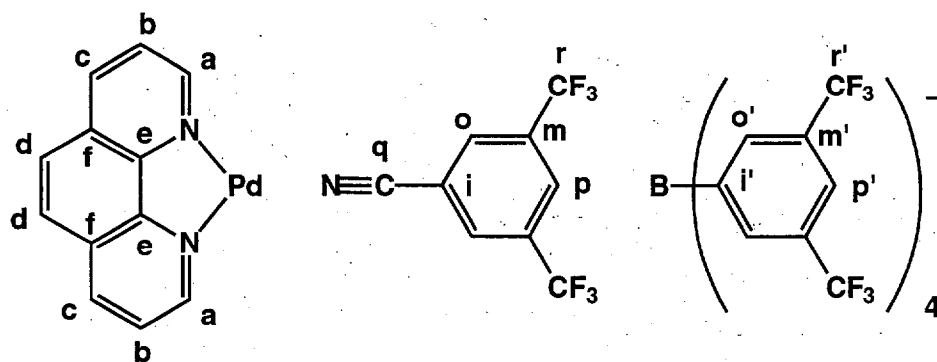


Experimental

General Methods. Anhydrous hexanes, triethylsilane, dimethyl malonate, 3,5-bis(trifluoromethyl)benzonitrile (Aldrich), $\text{H}^{13}\text{C}\equiv^{13}\text{C}^{13}\text{CH}_2\text{OH}$, and $(^{13}\text{CO}_2\text{Et})_2^{13}\text{CH}_2$ (Cambridge Isotope Laboratories), and dimethyl diallylmalonate (Lancaster) were used as received. Dichloromethane and dichloroethane were distilled from CaH_2 prior to use. $[(\text{phen})\text{Pd}(\text{Me})(\text{NCAr})]^+ [\text{BAR}_4]^-$ [$\text{Ar} = 3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2$],¹ $(\text{phen})\text{Pd}(\text{Me})\text{Cl}$,² NaBAR_4 ,³ and DSiEt_3 ⁴ were prepared according to known methods. Labelled dienes **1-2**, **6-d₂** and **1-3,3,5,5-d₄** have been previously synthesized in our laboratory.⁵ Elemental analysis was performed by Complete Analysis Laboratories, Inc. (Parsippany, NJ). Low temperature NMR were recorded at 500 MHz for ^1H and 125 MHz for ^{13}C except where noted; room temperature NMR were recorded at 400 MHz for ^1H and 100 MHz for ^{13}C . NMR Probe temperatures were measured using a methanol thermometer and were maintained to within ± 1 degree. Atom labeling schemes for phenanthroline, $\text{N}\equiv\text{CAr}$, and BAR_4^- are shown in Figure S1. NMR Yields for the conversion of **3** to **2**, **2** to **4**, **4** to **5** and **5** to **6** were obtained employing a 10 s delay between pulses. Error limits for rate constants refer to the deviation of multiple runs.

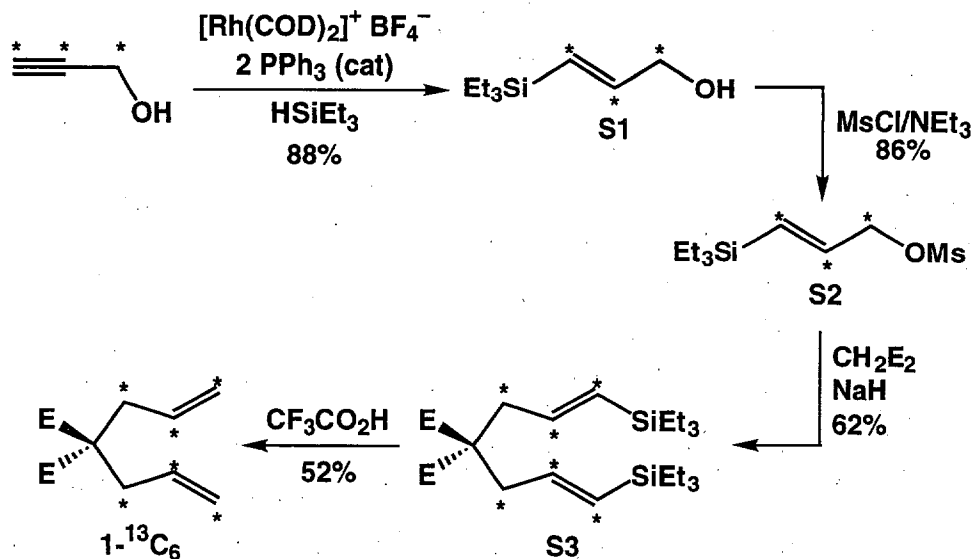
Figure S1. Atom labeling schemes for phenanthroline, $\text{N}\equiv\text{CAr}$, and BAR_4^- .



Labelled Dienes

$(^{13}\text{CO}_2\text{Et})_2^{13}\text{C}(\text{CH}_2\text{CH}=\text{CH}_2)_2$ (**1a- $^{13}\text{C}_3$**). A suspension of $(^{13}\text{CO}_2\text{Et})_2^{13}\text{CH}_2$ (150 μL , 1.0 mmol), allyl bromide (260 μL , 3.0 mmol) and NaH (140 mg, 6.0 mmol) in THF was stirred overnight at room temperature. Work up and chromatography (SiO_2 ; hexane–EtOAc = 24:1) gave **1a- $^{13}\text{C}_3$** (126 mg, 52%) as a colorless oil. ^1H NMR (CDCl_3 , 25 °C): δ 5.64 (dtdd, J = 1.4, 7.4, 10.6, 14.9 Hz, 2 H), 5.11 (dm, J = 1.2 Hz, 2 H), 5.08 (broad d, J = 2.0 Hz, 2 H), 4.17 (dq, J = 3.3, 7.2 Hz, 4 H), 2.63 (m, 4 H), 1.24 (d, J = 7.1 Hz, 6 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 25 °C): δ 171.0 (d, J = 57.2 Hz), 132.5, 119.4, 61.4, 57.4 (t, J = 57.3 Hz), 36.9 (d, J = 34.0 Hz), 14.3.

$(\text{CO}_2\text{Me})_2\text{C}(^{13}\text{CH}_2^{13}\text{CH}=\text{CH}_2)_2$ (**1- $^{13}\text{C}_6$**). Labelled diene **1- $^{13}\text{C}_6$** was synthesized in four steps from $\text{H}^{13}\text{C}\equiv^{13}\text{C}^{13}\text{CH}_2\text{OH}$ in 24% overall yield by the pathway depicted in Scheme S1. A solution of $\text{H}^{13}\text{C}\equiv^{13}\text{C}^{13}\text{CH}_2\text{OH}$ (250 mg, 4.2 mmol), HSiEt_3 (0.81 g, 7.0 mmol), $[\text{Rh}(\text{COD})_2]^+ \text{BF}_4^-$ (13 mg, 0.03 mmol), and PPh_3 (16 mg, 0.06 mmol) in acetone (7 mL) was stirred at room temperature for 40 min.⁶ The solvent was evaporated and the residue was chromatographed (SiO_2 ; hexanes–EtOAc = 50:1 \rightarrow 25:1) to give $\text{Et}_3\text{Si}^{13}\text{CH}=\text{CH}^{13}\text{CH}_2\text{OH}$ (**S1**) (0.65 g, 88%) as a colorless oil. A solution of **S1** (0.63 g, 3.6 mmol), methane sulfonylchloride (0.82 g, 7.2 mmol), and triethylamine (0.81 g, 8.0 mmol) in CH_2Cl_2 (15 mL) was warmed from 0 to 25 °C and stirred for 4 h. Solvent was evaporated and the residue was diluted with ether and washed with water, 1 N HCl, saturated NaHCO_3 , and brine, and dried (MgSO_4). Evaporation of ether gave $\text{Et}_3\text{Si}^{13}\text{CH}=\text{CH}^{13}\text{CH}_2\text{OMs}$ (**S2**) (0.79 g, 86%) as a pale yellow oil which was ~97% pure by GC and NMR analysis.



