

Nano-silica supported acidic ionic liquid as an efficient catalyst for the multi-component synthesis of indazolophthalazine-triones

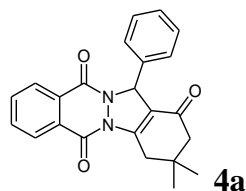
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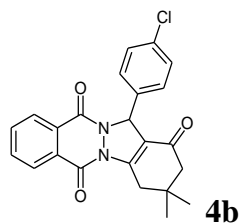
Spectroscopic data of the products	S2-S9
References	S9

Spectroscopic data of the products



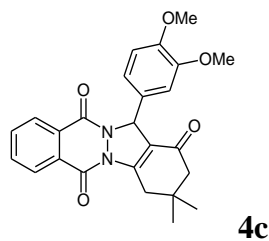
3,4-Dihydro-3,3-dimethyl-13-phenyl-2H-indazolo[1,2-*b*]phthalazine-1,6,11(13H)-trione (**4a**)^{1,2,3}

Mp. 205 °C. IR (KBr): ν_{\max} = 2958, 1661, 1575, 1362, 696 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 1.23 (s, 6H), 2.35 (s, 2H), 3.35 (AB system, J = 18.8 Hz, 2H), 6.46 (s, 1H), 7.30-7.44 (m, 5H), 7.86-8.36 (m, 4H).



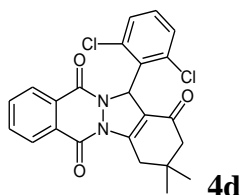
13-(4-Chlorophenyl)-3,4-dihydro-3,3-dimethyl-2H-indazolo[1,2-*b*]phthalazine-1,6,11(13H)-trione (**4b**)^{1,2,3}

Mp. 263 °C. IR (KBr): ν_{\max} = 3027, 2952, 1662, 1362, 696 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 1.22 (s, 3H), 1.23 (s, 3H), 2.36 (d, 2H), 3.35 (AB system, J = 17.2 Hz, 2H), 6.43 (s, 1H), 7.32 (d, J = 8.8 Hz, 2H), 7.38 (d, J = 8.8 Hz, 2H), 7.87-7.89 (m, 2H), 8.28-8.39 (m, 2H).



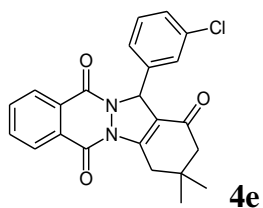
13-(3,4-Dimethoxyphenyl)-3,4-dihydro-3,3-dimethyl-2H-indazolo[1,2-*b*]phthalazine-1,6,11(13*H*)-trione (4c)²

Mp. 234 °C. IR (KBr): ν_{\max} = 3018, 2982, 1661, 1492, 787 cm^{-1} . ¹H NMR (400 MHz, CDCl₃): δ = 1.23 (s, 3H), 1.25 (s, 3H), 2.36 (s, 2H), 3.35 (AB system, J = 17.2 Hz, 2H), 6.43 (s, 1H), 6.82 (d, J = 8.2 Hz, 1H), 6.94 (dd, 1J = 8 Hz, 2J = 2.2 Hz, 1H), 7.01 (d, J = 2.4 Hz, 1H), 7.86-7.89 (m, 2H), 8.29-8.36 (m, 2H).



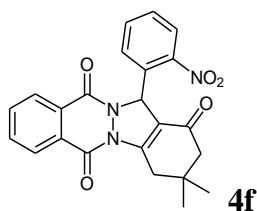
13-(2,6-Dichlorophenyl)-3,4-dihydro-3,3-dimethyl-2H-indazolo[1,2-*b*]phthalazine-1,6,11(13*H*)-trione (4d)

