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Full Paper

### **Crown Ether Derivatised Pyromellitic Diimides**

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Pyromellitic diimide functionalised on the aromatic core with azacrown ethers have been synthesised and characterised by analytical methods including X-ray crystallography. Changes in their UV-vis spectra by the addition of metal salts have been investigated.

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### Introduction

Tetracarboxylic diimide derivatives of rylenes, particularly of naphthalene (NDI) and perylene (PDI) (Chart 1), have been extensively studied for their well behaved redox and fluorescence properties, primarily towards components of photosynthetic mimics and as organic field-effect transistor materials for organic electronics.<sup>[1,2]</sup> While substitution of NDIs at the diimide nitrogens have very little influence on the photophysical and electrochemical properties, core substitution has been shown to drastically change the optical, electronic, and chemical properties.<sup>[3]</sup> What this means is that careful selection of substitution can fine-tune the properties of NDIs for specific applications. This is in contrast to the early development of NDIs, which, as a result of their unremarkable optical properties, were forgotten until the turn of the century.<sup>[3]</sup>

Outside of polymer science, the smallest member of the aromatic diimides, pyromellitic diimide (PMD), have received little attention, due in part to synthetic challenges in achieving stable derivatives, but more likely a result of the uninteresting optical and redox properties of the parent pyromellitic anhydride.<sup>[4]</sup> From our perspective, core substitution of the pyromellitic diimides is interesting due to the proximity of donating and withdrawing groups, leading to potential push–pull characteristics. Surprisingly, few attempts have been made to functionalise pyromellitic diimides in order to enhance the chromophoric properties.<sup>[5]</sup> In this paper, we investigate core functionalisation of pyromellitic diimides with amines and azacrown ethers and study their properties in the absence and presence of metal salts.

The target compounds **3a–d** were synthesised as outlined in Scheme 1. The dibromides **1a** and **1b** were prepared according to literature reported methods in four steps starting with commercially available 1,2,4,5-tetramethylbenzene.<sup>[6]</sup> The imide substitution using octyl and phenyl groups were chosen to aid solubility and crystallisation, respectively. Reaction of the dibromide **1a** or **1b** with 1-aza-15-crown-5 or 1-aza-18-crown-6 at elevated temperature in dimethylacetamide (DMA) gave the corresponding highly-coloured monobromides **2a–d** in good to excellent yields depending on the nature of the crown ether and the imide substitution. Generally, compounds

containing alkyl side chains gave higher yields than the corresponding phenyl derivatives. The stepwise addition of the secondary amine to **1a**, **b** is advantageous for the formation of more complex systems. In the course of this research, it appears the reaction temperature plays a critical role in this process. Too high an elevation does not lead to the intended disubstituted system, but instead begins to lead to degradation with a wide product distribution as evinced by TLC analysis. UV-vis absorption spectra of **2a**–**d** are very similar with maxima at 499 nm. The highly coloured nature of compounds **2a**–**d** compared with that of **1a**, **b** can be attributed in part to the introduction of nitrogen, leading to more extensive overlap of orbitals, as has been well reported in the related core-substituted NDIs.<sup>[7,8]</sup>

Reaction of **2a** or **2b** with excess dibutylamine, or **2c** or **2d** with morpholine, gives the target compounds **3a–d** in good yields following chromatography (Scheme 2).

Dark blue single crystals of **3c**, **d** suitable for X-ray crystallography were grown from MeCN solution. The molecular structure of each is shown in Fig. 1. As indicated, the groups extending from the pyromellitic core are all off-set to the PMD core as a result of the steric restrictions imposed by the imide oxygens. This effect makes it hard to deliver long-range ordering through  $\pi$ - $\pi$  interactions within the crystal lattice. As a result, the macromolecular structure is unremarkable. There is ordering in both **3c** and **3d** that results from regions containing the crown ether groups and phenyl groups but these might be better termed polar and less-polar regions.

Compound series **3a–d** are very weakly fluorescent however, they are intensely blue in colour with extinction coefficient ( $\varepsilon$ ) of 10500 M<sup>-1</sup> cm<sup>-1</sup> at 604 nm ( $\lambda_{CT}$ ) in methanol for both **3a** and **3b**, in stark contrast to **1a**, **b** which are both are pale yellow in colour ( $\lambda_{max}$  365 nm in CH<sub>2</sub>Cl<sub>2</sub>), the former attributable to the overlap of two amine lone pairs from crown nitrogen and morpholine nitrogen with the aromatic ring.

