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A Convenient and General Synthesis of 1-Mono-organyl- and 1,2-Diorganylcyclobutenes via Cyclialkylation

## Supplementary Data

**(Z)-1,4-Diiodo-3-(*n*-butyl)-3-octene (1b).** This compound was prepared in 71% isolated yield (>97% *Z*) from 4-octyne as in the preparation of 1a:  $^1\text{H}$  NMR  $\delta$  0.8-1.0 (m, 6 H), 1.2-1.6 (m, 8 H), 2.0-2.3 (m, 2 H), 2.50 (t,  $J = 7.5$  Hz, 2 H), 2.7-2.9 (m, 2 H), 3.05-3.25 (m, 2 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  1.39, 13.89, 14.00, 21.58, 22.57, 30.92, 31.54, 31.81, 40.97, 46.81, 107.75, 143.02 ppm.

**(E)-1,4-Diiodo-1,2-diphenyl-1-butene (1c).** This compound was prepared in 50% isolated yield (>97% *E*) from diphenylethyne as in the preparation of 1a:  $^1\text{H}$  NMR  $\delta$  3.10 (t,  $J = 7.7$  Hz, 2 H), 3.39 (t,  $J = 7.7$  Hz, 2 H), 6.8-7.2 (m, 10 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  1.50, 48.16, 103.85, 126.95, 127.10, 127.44, 127.93, 128.83, 129.36, 137.93, 143.83, 146.80 ppm.

**(E)-1,4-Diiodo-2-(*p*-chlorophenyl)-1-phenyl-1-butene and (E)-1,4-Diiodo-1-(*p*-chlorophenyl)-2-phenyl-1-butene (1d).** These two regioisomers were prepared from 1-(*p*-chlorophenyl)-2-phenylethyne as in the preparation of 1a as a roughly 1:1 mixture (by  $^1\text{H}$  NMR) in quantitative isolated yield (based on unreacted starting material) as an orange oil:  $^1\text{H}$  NMR (mixture of two isomers)  $\delta$  3.09 (t,  $J = 7$  Hz, 2 H), 3.38 (t,  $J = 7$  Hz, 2 H), 6.85-7.15 (m, 9 H) ppm;  $^{13}\text{C}$  NMR (mixture of two isomers)  $\delta$  1.30, 47.83, 48.12, 100.75, 103.30, 127.26, 127.42, 127.74, 128.19, 128.80, 129.30, 130.26, 130.83, 132.84, 136.38, 137.67, 142.39, 143.65, 145.54, 147.67 ppm; IR (neat) (mixture of two isomers) 1486, 1264  $\text{cm}^{-1}$ ; MS (EI, 70 eV) (mixture of two isomers)  $m/z$  (relative intensity) 494 ( $\text{M}^+$ , 12), 367 (100). The starting material 1-(*p*-chlorophenyl)-2-phenylethyne was prepared from 1-chloro-4-iodobenzene and phenyl acetylene in the presence of catalytic amount of  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (1 mol %) and  $\text{CuI}$  (0.5 mol %) in  $\text{Et}_2\text{NH}$  at 23  $^\circ\text{C}^a$  in 98% isolated yield: white crystalline solid, mp 79.5-81.0  $^\circ\text{C}$ ;  $^1\text{H}$  NMR  $\delta$  7.2-7.6 (m) ppm;  $^{13}\text{C}$  NMR  $\delta$  88.23, 90.30, 121.75, 122.90, 128.37, 128.46, 128.66, 131.57, 132.78, 134.22 ppm; IR ( $\text{CCl}_4$ ) 1496, 1266  $\text{cm}^{-1}$ .

**(Z)-1,4-Diiodo-2-methyl-1-phenyl-1-butene (1e).** This compound was prepared in 78% NMR yield (>97% Z, >97% regioisomeric pure) from 1-phenyl-1-propyne as in the preparation of **1a**:  $^1\text{H}$  NMR  $\delta$  1.67 (s, 3 H), 2.95 (t,  $J = 7.9$  Hz, 2 H), 3.25 (t,  $J = 7.5$  Hz, 2 H), 7.1-7.35 (m, 5 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  1.51, 18.94, 47.17, 97.81, 127.37, 127.91, 128.24, 141.22, 143.86 ppm.

