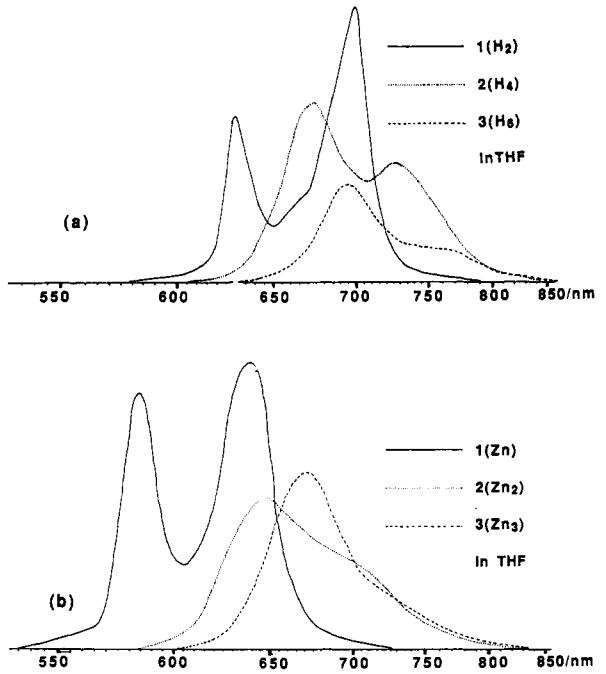

Figure 4. Fluorescence spectra of 1-H_2, 2-H_4, and 3-H_6 (the upper) and of 1-Zn, 2-Zn_2, and 3-Zn_3 (the lower) in THF excited at their respective Soret maxima. The fluorescence intensities of the monomers were one-fifth those of the dimers and trimers.

porphyrin 3-H_6 and was separated by flash chromatography on a silica gel column. The monomeric porphyrin 1 was eluted with CH_2Cl_2, and the diporphyrin 8 was eluted with CH_2Cl_2/THF (97/3 to 90/10). The triporphyrin 3-H_6 was eluted with CH_2Cl_2/THF (90/10 to 50/50), which was crystallized from CH_2Cl_2/MeOH to give blue crystals (45 mg, 0.026 mmol, 40% based on the amount of 8 used). Upon refluxing with $Zn(OAc)_2$ in CH_2Cl_2 or $CHCl_3$ solution for 4 h, 3-H_6 provided the bis-zinc complex of the triporphyrin 3-H_2Zn_2 (m/z 1892; calcd for $C_{122}H_{126}N_{12}Zn_2$ 1890.9) quantitatively. Complete zinc insertion in the porphyrin was achieved by refluxing for 2 h with $Zn(OAc)_2$ in either $CHCl_3$ containing a small quantity of triethylamine or in pyridine. 3-H_6: mp >300 °C; mass m/z 883 and 1765 (calcd for $C_{122}H_{130}N_{12}$ 1764.1); IR (KBr) 2962, 2927, 2870, 1460, 1448, and 752 cm^{-1}; ^1H NMR −8.32 (br, 2 H, NH), −7.05 (br, 2 H, NH), −5.74 (br, 2 H, NH), 0.88 (t, 12 H, Et), 1.10 (t, 12 H, Et), 1.21 (t, 12 H, Et), 2.16 (s, 12 H, Me), 2.54 (s, 12 H, Me), 2.62 (m, 4 H, Et), 2.73 (s, 6 H, tolyl-Me), 2.74 (s, 12 H, Me), 2.80 (m, 12 H, Et), 2.95 (m, 4 H, Et), 3.24 (m, 4 H, Et), 6.54 (s, 2 H, meso-H), 6.88 (d, 2 H, Ar), 7.18 (d, 2 H, Ar), 7.59 (s, 4 H, meso-H), 7.76 (d, 2 H, Ar), 8.05 (t, 2 H, Ar), 8.18 (t, 2 H, Ar), 8.23 (d, 2 H, Ar), 8.71 (d, 2 H, Ar), 8.89 (d, 2 H, Ar). 3-Zn_3: mp >300 °C; mass m/z 977, 1953 (calcd for $C_{122}H_{124}N_{12}Zn_3$ 1954.8); ^1H NMR (pyridine-d_6–$CDCl_3$ (1:1)) 1.12 (t, 12 H, Et), 1.44 (t, 24 H, Et), 2.43 (s, 12 H, Me), 2.77 (s, 6 H, tolyl-Me), 2.79 (s, 12 H, Me), 3.05 (s, 12 H, Me), 3.0–3.6 (m, 24 H, Et), 6.80 (s, 2 H, meso-H), 6.88 (br, 2 H, Ar), 6.95 (d, 2 H, Ar), 7.40 (s, 4 H, meso-H), 7.89 (broad, 2 H, Ar), 7.93 (d, 2 H, Ar), 8.08 (t, 2 H, Ar), 8.25 (t, 2 H, Ar), 8.80 (d, 2 H, Ar), and 9.14 (d, 2 H, Ar). The ^1H-NMR spectrum of 3-H_2Zn_2 could not be measured due to its limited solubility in most organic solvents.

