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Transition Metal-Free α-Csp^3-H Methylenation of Ketones to Form C=C Bond Using Dimethyl Sulfoxide as Carbon Source

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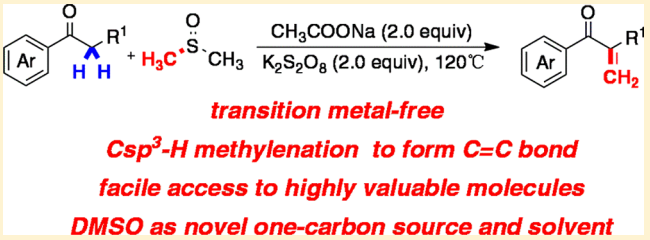
Supporting Information

ABSTRACT: A direct α-Csp^3-H methylenation of arylketones to form C=C bond using dimethyl sulfoxide as one-carbon source is achieved under transition metal-free reaction condition. Various aryl ketone derivatives react readily with DMSO, producing the α,β-unsaturated carbonyl compounds in yields of 42 to 90%. This method features a transition metal-free reaction condition, wide substrate scope and using DMSO as novel one-carbon source to form C=C bond, thus providing an efficient and expeditious approach to an important class of α,β-unsaturated carbonyl compounds. Based on the preliminary experiments, a plausible mechanism of this transformation is disclosed.



INTRODUCTION

The construction of C=C bond has been attracted continuous attention of chemists and great extensively studied because the compounds contained C=C bond are widely present in many naturally occurring and manmade compounds.[1] Generally, the traditional methods to form C=C bond is olefination of conbonyl compounds, the general strategy entails an electron-withdrawing group to stabilize carbanions formed by aldehydes or ketones. The electron-withdrawing group also acts as a good leaving group and forms some important reactions in organic chemistry, such as Witting reaction, Horner−Witting reaction, Horner−Wadsworth−Emmons reaction, Peterson olefination, and Julia olefination.[2] The other way is transition metal-catalyzed reactions of alcohols to form C=C bonds.[3] Considering the principle of atom-economic, sustainable, and environment-friendly organic synthesis, development of a simple and practical protocol to construct C=C bond is highly desirable.

Direct functionalization of C−H bonds is of great significance because it offers more efficient and economical ways to construct complex chemical frameworks.[4] Use of this process and a simple carbon source to construct C=C bond will undoubtedly have great importance in organic synthesis. Traditionally, these transformations include amine salt catalyzed/mediated α-methylenation using formaldehyde,[5] paraformaldehyde,[6] or CH_2Br_2[7] as the carbon sources and Mannich-type reaction with readily prepared Eschenmoser's salts followed by elimination.[8] However, the toxicity and the environment impact of these reagents have hindered its further application. Recently, a few elegant examples for the Csp^3-H methylenation to form C=C bonds have been reported. Xu and Wang developed an efficient protocol to form C=C bonds by direct Csp^3-H methylenation of quinolones.[9] Miura represented a method to construct of C=C bonds with benzylpyridines.[10] Lei reported a similar protocol for this conversion from benzylpyridines and the substrates scope of his method can be further applied to simple aryl-ketones.[11] Li developed an efficient conversion of Csp^3-H bond of ketones to form C=C bonds under aerobic conditions.[12] However, all of these methods employed transition-metal agent as catalysts and using *N*-methyl amides (DMA or DMF) as the carbon sources. Thus, the new one-carbon sources and efficient, economical, environmentally benign approach to form C=C bonds are still highly desirable. Dimethyl sulfoxide (DMSO) is a cheap, versatile solvent with low toxicity, great dissolving capacity, and relative stability.[13] Moreover, it is also widely used in organic synthesis serving as O,[14] Me,[15] SMe,[16] SOMe,[17] SO_2Me,[18] $MeSCH_2$,[19] $MeSOCH_2$,[20] and CN[21] source. Nevertheless, it is rare that using DMSO as one-carbon source to realize the Csp^3-H methylenation for the C=C bonds formation.[22] Herein, we report a transition metal-free method to realize the Csp^3-H methylenation for the C=C bonds formation using DMSO as novel one-carbon sources which provides a general, green, and practical approach to α,β-unsaturated ketones.

