

## Amination of vinylsilanes and vinylgermanes containing an activated double bond

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### Abstract

Mixtures of alkyl esters of 2-triethylsilyl(germyl)- and (*E*)-3-triethylsilyl(germyl)acrylic acids were obtained by hydrosilylation and hydrogermylation of alkyl esters of propiolic acids. Alkyl esters of organosilicon(germanium)  $\beta$ -amino(hydrazino)propionic acids were obtained by amination of the alkyl esters of 2-triethylsilyl(germyl)acrylic acids.

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### Introduction

Addition of *N*-nucleophiles to  $\alpha,\beta$ -unsaturated acids, esters, or nitriles provides a general method for the preparation of  $\beta$ -amino acids [1,2]. The quaternary nitrogen species formed by addition of dimethylhydrazine to alkyl esters of  $\alpha,\beta$ -unsaturated acids is an intermediate in the synthesis of 2-alkoxycarbonyl-1*H*-aziridines [3]. In continuation of our studies of the amination of vinylsilanes [4,5] we decided to explore the possibility of obtaining esters of  $\beta$ -amino(dimethylhydrazino)propionic acids with the triethylsilyl or triethylgermyl substituent in the  $\alpha$ -position.

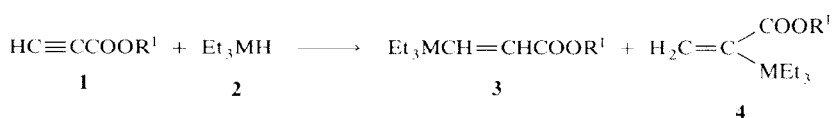
### Results and discussion

#### *The synthesis of alkyl esters of silyl- and germylacrylic acids*

We made use of the reaction of alkyl propiolates with triethylsilane and triethylgermane to prepare vinylsilanes and vinylgermanes containing an activated double bond.

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(a)  $\text{R}^1 = \text{H}$ ,  $\text{M} = \text{Si}$ ; (b)  $\text{R}^1 = \text{Et}$ ,  $\text{M} = \text{Si}$ ; (c)  $\text{R}^1 = \text{Me}$ ,  $\text{M} = \text{Si}$ ;  
 (d)  $\text{R}^1 = \text{Et}$ ,  $\text{M} = \text{Ge}$ ; (e)  $\text{R}^1 = \text{Me}$ ,  $\text{M} = \text{Ge}$

Scheme 1.

Hydrosilylation of alkyl propiolates with triethylsilane in the presence of Spayer's catalyst yielded two products, as a result of  $\alpha$ - and  $\beta$ -addition (Scheme 1). The ratio of regioisomers **3** and **4** depends on the nature of the ester group on the triple bond. Thus the mixture obtained from ethyl propiolate and silane **2** contained 52% of ethyl 2-triethylsilylacrylate and 48% of ethyl (*E*)-3-triethylsilylacrylate. In the case of methyl propiolate and propiolic acid the ratio of isomers **3** and **4** was 30:70 (see Table 1).

When the reactions were carried out in tetrahydrofuran (THF) or tetrahydropyran (THP), the proportion of the product **3** increased to 70%.

Hydrogermylation of ethyl propiolate by triethylgermane was carried out in THF in the presence of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ . When the reactions were performed without a solvent, the ratio of regioisomers **3d** and **4d** was similar to that obtained from addition of triethylsilane to ethyl propiolate. The product mixture contained 51% of ethyl 2-triethylgermylacrylate and 49% of ethyl (*E*)-3-triethylgermylacrylate (see Table 1). However the predominant direction of the addition of triethylgermane to ethyl propiolate was changed when the reaction was carried out in THF. Whereas the interaction of triethylsilane with ethyl propiolate yielded more  $\beta$ -product (70% of **3b**), in the case of triethylgermane the  $\alpha$ -addition product dominated (70% of ethyl 2-triethylgermylacrylate). Methyl propiolate was found to react with germane **2** in the same way as ethyl propiolate, and so the hydrogermylation reaction was optimized by use of methyl propiolate with the objective of maximizing the yield of the  $\alpha$ -product (see Table 2). In all cases hexachloroplatinic acid (0.1 *M* solution in THF) was added as the catalyst.

