## Supporting Information for Reduction of Alkynes into 1,2-Dideuterioalkenes with Hexamethyldisilane and Deuterium Oxide in the Presence of a Palladium Catalyst

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General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a nitrogen atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL JNM LA-500 (<sup>1</sup>H, 500 MHz; <sup>13</sup>C, 125 MHz) or a JEOL JNM FX-400 (<sup>1</sup>H, 400 MHz) spectrometer using tetramethylsilane (<sup>1</sup>H and <sup>13</sup>C) as an internal standard. GC-MS specta were taken on Shimadzu GCMS-QP5050A. Elemental analyses were performed at the Microanalytical Center, Kyoto University. Preparative recycling gel permeation chromatography was performed with JAI LC-908 equipped with JAIGEL-1H and -2H using chloroform as an eluent. Unless otherwise noted, reagents are commercially available and were used without further purification. Anhydrous DMA was purchased from Aldrich Chemical Co. and was dried further with molecular sieves 3A, which was evacuated at 260 °C for 12 h prior to use. Deuterium oxide (99.96%-d) was purchased from Cambridge Isotope Laboratories, Inc. Hexamethyldisilane was purchased from Tokyo Kasei Kogyo Co., Ltd. or Shin-Etsu Chemical Co., Ltd., and was fractionally distilled. Triphenylphosphine was purchased from Wako Pure Chemical Industries Ltd. and was recrystallized from hexane.  $[PdCl(\eta^3-C_3H_5)]_2$ ,<sup>1</sup>  $PdCp(\eta^3-C_3H_5)$ ,<sup>2</sup>  $PdH(Cl)(PPh_3)_2$ <sup>3</sup> and diarylacetylenes<sup>4</sup> were prepared according to the literature methods.

**Preparation of Methyl 4-(Phenylethynyl)benzoate.**<sup>4,5</sup> To a solution of  $Pd(OAc)_2$  (22 mg, 97  $\mu$ mol), PPh<sub>3</sub> (95 mg, 0.36 mmol) and K<sub>3</sub>PO<sub>4</sub> (770 mg, 3.6 mmol) in DMSO (6.0 mL) were added methyl 4-bromobenzoate (650 mg, 3.0 mmol) and phenylacetylene (0.50 mL, 4.6 mmol). After stirring at 80 °C for 24 h, water (20 mL) was added and the resulting mixture was extracted with diethyl ether (10 mL x 3). The combined organic layer was washed with brine (20 mL), and dried over anhydrous magnesium sulfate. Filtration and evaporation of the solvent followed by column chromatography on SiO<sub>2</sub> (hexane:ethyl acetate = 20:1) gave methyl 4-(phenylethynyl)benzoate (450 mg, 63%) as a white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  3.93 (s, 3 H), 7.33–7.40 (m, 3 H), 7.50–7.57 (m, 2 H), 7.59 (d, *J* = 8.6 Hz, 2 H), 8.02 (d, *J* = 8.6 Hz, 2 H).

**Preparation of 3,3-Dimethyl-1-phenyl-1-butyne.**<sup>6</sup> Prepared in a similar manner to methyl 4-(phenylethynyl)benzoate (90% yield). A colorless oil. Isolated by bulb-to-bulb distillation (100 °C/22 mmHg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.31 (s, 9 H), 7.19–7.31 (m, 3 H), 7.33–7.44 (m, 2 H).

