Tuning the Reaction Paths in Palladium(0)-Catalyzed Coupling-Cyclization Reaction of β -Amino Allenes with Organic Halides. A Substituent Switch.

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Supporting Information

Pd(0)-catalyzed coupling-cyclization reaction of β -amino allenes with organic halides: General procedure: A mixture of β -amino allene **1** (0.3 mmol), aryl or vinyl halide (0.45 mmol), K_2CO_3 (1.2 mmol) and $Pd(PPh_3)_4$ (5 mol%) was stirred at 70°C in DMF (2 mL). When the reaction was complete as monitored by TLC (eluent: petroleum ether/ ether), ether was added. The reaction mixture was washed with brine (three times) and dried over Na_2SO_4 . The product was purified by flash chromatography on silica gel (eluent: petroleum ether/ether).

2a

(1) **5-Benzyl-4-(n-butyl)-3-methyl-1-(toluene-4'-sulfonyl)-2,3-dihydro-1H-pyrrole (2a):** The reaction of **1a** (0.092 g, 0.30 mmol) with iodobenzene (51 μ L, 0.093 g, 0.46 mmol) afforded 0.090 g (78%) of **2a**: solid, mp 70-71°C (hexane); 1H NMR (300

MHz, CDCl₃) δ 7.59 (d, J = 8.2 Hz, 2 H), 7.40-7.16 (m, 7 H), 3.79 (d, J = 15.6 Hz, 1 H), 3.73 (dd, J = 12.2 and 8.0 Hz, 1 H), 3.65 (d, J = 15.6 Hz, 1 H), 3.17 (dd, J = 12.2 and 8.0 Hz, 1 H), 2.52-2.32 (m, 1 H), 2.38 (s, 3 H), 2.24-2.08 (m, 1 H), 2.05-1.90 (m, 1 H), 1.35-1.05 (m, 4 H), 0.83 (t, J = 6.9 Hz, 3 H), 0.73 (d, J = 6.7 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 143.38, 138.93, 134.71, 132.61, 129.40, 128.51, 128.27, 127.58, 126.10, 56.80, 36.34, 32.03, 29.77, 25.20, 22.39, 21.53, 18.02, 13.91; MS (m/z) 383 (M^+ , 10.64), 91 (100); IR (KBr) 1600, 1343, 1168 cm⁻¹; Anal. calcd for C₂₃H₂₉NO₂S: C, 72.03; H, 7.62; N, 3.65. Found: C, 71.97; H, 7.66; N, 3.66.

(2) ***trans*-(2,3)-3-Methyl-2-(1'-phenylvinyl)-1-(toluene-4'-sulfonyl)azetidine (3b)** and **3-Methyl-5-phenyl-1-(toluene-4'-sulfonyl)-1,2,3,6-tetrahydropyridine (4b)**: The reaction of **1b** (0.075 g, 0.30 mmol) with iodobenzene (51 μ L, 0.093 g, 0.46 mmol) afforded 0.014 g of (14%) of **3b** and 0.048 g (49%) of **4b**:

3b: liquid; ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 8.1 Hz, 2 H), 7.29 (d, J = 8.1 Hz, 2 H), 7.27-7.18 (m, 5 H), 5.52 (t, J = 1.3 Hz, 1 H), 5.29 (s, 1 H), 4.29 (d, J = 6.8 Hz, 1 H), 3.76 (t, J = 7.9 Hz, 1 H), 3.23 (t, J = 7.6 Hz, 1 H), 2.38 (s, 3 H), 2.25-2.10 (m, 1 H), 0.72 (d, J = 6.8 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 147.00, 144.29, 138.86, 132.60, 129.92, 128.62, 128.57, 128.05, 127.13, 114.93, 72.73, 54.68, 33.00, 21.86, 18.63; MS (m/z) 327 (M^+ , 8.98), 130 (100); IR (neat) 1598, 1347, 1162 cm⁻¹; HRMS calcd for C₁₉H₂₁NO₂S: 327.1293. Found: 327.1324.

The stereo chemistry of **3b** was confirmed by ¹H-¹H NOESY spectra.

: liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.64 (d, J = 8.0 Hz, 2 H), 7.36-7.16 (m, 7 H),

5.87 (bs, 1 H), 4.00 (d, $J = 15.6$ Hz, 1 H), 3.64 (d, $J = 15.6$ Hz, 1 H), 3.50-3.40 (m, 1 H), 2.62-2.44 (m, 2 H), 2.35 (s, 3 H), 1.01 (d, $J = 6.7$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 143.65, 138.52, 133.26, 132.54, 129.75, 128.58, 128.54, 127.76, 127.70, 125.29, 49.15, 46.36, 30.66, 21.55, 18.47; MS (m/z) 327 (M^+ , 7.43), 129 (100); IR (neat) 1598, 1346, 1167 cm^{-1} ; HRMS calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_2\text{S}$: 327.1293. Found: 327.1289.

