



SUPPLEMENTARY MATERIAL TO  
**Phospho sulfonic acid: a novel and efficient solid acid catalyst  
for the one-pot preparation of indazolo[1,2-*b*]-  
phthalazine-triones**

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*2,3,4,13-Tetrahydro-3,3-dimethyl-13-phenyl-1H-indazolo[1,2-*b*]phthalazine-1,6,11-trione (4a)*. Yellow powder; IR (KBr,  $\text{cm}^{-1}$ ): 2959, 1662, 1576;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 7.33–8.37 (9H, *m*, Ar-H), 6.47 (1H, *s*, CHN), 3.26 and 3.44 (2H, AB system,  $J = 18.6$  Hz,  $\text{CH}_a\text{H}_b\text{CO}$ ), 2.35 (2H, *s*,  $\text{CH}_2\text{C}$ ), 1.23 (6H, *s*, 2Me);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 28.5, 28.7, 34.7, 38.1, 50.9, 64.9, 118.6, 127.1, 127.7, 127.9, 128.7, 128.9, 129.1, 133.6, 134.5, 136.4, 150.9, 154.3, 156.1, 192.2.

*2,3,4,13-Tetrahydro-3,3-dimethyl-13-(4-nitrophenyl)-1H-indazolo[1,2-*b*]phthalazine-1,6,11-trione (4b)*. Yellow powder; IR (KBr,  $\text{cm}^{-1}$ ): 2923, 1695, 1659, 1615;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 7.61–8.41 (8H, *m*, Ar-H), 6.52 (1H, *s*, CHN), 3.26 and 3.43 (2H, AB system,  $J = 19.2$  Hz,  $\text{CH}_a\text{H}_b\text{CO}$ ), 2.33 and 2.38 (2H, AB system,  $J = 16.5$  Hz,  $\text{CH}_a\text{H}_b\text{C}$ ), 1.23 (3H, *s*, Me), 1.21 (3H, *s*, Me);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 28.4, 28.7, 34.7, 38.0, 50.8, 64.2, 117.3, 124.1, 127.8, 128.1, 128.3, 128.6, 128.9, 133.9, 134.9, 143.4, 147.9, 151.7, 154.6, 155.9, 192.1.

*2,3,4,13-Tetrahydro-3,3-dimethyl-13-(3-nitrophenyl)-1H-indazolo[1,2-*b*]phthalazine-1,6,11-trione (4c)*. Yellow powder; IR (KBr,  $\text{cm}^{-1}$ ): 2926, 1660, 1625;  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ,  $\delta$  / ppm): 7.60–8.37 (8H, *m*, Ar-H), 6.46 (1H, *s*, CHN), 3.23 (2H, *br s*,  $\text{CH}_2\text{CO}$ ), 2.27 (2H, *s*,  $\text{CH}_2\text{C}$ ), 1.12 (6H, *s*, 2Me);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ ,  $\delta$  / ppm): 28.3, 28.9, 34.6, 38.2, 51.5, 64.2, 116.9, 127.3, 127.3, 128.4, 128.7, 129.2, 129.8, 131.5, 132.7, 133.1, 133.6, 134.5, 135.5, 151.8, 154.4, 156.4, 192.2.

*13-(2-Chlorophenyl)-2,3,4,13-tetrahydro-3,3-dimethyl-1H-indazolo[1,2-*b*]phthalazine-1,6,11-trione (4d)*. Yellow powder; IR (KBr,  $\text{cm}^{-1}$ ): 2956, 1663,

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1625;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 7.25–8.40 (8H, *m*, Ar-H), 6.69 (1H, *s*, CHN), 3.24 and 3.42 (2H, AB system,  $J = 19.1$  Hz,  $\text{CH}_a\text{H}_b\text{CO}$ ), 2.33 (2H, *s*,  $\text{CH}_2\text{C}$ ), 1.23 (3H, *s*, Me), 1.22 (3H, *s*, Me);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 28.4, 28.8, 34.6, 38.0, 50.9, 64.0, 116.7, 127.2, 127.6, 128.0, 128.7, 129.0, 129.9, 130.5, 132.6, 133.0, 133.6, 134.5, 151.9, 154.2, 156.2, 192.1.

