H, 10.56. Found: C, 76.64; H, 10.81.

(7*R*)-7-(Benzyloxy)heptadec-1-en-6-one (14) was prepared similarly in 85% yield by the Collins oxidation of the alcohols **10** (oxathiane precursor de >98%): $[\alpha]^{20}_{D}$ +42.9° (*c* 2.13, $CHCl_3$), also $[\alpha]^{20}_{578}$ +45.0°, $[\alpha]^{20}_{546}$ +51.6°, $[\alpha]^{20}_{436}$ +96.4%, $[\alpha]^{20}_{365}$ +194°; ^1H NMR (250 MHz) δ 7.36–7.29 (m, 5 H), 5.75 (ddt, 1 H, *J* = 17.0, 10.3, 6.6 Hz), 5.04–4.93 (m, 2 H), 4.54, 4.39 (AB q, 2 H, *J* = 11.7 Hz), 3.76 (dd, 1 H, *J* = 7.5, 5.3 Hz), 2.53 (t, 2 H, *J* = 7.3 Hz), 2.05 (apparent q, 2 H, *J* = 7 Hz), 1.73–1.58 (m, 2 H), and others; ^{13}C NMR (62.89 MHz) δ 212.6, 137.9, 137.7, 128.4, 127.8, 115.1, 85.1, 72.4, 36.8, 33.2, 32.2, 31.9, 29.6, 29.4, 29.3, 25.3, 22.7, 22.3, 14.1; IR cm^{-1} 2920 vs, 2860 s, 1720 vs, 1460 s, 1100 s, and others.

(6*R*,7*S*)-6-(Benzyloxy)-7-(benzyloxy)-1-heptadecene (16). To a mixture of 0.35 g (0.97 mmol) of (6*R*,7*S*)-7-(benzyloxy)-heptadec-1-en-6-ol (**10**, oxathiane precursor de >98%), 0.24 g (1.97 mmol) of benzoic acid and 0.51 g (1.94 mmol) of triphenylphosphine in 5 mL of dry THF was added 0.36 g (1.96 mmol) of diethyl azodicarboxylate (DEAD) over 5 min at 0 °C. The yellow color of DEAD disappeared. The solution was stirred for 1 h at 0 °C. THF was removed under vacuum, and 50 mL of hexanes was added to the residue to dissolve the products soluble in hexanes. The hexanes solution was decanted and concentrated. The residue was subject to flash chromatography [hexanes–ethyl acetate (40:1)] to give 0.35 g (78%) of the benzoate **16** as an oil: $[\alpha]^{20}_{D}$ -8.1° (*c* 0.60, $CHCl_3$); ^1H NMR (250 MHz) δ 8.04 (d, 2 H, *J* = 7.9 Hz), 7.56–7.38 (m, 3 H), 7.32–7.18 (m, 5 H), 5.76 (ddt, 1 H, *J* = 17.0, 10.3, 6.6 Hz), 5.30 (dt, 1 H, *J* = 9.4, 3.0 Hz), 4.99 (d, 1 H, *J* = 17.0 Hz), 4.93 (d, 1 H, *J* = 10.2 Hz), 4.69, 4.50 (AB q, 2 H, *J* = 11.6 Hz), 3.60–3.57 (m, 1 H), 2.14–2.01 (m, 2 H) and others; ^{13}C NMR (62.89 MHz) δ 166.2, 138.6, 138.3, 132.8, 130.5, 129.6, 128.3, 128.2, 127.9, 127.5, 114.8, 80.4, 75.9, 72.5, 33.5, 31.9, 31.0, 29.6, 29.3, 28.7, 25.9, 25.1, 22.7, 14.1; IR (cm^{-1}) 2900 vs, 2860 vs, 1730 s, 1720 vs, 1440 m, 1270 vs, 1170 m, and others.

(6*S*,7*S*)-6-(Benzyloxy)-7-(benzyloxy)-1-heptadecene (16) was prepared by the benzoylation (benzoic anhydride, pyridine) of the (6*S*,7*S*)-alcohol **10**: ^1H NMR (250 NMR) δ 8.04 (d, 2 H, *J* = 8.0 Hz), 7.58–7.42 (m, 3 H), 7.34–7.28 (m, 5 H), 5.76 (ddt, 1 H, *J* = 17.0, 10.2, 6.7 Hz), 5.31 (dt, 1 H, *J* = 8.5, 4.4 Hz), 4.99 (d, 1 H, *J* = 17.0 Hz), 4.94 (d, 1 H, *J* = 10.2 Hz), 4.65, 4.62 (AB q, 2 H, *J* = 11.6 Hz), 3.60–3.53 (m, 1 H), 2.12–2.03 (m, 2 H) and others.

(5*R*,6*S*)-5-(Benzyloxy)-6-(benzyloxy)hexadecanal (33) was prepared in 81% yield by ozonolysis of (6*R*,7*S*)-6-(benzyloxy)-7-(benzyloxy)-1-heptadecene (**16**): $[\alpha]^{20}_{D}$ -6.1° (*c* 1.65, $CHCl_3$); ^1H NMR (250 MHz) δ 9.71 (t, 1 H, *J* = 1.3 Hz), 8.06 (d, 1 H, *J* = 7.9 Hz), 7.57–7.40 (m, 3 H), 7.33–7.22 (m, 5 H), 5.29 (dt, 1 H, *J* = 9.4, 3.0 Hz), 4.71, 4.52 (AB q, 2 H, *J* = 11.5 Hz), 3.63–3.60 (m, 1 H), 2.50–2.42 (m, 2 H), and others; ^{13}C NMR (62.89 MHz) δ 201.7, 166.1, 138.5, 132.9, 130.3, 129.6, 128.4, 128.3, 127.9, 127.5, 80.3, 75.6, 72.6, 43.5, 31.9, 29.6, 29.3, 28.8, 25.8, 22.7, 18.4, 14.1; IR cm^{-1} 2920 vs, 2860 s, 1730 vs, 1720 s, 1450 m, 1270 s, 1170 m, and others.

(5*R*,6*S*)-5-(Benzyloxy)-6-(benzyloxy)hexadecanoic acid (34) was prepared by the sodium chlorite oxidation of (5*R*,6*S*)-aldehyde **33**: ^1H NMR (250 MHz) δ 8.06 (d, 2 H, *J* = 7.9 Hz), 7.58–7.40 (m, 3 H), 7.30–7.24 (m, 5 H), 5.32–5.26 (m, 1 H), 4.71,4.52 (AB q, 2 H, *J* = 11.5 Hz), 3.64–3.58 (m, 1 H), 2.41–2.36 (m, 1 H), and others.

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Selective Reactions of Azide-Substituted α-Diazo Amides with Olefins and Alcohols Using Rhodium(II) Catalysts

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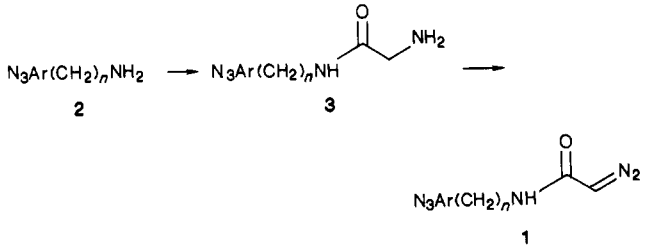
The synthesis and addition of azide-substituted α-diazo amides such as *N*-(4-azidophenyl)-α-diazoacetamide and *N*-(4-azido-2-hydroxyphenyl)-α-diazoacetamide to olefins and alcohols using either rhodium(II) acetate or preferably rhodium(II) pivalate provided cyclopropanecarboxamides and α-alkoxy amides, respectively, without disrupting the azide functionality. These azide-bearing α-diazo amides are potentially useful in the preparation of photoaffinity cross-linking reagents for studying the mechanism of action of natural products.

