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SOME REACTIONS OF 3-PHENYL-8-TRIPHENYLPHOSPHOIMINO-1-AZAAZULENE

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Abstract – Reaction of 3-phenyl-8-triphenylphosphoimino-1-azaazulene (**1**) with arylaldehyde gave 2-aryl-4-phenyl-3*H*-1,2a-diazacyclopent[*cd*]azulenes. Reaction of **1** with *trans*-cinnamaldehyde gave 3-benzyl-1-pheny-2a,5-diazabenz[*cd*]azulene as cyclization product. Cycloaddition reaction of **1** with dimethyl acetylenedicarboxylate gave tetramethyl 4-phenyl-9,9b-diazaindeno[4,3a,3,2-*bcd*]azulene-1,2,3,9a-tetracarboxylate and hexamethyl 6-phenyl-3a*H*-10c-azaacephenanthryene-1,2,3,3a,4,5-hexacarboxylate.

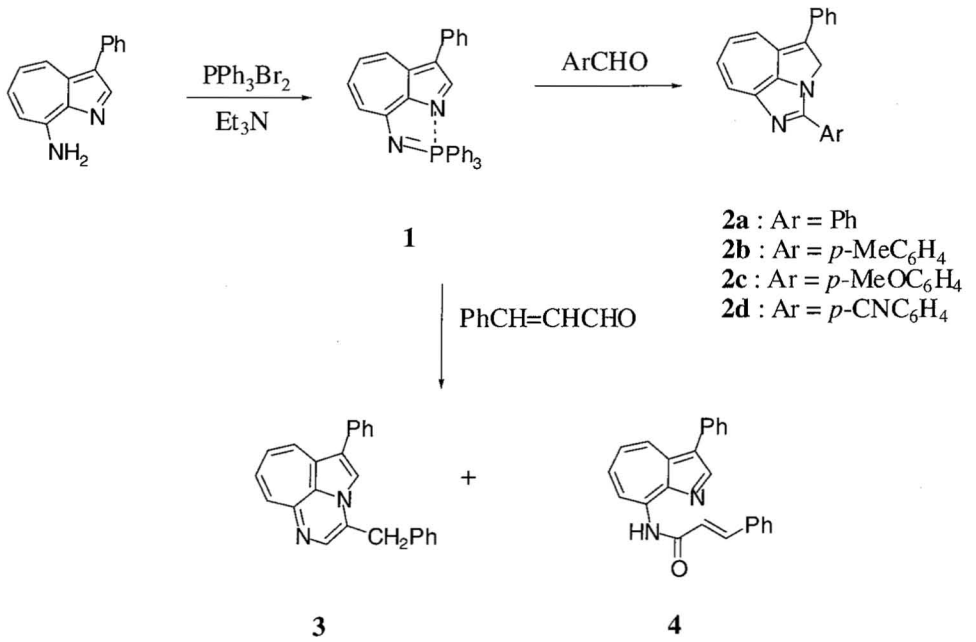
INTRODUCTION

It is known that the iminophosphoranes, chemical species having the nitrogen-phosphorus double bond, reveal synthetic versatility for the construction of fused heterocycles.[1] Recently we communicated the synthesis of the 8-phosphoimino-1-azaazulene derivative (**1**) from 8-amino-3-phenyl-1-azaazulene and dibromotriphenylphosphorane. Based on the X-Ray structure analysis of **1**, the interaction between N-1 and the P-atom was observed.[2] This suggests that **1** would have both the characters of an iminophosphorane and a tricyclic heterocycle. In addition, the ring nitrogen and the 8-position situated imionophosphorane moiety of **1** hold a suitable position for new ring construction. Therefore, it is expected that cyclization and cycloaddition reactions would produce a new class of heterocycles. For the extension of azaazulene chemistry[3,4] and a construction of novel fused heterocycles, we examined the reactions of **1** with arylaldehyde, where a cyclization attendant upon aza-Wittig reaction would be expected. Although heterocycles conjugated with iminophosphorane are considered as extended dipolar species and expected to proceed interesting cycloaddition reaction, the studies of cycloaddition reaction of such iminophosphoranes with acetylenic esters are few,[1,5] reaction of *N*-vinyl-iminophosphoranes with dimethyl acetylenedicarboxylate gave 1,2-λ^5-azaphosphorines or aminobutadiene derivatives, where Diels-Alder reaction or [2 + 2] cycloaddition occurred. Therefore we also examined the cycloaddition

reaction of **1** with dimethyl acetylenedicarboxylate.

