Electrochemically Induced Hetero-[4+2]-Cycloaddition Reactions Between 2-Vinylpyrroles and β-Acceptor-Substituted Enamines

Thomas Peglow, Siegfried Blechert,* and Eberhard Steckhan

Abstract: Recently, we reported on radical cation cycloaddition reactions between 2-vinylindoles and β-acceptor-substituted enamines, which provide a new pathway to pyrido[1,2-*a*]indoles.[1] In order to broaden the synthetic scope of this reaction, we have developed hetero-[4+2]-cycloaddition reactions between a number of readily accessible 2-vinylpyrroles, acting as heterodienes, and β-acceptor-substituted enamines. This reaction is induced by electrochemically generated radical cations of either the 2-vinylpyrrole diene or the enamine dienophile. These electron-transfer-induced reactions open up a novel route to highly substituted indolizines in moderate yields. We propose a mechanism that explains both the complete regiocontrol of this cycloaddition as well as the product formation, irrespective of the inducing radical cation species.

Keywords: cations · cycloadditions · electrochemistry · electron transfer · radical ions

Introduction

The synthetic applications of [4+2]-cycloaddition reactions are limited by the demand for reactants of complementary electronic character to ensure that the frontier orbitals can overlap sufficiently. In contrast, electron transfer, as the most simple method for a redox umpolung, permits [4+2] cycloadditions between reactants with similar HOMO energies under mild conditions via electrochemically or photochemically generated radical cations. These radical-cation-initiated reactions have a reaction rate several orders of magnitude greater than the neutral reactions owing to a very low activation barrier. Thus, electron-transfer-induced cycloadditions have proved to be a promising tool for organic synthesis.[2]

Originally, the application of this methodology was restricted to non-heterosubstituted dienes and dienophiles, for example cyclohexadienes,[3] 1,3-pentadienes[4] or styrenes.[5] Subsequently, heterosubstituted dienophiles were reported by Bauld in radical cation [4+2] cycloadditions by the reaction of butadiene-type dienes and phenylvinyl thioether as a step in the synthesis of (−)-β-selinene[6] and also by one of us in the very efficient application of indole as a heterodienophile.[7] We also demonstrated the ability of electron-transfer-induced cycloadditions to produce carbazole derivatives in good yields from reactions of several cyclohexadienes and styrenes (acting as dienophiles) with acceptor-substituted 2-vinylindoles (acting as heterodienes).[8] In conventional Diels–Alder reactions, these vinylindoles react only with very electron-deficient dienophiles, and often require drastic conditions.[9] In the course of these studies aimed at the use of heterosubstituted dienes and dienophiles in radical cation [4+2] cycloadditions, we recently developed a new annellation reaction between β-acceptor-substituted enamines, acting as dienophiles, and 2-vinylindoles to provide a method of synthesising pyrido[1,2 a]indoles.[1] Based on this work, we report here an electrochemically induced hetero-[4+2]-cycloaddition reaction between acceptor-substituted 2-vinylpyrroles and β-acceptor-substituted enamines, which opens up an efficient route to highly substituted indolizines.

[*] Prof. Dr. S. Blechert, Dipl.-Chem. T. Peglow
Institut für Organische Chemie der Technischen Universität Berlin
Strasse des 17. Juni 124, D-10623 Berlin (Germany)
Fax: Int. code + 49 30-31423619
e-mail: sibl@wap0105.chem.tu-berlin.de
Prof. Dr. E. Steckhan
Institut für Organische Chemie und Biochemie der Universität
Gerhard-Domagk-Strasse 1, D-53121 Bonn (Germany)
Fax: Int. code + 49 228-735683
e-mail: steckhan@uni-bonn.de

Results and Discussion

Diacceptor-substituted 2-vinylpyrroles **1** were chosen as suitable heterodienes for the anticipated electron-transfer-induced indolizine syntheses, since they are analogous to the successfully employed 2-vinylindoles.[1] These compounds, which must be completely substituted at the pyrrole nucleus to avoid polymerisation at the electrode surface,[10] are readily accessible by addition of dimethyl acetylenedicarboxylate (DMAD) or but-2-ynedinitrile to 2*H*-pyrroles. Mixtures of (*Z*)/(*E*) isomers were obtained from these reactions; however, except for **1c**, only the major isomers shown in Scheme 1 were employed in the single electron transfer (SET) reactions.

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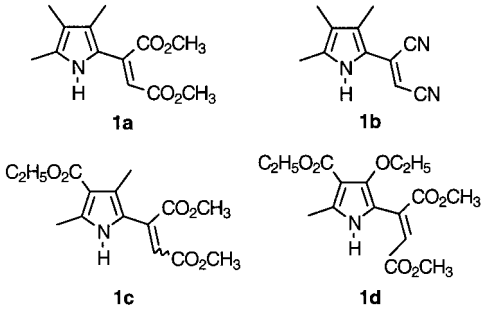
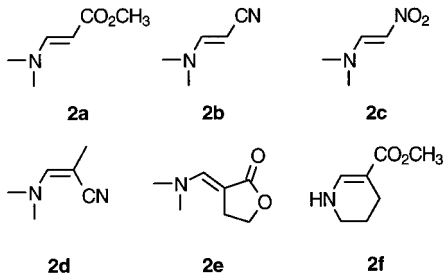


Scheme 1. 2-Vinylpyrroles **1** employed as dienes in electron-transfer-initiated cycloaddition reactions.

The dienophiles **2** (Scheme 2) were prepared by Michael addition of dimethylamine to α,β-acetylenic esters and nitriles (**2a** and **2b**),[11] treatment of β-bromo methacrylonitrile with



Scheme 2. β-Acceptor-substituted enamines **2** employed as dienophiles in electron-transfer-initiated cycloaddition reactions.

dimethylamine (**2d**),[12] condensation of γ-butyrolactone with Bredereck's reagent[13] (**2e**) or hydrogenation of the appropriate pyridine (**2f**).[14]

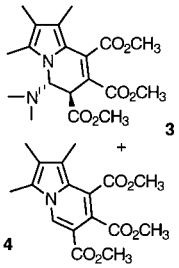
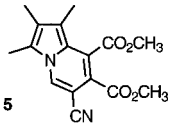
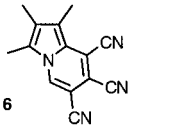
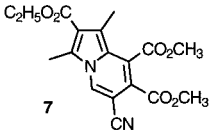
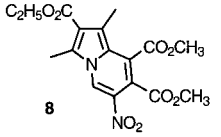
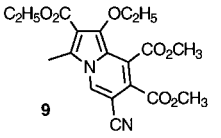
It has been previously shown that for an efficient radical-cation-induced [4+2] cycloaddition, the oxidation potentials of the diene and dienophile should not differ by much more than 500 mV.[8] Therefore, the oxidation potentials of the β-acceptor-substituted enamines and the 2-vinylpyrroles were measured by cyclic voltammetry in acetonitrile. At scan rates up to 400 mV s^{-1}, totally irreversible voltammograms were obtained in all cases. This indicates a fast follow-up reaction of the radical cations under these conditions. The linear dependence of the anodic peak current on the square root of the scan rate indicates a diffusion-controlled process. The anodic peak potentials are taken as a relative measure of the redox potentials of the compounds (Table 1). Thus, a hetero-[4+2]-cycloaddition reaction occurs between two compounds of nearly identical HOMO energies by a redox umpolung of either the diene or the dienophile to the corresponding radical cation. In all cases, the desired indolizines, which have a higher oxidation state than the reactants, were formed under complete regiocontrol in yields of 25 to 66% (Tables 2 and 3). No dimers of the diene or the dienophile were observed.

