# Congested C-C Bonds by Pd-Catalyzed Enantioselective Allyl-Allyl Cross-Coupling, A Mechanism-Guided Solution

Michael J. Ardolino, and James P. Morken*

*Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, MA 02467*

## Supporting Information

### Table of Contents

## General Information

$^{1}$H NMR spectra were recorded on a Varian Unity Inova 500 (500 MHz) or Varian VNMRS 600 (600 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet, app = apparent), and coupling constants (Hz). Coupling constants are reported to the nearest 0.5 Hz. $^{13}$C NMR spectra were recorded on a Varian Gemini-500 (125 MHz) or Varian VNMRS 600 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm). $^{31}$P NMR spectra were recorded on a Varian Gemini-500 (202 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with phosphoric acid as the external standard ($H_3PO_4$: 0.0 ppm). Infrared (IR) spectra were recorded on a Bruker alpha spectrophotometer, $\upsilon_{max}$ $cm^{-1}$. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). High resolution mass spectrometry (ESI) was performed at the Mass Spectrometry Facility, Boston College.

Liquid Chromatography was performed using forced flow (flash chromatography) on silica gel ($SiO_2$, 230 × 450 Mesh) purchased from Silicycle. Thin Layer Chromatography was performed on 25 µm silica gel plates purchased from Silicycle. Visualization was performed using ultraviolet light (254 nm), potassium permanganate ($KMnO_4$) in water, ceric ammonium molybdate (CAM) in water, or phosphomolybdic acid (PMA) in ethanol. Analytical chiral gas-liquid chromatography (GLC) was performed on a Hewlett-Packard 6890 Series chromatograph equipped with a split mode capillary injection system, a flame ionization detector, and a Supelco β-Dex 120 column, or a Supelco Asta Chiraldex B-DM with helium as the carrier gas. Analytical chiral supercritical fluid chromatography (SFC) was performed on a Thar SFC equipped with a Waters 2998 photodiode array detector and an analytical-2-prep column oven with isopropanol as the modifier. Optical rotations were measured on a Rudolph Analytical Research Autopol IV Polarimeter.

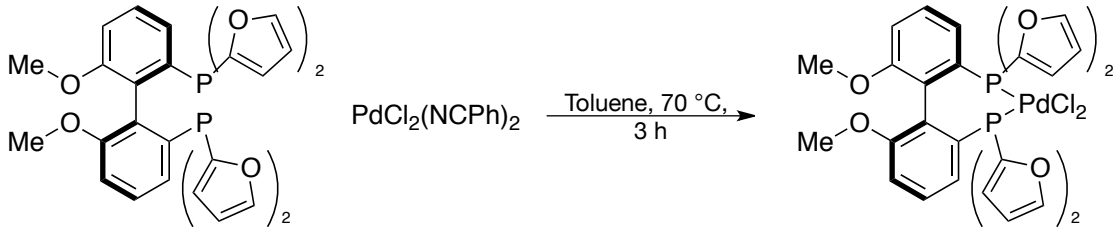
Reaction Calorimetry was carried out in a SuperCRC reaction calorimeter in a glass vial equipped with a teflon-lined septum-cap and magnetic stir bar. The calorimeter measures the heat released or consumed in a sample vial compared with that from a reference vial over the course of the reaction.

All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran (THF), Toluene (PhMe), and dichloromethane (DCM) were purified using a Pure Solv MD-4 solvent purification system from Innovative Technology Inc. by passing through two activated alumina columns after being purged with argon. Triethylamine (TEA) was distilled from calcium hydride. The deionized water used in the coupling reactions was purged with a vigorous stream of $N_2$ for at least two hours prior to use. Tris(dibenzylideneacetone) dipalladium(0) [$Pd_2(dba)_3$], bis(1,5-cyclooctadiene)nickel(0)

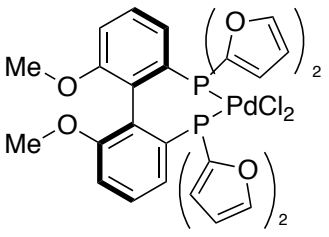
[$Ni(cod)_2$], Dichlorobis(benzonitrile)palladium(II) [$PdCl_2(NCPh)_2$], tricyclohexylphosphine ($PCy_3$), 1,2-bis(diphenylphosphino)benzene (dpp-Benzene), (*R*)-(+)-2,2′-bis(di-2-furanylphosphino)-6,6′-dimethoxy-1,1′-biphenyl [(*R*)-MeO(furyl)BIPHEP], and (*S*,*S*)-(-)-2,3-bis(*t*-butylmethylphosphino)quinoxaline [(*S*,*S*)-QuinoxP*], were purchased from Strem Chemicals, Inc. Pinacolborane (pinBH) was generously donated by BASF. Allylboronic acid pinacol ester (allyl Bpin) was generously donated by Frontier Scientific. bis(pinacolato) diboron [$B_2(pin)_2$] was generously donated by Allychem. All other reagents were purchased from either Fisher or Aldrich and used without further purification.

## Experimental Procedures

### Preparation $PdCl_2$-Ligand Complexes.[1]



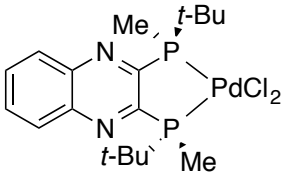

**Representative Procedure:** An oven-dried round-bottomed flask equipped with a magnetic stir bar was charged with bis(benzonitrile)palladium(II) chloride (83.9 mg, .219 mmol) and toluene (12.0 mL) in a dry-box under argon atmosphere to form a rust-brown solution. Also in the dry-box, an oven-dried 2 dram vial equipped with a magnetic stir bar was charged with *(R)*-(+)-2,2'-bis(di-2-furanylphosphino)-6,6'-dimethoxy-1,1'-biphenyl [*(R)*-Methoxy(furyl)BIPHEP] (120.0 mg, 0.221 mmol) and toluene (3.0 mL). Both vessels were sealed with septa, removed from the dry box, and heated to 70 °C with stirring under a positive pressure of dry nitrogen. The solution of ligand was added dropwise to the stirring solution of palladium complex over five minutes. The solution was stirred for three hours, over the course of which a bright yellow precipitate formed. The solution was slowly cooled to room temperature, and additional solids were crashed out of solution with the addition of pentane (30 mL). The solids were filtered away from the solution in a Buchner funnel with filter paper and washed with cold diethyl ether to yield a fine, dull yellow powder. This powder was dried for 12 hours under high-vacuum at 60 °C to yield a bright yellow powder (106 mg, 67% yield). The catalyst complex was effective without any further purification.




**[*(R)*-(+)-2,2'-bis(di-2-furanylphosphino)-6,6'-dimethoxy-1,1'-biphenyl]palladium(II) dichloride (4)**. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.80 (2H, s), 7.483 (2H, s), 7.22 (2H, dd, J = 3.0 Hz, 3.0 Hz), 7.16 (2H, ddd, J = 8.0 Hz, 8.0 Hz, 3.0 Hz), 6.93 (2H, d, J = 3.0 Hz), 6.85 (2H, dd, J = 12.5 Hz, 8.0 Hz), 6.76 (2H, d, J = 8.0 Hz), 6.45 (2H, ddd, J = 3.0 Hz, 1.5 Hz, 1.5 Hz), 6.24-6.43 (2H, m), 3.60 (6H, s); $^{31}$P NMR (202 MHz, $CDCl_3$): $\delta$ -11.56; IR (neat): 3109 (m), 3084 (m),

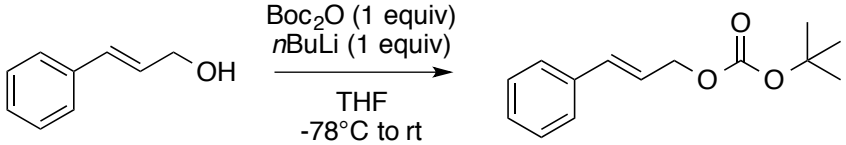
[1] Modified from: Sperrie, M.; Consiglio, G. *J. Am. Chem. Soc.* **1995**, *117*, 12130.

2937 (m), 2835 (w), 2228 (m), 1461 (s), 1267 (s), 1010 (s); A crystal structure of this catalyst complex has also been previously reported.[2]




**[*(S,S)*-2,3-bis(*tert*-butylmethylphosphino)quinoxaline]palladium(II) dichloride (Compound SI-1)**. The title compound was prepared *via* the representative procedure using *(S,S)*-2,3-*bis*(tert-butylmethylphosphino)quinoxaline (*(S,S)*-QuinoxP*) as the ligand with the following modifications: the reaction was run at 60 °C for three hours and the reaction was run on a 0.1 mmol scale. $^{1}$H NMR (600 MHz, CDCl3): δ 8.31 (2H, dd, *J* = 6.5 Hz, 3.5 Hz), 8.04 (2H, dd, *J* = 6.5 Hz, 3.5 Hz), 2.26 (3H, s), 2.24 (3H, s), 1.26 (9H, s), 1.23 (9H, s); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 133.3, 133.3, 130.2, 130.2, 27.9, 27.9, 27.9, 27.9, 27.9, 27.9 (unable to detect the carbons adjacent to phosphorous); $^{31}$P NMR (202 MHz, CDCl3): δ 55.5; IR (neat): 2983 (w), 2961 (m), 2922 (w), 2900 (w), 2866 (w), 2357 (w), 2344 (w), 2222 (w), 1559 (w), 1542 (w), 1473 (m), 1459 (w), 1416 (w), 1397 (w), 1334 (w), 1192 (w), 1019 (w), 896 (m), 777 (m), 729 (m), 644 (w); HRMS-(ESI+) for $C_{18}H_{32}Cl_2N_3P_2Pd_1$ [M+$NH_4$]: calculated: 530.0488, found: 530.0486. The resulting solid was dried at 80 °C under high vacuum overnight to yield 33.3 mg (65% yield) of a pale yellow/tan solid.

## Preparation of *tert*-Butyl Carbonates.[3]



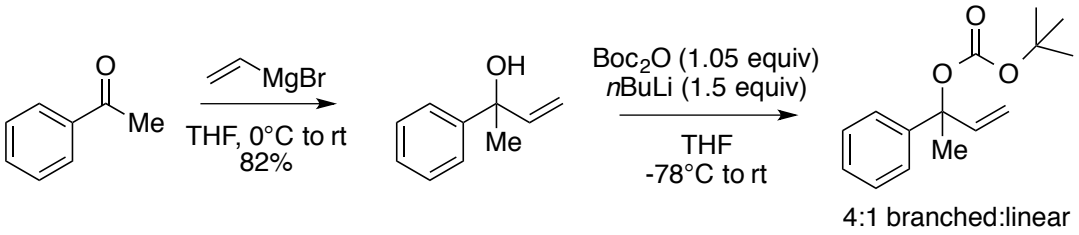

**Representative Procedure (Compound 1a):** A flame-dried round-bottomed flask equipped with a magnetic stir bar was charged with THF (30.0 mL) and cinnamyl alcohol (1.34 mg, 10.0 mmol) under a nitrogen atmosphere. The solution was cooled to –78 °C, and *n*-butyl lithium (10.0 mmol, 4.8 mL of a 2.1 M solution) was added dropwise over a period of 10 minutes, and the solution was stirred at –78 °C for 30 min. A separately prepared solution of di-*tert*-butyl dicarbonate (2.18 g, 10.0 mmol) dissolved in 5 mL of THF under a nitrogen atmosphere was added dropwise at –78 °C, and the solution was warmed to 0 °C for 2 hours followed by gradual warming to room temperature overnight. The reaction was re-cooled to 0 °C and quenched with 100 mL of a 3:2 mixture of diethyl ether and ice water, poured into a separatory funnel and extracted into diethyl ether (3 x 100 mL). The combined organics were dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (10:1 pentane:diethyl ether) to afford a clear, colorless oil (1.78 g, 76% yield) (compound **1a**). $R_f$

[2] Brozek, L. A.; Ardolino, M. J.; Morken, J. P. *J. Am. Chem. Soc.* **2011**, *133*, 16778.

[3] Adapted from: Trost, B. M.; Fraisse, P. L.; Ball, Z. T. *Angew. Chem. Int. Ed.* **2002**, *41*, 1059.

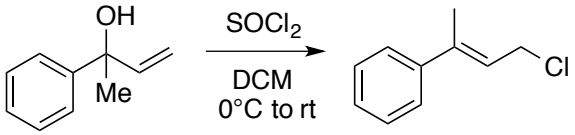
= 0.60 (10:1 pentane:diethyl ether, stain in $KMnO_4$) Spectral data is in accordance with the literature.[3]

***Preparation of tert-butyl (2-phenylbut-3-en-2-yl) carbonate (Compound 2a).*** From 2-phenylbut-3-en-2-ol, prepared from commercially available acetophenone as shown below, the representative procedure was followed with the following modifications: the reaction was run on a 3.0 mmol scale with 1.05 equiv *n*-butyl lithium and 1.5 equivalents of di-*tert*-butyl dicarbonate. The crude reaction mixture was purified on silica gel (10:1 pentane:diethyl ether) to afford a clear, colorless oil (714 mg, 96% yield). $R_f$ = 0.67 (10:1 pentane:diethyl ether, stain in $KMnO_4$). The product was isolated as a 4:1 mixture of branched:linear isomers, spectral data is in accordance with the literature.[4]




4:1 branched:linear

## Preparation of Substituted Allylic Chlorides.[5]




**Representative Procedure (Compound 2b):** An oven-dried round-bottomed flask equipped with a magnetic stir bar was charged with dichloromethane (40 mL) and 2-phenylbut-3-en-2-ol (1.33 g, 9.0 mmol) under a nitrogen atmosphere. The solution was cooled to 0 °C and thionyl chloride (2.4 mL, 36.0 mmol) was added dropwise. The solution was stirred at 0 °C for 2 h, then warmed to rt for 1 h. The reaction was quenched with ice water and extracted into dichloromethane (3 X 50 mL). The combined organics were dried over sodium sulfate, filtered, and concentrated *in vacuo*. The crude reaction mixture was purified by kugelrohr distillation (hi-vacuum, 140 °C) to afford a clear, colorless liquid (1.26 g, 85% yield) (compound **2b**). Spectral data is in accordance with the literature.[6]

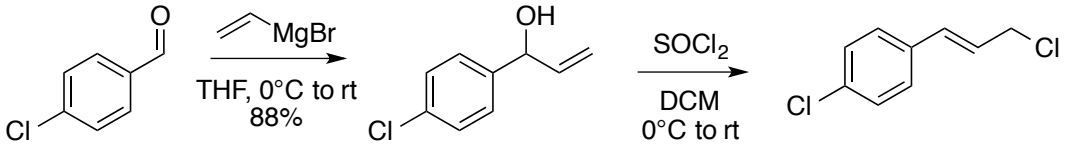
---

[4] Zhang, P.; Le, H.; Kyne, R. E.; Morken, J. P. *J. Am. Chem. Soc.* **2011**, *133*, 9716.

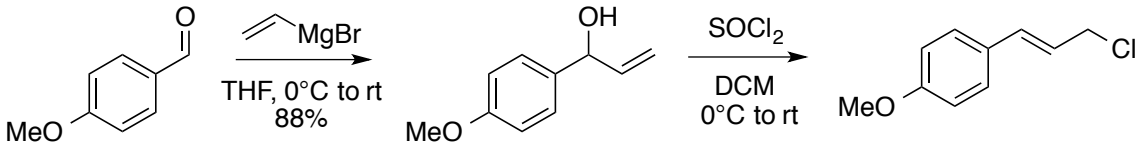
[5] Adapted from: Gissot, A.; Wagner, A.; Mioskowski, C. *Tetrahedron* **2004**, *60*, 6807.

[6] Falciola, C. A.; Tissot-Croset, K.; Reyneri, H.; Alexakis, A. *Adv. Synth. Catal.* **2008**, *350*, 1090.

***Preparation of (E)-1-chloro-4-(3-chloroprop-1-en-1-yl)benzene (Compound SI-2).*** From 1-(4-chlorophenyl)prop-2-en-1-ol, prepared from commercially available 4-chlorobenzaldehyde as shown below, the representative procedure was followed with the following modifications: the reaction was run on a 15.5 mmol scale with 10 equivalents of $SOCl_2$. After extraction and concentration *in vacuo*, the crude oil was dissolved in pentane and pushed through a plug of neutral allumina and concentrated *in vacuo* once more. The resulting wet, orange crystals were then purified by kugelrohr distillation (hi-vacuum, 180 °C) to afford a white, fluffy solid (966 mg, 34% yield). Spectral data is in accordance with the literature.[7]




***Preparation of (E)-1-(3-chloroprop-1-en-1-yl)-4-methoxybenzene (Compound SI-3).*** From 1-(4-methoxyphenyl)prop-2-en-1-ol, prepared from commercially available 4-methoxybenzaldehyde as shown below, the representative procedure was followed with the following modifications: the reaction was run on a 3.0 mmol scale with 10 equivalents of $SOCl_2$ to afford a off-white solid (483 mg, 87% yield). The crude product was used in the cross-coupling with no further purification. Spectral data is in accordance with the literature.[8]

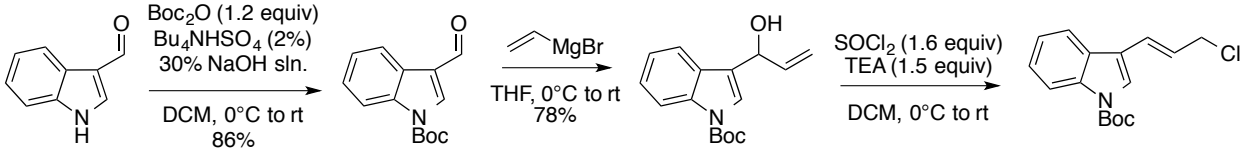


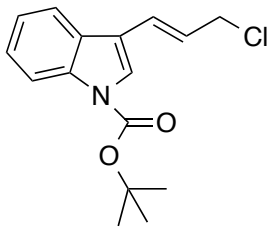

***Preparation of tert-butyl (E)-3-(3-chloroprop-1-en-1-yl)-1H-indole-1-carboxylate (Compound SI-4).*** From tert-butyl 3-(1-hydroxyallyl)-1H-indole-1-carboxylate, prepared from commercially available 1H-indole-3-carbaldehyde as shown below, the representative procedure was followed with the following modifications: the reaction was run on a 2.0 mmol scale with only 1.6 equivalents of $SOCl_2$ (380 mg, 3.2 mmol) and the addition of triethylamine (0.42 mL, 3.0 mmol) to afford a thick brown oil (561.4 mg, 90% yield). The crude product was used in the cross-coupling with no further purification.

---

[7] Lölsberg, W.; Ye, S.; Schmalz, H. G. *Adv. Synth. Catal.* **2010**, *352*, 2023.

[8] Penjšević, J.; Šukalović, V.; Andrić, D.; Kostić-Rajačić, S.; Šoškić, V.; Roglić, G. *Arch. Pharm. Chem. Life Sci.* **2007**, *340*, 456.

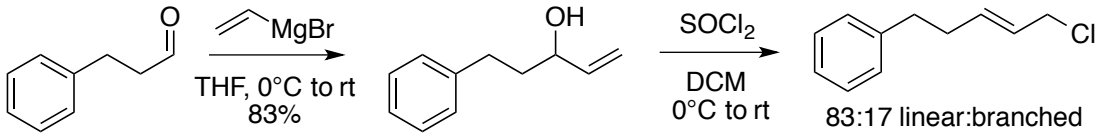


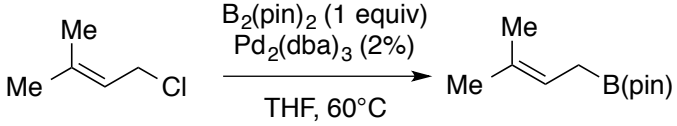
***tert-butyl (E)-3-(3-chloroprop-1-en-1-yl)-1H-indole-1-carboxylate. (Compound SI-4).***

$^1$H NMR (600 MHz, $CDCl_3$): δ 8.17 (1H, s), 7.76 (1H, d, *J* = 8.5 Hz), 7.66 (1H, s), 7.36 (1H, t, *J* = 7.8 Hz), 7.30 (1H, t, *J* = 6.0 Hz), 6.77 (1H, d, *J* = 15.6 Hz), 6.42 (1H, dt, *J* = 15.6 Hz, 7.2 Hz), 4.29 (2H, d, *J* = 7.2 Hz), 1.68 (9H, s); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 149.4, 135.9, 128.4, 125.7, 125.1, 125.1, 124.8, 124.8, 123.0, 119.8, 115.4, 84.1, 46.1, 28.2, 28.2, 28.2 ; IR (neat): 2979 (w) 2933 (w), 1732 (s), 1654 (w), 1607 (w), 1557 (w), 1476 (w), 1451 (m), 1368 (m), 1309 (m), 1254 (w), 1232 (m), 1153 (s), 1092 (w), 1043 (m), 1021 (w), 960 (w), 910 (w), 856 (w), 838 (w), 765 (w), 745 (m), 678 (m), 654 (m) cm$^{-1}$; HRMS-(ESI+) for $C_{16}H_{19}Cl_1N_1O_2$ [M+H]: calculated: 292.1104, found: 292.1116.

***Preparation of (E)-(5-chloropent-3-en-1-yl)benzene (Compound 35).*** From 5-phenylpent-1-en-3-ol, prepared from commercially available hydrocinnamaldehyde as shown below, the representative procedure was followed with the following modifications: the reaction was run on a 5.0 mmol scale and stirred for 3 hours at room temperature instead of only 1. The crude product was purified by kugelrohr distillation (hi-vacuum, 110 °C) to afford a clear, colorless oil (773.2 mg, 86% yield). Isolated as a 83:17 mixture of linear:branched isomers, spectral data is in accordance with the literature.[9]




**Preparation of 4,4,5,5-tetramethyl-2-(3-methylbut-2-en-1-yl)-1,3,2-dioxaborolane (Compound 9).[10]**

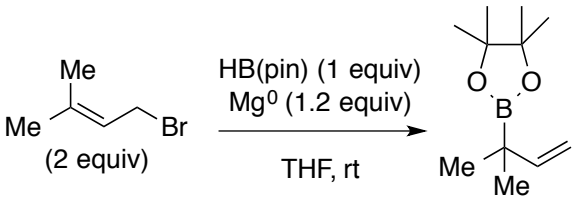



[9] Fuchter, M. J.; Levy, J.-N. *Org. Lett.* **2008**, *10*, 4919.

[10] Adapted from: Zhang, P.; Roundtree, I. A.; Morken, J. P. *Org. Lett.* **2012**, *14*, 1416.

An oven-dried scintillation vial equipped with a magnetic stir bar was charged with $Pd_2(dba)_3$ (54.9 mg, 0.06 mmol), bis(pinacolato)diboron (762.6 mg, 3.00 mmol), and tetrahydrofuran (1.5 mL) in a dry-box under argon atmosphere. The vial was capped and stirred for two minutes, then 1-chloro-3-methylbut-2-ene (313.7 mg, 3.00 mmol) was added. The vial was capped with a teflon cone-lined cap, sealed with electrical tape, removed from the dry-box, and heated to 60 °C and allowed to stir for 12 h. The reaction was then concentrated *in vacuo* and the crude reaction mixture was purified rapidly on oven-dried silica gel (fast gradient of 50:1-20:1 pentane:diethyl ether) to afford a clear, colorless oil (364 mg, 62% yield). $R_f$ = 0.53 (20:1 pentane:diethyl ether, stain in $KMnO_4$). Spectral data is in accordance with the literature.[11]

## Preparation of α,α-Disubstituted and Cyclic Allylboron Reagents.[12]




**Representative Procedure (Compound 19):** An oven-dried round-bottomed flask equipped with a magnetic stir bar was charged with magnesium turnings (292 mg, 12.0 mmol), pinacol borane (HBpin) (1.28 g, 10.0 mmol), and tetrahydrofuran (15 mL) in a dry-box under argon atmosphere. One equivalent of 1-bromo-3-methylbut-2-ene (1.49 g, 10.0 mmol) was added dropwise over 5 minutes with stirring, and the solution was capped and stirred an additional 30 minutes. A second equivalent of 1-bromo-3-methylbut-2-ene (1.49 g, 10.0 mmol) was added dropwise, and the solution was sealed with a septa and electrical tape, removed from the dry-box, and stirred under nitrogen for an additional 2 hours at room temperature. The solution was then cooled to 0 °C, dilluted with hexanes (50 mL) and quenched with dropwise addition of aqueous 0.1 M HCl (90 mL). After stirring for 10 minutes, the solution was transferred to a separatory funnel and extracted with hexanes (3 X 75 mL). The combined organics were dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The crude reaction mixture was purified by kugelrohr distillation (hi-vacuum, 80 °C) to afford a clear, colorless oil (1.42 g, 72% yield)(Compound **14**). Spectral data is in accordance with the literature.[12]

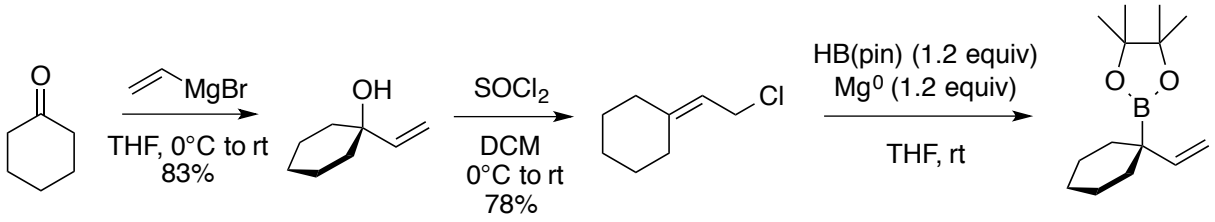
***Preparation of 4,4,5,5-tetramethyl-2-(1-vinylcyclohexyl)-1,3,2-dioxaborolane.*** From 1-(chloromethyl)cyclohex-1-ene, prepared from cyclohexanone as shown below, the representative procedure was followed with the following modifications: the reaction was run on a 4.0 mmol scale using only one equivalent of chloride and 1.2 equivalents of $Mg^0$ and HB(pin)

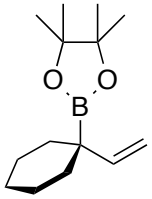
---

[11] Wu, J. Y.; Moreau, B.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 12915.

[12] Clary, J. W.; Rettenmaier, T. J.; Snelling, R.; Bryks, W.; Banwell, J.; Wipke, W. T.; Singaram, B. *J. Org. Chem.* **2011**, *76*, 9602.

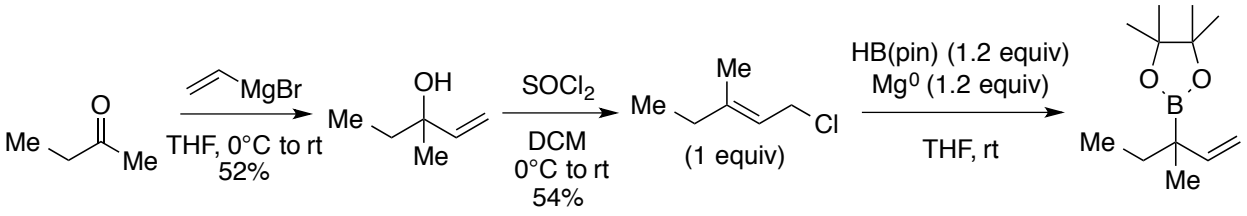
and was run for 5 hours. The crude reaction mixture was purified by kugelrohr distillation (hi-vacuum, 90 °C) to afford a clear, colorless oil (704 mg, 75% yield).

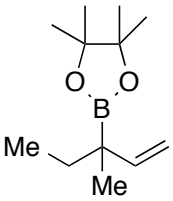


**4,4,5,5-tetramethyl-2-(1-vinylcyclohexyl)-1,3,2-dioxaborolane (Compound 23).** $^{1}$H NMR (600 MHz, $CDCl_3$): $\delta$ 5.78 (1H, dd, $J$ = 17.0 Hz, 11.5 Hz), 4.90-4.94 (2H, m), 1.95 (2H, d, $J$ = 13.0 Hz), 1.67 (2H, dt, $J$ = 14.0 Hz, 3.5 Hz), 1.26-1.34 (2H, m), 1.23 (12H, s), 1.19-1.20 (4H, m); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 145.6, 111.1, 85.1, 85.1, 33.7, 26.4, 26.4, 25.0, 24.8, 24.7, 24.7, 24.7, 24.7, 24.6; IR (neat): 2977 (w), 2924 (w), 2852 (w), 1449 (w), 1369 (s), 1336 (w), 1317 (w), 1306 (s), 1262 (w), 1231 (m), 1214 (w), 1165 (w), 1138 (s), 1109 (w), 1000 (m), 969 (w), 936 (m), 899 (m), 859 (w), 844 (w), 830 (w) cm$^{-1}$; HRMS-(ESI+) for $C_{14}H_{26}B_1O_2$ [M+H]: calculated: 237.2026, found: 237.2029.

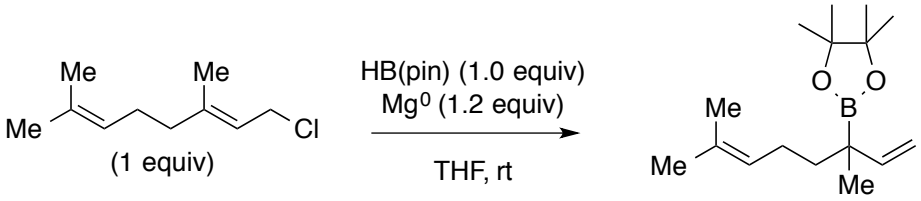
***Preparation of 4,4,5,5-tetramethyl-2-(3-methylpent-1-en-3-yl)-1,3,2-dioxaborolane.*** From (E)-1-chloro-3-methylpent-2-ene, prepared from 2-butanone as shown below, the representative procedure was followed with the following modifications: the reaction was run on a 2.8 mmol scale using only one equivalent of chloride and 1.2 equivalents of $Mg^0$ and HB(pin) and was run for 4 hours. The crude reaction mixture was purified by kugelrohr distillation (hi-vacuum, 90 °C) to afford a clear, colorless oil (381 mg, 64% yield).

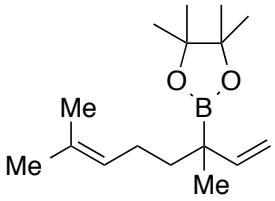


**4,4,5,5-tetramethyl-2-(3-methylpent-1-en-3-yl)-1,3,2-dioxaborolane (Compound 25).** $^{1}$H NMR (600 MHz, $CDCl_3$): $\delta$ 5.90 (1H, dd, $J$ = 17.0 Hz, 9.5 Hz), 4.94 (1H, dd, $J$ = 9.5 Hz, 1.0 Hz), 4.93 (1H, dd, $J$ = 17.0 Hz, 2.0 Hz), 1.53-1.60 (2H, m), 1.22 (12H, s), 1.03 (3H, s), 0.86 (3H, dd (app t), $J$ = 7.5 Hz, 7.5 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 145.5, 111.0, 83.1, 83.1, 30.8, 24.7, 24.7, 24.7, 24.7, 24.6, 19.1, 9.9; IR (neat): 2977 (m), 2931 (w), 2876 (w), 1627 (w), 1458 (m), 1371 (s), 1345 (s), 1131 (s), 1262 (m), 1214 (w), 1191 (w), 1165 (w), 1140 (s), 1113 (m), 1054 (w), 1030 (w), 1004 (w), 966 (m), 900 (s), 852 (w), 797 (w), 697 (w), 670 (m), 579 (w) cm$^{-1}$; HRMS-(ESI+) for $C_{12}H_{24}B_1O_2$ [M+H]: calculated: 211.1869, found: 211.1870.

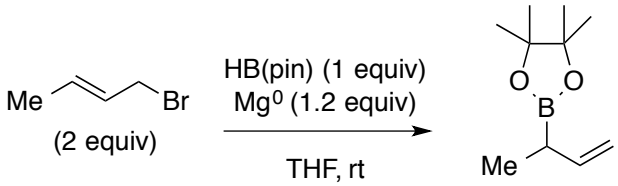
***Preparation of 2-(3,7-dimethylocta-1,6-dien-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.*** From commercially available geranyl chloride, the representative procedure was followed with the following modifications: the reaction was run on a 3.0 mmol scale using only one equivalent of chloride and HB(pin) and 1.2 equivalents of $Mg^0$ and was run for 4 hours. The crude reaction mixture was purified by kugelrohr distillation (hi-vacuum, 150 °C) to afford a clear, colorless oil (495 mg, 87% yield).



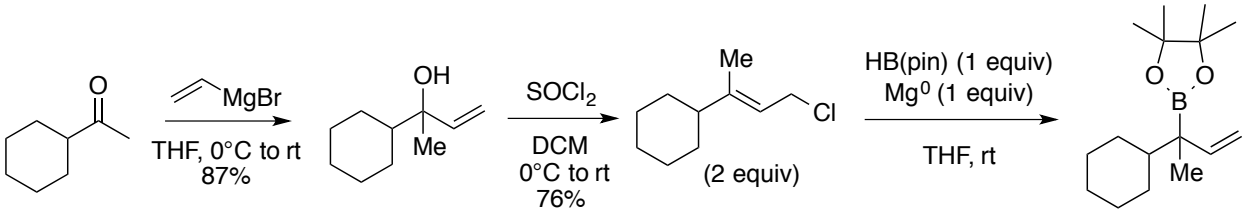

**2-(3,7-dimethylocta-1,6-dien-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound 27).** $^1$H NMR (600 MHz, $CDCl_3$): δ 5.91 (1H, dd, *J* = 17.5 Hz, 11.5 Hz), 5.12 (1H, dd (app t), *J* = 6.5 Hz, 6.5 Hz), 4.96 (1H, d, *J* = 11.5 Hz), 4.93 (1H, dd, *J* = 17.5 Hz, 2.0 Hz), 1.67 (3H, s), 1.59 (3H, s), 1.51 (1H, dddd (app dq), *J* = 14.0 Hz, 6.5 Hz, 6.5 Hz, 6.5 Hz), 1.36 (1H, dddd (app dq), *J* = 14.0 Hz, 6.5 Hz, 6.5 Hz, 6.5 Hz), 1.24 (2H, dd (app t), *J* = 6.5 Hz, 6.5 Hz), 1.22 (12H, s), 1.07 (3H, s); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 145.4, 131.0, 125.1, 111.0, 83.1, 83.0, 38.3, 25.7, 24.7, 24.7, 24.7, 24.7, 24.6, 24.4, 19.5, 17.5; IR (neat): 2977 (m), 2926 (w), 1628 (w), 1457 (w), 1410 (w), 1372 (m), 1346 (m), 1311 (s), 1273 (w), 1214 (w), 1186 (w), 1165 (w), 1143 (s), 1109 (m), 1002 (w), 976 (m), 901 (m), 853 (m), 710 (w), 671 (w), 579 (w), 456 (w) $cm^{-1}$; HRMS-(ESI+) for $C_{16}H_{30}B_1O_2$ [M+H]: calculated: 265.2399, found: 265.2346.

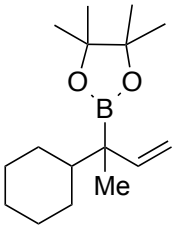
***Preparation of 2-(but-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound 29).*** From commercially available crotyl bromide, the representative procedure was followed on a 10 mmol scale. The crude reaction mixture was purified by kugelrohr distillation (hi-vacuum, 70 °C) to afford a clear, colorless oil (1.37 g, 75% yield). Spectral data is in accordance with the literature.[12]




***Preparation of 2-(2-cyclohexylbut-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.*** From (E)-(4-chlorobut-2-en-2-yl)cyclohexane, prepared as shown below, the representative procedure was followed with the following modifications: the reaction was run on a 3.0 mmol scale using two equivalents of the chloride and one equivalent of the $Mg^0$ and HB(pin), and was run for 4

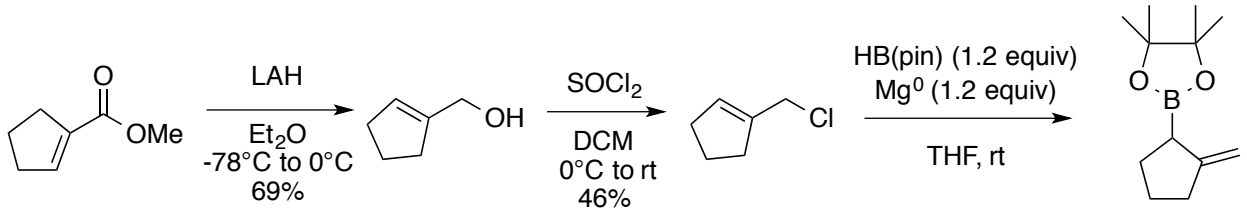
hours. The crude reaction mixture was purified by kugelrohr distillation (hi-vacuum, 180 °C) to afford a clear, colorless oil (827 mg, >96% yield) as a 8:1 mixture of branched product to regioisomers.

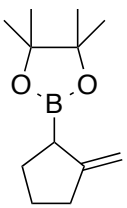



**2-(2-cyclohexylbut-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound 33).** $^{1}$H NMR (600 MHz, $CDCl_3$): δ 5.90 (1H, dd, *J* = 17.5 Hz, 11.0 Hz), 4.98 (1H, dd, *J* = 11.0 Hz, 2.0 Hz), 4.89 (1H, dd, *J* = 17.5 Hz, 1.0 Hz), 1.50-1.83 (11H, m), 1.21 (12H, s), 0.98 (3H, s); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 145.0, 111.5, 83.0, 83.0, 44.2, 29.8, 27.0, 26.8, 26.8, 24.7, 24.7, 24.7, 24.7, 24.5, 24.5, 14.3; IR (neat): 2977 (m), 2923 (s), 2852 (m), 1510 (w), 1448 (m), 1411 (w), 1371 (w), 1341 (m), 1311 (s), 1271 (w), 1246 (w), 1214 (w), 1192 (w), 1140 (w), 1010 9w), 1088 (w), 984 (w), 966 (w), 898 (w), 852 (m), 722 (w), 673 (m), 579 (w) $cm^{-1}$; HRMS-(ESI+) for $C_{16}H_{30}B_1O_2$ [M+H]: calculated: 265.2339, found: 265.2350.

***Preparation of 4,4,5,5-tetramethyl-2-(2-methylenecyclopentyl)-1,3,2-dioxaborolane.*** From 1-(chloromethyl)cyclopent-1-ene, prepared as shown below, the representative procedure was followed with the following modifications: the reaction was run on a 2.45 mmol scale using only one equivalent of chloride and 1.2 equivalents of $Mg^0$ and HB(pin) and was run for 5 hours. The crude reaction mixture was purified by kugelrohr distillation (hi-vacuum, 140 °C) to afford a clear, colorless oil (353.7 mg, 69% yield).

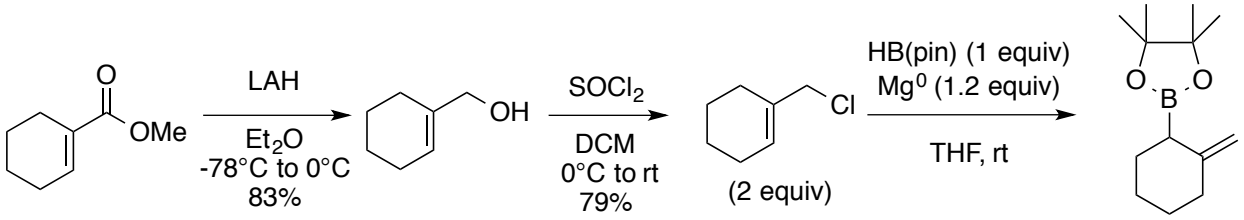


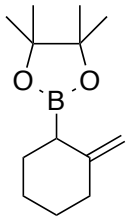




**4,4,5,5-tetramethyl-2-(2-methylenecyclopentyl)-1,3,2-dioxaborolane. (Compound SI-5).** $^{1}$H NMR (600 MHz, $CDCl_3$): δ 4.86 (1H, dd (app t), *J* = 2.5 Hz, 2.5 Hz), 4.84 (1H, dd (app t), *J* = 2.0 Hz, 2.0 Hz), 2.24-2.35 (2H, m), 2.06 (1H, dd (app t), *J* = 8.0 Hz, 8.0 Hz), 1.83-1.88 (1H, m), 1.66-1.78 (2H, m), 1.54-1.62 (1H, m), 1.24 (12H, s); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 154.6, 104.2, 83.0, 83.0, 34.4, 29.3, 27.2, 24.8, 24.7, 24.7, 24.6, 24.6; IR (neat): 2978 (w), 2951 (w), 2868 (w), 1644 (w), 1470 (w), 1450 (w), 1357 (s), 1319 (s), 1273 (w), 1213 (w), 1167 9w), 1143 (s), 1115

(w), 1007 (w), 970 (m), 872 (m), 853 (m), 672 (w), 579 (w) $cm^{-1}$; HRMS-(ESI+) for $C_{12}H_{22}B_1O_2$ [M+H]: calculated: 209.1713, found: 209.1722.

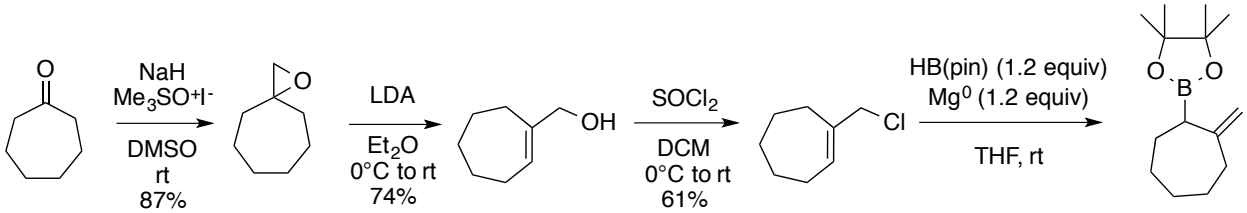
***Preparation of 4,4,5,5-tetramethyl-2-(2-methylenecyclohexyl)-1,3,2-dioxaborolane.*** From 1-(chloromethyl)cyclohex-1-ene, prepared as shown below, the representative procedure was followed with the following modifications: the reaction was run on a 3.1 mmol scale using only one equivalent of HB(pin) and 1.2 equivalents of $Mg^0$ and was run for 5 hours. The crude reaction mixture was purified by kugelrohr distillation (hi-vacuum, 140 °C) to afford a clear, colorless oil (422 mg, 61% yield).

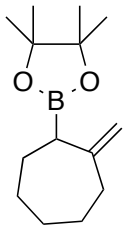



**4,4,5,5-tetramethyl-2-(2-methylenecyclohexyl)-1,3,2-dioxaborolane (Compound SI-6).** $^1H$ NMR (600 MHz, $CDCl_3$): δ 4.64 (1H, d, *J* = 1.0 Hz), 4.60 (1H, d, *J* = 2.5 Hz), 2.12-2.18 (2H, m), 1.91-2.01 (2H, m), 1.78-1.82 (1H, m), 1.35-1.71 (4H, m), 1.24 (12H, s); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 151.0, 106.6, 83.2, 83.2, 35.4, 29.7, 28.4, 25.6, 24.8, 24.8, 24.7, 24.7, 24.7; IR (neat): 2878 (w), 2926 (m), 2855 (w), 1644 (w), 1447 (w), 1379 (m), 1360 (s), 1314 (s), 1272 (w), 1243 (w), 1214 (w), 1186 (w), 1165 (w), 1143 (s), 1109 (w), 1064 (w), 1005 (w), 989 (w), 965 (w), 877 (m), 863 (m), 847 (m), 819 (w), 736 9w), 671 (w), 578 (w) $cm^{-1}$; HRMS-(ESI+) for $C_{13}H_{24}B_1O_2$ [M+H]: calculated: 223.1869, found: 223.1873.

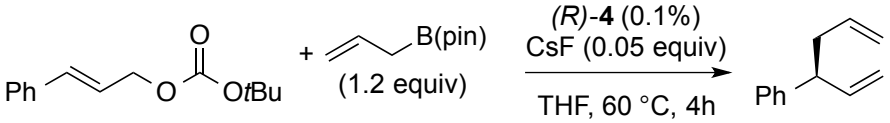
***Preparation of 4,4,5,5-tetramethyl-2-(2-methylenecycloheptyl)-1,3,2-dioxaborolane.*** From 1-(chloromethyl)cyclohept-1-ene, prepared as shown below,[6] the representative procedure was followed with the following modifications: the reaction was run on a 4.64 mmol scale using only one equivalent of chloride and 1.2 equivalents of $Mg^0$ and HB(pin) and was run for 5 hours. The crude reaction mixture was purified by kugelrohr distillation (hi-vacuum, 160 °C) to afford a clear, colorless oil (929.5 mg, 85% yield) as a 3.3:1 ratio of branched to linear product.





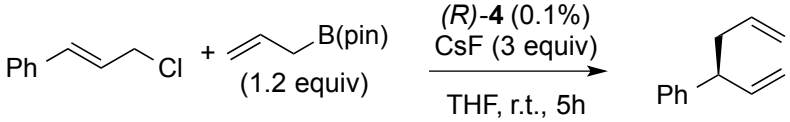
**4,4,5,5-tetramethyl-2-(2-methylenecycloheptyl)-1,3,2-dioxaborolane (Compound SI-7).** $^{1}$H NMR (500 MHz, $CDCl_3$): δ 4.73 (1H, dd (app t), *J* = 1.0, 1.0 Hz), 4.68 (1H, dd, 2.0 Hz, 1.0 Hz), 2.30 (1H, ddd, *J* = 11.0 Hz, 5.5 Hz, 2.0 Hz), 2.18 (1H, ddd, *J* = 10.5 Hz, 7.0 Hz, 2.5 Hz), 2.01-2.12 (2H, m), 1.65-1.81 (3H, m), 1.55-1.61 (1H, m), 1.4201.50 (1H, m), 1.25-1.40 (2H, m), 1.23 (12H, s); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 153.0, 110.5, 82.9, 82.9, 39.2, 36.1, 30.3, 30.0, 29.2, 29.1, 24.6, 24.6, 24.6, 24.6 ; IR (neat): 2977 (w), 2920 (m), 2850 (w), 1631 (w), 1446 (w), 1370 (s), 1356 (s), 1314 (s), 1272 (w), 1214 (w), 1197 (w), 1165 (w), 1143 (s), 1104 (w), 1005 (w), 984 (w), 877 (m), 850 (m), 737 (w), 670 (w), 579 (w) $cm^{-1}$; HRMS-(ESI+) for $C_{14}H_{26}B_1O_2$ [M+H]: calculated: 237.2026, found: 237.2027.

## Experimental Procedure for Allyl-Allyl Coupling.

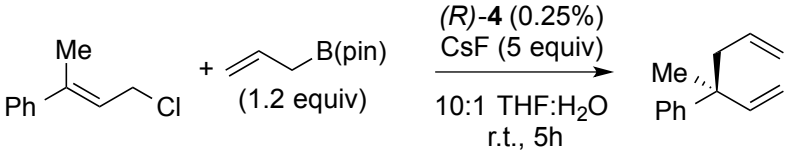



**Representative Procedure A:** An oven-dried scintillation vial equipped with a magnetic stir bar was charged successively with with *(R)*-**4** (0.29 mg, 0.4 µmol), THF (0.8 mL), *tert*-butyl cinnamyl carbonate (93.7 mg, 0.4 mmol), allylB(pin) (80.7 mg, 0.48 mmol), and cesium fluoride (3.1 mg, 0.02 mmol) in a dry-box under argon atmosphere. The vial was sealed, removed from the dry-box, and heated to 60 °C while allowing to stir for 4 h. After this time, the reaction mixture was diluted with diethyl ether, filtered through a plug of silica gel and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (60.0 mg, 95% yield).

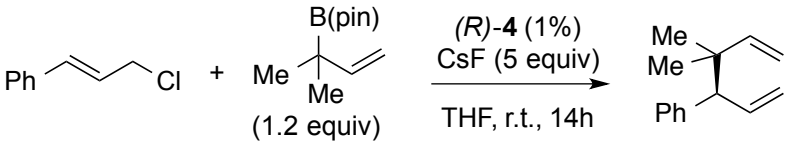
**Representative Procedure for Bench-top Reaction Setup:** An oven-dried scintillation vial equipped with a magnetic stir bar was charged with with *(R)*-**4** (0.58 mg, 0.8 µmol), cesium fluoride (6.1 mg, 0.04 mmol), and *tert*-butyl cinnamyl carbonate (187.4 mg, 0.8 mmol) on the benchtop. The vial was sealed with an open-top cap with a silicon/teflon septum and purged with nitrogen for 15 minutes. A solution of allylB(pin) (161.4 mg, 0.96 mmol) in dry THF (1.6 mL) was added under nitrogen. The vial was sealed with electrical tape and heated to 60 °C while allowing to stir for 4 h. After this time, the reaction mixture was diluted with diethyl ether, filtered through a plug of silica gel and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (122 mg, >96% yield).



**Representative Procedure B:** An oven-dried scintillation vial equipped with a magnetic stir bar was charged successively with with *(R)*-**4** (0.29 mg, 0.4 μmol), THF (0.8 mL), cinnamyl chloride (61.1 mg, 0.4 mmol), allylB(pin) (80.7 mg, 0.48 mmol), and cesium fluoride (182 mg, 1.2 mmol) in a dry-box under argon atmosphere. The vial was sealed, removed from the dry-box, and allowed to stir for 5 h at room temperature. After this time, the reaction mixture was diluted with diethyl ether, filtered through a plug of silica gel and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (58.0 mg, 92% yield).

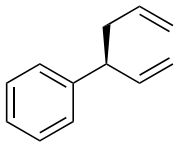



**Representative Procedure C:** An oven-dried scintillation vial equipped with a magnetic stir bar was charged successively with with *(R)*-**4** (0.36 mg, 0.5 μmol), THF (0.4 mL), (E)-(4-chlorobut-2-en-2-yl)benzene (33.2 mg, 0.2 mmol), allylB(pin) (40.4 mg, 0.24 mmol), and cesium fluoride (151.9 mg, 1.0 mmol) in a dry-box under argon atmosphere. The vial was sealed with an open-top cap with a silicon/teflon septum, removed from the dry-box, and degassed deionized water (0.04 mL) was added under nitrogen. The vial was sealed with electrical tape and allowed to stir for 5 h at room temperature. After this time, the reaction mixture was diluted with diethyl ether, filtered through a plug of silica gel and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (29.3 mg, 85% yield).




**Representative Procedure D:** An oven-dried scintillation vial equipped with a magnetic stir bar was charged successively with with *(R)*-**4** (1.44 mg, 2.0 μmol), THF (0.4 mL), cinnamyl chloride (30.5 mg, 0.2 mmol), 4,4,5,5-tetramethyl-2-(2-methylbut-3-en-2-yl)-1,3,2-dioxaborolane (47.1 mg, 0.24 mmol), and cesium fluoride (151.9.1 mg, 1.0 mmol) in a dry-box under argon atmosphere. The vial was sealed, removed from the dry-box, and allowed to stir for 14 h at room temperature. After this time, the reaction mixture was diluted with diethyl ether, filtered through a plug of silica gel and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (35.3 mg, 95% yield).

## Characterization of Products and Analysis of Stereochemistry



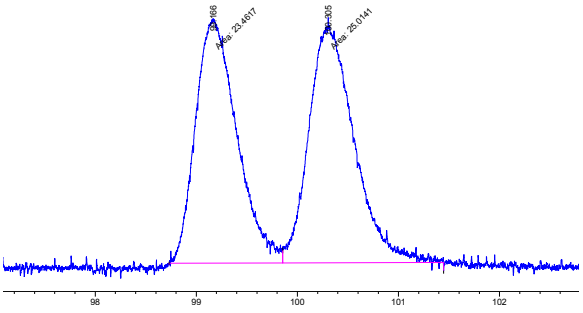
***(S)*-hexa-1,5-dien-3-ylbenzene (Compound 3a).** The title compound was prepared *via* representative procedure **B** for allyl-allyl coupling. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (58.1 mg, 92% yield). $R_f$ = 0.68 (pentane, stain in $KMnO_4$). Spectral data is in accordance with the literature.[13]

[13] Zhang, P.; Brozek, L. A.; Morken, J. P. *J. Am. Chem. Soc.* **2010**, *132*, 10686.

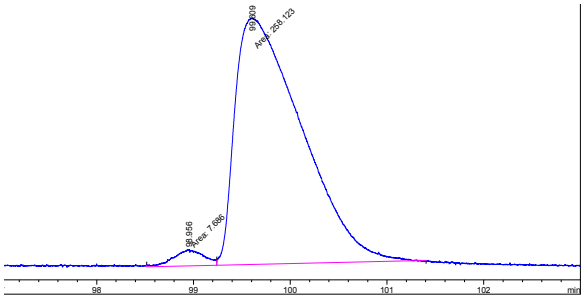
***Analysis of Stereochemistry:***

The enantiomer ratio was determined by GLC analysis of the title compound as compared to racemic material prepared by using 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (*rac*-BINAP) as the ligand in the allyl-allyl coupling reaction. The absolute stereochemistry for the product of allyl-allyl coupling with *(R)*-(+)-2,2'-bis(di-2-furanylphosphino)-6,6'-dimethoxy-1,1'-biphenyl [*(R)*-Methoxy(furyl)BIPHEP] has been previously proven.[13]

*Chiral GLC (CD-BDM, Supelco, 50 °C for 10 min, ramp 0.25 °C/min to 100 °C for 10 min, 20 psi) - analysis of title compound.*

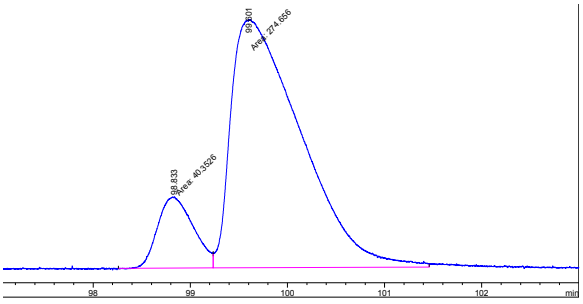



*Racemic Sample*

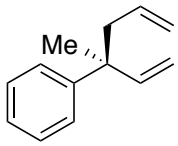



*Enantioenriched Sample*

| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 98.956 | MF | 0.3575 | 7.68600 | 3.58281e-1 | 2.89154 |
| 2 | 99.609 | FM | 0.7947 | 258.12347 | 5.41350 | 97.10846 |




*Co-Injection of Racemic and Enantioenriched Samples*

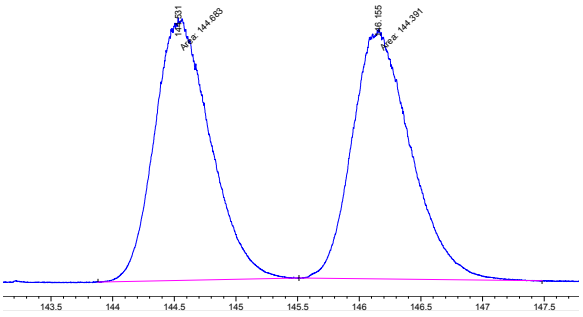



***(S)*-(3-methylhexa-1,5-dien-3-yl)benzene (Compound 3b).** The title compound was prepared *via* representative procedure **C** for allyl-allyl coupling. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (29.3 mg, 85% yield). $R_f$ = 0.83 (pentane, stain in $KMnO_4$).. Spectral data is in accordance with the literature.[4]

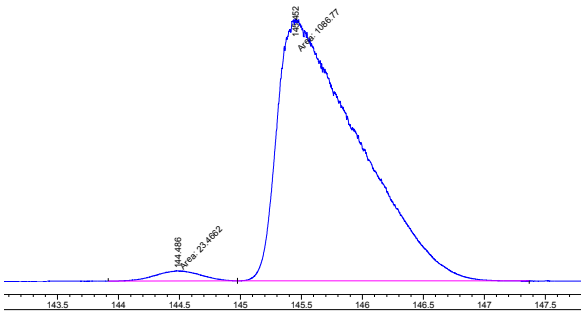
***Analysis of Stereochemistry:***

The enantiomer ratio was determined by GLC analysis of the title compound as compared to racemic material prepared by using 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (*rac*-BINAP) as the ligand in the allyl-allyl coupling reaction. The absolute stereochemistry for the product of allyl-allyl coupling with *(R)*-(+)-2,2'-bis(di-2-furanylphosphino)-6,6'-dimethoxy-1,1'-biphenyl [*(R)*-Methoxy(furyl)BIPHEP] has been previously proven.[4]

*Chiral GLC (β-dex, Supelco, 50 °C for 10 min, ramp 0.25 °C/min to 100 °C for 20 min, 20 psi) - analysis of title compound.*

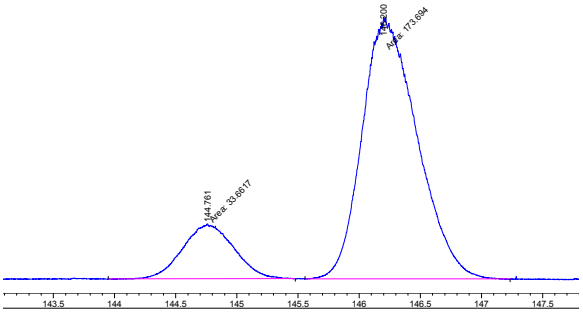



*Racemic Sample*

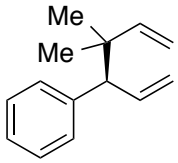



*Enantioenriched Sample*

| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 144.486 | MM | 0.4269 | 23.46618 | 9.16100e-1 | 2.11362 |
| 2 | 145.452 | MM | 0.7656 | 1086.76807 | 23.65905 | 97.88638 |




*Co-Injection of Racemic and Enantioenriched Samples*

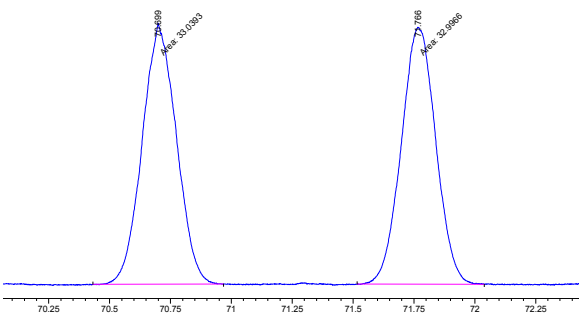



***(R)*-(4,4-dimethylhexa-1,5-dien-3-yl)benzene (Compound 10).** The title compound was prepared *via* representative procedure **D** for allyl-allyl coupling. $^1$H NMR (500 MHz, $CDCl_3$): δ 7.27 (2H, dd (app t), *J* = 8.0 Hz, 8.0 Hz), 7.20 (1H, dd (app t), *J* = 8.0 Hz, 8.0 Hz), 7.17 (2H, dd (app t), *J* = 8.0 Hz, 8.0 Hz), 6.20 (1H, ddd (app dt), *J* = 17.0 Hz, 10.0 Hz, 10.0 Hz), 5.87 (1H, dd, *J* = 17.5 Hz, 10.5 Hz), 5.09 (1H, dd, *J* = 10.0 Hz, 2.0 Hz), 5.03 (1H, dd, *J* = 17.0 Hz, 2.0 Hz), 5.00 (1H, dd, *J* = 10.5 Hz, 1.5 Hz), 4.89 (1H, dd, *J* = 17.5 Hz, 1.5 Hz), 3.10 (1H, d, *J* = 10.0 Hz), 1.03 (3H, s), 0.96 (3H, s); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 146.0, 142.0, 138.7, 129.3, 129.3, 127.7, 127.7, 126.1, 116.4, 111.8, 61.0, 39.8, 25.9, 25.2; IR (neat): 3081 (w), 3028 (w), 3006 (m), 2963 (w), 2928 (w), 2873 (w), 1637 (w), 1493 (w), 1453 (w), 1170 (w), 1072 (w), 994 (m), 912 (s), 783 (w), 732 (m), 701 (s), 668 (w), 521 (w) $cm^{-1}$; HRMS-(ESI+) for $C_{14}H_{19}$ [M+H]: calculated: 187.1487, found: 187.1489. $[\alpha]^{22}_D$ = + 76.8330 (*c* = 1.66, $CHCl_3$). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (35.3 mg, 95% yield). $R_f$ = 0.78 (pentane, stain in $KMnO_4$). Spectral data is also in accordance with the literature.[14]

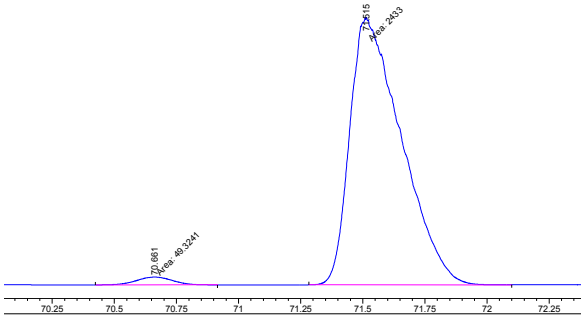
***Analysis of Stereochemistry:***

The enantiomer ratio was determined by GLC analysis of the title compound as compared to racemic material prepared by using 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (*rac*-BINAP) as the ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to product **3a**.

*Chiral GLC (β-dex, Supelco, 50 °C for 10 min, ramp 1 °C/min to 120 °C for 10 min, 20 psi) - analysis of title compound.*



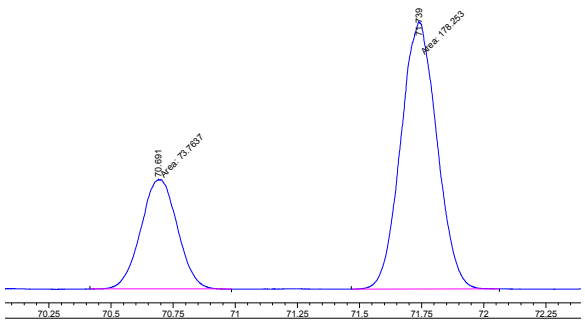

*Racemic Sample*



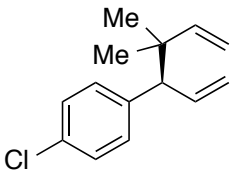

*Enantioenriched Sample*

| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 70.661 | MM | 0.1648 | 49.32411 | 4.98884 | 1.98702 |
| 2 | 71.515 | MM | 0.2400 | 2432.99634 | 168.98608 | 98.01298 |

[14] Hosomi, A.; Imai, T.; Endo, M.; Sakurai, H. *J. Organomet. Chem.* **1985**, *285*, 95.




*Co-Injection of Racemic and Enantioenriched Samples*

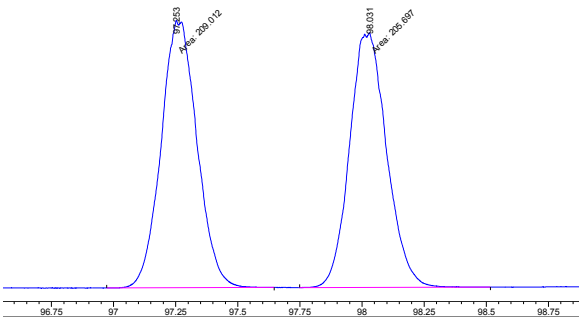



***(R)*-1-chloro-4-(4,4-dimethylhexa-1,5-dien-3-yl)benzene (Compound 20).** The title compound was prepared *via* representative procedure **D** for allyl-allyl coupling utilizing *(E)*-1-chloro-4-(3-chloroprop-1-en-1-yl)benzene. $^1$H NMR (500 MHz, $CDCl_3$): δ 7.23 (2H, ddd (app dt), *J* = 8.0 Hz, 2.0 Hz, 2.0 Hz), 7.08 (2H, ddd (app dt), *J* = 8.0 Hz, 2.0 Hz, 2.0 Hz), 6.13 (1H, ddd, *J* = 17.0 Hz, 10.5 Hz, 9.0 Hz), 5.82 (1H, dd, *J* = 17.5 Hz, 10.5 Hz), 5.10 (1H, dd, *J* = 10.5 Hz, 2.0 Hz), 5.02 (1H, ddd (app dt), *J* = 17.0 Hz, 2.0 Hz, 2.0 Hz), 5.00 (1H, dd, *J* = 10.5 Hz, 1.5 Hz), 4.87 (1H, dd, *J* = 17.5 Hz, 1.5 Hz), 3.08 (1H, d, *J* = 9.0 Hz), 1.01 (3H, s), 0.93 (3H, s); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 145.5, 140.5, 138.2, 131.9, 130.6, 130.6, 127.8, 127.8, 116.8, 112.3, 60.3, 39.8, 25.8, 25.2; IR (neat): 3081 (w), 2965 (m), 2928 (w), 2873 (w), 1637 (w), 1491 (s), 1461 (w), 1414 (w), 1406 (w), 1379 (w), 1363 (w), 1170 (w), 1092 (w), 1014 (m), 994 (m), 914 (s), 826 (s), 763 (m), 717 (w), 522 (m) cm$^{-1}$; HRMS-(ESI +) for $C_{14}H_{18}Cl$ [M+H]: calculated: 221.1097, found: 221.1104. $[\alpha]^{22}_D$ = + 93.3926 (*c* = 1.28, $CHCl_3$). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (40.5 mg, 92% yield). $R_f$ = 0.74 (pentane, stain in $KMnO_4$).

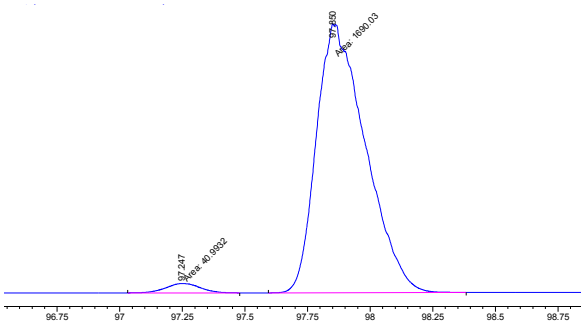
***Analysis of Stereochemistry:***

The enantiomer ratio was determined by GLC analysis of the title compound as compared to racemic material prepared by using 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (*rac*-BINAP) as the ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to compound **3a**.

*Chiral GLC (β-dex, Supelco, 50 °C for 50 min, ramp 1 °C/min to 140 °C for 10 min, 20 psi) - analysis of title compound.*

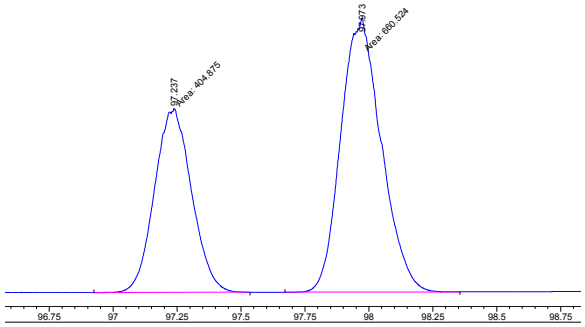



*Racemic Sample*

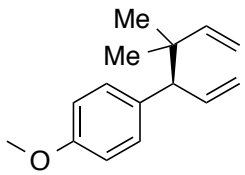



*Enantioenriched Sample*

| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 97.247 | MM | 0.1578 | 40.99323 | 4.33084 | 2.36815 |
| 2 | 97.850 | MM | 0.2270 | 1690.03235 | 124.09972 | 97.63185 |




*Co-Injection of Racemic and Enantioenriched Samples*



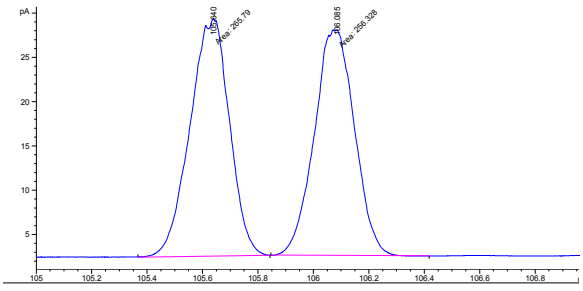

***(R)*-1-(4,4-dimethylhexa-1,5-dien-3-yl)-4-methoxybenzene (Compound 21).** The title compound was prepared *via* representative procedure **D** for allyl-allyl coupling with *(E)*-1-(3-chloroprop-1-en-1-yl)-4-methoxybenzene. $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.07 (2H, ddd (app dt), *J* = 9.0 Hz, 2.5 Hz, 2.5 Hz), 6.81 (2H, ddd (app dt), *J* = 9.0 Hz, 2.5 Hz, 2.5 Hz), 6.15 (1H, ddd, *J* = 17.5 Hz, 10.5 Hz, 9.5 Hz), 5.85 (1H, dd, *J* = 17.5, 10.5 Hz), 5.24 (1H, dd, *J* = 10.0 Hz, 2.5 Hz), 5.18 (1H, ddd, *J* = 17.0 Hz, 2.0 Hz, 1.0 Hz), 5.16 (1H, dd, *J* = 10.5 Hz, 1.5 Hz), 5.05 (1H, dd, *J* = 17.5 Hz, 1.5 Hz), 3.79 (3H, s), 3.05 (1H, d, *J* = 9.5 Hz), 1.00 (3H, s), 0.94 (3H, s); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 157.9, 146.2, 138.9, 134.2, 130.1, 130.1, 116.1,

113.1, 113.1, 111.8, 60.0, 55.2, 39.9, 25.9, 25.1; IR (neat): 3079 (w), 2961 (m), 2931 (w), 2835 (w), 1637 (w), 1610 (m), 1582 (w), 1510 (s), 1464 (w), 1442 (w), 1414 (w), 1378 (w), 1362 (w), 1332 (w), 1301 (w), 1268 (s), 1245 (m), 1179 (m), 1123 (m), 1100 (m), 1038 (m), 995 (s), 919 (w), 828 (w), 781 (w), 765 (w), 686 (w), 644 (w), 579 (w), 540 (w) $cm^{-1}$; HRMS-(ESI+) for $C_{15}H_{21}O_1$ [M+H]: calculated: 217.1592, found: 217.1598. $[\alpha]^{22}_D$ = + 81.6600 (*c* = 0.55, $CHCl_3$). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (19.4 mg, 90% yield). $R_f$ = 0.15 (pentane, stain in $KMnO_4$).

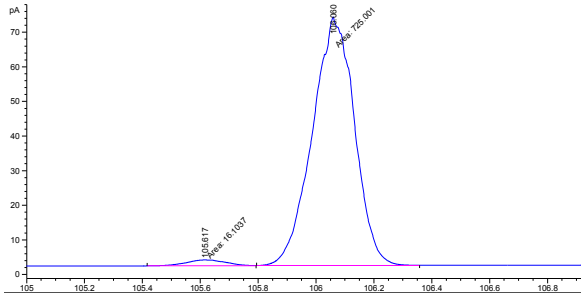
***Analysis of Stereochemistry:***

The enantiomer ratio was determined by GLC analysis of the title compound as compared to racemic material prepared by using 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (*rac*-BINAP) as the ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to product **3a**.

