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The Crossed [2+2] Cycloaddition of 1-Phenylcyclopropene and 1-Bromo-2-phenylcyclopropene

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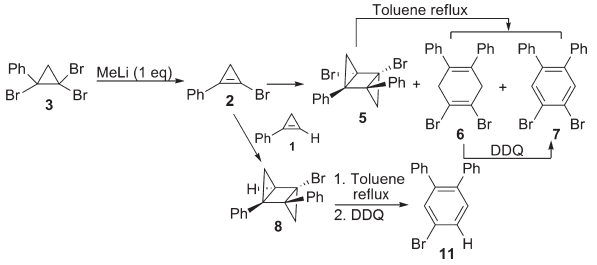

1-Bromo-2-phenylcyclopropene (**2**) underwent [2+2] dimerization to generate 1,2-dibromo-4,5-diphenyltricyclo[3.1.0.0^{2,4}]hexane (**5**), which was heated to form 1,2-dibromo-4,5-diphenylcyclohexa-1,4-diene (**6**) followed by oxidation to yield 4′,5′-dibromo-*o*-terphenyl (**7**). *o*-Terphenyl **7** could be synthesized in one-pot reactions from 1,1,2-tribromocyclopropane (**3**). When cyclopropane **3** was treated with 1.5 equiv of methyllithium followed by slowly adding the proton source, crossed [2+2] adduct **8** was isolated in 40% yield. Compound **8** was heated and oxidated to produce 4′-bromo-*o*-terphenyl (**11**).

Cyclopropene has attracted the attention of both theoretical and experimental chemists because of its special place as the simplest small ring cycloalkene.[1] Consequently, the chemistry of cyclopropenes is very rich, and contains many unusual processes, such as ene dimerizations,[2] coupling reactions,[3] rearrangement,[4] and [2+2] cyclizations to release strain energy.[5] Cyclopropenes usually will isomerize, dimerize, and/or react with other reagents to simultaneously form products due to their highly strained energy.

The control of the crossed reactions between two different cyclopropenes is an important issue to expand their applications. In the literature, there are only a few crossed reactions between two different cyclopropenes reported. Three types of cyclopropenes, bicyclo[5.1.0]oct-1,8-ene,[6] 1-phenylcyclopropene,[7] and 1-trimethylsilyl-3-phenylcyclopropene,[8] underwent ene trimerization, which was a type of crossed ene reaction of a monomer and an ene dimer. We also found that 1-trimethylsilyl-2-phenylcyclopropene was tetramerized via ene dimerizations to generate two different ene dimers, *exo*-form and *endo*-form, followed by crossed coupling to give a triene tetramer.[9] There is only one designed crossed reaction between two different cyclopropenes reported by Baird and co-workers. They claimed that 3,3-dimethylcyclopropenecarboxylic acid and 2-*tert*-butylcyclopropenecarboxylic acid underwent a crossed ene reaction. This crossed ene reaction

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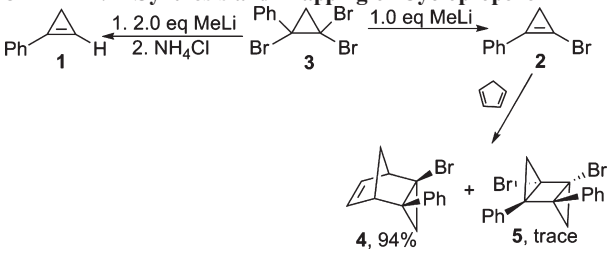
resulted from two different cyclopropenes but only one of them contained 3-hydrogen.[10]