Addition of alkali metal ions such as Na<sup>+</sup> or K<sup>+</sup>, as their acetate salts, leads to significant changes in the UV-vis absorption spectra of **3a**–**d** in methanol solution converting the deep blue solutions to bright red in colour ( $\Delta\lambda_{\rm CT}$  100 nm). The reference molecule **4**, which is dark blue in colour





Scheme 1. Synthesis of pyromellitic diimide dibromide (1). Reagents and conditions: (i) Br<sub>2</sub>, I<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>; (ii) (a) KMnO<sub>4</sub>, pyridine; (b) KMnO<sub>4</sub>, pyridine, H<sub>2</sub>O, NaOH; (iii) Ac<sub>2</sub>O, AcOH; (iv) C<sub>8</sub>H<sub>17</sub>NH<sub>2</sub> or aniline, AcOH.



Scheme 2. Synthesis of crown ether derivatives 2-3. Reagents and conditions: (i) crown ether, dimethylacetamide, 120°C; (ii) excess dibutylamine or morpholine, 140°C.

 $(\lambda_{CT} 630 \text{ nm})$  does not change its spectral properties with alkaline metal ions even at high concentrations indicating the importance of the crown ether group in characterising the change. The spectral changes that occur during sodium ion binding to compound **3a** in methanol are given in Fig. 2 as a representative example. Very similar spectral changes were observed for crown-6 derivative **3b**.

The interaction of nitrogen lone pair of the azacrown with the alkali metal ion combined with metal ion induced restriction on

rotation around nitrogen–carbon bond as a result of rigidifying the crown ether limits the characteristics of the charge-transfer band. This spectral change observed upon addition of metal ions to **3a** and **3b** is very similar to the changes observed upon addition of trifluoroacetic acid (TFA) to compounds **3a**, **3b**, and **4** (Chart 2). The absorption maxima for  $\lambda_{CT}$  are around 534 nm for all three molecules in the presence of acid.

The stability constants were calculated using Benesi– Hilderbrand equation and are given in Table 1. The metal ion



**Fig. 1.** Single-crystal X-ray structures of (a) **3c** and (b) **3d** drawn as *ORTEP* diagrams. The lattice solvent MeCN has been omitted for clarity. Part of the crown ether in **3d** was modelled as disordered over two positions, only the major component is shown.



Fig. 2. Sodium ion induced UV-vis spectral changes of 3a in CH<sub>3</sub>OH solution. The sodium ions were added as the acetate salts.



binding abilities of **3a** and **3b** are somewhat lower than its parent crown ether as given in Table 1. The metal binding nature of the parent crown ether has been altered by the presence of carbonyl groups close to the crown ether ring and the presence of the push–pull pyromellitic group. It is probable that the electron density shift/delocalisation of the nitrogen lone pair into the aromatic ring, supported by the strong electron pulling of two imide derivatives, could reduce the nitrogen–metal interaction

Table 1. Metal ion-crown ether complex stability constant, log  $\beta$  for 3a, 3b, their parent crown ethers *N*-methyl-monoaza-15-crown-5 and the corresponding 18-crown-6 analogue<sup>[9]</sup>

	3a	3b	<i>N</i> -methyl-monoaza- 15-crown-5	N-methyl-monoaza- 18-crown-6
Sodium	2.65	3.93	3.39	3.93
Potassium	2.66	3.91	3.07	5.33

reducing the total metal ion binding ability of the crown ether moiety, compared with the parent crown ether. The results clearly show the new compounds do not discriminate sodium from potassium ions. Interestingly, the addition of alkali metal ions does not significantly enhance the fluorescence of the system.

### Conclusion

Strong electron push–pull system has been created by introduction of tertiary amine into the core of pyromellitic diimide. The observed strong charge transfer band observed is attributed to charge transfer from nitrogen to the aromatic part of the molecule. The modulation of charge transfer site by metal ion binding created a very sensitive recognition system. This new electron push–pull system could be useful in designing molecular electronics due to its compact size and strong charge transfer nature.

