$ZrCl_4$-Mediated Regioselective Electrophilic Amination of Activated Arenes with New Alkyl Arylaminocarbonyldiazenecarboxylates: Intermolecular and Intramolecular Reactions†

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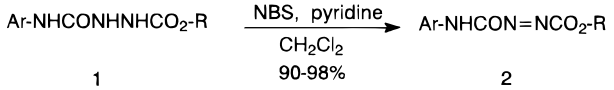
Introduction

Azo-diesters have been recognized as reagents for the amination of electron-rich arenes. A thermal and acid-catalyzed electrophilic amination of alkylbenzenes and some substituted phenols, which was published several decades ago and was limited to dialkyl azodicarboxylates, required high temperatures or strongly acidic conditions.[1] Recently, bis(2,2,2-trichloroethyl) azodicarboxylate was introduced as an efficient reagent for the synthesis of aromatic amines.[2] We herein report on hitherto unknown aminations of electron-rich arenes with alkyl arylaminocarbonyldiazenecarboxylates.

Our recently reported results on the reactions of mono- and disubstituted hydrazines demonstrated the variety of their applications in organic synthesis.[3] We also described a mild approach to 1,3,4-oxadiazoles and fused 1,2,4-triazoles from the corresponding 1,4-disubstituted semicarbazides via diazenes as intermediates. For example, ethyl phenylaminocarbonyldiazenecarboxylate[4] smoothly reacted with Ph_3P to give 2-ethoxy-5-phenylamino-1,3,4-oxadiazole.[5] Herein, we focus our attention on diazenes with respect to their potential as reagents for electrophilic amination. Diazenes **2a**−**g**, obtained in good yields by the oxidation of 1,4-disubstituted semicarbazides **1a**−**g** with NBS (Table 1), are stable compounds and can be kept in the refrigerator for months. There is only one report on diazene **2a** and its *tert*-butyl derivative dealing with their application in an azo−ene reaction.[4] To the best of our knowledge, diazene **2a** has not been previously used for electrophilic amination of arenes. Therefore, **2a** and new diazenes **2b**−**g** were employed in this investigation.

Table 1. Oxidation of 1,4-Disubstituted Semicarbazides[a] to Diazenes



1 2

Ar	R	time[b] (min)	product	yield[c] (%)
Ph	Et	50	**2a**	94[4]
Ph	*i*-Bu	30	**2b**	96
4-MeC_6H_4	Et	25	**2c**	98
4-$MeOC_6H_4$	Me	45	**2d**	94
4-FC_6H_4	Et	30	**2e**	90
3-ClC_6H_4	Et	55	**2f**	97
3,4-ClC_6H_3	Bn	25	**2g**	92

[a] Semicarbazides **1a**−**g** were prepared in 90−97% yield by the addition of aryl isocyanates (ArNCO) to alkoxycarbonylhydrazine (H_2NNHCO_2R). [b] Reactions were carried out at room temperature. [c] Isolated yields are given.

Results and Discussion

Diazenes **2a**−**g** can react with activated arenes under mild conditions. Our initial studies were devoted to the selection of the Lewis acid to enable the reaction of **2a** with anisole. Although ZnI_2, $ZnCl_2$, $BF_3{\cdot}Et_2O$, CF_3SO_3H, TFA, and $LiClO_4$ have already been used for electrophilic amination of arenes with bis(2,2,2-trichloroethyl) azodicarboxylate,[2a−d] we found $ZrCl_4$ to be a new reagent for the electrophilic amination of arenes with diazenes that was easy to handle and that led to the desired product in good yield. On the other hand, none of the other Lewis acids gave satisfactory results when **2a** was treated with anisole. Either this reaction resulted in a complex mixture of several products (the application of ZnI_2, $ZnCl_2$, $BF_3{\cdot}Et_2O$, CF_3SO_3H, or TFA) or the amination was much slower compared to that carried out in the presence of $ZrCl_4$ (in the case of $LiClO_4$). For the above reasons, $ZrCl_4$ was used throughout this paper. In a typical experiment, a solution of the diazene **2a** (1 mmol) and anisole (1 mmol) in CH_2Cl_2 (7 mL) was added dropwise to a stirred suspension of $ZrCl_4$ (1.1 mmol) in CH_2Cl_2 (2 mL) at −30 °C under argon. After 45 min, the reaction mixture was warmed to room temperature, quenched with H_2O (5 mL), and neutralized with a saturated aqueous solution of $NaHCO_3$, and the product **3a** was isolated from CH_2Cl_2 solution in 85% yield. Similar experiments of the diazenes **2b**−**g** led to the formation of the corresponding products **3b**−**g** (Table 2). Reactions took place with complete regioselectivity concerning both partners; the nitrogen atom, vicinal to the amide functionality of reagent **2**, always attacked *para* to the anisole methoxy group. There was no other regioisomer detected in the crude reaction mixture. This was evident from (i) ^1H NMR spectra as only the *ortho* coupling appeared for the protons of the aminated anisole moiety and (ii) typical fragments obtained in mass spectra (M^+ − ArNCO). In addition, anisole derivatives of type **3** could be easily transformed to 1,2-disubstituted hydrazines, unsymmetrical ureas, and unsymmetrical 1,2,4-triazoline-3,5-diones. Selected examples derived from **3a** are shown in

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† Dedicated with deep respect to Professor Henk C. van der Plas on the occasion of his 70th birthday.

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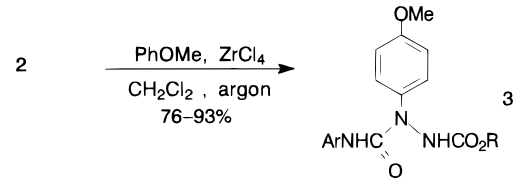
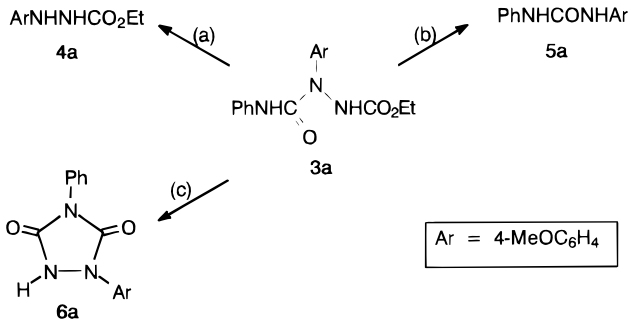
Table 2. Electrophilic Amination of Anisole



diazene	time (min)[a]	product	Ar	R	yield (%)[b]
2a	45	**3a**	Ph	Et	85
2b	90	**3b**	Ph	*i*-Bu	86
2c	75	**3c**	4-MeC_6H_4	Et	91
2d	180	**3d**	4-$MeOC_6H_4$	Me	87
2e	30	**3e**	4-FC_6H_4	Et	84
2f	75	**3f**	3-ClC_6H_4	Et	93
2g	120	**3g**	3,4-ClC_6H_3	Bn	76

[a] Reaction times at −30 °C. Reaction mixtures were then allowed to warm to room temperature. [b] Isolated yields are given.

