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Carbonylation of 1-Lithiobutadiene with Carbon Monoxide Followed by Intramolecular Acyllithiation of C═C Double Bond and Intermolecular Acylation with Acid Chloride: Scope, Applications, and Mechanistic Aspects

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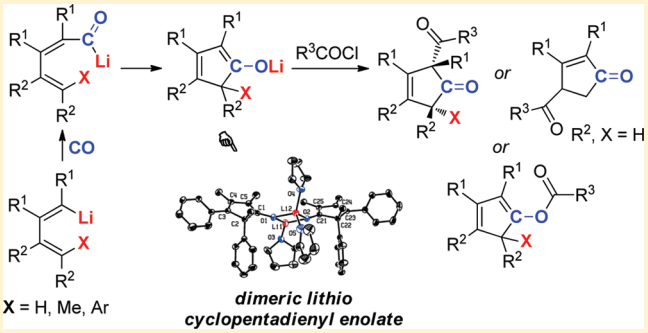
Supporting Information

ABSTRACT: The carbonylation of a 1-lithio-1,3-butadiene derivative with CO gave rise to a butadienyl acyllithio intermediate, which underwent an immediate intramolecular acyllithiation of the C═C double bond, affording a lithio cyclopentadienyl enolate. The X-ray structural analysis of the enolate revealed a dimer connected with a "Li_2O_2" four-membered ring. Subsequent intermolecular acylation of this enolate with acid chlorides afforded β-keto-3-cyclopentenones, γ-keto-2-cyclopentenones, or cyclopentadienyl ester derivatives. The stereo- and regioselectivity of the in situ generated lithio cyclopentadienyl enolate with various acid chlorides was investigated and analyzed, showing that the formation of the above products was significantly dependent on both the substituents on the butadienyl skeleton and the bulkiness of acid chlorides.

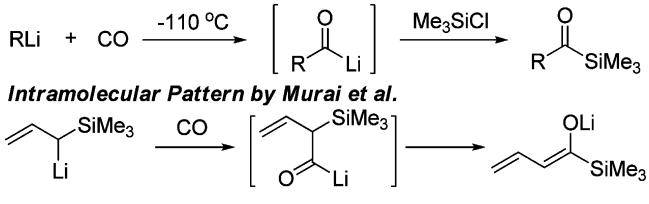


INTRODUCTION

For decades, the carbonylative reactions have been important methods for organic synthesis by direct application of carbon monoxide as a convenient one-carbon source.[1] Among them, the reaction of organolithium reagents with carbon monoxide has attracted much attention because it provides the most straightforward strategy to introduce a carbonyl group.[1b,2] Acyllithium species, which are of significant importance as reagents, have been commonly accepted as the initial intermediates.[3] However, because of their high reactivity, few selective and meaningful reactions have been developed using acyllithium compounds.[4,5] Generally, two different strategies have been successfully applied to control the complicated reactions. Seyferth and others reported the intermolecular pattern, in which electrophiles were used to trap the carbonyllithium species under careful reaction conditions.[6,7] Meanwhile, the other strategy involving an intramolecular pattern by converting reactive carbonyllithium species to enolates or ynolates was studied by Murai and others (Scheme 1).[8,9]

Cyclopentenones represent an important family of organic molecules widely existing in pharmaceuticals and natural products.[10] Many strategies for the synthesis of 2-cyclopentenones have been reported,[11−13] but the synthesis of 3-cyclopentenones is less studied.[14] Recently, we have demonstrated that 1,4-dilithio-1,3-diene derivatives **1** are of interesting and useful reactivities toward carbon monoxide. The reaction of 1,4-dilithio-1,3-diene derivatives **1** with carbon monoxide represents a novel example of highly efficient cyclocarbonylation of organolithium compounds generating 3-cyclopentenones **3** after hydrolysis.[15a] Additionally, the first oxycyclopentadienyl dilithium intermediates (OCp dianions) obtained from the reaction between 1,4-dilithio-1,3-diene **1** and carbon monoxide have been isolated and structurally

Scheme 1. Known Strategies to Apply Acyllithio Species Generated in situ from RLi and CO



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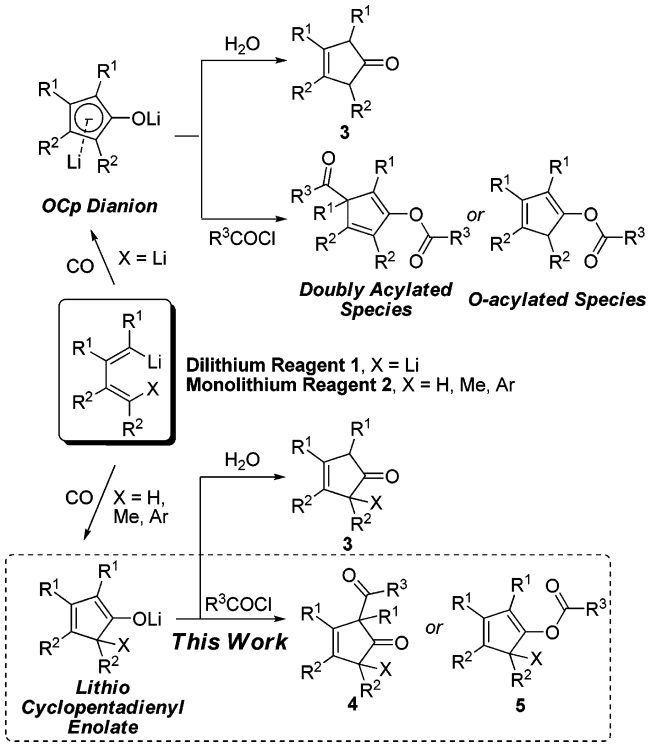
characterized.[15b] The OCp dianions displayed unique structures and novel reaction chemistry. By intermolecular acylation with acid chlorides, doubly acylated and O-acylated species could be obtained with perfect selectivity.[15] In 2002, the reaction between 1-lithio-1,3-diene derivatives **2** and carbon monoxide was reported, affording the same type product 3-cyclopentenones **3** in an unprecedented way (Scheme 2).[16]

