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The synthesis of Ni(II) and Al(III) 10-azacorroles through coordination-induced cyclisation involving 1,2-migration†

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We have synthesized Ni(II) and Al(III) 10-azacorroles through coordination-induced cyclisation of nitrogen-bridged bisdipyrrins. Al(III) 10-azacorrole displayed contrasting optoelectronic behaviours from Ni(II) 10-azacorrole, underlining the different electronic effects of the azacorrole ligand from the porphyrin.

Porphyrinoids are macrocycles with porphyrin-like skeletons.[1] The properties of porphyrinoids are substantially affected by their skeleton and structural factors. In particular, inclusion of heteroatoms into the aromatic π-conjugation circuit would result in a dramatic change of their electronic structures. Consequently, 10-heterocorroles (X = N, O, S and Se) have regained the spotlight as novel molecular entities as electronically tuneable porphyrin analogues with a similar divalent ligand skeleton and 18π aromatic conjugation as regular porphyrins (Fig. 1).[2–4]

Recently, Bröring and co-workers reported the synthesis of β-octaalkyl-10-oxa-, 10-thia- and 10-selenacorroles from dibromodipyrrins by treatment with copper(II) salts.[3] Our group independently developed the synthetic protocols of *meso*-diaryl-10-aza-, 10-oxa- and 10-thiacorroles.[4] In particular, 10-azacorroles can be regarded as electron-rich porphyrin analogues owing to

their low oxidation potentials. Ni(II) 10-azacorrole was synthesized *via* palladium-catalysed amination of the Ni(II) dipyrrin complex. However, the protocol was only applicable to the preparation of Ni(II) complexes.

Electrocyclisation is one of powerful methods for ring construction in organic synthesis. In porphyrin chemistry, Johnson and co-workers reported in the 1960s, the synthesis of corroles by oxidative cyclisation of a,c-biladienes with Co(II) or Ni(II) salts.[5] Despite this pioneering discovery, this synthetic protocol has been overshadowed for a long time because of difficulty in accessing a,c-biladienes.[6]

Herein we described the synthesis of Ni(II) and Al(III) 10-azacorroles from amine-bridged bisdipyrrins. Coordination of bisdipyrrins with Ni(II) and Al(III) induced efficient C–C bond formation between two pyrrole units to provide Ni(II) and Al(III) azacorroles with concomitant 1,2-migration of an α-substituent. This procedure enabled the first synthesis of Al(III) 10-azacorrole and regioselective introduction of various functionalities at the 2-position of Ni(II) 10-azacorroles. These two metal complexes exhibited significantly different optical and electrochemical properties.

Palladium-catalysed amination of dipyrrin 1 was performed with benzylamine (Scheme 1). Treatment of dibromodipyrrin
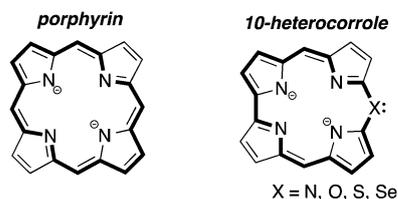

Fig. 1 Skeletons of porphyrin and 10-heterocorrole. The bold lines indicate 18π aromatic conjugation circuits.

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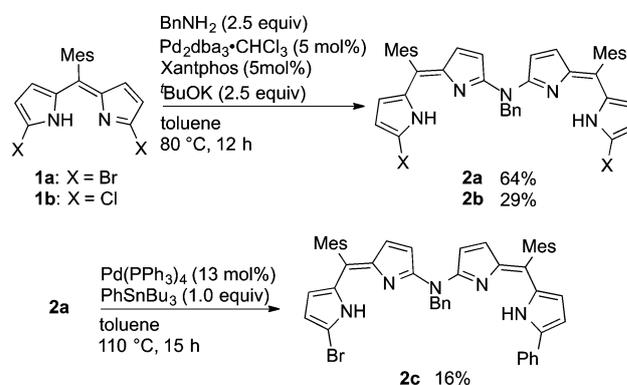
Scheme 1 Double amination of dihalodipyrrin and introduction of a phenyl group.
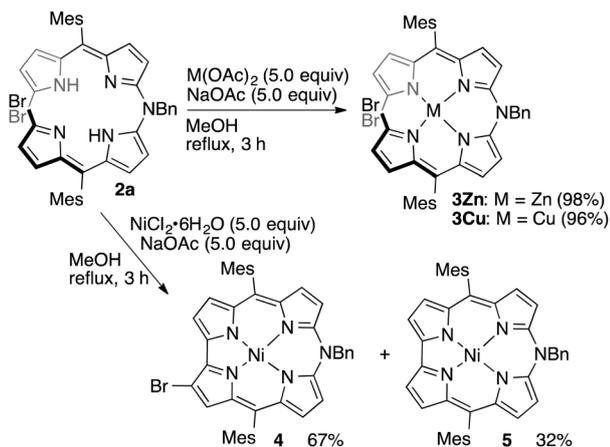
Scheme 2 Metallation of bisdipyrrins **2a** with Zn^{II}, Cu^{II} and Ni^{II} ions.

