Supporting Information

Copper(I)-Catalyzed Carbometalation of Nonfunctionalized Cyclopropenes with Organozinc and Grignard Reagents

Takeo Nakano¹, Kohei Endo¹,²*, Yutaka Ukaji¹

¹ Division of Material Sciences, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan
² PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama, 332-0012, Japan
kendo@se.kanazawa-u.ac.jp

List of Contents

Experimental details and characterization data for all products  S2
1H, 13C and 19F NMR spectra of products  S10
1H, 13C and 19F NMR spectra of substrates  S45
1H NMR of crude mixture 2g  S52
Information of relative configuration of products 5a and 5b  S53
Experimental Section

General Method. $^1$H NMR was recorded on a 400 MHz NMR spectrometer. Chemical shifts $\delta$ are reported in ppm using TMS as an internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant ($J$) and integration. $^{13}$C NMR spectra were recorded on 100 MHz NMR spectrometer. The chemical shifts were determined in the $\delta$-scale relative to CDCl$_3$ ($\delta = 77.0$ ppm). The wave numbers of maximum absorption peaks of IR spectroscopy are presented in cm$^{-1}$. HRMS (EI, positive) was measured with a quadrupole and TOF mass spectrometer. All of the melting points were measured with a micro melting point apparatus. All solvents were distilled and stored over drying agents.

General Procedure

To a solution of CuI (2.9 mg, 0.015 mmol) in toluene (1.5 mL), Et$_2$Zn (0.6 mL, 1.0 M in toluene) was added at room temperature. After stirring for 30 min, L1 (5.4 mg, 0.23 mmol) and cyclopropene 1a (57.7 mg, 0.3 mmol) were added at room temperature. The reaction mixture was stirred for 16 h and was quenched with a sat. NH$_4$Cl. The aqueous layer was separated and extracted with AcOEt. The combined organic layer was dried over Na$_2$SO$_4$. Concentration and purification by silica gel column chromatography (hexane) gave the 2a-Et in 86% yield.

(2-Ethylcyclopropane-1,1-diyl)dibenzene 2a-Et; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.67-0.80 (m, 1H), 0.89 (t, $J = 6.9$ Hz, 3H), 1.08-1.15 (m, 2H), 1.28-1.38 (m, 1H), 1.45-1.52 (m, 1H), 7.01-7.26 (m, 10H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.7, 20.5, 24.1, 28.4, 35.5, 125.5, 126.1, 127.7, 128.0, 128.1, 130.6, 141.9, 147.6; IR (neat, cm$^{-1}$) 3420, 3059, 3024, 2995, 2959, 2929, 2871, 1943, 1599, 1494, 1445, 1375, 1312, 1143, 1075, 1031, 933, 808, 748, 698; HRMS (APCI-TOF) $m/z$ calcd. C$_{17}$H$_{18}$ 222.1409 [M$^+$]; found: 222.1407.

(2-Isopropylcyclopropane-1,1-diyl)dibenzene 2a-i-Pr (57.3 mg, 0.24 mmol) was obtained in 81% yield.
yield; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.64-0.73 (m, 1H), 0.88 (d, $J = 6.4$ Hz, 3H), 0.92 (d, $J = 6.4$ Hz, 3H), 1.01 (dd, $J = 4.6$, 9.2 Hz, 1H), 1.18-1.22 (m, 1H), 1.31-1.37 (m, 1H), 7.03-7.26 (m, 10H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 18.5, 22.2, 22.6, 28.6, 34.5, 36.5, 125.7, 126.0, 127.9, 128.1, 128.6, 130.1, 141.8, 147.6; IR (neat, cm$^{-1}$) 3419, 3058, 3024, 2867, 1943, 1801, 1599, 1494, 1445, 1379, 1362, 1310, 1197, 1157, 1073, 1030, 965, 943, 916, 828, 751, 699; HRMS (APCI-TOF) m/z calcd. C$_{18}$H$_{20}$ 236.1562 [M$^+$]; found: 236.1562.

