JOC The Journal of Organic Chemistry

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Palladium-Catalyzed α-Ketocyclopropanation of Norbornenes with Propargyl Acetates

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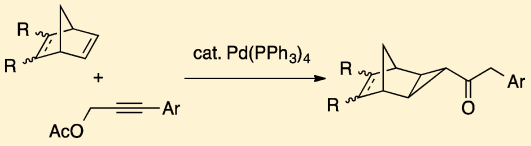
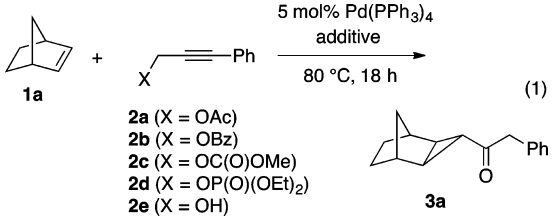
Supporting Information

ABSTRACT: Propargyl acetates reacted with norbornene in the presence of a catalytic amount of tetrakis(tripheylphosphine)palladium to give cyclopropyl ketones. The reaction proceeded with high stereoselectivity, affording a single stereoisomer. The reaction of various substituted norbornenes gave the corresponding cyclopropanes in moderate to good yields.



Transition-metal-catalyzed cycloaddition reactions are powerful and versatile methods for the synthesis of cyclic compounds.[1,2] Among them, [3 + 2] cycloaddition reactions that proceed via a trimethylenemethane palladium intermediate represent an important method for preparation of five-membered ring compounds.[3,4] On the other hand, the oxygen analogue, oxatrimethylenemethane palladium,[5−9] reacts with strained alkenes to give α-ketocyclopropanes with high regio- and stereoselectivity.[10−14] It is usual for the [2 + 1] cycloaddition reactions[15] to require that precursors of oxatrimethylenemethane bear an oxygen substituent at the center carbon. For example, 2-siloxy-[13,14] and 2-alkoxy-allylic compounds[11] or methylene-1,3-dioxalan-2-ones[12] have been used as the precursor. Recently, it was reported that propargyl alcohols, which have no oxygen substituent at the center carbon, reacted with norbornene under oxygen to yield alkenyl cyclopropyl ketones.[16] The oxidative reaction was limited to tertiary propargyl alcohols that have a methyl substituent at the propargyl position. Herein we report a palladium-catalyzed α-ketocyclopropanation of norbornenes with primary propargyl esters without oxygen as the oxidant.

We previously reported that the reaction of cinnamyl acetate and norbornene gave a [2 + 2] cycloaddition product and a [2 + 1] cycloaddition product in the presence of $Pd(PPh_3)_4$.[17] Under the same reaction conditions, the reaction of 3-phenyl-2-propynyl acetate **2a** and norbornene **1a** afforded benzyl cyclopropyl ketone **3a** in 44% yield with high stereoselectivity (eq 1, Table 1, entry 1). No stereoisomer was observed in GC,



GC−MS, or NMR analysis. Although the benzoate ester **2b** reacted similarly (entry 2), the reaction of the corresponding carbonate ester **2c** or phosphate ester **2d** did not afford **3a** (entries 3 and 4). In contrast to the oxidative cycloaddition,[16] the corresponding alcohol **2e** was much less reactive than the ester

Table 1. Palladium-Catalyzed α-Ketocyclopropanation of Norbornene with 3-Phenyl-2-propynyl Compounds[a]

entry	2	solvent	additive (mmol)	yield[b] (%)
1	**2a**	CH_3CN		44
2	**2b**	CH_3CN		31
3	**2c**	CH_3CN		0
4	**2d**	CH_3CN		0
5	**2e**	CH_3CN		trace
6[c]	**2a**	CH_3CN		32
7[d]	**2a**	CH_3CN		56
8	**2a**	ethanol		21
9	**2a**	DMF		trace
10	**2a**	AcOH		0
11	**2a**	dioxane		0
12	**2a**	toluene		0
13	**2a**	CH_3CN	Et_3N (0.45)	59
14	**2a**	CH_3CN	Et_2NiPr (0.45)	7
15	**2a**	CH_3CN	py (0.45)	6
16	**2a**	CH_3CN	2,6-Me_2py[e] (0.45)	4
17	**2a**	CH_3CN	AcOK (0.45)	7
18	**2a**	CH_3CN	H_2O (0.3)	54
19	**2a**	CH_3CN	H_2O (0.9)	37
20	**2a**	CH_3CN	MS4Å[f] (100 mg)	15
21	**2a**	CH_3CN[g]		63
22	**2a**	CH_3CN	O_2[h]	0

