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SUPPLEMENTARY MATERIAL TO Reductive Heck reactions of *N*-arylamino-substituted tricyclic imides

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CHARACTERIZATION DATA FOR 3

(3aR, 4S, 7R, 7aS)-rel-2-[(3-chloro-4-fluorophenyl)amino]-3a, 4, 7, 7a-tetrahydro-4, 7-methano-1H-isoindole-1,3(2H)-dione (3). Yield: 80 %; colorless crystals; m.p.: 207–210 °C, $R_{\rm f}$: 0.23 (20:1, dichloromethane/methanol); IR (ATR, cm⁻¹): 3272, 3055, 3024, 2970, 2944, 2873, 1712, 1692, 1636, 1608, 1496, 1414, 1199, 818; ¹H-NMR (500 MHz, CD₃OD, δ / ppm): 1.45–1.46 (2H, m, CH₂), 3.03 (1H, brs, NH), 3.12 (2H, brs, H4 & H4), 3.34–3.35 (2H, m, H7a & H3a), 6.08 (1H, dd, J = 3.4 & 5.6 Hz, =CH), 6.32 (1H, dd, J = 3.1 & 5.3 Hz, =CH), 6.75 (1H, ddd, J = 2.5, 6.6 & 8.8 Hz, Ar-H), 6.90 (1H, dd, J = 2.8 & 6.3 Hz, Ar-H), 7.03 (1H, t, J = 8.8 Hz, Ar-H); ¹³C-NMR (125 MHz, CD₃COCD₃, δ / ppm): 46.5 (CH), 46.7 (CH), 48.0 (CH), 48.4 (CH), 49.2 (CH₂), 113.1 (Ar-C), 113.9 (Ar-C), 114.5 (Ar-C), 115.4 (Cq), 133.7 (CH), 135.1 (CH), 136.5 (Cq), 147.9 (Cq), 173.3 (C=O), 174.1 (C=O); (+)ESI-LCMS (QTOF) (m/z): Calcd. for [C₁₅H₁₂ClFN₂O₂]: 306.0571. Found: 307.0632 [M + H]⁺.

CHARACTERIZATION DATA FOR 4a-d

(3aR, 4S, 7R, 7aS)-rel-2-[(3-chloro-4-fluorophenyl)amino]hexahydro-5-phenyl-4,7-methano-1H-isoindole-1,3(2H)-dione (4a). Yield: 55 %; colorless crystals; m.p.: 148–151 °C, $R_{\rm f}$: 0.47 (1:1, ethyl acetate/n-hexane); IR (ATR, cm⁻¹): 3287, 3064, 3024, 2948, 2913, 2881, 1768, 1706, 1598, 1496, 1452, 1178, 753, 698; ¹H-NMR (500 MHz, CDCl₃, δ / ppm): 1.63 (1H, d, J = 10.7 Hz, H8a), 1.88–1.90 (2H, m, H6n & H9x), 1.92 (1H, d, J = 10.7 Hz, H8s), 2.86 (1H, t, J = 7.5 Hz, H5n), 2.99 (1H, brs, H4), 3.01 (1H, d, J = 5.3 Hz, H4), 3.25 (1H, dd, J = 4.7 & 9.7 Hz, H7a), 3.31 (1H, dd, J = 5.3 & 9.7 Hz, H3a), 6.29 (1H, brs, NH), 6.83 (1H, ddd, J = 2.8, 6.6 & 8.8 Hz, Ar-H), 6.98 (1H, dd, J = 2.8 & 5.9 Hz, Ar-H), 7.05 (1H, t, J = 8.5 Hz, Ar-H), 7.17 (2H, d, J = 7.2 Hz, Ar-H), 7.23

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(1H, d, J = 7.2 Hz, Ar-H), 7.32 (2H, t, J = 7.5 Hz, Ar-H); ¹³C-NMR (125 MHz, CDCl₃, δ / ppm): 33.1 (CH₂), 39.4 (CH₂), 39.7 (CH), 41.8 (CH), 45.4 (CH), 46.3 (CH), 46.9 (CH), 115.7 (Ar-C), 117.0 (Ar-C), 117.9 (Ar-C), 126.4 (2×Ar-C), 126.8 (Ar-C), 128.6 (2×Ar-C), 142.1 (Cq), 144.0 (Cq), 153.3 (Cq), 155.3 (Cq), 175.6 (C=O), 175.7 (C=O). (+)ESI-LCMS (QTOF) (*m*/*z*): Calcd. for [C₂₁H₁₈ClFN₂O₂]: 384.1040. Found: 385.1110 [M + H]⁺.

