Studies on Pd(II)-Catalyzed Coupling-Cyclization of α - or β -Amino Allenes with Allylic Halides

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N-(2-Methyldeca-2,3-dienyl) *p*-toluenesulfonamide (2b): The reaction of 2-methyldeca-2,3-dien-1-ol (**1b**) (1.722 g, 10.3 mmol), pyridine (0.20 mL) and phosphorous tribromide (0.40 mL, 4.25 mmol) afforded 1.398 g (59%) of allenyl bromide: liquid; ^1H NMR (300 MHz, CDCl_3) δ 5.22-5.12 (m, 1 H), 4.03-3.94 (m, 2 H), 1.97 (q, $J = 6.9$ Hz, 2 H), 1.80 (d, $J = 2.7$ Hz, 3 H), 1.50-1.21 (m, 8 H), 0.87 (t, $J = 6.7$ Hz, 3 H); MS (m/z) 232 ($\text{M}^+(\text{Br}^{81})$, 22.39), 230 ($\text{M}^+(\text{Br}^{79})$, 22.47), 91 (100); IR(neat): 1961, 1462, 1442, 1202 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_{19}^{79}\text{Br}$ 230.0670. Found 230.0670.

A mixture of the above prepared allenyl bromide (0.887 g, 3.84 mmol), potassium carbonate (0.632 g, 4.58 mmol), *p*-toluenesulfonamide (2.581 g, 15.1 mmol), and 20 mL of acetone was heated to reflux for 17 hours to produce 0.894 g (73%) of **2b**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.72 (d, $J = 8.1$ Hz, 2 H), 7.28 (d, $J = 8.1$ Hz, 2 H), 5.21-5.07 (m, 1 H), 4.50-4.35 (m, 1 H), 3.53-3.36 (m, 2 H), 2.41 (s, 3 H), 2.00-1.82 (m, 2 H), 1.59 (d, $J = 2.8$ Hz, 3 H), 1.40-1.18 (m, 8 H), 0.86 (t, $J = 6.7$ Hz, 3 H); MS (m/z) 322 ($\text{M}^+ + 1$, 11.19), 321 (M^+ , 0.81), 155 (100); IR (neat) 3285, 1967, 1329, 1161 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{27}\text{NO}_2\text{S}$ 321.1763. Found 321.1740.

N-Deca-2,3-dienyl *p*-toluenesulfonamide (2c): The reaction of deca-2,3-dien-1-ol (**1c**) (3.098 g, 20.1 mmol), pyridine (0.20 mL) and phosphorous tribromide (0.75 mL, 7.97 mmol) afforded 2.882 g (66%) of the allenyl bromide:^{14b} liquid; ^1H NMR (300 MHz, CDCl_3) δ 5.36-5.13 (m, 2 H), 3.85 (dd, $J = 7.8$ and 2.0 Hz, 2 H), 1.96-1.80 (m, 2 H), 1.42-1.11 (m, 8 H), 0.80 (t, $J = 6.8$ Hz, 3 H); IR(neat): 1960, 1466, 1204 cm^{-1} .

A mixture of the above prepared allenyl bromide (2.117 g, 10.0 mmol), potassium carbonate (1.420 g, 10.3 mmol), *p*-toluenesulfonamide (6.860 g, 40.1 mmol), and 50 mL of acetone was heated to reflux for 13 hours to produce 2.483 g (81%) of **2c**: liquid; ^1H

NMR (300 MHz, CDCl₃) δ 7.76 (d, J = 8.1 Hz, 2 H), 7.31 (d, J = 8.1 Hz, 2 H), 5.24-5.12 (m, 1 H), 5.08-4.96 (m, 1 H), 4.48-4.36 (m, 1 H), 3.60-3.50 (m, 2 H), 2.43 (s, 3 H), 2.00-1.84 (m, 2 H), 1.40-1.15 (m, 8 H), 0.88 (t, J = 6.8 Hz, 3 H); MS (m/z) 307 (M^+ , 0.70), 155 (100); IR (neat) 3283, 1966, 1600, 1329, 1161 cm⁻¹; Anal. calcd for C₁₇H₂₅NO₂S (%): C, 66.41; H, 8.20; N, 4.56. Found: C, 66.62; H, 8.40; N, 4.38.

N-2-(3-Butyl-3,4-pentadienyl) p-toluenesulfonamide (2e): The reaction of 3-butylpenta-3,4-dien-2-ol (**1e**) (1.371 g, 9.79 mmol), triphenylphosphine (3.933 g, 15.0 mmol), phthalimide (1.468 g, 9.99 mmol), and diethyl azodicarboxylate (6.511 g, 40% in toluene, 15.0 mmol) afforded 1.477 g of the corresponding phthalimide. The resulting phthalimide (1.107 g, 4.12 mmol) was treated with hydrazine hydrate (0.48 mL, 85% purity, 8.32 mmol) in EtOH followed by tosylation to produce 0.741 g (overall yield: 34%) of **2e**; liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.74 (d, J = 8.2 Hz, 2 H), 7.28 (d, J = 8.2 Hz, 2 H), 4.82-4.64 (m, 2 H), 4.64-4.58 (m, 1 H), 3.84-3.68 (m, 1 H), 2.42 (s, 3 H), 1.84-1.72 (m, 2 H), 1.32-1.06 (m, 7 H), 0.81 (t, J = 6.9 Hz, 3 H); MS (m/z) 278 (M^+ -CH₃, 2.65), 155 (100); IR (neat) 3268, 1952, 1330, 1159 cm⁻¹; HRMS calcd for C₁₅H₂₀NO₂S(M^+ -CH₃) 278.1215. Found 278.1210.

N-(1-Phenyl-2-allylbuta-2,3-dienyl) p-toluenesulfonamide (2f): The reaction of 1-phenyl-2-allylbuta-2,3-dien-1-ol (**1f**) (1.205 g, 6.53 mmol), triphenylphosphine (2.659 g, 10.1 mmol), phthalimide (0.970 g, 6.77 mmol), and diethyl azodicarboxylate (4.3 mL, 40% in toluene, 9.9 mmol) afforded 0.454 g of the corresponding phthalimide. The resulting phthalimide (0.454 g, 1.44 mmol) was treated with hydrazine hydrate (0.18 mL, 85% purity, 3.12 mmol) in MeOH followed by tosylation to produce 0.253 g (overall yield: 11%) of **2f**; solid, mp 78-79 °C (*n*-hexane/ether); ¹H NMR (300 MHz, CDCl₃) δ

7.49 (d, $J = 7.2$ Hz, 2 H), 7.16-6.85 (m, 7 H), 5.62-5.34 (m, 2 H), 4.93-4.56 (m, 5 H), 2.52-2.24 (m, 2 H), 2.23 (s, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): $\delta = 204.61$, 142.74, 138.82, 137.53, 134.30, 129.00, 128.18, 127.47, 127.18, 126.97, 116.59, 103.47, 80.18, 57.75, 33.96, 21.26; MS m/z (%) 339 (M^+ , 0.24), 91 (100); IR (neat) 3270, 1953, 1325, 1159 cm^{-1} ; Anal. calcd for $\text{C}_{20}\text{H}_{21}\text{SNO}_2$ (%): C 70.77, H 6.24, N 4.13. Found: C 70.78, H 6.36, N 4.05.

2g

***N*-4-(3-Methyl-1,2-octadienyl) *p*-toluenesulfonamide (2g):** The reaction of 3-methylocta-1,2-dien-4-ol (**1g**) (0.612 g, 4.37 mmol), triphenylphosphine (1.753 g, 6.7 mmol), phthalimide (0.678 g, 4.61 mmol), and diethyl azodicarboxylate (2.9 ml, 40% in toluene, 6.7 mmol) afforded 0.423 g of the corresponding phthalimide. The resulting phthalimide (0.423 g, 1.57 mmol) was treated with hydrazine hydrate (0.19 mL, 85% purity, 3.3 mmol) in MeOH followed by tosylation to produce 0.249 g (overall yield: 19%) of **2g**: solid, mp 64-66 °C (*n*-hexane/ether); ^1H NMR (300 MHz, CDCl_3) δ 7.65 (d, $J = 8.4$ Hz, 2 H), 7.17 (d, $J = 8.4$ Hz, 2 H), 4.95 (brs, 1 H), 4.73-4.34 (m, 2 H), 3.58 (q, $J = 6.9$ Hz, 1 H), 2.31 (s, 3 H), 1.53-1.05 (m, 9 H), 0.72 (t, $J = 6.6$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): $\delta = 205.41$, 142.95, 137.99, 129.20, 127.03, 98.71, 76.53, 55.99, 33.60, 27.36, 22.12, 21.41, 14.65, 13.83; MS m/z (%) 293 (M^+ , 0.41), 91 (100); IR (neat) 3255, 1961, 1434, 1321, 1162 cm^{-1} ; Anal. calcd for $\text{C}_{16}\text{H}_{23}\text{SNO}_2$ (%): C 65.49, H 7.90, N 4.77. Found: C 65.20, H 7.75, N 4.57.

