Development, Synthetic Scope, and Mechanistic Studies of the Palladium-Catalyzed Cycloisomerization of Functionalized 1,6-Dienes in the Presence of Silane

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Supporting Information

Experimental procedures, analytical and spectroscopic data for new compounds (12 pages).

Experimental

General Methods. All reactions were performed under an atmosphere of nitrogen employing standard Schlenk or glovebox techniques. NMR were obtained on a General Electric QE 300 spectrometer operating at 300 MHz for ^1H and 75 MHz for ^{13}C in $CDCl_3$ unless otherwise noted. Gas chromatography was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a 25 m polydimethylsiloxane capillary column. Flash chromatography was performed employing 200-400 mesh silica gel (EM). Elemental analyses were performed by E+R Microanalytical Laboratories (Parsippany, NJ).

Methylene chloride and 1,2-dichloroethane (DCE) were distilled from CaH_2 under nitrogen. $Ti(O\textit{i}\text{-}Pr)_4$ (Aldrich) was distilled prior to use. Dimethyl malonate, dimethyl allylmalonate, dimethyl diallylmalonate (Lancaster), silanes (Aldrich), phosphines, phosphites, and $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (Strem) were used as received. 4,4-Dicarbomethoxy-oct-2-ene-6-yne,[1] 2-deuterio-prop-2-en-1-ol,[2] 1,1-dideuterio-prop-2-en-1-ol,[3] and 3,3-dideuterio-prop-2-en-1-ol,[4] dimethyl (1-phenyl-2-propenyl)malonate,[5] and the palladium complexes $[(\eta^3\text{-}CH_2C(Ph)CH_2)PdCl]_2$,[6] $[\eta^3\text{-}(CH_3)CHCHCH_2PdCl]_2$,[7] $[\eta^3\text{-}CH_2C(CH_3)CH_2PdCl]_2$,[7] were synthesized according to published procedures. Dimethyl (1-methyl-2-propenyl)malonate was synthesized from the reaction of dimethyl malonate and 2-chloro-3-butene in MeOH/MeONa. 4-Hydroxymethyl-4-phenyl-1,6-heptadiene was prepared by $LiAlH_4$ reduction of 4-phenyl-4-carbomethoxy-1,6-heptadiene.[8]

Palladium precatalysts

Palladium precatalysts were prepared employing a procedure analogous to published procedures.[9] The procedure given for the synthesis of **1b** was applied to the synthesis of all palladium complexes found in Table 2.

$[\eta^3\text{-}CH_2C(Ph)CH_2]Pd(Cl)PCy_3$ (1b). Tricyclohexylphophine (225 mg, 0.80 mmol) was added dropwise to a pale yellow suspension of $[\eta^3\text{-}CH_2C(Ph)CH_2]_2$ (200 mg, 0.39 mmol) in ether (20 mL) at 0 °C and stirred at room temperature for 1 h. The resulting white

suspension was concentrated to 10 mL under vacuum, filtered, washed with ether and hexane, and dried under vacuum to give **1b** (330 mg, 79 %) as an off-white solid. ^{1}H NMR: δ 7.46 (m, 2 H), 7.30 (m, 3 H), 4.72 (dd, *J* = 3.3, 6.0 Hz, 1 H), 4.71 (d, *J* = 9.0 Hz, 1 H), 3.57 (d, *J* = 2.0 Hz, 2 H), 2.60 (s, 1 H), 2.1 - 1.0 (m, 33 H). ^{13}C{^{1}H} NMR: δ 137.3, 130.0 (br), 128.2, 127.8, 126.0, 75.4 (d, *J* = 31 Hz), 49.1, 33.0 (d, *J* = 18 Hz), 29.3 (s), 26.8 (d, 7.0 Hz), 26.6 (s). Anal. calcd (found) for $C_{27}H_{42}PPdCl$: H, 7.85 (8.07); C, 60.12 (60.11).

[η^3-CH$_2$C(CH$_3$)CH$_2$]Pd(Cl)PCy$_3$ (1c). White solid, 70 %. ^{1}H NMR: δ 4.37 (dd, *J* = 2.7, 6.1 Hz, 1 H), 3.42 (d, *J* = 9.0 Hz, 1 H), 3.13 (br s, 1 H), 2.48 (s, 1 H), 2.10 (br q, *J* = 10.0 Hz, 3 H), 2.0 - 1.2 (m, 33 H). ^{13}C{^{1}H} NMR: δ 114.6 (s), 78.0 (d, *J* = 50 Hz), 51.0 (s), 33.3 (d, 19 Hz), 29.4 (d, *J* = 13 Hz), 26.8 (d, *J* = 10 Hz), 25.7 (s), 22.5 (s). Anal. calcd (found) for $C_{22}H_{40}PPdCl$: H, 8.45 (8.72); C, 55.35 (55.44).