RESULTS AND DISCUSSION

We initiated our studies with acetophenone (**1a**) as the model substrate to screen the optimal reaction conditions and the results are summarized in Table 1. To our delight, acetophenone (**1a**) gave the α-methylenation product **2a** in 85% isolated yield using acetophenone (0.5 mmol, 1.0 equiv), CH_3COONa (1 mmol, 2.0 equiv), $K_2S_2O_8$ (1.0 mmol, 2.0 equiv), DMSO (2.0 mL), 120 °C, 9 h in a sealed tube (entry 1).

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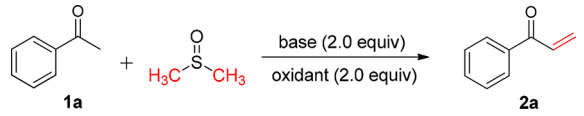
Table 1. Optimization of Reaction Conditions[a]



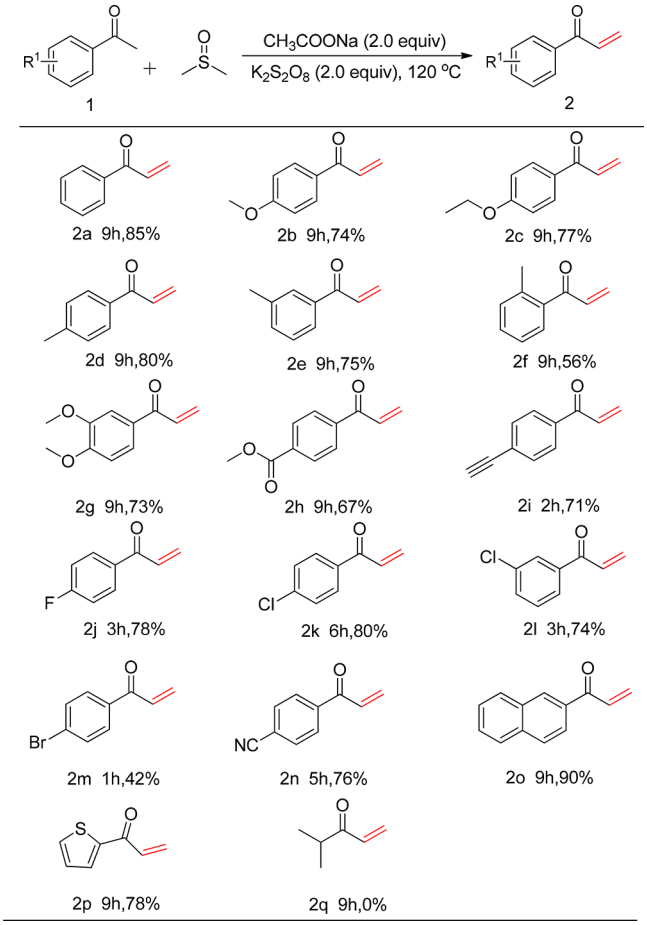
entry	base	oxidant	temp (°C)	yield[b] (%)
1	CH_3COONa	$K_2S_2O_8$	120	85
2		$K_2S_2O_8$	120	38
3	HCOONa	$K_2S_2O_8$	120	65
4	K_2CO_3	$K_2S_2O_8$	120	30
5	NaOH	$K_2S_2O_8$	120	56
6	DBU	$K_2S_2O_8$	120	trace
7	pyridine	$K_2S_2O_8$	120	trace
8	Et_3N	$K_2S_2O_8$	120	trace
9	DABCO	$K_2S_2O_8$	120	21%
10	CH_3COONa	oxone	120	trace
11	CH_3COONa	$Na_2S_2O_8$	120	70
12	CH_3COONa	$(NH_4)_2S_2O_8$	120	trace
13	CH_3COONa	H_2O_2	120	trace
14	CH_3COONa	TBHP	120	trace
15	CH_3COONa	$K_2S_2O_8$	110	60
16	CH_3COONa	$K_2S_2O_8$	130	83
17	CH_3COONa		120	0
17[c]	CH_3COONa	$K_2S_2O_8$	120	72

[a]Reaction conditions: acetophenone (**1a**, 0.5 mmol), base (1 mmol), oxidant (1 mmol), and solvent (2 mL) for 9 h. [b]Isolated yield. [c]Reaction time: 12 h.