Scheme S1

A suspension of **S2** (0.78 g, 3.1 mmol), dimethyl malonate (0.17 g, 1.3 mmol), and NaH (60% in mineral oil; 0.21 g, 5.2 mmol) in THF (15 mL) was refluxed overnight. Water and ether were added, the layers were separated, and the organic fraction was washed with water, 1 N HCl, saturated NaHCO₃, and brine, and dried (MgSO₄). Chromatography (SiO₂; hexane–EtOAc = 80:1 → 50:1) of the residue gave (CO₂Me)₂C(¹³CH₂¹³CH=¹³CHSiEt₃)₂ (**S3**) (0.36 g, 62 %) as a pale yellow oil. A solution of **S3** (0.35 g, 0.78 mmol) and CF₃CO₂H (1.0 mL, 13 mmol) in CH₂Cl₂ (3.2 mL) was stirred at room temperature for 24 h. The resulting solution was diluted with CH₂Cl₂, washed with saturated NaHCO₃, and dried (MgSO₄). Chromatography of the residue (SiO₂; hexane–EtOAc = 75:1 → 50:1) gave 1-¹³C₆ (89 mg, 52%) as a colorless oil.

For S1: ¹³C{¹H} NMR (CDCl₃, 25 °C), labelled carbons only: δ 146.4 (dd, *J* = 42, 60 Hz), 126.0 (d, *J* = 60 Hz), 66.1 (d, *J* = 43 Hz). HRMS Calcd. (found) for ¹²C₄¹³C₃H₁₅OSi (M⁺ – ¹²C₂H₅): 146.0993 (146.0996).

For S2: ¹³C{¹H} NMR (CDCl₃, 25 °C), labelled carbons only: δ 138.5 (dd, *J* = 45, 60 Hz), 134.0 (d, *J* = 60 Hz), 72.5 (d, *J* = 45 Hz). HRMS Calcd. (found) for ¹²C₄¹³C₃H₁₇O₃SSi (M⁺ – ¹²C₂H₅): 224.0768 (224.0764).

For S3: $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 25 °C), labelled carbons only: δ 141.6 (dd, $J = 41$, 60 Hz), 132.4 (d, $J = 60$ Hz), 40.6 (d, $J = 41$ Hz). HRMS Calcd. (found) for $^{12}\text{C}_{15}^{13}\text{C}_6\text{H}_{39}\text{O}_4\text{Si}_2$ ($\text{M}^+ - ^{12}\text{C}_2\text{H}_5$): 417.2588 (417.2581).

For 1- $^{13}\text{C}_6$: ^1H NMR (CDCl_3 , 25 °C): δ 5.62 (dm, $J_{\text{CH}} = 156$ Hz, 1 H), 5.08 (dm, $J_{\text{CH}} = 160$ Hz, 2 H), 3.71 (s, 6 H), 2.62 (dm, $J_{\text{CH}} = 132$ Hz, 4 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 25 °C), labelled carbons only: δ 132.5 (dd, $J = 43$, 69 Hz), 119.5 (d, $J = 69$ Hz), 37.2 (d, $J = 43$ Hz). HRMS Calcd. (found) for $^{12}\text{C}_4^{13}\text{C}_6\text{H}_{13}\text{O}_3$ ($\text{M}^+ - \text{O}^{12}\text{CH}_3$): 187.1066 (187.1065).

Palladium Complexes

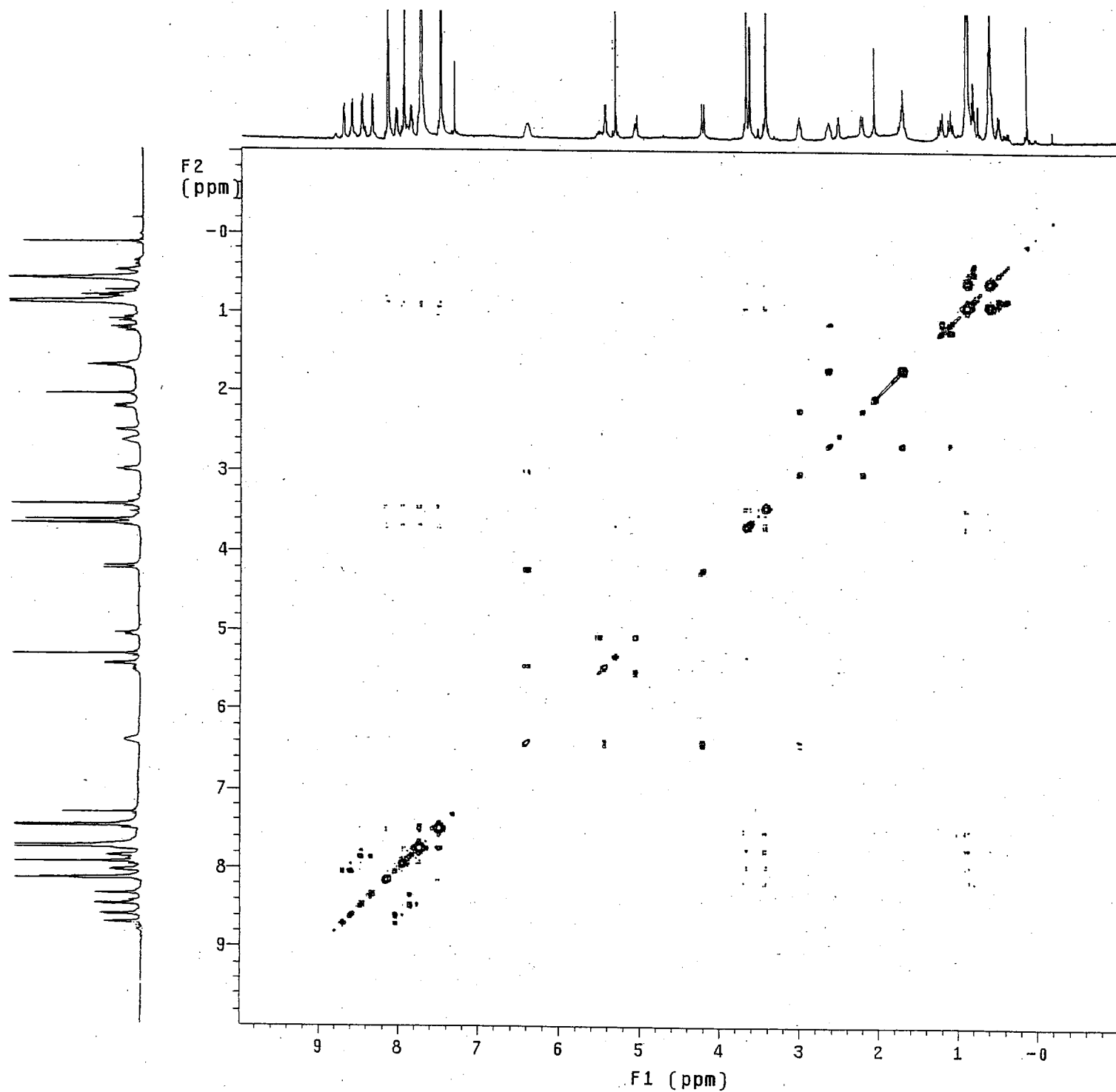
[(phen)Pd(SiEt₃)(NCAr)]⁺ [BAr₄]⁻ (2). HSiEt₃ (2.62 mg, 0.0225 mmol) was added via syringe to an NMR tube containing a solution of [(phen)Pd(Me)(NCAr)]⁺ [BAr₄]⁻ (3) at -78 °C. The tube was shaken briefly and placed in an NMR probe precooled to -81 °C. Reaction progress was determined by measuring disappearance of the Pd-CH₃ resonance of 2 (δ 1.26) relative to the para phenyl proton of the BAr₄⁻ counter ion (δ 7.76) in the ^1H NMR spectrum. After 20 min, 3 was completely consumed to form 2 in 101±10% yield. Complex 2 was thermally sensitive and characterized in solution by ^1H NMR spectroscopy. ^1H NMR (CD_2Cl_2 , -81 °C): δ 9.02 (d, $J = 4.9$ Hz, 1 H, H_{phen}), 8.83 (d, $J = 4.5$ Hz, 1 H, H_{phen}), 8.55 (d, $J = 8.2$ Hz, 1 H, H_{phen}), 8.43 (d, $J = 8.3$ Hz, 1 H, H_{phen}), 8.39 (s, 2 H, H_{O}), 8.36 (s, 1 H, H_{P}), 7.93 (m, 3 H, H_{phen}), 7.78 (dd, $J = 4.8$, 8.0 Hz, 1 H, H_{b}), 7.73 (s, 8 H, H_{O}), 7.46 (s, 4 H, H_{P}), 1.06 (t, $J = 7.5$ Hz, 9 H, SiCH₂CH₃), 0.97 (q, $J = 7.5$ Hz, 6 H, SiCH₂CH₃).