[η^3-(CH$_3$)CHCHCH$_2$]Pd(Cl)PCy$_3$ (1d). White solid, 70 %. ^{1}H NMR: δ 5.12 (dt, *J* = 6.9, 12.4 Hz, 1 H), 4.27 (quintet of doublets, *J* = 7.0, 13.6 Hz, 1 H), 3.11 (d, *J* = 6.5 Hz, 1 H), 2.37 (d, *J* = 11.5 Hz, 2.07 (q, *J* = 11.6 Hz, 3 H), 2.0 - 1.0 (m, 33 H). ^{13}C{^{1}H} NMR: δ 114.1 (d, *J* = 4.5 Hz), 99.4 (d, *J* = 50 Hz), 45.4 (s), 33.8 (d, *J* = 18 Hz), 29.5 (d, *J* = 3.0 Hz), 26.8 (d, 10.5 Hz), 25.7 (s), 16.6 (d, 3.0 Hz). Anal. calcd (found) for $C_{22}H_{40}PPdCl$: H, 8.45 (8.66); C, 55.35 (55.27).

{(η^3-C$_3$H$_5$)Pd(Cl)[P(cyclopentyl)$_3$]} (1e). ^{1}H NMR: δ 5.51 (tdd, *J* = 6.9, 9.8, 12.2 Hz, 1 H), 4.63 (dt, *J* = 1.9, 7.2 Hz, 1 H), 3.66 (d, *J* = 6.7 Hz, 1 H), 3.61 (dd, *J* = 9.0, 13.9 Hz, 1 H), 2.49 (d, *J* = 11.9 Hz, 1 H), 2.34 (m, 3 H), 2.0 - 1.5 (m, 24 H). ^{13}C{^{1}H}NMR: δ 115.7 (d, *J* = 4.7 Hz), 82.4 (d, *J* = 48.2 Hz), 48.7, 36.0 (d, *J* = 22.1 Hz), 30.5, 26.4 (d, *J* = 8.6 Hz). Anal. calcd (found) for $C_{18}H_{32}PPdCl$: H, 7.66 (7.89); C, 51.32 (51.40).

{(η^3-C$_3$H$_5$)Pd(Cl)[P(*i*-Pr)$_3$]} (1f). White solid, 88 %. ^{1}H NMR: δ 5.39 (tdd, *J* = 7.0, 9.6, 12.3 Hz, 1 H), 4.65 (dt, *J* = 2.2, 7.1 Hz, 1 H), 3.60 (dd, *J* = 9.0, 13.8 Hz, 1 H), 3.53 (d, *J* = 6.6 Hz, 1 H), 2.60 (d, *J* = 11.8 Hz, 1 H), 2.43 (qd, *J* = 7.2, 14.4 Hz, 3 H), 1.31 (dd, *J* = 3.0, 7.2 Hz, 9 H), 1.26 (dd, *J* = 2.8, 7.2 Hz, 9 H). ^{13}C{^{1}H}NMR: δ 116.3, 81.1 (d, *J*

= 28.9 Hz), 50.9, 24.8 (d, J = 19.4 Hz), 20.0. Anal. calcd (found) for $C_{12}H_{26}PPdCl$: H, 7.64 (7.84); C, 42.00 (42.24).

{(η^3-C_3H_5)Pd(Cl)[P(*o*-tolyl)$_3$]} (1i). Pale yellow solid, 83 %. ^{1}H NMR: δ 7.55 (dd, J = 7.6, 11.9 Hz, 3 H), 7.55 (t, J = 7.3 Hz, 3 H), 7.19 (m, 6 H), 5.52 (tt, J = 7.2, 13.4 Hz, 1 H), 4.64 (dt, J = 0.7, 6.8 Hz, 1 H), 3.57 (dd, J = 10.0, 13.6 Hz, 1 H), 3.13 (dd, J = 0.8, 5.2 Hz, 1 H), 2.30 (dd, J = 0.7, 11.8 Hz, 1 H), 2.19 (s, 9 H). ^{13}C{^{1}H}NMR: δ 142.8 (d, J = 9.0 Hz), 134.8 (d, J = 6.3 Hz), 132.1 (d, J = 7.2 Hz), 130.9, 128.5 (d, J = 40.4 Hz), 126.1 (d, J = 10.7 Hz), 116.9 (d, J = 5.0 Hz), 77.6 (d, J = 31.6 Hz), 61.7, 23.2 (d, J = 8.3 Hz). Anal. calcd (found) for $C_{24}H_{26}PPdCl$: H, 5.38 (5.35); C, 59.16 (59.29).

