BF_3·OEt_2-Mediated C–C Bond-Forming Reaction of α-Hydroxyketene-(*S*,*S*)-acetals with Active Methylene Compounds and Its Application in the Synthesis of Substituted 3,4-Dihydro-2-pyridones

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Abstract: The C–C bond-forming reaction between α-hydroxyketene-(*S*,*S*)-acetals **2** and active methylene compounds is described. Mediated by boron trifluoride etherate (BF_3·OEt_2), a series of C–C bond coupling products, 2-(2-acetyl-1-methyl-3-oxobutyl)-*N*-aryl-3,3-bis(ethylthio)acrylamides **3** was obtained in high to excellent yields by the reaction of **2a**–**e** (R^1 = Ar) with acetylacetone. Various *N*-aryl-substituted 3,4-dihydropyridones **5** were prepared in high yields from **3** via a two-step procedure. Upon the reaction of **2f** (R^1 = H) with active methylene compounds, 3,4-dihydropyridones **6** and/or **7**, were obtained in a one-pot reaction with moderate to good yields.

Keywords: C–C bond-forming reaction, α-hydroxyketene-(*S*,*S*)-acetals, active methylene compounds, substituted 3,4-dihydro-2-pyridones, one-pot synthesis

The carbon–carbon bond-forming reaction is one of the most fundamental approaches for the construction of molecular framework in organic chemistry.[1] In carbon–carbon bond-forming reactions, the direct displacement of the hydroxyl group of an allylic or benzylic alcohol by a carbon nucleophile would be quite useful since it would be both atom-efficient and environmentally benign because preparation of the reactive materials would not be required (alcohols are generally transformed into the corresponding halides or esters prior to reactions with nucleophiles due to the fact that the hydroxyl group is a poor leaving group) and only water would be generated as a side product.[2] In this context, expansion of substrates for this type of reaction to a wide range of active methylene compounds and other types of alcohols is desired and has stimulated much interest in organic chemists. Recently, Baba and co-workers described the direct carbon–carbon bond forming from alcohols and active methylenes, alkoxyketones, and indoles catalyzed by indium trichloride.[3] Kaneda et al. reported a Brønsted acid mediated heterogeneous addition reaction of 1,3-dicarbonyl compounds to alkenes and alcohols.[4] Hence, the selection of suitable substrates, especially the alcohol component, for the carbon–carbon bond-forming reaction is of great significance in achieving the synthetic applications.[2,3]

Over the past decades, the utility of α-oxoketene-(*S*,*S*)-acetals as versatile intermediates in organic synthesis has been recognized.[5] In our recent research, α-alkenoyl ketene-(*S*,*S*)-acetals, as five-carbon 1,5-bielectrophilic synthons, have been utilized to construct six-membered carbocycles and/or heterocycles including highly substituted phenols, functionalized 2,3-dihydro-4-pyridones, pyrido[2,3-*d*]pyrimidines and 2,3-dihydrothiopyran-4-ones based on [5C+1C],[6a] [5C+1N],[6b,c] and [5C+1S][6d] annulation strategies, respectively. On the other hand, as part of the synthetic applications of α-oxoketene-(*S*,*S*)-acetals,[7] a series of α-hydroxyketene-(*S*,*S*)-acetals was obtained based on the Morita–Baylis–Hillman (MBH) reactions of α-acetylketene-(*S*,*S*)-acetals (used as activated alkenes) with carbonyl compounds in the presence of titanium tetrachloride catalyst.[8] It was found that the resulting α-hydroxyketene-(*S*,*S*)-acetals, as a special type of allylic alcohol, may further react with α-acetylketene-(*S*,*S*)-acetals (activated alkene), furnishing the double MBH adducts.[8] This procedure provides a new entry to chemoselective C_{sp2}–C_{sp3} bond formation starting from the corresponding α-hydroxyketene-(*S*,*S*)-acetals. Asokan and co-workers also presented the utility of α-hydroxyketene dithioacetals in organic synthesis. For example, they reported the synthesis of substituted pyridines from Vilsmeier–Haack reactions of α-hydroxyketene-(*S*,*S*)-acetals[9] and the synthesis of α,β-unsaturated dithioesters from the reaction of α-hydroxyketene-(*S*,*S*)-acetals with Lawesson's reagent.[10] Inspired by the abovementioned MBH reactions, in our continuing research on the synthetic applications of α-oxoketene-(*S*,*S*)-acetals, we focused our attention on the construction of a C_{sp3}–C_{sp3} bond from α-hydroxyketene-(*S*,*S*)-acetals and active methylene compounds. The application of this methodology led to the formation of a C–C coupling product, which in turn could be used for the synthesis of 3,4-dihydro-2-pyridones, which serve as valuable building blocks in the construction of piperidines, perhydroquinolones, indolizidines, quinolizidines and other alkaloid ring systems and have a wide range of biological and pharmacological activities.[11] The general and common methods towards 3,4-dihydro-2-pyridones require multistep synthesis,[12–14] usually via a combination of three steps: (1) a condensation, (2) a conjugate addition, and (3) an N-acylation.[14a] Therefore, development of simple and convenient synthetic procedures for such nitrogen-containing heterocycles represents an attractive and interesting area of research in synthetic organic and medicinal chemistry. Herein, we wish to report our experimental results.

