Supporting information

Copper Catalyzed Aerobic Oxidative Carbocyclization Reactions of $N$-[(E)-Stilben-2-yl]amine Derivatives

Cheng-Yen Lu and Che-Ping Chuang

Department of Chemistry, National Cheng Kung University, Tainan, Taiwan 70101, Republic of China. Fax: +886-6-2740552; E-mail: cpchuang@mail.ncku.edu.tw

Contents

1) Optimization studies of the copper-catalyzed reactions.
3) Copies of $^1$H and $^{13}$C NMR spectra.
Optimization studies of the copper-catalyzed reactions.

Table 1. Optimization studies of the copper-catalyzed reactions with 2-Benzoyl-N-[E-stilben-2-yl]acetamide 1a.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cu salt</th>
<th>Base</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>T (h)</th>
<th>Yield(%)&lt;sup&gt;[a]&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuCl₂</td>
<td>DABCO/Phen</td>
<td>DMF</td>
<td>100</td>
<td>7</td>
<td>2a(71) 3a(8)</td>
</tr>
<tr>
<td>2&lt;sup&gt;[b]&lt;/sup&gt;</td>
<td>CuCl₂</td>
<td>DABCO/Phen</td>
<td>DMF</td>
<td>100</td>
<td>7</td>
<td>2a(72) 3a(7)</td>
</tr>
<tr>
<td>3</td>
<td>CuCl₂</td>
<td>DABCO</td>
<td>DMF</td>
<td>100</td>
<td>12</td>
<td>2a(58) 3a(7)</td>
</tr>
<tr>
<td>4</td>
<td>CuCl₂</td>
<td>DABCO/Phen</td>
<td>DMAc</td>
<td>100</td>
<td>7</td>
<td>2a(70) 3a(6)</td>
</tr>
<tr>
<td>5</td>
<td>CuCl₂</td>
<td>DABCO/Phen</td>
<td>DMSO</td>
<td>100</td>
<td>9</td>
<td>2a(11) 3a(7)</td>
</tr>
<tr>
<td>6</td>
<td>CuCl₂</td>
<td>Li₂CO₃/Phen</td>
<td>DMF</td>
<td>100</td>
<td>12</td>
<td>2a(58) 3a(6)</td>
</tr>
<tr>
<td>7</td>
<td>CuCl₂</td>
<td>NMP/Phen</td>
<td>DMF</td>
<td>100</td>
<td>7</td>
<td>2a(55) 3a(7)</td>
</tr>
<tr>
<td>8</td>
<td>CuCl₁</td>
<td>DABCO/Phen</td>
<td>DMF</td>
<td>100</td>
<td>7</td>
<td>2a(71) 3a(8)</td>
</tr>
<tr>
<td>9</td>
<td>CuCl₁</td>
<td>-</td>
<td>DMAc</td>
<td>100</td>
<td>7</td>
<td>2a(38) 3a(0)</td>
</tr>
<tr>
<td>10</td>
<td>CuBr</td>
<td>DABCO/Phen</td>
<td>DMF</td>
<td>100</td>
<td>9</td>
<td>2a(58) 3r(6)</td>
</tr>
<tr>
<td>11</td>
<td>CuI</td>
<td>DABCO/Phen</td>
<td>DMF</td>
<td>100</td>
<td>12</td>
<td>2a(43) 3a(5)</td>
</tr>
<tr>
<td>12</td>
<td>Cu(OAc)₂</td>
<td>DABCO/Phen</td>
<td>DMF</td>
<td>100</td>
<td>12</td>
<td>2a(43) 3a(5)</td>
</tr>
<tr>
<td>13&lt;sup&gt;[c]&lt;/sup&gt;</td>
<td>CuCl₂</td>
<td>DABCO/Phen</td>
<td>DMF</td>
<td>100</td>
<td>7</td>
<td>2a(70) 3a(8)</td>
</tr>
<tr>
<td>14</td>
<td>Cu(OAc)₂</td>
<td>NMP</td>
<td>Mesitylene</td>
<td>165</td>
<td>7</td>
<td>2a(7) 3a(0)</td>
</tr>
<tr>
<td>15</td>
<td>Cu(OAc)₂</td>
<td>DMAP</td>
<td>Mesitylene</td>
<td>165</td>
<td>8</td>
<td>2a(13) 3a(0)</td>
</tr>
</tbody>
</table>

[a] Yield of isolated product. [b] With 20 mol% of CuCl₂. [c] TEMPO (1 equiv) was added. DABCO = 1,4-diazabicyclo[2.2.2]octane; Phen = 1,10-phenanthroline; DMAc = N,N-dimethylacetamide; NMP = N-methylpiperidine; DMAP = N,N-dimethylpyridine; TEMPO = 2,2,6,6-tetramethyl-piperidinyloxy.
Table 2. Optimization studies of the copper-catalyzed reactions with dimethyl 2-[(E)-stilben-2-yl]aminofumarate 9j.

Table 2.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cu salt</th>
<th>Base</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>T (h)</th>
<th>Yield(%)&lt;sup&gt;[a]&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuCl₂</td>
<td>DABCO/Phen</td>
<td>DMF</td>
<td>100</td>
<td>1</td>
<td>10j(67) 11j(9)</td>
</tr>
<tr>
<td>2</td>
<td>CuCl₂</td>
<td>Phen</td>
<td>DMF</td>
<td>100</td>
<td>12</td>
<td>10j(41) 11j(12)</td>
</tr>
<tr>
<td>3</td>
<td>CuCl₂</td>
<td>NMP</td>
<td>DMAc</td>
<td>100</td>
<td>0.5</td>
<td>10j(66) 11j(9)</td>
</tr>
<tr>
<td>4</td>
<td>CuCl</td>
<td>NMP</td>
<td>DMAc</td>
<td>100</td>
<td>0.5</td>
<td>10j(84) 11j(8)</td>
</tr>
<tr>
<td>5</td>
<td>CuCl</td>
<td>DABCO</td>
<td>DMAc</td>
<td>100</td>
<td>0.5</td>
<td>10j(60) 11j(9)</td>
</tr>
<tr>
<td>6</td>
<td>CuCl</td>
<td>-</td>
<td>DMAc</td>
<td>100</td>
<td>1</td>
<td>10j(62) 11j(0)</td>
</tr>
<tr>
<td>7</td>
<td>Cu(OAc)₂</td>
<td>NMP</td>
<td>DMAc</td>
<td>100</td>
<td>0.5</td>
<td>10j(70) 11j(12)</td>
</tr>
<tr>
<td>8</td>
<td>Cu(OAc)₂</td>
<td>NMP</td>
<td>Mesitylene</td>
<td>165</td>
<td>0.5</td>
<td>10j(69) 11j(8)</td>
</tr>
<tr>
<td>9</td>
<td>Cu(OAc)₂</td>
<td>NMP</td>
<td>Mesitylene</td>
<td>130</td>
<td>8</td>
<td>10j(55) 11j(13)</td>
</tr>
<tr>
<td>10</td>
<td>Cu(OAc)₂</td>
<td>-</td>
<td>Mesitylene</td>
<td>165</td>
<td>0.5</td>
<td>10j(60) 11j(0)</td>
</tr>
<tr>
<td>11</td>
<td>Cu(OAc)₂</td>
<td>-</td>
<td>Mesitylene</td>
<td>130</td>
<td>8</td>
<td>10j(48) 11j(0)</td>
</tr>
</tbody>
</table>

[a] Yield of isolated product. DABCO = 1,4-diazobicyclo[2.2.2]octane; Phen = 1,10-phenanthroline; DMAc = N,N-dimethylacetamide; NMP = N-methylpiperidine.


