

# ***N*-Metalated Imines by Reaction of 1,1-Diethoxybuta-2-diene with Aromatic Nitriles, as Useful Intermediates for the Synthesis of Substituted Pyrimidines and Cyclopentenones**

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## **SUPPORTING INFORMATION**

**General.** All solvent were degassed before use. All reactions involving moisture-sensitive reagents were performed under nitrogen in oven-dried glassware using syringe-septum cap technique. Chromatographic separation were carried out on Merck silica gel 60 pretreated with Et<sub>3</sub>N (1%) using flash-column techniques, R<sub>f</sub> values refer to TLC carried out on 0.25 mm silica gel plates (Merck F254), visualization was accomplished by UV light (254 nm) or by spraying a solution of 5% (w/v) ammonium molibdate and heating to 200 °C or with 5% aqueous KMnO<sub>4</sub>. BuLi (1.6 M solution in hexanes) was purchased from Aldrich. *t*-BuOK was sublimed under vacuum (5.0 mm Hg) prior to the reaction. Anhydrous THF was freshly distilled under argon from Na/benzophenone ketyl. <sup>1</sup>H NMR spectra were recorded at 200 MHz, and <sup>13</sup>C NMR spectra at 50.33 MHz. MS spectra were recorded at an ionizing voltage of 70 eV.

### **Experimental Section**

**General procedure for the syntheses of dienyl imines:** a solution of freshly sublimated *t*-BuOK (6 mmol, 672 mg, 3.0 equiv) in 20 mL of THF was refrigerated to –78 °C. 1,1-diethoxybut-2-ene (2 mmol, 288 mg) in 2 mL of THF and BuLi (1.6 M in hexanes, 6 mmol, 3.75 mL, 3.0 equiv) were added in quick succession and the mixture was stirred for 2 h during which the temperature raised to –40 °C. Afterwards the reaction was refrigerated back to –78 °C and the appropriate nitrile (2.2 mmol, 1.1 equiv) in 5 mL of THF was added. The resulting mixture was stirred at –78 °C for 1 h. Then, a saturated NH<sub>4</sub>Cl aqueous solution (20 mL) was added, the mixture was extracted with Et<sub>2</sub>O (3 × 20 mL), washed with H<sub>2</sub>O (10 mL), brine (2 × 20 mL), and dried over anhydrous K<sub>2</sub>CO<sub>3</sub>. After filtration and evaporation of the solvent, crude products were purified by column flash chromatography.

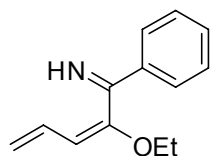
**General procedure for the syntheses of pyrimidines:** a solution of freshly sublimated *t*-BuOK (6 mmol, 672 mg, 3.0 equiv) in 20 mL of THF was refrigerated to –78 °C. 1,1-diethoxybut-2-ene (2 mmol, 288 mg) in 2 mL of THF and BuLi (1.6 M in hexanes, 6 mmol, 3.75 mL, 3.0 equiv) were added in quick succession and the mixture was stirred for 2 h during which the temperature raised to –40 °C. Afterwards the reaction was refrigerated again to –78 °C and a solution of the appropriate nitrile (5.0 mmol, 2.5 equiv) in 5 mL of THF was added. The resulting mixture was stirred at –78 °C for 1 h, after which the temperature was allowed to raise to r.t. and the reaction stirred overnight. Then, a saturated NH<sub>4</sub>Cl aqueous solution (20 mL) was added, the mixture was extracted with Et<sub>2</sub>O (3 × 20 mL), washed with H<sub>2</sub>O (10 mL), brine (2 × 20 mL), and dried over anhydrous K<sub>2</sub>CO<sub>3</sub>. After filtration and evaporation of the solvent, crude products were purified by column flash chromatography.