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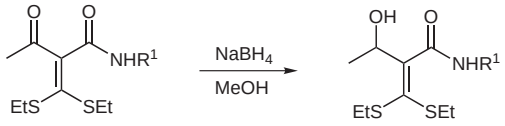
Initially, a variety of α-hydroxyketene-(*S*,*S*)-acetals **2** were prepared in excellent yields by reduction with sodium borohydride of the corresponding α-acetylketene-(*S*,*S*)-acetals **1**.[15] For example, upon treatment of **1a** with sodium borohydride (1.1 equiv) in methanol at 0 °C for about 55 minutes, alcohol **2a** was obtained in 96% isolated yield after workup (Table 1). Similarly, alcohols **2b–f** were obtained in 93–97% yields under the identical conditions.

Table 1 Reduction Reactions of α-Acetylketene-(*S*,*S*)-acetals **1**



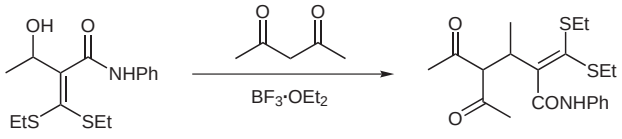
1a–f **2a–f**

Entry	Substrate	R^1	Product	Time (min)	Yield (%)[a]
1	**1a**	C_6H_5	**2a**	55	96
2	**1b**	4-ClC_6H_4	**2b**	45	97
3	**1c**	2-MeC_6H_4	**2c**	45	95
4	**1d**	2,4-$Me_2C_6H_3$	**2d**	60	93
5	**1e**	2-$MeOC_6H_4$	**2e**	50	93
6	**1f**	H	**2f**	30	95

[a] Isolated yields after silica gel chromatography.

With the readily available alcohols **2** in hand, we next turned to the study of the C–C cross-coupling reaction of **2** with active methylene compounds (Table 2 and Table 3). A model reaction between **2a** (R^1 = Ph) with acetylacetone was first examined to optimize the reaction conditions. Thus, the variation of solvents (THF, DMF, CH_2Cl_2 and MeCN) and temperature (0 °C to r.t.) were investigated (Table 2). It was found that either in dichloromethane or in *N*,*N*-dimethylformamide, no C–C cross-coupling products were detected when the reaction of **2a** with acetylacetone (1.2 equiv) proceeded at 0 °C for three hours in the presence of BF_3·OEt_2 (1.2 equiv) (Table 2, entries 1 and 2). When tetrahydrofuran or acetonitrile was used as the solvent (entries 3 and 4, respectively), the reaction afforded **3a** in low to moderate yields. However, when the reaction was carried out with neat acetylacetone (**2a**–acetylacetone = 1.0:15.0, molar ratio) and was catalyzed by BF_3·OEt_2 (1.2 equiv) at 0 °C for 40 minutes, the product **3a** was obtained in 87% yield (Table 2, entry 5). When the reaction was performed at room temperature, **3a** was produced in relatively low yield (70%, Table 2, entry 6). Under the optimized conditions as described above (Table 2, entry 5), the corresponding C–C coupling products **3b–e** (R^1 = Ar) were obtained in high to excellent yields (82–90%, Table 3, entries 1–4).[16]