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Supplementary Material Available: ^1H NMR spectra of 2, 3, 4, 6, 7, and 8 (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Ring Enlargement of Diaziridinone: Reactions with Bifunctionalized Carbanions Leading to Functionalized Pyrazolines or Novel Spiroheterocycles

Mitsuo Komatsu,* Yohko Kajihara, Mitsuharu Kobayashi, Shinobu Itoh, and Yoshiki Ohshiro*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565, Japan

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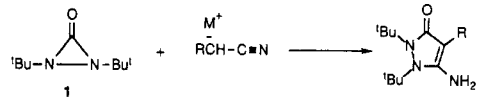
Much attention has been focused on the development of new synthetic reagents or new routes to functionalized heterocycles since the functional groups will allow novel uses of heterocycles. Ring enlargement reactions of small-ring heterocyclic compounds promoted by the release of large ring strain have provided versatile methods for the synthesis of medium-sized heterocycles.[1] Among these small rings, a diaziridinone[2] is expected to show high ring-opening reactivity because of its highly strained three-membered structure containing an sp^2 carbon and polar bonds.[1-3] In fact, cycloaddition and addition–cyclization reactions of diaziridinones leading to nitrogen-containing heterocycles have been reported by our group[4] and by Greene and co-workers.[5] In a previous paper,[4a] we reported that the ring enlargement reactions of *N,N'*-di-*tert*-butyldiaziridinone (1) with α-metalated nitriles led to aminopyrazolines via ring opening and recyclization.



(1)

The reactions of 1 with bifunctionalized carbanions derived from activated methylene compounds such as malononitrile and malonates instead of the above-mentioned monofunctionalized carbanions should give rise not only to multifunctionalized pyrazolines but also to novel spiroheterocyclic compounds. To test this hypothesis, we studied the ring enlargement reactions of diaziridinone 1 with some α-metalated malonic acid derivatives.

Treatment of *N,N'*-di-*tert*-butyldiaziridinone (1) with an equimolar amount of dicyano carbanion **3a**, generated from malononitrile (**2a**) and sodium hydride, in refluxing THF for 24 h afforded functionalized pyrazoline 3-amino-4-cyano-1,2-di-*tert*-butyl-3-pyrazolin-5-one (**4a**) in 31% yield. When 2 equiv of diaziridinone 1 was employed and the reaction was continued for 36 h, the isolated yield of pyrazolinone **4a** was improved to 92%. The structure of **4a** was determined from spectral data and elemental analysis. The amino group was detected by IR and ^1H NMR, and the existence of the cyano group was clearly supported by IR (2230 cm^{-1}) and ^{13}C NMR (δ 114.0). The

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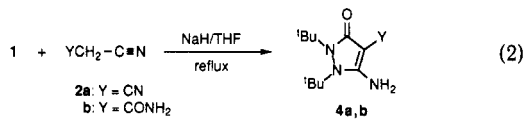
Table I. Formation of Aminopyrazolinones 4a,b from Diaziridinone 1 and Active Methylene Compounds 2a,b

substituent Y	mole ratio 1	2	NaH	reactn time (h)	yield of 4 (%)
2a: CN	1	1	1.4	24	31
	2	1	1.4	36	92
2b: $CONH_2$	1	1	1	24	4
	2	1	1	24	19

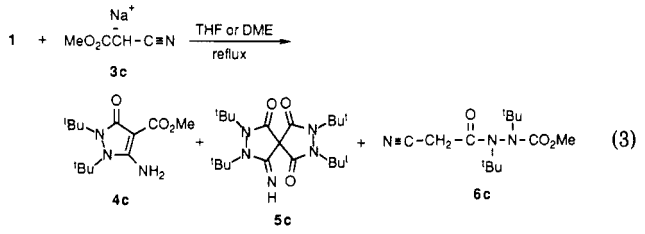
IR absorption of the carbonyl group was observed at 1650 cm^{-1}, which is characteristic of an α,β-unsaturated carbonyl group in a five-membered ring.



