Electronic Supplementary Information for


Asao Nakamura,*a Hiromi Irie,a Shuhei Hara,a Mai Sugawara,b and Shinji Yamada b

a Department of Chemistry, College of Engineering, Shibaura Institute of Technology, Saitama-shi, Saitama 337-8570, Japan. E-mail: asao@sic.shibaura-it.ac.jp; Fax: +81-48-687-5013; Tel: +81-48-687-5032
b Department of Chemistry, Faculty of Science, Ochanomizu University, Bunkyo-ku, Tokyo 112-8610, Japan. E-mail: yamada.shinji@ocha.ac.jp

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1. Experimental procedure and spectral data for trans-4-styrylpyridines 1a–1f

**Scheme S1.** Synthesis of 1a-1f by Horner-Wadsworth-Emmons reaction.

**General procedure for the preparation of 1a-1f**

A mixture of 0.04 mol corresponding benzyl bromide (or chloride) and 0.048 mol triethyl phosphite was heated at 180 °C for 17 h. After excess triethyl phosphite was removed by evaporation under reduced pressure, the residue was dissolved in dry THF and used without further purification.

To 0.08 mol sodium hydride dissolved in dry THF, the above obtained phosphonic diester was added dropwise for 30 min. 4-pyridinecarboxaldehyde (0.04 mol) was dissolved in THF separately and added dropwise to the reaction mixture for 30 min. The mixture was refluxed for 15 h. After sodium hydride was quenched by adding methanol, solvents were removed by evaporation. The residue was dissolved ethyl acetate, washed with 2 × water and saturated NaCl solution, dried with anhydrous sodium sulfate, and concentrated by vacuum evaporation. The crude product was purified by open column chromatography (eluent: hexane–ethyl acetate (1:1)) and recrystallization.

**trans-4-Styrylpyridine (1a)**

White crystals; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.38 (d, $J = 6.4$ Hz, 2H), 7.55 (d, $J = 6.4$ Hz, 2H), 7.39 (d, $J = 6.0$ Hz, 2H), 7.37 (d, $J = 6.0$ Hz, 2H), 7.33 (t, $J = 16.8$ Hz, 1H), 7.31 (d, $J = 16.0$ Hz, 1H), 7.03 (d, $J = 16.0$ Hz, 1H).

**trans-4-[2-(2-Methylphenyl)vinyl]pyridine (1b)**

White crystals; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.58 (d, $J = 6.4$ Hz, 2H), 7.63-7.59 (m, 1H), 7.56 (d, $J = 16.4$ Hz, 1H), 7.38 (d, $J = 6.0$ Hz, 2H), 7.26-7.22 (m, 3H), 6.92 (d, $J = 16.4$ Hz, 1H), 2.54 (s, 3H).

**trans-4-[2-(3-Methylphenyl)vinyl]pyridine (1c)**

White crystals; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.57 (d, $J = 6.0$ Hz, 2H), 7.36 (d, $J = 6.8$ Hz, 2H), 7.38-7.34 (m, 3H), 7.28 (d, $J = 16.4$ Hz, 1H), 7.15 (d, $J = 7.2$ Hz, 1H), 7.01 (d, $J = 16.4$ Hz, 1H), 2.39 (s, 3H).
**trans-4-[2-(4-Methylphenyl)vinyl]pyridine (1d)**
White crystals; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.56 (d, $J = 6.0$ Hz, 2H), 7.44 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 6.0$ Hz, 2H), 7.29 (d, $J = 16.0$ Hz, 1H), 7.20 (d, $J = 8.0$ Hz, 2H), 6.97 (d, $J = 16.0$ Hz, 1H), 2.38 (s, 3H).

**trans-4-[2-(3,4-Dimethylphenyl)vinyl]pyridine (1e)**
White crystals; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.57 (d, $J = 6.4$ Hz, 2H), 7.81 (d, $J = 6.8$ Hz, 2H), 7.56 (d, $J = 16$ Hz, 1H), 7.38 (d, $J = 16$ Hz, 1H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.08 (d, $J = 16$ Hz, 1H), 2.31 (s, 6H).