The best conditions involved keeping the reaction mixture at 60°C for 2 h with THF as solvent. More prolonged reaction lowered the yield of  $\alpha$ -product.

Table 1

Hydrosilylation and hydrogermylation of propiolic acid derivatives

Unsaturated compound <b>1</b>	$\text{Et}_3\text{MH}$ <b>M</b>	Solvent	B.p. (°C/mmHg) <b>3 + 4</b>	Yield (%) <b>3 + 4</b>	Products <sup>a</sup> (ratio, %) <b>3/4</b>
<b>a</b>	Si	—	112/1	60	30/70
<b>b</b>	Si	—	65/0.75	70	48/52
<b>b</b>	Si	THF	80–82/2	70	70/30
<b>b</b>	Si	THP	80–82/2	70	70/30
<b>c</b>	Si	—	50/0.75	70	30/70
<b>d</b>	Ge	—	74–76/1.5	68	49/51
<b>d</b>	Ge	THF	74–76/1.5	67	18/82

<sup>a</sup>  $^1\text{H}$  NMR data.

Table 2

Hydrogermylation of methyl propiolate with triethylgermane

Solvent	Temperature (°C)	Time (h)	Products <sup>a</sup> (ratio, %) <b>4e/3e</b>	Conversion <sup>b</sup> (%)
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	20	18	85/15	100
	50	3.5	75/25	100
CHCl <sub>3</sub>	20	15	87/13	90
	50	3.5	68/32	99
THF	20	18	89/11	99
	50	3.5	76/24	100
C <sub>6</sub> H <sub>14</sub>	20	18	80/20	99
	50	3.5	57/43	99
C <sub>6</sub> H <sub>6</sub>	20	15	88/12	99
	50	3.5	89/11	90

<sup>a</sup> Reactions were monitored by GLC. <sup>b</sup> Percentage of triethylgermane consumed

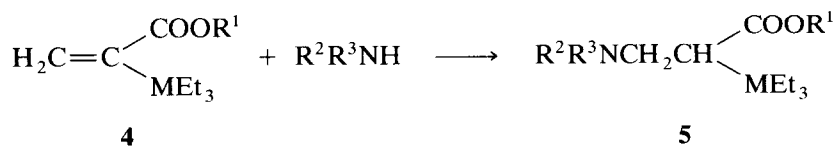
To increase the overall yield of the isomers **3** and **4** in all cases a slight excess of the acetylene derivative was used.

The mixtures of  $\alpha$ - and  $\beta$ -isomers of the alkyl esters of silyl-(or germyl-)acrylic acids were used as such in further reactions, because a control experiment showed that alkyl (*E*)-3-triethylsilyl(germyl)acrylates did not react with amines.

*Synthesis and properties of  $\beta$ -amino- and -hydrazinoethylsilyl(germyl)propionic acids*

We found that vinylsilanes and vinylgermanes with activated double bond **4b**, **c**, **e** readily underwent addition of primary or secondary amines or dimethylhydrazine (Scheme 2).

Compounds **4b** and **4c** reacted readily with tert-butylamine, diethylamine, and 1,1-dimethylhydrazine when the mixture was kept at 70–80°C for several hours under Ar, and yielded the alkyl esters of the organosilicon  $\beta$ -amino or  $\beta$ -hydrazino acids **5**. The triethylgermyl compound **4e** reacted under the same conditions with *N,N*-dimethylhydrazine to give 1,1-dimethyl-2-(2-ethoxycarbonyl-2-triethylgermyl-ethyl)hydrazine (see Table 3).



