Ring-Opening Cycloaddition of Aziridines to Ketenimines

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The Lewis acid-catalyzed addition of aziridines to ketenimines gave substituted pyrrolidonimines in 47−87% yields. The hard Lewis acid $LiClO_4$ proved to be superior to the soft $[(PhCN)_2PdCl_2]$, affording higher yields under milder conditions. The reaction is regioselective and occurs with complete stereoselectivity using $[(PhCN)_2PdCl_2]$ and with a small amount of racemization in the case of $LiClO_4$.

Introduction

Numerous methods have been described for the synthesis of five-membered heterocycles.[1] Among these, the ring-opening addition of three-membered heterocycles to cumulenes has particular potential. For example, the thermal reaction of oxiranes with isocyanates affords oxazolidinones[2] but requires severe reaction conditions. The introduction of catalysts allows the reaction to proceed under considerably milder conditions. Catalysts usually consist of main group element-based Lewis acids, e.g., organotin or organoantimony halides, which were successfully employed in the addition of oxiranes to isocyanates and carbodiimides.[3,4] Transition metal-based catalysts can either involve organometallic intermediates, as in the Pd(0)-catalyzed addition of vinyloxiranes to isocyanates,[5,6] or function as a soft Lewis acid, like $[(PhCN)_2PdCl_2]$. The latter has been shown to effectively catalyze the addition of N-heterocycles to various heterocumulenes, although reaction temperatures above 100 °C are still required.[7] Using aziridines and ketenimines as substrates, substituted pyrrolidine derivatives are easily accessible by this reaction. In this paper, we wish to report the Lewis acid-catalyzed synthesis of this class of interesting compounds using Li- or Pd-based catalysts.

Results and Discussion

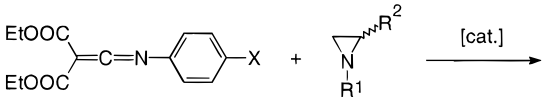
Treatment of dicarbethoxyketenimine **1a** or **1c** with substituted aziridine **2a** or **2c** in toluene in the presence of $[(PhCN)_2PdCl_2]$ afforded iminopyrrolidines of structural type **3** in 24−65% yield. The addition of the heterocycle occurred exclusively across the C−C double bond yielding highly substituted products with an exocyclic imino group. The aziridine underwent selective cleavage of the bond between nitrogen and the higher substituted C2 atom.

A reaction temperature of 75 °C was found to be optimal, while higher temperatures gave lower yields due to side reactions of the ketenimine. At lower temperatures, prolonged reaction times were required to achieve full conversion of the ketenimine. However, this did not result in increased product yields. Product yields decreased considerably when electron-withdrawing substituents were introduced at the C2 position of the aziridine. Thus, the ester-functionalized aziridine **2c** afforded the corresponding cycloadduct **3c** in only 24% yield (Table 1).

Table 1. $[(PhCN)_2PdCl_2]$-Catalyzed Reactions[a]

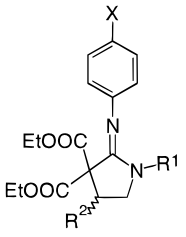
ketenimine	aziridine	*T* (°C)	yield (%)[c]	product
1a	**2a**	50[b]	54	**3a**
1a	**2a**	75	60	**3a**
1a	**2a**	100	41	**3a**
1c	**2a**	75	65	**3c**
1a	**2c**	75	24	**3f**

[a] Reaction conditions: 1 mmol each of **1** and **2**, 5 mL of toluene, 10 mol % $[(PhCN)_2PdCl_2]$; reaction time, 18 h. [b] 90 h. [c] Isolated yields.



1a: X = H
b: X = CH_3
c: X = Cl

2a: R^1 = *tert*Bu, R^2 = Ph
2b: R^1 = *n*Bu, R^2 = Ph
2c: R^1 = *tert*Bu, R^2 = $COOCH_3$
2d: R^1 = *tert*Bu, R^2 = $CH_2OpAnis$



3a-j

3a: X = H, R^1 = *tert*Bu, R^2 = Ph
3b: X = CH_3, R^1 = *tert*Bu, R^2 = Ph
3c: X = Cl, R^1 = *tert*Bu, R^2 = Ph
3d: X = H, R^1 = *n*Bu, R^2 = Ph
3e: X = CH_3, R^1 = *n*Bu, R^2 = Ph
3f: X = H, R^1 = *tert*Bu, R^2 = $COOCH_3$
3g: X = CH_3, R^1 = *tert*Bu, R^2 = $COOCH_3$
3h: X = Cl, R^1 = *tert*Bu, R^2 = $COOCH_3$
3i: X = H, R^1 = *tert*Bu, R^2 = $CH_2OpAnis$
3j: X = CH_3, R^1 = *tert*Bu, R^2 = $CH_2OpAnis$

