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Carbene Reactivity of 4-Diazo-4*H*-imidazoles toward Nucleophiles and Aromatic Compounds

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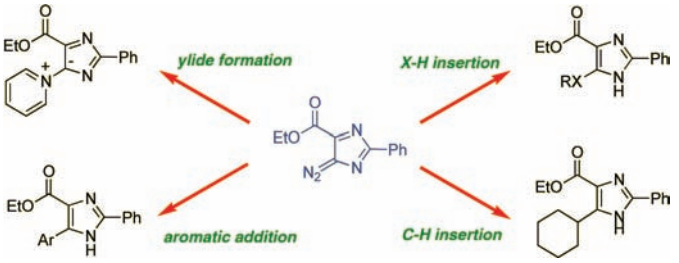

Carbenes derived from diazoimidazolecarboxylates **4** under thermal or photochemical conditions undergo O−H and N−H insertion reactions with alcohols and amines, respectively, in moderate yield, in competition with reduction in good H-donor solvents. Dichloromethane reacts to give the corresponding 4-chloroimidazole. Aromatic hydrocarbons are excellent traps for the imidazolylidene carbene and lead to a range of arylimidazole derivatives **7**. Reaction with pyridine leads to the first example of a pyridinium ylide **8** formed from an imidazolylidene carbene, whereas irradiation in hexafluorobenzene gives the imidazoazocine **11**, presumably by way of an initial norcaradiene intermediate.

Introduction

Diazo-azoles are heterocyclic analogues of diazocyclopentadiene[1] and are potential precursors to azolylidene carbenes, analogues of cyclopentadienylidene, a much investigated reactive intermediate.[2] Of the diazo-azoles, 4-diazoimidazoles are the best known, with 4-diazoimidazole-5-carboxamide **1** (Figure 1) the most widely studied. Azole **1** also serves as a precursor to two antitumor agents: reaction with dimethylamine gives 5-(3,3-dimethyl-1-triazenyl)imidazole-4-carboxamide (DIC, DCTIC),[3,4] and reaction with methyl isocyanate gives the imidazotetrazine **2**, the marketed drug temozolomide (www.temodar.com) used against aggressive brain tumors and now with sales of over $1 billion/year. Interestingly temozolomide is a prodrug for 5-(3-methyl-1-triazenyl)-imidazole-4-carboxamide (MTIC). Aside from the above, the dominant chemistry of **1** is its facile isomerization with cyclization into the imidazotriazinone **3** (azahypoxanthine).

Given the importance of the diazoimidazole **1** as a precursor to temozolomide, surprisingly little work has been done on this class of compound. The main study was carried out by Shechter and co-workers and described in two communications published in 1978 and 1986.[5,6] In these papers, the researchers showed that **1**, the parent compound 4-diazoimidazole itself, and the 2,5-diphenyl derivative served as carbene precursors upon heating or irradiation and that the resulting electrophilic imidazolylidenes underwent insertion into the C−H bonds of alcohols and addition to aromatic rings. The absence of kinetic isotope effects in the addition to C_6H_6/C_6D_6 mixtures and the failure to observe ESR spectra when 4-diazoimidazole was irradiated at 78 K in a range of solvent matrices suggested that imidazolylidene carbene had a singlet ground state. This is notwithstanding the fact that other studies had suggested

(1) Tisler, M.; Stanovnik, B. *Heterocycles* **1976**, *4*, 1115.
(2) Olson, D. R.; Platz, M. S. *J. Phys. Org. Chem.* **1996**, *9*, 759.
(3) Audette, R. C. S.; Connors, T. A.; Mandel, H. G.; Merai, K.; Ross, W. C. J. *Biochem. Pharmacol.* **1973**, *22*, 1855.
(4) Falkson, C. I. *Anti-Cancer Drugs* **1995**, *6*, 709.
(5) Kang, U. G.; Shechter, H. *J. Am. Chem. Soc.* **1978**, *100*, 651.
(6) Amick, T. J.; Shechter, H. *Tetrahedron Lett.* **1986**, *27*, 901.

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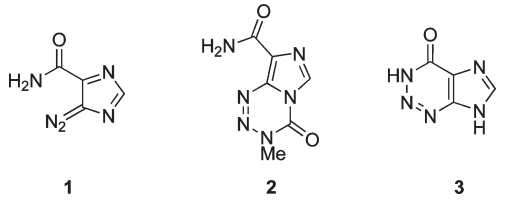


FIGURE 1. Structures of 4-diazoimidazole-5-carboxamide **1**, temozolomide **2**, and azahypoxanthine **3**.

that the carbene derived from **1** behaved as a triplet,[7] Much later, Maier and co-workers, with the benefit of more sophisticated experimental techniques, concluded that imidazolylidene was in fact a triplet ground state.[8]

We now report the details of an investigation into the synthetic utility of diazoimidazoles that sheds further light on the nature of the carbene intermediate produced upon heating or irradiation.

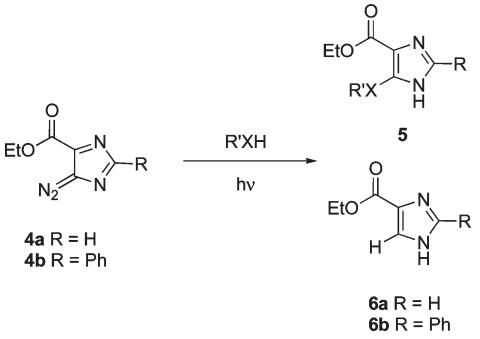
Results and Discussion

To avoid the problems associated with the facile isomerization and cyclization of 4-diazo-5-carboxamides, we used the corresponding carboxylates **4**, readily prepared by diazotization of the corresponding 4-amino heterocycles.[9] In view of our longstanding interest in carbene O−H insertion reactions,[10,11] we first investigated the dirhodium(II) tetraacetate catalyzed reaction of diazoimidazole **4b** with methanol, but in common with related work on diazoimidazole **1**,[12] this did not lead to the formation of any O−H insertion products. However, irradiation of **4a** in methanol did give the O−H insertion product, 5-methoxyimidazole-4-carboxylate **5a**, albeit in very poor yield (9%) along with the hydrogen abstraction product **6a** (38%). Irradiation in *tert*-butanol gave the O−H insertion product **5b** (6%) with no other identifiable products. These results compare with those of Kang and Shechter using 4-diazoimidazole-5-carboxamide **1** in that O−H insertion and hydrogen abstraction were observed,[5] although we did not isolate products of insertion into the C−H bonds of the alcohols with the 4-diazoimidazole-5-carboxylate precursor. The poor reactivity of the carbene derived from **4a** toward O−H insertion is further demonstrated by irradiation in methanol/dichloromethane, which results in preferential attack on dichloromethane (*q.v.*).

The 2-phenyl derivative **4b** behaved similarly upon irradiation, with the products being isolated in generally higher yields (Table 1). Thus irradiation of **4b** in methanol gave the 5-methoxyimidazole **5c** in 61% yield with no evidence for the formation of the hydrogen abstraction product **6b**. However, hydrogen abstraction did occur when the reaction was carried out using isopropanol, a better H-donor solvent: the O−H insertion product, ether **5d**, was formed in 29% yield, along with the hydrogen abstraction product **6b** (49%). With *tert*-butanol, only the O−H insertion product **5e** (65%) was observed. Again, we observed no products of insertion into the alcohol C−H bonds, as reported for both 4-diazoimidazole-5-carboxamide **1** and 4-diazo-2,5-diphenylimidazole.[5] Hydrogen abstraction was the major process observed under thermal conditions. For example, heating **4b** in cyclohexanol gave a quantitative yield of **6b**. Thiols were also very effective H-donors; irradiation of **4b** in the presence of 4-methoxybenzenethiol gave hydrogen abstraction product **6b** (100%). On the other hand, use of amines did lead to carbene N−H insertion products. Thus irradiation of **4b** in the presence of pyrrolidine or morpholine gave the corresponding N−H insertion products **5f** and **5g** in 50% and 31% yield, respectively (Table 1).