Scheme 2. Reactions of Dienyllithium Reagents with Carbon Monoxide

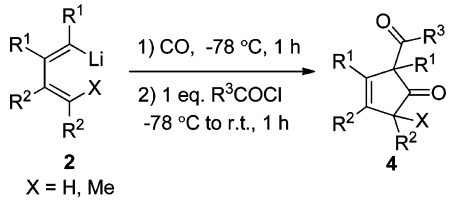


We tried to investigate further on the reaction of 1-lithio-1,3-diene derivatives **2** with carbon monoxide, with particular interest in the isolation and synthetic applications of the reactive carbonyllithio intermediates. In this paper, we report our systematic investigation of the cyclocarbonylation of substituted 1-lithio-1,3-diene derivatives **2** followed by acylation with acid chlorides. A wide variety of β-keto-3-cyclopentenone derivatives **4** and cyclopentadienyl ester derivatives **5** could be prepared (Scheme 2). Moreover, the reaction selectivity and mechanism were also studied by intermediate characterization and relevant LDA promoted deprotonation−lithiation experiments.

RESULTS AND DISCUSSION

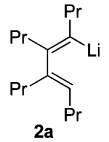
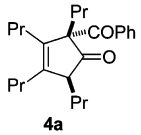
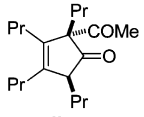
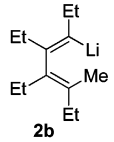
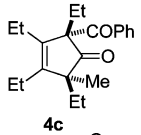
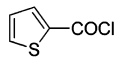
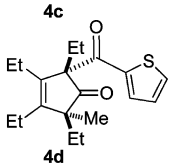
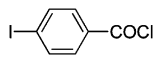
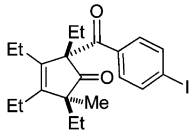
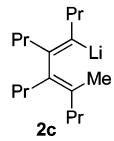
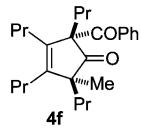
Reaction of 1-Lithio-1,3-dienes with Carbon Monoxide Followed by Intermolecular Trapping with Acid Chlorides: Formation of Multiply Substituted 3-Cyclopentenone. The 1-lithio-1,3-diene **2**, generated in situ from its corresponding monohalo compound and *t*-BuLi, was allowed to react with carbon monoxide at −78 °C for 1 h. After that, the corresponding reaction intermediate was trapped by an acid chloride, affording β-keto-3-cyclopentenone derivatives **4a**−**4f** in high isolated yields (Table 1). Only β-*C*-acylation product was observed. The regioselectivity was similar to the application of alkylation reagents, such as methyl iodide, benzyl halides,

Table 1. Formation of Multiply Substituted β-Keto-3-cyclopentenone Derivatives



2
X = H, Me

4

Entry	1-Lithio-1,3-diene	Acid chloride	Product	Yield (%)[a]
1	 **2a**	PhCOCl	 **4a**	76[b]
2	**2a**	MeCOCl	 **4b**	62[b]
3	 **2b**	PhCOCl	 **4c**	89[b]
4	**2b**		 **4d**	83[b]
5	**2b**		 **4e**	71[b]
6	 **2c**	PhCOCl	 **4f**	58[b]

[a]Isolated yields. [b]Only *cis* isomer. The two ethyl/propyl groups were in the same face.

and propargyl halides.[16] More importantly, these reactions proceeded in excellent regio- and stereoselectivity in which only *cis* products were obtained (*cis* here refers to the two identical substituents at positions 2 and 5). The structure of product **4e** was determined by single-crystal X-ray structural analysis. The two ethyl groups adjacent to the carbonyl group were confirmed in the *cis* positions (Figure 1).

In order to further investigate the effect of substitution patterns on the butadienyl skeletons, we prepared the 1,2-disubstitued 1-lithio-1,3-dienes **2d**. Interestingly, γ-*C*-acylation reactions took place to yield γ-keto-2-cyclopentenone derivatives **6** as sole products (Scheme 3). From the above experimental results, we found that the substitution patterns of the butadienyl skeleton of these monolithium reagents had important influences on the regioselectivity of their intermolecular acylation reactions.

According to the synthetic method mentioned above, multisubstituted stereodefined β-keto-3-cyclopentenone derivatives **4** and some γ-keto-2-cyclopentenone derivatives **6** could be easily constructed in one pot. In addition, the two carbonyl

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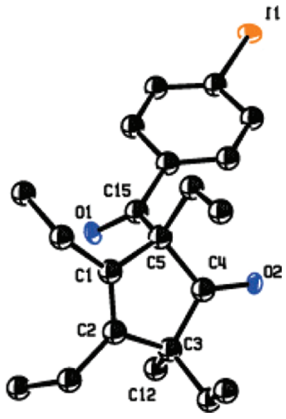
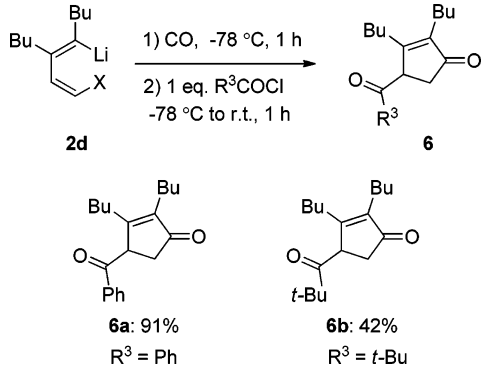


Figure 1. ORTEP drawings of **4e** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: C1−C5 1.516(6), C1−C2 1.337(6), C2−C3 1.519(6), C3−C4 1.517(6), C4−C5 1.549(6), C4−O2 1.210(5), C3−C12 1.542(6), C5−C15 1.550(6), C15−O1 1.214(5).

