Supporting Information

Allylic-type Diindium Reagents. Reactivity toward Electrophiles and Cascade

Coupling Reactions with Imines

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General. 1H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded on a Varian MERCURY spectrometer in $CDCl_3$ solutions containing tetramethylsilane as an internal standard.

***N*-(1-Phenylbut-3-enyl)benzeneamide (3a).**¹

***N*-(1-Phenylbut-3-enyl)benzenesulfonamide (3b).**²

(Z)-N-(1-Phenylpent-3-enyl)benzenesulfonamide (3c): colorless crystals, mp 80 - 81 °C (CH₂Cl₂-hexane); IR (KBr, cm⁻¹) 3265, 1448, 1314, 1160, 1092, 1056; ¹H NMR (200 MHz, CDCl₃) δ 7.70-7.66 (m, 2H), 7.49-7.02 (m, 8 H), 5.54 (dqt, *J* = 10.9, 6.8, 1.6 Hz, 1 H), 5.30-4.96 (m, 2 H), 4.37 (q, *J* = 6.9 Hz, 1 H), 2.60-2.36 (m, 2 H), 1.50 (d, *J* = 6.8 Hz, 3 H); ¹³C NMR (50 MHz, CDCl₃) δ 140.5, 140.3, 132.2, 128.6, 128.3, 127.9, 127.3, 127.0, 126.5, 124.5, 57.77, 34.87, 12.84; Anal. Calcd for C₁₇H₁₉NO₂S: C, 67.74; H, 6.35; N, 4.65. Found: C, 67.58; H, 6.43; N, 4.55.

N-(1-Phenyl-2-methylbut-3-enyl)benzenesulfonamide (4).³

1-Phenylbut-3-en-1-ol (5a).⁴

2-Methyl-1-phenylbut-3-en-1-ol (5b).⁵

N-(1,4-Diphenylbut-3-enyl)benzeneamide (6a): IR (neat, cm⁻¹) 3410, 1598, 1500, 1314; ¹H NMR (200 MHz, CDCl₃) δ 7.43-7.20 (m, 10 H), 7.07 (t, *J* = 7.3 Hz, 2 H), 6.64 (t, *J* = 7.3 Hz, 1 H), 6.57-6.48 (m, 3 H), 6.14 (dt, *J* = 16.4, 7.0 Hz, 1 H), 4.38 (dd, *J* = 7.8, 6.0 Hz, 1 H), 4.21 (br s, 1 H), 2.58-2.72 (m, 2 H); Anal. Calcd for C₂₂H₂₁N: C, 88.25; H, 7.07; N, 4.68. Found: C, 88.48; H, 7.28; N, 4.45.

N-(1,4-Diphenylbut-3-enyl)benzenesulfonamide (6b): colorless crystals, mp 62-63 °C; IR (neat, cm⁻¹) 3265, 1444, 1320, 1158; ¹H NMR (200 MHz, CDCl₃) δ 7.70-7.63 (m, 2 H), 7.49-7.01 (m, 13 H), 6.39 (d, *J* = 15.8 Hz, 1 H), 5.84 (dt, *J* = 15.8, 7.4 Hz, 1 H), 4.67 (d, *J* = 6.6 Hz, 1 H), 4.48 (q, *J* = 6.6 Hz, 1 H), 2.62 (dd, *J* = 7.4, 6.6 Hz, 2 H); ¹³C NMR (50 MHz, CDCl₃) δ 140.0, 136.4, 133.9, 132.1, 128.5, 128.3, 127.3, 126.8, 126.3, 126.0, 124.1, 57.61, 41.31; Anal. Calcd for C₂₂H₂₁NO₂S: C, 72.69; H, 5.82; N, 3.85. Found: C, 72.59; H, 5.71; N, 3.83.

***N*-(1-Phenylhept-3,6-dienyl)benzenesulfonamide (6c)**: IR (neat, cm^{-1}) 3290, 1446, 1324, 1162, 1094; ^1H NMR (200 MHz, CDCl_3) δ 7.70-7.63 (m, 2 H), 7.52-7.03 (m, 8 H), 5.82-5.63 (m, 1 H), 5.48 (dt, $J = 15.3, 6.4$ Hz, 1 H), 5.13 (dt, $J = 15.3, 7.0$ Hz, 1 H), 5.06-4.90 (m, 2 H), 4.85 (d, $J = 6.3$ Hz, 1 H), 4.36 (br q, $J = 6.5$ Hz, 1 H), 2.68 (t, $J = 6.4$ Hz, 2 H), 2.41 (t, $J = 7.0$ Hz, 2 H); Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_2\text{S}$: C, 69.69; H, 6.46; N, 4.28. Found: C, 69.79; H, 6.77; N, 4.58.