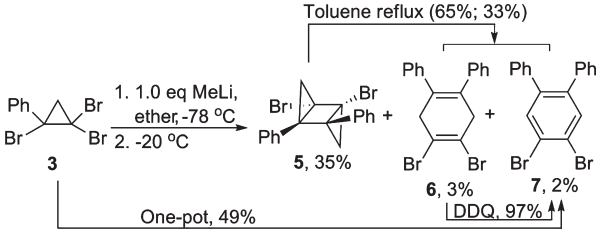
When cyclopropenes undergo [2 + 2] cyclizations, a stepwise diradical mechanism is consistent with the regiospecific formation of adducts based on the stabilization of the diradicals and on the reaction conditions.[11] Due to the highly strained energy, cyclopropenes usually undergo self- or intramolecular [2 + 2] cycloadditions to release the strain energy. To the best of our knowledge, no crossed [2+2] cycloaddition between two different cyclopropenes has been reported. Only the crossed [2 + 2] cycloaddition reaction of cyclopropenes with olefins has been reported. Padwa found that 1-phenyl-2-carbomethoxy-3,3-dimethylcyclopropene underwent photochemical [2 + 2] cycloaddition with alkenes and alkyne to give bicyclo[2.1.0]pentanes and bicyclo-[2.1.0]pent-2-ene. That reaction was carried out by using a slight excess of alkenes and alkyne in the presence of a triplet sensitizer. Dolgii and co-workers reported that both 3,3-dimethylcyclopropene and 3-cyclopropyl-3-methylcyclopropene underwent crossed [2 + 2] cycloaddition with norbornenes by using Ph_3P and CuCl as catalysts. Franck-Neumann reported that electrophilic *gem*-dimethylcyclopropenes underwent [2 + 2] cycloaddition with enamines and ynamines to give 2-aminobicyclo[2.1.0]pentanes and 2-aminobicyclo[2.1.0]pent-2-enes.[12]

Phenylcyclopropenes undergo [2 + 2] dimerizations to form diphenyltricyclo[3.1.0.0^{2,4}]hexanes that can isomerize to diphenylcyclohexa-1,4-dienes. Obata and Moritani have reported that both 3-acetyl- and 3-benzoyl-1,2-diphenylcyclopropenes undergo dimerizations to tricyclo[3.1.0.0^{2,4}]-hexanes upon irradiation.[13] Deboer also reported that sensitized irradiation of 1,2-diphenylcyclopropenes gives tricyclo-[3.1.0.0^{2,4}]hexanes.[11] The tricyclohexanes are thermally rearranged to 1,4-cyclohexadienes, which can be converted to benzenes. Weyerstahl reported that 1-chloro-2-phenylcyclopropene in benzene at rt for 2 days gave a 4% [2 + 2] dimer, which isomerized to 1,2-dichloro-4,5-diphenylcyclohexa-1,4-diene followed by oxidation to form 4′,5′-dichloro-*o*-terphenyl.[14] We have reported that 1-phenylcyclopropene

SCHEME 1. Synthesis and Trapping of Cyclopropene 2



SCHEME 2. Synthesis of Compounds 5, 6, and 7



(**1**) underwent [2 + 2] dimerization to generate 1,2-diphenyltricyclo[3.1.0.0^{2,4}]hexane that was heated to form 1,2-diphenylcyclohexa-1,4-diene followed by oxidation to yield *o*-terphenyl.[7] We now report that 1-bromo-2-phenylcyclopropene (**2**) undergoes [2 + 2] dimerization in 35% isolated yield. We also provided a method to synthesize the crossed [2 + 2] cycloadduct between cyclopropenes **1** and **2**.

1,1,2-Tribromocyclopropanes are very useful precursors for the synthesis of a series of 1-substituted cyclopropenes.[1e] Cyclopropenes **1** and **2** were prepared and trapped in solution by the method shown in Scheme 1. 1,1,2-Tribromo-2-phenylcycloproane (**3**)[7,9,15] was treated with 1.0 equiv of methyllithium followed by treatment with cyclopentadiene at rt, then two compounds, **4** and **5**, were isolated (94% and trace). The major product **4** was formed from cyclopropene **2** with cyclopentadiene (Scheme 1). The structure of the minor product **5** was shown by X-ray crystallography to be a dimer formed from *anti head-to-head* [2 + 2] cycloaddition of **2**.

Cyclopropene **2** under neat conditions at rt for 1 h gave 5% of dimer **5** along with a polymeric aromatic material. To improve the yield of **5**, cyclopropane **3** was treated with 1.0 equiv of methyllithium, and the reaction mixture was concentrated and kept at −20 °C until cyclopropene **2** completely disappeared, as monitored by ^{1}H NMR, and three compounds, **5**, **6**, and **7**, were isolated in yields of 35%, 3%, and 2%, respectively. The structures of **6** and **7**,[16] 1,2-dibromo-4,5-diphenylcyclohexa-1,4-diene and 4′-5′-dibromo-*o*-terphenyl, were shown by X-ray crystallography. When the adduct **5** was heated at toluene refluxing temperature for 24 h, compounds **6** and **7** were obtained in yields of 65% and 33%, respectively. Cyclohexadiene **6** was treated with DDQ to generate *o*-terphenyl **7** in 97% yield. In the one-pot synthesis of *o*-terphenyl **7**, when treated with methyllithium, heated at toluene refluxing temperature, and treated with DDQ, **7** was obtained in 49% isolated yield (Scheme 2).

