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Opening of Cyclopropyl Ketones with SmI$_2$. Synthesis of Spirocyclic and Bicyclic Ketones by Intramolecular Trapping of an Electrophile.

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Abstract: A method for the opening of cyclopropyl ketones with samarium(II) iodide followed by the intramolecular trapping of an electrophile is described. This process leads to the obtainment of functionalized spirocyclic, bicyclic, and tricyclic ketones in moderate to good yields. © 1997 Elsevier Science Ltd.

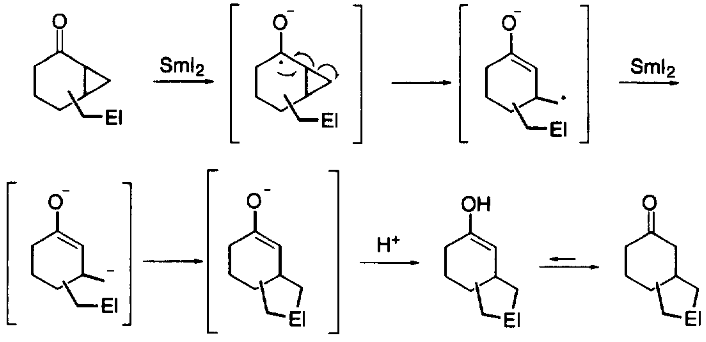
INTRODUCTION

Samarium(II) iodide (SmI$_2$) is a one-electron reducing agent capable of promoting a vast range of one-step and sequenced reactions.[1] Among them, SmI$_2$ is able to promote the reductive cleavage of cyclopropyl ketones.[2] In particular, bicyclic cyclopropyl ketones are stereoselectively opened with cleavage of the exocyclic carbon-carbon bond. As an extension of this process, the carbon radical that is formed during the course of the reaction has been successfully trapped by an unsaturated radicophilic acceptor.[2d] The same reaction has also been performed by *O*-stannyl ketyl promoted fragmentation[3] or by photoinduced electron transfer reactions,[4] affording in the second case the corresponding bicyclic and spirocyclic products with moderate yields.

It was the aim of this project to take advantage of the reducing strength of SmI$_2$ for further transformations. This reducing agent can convert the initially formed radical to a carbanion, opening the possibility of trapping an electrophile intramolecularly, a process that would lead to a variety of functionalized spirocyclic and bicyclic ring systems.

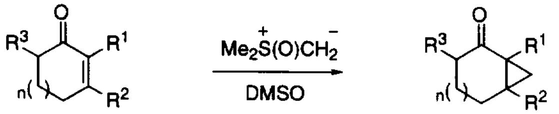
RESULTS AND DISCUSSION

The mechanism envisioned for this process would involve initial formation of the ketyl radical, followed by rapid cleavage of the cyclopropyl ring (Scheme 1). Further reduction of the carbon radical to the anion followed by intramolecular attack onto the electrophile would lead to the desired bicyclic or spirocyclic products after aqueous workup.



Scheme 1: Proposed mechanism for the cyclopropyl ketone opening / intramolecular trapping of an electrophile.

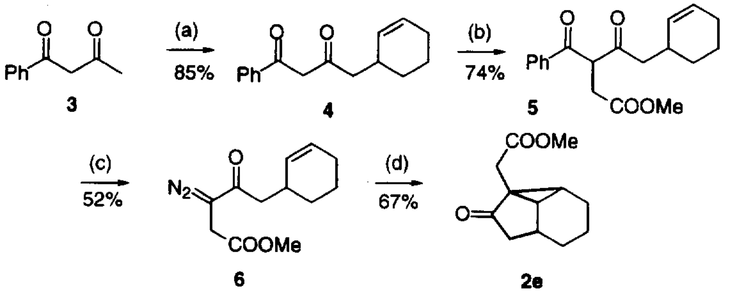
In order to study the scope of the reaction, a variety of substituted cyclopropyl ketones with properly functionalized lateral chains in different positions on the ring were prepared. These chains bore methyl ketones, esters, aldehydes, or epoxides as electrophilic moieties. Most of the keto esters were obtained from the readily available enones[5] by cyclopropanation of the double bond with trimethylsulfoxonium ylide (Scheme 2).[6]



1a; n = 1, $R^1 = R^3 = H$, $R^2 = CH_2CH_2COOMe$	**2a**; 26%
1b; n = 0, $R^1 = R^3 = H$, $R^2 = CH_2CH_2COOMe$	**2b**; 27%
1c; n = 1, $R^2 = R^3 = H$, $R^1 = CH_2COOEt$	**2c**; 75%
1d; n = 1, $R^1 = R^2 = H$, $R^3 = CH_2COOMe$	**2d**; 57% (1.7:1 ds)

Scheme 2: Synthesis of cyclopropyl keto esters **2a-d**.

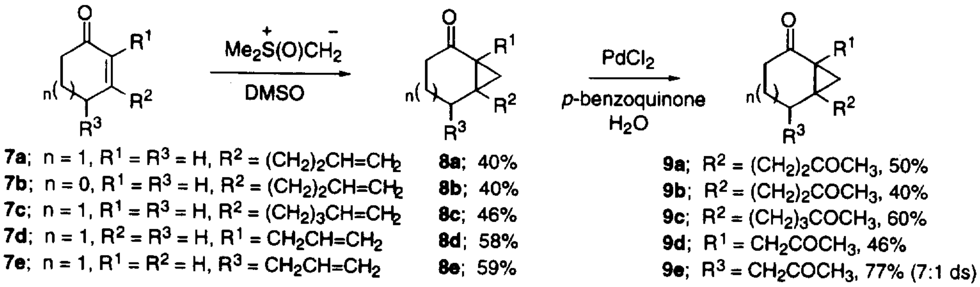
The tricyclic keto ester **2e** was obtained by copper catalyzed cyclopropanation of the diazo keto ester **6**.[7] Substrate **6** was synthesized by succesive α and γ alkylation of benzoylacetone followed by diazo transfer from *p*-nitrobenzenesulfonyl azide (*p*-NBSA) with debenzoylation of the substrate (Scheme 3).[8]



(a) LDA, 3-bromocyclohexene. (b) K_2CO_3, methyl bromoacetate. (c) *p*-NBSA, NaH. (d) $Cu(acac)_2$, $CuSO_4$.

Scheme 3: Synthesis of bicyclic ketone **2e**.

The diketone substrates were prepared from an appropiate dialkenone by a process that involved cyclopropanation of the conjugated double bond,[9] followed by Wacker oxidation of the terminal double bond (Scheme 4).[10] The first step of this pathway has been recently reported with similar results.[4a]



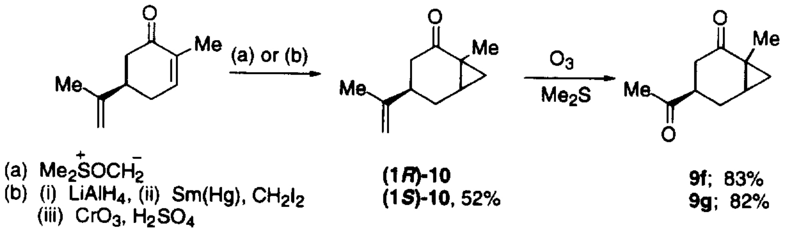
7a; n = 1, $R^1 = R^3 = H$, $R^2 = (CH_2)_2CH{=}CH_2$
7b; n = 0, $R^1 = R^3 = H$, $R^2 = (CH_2)_2CH{=}CH_2$
7c; n = 1, $R^1 = R^3 = H$, $R^2 = (CH_2)_3CH{=}CH_2$
7d; n = 1, $R^2 = R^3 = H$, $R^1 = CH_2CH{=}CH_2$
7e; n = 1, $R^1 = R^2 = H$, $R^3 = CH_2CH{=}CH_2$

8a; 40%
8b; 40%
8c; 46%
8d; 58%
8e; 59%

9a; $R^2 = (CH_2)_2COCH_3$, 50%
9b; $R^2 = (CH_2)_2COCH_3$, 40%
9c; $R^2 = (CH_2)_3COCH_3$, 60%
9d; $R^1 = CH_2COCH_3$, 46%
9e; $R^3 = CH_2COCH_3$, 77% (7:1 ds)

Scheme 4: Synthesis of the cyclopropyl diketones **9a-e**.

An exception to this procedure was the synthesis of diketones **9f** and **9g** (Scheme 5). Substrate **9f** was obtained by the usual direct cyclopropanation of (*R*)-(-)-carvone with methylsulfoxonium ylide to give **(1*R*)-10**,[11] followed by ozonolysis of the isolated double bond. The diastereomeric substrate **9g** was prepared by the hydroxyl-directed cyclopropanation of the corresponding carvol with samarium/mercury amalgam and diiodomethane,[12] Jones oxidation to the ketone **(1*S*)-10**, and finally ozonolysis. Aldehyde **11** and epoxide **12** were synthesized from the corresponding 3-alkenyl ketone **7a** by ozonolysis or epoxidation,[13] respectively, as shown in Scheme 6.

