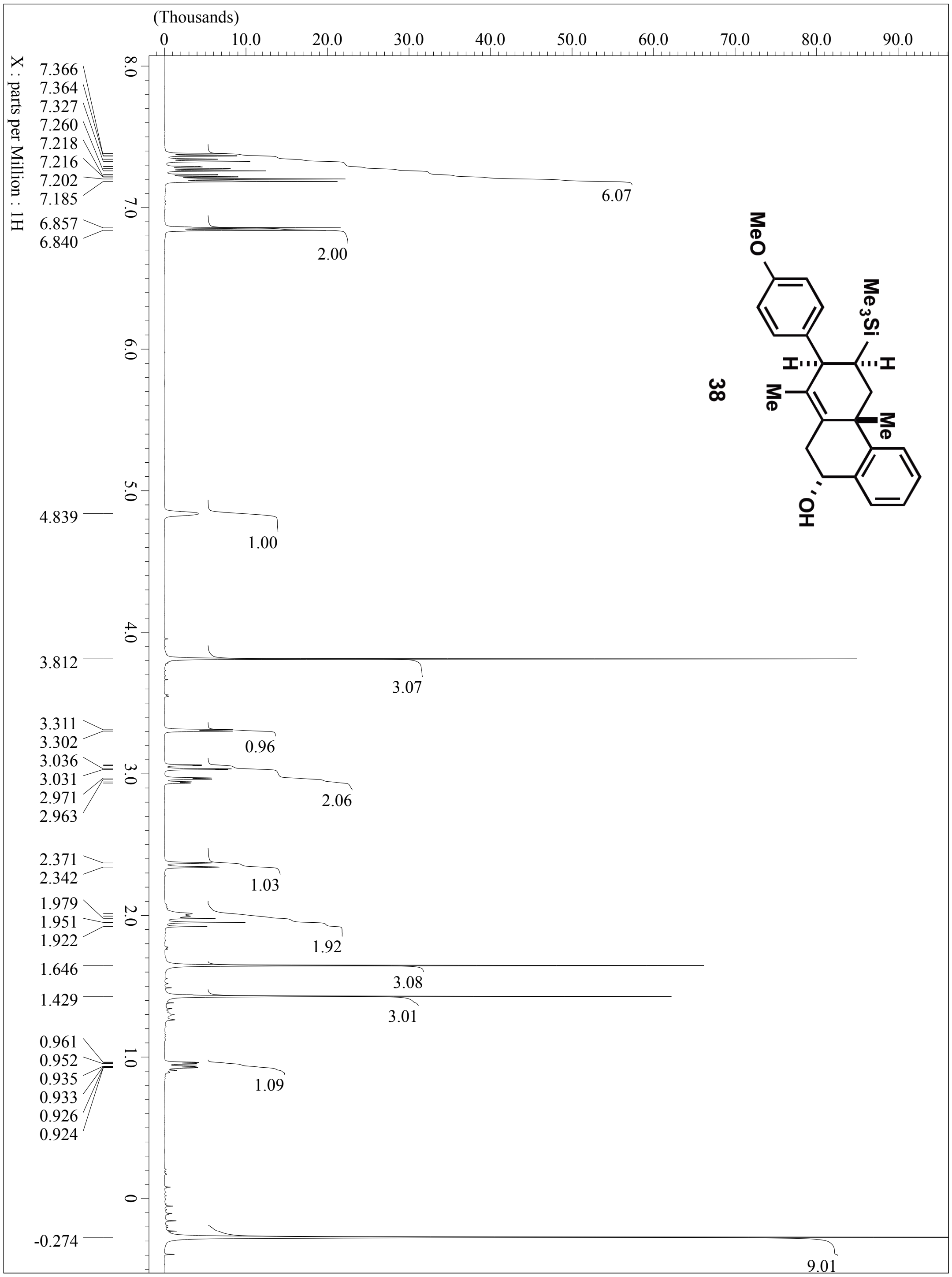


Figure S48: ^{13}C NMR (600 MHz, CDCl$_3$) of **37**.



38

Figure S49: ^{1}H NMR (600 MHz, CDCl$_3$) of **38**.

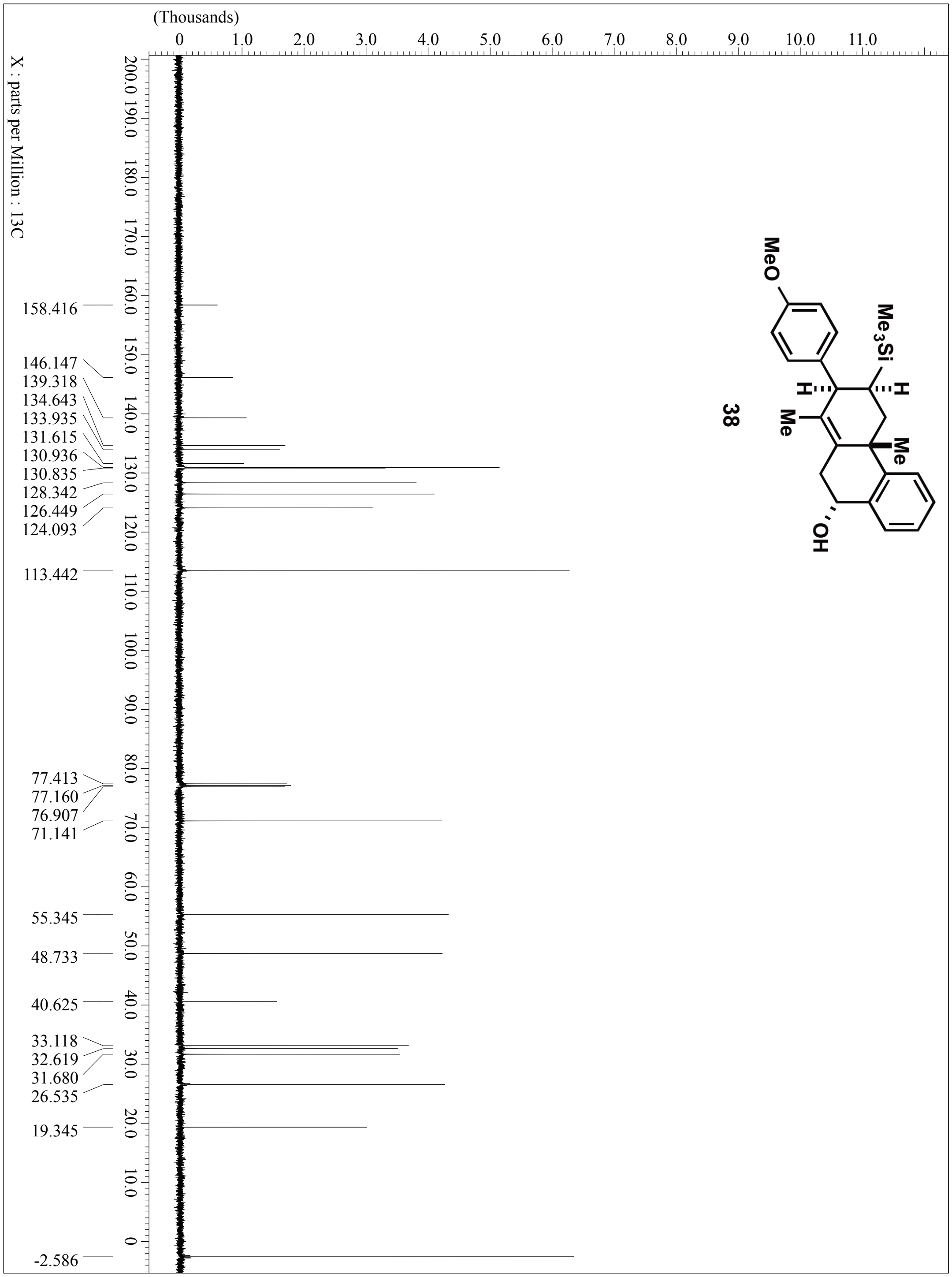


Figure S50: ^{13}C NMR (150 MHz, $CDCl_3$) of **38**.

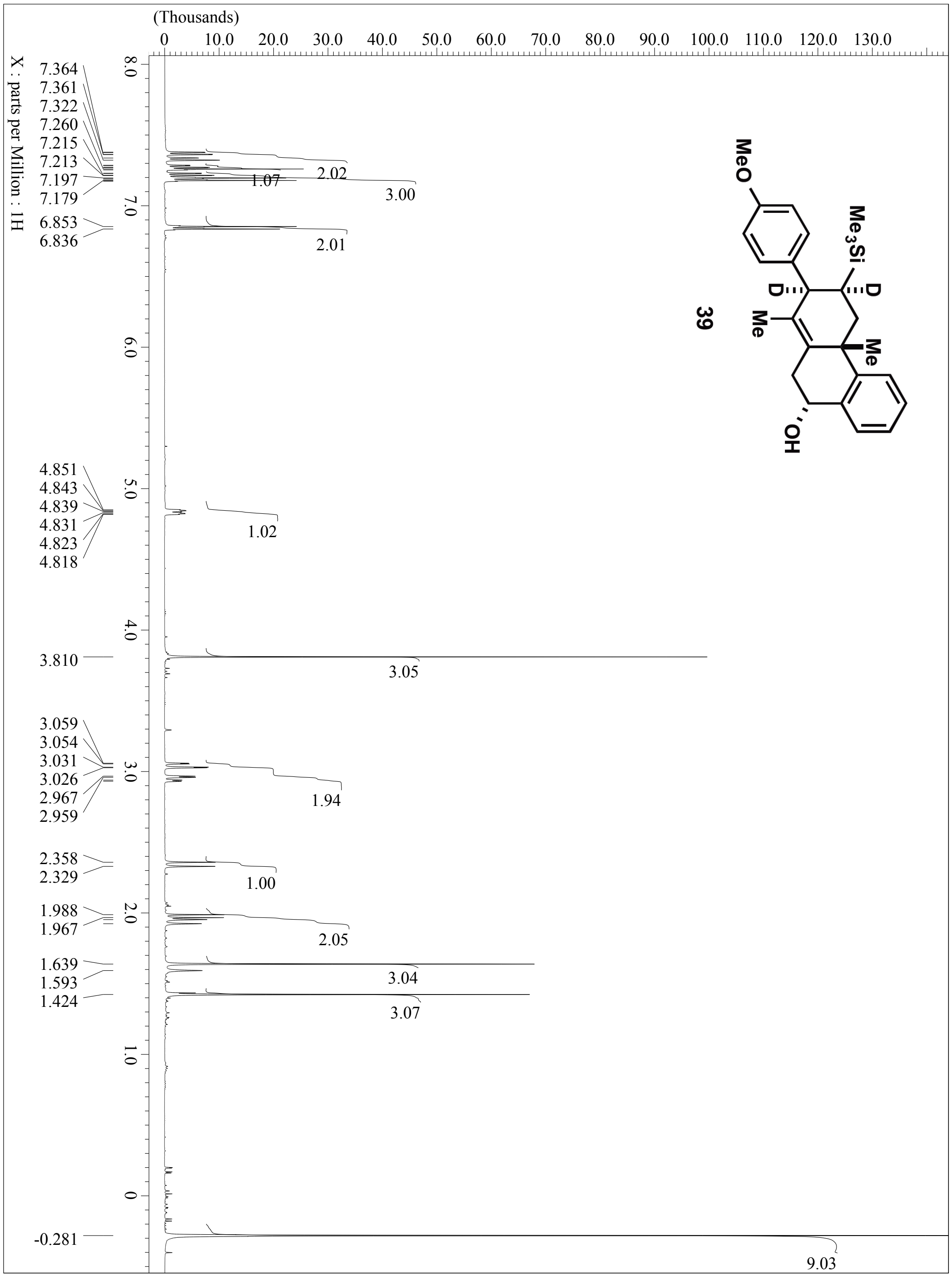


Figure S51: ^{1}H NMR (600 MHz, CDCl$_3$) of **39**.

