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A Palladium-Catalyzed Multicomponent Synthesis of Imidazolinium Salts and Imidazolines from Imines, Acid Chlorides, and Carbon Monoxide

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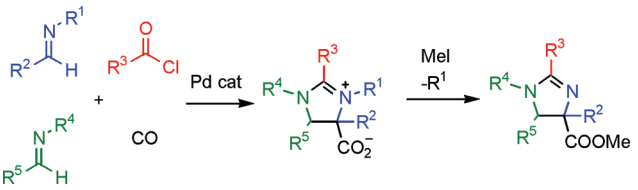

A palladium-catalyzed multicomponent synthesis of imidazolinium carboxylates and imidazolines is described. The palladium catalyst $[Pd(CH(R^1)N(R^2)COR^3)Cl]_2$, or $[Pd(allyl)Cl]_2$, with P(*t*-Bu)$_2$(2-biphenyl) can mediate the simultaneous coupling of two imines, acid chloride, and carbon monoxide into substituted imidazolinium carboxylates within hours under mild conditions (45 °C, 4 atm of CO). The reaction proceeds in good yield with aryl-, heteroaryl-, and alkyl-substituted acid chlorides, as well as variously functionalized imines. Imidazolines are formed via the initial generation of Münchnone intermediates, followed by their cycloaddition with an in situ generated protonated imine. The addition of an amine base can intercept catalysis at Münchnone formation, which allows the subsequent cycloaddition of a second imine. The latter provides a route for the assembly of complex, polysubstituted imidazolinium carboxylates with independent control of all five substituents. The subsequent removal of the nitrogen substituent(s) provides an overall synthesis of imidazolines.

Introduction

Imidazolines are found in a diverse range of biologically relevant compounds, including anticancer agents,[1] vasoregulators,[2] antidepressants,[3] antidiabetics,[4] and a variety of natural products.[5] In addition, imidazolines have been employed as components in peptidomimetics[6] and have found significant use as metal coordinating ligands,[7] precursors to chiral N-heterocyclic carbenes,[8] or building blocks in organic synthesis.[9] This utility has stimulated interest in the design of efficient routes to these heterocycles. The classic synthesis of imidazolines involves the

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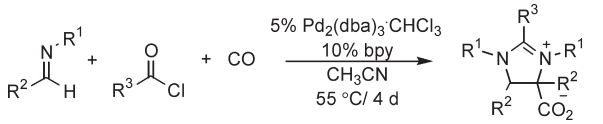
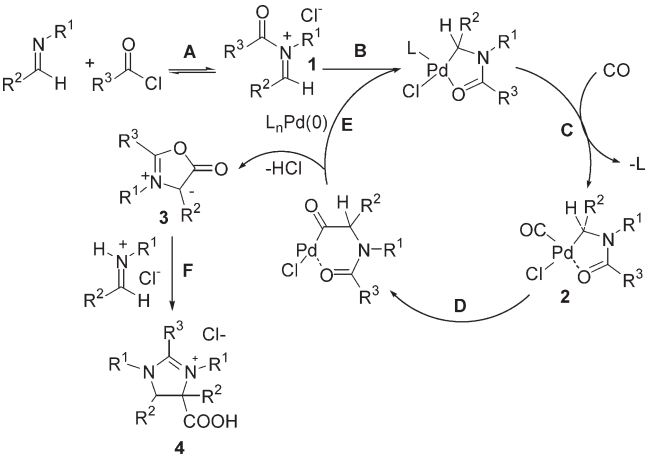
cyclization of substituted 1,2-diamines with electrophiles (e.g., esters,[10] amides,[11] imidates,[12] or aldehydes in concert with oxidants),[13] or β-substituted amidines.[14] Alternatively, a number of cycloaddition strategies have also been developed for the assembly of imidazolines. These include the reaction of isocyanides with imines,[15] the ring expansion of aziridines with nitriles,[16] and the cycloaddition of imines with imidate-derived azomethine ylides.[17]

While each of these approaches can be effective, one feature they typically share is the need to build up the precursor(s) with the desired substituents prior to cyclization. The latter can take multiple steps for highly substituted imidazolines, complicating not only its synthesis but also product diversification. An alternative is to assemble polysubstituted heterocycles such as imidazolines directly from multiple, available building blocks. As we[18] and others[19] have previously described, metal catalysis can provide a useful tool for mediating such reactions, by activating simple substrates toward reaction. We have previously reported that this approach can be applied to the synthesis of imidazolinium carboxylates, via the palladium-catalyzed coupling of imines, acid chlorides, and CO (Scheme 1).[20] Notably, this route avoids the need to construct complex substrates for cyclization and instead employs building blocks that are all either available (carbon monoxide and acid chlorides) or easily generated (imines, from aldehydes and amines).

SCHEME 1. Palladium-Catalyzed Imidazolinium Carboxylate Formation



SCHEME 2. Proposed Mechanism for Imidazoline Formation



The reaction in Scheme 1 has been postulated to proceed through a series of palladium-mediated operations to form Münchnone intermediates **3** (Scheme 2).[20] The latter dipolar compounds were initially reported by Huisgen in 1964 and are reactive 1,3-dipolar cycloaddition substrates.[21] Under the catalytic conditions shown in Scheme 1, protonated imine undergoes rapid cycloaddition to **3** to form the imidazoline core. The addition of the amine can block this cycloaddition, by inhibiting the formation of protonated imine leading to the catalytic synthesis of Münchnones.[22] More recently, Tepe[23] reported the synthesis of imidazoline carboxylic acids via TMS-mediated cycloaddition of imines with Münchnones.

Considering the efficiency of the palladium-catalyzed synthesis in Scheme 1, we became interested in the potential of using this methodology as a general approach to assemble the imidazoline core. However, the original report showed this reaction to be sluggish, typically requiring 4 days for complete conversion. In addition, the reaction has limited scope (R^1 = Ph or Me; R^3 = *p*-tolyl), requires the formation of products containing two identical imines, and thus generates only symmetrically substituted products. We describe herein our efforts toward addressing these issues. This includes the development of a highly active palladium catalyst for this synthesis, which can allow the coupling to proceed in hours under mild conditions. In addition, via modification of the reaction conditions, a diverse range of substituted imidazolinium salts and imidazolines can be generated, including the selective incorporation of different imines into the heterocyclic core. Overall, this provides a straightforward route to the formation of these products in a single operation, and with high atom economy.

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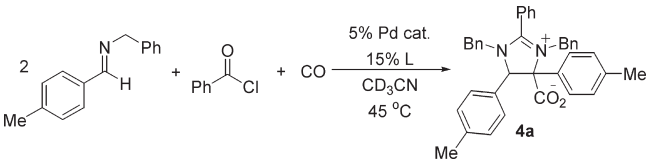
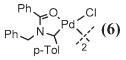
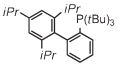
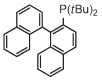
TABLE 1. Influence of Ligands on Imidazolinium Carboxylate Synthesis[a]



entry	Pd cat	L	time	yield
1	$Pd_2(dba)_3 \cdot CHCl_3$ (5)	bpy	96 h	82%
2	**5**	-	24 h	83%
3	 (6)	-	24 h	90%
4	**5**	-	3 h	21%
5	**6**	PPh_3	3 h	-
6	**6**	$P(OPh)_3$	3 h	-
7	**6**	P(*o*-tolyl)$_3$	3 h	10%
8	**6**		3 h	14%
9	**6**		3 h	15%
10	**6**	P(*t*Bu)$_3$	3 h	47%
11	**6**		3 h	33%
12	**6**		3 h	41%
13	**6**		3 h	47%
14	**6**		3 h	72%
15	**6**		3 h	33%
16	**6**	 7	3 h	84%
17	**5**	**7**	3 h	62%
18	$[Pd(C_3H_5)Cl]_2$	**7**	3 h	80%
19	$PdCl_2$	**7**	3 h	-
20	0.5 mol% **6**	1.5% **7**	96 h	92%

[a]General: imine (52 mg, 0.25 mmol), benzoyl chloride (17 mg, 0.12 mmol), 5% catalyst, 800 μL of CD_3CN, 4.0 atm of CO, in J. Young NMR tube, 45 °C. Yield based on ^1H NMR comparison to internal standard. For entry 18, 25 mol % **7** was used.

Results and Discussion

Catalyst Development. Our initial studies focused on developing a more active palladium catalyst for the imidazolinium carboxylate formation shown in Scheme 1. In considering the postulated mechanism for this reaction (Scheme 2), we noted that the bidentate bipyridine ligand present on the catalyst must be displaced by either iminium salt oxidative addition (step B) or CO coordination (step C) during the catalytic cycle, implying that the ligand may be slowing these steps. As shown in Table 1, performing this same coupling with only 5% $Pd_2dba_3 \cdot CHCl_3$ and no added ligand leads to the generation of **4a** in 24 h (entry 2), in contrast to the 4 days under analogous conditions with bipyridine present. Similar results are observed using the palladacycle intermediate **6** as a catalyst (generated by pretreating Pd_2dba_3 with imine and acid chloride, entry 3).