![Image](https://example.com/image1)

[1,1'-Bi(cyclopropane)]-2,2-diyl dibenzene 2a-$\text{-c}$-Pr (61.8 mg, 0.26 mmol) was obtained in 88% yield; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.11-0.18 (m, 1H), 0.20-0.32 (m, 3H), 0.42-0.51 (m, 1H), 1.21-1.30 (m, 3H), 7.07-7.13 (m, 3H), 7.18-7.22 (m, 3H), 7.30 (m, 2H), 7.45 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 4.44, 4.92, 11.8, 20.1, 30.8, 35.2, 125.4, 126.2, 127.2, 128.0, 128.1, 130.1, 142.2, 147.4; IR (neat, cm$^{-1}$) 3058, 3022, 2998, 1944, 1802, 1654, 1599, 1494, 1445, 1312, 1154, 1076, 1018, 961, 891, 817, 762, 701; HRMS (DART) m/z calcd. C$_{18}$H$_{19}$ 235.1486 [M+H$^+$]; found: 235.1476.

![Image](https://example.com/image2)

(2-Butylcyclopropane-1,1-diyl)dibenzene 2a-$\text{-n}$-Bu (63.0 mg, 0.25 mmol) was obtained in 84% yield; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.70-0.77 (m, 1H), 0.82 (t, $J = 6.9$ Hz, 3H), 1.16-1.29 (m, 4H), 1.35-1.48 (m, 3H), 1.55-1.62 (m, 1H), 7.08-7.33 (m, 10H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.1, 20.9, 22.5, 26.6, 30.6, 31.7, 35.2, 125.5, 126.1, 127.6, 128.1 (2 carbons overlapped), 130.6, 141.9, 147.7; IR (neat, cm$^{-1}$) 3058, 3023, 2996, 2955, 2927, 2855, 1943, 1801, 1599, 1494, 1445, 1377, 1325, 1143, 1076, 1027, 933, 824, 752, 699; HRMS (APCI-TOF) m/z calcd. C$_{19}$H$_{22}$ 250.1722 [M$^+$]; found: 250.1718.

![Image](https://example.com/image3)

(2-Allylcyclopropane-1,1-diyl)dibenzene 2a-$\text{-Allyl}$ (59.7 mg, 0.26 mmol) was obtained in 85% yield; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.64-0.73 (m, 1H), 0.88 (d, $J = 6.4$ Hz, 3H), 0.92 (d, $J = 6.4$ Hz, 3H), 1.01 (dd, $J = 4.6$, 9.2 Hz, 1H), 1.18-1.22 (m, 1H), 1.31-1.37 (m, 1H), 7.03-7.26 (m, 10H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 18.5, 22.2, 22.6, 28.6, 34.5, 36.5, 125.7, 126.0, 127.9, 128.1, 128.6, 130.1, 141.8, 147.6; IR (neat, cm$^{-1}$) 3419, 3058, 3024, 2867, 1943, 1801, 1599, 1494, 1445, 1379, 1362, 1310, 1197, 1157, 1073, 1030, 965, 943, 916, 828, 751, 699; HRMS (APCI-TOF) m/z calcd. C$_{18}$H$_{20}$ 236.1562 [M$^+$]; found: 236.1562.

![Image](https://example.com/image4)
yield; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.22-1.30 (m, 2H), 1.56-1.62 (m, 1H), 1.66-1.73 (m, 1H), 2.09-2.17 (m, 1H), 4.98 (d, $J = 10.1$ Hz, 1H), 5.04 (d, $J = 17.4$ Hz, 1H), 5.84-5.94 (m, 1H), 7.10-7.35 (m, 10H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 20.5, 25.2, 35.0, 35.4, 114.7, 125.6, 126.3, 127.6, 128.2 (2 carbons overlapped), 130.6, 137.7, 141.6, 147.2; IR (neat, cm$^{-1}$) 3419, 3059, 3023, 2999, 2976, 2906, 1944, 1802, 1749, 1639, 1599, 1494, 1445, 1314, 1261, 1077, 1027, 997, 912, 797, 752, 698; HRMS (APCI-TOF) m/z calcd. C$_{18}$H$_{18}$ 234.1409 [M$^+$]; found: 234.1403.

