Pyrido[1,2-a][1,2,4]triazol-3-ylidenes as a New Family of Stable Annulated N-Heterocyclic Carbenes: Synthesis, Reactivity, and Their Application in Coordination Chemistry and Organocatalysis

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General synthetic avenues to the pyrido-annulated triazolium salts with different steric and electronic properties have been developed. This architecture can be readily altered with different N-alkyl or aryl substituents at the N2 position of the triazole ring and modifications to the pyridine backbone. Deprotonation of the triazolium salts 12 with NaH led to formation of stable carbenes 11 at room temperature as clearly demonstrated through ESI mass spectra and by observation of the characteristic 13C NMR resonance for the carbene carbon at δ = 202–208 ppm. In sharp contrast, treatment of these triazolium salts with K2CO3 led to dimerization of free carbenes 11. The dimeric enetetramine (11b)2 could react with elemental sulfur to deliver the corresponding thiourea 16 in toluene at 80 °C in good yield. A silver complex with the pyrido[1,2-a][1,2,4]triazol-3-ylidene is described, and the molecular structure of complex 17 was established by X-ray crystallography. The triazolium salts 12 turned out to be powerful catalysts in catalytic benzoin condensations and transesterifications at 25 °C. The catalytic activity was largely dependent on the steric and electronic nature of the R1 and R2 substituents of the triazolium salt. We rationalized that this type of triazolium-catalyzed benzoin condensations should undergo the “traditional” Breslow mechanism rather than the pathway of the dimer (11)2 as the real catalytic species.

Introduction

The study of structure-reactivity relationships in dianocarbene is currently attracting intensive attention. It has been realized that several structural factors (e.g., the presence or absence of unsaturation at the C4–C5 bond in the imidazolide-dihydroimidazolide series, the steric bulkiness around the carbone carbon, and the presence of electron-withdrawing groups in the N-heterocyclic backbone or in N-aryl substituents, etc.) may have dramatic effects on the reactivity and stability of carbene. Much work has therefore been devoted to the design and development of carbene compounds with novel structures to tune their steric and electronic properties by slight modification of the ring framework. Some new families of stable carbene including those containing six-membered rings 4 and 5,6 seven-membered rings 6,7 and other cyclic/acyclic systems8 have been described recently. In addition, the construction of annulated NHCs by carbo- or heterocycles is also an efficient strategy to modify the properties of Arduengo’s “original” imidazol-2-yldienes 1.9 In particular, recent investigations indicate that the pyrido-annulation significantly influences the stability and the \( \alpha \)-donor/\( \pi \)-acceptor ligand properties of carbene and may be a tool for tuning their electronic properties, as was demonstrated in the bis(pyrido[1,2-al]imidazol-2-yldiene)7,10 the quinoline[\( \alpha \)]-annulated imidazol-2-yldiene 8,11 the pyrido[\( \alpha \)]-annulated carbene 9 and their homologous pyrido[\( b \)]- and pyrido[\( \alpha \)]-annulated NHCs 10.12 Although these pyrido-annulated NHCs fascinate chemists, only a few examples exist so far owing to the challenge posed by their synthesis.

Results and Discussion

Synthesis of the Pyrido-Annulated Triazolium Salts 12a–g

Several approaches to triazolium salts are conceivable. For example, 1,4-disubstituted triazolium salts can be prepared by condensation of an alkyl or aryl hydrazide with N,N-diformylhydrazine,15 followed by reaction with an amine. 3,4-Disubstituted 1-alkyl-4H-1,2,4-triazol-1-ium salts can be prepared from N-formylhydrazine and imidoyl chloride.16 1,3,4-Triphenyl-1,2,4-triazol-1-ium perchlorate can be synthesized via the cyclization of the N-phenylbenzamide phenyldrazonate with acetic anhydride and formic acid after treatment with perchloric acid.17 In addition, triazolium salts can also be accessible via