Table 1. Oxidative ($E_{p,ox}$) peak potentials (V) of the 2-vinylpyrroles (**1**) and the β-acceptor-substituted enamines (**2**).

2-Vinylpyrrole	$E_{p,ox}$ [a]	Enamine	$E_{p,ox}$ [a]
1a	0.61	**2a**	0.77
1b	0.85	**2b**	0.86
1c	0.92	**2c**	1.12
1d	0.79	**2d**	0.64
		2e	0.68
		2f	0.62

[a] Peak potentials from cyclic voltammograms at 25 to 400 mV s^{-1} scan rates vs. Ag/AgNO$_3$; electrolyte: acetonitrile (0.1M LiClO$_4$).

Table 2. Reactions of 2-vinylpyrroles **1a–d** with enamines **2a—c**.

Diene	Dienophile	Method	Product	Yield
1a	**2a**	SET, -2H$^+$, -2e$^-$, -HN(CH$_3$)$_2$, **A**	 **3** + **4**	8% + 49%
1a	**2b**	**A**	 **5**	43%
1b	**2b**	**A**	 **6**	60%
1c	**2b**	**A**	 **7**	47%
1c	**2c**	**A**	 **8**	43%
1d	**2b**	**A**	 **9**	66%

In cycloadditions with enamines **2a–c**, yields were generally good and were not affected by functional groups on the pyrrole nucleus (Scheme 3). However, subsequent aromatisation of the initially formed dihydroindolizines, with loss of dimethylamine, could not be prevented. This aromatisation occurred almost instantaneously in the reaction with nitroenamine **2c**, whereas the respective cycloadducts formed from cyanoenamine **2b** lost dimethylamine during work-up, and the dihydroindolizine **3a**, which decomposes within several weeks, was isolated. Consequently, the trend towards aromatisation increased with the strength of the acceptor adjacent to the dimethylamino moiety.

If the α'-methyl-substituted enamine **2d** was used, then aromatisation of the cycloadducts was impossible, but the yields were lower than those from the reactions of its α'-

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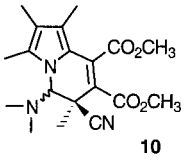
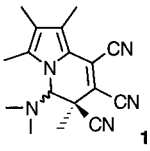
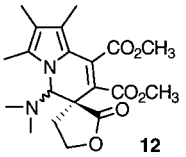
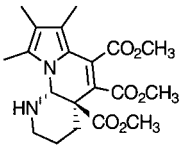
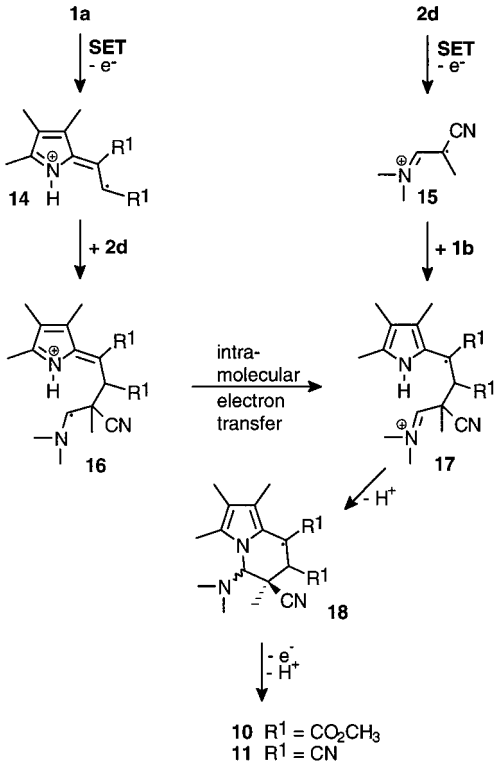
Table 3. Reactions of 2-vinylpyrroles **1a** and **1b** with enamines **2d–f**.

Diene	Dienophile	Method	Product	Yield
1a	**2d**	SET, - 2H⁺, -2e⁻ **A**	 **10**	37%
1b	**2d**	**A**	 **11**	54%
1a	**2e**	**A**	 **12**	33%
1a	**2f**	**A**	 **13**	25%

unsubstituted analogue **2b**, and dropped even further in reactions with the bulky enamines **2e** and **2f** (Table 3). This can be explained by a greater steric hindrance of the enamines **2d–f** compared to **2a–c**, rather than by a higher thermodynamic stability of the aromatic products, because aromatisation does not occur during the course of the cycloaddition reaction. In contrast to the stereoselective formation of **3** and **13**, the dihydro-indolizines **10**, **11** and **12** were obtained as a 1:1 (**10**, **11**) or 1:4 (**12**) mixture of the *cis*/*trans*-diastereomers, which we did not separate.



Scheme 3. Proposed mechanisms for electron-transfer-initiated cycloaddition reactions between 2-vinylpyrroles **1** and β-acceptor-substituted enamines **2**.

As a basis for the mechanistic interpretation of these reactions, ab initio calculations (UHF/3-21G+) of the radical cations **14**, derived from 2-vinylpyrroles **1**, were performed. These indicated the formation of a radical cation with the positive charge stabilised as an iminium ion, while the spin density is increased at the terminus of the former vinylic double bond. This was verified by the fact that a mixture of the (*E*) and (*Z*) isomers was found in the recovered material after the reaction: there had been a rotation around the former double bond at the radical cation stage. Consequently, product formation should not be sensitive to the double-bond configuration of the 2-vinylpyrroles. Because the oxidation potentials of several enamines **2** are lower than those of the applied 2-vinylpyrroles, the initial formation of the radical cations **15** must also be considered. On the basis of previous mechanistic investigations of radical cation [4+2] cycloadditions,[2a] we propose two reaction pathways starting with the attack of the electrophilic radical cation of either diene (**14**) or dienophile (**15**) at the nucleophilic site of the respective reactant to give the distonic radical cations **16** and **17**, respectively (Scheme 3). Radical cation **16** would then undergo an intramolecular electron transfer to give the thermodynamically favoured **17**. Thus, both pathways lead to the same key intermediate **17**, which would immediately undergo cyclisation by an intramolecular attack of the pyrrole nitrogen on the iminium carbon to give radical **18**. In both intermediates **17** and **18** the radical is stabilised by both an electron-donating and an electron-withdrawing group (*captodative effect*). The reaction is terminated by single-electron oxidation followed by deprotonation leading to the cycloadducts **10** and **11** as the only products.