(2-Benzylcyclopropane-1,1-diyl)dibenzene 2a-Bn (65.6 mg, 0.23 mmol) was obtained in 77% yield; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.34 (dd, $J = 5.5$, 8.7 Hz, 1H), 1.40 (t, $J = 5.5$ Hz, 1H), 1.91-1.98 (m, 1H), 2.07 (dd, $J = 9.2$, 14.6 Hz, 1H), 2.79 (dd, $J = 5.0$, 14.6 Hz, 1H), 7.01-7.26 (m, 10H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.2, 27.1, 35.5, 36.9, 125.6, 125.8, 126.4, 127.5, 128.1, 128.2 (2 carbons overlapped), 128.3, 130.7, 141.4, 141.6, 147.1; IR (neat, cm$^{-1}$) 3421, 3059, 3024, 2916, 1944, 1600, 1494, 1445, 1326, 1155, 1122, 1077, 1028, 916, 844, 753, 697; HRMS (APCI-TOF) m/z calcd. C$_{22}$H$_{20}$ 284.1565 [M$^+$]; found: 284.1568.

Cyclopropane-1,1,2-triylttribenzene 2a-Ph (75.4 mg, 0.28 mmol) was obtained in 93% yield; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.80 (dd, $J = 5.5$, 9.2 Hz, 1H), 1.97 (dd, $J = 5.5$, 6.4 Hz, 1H), 2.84 (dd, $J = 6.4$, 9.2 Hz, 1H), 6.85 (m, 2H), 7.01-7.18 (m, 9H), 7.24-7.30 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 20.9, 32.4, 39.3, 125.6, 125.9, 126.2, 127.4, 127.6, 127.9 (2 carbons overlapped), 128.3, 131.2, 138.7, 140.1, 147.0; IR (neat, cm$^{-1}$) 3055, 3027, 2998, 1597, 1496, 1457, 1445, 1314, 1210, 1186, 1157, 1132, 1094, 1074, 1032, 962, 931, 849, 825, 776, 758, 733, 696; HRMS (APCI-TOF) m/z calcd. C$_{21}$H$_{18}$ 270.1409 [M$^+$]; found: 270.1406.
4,4'-{(2-Ethylcyclopropane-1,1-diyl)bis(methylbenzene)} 2b (54.8 mg, 0.22 mmol) was obtained in 73% yield; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.69-0.79 (m, 1H), 0.89 (t, $J = 7.3$ Hz, 3H), 1.02-1.09 (m, 2H), 1.27-1.37 (m, 1H), 1.40-1.47 (m, 1H), 6.94 (m, 2H), 6.98-7.04 (m, 4H), 7.12 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.8, 20.4, 20.9, 21.1, 24.1, 28.1, 34.7, 127.5, 128.8 (2 carbons overlapped), 130.3, 134.9, 135.5, 139.1, 144.9; IR (neat, cm$^{-1}$) 3419, 2994, 2958, 2921, 2870, 1650, 1513, 1455, 1112, 1076, 1037, 821, 772, 726; HRMS (APCI-TOF) $m/z$ calcd. C$_{19}$H$_{22}$ 250.1722 [M$^+$]; found: 250.1720.

4,4'-{(2-Ethylcyclopropane-1,1-diyl)bis(fluorobenzene)} 2c (63.5 mg, 0.25 mmol) was obtained in 82% yield; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.72-0.86 (m, 1H), 0.97 (t, $J = 7.3$ Hz, 3H), 1.10-1.17 (m, 2H), 1.32-1.42 (m, 1H), 1.47-1.55 (m, 1H), 6.87-7.00 (m, 4H), 7.10-7.15 (m, 2H), 7.23-7.27 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.7, 20.5, 24.0, 28.2, 34.3, 114.9 (d, $J = 21.0$ Hz), 115.0 (d, $J = 21.0$ Hz), 129.2 (d, $J = 7.6$ Hz), 131.7 (d, $J = 7.6$ Hz), 137.6, 143.1, 161.0 (d, $J = 243$ Hz), 161.4 (d, $J = 243$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ −120.31, −119.39; IR (neat, cm$^{-1}$) 3384, 3067, 2961, 2931, 2873, 1888, 1602, 1509, 1456, 1405, 1375, 1296, 1221, 1157, 1095, 1076, 1033, 1015, 835, 782, 769, 730; HRMS (APCI-TOF) $m/z$ calcd. C$_{17}$H$_{16}$F$_2$ 258.1220 [M$^+$]; found: 258.1224.

