Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron Letters 47 (2006) 5775–5779
Tetrahedron Letters

Formation of novel polycyclic cage compounds through 'uncaging' of readily accessible higher cage compounds

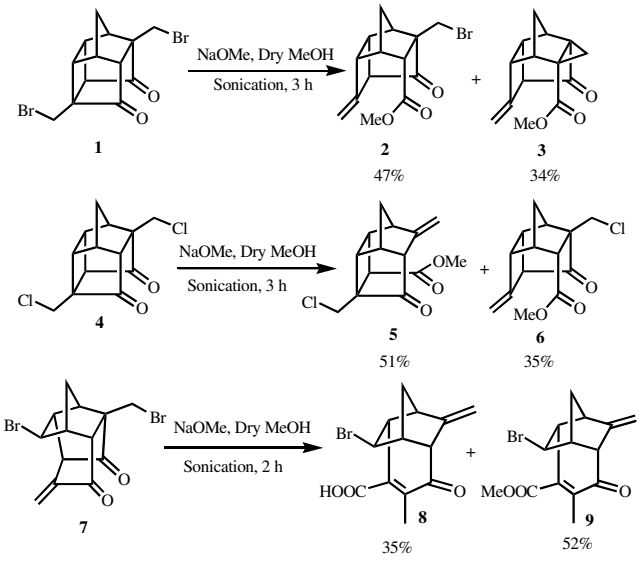
Beena James,[a] Nigam P. Rath,[b] E. Suresh[c] and Mangalam S. Nair[a,*]

[a]*Organic Chemistry Section, Chemical Sciences Division, Regional Research Laboratory (CSIR), Trivandrum 695 019, India*
[b]*Department of Chemistry and Biochemistry, University of Missouri, St. Louis, 63121-4499, USA*
[c]*Analytical Science Discipline, Central Salt and Marine Chemicals Research Institute (CSIR), Bhavnagar 364 002, India*

Received 16 March 2006; revised 19 May 2006; accepted 1 June 2006
Available online 23 June 2006

Abstract—The synthesis of the novel cage compounds 7-halomethyl-8-(carbomethoxy)tetracyclo[4.2.1.1^{4,7}.0^{2,5}]deca-3-(11)-ene-10-ones, methyl-4-methylene-6-oxopentacyclo[5.4.0.0.^{2,5}.0^{3,10}.0^{7,9}]undecane-9-carboxylate, 3-chloromethyl-4-(carbomethoxy)tetracyclo[4.2.1.1.^{3,8}.0^{2,5}]deca-7(11)ene-10-one, 2-bromo-5-methyl-8-methylene-6-oxotricyclo[5.3.0.0^{3,9}]decane-4-carboxylic acid and 2-bromo-5-methyl-8-methylene-6-oxotricyclo[5.3.0.0^{3,9}]decane-4-methyl carboxylate, achieved through base catalyzed rearrangement, is described.

Polycyclic cage compounds[1] continue to attract the attention of chemists as unique compounds with potential application in diverse fields such as high-energy compounds[2] and novel pharmaceutical agents,[3–5] in addition to their extensive utility as precursors for natural product synthesis.[6] Rigid cage molecules have proved to be valuable substrates for the study of organic reaction mechanisms. Molecular rearrangements in polycyclic cage compounds often occur in highly unexpected fashion because of spatial proximity effects leading to unusual products.[7,8] Herein we report the synthesis of an array of fascinating, hitherto unknown polycyclic cage structures **2**, **3**, **5**, **6**, **8** and **9** (Scheme 1) through base catalyzed rearrangement facilitated by the halo methyl substituents on the pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undeca-8,11-diones (PCUD)[9] **1** and **4** and tetracyclo[5.3.1.0^{2,6}.0^{4,8}]undecane systems (TCUD) **7**.[10] This methodology allows the preparation of novel polycyclic ring systems which are difficult to obtain through direct synthetic methodologies as the PCUD and TCUD systems can be readily synthesized through a two step protocol involving Cookson's method of [4+2] addition between cyclopentadiene and substituted benzoquinones, followed by photochemical [π2s+π2s] cycloaddition.[9c]



Scheme 1.

Having this strategy in mind, the two pentacyclic diones, **1**[10] and **4**,[11] and the tetracyclic dione[10] **7** were treated with sodium methoxide in dry methanol under sonication conditions, which provided novel cage compounds **2** and **3** in 47% and 34% yields, **5** and **6** in 51% and 35% yields and **8** and **9** in 35% and 52% yields, respectively (Scheme 1). Structural details of the products were confirmed through spectroscopic analysis.