Scheme 3. Formation of Multiply Substituted γ-Keto-2-cyclopentenone Derivatives



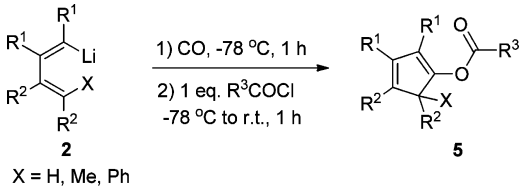
groups and the C−C double bonds in the relevant skeletons might be further modified for wider applications.[17]

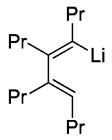
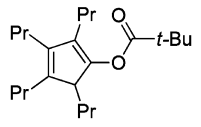
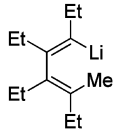
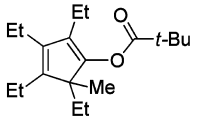
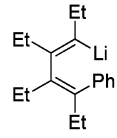
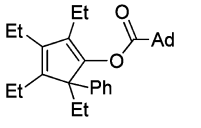
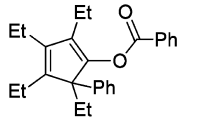
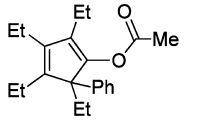
Reaction of 1-Lithio-1,3-dienes with Carbon Monoxide Followed by Intermolecular Trapping with Bulky Acid Chlorides: Formation of Multiply Substituted Cyclopentadienyl Ester. In order to study the steric effect deeply, bulky acid chlorides such as *t*-BuCOCl and AdCOCl were applied as the electrophiles. Surprisingly, *C*-acylation products were not observed. Instead, cyclopentadienyl ester derivatives **5a−c** were generated in moderate isolated yields (entries 1−3, Table 2). Moreover, when the reaction mixture of 1-lithio-4-phenyl-1,3-diene **2e** with carbon monoxide was treated with 1 equiv of relatively small PhCOCl or MeCOCl, only *O*-acylation products **5d**, **5e** were obtained in 57 and 72% yield, respectively (entries 4, 5, Table 2). This could be explained by the steric effect of the phenyl group on the skeleton of **2e**.

Cyclopentadienyl ester derivatives **5** are interesting and potential building blocks for synthetic chemistry and organometallic chemistry.[18] The reaction reported here provides a practical method for such compounds. Furthermore, these results indicate the existence of lithio cyclopentadienyl enolate intermediates.

Mechanistic Study on the Reaction of 1,2,3,4-Tetrasubstituted 1-Lithio-1,3-dienes with Carbon Monoxide. According to the proposed mechanism, the cyclo-

Table 2. Formation of Multiply Substituted Cyclopentadienyl Ester Derivatives



Entry	1-Lithio-1,3-diene	Acid chloride	Product	Yield (%)[a]
1	 **2a**	*t*-BuCOCl	 **5a**	55
2	 **2b**	*t*-BuCOCl	 **5b**	55
3	 **2e**	AdCOCl	 **5c**	59
4	**2e**	PhCOCl	 **5d**	57
5	**2e**	MeCOCl	 **5e**	72

[a]Isolated yields.

carbonylation of 1,2,3,4-tetrasubstituted 1-lithio-1,3-dienes and carbon monoxide could form a cyclic monoanion intermediate, which might be represented by three possible resonance structures **8−10** (Scheme 4). Because of the proposed intriguing transformation, we set our mind on making clear this novel cyclocarbonylation process by isolating the intermediates.

As shown in Scheme 5, the unsymmetrical substituted 1-lithio-1,3-diene **2f** was in situ generated from its corresponding monohalo compound with *t*-BuLi and was allowed to react with carbon monoxide under similar reaction conditions to those described above. Treatment of the reaction mixture with 1 equiv of *t*-BuCOCl afforded the cyclopentadienyl ester derivative **5f** in 67% isolated yield. This result is in consistence with the examples listed in Table 2. Hydrolysis of the reaction mixture afforded a mixture of two products, **3f** and **3f′**, which could be separated and obtained in 24 and 48% isolated yield, respectively. The structure of **3f** was determined by single-crystal X-ray structural analysis (see the Supporting Information for details).

The intermediate **10f** formed from the reaction of 1-lithio-1,3-diene **2f** with carbon monoxide was successfully obtained in

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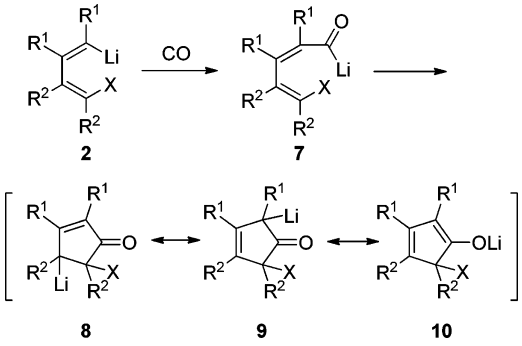
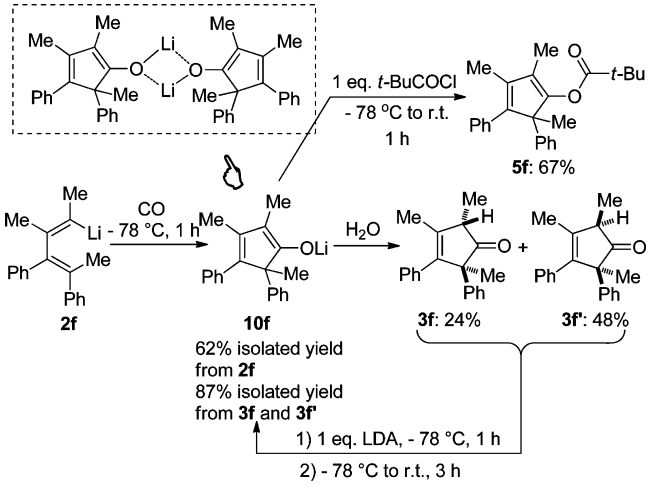
Scheme 4. Proposed Mechanism in Reactions of 1,2,3,4-Tetrasubstituted 1-Lithio-1,3-dienes with Carbon Monoxide

