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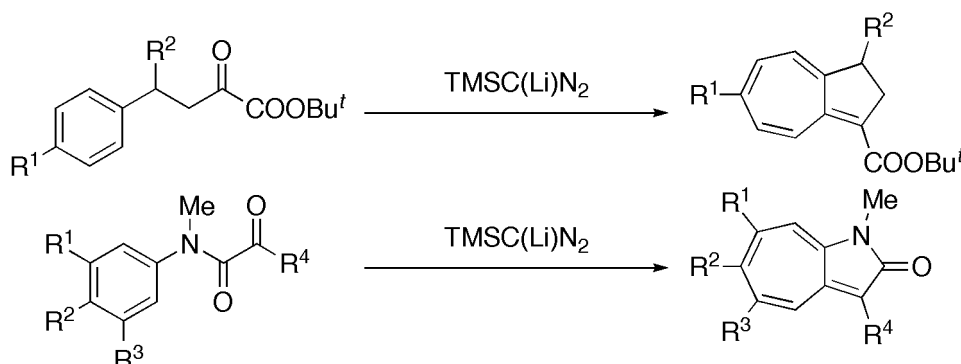
NEW SYNTHESIS OF *t*-BUTYL 1,2-DIHYDRO-1-OXAAZULENE-3-CARBOXYLATES USING LITHIUM TRIMETHYLSILYLDIAZOMETHANE

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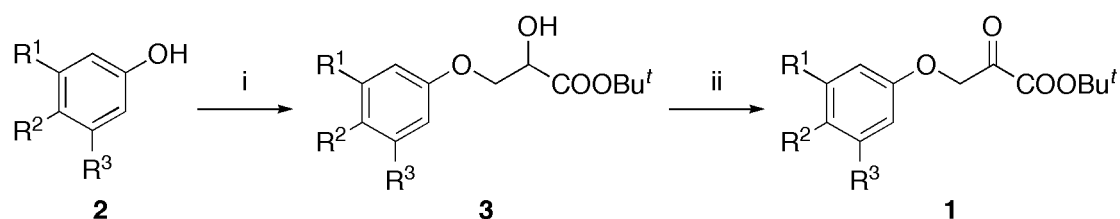
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Abstract – Lithium trimethylsilyldiazomethane reacts with *t*-butyl aryloxypruvates to give *t*-butyl 1,2-dihydro-1-oxaazulene-3-carboxylates *via* alkylidenecarbene intermediates.

Alkylidenecarbenes are attractive intermediates in organic synthesis.¹ We have already demonstrated that the lithium salt of trimethylsilyldiazomethane (TMSC(Li)N₂) smoothly reacts with carbonyl compounds to generate alkylidenecarbenes which undergo various types of reactions to give homologous alkynes, aldehydes, and heterocycles.² Furthermore, we have found that TMSC(Li)N₂ chemoselectively reacts with 4-aryl-2-oxobutanoates³ and *N*-methylanilides of α -keto acids⁴ at the carbonyl moiety giving 2,3-dihydroazulenes and 1-aza-1,2-dihydroazulen-2-ones *via* intramolecular cycloaddition of the generated alkylidenecarbenes to a benzene ring, followed by ring expansion, respectively (Scheme 1). Our continuous interest in this area has led us to investigate the reaction of aryloxypruvates with TMSC(Li)N₂ giving 1,2-dihydro-1-oxaazulene derivatives. In this paper, the details are described.

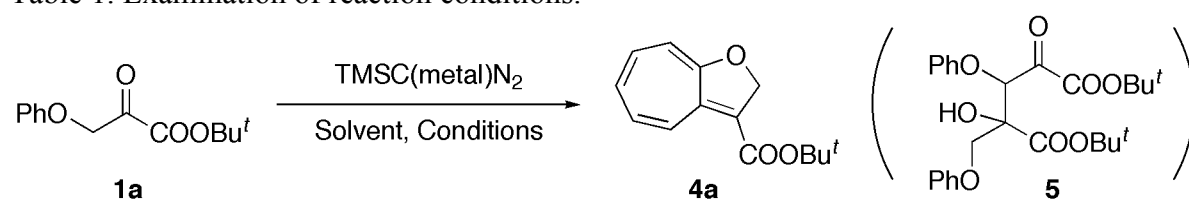


Scheme 1.



