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# A Convenient Synthesis of α-Methylene-γ-butyrolactones from Allenyl Carbonyl Units Mediated by $Mo(CO)_6$ through Intramolecular Cyclocarbonylation

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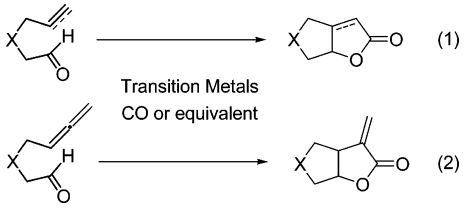
**Abstract:** A novel procedure for the synthesis of *cis*-fused bicyclic α-methylene-γ-butyrolactones from allenyl carbonyl functionalities via the molybdenum-mediated cyclocarbonylation is described. The use of $Mo(CO)_6$ with DMSO to promote reaction results in an efficient and convenient protocol through the three-component assembly in high yields.

The availability of efficient synthetic methods in the construction of a cyclic system via organotransition metal catalysts or reagents is of considerable current interest in organic chemistry. As a consequence, many advances in the cyclization mediated by transition metals have been made through a variety of ways in synthetic strategy.[1] Of particular interest is a cyclization strategy between carbonyl and unsaturated bonds to find practical way of chemical routes for the preparation of lactones mainly because the chemical process could dominate over the classical methods in simple trials as shown in eq 1 (Scheme 1).[2] For example, the use of titanium-mediated [2 + 2 + 1] cycloaddition of δ-unsaturated ketones or aldehydes to form fused bicyclic γ-butyrolactone via cyclocarbonylation known as the hetero-Pauson−Khand-type reaction has been developed by independently Buchwald[3] and Crowe laboratories.[4] Recently, Murai and co-workers disclosed elegant atom-economical method[5] in the preparation of α,β-unsaturated γ-butyrolactones from yne−aldehydes with carbon monoxide through the ruthenium-catalyzed cyclocarbonylation.[6]

**SCHEME 1. General Strategy**




As our continuous synthetic efforts to utilize allenyl moieties,[7] ruthenium-catalyzed carbonylative cycloaddition of allenyl aldehydes and ketones to provide fused bicyclic *cis*-α-methylene-γ-butyrolactone has been developed from this laboratory.[8] The characteristic features of this protocol in terms of chemical efficiency of three-component coupling process and structural aspects of products have encouraged us to carry out more investigations to screen other transition metals, which would expand the scope and utility of this reactions. Described herein is an extension of our strategy aimed at finding new reagents and realizing practical ways to advance new levels of transition-metal chemistry.

With this issue in mind, we set out to establish the scope of the reaction for the synthesis of **2** from **1** through the transition-metal-mediated cyclocarbonylation as outlined in eq 2 (Scheme 2). To find optimum conditions for this chemical process, a series of experiments have been performed with allenyl ketone **1a** as a model substrate. Preliminary investigations for the transformation of **1a** with various transition-metal complexes mainly employed for a Pauson−Khand-type reaction of enynes indicated that the conversion to the corresponding **2a** could not be satisfied with rhodium complexes,[9] $Ni(CO)_4(PPh_3)_2$,[10] and $[Ir(COD)Cl]_2$[11] under various conditions mainly due to a lack of reactivity. Fortunately, we found that molybdenum carbonyl complexes were able to promote the reaction process;[12] $Mo(CO)_6$ was generally superior to other molybdenum complexes such as $(C_7H_8)Mo(CO)_3$ and ($\eta^6$-mesitylene)$Mo(CO)_3$ and was chosen for systematic studies. After surveying numerous conditions for orienting experiments as summarized in Table 1, several key findings emerged. (i) 1.2 equiv of $Mo(CO)_6$ was required for optimal conditions in terms of chemical yields and reaction rates. (ii) The use of catalytic amounts of $Mo(CO)_6$ turned out to be unpromising, despite CO atmosphere under various pressures. (iii) We observed

(1) For excellent discussions, see: (a) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. *Chem Rev*. **1996**, *96*, 635−662. (b) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev*. **1996**, *96*, 49−92. (c) Trost, B. M.; Toste, F. D.; Pinkerton, A. B. *Chem. Rev*. **2001**, *101*, 2067−2096. (d) Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev*. **2002**, *102*, 813−834.