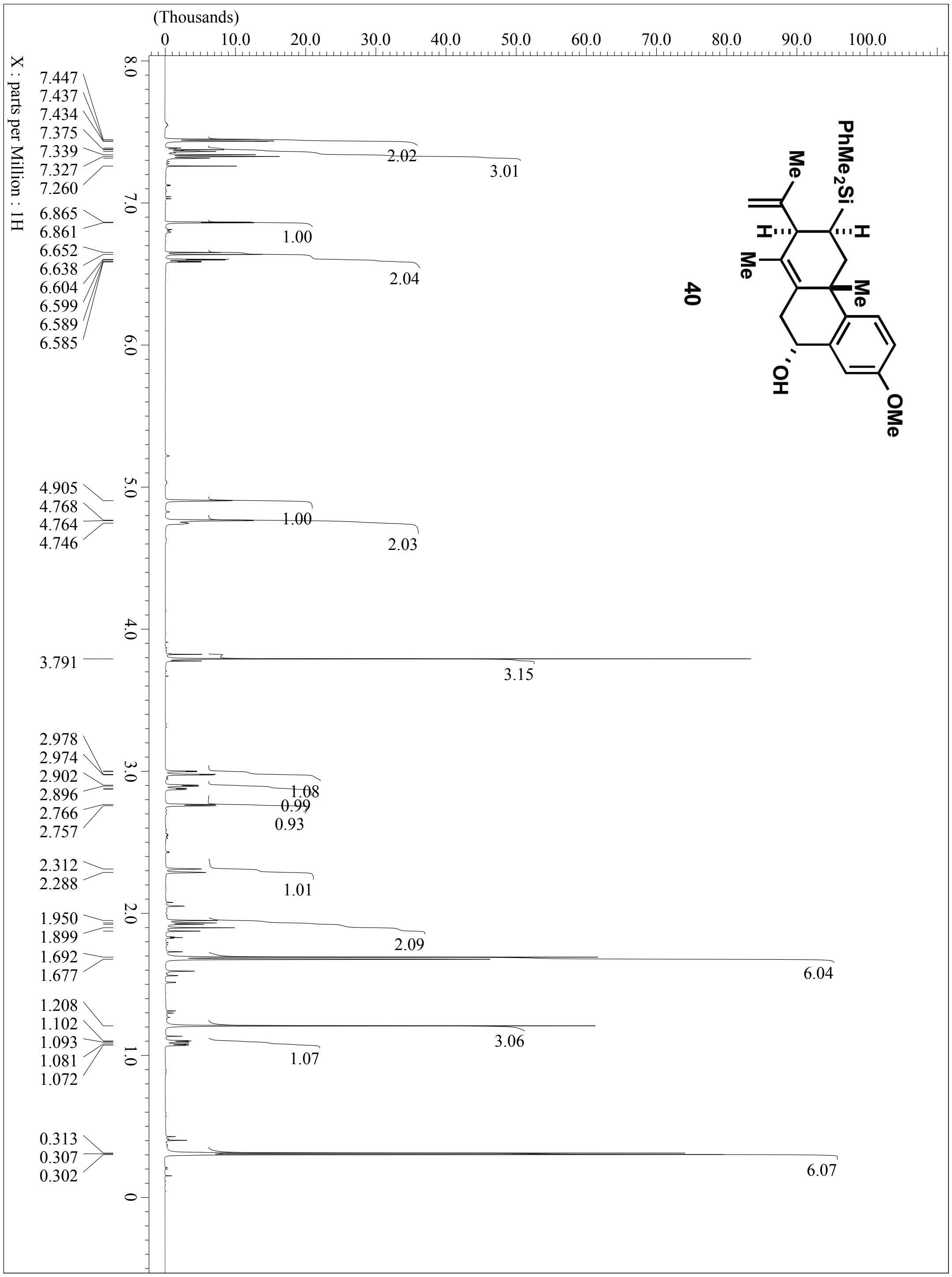


Figure S52: ^{1}H NMR (600 MHz, CDCl$_3$) of **40.**

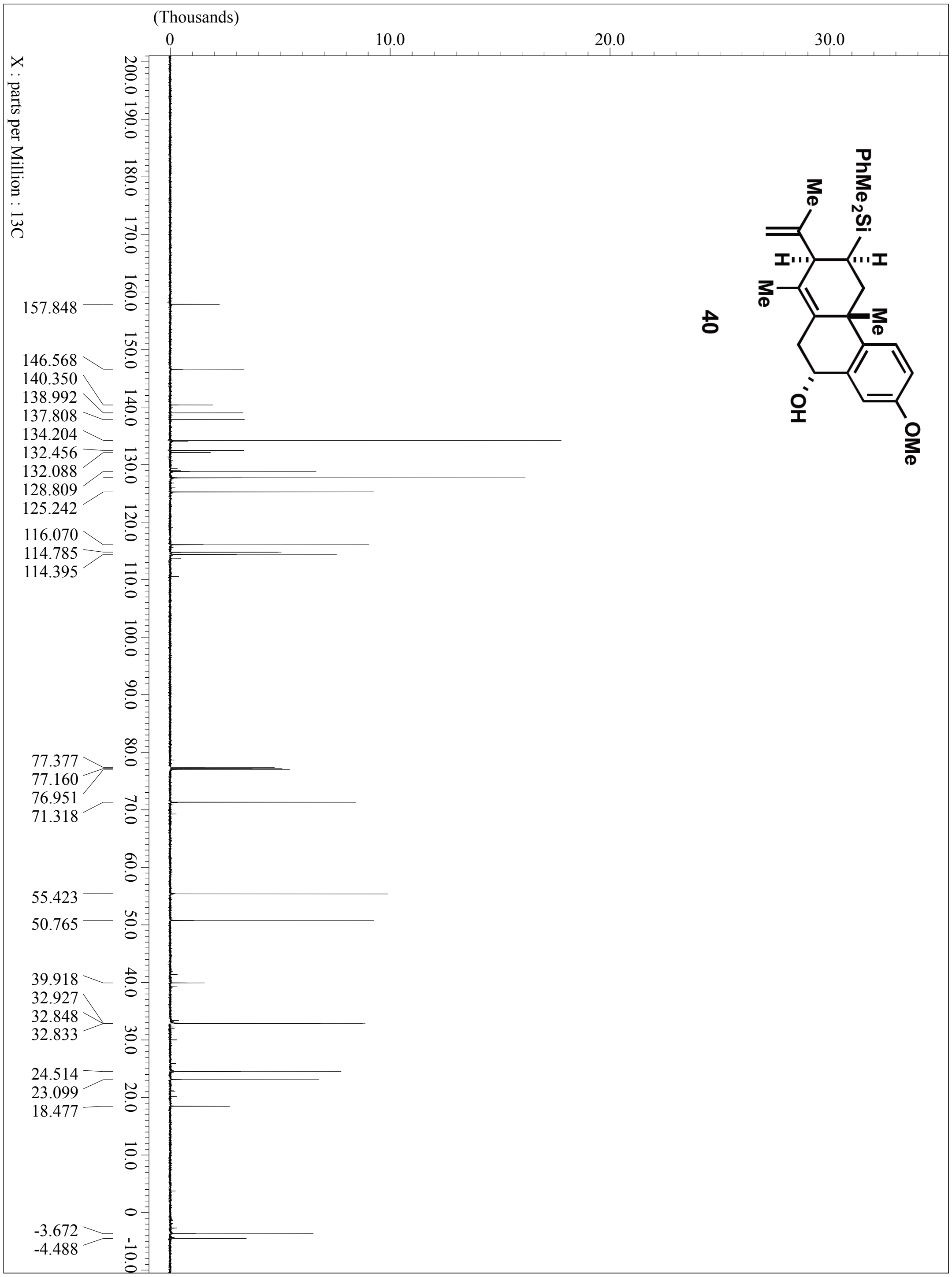


Figure S53: ^{13}C NMR (150 MHz, CDCl$_3$) of **40**.