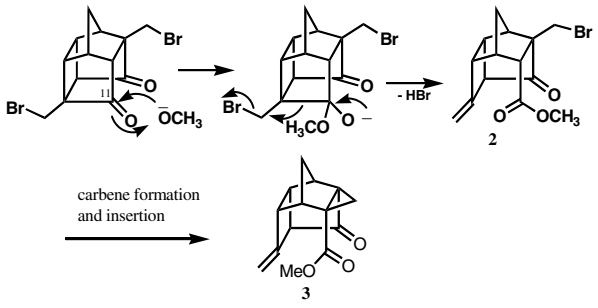
* Corresponding author. Tel.: +91 471 2515277; fax: +91 471 2491712; e-mail: msn555in@yahoo.co.in

0040-4039/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2006.06.005

Compound **2** showed the presence of an exocyclic olefin in its ^{1}H and ^{13}C NMR spectra. The presence of a methyl ester was also confirmed from the IR absorption at 1750 cm^{-1} as well as the characteristic –OMe protons appearing as a singlet at δ 3.46 and the ester carbonyl peak at δ 170.8 in the ^{1}H and ^{13}C NMR spectra, respectively. The presence of a strained cyclopentanone was confirmed through the carbonyl absorption at 1724 cm^{-1} in the IR spectrum and the resonance at δ 209.0 in the ^{13}C NMR spectrum. The protons of the bromomethyl group appeared as doublets at δ 3.73 and δ 3.35. The DEPT-135 NMR spectrum of **2** further indicated the presence of three $-CH_2$-groups. Taking into consideration the above structural details, the structure of **2** was proposed as 7-bromomethyl-8-(carbomethoxy)tetracyclo[4.2.1.1^{4,7}.0^{2,5}]deca-3-(11)-ene-10-one. This structure was based on a mechanism analogous to that proposed earlier for the reaction of **1** with amines, viz., attack of the nucleophile on one of the carbonyl carbons (C-11) followed by rearrangement and elimination of HBr resulting in the formation of the pentacyclo[5.4.1.0.^{2,6}.0^{5,9}.0^{8,11}]dodec-10(13)-ene-3-one system (Scheme 2), the structure of which was confirmed earlier by single crystal X-ray crystallography.[11]

The structure of **3**, however, could not be ascertained easily. The IR spectrum once again showed an absorption due to the ester moiety at 1743 cm^{-1} in addition to another carbonyl absorption at 1714 cm^{-1}. The ^{1}H and ^{13}C NMR spectra indicated the presence of an exocyclic olefin as well as a methyl ester. Surprisingly, while the protons expected for the bromomethyl substituents were absent, the DEPT-135 NMR spectrum still indicated the presence of three $-CH_2$-groups. Once again one cyclopentanone was intact as indicated by the IR absorption at 1714 cm^{-1} and the ^{13}C NMR peak at δ 202.2. The mass spectrum (M^+ 230.09) clearly indicated the loss of the Br atoms. Since the compound readily crystallized, an X-ray crystal structure determination was carried out which confirmed the structure as **3** having a propellane subsystem included[12] (Fig. 1).

The mechanism proposed for the formation of these novel cage compounds **2** and **3** envisages the initial nucleophilic attack of methoxide on one of the carbonyl carbons (C-11) of the pentacyclic dione. This leads to rupture of a five-membered ring, followed by the formation of an exocyclic double bond and loss of the halogen as shown in Scheme 2. The formation of **3** viz., methyl-



Scheme 2.

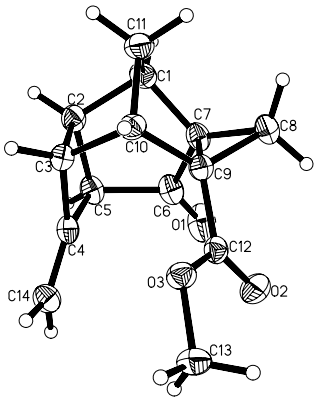


Figure 1. ORTEP plot for the X-ray crystal structure of **3**.

4-methylene-6-oxopentacyclo[5.4.0.0.^{2,5}.0^{3,10}.0^{7,9}]undecane-9-carboxylate can be attributed to the generation of a carbene, which inserts into the C–H bond under the base/sonication conditions.