Mp. 266 °C. IR (KBr): ν_{\max} = 3071, 2964, 1663, 1360, 703 cm^{-1} . ¹H NMR (400 MHz, CDCl₃): δ = 1.24 (s, 6H), 2.35 (AB system, J = 16.0 Hz, 2H), 3.38 (AB system, J = 17.2 Hz, 2H), 7.18 (s, 1H), 7.19 (d, J = 2.4 Hz, 1H), 7.46-7.48 (m, 2H), 7.86-7.89 (m, 2H), 8.25-8.40 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 28.56, 28.81, 34.57, 38.05, 50.85, 61.45, 114.96, 127.65, 128.09, 128.42, 129.05, 129.13, 129.42, 129.77, 129.89, 133.07, 133.64, 134.57, 137.50, 152.93, 154.12, 156.35, 192.09. MS: m/z = 440.02 ([M+4]⁺, 14.41), 442.02 ([M+2]⁺, 70.98), 440.03 ([M]⁺, 81.96), 294.98 (100), 103.62 (100), 77.04 (90.20). Anal. Calcd for C₂₃H₁₈Cl₂N₂O₃ (441.31): C, 62.60; H, 4.11; N, 6.35. Found: C, 62.59; H, 4.13; N, 6.33.



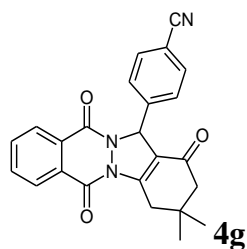
13-(3-Chlorophenyl)-3,4-dihydro-3,3-dimethyl-2H-indazolo[1,2-*b*]phthalazine-1,6,11(13*H*)-trione
(4e)

Mp. 190 °C. IR (KBr): ν_{\max} = 3019, 2960, 1659, 1355, 786 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 1.22 (s, 3H), 1.23 (s, 3H), 2.36 (s, 2H), 3.30 (AB system, J = 17.2 Hz, 2H), 6.42 (s, 1H), 7.29-7.40 (m, 3H), 7.88-7.91 (m, 2H), 8.28-8.38 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 28.53, 28.62, 34.71, 38.03, 50.92, 64.33, 117.97, 125.83, 126.94, 127.79, 128.11, 128.96, 129.97, 130.45, 132.22, 133.72, 133.80, 134.65, 139.04, 152.10, 154.44, 192.09. MS: m/z = 406.70 ($[\text{M}]^+$, 34.67), 295.07 (66.94), 103.80 (100), 77.83 (91.29). Anal. Calcd for $\text{C}_{23}\text{H}_{19}\text{ClN}_2\text{O}_3$ (406.86): C, 67.90; H, 4.71; N, 6.89. Found: C, 67.89; H, 4.75; N, 6.90.



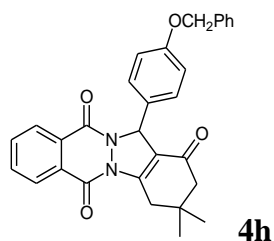
13-(2-Nitrophenyl)-3,4-dihydro-3,3-dimethyl-2H-indazolo[1,2-*b*]phthalazine-1,6,11(13*H*)-trione
(4f)

Mp. 236 °C. IR (KBr): ν_{\max} = 3074, 2959, 1664, 1526, 700 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 1.21 (s, 3H), 1.23 (s, 3H), 2.35 (AB system, J = 16.0 Hz, 2H), 3.34 (m, 2H), 6.45 (s, 1H), 7.34-7.59 (m, 3H), 7.87-7.96 (m, 3H), 8.26-8.39 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 28.52, 28.63, 34.67, 37.70, 50.77, 60.64, 118.40, 125.17, 127.79, 128.18, 128.61, 128.99, 129.49, 133.11, 133.88, 134.67, 136.04, 149.23, 152.01, 154.41, 155.98, 191.92. MS: m/z = 417.05 ($[\text{M}]^+$, 9.22), 295.07 (52.94), 103.99 (100), 77.07 (95.29). Anal. Calcd for $\text{C}_{23}\text{H}_{19}\text{N}_3\text{O}_5$ (417.41): C, 66.18; H, 4.59; N, 10.07. Found: C, 66.19; H, 4.63; N, 10.00.



