Supporting Information

Highly convergent modular access to poly-carbon substituted cyclopropanes via Cu(I)-catalyzed multicomponent cyclopropene carboallylation

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1. General information.

Instrumentation and software.

All $^1$H NMR and $^{13}$C NMR spectra were recorded at 25 °C on a Bruker 600 MHz spectrometer. Chemical shifts (δ) are given in parts per million (ppm) relative to internal standards (TMS, $^1$H-NMR: δ 0 ppm and $^{13}$C-NMR: δ 77.0 ppm for CDCl$_3$). The multiplicity of the NMR signals is assigned as follows: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, or combinations thereof. NMR yields were determined by addition of a known amount, approximately 20.5 ul, of nitromethane to the crude product and dissolving everything in CDCl$_3$, followed by $^1$HNMR-analysis. Flash chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Taizhou, China). Enantioselectivities were determined by Agilent 1260 HPLC system with Darcel Chiralpak columns.

Solvents and reagents.

Unless otherwise noted, all reactions were conducted under a nitrogen atmosphere. Copper salts and other commercial chemicals were used without further purification. Ether was distilled from sodium with benzophenone as indicator. Cyclopropenes 1a-1f, 1h-1j, \textsuperscript{[1a-1b]} 1g \textsuperscript{[1c]} and aryl boronic esters\textsuperscript{2]} were synthesized according to literature; the structure of existing compounds were verified by comparison with reported $^1$H NMR data. Allyl bromides were purchased from commercial sources or prepared from the literature [2-(bromomethyl)but-1-ene].\textsuperscript{[3]}
Experimental procedures

2.1 Preparation of starting materials

Cyclopropenes 1a-1f and 1h-1j used in this study (Scheme S1) were synthesized according to literature \[^{[1a-1b]}\] by a 4-step procedure typically from the corresponding ketones; cyclopropene 1g was synthesized according to literature by a 3-step procedure from Tosylhydrazone.\[^{[1c]}\]

\[\text{Schem S1.}\]

Substrates Preparation:

4,4′-(2-bromocyclopropane-1,1-diyl)bis(bromobenzene): Ti(OPr)\(_4\) (548 µL, 1.9 mmol) was added to a solution of 4,4′-(2,2-dibromocyclopropane-1,1-diyl)bis(bromobenzene) (9.36 g, 18.5 mmol) in and Et\(_2\)O (40 mL) at 0 °C. EtMgBr (7.5 mL, 22.2 mmol; 3.0 M solution in Et\(_2\)O) was added dropwise to it over 2 h and the mixture was further stirred for 1 h while gradually raising the temperature to room temperature. The reaction was slowly quenched with saturated NH\(_4\)Cl aq and 1 M HCl aq was added to it. After extraction with Et\(_2\)O, the organic layer was washed with saturated NaCl aq, dried over MgSO\(_4\), filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with petroleum ether to afford the title compound (6.17 g, 78% yield) as a yellow solid.

M.p. = 73 - 75°C. \(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)) \(\delta\) 7.50 - 7.46 (m, 2H), 7.40 - 7.36 (m, 2H), 7.25 – 7.21 (m, 2H), 7.08 – 7.05 (m, 2H), 3.64 - 3.60 (m, 1H), 1.87 - 1.82 (m, 1H), 1.80 – 1.76 (m, 1H). \(^1\text{C NMR}\) (151 MHz, CDCl\(_3\)) \(\delta\) 142.53, 139.18, 132.03, 131.79, 131.54, 129.36, 121.46, 120.85, 35.33, 27.50, 23.99. \(^{13}\text{C NMR}\) (ESI-TOF) (m/z): Calcd for C\(_{15}\)H\(_{12}\)Br\(_3\) ([M + H]\(^+\)), 428.8484; found 428.8486.
4,4’-(cycloprop-2-ene-1,1-diyl)bis(bromobenzene) (1f): KO'Bu (0.67 g, 6.0 mmol) was added portionwise to a solution of 4,4’-(2-bromocyclopropane-1,1-diyl)bis(bromobenzene) (2.14 g, 5.0 mmol) in DMSO (10 mL), and the mixture was stirred for 18 h. The reaction was quenched with H$_2$Oaq and extracted with Et$_2$O. The organic layer was washed with saturated NaClaq, dried over MgSO$_4$, and concentrated in vacuo. The residue was chromatographed on silica gel with petroleum ether to afford 1f (1.50 g, 86% yield) as a yellow solid.

M.p. = 83 - 88°C. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.47–7.44 (m, 1H), 7.40 (s, 2H), 7.27–7.24 (m, 1H), 7.23 – 7.19 (m, 1H), 7.17 – 7.12 (m, 2H), 7.07–7.00 (m, 1H), 6.90–6.86 (m, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 146.93, 145.09, 133.10, 131.34, 128.17, 127.83, 126.58, 125.33, 124.96, 113.02, 32.89. HRMS (ESI-TOF) (m/z): Calcd for C$_{15}$H$_{10}$Br$_2$ ([M+H]$^+$), 348.9222; found 348.9225.
### 2.2 Reaction optimization

**Table S1.** Optimization of the cyclopropene carboallylation (I): solvent screening.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield/%</th>
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<tbody>
<tr>
<td>1</td>
<td>THF</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>dioxane</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>Et$_2$O</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>Toluene</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>cyclohexane</td>
<td>20</td>
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</table>

**Table S2.** Optimization of the cyclopropene carboallylation (II): evaluation of ligands.

<table>
<thead>
<tr>
<th>Entry</th>
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<th>Yield/%</th>
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<tbody>
<tr>
<td>1</td>
<td>IMes</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>dcype</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>IPr</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>dppf</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>PPh$_3$</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>Phen</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>P(4-CF$_3$C$_6$H$_4$)$_3$</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>P(4-FC$_6$H$_4$)$_3$</td>
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<tr>
<td>9</td>
<td>P(4-ClC$_6$H$_3$)$_3$</td>
<td>50</td>
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<tr>
<td>10</td>
<td>P(3,5-di-CF$_3$C$_6$H$_3$)$_3$</td>
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<td>11</td>
<td>P(o-tol)$_3$</td>
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<tr>
<td>12</td>
<td>PCy$_3$</td>
<td>trace</td>
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<tr>
<td>13</td>
<td>P(n-Bu)$_3$</td>
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<tr>
<td>14</td>
<td>P(t-Bu)$_3$</td>
<td>trace</td>
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</tbody>
</table>
**Table S3.** Ligand effect on the enantioselective carboallylation.

<table>
<thead>
<tr>
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<th>Ligand</th>
<th>Yield/%</th>
<th>ee/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>((R, R))-DTBMSegPhos</td>
<td>38</td>
<td>-69</td>
</tr>
<tr>
<td>2</td>
<td>((R))-H(_8)-BINAP</td>
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</tr>
<tr>
<td>3</td>
<td>((R))-MeO-Tol-BIPHEP</td>
<td>28</td>
<td>-69</td>
</tr>
<tr>
<td>4</td>
<td>((R))-SegPhos</td>
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<td>-60</td>
</tr>
<tr>
<td>5</td>
<td>((R))-BINAP</td>
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<td>-66</td>
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<tr>
<td>6</td>
<td>((R, R))-Ph-BPE</td>
<td>11</td>
<td>88</td>
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2.3 Procedures

Typical procedure for Cu-catalyzed biscarbonation of cyclopropenes.

In a nitrogen filled glovebox, Cu(C₈H₁₁O₂)₂ (0.01 mmol, 5 mol%) and P(4-FC₆H₄)₃ (0.012 mmol, 6 mol%) were dissolved in anhydrous Et₂O (3 mL). The mixture was stirred at room temperature for ca. 2 min before NaOtBu (0.3 mmol, 1.5 equiv., 23 mg), boronic ester (0.30 mmol, 1.5 equiv.) and allyl bromide (0.6 mmol, 3.0 equiv.) were successively added. Then cyclopropene (0.20 mmol) was added dropwise into the solution. The resulting mixture was stirred at 70 °C for 24 h. After complete conversion, the solvent was removed in vacuo and residue was subjected to flash chromatography (eluent: petroleum ether/EtOAc = 200:1) to afford the title compound 4a (46.2 mg, 75% yield) as a colorless oil.