(2) For general discussions, see: *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 1998; Vols. I and II.

(3) (a) Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc*. **1995**, *117*, 6785−6786. (b) Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc*. **1996**, *118*, 3182−3191. (c) Kablaoui, N. M.; Hick, F. A.; Buchwald, S. L. *J. Am. Chem. Soc*. **1996**, *118*, 5818−5819. (d) Kablaoui, N. M.; Hick, F. A.; Buchwald, S. L. *J. Am. Chem. Soc*. **1997**, *119*, 4424−4431.

(4) (a) Crowe, W. E.; Vu, A. T. *J. Am. Chem. Soc*. **1996**, *118*, 1557−1558. (b) Crowe, W. E.; Rachita, M. *J. Am. Chem. Soc*. **1995**, *117*, 6787−6788.

(5) Trost, B. M. *Acc. Chem. Res.* **2002**, *35*, 695−705.

(6) Chatani, N.; Morimoto, T.; Fukumoto, Y.; Murai, S. *J. Am. Chem. Soc*. **1998**, *120*, 5335−5336.

(7) (a) Yu, C.-M.; Yoon, S.-K.; Baek, K.; Lee, J.-Y. *Angew. Chem., Int. Ed*. **1998**, *37*, 2392−2395. (b) Yu, C.-M.; Kim, Y.-M.; Kim, J.-M. *Synlett* **2003**, 1518−1520. (c) Kang, S.-K.; Hong, Y.-T.; Lee, J.-H.; Kim, W.-Y.; Lee, I.; Yu, C.-M. *Org. Lett.* **2003**, *5*, 2813−2816.

(8) Kang, S.-K.; Kim, K.-J.; Hong, Y.-T. *Angew. Chem., Int. Ed*. **2002**, *41*, 1584−1586.

(9) (a) Koga, Y.; Kobayashi, T.; Narasaka, K. *Chem. Lett.* **1998**, 249−250. (b) Jeong, N.; Lee, S.; Sung, B. K. *Organometallics* **1998**, *17*, 3642−3644. (c) Jeong, N.; Sung, B. K.; Choi, Y. K. *J. Am. Chem. Soc.* **2000**, *122*, 6771−6772.

(10) Semmelhack, M. F.; Brickner, S. J. *J. Org. Chem.* **1981**, *46*, 1723−1725.

(11) Shibata, T.; Takagi, K. *J. Am. Chem. Soc.* **2000**, *122*, 9852−9853.

(12) (a) Jeong, N.; Lee, S. J. *Tetrahedron Lett.* **1993**, *34*, 4027−4030. (b) Brummond, K. M.; Kerekes, A. D.; Wan, H. *J. Org. Chem*. **2002**, *67*, 5156−5163. (c) Brummond, K. M.; Lu, J.; Petersen, J. *J. Am. Chem. Soc*. **2000**, *122*, 4915−4920.

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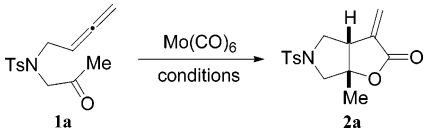
**TABLE 1. Selected Data from Preliminary Investigations**




| entry | additive (equiv) | solvent | *T* (°C) | time (h) | yield (%) |
|---|---|---|---|---|---|
| 1 | none | toluene | 100 | >24 | NR |
| 2 | none | $CH_3CN$ | 80 | 16 | 36 |
| 3 | $CH_3CN$ (10) | toluene | 100 | 4 | 54 |
| 4 | DMSO (10) | THF | 80 | >24 | trace |
| 5 | DMSO (10) | DMF | 100 | 16 | 47 |
| 6 | DMSO (10) | toluene | 100 | 6 | 80 |
| 7 | DMSO (5) | toluene | 100 | 6 | 72 |
| 8 | DMSO (2) | toluene | 100 | 6 | 69 |