*Chiral GLC (β-dex, Supelco, 50 °C for 10 min, ramp 1 °C/min to 160 °C for 10 min, 20 psi) - analysis of title compound.*

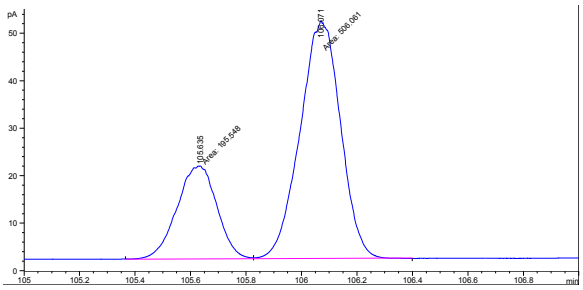


*Racemic Sample*

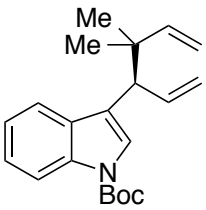


*Enantioenriched Sample*

| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 105.617 | MM | 0.1576 | 16.10371 | 1.70270 | 2.17293 |
| 2 | 106.060 | MM | 0.1682 | 725.00079 | 71.83309 | 97.82707 |



*Co-Injection of Racemic and Enantioenriched Samples*

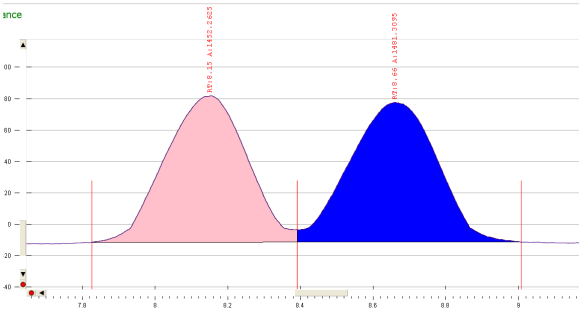


***tert-butyl (R)*-3-(4,4-dimethylhexa-1,5-dien-3-yl)-1H-indole-1-carboxylate (Compound 22).** The title compound was prepared *via* representative procedure **D** for allyl-allyl coupling with *tert*-butyl *(E)*-3-(3-chloroprop-1-en-1-yl)-1H-indole-1-carboxylate. $^{1}$H NMR (500 MHz, $CDCl_3$): δ 8.09 (1H, s (br)), 7.57 (1H, d, *J* = 7.5 Hz), 7.41 (1H, s (br)), 7.29 (1H, ddd (app dt), *J* = 8.0 Hz, 8.0 Hz, 1.5 Hz), 7.22 (1H, ddd (app dt), *J* = 8.0 Hz, 8.0 Hz, 1.5 Hz), 6.11 (1H, ddd, *J* = 18.0 Hz, 9.5 Hz, 9.0 Hz), 5.97 (1H, dd, *J* = 17.0 Hz, 11.0 Hz), 5.04-5.07 (2H, m), 5.02 (1H, dd, *J* = 10.5 Hz, 1.5 Hz), 4.98 (1H, dd, *J* = 17.0 Hz, 1.5 Hz), 3.44 (1H, d, *J* = 9.0 Hz), 1.68 (9H, s), 1.10 (3H, s), 1.05 (3H, s); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 146.2, 138.2, 131.3, 124.1, 123.1, 122.1, 121.0, 119.8, 115.9, 115.1, 115.1, 112.0, 110.0, 83.5, 51.1, 40.2, 28.2, 28.2, 28.2, 25.9, 25.2; IR (neat): 2975 (m), 2930 (w), 7314 (s), 1706 (w), 1637 (w), 1474 (w), 1452 (m), 1415 (w), 1368 (s), 1308 (w), 1252 (m), 1219 (w), 1156 (s), 1071 (m), 1017 (w), 913 (m), 860 (w), 839 (w), 767 (m), 744 (m) $cm^{-1}$; HRMS-(ESI+) for $C_{21}H_{28}N_1O_2$ [M+H]: calculated: 362.2118, found: 326.2120. $[\alpha]^{22}_D$ = + 29.7186 (*c* = 1.78, $CHCl_3$). The crude reaction mixture was purified on silica gel (50:1 pentane:diethyl ether) to afford a clear, colorless oil (53.3 mg, 82% yield). $R_f$ = 0.38 (50:1 pentane:diethyl ether, stain in $KMnO_4$).

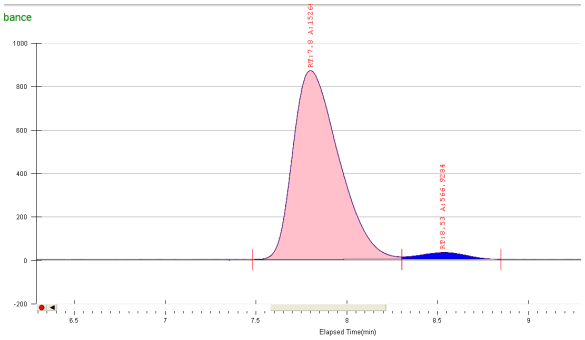
***Analysis of Stereochemistry:***

The enantiomer ratio was determined by SFC analysis of the title compound as compared to racemic material prepared by using 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (*rac*-BINAP) as the ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to product **3a**.

*Chiral SFC (ODR-H, Chiralpak, 1.5 mL/min, 1.0% i-PrOH, 100 bar, 35 °C) - analysis of title compound.*



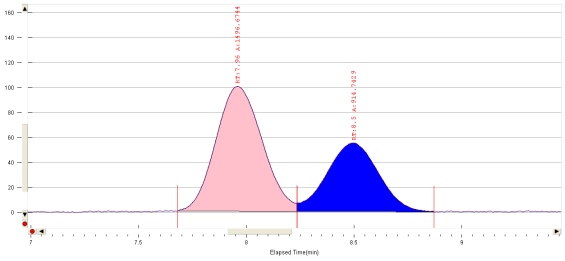
*Racemic Sample*



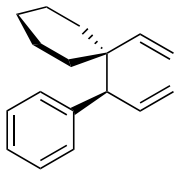
*Enantioenriched Sample*

Peak Info

| Peak No | % Area | Area | RT (min) | Height (mV) | K' |
|---|---|---|---|---|---|
| 1 | 96.419 | 15264.6999 | 7.8 | 869.3087 | 0.0101 |
| 2 | 3.581 | 566.9284 | 8.53 | 31.7582 | 0.011 |
| Total: | 100 | 15831.6283 | | | |



*Co-Injection of Racemic and Enantioenriched Samples*



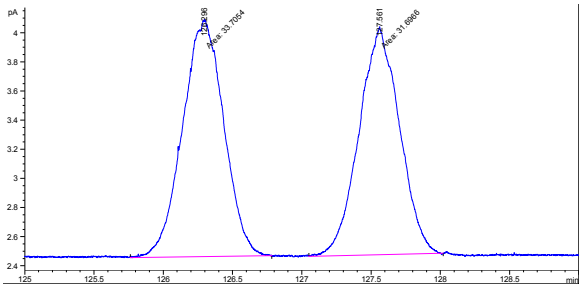
***(R)*-(1-(1-vinylcyclohexyl)allyl)benzene (Compound 24).** The title compound was prepared *via* representative procedure **D** for allyl-allyl coupling with 4,4,5,5-tetramethyl-2-(3-methylpent-1-en-3-yl)-1,3,2-dioxaborolane (Compound 18) and cinnamyl chloride. $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.24 (2H, dd (app t), *J* = 7.0 Hz, 7.0 Hz), 7.17 (1H, dddd (app tt), *J* = 7.5 Hz, 7.5 Hz, 1.5 Hz, 1.5 Hz), 7.15 (2H, dd (app t), *J* = 7.0 Hz, 7.0 Hz), 6.14 (1H, ddd (app dt), *J* = 7.0 Hz, 7.0 Hz), 5.54 (1H, dd, *J* = 18.0 Hz, 11.0 Hz), 5.26 (1H, dd, *J* = 11.5 Hz, 1.5 Hz), 5.06 (1H, dd, *J* = 10.0 Hz, 2.0 Hz), 5.02 (1H, dd, *J* = 17.0 Hz, 2.0 Hz), 4.89 (1H, dd, *J* = 18.0 Hz, 3.0 Hz), 3.12 (1H, d, *J* = 9.5 Hz), 1.83 (1H, d, *J* = 13.5 Hz), 1.38-1.53 (4H, m), 1.19-1.36 (5H, m); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 142.8, 141.7, 138.6, 129.5, 129.5, 127.5, 127.5, 126.1, 116.0, 115.6, 42.6, 35.0, 34.3, 26.4, 26.4, 22.2, 22.0; IR (neat): 3077 (w), 3028 (w), 2976 (w), 2931 (s), 2853 (m), 1635 (w), 1601 (w), 1492 (w), 1452 (m), 1416 (w), 995 (m), 913 (s), 731 (m), 701 (s), 669 (w),

522 (w) $cm^{-1}$; HRMS-(ESI+) for $C_{17}H_{23}$ [M+H]: calculated: 227.1780, found: 227.1807; $[\alpha]^{22}_D$ = + 70.272 (*c* = 0.91, $CHCl_3$). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (38.4 mg, 85% yield). $R_f$ = 0.75 (pentane, stain in $KMnO_4$).

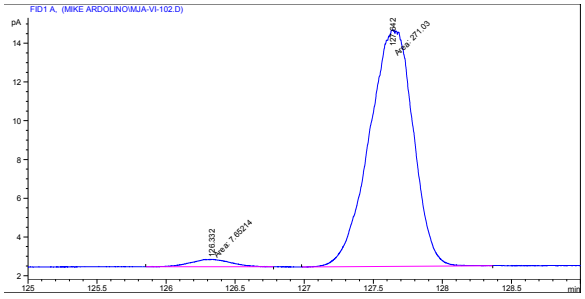
***Analysis of Stereochemistry:***

The enantiomer ratio was determined by GLC analysis of the title compound as compared to racemic material prepared by using 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (*rac*-BINAP) as the ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to product **3a**.

*Chiral GLC (β-dex, Supelco, 50 °C for 10 min, ramp 1 °C/min to 140 °C for 60 min, 20 psi) - analysis of title compound.*

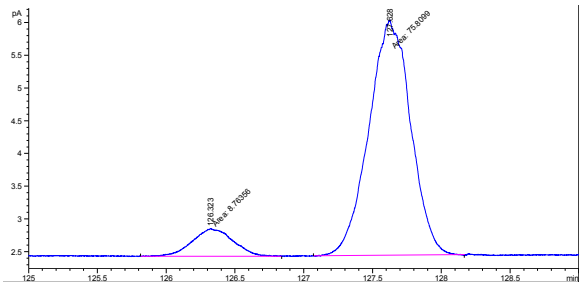



*Racemic Sample*

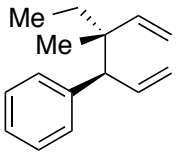



*Enantioenriched Sample*

| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 126.332 | MM | 0.3354 | 7.65214 | 3.80289e-1 | 2.74583 |
| 2 | 127.642 | MM | 0.3695 | 271.03003 | 12.22556 | 97.25417 |




*Co-Injection of Racemic and Enantioenriched Samples*

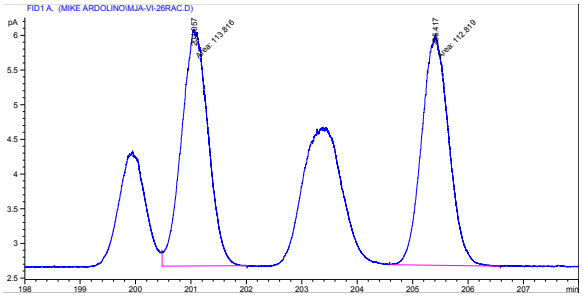



***((3R,4R)*-4-ethyl-4-methylhexa-1,5-dien-3-yl)benzene (Compound 26).** The title compound was prepared *via* representative procedure **D** for allyl-allyl coupling with 4,4,5,5-tetramethyl-2-(3-methylpent-1-en-3-yl)-1,3,2-dioxaborolane (Compound 20) and cinnamyl chloride. $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.26 (2H, dd (app t), *J* = 8.0 Hz, 8.0 Hz), 7.15-7.21 (3H, m), 6.19 (1H, ddd (app dt), *J* = 17.0 Hz, 10.0 Hz, 10.0 Hz), 5.76 (1H, dd, *J* = 18.0 Hz, 11.0 Hz), 5.13 (1H, dd, *J* = 11.0 Hz, 1.5 Hz), 5.08 (1H, dd, *J* = 17.0 Hz, 2.0 Hz), 5.02 (1H, dd, *J* = 11.0 Hz, 2.0 Hz), 4.86 (1H, dd, *J* = 18.0 Hz, 2.5 Hz), 3.17 (1H, d, *J* = 9.0 Hz), 1.49 (1H, (dq), *J* = 14.0 Hz, 7.5 Hz, 7.5 Hz, 7.5 Hz), 1.32 (1H, (dq), *J* = 14.0 Hz, 7.5 Hz, 7.5 Hz, 7.5 Hz), 0.87 (3H, s), 0.79 (3H, dd (app t), *J* = 7.5 Hz, 7.5 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 144.5, 141.9, 138.6, 129.6, 129.6, 127.6, 127.6, 126.1, 116.2, 113.7, 60.1, 43.3, 31.4, 19.4, 8.4; IR (neat): 3081 (w), 3028 (w), 2968 (m), 2934 (w), 2879 (w), 1637 (w), 1601 (w), 1492 (w), 1453 (m), 1414 (w), 1378 (w), 1135 (w), 1072 (w), 1061 (m), 1031 (w), 995 (w), 913 (s), 775 (w), 730 (m), 701 (s), 668 (w), 522 (w), 511 (w) $cm^{-1}$; HRMS-(ESI+) for $C_{15}H_{21}$ [M+H]: calculated: 201.1643, found: 201.1643. $[\alpha]^{22}_{D}$ = + 75.487 (*c* = 0.96, $CHCl_3$). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (38.4 mg, 96% yield). $R_f$ = 0.75 (pentane, stain in $KMnO_4$).

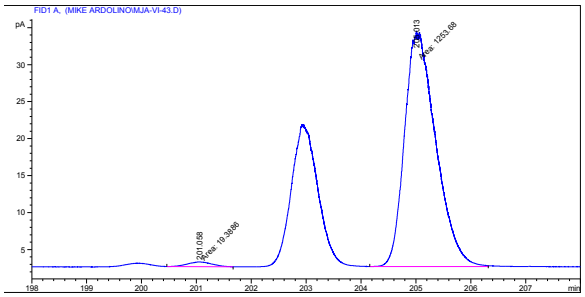
***Analysis of Stereochemistry:***

The enantiomer ratio was determined by GLC analysis of the title compound as compared to racemic material prepared by using 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (*rac*-BINAP) as the ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to products **3a** and **28**.

*Chiral GLC (β-dex, Supelco, 50 °C for 10 min, ramp 0.25 °C/min to 120 °C for 20 min, 20 psi) - analysis of title compound.*

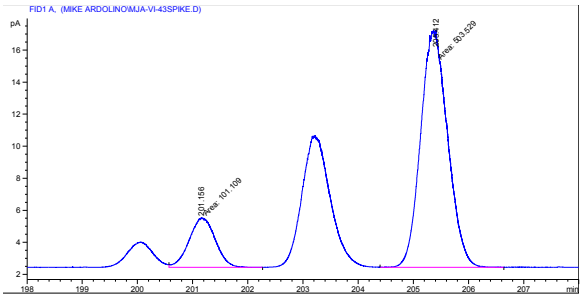



*Racemic Sample*

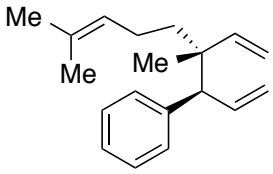



*Enantioenriched Sample*

| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 201.058 | MM | 0.5059 | 19.38857 | 6.38724e-1 | 1.52298 |
| 2 | 205.013 | MF | 0.6559 | 1253.68225 | 31.85507 | 98.47702 |



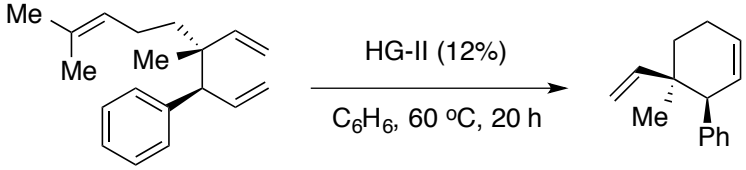

*Co-Injection of Racemic and Enantioenriched Samples*



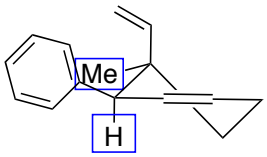

***((3R,4R)*-4,8-dimethyl-4-vinylnona-1,7-dien-3-yl)benzene (Compound 28).** The title compound was prepared *via* representative procedure **D** for allyl-allyl coupling with 2-(3,7-dimethylocta-1,6-dien-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound 22) and cinnamyl chloride. $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.25 (2H, ddd (app dt), *J* = 7.5 Hz, 7.5 Hz, 1.5 Hz), 7.17-7.21 (1H, m), 7.15 (2H, dd (app t), *J* = 7.5 Hz, 7.5 Hz), 6.18 (1H, ddd (app dt), *J* = 17.0 Hz, 10.0 Hz, 10.0 Hz), 5.78 (1H, dd, *J* = 17.5 Hz, 10.5 Hz), 4.99-5.13 (4H, m), 4.87 (1H, dd, *J* = 18.0 Hz, 1.5 Hz), 3.15 (1H, dd, *J* = 18.0 Hz, 1.5 Hz), 1.84-1.92 (2H, m), 1.67 (3H, d, *J* = 1.0 Hz), 1.57 (3H, s), 1.39-1.45 (1H, m), 1.26-1.34 (1H, m), 0.91 (3H, s); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 144.5, 141.8, 138.6, 129.6, 127.7, 127.7, 127.7, 127.7, 126.1, 124.9, 116.4, 113.7, 60.4, 42.7, 39.0, 25.7, 22.8, 20.1, 17.6; IR (neat): 3080 (w), 3029 (w), 2969 (m), 2922 (m), 2856 (w), 1636 (w), 1492 (w), 1453 (m), 1414 (w), 1374 (m), 1159 (w), 1121 (w), 1071 (w), 1030 (w), 995 (m), 913 (s), 828 (w), 782 (w), 734 (m), 702 (s), 669 (w), 523 (w) $cm^{-1}$; HRMS-(ESI+) for $C_{19}H_{27}$ [M+H]: calculated: 255.2107, found: 255.2113. $[\alpha]^{22}_{D}$ = + 26.470 (*c* = 0.92, $CHCl_3$). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (46.7 mg, 92% yield). $R_f$ = 0.64 (pentane, stain in $KMnO_4$).

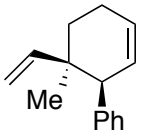
***Analysis of Stereochemistry:***

The title compound was treated with Hoveyda-Grubbs second generation catalyst to afford the ring closing metathesis product for GC analysis and determination of relative stereochemistry as depicted below. The analogous racemic material was prepared *via* the same route, using 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (*rac*-BINAP) as the ligand in the allyl-allyl coupling reaction.



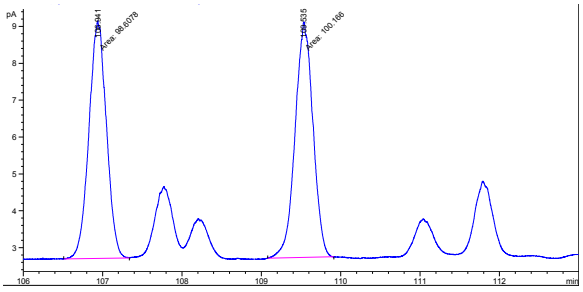
The absolute stereochemistry was assigned by analogy to compound **3a**. The relative stereochemistry was determined by NOESY analysis of the ring-closing metathesis product. The following NOE was observed:



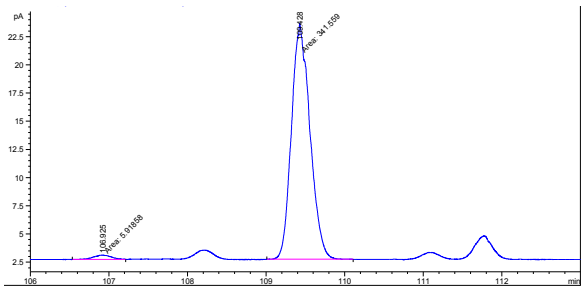




**(*1R,2R*)-2-methyl-2-vinyl-1,2,3,4-tetrahydro-1,1'-biphenyl (Compound SI-8).** $^{1}$H NMR (600 MHz, $CDCl_3$): δ 7.25 (2H, dd (app t), *J* = 7.0 Hz, 7.0 Hz), 7.19 (1H, dd, (app t), *J* = 7.5 Hz, 7.5 Hz), 7.14 (2H, dd (app t), *J* = 8.0 Hz, 8.0 Hz), 5.87-5.91 (1H, m), 5.81 (1H, dd, *J* = 17.5 Hz, 11.0 Hz), 5.68-5.70 (1H, m), 4.80 (1H, dd, *J* = 11.0 Hz, 1.0 Hz), 4.75 (1H, dd, *J* = 17.5 Hz, 2.0 Hz), 3.20-3.22 (1H, m), 2.23-2.30 (1H, m), 2.12-2.18 (1H, m), 1.69 (1H, ddd (app dt), *J* = 13.0 Hz, 7.0 Hz, 7.0 Hz), 1.54 (1H, ddd (app dt), *J* = 13.0 Hz, 7.0 Hz, 7.0 Hz), 1.13 (3H, s); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 144.4, 142.3, 130.0, 130.0, 129.4, 127.3, 127.3, 126.9, 126.1, 111.5, 52.4, 38.7, 32.5, 25.1, 22.8; IR (neat): 3082 (w), 3061 (w), 3024 (w), 2959 (m), 2923 (w), 2871 (w), 2848 (w), 2363 (w), 1637 (w), 1491 (w), 1452 (m), 1434 (w), 1416 (w), 1371 (w), 1006 (m), 911 (w), 757 (m), 702 (s), 668 (w), 532 (w) $cm^{-1}$; HRMS-(ESI+) for $C_{15}H_{19}$ [M+H]: calculated: 199.1487, found: 199.1484. $[\alpha]^{22}_{D}$ = – 114.26 (*c* = 1.00, $CHCl_3$). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (3.0 mg, 33% yield). $R_f$ = 0.66 (pentane, stain in $KMnO_4$).

*Chiral GLC (β-dex, Supelco, 50 °C for 10 min, ramp 1 °C/min to 120 °C for 10 min, then 0.5 deg/min to 150 °C, 60 min, 20 psi) - analysis of RCM product SI-X.*

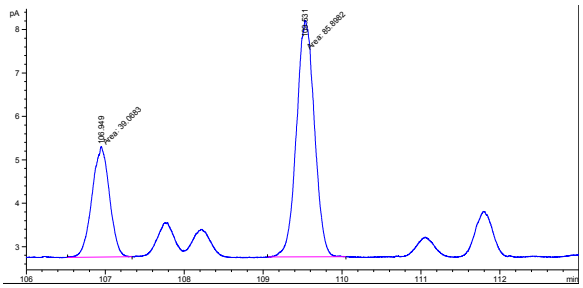


*Racemic Sample*

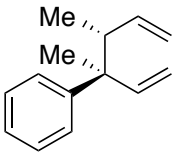


*Enantioenriched Sample*

| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 106.925 | MM | 0.2545 | 5.91858 | 3.87627e-1 | 1.70330 |
| 2 | 109.428 | MM | 0.2718 | 341.55917 | 20.94393 | 98.29670 |




*Co-Injection of Racemic and Enantioenriched Samples*

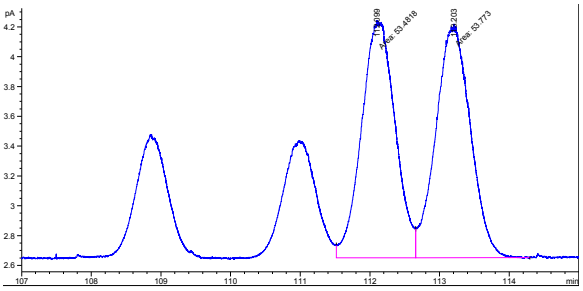



***((3R,4R)*-3,4-dimethylhexa-1,5-dien-3-yl)benzene (Compound 30).** The title compound was prepared *via* representative procedure **D** for allyl-allyl coupling with 2-(but-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound 24) and *(E)*-(4-chlorobut-2-en-2-yl)benzene. $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.22-7.29 (4H, m), 7.17 (1H, dddd (app tt), *J* = 7.0 Hz, 7.0 Hz, 1.5 Hz, 1.5 Hz,), 6.10 (1H, dd, *J* = 17.5 Hz, 11.5 Hz), 5.68 (1H, ddd, *J* = 18.0 Hz, 11.0 Hz, 7.0 Hz), 5.15 (1H, dd, *J* = 10.5 Hz, 1.5 Hz), 4.96-5.03 (3H, m), 2.66 (1H, dddddd (app dqt), *J* = 7.0 Hz, 7.0 Hz, 7.0 Hz, 7.0 Hz, 1.5 Hz, 1.5 Hz), 1.29 (3H, s), 0.80 (3H, d, *J* = 7.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 145.1, 140.9, 128.0, 128.0, 126.9, 126.9, 126.7, 125.7, 114.8, 113.2, 45.7, 38.1, 21.1, 14.5; IR (neat): 3082 (w), 3060 (w), 3021 (w), 2975 (w), 2931 (m), 2877 (w), 1636 (w), 1600 (w), 1493 (w), 1445 (w), 1413 (w), 1374 (w), 1079 (w), 1030 (w), 1000 (w), 912 (s), 761 (w), 732 (m), 699 (s), 542 (w) $cm^{-1}$; HRMS-(ESI+) for $C_{14}H_{19}$ [M+H]: calculated: 187.1487, found: 187.1491. $[\alpha]^{22}_{D}$ = + 63.841 (*c* = 0.775, $CHCl_3$). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (27.5 mg, 74% yield). $R_f$ = 0.73 (pentane, stain in $KMnO_4$).

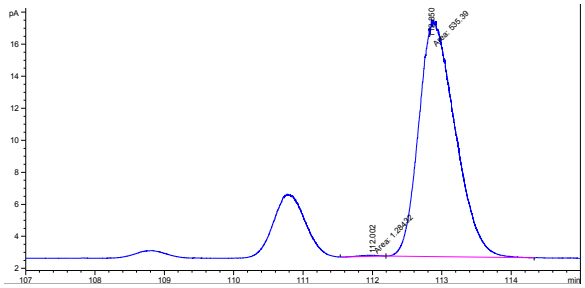
***Analysis of Stereochemistry:***

The enantiomer ratio was determined by GLC analysis of the title compound as compared to the analogous racemic material, prepared using 1,2-bis(diphenylphosphino)benzene as the ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to compounds **3a** and **31**.

*Chiral GLC (β-dex, Supelco, 40 °C for 10 min, ramp 1 °C/min to 90 °C for 60 min, 20 psi) - analysis of title compound.*

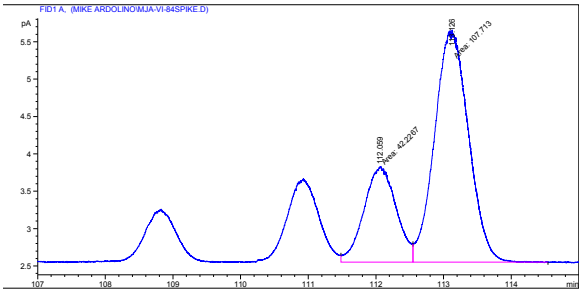


*Racemic Sample*

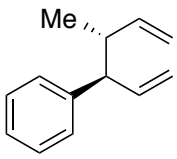


*Enantioenriched Sample*

| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 112.002 | MM | 0.3373 | 1.28432 | 6.34539e-2 | 0.23931 |
| 2 | 112.850 | MM | 0.6032 | 535.39044 | 14.79390 | 99.76069 |



*Co-Injection of Racemic and Enantioenriched Samples*

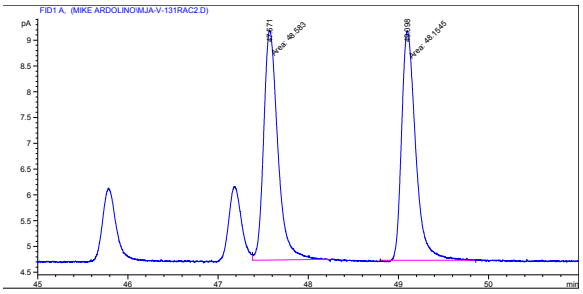



**((3R,4R)-4-methylhexa-1,5-dien-3-yl)benzene (Compound 31).** The title compound was prepared *via* representative procedure **A** for allyl-allyl coupling with 2-(but-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound 24) and *tert*-butyl cinnamyl carbonate. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (95.7 mg, 90% yield). $R_f$ = 0.45 (pentane, stain in $KMnO_4$). Spectral data is in accordance with the literature.[2]

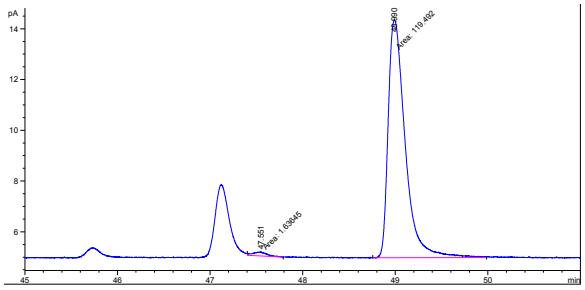
***Analysis of Stereochemistry:***

The enantiomer ratio was determined by GLC analysis of the title compound as compared to the analogous racemic material, prepared using 1,2-bis(diphenylphosphino)benzene as the ligand in the allyl-allyl coupling reaction. The absolute stereochemistry has been previously proven.[2]

*Chiral GLC (CD-BDM, Supelco, 50 °C for 10 min, ramp 1 °C/min to 110 °C for 20 min, 20 psi) - analysis of title compound.*

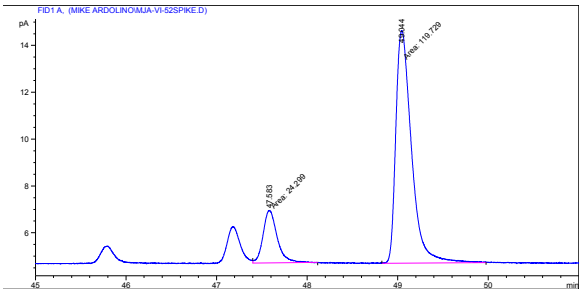



*Racemic Sample*

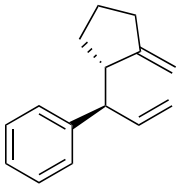



*Enantioenriched Sample*

| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 47.551 | FM | 0.1619 | 1.63645 | 1.68470e-1 | 1.35101 |
| 2 | 48.990 | MF | 0.2125 | 119.49178 | 9.37170 | 98.64899 |




*Co-Injection of Racemic and Enantioenriched Samples*

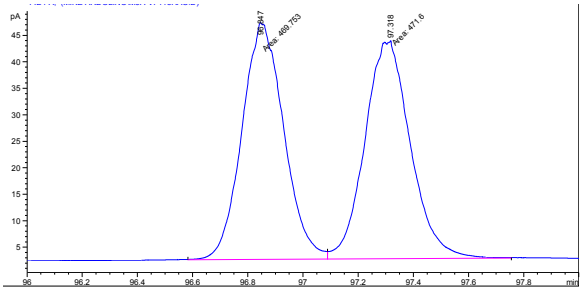


***((R)*-1-*((S)*-2-methylenecyclopentyl)allyl)benzene (Compound 37).** The title compound was prepared *via* representative procedure **D** for allyl-allyl coupling with 4,4,5,5-tetramethyl-2-(2-methylenecyclopentyl)-1,3,2-dioxaborolane and cinnamyl chloride with the following modification: the reaction was run for 24 hours. $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.29 (2H, dddd (app tt), *J* = 7.5 Hz, 7.5 Hz, 1.5 Hz, 1.5 Hz), 7.19 (3H, dd (app t), *J* = 7.5 Hz, 7.5 Hz), 6.11 (1H, ddd (app dt), *J* = 17.5 Hz, 9.5 Hz, 9.5 Hz), 5.07 (1H, ddd (app dt), *J* = 10.5 Hz, 1.5 Hz, 1.5 Hz), 5.00 (1H, ddd (app dt), *J* = 17.5 Hz, 1.5 Hz, 1.5 Hz), 4.96 (1H, s (br)), 4.91 (1H, s (br)), 3.28 (1H, dd (app t), *J* = 8.5 Hz, 8.5 Hz), 2.79-2.84 (1H, m), 2.18-2.34 (2H, m), 1.56-1.66 (2H, m), 1.45-1.54 (1H, m), 1.30-1.37 (1H, m); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 154.1, 143.6, 141.4, 128.3, 128.3, 128.2, 128.2, 126.0, 115.0, 107.2, 53.6, 48.3, 33.5, 31.0, 23.7; IR (neat): 3078 (w), 3027 (w), 2954 (m), 2868 (w), 1650 (w), 1638 (w), 1600 (w), 1492 (w), 1451 (w), 1434 (w), 1414 (w), 991 (w), 912 (m), 883 (m), 755 (m), 699 (s), 673 (w), 523 (w) cm$^{-1}$; HRMS-(ESI+) for $C_{15}H_{19}$ [M+H]: calculated: 199.1487, found: 199.1485. $[\alpha]^{22}_{D}$ = – 46.251 (*c* = 0.92, $CHCl_3$). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (38.0 mg, 96% yield). $R_f$ = 0.69 (pentane, stain in $KMnO_4$).

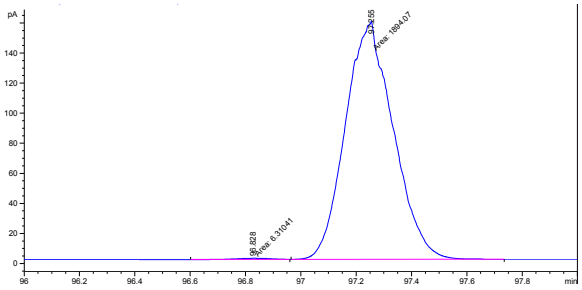
***Analysis of Stereochemistry:***

The enantiomer ratio was determined by GLC analysis of the title compound as compared to the analogous racemic material, prepared using 1,2-bis(diphenylphosphino)benzene as the ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to compounds **3a** and **38**.

*Chiral GLC (β-dex, Supelco, 50 °C for 10 min, ramp 1 °C/min to 140 °C for 30 min, 20 psi) - analysis of title compound.*

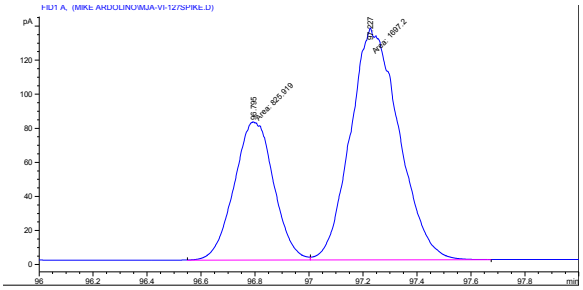


*Racemic Sample*

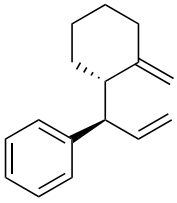


*Enantioenriched Sample*

| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 96.828 | MM | 0.1386 | 6.31041 | 7.58823e-1 | 0.33206 |
| 2 | 97.255 | MM | 0.1994 | 1894.06775 | 158.30048 | 99.66794 |



*Co-Injection of Racemic and Enantioenriched Samples*

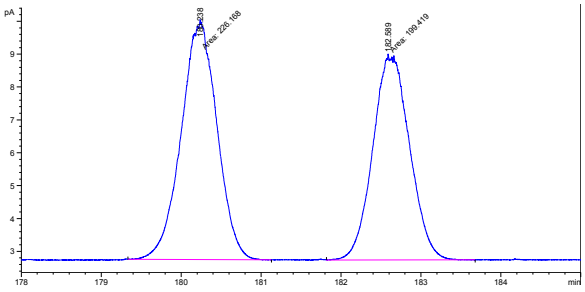


***((R)*-1-*((S)*-2-methylenecyclohexyl)allyl)benzene (Compound 38).** The title compound was prepared *via* representative procedure **D** for allyl-allyl coupling with 4,4,5,5-tetramethyl-2-(2-methylenecyclohexyl)-1,3,2-dioxaborolane and cinnamyl chloride with the following modification: the reaction was run for 24 hours on a 0.5 mmol scale. $^{1}$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.31 (2H, dd (app t), $J$ = 7.5 Hz, 7.5 Hz), 7.21 (3H, dd (app t), $J$ = 7.5 Hz, 7.5 Hz), 5.95 (1H, ddd, $J$ = 17.0 Hz, 10.0 Hz, 8.5 Hz), 4.94 (1H, dd, $J$ = 10.5 Hz, 1.5 Hz), 4.89 (1H, dd, $J$ = 17.0 Hz, 1.0 Hz), 4.77 (1H, s (br)), 4.73 (1H, d, $J$ = 2.5 Hz), 3.53 (1H, dd, $J$ = 11.5 Hz, 8.5 Hz), 2.56 (1H, ddd (app dt), $J$ = 11.5 Hz, 4.5 Hz, 4.5 Hz), 2.16-2.19 (2H, m), 1.75-1.80 (1H, m), 1.56-1.65 (1H, m), 1.37-1.46 (2H, m), 1.33 (2H, dddd (app p), $J$ = 4.0 Hz, 4.0 Hz, 4.0 Hz, 4.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 150.7, 143.7, 141.7, 128.5, 128.5, 128.1, 128.1, 126.2, 114.0, 108.8, 50.1, 48.4, 32.7, 30.1, 28.6, 21.6; IR (neat): 3065 (w), 3027 (w), 2977 (w), 2929 (s), 2855 (m), 1646 (w), 1600 (w), 1492 (w), 1448 (w), 1410 (m), 1070 (w), 986 (w), 909 (w), 888 (m), 857 (m), 779 (w), 750 (m), 699 (s), 674 (w), 577 (w), 521 (w) cm$^{-1}$; HRMS-(ESI+) for $C_{16}H_{21}$ [M+H]: calculated: 213.1643, found: 213.1651. $[\alpha]^{22}_{D}$ = + 60.601 ($c$ = 1.55, $CHCl_3$). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (100.0 mg, 94% yield). $R_f$ = 0.63 (pentane, stain in $KMnO_4$).

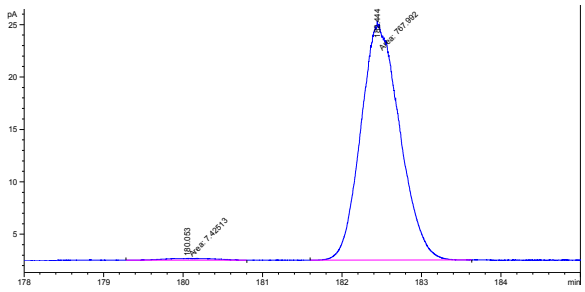
***Analysis of Stereochemistry:***

The enantiomer ratio was determined by GLC analysis of the title compound as compared to the analogous racemic material, prepared using 1,2-bis(diphenylphosphino)benzene as the ligand in the allyl-allyl coupling reaction. The relative stereochemistry was assigned as shown below. The absolute stereochemistry was assigned by analogy to compound **3a**.

*Chiral GLC (β-dex, Supelco, 50 °C for 10 min, ramp 0.5 °C/min to 120 °C for 40 min, 20 psi) - analysis of title compound.*

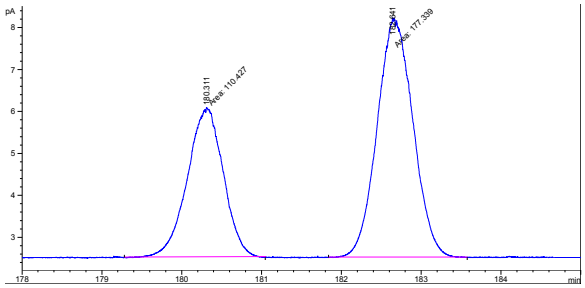


*Racemic Sample*



*Enantioenriched Sample*

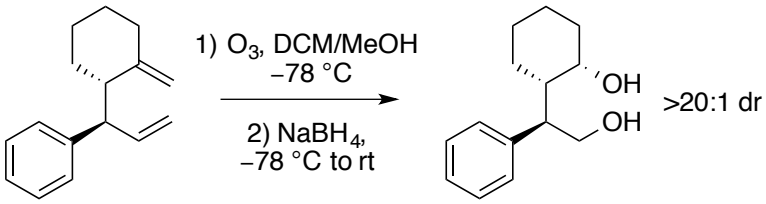
| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 180.053 | MM | 0.7482 | 7.42513 | 1.65393e-1 | 0.95757 |
| 2 | 182.444 | MM | 0.5607 | 767.99182 | 22.82834 | 99.04243 |

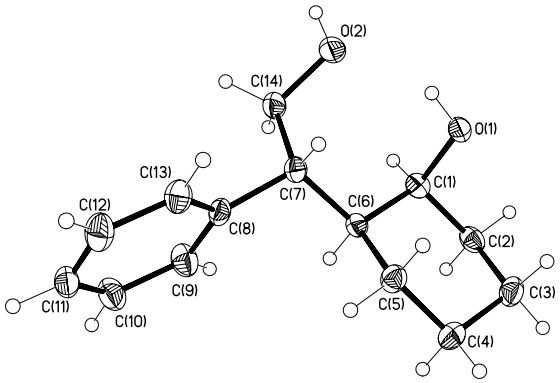


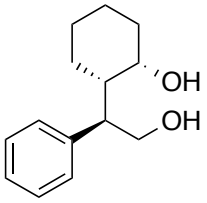
*Co-Injection of Racemic and Enantioenriched Samples*

***Proof of Relative Stereochemistry***

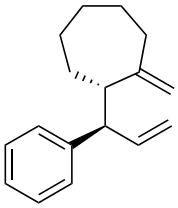
The title compound was subjected to ozonolysis/reduction as shown below. A crystal structure of the resulting diol was obtained, which showed an *anti*-relationship between the phenyl group and the unsubstituted methylene unit of the cyclohexane as shown.






***(1S,2S)*-2-(*(R)*-2-hydroxy-1-phenylethyl)cyclohexan-1-ol (Compound SI-9).**
$^1$H NMR (500 MHz, $CDCl_3$): δ 7.31 (2H, dd (app t), *J* = 8.0 Hz, 8.0 Hz), 7.22 (1H, dddd, app tt), *J* = 7.0 Hz, 7.0 Hz, 1.5 Hz, 1.5 Hz), 7.18-7.19 (2H, m), 4.26 (1H, s (br)), 4.00 (1H, dd, *J* = 11.0 Hz, 7.0 Hz), 3.81 (1H, dd, *J* = 11.0 Hz, 5.5 Hz), 2.77-2.82 (1H, m), 2.23 (2H, s (br)), 1.89-1.93 (1H, s), 1.69-1.75 (1H, m), 1.43-1.65 (4H, m), 1.26-1.35 (1H, m), 1.08-1.17 (2H, m); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 142.6, 128.6, 128.6, 128.3, 128.3, 126.6, 67.0, 65.6, 50.7, 45.0, 33.4, 25.8, 25.6, 20.1; IR (neat): 3342 (m, br), 3083 (w), 3061 (w), 3026 (w), 2927 (s), 2855 (m), 2363 (w), 1601 (w), 1493 (w), 1449 (m), 1074 (w), 1002 (m), 968 (m), 910 (w), 885 (w), 756 (m), 701 (s), 669 (w) cm$^{-1}$; HRMS-(ESI+) for $C_{14}H_{21}O_2$ [M+H]: calculated: 221.1542, found: 221.1550. $[\alpha]^{22}_D$ = + 10.258 (*c* = 1.31, $CHCl_3$). The crude reaction mixture was purified on silica gel (2:1 diethyl ether:pentane) to afford a clear, colorless oil (26.2 mg, 25% yield). $R_f$ = 0.14 (2:1 diethyl ether: pentane, stain in $KMnO_4$).



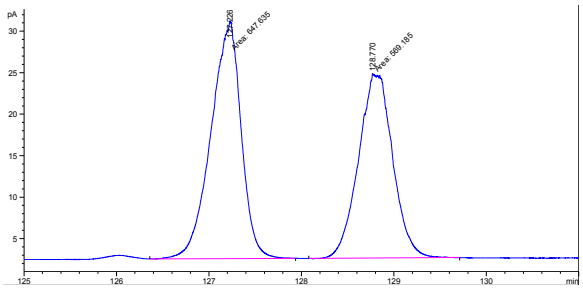
***(S)*-1-methylene-2-(*(R)*-1-phenylallyl)cycloheptane (Compound 39).** The title compound was prepared *via* representative procedure **D** for allyl-allyl coupling with 4,4,5,5-tetramethyl-2-(2-methylenecycloheptyl)-1,3,2-dioxaborolane and cinnamyl chloride with the following modification: the reaction was run for 24 hours. $^1$H NMR (500 MHz, $CDCl_3$): δ 7.30 (2H, dd (app t), *J* = 8.0 Hz, 8.0 Hz), 7.18-7.21 (3H, m), 5.99 (1H, ddd, *J* = 17.0 Hz, 10.0 Hz, 8.0 Hz), 4.94 (1H, ddd (app dt), *J* = 10.0 Hz, 1.0 Hz, 1.0 Hz), 4.91 (1H, d, *J* = 2.0 Hz), 4.84 (1H, ddd, *J* = 17.0 Hz, 2.0 Hz, 1.0 Hz), 4.73 (1H, d, *J* = 1.5 Hz), 3.16 (1H, dd (app t), *J* = 9.0 Hz, 9.0 Hz), 2.63 (1H, ddd (app dt), *J* = 10.5 Hz, 10.5 Hz, 6.0 Hz), 2.23 (1H, ddd (app dt), *J* = 10.0 Hz, 5.0 Hz, 5.0 Hz),1.95 (ddd (app dt)), *J* = 12.0 Hz, 12.0 Hz, 3.5 Hz), 1.81-1.84 (1H, m), 1.70-1.73 (1H, m), 1.51-1.60 (2H, m), 1.29-1.38 (1H, m), 1.15-1.27 (2H, m), 1.02-1.10 (1H, m); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 152.3, 143.5, 141.7, 128.3, 128.3, 128.2, 128.2, 126.1, 114.3, 114.1, 55.5, 51.7, 33.0, 32.4, 31.4, 30.5, 25.9; IR (neat): 3064 (w), 3027 (w), 2976 (w), 2923 (s), 2852 (m), 1638 (w), 1601 (w), 1493 (w), 1450 (m), 1414 (w), 986 (w), 908 (m), 893 (m), 883 (m), 852 (w), 826 (w), 763 (w), 728 (w), 699 (w), 677 (w), 527 (w) cm$^{-1}$; HRMS-(ESI+)

for $C_{17}H_{23}$ [M+H]: calculated: 227.1800, found: 227.1800. $[\alpha]^{22}_D$ = + 11.520 (*c* = 1.16, $CHCl_3$). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (43.4 mg, 96% yield). $R_f$ = 0.61 (pentane, stain in $KMnO_4$).

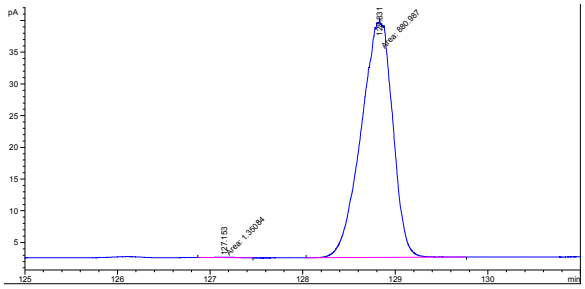
***Analysis of Stereochemistry:***

The enantiomer ratio was determined by GLC analysis of the title compound as compared to the analogous racemic material, prepared using 1,2-bis(diphenylphosphino)benzene as the ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to compounds **3a** and **38**.

*Chiral GLC (β-dex, Supelco, 50 °C for 10 min, ramp 1 °C/min to 140 °C for 90 min, 20 psi) - analysis of title compound.*

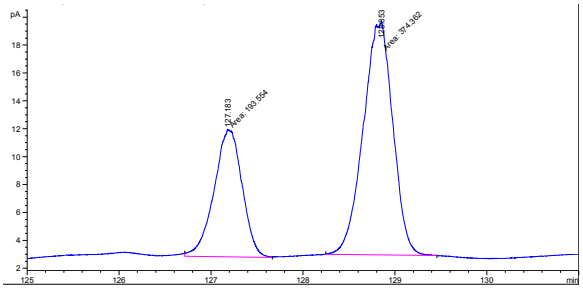



*Racemic Sample*

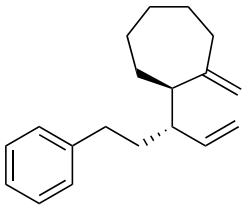



*Enantioenriched Sample*

| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 127.153 | MM | 0.2721 | 1.35084 | 8.27535e-2 | 0.15310 |
| 2 | 128.831 | MM | 0.3903 | 880.98737 | 37.62112 | 99.84690 |




*Co-Injection of Racemic and Enantioenriched Samples*

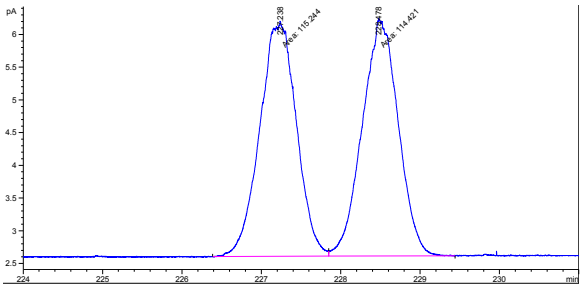


***(R)*-1-methylene-2-(*(S)*-5-phenylpent-1-en-3-yl)cycloheptane (Compound 40).** The title compound was prepared *via* representative procedure **C** for allyl-allyl coupling with 4,4,5,5-tetramethyl-2-(2-methylenecycloheptyl)-1,3,2-dioxaborolane and (E)-(5-chloropent-3-en-1-yl)benzene. The reaction was run with the following modifications: the reaction was run for 24 hours with 1 mol% [(*S,S*)-2,3-bis(tert-butylmethylphosphino)quinoxaline]palladium(II) dichloride as the catalyst and 10 equivalents of CsF. $^{1}$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.27 (2H, dd (app t), $J$ = 7.5 Hz, 7.5 Hz), 7.16-7.19 (3H, m), 5.52 (1H, ddd (app dt), $J$ = 17.0 Hz, 10.5 Hz, 10.5 Hz), 5.05 (1H, dd, $J$ = 10.5 Hz, 2.5 Hz), 4.96 (1H, dd, $J$ = 17.5 Hz, 2.0 Hz), 4.85 (1H, d, $J$ = 2.5 Hz), 4.68 (1H, d, $J$ = 2.0 Hz), 2.62-2.69 (1H, m), 2.47 (1H, ddd, $J$ = 14.0 Hz, 10.5 Hz, 6.5 Hz), 2.30 (1H, ddd (app dt), $J$ = 10.5 Hz, 5.5 Hz, 5.5 Hz), 2.17-2.22 (1H, m), 1.98 (1H, dddd (app tt), $J$ = 9.5 Hz, 9.5 Hz, 4.5 Hz, 4.5 Hz), 1.68-1.91 (6H, m), 1.56-1.65 (1H, m), 1.33-1.40 (1H, m), 1.17-1.23 (3H, m); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 253.2, 143.0, 141.2, 128.4, 128.4, 128.2, 128.2, 125.5, 115.4, 113.6, 50.7, 49.9, 34.5, 34.3, 33.9, 32.4, 31.5, 31.1, 26.3; IR (neat): 3065 (w), 3026 (w), 2975 (w), 2921 (s), 2852 (m), 1637 (w), 1604 (w), 1495 (w), 1452 (w), 1420 (w), 1004 (w), 911 (m), 893 (m), 793 (w), 747 (w), 698 (s) $cm^{-1}$; HRMS-(ESI+) for $C_{19}H_{27}$ [M+H]: calculated: 255.2113, found: 255.2102. $[\alpha]^{22}_{D}$ = + 76.855 ($c$ = 0.93, $CHCl_3$). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (41.7 mg, 82% yield). $R_f$ = 0.75 (pentane, stain in $KMnO_4$).

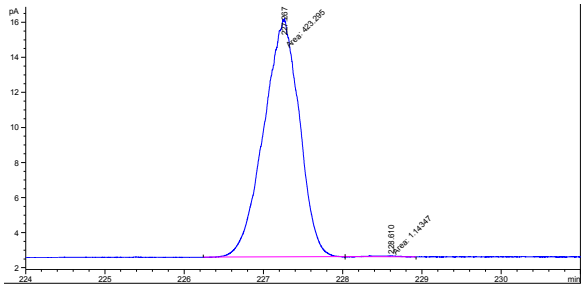
***Analysis of Stereochemistry:***

The enantiomer ratio was determined by GLC analysis of the title compound as compared to the analogous racemic material, prepared using 1,2-bis(diphenylphosphino)benzene as the ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to compounds **3a** and **40**. In related diastereoselective allyl-allyl couplings, *(R,R)*-QuinoxP* is known to give the same absolute stereochemistry as *(R)*-Methoxy(furyl)BIPHEP, therefore the catalyst derived from the *(S,S)*-QuinoxP* ligand should give the opposite enantiomer as with the *(R)*-Methoxy(furyl)BIPHEP.[2]

*Chiral GLC (β-dex, Supelco, 50 °C for 10 min, ramp 1 °C/min to 120 °C for 10 min, then ramp 0.25 °C/min to 160 °C for 10 min, 20 psi) - analysis of title compound.*

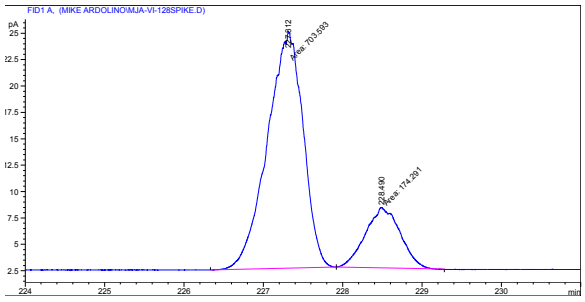



*Racemic Sample*




*Enantioenriched Sample*

| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 227.267 | MM | 0.5191 | 423.29474 | 13.59040 | 99.73059 |
| 2 | 228.610 | MM | 0.3587 | 1.14347 | 5.31343e-2 | 0.26941 |




*Co-Injection of Racemic and Enantioenriched Samples*

***Calorimeter Experiments***

*Representative Procedure for Allyl-Allyl Couplings in Calorimetry Study*

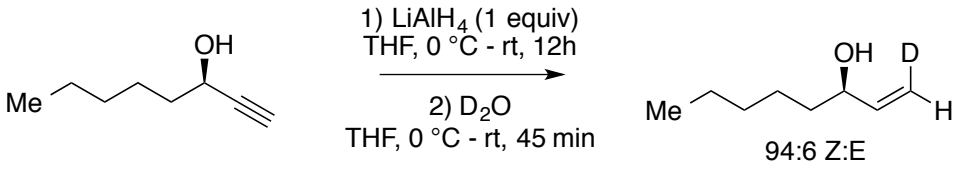
*Sample Vial:* An oven-dried calorimeter vial equipped with a magnetic stir bar was charged successively with *(R)*-**4** (0.6 mg, 0.8 μmol), THF (1.4 mL), allylB(pin) (161.4 mg, 0.96 mmol), and cesium fluoride (6.1 mg, 0.04 mmol) in a dry-box under argon atmosphere.

*Reference Vial:* An oven-dried calorimeter vial equipped with a magnetic stir bar was charged successively with THF (1.4 mL), allylB(pin) (161.4 mg, 0.96 mmol), and cesium fluoride (6.1 mg, 0.04 mmol) in a dry-box under argon atmosphere.

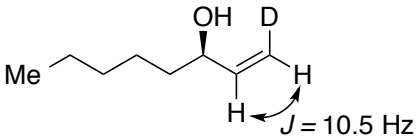
Both vials were sealed with a teflon-lined silicon septum cap and electrical tape and removed from the dry-box. The vials were placed in an Omnical SuperCRC calorimeter with vigorous stirring (450-480 rpm). A solution of *tert*-butyl cinnamyl carbonate (187.4 mg, 0.8 mmol) in dry THF (0.2 mL) was prepared under nitrogen and taken up in a 500 μL syringe which was placed in the sample syringe inlet and pushed through the septum of the sample vial but not injected. A second solution of *tert*-butyl cinnamyl carbonate (187.4 mg, 0.8 mmol) in dry THF (0.2 mL) was prepared under nitrogen and taken up in a 500 μL syringe, which was placed in the reference syringe inlet and pushed through the septum of the reference vial but not injected. The system was then warmed to 60 °C and allowed to stand for 30-60 minutes until thermal equilibrium was achieved. The reaction was then initiated by addition of the contents of both syringes simultaneously and rapidly to each vial. The microsyringes were not removed from the vials, and the top of the calorimeter was covered to fully insulate the system. The reaction was allowed to run without disturbance until the reaction showed no further heat output. After the reaction was complete, the instrument was re-equilibrated and a correction factor to account for the heat flow lag of the instrument was performed. The reaction vials were removed from the calorimeter, cooled, and the reaction mixture was analyzed to confirm full conversion of the reaction vial and no conversion in the reference vial. The data from the calorimeter was then analyzed using Microsoft Excel.

**Deuterium Labeling Studies**

**Preparation of *(R,Z)*-oct-1-en-1-D-3-ol**



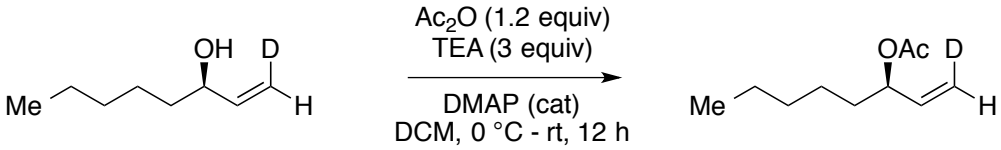

From commercially available *(R)*-1-octyn-3-ol, the literature procedure was followed on a 6.0 mmol scale.[15] The crude reaction mixture was purified on silica gel (4:1 pentane:diethyl ether) to afford a clear, colorless oil (691 mg, 89% yield). The product was contaminated with 25% of deuterated alkyne which was inseparable; however this was removed in the subsequent step. $R_f$ = 0.33 (4:1 pentane:diethyl ether, stain in $KMnO_4$).




***(R,Z)*-oct-1-en-1-D-3-ol (Compound SI-10).**

$^1$H NMR (500 MHz, $CDCl_3$): δ 5.86 (1H, dddd (app ddt), *J* = 11.0Hz, 10.5 Hz, 2.5 Hz, 2.5 Hz), 5.08 (1H, dd, *J* = 10.5 Hz, 1.5 Hz), 4.10 (1H, ddd (app dt), *J* = 11.0 Hz, 7.0 Hz, 7.0 Hz), 1.45-1.56 (2H, m), 1.27-1.37 (6H, m), 0.89 (3H, dd (app t), *J* = 7.0 Hz, 7.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 141.2, 114.2 (t), 73.2, 37.0, 31.7, 25.0, 22.6, 14.0.; IR (neat): 3366 (m, br), 2957 (m), 2931 (s), 2860 (m), 1521 (m), 1058 (w), 1029 (w), 809 (w) 669 (w) $cm^{-1}$; HRMS-(ESI+) for $C_8H_{14}D_1$ [M+H-$H_2O$]: calculated:112.1237, found:112.1241. $[\alpha]^{22}_D$ = – 2.480 (*c* = 1.50, $CHCl_3$).

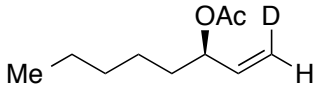
**Preparation of *(R,Z)*-oct-1-en-3-yl-1-D acetate**




An oven-dried round-bottomed flask equipped with a magnetic stir bar was charged with dichloromethane (30.0 mL), *(R,Z)*-oct-1-en-1-d-3-ol (473.2 mg, 3.7 mmol), and 4-dimethylamino pyridine (catalytic) under a nitrogen atmosphere. The solution was cooled to 0 °C and triethylamine (1.58 mL, 11.0 mmol) was added, followed by dropwise addition of acetic anhydride (0.42 mL, 4.4 mmol). The solution was gradually warmed to room temperature and stirred for 12 h. The reaction was concentrated *in vacuo*, and the crude reaction mixture was purified on silica gel (10:1 pentane:diethyl ether) to afford a clear, colorless oil (546 mg, 94% yield). $R_f$ = 0.77 (10:1 pentane:diethyl ether, stain in $KMnO_4$).

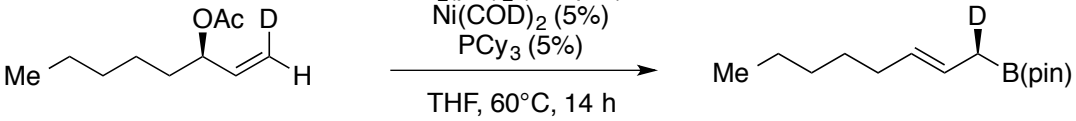
---

[15] Casey, C. P.; Strotman, N. A. *J. Am. Chem. Soc.* **2004**, *126*, 1699.

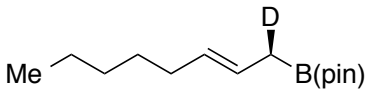



***(R,Z)*-oct-1-en-3-yl-1-D acetate (Compound SI-11).**
$^1$H NMR (500 MHz, $CDCl_3$): δ 5.74-5.78 (1H, m), 5.22 (1H, ddd (app q), *J* = 7.0 Hz, 7.0 Hz, 7.0 Hz), 5.14 (1H, dd, *J* = 10.5 Hz, 1.5 Hz), 2.06 (3H, s), 1.51-1.67 (2H, m), 1.26-1.34 (6H, m), 0.88 (3H, dd (app t), *J* = 7.0 Hz, 7.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 170.4, 136.6, 116.2 (t), 74.8, 34.1, 31.5, 24.7, 22.5, 21.2, 14.0; IR (neat): 2360 (s), 2342 (s), 1771 (m), 1734 (w), 1717 (w), 1699 (w), 1489 (w), 1473 (w), 1456 (w), 1436 (w), 1396 (w), 1387 (w), 1374 (w), 1363 (w), 669 (m), $cm^{-1}$; HRMS-(ESI+) for $C_{10}H_{16}D_1O_2$ [M+H]: calculated:170.1291, found:170.1299. $[\alpha]^{22}_D$ = + 13.936 (*c* = 0.80, $CHCl_3$).

**Preparation of *(S,E)*-4,4,5,5-tetramethyl-2-(oct-2-en-1-yl-1-D)-1,3,2-dioxaborolane**

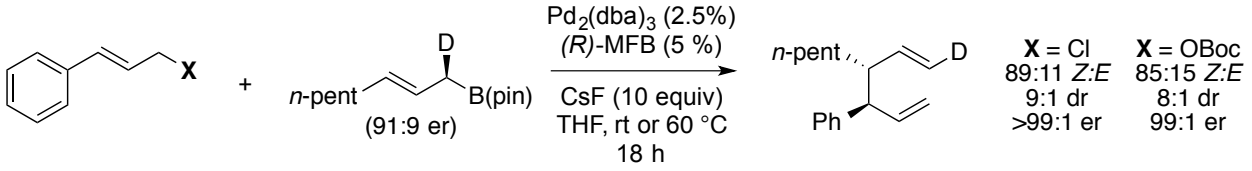



An oven-dried scintillation vial equipped with a magnetic stir bar was charged with $Ni(COD)_2$ (41.3 mg, 0.15 mmol), $PCy_3$ (42.1 mg, 0.15 mmol), bis(pinacolato)diboron (762.6 mg, 3.00 mmol), and tetrahydrofuran (3.0 mL) in a dry-box under an argon atmosphere. The vial was capped and stirred for two minutes, then *(R,Z)*-oct-1-en-3-yl-1-d acetate (510.4 mg, 3.00 mmol) was added. The vial was capped with a teflon cone-lined cap, sealed with electrical tape, removed from the dry-box, heated to 60 °C and allowed to stir for 14 h. The reaction was then cooled and concentrated *in vacuo*, and the crude reaction mixture was purified rapidly on oven-dried silica gel (fast gradient of 40:1-20:1 pentane:diethyl ether) to afford a clear, colorless oil (608 mg, 88% yield). $R_f$ = 0.72 (10:1 pentane:diethyl ether, stain in $KMnO_4$).

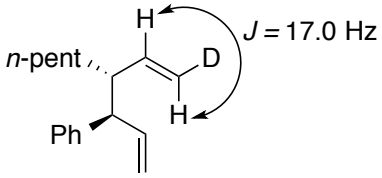



***(S,E)*-4,4,5,5-tetramethyl-2-(oct-2-en-1-yl-1-D)-1,3,2-dioxaborolane (Compound *(S)-E*-7).**
$^1$H NMR (500 MHz, $CDCl_3$): δ 5.35-5.45 (2H, m), 1.96 (2H, ddd (app q), *J* = 7.5 Hz, 7.5 Hz, 7.5 Hz), 1.61 (1H, d (br), *J* = 6.5 Hz), 1.24-1.37 (6H, m), 1.24 (12 H, s), 0.87 (3H, dd (app t), *J* = 7.0 Hz, 7.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 131.1, 128.6, 83.1, 83.1, 32.7, 31.4, 29.3, 24.8, 24.8, 24.8, 24.8, 22.6, 14.1; IR (neat): 2978 (w), 2958 (w), 2926 (m), 2856 (w), 1466 (w), 1370 (m), 1347 (s), 1320 (s), 1272 (w), 1215 (w), 1145 (s), 1110 (w), 968 (m), 862 (w), 672 (w) $cm^{-1}$; HRMS-(ESI+) for $C_{14}H_{27}D_1B_1O_2$ [M+H]: calculated: 240.2245, found: 240.2241. $[\alpha]^{22}_D$ = + 0.658 (*c* = 0.73, $CHCl_3$).

**Allyl-Allyl Coupling to give *((3R,4R)*-4-*((E)*-vinyl-2-D)non-1-en-3-yl)benzene (Compound *(R,R)-E*-8).**




An oven-dried two-dram vial equipped with a magnetic stir bar was charged successively with with $Pd_2(dba)_3$ (2.29 mg, 2.5 µmol), *(R)*-(+)-2,2'-bis(di-2-furanylphosphino)-6,6'-dimethoxy-1,1'-biphenyl [*(R)*-MFB] (2.71 mg, 5.0 µmol), and THF (0.2 mL) in a dry-box under an argon atmosphere. The vial was capped and allowed to stir for five minutes, then cinnamyl chloride (15.2 mg, 0.1 mmol) or *tert*-butyl cinnamyl carbonate (23.4 mg, 0.1 mmol) was added, followed by *(S,E)*-4,4,5,5-tetramethyl-2-(oct-2-en-1-yl-1-d)-1,3,2-dioxaborolane (28.6 mg, 0.12 mmol) and cesium fluoride (151.9 mg, 1.0 mmol). The vial was sealed, removed from the dry-box, and heated to room temperature (X=Cl) or 60 °C (X=OBoc) and stirred for 18 h. After this time, the reaction mixture was diluted with diethyl ether, filtered through a plug of silica gel and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (19.2 mg, 85% yield when X=Cl, 10.8 mg, 48% yield when X=OBoc). $R_f$ = 0.43 (pentane, stain in $KMnO_4$).

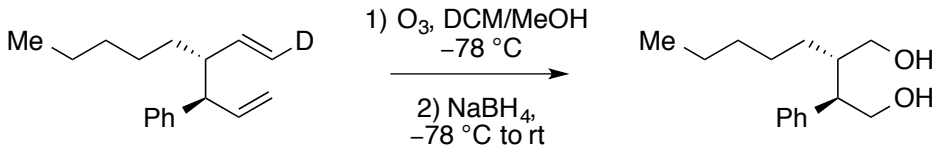



***((3R,4R)*-4-*((E)*-vinyl-2-D)non-1-en-3-yl)benzene (Compound *(R,R)-E*-8).**

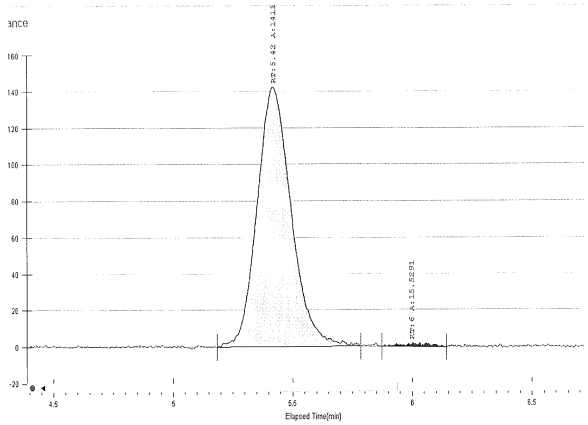
$^1$H NMR (500 MHz, $CDCl_3$): δ 7.30 (2H, dd (app t), *J* = 7.5 Hz, 7.5 Hz), 7.17-7.22 (3H, m), 5.99 (1H, ddd, *J* = 17.0 Hz, 10.0 Hz, 8.0 Hz), 5.56 (1H, dd, *J* = 17.0 Hz, 8.5 Hz), 5.02 (1H, dd, *J* = 10.0 Hz, 2.5 Hz), 4.94 (1H, ddd, *J* = 17.0 Hz, 1.5 Hz, 1.5 Hz), 4.94 (1H, dd, *J* = 17.0 Hz, 1.5 Hz), 3.18 (1H, dd (app t), *J* = 8.5 Hz, 8.5 Hz), 2.34 (1H, dddd (app dtd), *J* = 8.5 Hz, 8.5 Hz, 8.5 Hz, 2.5 Hz), 1.09-1.32 (8H, m), 0.83 (3H, dd (app t), *J* = 7.0 Hz, 7.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 143.5, 140.9, 140.7, 128.3, 128.3, 128.1, 128.1, 126.1, 115.1, 55.0, 49.2, 32.3, 31.7, 26.9, 26.7, 22.6, 14.0; IR (neat): 3080 (w), 3063 (w), 3028 (w), 2956 (m), 2928 (s), 2857 (m), 1637 (w), 1620 (w), 1601 (w), 1494 (w), 1453 (w), 1378 (w), 982 (m), 913 (m), 806 (w), 757 (w) 700 (s), 678 (w) $cm^{-1}$; HRMS-(ESI+) for $C_{17}H_{24}D_1$ [M+H]: calculated: 230.2019, found: 230.2013. $[\alpha]^{22}_D$ = + 32.954 (*c* = 1.46, $CHCl_3$).

***Analysis of Stereochemistry***

The title compound was subjected to ozonolysis and reduction to afford the 1,4-diol for SFC analysis as depicted below. The analogous racemic material was prepared *via* the same rout, using 1,2-bis(diphenylphosphino)benzene as the ligand in the allyl-allyl coupling reaction. the absolute stereochemistry was assigned by analogy to compound **31**.