Other reaction factors were investigated and the results are listed in entries 2−17. The efficiency of this conversion was improved by adding base to the reaction mixture, with CH_3COONa proving to be optimal (entries 2−5). Other organic base like DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), pyridine, Et_3N (triethylamine), and DABCO (1,4-diazabicyclo[2.2.2]octane) did not improve the yield compared with the reaction without any base (entry 6−9). Various oxidants, such as oxone, $Na_2S_2O_8$, $(NH_4)_2S_2O_8$, H_2O_2, and TBHP, were also applied in this reaction; $K_2S_2O_8$ afforded the best result (entries 10−14). Increasing the temperature did not improve the yield (entry 15) and at low temperature the acetophenone could not be fully converted to the product (entry 16). Control experiment showed that $K_2S_2O_8$ played an essential role in this transformation (entry 17). It is worth noting that the yield of product was decrease when prolonging the reaction time to 12 h (entry 17).

With the optimized reaction conditions in hand (Table 1, entry 1), we explored the scope of the α-methylenation protocol with the (hetero)aryl methyl ketones. The results are summarized in Table 2. Acetophenone derivatives bearing electron-donating substituents (Me, MeO, EtO) were successfully used to realize the Csp^3-H methylenation to form the C=C bonds in moderate to good yield (56%−85%, **2a**−**2g**). Triple bond and ester groups were successfully used to realize the Csp^3-H methylenation to form the C=C bonds in moderate to good yield (**2h** and **2i**). Much to our satisfaction, acetophenone derivatives with electron-withdrawing substituents (F, Cl, Br, CN) could be converted into corresponding products in 42−78% yield (**2j**−**2n**), which provided the possibility for further functionalization. Furthermore, acetophenone bearing the same substituents at different positions had influence on the efficiency of this transformation. For example, 2-methylacetophenone (**2f**) gave lower yield than 3-/4-methylacetophenone (**2e**/**2d**). 2-Acetonaphthone readily underwent the reaction to generate the expected products in high yield (**2o**). A heterocyclic, 2-acetylthiophene also provided the α-methylenation products in 78% yield (**2p**).

Table 2. Scope of Acetophenones[a,b]



[a]Reaction conditions: ketones (**1**, 0.5 mmol), CH_3COONa (1 mmol), $K_2S_2O_8$ (1 mmol) 120 °C, and DMSO (2 mL). [b]Yield of isolated product.

To expand the substrate scope of this transformation, α-monosubstituted ketones, aliphatic ketones, and cyclic ketones were also explored. As can be seen in Table 3, propiophenone derivatives appear slightly less reactive than corresponding acetophenone derivatives (**3a**−**3c**). Aryl (heterocyclic) ketones with long chain alkyl are compatible with the reaction conditions but in lower efficiency (**3d** and **3e**). Moreover, α-substituted acetophenone with aryl substituent resulted in moderate to good yield of product (**3f**). This methodology could be extended to cyclic ketone as well, although in moderate yield (**3g**).

In order to probe the mechanism of this α-methylenation method, several control experiments were investigated (Scheme 1). The reactions performed smoothly in the presence of radical inhibitors, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 2,6-di*tert*-butyl-4-methylphenol (BHT), producing the desired product **2a** in 62 and 80% yields, which might rule out a radical process in this transformation. When benzeneacetaldehyde (**D**) and benzoylformic acid (**E**), which is potentially generated by acetophenone, were employed as the substrates, the reactions did not proceed. These results exclude benzeneacetaldehyde and benzoylformic acid as intermediates in this transformation.

