C–C Coupling

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Regioselective Carbon–Carbon Bond Formation Reactions between TCNE or TCNQ and a Quinonoid Ring**

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Dedicated to Prof. Arthur J. Carty

Tetracyanoethylene (TCNE) and 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) are strong organic, one-electron acceptors, and as such are much used as precursors to electron-transfer salts and superconducting or magnetic materials.[1] The coordination chemistry of TCNE and TCNQ has been much

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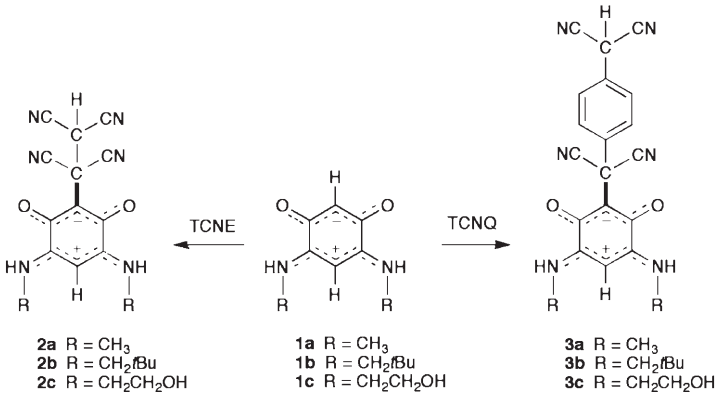
investigated,[2] and their reactions with organometallic compounds include: 1) insertion into M–H,[3a,b] M–C,[3c–f] or M–OR bonds;[3g] 2) [2+2], [4+2], or [3+2] additions on the ligand;[4] 3) α,β-additions to an acetylide group;[5] 4) cycloadditions;[6] and 5) insertions into an aromatic C–H bond.[7] Although numerous reactions of TCNE and TCNQ with organic compounds have been reported,[8] only insertion reactions into a C–C bond of a spiroanellated bicyclopropyl system[9] or a C–H bond of 4-hydroxycoumarins,[10] cyclic enol ethers,[11] phenols,[12] or a mesoionic thiazolium system[13] have been observed.

Quinonoid compounds also form an important class of molecules owing to their remarkable chemical and physical properties.[14] Recently, unusual quinonoid zwitterions (molecules of type **1** in Scheme 1) have been reported,[15,16b] the



Scheme 1. Reactions of zwitterions **1** with TCNE or TCNQ.

unprecedented electronic features of which immediately attracted considerable theoretical interest.[16] These molecules display interesting chemical and structural features, including when they act as ligands,[16b,17] and have relevant applications in color chemistry.[18] Whereas the reactivity at their oxygen and/or nitrogen centers has been demonstrated, a C-substitution reaction that preserves the zwitterionic form represented a challenge that could only be taken up by C–H insertion chemistry, so far unknown in quinonoid chemistry. Probably because quinones and TCNX (TCN = tetracyano; X = E or Q) are both well-known electron acceptors, to the best of our knowledge, no work has been reported so far on their reactivity with each other.

Notwithstanding the fact that quinonoids **1** are rather unusual as they have substituents that make them poorer electron acceptors than quinones, we describe herein the hitherto unknown reactions of TCNE and TCNQ with zwitterionic quinone monoimine derivatives, which afforded new C-substituted zwitterions.

When TCNE and the purple 6π + 6π zwitterions **1a–c**[15,16b,17c] were reacted together at room temperature in a 1:1 ratio, an orange precipitate (**2a,b**) or solution (**2c**) formed (see the Experimental section and Scheme 1).

The ^{1}H NMR data of **2a–c** are similar to those for **1a–c**, except for the C(sp^2)–H resonances of the latter, which are replaced with new, downfield shifted singlets (for example, δ(C-H) = 5.19 and 5.49 ppm for **1b**[15] and δ(C-H) = 5.39 and 6.00 ppm for **2b**). The ^{13}C{^{1}H} spectra (DEPT 135 experiment) revealed the presence of a new sp^3 carbon atom bearing only one proton (δ(C-H) = 31.25, 30.61, and 31.26 ppm for **2a**, **2b**, and **2c**, respectively) and showed that the O=C=*C*–H carbon atom in **1** has become a quaternary center in **2**. The formation of 1:1 addition products was further supported by mass-spectrometric, IR spectroscopic, and elemental-analysis data.