Scheme 1[a]



[a] Conditions: (a) **3a** (1 mmol), Zn (10 mmol), AcOH (6.5 mL), reflux, 4 h, 46% of **4a** (isolated yield); (b) **3a** (1 mmol), PPA (0.94 g), 100 °C, 1 h, 42% of **5a**; (c) **3a** (0.5 mmol), NaOH (10 mmol), H_2O−EtOH (1:5, 6 mL), rt, 1 h, 87% of **6a**.

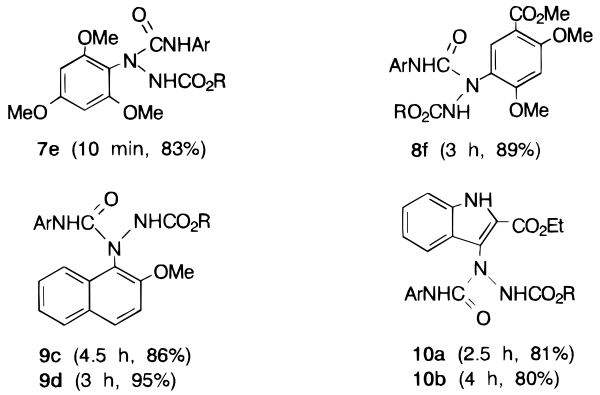
Scheme 1. Compounds **4a** and **5a** could arise only from **3a** and not from other regioisomers.

These results stimulated us to perform similar reactions on substrates such as 1,3,5-trimethoxybenzene, methyl 2,4-dimethoxybenzoate, 2-methoxynaphthalene and ethyl indole-2-carboxylate. It should be mentioned that complete regioselectivity on unsymmetrical substrates was again observed. Amination led to the formation of the products **7**−**10** (Chart 1).

Diazenes of type **2** suffered an intramolecular reaction when their CH_2Cl_2 solutions were treated with $ZrCl_4$ at room temperature. Namely, diazenes **2a**−**f** cyclized to the corresponding *N*-aminobenzimidazole-2-ones of type **11** or **12** (Table 3). It is worth noting that **11f** was obtained as the only regioisomer when **2f** was employed as a starting material. In the case of **2d**, an intramolecular process was presumably followed by an intermolecular one; the initially formed **11d** seems to be sufficiently activated, as a result of the presence of an electron-donating methoxy group on the benzene ring, to react with **2d**, giving **12d** in the final step (Scheme 2). Although several experiments were carried out at different temperatures (within the range of −78 °C to room temperature), all attempts to isolate **11d** failed.

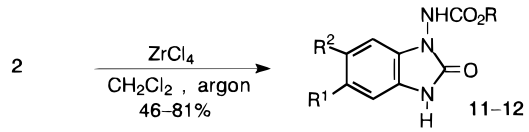
Having the above results in hand, it seemed reasonable to perform the electrophilic amination of less reactive arenes for comparison to those already mentioned; *m*-xylene, toluene, and benzene have been selected for that purpose. Thus, a treatment of *m*-xylene with **2a** led to

Chart 1[a]



[a] Products obtained from: (i) 1,3,5-trimethoxybenzene and **2e** (**7e**); (ii) methyl 2,4-dimethoxybenzoate and **2f** (**8f**); (iii) 2-methoxynaphthalene and **2c** or **2d** (**9c**, **9d**); (iv) ethyl indole-2-carboxylate and **2a** or **2b** (**10a**, **10b**). Experiments were carried out at −78 °C (for **8f** at 0 °C) as described for the synthesis of **3a** from anisole and **2a**.

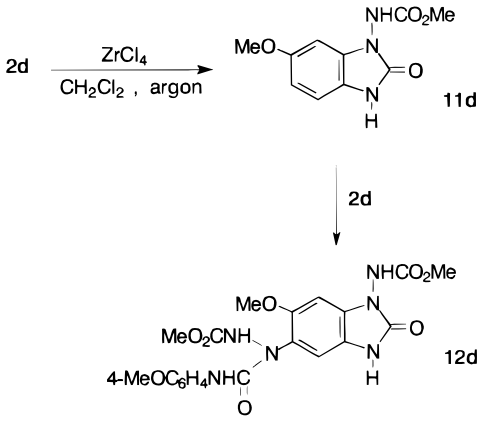
Table 3. Intramolecular Amination of Diazenes



diazene	time[a] (h)	product	R	R^1	R^2	yield[b] (%)
2a	20	**11a**	Et	H	H	58
2b	22	**11b**	*i*-Bu	H	H	81
2c	17	**11c**	Et	H	Me	58
2d	2	**12d**	Me	*c*	OMe	46
2e	19	**11e**	Et	H	F	74
2f	21	**11f**	Et	Cl	H	62

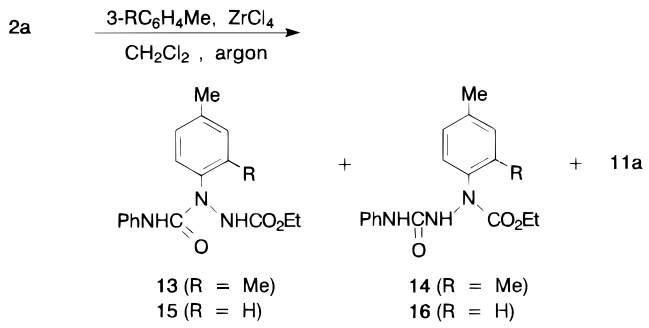
[a] Reactions were carried out at room temperature. [b] Isolated yields are given. [c] R^1 = $N(NHCO_2Me)CONHC_6H_4$(4-OMe).

Scheme 2



the formation of three products: two regioisomers regarding the diazene nitrogen, attached directly to the xylene ring (**13** and **14**), as well as *N*-aminobenzimidazole-2-one **11a** (Scheme 3). An intermolecular process, which gave almost equal amounts of **13** and **14**, obviously dominated over an intramolecular one. The formation of **11a** could not be avoided, although the experiment has been performed with a 20-fold excess of *m*-xylene. Similar amination of toluene with **2a** also gave three compounds: **15**, **16**, and **11a**. Aminated toluene derivative **15** was isolated as a minor product, contrary to reactions of diazenes with more electron-rich arenes, where only

Scheme 3



regioisomers of type **15** were formed. We have differentiated between regioisomers **13** and **14** or between **15** and **16** by mass spectrometry. Products **13** and **15** showed fragments ($M^+ - PhNCO$); signals for ($M^+ - ArNCO$) always appeared for the regioisomers of type **3**, **7**−**10**, and **12**. On the other hand, mass spectra of aminated xylene **14** and its toluene analogue **16** exhibited signals for ($M^+ - PhNCO$) but also peaks that seemed to belong to $(PhNHCONHNHAr)^+$ as supported by HRMS. (Fragment from **14**: $C_{15}H_{17}N_3O$ calcd 255.1372, found 255.1364; fragment from **16**: $C_{14}H_{15}N_3O$, calcd 241.1215, found 241.1206). The latter fragmentation has never been observed for the other regioisomers discussed above. Finally, a treatment of benzene with **2a** in the presence of $ZrCl_4$ led exclusively to the formation of **11a**. Benzene was obviously not reactive enough to compete with an intramolecular process that gave benzimidazolone **11a**.

