

Palladium(II)-Catalyzed Tandem Intramolecular Aminopalladation of Alkynes and Conjugate Addition. Synthesis of Oxazolidinones, Imidazolidinones and Lactams

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Spectra and analytical data of new compounds:

3e: Oil, ^1H NMR (300 MHz, CDCl_3) δ 7.89 (d, $J = 8.4\text{Hz}$, 2H), 7.80 (br, 1H), 7.46-7.26 (m, 7H), 6.29 (d, $J = 2.3\text{Hz}$, 1H), 2.67 (d, $J = 2.3\text{Hz}$, 1H), 2.43 (s, 3H); IR (neat): 3273, 2129, 1747, 1598, 1495, 1447, 1356, 1272, 1187, 1160, 1091, 861, 763, 698, 665, 546 cm^{-1} ; MS m/e : 329 (M^+), 330 (M^++1), 286, 155, 132, 131, 115, 91; HRMS Calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_4\text{S}$: 329.0722 Found: 329.0705.

3h: Oil, ^1H NMR (300 MHz, CDCl_3) δ 7.92 (d, $J = 8.4\text{Hz}$, 2H), 7.85 (br, 1H), 7.34 (d, $J = 8.4\text{Hz}$, 2H), 2.54 (s, 1H), 2.45 (s, 3H), 1.91-1.68 (m, 2H), 1.61 (s, 3H), 1.39-1.18 (m, 6H), 0.86 (t, $J = 6.7\text{Hz}$, 3H); IR (neat): 3271, 2957, 2932, 2872, 2121, 1754, 1599,

1440, 1378, 1228, 1164, 1090, 1038, 815, 663, 590, 548 cm^{-1} ; MS m/e : 338 (M^+), 339 (M^++1), 294, 216, 197, 198, 155, 91; HRMS Calcd for $C_{17}H_{23}NO_4S$: 338.1426 Found: 338.1420.

5a: oil, ^1H NMR (300 MHz, CDCl_3) δ 9.73 (s, 1H), 7.84 (d, $J = 8.4\text{Hz}$, 2H), 7.28 (d, $J = 8.4\text{Hz}$, 2H), 5.79 (tt, $J = 2.6, 7.9\text{Hz}$, 1H), 4.82 (t, $J = 2.6\text{Hz}$, 2H), 2.59 (t, $J = 6.8\text{Hz}$, 2H), 2.38 (s, 3H), 2.13 (dt, $J = 7.9, 6.8\text{Hz}$, 2H); IR (neat): 2852, 2747, 1792, 1725, 1692, 1391, 1160, 1089, 1060 cm^{-1} ; MS m/e 310 (M^++1), 309 (M^+), 253, 228, 155, 138, 91, 65. Anal.: Calcd for $C_{14}H_{15}NO_5S$: C, 54.36; H, 4.89; N, 4.53; Found: C, 54.33; H, 5.02; N, 4.73

5b: oil, ^1H NMR (300 MHz, CDCl_3) δ 7.87 (d, $J = 8.4\text{Hz}$, 2H), 7.32 (d, $J = 8.4\text{Hz}$, 2H), 5.75-5.82 (m, 1H), 4.88 (s, 2H), 2.55-2.62 (m, 2H), 2.39 (s, 3H), 2.07-2.23 (m, 5H); IR (neat): 2997, 2928, 2872, 1783, 1708, 1594.1419, 1384, 1365, 1229, 1190, 1175, 1164, 1110, 1089, 1060, 997 cm^{-1} ; MS m/e 324 (M^++1), 306, 280, 242, 168, 155, 152, 139, 108, 91; Anal.: Calcd for $C_{15}H_{17}NO_5S$: C, 55.71; H, 5.30; N, 4.33; Found: C, 55.73; H, 5.34; N, 4.36.

5c: oil, ^1H NMR (300 MHz, CDCl_3) δ 9.80 (s, 1H), 7.94 (d, $J = 8.4\text{Hz}$, 2H), 7.36 (d, $J = 8.4\text{Hz}$, 2H), 5.89 (dt, $J = 2.0, 7.3\text{Hz}$, 1H), 5.07-5.10 (m, 1H), 2.65 (t, $J = 6.9\text{Hz}$, 2H), 2.39 (s, 3H), 2.24-2.32 (m, 2H), 1.51-1.84 (m, 2H), 0.86 (t, $J = 7.3\text{Hz}$, 3H); IR (neat): 2974, 2940, 2732, 1787, 1722, 1687, 1598, 1460, 1172, 1091, 971, 815 cm^{-1} ; MS m/e : 338 (M^++1), 337 (M^+), 281, 182, 166, 155, 139, 109, 91, 65; Anal.: Calcd for $C_{16}H_{19}NO_5S$: C, 56.96; H, 5.68; N, 4.15; Found: C, 56.64; H, 5.79; N, 4.31.