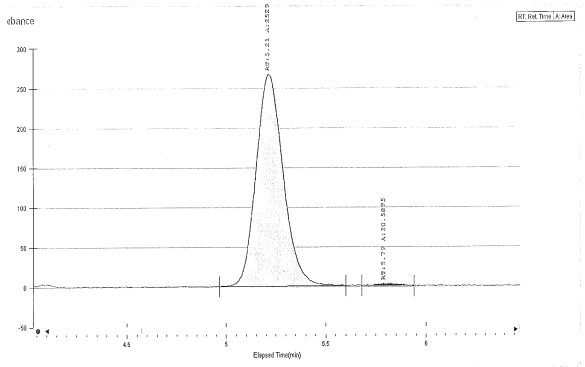



*Chiral SFC (OJ-H, Chiralpak, 3 mL/min, 5.0% i-PrOH, 100 bar, 35 °C) - analysis of title compound.*



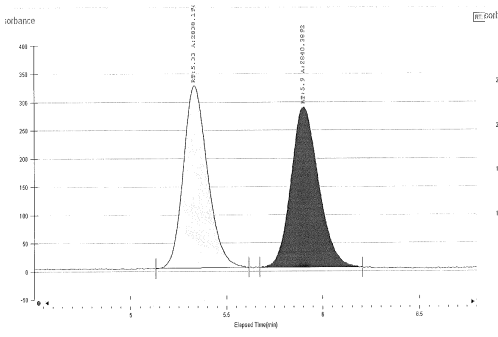
*Enantioenriched Sample (X=OBoc)*

| Peak No | % Area | Area | RT (min) |
|---|---|---|---|
| 1 | 98.9119 | 1411.6026 | 5.42 |
| 2 | 1.0881 | 15.5291 | 6 |
| Total: | 100 | 1427.1317 | |

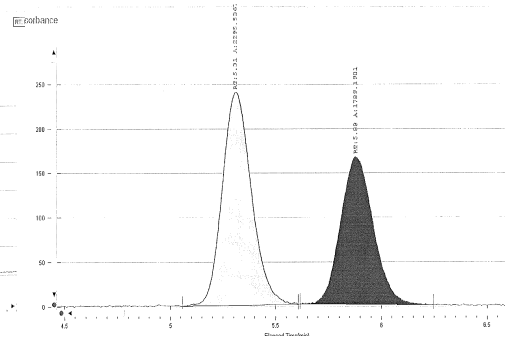


*Enantioenriched Sample (X=Cl)*

| Peak No | % Area | Area | RT (min) |
|---|---|---|---|
| 1 | 99.1925 | 2529.1009 | 5.21 |
| 2 | 0.8075 | 20.5895 | 5.79 |
| Total: | 100 | 2549.6904 | |

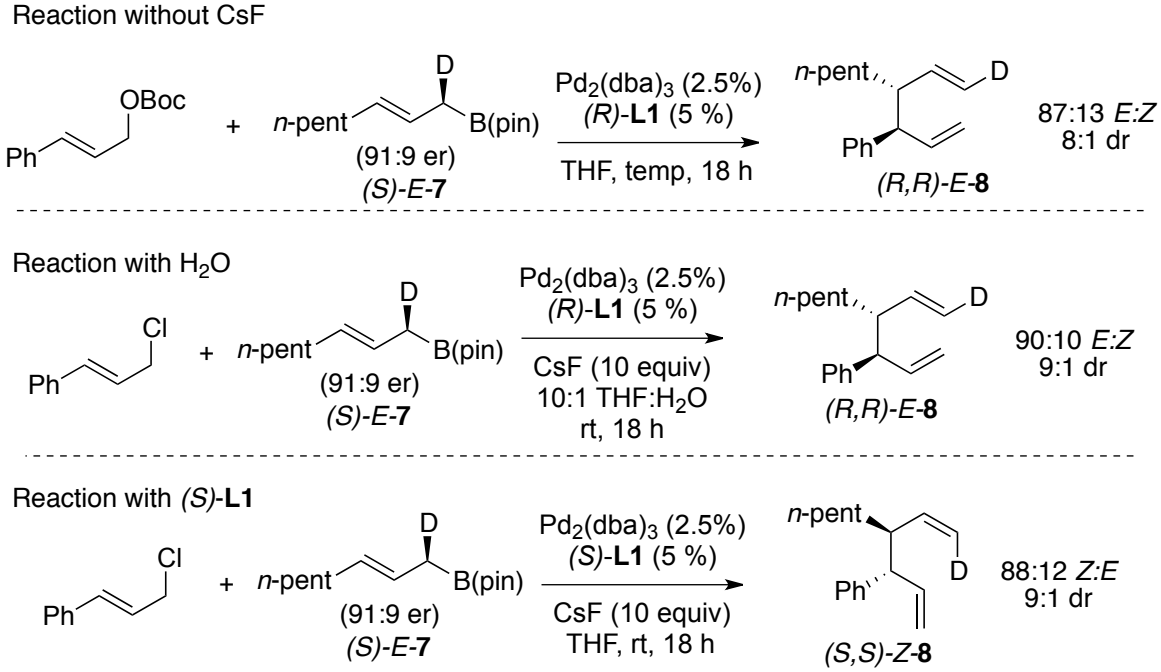


*Racemic Sample*

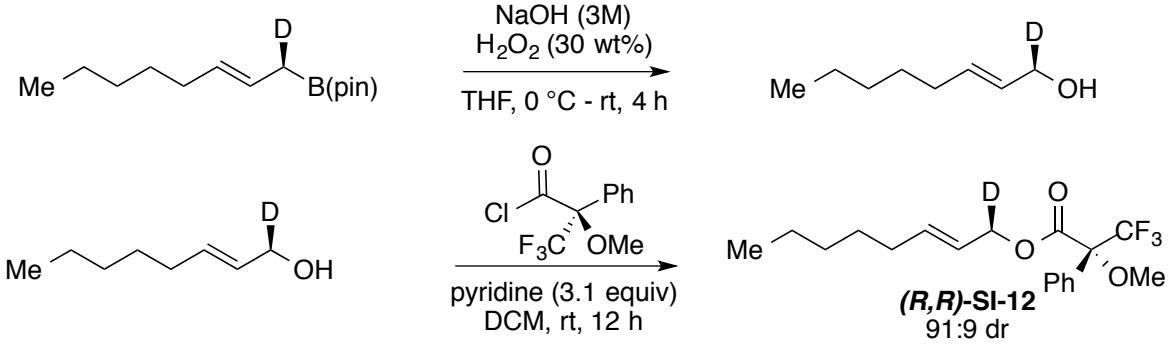


*Co-Injection of Racemic and Enantioenriched Samples*

***Additional Labeling Study Results***




***Determination of Absolute Configuration of Labeled Allylboron with Mosher's Ester Analysis***



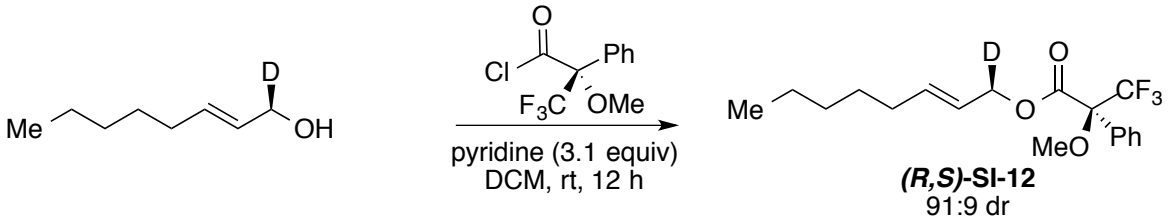

**Preparation of *(R,E)*-oct-2-en-1-yl-1-D *(R)*-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (Compound *(R,R)*-SI-12).**

To a scintillation vial with a magnetic stir-bar was added *(S,E)*-4,4,5,5-tetramethyl-2-(oct-2-en-1-yl-1-d)-1,3,2-dioxaborolane (40.0 mg, 0.17 mmol) and THF (1.5 mL). The solution was cooled to 0 °C, and 1.0 mL of aqueous NaOH (3M) was added followed by dropwise addition of 0.8 mL of hydrogen peroxide (30 wt% solution in $H_2O$). The solution was stirred at 0 °C for 15 minutes and then gradually warmed to room temperature for an additional 3.5 hours. The solution was then re-cooled to 0 °C and quenched with dropwise addition of saturated aqueous sodium thiosulfate. The solution was poured into a separatory funnel and extracted 3

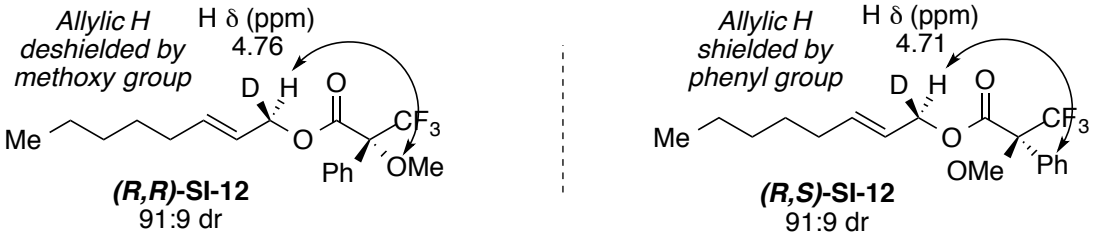
times with diethyl ether. The organics were combined, dried over magnesium sulfate and concentrated *in vacuo*. the crude reaction mixture was purified on silica gel (3:1 pentane:diethyl ether) to afford the corresponding allylic alcohol as a clear, colorless oil (13.2 mg, 61% yield). $R_f$ = 0.32 (3:1 pentane:diethyl ether, stain in $KMnO_4$).

The Mosher's ester (*R,R*-Si-X) was prepared using the literature procedure[16] with *(S)*-(+)-α-methoxy-α-trifluoromethylphenylacetyl chloride (*(S)*-MTPA-Cl). The crude reaction mixture was purified on silica gel (20:1 pentane:diethyl ether) to yield a clear, pale yellow oil (20.4 mg, 60% yield).

**Preparation of *(R,E)*-oct-2-en-1-yl-1-D *(S)*-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (Compound *(R,S)*-SI-12*).***



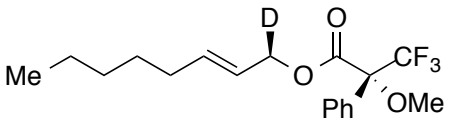

The opposite diasteromer was prepared using the same procedure as described above with *(R)*-(–)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (*(R)*-MTPA-Cl). The crude reaction mixture was purified on silica gel (20:1 pentane:diethyl ether) to yield a clear, pale yellow oil (39.8 mg, 82% yield).




The absolute configuration of the resulting Moshers' esters was determined as described in the literature.[17] The literature procedure relies on the assumption that the preferred conformation for the allylic esters is as shown above. In *(R,R)*-SI-12, the allylic proton is deshielded by the methoxy group resulting in a downfield shift to 4.76 ppm, whereas in *(R,S)*-SI-12, the allylic proton is shielded by the phenyl group, resulting in an upfield shift to 4.71 ppm.

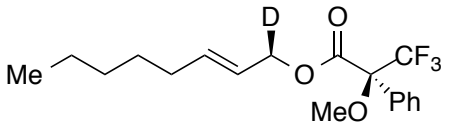
[16] Hoye, T. R.; Jeffry, C. S.; Shao, F. *Nature Protocols*, **2007**, *2*, 2451.

[17] Canon, J. S.; Olson, A. C.; Overman, L. E.; Solomon, N. S. *J. Org. Chem.* **2012**, *77*, 1961.




***(R,E)*-oct-2-en-1-yl-1-D-*(R)*-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (Compound *(R,R)*-SI-12*)*.**

$^1$H NMR (500 MHz, $CDCl_3$): δ 7.52-7.53 (2H, m), 7.37-7.41 (3H, m), 5.85 (1H, ddd (app dt), *J* = 15.0 Hz, 7.0 Hz, 7.0 Hz), 5.58 (1H, dd, *J* = 15.0 Hz, 6.0 Hz), 4.76 (1H, d, *J* = 6.0 Hz), 3.56 (3H, s), 2.05 (2H, ddd (app q), *J* = 7.0 Hz, 7.0 Hz, 7.0 Hz), 1.37 (2H, dddd (app p), *J* = 7.0 Hz, 7.0 Hz, 7.0 Hz, 7.0 Hz), 1.24-1.33 (4H, m), 0.88 (3H, dd (app t), *J* = 7.0 Hz, 7.0 Hz).; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 166.3, 138.7, 132.4, 129.5, 129.5, 128.3, 128.3, 127.3, 124.4, 122.3, 84.7, 66.7 (t), 55.4, 32.2, 31.2, 28.4, 22.5, 14.0; IR (neat): 2957 (w), 2930 (m), 2857 (w), 1747 (s), 1497 (w), 1452 (w), 1269 (m), 1244 (m), 1169 (s), 1123 (m), 1082 (w), 1023 (w), 996 (m), 970 (w), 919 (w), 765 (w), 716 (m), 697 (w), 646 (w) $cm^{-1}$; HRMS-(ESI+) for $C_{18}H_{26}D_1F_3N_1O_3$ [M+$NH_4$]: calculated: 363.2006, found: 363.1992. $[\alpha]^{22}_D$ = + 52.150 (*c* = 1.02, $CHCl_3$).




***(R,E)*-oct-2-en-1-yl-1-D-*(S)*-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (Compound *(R,S)*-SI-12*)*.**

$^1$H NMR (500 MHz, $CDCl_3$): δ 7.51-7.53 (2H, m), 7.37-7.41 (3H, m), 5.84 (1H, dddd (app dtd), *J* = 15.5 Hz, 7.0 Hz, 7.0 Hz, 1.0 Hz), 5.58 (1H, dd, *J* = 15.5 Hz, 6.5 Hz), 4.71 (1H, d, *J* = 6.5 Hz), 3.56 (3H, s), 2.05 (2H, ddd (app q), *J* = 7.0 Hz, 7.0 Hz, 7.0 Hz), 1.37 (2H, dddd (app p), *J* = 7.0 Hz, 7.0 Hz, 7.0 Hz, 7.0 Hz), 1.23-1.32 (4H, m), 0.88 (3H, dd (app t), *J* = 7.0 Hz, 7.0 Hz).; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 166.3, 138.7, 132.4, 129.5, 129.5, 128.3, 128.3, 127.3, 124.5, 122.3, 84.7, 66.7 (t), 55.5, 32.2, 31.2, 28.4, 22.5, 14.0; IR (neat): 2956 (w), 2929 (m), 2856 (w), 1746 (s), 1452 (w), 1269 (m), 1243 (m), 1167 (s), 1122 (m), 1081 (w), 1022 (w), 995 (m), 969 (w), 919 (m), 765 (w), 716 (w), 697 (m), 646 (w) $cm^{-1}$; HRMS-(ESI+) for $C_{18}H_{26}D_1F_3N_1O_3$ [M+$NH_4$]: calculated: 363.2006, found: 363.1990. $[\alpha]^{22}_D$ = – 53.038 (*c* = 1.99, $CHCl_3$).

### *Computational Details*

All calculations were performed using Gaussian 09 with all geometry optimizations, energies and frequencies were calculated at the DFT level utilizing the B3LYP hybrid functional.[18, 19] The 6-31G** basis set was used for the elements C, H, P, and O in conjunction with the LANL2DZ relativistic pseudopotential for Pd. The two oxygens and carbonyl carbon of the acetate group were augmented with diffuse functions. All free energies were calculated at 333.15 K. The PCM model was used to estimate the effect of solvation (THF).[20] The frequency calculations for transition states demonstrated one imaginary frequency each, and were found to connected with the correct ground states through IRC calculations. NBO analysis was carried out with Gaussian NBO version 3.1.[21] The three-dimensional structures presented in Figure 1 were visualized utilizing CYLview.[22]

### *Additional Computational Information:*

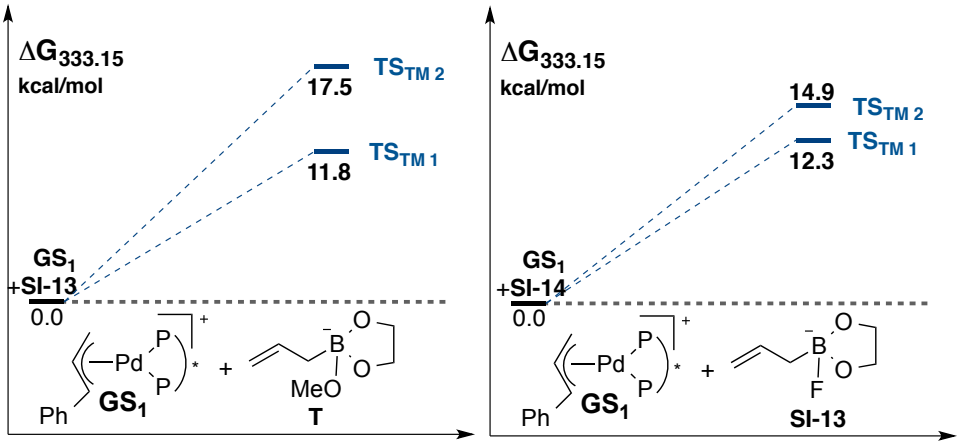



**Figure SI-1:** Calculated transition state energies for transmetallation with methoxide and fluoride.

---

[18] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

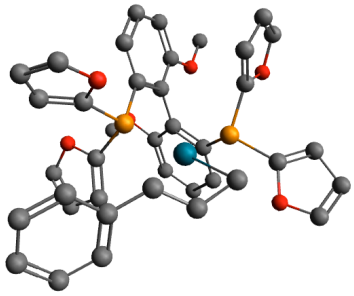
[19] (a) A. D. Becke*, Phys. Rev. A* 1988, *38*, 3098; (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* 1988, *37*, 785.

[20] (a) S. Miertus, E. Scrocco, J. Tomassi, *Chem. Phys.* **1981**, *55*, 117. (b) V. Barone, M. Cossi, J. Tomassi, *Chem. Phys.* **1997**, *107*, 3210.

[21] NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold.

[22] CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org).

***Structures and Energies from Figure 3***



**$GS_1$**

---

Cartesian coordinates (Angstroms):

---

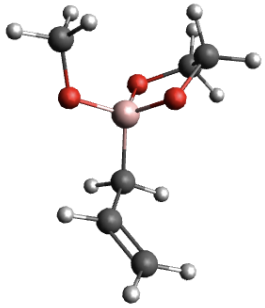
Pd -0.829 1.473 -0.366
C -1.185 3.611 -0.728
P 1.508 1.559 -0.008
O 3.898 1.080 -1.279
O 1.991 -3.267 1.833
O 1.350 3.876 1.431
C 2.544 1.253 -1.448
C 2.239 1.223 -2.783
H 1.253 1.330 -3.212
C 3.469 1.015 -3.478
H 3.612 0.933 -4.546
C 4.436 0.935 -2.521
H 5.505 0.786 -2.554
C 1.912 0.327 1.305
C 1.877 -1.057 1.051
C 2.034 -1.946 2.143
C 2.216 -1.461 3.443
H 2.337 -2.142 4.275
C 2.246 -0.086 3.666
H 2.393 0.289 4.675
C 2.093 0.809 2.612
H 2.112 1.874 2.809
C 2.156 -4.223 2.878
H 3.129 -4.116 3.370
H 2.100 -5.200 2.397
H 1.358 -4.140 3.625
C 2.163 3.136 0.601
C 2.029 5.016 1.745
H 1.515 5.703 2.400
C 3.248 5.029 1.137
H 3.992 5.809 1.205
C 3.338 3.810 0.396
H 4.168 3.470 -0.205
P -0.984 -0.923 -0.418
O -1.417 -3.085 1.222
O 4.063 -2.078 -0.155
O -2.468 -0.756 -2.688
C -1.418 -1.711 1.142
C -1.788 -1.180 2.349
H -1.873 -0.129 2.581
C -2.030 -2.284 3.224
H -2.339 -2.244 4.258
C -1.790 -3.408 2.490
H -1.838 -4.463 2.711
C 0.549 -1.754 -1.033
C 1.759 -1.654 -0.319
C 2.930 -2.208 -0.893
C 2.887 -2.838 -2.142
H 3.783 -3.262 -2.578
C 1.678 -2.924 -2.827
H 1.645 -3.419 -3.793
C 0.515 -2.386 -2.286
H -0.415 -2.465 -2.836
C 5.278 -2.624 -0.663
H 5.202 -3.708 -0.807
H 6.036 -2.413 0.092
H 5.565 -2.150 -1.608
C -2.282 -1.501 -1.544
C -3.455 -1.365 -3.405
H -3.713 -0.896 -4.342
C -3.909 -2.471 -2.750
H -4.689 -3.140 -3.082
C -3.147 -2.562 -1.543
H -3.221 -3.319 -0.777
C -2.343 3.129 -0.087
H -1.107 3.583 -1.814
H -0.559 4.337 -0.223
C -3.104 2.091 -0.653
H -2.523 3.424 0.944
C -4.242 1.429 -0.000
C -5.145 0.699 -0.794
C -4.489 1.517 1.385
C -5.605 0.905 1.946
C -6.262 0.085 -0.230
C -6.498 0.187 1.142
H -6.947 -0.472 -0.862
H -7.367 -0.290 1.585
H -4.969 0.617 -1.863
H -3.805 2.059 2.030
H -5.780 0.984 3.015
H -3.041 1.954 -1.732

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 12.0054 | 19.3890 | 28.3761 |
| Red. masses -- | 6.2586 | 5.8317 | 5.9247 |

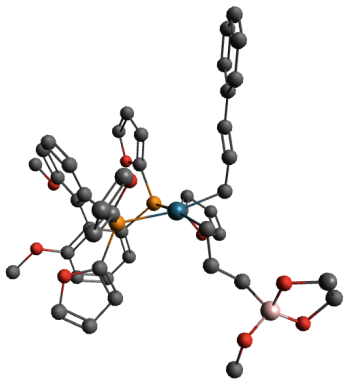
ZERO-POINT CORRECTION= 0.626388 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.681127
Thermal correction to Enthalpy= 0.682182
Thermal correction to Gibbs Free Energy= 0.528552
Sum of electronic and zero-point Energies= -2765.974536
Sum of electronic and thermal Energies= -2765.919798
Sum of electronic and thermal Enthalpies= -2765.918743
Sum of electronic and thermal Free Energies= -2766.072373

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000020 | 0.000450 | YES |
| RMS FORCE | 0.000003 | 0.000300 | YES |

---



**T**



**$TS_{TM\ 1}$**

---

Cartesian coordinates (Angstroms):

---

C -2.514 0.202 -0.135
C -3.417 -0.550 0.509
H -2.609 1.287 -0.052
H -4.217 -0.111 1.101
B 0.132 0.154 -0.278
C -1.337 -0.268 -0.919
H -1.373 0.181 -1.925
H -1.382 -1.358 -1.052
O 0.366 -0.517 1.043
O 0.144 1.623 -0.196
O 1.261 -0.339 -1.136
H -3.380 -1.638 0.475
C 1.871 -1.423 -0.486
C 1.610 -1.172 1.008
C 1.280 2.219 0.366
H 2.417 -0.544 1.433
H 1.585 -2.105 1.595
H 2.945 -1.477 -0.725
H 1.422 -2.390 -0.788
H 1.174 3.313 0.331
H 2.205 1.954 -0.173
H 1.429 1.933 1.420

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 43.7482 | 81.9629 | 93.6789 |
| Red. masses -- | 3.2096 | 2.6852 | 1.7032 |

ZERO-POINT CORRECTION= 0.180618 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.194238
Thermal correction to Enthalpy= 0.195293
Thermal correction to Gibbs Free Energy= 0.137067
Sum of electronic and zero-point Energies= -486.400757
Sum of electronic and thermal Energies= -486.387136
Sum of electronic and thermal Enthalpies= -486.386081
Sum of electronic and thermal Free Energies= -486.444307

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000014 | 0.000450 | YES |
| RMS FORCE | 0.000003 | 0.000300 | YES |

---

---

Cartesian coordinates (Angstroms):

---

Pd -0.864 0.245 0.197
P 0.391 -1.114 -1.446
O 1.264 -3.656 -2.081
O 5.248 -0.155 0.102
O -0.846 0.168 -3.507
C 0.540 -2.897 -1.189
C 0.025 -3.711 -0.214
H -0.567 -3.392 0.631
C 0.449 -5.041 -0.520
H 0.230 -5.942 0.034
C 1.195 -4.947 -1.657
H 1.716 -5.670 -2.266
C 2.112 -0.478 -1.714
C 3.089 -0.608 -0.709
C 4.350 0.007 -0.906
C 4.620 0.731 -2.071
H 5.584 1.200 -2.221
C 3.635 0.848 -3.051
H 3.847 1.406 -3.958
C 2.389 0.254 -2.880
H 1.638 0.360 -3.653
C 6.538 0.435 -0.030
H 7.076 0.036 -0.898
H 7.079 0.175 0.880
H 6.471 1.526 -0.114
C -0.365 -1.058 -3.099
C -1.430 -0.013 -4.726
H -1.850 0.872 -5.180
C -1.346 -1.318 -5.106
H -1.726 -1.748 -6.021
C -0.654 -1.998 -4.053
H -0.395 -3.044 -4.012
P 1.084 0.522 1.569
O 3.388 2.020 1.825
O 4.286 -3.017 -0.494
O -0.343 0.202 3.872
C 2.193 1.885 1.153
C 2.058 2.906 0.250
H 1.218 3.057 -0.412
C 3.230 3.715 0.367

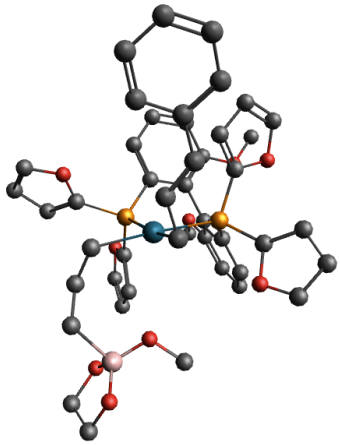
H 3.469 4.607 -0.194
C 3.998 3.133 1.332
H 4.956 3.375 1.766
C 2.126 -1.009 1.636
C 2.895 -1.426 0.532
C 3.569 -2.670 0.608
C 3.479 -3.468 1.753
H 3.998 -4.417 1.809
C 2.708 -3.036 2.830
H 2.637 -3.656 3.720
C 2.031 -1.822 2.778
H 1.435 -1.511 3.627
C 4.983 -4.260 -0.493
H 5.739 -4.296 0.299
H 5.475 -4.324 -1.464
H 4.294 -5.104 -0.379
C 0.721 0.877 3.316
C -0.465 0.631 5.159
H -1.264 0.183 5.729
C 0.484 1.566 5.442
H 0.621 2.080 6.382
C 1.256 1.725 4.248
H 2.106 2.374 4.101
C -1.936 1.724 1.308
C -2.071 2.851 0.385
C -1.369 4.010 0.461
H -2.788 2.728 -0.426
C -1.440 5.154 -0.449
C -0.697 6.313 -0.144
C -2.216 5.168 -1.629
C -2.247 6.289 -2.453
C -0.727 7.435 -0.971
C -1.504 7.431 -2.132
H -0.144 8.314 -0.709
H -1.531 8.302 -2.779
H -0.090 6.327 0.758
H -2.798 4.294 -1.905
H -2.853 6.272 -3.355
H -0.673 4.127 1.292
H -2.872 1.219 1.548
H -1.392 1.976 2.218
C -3.098 -1.355 0.111
C -2.834 -0.231 -0.713
H -2.610 -2.286 -0.180
H -3.489 0.627 -0.580
B -5.652 -2.158 0.478
C -3.988 -1.432 1.192
H -4.347 -0.492 1.610
H -3.783 -2.197 1.942
O -6.521 -2.120 1.634
O -5.359 -3.439 -0.065
O -6.139 -1.205 -0.484
H -2.582 -0.430 -1.752
C -7.347 -0.645 0.027
C -7.283 -0.921 1.537
C -5.037 -4.508 0.801
H -8.218 -1.141 -0.427
H -7.400 0.425 -0.205
H -8.270 -1.066 1.990
H -6.776 -0.099 2.067
H -4.066 -4.359 1.298
H -4.970 -5.425 0.205
H -5.800 -4.653 1.577

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -204.1962 | 8.9821 | 12.0045 |
| Red. masses -- | 7.8750 | 6.3836 | 6.1373 |

ZERO-POINT CORRECTION= 0.808419 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.878320
Thermal correction to Enthalpy= 0.879375
Thermal correction to Gibbs Free Energy= 0.688344
Sum of electronic and zero-point Energies= -3252.377796
Sum of electronic and thermal Energies= -3252.307895
Sum of electronic and thermal Enthalpies= -3252.306840
Sum of electronic and thermal Free Energies= -3252.497871

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000003 | 0.000450 | YES |
| RMS FORCE | 0.000001 | 0.000300 | YES |

---



**$TS_{TM\ 2}$**

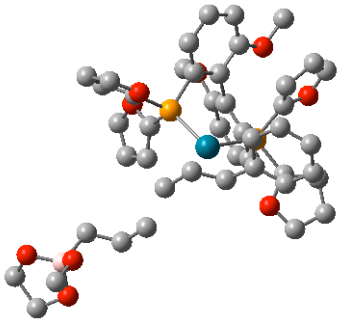
---
Cartesian coordinates (Angstroms):
---
Pd 0.206 -1.227 0.078
P -0.854 0.408 1.605
O -3.208 1.816 1.961
O 0.791 4.898 -0.423
O 0.163 -0.728 3.880
C -2.584 0.796 1.274
C -3.480 0.177 0.444
H -3.270 -0.663 -0.205
C -4.729 0.850 0.625
H -5.665 0.630 0.134
C -4.505 1.830 1.547
H -5.133 2.583 1.998
C 0.049 2.026 1.684
C 0.039 2.917 0.594
C 0.846 4.080 0.662
C 1.640 4.339 1.784

H 2.255 5.228 1.834
C 1.637 3.439 2.848
H 2.252 3.640 3.720
C 0.855 2.289 2.804
H 0.875 1.602 3.640
C 1.575 6.086 -0.423
H 1.291 6.757 0.397
H 1.372 6.576 -1.376
H 2.645 5.861 -0.353
C -0.950 -0.111 3.349
C -0.140 -1.073 5.164
H 0.646 -1.566 5.716
C -1.414 -0.703 5.469
H -1.920 -0.854 6.411
C -1.941 -0.078 4.294
H -2.924 0.351 4.168
P 0.763 0.525 -1.475
O 2.615 2.544 -1.832
O -2.140 4.481 0.265
O 0.243 -0.927 -3.737
C 2.293 1.416 -1.110
C 3.301 1.136 -0.226
H 3.324 0.302 0.460
C 4.297 2.144 -0.406
H 5.233 2.242 0.125
C 3.829 2.968 -1.386
H 4.220 3.856 -1.860
C -0.569 1.805 -1.636
C -0.828 2.739 -0.615
C -1.944 3.603 -0.755
C -2.772 3.531 -1.878
H -3.623 4.192 -1.983
C -2.498 2.594 -2.873
H -3.141 2.537 -3.746
C -1.412 1.734 -2.758
H -1.223 1.010 -3.540
C -3.242 5.378 0.192
H -3.167 6.039 -0.679
H -3.199 5.977 1.103
H -4.196 4.839 0.158
C 1.084 0.019 -3.196
C 0.690 -1.194 -4.996
H 0.120 -1.923 -5.551
C 1.798 -0.453 -5.275
H 2.365 -0.464 -6.195
C 2.055 0.335 -4.109
H 2.851 1.050 -3.968
C 1.347 -2.649 -1.046
C 2.557 -2.890 -0.257
C 3.795 -2.423 -0.557
H 2.432 -3.487 0.645
C 5.023 -2.614 0.217
C 6.246 -2.156 -0.317
C 5.060 -3.235 1.485
C 6.260 -3.395 2.172
C 7.447 -2.316 0.373
C 7.463 -2.938 1.623
H 8.373 -1.953 -0.068
H 8.397 -3.064 2.164
H 6.245 -1.672 -1.291
H 4.141 -3.591 1.939
H 6.258 -3.877 3.147
H 3.913 -1.847 -1.474
H 0.677 -3.507 -1.110
H 1.555 -2.252 -2.038
C -1.727 -3.169 1.384
C -0.318 -2.961 1.353
H -2.309 -2.464 1.981
H 0.090 -2.532 2.269
B -3.517 -3.466 -0.775
C -2.449 -4.170 0.733
H -3.359 -4.491 1.235
H -1.876 -4.978 0.279
O -3.918 -4.674 -1.441
O -2.623 -2.599 -1.453
O -4.686 -2.860 -0.198
H 0.250 -3.815 0.992
C -5.682 -3.867 -0.116
C -5.311 -4.866 -1.232
C -3.031 -2.210 -2.758
H -6.677 -3.427 -0.248
H -5.661 -4.357 0.872
H -5.861 -4.648 -2.161
H -5.524 -5.905 -0.953
H -3.949 -1.604 -2.730
H -3.221 -3.083 -3.396
H -2.232 -1.613 -3.203

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -303.4273 | 11.7917 | 14.8387 |
| Red. masses -- | 8.1807 | 6.2800 | 5.6666 |

ZERO-POINT CORRECTION= 0.809099 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.878623
Thermal correction to Enthalpy= 0.879678
Thermal correction to Gibbs Free Energy= 0.692415
Sum of electronic and zero-point Energies= -3252.372185
Sum of electronic and thermal Energies= -3252.302661
Sum of electronic and thermal Enthalpies= -3252.301606
Sum of electronic and thermal Free Energies= -3252.488870

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000004 | 0.000450 | YES |
| RMS FORCE | 0.000001 | 0.000300 | YES |



**TS$_{O.S.}$-*linear***

---
Cartesian coordinates (Angstroms):
---
Pd -0.071  0.709 -0.190
P  0.383 -1.553 -0.834
O  0.629 -4.141  0.102
O  5.538 -1.304 -0.247
O -1.109 -1.244 -3.090
C  0.187 -2.869  0.387
C -0.406 -2.858  1.622
H -0.837 -1.996  2.109
C -0.326 -4.192  2.129
H -0.690 -4.555  3.079
C  0.309 -4.923  1.170
H  0.595 -5.961  1.094
C  2.124 -1.645 -1.457
C  3.220 -1.502 -0.584
C  4.520 -1.422 -1.141
C  4.714 -1.464 -2.526
H  5.709 -1.396 -2.948
C  3.612 -1.597 -3.370
H  3.762 -1.634 -4.444
C  2.326 -1.687 -2.847
H  1.483 -1.790 -3.519
C  6.873 -1.224 -0.736
H  7.147 -2.120 -1.305
H  7.509 -1.150  0.147
H  7.018 -0.336 -1.362
C -0.625 -2.186 -2.208
C -1.866 -1.903 -4.010
H -2.316 -1.290 -4.776
C -1.887 -3.239 -3.742
H -2.412 -3.999 -4.302
C -1.081 -3.425 -2.576
H -0.861 -4.354 -2.072
P  2.027  1.127  0.868
O  4.640  1.831  0.335
O  3.874 -3.724  0.798
O  0.777  2.423  2.909
C  3.357  1.782 -0.163
C  3.334  2.316 -1.424
H  2.462  2.420 -2.052
C  4.674  2.714 -1.725
H  5.033  3.173 -2.635
C  5.419  2.395 -0.628
H  6.465  2.500 -0.385
C  2.707 -0.392  1.679
C  3.107 -1.506  0.913
C  3.492 -2.688  1.593
C  3.468 -2.756  2.990
H  3.761 -3.662  3.505
C  3.063 -1.643  3.724
H  3.048 -1.694  4.809
C  2.684 -0.469  3.081
H  2.375  0.385  3.671
C  4.267 -4.948  1.412
H  5.141 -4.812  2.059
H  4.527 -5.620  0.593
H  3.448 -5.385  1.994
C  1.958  2.359  2.202
C  0.908  3.425  3.824
H  0.056  3.592  4.465
C  2.135  4.009  3.719
H  2.509  4.830  4.314
C  2.818  3.318  2.669
C -2.740  0.746 -0.141
C -1.961  1.725 -0.799
C -1.137  2.647 -0.096
H -2.055  1.797 -1.878
C -0.464  3.801 -0.723
C -0.014  4.856  0.093
C -0.252  3.904 -2.113
C  0.379  5.019 -2.659
C  0.620  5.971 -0.455
C  0.820  6.059 -1.834
H  0.956  6.772  0.197
H  1.312  6.927 -2.263
H -0.167  4.798  1.167
H -0.574  3.104 -2.773
H  0.529  5.077 -3.734
H -1.311  2.749  0.974
H -3.120 -0.100 -0.698
H -2.665  0.627  0.932
C -5.464  0.612  0.651
C -4.846  1.616 -0.055
H -5.458  0.695  1.739
H -4.550  2.537  0.437
B -7.854 -0.351  0.261
C -6.142 -0.544  0.107
H -5.938 -1.452  0.686
H -5.928 -0.705 -0.954
O -8.516 -1.606 -0.142
O -8.197  0.764 -0.598
O -8.196 -0.172  1.693
H -4.942  1.656 -1.136
C -9.060 -1.217  2.088
C -8.843 -2.314  1.032
C -9.561  1.100 -0.666
H-10.114 -0.886  2.087
H -8.826 -1.560  3.107
H -9.733 -2.940  0.875
H -8.019 -2.984  1.341

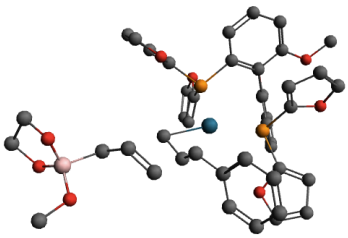
H-10.175 0.284 -1.078
H -9.682 1.977 -1.316
H -9.975 1.354 0.323
H 3.819 3.501 2.308

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -334.3002 | 6.7634 | 10.9959 |
| Red. masses -- | 9.7879 | 6.6342 | 6.1716 |

ZERO-POINT CORRECTION= 0.807659 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.877709
Thermal correction to Enthalpy= 0.878764
Thermal correction to Gibbs Free Energy= 0.686110
Sum of electronic and zero-point Energies= -3252.360635
Sum of electronic and thermal Energies= -3252.290585
Sum of electronic and thermal Enthalpies= -3252.289530
Sum of electronic and thermal Free Energies= -3252.482184

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000003 | 0.000450 | YES |
| RMS FORCE | 0.000001 | 0.000300 | YES |

---



**TS$_{O.S.}$-*Re***

---
Cartesian coordinates (Angstroms):
---
C 2.234 -0.699 -0.658
P -0.966 -1.969 0.024
O -2.516 -3.838 -1.306
O -5.473 0.176 1.469
O 0.968 -2.998 1.648
C -1.661 -2.766 -1.441
C -1.447 -2.518 -2.771
H -0.824 -1.732 -3.173
C -2.208 -3.486 -3.498
H -2.281 -3.591 -4.571
C -2.834 -4.254 -2.563
H -3.505 -5.098 -2.623
C -2.363 -1.697 1.210
C -3.467 -0.892 0.866
C -4.424 -0.594 1.868
C -4.274 -1.074 3.173
H -5.005 -0.841 3.937
C -3.169 -1.862 3.491
H -3.053 -2.237 4.504
C -2.219 -2.173 2.524
H -1.366 -2.784 2.794
C -6.478 0.508 2.422
H -6.967 -0.388 2.820
H -7.211 1.110 1.884
H -6.066 1.096 3.250
C -0.024 -3.343 0.755
C 1.574 -4.151 2.044
H 2.380 -4.039 2.754
C 1.007 -5.225 1.428
H 1.291 -6.261 1.549
C -0.032 -4.704 0.594
H -0.705 -5.262 -0.039
P -1.645 1.534 -0.292
O -3.408 2.840 1.398
O -5.336 -2.116 -0.638
O -0.590 3.057 -2.282
C -2.228 2.135 1.310
C -1.657 2.048 2.551
H -0.729 1.546 2.785
C -2.527 2.732 3.456
H -2.397 2.863 4.521
C -3.569 3.188 2.704
H -4.460 3.752 2.935
C -3.106 0.724 -1.103
C -3.742 -0.392 -0.522
C -4.755 -1.054 -1.260
C -5.113 -0.623 -2.541
H -5.886 -1.133 -3.103
C -4.464 0.477 -3.098
H -4.742 0.815 -4.092
C -3.470 1.147 -2.392
H -2.981 2.001 -2.845
C -6.354 -2.837 -1.324
H -7.216 -2.199 -1.553
H -6.665 -3.632 -0.645
H -5.974 -3.281 -2.252
C -1.462 3.092 -1.216
C -0.593 4.295 -2.847
H 0.049 4.423 -3.705
C -1.436 5.127 -2.172
H -1.630 6.166 -2.395
C -2.002 4.347 -1.115
H -2.724 4.667 -0.379
C 2.366 0.708 -0.773
C 2.666 1.540 0.347
H 2.383 1.152 -1.765
C 2.504 3.004 0.365
C 2.325 3.651 1.603
C 2.542 3.791 -0.801
C 2.398 5.174 -0.728
C 2.177 5.034 1.675
C 2.214 5.802 0.508
H 2.035 5.512 2.639
H 2.104 6.881 0.561
H 2.304 3.057 2.513
H 2.694 3.322 -1.768
H 2.431 5.766 -1.637
H 2.594 1.067 1.321
H 2.539 -1.197 0.257
H 2.280 -1.311 -1.554
Pd 0.241 0.033 -0.348
C 5.282 0.312 0.828
C 4.954 1.603 0.466
B 7.352 -0.970 -0.151

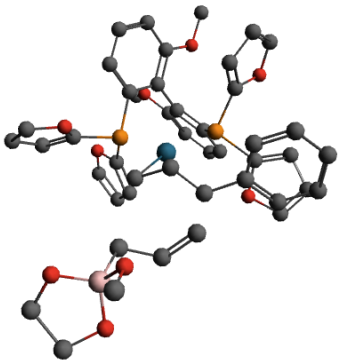
C 5.585 -0.770 -0.057
O 7.586 -2.112 -1.046
O 7.883 -1.366 1.157
O 7.839 0.296 -0.633
C 9.203 0.343 -0.981
C 8.009 -2.772 1.157
C 8.243 -3.133 -0.321
H 9.322 -3.142 -0.551
H 7.842 -4.124 -0.581
H 7.088 -3.256 1.530
H 8.834 -3.087 1.810
H 9.441 1.350 -1.347
H 9.453 -0.377 -1.775
H 9.859 0.130 -0.122
H 4.982 2.398 1.203
H 5.049 1.910 -0.571
H 5.335 0.097 1.897
H 5.267 -1.748 0.314
H 5.275 -0.605 -1.092

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -322.4118 | 7.5894 | 13.2829 |
| Red. masses -- | 9.4276 | 6.2624 | 6.2143 |

ZERO-POINT CORRECTION= 0.807768 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.877575
Thermal correction to Enthalpy= 0.878630
Thermal correction to Gibbs Free Energy= 0.688195
Sum of electronic and zero-point Energies= -3252.356921
Sum of electronic and thermal Energies= -3252.287114
Sum of electronic and thermal Enthalpies= -3252.286058
Sum of electronic and thermal Free Energies= -3252.476494

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000003 | 0.000450 | YES |
| RMS FORCE | 0.000000 | 0.000300 | YES |

---



**TS$_{O.S.}$-*Re***

---
Cartesian coordinates (Angstroms):
---
Pd -0.241 -0.060 -0.045
P 1.056 -2.044 -0.098
O 2.732 -3.672 1.397
O 5.382 0.458 -1.528
O -0.643 -3.404 -1.753
C 1.777 -2.680 1.432
C 1.479 -2.382 2.736
H 0.768 -1.639 3.066
C 2.293 -3.229 3.550
H 2.327 -3.267 4.629
C 3.031 -3.984 2.688
H 3.776 -4.754 2.825
C 2.438 -1.665 -1.272
C 3.484 -0.788 -0.922
C 4.391 -0.382 -1.933
C 4.252 -0.832 -3.250
H 4.945 -0.516 -4.019
C 3.210 -1.701 -3.570
H 3.105 -2.056 -4.591
C 2.308 -2.116 -2.597
H 1.499 -2.781 -2.871
C 6.315 0.930 -2.495
H 6.877 0.106 -2.950
H 7.004 1.578 -1.952
H 5.817 1.510 -3.281
C 0.303 -3.563 -0.763
C -1.111 -4.644 -2.071
H -1.864 -4.678 -2.843
C -0.499 -5.593 -1.310
H -0.676 -6.659 -1.345
C 0.420 -4.895 -0.464
H 1.088 -5.325 0.267
P 1.571 1.495 0.350
O 3.291 3.246 -0.936
O 5.454 -1.958 0.482
O 0.305 2.486 2.538
C 2.193 2.424 -1.072
C 1.748 2.472 -2.366
H 0.906 1.923 -2.763
C 2.612 3.370 -3.069
H 2.560 3.650 -4.111
C 3.524 3.806 -2.155
H 4.362 4.485 -2.208
C 3.081 0.729 1.121
C 3.763 -0.325 0.479
C 4.835 -0.954 1.160
C 5.208 -0.548 2.446
H 6.026 -1.032 2.964
C 4.518 0.494 3.061
H 4.810 0.814 4.057
C 3.465 1.128 2.411
H 2.946 1.939 2.908
C 6.536 -2.639 1.109
H 7.365 -1.958 1.333
H 6.870 -3.390 0.392
H 6.216 -3.137 2.032
C 1.160 2.832 1.514
C 0.143 3.590 3.319
H -0.505 3.471 4.174
C 0.860 4.636 2.821
H 0.913 5.634 3.232
C 1.523 4.145 1.652
H 2.193 4.687 1.002

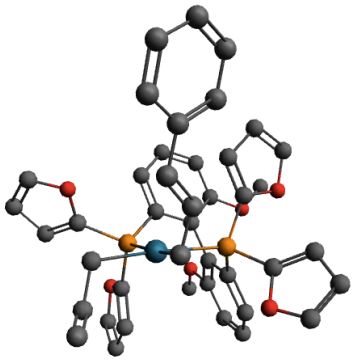
C -2.227 -0.819 -0.345
C -2.348 0.536 -0.728
C -2.745 1.581 0.159
H -2.285 0.770 -1.788
C -2.598 3.015 -0.160
C -2.534 3.944 0.895
C -2.542 3.500 -1.480
C -2.415 4.864 -1.731
C -2.405 5.308 0.643
C -2.345 5.775 -0.673
H -2.349 6.006 1.473
H -2.248 6.838 -0.872
H -2.580 3.587 1.920
H -2.610 2.812 -2.317
H -2.375 5.219 -2.757
H -2.732 1.346 1.217
H -2.229 -1.592 -1.105
H -2.575 -1.130 0.638
C -5.356 0.404 0.700
C -5.014 1.605 0.107
H -5.478 0.403 1.784
H -5.108 2.530 0.665
B -7.358 -1.071 -0.096
C -5.592 -0.837 0.033
H -5.295 -1.717 0.608
H -5.236 -0.873 -0.999
O -7.928 -1.090 1.259
O -7.579 -2.408 -0.647
O -7.799 -0.006 -0.958
H -5.048 1.696 -0.975
C -9.178 0.022 -1.249
C -7.862 -3.274 0.432
C -8.502 -2.362 1.493
H -9.598 -2.327 1.365
H -8.300 -2.702 2.518
H -6.938 -3.736 0.824
H -8.525 -4.088 0.109
H -9.387 0.888 -1.890
H -9.789 0.118 -0.338
H -9.512 -0.883 -1.778

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -342.5207 | 8.2593 | 14.1704 |
| Red. masses -- | 9.5609 | 6.2948 | 6.1750 |

ZERO-POINT CORRECTION= 0.807630 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.877624
Thermal correction to Enthalpy= 0.878679
Thermal correction to Gibbs Free Energy= 0.687747
Sum of electronic and zero-point Energies= -3252.355374
Sum of electronic and thermal Energies= -3252.285380
Sum of electronic and thermal Enthalpies= -3252.284325
Sum of electronic and thermal Free Energies= -3252.475258

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000005 | 0.000450 | YES |
| RMS FORCE | 0.000001 | 0.000300 | YES |

---



**$GS_2$**

---
Cartesian coordinates (Angstroms):
---

Pd 0.861 1.001 0.971
C 2.656 0.532 2.054
P 0.120 -1.336 0.909
O 0.093 -3.516 -0.807
O -4.799 -0.750 -0.685
O 0.834 -1.986 3.472
C 0.573 -2.243 -0.588
C 1.413 -1.891 -1.612
H 1.928 -0.947 -1.707
C 1.454 -3.001 -2.512
H 2.011 -3.077 -3.434
C 0.636 -3.951 -1.976
H 0.350 -4.945 -2.286
C -1.719 -1.494 1.105
C -2.607 -1.123 0.076
C -3.998 -1.122 0.349
C -4.485 -1.482 1.609
H -5.548 -1.482 1.814
C -3.586 -1.842 2.613
H -3.962 -2.121 3.592
C -2.217 -1.845 2.372
H -1.539 -2.115 3.171
C -6.208 -0.724 -0.484
H -6.598 -1.717 -0.228
H -6.638 -0.403 -1.434
H -6.489 -0.011 0.299
C 0.785 -2.463 2.180
C 1.407 -2.955 4.241
H 1.507 -2.723 5.290
C 1.736 -4.034 3.479
H 2.206 -4.945 3.822
C 1.333 -3.718 2.143
H 1.425 -4.345 1.269
P -1.055 1.674 -0.399
O -3.719 2.382 -0.110
O -3.013 -2.898 -1.916
O 0.379 3.344 -2.013
C -2.541 2.092 0.544
C -2.727 2.222 1.895

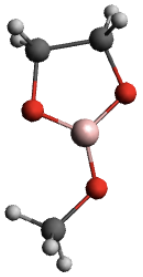
H -1.978 2.048 2.653
C -4.090 2.609 2.089
H -4.591 2.798 3.027
C -4.640 2.688 0.844
H -5.625 2.940 0.482
C -1.586 0.442 -1.681
C -2.176 -0.784 -1.318
C -2.440 -1.737 -2.334
C -2.120 -1.473 -3.669
H -2.323 -2.202 -4.443
C -1.530 -0.255 -4.003
H -1.281 -0.047 -5.040
C -1.260 0.695 -3.024
H -0.794 1.630 -3.308
C -3.311 -3.899 -2.883
H -4.024 -3.536 -3.633
H -3.760 -4.724 -2.329
H -2.404 -4.253 -3.388
C -0.826 3.204 -1.360
C 0.371 4.564 -2.621
H 1.259 4.815 -3.182
C -0.799 5.214 -2.370
H -1.077 6.197 -2.721
C -1.578 4.333 -1.554
H -2.571 4.508 -1.169
C 1.518 3.029 1.222
C 1.086 3.529 2.540
H 1.049 3.581 0.406
H 2.604 3.041 1.095
C 1.868 3.811 3.599
H 0.010 3.682 2.654
C 3.617 0.010 1.081
H 2.325 -0.216 2.776
H 2.990 1.434 2.564
C 4.696 0.670 0.589
H 3.423 -1.001 0.722
C 5.648 0.184 -0.412
H 4.904 1.668 0.977
C 6.781 0.967 -0.719
C 5.503 -1.041 -1.102
C 6.448 -1.458 -2.036
C 7.725 0.550 -1.656
C 7.568 -0.669 -2.321
H 8.587 1.178 -1.866
H 8.301 -0.997 -3.051
H 6.916 1.917 -0.207
H 4.639 -1.670 -0.910
H 6.309 -2.406 -2.549
H 1.450 4.159 4.540
H 2.950 3.711 3.553

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 9.6142 | 11.5893 | 17.2865 |
| Red. masses -- | 6.3842 | 6.1238 | 5.8262 |

ZERO-POINT CORRECTION= 0.695331 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.755747
Thermal correction to Enthalpy= 0.756803
Thermal correction to Gibbs Free Energy= 0.588320
Sum of electronic and zero-point Energies= -2883.324160
Sum of electronic and thermal Energies= -2883.263743
Sum of electronic and thermal Enthalpies= -2883.262688
Sum of electronic and thermal Free Energies= -2883.431170

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000015 | 0.000450 | YES |
| RMS FORCE | 0.000002 | 0.000300 | YES |

---



## MeOB(glycolato)

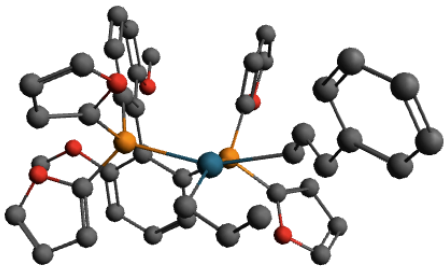
---
Cartesian coordinates (Angstroms):
---
B -0.261 -0.278 -0.008
O 0.175 1.029 0.063
O -1.559 -0.665 -0.025
O 0.757 -1.205 -0.067
C 1.991 -0.485 0.092
C 1.606 1.003 -0.083
C -2.606 0.307 0.018
H 2.713 -0.825 -0.655
H 2.397 -0.690 1.089
H 1.869 1.383 -1.077
H 2.063 1.650 0.670
H -2.893 0.507 1.055
H -3.467 -0.104 -0.514
H -2.303 1.246 -0.454

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 51.6488 | 105.4232 | 120.9307 |
| Red. masses -- | 1.0428 | 2.2443 | 2.9668 |

ZERO-POINT CORRECTION= 0.113305 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.122014
Thermal correction to Enthalpy= 0.123069
Thermal correction to Gibbs Free Energy= 0.076079
Sum of electronic and zero-point Energies= -369.081808
Sum of electronic and thermal Energies= -369.073099
Sum of electronic and thermal Enthalpies= -369.072044
Sum of electronic and thermal Free Energies= -369.119034

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000008 | 0.000450 | YES |
| RMS FORCE | 0.000002 | 0.000300 | YES |

---



**$TS_{3,3'\text{-}Si\ A}$**

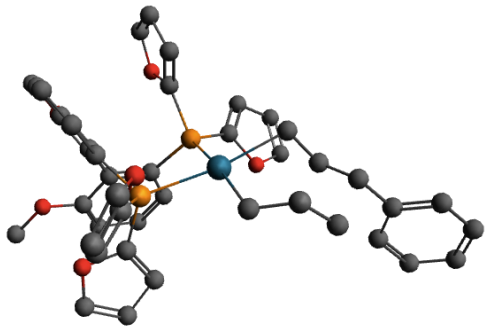
---
Cartesian coordinates (Angstroms):
---

| | | | |
|---|---|---|---|
| Pd | 1.053 | 0.021 | -0.530 |
| P | -0.652 | 1.776 | -0.232 |
| O | -1.973 | 3.386 | 1.615 |
| O | -4.955 | -1.130 | -0.257 |
| O | 0.409 | 3.150 | -2.326 |
| C | -0.985 | 2.445 | 1.420 |
| C | -0.367 | 2.186 | 2.615 |
| H | 0.435 | 1.479 | 2.769 |
| C | -1.002 | 3.007 | 3.599 |
| H | -0.774 | 3.064 | 4.654 |
| C | -1.965 | 3.709 | 2.938 |
| H | -2.693 | 4.445 | 3.247 |
| C | -2.305 | 1.279 | -0.910 |
| C | -3.070 | 0.275 | -0.285 |
| C | -4.258 | -0.165 | -0.918 |
| C | -4.662 | 0.372 | -2.144 |
| H | -5.569 | 0.032 | -2.627 |
| C | -3.883 | 1.358 | -2.749 |
| H | -4.196 | 1.777 | -3.701 |
| C | -2.715 | 1.809 | -2.145 |
| H | -2.124 | 2.575 | -2.632 |
| C | -6.156 | -1.625 | -0.838 |
| H | -6.902 | -0.830 | -0.960 |
| H | -6.538 | -2.373 | -0.142 |
| H | -5.967 | -2.097 | -1.809 |
| C | -0.263 | 3.313 | -1.133 |
| C | 0.662 | 4.393 | -2.823 |
| H | 1.183 | 4.425 | -3.768 |
| C | 0.183 | 5.350 | -1.980 |
| H | 0.247 | 6.420 | -2.118 |
| C | -0.419 | 4.651 | -0.886 |
| H | -0.913 | 5.083 | -0.028 |
| P | -0.563 | -1.761 | -0.094 |
| O | -2.587 | -3.331 | -1.172 |
| O | -4.461 | 1.046 | 1.898 |
| O | 1.302 | -3.173 | 1.304 |
| C | -1.596 | -2.410 | -1.436 |
| C | -1.555 | -2.167 | -2.784 |
| H | -0.886 | -1.481 | -3.283 |
| C | -2.570 | -2.977 | -3.384 |
| H | -2.824 | -3.040 | -4.432 |
| C | -3.162 | -3.657 | -2.362 |
| H | -3.965 | -4.376 | -2.315 |
| C | -1.743 | -1.292 | 1.258 |
| C | -2.738 | -0.315 | 1.054 |
| C | -3.515 | 0.102 | 2.164 |
| C | -3.300 | -0.434 | 3.437 |
| H | -3.895 | -0.111 | 4.282 |
| C | -2.304 | -1.393 | 3.616 |
| H | -2.137 | -1.811 | 4.605 |
| C | -1.530 | -1.820 | 2.544 |
| H | -0.758 | -2.563 | 2.707 |
| C | -5.253 | 1.538 | 2.973 |
| H | -5.849 | 0.742 | 3.434 |
| H | -5.921 | 2.280 | 2.535 |
| H | -4.632 | 2.017 | 3.739 |
| C | 0.184 | -3.312 | 0.509 |
| C | 1.751 | -4.425 | 1.598 |
| H | 2.627 | -4.475 | 2.226 |
| C | 0.961 | -5.365 | 1.008 |
| H | 1.084 | -6.437 | 1.065 |
| C | -0.056 | -4.646 | 0.304 |
| H | -0.868 | -5.061 | -0.273 |
| C | 2.316 | -1.462 | -1.672 |
| C | 2.667 | 1.576 | -0.044 |
| C | 3.840 | 0.941 | 0.395 |
| C | 5.004 | 0.795 | -0.376 |
| H | 3.829 | 0.509 | 1.395 |
| C | 3.435 | -0.855 | -2.282 |
| C | 4.718 | -0.877 | -1.750 |
| H | 3.259 | -0.255 | -3.177 |
| H | 4.954 | -1.621 | -0.994 |
| H | 5.559 | -0.570 | -2.364 |
| H | 2.728 | 2.190 | -0.941 |
| H | 2.047 | 2.006 | 0.740 |
| H | 2.525 | -2.239 | -0.938 |
| H | 1.484 | -1.700 | -2.334 |
| C | 6.296 | 0.396 | 0.220 |
| H | 5.098 | 1.481 | -1.215 |
| C | 6.390 | -0.506 | 1.300 |
| C | 7.626 | -0.861 | 1.837 |
| C | 8.809 | -0.336 | 1.306 |
| C | 7.498 | 0.904 | -0.308 |
| C | 8.736 | 0.547 | 0.226 |
| H | 9.646 | 0.962 | -0.201 |
| H | 9.771 | -0.617 | 1.724 |
| H | 5.485 | -0.940 | 1.716 |
| H | 7.668 | -1.556 | 2.672 |
| H | 7.454 | 1.596 | -1.146 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -374.5002 | 6.9123 | 13.6319 |
| Red. masses -- | 11.3678 | 6.0679 | 6.0301 |

ZERO-POINT CORRECTION= 0.694249 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.753963
Thermal correction to Enthalpy= 0.755018
Thermal correction to Gibbs Free Energy= 0.589128
Sum of electronic and zero-point Energies= -2883.303765
Sum of electronic and thermal Energies= -2883.244052
Sum of electronic and thermal Enthalpies= -2883.242996
Sum of electronic and thermal Free Energies= -2883.408886

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000003 | 0.000450 | YES |
| RMS FORCE | 0.000000 | 0.000300 | YES |



**$TS_{3,3'\text{-}Re\ a}$**

---
Cartesian coordinates (Angstroms):
---

| | | | |
|---|---|---|---|
| Pd | 1.018 | 0.594 | -0.760 |
| P | -0.147 | -1.599 | -0.303 |
| O | -1.867 | -3.422 | -1.517 |
| O | -4.471 | -0.003 | 2.110 |
| O | 1.964 | -2.792 | 0.963 |
| C | -1.078 | -2.304 | -1.690 |
| C | -1.109 | -1.929 | -3.007 |
| H | -0.589 | -1.083 | -3.433 |
| C | -1.960 | -2.857 | -3.684 |
| H | -2.218 | -2.867 | -4.734 |
| C | -2.392 | -3.734 | -2.734 |
| H | -3.042 | -4.596 | -2.759 |
| C | -1.325 | -1.557 | 1.132 |
| C | -2.528 | -0.826 | 1.070 |
| C | -3.318 | -0.716 | 2.242 |
| C | -2.913 | -1.308 | 3.442 |
| H | -3.517 | -1.220 | 4.336 |
| C | -1.713 | -2.017 | 3.482 |
| H | -1.396 | -2.479 | 4.413 |
| C | -0.922 | -2.141 | 2.346 |
| H | 0.008 | -2.692 | 2.406 |
| C | -5.312 | 0.149 | 3.248 |
| H | -5.669 | -0.820 | 3.617 |
| H | -6.163 | 0.742 | 2.912 |
| H | -4.799 | 0.678 | 4.059 |
| C | 0.925 | -3.026 | 0.086 |
| C | 2.682 | -3.947 | 1.062 |
| H | 3.531 | -3.917 | 1.727 |
| C | 2.142 | -4.912 | 0.267 |
| H | 2.505 | -5.922 | 0.145 |
| C | 1.004 | -4.318 | -0.365 |
| H | 0.322 | -4.790 | -1.056 |
| P | -1.037 | 1.812 | -0.133 |
| O | -2.450 | 2.618 | 2.125 |
| O | -4.592 | -2.003 | -0.204 |
| O | -0.869 | 3.769 | -2.038 |
| C | -1.274 | 2.085 | 1.642 |
| C | -0.400 | 1.902 | 2.681 |
| H | 0.597 | 1.494 | 2.600 |
| C | -1.068 | 2.340 | 3.868 |
| H | -0.682 | 2.338 | 4.877 |
| C | -2.303 | 2.759 | 3.471 |
| H | -3.153 | 3.167 | 3.997 |
| C | -2.582 | 0.985 | -0.750 |
| C | -3.066 | -0.212 | -0.186 |
| C | -4.170 | -0.855 | -0.803 |
| C | -4.764 | -0.326 | -1.951 |
| H | -5.605 | -0.821 | -2.421 |
| C | -4.261 | 0.854 | -2.498 |
| H | -4.721 | 1.269 | -3.391 |
| C | -3.182 | 1.504 | -1.912 |
| H | -2.807 | 2.415 | -2.361 |
| C | -5.689 | -2.707 | -0.775 |
| H | -6.600 | -2.097 | -0.781 |
| H | -5.845 | -3.580 | -0.140 |
| H | -5.466 | -3.037 | -1.796 |
| C | -1.225 | 3.529 | -0.726 |
| C | -1.009 | 5.107 | -2.261 |
| H | -0.772 | 5.445 | -3.258 |
| C | -1.432 | 5.735 | -1.129 |
| H | -1.623 | 6.792 | -1.013 |
| C | -1.572 | 4.715 | -0.134 |
| H | -1.902 | 4.842 | 0.885 |
| C | 2.103 | 2.586 | -0.833 |
| C | 2.791 | -0.559 | -1.688 |
| C | 3.862 | -0.567 | -0.782 |
| C | 5.025 | 0.222 | -0.916 |
| H | 3.759 | -1.187 | 0.105 |
| C | 3.427 | 2.585 | -1.313 |
| C | 4.551 | 2.230 | -0.563 |
| H | 3.574 | 2.762 | -2.380 |
| H | 4.450 | 2.179 | 0.520 |
| H | 5.529 | 2.558 | -0.902 |
| H | 2.217 | -1.475 | -1.782 |
| H | 2.942 | -0.040 | -2.634 |
| H | 1.381 | 3.125 | -1.439 |
| H | 1.982 | 2.740 | 0.242 |
| C | 6.186 | 0.013 | -0.018 |
| H | 5.307 | 0.461 | -1.938 |
| C | 6.035 | -0.280 | 1.351 |
| C | 7.144 | -0.465 | 2.175 |
| C | 8.438 | -0.350 | 1.659 |
| C | 7.496 | 0.138 | -0.518 |
| C | 8.607 | -0.043 | 0.306 |
| H | 9.607 | 0.053 | -0.110 |
| H | 9.302 | -0.491 | 2.303 |
| H | 5.037 | -0.354 | 1.775 |
| H | 6.998 | -0.693 | 3.228 |
| H | 7.640 | 0.371 | -1.571 |

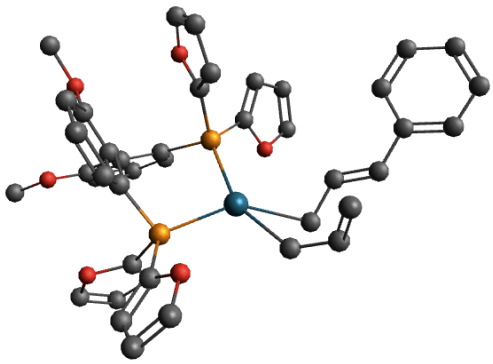
| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -430.3849 | 8.0689 | 12.1402 |
| Red. masses -- | 10.3665 | 6.3302 | 5.4390 |

ZERO-POINT CORRECTION= 0.694583 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.754164
Thermal correction to Enthalpy= 0.755219
Thermal correction to Gibbs Free Energy= 0.590177

Sum of electronic and zero-point Energies= -2883.298735
Sum of electronic and thermal Energies= -2883.239154
Sum of electronic and thermal Enthalpies= -2883.238099
Sum of electronic and thermal Free Energies= -2883.403141

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000011 | 0.000450 | YES |
| RMS FORCE | 0.000001 | 0.000300 | YES |

---



**$TS_{1,1'}$**

---
Cartesian coordinates (Angstroms):
---

| | | | |
|---|---|---|---|
| P | 1.744 | 1.654 | -0.071 |
| O | 4.255 | 1.530 | -1.271 |
| O | 2.942 | -3.069 | 1.764 |
| O | 1.345 | 3.905 | 1.413 |
| C | 2.891 | 1.513 | -1.469 |
| C | 2.631 | 1.436 | -2.812 |
| H | 1.648 | 1.399 | -3.259 |
| C | 3.895 | 1.405 | -3.480 |
| H | 4.075 | 1.343 | -4.544 |
| C | 4.840 | 1.462 | -2.499 |
| H | 5.919 | 1.466 | -2.507 |
| C | 2.382 | 0.491 | 1.231 |
| C | 2.496 | -0.893 | 0.989 |
| C | 2.829 | -1.746 | 2.071 |
| C | 3.023 | -1.238 | 3.359 |
| H | 3.270 | -1.894 | 4.183 |
| C | 2.896 | 0.133 | 3.577 |
| H | 3.049 | 0.532 | 4.576 |
| C | 2.580 | 0.992 | 2.530 |
| H | 2.483 | 2.053 | 2.726 |
| C | 3.263 | -3.985 | 2.804 |
| H | 4.237 | -3.760 | 3.255 |
| H | 3.303 | -4.968 | 2.334 |
| H | 2.494 | -3.988 | 3.586 |
| C | 2.242 | 3.295 | 0.561 |
| C | 1.840 | 5.139 | 1.713 |
| H | 1.243 | 5.736 | 2.385 |
| C | 3.023 | 5.345 | 1.070 |
| H | 3.636 | 6.233 | 1.121 |
| C | 3.286 | 4.151 | 0.326 |
| H | 4.144 | 3.946 | -0.297 |
| P | -0.475 | -1.188 | -0.314 |
| O | -0.345 | -3.247 | 1.558 |
| O | 4.719 | -1.619 | -0.340 |
| O | -2.098 | -1.738 | -2.436 |
| C | -0.616 | -1.913 | 1.342 |
| C | -1.017 | -1.338 | 2.518 |
| H | -1.288 | -0.301 | 2.650 |
| C | -0.995 | -2.366 | 3.513 |
| H | -1.250 | -2.274 | 4.559 |
| C | -0.579 | -3.496 | 2.875 |
| H | -0.409 | -4.512 | 3.200 |
| C | 1.141 | -1.813 | -0.996 |
| C | 2.368 | -1.524 | -0.367 |
| C | 3.570 | -1.911 | -1.012 |
| C | 3.550 | -2.549 | -2.255 |
| H | 4.471 | -2.839 | -2.746 |
| C | 2.325 | -2.812 | -2.867 |
| H | 2.305 | -3.308 | -3.833 |
| C | 1.133 | -2.452 | -2.249 |
| H | 0.195 | -2.667 | -2.746 |
| C | 5.964 | -1.963 | -0.935 |
| H | 6.054 | -3.046 | -1.087 |
| H | 6.731 | -1.634 | -0.233 |
| H | 6.106 | -1.450 | -1.894 |
| C | -1.703 | -2.213 | -1.202 |
| C | -3.062 | -2.578 | -2.908 |
| H | -3.466 | -2.334 | -3.879 |
| C | -3.306 | -3.572 | -2.010 |
| H | -4.022 | -4.375 | -2.119 |
| C | -2.426 | -3.339 | -0.905 |
| H | -2.328 | -3.935 | -0.011 |
| Pd | -0.618 | 1.202 | -0.463 |
| C | -2.587 | 1.886 | -1.563 |
| C | -1.669 | 3.295 | -0.166 |
| C | -2.941 | 3.804 | 0.363 |
| C | -3.374 | 3.644 | 1.623 |
| H | -3.578 | 4.350 | -0.334 |
| H | -2.787 | 3.101 | 2.361 |
| H | -4.324 | 4.052 | 1.955 |
| C | -3.643 | 1.022 | -1.053 |
| C | -4.894 | 1.424 | -0.717 |
| H | -3.375 | -0.023 | -0.933 |
| H | -1.220 | 3.929 | -0.929 |
| H | -0.968 | 3.121 | 0.656 |
| H | -1.908 | 1.395 | -2.274 |
| H | -2.937 | 2.818 | -2.000 |
| C | -5.976 | 0.579 | -0.203 |
| H | -5.158 | 2.470 | -0.860 |
| C | -5.801 | -0.770 | 0.173 |
| C | -7.268 | 1.129 | -0.073 |
| C | -8.338 | 0.371 | 0.401 |
| C | -6.870 | -1.527 | 0.646 |
| C | -8.146 | -0.965 | 0.762 |
| H | -4.819 | -1.229 | 0.102 |
| H | -6.706 | -2.563 | 0.929 |
| H | -9.322 | 0.824 | 0.488 |
| H | -8.976 | -1.559 | 1.133 |
| H | -7.428 | 2.168 | -0.352 |

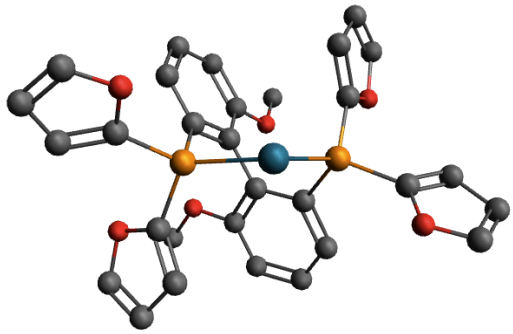
1 2 3

| | A | A | A |
|---|---|---|---|
| Frequencies -- | -388.2070 | 9.1092 | 14.9023 |
| Red. masses -- | 4.0109 | 6.4111 | 5.3768 |

ZERO-POINT CORRECTION= 0.693424 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.753758
Thermal correction to Enthalpy= 0.754813
Thermal correction to Gibbs Free Energy= 0.586713
Sum of electronic and zero-point Energies= -2883.275677
Sum of electronic and thermal Energies= -2883.215343
Sum of electronic and thermal Enthalpies= -2883.214288
Sum of electronic and thermal Free Energies= -2883.382388

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000003 | 0.000450 | YES |
| RMS FORCE | 0.000001 | 0.000300 | YES |

---



**PdL$_n$**

---
Cartesian coordinates (Angstroms):
---

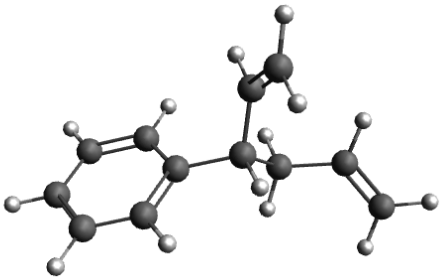
| | | | |
|---|---|---|---|
| Pd | -0.000 | 2.176 | 0.000 |
| P | 1.933 | 0.939 | 0.035 |
| O | 3.420 | -0.779 | -1.573 |
| O | -1.123 | -3.153 | 1.148 |
| O | 3.451 | 2.452 | 1.701 |
| C | 2.513 | 0.259 | -1.545 |
| C | 2.221 | 0.636 | -2.828 |
| H | 1.534 | 1.420 | -3.111 |
| C | 2.982 | -0.210 | -3.695 |
| H | 3.000 | -0.198 | -4.775 |
| C | 3.688 | -1.045 | -2.881 |
| H | 4.392 | -1.842 | -3.065 |
| C | 1.410 | -0.533 | 1.057 |
| C | 0.332 | -1.364 | 0.676 |
| C | -0.103 | -2.360 | 1.586 |
| C | 0.491 | -2.506 | 2.844 |
| H | 0.146 | -3.264 | 3.537 |
| C | 1.545 | -1.669 | 3.202 |
| H | 2.014 | -1.782 | 4.175 |
| C | 2.003 | -0.695 | 2.321 |
| H | 2.827 | -0.057 | 2.619 |
| C | -1.611 | -4.173 | 2.009 |
| H | -0.830 | -4.902 | 2.258 |
| H | -2.407 | -4.675 | 1.456 |
| H | -2.024 | -3.755 | 2.935 |
| C | 3.530 | 1.428 | 0.778 |
| C | 4.718 | 2.730 | 2.111 |
| H | 4.815 | 3.517 | 2.844 |
| C | 5.614 | 1.924 | 1.475 |
| H | 6.687 | 1.929 | 1.601 |
| C | 4.845 | 1.079 | 0.614 |
| H | 5.214 | 0.305 | -0.043 |
| P | -1.933 | 0.939 | -0.035 |
| O | -3.420 | -0.779 | 1.573 |
| O | 1.123 | -3.153 | -1.148 |
| O | -3.451 | 2.452 | -1.701 |
| C | -2.513 | 0.259 | 1.545 |
| C | -2.221 | 0.636 | 2.828 |
| H | -1.534 | 1.420 | 3.111 |
| C | -2.982 | -0.210 | 3.695 |
| H | -3.000 | -0.198 | 4.775 |
| C | -3.688 | -1.045 | 2.881 |
| H | -4.392 | -1.842 | 3.065 |
| C | -1.410 | -0.533 | -1.057 |
| C | -0.332 | -1.364 | -0.676 |
| C | 0.103 | -2.360 | -1.586 |
| C | -0.491 | -2.506 | -2.844 |
| H | -0.146 | -3.264 | -3.537 |
| C | -1.545 | -1.669 | -3.202 |
| H | -2.014 | -1.782 | -4.175 |
| C | -2.003 | -0.695 | -2.321 |
| H | -2.827 | -0.057 | -2.619 |
| C | 1.611 | -4.173 | -2.009 |
| H | 0.830 | -4.902 | -2.258 |
| H | 2.407 | -4.675 | -1.456 |
| H | 2.024 | -3.755 | -2.935 |
| C | -3.530 | 1.428 | -0.778 |
| C | -4.718 | 2.730 | -2.111 |
| H | -4.815 | 3.517 | -2.844 |
| C | -5.614 | 1.924 | -1.475 |
| H | -6.687 | 1.929 | -1.601 |
| C | -4.845 | 1.079 | -0.614 |
| H | -5.214 | 0.305 | 0.043 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -6.5886 | 22.7440 | 33.5422 |
| Red. masses -- | 6.8626 | 6.1981 | 4.8096 |

ZERO-POINT CORRECTION= 0.472498 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.515538
Thermal correction to Enthalpy= 0.516593
Thermal correction to Gibbs Free Energy= 0.390226
Sum of electronic and zero-point Energies= -2417.878301
Sum of electronic and thermal Energies= -2417.835261
Sum of electronic and thermal Enthalpies= -2417.834206
Sum of electronic and thermal Free Energies= -2417.960573