Catalytic enantioselective three-component arylallylation of cyclopropene:

In a nitrogen filled glovebox, Cu(C₈H₁₁O₂)₂ (0.01 mmol, 5 mol%) and (R,R)-Ph-BPE (0.012 mmol, 6 mol%) were dissolved in anhydrous Et₂O (3 mL) in a screw-cap tube. The mixture was stirred at room temperature for ca. 2 min before NaOtBu (0.3 mmol, 1.5 equiv., 23 mg), boronic ester (0.30 mmol, 1.5 equiv.) and allyl bromide (0.6 mmol, 3.0 equiv.) were successively added. Then cyclopropene (0.20 mmol) was added dropwise into the solution. The tube was sealed, taken out of the glovebox. The tube was stirred for 24 h in a 70 °C oil bath. After complete conversion, the solvent was removed in vacuo and residue was subjected to flash chromatography (eluent: petroleum ether/EtOAc = 200:1) to afford (+)-4e (7.5 mg, 11% yield, 94:6 e.r.) 
\([\alpha]_D^{20} = 19.7 \, (c = 0.5, \text{CHCl}_3)\)
2.4. Crystal structure of compound (±)-4e (CCDC# 1935679).

![ORTEP representation of compound (±)-4e](image)

**Figure S1.** ORTEP representation of compound (±)-4e.

<table>
<thead>
<tr>
<th>Bond precision:</th>
<th>C-C = 0.0034 Å</th>
<th>Wavelength=1.54178</th>
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<td>b=9.550(2)</td>
</tr>
<tr>
<td></td>
<td>alpha=90</td>
<td>beta=93.737(13)</td>
</tr>
<tr>
<td></td>
<td>c=20.071(5)</td>
<td>gamma=90</td>
</tr>
<tr>
<td>Temperature:</td>
<td>273 K</td>
<td></td>
</tr>
<tr>
<td>Volume</td>
<td>Calculated</td>
<td>Reported</td>
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<tr>
<td></td>
<td>1954.8(7)</td>
<td>1954.8(8)</td>
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<tr>
<td>Space group</td>
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<td>P 1 21/c 1</td>
</tr>
<tr>
<td>Hall group</td>
<td>-P 2ybc</td>
<td>-P 2ybc</td>
</tr>
<tr>
<td>Moiety formula</td>
<td>C25 H24 O</td>
<td>C25 H24 O</td>
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<tr>
<td>Sum formula</td>
<td>C25 H24 O</td>
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</tr>
<tr>
<td>Mr</td>
<td>340.44</td>
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<td>Z</td>
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<tr>
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<tr>
<td>F000</td>
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<td>h,k,lmax</td>
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<td>wR2(reflections)= 0.1530(3594)</td>
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<tr>
<td>S = 1.081</td>
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</table>

**Figure S2.** Crystal structure parameters.
3. Compound Characterization

((2S*,3S*)-3-allylcyclopropane-1,1,2-triyl)tribenzene (4a): following the general procedure, the reaction of 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 57.0 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4a (46.2 mg, 75% yield) as a colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.28–7.24 (m, 2H), 7.19–7.13 (m, 4H), 7.13–7.09 (m, 3H), 7.08–7.03 (m, 4H), 6.77–6.72 (m, 2H), 5.79–5.71 (m, 1H), 5.06–4.99 (m, 1H), 4.93–4.89 (m, 1H), 2.74 (d, $J$ = 10.2 Hz, 1H), 2.59–2.51 (m, 1H), 2.26–2.18 (m, 1H), 2.04–1.97 (m, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 149.07, 138.16, 137.77, 137.56, 132.01, 129.75, 128.42, 128.23, 127.57, 127.45, 126.55, 125.85, 125.37, 115.22, 40.82, 35.27, 31.79, 30.08.

HRMS (ESI-TOF) (m/z): Calcd for C$_{24}$H$_{22}$([M+H]$^+$), 311.1794; found 311.1782.

((2S*,3S*)-2-allyl-3-(p-tolyl)cyclopropane-1,1-diyl)dibenzene (4b): following the general procedure, the reaction of 5,5-dimethyl-2-(p-tolyl)-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 61.2 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 0.0720 g) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4b (46.6 mg, 72% yield) as a colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.33–7.31 (m, 2H), 7.26–7.21 (m, 4H), 7.21–7.16 (m, 3H), 7.14–7.09 (m, 1H), 6.97–6.92 (m, 2H), 6.72–6.68 (m, 2H), 5.87–5.79 (m, 1H), 5.14–5.07 (m, 1H), 5.01–4.96 (m, 1H), 2.78 (d, $J$ = 10.2 Hz, 1H), 2.63–2.56 (m, 1H), 2.31–2.24 (m, 4H), 2.08–2.01 (m, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 149.18, 138.16, 137.77, 137.56, 132.01, 129.75, 128.42, 128.39, 128.22, 128.19, 127.55, 126.50, 125.78, 115.15, 40.52, 35.04, 31.66, 30.12, 20.91.

HRMS (ESI-TOF) (m/z): Calcd for C$_{25}$H$_{24}$([M+H]$^+$), 325.1950; found 325.1955.

((2S*,3S*)-2-allyl-3-(4-(tert-butyl)phenyl)cyclopropane-1,1-diyl)dibenzene (4c): following the general procedure, the reaction of 2-(4-(tert-butyl)phenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 73.8 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4c (38.1 mg, 52% yield) as a colorless oil.
1H NMR (600 MHz, CDCl₃) δ 7.27–7.24 (m, 2H), 7.18–7.10 (m, 7H), 7.09–7.05 (m, 2H), 7.05–7.01 (m, 1H), 5.81–5.73 (m, 1H), 5.05–5.00 (m, 1H), 4.94–4.89 (m, 1H), 2.71 (d, J = 9.6 Hz, 1H), 2.53–2.46 (m, 1H), 2.22–2.16 (m, 1H), 1.99–1.93 (m, 1H), 1.20 (s, 9H).

13C NMR (151 MHz, CDCl₃) δ 149.25, 148.12, 138.00, 137.83, 134.89, 132.06, 129.40, 128.39, 128.16, 127.64, 126.45, 125.77, 124.34, 115.12, 77.21, 77.00, 76.79, 40.62, 34.83, 34.25, 31.56, 31.34, 30.24.

HRMS (ESI-TOF) (m/z): Calcd for C₂₈H₃₀ ([M+H]+), 367.2420; found 367.2418.

4d: following the general procedure, the reaction of 2-(1,1'-biphenyl)-4-yl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 79.8 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4d (67.5 mg, 87% yield) as a colorless oil.

1H NMR (600 MHz, CDCl₃) δ 7.59–7.55 (m, 2H), 7.43–7.37 (m, 4H), 7.37–7.33 (m, 2H), 7.32–7.28 (m, 1H), 7.26–7.23 (m, 4H), 7.23–7.20 (m, 3H), 7.16–7.12 (m, 1H), 6.90–6.86 (m, 2H), 5.90–5.82 (m, 1H), 5.16–5.10 (m, 1H), 5.03–4.99 (m, 1H), 2.855 (d, J = 10.2 Hz, 1H), 2.69–2.61 (m, 1H), 2.37–2.29 (m, 1H), 2.15–2.08 (m, 1H).

13C NMR (151 MHz, CDCl₃) δ 149.02, 140.76, 138.01, 137.74, 137.56, 137.40, 132.07, 130.15, 128.69, 128.45, 128.30, 127.56, 126.99, 126.80, 126.63, 126.02, 125.89, 115.31, 41.05, 35.10, 32.03, 30.14.

HRMS (ESI-TOF) (m/z): Calcd for C₃₀H₂₆ ([M+H]+), 387.2107; found 387.2102.

4e: following the general procedure, the reaction of 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4e (61.5 mg, 91% yield) as a yellow solid. M.p. = 87 - 89°C.

1H NMR (600 MHz, CDCl₃) δ 7.25–7.21 (m, 2H), 7.18–7.13 (m, 4H), 7.13–7.08 (m, 3H), 7.06–7.02 (m, 1H), 6.68–6.64 (m, 2H), 5.63–5.59 (m, 2H), 5.80–5.71 (m, 1H), 5.06–4.99 (m, 1H), 4.93–4.89 (m, 1H), 3.64 (s, 3H), 2.69 (d, J = 9.6 Hz, 1H), 2.55–2.48 (m, 1H), 2.22–2.15 (m, 1H), 1.99–1.92 (m, 1H).

13C NMR (151 MHz, CDCl₃) δ 157.46, 149.15, 137.88, 137.65, 132.10, 130.63, 129.98, 128.38, 128.20, 127.50, 126.49, 125.75, 115.17, 112.96, 55.09, 40.14, 34.67, 31.43, 30.12.

HRMS (ESI-TOF) (m/z): Calcd for C₂₅H₂₆O ([M + H]+), 341.1899; found 341.1892.
**((2S*,3S*)-2-Allyl-3-(4-phenoxyphenyl)cyclopropane-1,1-diyl)dibenzene (4f):** following the general procedure, the reaction of 5,5-dimethyl-2-(4-phenoxyphenyl)-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 84.6 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4f (72.7 mg, 90% yield) as a colorless oil.