An alternate approach for effecting the reaction of aziridines with ketenimines involved the use of the hard Lewis acid $LiClO_4$ as the catalyst. The same transformation was effected under milder conditions, resulting in higher yields at lower catalyst concentrations and shorter reaction times. For example, reaction of **1a** and **2a** with 5 mol % $LiClO_4$ in THF proceeded smoothly at room temperature within 5 h. In comparison, a temperature of 75 °C and a reaction time of 15 h were required when

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Table 2. $LiClO_4$-Catalyzed Reactions[a]

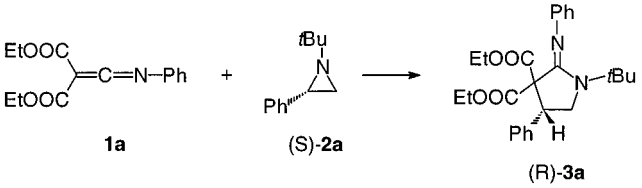
ketenimine	aziridine	*T* (°C)	time (h)	yield (%)[b]	product
1a	**2a**	rt	5	76	**3a**
1b	**2a**	rt	5	86	**3b**
1c	**2a**	rt	5	87	**3c**
1a	**2b**	rt	2	70	**3d**
1b	**2b**	rt	2	61	**3e**
1a	**2c**	50	18	65	**3f**
1b	**2c**	50	18	73	**3g**
1c	**2c**	50	18	69	**3h**
1a	**2d**	50	18	47	**3i**
1b	**2d**	50	18	62	**3j**

[a] Reaction conditions: 1 mmol each of **1** and **2**, 5 mL of THF, 5 mol % $LiClO_4$. [b] Isolated yields.

10 mol % of the Pd catalyst was employed. For the ester-substituted aziridine **2c**, the yield of **3f** was 65% using $LiClO_4$, significantly higher than that found with palladium (24%). The results of the reactions of a variety of aziridines and ketenimines are summarized in Table 2.

The reactivity of the ketenimine is not significantly influenced by the electronic nature of the aromatic substituent, since *p*-chloro- and *p*-methyl-substituted ketenimines **1b**,**c** give similar yields of iminopyrrolidines. On the other hand, substituents on the aziridine affect their reactivity. While 2-phenyl-substituted aziridines **2a**,**b** reacted at room temperature, no reaction was observed for the ester aziridine **2c** at this temperature. Due to the different electronegativities, the C2−N bond is polarized with a partial charge at the nitrogen atom. The ester unit as an electron-withdrawing group partially neutralizes this polarization, thus rendering the adjacent carbon atom less electrophilic and the nitrogen less nucleophilic compared to 2-phenyl-substituted aziridines. A higher reaction temperature of 50 °C is required for **2c**, which is also true for the ether-substituted aziridine **2d**. The higher reactivity of the *N*-*n*-butyl-substituted aziridine **2b** compared to that of the *N*-*tert*-butyl-substituted **2a** analogue is noteworthy.

To elucidate the stereochemical course of the reaction, (*S*)-1-*tert*-butyl-2-phenylaziridine, (*S*)-**2a**, was prepared in 93% ee according to a literature method.[8] When (*S*)-**2a** was subjected to the cycloaddition reaction with ketenimine **1a** under the above conditions, the same enantiomer of **3a** was formed in 83% ee for the Li-catalyzed reaction and in 93% ee for the palladium-catalyzed reaction. The absolute configuration of the cycloaddition product was determined by X-ray crystallography. The ORTEP plot (Figure 1) shows that the product has the *R*-configuration, which means that the stereochemistry of the aziridine C2 atom is retained throughout the reaction:



This finding as well as the reactivity pattern of the different substrates can be rationalized by a stepwise S_Ni-type reaction mechanism. The first step may involve nucleophilic attack of the aziridine at the central carbon atom of the ketenimine. Subsequent intramolecular nucleophilic attack of the resulting stabilized anion on the aziridine C2 atom furnishes the cycloaddition product, thereby retaining the stereochemistry of the former aziridine fragment. A similar mechanism has been postulated for the antimony-catalyzed cycloaddition of aziridines to isocyanates.[9]

