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Manganese(III) Acetate Mediated Oxidative Radical Cyclizations. Toward Vicinal All-Carbon Quaternary Stereocenters

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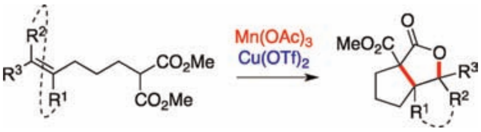
ABSTRACT



Manganese(III) acetate mediated oxidative radical cyclizations have been used to synthesize a range of densely functionalized and sterically congested cyclopentane-lactones. A number of the resulting lactones contain vicinal all-carbon quaternary stereocenters adjacent to a tertiary benzylic stereocenter and are formed with high levels of stereocontrol.

The direct stereocontrolled installation of all-carbon quaternary stereocenters adjacent to other stereocenters remains a considerable challenge in contemporary organic synthesis.[1] Even more challenging is the direct synthesis of vicinal all-carbon quaternary stereogenic centers.[1c,2] In this regard a number of methods have been developed to directly synthesize vicinal all-carbon quaternary centers, including pericyclic reactions, alkylation reactions, photochemical reactions, and transition metal catalyzed reactions to name but a few.[3,4] Additionally, radical reactions have been utilized for the direct synthesis of all-carbon quaternary centers.[5] Oxidative radical methods have also been used in the synthesis of highly congested vicinal stereocenters.[5a,h]

Previously we have reported the efficient synthesis of [3.3.0]-bicyclic γ-lactones by the cyclization of terminal 4-pentenyl malonates under the influence of manganese(III) acetate and copper(II) triflate.[6] Herein we report an extension of this methodology to the synthesis of bi- and tricyclic γ-lactones containing adjacent quaternary, tertiary, tertiary stereocenters; quaternary, quaternary, tertiary stereocenters; and quaternary, quaternary, quaternary stereocenters.

We envisaged that exposure of a suitably substituted pentenyl malonate **1** to manganese(III) acetate[7] would generate the corresponding electrophilic *C*-centered radical **2**, which would undergo 5-*exo*-trig radical cyclization to give adduct radical **3** (Scheme 1). The adduct radical would then undergo further single electron oxidation and hydrolysis to give the product [3.3.0]-bicyclic γ-lactone **5** potentially *via* the corresponding carbenium ion **4**.[8] Thus, in one step it would be possible to form up to three adjacent

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(1) For recent reviews, see: (a) Corey, E. J.; Guzman-Perez, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 388–401. (b) Douglas, C. J.; Overman, L. E. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5363–5367. (c) Peterson, E. A.; Overman, L. E. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 11943–11948. (d) *Quaternary Stereocenters: Challenges and Solutions for Organic Synthesis*; Christoffers, J., Baro, A., Eds.; Wiley-VCH: Weinheim, 2005. (e) Trost, B. M.; Jiang, C. *Synthesis* **2006**, 369–396. (f) Denissova, I.; Barriault, L. *Tetrahedron* **2003**, *59*, 10105–10146. (f) Christoffers, J.; Baro, A. *Adv. Synth. Catal.* **2005**, *347*, 1473–1482.

(2) For selected recent reviews which contain synthesis of natural products with adjacent all-carbon quaternary centers, see: (a) Pihko, A. J.; Koskinen, A. M. P. *Tetrahedron* **2005**, *61*, 8769–8807. (b) Steven, A.; Overman, L. E. *Angew. Chem., Int. Ed.* **2007**, *46*, 5488–5508. (c) Kim, J.; Movassaghi, M. *Chem. Soc. Rev.* **2009**, *38*, 3035–3050. (d) Zuo, Z. W.; Ma, D. W. *Isr. J. Chem.* **2011**, *51*, 434–441.

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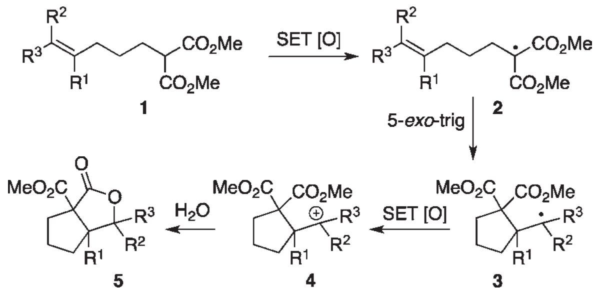
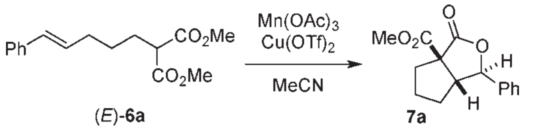
stereocenters including, with an appropriately substituted alkene, vicinal all-carbon quaternary stereocenters.