2b

(3) **4-(*n*-Butyl)-5-(4'-methoxybenzyl)-3-methyl-1-(toluene-4'-sulfonyl)-2,3-dihydro-1H-pyrrole (2b)**: The reaction of **1a** (0.092 g, 0.30 mmol) with *p*-methoxyphenyl iodide (0.105 g, 0.45 mmol) afforded 0.098 g (79%) of **2b**: solid, mp 74-76°C (hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.59 (d, $J = 8.6$ Hz, 2 H), 7.24 (d, $J = 8.6$ Hz, 2 H), 7.19 (d, $J = 8.7$ Hz, 2 H), 6.81 (d, $J = 8.7$ Hz, 2 H), 3.90 (dd, $J = 11.9$ and 8.3 Hz, 1 H), 3.89 (d, $J = 15.9$ Hz, 1 H), 3.79 (s, 3 H), 3.76 (d, $J = 15.9$ Hz, 1 H), 3.14 (dd, $J = 11.9$ and 8.3 Hz, 1 H), 2.50-2.28 (m, 1 H), 2.40 (s, 3 H), 2.22-2.10 (m, 1 H), 2.02-1.90 (m, 1 H), 1.35-1.00 (m, 4 H), 0.82 (t, $J = 6.9$ Hz, 3 H), 0.70 (d, $J = 7.5$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 158.20, 143.48, 135.37, 134.95, 132.37, 131.15, 129.66, 129.56, 127.78, 113.89, 57.00, 55.47, 36.52, 31.35, 30.01, 25.39, 22.60, 21.76, 18.22, 14.12; MS (m/z) 413 (M^+ , 33.71), 121 (100); IR (KBr) 1612, 1512, 1335, 1247, 1162 cm^{-1} ; Anal. calcd for $\text{C}_{24}\text{H}_{31}\text{NO}_3\text{S}$: C, 69.70; H, 7.55; N, 3.39. Found: C, 69.45; H, 7.46; N, 3.32.

2c

(4) **4-(*n*-Butyl)-5-(4'-methoxycarbonylbenzyl)-3-methyl-1-(toluene-4'-sulfonyl)-2,3-dihydro-1H-pyrrole (2c)**: The reaction of **1a** (0.093 g, 0.30 mmol) with *p*-(methoxycarbonyl)phenyl iodide (0.118 g, 0.45 mmol) afforded 0.097 g (73%) of **2c**: solid, mp 98-100°C (hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.92 (d, $J = 8.4$ Hz, 2 H),

7.58 (d, $J = 8.1$ Hz, 2 H), 7.32 (d, $J = 8.4$ Hz, 2 H), 7.22 (d, $J = 8.1$ Hz, 2 H), 3.99 (d, $J = 15.3$ Hz, 1 H), 3.94-3.80 (m, 5 H), 3.13 (dd, $J = 12.3$ and 7.8 Hz, 1 H), 2.42-2.35 (m, 1 H), 2.37 (s, 3 H), 2.15-2.02 (m, 1 H), 2.00-1.82 (m, 1 H), 1.30-0.98 (m, 4 H), 0.79 (t, $J = 7.0$ Hz, 3 H), 0.69 (d, $J = 6.9$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 167.38, 144.69, 143.75, 134.77, 134.10, 133.46, 129.85, 129.67, 128.71, 128.29, 127.74, 56.98, 52.21, 36.57, 32.33, 29.93, 25.41, 22.56, 21.76, 18.20, 14.10; MS (m/z) 441 (M^+ , 56.35), 398 (100); IR (KBr) 1714, 1609, 1285, 1165 cm^{-1} ; Anal. calcd for $\text{C}_{26}\text{H}_{33}\text{NO}_4\text{S}$: C, 68.00; H, 7.08; N, 3.17. Found: C, 68.02; H, 7.04; N, 3.12.

2d

(5) **5-(4'-Bromobenzyl)-4-(*n*-butyl)-3-methyl-1-(toluene-4'-sulfonyl)-2,3-dihydro-1*H*-pyrrole (2d)**: The reaction of **1a** (0.092 g, 0.30 mmol) with *p*-bromophenyl iodide (0.132 g, 0.47 mmol) afforded 0.113 g (82%) of **2d**: solid, mp 89-90°C (hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.57 (d, $J = 8.7$ Hz, 2 H), 7.37 (d, $J = 8.2$ Hz, 2 H), 7.24 (d, $J = 8.7$ Hz, 2 H), 7.13 (d, $J = 8.2$ Hz, 2 H), 3.91 (dd, $J = 12.1$ and 3.6 Hz, 1 H), 3.88 (d, $J = 16.2$ Hz, 1 H), 3.75 (d, $J = 16.2$ Hz, 1 H), 3.15 (dd, $J = 12.1$ and 8.1 Hz, 1 H), 2.45-2.32 (m, 1 H), 2.41 (s, 3 H), 2.20-2.06 (m, 1 H), 2.02-1.90 (m, 1 H), 1.30-1.00 (m, 4 H), 0.82 (t, $J = 6.9$ Hz, 3 H), 0.72 (d, $J = 6.6$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 143.75, 138.20, 134.82, 134.42, 133.16, 131.51, 130.55, 129.68, 127.73, 120.14, 57.01, 36.58, 31.71, 29.99, 25.41, 22.60, 21.79, 18.22, 14.14; MS (m/z) 463 ($\text{M}^+ + 1(^{81}\text{Br})$, 99.74), 461 ($\text{M}^+ + 1(^{79}\text{Br})$, 100); IR (KBr) 1596, 1343, 1166 cm^{-1} ; Anal. calcd for $\text{C}_{23}\text{H}_{28}\text{BrNO}_2\text{S}$: C, 59.74; H, 6.10; N, 3.03. Found: C, 59.72; H, 6.03; N, 2.94.

