

SUPPORTING INFORMATION

Palladium Functionalized Phosphinite Polyethyleneimine grafted Magnetic Silica Nanoparticles as an Efficient Catalyst for the Synthesis of Isoquinolino[1,2-*b*]quinazolin-8-ones

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Spectral data of 3-allyl-2-(2-bromophenyl)-2,3-dihydroquinazolin-4(1H)-one derivatives

5-methyl-8H-isoquinolino[1,2-b]quinazolin-8-one (4a)

Yield: 83%; white crystals; mp 143-145 °C; IR (KBr): ν = 1676, 1590 cm^{-1} ; ^1H NMR (DMSO- d_6 , 500 MHz): δ = 2.00 (3H, d, J = 1.5 Hz), 7.28-7.31 (3H, m), 7.35-7.38 (2H, m), 7.48-7.50 (1H, m), 7.69 (1H, q, J = 8.5 Hz), 7.82 (1H, d, J = 8.5 Hz), 8.01 (1H, s) ppm; ^{13}C NMR (DMSO- d_6 , 125 MHz): δ = 23.1, 112.6, 117.3, 117.4, 121.6, 125.3, 127.1, 128.3, 129.4, 130.8, 132.5, 133.2, 138.0, 138.3, 146.5, 156.7, 161.0 ppm; Anal. Calcd for $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}$: C: 78.44, H: 4.65, N: 10.76, O: 6.15, Found: C: 78.28, H: 4.81, N: 10.89, O: 6.02; MS (70 eV): m/z = 261 (M^+).

5-methyl-2-nitro-8H-isoquinolino[1,2-b]quinazolin-8-one (4b)

Yield: 87%; white crystals; mp 154-156°C; IR (KBr): ν = 1671, 1597 cm^{-1} ; ^1H NMR (DMSO- d_6 , 500 MHz): δ = 1.92 (3H, s), 6.82 (1H, s), 6.87 (1H, d, J = 8 Hz), 7.00 (1H, d, J = 7 Hz), 7.10-7.12 (1H, m), 7.15-7.20 (2H, m), 7.68 (1H, d, J = 1.5 Hz), 8.13 (1H, d, J = 7 Hz) ppm; ^{13}C NMR (DMSO- d_6 , 125 MHz): δ = 21.6, 114.4, 115.6, 116.6, 116.9, 118.7, 121.9, 126.0, 126.2, 127.3, 129.3, 133.0, 133.3, 139.2, 146.5, 154.5, 162.3 ppm; Anal. Calcd for $\text{C}_{17}\text{H}_{11}\text{N}_3\text{O}_3$: C: 66.88, H: 3.63, N: 13.76, O: 15.72, Found: C: 67.12, H: 3.47, N: 13.57, O: 15.93; MS (70 eV): m/z = 305 (M^+).

10-chloro-5-methyl-2-nitro-8H-isoquinolino[1,2-b]quinazolin-8-one (4c)

Yield: 85%; white crystals; mp 157-159 °C; IR (KBr): ν = 1601, 1583, 1527 cm^{-1} ; ^1H NMR (DMSO- d_6 , 500 MHz): δ = 1.99 (3H, s), 7.22 (1H, s), 7.35 (1H, d, J = 8 Hz), 7.51 (1H, s), 7.65 (1H, d, J = 8 Hz), 7.97 (1H, d, J = 8 Hz), 8.33 (1H, d, J = 8 Hz), 8.54 (1H, s) ppm; ^{13}C NMR (DMSO- d_6 , 125 MHz): δ = 18.3, 119.5, 121.9, 126.2, 127.0, 127.8, 128.1, 128.3, 128.4, 129.6, 129.7, 134.8, 136.3, 137.4, 145.9, 146.5, 160.3 ppm; Anal. Calcd for $\text{C}_{17}\text{H}_{10}\text{ClN}_3\text{O}_3$: C: 60.10, H: 2.97, N: 12.37, O: 14.13, Found: C: 60.24, H: 2.75, N: 12.22, O: 14.35; MS (70 eV): m/z = 339 (M^+).

