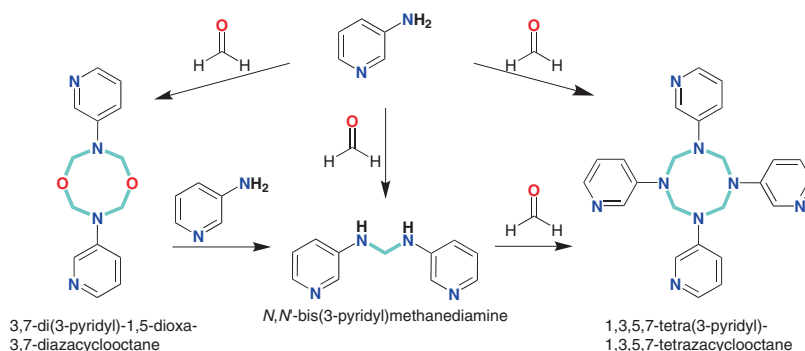


# Synthesis and Characterization of an Eight-Membered Heterocyclic 1,3,5,7-Tetra(3-pyridyl)-1,3,5,7-tetrazacyclooctane

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**Abstract** *N,N'*-Bis(3-pyridyl)methanediamine was prepared by treating 3-aminopyridine with formaldehyde in acetonitrile. By treating it with formaldehyde, the eight-membered heterocyclic ring compound 1,3,5,7-tetra(3-pyridyl)-1,3,5,7-tetrazacyclooctane was prepared. This could occur in a two-step manner in a [3+1+3+1] cycloaddition reaction. The compounds were characterized by X-ray crystallography, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, and mass spectrometry. The powder XRD pattern of 1,3,5,7-tetra(3-pyridyl)-1,3,5,7-tetrazacyclooctane was also determined and revealed an uncommon twist-crown conformation, which was further confirmed by DFT calculations.

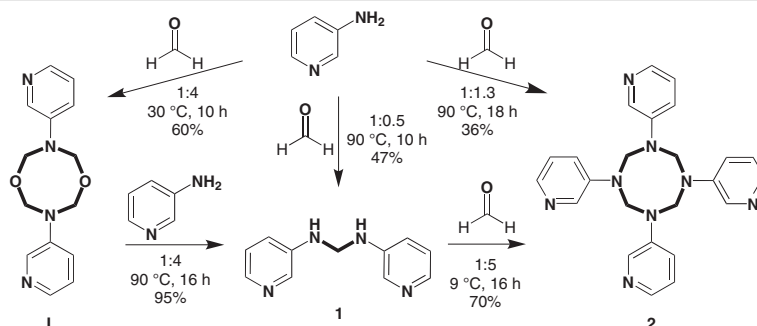
**Key words** *N,N'*-bis(3-pyridyl)methanediamine, 1,3,5,7-tetra(3-pyridyl)-1,3,5,7-tetrazacyclooctane, heterocycles, cyclooctanes, cycloaddition, twist-crown conformation, DFT calculations

Cyclooctane and its derivatives have been studied for decades. They have shown diverse conformations like boat-chair, crown, and boat-boat, among others.<sup>1</sup> Eight-membered rings with the methylene groups replaced by oxygen, sulfur, or nitrogen moieties have received relatively little attention. There are three bidentate heterocyclic compounds containing two sulfur or nitrogen heteroatoms (1,5-diazacyclooctane, 1,5-dithiacyclooctane,<sup>2</sup> and 1,5-dithiacyclooctane-1-oxide)<sup>3</sup> that have been employed as macrocyclic ligands. Kolar and Schendzielorz reported a few eight-membered heterocyclic compounds with alternate O and N atoms, namely 3,7-bis(4-trifluoromethylphenyl)-1,5,3,7-dioxadiazocine and its derivatives, in 1985.<sup>4</sup> Recently, two similar heterocyclic compounds, 3,7-bis(4-nitrophenyl)-1,5-dioxo-3,7-diazacyclooctane<sup>5</sup> and 3,7-di(3-nitrophenyl)-