Scheme 2. *Reagents and conditions.* i, *t*-butyl glycidate (1.1–2.2 eq.), NaH (0.3–1.0 eq.), *t*-BuOMe, rt–reflux, 43–65 h, 34–67 %; ii, Dess-Martin periodinane (3.0 eq.), CH₂Cl₂, rt, 3 h, 59–87 %. R¹, R², R³ = H, H, H (**a**); H, Me, H (**b**); H, MeO, H (**c**); H, Br, H (**d**); H, CF₃, H (**e**); Me, H, Me (**f**).

Table 1. Examination of reaction conditions.

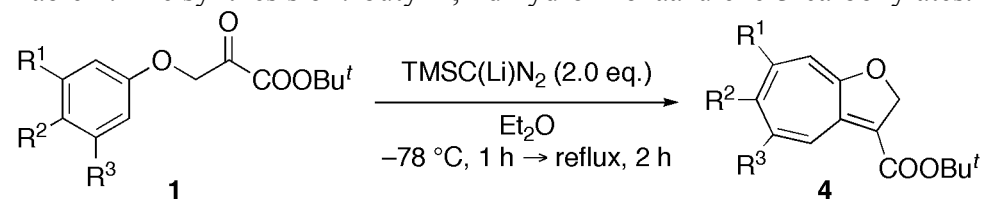


Entry	TMSC(metal)N ₂	Solvent	Conditions	Yield
1	TMSC(Li)N ₂ (1.2 eq.) ^a	Et ₂ O	–78 °C, 1 h → reflux, 2 h	19 %
2	TMSC(Li)N ₂ (1.2 eq.) ^a	THF	–78 °C, 1 h → 40 °C, 2 h	– ^f
3	TMSC(Li)N ₂ (1.2 eq.) ^a	<i>i</i> -Pr ₂ O	–78 °C, 1 h → 40 °C, 2 h	8 %
4	TMSC(Li)N ₂ (1.2 eq.) ^a	<i>t</i> -BuOMe	–78 °C, 1 h → 40 °C, 2 h	6 %
5	TMSC(Li)N ₂ (1.2 eq.) ^a	Et ₂ O-TMEDA (1.2 eq.)	–78 °C, 1 h → reflux, 2 h	– ^f (85 %) ^g
6	TMSC(Na)N ₂ (1.2 eq.) ^b	Et ₂ O	–78 °C, 1 h → reflux, 2 h	4 %
7	TMSC(K)N ₂ (1.2 eq.) ^c	Et ₂ O	–78 °C, 1 h → reflux, 2 h	– ^f
8	TMSC(MgBr)N ₂ (1.2 eq.) ^d	Et ₂ O	–78 °C, 1 h → reflux, 2 h	– ^f (42 %) ^g
9	TMSC(Li)N ₂ (2.0 eq.) ^a	Et ₂ O	–78 °C, 1 h → reflux, 2 h	28 %
10	TMSC(Li)N ₂ (2.0 eq.) ^e	Et ₂ O	–78 °C, 1 h → reflux, 2 h	27 %

^a Prepared from TMSCHN₂ and LDA. ^b Prepared from TMSCHN₂ and NaHMDS. ^c Prepared from TMSCHN₂ and KHMDS. ^d Prepared from TMSCHN₂, LDA and MgBr₂. ^e Prepared from TMSCHN₂ and *n*-BuLi. ^f Not obtained. ^g Obtained the aldol product (**5**).

The synthesis of *t*-butyl aryloxy pyruvates (**1**) as substrates is shown in Scheme 2. The epoxy-opening reaction of *t*-butyl glycidate⁵ by phenols (**2**) yielded α -hydroxy esters (**3**), which were oxidized by Dess-Martin periodinane giving the desired **1**.

The reaction conditions were optimized on the basis of reaction using *t*-butyl phenoxy pyruvate (**1a**) (Table 1). Treatment of **1a** with TMSC(Li)N₂ (1.2 eq.), prepared from TMSCHN₂ and LDA, in Et₂O gave the desired *t*-butyl 1,2-dihydro-1-oxaazulene-3-carboxylate (**4a**) in 19 % yield (Entry 1). Et₂O was found to be the solvent of choice though THF, *i*-Pr₂O and *t*-BuOMe were also tried (Entries 1–4). Interestingly, reaction in Et₂O containing TMEDA as an additive afforded the aldol product (**5**), and **4a** was not obtained at all (Entry 5). This result was probably due to an increase in basicity of TMSC(Li)N₂ by the addition of TMEDA. As shown in Entries 6–8, in this reaction, other metal salts of TMSCHN₂ such as TMSC(Na)N₂, TMSC(K)N₂ and TMSC(MgBr)N₂ were quite ineffective. When two equivalents of TMSC(Li)N₂ were used, the best result was obtained and the yield of **4a** increased to 28 % (Entry 9).⁶ The use of *n*-BuLi, instead of LDA, for the preparation of TMSC(Li)N₂ was also applicable in this reaction (Entry 10).