**Preparation of 1-(4-pentylphenyl)propyne.**<sup>7</sup> To a solution of 1-ethynyl-4-pentylbenzene (880 mg, 5.1 mmol) in THF (5 mL) was added a hexane solution of BuLi (1.6 M, 4.5 mL, 7.2 mmol) at 0 °C. After stirring at 0 °C for 15 min, methyl iodide (634  $\mu$ L, 10.2 mmol) was added. After stirring at room temperature for 5.5 h, water (20 mL) was added and the resulting mixture was extracted with diethyl ether (10 mL x 3). The combined organic layer was washed with brine (20 mL), and dried over anhydrous magnesium sulfate. Filtration and evaporation of the solvent followed by bulb-to-bulb distillation (100 °C/20 mmHg) gave 1-(4-pentylphenyl)propyne (844 mg, 89%) as a colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  0.88 (t, *J* = 7.0 Hz, 3 H), 1.24–1.39 (m, 4 H), 1.59 (quint, *J* = 7.6 Hz, 2 H), 2.03 (s, 3 H), 2.57 (t, *J* = 7.8 Hz, 2 H), 7.08 (d, *J* = 8.1 Hz, 2 H), 7.29 (d, *J* = 8.1 Hz, 2 H).

Reduction of Alkynes with Hexamethyldisilane and Deuterium Oxide. A General *Procedure.* A solution of PPh<sub>3</sub> (10.4 mg, 40 µmol) and  $[PdCl(\eta^3-C_3H_5)]_2$  (3.7 mg, 10 µmol) in DMA (0.50 mL) was stirred at room temperature for 10 min. To the resulting mixture were added an alkyne (0.40 mmol), hexamethyldisilane (88 mg, 0.60 mmol) and D<sub>2</sub>O (72 µL, 4.0 mmol). After stirring at 80 °C for 24 h, water (10mL) was added and the resulting mixture was extracted with diethyl ether (20 mL). The combined organic layer was washed with brine (10 mL x 4), and dried over anhydrous magnesium sulfate. Filtration and evaporation of the solvent followed by PTLC, bulb-to-bulb distillation or column chromatography on SiO<sub>2</sub> (hexane or hexane–ethyl acetate) gave the corresponding alkenes. Deuterium ratio and stereoselectivity were determined by <sup>1</sup>H NMR and GC/GC-MS, respectively.



(*E*)-1,2-Dideuterio-1,2-diphenylethene ((*E*)-3a).<sup>8</sup> A white solid. Isolated by column chromatography on SiO<sub>2</sub> (hexane). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.26 (t, *J* = 7.3 Hz, 2 H), 7.36 (t, *J* = 7.7 Hz, 4 H), 7.52 (d, *J* = 7.3 Hz, 4 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  126.5, 127.6, 128.2 (t, <sup>1</sup>*J*<sub>C-D</sub> = 23.2 Hz), 128.6, 137.2. Anal. Calcd for C<sub>14</sub>H<sub>10</sub>D<sub>2</sub>: C, 92.26; H, 7.74. Found: C, 92.11; H, 7.98.



(*E*)-1,2-Dideuterio-1,2-bis[4-(trifluoromethyl)phenyl]ethene. A white solid. Isolated by column chromatography on SiO<sub>2</sub> (hexane). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 (s, 8 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  124.3 (q, <sup>1</sup>*J*<sub>C-F</sub> = 270.4 Hz), 125.8 (q, <sup>3</sup>*J*<sub>C-F</sub> = 3.5 Hz), 126.9, 129.2 (t, <sup>1</sup>*J*<sub>C-D</sub> = 23.4 Hz), 130.0 (q, <sup>2</sup>*J*<sub>C-F</sub> = 31.9 Hz), 140.1. Anal. Calcd for C<sub>16</sub>H<sub>8</sub>D<sub>2</sub>F<sub>6</sub>: C, 60.38; H, 3.80. Found: C, 60.12; H, 3.79.



