Electronic Supplementary Information (ESI)

**Copper-Catalyzed Coupling Reaction of Unactivated Secondary Alkyl Iodides with Alkyl Grignard Reagents in the Presence of 1,3-Butadiene as an Effective Additive**

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**Additional Data**

**Condition screening**

Table S1. Screening of conditions

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<tr>
<th>Entry</th>
<th>Additive (1 equiv)</th>
<th>2a (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>3 (%)&lt;sup&gt;b,c&lt;/sup&gt;</th>
<th>4 (%)&lt;sup&gt;b&lt;/sup&gt;</th>
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<tbody>
<tr>
<td>1</td>
<td>1,3-Butadiene</td>
<td>90</td>
<td>1</td>
<td>&lt;1</td>
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<tr>
<td>2</td>
<td>None</td>
<td>56</td>
<td>15</td>
<td>8</td>
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<tr>
<td>3&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1,3-Butadiene</td>
<td>89</td>
<td>1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>4</td>
<td>1,3-Butadiene&lt;sup&gt;e&lt;/sup&gt;</td>
<td>81</td>
<td>2</td>
<td>2</td>
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<td>5</td>
<td>Isoprene</td>
<td>85</td>
<td>2</td>
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<td>1,3-Pentadiene</td>
<td>74</td>
<td>3</td>
<td>1</td>
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<tr>
<td>7&lt;sup&gt;f&lt;/sup&gt;</td>
<td>2,3-Dimethyl-1,3-butadiene</td>
<td>69</td>
<td>5</td>
<td>2</td>
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<td>8</td>
<td>1-Phenyl-1-propyne</td>
<td>69</td>
<td>12</td>
<td>6</td>
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<td>9</td>
<td>1,5-Cyclooctadiene</td>
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<td>10</td>
<td>2,5-Norbornadiene</td>
<td>57</td>
<td>13</td>
<td>6</td>
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<tr>
<td>11&lt;sup&gt;g&lt;/sup&gt;</td>
<td>1,3-Butadiene</td>
<td>N.R.</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>12&lt;sup&gt;g&lt;/sup&gt;</td>
<td>None</td>
<td>N.R.</td>
<td>–</td>
<td>–</td>
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<tr>
<td>13&lt;sup&gt;h&lt;/sup&gt;</td>
<td>1,3-Butadiene</td>
<td>N.D.</td>
<td>2</td>
<td>1</td>
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<sup>a</sup> To a mixture of 1a (0.5 mmol), n-BuMgCl (0.75 mmol, 0.61 M in THF) was added 1,3-butadiene (0.5 mmol, 11.2 mL) and CuI (0.015 mmol) at −78 °C. The reaction was then stirred at 0 °C. In each case, ca. 9-13% yield of n-octane resulted from homocoupling of n-BuMgCl was detected as byproduct. <sup>b</sup> GC yield based on 1a (n-decane as internal standard). <sup>c</sup> Combined GC yields of the olefin byproducts from 1a. <sup>d</sup> 1 mol% CuI. <sup>e</sup> 0.5 equiv. of 1,3-butadiene was used. <sup>f</sup> ca. 10% of 1a was recovered. <sup>g</sup> No CuI; N.R.: no reaction. <sup>h</sup> Et<sub>2</sub>O as solvent; N.D.: not detected; 1a was recovered.