The triazol-5-yldienes 3 have turned out to be powerful organocatalysts since the convenient preparation of 1,3,4-triphenyl-1,4-dihydro-1H-1,2,4-triazol-5-yldiene in 1995.13 Later, the triazolyl carbene annulated by aliphatic cyclic skeleton have been described and exhibited highly catalytic activity in umpolung aldehyde chemistry.14 Surprisingly, there is no information about the impact of the pyrido-annulation on the properties of triazol-5-yldienes so far. We herein wish to report the highly efficient methods for the preparation of the pyrido-annulated triazolium salts 12a–g in which R\(^2\) may be both N-alkyl or aryl substituents, and describe for the first time the properties of the pyrido[1,2-a][1,2,4]triazol-3-ylidene 11 as a new class of stable N-heterocyclic carbene.
FIGURE 1. Design of the pyrido-annulated triazolium salts 12a–g.

other routes such as those reported by Wanzlick and Becker. In this study, we take advantage of the cyclization of the pyridyldihydrazine derivative 13 with trimethyl orthoformate or triethyl orthoformate to construct the pyrido[1,2-a][1,2,4]-triazolium skeleton (Figure 1). Because the pyridyldihydrazine derivatives 13 are prepared easily and are even commercially available, structural variations of the pyrido-annulated triazolium salts can be simply achieved through the choice of both the R1 substituent of the pyridine ring and the R2 group at the N2 position of the triazole ring. These compounds are easily synthesized from inexpensive starting materials and are isolated in analytically pure form as crystalline solids in good to excellent yields, depending on the nature of the R1 and R2 substituents. Furthermore, these ligands are stable enough in the air and can be stored with no special precautions. It is noteworthy that the preparation of the annulated triazolium salts has been performed without problems on 10-g scales.

Method A. As shown in Scheme 1, the synthesis of the bicyclic triazolium salt 12a was a one-pot process from commercially available 1-(pyridin-2-yl)hydrazine 13a, trimethyl orthoformate tetrafluoroborate, and triethyl orthoformate for the two-step conversion in 86% yield, which is proposed to involve the initial N-alkylation of 13a with trimethyl orthoformate tetrafluoroborate to form the intermediate 1-methyl-2-(pyridin-2-yl)hydrazine, followed by the cyclization with triethyl orthoformate. Unfortunately, all attempts to isolate this intermediate were unsuccessful. While triethyl orthoformate tetrafluoroborate was used as an N-alkylating agent, 2-ethylpyrido[1,2-a][1,2,4]triazol-2-ium tetrafluoroborate 12b was formed in 91% yield. Alternatively, the diethyl ether solution of HBF₄ could be used as the N-alkylating agent in place of triethyl orthoformate tetrafluoroborate. The structure of 12b was confirmed by X-ray diffraction analysis (see Figure 1 in the Supporting Information). This protocol could also be extended to the synthesis of modified triazolium salts starting from 1-(substituted pyridin-2-yl)hydrazines, which are easily prepared from readily available pyridin-2-amine derivatives, as illustrated in the synthesis of 12c that contains a methyl group at the C6 of the pyridine ring.

Method B. Unfortunately, the protocols described above are limited to the synthesis of those bicyclic triazolium salts which bear the methyl or ethyl substituent at the N2 position of the triazole ring, and are inappropriate for the introduction of N-aryl substituents. To extend the possibilities of ligand tuning, we have developed another avenue to make the convenient introduction of aryl substituents at the N2 position of the triazole ring, as illustrated in the synthesis of 12d–g via the condensation of hydrazines 13c–f with triethyl orthoformate in the presence of ammonium hexafluoroaphosphoric acid to afford the desired triazolium salts 12d–g in 75%, 64%, 82%, and 77% yields, respectively (Scheme 2). Hydrazines 13c–f were prepared by using the synthetic methods described previously for the three-step conversion, involving treatment of aniline derivatives with m-chloroperoxybenzoic acid to generate nitrosobenzenes, condensation of nitrosobenzenes with pyridin-2-amine derivatives to form diazenes, and reduction of diazenes with zinc and ammonium acetate. The structure of 12d was confirmed by X-ray diffraction analysis (see Figure 2 in the Supporting Information). In comparison with the first route, this route is more versatile and offers less restriction in the nature of the N2 R2 group and involves more accessible starting materials.