2h

***N*-4-(3-methyl-1,2-nonadienyl) *p*-toluenesulfonamide (2h):** The reaction of 3-methylnona-1,2-dien-4-ol (**1h**) (0.304 g, 1.97 mmol), triphenylphosphine (0.786 g, 3.04 mmol), phthalimide (0.308 g, 2.16 mmol), and diethyl azodicarboxylate (1.3 ml, 40% in toluene, 3.0 mmol) afforded 0.234 g of the corresponding phthalimide. The resulting phthalimide (0.234 g, 0.83 mmol) was treated with hydrazine hydrate (0.09 mL, 85%

purity, 1.56 mmol) in MeOH followed by tosylation to produce 0.108 g (overall yield: 18%) of **2h**; liquid, ^1H NMR (300 MHz, CDCl_3) δ 7.64 (d, J = 8.4 Hz, 2 H), 7.17 (d, J = 8.4 Hz, 2 H), 5.02 (d, J = 8.7 Hz, 1 H), 4.50-4.33 (m, 2 H), 3.70-3.52 (m, 1 H), 2.31 (s, 3 H), 1.50-0.99 (m, 11 H), 0.72 (t, J = 6.6 Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ = 205.45, 142.92, 138.02, 129.19, 127.02, 98.71, 76.47, 56.01, 33.87, 31.19, 24.88, 22.35, 21.38, 14.62, 13.86; MS m/z (%) 308 (M^+ , 0.54), 91 (100); IR (neat) 3277, 1960, 1599, 1426, 1160, 814, 667 cm^{-1} ; Anal. calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_2\text{S}$ (%): C 66.41, H 8.20, N 4.56. Found: C 66.46, H 8.43, N 4.68.

N-(2-Methyl-1-phenylbuta-2,3-dienyl) p-toluenesulfonamide (2i): The reaction of 2-methyl-1-phenylbuta-2,3-dien-1-ol (**1i**) (0.786 g, 4.91 mmol), triphenylphosphine (1.978 g, 7.55 mmol), phthalimide (0.757 g, 5.15 mmol), and diethyl azodicarboxylate (3.3 ml, 40% in toluene, 7.6 mmol) afforded 0.467 g of the corresponding phthalimide. The resulting phthalimide (0.459 g, 1.59 mmol) was treated with hydrazine hydrate (0.18 mL, 85% purity, 3.12 mmol) in MeOH followed by tosylation to produce 0.342 g (overall yield: 22%) of **2i**: solid, mp 95-97 $^{\circ}\text{C}$ (*n*-hexane/ether); ^1H NMR (300 MHz, CDCl_3) δ 7.51 (d, J = 8.4 Hz, 2 H), 5.25-5.04 (m, 7 H), 4.99 (d, J = 6.9 Hz, 1 H), 4.82-4.71 (m, 1 H), 4.71-4.51 (m, 2 H), 2.31 (s, 3 H), 1.31 (t, J = 3.0 Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ = 204.72, 142.88, 138.91, 137.60, 129.17, 128.28, 127.58, 127.17, 127.01, 99.85, 78.61, 59.11, 21.37, 15.88; MS m/z (%) 313 (M^+ , 0.23), 260 ($\text{M}^+ - \text{C}_4\text{H}_5$, 50.68), 91 (100); IR (neat) 3268, 1959, 1598, 1494, 1325, 1163 cm^{-1} ; Anal. calcd for $\text{C}_{18}\text{H}_{19}\text{SNO}_2$ (%): C 68.98, H 6.11, N 4.47. Found: C 69.06, H 6.51, N 4.49.

N-(1-Benzyl-2-methylbuta-2,3-dienyl) p-toluenesulfonamide (2j): The reaction of 3-methyl-1-phenylpenta-3,4-dien-2-ol (**1j**) (0.133 g, 0.76 mmol), triphenylphosphine (0.311 g, 1.19 mmol), phthalimide (0.152 g, 1.03 mmol), and diethyl azodicarboxylate

(0.6 ml, 40% in toluene, 1.4 mmol) afforded the corresponding phthalimide. The resulting phthalimide was treated with hydrazine hydrate (0.09 mL, 85% purity, 1.56 mmol) in MeOH followed by tosylation to produce 0.123 g (overall yield: 50%) of **2j**: solid, mp 86-88 °C (*n*-hexane/ether); ¹H NMR (300 MHz, CDCl₃) δ 7.42 (d, *J* = 8.4 Hz, 2 H), 6.87-6.73(m, 5 H), 6.73-6.62(m, 2 H), 6.64(d, *J* = 8.4 Hz, 1 H), 4.29-4.13(m, 2 H), 3.71(q, *J* = 7.2 Hz, 1 H), 2.63(dd, *J* = 13.8, 26.7 Hz, 1 H), 2.61(dd, *J* = 13.8, 26.4 Hz, 1 H), 2.18(s, 3 H), 1.32(t, *J* = 3.0 Hz, 3 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 205.80, 143.01, 137.58, 136.55, 129.40, 129.31, 128.17, 126.96, 126.51, 98.69, 77.43, 56.80, 40.10, 21.45, 15.58; MS *m/z* (%) 327 (M⁺, 0.20), 274 (M⁺-C₄H₅, 9.38), 91 (100); IR (neat) 3256, 1959, 1596, 1496, 1442, 1322, 1155 cm⁻¹; Anal calcd for C₁₉H₂₁SNO₂ (%): C 69.69, H 6.46, N 4.28. Found: C 69.53, H 6.75, N 4.25.

2k

***N*-(3-Cyclohexylidene-2-propenyl) *p*-toluenesulfonamide (2k)**: The reaction of 3-cyclohexylideneprop-2-en-1-ol (**1k**) (0.189 g, 1.37 mmol), triphenylphosphine (0.556 g, 2.12 mmol), phthalimide (0.220 g, 1.50 mmol), and diethyl azodicarboxylate (0.9 ml, 40% in toluene, 2.1 mmol) afforded 0.170 g of the corresponding phthalimide. The resulting phthalimide (0.170 g, 0.64 mmol) was treated with hydrazine hydrate (0.08 mL, 85% purity, 1.39 mmol) in MeOH followed by tosylation to produce 0.131 g (overall yield: 33%) of **2k**: liquid ¹H NMR (300 MHz, CDCl₃) δ 7.76 (d, *J* = 6.6 Hz, 2 H), 7.31 (d, *J* = 6.6 Hz, 2 H), 4.96-4.87 (m, 1 H), 4.54 (t, *J* = 5.4 Hz, 1 H), 3.52 (t, *J* = 5.4 Hz, 2 H), 2.43 (s, 3 H), 2.10-1.97 (m, 4 H), 1.64-1.41 (m, 6 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 197.71, 143.20, 136.88, 129.52, 127.00, 106.10, 85.29, 42.31, 31.09, 27.13, 25.75, 21.39; MS *m/z* (%) 291 (M⁺, 1.38), 155 (100); IR (neat) 3279, 1965, 1598, 1495, 1445, 1160 cm⁻¹; Anal. calcd for C₁₆H₂₁NO₂S (%): C 65.95, H 7.26, N 4.81. Found: C 65.82, H 7.60, N 4.73.

6b

***N*-(3-(*n*-Butyl)-2-methyl-3,4-pentadienyl) *p*-nitro-benzenesulfonamide (6b):** The reaction of **5a** (1.153 g, 4.07 mmol) with hydrazine hydrate (0.50 mL, 85% purity, 8.63 mmol) followed by protection using 4-nitrobenzenesulfonyl chloride (0.884 g, 3.98 mmol) afforded 0.822 g (60%) of **6b**: solid, mp 59-61°C (hexane); ¹H NMR (300 MHz, CDCl₃) δ 8.37 (d, *J* = 8.1 Hz, 2 H), 8.04 (d, *J* = 8.1 Hz, 2 H), 4.80-4.64 (m, 3 H), 3.10-3.00 (m, 1 H), 2.98-2.88 (m, 1 H), 2.22-2.08 (m, 1 H), 1.92-1.72 (m, 2 H), 1.42-1.20 (m, 4 H), 0.99 (d, *J* = 7.2 Hz, 3 H), 0.87 (t, *J* = 7.2 Hz, 3 H); MS (*m/z*) 295 (*M*⁺-C₃H₇, 0.95), 152 (100); IR (KBr) 3435, 1953, 1607, 1535, 1177 cm⁻¹; Anal. calcd for C₁₆H₂₂N₂O₄S: C, 56.78; H, 6.55; N, 8.28. Found: C, 56.86; H, 6.59; N, 8.24.

6c

***N*-(2-Methyl-3-butylpenta-3,4-dienyl) acetamide (6c):** The reaction of **5a** (1.423 g, 5.00 mmol) with hydrazine hydrate (0.60 mL, 85% purity, 10.4 mmol) followed by protection using acetyl chloride (0.35 mL, 4.94 mmol) afforded 0.451 g (46%) of **6c**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 5.65 (brs, 1 H), 4.85-4.75 (m, 2 H), 3.40-3.28 (m, 1 H), 3.26-3.14 (m, 1 H), 2.28-2.12 (m, 1 H), 2.08-1.88 (m, 5 H), 1.50-1.22 (m, 4 H), 1.05 (d, *J* = 6.6 Hz, 3 H), 0.92 (t, *J* = 7.2 Hz, 3 H); MS (*m/z*) 196 (*M*⁺+1, 6.47), 110 (100); IR (neat) 3292, 1953, 1652, 1293 cm⁻¹; HRMS calcd for C₁₁H₁₈NO (*M*⁺-CH₃) 180.1388. Found 180.1369.

6d

***N*-(2-Methyl-3-butylpenta-3,4-dienyl) benzamide (6d):** The reaction of **5a** (1.133 g, 4.00 mmol) with hydrazine hydrate (0.50 mL, 85% purity, 8.63 mmol) followed by benzoylation using benzoyl chloride (0.50 mL, 4.14 mmol) afforded 0.813 g (79%) of **6d**:

liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.73 (d, $J = 7.3$ Hz, 2 H), 7.55-7.35 (m, 3 H), 6.29 (brs, 1 H), 4.79 (s, 2 H), 3.60-3.35 (m, 2 H), 2.40-2.26 (m, 1 H), 2.08-1.84 (m, 2 H), 1.50-1.20 (m, 4 H), 1.10 (d, $J = 6.1$ Hz, 3 H), 0.88 (t, $J = 7.0$ Hz, 3 H); MS (m/z) 258 ($M^+ + 1$, 18.09), 105 (100); IR (neat) 3323, 1952, 1640 cm^{-1} ; Anal. calcd for $\text{C}_{17}\text{H}_{23}\text{NO}$: C, 79.33; H, 9.01; N, 5.44. Found: C, 79.08; H, 9.07; N, 5.50.