In connection with the development of photoaffinity reagents[1] for studying the mechanism of action of natural products, we required a synthesis of various α-diazo amide reagents **1** bearing an aryl azide group and possessing the capacity for radioiodination.[2] The selection of the α-diazo amide functionality rather than the corresponding α-diazo ester functionality was based on the anticipated stability of the amide linkage relative to the ester linkage in the ultimate products of the cross-linking experiments. Although the reactions of α-diazo esters with olefins[3] and alcohols[4] have been investigated in some detail, the analogous synthesis and reactions of α-diazo amides **1** have been largely neglected.[5] As a consequence, we needed to develop an acceptable route to azide-substituted α-diazo amides **1** and to demonstrate the selective manipulation of the α-diazo amide functionality in the presence of an azide group.

(1) Bayley, H. *Photogenerated Reagents in Biochemistry and Molecular Biology*; Elsevier: New York, 1983.
(2) Seevers, R. H.; Counsell, R. E. *Chem. Rev.* **1982**, *82*, 575.
(3) (a) Noels, A. F.; Hubert, A. J.; Anciaux, A. J.; Petiniot, N.; Teyssie, P. *J. Org. Chem.* **1980**, 45, 695. (b) Hubert, A. J.; Noels, A. F.; Anciaux, A. J.; Teyssie, P. *Synthesis* **1976**, 600. (c) Doyle, M. P.; Leusen, D. V.; Tamblyn, W. H. *Synthesis* **1981**, 787.
(4) Paulissen, R.; Reimlinger, H.; Hayez, E.; Hubert, A. J.; Teyssie, P. *Tetrahedron Lett.* **1973**, *14*, 2233.
(5) (a) Kirmse, W.; Horner, L. *Liebigs Ann. Chem.* **1959**, *625*, 34. (b) Rando, R. R. *J. Am. Chem. Soc.* **1970**, 92, 6706. (c) Franich, R. A.; Lowe, G.; Parker, J., *J. Chem. Soc., Perkin Trans. 1* **1972**, 2034. (d) Tomioka, H.; Kondo, M.; Izawa, Y. *J. Org. Chem.* **1981**, *46*, 1090. (e) Wydila, J.; Thornton, E. R. *Tetrahedron Lett.* **1983**, *24*, 233. (f) Baines, K. M.; Vaughan, K.; Hooper, D. L.; Leveck, L. F. *Can. J. Chem.* **1983**, *61*, 1549. (g) Palmisano, G.; Danieli, B.; Lesma, G.; Riva, R. *J. Org. Chem.* **1985**, *50*, 3322. (h) Gamage Nicholas, K. U. K.; Vaughan, K. *Can. J. Chem.* **1986**, *64*, 799.

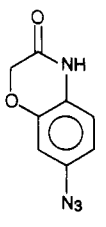
0022-3263/86/1951-5362$01.50/0



Although we were most interested in α-diazo amides **1** derived from aniline derivatives, we established that a general route to the α-diazo amides from various benzyl- and arylamines **2** involved the preparation of a glycyl amide derivative **3** and the subsequent diazotization of the glycyl amide. As illustrated in Scheme I, the simple cases of aniline and benzylamine provided the corresponding α-diazo amides **7** and **11**, respectively. Alternate approaches to the α-diazo amides such as **11**, which involved the nucleophilic substitution[6] of (4-nitrophenyl)- or (2,4-dinitrophenyl)-α-diazoacetate by amines was unsatisfactory.

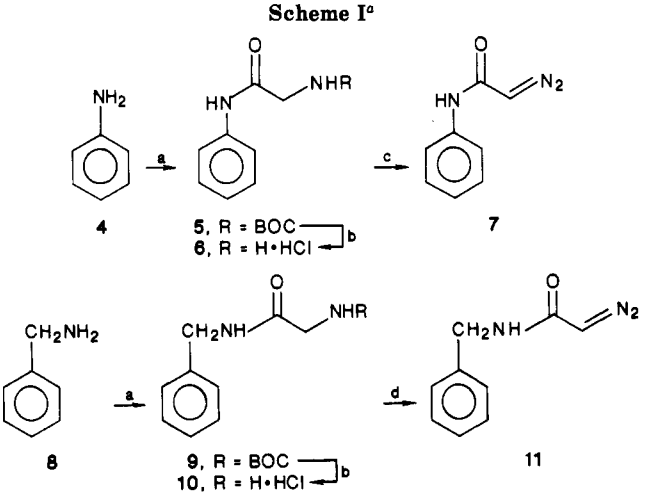
The former approach required us to prepare a variety of azide-substituted anilines, but we wanted to avoid a lengthy procedure for preparing azide-substituted anilines that involved the protection of a nitroaniline as its phthalimide derivative, conversion of the nitro group to an azide group, and deprotection of the phthalimide.[7] As shown in Scheme II, an alternate and reasonably efficient route to *N*-(4-azidophenyl)-α-diazoacetamide (**16**) from *p*-nitroaniline (**12**) relied on the protection of the amine as the *tert*-butoxycarbonyl (BOC) glycine derivative,[8] reduction of the nitro group in the presence of the BOC group, and diazotization. In the specific case of **16**, a second route was also developed that involved the monoprotection of *p*-phenylenediamine (**13**), diazotization, and azide substitution to afford **14**, as shown in Scheme II.

Unlike the symmetrical *p*-phenylenediamine example, in those cases where the corresponding diamines were unsymmetrical, we relied on the nitroaniline route as illustrated in Scheme II for the preparation of the hydroxy- and methoxy-substituted α-diazo amides **19a** and **19b**. In the case of *N*-(4-azido-2-hydroxyphenyl)-α-diazoacetamide (**19a**), the route was reasonably efficient except for the last step in which the diazotization was particularly troublesome. Although we suspected that the low yield was the result of a competitive insertion of the α-diazo amide functionality into the *o*-hydroxyl group, we did not isolate the anticipated heterocycle[9] **20**, and we found that the



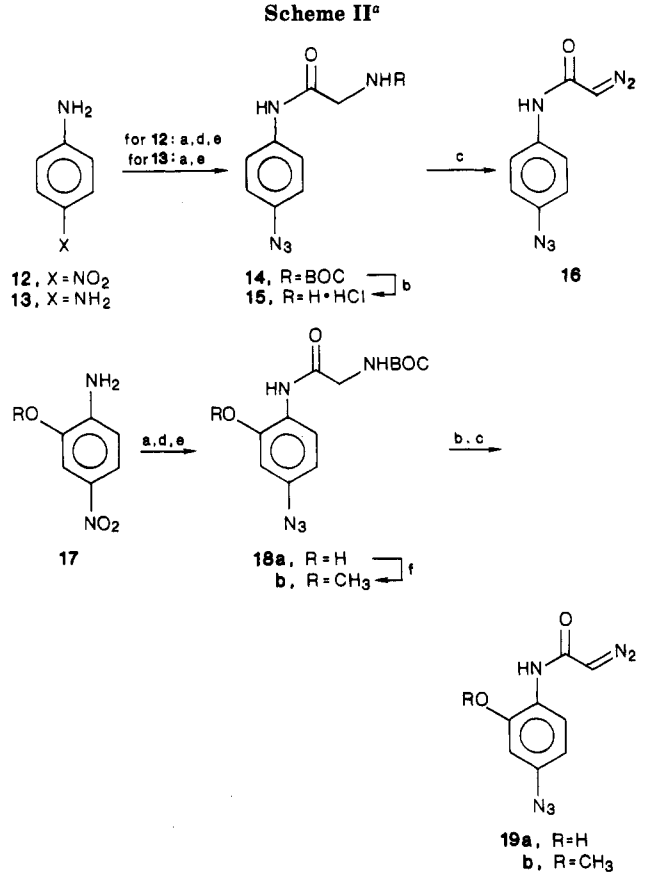
corresponding methoxy-substituted α-diazo amide **19b** was also plagued by a low yield in the diazotization step. Parenthetically, we would note that the hydroxyl group was necessary to facilitate the radioiodination[10] of the aryl azide nucleus, a requirement for biochemical studies utilizing natural products coupled to these reagents. It should also be noted that the incorporation of glycine in the synthesis of the α-diazo amide reagents provided an al-

Scheme I[a]



[a] Key: (a) BOCGly, DCC, THF; (b) glacial HOAc saturated with HCl, 25 °C; (c) $NaNO_2$, NaOAc, 2 M HCl, aqueous $CHCl_3$; (d) $NaNO_2$, HOAc, aqueous EtOAc.