Scheme 1. Proposed Mechanism for Oxidative Radical Cyclization



We began our investigations with the cyclization of the 1,2-disubstituted alkene substrate (*E*)-**6a** (Table 1) before moving to the more challenging trisubstituted and fully substituted alkene substrates (*vide infra*). Exposure of the malonate (*E*)-**6a**[9] to manganese(III) acetate and copper(II) triflate[10] in acetonitrile (0.1 M) at 80 °C gave rise to the desired [3.3.0]-bicyclic γ-lactone **7a** in 79% yield and 2:1 dr at the lactone stereocenter (Table 1, entry 1).[11] Variation of the concentration (Table 1, entries 1−6) gave rise to large changes in both dr and isolated yields, with the optimum concentration being 0.4 M. Lowering the temperature gave an increase in dr, but with a concomitant decrease in yield (Table 1, entries 7 and 8).

Table 1. Optimization of the Oxidative Radical Cyclization Reaction with Malonate **7a**[a]



entry	temp (°C)	concn (M)	yield (%)[b]	dr[c]
1	80	0.1	79	2.8:1
2	80	0.2	71	3.4:1
3	80	0.4	84	4.1:1
4	80	0.6	67	5.7:1
5	80	0.8	62	5.2:1
6	80	1.0	55	3.8:1
7	60	0.4	70	6.0:1
8	40	0.4	74	7.4:1

[a] All reactions were carried out with 2 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OTf)_2$ in N_2-sparged MeCN. [b] Isolated yield of mixture of diastereomers. [c] dr was established from the crude ^1H NMR; major diastereomer shown.

Control reactions demonstrated that both manganese(III) acetate and copper(II) triflate were required for efficient reaction.[12] Furthermore, resubmission of diastereomerically

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(3) For recent selected examples of the one-pot formation of vicinal all carbon quaternary stereocenters by the following methods, see: Thermal pericyclic: (a) Lemieux, R. M.; Meyers, A. I. *J. Am. Chem. Soc.* **1998**, *120*, 5453–5457. (b) Nicolaou, K. C.; Vassilikogiannakis, G.; Mägerlein, W.; Kranich, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 2482–2486. (c) Birman, V. B.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2002**, *124*, 2080–2081. (d) Denmark, S. E.; Baiazitov, R. Y. *Org. Lett.* **2005**, *7*, 5617–5620. (e) George, J.; Adlington, R. *Synlett* **2008**, 2093–2096. (f) Wu, H.; Xue, F.; Xiao, X.; Qin, Y. *J. Am. Chem. Soc.* **2010**, *132*, 14052–14054. (g) Matsuta, Y.; Kobari, T.; Kurashima, S.; Kumakura, Y.; Shinada, M.; Higuchi, K.; Kawasaki, T. *Tetrahedron Lett.* **2011**, *52*, 6199–6202. Photochemical: (h) Crimmins, M. T.; Pace, J. M.; Nantermet, P. G.; Kim-Meade, A. S.; Thomas, J. B.; Watterson, S. H.; Wagman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 10249–10250. (i) Ng, D.; Yang, Z.; Garcia-Garibay, M. A. *Org. Lett.* **2004**, *6*, 645–647. (j) Mortko, C. J.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2005**, *127*, 7994–7995. (k) Mehta, G.; Singh, S. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 953–955. (l) Inoue, M.; Sato, T.; Hirama, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 4843–4848. (m) Shi, L.; Meyer, K.; Greaney, M. F. *Angew. Chem., Int. Ed.* **2010**, *49*, 9250–9253. Alkylation: (n) Overman, L. E.; Larrow, J. F.; Stearns, B. A.; Vance, J. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 213–215. (o) Overman, L. E.; Peterson, E. A. *Tetrahedron* **2003**, *59*, 6905–6919. (p) Fuchs, J. R.; Funk, R. L. *J. Am. Chem. Soc.* **2004**, *126*, 5068–5069. (q) Clarke, P. A.; Black, R. J. G.; Blake, A. J. *Tetrahedron Lett.* **2006**, *47*, 1453–1455. (r) Feldman, K. S.; Nuriye, A. Y. *Tetrahedron Lett.* **2009**, *50*, 1914–1916. (s) Couladouros, E. A.; Dakanali, M.; Demadis, K. D.; Vidali, V. P. *Org. Lett.* **2009**, *11*, 4430–4433. (t) Sladojevich, F.; Michaelides, I. N.; Darses, B. D.; Ward, J. W.; Dixon, D. J. *Org. Lett.* **2011**, *13*, 5132–5135. Transition metal catalyzed: (u) Overman, L. E.; Paone, D. V.; Stearns, B. A. *J. Am. Chem. Soc.* **1999**, *121*, 7702–7703. (v) Chiba, S.; Kitamura, M.; Narasaka, K. *J. Am. Chem. Soc.* **2006**, *128*, 6931–6937. (w) Yang, J.; Wu, H.; Shen, L.; Qin, Y. *J. Am. Chem. Soc.* **2007**, *129*, 13794–13795. Oxidative: (x) Ishikawa, H.; Takayama, H.; Aimi, N. *Tetrahedron Lett.* **2002**, *43*, 5637–5639. (y) Snell, R. H.; Woodward, R. L.; Willis, M. C. *Angew. Chem., Int. Ed.* **2011**, *50*, 9116–9119.

