JOC The Journal of Organic Chemistry

Article

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Traceless OH-Directed Wacker Oxidation-Elimination, an Alternative to Wittig Olefination/Aldol Condensation: One-Pot Synthesis of α,β-Unsaturated and Nonconjugated Ketones from Homoallyl Alcohols

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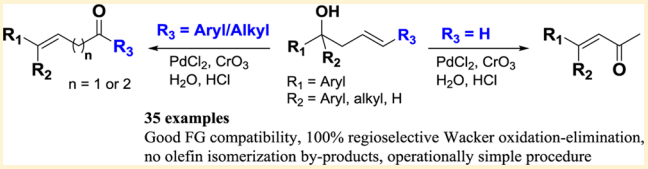
Supporting Information

ABSTRACT: A new method for one-pot synthesis of β-substituted and β,β-disubstituted α,β-unsaturated methyl ketones from homoallyl alcohols by sequential $PdCl_2/CrO_3$-promoted Wacker process followed by an acid-mediated dehydration reaction has been developed. Remarkably, internal homoallyl alcohols delivered regioselectively nonconjugated unsaturated carbonyl compounds under the same protocol. A new starting material-based synthesis of α,β-unsaturated and nonconjugated methyl ketones is demonstrated.



INTRODUCTION

Potential applications of α,β-unsaturated ketones are realized in various reactions in the main stream of organic synthesis, such as Michael addition,[1] cycloaddition,[2] cyclopropanation,[3] epoxidation,[4] hydrogenation,[5] Morita−Baylis−Hillman reaction,[6] and so forth. Similarly, β,γ-unsaturated carbonyl compounds are potential intermediates in synthetic chemistry as well as in photochemical reactions.[7,8]

The classical methods of Wittig,[9] Horner−Wadsworth−Emmons,[10] and Petersen olefination,[11] though widely used for the synthesis of α,β-unsaturated ketones, lead to stoichiometric P and Si byproducts, require sensitive reaction conditions, and have low atom economy. The traditional approach by Claisen−Schmidt condensation of aldehydes and ketones[12] by using a stoichiometric base sometimes leads to a mixture of self-condensed ketone and Michael addition products. Mukaiyama aldol reaction followed by subsequent dehydration catalyzed by a Lewis acid[13] or the Yanagisawa protocol of condensation of aldehydes with alkenyl trichloroacetates catalyzed by dibutyltin dimethoxide[14] are useful alternatives.

For the difficulties associated with classical methods to be overcome, a number of catalytic processes have been developed.[15] Similarly, the one-pot synthesis of enones from various starting materials has drawn significant attention. Over the past decade, organic chemists have made major progress in developing one-pot methods to avoid purification processes and minimize cost and waste production.[16] A representative example established by Pawluć and co-workers demonstrates the highly stereoselective synthesis of (*E*)-styryl ketones via vinyl silanes from readily available styrenes.[17] The Au-catalyzed Meyer−Schuster rearrangement of propargylic alcohols with small quantities of protic solvent to enones by Sheppard and co-workers is another notable example.[18] Recently, Sugiura and co-workers developed a one-pot synthesis of β,β-disubstituted α,β-unsaturated carbonyl compounds via a $TiCl_4$-promoted aldol reaction of ketones followed by base-induced elimination.[19] The cross-metathesis approach from olefins and vinyl ketones is also an efficient alternative.[15a] Wang and co-workers transformed simple terminal olefins into α,β-unsaturated methyl ketones via Wacker-type oxidation and a dehydrogenation sequence using $Pd(OAc)_2$ as catalyst and molecular oxygen (O_2) as the sole oxidant.[15e]

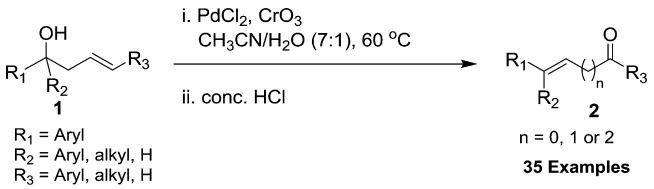
The syntheses of β,γ-unsaturated carbonyl compounds are well documented in the literature. The addition of allylic organometallic reagents with acyl halides is an important example.[20] In addition, the cross-coupling of allylic trifluoroacetates with acylsilanes/stannanes are also reported.[21] A series of β,γ-unsaturated carbonyl compounds were synthesized by cerium-mediated addition of organolithiums to silylated enaminones,[22] Ru−H catalyzed addition of aldehydes to dienes,[23] and acid-catalyzed opening of (1-hydroxyalkyl)-1-alkylcyclopropanols.[24] Recently, Trofimov and co-workers reported base-catalyzed stereoselective vinylation of ketones with arylacetylenes to deliver β,γ-unsaturated carbonyl compounds.[25a] Later, the same group employed superbase (KO^tBu) to synthesize β,γ-unsaturated carbonyl compounds with excellent stereoselectivity.[25b]