Additional results on condition screening are shown in Table S1. When a catalytic amount of copper(I) iodide was added to a solution of 4-phenylbutan-2-yl iodide (1a), n-BuMgCl (1.5 equiv) and 1,3-butadiene (1 equiv) in THF at −78 °C and then stirred at 0 °C for 4 h, the cross-coupled product 2a was obtained in 90% yield along with a small amount of the elimination products 3 (1%) and the hydrodehalided product 4 (<1%) (Table S1, entry 1). In contrast, the reaction catalyzed by CuI without 1,3-butadiene gave a mixture of 2a (56%), 3 (15%) and 4 (8%) (entry 2), clearly indicating that the presence of 1,3-butadiene is crucial on improving the yield and selectivity. Decreasing the catalytic CuI from 3 mol% to 1 mol% did not affect the reaction giving a good yield of product (entry 3). However, when the reaction was run with 0.5 equiv of 1,3-butadiene, the yield dropped to 81% (entry 4). We also examined other additives. As shown in Table S1, the use of isoprene gave 2a in 85% yield (entry 5), however, somewhat lower yields were observed when 2,3-dimethylbuta-1,3-diene or penta-1,3-diene was employed (entries 6 and 7). Although we have reported that an alkyne is effective additive in the Cu-catalyzed coupling reaction of primary alkyl halides, the use of 3-phenyl 2-propyne in the present reaction gave a moderate yield of 2a but with significant amount of byproducts 3 and 4 (entry 8). Neither 1,5-cyclooctadiene nor 2,5-norbornadiene was effective (entries 9 and 10). In addition, the use of other ligands or additives including...
TMEDA, PPh₃, NMP and PhCN did not improve the yields nor selectivity, and no reaction took place without a copper catalyst (entry 12). This coupling reaction did not proceed in Et₂O as the solvent resulting in a dark blue mixture, and most of the starting material 1a was recovered (entry 13).

Additional screening of substrates

It has been extremely reported that secondary alkyl halides couple with aryl Grignard reagents employing Fe S¹ and Co S² as a catalyst. We thus examined such sp³-sp² cross-coupling reaction though phenyl Grignard reagent retired the present catalyst and 1a was recovered (eq S1). In addition, sp³-sp coupling also resulted in no reaction (eq S2). S³ In the previous report, radical mechanism, namely SET from Fe or Co to secondary alkyl halides to generate alkyl radical intermediates and subsequent recombination with catalyst, was proposed. S¹, S² Based on experimental results (see also: eq 1 and Scheme 2), our Cu/butadiene system should proceed through a different mechanism, which is probably Sn² type mechanism as our previous report.¹¹c No reaction took place when 2-adamantyl iodide was used (eq S3). This result may consistent with proposed mechanism.
**General**

$^1$H NMR and $^{13}$C NMR spectra were recorded with a JEOL ECS-400 (400 MHz and 100 MHz, respectively) spectrometer. Chemical shifts were reported in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were recorded with a JASCO Corporation FT/IR-4200 instrument. Both conventional and high resolution mass spectra were recorded with a JEOL JMS-DX303HF spectrometer. GC Mass spectra (EI) were obtained using a JMS-mate operating in the electron impact mode (70 eV) equipped with a RTX-5 30MX.25MMX.25U column. GC analysis was performed on a Shimadzu GC-2014 instrument equipped with a GL Sciences InertCap 5 capillary column. GC yields were determined using n-decane as an internal standard. Grignard reagents were purchased from Aldrich Chemical Company or Kanto Chemical Company and used after titration by a method reported by Knochel, except for (2-(1,3-dioxolan-2-yl)ethyl)magnesium bromide, pent-4-enylmagnesium bromide and hex-5-enylmagnesium bromide which were prepared from the corresponding alkyl bromides and magnesium in THF. Secondary alkyl iodides were prepared from the corresponding alcohols according to the literature.

**Experimental Procedures and Analytical Data of Products**

**3-Methylheptyl benzene (2a)**

To a mixture of (3-iodobutyl)benzene (0.5 mmol, 130.0 mg) and butylmagnesium chloride (0.75 mmol, $C = 0.61 \text{ M in THF}$) cooled to −78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1.0 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 4 h. After completion as monitored by GC analysis, the reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL×3). The combined organic layers were dried over Na$_2$SO$_4$ and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 77.8 mg of 2a (82%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.29-7.25 (m, 2H), 7.19-7.14 (m, 3H), 2.68-2.52 (m, 2H), 1.68-1.54 (m, 1H), 1.47-1.12 (m, 8H), 0.93-0.87 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.2, 128.3, 128.2, 125.5, 39.0, 36.6, 33.5, 32.5, 29.2, 23.0, 19.6, 14.2.

**3-Methylbutyl benzene (2b)**

To a mixture of (3-iodobutyl)benzene (0.5 mmol, 130.0 mg) and methylmagnesium chloride (0.75 mmol, $C = 2.69 \text{ M in THF}$) cooled to −78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1.0 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 4 h. The reaction was quenched by 1 M HCl aq. Yield of 2b was determined by GC using n-decane as internal standard due to its volatile.

