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Synthesis and intramolecular ring transformation of *N,N'*-dialkylated 2,6,9-triazabicyclo[3.3.1]nonadienes†

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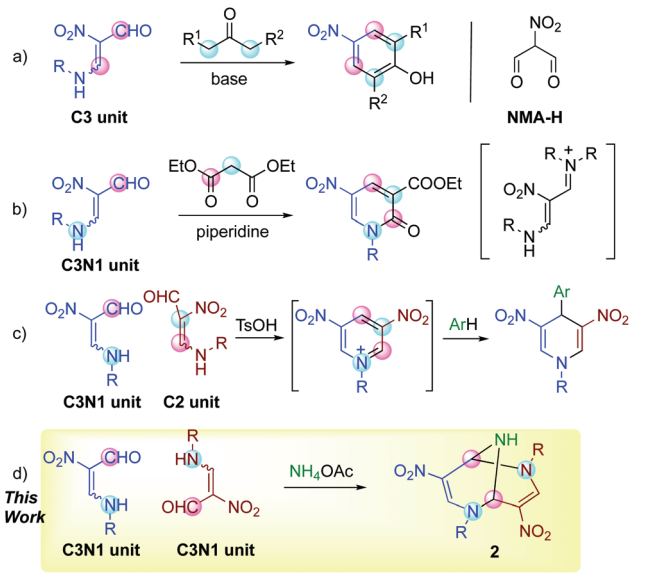
The first and facile synthesis of *N,N'*-dialkylated 2,6,9-triazabicyclo[3.3.1]nonadienes was achieved by the [4 + 4] self-condensation of β-formyl-β-nitroenamine in the presence of ammonium acetate. The 2,6- and 2,9-dialkylated products were found to be interconvertible when dissolved in a solvent. This isomerization proceeds through intramolecular ring transformation *via* a common intermediate under equilibrium.

Introduction

β-Formyl-β-nitroenamine **1** possesses multiple functionalities such as a formyl, nitro, and amino group, and a carbon–carbon double bond with biased electron density, which bring about diverse reactivities.[1] Two electrophilic sites of **1** react with dinucleophiles such as hydrazines, 1,2-diamines, and ketones to afford nitrated pyrazoles,[2] diazepines[2] and phenols (Scheme 1, a),[3] respectively, in which nitroenamine **1** serves as a synthetic equivalent of nitromalonaldehyde (**NMA-H**). Its sodium salt (**NMA-Na**) component has been used for this purpose for a long time. However, **NMA-Na** should be handled carefully because of the explosive impurity, and aqueous or alcoholic media should be used.[4] In contrast, nitroenamine **1** is safely handleable, and its high solubility in common organic solvents allows its reaction with versatile reagents in organic media.

The dipolar properties of nitroenamine **1** facilitate its reactions with 1,3-dicarbonyl compounds possessing both nucleophilic and electrophilic sites, and polyfunctionalized pyridones are synthesized through this process.[5] In these reactions, a secondary amine such as piperidine is found to be a suitable base for condensation, while a tertiary amine such as triethylamine causes no reaction, indicating that the intermediate formation of iminium species is crucial (Scheme 1, b). Furthermore, the [4 + 2] self-condensation of **1** proceeds in the presence of sulfonic acid to form a dinitropyridinium salt *in situ*, which can be trapped by electron-rich benzenes leading to the formation of 4-arylated 1,4-dihydropyridines (Scheme 1, c).[6]



Scheme 1 Reactions using nitroenamine **1**, in which the pink circles and blue circles indicate electrophilic and nucleophilic sites, respectively.

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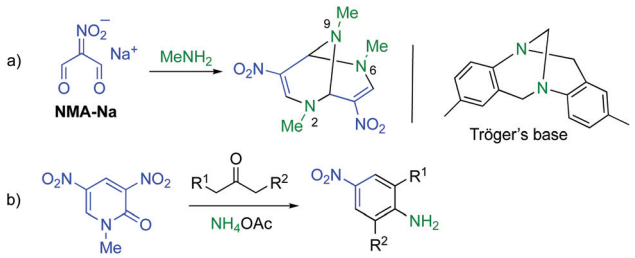
†Electronic supplementary information (ESI) available: Spectral data and copies of NMR spectra of compounds **2–6**, crystallographic data of **2a** and **3d**, and temperature-dependent NMR spectra. CCDC 2027731 and 2027735. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0ob01950j

These results prompted us to design a new synthetic method for the triazabicyclic framework, including the [4 + 4] self-condensation of nitroenamine **1**. Tröger's base[7] (3,7-dibenzo-2,6-diazabicyclo[3.3.1]nonane) with a V-shaped structure has attracted much attention because of its chirality,[8] biological activity,[9] molecular recognition ability,[10] and optoelectronic properties.[11] However, the bridgehead nitrogen atoms cannot be modified anymore. Hence, researchers' attention has recently turned towards its aza-analogue, 2,6,9-triazabicyclo[3.3.1]nonane (TABN), because of the availability of further interactions and modifiability of nitrogen atoms in the scaffold.[12] However, it is still difficult to introduce a functional group into the bicyclic framework,[13] except for two examples.[14,15] We focused on one of the examples, Ostercamp's work. The functionalized TABN derivative was first synthesized by the treatment of **NMA-Na** with methylamine (Scheme 2, a).[15] The use of safely handleable nitroenamine **1** was considered to represent a general synthetic method for diverse TABNs because the *N*-substituent of **1** can be easily modified. In Ostercamp's work, methylamine also serves as a nitrogen source to form a nitrogen bridge, which indicates that the addition of a nitrogen source to our reaction is also necessary. In our study of three-component ring transformation using dinitropyridone, ammonium acetate was found to serve as an excellent nitrogen source and an activator of the substrate (Scheme 2, b),[16] which prompted us to study the synthesis of TABNs using nitroenamine **1** and ammonium acetate (Scheme 1, d).