**trans-4-[2-(4-Isopropylphenyl)vinyl]pyridine (1f)**
White crystals; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.58 (d, $J = 6.0$ Hz, 2H), 7.37 (d, $J = 6.0$ Hz, 2H), 7.34 (d, $J = 6.0$ Hz, 2H), 7.29 (d, $J = 16.4$ Hz, 1H), 6.95 (d, $J = 6.1$ Hz, 2H), 7.08 (d, $J = 16$ Hz, 1H), 7.15 (d, $J = 16.4$ Hz, 1H), 2.38 (s, 6H), 1.65-1.61(m, 1H).

2. Determination of syn and anti stereochemistry by $^1$H NMR chemical shifts

The methine protons for syn dimers appear at higher field than those of anti dimers. In addition, the H$_a$ protons for the pyridine ring of syn dimers appear at lower field than those of anti dimers. The stereochemistry of these dimers was determined on the basis of these observations.

**Table S1. $^1$H NMR chemical shifts (ppm) for methine and H$_a$ protons of the photocyclodimerization products**

<table>
<thead>
<tr>
<th></th>
<th>$^1$H NMR chemical shift (ppm)</th>
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<tbody>
<tr>
<td></td>
<td>methine</td>
</tr>
<tr>
<td>2a (syn-HT)</td>
<td>4.46</td>
</tr>
<tr>
<td>2b (syn-HT)</td>
<td>4.49–4.56</td>
</tr>
<tr>
<td>2c (syn-HT)</td>
<td>4.39, 4.45</td>
</tr>
<tr>
<td>2d (syn-HT)</td>
<td>4.37, 4.45</td>
</tr>
<tr>
<td>3a (syn-HH)</td>
<td>4.48</td>
</tr>
<tr>
<td>3b (syn-HH)</td>
<td>4.41, 4.62</td>
</tr>
<tr>
<td>3c (syn-HH)</td>
<td>4.45, 4.39</td>
</tr>
<tr>
<td>3d (syn-HH)</td>
<td>4.39, 4.41</td>
</tr>
<tr>
<td>4a (anti-HT)</td>
<td>3.57, 3.67</td>
</tr>
<tr>
<td>4b (anti-HT)</td>
<td>3.78, 3.93</td>
</tr>
<tr>
<td>4c (anti-HT)</td>
<td>3.58, 3.73</td>
</tr>
<tr>
<td>4d (anti-HT)</td>
<td>3.57, 3.69</td>
</tr>
</tbody>
</table>
3. Determination of HH and HT orientation by mass spectrometry

The characteristic fragment peak of $m/z$ 208 was observed for the HH dimers, which enables to distinguish between HH and HT dimers.

![Diagram of HT and HH dimers]

Table S2. Relative intensities of the mass fragment peaks for the photocyclodimerization products

<table>
<thead>
<tr>
<th></th>
<th>$m/z$ 180 (%)</th>
<th>$m/z$ 181 (%)</th>
<th>$m/z$ 182 (%)</th>
<th>$m/z$ 195 (%)</th>
<th>$m/z$ 208 (%)</th>
</tr>
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<tbody>
<tr>
<td>2b (syn-HT)</td>
<td>81</td>
<td>12</td>
<td>1</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>2c (syn-HT)</td>
<td>90</td>
<td>14</td>
<td>2</td>
<td>100</td>
<td>2</td>
</tr>
<tr>
<td>2d (syn-HT)</td>
<td>78</td>
<td>12</td>
<td>2</td>
<td>100</td>
<td>2</td>
</tr>
<tr>
<td>3b (syn-HH)</td>
<td>90</td>
<td>15</td>
<td>2</td>
<td>100</td>
<td>15</td>
</tr>
<tr>
<td>3c (syn-HH)</td>
<td>62</td>
<td>10</td>
<td>2</td>
<td>100</td>
<td>13</td>
</tr>
<tr>
<td>3d (syn-HH)</td>
<td>72</td>
<td>16</td>
<td>5</td>
<td>100</td>
<td>52</td>
</tr>
<tr>
<td>4b (anti-HT)</td>
<td>41</td>
<td>5</td>
<td>1</td>
<td>100</td>
<td>2</td>
</tr>
<tr>
<td>4c (anti-HT)</td>
<td>34</td>
<td>6</td>
<td>1</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>4d (anti-HT)</td>
<td>72</td>
<td>12</td>
<td>3</td>
<td>100</td>
<td>7</td>
</tr>
</tbody>
</table>
4. Experimental procedure and spectral data for the photocyclodimerization products of 1b–1f