[a]A mixture of **1** (0.3 mmol), **2** (0.3 mmol), $Pd(PPh_3)_4$ (0.015 mmol), and additives in acetonitrile (1.0 mL) was heated at 80 °C for 18 h under nitrogen. [b]Determined by GC using dodecane as an internal standard. [c]Excess amount of acetate (1.5 mmol) was used. [d]Excess amount of norbornene (1.5 mmol) was used. [e]2,6-Mepy = 2,6-dimethylpyridine. [f]MS4Å = 4Å molecular sieves. [g]Degassed by freeze−pump−thaw cycles. [h]Carried out under oxygen (1 atm).

Received: February 13, 2014
Published: May 15, 2014

2a (entry 5). While the use of excess amounts of the acetate **2a** did not improve the yield of **3a** (entry 6), the reaction with excess amounts of norbornene **2a** gave **3a** in better yield (entry 7). The use of acetonitrile as a solvent is essential for the [2 + 1] cycloaddition. The yield of **3a** was lowered in the reaction in ethanol and DMF (entries 8 and 9). No products were obtained in the reaction in other solvents such as acetic acid, dioxane, and toluene (entries 10−12). Next, the addition of base was investigated because acetic acid is generated as the cycloaddition progresses. While the addition of various bases decreased the yield of **3a** (entries 14−17), only triethylamine was effective for the cycloaddition to afford **3a** in 59% yield (entry 13). The addition of 1 equiv of water slightly improved the yield of **3a** (entry 1 vs 18), although excess amounts of water exhibited the opposite effect (entry 19). The addition of MS4Å in the reaction decreased the yield of **3a** (entry 20). The reaction in acetonitrile degassed by freeze−pump−thaw cycles afforded **3a** in higher yield (entry 21). The cycloaddition did not proceed under oxygen (entry 22)

Table 2 summarizes the results of the α-ketocyclopropanation of several norbornene derivatives with **2a**. In the reaction of

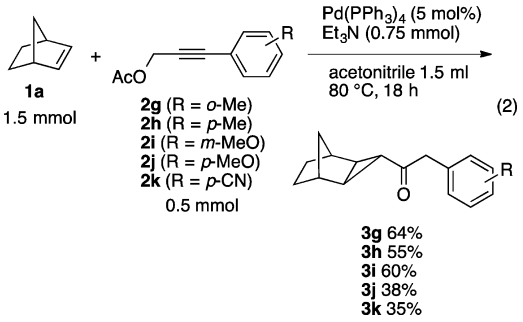
Table 2. Palladium-Catalyzed α-Ketocyclopropanation of Norbornene Derivatives with 3-Phenyl-2-propynyl Acetate 2a[a]

entry	norbornene	product	yield[b] (%)
1	**1a**	**3a**	68
2[c]	**1b** (E = CO_2Me)	**3b**	68
3[c,d]	**1c** (E = CO_2Me)	**3c**	69
4[c]	**1d** (E = CO_2Me)	**3d**	80
5[d]	**1e**	**3e**	64
6[d,e]	**1f**	**3f**	50

[a]A mixture of **1** (0.5 mmol), **2a** (0.5 mmol), $Pd(PPh_3)_4$ (0.025 mmol), and triethylamine (0.75 mmol) in acetonitrile (1.5 mL) was heated at 80 °C for 18 h under nitrogen. [b]Isolated yields. [c]Conducted with 1.0 mmol of **2a** at 120 °C. [d]Without triethylamine. [e]Conducted with 1.5 mmol of **1e**. [f]Conducted with 1.5 mmol of **1f** at 120 °C.