Scheme 3 1,2-Migration of a phenyl group in metallation of bisdipyrrin **2c** with Ni^{II} ions.

Scheme 4 Metallation of bisdipyrrins **2a** with AlCl$_3$.

Scheme 5 Reactions of Ni^{II} 2-bromo-10-azacorrole **5**.

1a with 1.1 equiv. of benzylamine and ^{t}BuOK in the presence of a catalytic amount of Pd$_2$dba$_3$·CHCl$_3$/DPPF (5 mol%) in toluene at 80 °C provided bisdipyrrin **2a** in 32% yield. The employment of Xantphos improved the yield to 45%, while DPEphos was not effective. Eventually, the reaction with 2.5 equiv. of benzylamine afforded **2a** in 64% yield. Dichlorobisdipyrrin **2b** was also prepared from dichlorodipyrrin **1b** in 29% yield. The introduction of a phenyl group at the α-position was achieved through Migita–Kosugi–Stille coupling to afford **2c**.

With bisdipyrrins **2** in hand, the metal coordination behaviour of **2** was investigated (Scheme 2).[7] Treatment of **2a** with 5.0 equiv. of Zn^{II} and Cu^{II} afforded the corresponding metal complexes **3Zn** and **3Cu** in 98 and 96% yields, respectively. The helical conformation of **3Cu** was elucidated by X-ray diffraction analysis (Fig. 2a). On the other hand, heating the mixture of **2a** with 5.0 equiv. of NiCl$_2$ furnished bromoazacorrole **4** and azacorrole **5** in 67% and 32% yields, respectively. Importantly, Ni^{II} bromoazacorrole **4** was obtained as a single regioisomer. X-ray diffraction analysis unambiguously determined the structure of **4**, revealing that the bromine atom shifted from the α- to β-positions during cyclisation (Fig. 2b). In the case of dichlorobisdipyrrin **2b**, **5** was obtained exclusively in 83% yield. Interestingly, treatment of phenylbisdipyrrin **2c** with NiCl$_2$ provided 2-phenyl-10-azacorrole **6** in 99% yield through 1,2-migration of the phenyl group (Scheme 3).

Treatment of **2a** with 10 equiv. of AlCl$_3$ also induced the similar cyclisation effectively (Scheme 4). In this case, a mixture
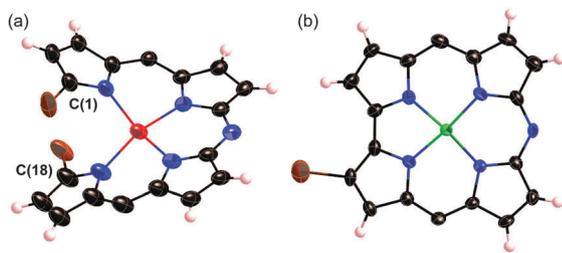
of regioisomeric bromoazacorroles and azacorrole **7** was obtained (Fig. S34, ESI†). Subsequent palladium-catalysed reductive dehalogenation afforded Al^{III} 10-azacorrole **7** in 67% yield in two steps from **2a**.[8] This result confirms that Ni^{II} metal ions work as neither a coupling reagent nor a catalyst in this cyclisation reaction.[9] Notably, the present cyclisation is highly dependent on the metal ions because Zn^{II} and Cu^{II} showed no similar reactivity.

The present methodology was employed to prepare functionalized azacorroles (Scheme 5). The reaction of **4** with pinacolborane under palladium catalysis provided **8** in 52% yield. In addition, treatment of **4** with Ni(cod)$_2$/2,2′-bipyridyl furnished the 2,2′-linked dimer **9** in 62% yield.