Table 2. The synthesis of *t*-butyl 1,2-dihydro-1-oxaazulene-3-carboxylates.

Entry	R ¹	R ²	R ³	Substrate	Yield
1 ^a	H	H	H	1a	28 %
2	H	Me	H	1b	31 %
3	H	MeO	H	1c	23 %
4	H	Br	H	1d	28 %
5	H	CF ₃	H	1e	22 %
6	Me	H	Me	1f	20 % ^b

^a Shown in Entry 9 of Table 1. ^b Obtained a mixture of **4f** and its isomer (1.7:1).

Next, reactions using other *t*-butyl aryloxypropionates were carried out under the optimized reaction conditions described above (Table 2). Various aryloxypropionates bearing methyl (**1b**), methoxy (**1c**), bromo (**1d**) and trifluoromethyl groups (**1e**) at the 4-position of the benzene ring reacted with TMSC(Li)N₂ to give the desired **4b-e** in 22-31 % yields (Entries 2-5). In these cases, substituents on the benzene ring of **1** had no effect on the yields of **4**. Reaction with (3,5-dimethylphenoxy)propionate (**1f**) also proceeded but the product was a mixture of **4f** and its isomer (concerning the position of double bonds) in 20 % yield (Entry 6). Unfortunately, reaction with *N,N*-diisopropyl-phenoxypropionamide⁷ or phenoxypropan-2-one gave a complex mixture and the desired 1,2-dihydro-1-oxaazulene derivative was not obtained.

In conclusion, we have found that the reaction of *t*-butyl aryloxypropionates with lithium trimethylsilyldiazomethane gave *t*-butyl 1,2-dihydro-1-oxaazulene-3-carboxylates bearing substituents on the 7-membered ring. Although the yield was still unsatisfactory, this synthetic method allows us to easily synthesize *t*-butyl 1,2-dihydro-1-oxaazulene-3-carboxylates from *t*-butyl acrylate.

EXPERIMENTAL

All melting points were measured on a Yanagimoto micro melting points apparatus and are uncorrected. IR spectra were recorded on a SHIMADZU FTIR-8400S spectrophotometer. ¹H and ¹³C NMR spectra were recorded on a JEOL JNM-EX-270 spectrometer (¹H, 270 MHz; ¹³C, 67.8 MHz). MS spectra were recorded on a JEOL JMS-SX-102A spectrometer.

***t*-Butyl 2-hydroxy-3-phenoxypropionate (3a).** To a stirred solution of phenol (1.88 g, 20 mmol) in *t*-butyl methyl ether (4 mL) were added NaH (400 mg, 60 % dispersion in oil, 10 mmol) and *t*-butyl glycidate (3.17 g, 22 mmol) under argon atmosphere. After being stirred at 45 °C for 43 h, the mixture was quenched with H₂O and extracted with EtOAc (2 times). The organic extracts were washed with water and saturated brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by Kugelrohr

distillation (1.0 mmHg, 150 °C) to give **3a** (3.17 g, 67 %). Colorless needles, mp 67-68 °C (Et₂O-hexane). IR (nujol): 3018, 1734 cm⁻¹. ¹H NMR (CDCl₃) δ: 1.48 (s, 9H), 3.21 (d, 1H, *J* = 6.5 Hz), 4.18-4.28 (m, 2H), 4.36-4.40 (m, 1H), 6.89-6.91 (m, 3H), 7.25-7.31 (m, 1H). ¹³C NMR (CDCl₃) δ: 28.0, 69.8, 70.3, 83.0, 114.6, 121.1, 129.0, 158.4, 171.2. MS (EI): *m/z* 238 (M⁺), 94 (bp). HRMS calcd for C₁₃H₁₈O₄: 238.1205, found: 238.1216.