{(η^3-C_3H_5)Pd(Cl)[P(OPh)$_3$]} (1j). White solid, 95 %. ^{1}H NMR: δ 7.32 - 7.17 (m, 15 H), 4.98 (quint, J = 10.2 Hz, 1 H), 4.5 - 2.0 (br, 4 H). ^{13}C{^{1}H}NMR: δ 150.9, 130.1, 125.7, 121.6 (d, J = 5.3 Hz), 118.8, 2° allylic carbon atoms not observed. Anal. calcd (found) for $C_{21}H_{20}O_3PPdCl$: H, 4.09 (4.08); C, 51.14 (52.00).

{(η^3-C_3H_5)Pd(Cl)[P(O*i*-Pr)$_3$]} (1k). Pale yellow needles (Et_2O, –30 °C), 81 %. ^{1}H NMR: δ 5.51 (q, J = 10.2 Hz, 1 H), 4.90 (m, 3 H), 4.5 - 2.0 (br, 4 H), 1.28 (d, J = 6.2 Hz, 18 H) ^{13}C{^{1}H}NMR: δ 119.0, 80.8 (br), 70.3, 56.3 (br), 24.4. Anal. calcd (found) for $C_{12}H_{26}PO_3PdCl$: H, 6.70 (6.99); C, 36.85 (37.19).

{(η^3-C_3H_5)Pd(Cl)[P(*t*-Bu)$_3$]} (1l). Yellow solid, 78 %. ^{1}H NMR: δ 5.40 (m, 1 H), 4.69 (t, J = 7.3 Hz, 1 H), 4.10 (br s, 1 H), 3.79 (dd, J = 8.5, 13.5 Hz, 1 H), 2.80 (br s, 1 H), 1.50 (d, J = 12.2 Hz, 27 H). ^{13}C{^{1}H}NMR: δ 113.9 (d, J = 4.5 Hz), 87.6 (d, J = 26.1 Hz), 57.1, 39.5 (d, J = 6.0 Hz), 32.9 (d, J = 4.9 Hz). Anal. calcd (found) for $C_{15}H_{32}PPdCl$: H, 8.37 (8.68); C, 46.77 (47.53).

[(η^3-C_3H_5)Pd(Cl)(pyridine)] (1m). Pale yellow solid, 85 %. ^{1}H NMR: δ 8.79 (td, J = 1.5, 4.8 Hz, 2 H), 7.78 (tt, J = 1.5, 7.9 Hz, 1 H), 7.36 (ddd, J = 1.5, 5.0, 7.6 Hz, 2 H), 5.59 (tt, J = 6.9,12.2 Hz, 1 H), 3.99 (d, J = 6.7 Hz, 2 H), 3.09 (d, J = 12.2 Hz, 2 H). ^{13}C{^{1}H}NMR: 152.7, 138.2, 125.3, 114.5, 61.0 (br). ^{13}C{^{1}H}NMR: δ Anal. calcd (found) for $C_8H_{10}NPdCl$: H, 3.85 (3.83); C, 36.67 (36.60); N, 5.35 (5.20).

{(η^3-C_3H_5)Pd(Cl)[P(*t*-Bu)$_2$(2-C_6H_4Ph)]} (1n). Yellow solid, 78 %. ^{1}H NMR: δ 7.79 (t, *J* = 6.7 Hz, 1 H), 7.56 (d, *J* = 6.6 Hz, 2 H), 7.42 - 7.08 (m, 6 H), 4.65 (m, 1 H), 4.80 (br s, 1 H), 3.40 (br s, 1 H), 2.80 (br s, 1 H), 1.38 (br s, 18 H), one allylic hydrogen not observed. ^{13}C{^{1}H}NMR: δ 148.3 (d, *J* = 16.6 Hz), 141.6 (d, *J* = 4.7 Hz), 134.3, 133.0 (d, *J* = 6.8 Hz), 129.8, 129.0, 127.5, 125.8, 124.7 (d, *J* = 3.7 Hz), 112.6 (d, *J* = 4.7 Hz), 81.0 (br), 57.0 (br), 36.3, 30.0, one aromatic carbon not observed. Anal. calcd (found) for $C_{23}H_{32}$PPdCl: H, 6.70 (6.66); C, 57.39 (57.39).