Fig. 3 displays the UV/vis absorption spectra of **5** and **7** in CH$_2$Cl$_2$. In contrast to Ni^{II} azacorrole **5**, Al^{III} azacorrole **7** exhibits
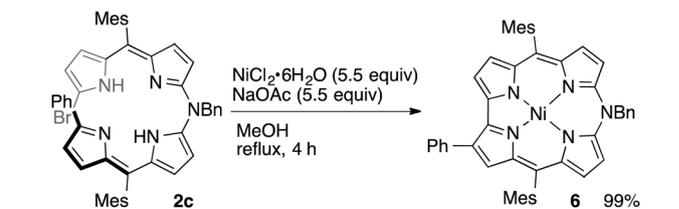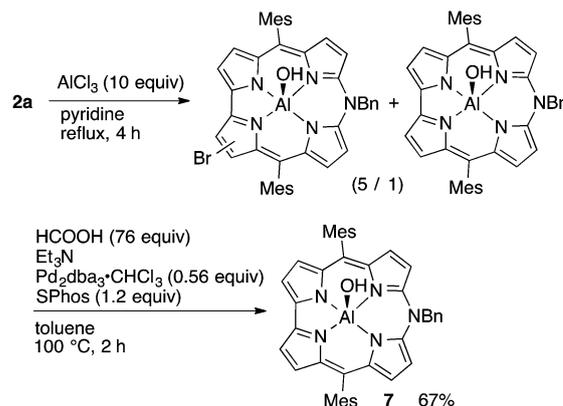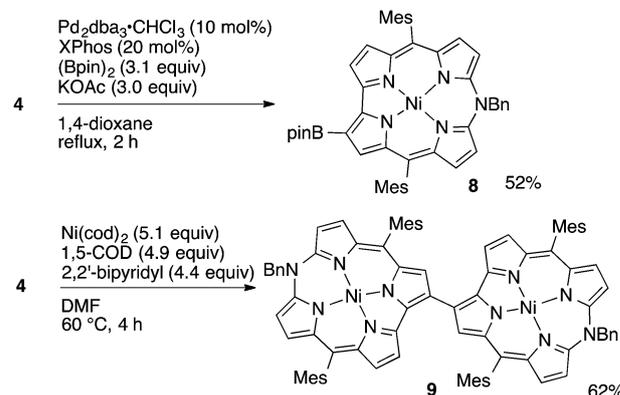
Fig. 2 X-ray crystal structures of (a) **3Cu** and (b) **4**. *meso*-Mesityl groups and the benzyl substituent are omitted for clarity. The thermal ellipsoids are scaled at 50% probability level.
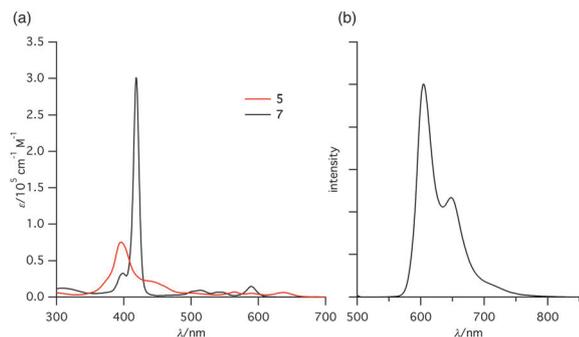
Fig. 3 (a) UV/vis absorption spectra of **5** (red) and **7** in CH_2Cl_2. (b) The emission spectrum of **7** in CH_2Cl_2.

a sharp and intense Soret band and blue-shift of the lowest energy absorption bands. This tendency is different from that observed in the corresponding porphyrin metal complexes: Al^{III} tetraphenylporphyrin (TPP) exhibits red-shifted absorption in comparison to that of Ni^{II} TPP.[10,11] These differences were analysed using theoretical calculations. Oscillator strengths for **5** and **7** calculated using the TD-DFT method were in good agreement with the experimental spectra. For Ni^{II} and Al^{III} TPPs, both the Soret and Q bands consist of the HOMO → LUMO and HOMO−1 → LUMO+1 transitions. On the other hand, the lowered symmetry of azacorroles results in the additional contribution of the HOMO−3 → LUMO transition in the Soret and Q bands. The HOMO−3 of **5** is significantly different from that of **7** because of the presence of the d–σ bond between nitrogen and Ni^{II} (Fig. S39, ESI†). Consequently, the Soret band of **5** is split and broad.