2e

(6) **4-(*n*-Butyl)-3-methyl-5-(2'-methylbenzyl)-1-(toluene-4'-sulfonyl)-2,3-dihydro-**

1*H*-pyrrole (2e): The reaction of **1a** (0.091 g, 0.30 mmol) with *o*-methylphenyl iodide (0.100 g, 0.46 mmol) afforded 0.099 g (84%) of **2e**: solid, mp 65-66.5°C (hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.60 (d, *J* = 7.9 Hz, 2 H), 7.23 (d, *J* = 7.9 Hz, 2 H), 7.18-7.05 (m, 4 H), 4.00 (dd, *J* = 11.0 and 9.6 Hz, 1 H), 3.96 (d, *J* = 16.5 Hz, 1 H), 3.76 (d, *J* = 16.5 Hz, 1 H), 3.26 (dd, *J* = 11.6 and 7.9 Hz, 1 H), 2.50-2.35 (m, 1 H), 2.40 (s, 3 H), 2.38 (s, 3 H), 2.10-1.98 (m, 1 H), 1.97-1.85 (m, 1 H), 1.30-1.00 (m, 4 H), 0.88-0.78 (m, 6 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 143.56, 136.89, 136.57, 135.14, 133.91, 133.52, 130.19, 129.61, 127.83, 127.81, 126.28, 126.09, 56.97, 36.66, 29.94, 29.53, 25.39, 22.69, 21.78, 20.11, 18.35, 14.14; MS (*m/z*) 397 (*M*⁺, 100); IR (KBr) 1598, 1462, 1346, 1165 cm⁻¹; Anal. calcd for C₂₄H₃₁NO₂S: C, 72.51; H, 7.86; N, 3.52. Found: C, 72.50; H, 7.71; N, 3.47.

2f

(7) **4-(*n*-Butyl)-3-methyl-5-(4'-methylbenzyl)-1-(toluene-4'-sulfonyl)-2,3-dihydro-1*H*-pyrrole (2f):** The reaction of **1a** (0.093 g, 0.30 mmol) with *p*-methylphenyl iodide (0.099 g, 0.45 mmol) afforded 0.100 g (83%) of **2f**: solid, mp 84-85.5°C (hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.60 (d, *J* = 8.4 Hz, 2 H), 7.24 (d, *J* = 8.4 Hz, 2 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 7.08 (d, *J* = 8.0 Hz, 2 H), 4.00-3.86 (m, 2 H), 3.77 (d, *J* = 15.0 Hz, 1 H), 3.14 (dd, *J* = 12.5 and 8.3 Hz, 1 H), 2.50-2.30 (m, 1 H), 2.41 (s, 3 H), 2.32 (s, 3 H), 2.22-2.10 (m, 1 H), 2.02-1.90 (m, 1 H), 1.30-1.00 (m, 4 H), 0.82 (t, *J* = 6.8 Hz, 3 H), 0.71 (d, *J* = 7.5 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 143.56, 136.08, 135.74, 135.20, 135.00, 132.62, 129.61, 129.20, 128.63, 127.81, 57.07, 36.57, 31.84, 30.02, 25.42, 22.62, 21.76, 21.31, 18.24, 14.15; MS (*m/z*) 397 (*M*⁺, 36.73), 105 (100); IR (KBr) 1597, 1343, 1169 cm⁻¹; Anal. calcd for C₂₄H₃₁NO₂S: C, 72.51; H, 7.86; N, 3.52. Found: C, 72.54; H, 7.93; N, 3.52.

2g

(8) **4-(*n*-Butyl)-3-methyl-5-(naphthalen-1'-ylmethyl)-1-(toluene-4'-sulfonyl)-2,3-dihydro-1*H*-pyrrole (2g)**: The reaction of **1a** (0.092 g, 0.30 mmol) with 1-iodonaphthalene (0.117 g, 0.46 mmol) afforded 0.104 g (80%) of **2g**: solid, mp 68-69°C (hexane); ¹H NMR (300 MHz, CDCl₃) δ 8.09 (d, *J* = 8.1 Hz, 1 H), 7.84 (d, *J* = 7.8 Hz, 1 H), 7.70 (d, *J* = 8.1 Hz, 1 H), 7.60 (d, *J* = 8.3 Hz, 2 H), 7.58-7.40 (m, 2 H), 7.38-7.24 (m, 2 H), 7.16 (d, *J* = 8.3 Hz, 2 H), 4.42 (d, *J* = 16.7 Hz, 1 H), 4.22 (d, *J* = 16.7 Hz, 1 H), 4.04 (dd, *J* = 12.1 and 8.5 Hz, 1 H), 3.32 (dd, *J* = 12.1 and 8.5 Hz, 1 H), 2.60-2.40 (m, 1 H), 2.36 (s, 3 H), 2.10-1.96 (m, 1 H), 1.94-1.80 (m, 1 H), 1.30-0.95 (m, 4 H), 0.81 (d, *J* = 6.6 Hz, 3 H), 0.75 (t, *J* = 6.8 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 143.60, 135.21, 134.52, 133.99, 133.94, 133.72, 132.28, 129.56, 128.91, 127.83, 127.01, 126.06, 125.73, 125.69, 125.40, 123.82, 56.96, 36.80, 29.92, 29.30, 25.42, 22.69, 21.74, 18.34, 14.13; MS (*m/z*) 433 (*M*⁺, 56.84), 141 (100); IR (KBr) 1597, 1346, 1164 cm⁻¹; Anal. calcd for C₂₇H₃₁NO₂S: C, 74.79; H, 7.21; N, 3.23. Found: C, 74.88; H, 7.22; N, 3.20.