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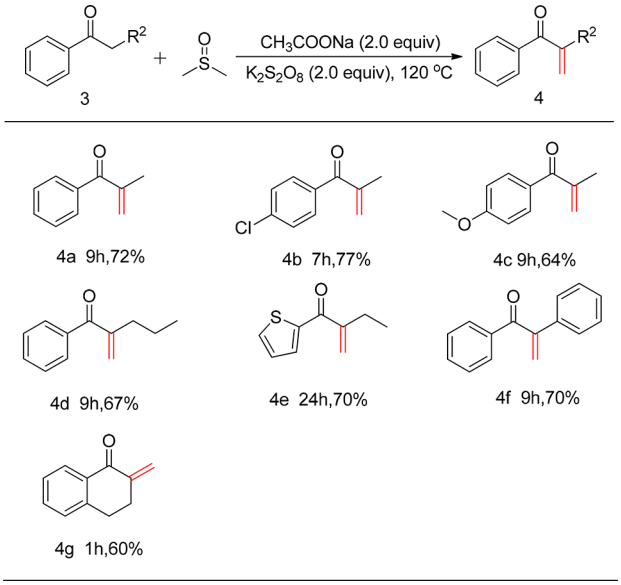
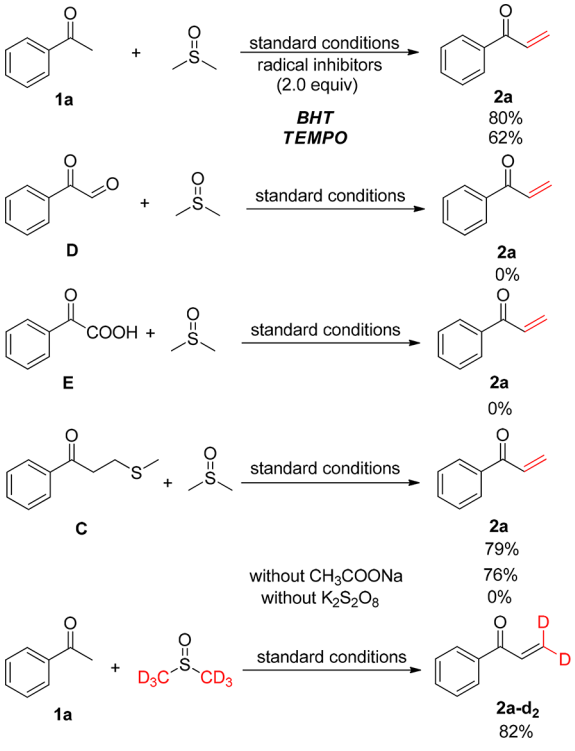
Table 3. Scope of Ketones[a,b]



[a]Reaction conditions: ketones (**3**, 0.5 mmol), CH_3COONa (1 mmol), $K_2S_2O_8$ (1 mmol) 120 °C, and DMSO (2 mL). [b]Yield of isolated product.

Scheme 1. Control Experiments



Furthermore, a key intermediate **C** was detected by GC-MS during the reaction. Pure **C** was isolated and could be converted to **2a** in 79% yields under the standard reaction conditions. In the absence of CH_3COONa, **C** could be converted to **2a** in 76% yield under the standard reaction conditions. Without addition of $K_2S_2O_4$, **C** remained intact and could be recovered in 96% yield under similar reaction conditions. The result showed that $K_2S_2O_8$ play an essential role in the transformation of **C** to **2a**. In addition, an isotope-labeling experiment was conducted and the result confirmed that the methylene was from dimethyl sulfoxide.

On the basis of the observed experimental results and previous literature,[19,22,23] a possible mechanism is proposed (Figure 1). Initially, DMSO is activated by $K_2S_2O_8$ to give **B**, which is coupled by **A** generated from **1a**, producing the intermediate **C**. In the presence of $K_2S_2O_8$, **C** undergoes demethylthioation to afford the α-methylenation product **2a**.