We then examined the electrochemistry of **5** and **7** by cyclic voltammetry, which showed two reversible oxidation and one reduction wave in both cases (Table 1 and Fig. S35, ESI†). All oxidation and reduction potentials of **7** are larger than that of **5** due to the electron-withdrawing nature of Al^{III}. The difference between the first oxidation and the reduction potentials (ΔE) of **7** is 2.33 V, which is smaller than that of **5** (2.19 V). This trend is opposite to that observed in the case of Ni^{II} and Al^{III} TPPs.[12,13] TPPs have the two degenerated HOMO and HOMO−1 with different symmetries, a_{1u} and a_{2u}. Central metals mainly affect the energy level of the a_{2u} orbital while that of the a_{1u} orbital remains rather unchanged. Therefore, the difference in the oxidation potentials of Ni^{II} and Al^{III} TPPs is rather small (Fig. S38, ESI†). The more positive Al^{III} lowers the LUMO energy more than Ni^{II}. Consequently, the HOMO–LUMO gap in Al^{III} TPP becomes smaller than that in Ni^{II} TPP. On the other hand,

Table 1 Results of electrochemical measurements for **5**, **7**, Ni^{II} TPP and Al^{III} TPP[a]

Compound	E_{red}	E_{ox}^1	E_{ox}^2	ΔE[b]
5	−2.01	0.181	0.718	2.19
7	−1.89	0.426	0.871	2.33
Ni^{II} TPP[c]	−1.75	0.55	—	2.30
Al^{III} TPP[d]	−1.69	0.43	—	2.12

[a] Unit: V. [b] $\Delta E = E_{ox}^1 - E_{red}$. [c] Ref. 12 (subtracted by −0.50 V). [d] Ref. 13.
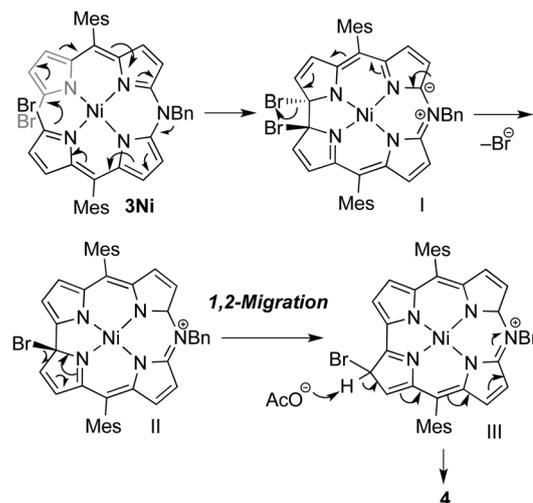
Scheme 6 Proposed mechanism of the cyclisation and rearrangement process.

both HOMO and LUMO of azacorrole have been influenced by metallation because of their substantial molecular orbital coefficients on the inner nitrogen atoms (Fig. S37, ESI†). Therefore, **7** has lower HOMO and LUMO energies than **5** due to the more electron-deficient nature of Al^{III} than Ni^{II}.

Compound **7** showed fluorescence with a moderate quantum yield ($\Phi_f = 0.117$, Fig. 3b). The emissive feature of Al^{III} complexes is also observed in corroles and porphyrins.[14] Compound **7** is the first example of emissive 10-azacorroles.

Cyclisation of bisdipyrrins in the presence of Ni^{II} and Al^{III} cations was intriguing in view of the reaction mechanism. Bromination of **5** with NBS afforded a mixture of regioisomeric bromoazacorroles. This fact negates that the introduction of the bromo substituent occurs after the formation of **5**. The possibility of nucleophilic substitution with a bromide anion should be excluded, considering the presence of a large amount of the chloride anion from $NiCl_2$. In addition, the reaction of **2a** with $NiBr_2$ afforded **4a** and **5** with almost the same selectivity (60% and 36% yields) as in the case of $NiCl_2$. This result negates the influence of the counter anion. The addition of TEMPO in the reaction had no effect, negating a radical mechanism.[15] On the basis of these findings, we propose the reaction mechanism involving electrocyclisation followed by 1,2-migration (Scheme 6).[16] Electrocyclisation of **3Ni** induced by electron pushing from the nitrogen atom provide the zwitterionic intermediate **I**. Elimination of a bromide anion yields the iminium species **II**, which then undergoes 1,2-migration of bromine to yield the cationic intermediate **III**. Deprotonation of **III** eventually furnishes 2-bromoazacorrole **4**. On the other hand, the attack of bromide on **II** affords azacorrole **5** through elimination of Br_2. In the case of **2b**, elimination predominantly proceeds to provide **5** because of the lower migratory ability of chloride.