**General procedure for the syntheses of protected dienyl imines:** a solution of freshly sublimated *t*-BuOK (6 mmol, 672 mg, 3.0 equiv) in 20 mL of THF was refrigerated to –78 °C. 1,1-diethoxybut-2-ene (2 mmol, 288 mg) in 2 mL of THF and BuLi (1.6 M in hexanes, 6 mmol, 3.75 mL, 3.0 equiv) were added in quick succession and the mixture

was stirred for 2 h during which the temperature raised to  $-40\text{ }^{\circ}\text{C}$ . Afterwards the reaction was refrigerated again to  $-78\text{ }^{\circ}\text{C}$  and a solution of the appropriate nitrile (2.2 mmol, 1.1 equiv) in 5 mL of THF was added. The resulting mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for 1 h, then  $\text{PhCOCl}$  (4.4 mmol, 2.2 equiv) was added dropwise. Then, a saturated  $\text{NH}_4\text{Cl}$  aqueous solution (20 mL) was added, the mixture was extracted with  $\text{Et}_2\text{O}$  ( $3 \times 20\text{ mL}$ ), washed with  $\text{H}_2\text{O}$  (10 mL), brine ( $2 \times 20\text{ mL}$ ), and dried over anhydrous  $\text{K}_2\text{CO}_3$ . After filtration and evaporation of the solvent, crude products were purified by column flash chromatography.

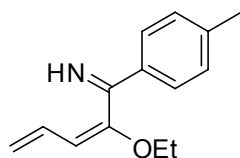
**General procedure for the syntheses of cyclopentenones:** a solution of protected dienyl imine (0.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was stirred in the presence of Amberlyst-15<sup>®</sup> and the reaction monitored by TLC. When the reaction was terminated, a small amount of anhydrous  $\text{K}_2\text{CO}_3$  was added, and after filtration and evaporation of the solvent, crude products were purified by column flash chromatography.

### Spectroscopic data



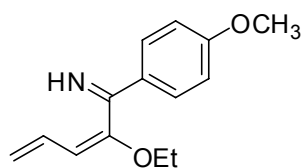
**(E)-2-ethoxy-1-phenylpenta-2,4-dien-1-imine.** Purified by flash chromatography

( $\text{Et}_2\text{O}$ :petroleum ether 3:7, 1%  $\text{Et}_3\text{N}$ ,  $R_f$  0.40) to give (289 mg, 72%):  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ).  $\delta$  ppm 7.78 (m, 2H), 7.44 (s, 1H), 7.41 (m, 3H), 6.23 (dt,  $J = 16.8, 10.5\text{ Hz}$ , 1H), 5.70 (d,  $J = 10.5\text{ Hz}$ , 1H), 5.13 (dd,  $J = 16.8, 1.2\text{ Hz}$ , 1H), 4.86 (dd,  $J = 10.5, 1.2\text{ Hz}$ , 1H), 3.91 (q,  $J = 7.0\text{ Hz}$ , 2H), 1.32 (t,  $J = 7.0\text{ Hz}$ , 3H).  $^{13}\text{C}$  NMR (50.33 MHz,  $\text{CDCl}_3$ ).  $\delta$  172.4 (s), 155.4 (s), 136.5 (s), 131.7 (d), 130.8 (d), 128.3 (d), 127.9 (d), 114.3 (t), 106.1 (d), 63.6 (t), 14.3 (q). MS  $m/z$  201 ( $\text{M}^+$ , 98), 186 (61), 172 (100), 157 (36). Anal. Calcd for  $\text{C}_{13}\text{H}_{15}\text{NO}$ : C, 77.58; H, 7.51. Found C, 77.46; H, 6.65.



**(E)-2-ethoxy-1-p-tolylpenta-2,4-dien-1-imine.** Purified by flash chromatography

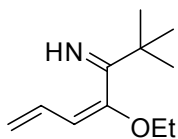
( $\text{Et}_2\text{O}$ :petroleum ether 3:7, 1%  $\text{Et}_3\text{N}$ ,  $R_f$  0.50) to give (202 mg, 47%):  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ).  $\delta$  ppm 7.83 (d,  $J = 8.2\text{ Hz}$ , 2H), 7.26 (d,  $J = 8.2\text{ Hz}$ , 2H) sovraimposed to 7.28 (s, 1H), 6.51 (dt,  $J = 17.3, 10.7\text{ Hz}$ , 1H), 5.81 (d,  $J = 10.7\text{ Hz}$ , 1H), 5.20 (dd,  $J = 17.3, 1.2\text{ Hz}$ , 1H), 4.97 (dd,  $J = 10.7, 1.2\text{ Hz}$ , 1H), 3.95 (q,  $J = 6.8\text{ Hz}$ , 2H), 2.43 (s, 3H), 1.35 (t,  $J = 6.8\text{ Hz}$ , 3H).  $^{13}\text{C}$  NMR (50.33 MHz,  $\text{CDCl}_3$ ).  $\delta$  191.3 (s), 153.9 (s), 144.2 (s), 133.5 (s), 131.3 (d), 129.9 (d), 128.9 (d), 115.9 (t), 108.8 (d), 63.8 (t), 21.6 (q), 14.3 (q). MS  $m/z$  215 ( $\text{M}^+$ , 58), 186 (32), 118 (100), 91 (44). Anal. Calcd for  $\text{C}_{14}\text{H}_{17}\text{NO}$ : C, 78.10; H, 7.96. Found C, 78.35; H, 7.85.