### Experimental

NMR experiments were carried out in CDCl<sub>3</sub> at 400 MHz (<sup>1</sup>H) or 100 MHz (<sup>13</sup>C) on a Bruker DRX400. <sup>1</sup>H NMR spectra are internally referenced to the residually protonated solvent peak (7.26 ppm) and <sup>13</sup>C NMR spectra are referenced to the central carbon peak (77.16 ppm) of CDCl<sub>3</sub>. In all spectra, chemical shifts are given in  $\delta$  relative to tetramethylsilane. Coupling constants are reported in Hz. High-resolution mass spectra were recorded on an Agilent ESI-TOF MS using electrospray ionisation (ESI). UV-vis analyses were carried out in methanol on an Agilent Cary 100 series UV-vis spectrometer.

### N,N-Di-n-octyl-3-(N'-aza-18-crown-6)-6-bromopyromellitic diimide **2a**

A mixture of N,N-di-n-octyl-3,6-dibromopyromellitic diimide **1a** (100 mg, 0.17 mmol), 1-aza-18-crown-6 (150 mg. 0.57 mmol), and dimethylacetamide (4 mL) was heated at 120°C, under nitrogen for 18h. Solvent was removed under reduced pressure and the crude material was chromatographed on flash silica (dichloromethane with 2-4 % v/v methanol). This material was redissolved in ethyl acetate and washed with deionised water  $(2 \times 50 \text{ mL})$ . The organic layer was separated and dried under reduced pressure to obtain 2a as a dark red film (135 mg, 99%).  $\delta_{\rm H}$  3.59–3.76 (m, 28H), 1.63–1.67 (m, 4H), 1.25–1.31 (m, 20H), 0.80–0.90 (m, 6H).  $\delta_{\rm C}$  165.33, 164.36, 146.15, 137.60, 130.32, 105.29, 71.66, 71.13, 71.06, 70.88, 70.54, 54.71, 38.93, 29.46, 29.43, 28.71, 27.23, 22.94, 14.39. m/z (ESI) 802.3, 804.3 [M + Na]<sup>+</sup>. m/z 802.3262, 804.3252. HRMS Anal. Calc. for  $C_{38}H_{58}BrN_3NaO_9 [M + Na]^+ 802.3254$ , 804.3234.

### N,N-Di-n-octyl-3-(N'-aza-15-crown-5)-6-bromopyromellitic diimide **2b**

A mixture of *N*,*N*-di-*n*-octyl-3,6-dibromopyromellitic diimide **1a** (63 mg, 0.11 mmol), 1-aza-18-crown-6 (75 mg, 0.34 mmol), and dimethylacetamide (4 mL) was heated at 120°C, under nitrogen for 18 h. Solvent was removed under reduced pressure and the crude material was chromatographed on flash silica (dichloromethane with 2–4 % v/v methanol). This material was redissolved in ethyl acetate and washed with deionised water (2 × 50 mL). The organic layer was separated and dried under reduced pressure to obtain **2b** as a dark red film (79 mg, 100 %).  $\delta_{\rm H}$  3.77–3.57 (m, 24H), 1.64–1.58 (m, 4H), 1.29–1.21 (m, 20H), 0.85–0.81 (m, 6H).  $\delta_{\rm C}$  165.14, 164.21, 145.83, 137.43, 130.29, 105.39, 71.61, 70.93, 70.77, 70.70, 54.61, 38.83, 31.98, 29.35, 29.31, 28.59, 27.11, 22.84, 14.12. *m/z* (ESI) 758.5, 760.5 [M + Na]<sup>+</sup>. *m/z* 758.2985, 760.2974. HRMS Anal. Calc. for C<sub>36</sub>H<sub>54</sub>BrN<sub>3</sub>NaO<sub>8</sub> [M + Na]<sup>+</sup> 758.2992, 760.2972.