2h

(9) **4-(*n*-Butyl)-3-methyl-5-(2'-thienylmethyl)-1-(toluene-4'-sulfonyl)-2,3-dihydro-1*H*-pyrrole (2h)**: The reaction of **1a** (0.093 g, 0.30 mmol) with 2-iodothiophene (0.095 g, 0.45 mmol) afforded 0.080 g (68%) of **2h**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.58 (d, *J* = 8.0 Hz, 2 H), 7.25 (d, *J* = 8.0 Hz, 2 H), 7.15-7.08 (m, 1 H), 6.97-6.88 (m, 2 H), 4.18 (d, *J* = 15.8 Hz, 1 H), 4.00 (d, *J* = 15.8 Hz, 1 H), 3.90 (dd, *J* = 12.2 and 8.9 Hz, 1 H), 3.18 (dd, *J* = 12.2 and 7.8 Hz, 1 H), 2.48-2.30 (m, 1 H), 2.40 (s, 3 H), 2.22-2.10 (m, 1 H), 2.05-1.94 (m, 1 H), 1.30-1.00 (m, 4 H), 0.84 (t, *J* = 6.7 Hz, 3 H), 0.70 (d, *J* = 7.3 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 143.67, 141.96, 134.75, 134.69, 132.80, 129.65, 127.79, 126.93, 125.68, 123.71, 56.96, 36.58, 29.96, 27.12, 25.42, 22.65, 21.79, 18.13, 14.15; MS (*m/z*) 389 (*M*⁺, 51.81), 97 (100); IR (neat) 1597, 1455, 1346, 1164 cm⁻¹; HRMS calcd for C₂₁H₂₇NO₂S₂: 389.1483. Found:

389.1509.

2i

(10) **4-(*n*-Butyl)-5-(2'-pyridinylmethyl)-3-methyl-1-(toluene-4'-sulfonyl)-2,3-dihydro-1H-pyrrole (2i):** The reaction of **1a** (0.091 g, 0.30 mmol) with 2-bromopyridine (0.074 g, 0.47 mmol) afforded 0.077 g (68%) of **2i**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 8.50-8.45 (m, 1 H), 7.64 (d, $J = 8.3$ Hz, 2 H), 7.60-7.52 (m, 1 H), 7.37 (d, $J = 7.9$ Hz, 1 H), 7.25 (d, $J = 8.3$ Hz, 2 H), 7.12-7.05 (m, 1 H), 4.13 (d, $J = 16.0$ Hz, 1 H), 4.01 (d, $J = 16.0$ Hz, 1 H), 3.92 (dd, $J = 12.0$ and 8.8 Hz, 1 H), 3.16 (dd, $J = 12.0$ and 7.8 Hz, 1 H), 2.42-2.30 (m, 1 H), 2.37 (s, 3 H), 2.20-2.08 (m, 1 H), 1.95-1.85 (m, 1 H), 1.25-0.94 (m, 4 H), 0.75 (t, $J = 7.0$ Hz, 3 H), 0.68 (d, $J = 6.8$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 159.11, 149.14, 143.69, 136.62, 134.67, 133.97, 133.19, 129.68, 127.80, 123.02, 121.50, 56.99, 36.63, 35.29, 29.94, 25.34, 22.48, 21.74, 18.14, 14.10; MS (m/z) 229 (100); IR (neat) 1591, 1347, 1164 cm^{-1} ; Anal. calcd for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_2\text{S}$: C, 68.72; H, 7.34; N, 7.29. Found: C, 68.87; H, 7.41; N, 7.30.

2j

(11) **5-Benzyl-4(*n*-butyl)-3(*n*-propyl)-1-(toluene-4'-sulfonyl)-2,3-dihydro-1H-pyrrole (2j):** The reaction of **1c** (0.102 g, 0.30 mmol) with iodobenzene (52 μL , 0.095 g, 0.47 mmol) afforded 0.092 g (74%) of **2j**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.55 (d, $J = 8.1$ Hz, 2 H), 7.30-7.02 (m, 7 H), 3.94 (d, $J = 15.6$ Hz, 1 H), 3.84 (d, $J = 15.6$ Hz, 1 H), 3.82 (dd, $J = 12.2$ and 9.2 Hz, 1 H), 3.26 (dd, $J = 12.2$ and 7.4 Hz, 1 H), 2.37 (s, 3 H), 2.36-2.21 (m, 1 H), 2.20-2.06 (m, 1 H), 2.02-1.88 (m, 1 H), 1.35-0.95 (m, 7 H), 0.81 (t, $J = 6.6$ Hz, 3 H), 0.75 (d, $J = 7.2$ Hz, 3 H), 0.60-0.48 (m, 1 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 143.20, 138.79, 134.51, 134.47, 131.46, 129.23, 128.36, 128.10, 127.39, 125.92, 54.35, 41.47, 34.47, 31.81, 29.81, 25.28, 22.28, 21.37, 19.99,

13.90, 13.78; MS (m/z) 411 (M^+ , 30.18), 368 (100); IR (neat) 1599, 1494, 1351, 1165 cm^{-1} ; HRMS calcd for $\text{C}_{25}\text{H}_{33}\text{NO}_2\text{S}$ 411.2232, Found 411.2196.