Penta-3,4-dienyl *p*-toluenesulfonamide (6e): The reaction of 3-butylpenta-3,4-dien-1-ol (**4b**) (2.093 g, 15.0 mmol), triphenylphosphine (5.890 g, 22.5 mmol), phthalimide (2.214 g, 15.1 mmol), and diethyl azodicarboxylate (9.792 g, 40% in toluene, 22.5 mmol) afforded 3.642 g of the phthalimide. The resulting phthalimide (3.227 g, 12.0 mmol) was treated with hydrazine hydrate (1.40 mL, 85% purity, 24.2 mmol) followed by tosylation using tosylate chloride (2.281 g, 11.9 mmol) to produce 2.727 g (overall yield: 70%) of **6e**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.73 (d, $J = 8.0$ Hz, 2 H), 7.29 (d, $J = 8.0$ Hz, 2 H), 4.78-4.58 (m, 3 H), 3.05 (q, $J = 6.3$ Hz, 2 H), 2.42 (s, 3 H), 2.10-1.98 (m, 2 H), 1.85-1.74 (m, 2 H), 1.40-1.15 (m, 4 H), 0.85 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 204.97, 143.19, 136.85, 129.53, 126.98, 100.14, 76.83, 40.94, 31.58, 31.53, 29.31, 22.15, 21.40, 13.78; MS (m/z) 293 (M^+ , 2.35), 96 (100); IR (neat) 3276, 1949, 1314, 1147 cm^{-1} ; HRMS calcd for $\text{C}_{16}\text{H}_{23}\text{NO}_2\text{S}$ 293.1450. Found 293.1443.

***N*-(2-Methyl-3-(*tert*-butyl)-3,4-pentadienyl) *p*-toluenesulfonamide (6f):** The reaction of 2-methyl-3-(*tert*-butyl)penta-3,4-dien-1-ol (**4c**) (1.089 g, 7.07 mmol), triphenylphosphine (2.749 g, 10.5 mmol), phthalimide (1.042 g, 7.09 mmol), and diethyl azodicarboxylate (4.560 g, 40% in toluene, 10.5 mmol) afforded 1.509 g of phthalimide. The resulting phthalimide was treated with hydrazine hydrate (0.65 mL, 85% purity, 11.2 mmol) followed by tosylation using tosylate chloride (1.020 g, 5.34 mmol) to produce

1.138 g (overall yield: 52%) of **6f**: solid, mp 78-79°C (hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.73 (d, $J = 8.3$ Hz, 2 H), 7.30 (d, $J = 8.3$ Hz, 2 H), 4.72 (d, $J = 9.8$ Hz, 1 H), 4.60 (d, $J = 9.8$ Hz, 1 H), 4.56-4.45 (m, 1 H), 2.90-2.75 (m, 2 H), 2.42 (s, 3 H), 2.30-2.18 (m, 1 H), 1.00 (s, 9 H), 0.98 (d, $J = 6.9$ Hz, 3 H); MS (m/z) 292 ($\text{M}^+ - \text{CH}_3$, 7.78), 91 (100); IR (neat) 3269, 1952, 1328, 1166 cm^{-1} ; $\text{C}_{17}\text{H}_{25}\text{NO}_2\text{S}$: C, 66.41; H, 8.20; N, 4.56. Found: C, 66.37; H, 8.11; N, 4.49.

6g

***N*-(3-(tert-butyl)-3,4-pentadienyl) *p*-toluenesulfonamide (6g)**: The reaction of 3-(tert-butyl)penta-3,4-dien-1-ol (**4d**) (0.554 g, 3.96 mmol), triphenylphosphine (1.570 g, 6.00 mmol), phthalimide (0.596 g, 4.05 mmol), and diethyl azodicarboxylate (2.638 g, 40% in toluene, 6.06 mmol) afforded 0.892 g of the phthalimide. The resulting phthalimide was treated with hydrazine hydrate (0.40 mL, 85% purity, 6.90 mmol) followed by tosylation using tosylate chloride (0.657 g, 3.44 mmol) to produce 0.707 g (overall yield: 61%) of **6g**: solid, mp 62-63°C (hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.73 (d, $J = 8.3$ Hz, 2 H), 7.30 (d, $J = 8.3$ Hz, 2 H), 4.67 (t, $J = 4.0$ Hz, 2 H), 4.63-4.58 (m, 1 H), 3.07 (q, $J = 6.5$ Hz, 2 H), 2.42 (s, 3 H), 2.15-2.06 (m, 2 H), 0.97 (s, 9 H); MS (m/z) 278 ($\text{M}^+ - \text{CH}_3$, 15.06), 91 (100); IR (neat) 3296, 1946, 1326, 1157 cm^{-1} ; Anal. calcd for $\text{C}_{16}\text{H}_{23}\text{NO}_2\text{S}$: C, 65.49; H, 7.90; N, 4.77. Found: C, 65.56; H, 7.98; N, 4.73.

6h

***N*-(2-Methyl-3,4-pentadienyl) *p*-toluenesulfonamide (6h)**: The reaction of 2-methylpenta-3,4-dien-1-ol (**4e**) (1.470 g, 15.0 mmol), triphenylphosphine (5.891 g, 22.5 mmol), phthalimide (2.197 g, 14.9 mmol), and diethyl azodicarboxylate (9.886 g, 40% in toluene, 22.7 mmol) afforded 3.121 g of the phthalimide. The resulting phthalimide (1.162 g, 5.12 mmol) was treated with hydrazine hydrate (0.60 mL, 85% purity, 10.4 mmol) followed by tosylation using tosyl chloride (0.954 g, 5.00 mmol) to

produce 0.449 g (overall yield: 32%) of **6h**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.74 (d, $J = 8.1$ Hz, 2 H), 7.30 (d, $J = 8.1$ Hz, 2 H), 4.96 (q, $J = 6.6$ Hz, 1 H), 4.80-4.62 (m, 3 H), 3.01-2.89 (m, 1 H), 2.88-2.78 (m, 1 H), 2.42 (s, 3 H), 2.40-2.25 (m, 1 H), 0.98 (d, $J = 6.9$ Hz, 3 H); MS (m/z) 236 ($\text{M}^+ - \text{CH}_3$, 3.87), 91 (100); IR (neat) 3278, 1952, 1321, 1162 cm^{-1} ; Anal. calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_2\text{S}$: C, 62.12; H, 6.82; N, 5.57. Found: C, 62.07; H, 7.03; N, 5.52.

6i

***N*-(2,3-Dimethylpenta-3,4-dienyl) *p*-toluenesulfonamide (6i)**: The reaction of 2,3-dimethylpenta-3,4-dien-1-ol (**4f**) (0.904 g, 8.07 mmol), triphenylphosphine (3.132 g, 12.0 mmol), phthalimide (1.306 g, 8.88 mmol), and diethyl azodicarboxylate (5.0 ml, 40% in toluene, 11.5 mmol) afforded 1.948 g of the corresponding phthalimide. The resulting phthalimide (1.840 g, 7.63 mmol) was treated with hydrazine hydrate (0.86 mL, 85% purity, 14.9 mmol) in MeOH followed by tosylation to produce 0.635 g (overall yield: 30%) of **6i**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.67 (d, $J = 8.4$ Hz, 2 H), 7.43-7.35 (m, 2 H), 4.49-4.42 (m, 2 H), 4.23 (t, $J = 6.2$ Hz, 1 H), 2.77-2.58 (m, 2 H), 2.36 (s, 3 H), 2.12-2.02 (m, 1 H), 1.50 (t, $J = 3.0$ Hz, 3 H), 0.91 (d, $J = 6.6$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): $\delta = 205.25, 143.33, 136.92, 129.64, 127.07, 99.99, 75.84, 46.75, 37.01, 21.50, 16.89, 16.61$; MS m/z (%) 265 (M^+ , 1.87), 110 (100); IR (neat) 3286, 2971, 1956, 1326, 1160, 1093 cm^{-1} ; HRMS m/z (EI) calcd for $\text{C}_{14}\text{H}_{19}\text{SNO}_2$: 265.11365. Found 265.11080.

6j

***N*-(2-Methyl-3-allylpenta-3,4-dienyl) *p*-toluenesulfonamide (6j)**: The reaction of 2-methyl-3-allylpenta-3,4-dien-1-ol (**4g**) (0.752 g, 5.45 mmol), triphenylphosphine (2.163 g, 8.26 mmol), phthalimide (0.890 g, 6.05 mmol), and diethyl azodicarboxylate (3.5 ml, 40% in toluene, 8.08 mmol) afforded the corresponding phthalimide. The

resulting phthalimide was treated with hydrazine hydrate (0.62 mL, 85% purity, 10.7 mmol) in MeOH followed by tosylation to produce 1.160 g (overall yield: 73%) of **6j**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.72 (d, J = 8.1 Hz, 2 H), 7.24 (d, J = 8.1 Hz, 2 H), 5.74-5.56 (m, 1 H), 5.23 (t, J = 6.0 Hz, 1 H), 4.98-4.80 (m, 2 H), 4.72-4.48 (m, 2 H), 2.92-2.74 (m, 2 H), 2.66-2.53 (m, 2 H) 2.35 (s, 3 H), 2.20-2.01 (m, 1 H), 0.93 (d, J = 7.2 Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ = 204.59, 142.85, 136.48, 134.78, 129.18, 126.59, 115.87, 103.42, 76.15, 46.60, 35.12, 34.92, 21.04, 16.84; MS m/z (%) 291 (M^+ , 0.71), 91 (100); IR (neat) 3287, 2968, 1954, 1667, 1326, 1160 cm^{-1} ; Anal. calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_2\text{S}$ (%): C 65.95, H 7.26, N 4.81. Found: C 65.69, H 6.99, N 5.18.