Conclusion

In conclusion, diazenes **2** were synthesized and introduced as new and convenient reagents for the regioselective electrophilic amination of various electron-rich arenes in the presence of $ZrCl_4$. The products can serve as easily available precursors of a number of aryl-substituted hydrazines, ureas, 1,2,4-triazolinediones, etc. In the absence of the arene, intramolecular reaction of **2** takes place. The latter process opens a simple and general entry to *N*-aminobenzimidazole-2-ones from aryl isocyanates via semicarbazides **1** and alkyl arylaminocarbonyldiazenecarboxylates **2**.

Experimental Section

General. Melting points are uncorrected. IR spectra were measured as KBr pellets. NMR spectra were recorded at 300.13 and 75.5 MHz, respectively, in DMSO-d_6 unless stated otherwise. Mass spectra were obtained on a VG-Analytical AutospecQ instrument. Elemental analyses (C, H, N) were performed in our analytical laboratory.

Typical Procedure for the Synthesis of Diazenes 2. NBS (0.934 g, 5.25 mmol) was slowly added to a stirred suspension of semicarbazide **1c** (1.186 g, 5 mmol) in CH_2Cl_2 (25 mL) and pyridine (0.791 g, 10 mmol) at room temperature. The reaction mixture was then stirred at room temperature for an additional 25 min, and H_2O was added (17 mL), followed by the addition of concentrated HCl (8 mL). The two phases were separated; the CH_2Cl_2 solution was treated with a solution of sodium thiosulfate pentahydrate (0.5 g) in H_2O (25 mL), saturated aqueous $NaHCO_3$ (25 mL), and H_2O (25 mL) and dried over anhydrous Na_2SO_4. Solvent was evaporated to dryness to afford **2c** (1.150 g, 98% yield). For reaction times and isolated yields of other products of type **2**, see Table 1.

Ethyl phenylaminocarbonyldiazenecarboxylate (2a): mp 80−81 °C (petroleum ether−benzene), lit.[4] mp 83−84 °C; ^1H NMR ($CDCl_3$) δ 1.46 (t, 3H, J = 7.2 Hz), 4.54 (q, 2H, J = 7.2 Hz), 7.25 (m, 1H), 7.43 (m, 2H), 7.67 (m, 2H), 8.32 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 65.5, 119.8, 126.1, 129.4, 136.0, 155.2, 161.6.

Isobutyl phenylaminocarbonyldiazenecarboxylate (2b): mp 50−54 °C (petroleum ether−ethyl acetate); IR 3300, 1750, 1720, 1230 cm^{-1}; ^1H NMR δ 0.97 (d, 6H, J = 6.8 Hz), 2.07 (m, 1H), 4.28 (d, 2H, J_1 = 6.8 Hz), 7.21 (m, 1H), 7.43 (m, 2H), 7.73 (m, 2H), 11.52 (s, 1H); ^{13}C NMR δ 18.4, 27.3, 74.5, 119.7, 125.1, 129.1, 137.2, 157.0, 161.5; MS (FAB) m/z 250 (M^+ + H, 35), 150 (30), 57 (100). Anal. Calcd for $C_{12}H_{15}N_3O_3$: C, 57.82; H, 6.07; N, 16.86. Found: C, 58.08; H, 6.30; N, 16.79.

Ethyl (4-tolyl)aminocarbonyldiazenecarboxylate (2c): mp 66.5−68 °C (toluene); IR 3280, 1760, 1730, 1240 cm^{-1}; ^1H NMR δ 1.37 (t, 3H, J = 7.2 Hz), 2.30 (s, 3H), 4.51, (q, 2H, J = 7.2 Hz), 7.23 (m, 2H), 7.62 (m, 2H), 11.44 (s, 1H); ^{13}C NMR δ 13.9, 20.5, 65.3, 119.6, 129.5, 134.3, 134.7, 156.9, 161.4; MS (EI) m/z 235 (M^+, 2), 134 (100), 106 (97); MS (FAB) m/z 236 (M^+ + H, 63), 107 (35). Anal. Calcd for $C_{11}H_{13}N_3O_3$: C, 56.16; H, 5.57; N, 17.86. Found: C, 56.20; H, 5.67; N, 18.05.

Methyl (4-methoxyphenyl)aminocarbonyldiazenecarboxylate (2d): mp 120−121 °C (petroleum ether−ethyl acetate); IR 3300, 1760, 1720, 1250 cm^{-1}; ^1H NMR δ 3.76 (s, 3H), 4.07 (s, 3H), 7.00 (m, 2H), 7.66 (m, 2H), 11.44 (s, 1H); ^{13}C NMR δ 55.2, 55.6, 114.3, 121.1, 130.2, 156.6, 156.7, 161.9; MS (EI) m/z 237 (M^+, 6), 149 (100), 122 (92); MS (FAB) m/z 238 (M^+ + H, 21), 123 (30), 55 (100). Anal. Calcd for $C_{10}H_{11}N_3O_4$: C, 50.63; H, 4.67; N, 17.71. Found: C, 50.44; H, 4.61; N, 17.99.

Ethyl (4-fluorophenyl)aminocarbonyldiazenecarboxylate (2e): mp 97−99 °C (toluene); IR 3290, 1750, 1730, 1500, 1240, 1210 cm^{-1}; ^1H NMR δ 1.38 (t, 3H, J = 7.2 Hz), 4.52 (q, 2H, J = 7.2 Hz), 7.28 (m, 2H), 7.76 (m, 2H) 11.58 (s, 1H); ^{13}C NMR δ 13.9, 65.4, 115.8 (d, J = 22.9 Hz), 121.6 (d, J = 8.0 Hz), 133.6 (d, J = 2.5 Hz), 157.0, 159.1 (d, J = 242.1 Hz), 161.3; MS (EI) m/z 239 (M^+, 6), 138 (100), 110 (89); MS (FAB) m/z 240 (M^+ + H, 66), 168 (34), 104 (64). Anal. Calcd for $C_{10}H_{10}FN_3O_3$: C, 50.21; H, 4.21; N, 17.57. Found: C, 50.05; H, 4.09; N, 17.72.

Ethyl (3-chlorophenyl)aminocarbonyldiazenecarboxylate (2f): mp 49.5−50.5 °C (cyclohexane-toluene); IR 3300, 1780, 1740, 1600, 1250 cm^{-1}; ^1H NMR δ 1.38 (t, 3H, J = 7.2 Hz), 4.53 (q, 2H, J = 7.2 Hz), 7.29 (ddd, 1H, J_1 = 8.0 Hz, J_2 = 2.1 Hz, J_3 = 1.0 Hz), 7.46 (dd, 1H, J_1 = 8.0 Hz, J_2 = 8.2 Hz), 7.66 (ddd, 1H, J_1 = 8.2 Hz, J_2 = 2.0 Hz, J_3 = 1.0 Hz), 7.85 (dd, 1H, J_1 = 2.1 Hz, J_2 = 2.0 Hz), 11.71 (s, 1H); ^{13}C NMR δ 13.9, 65.5, 118.2, 119.2, 124.9, 130.8, 133.4, 138.7, 157.0, 161.2; MS (FAB) m/z 256 (M^+ + H, 16). Anal. Calcd for $C_{10}H_{10}ClN_3O_3$: C, 46.98; H, 3.94; N, 16.44. Found: C, 47.20; H, 3.97; N, 16.36.