Obviously, the slightly improved yields obtained with dicyano-substituted 2-vinylpyrroles, as compared to the corresponding dialkoxycarbonyl-substituted substrates (Tables 2 and 3), can be rationalised by the enhanced stabilisation of the radical centre next to the cyano group, as well as by the lower steric demand.

The proposed mechanism also accounts for the mixtures of diastereomers observed when the dienophiles **2d** or **2e** were employed. Rotation around the newly formed single bond before ring-closure should be possible, especially if the substitutents at the newly built quaternary carbon are of similar size. On the other hand, an equilibration on the product stage due to ring opening of the aminal substructure, can be ruled out.[15] The highly diastereoselective addition of the tetrahydro-pyridine **2f** to give the pyrrolonaphthyridine **13** could be explained as a hindered rotation of the tetrahydropyridine ring at the stage of the intermediates **16** and **17**, respectively.

Experimental Section

Melting points: Leica Galan III. Melting points are uncorrected. Mass spectra and high-resolution MS: Varian MAT 711 and MAT 955Q mass spectrometer (EI) with an ionisation potential of 70 eV. Infrared spectra:

Nicolet 750 FT infrared spectrometer. ^{1}H NMR spectra: Bruker AM 400 and AC 200; chemical shifts relative to $CDCl_3$. ^{13}C NMR spectra including DEPT: Bruker AM 400 and AC 200. UV/Vis spectra: Beckman DU-64 spectrophotometer. Elemental analysis: Mikroanalytisches Labor Beller, Göttingen. Oxidation potentials: BAS (Bioanalytical System) CV-50W voltammetric analyser; platinum working electrode (1.6 mm diameter), $Ag/AgNO_3$ reference electrode, electrolyte: acetonitrile (0.1 M $LiClO_4$). Unless otherwise noted, all chemicals were of the highest purity commercially available, and were used without further purification. All the reactions were monitored by thin-layer chromatography on Merck 60 F_{254} (0.2 mm) sheets, which were visualised with ethanolic molybdophosphoric acid, UV light or a solution of *p*-dimethylaminobenzaldehyde in methanol/hydrochloric acid. Preparative flash chromatography was performed on Merck (0.04 – 0.063 mm) silica gel with positive air pressure. HPLC was performed on a Waters-590 module equipped with a Knaur refractometer, a Eurospher 100-C18 (7 μm) 20 × 300 mm column and a solvent rate of 20 mL min^{-1}. PE (light petroleum, b.p. 40 – 60°C), MTBE (methyl *tert*-butyl ether) and other solvents used for chromatography were distilled before use. Tetrahydrofuran (THF) was distilled from potassium.

Compounds **1a**,[16] **2a**,[11] **2d**,[12] **2e**[13] and **2f**[14] were prepared according to literature procedures. Compounds **2b** (Aldrich) and **2c** (Lancaster) were used as supplied.

General procedure: The reaction solution was potentiostatically electrolysed at the potentials given below in an electrochemical cell (undivided) (max. volume 100 mL) under vigorous stirring. Anode: carbon, 20 cm^2; cathode: carbon, 20 cm^2; reference electrode: $Ag/AgNO_3$; electrolyte: acetonitrile (0.1 M $LiClO_4$); separation of the electrodes: 3 cm. Prior to use, the electrodes were activated by ultrasonic treatment in acetonitrile. In the course of the electrolysis, the current dropped from 20 mA to 2 mA and the reaction solutions darkened slightly. The current consumption is given in Coulombs for each experiment. At the end of the reaction, the electrodes were subjected to ultrasonic treatment: i) 10 min in methanol (60 mL), ii) 5 min in acetonitrile (60 mL). The combined solutions were evaporated under reduced pressure and then treated with brine. The aqueous layer was extracted five times with chloroform and dried over $MgSO_4$ and the solvent evaporated. Chromatographic separation was performed on silica gel, unless otherwise stated. With the exception of **6**, yields are based on recovered material (90 % turnover).

2-(3,4,5-Trimethyl-1*H*-pyrrol-2-yl)-but-2-enedinitrile (**1b**): A solution of 2,3,4-trimethyl-1*H*-pyrrole[17] (86 mg, 0.79 mmol) and but-2-ynedinitrile[18] (60 mg, 0.79 mmol) in THF (3 mL) was stirred for 1 h at RT. Evaporation and separation of the reaction mixture by flash chromatography (MTBE/PE 1:5) afforded 93 mg of **1b** (63 %) and 13 mg of the (*Z*) isomer (9 %), which readily isomerises, to give a total yield of 72 % of the (*E*) isomer. **(*E*) Isomer 1b**: Bright yellow solid; m.p. 128 – 129 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 9.13 (br, 1H, NH), 5.21 (s, 1H, vinyl-H), 2.34 (s, 3H, 4′-CH_3), 2.27 (s, 3H, 5′-CH_3), 1.93 (s, 3H, 3′-CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 134.3 (s), 130.0 (s), 120.3 (s), 119.8 (s) 119.5 (s), 118.8 (s), 116.4 (s, Ar, C≡C), 89.1 (d, C≡C), 11.8 (q), 10.8 (q), 8.6 (q, CH_3) cm^{-1}; IR (film, CCl_4): $\tilde{\nu}_{max}$ = 3443 (m), 30.84 (w) 2923 (w), 2863 (w), 2198 (s), 1533 (vs), 1474 (vs), 1457 (s) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 185 (100, M$^+$), 170 (50), 158 (39), 143 (20); HR-MS calcd for $C_{11}H_{11}N_3$: 185.0953, found 185.0953; UV/Vis (MeOH): λ_{max} = 402, 270 nm.

