Steric Hinderance-Controlled Pd(0)-Catalyzed Coupling-Cyclization of 2,3-Allenamides and Organic Iodides. An Efficient Synthesis of Iminolactones and γ -Hydroxy- γ -lactams

Shengming Ma* and Hexin Xie

Supporting Information

Analytical Data for Starting Materials.

***N*-Benzyl 2-benzyl-4-methylpenta-2, 3-dienamide (1d).** white solid, mp 100-102 °C (petroleum ether); ^1H NMR (300 MHz, CDCl_3) δ 7.35-7.18 (m, 10H), 6.18 (bs, 1H), 4.48 (d, J = 6 Hz, 2H), 3.62 (s, 2H), 1.66 (s, 6H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 203.11, 166.67, 140.03, 138.74, 128.92, 128.59, 128.06, 127.43, 127.25, 125.91, 102.53, 101.46, 43.56, 34.79, 19.81; MS m/z 291 (M^+ , 30.21), 91 (100); IR (KBr) 3298, 1954, 1633 cm^{-1} ; Anal. Calcd for $\text{C}_{20}\text{H}_{21}\text{NO}$: C, 82.44; H, 7.26; N, 4.81 Found: C, 82.36; H, 7.41; N, 4.65.

***N*-Benzyl 4-methyl-penta-2, 3-dienamide (1e).** light yellow solid, mp 122-124 °C (*n*-hexane/diethyl ether); ^1H NMR (300 MHz, CDCl_3) δ 7.37-7.25 (m, 5H), 6.05 (bs, 1H), 5.53-5.47 (heptet, J = 3 Hz, 1H), 4.49 (d, J = 5.7 Hz, 2H), 1.80 (d, J = 3 Hz, 6H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 205.74, 166.06, 138.82, 128.88, 127.86, 127.60, 101.92, 89.44, 43.73, 20.01; MS m/z 201 (M^+ , 25.88), 91 (100); IR (KBr) 3265, 1964, 1626 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}$: C, 77.58; H, 7.51; N, 6.96 Found: C, 77.13; H, 7.59; N, 6.70.

***N*-(*n*-Butyl) 4-methylpenta-2, 3-dienamide (1f).** white solid, mp 91-93 °C (*n*-hexane); ^1H NMR (300 MHz, CDCl_3) δ 5.72 (bs, 1H), 5.45-5.39 (heptet, J = 3 Hz, 1H), 3.27 (q, J =

6.7 Hz, 2H), 1.80 (d, $J = 3$ Hz, 3H), 1.54-1.44 (m, 2H), 1.39-1.30 (m, 2H), 0.92 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 205.41, 165.99, 101.57, 89.61, 39.57, 32.00, 20.29, 19.97, 13.99; MS m/z 167 (M^+ , 30.62), 67 (100); IR (KBr) 3280, 1965, 1626 cm^{-1} ; Anal. Calcd for $\text{C}_{10}\text{H}_{17}\text{NO}$: C, 71.81; H, 10.25; N, 8.37 Found: C, 71.80; H, 10.06; N, 8.30.

4-Methylpenta-2, 3-dienamide (1g). white solid, mp 125-127 °C (diethyl ether) (mp 131 °C ($\text{CHCl}_3/\text{isohexane}$))¹; ^1H NMR (300 MHz, CDCl_3) δ 5.72 (bs, 1H), 5.42-5.40 (m, 1H), 5.40 (bs, 1H), 1.82 (d, $J = 3$ Hz, 6H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 206.34, 168.76, 101.22, 88.59, 19.51; MS m/z 111 (M^+ , 50.45), 110 (100); IR (KBr) 3385, 3331, 1963, 1656 cm^{-1} .

