Dutta, Dzieszkowski, Kijewska, Siczek, Orzeł, Pawlicki*

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1. General information

NMR Spectroscopy. ¹H NMR spectra were recorded on a high-field spectrometer (¹H 600.15 MHz and 400 MHz, ¹³C 150 MHz and 100 MHz), equipped with a broadband inverse gradient probehead. Spectra were referenced to the residual solvent signal (chloroform-*d*, 7.26 ppm, dichloromethane-*d*₂ 5.32 ppm). Two-dimensional NMR spectra were recorded with 2048 data points in the t2 domain and up to 1024 points in the t1 domain, with a 1s recovery delay.

Mass Spectrometry. The ESI-MS analysis was performed on Bruker qTOF (Bremen, Germany) equipped with a standard ESI source. Spectra were recorded using DCM or MeOH. The instruments parameters were as follows: positive-ion mode, calibration with the Tunemix[™] mixture (Agilent Technologies, Palo Alto, CA, USA), mass accuracy was better than 5 ppm, scan range: 50 - 1600 m/z; drying gas: nitrogen; flow rate: 3.0 L/min, temperature: 200 °C; potential between the spray needle and the orifice: 4.5 kV, analyte was introduced to the ESI source by pump (New Era Pump Systems, Inc., USA) with a flow rate: 3 µL/min.

UV-Vis Spectroscopy. Electronic spectra were recorded on a Varian Carry-50 Bio spectrophotometer with a 1 cm optical path in solutions in HPLC grade CH_2Cl_2 in 298 K using standard quartz cuvettes.

Fluorescence. Steady state fluorescence spectra were recorded with a Hitachi F-7000 spectrofluorometer apparatus. Time-dependent experiments (life-time measurements) was conducted with a picosecond Horiba Jobin Yvon spectrofluorometer (UV-Vis-NIR). The fluorescence quantum yield was established using a thiomethoxy BODIPY as a reference (QY = 0.03 in DMSO).

X-Ray Analysis. X-Ray quality crystals were prepared by diffusion method from HPLC grade DCM / hexane solvent combination (**1b** and **2**). For structure **1b** diffraction data was performed using Bruker D8 Quest Eco diffractometer at 100K equipped with Photon II CPAD detector, MoK α ($\lambda = 0.71073$ Å) sealed tube radiation source and Triumph® optics. For structure **2** diffraction data was collected on a Rigaku Oxford Diffraction XtaLAB Synergy-R DW diffractometer equipped with a HyPix ARC 150° Hybrid Photon Counting (HPC) detector using CuK α ($\lambda = 1.54184$ Å) at 100 K. Data were processed using the CrystAlisPro software. The structures were solved by intrinsic phasing with SHELXT (2015 release) and refined by full-matrix least-squares methods based F2 using SHELXL.^{1,2} For all structures, H atoms bound to C atoms were placed in the geometrically idealized positions and treated in riding mode, with C-H = 0.95Å and Uiso(H) = 1.2Ueq(C) for C-H groups, and C-H = 0.98Å and Uiso(H) = 1.5Ueq(C) for CH₃ groups and while the O- and N bound H atoms were refined freely.

Theoretical calculations. Geometry optimization for all analysed structures was carried out with the Gaussian 09³ software package within unconstrained C1 symmetry, with starting coordinates derived from semi-empirical calculations. Becke's three-parameter exchange functional with the gradient-corrected correlation formula of Lee, Yang and Parr (DFT-B3LYP)⁴ were used with the 6- 31G(d,p) basis set. The polarizable continuum model of solvation was used (PCM, standard chloroform parametrization) for all optimizations. Harmonic vibrational frequencies were calculated using analytical second derivatives as a verification of local minimum achievement with no negative frequencies observed. GIAO predicted chemical shifts for all structures were calculated for fully optimized geometries. The analysis of local

¹ G. M. Sheldrick, Acta Crystallogr. 2015, A71, 3–8; G. M. Sheldrick, Acta Crystallogr. 2015, C71, 3–8

² O. V. Dolomonov, L. J. Boutjis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Crystallogr. 2009, 42, 339–341

³ Gaussian 09, Revision E.01; M. J. Frisch et al., Gaussian, Inc.: Wallingford CT, 2009

⁴ a) C. T. Lee, W. T. Yang, R. G. Parr, Phys. Rev. B, 1988, 37, 785-789. b) A. D. Becke, Phys. Rev. A, 1988, 38, 3098-3100

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diatropic currents present in analysed systems were performed via calculation of NICS value and AICD currents calculated with Gaussian 09 software and visualized with the software provided by the Authors.⁵

2. Experimental section

All solvents (MeOH, Ethyl Acetate, $CHCl_3$, n-hexane, toluene, acetone, water) if not indicated differently were used without purification. CH_2Cl_2 was distilled over CaH_2 . Chloroform-*d* was prepared directly before using by passing through a basic alumina column. All reactions were performed under inert atmosphere. Compound **3** was synthesized according to the already reported procedure⁶.