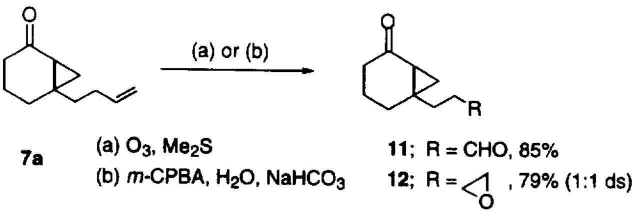


(a) $Me_2\overset{+}{S}O\overset{-}{C}H_2$
(b) (i) $LiAlH_4$, (ii) Sm(Hg), CH_2I_2
(iii) CrO_3, H_2SO_4

(1*R*)-10
(1*S*)-10, 52%

9f; 83%
9g; 82%

Scheme 5: Synthesis of cyclopropyl diketones **9f** and **9g** from (*R*)-(-)-carvone.



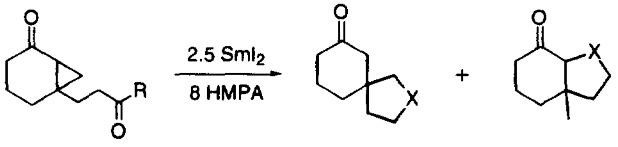
7a

(a) O_3, Me_2S
(b) *m*-CPBA, H_2O, $NaHCO_3$

11; R = CHO, 85%
12; R = , 79% (1:1 ds)

Scheme 6: Synthesis of epoxy cyclopropyl ketone **12** and cyclopropyl keto aldehyde **11**.

With these substrates in hand, the SmI_2 reductive cleavage / coupling sequence was tested (Scheme 7). The first experiments were carried out by slow, dropwise addition of the substrate to a solution of 2.5 equiv of SmI_2 in THF containing 8 equiv of hexamethylphosphoramide (HMPA) at -30 °C. Under these conditions, the diketone **9a** was consumed within 15 min to provide a mixture of compounds. The analysis of this mixture demonstrated that, along with the desired spirocyclic compound, an undesired bicyclic compound derived from attack of the enolate onto the electrophile was also formed. A similar result was observed when using the keto ester **2a**. In this case, the undesired condensation product was obtained as the major component.



9a; R = Me
2a; R = OMe

X = C(OH)Me, 32% (2:1)
X = CO, 30% (>1:9)

Scheme 7: First experiments on the SmI_2 reductive cleavage / coupling sequence.

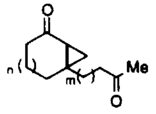
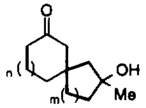
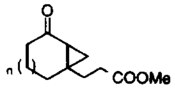
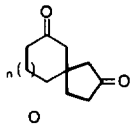
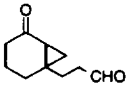
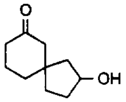
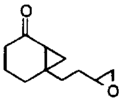
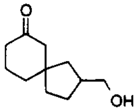
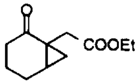
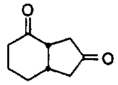
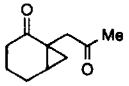
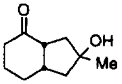
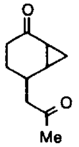
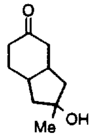
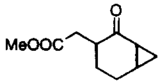
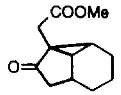
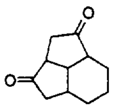
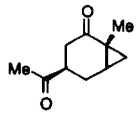
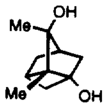
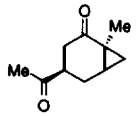
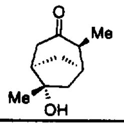
The reaction conditions were tuned in order to minimize the generation of the undesired product. By using the same amount of SmI_2 with only 2 equiv of HMPA at 0 °C, only the spirocyclic compounds **13a** and **13b** were obtained in good yield (Table 1, entries 1 and 4), with none of the enolate trapping product detected.

Other 3-substituted substrates were subjected to these standard reaction conditions. In general, the reactions provided the expected spirocyclic compounds in moderate to good yield when cyclization onto the electrophile gave rise to a second five-membered ring (entries 2, 5 and 6). The reaction of **9c** gave a complex mixture of products from which the corresponding spiro keto alcohol **13c** was isolated (entry 3). In this last case, there was some control over the formation of the second stereocenter, while other dicarbonyl substrates led to an equimolar mixture of diastereomeric keto alcohols. An epoxide proved to be a poor electrophile for this reaction (entry 7).

Two 2-substituted substrates were next tested under the standard reaction conditions. The keto ester **2c** gave cleanly the bicyclic diketone **14c** as a single diastereoisomer (entry 8). The stereochemistry of this compound was unambiguosly established by single crystal X-ray diffraction of the diol generated by reduction with L-Selectride®.[14] In a similar manner, the reaction of the diketone **9d** with SmI_2 gave the keto alcohol **13d** in good yield as an equimolar mixture of cis-fused diastereomers (entry 9). The inseparable mixture of isomers **9e** was subjected to the same reaction conditions, providing a mixture of diastereomers **13e** in 73% yield from which the trans-fused isomers were isolated (entry 10). The tricyclic keto ester **2e** yielded the expected tricyclic diketone **14e** with moderate yield (entry 12).

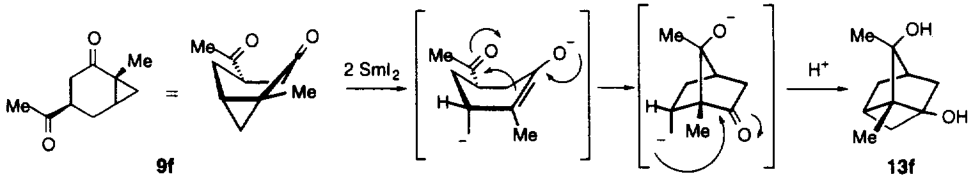
Both diastereomeric substrates derived from (*R*)-(-)-carvone gave unexpected results. Substrate **9f** reacted under the standard reaction conditions to afford a single compound in moderate yield, which proved to be the tricyclic diol **13f** as confirmed by X-ray diffraction techniques (entry 13, Figure 1).[14] The mechanism for this reaction can be envisioned as involving initial opening of the cyclopropyl ketone, followed by trapping of the carbonyl on the lateral chain by the enolate (Scheme 9). This process results in regeneration of the

Table 1: Results on the SmI$_2$ Reductive Cleavage / Coupling Sequence.

entry	substrate		product		% isoltd yld (ds)
1 2 3		**9a**; n=1, m=1 **9b**; n=0, m=1 **9c**; n=1, m=2		**13a** **13b** **13c**	79 (1:1) 61 (1.4:1) 30 (5:1) [a]
4 5		**2a**; n=1 **2b**; n=0		**14a** **14b**	64 40
6		**11**		**15**	42 (1.5:1)
7		**12**		**16**	27 (1.3:1) [b]
8		**2c**		**14c**	67
9		**9d**		**13d**	79 (1:1)
10		**9e** [c] (7:1 ds)		**13e**	73 [d]
11		**2d**	complex mixture		
12		**2e**		**14e**	39
13		**9f**		**13f**	40
14		**9g**		**13g**	79

(*a*) Substrate added as a 0.02 M solution in THF. **13c** was isolated with 90% purity (GC). (*b*) **16** was isolated with 70% purity (GC). (*c*) The trans-substituted isomer is the major compound. (*d*) Obtained as a mixture of four diastereomers. For the two trans-fused stereoisomers, the ratio of isomers owing to the carbinol stereocenter is 1:1.

ketone, which is then trapped by the primary carbanion result from the cyclopropyl opening. The diastereomeric substrate **9g** also reacted cleanly with SmI_2 to give a single enantiomeric product **13g** (entry 14). The stereochemistry was assigned according to the spectral data previously reported for this compound.[15] In both of the reactions of SmI_2 with **9f** and **9g** complete stereochemical control was established at the newly formed stereocenters. This is particularly surprising because no obvious stereocontrol element can be readily identified.



Scheme 8: Proposed mechanism for the formation of **13f**.

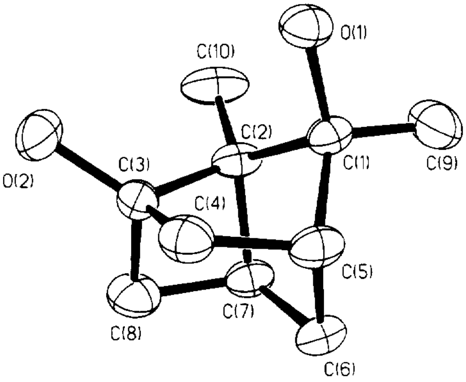
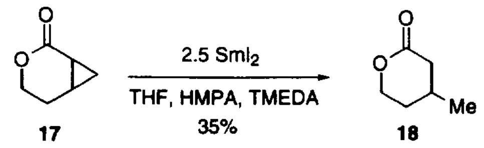


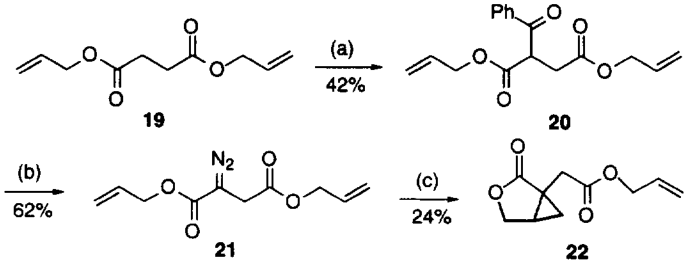
Figure 1: X-ray crystal structure of the tricyclic diol **13f**.