**(E)-2-ethoxy-1-(4-methoxyphenyl)penta-2,4-dien-1-imine.** Purified by flash

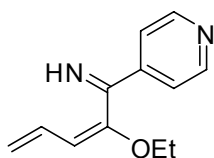
chromatography ( $\text{Et}_2\text{O}$ :petroleum ether 2:3, 1%  $\text{Et}_3\text{N}$ ,  $R_f$  0.40) to give (391 mg, 85%):  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ).  $\delta$  ppm 9.42 (br, 1H), 7.74 (d,  $J = 8.8\text{ Hz}$ , 2H), 6.90 (d,  $J = 8.8\text{ Hz}$ , 2H), 6.22 (dt,  $J = 16.9, 10.8\text{ Hz}$ , 1H), 5.65 (d,  $J = 10.8\text{ Hz}$ , 1H), 5.10 (dd,  $J = 16.9, 1.8\text{ Hz}$ , 1H), 4.83 (dd,  $J = 10.8, 1.8\text{ Hz}$ , 1H), 3.89 (q,  $J = 7.1\text{ Hz}$ , 2H), 3.82 (s, 3H), 1.31 (t,

$J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (50.33 MHz,  $\text{CDCl}_3$ ).  $\delta$  171.5 (s), 161.7 (s), 155.8 (s), 131.8 (d), 129.5 (d), 128.9 (s), 113.9 (t), 113.5 (d), 105.6 (d), 63.5 (t), 55.1 (q), 14.3 (q). MS  $m/z$  231 ( $\text{M}^+$ , 100), 216 (53), 200 (51), 186 (48). Anal. Calcd for  $\text{C}_{14}\text{H}_{17}\text{NO}_2$ : C, 72.70; H, 7.41. Found C, 72.44; H, 7.31.



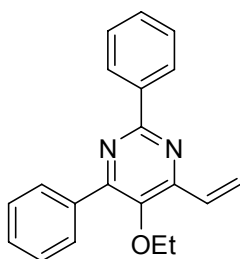
**(E)-4-ethoxy-2,2-dimethylhepta-4,6-dien-3-imine.** Purified by flash chromatography

( $\text{Et}_2\text{O}$ :petroleum ether 1:4, 1%  $\text{Et}_3\text{N}$ ,  $R_f$  0.50) to give (296 mg, 82%):  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ).  $\delta$  ppm 9.38 (br, 1H), 6.18 (m, 1H), 5.38 (d,  $J = 10.8$  Hz, 1H), 5.03 (dd,  $J = 17.1, 1.8$  Hz, 1H), 4.81 (d,  $J = 10.8, 1.8$  Hz, 1H), 3.80 (q,  $J = 6.8$  Hz, 2H), 1.32 (t,  $J = 6.8$  Hz, 3H), 1.18 (s, 9H).  $^{13}\text{C}$  NMR (50.33 MHz,  $\text{CDCl}_3$ ).  $\delta$  183.9 (s), 132.3 (d), 113.0 (t), 103.1 (d), 62.9 (t), 39.9 (s), 28.1 (q), 14.3 (q). MS  $m/z$  181 ( $\text{M}^+$ , 52), 97 (77), 69 (85), 57 (100). Anal. Calcd for  $\text{C}_{11}\text{H}_{19}\text{NO}$ : C, 72.88; H, 10.56. Found C, 72.96; H, 10.55.



