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Radical Cyclization

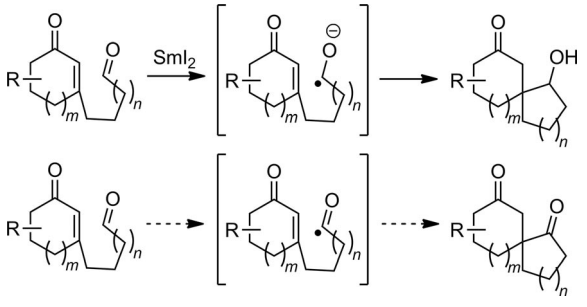
Synthesis of Spiranes by Thiol-Mediated Acyl Radical Cyclization

Day-Shin Hsu,*[a] Chih-Hao Chen,[a] and Chi-Wei Hsu[a]

Abstract: A general and efficient method for the preparation of spiro compounds is described. Various enone-aldehydes were exposed to *t*-dodecanethiol and AIBN at 75 °C in toluene to afford spirocyclic 1,4-diketones in moderate to good yields.

Introduction

Spiro compounds, bicyclic structures fused at single central carbon atoms, are of recent interest due to their interesting conformational features and structural implications in biological systems.[1] The asymmetry usually present in such molecules as a result of the presence of the chiral spiro carbon is one of the important criteria for showing biological activity. Spiro core systems are found in a variety of natural products with a wide range of biological activities.[1,2] Owing to the importance of spiro cores in nature, the development of new and efficient strategies for their construction has become a major focal point for synthetic chemistry. For this reason, there has been great interest in the development of a multitude of methods for their synthesis.[3] Among these, Tu et al. reported enantioselective preparation of spirocyclic 1,4-diketones from various cyclic hydroxy-enones, each containing a substituted cyclobutanol motif, through a semipinacol-type rearrangement.[4] Recently, we developed an intramolecular reductive cyclization of enone-aldehydes by treatment with samarium diiodide to prepare spirocyclic γ-hydroxy ketones (Scheme 1).[5] This strategy has since been successfully applied to the total synthesis of (±)-majusculone.[6] However, most of these intramolecular reductive cyclizations of enone-aldehydes resulted in mixtures of diastereomers.



Scheme 1. Strategies for constructing spiro skeletons.

[a] *Department of Chemistry and Biochemistry, National Chung Cheng University, Minhsiung, Taiwan 621*
E-mail: chedsh@ccu.edu.tw
http://deptche.ccu.edu.tw/faculty/dsh.html

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Moreover, samarium diiodide is an air-sensitive and relatively expensive reagent. These factors prompted us to develop another method for construction of spiro compounds.

In 2005, Tomioka et al. reported thiol-catalyzed acyl radical cyclization of alkenals to give five- and six-membered cyclic ketones.[7] In this strategy, the acyl radical was produced through reaction between an aldehyde and a thiyl radical. Thiyl radicals have found widespread use in organic synthesis for several decades and have proved to be valuable intermediates for the synthesis of natural products.[8] In our ongoing efforts to develop a general and efficient method for the preparation of spiro compounds, here we report another synthesis of spirocyclic 1,4-diketones based on thiol-mediated acyl radical cyclization (Scheme 1).

Results and Discussion

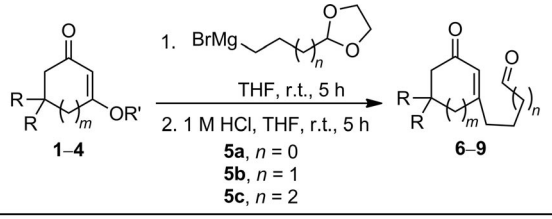
(a) Preparation of Enone-Aldehydes

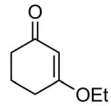
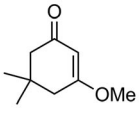
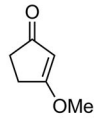
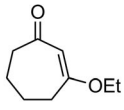
The spirane precursors, enone-aldehydes **6**–**9**, were prepared from 3-alkoxyenones **1**–**4**, which were in turn obtained either commercially or from the corresponding cyclic 1,3-diones by a method reported in the literature.[9] 1,2-Addition of Grignard reagents **5a**–**c**[10] to 3-alkoxyenones **1**–**4** and subsequent treatment of the resulting addition products with an acidic aqueous solution gave enone-aldehydes **6**–**8** in moderate to good yields, with the exception of **9b** (Table 1).

Because of the low yield of **9b**, we designed an alternative synthetic route to compounds **9**, as outlined in Scheme 2. Similarly, treatment of cyclohept-2-en-1-one (**10**) with Grignard reagents **5a**–**c** resulted in 1,2-addition, generating the tertiary allylic alcohols **11**. Oxidative rearrangement of compounds **11** to enones **12** was performed with pyridinium chlorochromate (PCC).[11] Without purification, compounds **12** were hydrolyzed under acidic conditions to give the desired enone-aldehydes **9b** and **9c** in good overall yields. However, cyclohept-2-en-1-one **12a**, with a three-carbon side chain, gave a complex mixture under these conditions. Gratifyingly, though, this problem could be solved by using a mild Lewis acid, $PdCl_2(CH_3CN)_2$,[12] to hydrolyze the acetal, affording the desired enone-aldehyde **9a** in 63 % overall yield.

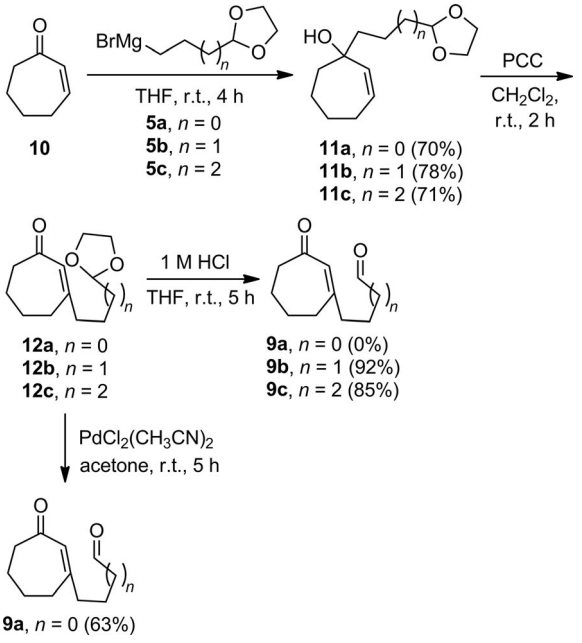
To examine their reactivity, *gem*-dimethylcyclohexenone derivatives **16** and **19** were also prepared (Scheme 3). Compounds

Table 1. Preparation of enone-aldehydes **6**–**9** from 3-alkoxyenones **1**–**4**.



Entry	3-Alkoxyenone	Grignard	Product	Yield (%)
1	 **1**	**5a**	**6a**, *n* = 0	37
2		**5b**	**6b**, *n* = 1	75
3		**5c**	**6c**, *n* = 2	80
4	 **2**	**5a**	**7a**, *n* = 0	40
5		**5b**	**7b**, *n* = 1	63
6		**5c**	**7c**, *n* = 2	57
7	 **3**	**5a**	**8a**, *n* = 0	38
8		**5b**	**8b**, *n* = 1	65
9		**5c**	**8c**, *n* = 2	68
10	 **4**	**5b**	**9b**, *n* = 1	20

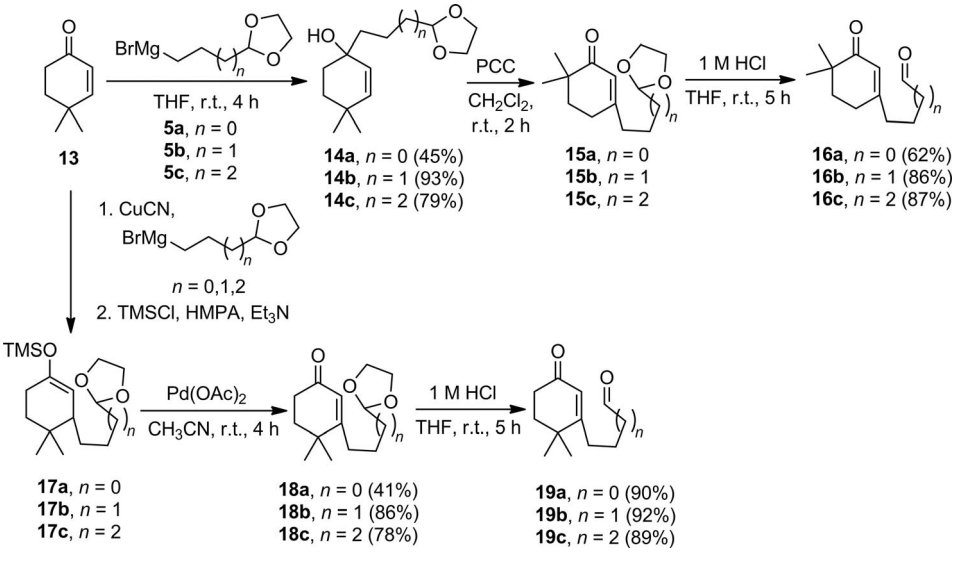
16a–**c** were prepared from 4,4-dimethylcyclohex-2-en-1-one (**13**) by a synthetic pathway similar to that in Scheme 2. 1,2-Addition of Grignard reagents **5a**–**c** to **13** and subsequent oxidation with pyridinium chlorochromate resulted in enones **15**. Acetal hydrolysis under acidic conditions gave 6,6-dimethylcyclohexenones **16a**–**c**. By an alternative route, 4,4-dimethylcyclohexenone derivatives **19** were also prepared from **13**. 1,4-



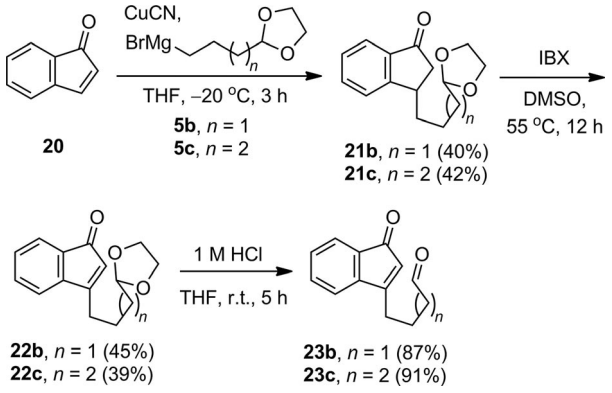
Scheme 2. Preparation of enone-aldehydes **9** from cyclohept-2-en-1-one (**10**).