4,4'-{(2-Ethylcyclopropane-1,1-diyl)bis(chlorobenzene)} 2d (85.2 mg, 0.29 mmol) was obtained in 98% yield; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.67-0.78 (m, 1H), 0.89 (t, $J = 6.8$ Hz, 3H), 1.05-1.11 (m, 2H), 1.24-1.34 (m, 1H), 1.42-1.49 (m, 1H), 6.98-7.01 (m, 2H), 7.09-7.19 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.6, 20.7, 24.0, 28.4, 34.4, 128.3, 128.4, 129.0, 131.5, 131.7, 132.2, 140.0, 145.5; IR (neat, cm$^{-1}$) 3418, 2960, 2929, 2817, 1723, 1593, 1492, 1455, 1398, 1092, 1014, 831, 808, 727; HRMS (APCI-TOF) $m/z$ calcd. C$_{17}$H$_{16}$Cl$_2$ 290.0629 [M$^+$]; S5
1-Phenylspiro[2.11]tetradecane 2e (73.7 mg, 0.27 mmol) was obtained in 91% yield; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.48-0.60 (m, 2H), 0.66 (t, $J = 6.4$ Hz, 1H), 0.78-0.92 (m, 2H), 0.99-1.16 (m, 5H), 1.21-1.37 (m, 4H), 1.39-1.59 (m, 5H), 1.66-1.86 (m, 5H), 2.07 (t, $J = 7.3$ Hz, 1H), 7.10-7.26 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.0, 26.5 (2 carbons overlapped), 26.8, 27.1, 27.2, 27.3, 29.7, 30.6, 32.1, 33.6, 36.3, 37.6, 43.5, 125.2, 127.5, 129.0, 139.9; IR (neat, cm$^{-1}$) 3384, 3060, 3024, 2923, 2850, 1602, 1497, 1448, 1073, 1041, 867, 774, 729, 698; HRMS (APCI-TOF) $m/z$ calcd. C$_{20}$H$_{30}$ 270.2348 [M$^+$]; found: 270.2343.

Dimethyl 2-ethylcyclopropane-1,1-dicarboxylate 2f (38.1 mg, 0.20 mmol) was obtained in 68% yield; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.94 (t, $J = 7.4$ Hz, 3H), 1.13-1.23 (m, 1H), 1.29-1.42 (m, 3H), 1.77-1.85 (m, 1H), 3.65 (s, 3H), 3.69 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.1, 21.1, 22.1, 30.4, 34.0, 52.4, 52.5, 168.7, 170.9; IR (neat, cm$^{-1}$) 3448, 2957, 2878, 1727, 1437, 1389, 1326, 1289, 1262, 1213, 1132, 1104, 1041, 990, 882, 808; HRMS (DART) $m/z$ calcd. C$_9$H$_{15}$O$_4$ 187.0970 [M+H$^+$]; found: 187.0970.

To a solution of CuI (2.9 mg, 0.015 mmol) in toluene (1.5 mL), Et$_2$Zn (0.6 mL, 1.0 M in toluene) was added at room temperature. After stirring for 30 min, L1 (5.4 mg, 0.23 mmol) and cyclopropene 1a (57.7 mg, 0.3 mmol) were added at room temperature. After stirred for 6 h, CuI (116 mg, 0.6 mmol) and the solution of I$_2$ (228 mg, 0.9 mmol) in CH$_2$Cl$_2$ (1.5 mL) were added. The reaction mixture was stirred for 15 h at 60 °C and was quenched with a sat. NH$_4$Cl. The aqueous layer was separated and extracted with AcOEt and dried over Na$_2$SO$_4$. Concentration and purification by silica gel column chromatography (hexane) gave the 3a-Et-I in 86% yield.
(2-Ethyl-3-iodocyclopropane-1,1-diyl)dibenzene 3a-Et-I; colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.92-1.05 (m, 4H), 1.32-1.37 (m, 1H), 1.78-1.85 (m, 1H), 3.44 (d, \(J = 8.2\) Hz, 1H), 7.03-7.09 (m, 3H), 7.12-7.20 (m, 3H), 7.27 (m, 2H), 7.35 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 10.3, 12.5, 26.4, 31.1, 37.1, 126.2, 126.9, 127.0, 128.2, 128.5, 131.5, 139.3, 146.3; IR (neat, cm\(^{-1}\)) 3025, 2962, 2927, 2870, 1597, 1493, 1445, 1375, 1247, 1201, 1078, 1030, 745, 703; HRMS (ESI-TOF) \(m/z\) calcd. C\(_{17}\)H\(_{17}\)INa 371.0273 [M+Na\(^+\)]; found: 371.0278.