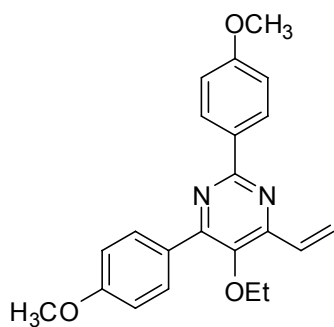
**(E)-2-ethoxy-1-(pyridin-4-yl)penta-2,4-dien-1-imine.** Purified by flash chromatography

(ethyl acetate, 1%  $\text{Et}_3\text{N}$ ,  $R_f$  0.50) to give (303 mg, 75%):  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ).  $\delta$  ppm 10.19 (br, 1H), 8.69 (d,  $J = 6.1$  Hz, 2H), 7.65 (d,  $J = 6.1$  Hz, 2H), 6.08 (dt,  $J = 16.5, 10.2$  Hz, 1H), 5.71 (d,  $J = 10.8$  Hz, 1H), 5.15 (dd,  $J = 16.5, 1.7$  Hz, 1H), 4.90 (dd,  $J = 10.8, 1.7$  Hz, 1H), 4.11 (q,  $J = 7.2$  Hz, 2H), 1.31 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (50.33 MHz,  $\text{CDCl}_3$ ).  $\delta$  170.8 (s), 153.7 (s), 150.1 (d), 143.8 (s), 131.0 (d), 121.7 (d), 115.6 (t), 106.9 (d), 63.8 (t), 14.2 (q). MS  $m/z$  202 ( $\text{M}^+$ , 72), 187 (77), 171 (100), 157 (32). Anal. Calcd for  $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}$ : C, 71.26; H, 6.98. Found C, 71.11; H, 6.65.

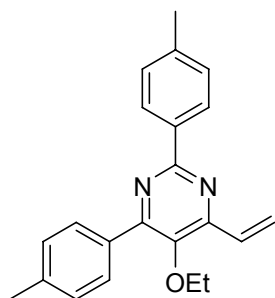


**5-ethoxy-2,4-diphenyl-6-vinylpyrimidine.** Purified by flash chromatography

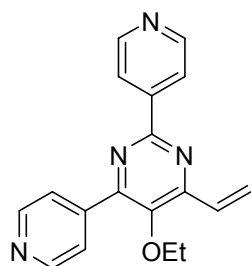
( $\text{Et}_2\text{O}$ :petroleum ether 5:95, 1%  $\text{Et}_3\text{N}$ ,  $R_f$  0.80) to give (387 mg, 64%):  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ).  $\delta$  ppm 8.57-8.52 (m, 2H), 7.75-7.70 (m, 2H), 7.51-7.46 (m, 6H), 6.68 (dd,  $J = 17.7, 11.9$  Hz, 1H), 6.12 (d,  $J = 17.7$  Hz, 1H), 5.49 (d,  $J = 11.9$  Hz, 1H), 4.73 (q,  $J = 7.1$  Hz, 2H), 1.57 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (50.33 MHz,  $\text{CDCl}_3$ ).  $\delta$  ppm 167.3 (s), 165.0 (s), 160.6 (s), 138.6 (s), 137.4 (s), 130.3 (d), 129.8 (d), 128.8 (d), 128.1 (d), 128.0 (d), 127.9 (d), 120.6 (t), 113.3 (s), 62.6 (t), 14.3 (q). MS  $m/z$  302 ( $\text{M}^+$ , 100), 275 (69), 230 (18), 77 (23). Anal. Calcd for  $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}$ : C, 79.44; H, 6.00. Found C, 79.42; H, 5.95.



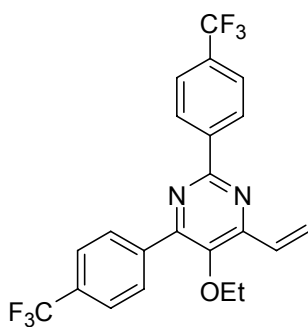
**5-ethoxy-2,4-bis(4-methoxyphenyl)-6-vinylpyrimidine.** Purified by flash chromatography (Et<sub>2</sub>O:petroleum ether 1:4, 1% Et<sub>3</sub>N, R<sub>f</sub> 0.60) to give (532 mg, 74%): <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>). δ ppm 8.47 (d, *J* = 8.7 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.00 (m, 4H), 6.67 (dd, *J* = 18.0, 12.0 Hz, 1H), 6.08 (d, *J* = 18.0 Hz, 1H), 5.45 (d, *J* = 12.0 Hz, 1H), 4.68 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 6H), 1.54 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (50.33 MHz, CDCl<sub>3</sub>). δ ppm 167.2 (s), 164.4 (s), 161.4 (s), 160.3 (s), 160.1 (s), 131.4 (d), 131.1 (s), 130.3 (s), 129.6 (d), 129.1 (d), 119.8 (t), 113.4 (d), 113.1 (d), 112.1 (s), 62.4 (t), 55.2 (q), 14.4 (q). MS *m/z* 361 (M<sup>+</sup>, 100), 348 (46), 335 (86), 317 (34). Anal. Calcd for C<sub>22</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>: C, 72.91; H, 6.12. Found C, 72.56; H, 6.10.