Synthesis, Characterization, Dimerization Behavior, and Reactivity of the Pyrido[1,2-a][1,2,4]triazol-3-ylidene 11. A distinguishing feature between unsaturated and saturated carbene precursors is their propensity to form enetetramines, the formal C=C dimers of the free carbene. N,N’-Substituted saturated dianimocarbene of type 2 show a tendency to dimerize to the enetetramines (2j) if the N-substituents are sterically less crowded. In sharp contrast, unsaturated dianimocarbene of type 1 seldom form enetetramines except under very specific circumstances such as after suitable bridging 14.12 1,2,4-Triazol-5-ylidene 15 is thermodynamically stable against dimerization to the enetetramine. To the best of our knowledge, no example describing the dimerization of triazol-5-ylidene has been clearly established so far. We herein present the synthesis, characterization, dimerization behavior, and reactivity of the first stable pyrido[1,2-a][1,2,4]triazol-3-ylidene 11.

Despite extensive application in organic catalysis, the structures, properties, and stability of triazol-5-ylidene has rarely been described. Deprotonation of appropriate cationic precursors by suitable bases is a widely applied, more convenient access to N-heterocyclic carbenes. In this study, our initial attempts focused on the direct deprotonation of the pyrido-annulated triazolium salts 12 in the presence of strong base (e.g., NaH, t-BuOK, NaOCH₃, etc.) at room temperature (Scheme 3). Perhaps the clearest spectroscopic evidence identifying 11 as an electron-rich NHCs is the appearance of a highly deshielded ¹³C NMR (THF-d₈) signal for the C_carbene at δ 202 to 208 ppm. The upfield shift of the pyrido-annulated NHCs 11 as compared to the nonannulated triazolylidene 15 (δ 214.6 ppm) reflects

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the influence of annulation on the divalent carbon. The chemical shifts are reminiscent of the unsaturated carbenes of type 1, which generally appear in the 205–220 ppm region. These values also fall in the range observed for the imidazo[1,5-a][1,2,4]triazol-3-ylidenes 9 (δ 206–209 ppm). Thus, annulation is a particularly suitable tool for tuning the electronic properties of N-heterocyclic carbenes.

As shown in Figure 2, after treatment of the triazolium salt 12b with 1.1 equiv of NaH in THF-d8 in a sealed NMR tube at room temperature, a very clean reaction occurred immediately. The 1H NMR resonance signal for the NCN proton at downfield chemical shift (δ 10.5 ppm) disappeared completely, suggesting the successful deprotonation of 12b (Figure 2b). Concomitant with this observation was the appearance of a 13C NMR signal at δ 203.8 ppm (Figure 2c). There was no evidence for dimerization of carbene, as this signal did not change even after the THF-d8 solution of 11b (R1 = H, R2 = ethyl) was kept for several days at room temperature, thereby demonstrating the stability of the free carbene in solution. Further removal of the solvent afforded the free carbene as a pale yellow solid, which is also stable for a long period at room temperature. The ESI mass spectrum of a mixture of 12b and NaH in a 1:1.1 ratio in THF showed the signal at m/z 148.9 assigned to the species 11b ([M + 2]+). In addition, treatment of the triazolium salts 12a, 12c and 12d–g with NaH afforded the values of the 13C resonance for C3 at δ 203.8, 201.8, 204.2, 204.7, 207.4, and 206.1 ppm, respectively. Notably, the salts 12d–g containing the aromatic R2 substituents at the N2 position of the triazole rings gave rise to the slight downfield shifts (204.2–207.4 ppm) as compared to 12a–c bearing the N-alkyl R2 substituents (201.8–203.8 ppm). Unfortunately, all tries to obtain single crystals suitable for X-ray crystallography were unsuccessful.

More interestingly, deprotonation of the pyrido-annulated triazolium salt 12b with K2CO3 did not lead to generation of the anticipated carbene 11b but instead yielded the enetetramine (11b)2, which has never previously been observed for triazol-5-ylidenes (Scheme 4). First, the ESI mass spectrum of a mixture of 12b and K2CO3 in a 1:1.1 ratio in THF showed the signal at