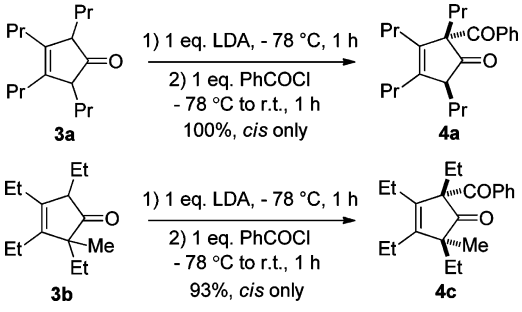


Scheme 5. Isolation of the Intermediate of 3-Cyclopentenones



62% isolated yield (Scheme 5). Meanwhile, treatment of the mixture of **3f**/**3f'** with LDA generated the same lithio species **10f** in 87% isolated yield. This result indicates that upon deprotonation–lithiation with LDA, the two isomers of **3f** and **3f'** were transformed into a single lithio intermediate. This deprotonation lithiation using LDA was also applied to other 3-cyclopentenone derivatives such as **3a** (a mixture of *cis* and *trans* isomers obtained via hydrolysis of the reaction mixture of **2a** with CO) and **3b**.[16] Similar reaction process took place, affording their corresponding acylated products **4a** and **4c** in excellent yields (Scheme 6). Thus, we confirmed that the same lithio cyclopentadienyl enolate intermediate could be obtained from both cyclocarbonylation of 1-lithio-1,3-dienes and LDA-promoted deprotonation–lithiation of 3-cyclopentenones.

Scheme 6. Deprotonation–Lithiation of 3-Cyclopentenones



Recrystallization of **10f** from THF/hexane mixed solvents afforded crystals suitable for single-crystal X-ray structural analysis (Figure 2). It features a dimeric lithio cyclopentadienyl

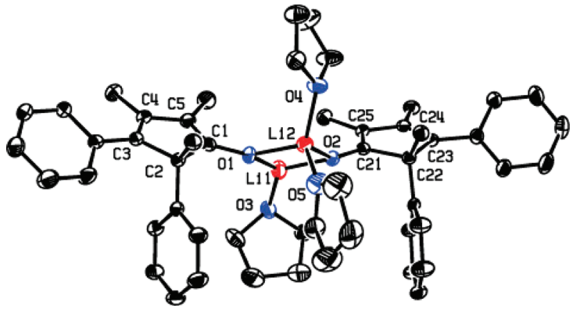


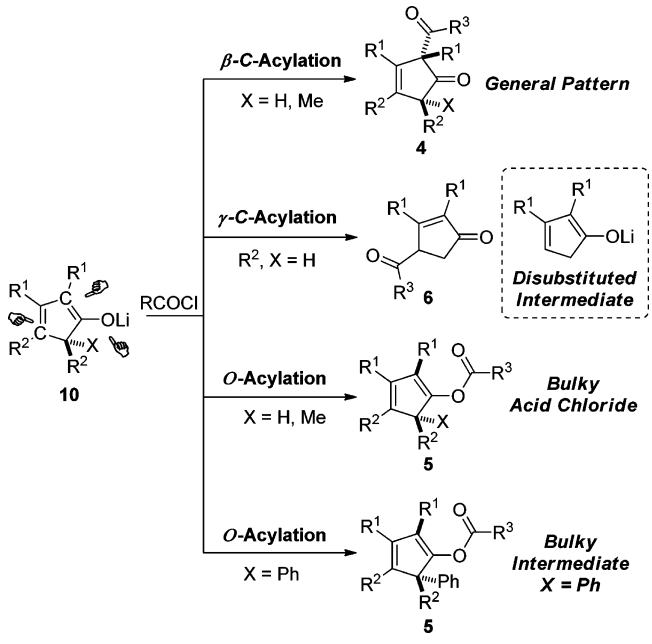
Figure 2. ORTEP drawing of **10f** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: C1–C2 1.535(4), C1–C5 1.350(4), C2–C3 1.534(4), C3–C4 1.358(4), C4–C5 1.456(4), C1–O1 1.317(3), O1–Li1 1.828(6), O1–Li2 1.913(5), O2–Li1 1.837(5), O2–Li2 1.908(5), C21–O2 1.307(3), C21–C22 1.549(4), C21–C25 1.358(4), C22–C23 1.532(4), C23–C24 1.357(4), C24–C25 1.455(4).

enolate structure, being connected through a 4-membered "Li_2O_2" moiety.[15b,19] Quantitative formation of **5f** or the mixture of **3f**/**3f'** (1:2 molar ratio) was observed when the isolated **10f** was treated with *t*-BuCOCl or H_2O, respectively.

Regioselectivity and Stereoselectivity Analysis. As described above, these reactions displayed high regioselectivity depending on the substituents on the butadienyl skeleton and the bulkiness of acid chlorides. Generally, the lithio cyclopentadienyl enolate intermediate **10** was trapped by acid chloride affording *β*-*C*-acylation products **4**. The regioselectivity is summarized in Scheme 7.

The *γ*-*C*-acylation species **6** could be obtained when the disubstituted enolate lithium intermediate was used. For the corresponding reaction intermediate, the *γ* position was sterically favored in nucleophilic substitution. However, if a

Scheme 7. Regioselectivity Analysis



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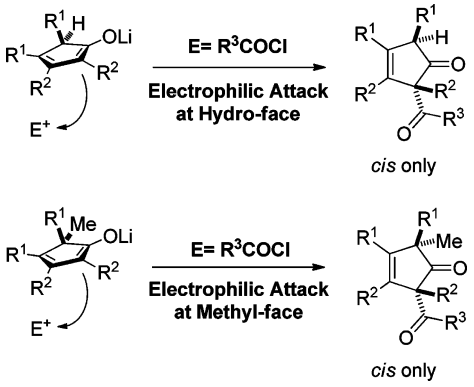
bulky lithio cyclopentadienyl enolate intermediate or acid chloride was tried, *O*-acylation cyclopentadienyl ester derivatives were formed. These results could be explained by the steric effect of the phenyl group in the corresponding lithio cyclopentadienyl enolate and bulky acid chloride.