Reactions of chloromethyl pentacyclic dione **4** with sodium methoxide yielded two compounds, **5** and **6** in 51% and 35% yields (Scheme 1). The salient structural features of both products were similar according to IR, ^{1}H and ^{13}C NMR spectral data. Both products were also found to have the same mass. Specifically, the spectral details of **5** included (i) an IR absorption at 1745 cm^{-1} indicating the presence of an ester functionality, (ii) the chloromethyl protons as doublets at δ 3.83 and δ 3.71 in the ^{1}H NMR spectra, (iii) ^{1}H and ^{13}C NMR spectra indicating the presence of an exocyclic olefin and a methyl ester. However, since the features of **5** and **6** were very similar, single crystal X-ray diffraction studies on **5** were carried out and the structure was confirmed as 3-(chloromethyl)-4-(carbomethoxy)tetracyclo[4.2.1.1^{3,8}.0^{2,5}]deca-7-(11)-ene-10-one (Fig. 2).[13] The mechanism for its formation is shown in Scheme 3.

Compound **6** showed the presence of an exocyclic olefin in its ^{1}H and ^{13}C NMR spectra. The presence of a methyl ester group was confirmed from its IR absorption at 1745 cm^{-1}, whilst the protons of the –OMe group appeared as a singlet at δ 3.53, and the ester car-

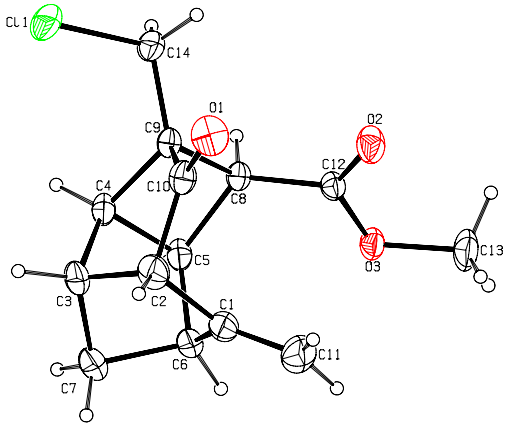
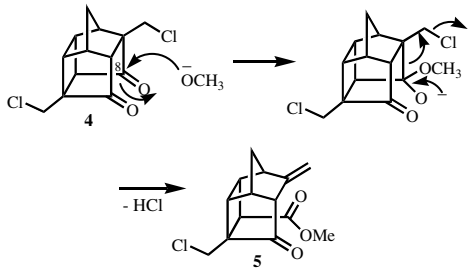


Figure 2. ORTEP plot for the X-ray crystal structure of **5**.



Scheme 3.

bonyl resonance occurred at δ 170.8 in the ^{1}H and ^{13}C NMR spectra, respectively. Considering all the features of the various spectra, the structure of compound **6** was proposed as 7-(chloromethyl)-8-(carbomethoxy)tetracyclo[4.2.1.1^{4,7}.0^{2,5}]deca-3-(11)-ene-10-one.

Since this method proved to facilitate the formation of new polycyclic cage compounds, reaction of tetracyclo[5.3.1.0^{2,6}.0^{4,8}]dione **7**, which was obtained through a photochemical rearrangement reported earlier from our own laboratory,[10a] with sodium methoxide under similar conditions was also studied. This yielded two novel products, **8** and **9** in 35% and 52% yields (Scheme 1). The presence of an acid group in compound **8** was confirmed from the IR absorption at 3575 cm^{-1} and the carbonyl absorption at 1681 cm^{-1}. The ^{1}H NMR spectrum showed the presence of methyl protons at δ 2.13 and exocyclic olefinic protons at δ 4.82 and δ 4.68. The ^{13}C NMR signals at δ 141.5, δ 107.7, δ 149.2 and δ 146.8 confirmed the presence of an exocyclic and an internal olefin, respectively. The structure of **8** was confirmed by single crystal X-ray analysis as 2-bromo-5-methyl-8-methylene-6-oxotricyclo[5.3.0.0^{3,9}]decane-4-carboxylic acid (Fig. 3).[14]