The efficacy of the SmI_2-induced reductive cleavage of cyclopropyl lactones was next examined. The reduction of esters with SmI_2 is known to be more difficult than that of ketones.[1a-c] In particular, the opening of cyclopropanecarboxylates with SmI_2 has only been achieved under very extreme conditions or with specially activated substrates.[16] As expected, the opening of the cyclopropyl lactone **17** did not take place using our standard reaction conditions. But the reaction proceeded smoothly at 0 °C when 5 equiv of HMPA and 2 equiv of tetramethylethylenediamine (TMEDA) were used as cosolvents (Scheme 9). The second additive is believed to serve as an aprotic Sm(III) chelator.[17]

An appropriate substrate was synthesized to test the opening of the bicyclic lactone followed by the intramolecular trapping of the electrophile. Benzoylation of the diester **19** followed by diazo transfer afforded the diazo diester **21**.[18] Copper catalyzed intramolecular cyclization of this compound gave the lactone **22** in moderate yield (Scheme 10).[7] Unfortunately, all efforts to reduce the cyclopropyl lactone **22** with SmI_2 failed. Either the substrate of the reaction was recovered or complex mixtures were obtained.



Scheme 9: SmI_2 reduction of cyclopropyl lactone **17**.



(a) NaH, allyl benzoate, (b) *p*-NBSA, DBU. (c) $Cu(acac)_2$, $CuSO_4$

Scheme 10: Synthesis of cyclopropyl lactone **22**.

CONCLUSIONS

A useful method for the synthesis of spirocyclic, bicyclic, and tricyclic ketones which bear additional functionality in their skeleton has been developed. A variety of compounds has been obtained in moderate to good yields, achieving high stereoselectivities in some particular cases.

ACKNOWLEDGEMENTS

C. Alonso-Alija is indebted to the Fundaciön Ramön Areces (Spain) for a Postdoctoral Fellowship. We thank Dr. Bruce C. Noll for performing the X-ray crystallographic analyses and the National Institutes of Health (NIH) for their generous support of our research program.

EXPERIMENTAL SECTION

Reagents: Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under Ar and then redistilled from sodium-benzophenone ketyl immediately prior to use. Samarium metal was purchased from Cerac, Inc. and stored under Ar. Diiodomethane (CH_2I_2) was purchased from Aldrich and was distilled prior to use and stored under Ar over copper turnings. HMPA was purchased from Aldrich and was distilled from CaH_2 and stored over 4Å molecular sieves under Ar. TMEDA was purchased from Aldrich and was distilled from KOH and stored over 4Å molecular sieves under Ar. All solvents were distilled prior to use. Commercially available reagents were used with no further purification. Standard benchtop techniques were employed for handling air-sensitive reagents, and all reactions were performed under Ar.

Methyl 3-(5-Oxobicyclo[4.1.0]heptan-1-yl)propionate (2a). General Procedure for the Cyclopropanation of α,β-Enones. To 127 mg (5.3 mmol) of sodium hydride (from 212 mg of 60% oil dispersion) in 6 mL of dimethylsulfoxide, 1.17 g (5.3 mmol) of trimethylsulfoxonium iodide were added in small portions at room temperature. After stirring for 2 h, 640 mg (3.52 mmol) of methyl 3-(3-oxo-1-cyclohexenyl)propionate (**1a**)[19] in 3 mL of DMSO were added dropwise. The mixture was stirred at 50 °C for 2 h, then quenched with saturated aqueous sodium chloride and extracted with diethyl ether. The organic layer was washed with water and dried over anhydrous magnesium sulfate. The product was isolated from the crude by flash chromatography with 30% ethyl acetate/hexanes over silica gel, and 182 mg (26% yield) of pure material was obtained: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.62 (s, 3H), 2.39 (t, *J* = 7.8 Hz, 2H), 2.23 (m, 1H), 2.05-1.86 (m, 2H), 1.82-1.50 (m, 6H), 1.35 (t, *J* = 5.1 Hz, 1H), 0.91 (dd, *J* = 10.5, 5.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.4, 173.5, 51.6, 36.0, 34.0, 33.2, 31.1, 27.2, 25.1, 18.0, 16.7; IR (neat) 2949, 1738, 1688 cm^{-1}; HRMS calcd for $C_{11}H_{16}O_3$: 196.1099, found 196.1089; LRMS (EI^+) *m/z* 196 (22), 165 (6.1), 136 (21), 123 (49), 109 (51), 95 (42), 81 (100), 79 (78), 67 (57), 55 (59), 41 (83).

Methyl 3-(4-Oxobicyclo[3.1.0]hexan-1-yl)propionate (2b). The title compound was prepared from methyl 3-(3-oxo-1-cyclopentenyl)propionate (**1b**)[19] according to the general procedure outlined for the preparation of **2a**. 350 mg (2.08 mmol) of substrate yielded 103 mg (27%) of **2b** after flash chromatography over silica gel with 35% ethyl acetate/hexanes: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.62 (s, 3H), 2.38 (t, *J* = 7.5 Hz, 2H), 2.10-1.86 (m, 5H), 1.77 (m, 1H), 1.60 (dd, *J* = 9.0, 3.6 Hz, 1H), 1.15-1.04 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.8, 173.4, 51.6, 33.9, 33.1, 31.4, 30.5, 26.3, 19.6; IR (neat) 2951, 1731, 1181 cm^{-1}; HRMS calcd for $C_{10}H_{14}O_3$: 182.0943, found 182.0933; LRMS (EI^+) *m/z* 182 (27), 150 (17), 122 (28), 109 (100), 94 (27), 81 (77), 79 (58), 67 (41), 55 (63), 41 (53).

Ethyl 2-(2-Oxobicyclo[4.1.0]heptan-1-yl)acetate (2c). The title compound was prepared from ethyl 2-(2-oxo-1-cyclohexenyl)acetate (**1c**)[5b] according to the general procedure outlined for the preparation of **2a**. 390 mg (2.14 mmol) of substrate yielded 290 mg (75%) of **2c** after flash chromatography over silica gel with 25% ethyl acetate/hexanes: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.08 (q, *J* = 7.2 Hz, 2H), 3.19 (d, *J* = 17.1 Hz, 1H), 2.28 (td, *J* = 16.4, 5.0 Hz, 1H), 2.17-1.88 (m, 3H), 1.85 (d, *J* = 17.1 Hz, 1H), 1.78-1.54 (m, 3H), 1.32 (t, *J* = 6.0 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.94 (dd, *J* = 8.4, 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.5, 171.6, 60.2, 39.1, 36.5, 30.3, 24.1, 21.6, 18.5, 15.9, 14.0; IR (neat) 2937, 1735, 1686, 1182 cm^{-1}; HRMS calcd for $C_{11}H_{16}O_3$: 196.1099, found 196.1109; LRMS (EI^+) *m/z* 196 (3.4), 168 (2.6), 151 (57), 150 (100), 122 (85), 94 (31), 79 (38), 67 (65), 55 (31), 41 (73).

Methyl 2-(2-Oxobicyclo[4.1.0]heptan-3-yl)acetate (2d). The title compound was prepared from methyl 2-(2-oxo-3-cyclohexenyl)acetate (**1d**)[20] according to the general procedure outlined for the preparation of **2a**. 357 mg (3.19 mmol) of substrate yielded 218 mg (57%) of **2d** after flash chromatography over silica gel with 20% ethyl acetate/hexanes, as a 1.7:1 diastereomeric mixture as determined by GC: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.63 (s, 1.1H), 3.62 (s, 1.9H), 2.73-2.58 (m, 2H), 2.26-1.40 (m, 7H), 1.28-1.20 (m, 1H), 1.12-0.95 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): (major) δ 209.8, 172.6, 51.6, 43.8, 34.7, 24.9, 21.7, 21.43, 15.9, 8.4; (minor) δ 208.4, 173.0, 40.8, 34.5, 31.7, 25.6, 22.2, 21.0, 18.0; IR (neat) 1735, 1686, 1351 cm^{-1}; HRMS calcd for $C_{10}H_{14}O_3$: 182.0943, found 182.0941; LRMS (EI^+) *m/z* 182 (24), 150 (82), 122 (32), 109 (54), 94 (28), 82 (64), 67 (26), 54 (100), 39 (55).