Dimethyl 2-(4-ethoxycarbonyl-3,5-dimethyl-1*H*-pyrrol-2-yl)-but-2-enedioate (**1c**): A solution of ethyl 2,4-dimethyl-1*H*-pyrrole-3-carboxylate[19] (150 mg, 0.90 mmol) and DMAD (127 mg, 0.90 mmol) in THF (3 mL) was stirred for 12 h at RT. Evaporation and separation of the reaction mixture by RP-HPLC (methanol/water 7:3) afforded 190 mg of **1c** (68 %) as a 1:3 mixture of (*Z*)/(*E*) isomers. Bright yellow solid; m.p. 94 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 11.70 (br, 0.75H, NH), 8.43 (br, 0.25H, NH), 5.97 (s, 0.75H, vinyl-H), 5.95 (s, 0.25H, vinyl-H), 4.28 (q, ^3J(H,H) = 7.0 Hz, 0.5H, OCH_2) 4.27 (q, ^3J(H,H) = 7.0 Hz, 1.5H, OCH_2) , 3.93 (s, 0.75H, OCH_3), 3.86 (s, 2.25H, OCH_3), 3.77 (s, 2.25H, OCH_3), 3.76 (s, 0.75H, OCH_3), 2.53 (s, 2.25H, 5′-CH_3), 2.48 (s, 0.75H, 5′-CH_3), 2.39 (s, 0.75H, 3′-CH_3), 2.29 (s, 2.25H, 3′-CH_3), 1.34 (t, ^3J(H,H) = 7.0 Hz, 3H, OCH_2CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 168.5 (s, 0.75C), 168.3 (s, 0.25C), 168.1 (s, 0.75C), 165.8 (s, 0.25C), 165.4 (s, 0.75C), 165.2 (s, 0.25C, C=O), 139.6 (s, 0.25C), 139.2 (s, 0.25C); 138.7 (s, 0.75C), 137.7 (s, 0.75C), 128.2 (s, 0.75C), 126.4 (s, 0.25C), 120.7 (s, 0.25C), 120.6 (s, 0.75C), 114.4 (d, 0.75C), 113.8 (s, 0.25C), 113.0 (s, 0.75C), 115.5 (d, 0.25C, Ar, C≡C), 59.3 (t, 1C, OCH_2), 52.9 (q, 0.75C), 52.7 (q, 0.25C), 52.2 (q, 0.75C), 51.6 (q, 0.25C, OCH_3), 14.5 (q, 1C), 14.3 (q, 0.25C), 14,0 (q, 0.75C), 12.0 (q, 0.75C), 11.4 (q, 0.25C, CH_3); IR (ATR): $\tilde{\nu}_{max}$ = 3315 (br m), 2981 (m), 2952 (m), 1697 (vs), 1592 (s), 1432 (s), 1256 (vs), 1205 (vs), 1092 (vs) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 309 (100, M$^+$), 278 (14), 264 (6), 249 (22); HR-MS calcd for $C_{15}H_{19}NO_6$: 309.1212, found 309.1212; UV/Vis (MeOH): λ_{max} = 360, 265 nm.

Dimethyl 2-(3-ethoxy-4-ethoxycarbonyl-5-methyl-1*H*-pyrrol-2-yl)-but-2-enedioate (**1d**): A solution of ethyl 4-ethoxy-5-methyl-1*H*-pyrrole-3-carboxylate[20] (115 mg, 0.58 mmol) and DMAD (81 mg, 0.58 mmol) in THF (3 mL) was stirred for 3 h at RT. Evaporation and separation of the reaction mixture by flash chromatography (MTBE/PE 1:1) afforded 132 mg of (*E*)-**1d** (67 %) and 14 mg of the (*Z*) isomer (7 %) to give a total yield of 74 %.

(*E*)-1d: Yellow solid; m.p. 72 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 12.14 (br, 1H, NH), 5.51 (s, 1H, vinyl-H), 4.29 (q, ^3J(H,H) = 7.0 Hz, 2H, $COOCH_2$), 3.96 (q, ^3J(H,H) = 7.0 Hz, 2H, OCH_2), 3.85 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 2.54 (s, 3H, 5′-CH_3), 1.35 (t, ^3J(H,H) = 7.0 Hz, 3H, $COOCH_2CH_3$), 1.32 (t, ^3J(H,H) = 7.0 Hz, 3H, OCH_2CH_3);^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 169.1 (s), 168.5 (s), 163.5 (s, C=O), 150.5 (s), 138.7 (s), 137.8 (s), 114.3 (s, Ar), 107.0 (d), 105.8 (s, C≡C), 71.8 (t, $COOCH_2$), 59.5 (t, OCH_2), 52.7 (q), 52.0 (q, OCH_3), 15.2 (q, $COOCH_2CH_3$), 15.0 (q, OCH_2CH_3), 14.2 (q, CH_3); IR (ATR): $\tilde{\nu}_{max}$ = 3205 (w), 2982 (m), 2951 (m), 1742 (s), 1700(s), 1567 (s), 1434 (s), 1285 (vs), 1205 (vs), 1084 (vs) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 339 (34, M$^+$), 265 (16), 233 (100), 121 (21); HR-MS calcd for $C_{16}H_{21}NO_7$: 339.1318, found 339.1318; UV/Vis (MeOH): λ_{max} = 356, 247(sh), 217(sh) nm.

(*Z*)-1d: Bright yellow solid; m.p. 142 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.38 (br, 1H, NH), 6.13 (s, 1H, vinyl-H), 4.29 (q, ^3J(H,H) = 7.0 Hz, 2H, $COOCH_2$), 4.00 (q, ^3J(H,H) = 7.0 Hz, 2H, OCH_2), 3.92 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 2.48 (s, 3H, 5′-CH_3), 1.35 (t, ^3J(H,H) = 7.0 Hz, 6H, $COOCH_2CH_3$, OCH_2CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 167.7 (s), 166.3 (s), 163.6 (s, C=O), 149.0 (s), 138.6 (s), 137.2 (s), 113.9 (s, Ar), 109.1 (d), 107.4 (s, C≡C), 71.3 (t, $COOCH_2$), 59.8 (t, OCH_2), 52.9 (q), 51.7 (q, OCH_3), 15.3 (q, $COOCH_2CH_3$), 14.8 (q, OCH_2CH_3), 14.4 (q, CH_3); IR (ATR): $\tilde{\nu}_{max}$ = 3310 (m), 2982 (m), 2952 (m), 1742 (vs), 1704 (vs), 1591 (vs), 1433 (vs), 1276 (vs), 1231 (vs), 1196 (vs), 1168 (vs), 1085 (vs) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 339 (31, M$^+$), 308 (4), 294 (6), 281 (10), 265 (16), 233 (100); HR-MS calcd for $C_{16}H_{21}NO_7$: 339.1318, found 339.1318; UV/Vis (MeOH): λ_{max} = 328, 260, 208 nm.

Trimethyl 5,6-*trans*-5-dimethylamino-1,2,3-trimethyl-5,6-dihydroindolizine-6,7,8-tricarboxylate (**3**) and **trimethyl 1,2,3-trimethylindolizine-6,7,8-tricarboxylate** (**4**): Following the general procedure above, 2-vinylpyrrole (**1a**, 30 mg, 0.12 mmol) and methyl 3-dimethylaminoacrylate (**2a**, 31 mg, 0.24 mmol) were electrolysed at 500 mV (current consumption 41 C). Separation of the reaction mixture by RP-HPLC (methanol/water 8:2) afforded 20 mg of **3** (49 %) and 3 mg of the aromatised product **4** (8 %) to give a total yield of 57 %.