An X-ray analysis of **2a** established that regioselective C–C bond formation had occurred between TCNE and the zwitterion CH carbon atom adjacent to the C=O bonds (Figure 1a).[20] The length of the newly formed C1–C9 bond

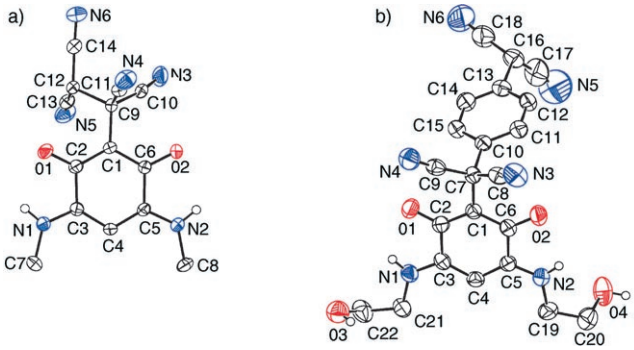


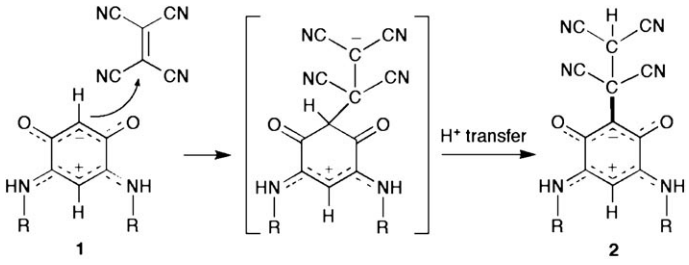
Figure 1. a) ORTEP view of the crystal structure of **2a** in **2a**·0.5 acetone. The H atom at C12 is not shown. Selected bond lengths [Å] and bond angles [°]: O1–C2 1.241(2), O2–C6 1.243(2), C1–C2 1.410(3), C1–C6 1.408(3), N1–C3 1.309(3), C5–N2 1.314(2), C4–C3 1.394(3), C4–C5 1.383(3), C2–C3 1.520(3), C5–C6 1.516(3), C1–C9 1.521(3), C12–C9 1.578(3), C12–C13 1.465(4), C10–N3 1.139(3); O1-C2-C1 125.9(2), O1-C2-C3 117.1(2), C2-C1-C9 120.6(2), C10-C9-C1 112.4(2), N3-C10-C9 169.2(2), C1-C9-C12 112.4(2), C11-C9-C10 108.1(2), N1-C3-C2 112.8(2), N1-C3-C4 125.1(2). b) ORTEP view of the crystal structure of **3c** in **3c**·0.5 Et$_2$O. The H atom at C16 is not shown. Selected bond lengths [Å] and bond angles [°]: C2–O1 1.246(4), O2–C6 1.238(4), C2–C1 1.400(4), C6–C1 1.408(4), N1–C3 1.311(4), N2–C5 1.310(4), C4–C3 1.384(4), C4–C5 1.381(4), C2–C3 1.521(5), C5–C6 1.533(5), C7–C1 1.530(4), C7–C8 1.500(5), C7–C10 1.549(4), C10–C11 1.378(4), C12–C11 1.393(5), C13–C16 1.535(5), C8–N3 1.133(4); O1-C2-C1 125.6(3), O1-C2-C3 116.6(3), C2-C1-C7 119.4(3), C8-C7-C1 110.8(3), N3-C8-C7 174.6(4), C1-C7-C10 112.5(2), C9-C7-C8 103.5(3), N1-C3-C2 113.2(3), N1-C3-C4 125.1(3).

(1.521(3) Å) corresponds to a C–C single bond. Examination of the bond lengths within the O1-C2-C1-C6-O2 and N1-C3-C4-C5-N2 moieties shows an equalization of the C–C and C–O bond lengths and the C–C and C–N bond lengths, respectively, which is consistent with the zwitterionic structure;[15,16b] that is, delocalization of the two 6π electrons subunits that remain connected by two single bonds: C2–C3 and C5–C6 (1.520(3) and 1.516(3) Å, respectively).

