



SUPPLEMENTARY MATERIAL TO
**Synthesis and electrochemical characterization of substituted
indolizine carboxylates**

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PHYSICAL, ANALYTIC AND SPECTRAL DATA OF THE COMPOUNDS AND DPV
AND CV CURVES OF GLASSY CARBON

Methyl 3-(4-chlorobenzoyl)-7-methylindolizine-1-carboxylate (IVa). Yellow crystals; yield: 52 %; m.p.: 175–176 °C; Anal. Calcd. for C₁₈H₁₄ClNO₃ (FW: 327.76): C, 65.96; H, 4.3; N, 4.27 %. Found: C, 65.72; H, 4.45; N, 4.21 %; IR (KBr, cm⁻¹): 1711, 1643, 1612, 1526, 1478, 1462, 1344, 1227; ¹H-NMR (300 MHz, CDCl₃, δ / ppm): 2.50 (3H, s, CH₃-7), 3.89 (3H, s, CH₃-ester), 6.94 (1H, dd, J = 1.9, 7.1 Hz, H-6), 7.48 (2H, d, J = 8.4 Hz, H-3'+H-5'), 7.73 (1H, s, H-2), 7.75 (2H, d, J = 8.4 Hz, H-2'+H-6'), 8.18 (1H, dd, J = 1.0, 2.0 Hz, H-8), 9.81 (1H, d, J = 7.1 Hz, H-5); ¹³C-NMR (75 MHz, CDCl₃, δ / ppm): 21.61 (CH₃), 51.21 (CH₃), 104.97, 117.91, 118.21, 121.86, 128.49, 128.61 (2C), 129.13, 130.25 (2C), 137.58, 138.25, 139.81, 140.48, 164.40 (CO₂), 183.71 (C=O); MS-ESI (m/z): 328/330 [M+1].

Ethyl 3-(4-fluorobenzoyl)-7-methylindolizine-1-carboxylate (IVb). Yellow crystals; yield: 69 %; m.p.: 146–148 °C; Anal. Calcd. for C₁₉H₁₆FNO₃ (FW: 325.34): C, 70.14; H, 4.96; N, 4.30 %. Found: C, 70.33; H, 5.10; N, 4.14 %; IR (KBr, cm⁻¹): 1710, 1643, 1610, 1526, 1477, 1462, 1343, 1227, 1176; ¹H-NMR (300 MHz, CDCl₃, δ / ppm): 1.40 (3H, t, J = 7.1 Hz, CH₃-ester), 2.50 (3H, s, CH₃-7), 4.38 (2H, q, J = 7.1 Hz, CH₂-ester), 6.93 (1H, dd, J = 2.0, 7.2 Hz, H-6), 7.19 (2H, t, J = 8.7 Hz, H-3'+H-5'), 7.73 (1H, s, H-2), 7.84 (2H, dd, J = 5.4, 8.8 Hz, H-2'+H-6'), 8.19 (1H, dd, J = 1.0, 2.0 Hz, H-8), 9.81 (1H, d, J = 7.2 Hz, H-5); ¹³C-NMR (75 MHz, CDCl₃, δ / ppm): 14.53 (CH₃), 21.61 (CH₃), 60.01

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(CH₂), 105.23, 115.27, 115.56, 117.76, 118.26, 121.68, 131.15, 131.26, 136.12, 136.17, 140.43, 163.55 ($J = 252.2$ Hz), 166.34 (CO₂), 183.69 (C=O); MS-ESI (m/z): 326 [M+1].

Ethyl 7-benzoyl-3-(4-fluorobenzoyl)indolizine-1-carboxylate (IVc). Yellow crystals; yield: 63 %; m.p.: 178–179 °C; Anal. Calcd. for C₂₅H₁₈FNO₄ (FW: 415.41): C, 72.28; H, 4.37; N, 3.37 %. Found: C, 72.43; H, 4.51; N, 3.19 %; IR (KBr, cm⁻¹): 1696, 1658, 1629, 1597, 1528, 1474, 1349, 1290, 1231, 1211; ¹H-NMR (300 MHz, CDCl₃, δ /ppm): 1.33 (3H, *t*, $J = 7.1$ Hz, CH₃-ester), 4.35 (2H, *q*, $J = 7.1$ Hz, CH₂-ester), 7.22 (2H, *d*, $J = 8.6$ Hz, H-3'+5'), 7.53–7.65 (3H, *m*, Ph+H-6), 7.64–7.69 (1H, *m*, Ph), 7.87 (1H, *s*, H-2), 7.90–7.92 (4H, *m*, Ph), 8.77 (1H, *s*, H-8), 9.94 (1H, *d*, $J = 7.4$ Hz, H-5); ¹³C-NMR (75 MHz, CDCl₃, δ /ppm): 14.34 (CH₃), 60.47 (CH₂), 109.45, 114.56, 115.55, 115.83, 122.66, 123.44, 128.60 (2C), 128.79, 129.91 (2C), 131.44, 131.56 (2C), 133.06, 134.86, 136.53, 137.89, 163.45 ($J = 251.92$ Hz), 166.74 (CO₂), 184.37 (C=O), 194.00 (C=O); MS-ESI (m/z): 416 [M+1].