1,5-dioxo-3,7-diazacyclooctane,<sup>6</sup> have been prepared and characterized by X-ray structure determination. Two compounds with alternate S and N heteroatoms have been reported. One is 1,5-dithia-3,7-diazacyclooctane with a crown conformation,<sup>7</sup> and the one is *trans*-5,10-bis-(methoxycarbonyl)-5,10-diphenyldipyrzolo[1,5-a:l',5'-e]-[1,5]-diaz[3,6]dithiocine.<sup>8</sup> Heterocyclic compounds with four nitrogen atoms have also been less reported; one is the energetic material 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane.<sup>9–13</sup> Another one is 1,3,5,7-tetraphenyltetrazocine with a twist-chair conformation.<sup>14</sup>

We have previously designed and prepared the clamp-like eight-membered heterocyclic compound 3,7-di(3-pyridyl)-1,5-dioxo-3,7-diazacyclooctane (**L**). The two pyridyl groups in **L** are separated by a distorted heterocycle, which adopts a crown conformation and elicited our interest in these structures.<sup>15,16</sup> During the synthesis of this compound, we unexpectedly obtained a 1,3,5,7-tetra(3-pyridyl)-1,3,5,7-tetrazacyclooctane by changing the reaction conditions. The molecule is centrosymmetric, being arranged about a crystallographic symmetry center. The eight-membered heterocyclic ring adopts a twist-crown conformation.<sup>1</sup> The formation of the heterocyclooctane compound might occur in a two-step manner through a [3+1+3+1] cycloaddition reaction. Hence, we tried to prepare **2** in a two-step process, and the intermediate product *N,N'*-bis(3-pyridyl)methanediamine, which is related to two eight-membered heterocyclic compounds (Scheme 1), was isolated and characterized.

Single crystals with dimensions of 0.20 mm × 0.25 mm × 0.37 mm (**1**) and 0.16 mm × 0.18 mm × 0.20 mm (**2**) were mounted on glass fibers. Single-crystal X-ray diffraction measurements were performed on a Bruker APEX II 4K CCD area detector equipped with graphite monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.071073$  nm) by using the  $\omega$ -scan mode on all observed reflections between  $\theta$  values of 2.42° to

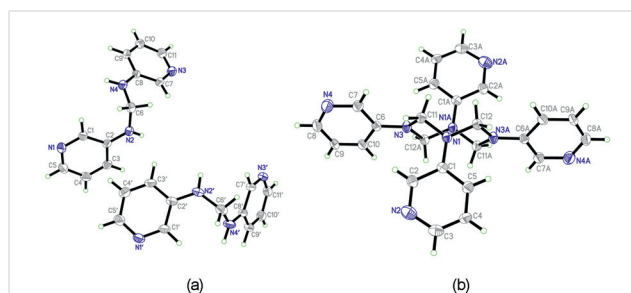


**Scheme 1** Preparation of compounds

27.38° (**1**) and 3.12° to 29.11° (**2**).<sup>17</sup> All absorption corrections were applied by using the SADABS program.<sup>17</sup> Structures were solved by direct methods and refined on  $F^2$  by the full-matrix least-squares method with the SHELXTL-97 program package.<sup>18,19</sup> All of the atoms were located from the e-maps, and hydrogen atoms were derived from the successive difference Fourier peaks. Crystallographic and structural refinement details for **1** and **2** are given in the Supporting Information.

Compound **1** crystallizes in the monoclinic space group  $P_{21/m}$ , and its asymmetric unit contains two  $N,N'$ -bis(3-pyridyl)methanediamine molecules. Compound **1** is Z-type in shape; the two pyridine rings are antiparallel (SI 1). Compound **2** crystallizes in the monoclinic space group  $P_{21/c}$ , and its asymmetric unit contains half of a **2** molecule. The pyridine rings are supported by an eight-membered ring in **2**. The four pyridine rings are arranged mutually perpendicular in space (Figure 1). The  $N_4C_4$  heterocyclic ring has a twist-crown conformation; the four symmetry-independent torsion angles are  $C12-N1-C11-N3 = 110.70(12)^\circ$ ,  $C11-N1-C12-N3A = -112.73(11)^\circ$ ,  $C12A-N3-C11-N1 = -31.72(15)^\circ$ , and  $C11-N3-C12A-N1A = -36.28(15)^\circ$ , respectively. These are different from those reported in 1,3,5,7-tetraphenyltetrazocine ( $-38.5^\circ$ ,  $113.8^\circ$ ,  $-108.0^\circ$ ,  $29.7^\circ$ ), which has a twist-chair conformation.<sup>14</sup> This symmetry is often coincidental with a crystallographic symmetry element. Usually, as for cyclooctane, the most common and stable conformation is boat-chair, which minimizes transannular interactions and has a lower torsional strain. The predominant conformation at room temperature is boat-chair, with remaining compounds in the crown conformation.<sup>1</sup> The conformation might be affected by steric hindrance from the pyridine rings, the reaction conditions, and the relatively small barriers of pseudorotation and ring inversion in compound **2**. The N–C bond lengths in the heterocyclic ring in **2** range from 1.4458(15) to 1.4646(16) Å; these are close to those of 1.45(1) to 1.47(2) Å reported in substituted tetrazocines.<sup>14</sup> Owing to the increase of s character and conjugation with the pyridine ring, the N atoms in the eight-membered ring show slightly shorter N–pyridine