10-chloro-5-methyl-8H-isoquinolino[1,2-b]quinazolin-8-one (4d)

Yield: 78%; white crystals; mp 149-151 °C; IR (KBr): ν = 1676, 1594 cm^{-1} ; ^1H NMR (DMSO- d_6 , 500 MHz): δ = 1.93 (3H, s), 6.99 (1H, d, J = 9 Hz), 7.04 (1H, s), 7.29-7.36 (2H, m), 7.47 (1H, d, J = 7 Hz), 7.51 (1H, d, J = 9 Hz), 7.66-7.68 (2H, m), 8.16 (1H, s) ppm; ^{13}C

NMR (DMSO- d_6 , 125 MHz): δ = 19.2, 107.7, 113.5, 117.3, 117.5, 127.2, 128.4, 129.4, 132.6, 133.3, 136.3, 138.0, 139.2, 143.2, 145.5, 157.1, 166.8 ppm; Anal. Calcd for $C_{17}H_{11}ClN_2O$: C: 69.28, H: 3.76, N: 9.59, O: 5.43, Found: C: 69.54, H: 3.58, N: 9.81, O: 5.13; MS (70 eV): m/z = 294 (M^+).

5-methyl-2-nitro-8H-pyrido[2',3':4,5]pyrimido[2,1-a]isoquinolin-8-one (4e)

Yield: 81%; white crystals; mp 177-179 °C; IR (KBr): ν = 1685, 1582 cm^{-1} ; 1H NMR (DMSO- d_6 , 500 MHz): δ = 1.99 (3H, s), 7.95 (1H, s), 8.13-8.19 (2H, m), 8.31-8.42 (2H, m), 7.58 (1H, t, J = 6 Hz), 8.92 (1H, s) ppm; ^{13}C NMR (DMSO- d_6 , 125 MHz): δ = 20.3, 127.4, 128.1, 128.9, 130.2, 130.4, 130.5, 131.0, 131.1, 132.7, 134.7, 135.1, 137.6, 146.7, 153.5, 161.3 ppm; Anal. Calcd for $C_{16}H_{10}N_4O_3$: C: 62.74, H: 3.29, N: 18.29, O: 15.67, Found: C: 62.97, H: 3.44, N: 18.04, O: 15.53; MS (70 eV): m/z = 306 (M^+).

5-methyl-8H-pyrido[2',3':4,5]pyrimido[2,1-a]isoquinolin-8-one (4f)

Yield: 75%; white crystals; mp 155-158 °C; IR (KBr): ν = 1676, 1606 cm^{-1} ; 1H NMR (DMSO- d_6 , 500 MHz): δ = 2.51 (3H, s), 6.98 (1H, d, J = 8 Hz), 7.26-7.28 (2H, m), 7.50 (1H, s), 7.60 (1H, t, J = 8 Hz), 7.71 (1H, d, J = 8 Hz), 7.88 (1H, t, J = 8 Hz), 8.21 (1H, d, J = 8 Hz) ppm; ^{13}C NMR (DMSO- d_6 , 125 MHz): δ = 20.9, 117.4, 118.8, 120.3, 126.4, 127.3, 128.2, 128.3, 129.8, 131.8, 133.7, 134.6, 134.7, 135.5, 146.8, 154.9, 161.3 ppm; Anal. Calcd for $C_{16}H_{11}N_3O$: C: 73.55, H: 4.24, N: 16.08, O: 6.12, Found: C: 73.14, H: 4.55, N: 16.27, O: 5.92; MS (70 eV): m/z = 261 (M^+).

5-methyl-2-nitro-8H-benzo[g]isoquinolino[1,2-b]quinazolin-8-one (4g)