Experimental Section

General considerations: Melting points are uncorrected. Infrared spectra were taken with a Hitachi 260-30 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AMX-400 spectrometer. Chemical shifts are reported in ppm relative to TMS as internal reference. The multiplicity of the <sup>13</sup>C NMR signals was determined by means of DEPT 135 experiments. Elemental analyses were performed with Heraeus CHN-Rapid Analyzer. Mass spectra were recorded on a Jeol JMS-SX 102A mass spectrometer. Analytical thin-layer chromatography was performed with precoated silica gel 60 F-254 plates (0.25 mm thick) from EM Laboratories and visualized by UV. The reaction mixture was purified by column chromatography over EM Laboratories silica gel (70-230 mesh).

Typical procedure for the preparation of 2-Benzoyl-N-[(E)-stilben-2-yl]acetamide: A solution of N-(2,4,6-trimethylbenzyl)-(E)-stilben-2-ylamine (526 mg, 1.61 mmol), 2-benzoylacetic acid (321 mg, 1.96 mmol) and DCC (442 mg, 2.14 mmol) in chloroform (15 mL) was stirred at room temperature for 10 h. The reaction mixture was then diluted with 100 mL of ethyl acetate washed with water (3 × 50 mL), dried (Na₂SO₄), and concentrated in vacuo. The residue was chromatographed over 20 g of silica gel (eluted with 20:1 hexane-ethyl
acetate) followed by recrystallization (ethyl acetate-hexane) to give 732 mg (96%) of 1a.

2-Benzoyl-N-(2,4,6-trimethylbenzyl)-N-[(E)-stilben-2-yl]acetamide (1a)

Yellow oils; yield: 96%.

IR (Neat): 1655, 1620, 1455, 1355, 1210 cm⁻¹.

1H NMR (400 MHz, CDCl₃): (keto form only), δ = 2.02 (s, 6H, 2 × CH₃), 2.10 (s, 3H, CH₃), 2.13 (s, 3H, CH₃), 3.64 (d, J = 15.9 Hz, 1H, CH₃), 3.80 (d, J = 14.1 Hz, 1H, CH₃), 4.79 (d, J = 14.1 Hz, 1H, NCH), 5.31 (d, J = 14.1 Hz, 1H, NCH), 6.54 (d, J = 8.0 Hz, 1H, ArH), 6.66 (d, J = 2.1 Hz, 1H, ArH), 6.82 (dd, J = 8.0, 1.3 Hz, 1H, ArH), 6.95 (d, J = 16.3 Hz, 1H, CH), 7.01 (d, J = 16.3 Hz, 1H, CH), 7.25 (t, J = 7.7 Hz, 2H, ArH), 7.32 (t, J = 7.4 Hz, 1H, ArH), 7.40 (t, J = 7.4 Hz, 2H, ArH), 7.43 (s, 1H, ArH), 7.46 (t, J = 7.7 Hz, 1H, ArH), 7.47 (d, J = 7.4 Hz, 2H, ArH), 7.71 (d, J = 7.7 Hz, 2H, ArH).

HMRS(EI) m/z [M]+ calcd for C₃₃H₃₁NO₂: 473.2355; found: 473.2364.

2-Benzoyl-N-[4-chloro-(E)-stilben-2-yl]-3-N-(2,4,6-trimethylbenzyl)acetamide (1b)

White crystals; mp 168-169 °C (ethyl acetate-hexane); yield: 99%.

IR (KBr): 1690, 1655, 1490, 1355, 1210 cm⁻¹.

1H NMR (400 MHz, CDCl₃): (keto form only), δ = 2.02 (s, 6H, 2 × CH₃), 2.10 (s, 3H, CH₃), 2.13 (s, 3H, CH₃), 3.64 (d, J = 15.9 Hz, 1H, CH₃), 3.80 (d, J = 14.1 Hz, 1H, CH₃), 4.79 (d, J = 14.1 Hz, 1H, NCH), 5.31 (d, J = 14.1 Hz, 1H, NCH), 6.54 (d, J = 8.0 Hz, 1H, ArH), 6.66 (d, J = 2.1 Hz, 1H, ArH), 6.82 (dd, J = 8.0, 1.3 Hz, 1H, ArH), 6.95 (d, J = 16.3 Hz, 1H, CH), 7.01 (d, J = 16.3 Hz, 1H, CH), 7.25 (t, J = 7.7 Hz, 2H, ArH), 7.32 (t, J = 7.4 Hz, 1H, ArH), 7.40 (t, J = 7.4 Hz, 2H, ArH), 7.43 (s, 1H, ArH), 7.46 (t, J = 7.7 Hz, 1H, ArH), 7.47 (d, J = 7.4 Hz, 2H, ArH), 7.71 (d, J = 7.7 Hz, 2H, ArH).

HMRS(EI) m/z [M]+ calcd for C₃₃H₃₁ClNO₂: 475.2344; found: 475.2345.

White crystals; mp 176-177 °C (ethyl acetate-hexane); yield: 95%.

IR (KBr): 1690, 1655, 1490, 1355, 1210 cm⁻¹.

1H NMR (400 MHz, CDCl₃): (keto form only), δ = 2.02 (s, 6H, 2 × CH₃), 2.10 (s, 3H, CH₃), 2.13 (s, 3H, CH₃), 3.64 (d, J = 15.9 Hz, 1H, CH₃), 3.80 (d, J = 14.1 Hz, 1H, CH₃), 4.79 (d, J = 14.1 Hz, 1H, NCH), 5.31 (d, J = 14.1 Hz, 1H, NCH), 6.54 (d, J = 8.0 Hz, 1H, ArH), 6.66 (d, J = 2.1 Hz, 1H, ArH), 6.82 (dd, J = 8.0, 1.3 Hz, 1H, ArH), 6.95 (d, J = 16.3 Hz, 1H, CH), 7.01 (d, J = 16.3 Hz, 1H, CH), 7.25 (t, J = 7.7 Hz, 2H, ArH), 7.32 (t, J = 7.4 Hz, 1H, ArH), 7.40 (t, J = 7.4 Hz, 2H, ArH), 7.43 (s, 1H, ArH), 7.46 (t, J = 7.7 Hz, 1H, ArH), 7.47 (d, J = 7.4 Hz, 2H, ArH), 7.71 (d, J = 7.7 Hz, 2H, ArH).
$^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ = 19.7 (2 × q), 20.8 (q), 21.3 (t), 44.7 (t), 45.8 (t), 122.5 (d), 126.2 (d), 126.8 (2 × d), 128.2 (d), 128.3 (2 × d), 128.4 (2 × d), 128.7 (2 × d), 129.2 (s + d), 130.3 (d), 131.5 (d), 133.1 (d), 135.6 (s), 135.7 (s), 136.4 (s), 138.5 (2 × s), 138.8 (s), 167.3 (s), 194.0 (s).