bond lengths (1.3893(16) and 1.3877(15) Å) than those of 1.392(5) and 1.390(5) Å in 1,3,5,7-tetraphenyltetrazocine. There are intermolecular hydrogen bonds of C–H...N in compound **2**; their bond lengths are 3.5629(19) and 3.5148(18) Å.



**Figure 1** Molecular structures of **1** (a) and **2** (b); symmetry code for **2**:  $x, -y, -z$

In the IR spectra, the bands at approximately 1585, 1563, and 1490  $\text{cm}^{-1}$  (**1**) and 1587, 1534, and 1478  $\text{cm}^{-1}$  (**2**) were assigned to the stretching vibrations of the pyridyl groups (SI 3). The strong peaks at around 3236 and 3156  $\text{cm}^{-1}$  (**2**) were attributed to the stretching vibrations of the N–H bonds. The peaks at 3035 and 2898  $\text{cm}^{-1}$  (**1**) and 3098 and 3037  $\text{cm}^{-1}$  (**2**) were attributed to the stretching vibrations of the  $\text{CH}_2$  groups. The UV/visible spectra of compounds **1** and **2** were found to have similar absorption peaks (SI 6). The normalized peak heights were also equivalent to each other. Peaks at around 267 and 292 nm corresponded to  $\pi$ – $\pi^*$  and  $n$ – $\pi^*$  transitions of the pyridine ring.

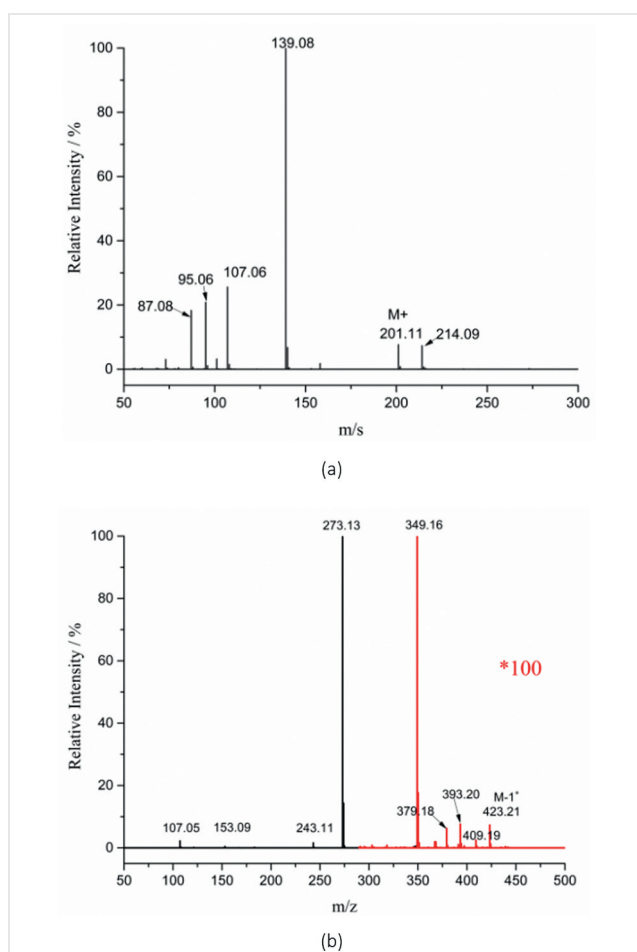
The  $^1\text{H}$  NMR spectrum, with the integral ratio, of compound **1** in *methanol-d*<sub>4</sub> was correct and is shown in SI 4. We also recorded the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound **2** (SI 5). The hydrogen spectrum in  $\text{CDCl}_3$  shows a singlet for the  $\text{CH}_2$  groups at 5.30 ppm and two multiplet peaks at 6.94–7.25 ppm and 7.95–8.43 ppm, with the correct integral ratios. However, in *methanol-d*<sub>4</sub>, the singlet was at 4.87 ppm and the multiplet peaks were at 6.99–7.02, 7.31–7.34, 7.74–7.75, and 8.12–8.13 ppm with the correct