**(E)-3,6-Diiodo-2-methyl-4-phenyl-1,3-hexadiene and (E)-2-(2-Iodoethyl)-3-methyl-1-phenyl-1,3-butadiene (1f).** These two compounds were prepared as in the preparation of **1a** from 2-methyl-4-phenyl-1-buten-3-yne in 79% isolated yield (based on unreacted starting material) as a 5:1 mixture (by  $^1\text{H}$  NMR) in which the former compound was the major isomer:  $^1\text{H}$  NMR (major isomer)  $\delta$  2.02 (d,  $J = 1.1$  Hz, 3 H), 2.9-3.3 (m, 4 H), 5.0-5.05 (m, 1 H), 5.13 (br s, 1 H), 7.05-7.4 (m, 5 H) ppm and (minor isomer)  $\delta$  1.76 (s, 3 H), 2.9-3.3 (m, 4 H), 4.6-4.7 (m, 1 H), 4.74 (br s, 1 H), 7.05-7.4 (m, 5 H) ppm;  $^{13}\text{C}$  NMR (major isomer)  $\delta$  3.23, 22.48, 38.59, 105.55, 115.02, 127.70, 128.31, 128.39, 143.44, 144.57, 146.65 and (minor isomer)  $\delta$  3.23, 22.59, 47.45, 106.76, 116.92, 127.35, 128.12, 128.18, 138.67, 144.46, 146.97 ppm; IR (neat) (mixture of two isomers) 2968, 1442  $\text{cm}^{-1}$ ; MS (EI, 70 eV) (mixture of two isomers)  $m/z$  (relative intensity) 424 ( $\text{M}^+$ , 8), 297 (12), 169 (17), 155 (41), 142 (100). The required starting material 2-methyl-4-phenyl-1-buten-3-yne was prepared as a yellow oil, in the same manner as that of 1-(*p*-chlorophenyl)-2-phenylethyne, from 2-methyl-1-buten-3-yne and iodobenzene in quantitative yield:  $^1\text{H}$  NMR  $\delta$  1.95-2.0 (m, 3 H), 5.25-5.45 (m, 2 H), 7.25-7.5 (m, 5 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  23.51, 88.42, 90.58, 121.95, 123.29, 126.87, 128.14, 128.29, 131.58 ppm; IR ( $\text{CCl}_4$ ) 3054, 1490, 1442  $\text{cm}^{-1}$ .

**(Z)-3-(*n*-butyl)-1,4-diiodo-3-decen-5-yne (1g).** This compound was prepared in 81% isolated yield from 5,7-dodecadiyne as in the preparation of **1a**:  $^1\text{H}$  NMR  $\delta$  0.92 (t,  $J = 7.0$  Hz, 6 H), 1.2-1.6 (m, 8 H), 2.25-2.5 (m, 4 H), 2.83 (t,  $J = 8.3$  Hz, 2 H), 3.15 (t,  $J = 7.5$  Hz, 2 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  - 0.07, 13.52, 13.80, 19.25, 21.84, 22.38, 30.10, 30.42, 34.12, 44.39, 73.56, 81.86, 96.16, 153.35 ppm.

**(E)-1,4-Diiodo-3-phenyl-3-decen-5-yne and (E)-1-Iodo-1-phenyl-2-(2-iodoethyl)-1-octen-3-yne (1h).** These two regioisomers were prepared as in the preparation of **1a** from 1-phenyl-1,3-octadiyne as a 2:3 mixture in 18% combined yield along with (Z)-4-(*n*-butyl)-3,6-diiodo-1-phenyl-3-hexen-1-yne (72%)