CONCLUSIONS

In summary, we have developed a novel and facile procedure to form C=C bond through transition metal-free α-Csp^3-H methylenation of ketones. Wide substrate scope, transition metal-free reaction condition, and using DMSO as solvent and a novel one-carbon source are the advantages of this method. A variety of α,β-unsaturated carbonyl compounds were produced in moderate to high yields. On the basis of control experiments, a plausible reaction path is proposed.

EXPERIMENTAL SECTION

General Methods. Materials obtained from commercial suppliers were used as received unless mentioned otherwise. Products were purified by flash chromatography on silica gel (300−400 mesh), and were characterized by ^1H NMR, and ^{13}C NMR. ^1H NMR spectra were recorded on 400 MHz spectrometer and the chemical shifts (δ) were reported in ppm relative to internal standard TMS (0 ppm) for $CDCl_3$. The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; q, quartet; brs, broad singlet. The coupling constants, J values, are given in Hertz (Hz).[13]C NMR spectra were obtained at 100 MHz and referenced to the internal solvent signals (central peak is 77.0 ppm in $CDCl_3$). Copies of ^1H NMR and ^{13}C NMR spectra are provided as Supporting Information. High-resolution mass spectra (HRMS) were measured on a double focusing mass spectrometer with an EI source.

Typical Experimental Procedure for the Formation of α,β-Unsaturated Ketones from Arylketones. In a Schlenk tube of 25 mL, CH_3COONa (1 mmol, 2.0 equiv), acetophenone **1** (0.5 mmol, 1.0 equiv), and $K_2S_2O_8$ (1 mmol, 2 equiv) were dissolved in DMSO (2 mL) and stirred at 120 °C for 9 h. After completion of the reaction, the resulting solution was cooled to room temperature; the solution was diluted with ethyl acetate (10 mL), washed with water (5 mL), extracted with ethyl acetate (3 × 5 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel to give the desired product.

Experimental Procedure for the Formation of Compound C from Acetophenone. In a Schlenk tube of 25 mL, CH_3COONa (1

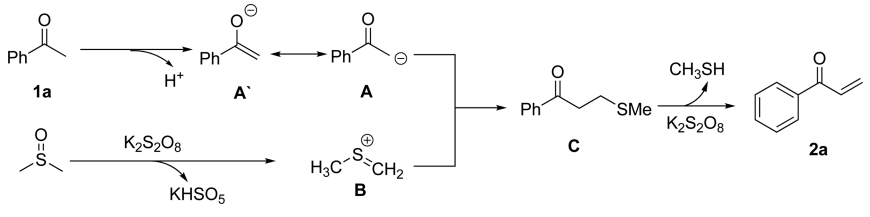


Figure 1. Possible mechanism.

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mmol, 2.0 equiv), acetophenone **1** (0.5 mmol, 1.0 equiv), and $K_2S_2O_8$ (0.5 mmol, 1 equiv) were dissolved in DMSO (2 mL) and stirred at 120 °C for 4 h. After completion of the reaction, the resulting solution was cooled to room temperature; the solution was diluted with ethyl acetate (10 mL), washed with water (5 mL), extracted with ethyl acetate (3 × 5 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel to give the desired product.

1-Phenylprop-2-en-1-one (2a).[12] Colorless oil, 56.1 mg, 85% yield, flash chromatography (petroleum ether/ethyl acetate, 40/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 7.7 Hz, 2H), 7.58 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.16 (dd, J = 17.1, 10.6 Hz, 1H), 6.44 (d, J = 17.1 Hz, 1H), 5.94 (d, J = 10.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 137.2, 133.0, 132.4, 130.2, 128.7, 128.6.

1-(4-Methoxyphenyl)prop-2-en-1-one (2b).[25] Pale yellow oil, 59.9 mg, 74% yield, flash chromatography (petroleum ether/ethyl acetate, 20/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.6 Hz, 2H), 7.18 (dd, J = 17.0, 10.5 Hz, 1H), 6.96 (d, J = 8.6 Hz, 2H), 6.42 (d, J = 17.0 Hz, 1H), 5.87 (d, J = 10.5 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.2, 163.5, 132.1, 131.0, 130.2, 129.3, 113.8, 55.5.