**3,5-Dimethylhexyl benzene (2c)**

To a mixture of (3-iodobutyl)benzene (0.5 mmol, 130.0 mg) and isobutylmagnesium chloride (0.75 mmol, $C = 2.0 \text{ M in THF}$) cooled to −78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I)
iodide (1 mol %, 1.0 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 6 h. The reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL×3). The combined organic layers were dried over Na₂SO₄ and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 78.5 mg of 2c (82%). \(^{1}H\) NMR (400 MHz, CDCl₃) δ 7.28-7.24 (m, 2H), 7.21-7.14 (m, 3H), 2.68-2.51 (m, 2H), 1.70-1.44 (m, 3H), 1.43-1.36 (m, 1H), 1.26-1.14 (m, 1H), 1.06-0.99 (m, 1H), 0.92-0.82 (m, 9H); \(^{13}C\) NMR (100 MHz, CDCl₃) δ 143.2, 128.2, 128.1, 125.5, 46.6, 39.3, 33.4, 30.1, 25.2, 23.4, 22.3, 19.7; IR (neat NaCl, ν/cm⁻¹) 3086, 3063, 3027, 2954, 1939, 1798, 1604, 1455, 1384, 1366, 1169, 1075, 1031, 969, 911, 744, 697; MS (EI) m/z (%) 190 (M⁺, 22), 105 (73), 92 (100); HRMS (EI) m/z calcd for C₁₄H₂₂ 190.1722, found 190.1730.

(3,5,5-Trimethylhexyl)benzene (2d)\(^{10}\)
To a mixture of (3-iodobutyl)benzene (0.5 mmol, 130.0 mg) and neopentylmagnesium chloride (0.75 mmol, C = 2.0 M in THF) and 0.5 mL of THF cooled to −78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1.0 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 6 h. The reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL×3). The combined organic layers were dried over Na₂SO₄ and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 80.2 mg of 2d (79%). \(^{1}H\) NMR (400 MHz, CDCl₃) δ 7.29-7.23 (m, 2H), 7.19-7.14 (m, 3H), 2.66-2.52 (m, 2H), 1.64-1.41 (m, 3H), 1.30-1.26 (m, 1H), 1.11-1.06 (m, 1H), 0.97 (d, J = 6.4 Hz, 3H), 0.88 (s, 9H). \(^{13}C\) NMR (100 MHz, CDCl₃) δ 143.1, 128.2, 128.1, 125.5, 51.2, 41.5, 33.7, 31.1, 30.0, 29.1, 22.6; MS (EI) m/z (%) 190 (M⁺, 22), 105 (73), 92 (100); HRMS (EI) m/z calcd for C₁₄H₂₂ 190.1722, found 190.1730.

(3-Methylhex-5-enyl)benzene (2e)\(^{11}\)
To a mixture of (3-iodobutyl)benzene (0.5 mmol, 130.0 mg) and allylmagnesium chloride (0.75 mmol, C = 0.66 M in THF) cooled to −78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1.0 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 4 h. The reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL×3). The combined organic layers were dried over Na₂SO₄ and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 76.6 mg of 2e (88%). \(^{1}H\) NMR (400 MHz, CDCl₃) δ 7.32-7.26 (m, 2H), 7.19-7.14 (m, 3H), 5.86-5.76 (m, 1H), 5.05-5.01 (m, 2H), 2.73-2.56 (m, 2H), 2.18-2.12 (m, 1H), 2.11-1.96 (m, 1H), 1.73-1.42 (m, 3H), 0.97 (d, J = 6.4 Hz, 6H); \(^{13}C\) NMR (100 MHz, CDCl₃) δ 142.9, 137.4, 128.3, 128.2, 125.6, 115.7, 41.2, 38.4, 33.4, 32.4, 19.3.