N-Benzyl 2, 4-dimethylpenta-2, 3-dienamide (1h). white solid, mp 87-88 °C (petroleum ether); ^1H NMR (300 MHz, CDCl_3) δ 7.35-7.25 (m, 5H), 6.26 (bs, 1H), 4.48 (d, $J = 6$ Hz, 2H), 1.87 (s, 3H), 1.76 (s, 6H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 202.42, 167.41, 138.81, 128.49, 127.30, 127.12, 100.26, 95.90, 43.45, 20.00, 14.61; MS m/z 215 (M^+ , 24.95), 91 (100); IR (KBr) 3331, 1961, 1639 cm^{-1} ; Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}$: C, 78.10; H, 7.96; N, 6.51 Found: C, 78.22; H, 8.08; N, 6.34.

N-Benzyl (4-*p*-tolyl-3-propyl-1-oxa-spiro[4,5]dec-3-enylidene) amine (4b) Starting from potassium carbonate (68 mg, 0.49 mmol), TBAB (4 mg, 0.012 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3 mg, 0.0026 mmol), allenamide **1c** (70 mg, 0.25 mmol) and 4-iodotoluene (59 mg, 0.27 mmol) in toluene (2 mL) at 70 °C for 47 h to afford 88 mg (95%) of **4b**: light yellow solid, m.p. 68-69 °C (*n*-hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.45 (d, $J = 7.2$ Hz, 2H), 7.34 (t,

$J = 7.5$ Hz, 2H), 7.26-7.21 (m, 3H), 7.03 (d, $J = 7.8$ Hz, 2H), 4.70 (s, 2H), 2.41 (s, 3H), 2.16 (t, $J = 7.7$ Hz, 2H), 1.72-1.52 (m, 11H), 1.13-1.00 (m, 1H), 0.82 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 163.50, 157.97, 141.65, 137.72, 131.01, 130.76, 129.03, 128.23, 128.07, 127.67, 126.04, 89.64, 50.94, 34.18, 26.16, 24.62, 22.14, 21.64, 21.27, 13.97; MS m/z 373 (M^+ , 100); IR (KBr) 1680 cm^{-1} ; Anal. Calcd for $\text{C}_{26}\text{H}_{31}\text{NO}$: C, 83.60; H, 8.36; N, 3.75. Found: C, 83.63; H, 8.21; N, 3.69.

***N*-Benzyl (4-(4-methoxyphenyl)-3-propyl-1-oxa-spiro[4,5]dec-3-enylidene) amine (4c)**

Starting from potassium carbonate (68 mg, 0.49 mmol), TBAB (4 mg, 0.012 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3 mg, 0.0026 mmol), allenamide **1c** (70 mg, 0.25 mmol) and 4-iodoanisole (65 mg, 0.28 mmol) in toluene (2 mL) at $70\text{ }^\circ\text{C}$ for 65 h to afford 91 mg (95%) of **4c**: light yellow solid, m.p. $89.5\text{-}90.5\text{ }^\circ\text{C}$ (*n*-hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.44-7.22 (m, 5H), 7.05 (d, $J = 9.2$ Hz, 2H), 6.95 (d, $J = 9.2$ Hz, 2H), 4.68 (s, 2H), 3.85 (s, 3H), 2.14 (t, $J = 7.6$ Hz, 2H), 1.77-1.47 (m, 11H), 1.15-1.00 (m, 1H), 0.81 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 163.90, 159.54, 158.07, 141.87, 131.40, 129.80, 128.34, 127.96, 126.33, 126.10, 114.04, 89.99, 55.50, 51.16, 34.45, 26.40, 24.90, 22.39, 21.89, 14.22; MS m/z 389 (M^+ , 25), 254 (100); IR (KBr) 1678 cm^{-1} ; Anal. Calcd for $\text{C}_{26}\text{H}_{31}\text{NO}_2$: C, 80.22; H, 8.03; N, 3.60. Found: C, 80.11; H, 7.94; N, 3.44.