integral ratios for the pyridine groups. The chemical shifts of the carbon spectrum were different to those for 3,7-di(3-pyridyl)-1,5-dioxo-3,7-diazacyclooctane (**L**) that we have previously studied.<sup>15</sup> The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2** also exhibited signals for the five different carbon atoms of the pyridyl groups at 142.30, 140.36, 137.07, 124.74, and 123.68 ppm; the methylene group peak was at 83.26 ppm. In **L**, these values were 140.98, 139.76, 136.92, 123.00, and 121.52 ppm for the pyridyl groups and 82.66 ppm for the methylene group.

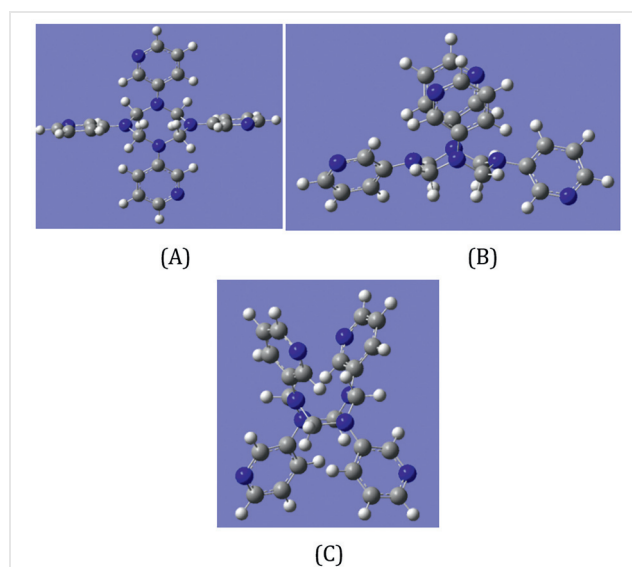
The positive-ion electron-impact mass spectra of **1** and **2** in methanol were measured. There are obvious molecular ion peaks in the spectra. Compound **1** has a peak at  $m/z$  201 for the molecular ion. Compound **2** displays a weak but distinct peak at  $m/z$  424 for the molecular ion, as shown in Figure 2. This is similar to that reported for 1,3,5,7-tetraphenyltetrazocine.<sup>14</sup> The phase purity of the bulk product of complex **2** was further confirmed by elemental analysis and

powder X-ray diffraction; the powder XRD patterns of the synthesized samples are consistent with those simulated from the respective single-crystal structures (SI 8).

For this study, we also used DFT calculations to confirm the possible structures for compound **2** obtained in the experiment. All possible geometries of the stable configurations were optimized at the B3LYP level of theory in combination with the 6-311++G\*\* basis set.<sup>20,21</sup> The nature of the stationary points was verified through a vibrational analysis (no imaginary frequencies). After optimization, we identified three stable configurations, and the spatial structures of these three compounds are shown in Figure 3. They are twist-crown (A), chair-chair (B), and twist-boat-boat (C) conformations. Table 1 lists the related energy data for these three configurations. The twist-crown conformation (A) represents the most stable conformation, followed by B, and the C conformation is the most unstable among them. This further proved the rationality of the previous structural tests. The calculated geometric parameters of this compound are also listed in Table 1. In Table 2, some available experimental values are listed for comparison. The theoretical values are well in agreement with the experimental findings, so the theoretical level chosen in this work is reliable for describing the features of compound **2**. Selected (left) and calculated (right) bond lengths (Å) and bond angles ( $^\circ$ ) for **2** are listed in Table 2.