Table 2 Reaction of **2a** with Acetylacetone under Different Conditions



2a **3a**

Entry[a]	**2a** (mmol)	Acetylacetone (mmol)	Solvent	Time (h)	Yield of **3a** (%)[b]
1	1.0	1.2	CH_2Cl_2	3.0	0[c]
2	1.0	1.2	DMF	3.0	0[c]
3	1.0	1.2	THF	2.0	12
4	1.0	1.2	MeCN	2.0	45
5	1.0	15.0	–	0.7	87
6	1.0	15.0	–	0.5	70

[a] BF_3 (1.2 equiv) was used in all the reactions.
[b] Isolated yields after silica gel chromatography.
[c] Complex product mixture was obtained.

Table 3 Reactions of α-Hydroxyketene-(*S*,*S*)-acetals **2** with Acetylacetone

Entry	Substrate	R^1	Time (min)	Product	Yield of **3** (%)[a]
1	**2b**	4-ClC_6H_4	30	**3b**	90
2	**2c**	2-MeC_6H_4	45	**3c**	82
3	**2d**	2,4-$Me_2C_6H_3$	50	**3d**	84
4	**2e**	2-$MeOC_6H_4$	50	**3e**	82

[a] Isolated yields after silica gel chromatography.

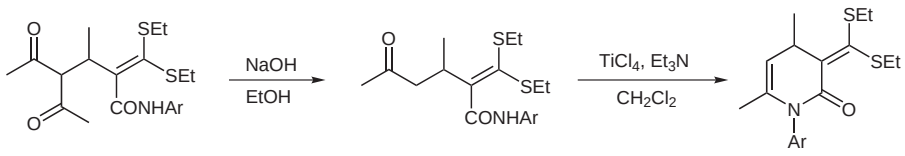
Once products **3a–e** were obtained, their transformation into pyridones was studied. However, direct transformation of **3** into pyridones with either BF_3·OEt_2 or titanium tetrachloride–triethylamine was unsuccessful after several attempts. Looking for an alternative route, compounds **3a–e** were then deacetylated by treatment with sodium hydroxide (1.2 equiv) in ethanol at 60 °C, affording products **4a–e** in 80–89% yields (Table 4). The aza-annulation of **4a–e** was tried in the presence of BF_3·OEt_2 (1.2 equiv) at 0 °C, but the desired products were not obtained. To our delight, by replacing BF_3·OEt_2 with titanium tetrachloride–triethylamine, the cyclization products *N*-aryl-substituted 3,4-dihydro-2-pyridones **5a–e** were generated in 81–88% yields (Table 4).[17]

Meanwhile, the reactions of alcohol **2f** (R^1 = H) with active methylene compounds were investigated under identical conditions as mentioned above. Interestingly, the formation of a pyridone ring was achieved by a one-pot process (Table 5). Thus, when **2f** was treated with acetylacetone (15.0 equiv) and boron trifluoride, pyridone **6a** was obtained as the sole product (Table 5, entry 1). To extend this interesting one-pot reaction, other active methylene compounds such as β-ketoesters, β-diesters and

benzoylacetone were subjected to the reaction sequences. When the reaction was performed with ethyl acetylacetate (Table 5, entry 2), the structure of the resulting product could not be easily determined from the corresponding ^{1}H and ^{13}C NMR spectra and mass spectrum. Fortunately, single-crystals could be grown in a mixture of petroleum ether and dichloromethane and the structure was established by X-ray diffraction analysis as **7b** (Figure 1).[18] In the case of using methyl acetylacetate as the carbon nucleophile, the reaction furnished two products, **6c** and **7c**, with respective yields of 23% and 35% (Table 5, entry 3). For benzoylacetone substrate, 5-benzoyl-3-[(difluoroboryloxy)(ethylthio)methylene]-4,6-dimethyl-3,4-dihydropyridone (**7d**) was the main product (66% yield, Table 5, entry 4). The diesters, such as ethyl malonate were found to be inert to the C–C bond coupling reaction under the identical conditions, probably due to its relatively weak acid character (pK_a = 16.4, while for acetylacetone, pK_a = 13.3; for ethyl acetylacetate, pK_a = 14.2).[19] Accordingly, a series of 5-substituted 3-[bis(ethylthio)methylene]-4,6-dimethyl-3,4-dihydropyridones **6** and/or 3-[(difluoroboryloxy)(ethylthio)methylene]-4,6-dimethyl-3,4-dihydropyridones **7** were successfully prepared in moderate to good yields.[20] Indeed, this protocol provides a convenient and efficient one-pot synthesis of polysubstituted 3,4-dihydro-2-pyridones.

