SUPPORTING INFORMATION
for
Straightforward Synthesis of Phenanthrenes from Styrenes and Arenes

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Contents

Table of Contents S1.
General Experimental Section S2.
General Experimental Procedures S3-S5.
Characterization of Products in Details S6-S13.
References S14.
NMR Spectra of Mechanistic Study Experiments S15.
NMR Spectra of Products S16-S55.
General Experimental Section

Analytic methods. $^1$H NMR and $^{13}$C NMR data were obtained on Bruker 400 M nuclear resonance spectrometers unless otherwise specified. CDCl$_3$ as solvent and tetramethylsilane (TMS) as the internal standard were employed. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the $^1$H NMR spectrum as 0.00 ppm. The data of $^1$H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant ($J$ values) in Hz and integration. Chemical shifts for $^{13}$C NMR spectra were recorded in ppm from TMS using the central peak of CDCl$_3$ (77.0 ppm) as the internal standard. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). HRMS (ESI and EI) analyses were performed by Analytical Instrumentation Center, Peking University, and Institute of Chemistry, Chinese Academy of Sciences, respectively. The AuLight™ photoreactor containing CEL-LAM500 high pressure mercury vapor lamp (hpmv) (500 W) was purchased from Beijing Zhongjiao AuLight Co., Ltd.

General preparation for chemicals. Palladium(II) acetate trimer (99.98%) and alkene substrates were purchased from Alfa Aesar. Other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. All the solvents were freshly distilled before used, and all the other reagents were directly used from purchased without any further purification unless otherwise specified.
General Experimental Procedures

General procedure for Pd(II)-catalyzed Heck-type coupling of styrene with benzene. Under air atmosphere, Pd(OAc)$_2$ (0.01 mmol, 2.2 mg), Ag$_2$CO$_3$ (0.24 mmol, 66 mg) and pivalic acid (0.20 mmol, 20 mg) were added into a dried Synthware™ sealed tube with a stir bar. The tube was stopped by a rubber plug and degassed with N$_2$ for three times. Then styrene (0.20 mmol, 21 mg), diisopropylsulfide (0.20 mmol, 24 mg) and benzene (2.0 mL) were added by syringe. Then the tube was sealed by the Teflon™ plug and the mixture was stirred at 120 °C. After 8 h, the reaction was cooled down to room temperature. The resultant mixture was evaporated in vacuum and further purified by flash chromatography on silica gel with petroleum ether to give the product trans-stilbene (30 mg, 82%) as a white solid.