***N*-Benzyl (4-(4-nitrophenyl)-3-propyl-1-oxa-spiro[4,5]dec-3-enylidene) amine (4d)**

Starting from potassium carbonate (68 mg, 0.49 mmol), TBAB (4 mg, 0.012 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3 mg, 0.0026 mmol), allenamide **1c** (70 mg, 0.25 mmol) and 1-iodo-4-nitrobenzene (68 mg, 0.28 mmol) in toluene (2 mL) at $70\text{ }^\circ\text{C}$ for 3 d to afford 94 mg (94%) of **4d**: white solid, m.p. $127\text{-}128\text{ }^\circ\text{C}$ (*n*-hexane); ^1H NMR (300 MHz, CDCl_3) δ 8.30-8.26 (d, $J = 8.8$ Hz, 2H), 7.43-7.20 (m, 7H), 4.68 (s, 2H), 2.13 (t, $J = 7.6$ Hz, 2H),

1.77-1.46 (m, 11H), 1.15-1.00 (m, 1H), 0.79 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 162.54, 155.48, 147.94, 141.51, 141.23, 133.11, 129.82, 128.39, 127.88, 126.47, 123.94, 89.75, 51.28, 34.68, 26.50, 24.78, 22.28, 21.84, 14.20; MS m/z 404 (M^+ , 100); IR (KBr) 1681 cm^{-1} ; Anal. Calcd for $\text{C}_{25}\text{H}_{28}\text{N}_2\text{O}_3$: C, 74.23; H, 6.98; N, 6.93. Found: C, 74.39; H, 7.20; N, 6.74.

***N*-Benzyl (4-(4-methoxycarbonylphenyl)-3-propyl-1-oxa-spiro[4,5]dec-3-enylidene)**

amine (4e) Starting from potassium carbonate (68 mg, 0.49 mmol), TBAB (4 mg, 0.012 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3 mg, 0.0026 mmol), allenamide **1c** (70 mg, 0.25 mmol) and 4-iodobenzoic acid methyl ester (71 mg, 0.27 mmol) in toluene (2 mL) at 70°C for 44 h to afford 103 mg (100%) of **4e**: light yellow solid, m.p. $77.5\text{--}78.5^\circ\text{C}$ (*n*-hexane); ^1H NMR (300 MHz, CDCl_3) δ 8.07 (d, $J = 8.6$ Hz, 2H), 7.43-7.19 (m, 7H), 4.67 (s, 2H), 3.93 (s, 3H), 2.11 (t, $J = 7.6$ Hz, 2H), 1.71-1.44 (m, 11H), 1.15-1.00 (m, 1H), 0.77 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 166.88, 163.04, 156.87, 141.73, 139.05, 132.19, 130.11, 129.84, 128.81, 128.33, 127.89, 126.35, 89.78, 52.48, 51.24, 34.60, 26.44, 24.84, 22.34, 21.82, 14.16; MS m/z 417 (M^+ , 17) 283 (100); IR (KBr) $1726, 1680.7\text{ cm}^{-1}$; Anal. Calcd for $\text{C}_{27}\text{H}_{31}\text{NO}_3$: C, 77.67; H, 7.48; N, 3.35. Found: C, 77.54; H, 7.42; N, 3.21.

***N*-Benzyl (3-benzyl-5,5-dimethyl-4-phenyl-5H-furan-2-ylidene) amine (4f)**

Starting from potassium carbonate (68 mg, 0.49 mmol), TBAB (4 mg, 0.012 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3 mg, 0.0026 mmol), allenamide **1d** (72 mg, 0.25 mmol) and iodobenzene (32 μL , 0.28 mmol) in toluene (2 mL) at 70°C for 65 h to afford 87 mg (96%) of **4f**: white solid, m.p. $69.5\text{--}70.5^\circ\text{C}$ (*n*-hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.43-7.15 (m, 15H), 4.70 (s, 2H), 3.60 (s, 2H), 1.50 (s, 6H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 162.43, 157.98, 141.58, 139.46,

133.18, 130.05, 128.74, 128.52, 128.34, 128.24, 128.10, 128.07, 127.45, 126.04, 125.86, 88.83, 50.67, 30.05, 26.03; MS m/z 367 (M^+ , 100); IR (KBr) 1680 cm^{-1} ; Anal. Calcd for $\text{C}_{26}\text{H}_{25}\text{NO}$: C, 84.98; H, 6.86; N, 3.81. Found: C, 84.89; H, 6.96; N, 3.68.