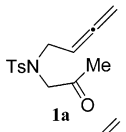
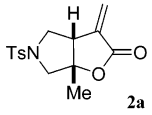
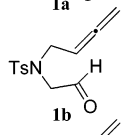
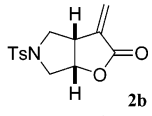
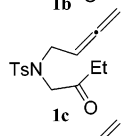
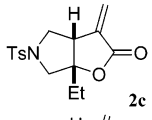
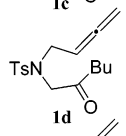
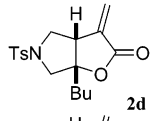
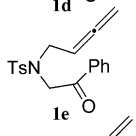
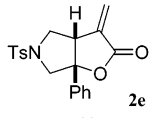
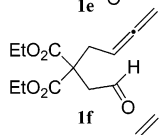
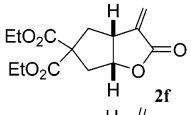
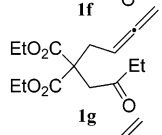
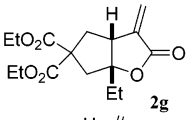
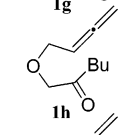
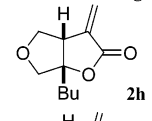
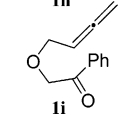
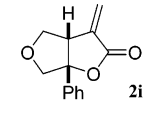
that the introduction of dimethyl sulfoxide (DMSO) as an additive proved to be effective in comparison with other inactive additives such as $H_2O$, NMO, and HMPA.[12a] (iv) The decreased chemical yields with the formation of undesired impurities were observed when DMSO was used as solvent. Also, the addition of $H_2O$ resulted in the decreased reactivity. (v) 10 equiv of DMSO was needed for optimum conditions whereas the reaction with reduced dosage of DMSO resulted in diminished chemical yield. (iv) Reaction performed at 100 °C in toluene resulted in the best chemical yields in comparison with other solvents such as THF, $CH_3CN$, and DMF. Under optimal conditions, the reaction was conducted by a dropwise addition of **1a** (1 equiv) in toluene at 20 °C to a mixture of $Mo(CO)_6$ (1.2 equiv) and DMSO (10 equiv) in toluene. After 6 h at 100 °C, volatile materials were removed under reduced pressure. Workup and chromatography gave **2a** in 80% yield.

With the notion that this approach might lead to a general and efficient method for the synthesis of **2**, we set out to determine the scope of reaction with various substrates **1** to produce carbo- and heterocycles as summarized in Table 2. Indeed, the method is successful with allenyl carbonyl units **1** to yield the five-membered bicyclic products **2** as diastereomerically pure form in moderate to high chemical yields as it can be seen in Table 2.

Although the exact mechanistic aspects of this transformation and the role of dimethyl sulfoxide as an additive have not been rigorously elucidated, the following pathway could be a probable stereochemical routes on the basis of product formation and our observations as illustrated in Scheme 2. The enhancing reactivity by the use of DMSO may be interpreted by assuming that the favorable ligand exchange between carbonyl and DMSO on molybdenum carbonyls resulted in the generation of vacant orbital to accommodate the allenyl moiety in forming the complex **A**.[13] Since the cyclization would lead to the particular metalacycles **B** via stereochemical model **A**, the origin of cis stereochemical outcomes for this transformation might be a geometrical preference for orientation in the transition states offered by substituents and ligands. Migratory insertion of the vinyl group to carbonyl in the molybdenum complex **B** to **C**