**1H NMR** (600 MHz, CDCl₃) δ 7.34–7.28 (m, 4H), 7.27–7.21 (m, 4H), 7.21–7.16 (m, 3H), 7.15–7.10 (m, 1H), 7.09–7.04 (m, 1H), 7.00–6.96 (m, 4H), 5.90–5.80 (m, 1H), 5.14–5.07 (m, 1H), 5.04–4.98 (m, 1H), 2.81 (d, *J* = 9.6 Hz, 1H), 2.67–2.59 (m, 1H), 2.34–2.27 (m, 1H), 2.12–2.05 (m, 1H).

**13C NMR** (151 MHz, CDCl₃) δ 157.38, 154.98, 149.01, 137.74, 137.53, 133.00, 132.03, 130.87, 129.63, 128.43, 128.25, 127.54, 126.59, 125.85, 123.00, 118.68, 118.00, 115.28, 40.50, 34.68, 31.59, 30.12.

**HRMS (ESI-TOF) (m/z):** Calcd for C_{30}H_{26}O ([M + H]^+), 403.2056; found 403.2048.

**((2S*,3S*)-2-Allyl-3-(4-fluorophenyl)cyclopropane-1,1-diyl)dibenzene (4g):** following the general procedure, the reaction of 2-(4-fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 62.4 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4g (46.3 mg, 71% yield) as a yellow solid. M.p. = 79 - 81°C.

**1H NMR** (600 MHz, CDCl₃) δ 7.34–7.29 (m, 2H), 7.27–7.18 (m, 5H), 7.18–7.10 (m, 3H), 6.85–6.80 (m, 2H), 6.79–6.74 (m, 2H), 5.86–5.77 (m, 1H), 5.12–5.06 (m, 1H), 2.80 (d, *J* = 10.2 Hz, 1H), 2.65–2.58 (m, 1H), 2.28–2.21 (m, 1H), 2.09–2.03 (m, 1H).

**13C NMR** (151 MHz, CDCl₃) δ 161.05 (d, *J* = 242.7 Hz), 148.85, 137.55, 137.30, 133.75 (d, *J* = 3.2 Hz), 131.99, 130.95 (d, *J* = 7.5 Hz), 128.45, 128.32, 127.49, 126.67, 125.91, 115.35, 114.31 (d, *J* = 20.9 Hz), 40.53, 34.51, 31.57, 29.97.

**19F NMR** (470 MHz, CDCl₃) δ –117.99 (tt, *J* = 8.9, 5.2 Hz).

**HRMS (ESI-TOF) (m/z):** Calcd for C_{24}H_{21}F ([M + H]^+), 329.1700; found 329.1708.

**((2S*,3S*)-2-Allyl-3-(4-chlorophenyl)cyclopropane-1,1-diyl)dibenzene (4h):** following the general procedure, the reaction of 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 67.3 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0
equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4h (59.5 mg, 87% yield) as a colorless oil.

**1H NMR** (600 MHz, CDCl₃) δ 7.32–7.30 (m, 2H), 7.27–7.18 (m, 5H), 7.18–7.14 (m, 2H), 7.14–7.11 (m, 1H), 7.01–7.08 (m, 2H), 6.75–6.69 (m, 2H), 5.85–5.75 (m, 1H), 5.12–5.06 (m, 1H), 5.02–4.98 (m, 1H), 2.78 (d, J = 9.6 Hz, 1H), 2.66–2.58 (m, 1H), 2.27–2.22 (m, 1H), 2.12–2.05 (m, 1H).

**13C NMR** (151 MHz, CDCl₃) δ 148.70, 137.36, 137.18, 136.75, 131.93, 131.25, 130.90, 128.47, 128.39, 127.57, 127.45, 126.76, 125.98, 115.44, 34.67, 31.90, 30.32, 29.90.

**HRMS** (ESI-TOF) (m/z): Calcd for C₂₄H₂₁Cl ([M + H]⁺), 345.1404; found 345.1406.

**((2S*,3S*)-2-Allyl-3-(4-bromophenyl)cyclopropane-1,1-diyl)dibenzene (4i):** following the general procedure, the reaction of 2-(4-bromophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 80.7 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4i (63.5 mg, 82% yield) as a colorless oil.

**1H NMR** (600 MHz, CDCl₃) δ 7.32–7.28 (m, 2H), 7.27–7.18 (m, 7H), 7.18–7.10 (m, 3H), 6.68–6.64 (m, 2H), 5.85–5.75 (m, 1H), 5.12–5.06 (m, 1H), 5.02–4.97 (m, 1H), 2.76 (d, J = 9.6 Hz, 1H), 2.66–2.57 (m, 1H), 2.26–1.90 (m, 1H), 2.12–2.05 (m, 1H).

**13C NMR** (151 MHz, CDCl₃) δ 148.66, 137.30, 137.15, 131.92, 131.29, 130.50, 128.47, 128.40, 127.45, 126.77, 125.99, 119.34, 115.45, 41.02, 34.73, 31.92, 29.87.

**HRMS** (ESI-TOF) (m/z): Calcd for C₂₄H₂₁Br([M + H]⁺), 389.0899; found 389.0901.

**((2S*,3S*)-2-Allyl-3-(4-iodophenyl)cyclopropane-1,1-diyl)dibenzene (4j):** following the general procedure, the reaction of 2-(4-iodophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 91.1 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4j (65.7 mg, 75% yield) as a colorless oil.

**1H NMR** (600 MHz, CDCl₃) δ 7.46–7.41 (m, 2H), 7.32–7.28 (m, 2H), 7.18–7.10 (m, 3H), 6.52–6.51 (m, 2H), 5.84–5.76 (m, 1H), 5.12–5.06 (m, 1H), 5.02–4.97 (m, 1H), 2.74 (d, J = 9.6 Hz, 1H), 2.65–2.57 (m, 1H), 2.26–2.18 (m, 1H), 2.12–2.05 (m, 1H).

**13C NMR** (151 MHz, CDCl₃) δ 148.66, 138.03, 137.28, 137.16, 136.45, 131.90, 131.66, 128.48, 128.42, 127.45, 126.78, 126.00, 125.51, 115.46, 34.84, 32.00, 30.32, 29.86.

**HRMS** (ESI-TOF) (m/z): Calcd for C₂₄H₂₁I ([M + H]⁺), 437.0760; found 437.0762.
Methyl 4-((1S*,3S*)-3-allyl-2,2-diphenylcyclopropyl)benzoate (4k): following the general procedure, the reaction of methyl 4-(5,5-dimethyl-1,3,2- dioxaborinan-2-yl)benzoate (0.30 mmol, 1.5 equiv., 74.4 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4k (27.4 mg, 37% yield) as a white solid. M.p. = 84 - 88°C.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.81–7.78 (m, 2H), 7.34–7.31 (m, 2H), 7.27–7.20 (m, 5H), 7.18–7.12 (m, 3H), 6.88–6.85 (m, 2H), 5.83–5.75 (m, 1H), 5.11–5.06 (m, 1H), 5.00–4.98 (m, 1H), 3.87 (s, 3H), 2.86 (d, $J = 9.6$ Hz, 1H), 2.71–2.64 (m, 1H), 2.32–2.25 (m, 1H), 2.20–2.13 (m, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 167.16, 148.55, 144.19, 137.22, 137.04, 131.84, 129.59, 128.64, 128.51, 128.44, 127.46, 127.15, 126.84, 126.07, 115.51, 51.91, 41.98, 35.38, 32.67, 29.92.

HRMS (ESI-TOF) (m/z): Calcd for C$_{26}$H$_{24}$O$_2$ ([M + H]$^+$), 369.1849; found 369.1856.

((2S*,3S*)-2-Allyl-3-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-diyl)dibenzene (4l): following the general procedure, the reaction of 5,5-dimethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 77.4 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 0.0384 g) afforded 4l (29.4 mg, 39% yield) as a white solid. M.p. = 236 - 240°C.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.39–7.36 (m, 2H), 7.34–7.31 (m, 2H), 7.28–7.20 (m, 5H), 7.19–7.12 (m, 3H), 6.91–6.87 (m, 2H), 5.83–5.75 (m, 1H), 5.12–5.06 (m, 1H), 5.02–4.97 (m, 1H), 2.86 (d, $J = 9.6$ Hz, 1H), 2.70–2.63 (m, 1H), 2.29–2.21 (m, 1H), 2.18–2.12 (m, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 148.49, 142.68, 137.15, 136.97, 130.84, 129.80, 128.54, 128.50, 127.52 (q, $J = 32.5$ Hz), 127.48, 126.91, 126.12, 124.38 (q, $^1$J$_{C,F} = 271.8$ Hz), 124.25 (q, $^1$J$_{C,F} = 4.5$ Hz), 115.57, 41.75, 34.98, 32.40, 29.84.

$^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –62.22 (s).