Ethyl 8-ethyl-5-methyl-3-(3-nitrobenzoyl)indolizine-1-carboxylate (IVd). Yellow crystals; Yield: 55 %; m.p.: 129–131 °C; Anal. Calcd. for C₂₁H₂₀N₂O₅ (FW: 380.39): C, 66.31; H, 5.30; N, 7.36 %. Found: C, 66.49; H, 5.16; N, 7.21 %; IR (KBr, cm⁻¹): 1702, 1615, 1528, 1471, 1348, 1220; ¹H-NMR (300 MHz, CDCl₃, δ /ppm): 1.27 (3H, *t*, $J = 7.4$ Hz, CH₃ from C₂H₅-8), 1.35 (3H, *t*, $J = 7.1$ Hz, CH₃-ester), 2.56 (3H, *s*, CH₃-5), 3.33 (2H, *q*, $J = 7.4$ Hz, CH₂ from C₂H₅-8), 4.32 (2H, *q*, $J = 7.1$ Hz, CH₂-ester), 6.96 (1H, *d*, $J = 7.3$ Hz, H-6), 7.33 (1H, *d*, $J = 7.3$ Hz, H-7), 7.71 (1H, *s*, H-2), 7.75 (1H, *t*, $J = 8.0$ Hz, H-5'), 8.38 (1H, *dt*, $J = 1.4, 7.7$ Hz, H-6'), 8.47–8.49 (1H, *m*, H-4'), 8.87 (1H, *t*, $J = 1.9$ Hz, H-2'); ¹³C-NMR (75 MHz, CDCl₃, δ /ppm): 14.41 (CH₃), 15.03 (CH₃), 23.22 (CH₃), 26.75 (CH₂), 60.53 (CH₂), 108.13, 117.52, 123.81, 124.78, 126.67, 128.14, 129.62, 131.72, 133.69, 135.56, 137.60, 140.25, 140.56, 148.13, 163.87 (CO₂), 179.07 (C=O); MS-ESI (m/z): 381 [M+1].

Diethyl 7-benzoylindolizine-1,3-dicarboxylate (IVe). Pale yellow crystals; yield: 57 %; m.p.: 136–138 °C; Anal. Calcd. for C₂₁H₁₉NO₅ (FW: 365.38): C, 69.03; H, 5.24; N, 3.83 %. Found: C, 69.31; H, 5.09; N, 3.68 %; IR (KBr, cm⁻¹): 1721, 1693, 1658, 1597, 1528, 1474, 1349, 1231, 1198; ¹H-NMR (300 MHz, CDCl₃, δ /ppm): 1.27 (3H, *t*, $J = 7.1$ Hz, CH₃-ester), 1.36 (3H, *t*, $J = 7.1$ Hz, CH₃-ester), 4.27 (2H, *q*, $J = 7.1$ Hz, CH₂-ester), 4.46 (2H, *q*, $J = 7.1$ Hz, CH₂-ester), 7.41–7.49 (3H, *m*, H-3', H-4', H-5'), 7.54–7.59 (1H, *m*, H-6), 7.77–7.81 (2H, *m*, H-2', H-6'), 7.98 (1H, *s*, H-2), 8.65 (1H, *dd*, $J = 1.0, 2.0$ Hz, H-8), 9.51 (1H, *dd*, $J = 1.0, 7.3$ Hz, H-5); ¹³C-NMR (75 MHz, CDCl₃, δ /ppm): 14.34 (CH₃), 14.40 (CH₃), 60.25 (CH₂), 60.73 (CH₂), 108.85, 113.60, 116.53, 123.13, 124.84, 127.65, 128.54 (2C), 129.84 (2C), 132.84, 132.91, 136.77, 136.85, 160.87 (CO₂), 163.67 (CO₂), 194.25 (C=O); MS-ESI (m/z): 366 [M+1].