These results prompted us to investigate the reaction with TCNQ. Orange-pink solids **3a–c** were similarly obtained from **1a–c**, respectively (Scheme 1), and fully characterized (see the Experimental Section). Owing to the weaker electron-withdrawing ability of the HC(CN)$_2$-C$_6$H$_4$-C(CN)$_2$ moiety, the ^{1}H NMR chemical shifts are shifted upfield with respect to those of **2**. The presence of well-defined resonances for AA′BB′ spin systems at approximately δ = 7.60 and 7.90 ppm,

with ^3J(H,H) and ^4J(H,H) coupling constants of 8.7 and 2.1 Hz, respectively, is consistent with the presence of aromatic protons in a *para*-disubstituted ring. An X-ray diffraction study of **3c**[20] also established the regioselective, formal insertion of TCNQ into the C–H bond of **1c** adjacent to the C=O bonds, which preserves the zwitterionic character of its core, as observed for TCNE (Figure 1b). Furthermore, the conversion of the quinonoid ring of TCNQ into an aromatic ring is confirmed by the C7–C10 and C13–C16 bond lengths of 1.535(4) and 1.535(5) Å, respectively, which correspond to a C–C single bond. The $CH(CN)_2$ and $C(CN)_2$ groups adopt a staggered conformation, similar to their orientation in **2a**.

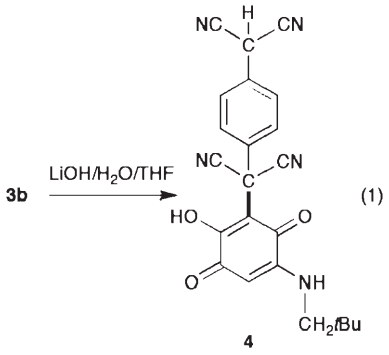
The cyclic voltammogram of **1b** reveals a reversible reduction process centered at −1.38 V and an irreversible oxidation wave at +0.96 V versus a Ag/Ag^+ electrode (that is, −1.09 and +1.25 V versus a saturated calomel electrode (SCE), respectively), which results from a one-electron oxidation process. When we compared these data with the first reduction potential of TCNE or TCNQ, in the range +0.10 to +0.25 V versus SCE,[21] it appears that the latter are much better one-electron acceptors than zwitterion **1b**. No reaction was observed between **1b** and dimethylacetylenedicarboxylate, maleic anhydride, or CO_2 in THF at room temperature or under reflux, thus it would appear that these reagents are not electrophilic enough. We have no spectroscopic indication that the formation of the C-substituted zwitterions **2** or **3** takes place by initial formation of charge-transfer complexes, as suggested in other cases.[3b,7c] Rather, we believe that C–C bond formation results from a Michael-type addition reaction, that is, the nucleophilic sp^2 C1 atom of the quinonemonoimine **1** attacks the double bond of TCNE or TCNQ (Scheme 2).



Scheme 2. Proposed mechanism for the formation of **2**.

Because the zwitterionic quinonoid compounds **1** can be considered as coupled polymethines composed from a cationic trimethine cyanine moiety and an anionic trimethine oxonol moiety that are chemically connected but electronically independent,[15,17c,22a–c] they should be able to react, as known from the chemistry of polymethines,[22d,e] with certain electrophiles. This behavior has now been demonstrated with TCNE and TCNQ, and the chemoselectivity of the reaction which occurs only on the electron-richer trimethine oxonol part of the molecule is fully consistent with the allopolarization principle.[23] This C–C bond formation reaction is thermally irreversible, as verified with **3b**.

In addition, **2** and **3** may be used to prepare C-substituted benzoquinones of type **4** in high yield [Eq. (1)].[17a] Related hydroxyquinones are known as efficient bioinhibitors.[19]



In conclusion, we have reported the first regioselective, formal insertion reactions of TCNE and TCNQ into a C–H bond of a quinonoid ring. This reaction between sp^2-hybridized carbon centers, which results in the formation of a new $C(sp^2)$–$C(sp^3)$ bond, provides general synthetic access to functional, C-substituted $6\pi+6\pi$ quinonoid zwitterions. The potential of these new multifunctional ligands, bearing two (N,O) chelation sites and four cyano groups, is particularly high in coordination chemistry, homogeneous catalysis (cooperative effects), and biochemistry.