Benzyl (3,4-dichlorophenyl)aminocarbonyldiazenecarboxylate (2g): mp 124−126 °C (petroleum ether−ethyl acetate); IR 3360, 1770, 1740, 1270, 1240 cm^{-1}; ^1H NMR δ 5.54 (s, 2H), 7.45 (m, 5H), 7.69 (m, 2H), 8.00 (dd, 1H, J_1 = 2.1 Hz, J_2 = 0.7 Hz), 11.82 (s, 1H); ^{13}C NMR δ 70.5, 119.8, 121.0, 126.9, 128.7, 128.97, 129.00, 131.1, 131.4, 134.1, 137.3, 156.8, 161.0; MS (EI) m/z 351 (M^+, 0.3), 187 (55), 91 (100). Anal. Calcd for $C_{15}H_{11}Cl_2N_3O_3$: C, 51.16, H, 3.15; N, 11.93. Found: C, 50.89; H, 3.18; N, 11.98.

Typical Procedure for the Preparation of 3. A solution of diazene **2a** (221 mg, 1 mmol) and anisole (108 mg, 1 mmol) in CH_2Cl_2 (7 mL) was added dropwise to a stirred suspension of $ZrCl_4$ (257 mg, 1.1 mmol) in CH_2Cl_2 (2 mL) at −30 °C under argon. After 45 min, the reaction mixture was warmed to room temperature, quenched with H_2O (5 mL), and neutralized with saturated $NaHCO_3$. The two phases were separated, and the aqueous solution was extracted with CH_2Cl_2 (4 × 5 mL). The combined CH_2Cl_2 extracts were then dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was treated with petroleum ether−ethyl acetate 5:1 (2 mL), and the solid material was filtered off to give **3a** (280 mg, 85% yield). For reaction temperatures, reaction times, and isolated yields of other products, see Table 2.

1-Ethoxycarbonyl-2-(4-methoxyphenyl)-4-phenylsemicarbazide (3a): mp 132−135 °C (ethyl acetate); IR 3380, 3260, 1720, 1690, 1530, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (t, 3H, J = 7.2 Hz), 3.83 (s, 3H), 4.23 (q, 2H, J = 7.2 Hz), 6.82 (broad s,

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1H), 6.93 (m, 2H), 7.04 (m, 1H), 7.11 (s, 1H), 7.26 (m, 2H), 7.37 (m, 2H), 7.44 (m, 2H); ^{13}C NMR δ 14.3, 55.2, 61.0, 113.6, 120.2, 122.4, 126.4, 128.2, 135.3, 139.4, 154.0, 155.7, 157.1; MS (EI) *m/z* 329 (M^+, 0.2), 210 (100), 137 (66), 122 (36); MS (FAB) *m/z* 330 ($M^+ + H$, 42), 241 (30), 210 (100), 122 (50). Anal. Calcd for $C_{17}H_{19}N_3O_4$: C, 62.00; H, 5.81; N, 12.76. Found: C, 61.81; H, 6.03; N, 12.62.

1-Isobutoxycarbonyl-2-(4-methoxyphenyl)-4-phenylsemicarbazide (3b): mp 143.5−145 °C (petroleum ether−ethyl acetate); IR 3380, 3300, 1730, 1670, 1460, 1250 cm^{-1}; ^{1}H NMR δ 0.88 (d, 6H, J = 5.6 Hz), 1.84 (m, 1H), 3.75 (s, 3H), 3.82 (d, 2H, J = 5.6 Hz), 6.91 (m, 2H), 7.00 (m, 1H), 7.28 (m, 4H), 7.54 (m, 2H), 8.89 (s, 1H), 9.88 (s, 1H); ^{13}C NMR δ 18.8, 27.5, 55.2, 70.8, 113.6, 120.3, 122.4, 126.3, 128.2, 135.3, 139.4, 154.0, 155.9, 157.0; MS (FAB) *m/z* 358 ($M^+ + H$, 55), 238 (100), 122 (51). Anal. Calcd for $C_{19}H_{23}N_3O_4$: C, 63.85; H, 6.49; N, 11.76. Found: C, 63.90; H, 6.63; 11.71.

1-Ethoxycarbonyl-2-(4-methoxyphenyl)-4-(4-tolyl)semicarbazide (3c): mp 167−168 °C (ethyl acetate); IR 3360, 3240, 1750, 1660, 1500, 1240 cm^{-1}; ^{1}H NMR δ 1.17 (t, 3H, J = 7.2 Hz), 2.24 (s, 3H), 3.75 (s, 3H), 4.07 (q, 2H, J = 7.2 Hz), 6.91 (m, 2H), 7.06 (m, 2H), 7.29 (m, 2H), 7.42 (m, 2H), 8.82 (s, 1H), 9.85 (s, 1H); ^{13}C NMR δ 14.3, 20.3, 55.2, 61.0, 113.5, 120.3, 126.3, 128.7, 131.3, 135.4, 136.8, 154.1, 155.7, 157.0; MS (FAB) *m/z* 344 ($M^+ + H$, 34), 210 (100), 122 (40). Anal. Calcd for $C_{18}H_{21}N_3O_4$: C, 62.96; H, 6.16; N, 12.24. Found: C, 62.88; H, 6.12; N, 12.20.

1-Methoxycarbonyl-2,4-bis(4-methoxyphenyl)semicarbazide (3d): mp 173−176 °C (ethyl acetate); IR 3400, 3280, 1760, 1670, 1510, 1240; ^{1}H NMR δ 3.63 (s, 3H), 3.71 (s, 3H), 3.74 (s, 3H), 6.85 (m, 2H), 6.90 (m, 2H), 7.29 (m, 2H), 7.42 (m, 2H), 8.83 (s, 1H), 9.92 (s, 1H); ^{13}C NMR δ 52.2, 55.1, 55.2, 113.5, 113.6, 122.1, 126.3, 132.4, 135.4, 154.2, 154.9, 156.2, 157.0; MS (EI) *m/z* 345 (M^+, 2), 196 (100), 137 (36), 122 (44); MS (FAB) *m/z* 346 ($M^+ + H$, 47), 196 (100), 122 (66). Anal. Calcd for $C_{17}H_{19}N_3O_5$: C, 59.12; H, 5.55; N, 12.17. Found: C, 59.10; H, 5.62; N, 12.14.