which can be chromatographically separated:  $^1\text{H}$  NMR (mixture of two isomers)  $\delta$  0.6-1.0 (m, 3 H), 1.0-1.8 (m, 4 H), 2.05-2.75 (m, 2 H), 2.8-3.35 (m, 4 H), 7.1-7.6 (m, 5 H) ppm;  $^{13}\text{C}$  NMR (mixture of two isomers)  $\delta$  0.71, 1.30, 13.54, 13.66, 19.25, 19.50, 21.60, 22.02, 30.01, 30.45, 41.06, 46.39, 71.02, 81.01, 83.41, 96.59, 127.95, 128.18, 128.36, 131.39, 137.82, 150.70, 151.88, 153.41 ppm. The required starting material 1-phenyl-1,3-octadiyne was prepared in 70% isolated yield as an orange oil from the reaction of bromophenylethyne (prepared from phenylacetylene and NBS (1.1 equiv.) in acetone catalyzed by  $\text{AgNO}_3$  (20 mol %))<sup>b</sup>, and 1-hexyne (1.2 equiv.) in the presence of  $\text{CuI}$  (5 mol %),  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (60 mol %), and  $\text{EtNH}_2$  (70 wt % in  $\text{H}_2\text{O}$ , 6 mL) in  $\text{CH}_3\text{OH}$  (6 mL) at 0 °C<sup>c</sup>:  $^1\text{H}$  NMR  $\delta$  0.92 (t,  $J$  = 7.0 Hz, 3 H), 1.3-1.6 (m, 4 H), 2.36 (t,  $J$  = 7.0 Hz, 2 H), 7.2-7.5 (m, 5 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  13.54, 19.29, 22.06, 30.41, 66.20, 75.30, 75.66, 85.06, 122.63, 128.53, 128.82, 132.73 ppm; IR (neat) 2958, 2246, 1490  $\text{cm}^{-1}$ ; MS (EI, 70 eV)  $m/z$  (relative intensity) 182 ( $\text{M}^+$ , 84), 167 (51), 152 (34), 139 (100). The byproduct of this reaction was diphenylbutadiyne formed in 30% yield which was separated by chromatography (hexanes):  $^1\text{H}$  NMR  $\delta$  7.2-7.6 (m) ppm;  $^{13}\text{C}$  NMR  $\delta$  73.92, 81.55, 121.77, 128.44, 129.20, 132.49 ppm; IR (neat) 3054, 1266  $\text{cm}^{-1}$ .

**(Z)-4-(*n*-Butyl)-3,6-diiodo-1-phenyl-3-hexen-1-yne (1i):**  $^1\text{H}$  NMR  $\delta$  0.94 (t,  $J$  = 7.2 Hz, 3 H), 1.2-1.65 (m, 4 H), 2.55 (t,  $J$  = 7.6 Hz, 2 H), 2.90 (t,  $J$  = 8.2 Hz, 2 H), 3.18 (t,  $J$  = 8.2 Hz, 2 H), 7.35-7.45 (m, 5 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  -0.33, 13.89, 22.45, 30.23, 34.55, 44.50, 72.29, 90.00, 93.92, 122.50, 127.81, 128.34, 131.34, 155.56 ppm; IR (neat) 2956, 1488, 754  $\text{cm}^{-1}$ .

**4-Iodo-2-methyl-1-butene.** This compound was prepared from 3-methyl-3-buten-1-ol in 68% yield in the same manner as that of (Z)-1,4-diiodo-3-octene:  $^1\text{H}$  NMR  $\delta$  1.73 (s, 3 H), 2.58 (t,  $J$  = 7.5 Hz, 2 H), 3.25 (t,  $J$  = 7.5 Hz, 2 H), 4.75 (br s, 1 H), 4.85 (br s, 1 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  3.50, 21.63, 41.80, 112.23, 143.79 ppm; IR (neat) 3078, 1650, 1234, 894  $\text{cm}^{-1}$ .

**(E)-1-Iodo-1-octene.** This compound was prepared from 1-octyne in 74% yield according to the published procedure<sup>d</sup>: bp 78-80 °C (2 mm Hg);  $^1\text{H}$  NMR  $\delta$  0.88 (t,  $J$  = 6.7 Hz, 3 H), 1.2-1.6 (m, 8 H), 2.05 (q,  $J$  = 7.0 Hz, 2 H), 5.97 (d,  $J$  = 14.3 Hz, 1 H), 6.51 (dt,  $J$  = 14.3 and 7.1 Hz, 1 H) ppm;  $^{13}\text{C}$  NMR

$\delta$  14.05, 22.54, 28.31, 28.58, 31.55, 36.04, 74.24, 146.76 ppm; IR (neat) 2926, 1466  $\text{cm}^{-1}$ .