In our previous report, cyclopropene **1** underwent ene trimerization to give ene trimer **10** and [2 + 2] dimerization to

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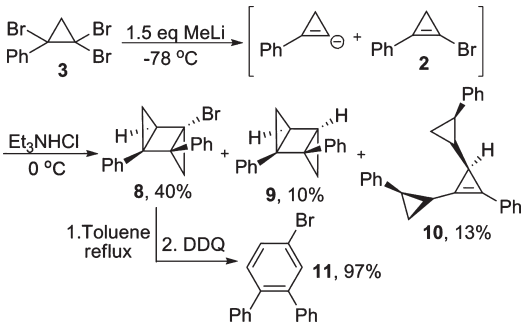
form 1,2-diphenyltricyclo[3.1.0.0^{2,4}]hexane (**9**) in the isolated yields of 88% and 8%, respectively.[7] Although both cyclopropenes **1** and **2** would undergo [2 + 2] cycloadditions, cyclopropene **2** was treated with **1** at rt to give a very low yield (> 1%) of 1-bromo-4,5-diphenyltricyclo[3.1.0.0^{2,4}]hexane (**8**). We attempted to design a method that would enhance the yield of the crossed [2 + 2] cycloaddition between **1** and **2** to expand the application of these phenylcyclopropenes.

Since the [2 + 2] cycloadditions of cyclopropenes are via stepwise diradical mechanisms, to find the difference in the energy gaps of HOMO−LUMO for these two cyclopropenes would be very important in the design of a method to control the crossed reaction. According to the theoretical calculations at the HF/6-31++G** level of ab initio theory, the energy difference (217.8 kcal/mol) between HOMO and LUMO of **1** is smaller than that for bromocyclopropene **2** (218.3 kcal/mol). We also simultaneously studied the stability of **1** and **2**, taking the ^{1}H NMR spectra for both at rt after they were synthesized at low temperature. Cyclopropene **1** was completely decomposed before the ^{1}H NMR spectrum was taken. The ^{1}H NMR spectrum of **2** could be taken with no decomposition, and the single CH_2 peak disappeared after 1 day. On the basis of the theoretical and experimental results, cyclopropene **1** is more easily excited to its diradical intermediate. When the less stable cyclopropene **1** in ether was slowly added to the more stable cyclopropene **2** at −78 °C in an ether solution, the yield of the crossed [2 + 2] adduct **8** increased to 10%.

According to the results, we designed the reaction conditions to enhance the yield of the crossed [2 + 2] cycloaddition. Cyclopropene **1** was slowly generated in a solution containing cyclopropene **2** at 0 °C. Tribromocyclopropane **3**, the immediate precursor of both **1** and **2**, was treated with 1.5 equiv of methyllithium followed by slowly adding proton source, and the yield of the crossed [2+2] adduct **8** rose to a 40% isolated yield. Compound **8** was treated with DDQ at toluene refluxing temperature to generate 4′-bromo-*o*-terphenyl (**11**)[17] in a 97% isolated yield (Scheme 3).

In summary, cyclopropene **2** underwent [2+2] dimerization to generate **5** in 35% isolated yield, which was heated to form compound **6** followed by oxidation to yield *o*-terphenyl **7**. *o*-Terphenyl **7** was synthesized in 49% isolated yield in a one-pot reaction from tribromocyclopropane **3**. We applied theoretical and experimental results to provide a method to synthesize a crossed [2+2] cycloadduct. When tribromocyclopropane **3** was treated with 1.5 equiv of methyllithium followed by slowly adding proton source, the yield of the crossed [2+2] adduct **8** rose to a 40% isolated yield. Compound **8** was heated and oxidated to produce **11**.