### N,N-Di-n-octyl-3-(N'-aza-18-crown-6)-6-N",N"-di-nbutylaminopyromellitic diimide **3a**

A mixture of **2a** (95 mg, 0.12 mmol) was dissolved in dibutylamine (2 mL) and heated at 140°C, under nitrogen for 18 h. Excess amine was removed under reduced pressure and the crude material was chromatographed on flash silica (dichloromethane with 0–10% v/v methanol). This material was redissolved in ethyl acetate and washed with deionised water (2 × 50 mL). The organic layer was separated and dried under reduced pressure to obtain **3a** as a dark blue film (76 mg, 77%).  $\delta_{\rm H}$  3.80–3.70 (m, 28H), 3.40 (t, *J* 12.3, 4H), 1.64–1.52 (m, 4H), 1.46–1.20 (m, 4H), 1.34–1.19 (m, 24H), 0.89–0.81 (m, 12H).  $\delta_{\rm C}$ 165.53, 165.36, 141.38, 140.79, 132.92, 131.70, 71.41, 71.27, 71.09, 71.03, 70.64, 54.45, 54.24, 38.50, 32.07, 31.06, 29.52, 29.47, 28.88, 27.30, 22.94, 20.36, 14.98, 14.30. *m/z* (ESI) 851.4 [M+H]<sup>+</sup>. *m/z* 851.5529. HRMS Anal. Calc. for C<sub>46</sub>H<sub>76</sub>N<sub>4</sub>NaO<sub>9</sub> [M+Na]<sup>+</sup> 851.5510.

### N,N-Di-n-octyl-3-(N'-aza-15-crown-5)-6-N",N"-di-nbutylaminopyromellitic diimide **3b**

A mixture of 2b (68 mg, 0.09 mmol) was dissolved in dibutylamine (2 mL) and heated at 140°C, under nitrogen for 18 h. Excess amine was removed under reduced pressure and the crude material was chromatographed on flash silica (dichloromethane with 0-10% v/v methanol). This material was redissolved in ethyl acetate and washed with deionised water  $(2 \times 50 \text{ mL})$ . The organic layer was separated and dried under reduced pressure to obtain **3b** as a dark blue film (45 mg, 64 %).  $\delta_{\rm H}$  3.74–3.59 (m, 24H), 3.41 (t, *J* 7.3, 4H), 1.62–1.65 (m, 4H), 1.43-1.50 (m, 4H), 1.34-1.19 (m, 24H), 0.89-0.81 (m, 12H).  $\delta_{\rm C}$  165.54, 165.39, 141.61, 140.94, 133.32, 131.63, 71.66, 71.39, 71.21, 70.77, 54.77, 54.32, 38.55, 32.10, 31.10, 30.03, 29.54, 29.49, 28.89, 27.33, 22.96, 20.38, 14.39, 14.29. m/z (ESI) 785.4  $[M+H]^+$ , 807.3  $[M+Na]^+$ . m/z 785.5421, 807.5242. HRMS Anal. Calc. for  $C_{44}H_{73}N_4O_8$  [M+H]<sup>+</sup> 785.5428,  $[M + Na]^+$  807.5247.

### N,N-Di-phenyl-3-(N'-aza-18-crown-6)-6bromopyromellitic diimide **2d**

A mixture of *N*,*N*-di-phenyl-3,6-dibromopyromellitic diimide **1b** (102 mg, 0.19 mmol), 1-aza-18-crown-6 (120 mg, 0.46 mmol), and dimethylacetamide (4 mL) was heated at 120°C, under nitrogen for 18 h. Solvent was removed under reduced pressure and the crude material was chromatographed on flash silica (dichloromethane with 2–4% v/v methanol). This material was crystallised from methanol to yield **2d** as dark purple/red crystals (96 mg, 70%).  $\delta_{\rm H}$  7.53–7.40 (m, 10H, ArH), 3.82–3.65 (m, 2H), 3.63–3.64 (m, 20H).  $\delta_{\rm C}$  164.12, 163.27, 146.86, 137.48, 131.43, 129.79, 129.42, 128.78, 127.00, 105.99, 71.57, 70.98, 70.93, 70.83, 70.42, 54.88. *m/z* (ESI) 730.3, 732.1 [M + Na]<sup>+</sup>. *m/z* 708.1546, 710.1531. HRMS Anal. Calc. for  $C_{34}H_{35}BrN_3NO_9$  [M + H]<sup>+</sup> 708.1557, 710.1536.