Anal. Calcd for C$_{34}$H$_{33}$NO$_2$: C, 83.74; H, 6.82; N, 2.87. Found: C, 83.73; H, 6.84; N, 2.82.

**2-Benzoyl-N-[4,5-dimethyl-(E)-stilben-2-yl]-N-(2,4,6-trimethylbenzyl)acetamide (1e)**

White crystals; mp 186-187 °C (ethyl acetate-hexane); yield: 98%.

IR (KBr): 1620, 1575, 1455, 1355, 1215 cm$^{-1}$.

$^{1}$H NMR (400 MHz, CDCl$_3$): (keto form only), $\delta$ = 1.98 (s, 3H, CH$_3$), 2.01 (s, 6H, 2 × CH$_3$), 2.11 (s, 3H, CH$_3$), 2.19 (s, 3H, CH$_3$), 3.66 (d, $J$ = 16.0 Hz, 1H, CH), 3.77 (d, $J$ = 16.0 Hz, 1H, CH), 4.87 (d, $J$ = 14.0 Hz, 1H, NCH), 5.21 (d, $J$ = 14.0 Hz, 1H, NCH), 6.39 (s, 1H, ArH), 6.65 (d, $J$ = 16.3 Hz, 1H, CH), 6.95 (d, $J$ = 16.3 Hz, 1H, CH), 7.23 (t, $J$ = 7.7 Hz, 2H, ArH), 7.30 (t, $J$ = 7.3 Hz, 1H, ArH), 7.36 (s, 1H, ArH), 7.38 (t, $J$ = 7.3 Hz, 2H, ArH), 7.41-7.47 (m, 1H, ArH), 7.44 (d, $J$ = 7.3 Hz, 2H, ArH), 7.69 (d, $J$ = 7.7 Hz, 2H, ArH).

$^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ = 19.1 (q), 19.5 (q), 19.8 (2 × q), 20.8 (q), 44.8 (t), 45.8 (t), 122.5 (d), 126.6 (d), 126.7 (2 × d), 127.9 (d), 128.2 (2 × d), 128.3 (2 × d), 128.6 (2 × d), 128.9 (2 × d), 129.3 (s), 130.5 (d), 131.3 (d), 133.0 (d), 133.2 (s), 135.8 (s), 136.5 (s), 137.0 (s), 137.1 (s), 137.3 (s), 137.4 (s), 138.4 (2 × s), 167.3 (s), 194.1 (s).

Anal. Calcd for C$_{35}$H$_{35}$NO$_2$: C, 83.80; H, 7.03; N, 2.79. Found: C, 83.57; H, 7.06; N, 2.70.

**2-Benzoyl-N-(2,4,6-trimethylbenzyl)-N-[4,6-dimethyl-(E)-stilben-2-yl]acetamide (1f)**

White crystals; mp 163-164 °C (ethyl acetate-hexane); yield: 97%.

IR (KBr): 1625, 1575, 1455, 1355, 1195 cm$^{-1}$.

$^{1}$H NMR (400 MHz, CDCl$_3$): (keto form : enol form = 1 : 12.8), $\delta$ = 1.95 (s, 3H, CH$_3$), 1.97 (s, 6H, 2 × CH$_3$), 2.02 (s, 3H, CH$_3$), 2.37 (s, 3H, CH$_3$), 4.80 (d, $J$ = 14.1 Hz, 1H, NCH), 5.19 (s, 1H, CH), 6.65 (d, $J$ = 16.2 Hz, 1H, CH), 6.70 (d, $J$ = 16.2 Hz, 1H, CH), 6.95 (s, 1H, ArH), 7.16-7.39 (m, 9H, ArH), 7.52 (d, $J$ = 7.3 Hz, 2H, ArH), 15.05 (s, 1H, OH).

$^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ = 17.3 (q), 19.8 (2 × q), 20.8 (q), 44.8 (t), 45.8 (t), 122.5 (d), 126.6 (d), 127.9 (d), 128.2 (2 × d), 128.3 (2 × d), 128.6 (2 × d), 128.9 (2 × d), 129.3 (s), 130.5 (d), 131.3 (d), 133.0 (d), 133.2 (s), 135.8 (s), 136.5 (s), 137.0 (s), 137.1 (s), 137.3 (s), 137.4 (s), 138.4 (2 × s), 167.3 (s), 194.1 (s).

Anal. Calcd for C$_{35}$H$_{35}$NO$_2$: C, 83.80; H, 7.03; N, 2.79. Found: C, 83.57; H, 7.06; N, 2.70.

**2-Benzoyl-N-benzyl-N-[4,6-dimethyl-(E)-stilben-2-yl]acetamide (1g)**

Colorless oils; yield: 98%.

IR (KBr): 1625, 1575, 1455, 1355, 1195 cm$^{-1}$.

$^{1}$H NMR (400 MHz, CDCl$_3$): (keto form: enol form = 1 : 1.60), $\delta$ = 1.87 (s, 3H, CH$_3$ enol), 2.04 (s, 3H, CH$_3$ keto), 2.33 (s, 3H, CH$_3$ enol), 2.40 (s, 3H, CH$_3$ keto), 3.46 (d, $J$ = 15.7 Hz, 1H, CH keto), 3.76 (d, $J$ = 15.7 Hz, 1H, CH keto), 4.49 (d, $J$ = 12.7 Hz, 1H, CH$_2$ enol), 4.81 (d, $J$ = 13.6 Hz, 1H, CH$_2$ enol), 4.88 (d, $J$ = 13.6 Hz, 1H, CH$_2$ enol), 5.14 (s, 1H, CH$_2$ enol), 5.16 (d, $J$ = 12.7 Hz, 1H, NCH$_2$ enol), 6.67 (d, $J$ = 16.3 Hz, 1H, CH), 6.72 (d, $J$ = 16.2 Hz, 1H, CH), 6.94 (d, $J$ = 16.3 Hz, 1H, CH), 6.95 (d, $J$ = 16.2 Hz, 1H, CH), 6.97 (s, 1H, ArH), 6.98 (s, 1H, ArH), 7.12-7.45 (m, 28H, ArH), 7.50 (d, $J$ = 7.5 Hz, 2H, ArH), 7.70 (d, $J$ = 7.8 Hz, 2H, ArH), 14.9 (s, 1H, OH enol).

HMRS(EI) m/z [M]$^+$ calcd for C$_{32}$H$_{29}$NO$_4$: 459.2198; found: 459.2201.

**Typical procedure for the preparation of 2-acetyl-N-[E-(E)-stilben-2-yl]acetamide**: A solution of N-(2,4,6-trimethylbenzyl)-(E)-stilben-2-ylamine (885 mg, 2.71 mmol), 2,2,6-trimethyl-4H-1,3-dioxin-4-one (461 mg, 3.25 mmol) in o-xylene (15 mL) was stirred at 120 °C for 7 h. The reaction mixture was then diluted with 100 mL of ethyl acetate, washed with water (3 × 50 mL), dried (Na$_2$SO$_4$), and concentrated in vacuo. The residue was chromatographed over 20 g of silica gel (eluted with 20:1 hexane-ethyl acetate) followed by recrystallization (ethyl...
acetate-hexane) to give 940 mg (85%) of 1h.

