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1,3-Dipolar Cycloaddition of Diazocompounds to 1-Alkenylboronic Esters

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ABSTRACT

A variety of diazo compounds was added to the parent vinylboronic ester derived from pinacol. The reactivity of some substituted 1-alkenylboronic esters is also briefly examined. The nonisolated primary adducts spontaneously rearrange via a 1,3-boron migration and lead to 1-borylated-2-pyrazolines. The structure of one of these compounds has been established by X-ray diffraction analysis.

INTRODUCTION

1,3-Dipolar cycloaddition reactions play a prominent role in organic synthesis [1]. Organoboron chemistry has also aroused considerable interest, the organoboranes being convenient precursors of a wide variety of compounds containing various function groups [2]. A combination of these two powerful synthetic tools would therefore be especially useful for the preparation of polyfunctionalized compounds.

This approach has been particularly well illustrated in the synthesis of cyclohexene derivatives via tandem sequences involving Diels–Alder reactions of 1-alkenylboranes followed by oxidation or amination of the cycloadducts [3–5] (Scheme 1).

Few studies have been conducted regarding 1,3-dipolar cycloadditions with α,β-unsaturated organoboranes. The preparation of boronate-substituted Δ^2-isoxazolines and isoazoles via nitrile oxides has been reported [6–9]. Thirty years ago, Matteson studied the cycloadditions of ethyl diazoacetate and diphenyldiazomethane with dibutyl vinylboronate **1a** [9] (Scheme 2). Boron migration from carbon to nitrogen to yield 2-pyrazolines **3** was proposed to rationalize the formation of **4** after ethanolysis. Compounds **2** and **3** were not characterized and were not isolated.

More recently, Brown et al. reported the synthesis of β,γ-unsaturated carboxylic esters **5** from 1-alkenyldichloroboranes and ethyl diazoacetate [10] (Scheme 3). A completely different reaction had been observed, and the Lewis acid properties of the boryl moiety apparently prevented any cycloaddition to the carbon=carbon double bond. Such behavior has been invoked to explain polymerization of diazomethane with boron reagents [11] and also enol borinate formation from diazocompounds bearing an electron-withdrawing group [12].

The presenting results led us to investigate the

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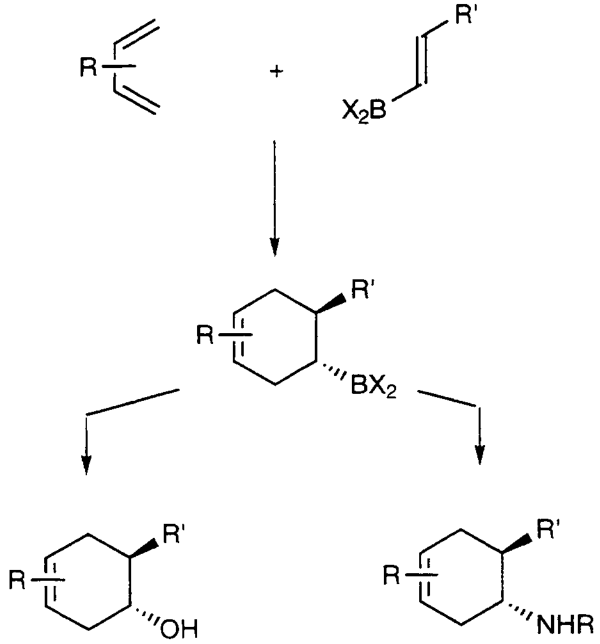
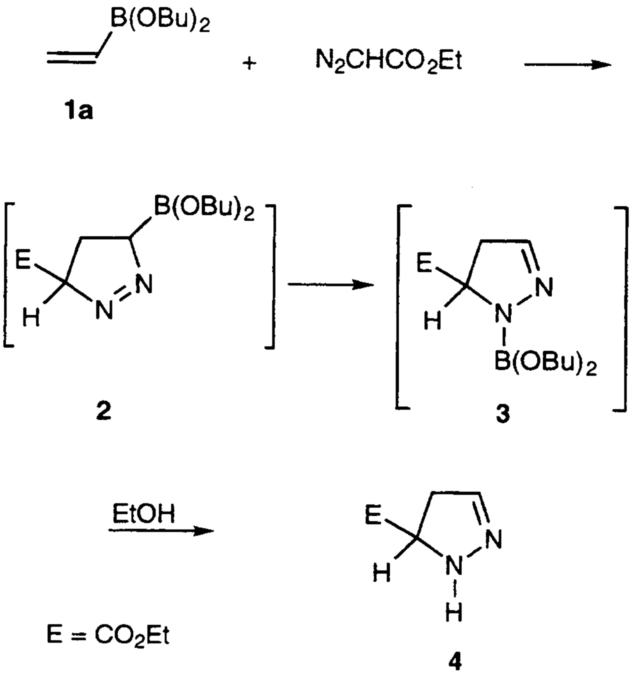