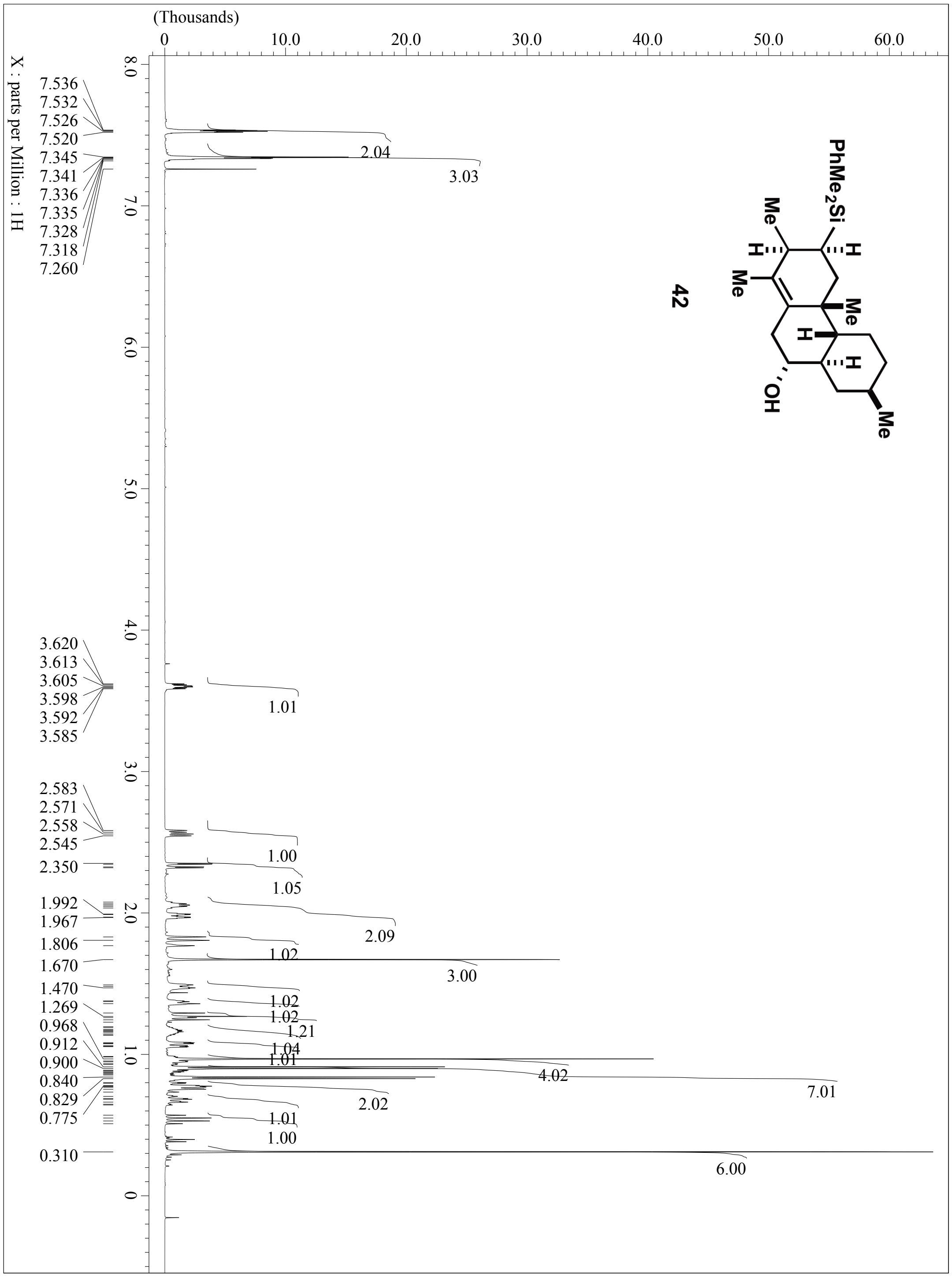


Figure S54: ^{1}H NMR (600 MHz, CDCl$_3$) of **42**.

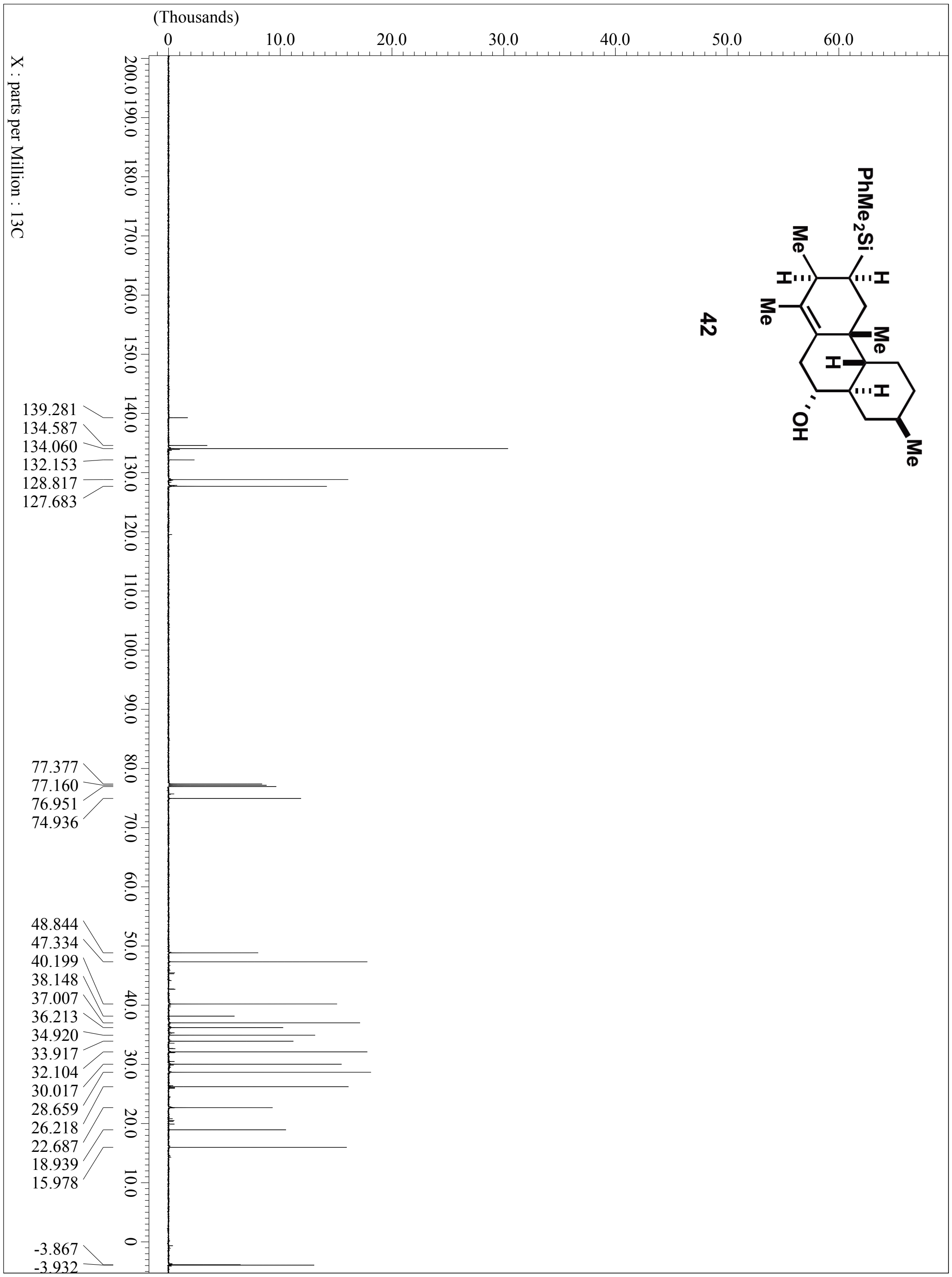


Figure S55: ^{13}C NMR (150 MHz, CDCl$_3$) of **42**.

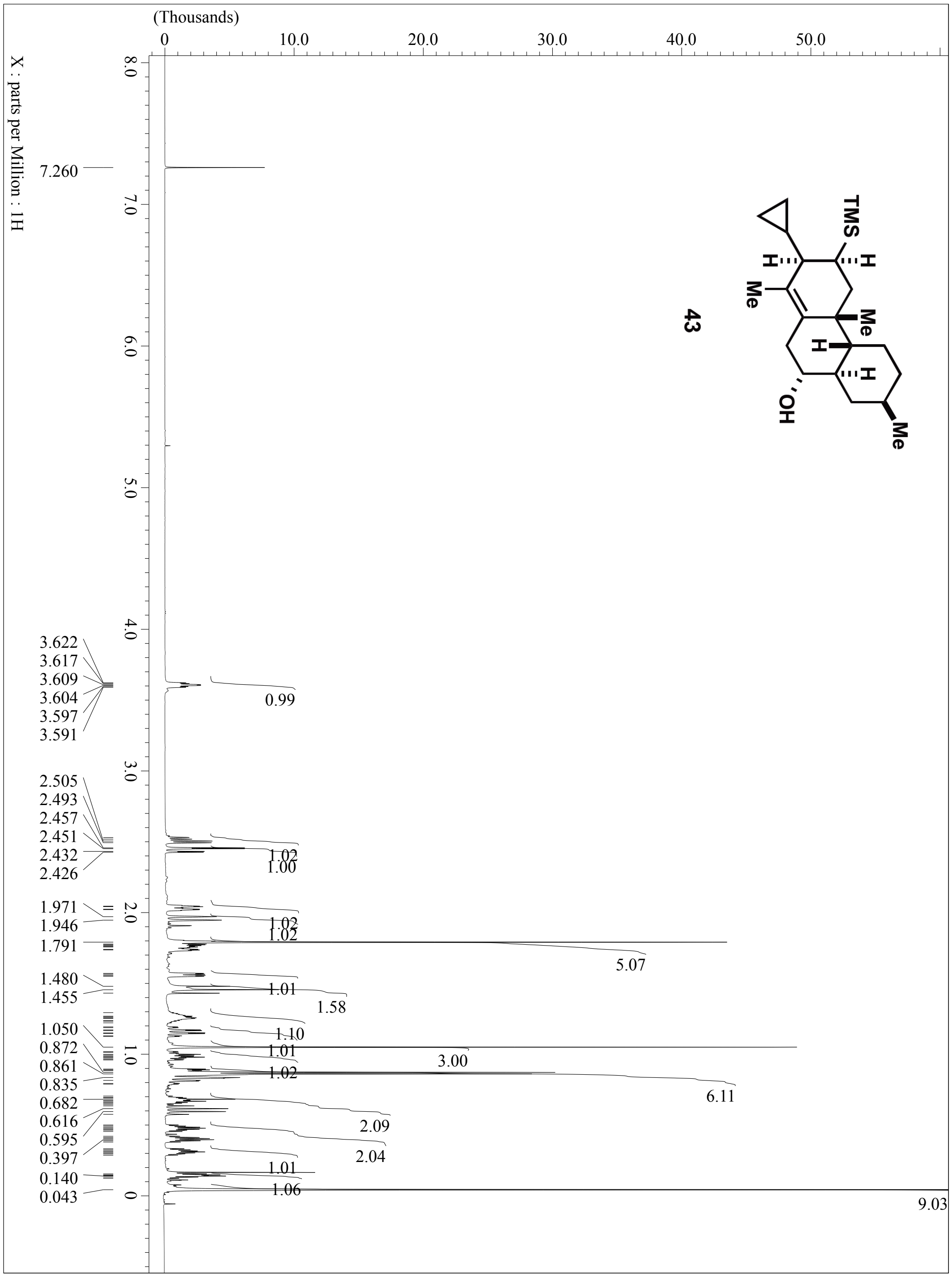


Figure S56: ^{1}H NMR (600 MHz, CDCl$_3$) of **43**.