TABLE 1. X-H Insertion Reactions of Ethyl 4-Diazoimidazole-5-carboxylates

diazo	R′XH	R	R′X	5	yield (%)	6	yield (%)
4a	MeOH	H	MeO	**5a**	9	**6a**	38
4a	*t*-BuOH	H	*t*-BuO	**5b**	6		
4b	MeOH	Ph	MeO	**5c**	61		
4b	*i*-PrOH	Ph	*i*-PrO	**5d**	29	**6b**	49
4b	*t*-BuOH	Ph	*t*-BuO	**5e**	65		
4b	4-MeOC$_6$H$_4$SH					**6b**	100
4b	pyrrolidine	Ph	pyrrolidino	**5f**	50		
4b	morpholine	Ph	morpholino	**5g**	31		

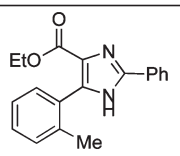
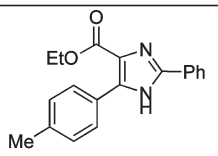
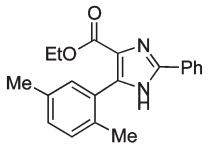
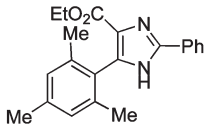
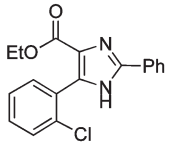
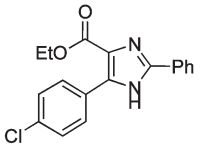
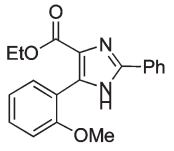
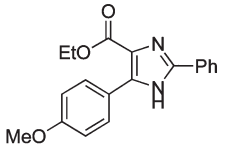
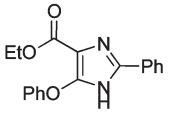
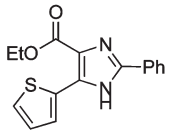
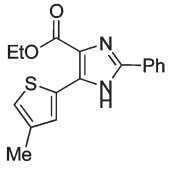
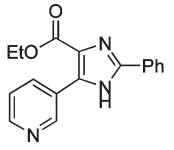
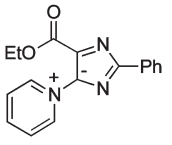


The reactions of carbenes with aromatic compounds is a well-known process and results in the formation of substituted benzenes by the isomerization of intermediate bicyclo-[4.1.0]heptadiene and/or direct C−H insertion processes.[13] 4-Imidazolyidene itself participates in such reactions, thought to proceed via the singlet carbene.[6] Therefore we investigated the photochemical reactions of diazoimidazole **4b** with a range of aromatic, including heteroaromatic, substrates, with some surprising results. Irradiation of **4b** in toluene gave a mixture of the *ortho*- and *para*-substituted products **7a** (41%) and **7b** (35%), in *p*-xylene the 5-(2,5-dimethylphenyl)imidazole **7c** (85%), and in mesitylene the corresponding 2,4,6-trimethyl derivative **7d**, again in good yield (89%) (Table 2). The reactions involving toluene, xylene, and mesitylene could also be conducted thermally in similar yields. In the reactions with methyl substituted benzenes, there was no evidence for insertion into C−H of methyl groups.

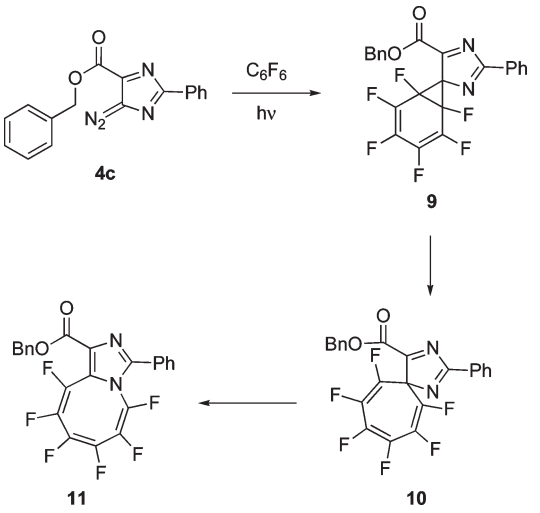
With chlorobenzene and anisole as substrates, the results mirrored those reported by Amick and Shechter for

(7) Ambroz, H. B.; Golding, B. T.; Kemp, T. J.; Shukla, V. S. *J. Chem. Soc., Chem. Commun.* **1982**, 414.
(8) Maier, G.; Endres, J. *Eur. J. Org. Chem.* **2000**, 2535.
(9) Andersen, K. E.; Pedersen, E. B. *Liebigs Ann.* **1986**, 1012.
(10) Kirmse, W. In *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI Press: Greenwich, CT, 1994; Vol. 1, p 1.
(11) Miller, D. J.; Moody, C. J. *Tetrahedron* **1995**, *51*, 10811.
(12) Hannah, D. R.; Stevens, M. F. G. *J. Chem. Res., Synop.* **2003**, 398.
(13) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971; Vol. 1.

TABLE 2. Photochemical Reactions of Ethyl 4-Diazo-2-phenylimidazole-4-carboxylate with Aromatic Substrates

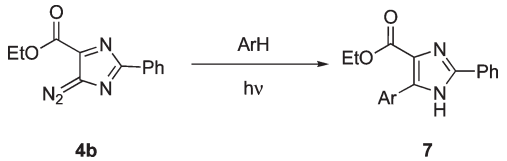
ArH	Products **7** (Yield)		
toluene	 **7a** (41%)	 **7b** (35%)	
p-xylene	 **7c** (85%)		
mesitylene	 **7d** (89%)		
chlorobenzene	 **7e** (28%)	 **7f** (32%)	
anisole	 **7g** (37%)	 **7h** (27%)	 **7i** (12%)
thiophene	 **7j** (98%)		
3-methylthiophene	 **7k** (48%)		
pyridine	 **7l** (29%)	 **8** (62%)	

SCHEME 1



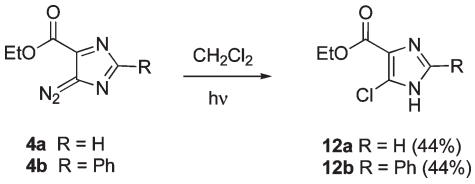
4-diazoimidazole.[6] Irradiation of **4b** in chlorobenzene gave a mixture of *ortho*- and *para*-substituted products **7e** (28%) and **7f** (32%), whereas anisole gave three products, the *ortho*- and *para*-compounds **7g** and **7h** and the 5-phenoxy compound **7i**. The latter product presumably results from attack of the carbene on the anisole oxygen to give an oxonium ylide that is subsequently demethylated. Interestingly, Amick and Shechter reported a similar process for chlorobenzene: attack on chlorine to give a chloronium ylide, which subsequently collapsed to give a 4-chloroimidazole, although we saw no corresponding products from **4b** and chlorobenzene.

When diazoimidazole **4b** was irradiated in thiophene, the 5-(2-thienyl)imidazole **7j** was formed in high yield. Likewise 3-methylthiophene gave the 5-thienyl derivative **7k** in modest yield. The formation of 2-substituted thiophenes presumably proceeds by attack of the carbene to give a norcaradiene type of intermediate, ring opening of which would be expected to lead a 2-substituted thiophene via the more stable cation. Irradiation in pyridine gave the 3-substituted pyridine **7l** in poor yield (28%). However, the major product (62%) from the irradiation of **4b** in pyridine was the pyridinium ylide **8**, the structure of which was confirmed by X-ray crystallography (see Supporting Information). This represents the first observation of the formation of a pyridinium ylide from an imidazolylidene carbene, mirrors the behavior of cyclopentadienylidene,[2] and is suggestive of the singlet nature of the carbene intermediate.

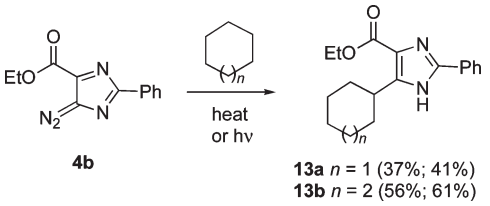


Given the apparent ease of additions of the imidazolylidene carbene derived from **4b** to aromatic rings, we attempted to effect an intramolecular version of the reaction. The diazoimidazole **4c** bearing a benzyl ester was irradiated in acetonitrile, but with no success. However, when the irradiation was repeated in hexafluorobenzene, a new product was formed and confirmed as the unusual 8−5 bicyclic

SCHEME 2



SCHEME 3[a]



[a]The first quoted yield refers to the reaction under thermal conditions, the second to photochemical conditions.

compound **11** by X-ray crystallography (see Supporting Information). Presumably this compound arises by formation of the norcaradiene **9** that undergoes ring opening to **10** followed by [1,5]-sigmatropic shift to the product **11** (Scheme 1). Although extremely unusual, a similar process has been observed in the reaction of 2,5-diphenyl-3-diazopyrrole with benzene that gave 1,3-diphenylcycloocta-[*c*]pyrrole in 31% yield.[14]

The poor reactivity of the carbene derived from **4a** toward O−H insertion has already been referred to and was further demonstrated by irradiation in methanol/dichloromethane, which results in formation of ethyl 5-chloroimidazole-4-carboxylate **12a** in 44% yield (Scheme 2). Presumably this results from initial attack of the carbene on the chlorine of dichloromethane; similar processes have been observed in dirhodium(II) catalyzed reactions of diazodicarbonyl compounds in dichloromethane.[15,16]

Finally, in a reaction similar to that reported for 4-diazoimidazole and its 2,5-diphenyl derivative,[5,6] heating diazoimidazole **4b** in cyclohexane or cycloheptane resulted in C−H insertion reaction to give the cycloalkylimidazoles **13** (Scheme 3). Similar yields were obtained under photochemical conditions.