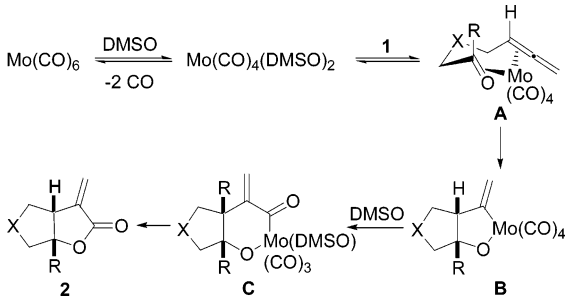
(13) Chung, Y. K.; Lee, B. Y.; Jeong, N.; Hudecek, M. H.; Pauson, P. L. *Organometallics* **1993**, *12*, 220−223.

**TABLE 2. $Mo(CO)_6$-Mediated Carbonylative Carbocyclization[a]**

| Entry | Substrate | Time (h) | Product | Yield (%)[b] |
|---|---|---|---|---|
| 1 |  **1a** | 6 |  **2a** | 80 |
| 2 |  **1b** | 5 |  **2b** | 75 |
| 3 |  **1c** | 6 |  **2c** | 82 |
| 4 |  **1d** | 6 |  **2d** | 81 |
| 5 |  **1e** | 6 |  **2e** | 83 |
| 6 |  **1f** | 6 |  **2f** | 58 |
| 7 |  **1g** | 8 |  **2g** | 51 |
| 8 |  **1h** | 6 |  **2h** | 59 |
| 9 |  **1i** | 6 |  **2i** | 67 |

[a] All reactions were carried out with $Mo(CO)_6$ (1.2 equiv) and DMSO (10 equiv) at 100 °C in toluene. [b] Refer to isolated and purified yields.

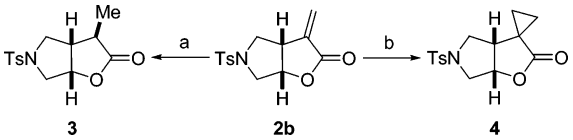
**SCHEME 2. Plausible Mechanistic Pathway**




probably by assistance of incoming ligand, DMSO, and then the reductive elimination of **C** provided the product **2**.

The products **2** are readily amenable for further conversion to useful synthetic intermediates by the functional group transformations as demonstrated in Scheme 3. For example, compound **3** was obtained by the treatment of **2b** with copper hydride in THF and HMPA

**SCHEME 3. Synthetic Manipulations of 2b**[a]




[a] Reagents and conditions: (a) $LiAlH_4$−CuI (1:1), THF−HMPA (4:1), −78 °C, 2 h; (b) $Me_2SOCH_2$, DMSO, 23 °C, 12 h.

in 67% yield.[14] Compound **2** was proved to be an excellent Michael acceptor: reaction of **2b** with dimethyloxosulfoxonium methylide gave **4** in 84% yield.[15]

In summary, this paper describes a new procedure for the synthesis of α-methylene-γ-bytyrolactones **2** from allenyl aldehydes and ketones **1** mediated by $Mo(CO)_6$ with DMSO. A variety of **1** including carbon, nitrogen, and oxygen linkages are converted to the corresponding **2** in good yields. Investigations into the versatility of this process including enantio- and diastereoselective routes are currently underway.

## Experimental Section

**General Methods.** All reactions were run in flame-dried glassware under an atmosphere of nitrogen. Diethyl ether ($Et_2O$) was dried by refluxing over sodium/benzophenone ketyl until a permanent purple coloration was presented and then distilled prior to use. Tetrahydrofuran (THF) was distilled from sodium−benzophenone ketyl under $N_2$. Dichloromethane ($CH_2Cl_2$) was distilled from $CaH_2$ prior to use. All liquid reagents purchased from the Aldrich were distilled properly prior to use, unless otherwise indicated. Diethyl ether was distilled from sodium−benzophenone ketyl under $N_2$. IR spectra were recorded on a Nicolet 320 FT-IR spectrometer. $^1H$ NMR and $^{13}C$ NMR were conducted at 500 and 300 MHz in $CDCl_3$, and chemical shifts are reported δ units relative to the tetramethylsilane (TMS) signal at 0.00 ppm. Coupling constants (*J*) are reported in Hz. For thin-layer chromatography (TLC), Merck precoated plates (silica gel 60 $F_{254}$, 0.25 mm) were used. Silica gel 60 (TA792685, 230−400 mesh) from Merck was used for column chromatography. The reported yields refer to chromatographically purified and isolated products.