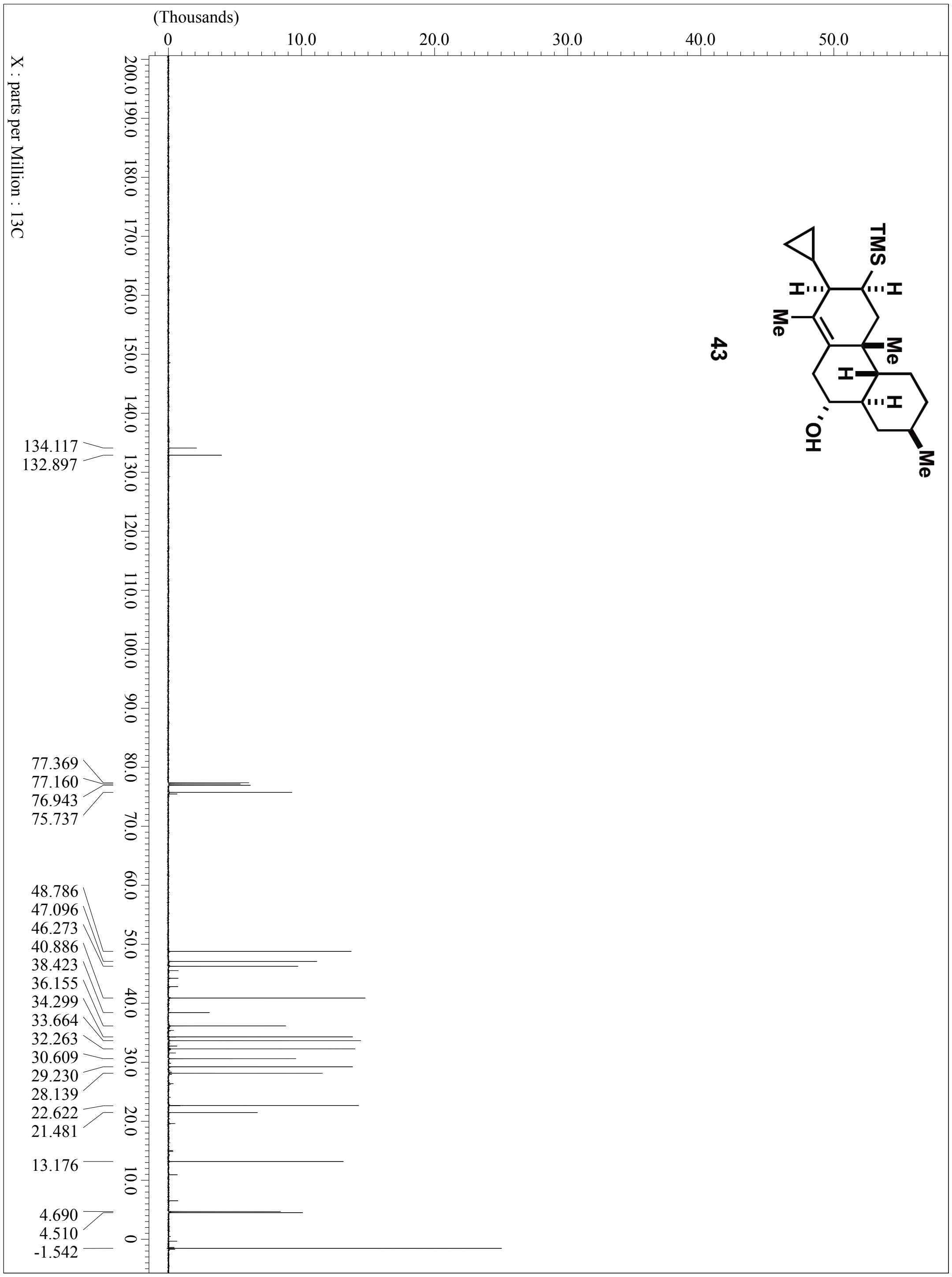


Figure S57: ^{13}C NMR (150 MHz, CDCl$_3$) of **43**.

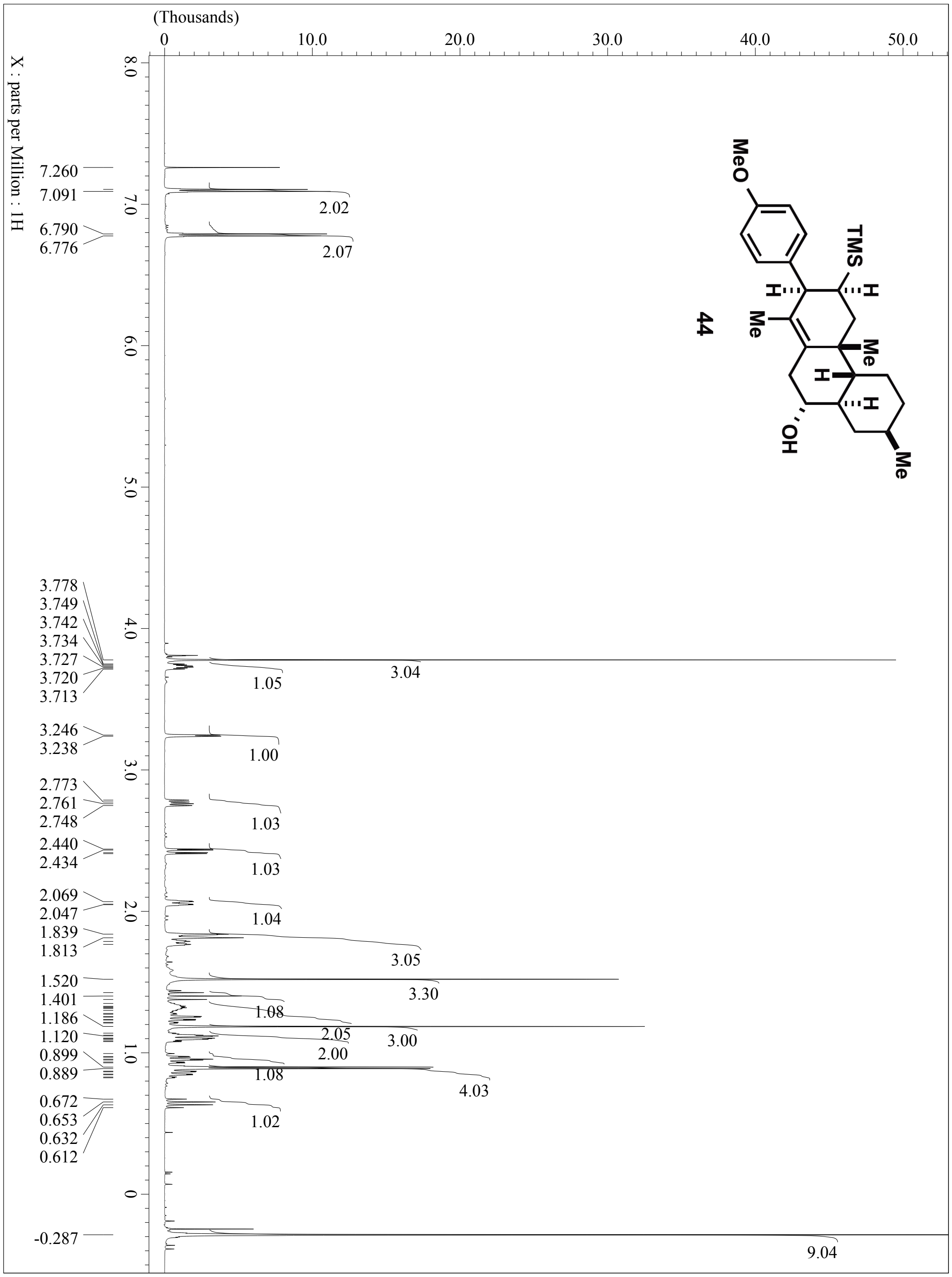


Figure S58: ^{1}H NMR (600 MHz, CDCl$_3$) of **44**.

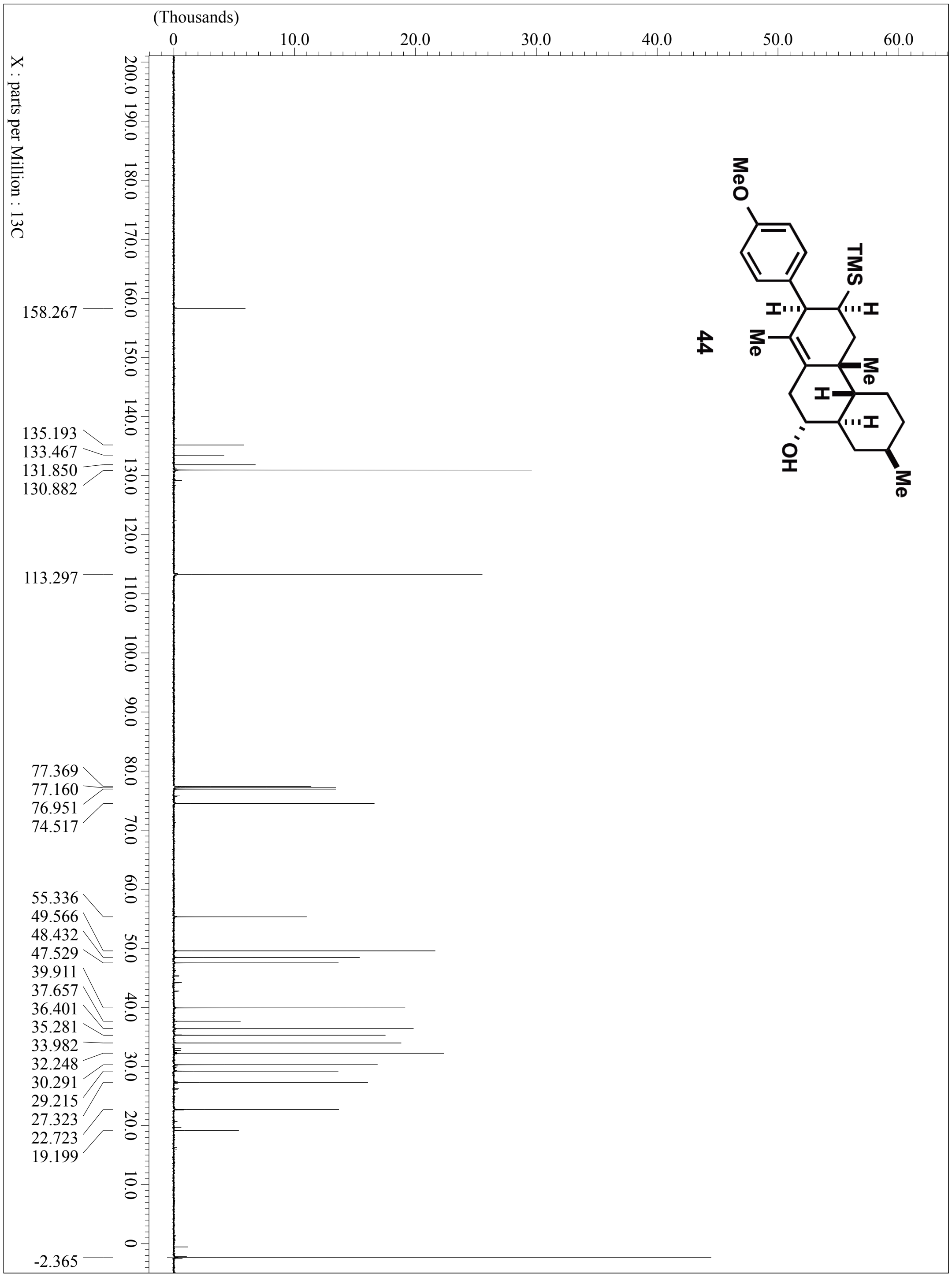


Figure S59: ^{13}C NMR (150 MHz, CDCl$_3$) of **44**.