*2,3,4,13-Tetrahydro-3,3-dimethyl-13-(4-methylphenyl)-1H-indazolo[1,2-b]phthalazine-1,6,11-trione (4e)*. Yellow powder; IR (KBr,  $\text{cm}^{-1}$ ) 2956, 1663, 1621;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 7.12–8.38 (8H, *m*, Ar-H), 6.43 (1H, *s*, CHN), 3.24 and 3.43 (2H, AB system,  $J = 18.5$  Hz,  $\text{CH}_a\text{H}_b\text{CO}$ ), 2.35 (2H, *s*,  $\text{CH}_2\text{C}$ ), 2.30 (3H, *s*,  $\text{CH}_3$ ), 1.23 (6H, *s*, 2Me);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 21.3, 28.5, 28.8, 34.7, 38.1, 50.9, 64.9, 118.7, 127.1, 127.7, 127.9, 128.9, 129.2, 129.5, 133.4, 133.5, 134.5, 138.5, 150.8, 154.2, 156.1, 192.2.

*13-(4-Chloro-2,3,4,13-Tetrahydro-3,3-dimethyl-1H-indazolo[1,2-b]phthalazine-1,6,11-trione (4f)*. Yellow powder; IR (KBr,  $\text{cm}^{-1}$ ): 2957, 1656, 1623;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 7.31–8.39 (8H, *m*, Ar-H), 6.43 (1H, *s*, CHN), 3.25 and 3.43 (2H, AB system,  $J = 19.1$  Hz,  $\text{CH}_a\text{H}_b\text{CO}$ ), 2.35 (2H, *s*,  $\text{CH}_2\text{C}$ ), 1.23 (3H, *s*, Me), 1.22 (3H, *s*, Me);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 28.5, 28.7, 34.7, 38.0, 50.9, 64.3, 118.1, 127.7, 128.1, 128.5, 128.8, 128.9, 129.0, 133.7, 134.5, 134.6, 134.9, 151.1, 154.3, 156.0, 192.2.

*2,3,4,13-Tetrahydro-3,3-dimethyl-13-(4-methoxyphenyl)-1H-indazolo[1,2-b]phthalazine-1,6,11-trione (4g)*. Yellow powder; IR (KBr,  $\text{cm}^{-1}$ ) 2959, 1655, 1626;  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 8.25–8.35 (2H, *m*, Ar-H), 7.82–7.85 (2H, *m*, Ar-H), 6.84–7.35 (4H, *m*, Ar-H), 6.42 (1H, *s*, CHN), 3.76 (3H, *s*, OMe), 3.23 and 3.42 (2H, AB system,  $J = 19.2$  Hz,  $\text{CH}_a\text{H}_b\text{CO}$ ), 2.34 (2H, *s*,  $\text{CH}_2\text{C}$ ), 1.21 (*s*, 6H, 2Me);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 28.51, 28.71, 34.65, 38.07, 50.99, 55.21, 64.59, 114.14, 118.58, 127.71, 127.93, 128.36, 128.51, 128.98, 129.18, 133.47, 134.47, 150.75, 154.28, 156.07, 159.74, 192.23.

*13-(2,4-Dichlorophenyl)-2,3,4,13-tetrahydro-1H-indazolo[1,2-b]phthalazine-1,6,11-trione (4h)*. Yellow powder; IR (KBr,  $\text{cm}^{-1}$ ): 2964, 1660, 1628;  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 8.37 (1H, *dd*,  $J = 3.3, 5.6$  Hz, Ar-H), 8.27 (1H, *dd*,  $J = 3.2, 5.4$  Hz, Ar-H), 7.26–7.88 (5H, *m*, Ar-H), 6.64 (1H, *s*, CHN), 3.40 (1H, *d*,  $J = 19.1$  Hz,  $\text{CH}_a\text{H}_b\text{CO}$ ), 3.24 (1H, *d*,  $J = 19.2$  Hz,  $\text{CH}_a\text{H}_b\text{CO}$ ), 2.34 (2H, *s*,  $\text{CH}_2\text{C}$ ), 1.22 (3H, *s*, Me), 1.21 (3H, *s*, Me);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 28.4, 28.8, 34.6, 38.0, 50.8, 63.6, 127.6, 127.7, 128.1, 128.6, 129.0, 130.4, 131.8, 133.3, 133.7, 134.6, 135.1, 152.1, 154.3, 156.1, 192.1.