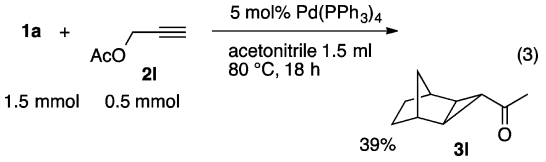
0.5 mmol of **1a** and **2a**, **3a** was isolated in 68% yield (entry 1). Methoxycarbonyl-substituted norbornene derivatives **1b**, **1c**, and **1d** were less reactive, and therefore their cycloaddition needed higher temperature to afford the corresponding cyclopropanes **3b**, **3c**, and **3d** in high yields (entries 2−4). The products were obtained with high stereoselectivity. In the reaction of dicyclopentadiene **1e**, one of two different double bonds selectively reacted to give **3e** as sole product (entry 5). The reaction using excess amounts of norbornadiene **1f** afforded monocyclopropanated product **3f** selectively (entry 6). No dicyclopropanated product was obtained even if excess amounts of **2a** were used. Only unidentified oligomers were observed. The reaction of other alkenes such as styrene, cyclohexene, 2-butene-1,4-diol, dimethyl maleate, and benzalacetone gave no products.

The reactions of other propargyl acetates were also investigated. Various 3-aryl-2-propynyl acetates **2g−k** reacted with **1a** as well as **2a**, giving cyclopropanes **3g−k** with high stereoselectivity in moderate to good yields (eq 2). Propargyl



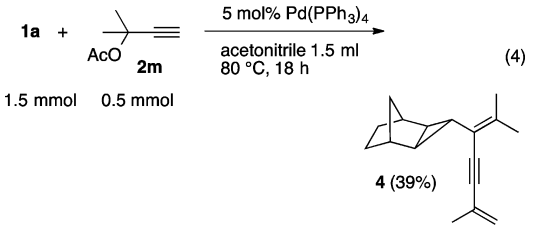
(2)

acetate **2l**, bearing a terminal alkyne, also can be used for the cycloaddition although the yield of cyclopropane **3l** was not high (eq 3). In the reaction of a 3-alkyl-substituted propargyl acetate



(3)

such as 2-pentynyl acetate, only a trace amount of product was observed under the similar reaction conditions. In contrast to the previous similar reaction of tertiary propargyl alcohols,[16] the reaction of acetate ester **2m**, derived from tertiary propargyl alcohol, gave dienynyl cyclopropane **4** in moderate yield instead of a ketocyclopropane (eq 4).

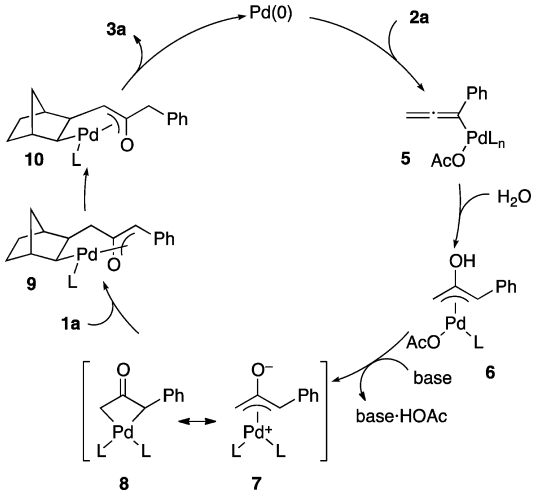


(4)

Since the yield of **3a** decreased under oxygen and increased in degassed acetonitrile (Table 1, entries 21 and 22), the oxygen atom of ketone does not seem to be derived from oxygen. The source of the oxygen atom could be residual water in acetonitrile or reagents because the yield of **3a** increased by the addition of water and decreased by the addition of MS4Å (Table 1, entries 18 and 20).[18] Alternatively, the inter- or intramolecular addition of an acetoxy group cannot be ruled out, although the use of acetic acid as a solvent and the addition of potassium acetate are not effective for the cycloaddition. A plausible mechanism for the reaction of **1a**, **2a**, and water are shown in Scheme 1. Oxidative addition of **2a** to Pd(0) would afford allenylpalladium intermediate **5**, which reacts with water to afford 2-hydroxyallylpalladium complex **6**.[19,20] Elimination of acetic acid from **6** would give

dx.doi.org/10.1021/jo500357f | J. Org. Chem. 2014, 79, 5301−5304

Scheme 1. Plausible Mechanism for the Cyclopropanation



oxatrimethylenemethane palladium intermediate **7**. Intermediate **9** would be formed by insertion of **1a** to **8** and isomerized to **10** via a hydroxyallylpalladium intermediate. Reductive elimination of **10** would afford **3a** and Pd(0).