1-Ethoxycarbonyl-4-(4-fluorophenyl)-2-(4-methoxyphenyl)semicarbazide (3e): mp 129−131 °C (petroleum ether−ethyl acetate); IR 3380, 3260, 1730, 1690, 1510, 1260 cm^{-1}; ^{1}H NMR δ 1.20 (t, 3H, J = 7.2 Hz), 3.75 (s, 3H), 4.07 (q, 2H, J = 7.2 Hz), 6.91 (m, 2H), 7.10 (m, 2H), 7.30 (m, 2H), 7.55 (m, 2H), 9.00 (s, 1H), 9.88 (s, 1H); ^{13}C NMR δ 14.3, 55.2, 61.0, 113.6, 114.7 (d, J = 22.2 Hz), 122.1 (d, J = 7.6 Hz), 126.4, 135.3, 135.8 (d, J = 2.2 Hz), 154.2, 155.7, 157.1, 157.7 (d, J = 238.8 Hz); MS (FAB) *m/z* 348 ($M^+ + H$, 64), 210 (100), 122 (32). Anal. Calcd for $C_{17}H_{18}FN_3O_4$: C, 58.79; H, 5.22; N, 12.10. Found: C, 59.10; H, 5.36; N, 11.94.

1-Ethoxycarbonyl-4-(3-chlorophenyl)-2-(4-methoxyphenyl)semicarbazide (3f): mp 139−140 °C (petroleum ether−ethyl acetate); IR 3410, 3200, 1760, 1670, 1510, 1230 cm^{-1}; ^{1}H NMR δ 1.20 (t, 3H, J = 7.2 Hz), 3.76 (s, 3H), 4.08 (q, 2H, J = 7.2 Hz), 6.93 (m, 2H), 7.04 (m, 1H), 7.29 (m, 3H), 7.57 (m, 1H), 7.74 (m, 1H), 9.15 (s, 1H), 9.91 (s, 1H); ^{13}C NMR δ 14.3, 55.2, 61.1, 113.6, 118.3, 119.3, 122.0, 126.5, 129.9, 132.7, 135.0, 141.1, 153.9, 155.7, 157.2; MS (EI) *m/z* 363 (M^+, 0.3), 210 (100), 122 (36); MS (FAB) *m/z* 364 ($M^+ + H$, 28), 210 (100), 122 (36). Anal. Calcd for $C_{17}H_{18}ClN_3O_4$: C, 56.13; H, 4.99; N, 11.55. Found: C, 56.12; H, 5.01; N, 11.48.

1-Benzyloxycarbonyl-4-(3,4-dichlorophenyl)-2-(4-methoxyphenyl)semicarbazide (3g): mp 155−157 °C (ethyl acetate); IR 3320, 1740, 1690, 1510, 1260 cm^{-1}; ^{1}H NMR δ 3.76 (s, 3H), 5.12 (s, 2H), 6.92 (m, 2H), 7.29 (m, 7H), 7.52 (d, 1H, J = 8.9 Hz), 7.63 (dd, 1H, J_1 = 8.9 Hz, J_2 = 2.5 Hz), 7.93 (d, 1H, J = 2.5 Hz), 9.31 (s, 1H), 10.11 (s, 1H); ^{13}C NMR δ 55.3, 66.6, 113.7, 119.9, 121.1, 123.8, 126.6, 127.9, 128.1, 128.4, 130.2, 130.6, 134.8, 136.1, 139.8, 153.9, 155.7, 157.4; MS (EI) *m/z* 459 (M^+, 0.4), 272 (37), 137 (98), 91 (100); MS (FAB) *m/z* 460 ($M^+ + H$, 24), 272 (62), 91 (100). Anal. Calcd for $C_{22}H_{19}Cl_2N_3O_4$: C, 57.40; H, 4.16; N, 9.13. Found: C, 57.14; H, 4.08; N, 9.15.

2-Ethoxycarbonyl-(4-methoxyphenyl)hydrazine (4a). Zinc dust (654 mg, 10 mmol) was added at room temperature to a solution of **3a** (329 mg, 1 mmol) in acetic acid (6.5 mL). The suspension was heated under reflux for 4 h and cooled to room temperature, and the solid material was filtered off. The filtrate was neutralized with 10 N NaOH and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was separated by radial chromatography using petroleum ether−ethyl acetate (5:3) as a solvent to give the title compound as a white solid (58 mg, 46%): mp 99.5−100.5 °C (petroleum ether−ethyl acetate); IR 3360, 3240, 1700, 1510, 1230 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (t, 3H, J = 7.0 Hz), 3.75 (s, 3H), 4.19 (q, 2H, J = 7.0 Hz), 5.60 (s, 1H), 6.46 (s, 1H), 6.81 (m, 4H); MS (EI) *m/z* 210 (M^+, 82), 137 (100), 122 (55). Anal. Calcd for $C_{10}H_{14}N_2O_3$: C, 57.13; H, 6.71; N, 13.33. Found: C, 56.90; H, 6.67; N, 13.42.

1-(4-Methoxyphenyl)-3-phenylurea (5a). A mixture of **3a** (329 mg, 1 mmol) and polyphosphoric acid (0.94 g) was heated at 100 °C for 1 h. Water (10 mL) was then added, and the resulting solution was neutralized with $NaHCO_3$ and extracted with CH_2Cl_2 (3 × 15 mL). The combined extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by radial chromatography using petroleum ether−ethyl acetate (5:2) as a solvent to afford **5a** as a white solid (102 mg, 42%): mp 193−194 °C (ethyl acetate), lit.[6] mp 193−194 °C; ^{1}H NMR δ 3.71 (s, 3H), 6.86 (m, 2H), 6.94 (m, 1H), 7.26 (m, 2H), 7.35 (m, 2H), 7.43 (m, 2H), 8.43 (s, 1H), 8.54 (s, 1H); MS (EI) *m/z* 242 (M^+, 81), 123 (100), 108 (91), 93 (69).

1-(Methoxyphenyl)-4-phenyl-1,2,4-triazoline-3,5-dione (6a). A solution of **3a** (165 mg, 0.5 mmol) and NaOH (40 mg, 10 mmol) in water−ethanol (1:5, 6 mL) was stirred at room temperature for 1 h. The solution was neutralized with 3 N HCl, extracted with CH_2Cl_2 (3 × 10 mL), and dried over anhydrous Na_2SO_4. The solvent was evaporated at a reduced pressure to give **6a** as a white solid (88 mg, 87%): mp 172−174 °C (ethyl acetate), lit.[7] mp 174 °C; ^{13}C NMR δ 55.6, 114.6, 121.9, 126.8, 128.4, 129.2, 129.7, 131.7, 150.0, 152.4, 157.3; MS (EI) *m/z* 283 (M^+, 100), 121 (87); HRMS calcd for $C_{15}H_{13}N_3O_3$ 283.0957, found 283.0966.

Typical Procedure for the Preparation of Semicarbazides 7−10. Aminated products **7**−**10** were obtained following the same procedure as described for the preparation of aminated anisoles **3**, using 1,3,5-trimethoxybenzene, methyl 2,4-dimethoxybenzoate, 2-methoxynaphthalene, or ethyl indole-2-carboxylate instead of anisole. For the selection of the appropriate diazene of type **2**, as well as for reaction temperatures, reaction times, and isolated yields, see Chart 1.