(*E*)-1,2-Dideuterio-1-phenyl-2-[4-(trifluoromethyl)phenyl]ethene. A white solid. Isolated by column chromatography on SiO<sub>2</sub> (hexane). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 (tt, *J* = 7.4, 2.0 Hz, 1 H), 7.39 (t, *J* = 7.8 Hz, 2 H), 7.51–7.56 (m, 2 H), 7.61 (s, 4 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  124.3 (q, <sup>1</sup>*J*<sub>C-F</sub> = 270.4 Hz), 125.6 (q, <sup>3</sup>*J*<sub>C-F</sub> = 3.6 Hz), 126.6, 126.8, 126.7 (t, <sup>1</sup>*J*<sub>C-D</sub> = 23.1 Hz), 128.3, 128.8, 129.3 (q, <sup>2</sup>*J*<sub>C-F</sub> = 32.3 Hz), 130.8 (t, <sup>1</sup>*J*<sub>C-D</sub> = 23.2 Hz), 136.6, 140.8. Anal. Calcd for C<sub>15</sub>H<sub>9</sub>D<sub>2</sub>F<sub>3</sub>: C, 71.99; H, 5.23. Found: C, 71.74; H, 5.17.



**Methyl 4-**[*(E)***-1,2-dideuterio-2-phenylethenyl]benzoate.** A white solid. Isolated by column chromatography on SiO<sub>2</sub> (hexane:ethyl acetate = 20:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  3.93 (s, 3 H), 7.30 (t, *J* = 7.5 Hz, 1 H), 7.38 (t, *J* = 7.6 Hz, 2 H), 7.54 (d, *J* = 7.2 Hz, 2 H), 7.57 (d, *J* = 8.2 Hz, 2 H), 8.03 (d, *J* = 8.2 Hz, 2 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  52.0, 126.3, 126.8, 127.2 (t, <sup>1</sup>*J*<sub>C-D</sub> = 23.4 Hz), 128.2, 128.8, 128.9, 130.0, 130.8 (t, <sup>1</sup>*J*<sub>C-D</sub> = 22.9 Hz), 136.7, 141.8, 166.9. Anal. Calcd for C<sub>16</sub>H<sub>12</sub>D<sub>2</sub>O<sub>2</sub>: C, 79.97; H, 6.71. Found: C, 79.68; H, 6.70.



(*E*)-1,2-Dideuterio-1-(4-methoxyphenyl)-2-phenylethene. A white solid. Isolated by column chromatography on SiO<sub>2</sub> (hexane:ethyl acetate = 20:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  3.82 (s, 3 H), 6.89 (d, *J* = 9.0 Hz, 2 H), 7.22 (t, *J* = 7.6 Hz, 1 H), 7.34 (t, *J* = 7.8 Hz, 2 H), 7.45 (d, *J* = 8.8 Hz, 2 H), 7.48 (d, *J* = 7.3 Hz, 2 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  55.3, 114.2, 126.22 (t, <sup>1</sup>*J*<sub>C-D</sub> = 22.9 Hz), 126.24, 127.2, 127.7, 127.8 (t, <sup>1</sup>*J*<sub>C-D</sub> = 22.9 Hz), 128.6, 130.1, 137.6, 159.3. Anal. Calcd for C<sub>15</sub>H<sub>12</sub>D<sub>2</sub>O: C, 84.87; H, 7.60. Found: C, 85.04; H, 7.43.



(*E*)-1,2-Dideuterio-1-(4-methylphenyl)-2-phenylethene. A white solid. Isolated by column chromatography on SiO<sub>2</sub> (hexane). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  2.35 (s, 3 H), 7.16 (d, *J* = 7.8 Hz, 2 H), 7.23 (t, *J* = 7.4 Hz, 1 H), 7.34 (t, *J* = 7.8 Hz, 2 H), 7.40 (d, *J* = 8.2 Hz, 2 H), 7.49 (d, *J* = 7.1 Hz, 2 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  21.2, 126.38, 126.42, 127.3 (t, <sup>1</sup>*J*<sub>C-D</sub> = 23.2 Hz), 127.4, 128.2 (t, <sup>1</sup>*J*<sub>C-D</sub> = 23.2 Hz), 128.7, 129.4, 134.5, 137.48, 137.51. Anal. Calcd for C<sub>15</sub>H<sub>12</sub>D<sub>2</sub>: C, 91.79; H, 8.21. Found: C, 91.55 H, 8.15.