Yield: 84%; white crystals; mp 187-189 °C; IR (KBr): ν = 1679, 1590 cm^{-1} ; 1H NMR (DMSO- d_6 , 500 MHz): δ = 2.00 (3H, d, 1.2 Hz), 7.26 (1H, t, J = 8.5 Hz), 7.32 (1H, t, 8.5 Hz), 7.56 (1H, d, 6 Hz), 7.66 (1H, s), 7.76 (1H, d, J = 8.5 Hz), 7.80 (1H, d, J = 8.5 Hz), 7.89 (1H, d, J = 6 Hz), 8.01 (1H, d, J = 8.5 Hz), 8.11 (1H, s), 8.42 (1H, s), 8.73 (1H, s) ppm; ^{13}C NMR (DMSO- d_6 , 125 MHz): δ = 45.6, 115.1, 115.9, 116.3, 116.5, 117.3, 118.2, 118.4, 119.7, 122.3, 123.4, 125.3, 127.3, 129.0, 129.4, 141.1, 142.6, 149.7, 150.5, 160.2 ppm; Anal. Calcd for $C_{21}H_{13}N_3O_3$: C: 70.98, H: 3.69, N: 11.83, O: 13.51, Found: C: 70.32, H: 3.45, N: 12.01, O: 13.23; MS (70 eV): m/z = 355 (M^+).

5-methyl-8H-benzo[g]isoquinolino[1,2-b]quinazolin-8-one (4h)

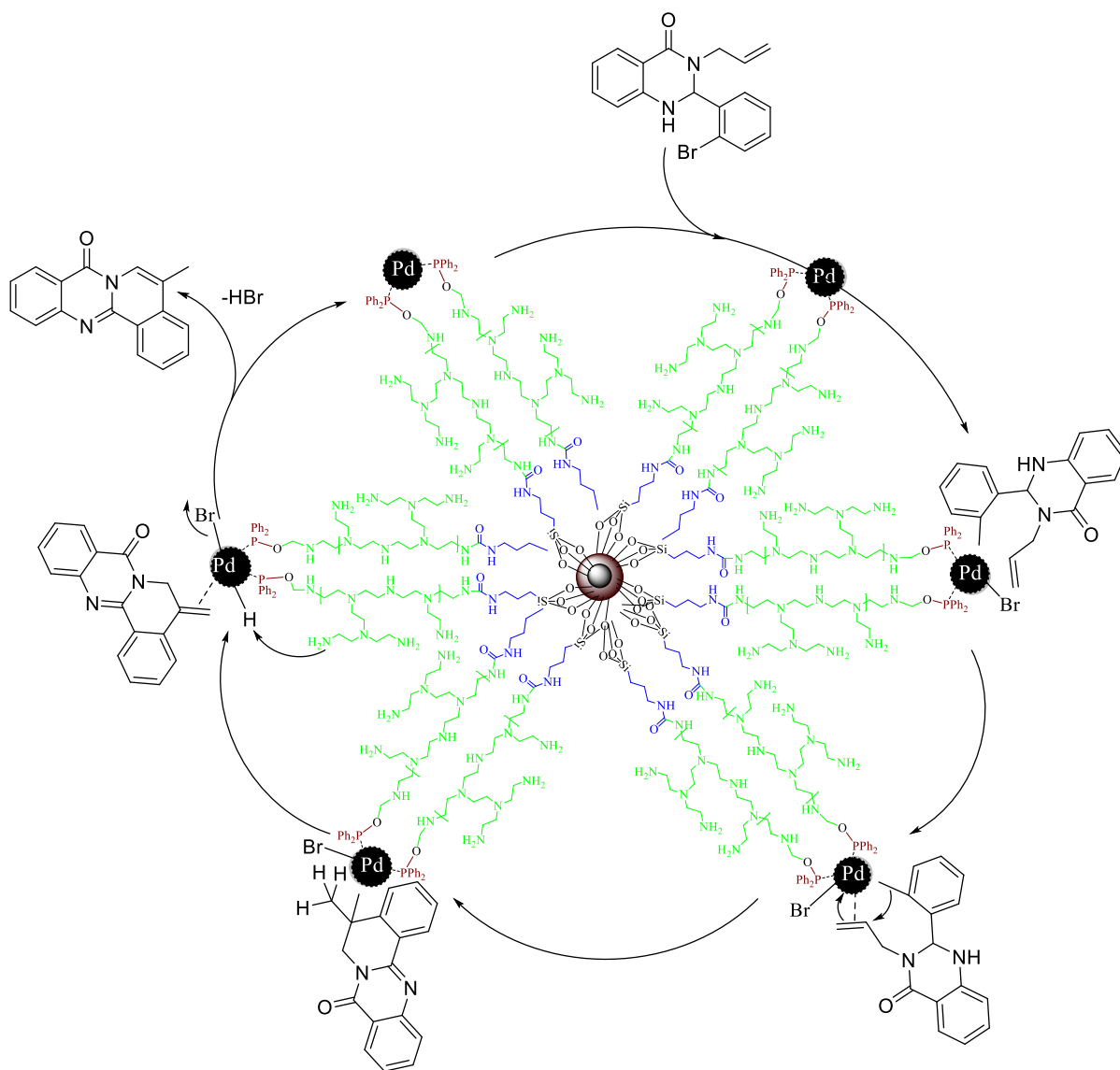
Yield: 80%; white crystals; mp 179-181 °C; IR (KBr): ν = 1675, 1588 cm^{-1} ; ^1H NMR (DMSO- d_6 , 500 MHz): δ = 2.02 (3H, d, J = 1 Hz), 7.14-7.22 (2H, m), 7.32-7.37 (2H, m), 7.41-7.49 (2H, m), 7.60-7.69 (2H, m), 7.91 (1H, d, J = 7 Hz), 8.27 (1H, s), 8.24 (1H, s) ppm; ^{13}C NMR (DMSO- d_6 , 125 MHz): δ = 15.8, 109.1, 117.5, 120.1, 120.4, 121.5, 123.7, 124.8, 125.2, 126.8, 128.1, 128.9, 129.6, 130.7, 132.9, 136.4, 136.8, 143.5, 147.1, 153.7, 162.5 ppm; Anal. Calcd for $\text{C}_{21}\text{H}_{14}\text{N}_2\text{O}$: C: 81.27, H: 4.55, N: 9.03, O: 5.16, Found: C: 81.55, H: 4.77, N: 9.52, O: 5.95; MS (70 eV): m/z = 310 (M^+).