2.1 Experimental procedures



Scheme S1. Conditions: a) (5-formylfuran-2-yl)boronic acid (3 equiv.), $Pd(PPh_3)_4$ (0.1 equiv.), K_2CO_3 (10 equiv.), THF/H₂O; b) furan-2-ylboronic acid (3 equiv.), $Pd(PPh_3)_4$ (0.1 equiv.), K_2CO_3 (10 equiv.), THF/H₂O; c) DMF (4 equiv.), POCl₃ (4 equiv.), DCE ; d) TiCl₄ (38 equiv.), Zn (75 equiv.), Cul (2 equiv.), THF, reflux.

Compound 5a. A mixture of THF (150 mL) and water (50 mL) was degassed via flushing with



argon for 45 min. **3** (1 g, 2.14 mmol), (5- formylfuran-2-yl)boronic acid (0.89 g, 6.42 mmol), Pd(PPh₃)₄ (0.24 g, 0.21 mmol) and K₂CO₃ (2.95 g, 21.40 mmol) were kept in vacuum for 45 mins and the mixture of degassed solvents was added to it under argon atmosphere. The mixture was allowed to reflux for 24 h with heat-onTM block. THF was evaporated on a rotary evaporator and the remaining organics were

extracted from the remaining water with 50 mL dichloromethane. After drying over anhydrous Na₂SO₄ solvent was evaporated under reduced pressure and the crude mixture was subjected to column chromatography on Silica 60 (0.063-0.200 mm) using a mixture of ethyl acetate and hexane (3:7) as eluent collecting the third fraction to obtain **5a** as yellow solid. Yield (0.54 g): 51 %; ¹**H NMR** (400 MHz, CDCl₃, 298K) δ (ppm): 10.25 (s, 1H), 9.56 (s, 2H), 8.63 (d, ⁴J = 2.4 Hz,

⁵ D. Geuenich, K. Hess, F. Köhler, R. Herges, *Chem. Rev.* 2005, **105**, 3758–3772

⁶ K. Yamamoto, S. Higashibayashi, *Chem. Eur. J.* 2016, **22**, 663-671.

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2H), 8.04 (d, ${}^{4}J$ = 2.4 Hz, 2H), 7.45 (d, ${}^{3}J$ = 3.8 Hz, 2H), 7.12 (d, ${}^{3}J$ = 3.8 Hz, 2H), 1.44 (s, 18H).; 13 C NMR (101 MHz, CDCl₃, 298K) δ (ppm): 178.0, 176.5, 157.6, 152.6, 144.9, 135.3, 132.0, 125.9, 122.1, 116.7, 111.0, 34.8, 31.4; HRMS (APCI) m/z calculated for C₃₁H₂₉NO₅ [M+H]⁺ : 496.2124; found : 496.2118.

Compound 4. A mixture of THF (75 mL) and water (25 mL) was degassed via flushing with



argon for 45 min. **3** (0.5 g, 1.07 mmol), 2-Furanylboronic acid (0.36 g, 3.21 mmol), $Pd(PPh_3)_4$ (0.12 g, 0.11 mmol) and K_2CO_3 (1.48 g, 10.70 mmol) were kept in vacuum for 45 mins and the mixture of degassed solvents was added to it under argon atmosphere. The mixture was allowed to reflux for 18 h with heat-onTM block. THF was evaporated on