2-Acetyl-N-(2,4,6-trimethylbenzyl)-N-[4-(E)-stilben-2-yl]acetamide (1h)

Light yellow crystals; mp 92-93 °C (ethyl acetate-hexane); yield: 85%.

IR (KBr): 1730, 1635, 1590, 1465, 1355 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): (keto form : enol form = 1: 2.1), δ = 1.77 (s, 3H, CH₃ enol), 1.97 (s, 6H, 2 × CH₃ enol), 2.00 (s, 6H, 2 × CH₃ keto), 2.03 (s, 3H, CH₃ keto), 2.09 (s, 3H, CH₃ keto), 2.12 (s, 3H, CH₃ keto), 3.18 (d, J = 16.4 Hz, 1H, CH₃ keto), 4.43 (s, 1H, CH enol), 4.76 (d, J = 14.1 Hz, 1H, NCH₃ keto), 4.83 (d, J = 14.1 Hz, 1H, NCH₃ enol), 5.19 (d, J = 14.1 Hz, 1H, NCH₃ enol), 6.57-6.67 (m, 4H, ArH), 6.59 (s, 2H, ArH), 6.81 (d, J = 16.2 Hz, 1H, CH), 6.88 (d, J = 16.2 Hz, 1H, CH), 6.92 (d, J = 16.2 Hz, 1H, CH), 7.00 (d, J = 16.2 Hz, 1H, CH), 7.04-7.14 (m, 2H, ArH), 7.27-7.47 (m, 12H, ArH), 7.62-7.68 (m, 2H, ArH), 14.39 (s, 1H, OH enol).

Anal. Calcd for C₂₈H₂₉NO₂: C, 81.72; H, 7.10; N, 3.40. Found: C, 81.73; H, 7.16; N, 3.35.

2-Acetyl-N-(2,4,6-trimethylbenzyl)-N-[4-methyl-(E)-stilben-2-yl]acetamide (1i)

White crystals; mp 134-135 °C (ethyl acetate-hexane); yield: 78% (Based on 94% conversion of starting aniline).

IR (KBr): 1720, 1660, 1595, 1375, 1355 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): (keto form: enol form = 1:2.4), δ = 1.77 (s, 3H, CH₃ enol), 1.98 (s, 6H, 2 × CH₃ enol), 2.01 (s, 6H, 2 × CH₃ keto), 2.04 (s, 3H, CH₃ keto), 2.07 (s, 3H, CH₃ keto), 2.35 (s, 3H, CH₃ keto), 2.37 (s, 3H, CH₃ keto), 3.19 (s, 2H, CH₂ keto), 4.45 (s, 1H, CH enol), 4.75 (d, J = 14.1 Hz, 1H, NCH₃ keto), 4.81 (d, J = 14.1 Hz, 1H, NCH₃ enol), 5.16 (d, J = 14.1 Hz, 1H, NCH₃ enol), 5.28 (d, J = 14.1 Hz, 1H, NCH₃ enol), 6.48 (d, J = 8.0 Hz, 1H, ArH), 6.52 (d, J = 8.5 Hz, 1H, ArH), 6.60 (s, 2H, ArH), 6.64 (s, 2H, ArH), 6.77 (d, J = 16.3 Hz, 1H, CH), 6.84 (d, J = 16.4 Hz, 1H, CH), 6.85-6.94 (m, 2H, ArH), 6.90 (d, J = 16.3 Hz, 1H, CH), 6.97 (d, J = 16.4 Hz, 1H, CH), 7.29 (t, J = 7.6 Hz, 1H, ArH), 7.33-7.46 (m, 11H, ArH), 14.41 (s, 1H, OH enol).


2-Acetyl-N-[4-chloro-(E)-stilben-2-yl]-N-(2,4,6-trimethylbenzyl)acetamide (1j)

White crystals; mp 140-141 °C (ethyl acetate-hexane); yield: 92% (Based on 94% conversion of starting aniline).

IR (KBr): 1720, 1660, 1635, 1480, 1355 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): (keto form: enol form = 1.3:1), δ = 1.79 (s, 3H, CH₃ enol), 1.99 (s, 6H, 2 × CH₃ enol), 2.02 (s, 6H, 2 × CH₃ keto), 2.05 (s, 3H, CH₃ keto), 2.10 (s, 3H, CH₃ keto), 2.12 (s, 3H, CH₃ keto), 3.17 (d, J = 16.0 Hz, 1H, CH₃ keto), 3.24 (d, J = 16.0 Hz, 1H, CH₃ keto), 4.40 (s, 1H, CH enol), 4.70 (d, J = 14.0 Hz, 1H, NCH₃ keto), 4.77 (d, J = 14.0 Hz, 1H, NCH₃ enol), 5.16 (d, J = 14.0 Hz, 1H, NCH₃ enol), 5.28 (d, J = 14.0 Hz, 1H, NCH₃ enol), 6.48 (d, J = 8.3 Hz, 1H, ArH), 6.55 (d, J = 8.5 Hz, 1H, ArH), 6.62 (s, 2H, ArH), 6.66 (s, 2H, ArH), 6.74 (d, J = 16.2 Hz, 1H, CH), 6.82 (d, J = 16.0 Hz, 1H, CH), 6.92 (d, J = 16.2 Hz, 1H, CH), 7.00 (d, J = 16.0 Hz, 1H, CH), 7.02 (dd, J = 8.3, 2.2 Hz, 1H, ArH), 7.06 (dd, J = 8.5, 1.8 Hz, 1H, ArH), 7.28-7.42 (m, 8H, ArH), 7.45 (d, J = 7.5 Hz, 2H, ArH), 7.63 (s, 2H, ArH), 14.31 (s, 1H, OH enol).


Typical procedure for the preparation of 2-cyano-N-[4-(E)-stilben-2-yl]acetamide: A solution of N-(2,4,6-trimethylbenzyl)-[4'-methoxy-(E)-stilben-2-yl]amine (765 mg, 2.14 mmol), 2-cyanoacetic acid (228 mg, 2.68 mmol) and DCC (572 mg, 2.78 mmol) in chloroform (15 mL) was stirred at 60 °C for 24 h. The reaction mixture was then diluted with 100 mL of ethyl acetate, washed with water (3 × 50 mL), dried (Na₂SO₄), and concentrated in vacuo. The residue was chromatographed over 20 g of silica gel (eluted with 20:1 hexane-ethyl acetate) followed by recrystallization (ethyl acetate-hexane) to give 604 mg (94%) of 1k and 223 mg of starting material.

2-Cyano-N-[4'-methoxy-(E)-stilben-2-yl]-N-(2,4,6-trimethylbenzyl)acetamide (1k)
White crystals; mp 187-188 °C (ethyl acetate-hexane); yield: 94% (Based on 71% conversion of starting aniline).