(*E*)-1,2-Dideuterio-1-(4-methoxyphenyl)-2-[4-(trifluoromethyl)phenyl]ethene. A white solid. Isolated by column chromatography on SiO<sub>2</sub> (hexane:ethyl acetate = 30:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  3.84 (s, 3 H), 6.92 (d, *J* = 8.8 Hz, 2 H), 7.47 (d, *J* = 8.7 Hz, 2 H), 7.57 (d, *J* = 8.9 Hz, 2 H), 7.59 (d, *J* = 8.9 Hz, 2 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  55.3, 114.3, 124.3 (q, <sup>1</sup>*J*<sub>C-F</sub> = 270.4 Hz), 124.6 (t, <sup>1</sup>*J*<sub>C-D</sub> = 23.2 Hz), 125.6 (q, <sup>3</sup>*J*<sub>C-F</sub> = 3.6 Hz), 126.3, 128.1, 128.8 (q, <sup>2</sup>*J*<sub>C-F</sub> = 32.0 Hz), 129.4, 130.3 (t, <sup>1</sup>*J*<sub>C-D</sub> = 22.7 Hz), 141.1, 159.9. Anal. Calcd for C<sub>16</sub>H<sub>11</sub>D<sub>2</sub>F<sub>3</sub>O: C, 68.56; H, 5.39. Found: C, 68.30; H, 5.32.



(*E*)-1,2-Dideuterio-1,2-bis(2-methylphenyl)ethene. A white solid. Isolated by column chromatography on SiO<sub>2</sub> (hexane). In this case, the deuteration ratio was determined not by <sup>1</sup>H NMR with CDCl<sub>3</sub> as a solvent but by that with DMSO. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  2.43 (s, 6 H), 7.15–7.26 (m, 6 H), 7.59 (d, *J* = 7.2 Hz, 2 H); (500 MHz, DMSO-*d*)  $\delta$  2.40 (s, 6 H), 7.16–7.25 (m, 6 H), 7.69 (d, *J* = 7.9 Hz, 2 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  19.9, 125.5, 126.2, 127.5, 127.6 (t, <sup>1</sup>*J*<sub>C-D</sub> = 23.2 Hz), 130.4, 135.8, 136.7. Anal. Calcd for C<sub>16</sub>H<sub>14</sub>D<sub>2</sub>: C, 91.38; H, 8.62. Found: C, 91.26; H, 8.32.



(*E*)-1,2-Dideuterio-3,3-dimethyl-1-phenyl-1-butene. <sup>9</sup> A colorless oil. Isolated by bulb-to-bulb distillation (110 °C/10 mmHg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  1.12 (s, 9 H), 7.18 (t, *J* = 7.4 Hz, 1 H), 7.29 (t, *J* = 7.7 Hz, 2 H), 7.36 (t, *J* = 7.3 Hz, 2 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  29.6, 33.2, 124.2 (t, <sup>1</sup>*J*<sub>C-D</sub> = 22.9 Hz), 126.0, 126.7, 128.4, 138.0, 141.3 (t, <sup>1</sup>*J*<sub>C-D</sub> = 22.6 Hz). Anal. Calcd for C<sub>12</sub>H<sub>14</sub>D<sub>2</sub>: C, 88.82; H, 11.18. Found: C, 88.54; H, 11.11.



(*E*)-1,2-Dideuterio-1-(4-pentylphenyl)propene. A colorless oil. Isolated by PTLC on SiO<sub>2</sub> (hexane) and gel permeation chromatography. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  0.88 (t, *J* = 6.9 Hz, 3 H), 1.25–1.38 (m, 4 H), 1.59 (quint, *J* = 7.5 Hz, 2 H), 1.85 (s, 3 H), 2.56 (2 H), 7.09 (d, *J* = 8.1 Hz, 2 H), 7.23 (d, *J* = 8.1 Hz, 2 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  14.0, 18.3, 22.6, 31.1, 31.5, 35.6, 124.2 (t, <sup>1</sup>*J*<sub>C-D</sub> = 22.7 Hz), 125.7, 128.5, 130.5 (t, <sup>1</sup>*J*<sub>C-D</sub> = 23.2 Hz), 135.3, 141.5. Anal. Calcd for C<sub>14</sub>H<sub>18</sub>D<sub>2</sub>: C, 88.35; H, 11.65. Found: C, 88.32; H, 11.42.