Trimethyl 5,6-*trans*-5-dimethylamino-1,2,3-trimethyl-5,6-dihydro-indolizine-6,7,8-tricarboxylate (**3**): Yellow solid; m.p. 107 – 109 °C, decomposition to **4**); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 5.18 (d, ^3J(H,H) = 1.0 Hz, 1H, H5), 4.10 (d, ^3J(H,H) = 1.0 Hz, 1H, H6), 3.92 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 2.17 (s, 9H, 3-CH_3, NCH_3), 1.95 (s, 3H, 1-CH_3), 1.89 (s, 3H, 2-CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 172.1 (s), 168.0 (s), 165.9 (s, C=O), 134.8 (s), 132.5 (s), 123.4 (s), 120.6 (s), 119.0 (s), 108.4 (s, Ar, C=C), 71.4 (d, C5), 52.9 (q), 52.4 (q), 52.1 (q, OCH_3), 39.8 (q, NCH_3), 39.2 (d, C6), 9.8 (q), 9.3 (q), 9.0 (q, CH_3); IR (film, CCl_4): $\tilde{\nu}_{max}$ = 2993 (w), 2951 (w), 2924 (w), 1731 (vs), 1438 (s), 1276 (s), 1240 (s), 1222 (s) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 333 (100, M$^+$ – $HNMe_2$), 302 (33), 275 (19), 251 (18), 215 (49), 157 (37), 121 (69); HR-MS calcd for $C_{17}H_{19}O_6N$: 333.1212, found 333.1212; UV/Vis (MeOH): λ_{max} = 380, 275 nm.

Trimethyl 1,2,3-trimethylindolizine-6,7,8-tricarboxylate (**4**): Bright yellow solid; m.p. 134 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.25 (s, 1H, H5), 3.96 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 2.42 (s, 3H, 3-CH_3), 2.19 (s, 3H, 1-CH_3), 2.15 (s, 3H, 2-CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 167.1 (s), 167.0 (s), 166.1 (s, C=O), 126.6 (d), 126.5 (s), 124.4 (s), 122.8 (s), 120.8 (s), 116.5 (s), 113.0 (s), 111.4 (s, Ar), 52.6 (q), 52.5 (q), 52.3 (q, OCH_3), 9.9 (q, q), 9.5 (q, CH_3); IR (film, CCl_4): $\tilde{\nu}_{max}$ = 3024 (w), 2996 (w), 2951 (w), 2925 (w), 1730 (vs), 1439 (s), 1276 (vs), 1240 (s), 1222 (s) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 333 (100, M$^+$), 302 (30), 286 (21), 215 (42), 157 (43), 69 (50), 57 (88), 55 (87); HR-MS calcd for $C_{17}H_{19}NO_6$: 333.1212, found 333.1212; UV/Vis (MeOH): λ_{max} = 399, 339, 275 nm.

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Dimethyl 6-cyano-1,2,3-trimethylindolizine-7,8-dicarboxylate (**5**): Following the general procedure, 2-vinylpyrrole (**1a**, 25 mg, 0.10 mmol) and 3-dimethylaminoacryl nitrile (**2b**, 19 mg, 0.20 mmol) were electrolysed at 500 mV (current consumption 60 C). Separation of the reaction mixture by flash chromatography (dichloromethane) afforded 12 mg of the indolizine **5** (43 %). Yellow solid; m.p. 220 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.06 (s, 1 H, H5), 4.02 (s, 3 H, OCH_3), 3.94 (s, 3 H, OCH_3), 2.43 (s, 3 H, 3-CH_3), 2.22 (s, 3 H, 2-CH_3), 2.19 (s, 3 H, 1-CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 166.9 (s), 163.7 (s, C=O), 129.7 (d), 129.3 (s), 128.1 (s), 123.1 (s), 122.6 (s), 117.4 (s), 116.6 (s), 110.0 (s), 93.3 (s, Ar, C≡N), 52.9 (q), 52.5 (q, OCH_3), 9.9 (q), 9.5 (q), 9.2 (q, CH_3); IR (film, CCl_4): $\tilde{\nu}_{max}$ = 2953 (s), 2924 (s), 2227 (s), 1733 (vs), 1705 (s), 1446 (m), 1282 (s), 1221 (vs) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 300 (79, M$^+$), 285 (10), 269 (22), 253 (26), 241 (4), 182 (100); HR-MS calcd for $C_{16}H_{16}N_2O_4$: 300.1110, found 300.1110; UV/Vis (MeOH): λ_{max} = 394, 353, 294, 268 nm.

6,7,8-Tricyano-1,2,3-trimethylindolizine (**6**): Following the general procedure, 2-vinylpyrrole (**1b**, 29 mg, 0.16 mmol) and 3-dimethylaminoacrylonitrile (**2b**, 31 mg, 0.32 mmol) were electrolysed at 610 mV (current consumption 58 C). Separation of the reaction mixture by flash chromatography (MTBE/PE 2:1) afforded 22 mg of the indolizine **6** (60 %). Bright red solid; m.p. 251 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.20 (s, 1 H, H5), 2.60 (s, 3 H, CH_3), 2.51 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 131.4 (s, s), 130.6 (d), 125.1 (s), 123.6 (s), 118.8 (s), 114.0 (s), 113.8 (s), 113.2 (s), 108.6 (s), 94.3 (s, Ar, C≡N), 10.1 (q), 9.7 (q), 9.5 (q, CH_3); IR (ATR): $\tilde{\nu}_{max}$ = 3157 (w), 3072 (m), 2925 (m), 2854 (s), 2232 (s), 2221 (s), 1507 (vs), 1435 (vs), 1393 (s) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 234 (86, M$^+$), 233 (100), 219 (25), 207 (7); HR-MS calcd for $C_{14}H_{10}N_4$: 234.0905, found 234.0905; UV/Vis (MeOH): λ_{max} = 463, 354, 271 nm.