(3aR, 4S, 7R, 7aS)-rel-2-[(3-chloro-4-fluorophenyl)amino]hexahydro-5-(4--thienyl)-4, 7-methano-1H-isoindole-1,3(2H)-dione (4b). Yield: 62 %; colorless crystals; m.p.: 130–133 °C, $R_{\rm f}$: 0.62 (2:1, ethyl acetate/n-hexane); IR (ATR, cm⁻¹): 3287, 3060, 2962, 2881, 1705, 1609, 1598, 1498, 1448, 1180, 754, 690; ¹H--NMR (500 MHz, CDCl₃, δ / ppm): 1.58 (1H, d, J = 10.7 Hz, H8a), 1.78–1.88 (2H, m, H6n & H6x), 1.96 (1H, d, J = 10.7 Hz, H8s), 289 (2H, d, J = 5.3 Hz, H4 & H4), 2.96 (1H, t, J = 7.2 Hz, H5n), 3.16 (1H, dd, J = 4.7 & 9.7 Hz, H7a), 3.21 (1H, dd, J = 5.3 & 9.4 Hz, H3a), 6.22 (1H, brs, NH), 6.68–6.71 (2H, m, Ar-H), 6.83–6.86 (2H, m, Ar-H), 6.95 (1H, t, J = 8.5 Hz, Ar-H), 7.07 (1H, d, J = 4.41 Hz, Ar-H); ¹³C-NMR (125 MHz, CDCl₃, δ / ppm): 35.3 (CH₂), 38.0 (CH), 39.4 (CH), 39.7 (CH₂), 46.0 (CH), 46.5 (CH), 46.9 (CH), 115.8 (Ar-C), 117.0 (Ar-C), 117.2 (Ar-C), 118.1 (Ar-C), 123.5 (Ar-C), 126.8 (Ar-C), 142.0 (Cq), 148.7 (Cq), 115.1 (Cq), 155.4 (Cq), 175.3 (C=O), 175.4 (C=O); (+)ESI-LCMS (QTOF) (m/z): Calcd. for [C₁9H₁₆CIFN₂O₂S]: 390.0605. Found: 391.0671 [M + H]⁺.

(3aR, 4S, 7R, 7aS)-rel-2-[(3-chloro-4-fluorophenyl)amino]-5-(4-chlorophenyl)hexahydro-4,7-methano-1H-isoindole-1,3(2H)-dione (4c). Yield: 58 %: colorless crystals; m.p.: 75-78 °C, Rf: 0.42 (20:1, dichloromethane/methanol); IR (ATR, cm⁻¹): 3291, 3033, 2973, 2877, 1777, 1709, 1607, 1404, 1376, 1177, 817; ¹H-NMR (500 MHz, CDCl₃, δ / ppm): 1.64 (1H, d, J = 10.7 Hz, H8a), 1.84– -1.87 (2H, *m*, H6n & H6x), 1.92 (1H, *d*, *J* = 10.7 Hz, H8s), 2.81 (1H, *t*, *J* = 7.2 Hz, H5n), 2.97 (1H, d, J = 5.0 Hz, H4), 3.00 (1H, brs, H4), 3.26 (1H, dd, J = 5.3 & 9.7 Hz, H7a), 3.32 (1H, dd, J = 5.0 & 9.7 Hz, H3a), 6.24 (1H, brs, NH), 6.83 (1H, *ddd*, *J* = 2.8, 6.6 & 8.8 Hz, Ar-H), 6.97 (1H, *dd*, *J* = 2.8 & 5.9 Hz, Ar-H), 7.05 (1H, t, J = 8.5 Hz, Ar-H), 7.09 (2H, d, J = 8.1 Hz, Ar-H), 7.28 (2H, d, J = = 8.5 Hz, Ar-H); ¹³C-NMR (125 MHz, CDCl₃, δ / ppm): 33.1 (CH₂), 39.2 (CH₂), 39.7 (CH), 41.2 (CH), 45.3 (CH), 46.2 (CH), 46.8 (CH), 115.4 (Ar-C), 117.1 (Ar-C), 117.6 (Ar-C), 121.6 (Cq), 128.1 (2×Ar-C), 128.6 (2×Ar-C), 132.1 (Cq), 142.1 (Cq), 153.2 (Cq), 155.1 (Cq), 175.6 (C=O), 175.7 (C=O); (+)ESI--LCMS (QTOF) (m/z): Calcd. for [C₂₁H₁₇Cl₂FN₂O₂]: 418.0651. Found: 419.0711 [M + H]⁺.