Although many of the reactions described above appear characteristic of the singlet carbene state, the ground state nature of imidazolylidenes seems a matter of debate (*vide supra*). Therefore in order to determine the effect of the ester substituent, we undertook a brief computational study of the carbene derived from the diazoimidazole **4a**. Calculations at the B3LYP level of theory using a 6-311+G** basis set predict a triplet ground state for the ester substituted imidazole carbene. The triplet to singlet gap is calculated to be 9.0 kcal mol^{-1}, which is in accord with the value of 10.7 kcal mol^{-1} calculated by Maier and Endres for the triplet to singlet gap of the parent 4*H*-imidazol-4-ylidene at the same level of theory.[8]

(14) Nagarajan, M.; Shechter, H. *J. Org. Chem.* **1984**, *49*, 62.
(15) Pirrung, M. C.; Zhang, J. C.; Lackey, K.; Sternbach, D. D.; Brown, F. *J. Org. Chem.* **1995**, *60*, 2112.
(16) Schulze, B.; Nikolaev, V. V.; Hennig, L.; Rodina, L. L.; Sieler, J.; Nikolaev, V. A. *Russ. J. Org. Chem.* **2004**, *40*, 740.

Conclusions

The work described herein both complements and extends that reported by Shechter and co-workers some 30 years ago. Carbenes derived from diazoimidazolecarboxylates participate in a range of processes: hydrogen abstraction, O−H and N−H insertion, ylide formation with ethers, chloro compounds and pyridine, and addition to aromatic rings. Apart from the hydrogen abstraction to give 5-unsubstituted imidazole-4-carboxylates, which only occurs in high yield in the presence of good H-donors, all of these processes are usually associated with singlet carbene reactivity. Hence singlet reactivity appears to dominate notwithstanding the fact that matrix isolation and computational evidence suggests that imidazolylidenes possess a triplet ground state. However, a prevalence of singlet carbene reactivity from ground state triplet carbenes is quite common and occurs with many carbenes such as cyclopentadienylidene, the all-carbon ring analogue of imidazolylidenes.[2] Irrespective of mechanism, many of the reactions proceed in synthetically useful yields and constitute a useful route to substituted imidazoles.

Experimental Section

Ethyl 5-Diazoimidazole-4-carboxylate 4a. To a solution of ethyl 5-aminoimidazole-4-carboxylate[17] (500 mg, 3.2 mmol) in hydrochloric acid (1 M; 10 mL) was added sodium nitrite (290 mg, 4.2 mmol) in water (1.5 mL) dropwise at 0 °C. After the addition was complete, the mixture was extracted with chloroform (10 mL), and the aqueous fraction extracted further with chloroform (3 × 10 mL). The organic extracts were combined and dried (Na_2SO_4), and the solvent was evaporated to give a dark orange oily residue. On cooling the product crystallized to crystals of the same color (388 mg, 73%), mp 46−48 °C (lit.,[9] mp 47−52 °C); λ_{max} (ethanol)/nm 205.6 (log ε 5.38), 270.4 (5.03), 320.2 (5.11); ν_{max} (solid)/cm^{-1} 2975, 2860, 2178, 1688, 1501, 1285, 1248, 1232; δ_H (400 MHz; DMSO-*d*) 7.70 (1H, s), 4.36 (2H, q, J = 7.2), 1.32 (3H, t, J = 7.2); δ_C (100 MHz; DMSO-*d*) 159.9 (C), 150.9 (C), 150.2 (CH), 105.3 (C), 62.0 (CH_2) 14.3 (Me); *m*/*z* (ESI) 167 (MNa+, 100%); (Found M + Na, 167.0571. $C_6H_6N_4O_2$ + Na requires 167.0569).

Ethyl 5-Diazo-2-phenylimidazole-4-carboxylate 4b. To a solution of ethyl 5-amino-2-phenylimidazole-4-carboxylate[18] (500 mg, 2.16 mmol) in hydrochloric acid (1 M; 15 mL) was added sodium nitrite (290 mg, 4.2 mmol) in water (2 mL) dropwise at 0 °C. After addition was complete the mixture was stirred for a further 30 min. The product precipitates from the concentrated solution and was extracted into chloroform. The organic extracts were combined, dried (Na_2SO_4), and then evaporated to dryness to give the product as bright yellow crystals (347 mg, 66%), mp 107−109 °C (lit.,[3] mp not given); λ_{max} (ethanol)/nm 203.7 (log ε 5.10), 254.4 (5.16) 362.9 (4.61); ν_{max} (solid)/cm^{-1} 3050, 2900, 2156, 1739, 1454, 1430, 1234, 1190, 1111, 1089, 1018; δ_H (400 MHz; DMSO-*d*) 8.13 (2H, dd, J = 6.8 1.6), 7.51−7.44 (3H, m), 4.39 (2H, q, J = 7.2), 1.35 (3H, t, J = 7.2); δ_C (100 MHz; DMSO-*d*) 159.9 (C), 158.9 (C), 151.9 (C), 133.3 (C), 130.0 (CH), 129.3 (CH), 127.0 (CH), 106.0 (C), 62.1 (CH_2), 14.4 (Me); *m*/*z* (ESI) 243 (MNa+, 100%); (Found M + Na, 243.0783. $C_{12}H_{11}N_4O_2$ + Na requires 243.0783).

Benzyl 5-Diazo-2-phenylimidazole-4-carboxylate 4c. Benzyl 5-amino-2-phenylimidazole-4-carboxylate, prepared in similar manner as the above ethyl ester,[18] (254 mg, 0.87 mmol) was suspended in hydrochloric acid (2 M; 5 mL), and the mixture was stirred at 0 °C. Sodium nitrite (119 mg, 1.73 mmol) in water (1 mL) was added dropwise, and the mixture was stirred for 30 min. The mixture was extracted with dichloromethane (2 × 5 mL), and the combined organic fractions were dried (Na_2SO_4), and evaporated. The residue was purified chromatography using a solvent gradient of 2% methanol in dichloromethane to give the title compound as an orange crystalline solid (160 mg, 60%), mp 92−94 °C; ν_{max} (solid)/cm^{-1} 2154, 1731, 1453, 1371, 1247, 1195, 1123, 1092; δ_H (400 MHz; $CDCl_3$) 8.23 (2H, dd, J = 8.0, 1.6), 7.51−7.37 (8H, m), 5.48 (2H, s); δ_C (100 MHz; $CDCl_3$) 158.7 (C), 157.4 (C), 150.8 (C), 132.3 (C), 130.1 (C), 127.6 (CH), 126.5 (CH), 126.4 (CH), 126.37 (CH), 126.2 (CH), 125.2 (CH), 101.1 (C), 65.6 (CH_2); *m*/*z* (ESI) 305 (MH+, 100%) 247 (12); (Found M + H, 305.1036. $C_{17}H_{12}N_4O_2$ + H requires 305.1039).