{(phen)Pd[η^1, η^2 -CH(CH₂SiEt₃)CH₂C(CO₂Me)₂CH₂CH=CH₂]}⁺ [BAr₄]⁻ (4). Dimethyldiallyl malonate (4.7 μL , 0.023 mmol) was added via syringe to an NMR tube containing a solution of [(phen)Pd(SiEt₃)(NCAr)]⁺ [BAr₄]⁻ (2) (0.023 mmol) in CD_2Cl_2 (0.6 mL) at -78 °C. The tube was shaken briefly and placed in the probe of an NMR spectrometer precooled to -81 °C. The probe was warmed to -62 °C and the solution was monitored periodically by ^1H NMR spectroscopy. Reaction progress was determined by integrating the carbomethoxy resonances of 4 (δ 3.69 and 3.43) relative to the para phenyl proton of the BAr₄⁻ counter ion (δ

7.74). After 20 min, **2** had been completely consumed to form **4** as the exclusive product in 84%±10% yield as a single diastereomer by ^1H NMR spectroscopy. Complex **4** was thermally sensitive and was characterized in solution by ^1H NMR spectroscopy at $-62\text{ }^\circ\text{C}$. Assignment of the proton resonances and coupling constants of **4** was aided by ^1H COSY analysis (Figure S2) and by spectroscopic analysis of the deuterium isotopomers $\{(\text{phen})\text{Pd}[\eta^1, \eta^2\text{-CD}(\text{CH}_2\text{SiEt}_3)\text{CH}_2\text{C}(\text{CO}_2\text{Me})_2\text{CH}_2\text{CD}=\text{CH}_2]\}^+ [\text{BAR}_4]^-$ (**4-d₂**) and $\{(\text{phen})\text{Pd}[\eta^1, \eta^2\text{-CH}(\text{CH}_2\text{SiEt}_3)\text{CD}_2\text{C}(\text{CO}_2\text{Me})_2\text{CD}_2\text{CH}=\text{CH}_2]\}^+ [\text{BAR}_4]^-$ (**4-d₄**) (see below).

For 4: ^1H NMR (CD_2Cl_2 , $-62\text{ }^\circ\text{C}$): δ 8.71 (d, $J = 4.4$ Hz, 1 H, H_a), 8.61 (d, $J = 8.1$ Hz, 1 H, H_c), 8.48 (dd, $J = 1.2, 8.2$ Hz, 1 H, H_c), 8.35 (dd, $J = 1.2, 4.9$ Hz, 1 H, H_a), 8.16 (s, 2 H, H_o), 8.14 (s, 1 H, H_p), 8.05 (dd, $J = 5.2, 8.0$ Hz, 1 H, H_b), 7.96 (s, 2 H, H_d), 7.87 (dd, $J = 4.9, 8.1$ Hz, 1 H, H_b), 7.74 (s, 8 H, H_o'), 7.49 (s, 4 H, H_p'), 6.41 (dtd, $J = 4.3, 8.4, 16.1$ Hz, 1 H, $-\text{CH}=\text{CH}_2$), 5.44 (d, $J = 9.0$ Hz, 1 H, $-\text{CH}=\text{CH}_2$), 4.22 (d, $J = 16.1$ Hz, 1 H, $-\text{CH}=\text{CH}_2$), 3.68 (s, 3 H, CO_2Me), 3.43 (s, 3 H, CO_2Me), 3.02 (dd, $J = 8.2, 12.7$ Hz, 1 H, $-\text{CH}_2\text{CH}=\text{CH}_2$), 2.66 (m, 1 H, Pd-CH), 2.22 (dd, $J = 4.0, 12.6$ Hz, 1 H, $-\text{CH}_2\text{CH}=\text{CH}_2$), 1.74, 1.70 [ABX, $J_{\text{AB}} = 15.6$ Hz, $J_{\text{AX}} = 10.9$ Hz, $J_{\text{BX}} = 5.4$ Hz, 2 H, Pd-CH(CH_2SiEt_3) CH_2], 1.23 [dd, $J = 2.6, 13.3$ Hz, 1 H, Pd-CH(CH_2SiEt_3) CH_2], 1.11 [t, $J = 13.3$ Hz, 1 H, Pd-CH(CH_2SiEt_3) CH_2], 0.94 (t, $J = 7.9$ Hz, 9 H, SiCH_2CH_3), 0.64 (q, $J = 7.9$ Hz, 6 H, SiCH_2CH_3).

Figure S2. ^1H COSY Spectrum of 4.



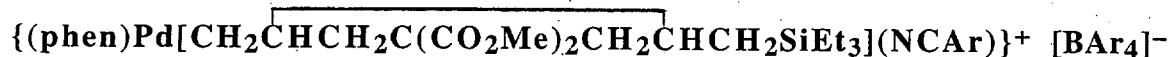
$\{(\text{phen})\text{Pd}[\eta^1, \eta^2\text{-CD}(\text{CH}_2\text{SiEt}_3)\text{CH}_2\text{C}(\text{CO}_2\text{Me})_2\text{CH}_2\text{CD}=\text{CH}_2]\}^+ [\text{BAR}_4]^-$ (**4-d₂**). Reaction of **1-2,6-d₂** (4.9 μL , 0.024 mmol) and **2** (0.024 mmol) in CD_2Cl_2 (0.6 mL) at -62°C employing a procedure analogous to that used in the synthesis of **4** gave **4-d₂** as the exclusive product by ^1H NMR analysis. ^1H NMR (CD_2Cl_2 , -62°C), hexenyl ligand only: δ 5.45 (s, 1 H, $-\text{CH}=\text{CH}_2$), 4.22 (s, 1 H, $-\text{CH}=\text{CH}_2$), 3.69 (s, 3 H, CO_2Me), 3.43 (s, 3 H, CO_2Me), 3.02 (d, $J = 12.7$ Hz, 1 H, $-\text{CH}_2\text{CD}=\text{CH}_2$), 2.22 (d, $J = 12.7$ Hz, 1 H, $-\text{CH}_2\text{CD}=\text{CH}_2$), 1.73, 1.70 [ABq, $J = 15.6$ Hz, 2 H, $\text{Pd-CD}(\text{CH}_2\text{SiEt}_3)\text{CH}_2$], 1.23, 1.11 [ABq, $J = 13.6$ Hz, 2 H, $\text{Pd-CD}(\text{CH}_2\text{SiEt}_3)\text{CH}_2$], 0.92 (t, $J = 7.8$ Hz, 9 H, SiCH_2CH_3), 0.62 (q, $J = 7.7$ Hz, 6 H, SiCH_2CH_3).