The salient spectral features of compound **9** include (i) IR absorptions at 1734 and 1687 cm^{-1} indicating the presence of an ester group and a carbonyl group, respectively, (ii) the presence of methyl and methyl ester protons easily identified as singlets at δ 2.03 and δ 3.82, respectively, in the ^{1}H NMR spectrum, (iii) the presence of exocyclic olefinic protons indicated by the signals at δ 4.79 and δ 4.65 in the ^{1}H NMR spectrum, (iv) the ^{13}C NMR spectrum confirmed the presence of a carbonyl group and a methyl ester group with signals at δ 203.1 and δ 167.5, whereas the signals at δ 142.7, δ 107.2 and δ 149.2 and δ 143.8 confirmed the presence of exocyclic and internal olefins, respectively and (v) the mass spectrum (M^{+} 310.0215) clearly indicated the loss of one bromine atom. Taking into consideration the above structural details, the structure of **9** was proposed as 2-bromo-5-methyl-8-methylene-6-oxotricyclo[5.3.0.0^{3,9}]-decane-4-methyl carboxylate.

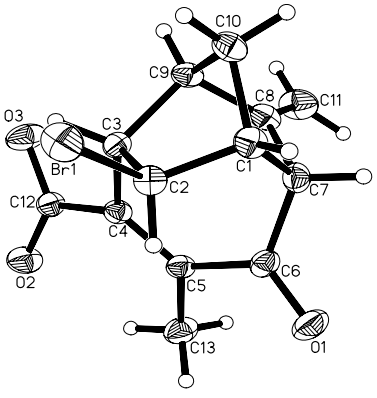
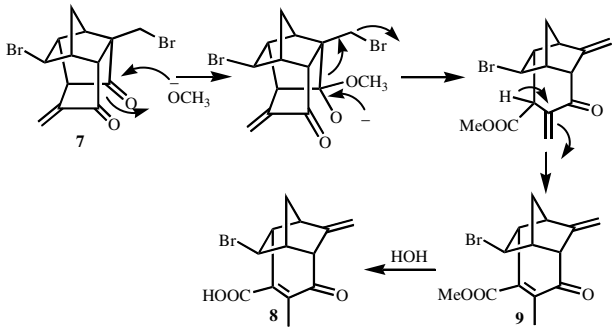


Figure 3. ORTEP plot for the X-ray crystal structure of **8**.



Scheme 4.

Formation of product **9** can be explained by the initial nucleophilic attack of a methoxide anion to the carbonyl group of the cyclopentanone moiety of the tetracyclic system **7**, followed by rearrangement and elimination of HBr resulting in the formation of an ester with an exocyclic methylene group and subsequent proton transfer leading to an internal olefin and a methyl group. Compound **8** was easily identified as the hydrolyzed product of compound **9** (Scheme 4).

In conclusion, we have synthesized several novel compounds, through 'uncaging' of cage systems that would be difficult to synthesize through direct methods.

Acknowledgements

B.J. thanks the Council of Scientific and Industrial Research, New Delhi, for a Senior Research Fellowship. We thank Ms. Soumini Mathew and Ms. S. Viji for recording NMR and HRMS spectra.

References and notes

1. (a) Kruger, H. G.; Martins, F. J. C.; Viljoen, A. M. *J. Org. Chem.* **2004**, *69*, 4863; (b) Mehta, G.; Vidya, R. *J. Org. Chem.* **2000**, *65*, 3497; (c) Marchand, A. P. *Aldrichim. Acta* **1995**, *28*, 95; (d) Osawa, E.; Yonemitsu, O. *Carbocyclic Cage Compounds*; VCH: New York, NY, 1992; (e) Marchand, A. P. *Synlett* **1991**, 73.
2. (a) Marchand, A. P.; Arney, B. E., Jr.; Dave, P. R. *J. Org. Chem.* **1988**, *53*, 443; (b) Marchand, A. P.; Dave, P. R.; Rajapaksa, D.; Arney, B. E., Jr.; Flippen-Anderson, J. L.; Gilardi, R.; George, C. *J. Org. Chem.* **1989**, *54*, 1769.
3. (a) Gedenhuys, W. J.; Malan, S. F.; Bloomquist, J. R.; Marchand, A. P.; Van der Schyf, C. *J. Med. Res. Rev.* **2005**, *25*, 21; (b) Eaton, P. E. *Angew. Chem., Int. Ed. Engl.*