***t*-Butyl 2-hydroxy-3-(4-methylphenoxy)propioate (3b)**. Prepared from 4-methylphenol (541 mg, 5.0 mmol) and *t*-butyl glycidate (865 mg, 6.0 mmol). The residue was purified by Kugelrohr distillation (1.2 mmHg, 140 °C) to give **3b** (516 mg, 41 %). Colorless crystals, mp 98-100 °C (hexane). IR (nujol): 3439, 1734 cm⁻¹. ¹H NMR (CDCl₃) δ: 1.47 (s, 9H), 2.28 (s, 3H), 3.21(br s, 1H), 4.14-4.24 (m, 2H), 4.35-4.37 (m, 1H), 6.80 (d, 2H, *J* = 8.4 Hz), 7.07 (d, 2H, *J* = 8.4 Hz). ¹³C NMR (CDCl₃) δ: 20.6, 28.1, 70.0, 70.3, 83.1, 114.5, 129.8, 130.4, 156.3, 171.3. MS (EI): *m/z* 252 (M⁺), 108 (bp). HRMS calcd for C₁₄H₂₀O₄: 252.1362, found: 252.1368.

***t*-Butyl 2-hydroxy-3-(4-methoxyphenoxy)propioate (3c)**. Prepared from 4-methoxyphenol (621 mg, 5.0 mmol) and *t*-butyl glycidate (865 mg, 6.0 mmol). The residue was purified by Kugelrohr distillation (1.0 mmHg, 150 °C) to give **3c** (644 mg, 48 %). Colorless needles, mp 74-75 °C (Et₂O-hexane). IR (nujol): 3439, 1740 cm⁻¹. ¹H NMR (CDCl₃) δ: 1.48 (s, 9H), 3.21 (d, 1H, *J* = 6.1 Hz), 3.77 (s, 3H), 4.16-4.19 (m, 2H), 4.30-4.35 (m, 1H), 6.79 (d, 2H, *J* = 8.4 Hz), 7.07 (d, 2H, *J* = 8.7 Hz). ¹³C NMR (CDCl₃) δ: 28.1, 55.7, 70.4, 70.7, 83.1, 114.5, 115.7, 152.6, 154.0, 171.3. MS (EI): *m/z* 268 (M⁺), 212 (bp). HRMS calcd for C₁₄H₂₀O₅: 268.1311, found: 268.1309.

***t*-Butyl 3-(4-bromophenoxy)-2-hydroxypropioate (3d)**. Prepared from 4-bromophenol (346 mg, 5.0 mmol) and *t*-butyl glycidate (634 g, 4.4 mmol). The residue was purified by Kugelrohr distillation (1.4 mmHg, 168 °C) to give **3d** (263 mg, 42 %). White powder, mp 96-97 °C. IR (nujol): 3434, 1732 cm⁻¹. ¹H NMR (CDCl₃) δ: 1.47 (s, 9H), 3.21 (d, 1H, *J* = 6.5 Hz), 4.14-4.24 (m, 2H), 4.36 (br s, 1H), 6.78 (d, 2H, *J* = 8.3 Hz), 7.37 (d, 2H, *J* = 8.3 Hz). ¹³C NMR (CDCl₃) δ: 28.1, 70.1, 70.2, 83.3, 113.4, 116.4, 132.2, 157.6, 171.0. MS (EI): *m/z* 318 (M⁺), 316 (M⁺), 57 (bp). HRMS calcd for C₁₃H₁₇O₄⁷⁹Br: 317.0310, found: 317.0337.

***t*-Butyl 2-hydroxy-3-(4-trifluoromethylphenoxy)propioate (3e)**. Prepared from 4-trifluoromethylphenol (811 mg, 5.0 mmol) and *t*-butyl glycidate (865 mg, 6.0 mmol). The residue was purified by Kugelrohr distillation (1.4 mmHg, 168 °C) to give **3e** (513 mg, 34 %). Colorless crystals, mp 121-122 °C (Et₂O). IR (nujol): 3437, 1730 cm⁻¹. ¹H NMR (CDCl₃) δ: 1.57 (s, 9H), 3.27 (br s, 1H), 4.22-4.32 (m, 2H), 4.38-4.42 (m, 1H), 6.96 (d, 2H, *J* = 8.7 Hz), 7.54 (d, 2H, *J* = 8.7 Hz). ¹³C NMR (CDCl₃) δ: 28.0, 70.0, 70.1, 83.5, 114.5, 115.4, 126.8, 126.9, 160.8, 170.9. MS (EI): *m/z* 306 (M⁺), 162 (bp). HRMS calcd for C₁₄H₁₇O₄F₃: 306.1079, found: 306.1087.