SCHEME 3. Enhanced Yield of Adduct 8 and Synthesized 11



Experimental Section

Trapping 1-Bromo-2-phenylcyclopropene (2) with Cp. Methyllithium (1.5 M in ether, 9.4 mL, 14.1 mmol) was added dropwise from a syringe to a stirred solution of compound **3** (5.0 g, 14.1 mmol) in 30.0 mL of dry ether at −78 °C. The mixture was allowed to warm to rt and stirred for 0.5 h. The mixture was cooled to −40 °C, and then cyclopentadiene (11.5 mL, 0.14 mol) was added. The mixture was allowed to warm to rt and stirred for 12 h. The mixture was poured into a 250-mL beaker with 100 g of crushed ice. The organic layer was separated and washed with water and brine, and then dried over anhydrous magnesium sulfate. After filtration, the solvent was removed on a rotary evaporator and the residue was purified by column chromatography (hexanes) to give colorless oil **4** (3.46 g, 94%) and white solid **5** (trace). Compound **4**: IR (neat, cm^{-1}) 3058, 2987, 2967, 2868, 1599, 1576, 1496, 1443, 1319, 1256, 1100, 1077, 1011, 854, 765, 737, 699; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42−7.33 (m, 4H), 7.30−7.25 (m, 1H), 6.22−6.18 (ddd, 1H, J = 1, 3.2, 5.4 Hz), 6.10 (dd, 1H, J = 3.2, 4.8 Hz), 3.27−3.24 (m, 1H), 3.09−3.06 (m, 1H), 2.64 (dt, 1H, J = 1.8, 7.4 Hz), 1.93 (dd, 1H, J = 1.1, 7.4 Hz), 1.81 (d, 1H, J = 6.3 Hz), 1.78 (d, 1H, J = 6.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4 (C), 135.8 (CH), 134.7 (CH), 128.5 (CH), 128.2 (CH), 126.5 (CH), 61.1 (CH_2), 54.9 (CH), 52.3 (CH), 47.0 (C), 33.3 (C), 32.8 (CH_2); MS m/z (%) 262 ($M^+ + 2$, 3.0), 260 (M^+, 3.1). HRMS calcd for $C_{14}H_{13}Br$ m/z 260.0201, found 260.0191. Anal. Calcd for $C_{14}H_{13}Br$: C 64.39, H 5.02. Found: C 64.56, H 4.78. Compound **5**: mp 93.5−94 °C; IR (neat, cm^{-1}) 3054, 3026, 2923, 2852, 1598, 1498, 1444, 1262, 1225, 1184, 1008, 965, 805, 775, 747, 695; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41−7.25 (m, 10H), 2.42 (d, 2H, J = 5.8 Hz), 2.22 (d, 2H, J = 5.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.5 (C), 128.6 (CH), 127.0 (CH), 126.4 (CH), 45.2 (C), 40.7 (C), 39.9 (CH_2); MS m/z (%) 392 ($M^+ + 4$, 5), 390 ($M^+ + 2$, 10), 388 (M^+, 6). HRMS calcd for $C_{18}H_{14}Br_2$ m/z 387.9462, found 387.9458. Anal. Calcd for $C_{18}H_{14}Br_2$: C 55.42, H 3.62. Found: C 55.34, H 3.53.

[2 + 2] Cycloaddition of 1-Bromo-2-phenylcyclopropene (2). To a stirred solution of compound **3** (5.0 g, 14.1 mmol) in 30 mL of dry ether at −78 °C was added methyllithium (1.5 M in ether, 9.4 mL, 14.1 mmol) dropwise from a syringe. The mixture was allowed to warm to rt and stirred for 0.5 h. Ether was removed under reduced pressure and the residue was kept at −20 °C until cyclopropene **2** had completely disappeared as monitored by ^{1}H NMR. About 30 mL of ether was added, then the mixture was poured into a 250-mL beaker with 100 g of crushed ice. The ether layer was separated, the aqueous layer was extracted with 30 mL of ether, and the combined ether solution was washed with about 100 mL of water and brine. The ether solution was dried with anhydrous magnesium sulfate. After filtration, the solvent was removed on a rotary evaporator and the residue was purified by column chromatography (hexanes) to give white solid **5** (0.96 g, 35%), **6** (82.5 mg, 3%), and **7** (54.7 mg, 2%). Compound **6**: mp 97.5−98.5 °C; IR (neat, cm^{-1}) 3059, 3028, 2866, 2809, 1667, 1599, 1490, 1441, 1419, 976, 758, 697; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18−7.10 (m, 6H), 7.01−6.98 (m, 4H), 3.65 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.2 (C), 131.5 (C), 128.6 (CH), 128.0 (CH), 126.8 (CH), 119.7 (C), 44.3 (CH_2); MS m/z (%) 392 ($M^+ + 4$, 23), 390 ($M^+ + 2$, 52), 388 (M^+, 26), 230 (100), 229 (72), 228 (39). HRMS calcd for $C_{18}H_{14}Br_2$ m/z 387.9462, found 387.9464. Anal. Calcd for $C_{18}H_{14}Br_2$: C 55.42, H 3.62. Found: C 55.66, H 3.75. Compound **7**: mp 110−111 °C; IR (neat, cm^{-1})