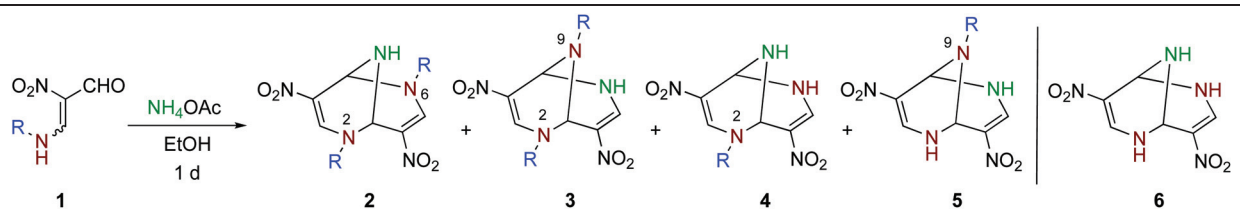


Scheme 2 Synthetic equivalents of **NMA-H**: (a) sodium salt **NMA-Na** and (b) 1-methyl-3,5-dinitro-2-pyridone.

Results and discussion

When a solution of nitroenamine **1a** in ethanol was heated at 80 °C for 1 d in the presence of ammonium acetate, four kinds of TABNs **2a–5a** were formed, among which **2a** and **3a** could not be separated by column chromatography (Table 1, entry 1). In the ^{1}H NMR spectrum of one major product **2a**, a singlet signal assigned to two equivalent olefinic protons and an NH signal showing coupling with the adjacent bridgehead protons were observed. Hence, this isomer was determined to be a 2,6-dipropyl derivative. The other major product **3a** possesses an unsymmetrical structure; one of the olefinic protons was observed as a singlet, and the other was observed as a doublet coupled with the adjacent NH proton, which was also supported by the ^{1}H–^{1}H COSY 2D NMR spectrum. The recrystallization of the **2a** and **3a** mixture afforded a single crystal of **2a**, which was subjected to X-ray crystallography to confirm the structure (Fig. 1, left). Fortunately, a single crystal of dibenzyl derivative **3d** was obtained, and the structure was confirmed to be a 2,9-disubstituted isomer (Fig. 1, right). The use of lower reaction temperature increased the total yield of products **2a–5a**, presumably because the competitive decomposition of

Table 1 Formation of four kinds of triazabicyclic compounds **2–5**



Entry	R		NH_4OAc (equiv.)	Temp. (°C)	Yield[a] (%) 2	3	4	5	Total	Recovery of **1**[a] (%)
1	Pr	**a**	1	80	25	12	7	2	46	20
2	Pr	**a**	1	50	51	20	19	1	90	10
3	Pr	**a**	1	rt	45	12	18	0	75	18
4	Pr	**a**	2	50	47	21	23	2	93	4
5	Pr	**a**	4	50	39	18	39	1	97	1
6	i-Pr	**b**	1	50	27	4	20	0	51	29
7[b]	*t*-Bu	**c**	1	50	0	0	0	0	0	30
8	$-CH_2Ph$	**d**	1	50	26	53	11	3	93	4
9	$-CH_2CH{=}CH_2$	**e**	1	50	21	41	15	3	80	6
10	$-CH_2CH_2OH$	**f**	1	50	37	24	8	12	81	4

[a] Determined by ^{1}H NMR. [b] Non-alkylated bicyclic compound **6** was obtained in 26% yield.

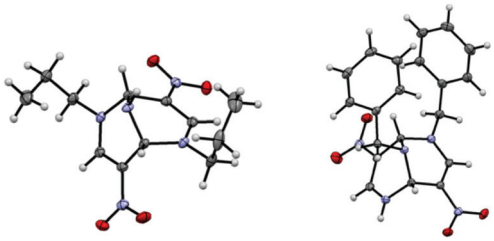


Fig. 1 ORTEP views of **2a** (left, 2,6-di-Pr) and **3d** (right, 2,9-di-Bn). Thermal ellipsoids are represented at probably the 50% level. CCDC: 2027731 (**2a**) and 2027735 (**3d**).†

ammonium acetate was suppressed (entry 2). Although this reaction proceeded even at room temperature, the total yield decreased to an extent (entry 3). The yields of dealkylated products **4a** and **5a** increased when larger amounts of ammonium acetate were used (entries 4 and 5).

The optimized conditions were applied to other nitroenamines **1b–f**. Bicyclic products **2b–5b** possessing bulkier isopropyl groups could be prepared by altering nitroenamine to **1b** (entry 6). When *tert*-butyl-substituted nitroenamine **1c** was employed, the corresponding bicyclic products **2c–5c** were not formed, and non-alkylated bicyclic product **6** was obtained with 26% yield, which was due to the easy elimination of the stable *tert*-butyl cation under acidic conditions (entry 7). It was also possible to introduce functional groups to the ring nitrogen atoms, such as benzyl, allyl, and 2-hydroxyethyl groups, efficiently (entries 8–10).

All attempts to control the selectivity between **2** and **3** failed. During this study, we noticed that the **2**/**3** ratio changed each time we performed ^{1}H NMR. This observation suggests that there is a relationship of equilibrium between **2** and **3**. To confirm this, the single crystals of **2a** and **3d** used for X-ray crystallography were dissolved in deuterated solvents, and the change in the mole fraction ([**2**]/([**2**] + [**3**]) was monitored by ^{1}H NMR at intervals of several minutes/hours (Fig. 2). Conversion from **2a** to **3a** was observed by only dissolving them in the solvents at room temperature, irrespective of the solvent, without the formation of any detectable byproduct. A different behavior was observed when **2a** was dissolved in chloroform-*d*, which might be due to a trace amount of hydrochloric acid in the solvent. Conversely, the formation of **2d** was also observed when **3d** was dissolved in deuterated solvents. The equilibrium constants (K = [**3**]/[**2**]) were temperature-dependent, as shown in Fig. 3. The K value for **3a**/**2a** increased upon increasing the temperature, whereas that for **3d**/**2d** decreased. The Gibbs energy differences between **2** and **3** determined by the Arrhenius-type fittings ($\ln K = -\Delta G/RT$) reveal that **3d** is more stable than **2d** ($\Delta G < 0$) in contrast to the **2a**/**3a** system (Table 2). The difference originated from the existence of π-stacking between the benzyl groups in **3d**. In addition, the K values in CD_3CN were smaller than the relevant values in $CDCl_3$, presumably due to the polarity and/or Lewis acidity/basicity of the solvent. These tendencies were qualitatively reproduced by theoretical calculations. Furthermore, when a mixture of **2a** and **3a** was heated in the presence of ammonium acetate, nitroenamine **1a** was formed in 10% yield in the reaction mixture, indicating the existence of equilibrium between **1a** and TABNs **2a** and **3a**.