(2-Allyl-3-ethylcyclopropane-1,1-diyl)dibenzene 3a-Et-Allyl (49.5 mg, 0.19 mmol) was obtained in 63% yield; colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.04 (t, \(J = 6.9\) Hz, 3H), 1.07-1.16 (m, 1H), 1.39-1.44 (m, 1H), 1.51-1.61 (m, 2H), 1.87-1.94 (m, 1H), 2.19-2.26 (m, 1H), 5.01 (d, \(J = 10.5\) Hz, 1H), 5.09 (d, \(J = 17.4\) Hz, 1H), 5.91-6.01 (m, 1H), 6.98-7.28 (m, 10H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.7, 19.9, 28.7, 30.5, 31.8, 37.1, 114.9, 125.3, 126.3, 127.0, 128.1, 128.3, 131.7, 138.4, 139.5, 149.1; IR (neat, cm\(^{-1}\)) 3057, 2961, 2872, 1638, 1599, 1494, 1445, 1376, 1077, 1031, 992, 911, 746, 705; HRMS (APCI-TOF) \(m/z\) calcd. C\(_{20}\)H\(_{22}\) 262.1721 [M\(^+\)]; found: 262.1698.

(3-Ethyl-2,2-diphenylcyclopropyl)(phenyl)methanone 3a-Et-Bz (84.1 mg, 0.26 mmol) was obtained in 86% yield; white solid of \(mp = 96-97\) °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.99 (t, \(J = 7.3\) Hz, 3H), 1.85-1.96 (m, 1H), 1.98-2.09 (m, 1H), 2.27-2.33 (m, 1H), 3.40 (d, \(J = 8.7\) Hz, 1H), 7.14-7.33 (m, 10H), 7.47-7.51 (m, 2H), 7.55-7.59 (m, 1H), 7.99-8.02 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.2, 18.6, 34.4, 39.5, 47.6, 126.4, 126.6, 126.7, 127.4, 128.2, 128.5, 128.6, 130.9, 132.3, 137.4, 140.2, 147.2, 196.9; IR (neat, cm\(^{-1}\)) 3057, 2958, 2928, 2873, 1734, 1670, 1578, 1493, 1446, 1409, 1381, 1214, 1178, 1078, 1020, 848, 741, 718, 702, 672; HRMS (EI) \(m/z\) calcd. C\(_{24}\)H\(_{23}\)O 326.1671 [M\(^+\)]; found: 326.1669.
3-Ethyl-2-methyl-2-phenylocyclopropyl)(phenyl)methanone 5a (47.4 mg, 0.18 mmol) was obtained in 60% yield; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) (major) $\delta$ 0.97 (t, $J$ = 6.9 Hz, 3H), 1.51 (s, 3H), 1.78-1.97 (m, 3H), 2.84 (d, $J$ = 8.2 Hz, 1H), 7.10-7.20 (m, 2H), 7.23-7.27 (m, 3H), 7.35-7.41 (m, 2H), 7.43-7.47 (m, 1H), 7.86-7.89 (m, 2H); (minor) $\delta$ 0.79 (t, $J$ = 6.9 Hz, 3H), 1.45 (s, 3H), 1.78-1.97 (m, 3H), 2.82 (d, $J$ = 7.3 Hz, 1H), 6.96-6.98 (m, 2H), 7.23-7.27 (m, 3H), 7.35-7.41 (m, 2H), 7.43-7.47 (m, 1H), 7.86-7.89 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) (major) $\delta$ 14.1, 15.3, 16.7, 33.2, 37.7 (2 carbons overlapped), 126.4, 127.4, 127.7, 128.4, 128.6, 132.3, 140.0, 148.2, 198.8; (minor) $\delta$ 14.3, 18.4, 32.3, 33.8, 39.8, 41.0, 126.3, 127.6, 128.1, 130.0, 132.0, 139.5, 140.4, 146.8, 197.2; IR (neat, cm$^{-1}$) 3058, 2959, 1665, 1597, 1579, 1494, 1447, 1414, 1379, 1214, 1179, 1065, 1023, 969, 892, 855, 764, 719, 700; HRMS (ESI-TOF) m/z calcd. C$_{19}$H$_{20}$ONa 287.1412 [M$+$Na$^+$]; found: 287.1420.