We have previously reported that the rate of iminium salt **1** carbonylation can be accelerated by the addition of monodentate phosphine ligands.[24] As shown in entries 5 and 6, the addition of smaller phosphines completely inhibits catalysis, presumably due to their strong coordination to palladium, which blocks carbonylation (step C). Interestingly, bulkier triarylphosphines, while allowing catalysis to proceed, had little influence on the rate of imidazoline formation, with the conversion at short reaction times similar to the results without ligand (entries 7−9). This includes P(*o*-tolyl)$_3$ (entry 7), which has been previously demonstrated to accelerate catalysis in related carbonylation reactions to form pyrroles and imidazoles.[25]

The lack of acceleration with the bulky triarylphosphine ligands may result from the relatively poor coordinating ability under the catalytic conditions, where there is both an excess of carbon monoxide and imine present. Therefore, several more strongly coordinating dialkyl- or trialkylphosphines were examined. As we had hoped, these ligands were found to significantly accelerate catalysis. From a survey of different ligands, the di-*tert*-butyl-2-biphenylphosphine **7** (entry 16) conveys the greatest rate enhancement, allowing imidazolinium formation to proceed to completion within a matter of hours at 45 °C. Notably, the commercial $Pd_2(dba)_3 \cdot CHCl_3$ can also be employed with this ligand (entry 17), as can $[Pd(allyl)Cl]_2$ (entry 18). With ligand **7**, the catalyst loadings can be decreased without a loss in yield (0.5 mol % **6**, entry 20).[26]

This optimized catalyst system provides an efficient method for generating a number of imidazolinium carboxylates (Table 2).[27] For example, aryl, heteroaryl, and even alkyl substituents can be incorporated into the 2-imidazoline position from the acid chloride (entries 3, 4, and 5, respectively). A range of imines derived from aromatic aldehydes are also viable substrates in the reaction. Examples include those with halo, thioether, ether, and even furanyl substituents (entries 3−6, respectively). However, enolizable imines (e.g., R^1 = *i*-Pr) and those with bulky nitrogen substituents (R^2 = *i*-Pr) are not compatible with the reaction, presumably because of the instability of these iminium salts.[28]

Selective Synthesis of Diversely Substituted Imidazolium Carboxylates. One limitation with this approach is the fact that the products all result from the coupling of two identical imines and thus generate only symmetrically substituted diaryl-substituted compounds. In general, attempts to employ two different imines in this reaction lead to mixtures of products. The latter is an issue often encountered in multicomponent synthesis, where two similar substrates can be difficult to differentiate.[29] However, as one can see from the mechanism of this catalytic coupling (Scheme 2), the imines are incorporated into the imidazolinium structure via fundamentally different operations, with the first undergoing carbonylation to form a Münchnone

(24) Dhawan, R.; Arndtsen, B. A. *J. Am. Chem. Soc.* **2004**, *126*, 468.
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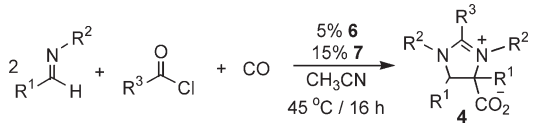
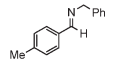
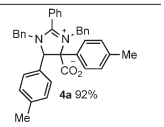
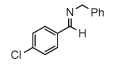
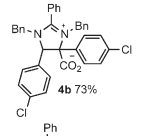
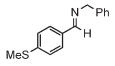
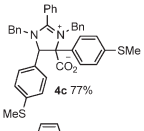
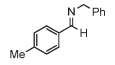
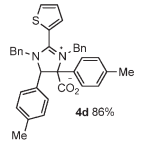
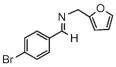
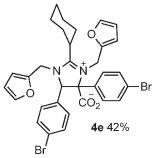
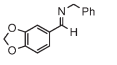
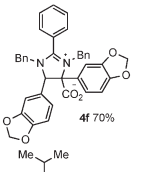
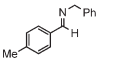
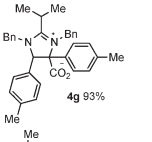
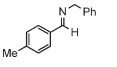
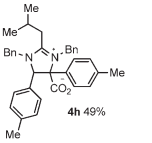
(26) In addition to enhancing the reaction rate, catalysis with bulky phosphines proceeds rapidly with the 2:1 imine:acid chloride ratio, rather than the excess acid chloride employed with bipyridine ligands. While the reason for this effect is as yet unclear, we postulate that the second imine acts as a base to accelerate HCl elimination.
(27) All products were formed as a single diastereomer and consistent with the trans orientation of the aryl groups previously noted.[20]
(28) For example, enolizable imines rapidly generate enamides from iminiium salts **1**. BnN=C(H)*t*-Bu has been previously employed to generate Münchnones,[22] but they are presumably too bulky to allow subsequent dipolar cycloaddition.
(29) For example: (a) Yamamoto, Y.; Saito, S. *Chem. Rev.* **2000**, *100*, 2901. (b) Gandon, V.; Aubert, C.; Malacria, M. *Chem. Commun.* **2006**, 2209.

TABLE 2. Substrate Diversity in Imidazoline Carboxylate Synthesis[a]



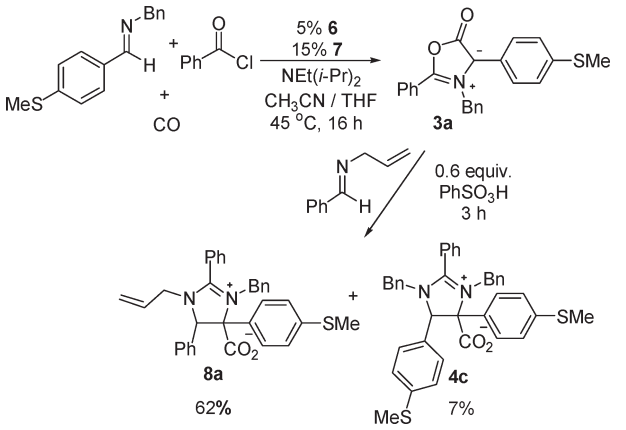
entry	imine	acid chloride	product
1			 **4a** 92%
2			 **4b** 73%
3			 **4c** 77%
4			 **4d** 86%
5			 **4e** 42%
6			 **4f** 70%
7			 **4g** 93%
8			 **4h** 49%

[a]General: imine (0.49 mmol), acid chloride (0.27 mmol), **5** (26 mg, 0.025 mmol), **7** (22 mg, 0.075 mmol), 15 mL of CH_3CN, 4.0 atm of CO, 45 °C, 16 h.

and the second involved in dipolar cycloaddition. Thus, construction of more complex imidazolines via the arrest of catalysis at Münchnone formation should be possible (steps A−E of Scheme 2), which could then be followed by the cycloaddition of a different imine in a subsequent step.

As we have previously reported, the addition of $NEt(i\text{-}Pr)_2$ base to the palladium-catalyzed reaction mixture can block the formation of imidazolinium carboxylates and instead allow the in situ formation of Münchnone **3a** (Scheme 3).[22] The addition

SCHEME 3. A Palladium-Catalyzed Route to Diversely Substituted Imidazolinium Salts



of imines to Münchnones is known to lead to the formation of β-lactams, via reaction with the ketene tautomer of **3**, rather than the Münchnones undergoing dipolar cycloaddition to form imidazolinium carboxylates.[30,31] This can be circumvented by the addition of benzenesulfonic acid, which catalyzes the dipolar cycloaddition of an N-allyl-substituted imine with Münchnone **3a** and forms **8a** within hours at ambient temperature (Scheme 3). A small amount of the inseparable homocoupled imidazoline product **4c** is generated under these conditions. The latter can be inhibited by the use of a slight excess of acid chloride in the initial Münchnone synthesis and allows the clean generation of **8a** in one pot and good yield (Table 3, entry 1).

The reaction in Table 3 provides what is to the best of our knowledge a unique method for constructing a diversely substituted imidazoline core from four separate and tunable substrates. The systematic variation of these building blocks can be used to form diverse families of products. Perhaps most notable is the diversity that can be incorporated into the second imine cycloaddition step. This includes not only relatively stabilized C-aryl-substituted imines but also a range of less stable imines. For example, C-heteroaryl imines, which cannot be incorporated into homocoupled imidazolines, can be used to form pyridinyl-substituted (entry 11) and furanyl-substituted (entry 12) products. N-Aryl-substituted imines can be used in the cycloaddition step (entry 3), as can N-allyl-protected imines (entry 1). Alternatively, polycyclic imidazolinium salts can be readily prepared via the cycloaddition of cyclic imines (entries 9 and 10), as can even less stable formaldimines (entries 13−16). The latter products lack substitution at the 4-position of the imidazoline ring. Overall, this provides a straightforward method for assembling small libraries of imidazolium salts in one pot, where any of the core substituents can be selectively modified from the appropriate imine(s) or acid chloride.