Based on these results, bicyclic products **2** and **3** are considered to be formed as shown in Scheme 3. The reaction is initiated by the conversion of a formyl group of **1** to iminium

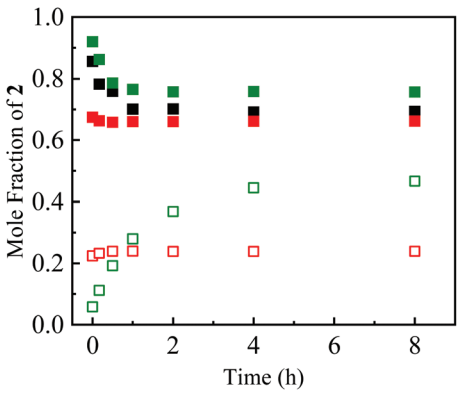


Fig. 2 Time courses of the mole fraction of **2a** (closed squares) and **3d** (open squares) in C_6D_6 (black), $CDCl_3$ (green) and CD_3CN (red).

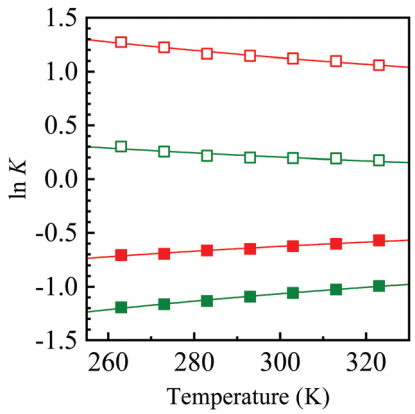
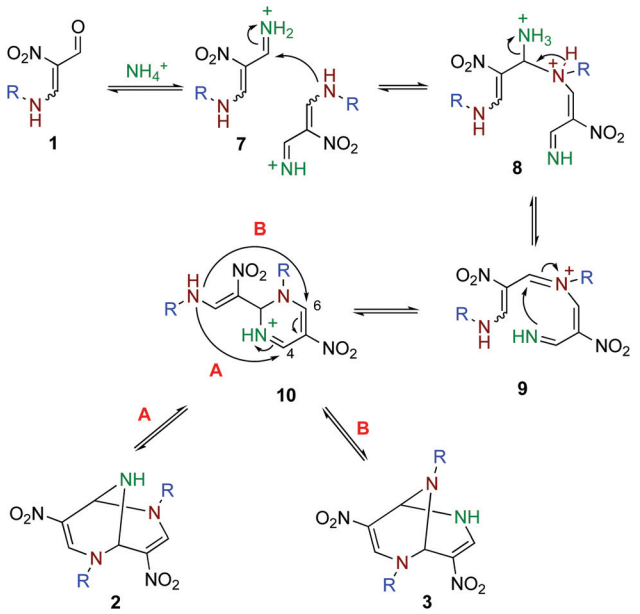


Fig. 3 Temperature dependences of equilibrium constants K for **3a**/**2a** (closed squares) and **3d**/**2d** (open squares) in $CDCl_3$ (green) and CD_3CN (red).

Table 2 Observed and calculated Gibbs energy differences in chloroform and acetonitrile

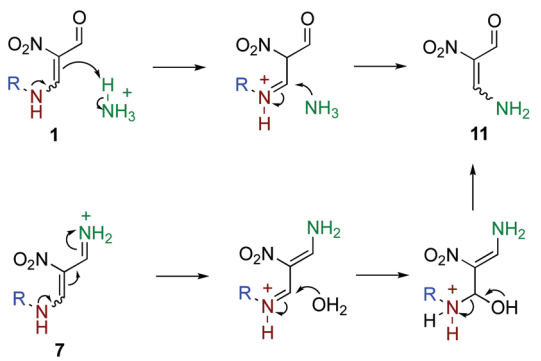
		ΔG (kJ mol^{-1})	
R	Solvent	Obsd[a]	Calcd[b]
–Pr	Chloroform	+2.40 ± 0.09	+5.22
	Acetonitrile	+1.58 ± 0.12	+5.29
–CH_2Ph	Chloroform	−1.36 ± 0.22	+1.87
	Acetonitrile	−2.38 ± 0.14	+0.69

[a] Determined using deuterated solvents. [b] Calculated at the B3LYP/6-311+G(d,p) level.



Scheme 3 A plausible mechanism for the formation of bicyclic compounds **2** and **3**.

ion **7**, which facilitates the attack of the less nucleophilic amino group of another molecule of **1** forming **8**. After the elimination of ammonia, the formed iminium ion is attacked by the imino group intramolecularly to form a six-membered ring. Dihydropyrimidine **10** is a common intermediate of **2** and **3**. When the amino group in the side chain attacks the 4-position (Path A), 2,6-dialkyl product **2** is formed. On the other hand, 2,9-dialkyl product **3** is formed when the amino group attacks the 6-position of **10** (Path B). A direct rearrangement between **2** and **3** is also possible if a stable cation such as a benzyl and allyl cation is released. However, ring transformation *via* intermediate **10** is considered to be more plausible based on our previous findings; 4,6-dinitro-2,8-diazabicyclo[3.3.1]nona-2-ene and 3-nitropyridine are interconvertible under equilibrium in the presence of ammonium acetate.[17] The use of larger amounts of ammonium acetate is subject to the conversion of nitroenamine **1** or iminium ion **7** to nitroenamine **11** (Scheme 4), which affords dealkylated products **4** and **5** in a manner similar to that shown in Scheme 3. Products **4** and **5** are also inseparable because there is a relationship between these compounds.



Scheme 4 Conversion of an alkylamino group to an amino group in the nitroenamine moiety.

Conclusions

TABN frameworks were efficiently constructed by the [4 + 4] self-condensation of nitroenamine **1** in the presence of ammonium acetate. Since the *N*-alkyl group of **1** is easily modified, versatile TABNs were available by this protocol. The major products, 2,6- and 2,9-dialkylated TABNs **2** and **3**, were found to be interconvertible when dissolved in a solvent and this isomerization proceeds through intramolecular ring transformation under equilibrium *via* the common intermediate **10**. Further studies on the physical properties of TABNs and chemical conversion using the functionalities are in progress, and the results will be presented in due course.