***t*-Butyl 3-(3,5-dimethylphenoxy)-2-hydroxypropioate (3f).** Prepared from 3,5-dimethylphenol (611 mg, 5.0 mmol) and *t*-butyl glycidate (793 g, 5.5 mmol). The residue was purified by Kugelrohr distillation (1.1 mmHg, 155 °C) to give **3f** (559 mg, 42 %). Colorless oil. IR (neat): 3434, 1736 cm⁻¹. ¹H NMR (CDCl₃) δ: 1.48 (s, 9H), 2.28 (s, 6H), 3.19 (d, 1H, *J* = 6.6 Hz) 4.13-4.23 (m, 2H), 4.35 (t, 1H, *J* = 3.0 Hz), 6.53 (s, 2H), 6.61 (s, 2H). ¹³C NMR (CDCl₃) δ: 21.4, 28.0, 69.7, 70.3, 112.3, 122.9, 139.0, 158.4, 171.3. MS (EI): *m/z* 266 (M⁺), 122 (bp). HRMS calcd for C₁₅H₂₂O₄: 266.1518, found: 266.1526.

***t*-Butyl phenoxypyruvate (1a).** To a solution of *t*-butyl 2-hydroxy-3-phenoxypropioate (**2a**) (218 mg, 0.91 mmol) in CH₂Cl₂ (4 mL) was added Dess-Martin periodinane (1.16 g, 2.74 mmol) and the mixture was stirred at rt for 3 h. After the mixture was diluted by Et₂O, a 1:1 mixture of saturated NaHCO₃ aq. and saturated Na₂S₂O₃ aq. was added and the mixture was further stirred overnight. The mixture was extracted with Et₂O (3 times). The organic extracts were washed with water and saturated brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (Fuji Sylisia BW-200MH, hexane:EtOAc = 7:1) to give **1a** (183 mg, 85 %). Pale yellow oil. IR (neat): 1746, 1734 cm⁻¹. ¹H NMR (CDCl₃) δ: 1.56 (s, 9H), 5.09 (s, 2H), 6.91 (d, 2H, *J* = 8.1 Hz), 7.01 (t, 1H, *J* = 7.6 Hz), 7.27-7.33 (m, 2H). ¹³C NMR (CDCl₃) δ: 27.9, 70.9, 85.1, 114.8, 121.9, 129.5, 157.4, 159.3, 189.7. MS (EI): *m/z* 236 (M⁺), 107 (bp). HRMS calcd for C₁₃H₁₆O₄: 236.1049, found: 236.1056.

***t*-Butyl (4-methylphenoxy)pyruvate (1b).** Prepared from **2b** (510 mg, 2.0 mmol) and Dess-Martin periodinane (2.57 g, 6.1 mmol). The residue was purified by column chromatography on silica gel (Fuji Sylisia BW-200MH, hexane:EtOAc = 7:1) to give **1b** (437 mg, 86 %). Pale yellow oil. IR (neat): 1755, 1720 cm⁻¹. ¹H NMR (CDCl₃) δ: 1.56 (s, 9H), 2.29 (s, 3H), 5.04 (s, 2H), 6.81 (d, 2H, *J* = 8.4 Hz), 7.08 (d, 2H, *J* = 8.4 Hz). ¹³C NMR (CDCl₃) δ: 20.6, 27.8, 71.3, 85.0, 114.7, 129.9, 131.2, 155.4, 159.4, 189.9. MS (EI): *m/z* 250 (M⁺), 121 (bp). HRMS calcd for C₁₄H₁₈O₄: 250.1205, found: 250.1200.

***t*-Butyl (4-methoxyphenoxy)pyruvate (1c).** Prepared from **2c** (553 mg, 2.1 mmol) and Dess-Martin periodinane (2.62 g, 6.2 mmol). The residue was purified by column chromatography on silica gel (Fuji Sylisia BW-200MH, hexane:EtOAc = 7:1) to give **1c** (430 mg, 78 %). Yellow oil. IR (neat): 1749, 1734 cm⁻¹. ¹H NMR (CDCl₃) δ: 1.56 (s, 9H), 3.77 (s, 3H), 5.09 (s, 2H), 6.80-6.87 (m, 4H). ¹³C NMR (CDCl₃) δ: 27.9, 55.7, 72.0, 85.0, 114.6, 116.1, 151.7, 154.6, 159.3, 190.1. MS (EI): *m/z* 266 (M⁺), 210 (M⁺ - ^tBu), 57 (bp). HRMS calcd for C₁₄H₁₈O₅: 266.1154, found: 266.1154.