Ethyl 5-Methoxyimidazole-4-carboxylate and Ethyl Imidazole-4-carboxylate 5a. Ethyl 5-diazoimidazole-4-carboxyate (100 mg, 0.64 mmol) was dissolved in dry methanol (10 mL) and irradiated under nitrogen for 1 h. Chromatography with a solvent gradient of 3% methanol in dichloromethane gave (i) ethyl 5-methoxyimidazole-4-carboxylate (10 mg, 9%), mp 157−159 °C; ν_{max}(solid)/cm^{-1} 1712, 1335, 1174, 1021, 763; δ_H (400 MHz; $CDCl_3$) 10.15 (1H, bs), 7.39 (1H, s), 4.37 (2H, q, J = 7.2), 4.09 (3H, s), 1.38 (3H, t, J = 7.2); δ_C (100 MHz; $CDCl_3$) 160.5 (C), 158.9 (C), 133.0 (CH), 102.3 (C), 62.3 (CH_2), 56.5 (Me), 14.5 (Me); *m*/*z* (ESI) 193 (MNa+, 100%), 171 (MH+, 28); (Found M + Na, 193.0589. $C_7H_{10}N_2O_3$ + Na requires 193.0589); and (ii) ethyl imidazole-4-carboxylate **6a** (30 mg, 38%), mp 158−160 °C (lit.,[19] mp 156−158 °C); ν_{max} (solid)/cm^{-1} 1713, 1335, 1174, 1021, 859 763; δ_H (400 MHz; $CDCl_3$) 12.80 (1H, bs) 7.86 (1H, s) 7.82 (1H, s) 4.37 (2H, q, J = 7.2) 1.36 (3H, t, J = 7.2); δ_C (100 MHz; $CDCl_3$) 162.5 (C) 137.0 (CH) 131.0 (C) 126.0 (CH) 60.6 (CH_2) 14.4 (Me); *m*/*z* (ESI) 163 (MNa+, 100%); (Found M + Na, 163.0478. $C_6H_8N_2O_2$ requires 163.0484).

Ethyl-5-*tert*-butoxyimidazole-4-carboxylate 5b. Ethyl-5-diazoimidazole-4-carboxylate (100 mg, 0.64 mmol) was dissolved in *tert*-butanol (10 mL) and stirred under nitrogen. The mixture was irradiated with a 300 W Ultra Vitalux lamp for 1 h. The solvent was removed under reduced pressure, and the residue was dissolved in chloroform (20 mL) and extracted with water (10 mL). The aqueous layer was extracted with chloroform (2 × 20 mL), and organic extracts were combined, dried (Na_2SO_4), and evaporated to dryness to give an orange oily residue. The product was purified by chromatography using a solvent gradient of 3% methanol in dichloromethane to give the title product as an orange crystalline solid (8 mg 6%), mp 117−120 °C; ν_{max} (cm^{-1}) 2970, 2940, 1693, 1558, 1500, 1404, 1379, 1350, 1166, 1095; δ_H (400 MHz; $CDCl_3$) 7.42 (1H, s), 4.34 (2H, q, J = 7.2), 1.54 (9H, s), 1.39 (3H, t, J = 7.2); δ_C (100 MHz; $CDCl_3$) 160.5 (C), 151.8 (C), 132.9 (CH), 107.6 (C), 82.2 (C), 60.5 (CH_2), 28.7 (Me) 14.3 (Me); *m*/*z* (ESI) 235 (MNa+, 100%); (Found M + Na, 235.1053. $C_{10}H_{16}O_3N_2$ + Na requires 235.1058).

Ethyl 5-Methoxy-2-phenylimidazole-4-carboxylate 5c. Ethyl 5-diazo-2-phenylimidazole-4-carboxylate (80 mg, 0.34 mmol) was dissolved in dry methanol (10 mL) under nitrogen. The mixture was irradiated for 1 h. The product was purified by chromatography using a solvent gradient of 5% methanol in dichloromethane to give the title compound as an orange powder (48 mg, 61%), mp 162−164 °C; ν_{max} (solid)/cm^{-1} 2995, 2890, 1660, 1561, 1452, 1278, 1133, 1114, 777; δ_H (400 MHz; $CDCl_3$) 11.11 (1H, bs), 8.02 (2H, dd, J = 7.8, 1.6), 7.43−7.40 (3H, m), 4.39 (2H, q, J = 7.2), 4.14 (3H, s), 1.38 (3H, t, J = 7.2); δ_C (100 MHz; $CDCl_3$) 161.4 (C), 159.9 (C), 144.5 (C), 129.2 (CH), 128.8 (C), 128.7 (CH), 126.1 (CH), 103.3 (C), 60.8 (CH_2), 56.5 (Me,) 14.6 (Me); *m*/*z* (ESI) 247 (MH+, 100%), 233 (15), 217 (43); (Found M + H, 247.1088. $C_{13}H_{14}N_2O_3$ + H requires 247.1082).

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Ethyl 5-Isopropoxy-2-phenylimidazole-4-carboxylate 5d. Ethyl 5-diazo-2-phenylimidazole-4-carboxylate (100 mg, 0.41 mmol) was dissolved in isopropyl alcohol (10 mL), and the mixture was irradiated for 1 h. The excess solvent was removed under reduced pressure, and the crude residue was purified by chromatography using a solvent gradient of 2% methanol in dichloromethane to give (i) ethyl 5-isopropoxy-2-phenylimidazole-4-carboxylate (31 mg, 29%), mp 115−118 °C; ν_{max} (solid)/cm^{-1} 3278, 2953, 1668, 1554, 1497, 1452, 1294, 1134, 1113, 774; δ_H (400 MHz; $CDCl_3$) 8.00 (2H, dd, J = 7.9, 1.6), 7.46−7.41 (3H, m), 5.26 (1H, hept, J = 6.2), 4.38 (2H, q, J = 7.2), 1.45 (6H, d, J = 6.2), 1.40 (3H, t, J = 7.2); δ_C (100 MHz; $CDCl_3$) 161.4 (C), 159.2 (C), 144.5 (C), 129.5 (CH), 129.3 (C), 128.7 (CH), 126.0 (CH), 104.4 (C), 72.6 (CH), 60.5 (CH_2), 22.3 (Me), 14.4 (Me); m/z (ESI) 273 (M − H, 100%), 215 (10); (Found M − H, 273.1234. $C_{15}H_{17}N_2O_3$ requires 273.1239); and (ii) ethyl 2-phenylimidazole-4-carboxylate **6b** (43 mg, 49%), mp 170−172 °C (lit.,[20] mp 174 °C); ν_{max} (solid)/cm^{-1} 1718, 1317, 1179, 1027; δ_H (400 MHz; $CDCl_3$) 8.03 (2H, dd, J = 7.2, 1.4), 7.93 (1H, s), 7.50−7.41 (3H, m), 4.27 (2H, q, J = 7.1), 1.30 (3H, t, J = 7.1); δ_C (100 MHz; $CDCl_3$) 161.4 (C), 148.4 (C), 131.7 (C), 130.4 (CH), 129.5 (C), 128.9 (CH), 127.3 (CH), 126.5 (CH), 61.0 (CH_2), 14.2 (Me); m/z (ESI) 217 (MH+, 100%) 203 (14); (Found M + H, 217.0974. $C_{12}H_{12}N_2O_2$ + H requires 217.0977).

Ethyl 5-*tert*-Butoxy-2-phenylimidazole-4-carboxylate 5e. Ethyl 5-diazo-2-phenylimidazole-4-carboxylate (59 mg, 0.24 mmol) was dissolved in *tert*-butanol (10 mL) and stirred under nitrogen. The mixture was irradiated for 1 h. The product was purified by chromatography using a solvent gradient of 5% methanol in dichloromethane to give the title compound as a dark orange crystalline solid (38 mg, 65%), mp 82−85 °C; ν_{max} (solid)/cm^{-1} 3275, 2953, 1671, 1438, 1296, 1274, 1172, 1129, 1106, 779; δ_H (400 MHz; $CDCl_3$) 8.00 (2H, dd, J = 7.9, 1.9), 7.42−7.39 (3H, m), 4.36 (2H, q, J = 7.2), 1.61 (9H, s), 1.40 (3H, t, J = 7.2); δ_C (100 MHz; $CDCl_3$) 161.6 (C), 157.9 (C), 144.3 (C), 129.5 (C), 128.8 (CH), 128.7 (CH), 125.92 (CH), 107.7 (C), 81.9 (C), 60.9 (CH_2), 28.8 (Me), 14.4 (Me); m/z (ESI) 289 (MH+, 100%), 271 (17), 233 (14); (Found M + H, 289.1569. $C_{16}H_{20}N_2O_3$ + H requires 289.1570).

Ethyl 2-Phenylimidazole-4-carboxylate 6b. Ethyl 2-phenyl-5-diazoimidazole-4-carboxylate (100 mg, 0.41 mmol) was dissolved in 4-methoxybenzenethiol (10 mL) and irradiated for 1 h. Excess 4-methoxybenenethiol was then removed under reduced pressure to give a dark yellow oily residue. The products were separated by chromatography using a solvent gradient of 2% methanol in dichloromethane to give the title compound as a colorless crystalline solid (93 mg, 100%), data as above.