(3-Methyloct-7-enyl)benzene (2f)
To a mixture of (3-iodobutyl)benzene (0.5 mmol, 130.0 mg) and pent-4-enylmagnesium bromide (0.75 mmol, C = 0.66 M in THF) cooled to −78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas)
through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1.0 mg), the system was closed, and the reaction was warmed to 0°C and stirred for 6 h. The reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL×3). The combined organic layers were dried over Na₂SO₄ and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 86.8 mg of 2f (86%). ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.24 (m, 2H), 7.21-7.14 (m, 3H), 5.86-5.75 (m, 1H), 5.01-4.92 (m, 1H), 2.68-2.52 (m, 2H), 2.05-2.00 (m, 2H), 1.68-1.58 (m, 1H), 1.50-1.31 (m, 5H), 1.20-1.13 (m, 1H), 0.93 (d, J = 6.0 Hz, 6H); ¹³C NMR (100 Hz, CDCl₃) δ 143.1, 139.1, 128.3, 128.2, 125.5, 114.2, 38.9, 36.3, 34.1, 33.4, 32.3, 26.3, 19.6; IR (neat NaCl, ν/cm⁻¹) 3063, 3026, 2927, 1940, 1820, 1802, 1640, 1603, 1496, 1455, 1377, 1065, 995, 909, 744, 697, 516; MS (EI) m/z 202 (M +, 18), 131 (44), 91 (100); HRMS (EI) m/z calcd for C₁₅H₂₂ 202.1722, found 202.1726.

2-(3-Methyl-5-phenylpentyl)-1,3-dioxolane (2g)
To a mixture of (3-iodobutyl)benzene (0.5 mmol, 130.0 mg) and (2-(1,3-dioxolan-2-yl)ethyl)magnesium bromide (1.0 mmol, = 1.0 M in THF) cooled to −78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (3 mol %, 3.0 mg), the system was closed, and the reaction was stirred at 0 °C for 4 h and 25 °C for another 20 h. The reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL×3). The combined organic layers were dried over Na₂SO₄ and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 70.9 mg of 2g (61%). 19.2 mg of the starting material (3-iodobutyl)benzene was recovered. ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.25 (m, 2H), 7.18-7.14 (m, 3H), 4.83 (t, J = 4.6 Hz, 1H), 3.98-3.82 (m, 4H), 2.69-2.53 (m, 2H), 1.75-1.26 (m, 8H), 0.95 (d, J = 6.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 142.9, 128.3, 128.2, 125.5, 104.9, 64.82, 64.8, 38.7, 33.3, 32.3, 31.4, 30.8, 19.4; IR (neat NaCl, ν/cm⁻¹) 3061, 3026, 2952, 2876, 1728, 1604, 1496, 1455, 1378, 1211, 1140, 1033, 973, 944, 876, 746, 699, 578, 514; MS (Cl) m/z (%) 235 (M+H⁺, 100); HRMS (Cl) m/z calcd for C₁₅H₂₃O₂ (M+H) 235.1698, found 235.1695.

(3-Propylheptyl)benzene (2h)
To a mixture of (3-iodohexyl)benzene (0.5 mmol, 114.1 mg) and butylmagnesium chloride (0.75 mmol, = 0.6 M in THF) cooled to −78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1.0 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 4 h. After completion as monitored by GC analysis, the reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL×3). The combined organic layers were dried over Na₂SO₄ and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 98.2 mg of 2h (85%). ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.23 (m, 2H), 7.19-7.14 (m, 3H), 2.59-2.55 (m, 2H), 1.59-1.53 (m, 2H), 1.35-1.26 (m, 11H), 0.90 (d, J = 6.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.3, 128.3, 128.2, 125.5, 37.1, 35.7, 33.2, 33.1, 28.9, 23.1, 14.2; IR (neat NaCl, ν/cm⁻¹) 3063, 3027, 2925, 2858, 1604, 1496, 1455, 1378, 1031, 902, 744,
697; MS (EI) m/z (%) 218 (M+, 12), 91 (100); HRMS (EI) m/z calcd for C₁₆H₂₆ 218.2035, found 218.2032.