(12) **3-(*n*-Butyl)-2-methylene-3-phenyl-1-(toluene-4'-sulfonyl)pyrrolidine (2k')**

and **5-Benzyl-4-(*n*-butyl)-1-(toluene-4'-sulfonyl)-2,3-dihydro-1*H*-pyrrole (2k)**:

The reaction of **1d** (0.295 g, 1.01 mmol) with iodobenzene (155 μL , 0.283 g, 1.39 mmol) afforded 0.036 g (10%) of **2k'** and 0.206 g (55%) of **2k**.

2k'

2k': solid, mp 119-121°C (hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.46 (d, J = 7.9 Hz, 2 H), 7.03 (d, J = 7.9 Hz, 2 H), 7.00-6.85 (m, 5 H), 5.33 (d, J = 1.5 Hz, 1 H), 4.32 (d, J = 1.5 Hz, 1 H), 3.79-3.67 (m, 1 H), 3.31-3.17 (m, 1 H), 2.42-2.21 (m, 1 H), 2.32 (s, 3 H), 1.90-1.78 (m, 1 H), 1.63-1.42 (m, 2 H), 1.25-0.98 (m, 3 H), 0.95-0.75 (m, 1 H), 0.71 (t, J = 7.0 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 149.93, 143.87, 141.81, 134.11, 129.35, 128.27, 127.49, 126.83, 126.27, 92.64, 54.36, 48.00, 39.49, 32.93, 27.00, 23.33, 21.75, 14.16; MS (m/z) 369 (M^+ , 4.93), 158 (100); IR (KBr) 1643, 1345, 1164 cm^{-1} ; Anal. calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_2\text{S}$: C, 71.51; H, 7.36; N, 3.79. Found: C, 71.49; H, 7.41; N, 3.75.

2k

2k: solid, mp 78-80°C (hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.55 (d, J = 7.9 Hz, 2 H), 7.29-7.06 (m, 7 H), 3.82 (s, 1 H), 3.64 (t, J = 8.3 Hz, 2 H), 2.34 (s, 3 H), 2.03 (t, J = 7.0 Hz, 2 H), 1.85 (t, J = 8.3 Hz, 2 H), 1.20-0.94 (m, 4 H), 0.74 (t, J = 7.0 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 143.43, 138.96, 135.44, 134.78, 129.43, 129.42, 128.64, 128.28, 127.51, 126.13, 49.55, 32.05, 30.96, 29.73, 27.57, 22.22, 21.56, 13.90; MS (m/z) 369 (M^+ , 40.22), 55 (100); IR (KBr) 1598, 1347, 1166 cm^{-1} ; Anal. calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_2\text{S}$: C, 71.51; H, 7.36; N, 3.79. Found: C, 71.47; H, 7.41; N, 3.75.

2l', 2l

(13) **3-(*n*-Butyl)-3-(4'-methoxyphenyl)-2-methylene-1-(toluene-4'-sulfonyl)pyrrolidine (2l')** and **4-(*n*-butyl)-5-(4'-methoxybenzyl)-1-(toluene-4'-sulfonyl)-2,3-dihydro-1H-pyrrole (2l)**: The reaction of **1d** (0.087 g, 0.30 mmol) with *p*-methoxyphenyl iodide (0.104 g, 0.44 mmol) afforded 0.081 g (68%) of **2l'** and **2l** as a mixture (14:86).

2l: solid; ^1H NMR (300 MHz, CDCl_3) δ 7.53 (d, $J = 7.9$ Hz, 2 H), 7.16 (d, $J = 8.6$ Hz, 2 H), 7.13 (d, $J = 7.9$ Hz, 2 H), 6.73 (d, $J = 8.6$ Hz, 2 H), 3.74 (s, 2 H), 3.69 (s, 3 H), 3.61 (t, $J = 8.3$ Hz, 2 H), 2.32 (s, 3 H), 2.01 (t, $J = 7.3$ Hz, 2 H), 1.82 (t, $J = 8.3$ Hz, 2 H), 1.20-0.92 (m, 4 H), 0.71 (t, $J = 7.0$ Hz, 3 H); MS (m/z) 399 (M^+ , 48.51), 121 (100); IR (neat) 1612, 1511, 1332, 1248, 1162 cm^{-1} ; Anal. calcd for $\text{C}_{23}\text{H}_{29}\text{NO}_3\text{S}$: C, 69.14; H, 7.32; N, 3.51. Found: C, 69.06; H, 7.50; N, 3.41. The following data are discernible for **2l'**: 7.43 (d, $J = 8.3$ Hz, 2 H), 7.01 (d, $J = 8.3$ Hz, 2 H), 6.45 (d, $J = 8.6$ Hz, 2 H), 5.29 (s, 1 H), 4.28 (s, 1 H), 2.29 (s, 3 H).