The role of Ni^{II} can be explained by the geometry of bisdipyrrin complexes. In the crystal structure of **3Cu**, the distance between C(1)–C(18) was 3.52 Å (Fig. 2a). This distance was reproduced well
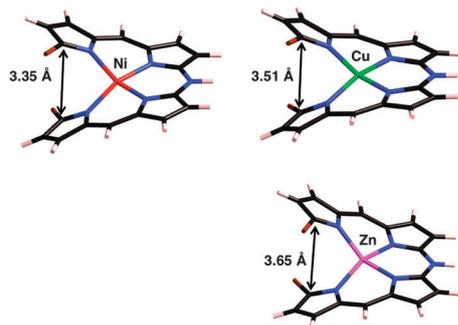
Fig. 4 Calculated structures of **3Ni**, **3Cu** and **3Zn** using the DFT method. The aryl and benzyl substituents are replaced with hydrogen.

by DFT calculations at the M06-2X/6-31G(d)+SDD level, showing the validity of the theory. The calculations also suggested that the distance between two α-carbon atoms in Ni^{II} bisdipyrrin complex **3Ni** to be 3.35 Å (Fig. 4). This distance is within the sum of van der Waals radii of two carbon atoms, facilitating the construction of a novel carbon–carbon bond. Thus, the Ni^{II} metal serves as a template to bring two reacting centres closer. Considering the formation of the Al^{III} complex **7**, the size of the metal ion should be critical. Al^{III} and Ni^{II} have similar ionic radii (0.48 and 0.49 Å), which are much smaller than those of Zn^{II} and Cu^{II} (0.60 and 0.57 Å). The mechanism was further investigated using DFT calculations (Fig. S36 and Table S2, ESI†). The transition state structure was obtained by bringing two reaction centres closer. Then the IRC calculation provided an intermediate species, which corresponds to iminium **II** in Scheme 4. The activation energy of the cyclisation process was calculated to be 45.0 kcal mol^{-1}.

In summary, we found that Ni^{II} and Al^{III} metallation of bisdipyrrins **2** efficiently provided Ni^{II} and Al^{III} 10-azacorroles. The cyclisation proceeds through electrocyclisation followed by 1,2-migration of bromo and phenyl substituents. Ni^{II} and Al^{III} 10-azacorroles exhibited significantly different optical and electrochemical properties from the corresponding porphyrin metal complexes. The present protocol would be also applicable to the chemistry of other types of 10-heterocorroles. Further investigation of the characteristics of *meso*-aryl-10-heterocorroles is underway in our group.