(4) For a recent example of the direct generation of vicinal all-carbon quaternary centers by reaction of a Grignard reagent with an α-chlorotosylhydrazone, see: Hatcher, J. M.; Coltart, D. M. *J. Am. Chem. Soc.* **2010**, *132*, 4546–4547.

(5) (a) Oumar-Mahamat, H.; Moustrou, C.; Surzur, J.-M.; Bertrand, M. P. *J. Org. Chem.* **1989**, *54*, 5684–5688. (b) Journet, M.; Malacria, M. *J. Org. Chem.* **1992**, *57*, 3085–3093. (c) Curran, D. P.; Shen, W. *Tetrahedron* **1993**, *49*, 755–770. (d) Leonetti, J. A.; Gross, T.; Little, R. D. *J. Org. Chem.* **1996**, *61*, 1787–1793. (e) Devin, P.; Fensterbank, L.; Malacria, M. *J. Org. Chem.* **1998**, *63*, 6764–6765. (f) Curran, D. P.; Sisko, J.; Balog, A.; Sonoda, N.; Nagahara, K.; Ryu, I. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1591–1594. (g) Pattenden, G.; Stoker, D. A.; Thomson, N. M. *Org. Biomol. Chem.* **2007**, *5*, 1776–1788. (h) Nicolaou, K. C.; Gray, D. *Angew. Chem., Int. Ed.* **2001**, *40*, 761–763. (i) Kim, J.; Ashenhurst, J. A.; Movassaghi, M. *Science* **2009**, *324*, 238–241. (j) Movassaghi, M.; Ahmad, O. K.; Lathrop, S. P. *J. Am. Chem. Soc.* **2011**, *133*, 13002–13005.

(6) (a) Davies, J. J.; Krulle, T. M.; Burton, J. W. *Org. Lett.* **2010**, *12*, 2738–2741. (b) Powell, L. H.; Docherty, P. H.; Hulcoop, D. G.; Kemmitt, P. D.; Burton, J. W. *Chem. Commun.* **2008**, 2559–2561.

(7) For reviews of manganese(III) acetate in organic synthesis, see: (a) Snider, B. B. *Chem. Rev.* **1996**, *96*, 339–363. (b) Melikyan, G. G. *Org. React.* **1997**, *49*, 427–675. (c) Demir, A. S.; Emrullahoglu, M. *Curr. Org. Synth.* **2007**, *4*, 321–351. Burton, J. W. In *Encyclopedia of Radicals in Chemistry, Biology and Materials*; Chatgilialoglu, C., Studer, A., Eds.; John Wiley & Sons Ltd.: Chichester, U.K., 2012; pp 901−942.

(8) For a review of the mechanisms of manganese(III) acetate mediated reactions, see: Snider, B. B. *Tetrahedron* **2009**, *65*, 10738–10744.

(9) For substrate synthesis see Supporting Information (SI).