***N*-Benzyl (3-benzyl-5,5-dimethyl-4-*p*-tolyl-5*H*-furan-2-ylidene) amine (4g)** Starting from potassium carbonate (68 mg, 0.49 mmol), TBAB (4 mg, 0.012 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3 mg, 0.0026 mmol), allenamide **1d** (72 mg, 0.25 mmol) and 1-iodotoluene (59 mg, 0.27 mmol) in toluene (2 mL) at 70 °C for 48 h to afford 87 mg (92%) of **4g**: white solid, m.p. 76-77 °C (*n*-hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.04 (m, 14H), 4.66 (s, 2H), 3.56 (s, 2H), 2.40 (s, 3H), 1.46 (s, 6H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 162.76, 158.31, 141.91, 139.86, 138.44, 130.43, 130.10, 129.49, 139.01, 128.38, 128.33, 128.30, 127.71, 126.26, 126.08, 89.07, 50.92, 30.36, 26.33, 21.54; MS m/z 381 (M^+ , 100); IR (KBr) 1677 cm^{-1} ; Anal. Calcd for $\text{C}_{27}\text{H}_{27}\text{NO}$: C, 85.00; H, 7.13; N, 3.67. Found: C, 84.94; H, 7.36; N, 3.64.

***N*-Benzyl (3-benzyl-5,5-dimethyl-4-(4-methoxyphenyl)-5*H*-furan-2-ylidene) amine (4h)** Starting from potassium carbonate (68 mg, 0.49 mmol), TBAB (4 mg, 0.012 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3 mg, 0.0026 mmol), allenamide **1d** (72 mg, 0.25 mmol) and 1-iodoanisole (65 mg, 0.27 mmol) in toluene (2 mL) at 70 °C for 65 h to afford 91 mg (93%) of **4h**: white solid, m.p. 94-95 °C (*n*-hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.37-6.91 (m, 14H), 4.66 (s, 2H), 3.85 (s, 3H), 3.58 (s, 2H), 1.47 (s, 6H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 162.83, 159.77, 158.05, 141.83, 139.82, 129.96, 129.70, 128.91, 128.32, 128.26, 127.65, 126.22, 126.04, 125.44, 114.18, 89.05, 55.49, 50.87, 30.32, 26.34; MS m/z 397 (M^+ , 100); IR (KBr) 1683 cm^{-1} ; Anal. Calcd for $\text{C}_{27}\text{H}_{27}\text{NO}_2$: C, 81.58; H, 6.85; N, 3.52. Found: C,

81.66; H, 6.88; N, 3.46.

***N*-Benzyl (3-benzyl-5,5-dimethyl-4-(4-nitrophenyl)-5*H*-furan-2-ylidene) amine (4i)**

Starting from potassium carbonate (68 mg, 0.49 mmol), TBAB (4 mg, 0.012 mmol), Pd(PPh₃)₄ (3 mg, 0.0026 mmol), allenamide **1d** (72 mg, 0.25 mmol) and 1-iodo-4-nitrobenzene (68 mg, 0.28 mmol) in toluene (2 mL) at 70 °C for 3 d to afford 96 mg (94%) of **4i**: white solid, m.p. 126-128 °C (*n*-hexane); ¹H NMR (300 MHz, CDCl₃) δ 8.24-8.21 (d, *J* = 8.3 Hz, 2H), 7.37-7.09 (m, 12H), 4.67 (s, 2H), 3.57 (s, 2H), 1.47 (s, 6H); ¹³C NMR (75.4 MHz, CDCl₃) δ 161.91, 155.55, 147.96, 141.41, 140.41, 138.90, 132.17, 129.63, 128.87, 128.53, 128.39, 127.73, 126.47, 126.44, 123.93, 88.84, 51.08, 30.40, 26.32; MS *m/z* 412 (M⁺, 82.62), 91 (100); IR (KBr) 1680 cm⁻¹; Anal. Calcd for C₂₆H₂₄N₂O₃: C, 75.71; H, 5.86; N, 6.79. Found: C, 75.68; H, 5.64; N, 6.75.