**(3-Ethylhex-5-enyl)benzene (2l)**

To a mixture of (3-iodohex-5-enyl)benzene (0.5 mmol, 143.1 mg) and ethylmagnesium bromide (0.75 mmol, C = 0.56 M in THF) cooled to −78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1.0 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 4 h. The reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL×3). The combined organic layers were dried over Na₂SO₄ and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 65.8 mg of 2l (70%). ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.24 (m, 2H), 7.19-7.15 (m, 3H), 5.83-5.73 (m, 1H), 5.04-4.99 (m, 1H), 2.61-2.57 (m, 2H), 2.12-2.05 (m, 2H), 1.60-1.54 (m, 2H), 1.42-1.32 (m, 3H), 0.88 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.1, 137.3, 128.3, 128.2, 125.6, 115.7, 38.5, 37.5, 34.9, 33.1, 25.6, 10.8.

**(3-Isopropylheptyl)benzene (2m)**

To a mixture of (3-iodo-4-methylpentyl)benzene (0.35 mmol, 100.8 mg) and butylmagnesium chloride (0.52 mmol, C = 0.60 M in THF) cooled to −78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 8.0 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (3 mol %, 2.1 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 6 h. After completion as monitored by GC analysis, the reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL×3). The combined organic layers were dried over Na₂SO₄ and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 60.4 mg of 2m (80%). ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.24 (m, 2H), 7.19-7.15 (m, 3H), 2.65-2.51 (m, 2H), 1.80-1.72 (m, 1H), 1.64-1.55 (m, 1H), 1.52-1.42 (m, 1H), 1.34-1.14 (m, 7H), 0.90 (t, J = 6.2 Hz, 3H), 0.84 (d, J = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): 143.4, 128.3, 128.2, 125.5, 43.4, 34.2, 32.7, 30.1, 29.9, 29.1, 23.1, 19.2, 19.1; IR (neat NaCl, ν/cm⁻¹) 3087, 3063, 3027, 2963, 2927, 2866, 1938, 1867, 1796, 1604, 1496, 1455, 1385, 1367, 1030, 968, 909, 747, 697, 588; MS (EI) m/z (%) 218 (M⁺, 12), 92 (100); HRMS (EI) m/z calcd for C₁₆H₂₆ 218.2135, found 218.2133.

**(3-Allylheptyl)benzene (2n)**

To a mixture of (3-iodohex-5-enyl)benzene (0.5 mmol, 143.1 mg) and butylmagnesium chloride (0.75 mmol, C = 0.60 M in THF) cooled to −78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1.0 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 4 h. The reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL×3). The combined organic layers were dried over Na₂SO₄ and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 105.8 mg of 2n (89%). ¹H NMR (400 MHz,
(3-Allylhex-5-enyl)benzene (2r)
To a mixture of (3-iodohex-5-enyl)benzene (0.5 mmol, 143.1 mg) and allylmagnesium chloride (0.75 mmol, C = 0.65 M in THF) cooled to −78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 4 h. After completion as monitored by GC analysis, the reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL×3). The combined organic layers were dried over Na₂SO₄ and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 86.0 mg of 2s (86%). ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.25 (m, 2H), 7.18-7.16 (m, 3H), 5.83-5.73 (m, 2H), 5.05-5.01 (m, 4H), 2.62 (t, J = 7.3 Hz, 3H), 2.12-2.09 (m, 4H), 1.62-1.55 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 142.8, 136.9, 128.32, 128.27, 125.6, 116.2, 37.6, 36.9, 34.9, 33.0; IR (neat NaCl, v/cm⁻¹) 3074, 3027, 2976, 2926, 2858, 1940, 1822, 1639, 1496, 1454, 1415, 1349, 1029, 994, 911, 745; MS (EI) m/z (%) 200 (M+, 2), 117 (26), 104 (15), 91 (100); HRMS (EI) m/z calcd for C₁₅H₂₀ 200.1565, found 200.1567.