1-Ethoxycarbonyl-4-(4-fluorophenyl)-2-(2,4,6-trimethoxyphenyl)semicarbazide (7e): mp 118−121 °C (petroleum ether−ethyl acetate); IR 3380, 1730, 1700, 1620, 1220, 1140 cm^{-1}; ^{1}H NMR δ 1.17 (t, 3H, J = 7.2 Hz), 3.74 (s, 6H), 3.79 (s, 3H), 4.03 (q, 2H, J = 7.2 Hz), 6.24 (s, 2H), 7.07 (m, 2H), 7.53 (m, 2H), 8.61 (broad s, 1H), 8.79 (s, 1H); ^{13}C NMR δ 14.4, 55.3, 55.8, 60.5, 91.2, 112.2, 114.7 (d, J = 21.8 Hz), 121.2 (d, J = 8.0 Hz), 136.2 (d, J = 2.9 Hz), 154.2, 155.4, 157.0, 157.4 (d, J = 238.4 Hz), 160.1; MS (FAB) *m/z* 408 ($M^+ + H$, 21), 319 (47), 270 (100). Anal. Calcd for $C_{19}H_{22}FN_3O_6$: C, 56.02; H, 5.44; N, 10.31. Found: C, 55.89; H, 5.48; N, 10.46.

4-(3-Chlorophenyl)-1-ethoxycarbonyl-2-(2,4-dimethoxy-5-methoxycarbonylphenyl)semicarbazide (8f): mp 191−194 °C (ethyl acetate), IR 3320, 1720, 1700, 1240 cm^{-1}; ^{1}H NMR δ 1.19 (t, 3H, J = 7.2 Hz), 3.74 (s, 3H), 3.88 (s, 3H), 3.90 (s, 3H), 4.07 (q, 2H, J = 7.2 Hz), 6.75 (s, 1H), 7.02 (ddd, 1H, J_1 = 8.0 Hz, J_2 = 2.1 Hz, J_3 = 1.0 Hz), 7.27 (dd, 1H, J_1 = J_2 = 8.0 Hz), 7.52 (m, 1H), 7.70 (dd, 1H, J_1 = J_2 = 2.1 Hz), 7.81 (s, 1H), 9.01 (s, 1H), 9.63 (s, 1H); ^{13}C NMR δ 14.3, 51.5, 56.1, 56.2, 61.0, 97.3, 110.3, 118.0, 119.1, 121.9, 122.5, 129.9, 132.4, 132.7, 141.2, 154.0, 155.9, 159.6, 160.3, 164.8; MS (FAB) *m/z* 452 ($M^+ + H$, 32), 298 (100), 210 (34). Anal. Calcd for $C_{20}H_{22}ClN_3O_7$: C, 53.16; H, 4.91; N, 9.30. Found: C, 53.37; H, 4.97; N, 9.01.

1-Ethoxycarbonyl-2-(2-methoxy-1-naphthyl)-4-(4-tolyl)-semicarbazide (9c): mp 135−136.5 °C (petroleum ether−ethyl acetate); IR 3440, 3260, 1750, 1700, 1520, 1280, 1240 cm^{-1}; ^{1}H NMR δ 1.15 (t, 3H, J = 7.1 Hz), 2.24 (s, 3H), 3.91 (s, 3H), 4.05 (q, 2H, J = 7.1 Hz), 7.06 (m, 2H), 7.39 (m, 3H), 7.48 (m, 2H), 7.87 (m, 1H), 7.96 (m, 1H), 8.32 (m, 1H), 8.71 (broad s, 1H), 9.26 (s, 1H); ^{13}C NMR δ 14.3, 20.3, 56.3, 60.8, 114.0, 119.9, 120.0, 123.5, 123.8, 126.3, 127.4, 128.6, 128.7, 129.6, 131.2, 131.9, 137.0, 152.9, 154.9, 156.0; MS (FAB) *m/z* 394 ($M^+ + H$, 40), 260 (100). Anal. Calcd for $C_{22}H_{23}N_3O_4$: C, 67.16; H, 5.89; N, 10.68. Found: C, 67.33; H, 5.95; N, 10.78.

(7) Wamhoff, H.; Wald, K. *Chem. Ber.* **1977**, *110*, 1699−1715.

1-Methoxycarbonyl-2-(2-methoxy-1-naphthyl)-4-(4-methoxyphenyl)semicarbazide (9d): mp 208−209 °C (ethyl acetate); IR 3400, 3360, 1770, 1690, 1520, 1240 cm^{-1}; ^1H NMR δ 3.58 (s, 3H), 3.70 (s, 3H), 3.92 (s, 3H), 6.83 (m, 2H), 7.38 (m, 3H), 7.48 (m, 2H), 7.86 (m, 1H), 7.96 (m, 1H), 8.29 (m, 1H), 8.66 (broad s, 1H), 9.32 (s, 1H); ^{13}C NMR δ 52.0, 55.1, 56.3, 113.5, 114.0, 121.8, 123.6, 123.8, 123.9, 126.3, 127.4, 128.6, 129.6, 132.0, 132.5, 152.9, 154.8, 155.1, 156.5; MS (FAB) *m/z* 396 ($M^+ + H$, 41), 246 (100), 122 (35). Anal. Calcd for $C_{21}H_{21}N_3O_5$: C, 63.79; H, 5.35; N, 10.63. Found: C, 63.73; H, 5.38; N, 10.49.

1-Ethoxycarbonyl-2-(2-ethoxycarbonyl-3-indolyl)-4-phenylsemicarbazide (10a): mp 189−190 °C (ethyl acetate); IR 3360, 1730, 1680, 1530, 1440, 1230 cm^{-1}; ^1H NMR δ 1.17 (t, 3H, J = 7.2 Hz), 1.21 (t, 3H, J = 7.2 Hz), 4.08 (q, 2H, J = 7.2 Hz), 4.25 (q, 2H, J = 7.2 Hz), 6.96 (m, 1H), 7.10 (m, 1H), 7.26 (m, 3H), 7.45 (m, 1H), 7.53 (m, 2H), 7.81 (m, 1H), 8.84 (s, 1H), 9.25 (s, 1H), 11.92 (s, 1H); ^{13}C NMR δ 13.9, 14.4, 60.6, 61.0, 112.6, 119.8, 119.9, 120.3, 120.9, 122.3, 122.6, 124.3, 125.0, 128.2, 134.9, 139.7, 154.5, 156.3, 160.7; MS (FAB) *m/z* 411 ($M^+ + H$, 48), 291 (100), 203 (68). Anal. Calcd for $C_{21}H_{22}N_4O_5$: C, 61.46; H, 5.40; N, 13.65. Found: C, 61.34; H, 5.43; N, 13.63.