**Figure 2** Positive-ion electron-impact mass spectra of **1** and **2** in methanol



**Figure 3** Three possible conformations of **2**

**Table 1** Gibbs Free Energy of the Three Possible Conformations

Species	Total Gibbs free energy (au)	Relative Gibbs free energy ( $\text{kJ mol}^{-1}$ )
A	-1366.903037	0.0
B	-1366.897414	14.76
C	-1366.895705	19.25

Reactions of anilines with CH<sub>2</sub>O are complex: they may form 1,4-diazacyclobutanes, cyclic trimers, tetrazocines,<sup>14</sup> 1,5-dioxa-3,7-diazacyclooctanes,<sup>6,15</sup> other oligomers, or products from more complicated reactions.<sup>22,23</sup> During the preparation of the eight-membered heterocyclic compound, there are two factors playing key roles. One is the ratio of the substrates, and the other is temperature. This can be seen from the synthesis of heterocyclic compounds with alternate O and N atoms. In our preliminary study, we prepared a 1,5-dioxa-3,7-diazacyclooctane by treating 3-aminopyridine with aqueous formaldehyde at ambient temperature. The 3,7-bis(4-X-aryl)-1,5,3,7-dioxadiazocines (X = CF<sub>3</sub>, COOCH<sub>3</sub>, CN, or NO<sub>2</sub>) were produced below zero degrees,<sup>2</sup> the 3,7-di(3-nitrophenyl)-1,5-dioxa-3,7-diazacyclooctane was prepared at room temperature,<sup>6</sup> and the 3,7-bis(4-nitrophenyl)-1,5-dioxa-3,7-diazacyclooctane was synthesized at ambient temperature.<sup>5</sup> Randaccio et al. reported a compound of 1,3,5,7-tetraphenyltetrazocine that was made under moderately high temperature conditions.<sup>14</sup> It was a slightly difficult reaction involving rapid addition of formaldehyde (in the form of solid, dry paraformaldehyde) to a refluxing concentrated solution of freshly distilled aniline. Herein, we have built the heterocyclooctane 1,3,5,7-tetra(3-pyridyl)-1,3,5,7-tetrazacyclooctane (**2**) by a convenient solvothermal method in a two-step way. This might provide a way to build other similar heterocyclooctane compounds.

3-Aminopyridine was purchased from the Aladdin reagents company. Formaldehyde (in solid form) and acetonitrile were purchased from commercial sources and used as received without further purification. Melting points were recorded by using an electrothermal melting point apparatus. Carbon, hydrogen, and nitrogen analyses were carried out by direct combustion on an EA1110-CHNSO elemental analyzer. FT-IR spectra were recorded on a Perkin Elmer Spectrum BXII spectrometer. Powder X-ray diffraction determination was performed on an X-ray diffractometer (X'Pert PRO MPOCPW 3040/60, Panalyti-

cal) with Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm), the operating voltage and current were 40 kV and 40 mA, respectively, and the measurement was carried out over a  $2\theta$  range of 10° to 50° in continuous scanning mode. The <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were measured on a Bruker AVANCE III 400MHz spectrometer by using CD<sub>3</sub>OD and CDCl<sub>3</sub> as solvents. Chemical shifts are quoted relative to the residual solvent signal. The positive-ion electron-impact mass spectra were measured on a high-resolution accurate-mass Thermo Scientific quadrupole-Orbitrap mass spectrometer by adopting atmospheric pressure chemical ionization mode. The samples were dissolved in the methanol before testing.

CCDC 855709 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

#### ***N,N'*-Bis(3-pyridyl)methanediamine (1)**

Formaldehyde (0.355 g, 11.83 mmol) was added to a solution of 3-aminopyridine (2.226 g, 23.65 mmol) in acetonitrile or water (10 mL). The reaction system was heated to reflux at 80 °C for 16 h and filtered immediately. After the filtrate had cooled to room temperature, light-pink block crystals were obtained. Compound **1** could also be prepared nearly quantitatively from 1,5-dioxa-3,7-diazacyclooctane (**L**) by treatment with 3-aminopyridine in a ratio of 1:4.

Light-pink block crystals; yield: 1.104 g (47%); mp 193 °C.