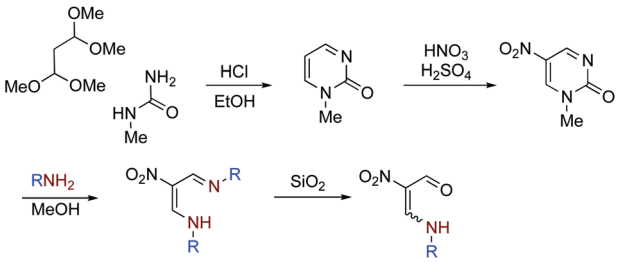
Experimental section

General

The melting points were determined using an SRS-Optimelt automated melting point system. All the reagents and solvents were commercially available and used as received. The ^{1}H NMR spectra were measured on a Bruker Ascend-400 at 400 MHz with tetramethylsilane as an internal standard. The ^{13}C NMR spectra were measured on a Bruker Ascend-400 at 100 MHz, and the assignments of the ^{13}C NMR spectra were performed by DEPT experiments. The high-resolution mass spectra were measured on an AB SCIEX Triple TOF 4600. The IR spectra were recorded on a JASCO FT/IR-4200 spectrometer.

Preparation of nitroenamines 1a–f

Nitroenamines **1a–f** were prepared according to our established method.[18] Nitropyrimidinone was prepared in 70% overall yield by the condensation of commercially available 1,1,3,3-tetramethoxypropane and *N*-methylurea in 12 M hydrochloric acid followed by nitration with nitric acid in sulfuric acid. To a solution of pyrimidinone (310 mg, 2 mmol) in methanol (40 mL), propylamine (410 μL, 5 mmol) was added, and the mixture was heated under reflux for 3 h. After evaporation, the residue was extracted with hexane (3 × 30 mL), and the removal of hexane afforded NMR pure azadienamine (390 mg, 1.96 mmol, 98%) as a pale yellow oil. A solution of azadienamine (200 mg, 1 mmol) in chloroform (5 mL) was charged on silica gel (20 g) in a column and allowed to stand at room temperature for 1 day, and then it was eluted with chloroform. The solvent was removed under reduced pressure to give nitroenamine **1a** (150 mg, 93%). Other nitroenamines **1b–f** were prepared in the same way by using the corresponding amines instead of propylamine (Scheme 5).



Scheme 5 Outline of the preparative method for nitroenamines **1a–f**.

4-Aza-2-nitro-2-heptenal (1a)[18]

Brown solid (*E*/*Z* = 76/24). (*E*)-Isomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (t, *J* = 7.4 Hz, 3H), 1.74 (tq, *J* = 7.3, 7.4 Hz, 2H), 3.45 (dt, *J* = 6.8, 7.3 Hz, 2H), 8.48 (dd, *J* = 3.6, 14.5 Hz, 1H), 10.14 (d, *J* = 3.6 Hz, 1H), 10.3–10.8 (br, 1H). (*Z*)-Isomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (t, *J* = 7.4 Hz, 3H), 1.76 (tq, *J* = 7.3, 7.4 Hz, 2H), 3.53 (dt, *J* = 6.8, 7.3 Hz, 2H), 8.48 (d, *J* = 15.3 Hz, 1H), 9.5–9.9 (br, 1H), 10.05 (s, 1H).

4-Aza-5-methyl-2-nitro-2-hexenal (1b)[19]

Brown solid (*E*/*Z* = 76/24). (*E*)-Isomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (d, *J* = 6.6 Hz, 6H), 3.75 (sep, *J* = 6.6 Hz, 1H), 8.52 (ddd, *J* = 0.6, 3.6, 14.6 Hz, 1H), 10.15 (d, *J* = 3.6 Hz, 1H), 10.3–10.8 (br, 1H). (*Z*)-Isomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (d, *J* = 6.6 Hz, 6H), 3.84 (sep, *J* = 6.6 Hz, 2H), 7.95 (d, *J* = 15.4 Hz, 1H), 9.4–9.9 (br, 1H), 10.56 (s, 1H).

4-Aza-5,5-dimethyl-2-nitro-2-hexenal (1c)[18]

White solid (*E*/*Z* = 79/21). (*E*)-Isomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 (s, 9H), 8.57 (dd, *J* = 3.6, 14.9 Hz, 1H), 10.15 (d, *J* = 3.6 Hz, 1H), 10.3–10.8 (br, 1H). (*Z*)-Isomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (s, 9H), 7.99 (d, *J* = 15.7 Hz, 1H), 9.7–10.1 (br, 1H), 9.94 (s, 1H).

4-Aza-2-nitro-5-phenyl-2-pentenal (1d)

White solid; mp 119.2–120.0 °C (*E*/*Z* = 77/23). (*E*)-Isomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64 (d, *J* = 5.9 Hz, 2H), 7.2–7.5 (m, 5H), 8.54 (dd, *J* = 3.6, 14.3 Hz, 1H), 10.16 (d, *J* = 3.6 Hz, 1H), 10.6–11.0 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.5 (CH_2), 126.3 (C), 127.8 (CH), 129.1 (CH), 129.5 (CH), 133.9 (CH), 155.0 (C), 186.4 (CH). (*Z*)-Isomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 (d, *J* = 6.0 Hz, 2H), 7.2–7.5 (m, 5H), 7.98 (d, *J* = 15.1 Hz, 1H), 9.7–10.0 (br, 1H), 10.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.7 (CH_2), 125.1 (C), 127.9 (CH), 129.2 (CH), 129.5 (CH), 133.9 (CH), 150.3 (C), 183.4 (CH). HRMS (ESI/TOF) calcd for $C_{10}H_{10}N_2O_3$(M − H^+): 205.0619, found: 205.0624; IR (KBr, cm^{-1}) 3212, 1656, 1606, 1505, 1317.

4-Aza-2-nitro-2,6-pentadienal (1e)[5]

Yellow oil (*E*/*Z* = 78/22). (*E*)-Isomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09 (br dd, *J* = 5.7, 5.7 Hz, 2H), 5.3–5.5 (m, 2H), 5.90 (ddt, *J* = 5.7, 11.2, 17.0 Hz, 1H), 8.48 (dd, *J* = 3.6, 14.4 Hz, 1H), 10.15 (d, *J* = 3.6 Hz, 1H), 10.3–10.8 (br, 1H). (*Z*)-Isomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 (br dd, *J* = 5.8, 5.8 Hz, 2H), 5.3–5.5 (m, 2H), 5.8–6.0 (m, 1H, overlapped with signals of *E*-isomer), 7.91 (d, *J* = 15.2 Hz, 1H), 9.5–9.9 (br, 1H), 10.06 (s, 1H).