Palladium (II)-catalyzed coupling-cyclization of α -amino allenes 2a-n with allylic halides. Synthesis of 2,5-dihydropyrrole products 7:

3-Allyl-2-hexyl-4-methyl-1-(*p*-toluenesulfonyl)-2,5-dihydro-1H-pyrrole (7b): The reaction of **2b** (0.095 g, 0.30 mmol), allyl bromide (0.183 g, 1.51 mmol), and PdCl_2 (5 mol%) at 25°C in 2 mL of DMA for 15 hours produced 0.101 g (95%) of **7b**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.67 (d, J = 8.3 Hz, 2 H), 7.27 (d, J = 8.3 Hz, 2 H), 5.56-5.40 (m, 1 H), 4.90 (d, J = 11.6 Hz, 1 H), 4.78 (d, J = 15.4 Hz, 1 H), 4.52-4.40 (m, 1 H), 3.98 (s, 2 H), 2.81 (dd, J = 15.5 and 5.5 Hz, 1 H), 2.46 (dd, J = 15.5 and 7.0 Hz, 1 H), 2.41 (s, 3 H), 1.96-1.80 (m, 1 H), 1.68-1.45 (m, 4 H), 1.40-1.05 (m, 8 H), 0.87 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 143.36, 135.15, 134.34, 131.14, 129.74, 127.96, 127.50, 116.33, 68.80, 59.37, 33.14, 32.13, 29.79, 29.59, 23.18, 22.91, 21.73, 14.37, 11.46; MS (m/z) 361 (M^+ , 0.57), 276 (100); IR (neat) 1635, 1343, 1162 cm^{-1} ; Anal. calcd for

C₂₁H₃₁NO₂S: C, 69.77; H, 8.64; N, 3.87. Found: C, 69.87; H, 8.69; N, 3.66.

(3) The reaction of **2c** (0.112 g, 0.36 mmol), allyl bromide (0.222 g, 1.83 mmol), K₂CO₃ (0.075 g, 0.54 mmol), and PdCl₂(PhCN)₂ (10 mol%) at 25°C in 2.5 mL of THF for 12 hours produced 0.049 g (39%) of **7c** and 0.028 g (22%) of N-allylation product **8c**.

7c

3-Allyl-2-hexyl-1-(p-toluenesulfonyl)-2,5-dihydro-1H-pyrrole (7c): solid, mp 41.5-43°C (hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.68 (d, *J* = 8.5 Hz, 2 H), 7.27 (d, *J* = 8.5 Hz, 2 H), 5.72-5.52 (m, 1 H), 5.27-5.23 (bs, 1 H), 4.99 (d, *J* = 16.2 Hz, 1 H), 4.95 (d, *J* = 23.0 Hz, 1 H), 4.44-4.36 (m, 1 H), 4.12-3.96 (m, 2 H), 2.70 (dd, *J* = 16.4 and 6.1 Hz, 1 H), 2.53 (dd, *J* = 16.4 and 7.3 Hz, 1 H), 2.40 (s, 3 H), 2.00-1.86 (m, 1 H), 1.64-1.48 (m, 1 H), 1.44-1.08 (m, 8 H), 0.87 (t, *J* = 6.7 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 143.39, 140.69, 135.50, 134.19, 129.79, 127.53, 119.52, 117.25, 68.09, 55.38, 32.98, 32.57, 32.08, 29.54, 22.97, 22.86, 21.70, 14.31; MS (*m/z*) 347 (M⁺, 0.22), 262 (100); IR (neat) 1637, 1346, 1165 cm⁻¹; Anal. calcd for C₂₀H₂₉NO₂S: C, 69.13; H, 8.41; N, 4.03. Found: C, 69.53; H, 8.26; N, 3.69.

8c

N-Allyl-N-deca-2,3-dienyl p-toluenesulfonamide (8c): liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.71 (d, *J* = 8.1 Hz, 2 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 5.75-5.60 (m, 1 H), 5.25-5.05 (m, 3 H), 4.94-4.78 (m, 1 H), 3.97-3.69 (m, 4 H), 2.43 (s, 3 H), 2.06-1.80 (m, 2 H), 1.50-1.32 (m, 8 H), 0.88 (t, *J* = 6.5 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 205.48, 143.37, 137.82, 132.90, 129.85, 127.37, 119.03, 92.72, 86.36, 49.24, 46.52, 31.83, 29.29, 28.94, 28.74, 22.80, 21.72, 14.28; MS (*m/z*) 347 (M⁺, 0.25), 224 (100); IR (neat) 1640, 1349, 1163 cm⁻¹; HRMS calcd for C₂₀H₂₉NO₂S 347.1919 Found 347.1882.

7d

4-Allyl-3-butyl-2-(methoxycarbonyl)-5-(isopropyl)-1-(*p*-toluenesulfonyl)-2,5-

dihydro-1*H*-pyrrole (7d): The reaction of **2d** (0.116 g, 0.31 mmol), allyl bromide (0.202 g, 1.67 mmol) and PdCl₂ (5 mol%) at 25°C in 2 mL of DMA for 44 hours produced 0.109 g (85%) of **7d**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.68 (d, *J* = 8.0 Hz, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 5.50-5.32 (m, 1 H), 4.92 (d, *J* = 10.1 Hz, 1 H), 4.75 (s, 1 H), 4.73 (d, *J* = 16.6 Hz, 1H), 4.32 (bs, 1 H), 3.74 (s, 3 H), 2.90 (dd, *J* = 15.7 and 4.9 Hz, 1 H), 2.55 (dd, *J* = 15.7 and 7.5 Hz, 1 H), 2.41 (s, 3 H), 2.22-1.85 (m, 3 H), 1.35-1.15 (m, 1 H), 1.08 (d, *J* = 6.9 Hz, 3 H), 1.05-0.80 (m, 3 H), 0.94 (d, *J* = 7.2 Hz, 3 H), 0.77 (t, *J* = 6.3 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 170.08, 143.68, 134.85, 133.97, 133.87, 131.64, 129.45, 127.75, 116.49, 73.85, 69.40, 52.04, 32.28, 30.39, 29.74, 25.11, 22.00, 21.33, 18.59, 18.44, 13.74; MS (*m/z*) 420, (*M*⁺+1, 5.53), 419 (*M*⁺, 0.53), 376 (100); IR (neat) 1763, 1733, 1639, 1599, 1353, 1168 cm⁻¹; HRMS caclcd for C₂₀H₂₆NO₄S (*M*⁺-C₃H₇) 376.1583. Found 376.1582.

7o

3-(But-2-enyl)-2-hexyl-4-methyl-1-(*p*-toluenesulfonyl)-2,5-dihydro-1*H*-pyrrole (7o):

The reaction of **2b** (0.061g, 0.19 mmol), 3-chlorobut-1-ene (0.103 g, 1.13 mmol), and PdCl₂ (5 mol%) in 1.4 mL of DMA at 25°C for 18 hours produced 0.059 g (83%) of **7o**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.75-7.62 (m, 2 H), 7.32-7.22 (m, 2 H), 5.50-4.98 (m, 2 H), 4.43 (bs, 1 H), 4.02-3.90 (m, 2 H), 2.81-2.68 (m, 1 H), 2.60-2.30 (m, 1 H), 2.41 (s, 3 H), 1.90-1.82 (m, 1 H), 1.70-1.40 (m, 7 H), 1.38-1.00 (m, 8 H), 0.87 (t, *J* = 6.7 Hz, 3 H); MS (*m/z*) 375 (*M*⁺, 1.19), 374 (*M*⁺-1, 6.42), 84 (100); IR (neat) 1344, 1165 cm⁻¹; IR

(neat) 2926, 2858, 1599, 1495, 1454, 1344, 1163, 1097, 664 cm^{-1} ; HRMS calcd for $\text{C}_{22}\text{H}_{33}\text{NO}_2\text{S}$ 375.2232 Found 375.2225.

7p

2-Hexyl-4-methyl-3-(2-methyl-2-propenyl)-1-(p-toluenesulfonyl)-2,5-dihydro-1H-pyrrole (7p): The reaction of **2b** (0.097 g, 0.30 mmol), 3-chloro-2-methyl-1-propene (0.145 g, 1.60 mmol), and PdCl_2 (5 mol%) in 2 mL of DMA at 25°C for 45 hours produced 0.077 g (68%) of **7p**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.66 (d, $J = 7.9$ Hz, 2 H), 7.25 (d, $J = 7.9$ Hz, 2 H), 4.70-4.49 (m, 1 H), 4.38-4.33 (m, 2 H), 3.99 (s, 2 H), 2.73 (d, $J = 15.0$ Hz, 1 H), 2.38 (s, 3 H), 2.47 (d, $J = 15.0$ Hz, 1 H), 1.87-1.77 (m, 1 H), 1.63-1.43 (m, 4 H), 1.36-0.95 (m, 11 H), 0.86 (t, $J = 6.0$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 143.36, 142.06, 134.96, 131.22, 129.72, 128.56, 127.50, 111.97, 68.66, 59.55, 33.96, 33.40, 32.15, 29.65, 23.23, 22.92, 21.98, 21.69, 14.36, 11.51; MS (m/z) 376 ($\text{M}^+ + 1$, 15.74), 375 (M^+ , 2.92), 374 ($\text{M}^+ - 1$, 15.61), 290 (100); IR (neat) 1648, 1343, 1162 cm^{-1} ; HRMS calcd for $\text{C}_{22}\text{H}_{33}\text{NO}_2\text{S}$ 375.2232. Found 375.2223.