**1,2-Di(*n*-butyl)cyclobutene (2b).** This compound was prepared from (*Z*)-1,4-diiodo-3-(*n*-butyl)-3-octene in 83% NMR yield:  $^1\text{H}$  NMR  $\delta$  0.89 (t,  $J = 7.0$  Hz, 6 H), 1.1-1.5 (m, 8 H), 1.98 (t,  $J = 7.0$  Hz, 4 H), 2.23 (s, 4 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  13.95, 22.62, 27.42, 27.96, 29.81, 140.44 ppm.

**1,2-Diphenylcyclobutene (2c).** This compound<sup>e</sup> was prepared from (*E*)-1,4-diiodo-1,2-diphenyl-1-butene in 73% yield (81% NMR yield):  $^1\text{H}$  NMR  $\delta$  2.76 (s, 4 H), 7.15-7.6 (m, 10 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  26.76, 126.02, 127.43, 128.27, 136.14, 138.68 ppm; IR ( $\text{CCl}_4$ ) 2916, 1498  $\text{cm}^{-1}$ .

**1-(*p*-Chlorophenyl)-2-phenylcyclobutene (2d).** This compound was prepared from a 1:1 mixture of (*E*)-1,4-diiodo-2-(*p*-chlorophenyl)-1-phenyl-1-butene and (*E*)-1,4-diiodo-1-(*p*-chlorophenyl)-2-phenyl-1-butene in 90% isolated yield (95% NMR yield) as a pale yellow oil (solidified while stored in refrigerator):  $^1\text{H}$  NMR  $\delta$  2.6-2.75 (m, 4 H), 7.15-7.5 (m, 9 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  26.68, 26.88, 126.01, 127.27, 127.66, 128.36, 128.45, 132.91, 134.49, 135.86, 137.32, 139.46 ppm; IR (neat) 2914, 1494  $\text{cm}^{-1}$ ; MS (EI, 70 eV)  $m/z$  (relative intensity) 240 ( $\text{M}^+$ , 36), 205 (100); HRMS calcd for  $\text{C}_{16}\text{H}_{13}\text{Cl}$  240.0706, found 240.0706.

**1-Phenyl-2-methylcyclobutene (2e).** This compound was prepared from (*Z*)-1,4-diiodo-2-methyl-1-phenyl-1-butene in 75% NMR yield:  $^1\text{H}$  NMR  $\delta$  1.99 (s, 3 H), 2.25 (br s, 2 H), 2.55-2.7 (m, 2 H), 7.1-7.4 (m, 5 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  16.10, 26.03, 29.73, 125.28, 126.28, 128.22, 136.22, 137.49, 138.81 ppm; IR (neat) 2900, 1640  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{11}\text{H}_{12}$ : C, 91.60; H, 8.39. Found: C, 91.57; H, 8.33.

**1-(1-Methylethenyl)-2-phenylcyclobutene (2f).** This compound was prepared from a 1:2 mixture of (*E*)-3,6-diiodo-2-methyl-4-phenyl-1,3-hexadiene and (*E*)-2-(2-iodoethyl)-3-methyl-1-phenyl-1,3-butadiene in 82% isolated yield (88% NMR yield) as a pale yellow oil:  $^1\text{H}$  NMR  $\delta$  1.87 (s, 3 H), 2.4-2.6 (m, 4 H), 4.88 (br s, 1 H), 5.01 (br s, 1 H), 7.0-7.4 (m, 5 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  20.82, 26.10, 26.79, 113.85, 127.06, 127.16, 128.02, 136.58, 139.14, 140.11, 140.74 ppm; IR (neat) 2918, 1446  $\text{cm}^{-1}$ ; MS (EI, 70 eV)  $m/z$  (relative intensity) 170 ( $\text{M}^+$ , 94), 155 (100), 141 (72); HRMS calcd for  $\text{C}_{13}\text{H}_{14}$  170.1096, found 170.1091.