1992, *31*, 1421; (c) Michalson, E. T.; Sqmurzkoviez, J. *Prog. Drug. Res.* **1989**, *33*, 135.
4. (a) Grobler, E.; Grobler, A.; Van der Schyf, C. J.; Malan, S. F. *Bioorg. Med. Chem.* **2006**, *14*, 1176; (b) Geldenhuys, W. J.; Malan, S. F.; Muruges, T.; Van der Schyf, C. J.; Bloomquist, J. R. *Bioorg. Med. Chem.* **2004**, *12*, 1799; (c) Zah, J.; Blanche, G. T.; Erasmus, E.; Malan, S. F. *Bioorg. Med. Chem.* **2003**, *11*, 3569.
5. (a) Gante, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1699; (b) Giannis, A.; Kolter, T. *Angew. Chem., Int. Ed. Engl.* **1993**, 1267.
6. (a) Mehta, G.; Srikrishna, A. *Chem. Rev.* **1997**, *97*, 671; (b) Mehta, G.; Reddy, A. V. *J. Chem. Soc., Chem. Commun.* **1984**, 1058; (c) Mehta, G.; Reddy, D. S.; Reddy, A. V. *Tetrahedron Lett.* **1984**, *25*, 2275; (d) Mehta, G.; Rao, K. S.; Marchand, A. P.; Kaya, R. *J. Org. Chem.* **1984**, *49*, 3848; (e) Mehta, G.; Reddy, A. V. *J. Chem. Soc., Chem. Commun.* **1981**, 756.
7. (a) Marchand, A. P.; Chong, H. S.; Shukla, R.; Sharma, G. V. M.; Kumar, K. A.; Zope, U. R.; Bott, S. G. *Tetrahedron* **1996**, *52*, 13531; (b) Martins, F. J. C.; Viljoen, A. M.; Coetzee, M.; Fourie, L.; Wessels, P. L. *Tetrahedron* **1991**, *47*, 9215.
8. (a) Marchand, A. P.; Aavula, B. R.; Bott, S. G. *Tetrahedron* **1998**, *54*, 5105; (b) Chow, T. J.; Wu, T.-K. *J. Org. Chem.* **1991**, *56*, 6833; (c) Marchand, A. P.; LaRoe, W. D.; Sharma, G. V. M.; Suri, S. C.; Reddy, D. S. *J. Org. Chem.* **1986**, *51*, 1622; (d) Craze, G. A.; Watt, I. *J. Chem. Soc., Perkin Trans. 2* **1981**, 175.
9. (a) Marchand, A. P.; Huang, C.; Kaya, R.; Baker, A. D.; Jemmis, E. D.; Dixon, D. A. *J. Am. Chem. Soc.* **1987**, *107*, 7095; (b) Marchand, A. P.; Kaya, R.; Baker, A. D. *Tetrahedron Lett.* **1984**, *25*, 795; (c) Cookson, R. C.; Crundwell, E.; Hill, R. R.; Hudec, J. *J. Chem. Soc.* **1964**, 3062.
10. (a) Nair, M. S.; Sudhir, U.; Joly, S.; Rath, N. P. *Tetrahedron* **1999**, *55*, 7653; (b) Suri, S. C. *J. Org. Chem.* **1993**, *58*, 4153; (c) Suri, S. C.; Hardcastle, K. I. *J. Org. Chem.* **1992**, *57*, 6357; (d) Suri, S. C. *Tetrahedron Lett.* **1990**, *31*, 3695.
11. Nair, M. S.; Sudhir, U.; Rath, N. P. *Tetrahedron* **2001**, *57*, 7749.
12. *Crystal data for* **3**: $C_{14}H_{14}O_3$, colourless crystalline solid, $0.38 \times 0.36 \times 0.20\ mm^3$; formula weight = 230.26. Orthorhombic, space group: *Pbca*. Unit cell dimensions: $a = 12.1677(2)$ Å $\alpha = 90°$; $b = 12.3939(2)$ Å $\beta = 90°$; $c = 14.2494(2)$ Å $\gamma = 90°$. *R* indices (all data): $R1 = 0.0538$, $wR2 = 0.1102$, Volume = 2148.88(6) Å^3 $Z = 8$. Density (calcd) = 1.423 Mg/m^3·F (000) = 976. Absorption coefficient = 0.099 mm^{-1}.
13. *Crystal data for* **5**: $C_{14}H_{15}O_3Cl$, colourless crystalline solid, $0.36 \times 0.29 \times 0.23\ mm^3$; formula weight = 266.71. Monoclinic, space group: *P*21/*n*. Unit cell dimensions: $a = 8.8657(10)$ Å $b = 8.2664(10)$ Å; $c = 18.523(2)$ Å $\beta = 101.467(2)°$; Volume = 1330.4(3) Å3; $Z = 4$. Density (calcd) = 1.332 Mg/m^3; F(000) = 560. Absorption coefficient = 0.284 mm^{-1}; GOF = 1.046; *R* indices ($I > 2\sigma$): $R1 = 0.0483$, $wR2 = 0.1352$.
The crystal structures for compounds **3** and **5** have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers 600719 and 600349, respectively.
14. *Crystal data for* **8**: $C_{13}H_{12}BrO_3$, colourless crystalline solid, $0.39 \times 0.28 \times 0.26\ mm^3$; formula weight = 296.1. Orthorhombic, space group: *Pbcn*. Unit cell dimensions: $a = 24.9991(12)$ Å $\alpha = 90°$; $b = 8.2241(4)$ Å $\beta = 90°$; $c = 11.9691(6)$ Å $\gamma = 90°$; *R* indices (all data): $R1 = 0.0722$, $wR2 = 0.1293$, Volume = 2460.8(2) Å^3; $Z = 8$. Density (calcd) = 1.599 Mg/m^3; F (000) = 1192. Absorption coefficient = 3.334 mm^{-1}.