{(η^3-C_3H_5)Pd(Cl)[P(Cy)$_2$(2-C_6H_4Ph)]} (1o). White solid, 88 %. ^{1}H NMR: δ 7.6 - 7.1 (m, 11 H), 4.82 (m, 1 H), 4.34 (t, *J* = 7.1 Hz, 1 H), 3.08 (m, 1 H), 2.10 (m, 1 H), 1.95 (m, 1 H), 1.9 - 1.4 (m, 22 H). ^{13}C{^{1}H}NMR: δ 148.1 (d, *J* = 11.4 Hz), 142.0 (d, *J* = 4.3 Hz), 134.4 (d, *J* = 5.3 Hz), 132.9 (d, *J* = 7.1 Hz), 130.1, 129.8, 128.4, 127.9 (d, *J* = 27.9 Hz), 127.2, 126.7 (d, *J* = 6.9 Hz), 115.1 (d, *J* = 5.0 Hz), 79.6 (d, *J* = 29.6 Hz), 54.7, 36.7 (d, *J* = 18.3 Hz), 36.1 (d, *J* = 20.0 Hz), 30.2 (br s), 28.9 (d, *J* = 22.4 Hz), 27.3 (d, *J* = 23.3 Hz), 27.1 (d, *J* = 13.4 Hz), 26.3. Anal. calcd (found) for $C_{27}H_{37}$PPdCl: H, 6.98 (6.95); C, 60.68 (60.96).

Dienes

Dimethyl (2-deuterio-2-propenyl)malonate (2a-2,6-d_2). Triethylamine (10 mL) and methanesulfonyl chloride (6 mL) were added sequentially to a solution of 2-deuterio-prop-2-en-1-ol (4.00 g, 69 mmol) in methylene chloride (60 mL) and the mixture was stirred for 30 minutes. Cold aqueous 1 N HCl (225 mL) was slowly added, the layers were separated, and the aqueous layer extracted with ether (3 × 50 mL). The combined organic layers were washed with 10% aqueous $NaHCO_3$ (50 mL) and brine (50 mL), dried ($MgSO_4$), concentrated, and chromatographed (ether–hexane = 7:3) to give crude 2-deuterio-3-methanesulfonyloxypropene (2.5 g, 27 %, ~75 % pure) which was employed in the following step without further purification. Dimethyl malonate (530 mg, 4.0 mmol) and a solution of the deuterated mesylate (1.2 g, 8.4 mmol) in THF (2 mL) were added sequentially to a suspension of

dry NaH (7.5 mmol) in THF (30 mL) and the resulting mixture was refluxed for 4 h, cooled to room temperature, and quenched with brine (0.3 mL). Hexane (20 mL) was added, the mixture was filtered, the residue was extracted with ether (2 × 20 mL), and the combined organic fractions were washed with brine (2 × 30 mL), dried ($MgSO_4$), concentrated, and chromatographed (SiO_2, hexanes) to give **2a**-2,6-d_2 as a colorless oil (425 mg, 50 %) which was 98 % deuterated by NMR and MS analysis. ^{1}H NMR: δ 4.99 (s, 4 H), 3.61 (s, 6 H), 2.53 (s, 4 H). ^{13}C{^{1}H}NMR: δ 171.2, 132.1 (t, J = 22 Hz), 119.1, 57.7, 52.4, 36.9.

Dimethyl (3,3-dideuterio-2-propenyl)malonate (**2a**-1,1,7,7d_4) was synthesized by an analogous procedures employing 3,3-dideuterio-prop-2-en-1-ol and was >95% isotopically pure by NMR and MS analysis. ^{1}H NMR: δ 5.61 (s, 2 H), 3.65 (s, 6 H), 2.57 (dd, J = 2.4, 5.2 Hz, 4 H). ^{13}C{^{1}H} NMR: δ 171.3, 132.2, 118.8 (m), 57.8, 52.4, 36.9.

4,4-Dicarboethoxy-1,5-heptadiene (5b). A mixture of (*E*/*Z*) – $CH_3CH{=}CHCH(CO_2Et)_2$ and $CH_3CH_2CH{=}C(CO_2Et)_2$ (436 mg, 2.18 mmol)[11] was added via syringe to a suspension of sodium hydride (96 mg, 4.0 mmol) in THF (60 mL), followed by addition of allyl bromide (360 mg, 3.0 mmol) via syringe. The resulting suspension was refluxed for two hours, cooled and quenched by a slow addition of cold water (20 mL). The layers were separated and the aqueous layer was extracted with ether (3 × 30 mL). The organic layers were combined, washed with brine, and dried ($MgSO_4$). Volatile material was evaporated under vacuum and the residue was chromatographed (ether–hexane = 0 → 30 %) to afford **5b** (219 mg, 42%) as predominantly (89%) the trans isomer. ^{1}H NMR (trans isomer): δ 5.88 (dq, J = 0.4, 16 Hz, 1 H), 5.62 (m, 2 H), 5.03 (m, 2 H), 4.15 (m, 4 H), 2.74 (d, J = 7.2 Hz, 2 H), 1.71 (dd, J = 1.6, 6.4 Hz, 3 H), 1.20 (dt, J =1.2, 6.8 Hz, 6 H). ^{13}C{^{1}H} NMR (trans isomer): δ 170.6, 132.9, 128.1, 127.4, 118.8, 61.5, 59.4, 39.9, 18.5, 14.2. IR (neat, cm^{-1}): 2981, 1732, 1641, 1445, 1366. HRMS (EI) calcd (found) for $C_{13}H_{20}O_4$: (M^+): 240.1362 (240.1368).