7q

2-Hexyl-4-methyl-3-(1-methyl-2-propenyl)-1-(p-toluenesulfonyl)-2,5-dihydro-1H-pyrrole (7q): The reaction of **2b** (0.065 g, 0.20 mmol), crotonyl chloride (0.104 g, 1.15 mmol), and PdCl_2 (5 mol%) in 1.4 mL of DMA at 25°C for 40 hours produced 0.018 g (24%) of a mixture of **7o** and **7q** (36:64). **7q**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.75-7.60 (m, 2 H), 7.35-7.20 (m, 2 H), 5.75-5.62 (m, 1 H), 5.00-4.82 (m, 2 H), 4.45 (bs, 1 H), 3.95 (s, 2 H), 3.00-2.82 (m, 1 H), 2.40 (s, 3 H), 1.92-1.78 (m, 1 H), 1.70-1.42 (m, 4 H), 1.40-1.12 (m, 8 H), 1.01 (d, $J = 7.2$ Hz, 3 H), 0.87 (t, $J = 6.7$ Hz, 3 H); MS (m/z) 375 (M^+ , 1.80), 84 (100).

7e

4-Allyl-3-butyl-2-methyl-1-(*p*-toluenesulfonyl)-2,5-dihydro-1*H*-pyrrole (7e): The reaction of **2e** (0.124 g, 0.42 mmol), allyl bromide (0.245 g, 2.02 mmol), and PdCl₂ (5 mol%) at 25°C in 2.5 mL of DMA for 12 hours produced 0.117 g (83%) of **7e**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.69 (d, *J* = 8.2 Hz, 2 H), 7.28 (d, *J* = 8.2 Hz, 2 H), 5.64-5.48 (m, 1 H), 4.92 (d, *J* = 21.9 Hz, 1 H), 4.88 (d, *J* = 28.90 Hz, 1H), 4.44-4.32 (m, 1 H), 4.01 (s, 2 H), 2.80-2.60 (m, 2 H), 2.41 (s, 3 H), 2.12-1.96 (m, 1 H), 1.90-1.76 (m, 1 H), 1.37 (d, *J* = 6.4 Hz, 3 H), 1.32-1.16 (m, 1 H), 1.12-0.92 (m, 3 H), 0.80 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 143.44, 136.83, 134.83, 134.57, 129.73, 127.54, 116.32, 64.86, 56.87, 30.57, 29.75, 24.84, 22.37, 21.71, 21.53, 14.09; MS (*m/z*) 335 (M⁺+2, 24.60), 333 (M⁺, 28.46), 319 (100); IR (neat) 1636, 1343, 1162 cm⁻¹; HRMS calcd for C₁₉H₂₇NO₂S 333.1763 Found 333.1721.

7f

3,4-Diallyl-2-phenyl-1-(*p*-toluenesulfonyl)-2,5-dihydro-1*H*-pyrrole (7f): The reaction of **2f** (0.091 g, 0.24 mmol), allyl bromide (0.14 mL, 1.61 mmol) and PdCl₂ (5 mol%) in 2 mL of DMA at 25°C for 5 hours produced 0.086 g (96%) of **7f**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.47 (d, *J* = 8.1 Hz, 2 H), 7.38-7.12 (m, 7 H), 5.85-5.60 (m, 1 H), 5.55-5.43 (m, 1 H), 5.43-5.38 (m, 1 H), 5.12-4.90 (m, 3 H), 4.84-4.73 (m, 1 H), 4.41-4.16 (m, 2 H), 2.87 (d, *J* = 4.4 Hz, 2 H), 2.80 (dd, *J* = 5.4, 15.6 Hz, 1 H), 2.41 (s, 3 H), 2.25 (dd, *J* = 7.8, 15.6 Hz, 1 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 142.86, 140.04, 135.56, 134.04, 133.86, 133.59, 129.88, 129.21, 128.31, 127.73, 127.70, 127.09, 116.59, 116.35, 72.25, 57.01, 30.54, 29.50, 21.39; MS *m/z* (%) 378 (M⁺, 53.25), 338 (100); IR (neat) 2919, 1638, 1594, 1494, 1455, 1347, 1163, 700 cm⁻¹; Anal. calcd for C₂₃H₂₅NO₂S (%): C

72.79, H 6.64, N 3.69. Found: C 72.66, H 6.72, N 3.60.

7g

4-Allyl-2-butyl-3-methyl-1-(*p*-toluenesulfonyl)-2,5-dihydro-1*H*-pyrrole (7g): The reaction of **2g** (0.087 g, 0.30 mmol), allyl bromide (0.14 mL, 1.61 mmol), and PdCl₂ (5 mol%) in 2 mL of DMA at 25°C for 3 hours produced 0.084 g (85%) of **7g**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.57 (d, *J* = 7.5 Hz, 2 H), 7.17 (d, *J* = 8.4 Hz, 2 H), 5.63-5.15 (m, 1 H), 4.78 (d, *J* = 24.0 Hz, 1 H), 4.73 (d, *J* = 30.0 Hz, 1 H), 4.25 (m, 1 H), 3.86 (s, 2 H), 2.57 (d, *J* = 6.0 Hz, 2 H), 2.29 (s, 3 H), 1.92-1.73 (m, 1 H), 1.57-1.41 (m, 1 H), 1.35 (s, 3 H), 1.32-0.87 (m, 4 H), 0.76 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 143.04, 134.77, 134.03, 130.03, 129.43, 127.96, 127.20, 115.81, 70.35, 57.30, 32.56, 30.24, 24.80, 22.64, 21.38, 14.02, 10.68; MS *m/z* (%) 331 (M⁺-2, 53.25), 276 (100); IR (neat) 1598, 1448, 1341, 1161, 674, 581 cm⁻¹; Anal. calcd for C₁₉H₂₇NO₂S (%): C 68.43, H 8.16, N 4.20. Found: C 68.12, H 8.20, N 4.25.

7h

4-Allyl-3-methyl-2-pentyl-1-(*p*-toluenesulfonyl)-2,5-dihydro-1*H*-pyrrole (7h): The reaction of **2h** (0.043 g, 0.14 mmol), allyl bromide (0.07 mL, 0.80 mmol), and PdCl₂ (10 mol%) in 2 mL of DMA at 25°C for 3 hours produced 0.038 g (75%) of **7h**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.62 (d, *J* = 8.4 Hz, 2 H), 7.21 (d, *J* = 8.1 Hz, 2 H), 5.57-5.41 (m, 1 H), 4.91-4.83 (m, 2 H), 4.30 (brs, 1 H), 3.91 (s, 2 H), 2.62 (d, *J* = 6.0 Hz, 2 H), 2.35 (s, 3 H), 1.94-1.78 (m, 1 H), 1.56-1.46 (m, 1 H), 1.46 (s, 3 H), 1.33-0.95 (m, 6 H), 0.80 (t, *J* = 6.3 Hz, 3 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 143.07, 134.98, 134.12, 130.37, 129.50, 128.06, 127.30, 115.90, 70.44, 57.38, 32.86, 31.85, 30.34, 22.64, 22.38, 21.47, 14.06, 10.78; MS *m/z* (%) 346 (M⁺-1, 0.15), 276 (100); IR (neat) 1638, 1598, 1494, 1448, 1342, 1160, 581 cm⁻¹; HRMS *m/z* (EI) calcd for C₂₀H₂₉NO₂S 347.19190. Found

347.19184.

7i

4-Allyl-3-methyl-2-phenyl-1-(*p*-toluenesulfonyl)-2,5-dihydro-1*H*-pyrrole (7i): The reaction of **2i** (0.093 g, 0.30 mmol), allyl bromide (0.14 mL, 1.61 mmol), and PdCl₂ (5 mol%) in 2 mL of DMA at 25°C for 3 hours produced 0.085 g (81%) of **7i**: solid; mp 64–66 °C (*n*-hexane/ether), ¹H NMR (300 MHz, CDCl₃) δ 7.46–7.37 (m, 2 H), 7.29–7.11 (m, 7 H), 5.75–5.60 (m, 1 H), 5.23 (s, 1 H), 5.07–4.94 (m, 2 H), 4.32–4.10 (m, 2 H), 2.82 (d, *J* = 6.3 Hz, 2 H), 2.37 (s, 3 H), 1.34 (s, 3 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 142.80, 140.30, 135.56, 134.04, 131.58, 129.23, 128.27, 128.23, 127.64, 127.50, 127.08, 116.29, 74.08, 56.97, 30.56, 21.38, 10.84; MS *m/z* (%) 353 (M⁺, 7.75), 198 (100); IR (neat) 1343, 1159, 1095, 822, 788, 587 cm⁻¹; Anal. calcd for C₂₁H₂₃SN₂O₂ (%): C 71.35, H 6.56, N 3.96. Found: C 71.34, H 6.48, N 3.75.

7j

4-Allyl-2-benzyl-3-methyl-1-(*p*-toluenesulfonyl)-2,5-dihydro-1*H*-pyrrole (7j): The reaction of **2j** (0.046 g, 0.14 mmol), allyl bromide (0.07 mL, 0.80 mmol), and PdCl₂ (5 mol%) in 2 mL of DMA at 25°C for 2 hours produced 0.051 g (98%) of **7j**: solid; mp 77–80 °C (*n*-hexane/ether), ¹H NMR (300 MHz, CDCl₃) δ 7.71 (d, *J* = 8.4 Hz, 2 H), 7.63–7.41 (m, 7 H), 5.36–5.19 (m, 1 H), 4.75 (dd, *J* = 1.2, 9.9 Hz, 1 H), 4.56 (brs, 1 H), 4.47 (dd, *J* = 1.2, 17.4 Hz, 1 H), 3.76 (d, *J* = 14.1 Hz, 1 H), 3.46 (dd, *J* = 1.8, 14.4 Hz, 1 H), 3.29 (dd, *J* = 5.4, 13.8 Hz, 1 H), 2.96 (dd, *J* = 2.4, 13.8 Hz, 1 H), 2.49 (t, *J* = 5.4 Hz, 2 H), 2.42 (s, 3 H), 1.52 (s, 3 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 143.20, 136.71, 134.85, 133.54, 130.14, 129.59, 19.56, 129.53, 127.74, 127.19, 126.20, 115.63, 71.10, 57.08, 39.55, 30.00, 21.47, 11.32; MS *m/z* (%) 276 (M⁺-Bn, 100); IR (neat) 1337, 1156, 675, 583 cm⁻¹; Anal. calcd for C₂₂H₂₅SN₂O₂ (%): C 71.90, H 6.86, N 3.81. Found: C 71.81,

H 6.77, N 3.59.