Reduction of Alkynes with Hexamethyldisilane and H<sub>2</sub>O. A General Procedure. A solution of PPh<sub>3</sub> (10.4 mg, 40  $\mu$ mol) and [PdCl( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)]<sub>2</sub> (3.7 mg, 10  $\mu$ mol) in DMA (0.50 mL) was stirred at room temperature for 10 min. To the resulting mixture were added an

alkyne (0.40 mmol), hexamethyldisilane (88 mg, 0.60 mmol) and  $H_2O$  (18 µL, 1.0 mmol). After stirring at 80 °C for 3 h, water (10 mL) was added and the resulting mixture was extracted with diethyl ether (20 mL). The combined organic layer was washed with brine (10 mL x 4), and dried over anhydrous magnesium sulfate. Filtration and evaporation of the solvent followed by PTLC and/or column chromatography on SiO<sub>2</sub> (hexane or hexane–ethyl acetate) gave the corresponding alkenes.



(*E*)-Stilbene ((*E*)-4a). A white solid. Isolated by PTLC on SiO<sub>2</sub> (hexane). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.11 (s, 2 H), 7.26 (t, *J* = 7.2 Hz, 2 H), 7.36 (t, *J* = 7.8 Hz, 4 H), 7.52 (d, *J* = 7.2 Hz, 4 H).



(*E*)-1,2-Bis[4-(trifluoromethyl)phenyl]ethene. <sup>10</sup> A white solid. Isolated column chromatography on SiO<sub>2</sub> (hexane) and PTLC on SiO<sub>2</sub> (hexane). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.21 (s, 2 H), 7.63 (s, 8 H).



(*E*)-1-(4-Methoxyphenyl)-2-[4-(trifluoromethyl)phenyl]ethene.<sup>11</sup> A white solid. Isolated by PTLC on SiO<sub>2</sub> (hexane:ethyl acetate = 10:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  3.84 (s, 3 H), 6.92 (d, *J* = 8.7 Hz, 2 H), 6.98 (d, *J* = 16.4 Hz, 1 H), 7.15 (d, *J* = 16.4 Hz, 1 H), 7.48 (d, *J* = 8.7 Hz, 2 H), 7.57 (d, *J* = 8.9 Hz, 2, H), 7.89 (d, *J* = 8.9 Hz, 2 H).



(*E*)-1,2-Bis(2-methylphenyl)ethene. <sup>12</sup> A white solid. Isolated by PTLC on SiO<sub>2</sub> (hexane:ethyl acetate = 20:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  2.43 (s, 6 H), 7.16–7.25 (m, 8 H), 7.59 (d, *J* = 7.4 Hz, 2 H); (500 MHz, DMSO-*d*)  $\delta$  2.40 (s, 6 H), 7.16–7.25 (m, 6 H), 7.26 (s, 2 H), 7.68 (d, *J* = 7.4, 2 H).

Cleavage of the Si–Si Bond of Hexamethyldisilane with a Palladium Catalyst and  $H_2O$ . A solution of PPh<sub>3</sub> (10.4 mg, 40 µmol) and a palladium complex (20 µmol of Pd) in DMA (0.50 mL) was stirred at room temperature for 10 min. To the resulting mixture were added hexamethyldisilane (88 mg, 0.60 mmol) and  $H_2O$  (18 µL, 1.0 mmol). After stirring at 80 °C for 3 h, the conversion of hexamethyldisilane to hexamethyldisiloxane was determined by GC.

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