Details of a typical experiment are as follows: The cage dione **1** (0.1 g, 0.28 mmol) was taken in dry methanol (10 mL) along with sodium methoxide (0.06 g, 1.11 mmol) and sonicated for 3 h under an argon atmosphere. After the reaction was complete, the reaction mixture was worked up by removing the solvent under reduced pressure and the crude product was diluted with distilled water and extracted with dichloromethane (3×20 mL). The combined extracts were washed with water, brine and dried over anhydrous sodium sulfate. The crude product thus obtained was purified by column chromatography to afford the products as white crystalline solids, **2** in 47% and **3** in 34% yields. The same methodology was used for the synthesis of compounds **5**, **6**, **8** and **9** which were obtained in 51%, 35%, 35% and 52% yields, respectively.

Spectral data for new compounds

7-Bromomethyl-8-(carbomethoxy)tetracyclo[4.2.1.1.^{4,7}.0^{2,5}]-deca-3-(11)-ene-10-one (**2**): Yield: 47%; crystallized from dichloromethane–petroleum ether (1:4). Mp: 62–64 °C; FT-IR (KBr, ν_{max}/cm^{-1}): 2986, 1750, 1724, 1667, 1439, 1237, 901; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.92 (s, 1H), 3.73 (d, $J = 10.5$ Hz, 1H), 3.50 (s, 1H), 3.46 (s, 3H), 3.35 (d, $J = 8.8$ Hz, 1H), 3.06–3.04 (m, 2H), 2.99–2.86 (m, 2H), 2.81 (br s, 1H), 1.63 (d, $J = 10.4$ Hz, 1H), 1.51 (d, $J = 10.4$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.0, 170.8, 147.2, 111.0, 57.9, 56.0, 51.5, 46.5, 43.9, 43.5, 41.5, 39.6, 37.8, 34.8. HRMS (M^+): 310.0200, $C_{14}H_{15}O_3Br$ requires 310.0205.

Methyl-4-methylene-6-oxopentacyclo[5.4.0.0.^{2,5}.0^{3,10}.0^{7,9}]-undecane-9-carboxylate (**3**): Yield: 34%; crystallized from ethyl acetate–petroleum ether (1:4). Mp: 100–102 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 2983, 1743, 1714, 1669, 1440, 1274, 1112, 985; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.99 (s, 1H), 4.71 (s, 1H), 3.55 (s, 3H) 3.37 (br s, 1H), 3.21 (br s, 1H), 3.11 (s, 1H), 3.03–2.96 (m, 1H), 2.87 (d, $J = 6.4$ Hz, 1H), 2.18 (d, $J = 6.5$ Hz, 1H), 1.69 (d, $J = 6.5$ Hz, 1H), 1.35 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.2, 170.9, 143.3, 111.5, 55.0, 54.3, 52.0, 44.6, 41.6, 41.2, 40.1, 36.1, 31.1, 19.2. HRMS (M^+): 230.0949, $C_{14}H_{14}O_3$ requires 230.0943.