7k

4-Allyl-1-(*p*-toluenesulfonyl)-1-azaspiro[4.5]dec-3-ene (7k): The reaction of **2k** (0.081 g, 0.28 mmol), allyl bromide (0.12 ml, 1.38 mmol), and PdCl₂ (5 mol%) in 2 mL of DMA at 25°C for 60 hours; 50 °C for 35 hours; 70 °C for 36 hours produced 0.017 g (18%) of **7k** and recovered 0.039 g (48%) of **2k**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.73 (d, *J* = 8.4 Hz, 2 H), 7.24 (d, *J* = 8.4 Hz, 2 H), 5.90-5.79 (m, 1 H), 5.27 (brs, 1 H), 5.11-5.04 (m, 2 H), 3.95 (d, *J* = 1.5 Hz, 2 H), 2.98 (d, *J* = 8.1 Hz, 2 H), 2.65 (dt, *J* = 5.4, 12.9 Hz, 2 H), 2.40 (s, 3 H), 1.95-1.30 (m, 8 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 148.22, 142.60, 138.74, 134.88, 129.30, 127.04, 117.46, 117.09, 75.37, 53.03, 35.80, 35.42, 24.14, 24.04, 21.43; MS *m/z* (%) 331 (M⁺, 1.86), 91 (100); IR (neat) 2925, 1641, 1598, 1494, 1454, 1332, 1159 cm⁻¹; HRMS *m/z* (EI) calcd for C₁₉H₂₅NO₂S 331.16060. Found 331.16063.

7l

4-Allyl-2-butyl-1-(*p*-toluenesulfonyl)-2,5-dihydro-1H-pyrrole (7l): The reaction of **2l** (0.090 g, 0.34 mmol), allyl bromide (0.14 ml, 1.61 mmol), and PdCl₂ (5 mol%) in 2 mL of DMA at 25°C for 48 hours; 50 °C for 36 hours produced 0.012 g (12%) of **7l**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.69 (d, *J* = 8.1 Hz, 2 H), 7.29 (d, *J* = 7.8 Hz, 2 H), 5.73-5.57 (m, 1 H), 5.24-5.22 (m, 1 H), 5.04-4.91 (m, 2 H), 4.41 (brs, 1 H), 4.06-3.92 (m, 2 H), 2.98-2.82 (m, 2 H), 2.41 (s, 3 H), 1.83-1.64 (m, 2 H), 1.39-1.19 (m, 4 H), 0.88 (t, *J* = 6.9 Hz, 3 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 143.20, 136.75, 134.77, 134.00, 129.56, 127.36, 123.79, 116.94, 67.64, 57.08, 36.02, 32.86, 26.74, 22.71, 21.50, 14.09; MS *m/z* (%) 262 (M⁺-C₄H₉, 100); IR (neat) 3077, 1638, 1598, 1494, 1347, 1162 cm⁻¹; Anal. calcd for C₁₈H₂₅NO₂S (%): C 67.67, H 7.89, N 4.38. Found: C 67.50, H 8.02, N

4.41.

Palladium (II)-catalyzed coupling-cyclization of β -amino allenes 6a-l with allylic halides. Synthesis of 1,2,3,6-tetrahydropyridine products 9

5-Allyl-4-butyl-3-methyl-1-(*p*-nitrobenzenesulfonyl)-1,2,3,6-tetrahydropyridine (9b):

The reaction of **6b** (0.175 g, 0.52 mmol), allyl bromide (0.310 g, 2.56 mmol), and PdCl₂ (5 mol%) in 3 mL of DMA at 25°C for 24 hours produced 0.150 g (77%) of **9b**: solid, mp 97-99°C (hexane); ¹H NMR (300 MHz, CDCl₃) δ 8.37 (d, J = 8.9 Hz, 2 H), 7.96 (d, J = 8.9 Hz, 2 H), 5.75-5.58 (m, 1 H), 5.06-4.94 (m, 2 H), 3.70 (d, J = 15.9 Hz, 1 H), 3.31 (dd, J = 11.0 and 3.7 Hz, 1 H), 3.18 (d, J = 15.9 Hz, 1 H), 2.85-2.62 (m, 3 H), 2.36-2.24 (m, 1 H), 2.23-2.10 (m, 1 H), 1.92-1.88 (m, 1 H), 1.40-1.05 (m, 4 H), 1.11 (d, J = 6.7 Hz, 3 H), 0.86 (t, J = 6.7 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 150.32, 142.59, 136.55, 135.30, 128.96, 124.51, 123.11, 116.26, 49.89, 47.62, 34.86, 32.53, 31.04, 29.98, 23.07, 18.02, 14.20; MS (m/z) 337 (M^+ , 100); IR (neat) 2931, 1635, 1351, 1173 cm⁻¹; Anal. calcd for C₁₉H₂₆N₂O₄S: C, 60.29; H, 6.92; N, 7.40. Found: C, 60.33; H, 6.99; N, 7.48.

5-Allyl-4-butyl-3-methyl-1-acetyl-1,2,3,6-tetrahydropyridine (9c): The reaction of **6c**

(0.100 g, 0.51 mmol), allyl bromide (0.308 g, 2.58 mmol), and PdCl₂ (5 mol%) in 3 mL of DMA at 25°C for 20 hours produced 0.054 g (45%) of **9c**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 5.84-5.66 (m, 1 H), 5.10-4.95 (m, 2 H), 4.28 (d, *J* = 18.3 Hz, 0.61 H), 4.00 (dd, *J* = 12.8 and 3.4 Hz, 0.39 H), 3.82 (d, *J* = 17.0 Hz, 0.39 H), 3.70 (d, *J* = 17.0 Hz, 0.39 H), 3.53 (d, *J* = 18.3 Hz, 0.61 H), 3.48 (dd, *J* = 12.7 and 2.7 Hz, 0.61 H), 3.30 (dd, *J* = 12.7 and 3.8 Hz, 0.61 H), 3.08 (dd, *J* = 12.8 and 3.8 Hz, 0.39 H), 2.85-2.60 (m, 2 H), 2.35-2.15 (m, 2 H), 2.11 (s, 1.83 H), 2.10 (s, 1.17 H), 1.95-1.80 (m, 1 H), 1.48-1.18 (m, 4 H), 1.04 (d, *J* = 6.6 Hz, 1.83 H), 0.99 (d, *J* = 6.9 Hz, 1.17 H), 0.91 (t, *J* = 7.0 Hz, 3 H); MS (*m/z*) 235 (M⁺, 9.82), 152 (100); IR (neat) 2958, 1647, 1452, 1243 cm⁻¹; HRMS calcd for C₁₅H₂₅NO 235.1936. Found 235.1985.

9e

5-Allyl-4-butyl-1-(*p*-toluenesulfonyl)-1,2,3,6-tetrahydropyridine (9e): The reaction of **6e** (0.099 g, 0.34 mmol), allyl bromide (0.212 g, 1.75 mmol), and PdCl₂ (5 mol%) in 2 mL of DMA at 25°C for 5 hours produced 0.086 g (76%) of **9e**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.65 (d, *J* = 7.9 Hz, 2 H), 7.29 (d, *J* = 7.9 Hz, 2 H), 5.72-5.56 (m, 1 H), 5.08-4.94 (m, 2 H), 3.42 (s, 2 H), 3.12 (t, *J* = 5.8 Hz, 2 H), 2.68 (d, *J* = 6.1 Hz, 2 H), 2.40 (s, 3 H), 2.20-2.08 (m, 2 H), 2.04-1.90 (m, 2 H), 1.35-1.12 (m, 4 H), 0.96-0.76 (m, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 143.42, 135.29, 133.30, 130.87, 129.57, 127.70, 123.66, 115.89, 47.35, 43.19, 34.84, 32.08, 30.18, 28.78, 22.65, 21.50, 14.00; MS (*m/z*) 333 (M⁺, 5.65), 292 (100); IR (neat) 1633, 1342, 1166 cm⁻¹; HRMS calcd for C₁₉H₂₇NO₂S 333.1763. Found 333.1792.