HRMS (ESI-TOF) (m/z): Calcd for C$_{25}$H$_{23}$F$_3$Na ([M + Na]$^+$), 401.1481; found 401.1488.
((2S*,3S*)-2-Allyl-3-(4-nitrophenyl)cyclopropane-1,1-diyl)dibenzene (4m): following the general procedure, the reaction of 5,5-dimethyl-2-(4-nitrophenyl)-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 70.5 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenylcyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4m (30.8 mg, 43% yield) as a colorless oil.

\[ \text{HRMS (ESI-TOF) (m/z): Calcd for C}_{24}\text{H}_{21}\text{NO}_2([M + H]^+), 356.1645; found 356.1641.} \]

((2S*,3S*)-2-Allyl-3-(4-vinylphenyl)cyclopropane-1,1-diyl)dibenzene (4n): following the general procedure, the reaction of 5,5-dimethyl-2-(4-vinylphenyl)-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 64.8 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenylcyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4n (45.4 mg, 68% yield) as a colorless oil.

\[ \text{HRMS (ESI-TOF) (m/z): Calcd for C}_{26}\text{H}_{24}([M + H]^+), 337.1950; found 337.1952.} \]

((2S*,3S*)-2-Allyl-3-(3-methoxyphenyl)cyclopropane-1,1-diyl)dibenzene (4o): following the general procedure, the reaction of 2-(3-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenylcyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4o (40.9 mg, 60% yield) as a colorless oil.

\[ \text{HRMS (ESI-TOF) (m/z): Calcd for C}_{24}\text{H}_{24}\text{O}[M + H]^+, 342.1650; found 342.1649.} \]
(m, 1H), 2.26–2.19 (m, 1H), 2.02–1.96 (m, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 158.72, 149.02, 139.75, 137.83, 137.55, 131.99, 128.43, 128.30, 128.25, 127.59, 126.57, 125.88, 122.54, 115.25, 115.02, 111.33, 54.84, 40.94, 35.11, 31.90, 30.18.

**HRMS (ESI-TOF) (m/z):** Caled for C$_{25}$H$_{24}$O ([M + H]$^+$), 341.1899; found 341.1893.

((2S*,3S*)-2-Allyl-3-(3-bromophenyl)cyclopropane-1,1-diyl)dibenzene (4p): following the general procedure, the reaction of 2-(3-bromophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 80.4 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclcopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4p (38.9 mg, 50% yield) as a colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.34–7.30 (m, 2H), 7.27–7.19 (m, 6H), 7.18–7.11 (m, 3H), 7.07–7.05 (m, 1H), 6.92 (t, J = 7.8 Hz, 1H), 6.63–6.60 (m, 1H), 5.86–5.78 (m, 1H), 5.13–5.07 (m, 1H), 5.03–4.99 (m, 1H), 2.75 (d, J = 9.6 Hz, 1H), 2.66–2.59 (m, 1H), 2.28–2.21 (m, 1H), 2.12–2.07 (m, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 148.58, 140.75, 137.23, 137.15, 132.85, 131.85, 128.81, 128.50, 128.42, 128.37, 127.96, 127.50, 126.82, 126.04, 121.60, 115.50, 41.28, 34.74, 32.05, 29.89.

**HRMS (ESI-TOF) (m/z):** Caled for C$_{24}$H$_{21}$Br ([M + H]$^+$), 389.0899; found 389.0902.

((2S*,3S*)-2-Allyl-3-(2-methoxyphenyl)cyclopropane-1,1-diyl)dibenzene (4q): following the general procedure, the reaction of 2-(2-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclcopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4q (10.9 mg, 16% yield) as a colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.48 (d, J = 7.8 z, 2H), 7.29–7.26 (m, 2H), 7.17–7.08 (m, 7H), 6.91 (d, J = 7.8 Hz, 1H), 6.66 (t, J = 7.8 Hz, 1H), 6.60 (d, J = 7.2 Hz, 1H), 5.99–5.91 (m, 1H), 5.19–5.04 (m, 2H), 3.91 (s, 3H), 3.15 (d, J = 9.6 Hz, 1H), 2.64–2.54 (m, 1H), 2.43–2.35 (m, 1H), 2.13–2.06 (m, 1H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ 159.15, 149.51, 139.27, 138.01, 131.32, 128.81, 128.28, 127.93, 127.06, 126.56, 126.06, 125.74, 119.63, 115.22, 110.04, 77.21, 77.00, 76.79, 55.53, 39.66, 30.82, 30.27, 27.59. **HRMS (ESI-TOF) (m/z):** Caled for C$_{25}$H$_{25}$O ([M + H]$^+$), 341.1900; found 341.1904.
((2S*,3S*)-2- Allyl-3-(3,5-dimethylphenyl)cyclopropane-1,1-diyl)dibenzene (4r): following the general procedure, the reaction of 2-(3,5-dimethylphenyl)-5,5- dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 65.0 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 83.4 mg) afforded 4r (39.2 mg, 58% yield) as a colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.27–7.24 (m, 2H), 7.18–7.13 (m, 4H), 7.13–7.09 (m, 3H), 7.06–7.03 (m, 1H), 6.70 (s, 1H), 6.34 (s, 2H), 5.82–5.74 (m, 1H), 5.07–5.01 (m, 1H), 4.95–4.91 (m, 1H), 2.66 (d, $J = 9.6$ Hz, 1H), 2.54–2.47 (m, 1H), 2.25–2.17 (m, 1H), 2.08 (s, 6H), 2.00–1.93 (m, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 149.24, 137.99, 137.97, 137.88, 136.71, 132.10, 128.44, 128.09, 127.85, 127.66, 127.07, 126.50, 125.83, 115.19, 40.72, 35.24, 31.82, 30.24, 21.40.

HRMS (ESI-TOF) (m/z): Calcd for C$_{26}$H$_{26}$ ([M + H]$^+$), 339.2107; found 339.2105.

5-((1S*,3S*)-3-Allyl-2,2-diphenylcyclopropyl)benzo[d][1,3]dioxole (4s): following the general procedure, the reaction of 2-(benzo[d][1,3] dioxol-5-yl)-5,5-dimethyl-1,3,2-dioxa-borinane (0.30 mmol, 1.5 equiv., 70.2 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4s (28.4 mg, 40% yield) as a colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.25–7.22 (m, 2H), 7.19–7.14 (m, 4H), 7.14–7.09 (m, 3H), 7.07–7.03 (m, 1H), 6.56 (d, $J = 7.8$ Hz, 1H), 6.37–6.34 (m, 1H), 6.16–6.14 (m, 1H), 5.82–5.79 (m, 2H), 5.79–5.73 (m, 1H), 5.07–5.02 (m, 1H), 4.96–4.92 (m, 1H), 2.68 (d, $J = 9.6$ Hz, 1H), 2.55–2.48 (m, 1H), 2.23–2.15 (m, 1H), 1.98–1.91 (m, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 149.06, 146.85, 145.34, 137.75, 137.55, 131.96, 131.82, 128.41, 128.25, 127.54, 126.61, 125.83, 123.07, 115.25, 109.94, 107.55, 100.71, 40.34, 35.07, 31.43, 30.11.

HRMS (ESI-TOF) (m/z): Calcd for C$_{25}$H$_{22}$O$_2$ ([M + H]$^+$), 355.1692; found 355.1699.

2-((1S*,3S*)-3-Allyl-2,2-diphenylcyclopropyl)naphthalene (4t): following the general procedure, the reaction of 5,5-dimethyl-2-(naphthalen-2-yl)-1,3,2- dioxaborinane (0.30
mmol, 1.5 equiv., 72.0 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4t (49.4 mg, 69% yield) as a colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.69–7.64 (m, 1H), 7.54–7.50 (m, 1H), 7.50–7.46 (m, 1H), 7.32–7.27 (m, 4H), 7.21–7.16 (m, 3H), 7.15–7.11 (m, 5H), 7.08–7.04 (m, 1H), 6.92–6.88 (m, 1H), 5.79–5.70 (m, 1H), 5.06–5.00 (m, 1H), 4.91–4.87 (m, 1H), 2.90 (d, $J = 9.6$ Hz, 1H), 2.67–2.59 (m, 1H), 2.34–2.27 (m, 1H), 2.12–2.05 (m, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 148.99, 137.77, 137.51, 135.86, 132.99, 132.06, 131.56, 128.60, 128.46, 128.28, 128.12, 127.58, 127.57, 127.35, 126.63, 125.91, 125.71, 125.13, 115.31, 41.08, 35.52, 32.22, 30.22.

HRMS (ESI-TOF) ($m/z$): Calcd for C$_{28}$H$_{24}$ ([M + H]$^+$), 361.1950; found 361.1948.