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000001 | 0.000015 | YES |
| RMS FORCE | 0.000000 | 0.000010 | YES |

---



**Branched**

---

Cartesian coordinates (Angstroms):

---

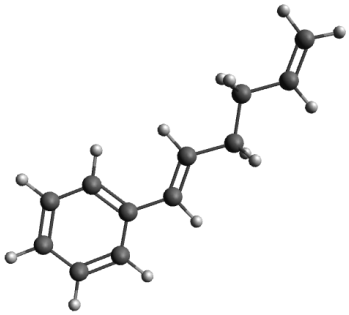
C 1.548 -0.857 -0.475
C 0.739 0.291 0.203
C 3.030 -0.766 -0.237
H 1.349 -0.831 -1.555
H 1.171 -1.817 -0.107
C 1.095 1.642 -0.380
C 1.653 2.645 0.298
H 0.864 1.777 -1.437
H 1.900 2.554 1.353
H 1.883 3.595 -0.177
C 3.765 -1.709 0.354
H 3.514 0.151 -0.574
H 3.324 -2.638 0.710
H 4.836 -1.592 0.500
H 1.010 0.299 1.265
C -0.763 0.032 0.109
C -1.413 -0.074 -1.130
C -1.529 -0.106 1.274
C -2.903 -0.344 1.208
C -2.787 -0.311 -1.200
C -3.538 -0.448 -0.030
H -3.271 -0.390 -2.170
H -4.607 -0.633 -0.084
H -0.847 0.028 -2.052
H -1.043 -0.025 2.243
H -3.476 -0.449 2.126

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 36.3057 | 60.4610 | 72.3007 |
| Red. masses -- | 3.6970 | 2.7976 | 3.0255 |

ZERO-POINT CORRECTION= 0.223164 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.237567
Thermal correction to Enthalpy= 0.238622
Thermal correction to Gibbs Free Energy= 0.177883
Sum of electronic and zero-point Energies= -465.461123
Sum of electronic and thermal Energies= -465.446719
Sum of electronic and thermal Enthalpies= -465.445664
Sum of electronic and thermal Free Energies= -465.506404

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000008 | 0.000450 | YES |
| RMS FORCE | 0.000002 | 0.000300 | YES |

---



**Linear**

---

Cartesian coordinates (Angstroms):

---

C -4.095 -0.814 -0.000
C -4.408 0.546 -0.000
C -2.763 -1.226 -0.000
C -3.373 1.487 0.000
C -2.043 1.075 0.000
C -1.709 -0.294 0.000
H -4.888 -1.556 -0.000
H -5.443 0.872 -0.000
H -2.528 -2.287 -0.000
H -3.604 2.548 0.000
H -1.258 1.825 0.000
C -0.324 -0.792 0.000
C 0.807 -0.069 0.000
H -0.235 -1.879 0.000
C 2.197 -0.663 0.000
H 0.751 1.019 0.000
C 3.307 0.397 -0.000
H 2.324 -1.316 -0.875
H 2.324 -1.316 0.875
C 4.699 -0.199 0.000
H 3.183 1.049 0.876
H 3.183 1.049 -0.876
C 5.835 0.499 -0.000
H 4.756 -1.288 0.000
H 5.842 1.587 -0.000
H 6.804 0.008 -0.000

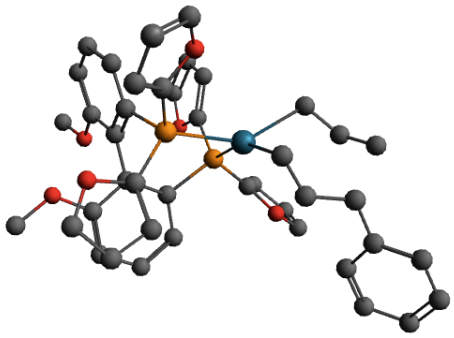
| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -141.2770 | -90.3086 | 22.1662 |
| Red. masses -- | 1.9790 | 2.0314 | 2.7343 |

ZERO-POINT CORRECTION= 0.222498 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.235410
Thermal correction to Enthalpy= 0.236465
Thermal correction to Gibbs Free Energy= 0.178360
Sum of electronic and zero-point Energies= -465.467778
Sum of electronic and thermal Energies= -465.454865
Sum of electronic and thermal Enthalpies= -465.453810
Sum of electronic and thermal Free Energies= -465.511915

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000055 | 0.000450 | YES |
| RMS FORCE | 0.000011 | 0.000300 | YES |

---

***Structures and Energies from Figure 4***



**$TS_{3,3'}$ *Si B***

---
Cartesian coordinates (Angstroms):
---

Pd 0.945 0.685 -0.920
P -1.135 1.797 -0.223
O -2.469 2.896 1.960
O -4.225 -2.335 0.364
O -0.996 3.438 -2.388
C -1.300 2.324 1.504
C -0.395 2.270 2.531
H 0.603 1.861 2.470
C -1.033 2.835 3.679
H -0.617 2.955 4.669
C -2.284 3.195 3.275
H -3.123 3.654 3.776
C -2.670 0.819 -0.583
C -2.921 -0.398 0.082
C -4.032 -1.176 -0.326
C -4.859 -0.758 -1.373
H -5.706 -1.356 -1.685
C -4.586 0.446 -2.022
H -5.230 0.774 -2.834
C -3.504 1.229 -1.637
H -3.310 2.162 -2.153
C -5.322 -3.167 0.006
H -6.280 -2.648 0.132
H -5.283 -4.020 0.684
H -5.236 -3.522 -1.028
C -1.421 3.382 -1.077
C -1.228 4.703 -2.837
H -0.949 4.897 -3.862
C -1.780 5.465 -1.852
H -2.062 6.506 -1.925
C -1.907 4.610 -0.712
H -2.316 4.866 0.254
P 0.079 -1.544 -0.444
O -1.617 -3.564 -1.323
O -3.936 -0.163 2.570
O 2.521 -2.441 0.365
C -0.996 -2.376 -1.644
C -1.296 -2.047 -2.939
H -0.959 -1.163 -3.461
C -2.144 -3.081 -3.446
H -2.577 -3.150 -4.434
C -2.305 -3.970 -2.425
H -2.850 -4.897 -2.326
C -0.866 -1.517 1.153
C -2.125 -0.891 1.256
C -2.716 -0.768 2.539
C -2.065 -1.241 3.682
H -2.518 -1.141 4.660
C -0.817 -1.849 3.556
H -0.310 -2.220 4.443
C -0.219 -1.988 2.309
H 0.753 -2.460 2.235
C -4.578 0.014 3.827
H -4.780 -0.947 4.316
H -5.524 0.513 3.611
H -3.981 0.644 4.496
C 1.324 -2.853 -0.181
C 3.341 -3.528 0.420
H 4.324 -3.351 0.827
C 2.709 -4.626 -0.082
H 3.120 -5.621 -0.168
C 1.402 -4.191 -0.469
H 0.615 -4.792 -0.899
C 2.217 -0.014 -2.742
C 2.222 2.500 -0.651
C 3.207 1.789 0.063
C 4.532 1.539 -0.371
H 2.926 1.408 1.045
C 3.499 -0.426 -2.368
C 4.594 0.430 -2.271
H 2.509 2.948 -1.603
H 1.508 3.093 -0.086
H 1.499 -0.774 -3.038
H 2.126 0.929 -3.283
C 5.484 0.821 0.500
H 4.986 2.329 -0.962
H 4.573 1.347 -2.854
H 5.584 0.020 -2.099
H 3.610 -1.439 -1.982
C 5.077 -0.217 1.363
C 6.853 1.150 0.476
C 7.774 0.488 1.287
C 5.996 -0.874 2.180
C 7.351 -0.527 2.149
H 7.193 1.944 -0.186
H 8.823 0.769 1.250
H 8.065 -1.044 2.784
H 4.034 -0.520 1.376
H 5.655 -1.665 2.843

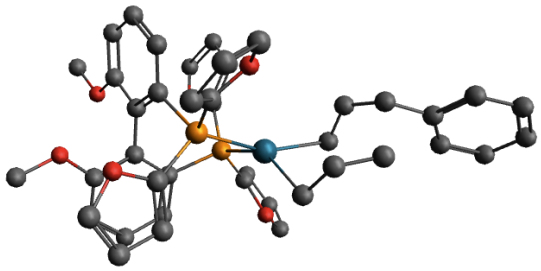
| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -399.6846 | 11.3389 | 20.3841 |
| Red. masses -- | 9.7657 | 5.9314 | 6.1455 |

ZERO-POINT CORRECTION= 0.694558 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.754052
Thermal correction to Enthalpy= 0.755107
Thermal correction to Gibbs Free Energy= 0.591602
Sum of electronic and zero-point Energies= -2883.298546
Sum of electronic and thermal Energies= -2883.239051
Sum of electronic and thermal Enthalpies= -2883.237996

Sum of electronic and thermal Free Energies= -2883.401502

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000004 | 0.000450 | YES |
| RMS FORCE | 0.000001 | 0.000300 | YES |

---



***trans*-TS$_{3,3'}$ *Si B***

---

Cartesian coordinates (Angstroms):

---

Pd 1.113 -0.076 -0.426
P -0.481 1.787 -0.225
O -1.876 3.411 1.553
O -4.927 -0.880 -0.554
O 0.776 3.137 -2.231
C -0.884 2.464 1.408
C -0.312 2.220 2.628
H 0.486 1.517 2.822
C -0.981 3.055 3.577
H -0.793 3.125 4.638
C -1.917 3.751 2.871
H -2.654 4.491 3.143
C -2.107 1.377 -1.015
C -2.971 0.421 -0.444
C -4.129 0.039 -1.166
C -4.408 0.583 -2.423
H -5.292 0.285 -2.972
C -3.533 1.520 -2.972
H -3.750 1.946 -3.947
C -2.393 1.916 -2.282
H -1.727 2.644 -2.728
C -6.097 -1.326 -1.230
H -6.794 -0.501 -1.419
H -6.569 -2.049 -0.564
H -5.849 -1.817 -2.179
C 0.043 3.312 -1.076
C 1.129 4.373 -2.681
H 1.706 4.395 -3.592
C 0.655 5.338 -1.844
H 0.789 6.405 -1.951
C -0.050 4.653 -0.805
H -0.569 5.093 0.033
P -0.613 -1.759 -0.033
O -2.592 -3.316 -1.207
O -4.479 1.305 1.607
O 1.062 -3.179 1.573
C -1.578 -2.408 -1.425
C -1.476 -2.161 -2.769
H -0.780 -1.480 -3.236
C -2.475 -2.955 -3.415
H -2.685 -3.012 -4.473
C -3.119 -3.631 -2.421
H -3.932 -4.341 -2.412
C -1.869 -1.204 1.217
C -2.780 -0.169 0.923
C -3.619 0.310 1.959
C -3.546 -0.222 3.250
H -4.188 0.148 4.040
C -2.633 -1.240 3.519
H -2.576 -1.657 4.521
C -1.799 -1.728 2.519
H -1.096 -2.517 2.753
C -5.340 1.848 2.602
H -6.019 1.088 3.007
H -5.923 2.621 2.101
H -4.769 2.299 3.422
C 0.032 -3.314 0.666
C 1.466 -4.433 1.919
H 2.269 -4.487 2.638
C 0.734 -5.370 1.253
H 0.841 -6.443 1.329
C -0.197 -4.646 0.443
H -0.949 -5.058 -0.214
C 2.326 -1.493 -1.780
C 2.926 1.204 -0.030
C 3.442 0.328 0.947
C 4.617 -0.463 0.922
H 2.814 0.192 1.830
C 3.218 -2.296 -1.054
C 4.527 -1.927 -0.767
H 3.488 1.368 -0.947
H 2.377 2.078 0.307
H 1.449 -1.971 -2.210
H 2.756 -0.707 -2.401
H 4.660 -1.188 1.735
C 5.974 0.012 0.561
H 5.009 -1.198 -1.411
H 5.200 -2.637 -0.296
H 2.819 -3.190 -0.576
C 7.082 -0.750 0.991
C 6.251 1.189 -0.163
C 8.391 -0.370 0.705
C 7.562 1.571 -0.450
C 8.643 0.796 -0.024
H 9.662 1.098 -0.249
H 7.737 2.488 -1.007
H 6.903 -1.658 1.564
H 9.217 -0.983 1.055
H 5.436 1.823 -0.491

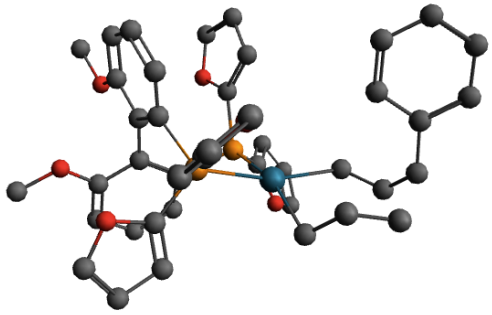
| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -390.5877 | 6.7309 | 13.9137 |
| Red. masses -- | 8.1521 | 6.2623 | 6.0650 |

ZERO-POINT CORRECTION= 0.694042 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.753819
Thermal correction to Enthalpy= 0.754874

Thermal correction to Gibbs Free Energy= 0.588612
Sum of electronic and zero-point Energies= -2883.290207
Sum of electronic and thermal Energies= -2883.230430
Sum of electronic and thermal Enthalpies= -2883.229375
Sum of electronic and thermal Free Energies= -2883.395637

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000012 | 0.000450 | YES |
| RMS FORCE | 0.000001 | 0.000300 | YES |

---



***trans*-TS$_{3,3'}$-*Re a***

---
Cartesian coordinates (Angstroms):
---

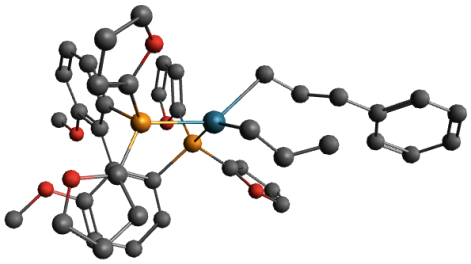
| | | | |
|---|---|---|---|
| Pd | 1.172 | 0.032 | -0.994 |
| P | -0.459 | 1.796 | -0.386 |
| O | -1.570 | 3.176 | 1.762 |
| O | -4.717 | -1.171 | 0.104 |
| O | 0.115 | 3.391 | -2.531 |
| C | -0.551 | 2.351 | 1.337 |
| C | 0.318 | 2.136 | 2.374 |
| H | 1.209 | 1.527 | 2.334 |
| C | -0.188 | 2.861 | 3.498 |
| H | 0.239 | 2.918 | 4.489 |
| C | -1.332 | 3.467 | 3.070 |
| H | -2.055 | 4.111 | 3.548 |
| C | -2.173 | 1.253 | -0.855 |
| C | -2.864 | 0.260 | -0.134 |
| C | -4.100 | -0.213 | -0.643 |
| C | -4.626 | 0.285 | -1.838 |
| H | -5.569 | -0.079 | -2.225 |
| C | -3.921 | 1.263 | -2.539 |
| H | -4.328 | 1.653 | -3.468 |
| C | -2.708 | 1.743 | -2.060 |
| H | -2.177 | 2.498 | -2.627 |
| C | -5.961 | -1.692 | -0.347 |
| H | -6.726 | -0.909 | -0.414 |
| H | -6.264 | -2.428 | 0.398 |
| H | -5.859 | -2.185 | -1.322 |
| C | -0.302 | 3.416 | -1.216 |
| C | 0.225 | 4.684 | -2.949 |
| H | 0.539 | 4.823 | -3.972 |
| C | -0.099 | 5.539 | -1.939 |
| H | -0.096 | 6.618 | -1.985 |
| C | -0.441 | 4.719 | -0.817 |
| H | -0.763 | 5.052 | 0.159 |
| P | -0.336 | -1.738 | -0.141 |
| O | -2.394 | -3.426 | -0.964 |
| O | -4.073 | 1.054 | 2.148 |
| O | 1.668 | -3.031 | 1.181 |
| C | -1.470 | -2.477 | -1.346 |
| C | -1.569 | -2.270 | -2.696 |
| H | -0.974 | -1.574 | -3.270 |
| C | -2.604 | -3.132 | -3.175 |
| H | -2.957 | -3.233 | -4.192 |
| C | -3.068 | -3.805 | -2.084 |
| H | -3.834 | -4.552 | -1.943 |
| C | -1.384 | -1.255 | 1.312 |
| C | -2.405 | -0.294 | 1.182 |
| C | -3.090 | 0.133 | 2.347 |
| C | -2.755 | -0.375 | 3.605 |
| H | -3.278 | -0.045 | 4.494 |
| C | -1.733 | -1.317 | 3.712 |
| H | -1.472 | -1.715 | 4.689 |
| C | -1.050 | -1.755 | 2.583 |
| H | -0.258 | -2.486 | 2.692 |
| C | -4.794 | 1.536 | 3.276 |
| H | -5.330 | 0.728 | 3.788 |
| H | -5.514 | 2.255 | 2.885 |
| H | -4.131 | 2.040 | 3.990 |
| C | 0.520 | -3.238 | 0.446 |
| C | 2.193 | -4.255 | 1.470 |
| H | 3.100 | -4.251 | 2.055 |
| C | 1.423 | -5.242 | 0.934 |
| H | 1.602 | -6.305 | 1.001 |
| C | 0.337 | -4.585 | 0.272 |
| H | -0.482 | -5.050 | -0.256 |
| C | 2.331 | -1.593 | -2.171 |
| C | 2.780 | 1.657 | -1.218 |
| C | 3.983 | 1.265 | -1.819 |
| C | 5.080 | 0.574 | -1.268 |
| H | 4.050 | 1.421 | -2.897 |
| C | 3.575 | -1.927 | -1.598 |
| C | 4.801 | -1.403 | -2.011 |
| H | 3.561 | -2.551 | -0.706 |
| H | 4.895 | -1.062 | -3.039 |
| H | 5.713 | -1.823 | -1.595 |
| H | 2.198 | 2.381 | -1.780 |
| H | 2.780 | 1.819 | -0.140 |
| H | 1.544 | -2.336 | -2.088 |
| H | 2.355 | -1.100 | -3.145 |
| H | 5.991 | 0.659 | -1.858 |
| C | 5.357 | 0.426 | 0.180 |
| C | 4.377 | 0.075 | 1.130 |
| C | 6.676 | 0.609 | 0.642 |
| C | 7.001 | 0.473 | 1.991 |
| C | 4.704 | -0.066 | 2.480 |
| C | 6.014 | 0.138 | 2.921 |
| H | 8.027 | 0.628 | 2.316 |
| H | 6.263 | 0.031 | 3.973 |
| H | 3.360 | -0.115 | 0.803 |
| H | 3.929 | -0.342 | 3.191 |
| H | 7.453 | 0.868 | -0.073 |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -409.1121 | 12.3309 | 17.7263 |
| Red. masses -- | 10.9456 | 6.0559 | 5.8831 |

ZERO-POINT CORRECTION= 0.695151 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.754466
Thermal correction to Enthalpy= 0.755521
Thermal correction to Gibbs Free Energy= 0.592838
Sum of electronic and zero-point Energies= -2883.294600
Sum of electronic and thermal Energies= -2883.235284
Sum of electronic and thermal Enthalpies= -2883.234229
Sum of electronic and thermal Free Energies= -2883.396913

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000028 | 0.000450 | YES |
| RMS FORCE | 0.000003 | 0.000300 | YES |

---



**$TS_{3,3'}$ *Re b***

---
Cartesian coordinates (Angstroms):
---

Pd 0.850 0.947 -0.219
P -1.427 1.774 -0.132
O -3.510 2.423 1.598
O -3.924 -2.722 -0.863
O -0.872 3.690 -1.987
C -2.181 2.071 1.490
C -1.618 2.049 2.738
H -0.591 1.798 2.961
C -2.647 2.405 3.666
H -2.563 2.487 4.740
C -3.768 2.617 2.921
H -4.781 2.899 3.166
C -2.601 0.665 -1.044
C -2.900 -0.627 -0.566
C -3.670 -1.490 -1.385
C -4.119 -1.080 -2.644
H -4.706 -1.743 -3.267
C -3.803 0.200 -3.099
H -4.153 0.521 -4.076
C -3.050 1.066 -2.314
H -2.813 2.054 -2.690
C -4.673 -3.651 -1.640
H -5.680 -3.277 -1.856
H -4.748 -4.554 -1.034
H -4.162 -3.888 -2.581
C -1.679 3.406 -0.905
C -1.161 4.958 -2.388
H -0.606 5.321 -3.239
C -2.124 5.503 -1.592
H -2.542 6.496 -1.676
C -2.462 4.498 -0.632
H -3.196 4.567 0.156
P 0.195 -1.410 -0.042
O -0.670 -3.719 -1.325
O -4.754 -0.707 1.389
O 2.282 -1.831 1.645
C -0.248 -2.416 -1.485
C -0.237 -2.107 -2.820
H 0.029 -1.151 -3.246
C -0.670 -3.276 -3.522
H -0.782 -3.396 -4.590
C -0.918 -4.217 -2.567
H -1.257 -5.241 -2.605
C -1.233 -1.603 1.132
C -2.517 -1.126 0.797
C -3.536 -1.175 1.780
C -3.280 -1.673 3.061
H -4.061 -1.704 3.810
C -2.001 -2.131 3.373
H -1.800 -2.520 4.367
C -0.985 -2.098 2.424
H 0.001 -2.460 2.689
C -5.821 -0.712 2.331
H -6.056 -1.727 2.670
H -6.683 -0.299 1.807
H -5.590 -0.083 3.200
C 1.495 -2.452 0.699
C 3.226 -2.729 2.042
H 3.915 -2.384 2.798
C 3.076 -3.906 1.371
H 3.686 -4.791 1.481
C 1.952 -3.729 0.503
H 1.528 -4.456 -0.172
C 2.598 0.574 -1.797
C 1.776 2.818 0.483
C 2.786 2.156 1.224
C 4.155 2.165 0.925
H 2.466 1.579 2.092
C 3.764 0.127 -1.196
C 4.828 0.970 -0.816
H 2.097 3.461 -0.338
H 0.922 3.213 1.030
H 1.959 -0.147 -2.297
H 2.579 1.581 -2.212
H 4.837 1.715 1.639
H 4.555 3.028 0.403
H 4.899 1.894 -1.382
C 6.130 0.461 -0.349
H 3.812 -0.925 -0.915
C 7.293 1.228 -0.560
C 6.276 -0.765 0.333
C 7.527 -1.205 0.763
C 8.544 0.790 -0.126
C 8.671 -0.433 0.537
H 9.422 1.404 -0.309

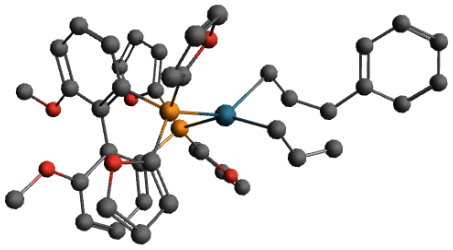
H 9.644 -0.778 0.876
H 5.402 -1.376 0.538
H 7.609 -2.156 1.283
H 7.209 2.179 -1.082

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -383.4892 | 16.3957 | 18.4342 |
| Red. masses -- | 10.4803 | 6.0149 | 5.9958 |

ZERO-POINT CORRECTION= 0.693895 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.753725
Thermal correction to Enthalpy= 0.754781
Thermal correction to Gibbs Free Energy= 0.589596
Sum of electronic and zero-point Energies= -2883.298986
Sum of electronic and thermal Energies= -2883.239155
Sum of electronic and thermal Enthalpies= -2883.238100
Sum of electronic and thermal Free Energies= -2883.403285

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000000 | 0.000450 | YES |
| RMS FORCE | 0.000000 | 0.000300 | YES |

---



***trans*-TS$_{3,3'}$ *Re b***

---
Cartesian coordinates (Angstroms):
---
Pd -1.083 0.422 -0.175
P 0.857 1.834 0.078
O 2.915 3.090 -1.307
O 4.425 -1.730 1.309
O -0.515 3.471 1.771
C 1.745 2.368 -1.411
C 1.433 2.203 -2.734
H 0.577 1.669 -3.119
C 2.459 2.855 -3.488
H 2.540 2.925 -4.563
C 3.328 3.370 -2.573
H 4.243 3.937 -2.656
C 2.151 1.111 1.190
C 2.875 -0.035 0.805
C 3.747 -0.633 1.747
C 3.881 -0.112 3.038
H 4.546 -0.574 3.757
C 3.146 1.016 3.400
H 3.251 1.424 4.402
C 2.287 1.625 2.492
H 1.726 2.501 2.794
C 5.321 -2.380 2.203
H 6.127 -1.710 2.525
H 5.749 -3.213 1.643
H 4.797 -2.769 3.084
C 0.491 3.456 0.828
C -0.684 4.763 2.166
H -1.443 4.931 2.914
C 0.178 5.582 1.499
H 0.261 6.654 1.608
C 0.941 4.736 0.633
H 1.729 5.033 -0.042
P 0.231 -1.679 -0.095
O 1.581 -3.520 1.491
O 4.921 0.425 -0.889
O -1.398 -2.830 -1.949
C 0.740 -2.428 1.476
C 0.399 -2.105 2.763
H -0.231 -1.280 3.061
C 1.058 -3.043 3.617
H 1.018 -3.090 4.696
C 1.759 -3.873 2.794
H 2.399 -4.725 2.968
C 1.804 -1.450 -1.057
C 2.839 -0.623 -0.576
C 3.953 -0.375 -1.417
C 4.026 -0.927 -2.699
H 4.878 -0.733 -3.339
C 2.985 -1.734 -3.157
H 3.040 -2.164 -4.152
C 1.883 -1.995 -2.350
H 1.086 -2.624 -2.727
C 6.059 0.734 -1.686
H 6.620 -0.169 -1.956
H 6.688 1.377 -1.070
H 5.775 1.271 -2.598
C -0.553 -3.119 -0.897
C -1.939 -4.006 -2.372
H -2.621 -3.938 -3.205
C -1.476 -5.042 -1.617
H -1.740 -6.085 -1.724
C -0.577 -4.469 -0.663
H -0.012 -4.989 0.096
C -2.963 -0.418 1.083
C -2.325 1.977 -1.073
C -2.988 1.110 -1.984
C -4.327 0.726 -1.883
H -2.406 0.725 -2.821
C -3.681 -1.237 0.227
C -4.878 -0.961 -0.476
H -2.940 2.462 -0.314
H -1.550 2.626 -1.476
H -2.210 -0.862 1.728
H -3.380 0.521 1.435
H -4.792 0.226 -2.727
H -4.990 1.352 -1.298
C -6.104 -0.340 0.064
H -5.111 -1.700 -1.242
H -3.176 -2.155 -0.070
C -7.269 -0.355 -0.735
C -6.213 0.249 1.341
C -7.415 0.803 1.782

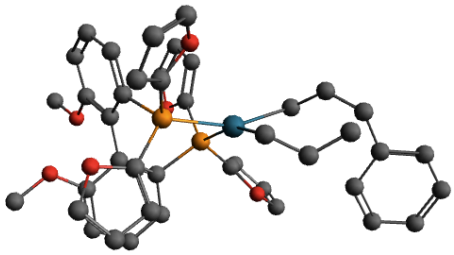
C -8.469 0.200 -0.295
C -8.551 0.790 0.970
H -9.484 1.223 1.318
H -9.344 0.168 -0.940
H -7.224 -0.815 -1.720
H -5.358 0.249 2.006
H -7.463 1.243 2.775

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -370.0475 | 14.7095 | 16.9664 |
| Red. masses -- | 8.6478 | 6.1878 | 5.7703 |

ZERO-POINT CORRECTION= 0.694058 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.753819
Thermal correction to Enthalpy= 0.754874
Thermal correction to Gibbs Free Energy= 0.589810
Sum of electronic and zero-point Energies= -2883.290741
Sum of electronic and thermal Energies= -2883.230980
Sum of electronic and thermal Enthalpies= -2883.229925
Sum of electronic and thermal Free Energies= -2883.394989

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000001 | 0.000450 | YES |
| RMS FORCE | 0.000000 | 0.000300 | YES |

---



**$TS_{3,3'}$ *Re c***

---
Cartesian coordinates (Angstroms):
---
Pd 1.087 0.717 -0.357
P -1.108 1.768 -0.073
O -2.930 2.642 1.838
O -4.278 -2.318 -0.593
O -0.524 3.626 -1.978
C -1.675 2.117 1.613
C -1.027 1.970 2.811
H -0.033 1.570 2.945
C -1.924 2.425 3.828
H -1.748 2.453 4.894
C -3.058 2.818 3.182
H -3.999 3.228 3.516
C -2.497 0.846 -0.883
C -2.927 -0.403 -0.390
C -3.901 -1.123 -1.127
C -4.420 -0.616 -2.322
H -5.162 -1.170 -2.883
C -3.972 0.616 -2.795
H -4.376 1.012 -3.723
C -3.020 1.343 -2.090
H -2.685 2.297 -2.477
C -5.252 -3.094 -1.282
H -6.206 -2.560 -1.369
H -5.396 -3.993 -0.681
H -4.904 -3.379 -2.282
C -1.220 3.435 -0.803
C -0.680 4.932 -2.335
H -0.191 5.231 -3.250
C -1.446 5.588 -1.420
H -1.727 6.631 -1.446
C -1.798 4.619 -0.428
H -2.411 4.774 0.448
P 0.105 -1.546 -0.209
O -1.294 -3.475 -1.643
O -4.559 -0.339 1.758
O 2.254 -2.535 1.147
C -0.621 -2.274 -1.702
C -0.585 -1.841 -3.002
H -0.134 -0.923 -3.349
C -1.271 -2.821 -3.786
H -1.440 -2.806 -4.853
C -1.679 -3.783 -2.912
H -2.225 -4.708 -3.026
C -1.217 -1.621 1.090
C -2.465 -0.991 0.910
C -3.371 -0.960 1.999
C -3.039 -1.533 3.230
H -3.734 -1.505 4.060
C -1.796 -2.145 3.387
H -1.537 -2.592 4.342
C -0.890 -2.189 2.334
H 0.072 -2.666 2.480
C -5.510 -0.253 2.813
H -5.828 -1.246 3.152
H -6.368 0.277 2.398
H -5.114 0.312 3.665
C 1.248 -2.885 0.269
C 3.032 -3.638 1.332
H 3.871 -3.514 1.999
C 2.563 -4.682 0.595
H 2.987 -5.675 0.544
C 1.407 -4.196 -0.094
H 0.767 -4.748 -0.765
C 2.879 -0.231 -1.452
C 1.996 2.720 0.213
C 3.341 2.617 0.640
C 4.445 2.887 -0.160
H 3.522 2.227 1.642
H 4.299 3.475 -1.062
H 5.425 2.978 0.297
C 3.831 0.701 -1.893
C 5.029 1.098 -1.279
H 3.567 1.269 -2.786
C 5.787 0.329 -0.265
H 5.679 1.691 -1.920
H 1.809 3.323 -0.675
H 1.275 2.896 1.009
H 3.190 -0.992 -0.743

H 2.202 -0.595 -2.223
C 7.190 0.261 -0.382
C 5.195 -0.315 0.841
C 7.968 -0.432 0.543
C 5.976 -1.003 1.772
C 7.364 -1.073 1.628
H 5.496 -1.478 2.624
H 7.966 -1.612 2.354
H 7.672 0.759 -1.220
H 9.047 -0.470 0.419
H 4.125 -0.250 0.990

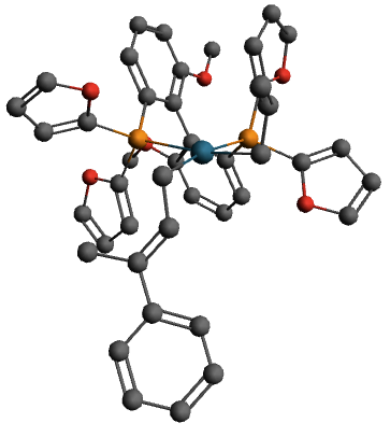
| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -368.6048 | 10.4918 | 20.0106 |
| Red. masses -- | 11.3121 | 6.0004 | 5.8267 |

ZERO-POINT CORRECTION= 0.694848 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.754340
Thermal correction to Enthalpy= 0.755395
Thermal correction to Gibbs Free Energy= 0.591290
Sum of electronic and zero-point Energies= -2883.298581
Sum of electronic and thermal Energies= -2883.239090
Sum of electronic and thermal Enthalpies= -2883.238035
Sum of electronic and thermal Free Energies= -2883.402139

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000009 | 0.000450 | YES |
| RMS FORCE | 0.000002 | 0.000300 | YES |

---

## ***Structures and Energies from Table 2***



**GS 13**

---
Cartesian coordinates (Angstroms):
---
Pd 0.787 0.814 1.159
C 2.602 0.153 2.102
P -0.026 -1.457 0.783
O -0.030 -3.489 -1.103
O -4.772 -0.551 -1.154
O 0.500 -2.263 3.338
C 0.511 -2.275 -0.738
C 1.454 -1.901 -1.658
H 2.043 -0.996 -1.624
C 1.501 -2.935 -2.644
H 2.130 -2.976 -3.521
C 0.583 -3.866 -2.258
H 0.262 -4.810 -2.674
C -1.879 -1.577 0.804
C -2.663 -1.058 -0.244
C -4.074 -1.067 -0.106
C -4.680 -1.576 1.047
H -5.758 -1.583 1.149
C -3.884 -2.076 2.075
H -4.353 -2.470 2.972
C -2.497 -2.076 1.964
H -1.901 -2.463 2.780
C -6.193 -0.519 -1.078
H -6.615 -1.527 -0.989
H -6.531 -0.068 -2.012
H -6.535 0.093 -0.236
C 0.477 -2.689 2.028
C 0.925 -3.312 4.097
H 0.992 -3.127 5.158
C 1.182 -4.395 3.313
H 1.537 -5.361 3.644
C 0.890 -3.994 1.970
H 0.964 -4.595 1.077
P -1.057 1.740 -0.160
O -3.726 2.470 0.026
O -2.878 -2.530 -2.505
O 0.506 3.623 -1.369
C -2.617 2.024 0.711
C -2.925 1.892 2.039
H -2.252 1.546 2.809
C -4.294 2.277 2.186
H -4.876 2.296 3.096
C -4.727 2.614 0.938
H -5.670 2.965 0.548
C -1.469 0.717 -1.654
C -2.097 -0.537 -1.530
C -2.263 -1.330 -2.693
C -1.812 -0.883 -3.938
H -1.941 -1.491 -4.825
C -1.186 0.359 -4.035
H -0.835 0.707 -5.002
C -1.010 1.154 -2.908
H -0.514 2.111 -3.008
C -3.086 -3.374 -3.631
H -3.723 -2.893 -4.383
H -3.589 -4.263 -3.249
H -2.136 -3.667 -4.094
C -0.753 3.396 -0.856
C 0.545 4.919 -1.789
H 1.478 5.244 -2.225
C -0.648 5.532 -1.553
H -0.899 6.559 -1.779
C -1.491 4.546 -0.949
H -2.516 4.669 -0.635
C 1.405 2.758 1.838
C 0.708 3.019 3.111
H 1.106 3.450 1.049

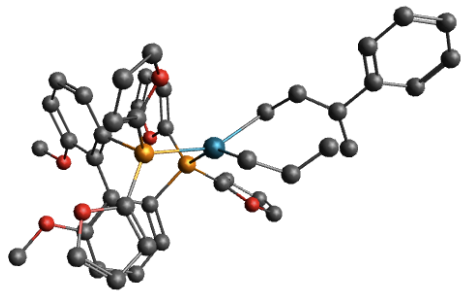
H 2.492 2.775 1.949
C 1.256 3.041 4.341
H -0.365 3.206 3.034
C 3.679 0.390 1.135
H 2.491 -0.885 2.413
H 2.668 0.798 2.980
C 4.423 -0.506 0.425
H 3.912 1.442 0.975
C 5.437 -0.036 -0.549
C 4.308 -2.001 0.627
C 6.549 -0.836 -0.888
C 5.334 1.218 -1.193
C 6.302 1.658 -2.093
C 7.518 -0.397 -1.792
C 7.406 0.856 -2.398
H 8.365 -1.038 -2.020
H 8.157 1.196 -3.105
H 6.669 -1.811 -0.428
H 4.468 1.845 -1.003
H 6.186 2.628 -2.571
H 0.657 3.221 5.229
H 2.322 2.884 4.493
H 4.270 -2.534 -0.330
H 3.413 -2.269 1.190
H 5.170 -2.403 1.179

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 8.1110 | 10.2300 | 18.4193 |
| Red. masses -- | 6.1703 | 6.0706 | 6.0566 |

ZERO-POINT CORRECTION= 0.723508 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.785613
Thermal correction to Enthalpy= 0.786668
Thermal correction to Gibbs Free Energy= 0.615473
Sum of electronic and zero-point Energies= -2922.610382
Sum of electronic and thermal Energies= -2922.548277
Sum of electronic and thermal Enthalpies= -2922.547222
Sum of electronic and thermal Free Energies= -2922.718418

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000011 | 0.000450 | YES |
| RMS FORCE | 0.000001 | 0.000300 | YES |

---



**$TS_{3,3'}$ 13**

---

Cartesian coordinates (Angstroms):

---

Pd -0.958 0.228 -0.215
P 0.534 -1.730 -0.064
O 1.995 -3.392 1.622
O 5.065 0.695 -0.864
O -0.974 -3.071 -1.894
C 1.062 -2.380 1.544
C 0.652 -2.049 2.809
H -0.063 -1.278 3.059
C 1.364 -2.896 3.714
H 1.293 -2.912 4.792
C 2.162 -3.685 2.941
H 2.871 -4.469 3.163
C 2.099 -1.413 -1.011
C 3.065 -0.500 -0.541
C 4.166 -0.190 -1.379
C 4.292 -0.764 -2.647
H 5.134 -0.523 -3.284
C 3.319 -1.658 -3.093
H 3.417 -2.107 -4.077
C 2.232 -1.981 -2.289
H 1.487 -2.676 -2.657
C 6.175 1.083 -1.666
H 6.813 0.227 -1.915
H 6.744 1.792 -1.064
H 5.848 1.573 -2.591
C -0.123 -3.253 -0.823
C -1.405 -4.302 -2.286
H -2.080 -4.319 -3.127
C -0.866 -5.270 -1.493
H -1.038 -6.335 -1.570
C -0.034 -4.593 -0.547
H 0.563 -5.038 0.235
P 0.882 1.803 0.035
O 2.811 3.261 -1.340
O 4.725 -1.423 1.378
O -0.652 3.314 1.698
C 1.744 2.394 -1.447
C 1.503 2.139 -2.772
H 0.736 1.483 -3.157
C 2.466 2.884 -3.522
H 2.575 2.921 -4.596
C 3.230 3.541 -2.605
H 4.069 4.216 -2.684
C 2.215 1.208 1.178
C 3.040 0.121 0.824
C 3.952 -0.378 1.787
C 4.031 0.183 3.065
H 4.727 -0.203 3.798
C 3.198 1.251 3.396
H 3.259 1.689 4.388
C 2.296 1.761 2.468
H 1.659 2.592 2.746
C 5.671 -1.968 2.290
H 6.412 -1.221 2.597
H 6.174 -2.773 1.753
H 5.181 -2.380 3.180
C 0.360 3.390 0.764

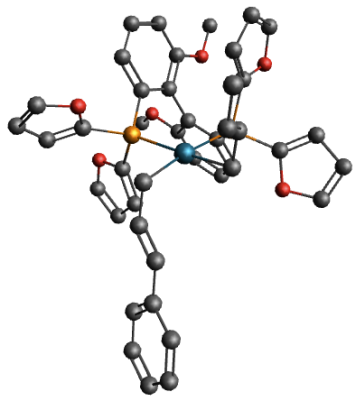
C -0.946 4.586 2.084
H -1.724 4.685 2.825
C -0.161 5.479 1.419
H -0.181 6.555 1.521
C 0.687 4.705 0.565
H 1.449 5.073 -0.105
C -2.163 1.837 -1.205
C -2.691 -1.104 0.620
C -3.939 -0.485 0.707
C -4.974 -0.556 -0.252
H -4.102 0.160 1.569
C -4.863 -1.632 -1.318
C -6.347 -0.156 0.181
C -3.206 1.227 -1.942
C -4.534 1.186 -1.527
H -2.936 0.716 -2.867
H -4.858 1.893 -0.771
H -5.303 0.901 -2.240
H -2.576 -1.961 -0.035
H -2.125 -1.169 1.548
H -2.459 2.521 -0.409
H -1.328 2.207 -1.798
H -5.039 -2.634 -0.903
H -3.865 -1.629 -1.761
H -5.581 -1.479 -2.129
C -6.565 0.937 1.049
C -7.488 -0.854 -0.261
C -8.773 -0.489 0.149
C -7.845 1.301 1.459
C -8.963 0.590 1.012
H -9.627 -1.058 -0.209
H -9.962 0.875 1.329
H -7.377 -1.706 -0.922
H -5.719 1.520 1.402
H -7.971 2.150 2.126

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -362.1616 | 10.8408 | 14.3521 |
| Red. masses -- | 10.1572 | 6.0517 | 6.3391 |

ZERO-POINT CORRECTION= 0.722591 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.783915
Thermal correction to Enthalpy= 0.784970
Thermal correction to Gibbs Free Energy= 0.616842
Sum of electronic and zero-point Energies= -2922.587111
Sum of electronic and thermal Energies= -2922.525787
Sum of electronic and thermal Enthalpies= -2922.524732
Sum of electronic and thermal Free Energies= -2922.692860

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000000 | 0.000450 | YES |
| RMS FORCE | 0.000000 | 0.000300 | YES |

---



**GS 14**

---
Cartesian coordinates (Angstroms):
---
Pd 0.970 0.841 0.695
C 2.713 0.301 1.837
P -0.151 -1.309 1.111
O -0.524 -3.793 -0.065
O -4.915 -0.320 -0.732
O 0.479 -1.445 3.768
C 0.147 -2.592 -0.128
C 1.019 -2.613 -1.184
H 1.668 -1.803 -1.482
C 0.880 -3.892 -1.809
H 1.410 -4.260 -2.676
C -0.066 -4.561 -1.092
H -0.503 -5.545 -1.174
C -1.994 -1.150 1.276
C -2.808 -0.857 0.166
C -4.185 -0.598 0.383
C -4.729 -0.633 1.670
H -5.781 -0.437 1.833
C -3.902 -0.921 2.755
H -4.323 -0.949 3.756
C -2.548 -1.174 2.568
H -1.926 -1.385 3.428
C -6.306 -0.055 -0.589
H -6.837 -0.912 -0.159
H -6.679 0.131 -1.597
H -6.483 0.831 0.032
C 0.331 -2.202 2.625
C 0.887 -2.285 4.761
H 1.041 -1.830 5.727
C 1.014 -3.556 4.288
H 1.326 -4.424 4.850
C 0.653 -3.504 2.904
H 0.623 -4.328 2.207
P -0.845 1.538 -0.788
O -3.374 2.667 -0.666
O -3.450 -2.915 -1.458
O 0.774 2.665 -2.677
C -2.243 2.329 0.043
C -2.388 2.725 1.347

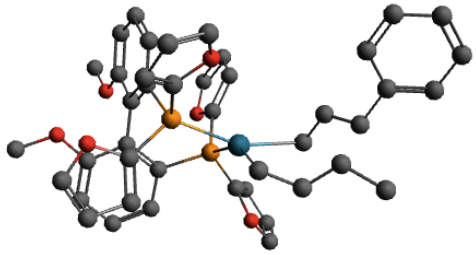
H -1.661 2.583 2.132
C -3.675 3.339 1.451
H -4.129 3.767 2.333
C -4.226 3.274 0.205
H -5.168 3.600 -0.208
C -1.552 0.169 -1.823
C -2.321 -0.863 -1.252
C -2.712 -1.951 -2.073
C -2.347 -2.003 -3.421
H -2.649 -2.834 -4.046
C -1.581 -0.972 -3.962
H -1.295 -1.011 -5.009
C -1.180 0.103 -3.176
H -0.576 0.884 -3.618
C -3.866 -4.045 -2.218
H -4.515 -3.754 -3.053
H -4.427 -4.677 -1.529
H -3.006 -4.605 -2.605
C -0.425 2.817 -2.016
C 0.920 3.740 -3.504
H 1.822 3.756 -4.097
C -0.145 4.580 -3.385
H -0.293 5.509 -3.915
C -1.019 3.983 -2.422
H -1.971 4.362 -2.082
C 1.951 2.738 0.552
C 1.531 3.587 1.684
H 1.636 3.148 -0.409
H 3.026 2.553 0.532
C 2.282 3.960 2.739
H 0.496 3.940 1.658
C 3.651 -0.344 0.916
H 2.328 -0.380 2.596
H 3.103 1.207 2.302
C 4.797 0.197 0.427
H 3.377 -1.350 0.595
C 5.725 -0.408 -0.530
H 5.082 1.189 0.779
C 6.907 0.286 -0.870
C 5.516 -1.663 -1.144
C 6.441 -2.190 -2.041
C 7.831 -0.242 -1.770
C 7.606 -1.486 -2.363
H 8.730 0.321 -2.008
H 8.324 -1.900 -3.065
H 7.094 1.256 -0.414
H 4.618 -2.231 -0.919
H 6.250 -3.159 -2.497
C 1.800 4.804 3.885
H 3.325 3.640 2.779
H 2.396 5.721 3.995
H 1.877 4.272 4.844
H 0.754 5.099 3.751

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 7.7735 | 12.1856 | 17.2224 |
| Red. masses -- | 6.0466 | 5.9485 | 6.0012 |

ZERO-POINT CORRECTION= 0.723520 (HARTREE/PARTICLE)

Thermal correction to Energy= 0.785765
Thermal correction to Enthalpy= 0.786820
Thermal correction to Gibbs Free Energy= 0.613584
Sum of electronic and zero-point Energies= -2922.616194
Sum of electronic and thermal Energies= -2922.553950
Sum of electronic and thermal Enthalpies= -2922.552895
Sum of electronic and thermal Free Energies= -2922.726130

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000003 | 0.000450 | YES |
| RMS FORCE | 0.000000 | 0.000300 | YES |



**$TS_{3,3'}$ 14**

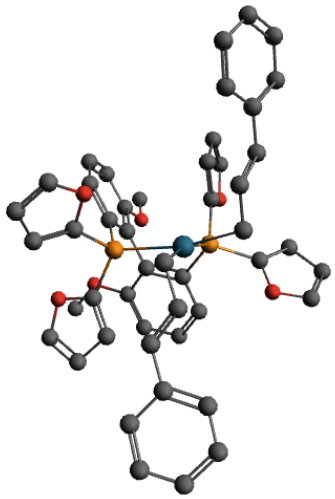
---
Cartesian coordinates (Angstroms):
---
Pd 0.945 0.283 -0.641
P -0.927 1.807 -0.210
O -2.296 3.161 1.799
O -4.856 -1.591 -0.107
O -0.145 3.397 -2.276
C -1.214 2.364 1.492
C -0.474 2.153 2.626
H 0.425 1.557 2.690
C -1.130 2.852 3.687
H -0.828 2.904 4.724
C -2.226 3.440 3.130
H -3.016 4.062 3.523
C -2.559 1.149 -0.797
C -3.157 0.034 -0.176
C -4.325 -0.518 -0.757
C -4.873 0.022 -1.925
H -5.765 -0.403 -2.368
C -4.260 1.120 -2.526
H -4.686 1.542 -3.431
C -3.113 1.681 -1.974
H -2.651 2.533 -2.457
C -6.030 -2.196 -0.636
H -6.870 -1.492 -0.663
H -6.271 -3.018 0.039
H -5.857 -2.594 -1.643
C -0.776 3.419 -1.050
C -0.066 4.683 -2.716
H 0.404 4.824 -3.677
C -0.618 5.534 -1.806
H -0.688 6.609 -1.889
C -1.080 4.715 -0.727
H -1.581 5.042 0.172
P -0.404 -1.693 -0.202

O -2.307 -3.405 -1.282
O -4.496 0.545 2.109
O 1.675 -2.984 0.998
C -1.433 -2.370 -1.534
C -1.486 -2.050 -2.865
H -0.920 -1.268 -3.350
C -2.439 -2.929 -3.468
H -2.738 -2.961 -4.505
C -2.904 -3.725 -2.463
H -3.623 -4.529 -2.425
C -1.559 -1.417 1.224
C -2.674 -0.562 1.114
C -3.429 -0.284 2.282
C -3.077 -0.834 3.518
H -3.656 -0.617 4.407
C -1.964 -1.670 3.603
H -1.689 -2.099 4.562
C -1.209 -1.960 2.473
H -0.345 -2.607 2.563
C -5.281 0.892 3.244
H -5.748 0.010 3.698
H -6.060 1.561 2.875
H -4.683 1.415 3.999
C 0.516 -3.193 0.279
C 2.245 -4.203 1.213
H 3.167 -4.198 1.775
C 1.495 -5.187 0.645
H 1.710 -6.246 0.653
C 0.374 -4.535 0.041
H -0.441 -4.999 -0.494
C 2.306 -0.985 -1.985
C 2.428 1.957 -0.235
C 3.484 1.250 0.360
C 4.755 1.049 -0.226
H 3.314 0.842 1.355
C 3.420 -0.280 -2.455
C 4.699 -0.349 -1.889
H 3.262 0.444 -3.258
H 4.883 -1.202 -1.237
C 5.898 0.114 -2.686
H 2.627 2.486 -1.166
H 1.756 2.487 0.434
H 2.496 -1.858 -1.363
H 1.469 -1.097 -2.674
C 5.850 0.492 0.599
H 5.070 1.822 -0.922
C 5.641 -0.600 1.467
C 6.677 -1.110 2.246
C 7.959 -0.555 2.174
C 7.149 1.033 0.534
C 8.189 0.518 1.310
H 9.179 0.962 1.244
H 8.767 -0.957 2.778
H 4.655 -1.053 1.518
H 6.487 -1.952 2.908
H 7.336 1.880 -0.121
H 6.757 0.339 -2.046
H 5.663 1.011 -3.270
H 6.221 -0.661 -3.394

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -391.4001 | 8.9269 | 13.0622 |
| Red. masses -- | 9.0631 | 6.1003 | 6.2120 |

ZERO-POINT CORRECTION= 0.722280 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.783724
Thermal correction to Enthalpy= 0.784779
Thermal correction to Gibbs Free Energy= 0.615855
Sum of electronic and zero-point Energies= -2922.592023
Sum of electronic and thermal Energies= -2922.530580
Sum of electronic and thermal Enthalpies= -2922.529525
Sum of electronic and thermal Free Energies= -2922.698448

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000018 | 0.000450 | YES |
| RMS FORCE | 0.000002 | 0.000300 | YES |



**GS 15**

---
Cartesian coordinates (Angstroms):
---
Pd 0.011 -1.321 0.018
C 0.985 -2.916 -1.044
P 0.751 0.372 -1.579
O 2.754 2.191 -2.158
O -1.598 4.581 0.369
O -0.137 -1.075 -3.719
C 2.392 1.106 -1.389
C 3.448 0.735 -0.600
H 3.456 -0.092 0.096
C 4.519 1.636 -0.894
H 5.507 1.644 -0.457
C 4.042 2.494 -1.839
H 4.471 3.333 -2.366
C -0.441 1.791 -1.663
C -0.538 2.728 -0.616
C -1.558 3.709 -0.676
C -2.455 3.750 -1.747

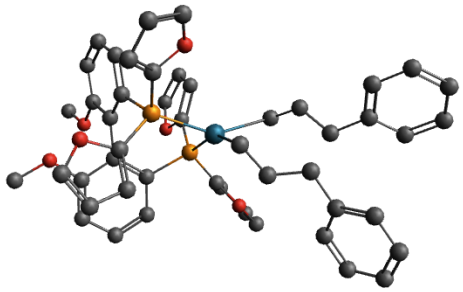
H -3.233 4.502 -1.790
C -2.345 2.807 -2.768
H -3.042 2.836 -3.600
C -1.353 1.833 -2.731
H -1.295 1.106 -3.532
C -2.609 5.583 0.382
H -2.522 6.257 -0.478
H -2.453 6.151 1.300
H -3.611 5.139 0.397
C 0.847 -0.205 -3.305
C 0.142 -1.418 -5.008
H -0.553 -2.099 -5.475
C 1.280 -0.799 -5.430
H 1.740 -0.891 -6.404
C 1.738 -0.011 -4.327
H 2.609 0.627 -4.297
P -0.729 0.394 1.595
O -2.801 2.106 2.253
O 1.342 4.668 -0.513
O 0.324 -1.000 3.688
C -2.412 1.044 1.464
C -3.468 0.637 0.694
H -3.456 -0.180 -0.012
C -4.569 1.489 1.022
H -5.566 1.459 0.607
C -4.107 2.357 1.966
H -4.560 3.171 2.512
C 0.380 1.882 1.623
C 0.415 2.783 0.540
C 1.363 3.835 0.562
C 2.252 3.978 1.632
H 2.976 4.784 1.647
C 2.206 3.069 2.688
H 2.896 3.179 3.519
C 1.284 2.028 2.688
H 1.270 1.332 3.518
C 2.261 5.753 -0.555
H 2.109 6.443 0.284
H 2.063 6.276 -1.491
H 3.299 5.400 -0.551
C -0.715 -0.172 3.326
C 0.131 -1.345 4.992
H 0.877 -1.995 5.422
C -1.005 -0.769 5.474
H -1.406 -0.873 6.473
C -1.555 -0.006 4.395
H -2.450 0.597 4.411
C -0.961 -2.903 1.105
C -2.138 -3.244 0.303
H -1.214 -2.558 2.109
H -0.225 -3.708 1.155
C -3.424 -2.937 0.613
H -1.942 -3.783 -0.624
C 2.183 -3.212 -0.255
H 1.209 -2.592 -2.061
H 0.267 -3.738 -1.059
C 3.455 -2.874 -0.589
H 2.015 -3.744 0.682
C 4.670 -3.122 0.188
C 5.924 -2.815 -0.385
C 4.671 -3.658 1.495
C 5.861 -3.883 2.181
C 7.115 -3.038 0.304
C 7.094 -3.577 1.592
H 8.063 -2.792 -0.168
H 8.019 -3.752 2.132
H 5.953 -2.399 -1.389
H 3.729 -3.895 1.981
H 5.829 -4.297 3.186
C -4.620 -3.223 -0.181
C -5.890 -2.944 0.368
C -4.585 -3.765 -1.485
C -7.064 -3.199 -0.338
C -5.758 -4.022 -2.190
C -7.007 -3.743 -1.624
H -5.946 -2.522 1.369
H -7.919 -3.943 -2.179
H -8.025 -2.973 0.116
H -3.630 -3.981 -1.955
H -5.699 -4.440 -3.192
H 3.613 -2.372 -1.543
H -3.610 -2.429 1.559

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 7.6804 | 13.8369 | 14.2759 |
| Red. masses -- | 6.3645 | 6.0458 | 6.1045 |

ZERO-POINT CORRECTION= 0.776603 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.842697
Thermal correction to Enthalpy= 0.843752
Thermal correction to Gibbs Free Energy= 0.661198
Sum of electronic and zero-point Energies= -3114.310616
Sum of electronic and thermal Energies= -3114.244522
Sum of electronic and thermal Enthalpies= -3114.243467
Sum of electronic and thermal Free Energies= -3114.426022

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000015 | 0.000450 | YES |
| RMS FORCE | 0.000002 | 0.000300 | YES |

---



**$TS_{3,3'}$ 15**

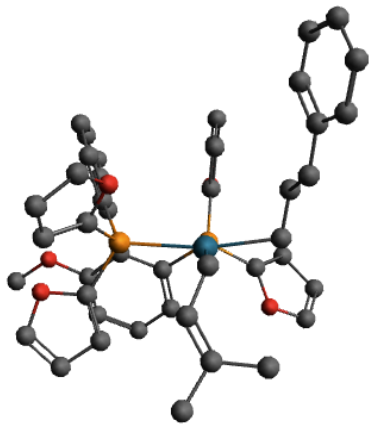
---
Cartesian coordinates (Angstroms):
---
Pd 0.488 0.305 -0.207
P -1.382 1.817 0.173
O -3.013 2.909 2.144

O -5.344 -1.356 -0.925
O -0.209 3.676 -1.429
C -1.932 2.095 1.880
C -1.422 1.628 3.063
H -0.583 0.955 3.165
C -2.223 2.180 4.110
H -2.111 2.026 5.174
C -3.170 2.945 3.496
H -3.986 3.551 3.859
C -2.917 1.354 -0.759
C -3.618 0.170 -0.452
C -4.705 -0.207 -1.279
C -5.071 0.568 -2.384
H -5.901 0.276 -3.017
C -4.357 1.729 -2.674
H -4.642 2.333 -3.531
C -3.288 2.122 -1.875
H -2.747 3.029 -2.116
C -6.439 -1.799 -1.717
H -7.254 -1.065 -1.727
H -6.791 -2.721 -1.251
H -6.129 -2.011 -2.747
C -1.055 3.532 -0.349
C -0.040 5.010 -1.639
H 0.601 5.280 -2.465
C -0.744 5.731 -0.721
H -0.788 6.808 -0.645
C -1.404 4.774 0.113
H -2.061 4.975 0.945
P -0.928 -1.651 -0.457
O -2.695 -3.000 -2.125
O -5.241 0.305 1.697
O 0.978 -3.260 0.644
C -1.772 -1.980 -2.029
C -1.626 -1.390 -3.257
H -0.982 -0.553 -3.484
C -2.499 -2.077 -4.157
H -2.646 -1.878 -5.209
C -3.121 -3.038 -3.417
H -3.854 -3.796 -3.649
C -2.266 -1.606 0.826
C -3.332 -0.686 0.747
C -4.234 -0.601 1.837
C -4.073 -1.402 2.972
H -4.765 -1.332 3.802
C -3.008 -2.300 3.030
H -2.882 -2.925 3.909
C -2.110 -2.403 1.974
H -1.288 -3.106 2.041
C -6.179 0.452 2.757
H -6.724 -0.480 2.947
H -6.882 1.219 2.429
H -5.690 0.782 3.681
C -0.125 -3.267 -0.186
C 1.465 -4.531 0.682
H 2.336 -4.682 1.301
C 0.716 -5.354 -0.103
H 0.876 -6.411 -0.266
C -0.315 -4.537 -0.665
H -1.104 -4.846 -1.333
C 2.026 -0.653 -1.718
C 1.907 1.684 0.899
C 2.797 0.707 1.357
C 4.150 0.585 0.933
H 2.445 0.028 2.132
C 3.169 0.128 -1.779
C 4.358 -0.159 -1.064
H 3.125 1.047 -2.362
H 4.449 -1.192 -0.732
C 5.642 0.449 -1.477
H 2.280 2.454 0.226
H 1.143 2.030 1.590
H 2.106 -1.661 -1.318
H 1.268 -0.513 -2.485
C 5.056 -0.306 1.692
H 4.611 1.519 0.620
C 4.642 -1.578 2.137
C 5.502 -2.402 2.862
C 6.805 -1.984 3.154
C 6.375 0.091 1.981
C 7.236 -0.733 2.706
H 8.246 -0.396 2.923
H 7.474 -2.627 3.718
H 3.639 -1.923 1.903
H 5.157 -3.377 3.197
H 6.719 1.064 1.641
C 5.740 1.790 -1.901
C 6.827 -0.309 -1.435
C 8.052 0.237 -1.822
C 8.127 1.563 -2.255
C 6.962 2.336 -2.289
H 9.079 1.990 -2.556
H 7.007 3.372 -2.615
H 6.780 -1.343 -1.104
H 8.948 -0.376 -1.786
H 4.850 2.413 -1.922

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -370.6500 | 8.9657 | 13.0828 |
| Red. masses -- | 10.9148 | 6.0021 | 5.9060 |

ZERO-POINT CORRECTION= 0.775519 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.840993
Thermal correction to Enthalpy= 0.842048
Thermal correction to Gibbs Free Energy= 0.662960
Sum of electronic and zero-point Energies= -3114.281630
Sum of electronic and thermal Energies= -3114.216156
Sum of electronic and thermal Enthalpies= -3114.215101
Sum of electronic and thermal Free Energies= -3114.394189

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000020 | 0.000450 | YES |
| RMS FORCE | 0.000002 | 0.000300 | YES |



**GS 16**

---
Cartesian coordinates (Angstroms):
---

| | | | |
|---|---|---|---|
| Pd | 1.027 | 0.481 | 0.724 |
| C | 2.636 | -0.469 | 1.810 |
| P | -0.530 | -1.357 | 1.218 |
| O | -1.274 | -3.904 | 0.413 |
| O | -4.850 | 0.219 | -1.194 |
| O | -0.051 | -1.132 | 3.890 |
| C | -0.400 | -2.858 | 0.215 |
| C | 0.490 | -3.191 | -0.772 |
| H | 1.279 | -2.556 | -1.149 |
| C | 0.152 | -4.510 | -1.207 |
| H | 0.639 | -5.092 | -1.975 |
| C | -0.922 | -4.890 | -0.458 |
| H | -1.521 | -5.787 | -0.420 |
| C | -2.322 | -0.874 | 1.184 |
| C | -2.960 | -0.551 | -0.029 |
| C | -4.291 | -0.068 | 0.013 |
| C | -4.959 | 0.095 | 1.230 |
| H | -5.976 | 0.465 | 1.260 |
| C | -4.303 | -0.222 | 2.419 |
| H | -4.821 | -0.096 | 3.365 |
| C | -2.997 | -0.701 | 2.404 |
| H | -2.507 | -0.937 | 3.340 |
| C | -6.189 | 0.702 | -1.229 |
| H | -6.891 | -0.027 | -0.806 |
| H | -6.422 | 0.856 | -2.283 |
| H | -6.287 | 1.653 | -0.693 |
| C | -0.310 | -2.044 | 2.890 |
| C | 0.131 | -1.836 | 5.042 |
| H | 0.340 | -1.249 | 5.923 |
| C | 0.005 | -3.172 | 4.810 |
| H | 0.105 | -3.964 | 5.538 |
| C | -0.283 | -3.309 | 3.415 |
| H | -0.457 | -4.225 | 2.870 |
| P | -0.543 | 1.429 | -0.901 |
| O | -2.893 | 2.876 | -1.154 |
| O | -3.747 | -2.619 | -1.576 |
| O | 1.406 | 2.165 | -2.673 |
| C | -1.887 | 2.482 | -0.299 |
| C | -2.086 | 3.052 | 0.931 |
| H | -1.448 | 2.925 | 1.793 |
| C | -3.278 | 3.836 | 0.835 |
| H | -3.740 | 4.424 | 1.614 |
| C | -3.723 | 3.690 | -0.445 |
| H | -4.571 | 4.082 | -0.986 |
| C | -1.344 | 0.095 | -1.914 |
| C | -2.331 | -0.753 | -1.374 |
| C | -2.799 | -1.836 | -2.159 |
| C | -2.295 | -2.065 | -3.443 |
| H | -2.656 | -2.892 | -4.040 |
| C | -1.314 | -1.217 | -3.954 |
| H | -0.921 | -1.394 | -4.951 |
| C | -0.836 | -0.149 | -3.202 |
| H | -0.067 | 0.488 | -3.618 |
| C | -4.262 | -3.727 | -2.308 |
| H | -4.752 | -3.405 | -3.234 |
| H | -4.999 | -4.198 | -1.656 |
| H | -3.474 | -4.451 | -2.546 |
| C | 0.183 | 2.533 | -2.158 |
| C | 1.787 | 3.137 | -3.549 |
| H | 2.735 | 2.981 | -4.041 |
| C | 0.849 | 4.123 | -3.603 |
| H | 0.889 | 5.017 | -4.208 |
| C | -0.193 | 3.732 | -2.703 |
| H | -1.109 | 4.264 | -2.495 |
| C | 2.334 | 2.171 | 0.628 |
| C | 1.653 | 3.328 | 1.240 |
| H | 2.498 | 2.306 | -0.443 |
| H | 3.271 | 1.897 | 1.108 |
| C | 1.817 | 3.863 | 2.473 |
| H | 0.906 | 3.811 | 0.607 |
| C | 3.588 | -0.959 | 0.811 |
| H | 2.157 | -1.280 | 2.360 |
| H | 3.068 | 0.251 | 2.508 |
| C | 4.817 | -0.447 | 0.542 |
| H | 3.254 | -1.823 | 0.234 |
| C | 5.758 | -0.901 | -0.483 |
| H | 5.171 | 0.379 | 1.159 |
| C | 7.061 | -0.360 | -0.507 |
| C | 5.442 | -1.865 | -1.466 |
| C | 6.384 | -2.271 | -2.408 |
| C | 8.003 | -0.764 | -1.452 |
| C | 7.673 | -1.726 | -2.410 |
| H | 8.998 | -0.326 | -1.440 |
| H | 8.403 | -2.042 | -3.149 |
| H | 7.332 | 0.388 | 0.235 |
| H | 4.445 | -2.294 | -1.499 |
| H | 6.109 | -3.014 | -3.152 |
| C | 1.007 | 5.058 | 2.914 |
| C | 2.787 | 3.343 | 3.503 |
| H | 0.425 | 4.836 | 3.821 |
| H | 0.309 | 5.388 | 2.139 |
| H | 1.654 | 5.909 | 3.171 |
| H | 3.416 | 2.536 | 3.123 |
| H | 2.255 | 2.964 | 4.387 |
| H | 3.445 | 4.145 | 3.863 |

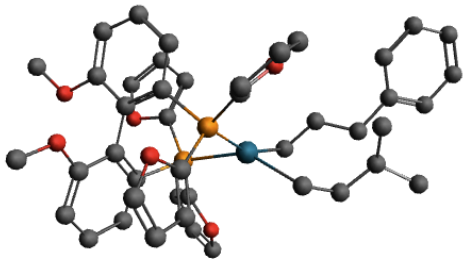
1 2 3

| | A | A | A |
|---|---|---|---|
| Frequencies -- | 10.8508 | 12.2808 | 14.5263 |
| Red. masses -- | 5.8759 | 6.1046 | 5.6659 |

ZERO-POINT CORRECTION= 0.751272 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.815377
Thermal correction to Enthalpy= 0.816432
Thermal correction to Gibbs Free Energy= 0.639731
Sum of electronic and zero-point Energies= -2961.906560
Sum of electronic and thermal Energies= -2961.842455
Sum of electronic and thermal Enthalpies= -2961.841400
Sum of electronic and thermal Free Energies= -2962.018101

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000015 | 0.000450 | YES |
| RMS FORCE | 0.000002 | 0.000300 | YES |

---



**$TS_{3,3'}$ 16**

---
Cartesian coordinates (Angstroms):
---

| | | | |
|---|---|---|---|
| Pd | 0.839 | 0.279 | -0.641 |
| P | -1.042 | 1.807 | -0.318 |
| O | -2.379 | 3.273 | 1.638 |
| O | -4.940 | -1.606 | 0.046 |
| O | -0.361 | 3.262 | -2.514 |
| C | -1.300 | 2.463 | 1.353 |
| C | -0.536 | 2.317 | 2.480 |
| H | 0.365 | 1.726 | 2.557 |
| C | -1.171 | 3.073 | 3.516 |
| H | -0.848 | 3.184 | 4.540 |
| C | -2.280 | 3.627 | 2.949 |
| H | -3.064 | 4.268 | 3.325 |
| C | -2.679 | 1.109 | -0.838 |
| C | -3.255 | 0.023 | -0.148 |
| C | -4.430 | -0.568 | -0.674 |
| C | -5.006 | -0.098 | -1.858 |
| H | -5.902 | -0.554 | -2.258 |
| C | -4.415 | 0.973 | -2.528 |
| H | -4.863 | 1.342 | -3.446 |
| C | -3.263 | 1.572 | -2.031 |
| H | -2.821 | 2.401 | -2.569 |
| C | -6.120 | -2.248 | -0.426 |
| H | -6.965 | -1.551 | -0.476 |
| H | -6.342 | -3.032 | 0.298 |
| H | -5.963 | -2.700 | -1.412 |
| C | -0.920 | 3.365 | -1.257 |
| C | -0.285 | 4.520 | -3.030 |
| H | 0.130 | 4.597 | -4.024 |
| C | -0.768 | 5.431 | -2.140 |
| H | -0.824 | 6.501 | -2.280 |
| C | -1.181 | 4.684 | -0.991 |
| H | -1.626 | 5.071 | -0.086 |
| P | -0.481 | -1.687 | -0.111 |
| O | -2.402 | -3.437 | -1.100 |
| O | -4.557 | 0.668 | 2.118 |
| O | 1.577 | -2.952 | 1.157 |
| C | -1.524 | -2.418 | -1.403 |
| C | -1.588 | -2.154 | -2.746 |
| H | -1.024 | -1.396 | -3.268 |
| C | -2.553 | -3.052 | -3.302 |
| H | -2.863 | -3.125 | -4.334 |
| C | -3.012 | -3.802 | -2.260 |
| H | -3.736 | -4.599 | -2.182 |
| C | -1.626 | -1.338 | 1.309 |
| C | -2.747 | -0.495 | 1.166 |
| C | -3.486 | -0.149 | 2.325 |
| C | -3.116 | -0.624 | 3.586 |
| H | -3.683 | -0.355 | 4.469 |
| C | -1.999 | -1.450 | 3.705 |
| H | -1.710 | -1.822 | 4.684 |
| C | -1.258 | -1.804 | 2.583 |
| H | -0.389 | -2.440 | 2.701 |
| C | -5.326 | 1.081 | 3.241 |
| H | -5.786 | 0.227 | 3.752 |
| H | -6.110 | 1.727 | 2.844 |
| H | -4.718 | 1.648 | 3.956 |
| C | 0.424 | -3.177 | 0.434 |
| C | 2.135 | -4.165 | 1.425 |
| H | 3.050 | -4.147 | 1.996 |
| C | 1.381 | -5.165 | 0.887 |
| H | 1.587 | -6.224 | 0.938 |
| C | 0.272 | -4.527 | 0.247 |
| H | -0.542 | -5.004 | -0.277 |
| C | 2.156 | -0.994 | -2.140 |
| C | 2.339 | 1.953 | -0.361 |
| C | 3.384 | 1.269 | 0.273 |
| C | 4.652 | 0.991 | -0.306 |
| H | 3.233 | 0.989 | 1.314 |
| C | 3.385 | -0.411 | -2.413 |
| C | 4.599 | -0.683 | -1.739 |
| H | 3.407 | 0.398 | -3.145 |
| C | 4.665 | -1.905 | -0.849 |
| C | 5.877 | -0.385 | -2.501 |
| H | 2.532 | 2.403 | -1.333 |
| H | 1.682 | 2.540 | 0.274 |
| H | 2.133 | -1.949 | -1.624 |
| H | 1.352 | -0.835 | -2.858 |
| C | 5.790 | 0.688 | 0.591 |
| H | 4.922 | 1.645 | -1.132 |
| C | 5.654 | -0.101 | 1.753 |
| C | 6.740 | -0.344 | 2.594 |
| C | 8.000 | 0.187 | 2.300 |
| C | 7.068 | 1.212 | 0.313 |
| C | 8.156 | 0.967 | 1.152 |
| H | 9.127 | 1.393 | 0.910 |
| H | 8.844 | -0.004 | 2.955 |
| H | 4.689 | -0.536 | 1.995 |

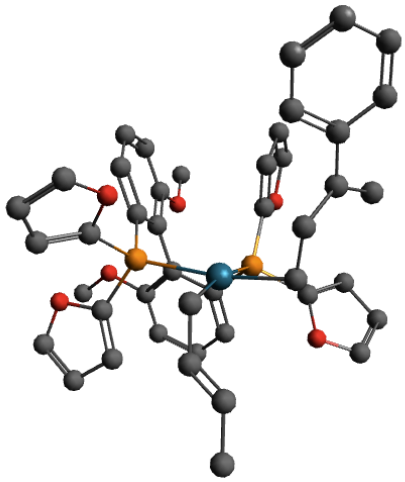
H 6.602 -0.955 3.482
H 7.201 1.838 -0.566
H 6.734 -0.254 -1.834
H 5.780 0.513 -3.121
H 6.120 -1.221 -3.173
H 5.607 -1.944 -0.296
H 4.596 -2.825 -1.448
H 3.845 -1.922 -0.125

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -374.2202 | 11.7269 | 13.5309 |
| Red. masses -- | 8.4878 | 6.0017 | 6.1207 |