Ethyl 2-Phenylimidazole-4-carboxylate 6b. Ethyl 5-diazo-2-phenylimidazole-4-carboxylate (50 mg, 0.2 mmol) dissolved in cyclohexanol (5 mL) and heated at reflux for 5 h. Excess cyclohexanol was then removed under reduced pressure, and the residue was purified by chromatography using a solvent gradient of 2% methanol in dichloromethane to give the title compound as a colorless crystalline solid (43 mg, 100%), data as above.

Ethyl 2-Phenyl-5-(pyrrolidin-1-yl)imidazole-4-carboxylate 5f. Ethyl 2-phenyl-5-diazoimidazole-4-carboxylate (100 mg, 0.41 mmol) was dissolved in pyrrolidine (10 mL) and irradiated for 1 h. The excess pyrrolidine was removed under reduced pressure to give the crude product as a dark brown oily residue. The product was purified using chromatography with a solvent gradient of 5% methanol in dichloromethane to give the title compound as a brown crystalline solid (59 mg, 50%), mp 151−153 °C; ν_{max} (solid)/cm^{-1} 3235, 2985, 1656, 1439, 1403, 1334, 1332, 1296, 1278, 1101, 784; δ_H (400 MHz; $CDCl_3$) 8.04 (2H, dd, J = 7.3, 1.9), 7.33−7.31 (3H, m), 4.34 (2H, q, J = 7.2), 3.79 (2H, bs), 3.69 (2H, bs), 2.0−1.91 (4H, br m), 1.32 (3H, t, J = 7.2); δ_C (100 MHz; $CDCl_3$) 161.4 (C), 147.0 (C), 138.1 (C), 129.3 (CH), 128.9 (CH), 127.6 (C), 126.2 (CH), 112.4 (C), 60.6 (CH_2), 51.1 (CH_2), 23.9 (CH_2), 14.4 (Me); m/z (ESI) 285 (M+, 18%) 284 (M − H, 100); (Found M − H, 284.1400. $C_{16}H_{18}N_3O_2$ requires 284.1399).

Ethyl 5-(Morpholin-4-yl)-2-phenylimidazole-4-carboxylate 5g. Ethyl 5-diazo-2-phenylimidazole-4-carboxylate (100 mg, 0.41 mmol) was dissolved in morpholine (10 mL) and stirred. The mixture was irradiated for 1 h. Excess morpholine was removed under reduced pressure, and the residue washed with water (3 × 5 mL). The residue was purified by chromatography using a solvent gradient of 2% methanol in dichloromethane with 0.2% triethylamine to give the title compound as brown crystals (38 mg, 31%), mp 96−99 °C; ν_{max} (solid)/cm^{-1} 2922, 2906, 1691, 1419, 1293, 1262, 1177, 1091, 1015; δ_H (400 MHz; $CDCl_3$) 8.00 (2H, dd, J = 7.5, 1.9), 7.43−7.40 (3H, m), 4.40 (2H, q, J = 7.1), 3.91 (4H, bs), 3.84 (4H, bs), 1.39 (3H, t, J = 7.1); δ_C (100 MHz; $CDCl_3$) 161.1 (C), 153.4 (C), 147.2 (C), 129.8 (C), 129.0 (CH), 128.7 (CH), 126.3 (CH), 113.9 (C), 66.4 (CH_2), 60.9 (CH_2), 43.5 (CH_2), 14.4 (Me); m/z (ESI) 301 (M+, 18%), 300 (M − H, 100); (Found M − H, 300.1340. $C_{16}H_{18}N_3O_3$ requires 300.1348).

Ethyl 2-Phenyl-5-(2-tolyl)imidazole-4-carboylate 7a and Ethyl 2-Phenyl-5-(4-tolyl)imidazole-4-carboxylate 7b. Ethyl 2-phenyl-5-diazoimidazole-4-carboxylate (100 mg, 0.41 mmol) was dissolved in toluene (10 mL) and stirred. The mixture was irradiated for 1 h. Excess solvent was removed under reduced pressure, and the residue was purified by chromatography, using a solvent gradient of 2% methanol in dichloromethane, to give (i) ethyl 2-phenyl-5-(4-tolyl)imidazole-4-carboxylate **7b** (44 mg, 35%) as a colorless solid, mp 195−198 °C; ν_{max} (solid)/cm^{-1} 1709, 1484, 1316, 1235, 1129, 1032; δ_H (400 MHz; $CDCl_3$) 7.97 (2H, dd, J = 7.9, 1.6), 7.79 (2H, d, J = 7.9), 7.46−7.44 (3H, m), 7.23 (2H, d, J = 7.9), 4.35 (2H, q, J = 7.1), 2.40 (3H, s), 1.33 (3H, t, J = 7.1); δ_C (100 MHz; $CDCl_3$) 161.2 (C), 147.3 (C), 138.6 (C), 130.0 (C), 129.8 (CH), 129.3 (CH), 128.9 (CH), 128.6 (CH), 127.7 (C), 126.6 (C), 126.1 (CH), 103.7 (C), 61.0 (CH_2), 21.4 (Me), 14.3 (Me); m/z (ESI) 305 (M − H, 100%); (Found M − H, 305.1290. $C_{19}H_{17}N_2O_2$ requires 305.1290); and (ii) ethyl 2-phenyl-5-(2-tolyl)imidazole-4-carboxylate **7a** (51 mg, 41%) as a colorless solid, mp 85−87 °C; ν_{max} (solid)/cm^{-1} 1712, 1484, 1322, 1225, 1139, 1110, 1025; δ_H (400 MHz; $CDCl_3$) 7.94 (2H, dd, J = 7.1, 1.6), 7.36−7.34 (3H, m), 7.19−7.03 (4H, m), 4.10 (2H q, J = 7.1), 2.12 (3H, s), 1.04 (3H, t, J = 7.1); δ_C (100 MHz; $CDCl_3$), 162.2 (C), 147.4 (C), 137.4 (C), 130.0 (CH), 129.6 (CH), 129.4 (CH), 129.2 (C), 128.7 (CH), 128.6 (CH), 128.5 (C), 128.3 (C), 126.1 (CH), 124.9 (CH), 102.5 (C), 60.5 (CH_2), 19.8 (Me), 13.9 (Me); m/z (ESI) 305 (M − H, 100%); (Found M − H, 305.1284. $C_{19}H_{17}N_2O_2$ requires 305.1290).

Ethyl 2-Phenyl-5-(2-tolyl)imidazole-4-carboxylate 7a and Ethyl 2-Phenyl-5-(4-tolyl)imidazole-4-carboxylate 7b. Ethyl 5-diazo-2-phenylimidazole-4-carboxylate (30 mg, 0.12 mmol) was dissolved in toluene (3 mL) and heated at reflux overnight. Excess toluene was removed under reduced pressure, and the residue was purified by chromatography using a solvent gradient of 2% methanol in dichloromethane to give (i) ethyl 2-phenyl-5-*p*-tolylimidazole-4-carboxylate **7b** (19 mg, 28%), data as above, and (ii) ethyl 2-phenyl-5-*o*-tolylimidazole-4-carboxylate **7a** (21 mg, 31%), data as above.

Ethyl 5-(2,5-Dimethylphenyl)-2-phenylimidazole-4-carboxylate 7c. Ethyl 5-diazo-2-phenylimidazole-4-carboxylate (100 mg, 0.41 mmol) was dissolved in anhydrous *p*-xylene (10 mL) and stirred. The mixture was then irradiated for 1 h. Excess xylene was removed under reduced pressure, and the residue was purified by chromatography with a solvent gradient of 2% methanol in dichloromethane to give the title compound as a pale yellow crystalline solid (112 mg, 85%), mp 202−204 °C; ν_{max} (solid)/cm^{-1} 2969, 2844,1703, 1485, 1326, 1231, 1190, 1151, 1120, 1036, 976; δ_H (400 MHz; $CDCl_3$) 7.94 (2H, dd, J = 7.9,

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1.6), 7.35−7.30 (3H, m), 6.99 (2H, d, J = 6.6), 6.93 (1H, s), 4.09 (2H, q, J = 7.1), 2.16 (3H, s), 2.05 (3H, s), 1.04 (3H, t, J = 7.1); δ_C (100 MHz; $CDCl_3$) 162.2 (C), 147.3 (C), 138.1 (C), 135.8 (C), 134.3 (C), 134.2 (C), 130.6 (CH), 129.6 (CH), 129.5 (CH), 129.4 (CH), 129.1 (C), 128.8 (CH), 126.1 (CH), 110.0 (C), 60.5 (CH_2), 20.8 (Me), 19.4 (Me), 13.9 (Me); m/z (ESI) 319 (M − H, 100%), 265 (16), 248 (17), 242 (14); (Found M − H, 319.1455. $C_{20}H_{19}N_2O_2$ requires 319.1447).