SCHEME 1

reactivity of several alkenyl boronic esters **1′**, **1″**, and **1‴** derived from pinacol, these being weak Lewis acids toward various diazo compounds (Figure 1).

The main goals of this study were to complete previous work concerning the scope and limitations of these reactions, to establish the exact nature of the intermediates, and, eventually, to find new experimental conditions that suppress the boron migration from carbon to nitrogen.



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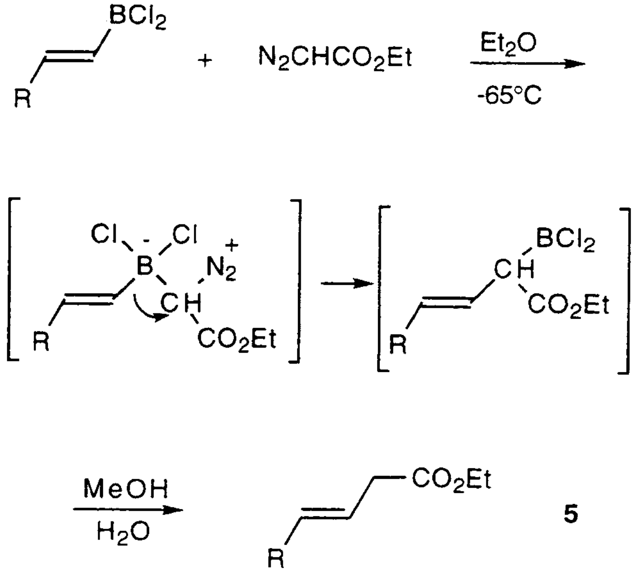


SCHEME 3

RESULTS AND DISCUSSION

Diazo compounds reacted with vinylboronate **1′** at 0°C for diazomethane **6a** and at room temperature for **6b–6f**. Heating at 40°C was necessary for methyl diazoacetate **6g** and diazoketones **6h** and **6i**. No addition was observed with diazomalonate **6j** (Scheme 4).

The cycloadditions of diazo compounds to vinyl boronic esters **1** are assumed to have led first to pyrazolines **7**. In spite of several attempts, these compounds were neither isolated nor characterized. We also never succeeded in obtaining the corresponding cyclopropyl boronic esters via a nitrogen extrusion reaction. For all of the experimental conditions we tried [13], 1,3-boratropy was faster and gave **8**. Compound **8b** was the only N-borylated 2-pyrazoline (vide infra) isolated. These moisture-sensitive compounds were usually hydrolyzed in situ to furnish the N–H derivatives **9**. The com-