$\{(\text{phen})\text{Pd}[\eta^1, \eta^2\text{-CH}(\text{CH}_2\text{SiEt}_3)\text{CD}_2\text{C}(\text{CO}_2\text{Me})_2\text{CD}_2\text{CH}=\text{CH}_2]\}^+ [\text{BAR}_4]^-$ (**4-d₄**). Addition of **1-3,3,5,5-d₄** (5.0 μL , 0.025 mmol) to a solution of **2** (0.025 mmol) in CD_2Cl_2 (0.6 mL) at -62°C gave a 5:6:10 mixture of **1-d₄**, **4-d₄**, and **5-d₄** by ^1H NMR analysis. From this mixture, the ^1H NMR resonances for the hexenyl ligand of **4-d₄** were determined. ^1H NMR (CD_2Cl_2 , -81°C), hexenyl ligand only: δ 6.41 (dd, $J = 9.0, 15.9$ Hz, 1 H, $-\text{CH}=\text{CH}_2$), 5.45 (d, $J = 9.0$ Hz, 1 H, $-\text{CH}=\text{CH}_2$), 4.23 (d, $J = 16.1$ Hz, 1 H, $-\text{CH}=\text{CH}_2$), 3.68 (s, 3 H, CO_2Me), 3.44 (s, 3 H, CO_2Me), 2.64 (dd, $J = 3.4, 12.4$ Hz, 1 H, Pd-CH), 0.61 (q, $J = 7.7$ Hz, 6 H, SiCH_2CH_3). The SiCH_2CH_3 resonances were obscured.

$\{(\text{phen})\text{Pd}[\eta^1, \eta^2\text{-CH}(\text{CH}_2\text{SiEt}_3)\text{CH}_2^{13}\text{C}(\text{CO}_2\text{Et})_2\text{CH}_2\text{CH}=\text{CH}_2]\}^+ [\text{BAR}_4]^-$ (**4a-¹³C₃**). Reaction of **1-¹³C₃** (4.7 μL , 0.023 mmol) and **2** (0.023 mmol) in CD_2Cl_2 (0.6 mL) at -62°C employing a procedure analogous to that used in the synthesis of **4** gave **4a-¹³C₃** as the exclusive product by ^1H NMR analysis. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -62°C), labelled carbon atoms only: δ 172.6 (dd, $J = 2.3, 55.3$ Hz), 172.5 (d, $J = 58.4$ Hz), 65.5 (dd, $J = 55.2, 58.4$ Hz).

$\{(\text{phen})\text{Pd}[\eta^1, \eta^2\text{-}^{13}\text{CH}(\text{CO}_2\text{Me})_2\text{CH}_2\text{C}(\text{CO}_2\text{Me})_2\text{CH}_2\text{CH}=\text{CH}_2]\}^+ [\text{BAR}_4]^-$ (**4-¹³C₆**). Reaction of **1-¹³C₆** (4.2 μL , 0.021 mmol) and **2** (0.022 mmol) in CD_2Cl_2 (0.6 mL) at -60°C employing a procedure analogous to that used in the synthesis of **4** gave **4-¹³C₆** as the exclusive

product by ^1H NMR analysis. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 75 MHz -60°C), labelled carbon atoms only: δ 103.7 (dd, $J = 41, 47$ Hz, $-\text{CH}=\text{CH}_2$), 87.5 (d, $J = 47$ Hz, $-\text{CH}=\text{CH}_2$), 50.0 [dd, $J = 30, 36$ Hz, $\text{Pd}-\text{CH}(\text{CH}_2\text{SiEt}_3)\text{CH}_2$], 39.2 [d, $J = 36$ Hz, $\text{Pd}-\text{CH}(\text{CH}_2\text{SiEt}_3)\text{CH}_2$], 32.5 (d, $J = 41$ Hz, $-\text{CH}_2\text{CH}=\text{CH}_2$), 20.3 [d, $J = 30$ Hz, $\text{Pd}-\text{CH}(\text{CH}_2\text{SiEt}_3)\text{CH}_2$].



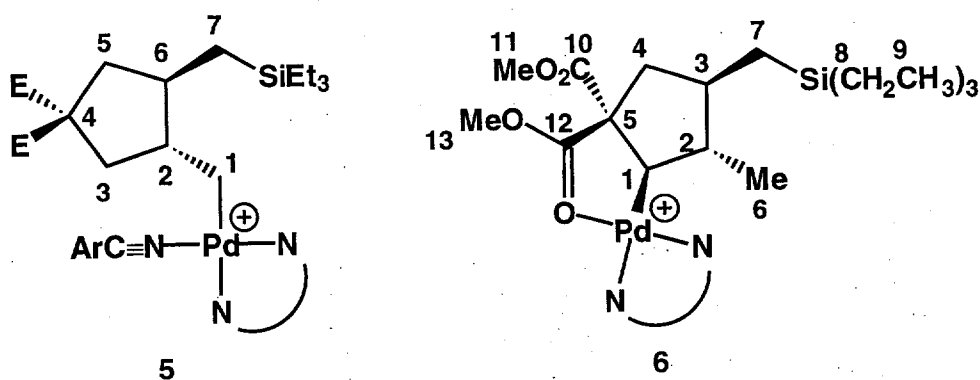
(5). An NMR tube containing a solution 4 (39 mM) and NCAr in CD_2Cl_2 was warmed at -41°C and monitored periodically by ^1H NMR spectroscopy; the progress of the reaction was determined by integrating the carbomethoxy resonances of 5 (δ 3.67 and 3.59) and 4 (δ 3.69 and 3.43) and the para phenyl resonance of the BAr_4^- counterion (δ 7.72). After 2 h, 4 had been completely consumed to form 5 in $96\% \pm 10\%$ yield by ^1H NMR analysis. Complex 5 was thermally sensitive and was characterized in solution by ^1H and ^{13}C NMR spectroscopy at -41°C . The ^1H and ^{13}C NMR labeling scheme for the cyclopentyl portion of 5 is shown in Figure S3. Assignment of proton resonances and J_{HH} coupling constants was aided by ^1H COSY analysis (Figure S4) and by ^1H NMR analysis of the labelled derivatives $\{(\text{phen})\text{Pd}[\text{CH}_2\text{CDCH}_2\text{C}(\text{CO}_2\text{Me})_2\text{CH}_2\text{CDCH}_2\text{SiEt}_3](\text{NCAr})\}^+ [\text{BAr}_4]^-$ (5- d_2) and $\{(\text{phen})\text{Pd}[\text{CH}_2\text{CHCD}_2\text{C}(\text{CO}_2\text{Me})_2\text{CD}_2\text{CHCH}_2\text{SiEt}_3](\text{NCAr})\}^+ [\text{BAr}_4]^-$ (5- d_4) (see below).

For 5: ^1H NMR (CD_2Cl_2 , -41°C): δ 8.86 (dd, $J = 1.0, 5.4$ Hz, 1 H, H_a), 8.84 (dd, $J = 1.5, 4.9$ Hz, 1 H, H_a), 8.65 (s, 2 H, H_o), 8.64 (dd, $J = 1.1, 8.6$ Hz, 1 H, H_c), 8.55 (dd, $J = 1.5, 8.4$ Hz, 1 H, H_c), 8.38 (s, 1 H, H_p), 8.02 (d, $J = 2.7$ Hz, 2 H, H_d), 7.99 (dd, $J = 5.4, 8.2$ Hz, 1 H, H_b), 7.86 (dd, $J = 4.8, 8.2$ Hz, 1 H, H_b), 7.72 (s, 8 H, H_o'), 7.51 (s, 4 H, H_p'), 3.67 (s, 3 H, CO_2CH_3), 3.59 (s, 3 H, CO_2CH_3), 2.93 (dd, $J = 7.4, 13.5$ Hz, 1 H, H_3), 2.62 (dd, $J = 6.3, 13.1$ Hz, 1 H, H_5), 2.52 (dd, $J = 4.0, 7.7$ Hz, 1 H, H_1), 2.18 (dd, $J = 10.4, 13.4$ Hz, 1 H, H_5), 2.09 (dd, $J = 8.3, 10.8$ Hz, 1 H, H_1), 1.80 (m, 1 H, H_2), 1.77 (dd, $J = 11.9, 12.9$ Hz, 1 H, H_5), 1.67 (m, 1 H, H_6), 1.26 (dd, $J = 3.0, 13.4$ Hz, 1 H, H_7), 0.92 (t, $J = 7.9$ Hz, 9 H, $-\text{SiCH}_2\text{CH}_3$), 0.55 (q, $J = 7.9$ Hz, 6 H, $-\text{SiCH}_2\text{CH}_3$), 0.46 (dd, $J = 11.9, 13.6$ Hz, 1 H, H_7).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -62°C): δ 175.4 (CO_2CH_3), 175.2 (CO_2CH_3), 163.8 (q, $J_{\text{C}11\text{B}} = 49.7$ Hz, superimposed on a septet, $J_{\text{C}10\text{B}} = 16.8$ Hz, C_i), 159.4, 150.5, 149.6, 145.4, 142.4,