Table S1. Condition screening for Pd(II)-catalyzed Heck-type coupling of styrene with benzene$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>ligand (mol%)</th>
<th>additive (equiv)</th>
<th>oxidant (equiv)</th>
<th>yield (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>—</td>
<td>—</td>
<td>Ag$_2$CO$_3$ (1.2)</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>iPr$_2$S (100)</td>
<td>—</td>
<td>Ag$_2$CO$_3$ (1.2)</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>iPr$_2$S (100)</td>
<td>HOAc (1.0)</td>
<td>Ag$_2$CO$_3$ (1.2)</td>
<td>37</td>
</tr>
<tr>
<td>4</td>
<td>iPr$_2$S (100)</td>
<td>EtCO$_2$H (1.0)</td>
<td>Ag$_2$CO$_3$ (1.2)</td>
<td>80 (78)</td>
</tr>
<tr>
<td>5</td>
<td>iPr$_2$S (100)</td>
<td>PivOH (1.0)</td>
<td>Ag$_2$CO$_3$ (1.2)</td>
<td>85 (82)</td>
</tr>
<tr>
<td>6</td>
<td>iPr$_2$S (100)</td>
<td>—</td>
<td>Phi(OAc)$_2$ (1.2)</td>
<td>34</td>
</tr>
<tr>
<td>7</td>
<td>iPr$_2$S (100)</td>
<td>EtCO$_2$H</td>
<td>Phi(OAc)$_2$ (1.2)</td>
<td>28</td>
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<tr>
<td>8</td>
<td>iPr$_2$S (100)</td>
<td>PivOH</td>
<td>Phi(OAc)$_2$ (1.2)</td>
<td>41</td>
</tr>
<tr>
<td>9</td>
<td>iPr$_2$S (100)</td>
<td>EtCO$_2$H (1.0)</td>
<td>Ag$_2$CO$_3$ (0.1), O$_2$</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>iPr$_2$S (100)</td>
<td>PivOH (1.0)</td>
<td>Ag$_2$CO$_3$ (0.1), O$_2$</td>
<td>9</td>
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<tr>
<td>11</td>
<td>iPr$_2$S (10)</td>
<td>PivOH (1.0)</td>
<td>Ag$_2$CO$_3$ (1.2)</td>
<td>55$^c$</td>
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<tr>
<td>12</td>
<td>PCy$_3$ (100)</td>
<td>PivOH (1.0)</td>
<td>Ag$_2$CO$_3$ (1.2)</td>
<td>5</td>
</tr>
<tr>
<td>13</td>
<td>PCy$_3$ (100)</td>
<td>PivOH (1.0)</td>
<td>Ag$_2$CO$_3$ (1.2)</td>
<td>—</td>
</tr>
<tr>
<td>14</td>
<td>Ph$_2$S (100)</td>
<td>PivOH (1.0)</td>
<td>Ag$_2$CO$_3$ (1.2)</td>
<td>38</td>
</tr>
<tr>
<td>15$^d$</td>
<td>iPr$_2$S (100)</td>
<td>PivOH (1.0)</td>
<td>Ag$_2$CO$_3$ (1.2)</td>
<td>75</td>
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<tr>
<td>16$^{gh}$</td>
<td>iPr$_2$S (100)</td>
<td>PivOH (1.0)</td>
<td>Ag$_2$CO$_3$ (1.2)</td>
<td>6</td>
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<tr>
<td>17$^{ih}$</td>
<td>iPr$_2$S (100)</td>
<td>PivOH (1.0)</td>
<td>Ag$_2$CO$_3$ (1.2)</td>
<td>6</td>
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<tr>
<td>18$^{ih}$</td>
<td>iPr$_2$S (100)</td>
<td>PivOH (1.0)</td>
<td>Ag$_2$CO$_3$ (1.2)</td>
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<tr>
<td>19$^i$</td>
<td>iPr$_2$S (100)</td>
<td>PivOH (1.0)</td>
<td>Ag$_2$CO$_3$ (1.2)</td>
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$^a$ Reactions were conducted with 0.20 mmol of 1a and 2.0 mL of 2a. $^b$ GC yields were given using dodecane as the internal standard. And isolated yields were shown in the parentheses. $^c$ Approx. 35% of triphenylethylene was detected. $^d$ 5.0 mol% of PdCl$_2$ and 50 mol% of LiCl were used. $^e$ Dioxane was used as solvent. $^f$ DMF was used as solvent. $^g$ Acetonitrile was used as solvent. $^h$ In these reactions, 10 equiv of 2a were used. $^i$ The reaction was conducted in the absence of transition-metal catalyst.
General procedure for photo-cyclization of trans-stilbene to phenanthrene. Under air atmosphere, trans-stilbene (0.20 mmol, 36 mg), iodosobenzene diacetate (0.24 mmol, 77 mg) and dioxane (2.0 mL) were added into a dried quartz tube with a stir bar. The mixture was stirred at room temperature in air and simultaneously exposed to light from a 500 W high pressure mercury vapor lamp (hpmv) in the AuLight™ photoreactor. After 8 h, the resultant mixture was evaporated in vacuum and further purified by flash chromatography on silica gel with petroleum ether to give the product phenanthrene (31 mg, 86%) as a white solid.