1-Benzoyl-3-(2-cyclohexenyl)-2-propanone (4). A solution of 4.4 mmol of LDA in 4 mL of THF was prepared from 0.62 mL (4.4 mmol) of diisopropylamine and 2.75 mL (4.4 mmol) of *n*-butyllithium (1.6 M solution in hexanes). The solution was cooled to -78 °C and 386 mg (2.4 mmol) of benzoylacetone (**3**) in 2 mL of THF were added dropwise. The reaction was warmed to -30 °C, stirred for 3 h and treated with 355 mg (2.2 mmol) of 3-bromocyclohexene dropwise over 10 min. The mixture was warmed to room temperature and stirred overnight. It was then diluted with 20 mL of saturated aqueous ammonium chloride and extracted with diethyl ether. The organic layer was washed with brine and dried over anhydrous magnesium sulfate. Purification by flash chromatography over silica gel with 3% ethyl acetate/hexanes yielded 455 mg (85%) of the title compound, mainly as its enolic form. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90-7.82 (m, 2H), 7.55-7.40 (m, 3H), 6.16 (s, 0.93H), 5.78-5.62 (m, 1H), 5.61-5.41 (m, 1H), 4.06 (s, 0.13H), 2.65 (m, 1H), 2.38 (m, 2H), 2.01-1.90 (m, 2H), 1.88-1.62 (m, 2H), 1.61-1.47 (m, 1H), 1.37-1.21 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): (enolic form) δ 195.1, 183.8, 135.1, 132.2, 130.2, 128.5, 128.1, 127.0, 96.9, 45.5, 32.9, 28.9, 25.0, 21.0; IR (neat) 2926, 1602 cm^{-1}; HRMS calcd for $C_{16}H_{18}O_2$: 242.1307, found 242.1297; LRMS (EI$^+$) *m/z* 242 (8.6), 161 (8.5), 147 (16), 120 (10), 105 (20), 77 (15), 41 (18), 28 (47), 18 (100).

Methyl 3-Benzoyl-5-(2-cyclohexenyl)-4-oxopentanoate (5). A mixture of 909 mg (6.58 mmol) of anhydrous potassium carbonate, 47.1 mg (0.146 mmol) of tetrabutylammonium bromide and 354 mg (1.46 mmol) of 1-benzoyl-3-(2-cyclohexenyl)-2-propanone (**4**) in 5 mL of toluene was heated to reflux for 3.5 h. The reaction was cooled to 40 °C, treated with a solution of 246 mg (1.61 mmol) of methyl bromoacetate in 1 mL of toluene, and stirred at 40 °C for 18 h. The mixture was cooled to 0 °C, filtered through a pad of Celite and the residue was washed with hexanes. Concentration of the filtrate and flash chromatography over silica gel with 12% ethyl acetate/hexanes yielded 338 mg (74%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, $J = 7.2$ Hz, 2H), 7.62-7.30 (m, 3H), 5.65-5.54 (m, 1H), 5.40-5.28 (m, 1H), 4.98 (m, 1H), 3.65 (s, 3H), 2.98 (m, 2H), 2.61 (m, 1H), 2.40 (d, $J = 7.5$ Hz, 2H), 1.98-1.40 (m, 5H), 1.08-0.99 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): it showed a high number of signals due to the keto-enolic equilibrium of the diastereomeric mixture of **5**; IR (neat) 2927, 1734, 1678 cm^{-1}; HRMS calcd for $C_{19}H_{22}O_4$: 314.1518, found 314.1507; LRMS (EI$^+$) *m/z* 314 (2.6), 232 (5.4), 192 (67), 160 (37), 133 (35), 105 (100), 81 (86), 43 (69).

Methyl 5-(Cyclohex-2-enyl)-3-diazo-4-oxopentanoate (6). 139 mg (5.8 mmol) of sodium hydride (from 232 mg of 60% oil dispersion) were suspended in 5 mL of THF. 870 mg (2.77 mmol) of compound **5** in 5 mL of THF were added dropwise at room temperature. The mixture was cooled to 0 °C, stirred for 10 min, and treated with a solution of 1.04 g (4.55 mmol) of *p*-nitrobenzenesulfonyl azide in 10 mL of THF. The mixture was warmed to room temperature and stirred for 2 h. Hexane was added and the crude mixture was filtered through a pad of Celite®. The organic solution was washed with water and brine and dried over anhydrous magnesium sulfate. Purification by flash chromatography over silica gel with 15% ethyl acetate/hexanes afforded 335 mg (52%) of the title compound. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.66 (m, 1H), 5.47 (m, 1H), 3.68 (s, 3H), 3.33 (s, 2H), 2.62 (m, 1H), 2.43-2.38 (m, 2H), 1.94 (m, 2H), 1.83-1.72 (m, 1H), 1.70-1.42 (m, 2H), 1.21 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.4, 169.9, 130.0, 128.2, 63.8, 52.3, 43.5, 32.3, 28.7, 27.8, 24.9, 20.8; IR (neat) 2927, 2081, 1743, 1634 cm^{-1}; HRMS calcd for $C_{12}H_{16}O_3$ ($M-N_2$): 208.1099, found 208.1092; LRMS (EI$^+$) *m/z* 208 (6.7), 176 (7.5), 148 (36), 127 (98), 99 (47), 91 (32), 81 (100), 79 (76), 59 (35), 41 (48).

Methyl 2-(8-Oxotricyclo[4.3.0.0^{2,8}]nonan-8-yl)acetate (2e). 335 mg (1.42 mmol) of methyl 5-(2-cyclohexenyl)-3-diazo-4-oxopentenoate (**6**) dissolved in 10 mL of benzene were added dropwise to a mixture of 1.00 g of anhydrous copper(II) sulfate and 39 mg (0.15 mmol) of copper(II) acetylacetonate in 15 mL of benzene heated at reflux. The mixture was mantained at reflux for 2 h, cooled to room temperature, and filtered through a pad of Celite®. The solvent was removed, the residue was suspended in diethyl ether and filtered again through Celite®. Removal of the solvent and flash chromatography of the residue over silica gel with 25% ethyl acetate/hexanes afforded 200 mg (67% yield) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.59 (s, 3H), 3.17 (d, *J* = 17.4 Hz, 1H), 2.87-2.70 (m, 2H), 2.09-1.80 (m, 5H), 1.43-1.33 (m, 4H), 1.20-1.01 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 216.0, 172.0, 51.5, 47.9, 39.2, 37.2, 30.9, 28.7, 26.3, 25.3, 19.6, 15.4; IR (neat) 2935, 1732, 1714, 1196 cm^{-1}; HRMS calcd for $C_{12}H_{16}O_3$: 208.1099, found 208.1104; LRMS (EI$^+$) *m/z* 208 (10), 176 (47), 148 (64), 135 (20), 120 (47), 105 (49), 91 (63), 79 (65), 67 (52), 53 (53), 41 (100).

5-(3-Butenyl)bicyclo[3.1.0]hexan-2-one (8b). The title compound was prepared from 3-(3-butenyl)-2-cyclopenten-1-one (**7b**) according to the general procedure outlined for the preparation of **2a**. 640 mg (4.71 mmol) of substrate yielded 283 mg (40%) of **8b** after flash chromatography over silica gel with 12% ethyl acetate/hexanes: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77 (m, 1H), 5.03-4.91 (m, 2H), 2.19-1.85 (m, 6H), 1.74 (m, 1H), 1.60-1.42 (m, 2H), 1.16-1.06 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.6, 137.9, 114.9, 34.7, 34.1, 33.8, 33.3, 31.0, 26.8, 20.0; IR (neat) 2922, 1729 cm^{-1}; LRMS (EI$^+$) *m/z* 150 (15), 122 (36), 108 (58), 93 (60), 81 (100), 79 (93), 67 (57), 53 (44), 41 (55).

6-(3-Oxobutyl)bicyclo[4.1.0]heptan-2-one (9a). General Procedure for the Preparation of Methyl Ketones from Terminal Alkenes. 1.109 g (6.76 mmol) of 6-(3-butenyl)bicyclo[4.1.0]heptan-2-one (**8a**)[21], 738 mg (6.82 mmol) of *p*-benzoquinone, 180 mg (1.01 mmol) of palladium chloride and 15 mL of *N,N*-dimethylformamide were placed in a flask and 0.6 mL of water were added. The solution was heated to 70 °C. After 30 min, 0.4 mL of water were added, and equal amounts of water were added after one hour and after 90 min. The temperature was maintained for a total period of 3 h, then the mixture was cooled and quenched with water. It was extracted with diethyl ether, and the organic layer was washed with water, saturated aqueous sodium bicarbonate and water and dried over anhydrous magnesium sulfate. Removal of the solvent, flash chromatography over silica gel with 50% ethyl acetate/hexanes and Kugelrohr distillation afforded 615 mg (3.42 mmol) of the title compound (50% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.49 (t, *J* = 7.8 Hz, 2H), 2.24-2.16 (m, 1H), 2.09 (s, 3H), 2.02-1.91 (m, 2H), 1.72-1.46 (m, 6H), 1.33 (t, *J* = 5.1 Hz, 1H), 0.88 (dd, *J* = 9.9, 5.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.6, 207.9, 40.4, 36.0, 33.3, 32.4, 29.9, 27.4, 25.3, 18.0, 16.9; IR (neat) 2934, 1714, 1683 cm^{-1}; HRMS calcd for $C_{11}H_{16}O_2$: 180.1150, found 180.1139; LRMS (EI$^+$) *m/z* 180 (8.0), 137 (9.0), 123 (25), 108 (22), 94 (10), 79 (26), 67 (15), 55 (19), 43 (100).