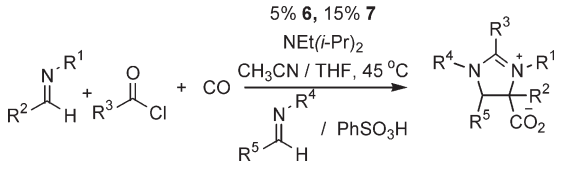
Imidazoline Synthesis. In addition to imidazolium salts, we have examined the application of this approach to the construction of imidazolines. A feature of the reaction in Table 3 is the ability to selectively incorporate removable substituents at either nitrogen of **8** from the appropriate imine(s). As shown in Scheme 4, coupling the catalytic synthesis with deprotection can allow the synthesis of variously substituted imidazoline esters.[32]

(30) (a) Dhawan, R.; Dghaym, R. D.; St. Cyr, D. J.; Arndtsen, B. A. *Org. Lett.* **2006**, *8*, 3927. (b) Croce, P. D.; Ferraccioli, R.; La Rosa, C. *Tetrahedron* **1995**, *51*, 9385. (c) Huisgen, R.; Funke, E.; Schaefer, F. C.; Knorr, R. *Agnew. Chem., Int. Ed.* **1967**, *6*, 367.

(31) Dhawan, R.; Dghaym, R. D.; Arndtsen, B. A. In *Catalysis of Organic Reactions*; Morrell, D., Ed.; Dekker: New York, 2003.

(32) It is necessary to introduce a methyl ester protecting group before nitrogen deprotection; otherwise, decarboxylation of the parent compound is observed.

TABLE 3. A Palladium-Catalyzed Route to Diversely Substituted Imidazoline Carboxylates[a]



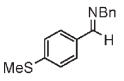
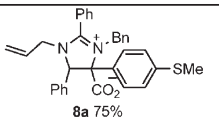
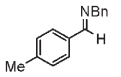
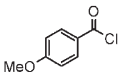
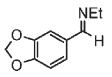
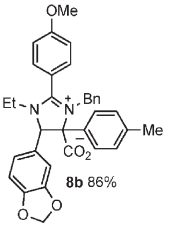
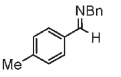
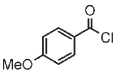
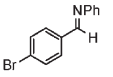
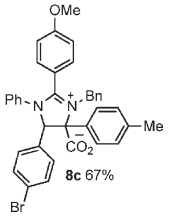
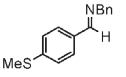
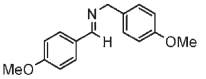
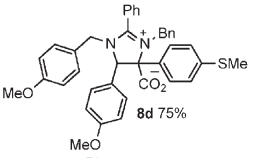
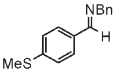
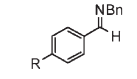
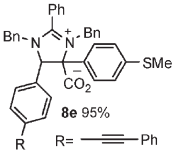
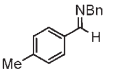
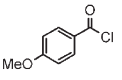
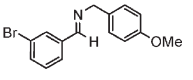
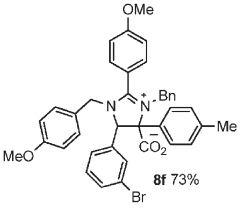
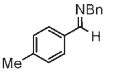
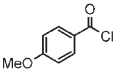
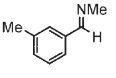
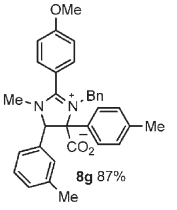
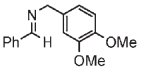
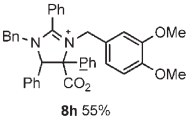
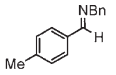
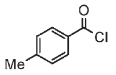
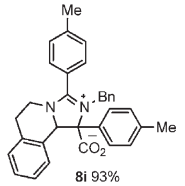
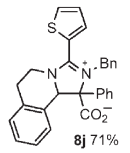
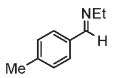
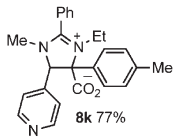
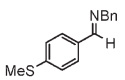
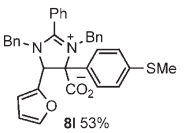
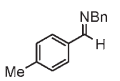
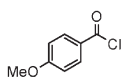
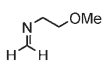
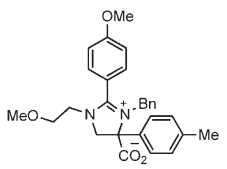
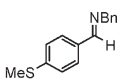
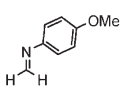
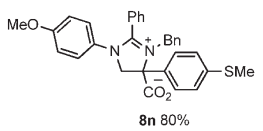
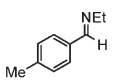
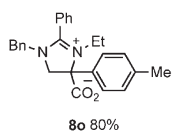
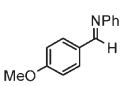
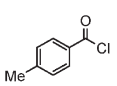
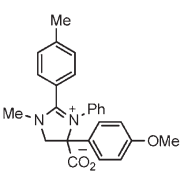
entry	imine	acid chloride	imine	product
1				 **8a** 75%
2				 **8b** 86%
3				 **8c** 67%
4				 **8d** 75%
5				 **8e** 95% R= Ph
6				 **8f** 73%
7				 **8g** 87%
8				 **8h** 55%

TABLE 3. Continued

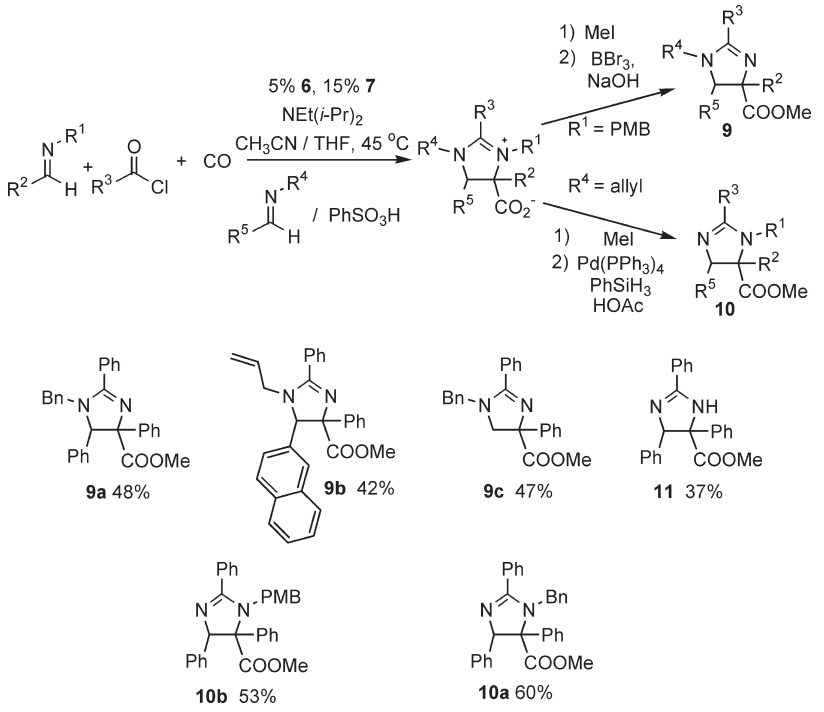
entry	imine	acid chloride	imine	product
9				 **8i** 93%
10				 **8j** 71%
11				 **8k** 77%
12				 **8l** 53%
13				 **8m** 93%
14				 **8n** 80%
15				 **8o** 80%
16				 **8p** 53%

[a]General: imine (0.22 mmol), acid chloride (0.31 mmol), 5% **6** (0.01 mmol), 15% **7** (10 mg, 0.03 mmol), 6 mL of a 1:1 THF/CH_3CN mixture, $NEt(i\text{-}Pr)_2$ (55 μL, 0.31 mmol), 4.0 atm of CO, 45 °C, 16 h, followed by addition of imine (0.44 mmol) and $PhSO_3H$ (28 mg, 0.18 mmol) in 2 mL of CH_3CN at room temperature for 3 h.