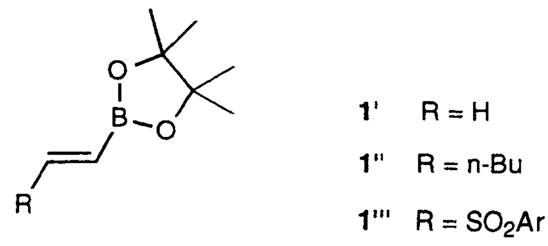
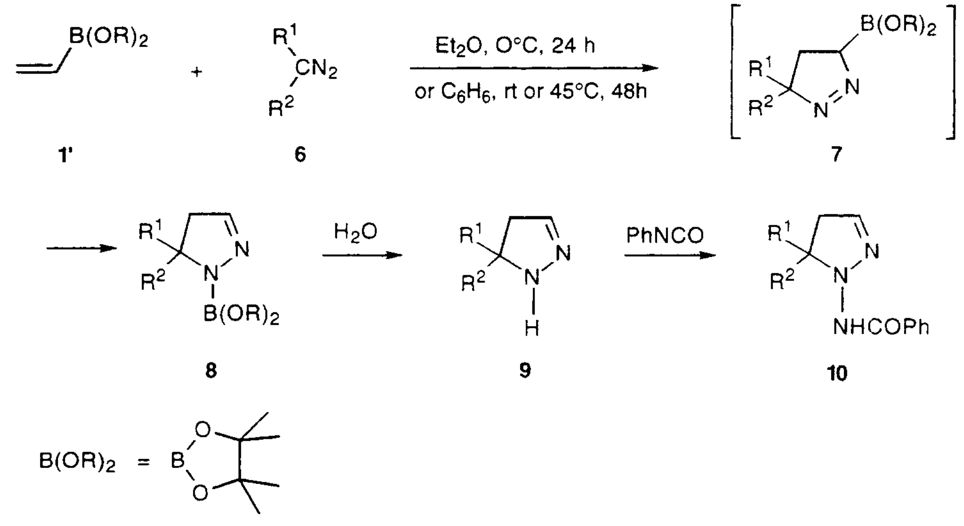


FIGURE 1

SCHEME 4



Entry	R^1	R^2	Entry	R^1	R^2
a	H	H	f	Ph	Bu^t
b	Ph	Ph	g	CO_2Me	H
c	Ph	Me	h	$-(CH_2)_5-CO$	
d	Ph	Et	i	$-(CH_2)_4-CO$	
e	Ph	Pr^i	j	CO_2Me	CO_2Me

pounds **9** were characterized only by ^1H NMR spectroscopy and then directly treated with phenyl isocyanate to afford the more stable ureas **10**. The products **10** were easily purified using column chromatography or recrystallization and fully characterized by ^1H and ^{13}C NMR spectroscopy and by elemental analysis (Table 1). To confirm their structures, independent syntheses of three 2-pyrazolines **9b**, **9d**, and **9h** were carried out starting from vinylphosphonium bromide according to the method of Schweizer and Kim [14].

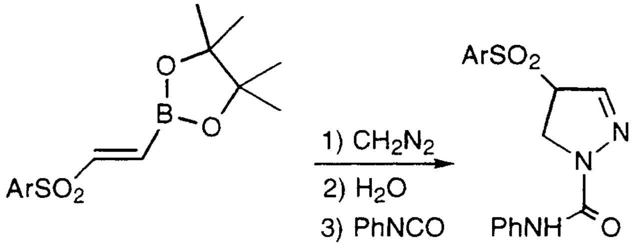
Attempts to obtain cycloadducts from 2-substituted-1-alkenyl boronic esters were unsuccessful when R = *n*-Bu. However, 2-pyrazoline **11** (R = $ArSO_2$) was prepared in good yield from **1'''**, diazomethane, and phenylisocyanate (Scheme 5). It is worthy of note that only one regioisomer was obtained.