**FIGURE 2.** 1H NMR and 13C NMR spectra (THF-d8) of 12b in the presence of 1.1 equiv of NaH at 298 K: (a) the 1H NMR spectrum before addition of NaH; (b) the 1H NMR spectrum after treatment with NaH; and (c) the 13C NMR spectrum after treatment with NaH.
mass 293 assigned to the species (11b)2 ([M – 1]+). The
dimerization behavior of the pyrido-annulated triazol-3-ylidene
11b was then clearly demonstrated by its time-resolved 1H NMR
and 13C NMR spectra by mixing a sample of 12b and K2CO3
(1.1 equiv) in a sealed NMR tube in THF-d8 at room temperature
(Figure 3). The first 1H NMR spectrum exhibited the signals
derived from the triazolium salt 12b (Figure 3a). Figure 3b
indicated the formation of enetetramine (11b)2, but was still
dominated by the resonance signals of 12b after 15 min. With
time, the intensities of (11b)2 resonance signals increased and
those of 12b decreased. After 24 h, the 1H NMR resonance
signal arising from the starting material 12b nearly disappeared
(Figure 3c). Furthermore, the 1H NMR and 13C NMR spectra
did not display any additional changes over several weeks at
room temperature (Figure 3d,e). The 1H NMR and 13C NMR
spectra gave two sets of resonance signals with different
intensities, which reveals the presence of both cis and trans
isomers of the enetetramine (11b)2 in an approximate 1:10 ratio.
We assume that the trans dimer is the major product due to
steric hindrance, but all attempts to isolate individual cis and
trans isomers failed at this stage.6e,25 It is notable that in these
1H NMR spectra the broad signals marked as H (δ 8.11 to 8.24
ppm) are possibly assigned to the released C3 protons of
triazolium ring after deprotonation with K2CO3 (Figure 3b-d).
Furthermore, the 13C NMR resonance signal at δ 203.8 ppm
was not detected over the period monitored, demonstrating the
rapid dimerization of the most likely intermediate carbene 11b.
For comparison, the rapid dimerization of carbene is typical
for saturated N-heterocyclic carbenes of the imidazolidin-2-
ylidene type 2. Therefore, the pyrido-annulated triazol-3-ylidenes
11 feature the spectroscopic properties of unsaturated
N-heterocyclic carbenes of type 1 but the dimerization of saturated
derivatives 2. We rationalize that the dimer (11b)2 should be
generated from the indirect proton-catalyzed carbene dimeriza-
tion pathway.26 In the presence of K2CO3, the deprotonation of
the triazolium salt 12b is slow so that relatively large quantities
of unreacted triazolium salt still remain in the reaction system,
which can serve as a protic catalyst for the dimerization of the
free carbene to the olefin (11b)2. To clarify the mechanism of
dimerization proposed, the triazolium salt 12b was added to a

**FIGURE 3.** Time-resolved 1H NMR and 13C NMR spectra (THF-d8) of 12b in the presence of 1.1 equiv of K2CO3 at 298 K: (a) the 1H NMR
spectrum prior to addition of K2CO3; (b) the 1H NMR spectrum after 15 min; (c) the 1H NMR spectrum after 24 h; (d) the 1H NMR spectrum after
several weeks; and (e) the 13C NMR spectrum after several weeks.
solution of the isolated carbene 11b in THF-d8. The 13C NMR resonance at δ 203.8 ppm disappeared but instead gave rise to the signals assigned to the enetetramine (11b). Thus, these results showed that addition of triazolium salt could efficiently catalyze its dimerization, clearly demonstrating the indirect proton-catalyzed pathway of carbene dimerization.

The dimer (11b)2 was found to be stable in air at room temperature. While the isolated sample (11b)2 was further heated to 80 °C in toluene-d8 in a sealed NMR tube for 24 h, we observed no evidence for an equilibrium between the NHC and its dimer in solution. However, it should be known that the C=C double bond of type (2)2 can be cleaved in reactions with electrophiles with the liberation of 2,2,2-trifluoroacetic acid.25 In this study, we found that the dimer (11b)2 could also react with elemental sulfur to deliver the thiourea 16 in toluene at 80 °C in 96% yield (Scheme 5). The thiourea 16 was characterized by X-ray structure analysis (see Figure 3 in the Supporting Information).