Besides the high regioselectivity, excellent stereoselectivity was also observed in these cyclocarbonylation reactions affording solely *cis* isomer products because of the acid chloride attack at the less-hindered face (Scheme 8). For the hydrolysis of the lithium dienolate, although the thermodynamically controlled process is possible, the kinetically controlled path seems more likely.

Scheme 8. Stereoselectivity Analysis



CONCLUSION

In summary, we have described a highly efficient and selective cyclocarbonylation of monolithiobutadienes with carbon monoxide affording 3-cyclopentenone derivatives. When various acid chlorides were used to trap the reaction mixture of monolithiobutadienes and carbon monoxide, 3-cyclopentenone and cyclopentadienyl ester derivatives could be obtained. Meanwhile, relevant results clearly demonstrated that the substitution patterns on the butadienyl skeletons and the bulkiness of acid chloride markedly influenced the regioselectivity and stereoselectivity. In order to understand the reaction mechanism deeply, the lithio cyclopentadienyl enolate intermediate was isolated and characterized by single-crystal X-ray structural analysis. The designed LDA-promoted deprotonation–lithiation experimental results confirmed the presence of an enolate–Li intermediate.

EXPERIMENTAL SECTION

General Method. All reactions were carried out under a slightly positive pressure of dry and oxygen-free nitrogen by using standard Schlenk line techniques or under a nitrogen atmosphere in a Glovebox. The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer to ensure both were always below 1 ppm. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvent was distilled from sodium/benzophenone ketyl under a nitrogen atmosphere. All 1-halo-1,3-butadiene derivatives used as starting materials were synthesized following the reported procedure.[20] 1-Lithio-1,3-butadienes were synthesized by lithium–halogen exchange reactions.

^{1}H NMR and ^{13}C NMR spectra were recorded on spectrometers (FT, 300 MHz for ^{1}H; 75 MHz for ^{13}C; FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C; FT, 500 MHz for ^{1}H; 125 MHz for ^{13}C) at room temperature. Infrared spectra (IR) were recorded on a FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a FTMS mass spectrometer using ESI (electrospray ionization) and FT-ICR mass analyzer or mass spectrometer using EI (electro-ionization). Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve NMR tubes.

Typical Procedure for Hydrolysis of the Carbonylation Reaction Mixture of the Full-Substituted 1-Lithio-1,3-dienes Derivatives and Carbon Monoxide. To a solution of 1-halo-1,3-butadienes (0.5 mmol) in THF–Et_2O (5 mL, 1:1) was added 2 equiv of *t*-BuLi at −78 °C. After it was stirred at −78 °C for 1 h, CO was then bubbled into the reaction mixture for 0.5 h. The above reaction mixture was stirred for an additional 0.5 h under CO atmosphere. Then, the reaction mixture was quenched by water and allowed to warm to room temperature. Aqueous layer of the above quenched mixture was extracted with Et_2O, and the combined organic layer was washed with brine. Solvent was evaporated, and the residue was purified by column chromatography to give corresponding product **3**. The isolated lithio cyclopentadienyl enolate **10f** was quenched by water affording the same results.

2,3,4,5-Tetraethyl-2-methylcyclopent-3-enone (3b). Yellow liquid: isolated yield 75% (78 mg); ^{1}H NMR (300 MHz, $CDCl_3$, $SiMe_4$) δ 0.64 (t, J = 7.5 Hz, 3H, CH_3), 0.90 (t, J = 7.5 Hz, 3H, CH_3), 1.01–1.10 (m, 9H, CH_3), 1.38–1.60 (m, 2H, CH_2), 1.64–1.82 (m, 2H, CH_2), 1.97–2.08 (m, 2H, CH_2), 2.15–2.22 (m, 1H, CH_2), 2.39–2.46 (m, 1H, CH_2), 2.85 (t, J = 5.7 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, $SiMe_4$) δ 9.8, 11.2, 12.5, 15.0, 18.0, 19.3, 20.9, 23.8, 28.5, 51.8, 56.5, 137.5, 140.8, 224.3; IR (neat) ν (C=O) = 1741 cm^{-1}; HRMS (ESI) calcd. for $C_{14}H_{25}O$ $[M + H]^+$ 209.1900, found 209.1902.

2,4,5-Trimethyl-2,3-diphenylcyclopent-3-enone (3f). White solid: isolated yield 24% (33 mg); mp 98–99 °C; ^{1}H NMR (300 MHz, $CDCl_3$, $SiMe_4$) 1.28 (d, J = 7.2 Hz, 3H, CH_3), 1.46 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 3.21 (q, J = 7.2 Hz, 1H, CH), 6.94–6.97 (m, 2H, CH), 7.19–7.35 (m, 8H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, $SiMe_4$) 13.4, 13.8, 20.0, 49.1, 60.7, 126.5, 126.9, 127.1, 127.9, 128.7, 129.0, 135.5, 136.8, 140.5, 140.7, 217.9; IR (neat) ν (C=O) = 1749 cm^{-1}; HRMS (ESI) calcd. for $C_{20}H_{21}O$ $[M + H]^+$ 277.1587, found 277.1581. Anal. Calcd. for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.96; H, 7.32. Recrystallization of **3f** from hexane at room temperature afforded single crystals for X-ray analysis.

2,4,5-Trimethyl-2,3-diphenylcyclopent-3-enone (3f′). Colorless liquid: isolated yield 48% (66 mg); ^{1}H NMR (300 MHz, $CDCl_3$, $SiMe_4$) 1.31 (d, J = 7.8 Hz, 3H, CH_3), 1.51 (s, 3H, CH_3), 1.89 (s, 3H, CH_3), 3.08 (q, J = 7.8 Hz, 1H, CH), 6.91–6.94 (m, 2H, CH), 7.17–7.29 (m, 8H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, $SiMe_4$) 13.4, 14.7, 20.6, 49.9, 61.2, 126.8, 127.0, 127.2, 127.8, 128.4, 129.2, 135.5, 136.7, 140.6, 141.6, 220.3; IR (neat) ν (C=O) = 1747 cm^{-1}; HRMS (ESI) calcd. for $C_{20}H_{21}O$ $[M + H]^+$ 277.1587, found 277.1581.