a rotary evaporator and the remaining organics were extracted from the remaining water with 50 mL dichloromethane. After drying over anhydrous Na₂SO₄ solvent was evaporated under reduced pressure and the crude mixture was subjected to column chromatography on Silica 60 (0.063-0.200 mm) using a mixture of ethyl acetate and hexane (1:9) as eluent collecting the second fraction to obtain **4** as yellow solid. Yield (0.3 g): 64 %; ¹**H** NMR (400 MHz, CDCl₃, 298K) δ (ppm): 10.88 (s, 1H), 8.51 (dd, ⁴*J* = 2.3, 0.9 Hz, 2H), 8.01 – 7.89 (m, 2H), 7.62 (dd, ⁴*J* = 2.3, 0.9 Hz, 2H), 6.79 (dd, ³*J* = 3.4, 0.9 Hz, 2H), 6.65 (dd, ³*J* = 3.4, 0.9 Hz, 2H), 1.43 (s, 18H).; ¹³C NMR (101 MHz, CDCl₃, 298K) δ (ppm): 152.4, 144.2, 142.4, 135.2, 129.9, 123.6, 121.8, 118.3, 112.0, 108.1, 34.8, 31.5; HRMS (ESI) m/z calculated for C₂₉H₂₉NO₃ [M+H]⁺ : 440.2226; found : 440.2171.

Compound 5b. DMF (0.20 mL, 2.54 mmol) was charged to a round-bottom flask at 0 °C. Freshly



distilled POCl₃ (0.24 mL, 2.54 mmol) was added to it slowly with continuous stirring. After complete addition, the reaction mixture was warmed to room temperature. After 0.5 h, **4** (0.28 g, 0.64 mmol) in 1,2-DCE (30 mL) was added to the Vilsmeier–Haack adduct at room temperature. Then the reaction mixture was refluxed by using a heat-onTM block for 2 h and cooled to room temperature. Saturated NaOAc

solution (1.05 g, 12.74 mmol in 16 mL of water) was added slowly to the reaction mixture and refluxed again for 2 h. After cooling the reaction mixture to room temperature, the organic layer was separated, and the aqueous layer was extracted with 50 ml CH₂Cl₂. Combined organic layers were passed through anhydrous Na₂SO₄ and evaporated to dryness. The crude reaction mixture was purified by Silica 60 (0.063-0.200 mm) column chromatography using ethyl acetate and hexane(3:7) collecting the second fraction followed by precipitation using DCM and hexane gave **5b** as yellowish solid, **5b**. Yield (0.19 g): 60 %; ¹H NMR (400 MHz, CDCl₃, 298K) δ (ppm): 9.77 (s, 2H), 8.49 (d, ⁴J = 2.2 Hz, 2H), 8.40 (d, ⁴J = 2.2 Hz, 2H), 7.73 (d, ³J = 3.7 Hz, 2H), 7.40 (d, ³J = 3.7 Hz, 2H), 1.54 (s, 18H); ¹³C NMR (101 MHz, CDCl₃, 298K) δ (ppm): 177.6, 157.3, 152.0, 149.9, 144.3, 141.7, 129.7, 127.8, 124.6, 120.8, 116.0, 77.4, 77.1, 76.8, 35.8, 31.0; HRMS (ESI) m/z calculated for C₃₁H₂₈ClNO4 [M+Na]⁺ : 536.1605; found : 536.1503.

Compound 1a and 1b. To a 250 mL three necked round bottom flask containing Zn dust (1 g,



15.26 mmol) and CuI (0.09 g, 0.48 mmol) in 50 mL dry, degassed THF under inert gas atmosphere, TiCl₄ (0.84 mL, 7.67 mmol) was added. The mixture was refluxed for 2 h under argon atmosphere with heat-onTM block and gradual changes of colour from green to grey were

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observed. To this generated low valent titanium (0) species, solution of the compound **5a** (0.1 g, 0.20 mmol) in 50 mL of degassed THF was added dropwise. The mixture was refluxed for 1.5 hour with heat-on block and quenched with 10 % aq. Solution of K₂CO₃ (34 mL), extracted two times with 50 mL ethyl acetate each time. The organic layer was washed with two times with 50 mL water each time, dried with Na₂SO₄, and evaporated under reduced pressure. The crude product was subjected to basic alumina (GII according to the Brockman activity grade) column chromatography using hexane / ethyl acetate (9:1). The first fraction was consisting of **1b** which was further purified by precipitation using DCM and hexane to obtain the product as red solid. Yield of compound **1b** (0.014 g): 16%. The last fraction was consisting of **1a** which was further purified by precipitation method from dichloromethane/hexane solvents to give orange solid. Yield of compound **1a** (0.04 g): 43 %.