1-((1S*,3S*)-3-Allyl-2,2-diphenylcyclopropyl)naphthalene (4u): following the general procedure, the reaction of 5,5-dimethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 72.0 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4u (12.3 mg, 17% yield) as a colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.22–8.18 (m, 1H), 7.89–7.85 (m, 1H), 7.71–7.67 (m, 1H), 7.52–7.47 (m, 2H), 7.37–7.30 (m, 4H), 7.24–7.18 (m, 2H), 7.14–7.10 (m, 1H), 7.09–7.01 (m, 3H), 6.96–6.92 (m, 2H), 6.07–5.98 (m, 1H), 5.25–5.20 (m, 1H), 5.12–5.08 (m, 1H), 3.23–3.19 (m, 1H), 2.59–2.52 (m, 1H), 2.51–2.43 (m, 2H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 148.62, 138.84, 137.97, 134.61, 134.42, 133.62, 131.64, 128.82, 128.51, 127.85, 127.31, 126.66, 126.20, 126.14, 125.81, 125.49, 125.08, 124.69, 115.60, 39.30, 33.36, 31.60, 30.19.

HRMS (ESI-TOF) ($m/z$): Calcd for C$_{28}$H$_{24}$ ([M + H]$^+$), 361.1950; found 361.1948.

3-((1R*,3S*)-3-Allyl-2,2-diphenylcyclopropyl)thiophene (4v): following the general procedure, the reaction of 5,5-dimethyl-2-(thiophen-3-yl)-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 58.8 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4v (11.2 mg, 18% yield) as a white solid.

M.p. 54-56 °C.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.23–7.20 (m, 2H), 7.19–7.16 (m, 4H), 7.15–7.13 (m, 3H), 7.07–7.03 (m, 2H), 6.55 (dd, $J = 4.8$, 1.2 Hz, 1H), 6.34 (dd, $J = 3.0$, 1.2 Hz, 1H), 5.74 (dddd, $J = 17.1$, 10.3, 6.7, 5.4 Hz, 1H), 5.01 (dq, $J = 17.2$, 1.7 Hz, 1H), 4.94–4.90 (m, 1H), 2.90 (d,
$J = 9.6 \text{ Hz}, \ 1\text{H}), 2.51 \ (\text{dtt}, J = 16.1, 6.8, 1.4 \text{ Hz}, \ 1\text{H}), 2.13 \ (\text{dddt}, J = 15.2, 7.3, 5.4, 1.7 \text{ Hz}, \ 1\text{H}), 1.96 - 1.91 \ (m, \ 1\text{H})$.

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 148.62, 138.00, 137.97, 137.44, 132.08, 129.97, 128.40, 128.21, 127.37, 126.65, 125.84, 123.50, 120.92, 115.20, 40.22, 31.30, 31.15, 30.74.

HRMS (ESI-TOF) (m/z): Calcd for C$_{22}$H$_{20}$S ([M + H]$^+$), 317.1358; found 317.1350.

5-((1S*, 3S*)-3-Allyl-2,2-diphenylcyclopropyl)-1-methyl-1H-indole (4w): following the general procedure, the reaction of 5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-1-methyl-1H-indole (0.30 mmol, 1.5 equiv., 72.9 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4w (43.2 mg, 60% yield) as a colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.29–7.25 (m, 2H), 7.17–7.13 (m, 2H), 7.12–7.06 (m, 5H), 7.05–6.98 (m, 3H), 6.86–6.84 (m, 1H), 6.68–6.64 (m, 1H), 6.22–6.19 (m, 1H), 5.81–5.72 (m, 1H), 5.05–5.01 (m, 1H), 4.91–4.85 (m, 1H), 3.59 (s, 3H), 2.85 (d, $J = 10.2$ Hz, 1H), 2.59–2.51 (m, 1H), 2.34–2.26 (m, 1H), 2.03–1.95 (m, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 149.55, 138.31, 138.01, 135.07, 132.16, 128.66, 128.45, 128.34, 128.04, 127.65, 126.53, 124.12, 121.63, 115.00, 108.13, 100.61, 40.00, 35.69, 32.71, 31.47, 30.35.

HRMS (ESI-TOF) (m/z): Calcd for C$_{27}$H$_{25}$N ([M + H]$^+$), 364.2059; found 364.2052.

4,4'-(2S*,3S*)-2-Allyl-3-(4-chlorophenyl)cyclopropane-1,1-diylbis(methylbenzene) (4x): following the general procedure, the reaction of 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.20 mmol, 1.0 equiv., 44.8 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 4,4'-(cycloprop-2-ene-1,1-diyl) bis (methylbenzene) (0.30 mmol, 1.5 equiv., 66.0 mg) afforded 4x (37.6 mg, 50% yield) as a colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.20–7.16 (m, 2H), 7.11–7.08 (m, 2H), 7.06–7.01 (m, 6H), 6.76–6.72 (m, 2H), 5.8–5.75 (m, 1H), 5.11–5.05 (m, 1H), 5.00–4.95 (m, 1H), 2.71 (d, $J = 9.6$ Hz, 1H), 2.64–2.56 (m, 1H), 2.31–2.25 (m, 6H), 2.25–2.18 (m, 1H), 2.07–2.01 (m, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 146.11, 137.33, 136.99, 136.21, 135.47, 134.42, 131.67, 131.09, 130.90, 129.12, 127.50, 127.24, 115.30, 40.28, 34.64, 31.80, 29.90, 21.11, 20.88.

HRMS (ESI-TOF) (m/z): Calcd for C$_{26}$H$_{26}$Cl ([M + H]$^+$), 373.1718; found 373.1719.
4,4’-((2S*,3S*)-2-Allyl-3-(4-chlorophenyl)cyclopropane-1,1-diyl)bis(methoxybenzene) (4y): following the general procedure, the reaction of 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.20 mmol, 1.0 equiv., 44.8 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 4,4’-(cycloprop-2-ene-1,1-diyl)bis(methoxybenzene) (0.30 mmol, 1.5 equiv., 75.6 mg) afforded 4y (46.5 mg, 58% yield) as a yellow solid. M.p. 38-40 °C.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.22–7.18 (m, 2H), 7.12–7.08 (m, 2H), 7.06–7.03 (m, 2H), 6.80–6.76 (m, 4H), 6.75–6.72 (m, 2H), 5.84–5.76 (m, 1H), 5.11–5.06 (m, 1H), 5.01–4.97 (m, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 2.69 (d, $J = 9.6$ Hz, 1H), 2.61–2.54 (m, 1H), 2.25–2.18 (m, 1H), 2.04–1.99 (m, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 146.13, 137.34, 137.01, 136.22, 135.48, 134.45, 131.69, 131.11, 129.13, 129.51, 127.25, 115.31, 40.29, 34.66, 31.82, 29.91, 21.11, 20.88.

HRMS (ESI-TOF) (m/z): Calcd for C$_{26}$H$_{26}$ClO$_2$ ([M + H]$^+$), 405.1616; found 405.1625.

4,4’-((2S*,3S*)-2-Allyl-3-(4-chlorophenyl)cyclopropane-1,1-diyl)bis(fluorobenzene) (4z): following the general procedure, the reaction of 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 67.3 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 4,4’-(cycloprop-2-ene-1,1-diyl)bis(fluorobenzene) (0.20 mmol, 1.0 equiv., 45.6 mg) afforded 4z (57 mg, 75% yield) as a colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.26–7.22 (m, 2H), 7.14–7.07 (m, 4H), 6.97–6.90 (m, 4H), 6.75–6.70 (m, 2H), 5.85–5.76 (m, 1H), 5.13–5.07 (m, 1H), 5.05–4.99 (m, 1H), 2.72 (d, $J = 9.6$ Hz, 1H), 2.61–2.52 (m, 1H), 2.28–2.20 (m, 1H), 2.07–2.01 (m, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 161.69 (d, $J = 245.0$ Hz), 144.30 (d, $J = 3.0$ Hz), 136.91, 136.24, 133.30 (d, $J = 7.8$ Hz), 133.14 (d, $J = 3.5$ Hz), 131.55, 130.80, 128.94 (d, $J = 8.0$ Hz), 127.76, 115.56 (d, $J = 29.3$ Hz), 115.47 (d, $J = 28.2$ Hz), 115.24, 39.51, 34.67, 31.89, 29.78.

$^{19}$F NMR (470 MHz, CDCl$_3$) δ –115.07 (tt, $J = 8.5$, 5.6 Hz, 1F), –116.66 (tt, $J = 8.5$, 5.2 Hz, 1F).