- (a)  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = {}^t\text{Bu}$ ,  $\text{R}^3 = \text{H}$ ,  $\text{M} = \text{Si}$ ; (b)  $\text{R}^1 = \text{Et}$ ,  $\text{R}^2 = \text{R}^3 = \text{Et}$ ,  $\text{M} = \text{Si}$ ;  
 (c)  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{Me}_2\text{N}$ ,  $\text{R}^3 = \text{H}$ ,  $\text{M} = \text{Si}$ ; (d)  $\text{R}^1 = \text{Et}$ ,  $\text{R}^2 = \text{Me}_2\text{N}$ ,  $\text{R}^3 = \text{H}$ ,  $\text{M} = \text{Si}$ ;  
 (e)  $\text{R}^1 = \text{Et}$ ,  $\text{R}^2 = \text{Me}_2\text{N}$ ,  $\text{R}^3 = \text{H}$ ,  $\text{M} = \text{Ge}$

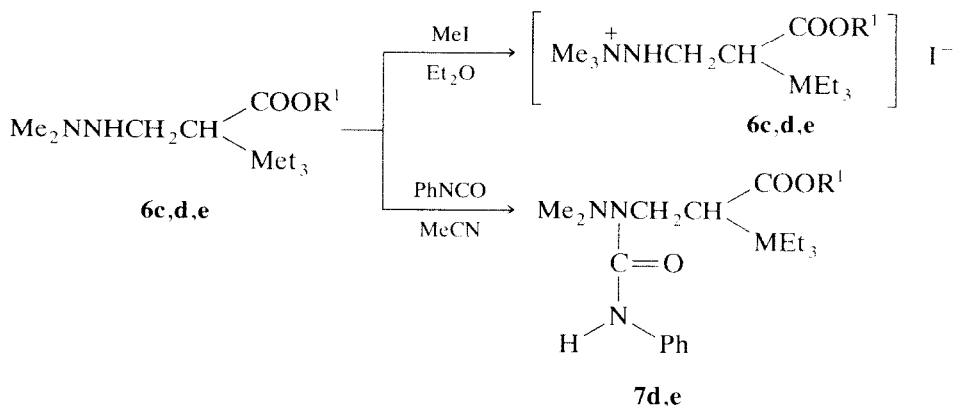
Scheme 2.

The products of addition to alkyl 2-triethylsilyl-(or trimethylgermyl-)acrylates **4c–e** were readily alkylated by MeI in diethyl-ether to give 1,1,1-trimethyl-2-[2'-alkoxycarbonyl-2'-triethylsilyl-(or triethylgermyl-)ethyl]hydrazinium iodides **6** in almost quantitative yields (see Scheme 3).

Table 3

Alkyl esters of organosilicon (germanium)  $\beta$ -amino and -hydrazino acids

Acrylate <b>4</b>	Time (h)	Product <b>5</b>	Yield (%)	B.p. (°C/mmHg)	<sup>1</sup> H NMR spectrum: <sup>a</sup> $\delta$ (ppm), $J$ (Hz)
<b>a</b>	6	<b>a</b>	40	134/13	0.58–0.91 (m, 15H, Et <sub>3</sub> Si), 1.04 (s, 9H, Me <sub>3</sub> C), 2.28 and 2.51 (dd $\times$ 2, 1H $\times$ 2, $J_1 = 12$ , $J_2 = 3$ , CH <sub>2</sub> N), 3.00 (dd, 1H, $J = 12$ , SiCH), 3.56 (s, 3H, MeO)
<b>b</b>	6	<b>b</b>	45	96/0.8	0.47–0.91 (m, 15H, Et <sub>3</sub> Si), 1.00 (s, 6H, CH <sub>3</sub> CH <sub>2</sub> N), 1.23 (t, 3H, $J = 7$ , CH <sub>3</sub> CH <sub>2</sub> O), 2.29–2.60 (m, 6H, CH <sub>2</sub> N and CH <sub>3</sub> CH <sub>2</sub> N), 3.13 (dd, 1H, $J_1 = 12$ , $J_2 = 14$ , SiCH), 4.09 (q, 2H, $J = 7$ , CH <sub>3</sub> CH <sub>2</sub> O)
<b>c</b>	4	<b>c</b>	60	93/0.7	0.47–0.96 (m, 15H, Et <sub>3</sub> Si), 2.37 (s, 6H, Me <sub>2</sub> N), 2.42 and 2.78 (dd $\times$ 2, 1H $\times$ 2, $J_1 = 12$ , $J_2 = 3$ , CH <sub>2</sub> N), 3.22 (dd, 1H, $J = 12$ , SiCH), 3.60 (s, 3H, MeO)
<b>d</b>	4	<b>d</b>	60	108/1.3	0.40–1.00 (m, 15H, Et <sub>3</sub> Si), 1.16 (t, 3H, $J = 7$ , CH <sub>3</sub> CH <sub>2</sub> O), 2.27 (s, 6H, Me <sub>2</sub> N), 2.29 and 2.69 (dd $\times$ 2, 1H $\times$ 2, $J_1 = 12$ , $J_2 = 3$ , CH <sub>2</sub> N), 3.18 (dd, 1H, $J = 12$ , SiCH), 4.00 (q, 2H, $J = 7$ , CH <sub>3</sub> CH <sub>2</sub> O)
<b>e</b>	4	<b>e</b>	60	110/2	0.74–1.19 (m, 15H, Et <sub>3</sub> Ge), 1.23 (t, 3H, $J = 7$ , CH <sub>3</sub> CH <sub>2</sub> O), 2.40 (s, 6H, Me <sub>2</sub> N), 2.46 and 2.80 (dd $\times$ 2, 1H $\times$ 2, $J_1 = 11$ , $J_2 = 3$ , CH <sub>2</sub> N), 3.22 (dd, 1H, $J = 11$ , GeCH), 4.10 (q, 2H, $J = 7$ , CH <sub>3</sub> CH <sub>2</sub> O)