2-(2-Ethoxycarbonyl-3-indolyl)-1-isobutoxylcarbonyl-4-phenylsemicarbazide (10b): mp 182−184 °C (ethyl acetate); IR 3360, 1730, 1690, 1540, 1210 cm^{-1}; ^1H NMR δ 0.84 (d, 6H, J = 6.8 Hz), 1.21 (t, 3H, J = 7.2 Hz), 1.84 (m, 1H), 3.83 (d, 2H, J = 6.4 Hz), 4.26 (q, 2H, J = 7.2 Hz), 6.96 (m, 1H), 7.09 (m, 1H), 7.25 (m, 3H), 7.45 (m, 1H), 7.52 (m, 2H), 7.80 (m, 1H), 8.79 (s, 1H), 9.27 (s, 1H), 11.91 (s, 1H); ^{13}C NMR δ 13.9, 18.7, 27.5, 60.6, 70.8, 112.6, 119.8, 119.9, 120.2, 120.8, 122.2, 122.5, 124.2, 124.9, 128.2, 134.8, 139.7, 154.3, 156.3, 160.6; MS (FAB) *m/z* 439 ($M^+ + H$, 32), 319 (100), 203 (91). Anal. Calcd for $C_{23}H_{26}N_4O_5$: C, 63.00; H, 5.98; N,12.78. Found: C, 63.12; H, 6.10; N, 12.83.

Typical Procedure for the Formation of 11−12. A solution of diazene **2b** (249 mg, 1 mmol) in CH_2Cl_2 (7 mL) was added dropwise to a stirred suspension of $ZrCl_4$ (257 mg, 1.1 mmol) in CH_2Cl_2 (2 mL) at room temperature under argon. After 22 h, the reaction mixture was quenched with H_2O (5 mL) and neutralized with saturated $NaHCO_3$. Isolation of the product, which was carried out as described above for the synthesis of **3a**, led to **11b** (201 mg, 81% yield). For reaction times and isolated yields of other products, see Table 3.

1-Ethoxycarbonylamino-2(3*H*)-benzimidazolone (11a): mp 197−199 °C (ethyl acetate); IR 3260, 1740, 1700, 1510, 1260 cm^{-1}; ^1H NMR δ 1.25 (t, 3H, J = 6.9 Hz), 4.15 (q, 2H, J = 6.9 Hz), 6.99 (m, 4H), 10.14 (s, 1H), 11.00 (s, 1H); ^{13}C NMR δ 14.3, 61.4, 106.9, 109.3, 122.0, 121.7, 126.4, 130.1, 152.7, 155.4; MS (EI) *m/z* 221 (M^+, 81), 175 (38), 148 (100), 133 (40), 106 (43); HRMS calcd for $C_{10}H_{11}N_3O_3$ 221.0800, found 221.0804. Anal. Calcd for $C_{10}H_{11}N_3O_3$: C, 54.30; H, 5.01; N, 19.00. Found: C, 54.06; H, 5.08; N, 18.99.

1-Isobutoxycarbonylamino-2(3*H*)-benzimidazolone (11b): mp 113−118 °C (petroleum ether−ethyl acetate); IR 3340, 1710, 1480, 1230 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (m, 6H), 1.92 (m, 1H), 3.98 (d, 2H, J = 6.4 Hz), 7.08 (m, 4H), 7.49 (s, 1H), 9.24 (s, 1H); ^{13}C NMR δ 18.7, 27.6, 71.1, 106.9, 109.3, 121.0, 121.7, 126.3, 130.1, 152.7, 155.6; MS (EI) *m/z* 249 (M^+, 51), 149 (100), 133 (30); HRMS calcd for $C_{12}H_{15}N_3O_3$ 249.1113, found 249.1121. Anal. Calcd for $C_{12}H_{15}N_3O_3$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.64; H, 5.97; N, 16.97.

1-Ethoxycarbonylamino-6-methyl-2(3*H*)-benzimidazolone (11c): mp 224−228 °C (MeOH); IR 3220, 1750, 1680, 1510, 1230 cm^{-1}; ^1H NMR δ 1.25 (t, 3H, J = 7.0 Hz), 2.30 (s, 3H), 4.14 (q, 2H, J = 7.0 Hz), 6.74 (m, 1H), 6.83 (ddd, 1H, J_1 = 7.9 Hz, J_2 = 0.7 Hz, J_3 = 1.6 Hz), 6.88 (dd, 1H, J_1 = 7.9 Hz, J_2 = 0.4 Hz), 10.11 (s, 1H), 10.87 (s, 1H); ^{13}C NMR δ 14.3, 20.9, 61.4, 107.4, 109.0, 122.1, 124.1, 130.1, 130.2, 152.8, 155.4; MS (EI) *m/z* 235 (M^+, 92), 189 (42), 162 (100), 147 (47); HRMS calcd for $C_{11}H_{13}N_3O_3$ 235.0957, found 235.0962. Anal. Calcd for $C_{11}H_{13}N_3O_3$: C, 56.16; H, 5.57; N, 17.86. Found: 56.21; H, 5.64; N, 17.87.

1-Ethoxycarbonylamino-6-fluoro-2(3*H*)-benzimidazolone (11e): mp 146−152 °C (ethyl acetate); IR 3260, 1740, 1710, 1680, 1490, 1260 cm^{-1}; ^1H NMR δ 1.26 (t, 3H, J = 7.1 Hz), 4.15 (q, 2H, J = 7.1 Hz), 6.85 (m, 2H), 6.99 (m, 1H), 10.20 (s, 1H), 11.07 (s, 1H); ^{13}C NMR δ 14.3, 61.5, 95.4 (d, J = 29.1 Hz), 107.9 (d, J = 24.0 Hz), 110.0 (d, J = 9.1 Hz), 122.6 (d, J = 1.1 Hz), 130.9 (d, J = 13.1 Hz), 153.1, 155.3, 157.9 (d, J = 235.9 Hz); MS (EI) *m/z* 239 (M^+, 86), 167 (100), 151 (47); HRMS calcd for $C_{10}H_{10}FN_3O_3$ 239.0706, found 239.0712. Anal. Calcd for $C_{10}H_{10}FN_3O_3$: C, 50.21; H, 4.21; N, 17.57. Found: C, 50.13; H, 4.18; N, 17.80.

1-Ethoxycarbonylamino-5-chloro-2(3*H*)-benzimidazolone (11f): mp 214−218 °C (ethyl acetate); IR 3280, 1740, 1720, 1680, 1500, 1270 cm^{-1}; ^1H NMR δ 1.25 (t, 3H, J = 6.8 Hz), 4.15 (q, 2H, J = 6.8 Hz), 6.95 (d, 1H, J = 8.9 Hz), 7.06 (d, 1H, J = 2.0 Hz), 7.06 (dd, 1H, J_1 = 8.9 Hz, J_2 = 2.0 Hz), 10.28 (s, 1H), 11.21 (broad s, 1H); ^{13}C NMR δ 14.3, 61.5, 108.2, 109.3, 120.8, 125.8, 127.5, 129.0, 152.6, 155.3; MS (EI) *m/z* 255 (M^+, 79), 182 (100), 167 (43); HRMS calcd for $C_{10}H_{10}ClN_3O_3$ 255.0411, found 255.0418. Anal. Calcd for $C_{10}H_{10}ClN_3O_3$: C, 46.98; H, 3.94; N, 16.44. Found: C, 46.83; H, 3.96; N, 16.16.