Experimental Section

NMR spectra were obtained by using a Bruker AC-300 instrument. MALDI-TOF mass spectra were recorded on a Biflex III Bruker mass spectrometer and ESI mass spectra on a Bruker micrOTOF instrument. Elemental analyses were performed by the "Service de Microanalyse, Université Louis Pasteur (Strasbourg, France)". All reactions were carried out under purified N_2, using Schlenk techniques, and the solvents were freshly distilled under nitrogen prior to use. Compounds **1a–c** were prepared following literature procedures.[15,16b,17a,c,d]

2a: A solution of TCNE (154 mg, 1.20 mmol) in THF (5 mL) was added to a solution of **1a** (200 mg, 1.20 mmol) in ethanol (30 mL). After the solution was stirred at room temperature for 3 h, the orange precipitate was filtered off, washed with ethanol, and dried in air (166 mg, 47% yield). Compound **2a** is highly soluble in acetone, poorly soluble in CH_2Cl_2, and almost insoluble in MeOH and EtOH. ^{1}H NMR (300 MHz, [D$_6$]acetone): $\delta = 3.31$ (d, ^3J(H,H) = 5.4 Hz, 6H, CH_3), 5.84 (s, 1H, C(sp^3)-H), 6.49 (s, 1H, N=C=C-H), 9.03 ppm (br s, 2H, N-H); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]acetone): $\delta = 29.80$ (CH_3-N), 31.25 (C(sp^3)-H), 37.80 (HC-*C*(CN)), 83.06 (N=C=*C*-H), 93.77 (O=C=*C*), 110.18 and 112.00 (C≡N), 155.45 (C=N), 170.00 ppm (C=O); IR (KBr): $\tilde{\nu} = \nu_{C\equiv N}$ 2246 (w), 2255 cm^{-1} (w); UV/Vis (CH_2Cl_2): $\lambda_{max} = 331$ nm (log $\varepsilon = 4.42$), 345 nm (log $\varepsilon = 4.43$), 475 nm (br, log $\varepsilon = 2.96$); HRMS (ESI): 317.08 ([*M*+Na]$^+$); found: 317.08; elemental analysis (%) calcd for $C_{14}H_{10}N_6O_2$: C 57.14, H 3.43, N 28.56; found: C 57.01, H 3.68, N 28.78.

2b: Solid TCNE (115 mg, 0.90 mmol) was added to a solution of **1b** (250 mg, 0.90 mmol) in THF (25 mL). After the solution was stirred at room temperature for 2 h, the solvent was evaporated to 5 mL and hexane was added. The orange precipitate was filtered off and **2b** was recrystallized from a dichloromethane/pentane mixture and dried in air (350 mg, 96% yield). Compound **2b** is highly soluble in chlorinated solvents, acetone, or THF. ^{1}H NMR (300 MHz,

$CDCl_3$): $\delta = 1.08$ (s, 18H, CH_3), 3.20 (d, $^3J(H,H) = 6.6$ Hz, 4H, CH_2), 5.39 (s, 1H, $C(sp^3)$-H), 6.00 (s, 1H, N=C=C-H), 8.28 (brt, 2H, N-H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 27.42$ (CMe_3), 30.61 ($C(sp^3)$-H), 32.63 (CMe_3), 37.63 (HC-C(CN)), 55.21 (CH_2-N), 82.72 (N=C=C-H), 94.25 (O=C=C), 111.05 and 108.86 (C≡N), 154.83 (C=N), 169.35 (C=O); IR (KBr): $\tilde{\nu} = \nu_{C\equiv N}$ 2243 (w), 2256 cm^{-1} (w); UV/Vis (CH_2Cl_2): $\lambda_{max} = 336$ nm (log $\varepsilon = 4.36$), 350 nm (log $\varepsilon = 4.35$), 478 nm (br, log $\varepsilon = 3.09$); HRMS (ESI): 429.20 ($[M+Na]^+$); found: 429.21; elemental analysis (%) calcd for $C_{22}H_{26}N_6O_2 \cdot 1/6\,CH_2Cl_2$: C 63.29, H 6.31, N 19.98; found: C 63.26, H 6.40, N 20.30.