13-(4-Cyanophenyl)-3,4-dihydro-3,3-dimethyl-2H-indazolo[1,2-*b*]phthalazine-1,6,11(13H)-trione (4g)

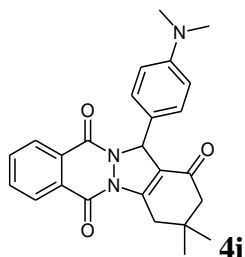
Mp. 206 °C. IR (KBr): ν_{\max} = 3040, 2958, 2229, 1655, 1364, 699 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 1.20 (s, 3H), 1.23 (s, 3H), 2.35 (AB system, J = 16.4 Hz, 2H), 3.34 (AB system, J = 17.2 Hz, 2H), 6.47 (s, 1H), 7.56 (dd, 1J = 7.2 Hz, 2J = 1.4 Hz, 2H), 7.65 (dd, 1J = 7.4 Hz, 2J = 2.4 Hz, 2H), 7.90 (dd, 1J = 6.0 Hz, 2J = 3.2 Hz, 2H), 8.26-8.40 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 28.43, 28.68, 34.75, 38.04, 50.82, 64.42, 112.54, 117.40, 118.44, 127.80, 127.89, 128.23, 128.66, 128.94, 129.07, 132.04, 133.95, 134.83, 141.56, 151.61, 154.55, 155.97, 192.10. MS: m/z = 399.07 ($[\text{M}+2]^+$, 1.92), 397.07 ($[\text{M}]^+$, 39.92), 295.07 (90.32), 104.03 (97.98), 76.06 (100). Anal. Calcd for $\text{C}_{24}\text{H}_{19}\text{N}_3\text{O}_3$ (397.43): C, 72.53; H, 4.82; N, 10.57. Found: C, 72.50; H, 4.84; N, 10.55.



13-(4-(Benzyloxy)phenyl)-3,4-dihydro-3,3-dimethyl-2H-indazolo[1,2-*b*]phthalazine-1,6,11(13H)-trione (4h)

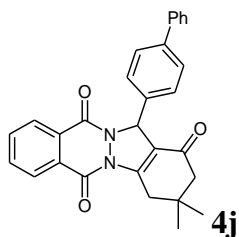
Mp. 221 °C. IR (KBr): ν_{\max} = 3074, 2959, 1664, 1526, 700 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 1.23 (s, 3H), 1.24 (s, 3H), 2.36 (s, 2H), 3.30 (AB system, J = 16.8 Hz, 2H), 5.02 (s, 2H), 6.44 (s, 1H), 6.95 (d, J = 8.4 Hz, 2H), 7.32-7.42 (m, 6H), 7.85-7.87 (m, 2H), 8.28-8.37 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 28.43, 28.61, 34.56, 37.95, 50.90, 60.42, 69.90, 114.84, 118.33, 125.50, 127.42, 127.53,

127.92, 128.50, 128.66, 128.90, 129.04, 132.34, 133.47, 134.44, 136.70, 150.79, 154.20, 158.91, 192.18. MS: m/z = 480.20 ($[M]^+$, 10.78), 478.19 ($[M]^+$, 72.94), 295.12 (83.92), 162.09 (80.00), 104.04 (96.47), 90.74 (100), 76.07 (96.86). Anal. Calcd for $C_{30}H_{26}N_2O_4$ (478.54): C, 75.30; H, 5.48; N, 5.85. Found: C, 75.29; H, 5.50; N, 5.80.



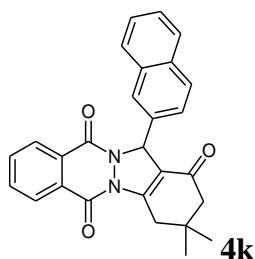
13-(4-(Dimethylamino)phenyl)-3,4-dihydro-3,3-dimethyl-2H-indazolo[1,2-*b*]phthalazine-1,6,11(13H)-trione (4i)