The reactivity order could be predicted from the consideration of frontier orbitals [1]. The boronic ester moiety is an electron-withdrawing group, although it is clearly less efficient than ester or nitro groups [15]. The LUMO of the alkenylboronic esters and the HOMO of the diazo compound control the cycloaddition. The introduction of substituents that lower this HOMO reduces the reactivity. The lack of reaction observed when there is an alkyl substituent in a β position to boron is the result of a steric effect on the cycloaddition [1]. By contrast, the introduction of a second electron-

TABLE 1 Yields, Melting Points, and Elemental Analysis of Compounds **10**

Compound	*R^1*	*R^2*	*Yield (%)[a]*	*Mp (°C)*	*Formula*	*C*	*H*	*N*	*C*	*H*	*N*
10a	H	H	52	118	$C_{10}H_{13}N_3O$	63.49	5.82	22.22	63.75	5.82	22.12
10b	Ph	Ph	60	184	$C_{22}H_{19}N_3O$	77.42	5.57	12.32	77.14	5.78	12.18
10c	Ph	Me	45	115	$C_{17}H_{17}N_3O$	73.12	6.09	15.05	73.34	6.27	15.13
10d	Ph	Et	42	123	$C_{18}H_{19}N_3O$	73.72	6.48	14.33	73.58	6.66	14.46
10e	Ph	Pr^i	47	165	$C_{19}H_{21}N_3O$	74.26	6.84	13.68	74.40	6.84	13.55
10f	Ph	Bu^t	43	135	$C_{20}H_{23}N_3O$	74.76	7.16	13.08	74.76	7.12	13.34
10g	CO_2Me	H	44	110	$C_{12}H_{13}N_3O_3$	58.29	5.26	17.00	58.57	5.32	17.06
10h	$(CH_2)_5-CO$		58	104	$C_{15}H_{17}N_3O_2$	66.40	6.27	15.49	66.62	6.28	15.34
10i	$(CH_2)_4-CO$		53	124	$C_{14}H_{15}N_3O_2$	65.36	5.83	16.34	65.49	5.88	15.79

[a] Yields in isolated products from diazo compounds and alkenyl boronic esters.



1'''

11

75 % yield

SCHEME 5

withdrawing group such as a sulfone, which decreases the LUMO of the alkene, favors the cycloaddition.

It is also of interest to point out that the vinylboronic ester **1**′ can be regarded as an efficient synthetic equivalent for ethene because of its good reactivity with diazo compounds and the easy elimination of the boryl group.

Structure of 2-Pyrazoline **8b**

Having been formed from diphenyldiazomethane and after solvent elimination under vacuum and recrystallization from diisopropyl ether, colorless crystals of **8b** were obtained. Its structure was confirmed by X-ray diffraction analysis [16,17] (Figure 2).

Examination of the X-ray data shows that the 2-pyrazoline ring is almost planar (±0.03 Å) and the boronic ester ring is twisted. Carbon atom C(1) appears at 0.23 Å above (or below), and carbon atom C(2) appears at 0.24 Å below (or above) the plane of atoms O(1)–B–O(2). Selected bond lengths (Å) are as follows: C(3)–C(4) 1.479(6), C(4)–C(5) 1.554(6), C(5)–N(1) 1.489(5), N(1)–N(2) 1.390(4), N(2)–C(3) 1.273(6), N(1)–B 1.414(6).

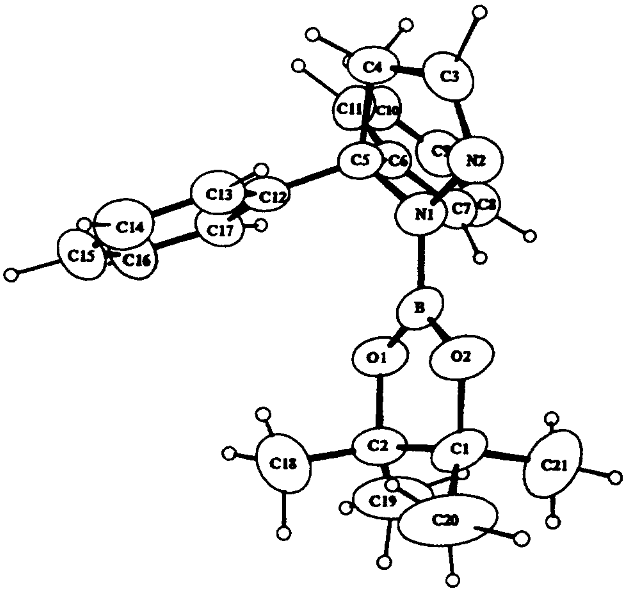


FIGURE 2 ORTEP representation of **8b** (probability ellipsoids: 50%).