**Synthesis of the Pyrido-Annulated Triazol-3-ylidene-Silver(I) Hexafluorophosphate Complex 17.** To further get structural information about carbenes, the triazolium salts 12 were expected to be coordinated to a silver unit to give the air-stable silver(I) complexes.26 In this study, we were fortunate to obtain both of the carbenes (11)2 and more importantly, there is no equilibrium observed between the NHCs and their dimers in solution at room temperature. We thereby felt that this was a chance to find evidence of the mechanism of the carbene-catalyzed benzoin condensation. By the NMR signals we observed the formation of free carbene arising from the deprotonation of the pyrido-annulated triazolium salt 12b in the presence of strong base at room temperature. After screening a variety of bases (i.e., NaH, DBU, Et3N, DIPEA, and t-BuOK), we found that t-BuOK was clearly the best choice in terms of yield. Thus, a typical benzoin condensation was carried out by treatment of benzaldehyde in the presence of 2 mol % of 12b and 2 mol % of t-BuOK in THF at 25 °C for 15 h. We were delighted to find that our catalytic system could afford excellent yields up to 93%. In sharp contrast, the isolated carbene dimer (11b)2 could not prompt the benzoin condensation at 25 °C. Therefore we rationalized that this type of triazolium-catalyzed benzoin condensation should undergo the "traditional" Breslow reaction.
mechanism 18 rather than the pathway of the bis(triazol-3-ylidene) dimer as the real catalytic species (Scheme 7).

The ligand survey for the catalytic benzoin condensation of benzaldehyde was carried out in the presence of 2 mol % of 12a and 2 mol % of t-BuOK in THF at 25 °C for 15 h, and the results are summarized in Table 1. We found that the yields of the benzoin condensations were largely dependent on the steric and electronic natures of the R1 and R2 substituents of the triazolium salts 12a–g. For example, the yields would decrease dramatically as the R2 substituent of the N2 position of the triazole ring varied from the N-alkyl group to the N-aryl group (compare entries 1, 2, 4, and 6). In particular, the presence of one methyl group at the C6 position of the pyridine ring would result in loss of catalytic activity (e.g., 12c, 12e, and 12g) possibly due to the steric hindrance created by the methyl group (entries 3, 5, and 7). The triazolium salt 12b thus turned out to be a particularly effective ligand, affording as high as 93% isolated yield (entry 2).

### TABLE 1. Screening of Ligand 12 for the Benzoin Condensation

<table>
<thead>
<tr>
<th>entry</th>
<th>ligand</th>
<th>yield (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>12a</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>12b</td>
<td>93</td>
</tr>
<tr>
<td>3</td>
<td>12c</td>
<td>47</td>
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<tr>
<td>4</td>
<td>12d</td>
<td>36</td>
</tr>
<tr>
<td>5</td>
<td>12e</td>
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<tr>
<td>6</td>
<td>12f</td>
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<tr>
<td>7</td>
<td>12g</td>
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*Reactions were performed on a 2.0 mmol scale with 2 mol % of ligand 12 and 2 mol % of t-BuOK in 2.0 mL of THF under N2 atmosphere at 25 °C for 15 h. Yield of isolated product based on benzaldehyde after chromatographic purification.

Catalytic Transesterification Reaction. The importance of esters in organic synthesis has encouraged the development of a variety of methods for their preparation, involving reaction of alcohol with carboxylic acid, ester interchange, and transesterification. In the past few years, the research groups of Nolan32 and Hedrick33 simultaneously reported the first use of various alkyl- or aryl-substituted imidazol-2-ylidenes as efficient transesterification catalysts in 2002.4 In this study, we were pleased to find that the transesterification of benzyl alcohol with isopropenyl acetate was able to proceed smoothly in the presence of the pyrido-annulated triazolium salt 12b. Under optimal conditions (5 mol % of 12b, 5 mol % of DBU, THF, 3 h), our catalytic system could afford the desired product 21 in 93% isolated yield at 25 °C (Scheme 8).