IR (KBr): 1665, 1515, 1410, 1245, 1175 cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 1.98 (s, 6H, CH₃), 2.14 (s, 3H, CH₃), 3.08 (d, J = 18.3 Hz, 1H, CH), 3.14 (d, J = 18.3 Hz, 1H, CH), 3.85 (s, 3H, OCH₃), 4.78 (d, J = 14.1 Hz, 1H, NCH), 5.30 (d, J = 14.1 Hz, 1H, NCH), 6.63 (d, J = 7.6 Hz, 1H, ArH), 6.64 (d, J = 16.3 Hz, 1H, CH), 6.68 (s, 2H, ArH), 6.70 (d, J = 16.3 Hz, 1H, CH), 6.92 (d, J = 8.2 Hz, 2H, ArH), 7.11 (t, J = 7.6 Hz, 1H, ArH), 7.34 (t, J = 7.6 Hz, 1H, ArH), 7.37 (t, J = 8.2 Hz, 2H, ArH), 7.66 (d, J = 7.6 Hz, 1H, ArH).

13C NMR (100.6 MHz, CDCl₃): δ = 19.7 (2 × q), 20.8 (q), 25.7 (t), 45.4 (t), 55.4 (q), 114.09 (2 × d), 118.7 (d), 126.1 (d), 128.22 (2 × d), 128.27 (d), 128.35 (s), 129.06 (s), 129.09 (2 × d), 129.6 (d), 129.9 (d), 132.6 (d), 136.4 (s), 136.5 (s), 137.6 (s), 138.3 (2 × s), 160.0 (s), 161.8 (s).


2-Cyano-N-[4’-methoxy-4-methyl-(E)]-stilben-2-yl]-N-(2,4,6-trimethylbenzyl)acetamide (1l)

White crystals; mp 175-176 °C (ethyl acetate-hexane); yield: 86% (Based on 79% conversion of starting aniline).

IR (KBr): 1600, 1510, 1400, 1250, 1020 cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 1.99 (s, 6H, CH₃), 2.15 (s, 3H, CH₃), 2.36 (s, 3H, CH₃), 3.07 (d, J = 18.2 Hz, 1H, CH), 3.13 (d, J = 18.2 Hz, 1H, CH), 3.85 (s, 3H, OCH₃), 4.76 (d, J = 13.8 Hz, 1H, NCH), 5.27 (d, J = 13.8 Hz, 1H, NCH), 6.50 (d, J = 8.4 Hz, 1H, ArH), 6.60 (d, J = 16.1 Hz, 1H, CH), 6.68 (s, 2H, ArH), 6.91 (d, J = 8.5 Hz, 2H, ArH), 6.97 (d, J = 16.1 Hz, 1H, CH), 7.36 (d, J = 8.5 Hz, 2H, ArH), 7.45 (s, 1H, ArH).

13C NMR (100.6 MHz, CDCl₃): δ = 19.8 (2 × q), 20.8 (q), 21.3 (q), 25.6 (t), 45.4 (t), 55.4 (q), 114.2 (2 × d), 118.9 (d), 126.5 (d), 128.2 (2 × d + s), 128.5 (s), 129.09 (2 × d), 129.15 (d), 129.21 (s), 132.2 (d), 134.2 (s), 135.9 (s), 137.6 (s), 138.3 (2 × s), 139.6 (s), 160.0 (s), 162.0 (s).


Typical procedure for the preparation of 2-ethoxycarbonyl-N-[4’-methoxy-4-methyl-(E)]-stilben-2-yl]-acetamide (1m)

White crystals; mp 175-176 °C (ethyl acetate-hexane); yield: 86% (Based on 79% conversion of starting aniline).

IR (KBr): 1740, 1660, 1510, 1395, 1250 cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 1.17 (t, J = 7.3 Hz, 3H, CH₃), 2.00 (s, 6H, 2 × CH₃), 2.13 (s, 3H, CH₃), 3.11 (s, 2H, CH₂), 3.85 (s, 3H, OCH₃), 3.99-4.13 (m, 2H, OCH₂), 4.70 (d, J = 14.1 Hz, 1H, NCH), 5.36 (d, J = 14.1 Hz, 1H, NCH), 6.58 (d, J = 7.7 Hz, 1H, ArH), 6.65 (s, 2H, ArH), 6.79 (d, J = 16.2 Hz, 1H, CH), 6.91 (d, J = 8.7 Hz, 2H, ArH), 6.96 (d, J = 16.2 Hz, 1H, CH), 7.03 (d, J = 7.7 Hz, 1H, ArH), 7.29 (t, J = 7.7 Hz, 1H, ArH), 7.39 (d, J = 8.7 Hz, 2H, ArH), 7.64 (d, J = 7.7 Hz, 1H, ArH).

13C NMR (100.6 MHz, CDCl₃): δ = 14.0 (q), 19.7 (2 × q), 20.8 (q), 41.8 (t), 44.7 (t), 55.4 (q), 114.2 (2 × d), 119.8 (d), 125.6 (d), 127.7 (d), 128.2 (2 × d), 128.92 (2 × d), 128.95 (d), 129.1 (s), 129.6 (s), 130.4 (d), 131.5 (d), 136.5 (s), 137.2 (s), 137.7 (s), 138.5 (2 × s), 159.8 (s), 165.9 (s), 167.6 (s).

Anal. Calcd for C₃₀H₃₃NO₄: C, 76.41; H, 7.05; N, 2.97. Found: C, 76.48; H, 7.11; N, 2.91.
Typical experimental procedure for the preparation of $N$-[(E)-stilben-2-yl]amines: A solution of dibenzoylmethane (507 mg, 2.26 mmol), [(E)-stilben-2-yl]amine (1.33 g, 6.82 mmol) and toluenesulfonic acid (50 mg, 0.26 mmol) in benzene (5 mL) was heated under reflux for 16 h using a Dean-Stark trap for azeotropic removal of water. The reaction mixture was diluted with ethyl acetate (100 mL), washed with saturated aqueous sodium bicarbonate (3 × 50 mL), water (3 × 50 mL), dried (Na$_2$SO$_4$), and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (20 g) (eluted with 1:10 ethyl acetate–hexane) to give 9a (862 mg, 95%).

(Z)-1,3-Diphenyl-3-[(E)-stilben-2-yl]amino-prop-2-en-1-one (9a)
Yellow crystals; mp 107-108 °C (ethyl acetate-hexane); yield: 95%.

IR (KBr): 1595, 1570, 1325, 755, 690 cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 6.18 (s, 1H, CH), 6.64 ($d$, $J$ = 8.0 Hz, 1H, ArH), 6.95 ($t$, $J$ = 7.5 Hz, 1H, ArH), 7.06 ($d$, $J$ = 7.5 Hz, 1H, ArH), 7.20-7.63 (m, 15 H, ArH + CH), 7.99 ($d$, $J$ = 7.1 Hz, 2H, ArH), 12.91 (s, 1 H, NH).