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3062, 3022, 2903, 1652, 1456, 1346, 1012, 775, 699; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (s, 2H), 7.23−7.21 (m, 6H), 7.10−7.07 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.2 (C), 139.1 (C), 135.2 (CH), 129.5 (CH), 128.1 (CH), 127.2 (CH), 123.6 (C); MS m/z (%) 390 ($M^+ + 4$, 50), 388 ($M^+ + 2$, 100), 386 (M^+, 52), 228 (59). HRMS calcd for $C_{18}H_{12}Br_2$ m/z 385.9306, found 385.9310. Anal. Calcd for $C_{18}H_{12}Br_2$: C 55.71, H 3.12. Found: C 55.95, H 3.34.

1,2-Dibromo-3,4-diphenylcyclohexa-1,4-diene (6) and 4′-5′-Dibromo-*o*-terphenyl (7). A solution of compound **5** (0.11 g, 0.28 mmol) in toluene (10 mL) was stirred and refluxed for 24 h. Toluene was removed under reduced pressure and the residue was purified by chromatography (hexanes) to give white solid **6** (72 mg, 65%) and **7** (36 mg, 33%).

Oxidation of Compound 6. A solution of **6** (30 mg, 0.077 mmol) in toluene (10 mL) containing DDQ (20.9 mg, 0.092 mmol) was refluxed for 3 h. Toluene was removed under reduced pressure and the residue was purified by column chromatography (hexanes) to give white solid **7** (29 mg, 97%).

One-Pot Synthesis of 4′-5′-Dibromo-*o*-terphenyl (7). To a stirred solution of cyclopropane **3** (5.0 g, 14.1 mmol) in 30 mL of dry ether at −78 °C was added methyllithium (1.5 M in ether, 9.4 mL, 14.1 mmol) dropwise from a syringe. The mixture was allowed to warm to rt and stirred for 0.5 h. The mixture was poured into a 250-mL beaker with 100 g of crushed ice. The ether layer was separated and the aqueous layer extracted with 30 mL of ether. The combined ether extracts were washed with about 100 mL of water and brine. The ether solution was dried with anhydrous magnesium sulfate. After fitration, ether was removed under reduced pressure and the residue was kept at −20 °C for 12 h. Toluene (50 mL) was added, and the mixture was refluxed for 24 h. The reaction mixture was cooled to rt and DDQ (1.59 g, 7 mmol) was added. The reaction mixture was refluxed for 3 h. Toluene was removed under reduced pressure and the residue was purified by column chromatography (hexanes) to give white solid **7** (1.34 g, 49%).