3-Ethyl-2-isopropyl-2-phenylocyclopropyl)(phenyl)methanone 5b (31.5 mg, 0.11 mmol) was obtained in 36% yield; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) (major) $\delta$ 0.79-0.86 (m, 9H), 1.20-1.30 (m, 1H), 1.58-1.68 (m, 2H), 1.70-1.84 (m, 1H), 2.80 (d, $J$ = 7.8 Hz, 1H), 6.85-6.87 (m, 1H), 7.13-7.21 (m, 3H), 7.22-7.26 (m, 1H), 7.38-7.42 (m, 2H), 7.44-7.49 (m, 1H), 7.90-7.94 (m, 2H); (minor) $\delta$ 0.66 (d, $J$ = 7.8 Hz, 3H), 0.78 (d, $J$ = 6.9 Hz, 3H), 0.94 (t, $J$ = 7.3 Hz, 3H), 1.15-1.30 (m, 1H), 1.91-2.09 (m, 2H), 2.73-2.78 (m, 1H), 2.91 (d, $J$ = 8.7 Hz, 1H), 6.85-6.87 (m, 3H), 7.13-7.21 (m, 1H), 7.22-7.26 (m, 1H), 7.38-7.42 (m, 2H), 7.44-7.49 (m, 1H), 7.90-7.94 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) (major) $\delta$ 14.3, 18.4, 19.5, 19.8, 33.8, 40.9, 41.8, 49.7, 126.4, 127.0, 127.6, 128.4, 131.1, 132.0, 132.5, 140.5, 197.0; (minor) $\delta$ 14.5, 16.1, 20.0, 20.7, 23.7, 32.4, 40.2, 49.5, 126.6, 127.6, 128.5, 130.6, 132.2, 133.1, 140.3, 143.4, 199.2; IR (neat, cm$^{-1}$) 3057, 2960, 2871, 1735, 1596, 1578, 1495, 1446, 1418, 1382, 1213, 1177, 1021, 913, 865, 804, 755, 705; HRMS (ESI-TOF) m/z calcd. C$_{21}$H$_{24}$ONa 315.1725 [M$+$Na$^+$]; found: 315.1726.
Cyclopropene substrates were synthesized from ketones for 4 steps. 

\[ \text{F} - \text{C} - \text{C} - \text{F} \]

4,4'-(Cycloprop-2-ene-1,1-diyl)bis(fluorobenzene) 1c (1.33 g, 5.8 mmol) was obtained in 39% yield (4 steps); colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.93-6.98 (m, 4H), 7.08-7.11 (m, 4H), 7.46 (s, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 30.6, 113.4, 114.8 (d, \(J = 21.0\) Hz), 129.4 (d, \(J = 7.6\) Hz), 142.6, 161.1 (d, \(J = 243\) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) –120.10; IR (neat, cm\(^{-1}\)) 3383, 1893, 1642, 1600, 1507, 1405, 1219, 1156, 1094, 1014, 995, 906, 863, 836, 814, 725; HRMS (APCI-TOF) \(m/z\) calcd. C\(_{15}\)H\(_{10}\)F\(_2\) 228.0751 [M\(^+\)]; found: 228.0748.

\[ \text{Cl} - \text{C} - \text{C} - \text{Cl} \]

4,4'-(Cycloprop-2-ene-1,1-diyl)bis(chlorobenzene) 1d (1.20 g, 4.6 mmol) was obtained in 31% yield (4 steps); colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.05-7.08 (m, 4H), 7.21-7.25 (m, 4H), 7.45 (s, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 30.9, 113.0, 128.2, 129.3, 131.6, 145.0; IR (neat, cm\(^{-1}\)) 3105, 1906, 1647, 1559, 1482, 1398, 1272, 1089, 1008, 946, 903, 859, 832, 795, 742, 722; HRMS (APCI-TOF) \(m/z\) calcd. C\(_{15}\)H\(_{10}\)Cl\(_2\) 260.0160 [M\(^+\)]; found: 260.0159.

\[ \text{C} - \text{C} - \text{C} - \text{C} \]

Spiro[2.11]tetradec-1-ene 1e (555 mg, 2.9 mmol) was obtained in 19% yield (4 steps); colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.51-0.62 (m, 4H), 0.91-1.03 (m, 2H), 1.15-1.28 (m, 4H), 1.41-1.48 (m, 6H), 1.56-1.60 (m, 2H), 1.64-1.69 (m, 4H), 7.10 (s, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 26.5, 26.6 (2 carbons overlapped), 30.9 (2 carbons overlapped), 34.9, 41.5, 113.9; IR (neat, cm\(^{-1}\)) 3420, 2920, 2849, 2667, 1630, 1447, 1382, 1306, 1008, 988, 933, 896, 851, 784, 698; HRMS (DART) \(m/z\) calcd. C\(_{14}\)H\(_{25}\) 193.1956 [M+H\(^+\)]; found: 193.1961.