The possible mechanism for the formation of pyridones **6** and/or **7** from substrate **2f** is proposed, as depicted in Scheme 1.[21,22] The carbon–carbon coupling depends on the formation of the allylic carbocation generated from **2f**. This is then followed by the azaannulation to give pyridone **6**. Clearly, the formation of **7** would involve the hydrolysis of **6** (S_NV, nucleophilic vinylic substitution)[22] and subsequent formation of the BF_3 complex.[23]

Table 4 Synthesis of *N*-Aryl-Substituted 3,4-Dihydro-2-pyridones from **3**

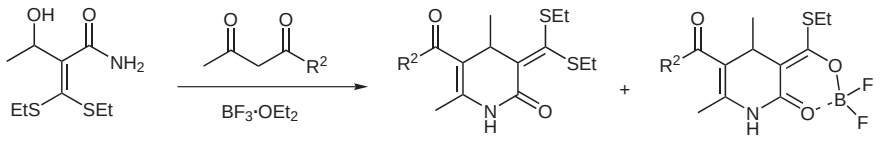


3a–e **4a–e** **5a–e**

Entry	Substrate	Ar	Product **4**	Yield of **4** (%)	Product **5**[a]	Yield of **5** (%)[b]
1	**3a**	Ph	**4a**	87	**5a**	85
2	**3b**	4-ClC_6H_4	**4b**	89	**5b**	88
3	**3c**	2-MeC_6H_4	**4c**	85	**5c**	85
4	**3d**	2,4-$Me_2C_6H_3$	**4d**	83	**5d**	81
5	**3e**	2-$MeOC_6H_4$	**4e**	80	**5e**	82

[a] The cyclization reactions were carried out in the presence of $TiCl_4$–Et_3N at 0 °C.
[b] Isolated yields.

Table 5 Reactions of α-Hydroxyketene-(*S*,*S*)-acetals **2f** with Active Methylenes



2f **6** **7**

Entry	Substrate	R^2	Time (h)	Product **6**	Yield (%)[a] **6**	Product **7**	Yield (%)[a] **7**
1	**2f**	Me	2.0	**6a**	89	**7a**	–[b]
2	**2f**	EtO	5.0	**6b**	–[b]	**7b**	54
3	**2f**	MeO	4.5	**6c**	23	**7c**	35
4	**2f**	Ph	6.0	**6d**	–[b]	**7d**[c]	66

[a] Isolated yields after silica gel chromatography.
[b] Not detected.
[c] MeCN was used as the solvent.

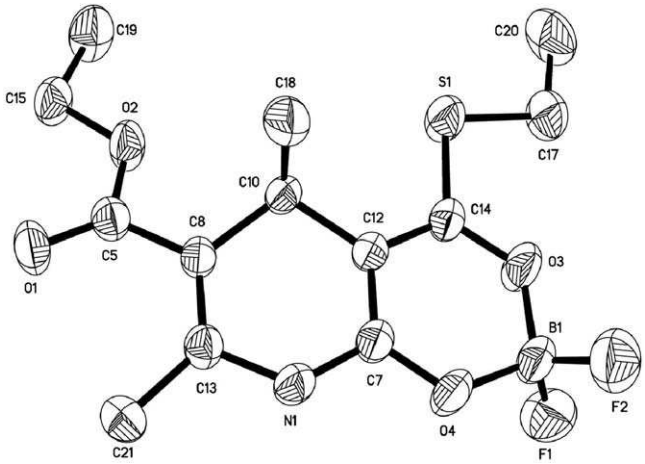
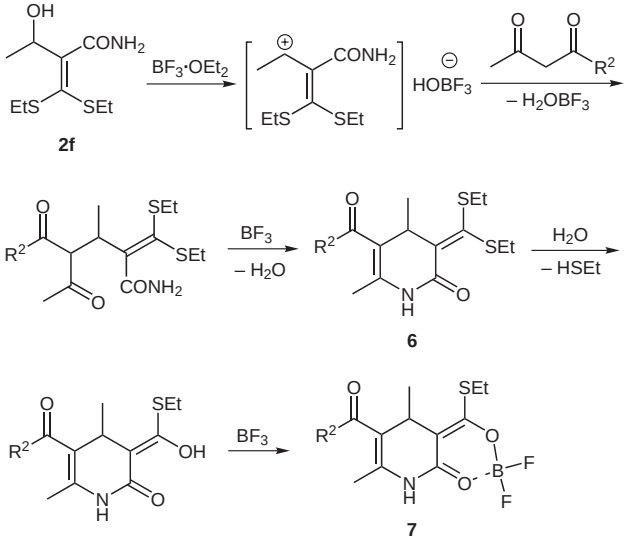