ZERO-POINT CORRECTION= 0.750389 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.813553
Thermal correction to Enthalpy= 0.814608
Thermal correction to Gibbs Free Energy= 0.642798
Sum of electronic and zero-point Energies= -2961.877664
Sum of electronic and thermal Energies= -2961.814500
Sum of electronic and thermal Enthalpies= -2961.813445
Sum of electronic and thermal Free Energies= -2961.985255

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000003 | 0.000450 | YES |
| RMS FORCE | 0.000000 | 0.000300 | YES |

---



## GS 17

---
Cartesian coordinates (Angstroms):
---
Pd 0.778 1.017 0.808
C 2.612 0.644 1.869
P -0.064 -1.258 1.110
O -0.130 -3.756 -0.101
O -4.817 -0.786 -0.961
O 0.516 -1.286 3.779
C 0.434 -2.500 -0.105
C 1.387 -2.430 -1.086
H 1.995 -1.565 -1.308
C 1.413 -3.708 -1.726
H 2.043 -4.017 -2.548
C 0.476 -4.467 -1.091
H 0.136 -5.485 -1.215
C -1.920 -1.299 1.182
C -2.709 -1.090 0.035
C -4.115 -0.994 0.186
C -4.712 -1.104 1.445
H -5.786 -1.032 1.558
C -3.910 -1.304 2.568
H -4.372 -1.389 3.547
C -2.528 -1.398 2.445
H -1.926 -1.544 3.333
C -6.234 -0.673 -0.884
H -6.691 -1.587 -0.486
H -6.576 -0.515 -1.907
H -6.534 0.182 -0.266
C 0.424 -2.084 2.660
C 0.914 -2.081 4.812
H 1.028 -1.590 5.766
C 1.087 -3.364 4.387
H 1.404 -4.204 4.988
C 0.768 -3.368 2.992
H 0.779 -4.214 2.321
P -1.024 1.536 -0.759
O -3.647 2.417 -0.926
O -3.021 -3.177 -1.659
O 0.686 2.831 -2.439
C -2.581 2.169 -0.088
C -2.929 2.494 1.196
H -2.297 2.389 2.066
C -4.277 2.969 1.153
H -4.878 3.312 1.982
C -4.659 2.898 -0.154
H -5.572 3.144 -0.675
C -1.488 0.119 -1.866
C -2.154 -1.012 -1.356
C -2.369 -2.119 -2.214
C -1.926 -2.097 -3.540
H -2.091 -2.944 -4.194
C -1.264 -0.969 -4.021
H -0.920 -0.950 -5.051
C -1.040 0.130 -3.198
H -0.517 0.990 -3.594
C -3.262 -4.327 -2.462
H -3.893 -4.090 -3.326
H -3.785 -5.036 -1.818
H -2.324 -4.777 -2.809
C -0.596 2.858 -1.936
C 0.825 3.914 -3.254
H 1.787 4.024 -3.730
C -0.327 4.640 -3.282
H -0.502 5.549 -3.838
C -1.251 3.956 -2.429
H -2.272 4.234 -2.216
C 1.386 3.076 0.932
C 0.828 3.643 2.176
H 0.978 3.561 0.044
H 2.477 3.125 0.904
C 1.510 3.984 3.287

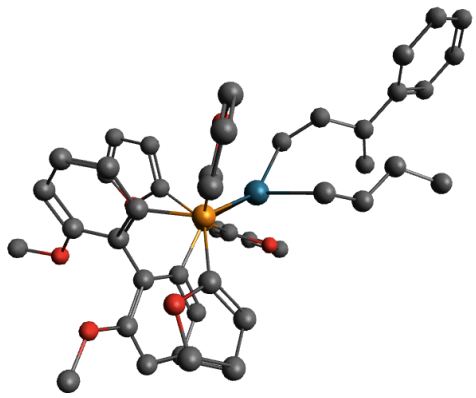
H -0.254 3.796 2.188
C 3.653 0.557 0.841
H 2.502 -0.248 2.484
H 2.713 1.524 2.506
C 4.365 -0.525 0.413
H 3.885 1.507 0.360
C 5.345 -0.392 -0.691
C 4.251 -1.883 1.070
C 6.441 -1.275 -0.803
C 5.224 0.603 -1.687
C 6.162 0.730 -2.709
C 7.379 -1.151 -1.829
C 7.251 -0.145 -2.788
H 8.215 -1.844 -1.875
H 7.978 -0.050 -3.590
H 6.573 -2.063 -0.068
H 4.369 1.271 -1.673
H 6.033 1.506 -3.459
C 0.892 4.536 4.541
H 2.595 3.867 3.294
H 1.087 3.892 5.410
H -0.194 4.639 4.440
H 1.300 5.525 4.795
H 4.177 -2.685 0.327
H 3.376 -1.950 1.717
H 5.130 -2.107 1.691

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 7.2125 | 12.2770 | 20.4200 |
| Red. masses -- | 5.9620 | 6.0465 | 6.0096 |

ZERO-POINT CORRECTION= 0.751572 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.815544
Thermal correction to Enthalpy= 0.816599
Thermal correction to Gibbs Free Energy= 0.640977
Sum of electronic and zero-point Energies= -2961.902613
Sum of electronic and thermal Energies= -2961.838641
Sum of electronic and thermal Enthalpies= -2961.837586
Sum of electronic and thermal Free Energies= -2962.013208

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000005 | 0.000450 | YES |
| RMS FORCE | 0.000001 | 0.000300 | YES |

---



**$TS_{3,3'}$ 17**

---
Cartesian coordinates (Angstroms):
---
Pd -0.860 0.241 -0.080
P 0.619 -1.724 -0.056
O 2.163 -3.415 1.522
O 5.126 0.696 -0.994
O -0.986 -3.024 -1.831
C 1.219 -2.410 1.512
C 0.857 -2.121 2.801
H 0.145 -1.365 3.102
C 1.612 -2.987 3.652
H 1.585 -3.035 4.731
C 2.386 -3.745 2.824
H 3.111 -4.527 2.994
C 2.144 -1.394 -1.060
C 3.136 -0.499 -0.611
C 4.200 -0.173 -1.489
C 4.268 -0.717 -2.775
H 5.082 -0.464 -3.443
C 3.271 -1.595 -3.199
H 3.323 -2.021 -4.197
C 2.218 -1.932 -2.357
H 1.453 -2.614 -2.708
C 6.204 1.094 -1.833
H 6.825 0.239 -2.126
H 6.803 1.786 -1.240
H 5.843 1.606 -2.733
C -0.075 -3.231 -0.815
C -1.436 -4.246 -2.229
H -2.158 -4.243 -3.031
C -0.851 -5.233 -1.494
H -1.025 -6.295 -1.589
C 0.032 -4.577 -0.579
H 0.673 -5.040 0.156
P 0.993 1.800 0.125
O 2.878 3.223 -1.348
O 4.876 -1.477 1.207
O -0.396 3.331 1.894
C 1.783 2.387 -1.398
C 1.455 2.153 -2.707
H 0.648 1.520 -3.049
C 2.391 2.879 -3.508
H 2.436 2.925 -4.587
C 3.228 3.505 -2.633
H 4.078 4.158 -2.758
C 2.377 1.171 1.187
C 3.177 0.089 0.769
C 4.130 -0.438 1.676
C 4.271 0.091 2.962
H 4.999 -0.317 3.653
C 3.461 1.155 3.357
H 3.571 1.569 4.356
C 2.521 1.692 2.485
H 1.902 2.518 2.813
C 5.867 -2.043 2.058
H 6.623 -1.302 2.344
H 6.341 -2.835 1.478

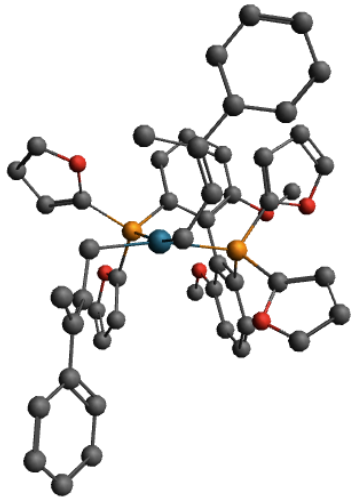
H 5.421 -2.474 2.962
C 0.549 3.394 0.892
C -0.645 4.608 2.299
H -1.368 4.717 3.093
C 0.104 5.490 1.581
H 0.106 6.566 1.684
C 0.879 4.705 0.670
H 1.599 5.063 -0.051
C -2.146 1.877 -0.971
C -2.576 -1.081 0.837
C -3.810 -0.445 0.882
C -4.845 -0.563 -0.085
H -3.975 0.244 1.708
C -3.140 1.259 -1.750
C -4.499 1.157 -1.400
H -2.835 0.832 -2.707
H -4.825 1.832 -0.613
C -5.514 0.964 -2.508
H -2.455 -1.960 0.214
H -1.992 -1.085 1.756
H -2.470 2.489 -0.130
H -1.313 2.306 -1.524
C -6.224 -0.225 0.383
C -6.476 0.888 1.215
C -7.760 1.193 1.661
C -8.849 0.398 1.290
C -7.338 -1.008 0.018
C -8.626 -0.704 0.465
H -9.457 -1.338 0.166
H -9.850 0.636 1.637
H -5.655 1.533 1.515
H -7.911 2.060 2.299
H -7.199 -1.881 -0.611
H -6.468 0.574 -2.140
H -5.140 0.285 -3.280
H -5.730 1.924 -2.997
C -4.705 -1.698 -1.086
H -3.716 -1.674 -1.549
H -5.447 -1.636 -1.885
H -4.821 -2.678 -0.603

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -378.6280 | 9.6581 | 13.1642 |
| Red. masses -- | 8.7143 | 6.0104 | 5.8732 |

ZERO-POINT CORRECTION= 0.750711 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.813845
Thermal correction to Enthalpy= 0.814900
Thermal correction to Gibbs Free Energy= 0.642827
Sum of electronic and zero-point Energies= -2961.873604
Sum of electronic and thermal Energies= -2961.810470
Sum of electronic and thermal Enthalpies= -2961.809415
Sum of electronic and thermal Free Energies= -2961.981488

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000004 | 0.000450 | YES |
| RMS FORCE | 0.000001 | 0.000300 | YES |

---



## GS 18

---
Cartesian coordinates (Angstroms):
---

Pd 0.807 0.659 0.396
C 1.293 2.615 -0.349
P -0.785 0.197 -1.427
O -3.445 0.325 -2.185
O -2.017 -4.748 -0.389
O 0.980 0.993 -3.359
C -2.505 0.734 -1.264
C -3.092 1.576 -0.358
H -2.594 2.059 0.470
C -4.466 1.694 -0.734
H -5.231 2.280 -0.246
C -4.622 0.915 -1.843
H -5.464 0.689 -2.479
C -0.855 -1.614 -1.830
C -1.483 -2.532 -0.967
C -1.390 -3.915 -1.264
C -0.687 -4.364 -2.385
H -0.618 -5.421 -2.609
C -0.066 -3.437 -3.221
H 0.480 -3.785 -4.093
C -0.143 -2.075 -2.951
H 0.353 -1.375 -3.611
C -1.963 -6.151 -0.624
H -2.423 -6.417 -1.583
H -2.528 -6.611 0.187
H -0.931 -6.521 -0.602
C -0.356 0.971 -3.021
C 1.089 1.658 -4.544
H 2.088 1.750 -4.940
C -0.137 2.070 -4.972
H -0.350 2.622 -5.876
C -1.075 1.624 -3.987
H -2.146 1.760 -3.998
P 0.082 -1.356 1.590
O 0.523 -4.085 1.812

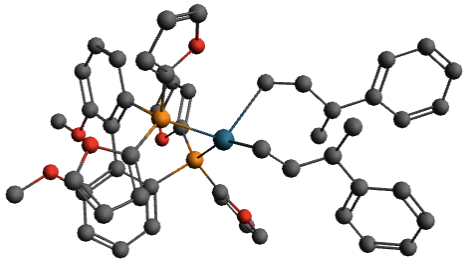
O -4.182 -2.690 -1.063
O 0.085 -0.037 3.976
C 0.919 -2.912 1.206
C 1.975 -3.166 0.372
H 2.477 -2.436 -0.245
C 2.249 -4.566 0.464
H 3.016 -5.121 -0.057
C 1.341 -5.070 1.347
H 1.154 -6.059 1.738
C -1.736 -1.696 1.443
C -2.297 -2.132 0.227
C -3.705 -2.256 0.136
C -4.526 -1.944 1.224
H -5.603 -2.038 1.151
C -3.949 -1.504 2.413
H -4.586 -1.260 3.259
C -2.569 -1.377 2.529
H -2.143 -1.028 3.461
C -5.588 -2.835 -1.227
H -6.003 -3.566 -0.523
H -5.734 -3.193 -2.246
H -6.106 -1.876 -1.102
C 0.353 -1.254 3.388
C 0.402 -0.148 5.297
H 0.237 0.735 5.895
C 0.872 -1.396 5.572
H 1.202 -1.763 6.533
C 0.839 -2.116 4.335
H 1.130 -3.142 4.169
C 2.504 0.914 1.701
C 3.696 0.561 0.918
H 2.328 0.199 2.506
H 2.503 1.924 2.110
C 4.746 1.333 0.517
H 3.742 -0.491 0.635
C 0.090 3.444 -0.239
H 1.572 2.417 -1.385
H 2.150 2.980 0.211
C -0.267 4.316 0.747
H -0.627 3.309 -1.048
C -1.545 5.062 0.679
C 0.588 4.522 1.977
C -2.180 5.522 1.852
C -2.178 5.361 -0.549
C -3.387 6.051 -0.596
C -3.391 6.215 1.805
C -4.006 6.482 0.581
H -3.854 6.545 2.731
H -4.945 7.027 0.542
H -1.730 5.320 2.819
H -1.699 5.074 -1.480
H -3.840 6.268 -1.560
C 5.817 0.757 -0.332
C 4.925 2.770 0.960
H 0.620 5.576 2.274
H 1.614 4.188 1.811
H 0.206 3.959 2.840
C 7.132 1.269 -0.303
C 5.569 -0.314 -1.219
C 8.147 0.718 -1.086
C 6.582 -0.867 -1.998
C 7.883 -0.358 -1.937
H 7.373 2.100 0.351
H 8.672 -0.784 -2.550
H 9.150 1.133 -1.029
H 4.559 -0.698 -1.317
H 6.351 -1.688 -2.672
H 4.054 3.140 1.502
H 5.104 3.439 0.110
H 5.787 2.878 1.632

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 7.1321 | 10.4356 | 13.1313 |
| Red. masses -- | 6.0426 | 6.0869 | 6.0654 |

ZERO-POINT CORRECTION= 0.833065 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.902692
Thermal correction to Enthalpy= 0.903747
Thermal correction to Gibbs Free Energy= 0.713775
Sum of electronic and zero-point Energies= -3192.878300
Sum of electronic and thermal Energies= -3192.808673
Sum of electronic and thermal Enthalpies= -3192.807618
Sum of electronic and thermal Free Energies= -3192.997590

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000011 | 0.000450 | YES |
| RMS FORCE | 0.000001 | 0.000300 | YES |

---



**$TS_{3,3'}$ 18**

---
Cartesian coordinates (Angstroms):
---
Pd -0.291 0.480 -0.208
P 1.732 1.822 -0.233
O 3.793 2.787 -1.839
O 5.090 -1.785 1.399
O 0.518 3.738 1.270
C 2.599 2.096 -1.802
C 2.251 1.734 -3.077
H 1.373 1.169 -3.353
C 3.276 2.225 -3.946
H 3.331 2.122 -5.020
C 4.181 2.851 -3.142
H 5.109 3.369 -3.332
C 3.032 1.183 0.927
C 3.633 -0.072 0.706
C 4.527 -0.576 1.682

C 4.796 0.141 2.853
H 5.476 -0.249 3.599
C 4.177 1.373 3.057
H 4.386 1.933 3.965
C 3.304 1.894 2.108
H 2.838 2.857 2.284
C 6.001 -2.348 2.335
H 6.877 -1.704 2.483
H 6.322 -3.297 1.904
H 5.520 -2.534 3.302
C 1.488 3.547 0.308
C 0.431 5.078 1.500
H -0.291 5.381 2.243
C 1.308 5.756 0.709
H 1.450 6.826 0.676
C 1.996 4.765 -0.062
H 2.775 4.929 -0.791
P 0.798 -1.627 0.252
O 2.166 -3.207 2.083
O 5.568 -0.067 -1.167
O -0.971 -3.052 -1.259
C 1.370 -2.094 1.912
C 1.123 -1.528 3.135
H 0.542 -0.636 3.314
C 1.795 -2.330 4.110
H 1.819 -2.179 5.180
C 2.409 -3.329 3.416
H 3.024 -4.167 3.708
C 2.324 -1.686 -0.815
C 3.449 -0.878 -0.548
C 4.510 -0.864 -1.487
C 4.449 -1.623 -2.659
H 5.261 -1.607 -3.376
C 3.324 -2.408 -2.906
H 3.274 -3.001 -3.815
C 2.271 -2.442 -1.999
H 1.406 -3.058 -2.214
C 6.667 0.003 -2.068
H 7.139 -0.978 -2.205
H 7.384 0.686 -1.611
H 6.362 0.399 -3.044
C -0.079 -3.162 -0.211
C -1.541 -4.277 -1.439
H -2.259 -4.349 -2.241
C -1.053 -5.168 -0.532
H -1.330 -6.208 -0.438
C -0.104 -4.448 0.261
H 0.496 -4.835 1.070
C -1.712 0.670 1.992
C -1.549 1.835 -1.394
C -2.524 0.836 -1.524
C -3.897 0.892 -1.069
H -2.280 0.030 -2.210
C -2.989 1.035 1.683
C -4.018 0.160 1.189
C -5.429 0.457 1.541
H -1.773 2.763 -0.877
H -0.823 1.940 -2.197
H -1.440 -0.370 2.115
H -1.011 1.410 2.365
C -4.817 -0.085 -1.709
C -4.387 -1.381 -2.082
C -5.242 -2.281 -2.713
C -6.564 -1.926 -3.002
C -6.157 0.245 -2.003
C -7.012 -0.655 -2.642
H -8.034 -0.356 -2.859
H -7.228 -2.628 -3.498
H -3.372 -1.693 -1.863
H -4.875 -3.269 -2.981
H -6.540 1.226 -1.749
C -5.796 1.610 2.277
C -6.481 -0.421 1.190
C -7.806 -0.158 1.539
C -8.140 0.993 2.253
C -7.120 1.876 2.619
H -9.171 1.195 2.528
H -7.353 2.771 3.189
H -6.268 -1.324 0.632
H -8.580 -0.863 1.248
H -5.033 2.303 2.612
H -3.223 2.095 1.749
C -3.628 -1.293 1.057
H -4.364 -1.885 0.514
H -3.503 -1.753 2.048
H -2.673 -1.382 0.530
C -4.454 2.286 -0.838
H -3.754 2.908 -0.278
H -5.394 2.277 -0.286
H -4.633 2.787 -1.799

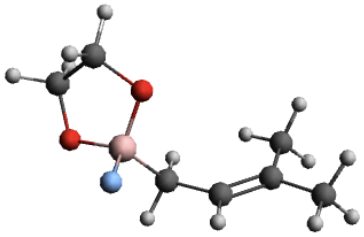
| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -252.3017 | 11.0594 | 14.8511 |
| Red. masses -- | 7.6328 | 5.7524 | 5.9998 |

ZERO-POINT CORRECTION= 0.832197 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.900974
Thermal correction to Enthalpy= 0.902029
Thermal correction to Gibbs Free Energy= 0.718231
Sum of electronic and zero-point Energies= -3192.838701
Sum of electronic and thermal Energies= -3192.769925
Sum of electronic and thermal Enthalpies= -3192.768870
Sum of electronic and thermal Free Energies= -3192.952668

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000001 | 0.000450 | YES |
| RMS FORCE | 0.000000 | 0.000300 | YES |

---

***Structures and Energies from Figure 6***



**V**

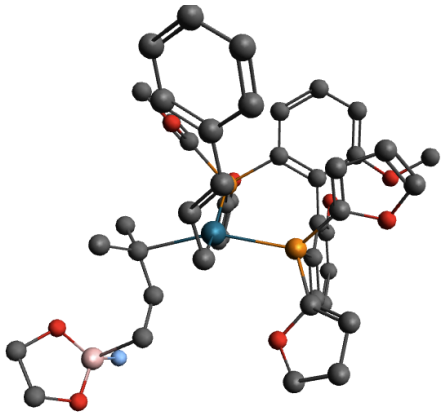
---
Cartesian coordinates (Angstroms):
---

C -1.550 0.662 -0.357
C -2.614 -0.102 -0.046
H -1.576 1.692 0.010
C -3.766 0.451 0.762
B 1.071 0.492 -0.173
C -0.287 0.313 -1.079
H -0.178 0.992 -1.942
H -0.326 -0.703 -1.491
O 1.122 -0.465 0.955
F 1.125 1.849 0.313
O 2.305 0.222 -0.962
C -2.770 -1.550 -0.442
C 3.054 -0.771 -0.302
C 2.476 -0.818 1.122
H 3.009 -0.098 1.772
H 2.568 -1.810 1.589
H 4.131 -0.536 -0.310
H 2.936 -1.756 -0.794
H -3.612 1.503 1.023
H -3.909 -0.108 1.698
H -4.718 0.374 0.215
H -1.951 -1.904 -1.072
H -3.711 -1.712 -0.986
H -2.814 -2.201 0.443

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 32.9174 | 47.6080 | 77.0765 |
| Red. masses -- | 3.1012 | 3.7338 | 3.2159 |

ZERO-POINT CORRECTION= 0.197792 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.212417
Thermal correction to Enthalpy= 0.213472
Thermal correction to Gibbs Free Energy= 0.152545
Sum of electronic and zero-point Energies= -549.760118
Sum of electronic and thermal Energies= -549.745492
Sum of electronic and thermal Enthalpies= -549.744437
Sum of electronic and thermal Free Energies= -549.805364

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000014 | 0.000450 | YES |
| RMS FORCE | 0.000002 | 0.000300 | YES |



**$TS_{TM}$ V**

---
Cartesian coordinates (Angstroms):
---

Pd -0.975 0.291 0.092
P 0.515 -0.746 -1.661
O 1.467 -3.026 -2.908
O 5.111 -0.817 0.767
O -0.383 1.158 -3.375
C 0.601 -2.533 -1.956
C -0.064 -3.575 -1.367
H -0.791 -3.494 -0.572
C 0.408 -4.773 -1.988
H 0.100 -5.786 -1.775
C 1.331 -4.380 -2.910
H 1.947 -4.914 -3.618
C 2.294 -0.237 -1.464
C 3.078 -0.745 -0.411
C 4.409 -0.282 -0.269
C 4.935 0.669 -1.148
H 5.953 1.022 -1.039
C 4.135 1.171 -2.172
H 4.541 1.913 -2.854
C 2.826 0.728 -2.334
H 2.227 1.128 -3.142
C 6.466 -0.422 0.951
H 7.080 -0.672 0.077
H 6.825 -0.981 1.816
H 6.547 0.652 1.155
C 0.113 -0.126 -3.324
C -0.666 1.430 -4.680
H -1.061 2.415 -4.880
C -0.369 0.357 -5.465
H -0.495 0.289 -6.536
C 0.139 -0.652 -4.587
H 0.485 -1.638 -4.856
P 0.852 0.158 1.709
O 3.232 1.179 2.677
O 3.974 -3.302 -0.583
O -0.976 -0.400 3.656
C 2.187 1.377 1.800
C 2.368 2.562 1.138

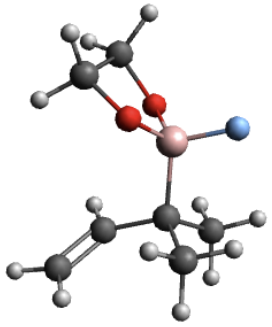
H 1.711 2.974 0.386
C 3.585 3.128 1.630
H 4.041 4.061 1.330
C 4.064 2.249 2.555
H 4.938 2.240 3.188
C 1.676 -1.498 1.587
C 2.588 -1.781 0.552
C 3.101 -3.096 0.440
C 2.708 -4.098 1.333
H 3.100 -5.103 1.245
C 1.795 -3.797 2.343
H 1.488 -4.575 3.035
C 1.277 -2.513 2.473
H 0.565 -2.304 3.262
C 4.538 -4.600 -0.748
H 5.110 -4.906 0.136
H 5.209 -4.526 -1.604
H 3.764 -5.347 -0.959
C 0.238 0.207 3.423
C -1.283 -0.201 4.968
H -2.215 -0.631 5.302
C -0.307 0.524 5.582
H -0.290 0.834 6.617
C 0.682 0.789 4.582
H 1.607 1.331 4.706
C -1.937 1.754 1.316
C -1.836 2.959 0.499
C -0.968 3.981 0.725
H -2.505 3.022 -0.357
C -0.791 5.187 -0.082
C 0.052 6.213 0.397
C -1.418 5.390 -1.332
C -1.217 6.564 -2.053
C 0.253 7.387 -0.327
C -0.382 7.571 -1.557
H 0.906 8.159 0.070
H -0.227 8.484 -2.125
H 0.548 6.080 1.355
H -2.061 4.619 -1.744
H -1.712 6.693 -3.012
H -0.337 3.923 1.612
H -2.940 1.362 1.462
H -1.411 1.833 2.267
C -3.220 -1.150 0.314
C -3.042 -0.261 -0.808
H -2.636 -2.070 0.268
C -4.044 0.874 -0.971
B -5.615 -2.419 0.644
C -4.129 -1.071 1.356
H -4.708 -0.163 1.511
H -3.952 -1.665 2.249
O -6.569 -2.305 1.673
F -4.871 -3.564 0.605
O -6.110 -1.895 -0.569
C -2.864 -0.983 -2.143
C -7.429 -1.405 -0.318
C -7.546 -1.368 1.221
H -8.165 -2.089 -0.762
H -7.561 -0.417 -0.772
H -8.537 -1.662 1.581
H -7.320 -0.367 1.615
H -3.840 -1.377 -2.466
H -2.181 -1.833 -2.077
H -2.510 -0.312 -2.929
H -5.018 0.457 -1.263
H -3.729 1.559 -1.766
H -4.209 1.460 -0.065

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -263.9970 | 12.6109 | 15.7265 |
| Red. masses -- | 8.9817 | 6.3858 | 6.1630 |

ZERO-POINT CORRECTION= 0.825225 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.896201
Thermal correction to Enthalpy= 0.897256
Thermal correction to Gibbs Free Energy= 0.706902
Sum of electronic and zero-point Energies= -3315.710373
Sum of electronic and thermal Energies= -3315.639397
Sum of electronic and thermal Enthalpies= -3315.638342
Sum of electronic and thermal Free Energies= -3315.828696

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000002 | 0.000450 | YES |
| RMS FORCE | 0.000000 | 0.000300 | YES |

---



**W**

---
Cartesian coordinates (Angstroms):
---
C 1.324 1.108 0.633
C 1.965 2.149 0.083
H 0.840 1.269 1.598
H 2.001 3.117 0.578
B -0.486 -0.563 -0.147
C 1.139 -0.280 0.090
C 1.662 -1.285 1.145
C 1.893 -0.492 -1.231
O -1.262 -0.308 1.091
F -0.635 -1.930 -0.571
O -1.095 0.316 -1.176
H 2.468 2.083 -0.878
C -2.070 1.119 -0.555
C -2.455 0.340 0.711
H -3.258 -0.387 0.479
H -2.824 0.989 1.519

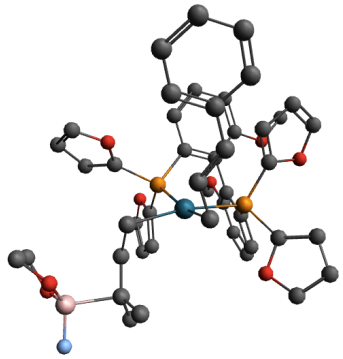
H -2.928 1.292 -1.224
H -1.660 2.109 -0.281
H 1.730 -1.511 -1.597
H 2.978 -0.340 -1.127
H 1.532 0.195 -2.005
H 1.467 -2.312 0.818
H 1.158 -1.147 2.108
H 2.745 -1.183 1.317

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 76.3682 | 104.8474 | 111.5862 |
| Red. masses -- | 3.9750 | 3.2842 | 3.2093 |

ZERO-POINT CORRECTION= 0.198015 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.212261
Thermal correction to Enthalpy= 0.213316
Thermal correction to Gibbs Free Energy= 0.155570
Sum of electronic and zero-point Energies= -549.750417
Sum of electronic and thermal Energies= -549.736172
Sum of electronic and thermal Enthalpies= -549.735117
Sum of electronic and thermal Free Energies= -549.792862

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000040 | 0.000450 | YES |
| RMS FORCE | 0.000008 | 0.000300 | YES |

---



**$TS_{TM}$ W**

---
Cartesian coordinates (Angstroms):
---
Pd -0.763 0.474 0.544
P -0.055 -1.102 -1.258
O 0.477 -3.718 -1.950
O 5.095 -0.719 -0.783
O -1.551 0.246 -3.100
C -0.022 -2.886 -0.972
C -0.437 -3.636 0.096
H -0.860 -3.255 1.013
C -0.186 -5.003 -0.238
H -0.390 -5.874 0.368
C 0.367 -4.991 -1.484
H 0.717 -5.767 -2.149
C 1.629 -0.657 -1.889
C 2.776 -0.907 -1.111
C 4.029 -0.446 -1.582
C 4.129 0.245 -2.794
H 5.088 0.595 -3.155
C 2.979 0.487 -3.543
H 3.057 1.024 -4.484
C 1.736 0.046 -3.100
H 0.855 0.249 -3.697
C 6.391 -0.311 -1.209
H 6.666 -0.778 -2.162
H 7.079 -0.646 -0.432
H 6.457 0.779 -1.306
C -1.119 -1.010 -2.731
C -2.369 0.090 -4.180
H -2.782 0.999 -4.590
C -2.481 -1.227 -4.507
H -3.066 -1.642 -5.315
C -1.670 -1.943 -3.569
H -1.508 -3.009 -3.528
P 1.438 0.464 1.490
O 3.934 1.618 1.300
O 3.723 -3.438 -1.077
O 0.425 0.332 4.016
C 2.632 1.659 0.852
C 2.489 2.688 -0.041
H 1.579 2.958 -0.554
C 3.768 3.316 -0.152
H 4.030 4.163 -0.769
C 4.601 2.628 0.679
H 5.646 2.726 0.933
C 2.262 -1.193 1.385
C 2.749 -1.695 0.163
C 3.275 -3.011 0.134
C 3.309 -3.796 1.290
H 3.712 -4.801 1.266
C 2.812 -3.280 2.486
H 2.836 -3.891 3.383
C 2.288 -1.993 2.540
H 1.903 -1.615 3.479
C 4.259 -4.753 -1.182
H 5.141 -4.881 -0.543
H 4.550 -4.873 -2.226
H 3.510 -5.511 -0.925
C 1.459 0.848 3.267
C 0.601 0.761 5.297
H -0.139 0.430 6.008
C 1.713 1.542 5.390
H 2.091 2.021 6.282
C 2.273 1.599 4.074
H 3.167 2.119 3.765
C -1.311 2.153 1.744
C -1.537 3.223 0.770
C -0.703 4.272 0.558
H -2.451 3.155 0.182
C -0.875 5.361 -0.405
C 0.040 6.435 -0.389
C -1.912 5.400 -1.362
C -2.028 6.467 -2.249
C -0.077 7.502 -1.279
C -1.114 7.525 -2.215
H 0.642 8.315 -1.241
H -1.208 8.354 -2.910

H 0.848 6.426 0.338
H -2.630 4.588 -1.415
H -2.836 6.472 -2.976
H 0.193 4.340 1.175
H -2.210 1.827 2.267
H -0.515 2.381 2.452
C -3.176 -0.939 0.562
C -2.938 0.350 0.035
H -2.841 -1.772 -0.057
H -3.450 1.179 0.513
B -5.586 -1.683 0.912
C -3.884 -1.316 1.727
C -4.173 -0.252 2.781
C -3.476 -2.660 2.338
O -6.097 -0.478 0.321
F -6.278 -2.118 2.044
O -5.476 -2.693 -0.103
H -2.865 0.438 -1.046
C -5.656 -2.056 -1.358
C -6.436 -0.769 -1.028
H -6.199 -2.718 -2.044
H -4.684 -1.820 -1.820
H -7.522 -0.932 -1.124
H -6.163 0.069 -1.683
H -4.593 0.658 2.343
H -3.259 0.022 3.328
H -4.897 -0.631 3.507
H -3.330 -3.422 1.567
H -4.247 -3.022 3.022
H -2.540 -2.566 2.909

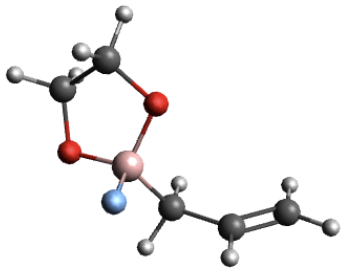
| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -151.0941 | 9.4811 | 11.1710 |
| Red. masses -- | 5.3081 | 6.2993 | 6.4266 |

ZERO-POINT CORRECTION= 0.825403 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.896177
Thermal correction to Enthalpy= 0.897232
Thermal correction to Gibbs Free Energy= 0.706032
Sum of electronic and zero-point Energies= -3315.722527
Sum of electronic and thermal Energies= -3315.651752
Sum of electronic and thermal Enthalpies= -3315.650697
Sum of electronic and thermal Free Energies= -3315.841898

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000003 | 0.000450 | YES |
| RMS FORCE | 0.000001 | 0.000300 | YES |

---

## ***Structures and Energies from Figure SI-1***



**SI-14**

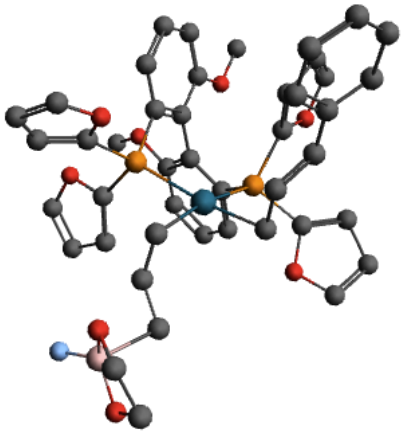
---
Cartesian coordinates (Angstroms):
---
C 2.400 0.155 0.002
C 3.247 -0.879 0.075
H 2.580 0.903 -0.774
H 4.086 -0.986 -0.608
B -0.217 0.432 -0.044
C 1.179 0.392 0.826
H 1.264 1.376 1.316
H 1.109 -0.357 1.627
O -0.529 -0.876 -0.659
F -0.093 1.455 -1.054
O -1.390 0.747 0.813
H 3.123 -1.666 0.818
C -2.332 -0.292 0.688
C -1.928 -1.033 -0.598
H -2.431 -0.577 -1.472
H -2.203 -2.098 -0.583
H -3.360 0.101 0.641
H -2.288 -0.981 1.554

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 56.8402 | 91.8408 | 103.6136 |
| Red. masses -- | 3.5729 | 3.3961 | 2.5785 |

ZERO-POINT CORRECTION= 0.141412 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.152569
Thermal correction to Enthalpy= 0.153624
Thermal correction to Gibbs Free Energy= 0.101269
Sum of electronic and zero-point Energies= -471.177542
Sum of electronic and thermal Energies= -471.166385
Sum of electronic and thermal Enthalpies= -471.165330
Sum of electronic and thermal Free Energies= -471.217685

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000050 | 0.000450 | YES |
| RMS FORCE | 0.000007 | 0.000300 | YES |

---



**$TS_{TM\ 1}$**

---
Cartesian coordinates (Angstroms):
---

| | | | |
|---|---|---|---|
| Pd | -0.966 | 0.092 | 0.300 |
| P | 0.332 | -1.279 | -1.287 |
| O | 1.521 | -3.750 | -1.627 |
| O | 5.141 | 0.396 | -0.268 |
| O | -1.195 | -0.485 | -3.404 |
| C | 0.729 | -2.976 | -0.808 |
| C | 0.354 | -3.708 | 0.288 |
| H | -0.256 | -3.356 | 1.106 |
| C | 0.943 | -5.002 | 0.140 |
| H | 0.860 | -5.840 | 0.816 |
| C | 1.636 | -4.969 | -1.033 |
| H | 2.232 | -5.696 | -1.565 |
| C | 1.936 | -0.476 | -1.755 |
| C | 2.999 | -0.390 | -0.837 |
| C | 4.152 | 0.350 | -1.201 |
| C | 4.234 | 0.983 | -2.445 |
| H | 5.115 | 1.547 | -2.723 |
| C | 3.166 | 0.888 | -3.335 |
| H | 3.230 | 1.379 | -4.302 |
| C | 2.023 | 0.170 | -3.000 |
| H | 1.203 | 0.115 | -3.705 |
| C | 6.332 | 1.115 | -0.571 |
| H | 6.843 | 0.698 | -1.447 |
| H | 6.974 | 1.010 | 0.304 |
| H | 6.125 | 2.178 | -0.743 |
| C | -0.500 | -1.555 | -2.882 |
| C | -1.779 | -0.908 | -4.560 |
| H | -2.361 | -0.169 | -5.090 |
| C | -1.487 | -2.218 | -4.790 |
| H | -1.821 | -2.814 | -5.627 |
| C | -0.657 | -2.639 | -3.704 |
| H | -0.223 | -3.616 | -3.555 |
| P | 1.043 | 0.729 | 1.483 |
| O | 3.159 | 2.504 | 1.414 |
| O | 4.519 | -2.597 | -0.495 |
| O | -0.151 | 0.480 | 3.923 |
| C | 1.947 | 2.162 | 0.855 |
| C | 1.620 | 3.069 | -0.117 |
| H | 0.723 | 3.053 | -0.719 |
| C | 2.684 | 4.022 | -0.165 |
| H | 2.766 | 4.880 | -0.816 |
| C | 3.585 | 3.631 | 0.781 |
| H | 4.532 | 4.027 | 1.114 |
| C | 2.271 | -0.656 | 1.607 |
| C | 3.006 | -1.091 | 0.487 |
| C | 3.839 | -2.229 | 0.624 |
| C | 3.930 | -2.911 | 1.841 |
| H | 4.568 | -3.780 | 1.943 |
| C | 3.185 | -2.467 | 2.932 |
| H | 3.254 | -2.997 | 3.878 |
| C | 2.359 | -1.354 | 2.823 |
| H | 1.786 | -1.033 | 3.683 |
| C | 5.387 | -3.725 | -0.427 |
| H | 6.187 | -3.573 | 0.307 |
| H | 5.824 | -3.824 | -1.421 |
| H | 4.836 | -4.640 | -0.181 |
| C | 0.772 | 1.217 | 3.215 |
| C | -0.239 | 1.030 | 5.166 |
| H | -0.929 | 0.551 | 5.844 |
| C | 0.593 | 2.103 | 5.273 |
| H | 0.725 | 2.732 | 6.142 |
| C | 1.252 | 2.225 | 4.008 |
| H | 1.992 | 2.958 | 3.725 |
| C | -2.146 | 1.499 | 1.396 |
| C | -2.458 | 2.554 | 0.431 |
| C | -1.873 | 3.778 | 0.394 |
| H | -3.214 | 2.314 | -0.316 |
| C | -2.124 | 4.855 | -0.565 |
| C | -1.471 | 6.092 | -0.387 |
| C | -2.992 | 4.731 | -1.673 |
| C | -3.196 | 5.794 | -2.548 |
| C | -1.675 | 7.156 | -1.265 |
| C | -2.541 | 7.015 | -2.351 |
| H | -1.157 | 8.097 | -1.099 |
| H | -2.702 | 7.842 | -3.037 |
| H | -0.796 | 6.213 | 0.457 |
| H | -3.508 | 3.793 | -1.853 |
| H | -3.869 | 5.670 | -3.392 |
| H | -1.133 | 4.009 | 1.160 |
| H | -3.009 | 0.917 | 1.720 |
| H | -1.582 | 1.859 | 2.256 |
| C | -3.016 | -1.804 | 0.432 |
| C | -2.896 | -0.662 | -0.424 |
| H | -2.423 | -2.676 | 0.155 |
| H | -3.657 | 0.102 | -0.282 |
| B | -5.425 | -2.950 | 0.645 |
| C | -3.865 | -1.959 | 1.516 |
| H | -4.382 | -1.085 | 1.909 |
| H | -3.646 | -2.738 | 2.242 |
| O | -6.304 | -3.120 | 1.742 |
| F | -4.803 | -4.085 | 0.189 |
| O | -5.987 | -2.067 | -0.309 |
| H | -2.703 | -0.875 | -1.473 |
| C | -7.276 | -1.683 | 0.169 |
| C | -7.267 | -2.073 | 1.661 |

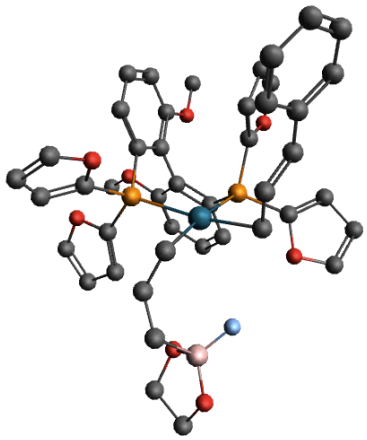
H -8.055 -2.231 -0.381
H -7.440 -0.611 0.013
H -8.239 -2.431 2.016
H -6.963 -1.225 2.292

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -246.1626 | 6.6284 | 10.8363 |
| Red. masses -- | 8.7941 | 6.5061 | 6.3592 |

ZERO-POINT CORRECTION= 0.769045 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.836570
Thermal correction to Enthalpy= 0.837625
Thermal correction to Gibbs Free Energy= 0.650627
Sum of electronic and zero-point Energies= -3237.152036
Sum of electronic and thermal Energies= -3237.084511
Sum of electronic and thermal Enthalpies= -3237.083456
Sum of electronic and thermal Free Energies= -3237.270453

| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000002 | 0.000450 | YES |
| RMS FORCE | 0.000000 | 0.000300 | YES |

---



**TS TM 2**

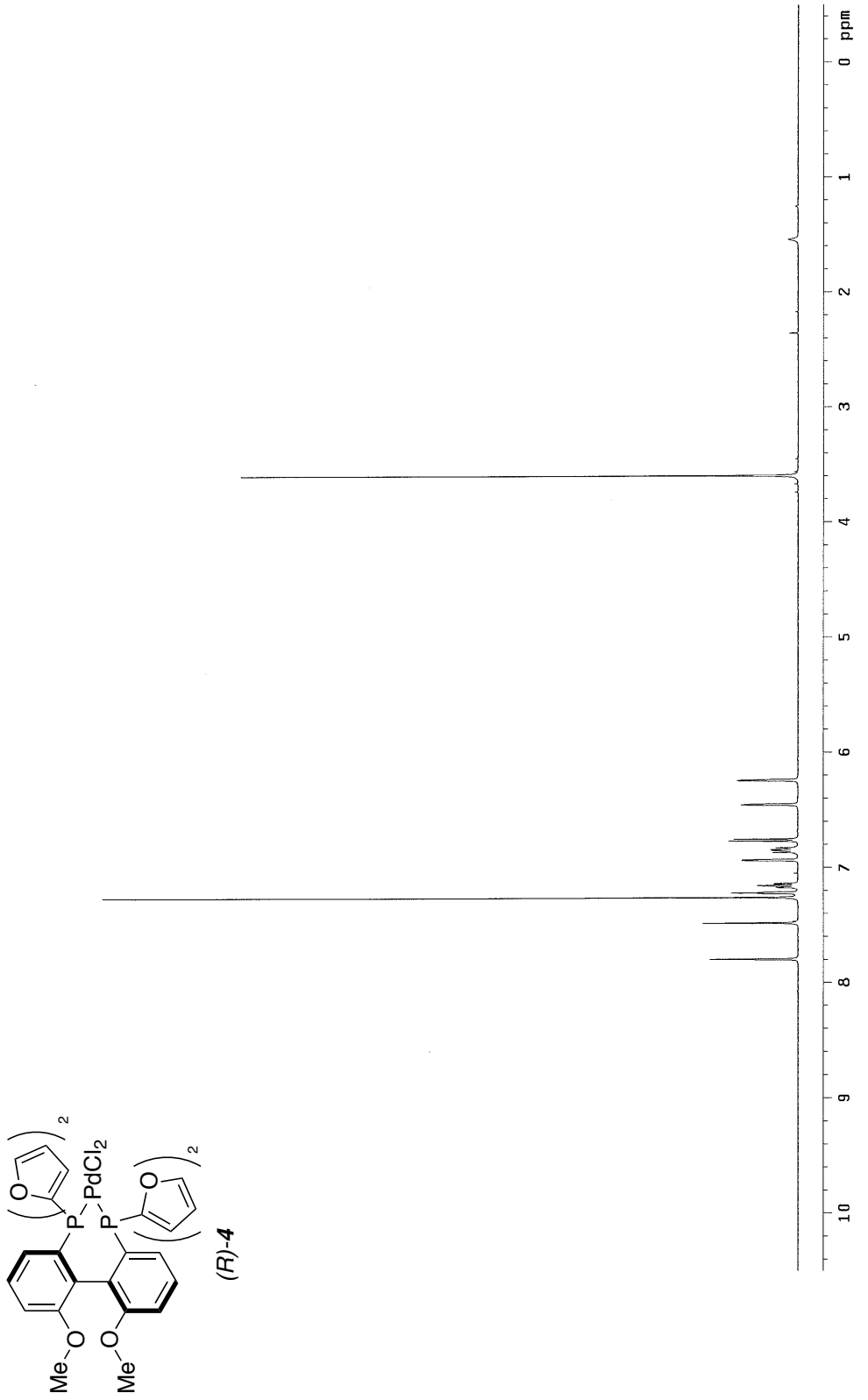
---
Cartesian coordinates (Angstroms):
---
Pd -0.529 1.166 0.123
P 0.956 -0.118 1.648
O 3.565 -0.769 2.250
O 1.041 -4.733 -0.734
O -0.589 0.445 3.838
C 2.749 0.071 1.521
C 3.516 0.965 0.821
H 3.159 1.751 0.166
C 4.879 0.660 1.133
H 5.762 1.159 0.760
C 4.847 -0.395 1.996
H 5.612 -0.967 2.499
C 0.639 -1.944 1.570
C 1.016 -2.697 0.441
C 0.647 -4.063 0.383
C -0.078 -4.656 1.421
H -0.357 -5.702 1.376
C -0.446 -3.890 2.525
H -1.009 -4.350 3.332
C -0.098 -2.545 2.604
H -0.402 -1.969 3.469
C 0.706 -6.111 -0.858
H 1.153 -6.708 -0.055
H 1.115 -6.432 -1.816
H -0.380 -6.260 -0.860
C 0.712 0.281 3.410
C -0.541 0.790 5.157
H -1.496 0.947 5.635
C 0.749 0.860 5.584
H 1.085 1.114 6.579
C 1.563 0.529 4.454
H 2.641 0.470 4.422
P -0.364 -0.546 -1.553
O -1.397 -3.041 -2.152
O 3.616 -3.408 0.204
O -0.240 1.156 -3.692
C -1.512 -1.927 -1.350
C -2.596 -2.066 -0.525
H -2.933 -1.341 0.201
C -3.183 -3.334 -0.829
H -4.055 -3.779 -0.372
C -2.416 -3.879 -1.816
H -2.461 -4.807 -2.365
C 1.339 -1.269 -1.663
C 1.841 -2.144 -0.681
C 3.193 -2.562 -0.773
C 4.014 -2.112 -1.811
H 5.046 -2.433 -1.880
C 3.498 -1.235 -2.763
H 4.137 -0.880 -3.566
C 2.176 -0.810 -2.695
H 1.802 -0.119 -3.439
C 4.959 -3.878 0.167
H 5.163 -4.443 -0.751
H 5.067 -4.539 1.027
H 5.675 -3.052 0.252
C -0.737 -0.055 -3.267
C -0.674 1.346 -4.969
H -0.355 2.263 -5.440
C -1.441 0.295 -5.373
H -1.920 0.180 -6.334
C -1.483 -0.615 -4.270
H -1.991 -1.567 -4.229
C -2.077 2.163 -0.967
C -3.305 1.956 -0.201
C -4.317 1.121 -0.549
H -3.396 2.521 0.726
C -5.549 0.865 0.199
C -6.547 0.055 -0.382
C -5.805 1.385 1.488
C -6.999 1.114 2.149
C -7.743 -0.218 0.281
C -7.979 0.312 1.552
H -8.492 -0.844 -0.196
H -8.909 0.102 2.073

H -6.375 -0.361 -1.372
H -5.059 2.003 1.979
H -7.168 1.528 3.139
H -4.228 0.578 -1.490
H -1.710 3.188 -0.985
H -2.127 1.757 -1.977
C 0.631 3.527 1.496
C -0.652 2.897 1.488
H 1.435 2.969 1.980
H -0.880 2.328 2.389
B 1.673 4.491 -0.966
C 0.982 4.747 0.933
H 1.896 5.211 1.294
H 0.183 5.440 0.672
O 1.972 5.828 -1.327
F 0.593 3.906 -1.572
O 2.862 3.722 -0.896
H -1.470 3.547 1.183
C 3.944 4.648 -0.816
C 3.389 5.936 -1.459
H 4.816 4.249 -1.343
H 4.224 4.815 0.234
H 3.655 5.999 -2.523
H 3.754 6.843 -0.963

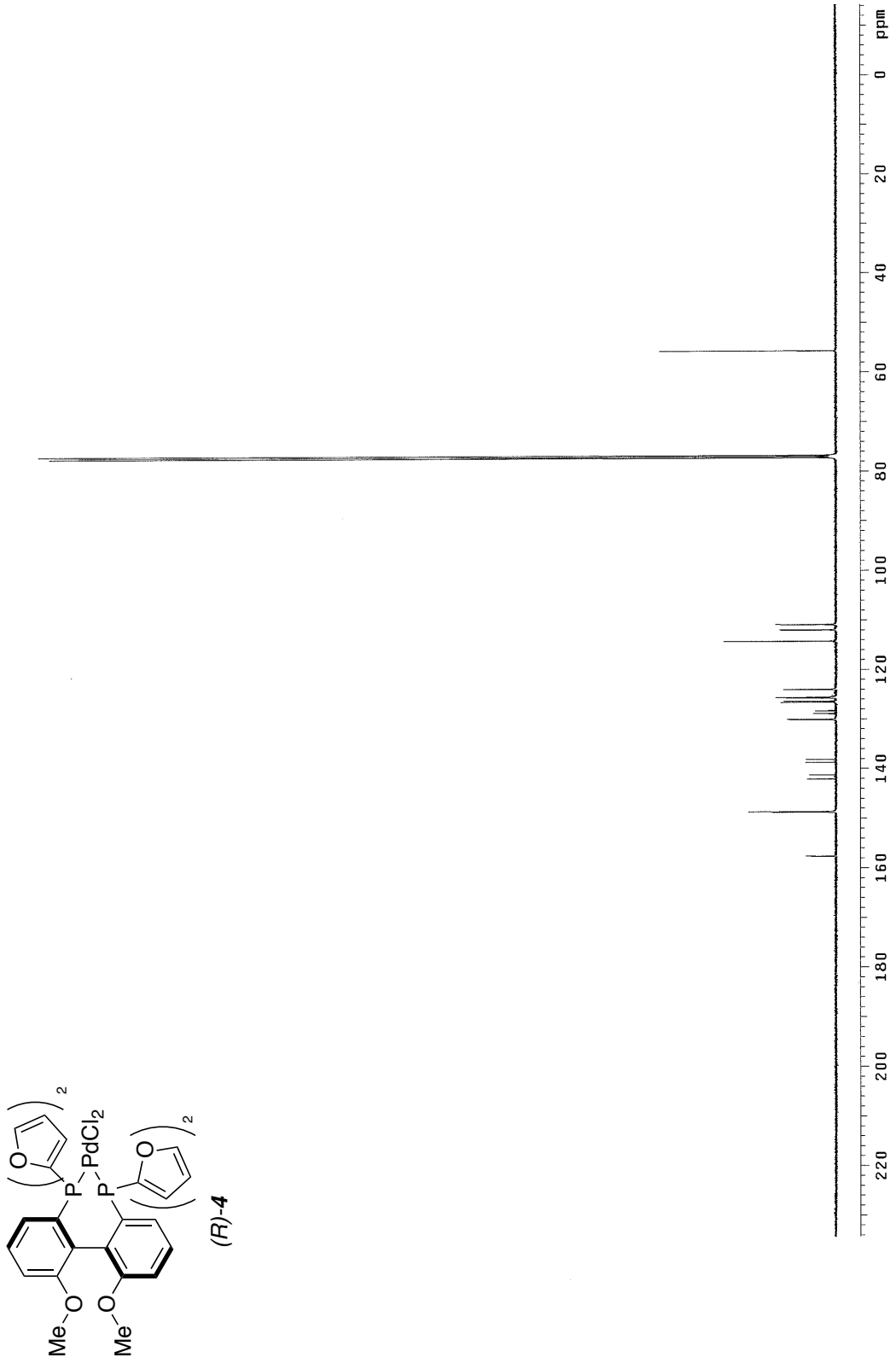
| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | -345.7525 | 10.0517 | 13.7463 |
| Red. masses -- | 9.7489 | 6.4223 | 6.1187 |

ZERO-POINT CORRECTION= 0.769051 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.836436
Thermal correction to Enthalpy= 0.837491
Thermal correction to Gibbs Free Energy= 0.653694
Sum of electronic and zero-point Energies= -3237.150946
Sum of electronic and thermal Energies= -3237.083560
Sum of electronic and thermal Enthalpies= -3237.082505
Sum of electronic and thermal Free Energies= -3237.266302

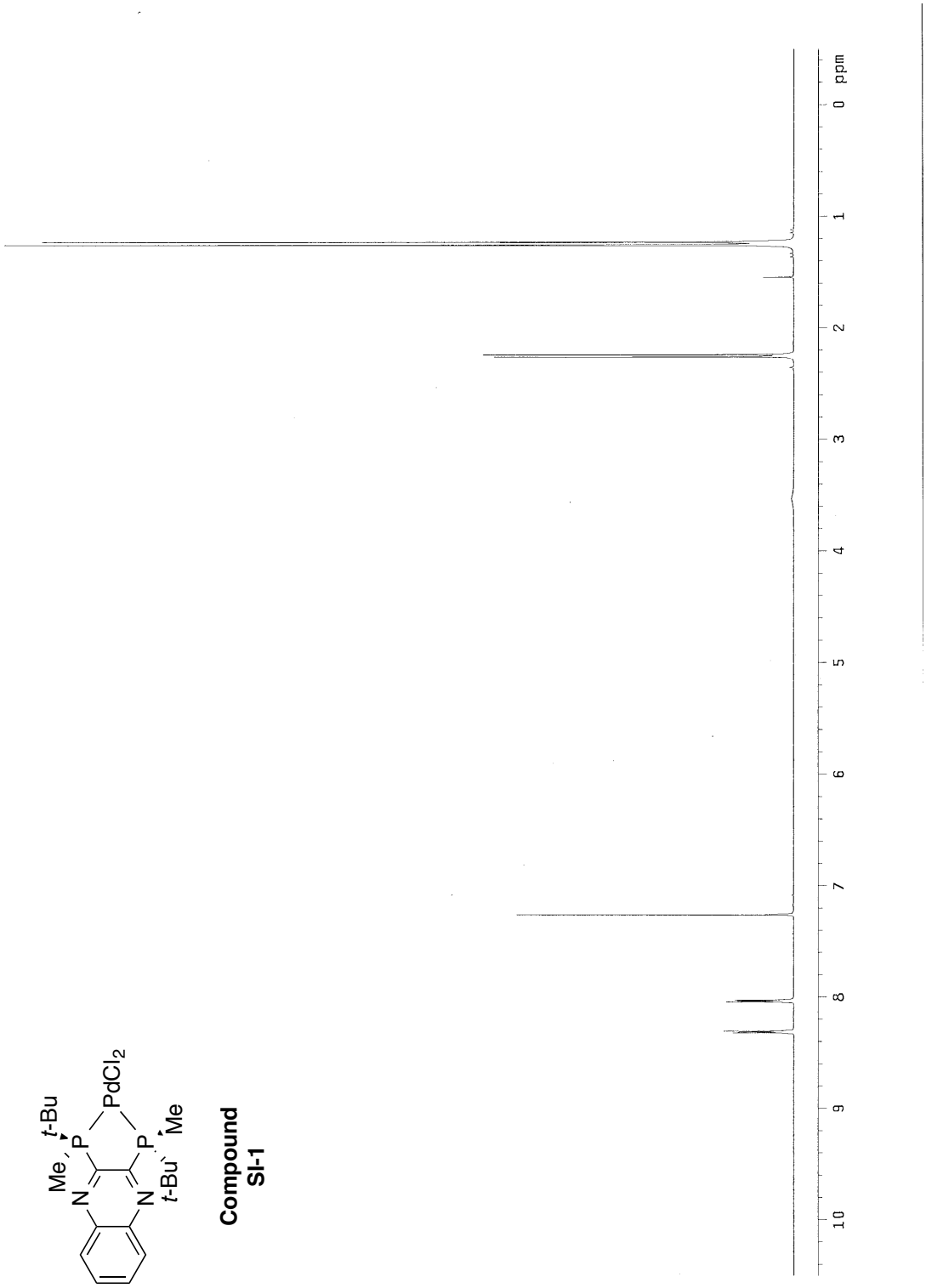
| ITEM | VALUE | THRESHOLD | CONVERGED? |
|---|---|---|---|
| MAXIMUM FORCE | 0.000016 | 0.000450 | YES |
| RMS FORCE | 0.000001 | 0.000300 | YES |