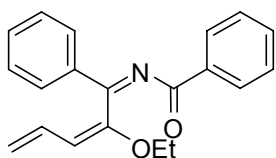
**5-ethoxy-2,4-di-*p*-tolyl-6-vinylpyrimidine.** Purified by flash chromatography (Et<sub>2</sub>O:petroleum ether 1:9, 1% Et<sub>3</sub>N, R<sub>f</sub> 0.50) to give (413 mg, 63%): <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>). δ ppm 8.42 (d, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.29 (m, 4H), 6.68 (dd, *J* = 17.8, 11.8 Hz, 1H), 6.11 (d, *J* = 17.8 Hz, 1H), 5.46 (d, *J* = 11.8 Hz, 1H), 4.71 (q, *J* = 7.1 Hz, 2H), 2.45 (s, 6H), 1.56 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (50.33 MHz, CDCl<sub>3</sub>). δ ppm 167.2 (s), 165.0 (s), 160.6 (s), 140.4 (s), 138.8 (s), 135.8 (s), 134.8 (s), 129.7 (d), 129.0 (d), 128.9 (d), 128.6 (d), 128.0 (d), 120.1 (t), 112.8 (s), 62.5 (t), 21.3 (q), 14.4 (q). MS *m/z* 330 (M<sup>+</sup>, 100), 316 (22), 303 (68), 91 (23). Anal. Calcd for C<sub>22</sub>H<sub>22</sub>N<sub>2</sub>O: C, 79.97; H, 6.71. Found C, 79.89; H, 6.42.



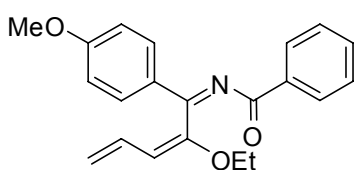
**5-ethoxy-2,4-di(pyridin-4-yl)-6-vinylpyrimidine.** Purified by flash chromatography (ethyl acetate, 1% Et<sub>3</sub>N, R<sub>f</sub> 0.30) to give (493 mg, 81%): <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>). δ ppm 8.73-8.61 (m, 4H), 8.18 (d, *J* = 6.1 Hz, 2H), 7.48 (d, *J* = 6.1 Hz, 2H), 6.49 (dd, *J* = 17.7, 11.8 Hz, 1H), 6.00 (dd, *J* = 17.7, 1.8 Hz, 1H), 5.48 (dd, *J* = 11.8, 1.8 Hz, 1H), 4.60 (q, *J* = 7.1 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (50.33 MHz, CDCl<sub>3</sub>) δ ppm 167.4 (s), 162.0 (s), 158.8 (s), 150.1 (d), 149.6 (d), 145.5 (s), 144.1 (s), 127.2 (d), 123.9 (d), 123.0 (t), 121.6 (d), 115.4 (s), 63.2 (t), 14.1 (q). MS *m/z* 304 (M<sup>+</sup>, 15), 277 (100), 248 (49), 78 (22). Anal. Calcd for C<sub>18</sub>H<sub>16</sub>N<sub>4</sub>O: C, 71.04; H, 5.30. Found C, 70.99; H, 5.12.