RESULTS AND DISCUSSION

Reaction with aryl aldehydes. Reaction of 8-phosphoimino-1-azaazulene derivative (**1**) with benzaldehyde at room temperature did not proceed (Entry 1), but when the reaction was performed at elevated temperature, 2,4-diphenyl-3*H*-1,2a-diazacyclopent[*cd*]azulene (**2a**) was isolated. Thus **1** was heated with benzaldehyde in toluene under reflux for 137 h to give **2a** in 10 % yield along with recovered **1a** (78%) (Entry 2). It seems that higher temperature (125 ℃) and prolonged reaction slightly improved the yield (Entry 3), but further elevation of the temperature (175 ℃) led to give a complex mixture (Entry 4). For the improvement of the reaction, we tried to adopt a Lewis acid as catalyst. Thus the reaction was carried out in the presence of 5% molar $ZnCl_2$, but the improvement of the yield was not achieved (Entry 5). When $Y(OTf)_3$ was used in the reaction, complex mixture was produced and no distinct product was isolated (Entry 6). Using of $Pd(OAc)_2$ as catalyst produced an enhancement of the yield, and the reaction under the presence of 5% molar $Pd(OAc)_2$ afforded **2a** in 61% yield (Entry 7).



In the ^{1}H NMR spectrum of **2a**, 2H singlet assignable to H-3 appeared at δ 5.28, and the seven-membered protons resonated at rather high field [δ 5.69 (dd, *J* 11.9 and 8.5), 5.96 (dd, *J* 7.4 and 7.2), 6.01 (d, *J* 11.9), and 6.62 (d, *J* 11.9)], appropriated as a heptafulvene structure, together with phenyl protons (10H). In

the ^{13}C NMR spectrum, a methylene carbon was appeared at δ 56.45. From the results, we assigned the structure of **2a** as 2,4-diphenyl-3*H*-1,2a-diazacyclopent[*cd*]azulene.[6] Its MS spectrum (*m/z* 308, M^+) and elemental analysis of the picrate of **2a** consisted with the structure. Compound (**2a**) was stable in solution, but the concentrated oil decomposed gradually at room temperature. Therefore the elemental analysis of **2a** was performed as the picrate.

In the similar manner, some aryl aldehydes were reacted with **1**. Reactions of **1** with *p*-tolualdehyde showed similar results as a case of benzaldehyde, although slightly lowering of the yield of **2b** was seen in spite of using $Pd(OAc)_2$ (Entries 8—10). Reaction of **1** with *p*-anisaldehyde brought to the lowering of the yield, and even using of $Pd(OAc)_2$ led a decrease of the yield (Entry 12). These results suggested that electron-donating group would suppress the reaction. On the contrary, electron-withdrawing group

Table 1. Reactions of **1** with aryl aldehydes.