EXPERIMENTAL SECTION

General. All reactions were carried out under nitrogen atmosphere. Dry solvents were purchased and used directly as received. Propargyl acetates were prepared by acetylation of corresponding alcohols. Norbornene derivatives were prepared by Diels–Alder reaction or purchased and used without further purification. ^{1}H NMR spectra were measured at 25 °C on a 600 MHz spectrometer. Chemical shifts are reported in the scale relative to tetramethylsilane (0 ppm). ^{13}C{^{1}H} NMR spectra were measured at 25 °C on a 151 MHz spectrometer. Chemical shifts are reported in the scale relative to $CDCl_3$ (77.1 MHz) as an internal reference. High-resolution mass spectra were obtained by electrospray ionization or electron ionization time-of-flight reflectron experiments.

General Procedure for Cyclopropanation of Norbornenes with Propargyl Acetates. To a mixture of $Pd(PPh_3)_4$ and norbornene derivatives were added acetonitrile and then triethylamine and propargyl acetates in a pressure vial. In all reactions in Tables 1 and 2 and eqs 2–4, commercial dry acetonitrile was used without further drying. After stirring at 80 or 120 °C for 18 h, the mixture was cooled to room temperature and filtered through a short plug of silica gel using ether as an eluent. The yield of **3a** was determined by a GC analysis of the filtrate using dodecane as an internal standard. For all products, the yields were determined by isolation. After evaporation of volatiles in the filtrate, the products were separated from the residue by silica gel column chromatography (hexane/ethyl acetate). See Tables 1 and 2 and eqs 2–4 for specific solvent volumes, temperature, amounts of substrates, and additives such as triethylamine for every example.

Data for 3a. 76.8 mg, 68%. Pale yellow amorphous solid. ^{1}H NMR ($CDCl_3$): δ 7.32 (t, J = 6.6 Hz, 2H), 7.26 (t, J = 4.8 Hz, 1H), 7.20 (d, J = 7.2 Hz, 2H), 3.76 (s, 2H), 2.30 (s, 2H), 1.91 (t, J = 2.4 Hz, 1H), 1.44 (m, 2H), 1.39 (d, J = 2.4 Hz, 2H), 1.28 (m, 2H), 0.87 (d, J = 11.4 Hz, 1H), 0.67 (d, J = 10.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 207.8, 134.6, 129.4, 128.6, 126.8, 50.9, 36.0, 29.3, 28.8, 28.6, 24.2. HRMS (ESI): m/z calcd for $C_{16}H_{19}O^+$ $[M + H]^+$ 227.1430, found 227.1442.

Data for 3b. 96.2 mg, 68%. Orange amorphous solid. ^{1}H NMR ($CDCl_3$): δ 7.32 (t, J = 7.2 Hz, 2H), 7.26 (t, J = 4.2 Hz, 1H), 7.19 (d, J = 7.8 Hz, 2H), 3.75 (s, 2H), 3.61 (s, 3H), 2.74 (dt, J = 9.6 Hz, J = 4.2 Hz, 1H), 2.69 (m, 1H), 2.38 (m, 1H), 1.97 (t, J = 2.4 Hz, 1H), 1.74 (m, 2H), 1.47 (q, J = 10.2 Hz, 2H), 0.99 (d, J = 11.1 Hz, 1H), 0.83 (d, J = 10.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 206.9, 174.1, 134.3, 129.4, 128.6, 126.8, 51.7, 50.8, 46.3, 39.6, 36.5, 31.3, 29.8, 28.3, 24.9, 23.4. HRMS (ESI): m/z calcd for $C_{18}H_{20}NaO_3^+$ $[M + Na]^+$ 307.1305, found 307.1283.

Data for 3c. 119 mg, 69%. Brown amorphous solic. ^{1}H NMR ($CDCl_3$): δ 7.32 (t, J = 7.2 Hz, 2H), 7.27–7.23 (m, 1H), 7.19 (d, J = 7.2 Hz, 2H), 3.74 (s, 2H), 3.66 (s, 6H), 3.01 (s, 2H), 2.71 (s, 2H), 2.04 (m, 1H), 1.93 (s, 2H), 1.10 (d, J = 11.4 Hz, 1H), 0.81 (d, J = 11.4 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 206.1, 171.8, 134.3, 129.4, 128.5, 126.8, 51.5, 50.4, 47.8, 40.0, 29.3, 24.2, 23.1. HRMS (ESI): m/z calcd for $C_{20}H_{22}NaO_5^+$ $[M + Na]^+$ 365.1359, found 365.1373.