HRMS (ESI-TOF) (m/z): Calcd for C$_{24}$H$_{19}$ClF$_2$ ([M + H]$^+$), 381.1216; found 381.1208.
4,4',4''-((2S*,3S*)-3-Allylcyclopropane-1,1,2-triy)tris(chlorobenzene) (4za): following the general procedure, the reaction of 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 67.3 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 4,4'-(cycloprop-2-ene-1,1-diyl)bis(chlorobenzene) (0.20 mmol, 1.0 equiv., 52.0 mg) afforded 4za (55.4 mg, 67% yield) as a yellow solid. M.p. 98-100 °C.

\[ \text{^1}H \text{ NMR (600 MHz, CDCl}_3\text{)} \delta 7.25-7.18 (m, 6H), 7.15-7.11 (m, 2H), 7.07-7.03 (m, 2H), 6.75-6.72 (m, 2H), 5.84-5.76 (m, 1H), 5.12-5.07 (m, 1H), 5.04-5.00 (m, 1H), 2.72 (d, J = 10.2 Hz, 1H), 2.59-2.52 (m, 1H), 2.27-2.21 (m, 1H), 2.08-2.03 (m, 1H).

\[ \text{^13}C \text{ NMR (151 MHz, CDCl}_3\text{)} \delta 146.60, 136.75, 135.92, 135.57, 133.12, 133.01, 131.98, 131.69, 130.80, 128.81, 128.76, 128.69, 127.84, 115.81, 39.62, 34.77, 31.82, 29.74.

\[ \text{HRMS (ESI-TOF) (m/z): Calcd for C}_{24}\text{H}_{19}\text{Cl}_3 ([M + H]^+), 413.0625; found 413.0620.}

4,4',((2S*,3S*)-2-Allyl-3-(4-chlorophenyl)cyclopropane-1,1-diy)bis(bromobenzene)(4zb): following the general procedure, the reaction of 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 67.3 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 4,4'-(cycloprop-2-ene-1,1-diyl) bis(bromobenzene) (0.20 mmol, 1.0 equiv., 69.5 mg) afforded 4zb (79 mg, 79% yield) as a colorless oil.

\[ \text{^1}H \text{ NMR (600 MHz, CDCl}_3\text{)} \delta 7.40-7.34 (m, 4H), 7.15-7.11 (m, 4H), 7.01-6.96 (m, 2H), 6.76-6.72 (m, 2H), 5.84-5.75 (m, 1H), 5.12-5.06 (m, 1H), 5.05-5.00 (m, 1H), 2.72 (d, J = 9.6 Hz, 1H), 2.58-2.51 (m, 1H), 2.28-2.20 (m, 1H), 2.08-2.02 (m, 1H).

\[ \text{^13}C \text{ NMR (151 MHz, CDCl}_3\text{)} \delta 147.02, 136.70, 136.00, 135.85, 133.48, 131.77, 131.71, 131.64, 130.79, 129.14, 127.85, 121.23, 120.04, 115.83, 39.74, 34.73, 31.74, 29.72.

\[ \text{HRMS (ESI-TOF) (m/z): Calcd for C}_{24}\text{H}_{19}\text{Br}_2\text{Cl ([M + H]^+), 500.9614; found 500.9606.}

4,4',((2S*,3S*)-2-Allyl-3-(4-chlorophenyl)spiro[cyclopropane-1,9'-fluorene] (4zc): following the general procedure, the reaction of 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 67.3 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and spiro[cyclopropane-1,9'-fluoren]-2-ene (0.20 mmol, 1.0 equiv., 38.0 mg) afforded 4zc (44.7 mg, 65% yield) as a white solid. M.p. 45-47°C.
\textbf{H NMR} (600 MHz, CDCl$_3$) $\delta$ 7.89–7.83 (m, 2H), 7.41–7.30 (m, 3H), 7.26–7.21 (m, 2H), 7.16–7.12 (m, 1H), 7.05–6.97 (m, 3H), 6.25 (d, $J$ = 7.8 Hz, 1H), 5.70–5.61 (m, 1H), 4.94–4.89 (m, 1H), 4.89–4.85 (m, 1H), 3.42 (d, $J$ = 8.4 Hz, 1H), 2.70–2.62 (m, 1H), 2.38–2.31 (m, 2H).

\textbf{C NMR} (151 MHz, CDCl$_3$) $\delta$ 148.82, 141.44, 141.41, 139.12, 136.57, 132.82, 132.77, 132.73, 128.35, 127.01, 126.07, 125.90, 125.53, 125.09, 119.93, 119.63, 118.37, 115.52, 37.74, 35.87, 33.60, 29.51.

\textbf{HRMS} (ESI-TOF) ($m/z$): Calcd for C$_{24}$H$_{19}$Cl ([M + H]$^+$), 343.1248; found 343.1256.

1-((1S*,2R*,3S*)-3-allyl-2-(4-bromophenyl)-2-methylcyclopropyl)-4-methoxybenzene (4zd): following the general procedure, the reaction of 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinan (0.30 mmol, 1.5 equiv., 66.6 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 1-bromo-4-(1-methyl-cycloprop-2-en-1-yl)benzene (0.20 mmol, 1.0 equiv., 41.5 mg) afforded 4zd (28.5 mg, 40% yield, 84:16 d.r.) as a colorless oil.

\textbf{H NMR} (600 MHz, CDCl$_3$) $\delta$ 7.46-7.41 (m, 2H), 7.40-7.37 (0.48H, ArH of the minor isomer), 7.28-7.23 (m, 2H), 7.22-7.17 (m, 2H), 7.01-6.97 (m, 0.44H, ArH of the minor isomer), 6.91-6.84 (m, 2H), 6.68-6.63 (m, 0.38H), 6.62-6.58 (m, 0.36H, ArH of the minor isomer), 6.00 (ddt, $J$ = 17.4, 10.8, 6.0 Hz, 1H), 5.71 (ddt, $J$ = 17.4, 10.8, 6.0 Hz, 0.19H, C=CH of the minor isomer), 5.18-5.10 (m, 1H), 5.10-5.05 (m, 1H), 5.04-4.99 (m, 0.23H, C=CH of the minor isomer), 4.96-4.91 (m, 0.19H, C=CH of the minor isomer), 3.80 (s, 3H), 3.93 (s, 0.54H, OMe of the minor isomer), 2.45-2.36 (m, 2H), 2.36-2.30 (m, 0.21H), 2.20 (d, $J$ = 9.6 Hz, 0.20H), 2.08-1.96 (m, 1.22H), 1.51-1.46 (m, 1H), 1.46 (s, 0.6H, Me of the minor isomer), 1.19 (s, 3H);

\textbf{C NMR} (151 MHz, CDCl$_3$) $\delta$ (peaks of isomers were recorded together and not assigned to each isomer) 158.09, 157.23, 148.42, 139.23, 137.99, 137.82, 132.84, 131.81, 131.40, 131.39, 130.26, 130.20, 129.22, 128.82, 120.18, 119.36, 115.10, 114.79, 113.73, 112.92, 55.21, 55.08, 33.37, 33.13, 30.93, 30.71, 30.59, 30.22, 29.78, 27.91, 27.68, 17.47.

\textbf{HRMS} (ESI-TOF) ($m/z$): Calcd for C$_{20}$H$_{19}$ClO ([M + H]$^+$), 357.0849; found 357.0856.

2-((1R*,2S*,3S*)-2-allyl-3-(4-chlorophenyl)-1-methylcyclopropyl)naphthalene (4ze): following the general procedure, the reaction of 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinan (0.30 mmol, 1.5 equiv., 66.6 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 2-(1-methylcycloprop-2-en-1-yl)naphthalene (0.20 mmol, 1.0 equiv.,
36.0 mg) afforded 4ze (15.7 mg, 24% yield, 78:22 d.r.) as a colorless oil.

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (overlapped peaks of isomers were assigned together) 7.86-7.77 (m, 4.3H), 7.77-7.71 (m, 0.6H), 7.63 (s, 0.3H), 7.55-7.50 (m, 1H), 7.50-7.41 (m, 2.6H), 7.36-7.27 (m, 4H), 7.22-7.17 (m, 0.3H), 7.02-6.97 (m, 0.6H), 6.64-6.58 (m, 0.6H), 6.06 (ddt, \(J = 17.4, 10.8, 6.0\) Hz, 1H), 5.72 (ddt, \(J = 17.4, 10.8, 6.0\) Hz, 0.3H), 5.24-5.17 (m, 1H), 5.16-5.09 (m, 1H), 5.07-5.01 (m, 0.3H), 4.99-4.93 (m, 0.3H), 2.54 (d, \(J = 9.6\) Hz, 1H), 2.51 (t, \(J = 6.0\) Hz, 0.3H), 2.47-2.37 (m, 1H), 2.32-2.24 (m, 0.3H), 2.13-2.01 (m, 1.3H); 1.67 (dt, \(J = 9.0, 6.0\) Hz, 1H), 1.60-1.56 (m, 0.3H), 1.56 (s, 1H, methyl of the minor isomer), 1.30 (s, 3H, methyl of the major isomer); 

\(^13\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) (peaks correspond to both isomers and are not assigned to each isomer) 146.29, 137.87, 137.62, 137.36, 137.23, 135.81, 135.6, 133.55, 133.52, 132.31, 132.13, 132.10, 131.96, 130.72, 130.50, 129.53, 129.16, 128.46, 128.14, 127.95, 127.71, 127.64, 127.58, 127.55, 127.40, 126.26, 126.07, 125.82, 125.66, 125.45, 125.40, 115.30, 114.98, 33.63, 33.31, 32.55, 31.60, 30.57, 30.28, 29.73, 28.54, 27.61, 17.68.