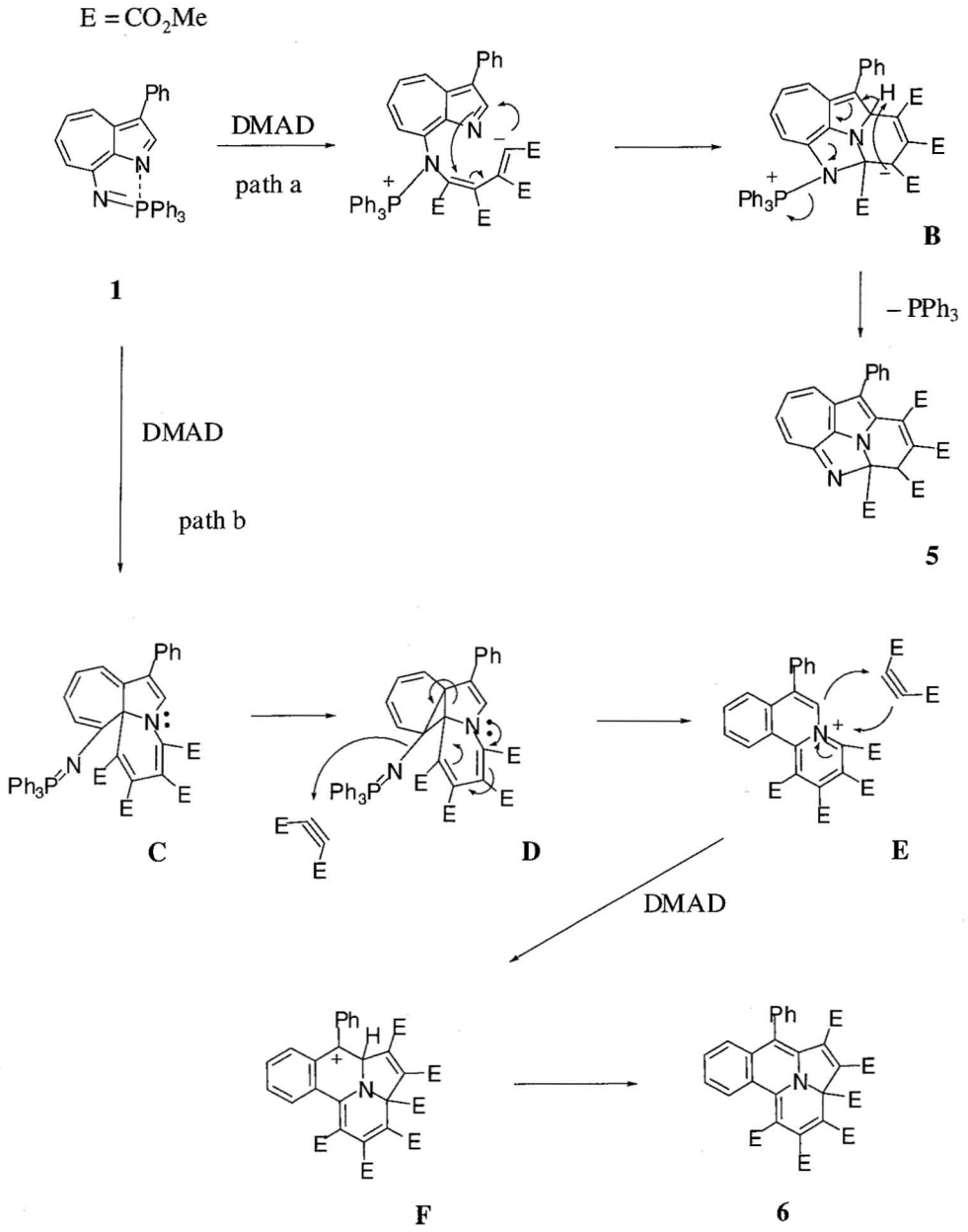
Entry	Aldehyde	Conditions			Products (Yield / %)
		Catalyst	Temp / ℃	Time / h	
1	PhCHO	—	35	90	No reaction
2	PhCHO	—	110	137	**2a** (10) **1**(78)
3	PhCHO	—	125	200	**2a** (27) **1**(10)
4	PhCHO	—	175	24	Complex mixture, **1**(28)
5	PhCHO	$ZnCl_2$	125	200	**2a**(23.5) **1**(14)
6	PhCHO	$Yb(OTf)_3$	125	24	Complex mixture, **1**(—)
7	PhCHO	$Pd(OAc)_2$	125	200	**2a** (61) **1**(—)
8	*p*-MeC_6H_4CHO	—	120	21	**2b** (trace) **1**(83)
9	*p*-MeC_6H_4CHO	—	125	200	**2b** (26) **1**(36)
10	*p*-MeC_6H_4CHO	$Pd(OAc)_2$	125	200	**2b** (39) **1**(10)
11	*p*-$MeOC_6H_4CHO$	—	125	200	**2c** (15) **1**(—)
12	*p*-$MeOC_6H_4CHO$	$Pd(OAc)_2$	125	200	**2c** (7.5) **1**(—)
13	*p*-CNC_6H_4CHO	—	120	17	**2d** (24) **1**(—)
14	*p*-CNC_6H_4CHO	—	125	20	**2d** (27) **1**(—)
15	*p*-CNC_6H_4CHO	—	125	200	**2d** (6) **1**(—)
16	*p*-CNC_6H_4CHO	$Pd(OAc)_2$	125	24	Complex mixture, **1**(12)
17	crotonaldehyde	—	120	200	No reaction
18	*trans*-cinnamaldehyde	—	120	21	**3**(4) **4**(13) **1**(35)
19	*trans*-cinnamaldehyde	—	125	200	**3**(7) **4**(—) **1**(15)

facilitated the reaction; the reaction of **1** with *p*-cyanobenzaldehyde for 20 h gave **2d** in 27% yield (Entry 13). Prolonged reaction led to decrease of the yield (Entry 14). The use of $Pd(OAc)_2$ on the reaction of **1** with *p*-cyanobenzaldehyde gave complex feature and **2d** was not obtained (Entry 16).