2-Ethyl-7,8-dimethyl 6-cyano-1,3-dimethylindolizine-2,7,8-tricarboxylate (**7**): Following the general procedure, 2-vinylpyrrole (**1c**, 30 mg, 0.10 mmol) and 3-dimethylaminoacrylonitrile (**2b**, 19 mg, 0.20 mmol) were electrolysed at 700 mV (current consumption 73 C). Separation of the reaction mixture by flash chromatography (MTBE/PE 1:1) afforded 14 mg of the indolizine **7** (47 %). Orange solid; m.p. 188–189 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.17 (s, 1 H, H5), 4.39(q, ^3J(H,H) = 7.0 Hz, 2 H, OCH_2), 4.02 (s, 3 H, OCH_3), 3.95 (s, 3 H, OCH_3), 2.74 (s, 3 H, 3-CH_3), 2.45 (s, 3 H, 1-CH_3), 1.40 (t, ^3J(H,H) = 7.0 Hz, 3 H, OCH_2CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 166.1 (s), 164.6 (s), 163.1 (s, C=O), 131.8 (s), 131.0 (d), 128.7 (s), 123.3 (s), 121.4 (s), 119.3 (s), 116.3 (s), 112.3 (s), 96.4 (s; Ar, C≡N), 60.8 (t, OCH_2), 53.1 (q), 52.8 (q, OCH_3), 14.2 (q, OCH_2CH_3), 11.0 (q), 10.3 (q, CH_3); IR (ATR): $\tilde{\nu}_{max}$ = 2980 (m), 2955 (m), 2918 (m), 2849 (w), 2231 (m), 1718 (vs), 1543 (m), 1441 (s), 1278 (vs), 1254 (vs), 1201 (vs), 1108 (vs) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 358 (100, M$^+$), 343 (12), 331 (62), 309 (59), 278 (17), 240 (36), 220 (20); HR-MS calcd for $C_{18}H_{18}N_2O_6$: 358.1165, found 358.1165; UV/Vis (MeOH): λ_{max} = 403, 341, 272 nm.

2-Ethyl-7,8-dimethyl 1,3-dimethyl-6-nitroindolizine-2,7,8-tricarboxylate (**8**): Following the general procedure, 2-vinylpyrrole (**1c**, 29 mg, 0.09 mmol) and dimethyl(2-nitrovinyl)amine (**2c**, 22 mg, 0.19 mmol) were electrolysed at 800 mV (current consumption 37 C). Separation of the reaction mixture by flash chromatography (MTBE/PE 1:3) afforded 14 mg of the indolizine **8** (43 %). Orange solid; m.p. 117–119 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.64 (s, 1 H, H5), 4.40 (q, ^3J(H,H) = 7.0 Hz, 2 H, OCH_2), 3.99 (s, 3 H, OCH_3), 3.96 (s, 3 H, OCH_3), 2.77 (s, 3 H, 3-CH_3), 2.51 (s, 3 H, 1-CH_3), 1.41 (t, ^3J(H,H) = 7.0 Hz, 3 H, OCH_2CH_3);^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 165.3 (s), 164.6 (s), 164.1 (s, C=O), 135.9 (s), 129.8 (s), 127.8 (s), 124.1 (d), 123.0 (s), 122.0 (s), 117.9 (s), 113.6 (s, Ar), 60.8 (t, OCH_2), 53.2 (q, q, OCH_3), 14.3 (q, OCH_2CH_3), 11.1 (q), 10.6 (q, CH_3); IR (ATR): $\tilde{\nu}_{max}$ = 2983 (w), 2953 (w),1741 (vs), 1718 (s), 1536 (s), 1325 (s), 1312 (s), 1263 (vs) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 378 (100, M$^+$), 349 (24), 333 (18), 309 (8), 215 (21), 187 (18); HR-MS calcd for $C_{17}H_{18}N_2O_8$: 378.1063, found 378.1063; UV/Vis (MeOH): λ_{max} = 353, 294, 255 nm.

2-Ethyl-7,8-dimethyl 6-cyano-1-ethoxy-3-methylindolizine-2,7,8-tricarboxylate (**9**): Following the general procedure, 2-vinylpyrrole (**1d**, 25 mg, 0.07 mmol) and 3-dimethylaminoacrylonitrile (**2b**, 14 mg, 0.15 mmol) were electrolysed at 550 mV (current consumption 51 C). Separation of the reaction mixture by RP-HPLC (methanol/water 7:3) afforded 16 mg of the indolizine **9** (66 %). Bright yellow solid; m.p. 155–156 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.09 (s, 1 H, H5), 4.40 (q, ^3J(H,H) = 7.0 Hz, 2 H, $COOCH_2$), 4.03 (q, ^3J(H,H) = 7.0 Hz, 2 H, OCH_2), 4.00 (s, 3 H, OCH_3), 3.93 (s, 3 H, OCH_3), 2.75 (s, 3 H, 3-CH_3), 1.42 (t, ^3J(H,H) = 7.0 Hz, 3 H, $COOCH_2CH_3$). 1.40 (t, ^3J(H,H) = 7.0 Hz, 3 H, OCH_2CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 165.4 (s), 163.2 (s), 162.8 (s, C=O), 142.0 (s), 131.2 (s), 130.2 (d), 127.6 (s), 117.6 (s), 116.2 (s), 113.8 (s), 110.9 (s), 97.3 (s, Ar, C≡N), 72.8 (t, $COOCH_2$), 60.9 (t, OCH_2), 53.0 (q), 52.8 (q, OCH_3), 15.3 (q, $COOCH_2CH_3$), 14.3 (q, OCH_2CH_3), 10.8 (q, CH_3); IR (ATR): $\tilde{\nu}_{max}$ = 2983 (w), 2954 (w), 2931 (w), 2856 (w), 2232 (w), 1748 (s), 1727 (s), 1551 (m), 1460 (m), 1435 (m), 1278 (vs), 1205 (m) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 388 (36, M$^+$), 361 (11), 359 (26), 345 (19), 313 (87), 247 (63), 167 (31), 149 (100); HR-MS calcd for $C_{19}H_{20}N_2O_7$: 388.1271, found 388.1271; UV/Vis (MeOH): λ_{max} = 415, 345, 273; $C_{19}H_{20}N_2O_7$: calcd C 58.76, H 5.19, N 7.21; found C 58.87, H 5.34, N 7.13 nm.