Typical Procedure for the Reaction of 1-Lithio-1,3-dienes with Carbon Monoxide Followed by Intermolecular Trapping with Acid Chlorides in Et_2O–THF. To a solution of 1-halo-1,3-butadienes (0.5 mmol) in THF–Et_2O (5 mL, 1:1) was added 2 equiv of *t*-BuLi at −78 °C. After it was stirred at −78 °C for 1 h, CO was then bubbled into the reaction mixture for 0.5 h. The above reaction mixture was stirred for an additional 0.5 h under CO atmosphere. Next, for **4**–**6**, acid chloride (0.5 mmol) was added, and the reaction mixture was allowed to warm to room temperature. Then, the reaction mixture was quenched by water after 1 h. Aqueous layer of the above quenched mixture was extracted with Et_2O, and the combined organic layer was washed with brine. Solvent was evaporated, and the residue was purified by column chromatography to give products **4**–**6**. The isolated lithio cyclopentadienyl enolate **10f** was allowed to react with acid chlorides to afford the same results.

2-Benzoyl-2,3,4,5-tetrapropylcyclopent-3-enone (4a). Colorless liquid: isolated yield 76% (135 mg); ^{1}H NMR (300 MHz, $CDCl_3$, $SiMe_4$) δ 0.84–0.97 (m, 12H, CH_3), 1.03–1.81 (m, 12H, CH_2), 2.00–2.44 (m, 4H, CH_2), 3.03 (t, J = 4.5 Hz, 1H, CH), 7.27–7.43 (m, 3H, CH), 7.59–7.62 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, $SiMe_4$) δ

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14.1, 14.1, 14.4, 14.6, 17.6, 20.3, 20.5, 22.7, 28.5, 28.8, 31.5, 35.5, 53.7, 74.8, 127.6, 128.1, 131.7, 137.6, 139.1, 141.3, 198.9, 217.9; IR (neat) ν (C═O) = 1676, 1740 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{35}O_2$ $[M + H]^+$ 355.2632, found 355.2636.

2-Acetyl-2,3,4,5-tetrapropylcyclopent-3-enone (4b). Colorless liquid: isolated yield 62% (91 mg); ^1H NMR (300 MHz, $CDCl_3$, $SiMe_4$) δ 0.90−1.01 (m, 12H, CH_3), 1.26−1.74 (m, 10H, CH_2), 1.90−2.15 (m, 7H, $1CH_3$, $2CH_2$), 2.35−2.45 (m, 2H, CH_2), 3.07 (t, J = 6 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, $SiMe_4$) δ 14.2, 14.3, 14.5, 14.7, 17.9, 20.3, 20.9, 22.6, 26.7, 28.5, 28.7, 30.9, 32.5, 53.4, 76.4, 136.1, 142.2, 203.9, 218.0; IR (neat) ν (C═O) = 1708, 1742 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{33}O_2$ $[M + H]^+$ 293.2475, found 293.2478.

2-Benzoyl-2,3,4,5-tetraethyl-5-methylcyclopent-3-enone (4c). Colorless liquid: isolated yield 89% (139 mg); ^1H NMR (300 MHz, $CDCl_3$, $SiMe_4$) δ 0.79 (t, J = 7.5 Hz, 3H, CH_3), 0.87 (t, J = 7.5 Hz, 3H, CH_3), 0.97 (s, 3H, CH_3), 1.05 (t, J = 7.5 Hz, 3H, CH_3), 1.17 (t, J = 7.5 Hz, 3H, CH_3), 1.44−1.73 (m, 3H, CH_2), 2.16−2.37 (m, 4H, CH_2), 2.53−2.60 (m, 1H, CH_2), 7.29−7.41 (m, 3H, CH), 7.67−7.69 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, $SiMe_4$) δ 9.1, 9.7, 14.1, 14.3, 18.9, 19.8, 21.9, 27.3, 30.3, 56.8, 74.8, 127.9, 128.1, 131.3, 137.8, 139.4, 145.7, 200.0, 218.4; HRMS (EI) calcd. for $C_{21}H_{28}O_2$ 312.2089, found 312. 2092.

2,3,4,5-Tetraethyl-2-methyl-5-(thiophene-2-carbonyl)-cyclopent-3-enone (4d). Colorless liquid: isolated yield 83% (132 mg); ^1H NMR (300 MHz, $CDCl_3$, $SiMe_4$) δ 0.80 (t, J = 7.5 Hz, 3H, CH_3), 0.90 (t, J = 7.5 Hz, 3H, CH_3), 1.07 (t, J = 7.5 Hz, 3H, CH_3), 1.10 (s, 3H, CH_3), 1.20 (t, J = 7.5 Hz, 3H, CH_3), 1.51−1.56 (m, 1H, CH_2), 1.72−1.86 (m, 2H, CH_2), 2.14−2.38 (m, 4H, CH_2), 2.56−2.60 (m, 1H, CH_2), 7.04 (t, J = 4.5 Hz, 1H, CH), 7.54 (d, J = 5.1 Hz, 1H, CH), 7.94 (d, J = 4.2 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, $SiMe_4$) δ 9.1, 10.0, 14.1, 14.2, 19.0, 20.4, 22.4, 28.1, 29.7, 56.7, 74.2, 127.8, 133.3, 133.4, 138.4, 143.1, 145.3, 190.4, 216.9; HRMS (EI) calcd. for $C_{19}H_{26}O_2S$ 318.1654, found 318.1651.