(2)

The reaction of diaziridinone 1 with carbanion **3b**, generated from α-cyanoacetamide (**2b**), gave the corresponding pyrazolinone 3-amino-4-carbamoyl-1,2-di-*tert*-butyl-3-pyrazolin-5-one (**4b**), but in a very low yield. The lower electronegative character of the carbamoyl group and the presence of active hydrogens on the nitrogen seem to have made the reaction more complicated.

Pyrazolinone **4c** precipitated from the reaction mixture of diaziridinone 1 and methyl α-sodio-α-cyanoacetate (**3c**), generated from methyl 2-cyanoacetate (**2c**), and column chromatography of the filtrate afforded a new spiroheterocyclic compound, 9-imino-2,3,7,8-tetraazaspiro-[4.4]nonane-1,4,6-trione (**5c**), and acyclic 1:1 adduct **6c**.



(3)

The IR spectrum of spiro compound **5c** showed absorptions at 3400 (NH), 1740 and 1720 (C=O), and 1660 cm^{-1} (C=N). In the ^1H NMR spectrum, four *tert*-butyl singlets together with a broad NH singlet (δ 6.9–7.1) were observed. Signals in the ^{13}C NMR spectrum were also in good agreement with the spiro structure (see Experimental Section). In contrast to the cyano group of malononitrile, the ester group of the cyanoacetate did take part in the ring formation reaction.

Since the biological activity, as well as other functions, of spiro compounds is of recent interest[6] and since spiro compounds **5c** has a novel skeleton, the effect of the reaction conditions on the product distribution was further studied. The reaction did not proceed in nonpolar solvents such as benzene probably because of the low solubility of sodiocyanoacetate **3c** in such solvents, but pyrazolinone **4c** was obtained in good yields in THF. An increase in the amount of diaziridinone 1 caused a slight increase in the yields of **4c** and **5c**. Addition of HMPA to this system gave no positive effect. In refluxing DME, a considerable amount of spiro compound **5c** was obtained without a decrease in the yield of **4c** (see Table II).

Table II. Formation of Aminopyrazolinone 4c and Spiroheterocycle 5c from Diaziridinone 1 and Active Methylene Compound 2c

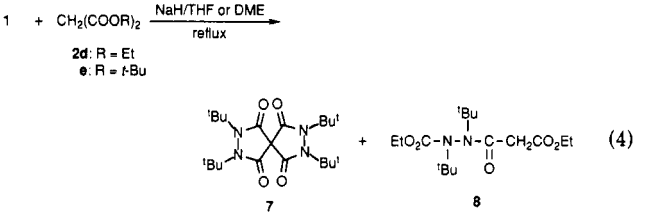
mole ratio 1	2	NaH	solv	reactn time (h)	yield (%) 4c	5c	6c
1	1	1	THF	24	53	4	4
2	1	1	THF	24	60	6	6
2	1	1	PhH	24	0	0	trace[a]
2	1	1	DME	24	47	10	7
2.5	1	1.5	DME	72	58	19	6
4.5	1	1.2	DME	36	64	15	17

[a] Ester **2c** was recovered (92%).

Formation of functionalized pyrazolinones **4a–c** is explained by the path assumed for the reaction of 1 with α-metalated nitriles.[4a] The reaction of 1 and **3c** affords **4c** via path a as shown in Scheme I. The anion of the 1:1 cycloadduct generated from 1 and **3c** via path a was expected to react with another molecule of diaziridinone 1 to give spiroheterocycle **5c**. However, when isolated pyrazolinone **4c** was deprotonated with LDA or NaH and then treated with diaziridinone 1 in refluxing DME for 48 h, no spiro compound **5c** was obtained, and unchanged **4c** was recovered almost quantitatively after workup. Accordingly, the formation of **5c** via path a is rather unlikely.