Dimethyl 6-cyano-5-dimethylamino-1,2,3,6-tetramethyl-5,6-dihydro-indolizine-7,8-dicarboxylate (**10**): Following the general procedure, 2-vinylpyrrole (**1a**, 30 mg, 0.12 mmol) and 3-dimethylamino-2-methylacrylonitrile (**2d**, 27 mg, 0.24 mmol) were electrolysed at 500 mV (current consumption 71 C). Separation of the reaction mixture by flash chromatography (MTBE/PE 1:1) afforded 14 mg of **10** (37 %) as a 1:1 mixture of diastereomers. Yellow solid; m.p. 92 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.58 (s, 0.5 H, H5), 4.47 (s, 0,5 H, H5), 3.63 (s, 1.5 H, OCH_3), 3.55 (s, 1.5 H, OCH_3), 3.52 (s, 1.5 H, OCH_3), 3.42 (s, 1.5 H, OCH_3), 2.26 (s, 3 H, NCH_3), 2.01 (s, 1.5 H, CH_3), 1.91 (s, 1.5 H, CH_3), 1.90 (s, 3 H, NCH_3), 1.83 (s, 1.5 H, CH_3), 1.77 (s, 1.5 H, CH_3), 1.75 (s, 3 H, 2 CH_3), 1.74 (s, 1.5 H, CH_3), 1.42 (s. 1.5 H, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 167.2 (s, 0.5 C), 167.1 (s, 0.5 C), 165.2 (s, 0.5 C), 164.6 (s, 0.5 C, C=O), 134.8 (s, 0.5 C), 133.2 (s, 0.5 C), 132.1 (s, 0.5 C), 132.0 (s, 0.5 C), 124.1 (s, 0.5 C), 123.9 (s, 0.5 C), 121.7 (s, 0.5 C), 120.6 (s, 0.5 C), 120.5 (s, 0.5 C), 119.9 (s, 0.5 C), 119.7 (s, 1 C); 112.6 (s, 0.5 C), 111.7 (s, 0.5 C, Ar, C=C, C≡N), 76.8 (d, 0.5 C), 76.7 (d, 0.5 C, C5), 52.6 (q, 0.5 C), 52.5 (q, 0.5 C), 52.1 (q, 0.5 C), 52.0 (q, 0.5 C, OCH_3), 42.1 (q, 1 C), 41.8 (q, 1 C, NCH_3), 41.6 (s, 0.5 C), 39.0 (s, 0.5 C, C6), 25.0 (q, 0.5 C), 20.7 (q, 0.5 C, 6-CH_3), 10.7 (q, 0.5 C), 10.5 (q, 0.5 C), 9.5 (q, 0.5 C), 9.3 (s, 0.5 C), 9.1 (q, 1 C, CH_3); IR (ATR): $\tilde{\nu}_{max}$ = 2951 (m), 2924 (m), 2221 (w), 1740 (s), 1707 (s), 1577 (m), 1435 (s), 1269 (vs), 1242 (vs), 1221 (s) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 359 (68, M$^+$), 328 (19), 315 (15), 300 (45), 88 (100); HR-MS calcd for $C_{19}H_{25}N_3O_4$: 359.1845, found 359.1848; UV/Vis (MeOH): λ_{max} = 376 nm.

5-Dimethylamino-1,2,3,6-tetramethyl-6,7,8-tricyano-5,6-dihydro-indolizine (**11**): Following the general procedure, 2-vinylpyrrole (**1b**, 30 mg, 0.16 mmol) and 3-dimethylamino-2-methylacrylonitrile (**2d**, 35 mg, 0.32 mmol) were electrolysed at 500 mV (current consumption 56 C). Separation of the reaction mixture by flash chromatography (MTBE/PE 1:1) afforded 16 mg of **11** (54 %) as a 1:1 mixture of diastereomers. Yellow solid; m.p. 143 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.95 (s, 0.5 H, H5), 4.89 (s, 0,5 H, H5), 2.36 (s, 3 H, NCH_3), 2.34 (s, 1.5 H, CH_3), 2.32 (s, 1.5 H, CH_3), 2.29 (s, 1.5 H, CH_3), 2.25 (s, 1.5 H, CH_3), 2.24 (s, 3 H, NCH_3), 1.98 (s, 1.5 H, CH_3), 1.96 (s, 1.5 H, CH_3), 1.84 (s, 1.5 H, CH_3), 1.59 (s, 1.5 H, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 136.8 (s, 0.5 C), 135.8 (s, 0.5 C), 128.6 (s, 0.5 C), 127.5 (s, 0.5 C), 122.2 (s, 0.5 C), 121.7 (s, 1 C), 121.5 (s, 0.5 C), 119.9 (s, 0.5 C), 119.4 (s, 0.5 C), 117.5 (s, 0.5 C), 117.0 (s, 0.5 C), 115.1 (s, 0.5 C), 114.5 (s, 0.5 C), 113.2 (s, 1 C), 104.0 (s, 0.5 C), 101.1 (s, 0.5 C, Ar, C=C, C≡N), 76.1 (d, 0.5 C), 76.0 (d, 0.5 C, C5), 42.5 (s, 0.5 C, C6), 41.6 (q, 1 C), 41.2 (q, 1 C, NCH_3), 39.5 (s, 0.5 C, C6), 24.6 (q, 0.5 C), 20.7 (q, 0.5 C, 6-CH_3), 11.0 (q, 0.5 C), 10.7 (q, 0.5 C), 10.0 (q, 0.5 C), 9.8 (q, 0.5 C), 9.0 (q, 1 C, CH_3); IR (ATR): $\tilde{\nu}_{max}$ = 2954 (m), 2924 (m), 2858 (m), 2797 (w), 2235 (m), 2198 (s), 1569 (vs), 1530 (vs), 1475 (vs), 1434 (vs), 1342 (s) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 293 (100, M$^+$), 278 (20), 249 (28), 235 (25), 233 (33), 222 (13), 202 (58); HR-MS calcd for $C_{17}H_{19}N_5$: 293.1640, found 293.1640; UV/Vis (MeOH): λ_{max} = 426, 266 nm.

Spiro[γ-butyrolactone-2,6′-(7,8-dicarbomethoxy-5-dimethylamino-1,2,3-trimethyl)]-5,6-dihydroindolizine (**12**): Following the general procedure described above, 2-vinylpyrrole (**1a**, 35 mg, 0.14 mmol) and 3-dimethylaminomethylenedihydrofuran-2-one (**2e**, 40 mg, 0.28 mmol) were electrolysed at 420 mV (current consumption 60 C). Separation of the reaction mixture by flash chromatography (MTBE/PE 1:1) afforded 17 mg of **12** (33 %) as a 1:4 mixture of diastereomers. Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.85 (s, 0.8 H, H5), 4.70 (s, 0.2 H, H5), 4.57 (m, 0.2 H, H4′), 4.52 (m, 0.8 H, H4′), 4.42 (m, 0.8 H, H4′), 4.34 (m, 0.2 H, H4′), 3.90 (s, 2.4 H, OCH_3), 3.86 (s, 0.6 H, OCH_3), 3.74 (s, 3 H, OCH_3), 3.02 (m, 0.2 H, H3′), 2.63 (m, 1 H, H3′), 2.36 (s, 4.8 H, NCH_3), 2.27 (s, 1.2 H, NCH_3), 2.24 (s, 2.4 H, CH_3), 2.18 (s, 0.6 H, CH_3), 2.16 (m, 0.8 H, H3′), 1.93 (s, 4.8 H, CH_3), 1.92 (s, 0.6 H, CH_3), 1.91 (s, 0.6 H, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 174.6 (s), 167.6 (s), 165.5 (s, C=O), 134.0 (s), 131.4 (s), 122.5 (s), 120.7 (s),

119.3 (s), 114.7 (s, Ar, C=C), 73.3 (d, C5), 64.8 (t, OCH_2), 52.6 (q), 52.0 (q, OCH_3), 50.5 (s, C6), 41.4 (q, NCH_3), 34.5 (t, 6-CH_2), 10.6 (q), 9.2 (q), 9.1 (q, CH_3); IR (ATR): $\tilde{\nu}_{max} = 2951$ (m), 2923 (m), 1775 (s), 1739 (vs), 1703 (vs), 1583 (m), 1434 (s), 1280 (vs), 1212 (vs) cm^{-1}; MS (70 eV, EI): m/z (%) = 390 (14, M^+), 331 (32), 229 (15), 169 (56), 43 (100); HR-MS calcd for $C_{20}H_{26}N_2O_6$: 390.1791, found 390.1790; UV/Vis (MeOH): $\lambda_{max} = 374$ nm.