***t*-Butyl (4-bromophenoxy)pyruvate (1d).** Prepared from **2d** (266 mg, 0.84 mmol) and Dess-Martin periodinane (1.07 g, 2.5 mmol). The residue was purified by column chromatography on silica gel (Fuji Sylisia BW-200MH, hexane:EtOAc = 7:1) to give **1d** (227 mg, 86 %). Pale yellow oil. IR (neat): 1747, 1732 cm⁻¹. ¹H NMR (CDCl₃) δ: 1.56 (s, 9H), 5.07 (s, 2H), 6.79 (d, 2H, *J* = 9.1 Hz), 7.39 (d, 2H, *J* = 9.1 Hz). ¹³C NMR (CDCl₃) δ: 27.9, 71.1, 85.3, 114.2, 116.5, 132.3, 156.6, 159.1, 189.1. MS (EI): *m/z* 316 (M⁺), 314 (M⁺), 57 (bp). HRMS calcd for C₁₃H₁₅O₄⁷⁹Br: 314.0154, found: 314.0152.

***t*-Butyl (4-trifluoromethoxy)pyruvate (1e).** Prepared from **2e** (500 mg, 1.6 mmol) and Dess-Martin periodinane (2.08 g, 4.9 mmol). The residue was purified by column chromatography on silica gel (Fuji Sylisia BW-200MH, hexane:EtOAc = 7:1) to give **1e** (295 mg, 59 %). Colorless crystals, mp 78-79 °C (hexane). IR (nujol): 1751 cm⁻¹. ¹H NMR (CDCl₃) δ: 1.57 (s, 9H), 5.15 (s, 2H), 6.97 (d, 2H, *J* = 8.6 Hz), 7.56 (d, 2H, *J* = 8.6 Hz). ¹³C NMR (CDCl₃) δ: 27.9, 70.7, 85.4, 114.7, 122.1, 123.8, 124.3, 126.1, 159.0, 159.8, 188.7. MS (EI): *m/z* 304 (M⁺), 248 (M⁺ - ^tBu), 175 (bp). HRMS calcd for C₁₄H₁₇O₄F₃: 304.0922, found: 304.0929.

***t*-Butyl (3,5-dimethylphenoxy)pyruvate (1f).** Prepared from **2f** (175 mg, 0.66 mmol) and Dess-Martin periodinane (936 mg, 2.0 mmol). The residue was purified by column chromatography on silica gel (Fuji Sylisia BW-200MH, hexane:EtOAc = 7:1) to give **1f** (121 mg, 70 %). Yellow needles, mp 84-85 °C (Et₂O-hexane). IR (nujol): 1751, 1726 cm⁻¹. ¹H NMR (CDCl₃) δ: 1.56 (s, 9H), 2.28 (s, 6H), 5.04 (s, 2H), 6.53 (s, 2H), 6.65 (s, 1H). ¹³C NMR (CDCl₃) δ: 21.5, 27.9, 70.9, 85.0, 112.5, 123.7, 139.3, 157.5, 159.4, 190.0. MS (EI): *m/z* 264 (M⁺), 135 (M⁺ - COCO₂^tBu), 57 (bp). HRMS calcd for C₁₅H₂₀O₄: 264.1362, found: 264.1368.