$^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ = 96.9 (d), 123.6 (d), 125.4 (d), 126.1 (d), 126.7 (d), 126.9 (2 × d), 127.5 (d), 127.9 (d), 128.34 (2 × d), 128.36 (4 × d), 128.7 (2 × d), 129.6 (d), 131.24 (d), 131.28 (d), 132.2 (s), 135.9 (s), 137.3 (s), 137.4 (s), 139.9 (s), 162.8 (s), 189.8 (s).

Anal. Calcd for C$_{29}$H$_{23}$NO: C, 86.75; H, 5.77; N, 3.49. Found: C, 86.63; H, 5.80; N, 3.42.

(Z)-3-[4-Methyl-[(E)-stilben-2-yl]amino]-1,3-diphenyl-prop-2-en-1-one (9b)
Yellow crystals; mp 135-136 °C (ethyl acetate-hexane); yield: 95%.

IR (KBr): 1585, 1560, 1325, 755, 690 cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.29 (s, 1H, CH$_3$), 6.15 (d, $J$ = 8.1 Hz, 1H, ArH), 6.55 ($d$, $J$ = 8.1, 1.6 Hz, 1H, ArH), 7.05 ($d$, $J$ = 16.2 Hz, 1H, CH), 7.22–7.39 (m, 8 H, ArH + CH), 7.40 (d, $J$ = 1.6 Hz, 1H, ArH), 7.42–7.52 (m, 4H, ArH + CH), 7.55 ($d$, $J$ = 7.2 Hz, 2H, ArH), 7.97–8.01 (m, 2H, ArH), 12.86 (s, 1H, NH).

$^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ = 21.0 (q), 96.5 (d), 123.7 (d), 126.4 (d), 126.6 (d), 126.8 (2 × d), 127.3 (2 × d), 127.8 (d), 128.27 (2 × d), 128.32 (2 × d), 128.4 (d), 128.6 (2 × d), 129.5 (d), 130.9 (d), 131.2 (d), 132.0 (s), 134.9 (s), 135.0 (s), 135.9 (s), 137.3 (s), 140.0 (s), 163.1 (s), 189.6 (s).

Anal. Calcd for C$_{30}$H$_{25}$NO: C, 86.71; H, 6.06; N, 3.37. Found: C, 86.77; H, 6.05; N, 3.31.

(Z)-3-[4-Chloro-[(E)-stilben-2-yl]amino]-1,3-diphenyl-prop-2-en-1-one (9c)
Yellow needles; mp 157-158 °C (ethyl acetate-hexane); yield: 93%.

IR (KBr): 1595, 1565, 1325, 1280, 755 cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 6.20 (s, 1H, CH), 6.54 ($d$, $J$ = 8.6 Hz, 1H, ArH), 6.90 ($dd$, $J$ = 8.6, 2.3 Hz, 1H, ArH), 7.07 ($d$, $J$ = 16.2 Hz, 1H, CH), 7.26-7.41 (m, 8 H, ArH + CH), 7.42–7.54 (m, 4H, ArH + CH), 7.57 ($d$, $J$ = 7.2 Hz, 2H, ArH), 7.96-8.02 (m, 2H, ArH), 12.84 (s, 1H, NH).

$^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ = 97.4 (d), 122.3 (d), 125.9 (d), 127.0 (2 × d), 127.33 (d), 127.35 (2 × d), 127.6 (d), 128.26 (d), 128.31 (2 × d), 128.4 (2 × d), 128.5 (2 × d), 128.8 (2 × d), 129.8 (2 × d), 130.8 (s), 131.5 (d), 132.5 (d), 133.7 (s), 135.6 (s), 136.1 (s), 136.8 (s), 137.9 (s), 162.4 (s), 190.1 (s).


(Z)-1-phenyl-3-[(E)-stilben-2-yl]amino-but-2-en-1-one (9d)
Yellow crystals; mp 87-88 °C (ethyl acetate-hexane); yield: 74%.

IR (KBr): 1580, 1320, 1280, 685, 540 cm$^{-1}$.
$^{13}$C NMR (100.6 MHz, CDCl$_3$): δ = 20.3 (q), 93.7 (d), 123.5 (d), 126.1 (d), 126.8 (2 × d), 127.1 (2 × d), 127.3 (d), 127.6 (d), 128.0 (2 × d), 128.3 (2 × d), 128.7 (2 × d), 130.9 (d), 131.3 (d), 134.3 (s), 136.4 (s), 137.1 (s), 140.0 (s), 163.7 (s), 188.9 (s).

Anal. Caled for C$_{24}$H$_{21}$NO: C, 84.92; H, 6.24; N, 4.13. Found: C, 84.84; H, 6.33; N, 4.12.

(Z)-3-[4-Methyl-(E)-stilben-2-yl]amino-1-phenyl-but-2-en-1-one (9e)

Yellow needles; mp 89-90 °C (ethyl acetate-hexane); yield: 77%.

IR (KBr): 1600, 1575, 1545, 1320, 730 cm$^{-1}$.

1H NMR (400 MHz, CDCl$_3$): δ = 1.93 (s, 3H, CH$_3$), 2.41 (s, 3H, CH$_3$), 5.93 (s, 1H, CH), 7.05-7.16 (m, 3H, CH + ArH), 7.21-7.29 (m, 2H, CH + ArH), 7.32 (t, J = 7.5 Hz, 2H, ArH), 7.42-7.52 (m, 5H, ArH), 7.54 (s, 1H, ArH), 7.95 (dd, J = 7.5, 1.7 Hz, 2H, ArH), 12.86 (s, 1H, NH).

13C NMR (100.6 MHz, CDCl$_3$): δ = 20.1 (q), 21.1 (q), 93.4 (d), 123.4 (d), 126.4 (d), 126.7 (2 × d), 127.0 (2 × d), 127.3 (d), 127.8 (d), 128.1 (2 × d), 128.5 (2 × d), 128.7 (d), 130.7 (d), 130.8 (d), 133.8 (2 × s), 136.9 (s), 137.0 (s), 140.0 (s), 163.9 (s), 188.5 (s).

Anal. Calcd for C$_{25}$H$_{23}$NO: C, 84.95; H, 6.56; N, 3.96. Found: C, 84.79; H, 6.67; N, 3.93.

(Z)-3-[4-Chloro-(E)-stilben-2-yl]amino-1-phenyl-but-2-en-1-one (9f)

Yellow needles; mp 89-90 °C (ethyl acetate-hexane); yield: 78%.

IR (KBr): 1600, 1575, 1285, 740, 695 cm$^{-1}$.

1H NMR (400 MHz, CDCl$_3$): δ = 1.95 (s, 3H, CH$_3$), 5.97 (s, 1H, CH), 7.12 (d, J = 16.6 Hz, 1H, CH), 7.13 (d, J = 9.5 Hz, 1H, CH), 7.22 (d, J = 16.6 Hz, 1H, CH), 7.26 (t, J = 7.5 Hz, 2H, ArH), 7.33 (t, J = 7.5 Hz, 2H, ArH), 7.42-7.51 (m, 5H, ArH), 7.71 (d, J = 2.3 Hz, 1H, ArH), 7.95 (dd, J = 7.5, 1.4 Hz, 2H, ArH), 12.90 (s, 1H, NH).