Figure 1 ORTEP drawing of compound **7b**



Scheme 1 Possible mechanism for the formation of **6** and/or **7**

In summary, the C–C bond-forming reaction of α-hydroxyketene-(*S*,*S*)-acetals and active methylene compounds has been described. The utility of the C–C bond formation products has been demonstrated in the synthesis of *N*-aryl-substituted 3-[bis(ethylthio)methylene]-4,6-dimethyl-3,4-dihydropyridones **5** and substituted 2,3-dihydro-3-[bis(ethylthio)methylene]-4,6-dimethyl-3,4-dihydropyridones **6** and/or 3-[(difluoroboryloxy)(ethylthio)methylene]-4,6-dimethyl-3,4-dihydropyridones **7** in concise steps and good to high yields. The protocol provides a simple, straightforward, and efficient synthesis of polysubstituted 3,4-dihydro-2-pyridones. Further studies on the extension on the scope of this C–C bond-forming reaction, as well as synthetic applications, are ongoing.

Acknowledgment

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(16) **Preparation of 3 (3a as an example); Typical Procedure**: To a well-stirred suspension of **2a** (1.0 mmol, 0.31 g) in

anhyd acetylacetone (15 mmol, 1.55 mL) was added $BF_3{\cdot}OEt_2$ (1.2 mmol, 0.15 mL). The mixture was stirred for 40 min at 0 °C until the reaction was complete (as indicated by TLC) and neutralized with aq $NaHCO_3$ (10%). After workup, the crude product was purified by column chromatography (eluent: PE–EtOAc, 5:1) to give **3a** in 87% yield.

Selected data for compounds **3**:

2-(2-Acetyl-1-methyl-3-oxobutyl)-*N*-phenyl-3,3-bis(ethylthio)acrylamide (3a): white solid; mp 88–91 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.15 (d, *J* = 6.5 Hz, 3 H), 1.17–1.21 (m, 3 H), 1.25–1.66 (m, 3 H), 2.23 (s, 3 H), 2.24 (s, 3 H), 2.61–2.92 (m, 4 H), 4.06 (d, *J* = 11.5 Hz, 1 H), 4.21 (m, 1 H), 7.12–7.15 (m, 1 H), 7.34 (t, *J* = 7.5 Hz, 2 H), 7.58 (t, *J* = 7.5 Hz, 2 H), 7.75 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 204.0, 202.6, 164.7, 146.6, 136.7, 132.8, 128.1 (2 × C), 123.6, 118.8 (2 × C), 71.8, 37.4, 30.1, 28.5, 26.8, 26.5, 17.0, 14.3, 13.8. IR (KBr): 3340, 2968, 2360, 1732, 1698, 1653, 1529, 760 cm^{-1}. MS: *m*/*z* = 394.1 $[M + H]^+$. Anal. Calcd for $C_{20}H_{27}NO_3S_2$: C, 61.04; H, 6.91; N, 3.56. Found: C, 60.90; H, 6.75; N, 3.44.