2m', 2m

(14) **3-(*n*-Butyl)-3-(4'-methoxycarbonylphenyl)-2-methylene-1-(toluene-4'-sulfonyl)pyrrolidine (2m')** and **4-(*n*-butyl)-5-(4'-methoxycarbonylbenzyl)-1-(toluene-4'-sulfonyl)-2,3-dihydro-1H-pyrrole (2m)**: The reaction of **1d** (0.087 g, 0.30 mmol) with *p*-(methoxycarbonyl)phenyl iodide (0.119 g, 0.45 mmol) afforded 0.097 g (77%) of **2m'** and **2m** as a mixture (15:85).

2m: solid; ^1H NMR (300 MHz, CDCl_3) δ 7.93 (d, $J = 7.9$ Hz, 2 H), 7.61 (d, $J = 8.3$ Hz, 2 H), 7.34 (d, $J = 7.9$ Hz, 2 H), 7.23 (d, $J = 8.3$ Hz, 2 H), 3.92 (s, 2 H), 3.88 (s, 3 H),

3.69 (t, $J = 8.3$ Hz, 2 H), 2.39 (s, 3 H), 2.08 (t, $J = 7.1$ Hz, 2 H), 1.92 (t, $J = 8.3$ Hz, 2 H), 1.25-1.00 (m, 4 H), 0.79 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 167.13, 144.48, 143.60, 134.63, 134.56, 130.15, 129.61, 129.49, 128.61, 128.07, 127.43, 51.96, 49.53, 32.12, 30.95, 29.66, 27.52, 22.16, 21.52, 13.84; MS (m/z) 427 (M^+ , 79.02), 55 (100); IR (neat) 1711, 1611, 1346, 1287, 1163 cm^{-1} ; Anal. calcd for $\text{C}_{24}\text{H}_{29}\text{NO}_4\text{S}$: C, 67.42; H, 6.84; N, 3.28. Found: C, 67.37; H, 7.08; N, 3.29. The following data are discernible for **2m'**: 7.45 (d, $J = 8.1$ Hz, 2 H), 7.02 (d, $J = 8.4$ Hz, 2 H), 6.98 (d, $J = 8.1$ Hz, 2 H), 5.45 (s, 1 H), 4.45 (s, 1 H), 2.32 (s, 3 H).

2n

(15) **5-Benzyl-4-(tert-butyl)-1-(toluene-4'-sulfonyl)-2,3-dihydro-1H-pyrrole (2n)**:

The reaction of **1e** (0.089 g, 0.30 mmol) with iodobenzene (50 μL , 0.092 g, 0.45 mmol) afforded 0.073 g (65%) of **2n**: solid, mp 94-95°C (hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.68 (d, $J = 7.9$ Hz, 2 H), 7.32-7.15 (m, 7 H), 4.16 (s, 2 H), 3.65 (t, $J = 7.9$ Hz, 2 H), 2.42 (s, 3 H), 1.86 (t, $J = 7.9$ Hz, 2 H), 1.03 (s, 9 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 143.75, 139.61, 139.29, 135.05, 134.81, 129.51, 128.62, 128.48, 127.83, 126.20, 49.49, 33.90, 32.78, 31.07, 30.40, 21.82; MS (m/z) 369 (M^+ , 100); IR (KBr) 1599, 1348, 1165 cm^{-1} ; Anal. calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_2\text{S}$: C, 71.51; H, 7.36; N, 3.79. Found: C, 71.57; H, 7.52; N, 3.73.

2o

(16) **4-(tert-Butyl)-5-(4'-methoxybenzyl)-1-(toluene-4'-sulfonyl)-2,3-dihydro-1H-pyrrole (2o)**:

The reaction of **1e** (0.088 g, 0.30 mmol) with *p*-methoxyphenyl iodide (0.106 g, 0.45 mmol) afforded 0.092 g (77%) of **2o**: solid, mp 100-102°C (hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.67 (d, $J = 8.1$ Hz, 2 H), 7.26 (d, $J = 8.14$ Hz, 2 H), 7.21 (d, $J = 8.7$ Hz, 2 H), 6.82 (d, $J = 8.7$ Hz, 2 H), 4.07 (s, 2 H), 3.77 (s, 3 H), 3.63 (t, $J =$

7.9 Hz, 2 H), 2.41 (s, 3 H), 1.84 (t, $J = 7.9$ Hz, 2 H), 1.03 (s, 9 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 158.09, 143.70, 138.91, 135.25, 135.04, 131.58, 129.58, 129.48, 127.81, 113.89, 55.46, 49.50, 33.00, 32.73, 31.04, 30.43, 21.81; MS (m/z) 399 (M^+ , 37.01), 97 (100); IR (KBr) 1611, 1513, 1330, 1248, 1162 cm^{-1} ; Anal. calcd for $\text{C}_{23}\text{H}_{29}\text{NO}_3\text{S}$: C, 69.14; H, 7.32; N, 3.51. Found: C, 69.18; H, 7.35; N, 3.42.