**General Procedure (Entry 1 in Table 2). (3a*S**,6a*S**)-Hexahydro-6a-methyl-3-methylene-5-tosylfuro[3,2-*c*]pyrrol-2-one (2a).** To a solution of $Mo(CO)_6$ (126.8 mg, 0.48 mmol) in toluene (7 mL) were added allenyl ketone **1a** (112 mg, 0.40 mmol) and DMSO (313 mg, 4.0 mmol) at room temperature under nitrogen. The reaction mixture was stirred at 100 °C for 6 h. After the reaction was complete, the solvent was removed and the residue treated with EtOAc and washed with brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by $SiO_2$ column chromatography (EtOAc/hexane 1:1) to give the cyclized product **2a** (98 mg, 0.21 mmol, 80%) as a white solid: mp 156 °C; $R_f$ = 0.44 (EtOAc/hexane 1:1); IR (film) 3064, 2987, 1752, 1659, 1598, 1311, 893 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 1.48 (s, 3H), 2.45 (s, 3H), 2.96 (d, 1H, *J* = 11.1 Hz), 3.14 (m, 1H), 3.27 (dd, 1H, *J* = 10.0, 3.5 Hz), 3.39 (dd, 1H, *J* = 10.0, 8.0 Hz), 3.56 (d, 1H, *J* = 11.1 Hz), 5.72 (d, 1H, *J* = 2.4 Hz), 6.33 (d, 1H, *J* = 2.4 Hz), 7.35 (d, 2H, *J* = 8.2 Hz), 7.67 (d, 2H, *J* = 8.2 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 168.7, 144.8, 138.3, 132.2, 130.3, 128.4, 125.5, 88.6, 59.0, 55.3, 48.7, 24.6, 22.0; HRMS calcd for $C_{15}H_{17}NO_4S$ 307.0878, found 307.0883.

**(3a*S**,6a*S**)-Hexahydro-3-methylene-5-tosylfuro[3,2-*c*]-pyrrol-2-one (2b):** white solid; mp 115 °C; TLC, $R_f$ = 0.48 (EtOAc/hexane 1:1); IR (film) 3061, 2981, 1745, 1661, 1599, 890 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 2.45 (s, 3H), 3.07 (dd, 1H, *J* = 5.3, 11.7 Hz), 3.22 (dd, 1H, *J* = 10.0, 7.6 Hz), 3.37 (dd, 1H, *J* = 10.0, 2.9 Hz), 3.55 (m, 1H), 3.63 (dd, 1H, *J* = 0.6, 11.7 Hz), 4.97 (m, 1H), 5.77 (d, 1H, *J* = 2.4 Hz), 6.35 (d, 1H, *J* = 2.4 Hz), 7.36 (d, 2H, *J* = 8.2 Hz), 7.68 (d, 2H, *J* = 8.2 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 169.6, 145.2, 137.4, 132.1, 130.6, 128.7, 125.8, 79.7, 55.2, 54.7, 42.6, 22.3; HRMS calcd for $C_{14}H_{15}NO_4S$ 293.0776, found 293.0705.