Data for 3d. 136 mg, 80%. Orange viscous oil. ^{1}H NMR ($CDCl_3$): δ 7.32–7.31 (m, 2H), 7.27–7.25 (m, 1H), 7.19–7.17 (m, 2H), 3.76 (s, 2H), 3.71 (s, 3H), 3.68 (s, 3H), 3.21 (s, 1H), 2.94 (s, 1H), 2.76 (s, 1H), 2.68 (s, 1H), 2.08 (s, 1H), 1.54 (s, 1H), 1.48 (s, 1H), 1.06 (d, J = 12.0 Hz, 1H), 0.96 (d, J = 11.4 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 206.0, 174.2, 172.5, 134.0, 129.3, 128.6, 126.9, 52.1, 52.0, 50.9, 50.2, 48.2, 41.4, 39.4, 27.9, 27.7, 25.3, 24.1. HRMS (ESI): m/z calcd for $C_{20}H_{22}NaO_5^+$ $[M + Na]^+$ 365.1359, found 365.1373.

Data for 3e. 84.9 mg, 64%. Pale brown amorphous solid. ^{1}H NMR ($CDCl_3$): δ 7.31 (t, J = 7.2 Hz, 2H), 7.24 (t, J = 5.4 Hz, 1H), 7.18 (d, J = 7.8 Hz, 2H), 5.71 (m, 1H), 5.51 (m, 1H), 3.74 (s, 2H), 3.10–3.06 (m, 1H), 2.54 (dt, J = 7.2 Hz, J = 10.2 Hz, 1H), 2.38 (m, 1H), 2.29 (m, 2H), 2.23–2.17 (m, 1H), 1.99 (t, J = 2.4 Hz, 1H), 1.53 (d, J = 7.2 Hz, 1H), 1.24 (d, J = 6.6 Hz, 1H), 0.99 (d, J = 10.8 Hz, 1H), 0.89 (d, J = 10.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 207.8, 134.6, 132.7, 130.0, 129.4, 128.5, 126.7, 54.5, 50.9, 42.8, 39.6, 38.3, 31.6, 31.4, 27.4, 24.4, 23.3. HRMS (ESI): m/z calcd for $C_{19}H_{20}NaO^+$ $[M + Na]^+$ 287.1406, found 287.1394

Data for 3f. 56.4 mg, 50%. Pale yellow amorphous solid. ^{1}H NMR ($CDCl_3$): δ 7.33 (t, J = 7.8 Hz, 2H), 7.26 (t, J = 7.2 Hz, 1H), 7.20 (d, J = 6.6 Hz, 2H), 6.39 (s, 2H), 3.76 (s, 2H), 2.90 (t, J = 2.4 Hz, 1H), 2.86 (s, 2H), 1.68 (s, 2H), 1.10 (d, J = 9.0 Hz, 1H), 0.99 (d, J = 9.0 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 204.7, 140.9, 134.3, 129.5, 128.6, 126.9, 50.4, 42.0, 40.2, 39.9, 34.7. HRMS (EI): m/z calcd for $C_{16}H_{16}O^+$ M^+ 224.1196, found 224.1174.

Data for 3g. 76.6 mg, 64%. Pale yellow amorphous solid. ^{1}H NMR ($CDCl_3$): δ 7.18–7.11 (m, 4H), 3.77 (s, 2H), 2.30 (s, 2H), 2.23 (s, 3H), 1.91 (t, J = 1.8 Hz, 1H), 1.44 (m, 2H), 1.39 (d, J = 2.4 Hz, 2H), 1.28 (m, 2H), 0.85 (d, J = 10.2, 1H), 0.66 (d, J = 10.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 207.6, 136.9, 133.4, 130.3, 130.3, 127.1, 126.1, 49.1, 36.0, 29.1, 28.8, 28.5, 23.9, 19.7. HRMS (ESI): m/z calcd for $C_{17}H_{20}NaO^+$ $[M + Na]^+$ 263.1406, found 263.1402.