5d: oil, ^1H NMR (300 MHz, CDCl_3) δ 7.91 (d, $J = 8.3\text{Hz}$, 2H), 7.36 (d, $J = 8.3\text{Hz}$, 2H), 5.87 (dt, $J = 2.0, 7.4\text{Hz}$, 1H), 5.08-5.10 (m, 1H), 2.61 (t, $J = 7.7\text{Hz}$, 2H), 2.52 (s, 3H),

2.15-2.28 (m, 5H), 1.75-1.84 (m, 2H), 0.86 (t, $J = 7.3\text{Hz}$, 3H); IR (neat): 2972, 2927, 1787, 1716, 1689, 1352, 1166, 1091, 1057 cm^{-1} ; MS m/e: 352 ($M^+ + 1$), 334, 308, 290, 270, 226, 196, 180, 155, 136, 110, 91, 65, 43; Anal.: Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_5\text{S}$: C, 58.10; H, 6.02; N, 3.99; Found: C, 57.78; H, 6.11; N, 4.25

5e: oil, ^1H NMR (300 MHz, CDCl_3) δ 7.97 (d, $J = 8.4\text{Hz}$, 2H), 7.39 (d, $J = 8.4\text{Hz}$, 2H), 7.20-7.35 (m, 3H), 7.14-7.16 (m, 2H), 5.99-6.05 (m, 2H), 2.34-2.48 (m, 5H), 2.07-2.23 (m, 2H), 2.03 (s, 3H); IR (neat): 1798, 1773, 1712, 1687, 1594, 1493, 1458, 1425, 1389, 1369, 1316, 1305, 1270, 1101, 1086, 1039, 990, 855, 823, 762, 748, 705, 669, 593, 571, 547 cm^{-1} ; MS m/e: 400 ($M^+ + 1$), 356, 338, 244, 228, 200, 184, 169, 158, 155, 143, 105, 91, 65, 43; Anal.: Calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_5\text{S}$: C, 63.14; H, 5.30; N, 3.51; Found: C, 62.88; H, 5.32; N, 3.65.

5f: oil, ^1H NMR (300 MHz, CDCl_3) δ 9.79 (s, 1H), 7.84 (d, $J = 8.1\text{Hz}$, 2H), 7.33 (d, $J = 8.1\text{Hz}$, 2H), 5.91 (t, $J = 8.0\text{Hz}$, 1H), 2.63 (t, $J = 7.2\text{Hz}$, 2H), 2.36-2.48 (m, 5H), 1.45 (s, 6H); IR (neat): 2982, 2933, 2732, 1790, 1722, 1683, 1597, 1494, 1449, 1388, 1373, 1272, 1191, 1090, 1051, 974, 816, 758, 705, 666, 611, 572, 545 cm^{-1} ; MS m/e: 338 ($M^+ + 1$), 281, 182, 155, 139, 122, 109, 110, 91, 65; Anal.: Calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_5\text{S}$: C, 56.96; H, 5.68; N, 4.15; Found: C, 56.60; H, 5.89; N, 4.40.

5g: oil, ^1H NMR (300 MHz, CDCl_3) δ 7.85 (d, $J = 8.3\text{Hz}$, 2H), 7.36 (d, $J = 8.3\text{Hz}$, 2H), 5.92 (t, $J = 6.7\text{Hz}$, 1H), 2.62 (t, $J = 6.6\text{Hz}$, 2H), 2.52 (s, 3H), 2.20-2.52 (m, 2H), 2.20 (s, 3H), 1.51 (s, 6H); IR (neat): 2984, 1782, 1717, 1686, 1596, 1496, 1390, 1375, 1281, 1189, 1174, 1156, 1089, 1049, 1020, 973, 908, 828, 815, 757, 668, 609, 571, 546 cm^{-1} ; MS m/e: 352 ($M^+ + 1$), 334, 308, 290, 250, 226, 196, 180, 155, 136, 110, 91, 65, 43;

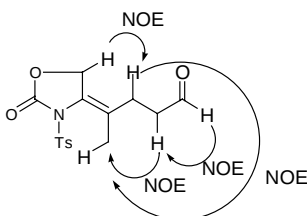
Anal.: Calcd for $C_{17}H_{21}NO_5S$: C, 58.10; H, 6.02; N, 3.99; Found: C, 57.99; H, 6.09; N, 3.97.