**(3a*S**,6a*S**)-6a-Ethylhexahydro-3-methylene-5-tosylfuro-[3,2-*c*]pyrrol-2-one (2c):** white solid; mp 120 °C; TLC, $R_f$ = 0.38 (EtOAc/hexane 1:1); IR (film) 3061, 2977, 1762, 1659, 1597, 1346, 1159 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 0.92 (t, 3H, *J* = 7.3 Hz), 1.69 (m, 1H), 1.79 (m, 1H), 2.45 (s, 3H), 2.93 (d, 1H, *J* = 11.3 Hz), 3.18 (m, 1H), 3.32 (m, 2H), 3.54 (d, 1H, *J* = 11.0 Hz), 5.72 (d, 1H, *J* = 2.3 Hz), 6.30 (d, 1H, *J* = 2.3 Hz), 7.34 (d, 2H, *J* = 8.2 Hz), 7.66 (d, 2H, *J* = 8.2 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 169.1, 144.9, 138.5, 131.8, 130.3, 128.4, 125.2, 91.7, 57.7, 55.6, 46.6, 31.0, 22.0, 8.3; HRMS calcd for $C_{16}H_{19}NO_4S$ 321.1035, found 321.1095.

**(3a*S**,6a*S**)-6a-Butylhexahydro-3-methylene-5-tosylfuro-[3,2-*c*]pyrrol-2-one (2d):** white solid; mp 104 °C; TLC, $R_f$ = 0.48 (EtOAc/hexane 1:1); IR (film) 3061, 2932, 1763, 1660, 1597, 1348, 1163, 863 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 0.86 (m, 3H), 1.28 (m, 4H), 1.62 (m, 1H), 1.74 (m, 1H), 2.45 (s, 3H), 2.90 (d, 1H, *J* = 11.0 Hz), 3.18 (m, 1H), 3.28 (m, 2H), 3.56 (d, 1H, *J* = 11.2 Hz), 5.72 (d, 1H, *J* = 2.3 Hz), 6.30 (d, 1H, *J* = 2.3 Hz), 7.35 (d, 2H, *J* = 8.2 Hz), 7.67 (d, 2H, *J* = 8.2 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 169.0, 144.7, 138.4, 131.6, 130.2, 128.3, 125.1, 91.2, 57.9, 55.5, 46.8, 37.6, 25.8, 22.9, 21.9, 14.1; HRMS calcd for $C_{18}H_{23}NO_4S$ 349.1348, found 349.1359.

**(3a*S**,6a*S**)-6a-Phenylhexahydro-3-methylene-5-tosylfuro[3,2-*c*]pyrrol-2-one (2e):** white solid; mp 130 °C; TLC, $R_f$ = 0.44 (EtOAc/hexane 1:1); IR (film) 3062, 2923, 1769, 1662, 1597, 1350, 1166 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 2.46 (s, 3H), 3.33 (d, 1H, *J* = 11.52 Hz), 3.43 (dd, 1H, *J* = 7.87, 7.59 Hz), 3.59 (dd, 1H, *J* = 8.43, 7.59 Hz), 3.61 (dd, 1H, *J* = 8.43, 7.87 Hz), 3.83 (d, 1H, *J* = 11.52 Hz), 5.74 (d, 1H, *J* = 1.4 Hz), 6.32 (d, 1H, *J* = 1.4 Hz), 7.31 (m, 7H), 7.69 (d, 2H, *J* = 8.4 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 168.6, 144.9, 139.6, 137.4, 131.8, 130.3, 129.2, 129.0, 128.3, 125.7, 124.8, 90.8, 61.1, 56.1, 50.8, 21.9; HRMS calcd for $C_{20}H_{19}NO_4S$ 369.1035, found 369.1031.