1-(4-Ethoxyphenyl)prop-2-en-1-one (2c).[27] Pale yellow oil, 67.8 mg, 77% yield, flash chromatography (petroleum ether/ethyl acetate, 20/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.6 Hz, 2H), 7.17 (dd, J = 17.1, 10.5 Hz, 1H), 6.94 (d, J = 8.6 Hz, 2H), 6.42 (d, J = 17.0 Hz, 1H), 5.86 (d, J = 10.5 Hz, 1H), 4.10 (q, J = 7.0 Hz, 2H), 1.44 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.2, 163.0, 132.1, 131.0, 130.0, 129.1, 114.2, 63.7, 14.6.

1-(*p*-Tolyl)prop-2-en-1-one (2d).[26] Colorless oil, 58.4 mg, 80% yield, flash chromatography (petroleum ether/ethyl acetate, 40/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 7.9 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 7.16 (dd, J = 17.1, 10.5 Hz, 1H), 6.43 (d, J = 17.1 Hz, 1H), 5.90 (d, J = 10.5 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.5, 143.8, 134.7, 132.3, 129.7, 129.3, 128.8, 21.7.

1-(*m*-Tolyl)prop-2-en-1-one (2e).[26] Colorless oil, 54.8 mg, 75% yield, flash chromatography (petroleum ether/ethyl acetate, 40/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72−7.63 (m, 2H), 7.34−7.25 (m, 2H), 7.08 (dd, J = 17.2, 10.5 Hz, 1H), 6.35 (d, J = 17.1 Hz, 1H), 5.84 (d, J = 10.5 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.2, 138.4, 137.3, 133.8, 132.5, 130.0, 129.2, 128.4, 125.9, 21.3.

1-(*o*-Tolyl)prop-2-en-1-one (2f).[12] Colorless oil, 40.9 mg, 56% yield, flash chromatography (petroleum ether/ethyl acetate, 40/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 7.5 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.30−7.16 (m, 2H), 6.79 (dd, J = 17.4, 10.6 Hz, 1H), 6.15 (d, J = 17.4 Hz, 1H), 6.01 (d, J = 10.6 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 137.9, 137.3, 136.6, 131.4, 131.2, 130.7, 128.4, 125.3, 20.3.

1-(3,4-Dimethoxyphenyl)prop-2-en-1-one (2g).[25] Pale yellow solid, 70.1 mg, 73% yield, flash chromatography (petroleum ether/ethyl acetate, 10/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 8.5 Hz, 1H), 7.57 (s, 1H), 7.20 (dd, J = 17.0, 10.5 Hz, 1H), 6.91 (d, J = 8.3 Hz, 1H), 6.44 (d, J = 17.0 Hz, 1H), 5.88 (d, J = 10.5 Hz, 1H), 3.96 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$): δ 189.1, 153.4, 149.2, 131.9, 130.3, 129.2, 123.4, 110.7, 109.9, 56.1, 56.0.

Methyl 4-Acryloylbenzoate (2h).[9] Pale yellow solid, 63.7 mg, 67% yield, flash chromatography (petroleum ether/ethyl acetate, 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 7.9 Hz, 2H), 7.98 (d, J = 7.9 Hz, 2H), 7.15 (dd, J = 17.1, 10.6 Hz, 1H), 6.46 (d, J = 17.1 Hz, 1H), 6.00 (d, J = 10.6 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 166.2, 140.6, 133.7, 132.2, 131.1, 129.8, 128.5, 52.4.

1-(4-Ethynylphenyl)prop-2-en-1-one (2i).[9] Pale yellow solid, 70.1 mg, 71% yield, flash chromatography (petroleum ether/ethyl acetate, 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 7.9 Hz, 2H), 7.98 (d, J = 7.9 Hz, 2H), 7.15 (dd, J = 17.1, 10.6 Hz, 1H), 6.46 (d, J = 17.1 Hz, 1H), 6.00 (d, J = 10.6 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 137.0, 132.3, 132.0, 130.6, 128.6, 126.8, 82.7, 80.4.