Scheme II[a]



[a] Key: (a) BOCGly, DCC, THF; (b) glacial HOAc saturated with HCl, 25 °C; (c) $NaNO_2$, HOAc, aqueous THF–EtOAc; (d) Fe, aqueous HOAc, acetone; (e) $NaNO_2$, HCl, THF, 0 °C followed by NaN_3; (f) NaH, CH_3I.

(6) (a) Westheimer, F. H.; Stefanovsky, Y. *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 1132. (b) Westheimer, F. H.; Thornton, E. R.; Singh, A. *J. Biol. Chem.* **1962**, *237*, 3006. (c) Takamura, N.; Mizogushi, T.; Koga, K.; Yamada, S. *Tetrahedron* **1975**, *31*, 227.

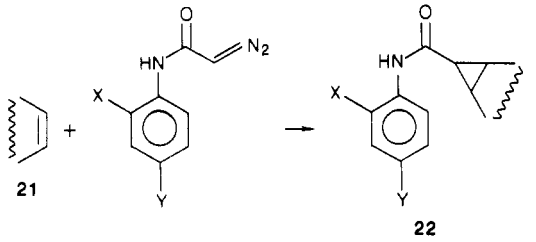
(7) (a) Meyer, R.; Luders, H. *Liebigs Ann. Chem.* **1918**, *415*, 29. (b) Smith, P. A. S.; Hall, J. H.; Kan, R. O. *J. Am. Chem. Soc.* **1962**, *84*, 485.

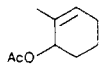
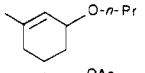
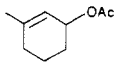
(8) Itoh, M.; Hagiwara, D.; Kamiya, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 718.

(9) For a leading reference to the (2*H*)-1,4-benzoxazin-3-ones, see: Mazharuddin, M.; Thyagarajan, G. *Tetrahedron* **1969**, *25*, 517.

(10) (a) Kometani, T.; Watt, D. S.; Ji, T. *Tetrahedron Lett.* **1985**, *26*, 2043. (b) Kometani, T.; Watt, D. S.; Ji, T.; Fitz, T. *J. Org. Chem.* **1985**, *50*, 5384.

Table I. Addition of α-Diazo Amides to Olefins 21 in the Presence of Various Transition-Metal Catalysts



	olefin 21	α-diazo amide	conditions[c] catalyst	conditions[c] temp, °C	conditions[c] time, h	isolated yield[a] of 22, %
a	(*E*)-2-octene	7	$Rh_2(OAc)_4$	25	4	51
		7	$Rh_2(OPv)_4$	25	4	59
		7	$Rh_2(OPv)_4$	85	4	9
		7	$Rh_6(CO)_{16}$	25	12	14
		7	$Cu(BSI)_2$[e]	25	12	5
b	(*E*)-4-octene	7	$Rh_2(OPv)_4$	25	4	54
c	(*E*)-stilbene	7	$Rh_2(OAc)_4$	25	4	42
		7	$Rh_2(OPv)_4$	25	4	55
		16	$Rh_2(OPv)_4$	25	4	30
d	methylenecyclohexane	7	$Rh_2(OPv)_4$	25	4	64
		16	$Rh_2(OPv)_4$	25	4	74
e	(*Z*)-cyclooctene	7	$Rh_2(OPv)_4$	25	4	68
		16	$Rh_2(OPv)_4$	25	4	31
f	1-methylcyclohexene	7	$Rh_2(OAc)_4$	25	3	30
		7	$Rh_2(OPv)_4$	25	4	56
		7	CuCl, $P(OMe)_3$	25	3	6
		16	$Rh_2(OAc)_4$	25	3	37[b]
		19a	$Rh_2(OAc)_4$	25	1	31
g	norbornene	7	$Rh_2(OPv)_4$	25	4	44[b]
h	dihydropyran	7	$Rh_2(OPv)_4$	25	4	83[b]
		16	$Rh_2(OPv)_4$	25	4	75[b]
i[d]		7	$Rh_2(OPv)_4$	25	2.5	13
		16	$Rh_2(OPv)_4$	25	5	22
		16	$Rh_2(OPv)_4$	80	4	21
		16	$Pd(OAc)_2$	25	4	0
j		16	$Rh_2(OPv)_4$	25	4	6
		16	$Rh_6(CO)_{16}$	25	4	2
k		7	$Rh_2(OPv)_4$	25	4	18

[a] Yield based on α-diazo amide; product isolated as a mixture of diastereomers except where noted. [b] Diastereomers separated. [c] α-Diazo amide in 1,2-dimethoxyethane was added over the stated time period by a motor-driven syringe pump to the substrate and catalyst. [d] Treibs, W.; Weissenfels, M. *Chem. Ber.* **1960**, *93*, 1374. [e] Charles, R. G. *J. Org. Chem.* **1957**, *22*, 677. [f] Solvent was THF.

ternate route for incorporating a ^3H or ^{14}C radiolabel.

Drawing on obvious precedent for the addition of α-diazo esters to olefins,[3] we examined the copper- and rhodium-catalyzed cyclopropanation of olefins **21** to furnish the cyclopropylcarboxanilides **22** shown in Table I. We noted that modest but acceptable yields of **22** were obtained with rhodium(II) acetate or, preferably, rhodium(II) pivalate,[11] in 1,2-dimethoxyethane solution. The azide group in **16** and **19a** was not affected under these conditions. The cyclopropanation yields were, however, quite sensitive to substituent effects: allylic hydroxyl, ether, or ester functionalities diminished the yields of **22** appreciably whereas vinylic ether functionality enhanced the yields. Similarly, the reactions of **7** and **16** with several alcohols **23** in the presence of rhodium(II) pivalate furnished the corresponding α-alkoxy amides **24** as shown in Table II. Applications of these reagents to the preparation of photoaffinity probes of selected natural products will be reported in due course.

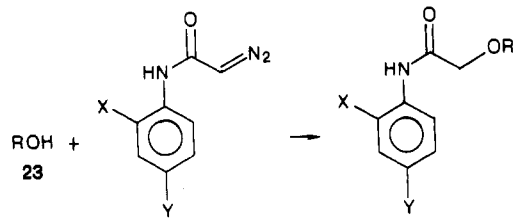
(11) Rhodium(II) pivalate was prepared by a modification of the procedure described for the preparation of rhodium(II) acetate: Legzdins, P.; Mitchell, R. W.; Rempel, G. L.; Ruddick, J. D.; Wilkinson, G. *J. Chem. Soc. A* **1970**, 3322.

Experimental Section

Infrared spectra were determined on a Beckman Microlab 600 spectrometer. The abbreviation TF denotes thin film. NMR spectra were determined on a JEOL 270-MHz or Varian XL-200 spectrometer. Mass spectra were determined on VG ZAB mass spectrometer. Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. Column chromatography using Macherey Nagel silica gel 60 is referred to as "silica gel chromatography", and the drying of an organic phase over anhydrous magnesium sulfate is simply indicated by the phrase "dried".