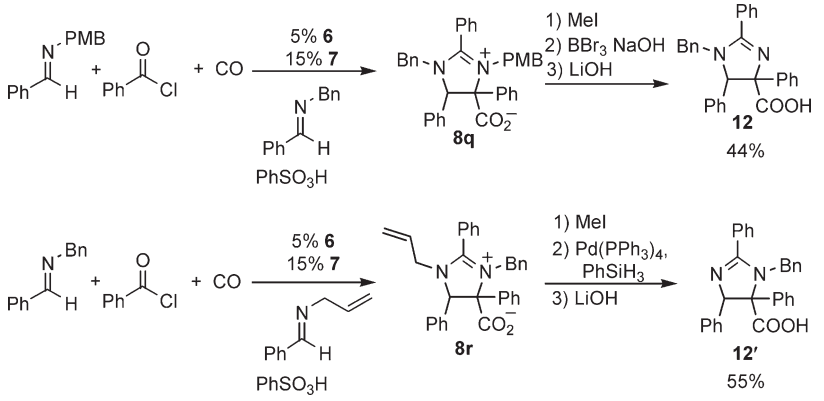
For example, BBr_3 treatment of the R^1 = *p*-methoxybenzyl-subtituted **8** allows the formation of imidazoline **9a** in 48% overall yield from imines and acid chloride. Alternatively, the use of N-allyl imines for cycloaddition followed by palladium-catalyzed deprotection can be used to form the 5-ester-substituted isomer **10a**. By changing the position of the protecting group, this strategy can access various isomers of imidazolines, or even the stepwise formation of N,N′-unsubstituted products (**11**). Relative to traditional approaches to polysubstituted imidazolines, this represents an effective and modular synthesis of these products from simple imines, acid chloride, and CO.

As an illustration of the potential utility of this reaction, we have examined its application to the synthesis of imidazoline **12** (Scheme 5). The latter has been identified by Tepe and

SCHEME 4. Synthesis of Polysubstituted Imidazolines



SCHEME 5. Synthesis of Imidazoline 12 and Its 5-Carboxylic Acid Isomer



Sharma as a potent sensitizer for cancer treatment.[33] As shown, the palladium-catalyzed formation of **8q** followed by deprotection can provide an efficient overall synthesis of **12** in good yield. In addition to forming **12**, a potentially useful feature of this chemistry is its ability to access variants of these products. For example, via variation of the position of the protecting group on the imines employed, a new 5-carboxylic acid isomer of **12**, **12′**, can be generated using the same acid chloride, and a simple N-allyl imine for cycloaddition. In principle, this modularity can be applied to access a range of new variants to these heterocycles.

Conclusions

In conclusion, we have described a straightforward, palladium-catalyzed approach to the assembly of substituted imidazolinium carboxylates directly from acid chlorides, imines, and carbon monoxide. When coupled with N-deprotection, this provides one-pot access to imidazolines where each substituent can be independently varied from the appropriate imine(s) or acid chlorides. Considering the availability of the building blocks, this provides an efficient and tunable alternative to classic synthesis of these heterocycles. Experiments directed toward the application of this method to alternative imidazoline targets are currently underway.

Experimental Section

General Considerations. All manipulations were conducted in a glovebox under a nitrogen atmosphere. Unless otherwise noted, all reagents were purchased from commercial sources and used without purification. Carbon monoxide (99.99%) was used as received. Solvents were dried by being passed through alumina except acetonitrile, which was distilled from CaH_2 and degassed. Once collected, solvents were stored under nitrogen over activated molecular sieves inside the glovebox. $Pd_2(dba)_3 \cdot CHCl_3$ was prepared using literature techniques.[34] Aldimines were prepared from the condensation of aldehyde and amine

(33) Sharma, V.; Peddibhotla, S.; Tepe, J. J. *J. Am. Chem. Soc.* **2006**, *128*, 9137.

using concentrated aqueous NaCl as a drying agent and then distilled under vacuum. Formaldimines were prepared following literature procedures[35] or purchased as the trisubstituted triazine. Amide-chelated palladacycle catalysts **6** were prepared by pretreating $Pd_2(dba)_3 \cdot CHCl_3$ with imine and acid chloride as previously reported.[22] Benzenesulfonic acid was purchased as the dry acid (not as the monohydrate) and dried under vacuum for 48 h. Iminium salt (imine·$PhSO_3H$) hydrolysis was tested by ^{1}H NMR to ensure dryness. Deuterated acetonitrile was stirred with CaH_2, vacuum transferred, degassed, and stored over 4 Å molecular sieves.

Nuclear magnetic resonance (NMR) characterization was realized at 200, 300, 400, and 500 MHz for ^{1}H NMR and at 75, 100, and 125 MHz for ^{13}C NMR. ^{1}H and ^{13}C NMR chemical shifts were referenced to residual solvent. ^{13}C NMR spectra had no signals in the regions not recorded (0−20 ppm). Mass spectra were recorded on a high-resolution electrospray ionization quadrupole mass spectrometer. Compounds **4a**−**c** and **12** were characterized by comparison to previous reports.[20,33]

Ligand Screening. Reactions were set up in J. Young NMR tubes fitted with PTFE valves. (4-$CH_3C_6H_4$)HC=$NCH_2C_6H_5$ (52.3 mg, 0.25 mmol), benzoyl chloride (17.0 mg, 0.12 mmol), palladium catalyst (0.007 mmol), ligand (0.018 mmol), and benzyl benzoate NMR standard (0.25 mmol) were combined in 800 μL of CD_3CN, stirred until the mixture was homogeneous, and transferred to the NMR tube. One freeze−pump−thaw cycle was conducted before the tube's contents were pressurized with 4.0 atm of CO. The conversion to product was determined by ^{1}H NMR analysis by comparison to the benzyl benzoate standard.

Typical Synthesis of Homocoupled Imidazolinium Carboxylates (4a). In a 50 mL sealed glass reaction bomb equipped with a magnetic stir bar, (4-$CH_3C_6H_4$)HC=$NCH_2C_6H_5$ (102 mg, 0.49 mmol), benzoyl chloride (38 mg, 0.27 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ **5** (26 mg, 0.025 mmol), and di-*tert*-butyl-2-biphenylphosphine **7** (22 mg, 0.75 mmol) were combined in 15 mL of acetonitrile and stirred for 15 min until the mixture was homogeneous. One freeze−pump−thaw cycle was conducted before the bomb's contents were pressurized with 4.0 atm of CO. The reaction mixtures were left for 16 h at 45 °C; the solvent was removed in vacuo and the residue dissolved in CH_2Cl_2 and filtered through Celite.[36] The organic phase was washed sequentially with brine, 0.1 M HCl, and concentrated Na_2CO_3. The organic phase was dried over Mg_2SO_4, filtered, concentrated to ca. 0.5 mL, and then diethyl ether was added. Precipitation at −35 °C afforded **4a** as a solid (0.23 mmol, 92%).[37]

(i) 1,3-Dibenzyl-2-thiophen-2-yl-4,5-di-*p*-tolyl-2-imidazolinium-4-carboxylate (4d). Yield of 86%. ^{1}H NMR (300 MHz, CD_3OD): δ 7.89 (d, J = 4.7 Hz, 1H), 7.53−6.92 (m, 18H), 6.63 (d, J = 7.4 Hz, 2H), 5.55 (s, 1H), 5.06 (d, J = 15.9 Hz, 1H), 4.71 (d, J = 16.0 Hz, 1H), 4.58 (d, J = 14.7 Hz, 1H), 4.02 (d, J = 14.8 Hz, 1H), 2.45 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (75.46 MHz, CD_3OD): δ 168.8, 160.5, 139.60, 139.5, 136.5, 135.3, 133.7, 133.1, 132.3, 130.6, 129.4, 129.3, 129.1, 128.8, 128.6, 128.3, 127.9, 127.7, 127.4, 127.0, 120.3, 83.0, 71.9, 50.6, 49.5, 20.0, 19.7. HRMS ($C_{36}H_{32}N_2O_2S$): calcd (M + 1) 557.2257, observed 557.2256. IR: ν_{CO} 1637, 1533 cm^{-1}.

(ii) 4,5-Bis(4-bromophenyl)-2-cyclohexyl-1,3-bis-furan-2-yl-methyl-2-imidazolinium-4-carboxylate (4e). The product was precipitated from ethyl acetate with diethyl ether at room temperature. Yield of 42%. ^{1}H NMR (400 MHz, CD_3OD): δ 7.73 (m, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.28 (s, 1H), 7.18 (t, J = 5.8 Hz, 4H), 6.50 (m, 1H), 6.37 (m, 1H), 6.19 (m, 1H), 5.63 (m, 1H), 5.38 (d, J = 16.1 Hz, 1H), 5.18 (d, J = 16.1 Hz, 1H), 4.83 (d, J = 15.9 Hz, 1H), 4.13 (d, J = 15.9 Hz, 1H), 3.42−3.35 (m, 1H), 2.22−2.19 (m, 1H), 2.07−1.88 (m, 4H), 1.80−1.75 (m, 2H), 1.55−1.34 (m, 3H). ^{13}C NMR (125.71 MHz, CD_3OD): δ 169.7, 167.9, 148.5, 145.6, 144.2, 142.2, 139.2, 133.6, 131.6, 131.5$_5$, 129.7, 123.4, 123.0, 112.0, 111.0, 110.8, 110.5, 109.0, 81.3, 72.8, 42.6, 42.4, 37.4, 27.3, 27.0, 25.5 (two carbons), 24.6. HRMS ($C_{32}H_{30}Br_2N_2O_4$): calcd (M + 1) 665.0651, observed 665.0652. IR: ν_{CO} 1630, 1568 cm^{-1}.