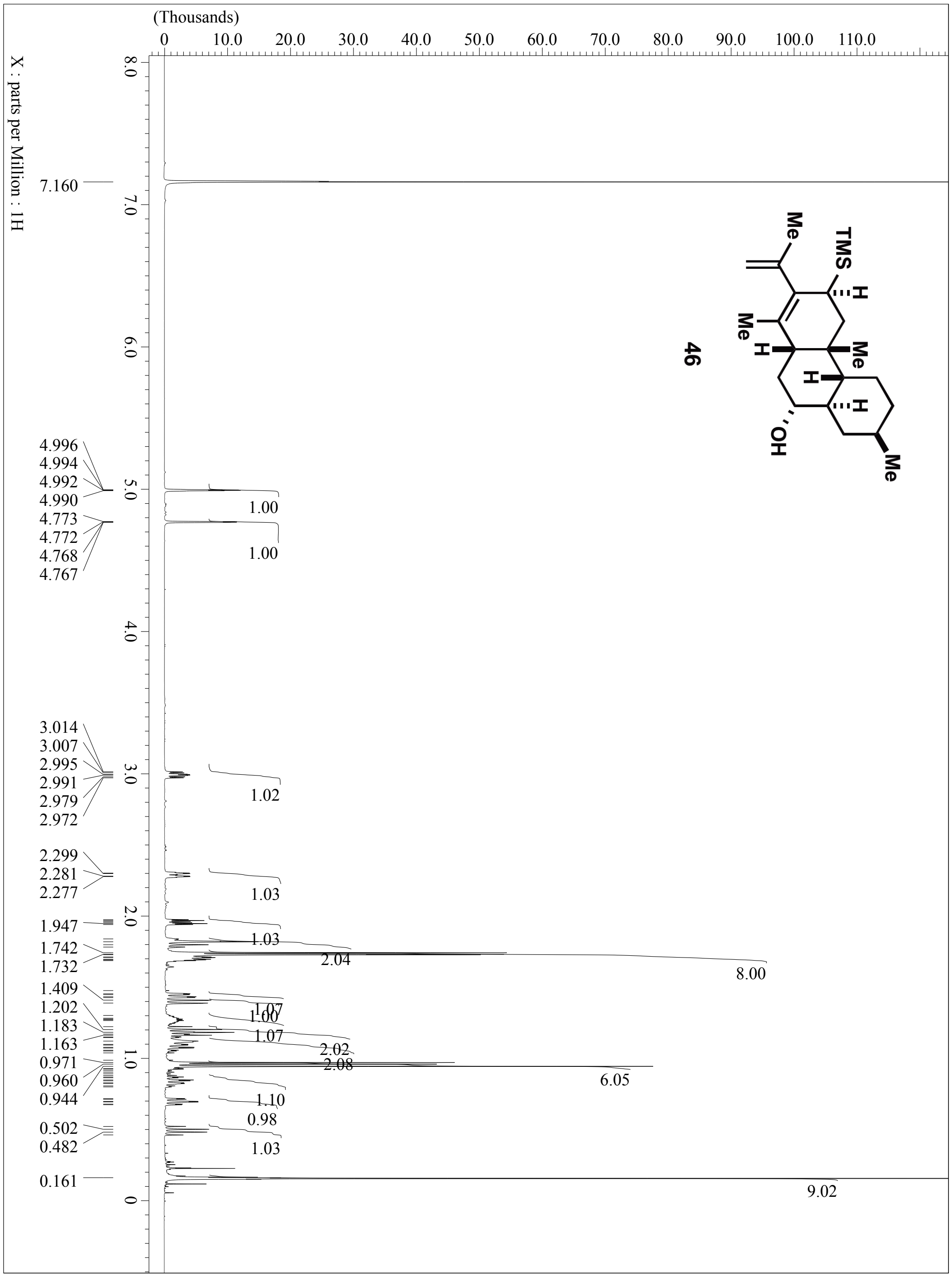


Figure S60: ^{1}H NMR (600 MHz, C_6D_6) of **46.**

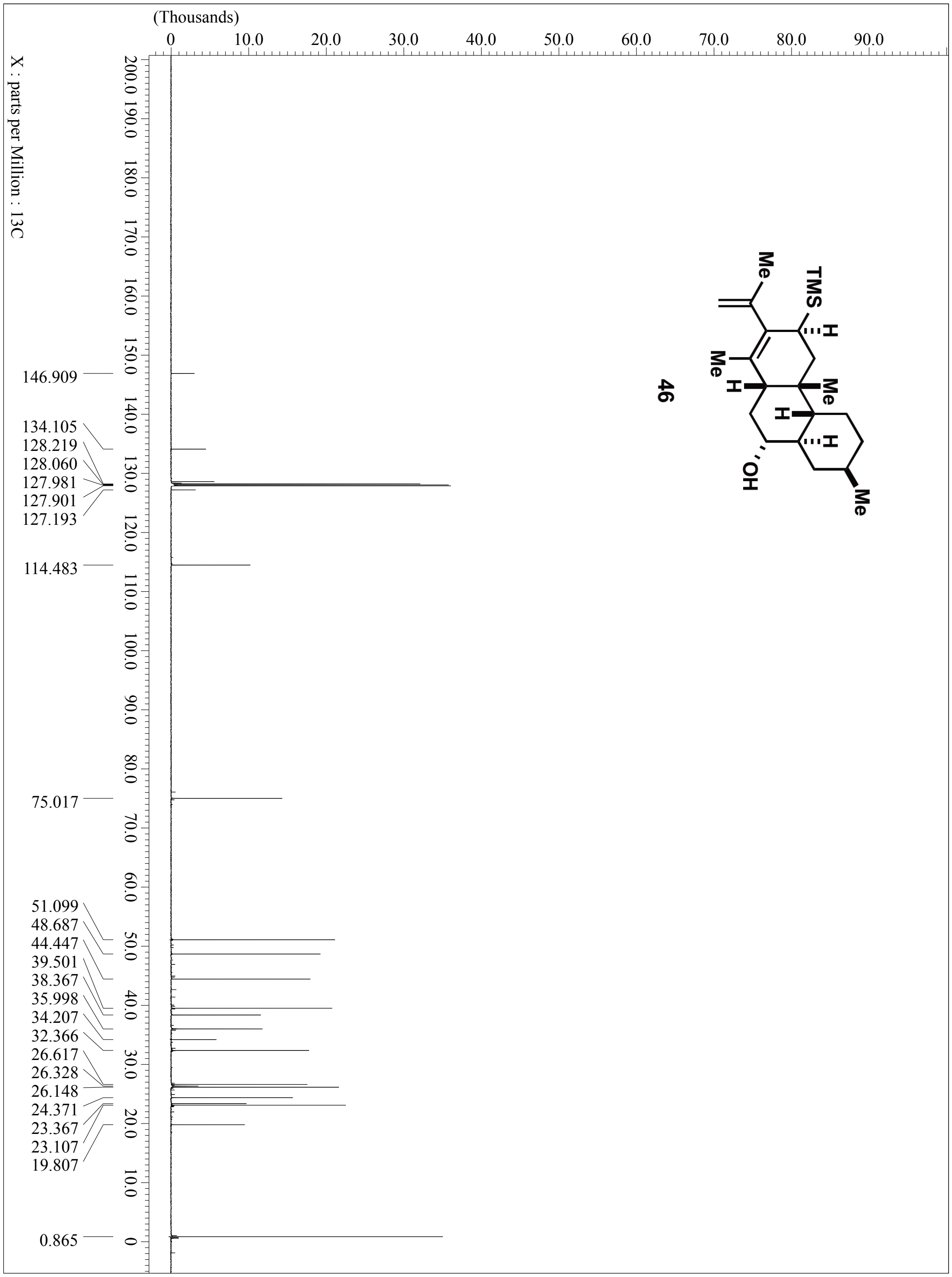


Figure S61: ^{13}C NMR (150 MHz, C_6D_6) of **46**.

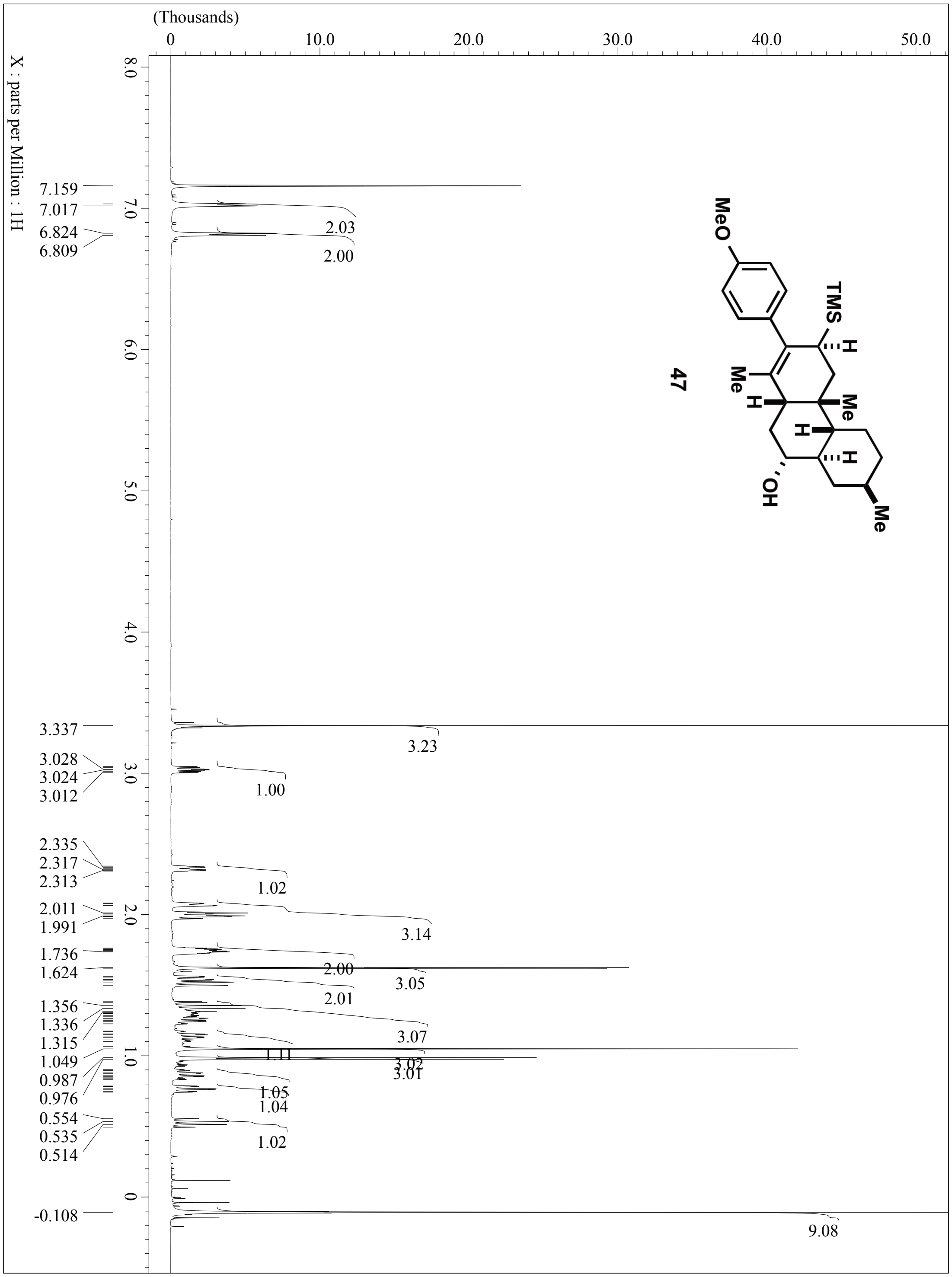


Figure S62: ^{1}H NMR (600 MHz, C_6D_6) of **47**.