Addition of Grignard reagents **5a**–**c** to **13** was performed in the presence of copper(I) cyanide, and the resulting enolates were trapped with TMSCl to form silyl enol ethers **17**. These crude products were then subjected to Saegusa oxidation[13] to give cyclohexenones **18a**–**c**. Acidic conditions were again used to hydrolyze the acetals, affording the desired products **19a**–**c** in excellent yields.

In order to extend the scope of the acyl radical cyclization, indenone-aldehydes **23** were also prepared (Scheme 4). Treatment of indenone (**20**)[14] with Grignard reagents **5b**–**c** in the presence of copper(I) cyanide, followed by oxidation with *o*-iodoxybenzoic acid (IBX),[15] afforded enones **22**. Hydrolysis of the acetal moiety with 1 M HCl in THF afforded indenone-aldehydes **23** in good yields.



Scheme 3. Preparation of *gem*-dimethylcyclohexenones from 4,4-dimethylcyclohex-2-en-1-one (**13**).



Scheme 4. Preparation of indenone-aldehydes **23** from indenone (**20**).

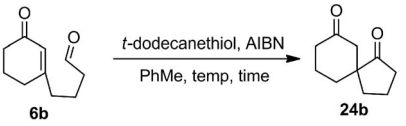
(b) Intramolecular Acyl Radical Cyclization

Having obtained the enone-aldehydes, we first used **6b** to explore the reaction conditions. Acyl radical generation from an aldehyde can be accelerated by thiols, especially tertiary thiols, which give the best yields.[7] Therefore, we first carried out this reaction with 1 equiv. of azoisobutyronitrile (AIBN) in the presence of 0.3 equiv. of *t*-dodecanethiol in toluene at 75 °C. The reaction mixture was stirred at this temperature for 19 h, after which the reaction was still incomplete. An additional 1 equiv. of AIBN was added, and the mixture was stirred at 75 °C for a further 12 h. The desired product **24b** was obtained in 38 % yield. In order to improve the yield further, we increased the amount of *t*-dodecanethiol, finding that 5 equiv. gave the best yield of 71 % (Table 2, Entries 1–7). In the absence of *t*-dodecanethiol, the reaction was found to be sluggish and low-yielding (Entry 8). When the reaction was attempted at higher or lower concentrations, the yields also dropped (Entries 9–10). The best yield was achieved when the reaction was carried out in toluene at reflux, although a large amount of AIBN was required under these conditions (Entry 11). We reasoned that the quantity of AIBN needed to drive the reaction to completion was due to its poor thermal stability at higher temperatures and so tried to improve the yield by replacing AIBN with 1,1′-azobis-(cyclohexanecarbonitrile) (V-40), which is more stable at higher temperatures, but at 75 °C and reflux the reactions were unsuccessful (Entries 12–13). Alternatively, use of a syringe pump to add 1 equiv. of AIBN to the reaction mixture over 7 h, with various amount of *t*-dodecanethiol, either at 75 °C or at reflux, also did not improve yields (Entries 14–23). Although the best yield was observed with 5 equiv. of *t*-dodecanethiol and 7 equiv. of AIBN in toluene at reflux (Entry 11), the amount of AIBN used was considerable. Thus, in subsequent syntheses of other enone-aldehyde substrates, we used 5 equiv. of *t*-dodecanethiol and 2 equiv. of AIBN at 75 °C in toluene (Entry 6).

Other thiols were also tested under the optimized conditions, but the yields were lower (Table 3, Entries 2–5). Tertiary thiols afforded the best yields in the reaction, probably due to their ability to prevent hemithioacetal formation from aldehydes and conjugate addition to the α,β-unsaturated ketone.[7a]

With optimized conditions in hand, other enone-aldehydes were subjected to them. In most cases the desired products were obtained in moderate to good yields (Table 4). Formation of four-membered rings in these substrates was difficult: the desired spiro[3.5]nonane and spiro[3.4]octane skeletons could not be obtained, with only complex mixtures being produced (Entries 1, 4, 7, 10, and 13). However, in the case of the seven-membered-ring enone with a three-carbon side chain, the desired spiro[3.6]decane was obtained in 36 % yield (Entry 16). Spiro[3.5]nonane and spiro[3.4]octane skeletons were not observed, presumably because of ring strain. Substrates with geminal dimethyl systems at the γ-position gave slightly lower yields (Entries 11 and 12). This was probably due to steric hin-

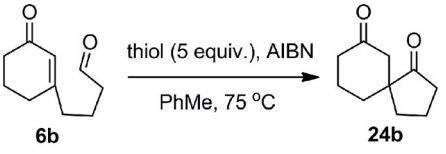
Table 2. Conditions for attempted intramolecular acyl radical cyclization.



Entry	t-$C_{12}H_{25}SH$ (equiv.)	AIBN (equiv.)	Conc. (M)	T (°C)	Time (h)	Yield (%)
1	0.3	1 + 1[a]	0.0150	75	19 + 12	38
2	1	1 + 1[a]	0.0150	75	19 + 12	56
3	2	1 + 1[a]	0.0150	75	19 + 12	67
4	3	1 + 1[a]	0.0150	75	19 + 12	59
5	4	1 + 1[a]	0.0150	75	19 + 12	64
6	5	1 + 1[a]	0.0150	75	19 + 12	71
7	10	1	0.0150	75	19 + 12	55
8	0	1 + 1	0.0150	75	19 + 12	18 (37)[b]
9	5	1 + 1[a]	0.0300	75	19 + 12	34
10	5	1 + 1[a]	0.0075	75	19 + 12	27
11	5	1 + 6[a]	0.0150	reflux	19 + 72	80
12	5	V-40 (1)	0.0150	75	26	–[c]
13	5	V-40 (1)	0.0150	reflux	26	42
14[d]	0.3	1	0.0150	75	7 + 20	38 (76)[b]
15[d]	1	1	0.0150	75	7 + 20	49
16[d]	3	1	0.0150	75	7 + 20	48
17[d]	5	1	0.0150	75	7 + 20	63
18[d]	10	1	0.0150	75	7 + 20	67
19[d]	0.3	1	0.0150	reflux	7 + 20	24 (62)[b]
20[d]	1	1	0.0150	reflux	7 + 20	33
21[d]	3	1	0.0150	reflux	7 + 20	40
22[d]	5	1	0.0150	reflux	7 + 20	53
23[d]	10	1	0.0150	reflux	7 + 20	73

[a] An additional 1 equiv. of AIBN was added to the reaction mixture after 19 h and this addition was repeated every 12 h until enone-aldehyde was completely consumed. [b] Based on recovery of starting material. [c] Recovery of starting material. [d] A solution of AIBN in toluene was added to the reaction mixture over 7 h by syringe pump.

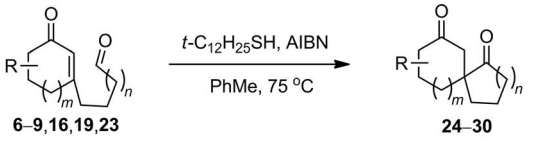
Table 3. Intramolecular acyl radical cyclization in the presence of various thiols.

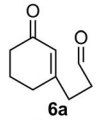
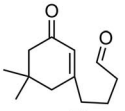
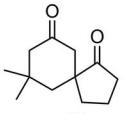
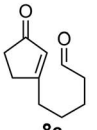
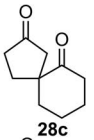
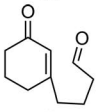
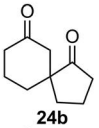
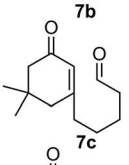
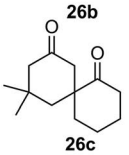
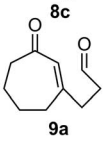
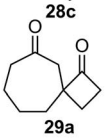
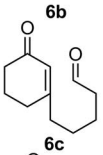
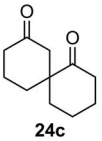
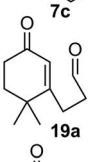
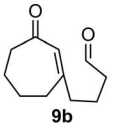
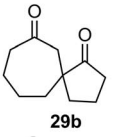
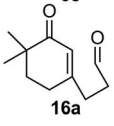
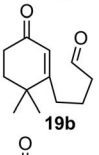
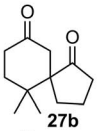
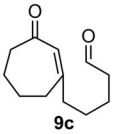
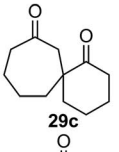
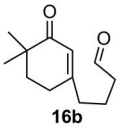
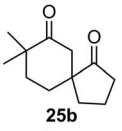
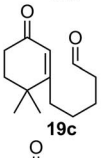
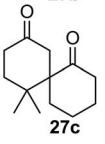
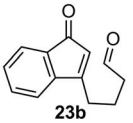
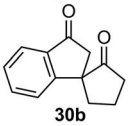
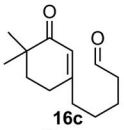
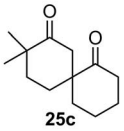
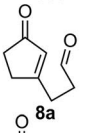
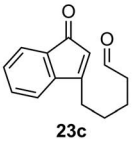
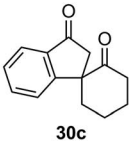
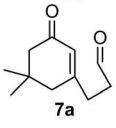
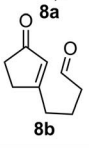
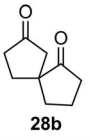


Entry	Thiol	AIBN[a] (equiv.)	Time (h)	Yield (%)
1	*t*-dodecanethiol	1 + 1	19 + 12	71
2	1-decanethiol	1 + 1	19 + 12	40
3	1-undecanethiol	1 + 2	19 + 24	42
4	1-octanethiol	1 + 1	19 + 12	45
5	benzyl mercaptan	1 + 2	19 + 24	36

[a] An additional 1 equiv. of AIBN was added to the reaction mixture after 19 h and this addition was repeated every 12 h until enone-aldehyde was completely consumed.