5-(3-Oxobutyl)bicyclo[3.1.0]hexan-2-one (9b). The title compound was prepared from 5-(3-butenyl)bicyclo[3.1.0]hexan-2-one (**8b**) according to the general procedure outlined for the preparation of **9a**. 270 mg (1.80 mmol) of substrate yielded 140 mg (40%) of **9b** after flash chromatography over silica gel with 50% ethyl acetate/hexanes: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.47 (t, *J* = 7.5 Hz, 2H), 2.08 (s, 3H), 2.06-1.92 (m, 3H), 1.90-1.78 (m, 2H), 1.67 (m, 1H), 1.54 (dd, *J* = 9.0, 3.6 Hz, 1H), 1.07-1.01 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.8, 207.6, 40.5, 33.9, 33.2, 33.1, 29.8, 28.8, 26.5, 19.7; IR (neat) 2935, 1721, 1363 cm^{-1};

HRMS calcd for $C_{10}H_{14}O_2$: 166.0994, found 166.0984; LRMS (EI$^+$) m/z 166 (5.2), 148 (6.0), 109 (45), 95 (11), 81 (21), 67 (12), 55 (15), 43 (100).

6-(4-Oxopentyl)bicyclo[4.1.0]heptan-2-one (9c). The title compound was prepared from 6-(4-pentenyl)bicyclo[4.1.0]heptan-2-one (**8c**)[21] according to the general procedure outlined for the preparation of **9a**. 707 mg (3.97 mmol) of substrate yielded 461 mg (60%) of **9c** after flash chromatography over silica gel with 50% ethyl acetate/hexanes: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (t, *J* = 7.2 Hz, 2H), 2.22 (m, 1H), 2.07 (s, 3H), 2.02-1.85 (m, 2H), 1.75-1.47 (m, 6H), 1.42-1.19 (m, 3H), 0.87 (dd, *J* = 10.2, 5.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.1, 208.4, 43.2, 38.2, 36.1, 33.4, 29.9, 27.9, 25.3, 20.3, 18.1, 17.0; IR (neat) 2938, 1713, 1683, 1359 cm^{-1}; HRMS calcd for $C_{12}H_{18}O_2$: 194.1307, found 194.1303; LRMS (EI$^+$) m/z 194 (11), 151 (5.0), 136 (88), 123 (28), 109 (19), 93 (35), 79 (53), 67 (23), 55 (30), 43 (100).

1-(2-Oxopropyl)bicyclo[4.1.0]heptan-2-one (9d). The title compound was prepared from 1-(2-propenyl)bicyclo[4.1.0]heptan-2-one (**8d**)[21] according to the general procedure outlined for the preparation of **9a**. 545 mg (3.63 mmol) of substrate yielded 275 mg (46%) of **9d** after flash chromatography over silica gel with 35% ethyl acetate/hexanes: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.27 (d, *J* = 17.7 Hz, 1H), 2.23 (m, 1H), 2.12 (m, 1H), 2.07 (s, 3H), 2.05-1.84 (m, 3H), 1.76-1.50 (m, 2H), 1.44 (m, 1H), 1.27 (t, *J* = 5.7 Hz, 1H), 0.87 (dd, *J* = 8.1, 5.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.9, 206.5, 48.3, 36.4, 30.3, 29.7, 24.1, 21.6, 18.5, 15.6; IR (neat) 2937, 1715, 1682, 1359 cm^{-1}; HRMS calcd for $C_{10}H_{14}O_2$: 166.0994, found 166.0992; LRMS (EI$^+$) m/z 166 (6.8), 135 (16), 124 (37), 109 (24), 96 (46), 79 (18), 67 (25), 53 (18), 43 (100).

5-(2-Oxopropyl)bicyclo[4.1.0]heptan-2-one (9e). The title compound was prepared from 5-(2-propenyl)bicyclo[4.1.0]heptan-2-one (**8e**)[21] according to the general procedure outlined for the preparation of **9a**. 354 mg (2.36 mmol) of substrate yielded 300 mg (77%) of **9e** after flash chromatography over silica gel with 50% ethyl acetate/hexanes. The product was obtained as a 7:1 diastereomeric mixture, as determined by GC: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.64-2.42 (m, 3H), 2.12 (s, 3H), 2.23-2.00 (m, 2H), 1.88-1.63 (m, 2H), 1.61-1.42 (m, 2H), 1.26-1.08 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): (major) δ 208.7, 207.1, 47.9, 32.6, 30.3, 26.7, 25.3, 23.7, 23.3, 12.1; IR (neat) 2923, 1713, 1688, 1356 cm^{-1}; HRMS calcd for $C_{10}H_{14}O_2$: 116.0994, found 116.0988; LRMS (EI$^+$) m/z 166 (0.9), 105 (13), 91 (7.0), 79 (9.6), 71 (11), 69 (11), 57 (27), 55 (30), 43 (39), 41 (45), 18 (100).

(1*R*,4*R*,6*S*)-4-Acetyl-1-methylbicyclo[4.1.0]heptan-2-one (9f). 500 mg (3.05 mmol) of (1*R*,4*R*)-4-isopropenyl-1-methylbicyclo[4.1.0]heptan-2-one ((**1*R*)-10**)[11] were dissolved in 3 mL of dichloromethane and 3 mL of methanol. 512 mg (6.1 mmol) of sodium bicarbonate were added, and the reaction mixture was cooled to -78 °C. Ozone was bubbled through the solution until the blue color persisted. 2.3 mL (1.9 g, 31 mmol) of dimethylsulfide were added and the mixture was stirred overnight while the reaction temperature warmed to room temperature. The solvent was removed, diethyl ether was added and the organic layer was washed with water and dried over anhydrous magnesium sulfate. Kugelrohr distillation afforded 420 mg (83%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.73 (m, 1H), 2.35 (dd, *J* = 17.7, 5.7 Hz, 1H), 2.27-2.17 (m, 2H), 2.12 (s, 3H), 1.87 (m, 1H), 1.56 (m, 1H), 1.23 (t, *J* = 5.7 Hz, 1H), 1.17 (s, 3H), 0.87 (dd, *J* = 7.8, 5.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.3, 208.2, 43.3, 37.2, 29.2, 28.1, 24.4, 24.3, 19.4, 17.4; IR (neat) 2931, 1712, 1682, 1355 cm^{-1}; HRMS calcd for $C_{10}H_{14}O_2$: 166.0994, found 166.1000; LRMS (EI$^+$) m/z 167 (1.5), 138 (22), 123 (42), 109 (24), 95 (56), 81 (25), 67 (45), 53 (25), 43 (100). $[\alpha]^D_{20}$ -0.857° (c = 0.35, $CHCl_3$).

(1*S*,4*R*,6*R*)-4-Isopropenyl-1-methylbicyclo[4.1.0]heptan-2-one ((1*S*)-10). 1.58 g (10.5 mmol) of samarium metal were suspended in 20 mL of THF. 272 mg (1 mmol) of mercury chloride (II) were added and the suspension was stirred for 15 min at room temperature. After this time, 430 mg (2.83 mg) of (1*R*,5*R*)-5-isopropenyl-2-methyl-2-cyclohexen-1-ol [11] in 10 mL of THF were added dropwise. The mixture was cooled to -78 °C and 2.68 g (10.0 mmol) of diiodomethane were added dropwise. The reaction was warmed to room temperature and stirred for 2.5 h. It was then quenched with saturated potassium carbonate, extracted with diethyl ether, washed with brine and dried over anhydrous magnesium sulfate. Flash chromatography over silica gel with 15% ethyl acetate/hexanes afforded 272 mg (58% yield) of (1*S*,2*R*,4*R*,6*R*)-4-isopropenyl-1-methylbicyclo[4.1.0]heptan-2-ol: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.63-4.60 (m, 2H), 3.90 (dd, *J* = 10.5, 6.0 Hz, 1H), 2.04-1.97 (m, 1H), 1.90-1.70 (m, 2H), 1.63 (s, 3H), 1.43 (bs, 1H), 1.22-1.08 (m, 1H), 1.17 (s, 3H), 0.94 (m, 1H), 0.82 (q, *J* = 10.8 Hz, 1H), 0.41 (dd, *J* = 9.0, 4.8 Hz, 1H), 0.31 (t, *J* = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 108.8, 74.0, 41.9, 35.2, 29.9, 24.1, 22.6, 21.7, 20.6, 16.5. Further Jones oxidation of this compound yielded 240 mg (88%) of the title compound **(1*S*)-10**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.66 (m, 1H), 4.60 (m, 1H), 2.45-2.32 (m, 1H), 2.24-2.02 (m, 3H), 1.62 (s, 3H), 1.60-1.41 (m, 2H), 1.15 (s, 3H), 1.04-0.96 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.0, 146.9, 109.8, 46.2, 41.6, 29.8, 28.9, 27.7, 27.0, 20.3, 19.3.