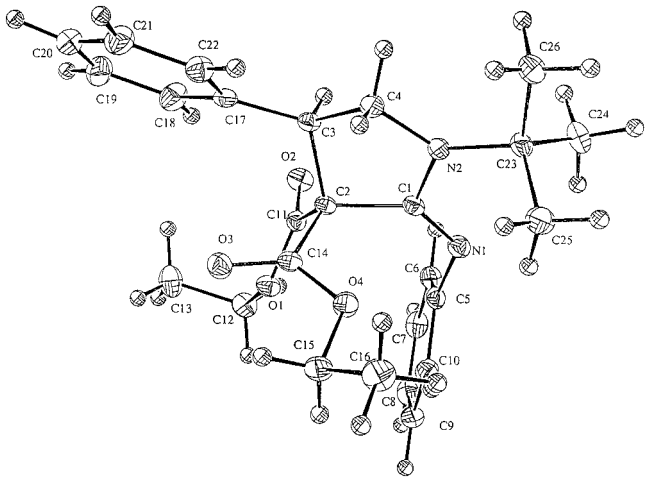
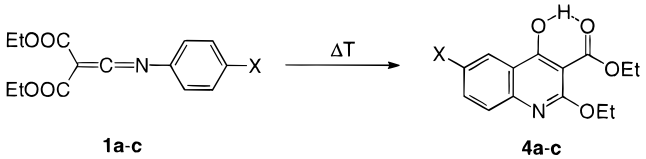


Figure 1.

For a pure S_Ni-type mechanism the overall reaction should occur with complete retention of configuration of the aziridine. However, the Li-catalyzed reaction proceeds with racemization to a minor extent, whereas with palladium the reaction proceeds in a completely stereoselective manner. This different behavior might be due to the fact that for solubility reasons, the $LiClO_4$-catalyzed reaction was carried out in THF. In a polar, coordinating solvent the reaction obviously does not occur in a pure S_Ni fashion, but solvation effects result in partial racemization. Alternatively, the Pd-catalyzed reaction may be concerted, while the Li^+-catalyzed process may be, as proposed, stepwise in nature.

The reason that Li-catalyzed reactions gave better yields than Pd-catalyzed processes is that side reactions of the ketenimine acquire greater importance at temperatures above 75 °C, conditions which are required with Pd catalysts. One side reaction is the thermal rearrangement of the ketenimines to oxoquinolines, which has been described previously for **1a**,**b** affording **4a**,**b**,[10,11] respectively. We isolated the oxoquinolines **4a**−**c** in up to 10% yield from reactions at 100 °C.



In conclusion, we have demonstrated the catalytic regio- and stereoselective synthesis of pyrrolidonimines from ketenimines and aziridines in moderate to excellent yields under mild conditions.

Experimental Section

All reactions were carried out using standard Schlenk technique in an N_2 atmosphere. Solvents were dried by standard methods and distilled under N_2. ^1H and ^{13}C NMR

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spectra were recorded on a Bruker AMX500 instrument, and infrared spectra were obtained on a Bomem MB-100 spectrometer. Mass spectra were obtained with a VG 7070 E spectrometer. A JAI LC-908 instrument was used for preparative HPLC (chloroform as eluant, 3−5 mL/min flow rate). Melting points are uncorrected. Aziridines were prepared as reported,[8,12] and ketenimines were prepared from the corresponding amides.[13]

General Procedure for the Pd-Catalyzed Reactions. $[(PhCN)_2PdCl_2]$ (38.4 mg, 0.1 mmol) was dissolved in 3 mL of toluene, 1.0 mmol of the aziridine and 1.0 mmol of the ketenimine dissolved in 1 mL of toluene each were added to the catalyst solution, and the Schlenk tube was immersed in a preheated oil bath. After the reaction, the solution was cooled to room temperature, and an IR spectrum of the reaction mixture showed complete conversion of the ketenimine. The catalyst was removed by filtration over Florisil, the filtrate was evaporated, and pyrrolidonimine **3** and oxoquinoline **4** were isolated by preparative HPLC.

General Procedure for the Li-Catalyzed Reactions. $LiClO_4$ (5.3 mg, 0.05 mmol) was dissolved in 3 mL of THF, 1.0 mmol of the aziridine and 1.0 mmol of the ketenimine dissolved in 1 mL of THF each were added to the catalyst solution, and for reactions at elevated temperatures the Schlenck tube was immersed in a preheated oil bath. After the reaction, the solution was cooled to room temperature, and an IR spectrum of the reaction mixture showed the complete conversion of the ketenimine. The mixture was evaporated, and the product was isolated by preparative HPLC.