Table S2. Condition screening of photo-cyclization of trans-stilbene

<table>
<thead>
<tr>
<th>entry</th>
<th>variation from &quot;standard condition&quot;</th>
<th>cis-3aa (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>trans-3aa (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>4aa (%)&lt;sup&gt;b&lt;/sup&gt;</th>
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<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>–</td>
<td>–</td>
<td>87 (85)</td>
</tr>
<tr>
<td>2</td>
<td>Pd(OAc)&lt;sub&gt;2&lt;/sub&gt;, Ph3P, Ph(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>–</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ph3P, Ph(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>–</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Ph(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>–</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>in the absence of Ph(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>–</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Pd(OAc)&lt;sub&gt;2&lt;/sub&gt;, Ph3P, Ph(OAc)&lt;sub&gt;2&lt;/sub&gt;, Ag2CO3</td>
<td>–</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Ph3P, Ph(OAc)&lt;sub&gt;2&lt;/sub&gt;, Ag2CO3</td>
<td>–</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Ag2CO3</td>
<td>–</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>I2</td>
<td>11</td>
<td>7</td>
<td>50</td>
</tr>
<tr>
<td>10</td>
<td>benzene</td>
<td>7</td>
<td>9</td>
<td>44</td>
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<td>11</td>
<td>MeOH</td>
<td>3</td>
<td>2</td>
<td>69 (65)</td>
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<tr>
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<td>68</td>
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<tr>
<td>13</td>
<td>THF</td>
<td>2</td>
<td>1</td>
<td>75 (74)</td>
</tr>
<tr>
<td>14</td>
<td>DCE</td>
<td>1</td>
<td>1</td>
<td>50 (41)</td>
</tr>
<tr>
<td>15</td>
<td>CH2Cl2</td>
<td>3</td>
<td>5</td>
<td>61</td>
</tr>
<tr>
<td>16</td>
<td>decalin</td>
<td>5</td>
<td>3</td>
<td>45</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reactions were conducted with 0.20 mmol of 3aa and 2.0 mL of dioxane. <sup>b</sup>GC yields were given using dodecane as the internal standard. And isolated yields were shown in the parentheses.

General procedure for semi-one-pot synthesis of phenanthrene from styrene and benzene.

Under air atmosphere, Pd(OAc)<sub>2</sub> (0.01 mmol, 2.2 mg), Ag2CO3 (0.24 mmol, 66 mg) and pivalic acid (0.20 mmol, 20 mg) were added into a dried Synthware™ sealed tube with a stir bar. The tube was stopped by a rubber plug and degassed with N₂ for three times. Then styrene (0.20 mmol, 21 mg), diisopropylsulfide (0.20 mmol, 24 mg) and benzene (2.0 mL) were added by syringe. Then the tube was sealed by the Teflon™ plug and the mixture was stirred at 120 °C. After 8 h, the reaction was cooled down to room temperature. The resultant mixture was filtered through a celite plug, evaporated in vacuum and dissolved in dioxane (3.0 mL). The obtained solution was transferred to a dried quartz tube containing iodosobenzene diacetate (0.24 mmol, 77 mg) with a stir bar. The mixture was stirred at room temperature in air and simultaneously exposed to light from a 500 W high pressure mercury vapor lamp (hpmv) in the AuLight™ photoreactor. After 8 h, the resultant mixture was evaporated in vacuum and further...
purified by flash chromatography on silica gel with petroleum ether to give the product phenanthrene (21 mg, 58%) as a white solid.
Characterization of Products in Details

**trans-Stilbene (3aa).** White solid (30 mg, 82%). NMR spectral data of the compound are in accordance with previous report.¹

**(E)-2-Methylstilbene (3ba).** White solid (28 mg, 72%). NMR spectral data of the compound are in accordance with previous report.²

**(E)-3-Methylstilbene (3ca).** White solid (24 mg, 62%). NMR spectral data of the compound are in accordance with previous report.³

**(E)-4-Methylstilbene (3da).** White solid (29 mg, 75%). NMR spectral data of the compound are in accordance with previous report.²⁴

**(E)-2,5-Dimethylstilbene (3ea).** White solid (32 mg, 76%). NMR spectral data of the compound are in accordance with previous report.⁵