***N*-Benzyl (3-benzyl-5,5-dimethyl-4-(4-methoxycarbonylphenyl)-5*H*-furan-2-ylidene) amine (4j)**

Starting from potassium carbonate (68 mg, 0.49 mmol), TBAB (4 mg, 0.012 mmol), Pd(PPh₃)₄ (3 mg, 0.0026 mmol), allenamide **1d** (72 mg, 0.25 mmol) and 4-iodobenzoic acid methyl ester (71 mg, 0.27 mmol) in toluene (2 mL) at 70 °C for 3 d to afford 101 mg (96%) of **4j**: white solid, m.p. 49-50 °C (*n*-hexane); ¹H NMR (300 MHz, CDCl₃) δ 8.07-8.04 (d, *J* = 8.6 Hz, 2H), 7.36-7.13 (m, 12H), 4.66 (s, 2H), 3.95 (s, 3H), 3.55 (s, 2H), 1.46 (s, 6H); ¹³C NMR (75.4 MHz, CDCl₃) δ 166.85, 162.34, 157.02, 141.61, 139.31, 138.28, 131.14, 130.32, 129.96, 128.93, 128.64, 128.42, 128.35, 127.71, 126.37, 126.26, 88.98, 52.58, 51.00, 30.31, 26.31; MS *m/z* 425 (M⁺, 100); IR (KBr) 1725, 1682 cm⁻¹; Anal. Calcd for C₂₈H₂₇NO₃: C, 79.03; H, 6.40; N, 3.29. Found: C, 79.08; H, 6.33; N, 3.08.

***N*-Benzyl (5,5-dimethyl-4-phenyl-5*H*-furan-2-ylidene) amine (4k)** Starting from potassium carbonate (68 mg, 0.49 mmol), TBAB (4 mg, 0.012 mmol), Pd(PPh₃)₄ (3 mg, 0.0026 mmol), allenamide **1e** (50 mg, 0.25 mmol) and iodobenzene (32 μ L, 0.28 mmol) in toluene (2 mL) at 70 °C for 22 h to afford 62 mg (90%) of **4k**: light yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.50-7.23 (m, 10H), 6.33 (s, 1H), 4.58 (s, 2H), 1.68 (s, 6H); ¹³C NMR (75.4 MHz, CDCl₃) δ 162.39, 161.87, 141.13, 131.44, 129.44, 128.85, 128.32, 127.94, 127.09, 126.39, 118.80, 90.18, 51.34, 26.88; MS *m/z* 277 (M⁺, 32.49), 172 (100); IR (KBr) 1677 cm⁻¹; Anal. Calcd for C₁₉H₁₉NO: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.13; H, 6.56; N, 4.91.

***N*-*n*-Butyl-(5,5-dimethyl-4-phenyl-5*H*-furan-2-ylidene)amine (4l)** Starting from potassium carbonate (137 mg, 0.99 mmol), TBAB (8 mg, 0.025 mmol), Pd(PPh₃)₄ (6 mg, 0.0052 mmol), allenamide **1f** (83 mg, 0.50 mmol) and iodobenzene (64 μ L, 0.56 mmol) in toluene (2 mL) at 70 °C for 24 h to afford 110 mg (91%) of **4l**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.40-7.33 (m, 5H), 6.21 (s, 1H), 3.30 (t, *J* = 7.33 Hz, 2H), 1.58 (s, 6H), 1.60-1.50 (m, 2H), 1.40-1.30 (m, 2H), 0.89 (t, *J* = 7.34 Hz, 3H); ¹³C NMR (75.4 MHz, CDCl₃) δ 168.08, 161.78, 131.84, 129.58, 129.05, 127.34, 119.04, 90.16, 47.06, 33.48, 27.06, 20.91, 14.23; MS *m/z* 244 (M⁺+1, 100); IR (KBr) 1678 cm⁻¹; Anal. Calcd for C₁₆H₂₁NO: C, 78.97; H, 8.70; N, 5.76. Found: C, 79.04; H, 8.58; N, 5.78.