### N,N-Di-phenyl-3-(N'-aza-15-crown-5)-6bromopyromellitic diimide **2***c*

A mixture of *N*,*N*-di-phenyl-3,6-dibromopyromellitic diimide **1b** (140 mg, 0.27 mmol), 1-aza-15-crown-5 (140 mg, 0.64 mmol), and dimethylacetamide (4 mL) was heated at 120°C, under nitrogen for 18 h. Solvent was removed under reduced pressure and the crude material was chromatographed on flash silica (dichloromethane with 2–4 % v/v methanol). This material was crystallised from methanol to yield **2c** as dark purple/red crystals (116 mg, 66 %).  $\delta_{\rm H}$  7.52–7.25 (m, 10H, ArH), 3.82–3.80 (m, 8H), 3.69–3.64 (m, 12H).  $\delta_{\rm C}$  164.08, 163.28, 146.65, 137.52, 131.42, 129.93, 129.47, 128.85, 127.02, 106.35, 71.69, 70.99, 70.84, 70.81, 54.92. *m/z* (ESI) 686.3, 688.3 [M + Na]<sup>+</sup>. *m/z* 686.1099, 688.1081. HRMS Anal. Calc. for C<sub>32</sub>H<sub>30</sub>BrN<sub>3</sub>NaO<sub>8</sub> [M + Na]<sup>+</sup> 686.1114, 688.1081.

# N,N-Di-phenyl-3-(N'-aza-15-crown-5)-6-(N"-morpholino) pyromellitic diimide **3***c*

A mixture of **2c** (35 mg, 0.05 mmol) and morpholine (250 mg, 2.87 mmol) was dissolved in dimethylacetamide (2 mL) and heated at 140°C, under nitrogen for 3 h. Excess amine was removed under reduced pressure and the crude material was chromatographed on flash silica (dichloromethane with 0–10 % v/v methanol). This material was crystallised from methanol to yield **3c** as dark blue crystals (16 mg, 43 %), mp 210–211°C.  $\lambda_{max}/mm$  608, 362 (CH<sub>2</sub>Cl<sub>2</sub>).  $\delta_{H}$  7.55–7.40 (m, 10H, ArH), 3.91 (t, *J* 4.5, 4H, CH<sub>2</sub>O of morpholine), 3.77 (t, *J* 4.5, 4H, NCH<sub>2</sub>), 3.70–3.64 (m, 16H), 3.51 (t, *J* 4.5, 4H, CH<sub>2</sub>N of morpholine).  $\delta_{C}$  164.68, 164.13, 142.36, 141.76, 132.88, 131.82, 130.86, 129.55, 128.77, 127.32, 71.64, 71.29, 71.15, 70.78, 68.04, 54.95, 53.33. *m/z* (ESI) 693.2 [M + Na]<sup>+</sup>. *m/z* 693.2541. HRMS Anal. Calc. for C<sub>36</sub>H<sub>38</sub>N<sub>4</sub>NaO<sub>9</sub> [M + Na]<sup>+</sup> 693.2536.

# N,N-Di-phenyl-3-(N'-aza-18-crown-6)-6-(N''-morpholino) pyromellitic diimide **3d**

A mixture of **2d** (106 mg, 0.14 mmol) and morpholine (250 mg, 2.87 mmol) was dissolved in dimethylacetamide (2 mL) and heated at 140°C, under nitrogen for 3 h. Excess amine was removed under reduced pressure and the crude material was chromatographed on flash silica (dichloromethane with 0–10 % v/v methanol). This material was crystallised from methanol to yield **3d** as dark blue crystals (82 mg, 74 %), mp 200–201°C.  $\lambda_{max}$ /nm 609, 363 (CH<sub>2</sub>Cl<sub>2</sub>).  $\delta_{\rm H}$  7.56–7.49 (m, 4H, ArH), 7.45–7.39 (m, 6H, ArH), 3.93–3.88 (m, 4H), 3.74–3.59 (m, 24H), 3.52–3.48 (m, 4H).  $\delta_{\rm C}$  164.69, 164.11, 142.43, 141.52, 132.49, 131.85, 131.06, 129.53, 128.73, 127.29, 71.48, 71.25, 71.04 (broad), 70.60, 68.02, 54.75, 53.14. *m/z* (ESI) 737.1 [M + Na]<sup>+</sup>. *m/z* 737.2797. HRMS Anal. Calc. for C<sub>38</sub>H<sub>42</sub>N<sub>4</sub>NaO<sub>10</sub> [M + Na]<sup>+</sup> 737.2799.