Dimethylphenyl-2-phenylimidazole-4-carboxylate 7c. Ethyl 5-diazo-2-phenylimidazole-4-carboxylate (50 mg, 0.2 mmol) was dissolved in *p*-xylene (5 mL) and heated to reflux for 1.5 h. Excess xylene was removed under reduced pressure, and the residue was purified by chromatography using a solvent gradient of 2% methanol in dichloromethane to give the title compound as a colorless crystalline solid (54 mg, 84%), data as above.

Ethyl 2-Phenyl-5-(2,4,6-trimethylphenyl)imidazole-4-carboxylate 7d. Ethyl 5-diazo-2-phenylimidazole-4-carboxylate (100 mg, 0.41 mmol) was dissolved in mesitylene (10 mL) and stirred. The mixture was then irradiated for 1 h. Excess mesitylene was removed under reduced pressure, and the residue was purified by chromatography, using a solvent gradient of 2% methanol in dichloromethane to give the title compound as a pale yellow crystalline solid (122 mg, 89%), mp 194−196 °C; ν_{max} (solid)/cm^{-1} 2969, 2922, 1711, 1482, 1457, 1404, 1323, 1222, 1173, 1121, 1026; δ_H (400 MHz; $CDCl_3$) 7.96 (2H, dd, J = 7.8, 1.6), 7.33−7.28 (3H, m), 6.73 (2H, s), 3.99 (2H, q, J = 7.1), 2.23 (3H, s), 1.89 (6H, s), 0.97 (3H, t, J = 7.1); δ_C (100 MHz; $CDCl_3$) 162.6 (C), 147.5 (C), 137.9 (C), 137.2 (C), 129.5 (C), 129.1 (CH), 128.7 (CH), 128.5 (C), 127.7 (CH), 126.5 (C), 126.2 (CH), 60.1 (CH_2), 21.2 (Me), 20.0 (Me) 13.9 (Me); m/z (ESI) 333 (M − H, 100%); (Found M − H, 333.1597. $C_{21}H_{21}N_2O_2$ requires 333.1603).

Ethyl 2-Phenyl-5-(2,4,6-trimethylphenyl)imidazole-4-carboxylate 7d. Ethyl 2-phenyl-5-diazoimidazole-4-carboxylate (50 mg, 0.2 mmol) was dissolved in mesitylene (5 mL) and heated to reflux for 1.5 h. Excess mesitylene was removed under reduced pressure, and the residue was purified by chromatography using a solvent gradient of 2% methanol in dichloromethane to give the title compound as a colorless crystalline solid (60 mg, 90%), data as above.

Ethyl 5-(2-Chloro-phenyl)-2-phenylimidazole-4-carboxylate 7e and Ethyl 5-(4-Chlorophenyl)-2-phenylimidazole-4-carboxylate 7f. Ethyl 5-diazo-2-phenylimidazole-4-carboxylate (100 mg, 0.41 mmol) was dissolved in chlorobenzene (10 mL) and stirred. The mixture was then irradiated for 1 h. Excess chlorobenzene was removed under reduced pressure to give a yellow solid. The residue was purified by chromatography using a solvent gradient of 2% methanol in dichloromethane to give (i) ethyl 5-(4-chlorophenyl)-2-phenylimidazole-4-carboxylate **7f** (43 mg, 32%) as a pale yellow crystalline solid, mp 168−170 °C; ν_{max} (solid)/cm^{-1} 3279, 1666, 1473, 1427, 1295, 1273, 1151, 1111, 1026; δ_H (400 MHz; $CDCl_3$) 7.99 (2H, dd, J = 6.9, 3.1), 7.82 (2H, d, J = 8.5), 7.44−7.40 (3H, m), 7.36 (2H, d, J = 8.5), 4.32 (2H, q, J = 7.1), 1.29 (3H, t, J = 7.1); δ_C (100 MHz; $CDCl_3$) 160.1 (C), 147.6 (C), 134.4 (C), 130.8 (CH), 130.3 (C), 129.9 (CH), 128.9 (CH), 128.4 (C), 128.2 (C), 128.0 (CH), 126.2 (CH), 126.1 (C), 61.2 (CH_2), 14.2 (Me); m/z (ESI) 327/325 (M − H, 34/100%), 249 (14); (Found M − H, 325.0748. $C_{18}H_{13}{}^{35}ClN_2O_2$ requires 325.0744); and (ii) ethyl 5-(2-chlorophenyl)-2-phenyl imidazole-4-carboxylate **7e** (38 mg, 28%) as a pale yellow crystalline solid, mp 88−90 °C; ν_{max} (solid)/cm^{-1} 2970, 1714, 1480, 1321, 1297, 1224, 1142, 1070, 1024; δ_H (400 MHz; $CDCl_3$) 7.99 (2H, dd, J = 7.1, 3.5), 7.43−7.38 (5H, m), 7.32−7.24 (2H, m), 4.21 (2H, q, J = 7.1), 1.12 (3H, t, J = 7.1); δ_C (100 MHz; $CDCl_3$) 161.4 (C), 148.2 (C), 134.0 (C), 131.8 (CH), 129.7 (CH), 129.5 (C), 129.2 (CH), 129.0 (CH), 128.8 (CH), 128.5 (C), 127.8 (C), 126.3 (CH), 126.2 (CH), 61.0 (CH_2), 13.8 (Me); m/z (ESI) 327/325 (M − H, 39/100%), 249 (12); (Found M − H, 325.0755. $C_{18}H_{13}{}^{35}ClN_2O_2$ requires 325.0744).

Ethyl 5-(2-Methoxyphenyl)-2-phenylimidazole-4-carboxylate 7g, Ethyl 5-(4-Methoxyphenyl)-2-phenylimidazole-4-carboxylate 7h, and Ethyl 5-Phenoxy-2-phenylimidazole-4-carboxylate 7i. Ethyl 5-diazo-2-phenylimidazole-4-carboxylate (100 mg, 0.41 mmol) was dissolved in anisole (10 mL) and stirred. The mixture was irradiated with a 300 W Ultra Vitalux lamp for 1 h. Excess anisole was removed under reduced pressure, and the residue was purified by chromatography using a solvent gradient of 30% ethyl acetate in light petroleum to give (i) ethyl 5-phenoxy-2-phenylimidazole-4-carboxylate **7i** (15 mg, 12%) as a colorless solid, mp 180−182 °C; ν_{max} (solid)/cm^{-1} 3204, 2990, 2922, 1648, 1539, 1488, 1446, 1305, 1282, 1238, 1201, 1133, 1111, 1021; δ_H (400 MHz; $CDCl_3$) 10.82 (1H, bs), 7.99 (2H, dd, J = 7.0, 2.0), 7.45−7.43 (3H, m), 7.34 (2H, t, J = 7.3), 7.19 (2H, d, J = 7.7), 7.12 (1H, t, J = 7.3), 4.33 (2H, q, J = 7.1), 1.25 (3H, t, J = 7.1); δ_C (100 MHz; $CDCl_3$) 160.6 (C), 156.8 (C), 155.6 (C), 145.0 (C), 130.0 (CH), 129.3 (CH), 128.81 (CH), 128.80 (C), 126.0 (CH), 123.2 (CH), 117.7 (CH), 108.1 (C), 61.1 (CH_2), 14.2 (Me); m/z (ESI) 307 (M − H, 100%); (Found M − H, 307.1080. $C_{18}H_{15}N_2O_3$ requires 307.1083); (ii) ethyl 5-(4-methoxyphenyl)-2-phenylimidazole-4-carboxylate **7h** (36 mg, 27%) as a colorless solid, mp 158−160 °C; ν_{max} (solid)/cm^{-1} 1673, 1496, 1427, 1244, 1191, 1175, 1130, 1026; δ_H (400 MHz; MeOH-d) 8.10 (2H, d, J = 6.8), 7.67 (2H, d, J = 8.8), 7.51−7.45 (3H, m), 7.00 (2H, d, J = 8.8), 4.30 (2H, q, J = 7.1), 3.86 (3H, s), 1.30 (3H, t, J = 7.1); δ_C (100 MHz; $CDCl_3$) 160.0 (C), 147.3 (C), 138.1 (C), 130.8 (CH), 129.8 (CH), 129.3 (C), 128.9 (CH), 126.1 (CH), 125.9 (CH), 117.8 (C), 113.3 (CH), 61.0 (CH_2), 55.3 (Me), 14.3 (Me); m/z (ESI) 321 (M − H, 100%); (Found M − H, 321.1247. $C_{19}H_{17}N_2O_3$ requires 321.1239); and (iii) ethyl 5-(2-methoxyphenyl)-2-phenylimidazole-4-carboxylate **7g** (49 mg, 37%) as a colorless solid, mp 122−124 °C; ν_{max} (solid)/cm^{-1} 1704, 1483, 1460, 1252, 1219, 1112, 1025; δ_H (400 MHz; $CDCl_3$) 7.95 (2H, d, J = 6.1), 7.61 (1H, d, J = 7.2), 7.41−7.34 (4H, m), 7.00 (1H, t, J = 7.5), 6.95 (1H, d, J = 8.2), 4.28 (2H, q, J = 7.1), 3.81 (3H, s), 1.24 (3H, t, J = 7.1); δ_C (100 MHz; $CDCl_3$) 162.4 (C), 156.7 (C), 146.1 (C), 132.0 (CH), 130.8 (C), 130.4 (CH), 129.5 (CH), 129.0 (C,) 128.8 (CH), 126.1 (CH), 125.9 (CH), 120.5 (CH), 60.6 (CH_2) 55.7 (Me), 14.2 (Me); m/z (ESI) 321 (M − H, 100%); (Found M − H, 321.1254. $C_{19}H_{17}N_2O_3$ requires 321.1239).

