

Supportion Information

Palladium(0)-Catalyzed Carbonylation-Coupling-Cyclization of Allenic Sulfonamides with Aryl Iodides and Carbon Monoxide

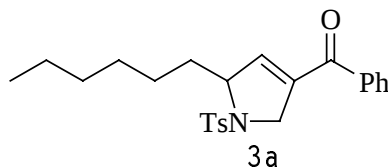
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Typical experimental procedures for the preparation of **3a-4a**, and spectroscopic and analytical data for **3a-4e**, **5a**, **5b**, **5c** and **5d**

The typical procedure is as follows. A stainless autoclave was charged with α -allenic *p*-toluenesulfonamide **1a** (100 mg, 0.33 mmol), CH₃CN (3 mL), iodobenzene (99.4 mg, 0.49 mmol), K₂CO₃ (179 mg, 1.30 mmol) and Pd(PPh₃)₄ (18.7 mg, 5 mol %). It was flushed with 20 atm of CO three times. And then it was pressurized to 20 atm and stirred at 90 °C for 6 h. The resulting mixture was cooled and then quenched with saturated NH₄Cl solution. The reaction mixture was extracted with ether (20 mL $\times$ 3) and the organic layer was dried over anhydrous MgSO₄ and evaporated *in vacuo*. The crude product was separated by SiO₂ column chromatography (hexanes/EtOAc, 6 : 1) to give 3-pyrroline **3a** (32.0 mg, 24%) and 2-pyrroline **4a** (76.0 mg, 57%).

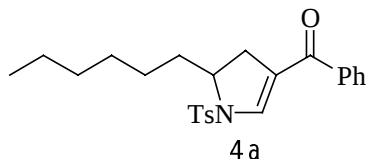
[5-Hexyl-1-(toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrol-3-yl]phenylmethanone (**3a**)



TLC, SiO₂, EtOAc / hexanes 1 : 2, R_f = 0.55. IR (neat) 3061, 2929, 1701, 1653, 1356, 1272, 1170 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 0.87 (t, 3H, *J* = 6.75 Hz), 1.25 (m, 8H), 1.96 (m, 2H), 2.44 (s, 3H), 3.31 (ddd, 1H *J* = 2.64, 2.93, 21.71 Hz), 3.49 (dd, 1H, *J* = 1.17, 21.71 Hz), 5.29 (m, 1H), 6.67 (dd, 1H, *J* = 2.93, 5.87 Hz), 7.33 (d, 2H, *J* = 8.21 Hz), 7.49 (m, 2H), 7.59 (m, 1H), 7.67 (m, 2H), 7.95 (d, 2H, *J* = 8.21 Hz). ¹³C NMR (125 MHz, CDCl₃) δ 194.5, 168.3, 145.8, 139.1, 137.3,

136.7, 134.2, 133.3, 130.0, 129.9, 129.2, 58.6, 36.9, 34.4, 32.2, 29.6, 25.1, 23.2, 22.3, 14.7. HRMS calcd. for $C_{24}H_{29}NO_3S$: 411.1868 found: 411.1874.

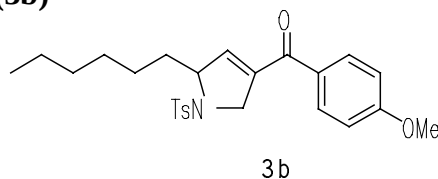
[5-Hexyl-1-(toluene-4-sulfonyl)-4,5-dihydro-1H-pyrrol-3-yl]phenylmethanone (4a)



TLC, SiO_2 , EtOAc / hexanes 1 : 2, R_f = 0.59. IR (neat) 3058, 2930, 1686, 1660, 1354, 1273, 1169 cm^{-1} . 1H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, 3H, J = 6.75 Hz), 1.26 (m, 8H), 1.78 (m, 2H), 2.44 (s, 3H), 2.88 (ddd, 1H J = 2.93, 6.16, 18.19 Hz), 3.04 (dd, 1H, J = 1.47, 18.19 Hz), 4.93 (m, 1H), 6.17 (d, 1H, J = 2.93 Hz), 7.33 (d, 2H, J = 8.21 Hz), 7.47 (m, 2H), 7.60 (m, 1H), 7.74 (m, 2H), 7.98 (d, 2H, J = 8.21 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.7, 162.9, 148.2, 145.7, 136.9, 136.