<sup>a</sup> MHz, in CDCl<sub>3</sub>, TMS as internal standard.

Scheme 3.

The reaction of phenyl isocyanate with alkyl 2-triethylsilyl-(or triethylgermyl)-3-(2,2-dimethylhydrazino)propionate **5d**, **e**, yielded the corresponding silyl-(or germyl)-containing semicarbazide **7**.

## Experimental

The  $^1\text{H}$  NMR spectra were recorded on a WH-90/DS instrument (Bruker). The GLC analyses were carried out with a Varian 3700 apparatus fitted with a flame-ionization detector. A steel column (2 m  $\times$  1.8 mm) was packed with 5% OV-17/Chromosorb W/HP-AW DMCS (80–100 mesh); helium was used as carrier gas (20 cm<sup>3</sup>/min). Melting points were determined with a Fisher digital melting point analyser and are uncorrected.

### *Synthesis of alkyl 2-triethylsilyl(triethylgermyl)acrylates (general method)*

Three drops of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (0.1 M in THF) were added to an equimolar mixture of alkyl propiolate and triethylsilane (or triethylgermane). The mixture was heated to 50°C, at which an exothermic reaction took place. The mixture was stirred until the temperature fell to ambient. Products **3** and **4** were isolated by distillation under vacuum (see Table 1).

$^1\text{H}$  NMR spectrum of ethyl (*E*)-3-triethylsilylacrylate (90 MHz,  $\text{CDCl}_3/\text{TMS}$ ), ppm:  $\delta$  0.47–0.96 (m, 15H,  $\text{SiEt}_3$ ), 1.27 (t, 3H,  $J$  7.0 Hz,  $\text{CH}_3\text{CH}_2\text{O}$ ), 4.16 (q, 2H,  $J$  7.0 Hz,  $\text{CH}_3\text{CH}_2\text{O}$ ), 6.22 (d, 1H,  $J$  19.0 Hz,  $\text{SiCH=}$ ), 7.20 (d, 1H,  $J$  19.0 Hz,  $=\text{CHC(O)}$ ).

$^1\text{H}$  NMR spectrum of ethyl 2-triethylsilylacrylate (90 MHz,  $\text{CDCl}_3/\text{TMS}$ ), ppm:  $\delta$  0.47–0.96 (m, 15H,  $\text{SiEt}_3$ ), 1.27 (t, 3H,  $J$  7.0 Hz,  $\text{CH}_3\text{CH}_2\text{O}$ ), 4.16 (q, 2H,  $J$  7.0 Hz,  $\text{CH}_3\text{CH}_2\text{O}$ ), 5.93 (d, 1H,  $J$  3.0 Hz,  $\text{CH=}$ ), 6.80 (d, 1H,  $J$  3.0 Hz,  $\text{CH=}$ ).