In conclusion, this work contributes to the study of the behavior of alkenylboronic esters toward 1,3-dipolar compounds. This reactivity and the nature of the products thus obtained have been clarified. Spontaneous 1,3-migration of boron prevents any further functionalization of the adducts by the transformation of the boron–carbon bond to a carbon–heteroatom or carbon–carbon bond. However, it enables us to prepare a large variety of 2-pyrazolines not easily accessible via other routes. The vinylboronic ester must therefore be regarded as a useful synthetic equivalent for ethene.

EXPERIMENTAL SECTION

^1H and ^{13}C spectra were recorded on a Bruker AM 300 Spectrometer (75.5 MHz for ^{13}C). Chemical shifts are reported in δ and coupling constants are given in hertz. Deuterochloroform was used as the solvent. Elemental analyses were performed by the "Laboratoire Central d'Analyses du CNRS," Lyon. All melting points were determined with a Kofler apparatus and were uncorrected. Flash chromatography was carried out using E. MERCK 60 silica gel (250–400 mesh).

The following starting materials were prepared according to reported procedures: alkenyl boronic esters **1**′ [18], **1**″ [19], and **1**‴ [20] and diazo compounds **6a** [21], **6b–6f** [22], **6g** [23], **6h–6i** [24], and **6j** [25].

Cycloadditions with Diazomethane **6a**

A previously cooled ether solution (80 mL) of diazomethane (67 mmol) was dried over KOH for one night (−20°C). To this solution, after filtration and cooling at −78°C, was added dropwise 1.00 g of the alkenyl boronic ester (0.65 mmol) dissolved in dried ether (10 cm^3). When the addition was finished, the solution was kept at 0°C for 24 hours. The solution became cloudy and the formation of small amounts of (probably) polyethylene was observed. After filtration, ether was distilled under vacuum at room temperature. The crude mixture was used further without purification.

Cycloadditions with Diazocompounds **6b–6j**

To a solution of 6.5 mmol of each diazocompound in 2 mL of dried benzene was added dropwise 1.00 g (1 equivalent) of the alkenyl boronic ester. After 48 hours at room temperature (45°C for **6g–6i**) under nitrogen, solvent was removed under vacuum. The crude mixture was used in the next step without purification, except for **8b**, which was isolated by filtration after addition of diethyl ether.

8b: Yield = 75%; mp = 148–150°C (diisopropyl ether). ^{1}H NMR, δ (C_6D_6): 1.02 (s, $-OC(C\underline{H}_3)_2-$, 12H); 3.12 (d, H-4 and H-4′, ^{3}J = 1.6); 6.27 (t, H-3, ^{3}J = 1.6); 6.9–7.2 (m, 10H, aromatic protons). ^{13}C NMR, δ: 24.3 ($-OC(\underline{C}H_3)_2-$, $^{1}J_{CH}$ = 126); 55.8 (C-4, $^{1}J_{CH}$ = 134); 71.9 (C-5); 82.5 ($-O\underline{C}(CH_3)_2-$); 146.6 (s, aromatic carbons bound to C-5); 126.9, 127.9, and 128.4 (other aromatic carbons); 139.7 (d, C-3, $^{1}J_{CH}$ = 189).

Alkaline Hydrolysis of Compounds 8

To the previously obtained crude mixture (2.0 g) was added 20 cm^3 of 10% aqueous sodium hydroxide. After 1 hour at 80°C (room temperature for **8i** and **8j**), the reaction mixture was cooled and extracted with 3 × 30 cm^3 of diethyl ether. The extract was dried with $MgSO_4$ and concentrated. As a rule, 2-pyrazolines **9** are relatively unstable and cannot be isolated in pure form. They were only characterized by ^{1}H NMR spectroscopy before being converted to the corresponding ureas **10**.