We next examined the reaction of **1** with α,β-conjugated aldehydes. Although crotonaldehyde did not react with **1**, the treatment of **1** with *trans*-cinnamaldehyde in dry xylene under heating at 120 ℃ for 21 h gave **3** and **4** in 4% and 13% yields, respectively. In the ^{1}H NMR spectrum of **3**, 2H singlet assignable to methylene protons appeared at δ 5.21 and two 1H singlets assignable to H-2 and H-4 appeared at δ 6.98 and 6.99. The seven-membered protons resonated at δ 5.74 (1H, dd, *J* 11.2 and 8.5), 6.00 (1H, dd, *J* 11.8 and 8.5), 6.51 (1H, d, *J* 11.2) and 6.66 (1H, d, *J* 11.8); these results are comparable to 3,4-dibenzoyl-1-pheny-2a,5-diazabenz[*cd*]azulene.[7] In its MS spectrum, the molecular peak was seen at *m/z* 334 (100%). From these results, we assigned the structure of **3** as 3-benzyl-1-pheny-2a,5-diazabenz[*cd*]azulene. The molecular peak appeared at *m/z* 334 (100%) in the MS spectrum of **4**. In its IR spectrum, signals, 3292 (NH), 1692 (C=O), and 1625 (C=C), were seen, and these suggest that **4** has conjugated amide moiety. In the ^{1}H NMR spectrum of **4**, the *trans*-situated vinylic protons appeared at δ 6.92 (d, *J* 15.5) and 7.90 (d, *J* 15.5), and the seven-membered ring protons resonated at ordinal region for 1-azaazulene. From the results, we assigned the structure. The reaction mechanisms would be considered as follows. At first the Schiff base would be produced by the aza-Wittig reaction of **1** with *trans*-cinnamaldehyde. Following cyclisation of the Schiff base gave **3**. Hydrolysis of the Schiff base and successive oxydation under work-up would give **4**.

Reaction with DMAD. We next examined the cycloaddition reaction of **1**. When **1** was treated with dimethyl acetylenedicarboxylate (DMAD) in benzene at room temperature, a complex mixture was obtained. From the mixture, two cycloadducts, green prisms (**5**, 6%) and red needles (**6**, 29%), were isolated. In the reaction, the formation of triphenylphosphine was confirmed. For the improvement of the reaction, $Pd(OAc)_2$ or Pd-C was used as catalyst, but desirable results were not obtained. When the reaction was carried out under the presence of 5% molar $Pd(OAc)_2$, the reaction showed complex feature , and no distinct product was isolated. When the reaction was carried out in the presence of 5% Pd-C for 24 h at room temperature, complex mixture were also produced, and **5** (3%) and **6** (10%) were isolated only low yields. The reaction of **1** with DMAD in the presence of 5% Pd-C for under irradiation of ultrasonic waves for 7 h gave and **5** (5%) and **6** (19%). In these reactions, a significant improvement could not be achieved. Compound (**5**) was analyzed as $C_{27}H_{22}N_2O_8$ from its elemental analysis and MS spectrum [*m/z* 502 (M^+)]; compound (**5**) would have a structure where triphenylphosphine was eliminated from a 1:2-adduct of **1** and DMAD. In the ^{1}H NMR spectrum of **5**, a methine singlet at δ 5.41 and the higher field resonated seven-membered protons at δ 5.63-5.71 (1H, m), 6.12 (1H, d, *J* 12.2), 6.23-6.28

(1H, m), 6.61 (1H, d, *J* 11.1) were seen, besides of four methyl ester protons and phenyl protons. In the ^{13}C NMR spectrum, a methine carbon and a quaternary