(1*S*,4*R*,6*R*)-4-Acetyl-1-methylbicyclo[4.1.0]heptan-2-one (9g). The title compound was prepared from (1*S*,4*R*,6*R*)-4-isopropenyl-1-methylbicyclo[4.1.0]heptan-2-one (**(1*S*)-10**) by following the procedure described for the preparation of **9f**. 218 mg (1.33 mmol) of substrate yielded 181 mg (82%) of **9g** after flash chromatography over silica gel with 50% ethyl acetate/hexanes: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.87 (m, 1H), 2.40-2.29 (m, 3H), 2.12 (s, 3H), 1.79 (m, 1H), 1.58 (m, 1H), 1.18 (s, 3H), 1.05 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.6, 207.9, 50.9, 37.6, 29.1, 28.2, 27.2, 26.1, 25.7, 19.1; IR (neat) 2965, 1711, 1687, 1354 cm^{-1}; HRMS calcd for $C_{10}H_{14}O_2$: 166.0994, found 166.1000; LRMS (EI$^+$) *m/z* 166 (0.1), 138 (6.0), 123 (9.1), 95 (15), 77 (10), 67 (23), 53 (29), 43 (100), 39 (80). $[\alpha]^D{}_{20}$ +31.80° (c = 1.39, $CHCl_3$).

6-(3-Oxopropyl)bicyclo[4.1.0]heptan-2-one (11). The title compound was prepared from 6-(3-butenyl) bicyclo[4.1.0]heptan-2-one (**8a**)[21] by following the procedure described for the preparation of **9f**. 164 mg (1.0 mmol) of substrate yielded 140 mg (85%) of **11** after purification by flash chromatography over silica gel with 50% ethyl acetate/hexanes: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.77 (t, *J* = 1.5 Hz, 1H), 2.55 (td, *J* = 7.5, 1.5 Hz, 2H), 2.28 (m, 1H), 2.06-1.87 (m, 2H), 1.80-1.47 (m, 6H), 1.39 (t, *J* = 5.1 Hz, 1H), 0.93 (dd, *J* = 10.2, 5.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.2, 201.3, 40.8, 35.9, 33.3, 30.8, 27.1, 25.2, 17.9, 16.7; IR (neat) 2927, 1721, 1682 cm^{-1}; HRMS calcd for $C_{10}H_{14}O_2$: 166.0994, found 166.1007; LRMS (EI$^+$) *m/z* 166 (0.3), 110 (11), 91 (10), 79 (38), 67 (44), 55 (77), 53 (43), 41 (65), 39 (99), 29 (61), 27 (100).

6-(3,4-Epoxybutyl)bicyclo[4.1.0]heptan-2-one (12). 177 mg (1.08 mmol) of 6-(3-butenyl) bicyclo[4.1.0]heptan-2-one (**8a**)[21] dissolved in 7 mL of 0.3 N sodium bicarbonate aqueous solution were cooled to 0 °C. 237 mg (1.37 mmol) of *m*-chloroperoxybenzoic acid were added in portions. The mixture was slowly warmed to room temperature and stirred for 2 h. Diethyl ether was added and the resulting organic layer was washed with 10% sodium hydroxide solution and brine and dried over anhydrous magnesium sulfate. Purification by flash chromatography over silica gel with 40% ethyl acetate/hexanes afforded 153 mg (0.85 mmol) of the title compound (79% yield), as a 1:1 diastereomeric mixture as determined by GC: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.88 (m, 1H), 2.73 (m, 1H), 2.44 (m, 1H), 2.25 (m, 1H), 2.02-1.83 (m, 2H), 1.79-1.37 (m, 9H), 0.93 (dd, *J* = 9.9, 5.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.6 (2), 51.7, 51.6, 46.9 (2), 35.9 (2), 35.1, 34.9, 33.5, 33.4, 29.3, 29.1, 27.5, 27.3, 25.2 (2), 18.0 (2), 17.0, 16.9; IR (neat) 2924, 1682 cm^{-1}; HRMS calcd for $C_{11}H_{16}O_2$: 180.1150, found 180.1151; LRMS (EI$^+$) *m/z* 180 (0.3), 105 (6.5), 93 (36), 79 (49), 67 (16), 55 (40), 39 (74), 27 (100).

2-Hydroxy-2-methylspiro[4.5]decan-7-one (13a). General Procedure for the SmI_2-Induced Opening of Cyclopropyl Ketones / Intramolecular Trapping of an Electrophile. 446 mg (1.67 mmol) of diiodomethane were added to a vigorously stirred suspension of 276 mg (1.84 mmol) of samarium metal in 17 mL of THF. The resultant blue-green slurry was stirred vigorously for 2 h at room temperature, then cooled to 0 °C and 0.6 mL (3.34 mmol) of HMPA were added. After 10 min, 117 mg (0.65 mmol) of substrate **9a** were added slowly dropwise as a 0.045 M solution in THF. After 30 min at 0 °C, TLC analysis revealed the consumption of substrate and the reaction was quenched with a saturated aqueous solution of Rochelle's salt.[22] The organic materials were extracted with diethyl ether, washed with brine and dried over anhydrous magnesium sulfate. Flash chromatography over silica gel with 50% ethyl acetate/hexanes afforded 93 mg (79%) of the title compound, isolated as a 1:1 mixture of diastereomers, as determined by GC: ^1H NMR (300 MHz, $CDCl_3$) δ 2.46-2.39 (m, 1H), 2.27-2.21 (m, 3H), 1.86-1.46 (m, 11H), 1.33 (s, 1.5H), 1.31 (s, 1.5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.4, 211.9, 79.9, 79.8, 54.7, 54.4, 53.2, 52.8, 47.1, 47.0, 41.0, 41.0, 40.3, 40.2, 38.1, 38.0, 37.5, 36.9, 29.1 (2), 23.6, 23.5; IR (neat) 3418, 2937, 1704 cm^{-1}; HRMS calcd for $C_{11}H_{18}O_2$: 182.1307, found 182.1310; LRMS (EI$^+$) *m/z* 182 (1.3), 167 (1.2), 153 (9.0), 125 (10), 111 (15), 97 (13), 67(15), 53 (22), 43 (100), 39 (61).

7-Hydroxy-7-methylspiro[4.4]nonan-2-one (13b). This compound was prepared from **9b** according to the general procedure outlined for the synthesis of **13a**. 83 mg (0.50 mmol) of substrate yielded 52 mg (61%) of the title compound after flash chromatography over silica gel with 60% ethyl acetate/hexanes, isolated as a 1.4:1 mixture of diastereomers, as determined by GC: ^1H NMR (300 MHz, $CDCl_3$) δ 2.31-2.09 (m, 4H), 2.01-1.98 (m, 1H), 1.86-1.58 (m, 8H), 1.31 (s, 1.8H), 1.30 (s, 1.2H); ^{13}C NMR (75 MHz, $CDCl_3$): (major) δ 219.9, 79.7, 53.8, 53.1, 46.9, 41.0, 37.8, 37.4, 36.7, 29.3; (minor) δ 219.7, 79.7, 53.5, 52.7, 47.0, 41.2, 37.9, 37.6, 36.9, 29.4; IR (neat) 3435, 2958, 1738 cm^{-1}; HRMS calcd for $C_{10}H_{16}O_2$: 168.1150, found 168.1147; LRMS (EI$^+$) *m/z* 168 (0.8), 139 (9.2), 97 (13), 79 (8.8), 67 (15), 53 (22), 43 (100), 39 (57).

8-Hydroxy-8-methylspiro[5.5]decan-2-one (13c). This compound was prepared from **9c** according to the general procedure outlined for the synthesis of **13a**. 81 mg (0.42 mmol) of substrate yielded 25 mg (30% yield, 90% pure by GC) of the title compound after flash chromatography over silica gel with 30% ethyl acetate/hexanes, isolated as a 5:1 mixture of diastereomers as determined by GC: ^1H NMR (300 MHz, $CDCl_3$) δ 2.69 (d, J = 13.2 Hz, 0.16H), 2.47 (d, J = 13.2 Hz, 0.16H), 2.25 (m, 1.7H), 2.04 (m, 1.7H), 2.00-0.93 (m, rest H), 1.17 (s, 2.5H), 1.14 (s, 0.5H); ^{13}C NMR (75 MHz, $CDCl_3$): (major) δ 212.2, 70.5, 57.1, 47.7, 41.3, 39.5, 39.2, 36.1, 33.1, 32.8, 22.3, 18.0; (minor) δ 213.7, 70.1, 50.6, 47.8, 41.1, 40.3, 39.2, 38.8, 36.6, 32.9, 21.5, 17.6; IR (neat) 3460, 2932, 1698 cm^{-1}; HRMS calcd for $C_{12}H_{20}O_2$: 196.1463, found 196.1470; LRMS (EI$^+$) *m/z* 196 (5.0), 181 (11), 178 (14), 153 (38), 123 (26), 111 (81), 95 (26), 55 (24), 43 (69), 18 (100).

Spiro[4.5]decan-2,7-dione (14a). This compound was prepared from **2a** according to the general procedure outlined for the synthesis of **13a**. 118 mg (0.60 mmol) of substrate yielded 64 mg (64%) of the title compound after flash chromatography over silica gel with 50% ethyl acetate/hexanes: ^1H NMR (300 MHz, $CDCl_3$) δ 2.38-2.23 (m, 6H), 2.10 (m, 2H), 2.00-1.65 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 217.2, 209.9, 52.1, 50.3, 44.4, 40.8, 36.2, 35.6, 33.9, 22.7; IR (neat) 2940, 1740, 1710 cm^{-1}; HRMS calcd for $C_{10}H_{14}O_2$: 166.0994, found 166.0996; LRMS (EI$^+$) *m/z* 166 (5.7), 138 (7.0), 123 (7.1), 110 (15), 95 (15), 81 (22), 67 (77), 53 (53), 41 (80), 39 (100).