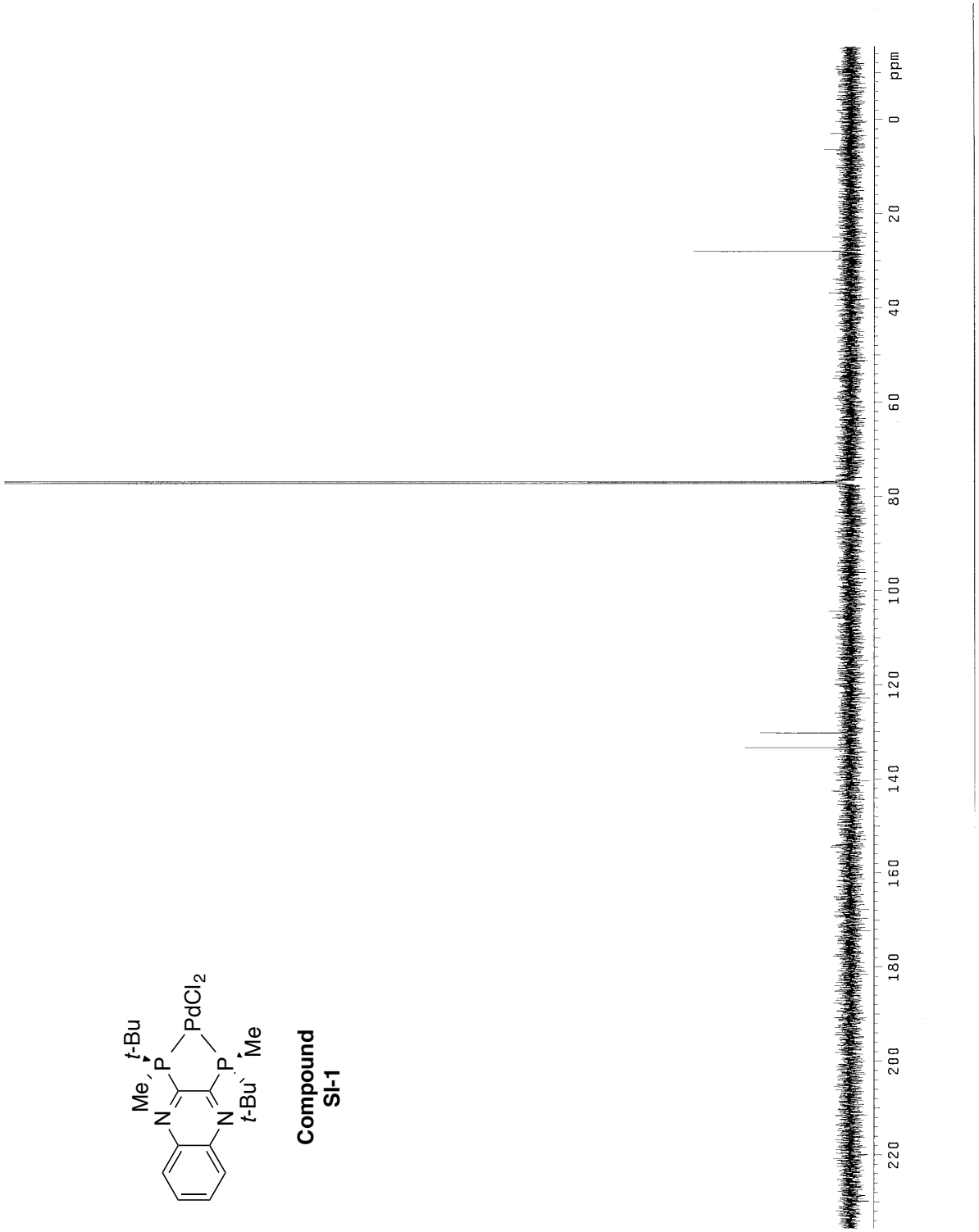

*(R)*-**4**



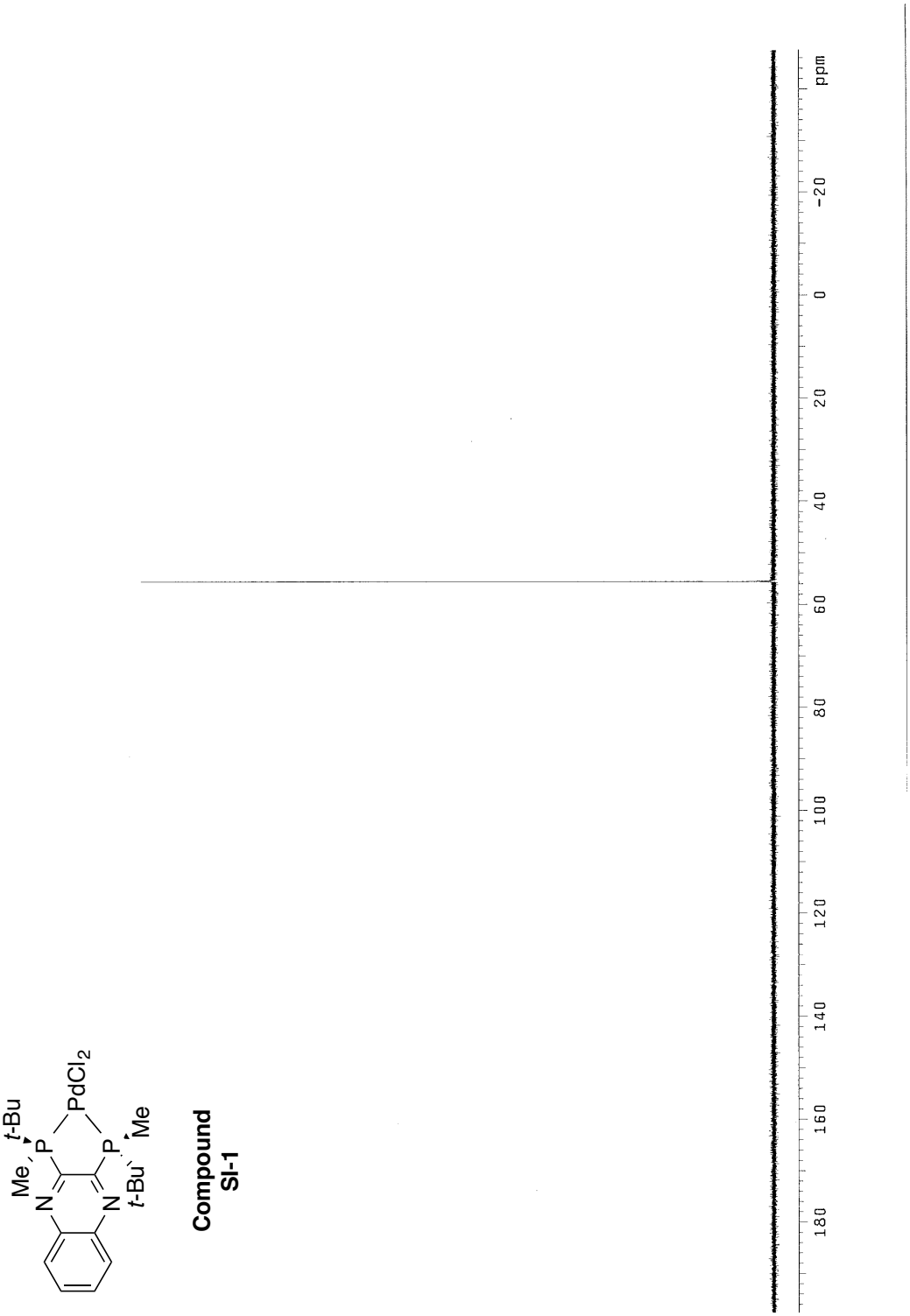

*(R)*-**4**



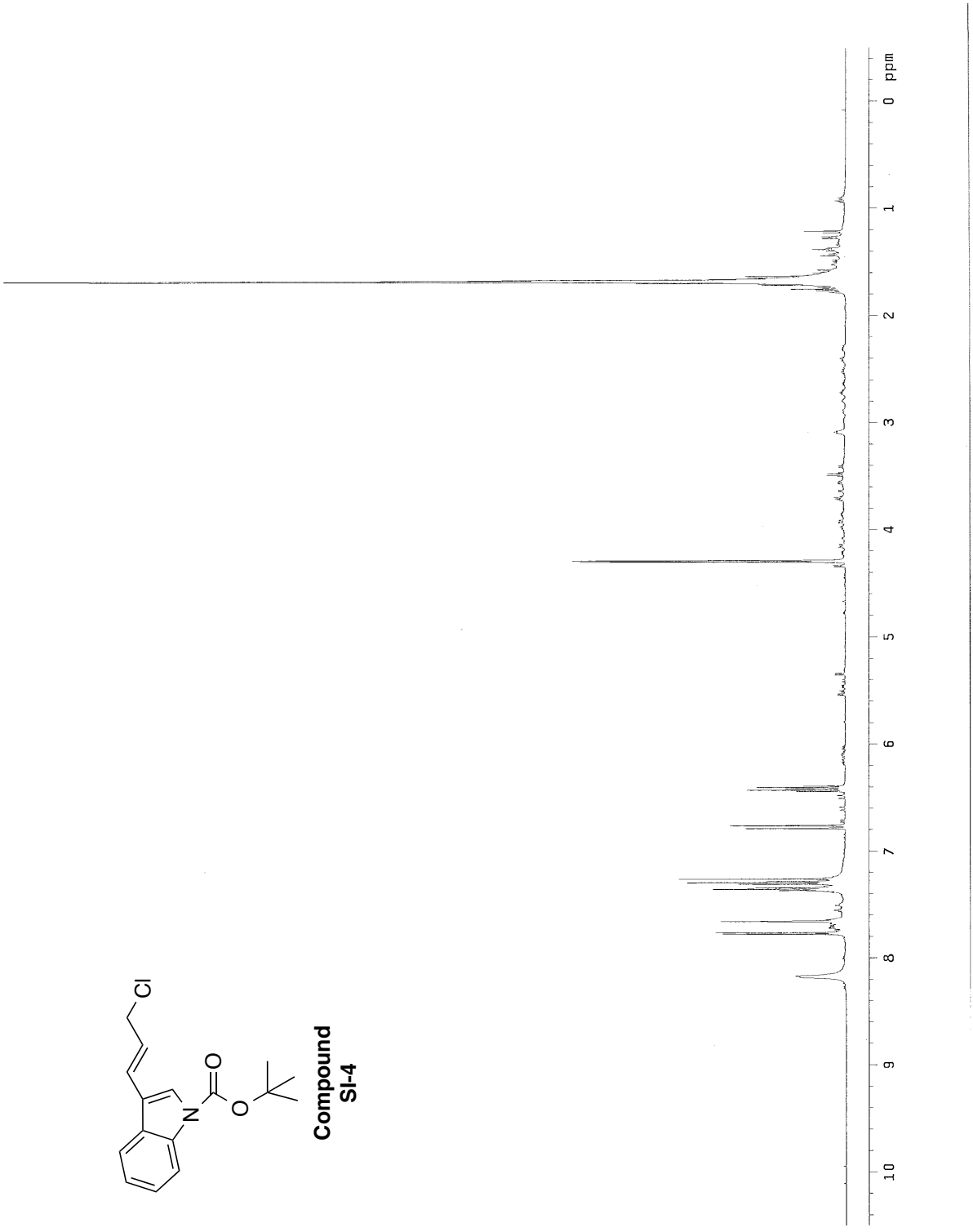

**Compound SI-1**



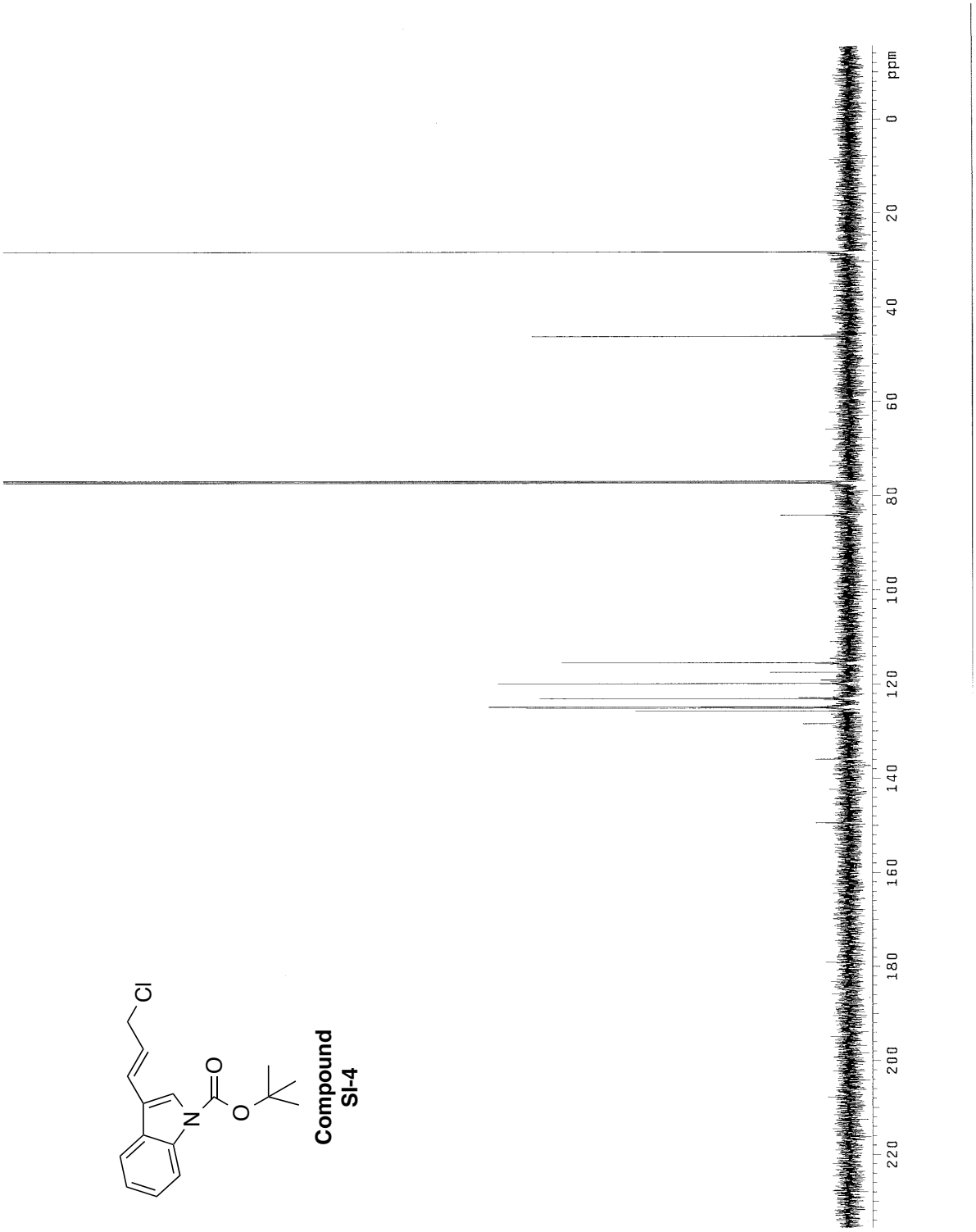

**Compound SI-1**



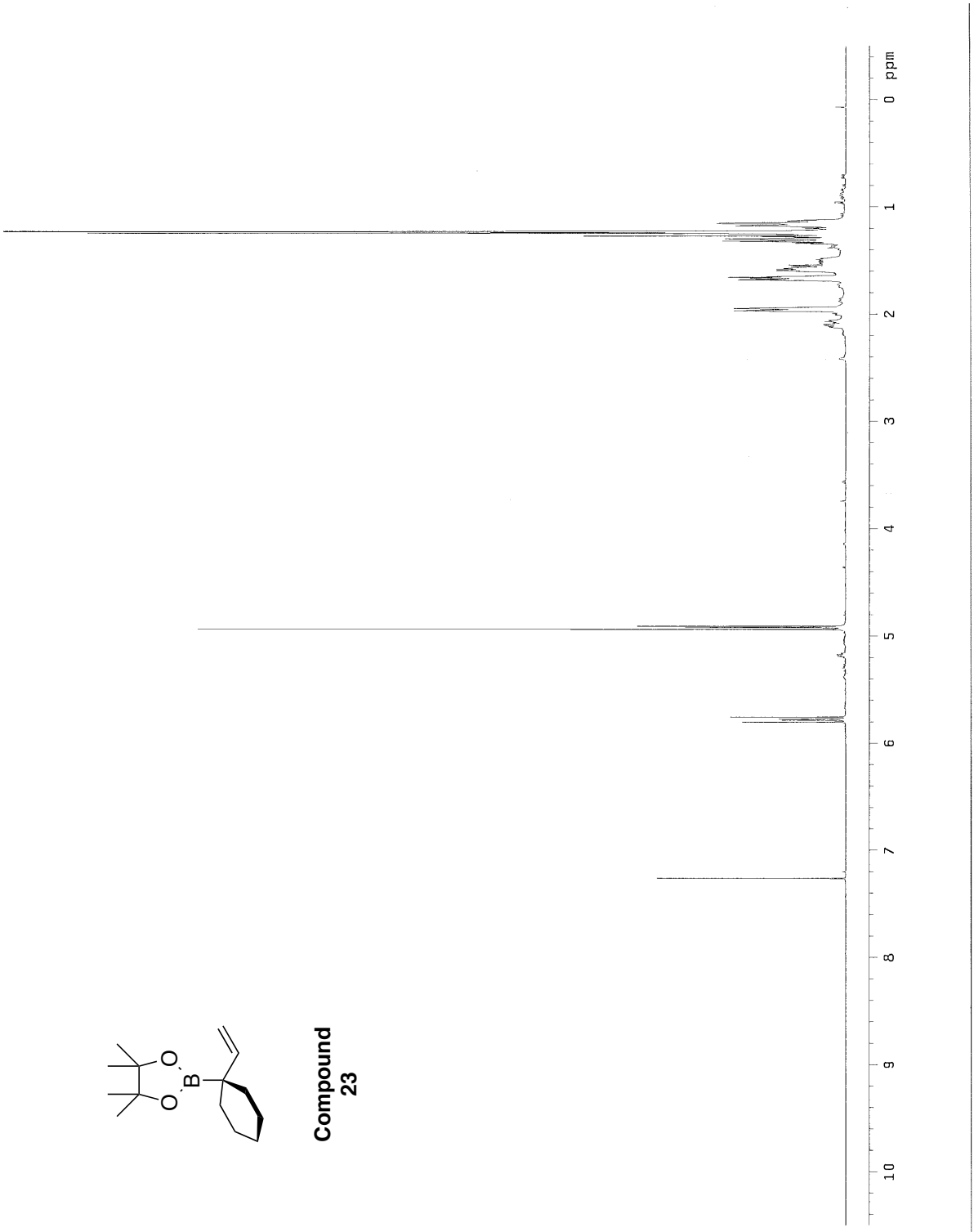

**Compound SI-1**




**Compound SI-4**



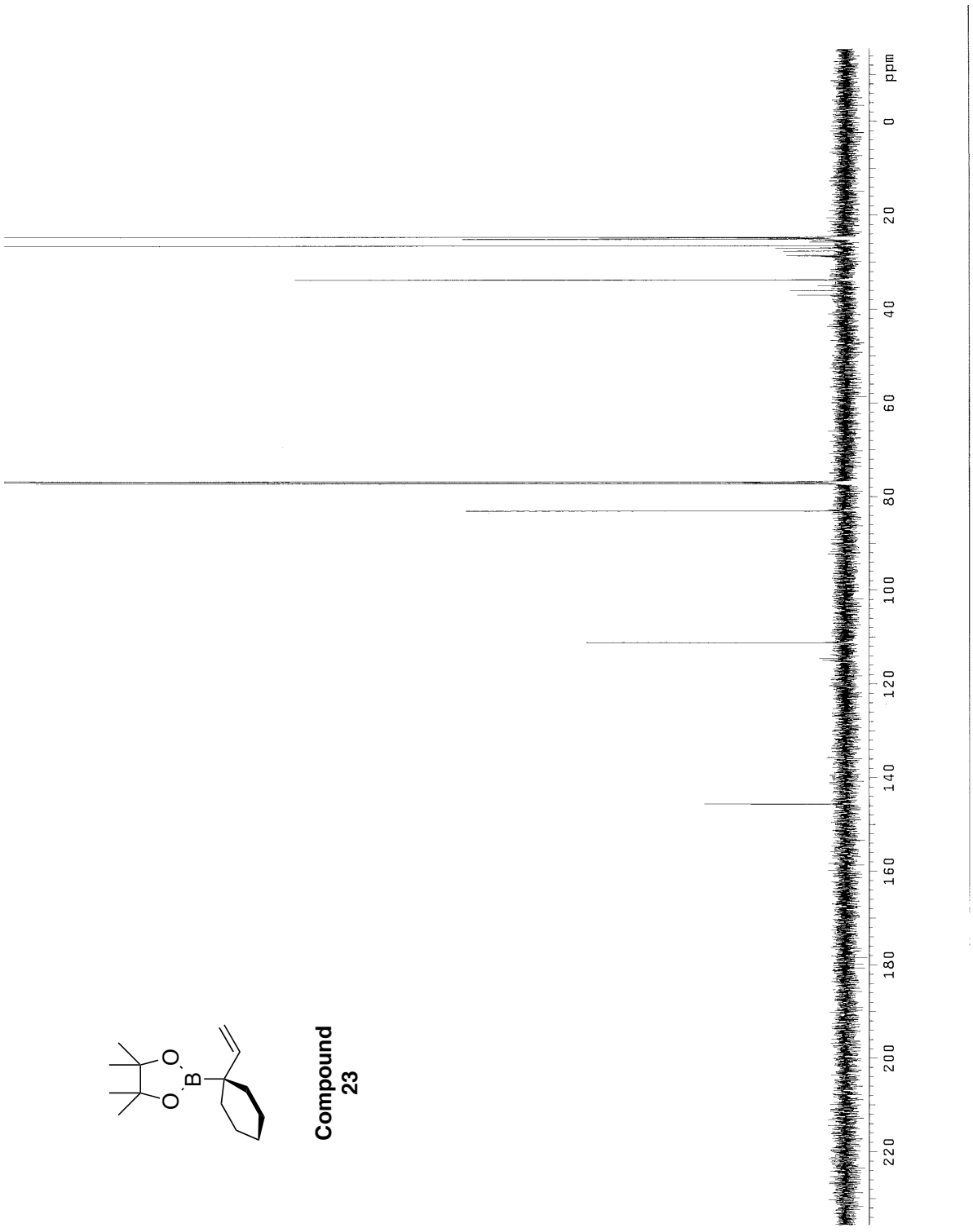

**Compound SI-4**



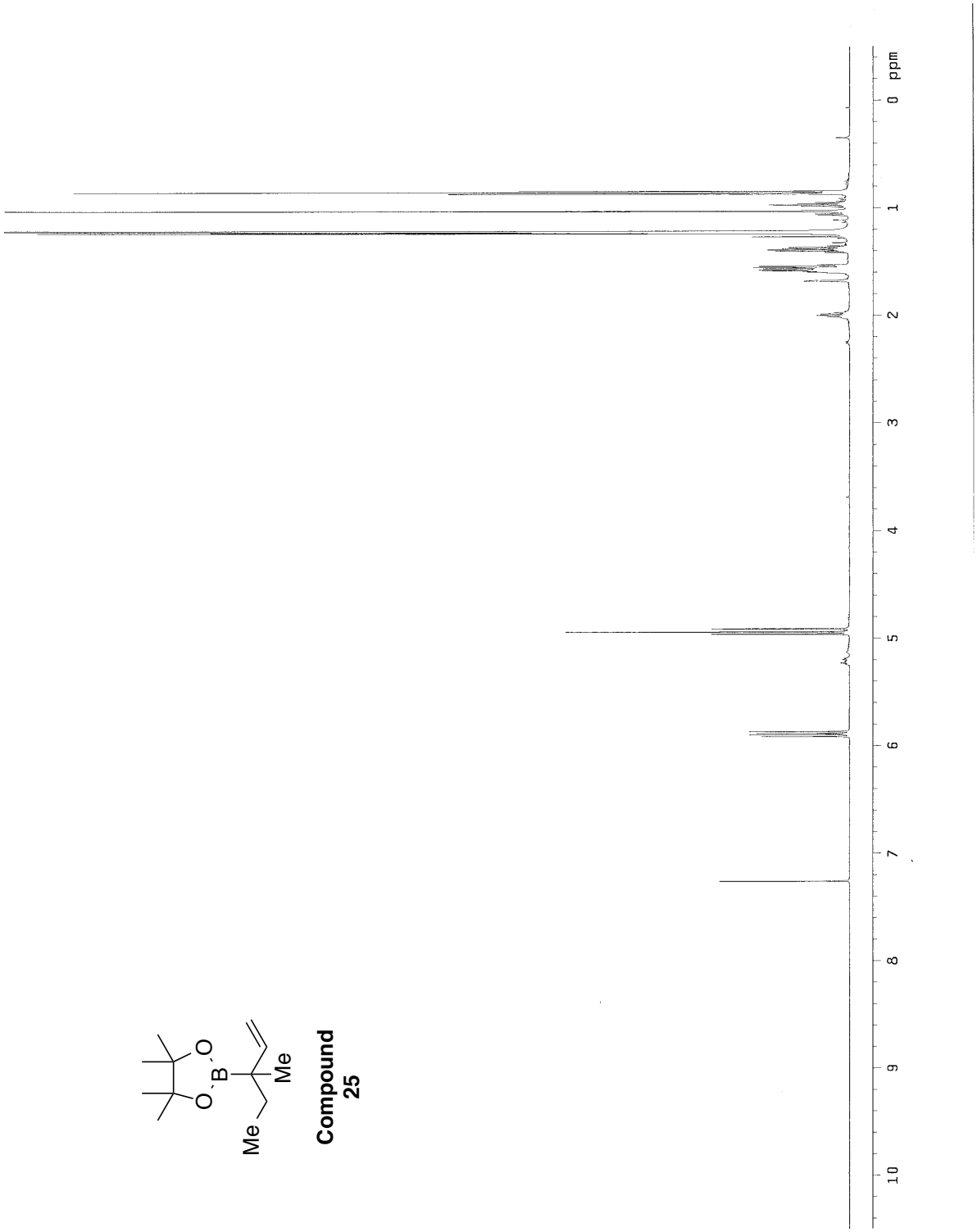




**Compound 23**



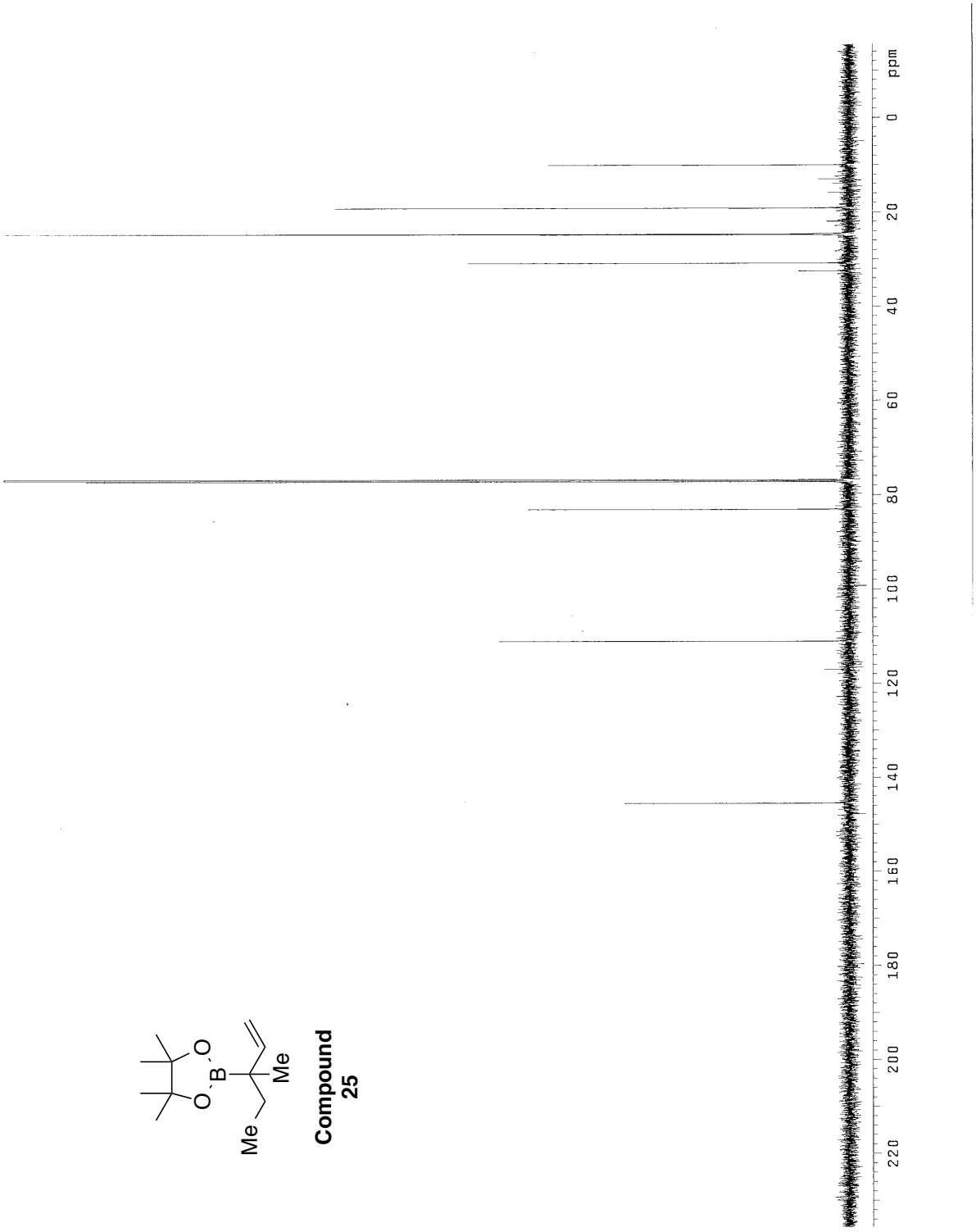

**Compound 23**



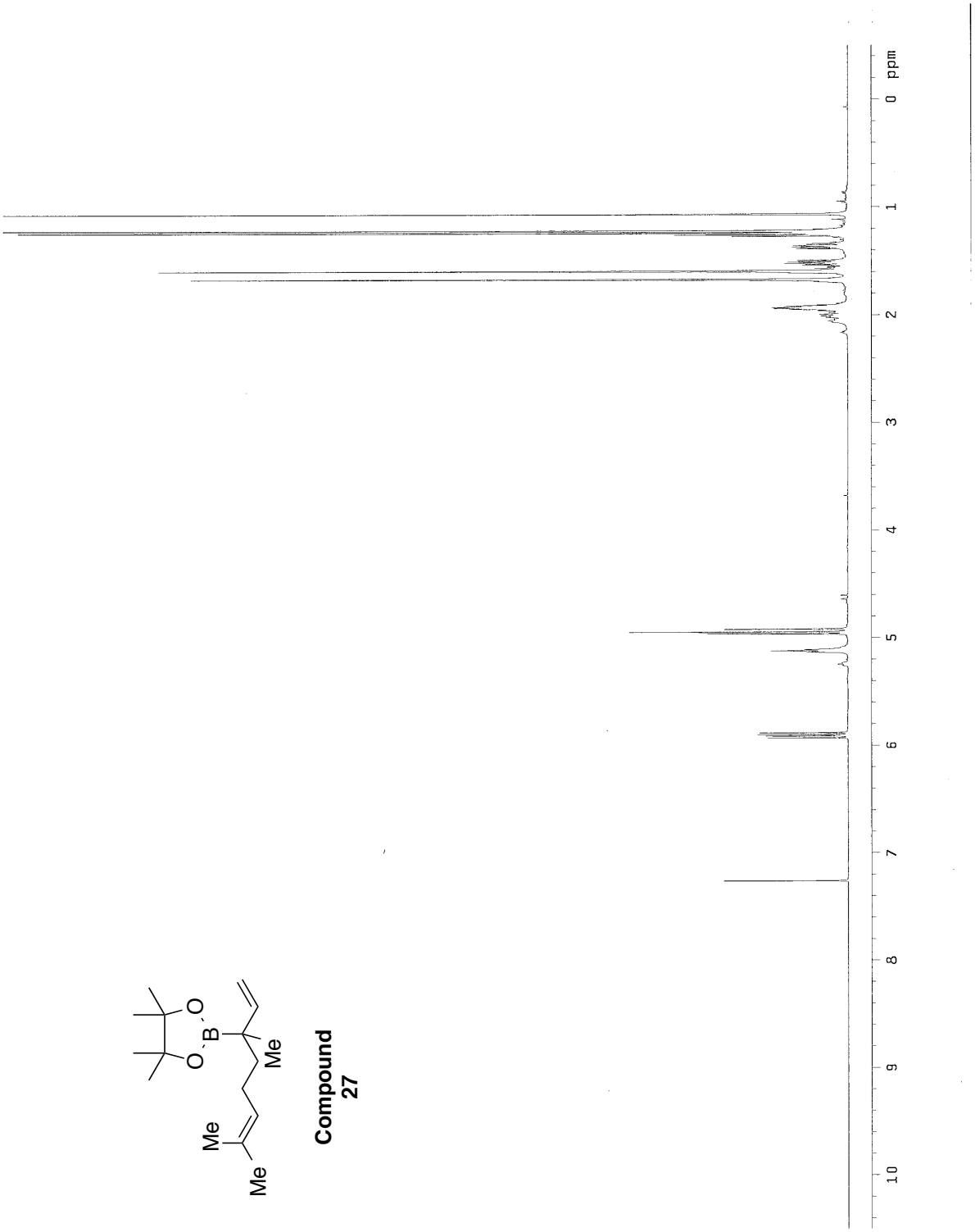


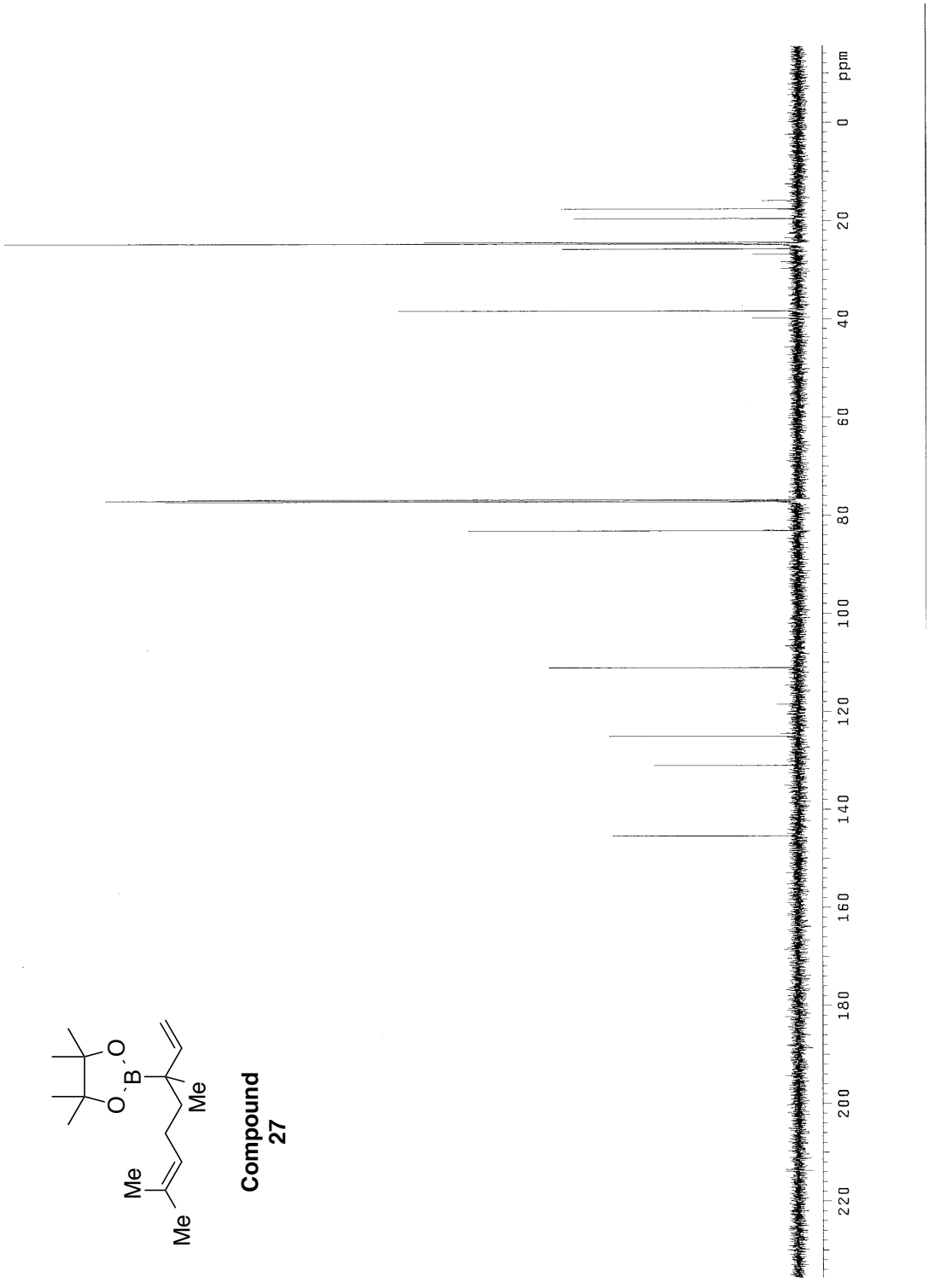


**Compound 25**

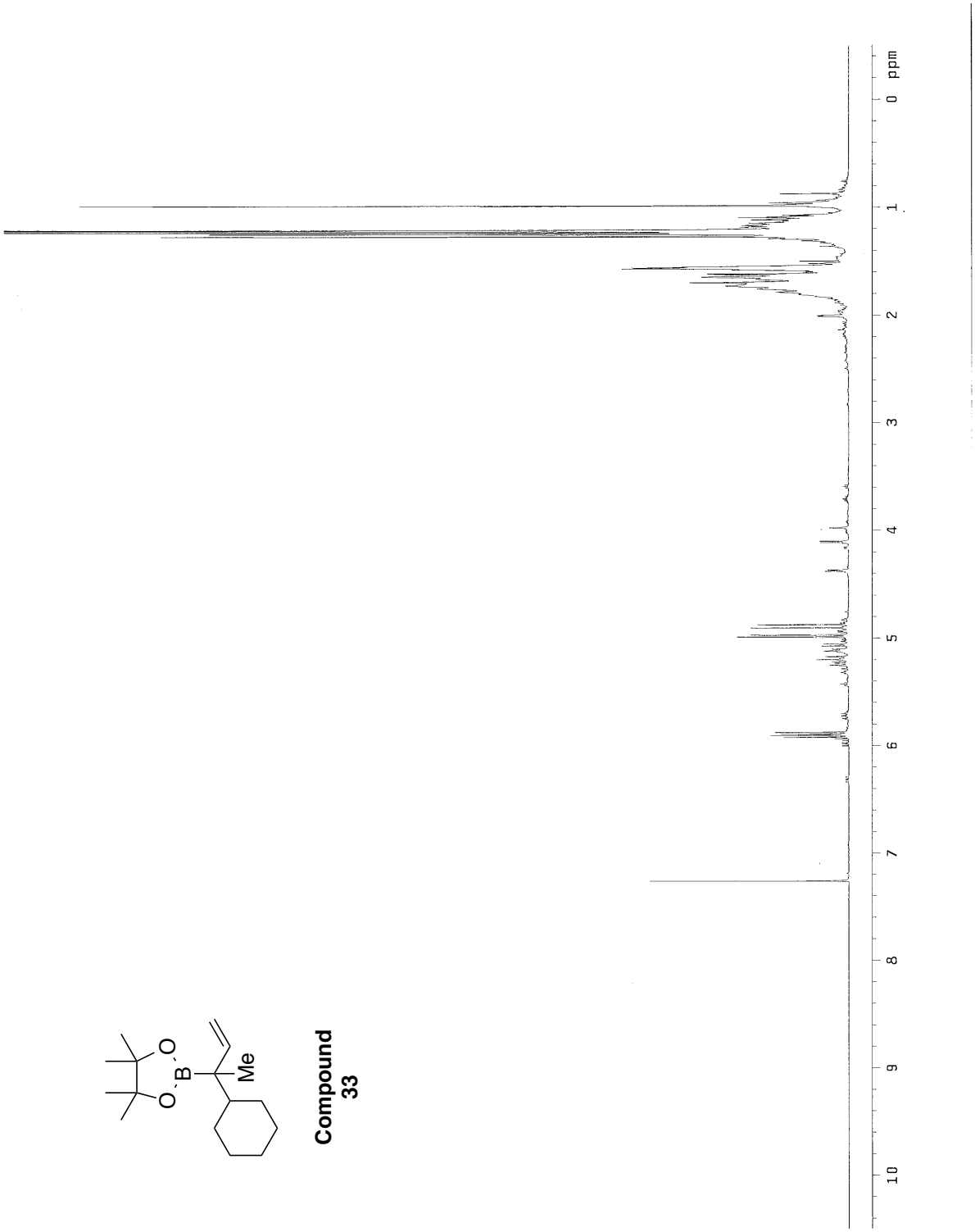



**Compound 25**

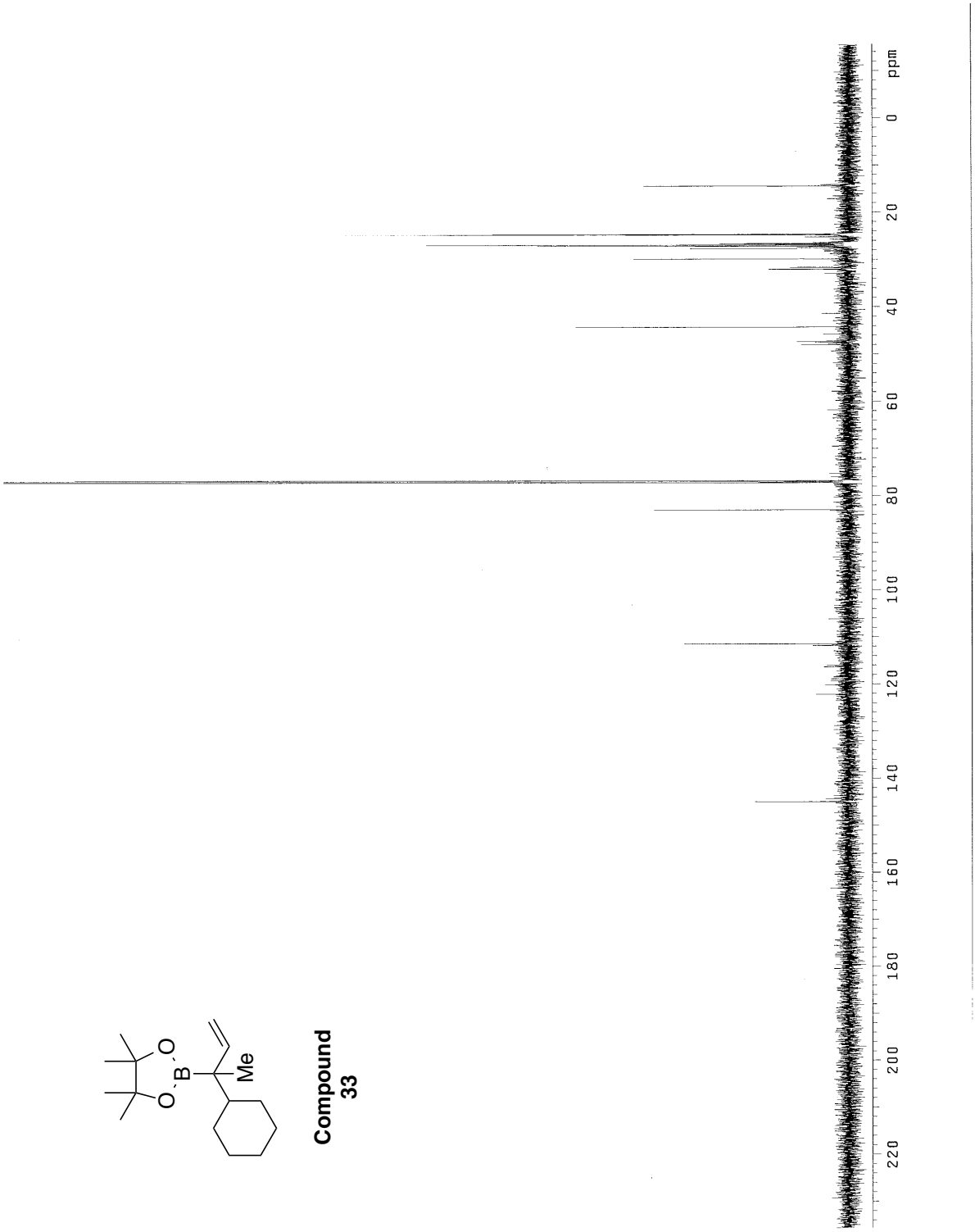

O
B
O
Me
Me
Me
Compound
27
10
9
8
7
6
5
4
3
2
1
0 ppm



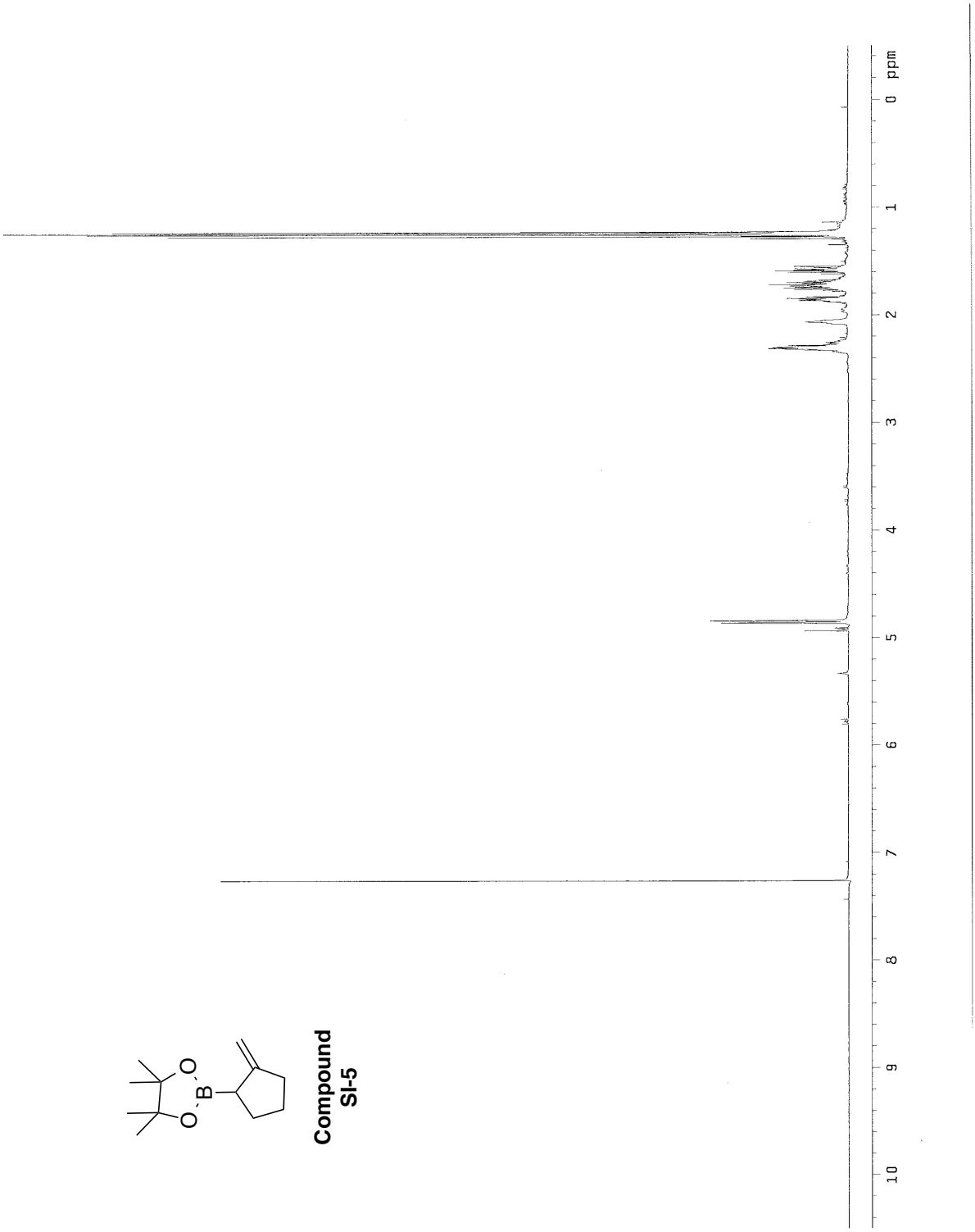

**Compound 27**




**Compound 33**



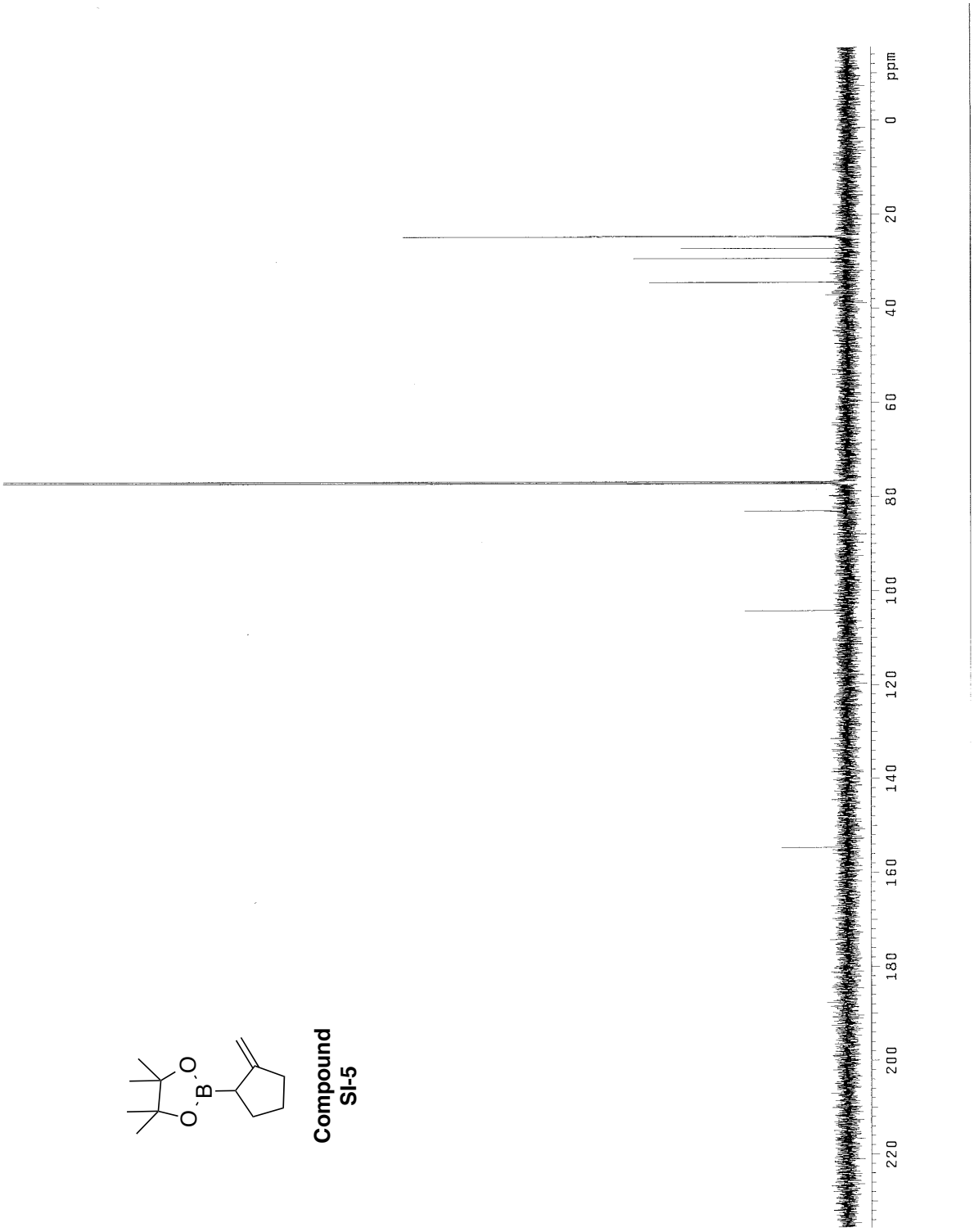

**Compound 33**



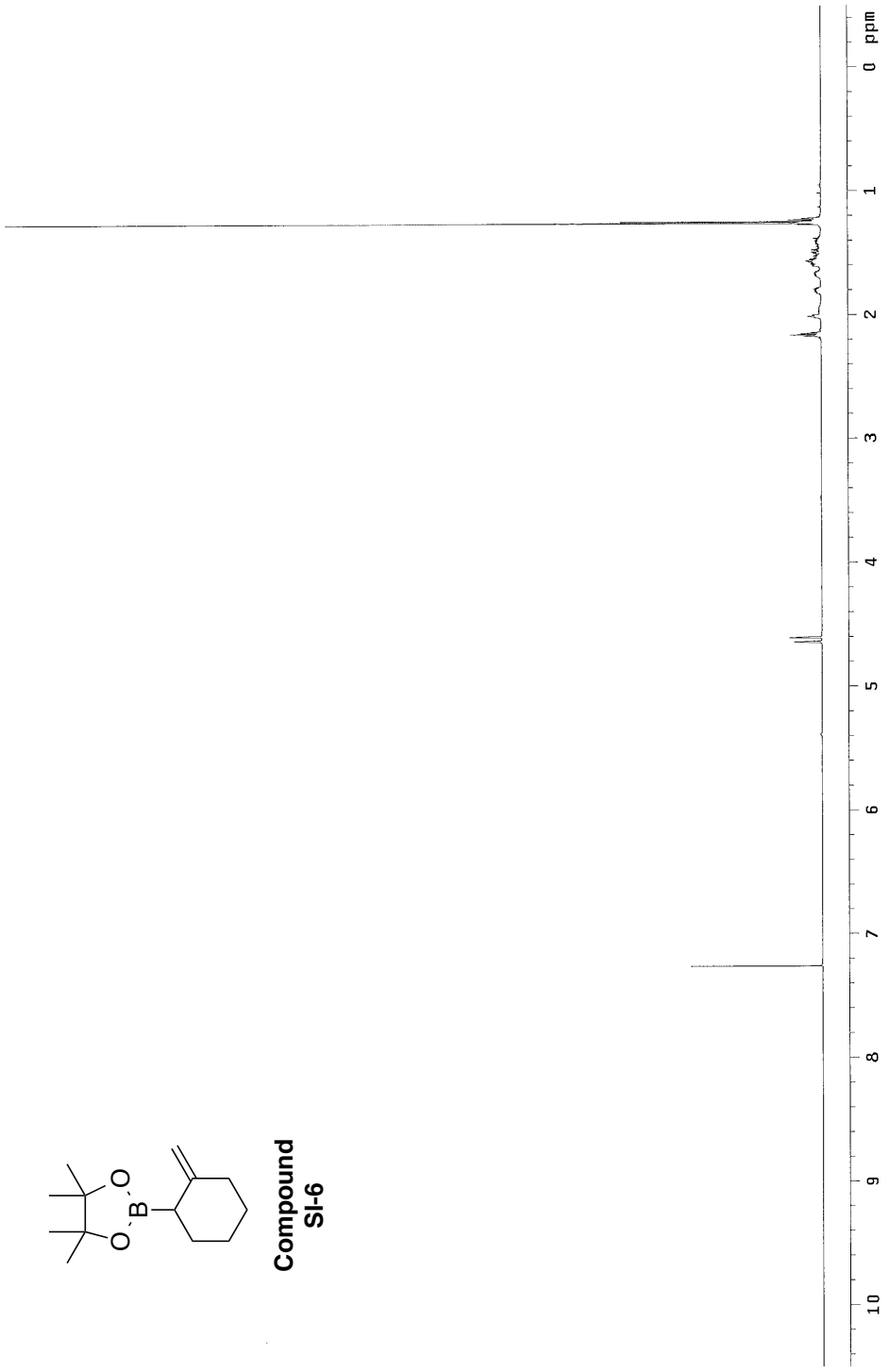




**Compound SI-5**



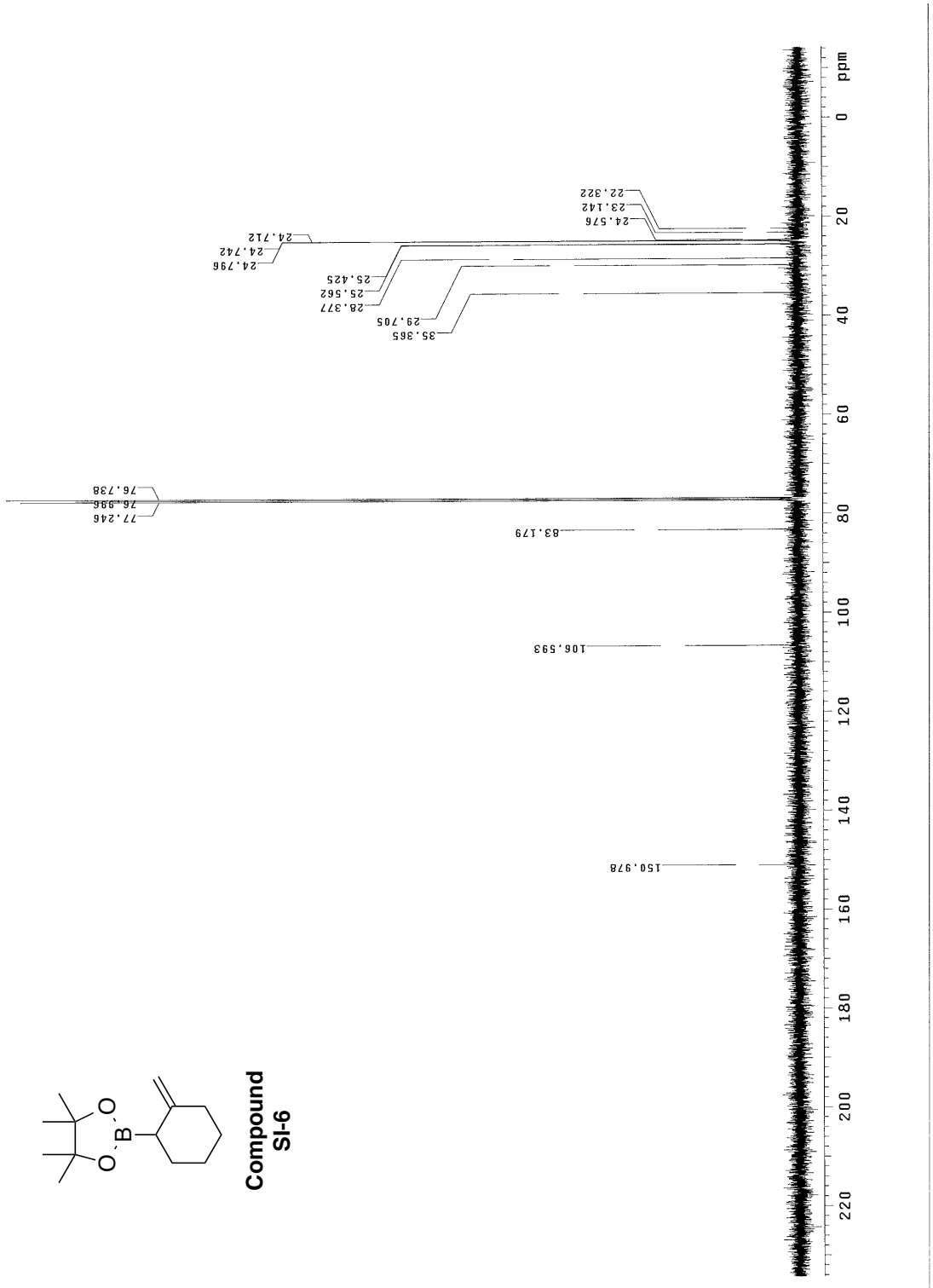

**Compound SI-5**





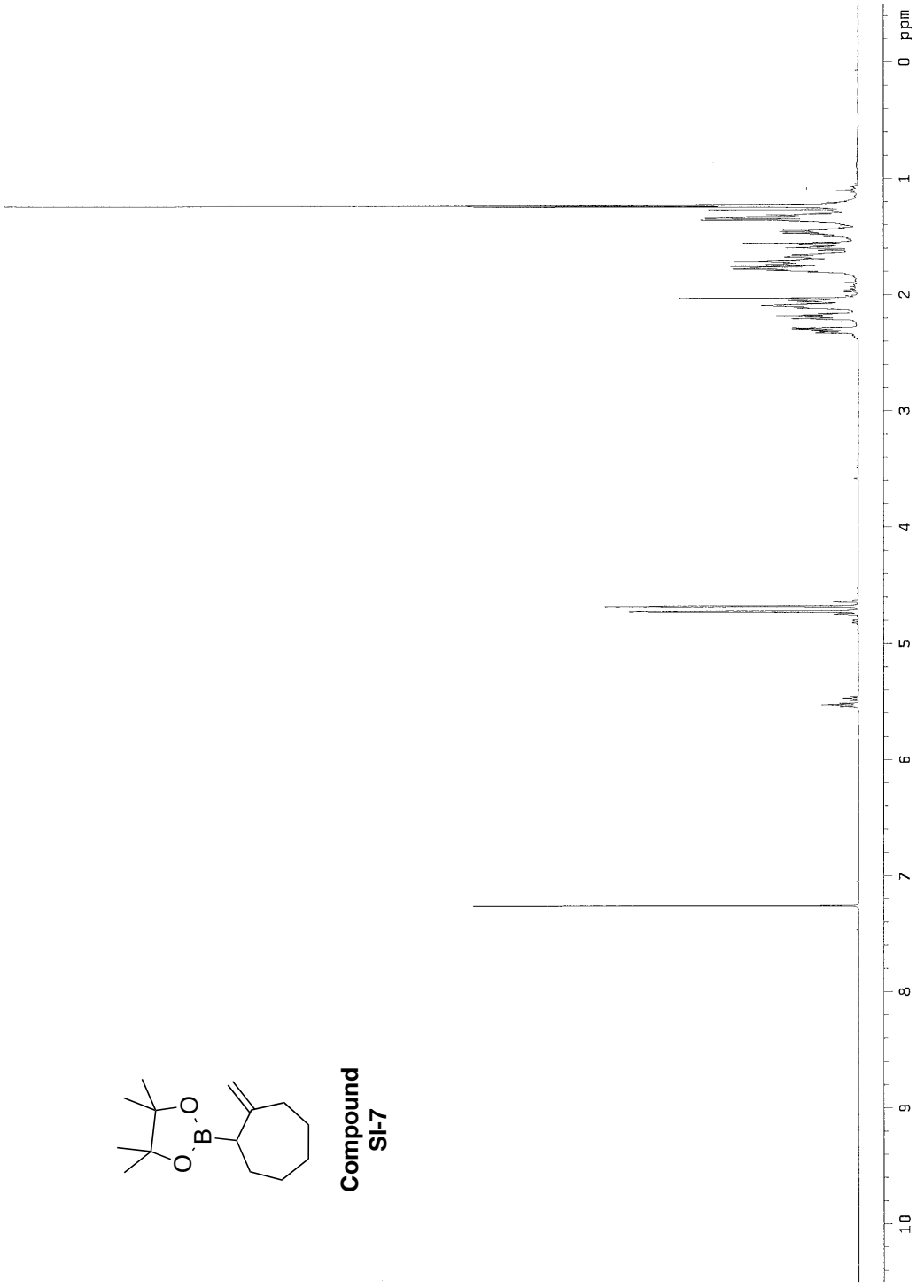


**Compound SI-6**



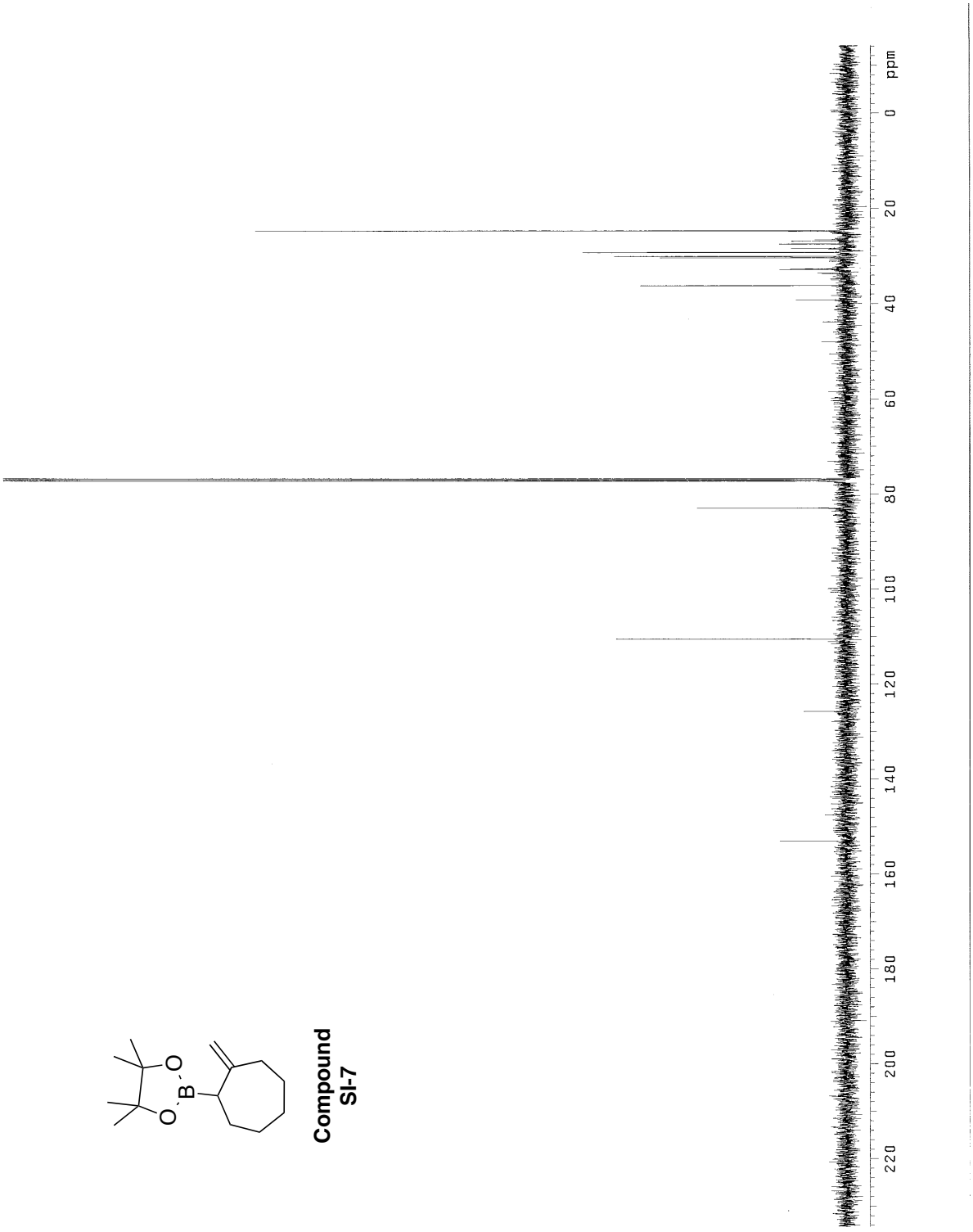



**Compound SI-6**

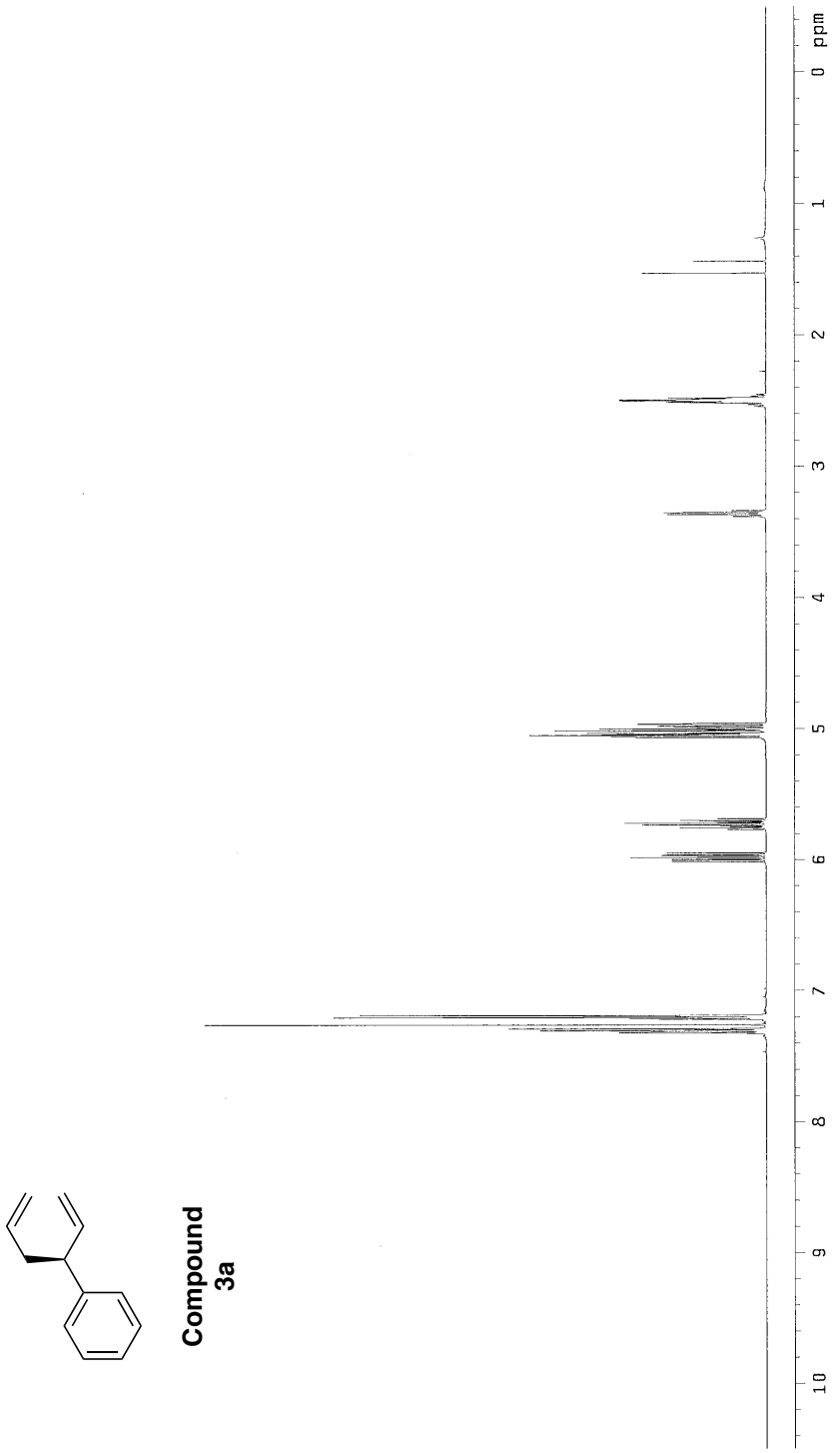





**Compound SI-7**

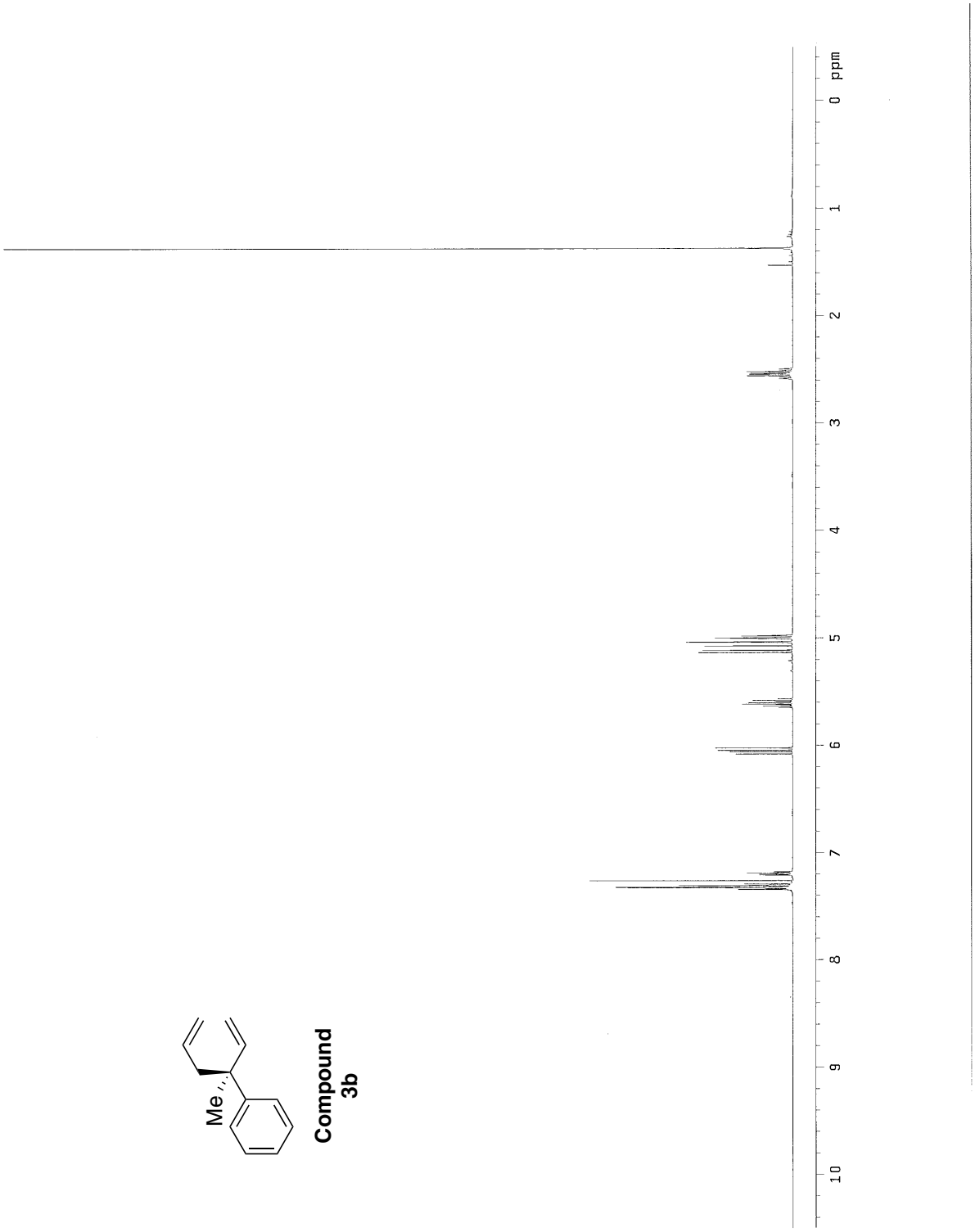


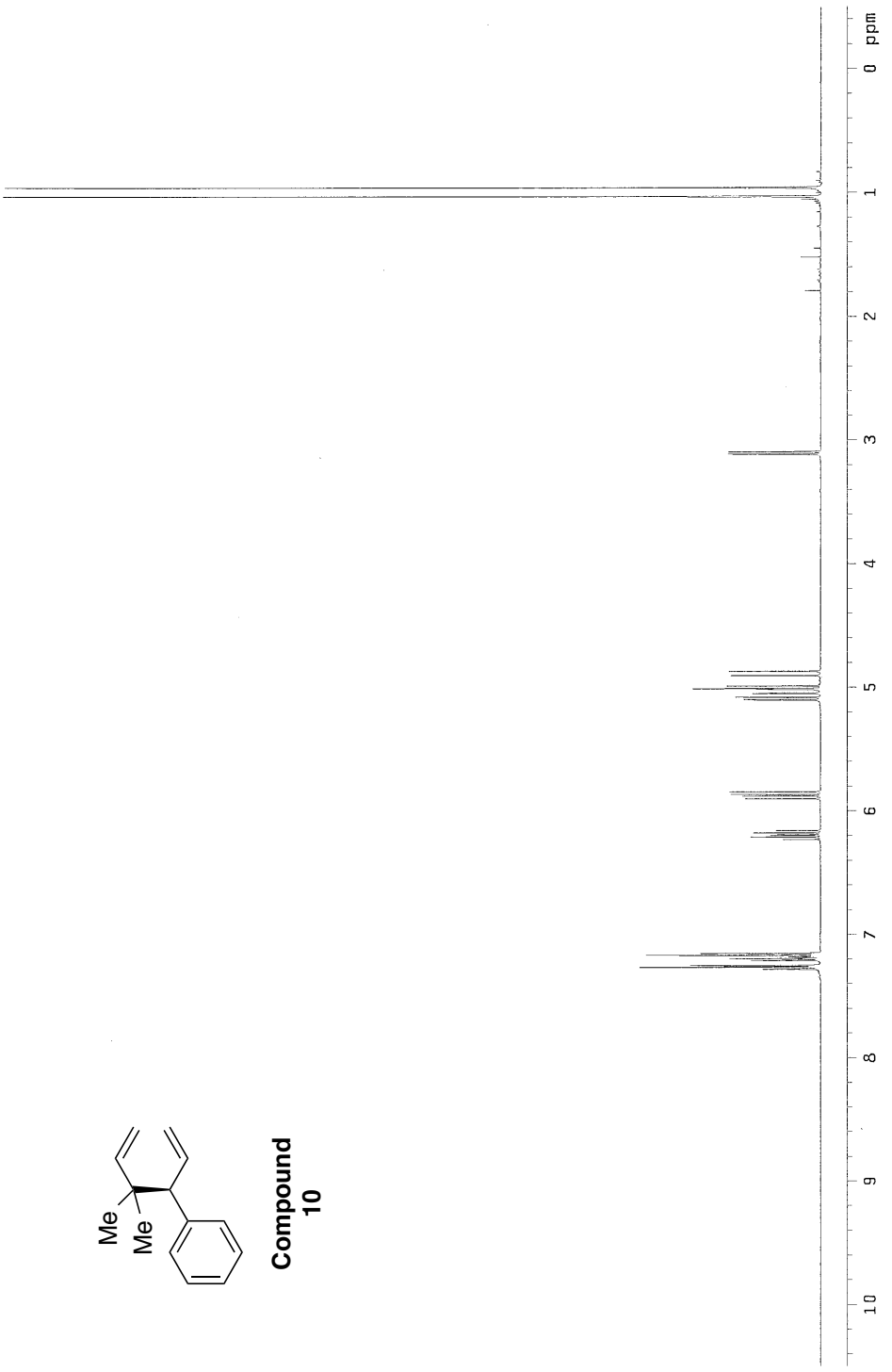

**Compound SI-7**

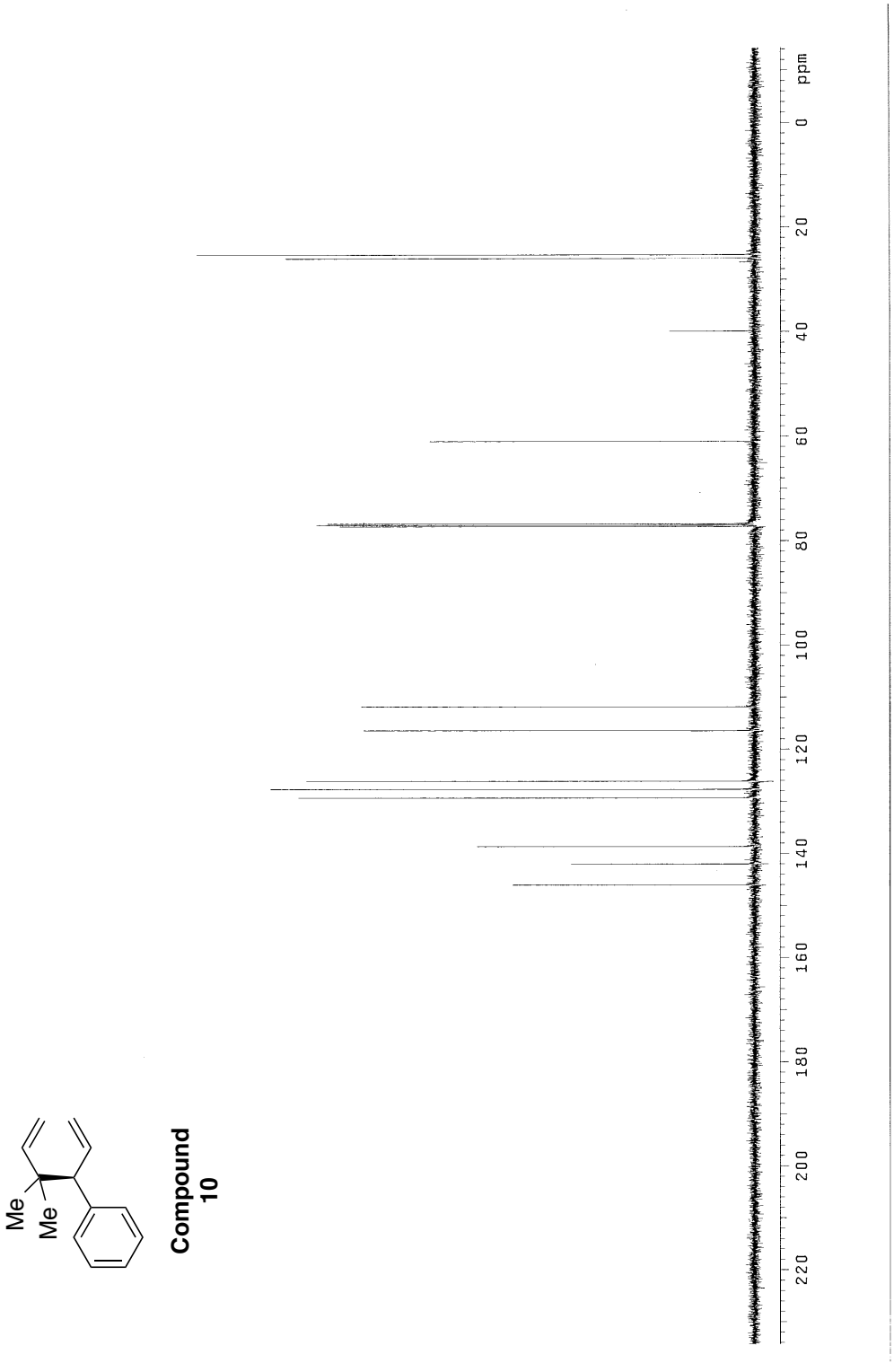


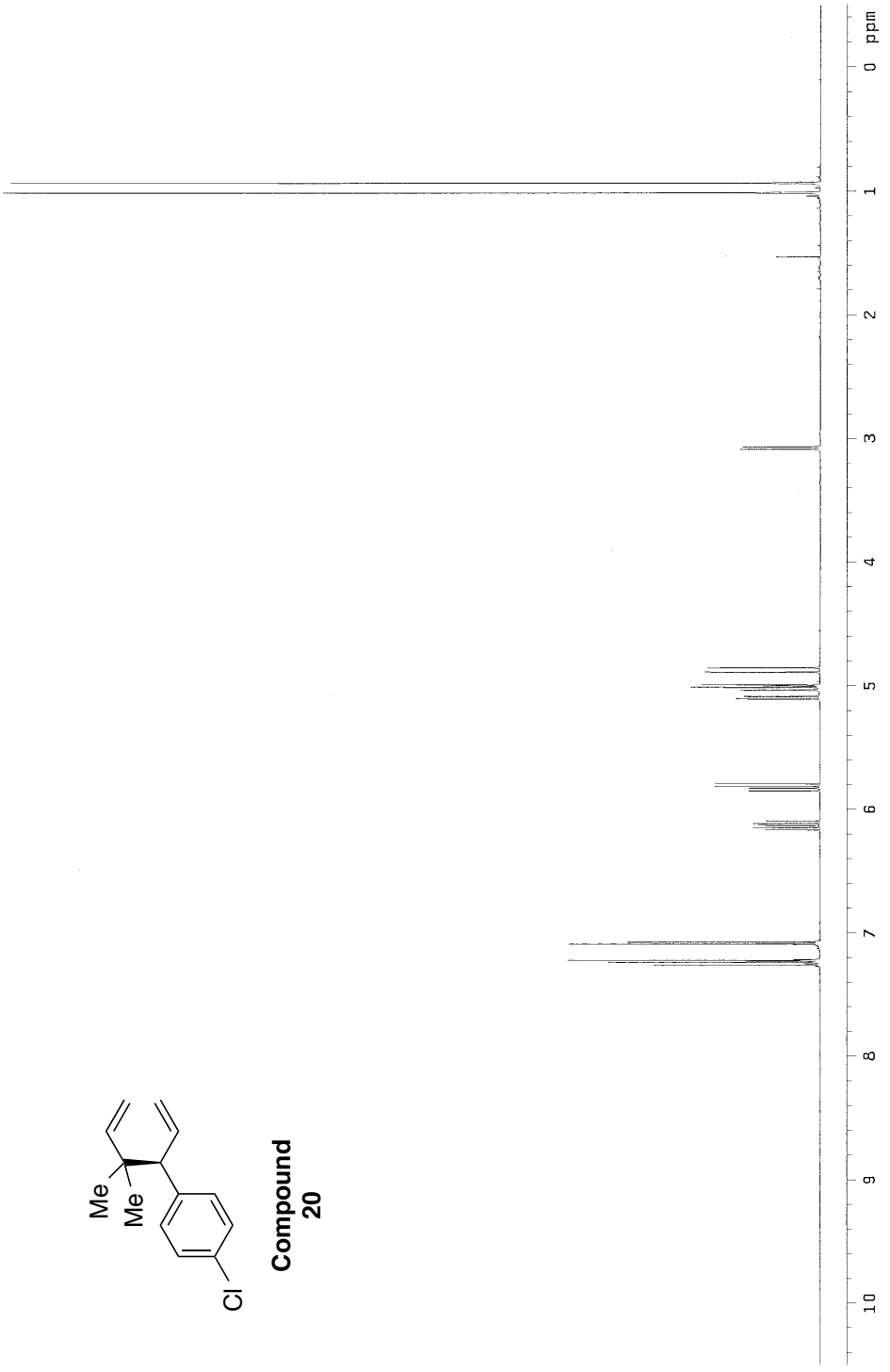


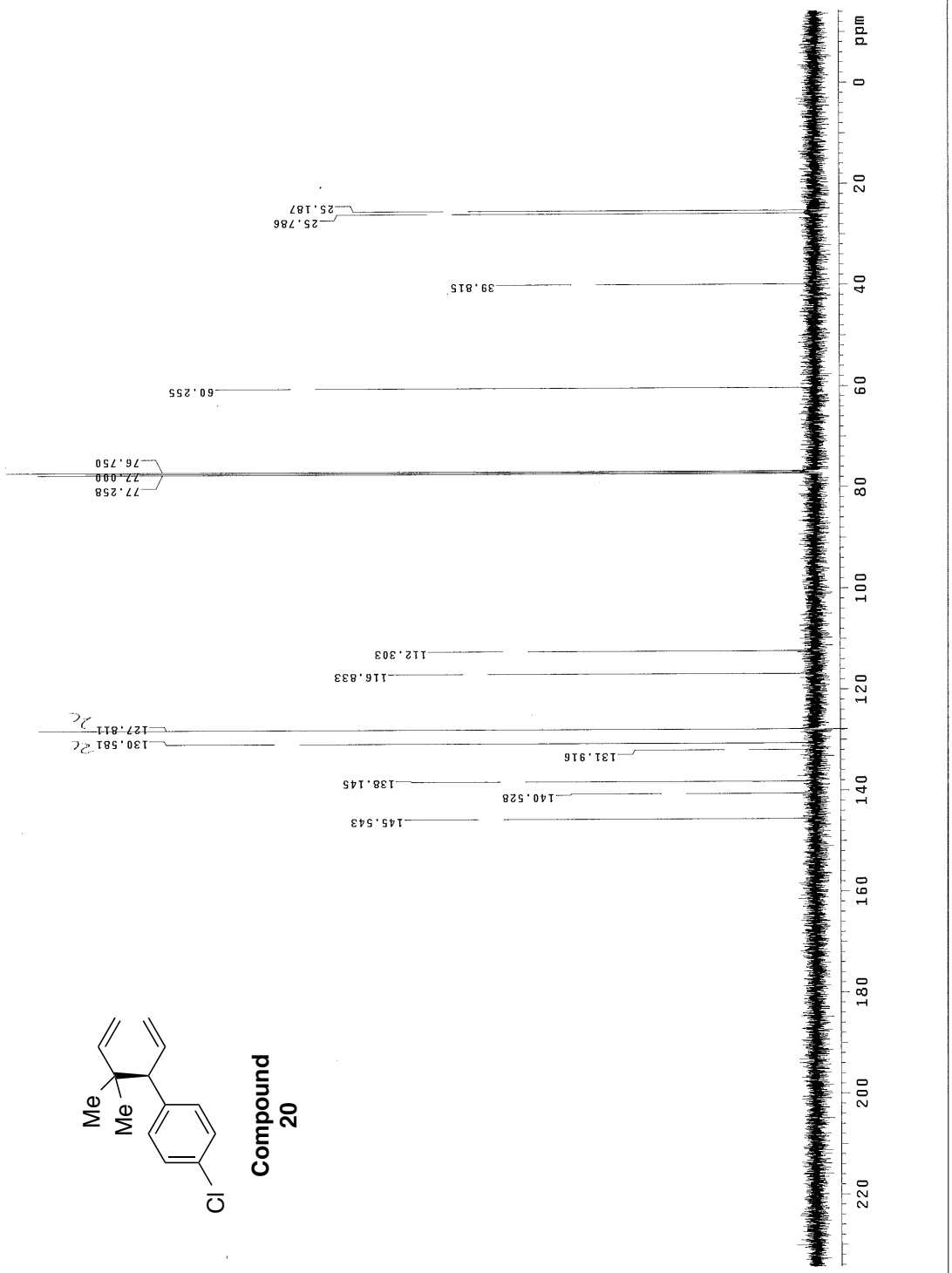

**Compound 3a**

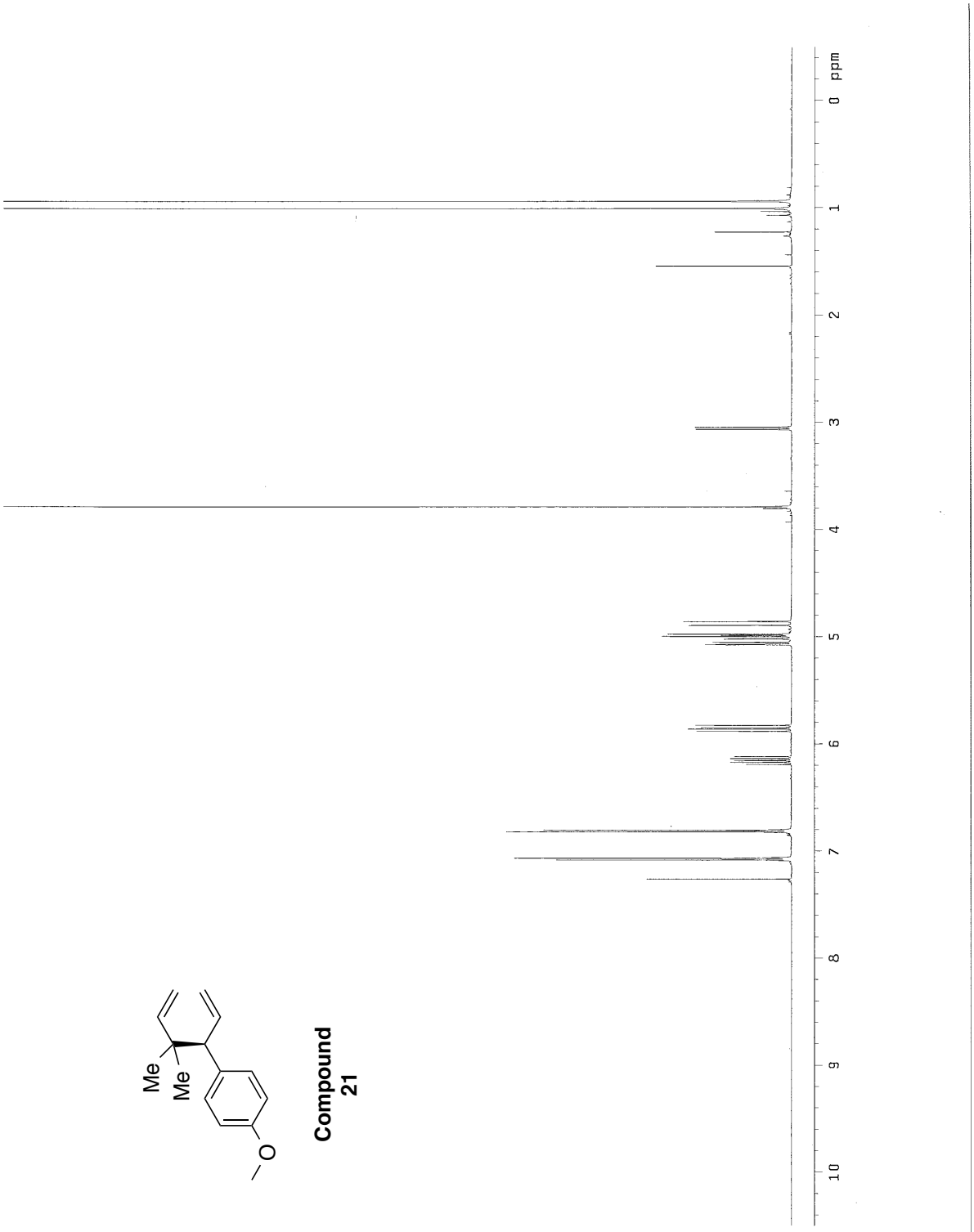

Me
Compound
3b
0 ppm
1
2
3
4
5
6
7
8
9
10

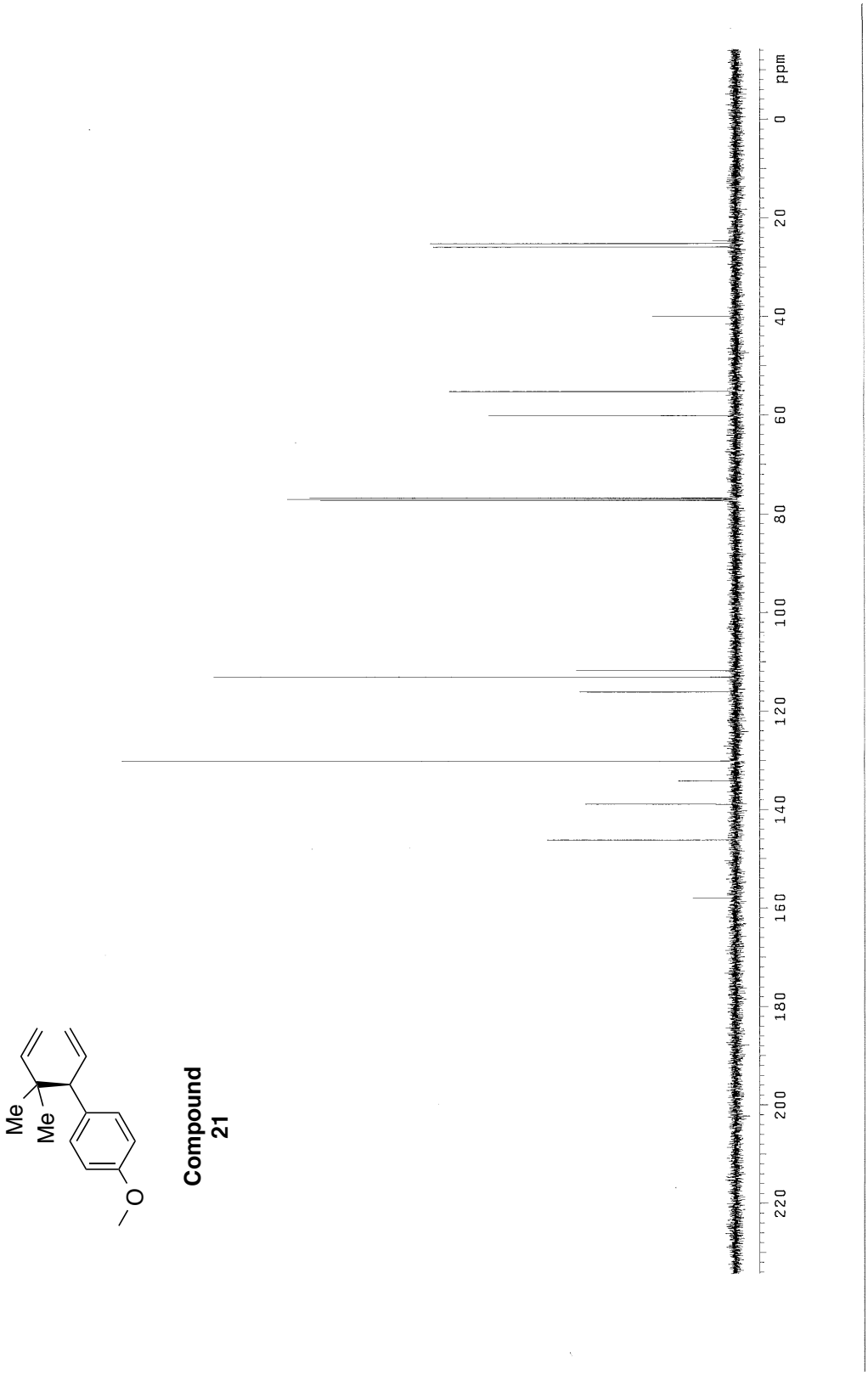

Me
Me
Compound
10
10
9
8
7
6
5
4
3
2
1
0 ppm


Me
Me
Compound
10
ppm
0
20
40
60
80
100
120
140
160
180