**Conclusion**

In summary, the pyrido-annulated triazolium salts 12a–g have been readily synthesized in a straightforward fashion from inexpensive starting materials in good yields. Novel stable pyrido[1,2-a][1,2,4]triazol-3-ylidenes 11 have been prepared by deprotonation of triazolium salts 12. The triazolium salts can be modified by changing the R1 substituent on pyridine and the R2 group on the N2 position of the triazole to tune the electronic and steric nature of the derived carbenes. These carbenes exhibit the spectroscopic properties of unsaturated N-heterocyclic carbenes but undergo dimerizations reminiscent of saturated derivatives. The dimeric enetetramine 11b2 could react with elemental sulfur to deliver the corresponding thiourea 16 in toluene at 80 °C in good yield. The pyrido-annulated triazolium salt 12d could react with Ag2O to form the silver(I) bis-carbene complex 17 with a two-coordinate Ag(I) atom in a close linear environment. The triazolium salts 12 turned out to be powerful...
catalysts in catalytic benzoine condensation and transetherification at 25 °C. The catalytic activity was largely dependent on the steric and electronic nature of the R1 and R2 substituent of the triazolium salt. The triazolium-catalyzed benzoine condensations are proposed to undergo the “traditional” Breslow mechanism rather than the dimer pathway. Further investigations into other versions of organocatalysis, organometallic catalysis, as well as the related reaction mechanisms are currently underway and will be reported in due course.

Experimental Section

General Remarks. 1H NMR spectra were obtained with a Bruker AV-300, a Varian Inova-400, or a Varian Inova-600 spectrometer, while 13C NMR spectra were recorded with a Bruker AV-300, a Varian Inova-400, or a Varian Inova-600. The 1H chemical shifts were measured relative to tetramethylsilane as the internal reference, while the 13C NMR chemical shifts were recorded with THF-d8, CDCl3, or CD3OD as the internal standard. Elemental analyses were performed with a CARLO ERBA1106 instrument. The mass spectra (ESI+) were measured relative to tetramethylsilane as the internal reference, performed with a CARLO ERBA1106 instrument. The mass spectra (ESI+) were obtained as colorless crystals in 65% yield after crystallization from acetone. Mp 185–187 °C. 1H NMR (600 MHz, CD3OD) δ 1.72 (t, J = 7.2 Hz, 3 H), 2.81 (s, 1 H), 4.70 (q, J = 7.8 Hz, 2 H), 7.25 (d, J = 6.6 Hz, 1 H), 7.77–7.80 (m, 1 H), 7.84 (d, J = 9.0 Hz, 1 H). 13C NMR (150 MHz, CD3OD) δ 14.4, 17.8, 50.2, 113.7, 118.1, 135.1, 137.6, 139.1, 149.8. MS (ESI+) m/z 161 [M – BF4–]+. Anal. Calcd for C9H10BF4N3: C, 42.56; H, 3.01; N, 12.29. Found: C, 42.46; H, 3.33; N, 11.85. 5-Methyl-2-phenylpyridin-2-ium hexafluorophosphate (12e): This compound was prepared following the same procedure as described above for 12a, using 13e as the starting material. Compound 12e was obtained as a white solid in 86% yield after crystallization from acetone. Mps 274–276 °C. 1H NMR (600 MHz, DMSO-d6) δ 2.83 (s, 3 H), 7.39 (d, J = 6.6 Hz, 1 H), 7.72 (t, J = 7.2 Hz, 1 H), 11.56 (s, 1 H). 13C NMR (150 MHz, DMSO-d6) δ 113.5, 113.4, 134.5, 135.2, 147.3. MS (ESI+) m/z 209 [M – PF6–]+. Anal. Calcd for C13H11F6N3P: C, 43.96; H, 3.41; N, 11.83. Found: C, 44.02; H, 3.45; N, 11.85. 2-(2-Isopropylphenyl)pyridin-2-ium hexafluorophosphate (12f): This compound was prepared following the same procedure as described above for 12a, using 13f as the starting material. Compound 12f was obtained as a white solid in 64% yield after crystallization from acetone. Mps 214–215 °C. 1H NMR (400 MHz, DMSO-d6) δ 1.20 (d, J = 6.8 Hz, 6 H), 2.86–2.93 (m, 1 H), 7.52–7.58 (m, 2 H), 7.61 (d, J = 8.0 Hz, 1 H), 7.75 (d, J = 3.6 Hz, 2 H), 7.94–7.98 (m, 1 H), 8.19 (d, J = 9.2 Hz, 1 H), 8.88 (d, J = 6.8 Hz, 1 H), 11.33 (s, 1 H). 13C NMR (100 MHz, DMSO-d6) δ 24.1, 27.6, 115.6, 119.0, 127.1, 127.4, 128.0, 132.8, 134.8, 137.8, 145.2, 147.3. MS (ESI+) m/z 238 [M – PF6–]++. Anal. Calcd for C15H14F6N3P: C, 47.35; H, 3.35; N, 12.29. 2-(2-Isopropylphenyl)-5-methylpyrido[1,2-a][1,2,4]triazol-2-ium hexafluorophosphate (12g): This compound was prepared following the same procedure as described above for 12a, using 13f as the starting material. Compound 12g was obtained as a white solid in 75% yield after crystallization from acetone. Mps 274–276 °C. 1H NMR (400 MHz, DMSO-d6) δ 2.83 (s, 3 H), 7.39 (d, J = 6.6 Hz, 1 H), 7.72 (t, J = 7.2 Hz, 1 H), 11.56 (s, 1 H). 13C NMR (150 MHz, DMSO-d6) δ 113.5, 113.4, 134.5, 134.6, 147.6. MS (ESI+) m/z 209 [M – PF6–]++. Anal. Calcd for C13H11F6N3P: C, 43.96; H, 3.41; N, 11.83. Found: C, 44.02; H, 3.45; N, 11.85. 5-Methyl-2-phenylpyrido[1,2-a][1,2,4]triazol-2-ium hexafluorophosphate (12e): This compound was prepared following the same procedure as described above for 12a, using 13e as the starting material. Compound 12e was obtained as a white solid in 86% yield after crystallization from acetone. Mps 274–276 °C. 1H NMR (600 MHz, DMSO-d6) δ 2.83 (s, 3 H), 7.39 (d, J = 6.6 Hz, 1 H), 7.72 (t, J = 7.2 Hz, 1 H), 11.56 (s, 1 H). 13C NMR (150 MHz, DMSO-d6) δ 113.5, 113.4, 134.5, 134.6, 147.6. MS (ESI+) m/z 209 [M – PF6–]++. Anal. Calcd for C13H11F6N3P: C, 43.96; H, 3.41; N, 11.83. Found: C, 44.02; H, 3.45; N, 11.85.
C_{15}H_{28}N_{3}P_{2}: C, 38.47; H, 4.57; N, 10.58. Found: C, 38.57; H, 4.66; N, 10.85.