(iii) 4,5-Bisbenzo[1,3]dioxol-5-yl-1,3-dibenzyl-2-*p*-tolyl-2-imidazolinium-4-carboxylate (4f). Yield of 70%. ^{1}H NMR (400 MHz, CD_3OD): δ 7.41 (s, 2H), 7.35−6.61 (m, 18H), 6.05 (s, 2H), 5.95 (d, J=14.1 Hz, 2H), 5.45 (s, 1H), 4.89 (d, J=14.9 Hz, 1H), 4.45 (m, 2H), 4.05 (d, J = 14.9 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100.62 MHz, DMSO): δ 165.7, 164.6, 148.2, 147.4, 147.3, 142.7, 136.3, 134.4, 133.5, 130.4, 130.3, 130.2, 128.8, 128.6, 129.4, 128.4, 128.0, 123.7, 123.7, 122.4, 120.6, 109.7, 109.3, 108.0, 101.6, 101.5, 73.7, 83.0, 50.3, 49.2, 21.5. HRMS ($C_{39}H_{32}N_2O_6$): calcd (M + 1) 625.23389, observed 625.2334. IR: ν_{CO} 1639, 1556 cm^{-1}.

(iv) 1,3-Dibenzyl-2-isopropyl-4,5-di-*p*-tolyl-2-imidazolinium-4-carboxylate (4g). Yield of 93%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50−7.00 (m, 16H), 6.69−6.92 (m, 2H), 5.20 (d, J = 17.6 Hz, 1H), 5.17 (s, 1H), 4.95 (d, J = 14.7 Hz, 1H), 4.90 (d, J = 17.2 Hz, 1H), 4.05 (d, J = 14.7 Hz, 1H), 3.25 (m, 1H), 2.35 (s, 3H), 2.29 (s, 3H), 1.50−1.39 (d, J = 7.3 Hz, 3H), 1.15−1.03 (d, J = 7.2 Hz, 3H). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 169.3, 166.6, 139.4, 138.8, 137.5, 136.9, 132.0, 131.3, 129.8, 129.7, 129.5, 129.1, 128.9, 128.5, 128.0, 127.4, 83.6, 72.7, 51.5, 49.3, 27.2, 21.7, 21.3, 18.3, 18.2. HRMS ($C_{35}H_{36}N_2O_2$): calcd (M + 1) 517.2855, observed 517.2850. IR: ν_{CO} 1635, 1557 cm^{-1}.

(v) 1,3-Dibenzyl-2-isobutyl-4,5-di-*p*-tolyl-2-imidazolinium-4-carboxylate (4h). Yield of 49%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45−6.56 (m, 16H), 5.25 (s, 1H), 5.09 (d, J = 17.0 Hz, 1H), 4.80 (d, J = 15.4 Hz, 1H), 4.65 (d, J = 16.7 Hz, 1H), 4.00 (d, J = 15.2 Hz, 1H), 2.50 (m, 1H), 2.38−2.30 (m, 2H), 2.29 (s, 3H), 2.23 (s, 3H), 1.05 (m, 6H). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 166.1, 165.5, 138.9, 138.4, 135.4, 132.4, 131.1, 129.5, 129.4, 129.3, 129.2, 129.1, 128.8, 128.2, 127.8, 127.0, 126.7, 83.4, 77.4, 72.9, 50.7, 48.9, 33.6, 27.5, 23.1, 22.6, 21.4, 20.9. HRMS ($C_{36}H_{38}N_2O_2$): calcd (M + 1) 531.3006, observed 531.3009. IR: ν_{CO} 1637, 1566 cm^{-1}.

Typical Procedure for the Synthesis of Heterocoupled Imidazoline Carboxylates (8a). In a 50 mL reaction bomb under nitrogen, (4-$CH_3SC_6H_4$)HC=N(CH_2Ph) (53 mg, 0.22 mmol) and benzoyl chloride (44 mg, 0.31 mmol) were dissolved in 3 mL of acetonitrile and stirred for ca. 10 min. [Pd(Cl)[η^2-CH(4-$CH_3SC_6H_4$)N(CH_2Ph)-COPh]] (9.8 mg, 0.01 mmol) and P(t-Bu)$_2$(2-biphenyl) **2.7** (10 mg, 0.03 mmol) were then added as a solution in 3 mL of THF and stirred for 5 min. Diisopropylethylamine (50 μL, 0.31 mmol) was added via microsyringe, and the vessel was removed from the glovebox. One freeze−pump−thaw cycle was performed before the vessel was pressurized with 4.0 atm of CO. The reaction mixture was allowed to stir at 45 °C for 16 h. CO was removed under vacuum, and the reaction bomb was brought back into the drybox. PhHC=N($CH_2CH=CH_2$) (64 mg 0.44 mmol) and $PhSO_3H$ (28 mg, 0.18 mmol) were added as a solution in 2 mL of acetonitrile. The reaction mixture was stirred at room temperature until the Münchnone was completely consumed as observed by ^{1}H NMR (3 h). The product was purified as described above to give imidazoline carboxylate **8a** (0.17 mmol, 75%). ^{1}H NMR (400 MHz, CD_3OD): δ 7.65−7.60 (m, 2H), 7.47−7.41 (m, 6H), 7.32 (d, J=8.0 Hz, 2H), 7.00 (t, J = 7.3 Hz, 2H), 6.95−6.88 (m, 3H), 6.49−6.33 (m, 2H), 5.91 (s, 1H), 5.91−5.76 (m, 1H), 5.28 (d, J = 10.1 Hz, 1H), 4.97

(34) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.

(35) Giumanini, A. G.; Toniutti, N.; Verardo, G.; Merli, M. *Eur. J. Org. Chem.* **1999**, 141.

(36) Celite filtration was performed when palladium black formed in the crude solution. If the brine wash is neglected, unidentified phosphine species contaminate the products and are very difficult to remove.

(37) To ensure the stability of these products during isolation, care must be taken to avoid prolonged contact with $CHCl_3$ or wet organic solvents. Decarboxylation to 4,5-dihydroimidazolinium salts is commonly observed when these precautions are not taken. Similarly, precipitation at −35 °C and collection of the precipitate should be conducted with care under a dry atmosphere as condensation of water vapor from the air can elicit the same decomposition.

(d, J = 17.0 Hz, 1H), 4.91 (d, J = 15.8 Hz, 1H), 4.46 (d, J = 15.8 Hz, 1H), 3.88 (dd, J = 15.5, 5.0 Hz, 1H), 3.48 (dd, J = 15.3, 8.1 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100.62 MHz, CD_3OD): δ 168.7, 165.7, 141.2, 135.3, 135.1, 133.8, 132.1, 129.5, 129.3, 129.3, 129.1, 128.9, 128.5, 127.8, 127.7, 127.6, 127.2, 127.0, 126.1, 123.1, 121.3, 83.4, 72.8, 50.2, 13.8. HRMS ($C_{33}H_{30}N_2O_2S$): calcd (M + 1) 519.2106, observed 519.2094. IR: ν_{CO} 1638, 1549 cm^{-1}.

(i) 5-Benzo[1,3]dioxol-5-yl-3-benzyl-1-ethyl-2-(4-methoxyphenyl)-4-*p*-tolyl-2-imidazolinium-4-carboxylate (8b). Yield of 86%. ^{1}H NMR (400 MHz, CD_3OD): δ 7.65 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.1 Hz, 1H), 7.03−6.82 (m, 12H), 6.42 (d, J = 7.4 Hz, 2H), 4.85 (d, J = 15.8 Hz, 1H), 4.40 (d, J = 15.8 Hz, 1H), 3.35−3.24 (m, 1H), 3.10−2.97 (m, 1H), 2.38 (s, 3H), 1.18−1.10 (m, 3H). ^{13}C NMR (100.62 MHz, CD_3OD): δ 169.5, 165.8, 162.8, 149.1, 148.3, 139.7, 136.8, 135.7, 129.7, 129.4, 129.0, 128.4, 128.0, 127.9, 127.8, 127.1, 123.2, 115.1, 115.0, 107.1, 101.7, 83.2, 72.3, 55.0, 50.3, 40.8, 20.0, 11.8. HRMS ($C_{34}H_{32}N_2O_5$): calcd (M + 1) 549.2390, observed 549.2369. IR: ν_{CO} 1641, 1552 cm^{-1}.