### N,N-Di-n-octyl-3,6-di-(di-n-butylamino)pyromellitic diimide **4**

A mixture of *N*,*N*-di-*n*-octyl-3,6-dibromopyromellitic diimide (**1a**) (100 mg, 0.17 mmol) and dibutylamine (250 mg, 1.94 mmol) was heated at 120°C, under nitrogen for 18 h. The resulted crude material was chromatographed on flash silica (dichloromethane with 2–4 % v/v methanol) to obtain **4** as a blue

film (63 mg, 54 %).  $\lambda_{max}$ /nm 630 (methanol).  $\delta_{H}$  3.63 (t, *J* 7.4, 4H), 3.39 (t, *J*7.4, 8H), 1.57–1.68 (m, 4H), 1.19–1.35 (m, 8H), 1.38–1.44 (m, 28H), 0.81–0.90 (m, 18H).  $\delta_{C}$  165.57, 140.66, 132.31, 54.26, 38.55, 32.08, 31.16, 30.04, 29.56, 29.50, 28.89, 27.33, 22.95, 20.12, 14.37, 14.30. *m/z* (ESI) 695.6 [M + H]<sup>+</sup>. *m/z* 695.5477. HRMS Anal. Calc. for C<sub>42</sub>H<sub>71</sub>N<sub>4</sub>O<sub>4</sub> 695.5475.

### Determination of Association Constants

A 100 mL solution of each compound, with absorbance adjusted to between 0.3–0.6, were titrated with appropriate amounts of 2.0 M stock solution of sodium acetate, potassium acetate, and TFA in methanol. UV-vis spectra were recorded after each addition.

### X-Ray Structure Determinations

Single crystal X-ray data for compounds **3c** and **3d** were collected at 123 K using an Oxford Gemini Ultra CCD with  $Cu_{K\alpha}$  and  $Mo_{K\alpha}$  radiation, respectively. The diffraction images were processed, including a multi-scan absorption correction, using the *CrysAlisPro* software package.<sup>[10]</sup> Both structures were solved by standard methods and refined by full matrix least-squares using the *SHELX-97* program.<sup>[11]</sup> Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions using a riding model with C–H distances of 0.95–0.99 Å and  $U_{iso}(H) = 1.2 - 1.5 \times U_{eq}(C)$ . For the structure of **3d**, part of the crown ether moiety was modelled as disordered over two positions, as detailed in the Supplementary Material.

### Crystal Data for 3c

 $C_{36}H_{38}N_4O_9, M = 670.70$ , monoclinic, space group  $P2_1/n$ , a = 16.1981(6), b = 12.6027(4), c = 15.6378(6)Å;  $\alpha = 90$ ,  $\beta = 95.855(3), \gamma = 90^{\circ}; V = 3175.6(2)$ Å<sup>3</sup>;  $Z = 4; D_c = 1.403$ Mg m<sup>-3</sup>;  $\mu = 0.843$  mm<sup>-1</sup>; specimen:  $0.20 \times 0.12 \times 0.02$  mm<sup>3</sup>;  $Cu_{K\alpha} = 1.54184$ Å;  $\theta_{max} = 66.8243^{\circ}; 5564$  reflections collected; 4719 unique ( $R_{int} = 0.0309$ ); GOF = 1.038;  $R_1 = 0.0447$ , w $R_2 = 0.0925$  [ $I > 2\sigma(I$ )].

### Crystal Data for 3d

 $C_{38}H_{42}N_4O_{10}.CH_3CN, M = 755.81$ , monoclinic, space group  $P2_1/n, a = 18.1027(8), b = 9.5146(4), c = 21.6931(9)$  Å;  $\alpha = 90$ ,  $\beta = 95.487(4), \gamma = 90^{\circ}; V = 3719.3(3)$  Å<sup>3</sup>;  $Z = 4; D_c = 1.350$  Mg m<sup>-3</sup>;  $\mu = 0.098$  mm<sup>-1</sup>; specimen:  $0.25 \times 0.12 \times 0.12$  mm<sup>3</sup>; Mo<sub>K $\alpha</sub> = 0.71073$  Å;  $\theta_{max} = 30.5135^{\circ}$ ; 8548 reflections collected; 6500 unique ( $R_{int} = 0.0391$ ); GOF = 1.014;  $R_1 = 0.0667$ , w $R_2 = 0.1157$  [ $I > 2\sigma(I$ )].</sub>

### Supplementary Material

<sup>1</sup>H, <sup>13</sup>C, and mass spectroscopy data for compound families **2-3** are available on the Journal's website. Detailed crystallographic data are available from the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 986234 and 986235. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or email: deposit@ccdc.cam.ac.uk).

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