Ethyl 2-Phenyl-5-(thien-2-yl)imidazole-4-carboxylate 7j. Ethyl 5-diazo-2-phenylimiazole-4-carboxylate (100 mg, 0.41 mmol) was dissolved in thiophene (10 mL) and stirred. The mixture was then irradiated for 1 h. Excess thiophene was then removed under reduced pressure, and the residue was purified by chromatography using a solvent gradient of 2% methanol in dichloromethane to give the title compound as a off white solid (120 mg, 98%), mp 132−134 °C; ν_{max} (solid)/cm^{-1} 3296, 1669, 1274, 1447, 1270, 1108, 1025; δ_H (400 MHz; $CDCl_3$) 10.07 (1H, bs), 8.13 (1H, d, J = 3.2), 7.98 (2H, d, J = 7.0), 7.51−7.45 (3H, m), 7.42 (1H, d, J = 5.0), 7.14 (1H, t, J = 4.8), 4.45 (2H, q, J = 7.1), 1.46 (3H, t, J = 7.1); δ_C (100 MHz; $CDCl_3$) 160.2 (C), 147.8 (C), 142.3 (C), 136.4 (C), 130.1 (CH), 128.9 (CH), 128.6 (C), 128.3 (CH), 127.5 (CH), 127.0 (CH), 126.2 (CH), 117.1 (C), 61.3 (CH_2), 14.5 (Me); m/z (ESI) 297 (M − H, 100%); (Found M − H, 297.0697. $C_{16}H_{13}N_2O_2S$ requires 297.0698).

Ethyl 5-(3-Methylthien-5-yl)-2-phenylimidazole-4-carboxylate 7k. Ethyl 5-diazo-2-phenylimidazole-4-carboxylate (100 mg, 0.41 mmol) was dissolved in 3-methylthiophene (10 mL) and stirred. The mixture was then irradiated with a 300 W Ultra Vitalux lamp for 1 h. Excess 3-methylthiophene was removed under reduced pressure to give a dark orange solid. The product was purified by chromatography using a solvent gradient of 2% methanol in dichloromethane to give the title compound as a pale orange solid (61 mg, 48%), mp 152−154 °C; ν_{max} (solid)/cm^{-1}

3311, 1666, 1447, 1270, 1108, 1025; δ_H (400 MHz; $CDCl_3$) 10.25 (1H, bs), 7.98 (2H, d, J = 5.8), 7.95 (1H, s), 7.47−7.45 (3H, m), 6.99 (1H, s), 4.45 (2H, q, J = 7.0), 1.45 (3H, t, J = 7.0); δ_C (100 MHz; $CDCl_3$) 160.2 (C), 147.8 (C), 142.6 (C), 138.0 (C), 135.9 (C), 130.6 (CH), 130.0 (CH), 128.9 (CH), 128.6 (C) 126.2 (CH), 122.6 (CH), 116.9 (C), 61.3 (CH_2), 15.6 (Me), 14.4 (Me); m/z (ESI) 312 (M+, 20%) 311 (M − H, 100); (Found M − H, 311.0858. $C_{17}H_{15}N_2O_2S$ requires 311.0854).

Ethyl 2-Phenyl-5-(pyridin-3-yl)imidazole-4-carboxylate 7l and 1-(4-Ethoxycarbonyl-2-phenylimidazolidin-4-yl)pyridinium inner Salt 8. Ethyl 5-diazo-2-phenylimidazole-4-carboxylate (100 mg, 0.41 mmol) was dissolved in anhydrous pyridine (10 mL) and stirred. The mixture was then irradiated 300W Ultra Vitalux lamp for 1 h. Excess pyridine was removed under reduced pressure, and the residue was purified by chromatography using a solvent gradient of 2% methanol in dichloromethane, increasing to 5% methanol to give (i) ethyl 2-phenyl-5-(pyridin-3-yl)imidazole-4-carboxylate **7l** (35 mg, 29%) as a brown crystalline solid, mp 130−132 °C; ν_{max} (solid)/cm^{-1} 1710, 1473, 1419, 1302, 1280, 1141, 1110, 1024; δ_H (400 MHz; $CDCl_3$) 9.13 (1H, s), 8.57 (1H, d, J = 4.8), 8.28 (1H, d, J = 7.8), 8.04 (2H, d, J = 7.6), 7.44−7.40 (3H, m), 7.38−7.34 (1H, m), 4.30 (2H, q, J = 7.1), 1.25 (3H, t, J = 7.1); δ_C (100 MHz; $CDCl_3$) 160.8 (C), 149.9 (CH), 148.8 (C), 148.7 (C), 137.2 (CH), 129.9 (CH), 129.3 (C), 128.9 (CH), 128.4 (C), 127.8 (C), 126.3 (CH), 122.9 (CH), 61.2 (CH_2), 14.1 (Me); m/z (ESI) 293 (M+, 23%), 292 (M − H, 100); (Found M − H, 292.1079. $C_{17}H_{14}N_3O_2$ requires 292.1080); and (ii) 1-(4-ethoxycarbonyl-2-phenylimidazolidin-4-yl)pyridinium inner salt **8** (73 mg, 62%) as yellow crystalline solid, mp 224−226 °C; ν_{max} (solid)/cm^{-1} 1689, 1659, 1627, 1494, 1470, 1421, 1243, 1230, 1033; δ_H (400 MHz; $CDCl_3$) 9.44 (2H, d, J = 6.5), 8.26 (1H, dd, J = 6.5, 1.2), 8.21 (2H, d, J = 7.9), 7.89 (2H, t, J = 6.5), 7.41−7.37 (2H, m), 7.30−7.26 (1H, m), 4.37 (2H, q, J = 7.1), 1.41 (3H, t, J = 7.1); δ_C (100 MHz; $CDCl_3$) 164.3 (C), 154.7 (C), 143.6 (CH), 142.9 (CH), 135.0 (C), 128.2 (CH), 127.3 (CH), 126.2 (CH), 125.9 (CH), 122.1 (C), 100.6 (C), 60.6 (CH_2), 14.5 (Me); m/z (ESI) 294 (MH+, 100%); (Found M + H^+, 294.1241. $C_{17}H_{15}N_3O_2$ + H requires 294.1243).