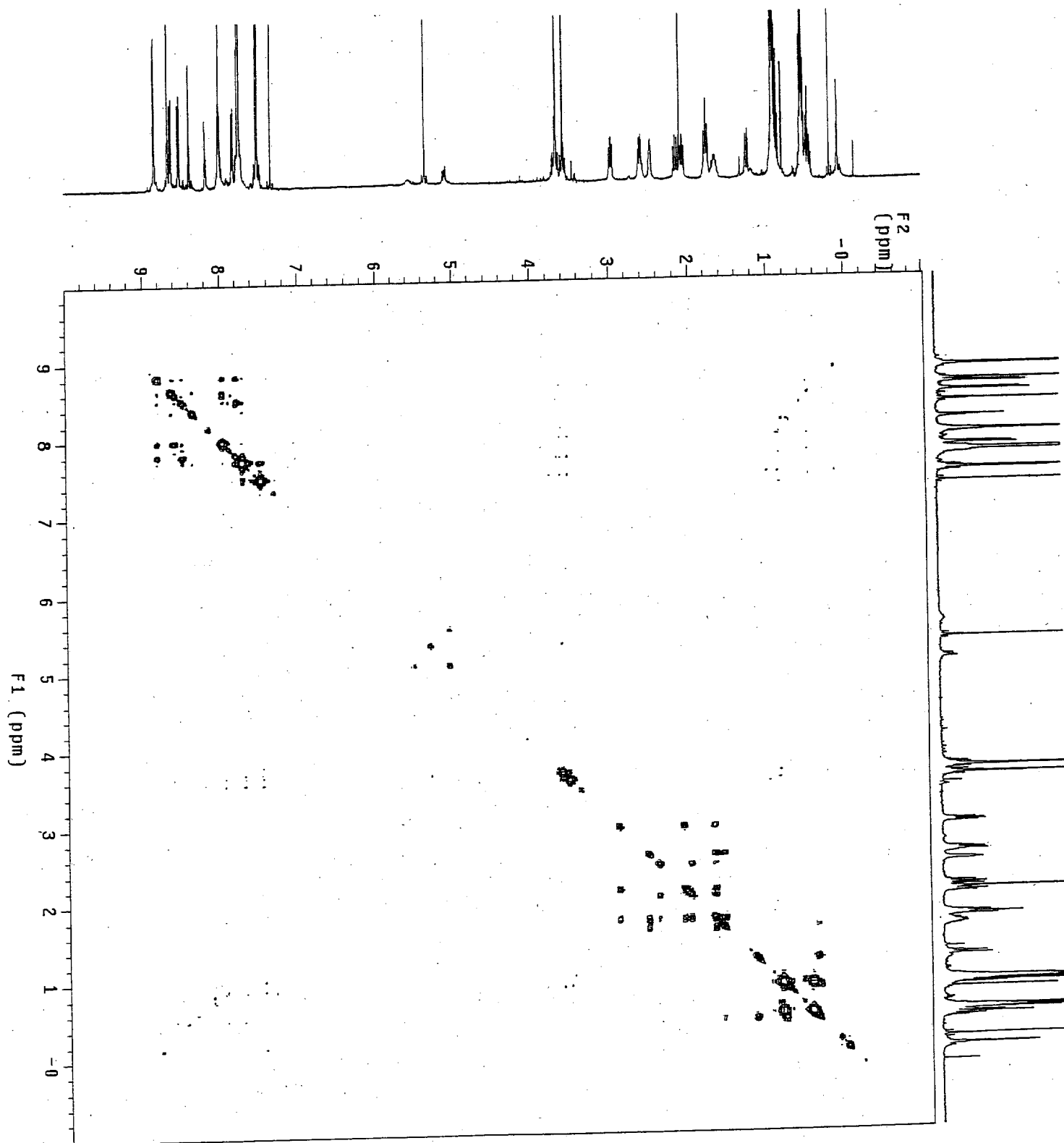
141.4 (C_{phen}), 136.6 (C_{O}), 136.1 (C_{O}), 134.9 (q, $^2J_{\text{CF}} = 35.1$ Hz, C_{m}), 132.6, 132.0 (C_{phen}), 131.3 (C_{p}), 130.6 (q, $^2J_{\text{CF}} = 31.4$ Hz, C_{m}), 129.9, 129.6, 127.9, 127.8 (C_{phen}), 126.4 (q, $^1J_{\text{CF}} = 273$ Hz, C_{r}), 124.1 (q, $^1J_{\text{CF}} = 274$ Hz, C_{r}), 121.5, 113.8 (C_{i} and C_{q}), 119.5 (C_{p}), 59.2 (C_4), 55.3 (CO_2CH_3), 55.2 (CO_2CH_3), 53.6 (C_2), 45.2, 44.8, 43.9 (C_3 , C_5 , and C_6), 32.4 (C_1), 16.0 (C_7), 9.5 (SiCH_2CH_3), 5.2 (SiCH_2CH_3).

Figure S3. Atom labeling Schemes for complexes **5** and **6**.



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Figure S4. ^1H NMR COSY Spectrum of 5.



$\{(\text{phen})\text{Pd}[\text{CH}_2\overline{\text{CDCH}_2\text{C}(\text{CO}_2\text{Me})_2\text{CH}_2\text{CDCH}_2\text{SiEt}_3](\text{NCAr})\}^+ [\text{BAR}_4]^-$ (**5-*d*₂**). Warming a solution of **4-*d*₂** (0.023 mmol) in CD_2Cl_2 (0.6 mL) at -41°C for 90 min formed **5-*d*₂** as the exclusive product by ^1H NMR analysis. ^1H NMR (CD_2Cl_2 , -41°C): δ 3.66 (s, 3 H, CO_2CH_3), 3.57 (s, 3 H, CO_2CH_3), 2.92 (d, $J = 13.6$ Hz, 1 H, H_3), 2.59 (d, $J = 13.4$ Hz, 1 H, H_5), 2.48 (d, $J = 8.2$ Hz, 1 H, H_1), 2.15 (d, $J = 13.5$ Hz, 1 H, H_3), 2.06 (d, $J = 8.1$ Hz, 1 H, H_1), 1.74 (d, $J = 13.5$ Hz, 1 H, H_5), 1.23 (d, $J = 14.3$ Hz, 1 H, H_7), 0.90 (t, $J = 7.8$ Hz, 9 H, $-\text{SiCH}_2\text{CH}_3$), 0.53 (q, $J = 7.8$ Hz, 6 H, $-\text{SiCH}_2\text{CH}_3$). One of the two diastereotopic $-\text{CH}_2\text{SiEt}_3$ protons (H_7) was obscured.