(10) For the use of copper(II) triflate in conjunction with manganese(III) acetate, see: (a) Toyao, A.; Chikaoka, S.; Takeda, Y.; Tamura, O.; Muraoka, O.; Tanabe, G.; Ishibashi, H. *Tetrahedron Lett.* **2001**, *42*, 1729–1732. (b) Hulcoop, D. G.; Burton, J. W. *Chem. Commun.* **2005**, 4687–4689. (c) Hulcoop, D. G.; Sheldrake, H. M.; Burton, J. W. *Org. Biomol. Chem.* **2004**, *2*, 965–967 and ref 6.

(11) The cyclization of the diethyl malonate analogue of **6a** to give the lactone corresponding to **7a** has previously been reported under various oxidative radical conditions: with manganese(III) acetate in acetic acid at 60 °C gives the lactone in 69% yield (10:1 dr) along with 25% of a benzylic acetate; see: (a) Citterio, A.; Sebastiano, R.; Nicolini, M. *Tetrahedron* **1993**, *49*, 7743–7760. With ferrocenium hexafluorophosphate or copper(II) chloride gives the lactone with up to 28% yield (10:1 dr) along with dimers; see: (b) Jahn, U.; Hartmann, P. *Chem. Commun.* **1998**, 209–210. (c) Jahn, U.; Hartmann, P.; Dix, I.; Jones, P. G. *Eur. J. Org. Chem.* **2001**, 3333–3355.

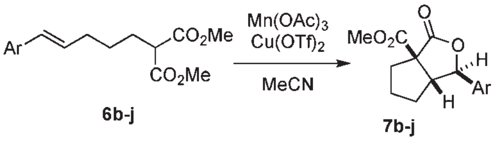
(12) In the absence of copper(II) triflate the yield of **7a** was only 28% (4.2:1 dr). In the absence of manganese(III) acetate substrate decomposition occurred.

pure lactone **7a** to the reaction conditions did not lead to epimerization, indicating that product formation is a kinetically controlled process. Cyclization of (*Z*)-**6a** gave the γ-lactone **7a** with the same yield and dr as those for (*E*)-**6a** in keeping with the proposed mechanism shown in Scheme 1.

Having developed conditions (Table 1, entry 3) for the efficient cyclization of **6a** we moved to investigate the cyclization onto a range of substituted styrenes. The results are summarized in Table 2.[9] More electron-rich substrates gave the γ-lactone products **7** with reduced diastereocontrol (Table 2, entries 4, 5, and 9), with the most electron-rich substrate **6h** giving an intractable mixture of products in which the desired γ-lactone was only a minor constituent.

The stereochemistry of the products was established by ^{1}H NMR NOE experiments on diastereomerically pure cyclopentane-lactones **7a**, **7b**, and **7i** and confirmed by single crystal X-ray diffraction of cyclopentane-lactone **7i** (Figure 1).[13,14] The stereochemistry of the remaining cyclopentane-lactone products, **7c**–**7g** and **7j**, were established by analogy, as the ^{1}H NMR chemical shift of the benzylic protons of the major and minor isomers fell in characteristic regions (δ_H = 5.00–5.40 and 5.80–6.10 ppm respectively).

Table 2. Manganese(III) Acetate Mediated Oxidative Radical Cyclization of Aryl Substituted Malonates **6b**–**6j**[a]



entry	**6**, Ar	**7**, yield (%)[b]	dr[c]
1	**6b**, 4-FC$_6$H$_4$	**7b**, 72	4.1:1
2	**6c**, 2-FC$_6$H$_4$	**7c**, 54	4.8:1
3	**6d**, 4-BrC$_6$H$_4$	**7d**, 74	4.2:1
4	**6e**, 4-MeC$_6$H$_4$	**7e**, 58	1.5:1
5	**6f**, 2-MeC$_6$H$_4$	**7f**, 72	1.3:1
6	**6g**, 3-MeOC$_6$H$_4$	**7g**, 73	6.0:1
7	**6h**, 4-MeOC$_6$H$_4$	**7h**, n.d.[d]	n.d.[d]
8	**6i**, 3-NO$_2$C$_6$H	**7i**, 66	3.4:1
9	**6j**, 2-naphthyl	**7j**, 83	1.9:1

[a] All reactions were carried out with 2 equiv of Mn(OAc)$_3$·2H$_2$O and 1 equiv of Cu(OTf)$_2$ in sparged MeCN at 80 °C. [b] Isolated yield. [c] dr was established from the crude ^{1}H NMR; major diastereomer shown. [d] Not determined.