(ii) 3-Benzyl-5-(4-bromophenyl)-2-(4-methoxyphenyl)-1-phenyl-4-*p*-tolyl-2-imidazolinium-4-carboxylate (8c). Yield of 67%. ^{1}H NMR (400 MHz, CD_3OD): δ 7.89−7.80 (d, J = 8.5 Hz, 2H), 7.46−6.79 (m, 10H), 6.67 (s, 1H), 6.45−6.32 (d, J = 7.4 Hz, 2H), 5.05 (d, J = 15.8 Hz, 1H), 4.55 (d, J = 15.8 Hz, 1H), 3.70 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100.62 MHz, CD_3OD): δ 168.9, 165.3, 162.8, 139.9, 135.6, 134.9, 134.3, 133.3, 131.2, 130.9, 130.6, 129.8, 129.6, 129.2, 128.5, 127.8, 127.7, 127.1, 127.0, 123.0, 115.2, 114.6, 84.4, 75.5, 54.9, 50.3, 20.0. HRMS ($C_{37}H_{31}BrN_2O_3$): calcd (M + 1) 631.1596, observed 631.1586. IR: ν_{CO} 1635, 1567 cm^{-1}.

(iii) 3-Benzyl-1-(4-methoxybenzyl)-5-(4-methoxyphenyl)-4-(4-methylsulfanylphenyl)-2-phenyl-2-imidazolinium-4-carboxylate (8d). Yield of 75%. ^{1}H NMR (300 MHz, CD_3OD): δ 7.63−7.16 (m, 11H), 7.05−6.83 (m, 9H), 6.67−6.58 (d, J = 7.4 Hz, 2H), 5.47 (s, 1H), 4.95 (m, 1H), 4.44−4.33 (m, 2H), 3.95−3.72 (m, 7H), 2.45 (s, 3H). ^{13}C NMR (75.46 MHz, CD_3OD): δ 169.2, 165.2, 161.1, 160.7, 141.2, 136.3, 135.6, 132.3, 130.5, 129.9, 129.5, 128.4, 128.2, 128.1, 128.0, 127.4, 127.2, 126.3, 125.5, 124.1, 123.4, 114.5, 114.2, 83.0, 72.0, 54.7, 54.7, 54.7, 50.5, 48.8, 48.7. HRMS ($C_{39}H_{36}N_2O_4S$): calcd (M + 1) 629.2474, observed 629.2473. IR: ν_{CO} 1638, 1547 cm^{-1}.

(iv) 1,3-Dibenzyl-4-(4-methylsulfanylphenyl)-2-phenyl-5-(4-phenylethynylphenyl)-2-imidazolinium-4-carboxylate (8e). Yield of 95%. ^{1}H NMR (400 MHz, CD_3OD): δ 7.63−7.35 (m, 17H), 7.28−7.21 (m, 2H), 7.09−7.02 (m, 2H), 6.99−6.93 (m, 2H), 6.60 (m, 2H), 5.58 (s, H), 4.9 (d, J = 15.6 Hz, 1H), 4.50 (d, J = 14.8 Hz, 1H), 4.45 (d, J = 15.5 Hz, 1H), 4.02 (d, J = 14.9 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (100.62 MHz, CD_3OD): δ 168.6, 165.8, 141.4, 135.8, 135.4, 134.0, 132.4, 132.3, 131.8, 131.4, 129.9, 129.6, 129.3, 129.1, 128.5, 128.4$_7$, 128.4, 128.2, 128.1, 127.5, 127.3, 126.3, 124.9, 123.2, 123.1, 90.3, 88.4, 83.5, 72.3, 53.6, 50.6, 49.7, 14.0. HRMS ($C_{45}H_{36}N_2O_2S$): calcd (M + 1) 669.2576, observed 669.2568. IR: ν_{CO} 1637, 1567 cm^{-1}.

(v) 3-Benzyl-5-(3-bromophenyl)-1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-4-*p*-tolyl-2-imidazolinium-4-carboxylate (8f). Yield of 73%. ^{1}H NMR (200 MHz, CD_3OD): δ 7.62−7.53 (m, 2H), 7.50−6.83 (m, 21H), 6.65 (d, J = 7.4 Hz, 2H), 5.55 (s, 1H), 5.01 (d, J = 15.4 Hz, 1H), 4.49 (d, J = 14.8 Hz, 1H), 4.36 (d, J = 14.8 Hz, 1H), 3.91 (d, J = 14.9 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (75.46 MHz, CD_3OD): δ 168.9, 165.7, 163.0, 160.7, 139.7, 139.1, 136.9, 136.8, 135.8, 132.6, 130.5, 129.9, 129.7, 129.2, 128.1, 128.0, 127.7, 127.2, 124.1, 122.5, 115.3, 115.1, 114.6, 114.5, 83.5, 71.2, 55.0, 54.7, 50.3, 49.1, 19.9. HRMS ($C_{39}H_{35}BrN_2O_4$): calcd (M + 1) 675.1853, observed 675.1846. IR: ν_{CO} 1640, 1561 cm^{-1}.

(vi) 3-Benzyl-2-(4-methoxyphenyl)-1-methyl-5-*m*-tolyl-4-*p*-tolyl-2-imidazolinium-4-carboxylate (8g). Yield of 87%. ^{1}H NMR (200 MHz, CD_3OD): δ 7.68 (d, J = 8.2 Hz, 2H), 7.33−7.17 (m, 8H), 7.00−6.83 (m, 3H), 6.43 (d, J = 7.5 Hz, 2H), 5.90 (s, 1H), 4.86 (d, J = 16.8 Hz, 1H), 4.40 (d, J = 15.6 Hz, 1H), 3.80 (s, 3H), 2.79 (s, 3H), 2.35 (s, 6H). ^{13}C NMR (75.46 MHz, CD_3OD): δ 169.5, 166.2, 162.8, 139.5, 139.1, 138.4, 136.1, 135.8, 134.3, 130.0, 129.6, 129.5, 128.9, 128.6, 127.8, 127.0, 125.6, 115.1, 114.9, 83.7, 74.9, 55.0, 50.2, 32.4, 20.3, 20.0. HRMS ($C_{33}H_{32}N_2O_3$): calcd (M + 1) 505.2491, observed 505.2486. IR: ν_{CO} 1639, 1548 cm^{-1}.

(vii) 1-Benzyl-3-(3,4-dimethoxybenzyl)-2,4,5-2-imidazolinium-4-carboxylate (8h). Yield of 44%. ^{1}H NMR (400 MHz, CD_3OD): δ 7.61−7.38 (m, 19H), 7.14 (d, J = 7.6 Hz, 1H), 7.03 (m, 2H), 6.45 (d, J = 8.3 Hz, 1H), 6.39 (s, 1H), 5.99 (d, J = 8.0 Hz, 1H), 5.58 (s, 1H), 4.95 (d, J = 15.2 Hz, 1H), 4.42 (d, J = 14.8 Hz, 1H), 4.30 (d, J = 15.1 Hz, 1H), 3.92 (d, J = 14.8 Hz, 1H), 3.71 (s, 3H), 3.61 (s, 3H). ^{13}C NMR (100.62 MHz, CD_3OD): δ 168.7, 165.1, 148.7, 148.4, 140.1, 132.2, 132.0, 129.6, 129.5, 129.3, 129.2, 129.1, 129.0, 128.98, 128.95, 128.6, 127.9, 127.7, 127.5, 127.1, 123.3, 121.1, 111.5, 110.9, 83.2, 82.2, 54.99, 54.98, 50.0, 49.1. HRMS ($C_{38}H_{34}N_2O_4$): calcd (M + 1) 583.2597, observed 583.2597. IR: ν_{CO} 1642, 1551 cm^{-1}.

(viii) 2-Benzyl-1,3-di-*p*-tolyl-1,5,6,10b-tetrahydroimidazolinium-[5,1-*a*]isoquinoline-1-carboxylate (8i). Yield of 93%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11 (d, J = 7.3 Hz, 1H), 7.99 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 7.7 Hz, 1H), 7.15−6.83 (m, 10H), 6.40 (d, J = 7.3 Hz, 1H), 6.05 (s, 1H), 4.75 (d, J = 15.7 Hz, 1H), 4.20 (d, J = 15.7 Hz, 1H), 3.65 (m, 1H), 3.18−3.41 (m, 2H), 2.63 (d, J = 14.8 Hz, 1H), 2.41 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 166.0, 165.4, 143.4, 138.9, 135.8, 132.8, 132.2, 131.4, 129.9, 129.7, 129.4, 129.2, 129.0, 128.1, 128.0, 127.9, 127.8$_9$, 127.3, 126.9, 120.9, 86.8, 68.2, 49.6, 43.2, 29.9, 21.9, 21.3. HRMS ($C_{33}H_{30}N_2O_2$): calcd (M + 1) 487.2386, observed 487.2382. IR: ν_{CO} 1616, 1545 cm^{-1}.