1, 134.4, 130.3, 130.1, 129.8, 129.6, 56.4, 34.3, 32.3, 29.6, 28.9, 27.0, 23.2, 22.4, 14.7. HRMS calcd. for $C_{24}H_{29}NO_3S$: 411.1868 found: 411.1861.

[5-Hexyl-1-(toluene-4-sulfonyl)-2,5-dihydro-1H-pyrrol-3-yl]-(4-methoxyphenyl)ethanone (3b)



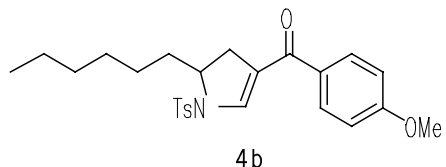
TLC, SiO_2 , EtOAc / hexanes 1 : 2, R_f = 0.46. IR (neat) 3057, 2929, 1700, 1644, 1356, 1259, 1170 cm^{-1} . 1H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, 3H, J = 6.75 Hz), 1.27 (m, 8H), 1.96 (m, 2H), 2.44 (s, 3H), 3.33 (ddd, 1H J = 2.64, 2.93, 21.71 Hz), 3.44 (dd, 1H, J = 1.17, 21.71 Hz), 5.28 (m, 1H), 6.61 (dd, 1H, J = 2.93, 5.87 Hz), 6.96 (d, 2H, J = 9.09 Hz), 7.33 (d, 2H, J = 8.21 Hz), 7.72 (d, 2H, J = 9.09 Hz), 7.95 (d, 2H, J = 8.21 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.3, 168.6, 164.2, 145.8

, 137.3, 136.7, 134.2, 132.4, 130.0, 129.7, 114.6, 58.5, 56.3, 36.9, 34.8, 32.3, 29.6, 25.1, 23.2, 22.4, 14.7. HRMS calcd. for $C_{25}H_{31}NO_4S$: 441.1974 found: 441.1983.

[5-Hexyl-1-(toluene-4-sulfonyl)-4,5-dihydro-1H-pyrrol-3-yl]-(4-methoxy-

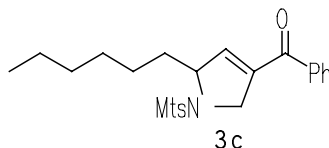
phenyl)methan

onoe (4b)



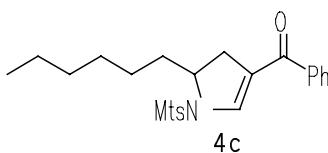
TLC, SiO₂, EtOAc / hexanes 1 : 2, R_f = 0.51. IR (neat) 3055, 2930, 1685, 1653, 1354, 1265, 1170 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 0.89 (t, 3H, *J* = 6.75 Hz), 1.29 (m, 8H), 1.78 (m, 2H), 2.44 (s, 3H), 2.88 (ddd, 1H *J* = 2.93, 6.16, 18.19 Hz), 2.99 (dd, 1H, *J* = 1.47, 18.19 Hz), 4.92 (m, 1H), 6.11 (d, 1H, *J* = 2.93 Hz), 6.94 (d, 2H, *J* = 9.09 Hz), 7.33 (d, 2H, *J* = 8.21 Hz), 7.78 (d, 2H, *J* = 9.09 Hz), 7.98 (d, 2H, *J* = 8.21 Hz). ¹³C NMR (125 MHz, CDCl₃) δ 194.0, 165.0, 163.0, 149.0, 145.6, 137.0, 132.9, 130.0, 129.8, 128.6, 114.8, 56.4, 56.3, 34.3, 32.3, 29.6, 29.4, 27.0, 23.2, 22.4, 14.7. HRMS calcd. for C₂₅H₃₁NO₄S: 441.1974 found: 441.1983.