(3-Allyloct-7-enyl)benzene (2s)
To a mixture of (3-iodooct-7-enyl)benzene (0.5 mmol, 157.1 mg) and allylmagnesium chloride (0.75 mmol, C = 0.65 M in THF) cooled to −78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 4 h. After completion as monitored by GC analysis, the reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL×3). The combined organic layers were dried over Na₂SO₄ and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 91.2 mg of 2t (80%). ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.27 (m, 3H), 7.22-7.19 (m, 3H), 5.89-5.76 (m, 2H), 5.01-4.96 (m, 4H), 2.65-2.61 (m, 2H), 2.14-2.04 (m, 4H), 1.65-1.33 (m, 7H); ¹³C NMR (100 MHz, CDCl₃) δ 143.0, 139.0, 137.1, 128.31, 128.26, 125.6, 115.9, 114.3, 37.9, 36.9, 35.3, 34.1, 33.0, 32.7, 25.9; IR (neat NaCl, v/cm⁻¹) 3075, 3027, 2976, 2926, 2858, 1940, 1822, 1639, 1604, 1496, 1455, 1415, 1361, 1031, 993, 910, 745, 698; MS (EI) m/z (%) 228 (M⁺, 2), 117 (26), 104 (15), 91 (100); HRMS (EI) m/z calcd for C₁₇H₂₄ 228.1878, found 228.1879.

(3-(Pent-4-enyl)oct-7-enyl)benzene (2t)
To a mixture of (3-iodooct-7-enyl)benzene (0.5 mmol, 157.1 mg) and pent-4-enylmagnesium bromide (1.0 mmol, C =
0.66 M in THF) cooled to −78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 6 h. The reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL × 3). The combined organic layers were dried over Na2SO4 and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 103.8 mg of 2t (81%). 1H NMR (400 MHz, CDCl3) δ 7.29-7.26 (m, 3H), 7.19-7.15 (m, 3H), 5.87-5.77 (m, 2H), 5.02-4.93 (m, 4H), 2.58 (t, J = 8.2 Hz, 2H), 2.06-2.01 (m, 4H), 1.59-1.54 (m, 2H), 1.40-1.31 (m, 11H); 13C NMR (100 MHz, CDCl3) δ 143.1, 139.1, 128.3, 128.2, 125.5, 114.3, 36.9, 35.6, 34.2, 33.1, 32.9, 25.9; IR (neat NaCl, ν/cm–1) 3076, 3026, 2975, 2927, 2856, 1939, 1820, 1640, 1604, 1496, 1455, 1415, 1369, 1031, 992, 745, 698, 638; MS (EI) m/z (%) 256 (M+, 7), 185 (17), 91 (100); HRMS (EI) m/z calcd for C19H28 256.2191, found 256.2197.

(3-(Pent-4-enyl)non-8-enyl)benzene (2u)
To a mixture of (3-iodooct-7-enyl)benzene (1.0 mmol, 314.2 mg) and hex-5-enylmagnesium bromide (2 mmol, C = 0.66 M in THF) cooled to −78 °C, was introduced 1 equiv. of 1,3-butadiene (1 mmol, 22.4 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 2.0 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 6 h. The reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL × 3). The combined organic layers were dried over Na2SO4 and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 195.8 mg of 2u (73%). 1H NMR (400 MHz, CDCl3) δ 7.29-7.24 (m, 3H), 7.18-7.15 (m, 3H), 5.86-5.76 (m, 2H), 5.02-4.93 (m, 4H), 2.59-2.55 (m, 2H), 2.08-2.00 (m, 4H), 1.59-1.53 (m, 2H), 1.40-1.30 (m, 11H); 13C NMR (100 MHz, CDCl3) δ 143.2, 139.1, 128.3, 128.2, 125.5, 114.3, 114.2, 37.0, 35.6, 34.2, 33.8, 33.2, 32.9, 29.3, 26.0, 25.9; IR (neat NaCl, ν/cm–1) 3076, 3026, 2975, 2927, 2857, 1940, 1821, 1640, 1496, 1455, 1369, 1031, 992, 909, 745, 698, 641; MS (EI) m/z (%) 270 (M+, 10), 91 (100); HRMS (EI) m/z calcd for C20H30 270.2348, found 270.2349.