### *Synthesis of ethyl 2-triethylgermylacrylate in THF*

A 0.1 M solution of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  in THF (160  $\mu\text{l}$ ) was added to a mixture of 8.24 g (0.084 mol) of ethyl propiolate and 12.88 g (0.080 mol) of triethylgermane in 90 ml of THF. The mixture was boiled for 2 h, the solvent then distilled off, and the products separated by distillation under vacuum (see Table 1).

$^1\text{H}$  NMR spectrum of ethyl (*E*)-3-triethylgermylacrylate (90 MHz,  $\text{CDCl}_3/\text{TMS}$ ), ppm:  $\delta$  0.83–1.18 (m, 15H,  $\text{GeEt}_3$ ), 1.29 (t, 3H,  $J$  7.0 Hz,  $\text{CH}_3\text{CH}_2\text{O}$ ), 4.18 (q, 2H,  $J$  7.0 Hz,  $\text{CH}_3\text{CH}_2\text{O}$ ), 6.19 (d, 1H,  $J$  19.0 Hz,  $\text{GeCH=}$ ), 7.40 (d, 1H,  $J$  19.0 Hz,  $=\text{CHC(O)}$ ).

$^1\text{H}$  NMR spectrum of ethyl 2-triethylgermylacrylate (90 MHz,  $\text{CDCl}_3/\text{TMS}$ ), ppm:  $\delta$  0.83–1.18 (m, 15H,  $\text{GeEt}_3$ ), 1.29 (t, 3H,  $J$  7.0 Hz,  $\text{CH}_3\text{CH}_2\text{O}$ ), 4.18 (q, 2H,  $J$  7.0 Hz,  $\text{CH}_3\text{CH}_2\text{O}$ ), 5.88 (d, 1H,  $J$  3.0 Hz,  $\text{CH=}$ ), 6.81 (d, 1H,  $J$  3.0 Hz,  $\text{CH=}$ ).

### *Synthesis of ethyl esters of organosilicon (germanium) $\beta$ -amino and -hydrazino acids (general method)*

The amino compound (0.12 molar proportion based on **4**) was added to a mixture of 0.1 mol of silyl(germyl)acrylates **3** and **4** and the mixture was stirred under an Ar atmosphere at 70°C for 4–6 h then cooled. The residual amine or hydrazine was distilled off and the residue purified by distillation under vacuum (see Table 3).

*Synthesis of 1,1,1-trimethyl-2-(2'-methoxycarbonyl-2'-triethylsilylethyl)hydrazinium iodide (6c)*

A mixture of 2.6 g (0.01 mol) 1,1-dimethyl-2-(2'-methoxycarbonyl-2'-triethylsilylethyl)hydrazine (**5c**) and 1.42 g (0.01 mol) MeI in 15 ml of dry ether was stirred for 20 hours at room temperature. The solid was filtered off and recrystallized from water to give **6c** (3.9 g, 98%), m.p. 127°C.

<sup>1</sup>H NMR spectrum (90 MHz, CDCl<sub>3</sub>/TMS), ppm: δ 0.52–1.13 (m, 15H, SiEt<sub>3</sub>), 2.49 (dd, 1H, *J*<sub>1</sub> 5.2 Hz, *J*<sub>2</sub> 9.8 Hz, SiCH), 3.24 (m, 2H, CH<sub>2</sub>N), 3.57 (s, 9H, Me<sub>3</sub>N<sup>+</sup>), 3.67 (s, 3H, OMe), 6.89 (t, 1H, *J* 8.2 Hz, NH).

*Synthesis of 1,1,1-trimethyl-2-(2'-ethoxycarbonyl-2'-triethylsilylethyl)hydrazinium iodide (6d)*

The procedure described above but starting from 2.7 g (0.01 mol) of 1,1-dimethyl-2-(2'-ethoxycarbonyl-2'-triethylsilylethyl)hydrazine (**5d**) and 1.42 g (0.01 mol) of MeI gave 3.7 g (90%) of **6d**, m.p. 169°C.