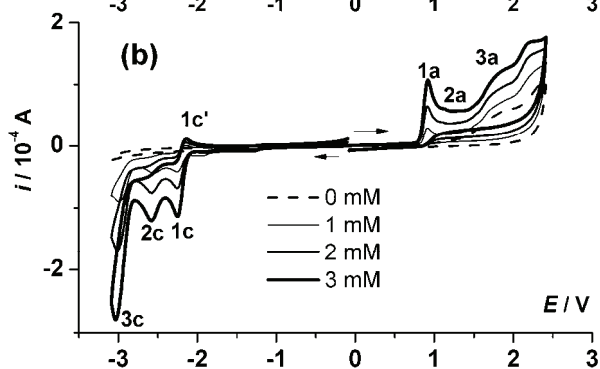
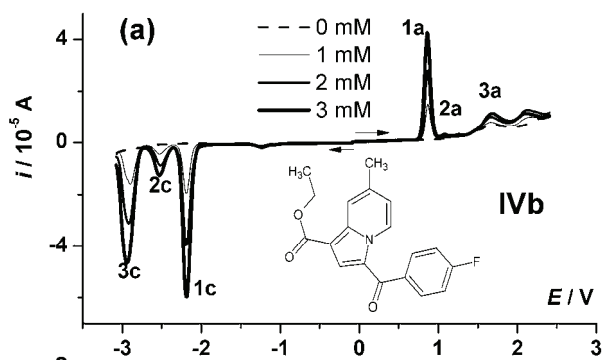


Fig. 1S. a) DPV and b) CV curves for different concentrations of **IVb** in 0.1 M TBAP, CH₃CN.

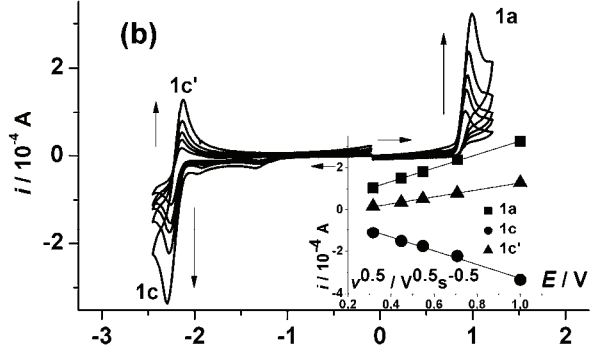
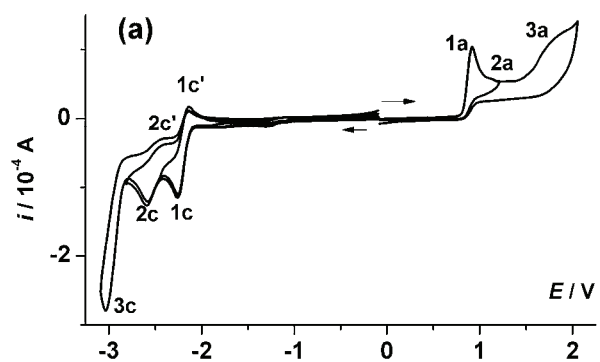


Fig. 2S. CV curves for various scan domains at 0.1 V s⁻¹ (a) and different scan rates: 0.1, 0.2, 0.3, 0.5 and 1 V s⁻¹ in the domains of peaks 1c and 1a (b) for **IVb** (3 mM) in 0.1 M TBAP, CH₃CN.

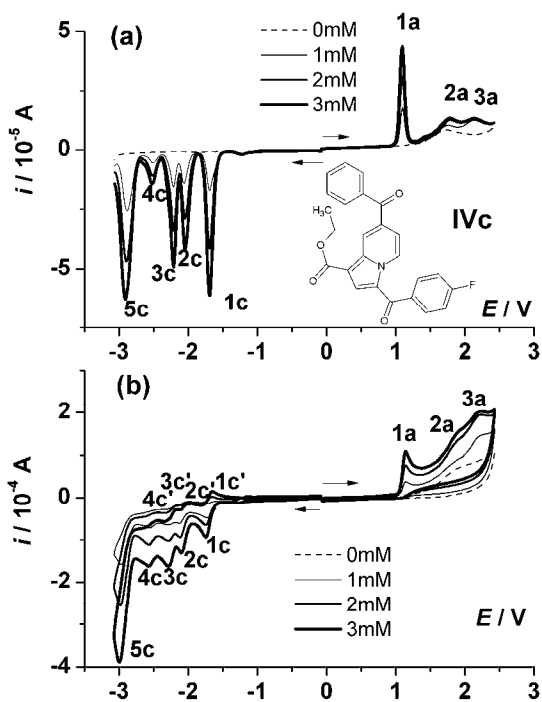


Fig. 3S. a) DPV and b) CV curves for different concentrations of **IVc** in 0.1 M TBAP, CH_3CN .