2-(2-Acetyl-1-methyl-3-oxobutyl)-*N*-*o*-tolyl-3,3-bis(ethylthio)acrylamide (3c): white solid; mp 97–99 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.17 (d, *J* = 7.0 Hz, 3 H), 1.18–1.21 (m, 3 H), 1.29–1.31 (m, 3 H), 2.25 (s, 3 H), 2.26 (s, 3 H), 2.35 (s, 3 H), 2.63–2.92 (m, 4 H), 4.10 (d, *J* = 11.0 Hz, 1 H), 4.24–4.27 (m, 1 H), 7.08 (t, *J* = 7.5 Hz, 1 H), 7.21 (t, *J* = 7.5 Hz, 2 H), 7.62 (s, 1 H), 7.98 (d, *J* = 7.5 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 203.6, 202.7, 164.9, 146.8, 134.6, 132.6, 129.6, 128.0, 125.8, 124.2, 121.6, 71.7, 37.3, 30.0, 28.6, 26.9, 26.5, 17.2, 17.0, 14.1, 13.7. IR (KBr): 3364, 2975, 2924, 2360, 2170, 1694, 1668, 1517, 1456, 769 cm^{-1}. MS: *m*/*z* $[M + H]^+$ calcd for $C_{21}H_{29}NO_3S_2$: 407.2; found: 408.6. Anal. Calcd for $C_{21}H_{29}NO_3S_2$: C, 61.88; H, 7.17; N, 3.44. Found: C, 61.57; H, 6.81; N, 3.23.

(17) **Preparation of 5 (5a as an example); Typical Procedure**: To a well-stirred suspension of **3a** (1.0 mmol, 0.43 g) in EtOH (10 mL) was added NaOH (1.2 mmol, 0.05 g). The mixture was stirred at 60 °C for 1.0 h, and then poured into H_2O (80 mL) under stirring. The precipitated solid was collected by filtration, washed with H_2O (3 × 30 mL) and then dried in vacuo to afford the product **4a** (0.31 g, 87%) as a white solid. To a well-stirred suspension of **4a** (1.0 mmol, 0.35 g) in anhyd CH_2Cl_2 (10 mL) were added $TiCl_4$ (1.2 mmol, 0.14 mL) and Et_3N (1.4 mmol, 0.20 mL). The mixture was stirred for about 2 h until the reaction was complete (as indicated by TLC) and neutralized with aq $NaHCO_3$ (10%). After workup, the crude product was purified by column chromatography (eluent: PE–EtOAc = 15:1) to give **5a** in 85% yield.

Selected data for compounds **5**:

3-[Bis(ethylthio)methylene]-4,6-dimethyl-1-phenyl-3,4-dihydropyridin-2(1*H*)-one (5a): yellow solid; mp 87–89 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.16 (d, *J* = 6.5 Hz, 3 H), 1.25–1.30 (m, 6 H), 1.55 (s, 3 H), 2.82–2.94 (m, 4 H), 4.00–4.02 (q, *J* = 6.5 Hz, 1 H), 5.21 (d, *J* = 6.5 Hz, 1 H), 7.19 (d, *J* = 7.5 Hz, 2 H), 7.31 (t, *J* = 7.5 Hz, 1 H), 7.40 (t, *J* = 7.5 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.4, 141.4, 137.6, 137.3, 133.4, 128.4, 128.0 (2 × C), 126.6, 109.0 (2 × C), 33.5, 28.1, 27.8, 19.3, 19.1, 14.2, 13.4. IR (KBr): 3063, 2962, 2921, 2867, 2360, 2170, 1648, 1595, 1539, 1489, 699 cm^{-1}. MS: *m*/*z* = 334.3 $[M + H]^+$. Anal. Calcd for $C_{18}H_{23}NOS_2$: C, 64.82; H, 6.95; N, 4.20. Found: C, 64.64; H, 6.79; N, 4.04.

3-[Bis(ethylthio)methylene]-1-(4-chlorophenyl)-4,6-dimethyl-3,4-dihydropyridin-2(1*H*)-one (5b): yellow solid; mp 136–137 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.14 (d, *J* = 6.5 Hz, 3 H), 1.23–1.32 (m, 6 H), 1.55 (s, 3 H), 2.81–2.95 (m, 4 H), 3.99–4.02 (q, *J* = 6.5 Hz, 1 H), 5.22 (d, *J* = 7.5 Hz, 1 H), 7.10 (t, *J* = 8.5 Hz, 2 H), 7.37 (d, *J* = 8.5 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.4, 142.2, 136.7, 136.2, 132.9, 132.4, 129.4, 128.2 (2 × C), 109.5 (2 × C), 33.4, 28.2, 27.7, 19.3, 19.0, 14.2, 13.4. IR (KBr): 3070, 2964, 2927, 2865, 1644, 1487, 1454, 1085, 775 cm^{-1}. MS: *m*/*z* = 368.1 $[M + H]^+$. Anal. Calcd for $C_{18}H_{22}ClNOS_2$: C, 58.75; H, 6.03; N, 3.81. Found: C, 58.58; H, 5.96; N, 3.70.