2a-Et

$^1$H NMR (in CDCl$_3$, 400 MHz)
2a-Et

$^{13}$C NMR (in CDCl$_3$, 100 MHz)
2a-i-Pr

$^1$H NMR (in CDCl$_3$, 400 MHz)
$2a$-$i$-Pr

$^{13}$C NMR (in CDCl$_3$, 100 MHz)
2a-c-Pr

$^1$H NMR (in CDCl₃, 400 MHz)
2a-c-Pr

$^{13}$C NMR (in CDCl$_3$, 100 MHz)
2a-\textit{t}-Bu

$^1$H NMR (in CDCl$_3$, 400 MHz)
$\text{2a-n-Bu}$

$^{13}$C NMR (in CDCl$_3$, 100 MHz)
2a- Allyl

$^1$H NMR (in CDCl$_3$, 400 MHz)
2a-Allyl

$^{13}$C NMR (in CDCl$_3$, 100 MHz)
2a-Bn

$^1$H NMR (in CDCl$_3$, 400 MHz)
$^{13}$C NMR (in CDCl$_3$, 100 MHz)
2a-Ph

$^1$H NMR (in CDCl$_3$, 400 MHz)
2a-Ph

$^{13}$C NMR (in CDCl$_3$, 100 MHz)
$\text{Me-} \quad \text{Me}$

2b

$^1\text{H NMR (in CDCl}_3\text{, 400 MHz)}$
2b

$^{13}$C NMR (in CDCl$_3$, 100 MHz)
$2c$

$^{1}\text{H NMR (in CDCl}_3\text{, 400 MHz)}$
$^{13}$C NMR (in CDCl$_3$, 100 MHz)
$^{19}$F NMR (in CDCl$_3$, 376 MHz)
2d

$^1$H NMR (in CDCl$_3$, 400 MHz)
$^{13}$C NMR (in CDCl$_3$, 100 MHz)
$^{1}$H NMR (in CDCl$_3$, 400 MHz)
$^{13}$C NMR (in CDCl$_3$, 100 MHz)
$^1$H NMR (in CDCl$_3$, 400 MHz)
2f

$^{13}$C NMR (in CDCl$_3$, 100 MHz)
$^{1}$H NMR (in CDCl$_3$, 400 MHz)
$^{13}$C NMR (in CDCl$_3$, 100 MHz)
2a-Et-Allyl

$^{13}$C NMR (in CDCl$_3$, 100 MHz)
2a-Et-Bz

$^1$H NMR (in CDCl$_3$, 400 MHz)
$^{13}$C NMR (in CDCl$_3$, 100 MHz)
$^1$H NMR (in CDCl$_3$, 400 MHz)

5a
$^{13}$C NMR (in CDCl$_3$, 100 MHz)
$^1$H NMR (in CDCl$_3$, 400 MHz)
$^{13}$C NMR (in CDCl$_3$, 100 MHz)
1c

$^1$H NMR (in CDCl$_3$, 400 MHz)
$1^3\text{C NMR (in CDCl}_3$, 100 MHz$]
$^{19}$F NMR (in CDCl$_3$, 376 MHz)
1H NMR (in CDCl₃, 400 MHz)
$^{13}$C NMR (in CDCl$_3$, 100 MHz)
$^1$H NMR (in CDCl$_3$, 400 MHz)
$^{13}$C NMR (in CDCl$_3$, 100 MHz)
^1H NMR spectrum of crude product 2g

A single spot on TLC analysis was observed after the reaction of 1g and Et₂Zn. The desired product should be obtained, but the decomposition took place even under neutral conditions. The 1H NMR spectrum of the crude mixture indicated the presence of the desired product 2g.
The nosey analysis of products 2g and 2h did not show the correlation; thus, the relative configuration could not be determined.