**(E)-2,4,6-Trimethylstilbene (3fa).** White solid (31 mg, 69%). NMR spectral data of the compound are in accordance with previous report.⁵
(E)-4-Methoxystilbene (3ga). White solid (26 mg, 62%). NMR spectral data of the compound are in accordance with previous report.6

(E)-4-Acetoxystilbene (3ha). White solid (30 mg, 63%). NMR spectral data of the compound are in accordance with previous report.7

(E)-4-Fluorostilbene (3ia). White solid (31 mg, 78%). NMR spectral data of the compound are in accordance with previous report.8

(E)-2,3,4,5,6-Pentafluorostilbene (3ja). White solid (37 mg, 68%). NMR spectral data of the compound are in accordance with previous report.9

(E)-4-Chlorostilbene (3ka). White solid (27 mg, 63%). NMR spectral data of the compound are in accordance with previous report.10

(E)-2,6-Dichlorostilbene (3la). White solid (38 mg, 76%). NMR spectral data of the compound are in accordance with previous report.11
(E)-4-Cyanostilbene (3ma). White solid (33 mg, 81%). NMR spectral data of the compound are in accordance with previous report.\textsuperscript{12,13}

(E)-4-Nitrostilbene (3na). Yellow solid (35 mg, 77%). NMR spectral data of the compound are in accordance with previous report.\textsuperscript{5,14}

(E)-2-Styrylnaphthalene (3oa). White solid (28 mg, 61%). NMR spectral data of the compound are in accordance with previous report.\textsuperscript{15}

(E)-α-Methylstilbene (3pa). White solid (23 mg, 60%). NMR spectral data of the compound are in accordance with previous report.\textsuperscript{16}

Methyl 3,3-diphenylacrylate (3qa). White solid (39 mg, 82%). NMR spectral data of the compound are in accordance with previous report.\textsuperscript{17}

(E)-2,5-Dimethylstilbene (3ab). White solid (30 mg, 73%). The structure is same as 3ea.
**S9**

(E)-2,5-Difluorostilbene (3ac). White solid (30 mg, 69%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 6.87-6.93\) (m, 1H), 6.99-7.02 (m, 1H), 7.13 (d, \(J = 16.0, 1H\)), 7.22 (d, \(J = 20.0, 1H\)), 7.26-7.29 (m, 2H), 7.37 (t, \(J = 8.0, 2H\)), 7.53 (d, \(J = 8.0, 2H\)). \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 112.73\) (dd, \(J = 24, 4\)), 115.92 (ddd, \(J = 171, 24, 9\)), 119.84-119.90 (m), 126.61 (dd, \(J = 15, 8\)), 126.81, 128.32, 128.76, 131.98 (d, \(J = 4\)), 136.70, 155.17 (d, \(J = 2\)), 157.65 (dd, \(J = 8, 3\)), 160.09 (d, \(J = 3\)). HRMS (ESI): found: 217.08220, calcd. for C\(_{14}\)H\(_{11}\)F\(_2\) ([M+H]+): 217.08233.

(E)-2,4,6-Trimethylstilbene (3ad). White solid (15 mg, 33%). The structure is same as 3fa.

(E)-2,3-Dimethylstilbene and (E)-3,4-dimethylstilbene (3ae). White solid (29 mg, 70%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 2.27\) (d, \(J = 8.0, 3,4\)-dimethyl), 2.32 (d, \(J = 4.0, 2,3\)-dimethyl) (6H, the radio of above two compounds was 1:2.67, which were in accordance with previous report\(^{29}\)), 7.06-7.12 (m, 3H), 7.23-7.41 (m, 5H), 7.48-7.52 (m, 2H). \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 15.46, 19.55, 19.80, 20.63, 123.83, 124.01, 125.62, 126.36, 126.51, 127.31, 127.48, 127.52, 127.62, 127.76, 128.62, 128.65, 128.73, 129.27, 129.95, 130.42, 134.35, 134.98, 136.24, 136.74, 136.83, 136.85, 137.61, 137.80. HRMS (ESI): found: 209.13283, calcd. for C\(_{16}\)H\(_{17}\) ([M+H]+): 209.13248.