9a, δ: 2.67 (dt, H-4 and H-4′, ^{3}J = 1.6 and 9.7); 3.29 (t, H-5 and H-5′, ^{3}J = 9.7); 6.65 (s large, NH); 6.91 (t, H-3, ^{3}J = 1.6).

9b, C_6D_6, δ: 5.32 (d, H-4 and H-4′, ^{3}J = 1.5); 6.01 (s large, N$\underline{H}$); 6.81 (t, H-3, ^{3}J = 1.5); 7.1–7.4 (m, 10H, aromatic protons).

9c, δ: 1.45 (s, $C\underline{H}_3$); 2.7–2.9 (m, H-4 and H-4′); 5.63 (s large, N$\underline{H}$); 6.65 (t, H-3, ^{3}J = 1.6); 7.0–7.5 (m, 5H, aromatic protons).

9d, δ: 0.72 (t, $CH_2C\underline{H}_3$, ^{3}J = 7.0); 1.88 (q, $C\underline{H}_2CH_3$, ^{3}J = 7.0); 2.6–3.1 (m, H-4 and H-4′); 5.95 (s large, N$\underline{H}$); 6.70 (t, H-3, ^{3}J = 1.6); 7.0–7.6 (m, 5H, aromatic protons).

9e, δ: 0.75 (d, $CHC\underline{H}_3$, ^{3}J = 7.6); 0.90 (d, $CHC\underline{H}_3$, ^{3}J = 7.6); 2.11 (quint, $C\underline{H}CH_3$, ^{3}J = 7.6); 2.80 (H-4), 3.06 (H-4′), and 6.61 (H-3) (ABX system, $^{2}J_{4,4'}$ = 17.6, $^{3}J_{4',3}$ = $^{3}J_{4,3}$ = 1.8); 4.81 (s large, N$\underline{H}$); 7.0–7.6 (m, 5H, aromatic protons).

9f, δ: 0.80 (s, 9H, $C(C\underline{H}_3)_3$); 2.99 (H-4), 3.21 (H-4′), and 6.82 (H-3) (ABX system, $^{2}J_{4,4'}$ = 17.6, $^{3}J_{4',3}$ = $^{3}J_{4,3}$ = 1.6); 6.17 (s large N$\underline{H}$); 6.8–7.6 (m, 5H, aromatic protons).

9g, δ: 2.82 (H-4, ddd, $^{2}J_{4,4'}$ = 17.6, $^{3}J_{4,3}$ = 1.6, $^{3}J_{4,5}$ = 6.6); 3.09 (H-4′, ddd, $^{2}J_{4,4'}$ = 17.6, $^{3}J_{4',3}$ = 1.6, $^{3}J_{4',5}$ = 10.0); 3.72 (s, $C\underline{H}_3$); 4.22 (dd, H-5, $^{3}J_{4,5}$ = 6.6, $^{3}J_{4',5}$ = 10.0); 5.95 (s large, N$\underline{H}$); 6.77 (t, H-3, ^{3}J = 1.6).

9h, δ: 1.5–2.5 (m, 10H, $(C\underline{H}_2)_5$); 2.66 (H-4), 3.16 (H-4′), and 6.63 (H-3) (ABX system, $^{2}J_{4,4'}$ = 17.6, $^{3}J_{4,3}$ = $^{3}J_{4',3}$ = 1.8); 6.25 (s large, N$\underline{H}$).

9i, δ: 1.6–2.4 (m, 8H, R^1 and R^2); 3.65 (H-4), 2.95 (H-4′), and 6.66 (H-3) (ABX system, $^{2}J_{4,4'}$ = 17.4, $^{3}J_{4,3}$ = $^{3}J_{4',3}$ = 1.7); 5.50 (s large, N$\underline{H}$).