4-Trimethylacetoxymethyl-4-phenyl-1,6-heptadiene (9). Trimethylacetyl chloride (2.5 g, 21 mmol) was added slowly to a solution of 4-hydroxymethyl-4-phenyl-1,6-heptadiene (2.0 g, 10 mmol), NEt_3 (1.6 g, 18 mmol), and dimethylaminopryridine (100 mg, 1

mmol), in CH_2Cl_2 (25 mL) at 0 °C and the resulting solution was stirred overnight at room temperature. Water (25 mL) and CH_2Cl_2 (25 mL) were added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 25 mL) and the combined organic fractions were washed with water and brine, dried ($MgSO_4$), concentrated and distilled under vacuum (0.1 torr, 120 °C) to give **9** (2.1 g, 70 %) as a pale yellow oil. ^1H NMR: δ 7.28 (m, 5 H), 5.51 (tdd, J = 7.35, 10.5, 17.2 Hz, 2 H), 5.00 (m, 4 H), 4.29 (s, 2 H), 2.51 (d, J = 7.5 Hz, 4 H), 1.12 (s, 9 H). $^{13}C\{^1H\}$NMR: δ 178.0, 143.1, 133.7, 128.3, 126.5, 126.3, 118.3, 67.2, 44.2, 40.9, 38.9, 27.2, 26.6. HRMS (EI) calcd (found) for $C_{19}H_{25}O_2$ ($M-H^+$): 285.1854 (285.1850). Anal. calcd (found) for $C_{19}H_{26}O_2$: H, 9.15 (9.41); C, 79.68 (79.84).

4-Phenylsulfonyl-4-phenyl-1,6-heptadiene (22). Allyl bromide (4.36 mL, 52 mmol) was added via syringe to a milky suspension of to benzyl phenylsulfone (2.00 g, 8.6 mmol) and NaH (1.4 g, 35.1 mmol) in THF (15 mL) and the resulting solution was refluxed for 36 hours. The mixture was cooled, water (20 mL) was added, the layers were separated, and the aqueous layer was extracted with ether (3 × 50 mL). The combined organic fractions were washed with brine, and dried ($MgSO_4$), and concentrated under vacuum to give an oily residue which was triturated with hexane to give **22** (1.24 g, 30% yield) as a white powder. ^1H NMR: δ 7.47 (tt, J = 1.2, 7.2 Hz, 1 H), 7.18-7.27 (br 9 H), 5.85 (m, 2 H), 5.14 (m, 4 H), 3.14 (dd, J = 7.2, 11.2 Hz, 4 H). $^{13}C\{^1H\}$ NMR: δ 135.4, 134.9, 133.6, 132.2, 130.5, 129.8, 128.6, 128.3, 128.1, 119.8, 71.1, 35.5. IR (neat, cm^{-1}): 3074, 1642, 1446, 1303, 1147, 1081. Anal. calcd (found) for $C_{19}H_{20}O_2$: H, 6.45 (6.40); C, 73.04 (73.14); S, 10.26 (10.19).

4,4-Dicarbomethoxy-3-phenyl-1,6-heptadiene (26). A suspension of dimethyl (1-phenyl)-2-propenylmalonate (374 mg, 1.5 mmol), NaH (60 % in oil, 100 mg, 2.5 mmol), and allyl bromide (0.5 g, 3.0 mmol) in THF (10 mL) was refluxed for 12 h. Water (10 mL) and ether (10 mL) were added and the layers were separated. The aqueous layer was extracted with ether (2 × 10 mL) and the combined ether fractions were washed with water and brine, dried ($MgSO_4$), concentrated, and chromatographed (12:1) to give **26** (305 mg, 71 %) as a colorless oil. ^1H NMR: δ 7.25 (m, 3 H), 7.12 (d, J = 6.62 Hz, 2 H), 6.37 (ddd, J = 8.6, 10.2, 17.2 Hz, 1 H),

5.74 (m, 1 H), 5.14 - 4.96 (m, 4 H), 3.99 (d, J = 8.5 Hz, 1 H), 3.72 (s, 3 H), 3.65 (s, 3 H), 2.57 (ddd, J = 1.1, 6.3, 14.1 Hz, 1 H), 2.39 (dd, J = 8.2, 14.1 Hz, 1 H). $^{13}C\{^1H\}$NMR: δ 170.6, 170.4, 139.0, 137.8, 133.4, 129.3, 128.4, 127.3, 118.6, 117.3, 63.1, 54.6, 52.1, 52.0, 39.6. IR (neat, cm^{-1}): 3079, 3028, 2982, 2950, 1729, 1453, 1220, 1065. Anal. calcd (found) for $C_{17}H_{20}O_4$: H, 6.99 (6.92); C, 70.81 (70.69).

