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Base-catalyzed α-vinylation of ketones with acetylenes as a key step in one-pot synthesis of pyrazolines and pyrazoles

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5-Benzyl-3-[1,1'-biphenyl]-4-yl-1-ethyl-4,5-dihydro-1H-pyrazole **6b** with admixture of pyrazoles **7b** and **8b**: yield: 1.037 g, 61%; pale-yellow oil. IR (film, ν/cm^{-1}): 3027, 2971, 2932, 2850, 1680, 1602, 1572, 1487, 1448, 1407, 1369, 1281, 1160, 1126, 1076, 1005, 837, 767, 725, 698. ^{1}H NMR for **6b**, δ: 7.89-7.24 (m, 14H$_{Ar}$), 3.62-3.60 (m, 1H, H^{5}), 3.32-3.30, 3.02-3.00 (m, 2H, N-CH_2), 3.22 (dd, 1H, CH_2-Ph, ^{2}J 13.7 Hz, ^{3}J 4.9 Hz), 3.06 (dd, 1H, H^{4}, ^{2}J 16.2 Hz, ^{3}J 9.5 Hz), 2.91 (dd, 1H, CH_2-Ph, ^{2}J 13.7 Hz, ^{3}J 9.3 Hz), 2.78 (dd, 1H, H^{4}, ^{2}J 16.2 Hz, ^{3}J 13.0 Hz), 1.39 (t, 3H, Me, ^{3}J 7.1 Hz). ^{13}C NMR for **6b**, δ: 150.3 (C^{3}), 141.9-125.9 (18C$_{Ar}$), 67.5 (C^{5}), 48.1 (N-*C*H$_2$), 39.6 (*C*H$_2$-Ph), 38.9 (C^{4}), 12.8 (Me). ^{15}N NMR for **6b**, δ: -228.5 (N1), -35.5 (N2). ^{1}H NMR for **7b**, δ: 7.89-7.24 (m, 14H$_{Ar}$), 6.36 (s, 1H, H^{4}), 4.11 (q, 2H, N-CH_2, ^{3}J 7.2 Hz), 4.07 (s, 2H, CH_2-Ph), 1.38 (t, 3H, Me, ^{3}J 7.2 Hz). ^{13}C NMR for **7b**, δ: 149.9 (C^{3}), 141.9-125.9 (18C$_{Ar}$), 141.1 (C^{5}), 103.5 (C^{4}), 44.4 (N-*C*H$_2$), 32.0 (*C*H$_2$-Ph), 15.6 (Me). ^{15}N NMR for **7b**, δ: -169.6 (N1), -85.2 (N2). ^{1}H NMR for **8b**, δ: 7.89-7.24 (m, 14H$_{Ar}$), 6.06 (s, 1H, H^{4}), 4.24 (q, 2H, N-CH_2, ^{3}J 7.2 Hz), 4.07 (s, 2H, CH_2-Ph), 1.48 (t, 3H, Me, ^{3}J 7.2 Hz). ^{13}C NMR for **8b**, δ: 151.6 (C^{3}), 144.2 (C^{5}), 141.9-125.9 (18C$_{Ar}$), 105.4 (C^{4}), 44.5 (N-*C*H$_2$), 35.0 (*C*H$_2$-Ph), 16.1 (Me). ^{15}N NMR for **8b**, δ: -174.1 (N1). -82.9 (N2).

5-Benzyl-1-ethyl-3-(2-naphthyl)-4,5-dihydro-1H-pyrazole **6c** with admixture of pyrazoles **7c** and **8c**: yield: 1.02 g, 65%; yellow oil. IR (film, ν/cm^{-1}): 3060, 3027, 2972, 2934, 2850, 1677, 1601, 1551, 1496, 1454, 1374, 1285, 1164, 1128, 1083, 1031, 969, 932, 858, 821, 748, 701, 476. ^{1}H NMR for **6c**, δ: 7.97-7.24 (m, 12H$_{Ar}$), 3.65-3.56 (m, 1H, H^{5}), 3.32-3.29, 3.04-2.99 (m, 2H, N-CH_2), 3.29 (dd, 1H, CH_2-Ph, ^{2}J 13.6 Hz, ^{3}J 4.8 Hz), 3.11 (dd, 1H, H^{4}, ^{2}J 16.3 Hz, ^{3}J 9.4 Hz), 2.90 (dd, 1H, CH_2-Ph, ^{2}J 13.6 Hz, ^{3}J 9.4 Hz,), 2.80 (dd, 1H, H^{4}, ^{2}J 16.3 Hz, ^{3}J 13.0 Hz), 1.36 (t, 3H, Me, ^{3}J 7.1 Hz). ^{13}C NMR for **6c**, δ: 153.3 (C^{3}), 138.9-123.6 (16C$_{Ar}$), 66.5 (C^{5}), 48.7 (N-*C*H$_2$), 39.7 (*C*H$_2$-Ph), 38.6 (C^{4}), 12.8 (Me). ^{1}H NMR for **7c**, δ: 7.97-7.24 (m, 12H$_{Ar}$), 6.40 (s, 1H, H^{4}), 4.09 (q, 2H, N-CH_2, ^{3}J 7.2 Hz), 4.03 (s, 2H, CH_2-Ph), 1.36 (t, 3H, Me, ^{3}J 7.2 Hz). ^{13}C NMR for

7c, *δ*: 150.1 (C^3), 138.9-123.6 ($16C_{Ar}$), 141.9 (C^5), 105.5 (C^4), 44.1 (N-*C*H_2), 34.9 (*C*H_2-Ph), 15.5 (Me). ^{1}H NMR for **8c**, *δ*: 7.97-7.24 (m, $12H_{Ar}$), 6.08 (s, 1H, H^4), 4.18 (q, 2H, N-C*H*$_2$, ^3J 7.2 Hz), 4.03 (s, 2H, C*H*$_2$-Ph), 1.41 (t, 3H, Me, ^3J 7.2 Hz). ^{13}C NMR for **8c**, *δ*: 151.3 (C^3), 140.7 (C^5), 138.9-123.6 ($16C_{Ar}$), 105.7 (C^4), 45.5 (N-*C*H_2), 35.6 (*C*H_2-Ph), 16.3 (Me).