Compound 1a: ¹**H NMR** (400 MHz, CDCl₃, 298K) δ(ppm): 15.86 (s, 1H), 8.16 (d, ${}^{4}J$ = 2.2 Hz, 2H), 7.55 (d, ${}^{4}J$ = 2.2 Hz, 2H), 6.50 (d, ${}^{3}J$ = 3.6 Hz, 2H), 6.15 (d, ${}^{3}J$ = 3.6 Hz, 2H), 5.52 (s, 2H), 1.35 (s, 18H); ¹³**C NMR** (101 MHz, CDCl₃, 298K) δ(ppm): 177.8, 155.0, 152.8, 144.2, 136.0, 126.9, 123.4, 122.2, 118.8, 115.9, 112.1, 109.1, 34.6, 31.1.; **HRMS (APCI)** m/z calculated for C₃₁H₃₀NO₃ [M+H]⁺ : 464.2226; found : 464.2220; **UV/Vis** (CH₂Cl₂, 298K, λ (nm), log ε): 277(4.77), 471(3.86).

Compound 1b: ¹**H NMR** (400 MHz, CDCl₃, 298K) δ(ppm): 8.39 (s, 1H), 7.95 (d, ⁴*J* = 2.0 Hz, 2H), 7.60 (d, ⁴*J* = 2.0 Hz, 2H), 6.97 (d, ³*J* = 3.5 Hz, 2H), 6.48 (d, ³*J* = 3.5 Hz, 2H), 6.03 (s, 2H), 1.44 (s, 18H).; ¹³**C NMR** (101 MHz, CDCl₃, 298K) δ(ppm): 155.4, 154.1, 148.4, 145.1, 134.4, 129.6, 127.5, 124.4, 121.7, 115.3, 112.7, 110.9, 35.1, 31.1; **HRMS (APCI)** m/z calculated for C₃₁H₃₀NO₂ [M+H]⁺ : 448.2277; found : 448.2271; **UV/Vis** (CH₂Cl₂, 298K, λ (nm), log ϵ): 283(4.51), 442(3.65).

Compound 2. To a 500 mL three necked round bottom flask containing Zn dust (1.68 g, 25.77



mmol) and CuI (0.157 g, 0.82 mmol) in 85 mL dry, degassed THF under inert gas atmosphere, TiCl₄ (1.43 mL, 13.06 mmol) was added. The mixture was refluxed with heat-on block for 2 h under argon atmosphere and gradual changes of colour from green to grey were observed. To this generated low valent titanium (0) species, solution of the compound **5b** (0.17 g, 0.343 mmol) in 85 mL of degassed THF was added dropwise. The mixture was refluxed for 2 hours with heatonTM block and after cooling down to room temperature the reaction

mixture was quenched with 10 % aq. solution of K₂CO₃ (57 mL), extracted two times with 100 mL ethyl acetate each time. The organic layer was washed two times with 100 mL water each time, dried with Na₂SO₄, and evaporated under reduced pressure. The crude product was subjected size exclusion column chromatography (SEC) using THF and reduced under pressure to obtain the desired compound as dark red solid. Yield (0.062 g): 40 % ; ¹H NMR (400 MHz, CDCl₃, 298K), δ (ppm): 8.01 (d, ⁴*J* = 2.0 Hz, 4H), 7.06 (d, ³*J* = 3.5 Hz, 4H), 6.83 (d, ⁴*J* = 2.0 Hz, 4H), 6.57 (d, ³*J* = 3.5 Hz, 4H), 6.13 (s, 4H), 1.05 (s, 36H); ¹³C NMR (101 MHz, CDCl₃, 298K), δ (ppm): 155.3, 154.3, 149.1, 144.9, 129.7, 125.9, 124.4, 120.6, 115.6, 112.7, 111.5, 35.1, 30.9; HRMS (ESI): *m/z*: calculated for C₆₂H₅₆N₂O₄ [M+H]⁺: 893.4318; found: 888.4313. UV/Vis (CH₂Cl₂, 298K, λ (nm), log ϵ): 286(4.97), 531(3.98).

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3. NMR spectra



Fig. S1 ¹H NMR (CDCl₃, 400 MHz, 298K) spectrum of 5a.



Fig. S2 ¹³C NMR (CDCl₃, 101 MHz, 298K) spectrum of 5a.



Fig. S3 ¹H NMR (CDCl₃, 400 MHz, 298K) spectrum of **4**.



Fig. S4 ¹³C NMR (CDCl₃, 101 MHz, 298K) spectrum of 4.



Fig. S5 ¹H-¹H COSY (CDCl₃, 400 MHz, 298K) spectrum of **4**.



Fig. S6 ¹H-¹H NOESY (CDCl₃, 400 MHz, 298K) spectrum of **4**.