***N*-(3*E*,5*E*-1,6-Diphenylhexa-3,5-dienyl)benzenesulfonamide (6d)**: colorless crystals, mp 129-130 °C (CH_2Cl_2 -hexane); IR (neat, cm^{-1}) 3260, 1444, 1314, 1152; ^1H NMR (200 MHz, CDCl_3) δ 7.70-7.64 (m, 2 H), 7.52-7.04 (m, 13 H), 6.59 (dd, $J = 15.5, 9.7$ Hz, 1 H), 6.44 (d, $J = 15.5$ Hz, 1 H), 6.19 (dd, $J = 15.2, 9.7$ Hz, 1 H), 5.42 (dt, $J = 15.2, 7.5$ Hz, 1 H), 4.85 (d, $J = 6.5$ Hz, 1 H), 4.45 (br q, $J = 6.8$ Hz, 1 H), 2.56 (br t, $J = 7.2$ Hz, 2 H); ^{13}C NMR (50 MHz, CDCl_3) δ 140.5, 140.2, 137.1, 134.3, 132.2, 131.7, 128.7, 128.5, 128.4, 127.4, 127.1, 126.5, 126.2, 57.73, 40.89; Anal. Calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_2\text{S}$: C, 74.00; H, 5.95; N, 3.60. Found: C, 73.53; H, 5.98; N, 3.66.

***N*-(1-*n*-Butyl-4-phenylbut-3-enyl)-*p*-toluenesulfonamide (6e)**: colorless crystals, mp 72-73 °C (CH_2Cl_2 -hexane); IR (neat, cm^{-1}) 3300, 2875, 1324, 1162; ^1H NMR (200 MHz, CDCl_3) δ 7.77-7.72 (m, 2 H), 7.33-7.18 (m, 7 H), 6.27 (d, $J = 15.8$ Hz, 1 H), 5.87 (dt, $J = 15.8, 7.4$ Hz, 1 H), 4.35 (d, $J = 5.1$ Hz, 1 H), 3.39-3.29 (m, 1 H), 2.41 (s, 3 H), 2.32-2.21 (m, 2 H), 1.50-1.38 (m, 2 H), 1.29-1.12 (m, 4 H), 0.86-0.78 (m, 3 H); ^{13}C NMR (50 MHz, CDCl_3) δ 142.8, 137.8, 136.7, 133.2, 129.3, 128.2, 127.1, 126.8, 125.9, 124.8, 53.82, 38.50, 34.85, 27.70, 22.54, 21.65, 14.11; Anal. Calcd for $\text{C}_{21}\text{H}_{27}\text{NO}_2\text{S}$: C, 70.54; H, 7.61; N, 3.92. Found: C, 70.60; H, 7.74; N, 3.88.

***N*-(1-*i*-Propyl-4-phenylbut-3-enyl)-*p*-toluenesulfonamide (6f):** colorless crystals, mp 122-124 °C (CH₂Cl₂-hexane); IR (neat, cm⁻¹) 3280, 1598, 1410, 1314, 1154; ¹H NMR (200 MHz, CDCl₃) δ 7.72-7.69 (m, 2 H), 7.33-7.14 (m, 7 H), 6.25 (d, *J* = 15.6 Hz, 1 H), 5.77 (dt, *J* = 15.6, 7.2 Hz, 1 H), 4.32 (d, *J* = 7.4 Hz 1 H), 3.21-3.10 (m, 1 H), 2.37 (s, 3 H), 2.28-2.17 (m, 2 H), 1.93-1.84 (m, 1 H), 0.88 (dd, *J* = 6.8, 1.7 Hz, 6 H); Anal. Calcd for C₂₀H₂₅NO₂S: C, 69.93; H, 7.34; N, 4.08. Found: C, 69.52; H, 7.45; N, 4.04.