(3aR, 4S, 7R, 7aS)-rel-2-[(3-chloro-4-fluorophenyl)amino]-5-(6-chloropyridin-3-yl)hexahydro-4, 7-methano-1H-isoindole-1,3(2H)-dione (4d). Yield: 62 %; yellow oil; R_{f} : 0.03 (100:1, dichloromethane/methanol); IR (ATR, cm⁻¹): 3239, 3033, 2967, 2930, 2881, 1715, 1659, 1607, 1496, 1455, 1180, 828; ¹H-NMR (500 MHz, CDCl₃, δ / ppm): 1.58 (1H, d, J = 10.7 Hz, H8a), 1.66 (1H, d, J =

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= 12.9 Hz, H6n), 1.75 (1H, d, J = 10.7 Hz, H8s), 1.82 (1H, dt, J = 12.9 Hz, H6x), 2.74 (1H, t, J = 7.2 Hz, H5n), 2.78 (1H, brs, H4), 2.87 (1H, d, J = 11.9 Hz, H4), 3.20 (1H, dd, J = 4.7 & 9.4 Hz, H7a), 3.26 (1H, dd, J = 5.0 & 9.4 Hz, H3a), 6.67 (1H, dd, J = 2.8 & 6.6 Hz, Ar-H), 6.80 (1H, dd, J = 2.8 & 5.9 Hz, Ar-H), 6.91 (1H, t, J = 8.5 Hz, Ar-H), 7.17 (1H, d, J = 8.5 Hz, Ar-H), 7.24 (1H, brs, NH), 7.35 (1H, d, J = 8.5 Hz, Ar-H), 7.91 (1H, s, Ar-H); ¹³C-NMR (125 MHz, CDCl₃, δ / ppm): 33.1 (CH₂), 39.1 (CH), 39.3 (CH₂), 39.7 (CH), 44.9 (CH), 46.0 (CH), 46.7 (CH), 115.6 (Ar-C), 117.0 (Ar-C), 117.7 (Ar-C), 124.1 (Ar-C), 137.8 (Ar-C), 138.4 (Cq), 142.2 (Cq), 148.3 (Ar-C), 149.5 (Cq), 153.2 (Cq), 155.2 (Cq), 175.2 (C=O), 175.3 (C=O); (+)ESI-LCMS (QTOF) (m/z): Calcd. for [C₂₀H₁₆Cl₂FN₃O₂]: 419.0603. Found: 420.0689 [M + H]⁺.

CHARACTERIZATION DATA FOR 7a-d

(3aR, 4S, 7R, 7aS)-rel-2-[(2,4-dinitrophenyl)amino]hexahydro-5-phenyl-4,7--methano-IH-isoindole-1,3(2H)-dione (7a). Yield: 85 %; yellow crystals; m.p.: 213–215 °C, $R_{\rm f}$: 0.70 (2:1, ethyl acetate/n-hexane); IR (ATR, cm⁻¹): 3317, 3100, 3052, 2956, 2924, 2874, 1724, 1616, 1594, 1500, 1336, 1426, 1390, 1172, 833; ¹H-NMR (500 MHz, DMSO-d₆, δ / ppm): 1.61 (1H, d, J = 10.0 Hz, H8a), 1.78 (2H, d, J = 10.0 Hz, H8s & H6n), 1.95–2.00 (1H, m, H6x), 2.78 (1H, brd, J = 4.7 Hz, H4), 2.84 (1H, brs, H4), 3.04–3.06 (1H, m, H8x), 3.40 (1H, dd, J = 5.0 & 9.4 Hz, H7a), 3.46 (1H, dd, J = 5.0 & 9.4 Hz, H3a), 7.19 (1H, t, J = 7.5 Hz, Ar-H), 7.23 (2H, d, J = 7.5 Hz, Ar-H), 7.33 (3H, t, J = 7.5 Hz, Ar-H), 8.28 (1H, brs, Ar-H), 8.90 (1H, d, J = 2.5 Hz, Ar-H), 10.71 (1H, brs, NH); ¹³C-NMR (100 MHz, DMSO-d₆, δ / ppm): 32.9 (CH₂), 39.7 (CH₂), 41.5 (CH), 43.4 (CH), 45.7 (CH), 46.5 (CH), 47.3 (CH), 109.1 (Ar-C), 123.6 (Ar-C), 126.3 (Ar-C), 127.4 (2×Ar-C), 128.8 (2×Ar-C), 130.7 (Cq), 131.3 (Ar-C), 143.0 (Cq), 144.5 (Cq), 145.4 (Cq), 175.3 (C=O), 175.4 (C=O); (+)ESI-LCMS (QTOF) (m/z): Calcd. for [C₂₁H₁₈N₄O₆]: 422.1192. Found: 445.1083 [M + Na]⁺.