Benzyl 5,6,7,8,9,10-Hexafluoro-2-phenylimidazo[1,5-*a*]azocine-4-carboxylate 11. Benzyl 5-diazo-2-phenylimidazole-4-carboxylate (100 mg, 0.33 mmol) was dissolved in hexafluorobenzene (10 mL) and stirred. The mixture was irradiated for 1 h. Excess hexafluorobenzene was removed under reduced pressure, and the residue was purified by chromatography using a solvent gradient of 2% methanol in dichloromethane to give the title compound as a colorless crystalline solid (61 mg, 51%), mp 94−96 °C; ν_{max} (solid)/cm^{-1} 2927, 1740, 1406, 1340, 1313, 1214, 1179, 1109, 1018, 971, 911; δ_H (400 MHz; $CDCl_3$) 7.81 (2H, d, J = 7.7), 7.58−7.52 (3H, m), 7.48 (2H, d, J = 6.8), 7.42−7.36 (3H, m), 5.46 (2H, s); δ_C (125 MHz; $CDCl_3$) 160.2 (C), 149.6 (C), 139.8 (dt, J = 270.3, 23.6, CF), 138.9 (dt, J = 250.9, 24.0, CF), 137.7 (C), 136.8 (dt, J = 248.1, 25.4, CF), 135.6 (C), 135.1 (C), 132.0 (dt, J = 260.2, 27.8, CF), 131.5 (CH) 129.3 (CH), 128.6 (CH), 128.5 (CH), 127.7 (CH), 126.9 (C), 67.6 (CH_2); δ_F (376 MHz; $CDCl_3$) −94.11 (s), −108.97 (d, J = 20.3), −122.97 (dd, J = 38.0, 17.8), −127.17 (dd, J = 37.4, 17.8), −129.95 (dd, J = 38.0, 20.3), −134.41 (d, J = 37.4); m/z (ESI) 463 (MH+, 100%); (Found M + H, 463.0906. $C_{23}H_{12}F_6N_2O_2$ requires 463.0881).

Ethyl 5-Chloroimidazole-4-carboxylate 12a. Ethyl 5-diazoimidazole-4-carboxylate (73.4 mg, 0.47 mmol) was dissolved in dichloromethane (10 mL) and stirred. Dry methanol (22.5 mg, 28.5 μL) was added, and the mixture was irradiated for 2 h. Solvent was removed under reduced pressure to give a pale brown residue. The residue was purified with chromatography using a solvent gradient of 3% methanol in dichloromethane to give the title compound as a pale yellow crystalline solid (32 mg, 44%), mp 183−185 °C (lit.,[17] mp 178 °C); ν_{max}(solid)/cm^{-1} 3280, 1710, 1553, 1344, 1222, 1197, 1160, 1050, 836; δ_H (400 MHz; $CDCl_3$) 7.75 (1H, s), 4.41 (2H, q, J = 7.2), 1.42 (3H, t, J = 7.2); δ_C (100 MHz; $CDCl_3$) 159.4 (C), 136.0 (CH), 134.8 (C), 117.0 (C), 61.5 (CH_2), 14.3 (Me); m/z (ESI) 175 (MH+, 34%), 173 (M − H, 100); (Found M − H, 173.0125. $C_6H_6{}^{35}ClN_2O_2$ requires 173.0118).

Ethyl 5-Chloro-2-phenylimidazole-4-carboxylate 12b. Ethyl 5-diazo-2-phenylimidazole-4-carboxylate (100 mg, 0.41 mmol) was dissolved in dry dichloromethane (10 mL) and stirred. Methanol (25 μL) was added, and the mixture was irradiated for 1 h. The solvent was removed under reduced pressure to give dark yellow residue. The crude residue was purified by chromatography using as solvent gradient of 2% methanol in dichloromethane to give the title compound (45 mg, 44%), mp 162−165 °C; ν_{max} (solid)/cm^{-1} 3275, 1671, 1516, 1466, 1413, 1389, 1296, 1267, 1210, 1038; δ_H (360 MHz; $CDCl_3$) 8.00 (2H, dd, J = 6.6, 2.9), 7.49−7.47 (3H, m), 4.43 (2H, q, J = 7.2), 1.44 (3H, t, J = 7.2); δ_C (90 MHz; $CDCl_3$) 160.1 (C), 147.6 (C), 130.4 (CH), 129.1 (C), 129.0 (CH), 128.1 (C), 126.1 (CH), 118.2 (C), 61.7 (CH_2), 14.3 (Me); m/z (ESI) 251 (MH+, 31%) 249 (M − H, 100); (Found M − H, 249.0422. $C_{12}H_{10}{}^{35}ClN_2O_2$ requires 249.0431).

Ethyl 5-Cyclohexyl-2-phenylimidazole-4-carboxylate 13a. (a) Ethyl 5-diazo 2-phenylimidazole-4-carboxylate (50 mg, 0.2 mmol) was dissolved in cyclohexane (5 mL) and heated at reflux overnight. Excess cyclohexane was removed under reduced pressure, and the residue was purified by chromatography using a solvent gradient of 2% methanol in dichloromethane to give the residual starting material (28 mg, 56%) and the title compound as a colorless crystalline solid (22 mg, 37%), mp 188−190 °C; ν_{max} (solid)/cm^{-1} 2925, 1706, 1485, 1327, 1201, 1087; δ_H (400 MHz; $CDCl_3$) 7.93 (2H, dd, J = 7.7, 1.6), 7.42−7.39 (3H, m), 4.37 (2H, q, J = 7.1), 3.40 (1H, br m), 1.94−1.85 (4H, m), 1.77−1.68 (3H, m), 1.48−1.31 (3H, m), 1.38 (3H, t, J = 7.1); δ_C (100 MHz; $CDCl_3$) 161.7 (C), 146.4 (C), 138.1 (C), 129.8 (CH), 128.8 (CH), 128.5 (C), 128.1 (C), 126.2 (CH), 60.7 (CH_2), 36.2 (CH), 32.1 (CH_2), 26.5 (CH_2), 25.9 (CH_2), 14.3 (Me); m/z (ESI) 297 (M − H, 100%); (Found M − H, 297.1603. $C_{18}H_{21}N_2O_2$ requires 297.1603).

(b) Ethyl 5-diazo-2-phenylimidazole-4-carboxylate (50 mg, 0.21 mmol) was dissolved in cyclohexane (5 mL) and stirred. The mixture was irradiated with a 300 W Ultra Vitalux lamp for 1 h. Excess cyclohexane was removed under reduced pressure, and the residue was purified by chromatography using a solvent gradient of 2% methanol in dichloromethane to give the title compound (26 mg, 41%); data as above.

Ethyl 5-Cycloheptyl-2-phenylimidazole-4-carboxylate 13b. (a) Ethyl 5-diazo-2-phenylimiazole-4-carboxylate (50 mg, 0.2 mmol) was dissolved in cycloheptane (5 mL) and heated at reflux for 3 h. Excess cycloheptane was then removed under reduced pressure, and the crude residue was purified by chromatography using a solvent gradient of 2% methanol in dichloromethane to give the title compound as a colorless crystalline solid (35 mg, 56%), mp 180−182 °C; ν_{max} (solid)/cm^{-1} 2923, 1704, 1458, 1326, 1197, 1086; δ_H (400 MHz; $CDCl_3$) 7.93 (2H, dd, J = 7.9, 1.6), 7.40−7.37 (3H, m), 4.35 (2H, q, J = 7.1), 3.56 (1H, br m), 1.97−1.92 (2H, m), 1.81−1.77 (4H, m), 1.70−1.67 (2H, m), 1.61−1.54 (4H, m), 1.35 (3H, t, J = 7.1); δ_C (100 MHz; $CDCl_3$) 162.3 (C), 146.6 (C), 138.1 (C), 129.4 (CH), 129.0 (C), 128.8 (CH), 126.0 (CH), 125.9 (C), 60.5 (CH_2), 38.1 (CH), 34.2 (CH_2), 27.8 (CH_2), 27.2 (CH_2), 14.4 (Me); m/z (ESI) 311 (M − H, 100%); (Found M − H, 311.1759. $C_{19}H_{23}N_2O_2$ requires 311.1760).

(b) Ethyl 5-diazo-2-phenylimidazole-4-carboxylate (50 mg, 0.21 mmol) was dissolved in cycloheptane (5 mL) and stirred. The mixture was irradiated with a 300 W Ultra Vitalux lamp for 1 h. Excess cycloheptane was removed under reduced pressure, and the residue was purified by chromatography using a solvent gradient of 2% methanol in dichloromethane to give th etitle compound (40 mg, 61%); data as above.

Computational Methods. Calculations were performed on the singlet and triplet carbenes derived from diazoimidazole **4a**. Geometry optimizations were performed at the B3LYP/6-311+G** level of theory for the singlet carbene and UB3LYP/6-311+G** for the triplet carbene using Q-Chem. Zero point vibrational energies were calculated for all structures, and the absence of imaginary frequencies was used to characterize the structures as minima on their potential energy surfaces.

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Supporting Information Available: General experimental details, calculated coordinates for singlet and triplet carbenes derived from diazoimidazole **4a**, copies of ^{1}H and ^{13}C NMR spectra, and files in CIF format for compounds **8** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.