9f

5-Allyl-4-(*tert*-butyl)-3-methyl-1-(*p*-toluenesulfonyl)-1,2,3,6-tetrahydropyridine (9f):

The reaction of **6f** (0.155 g, 0.50 mmol), allyl bromide (0.309 g, 2.55 mmol), and PdCl₂ (5 mol%) in 3 mL of DMA at 25°C for 96 hours produced 0.080 g (46%) of **9f** and 0.053 g (34%) of **6f** was recovered. When the reaction was performed at 50-55°C for 48 h, the yield of **9f** was improved to 79%. **9f**: solid, mp 105-107°C (hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.64 (d, *J* = 8.1 Hz, 2 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 5.75-5.60 (m, 1 H), 5.05-4.95 (m, 2 H), 3.78 (d, *J* = 16.4 Hz, 1 H), 3.49 (dd, *J* = 10.4 and 2.1 Hz, 1 H), 3.00 (d, *J* = 16.4 Hz, 1 H), 2.94-2.86 (m, 2 H), 2.56-2.46 (m, 1 H), 2.42 (s, 3 H), 2.37 (dd, *J* = 10.2 and 2.7 Hz, 1 H), 1.17 (d, *J* = 6.6 Hz, 3 H), 1.14 (s, 9 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 143.52, 136.05, 133.34, 129.79, 127.91, 124.37, 116.87, 50.17, 48.29, 37.05, 35.59, 31.84, 31.40, 21.62, 20.57; MS (*m/z*) 347 (*M*⁺, 2.28), 91 (100); IR (neat) 1636, 1344, 1165 cm⁻¹; Anal. calcd for C₂₀H₂₉NO₂S: C, 69.13; H, 8.41; N, 4.03. Found: C, 69.19; H, 8.57; N, 4.00.

9g

5-Allyl-4-(tert-butyl)-1-(p-toluenesulfonyl)-1,2,3,6-tetrahydropyridine (9g): The reaction of **6g** (0.146 g, 0.50 mmol), allyl bromide (0.310 g, 2.56 mmol), and PdCl₂ (5 mol%) in 3 mL of DMA at 25°C for 30 hours produced 0.132 g (79%) of **9g**: solid, mp 98.5-100°C (hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.65 (d, *J* = 8.3 Hz, 2 H), 7.30 (d, *J* = 8.3 Hz, 2 H), 5.80-5.64 (m, 1 H), 5.10-5.00 (m, 2 H), 3.37 (s, 2 H), 3.04 (t, *J* = 6.1 Hz, 2 H), 2.88 (d, *J* = 6.1 Hz, 2 H), 2.42 (s, 3 H), 2.26-2.18 (m, 2 H), 1.08 (s, 9 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 143.68, 137.92, 136.03, 133.13, 129.76, 128.06, 124.58, 116.96, 48.99, 44.07, 36.90, 36.04, 30.66, 27.77, 21.75; MS (*m/z*) 333 (*M*⁺, 1.39), 91 (100); IR (neat) 1639, 1340, 1165 cm⁻¹; Anal. calcd for C₁₉H₂₇NO₂S: C, 68.43; H, 8.16; N, 4.20. Found: C, 68.35; H, 8.11; N, 4.13.

9h

5-Allyl-3-methyl-1-(*p*-toluenesulfonyl)-1,2,3,6-tetrahydropyridine (9h): The reaction of **6h** (0.080 g, 0.29 mmol), allyl bromide (0.14 ml, 1.61 mmol), and PdCl₂ (5 mol%) in 2 mL of DMA at 25°C for 48 hours; 50 °C for 72 hours; 70 °C for 51 hours produced 0.012 g (14%) of **9h** with 0.025 g (31%) of **6h** recovered. **9h**: solid; mp 96-97 °C

(*n*-hexane/ether), ¹H NMR (300 MHz, CDCl₃) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 5.79-5.63 (m, 1 H), 5.35 (brs, 1 H), 5.15-4.98 (m, 2 H), 3.57 (d, *J* = 15.9 Hz, 1 H), 3.46-3.34 (m, 1 H), 3.22 (d, *J* = 15.6 Hz, 1 H), 2.66 (d, *J* = 6.6 Hz, 2 H), 2.48-2.35 (m, 5 H), 0.97 (d, *J* = 6.3 Hz, 3 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 143.41, 135.06, 131.41, 129.61, 127.64, 126.69, 116.95, 94.74, 49.41, 47.01, 38.97, 30.13, 21.52, 18.50; MS *m/z* (%) 291 (M⁺, 16.39), 93 (100); IR (neat) 3437, 1642, 1598, 1344, 1156 cm⁻¹; Anal. calcd for C₁₆H₂₁NO₂ (%): C 65.95, H 7.26, N 4.81. Found: C 65.58, H 7.07, N 4.99.

9i

5-Allyl-3,4-dimethyl-1-(*p*-toluenesulfonyl)-1,2,3,6-tetrahydropyridine (9i): The reaction of **6i** (0.086 g, 0.32 mmol), allyl bromide (0.15 ml, 1.72 mmol), and PdCl₂ (5 mol%) in 2 mL of DMA at 25°C for 4 hours produced 0.074 g (80%) of **9i**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.54 (d, *J* = 8.1 Hz, 2 H), 7.20 (d, *J* = 8.4 Hz, 2 H), 5.69-5.43 (m, 1 H), 4.97-4.81 (m, 2 H), 4.45 (d, *J* = 15.3 Hz, 1 H), 3.11-2.92 (m, 2 H), 2.71 (dd, *J* = 3.6, 11.1 Hz, 1 H), 2.64-2.46 (m, 2 H), 2.30 (s, 3 H), 2.06 (brs, 1 H), 1.50 (s, 3 H), 0.99 (d, *J* = 6.6 Hz, 3 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 143.29, 134.55, 132.93, 131.23, 129.46, 127.60, 123.13, 115.42, 49.44, 47.68, 35.05, 34.88, 21.42, 17.35, 16.37; MS *m/z* (%) 306 (M⁺, 1.96), 264 (100); IR (neat) 2925, 1637, 1460, 1343, 1165 cm⁻¹; Anal. calcd for C₁₇H₂₃NO₂S (%): C 66.85, H 7.59, N 4.59. Found: C 66.59, H 7.81, N 4.32.

9j

4,5-Diallyl-3-methyl-1-(*p*-toluenesulfonyl)-1,2,3,6-tetrahydropyridine (9j): The reaction of **6j** (0.083 g, 0.29 mmol), allyl bromide (0.14 ml, 1.61 mmol), and PdCl₂ (5 mol%) in 2 mL of DMA at 25°C for 17 hours produced 0.092 g (97%) of **9j**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.59 (d, *J* = 8.1 Hz, 2 H), 7.25 (d, *J* = 8.4 Hz, 2 H), 5.71-5.48 (m, 2 H), 5.02-4.84 (m, 4 H), 3.62 (d, *J* = 15.9 Hz, 1 H), 3.20 (dd, *J* = 3.6, 15.1 Hz, 1 H), 3.06 (d, *J* = 15.9, 1 H), 2.85 (dd, *J* = 5.4, 15.3 Hz, 1 H), 2.75-2.47 (m, 4 H), 2.36 (s, 3 H), 2.19 (brs, 1 H), 1.06 (d, *J* = 6.9, 3 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 143.35, 135.59, 134.89, 133.14, 129.54, 127.64, 125.14, 115.90, 115.53, 109.71, 49.61, 47.64, 34.70, 34.42, 32.60, 21.45, 17.60; MS *m/z* (%) 331 (M⁺, 8.60), 290 (100); IR (neat) 2974, 1636, 1344, 1167 cm⁻¹; Anal. calcd for C₁₉H₂₅NO₂S (%): C 68.10, H 7.30, N 4.41. Found: C 68.35, H 7.50, N 4.21.

9k

3-Allyl-1-(*p*-toluenesulfonyl)-1,2,5,6-tetrahydropyridine (9k): The reaction of **6k** (0.054 g, 0.23 mmol), allyl bromide (0.10 ml, 1.15 mmol), and PdCl₂ (5 mol%) in 2 mL of DMA at 25°C for 18 hours, 70 °C for 7 hours produced 0.020 g (32%) of **9k**: liquid, ¹H NMR (300 MHz, CDCl₃) δ 7.68 (d, *J* = 8.4 Hz, 2 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 5.79-5.60 (m, 1 H), 5.53-5.45 (m, 1 H), 5.12-4.97 (m, 2 H), 3.51-3.41 (m, 2 H), 3.13 (t, *J* = 6.0 Hz, 2 H), 2.67 (d, *J* = 6.0 Hz, 2 H), 2.44 (s, 3 H), 2.23-2.15 (m, 2 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 143.44, 135.02, 133.28, 132.31, 129.59, 127.65, 120.07, 116.96, 47.04, 42.62, 39.20, 25.10, 21.52; MS *m/z* (%) 277 (M⁺, 41.68), 236 (100); IR (neat) 2923, 1643, 1597, 1430, 1343, 1161 cm⁻¹; HRMS *m/z* (EI) calcd for C₁₅H₁₉SNO₂ 277.11365. Found 277.11019.

9l

5-Allyl-4-butyl-3-(isopropyl)-1-(*p*-toluenesulfonyl)-1,2,3,6-tetrahydropyridine (9l):

The reaction of **6l** (0.100 g, 0.30 mmol), allyl bromide (0.14 ml, 1.61 mmol), and PdCl₂ (5 mol%) in 2 mL of DMA at 25°C for 4 hours produced 0.074 g (67%) of **9m**: solid; mp 84-86 °C (*n*-hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.65 (d, *J* = 8.4 Hz, 2 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 5.68-5.52 (m, 1 H), 5.02-4.95 (m, 2 H), 3.71 (d, *J* = 15.3 Hz, 1 H), 3.57 (dd, *J* = 2.1, 8.1 Hz, 1 H), 3.01 (d, *J* = 15.6 Hz, 1 H), 2.77 (dd, *J* = 5.4, 15.6 Hz, 1 H), 2.48 (dd, *J* = 6.3, 18.0 Hz, 1 H), 2.43 (dd, *J* = 4.8, 11.7 Hz, 1 H), 2.41 (s, 3 H), 2.20-2.08 (m, 1 H), 2.01 (d, *J* = 8.4 Hz, 1 H), 1.49 (t, *J* = 9.6 Hz, 1 H), 1.54-1.09 (m, 8 H), 0.90 (t, *J* = 6.6 Hz, 3 H), 0.85 (t, *J* = 6.9 Hz, 3 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ = 143.24, 135.58, 135.25, 133.04, 129.46, 127.60, 123.33, 115.65, 47.33, 45.96, 37.56, 34.63, 33.29, 30.88, 29.87, 22.78, 21.43, 20.56, 14.10, 13.91; MS *m/z* (%) 376 (M⁺, 1.02), 334 (100); IR (neat) 1635, 1595, 1463, 1343, 1168 cm⁻¹; Anal. calcd for C₂₂H₃₃SNO₂ (%): C 70.36, H 8.86, N 3.73. Found: C 70.31, H 8.74, N 3.65.