Spiro[4.4]nonan-2,7-dione (14b). This compound was prepared from **2b** according to the general procedure outlined for the synthesis of **13a**. 82 mg (0.45 mmol) of substrate yielded 27 mg (40%) of the title compound after flash chromatography over silica gel with 60% ethyl acetate/hexanes: ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.32 (m, 4H), 2.25 (s, 4H), 1.99 (t, J = 8.1 Hz, 4H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 217.2 (2), 50.3 (2), 44.4, 37.3 (2), 34.4 (2); IR (neat) 2953, 1738 cm^{-1}; HRMS calcd for $C_9H_{12}O_2$: 152.0837, found 152.0837; LRMS (EI$^+$) *m/z* 152 (3.6), 109 (4.6), 96 (10), 81 (14), 67 (45), 53 (45), 41 (45), 39 (100). Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 71.03; H, 8.34.

2-Hydroxyspiro[4.5]decan-7-one (15). This compound was prepared from **11** according to the general procedure outlined for the synthesis of **13a**. 78 mg (0.47 mmol) of substrate yielded 33 mg (42%) of the title compound after flash chromatography over silica gel with 50% ethyl acetate/hexanes, isolated as a 1.5:1 diastereomeric mixture as determined by GC: ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.40-4.27 (m, 1H), 2.40 (s, 0.8H), 2.27 (t, J = 9.0 Hz, 2H), 2.19 (s, 1.2H), 1.97-1.40 (m, 11H); ^{13}C NMR (75 MHz, CDCl$_3$): (major) δ 211.8, 73.1, 53.9, 47.5, 46.5, 41.0, 38.1, 35.9, 34.3, 23.6; (minor) δ 212.1, 73.3, 54.6, 47.4, 46.4, 41.0, 37.4, 36.1, 34.3, 23.4; IR (neat) 3414, 2939, 1702 cm^{-1}; HRMS calcd for $C_{10}H_{16}O_2$: 168.1150, found 168.1142; LRMS (EI$^+$) *m/z* 168 (3.0), 125 (8.6), 79 (17), 67 (27), 55 (52), 41 (77), 39 (100).

2-Hydroxymethylspiro[4.5]decan-7-one (16). This compound was prepared from **12** according to the general procedure outlined for the synthesis of **13a**. 110 mg (0.61 mmol) of substrate yielded 30 mg (27% yield, 70% pure by GC) of the title compound after flash chromatography over silica gel with 50% ethyl acetate/hexanes, isolated as a 1.3:1 diastereomeric mixture as determined by GC: ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.56-3.41 (m, 1.3H), 3.33 (dd, J = 9.9, 3.9 Hz, 1H), 3.20 (dd, J = 9.9, 6.3 Hz, 1H), 2.30-0.87 (m, rest H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 209.1 (2), 70.7, 70.6, 36.2, 36.1, 35.0, 34.9, 33.7, 33.5, 33.3, 33.2, 27.9, 27.7, 25.5 (2), 18.2 (2), 17.1, 17.1, 16.2 (2); IR (neat) 3407, 2938, 1676 cm^{-1}; HRMS calcd for $C_{11}H_{18}O_2$: 182.1307, found 182.1283; LRMS (EI$^+$) *m/z* 182 (4.2), 151 (6.0), 139 (16), 123 (13), 111 (43), 93 (20), 81 (28), 67 (35), 55 (100), 43 (93).

(1*R,6*S**)-Bicyclo[4.3.0]nonan-2,8-dione (14c).** This compound was prepared from **2c** according to the general procedure outlined for the synthesis of **13a**. 150 mg (0.77 mmol) of substrate yielded 77 mg (67%) of the title compound after flash chromatography over silica gel with 50% ethyl acetate/hexanes, isolated as a single diastereomer as determined by GC: ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.04 (m, 1H), 3.00-2.90 (m, 2H), 2.46-2.28 (m, 2H), 2.17 (m, 2H), 2.05-1.86 (m, 4H), 1.72 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 216.0, 210.5, 49.4, 41.9, 40.0, 39.6, 38.5, 26.4, 23.1; IR (neat) 2933, 1743, 1708 cm^{-1}; HRMS calcd for $C_9H_{12}O_2$: 152.0837, found 152.0837; LRMS (EI$^+$) *m/z* 152 (8.1), 124 (6.4), 98 (11), 81 (8.1), 67 (21), 53 (33), 41 (66), 39 (100).

(1*R,6*S**,8*R**/*S**)-8-Hydroxy-8-methylbicyclo[4.3.0]nonan-2-one (13d).** This compound was prepared from **9d** according to the general procedure outlined for the synthesis of **13a**. 109 mg (0.66 mmol) of substrate yielded 87 mg (79%) of the title compound, isolated as a 1:1 mixture of diastereomers which could be separated after flash chromatography over silica gel with 50% ethyl acetate/hexanes: ^{1}H NMR (300 MHz, CDCl$_3$): (higher Rf) δ 2.70-2.60 (m, 2H), 2.40-2.20 (m, 3H), 1.98-1.71 (m, 4H), 1.70-1.42 (m, 4H), 1.29 (s, 3H); (lower Rf) δ 2.95-2.82 (m, 2H), 2.33-2.18 (m, 3H), 1.96-1.68 (m, 6H), 1.41-1.23 (m, 2H), 1.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): (higher Rf) δ 214.6, 78.6, 52.2, 45.9, 42.8, 41.6, 40.3, 29.1, 27.4, 22.8; (lower Rf) δ 214.0, 78.5, 51.2, 46.7, 41.4, 40.6, 40.0, 28.7, 27.7, 22.7; IR (neat) 3438, 2934, 1704 cm^{-1}; HRMS calcd for $C_{10}H_{16}O_2$: 168.1150, found 168.1146; LRMS (EI^+) *m/z* 168 (5.9), 125 (24), 110 (23), 97 (17), 81 (30), 67 (18), 55 (70), 43 (100).

(1*R,6*S**,8*R**/*S**)-8-Hydroxy-8-methylbicyclo[4.3.0]nonan-3-one (13e).** This compound was prepared from **9e** according to the general procedure outlined for the synthesis of **13a**. 100 mg (0.60 mmol) of substrate yielded 73 mg (73%) of the title compound, isolated as a mixture of diastereomers. The two trans-fused diastereomers were obtained as a 1:1 mixture as determined by GC, and could be isolated separately after flash chromatography over silica gel with 50% ethyl acetate/hexanes: ^1H NMR (300 MHz, $CDCl_3$): (higher Rf) δ 2.52 (m, 1H), 2.40 (m, 1H), 2.28 (m, 1H), 2.18-1.82 (m, 5H), 1.80-1.35 (m, 5H), 1.40 (s, 3H); (lower Rf) δ 2.50 (m, 1H), 2.42-1.92 (m, 7H), 1.78-1.22 (m, 5H), 1.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): (higher Rf) δ 211.2, 79.5, 49.1, 47.5, 46.9, 45.1, 44.6, 40.9, 31.2, 29.5; (lower Rf) δ 211.3, 79.5, 48.8, 47.6, 47.1, 46.1, 43.6, 40.9, 31.1, 29.3; IR (neat) 3427, 2957, 1709 cm^{-1}; HRMS calcd for $C_{10}H_{16}O_2$: 168.1150, found 168.1142; LRMS (EI^+) *m/z* 168 (1.8), 150 (7.5), 111 (47), 95 (23), 81 (17), 67 (19), 55 (18), 43 (100).

(1*R,4*R**,8*R**,11*R**)-Tricyclo[6.2.1.0^{4,11}]undecan-2,9-dione (14e).** This compound was prepared from **2e** according to the general procedure outlined for the synthesis of **13a**. 90 mg (0.43 mmol) of substrate yielded 30 mg (39%) of the title compound, isolated as a single diastereomer after flash chromatography over silica gel with 30% ethyl acetate/hexanes ^1H NMR (300 MHz, $CDCl_3$) δ 3.20 (dd, *J* = 19.5, 9.6 Hz, 1H), 2.97-2.88 (m, 1H), 2.68 (ddd, *J* = 19.1, 12.9, 2.1 Hz, 1H), 2.53-2.24 (m, 4H), 2.11-2.00 (m, 2H), 1.60-1.35 (m, 4H), 1.26-1.13 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 219.1, 216.7, 45.1, 44.7, 42.8, 39.8, 38.1, 31.6, 26.0, 20.0, 16.5; IR (neat) 2932, 1736 cm^{-1}; HRMS calcd for $C_{11}H_{14}O_2$: 178.1017, found 177.0994; LRMS (EI^+) *m/z* 178 (4.5), 97 (20), 81 (100), 69 (34), 57 (58), 55 (55), 43 (61), 41 (65).