(ix) 2-Benzyl-1-phenyl-3-thiophen-2-yl-1,5,6,10b-tetrahydroimidazolinium[5,1-*a*]isoquinoline-1-carboxylate (8j). Yield of 71%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.09 (d, J = 6.6 Hz, 2H), 7.71 (m, 2H), 7.40−6.75 (m, 11H), 6.49 (d, J = 7.3 Hz, 2H), 6.09 (s, 1H), 4.91 (d, J = 15.9 Hz, 1H), 4.22 (d, J = 15.9 Hz, 1H), 3.85 (m, 1H), 3.50−3.12 (m, 2H), 2.63 (d, J = 15.0 Hz, 1H). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 165.0, 161.3, 135.1, 134.6, 134.0, 132.8, 132.7, 131.3, 129.3, 129.0, 128.8, 128.6, 128.2, 128.1, 127.8, 127.6, 127.5, 127.3, 126.7, 121.1, 86.6, 68.0, 49.7, 43.6, 29.7. HRMS ($C_{29}H_{24}N_2O_2S$): calcd (M + 1) 465.1631, observed 465.1645. IR: ν_{CO} 1639, 1555 cm^{-1}.

(x) 3-Ethyl-1-methyl-2-phenyl-5-pyridin-4-yl-4-*p*-tolyl-2-imidazolinium-4-carboxylate (8k). Yield of 77%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (m, 2H), 7.85−7.52 (m, 8H), 7.34−7.18 (m, 8H), 5.44 (s, 1H), 3.58 (m, 2H), 2.74 (s, 3H), 2.36 (s, 3H), 0.54 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125.71 MHz, $CDCl_3$): δ 166.0, 164.8, 150.1, 143.7, 139.2, 136.4, 133.0, 130.1, 129.6, 129.3, 128.1, 123.6, 123.3, 84.8, 76.3, 43.0, 33.6, 21.0, 14.8. HRMS ($C_{25}H_{25}N_3O_2$): calcd (M + 1) 400.2025, observed 400.2017.

(xi) 1,3-Dibenzyl-5-furan-2-yl-4-(4-methylsulfanylphenyl)-2-phenyl-2-imidazolinium-4-carboxylate (8l). Yield of 53%. ^{1}H NMR (500 MHz, CD_3OD): δ 7.68 (s, 1H), 7.57−7.51 (m, 1H), 7.48−7.33 (m, 10H), 7.25 (d, J = 8.2 Hz, 4H), 7.10−6.90 (m, 6H), 6.67 (m, 4H), 6.53 (s, 1H), 5.72 (s, 1H), 5.14 (d, J = 15.6 Hz, 1H), 4.45 (m, 1H), 4.35 (m, 1H), 3.97 (d, J = 14.9 Hz, 1H), 2.45 (3s, H). ^{13}C NMR (125.71 MHz, CD_3OD): δ 167.7, 164.4, 145.1, 143.1, 140.0, 134.3, 134.2, 131.4, 131.0, 128.4, 128.2, 127.8, 127.7, 127.5, 126.8, 126.7, 126.6, 125.9, 125.0, 121.9, 112.1, 109.6, 79.3, 65.2, 49.0, 48.2, 12.7. HRMS ($C_{35}H_{30}N_2O_3S$): calcd (M + 1) 559.2055, observed 559.2051. IR: ν_{CO} 1640, 1567 cm^{-1}.

(xii) 3-Benzyl-1-(2-methoxyethyl)-2-(4-methoxyphenyl)-4-*p*-tolyl-2-imidazolinium-4-carboxylate (8m). Yield of 93%. ^{1}H NMR (400 MHz, CD_3OD): δ 7.60−6.85 (m, 11H), 6.51−6.42 (d, J = 7.4 Hz, 2H), 4.83−4.72 (m, 2H), 4.60 (d, J = 12.4 Hz, 1H), 4.45 (d, J = 16.2 Hz, 1H), 3.85 (s, 3H), 3.55 (m, 2H), 3.39−3.27 (m, 5H), 2.31 (s, 3H). ^{13}C NMR (100.62 MHz, CD_3OD): δ 174.0, 165.6, 162.9, 139.5, 135.8, 133.5, 130.3, 130.5, 129.4, 129.0, 127.8, 127.5, 127.0, 114.7, 77.6, 68.1, 59.5, 58.1, 55.0, 49.4, 48.4, 19.9. HRMS ($C_{28}H_{30}N_2O_4$): calcd (M + 1) 459.2284, observed 459.2278. IR: ν_{CO} 1628, 1551 cm^{-1}.

(xiii) 3-Benzyl-1-(4-methoxyphenyl)-4-(4-methylsulfanylphenyl)-2-phenyl-2-imidazolinium-4-carboxylate (8n). Yield of 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.5 Hz, 2H), 7.41−7.21

(m, 6H), 7.11 (m, 2H), 6.99−6.81 (m, 6H), 6.63 (d, J = 8.9 Hz, 2H), 6.40 (d, J = 7.2 Hz, 2H), 5.22 (d, J = 11.8 Hz, 1H), 5.00 (d, J = 16.2 Hz, 1H), 4.81−4.70 (m, 2H), 3.63 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (125.71 MHz, $CDCl_3$): δ 170.9, 163.2, 159.6, 140.5, 135.5, 132.3, 130.3, 129.5, 129.1, 128.9, 128.3, 128.1, 127.5, 126.8, 126.6, 126.5, 123.7, 115.0, 78.8, 64.5, 55.6, 50.6, 15.7. HRMS ($C_{31}H_{28}N_2O_3S$): calcd (M + 1) 509.1899, observed 509.1898. IR: ν_{CO} 1633, 1555 cm^{-1}.

(xiv) 1-Benzyl-3-ethyl-2-phenyl-4-*p*-tolyl-2-imidazolinium-4-carboxylate (8o). Yield of 80%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71−7.09 (m, 14H), 4.89 (d, J = 11.8 Hz, 1H), 4.47−4.33 (m, 4H), 4.09 (d, J = 11.7 Hz, 1H), 3.76−3.67 (m, 1H), 3.57−3.49 (m, 1H), 2.28 (s, 3H), 0.48 (m, 3H). ^{13}C NMR (125.71 MHz, $CDCl_3$): δ 170.6, 163.4, 138.9, 135.2, 133.0, 132.9, 130.3, 130.0, 129.7, 129.6, 129.1, 128.9, 127.8, 123.4, 77.8, 61.2, 51.5, 42.1, 21.3, 15.4. HRMS ($C_{26}H_{26}N_2O_2$): calcd (M + 1) 399.2073, observed 399.2063. IR: ν_{CO} 1628, 1568 cm^{-1}.

(xv) 4-(4-Methoxyphenyl)-1-methyl-3-phenyl-2-*p*-tolyl-2-imidazolinium-4-carboxylate (8p). Yield of 53%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.49 (d, J = 8.6 Hz, 2H), 7.40 (d, J = 7.2 Hz, 2H), 7.27 (t, J = 6.8 Hz, 4H), 6.98−6.90 (m, 3H), 6.72 (d, J = 8.7 Hz, 2H), 4.69 (d, J = 11.5 Hz, 1H), 4.46 (d, J = 11.3 Hz, 1H), 3.63 (s, 3H), 3.13 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (125.71 MHz, D_2O): δ 176.1, 164.8, 159.5, 144.4, 135.7, 130.6, 129.9, 129.7, 129.5, 128.7, 128.6, 128.3, 119.5, 114.2, 78.8, 63.2, 55.5, 34.9, 20.9. HRMS ($C_{25}H_{24}N_2O_3$): calcd (M + 1) 401.1865, observed 401.1856.

Typical Protocol for Removal of the Paramethoxybenzyl (PMB) Group (9a). Imidazolinium-carboxylate **8q** (111 mg, 0.2 mmol) was charged into a 50 mL oven-dried Schlenk flask under a positive atmosphere of nitrogen. Five milliliters of dry CH_3CN was added by syringe. MeI (0.125 mL, 2.0 mmol) was then added by microsyringe. The resulting solution was allowed to stir at 45 °C for 2 h. The solvent and MeI were then removed in vacuo, and the resulting residue was dissolved with 5 mL of dry CH_2Cl_2 under an atmosphere of nitrogen. The solution was then cooled to 0 °C, and 1 M BBr_3 in CH_2Cl_2 (2 mL, 2 mmol) was added dropwise. The mixture was allowed to gradually warm to ambient temperature and stirred for 2 h, after which it was rapidly added to a stirring 1 M NaOH solution (20 mL). The product was extracted with additional CH_2Cl_2, and the combined organic layers were dried with Na_2SO_4, filtered, and condensed to give a yellow oil that was purified by silica gel chromatography (40% EtOAc in hexanes) to give a yellow solid (0.13 mmol, 66%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (m, 2H), 7.75 (d, J = 7.4 Hz, 2H), 7.49 (m, 3H), 7.41−7.28 (m, 8H), 7.09 (m, 3H), 6.75 (d, J = 7.2 Hz, 2H), 4.93 (s, 1H), 4.65 (d, J = 15.8 Hz, 1H), 3.85 (d, J = 15.8 Hz, 1H), 3.19 (s, 3H). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 171.4, 165.7, 144.0, 137.8, 136.6, 130.5, 130.4, 128.9, 128.7, 128.5, 128.4$_3$, 128.3$_6$, 128.1, 128.0, 127.5, 127.4, 127.2, 126.8, 83.1, 73.9, 51.9, 48.7. HRMS ($C_{30}H_{27}O_2N_2$): calcd (M + 1) 447.2067, observed 447.2061. IR: ν_{CO} 1732 cm^{-1}.