Notes and references

1 (a) *The Porphyrin Handbook*, ed. K. Kadish, K. M. Smith and R. Guilard, Academic Press, Boston, 2003, vol. 11–20; (b) *Handbook of Porphyrin Science*, ed. K. Kadish, K. M. Smith and R. Guilard, World Scientific Publishing Co. Pte. Ltd., Singapore, 2010, vol. 1–30.
2 (a) H. M. Neu, J. Jung, R. A. Baglia, M. A. Siegler, K. Ohkubo, S. Fukuzumi and D. P. Goldberg, *J. Am. Chem. Soc.*, 2015, **137**, 4614; (b) S. Fukuzumi, H. Kotani, K. A. Prokop and D. P. Goldberg, *J. Am. Chem. Soc.*, 2011, **133**, 1859; (c) A. J. McGown, W. D. Kerber, H. Fujii and D. P. Goldberg, *J. Am. Chem. Soc.*, 2009, **131**, 8040; (d) B. Ramdhanie, J. Telser, A. Caneschi, L. N. Zakharov, A. L. Rheingold and D. P. Goldberg, *J. Am. Chem. Soc.*, 2004, **126**, 2515.
3 (a) D. Sakow, B. Böker, K. Brandhorst, O. Burghaus and M. Bröring, *Angew. Chem., Int. Ed.*, 2013, **52**, 4912; (b) M. Bröring, S. Köhler and C. Pietzonka, *J. Porphyrins Phthalocyanines*, 2012, **16**, 641; (c) M. Bröring, F. Brégier, E. C. Tejero, C. Hell and M. C. Holthausen, *Angew. Chem., Int. Ed.*, 2007, **46**, 445; (d) M. J. Broadhurst, R. Grigg and A. W. Johnson, *J. Chem. Soc., Perkin Trans. 1*, 1972, 1124; (e) A. W. Johnson, I. T. Kay and R. Rodrigo, *J. Chem. Soc.*, 1963, 2336.
4 (a) M. Horie, Y. Hayashi, S. Yamaguchi and H. Shinokubo, *Chem. – Eur. J.*, 2012, **18**, 5919; (b) H. Kamiya, T. Kondo, T. Sakida, S. Yamaguchi and H. Shinokubo, *Chem. – Eur. J.*, 2012, **18**, 16129; (c) T. Ito, Y. Hayashi, S. Shimizu, J.-Y. Shin, N. Kobayashi and H. Shinokubo, *Angew. Chem., Int. Ed.*, 2012, **51**, 8542.
5 A. W. Johnson, *Porphyrins and Metalloporphyrins*, Elsevier, Amsterdam, 1975, p. 732.
6 (a) Y. Murakami, S. Yamada, Y. Matsuda and K. Sakata, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 123; (b) M. Bröring and C. Hell, *Chem. Commun.*, 2001, 2336.
7 For excellent reviews on metal complexes of bisdipyrrins, see: (a) M. Bröring, in *Handbook of Porphyrin Science*, ed. K. M. Kadish, K. M. Smith and R. Guilard, World Scientific Publishing, Singapore, 2010, vol. 8, p. 343; (b) A. L. Balch and F. L. Bowles, in *Handbook of Porphyrin Science*, ed. K. M. Kadish, K. M. Smith and R. Guilard, World Scientific Publishing, Singapore, 2010, vol. 8, p. 293; (c) T. E. Wood, M. I. Uddin and A. Thompson, in *Handbook of Porphyrin Science*, ed. K. M. Kadish, K. M. Smith and R. Guilard, World Scientific Publishing, Singapore, 2010, vol. 8, p. 343; (d) T. E. Wood and A. Thompson, *Chem. Rev.*, 2007, **107**, 1831.
8 (a) A. K. Sahoo, Y. Nakamura, N. Aratani, K. S. Kim, S. B. Noh, H. Shinokubo, D. Kim and A. Osuka, *Org. Lett.*, 2006, **8**, 4141; (b) A. Kato, R. D. Hartnell, M. Yamashita, H. Miyasaka, K. Sugiura and D. P. Arnold, *J. Porphyrins Phthalocyanines*, 2004, **8**, 1222.
9 Non-cyclised complex **3Ni** was isolated with other *meso*-substituents. See the ESI† (Scheme S1).
10 A. Muranaka, M. Yokoyama, Y. Matsumoto, M. Uchiyama, A. Tsuda, A. Osuka and N. Kobayashi, *ChemPhysChem*, 2005, **6**, 171.
11 A. Harriman and A. D. Osborne, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 765.
12 D. Chang, T. Malinski, A. Ulman and K. M. Kadish, *Inorg. Chem.*, 1984, **23**, 817.
13 P. K. Poddutoori, G. N. Lim, S. Vassiliev and F. D'Souza, *Phys. Chem. Chem. Phys.*, 2015, **17**, 26346.
14 (a) A. Mahammed and Z. Gross, *J. Inorg. Biochem.*, 2002, **88**, 305; (b) D. Kowalska, X. Liu, U. Tripathy, A. Mahammed, Z. Gross, S. Hirayama and R. P. Steer, *Inorg. Chem.*, 2009, **48**, 2670.
15 K. M. Smith and O. M. Minnetian, *J. Org. Chem.*, 1985, **50**, 2073.
16 Electrocyclisation involving 1,2-migration was observed in Nazarov cyclisation; (a) D. Lebœuf, E. Theiste, V. Gandon, S. L. Daifuku, M. L. Neidig and A. J. Frontier, *Chem. – Eur. J.*, 2013, **19**, 4842; (b) D. Lebœuf, V. Gandon, J. Ciesielski and A. J. Frontier, *J. Am. Chem. Soc.*, 2012, **134**, 6296.