Reactions of 9 *with Phenyl Isocyanate*

To 8.6 mmol of crude 2-pyrazoline **9** dissolved in 10 mL of diethyl ether was added 8.6 mmol of phenyl isocyanate. The reaction mixture was kept at room temperature for 12 hours. Ether was distilled under vacuum and compounds **10** were purified by chromatography or recrystallization.

10a: Mp = 118°C (diisopropyl ether). Yield = 52%. ^{1}H NMR, δ: 2.92 (td, H-4 and H-4′, ^{3}J = 1.8 and 10.1); 3.86 (t, H-5 and H-5′, ^{3}J = 10.1); 6.83 (t, H-3, ^{3}J = 1.6); 6.8–7.6 (m, 5H, aromatic protons); 7.89 (broad s, N$\underline{H}$). ^{13}C NMR, δ: 33.7 ($^{1}J_{CH}$ = 135) and 42.3 ($^{1}J_{CH}$ = 146) (2t, C-4 and C-5); 138.5 (s, aromatic carbon bound to NH); 118.5, 122.8, and 128.9 (other aromatic carbons); 145.0 (d, C-3, $^{1}J_{CH}$ = 193); 152.3 (s, $\underline{C}$=0).

10b: Mp = 184°C (diisopropyl ether). Yield = 60%. ^{1}H NMR, δ: 3.67 (d, H-4 and H-4′, ^{3}J = 1.9); 6.8–7.6 (m, 15H, aromatic protons); 6.82 (t, H-3, ^{3}J = 1.9); 8.12 (broad s, NH).

10c: Mp = 115°C after chromatography on silica gel. Eluent petroleum ether/ether (1/1). R_f = 0.38. Yield = 45%. ^{1}H NMR, δ: 1.99 (s, $C\underline{H}_3$); 2.95 (H-4), 3.17 (H-4′), and 6.70 (H-3) (ABX system, $^{2}J_{4,4'}$ = 17.9, $^{3}J_{3,4}$ = $^{3}J_{3,4'}$ = 1.6); 6.8–7.6 (m, 10H, aromatic protons); 8.07 (broad s, N$\underline{H}$).

10d: Mp = 123°C (methanol). Yield = 42%. ^{1}H NMR, δ: 0.92 (t, $CH_2C\underline{H}_3$, ^{3}J = 7.0); 2.15 (q, $C\underline{H}_2CH_3$, ^{3}J = 7.0); 2.99 (H-4), 3.17 (H-4′), and 6.70 (H-3) (ABX system, $^{2}J_{4,4'}$ = 19.0; $^{3}J_{3,4}$ = $^{3}J_{3,4'}$ = 1.6); 6.8–7.6 (m, 10H, aromatic protons); 8.11 (broad s, N$\underline{H}$).

10e: Mp = 165°C after chromatography on silica gel, eluent petroleum ether/ether (2/3). R_f = 0.63. Yield: 53%. NMR ^{1}H, δ: 0.97 (d, $CHC\underline{H}_3$, ^{3}J = 6.7); 3.19 (H-4), 3.48 (H-4′), and 6.81 (H-3) (ABX system, $^{2}J_{4,4'}$ = 19.3, $^{3}J_{4',3}$ = $^{3}J_{4,3}$ = 1.6); 3.63 (quint. $C\underline{H}CH_3$, ^{3}J = 6.7); 6.8–7.6 (m, 10H, aromatic protons); 7.93 (broad s, N$\underline{H}$). ^{13}C NMR, δ: 17.5 and 18.3 (2q, $\underline{C}H_3$, $^{1}J_{CH}$ = 126); 29.9 (d, $\underline{C}HCH_3$, $^{1}J_{CH}$ = 132); 44.7 (t, C-4, $^{1}J_{CH}$ = 134); 71.9 (s, C-5); 138.8 (s, aromatic carbon bound to NH); 143.5 (s, aromatic carbon bound to C-5); 118.9, 122.5, 127.2, 127.5, 128.2, and 128.7 (other aromatic carbons); 141.7 (t, C-3, $^{1}J_{CH}$ = 190); 150.8 (s, $\underline{C}$=0).