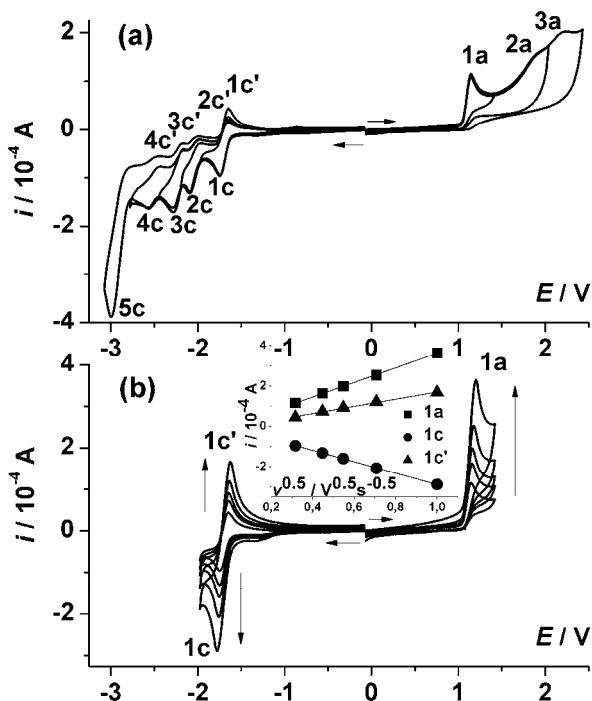


Fig. 4S. CV curves for various scan domains at 0.1 V s^{-1} (a) and at different scan rates: 0.1, 0.2, 0.3, 0.5 and 1 V s^{-1} (b) in the domain of peaks 1c and 1a for **IVc** (3 mM) in 0.1 M TBAP, CH_3CN .

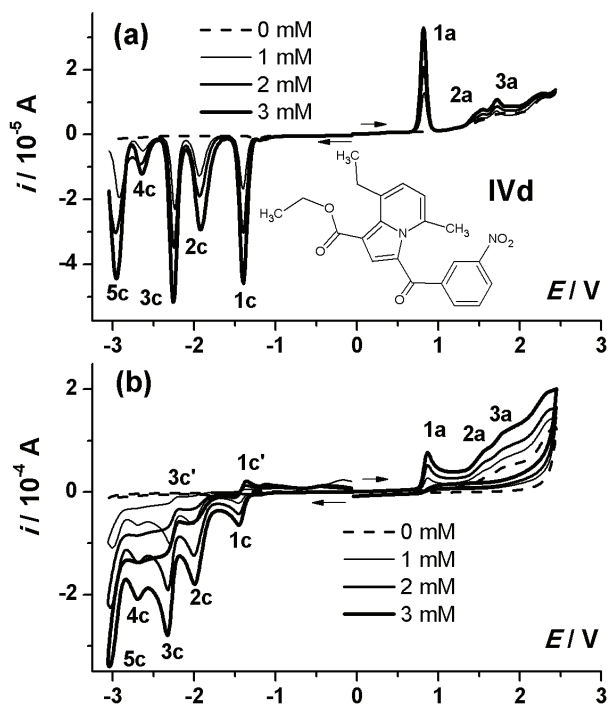


Fig. 5S. a) DPV and b) CV curves for different concentrations of **IVd** in 0.1 M TBAP, CH₃CN.