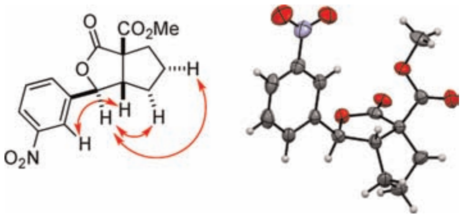
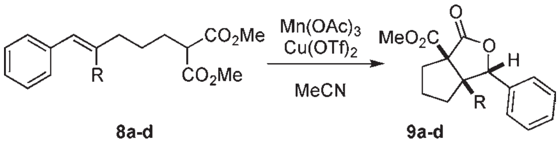


Figure 1. ^{1}H NMR NOE data and single crystal X-ray structure of lactone **7i** determined from single crystal diffraction data (thermal ellipsoids drawn at 50% probability).

Having established an efficient protocol for the synthesis of [3.3.0]-bicyclic γ-lactones containing adjacent quaternary, tertiary, tertiary stereocenters we sought to extend this methodology to the synthesis of products with vicinal all-carbon quaternary stereocenters.

Pleasingly, on submission to the previously optimized cyclization conditions, the trisubstituted alkenes **8a**–**d**[9] underwent efficient and highly diastereoselective cyclization to give the corresponding [3.3.0]-bicyclic γ-lactones **9a**–**d** containing vicinal all-carbon quaternary stereocenters (Table 3). Importantly, both unsaturation and oxygenation (Table 3, entries 3 and 4) are tolerated in the cyclization substrate. The high yielding formation of the γ-lactones **9a**–**d** is noteworthy given the significantly reduced rate of 5-*exo*-trig cyclization onto 2,2-disubstituted alkenes, compared with monosubstituted alkenes.[15]

Table 3. Cyclization of Trisubstituted Pentenyl Malonates **8a**–**d**[a]



entry	**8**, R	**9**, yield (%)[b]	dr[c]
1	**8a**, Me	**9a**, 83	8.0:1
2	**8b**, *n*-Bu	**9b**, 91	10.7:1
3	**8c**, CH$_2$C≡CH	**9c**, 74	11.9:1
4	**8d**, (CH$_2$)$_2$OTBDPS[d]	**9d**, 96	10.2:1

[a] All reactions were carried out with 2 equiv of Mn(OAc)$_3$·2H$_2$O and 1 equiv of Cu(OTf)$_2$ in sparged MeCN at 80 °C. [b] Isolated yield. [c] dr was established from the crude ^{1}H NMR. [d] TBDPS = *tert*-butyldiphenylsilyl.

In order to test the limits of steric bulk tolerated on the alkene moiety, substrates containing an *i*-Pr or *t*-Bu group, **8e** and **8f** respectively,[9] were submitted to the optimized reaction conditions (Table 4). Under these conditions, substrate **8e** underwent competitive 5-*exo*/6-*endo*-trig cyclization to give the desired γ-lactone **9e** (39% as a single

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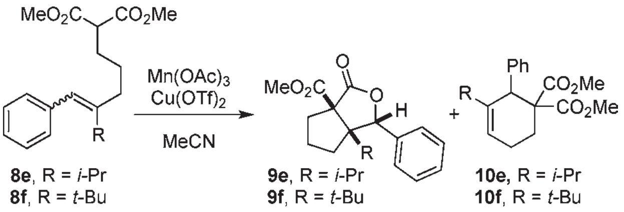
(13) Low temperature, single crystal diffraction data were collected using a Nonius Kappa CCD, reduced using DENZO/SCALEPACK [(a) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307–326] and were solved using SIR92[(b) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435–435]. Refinement was carried out within the CRYSTALS suite[(c) Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Crystallogr.* **2003**, *36*, 1487–1487; (d) Thompson, A. L.; Watkin, D. J. *J. Appl. Crystallogr.* **2011**, *44*, 1017–1022] using a Chebychev polynomial weighting scheme [(e) Carruthers, J. R.; Watkin, D. J. *Acta Crystallogr.* **1979**, *A35*, 698–699] with the hydrogen atoms treated in the usual fashion[(f) Cooper, R. I.; Thompson, A. L.; Watkin, D. J. *J. Appl. Crystallogr.* **2010**, *43*, 1100–1107]. (g) For full experimental details, see SI (CIF); crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre (CCDC 879276 and 879277) and can be obtained *via* http://www.ccdc.cam.ac.uk/data_request/cif.

(14) The stereochemistry of the minor diastereomers of lactones **7a** and **7b** was assigned on the basis of ^{1}H NMR NOE experiments.