Spectral and analytical data for cycloaddition products **3a**−**j** and rearrangement product **4c** are as follows.

3a (R_1 = Ph, R_2 = *t*-Bu, X = H): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (m, 3H), 7.11 (m, 4H), 6.83 (m, 1H), 6.69 (m, 2H), 4.33 (dd, 1H, J = 9.7, 7.2 Hz), 3.92 (m, 2H), 3.77 (m, 2H), 3.63 (m, 1H), 3.53 (m, 1H), 1.58 (s, 9H), 0.99 (t, 3H, J = 7.1 Hz), 0.90 (t, 3H, J = 7.1 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.1, 166.3, 151.8, 149.5, 136.2, 128.3, 128.2, 128.0, 127.8, 121.8, 121.3, 67.2, 61.9, 61.0, 55.3, 49.1, 48.0, 27.4, 13.5; IR (CH_2Cl_2) $\nu_{C=N}$ 1656 cm^{-1}, $\nu_{C=O}$ 1716 cm^{-1}; MS *m/e* 436 [M$^+$]; mp 94−95 °C. Anal. Calcd for $C_{26}H_{32}N_2O_4$: C, 71.54; H, 7.39; N, 6.42. Found: C, 71.82; H, 7.20; N, 6.25.

3b (R_1 = Ph, R_2 = *t*-Bu, X = CH_3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (m, 3H), 7.10 (m, 2H), 6.91 (d, 2H, J = 8.3 Hz), 6.58 (d, 2H, J = 8.2 Hz), 4.32 (dd, 1H, J = 9.5, 7.4 Hz), 3.91 (m, 2H), 3.76 (m, 2H), 3.64 (m, 1H), 3.56 (m, 1H), 2.22 (s, 3H), 1.58 (s, 9H), 0.99 (t, 3H, J = 7.2 Hz), 0.91 (d/t, 3H, J = 7.1, 0.7 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.2, 166.3, 152.2, 147.0, 136.2, 130.3, 128.8, 128.3, 128.1, 127.9, 121.8, 67.0, 61.9, 60.9, 55.3, 49.2, 48.0, 27.4, 20.7, 13.5, 13.4; IR (CH_2Cl_2) $\nu_{C=N}$ 1655 cm^{-1}, $\nu_{C=O}$ 1712 cm^{-1}; MS *m/e* 450 [M$^+$]; mp 90−91 °C. Anal. Calcd for $C_{27}H_{34}N_2O_4$: C, 71.97; H, 7.61; N, 6.22. Found: C, 71.60; H, 7.34; N, 6.11.

3c (R_1 = Ph, R_2 = *t*-Bu, X = Cl): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (m, 3H), 7.06 (m, 4H), 6.60 (m, 2H), 4.32 (dd, 1H, J = 9.6, 7.3 Hz), 3.91 (m, 2H), 3.74 (m, 2H), 3.56 (m, 2H), 1.54 (s, 9H), 0.99 (t, 3H, J = 7.1 Hz), 0.86 (t, 3H, J = 7.2 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.1, 166.3, 152.1, 148.1, 136.0, 126.2, 128.3, 128.1, 128.0, 127.8, 123.1, 67.4, 62.2, 61.2, 55.4, 49.0, 48.1, 27.3, 13.4; IR (CH_2Cl_2) $\nu_{C=N}$ 1654 cm^{-1}, $\nu_{C=O}$ 1716 cm^{-1}; MS *m/e* 471, 473 [M$^+$]; mp 57−59 °C. Anal. Calcd for $C_{26}H_{31}ClN_2O_4$: C, 66.30; H, 6.63; N, 5.95. Found: C, 66.05; H, 6.50; N, 5.66.

3d (R_1 = Ph, R_2 = *n*-Bu, X = H): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27−6.75 (m, 10H), 4.46 (t, 1H, J = 8.4 Hz), 4.01 (m, 1H), 3.86 (m, 1H), 3.82 (t, 1H, J = 9.3 Hz), 3.71 (m, 1H), 3.63 (m, 2H), 3.45 (m, 1H), 3.30 (m, 1H), 1.69−1.16 (m, 4H), 1.01 (m, 3H), 0.87 (m, 3H), 0.83 (t, 3H, J = 7.2 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 167.7, 166.2, 152.8, 149.5, 136.1, 128.7, 128.2, 128.0, 127.8, 121.9, 121.6, 67.6, 62.0, 61.1, 50.9, 48.8, 45.2, 28.7, 20.1, 14.8, 13.8, 13.4; IR (CH_2Cl_2) $\nu_{C=N}$ 1659 cm^{-1}, $\nu_{C=O}$ 1718 cm^{-1}; MS *m/e* 436 [M$^+$]. Anal. Calcd for $C_{26}H_{32}N_2O_4$: C, 71.54; H, 7.39; N, 6.42. Found: C, 71.44; H, 7.34; N, 6.59.