Procedure for the Preparation of 2-Ethylpyrido[1,2-a][1,2,4]triazol-3-thione 16. The mixture of 12b (117.5 mg, 0.5 mmol) and K_{2}CO_{3} (75.9 mg, 0.55 mmol) in THF (5.0 mL) was stirred under N_{2} atmosphere for 24 h and then filtered through a celite plug. The filtrate was evaporated under vacuum, and the resulting residue was purified by crystallization from hexane to give the enetetramine (11b) as a white solid. The enetetramine (11b) further reacted with S_{8} (9.6 mg, 0.3 mmol) in toluene (10 mL) at 80 °C for 6 h. The mixture was then cooled to room temperature and concentrated in vacuo. The resulting residue was recrystallized from hexane to afford the colorless crystalline product (11b) as a white solid. The enetetramine (11b) further reacted with S_{8} (9.6 mg, 0.3 mmol) in toluene (10 mL) at 80 °C for 6 h. The mixture was then cooled to room temperature and concentrated in vacuo. The resulting residue was recrystallized from hexane to afford the thiourea (16) as colorless crystals in 92% yield. Mp 59–60 °C. 1H NMR (300 MHz, CDCl_{3}) δ 1.43 (t, J = 7.2 Hz, 3 H), 4.40 (q, J = 7.2 Hz, 2 H), 6.74 (s, J = 6.5 Hz, 1 H), 7.20–7.35 (m, 2 H), 8.28 (d, J = 7.1 Hz, 1 H). 13C NMR (75 MHz, CDCl_{3}) δ 13.3, 44.9, 113.0, 115.1, 126.2, 130.7, 145.5, 158.5. MS (ESI) m/z 181 [M + H]+. Anal. Calcd for C_{4}H_{9}N_{3}S: C, 53.61; H, 5.06; N, 23.44; S, 17.89. Found: C, 53.46; H, 4.66; N, 22.23; S, 17.70.