2,3,4,5-Tetraethyl-2-(4-iodobenzoyl)-5-methylcyclopent-3-enone (4e). Colorless solid: isolated yield 71% (155 mg); ^1H NMR (300 MHz, $CDCl_3$, $SiMe_4$) δ 0.79 (t, J = 7.5 Hz, 3H, CH_3), 0.85 (t, J = 7.5 Hz, 3H, CH_3), 1.03 (t, J = 7.5 Hz, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.17(t, J = 7.5 Hz, 3H, CH_3), 1.45−1.52 (m, 1H, CH_2), 1.62−1.74 (m, 2H, CH_2), 2.12−2.37 (m, 4H, CH_2), 2.50−2.58 (m, 1H, CH_2), 7.45−7.48 (m, 2H, CH), 7.68−7.71 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, $SiMe_4$) δ 9.0, 9.7, 14.1, 14.3, 18.8, 19.8, 22.0, 27.5, 30.2, 56.8, 74.6, 98.9, 129.8, 137.1, 137.8, 138.3, 145.8, 198.9, 218.1; HRMS (EI) calcd. for $C_{21}H_{27}IO_2$ 438.1056, found 438.1060. Recrystallization of **4e** from hexane solvent at room temperature afforded single crystals for X-ray analysis.

2-Benzoyl-5-methyl-2,3,4,5-tetrapropylcyclopent-3-enone (4f). Colorless liquid: isolated yield 58% (107 mg); ^1H NMR (300 MHz, $CDCl_3$, $SiMe_4$) δ 0.82−1.05 (m, 15H, CH_3), 1.00−1.60 (m, 12H, CH_2), 2.04−2.21 (m, 3H, CH_2), 2.44 (m, 1H, CH_2), 7.29−7.41 (m, 3H, CH), 7.65−7.68 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, $SiMe_4$) δ 14.7 (2 CH_3), 15.0, 15.1, 17.8, 18.3, 22.4, 22.9, 23.0, 28.6, 29.6, 36.7, 40.0, 56.7, 74.6, 127.9, 128.1, 131.3, 137.1, 139.3, 144.5, 199.9, 218.5; HRMS (EI) calcd. for $C_{25}H_{36}O_2$ 368.2715, found 368.2717.

4-Benzoyl-2,3-dibutylcyclopent-2-enone (6a). Colorless liquid: isolated yield 91% (136 mg); ^1H NMR (300 MHz, $CDCl_3$, $SiMe_4$) δ 0.85 (t, J = 6.6 Hz, 3H, CH_3), 0.92 (t, J = 6.6 Hz, 3H, CH_3), 1.31−1.47 (m, 8H, CH_2), 2.23−2.32 (m, 3H, CH_2), 2.53−2.60 (m, 1H, CH_2), 2.39−2.46 (m, 1H, CH_2), 2.70−2.79 (m, 1H, CH_2). 4.71−4.73 (m, 1H, CH), 7.49−7.65 (m, 3H, CH), 7.99−8.01 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, $SiMe_4$) δ 13.7, 14.0, 22.7, 22.8, 23.2, 29.6, 29.7, 30.6, 39.4, 47.6, 128.5, 129.0, 133.8, 136.4, 143.0, 171.4, 199.4, 206.9; IR (neat) ν (C═O) = 1682, 1702 cm^{-1}; HRMS (EI) calcd. for $C_{20}H_{26}O_2$ 298.1933, found 298.1934.

2,3-Dibutyl-4-pivaloylcyclopent-2-enone (6b). Colorless liquid: isolated yield 42% (58 mg); ^1H NMR (300 MHz, $CDCl_3$, $SiMe_4$) δ 0.88−0.94 (m, 6H, CH_3), 1.22−1.52 (m, 17H, 4 CH_2, 3 CH_3), 2.02−2.23 (m, 4H, CH_2), 2.46−2.61 (m, 2H, CH_2), 4.23−4.25 (m, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, $SiMe_4$) δ 13.8, 14.0, 22.7, 22.9, 23.2, 26.2, 29.6, 29.9, 30.6, 40.2, 44.9, 46.6, 143.3, 171.7, 207.2, 215.3; HRMS (EI) calcd. for $C_{18}H_{30}O_2$ 278.2246, found 278.2244.

2,3,4,5-Tetrapropylcyclopenta-1,3-dien-1-yl Pivalate (5a). Colorless liquid: isolated yield 55% (92 mg); ^1H NMR (300 MHz, $CDCl_3$, $SiMe_4$) δ 0.79−1.21 (m, 14H, $1CH_2$, $4CH_3$), 1.30−1.50 (m, 17H, $4CH_2$, $3CH_3$), 1.96−2.34 (m, 6H, CH_2), 3.37 (t, J = 3.2 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, $SiMe_4$) δ 14.2, 14.2, 14.3, 14.6, 17.4, 22.3, 23.5, 23.9, 26.3, 27.3, 27.8, 28.6, 29.8, 39.1, 48.3, 129.3, 137.4, 137.7, 150.6, 177.2; HRMS (EI) calcd. for $C_{22}H_{38}O_2$ 334.2872, found 334.2875.

2,3,4,5-Tetraethyl-5-methylcyclopenta-1,3-dien-1-yl Pivalate (5b). Colorless liquid: isolated yield 55% (80 mg); ^1H NMR (300 MHz, $CDCl_3$, $SiMe_4$) δ 0.53 (t, J = 7.2 Hz, 3H, CH_3), 0.98−1.08 (m, 12H, CH_3), 1.31 (s, 9H, CH_3), 1.47 (q, J = 7.2 Hz, 2H, CH_2), 2.00−2.27 (m, 6H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$, $SiMe_4$) δ 8.1, 13.2, 14.6, 15.0, 17.7, 17.9, 19.0, 21.0, 27.4, 27.8, 39.1, 54.2, 130.2, 138.8, 141.3, 151.4, 176.1; HRMS (EI) calcd. for $C_{19}H_{32}O_2$ 292.2402, found 292.2400.