Table 4. Intramolecular acyl radical cyclization.



Entry	Enone-aldehyde	Product (yield)	Entry	Enone-aldehyde	Product (yield)	Entry	Enone-aldehyde	Product (yield)
1	 6a	– (–)[a]	8	 7b	 26b (64%)	15	 8c	 28c (75%)
2	 6b	 24b (71%)	9	 7c	 26c (71%)	16	 9a	 29a (36%)
3	 6c	 24c (73%)	10	 19a	– (–)[a]	17	 9b	 29b (80%)
4	 16a	– (–)[a]	11	 19b	 27b (55%)	18	 9c	 29c (69%)
5	 16b	 25b (62%)	12	 19c	 27c (53%)	19	 23b	 30b (23%)
6	 16c	 25c (66%)	13	 8a	– (–)[a]	20	 23c	 30c (22%)
7	 7a	– (–)[a]	14	 8b	 28b (78%)			

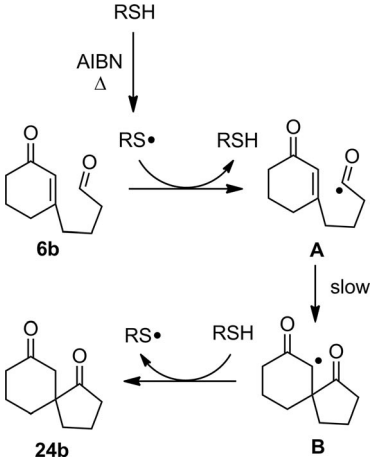
[a] Complex mixtures of products.

drance between the geminal dimethyl system and the acyl radical side chain in the cyclization. In contrast to simple aliphatic enone-aldehydes, indenone-aldehydes gave poor yields under the same conditions (Entries 19 and 20).

The structures of **24**–**30** were characterized by IR, ^{1}H and ^{13}C NMR, and low- and high-resolution mass spectrometry. For spiro compounds containing cyclopentanone rings, carbonyl absorptions were observed around 1740 cm^{-1} in the IR spectra. For **29a**, carbonyl absorption in the four-membered ring was observed at 1780 cm^{-1}.

(c) Reaction Mechanism

A plausible mechanism for the formation of a spirocyclic 1,4-diketone from an enone-aldehyde is depicted in Scheme 5.[16] Firstly, a thiyl radical could be generated by the reaction between the thiol and AIBN. The thiyl radical could then react



Scheme 5. A plausible reaction mechanism.

with **6b** to form acyl radical **A**, with subsequent cyclization to form intermediate **B**. Hydrogen abstraction from thiol could then give the desired product **24b**. Large quantities of reagents are used in this reaction, probably due to the steric hindrance between the β-disubstituted double bond and the acyl radical in cyclization. The generation of the spiro atom by 1,4-addition of the acyl radical to the β-disubstituted enone is slow. Consequently, use of excess reagents helped the reaction to proceed to completion.

Conclusions

In summary, we have developed a general method for the preparation of various all-carbon spirocyclic 1,4-diketones through an acyl radical cyclization. Although intramolecular acyl radical cyclization is well-known, use of this methodology to generate a quaternary carbon center is rare. The ring sizes of the spiro compounds are easily controlled either by using different cyclic enones or by altering the length of the side chain. The application of this efficient method to the preparation of heteroatomic spirocyclic 1,4-diketones and natural product synthesis is currently under investigation.

Experimental Section

General Information: Unless stated otherwise, reagents were obtained from commercial sources and used without further purification. All reactions were performed under nitrogen in anhydrous solvents, which were dried prior to use by standard procedures. Reactions were monitored by thin-layer chromatography with 0.25 mm E. Merck silica gel plates (60F-254) and ethanolic phosphomolybdic acid (7 %) as developing agent. Merck silica gel 60 (particle size 0.04–0.063 mm) was employed for flash chromatography. Melting points are uncorrected. IR spectra were recorded as films on KBr plates. ^{1}H NMR spectra were obtained in $CDCl_3$ unless otherwise noted, at 400 MHz. ^{13}C NMR spectra were obtained at 100 MHz. Chemical shifts are reported in δ (ppm) with the solvent resonance as the internal reference.

General Procedure for Preparation of Enone-Aldehydes: The appropriate 3-alkoxyenone (2.1 mmol) was added at room temperature to a stirred solution of the appropriate Grignard reagent (2.5 mmol) in THF (5 mL). The mixture was stirred at room temperature for another 5 h and then quenched with HCl (1 M, 5 mL) at 0 °C and stirred at room temperature for 5 h. The aqueous layer was extracted with EtOAc. The combined extracts were washed with brine, dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by silica gel chromatography with EtOAc/hexanes as the eluent to furnish the enone-aldehydes **6**–**8** and **9b**.

3-(3-Oxocyclohex-1-enyl)propanal (6a):[17] Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.81 (br. s, 1 H), 5.82 (br. s, 1 H), 2.69 (t, J = 7.4 Hz, 2 H), 2.53 (t, J = 7.4 Hz, 2 H), 2.36 (t, J = 6.0 Hz, 2 H), 2.30 (t, J = 6.0 Hz, 2 H), 2.03–1.98 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.1, 199.4, 163.7, 125.6, 40.7, 37.2, 29.9, 29.6, 22.5 ppm. IR (neat): $\tilde{\nu}$ = 2949, 2825, 2730, 1723, 1665, 1625, 1254, 1193, 890 cm^{-1}. MS (EI): m/z (%) = 152 (45) [M]$^+$, 124 (58), 110 (41), 96 (56), 82 (100), 67 (50). HRMS (EI) calcd. for $C_9H_{12}O_2$ 152.0837; found 152.0839.

4-(3-Oxocyclohex-1-enyl)butanal (6b):[18] Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.66 (t, J = 1.3 Hz, 1 H), 5.75 (t, J = 1.2 Hz, 1 H), 2.40 (t, J = 7.3 Hz, 2 H), 2.26–2.12 (m, 6 H), 1.90–1.85 (m, 2 H), 1.75–1.68 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.4, 199.6, 165.1, 125.6, 42.7, 37.0, 36.8, 29.2, 22.3, 18.9 ppm. IR (neat): $\tilde{\nu}$ = 2941, 2871, 1721, 1665, 1624 cm^{-1}. MS (EI): m/z (%) = 166 (4) [M]$^+$, 138 (21), 123 (22), 110 (70), 95 (12), 82 (100). HRMS (EI) calcd. for $C_{10}H_{14}O_2$ 166.0994; found 166.0999.

5-(3-Oxocyclohex-1-enyl)pentanal (6c): Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.75 (m, 1 H), 5.84 (br. s, 1 H), 2.46 (t, J = 7.2 Hz, 2 H), 2.36–2.21 (m, 6 H), 2.00–1.94 (m, 2 H), 1.65–1.59 (m, 2 H), 1.56–1.48 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.1, 200.0, 165.8, 126.0, 43.7, 37.9, 37.5, 29.8, 26.5, 22.9, 21.7 ppm. IR (neat): $\tilde{\nu}$ = 2943, 2868, 2726, 1721, 1659, 1414 cm^{-1}. MS (EI): m/z (%) = 180 (2) [M]$^+$, 152 (21), 123 (75), 110 (53), 95 (56), 82 (100). HRMS (EI) calcd. for $C_{11}H_{16}O_2$ 180.1150; found 180.1152.

3-(5,5-Dimethyl-3-oxocyclohex-1-enyl)propanal (7a):[19] Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.78 (br. s, 1 H), 5.81 (s, 1 H), 2.67 (t, J = 7.3 Hz, 2 H), 2.48 (t, J = 7.3 Hz, 2 H), 2.19 (s, 2 H), 2.17 (s, 2 H), 1.01 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.1, 199.6, 161.3, 124.5, 50.9, 44.1, 40.6, 33.5, 29.6, 28.1 ppm. IR (neat): $\tilde{\nu}$ = 2958, 2869, 2818, 2721, 1723, 1665, 1360, 1299, 1280, 1248, 1196, 1138, 902 cm^{-1}. MS (EI): m/z (%) = 180 (2) [M]$^+$, 101 (12), 83 (13), 73 (12), 59 (47), 58 (100), 57 (12). HRMS (EI) calcd. for $C_{11}H_{16}O_2$ 180.1150; found 180.1153.

4-(5,5-Dimethyl-3-oxocyclohex-1-enyl)butanal (7b): Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.78 (br. s, 1 H), 5.86 (br. s, 1 H), 2.49 (t, J = 7.2 Hz, 2 H), 2.22–2.17 (m, 2 H), 2.21 (s, 2 H), 2.16 (s, 2 H), 1.86–1.79 (m, 2 H), 1.02 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.3, 199.8, 162.4, 125.0, 51.0, 43.8, 43.0, 37.0, 33.6, 28.2, 19.1 ppm. IR (neat): $\tilde{\nu}$ = 2956, 2870, 2723, 1723, 1666, 1628, 1596, 1369, 1247, 903 cm^{-1}. MS (EI): m/z (%) = 194 (5) [M]$^+$, 177 (22), 151 (33), 138 (21), 125 (21), 112 (56), 97 (28), 83 (100). HRMS (EI) calcd. for $C_{12}H_{18}O_2$ 194.1307; found 194.1311.