General procedure for the irradiation of 1b-1f

A solution of 0.0579 mmol of corresponding alkene in 100 µL of MeOH containing various amounts of HCl was irradiated with a 450 W high-pressure mercury lamp for 15 h. After the irradiation, solvent was evaporated to give a crude product, which was neutralized with 2 M NaOH aq. and extracted with CH₂Cl₂. The organic layer was dried over anhydrous MgSO₄ and the solvent was evaporated in vacuo to give a neutralized reaction mixture. The product ratio was determined by ¹H NMR spectroscopy. The mixture was separated by column chromatography on silica gel employing hexane-ethyl acetate as an eluent.

Irradiation of 1b

The products were photodimers 2b, 3b, 4b, 6b and cis-isomer 5b. 6b was afforded when the reaction was carried out at 1.480 mol/L.

**syn** head-to-tail dimer of 1b (2b)

Yellow crystals; mp 178.5-179.8 °C; IR (KBr) 3025, 2955, 1597, 1554, 1489, 1459, 1415, 994, 828, 802, 773, 754, 575, 546 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 8.33 (d, J = 6.1 Hz, 4H), 7.28 (d, J = 7.6 Hz, 2H), 7.13 (t, J = 7.1 Hz, 2H), 7.02 (d, J = 7.3 Hz, 2H), 6.98 (d, J = 6.1 Hz, 4H), 4.56-4.49 (m, 4H), 2.16 (s, 6H); MS m/z 391 (M⁺, 0.38 %), 196 (18), 195 (100), 194 (61), 181 (12), 180 (81); HRMS calcld for C₂₈H₂₆N₂ 390.2096, found 390.2059.

**syn** head-to-head dimer of 1b (3b)

Yellow crystals; mp 176.5-177.0 °C; IR (KBr) 3025, 2949, 1599, 1556, 1491, 1462, 993, 815, 753, 730, 561 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 8.39 (d, J = 6.1 Hz, 4H), 7.14 (d, J = 7.6 Hz, 2H), 7.09-7.02 (m, 6H), 7.00 (d, J = 6.1 Hz, 4H), 4.62-4.61 (m, 2H), 4.41-4.40 (m, 2H), 2.15 (s, 6H); MS m/z 390 (M⁺, 0.94 %), 208 (15), 196 (36), 195 (100), 194 (51), 181 (15), 180 (90), 178 (10); HRMS calcld for C₂₈H₂₆N₂ 390.2096, found 390.2086.

**anti** head-to-tail dimer of 1b (4b)

Pale yellow crystals; mp 181.1-182.5 °C; IR (KBr) 3019, 2956, 2926, 1599, 1557, 1493, 1462, 1412, 993, 799, 746, 720, 649, 539 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 8.48 (d, J = 6.0 Hz, 4H), 7.64 (d, J = 7.7 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H),
7.18 (t, \( J = 7.4 \text{ Hz}, 2\text{H} \)), 7.12 (d, \( J = 6.0 \text{ Hz}, 6\text{H} \)), 3.93 (t, \( J = 9.7 \text{ Hz}, 2\text{H} \)), 3.78 (t, \( J = 9.7 \text{ Hz}, 2\text{H} \)), 2.04 (s, 6H); MS m/z 391 (M⁺, 0.55 %), 390 (1.4), 196 (27), 195 (100), 194 (29), 180 (41); HRMS calcd for C₂₈H₂₆N₂ 390.2096, found 390.2053.

**anti** head-to-head dimer of 1b (6b)

Pale yellow crystals; mp 226.5-227.0 °C IR (KBr) 3025, 1599, 1557, 1491, 1463, 1413, 993, 759, 723, 545 cm⁻¹; \(^1\)H NMR (600 MHz, CDCl₃) \( \delta \) 8.53 (d, \( J = 6.1 \text{ Hz}, 4\text{H} \)), 7.61 (d, \( J = 7.6 \text{ Hz}, 2\text{H} \)), 7.29 (t, \( J = 7.5 \text{ Hz}, 2\text{H} \)), 7.18 (d, \( J = 6.1 \text{ Hz}, 4\text{H} \)), 7.14 (t, \( J = 7.8 \text{ Hz}, 2\text{H} \)), 7.07 (d, \( J = 7.5 \text{ Hz}, 2\text{H} \)), 3.87-3.83 (m, 4H), 1.92 (s, 6H); MS m/z 391 (M⁺, 1.2 %), 390 (2.4), 209 (9), 208 (49), 196 (22), 195 (100), 194 (25), 193 (19), 181 (7), 180 (30), 178 (11); HRMS calcd for C₂₈H₂₆N₂ 390.2096, found 390.2117.