**1-(1-Hexynyl)-2-(*n*-butyl)cyclobutene (2g).** This compound was prepared from (*Z*)-3-(*n*-butyl)-1,4-diiodo-3-decen-5-yne in 80% isolated yield (90% NMR yield):  $^1\text{H}$  NMR  $\delta$  0.91 (t,  $J = 7.2$  Hz, 3 H), 0.92 (t,  $J = 7.2$  Hz, 3 H), 1.15-1.85 (m, 8 H), 2.12 (t,  $J = 7.2$  Hz, 2 H), 2.2-2.5 (m, 6 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  13.57, 13.84, 18.85, 19.18, 21.94, 22.58, 28.90, 29.73, 30.22, 30.95, 75.94, 91.55, 119.74, 154.24 ppm; IR (neat) 2958, 2218, 1466  $\text{cm}^{-1}$ ; MS (EI, 70 eV)  $m/z$  (relative intensity) 190 ( $\text{M}^+$ , 66), 175 (3), 161 (9), 147 (18), 133 (21), 119 (48), 105 (85), 91 (100); HRMS calcd for  $\text{C}_{14}\text{H}_{22}$  190.1722, found 190.1712.

**1-Hexynyl-2-phenylcyclobutene (2h).** This compound was prepared from a 1:1 mixture of (*E*)-1,4-diiodo-3-phenyl-3-dec-5-yne and (*E*)-1-iodo-1-phenyl-2-(2-iodoethyl)-1-octen-3-yne in 86% isolated yield (95% NMR yield) as an orange oil:  $^1\text{H}$  NMR  $\delta$  0.95 (t,  $J = 7.1$  Hz, 3 H), 1.35-1.7 (m, 4 H), 2.46 (t,  $J = 6.8$  Hz, 2 H), 2.66 (d,  $J = 5.4$  Hz, 4 H), 7.2-7.65 (m, 5 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  13.63, 19.51, 22.02, 26.55, 29.75, 30.84, 77.53, 95.65, 119.43, 124.99, 127.77, 128.20, 134.97, 147.38 ppm; IR (neat) 2924, 1492  $\text{cm}^{-1}$ ; MS (EI, 70 eV)  $m/z$  (relative intensity) 210 ( $\text{M}^+$ , 100), 195 (6), 181 (12), 167 (89); HRMS calcd for  $\text{C}_{16}\text{H}_{18}$  210.1409, found 210.1409.

**1-(2-Phenylethynyl)-2-(*n*-butyl)cyclobutene (2i).** This compound was prepared from (*Z*)-4-(*n*-butyl)-3,6-diiodo-1-phenyl-3-hexen-1-yne in 87% isolated yield (90% NMR yield) as an orange oil:  $^1\text{H}$  NMR  $\delta$  0.92 (t,  $J = 7.3$  Hz, 3 H), 1.1-1.7 (m, 4 H), 2.0-2.75 (m, 6 H), 7.15-7.6 (m, 5 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  13.88, 22.58, 28.85, 29.44, 29.68, 30.56, 84.77, 90.47, 119.22, 123.58, 127.81, 128.18, 131.35, 156.79 ppm; IR (neat) 2956, 1638, 1490  $\text{cm}^{-1}$ ; MS (EI, 70 eV)  $m/z$  (relative intensity) 210 ( $\text{M}^+$ , 100), 195 (13), 181 (29), 167 (84); HRMS calcd for  $\text{C}_{16}\text{H}_{18}$  210.1409, found 210.1407.

**1-(*n*-Butyl)cyclobutene (2j).** This compound was prepared from (*Z*)-1,4-diiodo-3-octene in 45% isolated yield as a colorless oil:  $^1\text{H}$  NMR  $\delta$  0.90 (t,  $J = 7.1$  Hz, 3 H), 1.2-1.5 (m, 4 H), 1.9-2.1 (m, 2 H), 2.3-2.45 (m, 4 H), 5.65 (d,  $J = 0.5$  Hz, 1 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  13.95, 22.51, 26.46, 28.97, 30.82, 31.12, 126.42, 150.97 ppm. Conversion of this compound to 4-oxo-1-octanal using  $\text{OsO}_4$  (1 mol %) and 4-methylmorpholine *N*-oxide (2 equiv)<sup>f</sup> gave the following data which are consistent with those reported<sup>g</sup>:  $^1\text{H}$  NMR  $\delta$  0.90 (t,  $J = 7.3$  Hz, 3 H), 1.31 (sex,  $J = 7.6$  Hz, 2 H), 1.56 (quint.  $J = 7.6$  Hz, 2 H), 2.46 (t,

$J = 7.4$  Hz, 2 H), 2.6-2.9 (m, 4 H), 9.80 (s, 1 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  13.79, 22.25, 25.90, 34.56, 37.42, 42.42, 200.55, 208.90 ppm.