(i) Methyl 1-Allyl-5-(naphthalen-2-yl)-2,4-diphenyl-4,5-dihydro-1*H*-imidazole-4-carboxylate (9b). Yield of 42%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 7.9 Hz, 2H), 7.87 (m, 4H), 7.79 (m, 2H), 7.58 (m, 1H), 7.51 (m, 5H), 7.44 (t, J = 7.4 Hz, 2H), 7.34 (t, J = 7.3 Hz, 2H), 5.41 (m, 1H), 5.26 (s, 1H), 4.92 (d, J = 10.2 Hz, 1H), 4.79 (d, J = 17.1 Hz, 1H), 3.94 (dt, J = 16.1, 2.2 Hz, 1H), 3.36 (dd, J = 16.3, 7.0 Hz, 1H), 3.15 (s, 3H). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 171.4, 166.0, 144.3, 135.7, 133.3, 133.2, 133.0, 130.6, 130.4, 128.7, 128.5, 128.3, 128.2, 128.1, 127.7, 127.6, 127.5, 126.9, 126.3, 126.2, 125.4, 117.7, 83.0, 75.4, 52.0, 48.1. HRMS ($C_{30}H_{27}O_2N_2$): calcd (M + 1) 447.2067, observed 447.2057. IR: ν_{CO} 1734 cm^{-1}.

(ii) Methyl 1-Benzyl-2,4-diphenyl-4,5-dihydro-1*H*-imidazole-4-carboxylate (9c). Yield of 47%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 6.5 Hz, 2H), 7.44 (m, 5H), 7.31 (m, 6H), 7.19 (d, J = 7.2 Hz, 2H), 4.59 (d, J = 10.1 Hz, 1H), 4.45 (d, J = 15.9 Hz, 1H), 4.23 (d, J = 15.9 Hz, 1H), 3.71 (s, 3H), 3.45 (d, J = 10.1 Hz, 1H). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 173.9, 167.0, 143.9, 137.1, 130.4, 130.3, 128.8, 128.64, 128.6 (two carbons), 127.48, 127.46, 126.9, 125.6, 77.9, 60.6, 53.0, 52.2. HRMS ($C_{24}H_{23}O_2N_2$): calcd (M + 1) 371.1754, observed 371.1748. IR: ν_{CO} 1726 cm^{-1}.

Typical Protocol for Deallylation (10b). Imidazolinium-carboxylate (86 mg, 0.17 mmol) was charged into a 50 mL oven-dried Schlenk flask under a positive atmosphere of nitrogen. Five milliliters of dry CH_3CN was added by syringe. MeI (0.100 mL, 1.6 mmol) was then added by microsyringe. The resulting solution was allowed to stir at 45 °C for 2 h. The solvent and MeI were then removed in vacuo, and the resulting residue was placed under an atmosphere of nitrogen. $Pd(PPh_3)_4$ (20.6 mg 0.017 mmol) was then added by syringe as a solution in 2 mL of dry CH_2Cl_2 followed by $PhSiH_3$ (80 μL, 0.65 mmol) and glacial acetic acid (40 μL, 0.7 mmol). Upon completion of the deallylation as observed by ^{1}H NMR (20 h), the solution was washed with saturated $NaHCO_3$ followed by brine extraction. The combined organic layers were dried with Na_2SO_4, filtered, and condensed to give a yellow oil that was purified by silica gel chromatography (40% EtOAc in hexanes) to give a yellow solid (0.15 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 6.4 Hz, 2H), 7.43−7.24 (m, 13H), 6.66 (d, J = 8.8 Hz, 2H), 6.54 (d, J = 8.8 Hz, 2H), 5.92 (s, 1H), 4.34 (d, J = 16.0 Hz, 1H), 3.95 (d, J = 16.0 Hz, 1H), 3.71 (s, 3H), 3.13 (s, 3H). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 171.0, 166.1, 158.1, 139.9, 139.5, 131.7, 130.3, 129.4, 128.8, 128.6, 128.4, 128.2, 128.11, 128.08, 128.0, 127.8, 127.6, 113.1, 83.0, 79.8, 55.2, 51.4, 48.2. HRMS ($C_{31}H_{29}O_3N_2$): calcd (M + 1) 477.2173, observed 477.2163. IR: ν_{CO} 1733 cm^{-1}.

Methyl 1-Benzyl-2,4,5-triphenyl-4,5-dihydro-1*H*-imidazole-5-carboxylate (10a). Yield of 60%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 6.8 Hz, 2H), 7.41 (d, J = 8.2 Hz), 7.37−7.25 (m, 11H), 7.01 (m, 3H), 6.80 (m, 2H), 5.96 (s, 1H), 4.44 (d, J = 16.3 Hz, 1H), 4.02 (d, J = 16.3 Hz, 1H), 3.13 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.9, 166.1, 139.7, 139.5, 138.3, 131.6, 129.5, 128.6, 128.5, 128.2, 128.13, 128.10, 128.0, 127.9, 127.7 (two carbons), 127.5, 126.4, 83.1, 79.5, 51.4, 48.8. HRMS ($C_{30}H_{27}O_2N_2$): calcd (M + 1) 447.2067, observed 447.2057. IR: ν_{CO} 1734 cm^{-1}.

Synthesis of 12. In a 50 mL round-bottom flask equipped with a reflux condenser, compound **9a** (59 mg, 0.13 mmol) was dissolved in 20 mL of a 1:1 EtOH/2 M NaOH solution. This mixture was heated at reflux until the ester was completely consumed as observed by TLC (40% EtOAc in hexanes) (24 h). The solution was then brought to pH 0 by HCl, and the product was extracted into $CHCl_3$. The combined organic layers were dried with Na_2SO_4, filtered, and condensed, and the resulting off-white solid was purified by silica gel chromatography (10% MeOH in CH_2Cl_2 with 1% acetic acid) to afford the product **12** as an off-white solid (0.12 mmol, 91%). This compound has been previously described.[33]

1-Benzyl-2,4,5-triphenyl-4,5-dihydro-1*H*-imidazole-5-carboxylic Acid (12′). Yield of 55%. ^{1}H NMR (400 MHz, CD_3OD): δ 7.83 (d, J = 7.1 Hz, 2H), 7.61−7.53 (m, 3H), 7.44−7.33 (m, 10H), 6.92−6.83 (m, 3H), 6.39 (d, J = 7.1 Hz, 2H), 6.13 (s, 1H), 4.99 (d, J = 16.4 Hz, 1H), 4.53 (d, J = 16.4 Hz, 1H) (the CO_2H signal is not observed due to exchange with solvent). ^{13}C NMR (125.71 MHz, CD_3OD): δ 169.1, 166.0, 138.7, 136.6, 135.1, 132.3, 129.1, 129.0, 128.8, 128.7, 128.6, 128.0, 127.7$_9$, 127.6, 127.5, 127.3, 126.7, 124.4, 85.8, 69.5, 49.3. HRMS ($C_{29}H_{24}O_2N_2$): calcd (M + 1) 433.1911, observed 433.1901. IR: ν_{CO} 1624, 1559 cm^{-1}.

Synthesis of 11. In a 25 mL round-bottom flask, compound **10b** (133 mg, 0.28 mmol) was dissolved in 4 mL of CH_3CN along with ca. 2 drops of distilled water. To this solution was added cerium ammonium nitrate (765 mg, 1.4 mmol). The mixture was stirred at ambient temperature for 24 h. Then 20 mL of 1 M NaOH was added, and the resulting mixture was filtered over Celite. The organic phase was extracted with CH_2Cl_2 and washed with saturated $NaHCO_3$ followed by brine. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated to give a yellow oil, which was purified by silica gel chromatography (40% EtOAc in hexanes) to give a white solid (0.18 mmol, 65%).

^{1}H NMR (400 MHz, CD_3OD): δ 8.00−7.98 (m, 2H), 7.77−7.74 (m, 2H), 7.57−7.47 (m, 3H), 7.36 (m, 8H), 5.47 (s, 1H), 3.14 (s, 3H) (the N*H* signal not observed due to exchange with solvent). ^{13}C NMR (75.46 MHz, CD_3OD): δ 171.3, 164.3, 143.0, 139.8, 131.2, 129.2, 128.3, 128.0, 127.8_5, 127.7_9, 127.6, 127.5_2, 127.5_0, 126.2, 80.6, 76.9, 50.9. HRMS ($C_{23}H_{20}O_2N_2$): calcd (M + 1) 357.1598, observed 357.1590. IR: ν_{CO} 1733 cm^{-1}.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra of all synthesized products. This material is available free of charge via the Internet at http://pubs.acs.org.