**cis**-4-[2-(2-Methylphenyl)vinyl]pyridine (5b)

Pale yellow oil; \(^1\)H NMR (600 MHz, CDCl₃) \( \delta \) 8.38 (d, \( J = 6.1 \text{ Hz}, 2\text{H} \)), 7.22-7.18 (m, 2H), 7.07-7.04 (m, 2H), 6.95 (d, \( J = 6.1 \text{ Hz}, 2\text{H} \)), 6.87 (d, \( J = 12.1 \text{ Hz}, 1\text{H} \)), 6.54 (d, \( J = 12.1 \text{ Hz}, 1\text{H} \)), 2.27 (s, 3H).

Irradiation of 1c

The products were photodimers 2c, 3c, 4c and **cis**-isomer 5c.

**syn** head-to-tail dimer of 1c (2c)

Pale yellow crystals; mp 64.0-64.8°C; IR (KBr) 3438, 3052, 1599, 1555, 1492, 1414, 1220, 994, 789, 702, 552 cm⁻¹; \(^1\)H NMR (600 MHz, CDCl₃) \( \delta \) 8.35 (d, \( J = 6.1 \text{ Hz}, 4\text{H} \)), 7.06 (t, \( J = 7.9 \text{ Hz}, 2\text{H} \)), 6.99 (d, \( J = 6.0 \text{ Hz}, 4\text{H} \)), 6.91 (d, \( J = 7.6 \text{ Hz}, 2\text{H} \)), 6.88 (d, \( J = 6.2 \text{ Hz}, 4\text{H} \)), 4.45 (t, \( J = 9.2 \text{ Hz}, 2\text{H} \)), 4.39 (t, \( J = 9.2 \text{ Hz}, 2\text{H} \)), 2.22 (s, 6H); MS m/z 390 (M⁺, 0.94 %), 196 (50), 195 (100), 194 (77), 181 (14), 180 (90); HRMS calcd for C₂₈H₂₆N₂ 390.2096, found 390.2113.

**syn** head-to-head dimer of 1c (3c)

Yellow crystals; mp 128.3-129.5 °C; IR (KBr) 3025, 2924, 1600, 1556, 1491, 1419, 994, 841, 815, 795, 764, 701, 690, 544 cm⁻¹; \(^1\)H NMR (600 MHz, CDCl₃) \( \delta \) 8.38 (d, \( J = 6.1 \text{ Hz}, 4\text{H} \)), 7.04 (t, \( J = 7.6 \text{ Hz}, 2\text{H} \)), 7.01 (d, \( J = 6.0 \text{ Hz}, 4\text{H} \)), 6.90 (d, \( J = 7.4 \text{ Hz}, 2\text{H} \)), 6.86 (m, 4H), 4.45 (m, 2H), 4.39-4.38 (m, 2H), 2.21 (s, 6H); MS m/z 390 (M⁺, 1.1 %), 208 (13), 196 (42), 195 (100), 194 (72), 193 (13), 181 (10), 180 (62), 178 (13), 152 (13); HRMS calcd for C₂₈H₂₆N₂ 390.2096, found 390.2113.
\textit{anti} head-to-tail dimer of 1c (4c)

white crystals; mp 152.5-153.8 °C; IR (KBr) 3027, 2917, 1601, 1552, 1498, 1460, 1414, 992, 809, 801, 794, 770, 699, 560, 2530 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.51 (d, $J = 4.6$ Hz, 4H), 7.25 (t, $J = 7.7$ Hz, 2H), 7.15 (d, $J = 6.0$ Hz, 4H), 7.12 (s, 2H), 7.10 (d, $J = 6.1$ Hz, 4H), 3.73 (t, $J = 9.7$ Hz, 2H), 3.58 (t, $J = 9.7$ Hz, 2H), 2.36 (s, 6H); MS m/z 390 (M$^+$, 1.2 %), 196 (22), 195 (100), 194 (32), 180 (34); HRMS calcd for C$_{28}$H$_{26}$N$_2$ 390.2096, found 390.2078.