FT-IR (KBr): 3422 (m), 3236 (vs), 3156 (s), 3098 (s), 3037 (vs), 2996 (s), 1587 (vs), 1534 (s), 1478 (vs), 1426 (s), 1386 (s), 1343 (m), 1282 (vs), 1247 (s), 1192 (m), 1137 (m), 1090 (vs), 1016 (s), 879 (w), 796 (s), 705 (s), 629 (m), 513 (w), 468 (w), 411 (w).

<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD):  $\delta$  = 7.95 (d,  $J$  = 2 Hz, 2 H), 7.85 (t,  $J$  = 2.8, 3.2 Hz, 2 H), 7.19 (t,  $J$  = 1.6, 2.8 Hz, 2 H), 7.06–7.12 (m, 2 H), 4.88 (s, 2 H), 4.63 (s, 2 H).

Anal. Calcd for C<sub>11</sub>H<sub>12</sub>N<sub>4</sub>: C, 65.98; H, 6.04; N, 27.98. Found: C, 65.80; H, 6.01; N, 27.80.

#### **1,3,5,7-Tetra(3-pyridyl)-1,3,5,7-tetrazacyclooctane (2)**

A mixture of analytical-grade 3-aminopyridine (1.527 g, 16.23 mmol), solid formaldehyde (0.633 g, 21.09 mmol), and acetonitrile (30 mL, 574.42 mmol) in a mole ratio of 1:1.3:35.39 was sealed in a 50 mL Teflon-lined stainless container, which was heated to 90 °C and

**Table 2** Selected (Left) and Calculated (Right) Bond Lengths (Å) and Bond Angles (°) for **2**<sup>a</sup>

Bond lengths					
N1–C1	1.3889(16)	1.3993	N1–C11	1.4447(15)	1.4504
N1–C12	1.4457(15)	1.4478	N3–C6	1.3877(15)	1.3930
N3–C11	1.4651(15)	1.4673	N3–C12A	1.4616(16)	1.4643
C12–N3A	1.4616(15)	1.4643	C1–C2	1.4004(18)	1.4054
C1–C5	1.4033(18)	1.4120	C6–C7	1.4013(18)	1.4130
C6–C10	1.3993(18)	1.4069			
Bond angles					
C1–N1–C11	121.10(10)	120.77	C1–N1–C12	121.29(10)	120.97
C11–N1–C12	117.54(10)	118.14	C6–N3–C12A	120.46(10)	120.76
C6–N3–C11	120.01(10)	120.25	C12A–N3–C11	118.93(9)	118.92
N1–C11–N3	113.37(10)	114.18	N1–C12–N3A	112.23(10)	113.85

<sup>a</sup> Symmetry code for **2**: x, –y, –z.

maintained at that temperature for 10 h. After the sample had cooled to room temperature and was filtered, the desired product was afforded as white rectangular crystals. Compound **2** could also be prepared in 70% yield by treating **1** with formaldehyde in a ratio of 1:5.

White rectangular crystals; yield: 0.620 g (36%); mp 225 °C.

FT-IR (KBr): 3430 (m), 3036 (w), 2898 (w), 1585 (vs), 1563 (s), 1490 (vs), 1471 (s), 1438 (s), 1404 (m), 1377 (s), 1364 (s), 1351 (vs), 1302 (vs), 1275 (s), 1249 (s), 1189 (m), 1166 (s), 1133 (m), 1029 (m), 1008 (m), 970 (m), 937 (m), 798 (s), 777 (m), 709 (s), 617 (w), 582 (w), 536 (w), 518 (w), 458 (w).

<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD): δ = 8.13 (d, *J* = 2.8 Hz, 4 H), 7.74 (dd, *J* = 1.2, 0.8 Hz, 4 H), 7.31–7.34 (dq, 4 H), 6.99–7.02 (q, 4 H), 4.87 (s, 8 H).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.95–8.43 (m, 8 H), 6.94–7.25 (m, 8 H), 5.30 (s, 8 H).

<sup>13</sup>C{<sup>1</sup>H} NMR (400 MHz, CD<sub>3</sub>OD): δ = 142.30, 140.36, 137.07, 124.74, 123.68, 83.26.

Anal. Calcd for C<sub>24</sub>H<sub>24</sub>N<sub>8</sub>: C, 67.91; H, 24.19; N, 26.40. Found: C, 67.83; H, 24.09; N, 26.33.

## Conflict of Interest

The authors declare no conflict of interest.

## Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0042-1751494>.

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