(E)-2,4-Dimethylstilbene, (E)-3,5-dimethylstilbene and (E)-2,6-dimethylstilbene (3af). White solid (27 mg, 65%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 2.33\) (d, \(J = 8.0, 2,4\)-dimethyl), 2.37 (s, 2,6-dimethyl), 2.39 (s, 3,5-dimethyl) (6H, the radio of above three compounds was 1.81:1.0.16, which were in accordance with previous report\(^{29,30}\)), 6.91-7.07 (m, 3H), 7.14-7.29 (m, 2H), 7.33-7.37 (m, 2H), 7.49-7.52 (m, 3H). \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 19.80, 21.10, 21.28, 124.42, 125.29, 126.45, 126.94, 127.38, 127.44, 127.85, 128.29, 128.64, 128.90, 129.08, 129.42, 131.18, 133.54, 135.65, 137.23, 137.35, 137.53, 137.87, 138.10. HRMS (ESI): found: 209.13281, calcd. for
C_{16}H_{17} ([M+H]^+): 209.13248.

**Phenanthrene (4aa).** White solid (21 mg, 58%). NMR spectral data of the compound are in accordance with previous report.\(^{18}\)

1-Methylphenanthrene (4ba). White solid (14 mg, 36%). NMR spectral data of the compound are in accordance with previous report.\(^{19}\)

2-Methylphenanthrene and 4-methylphenanthrene (4ca). White solid (18 mg, 47%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 2.55\) (s, 3H, 2-methyl), 3.14 (s, 3.06H, 4-methyl) (the radio of above two compounds was 1:1.02, which were in accordance with previous report\(^{19,20}\), 7.46-7.49 (m, 3H), 7.53-7.71 (m, 9H), 7.76 (m, 1H), 7.86 (d, \(J = 8.0\), 1H), 7.91 (d, \(J = 8.0\), 1H), 8.56 (d, \(J = 8.0\), 1H), 8.63 (d, \(J = 8.0\), 1H), 8.91 (d, \(J = 8.0\), 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 21.44, 27.38, 122.44, 122.55, 125.77, 125.86, 125.95, 126.46, 126.66, 126.90, 127.07, 127.44, 127.50, 127.99, 128.12, 128.15, 128.32, 128.50, 128.69, 130.09, 130.35, 131.21, 131.67, 131.72, 132.20, 133.49, 133.74, 135.52, 136.30\). HRMS (ESI): found: 193.10114, calcd. for C\(_{15}\)H\(_{13}\) ([M+H]^+): 193.10118.

3-Methylphenanthrene (4da). White solid (17 mg, 43%). NMR spectral data of the compound are in accordance with previous report.\(^{20}\)

3-Acetoxyphenanthrene (4ha). White solid (23 mg, 49%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 2.39\) (s, 3H), 7.34 (d, \(J = 8.0\), 1H), 7.57-7.63 (m, 2H), 7.71 (s, 2H), 7.87-7.89 (m, 2H), 8.35 (s, 1H), 8.55 (d, \(J = 8.0\), 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 21.21, 114.73, 121.02, 122.78, 126.28, 126.56, 126.76, 126.95, 128.57, 129.74, 129.86, 129.92, 131.22, 132.11, 149.25, 169.68\). HRMS (ESI): found: 259.07354, calcd. for C\(_{16}\)H\(_{12}\)O\(_2\)Na ([M+Na]^+): 259.07295.
3-Fluorophenanthrene (4ia). White solid (24 mg, 60%). NMR spectral data of the compound are in accordance with previous report.21

3-Chlorophenanthrene (4ka). White solid (22 mg, 51%). NMR spectral data of the compound are in accordance with previous report.22

3-Cyanophenanthrene (4ma). White solid (19 mg, 46%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.67$-$7.71$ (m, 1H), 7.73-$7.78$ (m, 3H), 7.90 (d, $J = 8.0$, 1H), 7.95 (t, $J = 8.0$, 2H), 8.64 (d, $J = 8.0$, 1H), 9.01 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 109.82$, 119.54, 122.57, 126.05, 127.72, 127.83, 127.96, 128.21, 128.90, 129.36 129.50, 130.00, 130.36, 132.24, 134.27. HRMS (ESI): found: 204.08121, calcd. for C$_{15}$H$_{10}$N ([M+H]+): 204.08078.