4-Aza-6-hydroxy-2-nitro-2-hexenal (1f)

Brown solid; mp 125.4–126.5 °C (*E*/*Z* = 71/29). (*E*)-Isomer; ^{1}H NMR (400 MHz, CD_3CN) δ 3.1–3.4 (br, 1H), 3.5–3.6 (m, 2H), 3.70 (t, *J* = 5.2 Hz, 2H), 8.58 (br d, *J* = 8.8 Hz, 1H), 10.10 (d, *J* = 3.6 Hz, 1H), 10.3–10.7 (br, 1H); ^{13}C NMR (100 MHz, CD_3CN) δ 53.3 (CH_2), 60.8 (CH_2), 126.8 (C), 157.4 (CH), 186.3 (CH). (*Z*)-Isomer; ^{1}H NMR (400 MHz, CD_3CN) δ 3.2–3.4 (br, 1H), 3.62 (t, *J* = 4.7 Hz, 2H), 3.6–3.8 (m, 2H), 7.96 (d, *J* = 15.2 Hz, 1H), 9.5–9.9 (br, 1H), 9.98 (s, 1H); ^{13}C NMR (100 MHz, CD_3CN) δ 53.4 (CH_2), 60.8 (CH_2), 125.6 (C), 152.7 (CH), 183.8 (CH). HRMS (ESI/TOF) calcd for $C_5H_8N_2O_4$(M − H^+): 159.0411, found: 159.0416; IR (KBr, cm^{-1}) 3494, 3216, 1674, 1589, 1491, 1314.

Synthesis of triazabicyclic compounds

To a solution of formylnitroenamine **1a** (158.2 mg, 1.0 mmol) in ethanol (4 mL), ammonium acetate (78.5 mg, 1.0 mmol) was added, and the resultant mixture was heated at 50 °C for 1 day. After the removal of the solvent under reduced pressure, the residual brown solid was dissolved in dichloromethane (30 mL) and washed with water (30 mL × 1). The aqueous layer was extracted with dichloromethane (30 mL × 3). The combined organic layer was dried over magnesium sulfate and evaporated to afford a brown solid as a residue. The solid was subjected to column chromatography on silica gel using ethyl acetate/dichloromethane (1/9) as an eluent to afford a mixture of **2a** and **3a** as a yellow solid (81.0 mg, 0.27 mmol, 55%) and a mixture of **3a** and **4a** as a brown solid (17.9 mg, 0.07 mmol, 14%). However, further separation could not be achieved. When other nitroenamines **1b–f** were used, the experiments were performed in the same way. In the cases of **1b** and **1f**, ethyl acetate was used as an extraction solvent instead of dichloromethane. In the case of **1f**, ethyl acetate was used as an eluent for column chromatography.

The NMR spectra were analyzed using a mixture of **2** and **3** because these products are interconvertible under equilibrium when dissolved in solvents. Hence, the content ratio varied in each measurement. With regard to bicyclic products **3** and **4**, the NMR spectra were measured using a mixture because they were inseparable despite several attempts. The yields of **3** and **4** were determined on the basis of the integral ratio.

2,6,9-Triaza-4,8-dinitro-2,6-dipropylbicyclo[3.3.1]nona-3,7-diene (2a) and 2,6,9-triaza-4,8-dinitro-2,9-dipropylbicyclo[3.3.1]nona-3,7-diene (3a)

Yellow solid, mp 152.5–153.3 °C, R_f = 0.43 (SiO_2, dichloromethane/methanol = 20/1). **2a**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.4 Hz, 6H), 1.6–1.9 (m, 4H), 2.2–2.3 (br, 1H), 3.43 (ddd, *J* = 7.7, 7.7, 13.9 Hz, 2H), 3.98 (ddd, *J* = 5.8, 7.8, 13.9 Hz, 2H), 5.68 (d, *J* = 2.8 Hz, 2H), 8.20 (s, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 11.1 (CH3), 23.3 (CH2), 56.9 (CH2), 61.9 (CH), 122.4 (C), 144.6 (CH). **3a**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J* =

7.4 Hz, 3H), 1.00 (t, J = 7.4 Hz, 3H), 1.56 (ddq, J = 7.2, 7.2, 7.4 Hz, 2H), 1.6–1.9 (m, 2H), 2.37 (dt, J = 7.2, 12.6 Hz, 1H), 2.41 (dt, J = 7.4, 12.6 Hz, 1H), 3.39 (ddd, J = 7.8, 7.8, 14.0 Hz, 1H), 3.95 (ddd, J = 5.4, 8.1, 14.0 Hz, 1H), 5.34 (d, J = 1.4 Hz, 1H), 5.32 (s, 1H), 7.0–7.2 (br, 1H), 8.16 (s, 1H), 8.29 (d, J = 4.7, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.1 (CH_3), 11.6 (CH_3), 20.8 (CH_2), 23.2 (CH_2), 51.4 (CH_2), 56.8 (CH_2), 61.3 (CH), 66.9 (CH), 122.2 (C), 122.7 (C), 142.2 (CH), 144.4 (CH). HRMS (ESI/TOF) calcd for $C_{12}H_{19}N_5O_4$ ($M + H^+$): 298.1510, found: 298.1515; IR (KBr, cm^{-1}) 3291, 2965, 1613, 1304, 1226. A single crystal of **2a** was obtained as yellow needles by recrystallization from dichloromethane/hexane.

2,6,9-Triaza-4,8-dinitro-2-propylbicyclo[3.3.1]nona-3,7-diene (4a) and 2,6,9-triaza-4,8-dinitro-9-propylbicyclo[3.3.1]nona-3,7-diene (5a)