13C NMR (100.6 MHz, CDCl$_3$): δ = 20.2 (q), 94.2 (d), 122.2 (d), 125.9 (d), 127.0 (2 × d), 127.1 (2 × d), 127.8 (d), 128.3 (3 × d), 130.7 (d), 132.9 (s), 134.9 (s), 135.9 (s), 136.6 (s), 139.8 (s), 163.2 (s), 189.1 (s).

Anal. Caled for C$_{24}$H$_{20}$ClNO: C, 77.10; H, 5.39; N, 3.75. Found: C, 76.94; H, 5.46; N, 3.74.

(Z)-3-Phenyl-3-[((E))-stilben-2-y]aminoacrylonitrile (9g)

Colorless needles; mp 152-153 °C (ethyl acetate-hexane); yield: 54%.

IR (KBr) 3270, 2190, 1590, 970, 695 cm$^{-1}$.

1H NMR (400 MHz, CDCl$_3$): δ = 4.27 (s, 1H, CH), 5.82 (s, 1H, NH), 7.11 (d, J = 16.3 Hz, 1H, CH), 7.18 (d, J = 16.3 Hz, 1H, CH), 7.26-7.40 (m, 6H, ArH), 7.42-7.51 (m, 5H, ArH), 7.50-7.56 (m, 3H, ArH), 7.71-7.80 (m, 3H, ArH).

13C NMR (100.6 MHz, CDCl$_3$): δ = 67.0 (d), 120.7 (s), 122.9 (d), 126.7 (2 × d), 126.80 (d), 126.86 (d), 127.5 (d), 127.9 (2 × d), 128.2 (d), 128.7 (d), 128.8 (2 × d), 129.1 (2 × d), 130.9 (d), 132.0 (d), 133.8 (s), 135.1 (s), 135.9 (s), 136.8 (s), 161.1 (s).

HMRS(EI) m/z [M$^+$] calcd for C$_{23}$H$_{18}$N$_2$: 322.1470; found: 322.1475.

(Z)-3-[4-Methyl-(E)-stilben-2-yl]amino-3-phenylacrylonitrile (9h)

Colorless needles; mp 174-175 °C (ethyl acetate-hexane); yield: 57%.

IR (KBr): 3270, 2190, 1590, 970, 695 cm$^{-1}$.

1H NMR (400 MHz, CDCl$_3$): δ = 2.42 (s, 3H, CH$_3$), 4.20 (s, 1H, CH), 5.75 (s, 1H, NH), 7.10 (d, J = 16.4 Hz, 1H, CH), 7.13-7.20 (m, 2H, ArH), 7.16 (d, J = 16.4 Hz, 1H, CH), 7.28 (t, J = 7.5 Hz, 1H, ArH), 7.36 (t, J = 7.5 Hz, 2H, ArH), 7.47 (d, J = 7.5 Hz, 2H, ArH), 7.50-7.54 (m, 3H, ArH), 7.55 (s, 1H, ArH), 7.73-7.79 (m, 2H, ArH).

13C NMR (100.6 MHz, CDCl$_3$): δ = 21.2 (q), 66.4 (d), 120.9 (s), 123.0 (d), 126.7 (2 × d), 127.0 (d), 127.2 (d), 127.9 (2 × d), 128.1 (d), 128.8 (2 × d), 129.1 (2 × d), 129.6 (d), 130.8 (d), 131.6 (d), 133.3 (s), 133.7 (s), 135.2 (s), 136.9 (s), 137.5 (s), 161.5 (s).

HMRS(EI) m/z [M$^+$] calcd for C$_{24}$H$_{20}$N$_2$: 336.1626; found: 336.1626.

(Z)-3-[4-Chloro-(E)-stilben-2-yl]amino-3-phenylacrylonitrile (9i)

Colorless needles; mp 175-176 °C (ethyl acetate-hexane); yield: 58%.

IR (KBr): 3270, 2195, 1565, 1505, 695 cm$^{-1}$.
**1H NMR (400 MHz, CDCl₃):** δ = 4.23 (s, 1H, CH), 5.81 (s, 1H, NH), 7.09 (s, 2H, CH), 7.21 (d, J = 8.4 Hz, 1H, ArH), 7.24-7.33 (m, 2H, ArH), 7.36 (t, J = 7.4 Hz, 2H, ArH), 7.47 (d, J = 7.4 Hz, 2H, ArH), 7.50-7.57 (m, 3H, ArH), 7.70 (d, J = 1.9 Hz, 1H, ArH), 7.71-7.77 (m, 2H, ArH).

**13C NMR (100.6 MHz, CDCl₃):** δ = 67.6 (d), 120.4 (s), 121.6 (d), 126.6 (d), 126.8 (2 × d), 127.9 (2 × d), 128.2 (d), 128.9 (2 × d), 129.1 (2 × d), 131.0 (d), 133.1 (s), 133.2 (d), 134.3 (s), 134.7 (s), 135.5 (s), 136.3 (s), 161.0 (s).

**HMRS(EI) m/z [M]+ calcd for C₂₃H₁₇ClN₂: 356.1080; found: 356.1072.**

**Typical experimental procedure for the preparation of dimethyl 2-[[(E)-stilben-2-yl]aminofumarates:**

A solution of dimethyl acetylenedicarboxylate (548 mg, 3.86 mmol), [(E)-stilben-2-yl]amine (602 mg, 3.09 mmol) in methanol (10 mL) was stirred at room temperature for 2 h. The reaction mixture was diluted with ethyl acetate (100 mL), washed with saturated aqueous sodium bicarbonate (3 × 50 mL), water (3 × 50 mL), dried (Na₂SO₄), and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (20g) (eluted with 1:10 ethyl acetate–hexane) to give 9j (887 mg, 86%).

**Dimethyl 2-[(E)-stilben-2-yl]aminofumarate (9j):**
White crystals; mp 81-82 °C (ethyl acetate-hexane); yield: 86%.

**IR (KBr):** 3245, 1730, 1670, 1610, 1430, 1270 cm⁻¹.

**1H NMR (400 MHz, CDCl₃):** δ = 3.61 (s, 3H, OCH₃), 3.75 (s, 3H, OCH₃), 5.49 (s, 1H, CH), 6.84 (d, J = 7.9 Hz, 1H, ArH), 7.07 (d, J = 16.4 Hz, 1H, CH), 7.13-7.22 (m, 2H, ArH), 7.27 (t, J = 7.5 Hz, 1H, ArH), 7.34 (d, J = 16.4 Hz, 1H, CH), 7.36 (t, J = 7.5 Hz, 2H, ArH), 7.53 (d, J = 7.5 Hz, 2H, ArH), 7.62 (d, J = 7.9 Hz, 1H, ArH), 9.61 (s, 1H, NH).

**13C NMR (100.6 MHz, CDCl₃):** δ = 51.2 (q), 52.7 (q), 93.6 (d), 122.9 (d), 123.4 (d), 125.3 (d), 126.5 (d), 126.8 (2 × d), 127.8 (d), 128.0 (d), 128.6 (2 × d), 131.28 (s), 131.30 (d), 137.2 (s), 138.2 (s), 148.9 (s), 164.5 (s), 170.0 (s).