Benzo[c]phenanthrene (4oa). White solid (9 mg, 20%). NMR spectral data of the compound are in accordance with previous report.23

Chrysene (4ra). White solid (14 mg, 30%). NMR spectral data of the compound are in accordance with previous report.24

9-Phenylphenanthrene (4sa). White solid (20 mg, 39%). NMR spectral data of the compound are in accordance with previous report.25
9-Methylphenanthrene (4pa). White solid (15 mg, 39%). NMR spectral data of the compound are in accordance with previous report.\textsuperscript{26}

1,4-Dimethylphenanthrene (4ab). White solid (20 mg, 48%). NMR spectral data of the compound are in accordance with previous report.\textsuperscript{27}

1,4-Difluorophenanthrene (4ac). White solid (21 mg, 49%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 7.20-7.31 (m, 2H), 7.64-7.71 (m, 2H), 7.82 (d, J = 8.0, 1H), 7.92 (d, J = 8.0, 1H), 7.98 (d, J = 8.0, 1H), 9.09 (d, J = 8.0, 1H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 110.80 (dd, J = 24, 10), 112.61 (dd, J = 27, 9), 118.22 (dd, J = 8, 2), 120.43 (dd, J = 11, 4), 123.23 (dd, J = 17, 5), 127.40, 127.56 (d, J = 2), 127.65, 127.91 (dd, J = 6, 2), 128.68, 128.80-128.83 (m), 132.62, 156.08-156.15 (m), 156.13 (dd, J = 487, 3). HRMS (EI): found: 214.0597, calcd. for C\textsubscript{14}H\textsubscript{8}F\textsubscript{2} (M\textsuperscript{+}): 214.0594.

1,4-Difluorobenzo[c]phenanthrene (4oc). White solid (13 mg, 25%). NMR spectral data of the compound are in accordance with previous report.\textsuperscript{28}

1,4-Dimethylchrysene (4rb). White solid (13 mg, 25%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 2.79 (s, 3H), 3.14 (s, 3H), 7.40 (dd, J = 24.0, 8.0, 2H), 7.64-7.70 (m, 2H), 7.91 (d, J = 8.0, 1H), 7.98 (d, J = 8.0, 1H), 8.18 (d, J = 8.0, 1H), 8.73 (d, J = 8.0, 1H), 8.80 (d, J = 8.0, 1H), 8.86 (d, J = 8.0, 1H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 20.11, 27.22, 120.95, 123.04, 123.36, 123.90, 125.05, 126.12, 126.34, 127.06, 128.04, 129.33, 129.75, 130.36, 130.76, 131.19, 131.45, 132.27, 132.68, 133.12. HRMS (ESI): found: 257.13289, calcd. for C\textsubscript{20}H\textsubscript{17} (\textsuperscript{[M+H]}\textsuperscript{+}): 257.13248.
1,4-Difluorochrysene (4rc). White solid (18 mg, 34%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.19-7.23$ (m, 1H), 7.26-7.32 (m, 1H), 7.65-7.74 (m, 2H), 7.98-8.02 (m, 2H), 8.22 (dd, $J = 12.0, 4.0, 1H$), 8.77 (d, $J = 8.0, 1H$), 8.81 (d, $J = 8.0, 1H$), 9.11 (dd, $J = 8.0, 4.0, 1H$). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta =$ 110.16 (dd, $J = 22.5, 10.0$), 112.38 (dd, $J = 28.8, 8.8$), 118.94 (dd, $J = 7.5, 2.5$), 120.94 (dd, $J = 10.0, 3.8$), 122.80-122.82 (m), 123.24, 123.53 (dd, $J = 17.5, 5.0$), 124.92 (d, $J = 26.3$), 126.46 (dd, $J = 6.3, 1.3$), 126.75, 126.97, 128.01 (d, $J = 2.5$), 128.35, 129.36, 129.95, 132.11 (d, $J = 2.5$), 154.92 (dd, $J = 245.0, 2.5$), 157.21 (dd, $J = 247.5, 2.5$). HRMS (EI): found: 264.0755, calcd. for C$_{18}$H$_{10}$F$_2$ (M$^+$): 264.0751.