5-(5,5-Dimethyl-3-oxocyclohex-1-enyl)pentanal (7c): Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.76 (t, J = 1.4 Hz, 1 H), 5.86 (br. s, 1 H), 2.47 (dt, J = 7.2, 1.4 Hz, 2 H), 2.22–2.17 (m, 2 H), 2.20 (s, 2 H), 2.16 (s, 2 H), 1.66–1.62 (m, 2 H), 1.54–1.50 (m, 2 H), 1.02 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.9, 200.0, 163.1, 124.8, 51.0, 43.8, 43.5, 37.7, 33.6, 28.2, 26.2, 21.6 ppm. IR (neat): $\tilde{\nu}$ = 2941, 2869, 2729, 1723, 1664, 1194 cm^{-1}. MS (EI): m/z (%) = 208 (3) [M]$^+$, 191 (20), 165 (19), 151 (100), 138 (18), 121 (17), 109 (19), 95 (28), 82 (74). HRMS (EI) calcd. for $C_{13}H_{20}O_2$ 208.1463; found 208.1462.

3-(3-Oxocyclopent-1-enyl)propanal (8a): Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.79 (br. s, 1 H), 5.87 (s, 1 H), 2.77 (t, J = 6.9 Hz, 2 H), 2.68 (t, J = 6.9 Hz, 2 H), 2.57 (t, J = 3.7 Hz, 2 H), 2.38–2.35 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.5, 199.9, 180.3, 129.4, 40.8, 35.1, 31.6, 25.4 ppm. IR (neat): $\tilde{\nu}$ = 2923, 2842, 2726, 1705, 1675, 1612, 1439, 1280, 1191, 1112, 1051 cm^{-1}. MS (EI): m/z (%) = 138 (3) [M]$^+$, 110 (100), 109 (21), 81 (46), 67 (30), 53 (27). HRMS (EI) calcd. for $C_8H_{10}O_2$ 138.0681; found 138.0681.

4-(3-Oxocyclopent-1-enyl)butanal (8b): Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.79 (br. s, 1 H), 5.95 (t, J = 1.3 Hz, 1 H), 2.58–2.54 (m, 2 H), 2.53 (t, J = 7.2 Hz, 2 H), 2.45–2.39 (m, 4 H), 1.95–1.89 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.7, 201.2, 181.2, 129.8, 43.1, 35.2, 32.6, 31.4, 19.3 ppm. IR (neat): $\tilde{\nu}$ = 2925, 2729, 1704, 1673, 1613, 1186, 842 cm^{-1}. MS (EI): m/z (%) = 152 (5) [M]$^+$, 150 (12), 138 (48), 124 (34), 109 (100), 96 (92), 81 (60), 67 (54), 55 (91). HRMS (EI) calcd. for $C_9H_{12}O_2$ 152.0837; found 152.0843.

5-(3-Oxocyclopent-1-enyl)pentanal (8c): Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.79 (t, J = 1.4 Hz, 1 H), 5.96 (br. s, 1 H), 2.59–2.57 (m, 2 H), 2.50 (dt, J = 6.3, 1.4 Hz, 2 H), 2.43–2.39 (m, 4 H), 1.69–1.64 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.9, 201.8,

181.9, 129.6, 43.5, 35.3, 33.2, 31.5, 26.5, 21.7 ppm. IR (neat): $\tilde{\nu}$ = 2930, 1727, 1657, 1600, 1408, 1281, 1180 cm^{-1}. MS (EI): *m/z* (%) = 166 (0.8) $[M]^+$, 148 (3), 138 (23), 122 (11), 109 (100), 96 (62), 81 (28). HRMS (EI) calcd. for $C_{10}H_{14}O_2$ 166.0994; found 166.0986.

4-(3-Oxocyclohept-1-enyl)butanal (9b): Yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.78 (br. s, 1 H), 5.90 (br. s, 1 H), 2.58 (t, *J* = 6.2 Hz, 2 H), 2.49 (t, *J* = 7.5 Hz, 2 H), 2.41 (t, *J* = 5.8 Hz, 2 H), 2.22 (t, *J* = 7.5 Hz, 2 H), 1.85–1.58 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.9, 201.5, 160.5, 129.8, 43.1, 42.2, 40.1, 32.5, 25.1, 21.2, 19.8 ppm. IR (neat): $\tilde{\nu}$ = 2936, 2867, 2724, 1722, 1658, 1451, 1267 cm^{-1}. MS (EI): *m/z* (%) = 180 (24) $[M]^+$, 152 (19), 137 (19), 124 (34), 109 (51), 98 (100), 81 (64), 55 (76). HRMS (EI) calcd. for $C_{11}H_{16}O_2$ 180.1150; found 180.1158.

General Procedure for 1,2-Addition of Grignard Reagents: The appropriate cyclic enone (1.8 mmol) was added at room temperature to a stirred solution of the appropriate Grignard reagent (2.5 mmol) in THF (5 mL). The mixture was stirred at room temperature for 4 h and then quenched with water and extracted with EtOAc. The combined extracts were washed with brine, dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by silica gel chromatography with EtOAc/hexanes as the eluent to furnish adducts **11** or **14**.

1-[2-(1,3-Dioxolan-2-yl)ethyl]cyclohept-2-enol (11a): Yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.72–5.66 (m, 1 H), 5.59 (d, *J* = 11.9 Hz, 1 H), 4.89 (t, *J* = 4.3 Hz, 1 H), 3.99–3.83 (m, 4 H), 2.17–2.02 (m, 3 H), 1.85–1.58 (m, 10 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.9, 129.8, 104.6, 75.3, 64.8, 38.6, 34.5, 27.9, 27.5, 27.3, 24.1 ppm. IR (neat): $\tilde{\nu}$ = 3453, 2927, 2862, 1450, 1408, 1140, 1103, 1035, 956, 939, 796, 751, 691 cm^{-1}. MS (EI): *m/z* (%) = 212 (2) $[M]^+$, 111 (46), 99 (60), 93 (34), 79 (39), 73 (100). HRMS (EI) calcd. for $C_{12}H_{20}O_3$ 212.1412; found 212.1414.

1-[3-(1,3-Dioxolan-2-yl)propyl]cyclohept-2-enol (11b): Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.70 (dt, *J* = 12.0, 5.8 Hz, 1 H), 5.59 (d, *J* = 12.0 Hz, 1 H), 4.86 (t, *J* = 4.7 Hz, 1 H), 3.94–3.82 (m, 4 H), 2.20–2.01 (m, 2 H), 1.85–1.53 (m, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.9, 130.2, 104.6, 76.0, 64.8, 41.2, 38.5, 34.3, 27.6, 27.4, 24.0, 18.1 ppm. IR (neat): $\tilde{\nu}$ = 3465, 2925, 2878, 1454, 1409, 1141, 1104, 1045, 941 cm^{-1}. MS (EI): *m/z* (%) = 226 (0.3) $[M]^+$, 164 (4), 136 (4), 111 (100), 88 (23), 73 (76). HRMS (EI) calcd. for $C_{13}H_{22}O_3$ 226.1569; found 226.1571.

1-[4-(1,3-Dioxolan-2-yl)butyl]cyclohept-2-enol (11c): Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.67 (dt, *J* = 12.0, 5.7 Hz, 1 H), 5.58 (d, *J* = 12.0 Hz, 1 H), 4.84 (t, *J* = 4.8 Hz, 1 H), 3.97–3.82 (m, 4 H), 2.23–2.03 (m, 2 H), 1.74–1.44 (m, 12 H), 1.43–1.41 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.0, 130.0, 104.6, 76.0, 64.8, 41.2, 38.6, 33.8, 27.6, 27.4, 24.6, 24.1, 23.4 ppm. IR (neat): $\tilde{\nu}$ = 3482, 2926, 2860, 1456, 1407, 1140, 1032, 944 cm^{-1}. MS (EI): *m/z* (%) = 240 (2) $[M]^+$, 239 (8), 178 (3), 155 (17), 111 (17), 99 (20), 73 (100). HRMS (EI) calcd. for $C_{14}H_{24}O_3$ 240.1725; found 240.1725.

1-[2-(1,3-Dioxolan-2-yl)ethyl]-4,4-dimethylcyclohex-2-enol (14a): Yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.46 (d, *J* = 10.0 Hz, 1 H), 5.42 (d, *J* = 10.0 Hz, 1 H), 4.86 (t, *J* = 4.5 Hz, 1 H), 3.96–3.81 (m, 4 H), 2.02 (br. s, 1 H), 1.79–1.54 (m, 6 H), 1.43–1.39 (m, 1 H), 0.98 (s, 3 H), 0.91 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.0, 129.8, 104.6, 69.0, 64.8, 35.7, 33.5, 32.5, 31.9, 29.8, 28.0, 27.7 ppm. IR (neat): $\tilde{\nu}$ = 3460, 2951, 2871, 1460, 1405, 1235, 1202, 1140, 1030 cm^{-1}. MS (EI): *m/z* (%) = 226 (1) $[M]^+$, 209 (30), 125 (100), 73 (27), 59 (40), 58 (25). HRMS (EI) calcd. for $C_{13}H_{22}O_3$ 226.1569; found 226.1570.

1-[3-(1,3-Dioxolan-2-yl)propyl]-4,4-dimethylcyclohex-2-enol (14b): Yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.50 (d, *J* = 10.0 Hz, 1 H), 5.45 (d, *J* = 10.0 Hz, 1 H), 4.86 (t, *J* = 4.7 Hz, 1 H), 3.98–3.84 (m, 4 H), 1.68–1.47 (m, 10 H), 1.01 (s, 3 H), 0.94 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.9, 129.9, 104.4, 69.6, 64.7, 41.8, 34.2, 33.5, 32.3, 31.8, 29.8, 27.7, 18.2 ppm. IR (neat): $\tilde{\nu}$ = 3450, 2951, 2871, 1204, 1139, 1051, 1027, 938, 905, 793 cm^{-1}. MS (EI): *m/z* (%) = 240 (2) $[M]^+$, 223 (48), 126 (34), 125 (100), 88 (41), 73 (92), 59 (29), 58 (38). HRMS (EI) calcd. for $C_{14}H_{24}O_3$ 240.1725; found 240.1725.