5,5-dimethyl-4-*p*-tolyl-5*H*-furan-2-ylideneamine (4m) Starting from potassium carbonate (195 mg, 1.4 mmol), TBAB (11 mg, 0.034 mmol), Pd(PPh₃)₄ (8 mg, 0.007 mmol), allenamide **1g** (78 mg, 0.70 mmol) and 1-iodotoluene (169 mg, 0.77 mmol) in toluene (4 mL) at 70 °C for 22 h to afford 133 mg (94%) of **4m**: light yellow solid, m.p.

94-95 °C (*n*-hexane-CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.39 (d, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 6.26 (s, 1H), 2.38 (s, 3H), 1.63 (s, 6H); ¹³C NMR (75.4 MHz, CDCl₃) δ 170.48, 164.28, 140.48, 129.83, 128.27, 127.38, 116.71, 89.99, 26.85, 21.54; MS *m/z* 201 (M⁺, 52.43), 158 (100); IR (KBr) 1656 cm⁻¹; Anal. Calcd for C₁₃H₁₅NO: C, 77.58; H, 7.51; N, 6.96 Found: C, 77.38; H, 7.51; N, 6.85.

5,5-dimethyl-4-(4-methoxyphenyl)-5*H*-furan-2-ylideneamine (4n) Starting from potassium carbonate (194 mg, 1.4 mmol), TBAB (11 mg, 0.034 mmol), Pd(PPh₃)₄ (8 mg, 0.007 mmol), allenamide **1g** (78 mg, 0.70 mmol) and 1-iodoanisole (181 mg, 0.77 mmol) in toluene (4 mL) at 70 °C for 22 h to afford 141 mg (93%) of **4n**: light yellow solid, m.p. 99-100 °C (*n*-hexane-CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.46 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.22 (s, 1H), 3.85 (s, 3H), 1.65 (s, 6H); ¹³C NMR (75.4 MHz, CDCl₃) δ 170.59, 163.97, 161.13, 128.97, 123.42, 115.33, 114.50, 89.73, 55.54, 26.91; MS *m/z* 217 (M⁺, 77.57), 132 (100); IR (KBr) 3430, 1656 cm⁻¹; Anal. Calcd for C₁₃H₁₅NO₂: C, 71.87; H, 6.96; N, 6.45 Found: C, 71.87; H, 6.94; N, 6.30.

5,5-dimethyl-4-(4-methoxycarbonylphenyl)-5*H*-furan-2-ylideneamine (4o) Starting from potassium carbonate (198 mg, 1.4 mmol), TBAB (11 mg, 0.034 mmol), Pd(PPh₃)₄ (8 mg, 0.007 mmol), allenamide **1g** (78 mg, 0.70 mmol) and 4-iodobenzoic acid methyl ester (203 mg, 0.77 mmol) in toluene (4 mL) at 70 °C for 22 h to afford 155 mg (90%) of **4o**: light yellow solid, m.p. 117.5-118.5 °C (*n*-hexane-CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 8.08 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 8.7 Hz, 2H), 6.36 (s, 1H), 3.94 (s, 3H), 1.64 (s, 6H); ¹³C NMR (75.4 MHz, CDCl₃) δ 169.45, 166.35, 163.13, 135.57, 131.18,

130.21, 127.40, 119.56, 89.98, 52.54, 26.68; MS m/z 245 (M^+ , 27), 170 (100); IR (KBr) 3413, 1717, 1668 cm^{-1} ; Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_3$: C, 68.56; H, 6.16; N, 5.71 Found: C, 68.75; H, 6.07; N, 5.58.