2p

(17) **4-(*tert*-Butyl)-5-[4'-(methoxycarbonyl)benzyl]-1-(toluene-4'-sulfonyl)-2,3-dihydro-1H-pyrrole (2p)**: The reaction of **1e** (0.088 g, 0.30 mmol) with *p*-methoxycarbonylphenyl iodide (0.119 g, 0.45 mmol) afforded 0.058 g (45%) of **2p** and 0.025 g (28%) of starting material **1e** was recovered. **2p**: solid, mp 126-129°C (hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.93 (d, $J = 8.6$ Hz, 2 H), 7.65 (d, $J = 8.3$ Hz, 2 H), 7.33 (d, $J = 8.6$ Hz, 2 H), 7.26 (d, $J = 8.3$ Hz, 2 H), 4.18 (s, 2 H), 3.88 (s, 3 H), 3.64 (t, $J = 8.1$ Hz, 2 H), 2.41 (s, 3 H), 1.86 (t, $J = 8.1$ Hz, 2 H), 1.01 (s, 9 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 167.39, 145.18, 143.86, 139.79, 134.91, 133.93, 129.84, 129.52, 128.56, 128.18, 127.77, 52.22, 49.43, 33.98, 32.77, 31.03, 30.33, 21.80; MS (m/z) 427 (M^+ , 36.91), 412 (100); IR (KBr) 1712, 1609, 1288, 1164 cm^{-1} ; Anal. calcd for $\text{C}_{24}\text{H}_{29}\text{NO}_4\text{S}$: C, 67.42; H, 6.84; N, 3.28. Found: C, 67.45; H, 6.85; N, 3.27.

2q

(18) **5-Benzyl-4-(*tert*-butyl)-3-methyl-1-(toluene-4'-sulfonyl)-2,3-dihydro-1H-pyrrole (2q)**: The reaction of **1f** (0.091 g, 0.30 mmol) with iodobenzene (50 μL , 0.092 g, 0.45 mmol) afforded 0.086 g (76%) of **2q**: solid, mp 88-90°C (hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.48 (d, $J = 8.1$ Hz, 2 H), 7.30-7.12 (m, 7 H), 4.18 (d, $J = 17.0$ Hz, 1 H), 4.06 (d, $J = 17.0$ Hz, 1 H), 3.66 (dd, $J = 11.3$ and 8.3 Hz, 1 H), 3.48 (dd, $J = 11.3$ and 1.7 Hz, 1 H), 2.65-2.55 (m, 1 H), 2.37 (s, 3 H), 1.12 (s, 9 H), 0.73 (d, $J =$

6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 143.29, 139.65, 138.95, 135.93, 133.67, 129.48, 128.35, 128.31, 127.53, 126.01, 56.80, 37.92, 33.41, 32.29, 31.36, 21.73, 21.34; MS (m/z) 383 (M^+ , 40.43), 368 (100); IR (KBr) 1597, 1346, 1161, 1050 cm^{-1} ; Anal. calcd for $\text{C}_{23}\text{H}_{29}\text{NO}_2\text{S}$: C, 72.03; H, 7.62; N, 3.65. Found: C, 71.90; H, 7.66; N, 3.61.

2r

(19) **4-(*tert*-Butyl)-5-(hept-2'-enyl)-3-methyl-1-(toluene-4'-sulfonyl)-2,3-dihydro-1H-pyrrole (2r)**: The reaction of **1f** (0.092 g, 0.30 mmol) with (*E*)-1-iodohex-1-ene (0.095 g, 0.48 mmol) afforded 0.072 g (62%) of **2r**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.64 (d, $J = 7.9$ Hz, 2 H), 7.30 (d, $J = 7.9$ Hz, 2 H), 5.52-5.44 (m, 2 H), 3.59 (dd, $J = 11.6$ and 8.6 Hz, 1 H), 3.51-3.28 (m, 3 H), 2.50-2.35 (m, 1 H), 2.41 (s, 3 H), 2.00-1.90 (m, 2 H), 1.40-1.15 (m, 4 H), 1.09 (s, 9 H), 0.87 (t, $J = 7.0$ Hz, 3 H), 0.50 (d, $J = 6.7$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 143.31, 137.67, 135.90, 134.79, 132.16, 129.53, 127.70, 126.51, 56.83, 37.62, 32.51, 32.09, 31.79, 31.30, 30.99, 22.43, 21.74, 21.52, 14.21; MS (m/z) 389 (M^+ , 30.30), 69 (100); IR (neat) 1627, 1598, 1351, 1166 cm^{-1} ; HRMS calcd for $\text{C}_{23}\text{H}_{35}\text{NO}_2\text{S}$: 389.2388. Found: 389.2349.