(18) X-ray diffraction data for **7b** has been deposited at the Cambridge Crystallographic Data Centre with supplementary publication number CCDC 611469.

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(20) **Preparation of 6 and 7 (6a as an example); Typical Procedure**: To a well-stirred suspension of **2f** (1.0 mmol, 0.235g) in acetylacetone (15 mmol, 1.55 mL) was added $BF_3{\cdot}OEt_2$ (1.2 mmol, 0.2 mL). The mixture was stirred at 0 °C for 2 h until the reaction was complete (as indicated by TLC) and neutralized with aq $NaHCO_3$ (10%). After workup, the crude product was purified by column chromatography (eluent: PE–EtOAc = 5:1) to give **6a** in 89% yield.

Selected data for compounds **6** and **7**:

5-Acetyl-3-[bis(ethylthio)methylene]-4,6-dimethyl-3,4-dihydropyridin-2(1*H*)-one (6a): yellow solid; mp 66–68 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.15 (d, *J* = 7.0 Hz, 3 H), 1.17–1.34 (m, 6 H), 2.28 (s, 3 H), 2.34 (s, 3 H), 2.81–3.03 (m, 4 H), 4.60 (q, *J* = 7.0 Hz, 1 H), 7.98 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.9, 162.7, 146.7, 142.6, 132.8, 117.1, 35.8, 29.0, 28.7, 28.1, 18.7, 18.5, 14.3, 13.6. IR (KBr): 3246, 3093, 2963, 2924, 2865, 2360, 2342, 1673, 1617, 1577, 1230, 786 cm^{-1}. MS: *m*/*z* = 300.0 $[M + H]^+$. Anal. Calcd for $C_{14}H_{21}NO_2S_2$: C, 56.15; H, 7.07; N, 4.68. Found: C, 56.08; H, 6.95; N, 4.43.

3-[Bis(ethylthio)methylene]-4,6-dimethyl-5-methyloxycarbonyl-3,4-dihydropyridin-2(1*H*)-one (6c): yellow solid; mp 115–116 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.12 (d, *J* = 7.5 Hz, 3 H), 1.24–1.31 (m, 6 H), 2.30 (s, 3 H), 2.83–3.01 (m, 4 H), 3.77 (s, 3 H), 4.59–4.60 (q, *J* = 7.5 Hz, 1 H), 7.46 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.1, 163.3, 148.0, 143.8, 133.6, 109.1, 51.4, 36.2, 30.1, 29.2, 19.8, 18.8, 15.1, 14.5. IR (KBr): 3187, 3090, 2943, 2927, 1709, 1673, 1629, 1525, 1486, 1345, 1217, 1182, 772 cm^{-1}. MS: *m*/*z* = 316.1 $[M + H]^+$. Anal. Calcd for $C_{14}H_{21}NO_3S_2$: C, 53.30; H, 6.71; N, 4.44. Found: C, 53.13; H, 6.63; N, 4.29.

3-[(Difluoroboryloxy)(ethylthio)methylene]-4,6-dimethyl-5-methyloxycarbonyl-3,4-dihydropyridin-2(1*H*)-one (7c): yellow solid; mp 98–100 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.16 (d, *J* = 6.5 Hz, 3 H), 1.37 (t, *J* = 7.5 Hz, 3 H), 2.32 (s, 3 H), 3.12–3.17 (q, *J* = 7.5 Hz, 2 H), 3.78 (s, 3 H), 3.79–3.81 (q, *J* = 6.5 Hz, 1 H), 6.84 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ =185.6, 166.5, 160.8, 141.2, 110.6, 95.4, 51.8, 28.9, 24.4, 21.7, 19.0, 14.7. IR (KBr): 2927, 2284, 1786, 1758, 1731, 1592, 1491, 1383, 1028 cm^{-1}. MS: *m*/*z* = 320.1 $[M + H]^+$. Anal. Calcd for $C_{12}H_{16}BF_2NO_4S$: C, 45.16; H, 5.05; N, 4.39. Found: C, 45.05; H, 4.99; N, 4.15.

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