HRMS (ESI-TOF) (m/z): Calcd for C\(_{23}\)H\(_{21}\)Cl ([M + H])\(^+\), 333.1405; found 333.1412.

\((1R,2S*,3S*)\)-2-Allyl-3-(4-chlorophenyl)-3',4'-dihydro-2'H-spiro[cyclopropane-1,1'-naphthalene] (4zf): following the general procedure, the reaction of 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 67.3 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3',4'-dihydro-2'H-spiro[cyclopropane-1,1'-naphthalene]-2-ene (0.20 mmol, 1.0 equiv., 31.2 mg) afforded 4zf (27 mg, 44% yield) as a colorless oil.

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.28–7.25 (m, 2H), 7.23–7.19 (m, 2H), 7.19–7.14 (m, 1H), 7.11–7.06 (m, 2H), 6.85 (d, \(J = 7.8\) Hz, 1H), 6.03–5.94 (m, 1H), 5.14–5.08 (m, 1H), 5.07–5.03 (m, 1H), 2.93–2.80 (m, 2H), 2.57 (d, \(J = 9.6\) Hz, 1H), 2.40–2.33 (m, 1H), 2.21–2.14 (m, 1H), 1.87–1.81 (m, 2H), 1.68–1.62 (m, 1H), 1.55–1.52 (m, 2H).

\(^13\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 142.42, 137.79, 137.45, 135.55, 132.06, 132.01, 128.82, 128.39, 126.37, 124.75, 121.83, 115.24, 35.35, 32.16, 30.82, 29.77, 25.37, 25.11, 22.16.

HRMS (ESI-TOF) (m/z): Calcd for C\(_{21}\)H\(_{21}\)Cl ([M + H])\(^+\), 309.1404; found 309.1409.

\((2S*,3S*)\)-2-(4-Methoxyphenyl)-3-(2-methylallyl)cyclopropane-1,1-diyldibenzene (4zg): following the general procedure, the reaction of 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg), 3-bromo-2-methylprop-1-ene (0.60 mmol, 3.0 equiv., 81.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg)
afforded 4zg (47.5 mg, 67% yield) as a colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.27–7.23 (m, 2H), 7.18–7.09 (m, 7H), 7.06–7.01 (m, 1H), 6.67–6.59 (m, 4H), 4.80 (s, 1H), 4.71 (s, 1H), 3.66 (s, 3H), 2.73 (d, $J = 9.6$ Hz, 1H), 2.49–2.40 (m, 1H), 2.12–2.01 (m, 2H), 1.61 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 157.43, 149.29, 145.27, 138.03, 132.05, 130.73, 130.11, 128.39, 128.18, 127.45, 126.44, 125.72, 112.89, 110.33, 55.08, 39.68, 34.79, 33.39, 30.63, 23.48.

HRMS (ESI-TOF) ($m$/z): Calcd for C$_{26}$H$_{26}$NaO ([M + Na$^+$]), 377.1863; found 377.1876.

((2S*,3S*)-2-(4-Methoxyphenyl)-3-(2-methylenebutyl)cyclopropane-1,1-diyl)dibenzene (4zh): following the general procedure, the reaction of 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg), 2-(bromomethyl) but-1-ene (0.60 mmol, 3.0 equiv., 88.8 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4zh (51.4 mg, 70% yield) as a colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.27–7.23 (m, 2H), 7.1–7.13 (m, 4H), 7.13–7.09 (m, 3H), 7.07–7.03 (m, 1H), 6.67–6.63 (m, 2H), 6.63–6.59 (m, 2H), 4.85 (s, 1H), 4.73 (s, 1H), 3.67 (s, 3H), 2.74 (d, $J = 9.6$ Hz, 1H), 2.48–2.41 (m, 1H), 2.13–2.04 (m, 2H), 1.97–1.86 (m, 2H), 0.92–0.87 (t, $J = 7.8$ Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 157.41, 151.87, 149.30, 138.02, 132.07, 130.73, 130.13, 128.38, 128.16, 127.43, 126.44, 125.70, 112.87, 108.22, 55.09, 39.68, 34.84, 31.88, 30.61, 29.84, 12.51.

HRMS (ESI-TOF) ($m$/z): Calcd for C$_{27}$H$_{26}$NaO ([M + Na$^+$]), 391.2032; found 391.2033.

((2S*,3S*)-2-(2-Bromoallyl)-3-(4-methoxyphenyl)cyclopropane-1,1-diyl)dibenzene (4zi): following the general procedure, the reaction of 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg), 2,3- dibromoprop-1-ene (0.60 mmol, 3.0 equiv., 88.8 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4zi (56.0 mg, 67% yield) as a colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.30–7.26 (m, 2H), 7.20–7.15 (m, 4H), 7.15–7.10 (m, 3H), 7.08–7.04 (m, 1H), 6.62 (s, 4H), 5.45 (s, 1H), 5.31 (s, 1H), 3.67 (s, 3H), 2.95–2.89 (m, 1H), 2.76 (d, $J = 9.6$ Hz, 1H), 2.57–2.51 (m, 1H), 2.21–2.15 (m, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 157.62, 148.68, 137.51, 132.92, 131.82, 130.63, 129.17, 128.49, 128.37, 127.56, 126.70, 126.00, 117.02, 113.04, 55.11, 39.93, 37.77, 34.35, 30.35.

HRMS (ESI-TOF) ($m$/z): Calcd for C$_{25}$H$_{23}$BrO ([M + H$^+$]), 419.1005; found 419.1012.
((2S*,3S*)-2-(4-methoxyphenyl)-3-(3-methylbut-2-en-1-yl)cyclopropane-1,1-diyl)dibenzen (4zj): following the general procedure, the reaction of 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg), 1-bromo-3-methylbut-2-ene (0.60 mmol, 3.0 equiv., 89.4 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4zj (44.2 mg, 60% yield) as a colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.22–7.19 (m, 2H), 7.17–7.12 (m, 4H), 7.12–7.06 (m, 3H), 7.05–7.00 (m, 1H), 6.70–6.65 (m, 2H), 6.64–6.60 (m, 2H), 5.15–5.10 (m, 1H), 3.67 (s, 3H), 2.64 (d, $J$ = 9.6 Hz, 1H), 2.47–2.40 (m, 1H), 2.11–2.03 (m, 1H), 1.91–1.85 (m, 1H), 1.61 (s, 3H), 1.49 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 157.40, 149.40, 139.00, 132.25, 131.97, 130.68, 130.29, 128.32, 128.16, 127.50, 126.37, 125.64, 123.59, 112.96, 55.10, 40.24, 34.92, 33.07, 25.79, 24.77, 18.05.

HRMS (ESI-TOF) ($m/z$): Calcd for C$_{27}$H$_{28}$O ($[M + H]^+$), 369.2212; found 369.2220.

((2S*,3S*)-2-((E)-3,7-Dimethyllocta-2,6-dien-1-yl)-3-(4-methoxyphenyl)cyclopropane-1,1-diyl)dibenzen (4zk): following the general procedure, the reaction of 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg), (E)-1-bromo-3,7-dimethyllocta-2,6- diene (0.60 mmol, 1.5 equiv., 64.8 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4zk (35.8 mg, 41% yield) as a white solid. M.p.116-119°C.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.32–7.29 (m, 2H), 7.25–7.20 (m, 4H), 7.19–7.15 (m, 3H), 7.13–7.09 (m, 1H), 6.78–6.74 (m, 2H), 6.71–6.68 (m, 2H), 5.26–5.22 (m, 1H), 5.12–5.07 (m, 1H), 3.75 (s, 3H), 2.72 (d, $J$ = 10.2 Hz, 1H), 2.53–2.46 (m, 1H), 2.20–2.13 (m, 1H), 2.12–2.04 (m, 2H), 2.04–1.92 (m, 3H), 1.68–1.66 (m, 3H), 1.61–1.59 (m, 3H), 1.57–1.54 (m, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 157.39, 149.45, 139.08, 135.55, 132.20, 131.34, 130.68, 130.30, 128.33, 128.16, 127.60, 126.34, 125.65, 124.26, 123.68, 112.95, 55.10, 40.34, 39.67, 34.78, 32.99, 26.59, 25.70, 24.67, 17.71, 16.34.