Data for 3h. 66.2 mg, 55%. Pale yellow amorphous solid. ^{1}H NMR ($CDCl_3$): δ 7.13 (d, J = 7.8 Hz, 2H), 7.08 (d, J = 7.8 Hz, 2H), 3.72 (s, 2H), 2.33 (s, 3H), 2.30 (s, 2H), 1.91 (s, 1H), 1.43 (m, 2H), 1.38 (s, 2H), 1.28 (m, 2H), 0.87 (d, J = 10.2 Hz, 1H), 0.67 (d, J = 10.8, 1H). ^{13}C NMR ($CDCl_3$): δ 208.0, 136.3, 131.5, 129.3, 50.6, 36.0, 29.2, 28.8, 28.6, 24.0, 21.1. HRMS (ESI): m/z calcd for $C_{17}H_{20}NaO^+$ $[M + Na]^+$ 263.1406, found 263.1417.

Data for 3i. 76.3 mg, 60%. Pale yellow amorphous solid. ^{1}H NMR ($CDCl_3$): δ 7.26–7.22 (m, 1H), 6.81–6.79 (m, 2H), 6.75–6.74 (m, 1H), 3.79 (s, 3H), 3.73 (s, 2H), 2.31 (s, 2H), 1.92 (t, J = 3.0 Hz, 1H), 1.44 (m, 2H), 1.39 (d, J = 2.4 Hz, 2H), 1.28 (m, 2H), 0.87 (d, J = 10.8 Hz, 1H), 0.67 (d, J = 10.8, 1H). ^{13}C NMR ($CDCl_3$): δ 207.64, 159.68, 136.0, 129.5, 121.8, 115.0, 112.3, 55.1, 51.0, 36.0, 29.3, 28.8, 28.5, 24.1. HRMS (ESI): m/z calcd for $C_{17}H_{20}NaO_2^+$ $[M + Na]^+$ 279.1356, found 279.1366.

Data for 3j. 49.7 mg, 38%. Pale yellow amorphous solid. ^{1}H NMR ($CDCl_3$): δ 7.11 (d, J = 7.2 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 3.79 (s, 3H), 3.70 (s, 2H), 2.30 (s, 2H), 1.91 (s, 1H), 1.43 (m, 2H), 1.38 (s, 2H), 1.28 (s, 2H), 0.87 (d, J = 10.2 Hz, 1H), 0.67 (d, J = 10.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 208.1, 158.4, 130.4, 126.6, 114.0, 55.2, 50.0, 36.0, 29.2, 28.8, 28.5, 23.9. HRMS (ESI): m/z calcd for $C_{17}H_{20}NaO_2^+$ $[M + Na]^+$ 279.1356, found 279.1356.

Data for 3k. 44.5 mg, 35%. Pale yellow amorphous solid. ^{1}H NMR ($CDCl_3$): δ 7.61(d, J = 7.8 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 3.86 (s, 2H), 2.34 (s, 2H), 1.91 (t, J = 1.8 Hz, 1H), 1.46 (d, J = 7.8 Hz, 2H), 1.42 (m, 2H), 1.29 (m, 2H), 0.90 (d, J = 11.4 Hz, 1H), 0.72 (d, J = 10.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 206.0, 139.9, 132.3, 130.3, 118.8, 110.8, 50.5, 36.0, 29.7, 28.8, 28.5, 24.6. HRMS (ESI): m/z calcd for $C_{17}H_{16}NO^-$ $[M - H]^-$ 250.1237, found 250.1215

Data for 3l. 25.4 mg, 34%. Pale yellow amorphous solid. ^{1}H NMR ($CDCl_3$): δ 2.36 (s, 2H), 2.19 (s, 3H), 1.89 (t, J = 2.4 Hz, 1H), 1.46 (m, 2H), 1.38 (d, J = 1.8 Hz, 2H), 1.30 (m, 2H), 0.95 (dt, J = 11.4 Hz, J = 4.2

dx.doi.org/10.1021/jo500357f | J. Org. Chem. 2014, 79, 5301–5304

Hz, 1H), 0.71 (d, J = 10.8 Hz, 1H). The NMR spectrum matches that reported in the literature.[21]