<sup>1</sup>H NMR spectrum (90 MHz, CDCl<sub>3</sub>/TMS), ppm: δ 0.60–1.25 (m, 15H, SiEt<sub>3</sub>), 1.25 (t, 3H, *J* 7.0 Hz, CH<sub>3</sub>CH<sub>2</sub>O), 2.42 (dd, 1H, *J*<sub>1</sub> 5.0 Hz, *J*<sub>2</sub> 10.0 Hz, SiCH), 3.22 (m, 2H, CH<sub>2</sub>N), 3.56 (s, 9H, Me<sub>3</sub>N<sup>+</sup>), 4.11 (q, 2H, *J* 7.0 Hz, CH<sub>3</sub>CH<sub>2</sub>O), 6.93 (t, 1H, *J* 8 Hz, NH).

*Synthesis of 1,1,1-trimethyl-2-(2'-ethoxycarbonyl-2'-triethylgermylethyl)hydrazinium iodide (6e)*

The same procedure but starting from 3.1 g (0.01 mol) of 1,1-dimethyl-2-(2'-ethoxycarbonyl-2'-triethylgermylethyl)hydrazine (**5e**) and 1.42 g (0.01 mol) of MeI and with recrystallization from 9/1 ethyl acetate/ethanol gave 3.8 g (85%) of **6e**, m.p. 167°C.

<sup>1</sup>H NMR spectrum (90 MHz, CDCl<sub>3</sub>/TMS), ppm: δ 0.84–1.13 (m, 15H, GeEt<sub>3</sub>), 1.25 (t, 3H, *J* 7.0 Hz, CH<sub>3</sub>CH<sub>2</sub>O), 2.49 (dd, 1H, *J*<sub>1</sub> 5.4 Hz, *J*<sub>2</sub> 10.1 Hz, GeCH), 3.22 (m, 2H, CH<sub>2</sub>N), 3.55 (s, 9H, Me<sub>3</sub>N<sup>+</sup>), 4.10 (q, 2H, *J* 7.0 Hz, CH<sub>3</sub>CH<sub>2</sub>O), 6.83 (t, 1H, *J* 8.2 Hz, NH).

*Synthesis of silicon-containing semicarbazide 7d*

Phenyl isocyanate (0.56 g, 0.005 mol) was added to a solution of 1.35g (0.005 mol) of 1,1-dimethyl-2-(2'-ethoxycarbonyl-2'-triethylsilylethyl)hydrazine (**5d**) in 20 ml of acetonitrile. The mixture was boiled for 3 h the solvent then distilled off, and the residue recrystallized from hexane to give 1.3 g (70%) of **7d**, m.p. 50°C.

<sup>1</sup>H NMR spectrum (90 MHz, CDCl<sub>3</sub>/TMS), ppm: δ 0.69–0.98 (m, 15H, SiEt<sub>3</sub>), 1.19 (t, 3H, *J* 6.7 Hz, CH<sub>3</sub>CH<sub>2</sub>O), 2.48 (s, 6H, Me<sub>2</sub>N), 2.92 (dd, 1H, *J* 5.0 Hz, SiCH), 3.53 (m, 2H, *J*<sub>1</sub> 5.0 Hz, *J*<sub>2</sub> 2 Hz, CH<sub>2</sub>N), 4.04 (q, 2H, *J* 6.7 Hz, CH<sub>3</sub>CH<sub>2</sub>O), 6.82–7.44 (m, 5H, Ph), 8.58 (bs, 1H, NH).

*Synthesis of germanium-containing semicarbazide 7e*

A similar procedure but starting from 1.55 g (0.005 mol) of **5e** and 0.56 g (0.005 mol) of phenyl isocyanate gave 1.48 g (70%) of **7e**, m.p. 52°C.

<sup>1</sup>H NMR spectrum (90 MHz, CDCl<sub>3</sub>/TMS), ppm: δ 0.73–1.15 (m, 15H, GeEt<sub>3</sub>), 1.22 (t, 3H, *J* 7.0 Hz, CH<sub>3</sub>CH<sub>2</sub>O), 2.51 (s, 6H, Me<sub>2</sub>N), 2.93 (dd, 1H, *J*<sub>1</sub> 5.0 Hz, *J*<sub>2</sub> 8.0 Hz, GeCH), 3.53 (m, 2H, CH<sub>2</sub>N), 4.04 (q, 2H, *J* 7.0 Hz, CH<sub>3</sub>CH<sub>2</sub>O), 6.87–7.49 (m, 5H, Ph), 8.58 (bs, 1H, NH).

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