[5-Hexyl-1-(2,4,6-trimethyl-benzensulfonyl)-2,5-dihydro-1H-pyrrol-3-yl]phenylmethanone (3c)



TLC, SiO₂, EtOAc / hexanes 1 : 3, R_f = 0.46. IR (neat) 2937, 2863, 1696, 1657, 1339, 1270, 1169 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 0.87 (t, 3H, *J* = 6.75 Hz), 1.30 (m, 8H), 2.02 (m, 2H), 2.30 (s, 3H), 2.62 (s, 6H), 3.34 (ddd, 1H *J* = 2.64, 2.93, 21.71 Hz), 3.47 (dd, 1H, *J* = 1.17, 21.71 Hz), 5.24 (m, 1H), 6.72 (dd, 1H, *J* = 2.93, 5.87 Hz), 6.95 (m, 2H), 7.49 (m, 2H), 7.60 (m, 1H), 7.66 (d, 2H, *J* = 8.21 Hz). ¹³C NMR (125 MHz, CDCl₃) δ 194.6, 168.7, 144.2, 138.8, 137.3, 134.9, 134.2, 133.4, 132.7, 129.9, 129.3, 57.9, 37.2, 34.1, 32.3, 29.7, 25.4, 23.2, 21.8, 14.7. HRMS calcd. for C₂₆H₃₃NO₃S: 439.2181 found: 439.2132.

[5-Hexyl-1-(2,4,6-trimethyl-benzensulfonyl)-4,5-dihydro-1H-pyrrol-3-yl]phenylmethanone (4c)

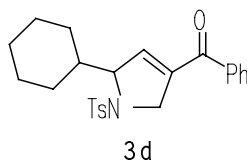


TLC, SiO₂, EtOAc / hexanes 1 : 3, R_f = 0.49. IR (neat) 2950, 2850, 1694, 1655, 1346, 1266, 1168

cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 0.88 (t, 3H, *J* = 6.75 Hz), 1.30 (m, 8H), 1.93 (m, 2H), 2.23 (s, 3H), 2.29 (s, 6H), 2.90 (ddd, 1H *J* = 2.93, 6.16, 18.19 Hz), 3.10 (dd, 1H, *J* = 1.47, 18.19 Hz), 4.87 (m, 1H), 6.16 (d, 1H, *J* = 2.93 Hz), 6.97 (s, 2H), 7.46 (d, 2H, *J* = 8.21 Hz), 7.61 (m, 2H), 7.75 (d, 2H, *J* = 8.21 Hz). ¹³C NMR (125 MHz, CDCl₃) δ 195.7, 163.5, 147.5, 144.3, 141.3, 136.1, 134.4,

132.6, 130.3, 129.8, 129.4, 55.7, 34.9, 32.3, 29.6, 28.1, 27.0, 23.2, 21.7, 14.7 HRMS calcd. for C₂₆H₃₃NO₃S: 439.2181 found: 439.2178.

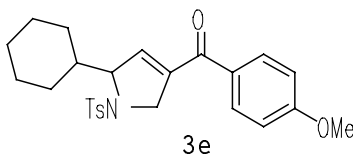
[5-Cyclohexyl-1-(toluene-4-sulfonyl)-2,5-dihydro-1H-pyrrol-3-yl]phenylmethanone (3d)



TLC, SiO₂, EtOAc / hexanes 1 : 2, R_f = 0.48. IR (neat) 2960, 2925, 1684, 1656, 1350, 1165, 1092 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 0.95 (m, 2H), 1.05 (m, 2H), 1.26 (m, 2H), 1.75 (m, 3H), 1.87 (m, 1H), 2.25 (m, 1H), 2.44 (s, 3H), 3.28 (ddd, 1H *J* = 2.64, 2.93, 21.71 Hz), 3.46 (dd, 1H, *J* = 1.17, 21.71 Hz), 5.18 (m, 1H), 6.65 (dd, 1H, *J* = 2.93, 5.87 Hz), 7.33 (d, 2H, *J* = 8.21 Hz), 7.49 (m, 2H), 7.60 (m, 1H), 7.68 (m, 2H), 7.93 (d, 2H, *J* = 8.21 Hz). ¹³C NMR (125 MHz, CDCl₃)

δ 194.0, 170.0, 145.0, 136.6, 135.9, 134.4, 132.7, 129.2, 129.2, 128.5, 62.6, 45.3, 33.9, 29.8, 26.4, 26.2, 26.0, 25.6, 21.7. HRMS calcd. for C₂₄H₂₇NO₃S: 409.1712 found: 409.1753.