Scheme 1

carbon were appeared at δ 41.16 and 46.54. From the results, we assigned the structure of **5** as

tetramethyl 4-phenyl-9,9b-diazaindeno[4,3a,3,2-*bcd*]azulene-1,2,3,9a-tetracarboxylate. Compound (**6**) was analyzed as $C_{33}H_{27}NO_{12}$ from its elemental analysis and MS spectrum [*m/z* 629 (M^+)]. Therefore compound (**6**) would have a structure where $NPPh_3$ moiety was eliminated from a 1:3-adduct of **1** and DMAD. In the ^1H NMR spectrum of **6**, seven-membered protons were not observed. Instead benzene ring protons were seen at δ 7.17 (1H, ddd, *J* 8.3, 1.4 and 0.4), 7.56 (1H, ddd, *J* 8.4, 7.2, and 1.4), 7.62 (1H, ddd, *J* 8.3, 7.2 and 1.2), 7.87 (1H, ddd, *J* 8.4, 1.2 and 0.4), besides of six methyl ester protons and phenyl protons. From theresults, we assigned the structure of **6** as hexamethyl 6-phenyl-3a*H*-10c-azaacephenanthryene-1,2,3,3a,4,5-hexacarboxylate.

Plausible mechanism is shown in Scheme 1. Attack of DMAD at nitrogen of the phosphoimine moiety and a successive cyclization would produce **B** (path a). Hydrogen transfer and elimination of triphenylphosphine from **B** furnishes **5**. When first attack of DMAD occurred at ring nitrogen, an intermediate **C** would produce (path b). Transformation of **C** affords a norcaradiene intermediate (**D**). Ring transformation of **D** attended with the elimination of a phosphoimine moiety gives **E**. It is conceived that a phosphoimine moiety reacts with DMAD, but the product could not be detected. Cycloaddition of **E** with DMAD furnishes **6**. Resemble cycloaddition reactions of 1-azaazulene derivative with two or more equivalent of DMAD were known.[8]

CONCLUSION

8-Phosphoimino-1-azaazulene derivative (**1**), having both the characters of iminophosphorane and tricyclic heterocycles, reacted with arylaldehydes to give tricyclic heterocycles, 2-aryl-4-phenyl-3*H*-1,2a-diazacyclopent[*cd*]azulenes. Compound (**1**) performed the aza-Wittig reaction when treated with *trans*-cinnamaldehyde and gave 2a,5-diazabenz[*cd*]azulene system. Reaction of **1** with DMAD pursued a rather complicated process and gave two tetracyclic compounds (**5** and **6**). Thus, the phosphoimines conjugated with azaazulene system were expected to produce new heterocyclic systems by cycloaddition.

EXPERIMENTAL

Mps are measured using a Yanagimoto micro-melting apparatus and uncorrected. ^1H NMR spectra (including 2D NMR) were recorded on a Bruker AVANCE 400S (400 MHz) and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400S (100.6 MHz) using deuteriochloroform as a solvent with tetramethylsilane as an internal standard unless otherwise stated; *J* values are recorded in Hz. ^{31}P NMR spectra were recorded on a Bruker AVANCE 400S using deuteriochloroform as a solvent with triphenylphosphine as an internal standard. IR spectra were recorded for KBr pellets on a Nicolet FT-IR Impact 410 unless otherwise stated. MS spectra were taken with on an LC-MS Waters Integrity System. Elemental analyses were taken with a Perkin Elmer 2400II. Kieselgel 60 was used for column chromatography and Kieselgel 60G was used for thin-layer chromatography.

Synthesis of 3-phenyl-8-triphenylphosphoimino-1-azaazulene (1)

Under argon atmosphere, a mixture of 8-amino-3-phenyl-1-azaazulene (0.442 g, 2.01 mmol), dibromotriphenylphosphorane (1.231 g, 2.92 mmol), triethylamine (1.20 mL, 8.64 mmol), and dry benzene (6.0 mL) in a sealed tube was stirred for 24 h at rt. To the mixture, dry benzene (10 mL) was added, and the precipitate was filtered off. The filtrate was evaporated, and the residue was recrystallized from hexane-chloroform to give orange prisms (0.866 g, 90%).