Yellow solid, mp 91.5–93.6 °C (**4a**/**5a** = 89/11). **4a**; ^{1}H NMR (400 MHz, CD_3CN) δ 0.92 (t, J = 7.4 Hz, 3H), 1.6–1.9 (m, 2H), 2.7–2.9 (br, 1H), 3.45 (ddd, J = 7.7, 7.7, 13.8 Hz, 1H), 3.87 (ddd, J = 5.5, 7.8, 13.8 Hz, 1H), 5.57 (d, J = 1.6 Hz, 1H), 5.68 (d, J = 2.0 Hz, 1H), 7.6–8.1 (br, 1H), 8.20 (s, 1H), 8.22 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.1 (CH_3), 23.6 (CH_2), 55.6 (CH_2), 55.7 (CH), 61.5 (CH), 124.0 (C), 124.3 (C), 143.5 (CH), 145.35 (CH). **5a**; ^{1}H NMR (400 MHz, CD_3CN) δ 0.87 (t, J = 7.4 Hz, 3H), 1.51 (ddq, J = 6.7, 6.8, 7.4 Hz, 2H), 2.34 (dt, J = 6.7, 14.7 Hz, 1H), 2.36 (dt, J = 6.8, 14.7 Hz, 1H), 5.33 (s, 2H), 7.6–8.1 (br, 2H), 8.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7 (CH_3), 21.2 (CH_2), 51.3 (CH_2), 62.0 (CH), 124.0 (C), 142.8 (CH). HRMS (ESI/TOF) calcd for $C_9H_{13}N_5O_4$ ($M - H^+$): 254.0895, found: 254.0890; IR (KBr, cm^{-1}) 3283, 2965, 1611, 1340, 1225, 1139, 926.

2,6,9-Triaza-2,6-di(2-methylethyl)-4,8-dinitrobicyclo[3.3.1]nona-3,7-diene (2b) and 2,6,9-triaza-2,9-di(2-methylethyl)-4,8-dinitrobicyclo[3.3.1]nona-3,7-diene (3b)

Yellow solid, mp 160.6–162.1 °C. Signals of **3b** were too small to be assigned. **2b**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (d, J = 6.6 Hz, 12H), 2.1–2.3 (br, 1H), 4.36 (sep, J = 6.6 Hz, 2H), 5.69 (d, J = 2.7 Hz, 2H), 8.27 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3 (CH_3), 24.2 (CH_3), 55.5 (CH), 63.4 (CH), 122.7 (C), 140.9 (CH); HRMS (ESI/TOF) calcd for $C_{12}H_{18}N_5O_4$ ($M - H^+$): 296.1364, found: 296.1375; IR (KBr, cm^{-1}) 3291, 2973, 1609, 1338, 1259, 1230, 1181.

2,6,9-Triaza-2-(2-methylethyl)-4,8-dinitrobicyclo[3.3.1]nona-3,7-diene (4b)

Brown solid, mp 126.2–127.9 °C. Signals of **5b** were too small to be assigned. ^{1}H NMR (400 MHz, CD_3CN) δ 1.30 (d, J = 6.6 Hz, 3H), 1.33 (d, J = 6.6 Hz, 3H), 2.7–2.9 (br, 1H), 4.24 (qq, J = 6.6, 6.6 Hz, 1H), 5.57 (d, J = 1.1 Hz, 1H), 5.70 (d, J = 1.2 Hz, 1H), 7.7–8.0 (br, 1H), 8.21 (s, 1H), 8.26 (s, 1H); ^{13}C NMR (100 MHz, CD_3CN) δ 21.2 (CH_3), 23.9 (CH_3), 56.2 (CH), 57.4 (CH), 64.4 (CH), 124.1 (C), 124.9 (C), 141.4 (CH), 143.4 (CH); HRMS (ESI/TOF) calcd for $C_9H_{12}N_5O_4$ ($M - H^+$): 254.0895, found: 254.0898; IR (KBr, cm^{-1}) 3283, 1609, 1342, 1232.

2,6,9-Triaza-4,8-dinitro[3.3.1]nona-3,7-diene (6)

Yellow solid, mp 207.0–208.1 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.72 (t, J = 2.7 Hz, 1H), 5.51 (d, J = 2.7 Hz, 2H), 8.24 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 56.2 (CH), 123.1 (C), 142.8 (CH); HRMS (ESI/TOF) calcd for $C_6H_7N_5O_4$ ($M - H^+$): 212.0425, found: 212.0427; IR (KBr, cm^{-1}) 3166, 3012, 1607, 1353, 1223.

2,6,9-Triaza-2,6-dibenzyl-4,8-dinitrobicyclo[3.3.1]nona-3,7-diene (2d) and 2,6,9-triaza-2,9-dibenzyl-4,8-dinitrobicyclo[3.3.1]nona-3,7-diene (3d)

Brown solid, mp 155.8–157.5 °C, R_f = 0.29 (SiO_2, hexane/ethyl acetate/triethylamine = 6/4/0.5). **2d**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.9–2.1 (br, 1H), 4.68 (d, J = 14.8 Hz, 2H), 5.08 (d, J = 14.8 Hz, 2H), 5.65 (d, J = 2.6 Hz, 2H), 6.9–7.5 (m, 10H), 8.26 (s, 2H). **3d**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.29 (d, J = 13.4 Hz, 1H), 3.35 (d, J = 13.4 Hz, 1H), 4.63 (d, J = 14.7 Hz, 1H), 4.99 (d, J = 14.7 Hz, 1H), 5.24 (d, J = 1.3 Hz, 1H), 5.35 (d, J = 1.3 Hz, 1H), 6.9–7.5 (m, 10H), 8.30 (s, 1H), 8.38 (s, 1H). A signal of N–H was absent, which was presumably due to overlapping. The ^{13}C NMR (100 MHz, $CDCl_3$) measurement was performed using a mixture of two isomers **2d** and **3d**. δ 53.7 (CH_2), 59.1 (CH_2), 59.1 (CH_2), 60.7 (CH), 61.1 (CH), 65.8 (CH), 121.8 (C), 122.8 (C), 123.0 (C), 128.2 (CH), 128.4 (CH), 128.6 (CH), 128.7 (CH), 128.9 (CH), 129.0 (CH), 129.0 (CH), 129.4 (CH), 129.4 (CH), 134.5 (C), 134.7 (C), 135.0 (C), 142.8 (CH), 144.6 (CH), 144.8 (CH); HRMS (ESI/TOF) calcd for $C_{20}H_{19}N_5O_4$($M + H^+$): 394.1510, found: 394.1525; IR (KBr, cm^{-1}) 3279, 3057, 1614, 1318, 1209. A single crystal of **3d** was obtained as yellow blocks by recrystallization from ethanol/diethyl ether.