***N*-Phenyl-α-[(*tert*-butoxycarbonyl)amino]acetamide (5).** To a solution of 2.04 g (22.0 mmol, 1.0 equiv) of aniline in 50 mL of anhydrous THF at 25 °C was added 3.84 g (22.0 mmol, 1.0 equiv) of *N*-(*tert*-butoxycarbonyl)glycine and 4.71 g (23.0 mmol, 1.04 equiv) of 1,3-dicyclohexylcarbodiimide. The mixture was stirred at 25 °C for 5 h, diluted with 200 mL of ethyl acetate, filtered to remove the urea byproduct, and concentrated to afford 5.50 g (100%) of crude **5** which was sufficiently pure for direct use in the subsequent step: IR (KBr) 3359, 3308, 1681, 1675 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48 [s, 9, $C(CH_3)_3$], 3.93 (d, J = 5.8 Hz, 2, CH_2), 5.35 [br s, 1, $NHCO_2C(CH_3)_3$], 7.11 (t, J = 7.3 Hz, 1, C-4 aromatic H), 7.31 (dd, J = 8.1 and 7.3 Hz, 2, C-3, 5 aromatic H), 7.52 (d, J = 8.1 Hz, 2, C-2, 6 aromatic H), 8.25 (br s, 1, C_6H_5NHCO).

Table II. Reaction of α-Diazo Amides with Alcohols 23 in the Presence of Rhodium(II) Pivalate



	alcohol 23	α-diazo amide	conditions temp, °C	conditions time, h	isolated yield[a] of 24, %
a	cyclohexanol	16	25	4	59
b	3-methyl-2-cyclohexenol	7	25	4	36
c	*exo*-norborneol	16	25	4	39

[a] Yield based on α-diazo amide.

***N*-Phenyl-α-aminoacetamide Hydrochloride (6).** To 3.0 g (12 mmol) of **5** was added 15 mL of glacial acetic acid saturated with hydrogen chloride. The solution was allowed to stand for 30 min at 25 °C, diluted with 45 mL of ether, filtered, and extracted to obtain, after the solvent was evaporated, 1.92 g (86%) of crude **6**, which was sufficiently pure to be used directly in the subsequent step: mp 216–220 °C; IR (KBr) 1673 cm^{-1}.

***N*-Phenyl-α-diazoacetamide (7).** To a solution of 3.95 g (21.2 mmol, 1 equiv) of **6** and 17.4 mg (0.21 mmol, 0.01 equiv) of sodium acetate in 8 mL of water was added 100 mL of chloroform and a solution of 1.9 g (27.6 mmol, 1.3 equiv) of sodium nitrite in 3 mL of water. To this solution was added 1.5 mL of 2 M hydrochloric acid solution dropwise. After the mixture was stirred for 0.5 h, the chloroform layer was separated, and the product was extracted with an additional 50 mL of ethyl acetate. The combined organic solutions were washed successively with saturated sodium bicarbonate solution and brine and dried. Crystallization of the crude product by trituration with hexane afforded 1.97 g (58%) of **7**: dec pt 148–150 °C; IR (KBr) 3250 (br), 3080, 2080, 1675, 1627 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.92 (s, 1, C*H*), 6.9 (br s, 1, N*H*), 7.11 (t, *J* = 7.2 Hz, 1, C-4 aromatic H), 7.3 (dd, *J* = 14.8 and 7.3 Hz, 2, C-3, 5 aromatic H), 7.42 (d, *J* = 7.9 Hz, 2, C-2 aromatic H); exact mass spectrum for $C_8H_7N_3O$, calcd 161.0589, found 161.0589.

***N*-Benzyl-α-[(*tert*-butoxycarbonyl)amino]acetamide (9).** The procedure described for the preparation of **5** was repeated using 1.07 (10.0 mmol, 1.0 equiv) of benzylamine, 1.75 g (10.0 mmol, 1.0 equiv) of *N*-(*tert*-butoxycarbonyl)glycine, and 2.14 g (10.4 mmol, 1.04 equiv) of 1,3-dicyclohexylcarbodiimide in 40 mL of anhydrous THF for 3 h to aford, after chromatography on silica gel using 1:1 ethyl acetate–hexane, 2.04 g (77%) of **9**: IR (KBr) 3307, 3056, 3023, 2964, 2923, 1697, 1647, 1547, 1507 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.41 [s, 9, $C(CH_3)_3$], 3.81 (d, *J* = 5.3 Hz, 2, $COCH_2NH$), 4.43 (d, *J* = 6.2 Hz, $ArCH_2NH$), 5.36 (br s, 1, N*H*COO-*t*-Bu), 6.74 (br s, 1, $ArCH_2NH$), 7.24–7.30 (m, 5, aromatic H); exact mass spectrum for $C_{10}H_{12}N_2O_3$–isobutylene, calcd 208.0848, found 208.0881.

***N*-Benzylglycinamide Hydrochloride (10).** The procedure described for the preparation of **6** was repeated using 2.47 g (9.35 mmol) of **9** and 15 mL of acetic acid saturated with hydrogen chloride to afford 1.49 g (80%) of **10**: mp 169–171 °C; IR (KBr) 3293, 3181, 2976 (br), 1708, 1666, 1561, 1522 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 3.61 (s, 2, $COCH_2NH$), 4.35 (d, *J* = 6 Hz, 2, $ArCH_2NH$), 7.29–7.35 (m, 5, aromatic H), 8.24 (br s, 3, NH_3^+), 9.04 (br s, 1, $ArCH_2NH$). Anal. Calcd for $C_9H_{13}N_2OCl$: C, 53.87; H, 6.53. Found: C, 54.03; H, 6.65.

***N*-Benzyl-α-diazoacetamide (11).** To a solution of 201 mg (1.0 mmol, 1.0 equiv) of **10** in 4 mL of water was added 97 mg (1.4 mmol, 1.4 equiv) of sodium nitrite in 1 mL of water followed by 10 mL of ethyl acetate. The solution was stirred rapidly, and 2 mL of 10% acetic acid was added dropwise. The stirring was continued for 1 h at 25 °C. The ethyl acetate layer was separated, washed successively with saturated sodium bicarbonate solution and brine, and dried. The solvent was evaporated to afford 132 mg (75%) of **11**: dec pt 75–80 °C; IR (KBr) 3281, 3079, 3025, 2918, 2870, 2100, 1661, 1653, 1602, 1543 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.45 (d, *J* = 5.5 Hz, 2, $ArCH_2NH$), 4.75 (s, 1, CHN_2), 6.94 (br s, 1, $ArCH_2NH$), 7.21–7.34 (m, 5, aromatic H). Anal. Calcd for $C_9H_9N_3O$: C, 61.70; H, 5.18. Found: C, 61.98; H, 5.28.

***N*-(4-Nitrophenyl)-α-[(*tert*-butoxycarbonyl)amino]acetamide.** The procedure described for the preparation of **5** was repeated using 2.0 g (14.5 mmol, 1.0 equiv) of *p*-nitroaniline (**12**), 2.54 g (14.5 mmol, 1.0 equiv) of *N*-(*tert*-butoxycarbonyl)glycine, and 3.11 g (15.1 mmol, 1.04 equiv) of 1,3-dicyclohexylcarbodiimide in 40 mL of anhydrous THF for 18 h to afford 1.4 g (33%) of *N*-(4-nitrophenyl)-α-[(*tert*-butoxycarbonyl)amino]acetamide: mp 170–180 °C; IR (KBr) 3385, 3210, 3185, 3120, 3000, 2940, 2865, 1690, 1630, 1610, 1575, 1535 cm^{-1}; ^1H NMR ($CDCl_3$–Me_2SO-d_6) δ 1.47 [s, 9, $C(CH_3)_3$], 3.92 (d, *J* = 6 Hz, 2, CH_2), 6.16 [br s, 1, $NHCO_2C(CH_3)_3$], 7.79 (d, *J* = 9 Hz, 2, C-2 and C-6 aromatic H), 8.13 (d, *J* = 9 Hz, 2, C-3 and C-5 aromatic H), 10.17 (br s, 1, $NHCOCH_2$); exact mass spectrum for $C_{13}H_{17}N_3O_5$ calcd 295.1168, found 295.1156.