1: Orange prisms (from hexane-chloroform), mp 207-208 ℃; δ_H 6.88 (1H, dd, *J* 10.2 and 9.4), 7.19-7.23 (1H, m), 7.32-7.40 (13H, m), 7.42 (1H, dd, *J* 10.7 and 9.4), 7.64 (1H, s), 7.70 (1H, d, *J* 10.7), 7.82-7.88 (6H, m), and 8.12 (1H, d, *J* 10.2); δ_C 120.95, 125.57, 128.10 (d, *J* 12.2), 130.70 (d, *J* 24.8), 132.53 (d, *J* 7.7), 133.18, 135.29 (d, *J* 4.6), 135.30, 143.50, and 163.12; δ_P 16.133; ν_{max} / cm^{-1} 1464 (P–Ph); λ_{max}(EtOH) / nm (log ε) 229 (4.52), 256 (4,35), 268 (3.87), 319 (4.30), and 412 (4.00); *m/z* (rel intensity) 480 (M^+, 32), 403 (71), 277 (100), 262 (10), 183 (67). *Anal.* Calcd for $C_{33}H_{25}N_2P$: C, 82.48; H, 5.24; N, 5.83. Found: C, 82.80; H, 5.47; N, 5.74.

Reaction of 1 with aryl aldehydes

Typical procedure A -Under argon atmosphere, a mixture of **1** (0.120 g, 0.25 mmol) and benzaldehyde (0.026 mL, 0.25 mmol) in dry xylene (3.0 mL) was heated at 125 ℃ for 200 h, then the mixture was evaporated. Chromatography of the residue on silica gel with hexane—ethyl acetate (4 : 1) gave **2a** (0.021 g, 27%) and recovered **1** (0.012g, 10%).

Typical procedure B -Under argon atmosphere, a mixture of **1** (0.240 g, 0.50 mmol), benzaldehyde (0.052 mL, 0.50 mmol), palladium(II) acetate(0.0056 g, 0.025 mmol), and dry xylene (5.0 mL) in a sealed tube was heated at 125 ℃ for 200 h. The mixture was evaporated and chromatography of the residue on silica gel with hexane—ethyl acetate (4 : 1) gave **2a** (0.094 g, 61%).

2a: Red oil; δ_H 5.28 (2H, s), 5.69 (1H, dd, *J* 11.9 and 8.5), 5.96 (1H, dd, *J* 7.4 and 7.2), 6.01 (1H, d, *J* 11.9), 6.62 (1H, d, *J* 11.9), 7.10-7.19 (1H, m), 7.29-7.34 (5H, m), 7.40 (2H, t, *J* 7.3), and 7.79 (2H, d, *J* 7.3); δ_C 56.45, 121.94, 123.10, 125.02, 125.11, 125.21, 126.56, 128.72, 128.86, 128.87, 129.40, 129.45, 130.94, 131.89, 132.65, 134.79, 144.86, and 150.79; ν_{max}(neat) / cm^{-1} 769 and 704 (phenyl); *m/z* (rel intensity) 308 (M^+, 100), 307 (54), 231 (29), 205 (26), 204 (27), 176 (10), 154 (11). Picrate of **2a**: Yellow needles (from ethanol), mp 169.5-170.5 ℃ *Anal.* Calcd for $C_{28}H_{19}N_5O_7$: C, 62.57; H, 3.56; N, 13.03. Found: C, 62.54; H, 3.56; N, 12.83.

In a similar manner, the reactions of **1** with some arylaldehydes were performed. The results were listed in Table 1.

2b: Red oil; δ_H 2.34 (3H, s), 5.26 (2H, s), 5.68 (1H, dd, *J* 11.3 and 8.5), 5.96 (1H, dd, *J* 11.9 and 8.5), 6.51 (1H, d, *J* 11.3), 6.62 (1H, d, *J* 11.9), 7.15-7.20 (1H, m), 7.22 (2H, d, *J* 8.2), 7.28-7.32 (4H, m), and

7.68 (2H, d, *J* 8.2); δ_C 29.71, 56.40, 123.00, 125.00, 125.10, 125.22, 126.50, 126.54, 126.66, 128.64, 128.85, 129.27, 129.58, 130.11, 131.89, 134.86, 138.93, 143.83, and 150.79; ν_{max}(neat) / cm^{-1} 801, 769 and 703 (phenyl); *m/z* (rel intensity) 322 (M^+, 100), 321 (41), 320 (41), 245 (31), 205 (43), 204 (42), 176 (18), 161 (47). Picrate of **2b**: Yellow needles (from ethanol), mp 179-180 ℃. *Anal.* Calcd for $C_{29}H_{21}N_5O_7$: C, 63.16; H, 3.84; N, 12.70. Found: C, 63.44; H, 3.91; N, 12.46.