Fig. S8 $^{\rm 13}C$ NMR (CDCl₃, 101 MHz, 298K) spectrum of 5b.



Fig. S9 ¹H-¹H COSY (CDCl₃, 400 MHz, 298K) spectrum of **5b**.









Fig. S16 ¹H-NMR (CDCl₃, 400 MHz, 298K) spectrum of **1b**.



Fig. S18 ¹H-¹H COSY (CDCl₃, 400 MHz, 298K) spectrum of **1b**.



Fig. S19 ¹H-¹H NOESY (CDCl₃, 400 MHz, 298K) spectrum of **1b**.



Fig. S20 ¹H-¹³C HSQC (CDCl₃, 400 MHz, 298K) spectrum of **1b**.



Fig. S22 ¹H-NMR (CDCl₃, 400 MHz, 298K) spectrum of **2**.



Fig. S23 ¹³C-NMR (CDCl₃, 101 MHz, 298K) spectrum of 2.



Fig. S24 ¹H-¹H COSY (CDCl₃, 400 MHz, 298K) spectrum of **2**.



9	8	7	ppm 6

Fig. S26: ¹H NMR-monitored titration of **1b** with TFA (CDCl₃, 400 MHz, 298 K); A – without; B - 1 eq. TFA. Assignment follows the numbering system presented in **Scheme 1**.

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Fig. S27: ¹H NMR-monitored titration of **2** with TFA followed by DBU (CD₃CN, 400 MHz, 298 K); **A** – without TFA; **B** – 1 eq. TFA; **C** – 2 eq. TFA; **D** – 3 eq. TFA; **E** – 3 eq. TFA + 3 eq. DBU.

4. UV-VIS spectra



Fig. S28 Extinction spectra of the neutral macrocycle 1a, 1b and 2 in CH₂Cl₂ at 298K.

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Fig. S29 UV-Vis spectra recorded during titration of 1b (bottom) and 2 (top) with TFA followed by **DBU** in dichloromethane at rt.

5. Emission spectra



Fig. S30 Normalized emission spectra of the neutral macrocycle 1b (red) and 2 (blue) in Dichloromethane at 295K (left) in solid state (right).

Table S1. Emission properties for neutral macrocycle 1b and 2.							
Compounds	$\lambda_{\text{emission}}^{[a]},$	$\lambda_{\text{emission}}^{[a]}, \qquad \lambda_{\text{exitation}}^{[b]},$		$\Phi^{[c]}$			
	nm (solid)	nm	nm (DCM)	(DCM)			
1b	644	471	627	64 %			
2	686	261	642	46 %			

-. ~ . . 1.7

[a] Emission maxima. [b] Excitation wavelength. [c] Quantum yield.

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Fig. S31 Emission recorded during titration of **1b** with **TFA** followed by **DBU** in dichloromethane at rt.



Fig. S32 Emission recorded during titration of 2 with TFA in dichloromethane at rt.

5. Lifetime Measurement



Fig. S33 Fluorescence decay profile of 1b in CH₂Cl₂ at 298K.

Supporting information



Fig. S34 Fluorescence decay profile of 2 in CH₂Cl₂ at 298K.



Fig. S35. TFA titration of **1b** (concentration in each attempt: 2.3·10⁻⁵ M) in different solvents.



Fig. S36. 1b in different solvents $(2.3 \cdot 10^{-5} \text{ M})$ registered after keeping in different temperatures with no changes.

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Fig. S37. 2 in different solvents (*conc.* $5.2 \cdot 10^{-6}$ M).



Fig. S38. **1b** (*conc.* $2.3 \cdot 10^{-5}$ M) protonated with TFAH at different temperatures showing no change.



Fig. S39. Emission spectra of 1b (4.6·10⁻⁶ M) in different solvents.

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6. ESI-MS spectra



Fig. S40 APCI-MS spectrum of **5a** with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).



Fig. S41 ESI-MS spectrum of **1b** with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).



Fig. S42 APCI-MS spectrum of **1a** with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).



Fig. S43 ESI-MS spectrum of **4** with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).



Fig. S44 ESI-MS spectrum of **5b** with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).



Fig. S45 ESI-MS spectrum of **2** with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).

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7. Theoretical calculations

7.1 NICS and GIAO calculations

Table S2. Comparison of ¹H chemical shifts recorded and predicted with GIAO calculations.