Carbocycles

4,4-Dicarbobenzyloxy-1,2-dimethylcyclopentene (3c). ^1H NMR: δ 7.25 (m, 10 H), 5.10 (s, 4 H), 2.94 (s, 4 H), 1.56 (s, 6 H). $^{13}C\{^1H\}$NMR: δ 172.3, 135.8, 128.7, 128.4, 128.3, 128.1, 67.2, 57.5, 46.0, 13.5. IR (neat, cm^{-1}): 3033, 1731, 1454, 1241, 1162, 1064. Anal. calcd (found) for $C_{23}H_{24}O_4$: H, 6.64 (6.52); C, 75.80 (75.86).

4,4-Dicarbo-*t*-butoxy-1,2-dimethylcyclopentene (3d). ^1H NMR: δ 2.80 (s, 4 H), 1.56 (s, 6 H), 1.43 (s, 18 H). $^{13}C\{^1H\}$NMR: δ 172.0, 128.2, 81.0, 58.3, 45.9, 28.1, 13.6. Anal. calcd (found) for $C_{17}H_{28}O_4$: H, 9.53 (9.63); C, 68.87 (68.79).

4,4-Dicarbomethoxy-1,2,3-trimethylcyclopentene (28a). ^1H NMR: δ 3.67 (s, 6 H), 3.31 (m, 1 H), 3.17 (m, 1 H), 2.52 (dd, J = 0.8, 16.4 Hz, 1 H), 1.54 (m, 6 H), 0.88 (d, J = 7.2, 3 H). $^{13}C\{^1H\}$NMR: δ 173.3, 171.5, 133.3, 127.2, 62.6, 52.8, 52.3, 49.2, 44.0, 14.3, 13.7, 12.0. IR (neat, cm^{-1}): 2964, 1732, 1444, 1250. Anal. calcd (found) for $C_{12}H_{18}O_4$: H, 8.02 (8.11); C, 63.70 (63.50).

4,4-Dicarbomethoxy-2-methyl-1-ethylidenecyclopentane (33). Dimethyl allylmalonate (3.0 g, 15 mmol), and 1-bromo-2-butyne (2.5 g, 15 mmol) were added sequentially to a solution of NaOMe in MeOH (generated from 900 mg sodium in 200 mL MeOH) and the mixture was stirred at room temperature for 2.5 h. The volatile material was evaporated and the residue was dissolved in water (40 mL) and extracted with chloroform (3 × 50 mL). The combined organic extracts were washed with brine, dried ($MgCl_2$) and concentrated to afford a pale yellow liquid which was filtered through a plug of silica gel with 40% ethyl ether in hexane (50 mL) to give 4,4-dicarbomethoxy-oct-1-ene-6-yne (2.32 g, 71 %) as a colorless oil which was

96 % pure by GC analysis. Reaction of 4,4-dicarbomethoxy-oct-1-ene-6-yne (670 mg, 3 mmol), $Ti(O\text{-}i\text{-}Pr)_4$ (1.1 mL, 3.8 mmol), and *i*-PrMgCl (4.1 mL of 2.0 M ether solution, 8.4 mmol) employing the procedure of Sato[11] gave **33** (371 mg, 55 %).

For 4,4-dicarbomethoxy-oct-1-ene-6-yne: ^1H NMR: δ 5.56 (m, 1 H), 5.09 (m, 2 H), 3.66 (s, 6 H), 2.67-2.73 (overlapping region, 4 H), 1.69 (m, 3 H). $^{13}C\{^1H\}$ NMR: δ 170.6, 132.1, 119.6, 79.0, 73.3, 57.4, 52.7, 36.7, 23.2, 3.6. Anal. calcd (found) for $C_{12}H_{16}O_4$: H, 7.19 (7.28); C, 64.27 (64.25).

Figure S1. Concentration versus time plot for the disappearance of **2b** ($[\mathbf{2b}]_0 = 0.05$ M) in the presence of $HSiEt_3$ (0.095 M) and a catalytic mixture of **1a**/$NaBAr_4$ (2.5 mM) in CH_2Cl_2 at 0 C.