200
220

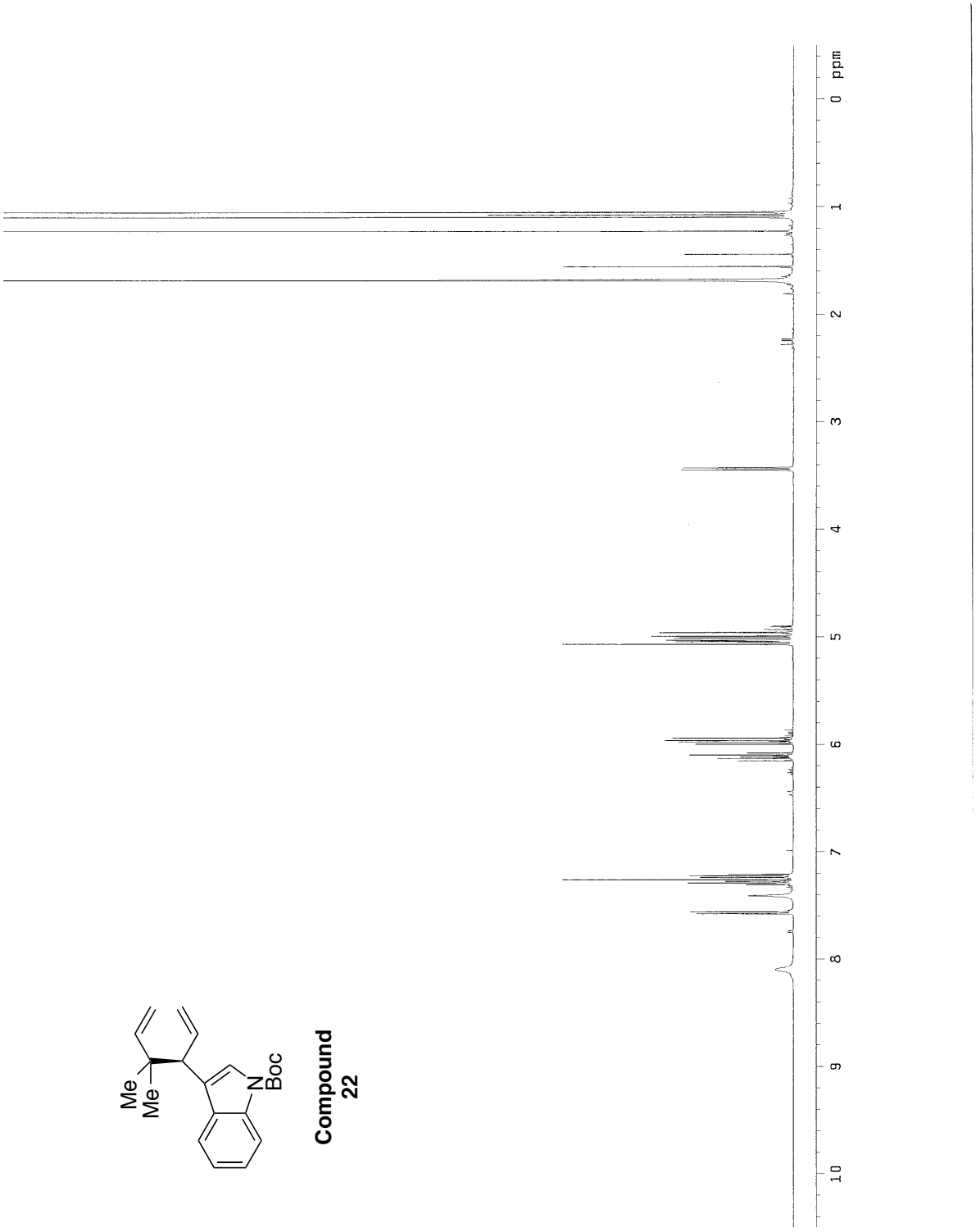

Me
Me
Cl
Compound
20
10
9
8
7
6
5
4
3
2
1
0 ppm

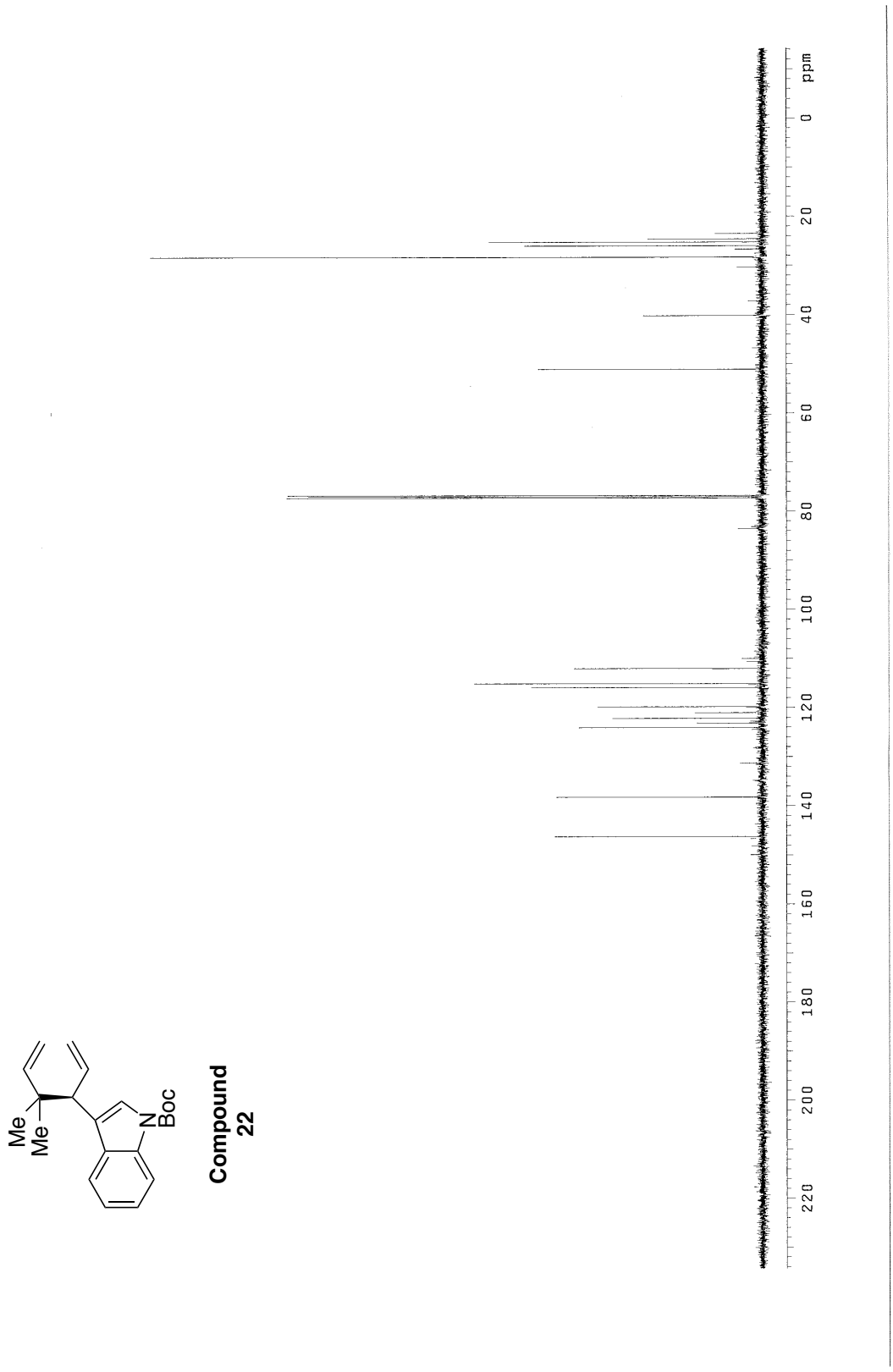

25.187
25.786
39.815
60.255
76.750
77.000
77.258
112.303
116.833
127.811
130.581
131.916
138.145
140.528
145.543
ppm
0
20
40
60
80
100
120
140
160
180
200
220
Me
Me
Cl
Compound
20


Me
Me
O
Compound
21
10
9
8
7
6
5
4
3
2
1
0 ppm

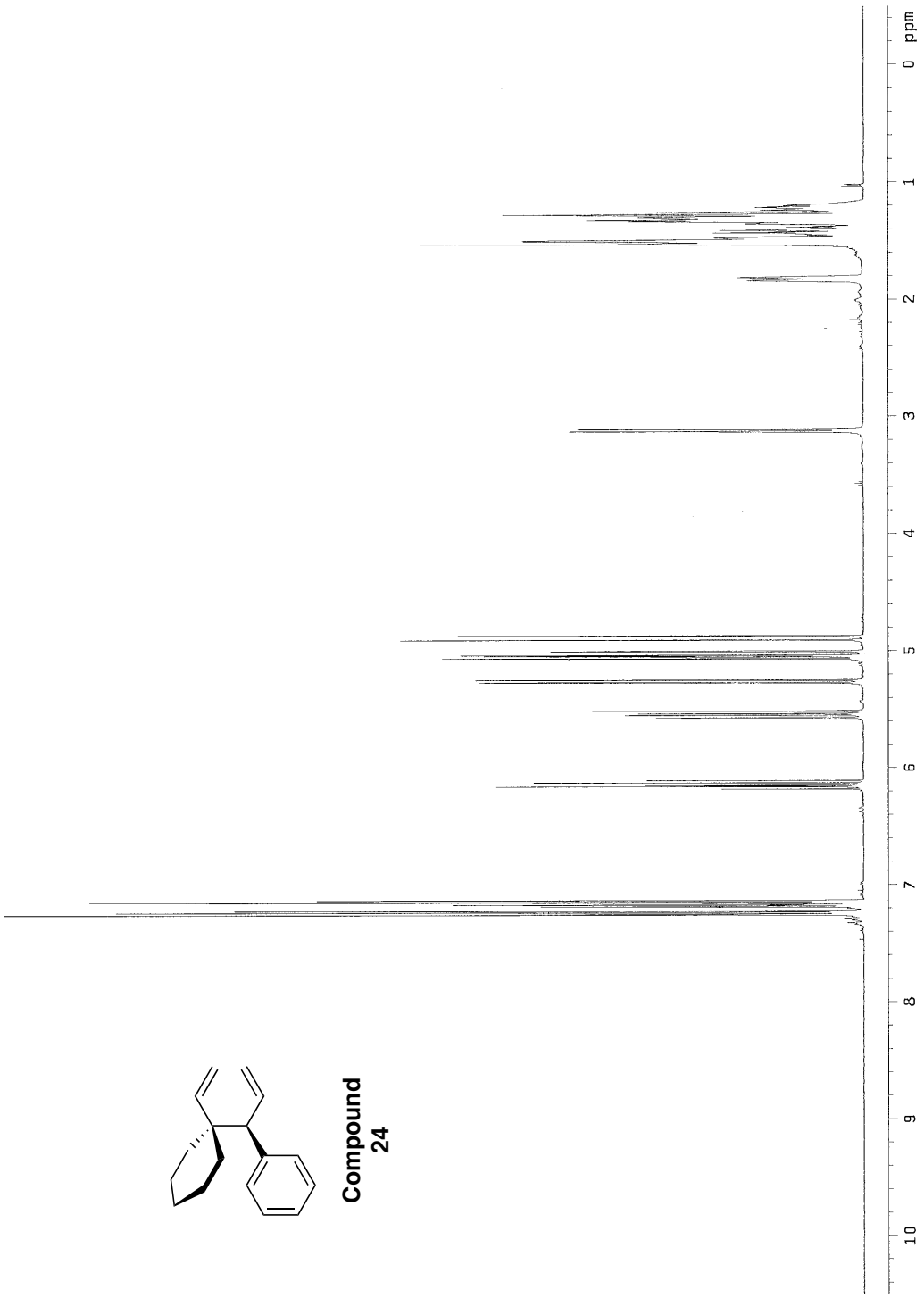



**Compound 21**


Me
Me
N
Boc
Compound
22
0 ppm
1
2
3
4
5
6
7
8
9
10

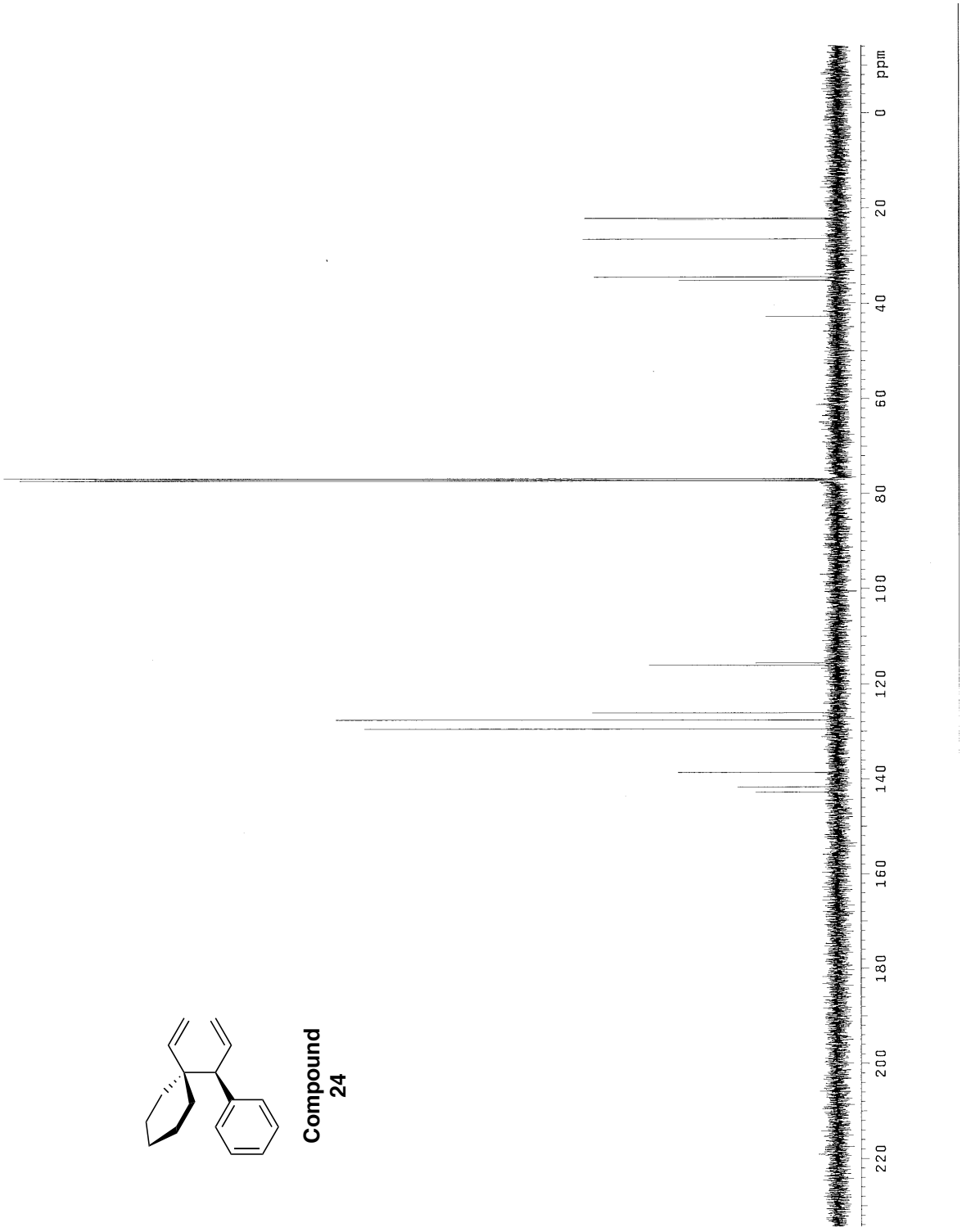



**Compound 22**



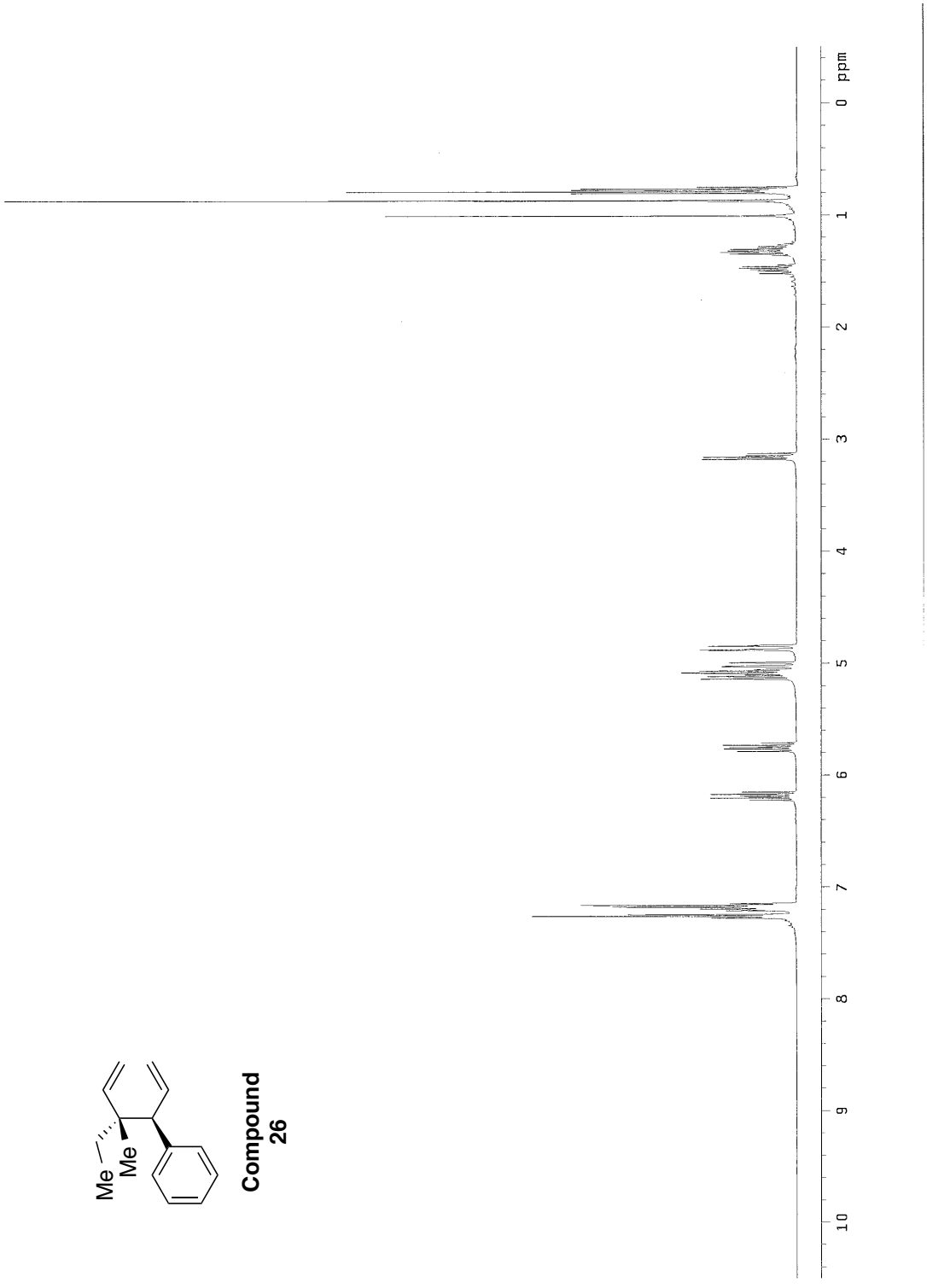


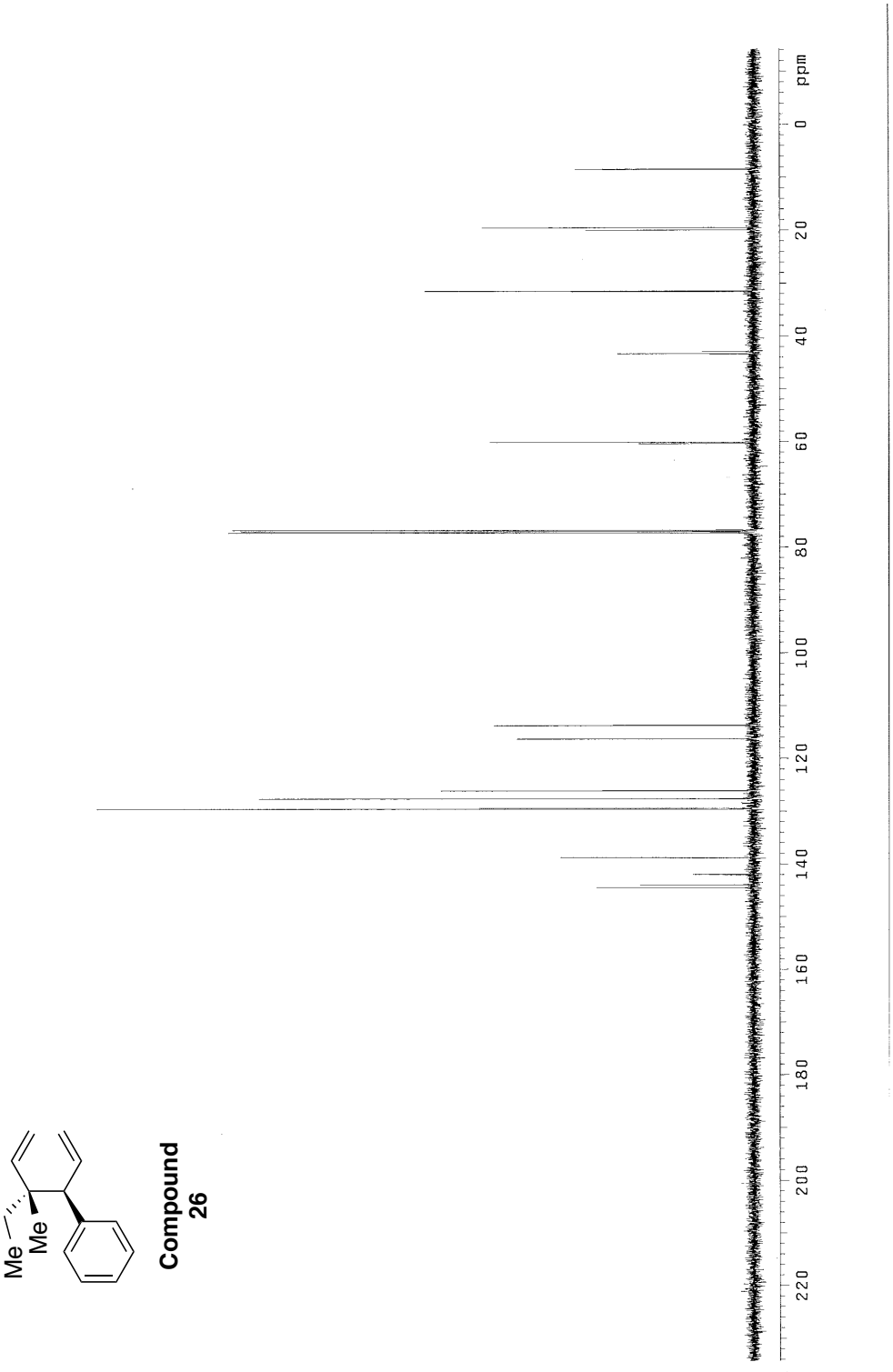

**Compound 24**



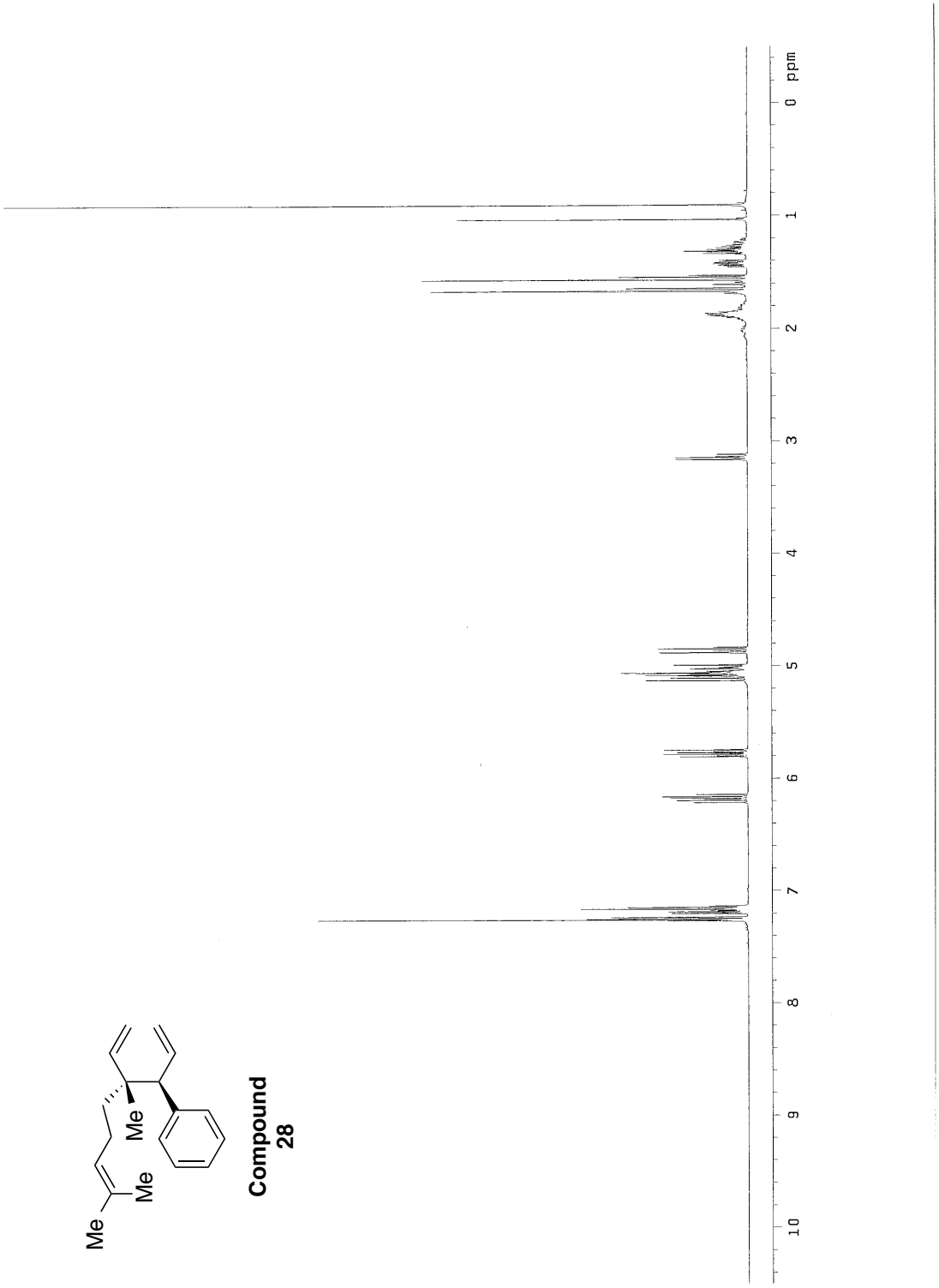


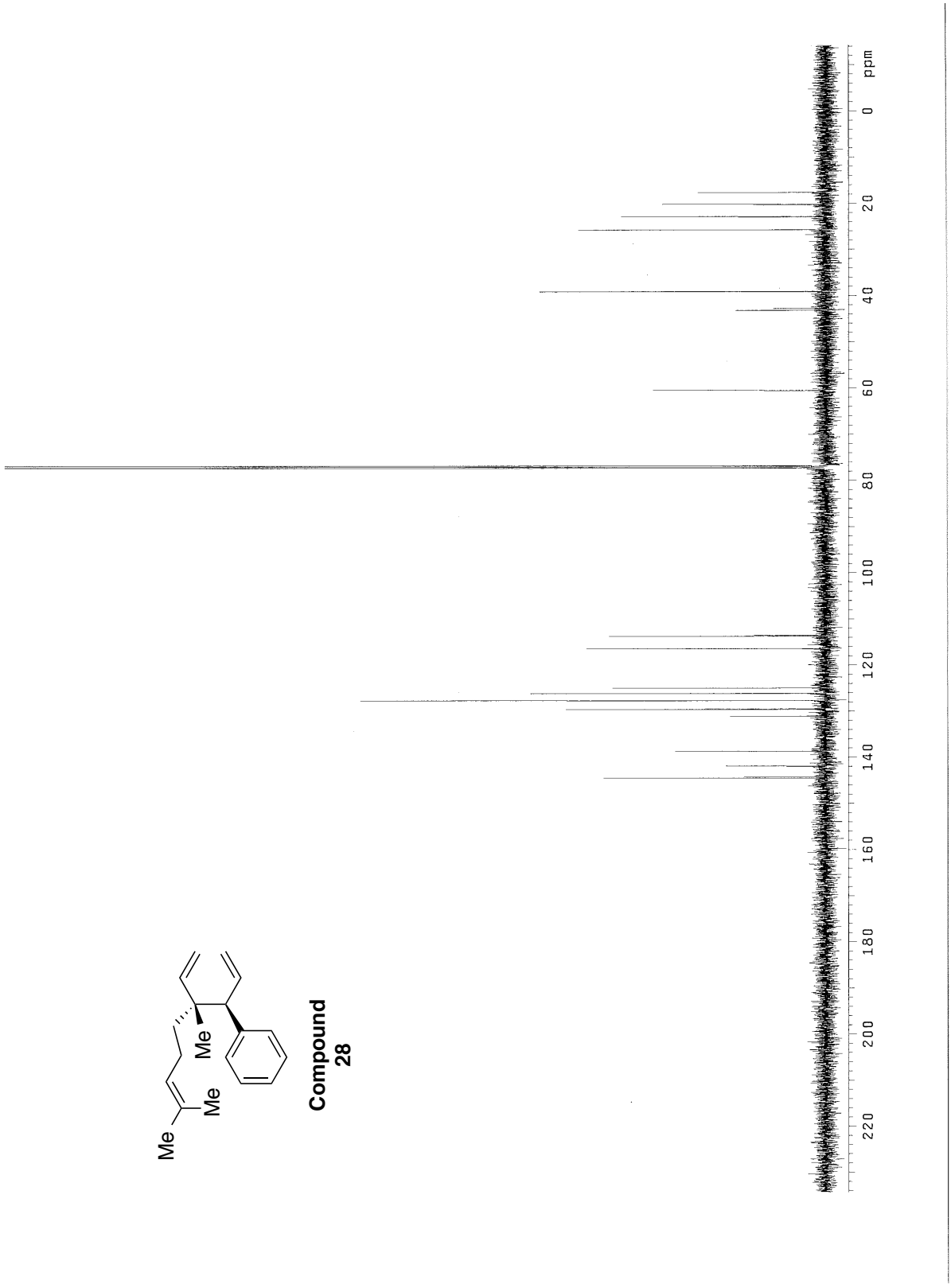

**Compound 24**

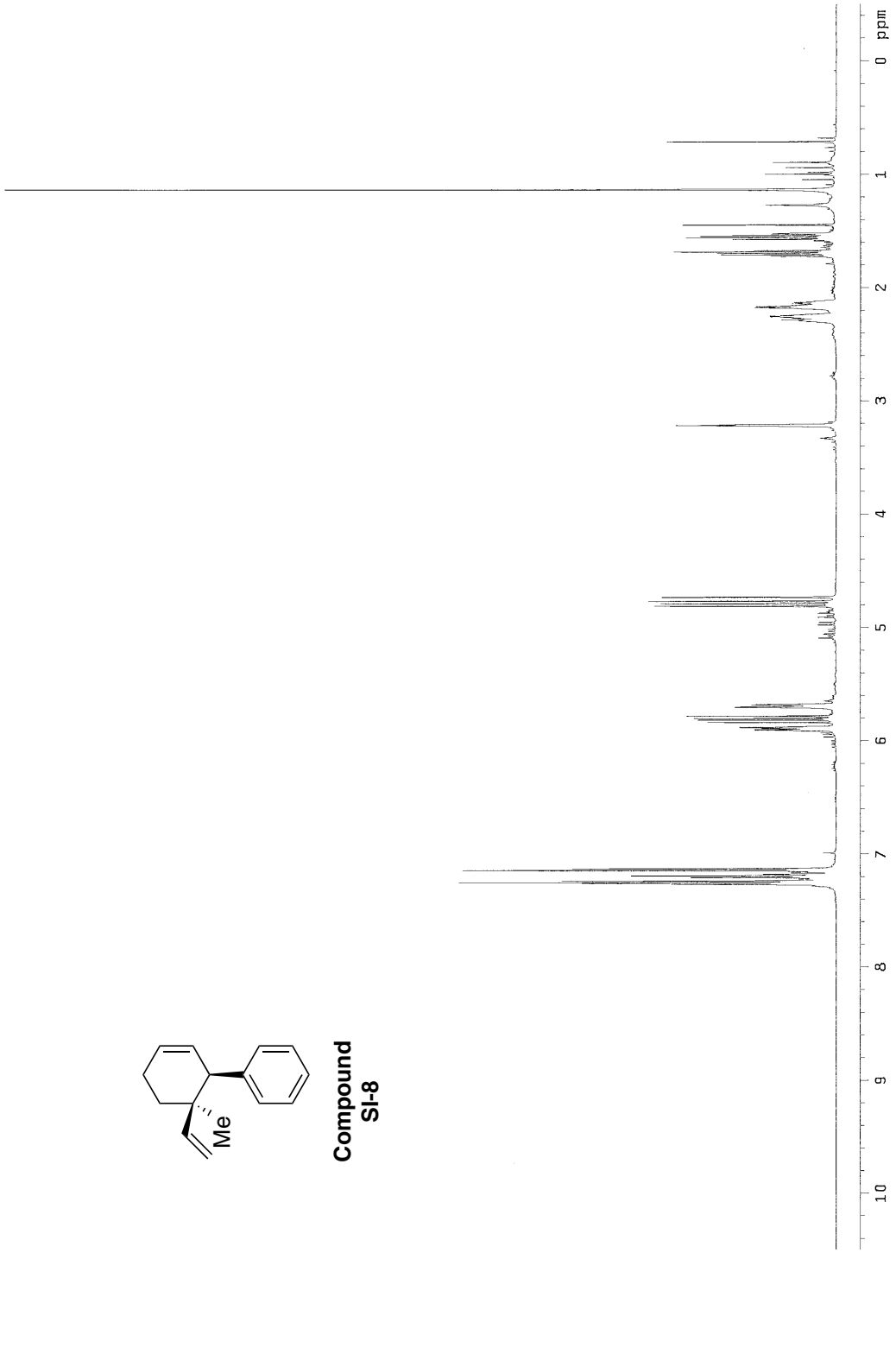

Me
Me
Compound
26
10
9
8
7
6
5
4
3
2
1
0 ppm

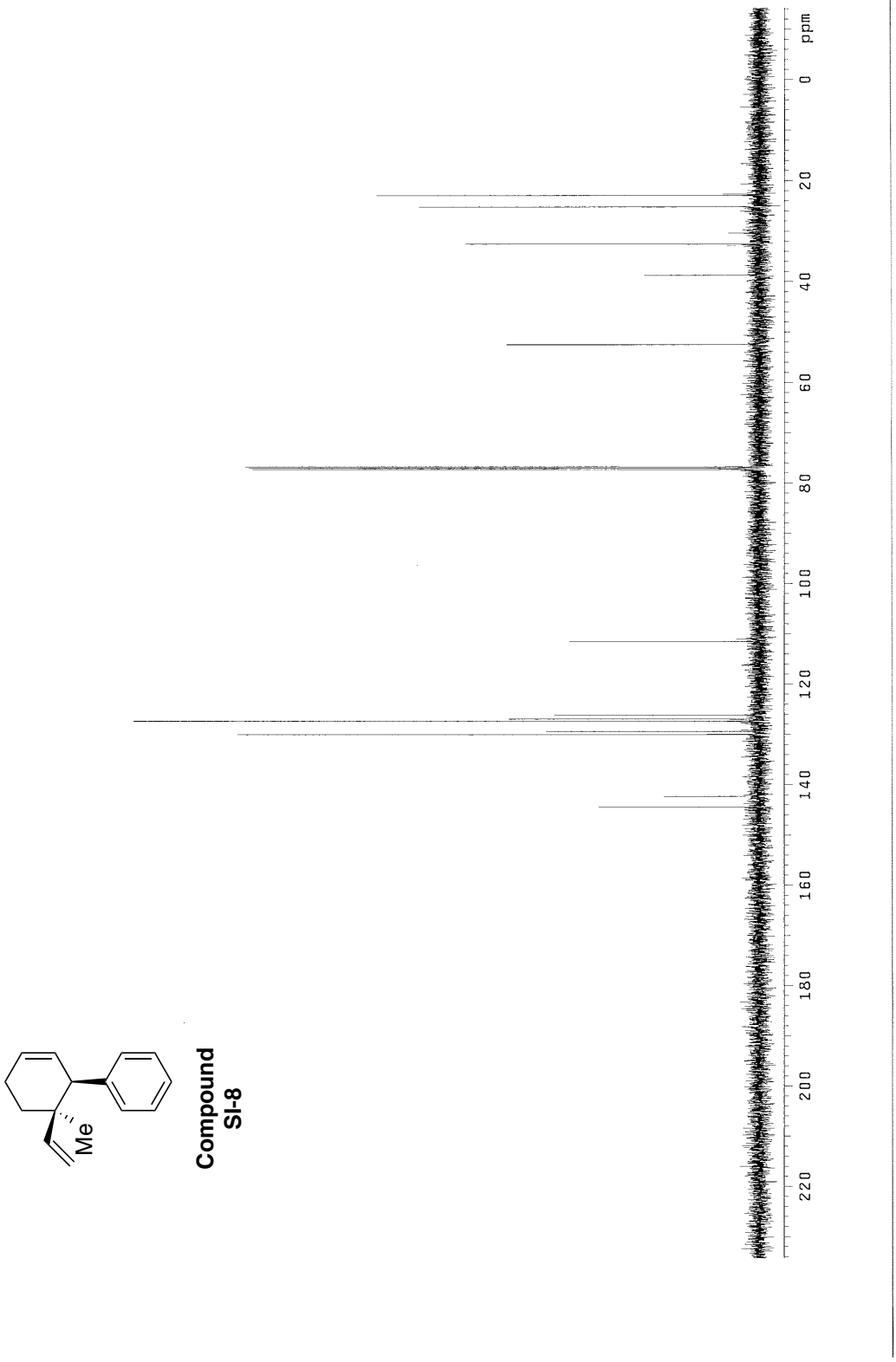



**Compound 26**

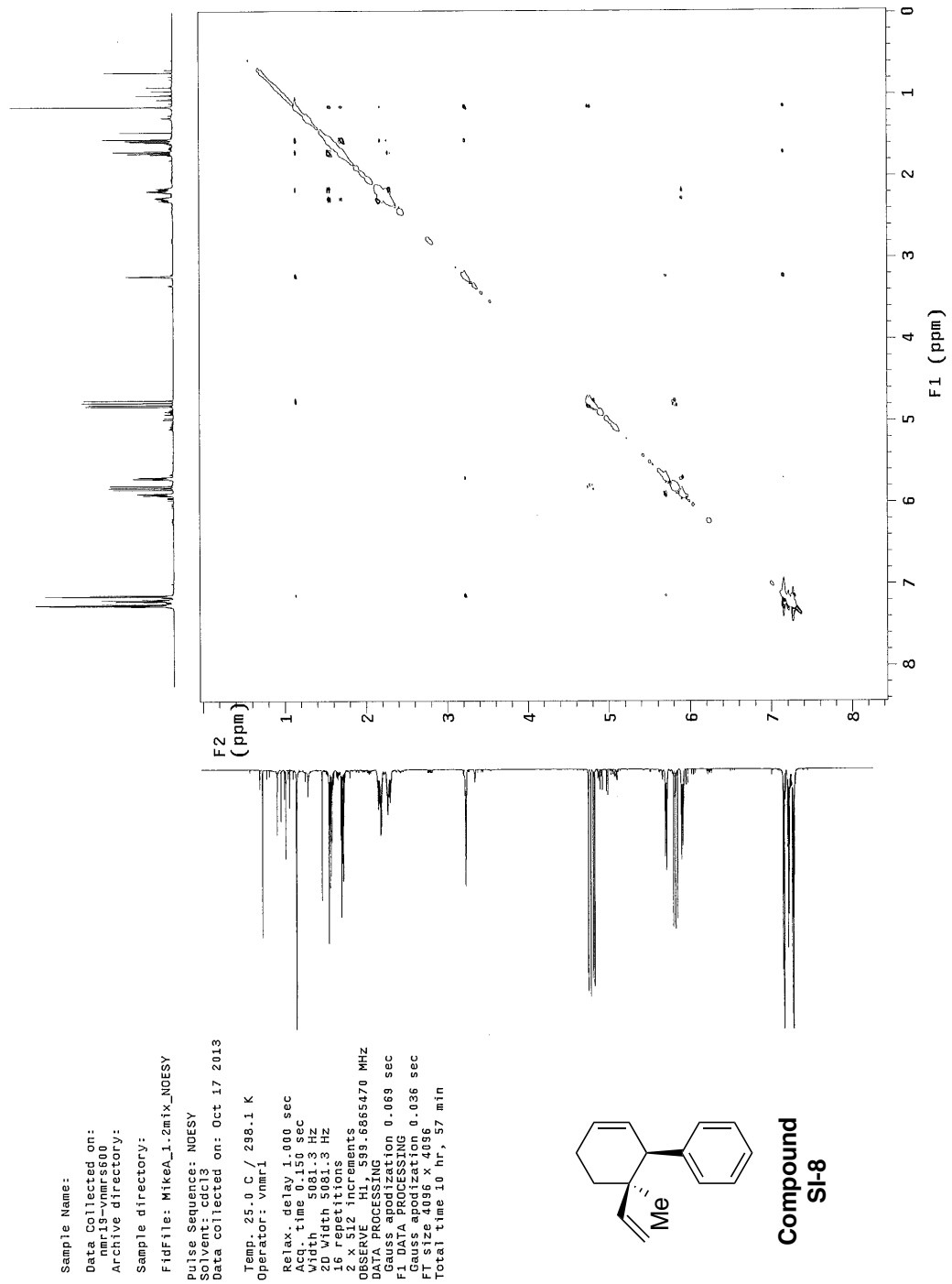

Me
Me
Me
Compound
28
10
9
8
7
6
5
4
3
2
1
0 ppm

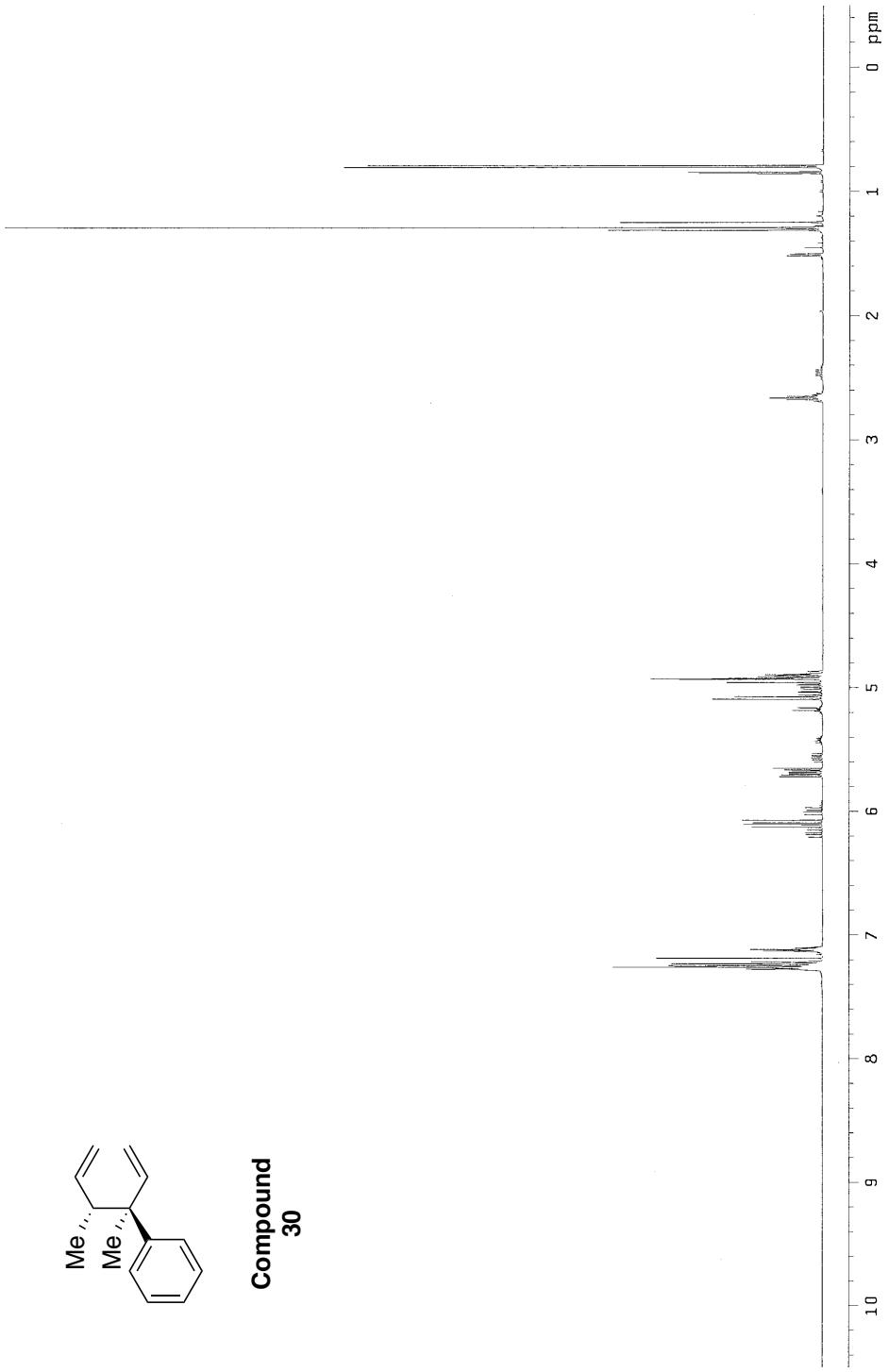

Me
Me
Me
Compound
28
ppm
0
20
40
60
80
100
120
140
160
180
200
220


Me
Compound
SI-8
10
9
8
7
6
5
4
3
2
1
0 ppm




**Compound SI-8**

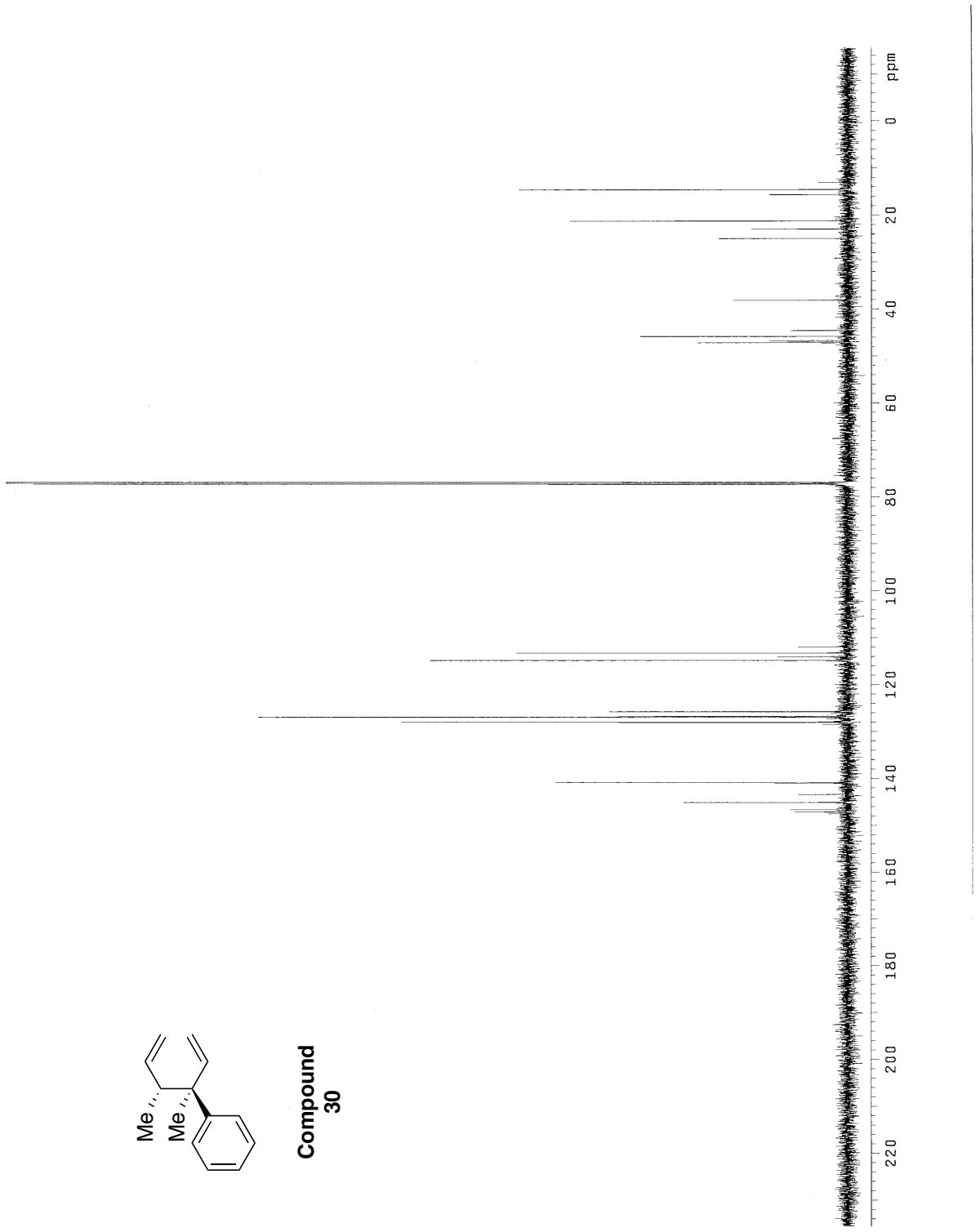

Sample Name:
Data Collected on:
nmr19-vnmrs600
Archive directory:
Sample directory:
FidFile: MikeA_1.2mix_NOESY
Pulse Sequence: NOESY
Solvent: cdcl3
Data collected on: Oct 17 2013
Temp. 25.0 C / 298.1 K
Operator: vnmr1
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 5081.3 Hz
2D Width 5081.3 Hz
16 repetitions
2 x 512 increments
OBSERVE H1, 599.6865470 MHz
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.036 sec
FT size 4096 x 4096
Total time 10 hr, 57 min
F2 (ppm)
F1 (ppm)
Me
Compound SI-8