Crossed [2+2] Cycloaddition of Cyclopropenes 1 and 2: Preparation of Cyclopropene 1: Methyllithium (1.5 M in ether, 23.5 mL, 35.3 mmol) was added dropwise from a syringe to a stirred solution of compound **3** (5.0 g, 14.1 mmol) in 30.0 mL of dry ether at −78 °C. The mixture was allowed to warm to rt and stirred for 0.5 h. Ammonium chloride (5.6 g, 0.105 mol) was added at −78 °C. **Preparation of cyclopropene 2:** Methyllithium (1.5 M in ether, 9.4 mL, 14.1 mmol) was added dropwise from a syringe to a stirred solution of compound **3** (5.0 g, 14.1 mmol) in 30.0 mL of dry ether at −78 °C. The mixture was allowed to warm to rt and stirred for 0.5 h. A solution of cyclopropene **1** was transferred to the solution of cyclopropene **2** at −78 °C. After the solution was added, the mixture was allowed to warm to rt and stirred for 12 h. The mixture was poured into a 250-mL beaker with 100 g of crushed ice. The organic layer was separated and washed with water and brine, and then dried over anhydrous magnesium sulfate. After filtration, the solvent was removed on a rotary evaporator and the residue was purified by column chromatography (hexanes) to give white solid **5** (0.14 g, 5%), **8** (0.44 g, 10%), **9** (0.16 g, 10%), and **10** (0.49 g, 30%). Compound **8**: decomposition temperature 44 °C; IR (neat, cm^{-1}) 3060, 3033, 2984, 2920, 1603, 1498, 1448, 1285, 1224, 1137, 1022, 756, 695; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38−7.12 (m, 10H), 2.55 (dd, 1H, J = 2.7, 3.9 Hz), 2.31 (d, 1H, J = 5.2 Hz), 2.12 (dd, 1H, J = 1.4, 5.2 Hz), 2.01−1.98 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.9 (C), 135.5 (C), 128.45 (CH), 128.40 (CH), 126.5 (CH), 126.3 (CH), 126.0 (CH), 125.5 (CH), 42.0 (C), 38.8 (CH_2), 38.5 (C), 34.9 (CH), 34.8 (C), 32.6 (CH_2); MS m/z (%) 312 ($M^+ + 2$, 13), 310 (M^+, 15), 231 (100), 216 (57), 215 (84), 153 (46). HRMS calcd for $C_{18}H_{15}Br$ m/z 310.0357, found 310.0359. Anal. Calcd for $C_{18}H_{15}Br$: C 69.47, H 4.86. Found: C, 69.14, H 5.14. Compound **9**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32−7.14 (m, 10H), 2.02 (dd, 2H, J = 2.5, 3.7 Hz), 1.85−1.82 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4 (C), 128.3 (CH), 125.5(CH), 125.1 (CH), 32.4 (C), 31.3 (CH_2), 29.3 (CH). Compound **10**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54−7.07 (m, 15H), 2.43−2.30 (m, 2H), 2.03 (d, 1H, J = 3.9 Hz), 1.80−1.74 (m, 1H), 1.67−1.53 (m, 2H), 1.31−1.21 (m, 1H), 1.02−0.92 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8 (C), 143.3 (C), 130.1 (C), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 127.5 (CH), 126.1 (CH), 126.0 (CH), 125.9 (CH), 125.2 (CH), 120.7 (C), 111.4 (C), 27.6 (CH), 26.3 (CH), 22.5 (CH), 21.8 (CH), 20.5 (CH), 16.3 (CH_2), 15.7 (CH_2).

Enhanced Yield of Crossed [2 + 2] Cycloaddition of Cyclopropene 1 and 2. Methyllithium (1.5 M in ether, 14.1 mL, 21.2 mmol) was added dropwise from a syringe to a stirred solution of compound **3** (5.0 g, 14.1 mmol) in 30.0 mL of dry ether at −78 °C. The mixture was allowed to warm to rt and stirred for 0.5 h. A solution of Et_3NHCl (0.92 g, 16.8 mmol) in dry THF (25 mL) was added slowly (over 1 h) to the vigorously stirred ether solution at 0 °C, which was then stirred for 24 h. The mixture was poured into a 250-mL beaker with 100 g of crushed ice. The organic layer was separated and washed with water and brine, and then dried over anhydrous magnesium sulfate. After filtration, the solvent was removed on a rotary evaporator and the residue was purified by column chromatography (hexanes) to give white solid **8** (0.88 g, 40%), **9** (82 mg, 10%), and **10** (0.11 g, 13%)

Synthesis of 4′-Bromo-*o*-terphenyl (11). A solution of **8** (0.1 g, 0.32 mmol) in toluene (10 mL) was refluxed for 24 h. The reaction was cooled to rt and DDQ (87 mg, 0.35 mmol) was added. The reaction mixture was refluxed for 3 h. Toluene was removed under reduced pressure and the residue was purified by column chromatography (hexanes) to give white solid **11** (96 mg, 97%). Compound **11**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, 1H, J = 2.1 Hz), 7.54 (dd, 1H, J = 2.1, 8.2 Hz), 7.29 (d, 1H, J = 8.2 Hz), 7.23−7.19 (m, 6H), 7.14−7.08 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5 (C), 140.4 (C), 140.2 (C), 139.5 (C), 133.3 (CH), 132.1 (CH), 130.4 (CH) 129.7 (CH), 129.69 (CH), 128.0 (CH), 127.99 (CH), 126.98 (CH), 126.8 (CH), 121.4 (C).

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Supporting Information Available: X-ray structure determinations for **5**, **6**, **7**, **8**, and **11** in CIF format and ^{1}H, ^{13}C, and DEPT NMR spectra for compounds **4**, **5**, **6**, **7**, **8**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.