5h: oil, 1H NMR (300 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.89 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.4$ Hz, 2H), 6.00 (t, $J = 7.9$ Hz, 1H), 2.62-2.67 (m, 2H), 2.35-2.44 (m, 5H), 1.71 (t, $J = 7.6$ Hz, 2H), 1.51 (s, 3H); 1.09-1.25 (m, 6H), 0.80 (t, $J = 7.2$ Hz, 3H); IR (neat): 2957, 2932, 2862, 1789, 1723, 1680, 1598, 1456, 1383, 1370, 1288, 1257, 1190, 1178, 1146, 1091, 1049, 815, 755 cm^{-1} ; MS m/e 394 ($M^+ + 1$), 350, 267, 238, 222, 194, 178, 166, 155, 91, 65, 43; Anal.: Calcd for $C_{20}H_{27}NO_5S$: C, 61.05; H, 6.92; N, 3.56; Found: C, 60.78; H, 7.12; N, 3.67.

6h: oil, 1H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, $J = 8.3$ Hz, 2H), 7.35 (d, $J = 8.3$ Hz, 2H), 6.54 (d, $J = 3.0$ Hz, 1H), 4.38 (d, $J = 3.0$ Hz, 1H), 2.44 (s, 3H), 1.75-1.49 (m, 2H), 1.43 (s, 3H), 0.95-1.15 (m, 6H), 0.79 (t, $J = 6.6$ Hz, 3H); IR (neat): 2958, 2935, 1795, 1666, 1599, 1495, 1456, 1403, 1383, 1285, 1192, 1180, 1151, 1123, 1092, 1072, 1056, 1021, 815, 759, 704, 674, 575, 545 cm^{-1} ; MS m/e 338 ($M^+ + 1$), 294, 267, 236, 218, 203, 182, 166, 155, 138, 112, 91, 65, 43; HRMS: Calcd for $C_{17}H_{23}NO_4S$: 337.1348; Found: 337.1327.

5i: oil, 1H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, $J = 8.2$ Hz, 2H), 7.35 (d, $J = 8.2$ Hz, 2H), 5.98 (t, $J = 7.9$ Hz, 1H), 2.60 (t, $J = 7.4$ Hz, 2H), 2.45 (s, 3H), 2.29-2.37 (m, 2H), 2.20 (s, 3H), 1.72 (t, $J = 8.8$ Hz, 2H), 1.50 (s, 3H); 0.92-1.28 (m, 6H), 0.82 (t, $J = 6.7$ Hz, 3H); IR (neat): 2956, 2928, 2862, 1786, 1716, 1678, 1597, 1458, 1369, 1287, 1254, 1177, 1090, 1047, 815, 754, 704, 668, 570, 545 cm^{-1} ; MS m/e : 408 ($M^+ + 1$), 252, 190, 155, 91, 65, 43; Anal.: Calcd for $C_{21}H_{29}NO_5S$: C, 61.89; H, 7.17; N, 3.44; Found: C, 61.58; H, 7.33; N, 3.52.

5j: oil, ^1H NMR (300 MHz, CDCl_3) δ 9.79 (s, 1H), 7.83 (d, $J = 8.3\text{Hz}$, 2H), 7.33 (d, $J = 8.3\text{Hz}$, 2H), 4.76 (s, 2H), 2.71 (t, $J = 6.9\text{Hz}$, 2H), 2.42 (s, 3H), 2.29 (t, $J = 6.9\text{Hz}$, 2H), 1.86 (s, 3H); IR (neat): 3063, 2925, 2733, 1800, 1724, 1597, 1494, 1451, 1370, 1270, 1176, 1088, 1045, 1019, 970, 816, 768, 736, 664, 589, 572, 543 cm^{-1} ; MS m/e 323 (M^+), 279, 168, 155, 150, 139, 123, 108, 95, 91, 65, 43; HRMS: Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_5\text{S}$: 323.0827 Found: 323.0847