3e (R_1 = Ph, R_2 = *n*-Bu, X = CH_3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24−6.61 (m, 9H), 4.43 (t, 1H, J = 8.5 Hz), 3.97 (m, 1H), 3.87 (m, 1H), 3.79 (t, 1H, J = 9.4 Hz), 3.68 (m, 1H), 3.60 (m, 2H), 3.42 (m, 1H), 3.28 (m, 1H), 2.19 (s, 3H), 1.69−1.12 (m, 4H), 1.02 (m, 3H), 0.87 (m, 3H), 0.85 (t, 3H, J = 7.2 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 167.8, 166.1, 153.3, 146.6, 136.0, 130.9, 128.8, 128.3, 128.0, 127.8, 121.9, 67.6, 62.1, 61.4, 50.7, 49.0, 45.3, 28.7, 20.7, 20.1, 14.8, 13.9, 13.5 ppm; IR (CH_2Cl_2) $\nu_{C=N}$ 1660 cm^{-1}, $\nu_{C=O}$ 1718 cm^{-1}, MS *m/e* 450 [M$^+$]. Anal. Calcd for $C_{27}H_{34}N_2O_4$: C, 71.97; H, 7.61; N, 6.22. Found: C, 71.53; H, 7.34; N, 6.11.

3f (R_1 = $COOCH_3$, R_2 = *t*-Bu, X = H): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (m, 2H), 6.82 (m, 3H), 4.21 (m, 2H), 3.79 (dd, 1H, J = 9.3, 8.7 Hz), 3.70 (m, 1H), 3.62 (s, 3H), 3.61 (t, 1H, J = 8.7 Hz), 3.50 (t, 1H, J = 9.6 Hz), 3.40 (m, 1H), 1.44 (s, 9H), 1.28 (t, 3H, J = 7.2 Hz), 0.95 (t, 3H, J = 7.2 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.7, 166.6, 165.9, 148.7, 147.9, 127.8, 122.2, 121.5, 64.5, 62.1, 62.0, 55.0, 51.8, 48.0, 44.4, 27.1, 13.9, 13.4 ppm; IR (CH_2Cl_2) $\nu_{C=N}$ 1660 cm^{-1}, $\nu_{C=O}$ 1742 cm^{-1}; MS *m/e* 418 [M$^+$]; mp 83−84 °C. Anal. Calcd for $C_{22}H_{30}N_2O_6$: C, 63.14; H, 7.23; N, 6.69. Found: C, 62.92; H, 7.18; N, 6.69.

3g (R_1 = $COOCH_3$, R_2 = *t*-Bu, X = CH_3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (m, 2H), 6.70 (m, 2H), 4.21 (m, 2H), 3.78 (dd, 1H, J = 10.0, 7.7 Hz), 3.70 (m, 1H), 3.62 (s, 3H), 3.61 (t, 1H, J = 7.7 Hz), 3.50 (t, 1H, J = 10.0 Hz), 3.42 (m, 1H), 2.21 (s, 3H), 1.44 (s, 9H), 1.28 (t, 3H, J = 7.2 Hz), 0.96 (t, 3H, J = 7.1 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.8, 166.7, 165.9, 148.9, 145.4, 130.5, 128.3, 122.1, 64.4, 62.1, 62.0, 55.0, 51.8, 48.1, 44.3, 27.1, 20.6, 13.9, 13.3; IR (CH_2Cl_2) $\nu_{C=N}$ 1660 cm^{-1}, $\nu_{C=O}$ 1742 cm^{-1}; MS *m/e* 432 [M$^+$]; mp 100−102 °C. Anal. Calcd for $C_{23}H_{32}N_2O_6$: C, 63.87; H, 7.46; N, 6.48. Found: C, 63.47; H, 7.44; N, 6.20.