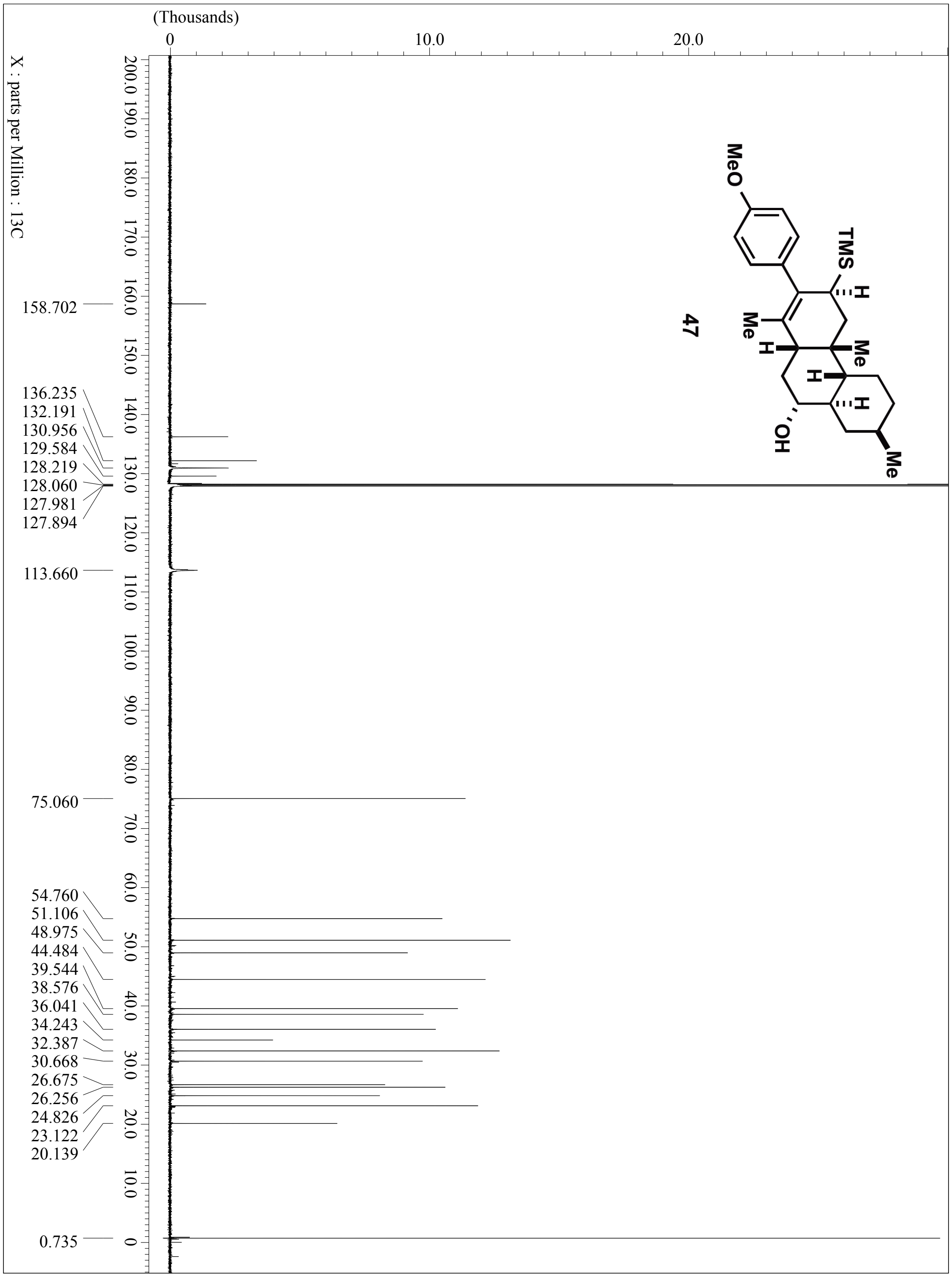


Figure S63: ^{13}C NMR (150 MHz, C_6D_6) of **47**.

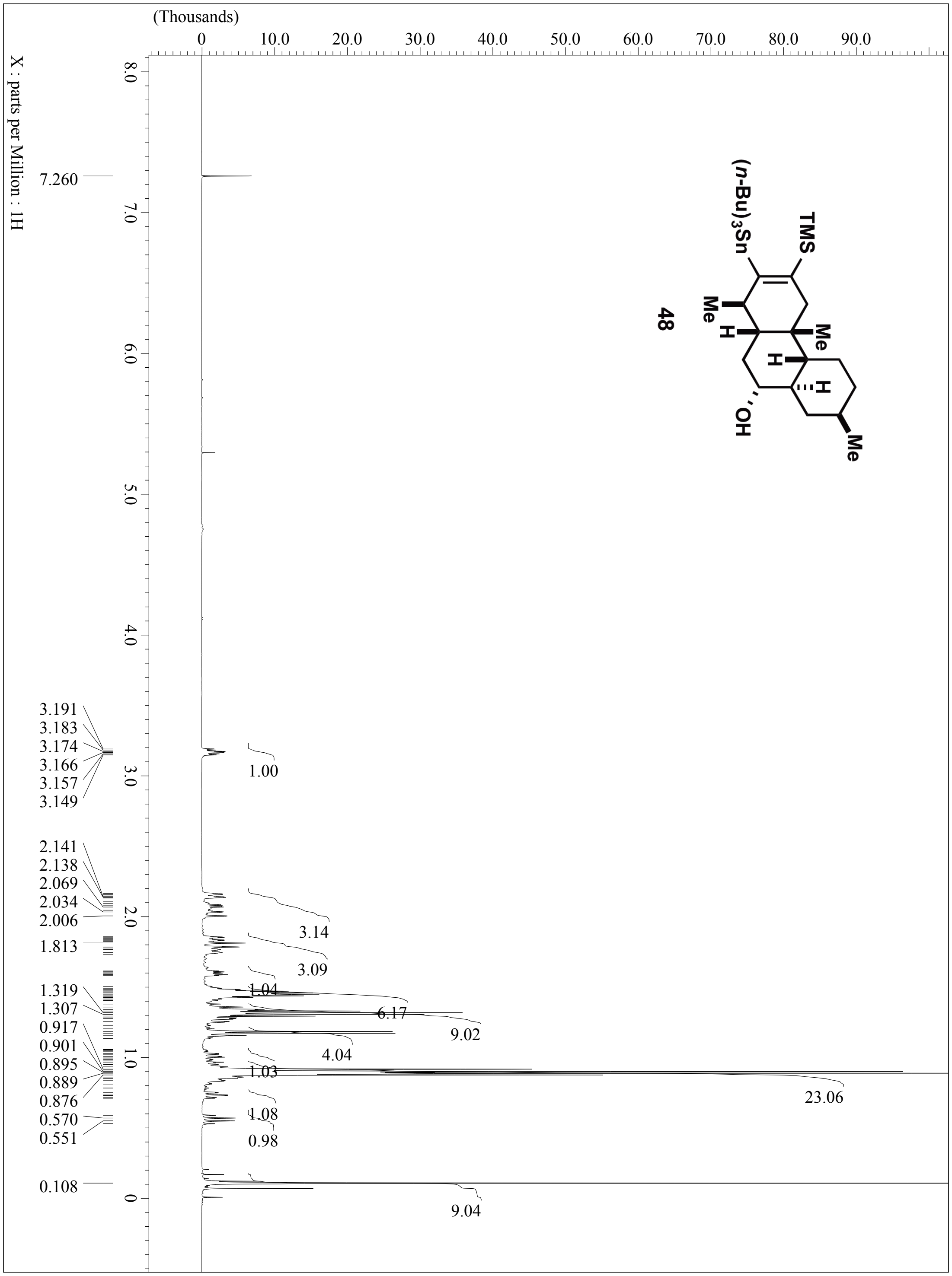


Figure S64: ^{1}H NMR (600 MHz, CDCl$_3$) of **48**.