2c: Red oil; δ_H 3.80 (3H, s), 5.27 (2H, s), 5.68 (1H, dd, *J* 11.7 and 8.5), 5.96 (1H, dd, *J* 11.9 and 8.5), 6.50 (1H, d, *J* 11.7), 6.62 (1H, d, *J* 11.9), 6.94 (2H, d, *J* 8.9), 7.26-7.29 (2H, m), 7.30-7.32 (3H, m), and 7.74 (2H, d, *J* 8.9); δ_C 55.40, 56.29, 114.81, 116.07, 121.28, 122.27, 122.91, 124.94, 125.10, 126.43, 126.84, 128.84, 129.49, 129.99, 130.11, 131.91, 132.37, 145.01, and 160.09; ν_{max}(neat) / cm^{-1} 2850 (OMe), 800, 760, and 700 (phenyl); *m/z* (rel intensity) 338 (M^+, 100), 337 (26), 261 (19), 205 (21), 204 (21), 169 (14), 149(9). Picrate of **2c**: Yellow needles (from ethanol), mp 175.5-176 ℃. *Anal.* Calcd for $C_{29}H_{21}N_5O_8$: C, 61.38; H, 3.73; N, 12.34. Found: C, 61.72; H, 3.94; N, 11.97.

2d: Red needles (from hexane-dichloromethane), mp 217.5-218 ℃; δ_H 5.35 (2H, s), 5.81 (1H, dd, *J* 11.3 and 8.5), 6.04 (1H, dd, *J* 11.9 and 8.5), 6.54 (1H, d, *J* 11.3), 6.69 (1H, d, *J* 11.9), 7.25-7.29 (2H, m), 7.35-7.40 (3H, m), 7.75 (2H, d, *J* 8.4), and 7.92 (2H, d, *J* 8.4); δ_C 57.07, 111.78, 118.03, 118.09, 119.07, 123.97, 124.42, 125.59, 127.47, 129.36, 130.28, 132.24, 133.05, 133.52, 133.96, 134.67, 139.14, 143.03, and 150.79; ν_{max} / cm^{-1} 2234 (CN), 800, 754, and 700 (phenyl); *m/z* (rel intensity) 333 (M^+, 100), 332 (99), 256 (38), 255 (25), 204 (48), 176 (13). *Anal.* Calcd for $C_{23}H_{15}N_3$: C, 82.86; H, 4.54; N, 12.60. Found: C, 82.63; H, 4.56; N, 12.58. Picrate of **2d**: Yellow needles (from ethanol), mp 176-177 ℃. *Anal.* Calcd for $C_{29}H_{18}N_6O_7$: C, 61.92; H, 3.23; N, 14.94. Found: C, 62.33; H, 3.56; N, 14.58.

Reaction of 1 with *trans*-cinnamaldehyde

Under argon atmosphere, a mixture of **1** (0.192 g, 0.40 mmol), *trans*-cinnamaldehyde (0.0051 mL, 0.40 mmol) and dry xylene (3.0 mL) in a sealed tube was heated at 120 ℃ for 21 h, then the mixture was evaporated. Chromatography of the residue on silica gel with hexane—ethyl acetate (4 : 1) gave **3** (0.005 g, 4%), **4** (0.018 g, 13%) and recovered 1 (0.068 g, 35%).

3: Red oil; δ_H 5.21 (2H, s), 5.74 (1H, dd, *J* 11.2 and 8.5), 6.00 (1H, dd, *J* 11.8 and 8.5), 6.51 (1H, d, *J* 11.2), 6.66 (1H, d, *J* 11.8), 6.98 (1H, s), 6.99 (1H, s), 7.20-7.39 (8H, m), and 7.51 (2H, d, *J* 7.5)); δ_C 55.21, 116.24, 122.83, 123.31, 125.7, 126.66, 126.72, 128.08, 128.51, 128.90, 129.24, 129.85, 131.63, 131.79, 134.81, 136.32, 136.71, 144.28, and 150.51; ν_{max}(neat) / cm^{-1} 1633 (C=C and C=N), 754, and 688 (phenyl); *m/z* (rel intensity) 334 (M^+, 100), 333 (47), 257 (15), 242 (7), 205 (16), 204 (18). Picrate of 3: Red micro needles (from ethanol), mp 183-184 ℃. *Anal.* Calcd for $C_{30}H_{21}N_5O_7$: C, 63.94; H, 3.76; N, 12.43. Found: C, 63.76; H, 3.51; N, 12.58.