***N*-Benzyl (4-(hex-1-enyl)-5,5-dimethyl-5*H*-furan-2-ylidene) amine (4p)** Starting from potassium carbonate (91 mg, 0.66 mmol), TBAB (11 mg, 0.034 mmol), $\text{Pd}(\text{PPh}_3)_4$ (19 mg, 0.016 mmol), allenamide **1h** (70 mg, 0.33 mmol) and (*E*)-1-iodo-1-hexenyl (104mg, 0.50 mmol) in toluene (2 mL) at 70 °C for 17 h to afford 73 mg (75%) of **4p**: light yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.17 (m, 5H), 6.16 (dt, $J = 16.2$ and 2.4 Hz, 1H), 5.94 (dt, $J = 16.2$ and 6.9 Hz, 1H), 4.58 (s, 2H), 2.22 (q, $J = 6.8$ Hz, 2H), 1.91 (s, 3H), 1.48 (s, 6H), 1.50-1.31(m, 4H), 0.93 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 164.87, 152.70, 141.40, 138.13, 128.39, 128.05, 126.49, 124.93, 120.53, 88.28, 50.91, 34.00, 31.50, 26.92, 22.52, 14.21, 9.71; MS m/z 297 (M^+ , 7.99), 105 (100); IR (KBr) 1678 cm^{-1} ; HRMS calcd for $\text{C}_{20}\text{H}_{27}\text{NO}$ 297.20926 Found 297.21308.

***N*-Benzyl (4-(*Z*-2'-methoxycarbonylvinyl)-3,5,5-trimethyl-5*H*-furan-2-ylidene) amine (4q)** Starting from potassium carbonate (90 mg, 0.66 mmol), TBAB (12 mg, 0.037 mmol), $\text{Pd}(\text{PPh}_3)_4$ (19 mg, 0.016 mmol), allenamide **1h** (70 mg, 0.33 mmol) and methyl 3-iodo-(*2Z*) propenoate (106mg, 0.50 mmol) in toluene (2 mL) at 70 °C for 20 h to afford 96 mg (99%) of **4q**: light yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.20 (m, 5H), 6.43 (dq, $J = 12.3$ and 1.5 Hz, 1H), 6.15 (d, $J = 12.0$ Hz, 1H), 4.58 (s, 2H), 3.71 (s, 3H), 1.74 (d, $J = 1.2$ Hz, 3H), 1.43 (s, 6H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 165.59, 163.48, 150.87, 141.41, 133.68, 128.50, 128.41, 127.98, 126.49, 125.60, 88.21, 52.05, 51.22, 26.08, 10.91; MS m/z 299 (M^+ , 17.62), 91 (100); IR (KBr) 1732, 1681 cm^{-1} ; HRMS calcd

for C₁₈H₂₁NO₃ 299.15214 Found 299.15417.

***N*-Benzyl (4-(*E*-2'-methoxycarbonylvinyl)-3,5,5-trimethyl-5*H*-furan-2-ylidene)**

amine (4r) Starting from potassium carbonate (92 mg, 0.67 mmol), TBAB (11 mg, 0.034 mmol), Pd(PPh₃)₄ (19 mg, 0.016 mmol), allenamide **1h** (70 mg, 0.33 mmol) and methyl 3-iodo-(2*E*) propenoate (105mg, 0.50 mmol) in toluene (2 mL) at 70 °C for 20 h to afford 96 mg (99%) of **4r**: white solid, m.p. 71-72 °C (*n*-hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.51 (d, *J* = 16.5, 1H), 7.40-7.21 (m, 5H), 6.07 (d, *J* = 16.2 Hz, 1H), 4.60 (s, 2H), 3.81 (s, 3H), 2.05 (s, 3H), 1.53 (s, 6H); ¹³C NMR (75.4 MHz, CDCl₃) δ 166.71, 162.52, 148.87, 140.83, 135.00, 133.27, 128.19, 127.70, 126.35, 121.73, 87.53, 51.98, 51.12, 26.52, 9.99; MS *m/z* 299 (M⁺, 16.20), 91 (100); IR (KBr) 1718, 1672 cm⁻¹; Anal. Calcd for C₁₈H₂₁NO₃: C, 72.22; H, 7.07; N, 4.68 Found: C, 72.20; H, 7.14; N, 4.58.

References:

1. Greaves P. M.; Landor P.D.; Landor S. R.; Odyek O. *Tetrahedron* **1974**, *30*, 1427.