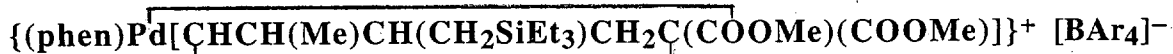
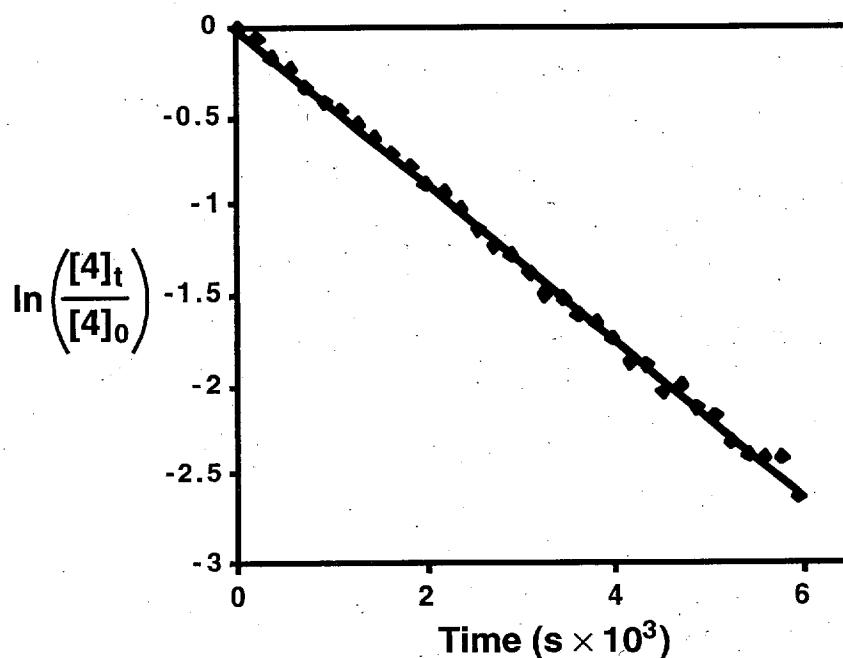
$\{(\text{phen})\text{Pd}[\text{CH}_2\overline{\text{CHCD}_2\text{C}(\text{CO}_2\text{Me})_2\text{CD}_2\text{CHCH}_2\text{SiEt}_3](\text{NCAr})\}^+ [\text{BAR}_4]^-$ (**5-*d*₄**). Warming a 5:6:10 mixture of **1-*d*₄**, **4-*d*₄**, and **5-*d*₄** (0.023 mmol combined) in CD_2Cl_2 (0.6 mL) at -41°C for 90 min formed **5-*d*₄** as the exclusive product by ^1H NMR analysis. ^1H NMR (CD_2Cl_2 , -41°C): δ 3.67 (s, 3 H, CO_2CH_3), 3.58 (s, 3 H, CO_2CH_3), 2.50 (dd, $J = 4.1, 8.0$ Hz, 1 H, H_1), 2.08 (dd, $J = 8.6, 10.7$ Hz, 1 H, H_1), 1.77 (dt, $J = 4.2, 10.3$ Hz, 1 H, H_2), 1.64 (dd, $J = 10.0, 11.8$ Hz, 1 H, H_6), 1.24 (d, $J = 13.7$ Hz, 1 H, H_7), 0.91 (t, $J = 8.0$ Hz, 9 H, $-\text{SiCH}_2\text{CH}_3$), 0.54 (q, $J = 7.9$ Hz, 6 H, $-\text{SiCH}_2\text{CH}_3$). One of the two diastereotopic $-\text{CH}_2\text{SiEt}_3$ protons (H_7) was obscured.

$\{(\text{phen})\text{Pd}[\text{CH}_2\overline{\text{CHCH}_2^{13}\text{C}(\text{CO}_2\text{Et})_2\text{CH}_2\text{CHCH}_2\text{SiEt}_3](\text{NCAr})\}^+ [\text{BAR}_4]^-$ (**5a-¹³C₃**). Warming a solution of **4a-¹³C₃** (4.66 μL , 0.023 mmol) in CD_2Cl_2 (0.6 mL) at -41°C for 90 min formed **5a-¹³C₃** as the exclusive product by ^1H NMR analysis. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -41°C), labelled carbon atoms only: δ 175.4 (dd, $J = 1.4, 58.4$ Hz, CO_2CH_3), 175.2 (dd, $J = 1.4, 58.4$ Hz, CO_2CH_3), 59.2 (t, $J = 58.4$ Hz, C_4).

$\{[(\text{phen})\text{Pd}[\text{CH}_2\overline{\text{CH}^{13}\text{CH}_2\text{C}(\text{CO}_2\text{Me})_2\text{CH}_2\text{CH}^{13}\text{CH}_2\text{SiEt}_3](\text{NCAr})\}^+ [\text{BAR}_4]^-$ (**5-¹³C₆**). Warming a solution of **4-¹³C₆** (0.021 mmol) in CD_2Cl_2 (0.6 mL) at -40°C for 90 min formed **5-¹³C₆** as the exclusive product by ^1H NMR analysis. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 75 MHz -40°C), labelled carbon atoms only: δ [51.8 (q), 43.3 (q), C_2 and C_6], [42.7 (d), 42.2 (d), 31.0 (d), C_1, C_3 and C_5], 14.8 (d, C_7); all $^1J_{\text{CC}} = 31\text{--}34$ Hz.

Kinetics of the Conversion of 4 to 5. An NMR tube containing an equimolar solution **4** and $\text{N}\equiv\text{CAr}$ (0.0213 mmol) in CD_2Cl_2 (0.6 mL) was warmed at -41°C and monitored periodically by ^1H NMR spectroscopy. The concentration of **4** was determined by integrating the carbomethoxy resonances of **4** (δ 3.69 and 3.43) relative to the para phenyl resonance of the BAr_4^- counterion (δ 7.72). A plot of $\ln\{[\mathbf{4}]_t/[\mathbf{4}]_0\}$ was linear to >3 half-lives with a first-order rate constant of $k = 4.7 \pm 0.3 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ (Figure S5). The absence of curvature in the first-order plot indicates that the rate of conversion of **4** to **5** is independent of $[\text{N}\equiv\text{CAr}]$ from 0 to 35.5 mM.

Figure S5: First-order plot for the conversion of **4** to **5** at -41°C in CD_2Cl_2 .