Trimethyl 7,8,9-trimethyl-1,3,4,10a-tetrahydro-2*H*-pyrrolo[1,2-*a*][1,8]naphthyridine-4a,5,6-tricarboxylate (**13**): Following the general procedure, 2-vinylpyrrole (**1a**, 30 mg, 0.12 mmol) and methyl 1,4,5,6-tetrahydropyridine-3-carboxylate (**2f**, 34 mg, 0.24 mmol) were electrolysed at 420 mV (current consumption 96 C). Separation of the reaction mixture by flash chromatography (MTBE) afforded 9 mg of **13** (25%) as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 5.02$ (s, 1H, H10a), 3.89 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 3.07 (m, 1H, H4), 2.99 (m, 1H, H2), 2.75 (m, 1H, H2′), 221 (s, 3H, CH_3), 1.95 (m, 1H, H4′), 1.88 (s, 3H, CH_3), 1.85 (s, 3H, CH_3), 1.51 (m, 1H, H3), 1.14 (m, 1H, H3′); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 174.3$ (s), 168.0 (s), 166.5 (s, C=O), 135.5 (s), 131.0 (s), 124.2 (s), 119.1 (s), 119.0 (s), 112.4 (s; Ar, C=C), 69.0 (d, C10a), 52.8 (q), 52.4 (q), 51.8 (q, OCH_3), 50.8 (s, C4a), 44.8 (t, C2), 30.7 (t, C4), 22.5 (t, C3), 9.5 (q), 9.3 (q), 8.9 (q, CH_3); IR (ATR): $\tilde{\nu}_{max} = 3316$ (w), 2950 (m), 2861 (w), 1739 (vs), 1709 (vs), 1550 (m), 1434 (s), 1258 (vs), 1221 (vs), 1200 (s) cm^{-1}; MS (70 eV, EI): m/z (%) = 390 (90, M^+), 359 (19), 331 (100), 299 (61), 251 (40); HR-MS calcd for $C_{20}H_{26}N_2O_6$: 390.1791, found 390.1797; UV/Vis (MeOH): $\lambda_{max} = 370$, 281 nm.

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[1] a) C. F. Gürtler, E. Steckhan, S. Blechert, *Synlett* **1994**, 141; b) C. F. Gürtler, E. Steckhan, S. Blechert, *Angew. Chem.* **1995**, *107*, 2025; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1901; c) C. F. Gürtler, E. Steckhan, S. Blechert, *J. Org. Chem.* **1996**, *61*, 4136.

[2] For a review see: a) N. L. Bauld, *Tetrahedron* **1989**, *45*, 5307; b) N. L. Bauld, D. J. Bellville, B. Harirchian, K. T. Lorenz, R. A. Pabon, D. W. Reynolds, D. D. Wirth, H. Chiou, B. K. Marsh, *Acc. Chem. Res.* **1987**, *20*, 371; c) H. Chanon, L. Eberson in *Photoinduced Electron Transfer Reactions* (Eds.: M. A. Fox, M. Chanon), Elsevier, Amsterdam, **1988**, p. 409.

[3] a) G. O. Schenk, S. P. Mannsfield, G. Schomburg, C. H. Krauch, *Z. Naturforsch.* **1964**, *B19*, 18; b) R. Schutte, G. R. Freeman, *J. Am. Chem. Soc.* **1969**, *91*, 3715; c) G. S. Hammond, T. L. Penner, D. G. Whitten, *ibid.* **1970**, *92*, 2861.

[4] a) D. W. Raynolds, N. L. Bauld, *Tetrahedron* **1986**, *42*, 6189; b) P. G. Gassmann, D. A. Singleton, *J. Am. Chem. Soc.* **1984**, *106*, 7993.

[5] J. Mlcoch, E. Steckhan, *Tetrahedron Lett.* **1987**, *28*, 1081.

[6] B. Harirchian, N. L. Bauld, *J. Am. Chem. Soc.* **1989**, *111*, 1826.

[7] a) A. Gieseler, E. Steckhan, O. Wiest, F. Knoch, *J. Org. Chem.* **1991**, *56*, 1405; b) O. Wiest, E. Steckhan, F. Grein, *ibid*. **1992**, *57*, 4034; c) O. Wiest, E. Steckhan, *Tetrahedron Lett.* **1993**, *34*, 6391.

[8] O. Wiest, E. Steckhan, *Angew. Chem.* **1993**, *105*, 932; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 901.

[9] T. Wirth, S. Blechert, *Tetrahedron Lett.* **1992**, *33*, 6621.

[10] a) P. G. Pickup, R. A. Osteryoung, *J. Am. Chem. Soc.* **1984**, *106*, 2294; b) G. Tourillon, F. Garnier, *J. Electroanal.* **1982**, *135*, 173.

[11] E. Winterfeldt, H. Preuss, *Chem. Ber.* **1966**, *99*, 450.

[12] D. V. Gardner, D. E. McGreer, *Can. J. Chem.* **1970**, *48*, 2104.

[13] a) H. H. Wasserman, J. L. Ives, *J. Org. Chem* **1978**, *43*, 3228; b) H. Bredereck, F. Effenberger, T. Brendle, H. Muffler, *Chem. Ber.* **1968**, *101*, 1885.

[14] E. Wenkert, K. G. Dave, F. Haglid, R. G. Lewis, T. Oishi, R. V. Stevens, M. Terashima, *J. Org. Chem.* **1968**, *33*, 747.

[15] Ring opening is achieved by refluxing in methanolic hydrochloric acid. See: S. Takano, T. Sato, K. Inomato, K. Ogasawara *J. Chem. Soc. Chem. Commun.* **1991**, 462.

[16] O. Diels, K. Alder, *Justus Liebigs Ann. Chem.* **1932**, *498*, 1.

[17] A. Treibs, R. Zinsmeister, *Chem. Ber.* **1957**, *90*, 87.

[18] A. J. Saggiomo, *J. Org. Chem.* **1957**, *22*, 1171.

[19] A. Treibs, R. Schmidt, R. Zinsmeister, *Chem. Ber.* **1957**, *90*, 79.

[20] H. Berner, G. Schulz, H. Reinshagen, *Monatsh. Chem.* **1977**, *108*, 915.