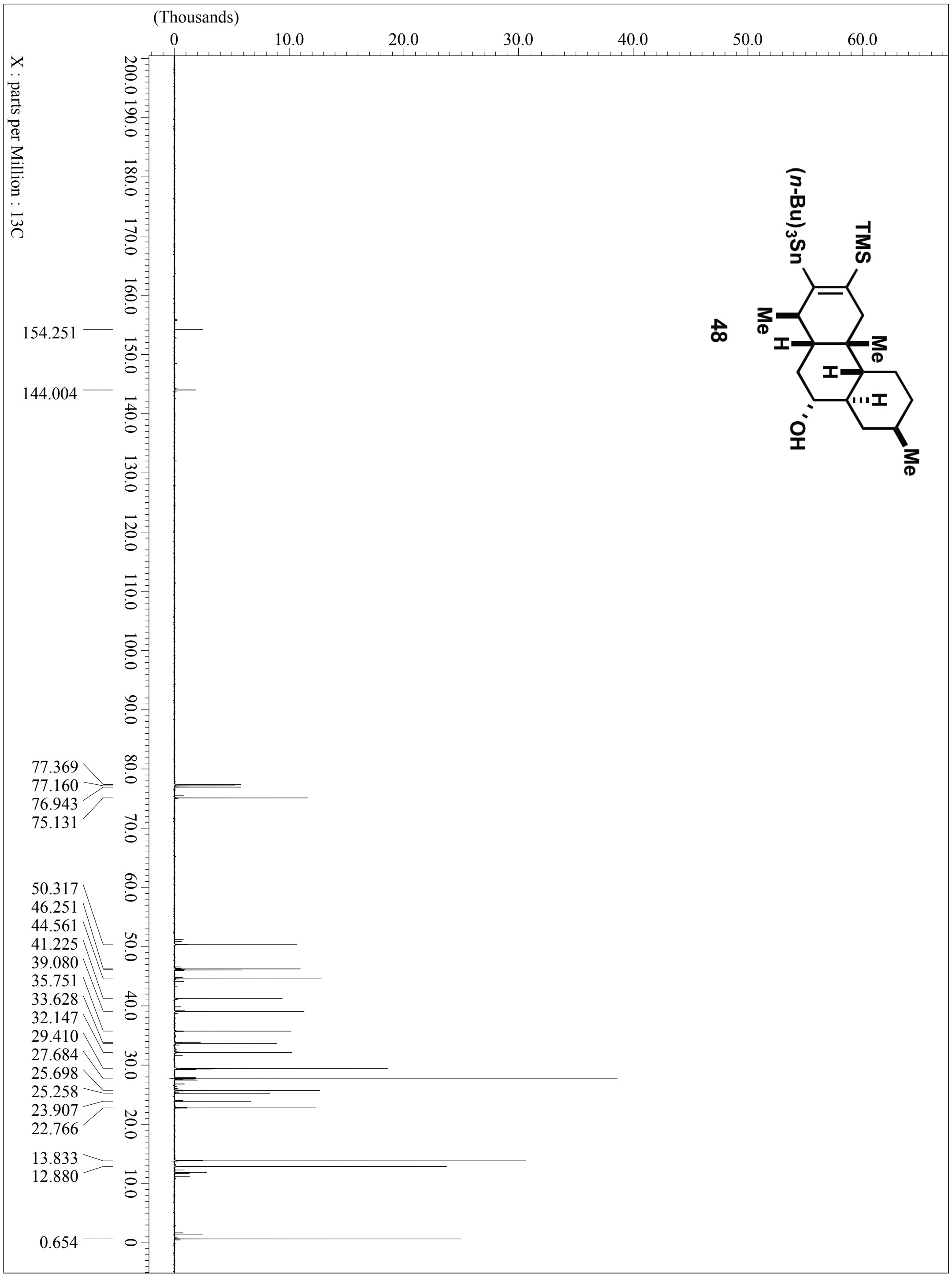


Figure S65: ^{13}C NMR (150 MHz, CDCl$_3$) of **48**.

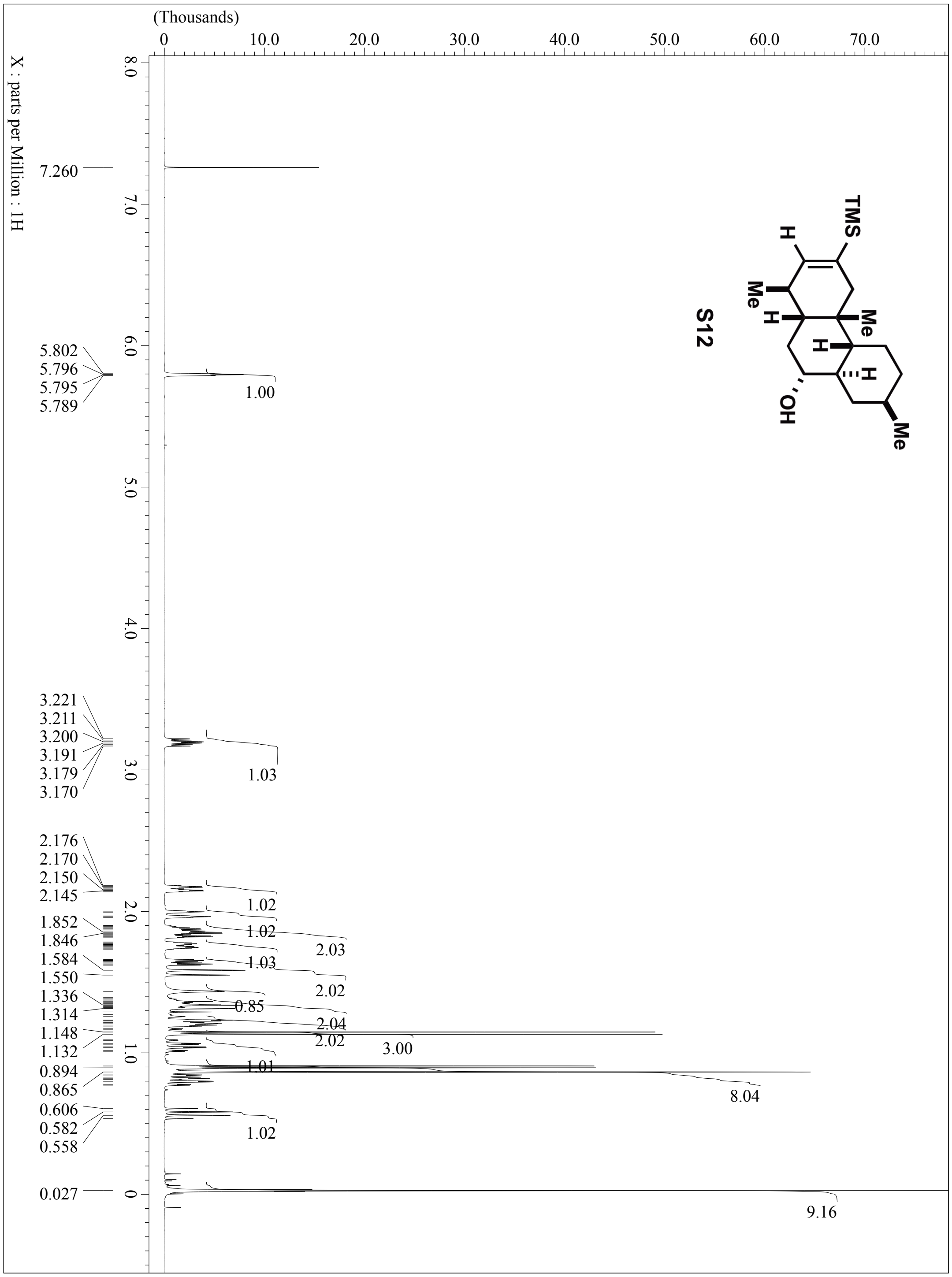


Figure S66: ^{1}H NMR (600 MHz, $CDCl_3$) of **S12**.

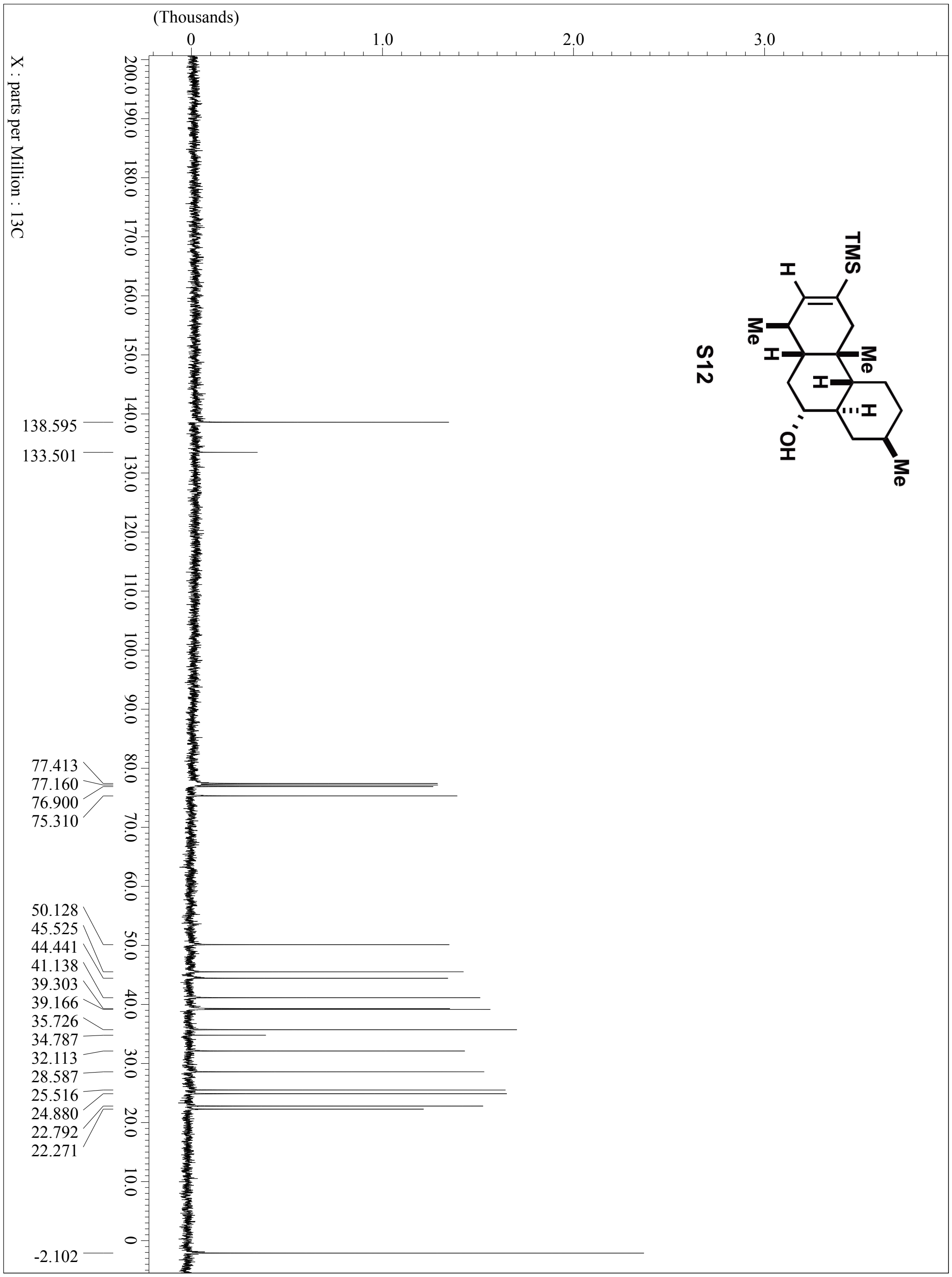


Figure S67: ^{13}C NMR (150 MHz, CDCl$_3$) of **S12**.