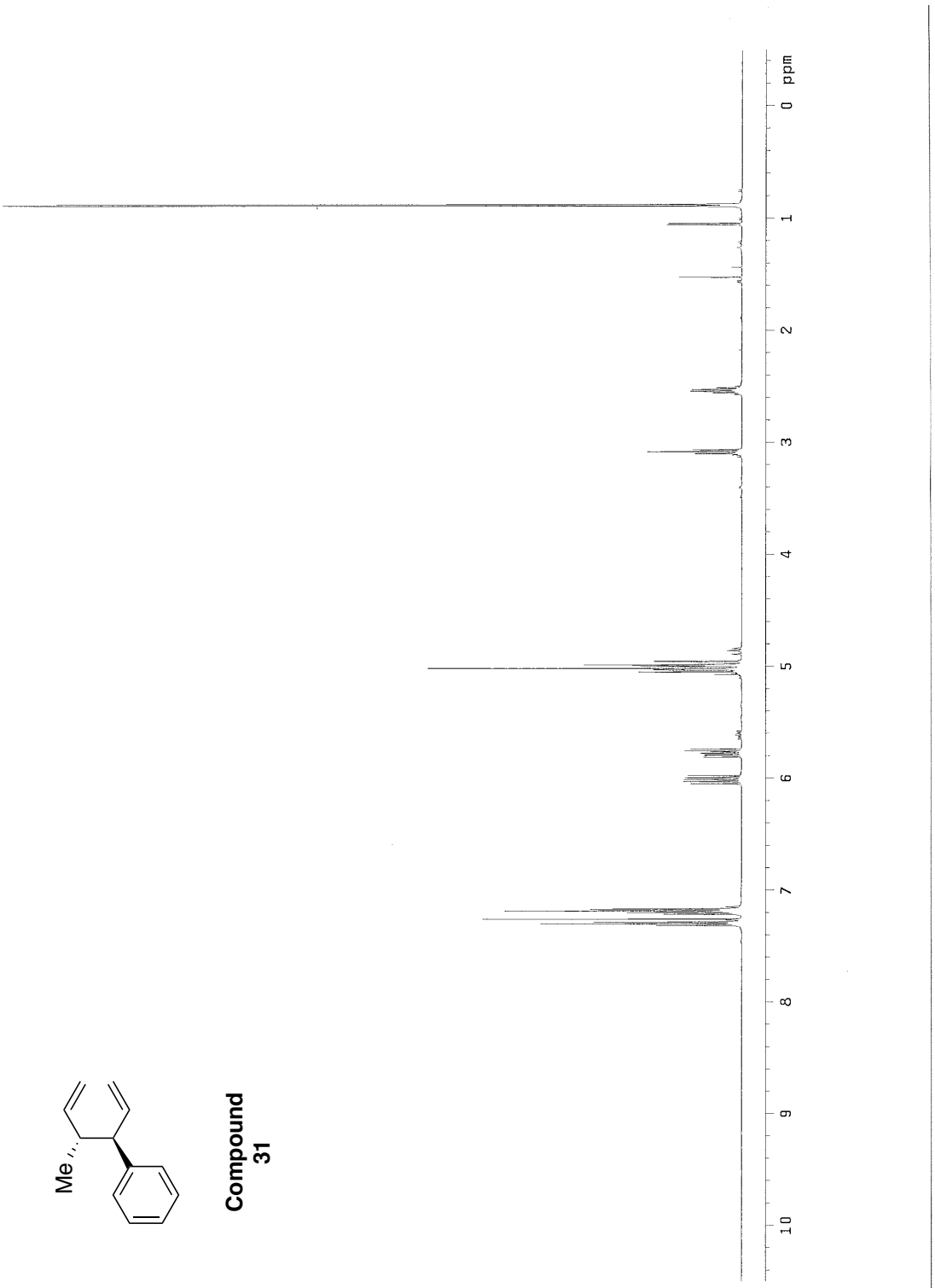


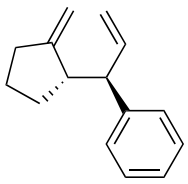


**Compound 30**

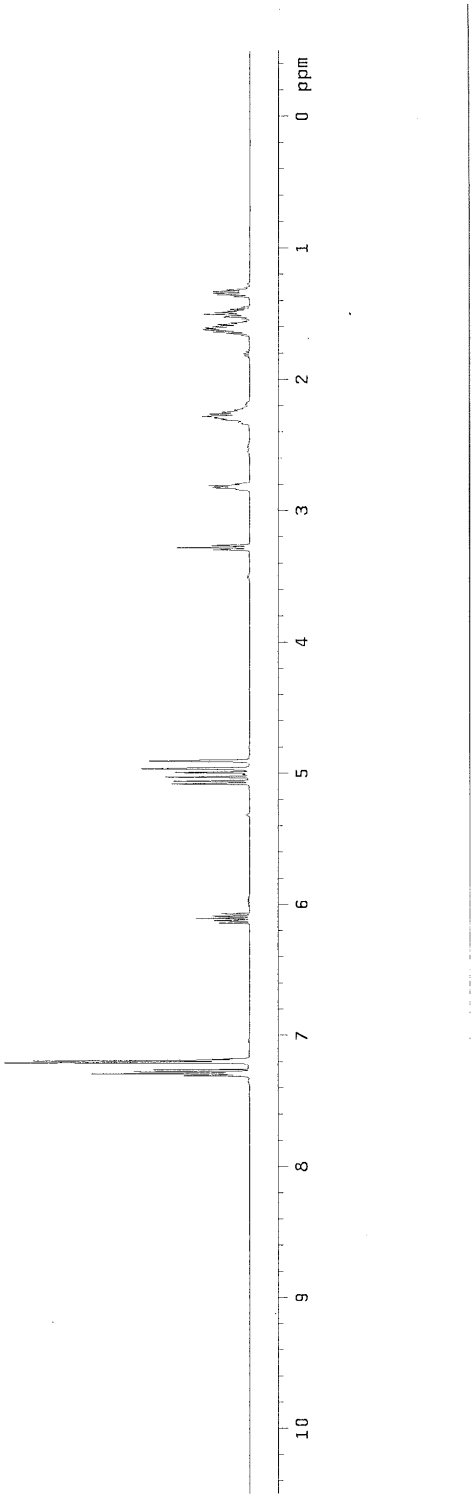


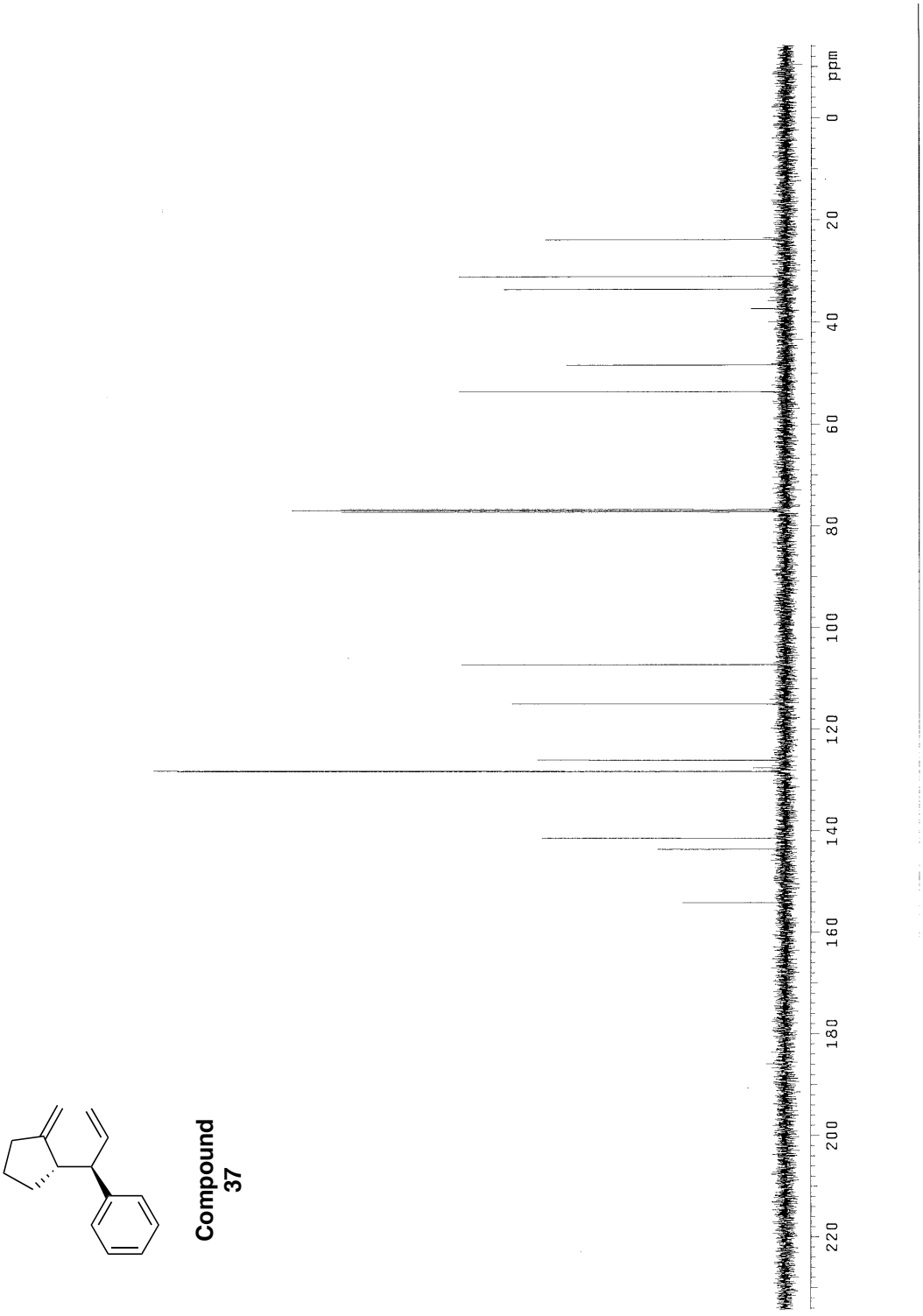

**Compound 30**


Me
Compound
31
10
9
8
7
6
5
4
3
2
1
0 ppm



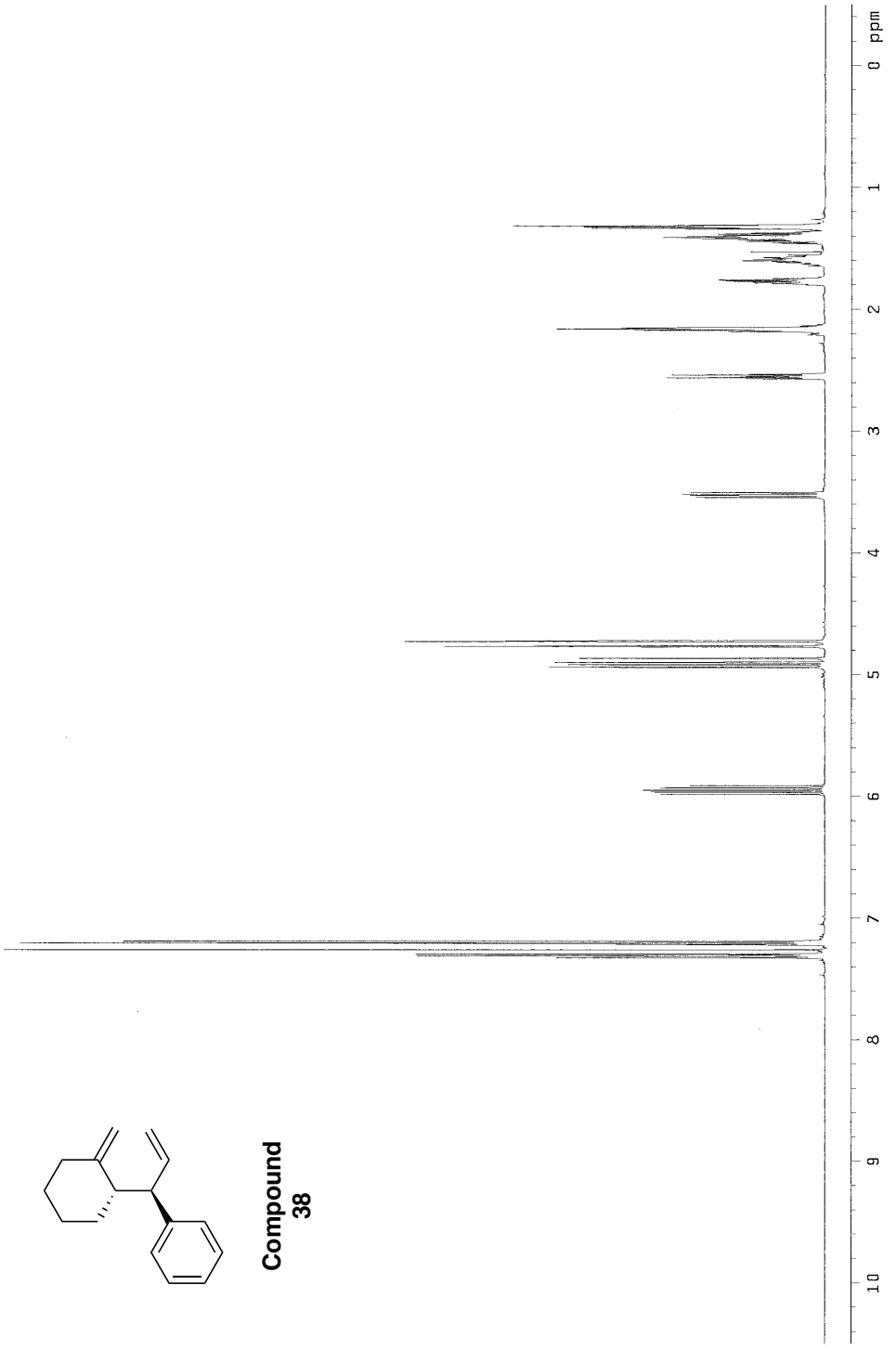
**Compound 37**





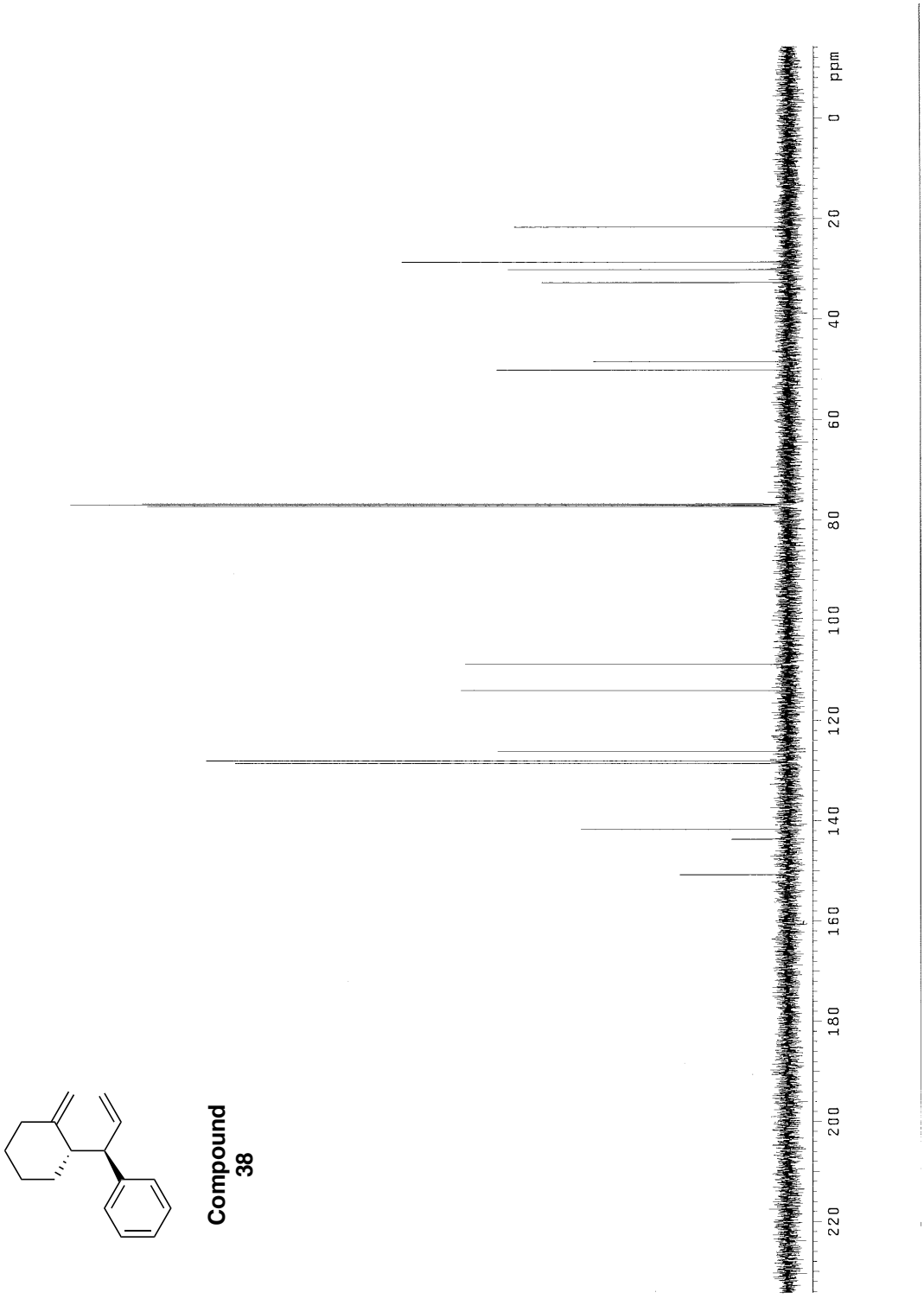



**Compound 37**



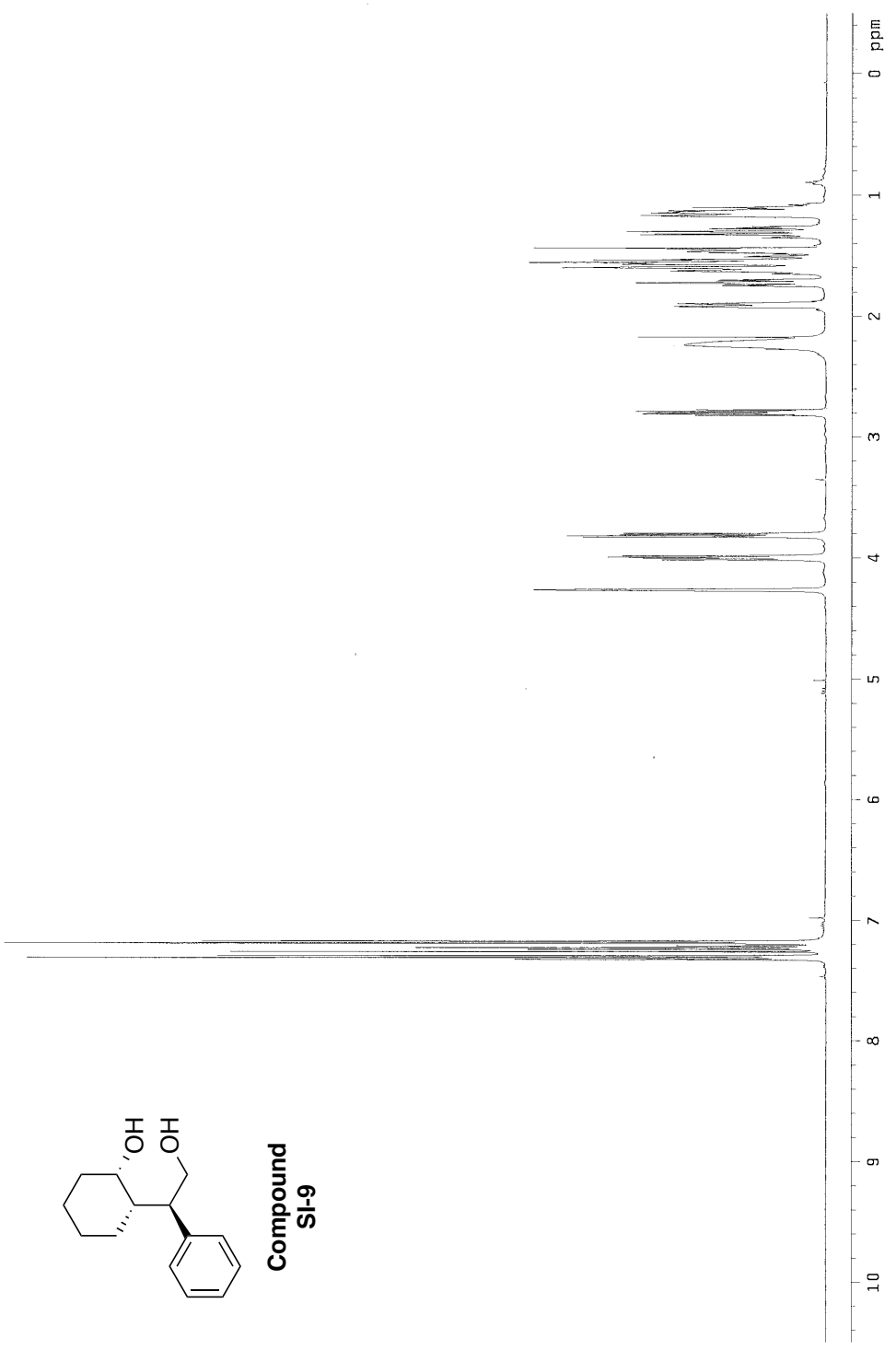


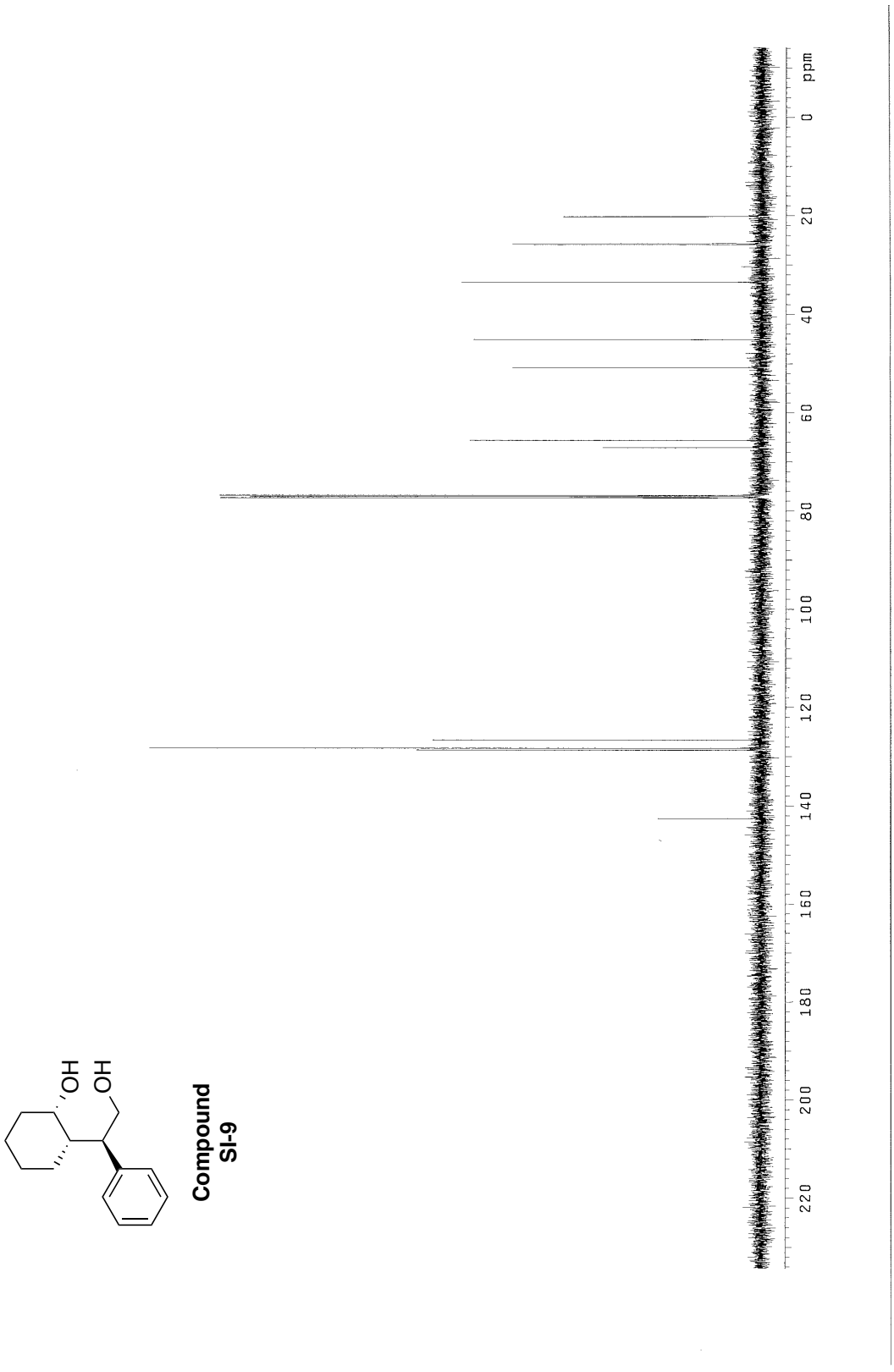

**Compound 38**



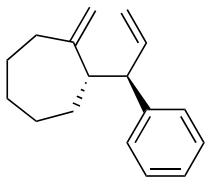



**Compound 38**

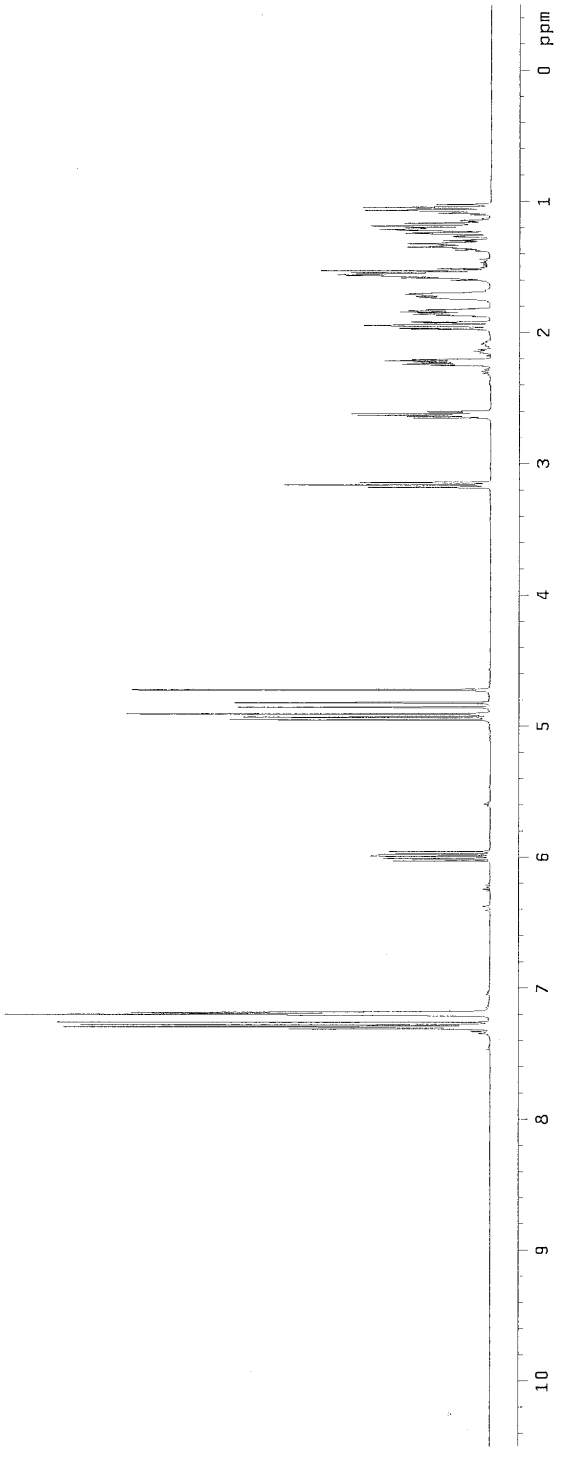

OH
OH
Compound
SI-9
10
9
8
7
6
5
4
3
2
1
0 ppm

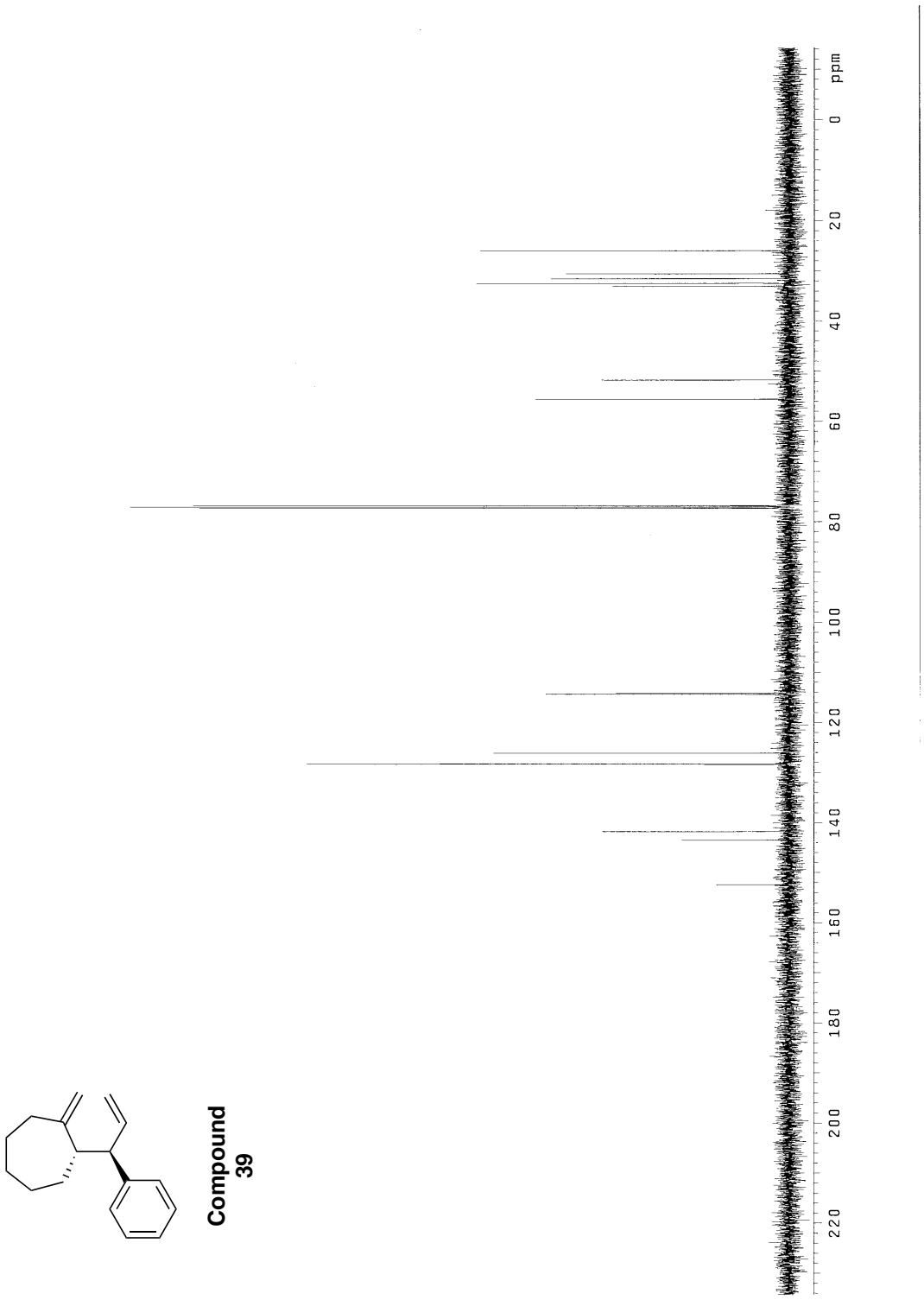



**Compound SI-9**



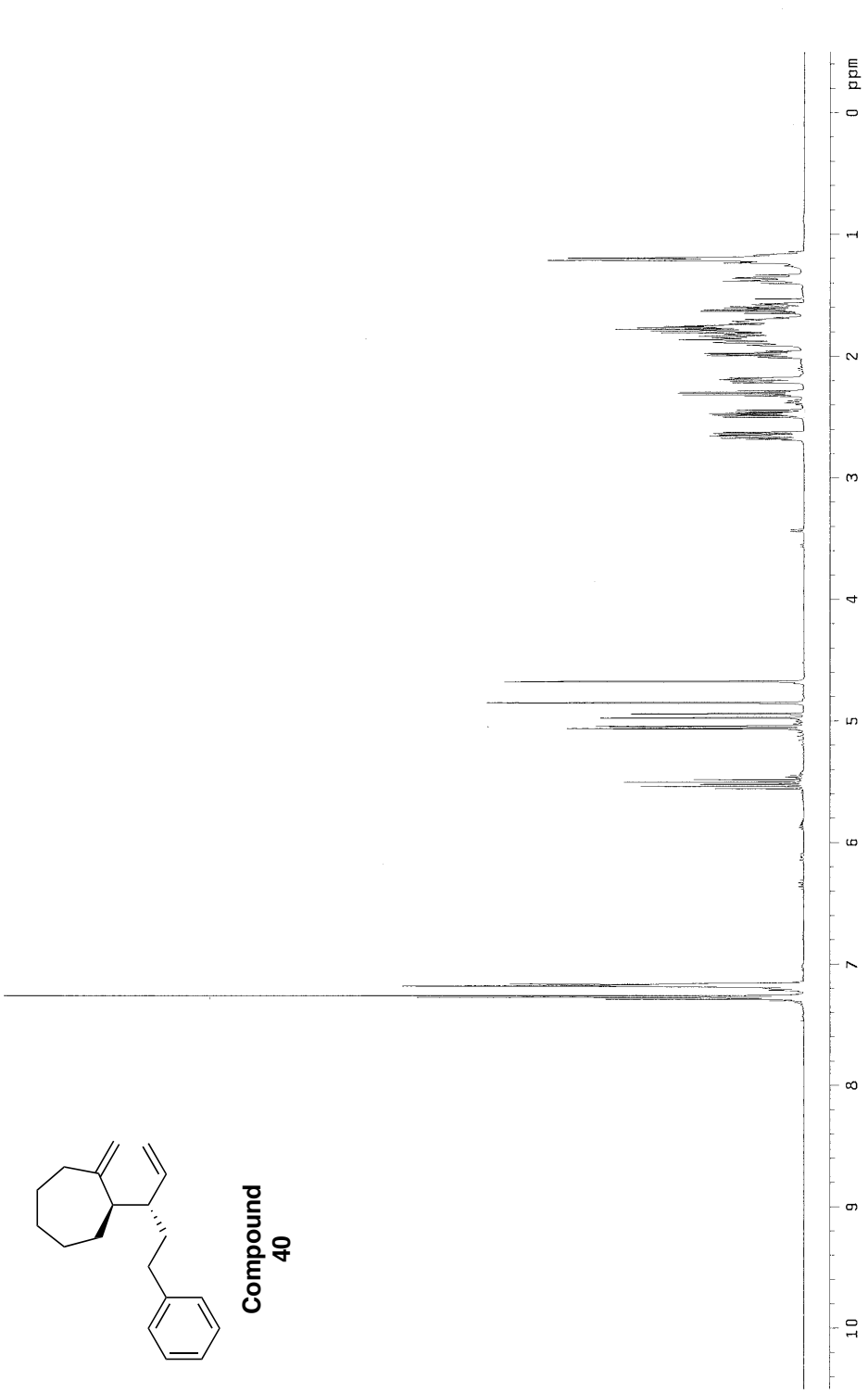
**Compound 39**





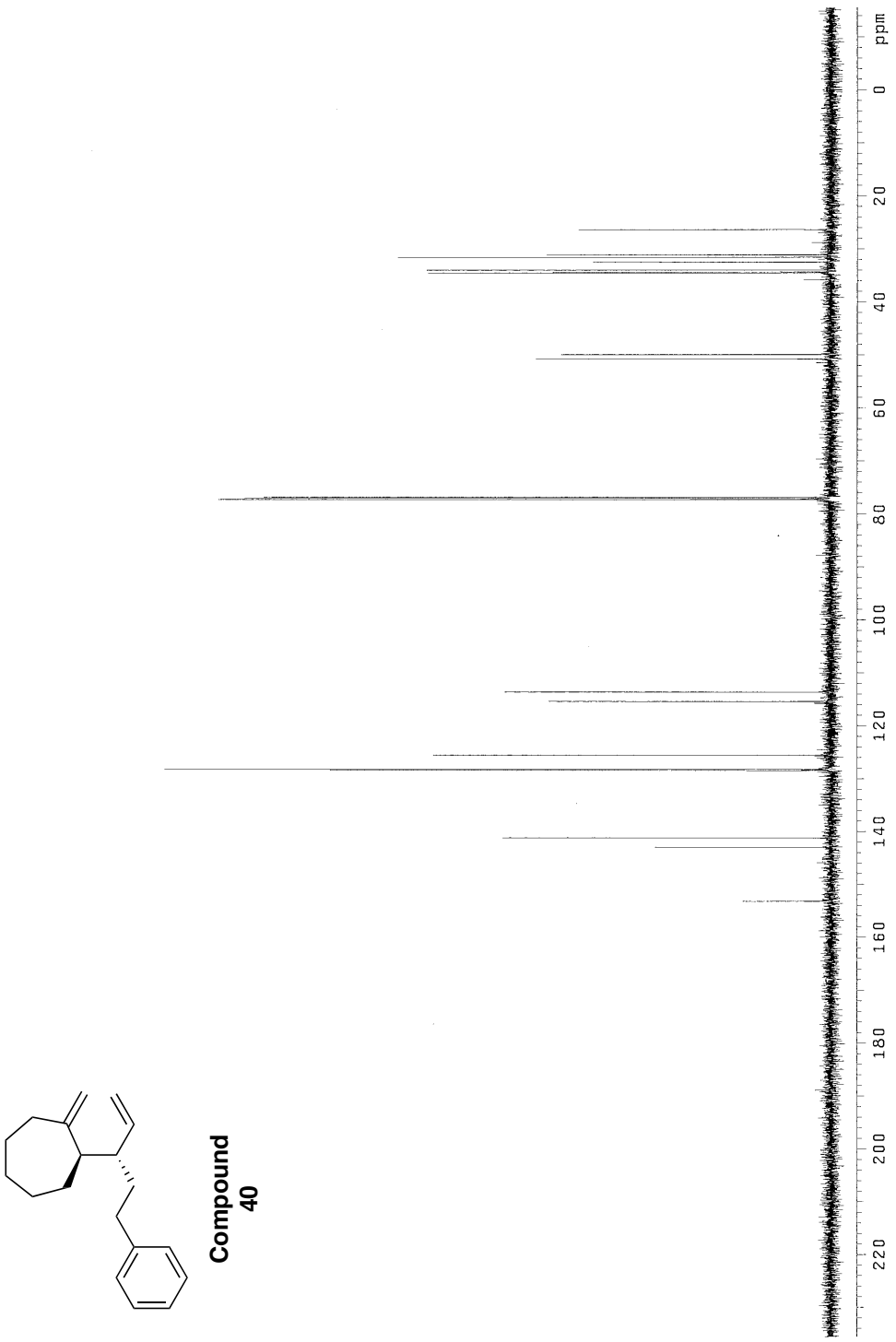



**Compound 39**

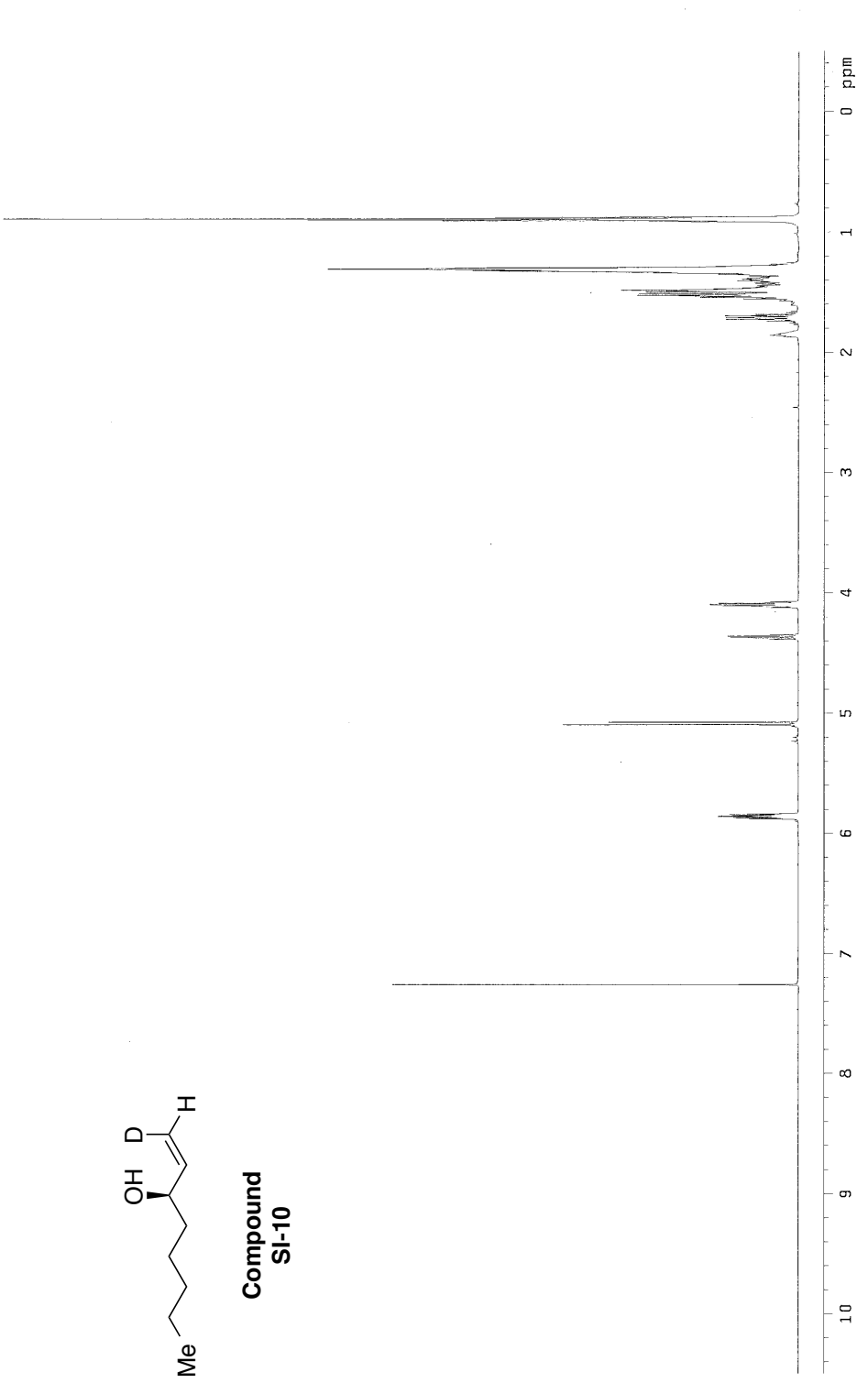




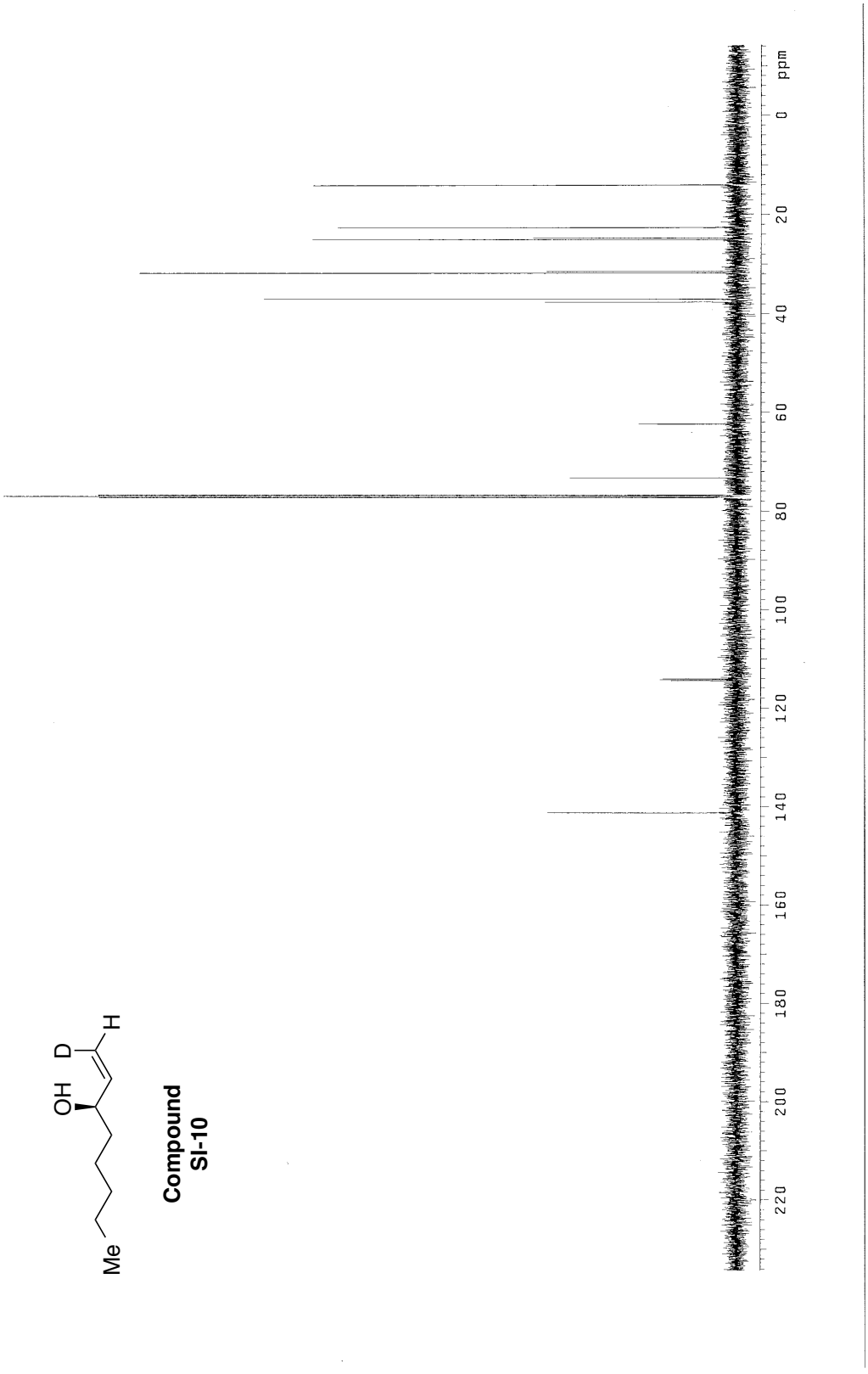

**Compound 40**



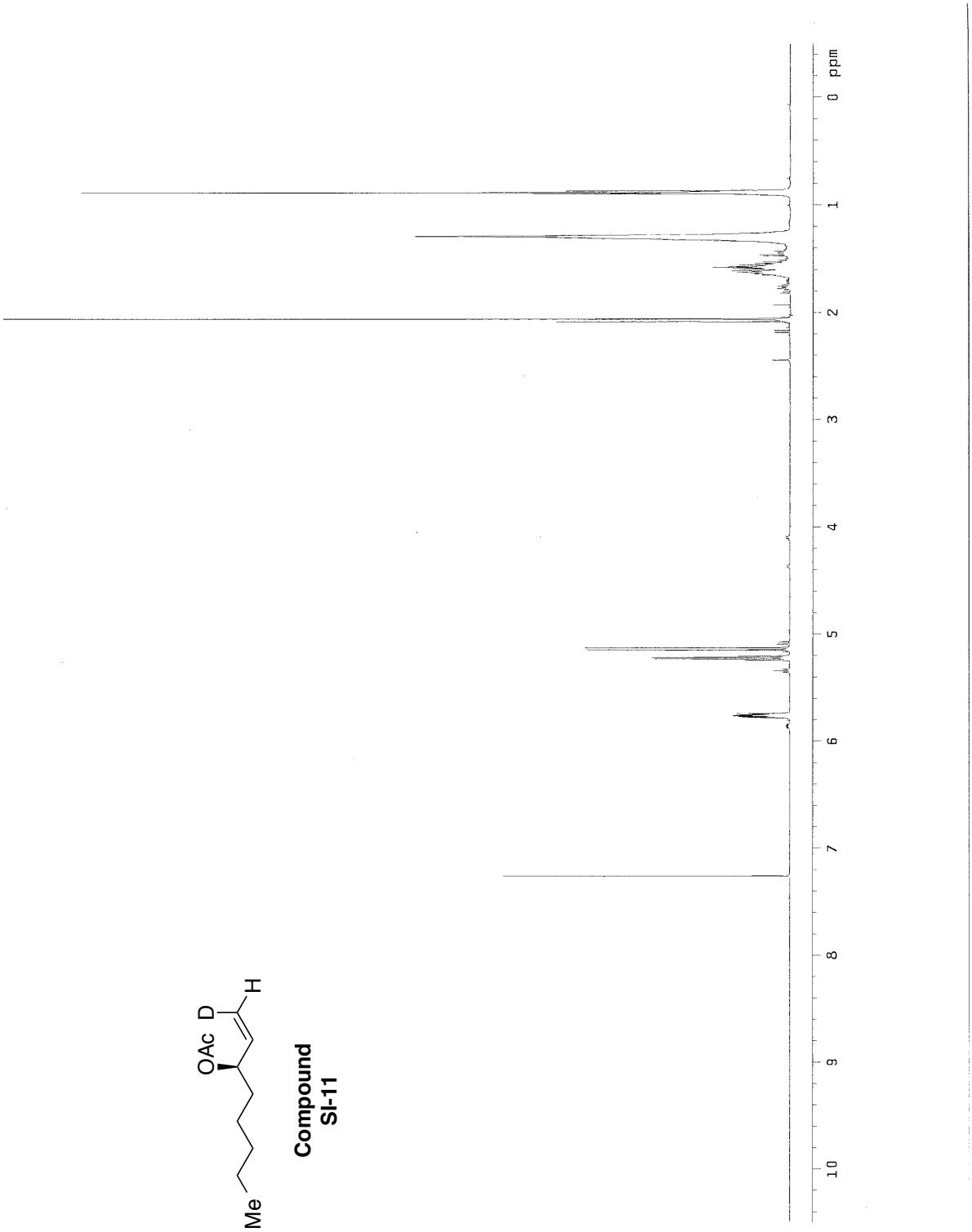

**Compound 40**



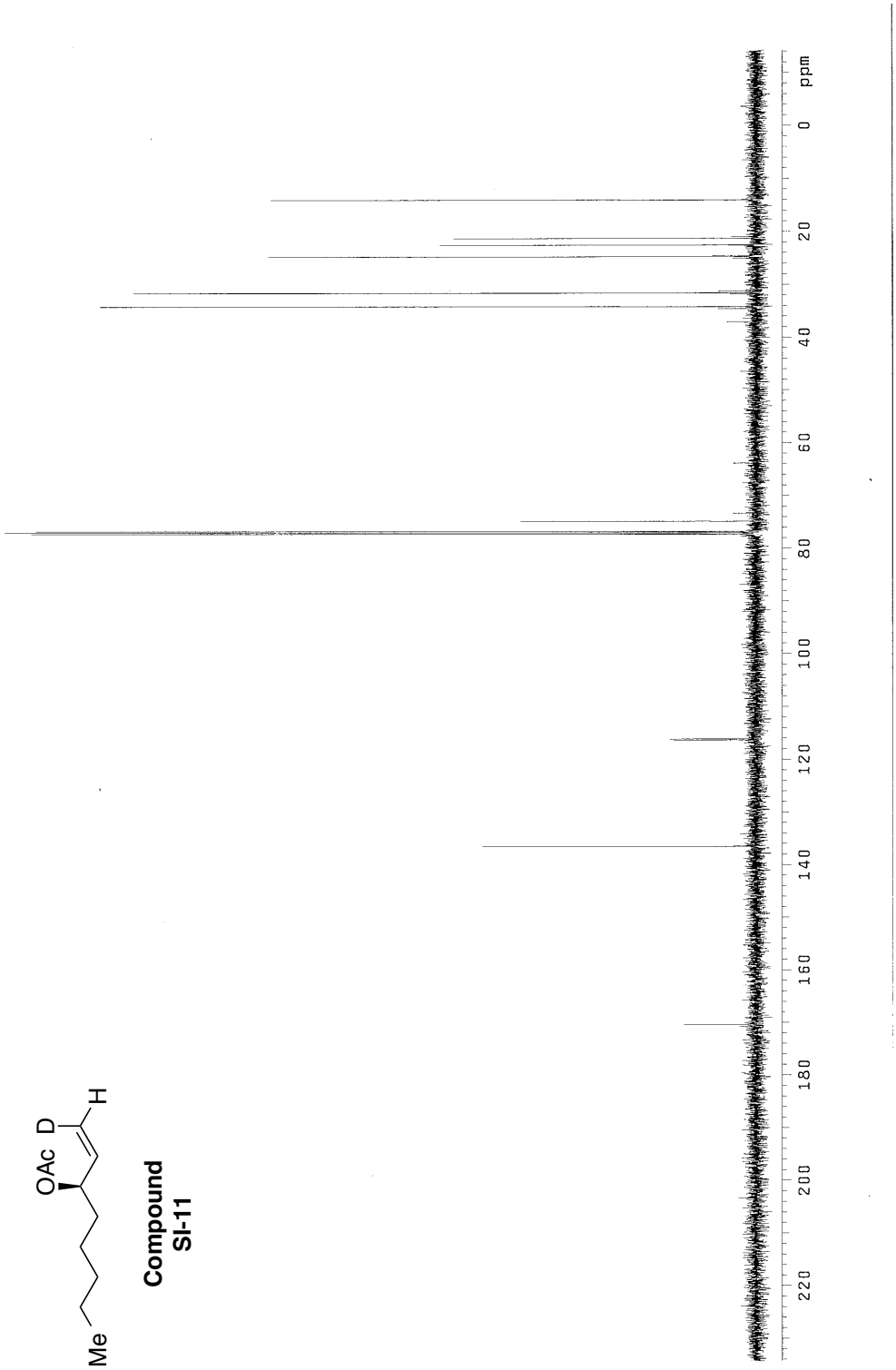

**Compound SI-10**



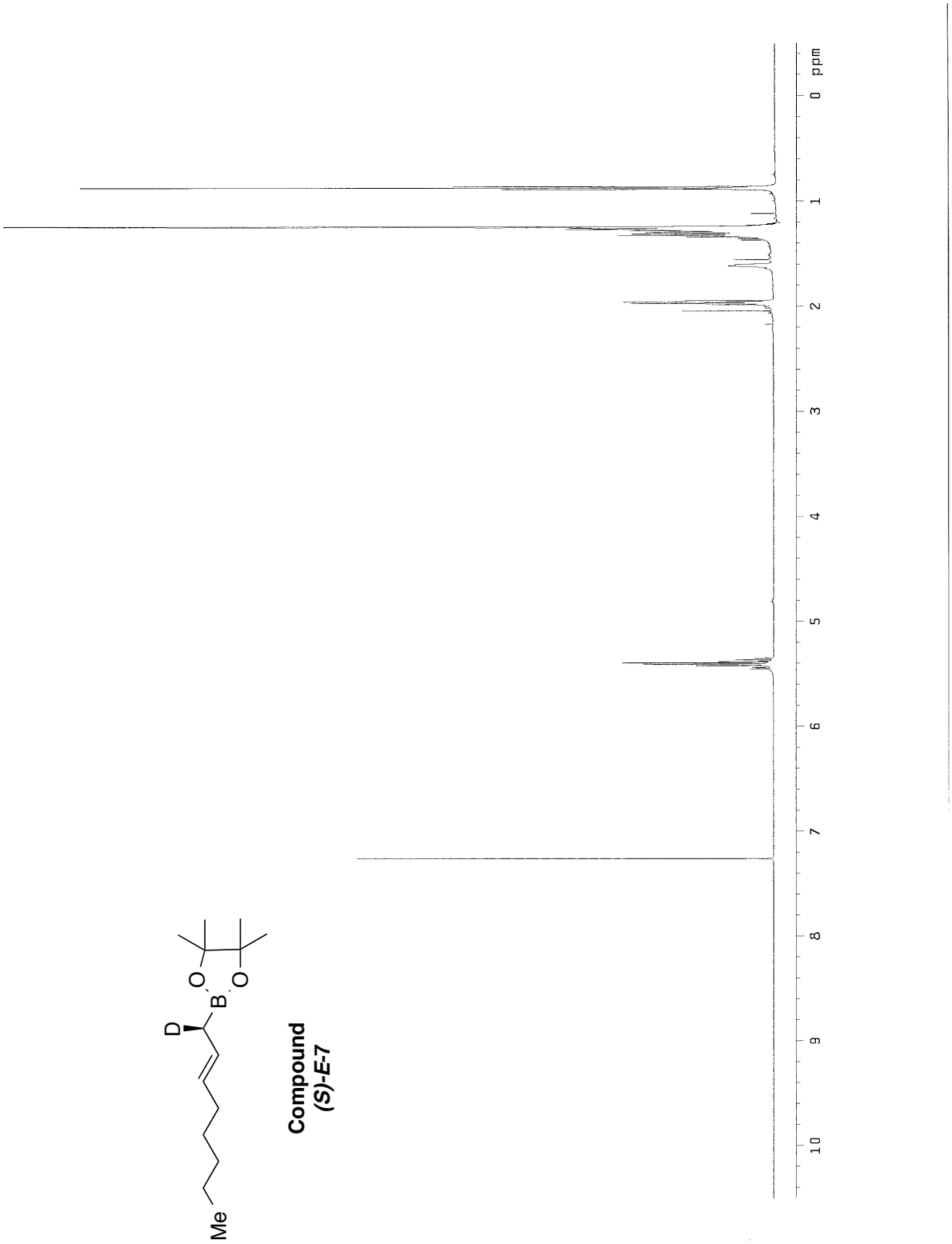

**Compound SI-10**



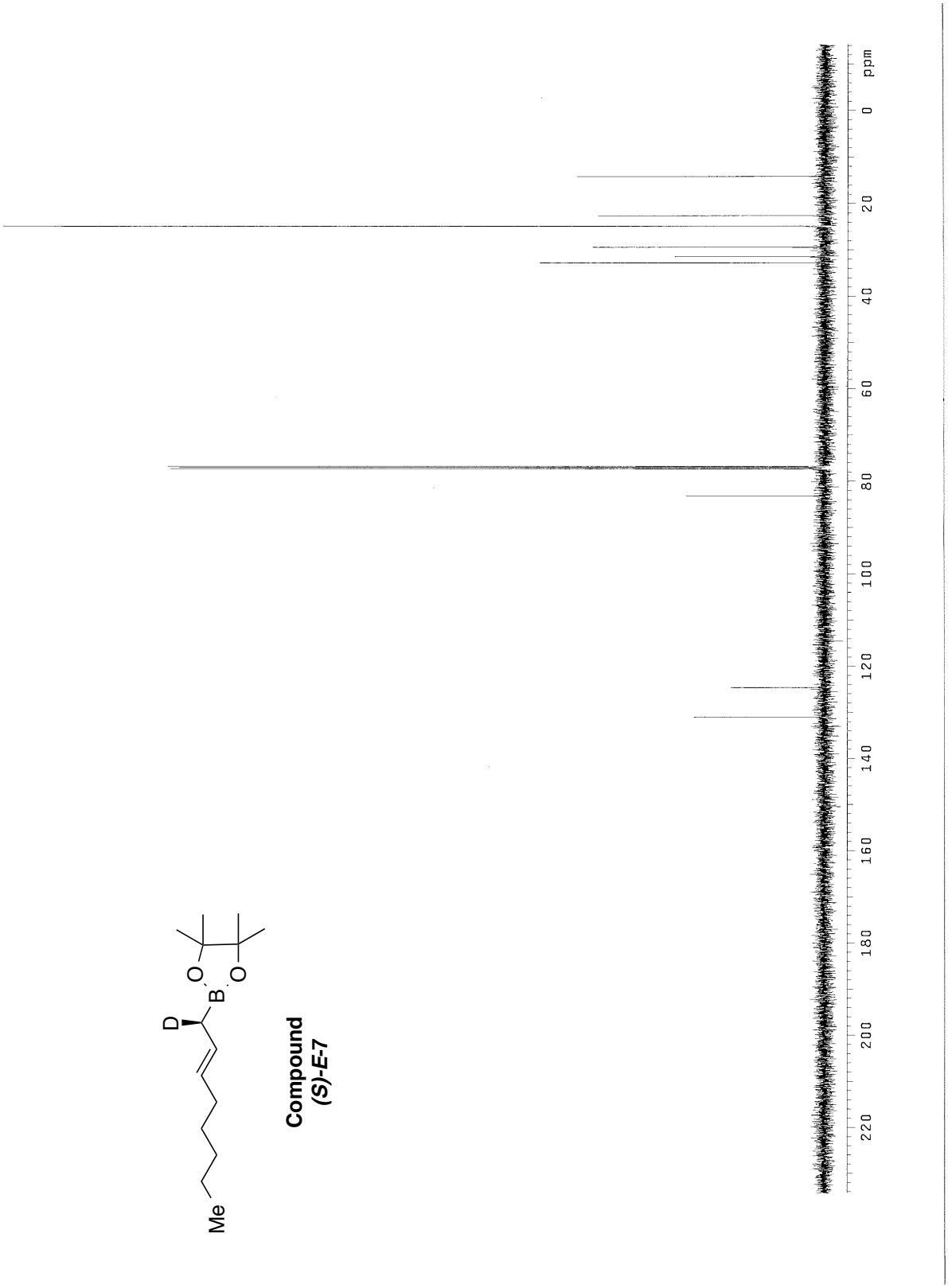

**Compound SI-11**



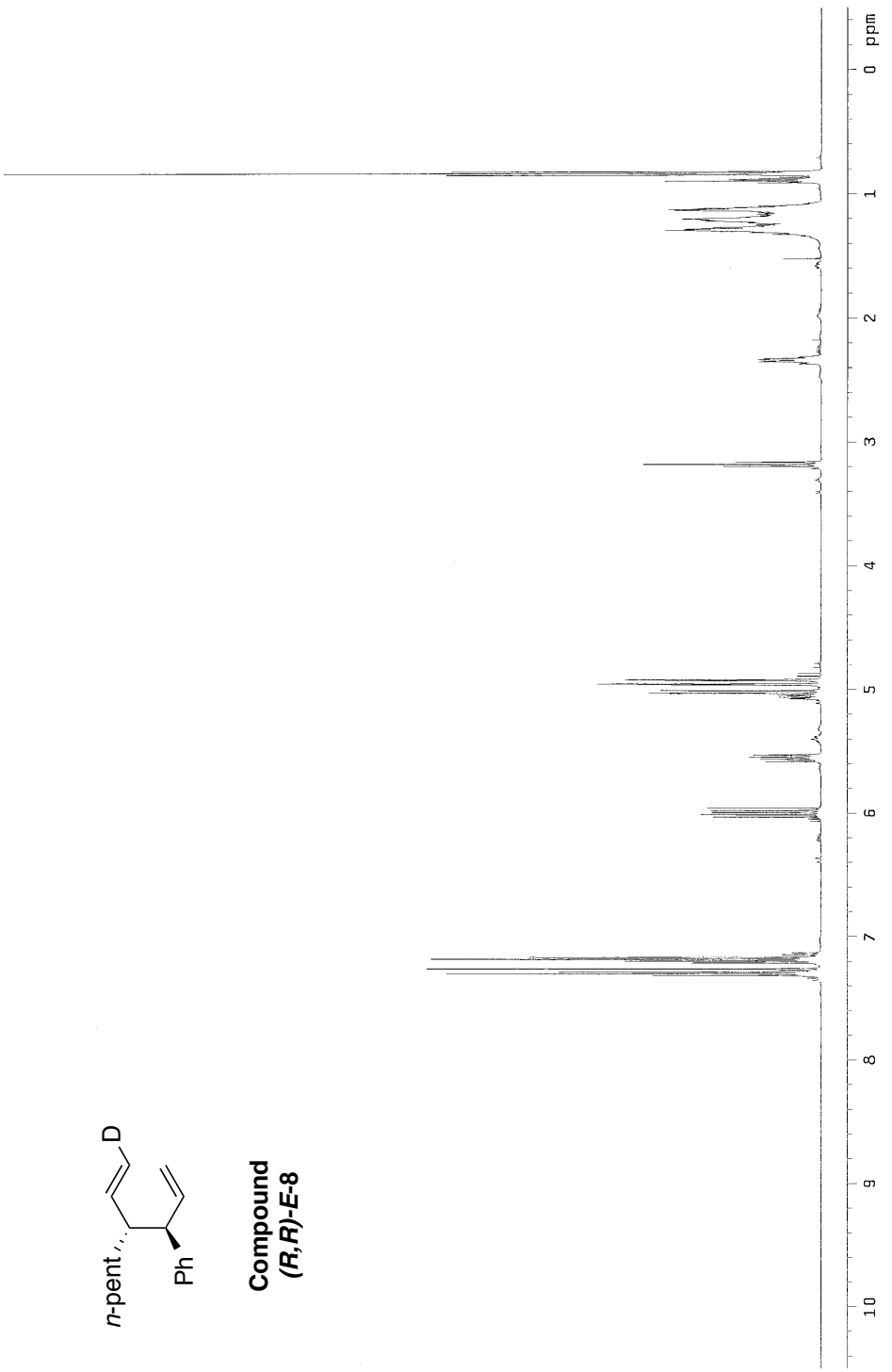

**Compound SI-11**



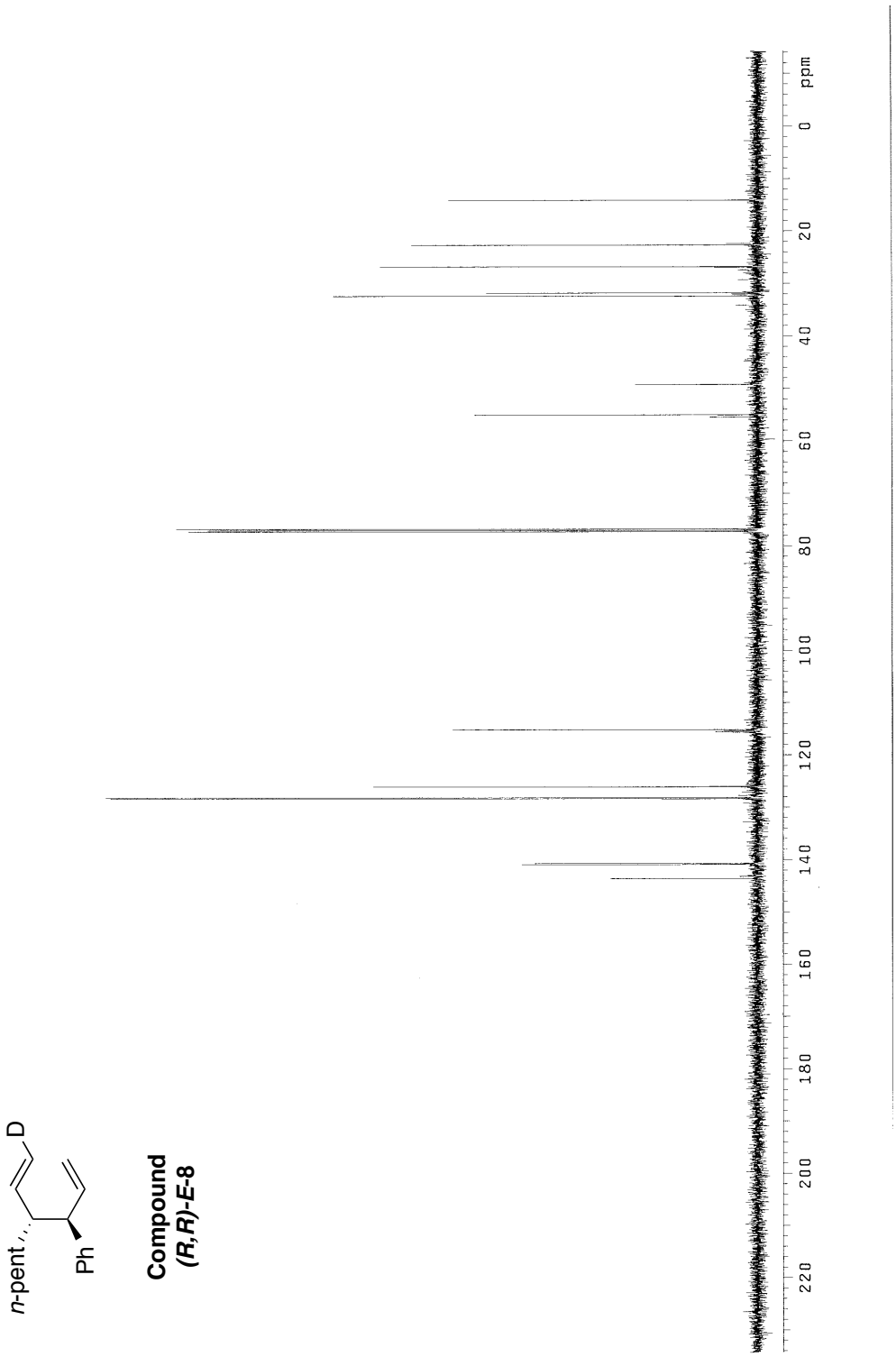

**Compound *(S)-E-7***



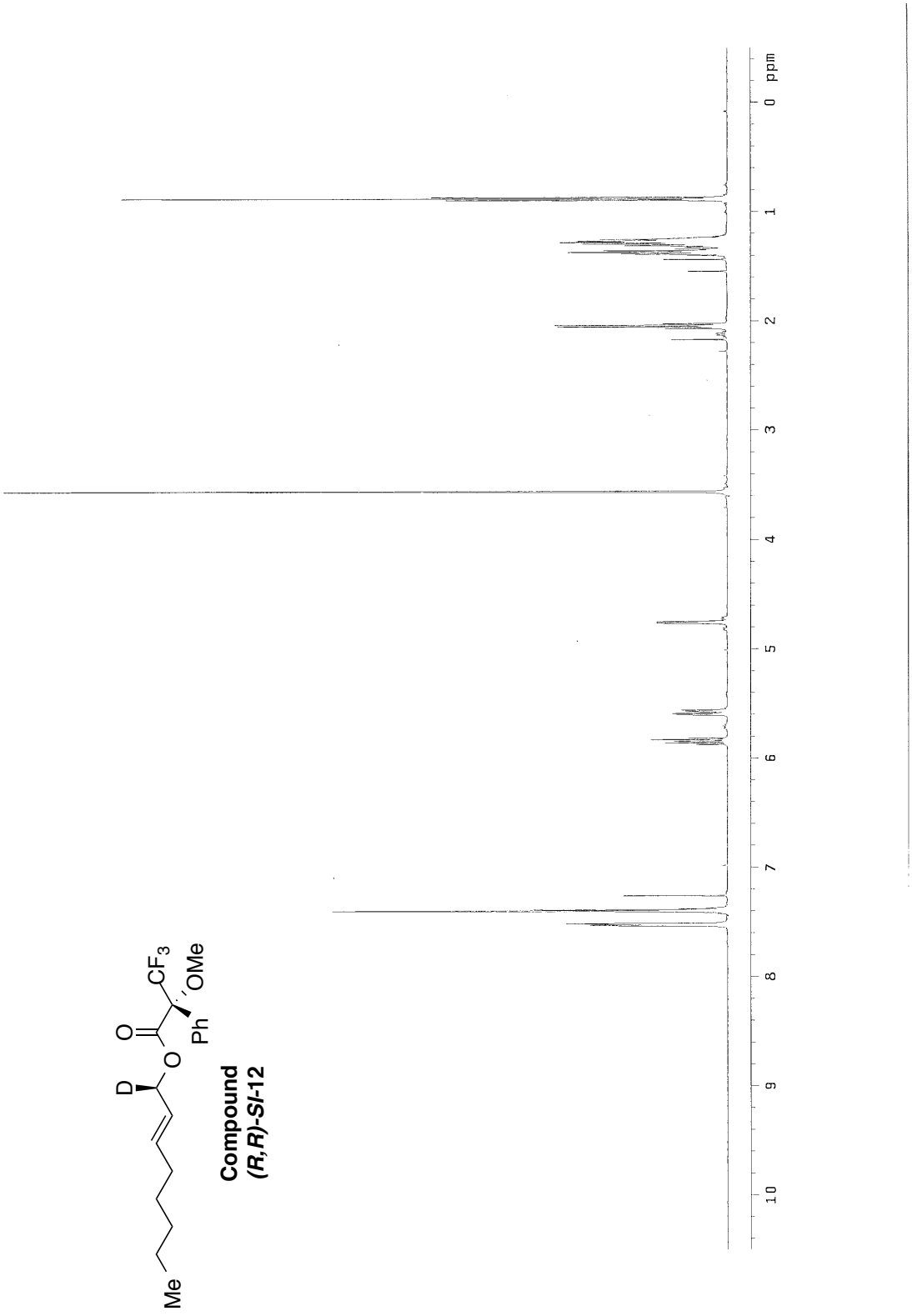

**Compound**
***(S)-E-7***



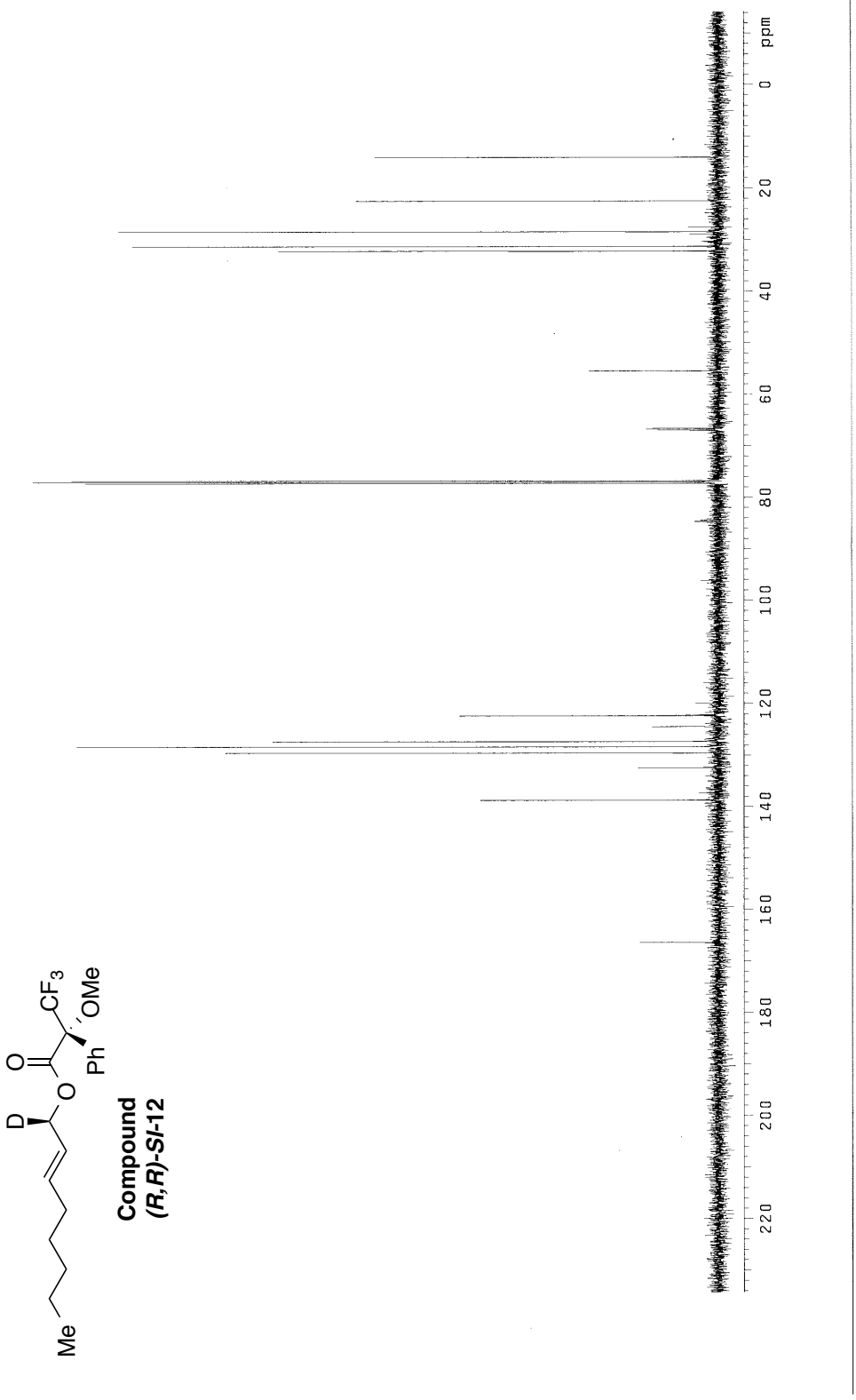

**Compound**
***(R,R)-E-8***



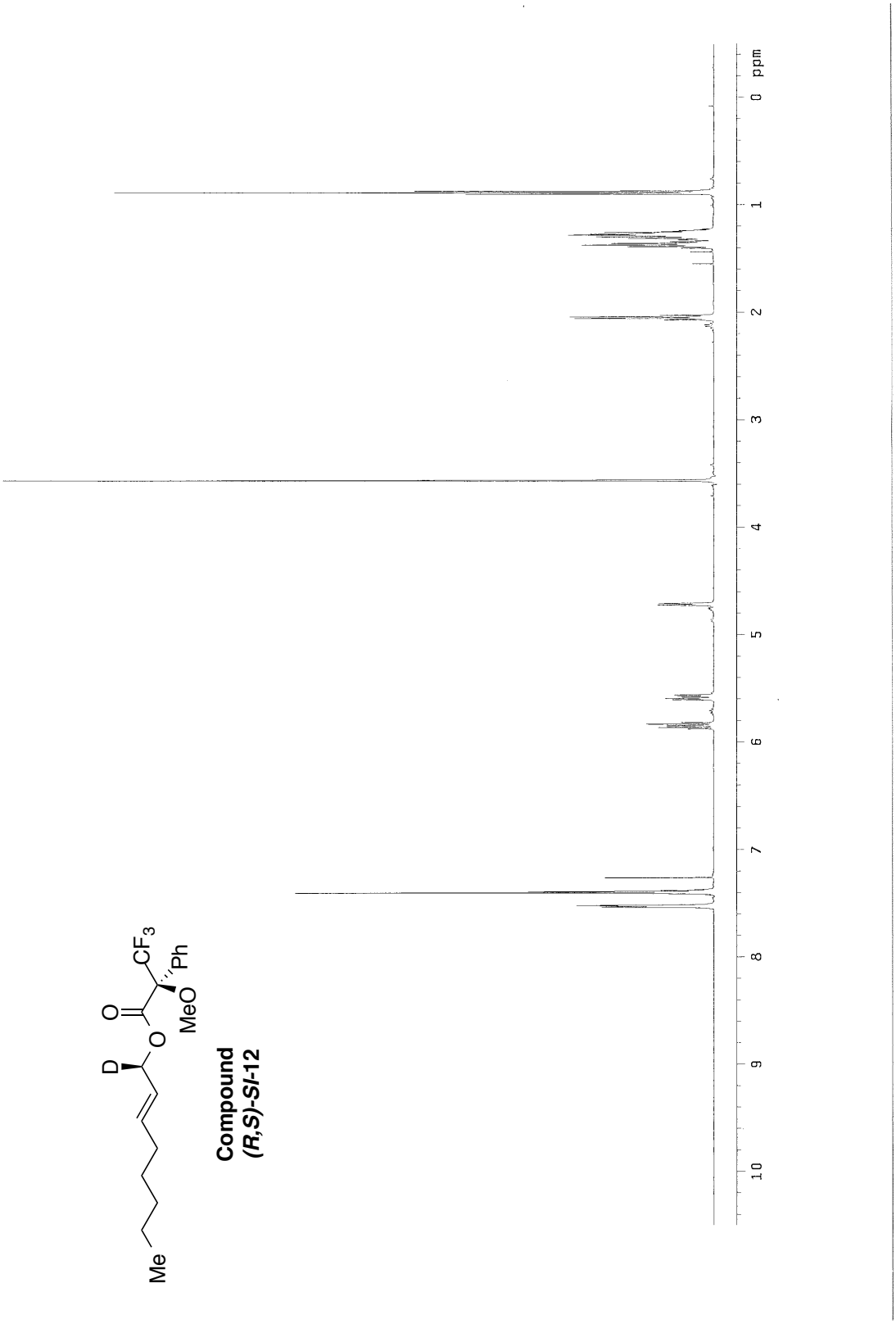

**Compound**
***(R,R)-E-8***



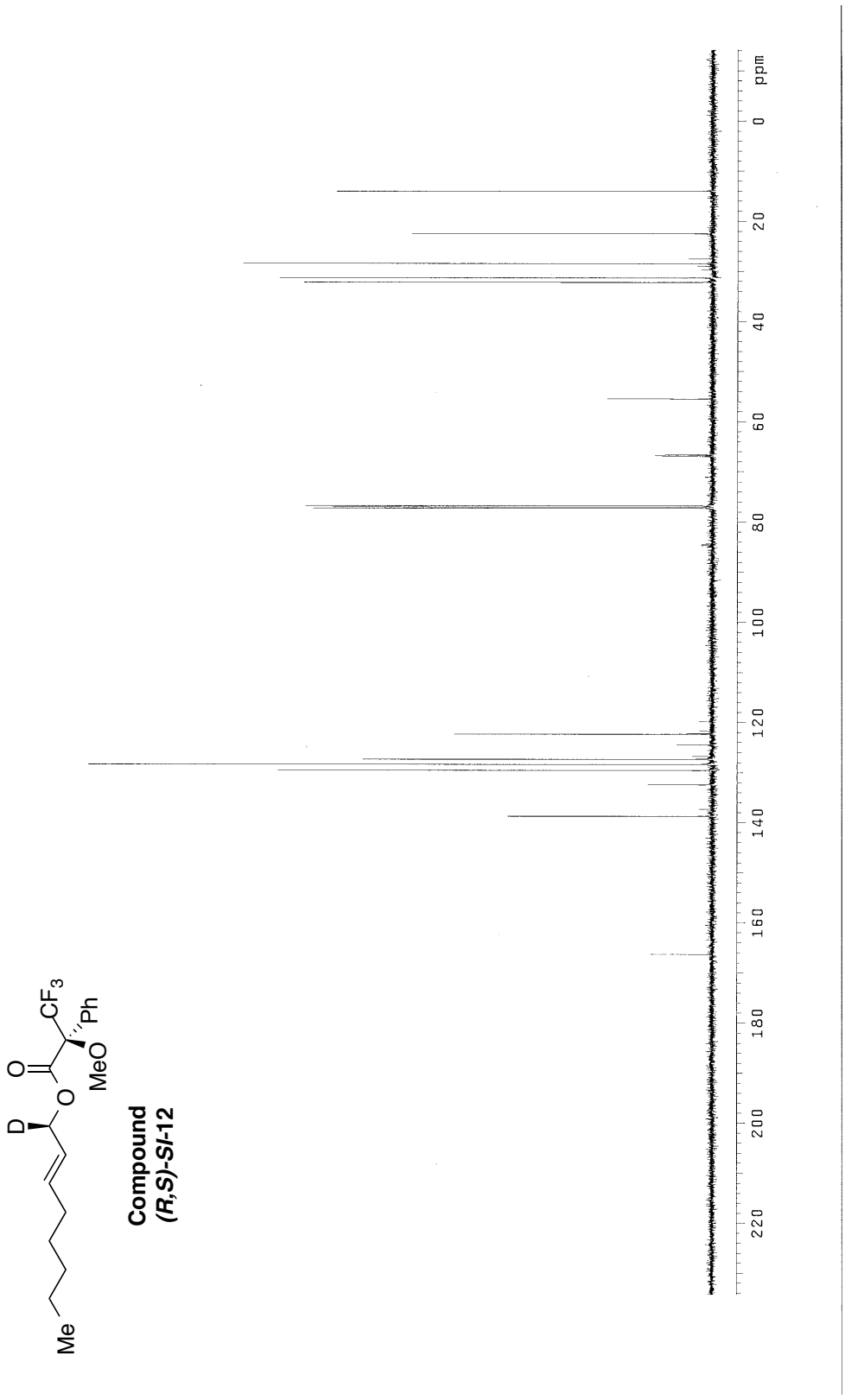

**Compound *(R,R)-SI-12***




**Compound *(R,R)-SI-12***




**Compound**
***(R,S)-SI-12***




**Compound**
***(R,S)-SI-12***