3h (R_1 = $COOCH_3$, R_2 = *t*-Bu, X = Cl): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (m, 2H), 6.73 (m, 2H), 4.19 (m, 2H), 3.76 (m, 2H), 3.60 (s, 3H), 3.60 (t, 1H, J = 8.7 Hz), 3.46 (m, 2H), 1.41 (s, 9H), 1.25 (t, 3H, J = 7.2 Hz), 0.95 (t, 3H, J = 7.1 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.5, 166.6, 165.7, 149.3, 146.7, 126.5, 127.7, 123.7, 64.7, 62.3, 62.2, 55.2, 51.9, 48.1, 44.5, 27.1, 13.9, 13.4; IR (CH_2Cl_2) $\nu_{C=N}$ 1658 cm^{-1}; $\nu_{C=O}$ 1742 cm^{-1}; MS *m/e* 452, 454 [M$^+$]; mp 86−87 °C. Anal. Calcd for $C_{22}H_{29}ClN_2O_6$: C, 58.34; H, 6.45; N, 6.18. Found: C, 58.56; H, 6.31; N, 6.02.

3i (R_1 = CH_2O-*p*-Anis, R_2 = *t*-Bu, X = H): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (m, 2H), 6.76 (m, 7H), 4.18 (m, 1H), 4.08 (m, 1H), 3.98 (m, 1H), 3.83 (m, 2H), 3.74 (m, 1H), 3.72 (s, 3H), 3.51 (m, 1H), 3.43 (m, 1H), 3.24 (m, 1H), 1.49 (s, 9H), 1.22 (t, 3H, J = 7.2 Hz), 1.00 (t, 3H, J = 7.1 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 167.5, 166.4, 154.7, 152.6, 151.0, 149.1, 128.1, 121.8, 121.3, 115.4, 114.7, 66.8, 63.7, 61.9, 61.6, 55.6, 55.0, 47.3, 43.7, 27.2, 13.9, 13.5; IR (CH_2Cl_2) $\nu_{C=N}$ 1656 cm^{-1}, $\nu_{C=O}$ 1732 cm^{-1}; MS *m/e* 496 [M$^+$]. Anal. Calcd for $C_{28}H_{36}N_2O_6$: C, 67.72; H, 7.31; N, 5.64. Found: C, 67.85; H, 7.41; N, 5.70.

3j (R_1 = CH_2O-*p*-Anis, R_2 = *t*-Bu, X = CH_3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (m, 2H), 6.76 (m, 4H), 6.58 (m, 2H), 4.17 (m, 1H), 4.08 (m, 1H), 3.97 (m, 1H), 3.82 (m, 2H), 3.74 (m, 1H), 3.72 (s, 3H), 3.54 (m, 1H), 3.50 (m, 1H), 3.23 (m, 1H), 2.22 (s, 3H), 1.49 (s, 9H), 1.22 (t, 3H, J = 7.2 Hz), 1.00 (t, 3H, J = 7.1 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 167.7, 166.4, 154.1, 152.5, 151.3, 146.6, 130.3, 128.7, 121.6, 115.4, 114.6, 66.9, 63.5, 62.0, 61.6, 55.7, 55.0, 47.4, 43.8, 27.2, 20.6, 13.9, 13.4; IR (CH_2Cl_2) $\nu_{C=N}$ 1657 cm^{-1}, $\nu_{C=O}$ 1729 cm^{-1}; MS *m/e* 510 [M$^+$]. Anal. Calcd for $C_{29}H_{38}N_2O_6$: C, 68.21; H, 7.50; N, 5.49. Found: C, 67.90; H, 7.58; N, 5.16.

4c (X = Cl): ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.40 (s, 1H), 8.09 (m, 1H), 7.56 (m, 2H), 4.49 (q, 2H, J = 7.1 Hz), 4.42 (q, 2H, J = 7.2 Hz), 1.43 (t, 3H, J = 7.1 Hz), 1.42 (t, 3H, J = 7.2 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 171.3, 169.3, 160.2, 146.1, 133.2, 129.1, 128.2, 122.8, 118.5, 95.3, 62.6, 62.1, 14.3, 13.9; IR (CH_2Cl_2) $\nu_{C=O}$ 1630 cm^{-1}; MS *m/e* 295, 297 [M$^+$]; mp 120−

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121 °C. Anal. Calcd for $C_{14}H_{14}ClNO_4$: C, 56.86; H, 4.77; N, 4.74. Found: C, 56.81; H, 4.55; N, 4.98.

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Supporting Information Available: Crystal data collection, data reduction, and structure solution and refinement (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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