**Diethyl (3a*R**,6a*R**)-hexahydro-3-methylene-2-oxocyclopenta[*b*]furan-5,5-dicarboxylate (2f):** colorless oil; TLC, $R_f$ = 0.40 (EtOAc/hexane 1:2); IR (neat) 3059, 2987, 1763, 1740, 1651, 1173 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 1.25 (dt, 6H, *J* = 7.3, 4.7 Hz), 2.46 (dd, 1H, *J* = 13.6, 5.3 Hz), 2.56 (dd, 1H, *J* = 13.6, 9.7 Hz), 2.62 (dd, 1H, *J* = 13.6, 3.4 Hz), 2.66 (dd, 1H, *J* = 13.6, 6.0 Hz), 3.57 (m, 1H), 4.19 (m, 4H), 5.01 (ddd, 1H, *J* = 7.3, 5.6, 3.2 Hz), 5.67 (d, 1H, *J* = 2.4 Hz), 6.26 (d, 1H, *J* = 2.4 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 170.9, 170.3, 139.3, 122.9, 81.9, 62.1, 60.4, 42.7, 41.9, 40.8, 14.0; HRMS calcd for $C_{14}H_{18}O_6$ 282.1103, found 282.1103.

**Diethyl (3a*R**,6a*R**)-6a-Ethylhexahydro-3-methylene-2-oxocyclopenta[*b*]furan-5,5-dicarboxylate (2g):** colorless oil; TLC, $R_f$ = 0.25 (EtOAc/hexane 1:3); IR (neat) 3058, 2981, 1763, 1730, 1663, 1267 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 0.96 (t, 3H, *J* = 7.5 Hz), 1.25 (t, 6H, *J* = 7.2 Hz), 1.72 (q, 1H, *J* = 7.5 Hz), 1.80 (q, 1H, *J* = 7.5 Hz), 2.54 (m, 3H), 2.78 (dd, 1H, *J* = 15.0, 1.2 Hz), 3.22 (m, 1H), 4.18 (q, 4H, *J* = 7.2 Hz), 5.64 (d, 1H, *J* = 2.0 Hz), 6.21 (d, 1H, *J* = 2.0 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 171.3, 170.8, 170.0, 141.0, 122.8, 94.5, 62.5, 62.3, 60.7, 47.4, 44.6, 41.6, 32.8, 14.4, 14.3, 8.5; HRMS calcd for $C_{16}H_{22}O_6$ 310.1416, found 310.1411.

**(3a*S**,6a*S**)-6a-Butyltetrahydro-3-methylenefuro[3,4-*b*]-furan-2(3*H*)-one (2h):** yellow oil; TLC, $R_f$ = 0.26 (EtOAc/hexane 1:3); IR (neat) 2958, 1762, 1661, 1113, 948 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 0.91 (m, 3H), 1.37 (m, 4H), 1.81 (m, 2H), 3.22 (m, 1H), 3.52 (d, 1H, *J* = 10.9 Hz), 3.94 (m, 2H), 4.10 (d, 1H, *J* = 10.6 Hz), 5.71 (d, 1H, *J* = 2.0 Hz), 6.31 (d, 1H, *J* = 2.0 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 169.9, 139.8, 128.6, 93.4, 76.5,

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48.9, 36.1, 30.7, 26.4, 23.1, 14.3; HRMS calcd for $C_{11}H_{16}O_3$ 196.1099, found 196.1098.

**(3a*S**,6a*S**)-6a-Phenyltetrahydro-3-methylenefuro[3,4-*b*]furan-2(3*H*)-one (2i):** white solid; mp 80 °C; TLC, $R_f = 0.28$ (EtOAc/hexane 1:3); IR (film) 3022, 2922, 1755, 1661, 1092, 943 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 3.65 (m, 1H), 3.87 (d, 1H, $J$ = 10.9 Hz), 4.09 (d, 1H, $J$ = 8.9 Hz), 4.28 (m, 2H), 5.75 (d, 1H, $J$ = 2.0 Hz), 6.35 (d, 1H, $J$ = 2.0 Hz), 7.39 (m, 5H). $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 169.5, 139.1, 138.9, 129.3, 128.8, 125.3, 124.8, 93.1, 80.5, 77.7, 53.3; HRMS calcd for $C_{13}H_{12}O_3$ 216.0786, found 216.0788.