5k: oil, ^1H NMR (300 MHz, CDCl_3) δ 7.78 (d, $J = 8.4\text{Hz}$, 2H), 7.30 (d, $J = 8.4\text{Hz}$, 2H), 4.72 (s, 2H), 2.61 (t, $J = 6.9\text{Hz}$, 2H), 2.38 (s, 3H), 2.25-1.90 (m, 5H), 1.80 (s, 3H); IR (neat): 2957, 2925, 1799, 1715, 1597, 1494, 1450, 1407, 1368, 1270, 1407, 1368, 1270, 1190, 1175, 1087, 1044, 1019, 971, 817, 769, 730, 705, 665, 589, 573, 542 cm^{-1} ; MS m/e 338 ($\text{M}^+ + 1$), 317, 294, 182, 166, 155, 138, 122, 96, 91, 65, 43; HRMS: Calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_5\text{S}$: 337.0984 Found: 337.0982

7b: oil, ^1H NMR (300 MHz, CDCl_3) δ 7.87 (d, $J = 8.1\text{Hz}$, 2H), 7.36-7.19 (m, 7H), 4.53 (s, 2H), 4.08 (s, 2H), 2.43 (s, 3H), 2.31 (s, 1H); IR (neat): 3282, 3030, 2925, 1746, 1677, 1598, 1466, 1453, 1340, 1230, 1165, 1085, 854, 752, 701, 665, 547 cm^{-1} ; MS m/e : 342 (M^+), 343 ($\text{M}^+ + 1$), 278, 197, 187, 155, 144, 91; HRMS Calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$: 342.1038 Found: 342.1027.

8b: oil, ^1H NMR (300 MHz, CDCl_3) δ 9.70 (t, $J = 1.0\text{Hz}$, 1H), 7.84 (d, $J = 8.3\text{Hz}$, 2H), 7.28-7.19 (m, 5H), 7.05 (d, $J = 7.2\text{Hz}$, 2H), 5.85-5.80 (m, 1H), 4.3 (s, 2H), 3.78-3.76 (m,

2H), 2.53 (t, $J = 7.1\text{Hz}$, 2H), 2.38 (s, 3H), 2.13-2.05 (m, 2H); IR (neat): 3066, 3032, 2957, 2926, 1747, 1720, 1682, 1598, 1496, 1455, 1425, 1380, 1359, 1251, 1188, 1176, 1091, 815, 745, 730, 703, 665, 581, 546 cm^{-1} ; MS m/e 398 (M^+), 342, 278, 243, 215, 187, 155, 91, 65; HRMS: Calcd for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_4\text{S}$: 398.1300; Found: 398.1337.

9: colorless crystal: m.p.130.5-131.5°C, ^1H NMR(300 MHz, CDCl_3) δ 9.2(br, 1H), 7.92(d, $J = 8.4\text{Hz}$, 2H), 7.32(d, $J = 8.4\text{Hz}$, 2H), 2.52-2.39(m, 7H), 1.94(t, $J = 2.5\text{Hz}$, 1H); IR(neat): 3278, 2929, 1729, 1596, 1438, 1412, 1334, 1167, 1121, 1083, 1034, 857, 810, 691, 667, 587, 554, 509 cm^{-1} ; MS m/e : 155, 154, 108, 107, 91, 65, 53, 52; Anal: Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_5\text{S}$: C, 57.35; H, 5.21; N, 5.57; Found: C, 56.95; H, 5.04; N, 5.55.

10: oil, ^1H NMR (300 MHz, CDCl_3) δ 9.82 (t, $J = 1.1\text{Hz}$, 1H), 7.91 (d, $J = 8.5\text{Hz}$, 2H), 7.35 (d, $J = 8.5\text{Hz}$, 2H), 5.92 (tt, $J = 2.2, 7.6\text{Hz}$, 1H), 2.72-2.61 (m, 4H), 2.51-2.32 (m, 7H); IR (neat): 2927, 2733, 1758, 1722, 1675, 1598, 1495, 1445, 1380, 1353, 1303, 1164, 1090, 942, 815, 706, 665, 598, 562, 539 cm^{-1} ; MS m/e : 307 (M^+), 279, 251, 243, 187, 155, 134, 91, 65; HRMS: Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_4\text{S}$: 307.0878; Found: 307.0864