***N*-(1,4-Diphenylbut-3-enyl)benzenesulfonamide (6g):** colorless crystals, mp 115 - 116 °C (CH₂Cl₂-hexane); IR (KBr, cm⁻¹) 3340, 1496, 1324, 1158; ¹H NMR (200 MHz, CDCl₃) δ 7.70-7.66 (m, 2 H), 7.46-7.08 (m, 13 H), 5.47 (t, *J* = 7.4 Hz, 1 H), 5.09 (br s, 1 H), 4.45 (q, *J* = 7.0 Hz, 1 H), 2.63 (m, 2 H), 1.90 (s, 3 H); ¹³C NMR (50 MHz, CDCl₃) δ 143.1, 140.5, 140.4, 138.2, 132.1, 128.6, 128.3, 128.0, 127.3, 126.9, 126.8, 126.4, 125.6, 122.3, 58.17, 36.85, 15.9; Anal. Calcd for C₂₃H₂₃NO₂S: C, 73.17; H, 6.14; N, 3.71. Found: C, 73.15; H, 6.20; N, 3.60.

***N*-(3*E*,5*E*-1,6-Diphenylhexa-3,5-dienyl)benzenesulfonamide (6h):** colorless crystals, mp 148 - 150 °C (CH₂Cl₂-hexane); IR (KBr, cm⁻¹) 3280, 1484, 1308, 1148; ¹H NMR (200 MHz, CDCl₃) δ 7.74-7.66 (m, 2 H), 7.52-7.00 (m, 13 H), 6.62 (d, *J* = 16.3 Hz, 1 H), 6.44 (d, *J* = 16.3 Hz, 1 H), 5.31 (t, *J* = 7.5 Hz, 1 H), 4.92 (d, *J* = 6.9 Hz, 1 H), 4.44 (q, *J* = 6.9 Hz, 1 H), 2.68-2.62 (m, 2 H), 1.76 (s, 3 H); ¹³C NMR (50 MHz, CDCl₃) δ 140.5, 140.3, 137.5, 137.1, 133.1, 132.3, 128.8, 128.6, 128.4, 127.5, 127.2, 127.1, 127.0, 127.0, 126.5, 126.3, 58.93, 36.52, 15.56; Anal. Calcd for C₂₅H₂₅NO₂S: C, 74.41; H, 6.24; N, 3.47. Found: C, 73.91; H, 6.18; N, 3.50.

1-Phenylpent-3-en-1-ol (7).⁵

1,5-Diphenyl-2-methylpent-2-en-1,5-diol (8a): IR(neat, cm^{-1}) 3475, 2910, 1494, 1448, 1016; ^1H NMR (200 MHz, CDCl_3) δ 7.40 – 7.22 (m, 10 H), 5.70 (t, $J = 7.3$ Hz, 1 H), 5.09 (s, 1 H), 4.78 (t, $J = 6.5$ Hz, 1 H), 2.61 – 2.50 (m, 2 H), 2.18 (br s, 2 H), 1.44 (s, 3 H); ^{13}C NMR (50 MHz, CDCl_3) δ 144.03, 142.09, 140.0, 128.4, 128.29, 127.56, 127.37, 126.29, 121.67, 79.00, 74.02, 37.4, 25.86, 12.48; Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_2$ C: 80.56, H: 7.51 found C: 79.96, H: 7.56.

1,3-Diphenyl-2-methyl-2-vinylpropan-1,3-diol (8b): colorless needles, mp 142-143 $^{\circ}\text{C}$ (CH_2Cl_2 – hexane); IR (KBr, cm^{-1}) 3325, 2890, 1496, 1450, 1042, 920; ^1H NMR (200 MHz, CDCl_3) δ 7.31 - 7.26 (m, 10 H), 6.61 (dd, $J = 17.8, 11.1$ Hz, 1 H), 5.36 (d, $J = 11.1$ Hz, 1 H), 4.87 (s, 2 H), 4.73 (d, $J = 7.1$ Hz, 1 H), 2.8 (br s, 2 H), 0.56 (s, 3 H, Me); ^{13}C NMR (50 MHz, CDCl_3) δ 140.63, 136.95, 128.13, 127.65, 127.45, 118.48, 80.49, 49.91, 16.18; Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_2$ C: 80.56, H: 7.51 found C: 80.17, H: 7.50.

2-Methyl-2-phenyl-but-3-enal (9).⁶

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