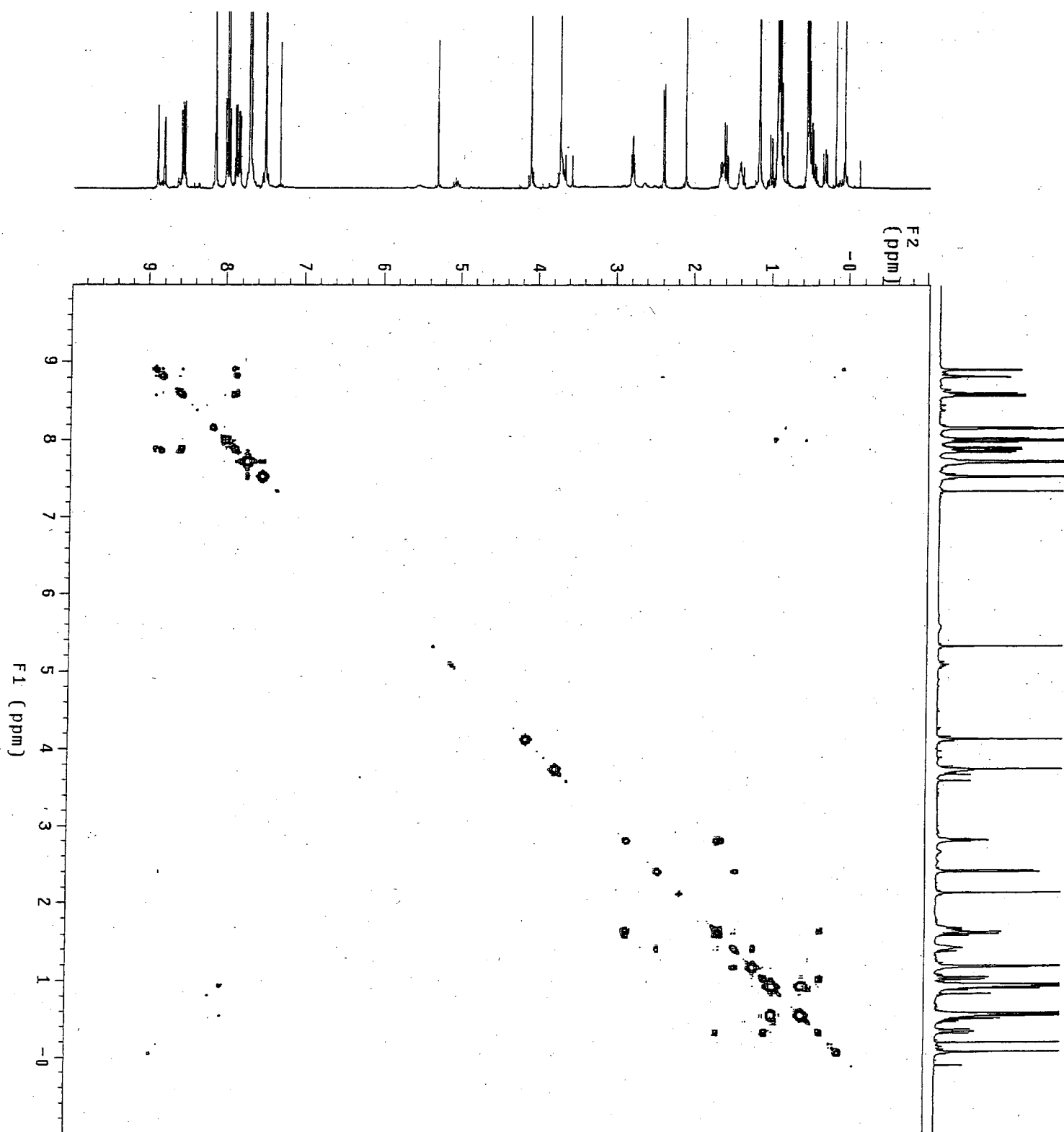


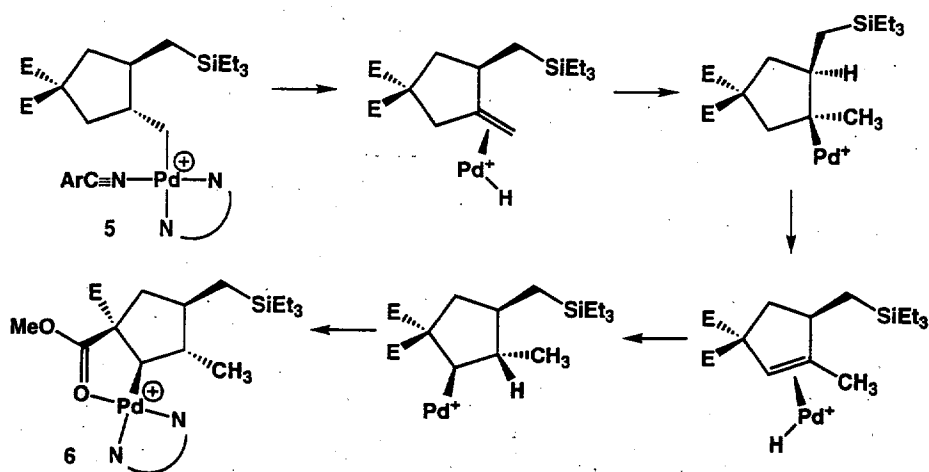
(6). Triethylsilane (12.3 μL , 0.077 mmol) was added via syringe to a solution of $\{(\text{phen})\text{Pd}(\text{Me})(\text{N}\equiv\text{CMe})\}^+ [\text{BAr}_4]^-$ (**3a**) (93 mg, 0.077 mmol) in CH_2Cl_2 (25 mL) at -78°C , stirred for 30 minutes, and treated with **1** (16 μL , 0.077 mmol). The resulting solution was warmed to room temperature and stirred for 120 min. Solvent was evaporated under vacuum to

form a yellow glass which was triturated with hexanes (3×5 mL) and dried under vacuum to give **6** (52 mg, 49%) as a yellow microcrystals. The ^1H and ^{13}C NMR labeling scheme for the cyclopentyl portion of **6** is shown in Figure S3. ^1H NMR resonances were assigned based on COSY analysis (Figure S6). The stereochemistry of **6** was assigned assuming non-dissociative rearrangement of **5** (Scheme S2).

For 6: ^1H NMR (CDCl_3 , 23 °C): δ 8.92 (dd, $J = 1.4, 4.9$ Hz, 1 H, H_c), 8.85 (dd, $J = 1.4, 5.4$ Hz, 1 H, H_c), 8.64 (dd, $J = 1.2, 8.2$ Hz, 1 H, H_a), 8.62 (dd, $J = 1.6, 8.4$ Hz, 1 H, H_a), 8.07, 8.03 (ABq, $J = 8.9$ Hz, 2 H, H_d), 7.95 (dd, $J = 4.8, 8.3$ Hz, 1 H, H_b), 7.89 (dd, $J = 5.3, 8.2$ Hz, 1 H, H_b), 7.72 (t, $J = 2.4$ Hz, 8 H, H_o), 7.55 (s, 4 H, H_p), 4.16 (s, 3 H, H_{13}), 3.78 (s, 3 H, H_{11}), 2.85 (dd, $J = 7.1, 13.0$ Hz, 1 H, H_4), 2.47 (d, $J = 10.5$ Hz, 1 H, H_1), 1.70 (m, 1 H, H_3), 1.67 (d, $J = 12.8$ Hz, 1 H, H_4), 1.47 (m, 1 H, H_2), 1.20 (d, $J = 6.5$ Hz, 3 H, H_6), 1.06 (dd, $J = 2.4, 14.4$ Hz, 1 H, H_7), 0.97 (t, $J = 7.9$ Hz, 9 H, H_9), 0.58 (q, $J = 7.8$ Hz, 6 H, H_8), 0.37 (dd, $J = 11.2, 14.4$ Hz, 1 H, H_7). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 23 °C): δ 191.5 (C_{12}), 171.7 (C_{10}), 161.9 (q, $J_{\text{CB}} = 50.0$ Hz, C_i), 151.7, 149.1 (C_a), 147.8, 143.8 (C_e), 139.7, 139.1 (C_b), 134.9 (C_o), 130.9, 130.2 (C_f), 129.2 (q, $^2J_{\text{CF}} = 31.7$ Hz, C_m), 128.0, 127.5, 126.0, 125.4 (C_b and C_c), 124.6 (q, $^1J_{\text{CF}} = 272.8$ Hz, C_r), 117.6 (C_p), 68.5, 56.5, 53.8, 53.2, 42.1, (C_1, C_2, C_5, C_{11} , and C_{13}), 42.9, 40.9 (C_3 and C_4), 17.3 (C_6), 15.8 (C_7), 7.5 (C_9), 4.0 (C_8). IR (neat, cm^{-1}): 2960, 2887, 1746, 1612, 1457, 1355, 1275, 1122, 889, 841. Anal. Calcd (found) for $\text{C}_{61}\text{H}_{51}\text{N}_2\text{O}_4\text{F}_{24}\text{PdSiB}$: H 3.48 (3.14), C 49.59 (49.47), N 1.90 (2.02).