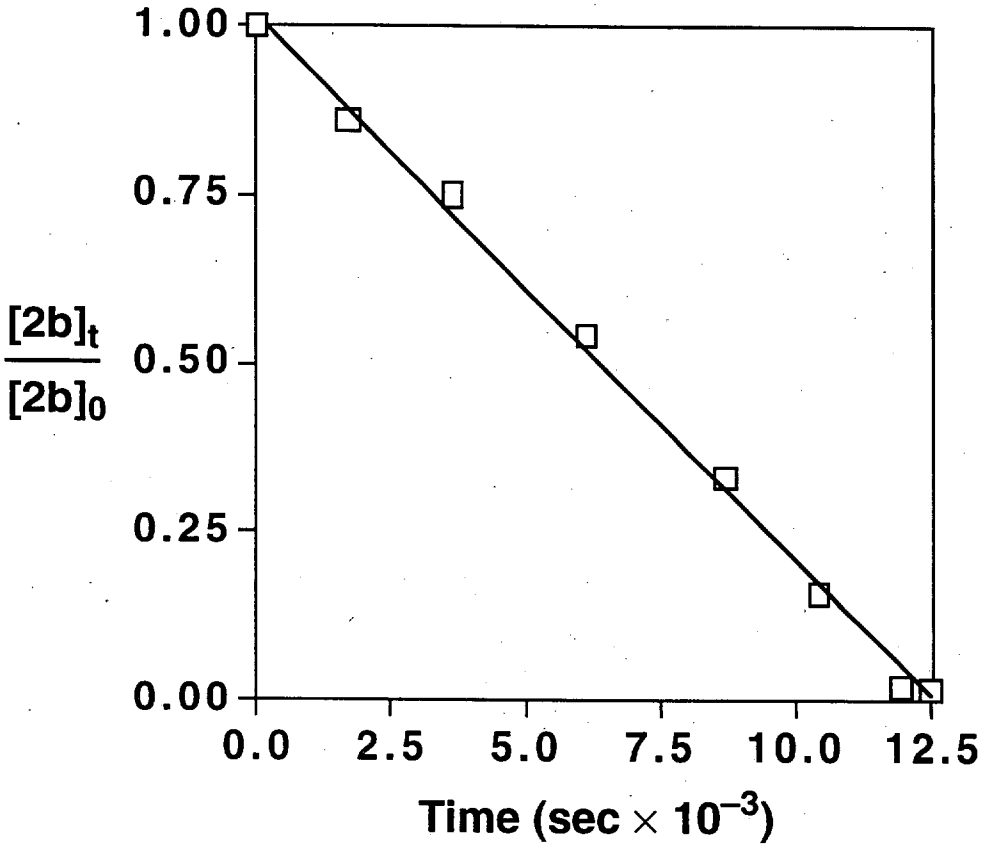


Figure S2. Concentration versus time plot for the disappearance of **4b** in the presence of $HSiEt_3$ (0.095 M) and a catalytic mixture of **1a**/$NaBAr_4$ (2.5 mM) in CH_2Cl_2 at 0 C.