3-Chloromethyl-4-(carbomethoxy)tetracyclo[4.2.1.1^{3,8}.0^{2,5}]-deca-7(11)-ene-10-one (**5**): Yield: 51%; crystallized from dichloromethane–petroleum ether (1:4). Mp: 51–53 °C; FT-IR (KBr, ν_{max}/cm^{-1}): 2945, 1745, 1724, 1659, 1434, 1295, 897, 738; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.99 (s, 1H), 4.95 (s, 1H), 3.83 (d, $J = 11.5$ Hz, 1H), 3.71 (d, $J = 11.5$ Hz, 1H), 3.53 (s, 3H), 3.48 (d, $J = 9.0$ Hz, 1H), 3.13–3.04 (m, 2 H), 3.02–2.94 (m, 2H), 2.87–2.86 (m, 1H), 1.70 (d, $J = 10.2$ Hz, 1H), 1.58 (d, $J = 10.3$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.5, 171.0, 147.2, 111.1, 58.1, 56.4, 51.2, 46.6, 45.6, 42.6, 41.9, 41.6, 39.7, 38.4. HRMS (M^+): 266.0686, $C_{14}H_{15}O_3Cl$ requires 266.0710.

7-Chloromethyl-8-(carbomethoxy)tetracyclo[4.2.1.1^{4,7}.0^{2,5}]-deca-3-(11)-ene-10-one (**6**): Yield: 35%; crystallized from dichloromethane–petroleum ether (1:4). Mp: 50–52 °C; FT-IR (KBr, ν_{max}/cm^{-1}): 2979, 1745, 1732, 1659, 1427, 1208, 1043, 890; ^{1}H NMR (300 MHz, $CDCl_3$): δ δ 5.01 (s, 1H), 4.83 (s, 1H), 3.86 (s, 2H), 3.53 (s, 3H), 3.34 (s, 1H), 3.30 (s, 1H), 3.09–2.97 (m, 3H), 2.82–2.81 (d, $J = 4.5$ Hz, 1H), 2.09 (d, $J = 10.6$ Hz, 1H), 1.58 (d, $J = 10.7$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 210.1, 170.8, 140.4, 112.3, 55.7, 55.1 53.7, 51.4, 50.2, 49.0, 46.9, 42.5, 40.5, 38.0. HRMS (M^+): 266.0710, $C_{14}H_{15}O_3Cl$ requires 266.0710.

2-Bromo-5-methyl-8-methylene-6-oxotricyclo[5.3.0.0^{3,9}]-decane-4-carboxylic acid (**8**): Yield: 35%; crystallized from dichloromethane–petroleum ether (1:4). Mp: 67–69 °C; FT-IR (KBr, ν_{max}/cm^{-1}): 3575, 1681, 1606, 1245, 894, 576,

433; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.32 (br s, 1H), 4.82 (s, 1H), 4.68 (s, 1H), 3.89 (d, $J = 4.7$ Hz, 1H), 3.82 (s, 1H), 3.50 (d, $J = 5.0$ Hz, 1H), 3.08 (d, $J = 5.3$ Hz, 1H), 2.90 (d, $J = 5.7$ Hz, 1H), 2.73 (d, $J = 10.6$ Hz, 1H), 2.13 (s, 3 H), 1.75 (d, $J = 10.6$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.2, 172.6, 149.2, 146.8, 141.5, 107.7, 59.1, 57.1, 50.6, 48.2, 46.4, 38.7, 16.1. HRMS (M^+): 296.0042, $C_{13}H_{13}O_3Br$ requires 296.0048.

2-Bromo-5-methyl-8-methylene-6-oxotricyclo[5.3.0.0^{3,9}]-decane-4-methylcarboxylate (**9**): Yield: 52%; crystallized from dichloromethane–petroleum ether (1:4). Mp: 70–72 °C; FT-IR (KBr, ν_{max}/cm^{-1}): 1734, 1687, 1517, 1237, 1062, 772, 694; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.79 (s, 1H), 4.65 (s, 1H), 3.82 (s, 3H), 3.79 (d, $J = 5.7$ Hz, 2H), 3.48 (d, $J = 6.0$ Hz, 1H), 3.06 (d, $J = 6.9$ Hz, 1H), 2.88 (d, $J = 5.6$ Hz, 1H), 2.71 (d, $J = 10.5$ Hz, 1H), 2.03 (s, 3H), 1.77 (d, $J = 10.6$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.1, 167.5, 149.2, 143.8, 142.7, 107.2, 59.4, 57.0, 52.1, 50.6, 47.9, 46.0, 38.6, 15.6. HRMS (M^+): 310.0198, $C_{14}H_{15}O_3Br$ requires 310.0205.