1-(4-Fluorophenyl)prop-2-en-1-one (2j).[12] Colorless oil, 58.5 mg, 78% yield, flash chromatography (petroleum ether/ethyl acetate, 40/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03−7.95 (m, 2H), 7.19−7.10 (m, 3H), 6.45 (d, J = 17.1 Hz, 1H), 5.94 (d, J = 10.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 165.7(d, J = 255.0 Hz), 133.6 (d, J = 3.0 Hz), 132.0, 131.3 (d, J = 9.3 Hz), 130.4, 115.8 (d, J = 21.9 Hz).

1-(4-Chlorophenyl)prop-2-en-1-one (2k).[12] Pale yellow oil, 66.4 mg, 80% yield, flash chromatography (petroleum ether/ethyl acetate, 40/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 7.12 (dd, J = 17.1, 10.6 Hz, 1H), 6.45 (d, J = 17.1 Hz, 1H), 5.96 (d, J = 10.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 139.5, 135.5, 131.9, 130.7, 130.1, 128.9.

1-(4-Bromophenyl)prop-2-en-1-one (2l).[12] Pale yellow oil, 44.1 mg, 42% yield, flash chromatography (petroleum ether/ethyl acetate, 40/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 7.9 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.11 (dd, J = 17.1, 10.6 Hz, 1H), 6.45 (d, J = 17.1 Hz, 1H), 5.96 (d, J = 10.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.9, 135.9, 132.0, 131.9, 130.7, 130.2, 128.2.

4-Acryloylbenzonitrile (2m).[12] Yellow oil, 59.7 mg, 76% yield, flash chromatography (petroleum ether/ethyl acetate, 10/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.1 Hz, 2H), 7.80 (d, J = 8.1 Hz, 2H), 7.11 (dd, J = 17.1, 10.6 Hz, 1H), 6.48 (d, J = 17.1 Hz, 1H), 6.05 (d, J = 10.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 140.4, 132.5, 132.0, 131.7, 129.0, 117.9, 116.2.

1-(3-Chlorophenyl)prop-2-en-1-one (2n).[12] Pale yellow oil, 59.7 mg, 76% yield, flash chromatography (petroleum ether/ethyl acetate, 40/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.74 (d, J = 7.7 Hz, 1H), 7.47 (d, J = 7.9 Hz, 1H), 7.35 (t, J = 7.8 Hz, 1H), 7.03 (dd, J = 17.1, 10.6 Hz, 1H), 6.38 (d, J = 17.1 Hz, 1H), 5.90 (d, J = 10.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 138.8, 134.9, 132.9, 131.9, 131.0, 129.9, 128.7, 126.7.

1-(Naphthalen-2-yl)prop-2-en-1-one (2o).[12] Colorless oil, 81.9 mg, 90% yield, flash chromatography (petroleum ether/ethyl acetate, 40/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 8.03 (d, J = 8.6 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.6 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.60 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.32 (dd, J = 17.1, 10.6 Hz, 1H), 6.50 (d, J = 17.1 Hz, 1H), 5.97 (d, J = 10.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 135.5, 134.6, 132.5, 132.4, 130.4, 130.1, 129.5, 128.6, 128.5, 127.8, 126.8, 124.4.

1-(Thiophen-2-yl)prop-2-en-1-one (2p).[25] Yellow oil, 53.8 mg, 78% yield, flash chromatography (petroleum ether/ethyl acetate, 15/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 1.0 Hz, 1H), 7.69 (d, J = 4.8 Hz, 1H), 7.20−7.14(m, 1H), 7.09 (dd, J = 17.0, 10.4 Hz, 1H), 6.51 (d, J = 17.0 Hz, 1H), 5.89 (d, J = 10.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.4, 144.6, 134.4, 132.5, 131.8, 129.5, 128.3.

2-Methyl-1-phenylprop-2-en-1-one (4a).[6] Pale yellow oil, 52.6 mg, 72% yield, flash chromatography (petroleum ether/ethyl acetate, 40/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 7.7 Hz, 2H), 7.45 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.6 Hz, 2H), 5.83 (s, 1H), 5.54 (s, 1H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.3, 143.7, 137.7, 132.0, 129.4, 128.1, 127.1, 18.6.