2,3,4,5-Tetraethyl-5-phenylcyclopenta-1,3-dien-1-yl Adamantane-1-carboxylate (5c). Colorless liquid: isolated yield 59% (128 mg); ^1H NMR (300 MHz, $CDCl_3$, $SiMe_4$) δ 0.70−0.75 (m, 6H, CH_3), 1.04−1.13 (m, 6H, CH_3), 1.59−1.74 (m, 11H, 3CH, $4CH_2$), 1.93−2.21 (m, 10H, CH_2), 2.32 (q, J = 7.5 Hz, 2H, CH_2), 7.11−7.21 (m, 5H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, $SiMe_4$) δ 7.7, 13.1, 14.2, 14.9, 18.1, 18.8, 19.1, 23.2, 27.9, 36.4, 38.7, 40.9, 61.6, 126.1, 126.9, 127.7, 131.9, 140.0, 140.8, 142.3, 151.8, 174.0; HRMS (EI) calcd. for $C_{30}H_{40}O_2$ 432.3028, found 432.3030.

2,3,4,5-Tetraethyl-5-phenylcyclopenta-1,3-dien-1-yl Benzoate (5d). Colorless liquid: isolated yield 57% (107 mg); ^1H NMR (300 MHz, $CDCl_3$, $SiMe_4$) δ 0.74 (t, J = 7.5 Hz, 3H, CH_3), 0.82 (t, J = 7.5 Hz, 3H, CH_3), 1.07−1.17 (m, 6H, CH_3), 1.97−2.16 (m, 4H, CH_2), 2.23−2.40 (m, 4H, CH_2), 7.13−7.34 (m, 5H, CH), 7.34−7.39 (m, 2H, CH), 7.48−7.53 (m, 1H, CH), 7.91−7.93 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, $SiMe_4$) δ 7.8, 13.0, 14.2, 14.9, 18.3, 18.8, 19.1, 23.1, 61.8, 126.2, 126.8, 128.0, 128.3, 129.8, 130.0, 132.6, 133.0, 140.0, 140.5, 143.0, 151.7, 163.0; HRMS (EI) calcd. for $C_{26}H_{30}O_2$ 374.2246, found 374.2244.

2,3,4,5-Tetraethyl-5-phenylcyclopenta-1,3-dien-1-yl Acetate (5e). Colorless liquid: isolated yield 72% (112 mg); ^1H NMR (300 MHz, $CDCl_3$, $SiMe_4$) δ 0.68−0.74 (m, 6H, CH_3), 1.06−1.13 (m, 6H, CH_3), 1.90−2.08 (m, 7H, $2CH_2$, $1CH_3$), 2.20 (q, J = 7.5 Hz, 2H, CH_2), 2.32 (q, J = 7.5 Hz, 2H, CH_2), 7.18 (s, 5H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, $SiMe_4$) δ 7.6, 12.9, 14.1, 14.9, 18.2, 18.7, 19.1, 20.7, 22.9, 61.5, 126.2, 126.8, 127.9, 132.3, 140.0, 140.4, 142.8, 151.8, 167.5; HRMS (EI) calcd. for $C_{21}H_{28}O_2$ 312.2098, found 312.2092.

2,3,5-Trimethyl-4,5-diphenylcyclopenta-1,3-dien-1-yl Pivalate (5f). White solid: isolated yield 67% (121 mg); mp 76−78 °C; ^1H NMR (400 MHz, $CDCl_3$, $SiMe_4$) δ 1.12 (s, 9H, CH_3), 1.41 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 6.83−6.85 (m, 2H, CH), 7.14−7.23 (m, 8H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$) δ 10.2, 12.8, 18.2, 27.1, 39.0, 58.2, 125.0, 126.3, 126.4, 126.6, 127.8, 128.1, 128.9, 135.9, 136.1, 139.3, 143.4, 156.2, 175.2; IR (neat) ν (C═O) = 1751 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{29}O_2$ $[M + H]^+$ 361.2162, found 361.2171.

Typical Procedure for the Isolation of Intermediate 10f from the Reaction of 1-Lithio-1,3-diene 2f with Carbon Monoxide. To a solution of 1-halo-1,3-butadienes (0.5 mmol) in THF−Et_2O (5 mL, 1:1) was added 2 equiv of *t*-BuLi at −78 °C. After it was stirred at −78 °C for 1 h, CO was then bubbled into the reaction mixture for 0.5 h. The above reaction mixture was stirred for additional 0.5 h under CO atmosphere. Next, the reaction mixture was allowed to warm to room temperature. Then, the solvents were removed under vacuum in glovebox, and the residue was dissolved in hexane and filtered. This step may need to be repeated several times until the residue powder can be totally dissolved in hexane to form a clear solution. Thus obtained powder as salt free **10f** is pure enough for NMR analysis.

Lithio Cyclopentadienyl Enolate Intermediate (10f). Yellow solid: ^1H NMR (500 MHz, C_4D_8O) δ 1.30 (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 6.75−7.18 (m, 10H, CH); ^{13}C NMR (100 MHz, C_4D_8O) δ 9.5, 14.6, 20.3, 58.9, 101.3, 123.0, 125.2, 127.6, 127.8,

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127.9, 128.3, 130.1, 139.7, 143.8, 147.5, 182.8. Recrystallization of **10f** from THF−hexane at room temperature afforded single crystals for X-ray analysis.

Typical Procedure for the Preparation of Intermediate 10f from the Deprotonation Lithiation of 3-Cyclopentenones Using LDA. One equivalent of LDA was added into the solution of 3-cyclopentenones **3f**−**3f′** (0.5 mmol, 1:2) in Et_2O−THF (5 mL, 1:1) at −78 °C. After it was stirred at −78 °C for 1 h, the reaction mixture was allowed to warm to room temperature for 3 h. Then, the solvents were removed under vacuum in a glovebox, and the residue was dissolved in hexane and filtered. The resulting powders **10f** were recrystallized from hexane at −30 °C, affording suitable crystals for NMR analysis and X-ray analysis.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data for **3f**, **4e**, and **10f** and NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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