Mp. 215 °C. IR (KBr): ν_{max} = 3019, 2958, 1661, 1493, 789 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$): δ = 1.02 (s, 3H), 1.12 (s, 3H), 2.22 (AB system, J = 16.2 Hz, 2H), 2.48 (AB system, J = 18.0 Hz, 2H), 4.72 (s, 1H), 7.08 (d, J = 8.4 Hz, 2H), 7.30-7.32 (m, 2H), 7.54-8.04 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.55, 29.18, 31.27, 32.25, 40.83, 44.15, 50.74, 115.33, 116.15, 116.33, 116.58, 122.62, 124.45, 129.80, 132.45, 135.11, 140.04, 144.79, 162.43, 196.62. MS: m/z = 400.25 ($[M]^+$, 9.67), 273.14 (44.34), 103.97 (100), 76.01 (94.54). Anal. Calcd for $C_{25}H_{25}N_3O_3$ (415.48): C, 72.27; H, 6.06; N, 10.11. Found: C, 72.20; H, 6.09; N, 10.15.



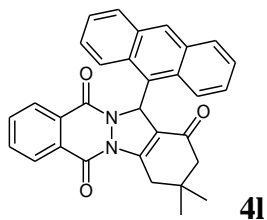
13-(Biphenyl-4-yl)-3,4-dihydro-3,3-dimethyl-2H-indazolo[1,2-*b*]phthalazine-1,6,11(13H)-trione (4j)

Mp. 258 °C. IR (KBr): $\nu_{\max} = 3023, 2956, 1666, 1363, 699 \text{ cm}^{-1}$. ^1H NMR (400 MHz, CDCl_3): $\delta = 1.24$ (s, 3H), 1.25 (s, 3H), 2.38 (s, 2H), 3.32 (AB system, $J = 18.8 \text{ Hz}$, 2H), 6.52 (s, 1H), 7.33-7.58 (m, 8H), 7.86-7.89 (m, 2H), 8.30-8.40 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 28.42, 28.65, 34.63, 37.99, 50.91, 64.64, 118.32, 127.05, 127.32, 127.42, 128.54, 127.61, 128.66, 128.95, 128.97, 133.57, 134.52, 135.36, 140.51, 141.42, 151.01, 154.32, 155.97, 192.20$. MS: $m/z = 448.14$ ($[\text{M}]^+$, 15), 295.04 (95.33), 152.05 (73.65), 103.97 (100), 76.02 (100). Anal. Calcd for $\text{C}_{29}\text{H}_{24}\text{N}_2\text{O}_3$ (448.51): C, 77.66; H, 5.39; N, 6.25. Found: C, 77.65; H, 5.40; N, 6.30.



3,4-Dihydro-3,3-dimethyl-13-(naphthalen-2-yl)-2H-indazolo[1,2-*b*]phthalazine-1,6,11(13H)-trione
(4k)^{2,3}

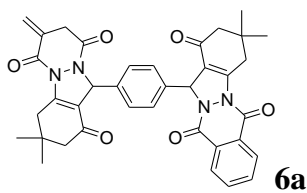
Mp. 252 °C. IR (KBr): $\nu_{\max} = 3055, 2953, 1665, 1361, 696 \text{ cm}^{-1}$. ^1H NMR (400 MHz, CDCl_3): $\delta = 1.24$ (s, 6H), 2.35 (s, 2H), 3.40 (AB system, $J = 19.2 \text{ Hz}$, 2H), 6.63 (s, 1H), 7.45-7.50 (m, 3H), 7.87-7.94 (m, 5H), 7.94 (d, $J = 1.6 \text{ Hz}$, 1H), 8.26-8.41 (m, 2H).