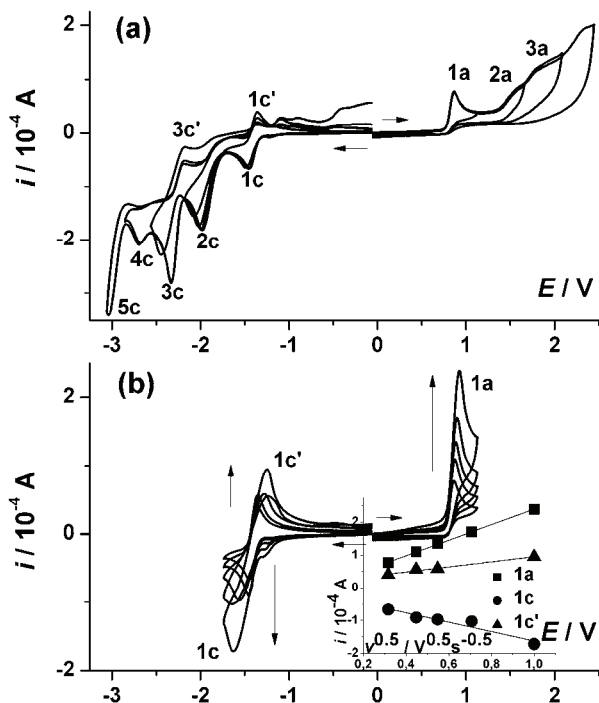


Fig. 6S. CV curves for various scan domains at 0.1 V s⁻¹ (a) and at different scan rates: 0.1, 0.2, 0.3, 0.5 and 1 V s⁻¹ (b) in the domain of peaks 1c and 1a for **IVd** (3 mM) in 0.1 M TBAP, CH₃CN.

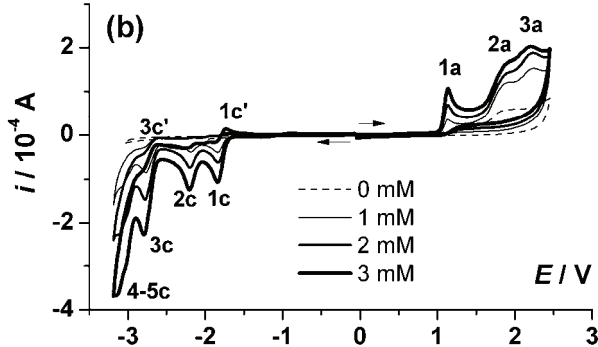
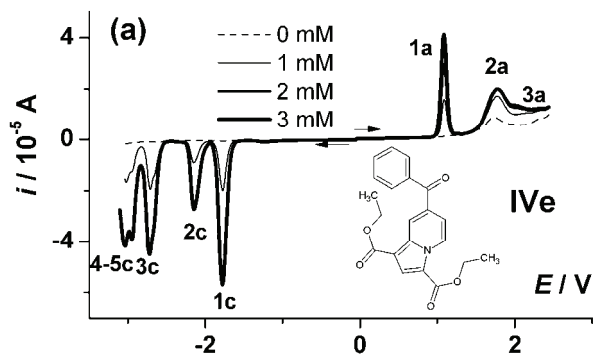


Fig. 7S. a) DPV and b) CV curves for different concentrations of **IVe** in 0.1 M TBAP, CH_3CN .

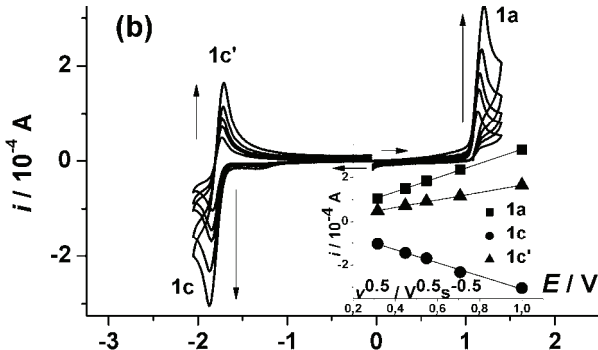
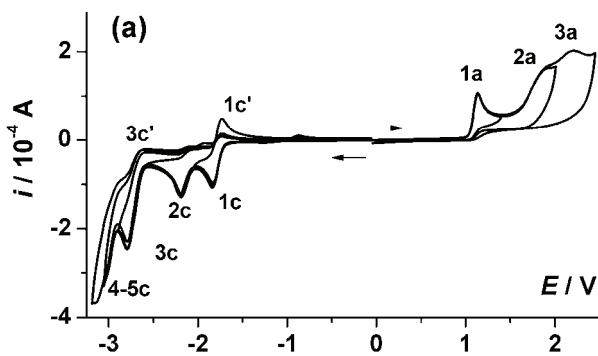


Fig. 8S. CV curves for various scan domains at 0.1 V s^{-1} (a) and different scan rates: 0.1, 0.2, 0.3, 0.5 and 1 V s^{-1} (b) in the domain of peaks 1c and 1a for **IVe** (3 mM) in 0.1 M TBAP, CH_3CN .