***N*-(4-Aminophenyl)-α-[(*tert*-butoxycarbonyl)amino]acetamide from *N*-(4-Nitrophenyl)-α-[(*tert*-butoxycarbonyl)amino]acetamide.** To a solution of 590 mg (2.0 mmol, 1.0 equiv) of *N*-(4-nitrophenyl)-α-[(*tert*-butoxycarbonyl)amino]acetamide in 50 mL of acetone, 8 mL of glacial acetic acid, and 8 mL of water at reflux was added 1.34 g (24 mmol, 6.0 equiv) of iron powder. The mixture was refluxed for 5 h. The solution was filtered, neutralized by the slow addition of saturated sodium bicarbonate solution, and extracted with ethyl acetate. The ethyl acetate solution was washed with brine and dried. The crude product was chromatographed on silica gel with 1:48 methanol–ethyl acetate to afford 200 mg (38%) of *N*-(4-aminophenyl)-α-[(*tert*-butoxycarbonyl)amino]acetamide: mp 151–152 °C; IR (KBr) 3420, 3398, 3325, 3220, 3180, 3115, 2995, 2940, 1695, 1670, 1640, 1560, 1520 cm^{-1}; ^1H NMR ($CDCl_3$–Me_2SO-d_6) δ 1.43 [s, 9, $C(CH_3)_3$], 3.22 (br s, 2, NH_2), 3.73 (d, *J* = 6 Hz, 2, CH_2), 6.37 [br s, 1, $NHCO_2C(CH_3)_3$], 6.50 (d, *J* = 8 Hz, 2, C-2 and C-6 aromatic H), 7.18 (d, *J* = 8 Hz, 2, C-3 and C-5 aromatic H), 9.16 (br s, 1, $NHCOCH_2$).

***N*-(4-Aminophenyl)-α-[(*tert*-butoxycarbonyl)amino]acetamide from *p*-Phenylenediamine (13).** The procedure described above for the preparation of **5** was repeated using 1.73 g (16.0 mmol, 1.0 equiv) of *p*-phenylenediamine (**13**), 3.06 g (17.5 mmol, 1.1 equiv) of *N*-(*tert*-butoxycarbonyl)glycine, and 3.61 g (17.5 mmol, 1.1 equiv) of 1,3-dicyclohexylcarbodiimide in 60 mL of anhydrous THF for 24 h to afford, after chromatography on silica gel using 1:48 methanol–ethyl acetate, 3.46 g (65%) of *N*-(4-aminophenyl)-α-[(*tert*-butoxycarbonyl)amino]acetamide, having the same properties as material described above.

***N*-(4-Azidophenyl)-α-[(*tert*-butoxycarbonyl)amino]acetamide (14).** To 2.65 g (10 mmol, 1.0 equiv) of *N*-(4-aminophenyl)-α-[(*tert*-butoxycarbonyl)amino]acetamide in 40 mL of THF and 40 mL of water was added 4 mL of concentrated hydrochloric acid. The solution was cooled to 0–5 °C, and a cold solution of 760 mg (11 mmol, 1.1 equiv) of sodium nitrite in 4 mL of water was added dropwise. The solution was stirred for 30 min, filtered, and treated with a solution of 715 mg (11 mmol, 1.1 equiv) of sodium azide in 6 mL of water for 30 min. The product was extracted with ethyl acetate, washed successively with a saturated sodium bicarbonate solution and brine, and dried. The solvent was evaporated to afford 2.85 g (98%) of **14**: dec pt 158–159 °C; IR (KBr) 3337, 3313, 2075, 1665, 1602 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48 [s, 9, $C(CH_3)_3$], 3.93 (d, *J* = 6 Hz, 2, CH_2), 5.35 (br s, 1, CH_2NH), 6.97 (d, *J* = 9.2 Hz, 2, C-2, 6 aromatic H), 7.51 (d, *J* = 8.6 Hz, 2, C-3, 5 aromatic H), 8.37 (br s, 1, NHCO); exact mass spectrum for $C_{13}H_{17}N_5O_3$, calcd 291.1333, found 291.1329. Anal. Calcd for $C_{13}H_{17}N_5O_3$: C, 53.60; H, 5.88. Found: C, 53.67; H, 5.89.

***N*-(4-Azidophenyl)-α-aminoacetamide Hydrochloride (15).** The procedure described for the preparation of **6** was repeated using 1.0 g (3.4 mmol) of **14** to afford 0.62 g (80%) of **15**: no sharp mp; sample darkened and decomposed at 190 °C; IR (KBr) 2104, 1664 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 3.79 (s, 2, CH_2), 7.12 (d, *J* = 11.2 Hz, 2, C-2, 6 aromatic H), 7.68 (d, *J* = 11.2 Hz, 2, C-3, 5 aromatic H), 8.31 (br s, 3, NH_3^+). Anal. Calcd for $C_8H_{10}N_5OCl$: C, 42.21; H, 4.43. Found: C, 42.20; H, 4.47.

***N*-(4-Azidophenyl)-α-diazoacetamide (16).** To a solution

of 5.16 g (22.7 mmol, 1 equiv) of **15** in 160 mL of 1:1 water–THF was added 1.88 g (27.2 mmol, 1.2 equiv) of sodium nitrite in 10 mL of water, 100 mL of ethyl acetate, and 4.5 mL of glacial acetic acid. The mixture was stirred for 1.5 h. The organic layer was separated, washed successively with sodium bicarbonate solution and brine, and dried. The crude product was chromatographed on silica gel using 1:1 ethyl acetate–hexane to afford 3.16 g (69%) of **16**: dec pt 147–149 °C; IR (KBr) 3278, 2084, 1619, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.88 (s, 1, CH), 6.73 (br s, 1, NH), 6.98 (d, J = 6.6 Hz, 2, C-2, 6 aromatic H), 7.43 (d, J = 8.6 Hz, 2, C-3, 5 aromatic H); exact mass spectrum for $C_8H_6N_6O$, calcd 202.0605, found 202.0619.

***N*-(2-Hydroxy-4-nitrophenyl)-α-[(*tert*-butoxycarbonyl)amino]acetamide.** The procedure described for the preparation of **5** was repeated using 2.64 g (17.1 mmol) of 2-hydroxy-4-nitroaniline (**17**), 3.0 g (17.1 mmol, 1 equiv) of *N*-(*tert*-butoxycarbonyl)glycine, and 3.89 g (18.9 mmol, 1.1 equiv) of 1,3-dicyclohexylcarbodiimide in 50 mL of anhydrous THF to afford 3.19 g (60%) of *N*-(2-hydroxy-4-nitrophenyl)-α-[(*tert*-butoxycarbonyl)amino]acetamide: mp 187–188 °C; IR (KBr) 3355, 3320, 3160, 2980, 1654, 1500 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 1.41 [s, 9, $C(CH_3)_3$], 3.81 (d, J = 6 Hz, 2, CH_2), 7.33 (br s, 1, CH_2NH), 7.66–8.36 (m, 3, C-3, 5, 6 aromatic H), 9.38 (br s, 1, CONH), 11.18 (br s, 1, OH); exact mass spectrum for $C_{13}H_{17}N_3O_6$–isobutylene, calcd 255.0492, found 255.0495. Anal. Calcd for $C_{13}H_{17}N_3O_6$: C, 50.16; H, 5.50. Found: C, 50.08; H, 5.55.