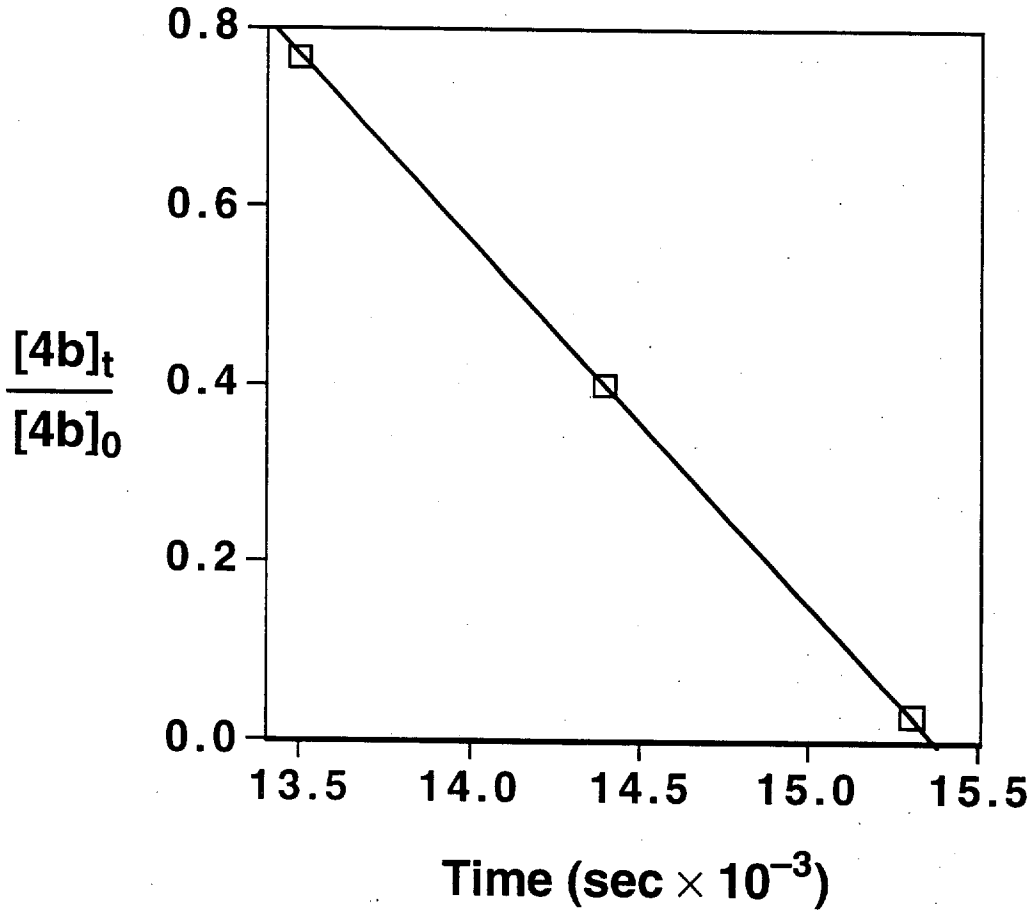
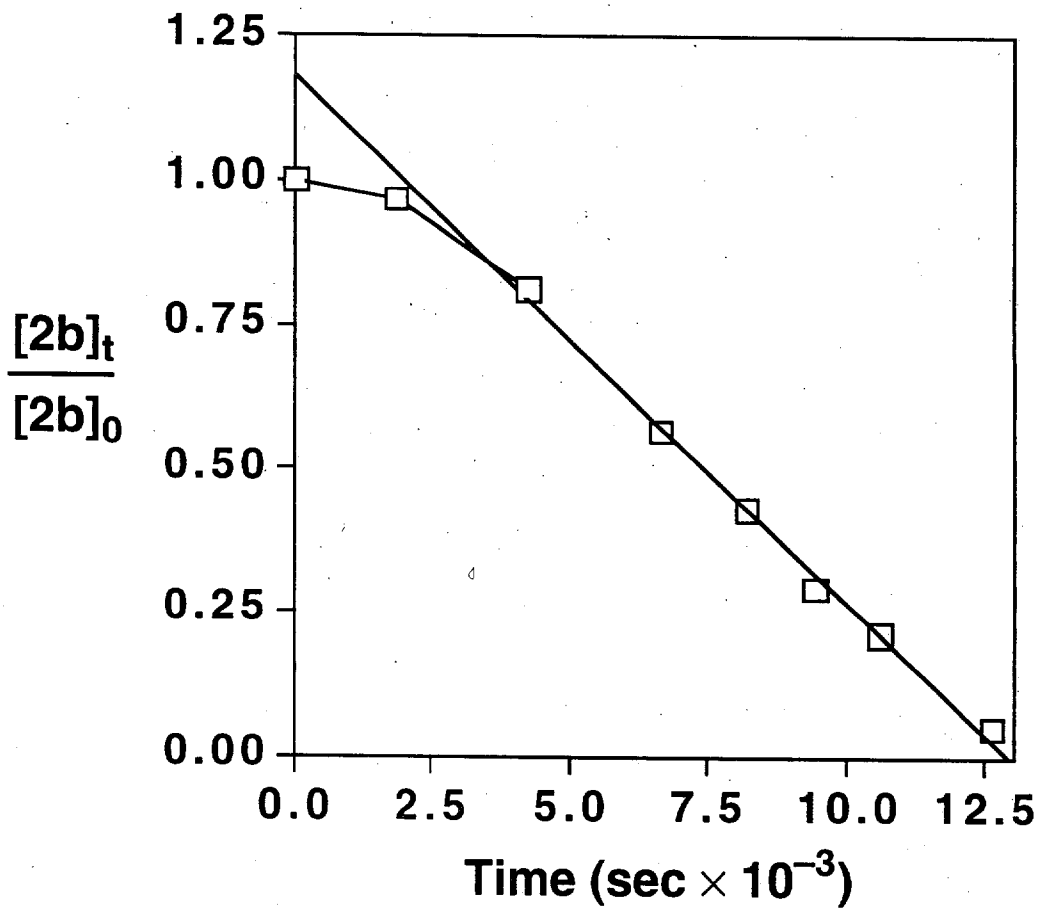


Figure S3. Concentration versus time plot for the disappearance of **2b** ($[\mathbf{2b}]_0 = 0.05$ M) in the presence of $DSiEt_3$ (0.095 M) and a catalytic mixture of **1a**/$NaBAr_4$ (2.5 mM) in CH_2Cl_2 at 0 C.



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