11-chloro-5-methyl-8*H*-isoquinolino[1,2-*b*]quinazolin-8-one (4i)

Yield: 76%; white crystals; mp 153-155 °C; IR (KBr): ν = 1673, 1561 cm^{-1} ; ^1H NMR (DMSO- d_6 , 500 MHz): δ = 1.99 (3H, s), 6.72 (1H, d, J = 8 Hz), 7.00 (1H, s), 7.21-7.35 (3H, m), 7.39 (1H, d, J = 7 Hz), 7.68 (1H, d, J = 8 Hz), 8.04 (1H, s) ppm; ^{13}C NMR (DMSO- d_6 , 125 MHz): δ = 23.1, 112.9, 117.3, 117.5, 122.0, 127.6, 128.9, 129.9, 131.2, 135.1, 135.6, 139.8, 140.1, 149.7, 150.0, 158.5, 161.4 ppm; Anal. Calcd for $\text{C}_{17}\text{H}_{11}\text{ClN}_2\text{O}$: C: 69.28, H: 3.76, N: 9.50, O: 5.43, Found: C: 69.14, H: 3.95, N: 9.77, O: 5.70; MS (70 eV): m/z = 294 (M^+).

Suggested mechanism

For understanding the role of the catalyst in this step, a possible mechanism was proposed, which is presented in Scheme S1. Initially, 3-allyl-2-(2-bromophenyl)-2,3-dihydroquinazolin-4(1*H*)-one attaches to palladium by C-Br bond. Then, double bond of allyl group coordinated to the palladium, followed by intramolecular cyclization reaction between phenyl and allyl group, which finally converts to 5-methylene-5,6-dihydro-8*H*-isoquinolino[1,2-*b*]quinazolin-8-one via a β -hydride elimination. In this step, cyclization reaction occurs such that, a 6 membered ring is formed, while the formation of 6 membered ring is more favourable. The final 5-methyl-8*H*-isoquinolino[1,2-*b*]quinazolin-8-one product obtains by a hydrogen shift. The hydrogen shift is a desired transformation, due to the aromaticity of the product. The catalyst is free at the end of the reaction cycle and can start another cycle. The suggested mechanism is shown in Scheme S1.



Scheme S1. Proposed mechanism for Pd@Ph₂PO-PEI-mSiO₂ catalyzed synthesis of 5-methyl-13,13a-dihydro-8H-isoquinolino[1,2-*b*]quinazolin-8-one derivatives