\textit{cis}-4-[2-(3-Methylphenyl)vinyl]pyridine (5c)

Pale yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.45 (d, $J = 6.4$ Hz, 2H), 7.35-7.37 (m, 3H), 7.30-7.26 (m, 3H), 7.15 (d, $J = 7.6$ Hz, 1H), 6.76 (d, $J = 12.4$ Hz, 1H), 6.47 (d, $J = 12.4$ Hz, 1H), 2.27 (s, 3H).

Irradiation of 1d

The products were photodimers 2d, 3d, 4d and \textit{cis}-isomer 5d.

\textit{syn} head-to-tail dimer of 1d (2d)

Yellow crystals; mp 82.2-83.0 °C IR (KBr) 3028, 2924, 1598, 1557, 1515, 1417, 817, 533 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.34 (d, $J = 6.1$ Hz, 4H), 6.98-6.95 (m, 12H), 4.45-4.44 (m, 2H), 4.37 (m, 2H), 2.23 (s, 6H); MS m/z 390 (M$^+$, 0.39 %), 196 (46), 195 (100), 194 (61), 181 (12), 180 (78), 152 (17); HRMS calcd for C$_{28}$H$_{26}$N$_2$ 390.2096, found 390.2076.

\textit{syn} head-to-head dimer of 1d (3d)

Yellow crystals; mp 94.5-95.3 °C IR (KBr) 3028, 2921, 1600, 1557, 1515, 1415, 1264, 817, 543 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.37 (d, $J = 6.1$ Hz, 4H), 7.00-6.95 (m, 12H), 4.42-4.41 (m, 2H), 4.39-4.38 (m, 2H), 2.24 (s, 6H); MS m/z 391 (M$^+$, 0.63 %), 390 (1.4), 389 (1.3), 208 (52), 196 (51), 195 (100), 194 (60), 181 (16), 180 (72), 179 (11); HRMS calcd for C$_{28}$H$_{26}$N$_2$ 390.2096, found 390.2141.

\textit{anti} head-to-tail dimer of 1d (4d)

Yellow crystals; mp 152.8-153.2 °C; IR (KBr) 3024, 2921, 1596, 1555, 1515, 1413, 993, 828, 809, 531 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.50 (d, $J = 6.1$ Hz, 4H), 7.20 (d, $J = 8.1$ Hz, 4H), 7.17 (d, $J = 8.1$ Hz, 4H), 7.14 (d, $J = 6.0$ Hz, 4H), 3.69 (t, $J = 10$ Hz, 2H), 3.57 (t, $J = 10$ Hz, 2H), 2.35 (s, 6H); MS m/z 390 (M$^+$, 0.65 %), 389 (0.55), 196 (38), 195
(100), 194 (53), 180 (72); HRMS calcd for C_{28}H_{26}N_{2} 390.2096, found 390.2117.

cis-4-[2-(4-Methylphenyl)vinyl]pyridine (5d)
Pale yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 8.45 (d, J = 6.1 Hz, 2H), 7.19 (d, J = 7.2 Hz, 2H), 7.11 (d, J = 5.8 Hz, 2H), 7.04 (d, J = 7.3 Hz, 2H), 6.74 (d, J = 12.2 Hz, 1H), 6.54 (d, J = 12.1 Hz, 1H), 2.32 (s, 3H).
5. $^1$H NMR spectra of photocyclodimerization products of 1b–1d
Figure S1. $^1$H NMR spectrum of 2b.
Figure S2. $^1$H NMR spectrum of 2c.
Fig. S3. $^1$H NMR spectrum of 2d.

S12
Figure S4. $^1$H NMR spectrum of 3b.
Figure S5. $^1$H NMR spectrum of 3c.
Figure S6. $^1$H NMR spectrum of 3d.

S15
Figure S7. $^1$H NMR spectra of 4b.
Figure S8. $^1$H NMR spectrum of 4c.
Figure S9. $^1$H NMR spectrum of 4d.
Figure S10. $^1$H NMR spectrum of 6b.