HRMS (ESI-TOF) ($m/z$): Calcd for C$_{32}$H$_{36}$O ($[M + H]^+$), 437.2838; found 437.2846.

((2S*,3S*)-2-((S)-Cyclohex-2-en-1-yl)-3-(4-methoxyphenyl)cyclopropane-1,1-diyl)dibenzen (4zi)
ene (4zl): following the general procedure, the reaction of 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg), 1-(bromomethyl)cyclohex-1-ene (0.60 mmol, 3.0 equiv., 96.6 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4zl (47.7 mg, 63% yield, 5:3 d.r.) as a colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (most peaks of the two diastereomers overlap and have been integrated and assigned together) 7.31–7.21 (m, 3.51H), 7.18–7.06 (m, 11.7H), 7.06–7.00 (m, 1.72H), 6.69–6.64 (m, 1.25H), 6.63–6.57 (m, 5.20H), 6.19–6.14 (m, 1H, $H_a$ (vinyl) of the major isomer), 5.82–5.76 (m, 1H, $H_b$ (vinyl) of the major isomer), 5.50–5.44 (m, 1H, $H_b$ (vinyl) of the minor isomer), 5.07–5.02 (m, 1H, $H_a$ (vinyl) of the major isomer), 3.67 (s, 5H), 2.65 (d, $J = 10.2$ Hz, 0.60H), 2.63 (d, $J = 9.6$ Hz, 1H), 2.43–2.35 (m, 0.6H), 2.35–2.27 (m, 1H), 2.27–2.21 (m, 0.6H), 2.04–1.83 (m, 3.6H), 1.83–1.72 (m, 2H), 1.72–1.65 (m, 1H), 1.64–1.55 (m, 0.8H), 1.55–1.47 (m, 1.2H), 1.31–1.21 (m, 2.3H), 1.11–1.00 (m, 1H), 0.84–0.76 (m, 0.50H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ (peaks of each diastereomer were not assigned) $\delta$ 157.42, 157.37, 149.48, 149.47, 138.36, 138.23, 132.03, 131.89, 131.71, 130.62, 130.60, 130.52, 130.35, 130.23, 128.36, 128.25, 128.22, 128.20, 127.81, 127.72, 127.57, 126.40, 126.38, 125.71, 125.69, 112.98, 112.91, 55.07, 41.28, 41.13, 39.01, 38.90, 34.46, 34.18, 31.50, 30.95, 30.72, 28.10, 25.26, 25.07, 21.33, 21.11.

HRMS (ESI-TOF) (m/z): Calcd for C$_{29}$H$_{30}$O ($[M + H]^+$), 395.2369; found 395.2377.

((2S*,3S*)-2-(3,3-Difluoroallyl)-3-(4-methoxyphenyl)cyclopropane-1,1-diyl)dibenzene (4zm): following the general procedure, the reaction of 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg), 3-bromo-3,3-difluoroprop-1-ene (0.60 mmol, 3.0 equiv., 93.5 mg) and 3,3-diphenylcyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4zm (34.6mg, 46% yield) as a colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.23–7.20 (m, 2H), 7.19–7.11 (m, 5H), 7.09–88.67 7.03 (m, 3H), 6.66–6.61 (m, 4H), 3.98–3.89 (m, 1H), 3.67 (s, 3H), 2.67 (d, $J = 9.6$ Hz, 1H), 2.59–2.52 (m, 1H), 2.09–2.01 (m, 1H), 1.93–1.87 (m, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 157.60, 156.06 (t, $^1J_{C,F} = 286.9$ Hz), 148.76, 137.46, 131.92, 130.53, 129.35, 128.44, 128.35, 127.46, 126.67, 125.91, 113.13, 77.26 (t, $^2J_{C,F} = 21.1$ Hz), 55.12, 40.43, 34.45, 31.81 (t, $^4J_{C,F} = 2.3$ Hz), 19.43 (d, $^3J_{C,F} = 4.5$ Hz).

$^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ – 88.67 (d, $^2J_{F,F} = 47.0$ Hz, 1F); – 90.35 (dd, $^2J_{F-F} = 47.0$ Hz, $^3J_{F,H_{(trans)}} = 25.6$ Hz, 1F).

HRMS (ESI-TOF) (m/z): Calcd for C$_{25}$H$_{22}$F$_2$O ($[M + H]^+$), 377.1711; found 377.1719.
((2S*,3S*)-2-(3,3-Difluoroallyl)-3-(4-methoxyphenyl)cyclopropane-1,1-diyldibenzene (4zn): following the general procedure, the reaction of 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinanene (0.30 mmol, 1.5 equiv., 66.0 mg), 3-bromo-2-(bromomethyl)prop-1-ene (0.60 mmol, 3.0 equiv., 127.1mg) and 3,3-diphenylcyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4zn (32.0mg, 37%yield) as a pair of atropoisomeric isomers (ratio: 3:2).

\[ \text{H NMR} \quad (600 MHz, C}_6D_6 \delta \text{ (overlapped peaks of the isomers are assigned together)} \]
7.31-7.22 (m, 4H), 7.16 (s, 4H), 7.14-7.07 (m, 4H), 7.04-6.97 (m, 2H), 6.76-6.70 (m, 2H), 6.65-6.59 (m, 2H), 4.98 (s, 0.4H), 4.96 (s, 0.6H), 4.89 (s, 0.4H), 4.87 (s, 0.6H), 3.64 (d, \( J = 11.4 \) Hz, 0.4H), 3.55 (d, \( J = 10.2 \) Hz, 0.6H), 3.53 (d, \( J = 11.4 \) Hz, 0.4H), 3.44 (d, \( J = 10.2 \) Hz, 0.6H), 3.24 (s, 3H), 2.91 (dd, \( J = 17.4, 6.0 \) Hz, 0.6H), 2.85 (dd, \( J = 16.2, 6.0 \) Hz, 0.4H), 2.74 (d, \( J = 9.6 \) Hz, 1H), 2.40-2.28 (m, 1H), 2.07-2.00 (m, 1H);

\[ \text{C NMR} \quad (151 MHz, CDCl}_3 \delta \text{ (peaks of two isomers were not assigned and recorded together)} \]
157.56, 148.98, 144.72, 144.45, 137.70, 137.68, 131.94, 130.64, 129.63, 128.45, 128.31, 127.39, 127.38, 126.63, 125.86, 115.74, 115.11, 113.01, 113.00, 55.11, 48.89, 39.75, 39.73, 37.33, 34.64, 34.62, 30.24, 30.18, 29.57, 29.21.

\[ \text{HRMS (ESI-TOF) (m/z): Calcd for C}_{25}H_{22}F_2O ([M + H]^+) 433.1162; found 433.1170.} \]

5-((1S*,3S*)-3-benzyl-2,2-diphenylcyclopropyl)-1-methyl-1H-indole (4zo): following the general procedure, the reaction of 5-(5,5-dimethyl- 1,3,2-dioxaborinan-2-yl)-1-methyl-1H-indole (0.30 mmol, 1.5 equiv.,72.9 mg), benzyl bromide (0.60 mmol, 3.0 equiv., 51.0 mg) and 3,3-diphenylcyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded 4zo (19.8 mg, 24% yield) as a colorless oil.

\[ \text{H NMR} \quad (600 MHz, C}_6D_6 \delta \text{ (overlapped peaks of the isomers are assigned together)} \]
7.38-7.30 (m, 2H), 7.30-7.17 (m, 9H), 7.17-7.07 (m, 6H), 7.02-6.94 (m, 1H), 6.85-6.77 (m, 1H), 6.31 (d, \( J = 3.0 \) Hz, 1H), 3.74 (s, 3H), 3.23 (dd, \( J = 15.6, 6.6 \) Hz, 1H), 3.08-2.96 (m, 2H), 2.38-2.30 (m, 1H);

\[ \text{C NMR} \quad (151 MHz, CDCl}_3 \delta \text{ (overlapped peaks of the isomers are assigned together)} \]
149.50, 148.98, 144.72, 144.45, 137.70, 137.68, 131.94, 130.64, 129.63, 128.45, 128.31, 128.43, 128.36, 128.26, 128.10, 128.08, 127.60, 126.33, 125.70, 125.64, 124.43, 121.99, 108.22, 100.71, 39.89, 36.25, 33.43, 32.79, 31.60.

\[ \text{HRMS (ESI-TOF) (m/z): Calcd for C}_{25}H_{22}F_2O ([M + H]^+) 414.2216; found 414.2223.} \]
References


4. NMR spectra and HPLC chromatographs of new compounds
**HPLC traces of (+)-4e.**

HPLC conditions: chiralpak OD-H column, hexanes/i-PrOH = 99/1, 1 mL/min, \( \tau \) (major) = 4.9 min; \( \tau \) (minor) = 5.6 min.

![HPLC traces](image)

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