A possible alternative route to **5c** is a combination of paths b and c in Scheme I. Acyclic adduct **6c** is formed by nucleophilic attack of methoxide ion, liberated by cyclization, on the carbonyl carbon of the cyclic 1:1 adduct, pyrazolidinedione (paths b and d), and spiro compound **5c** may be formed by the reaction of diaziridinone 1 with the anion generated by deprotonation of the cyclic adduct by methoxide ion (paths b and c).

As the methoxycarbonyl group was effective in producing spiroheterocycle **5c**, diaziridinone 1 was allowed to react with carbanions having two alkoxycarbonyl substituents. When a mixture of 1 and diethyl sodiomalonate (**3d**), generated from malonate **2d** and sodium hydride, was refluxed in THF, only a slight amount of the anticipated tetraazaspirononanetetrone **7** was obtained, along with a considerable amount of 1:1 acyclic adduct **8**.



(4)

Spiro compound **7** and acyclic product **8** were formed in a manner similar to that for **5c** and **6c**. Because nucleophilic attack of the eliminated ethoxide ion caused the formation of acyclic compound **8**, it was expected that an alkoxide with lower nucleophilicity would give rise to a higher yield of the spiro compound **7**. Thus, di-*tert*-butyl malonate (**2e**) was successfully employed in place of **2d** to increase the yield of **7**. Although the bulky *tert*-butoxy group retards the initial cyclization reaction, its lower nucleophilicity prevents attack of the carbonyl carbon of the initial cycloadduct to form the ring-opened product leading to **8**. Instead, *tert*-butoxide acts as a strong base to abstract a proton from the cycloadduct, the anion of which reacts with diaziridinone 1 to form spiro compound **7**.

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Scheme I

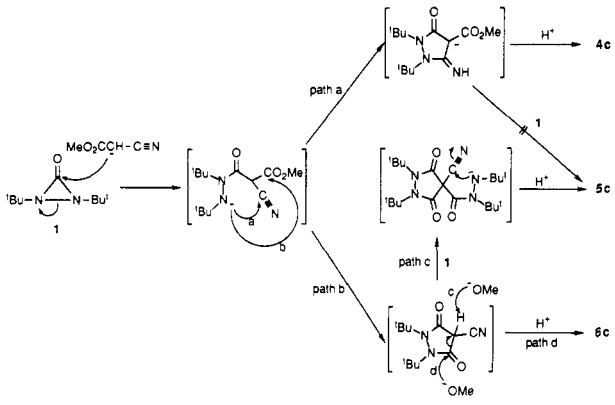

Table III. Formation of Spiroheterocycle 7 from Diaziridinone 1 and Malonates 2d,e

R of 2	mole ratio 1	2	NaH	solv	reactn time (h)	yield (%) 7	8
Et	1	1	1	THF	32	1	20
t-Bu	1	1	1	THF	24	11	
t-Bu	2	1	1	THF	24	8	
t-Bu	2.5	1	1.2	DME	24	23	*a*
t-Bu	2.5	1	1.7	DME	48	55	*a*

[a] A considerable amount of *tert*-butyl N^1,N^2-di-*tert*-butylcarbazate was detected.[8]

Experimental Section

General. All reactions were carried out under a nitrogen atmosphere. *N*,*N*'-Di-*tert*-butyldiaziridinone (1) and di-*tert*-butyl malonate (**2e**) were prepared according to known methods.[2,7] Malononitrile (**2a**), cyanoacetamide (**2b**), ethyl cyanoacetate (**2c**), and diethyl malonate (**2d**) were purchased and recrystallized or distilled prior to use. Organic solvents such as tetrahydrofuran (THF) and dimethoxyethane (DME) were dried and distilled according to conventional methods. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 90 and 22.5 MHz, respectively, with tetramethylsilane as an internal standard. Mass spectra were obtained by electron impact (EI) at 70 eV.