C=C(C)C(S(=O)(=O)N)C1CCCCCCCC1
 TsHN
 $n\text{-C}_8\text{H}_{17}$
 2b
 ry: /export/home/mase/vnmr/sys/data
 122p1
 Solvent: CDCl_3
 Ambient temperature
 File: yf-1-114-1-cur5
 Mercury-300SB "QNP300"
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 0.500 sec
 Width 10007.5 Hz
 32 repetitions
 OBSERVE Cl , 75.4421034 MHz
 DECOUPLE H , 300.0294698 MHz
 Power 36 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 40536
 Total time 95 hr, 5 min, 35 sec

C=C(C)C(S(=O)(=O)N)C1=CC=CC=C1
 TsHN
 Ph
 2b
 1
 /export/home/mase/vnmr/sys/data
 Mercury-300SB "QNP300"
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.500 sec
 Width 10007.5 Hz
 36 repetitions
 OBSERVE Cl , 75.4421045 MHz
 DECOUPLE H , 300.0294698 MHz
 Power 36 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 40536
 Total time 95 hr, 5 min, 35 sec

gw2-12-37-1
Pulse Sequence: zgpg30

CC(C)=CCc1ccc(C)cc1
 61
 :story: /export/home/masm/vnmrsys/data
 :ory:
 1: 62pul
 3
 rature
 1-C
 "HNC300"
 0
 ... 1.000 sec
 Pulse 45.0 degree
 Acq. time 1.815 sec
 Width 10007.0 Hz
 100000 repetitions
 OBSERVE CH1 75.4428558 MHz
 DECOUPLE H1 300.0234658 MHz
 Power 40.00
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total time 138 hr 13 min, 8 sec

Archive directory: /s/
 Sample directory: yf-
 Pulse Sequence: COSY
 Solvent: CDCl₃
 Ambient Temperature
 File: COSY
 Mercury-30000 "QWC300"
 Relax. delay 1.000 sec
 Acq. time 0.213 sec
 Width 4007.7 Hz
 2D Width 4007.7 Hz
 8 repetitions
 128 increments
 OBSERVE: H1, 300.0278985 MHz
 DATA PROCESSING
 Sg. sine bell 0.107 sec
 F1 DATA PROCESSING
 Sg. sine bell 0.027 sec
 F1 size 2048 x 2048
 Total time 25 min, 23 sec

sys/data

Chemical structure of 9a: CC1=CC(C=C1)N(C)C(C=C)C2=CC=CC=C2

¹H NMR spectrum (CDCl₃) of compound 9a. The x-axis represents the chemical shift in ppm, ranging from 0.5 to 7.5. The y-axis represents the integral of the signal.

Integration values (from left to right): 21.65, 24.22, 6.90, 21.24, 9.92, 21.49, 24.33, 15.18, 39.37, 28.63, 12.52, 9.92, 109.37, 48.46.

Peak list (ppm): 7.59754, 7.59771, 7.59781, 7.25777, 7.25793, 7.19775, 6.25466, 6.25482, 6.25497, 6.25512, 6.25527, 6.25542, 6.25557, 6.25572, 6.25587, 6.25602, 6.25617, 6.25632, 6.25647, 6.25662, 6.25677, 6.25692, 6.25707, 6.25722, 6.25737, 6.25752, 6.25767, 6.25782, 6.25797, 6.25812, 6.25827, 6.25842, 6.25857, 6.25872, 6.25887, 6.25902, 6.25917, 6.25932, 6.25947, 6.25962, 6.25977, 6.25992, 6.26007, 6.26022, 6.26037, 6.26052, 6.26067, 6.26082, 6.26097, 6.26112, 6.26127, 6.26142, 6.26157, 6.26172, 6.26187, 6.26202, 6.26217, 6.26232, 6.26247, 6.26262, 6.26277, 6.26292, 6.26307, 6.26322, 6.26337, 6.26352, 6.26367, 6.26382, 6.26397, 6.26412, 6.26427, 6.26442, 6.26457, 6.26472, 6.26487, 6.26502, 6.26517, 6.26532, 6.26547, 6.26562, 6.26577, 6.26592, 6.26607, 6.26622, 6.26637, 6.26652, 6.26667, 6.26682, 6.26697, 6.26712, 6.26727, 6.26742, 6.26757, 6.26772, 6.26787, 6.26802, 6.26817, 6.26832, 6.26847, 6.26862, 6.26877, 6.26892, 6.26907, 6.26922, 6.26937, 6.26952, 6.26967, 6.26982, 6.26997, 6.27012, 6.27027, 6.27042, 6.27057, 6.27072, 6.27087, 6.27102, 6.27117, 6.27132, 6.27147, 6.27162, 6.27177, 6.27192, 6.27207, 6.27222, 6.27237, 6.27252, 6.27267, 6.27282, 6.27297, 6.27312, 6.27327, 6.27342, 6.27357, 6.27372, 6.27387, 6.27402, 6.27417, 6.27432, 6.27447, 6.27462, 6.27477, 6.27492, 6.27507, 6.27522, 6.27537, 6.27552, 6.27567, 6.27582, 6.27597, 6.27612, 6.27627, 6.27642, 6.27657, 6.27672, 6.27687, 6.27702, 6.27717, 6.27732, 6.27747, 6.27762, 6.27777, 6.27792, 6.27807, 6.27822, 6.27837, 6.27852, 6.27867, 6.27882, 6.27897, 6.27912, 6.27927, 6.27942, 6.27957, 6.27972, 6.27987, 6.28002, 6.28017, 6.28032, 6.28047, 6.28062, 6.28077, 6.28092, 6.28107, 6.28122, 6.28137, 6.28152, 6.28167, 6.28182, 6.28197, 6.28212, 6.28227, 6.28242, 6.28257, 6.28272, 6.28287, 6.28302, 6.28317, 6.28332, 6.28347, 6.28362, 6.28377, 6.28392, 6.28407, 6.28422, 6.28437, 6.28452, 6.28467, 6.28482, 6.28497, 6.28512, 6.28527, 6.28542, 6.28557, 6.28572, 6.28587, 6.28602, 6.28617, 6.28632, 6.28647, 6.28662, 6.28677, 6.28692, 6.28707, 6.28722, 6.28737, 6.28752, 6.28767, 6.28782, 6.28797, 6.28812, 6.28827, 6.28842, 6.28857, 6.28872, 6.28887, 6.28902, 6.28917, 6.28932, 6.28947, 6.28962, 6.28977, 6.28992, 6.29007, 6.29022, 6.29037, 6.29052, 6.29067, 6.29082, 6.29097, 6.29112, 6.29127, 6.29142, 6.29157, 6.29172, 6.29187, 6.29202, 6.29217, 6.29232, 6.29247, 6.29262, 6.29277, 6.29292, 6.29307, 6.29322, 6.29337, 6.29352, 6.29367, 6.29382, 6.29397, 6.29412, 6.29427, 6.29442, 6.29457, 6.29472, 6.29487, 6.29502, 6.29517, 6.29532, 6.29547, 6.29562, 6.29577, 6.29592, 6.29607, 6.29622, 6.29637, 6.29652, 6.29667, 6.29682, 6.29697, 6.29712, 6.29727, 6.29742, 6.29757, 6.29772, 6.29787, 6.29802, 6.29817, 6.29832, 6.29847, 6.29862, 6.29877, 6.29892, 6.29907, 6.29922, 6.29937, 6.29952, 6.29967, 6.29982, 6.29997, 6.30012, 6.30027, 6.30042, 6.30057, 6.30072, 6.30087, 6.30102, 6.30117, 6.30132, 6.30147, 6.30162, 6.30177, 6.30192, 6.30207, 6.30222, 6.30237, 6.30252, 6.30267, 6.30282, 6.30297, 6.30312, 6.30327, 6.30342, 6.30357, 6.30372, 6.30387, 6.30402, 6.30417, 6.30432, 6.30447, 6.30462, 6.30477, 6.30492, 6.30507, 6.30522, 6.30537, 6.30552, 6.30567, 6.30582, 6.30597, 6.30612, 6.30627, 6.30642, 6.30657, 6.30672, 6.30687, 6.30702, 6.30717, 6.30732, 6.30747, 6.30762, 6.30777, 6.30792, 6.30807, 6.30822, 6.30837, 6.30852, 6.30867, 6.30882, 6.30897, 6.30912, 6.30927, 6.30942, 6.30957, 6.30972, 6.30987, 6.31002, 6.31017, 6.31032, 6.31047, 6.31062, 6.31077, 6.31092, 6.31107, 6.31122, 6.31137, 6.31152, 6.31167, 6.31182, 6.31197, 6.31212, 6.31227, 6.31242, 6.31257, 6.31272, 6.31287, 6.31302, 6.31317, 6.31332, 6.31347, 6.31362, 6.31377, 6.31392, 6.31407, 6.31422, 6.31437, 6.31452, 6.31467, 6.31482, 6.31497, 6.31512, 6.31527, 6.31542, 6.31557, 6.31572, 6.31587, 6.31602, 6.31617, 6.31632, 6.31647, 6.31662, 6.31677, 6.31692, 6.31707, 6.31722, 6

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Fig. 1. ORTEP representation of **7i**

Fig. 2. ORTEP representation of **9b**