1,2,3,4-Tetrafluorophenanthrene (4ag). White solid (22 mg, 44%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.67-7.74 (m, 2H), 7.82 (d, $J = 8.0, 1H$), 7.91-7.94 (m, 2H), 8.98 (d, $J = 8.0, 1H$). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta =$ 115.81-115.92 (m), 116.82-116.95 (m), 118.30 (dm, $J = 12.5$), 126.95, 127.14, 127.88, 128.08-128.09 (m), 129.00, 129.07, 132.34, 137.64 (dm, $J = 183.8$), 139.66 (dm, $J = 186.3$), 142.46 (dm, $J = 246.3$), 146.00 (dm, $J = 251.3$). HRMS (EI): found: 250.0409, calcd. for C$_{14}$H$_6$F$_4$ (M$^+$): 250.0406.
References

NMR Spectra of Mechanistic Study Experiments

Intermolecular kinetic isotopic effect (KIE)

\[
\text{Pd(OAc)}_2 (5.0 \text{ mol}) / \text{PPh}_3 (1.0 \text{ equiv}) \quad \text{PrvOH (1.0 equiv)} \\
\text{Ag}_2\text{CO}_3 (12 \text{ equiv}) \quad 120^\circ\text{C}, 8 \text{ h}
\]

\[
\text{1d} + \text{C}_6\text{H}_5\text{C}_6\text{D}_6 \quad 1:1 \\
\text{3da/3da-d}_5 \quad k_{\text{H}}/k_{\text{D}} = 2.33
\]
NMR Spectra of Products

trans-Stilbene (3aa)
(E)-2-Methylstilbene (3ba)
(E)-3-Methylstilbene (3ca)
(E)-4-Methylstilbene (3da)
(E)-2,5-Dimethylstilbene (3ea or 3ab)
(E)-2,4,6-Trimethylstilbene (3fa or 3ad)
(E)-4-Acetoxystilbene (3ha)
(E)-4-Fluorostilbene (3ia)
(E)-2,3,4,5,6-Pentafluorostilbene (3ja)
(E)-4-Chlorostilbene (3ka)
(E)-2,6-Dichlorostilbene (3la)
(E)-4-Cyanostilbene (3ma)
(E)-4-Nitrostilbene (3na)
(E)-2-Styrylnaphthalene (3oa)
Methyl 3,3-diphenylacrylate (3qa)
(E)-2,5-Difluorostilbene (3ac)
(E)-2,3-Dimethylstilbene and (E)-3,4-dimethylstilbene (3ae)
(E)-2,4-Dimethylstilbene, (E)-3,5-dimethylstilbene and (E)-2,6-dimethylstilbene (3af)
Phenanthrene (4aa)
1-Methylphenanthrene (4ba)
2-Methylphenanthrene and 4-methylphenanthrene (4ca)

1 : 1.02
3-Methylphenanthrene (4da)
3-Acetoxyphenanthrene (4ha)
3-Fluorophenanthrene (4ia)
3-Chlorophenanthrene (4ka)
3-Cyanophenanthrene (4ma)
Benzo[c]phenanthrene (4oa)
9-Phenylphenanthrene (4sa)
9-Methylphenanthrene (4pa)
1,4-Dimethylphenanthrene (4ab)
1,4-Difluorophenanthrene (4ac)
1,4-Difluorobenzo[c]phenanthrene (4oc)
1,4-Dimethylchrysene (4rb)
1,4-Difluorochrysene (4rc)
1,2,3,4-Tetrafluorophenanthrene (4ag)