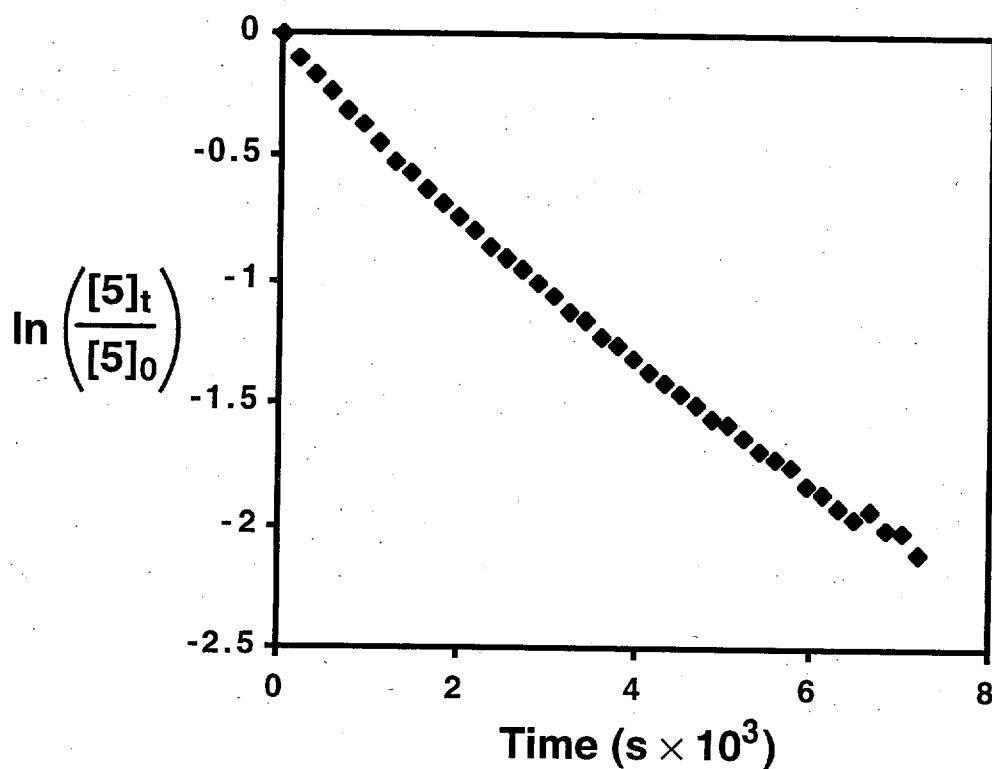
Figure S5. ^1H COSY Spectrum of 6.





Scheme S2. Stereochemical model for the non-dissociative conversion of **5** to **6**.

Conversion of 5 to 6. An NMR tube containing a solution of **5** (0.0214 mmol) in CD_2Cl_2 (0.6 mL) was warmed at -9°C and monitored periodically by ^1H NMR spectroscopy. The concentration of **5** and **6** were determined by integrating the carbomethoxy resonances of **5** (δ 3.67 and 3.59) and **6** (δ 4.13 and 3.75) and the para phenyl resonance of the BAR_4^- counterion (δ 7.72). A plot of $\ln \{[\mathbf{5}]_t/[\mathbf{5}]_0\}$ versus time revealed a slight positive deviation from linearity with an initial half-life of 32 min (Figure S7). The solution was then warmed at 25°C for 30 min to form **6** in $110\% \pm 10\%$ by ^1H NMR analysis.

Figure S7. First-order plot for the conversion of **5** to **6** at $-9\text{ }^{\circ}\text{C}$ in CD_2Cl_2 .

***trans*-1,1-Dicarbomethoxy-4-deuteriomethyl-3-triethylsilylmethyl cyclopentane (7-*d*₁).** DSiEt_3 (300 μL , 1.88 mmol) was added to a solution of dimethyl diallylmalonate (100 μL , 0.50 mmol), (phen) PdMeCl (8 mg, 0.024 mmol), and NaBAR_4 (23 mg, 0.027 mmol) in DCE (10 mL) at room temperature and stirred for 30 min. Solvent and excess silane were evaporated and the residue was chromatographed (SiO_2 ; hexanes–EtOAc = 24:1) to give **7-*d*₁** (167 mg, 102%) as a colorless oil. MS analysis of **7-*d*₁** revealed exclusive ($\geq 98\%$) formation of the *d*₁ isotopomer. ^1H and ^{13}C NMR analysis of **7-*d*₁** indicated complete ($\geq 95\%$) deuteration at the C(4) methyl group. ^1H NMR (CDCl_3): δ 3.64 (s, 6 H), 2.51 (dd, $J = 6.8$, 13.3 Hz, 1 H), 2.44 (dd, $J = 6.8$, 13.3 Hz, 1 H), 1.61 (d, $J = 13.3$ Hz, 1 H), 1.58 (d, $J = 13.2$ Hz, 1 H), 1.36 (m, 2 H), 0.86 (t, $J = 7.9$ Hz, 9 H), 0.81 (dd, $J = 2.3$, 14.6 Hz, 1 H), 0.46 (q, $J = 7.9$ Hz, 6 H), 0.21 (dd, $J = 11.5$, 14.5 Hz, 1 H), $-\text{CH}_2\text{D}$ doublet obscured by resonance at δ

0.86. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 173.6, 58.3, 52.7, 43.8, 43.5, 43.1, 42.3, 17.1 (t, $J_{\text{CD}} = 19.1$ Hz, isotopic shift = 360 ppb), 14.9, 7.6, 4.0.

Reaction of 5 and DSiEt₃. DSiEt₃ (5 μL , 0.031 mmol) was added via syringe to an NMR tube containing a solution of **5** (0.019 mmol) in CH_2Cl_2 (0.6 mL) at -78 °C and placed in the probe of an NMR spectrometer precooled at -41 °C and monitored periodically by ^1H NMR spectroscopy. Reaction progress was determined by integrating the carbomethoxy resonances of **5** (δ 3.67 and 3.59) relative to the para phenyl resonance of the BAr_4^- counterion (δ 7.72). After 5 minutes, resonances corresponding to **5** could no longer be observed and resonances corresponding to **2** and **7-d₁** were formed as the only observable products in a 1:1 ratio. The solution was then warmed to room temperature (leading to decomposition of **2**), filtered through a plug of Celite, and analyzed by ^{13}C NMR spectroscopy. The predominance ($\geq 90\%$) formation of the **7-d₁** isotopomer was established by the predominance of the 1:1:1 triplet at δ 17.1 [t, $J_{\text{CD}} = 19.1$ Hz, $-\text{C}(4)\text{CH}_2\text{D}$] relative to the singlet at δ 17.4 [$-\text{C}(4)\text{CH}_3$] in the ^{13}C NMR spectrum.

***trans*-2-Deuterio-1,1-dicarbomethoxy-3-methyl-4-(triethylsilyl)methyl cyclopentane (7-d₁').** DSiEt₃ (107 μL , 0.67 mmol) was added via syringe to a solution of **6** (161 mg, 0.13 mmol) in CH_2Cl_2 (1.6 mL) at room temperature and the resulting solution was stirred for two hours to form a dark brown solution. The solvent was evaporated and the residue was chromatographed (SiO_2 ; hexane–EtOAc = 24:1) to give **7-d₁'** (20 mg, 46%) as a colorless oil. MS analysis of **7-d₁'** revealed an 83:17 ratio of $d_1:d_0$ isotopomers. ^1H and ^{13}C NMR analysis revealed predominant $\geq 80\%$ deuteration of the C(2) ring carbon without formation of significant amounts of **7-d₁**. The stereochemistry of **7-d₁'** was assigned assuming retention of stereochemistry in the silylation of **6**. ^1H NMR (CDCl_3): δ 3.68 (s, 6 H), 2.55 (dd, $J = 6.6$, 13.3 Hz, 1 H), 1.63 (m, 2 H), 1.40 (m, 2 H), 0.93 (d, $J = 6.3$ Hz, 3 H), 0.90 (t, $J = 7.8$ Hz, 9 H), 0.83 (dd, $J = 2.4$, 14.6 Hz, 1 H), 0.49 (q, $J = 7.8$ Hz, 9 H), 0.25 (dd, $J = 11.1$, 14.6 Hz, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 173.7, 58.3, 52.8, 43.8, 43.5, 43.1, 42.0 (t, $J_{\text{CD}} = 20.6$ Hz, isotopic shift = 315 ppb), 17.4, 14.9, 7.6, 4.0.

References

- 1) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746.
- 2) De Delice, V.; Albano, B. G.; Castellari, C.; Cucciolito, M. E.; De Renzi, A. *J. Organomet. Chem.* **1991**, *403*, 269.
- 3) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.
- 4) Doyle, M. P.; McOsker, C. C.; West, C. T. *J. Org. Chem.* **1976**, *41*, 1393.
- 5) Kisanga, P.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2000**, *122*, 10017.
- 6) Takeuchi, R.; Nitta, S.; Watanabe, D. *J. Org. Chem.* **1995**, *60*, 3045.