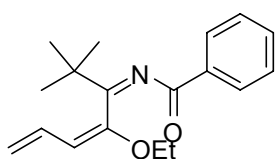
**5-ethoxy-2,4-bis(4-(trifluoromethyl)phenyl)-6-vinylpyrimidine.** Purified by flash chromatography (Et<sub>2</sub>O:petroleum ether 2:98, 1% Et<sub>3</sub>N, R<sub>f</sub> 0.70) to give (569 mg, 65%): <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>). δ ppm 8.70-8.53 (m, 2H), 7.97-7.61 (m, 6H), 6.60 (dd, *J* = 17.6, 12.0 Hz, 1H), 6.11 (dd, *J* = 17.6, 1.6 Hz, 1H), 5.55 (dd, *J* = 12.0, 1.6 Hz, 1H), 4.73 (q, *J* = 6.9 Hz, 2H), 1.58 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (50.33 MHz, CDCl<sub>3</sub>). δ 167.4 (s), 163.4 (s), 159.4 (s), 141.8 (s), 140.4 (s), 130.1 (d), 128.2 (d), 127.8 (d), 125.1 (d), 125.0 (d), 124.9 (s), 122.1 (t), 114.5 (s), 63.0 (t), 14.2 (q). MS *m/z* 438 (M<sup>+</sup>, 100), 411 (96), 369 (39), 342 (42). Anal. Calcd for C<sub>22</sub>H<sub>16</sub>F<sub>6</sub>N<sub>2</sub>O: C, 60.28; H, 3.68. Found C, 59.96; H, 3.58.



***N*-((*E*)-2-ethoxy-1-phenylpenta-2,4-dienylidene)benzamide.** Purified by flash chromatography (Et<sub>2</sub>O:petroleum ether 3:7, 1% Et<sub>3</sub>N, R<sub>f</sub> 0.30) to give (430 mg, 70%): <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>). δ ppm 8.12-7.86 (m, 4H), 7.68-7.34 (m, 6H), 6.06 (dt, *J* = 16.6, 10.5 Hz, 1H), 5.66 (d, *J* = 10.5 Hz, 1H), 5.02 (dd, *J* = 16.6, 1.4 Hz, 1H), 4.78 (dd, *J* = 10.5, 1.4 Hz, 1H), 3.71 (q, *J* = 6.9 Hz, 2H), 0.92 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (50.33 MHz, CDCl<sub>3</sub>). δ 179.3 (s), 162.5 (s), 149.7 (s), 135.1 (s), 133.1 (s), 132.6 (d), 132.0 (d), 131.3 (d), 129.2 (d), 129.0 (d), 128.5 (d), 127.9 (d), 114.8 (t), 107.5 (d), 63.8 (t), 13.6 (q). MS *m/z* 305 (M<sup>+</sup>, 41), 200 (56), 105 (100), 77 (68). Anal. Calcd for C<sub>20</sub>H<sub>19</sub>NO<sub>2</sub>: C, 78.66; H, 6.27. Found C, 78.23; H, 6.15.

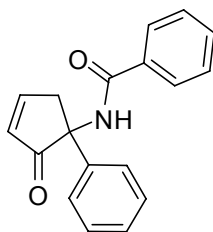


***N*-((*E*)-2-ethoxy-1-(4-methoxyphenyl)penta-2,4-dienylidene)benzamide.** Purified by flash chromatography (methylene chloride, 1% Et<sub>3</sub>N, R<sub>f</sub> 0.50) to give (430 mg, 64%): <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>). δ ppm 8.06-7.83 (m, 4H), 7.59-7.34 (m, 4H), 6.96 (d, *J* = 8.9 Hz, 2H), 6.08 (dt, *J* = 16.6, 10.5 Hz, 1H), 5.62 (d, *J* = 10.5 Hz, 1H), 5.00 (dd, *J* = 16.6, 0.9 Hz, 1H), 4.77 (dd, *J* = 10.5, 0.9 Hz, 1H), 3.87 (s, 3H), 3.69 (q, *J* = 7.0 Hz, 2H), 0.91 (t, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (50.33 MHz, CDCl<sub>3</sub>). δ 179.4 (s), 162.8 (s), 161.7 (s), 150.0 (s), 133.4 (s), 132.4 (d), 131.5 (d), 131.0 (d), 129.2 (d), 127.8 (d), 127.6 (s), 114.5 (t), 113.9 (d), 107.0 (d), 63.8 (t), 55.2 (q), 13.6 (q). MS *m/z* 335 (M<sup>+</sup>, 100), 230 (53), 199 (88), 105 (100). Anal. Calcd for C<sub>21</sub>H<sub>21</sub>NO<sub>3</sub>: C, 75.20; H, 6.31. Found C, 74.95; H, 6.10.