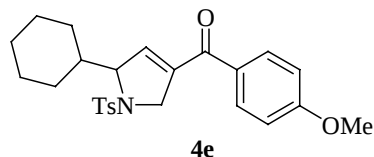
[5-Cyclohexyl-1-(toluene-4-sulfonyl)-2,5-dihydro-1H-pyrrol-3-yl]-(4-methoxyphenyl) methanone (3e)



TLC, SiO₂, EtOAc / hexanes 1 : 2, R_f = 0.45. IR (neat) 2983, 2976, 1680, 1652, 1354, 1259,

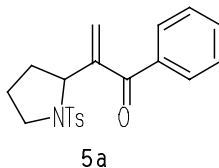
1170 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 0.93 (m, 2H), 1.07 (m, 2H), 1.23 (m, 2H), 1.75 (m, 3H), 1.87 (m, 1H), 2.25 (m, 1H), 2.44 (s, 3H), 3.30 (ddd, 1H J = 2.64, 2.93, 21.71 Hz), 3.42 (dd, 1H, J = 1.17, 21.71 Hz), 5.18 (m, 1H), 6.59 (dd, 1H, J = 2.93, 5.87 Hz), 6.97 (d, 2H J = 9.09 Hz), 7.33 (d, 2H, J = 8.21 Hz), 7.73 (d, 2H, J = 9.09 Hz), 7.94 (d, 2H, J = 8.21 Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 192.6, 168.2, 163.5, 145.1, 136.1, 134.8, 132.1, 131.7, 129.3, 129.2, 113.9, 62.6, 55.6, 45.4, 34.4, 29.8, 29.7, 26.3, 26.1, 25.7, 21.7. HRMS calcd. for $\text{C}_{25}\text{H}_{29}\text{NO}_4\text{S}$: 439.1817 found: 439.1853.

[5-Cyclohexyl-1-(toluene-4-sulfonyl)-2,5-dihydro-1H-pyrrol-3-yl]-(4-methoxyphenyl) methanone (4e)



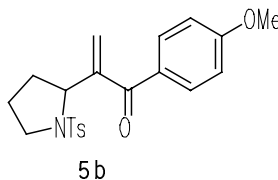
TLC, SiO_2 , EtOAc / hexanes 1 : 2, R_f = 0.45. IR (neat) 2982, 2965, 1685, 1640, 1350, 1259, 1170 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 1.16 (m, 2H), 1.22 (m, 4H), 1.74 (m, 4H), 1.89 (m, 1H), 2.44 (s, 3H), 2.79 (ddd, 1H J = 2.93, 6.75, 18.19 Hz), 3.11 (dd, 1H, J = 1.17, 18.19 Hz), 3.87 (s, 3H), 4.70 (m, 1H), 6.08 (d, 2H J = 2.93 Hz), 6.93 (d, 2H J = 9.09 Hz), 7.32 (d, 2H, J = 8.21 Hz), 7.75 (d, 2H, J = 9.09 Hz), 7.95 (d, 2H, J = 8.21 Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 193.2, 164.3, 162.6, 148.5, 144.9, 136.3, 132.1, 129.4, 129.1, 128.0, 114.1, 60.5, 55.6, 41.7, 30.2, 30.0, 27.0, 26.3, 26.2, 26.0, 21.7. HRMS calcd. for $\text{C}_{25}\text{H}_{29}\text{NO}_4\text{S}$: 439.1817 found: 439.1820

Phenyl-2-[1-(toluene-4-sulfonyl)-pyrrolidin-2-yl]propenone (5a)



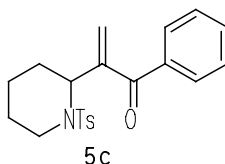
TLC, SiO_2 , EtOAc / hexanes 1 : 3, R_f = 0.41. IR (neat) 3062, 2977, 1654, 1349, 1155 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 1.63 (m, 1H), 1.82 (m, 3H), 2.44 (s, 3H), 3.23 (m, 1H), 3.63 (m, 1H), 4.71 (dd, 1H J = 3.52, 6.75 Hz), 5.85 (s, 1H), 6.33 (s, 1H), 7.33 (d, 2H, J = 8.21 Hz), 7.45 (m, 2H), 7.55 (m, 1H), 7.76 (d, 2H, J = 8.21 Hz), 7.78 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 197.7, 148.7, 143.9, 138.1, 134.2, 132.7, 130.0, 129.8, 128.5, 127.8, 127.5, 60.4, 49.6, 33.2, 24.0, 21.8. HRMS calcd. for $\text{C}_{21}\text{H}_{23}\text{NO}_3\text{S}$: 335.1242 found: 335.1246