***t*-Butyl 1,2-dihydro-1-oxaazulene-3-carboxylate (4a).** To a stirred solution of diisopropylamine (95 mg, 0.94 mmol) in Et₂O (4 mL) was added dropwise *n*-butyllithium (1.60 M in hexane solution, 0.59 mL, 0.94 mmol) at -78 °C under argon atmosphere, and the mixture was stirred for 20 min. TMSCHN₂ (1.55 M in hexane solution, 0.60 mL, 0.94 mmol) was added dropwise at -78 °C, and the mixture was stirred for 10 min. A solution of *t*-butyl phenoxy pyruvate (**3a**) (111 mg, 0.47 mmol) in Et₂O (0.6 mL) was added dropwise. This mixture was stirred at -78 °C for 1 h, then refluxed for 2 h. After being quenched with H₂O, the mixture was extracted with EtOAc (3 times). The organic extracts were washed with water and saturated brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (Fuji Sylisia BW-200MH, hexane:EtOAc = 30:1) to give **4a** (29 mg, 27 %). Red oil. IR (neat): 1686 cm⁻¹. ¹H NMR (CDCl₃) δ: 1.46 (s, 9H), 5.36 (s, 2H), 5.63 (d, 1H, *J* = 9.3 Hz), 5.79 (dd, 1H, *J* = 8.2 and 11.0 Hz), 6.12 (dd, 1H, *J* = 9.3 and 11.0 Hz), 6.23 (dd, 1H, *J* = 8.2 and 11.9 Hz), 7.22 (d, 1H, *J* = 11.9 Hz). ¹³C NMR (CDCl₃) δ: 27.8, 78.1, 79.7, 104.9, 112.7, 123.3, 123.8, 133.5, 134.4, 144.6, 162.1, 172.1. MS (EI): *m/z* 232 (M⁺), 176 (M⁺ - ^tBu), 131(bp). HRMS calcd for C₁₄H₁₆O₃: 232.1100, found: 232.1100.

***t*-Butyl 4-(*t*-butoxycarbonyl)-3,5-diphenoxy-4-hydroxy-2-oxopentanoate (5).** Prepared from **3a** (61 mg, 0.26 mmol), TMS(Li)N₂ (0.31 mmol) and TMEDA (36 mg, 0.31 mmol). The residue was purified by column chromatography on silica gel (Fuji Sylisia BW-200MH, hexane:EtOAc = 30:1) to give **5** (52 mg, 85 %). Colorless needles, mp 127-128 °C (Et₂O). IR (nujol): 3522, 1747, 1728 cm⁻¹. ¹H NMR (CD₂Cl₂) δ: 1.36 (s, 9H), 1.42 (s, 9H), 3.99 (br s, 1H), 4.30 (d, 1H, *J* = 9.6 Hz), 4.34 (d, 1H, *J* = 9.6 Hz), 5.71 (s, 1H), 6.87-7.02 (m, 6H), 7.29 (m, 4H). ¹³C NMR (CD₂Cl₂) δ: 27.8, 27.8, 69.8, 79.2, 79.5, 84.3,

85.0, 114.8, 115.1, 121.5, 122.2, 129.3, 129.5, 156.9, 158.0, 161.0, 168.9, 191.3. MS (FAB): m/z 473 (MH^+). Anal. Calcd for $C_{26}H_{32}O_8$: C, 66.09; H, 6.83. Found: C, 65.79; H, 6.85.

***t*-Butyl 1,2-dihydro-6-methyl-1-oxaazulene-3-carboxylate (4b).** Prepared from **3b** (132 mg, 0.53 mmol) and $TMSC(Li)N_2$ (1.1 mmol). The residue was purified by column chromatography on silica gel (Fuji Sylisia BW-200MH, hexane:EtOAc = 30:1) to give **4b** (41 mg, 31 %). Red solid, mp 46-48 °C. IR (nujol): 1682 cm^{-1} . 1H NMR (CD_2Cl_2) δ : 1.46 (s, 9H), 1.90 (s, 3H), 5.32 (s, 2H), 5.56 (d, 1H, $J = 9.3$ Hz), 6.03 (d, 1H, $J = 9.3$ Hz), 6.20 (d, 1H, $J = 12.2$ Hz), 7.23 (d, 1H, $J = 12.2$ Hz). ^{13}C NMR (CD_2Cl_2) δ : 25.3, 27.8, 77.5, 79.6, 104.3, 112.2, 123.4, 130.7, 132.4, 137.8, 143.9, 162.3, 169.8. MS (EI): m/z 246 (M^+), 190 (bp). HRMS calcd for $C_{15}H_{18}O_3$: 246.1256, found: 246.1257.

***t*-Butyl 1,2-dihydro-6-methoxy-1-oxaazulene-3-carboxylate (4c).** Prepared from **3c** (99 mg, 0.37 mmol) and $TMSC(Li)N_2$ (0.75 mmol). The residue was purified by column chromatography on silica gel (Fuji Sylisia BW-200MH, hexane:EtOAc = 30:1) to give **4c** (23 mg, 23 %). Red solid, mp; 73-74 °C. IR (nujol): 1678 cm^{-1} . 1H NMR (CD_2Cl_2) δ : 1.47 (s, 9H), 3.56 (s, 3H), 5.28 (s, 2H), 5.51 (d, 1H, $J = 9.4$ Hz), 5.63 (d, 1H, $J = 9.4$ Hz), 6.19 (d, 1H, $J = 12.8$ Hz), 7.36 (d, 1H, $J = 12.8$ Hz). ^{13}C NMR (CD_2Cl_2) δ : 27.8, 54.7, 76.9, 79.7, 101.8, 106.5, 113.0, 124.1, 132.0, 142.5, 154.8, 162.3, 165.4. MS (EI): m/z 262 (M^+), 205 (bp). HRMS calcd for $C_{15}H_{18}O_4$: 262.1205, found: 262.1205.