2a-Ns

(20) **5-Benzyl-4-(*n*-butyl)-3-methyl-1-(4'-nitrobenzenesulfonyl)-2,3-dihydro-1H-pyrrole (2a-Ns)**: The reaction of **1a-Ns** (0.106 g, 0.31 mmol) with iodobenzene (52 μL , 0.095 g, 0.47 mmol) afforded 0.072 g (55%) of **2a-Ns**: solid, mp 115-117°C (hexane); ^1H NMR (300 MHz, CDCl_3) δ 8.19 (d, $J = 8.7$ Hz, 2 H), 7.69 (d, $J = 8.7$ Hz, 2 H), 7.32-7.15 (m, 5 H), 3.95 (dd, $J = 11.7$ and 9.0 Hz, 1 H), 3.93 (d, $J = 15.9$ Hz, 1 H), 3.84 (d, $J = 15.9$ Hz, 1 H), 3.26 (dd, $J = 11.7$ and 7.2 Hz, 1 H), 2.62-2.48 (m, 1 H), 2.25-2.12 (m, 1 H), 2.08-1.85 (m, 1 H), 1.40-1.08 (m, 4 H), 0.84 (t, $J = 6.9$ Hz, 3 H),

0.81 (d, $J = 7.2$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 150.00, 144.00, 138.46, 133.96, 132.94, 128.74, 128.65, 128.62, 126.64, 124.09, 56.98, 36.60, 31.85, 30.20, 25.48, 22.73, 18.47, 14.05; MS (m/z) 414 (M^+ , 35.33), 91 (100); IR (KBr) 1528, 1348, 1169 cm^{-1} ; Anal. calcd for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_4\text{S}$: C, 63.75; H, 6.32; N, 6.76. Found: C, 63.71; H, 6.45; N, 6.75.

3a-Bz

(21) **2-(*n*-Butyl)-3-methyl-2-(1'-phenylethenyl)-1-(toluene-4'-sulfonyl)-azetidine**

(3a-Bz): The reaction of **1a-Bz** (0.129 g, 0.50 mmol) with iodobenzene (85 μL , 0.156 g, 0.76 mmol) afforded 0.031 g (19%) of **3a-Bz**: liquid; ^1H NMR (600 MHz, CDCl_3) δ 7.95-7.91 (m, 2 H), 7.43-7.34 (m, 3 H), 7.30-7.23 (m, 5 H), 5.27 (d, $J = 0.9$ Hz, 1 H), 5.20 (d, $J = 0.9$ Hz, 1 H), 3.67 (dd, $J = 16.8$ and 5.4 Hz, 1 H), 3.26 (dd, $J = 16.8$ and 3.3 Hz, 1 H), 2.00-1.94 (m, 1 H), 1.93-1.87 (m, 1 H), 1.84-1.78 (m, 1 H), 1.74-1.64 (m, 1 H), 1.60-1.51 (m, 1 H), 1.50-1.35 (m, 2 H), 1.01-0.95 (m, 6 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 154.11, 149.81, 140.51, 134.10, 130.53, 128.70, 128.30, 128.24, 127.59, 127.14, 117.51, 84.38, 48.84, 34.68, 30.77, 26.05, 23.25, 14.43, 13.74; MS (m/z) 333 (M^+ , 28.42), 105 (100); IR (neat) 1657, 1289, 1128 cm^{-1} ; HRMS calcd for $\text{C}_{23}\text{H}_{27}\text{NO}$: 333.2093. Found: 333.2108.

The stereo chemistry of **3a-Bz** was confirmed by the ^1H - ^1H NOESY spectra.

(22) **2-(1'-Phenylvinyl)-1-(toluene-4'-sulfonyl)azetidine and 5-phenyl-1-(toluene-4'-sulfonyl)-1,2,3,6-tetrahydropyridine**

We have repeated the Pd(0)-catalyzed coupling-cyclization reaction of simple N-(3,4-pentadienyl)sulfonamide with PhI .⁴ The reaction of N-(3,4-pentadienyl)sulfonamide (0.120 g, 0.51 mmol) with iodobenzene (280 μL , 0.512 g, 2.51 mmol) afforded 0.084 g (53%) of four-membered and six-membered product (79:21).

liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.75 (d, $J = 8.0$ Hz, 2 H), 7.37 (d, $J = 8.0$ Hz, 2 H), 7.35-7.20 (m, 5 H), 5.70 (t, $J = 1.2$ Hz, 1 H), 5.50 (t, $J = 0.9$ Hz, 1 H), 4.79 (t, $J = 8.4$ Hz, 1 H), 3.80-3.71 (m, 2 H), 2.46 (s, 3 H), 2.28-2.16 (m, 1 H), 2.08-1.94 (m, 1 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 146.74, 144.31, 138.28, 132.45, 130.01, 128.68, 128.10, 126.47, 114.43, 65.36, 47.51, 24.82, 21.87; MS (m/z) 313 (M^+ , 13.88), 91 (100); IR (neat) 1624, 1595, 1494, 1348, 1163.

solid; mp 98-99 $^\circ\text{C}$ (EtOAc-hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.72 (d, $J = 8.4$ Hz, 2 H), 7.40-7.22 (m, 7 H), 6.10-6.04 (m, 1 H), 3.94 (q, $J = 2.4$ Hz, 2 H), 3.24 (t, $J = 5.9$ Hz, 2 H), 2.42 (s, 3 H), 2.41-2.35 (m, 2 H); ^{13}C NMR (300 MHz, CDCl_3) δ 143.61, 138.69, 133.40, 133.24, 129.69, 128.51, 127.69, 125.19, 122.17, 46.38, 42.34, 25.62, 21.53; MS (m/z) 313 (M^+ , 20.70), 130 (100); IR (neat) 1596, 1494, 1345, 1164. As compared with the literature data,⁶ due to the difference of ^1H NMR data we observed for the six-membered product, the structure of the six-membered product was established by X-ray diffraction study.