(1*R*,3*R*,5*S*,6*S*,7*S*)-6,7-Dimethyltricyclo[3.2.1.0^{3,6}]octan-3,7-diol (13f).[14] This compound was prepared from **9f** according to the general procedure outlined for the synthesis of **13a**. 118 mg (0.71 mmol) of substrate yielded 47 mg (40%) of the title compound, isolated as a single enantiomer after flash chromatography over silica gel with 60% ethyl acetate/hexanes ^1H NMR (300 MHz, $CDCl_3$) δ 2.28-2.18 (m, 2H), 2.10 (bs, 2H), 2.01 (m, 1H), 1.80-1.70 (m, 4H), 1.28-1.19 (m, 1H), 1.09 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 86.2 (Cq), 76.4 (Cq), 56.0 (Cq), 46.3 (CH), 44.0 (CH_2), 41.7 (CH_2), 33.6 (CH_2), 31.6 (CH), 18.7 (CH_3), 6.5 (CH_3); IR (neat) 3386, 2954, 1734, 1701 cm^{-1}; HRMS calcd for $C_9H_{13}O_2$ ($M-CH_3$): 153.0916, found 153.0921; LRMS (EI^+) *m/z* 153 (31), 150 (23), 135 (16), 107 (91), 93 (59), 79 (20), 71 (15), 55 (16), 43 (100). $[\alpha]^D{}_{20}$ +26.47° (c = 0.34, $CHCl_3$).

(1*R*,2*S*,5*R*,6*S*)-6-Hydroxy-2,6-dimethylbicyclo[3.2.1]octan-3-one (13g).[15] This compound was prepared from **9g** according to the general procedure outlined for the synthesis of **13a**. 70 mg (0.42 mmol) of substrate yielded 56 mg (79%) of the title compound, isolated as a single enantiomer after flash chromatography over silica gel with 50% ethyl acetate/hexanes ^1H NMR (300 MHz, $CDCl_3$) δ 2.46-2.38 (m, 4H), 2.37-2.30 (m, 1H), 2.21-2.14 (m, 1H), 1.86-1.74 (m, 2H), 1.53-1.36 (m, 2H), 1.26 (s, 3H), 0.95 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.4, 80.4, 51.7, 49.2, 45.5, 42.1, 41.6, 38.1, 25.4, 12.7; IR (neat) 3435, 2934, 1703 cm^{-1}; HRMS calcd for $C_{10}H_{16}O_2$: 168.1150, found 168.1142; LRMS (EI^+) *m/z* 168 (3.5), 110 (27), 95 (19), 79 (11), 67 (24), 55 (20), 43 (100). $[\alpha]^D{}_{20}$ +13.97° (c = 0.68, $CHCl_3$).

4-Methyltetrahydro-2*H*-pyran-2-one (18). A 0.1 M samarium diiodide solution in THF was prepared from 145 mg (0.96 mmol) of samarium metal and 234 mg (0.88 mmol) of diiodomethane. The solution was cooled to 0 °C and 0.76 mL (4.38 mmol) of HMPA and 0.26 mL (1.75 mmol) of TMEDA were added. After 10 min, 39 mg (0.35 mmol) of 3-oxabicyclo[4.1.0]heptan-2-one (**17**) were added slowly dropwise as a 0.045 M solution in THF. After 1 h at 0 °C, the reaction was quenched with saturated aqueous solution of Rochelle's salt.[22] The organic materials were extracted with diethyl ether, washed with brine and dried over anhydrous magnesium sulfate. Flash chromatography over silica gel with 25% diethyl ether/pentane afforded 15 mg (35%) of the title compound, which slowly decomposed at room temperature: ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.39 (m, 1H), 4.22 (m, 1H), 2.63 (m, 1H), 2.17-2.02 (m, 2H), 1.95-1.82 (m, 1H), 1.58-1.42 (m, 1H), 1.04 (d, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 68.6, 38.3, 30.7, 26.6, 21.5; IR (neat) 2958, 1728, 1256 cm^{-1}; HRMS calcd for $C_6H_{10}O_2$: 114.0681, found 114.0649; LRMS (EI$^+$) *m/z* 114 (19), 97 (20), 85 (27), 69 (68), 55 (92), 41 (100).

Diallyl 2-Benzoylsuccinate (20). A suspension of 467 mg (19.5 mmol) of sodium hydride (from 780 mg of 60% oil dispersion) in 20 mL of DME was cooled to 0 °C. A solution of 2.97 g (14.99 mmol) of diallyl succinate (**19**) in 7 mL of DME was added dropwise. The mixture was stirred for 10 min at 0 °C, and a solution of 1.35 g (19.5 mmol) of allyl benzoate in 7 mL of DME was added dropwise. One drop of allylic alcohol was added and the mixture was heated to reflux for 2 h. After this period, the reaction was cooled to 0 °C and quenched with 1 N hydrochloric acid until pH = 4. The organic materials were extracted with diethyl ether, washed with brine and dried over anydrous magnesium sulfate. The product was purified by flash chromatography over silica gel with 10% ethyl acetate/hexanes to obtain 1.90 g (42%) of the title compound, as a mixture of the keto and the enolic forms: ^{1}H NMR (300 MHz, CDCl$_3$): (ketonic form) δ 8.01 (m, 2H), 7.57 (m, 1H), 7.46 (m, 2H), 5.83 (m, 2H), 5.36-5.10 (m, 4H), 4.89 (t, J = 7.2 Hz, 1H), 4.54 (d, J = 6.0 Hz, 4H), 3.08 (m, 2H); (enolic form, distinctive signals) δ 12.09 (s), 4.66 (m), 3.19 (s); ^{13}C NMR (75 MHz, CDCl$_3$): (ketonic form) δ 193.9, 170.8, 168.2, 135.7, 133.7, 131.7, 131.1, 128.8, 128.7, 118.5, 118.4, 66.1, 65.6, 49.3, 33.1; (enolic form, distinctive signals) δ 170.7, 168.7, 118.3, 93.0, 65.1, 28.4; IR (neat) 1738, 1687, 1649 cm^{-1}; HRMS calcd for $C_{17}H_{18}O_5$: 302.1154, found 302.1152; LRMS (EI$^+$) *m/z* 302 (0.2), 245 (4.3), 105 (100), 77 (42), 41 (46).

Diallyl 2-Diazosuccinate (21). A solution of 1.51 g (5.0 mmol) of diallyl 2-benzoylsuccinate (**20**) in 10 mL of dichloromethane was cooled to 0 °C. 1.60 g (10.5 mmol) of DBU were added in one portion. After 10 min, a solution of 2.39 g (10.5 mmol) of *p*-nitrobenzenesulfonyl azide in 10 mL of dichloromethane was added dropwise. The mixture was stirred at 0 °C for 1 h. It was then quenched with 15 mL of pH 7 phosphate buffer and 20 mL of water, and the organic materials were extracted with dichloromethane and dried over anhydrous magnesium sulfate. Flash chromatography of the crude product over silica gel with 15% ethyl acetate/hexanes afforded 689 mg (62%) of the title compound: ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.87 (m, 2H), 5.33-5.18 (m, 4H), 4.66-4.59 (m, 4H), 3.33 (s, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 169.2 (2), 132.0, 131.5, 118.8, 118.1, 66.1 (2), 65.6, 28.8; IR (neat) 2096, 1743, 1694 cm^{-1}; HRMS calcd for $C_{10}H_{12}O_4N_2$: 224.0797, found 224.0791; LRMS (EI$^+$) *m/z* 224 (1.5), 167 (1.4), 139 (6.5), 111 (6.5), 99 (15), 55 (10), 41 (100).

Allyl 2-(3-Oxa-2-oxobicyclo[3.1.0]hexan-1-yl)acetate (22). A solution of 455 mg (2.03 mmol) of diallyl 2-diazosuccinate (**21**) in 10 mL of benzene was added dropwise to a slurry of 1.43 g of anhydrous copper(II) sulfate and 57 mg (0.218 mmol) of copper(II) acetylacetonate in 15 mL of benzene heated at reflux.

The temperature was mantained for 3 h, and the mixture was cooled and filtered through a pad of Celite®. The filtrate was concentrated, dissolved in diethyl ether and filtered again. Concentration and purification by flash chromatography over silica gel with 50% ethyl acetate/hexanes afforded 95 mg (24%) of the title compound: ^1H NMR (300 MHz, $CDCl_3$) δ 5.84 (m, 1H), 5.30-5.16 (m, 2H), 4.55 (m, 2H), 4.34 (dd, J = 9.0 Hz, 4.5H), 4.15 (d, J = 9.0 Hz, 1H), 3.26 (d, J = 17.7 Hz, 1H), 2.30 (d, J = 17.7 Hz, 1H), 2.16 (m, 1H), 1.19 (dd, J = 7.5, 4.8 Hz, 1H), 0.97 (t, J = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 170.2, 131.6, 118.5, 68.3, 65.5, 33.7, 24.6, 22.0, 17.2; IR (neat) 2971, 2910, 1769, 1732 cm^{-1}; HRMS calcd for $C_{10}H_{12}O_4$: 196.0736, found 196.0705; LRMS (EI^+) *m/z* 196 (0.2), 155 (1.1), 139 (58), 111 (20), 83 (26), 67 (20), 55 (35), 41 (100).

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