***t*-Butyl 6-bromo-1,2-dihydro-1-oxaazulene-3-carboxylate (4d).** Prepared from **3d** (172 mg, 0.55 mmol) and $TMSC(Li)N_2$ (1.1 mmol). The residue was purified by column chromatography on silica gel (Fuji Sylisia BW-200MH, hexane:EtOAc = 30:1) to give **4d** (48 mg, 28 %). Red solid, mp 121-123 °C. IR (nujol): 1688 cm^{-1} . 1H NMR (CD_2Cl_2) δ : 1.47 (s, 9H), 5.33 (s, 2H), 5.40 (d, 1H, $J = 9.7$ Hz), 6.40 (d, 1H, $J = 11.7$ Hz), 6.51 (d, 1H, $J = 9.7$ Hz), 7.08 (d, 1H, $J = 11.7$ Hz). ^{13}C NMR (CD_2Cl_2) δ : 27.7, 78.0, 80.4, 102.9, 115.7, 116.5, 123.6, 134.9, 137.8, 142.4, 161.7, 171.4. MS (EI): m/z 312 (M^+), 310 (M^+), 254 (bp). HRMS calcd for $C_{14}H_{15}O_3^{79}Br$: 310.0205, found: 310.0202.

***t*-Butyl 1,2-dihydro-1-oxa-6-trifluoromethylazulene-3-carboxylate (4e).** Prepared from **3e** (273 mg, 0.90 mmol) and $TMSC(Li)N_2$ (1.8 mmol). The residue was purified by column chromatography on silica gel (Fuji Sylisia BW-200MH, hexane:EtOAc = 30:1) to give **4e** (60 mg, 22 %). Red solid, mp <30 °C. IR (nujol): 1659 cm^{-1} . 1H NMR (CD_2Cl_2) δ : 1.47 (s, 9H), 5.39 (s, 2H), 5.58 (d, 1H, $J = 9.6$ Hz), 6.24 (d, 1H, $J = 12.5$ Hz), 6.55 (d, 1H, $J = 9.6$ Hz), 7.27 (d, 1H, $J = 12.5$ Hz). ^{13}C NMR (CD_2Cl_2) δ : 27.7, 78.6, 80.8, 101.8, 124.3, 128.6, 128.7, 132.8, 142.4, 161.5, 174.7. MS (EI): m/z 300 (M^+), 244 ($M^+ - ^tBu$), 199 (bp). HRMS calcd for $C_{15}H_{15}O_3F_3$: 300.0973; found: 300.0979.

***t*-Butyl 1,2-dihydro-3,5-dimethyl-1-oxaazulene-3-carboxylate (4f).** Prepared from **3f** (86 mg, 0.33 mmol) and $TMSC(Li)N_2$ (0.65 mmol). The residue was purified by column chromatography on silica gel (Fuji Sylisia BW-200MH, hexane:EtOAc = 30:1) to give a mixture of **4f** and its isomer (17 mg, 20 %, **4f** : its isomer = 1.7 : 1). Red oil. IR (nujol): 1688 cm^{-1} . **4f**, 1H NMR (CD_2Cl_2) δ : 1.70 (s, 9H), 2.27 (s, 3H),

2.30 (s, 3H), 5.30 (s, 2H), 5.62 (s, 1H), 5.72 (s, 1H), 7.17 (s, 1H); its isomer, ^1H NMR (CD_2Cl_2) δ : 1.54 (s, 9H), 1.95 (s, 3H), 2.00 (s, 3H), 4.86 (s, 2H), 6.54 (s, 1H), 6.63 (s, 1H), 7.55 (s, 1H). MS (EI): m/z 260 (M^+), 203 ($\text{M}^+ - \text{t-Bu}$), 159 (bp). HRMS calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$: 260.1412; found: 260.1414.

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