1-[4-(1,3-Dioxolan-2-yl)butyl]-4,4-dimethylcyclohex-2-enol (14c): Yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.42 (d, *J* = 10.0 Hz, 1 H), 5.38 (d, *J* = 10.0 Hz, 1 H), 4.79 (t, *J* = 4.7 Hz, 1 H), 3.92–3.76 (m, 4 H), 1.80 (br. s, 1 H), 1.71–1.31 (m, 12 H), 0.95 (s, 3 H), 0.89 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.7, 130.1, 104.4, 69.5, 64.7, 41.9, 33.7, 33.5, 32.3, 31.8, 29.8, 27.7, 24.5, 23.4 ppm. IR (neat): $\tilde{\nu}$ = 3458, 2947, 2865, 1464, 1408, 1361, 1228, 1140, 1032, 945, 906, 853, 772 cm^{-1}. MS (EI): *m/z* (%) = 254 (3) $[M]^+$, 148 (58), 125 (42), 99 (38), 73 (75), 59 (43), 58 (100). HRMS (EI) calcd. for $C_{15}H_{26}O_3$ 254.1882; found 254.1881.

3-(3-Oxocyclohept-1-enyl)propanal (9a): Compound **11a** (300 mg, 1.41 mmol) was added at room temperature to a stirred mixture of PCC (609 mmg, 2.82 mmol) and celite (1.22 g) in CH_2Cl_2 (10 mL). After having been stirred at room temperature for 2 h, the reaction mixture was diluted with Et_2O (20 mL) and filtered through a pad of celite. The filtrate was concentrated, the crude product was dissolved in acetone (114 mL), and $PdCl_2(CH_3CN)_2$ (36.6 mg, 0.14 mmol) was added. The mixture was stirred at room temperature for 5 h and then filtered through a pad of celite. The filtrate was concentrated, and the crude product was dissolved in water and extracted with CH_2Cl_2. The combined extracts were washed with brine, dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by silica gel chromatography (EtOAc/hexanes 1:2) to furnish **9a** (148 mg, 63 %) as a yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.80 (br. s, 1 H), 5.87 (s, 1 H), 2.66 (t, *J* = 7.3 Hz, 2 H), 2.57 (t, *J* = 6.2 Hz, 2 H), 2.53 (t, *J* = 7.3 Hz, 2 H), 2.43 (t, *J* = 6.2 Hz, 2 H), 1.82–1.77 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.7, 200.4, 159.3, 129.1, 42.0, 41.3, 32.7, 32.4, 24.9, 21.0 ppm. IR (neat): $\tilde{\nu}$ = 2934, 2866, 2728, 1723, 1653, 1452, 1418, 1344, 1267, 1183, 1056, 879 cm^{-1}. MS (EI): *m/z* (%) = 166 (10) $[M]^+$, 167 (100), 124 (76), 111 (57), 98 (75), 81 (53), 55 (66). HRMS (EI) calcd. for $C_{10}H_{14}O_2$ 166.0994; found 166.0992.

General Procedure for PCC Oxidation and Acetal Hydrolysis: The appropriate compound **11** or **14** (2.20 mmol) was added at room temperature to a stirred mixture of PCC (4.40 mmol) and celite (2.0 g) in CH_2Cl_2 (20 mL). After having been stirred at room temperature for 2 h, the reaction mixture was diluted with Et_2O (20 mL) and filtered through a pad of celite. The filtrate was concentrated, the crude product was dissolved in THF (20 mL), and HCl (1 M, 20 mL) was added. The mixture was stirred at room temperature for 4 h. The aqueous layer was extracted with EtOAc. The combined extracts were washed with brine, dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by silica gel chromatography with EtOAc/hexanes as the eluent to furnish the enone-aldehydes **9** or **16**.

5-(3-Oxocyclohept-1-enyl)pentanal (9c): Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.76 (t, *J* = 1.4 Hz, 1 H), 5.89 (br. s, 1 H), 2.56 (t, *J* = 5.8 Hz, 2 H), 2.46 (dt, *J* = 7.2, 1.4 Hz, 2 H), 2.39 (t, *J* = 5.8 Hz, 2 H), 2.20 (t, *J* = 7.3 Hz, 2 H), 1.79–1.77 (m, 4 H), 1.65–1.59 (m, 2 H), 1.55–1.49 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.0, 202.0, 161.3, 129.4, 43.5, 42.1, 40.6, 32.5, 27.0, 25.1, 21.6, 21.2 ppm. IR (neat): $\tilde{\nu}$ = 2936, 2865, 2722, 1724, 1656, 1458, 1266 cm^{-1}. MS (EI): *m/z* (%) = 194 (18) $[M]^+$, 166 (12), 150 (16), 137 (41), 124 (38), 109

(100), 98 (38), 81 (52), 67 (49). HRMS (EI) calcd. for $C_{12}H_{18}O_2$ 194.1307; found 194.1306.

3-(4,4-Dimethyl-3-oxocyclohex-1-enyl)propanal (16a): Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.82 (br. s, 1 H), 5.74 (t, J = 1.3 Hz, 1 H), 2.70 (t, J = 7.2 Hz, 2 H), 2.52 (t, J = 7.2 Hz, 2 H), 2.33 (t, J = 5.9 Hz, 2 H), 1.82 (t, J = 5.9 Hz, 2 H), 1.09 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.3, 200.3, 161.4, 124.1, 40.8, 40.4, 36.2, 29.2, 27.3, 24.1 ppm. IR (neat): $\tilde{\nu}$ = 2964, 2924, 2726, 1722, 1665, 1460, 1378, 1310, 1217, 1166, 881 cm^{-1}. MS (EI): m/z (%) = 180 (5) $[M]^+$, 140 (87), 112 (100), 96 (34), 95 (41), 82 (31). HRMS (EI) calcd. for $C_{11}H_{16}O_2$ 180.1150; found 180.1147.

4-(4,4-Dimethyl-3-oxocyclohex-1-enyl)butanal (16b): Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.77 (t, J = 1.3 Hz, 1 H), 5.75 (t, J = 1.2 Hz, 1 H), 2.48 (dt, J = 7.5, 1.3 Hz, 2 H), 2.29 (t, J = 5.6 Hz, 2 H), 2.21 (t, J = 7.6 Hz, 2 H), 1.86–1.78 (m, 4 H), 1.08 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.4, 201.4, 162.5, 124.4, 42.9 40.3, 36.6, 36.1, 26.8, 24.0, 19.1 ppm. IR (neat): $\tilde{\nu}$ = 2958, 2926, 2871, 2722, 1723, 1667, 1453, 1381, 1310, 1209, 1166, 1122, 877 cm^{-1}. MS (EI): m/z (%) = 194 (27) $[M]^+$, 110 (38), 97 (59), 95 (35), 82 (100), 69 (35), 67 (35). HRMS (EI) calcd. for $C_{12}H_{18}O_2$ 194.1307; found 194.1307.

5-(4,4-Dimethyl-3-oxocyclohex-1-enyl)pentanal (16c): Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.75 (t, J = 1.4 Hz, 1 H), 5.74 (s, 1 H), 2.46 (dt, J = 7.0, 1.4 Hz, 2 H), 2.28 (t, J = 6.0 Hz, 2 H), 2.19 (t, J = 7.4 Hz, 2 H), 1.79 (t, J = 6.1 Hz, 2 H), 1.66–1.48 (m, 4 H), 1.07 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.5, 201.9, 163.2, 124.2, 43.4, 40.3, 37.2, 36.2, 26.9, 26.3, 24.1, 21.5 ppm. IR (neat): $\tilde{\nu}$ = 2927, 2865, 2720, 1721, 1667, 1454, 1423, 1382, 1311, 1212, 1167, 1123, 790 cm^{-1}. MS (EI): m/z (%) = 208 (3) $[M]^+$, 101 (36), 82 (100), 69 (43), 67 (36), 59 (60), 55 (32). HRMS (EI) calcd. for $C_{13}H_{20}O_2$ 208.1463; found 208.1461.

General Procedure for 1,4-Addition and Saegusa Oxidation: A solution of Grignard reagent (4.0 mmol) in THF (8 mL) was added at –20 °C under Ar to a suspension of copper(I) cyanide (0.8 mmol) in THF (1 mL). After the mixture had been stirred at –20 °C for 40 min, HMPA (4.0 mmol) was added, and the mixture was stirred for another 10 min. TMSCl (8.0 mmol) and 4,4-dimethylcyclohex-2-en-1-one (**13**, 2.0 mmol) were added, the mixture was stirred at –20 °C for 30 min, Et_3N (8.0 mmol) was then added, and the mixture was stirred at –20 °C for 2 h, quenched with saturated aqueous $NaHCO_3$, and extracted with EtOAc. The combined extracts were washed with brine, dried with $MgSO_4$, filtered, and concentrated to give the crude product. The crude product was then dissolved in CH_3CN (14 mL), and $Pd(OAc)_2$ (2.4 mmol) was added to the solution. The mixture was stirred at room temperature for 4 h, filtered through a pad of celite, and washed with EtOAc. The filtrate was concentrated to give the residue and purified by silica gel chromatography with EtOAc/hexanes as the eluent to furnish cyclohex-2-en-1-ones **18**.