2,6,9-Triaza-2-benzyl-4,8-dinitrobicyclo[3.3.1]nona-3,7-diene (4d) and 2,6,9-triaza-9-benzyl-4,8-dinitrobicyclo[3.3.1]nona-3,7-diene (5d)

Yellow solid, mp 155.0–155.8 °C. **4d**; ^{1}H NMR (400 MHz, CD_3CN) δ 2.6–2.8 (br, 1H), 4.78 (d, J = 15.0 Hz, 1H), 4.99 (d, J = 15.0 Hz, 1H), 5.56 (dd, J = 1.0, 2.7 Hz, 1H), 5.63 (d, J = 2.7 Hz, 1H), 7.1–7.5 (m, 5H), 8.24 (s, 1H), 8.26 (s, 1H). **5d**; ^{1}H NMR (400 MHz, CD_3CN) δ 3.54 (d, J = 13.3 Hz, 1H), 3.59 (d, J = 13.3 Hz, 1H), 5.25 (s, 2H), 7.1–7.5 (m, 5H), 8.27 (s, 2H). A signal of *N*–H was absent, which was presumably due to overlapping. The ^{13}C NMR (100 MHz, CD_3CN) measurement was performed using a mixture of two isomers **4d** and **5d**. δ 53.7 (CH_2), 57.1 (CH), 58.9 (CH_2), 61.5 (CH), 62.5 (CH), 123.8 (C), 124.1 (C), 124.9 (C), 128.8 (CH), 129.2 (CH), 129.3 (CH), 129.6 (CH), 129.9 (CH), 130.0 (CH), 136.9 (C), 137.4 (C), 142.9 (CH), 143.5 (CH), 145.3 (CH); HRMS (ESI/TOF) calcd for $C_{13}H_{13}N_5O_4$ ($M - H^+$): 302.0895, found: 302.0895; IR (KBr, cm^{-1}) 3276, 1705, 1610, 1320, 1204, 928.

2,6,9-Triaza-4,8-dinitro-2,6-di(3-propen-1-yl)bicyclo[3.3.1]nona-3,7-diene (2e) and 2,6,9-triaza-4,8-dinitro-2,9-di(3-propen-1-yl)bicyclo[3.3.1]nona-3,7-diene (3e)

Brown solid, mp 60.5–62.0 °C. **2e**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.20 (br, 1H), 4.17 (dddd, J = 1.5, 1.5, 5.0, 15.4 Hz, 2H), 3.60

(br dd, J = 7.1, 15.4 Hz, 2H), 5.82 (dddd, J = 1.2, 1.2, 1.2, 17.2 Hz, 2H), 5.3–5.5 (m, 2H), 5.69 (d, J = 2.8 Hz, 2H), 5.87 (dddd, J = 5.0, 7.1, 10.2, 17.2 Hz, 2H), 8.18 (s, 2H). **3e**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.01 (dddd, J = 1.2, 1.2, 6.4, 13.5 Hz, 1H), 3.08 (dddd, J = 1.2, 1.2, 6.3, 13.5 Hz, 1H), 4.13 (dddd, J = 1.3, 1.3, 5.1, 15.3 Hz, 1H), 4.44 (br dd, J = 7.2, 15.3 Hz, 1H), 5.26 (dddd, J = 1.2, 1.2, 1.2, 17.1 Hz, 1H), 5.29 (dddd, J = 1.3, 1.3, 1.3, 10.2 Hz, 1H), 5.3–5.5 (m, 2H), 5.47 (dddd, J = 1.3, 1.3, 1.3, 17.0 Hz, 1H), 5.34 (d, J = 1.5 Hz, 1H), 5.38 (d, J = 1.5 Hz, 1H), 5.82 (dddd, J = 6.3, 6.4, 10.2, 17.1 Hz, 1H), 5.86 (dddd, J = 5.1, 7.2, 10.2, 17.0 Hz, 1H), 6.2–6.8 (br, 1H), 8.18 (s, 1H), 8.30 (s, 1H). The ^{13}C NMR (100 MHz, $CDCl_3$) measurement was performed using a mixture of two isomers **2e** and **3e**. δ 52.6 (CH_2), 57.5 (CH_2), 57.5 (CH_2), 60.7 (CH), 61.7 (CH), 66.2 (CH), 120.6 (CH_2), 121.1 (CH_2), 121.4 (CH_2), 121.8 (C), 122.8 (C), 122.9 (C), 131.5 (CH), 131.7 (CH), 132.4 (CH), 142.8 (CH), 144.3 (CH), 144.6 (CH); HRMS (ESI/TOF) calcd for $C_{12}H_{15}N_5O_4$ (M − H$^+$): 292.1051, found: 292.1054; IR (KBr, cm^{-1}) 3283, 1613, 1482, 1416, 1309, 920, 760.

2,6,9-Triaza-4,8-dinitro-2-(3-propen-1-yl)bicyclo[3.3.1]nona-3,7-diene (4e) and 2,6,9-triaza-4,8-dinitro-9-(3-propen-1-yl)bicyclo[3.3.1]nona-3,7-diene (5e)

Yellow solid, mp 135.4–137.5 °C. **4e**; ^{1}H NMR (400 MHz, CD_3CN) δ 2.7–2.9 (br, 1H), 4.19 (dddd, J = 1.4, 1.4, 5.0, 15.6 Hz, 1H), 4.43 (dddd, J = 1.4, 1.4, 6.8, 15.6 Hz, 1H), 5.30 (dddd, J = 1.4, 1.4, 1.4, 10.2 Hz, 1H), 5.39 (dddd, J = 1.4, 1.4, 1.4, 17.1 Hz, 1H), 5.57 (dd, J = 1.1, 2.7 Hz, 1H), 5.65 (br d, J = 2.8 Hz, 1H), 5.94 (dddd, J = 5.0, 6.9, 10.2, 17.1 Hz, 1H), 7.5–8.1 (br, 1H), 8.18 (s, 1H), 8.22 (s, 1H). **5e**; ^{1}H NMR (400 MHz, CD_3CN) δ 3.00 (dddd, J = 1.3, 1.3, 6.4, 13.7 Hz, 1H), 3.05 (dddd, J = 1.3, 1.3, 6.4, 13.7 Hz, 1H), 5.30 (dddd, J = 1.3, 1.3, 1.3, 10.2 Hz, 1H), 5.39 (dddd, J = 1.3, 1.3, 1.3, 17.1 Hz, 1H), 5.33 (s, 2H), 5.85 (dddd, J = 6.4, 6.4, 10.2, 17.1 Hz, 1H), 7.5–8.1 (br, 2H), 8.23 (s, 2H). The ^{13}C NMR (100 MHz, CD_3CN) measurement was performed using a mixture of two isomers **4e** and **5e**. δ 52.6 (CH_2), 57.1 (CH), 57.7 (CH_2), 61.5 (CH), 62.8 (CH), 119.9 (CH_2), 119.9 (CH_2), 123.8 (C), 124.1 (C), 124.9 (C), 134.0 (CH), 134.4 (CH), 142.8 (CH), 143.4 (CH), 145.1 (CH); HRMS (ESI/TOF) calcd for $C_9H_{11}N_5O_4$ (M − H$^+$): 252.0738, found: 252.0740; IR (KBr, cm^{-1}) 3278, 1610, 1423, 1334, 1215, 927.