1-(4-Methoxy-phenyl)-2-[1-(toluene-4-sulfonyl)-pyrrolidin-2-yl]propenone (5b)



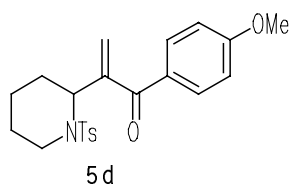
TLC, SiO₂, EtOAc / hexanes 1 : 2, R_f = 0.39. IR (neat) 3055, 2985, 1647, 1345, 1162 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 1.63 (m, 1H), 1.83 (m, 3H), 2.43 (s, 3H), 3.21 (m, 1H), 3.61 (m, 1H), 3.88 (s, 3H), 4.66 (t, 1H *J* = 5.58 Hz), 5.75 (s, 1H), 6.20 (s, 1H), 6.95 (d, 2H, *J* = 8.80 Hz), 7.32 (d, 2H, *J* = 8.21 Hz), 7.74 (d, 2H, *J* = 8.21 Hz), 7.84 (d, 2H, *J* = 8.80 Hz). ¹³C NMR (125 MHz, CDCl₃) δ 196.5, 163.6, 148.8, 143.8, 134.3, 132.3, 130.6, 130.0, 127.9, 125.2, 113.8, 60.8, 55.7, 49.6, 33.2, 23.9, 21.8. HRMS calcd. for C₂₂H₂₅NO₄S: 385.1348 found: 385.1348

Phenyl-2-[1-(toluene-4-sulfonyl)-piperidin-2-yl]propenone (5c)



TLC, SiO₂, EtOAc / hexanes 1 : 3, R_f = 0.41. IR (neat) 3055, 2934, 1656, 1597, 1336, 1157, cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 1.27 (m, 1H), 1.48 (m, 4H), 1.80 (m, 1H), 2.42 (s, 3H), 3.30 (ddd, 1H *J* = 3.17, 12.67, 13.73 Hz), 3.86 (d, 1H, *J* = 13.73 Hz), 5.27 (d, 1H, *J* = 3.17 Hz), 5.74 (d, 1H *J* = 2.11 Hz), 5.98 (d, 1H *J* = 2.11 Hz), 7.28 (d, 2H, *J* = 8.45 Hz), 7.50 (m, 2H), 7.57 (m, 1H), 7.75 (d, 2H, *J* = 8.45 Hz), 7.83 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 196.9, 146.3, 14.3, 13.1, 138.1, 137.1, 132.9, 129.4, 128.4, 126.9, 125.4, 54.2, 41.8, 27.1, 24.5, 21.5, 19.6. HRMS calcd. for C₂₁H₂₃NO₃S: 369.1398 found: 369.1397

1-(4-Methoxy-phenyl)-2-[1-(toluene-4-sulfonyl)-piperidin-2-yl]propenone (5d)



TLC, SiO₂, EtOAc / hexanes 1 : 2, R_f = 0.38. IR (neat) 3056, 2986, 1651, 1600, 1333, 1157 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 1.26 (m, 1H), 1.45 (m, 4H), 1.77 (m, 1H), 2.41 (s, 3H), 3.29 (ddd, 1H *J* = 3.17, 12.67, 13.73 Hz), 3.85 (d, 1H, *J* = 13.73 Hz), 3.86 (s, 3H), 5.26 (d, 1H, *J* = 3.17 Hz), 5.65 (d, 1H *J* = 2.11 Hz), 5.87 (d, 1H *J* = 2.11 Hz), 6.94 (d, 2H, *J* = 8.98 Hz), 7.28 (d, 2H, *J* = 8.45 Hz), 7.75 (d, 2H, *J* = 8.45 Hz), 7.87 (d, 2H, *J* = 8.98 Hz). ¹³C NMR (125 MHz, CDCl₃)

δ 195.7, 163.6, 146.4, 143.0, 138.2, 132.1, 129.6, 129.6, 126.9, 123.2, 113.7, 55.5, 54.4, 41.7, 27.0, 24.5, 21.5, 19.6. HRMS calcd. for C₂₂H₂₅NO₄S: 399.1504 found: 399.1500