3-[2-(1,3-Dioxolan-2-yl)ethyl]-4,4-dimethylcyclohex-2-en-1-one (18a): Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.70 (s, 1 H), 4.84 (t, J = 4.6 Hz, 1 H), 3.91–3.77 (m, 4 H), 2.36 (t, J = 6.9 Hz, 2 H), 2.27 (t, J = 8.1 Hz, 2 H), 1.80–1.73 (m, 4 H), 1.11 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.2, 171.6, 124.0, 103.4, 64.8, 37.7, 35.6, 34.1, 31.4, 26.2, 25.7 ppm. IR (neat): $\tilde{\nu}$ = 2958, 2885, 1670, 1613, 1473, 1419, 1330, 1277, 1242, 1201, 1141, 1028, 945, 902 cm^{-1}. MS (EI): m/z (%) = 224 (1) $[M]^+$, 99 (15), 86 (57), 73 (64), 59 (26), 58 (100). HRMS (EI) calcd. for $C_{13}H_{20}O_3$ 224.1412; found 224.1412.

3-[3-(1,3-Dioxolan-2-yl)propyl]-4,4-dimethylcyclohex-2-en-1-one (18b): Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.76 (s, 1 H), 4.84 (t, J = 4.3 Hz, 1 H), 3.94–3.80 (m, 4 H), 2.39 (t, J = 6.6 Hz, 2 H), 2.21 (t, J = 7.6 Hz, 2 H), 1.81 (t, J = 6.8 Hz, 2 H), 1.68–1.57 (m, 4 H), 1.13 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.4, 172.1, 124.3, 104.0, 64.8, 37.8, 35.5, 34.2, 33.3, 31.6, 26.3, 21.5 ppm. IR (neat): $\tilde{\nu}$ = 2958, 2926, 2873, 1732, 1667, 1612, 1466, 1415, 1275, 1242, 1139, 1031, 945, 865 cm^{-1}. MS (EI): m/z (%) = 238 (6) $[M]^+$, 138 (20), 112 (18), 99 (39), 73 (100). HRMS (EI) calcd. for $C_{14}H_{22}O_3$ 238.1569; found 238.1566.

3-[4-(1,3-Dioxolan-2-yl)butyl]-4,4-dimethylcyclohex-2-en-1-one (18c): Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.78 (s, 1 H), 4.85 (t, J = 4.7 Hz, 1 H), 3.96–3.83 (m, 4 H), 2.43 (t, J = 6.7 Hz, 2 H), 2.20 (t, J = 7.1 Hz, 2 H), 1.84 (t, J = 6.8 Hz, 2 H), 1.71–1.66 (m, 2 H), 1.62–1.45 (m, 4 H), 1.15 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.4, 172.4, 124.2, 104.3, 64.8, 37.8, 35.5, 34.2, 33.5, 31.7, 27.3, 26.3, 23.8 ppm. IR (neat): $\tilde{\nu}$ = 2943, 2871, 1731, 1663, 1466, 1418, 1242, 1197, 1030, 947 cm^{-1}. MS (EI): m/z (%) = 252 (2) $[M]^+$, 151 (59), 124 (51), 109 (29), 99 (26), 95 (25), 73 (100). HRMS (EI) calcd. for $C_{15}H_{24}O_3$ 252.1725; found 252.1724.

General Procedure for Acetal Hydrolysis: HCl (1 M, 10 mL) was added to a stirred solution of the appropriate acetal (0.6 mmol) in THF (10 mL). The mixture was stirred at room temperature for 5 h. The aqueous layer was extracted with EtOAc. The combined extracts were washed with saturated aqueous $NaHCO_3$ and brine, dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by silica gel chromatography with EtOAc/hexanes as the eluent to furnish the enone-aldehydes **19** or **23**.

3-(6,6-Dimethyl-3-oxocyclohex-1-enyl)propanal (19a): Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.76 (br. s, 1 H), 5.61 (s, 1 H), 2.64 (t, J = 7.2 Hz, 2 H), 2.49 (t, J = 7.2 Hz, 2 H), 2.37 (t, J = 6.8 Hz, 2 H), 1.80 (t, J = 6.8 Hz, 2 H), 1.14 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.3, 199.1, 170.2, 123.9, 40.8, 37.6, 35.6, 34.0, 26.2, 23.6 ppm. IR (neat): $\tilde{\nu}$ = 2961, 2927, 2873, 2723, 1716, 1665, 1613, 1120, 1164, 1115, 1056, 991, 787 cm^{-1}. MS (EI): m/z (%) = 180 (25) $[M]^+$, 142 (70), 124 (47), 95 (63), 85 (73), 71 (62), 58 (100). HRMS (EI) calcd. for $C_{11}H_{16}O_2$ 180.1150; found 180.1153.

4-(6,6-Dimethyl-3-oxocyclohex-1-enyl)butanal (19b): Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.78 (t, J = 1.2 Hz, 1 H), 5.78 (s, 1 H), 2.52 (t, J = 7.0 Hz, 2 H), 2.44 (dt, J = 6.9, 1.2 Hz, 2 H), 2.23 (t, J = 7.7 Hz, 2 H), 1.87–1.81 (m, 4 H), 1.16 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.5, 199.4, 171.3, 124.5, 43.2, 37.8, 35.6, 34.2, 31.0, 26.4, 19.7 ppm. IR (neat): $\tilde{\nu}$ = 2963, 2873, 2726, 1716, 1658, 1469, 1413, 1279, 1243, 1200, 1164 cm^{-1}. MS (EI): m/z (%) = 194 (14) $[M]^+$, 140 (16), 138 (23), 97 (31), 58 (100). HRMS (EI) calcd. for $C_{12}H_{18}O_2$ 194.1307; found 194.1304.

5-(6,6-Dimethyl-3-oxocyclohex-1-enyl)pentanal (19c): Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.74 (t, J = 1.4 Hz, 1 H), 5.73 (s, 1 H), 2.45 (dt, J = 7.1, 1.4 Hz, 2 H), 2.40 (t, J = 6.6 Hz, 2 H), 2.19 (t, J = 7.6 Hz, 2 H), 1.81 (t, J = 6.6 Hz, 2 H), 1.67–1.61 (m, 2 H), 1.51–1.47 (m, 2 H), 1.13 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.0, 199.5, 172.0, 124.2, 43.6, 37.8, 35.6, 34.1, 31.5, 26.8, 26.3, 21.7 ppm. IR (neat): $\tilde{\nu}$ = 2940, 2869, 2722, 1725, 1667, 1612, 1467, 1415, 1243, 1198 cm^{-1}. MS (EI): m/z (%) = 208 (8) $[M]^+$, 109 (31), 69 (34), 67 (33), 58 (100). HRMS (EI) calcd. for $C_{13}H_{20}O_2$ 208.1463; found 208.1462.

4-(1-Oxo-1*H*-inden-3-yl)butanal (23b): Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.82 (br. s, 1 H), 7.40 (d, J = 7.2 Hz, 1 H), 7.36 (dd, J = 7.2, 7.2 Hz, 1 H), 7.24 (dd, J = 7.2, 7.2 Hz, 1 H), 7.12 (d, J = 7.2 Hz, 1 H), 5.68 (s, 1 H), 2.63–2.57 (m, 4 H), 2.06–2.01 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.3, 197.5, 165.2, 144.8, 133.1, 131.3, 129.1, 122.4, 121.8, 119.5, 43.0, 27.4, 19.0 ppm. IR (neat): $\tilde{\nu}$ = 2925, 2732, 1706, 1604, 1574, 1454, 1389, 1279, 1191, 1082 cm^{-1}. MS (EI): m/z (%) = 200 (34) $[M]^+$, 145 (31), 144 (100), 128 (55), 116

(35), 115 (61). HRMS (EI) calcd. for $C_{13}H_{12}O_2$ 200.0837; found 200.0837.

5-(1-Oxo-1*H*-inden-3-yl)pentanal (23c): Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.79 (br. s, 1 H), 7.41 (d, J = 7.2 Hz, 1 H), 7.37 (dd, J = 7.2, 7.2 Hz, 1 H), 7.25 (dd, J = 7.2, 7.2 Hz, 1 H), 7.10 (d, J = 7.2 Hz, 1 H), 5.68 (s, 1 H), 2.58 (t, J = 6.6 Hz, 2 H), 2.53 (t, J = 6.5 Hz, 2 H), 1.80–1.65 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.9, 197.7, 165.8, 145.1, 133.1, 131.5, 129.2, 122.4, 121.9, 119.4, 43.5, 28.1, 26.2, 21.8 ppm. IR (neat): $\tilde{\nu}$ = 2937, 2869, 2723, 1707, 1606, 1573, 1454, 1385, 1275, 1188, 1179, 834 cm^{-1}. MS (EI): m/z (%) = 214 (19) $[M]^+$, 170 (89), 157 (50), 144 (100), 115 (67), 58 (74). HRMS (EI) calcd. for $C_{14}H_{14}O_2$ 214.0994; found 214.0995.

General Procedure for 1,4-Addition to Indenone: A solution of Grignard reagent (5.7 mmol) in THF (8 mL) was added at –20 °C under Ar to a suspension of copper(I) cyanide (1.5 mmol) in THF (3 mL). After the mixture had been stirred at –20 °C for 40 min, indenone (**20**, 3.8 mmol) was added, and the mixture was stirred for another 3 h. The mixture was quenched with water and extracted with Et_2O. The combined extracts were washed with brine, dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by silica gel chromatography with EtOAc/hexanes as the eluent to furnish the enone-aldehydes **21**.