2,6,9-Triaza-2,6-di(2-hydroxyethyl)-4,8-dinitro[3.3.1]nona-3,7-diene (2f) and 2,6,9-triaza-2,9-di(2-hydroxyethyl)-4,8-dinitro[3.3.1]nona-3,7-diene (3f)

Brown solid, mp 68.1–70.7 °C. **2f**; ^{1}H NMR (400 MHz, CD_3CN) δ 2.8–3.0 (br, 1H), 3.0–3.3 (br, 2H), 3.44 (ddd, J = 3.8, 7.0, 14.2 Hz, 2H), 3.69 (ddd, J = 3.8, 6.0, 11.8 Hz, 2H), 3.77 (ddd, J = 3.4, 7.0, 11.8 Hz, 2H), 4.01 (ddd, J = 3.4, 6.0, 14.2 Hz, 2H), 5.71 (d, J = 1.0 Hz, 2H), 8.24 (s, 2H); ^{13}C NMR (100 MHz, CD_3CN) δ57.4 (CH_2), 61.5 (CH_2), 63.3 (CH), 123.5 (C), 144.6 (CH). **3f**; ^{1}H NMR (400 MHz, CD_3CN) δ 2.49 (ddd, J = 5.2, 5.2, 13.7 Hz, 1H), 2.64 (ddd, J = 5.0, 5.0, 13.7 Hz, 1H), 2.9–3.1 (br, 1H), 3.0–3.3 (br, 1H), 3.5–3.8 (m, 5H, overlapped with signals of **3f**), 3.97 (ddd, J = 3.3, 6.0, 14.7 Hz, 1H), 5.42 (d, J = 1.5 Hz, 1H), 5.61 (d, J = 1.5 Hz, 1H), 7.5–8.2 (br, 1H), 8.26 (s, 1H), 8.27 (s, 1H); ^{13}C NMR (100 MHz, CD_3CN) δ 51.9 (CH_2), 57.3 (CH_2), 60.7 (CH_2), 61.4 (CH_2), 62.1 (CH), 68.4 (CH), 122.9 (C), 123.1 (C), 143.4 (CH), 145.9 (CH). HRMS (ESI/TOF) calcd for $C_{10}H_{15}N_5O_6$ (M − H$^+$): 300.0950, found: 300.0954; IR (KBr, cm^{-1})1209, 1307, 1612, 2359, 3307.

2,6,9-Triaza-2-(2-hydroxyethyl)-4,8-dinitro[3.3.1]nona-3,7-diene (4f) and 2,6,9-triaza-9-(2-hydroxyethyl)-4,8-dinitro[3.3.1]nona-3,7-diene (5f)

Brown solid, mp 95.6–97.2 °C. **4f**; ^{1}H NMR (400 MHz, CD_3CN) δ 2.8–3.0 (br, 1H), 2.9–3.4 (br, 1H), 3.57 (ddd, J = 3.8, 6.9, 14.3 Hz, 1H), 3.67 (ddd, J = 3.8, 6.2, 11.6 Hz, 1H), 3.77 (ddd, J = 3.5, 6.9, 11.6 Hz, 1H), 3.99 (ddd, J = 3.5, 6.2, 14.3 Hz, 1H), 5.57 (s, 1H), 5.73 (s, 1H), 7.4–8.2 (br, 1H), 8.21 (s, 1H), 8.23 (s, 1H); ^{13}C NMR (100 MHz, CD_3CN) δ 57.0 (CH_2), 57.2 (CH), 61.5 (CH_2), 63.8 (CH), 124.0 (C), 124.7 (C), 143.5 (CH), 145.6 (CH). **5f**; ^{1}H NMR (400 MHz, CD_3CN) δ 2.49 (ddd, J = 5.5, 5.5, 13.4 Hz, 1H), 2.55 (ddd, J = 5.1, 5.1, 13.4 Hz, 1H), 2.9–3.4 (br, 1H), 3.5–3.7 (m, 2H, overlapped with signals of **4f**), 5.44 (s, 2H), 7.4–8.2 (br, 2H), 8.23 (s, 2H); ^{13}C NMR (100 MHz, CD_3CN) δ 51.9 (CH_2), 60.7 (CH_2), 62.5 (CH), 124.0 (C), 142.7 (CH). HRMS (ESI/TOF) calcd for $C_8H_{11}N_5O_5$ (M − H$^+$): 256.0687, found: 256.0685; IR (KBr, cm^{-1}) 1208, 1226, 1317, 1609, 2359, 3251.

X-Ray crystallographic analysis

Diffraction data were collected at 93 or 123 K under a cold N_2-gas stream using a Rigaku XtaLAB Synergy-S/Mo system (λ = 0.71073 Å (Mo-Kα)). The integrated data were analyzed using the Olex2 crystallographic software package.[20] The structures were solved with the ShelXT structure solution program[21] using Intrinsic Phasing and refined with the ShelXL refinement package[22] using least-squares minimization. Anisotropic refinement was performed for all non-hydrogen atoms, and all the hydrogen atoms were placed at the calculated positions.

Temperature dependent NMR spectra

^{1}H NMR spectra were obtained by using the variable-temperature (VT) NMR technique. The sample solutions were stored at −10–50 °C for over 12 h prior to the measurements.

Theoretical calculations

Density functional theory (DFT) calculations for **2a**, **2d**, **3a** and **3d** were conducted using Gaussian 16 W software (revision A.03)[23] using the restricted Becke three-parameter hybrid functionals with the Lee–Yang–Parr correlation (RB3LYP)[24,25] and 6-311+G(d,p) basis set.[26,27] Ground-state geometries were optimized and, then, the Gibbs energies of the molecules were calculated. Solvation was considered using the conductor-like polarizable continuum model.[28,29]

Conflicts of interest

There are no conflicts to declare.

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