***N*-(4-Amino-2-hydroxyphenyl)-α-[(*tert*-butoxycarbonyl)amino]acetamide.** The procedure described for the preparation of *N*-(4-aminophenyl)-α-[(*tert*-butoxycarbonyl)amino]acetamide was repeated using 2.94 g (9.5 mmol, 1.0 equiv) of *N*-(4-nitro-2-hydroxyphenyl)-α-[(*tert*-butoxycarbonyl)amino]acetamide and 6.3 g (113 mmol, 6.0 equiv) of iron powder to afford, after chromatography on silica gel using 1:49 methanol–ethyl acetate, 2.14 g (80%) of *N*-(4-amino-2-hydroxyphenyl)-α-[(*tert*-butoxycarbonyl)amino]acetamide: IR (KBr) 3385, 3310, 3090 (br), 2980, 1670, 1635, 1500 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 1.40 [s, 9, $C(CH_3)_3$], 3.66 (d, J = 6 Hz, 2, CH_2), 4.84 (s, 2, NH_2), 5.97–6.12 (m, 2, C-5, 6 aromatic H), 7.20 (br s, 1, CH_2NH), 7.30–7.36 (m, 1, C-3 aromatic H), 8.67 (br s, 1, CONH), 9.36 (br s, 1, OH); exact mass spectrum for $C_{13}H_{19}N_3O_4$, calcd 281.1375, found 281.1339.

***N*-(4-Azido-2-hydroxyphenyl)-α-[(*tert*-butoxycarbonyl)amino]acetamide (18a).** To 1.4 g (5.0 mmol) of *N*-(4-amino-2-hydroxyphenyl)-α-[(*tert*-butoxycarbonyl)amino]acetamide in 25 mL of water, 20 mL of THF, and 4.5 mL of concentrated hydrochloric acid was added 378 mg (5.5 mmol, 1.1 equiv) of sodium nitrite in 2 mL of water at 0–5 °C. The mixture was stirred for 30 min and filtered. The cold filtrate was treated with 358 mg (5.5 mmol, 1.1 equiv) of sodium azide in 2 mL of water. After the mixture was stirred for 20 min at 25 °C, the product was extracted with three 100-mL portions of ethyl acetate. The ethyl acetate solution was washed successively with saturated sodium bicarbonate solution and brine and dried. The solvent was evaporated to afford 1.32 g (86%) of **18a**, which was sufficiently pure for use in the next step: dec pt 174–176 °C; IR (KBr) 3350, 3200 (br), 2980, 2100, 1650, 1510 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 1.40 [s, 9, $C(CH_3)_3$], 3.72 (d, J = 6 Hz, 2, CH_2), 6.52–6.8 (m, 2, C-5, 6 aromatic H), 7.27 (br s, 1, CH_2NH), 7.93–7.98 (m, 1, C-3 aromatic H), 9.0 (br s, 1, CONH); exact mass spectrum for $C_{13}H_{17}N_5O_4$, calcd 307.1282, found 307.1286.

An analytical sample was prepared by two recrystallizations from ethyl acetate–hexane. Anal. Calcd for $C_{13}H_{17}N_5O_4$: C, 50.81; H, 5.58. Found: C, 50.85; H, 5.74.

***N*-(4-Azido-2-hydroxyphenyl)-α-aminoacetamide Hydrochloride.** The procedure described for the preparation of **15** was repeated using 1.23 g (4.0 mmol) of **18a** to afford 0.93 g (96%) of *N*-(4-azido-2-hydroxyphenyl)-α-aminoacetamide hydrochloride: no melting point at temperatures <245 °C; IR (KBr) 3100 (br), 2110, 1675, 1595, 1250 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 3.82 (d, J = 5 Hz, 2, CH_2), 6.54–6.70 (m, 2, C-5, 6 aromatic H), 7.88–7.92 (m, 1, C-3 aromatic H), 8.20 (br s, 3, NH_3^+), 9.80 (br s, 1, NH), 10.56 (br s, 1, OH).

***N*-(4-Azido-2-hydroxyphenyl)-α-diazoacetamide (19a).** To 244 mg (1.0 mmol, 1.0 equiv) of *N*-(4-azido-2-hydroxyphenyl)-α-aminoacetamide hydrochloride in 8 mL of water and 20 mL of ethyl acetate was added 83 mg (1.2 mmol, 1.2 equiv) of sodium nitrite, 10 mg (0.12 mmol, 0.12 equiv) of sodium acetate, and 0.2 mL of 2 M hydrochloric acid solution. The mixture was stirred for 1 h at 25 °C. The ethyl acetate layer was separated, washed successively with saturated sodium bicarbonate solution and brine, and dried. The crude product was chromatographed on silica gel (F254 preparative layer) with 1:1 ethyl acetate–hexane to afford 29 mg (13%) of **19a**: IR (KBr) 3360, 2090, 1600 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 5.88 (s, 1, CHN_2), 6.50–6.80 (m, 2, C-5, 6 aromatic H), 7.90–7.95 (m, 1, C-3 aromatic H), 9.0 (br s, 1, NH) 9.07 (br s, 1, OH).

***N*-(4-Azido-2-methoxyphenyl)-α-[(*tert*-butoxycarbonyl)amino]acetamide (18b).** To 25 mg (1.05 mmol, 1.05 equiv) of sodium hydride in 2 mL of THF at 0 °C under a nitrogen atmosphere was added 307 mg (1 mmol, 1 equiv) of **18a** in 10 mL of THF. The mixture was stirred for 1 h, and 156 mg (1.1 mmol, 1.1 equiv) of methyl iodide was added. The mixture was stirred for 20 h at 25 °C. The product was diluted with ethyl acetate, washed with water, and dried. The crude product was chromatographed on silica gel with 1:1 ethyl acetate–hexane to afford 132 mg (41%) of **18b**: IR (THF) 3375, 3310, 2960, 2910, 2090, 1660, 1590, 1520 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48 [s, 9, $C(CH_3)_3$], 3.80 (s, 3, OCH_3), 3.90 (d, J = 6 Hz, 2, CH_2NH), 5.45 (br s, 1, CH_2NH), 6.46 (d, J = 3 Hz, 1, C-6 aromatic H), 6.60 (dd, J = 9, 3 Hz, 1, C-5 aromatic H), 8.27 (d, J = 9 Hz, 1, C-3 aromatic H), 8.33 (br s, 1, ArNHCO).

***N*-(4-Azido-2-methoxyphenyl)glycinamide Hydrochloride.** The procedure described for the preparation of *N*-phenyl-α-aminoacetamide hydrochloride was repeated using 132 mg (0.41 mmol) of **18b** in 2 mL of ether and 3 mL of acetic acid saturated with hydrogen chloride to afford 52 mg (49%) of *N*-(4-azido-2-methoxyphenyl)-α-aminoacetamide hydrochloride: IR (KBr) 3220 (br), 3110 (br), 2900 (br), 2090, 1665, 1590 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 3.85 (br s, 2, CH_2NH), 3.90 (s, 3, OCH_3), 6.72–6.82 (m, 2, C-5, C-6 aromatic H), 7.99 (d, J = 8 Hz, 1, C-3 aromatic H), 8.22 (br s, 3, NH_3^+), 9.80 (br s, 1, ArNHCO).