3-[3-(1,3-Dioxolan-2-yl)propyl]-2,3-dihydro-1*H*-inden-1-one (21b): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, J = 7.4 Hz, 1 H), 7.58 (dd, J = 7.4, 7.4 Hz, 1 H), 7.49 (d, J = 7.4 Hz, 1 H), 7.35 (dd, J = 7.4, 7.4 Hz, 1 H), 4.84 (t, J = 4.7 Hz, 1 H), 3.96–3.81 (m, 4 H), 3.40–3.30 (m, 1 H), 2.84 (dd, J = 19.0, 7.4 Hz, 1 H), 2.35 (dd, J = 19.0, 3.4 Hz, 1 H), 1.99–1.92 (m, 1 H), 1.72–1.51 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.3, 158.6, 136.6, 134.6, 127.4, 125.5, 123.5, 104.2, 64.8, 64.7, 42.9, 38.2, 35.9, 33.7, 22.0 ppm. IR (neat): $\tilde{\nu}$ = 2923, 2880, 1713, 1604, 1462, 1406, 1281, 1137, 1045, 761 cm^{-1}. MS (EI): m/z (%) = 246 (8) $[M]^+$, 185 (8), 184 (39), 131 (12), 73 (100). HRMS (EI) calcd. for $C_{15}H_{18}O_3$ 246.1256; found 246.1257.

3-[4-(1,3-Dioxolan-2-yl)butyl]-2,3-dihydro-1*H*-inden-1-one (21c): Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, J = 7.6 Hz, 1 H), 7.58 (dd, J = 7.6, 7.6 Hz, 1 H), 7.48 (d, J = 7.6 Hz, 1 H), 7.33 (dd, J = 7.6, 7.6 Hz, 1 H), 4.82 (t, J = 4.7 Hz, 1 H), 3.96–3.80 (m, 4 H), 3.40–3.30 (m, 1 H), 2.83 (dd, J = 19.0, 7.5 Hz, 1 H), 2.33 (dd, J = 19.0, 3.2 Hz, 1 H), 1.85–1.95 (m, 1 H), 1.70–1.60 (m, 2 H), 1.49–1.30 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.4, 158.8, 136.7, 134.6, 127.4, 125.5, 123.5, 104.3, 64.8, 43.0, 38.1, 35.9, 33.6, 27.4, 24.0 ppm. IR (neat): $\tilde{\nu}$ = 2929, 2861, 1712, 1605, 1463, 1408, 1333, 1283, 1241, 1139, 1041, 943, 760 cm^{-1}. MS (EI): m/z (%) = 260 (6) $[M]^+$, 198 (18), 132 (13), 131 (17), 73 (100). HRMS (EI) calcd. for $C_{16}H_{20}O_3$ 260.1412; found 260.1409.

General Procedure for IBX Oxidation: A mixture of the appropriate compound **21** (1.4 mmol) and IBX (7.0 mmol) in DMSO (28 mL) was stirred at 55 °C for 12 h. The reaction mixture was quenched with water and filtered through a pad of celite. The filtrate was extracted with Et_2O, and the combined extracts were washed successively with water and brine, dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by silica gel chromatography with EtOAc/hexanes as the eluent to furnish indenones **22**.

3-[3-(1,3-Dioxolan-2-yl)propyl]-1*H*-inden-1-one (22b): Bright yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 7.2 Hz, 1 H), 7.36 (dd, J = 7.2, 7.2 Hz, 1 H), 7.24 (dd, J = 7.2, 7.2 Hz, 1 H), 7.11 (d, J = 7.2 Hz, 1 H), 5.70 (s, 1 H), 4.91 (t, J = 4.1 Hz, 1 H), 4.00–3.84 (m, 4 H), 2.61 (t, J = 6.4 Hz, 2 H), 1.90–1.78 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.8, 166.1, 145.2, 133.1, 131.6, 129.1, 122.4, 121.9, 119.5, 104.1, 64.9, 33.4, 28.2, 21.1 ppm. IR (neat): $\tilde{\nu}$ = 2923, 2880, 1707, 1604, 1191, 1135, 1082, 946 cm^{-1}. MS (EI): m/z (%) = 244 (9) $[M]^+$, 180 (88), 109 (50), 97 (83), 82 (42), 81 (100). HRMS (EI) calcd. for $C_{15}H_{16}O_3$ 244.1099; found 244.1101.

3-[4-(1,3-Dioxolan-2-yl)butyl]-1*H*-inden-1-one (22c): Bright yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, J = 7.2 Hz, 1 H), 7.33 (dd, J = 7.2, 7.2 Hz, 1 H), 7.21 (dd, J = 7.2, 7.2 Hz, 1 H), 7.07 (d, J = 7.2 Hz, 1 H), 5.65 (s, 1 H), 4.84 (t, J = 4.7 Hz, 1 H), 3.96–3.80 (m, 4 H), 2.54 (t, J = 6.7 Hz, 2 H), 1.74–1.68 (m, 4 H), 1.58–1.52 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.7, 166.3, 145.2, 133.0, 131.5, 129.0, 122.3, 121.7, 119.4, 104.2, 64.8, 33.4, 28.2, 26.6, 23.7 ppm. IR (neat): $\tilde{\nu}$ = 2945, 2869, 1708, 1605, 1575, 1454, 1412, 1282, 1137, 1034, 945, 766, 695 cm^{-1}. MS (EI): m/z (%) = 258 (7) $[M]^+$, 180 (50), 111 (79), 99 (53), 128 (49), 81 (61), 73 (100). HRMS (EI) calcd. for $C_{16}H_{18}O_3$ 258.1256; found 258.1258.

General Procedure for the Intramolecular Acyl Radical Cyclization: A solution of the appropriate enol-aldehyde (0.9 mmol) and *t*-dodecanethiol (4.5 mmol) in toluene (5 mL) was added at room temperature to a stirred solution of AIBN (0.9 mmol) in toluene (55 mL). The mixture was stirred at 75 °C for 19 h and then additional AIBN (0.9 mmol) was added to the reaction mixture. The stirring was continued at 75 °C for a further 12 h. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography with EtOAc/hexanes as the eluent to furnish the spiro compounds **24**–**30**.

Spiro[4.5]decane-1,7-dione (24b):[4] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (d, J = 14.3 Hz, 1 H), 2.43–2.22 (m, 4 H), 2.11–2.03 (m, 2 H), 1.96–1.78 (m, 6 H), 1.59–1.55 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 219.8, 209.8, 52.7, 47.1, 40.9, 36.8, 34.2, 30.9, 22.7, 18.6 ppm. IR (neat): $\tilde{\nu}$ = 2952, 2872, 1735, 1715, 1448, 1406, 1228, 1187, 1161 cm^{-1}. MS (EI): m/z (%) = 166 (66) $[M]^+$, 138 (34), 123 (35), 110 (100), 97 (41), 82 (61), 67 (93), 55 (80). HRMS (EI) calcd. for $C_{10}H_{14}O_2$ 166.0994; found 166.0985.

Spiro[5.5]undecane-1,8-dione (24c): White solid, m.p. 72–73 °C (Et_2O/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.64 (d, J = 14.7 Hz, 1 H), 2.55–2.33 (m, 3 H), 2.25–2.17 (m, 2 H), 2.02–1.98 (m, 2 H), 1.87–1.59 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.5, 209.4, 52.9, 49.1, 40.3, 38.3, 37.9, 31.7, 27.0, 21.0, 20.7 ppm. IR (neat): $\tilde{\nu}$ = 2937, 2871, 1706, 1559, 1457 cm^{-1}. MS (EI): m/z (%) = 180 (82) $[M]^+$, 152 (28), 137 (46), 123 (65), 109 (83), 95 (43), 81 (56), 67 (68), 55 (100). HRMS (EI) calcd. for $C_{11}H_{16}O_2$ 180.1150; found 180.1152.

8,8-Dimethylspiro[4.5]decane-1,7-dione (25b): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.63 (d, J = 14.2 Hz, 1 H), 2.32–2.20 (m, 2 H), 2.02 (dd, J = 14.2, 2.0 Hz, 1 H), 2.04–1.70 (m, 6 H), 1.67–1.58 (m, 1 H), 1.48–1.42 (m, 1 H), 1.19 (s, 3 H), 1.05 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 219.9, 214.1, 53.4, 44.6, 43.6, 36.8, 36.8, 34.1, 27.8, 25.2, 24.8, 18.6 ppm. IR (neat): $\tilde{\nu}$ = 2956, 2873, 1736, 1707, 1460, 1192, 1107, 1017 cm^{-1}. MS (EI): m/z (%) = 194 (100) $[M]^+$, 135 (87), 110 (88), 97 (78), 95 (72), 82 (91), 67 (53). HRMS (EI) calcd. for $C_{12}H_{18}O_2$ 194.1307; found 194.1310.

9,9-Dimethylspiro[5.5]undecane-1,8-dione (25c): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.66 (dd, J = 14.7, 1.4 Hz, 1 H), 2.48–2.40 (m, 1 H), 2.35–2.29 (m, 1 H), 2.16–2.10 (m, 1 H), 2.08 (d, J = 14.7 Hz, 1 H), 2.00–1.92 (m, 1 H), 1.84–1.44 (m, 8 H), 1.08 (s, 3 H), 1.06 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.9, 213.6, 53.5, 45.6, 44.0, 38.2, 37.7, 35.4, 28.6, 27.0, 25.6, 25.1, 20.6 ppm. IR (neat): $\tilde{\nu}$ = 2933, 2865, 1708, 1707, 1453, 1384, 1362, 1307, 1218, 1115 cm^{-1}. MS (EI): m/z (%) = 208 (54) $[M]^+$, 149 (47), 138 (100), 109 (58), 81 (42). HRMS (EI) calcd. for $C_{13}H_{20}O_2$ 208.1463; found 208.1465.

9,9-Dimethylspiro[4.5]decane-1,7-dione (26b): White solid, m.p. 46–47 °C (Et_2O/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.37–1.72 (m, 11 H), 1.35 (d, J = 14.2 Hz, 1 H), 1.09 (s, 3 H), 0.99 (s, 3 H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 220.6, 210.1, 54.4, 52.6, 45.9, 44.8, 37.0, 36.6, 36.1, 33.0, 27.6, 19.0 ppm. IR (neat): $\tilde{\nu}$ = 2958, 2871, 1737, 1709, 1277, 1151 cm^{-1}. MS (EI): *m/z* (%) = 194 (49) [M]$^+$, 179 (74), 166 (39), 151 (42), 138 (79), 110 (55), 95 (32), 83 (100). HRMS (EI) calcd. for $C_{12}H_{18}O_2$ 194.1307; found 194.1310.