1-Methoxycarbonyl-2-(6-methoxy-1-methoxycarbonylamino-2(3*H*)-benzimidazolone-5-yl)-4-methoxyphenylsemicarbazide (12d): mp 231−233 °C (ethyl acetate); IR 3300, 3180, 1720, 1670, 1510, 1240 cm^{-1}; ^1H NMR δ 3.61 (s, 3H), 3.70 (s, 3H), 3.72 (s, 3H), 3.75 (s, 3H), 6.70 (s, 1H), 6.83 (m, 2H), 7.06 (s, 1H), 7.39 (m, 2H), 8.59 (s, 1H), 9.53 (s, 1H), 10.23 (s, 1H), 10.87 (s, 1H); ^{13}C NMR δ 52.1, 52.7, 55.1, 56.4, 92.8, 111.0, 113.5, 118.7, 121.7, 124.7, 130.1, 132.6, 151.2, 152.9, 154.5, 154.8, 155.9, 156.6; MS (FAB) *m/z* 475 ($M^+ + H$, 27), 325 (73), 122 (34); HRMS (FAB) calcd for $C_{20}H_{23}N_6O_8$ 475.1577, found 475.1593. Anal. Calcd for $C_{20}H_{22}N_6O_8$ x 0.5 H_2O: C, 49.69; H, 4.80; N, 17.38. Found: C, 49.80; H, 4.71; N, 17.38.

Reaction of 2a with *m*-Xylene. A solution of **2a** (442 mg, 2 mmol) and *m*-xylene (4.92 mL, 40 mmol) in CH_2Cl_2 (14 mL) was added dropwise to a stirred suspension of $ZrCl_4$ (513 mg, 2.2 mmol) in CH_2Cl_2 (4 mL) at 0 °C under argon. After 3 h, the reaction mixture was warmed to room temperature, quenched with H_2O (10 mL), and neutralized with aqueous solution of $NaHCO_3$. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The products were separated by radial chromatography using petroleum ether−ethyl acetate (5:2) to give **13** (298 mg, 46%), **14** (269 mg, 41%), and **11a** (17 mg, 4%).

1-Ethoxycarbonyl-2-(2,4-dimethylphenyl)-4-phenylsemicarbazide (13): mp 64−67 °C (petroleum ether−ethyl acetate); IR 3410, 3220, 1750, 1680, 1520, 1230 cm^{-1}; ^1H NMR δ 1.18 (t, 3H, J = 7.1 Hz), 2.24 (s, 3H), 2.27 (s, 3H), 4.06 (q, 2H, J = 7.1 Hz), 6.99 (m, 3H), 7.26 (m, 3H), 7.53 (m, 2H), 8.81 (s, 1H), 9.88 (s, 1H); ^{13}C NMR δ 14.3, 17.7, 20.5, 60.9, 120.1, 122.4, 126.6, 126.9, 128.3, 130.8, 136.0, 136.5, 138.9, 139.5, 153.8, 155.9; MS (FAB) *m/z* 328 ($M^+ + H$, 62), 208 (100), 120 (76); HRMS (FAB) calcd for $C_{18}H_{22}N_3O_3$ ($M^+ + H$) 328.1661, found 328.1672. Anal. Calcd for $C_{18}H_{21}N_3O_3$: C, 66.04; H, 6.47; N, 12.84. Found: C, 65.99; H, 6.66; N, 12.68.

1-Ethoxycarbonyl-1-(2,4-dimethylphenyl)-4-phenylsemicarbazide (14): mp 156−157.5 °C (petroleum ether−ethyl acetate); IR 3300, 1680, 1600, 1540, 1220 cm^{-1}; ^1H NMR δ 1.18 (t, 3H J = 7.1 Hz), 2.24 (s, 3H), 2.26 (s, 3H), 4.10 (q, 2H, J = 7.1 Hz), 6.99 (m, 3H), 7.25 (m, 2H), 7.33 (d, 1H, J = 8 Hz), 7.43 (m, 2H), 8.73 (s, 1H), 8.93 (s, 1H); ^{13}C NMR δ 14.6, 17.4, 20.6, 61.9, 118.5, 122.2, 127.0, 127.4, 128.8, 131.0, 134.9, 137.0, 138.9, 139.5, 154.8, 155.2; MS (FAB) *m/z* 328 ($M^+ + H$, 60), 208 (94), 192 (100), 120 (35). Anal. Calcd for $C_{18}H_{21}N_3O_3$: C, 66.04; H, 6.47; N, 12.84. Found: C, 66.00; H, 6.63; N, 12.81.

Reaction of 2a with Toluene. This was performed as described above for the amination of *m*-xylene, using toluene, **2a**, and $ZrCl_4$. Reaction time: 16 h; isolated products: **15** (33 mg, 5%), **16** (267 mg, 41%), and **11a** (188 mg, 42%).

1-(Ethoxycarbonyl)-4-phenyl-2-(4-tolyl)semicarbazide (15): mp 54.5−57.5 °C (petroleum ether−ethyl acetate); IR 3300, 1740, 1680, 1530, 1430, 1220 cm^{-1}; ^1H NMR δ 1.26 (t, 3H, J = 7.1 Hz), 2.37 (s, 3H), 4.22 (q, 2H, J = 7.1 Hz), 6.94 (s, 1H), 7.04 (m, 1H), 7.24 (m, 5H), 7.37 (m, 4H); MS (FAB) *m/z* 314 ($M^+ + H$, 59), 194 (100); HRMS (FAB) calcd for $C_{17}H_{20}N_3O_3$ ($M^+ + H$) 314.1505, found 314.1492. Anal. Calcd for $C_{17}H_{19}N_3O_3$: C, 65.16; H, 6.11; N, 13.41. Found: C, 65.40; H, 6.11; N, 13.48.

1-(Ethoxycarbonyl)-4-phenyl-1-(4-tolyl)semicarbazide (16): mp 152−153 °C (petroleum ether−ethyl acetate); IR 3380, 3280, 1700, 1670, 1530, 1340 cm^{-1}; ^1H NMR δ 1.18 (t, 3H, J = 7.2 Hz), 2.28 (s, 3H), 4.14 (q, 2H, J = 7.2 Hz), 6.96 (m, 1H), 7.15 (m, 2H), 7.25 (m, 2H), 7.34 (m,2H), 7.45 (m, 2H), 8.90 (s, 1H), 8.92 (s, 1H); ^{13}C NMR δ 14.3, 20.4, 61.9, 118.5, 122.0, 123.6, 128.6, 128.7, 134.6, 139.4, 140.2, 154.67, 154.74; MS (FAB) *m/z*

314 ($M^+ + H$, 68), 195 (100), 194 (85), 178 (47), 121 (46). Anal. Calcd for $C_{17}H_{19}N_3O_3$: C, 65.16; H, 6.11; N, 13.41. Found: C, 65.03; H, 6.19; N, 13.39.

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