***N*-(4-Azido-2-methoxyphenyl)-α-diazoacetamide (19b).** The procedure described for the preparation of **19a** was repeated using 45 mg (0.18 mmol, 1.0 equiv) of *N*-(4-azido-2-methoxyphenyl)-α-aminoacetamide hydrochloride, 2 mg (0.02 mmol, 0.14 equiv) of sodium acetate in 2 mL of water, 15 mg (0.23 mmol, 1.3 equiv) of sodium nitrite in 0.5 mL of water, and 0.1 mL of 2 M hydrochloric acid to afford, after chromatography on silica gel using 1:1 ethyl acetate–hexane, 10 mg (25%) of **19b**: IR (KBr) 3310 (br), 3100, 2100, 1620, 1540 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.87 (s, 3, OCH_3), 4.96 (s, 1, CHN_2), 6.5 (d, J = 3 Hz, 1, C-6 aromatic H), 6.67 (dd, J = 10, 4 Hz, 1, C-5 aromatic H), 7.24 (br s, 1, NH), 8.3 (d, J = 10 Hz, 1, C-3 aromatic H).

General Procedure for the Reaction of Olefins 21 with α-Diazo Amides and Rhodium(II) Catalysts. Preparation of Cyclopropanecarboxamide 22h (X = H, Y = N_3). To a stirred solution of 168 mg (2.0 mmol, 2.0 equiv) of dihydropyran (**21h**) and 18 mg (0.03 mmol, 0.03 equiv) of rhodium pivalate[11] was added a solution of 202 mg (1.0 mmol, 1.0 equiv) of *N*-(4-azidophenyl)-α-diazoacetamide (**16**) in 6 mL of 1,2-dimethoxyethane by a motor-driven syringe pump over a 4-h period. The solvent was evaporated, and the crude product was chromatographed on silica gel (F254 preparative layer) with 1:1 ethyl acetate–hexane to afford 195 mg (75%) of **22h** (X = H, Y = N_3): IR (KBr) 3320, 3120, 2940, 2860, 2100, 1665, 1600, 1530, 1505, 1410 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.4–2.06 (m, 6, aliphatic H), 3.44–3.9 (m, 3, CH_2OCH), 6.98 (d, J = 11 Hz, 2, C-2, C-6 aromatic H), 7.54 (d, J = 11 Hz, 2, C-3, C-5 aromatic H), 8.6 (br s, 1, NH); exact mass spectrum for $C_{13}H_{14}N_4O_2$, calcd 258.1157, found 258.1110.

Spectral Data for Cyclopropanes 22 in Table I. Compound 22a (X = H, Y = H): IR (TF) 3315, 3060, 2980, 2945, 2875, 1665, 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.73–1.93 (m, 17, aliphatic H), 6.90–7.67 (m, 6, aromatic H and NH); exact mass spectrum for $C_{16}H_{23}NO$, calcd 245.1781, found 245.1803.

Compound 22b (X = H, Y = H): IR (KBr) 3300, 3090, 2980, 2920, 2860, 1665, 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.5–1.83 (m, 17, aliphatic H), 6.87–7.63 (m, 6, aromatic H and NH); exact mass spectrum for $C_{16}H_{23}NO$, calcd 245.1781, found 245.1802.

Compound 22c (X = H, Y = H): mp 192–194 °C; IR (KBr) 3310, 3270, 3090, 3065, 3035, 2925, 1660, 1605, cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.28 (dd, J = 3, 6 Hz, 1, CHCONH), 2.87 (dd, J = 4,

6 Hz, 1, CHAr), 3.27 (dd, J = 3, 4 Hz, 1, CHAr), 7.20 (m, 16, aromatic H and NH); exact mass spectrum for $C_{22}H_{19}NO$, calcd 313.1513, found 313.1467.

Compound 22c (X = H, Y = N_3): dec pt 163–166 °C; IR (KBr) 3270, 3230, 3180, 3110, 3050, 2100, 1660, 1610, 1550, 1505 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.32 (dd, J = 9, 5 Hz, 1, C*H*CONH), 2.95 (dd, J = 9, 7 Hz, 1, CHAr), 3.31 (dd, J = 7, 5 Hz, 1, CHAr), 6.86–7.41 (m, 15, aromatic and NH); exact mass spectrum for $C_{22}H_{18}N_4ON_2$, calcd 326.1419, found 326.1428.

Compound 22d (X = H, Y = H): mp 106.5–108 °C; IR (KBr) 3280, 3080, 2920, 2845, 1645, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80 (dd, J = 5, 8 Hz, 1, cyclopropane H), 1.16–1.76 (m, 12, CH_2 of cyclohexane and cyclopropane H), 7.07 (t, J = 7 Hz, 1, C-4 aromatic H), 7.30 (t, J = 7 Hz, 2, C-3 and C-5 aromatic H), 7.51 (d, J = 7 Hz, 1, 2, C-2 and C-6 aromatic H), 7.62 (br s, 1, NH); exact mass spectrum for $C_{15}H_{19}NO$, calcd 229.1468, found 229.1505.

Compound 22d (X = H, Y = N_3): dec pt 114–117 °C; IR (KBr) 3275, 2910, 2850, 2100, 1650, 1600, 1540, 1510 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.79 (dd, J = 8, 5 Hz, 1, cyclopropane CH), 1.18–1.64 (m, 12, CH_2), 6.92 (d, J = 9 Hz, 2, C-2, C-6 aromatic H), 7.49 (d, J = 9 Hz, 2, C-3, C-5 aromatic H), 7.82 (br s, 1, NH); exact mass spectrum for $C_{15}H_{18}N_4O$, calcd 270.1480, found 270.1466.

Compund 22e (X = H, Y = H): mp 133–135 °C; IR (KBr) 3320, 3010, 2940, 2850, 1650, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.77–2.10 (m, 15, aliphatic H), 6.87–7.53 (m, 6, aromatic H and NH); exact mass spectrum for $C_{16}H_{21}NO$, calcd 243.1624, found 243.1665.

Compound 22e (X = H, Y = N_3): mp 155–156 °C; IR (KBr) 3300, 3000, 2930, 2860, 2120, 1650, 1520, 1510 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96–2.12 (m, 15, aliphatic H), 6.96 (d, J = 11 Hz, 2, C-2, C-6 aromatic H), 7.27 (br s, 1, NH), 7.50 (d, J = 11 Hz, 2, C-3, C-5 aromatic H); exact mass spectrum for $C_{16}H_{20}N_4O$, calcd 284.1639, found 284.1613.

Compound 22f (X = H, Y = H): IR (KBr) 3278, 3269, 1646, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1–1.88 (m, 13, aliphatic H), 7.06 (t, J = 7.3 Hz, 1, C-4 aromatic H), 7.28 (t, J = 8.6 Hz, 2, C-3, 5 aromatic H), 7.50 (d, J = 8.6 Hz, 2, C-2, 6 aromatic H), 7.75 (br s, 1, NH). Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35. Found: C, 78.53; H, 8.36.

Compound 22f (X = H, Y = N_3): The product [20 mg (37%)] was isolated as a mixture of two isomers that were separated by chromatography on silica gel (F254 analytical layer) using 1:5 ethyl acetate–hexane (three developments) to afford two bands.

A band (R_f 0.84) afforded **22f** (X = H, Y = N_3): ^1H NMR ($CDCl_3$) δ 1.24 (s, 3, C-1 CH_3), 1.35–2.05 (m, 10, aliphatic H), 6.96 (d, J = 8.6 Hz, 2, C-2, 6 aromatic H), 7.25 (br s, 1, NH), 7.55 (d, J = 8.6 Hz, 2, C-3, 5 aromatic H); exact mass spectrum for $C_{15}H_{18}N_4O$, calcd 270.1481, found 270.1479.