4: Yellow oil; δ_H 6.92 (1H, d, *J* 15.5), 7.36-7.48 (4H, m), 7.50-7.55 (3H, m), 7.61 (2H, dd, *J* 8.0 and 1.2), 7.62-7.68 (2H, m), 7.90 (1H, d, *J* 15.5), 8.00 (1H, dd, *J* 11.4 and 9.3), 8.50 (1H, s), 8.66 (1H, d, *J* 9.8), and 9.52 (1H, d, *J* 11.4) (NH was not observed); ν_{max}(neat) / cm^{-1} 3292 (NH), 1692 (C=O), 1625 (C=C), 758, and 704 (phenyl); *m/z* (rel intensity) 350 (M^+, 100), 321 (30), 320 (31), 273 (29), 272 (34), 247 (49),

193 (43), 103 (39).

Reaction of 1 with DMAD

Procedure A - Under argon atmosphere, a solution of **1** (0.264 g, 0.55 mmol) and DMAD (0.2 mL, 1.65 mmol) in dry benzene (5.0 mL) was stirred for 24 h at rt, then the mixture was evaporated. Chromatography of the residue on silica gel with hexane—ethyl acetate (4 : 1) gave **5** (0.016 g, 6%) and **6** (0.101 g, 29%).

Procedure B - Under argon atmosphere, a mixture of **1** (0.240 g, 0.50 mmol), DMAD (0.18 mL, 1.50 mmol) and 5% Pd-C (0.050 g) in dry benzene (10.0 mL) was irradiated with ultra sonic wave for 7 h at rt , then the mixture was evaporated. Chromatography of the residue on silica gel with hexane—ethyl acetate (4 : 1) gave **5** (0.012 g, 5%) and **6** (0.065 g, 19%).

5: Green micro needles (from hexane), mp 194-195 ℃; δ_H 3.42 (3H, s), 3.65 (3H, s), 3.76 (3H, s), 3.83 (3H, s), 5.41 (1H, s), 5.63-5.71 (1H, m), 6.12 (1H, d, *J* 12.2), 6.23-6.28 (1H, m), 6.61 (1H, d, *J* 11.1), 7.16-7.18 (2H, m), and 7.31-7.39 (3H, m); δ_C 41.16, 46.54, 52.65, 52.93, 53.04, 54.93, 103.89, 118.22, 123.82, 124.01, 124.59, 128.16, 129.14, 130.20, 132.11, 133.83, 135.03, 139.01, 156.99, 157.85, 165.05, 167.55, and 170.45; ν_{max} / cm^{-1} 1742, 1708, and 1691 (C=O); *m/z* (rel intensity) 502 (M^+, 1), 428 (8), 311 (33), 279 (56), 267 (46), 198 (58), 149 (100) . *Anal.* Calcd for $C_{27}H_{22}N_2O_8$: C, 64.54; H, 4.41; N, 5.58. Found: C, 64.64; H, 4.51; N, 5.36.

6: Red needles (from hexane-dichloromethane), mp 251-252.5 ℃; δ_H 3.56 (6H, s), 3.61 (3H, s), 3.83 (3H, s), 3.86 (3H, s), 3.93 (3H, s), 7.17 (1H, ddd, *J* 8.3, 1.4 and 0.4), 7.48-7.51 (2H, m), 7.56 (1H, ddd, *J* 8.4, 7.2, and 1.4), 7.62 (1H, ddd, *J* 8.3, 7.2 and 1.2), and 7.87 (1H, ddd, *J* 8.4, 1.2 and 0.4); ν_{max} / cm^{-1} 1758, 1749, 1733, 1717, and 1682 (C=O); *m/z* (rel intensity) 629 (M^+, 1), 570 (100), 512 (2), 395 (3), 277 (2). *Anal.* Calcd for $C_{33}H_{27}NO_{12}$: C, 62.96; H, 4.32; N, 2.22. Found: C, 62.82; H, 4.18; N, 2.43.

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