(3aR,4S,7R,7aS)-rel-2-[(2,4-dinitrophenyl)amino]hexahydro-5-(2-thienyl)--phenyl-4,7-methano-1H-isoindole-1,3(2H)-dione (7b). Yield: 60 %; brownish crystals; m.p.: 269–271 °C, $R_{\rm f}$: 0.78 (2:1, ethyl acetate/n-hexane); IR (ATR, cm⁻¹): 3332, 3086, 3061, 2973, 2916, 2857, 1730, 1660, 1608, 1534, 1324, 1425, 1382, 1170, 832; ¹H-NMR (500 MHz, DMSO-d₆, δ / ppm): 1.66 (1H, d, J = 10.0 Hz, H8a), 1.81 (2H, d, J = 10.0 Hz, H8s & H6n), 2.05 (1H, dd, J = 1.8 & 8.5 Hz, H6x), 2.77 (1H, brd, J = 5.0 Hz, H4), 2.83 (1H, brs, H4), 3.23–3.26 (1H, m, H8x), 3.41 (1H, dd, J = 5.0 & 9.4 Hz, H7a), 3.46 (1H, dd, J = 5.0 & 9.4 Hz, H3a), 6.89 (1H, d, J = 3.4 Hz, Ar-H), 6.97 (1H, dd, J = 3.4 & 5.0 Hz, Ar-H), 7.36 (2H, dd, J = 0.9 & 5.0 Hz, Ar-H), 8.27 (1H, brd, J = 8.5 Hz, Ar-H), 8.90 (1H, d, J = 2.5 Hz, Ar-H), 10.70 (1H, brs, NH); ¹³C-NMR (100 MHz, DMSO-d₆, δ / ppm): 34.8 (CH₂), 37.7 (CH₂), 46.3 (CH), 46.8 (CH), 47.3 (CH), 42.0 (CH), 63.2 (CH), 115.8 (Ar-C), 123.5 (Ar-C), 123.7 (Ar-C), 124.2 (Ar-C), 127.4 (Ar-C),

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130.4 (Cq), 131.2 (Ar-C), 139.0 (Cq), 150.0 (Cq), 175.1 (C=O), 175.2 (C=O); (+)ESI-LCMS (QTOF) (m/z): Calcd. for [C₁₉H₁₆N₄O₆S]: 428.0755. Found: 451.0646 [M + Na]⁺.

(3aR,4S,7R,7aS)-rel-5-(4-chlorophenyl)-2-[(2,4-dinitrophenyl)amino]hexahydro-4,7-methano-1H-isoindole-1,3(2H)-dione (7c). Yield: 60 %; yellow crystals; m.p.: 267–268 °C, $R_{\rm f}$: 0.74 (2:1, ethyl acetate/n-hexane); IR (ATR, cm⁻¹): 3314, 3100, 3052, 2976, 2952, 2883, 1725, 1617, 1597, 1502, 1339, 1425, 1388, 1170, 819); ¹H-NMR (500 MHz, DMSO- d_6 , δ / ppm): 1.67 (1H, d, J = 10.0 Hz, H8a), 1.80 (2H, d, J = 10.0 Hz, H8s & H6n), 1.99–2.03 (1H, m, H6x), 2.82 (1H, brd, J = 4.4 Hz, H4), 2.89 (1H, brs, H4), 3.07–3.09 (1H, m, H8x), 3.46 (1H, dd, J = 4.4 & 6.3 Hz, H7a), 3.51 (1H, dd, J = 5.0 & 9.4 Hz, H3a), 7.31 (2H, d, J = 8.1 Hz, Ar-H), 8.24 (3H, d, J = 8.5 Hz, Ar-H), 8.32 (1H, brs, Ar-H), 8.96 (1H, brd, J = 1.89 Hz, Ar-H), 10.76 (1H, brs, NH); ¹³C-NMR (100 MHz, DMSO- d_6 , δ / ppm): 32.5 (CH₂), 35.2 (CH₂), 40.6 (CH), 45.2 (CH), 46.0 (CH), 46.8 (CH), 48.5 (CH), 115.4 (Ar-C), 117.1 (Ar-C), 123.1 (Ar-C), 126.9 (Cq), 128.3 (Ar-C), 130.4 (Ar-C), 130.8 (Ar-C), 131.3 (Ar-C), 143.9 (Cq), 148.1 (Cq), 151.0 (Cq), 154.8 (Cq), 174.8 (C=O), 174.9 (C=O); (+)ESI-LCMS (QTOF) (m/z): Calcd. for [C₂₁H₁₇Cl₂N₄O₆] 456.0837. Found: 457.0902 [M + H]⁺.