**Anal. Calcd for C₂₀H₁₉NO₄: C, 71.20; H, 5.68; N, 4.15. Found: C, 71.12; H, 5.73; N, 4.14.**

**Dimethyl 2-4-methyl-[(E)-stilben-2-yl]aminofumarate (9k):**
Yellow solids; mp 90-91 °C (ethyl acetate-hexane); yield: 85%.

**IR (KBr):** 3245, 1740, 1615, 1435, 1260, 1140 cm⁻¹.

**1H NMR (400 MHz, CDCl₃):** δ = 2.35 (s, 3H, CH₃), 3.61 (s, 3H, OCH₃), 3.74 (s, 3H, OCH₃), 5.44 (s, 1H, CH), 6.76 (d, J = 8.0 Hz, 1H, ArH), 6.99 (dd, J = 8.0, 1.5 Hz, 1H, ArH), 7.06 (d, J = 16.3 Hz, 1H, CH), 7.26 (t, J = 7.4 Hz, 1H, ArH), 7.31 (d, J = 16.3 Hz, 1H, CH), 7.36 (t, J = 7.4 Hz, 2H, ArH), 7.44 (s, 1H, ArH), 7.52 (d, J = 7.4 Hz, 2H, ArH), 9.55 (s, 1H, NH).

**13C NMR (100.6 MHz, CDCl₃):** δ = 21.0 (q), 51.2 (q), 52.7 (q), 92.6 (d), 123.2 (d), 123.6 (d), 126.7 (2 × d), 127.8 (d), 128.6 (2 × d), 131.28 (s), 131.30 (d), 137.2 (s), 138.2 (s), 148.9 (s), 164.5 (s), 170.1 (s).

**Anal. Calcd for C₂₁H₂₁NO₄: C, 71.78; H, 6.02; N, 3.99. Found: C, 71.80; H, 6.02; N, 3.96.**

**Dimethyl 2-4-chloro-[(E)-stilben-2-yl]aminofumarate (9l):**
Yellow needles; mp 117-118 °C (ethyl acetate-hexane); yield: 89%.

**IR (KBr):** 1740, 1605, 1440, 1140, 960 cm⁻¹.

**1H NMR (400 MHz, CDCl₃):** δ = 3.64 (s, 3H, OCH₃), 3.75 (s, 3H, OCH₃), 5.53 (s, 1H, CH), 6.77 (d, J = 8.5 Hz, 1H, ArH), 7.07 (d, J = 16.2 Hz, 1H, CH), 7.14 (dd, J = 8.5, 2.4 Hz, 1H, ArH), 7.25 (d, J = 16.2 Hz, 1H, CH), 7.29 (t, J = 7.5 Hz, 1H, ArH), 7.37 (t, J = 7.5 Hz, 2H, ArH), 7.52 (d, J = 7.5 Hz, 2H, ArH), 7.59 (d, J = 2.4 Hz, 1H, ArH), 9.53 (s, 1H, NH).

**13C NMR (100.6 MHz, CDCl₃):** δ = 51.3 (q), 52.8 (q), 92.4 (d), 122.2 (d), 124.2 (d), 126.2 (d), 126.9 (2 × d), 127.8 (d), 128.2 (d), 128.7 (2 × d), 130.8 (s), 132.5 (d), 133.0 (s), 136.76 (s), 136.81 (s), 148.5 (s), 164.2 (s), 170.0 (s).

**Anal. Calcd for C₂₀H₁₈ClNO₄: C, 64.61; H, 4.88; N, 3.77. Found: C, 64.53; H, 4.92; N, 3.75.
Dimethyl 2-[4,5-dimethyl-(E)-stilben-2-yl]aminofumarate (9m)

Yellow needles; mp 112-113 °C (ethyl acetate-hexane); yield: 83%.

IR (KBr): 3240, 1735, 1670, 1615, 1275, 1210 cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ = 2.20 (s, 3H, CH\(_3\)), 2.26 (s, 3H, CH\(_3\)), 3.60 (s, 3H, OCH\(_3\)), 3.74 (s, 3H, OCH\(_3\)), 5.41 (s, 1H, CH), 6.66 (s, 1H, ArH), 7.02 (d, \(J = 16.3\) Hz, 1H, CH), 7.25 (t, \(J = 7.4\) Hz, 1H, ArH), 7.27 (d, \(J = 16.3\) Hz, 1H, CH), 7.35 (t, \(J = 7.4\) Hz, 2H, ArH), 7.39 (s, 1H, ArH), 7.51 (d, \(J = 7.4\) Hz, 2H, ArH), 9.53 (s, 1H, NH);

\(^1\)C NMR (100.6 MHz, CDCl\(_3\)): δ = 19.4 (q), 19.5 (q), 51.1 (q), 52.6 (q), 92.2 (d), 123.6 (d), 124.6 (d), 126.6 (2 \(\times\) d), 127.3 (d), 127.6 (d), 128.6 (2 \(\times\) d), 129.0 (s), 129.9 (d), 133.9 (s), 135.9 (s), 136.9 (s), 137.5 (s), 149.5 (s), 164.6 (s), 170.2 (s).

Anal. Calcd for C\(_{22}\)H\(_{23}\)NO\(_4\): C, 72.31; H, 6.34; N, 3.83. Found: C, 72.31; H, 6.36; N, 3.81.

Dimethyl 2-[4,6-dimethyl-(E)-stilben-2-yl]aminofumarate (9n)

White crystals; mp 91-92 °C (ethyl acetate-hexane); yield: 78%.

IR (KBr): 3275, 1745, 1675, 1595, 1440, 1220 cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ = 2.26 (s, 3H, CH\(_3\)), 2.33 (s, 3H, CH\(_3\)), 3.47 (s, 3H, OCH\(_3\)), 3.77 (s, 3H, OCH\(_3\)), 5.36 (s, 1H, CH), 6.96 (s, 1H, ArH), 6.98 (d, \(J = 16.2\) Hz, 1H, CH), 7.19 (d, \(J = 16.2\) Hz, 1H, CH), 7.25 (t, \(J = 7.4\) Hz, 1H, ArH), 7.29 (s, 1H, ArH), 7.34 (t, \(J = 7.4\) Hz, 2H, ArH), 7.46 (d, \(J = 7.4\) Hz, 2H, ArH), 9.39 (s, 1H, NH).

\(^1\)C NMR (100.6 MHz, CDCl\(_3\)): δ = 18.4 (q), 21.1 (q), 51.0 (q), 52.5 (q), 88.7 (d), 124.2 (d), 124.8 (d), 126.6 (2 \(\times\) d), 127.6 (d), 128.6 (2 \(\times\) d), 130.4 (d), 130.7 (d), 134.2 (s), 134.3 (s), 134.7 (s), 136.1 (s), 137.5 (s), 151.5 (s), 163.6 (s), 170.7 (s).

Anal. Calcd for C\(_{22}\)H\(_{23}\)NO\(_4\): C, 72.31; H, 6.34; N, 3.83. Found: C, 72.28; H, 6.38; N, 3.81.

2) Copies of \(^1\)H and \(^1\)C NMR spectra