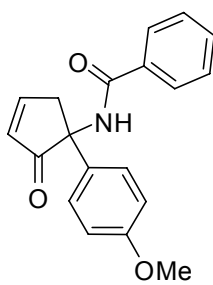
***N*-((*E*)-4-ethoxy-2,2-dimethylhepta-4,6-dien-3-ylidene)benzamide.** Purified by flash chromatography (Et<sub>2</sub>O:petroleum ether 1:9, 1% Et<sub>3</sub>N, R<sub>f</sub> 0.80) to give (413 mg, 72%): <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>). δ

ppm 7.59-7.32 (m, 5H), 6.09 (dt,  $J = 16.6, 10.5$  Hz, 1H), 5.25 (d,  $J = 10.5$  Hz, 1H), 4.89 (dd,  $J = 16.6, 1.6$  Hz, 1H), 4.74 (dd,  $J = 10.5, 1.6$  Hz, 1H), 3.53 (q,  $J = 6.9$  Hz, 2H), 1.31 (s, 9H), 1.05 (t,  $J = 6.9$  Hz, 3H).  $^{13}\text{C}$  NMR (50.33 MHz,  $\text{CDCl}_3$ ).  $\delta$  179.0 (s), 174.5 (s), 152.6 (s), 132.5 (d), 131.9 (d), 129.4 (s), 129.2 (d), 127.8 (d), 113.3 (t), 103.6 (d), 63.1 (t), 39.6 (s), 28.1 (q), 14.0 (q). MS  $m/z$  285 ( $\text{M}^+$ , 39), 228 (26), 180 (67), 57 (100). Anal. Calcd for  $\text{C}_{18}\text{H}_{23}\text{NO}_2$ : C, 75.76; H, 8.12. Found C, 75.41; H, 8.00.



***N*-(2-oxo-1-phenylcyclopent-3-enyl)benzamide.** Purified by flash chromatography

( $\text{Et}_2\text{O}$ :petroleum ether 4:1, 1%  $\text{Et}_3\text{N}$ ,  $R_f$  0.80) to give (127 mg, 92%):  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ).  $\delta$  ppm 7.95-7.87 (m, 1H), 7.84 (d,  $J = 6.7$  Hz, 2H), 7.59-7.27 (m, 8H), 7.05 (br, 1H), 6.31 (d,  $J = 3.9$  Hz, 1H), 3.59 (d,  $J = 6.9$  Hz, 2H).  $^{13}\text{C}$  NMR (50.33 MHz,  $\text{CDCl}_3$ ).  $\delta$  204.8 (s), 166.5 (s), 162.7 (d), 138.2 (s), 133.4 (s), 131.7 (d), 130.7 (d), 128.8 (d), 128.4 (d), 127.8 (d), 126.9 (d), 125.0 (d), 65.0 (s), 44.0 (t). MS  $m/z$  277 ( $\text{M}^+$ , 38), 172 (52), 105 (100), 77 (95). Anal. Calcd for  $\text{C}_{18}\text{H}_{15}\text{NO}_2$ : C, 77.96; H, 5.45. Found C, 77.86; H, 5.25.



***N*-(1-(4-methoxyphenyl)-2-oxocyclopent-3-enyl)benzamide.** Purified by flash chromatography

( $\text{Et}_2\text{O}$ :petroleum ether 9:1, 1%  $\text{Et}_3\text{N}$ ,  $R_f$  0.70) to give (146 mg, 95%):  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ).  $\delta$  ppm 7.91-7.77 (m, 3H), 7.59-7.34 (m, 5H), 6.99-6.92 (m, 1H), 6.91-6.84 (m, 2H), 6.30 (d,  $J = 5.97$  Hz, 1H), 3.78 (s, 3H), 3.57 (d,  $J = 3.59$  Hz, 2H).  $^{13}\text{C}$  NMR (50.33 MHz,  $\text{CDCl}_3$ ).  $\delta$  204.9 (s), 166.5 (s), 162.2 (d), 159.1 (s), 133.4 (s), 131.7 (d), 130.8 (d), 130.1 (s), 128.4 (d), 126.8 (d), 126.5 (d), 114.1 (d), 64.5 (s), 55.1 (q), 43.6 (t). MS  $m/z$  307 ( $\text{M}^+$ , 50), 202 (55), 105 (100), 77 (72). Anal. Calcd for  $\text{C}_{19}\text{H}_{17}\text{NO}_3$ : C, 74.25; H, 5.58. Found C, 74.12; H, 5.43.