(3aR,4S,7R,7aS)-rel-5(6-chloropyridin-3-yl)-2-[(2,4-dinitrophenyl)amino]hexahydro-4,7-methano-1H-isoindole-1,3(2H)-dione (7d). Yield: 87 %; yellow crystals; m.p.: 255–257 °C, $R_{\rm f}$: 0.42 (2:1, ethyl acetate/n-hexane); IR (ATR, cm⁻¹): 3318, 3104, 2956, 2931, 2877, 1725, 1616, 1594, 1501, 1337, 1425, 1390, 1173, 829; ¹H-NMR (500 MHz, DMSO- d_6 , δ / ppm): 1.65 (1H, d, J = 10.4 Hz, H8a), 1.78 (2H, d, J = 10.4 Hz, H8s & H6n), 1.97–2.03 (1H, m, H6x), 2.85 (1H, brs, H4), 3.07 (1H, brs, H7), 3.39–3.40 (1H, m, H8x), 3.44 (1H, dd, J = 5.0 & 9.4 Hz, H7a), 3.49 (1H, dd, J = 5.0 & 9.4 Hz, H3a), 7.39 (1H, brs, Ar-H), 7.47 (1H, d, J = 8.1 Hz, Ar-H), 7.73 (1H, dd, J = 1.8 & 8.1 Hz, Ar-H), 8.28 (2H, brd, J = 1.8 Hz, Ar-H), 8.90 (1H, d, J = 2.5 Hz, Ar-H), 10.66 (1H, brs, NH); ¹³C-NMR (100 MHz, DMSO- d_6 , δ / ppm): 33.0 (CH₂), 38.9 (CH₂), 39.8 (CH), 45.1 (CH), 46.4 (CH), 47.2 (CH), 63.2 (CH), 115.8 (Ar-C), 123.5 (Ar-C), 124.4 (Ar-C), 130.5 (Cq), 131.3 (Ar-C), 138.5 (Ar-C), 138.8 (Ar-C), 140.2 (Cq), 146.6 (Cq), 148.4 (Cq), 149.0 (Cq), 175.2 (C=O), 175.3 (C=O); (+)ESI-LCMS (QTOF) (m/z): Calcd. for [C₂₀H₁₆CIN₅O₆]: 457.0787. Found: 458.0861 [M + H]⁺.

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CHARACTERIZATION SPECTRA OF THE SYNTHESIZED COMPOUNDS





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HYDROARYLATIONS OF TRICYCLIC IMIDES





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Fig. S-6. ¹H-NMR spectrum of compound 4a (CDCl₃).





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Fig. S-9. IR spectrum of compound 4b.

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S288 ATBAKAR et al. Π-7 -4E+08 -3E+08 lĺ -2E+08 -2E+08 -2E+08 -1E+08 -5E+07 -0 1.51<u>4</u> 2.04<u>4</u> 1.70<u>4</u> 2222 1.00-1 1.11/1 1.11/1 2.19 3.0 7.0 4.0 3.5 f1 (ppm) 2.0 7.5 6.5 6.0 5.5 5.0 4.5 2.5 1.5 1.0 0.5 0.0 -0.5

Fig. S-10. 1 H-NMR spectrum of compound **4b** (CDCl₃).





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Fig. S-14. 1 H-NMR spectrum of compound **4c** (CDCl₃).







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Fig. S-18. ¹H-NMR spectrum of compound 4d (CDCl₃).





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Fig. S-20. ¹³C-NMR spectrum of compound 4d (CDCl₃).



Fig. S-21. IR spectrum of compound 7a (ATR).



Fig. S-22. ¹H-NMR spectrum of compound 7a (DMSO-*d*₆).





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Fig. S-25. IR spectrum of compound **7b** (ATR).

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Fig. S-26. ¹H-NMR spectrum of compound **7b** (DMSO- d_6).





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Fig. S.29. IR spectrum of compound 7c (ATR).



Fig. S-30. ¹H-NMR spectrum of compound 7c (DMSO-*d*₆).





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Fig. S-33. IR spectrum of compound **7d** (ATR).

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Fig. S-34. ¹H-NMR spectrum of compound 7d (DMSO-*d*₆)





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Fig. S-36. ¹³C-NMR spectrum of compound **7d** (DMSO-*d*₆).