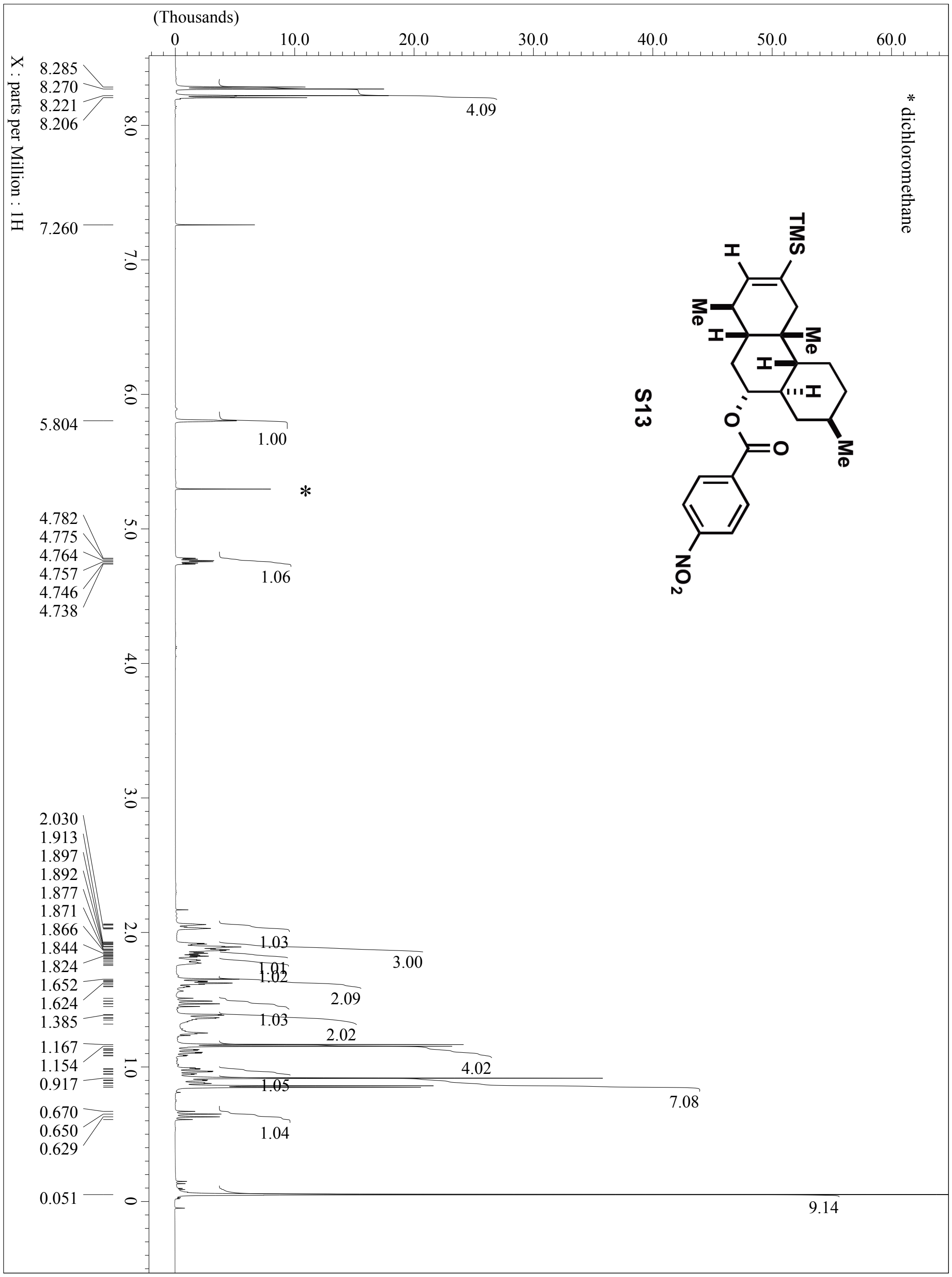


Figure S68: ^{1}H NMR (600 MHz, CDCl$_3$) of **S13.**

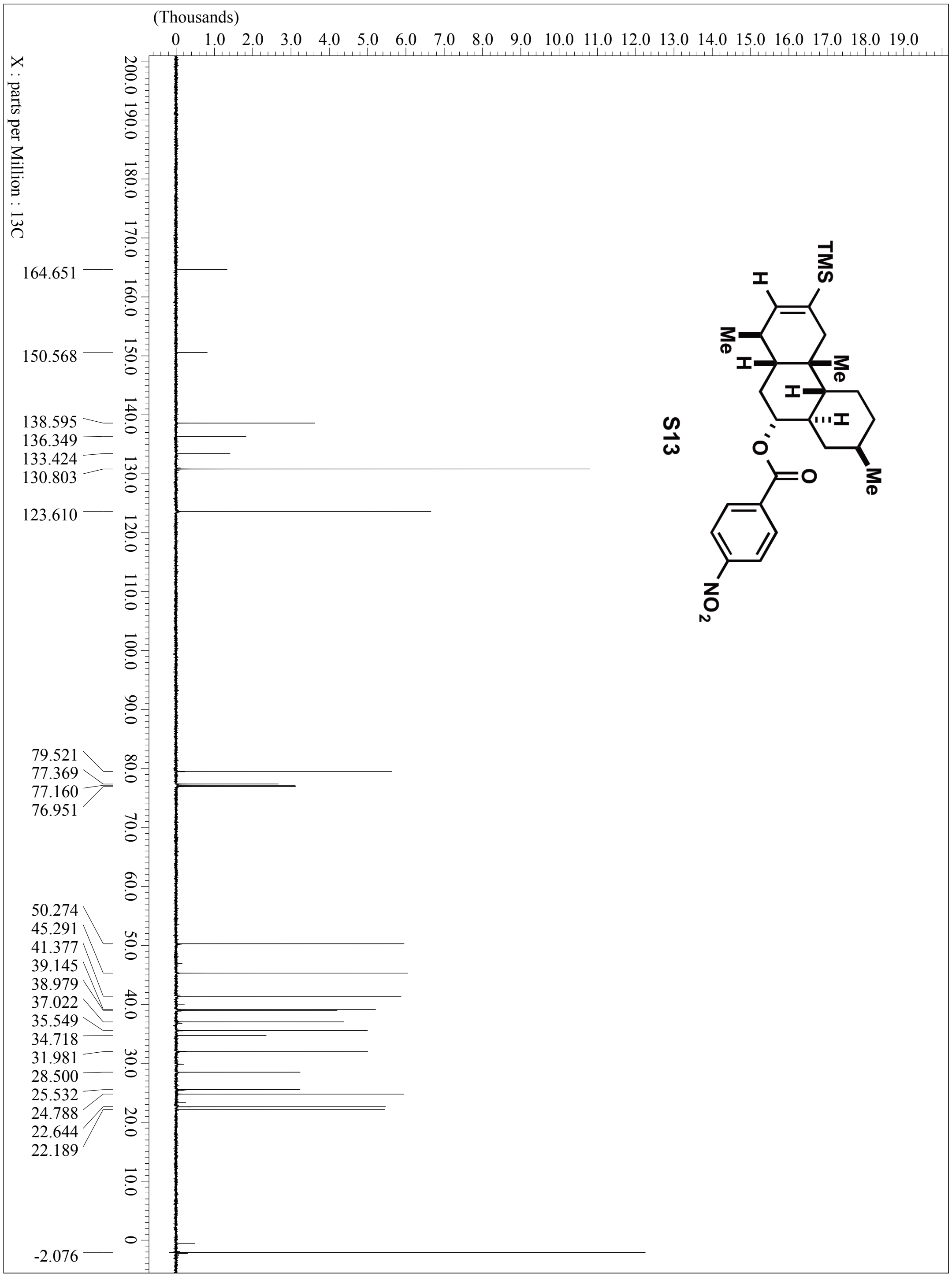


Figure S69: ^{13}C NMR (150 MHz, CDCl$_3$) of **S13**

4. X-ray Crystallographic Data

X-ray crystallographic data for S13

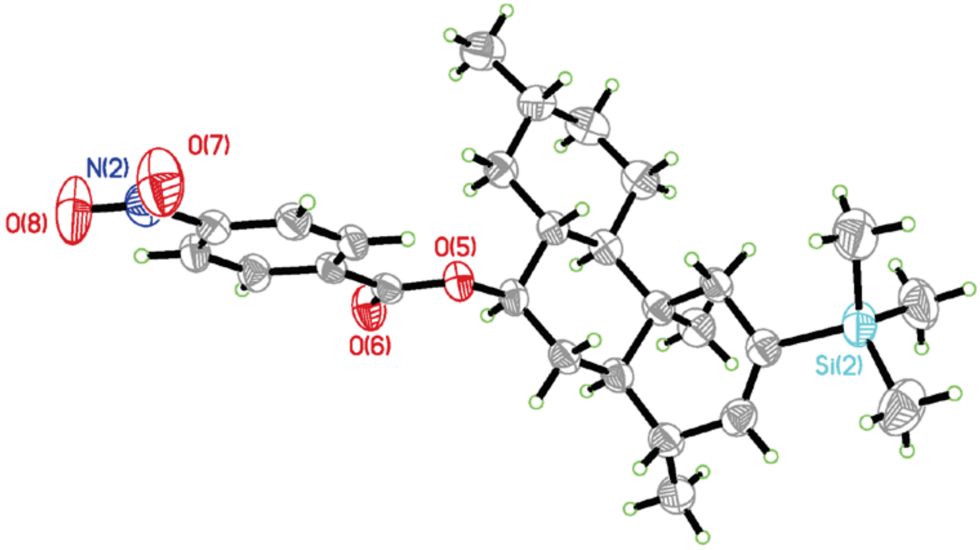


Figure S70. ORTEP representation of X-ray crystallographic structure of **S13**

Table S1. Crystal data and structure refinement for **S13**

Formula	$C_{54}H_{78}N_2O_8Si_2$
$D_{calc.}$/ g cm^{-3}	1.148
m/mm^{-1}	0.117
Formula Weight	939.36
Colour	colourless
Shape	chunk
Max Size/mm	0.31
Mid Size/mm	0.22
Min Size/mm	0.14
T/K	173(2)
Crystal System	monoclinic
Flack Parameter	-0.05(4)
Hooft Parameter	-0.05(4)
Space Group	$P2_1$
a/Å	13.4286(9)
b/Å	9.6835(6)
c/Å	21.6664(14)
a/°	90
b/°	105.3750(10)
g/°	90
V/Å^3	2716.6(3)
Z	2
Z'	1
Q_{min}/°	1.573
Q_{max}/°	25.375
Measured Refl.	45415
Independent Refl.	9961
Reflections Used	8457
R_{int}	0.0361
Parameters	607
Restraints	1
Largest Peak	0.215
Deepest Hole	-0.167
GooF	1.023
wR_2 (all data)	0.0979
wR_2	0.0910
R_1 (all data)	0.0504
R_1	0.0393