1-(4-Chlorophenyl)-2-methylprop-2-en-1-one (4b).[24] Yellow oil, 69.3 mg, 77% yield, flash chromatography (petroleum ether/ethyl acetate, 40/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 7.9 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 5.92 (s, 1H), 5.60 (s, 1H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 143.6, 138.4, 135.9, 130.8, 128.5, 127.1, 18.6.

1-(4-Methoxyphenyl)-2-methylprop-2-en-1-one (4c).[24] Yellow oil, 56.3 mg, 64% yield, flash chromatography (petroleum ether/ethyl acetate, 20/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 5.80 (s, 1H), 5.53 (s, 1H), 3.86 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 163.0, 143.9, 131.9, 130.0, 124.8, 113.4, 55.4, 19.1.

2-Methylene-1-phenylpentan-1-one (4d).[24] Yellow oil, 58.3 mg, 67% yield, flash chromatography (petroleum ether/ethyl acetate, 50/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 7.7 Hz, 2H), 7.53 (t, J = 7.3 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 5.82 (s, 1H), 5.58 (s, 1H), 2.46 (t, J = 7.6 Hz, 2H), 1.62−1.47 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5, 148.2, 137.9, 132.1, 129.5, 128.1, 125.3, 34.3, 21.3, 13.8.

2-Methylene-1-(thiophen-2-yl)butan-1-one (4e).[24] Yellow oil, 58.1 mg, 70% yield, flash chromatography (petroleum ether/ethyl acetate, 15/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 4.3 Hz,

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2H), 7.12 (t, J = 4.3 Hz, 1H), 5.75 (s, 1H), 5.70 (s, 1H), 2.48 (q, J = 7.4 Hz, 2H), 1.11 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.1, 150.0, 143.8, 133.9, 133.9, 127.8, 121.3, 25.6, 12.3.

1,2-Diphenylprop-2-en-1-one (4f).[6] White solid, 72.8 mg, 70% yield, flash chromatography (petroleum ether/ethyl acetate, 30/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 7.9 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.45−7.41 (m, 4H), 7.37−7.31 (m, 3H), 6.07 (s, 1H), 5.64 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 148.3, 137.1, 137.0, 133.1, 130.0, 128.6, 128.4, 127.0, 121.0.

2-Methylene-3,4-dihydronaphthalen-1(2H)-one (4g).[24] Yellow oil, 47.4 mg, 60% yield, flash chromatography (petroleum ether/ethyl acetate, 40/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 7.8 Hz, 1H), 7.48 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.25 (d, J = 7.1 Hz, 1H), 6.23 (s, 1H), 5.45 (s, 1H), 3.01 (t, J = 6.3 Hz, 2H), 2.87 (t, J = 6.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.6, 144.1, 143.3, 133.4, 133.1, 128.5, 128.2, 127.0, 121.7, 31.7, 29.7.

1-Phenylprop-2-en-1-one (2a−d_2). Colorless oil, 56.1 mg, 82% yield, flash chromatography (petroleum ether/ethyl acetate, 40/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.8 Hz, 2H), 7.58 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H), 7.15 (s, 1H).

3-(Methylthio)-1-phenylpropan-1-one (C)^{new}. Yellow oil, 23.4 mg, 26% yield, flash chromatography (petroleum ether/ethyl acetate, 40/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.96 (d, J = 7.9 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 3.29 (t, J = 7.3 Hz, 2H), 2.91 (t, J = 7.4 Hz, 2H), 2.16 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ198.4, 136.6, 133.2, 128.6, 128.0, 38.6, 28.5, 15.9. HRMS (EI) m/z: [M^+] calcd for $C_{10}H_{12}OS$: 180.0609; found: 180.0611

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00619.

Copies of ^{1}H and ^{13}C spectra for all products and the GC-MS data of intermediate **C** (PDF)

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Notes

The authors declare no competing financial interest.

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