A band (R_f 0.79) afforded 22f (X = H, Y = N_3): ^1H NMR ($CDCl_3$) δ 1.19 (s, 3, C-1 CH_3), 1.30–2.05 (m, 10, aliphatic H), 6.97 (d, J = 9.2 Hz, 2, C-2, 6 aromatic H), 7.17 (br s, 1, NH), 7.50 (d, J = 9.2 Hz, 2, C-3, 5 aromatic H); exact mass spectrum for $C_{15}H_{18}N_4O$, calcd 270.1481, found 270.1477.

Compound 22f (X = OH, Y = N_3): ^1H NMR ($CDCl_3$) δ 1.16–1.86 (m, 13, aliphatic H), 6.46 (m, 1, C-5 aromatic H), 6.61 (d, J = 4 Hz, 1, C-6 aromatic H), 7.18 (d, J = 8 Hz, 1, C-3 aromatic H), 8.2 (br s, 1, NH), 8.23 (br s, 1, OH); exact mass spectrum for $C_{15}H_{18}N_4O_2$, calcd 286.1430, found 286.1428.

Compound 22g (X = H, Y = H): The product was isolated as a mixture of two isomers that were separated by chromatography on silica gel using 1:4 ethyl acetate–hexane to afford two bands.

A band (R_f 0.33) afforded 43 mg (30%) of **22g** (X = H, Y = H): mp 204–205 °C; IR (KBr) 3280, 3045, 2970, 2890, 1660, 1610 cm^{-1}; ^1H NMR ($CDCl_3$, Me_2SO-d_6) δ 0.70–1.80 (m, 11, CH and CH_2), 6.93–7.63 (m, 5, aromatic H), 9.33 (br s, 1, NH); exact mass spectrum for $C_{15}H_{17}NO$, calcd 227.1311, found 227.1310.

A band (R_f 0.13) afforded 19 mg (14%) of **22g** (X = H, Y = H): mp 129–130 °C; IR (KBr) 3260, 3015, 2950, 2865, 1660, 1595 cm^{-1}; ^1H NMR ($CDCl_3$, Me_2SO-d_6) δ 0.70–1.58 (m, 11, CH and CH_2), 7.07 (t, J = 8 Hz, 1, C-4 aromatic H), 7.31 (t, J = 8 Hz, 2, C-3 and C-5 aromatic H), 7.58 (d, J = 7 Hz, 2, C-2 and C-6 aromatic H), 8.21 (br s, 1, NH); exact mass spectrum for $C_{15}H_{17}NO$, calcd 227.1311, found 227.1334.

Compound 22h (X = H, Y = H): The product was isolated as a mixture of two isomers that were not separated but were characterized as a mixture. IR (THF) 3300, 3010, 2940, 2860, 1660, 1595 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06–2.16 (m, 6, aliphatic H), 3.27–4.00 (m, 3, $CHOCH_2$), 6.87–7.63 (m, 5, aromatic H), 8.27 and 8.53 (two br s, 1, NH from two isomers); exact mass spectrum for $C_{13}H_{15}NO_2$, calcd 217.1104, found 217.1119.

Compound 22i (X = H, Y = H): IR (TF) 3310, 2940, 2885, 1725, 1665, 1600, 1535, 1500, 1445 cm^{-1}; ^1H NMR ($CDCl_3$, Me_2SO-d_6) δ 1.12 (s, 3, CH_3), 1.24–2.22 (m, 8, CH and CH_2), 2.14 (s, 3, $COCH_3$), 4.96 (m, 1, C*H*OAc), 7.06 (m, 1, C-4 aromatic H), 7.30 (m, 2, C-3, C-5 aromatic H), 7.62 (m, 2, C-2, C-6 aromatic H), 9.14 (br s, 1, NH); exact mass spectrum for $C_{17}H_{21}NO_3$, calcd 287.1522, found 287.1512.

Compound 22i (X = H, Y = N_3): IR (TF) 3300, 2930, 2870, 2100, 1720, 1665, 1600, 1530, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (s, 3, CH_3), 0.90–2.15 (m, 8, CH and CH_2), 2.13 (s, 3, $COCH_3$), 4.63 (m, 1, C*H*OAc), 6.92 (d, J = 9 Hz, 2, C-2, C-6 aromatic H), 7.60 (d, J = 9 Hz, 2, C-2, C-5 aromatic H), 8.87 (br s, 1, NH); exact mass spectrum for $C_{17}H_{20}N_4O_3$, calcd 328.1535, found 328.1538.

Compound 22j (X = H, Y = N_3): IR (TF) 3290, 2940, 2885, 2100, 1660, 1600, 1535, 1505 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 3, $CH_2CH_2CH_3$), 1.23–1.85 (m, 12, CH, CH_2, and CH_3), 3.48 (t, J = 6.7 Hz, 2, $CHOCH_2$), 3.95 (br s, 1, C*H*OCH_2), 6.98 (d, J = 8.6 Hz, 2, C-3, C-5 aromatic H), 7.27 (br s, 1, NH), 7.49 (d, J = 8.6 Hz, 2, C-2, C-6 aromatic H); exact mass spectrum for $C_{18}H_{24}N_4O_2$, calcd 328.1899, found 328.1893.

Compound 22k (X = H, Y = H): IR (KBr) 3310, 1730, 1680, 1605, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00–2.20 (m, 14, CH, CH_2, and CH_3), 4.71 (m, 1, C*H*OAc), 7.10–7.67 (m, 5, aromatic H), 8.35 (br s, 1, NH).

General Procedure for the Reaction of Alcohols 23 with α-Diazo Amides and Rhodium(II) Catalysts. The procedure described for the preparation of the cyclopropanecarboxamides was repeated with the alcohols **23** instead of the olefins **21**.

Spectral Data for α-Alkoxy Amides 24 in Table II. α-Alkoxy Amide 24a (X = H, Y = N_3): IR (TF) 3380, 2930, 2850, 2100, 1690, 1600, 1520 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22–2.05 (m, 10, aliphatic H), 3.42 (m, 1, C*H*OCH_2), 4.08 (s, 2, CH_2CO), 7.01 (d, J = 8.8 Hz, 2, C-2 and 6 aromatic H), 7.58 (d, J = 8.9 Hz, 2, C-3 and 5 aromatic H), 8.4 (br s, 1, NH); exact mass spectrum for $C_{14}H_{18}N_4O_2$, calcd 274.1429, found 274.1418.

α-Alkoxy Amide 24b (X = H, Y = H): IR (THF) 3390, 3060, 2930, 2860, 1690, 1600, 1525 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.49–2.0 (m, 9, aliphatic H including CH_3 s at 1.73), 4.0 (br d, J = 3 Hz, 1, C*H*OCH_2), 4.1 (d, J = 1.7 Hz, 2, CH_2CO), 5.55 (br s, 1, vinylic H), 7.1 (m, 1, C-4 aromatic H), 7.34 (m, 2, C-3 and 5 aromatic H), 7.57 (d, J = 8.3 Hz, 2, C-2 and 6 aromatic H), 8.40 (br s, 1, NH); exact mass spectrum for $C_{15}H_{19}NO_2$, calcd 245.1416, found 245.1393.

α-Alkoxy Amide 24c (X = H, Y = N_3): IR (TF) 3390, 2960, 2870, 2100, 1695, 1600, 1520 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99–1.65 (m, 8, aliphatic H), 2.05–2.39 (m, 2, aliphatic H), 3.50 (br d, J = 6.7 Hz, 1, C*H*OCH_2), 4.02 (s, 2, CH_2CO), 7.00 (d, J = 9.0 Hz, 2, C-2 and 6 aromatic H), 7.57 (d, J = 9.0 Hz, 2, C-3 and 5 aromatic H), 8.34 (br s, 1, NH); exact mass spectrum for $C_{15}H_{18}N_4O_2$, calcd 286.1430, found 286.1432.

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