Reaction of Diaziridinone 1 and α-Sodiomalononitrile (3a). Sodium hydride (50% in mineral oil, 340 mg, 7.0 mmol) was washed with dry hexane, dried, and suspended in THF (5 mL). To the suspension cooled with an ice bath was added dropwise a solution of malononitrile (**2a**: 3.3 g, 5.0 mmol) in THF (5 mL), and the mixture was stirred for 1 h at room temperature. Then a solution of 1 (850 mg, 5.0 mmol) in THF (5 mL) was added to the above solution, and the mixture was refluxed for 24 h. The reaction mixture was quenched with wet THF, neutralized with 1 N HCl, and concentrated under reduced pressure. Upon addition of ether to the residue, 362 mg (31%) of 3-amino-4-cyano-1,2-di-*tert*-butyl-3-pyrazolin-5-one (**4a**) was obtained as a white precipitate. Similarly, the reaction of 1.70 g (10 mmol) of 1 for a longer reflux time (36 h) afforded 1.085 g (92% based on **2a**) of pyrazolinone **4a**. Recrystallization of the white precipitate from methanol gave colorless needles: mp 266 °C; IR (KBr) 3315, 3175 (NH_2), 2230 (CN), 1650 (C=O), 1600 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.20 (18 H, s, 2 *t*-Bu), 8.14 (2 H, br s, NH_2); ^{13}C NMR (DMSO-d_6) δ 27.3 (Me_3C), 27.5 (Me_3C), 61.6 (Me_3C), 64.3 (Me_3C), 69.5 (=CCN), 114.0 (CN), 176.7 (=CNH_2), 179.8 (C=O); MS *m*/*z* 236 (M^+). Anal. Calcd for $C_{12}H_{20}N_4O$: C, 60.99; H, 8.53; N, 23.71. Found: C, 61.13; H, 8.75; N, 23.77.

Reaction of Diaziridinone 1 and α-Sodio-α-cyanoacetamide (3b). The reaction of 1 (0.85 g, 5.0 mmol), α-cyanoacetamide (**2b**: 0.42 g, 5.0 mmol), and sodium hydride (50% in mineral oil, 0.24 g, 5.0 mmol) was performed as described for the above reaction. After 24 h, the reaction mixture was quenched with wet THF, neutralized with 1 N HCl, and concentrated under reduced pressure. The residue was extracted with ether (20 mL × 3) and water (10 mL) to afford 55 mg (4%) of 3-amino-4-carbamoyl-1,2-di-*tert*-butyl-3-pyrazolin-5-one (**4b**) as a white solid upon concentration of the organic extract. The yield was 19% when the reaction was carried out with 4.0 mmol of 1, 0.2 mmol of **2b**, and 0.2 mmol of sodium hydride. Pyrazolinone **4b**: mp 192 °C (colorless cubes from $CHCl_3$); IR (KBr) 3680, 3412 (NH), 1660, 1620 (C=O) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.30 (9 H, s, *t*-Bu), 1.33 (9 H, s, *t*-Bu), 5.15 (2 H, br s, $CONH_2$), 7.74 (2 H, br s, NH_2); MS *m*/*z* 198 ($M^+ - Me_2C{=}CH_2$). Anal. Calcd for $C_{12}H_{22}N_4O_2$: C, 56.67; H, 8.72; N, 22.03. Found: C, 56.47; H, 8.68; N, 21.83.

Reactions of Diaziridinone 1 and Methyl α-Sodio-α-cyanoacetate (3c). The reactions were performed as described for **3a** according to the conditions given in Table II. In the cases with THF as a solvent (runs 1 and 2), 3-amino-4-carbomethoxy-1,2-di-*tert*-butyl-3-pyrazolin-5-one (**4c**) precipitated out after neutralization and trituration with ether. In the other cases (runs 4–5), **4c** was isolated as a solid material by extraction with $CHCl_3/H_2O$ and successive trituration of the organic extract with ether. Column chromatography of the filtrate (neutral Al_2O_3/hexane–$CHCl_3$) afforded 9-imino-2,3,7,8-tetra-*tert*-butyl-2,3,7,8-tetraazaspiro[4.4]nonane-1,4,6-trione (**5c**) and/or methyl N^1,N^2-di-*tert*-butyl-N^1-(cyanoacetyl)carbazate (**6c**).

Pyrazolinone 4c: mp 167 °C (colorless needles from THF); IR (KBr) 3410, 3135 (NH), 1675, 1630 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30 (9 H, s, *t*-Bu), 1.32 (9 H, s, *t*-Bu), 3.83 (3 H, s, OMe), 6.75 (2 H, br s, NH_2); MS *m*/*z* 213 ($M^+ - Me_2C{=}CH_2$). Anal. Calcd for $C_{13}H_{23}N_3O_3$: C, 57.97; H, 8.61; N, 15.60. Found: C, 57.87; H, 8.61; N, 15.50.