10f: Mp = 135°C (methanol). Yield = 43%. NMR ^{1}H, δ: 1.21 (s, $C(C\underline{H}_3)_3$); 3.14 (H-4), 3.48 (H-4′), and 6.72 (H-3) (ABX system, $^{2}J_{4,4'}$ = 17.9, $^{3}J_{4',3}$ = $^{3}J_{4,3}$ = 1.6); 6.8–7.7 (m, 10H aromatic protons); 8.41 (broad s, N$\underline{H}$).

10g: Mp = 110°C (methanol). Yield = 44%. NMR ^{1}H, δ: 2.84 (H-4, ddd, $^{2}J_{4,4'}$ = 18.4, $^{3}J_{4,3}$ = 1.6, $^{3}J_{4,5}$ = 7.4); 3.36 (H-4′, ddd, $^{2}J_{4,4'}$ = 18.4, $^{3}J_{4',3}$ = 1.6, $^{3}J_{4',5}$ = 11.8); 3.71 (s, CH_3 in R^1); 4.81 (dd, H-5, $^{3}J_{4,5}$ = 7.4, $^{3}J_{4',5}$ = 11.8); 6.71 (t, H-3, ^{3}J = 1.6); 6.8–7.6 (m, 10H, aromatic protons); 7.92 (broad s, NH).

10h: Mp = 104°C (methanol). Yield = 58%. ^{1}H NMR, δ: 1.5–2.7 (m, 10H, $(C\underline{H}_2)_5$); 2.79 (H-4), 2.96 (H-4′), and 6.63 (H-3) (ABX system, $^{2}J_{4,4'}$ = 18.4, $^{3}J_{4,3}$ = $^{3}J_{4',3}$ = 1.8); 6.8–7.6 (m, 5H, aromatic protons); 7.95 (broad s, N$\underline{H}$). ^{13}C NMR, δ: 22.7 (t, $^1J_{CH}$ = 130); 24.5 (t, $^1J_{CH}$ = 125); 36.5 (t, $^1J_{CH}$ = 131), 38.4 (t, $^1J_{CH}$ = 130); 46.9 (t, C-4, $^1J_{CH}$ = 137); 70.9 (s, C-5); 138.8 (other aromatic carbons); 140.2 (d, C-3, $^1J_{CH}$ = 193); 151.8 (s, $\underline{C}$ = 0 bound to nitrogen); 207.6 (s, $(CH_2)_5\underline{C}O$).

10i: Mp = 124°C (diisopropyl ether). Yield = 53%. ^{1}H NMR, δ: 1.5–2.5 (m, 6H, $(C\underline{H}_2)_4$); 2.79 (H_4), 2.99 ($H_{4'}$), and 6.71 (H_3) (ABX system, $^2J_{4,4'}$ = 18.2, $^3J_{3,4}$ = $^3J_{3,4'}$ = 1.8); 6.9–7.5 (m, 5H, aromatic protons); 7.81 (broad s, N$\underline{H}$).

11: Mp = 202°C. Yield = 75%. ^{1}H NMR, δ $(CD_3)_2SO$: 4.08 (dd, H-5′, J = 12.0 and 13.0); 4.27 (dd, H-5, J = 13.0 and 5.4); 5.13 (ddd, H-4, J = 5.4, 12.0, and 1.5); 7.05 (t, H-3, J = 1.5); 6.98–7.04 (m, 2H); 7.21–7.32 (m, 2H); 7.52 (d, 2H, J = 8.0); 7.64 (d, 2H, J = 7.8); 7.84 (d, 2H, J = 8.3); 8.31 (broad s, N$\underline{H}$). Anal. calcd for $C_{17}H_{17}N_3SO_3$: C, 59.48; H, 4.95; N, 12.24. Found: C, 59.12; H, 5.11; N, 12.31.

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