General Procedure for the Preparation of 2-Phenylpyrido[1,2-a][1,2,4]triazol-3-ylidene-Silver(I) Hexafluorophosphate Complex (17). 2-Phenylpyrido[1,2-a][1,2,4]triazol-2-ium hexafluorophosphate 12d (412 mg, 1.2 mmol) and silver oxide (139 mg, 0.6 mmol) were added to CH_{2}Cl_{2} (15 mL). The suspension became clear after stirring for 6 h at room temperature and the mixture was filtered through celite. The solvent was removed in vacuo at room temperature to give a white solid, which was recrystallized from CH_{2}Cl_{2} to afford the colorless crystalline product 17 in 98% yield. Mp 293–294 °C. 1H NMR (300 MHz, DMSO-d_{6}) δ 7.36 (t, J = 6.6 Hz, 1 H), 7.40–7.68 (m, 3 H), 7.80–7.86 (m, 1 H), 8.05–8.11 (m, 3 H), 9.23 (d, J = 7.0 Hz, 1 H). 13C NMR (75 MHz, DMSO-d_{6}) δ 115.2, 116.3, 124.2, 130.2, 130.4, 131.1, 133.7, 140.1, 148.7. Anal. Calcd for C_{23}H_{13}AgFeN_{6}P_{2}: C, 44.81; H, 2.82; N, 13.06. Found: C, 44.65; H, 2.92; N, 12.87.

Procedure for the Catalytic Benzoin Condensation by the Pyrido-Annulated Triazolium Salts 12. A flame-dried Schlenk tube with a magnetic stirring bar was charged with the triazolium salt 12 (0.04 mmol) and dry THF (2 mL) at 25 °C, followed by addition of a THF solution of t-BuOK (0.4 M, 100 μL, 0.04 mmol). After the mixture was stirred for 10 min, benzaldehyde (202 μL, 2 mmol) was added. The reaction mixture was then stirred at the same temperature for 15 h, poured into water, and extracted twice with dichloromethane. The combined organic layers were evaporated and the resulting residue was purified by column chromatography on silica gel eluting with ethyl acetate/petroleum ether (1/9) to afford 2-hydroxy-1,2-diphenylethanone (20): 1H NMR (400 MHz, CDCl_{3}) δ 4.54 (br s, 1 H), 5.96 (s, 1 H), 7.26–7.34 (m, 5 H), 7.38–7.54 (m, 3 H), 7.91–7.93 (m, 2 H). 13C NMR (100 MHz, CDCl_{3}) δ 76.2, 127.8, 128.5, 128.7, 129.1, 133.6, 133.8, 139.0, 199.0. GC-MS (EI+) m/z 211 [M + H]+.

Procedure for the Catalytic Transesterification Reaction. A flame-dried Schlenk tube with a magnetic stirring bar was charged with 12b (23.6 mg, 0.1 mmol), DBU (15 µL, 0.1 mmol), and THF (1.0 mL) under N_{2} atmosphere at 25 °C. After the mixture was stirred for 10 min, benzyl alcohol (208 µL, 2 mmol) and isopropenyl acetate (262 µL, 2.4 mmol) were added. After the reaction mixture was stirred at the same temperature for 3 h, the volatiles were removed and the resulting residue was purified by column chromatography on silica gel eluting with ethyl acetate/petroleum ether (1/12) to give the benzyl acetate (21) as a viscous oil in 93% yield. 1H NMR (400 MHz, CDCl_{3}) δ 2.10 (s, 3 H), 5.11 (s, 2 H), 7.35–7.37 (m, 5 H). 13C NMR (100 MHz, CDCl_{3}) δ 20.9, 38.3, 66.2, 128.2, 128.5, 135.9, 170.8. GC-MS (EI+) m/z 149 [M + H]+.

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Supporting Information Available: Copies of 1H and 13C NMR spectra for compounds 12a–g, (11b)2, 16, 17, 20, and 21. ORTEP drawings of 12b, 12d, and 16, and X-ray crystallographic data in CIF format for 12b, 12d, 16, and 17. This material is available free of charge via the Internet at http://pubs.acs.org.

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