*2,3,4,13-Tetrahydro-3,3-dimethyl-13-[3-(trifluoromethyl)phenyl]-1H-indazolo[1,2-b]phthalazine-1,6,11-trione (4i)*. Yellow powder; IR (KBr,  $\text{cm}^{-1}$ ) 1635, 1616;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm) 8.36–8.39 (1H, *m*, Ar-H), 8.25–8.28 (1H, *m*, Ar-H), 7.85–7.89 (2H, *m*, Ar-H), 7.68 (1H, *d*,  $J = 8.0$  Hz, Ar-H), 7.60 (1H, *s*, Ar-H), 7.55 (1H, *d*,  $J = 8.0$  Hz, Ar-H), 7.48 (1H, *t*,  $J = 8.0$  Hz, Ar-H), 6.49 (1H, *s*, CHN), 3.24 and 3.43 (AB system,  $J = 19.0$  Hz, 2H,  $\text{CH}_a\text{H}_b\text{CO}$ ), 2.34 (2H,

*s*, CH<sub>2</sub>C), 1.22 (3H, *s*, Me), 1.21 (*s*, 3H, Me); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, δ / ppm) 28.3, 28.8, 34.7, 38.1, 50.9, 64.3, 117.1, 123.5, 123.6 (*q*, *J* = 3.7 Hz), 125.6 (*q*, *J* = 3.6 Hz), 126.5 (*q*, *J* = 270.8 Hz), 127.8, 128.2, 128.9, 129.0, 129.2, 131.1, 131.2 (*q*, *J* = 37.5 Hz), 133.8, 134.7, 137.5, 151.4, 154.6, 156.1, 192.1.

*2,3,4,13-Tetrahydro-3,3-dimethyl-13-(3-methylphenyl)-1H-indazolo[1,2-b]-phthalazine-1,6,11-trione (4j)*. Yellow powder; IR (KBr, cm<sup>-1</sup>) 1639, 1616; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ / ppm): 8.34–8.37 (1H, *m*, Ar-H), 8.26–8.30 (1H, *m*, Ar-H), 7.83–7.87 (2H, *m*, Ar-H), 7.18–7.23 (3H, *m*, Ar-H), 7.08 (1H, *d*, *J* = 7.5 Hz, Ar-H), 6.40 (1H, *s*, CHN), 3.23 and 3.41 (AB system, *J* = 19.0 Hz, 2H, CH<sub>a</sub>H<sub>b</sub>CO), 2.33 (2H, *s*, CH<sub>2</sub>C), 2.32 (3H, *s*, Ar-Me), 1.21 (3H, *s*, Me), 1.20 (3H, *s*, Me); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, δ / ppm): 21.5, 28.5, 28.6, 34.9, 38.1, 51.0, 65.0, 118.8, 124.1, 127.7, 127.9, 128.0, 128.6, 129.0, 129.2, 129.6, 133.4, 134.4, 136.3, 138.3, 150.7, 154.2, 156.1, 192.1

*13-(Trifluoromethyl)-2,3,4,13-tetrahydro-1H-indazolo[1,2-b]phthalazine-1,6,11-trione (4k)*. Yellow powder; IR (KBr, cm<sup>-1</sup>) 2972, 2958, 1695, 1660; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ / ppm): 8.27–8.40 (2H, *m*, Ar-H), 7.88–7.90 (2H, *m*, Ar-H), 7.5–7.6 (4H, *m*, Ar-H), 6.50 (1H, *s*, CHN), 3.33–3.61 (2H, *m*, CH<sub>2</sub>CO), 2.47–2.50 (2H, *m*, CH<sub>2</sub>), 2.25–2.27 (2H, *m*, CH<sub>2</sub>); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, δ / ppm) 22.25, 24.53, 36.85, 64.46, 118.94, 122.54, 125.73, 125.80, 127.53, 127.79, 128.16, 128.80, 128.932, 133.83, 134.74, 140.27, 152.77, 154.44, 156.03, 192.48.