(15) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073–3100.

Table 4. Cyclization of More Hindered Substrates **8e** and **8f**[a]



entry	**8**, R	**9**, yield (%)[b]	**10**, yield (%)[b]
1[c]	**8e**, *i*-Pr	**9e**, 39	**10e**, 48
2[d]	**8f**, *t*-Bu	**9f**, 0	**10f**, 23

[a] All reactions were carried out with 2 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OTf)_2$ in sparged MeCN at 80 °C. [b] Isolated yield. [c] Substrate **8e** was a *ca.* 5:1 mixture of (*Z*)/(*E*) geometrical isomers. [d] Substrate **8f** was 100% (*E*)-isomer.

diastereomer) and cyclohexene **10e** (48%). In contrast, the *t*-Bu substituted substrate **8f** underwent 6-*endo*-trig cyclization to give the cyclohexene **10f** in 23% yield.[16]

The stereochemistry of **9e** was assigned by ^{1}H NMR NOE experiments and confirmed by single crystal X-ray analysis, and the stereochemistry of the remaining γ-lactones **9** was assigned by analogy with **9e** (Figure 2).[13] The major diastereomer of the γ-lactones **9** had the opposite configuration at the benzylic stereocenter compared with the γ-lactones **7**, with the phenyl group positioned on the concave face of the [3.3.0]-bicyclic system most probably to avoid interaction with the non-hydrogen bridgehead substituent. The ^{1}H NMR chemical shifts for the benzylic protons of the γ-lactones **9** were higher for the major diastereomers compared with the minor diastereomers and followed the same trend as observed with the γ-lactones **7**.

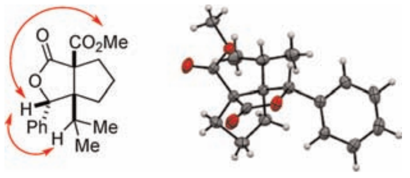
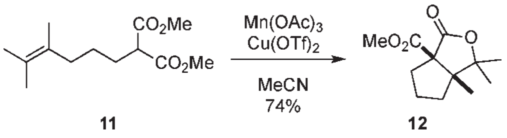


Figure 2. ^{1}H NMR NOE data and single crystal X-ray structure of lactone **9e** determined from single crystal diffraction data (thermal ellipsoids drawn at 50% probability).

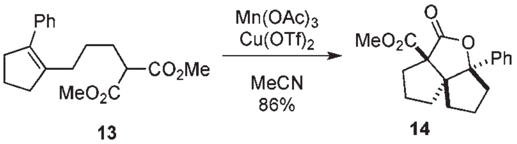
It also proved possible to perform cyclizations on substrates which did not contain an aryl group to stabilize the adduct radical. The fully substituted alkene substrate **11**[9] underwent oxidative radical cyclization to give the [3.3.0]-bicyclic γ-lactone **12** in 74% yield (Scheme 2). In this instance, the adduct radical is stabilized by three alkyl substituents.

Scheme 2. Oxidative Radical Cyclization of Malonate **11**



With these results in hand substrate **13**,[9] which contains an internal tetrasubstituted alkene, was synthesized. Upon exposure to the conditions developed above, tricyclic γ-lactone **14** was formed in good yield as a single diastereomer containing vicinal all-carbon quaternary centers adjacent to a further quaternary stereocenter (Scheme 3); the stereochemistry of **14** was assigned on the basis of ^{1}H NMR NOE experiments.[17]

Scheme 3. Oxidative Radical Cyclization of Tetrasubstituted Alkene **8**



In summary, we have developed a robust methodology for synthesizing highly functionalized and sterically congested [3.3.0]-bicyclic γ-lactones containing vicinal all-carbon quaternary stereocenters from simple linear precursors. Delicate functionalities, such as alkynes and silyl protecting groups, are tolerated under the reaction conditions. We are further investigating this oxidative radical cyclization in the context of natural product synthesis.

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Supporting Information Available. Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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[16] A small amount of the dimer formed from two molecules of **8f** and trace amounts of a product with the molecular mass corresponding to **9f** were also detected.

[17] For a related ionic iodocarbocylization and lactonization to give a compound with adjacent all-carbon quaternary centers, see: Kitagawa, O.; Inoue, T.; Hirano, K.; Taguchi, T. *J. Org. Chem.* **1993**, *58*, 3106–3112.