13-(Anthracen-10-yl)-3,4-dihydro-3,3-dimethyl-2H-indazolo[1,2-*b*]phthalazine-1,6,11(13H)-trione
(4l)

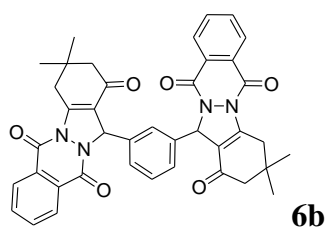
Mp. 235 °C. IR (KBr): $\nu_{\max} = 3049, 2957, 1728, 1361, 700 \text{ cm}^{-1}$. ^1H NMR (400 MHz, CDCl_3): $\delta = 1.16$ (s, 3H), 1.18 (s, 3H), 2.16 (AB system, $J = 16.4 \text{ Hz}$, 2H), 3.40 (AB system, $J = 16.2 \text{ Hz}$, 2H), 4.02 (s,

1H), 7.20-8.33 (m, 10H), 8.34 (dd, $^1J = 8$ Hz, $^2J = 1.2$ Hz, 1H), 8.40 (s, 1H), 8.73 (d, $J = 8.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 28.93, 30.36, 34.50, 38.72, 50.86, 68.16, 121.82, 123.41, 124.15, 125.12, 126.34, 127.05, 127.67, 128.05, 128.81, 129.54, 130.15, 130.45, 130.90, 131.57, 132.45, 133.53, 134.16, 134.61, 150.79, 167.79, 192.13$. MS: $m/z = 472.58$ ($[\text{M}]^+$, 2.09), 295.08 (15.67), 152.09 (22.69), 104.05 (66.92), 76.08 (87.31). Anal. Calcd for $\text{C}_{31}\text{H}_{24}\text{N}_2\text{O}_3$ (472.53): C, 78.79; H, 5.12; N, 5.93. Found: C, 78.77; H, 5.17; N, 5.94.



3,4-Dihydro-13-(4-(2,3,4,6,11,13-hexahydro-3,3-dimethyl-1,6,11-trioxo-1H-indazolo[1,2-*b*]phthalazin-13-yl)phenyl)-3,3-dimethyl-2H-indazolo[1,2-*b*]phthalazine-1,6,11(13H)-trione (6a)

Mp. >320 °C. IR (KBr): $\nu_{\text{max}} = 3074, 2958, 1662, 1360, 696$ cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\delta = 1.19$ (s, 3H), 1.20 (s, 3H), 1.24 (s, 3H), 1.25 (s, 3H), 2.27-2.42 (m, 2H), 3.21-3.41 (m, 2H), 6.46 (s, 1H), 6.47 (s, 1H), 7.40 (d, $J = 4.0$ Hz, 4H), 7.84-7.88 (m, 4H), 8.22-8.37 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 28.44, 28.95, 34.73, 37.98, 50.98, 64.05, 127.53, 127.69, 127.74, 127.80, 128.01, 128.93, 129.06, 133.55, 134.53, 134.57, 136.46, 151.11, 151.23, 192.13$. Anal. Calcd for $\text{C}_{40}\text{H}_{34}\text{N}_4\text{O}_6$ (666.72): C, 72.06; H, 5.14; N, 8.40. Found: C, 72.05; H, 5.19; N, 8.45.



3,4-Dihydro-13-(3-(2,3,4,6,11,13-hexahydro-3,3-dimethyl-1,6,11-trioxo-1*H*-indazolo[1,2-*b*]phthalazin-13-yl)phenyl)-3,3-dimethyl-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione (6b)

Mp. 280 °C decomposes. IR (KBr): ν_{\max} = 3074, 2957, 1667, 1361, 697 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 1.16 (s, 3H), 1.17 (s, 3H), 2.31 (m, 2H), 3.30 (AB system, J = 18.8 Hz, 2H), 6.44 (s, 1H), 7.31-7.41 (m, 2H), 7.85-7.87 (m, 2H), 8.18-8.36 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 28.37, 28.71, 34.59, 37.98, 50.87, 64.24, 118.34, 125.09, 127.63, 127.72, 127.78, 127.99, 128.95, 129.02, 129.08, 133.48, 134.44, 136.83, 150.85, 156.08, 191.96. Anal. Calcd for $\text{C}_{40}\text{H}_{34}\text{N}_4\text{O}_6$ (666.72): C, 72.06; H, 5.14; N, 8.40. Found: C, 72.04; H, 5.17; N, 8.38.

References

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- [2] J. M. Khurana, D. Magoo, *Tetrahedron Lett.* 50 (2009) 7300-7303.
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