2c: Solid TCNE (170 mg, 1.33 mmol, 1 equiv) was added to a suspension of **1c** (300 mg, 1.33 mmol) in acetonitrile (50 mL), and the solution was stirred overnight at room temperature. After filtration to remove the small amount of unreacted **1c**, the filtrate was concentrated and diethyl ether was added to precipitate the product. After filtration, washing with diethyl ether, and drying in air, **2c** was obtained as an orange powder (362 mg, 77% yield). Compound **2c** is highly soluble in acetone and poorly soluble in CH_2Cl_2. ^1H NMR (300 MHz, [D$_6$]acetone): $\delta = 3.78$ (m, 4H, NHCH_2), 3.95 (q, $^3J(H,H) = 5.5$ Hz, 4H, CH_2OH), 4.36 (t, $^3J(H,H) = 5.5$ Hz, 2H, OH), 6.09 (s, 1H, $C(sp^3)$-H), 6.49 (s, 1H, N=C=CH), 8.84 ppm (brs, 2H, NH); $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]acetone): $\delta = 31.26$ ($C(sp^3)$-H), 37.86 (HC-C(CN)$_2$), 45.90 and 46.03 (CH_2NH), 59.23 and 59.35 (CH_2OH), 84.05 (N=C=C), 93.69 (O=C=C), 110.18 (C≡N), 111.98 (C≡N), 155.06 (N=C), 169.98 ppm (O=C); IR (KBr): $\tilde{\nu} = \nu_{C\equiv N}$ 2113 (w), 2216 cm^{-1} (w); MALDI-TOF: m/z 353.1 $[M-1]^-$; elemental analysis (%) calcd for $C_{16}H_{14}N_6O_4$: C 54.24, H 3.98, N 23.72; found: C 54.24, H 4.17, N 23.86.

3a: Prepared by a similar method to that of **2a**, from **1a** (100 mg, 0.60 mmol) and TCNQ (123 mg, 0.60 mmol, 1 equiv), instead of TCNE. Yield of isolated product = 48% (107 mg). Compound **3a** is soluble in dimethyl sulfoxide (DMSO) and almost insoluble in most common organic solvents. ^1H NMR (300 MHz, [D$_6$]DMSO): $\delta = 3.10$ (d, $^3J(HH) = 5.4$ Hz, 6H, CH_3), 5.48 (s, 1H, $C(sp^3)$-H), 5.60 (s, 1H, N=C=C-H), 7.64 (dt, AA′ part of an AA′BB′ spin system, 2H, $^3J(HH) = 8.7$ Hz, $^4J(HH) = 2.1$ Hz, aromatic C-H), 7.82 (dt, BB′ part of an AA′BB′ spin system, 2H, $^3J(H,H) = 8.7$ Hz, $^4J(H,H) = 2.1$ Hz, aromatic C-H), 8.38 ppm (brs, 2H, N-H); $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]DMSO): $\delta = 30.50$ (CH_3-N), 38.97 ($C(sp^3)$-H), 82.91 (N=C-C-H), 100.65 (O=C=C), 116.26 (C≡N), 127.49 (aromatic C-H), 155.80 (C=N), 169.35 ppm (C=O); we could not observe all ^{13}C NMR resonances owing to the poor solubility of **3a** in DMSO; IR (KBr): $\tilde{\nu} = \nu_{C\equiv N}$ 2250 cm^{-1} (vw); UV/Vis (CH_2Cl_2): $\lambda_{max} = 333$ nm (log $\varepsilon = 4.42$), 347 nm (log $\varepsilon = 4.45$), 478 nm (br, log $\varepsilon = 2.99$); HRMS (ESI): 393.11 ($[M+Na]^+$); found: 393.15; elemental analysis (%) calcd for $C_{20}H_{14}N_6O_2$: C 64.86, H 3.81, N 22.69; found: C 64.23, H 4.19, N 22.39.

3b: Prepared by a similar method to that of **2a**, from **1b** (100 mg, 0.36 mmol) with TCNQ (73 mg, 0.36 mmol, 1 equiv), instead of TCNE. Yield of isolated product = 98% (170 mg). Compound **3b** is highly soluble in chlorinated solvents, acetone, and THF. It remains unchanged after refluxing in a solution of THF overnight. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.06$ (s, 18H, CH_3), 3.14 (d, $^3J(H,H) = 6.3$ Hz, 4H, CH_2), 5.16 (brs, 1H, $C(sp^3)$-H), 5.28 (s, 1H, N=C=C-H), 7.54 (dt, AA′ part of an AA′BB′ spin system, 2H, $^3J(H,H) = 8.7$ Hz, $^4J(H,H) = 2.1$ Hz, C-H aromatic), 7.93 (dt, BB′ part of an AA′BB′ spin system, 2H, $^3J(H,H) = 8.7$ Hz, $^4J(H,H) = 2.1$ Hz, C-H aromatic), 8.30 ppm (brt, 2H, N-H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 27.47$ (CMe_3), 27.81 (C_{sp3}-H), 32.54 (CMe_3), 32.76 (aryl-C(CN)), 55.16 (CH_2-N), 81.74 (N=C-C-H), 101.35 (O=C=C), 111.48 and 114.78 (C≡N), 126.84 and 138.07 (aromatic C), 127.98 and 128.06 (aromatic C-H), 155.62 (C=N), 168.02 ppm (C=O); IR (KBr): $\tilde{\nu} = \nu_{C\equiv N}$ 2243 cm^{-1} (vw); UV/Vis (CH_2Cl_2): $\lambda_{max} = 338$ nm (log $\varepsilon = 4.31$), 351 nm (log $\varepsilon = 4.33$), 478 nm (br, log $\varepsilon = 3.04$); HRMS (ESI): 505.23 ($[M+Na]^+$); found: 505.27; elemental analysis (%) calcd for $C_{26}H_{30}N_6O_2 \cdot 1/2\,C_4H_8O$: C 69.48, H 6.61, N 16.20; found: C 69.45, H 6.64, N 16.38.