**1-Methylcyclobutene (2k).** This compound<sup>h</sup> was prepared from (*Z*)-1,4-diiodo-2-methyl-1-butene in 75% NMR yield:  $^1\text{H}$  NMR  $\delta$  1.69 (br s, 3 H), 2.25-2.35 (m, 2 H), 2.35-2.45 (m, 2 H), 5.66 (br s, 1 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  16.89, 26.46, 33.00, 127.76, 152.20 ppm. Examination of the reaction of (*E*)-1,4-diiodo-2-methyl-1-butene by NMR spectroscopy indicated the formation of 2-methyl-1,3-butadiene<sup>i</sup> in 60% yield and the title compound in 5-10% yield.

**1-(1-Octynyl)-2-methylcyclobutene (2n).** To a solution of 1-octyne (1.10 g, 10 mmol) in THF (10 mL) was added *n*-BuLi (2.6 *M* in hexane, 4.23 mL, 11 mmol) at  $-78$  °C. Conversion of 1-octynyllithium to the corresponding Zn reagent, its Pd-catalyzed cross coupling reaction and the workup were performed on a 10 mmol scale as described in detail for **2e**. Distillation yielded 1.37 g (78%) of the title compound as a colorless oil ( $\geq 98\%$  pure by GLC): bp  $132$ - $134$  °C (31 mm Hg);  $n_D^{27}$  1.4864;  $^1\text{H}$  NMR  $\delta$  0.88 (br s, 3 H), 1.35 (br s, 10 H), 1.73 (s, 3 H), 2.30 (br s, 4 H) ppm; IR (neat) 2950, 2230,  $1640\text{ cm}^{-1}$ . Anal. calcd for  $\text{C}_{13}\text{H}_{20}$ : C, 88.63; H, 11.36. Found: C, 88.77; H, 11.52.

**(*E*)-1-Hexenyl-2-allylcyclobutene (2p).** This compound was prepared in 62% NMR yield by Pd-catalyzed cross coupling using **4b** generated *in situ* and (*E*)-1-iodo-1-octene. Its spectral data are as follows:  $^1\text{H}$  NMR  $\delta$  0.85-1.0 (m, 3 H), 1.2-1.4 (m, 4 H), 2.0-2.2 (m, 2 H), 2.3-2.45 (m, 4 H), 2.8-2.9 (m, 2 H), 5.0-5.15 (m, 2 H), 5.5-5.7 (m, 1 H), 5.7-6.0 (m, 1 H), 6.13 (d,  $J = 15$  Hz, 1 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  14.42, 22.76, 26.04, 28.24, 32.09, 32.84, 34.30, 116.06, 123.39, 131.36, 135.67, 138.80, 139.37 ppm; HRMS calcd for  $\text{C}_{13}\text{H}_{20}$  176.1566, found 176.1568.

This compound was also prepared in 95% yield by generating **4b** via treatment of **5b** with 2 equiv. of *t*-BuLi followed by addition of dry  $\text{ZnBr}_2$ .

**1-(1-Hexynyl)-2-allylcyclobutene (2q).** This compound was prepared in 68% NMR yield by Pd-catalyzed cross coupling using **4b** generated *in situ* and 1-iodo-1-hexyne. The title compound yielded the following data:  $^1\text{H}$  NMR  $\delta$  0.85-0.95 (m, 3 H), 1.2-1.4 (m, 4 H), 1.95-2.05 (m, 2 H), 2.25 (s, 4 H), 2.76

(d,  $J = 7$  Hz, 2 H), 4.95-5.1 (m, 2 H), 5.7-5.9 (m, 1 H) ppm;  $^{13}\text{C}$  NMR  $\delta$  13.62, 19.20, 21.96, 28.91, 30.04, 30.88, 35.27, 75.63, 92.27, 116.07, 120.88, 134.20, 150.81 ppm; IR (neat) 2210, 1720, 1680  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{13}\text{H}_{18}$  174.1409, found 174.1405.

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