Tetraazaspirononane 5c: mp 129–130 °C (colorless cubes from CH_2Cl_2–MeOH); IR (KBr) 3400 (NH), 1740, 1720 (C=O), 1660 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.47 (9 H, s, *t*-Bu), 1.49 (9 H, s, *t*-Bu), 1.60 (9 H, s, *t*-Bu), 1.65 (9 H, s, *t*-Bu), 6.92–7.07 (1 H, br s, NH); ^{13}C NMR ($CDCl_3$) δ 27.9 (Me_3C), 28.6 (Me_3C), 57.4 (Me_3C), 57.9 (Me_3C), 58.7 (Me_3C), 58.9 (Me_3C), 79.7 (spiro C), 155.8 (C=N), 156.6 (C=O), 160.9 (C=O), 168.5 (C=O); MS *m*/*z* 407 (M^+). Anal. Calcd for $C_{21}H_{37}N_5O_3$: C, 61.89; H, 9.15; N, 17.18. Found: C, 61.64; H, 9.15; N, 17.06.

Carbazate 6c: mp 84–85 °C (colorless needles from MeOH); IR (KBr) 2260 (CN), 1720, 1685 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45 (9 H, s, *t*-Bu), 1.47 (9 H, s, *t*-Bu), 3.48 (1 H, s, C*H*H), 3.54 (1 H, s, CH*H*), 3.78 (3 H, s, OMe); MS *m*/*z* 213 ($M^+ - Me_2C{=}CH_2$). Anal. Calcd for $C_{13}H_{23}N_3O_3$: C, 57.97; H, 8.61; N, 15.60. Found: C, 58.21; H, 8.64; N, 15.54.

Reaction of Diaziridinone 1 and Diethyl Sodiomalonate (3d). The reaction of 1 (3.4 g, 20 mmol), diethyl malonate (**2d**, 3.2 g, 20 mmol), and sodium hydride (50% in mineral oil, 0.96 g, 20 mmol) was performed as for **3a**. After a 38-h reflux period, the reaction mixture was quenched with water and extracted with ether (50 mL × 3). The organic layer was concentrated and distilled to give 0.6 g (19%) of the starting malonate. The residue was chromatographed (SiO_2/hexane–benzene) to give 60 mg (1%) of 2,3,7,8-tetra-*tert*-butyl-2,3,7,8-tetraazaspiro[4.4]nonane-1,4,6,9-tetrone (**7**) and 1.3 g (20%) of ethyl N^1,N^2-di-*tert*-butyl-N^1-((ethoxycarbonyl)acetyl)carbazate (**8**).

Tetraazaspirononanetetrone 7: mp 137–138 °C (colorless cubes from CH_2Cl_2–MeOH); IR (KBr) 1720 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.49 (18 H, s, 2 *t*-Bu), 1.59 (18 H, s, 2 *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 28.0 (Me_3C), 28.7 (Me_3C), 58.1 (Me_3C), 59.2 (Me_3C), 80.2 (spiro C), 156.1 (C=O), 167.7 (C=O); MS *m*/*z* 408 (M^+). Anal. Calcd for $C_{21}H_{36}N_4O_4$: C, 61.74; H, 8.88; N, 13.72. Found: C, 61.73; H, 8.89; N, 13.69.

Carbazate 8: bp 125–138 °C/1 mmHg (by pot distillation, colorless liquid); IR (neat) 1740, 1710 and 1670 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.28 (6 H, t, *J* = 7.0 Hz, 2 Me), 1.42 (9 H, s, *t*-Bu), 1.48 (9 H, s, *t*-Bu), 3.25 (2 H, d, *J* = 16.1 Hz, C*H*H), 3.48 (2 H, d, *J* = 16.1 Hz, CH*H*), 4.18 (q, *J* = 7.0 Hz, 4 H, 2 CH_2); MS *m*/*z* 228 ($M^+ - Me_2C{=}CH_2 - EtOH$). Anal. Calcd for $C_{16}H_{30}N_2O_5$: C, 58.16; H, 9.15; N, 8.48. Found: C, 57.84; H, 9.48; N, 8.62.

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(8) *tert*-Butyl carbazate: colorless liquid; IR (neat) 3295 (NH), 1700 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.02 (9 H, s, *t*-Bu), 1.31 (9 H, s, *t*-Bu), 1.48 (9 H, s, *t*-Bu), 4.00 (1 H, br s, NH); MS *m*/*z* 244 (M^+).