10,10-Dimethylspiro[5.5]undecane-1,8-dione (26c): White solid, m.p. 85–86 °C (Et_2O/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.81 (d, *J* = 14.4 Hz, 1 H), 2.66 (ddd, *J* = 14.4, 6.4, 6.4 Hz, 1 H), 2.38–2.29 (m, 2 H), 2.18–2.04 (m, 3 H), 1.92–1.87 (m, 2 H), 1.83 (d, *J* = 14.4 Hz, 1 H), 1.71–1.55 (m, 4 H), 1.05 (s, 3 H), 0.99 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.9, 209.4, 54.0, 52.9, 47.8, 46.0, 43.3, 38.8, 35.1, 32.6, 28.5, 27.5, 21.0 ppm. IR (neat): $\tilde{\nu}$ = 2945, 2870, 1712, 1445, 1280, 1236, 1129 cm^{-1}. MS (EI): *m/z* (%) = 208 (46) [M]$^+$, 193 (18), 180 (45), 175 (48), 165 (53), 151 (69), 138 (46), 124 (39), 109 (57), 91 (44), 83 (100), 55 (90). HRMS (EI) calcd. for $C_{13}H_{20}O_2$ 208.1463; found 208.1462.

10,10-Dimethylspiro[4.5]decane-1,7-dione (27b): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.47–2.40 (m, 1 H), 2.36–2.12 (m, 4 H), 2.02 (d, *J* = 14.7 Hz, 1 H), 1.97–1.62 (m, 6 H), 1.06 (s, 3 H), 0.87 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 220.7, 210.0, 58.5, 42.2, 41.2, 40.1, 33.6, 33.5, 26.6, 24.8, 23.0, 20.5 ppm. IR (neat): $\tilde{\nu}$ = 2954, 2876, 1733, 1708, 1466, 1412, 1317, 1236, 1119, 1048, 945 cm^{-1}. MS (EI): *m/z* (%) = 194 (100) [M]$^+$, 179 (41), 138 (54), 110 (43), 95 (36). HRMS (EI) calcd. for $C_{12}H_{18}O_2$ 194.1307; found 194.1305.

11,11-Dimethylspiro[5.5]undecane-1,8-dione (27c): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.48 (dd, *J* = 15.3, 1.4 Hz, 1 H), 2.41–2.26 (m, 3 H), 2.10 (d, *J* = 15.3 Hz, 1 H), 2.12–1.95 (m, 3 H), 1.88–1.70 (m, 3 H), 1.57–1.45 (m, 3 H), 1.09 (s, 3 H), 1.04 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 215.8, 209.7, 56.8, 45.5, 39.7, 37.4, 36.9, 35.3, 32.1, 25.2, 23.3, 22.9, 19.1 ppm. IR (neat): $\tilde{\nu}$ = 2951, 2873, 1707, 1453, 1420, 1371, 1324, 1241, 1117, 1021, 736, 700 cm^{-1}. MS (EI): *m/z* (%) = 208 (84) [M]$^+$, 152 (37), 139 (44), 111 (100), 108 (42), 91 (49). HRMS (EI) calcd. for $C_{13}H_{20}O_2$ 208.1463; found 208.1463.

Spiro[4.4]nonane-1,7-dione (28b):[20] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.45–2.20 (m, 5 H), 2.09–1.77 (m, 7 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 220.8, 216.5, 52.7, 46.8, 37.0, 36.7, 35.9, 31.4, 19.2 ppm. MS (EI): *m/z* (%) = 152 (41) [M]$^+$, 124 (100), 110 (20), 96 (39), 82 (52), 68 (57). IR (neat): $\tilde{\nu}$ = 2960, 2884, 1742, 1453, 1404, 1264, 1138 cm^{-1}. HRMS (EI) calcd. for $C_9H_{12}O_2$ 152.0837; found 152.0846.

Spiro[4.5]decane-2,6-dione (28c):[20] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.79 (d, *J* = 18.0 Hz, 1 H), 2.60–2.25 (m, 5 H), 2.00 (d, *J* = 18.0 Hz, 1 H), 1.97–1.70 (m, 7 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 216.6, 212.5, 53.7, 47.3, 38.6, 38.5, 36.3, 31.4, 27.0, 21.9 ppm. IR (neat): $\tilde{\nu}$ = 2928, 2857, 1744, 1704, 1449, 1163, 1127 cm^{-1}. MS (EI): *m/z* (%) = 166 (12) [M]$^+$, 149 (13), 138 (100), 125 (9), 110 (16), 97 (8), 82 (12). HRMS (EI) calcd. for $C_{10}H_{14}O_2$ 166.0994; found 166.0991.

Spiro[3.6]decane-1,6-dione (29a): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.99 (dd, *J* = 14.0, 1.1 Hz, 1 H), 2.81 (d, *J* = 14.0 Hz, 1 H), 2.67–2.59 (m, 3 H), 2.52–2.44 (m, 1 H), 2.14–2.04 (m, 3 H), 1.97–1.83 (m, 3 H), 1.79–1.68 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.9, 175.7, 84.5, 54.2, 43.8, 41.5, 33.9, 28.1, 24.2, 23.4 ppm. IR (neat): $\tilde{\nu}$ = 2926, 2856, 1772, 1698, 1457, 1304, 1233, 1181, 1022, 933, 796 cm^{-1}. MS (EI): *m/z* (%) = 166 (1) [M]$^+$, 124 (88), 111 (83), 98 (100), 55 (84). HRMS (EI) calcd. for $C_{10}H_{14}O_2$ 166.0994; found 166.0993.

Spiro[4.6]undecane-1,7-dione (29b): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.87 (d, *J* = 12.7 Hz, 1 H), 2.63–2.56 (m, 1 H), 2.40–2.27 (m, 3 H), 2.19 (dd, *J* = 12.7, 1.4 Hz, 1 H), 2.00–1.65 (m, 9 H), 1.47–1.37 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 220.7, 212.1, 49.2, 48.7, 43.7, 36.4, 36.2, 33.1, 25.0, 23.5, 18.4 ppm. IR (neat): $\tilde{\nu}$ = 2930, 2862, 1736, 1698, 1452, 1406, 1334, 1248, 1141, 1000, 813 cm^{-1}. MS (EI): *m/z* (%) = 180 (80) [M]$^+$, 123 (36), 109 (43), 97 (65), 81 (100), 67 (40). HRMS (EI) calcd. for $C_{11}H_{16}O_2$ 180.1150; found 180.1148.

Spiro[5.6]dodecane-1,8-dione (29c): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.92 (d, *J* = 14.0 Hz, 1 H), 2.52–2.33 (m, 5 H), 2.28–2.19 (m, 1 H), 2.01–1.90 (m, 1 H), 1.79–1.50 (m, 10 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.0, 212.8, 51.4, 50.6, 43.7, 39.1, 38.6, 37.6, 27.4, 24.9, 23.9, 20.7 ppm. IR (neat): $\tilde{\nu}$ = 2933, 2861, 1701, 1453, 1127 cm^{-1}. MS (EI): *m/z* (%) = 194 (65) [M]$^+$, 166 (9), 150 (38), 137 (51), 111 (100), 95 (39), 81 (67), 67 (73). HRMS (EI) calcd. for $C_{12}H_{18}O_2$ 194.1307; found 194.1299.

Spiro[cyclopentane-1,1′-indene]-2,3′(2′*H*)-dione (30b): Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 7.6 Hz, 1 H), 7.65–7.61 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.44 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.25 (d, *J* = 7.6 Hz, 1 H), 2.87 (d, *J* = 18.3 Hz, 1 H), 2.58–2.42 (m, 3 H), 2.52 (d, *J* = 18.3 Hz, 1 H), 2.33–2.26 (m, 2 H), 2.12–2.03 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 218.6, 203.5, 156.3, 136.9, 135.3, 128.6, 124.4, 124.0, 65.9, 47.9, 38.4, 37.6, 20.1 ppm. IR (neat): $\tilde{\nu}$ = 2957, 1714, 1599, 1462, 1399, 1283, 1241, 1160, 1041, 763 cm^{-1}. MS (EI): *m/z* (%) = 200 (63) [M]$^+$, 145 (28), 144 (100), 116 (28), 115 (37). HRMS (EI) calcd. for $C_{13}H_{12}O_2$ 200.0837; found 200.0839.

Spiro[cyclohexane-1,1′-indene]-2,3′(2′*H*)-dione (30c): Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 7.6 Hz, 1 H), 7.67 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.54 (d, *J* = 7.6 Hz, 1 H), 7.45 (dd, *J* = 7.6, 7.6 Hz, 1 H), 2.88 (d, *J* = 18.6 Hz, 1 H), 2.79 (d, *J* = 18.6 Hz, 1 H), 2.65–2.59 (m, 2 H), 2.22–2.14 (m, 2 H), 2.04–1.80 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.8, 203.1, 156.7, 136.1, 134.8, 128.5, 126.6, 123.8, 56.6, 47.1, 41.0, 40.0, 27.0, 22.9 ppm. IR (neat): $\tilde{\nu}$ = 2933, 2862, 1711, 1602, 1463, 1289, 1260, 1127, 1049, 762 cm^{-1}. MS (EI): *m/z* (%) = 214 (75) [M]$^+$, 170 (100), 158 (85), 157 (59), 144 (96), 129 (60), 115 (60). HRMS (EI) calcd. for $C_{14}H_{14}O_2$ 214.0994; found 214.0993.

Supporting Information (see footnote on the first page of this article): Copies of ^{1}H and ^{13}C NMR for compounds **6**–**9**, **11**, **14**, **16**, **18**–**19**, and **21**–**30**.

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