**(3*R**,3a*S**,6a*S**)-Hexahydro-3-methyl-5-tosylfuro[3,2-*c*]pyrrol-2-one (3).** To a suspension of $LiAlH_4$ (7.1 mg, 0.19 mmol) in THF (2 mL) at −78 °C was added CuI (35.6 mg, 0.19 mmol) dissolved in THF−HMPA (1:1, 1 mL each). The resulting mixture was stirred for 30 min at −78 °C, and then **2b** (50 mg, 0.17 mmol) in THF (1 mL) was added. The reaction mixture was stirred at −78 °C for 2 h. The mixture was treated with saturated aqueous $NH_4Cl$ followed by $Et_2O$. The organic layers were dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by $SiO_2$ column chromatography to give the product **3** (33.6 mg, 0.11 mmol, 67%) as a white solid: mp 114 °C; TLC, $R_f = 0.48$ (EtOAc/hexane 1:1); IR (film) 3061, 2977, 1771, 1597, 1347, 1160 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.23 (d, 3H, $J$ = 7.3 Hz), 2.45 (s, 3H), 2.84 (dq, 1H, $J$ = 7.3, 15.0 Hz), 3.07 (m, 2H), 3.28 (m, 1H), 3.40 (dd, 1H, $J$ = 4.7, 12.0 Hz), 3.51 (dd, 1H, $J$ = 1.3, 12.0 Hz), 4.90 (ddd, 1H, $J$ = 1.3, 4.7, 6.0 Hz), 7.36 (d, 2H, $J$ = 8.3 Hz), 7.69 (d, 2H, $J$ = 8.3 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 177.6, 144.6, 132.5, 130.1, 128.2, 80.3, 53.9, 47.9, 43.1, 37.1, 21.8, 11.2; HRMS calcd for $C_{14}H_{17}NO_4S$ 295.0878, found 295.0881.

**3-Cyclopropyl-5-(toluene-4-sulfonyl)hexahydrofuro[2,3-*c*]pyrrol-2-one (4).** To a solution of dimethyloxosulfonoim methylide (17.5 mg, 0.19 mmol) prepared according to the established procedure[14a] in DMSO (2 mL) was added **2b** (50 mg, 0.17 mmol) in DMSO (1 mL) at 23 °C. The resulting reaction mixture was allowed to proceed for 12 h. The mixture was then poured into water and extracted with ether (15 mL × 3). The ether extract was washed with water (2×) and brine (1×), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by $SiO_2$ column chromatography (EtOAc/hexane, 1:1) to give **4** (43.9 mg, 0.14 mmol, 84%) as a colorless oil: TLC, $R_f = 0.37$ (EtOAc/hexane 1:1); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.03 (dt, 2H, $J$ = 3.1, 5.6 Hz), 1.31 (dt, 2H, $J$ = 3.1, 8.2 Hz), 2.45 (s, 3H), 2.82 (ddd, 1H, $J$ = 3.9, 8.2, 7.6 Hz), 3.06 (dd, 1H, $J$ = 7.6, 10.4 Hz), 3.19 (dd, 1H, $J$ = 3.9, 10.4 Hz), 3.22 (dd, 1H, $J$ = 5.3, 11.5 Hz), 3.61 (d, 1H, $J$ = 11.5 Hz), 5.06 (ddd, 1H, $J$ = 0.6, 5.3, 8.2 Hz), 7.35 (d, 2H, $J$ = 8.2 Hz), 7.69 (d, 2H, $J$ = 8.2 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 178.6, 144.6, 132.1, 130.1, 128.2, 79.7, 54.6, 52.3, 44.1, 24.8, 21.8, 18.4, 13.0; HRMS calcd for $C_{15}H_{17}NO_4S$ 307.0878, found 307.0881.

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**Supporting Information Available:** Characterization of all starting materials and copies of $^1H$ and $^{13}C$ NMR spectra of **2a**−**i**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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