Data for 4. 21.5 mg, 38%. Yellow viscous oil. ^{1}H NMR ($CDCl_3$): δ 5.21 (s, 1H), 5.15 (m, 1H), 2.32 (s, 2H), 1.93 (s, 3H), 1.91 (s, 3H), 1.86 (s, 3H), 1.49 (m, 1H), 1.44 (m, 2H), 1.28 (m, 2H), 1.04 (d, J = 10.8 Hz, 1H), 1.01 (d, J = 2.4 Hz, 2H), 0.68 (d, J = 10.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 140.6, 127.4, 119.9, 117.1, 93.7, 87.3, 43.8, 43.0, 36.0, 29.5, 28.6, 24.0, 23.8, 23.6, 20.2, 14.4. HRMS (EI): m/z calcd for $C_{17}H_{22}^{+}$ M^+ 226.1717, found 226.1702.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Wenders, P. A.; Croatt, M. P.; Deschamps, N. M. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: Oxford, 2007; Vol. *10*, pp 603−647.

(2) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49−92.

(3) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1979**, *101*, 6429−6432.

(4) Yamago, S.; Nakamura, E. *Org. React.* **2002**, *61*, 1−217.

(5) Mentes, A.; Kemmitt, R. D. W. *Polyhedron* **2002**, *21*, 2653−2657.

(6) Nielsen, D. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **2001**, *20*, 995−1000.

(7) Ohsuka, A.; Wardhana, T. W.; Kurosawa, H.; Ikeda, I. *Organometallics* **1997**, *16*, 3038−3043.

(8) Ohsuka, A.; Hirao, T.; Kurosawa, H.; Ikeda, I. *Chem. Lett.* **1996**, 163−164.

(9) Ohsuka, A.; Hirao, T.; Kurosawa, H.; Ikeda, I. *Organometallics* **1995**, *14*, 2538−2542.

(10) Ogoshi, S. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; John Wiley & Sons: New York, 2002; Vol. *2*, pp 1995−2009.

(11) Ikeda, I.; Ohsuka, A.; Tani, K.; Hirao, T.; Kurosawa, H. *J. Org. Chem.* **1996**, *61*, 4971−4974.

(12) Ohe, K.; Matsuda, H.; Ishihara, T.; Ogoshi, S.; Chatani, N.; Murai, S. *J. Org. Chem.* **1993**, *58*, 1173−1177.

(13) Trost, B. M.; Urabe, H. *Tetrahedron Lett.* **1990**, *31*, 615−618.

(14) Trost, B. M.; Schneider, S. *J. Am. Chem. Soc.* **1989**, *111*, 4430−4433.

(15) For recent examples of palladium-catalyzed cyclopropanation of norbornene, see: (a) Horino, Y.; Homura, N.; Inoue, K.; Yoshikawa, S. *Adv. Synth. Catal.* **2012**, *354*, 828−834. (b) Khanna, A.; Premachandra, I. D. U. A.; Sung, P. D.; Van Vranken, D. L. *Org. Lett.* **2013**, *15*, 3158−3161. (c) Clavier, H.; Lepronier, A.; Bengobesse-Mintsa, N.; Gatineau, D.; Pellissier, H.; Giordano, L.; Tenaglia, A.; Buono, G. *Adv. Synth. Catal.* **2013**, *355*, 403−408. (d) den Hartog, T.; Toro, J. M. S.; CHen, P. *Org. Lett.* **2014**, *16*, 1100−1103.

(16) Wu, W.; Jiang, H.; Gao, Y.; Huang, H.; Zei, W.; Cao, D. *Chem. Commun.* **2012**, *48*, 10340−10342.

(17) Tsukada, N.; Sato, T.; Inoue, Y. *Tetrahedron Lett.* **2000**, *41*, 4181−4184.

(18) Water was demonstrated to be important for a successful reaction. However, the amount of adventitious water entering the system from the commercial dry solvents, reactor, and substrates was not defined. Addition of water up to 1.0 equiv relative to the substrate may be required for reproducibility depending on the solvent and substrate quality as well as experimental techniques.

(19) Daniel, K. L.; Furilla, J. L.; Wojcicki, A. *J. Organomet. Chem.* **2002**, *655*, 192−203.

(20) Huang, T.-M.; Hsu, R.-H.; Yang, C.-S.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *Organometallics* **1994**, *13*, 3657−3663.

(21) Matsushima, Y.; Kikuchi, H.; Uno, M.; Takahashi, S. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2475−2482.