3c: Prepared by a similar method to that of **2c**, from **1c** (100 mg, 0.44 mmol) with of TCNQ (90 mg, 0.44 mmol, 1 equiv), instead of TCNE. Yield of isolated product = 91% (173 mg). Compound **3c** is highly soluble in acetone and poorly soluble in CH_2Cl_2. ^1H NMR (300 MHz, [D$_6$]acetone): $\delta = 3.71$ (q, $^3J(H,H) = 5.6$ Hz, 4H, NHCH_2), 3.91 (q, $^3J = 5.3$ Hz, 4H, CH_2OH), 4.34 (t, $^3J(H,H) = 5.6$ Hz, 2H, OH), 5.92 (s, 1H, C_{sp3}-H), 6.13 (s, 1H, N=C=CH), 7.75 and 7.91 (AA′BB′ spin system, 4H, aromatic C-H), 8.70 ppm (brs, NH); IR (KBr): $\tilde{\nu} = \nu_{C\equiv N}$ 2121 (w), 2174 (w); 2250 cm^{-1} (w); MALDI-TOF: m/z 429.2 $[M-1]^-$; elemental analysis (%) calcd for $C_{22}H_{18}N_6O_4 \cdot 1/2\,(CH_3CH_2)_2O$: C 61.66, H 4.96, N 17.98; found: C 61.04, H 4.94, N 18.08.

4: Compound **3b** (200 mg, 0.414 mmol) was dissolved in a solution of LiOH in THF/H_2O (100 mL, pH > 10) and then stirred overnight at room temperature. Protonation of the alcoholate, followed by extraction with CH_2Cl_2 and evaporation of the solvent afforded **4** as a purple powder (158 mg, 92% yield). ^1H NMR (300 MHz, [D$_6$]acetone): $\delta = 1.05$ (s, 9H, CH_3), 3.35 (brd, 2H, CH_2), 5.93 (s, 1H, $C(sp^3)$-H), 6.18 (s, 1H, NC=CH), 7.84 and 7.97 ppm (AA′BB′ spin system, 4H, aromatic C-H); the OH and NH protons could not be observed; IR (KBr): $\tilde{\nu} = \nu_{C\equiv N}$ 2121 (w), 2253 cm^{-1} (w); MALDI-TOF: m/z 412.1 $[M-1]^-$; elemental analysis (%) calcd for $C_{23}H_{19}N_5O_3$: C 66.82, H 4.63, N 16.94; found: C 66.25, H 5.18, N 16.52.

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[20] Red crystals of **2a**·0.5 suitable for X-ray diffraction studies were obtained by slow diffusion of heptane into an solution of **2a** in acetone. Data for **2a**·0.5 acetone: triclinic space group, $P\bar{1}$, a = 9.7610(2), b = 11.9030(3), c = 15.8030(4) Å, α = 68.040(14), β = 80.380(12), γ = 73.100(11)°, 173(2) K, Z = 2; refinement of 10326 reflections and 465 parameters, yielded $R1$ = 0.0859 and $wR2$ = 0.1757 for all data (5599 reflections with $I > 2\sigma(I)$). Single crystals of **3c**·0.5 Et_2O suitable for X-ray diffraction studies were obtained from a mixture of acetone/Et_2O; data for **3c**·0.5 Et_2O: triclinic space group, $P\bar{1}$, with a = 11.617(5), b = 14.726(5), c = 14.990(5) Å, α = 80.25(5), β = 74.05(5), γ = 67.78(5)°, 173(2) K, Z = 2; refinement of 13224 reflections and 630 parameters yielded $R1$ = 0.0902 and $wR2$ = 0.2336 for all data (7537 reflections with $I > 2\sigma(I)$). CCDC-279100 and -279101 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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