Observed vs predicted NMR chemical shifts									
	2		1b		1b + TFA		1a		
Positions	Observed chemical shift (ppm)	calculated chemical shift (ppm)	Observed chemical Shift (ppm)	calculated chemical shift (ppm)	Observed chemical Shift (ppm)	calculated chemical shift (ppm)	Observed chemical shift (ppm)	Calculated chemical shift (ppm)	
2 ¹ , 4 ¹	6.84	6.83	7.60	7.58	7.87	7.68	8.18	7.96	
6 ¹ ,17 ¹	8.02	8.24	7.96	8.25	8.13	8.32	7.58	7.61	
8,15	7.07	7.25	6.97	7.21	7.06	7.14	6.56	6.52	
9,14	6.57	6.65	6.49	6.54	6.49	6.49	6.22	6.00	
11,12	6.14	5.85	6.04	5.70	5.91	5.52	5.62	4.94	
3			8.39	8.13	9.29	8.68			
18					18.27	18.76	15.85	17.16	

Table S3. Compa	rison NICS(0)iso a	nd NICS(0)zz for	compound 1a	, 1b and 2 .

	2			2 1b				3a				
Positions	NICS(0) _{iso}	NICS(0)zz	NICS(1) _{iso}	NICS(1) _{ZZ}	NICS(0) _{iso}	NICS(0) _{ZZ}	NICS(1) _{iso}	NICS(1)zz	NICS(0) _{iso}	NICS(0) _{ZZ}	NICS(1) _{iso}	NICS(1)zz
а	-7.19	-3.93	-9.64	-17.43	-6.73	-0.62	-8.68	-18.73	-6.71	3.88	-8.07	-14.94
b	-10.61	-20.67	-10.50	-20.25	-9.92	-10.78	-12.38	-28.83	-2.77	11.72	-5.18	-8.55
С	-9.34	4.33	-6.42	-16.00	-9.17	6.13	-7.69	-15.95	-7.27	13.64	-5.50	-9.98
d	1.66	23.78	0.41	6.59	2.01	24.98	0.83	9.12	5.73	37.08	4.22	19.31
e	3.75	31.55	0.99	10.18	3.92	33.14	1.44	11.47	4.76	42.93	3.49	19.56







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7.2. AICD plots.



Fig. S46 AICD plots for 1a (A), 1b (B) and 2 (C).

7.3. Cartesian Coordinates.

Provided as pdb files.

8. X-Ray Analysis

Identification code	1b	2		
Empirical formula	C ₃₁ H ₂₉ NO ₂	C64.50H58.75N2O4		
CCDC number	2428088	2428089		
Formula weight	447.55	925.88		
Temperature [K]	100(1)	100(1)		
Wavelength [Å]	0.71073	1.54184		
Crystal system, space group	monoclinic, $P2_1/c$	monoclinic, P-1		
Unit cell dimensions [Å] and [°]				
Volume [Å ³]	2297.0(3)	2591.0(12)		
Z, Calculated density [Mg·m ⁻³]	4, 1.294	2, 1.177		
Absorption coefficient [mm ⁻¹]	0.080	0.845		
F(000)	952.0	973.0		
Crystal size [mm]	0.15 imes 0.10 imes 0.05	$0.10\times0.07\times0.02$		
20 range for data collection [°]	4.296 to 52.744	6.998 to 151.032		
Limiting indices	$-25 \le h \le 25$ $-13 \le k \le 13$ $-13 \le 1 \le 13$	$-15 \le h \le 15$ $-16 \le k \le 17$ $-17 \le l \le 17$		
Reflections collected/unique	$44386/4279 (R_{int} = 0.2441)$	45973/10371 (R _{int} = 0.0207)		
Completeness [%] to theta [°]	91.1 to 26.37	96.6 to 75.52		
Absorption correction	multi-scan	gaussian		
Max. and min. transmission	0.726/0.618	1.000/0.809		
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²		
Data/restraints/parameters	4279/45/321	10371/75/688		
Goodness-of-fit on F ²	1.190	1.066		
Final R indices [I>2 σ (I)]	$R_1 = 0.1923, wR_2 = 0.3271$	$R_1 = 0.0532, wR_2 = 0.1479$		
R indices (all data)	$R_1 = 0.2417, wR_2 = 0.3512$	$R_1 = 0.0622, wR_2 = 0.1549$		
Largest diff. peak and hole $[eÅ^{-3}]$	0.62/-0.51	0.50/-0.21		



Fig. S47 Crystal structures of 1b (left) and 2 (right).