1,5-Dibenzyl-3-phenyl-4,5-dihydro-1H-pyrazole **6d** with admixture of pyrazoles **7d** and **8d**: yield: 1.42 g, 87%; yellow oil. IR (film, ν/cm^{-1}): 3086, 3062, 3029, 2929, 2851, 1955, 1681, 1604, 1583, 1546, 1496, 1486, 1454, 1399, 1361, 1121, 1075, 1030, 985, 926, 782, 759, 728, 699. ^{1}H NMR for **6d**, *δ*: 7.60-7.03 (m, $15H_{Ar}$), 4.50 (d, 1H, N-C*H*$_2$, ^2J 14.3 Hz), 4.25 (d, 1H, N-C*H*$_2$, ^2J 14.3 Hz), 3.56-3.47 (m, 1H, H^5), 3.11 (dd, 1H, C*H*$_2$-Ph, ^2J 13.7 Hz, ^3J 4.8 Hz), 2.94 (dd, 1H, H^4, ^2J 16.0 Hz, ^3J 9.8 Hz), 2.79 (dd, 1H, H^4, ^2J 16.0 Hz, ^3J 13.7 Hz,), 2.69 (dd, 1H, C*H*$_2$-Ph, ^2J 13.7 Hz, ^3J 9.3 Hz). ^{13}C NMR for **6d**, *δ*: 149.7 (C^3), 139.2-125.6 ($18C_{Ar}$), 66.3 (C^5), 57.6 (N-*C*H_2), 43.1 (C^4), 38.8 (*C*H_2-Ph). ^{1}H NMR for **7d**, *δ*: 7.58-7.14 (m, $15H_{Ar}$), 6.34 (s, 1H, H^4), 5.34 (s, 2H, N-C*H*$_2$), 4.03 (s, 2H, C*H*$_2$-Ph). ^{13}C NMR for **7d**, *δ*: 151.7 (C^3), 144.0 (C^5), 139.2-125.6 ($18C_{Ar}$), 106.3 (C^4), 53.1 (N-*C*H_2), 34.8 (*C*H_2-Ph). ^{1}H NMR for **8d**, *δ*: 7.58-7.14 (m, $15H_{Ar}$), 6.07 (s, 1H, H^4), 5.32 (s, 2H, N-C*H*$_2$), 3.86 (s, 2H, C*H*$_2$-Ph). ^{13}C NMR for **8d**, *δ*: 149.8 (C^3), 144.0 (C^5), 139.2-125.6 ($18C_{Ar}$), 105.6 (C^4), 52.8 (N-*C*H_2), 31.9 (*C*H_2-Ph).

1,5-Dibenzyl-3-[1,1'-biphenyl]-4-yl-4,5-dihydro-1H-pyrazole **6e** with admixture of pyrazoles **7e** and **8e**: yield: 1.59 g, 79%; yellow oil. ^{1}H NMR for **6e**, *δ*: 7.55-6.97 (m, $19H_{Ar}$), 4.43 (d, 1H, N-C*H*$_2$, ^2J 14.3 Hz), 4.17 (d, 1H, N-C*H*$_2$, ^2J 14.3 Hz), 3.51-3.47 (m, 1H, H^5), 2.97 (dd, 1H, C*H*$_2$-Ph, ^2J 13.3 Hz, ^3J 4.6 Hz), 2.85 (dd, 1H, H^4, ^2J 16.1 Hz, ^3J 10.0 Hz), 2.69 (dd, 1H, H^4, ^2J 16.1 Hz, ^3J = 13.0 Hz), 2.61 (dd, 1H, C*H*$_2$-Ph, ^2J 13.3 Hz, ^3J 9.3 Hz). ^{13}C NMR for **6e**, *δ*: 149.4 (C^3), 141.3-126.1 ($24C_{Ar}$), 66.3 (C^5), 53.1 (N-*C*H_2), 39.6 (C^4), 38.8 (*C*H_2-Ph). ^{1}H NMR for **7e**, *δ*: 7.55-6.97 (m, $19H_{Ar}$), 6.28 (s, 1H, H4), 5.28 (s, 2H, N-C*H*$_2$), 3.96 (s, 2H, C*H*$_2$-Ph). ^{13}C NMR for **7e**, *δ*: 151.7 (C^3), 144.0 (C^5), 141.3-126.1 ($24C_{Ar}$), 106.4 (C^4), 52.9 (N-*C*H_2), 34.8 (*C*H_2-Ph). ^{1}H NMR for **8e**, *δ*: 7.55-6.97 (m, $19H_{Ar}$), 6.02 (s, 1H, H^4), 5.25 (s, 2H, N-C*H*$_2$), 4.30 (s, 2H, C*H*$_2$-Ph). ^{13}C NMR for **8e**, *δ*: 151.7 (C^3), 143.2 (C^5), 141.3-126.1 ($24C_{Ar}$), 104.7 (C^4), 51.6 (N-*C*H_2), 29.7 (*C*H_2-Ph).