(4-Ethylhept-6-en-1-ynyl)benzene (2v)
To a mixture of (4-iodohex-1-ynyl)benzene (0.5 mmol, 142.1 mg) and allylmagnesium chloride (0.75 mmol, C = 0.66 M in THF) cooled to −78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 4 h. After completion as monitored by GC analysis, the reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL × 3). The combined organic layers were dried over Na2SO4 and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 55.6 mg of 2v (56%). 1H NMR (400 MHz, CDCl3) δ 7.41-7.39 (m, 2H), 7.29-7.25 (m, 3H), 5.86-5.75 (m, 1H), 5.10-5.03 (m, 2H), 2.40 (d, J = 6.0 Hz, 2H), 2.20 (t, J = 6.9 Hz, 2H), 1.67-1.58 (m, 1H), 1.53-1.43 (m, 2H), 0.94 (t, J = 7.6 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 136.7, 131.5, 128.1, 127.4, 124.1, 116.4, 88.7, 81.6, 38.9, 37.5, 25.8, 22.9, 11.3; IR (neat
NaCl, ν/cm⁻¹) 3019, 2966, 2924, 2400, 1711, 1490, 1428, 1363, 1216, 928, 956, 670; MS (EI) m/z (%) 198 (M⁺, 15), 169 (83), 142 (68), 115 (100); HRMS (EI) m/z calcd for C₁₅H₁₈ 198.1409, found 198.1410.

(2-(Cyclopent-3-enyl)ethyl)benzene (5a)
To a solution of (3-allylhex-5-enyl)benzene (0.35 mmol, 70.0 mg) in 1 mL of CH₂Cl₂, was added the Grubbs 1st catalyst (5 mol%, 14.3 mg) under N₂. After the reaction was stirred at 40 °C for 24 h, the mixture was concentrated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 55.4 mg of 5a (92%). ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.24 (m, 2H), 7.19-7.15 (m, 3H), 5.67 (s, 2H), 2.63 (t, J = 7.8 Hz, 2H), 2.63-2.48 (m, 2H), 2.31-2.20 (m, 1H), 2.05-1.99 (m, 2H), 1.75-1.69 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 142.8, 129.9, 128.4, 128.2, 128.2, 125.6, 38.9, 38.4, 37.1, 34.7.

4-Phenethylcyclohept-1-ene (5b)
Following a similar procedure as described above from 2s (0.41 mmol, 92.5 mg) afforded 70.6 mg of 5b (87%). ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.25 (m, 2H), 7.18-7.15 (m, 3H), 5.84-5.71 (m, 2H), 2.65-2.59 (m, 2H), 2.21-1.93 (m, 4H), 1.82-1.15 (m, 7H); ¹³C NMR (100 MHz, CDCl₃) δ 143.0, 132.7, 130.4, 128.3, 128.2, 125.5, 38.8, 38.0, 36.9, 34.4, 33.6, 28.8, 25.5. IR (neat NaCl, ν/cm⁻¹): 3085, 3062, 3022, 2918, 1940, 1865, 1799, 1653, 1604, 1496, 1453, 1348, 1280, 1178, 1053, 1117, 1078, 1031, 903, 835, 748, 698, 639, 573; MS (EI) m/z (%) 200 (M⁺, 65), 129 (13), 104 (100), 91 (88), 67 (29); HRMS (EI) m/z calcd for C₁₅H₂₀ 200.1565, found 200.1571.
References


S8 D. H. R. Barton, L. Bohe and X. Lusinchi, Tetrahedron, 1990, 46, 5273.


$^1$H and $^{13}$C NMR Spectra Copies of the Products

Ph

2a

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

Ph

2d

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

Ph

2e

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$^1$H NMR (400MHz, CDCl$_3$)

Ph

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$^{13}$C NMR (100MHz, CDCl$_3$)
$^1$H NMR (400MHz, CDCl$_3$)
$^{13}$C NMR (100MHz, CDCl₃)
$^1$H NMR (400MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)

Electronic Supplementary Material (ESI) for Chemical Communications
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$^1$H NMR (400MHz, CDCl$_3$)
$^{13}$C NMR (100MHz, CDCl$_3$)
$^1$H NMR (400MHz, CDCl$_3$)
$^{13}$C NMR (100MHz, CDCl$_3$)
$^1$H NMR (400MHz, CDCl$_3$)
$^{13}$C NMR (100MHz, CDCl$_3$)
$^{13}$C NMR (100MHz, CDCl$_3$)

Ph

$2r$

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$^1$H NMR (400MHz, CDCl$_3$)
13C NMR (100 MHz, CDCl₃)
$^{13}$C NMR (100MHz, CDCl$_3$)
1H NMR (400 MHz, CDCl3)

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

Ph

2v

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

Ph

5a
$^1$H NMR (400MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)