We recently developed new alternatives to the well-known Wacker oxidation of terminal olefins to methyl ketones using Pd catalyst and various oxidants, such as CrO_3,[26a] $Fe_2(SO_4)_3 \cdot nH_2O$,[26b] or DMP.[26c] When a similar oxidation of aryl homoallyl alcohol was investigated (using the catalytic system as in ref 26a), we observed the Wacker oxidation-elimination product α,β-unsaturated methyl ketone (Scheme 1). When the reaction was assisted by the addition of acids, the major product

Received: August 4, 2016
Published: August 26, 2016

DOI: 10.1021/acs.joc.6b01899
J. Org. Chem. 2016, 81, 8577−8584

Scheme 1. Synthesis of α,β-Unsaturated and Non-Conjugated Ketones

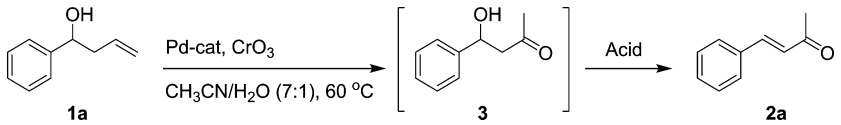


was α,β-unsaturated ketone. This method is substrate selective in delivering the conjugated methyl ketones and deconjugated carbonyl compounds with high regio- and stereoselectivity. Terminal homoallyl alcohols delivered the conjugated methyl ketones whereas internal homoallyl alcohols gave deconjugated carbonyl compounds. A remarkable OH-directed regioselective Wacker oxidation was observed. We consider this method to have advantages for the synthesis of conjugated/deconjugated carbonyl compounds from a different starting material and also to be able to overcome some of the disadvantages of classical condensation methods. The requirement of cheap CrO_3 (0.5 equiv) as oxidant (having good water solubility) and no dry conditions makes this method operationally simple. The exclusive delivery of *E*-double bonds for noncyclic compounds is also a notable feature.

RESULTS AND DISCUSSION

We initiated our studies by choosing homoallyl alcohol **1a** as a model substrate to optimize the reaction conditions (Table 1). On the basis of our previous report,[26a] we carried out the reaction of **1a** using $PdCl_2$ (10 mol %) and CrO_3 (1.5 equiv) in CH_3CN/H_2O (7:1) at 60 °C for 3 h. The desired product, α,β-unsaturated methyl ketone **2a**, was formed in 12% yield along with β-hydroxy methyl ketone **3** in 60% yield (Table 1, entry 1). The reaction without $PdCl_2$ resulted in oxidation of **1a** to the corresponding ketone (1-phenyl-3-buten-1-one) obtained in 65% yield (entry 2). Desired product **2a** was assumed to be generated from **3** and mediated by the acidic nature of CrO_3. The reaction without the use of CrO_3 delivered no product (entry 3). Lowering the concentration of CrO_3 (0.5 equiv) gave **3** in 71% yield (entry 4) with no trace of **2a**. An increase in CrO_3 concentration (3.0 equiv) resulted in increased yield of **2a** to 22% (entry 5). This indicated the need of excess CrO_3 to effect both Wacker oxidation and the β-hydroxy elimination. A reaction at higher temperature (100 °C) resulted in decomposition and lower yield of **2a** (16%, entry 6). We expected that addition of a protic acid would facilitate the elimination process after Wacker oxidation in the one-pot process. Thus, the reaction of **1a** using $PdCl_2$ (10 mol %) and CrO_3 (1.5 equiv) in CH_3CN/H_2O (7:1) at 60 °C was run for 3 h, during which the starting material was consumed (TLC monitoring). In the same vessel, we added CH_3COOH (2.0 equiv) and stirred for another 12 h. Desired product **2a** was then obtained in increased yield of 30% (entry 7). Encouraged by this result, we screened a series of acids with $PdCl_2$ (10 mol %) and CrO_3 (1.5 equiv) in CH_3CN/H_2O (7:1) at 60 °C. Strong acids such as H_3PO_4, HNO_3, H_2SO_4, HCl, and oxalic acid were employed in the one-pot dehydration process (entries 8–12). Among these, to our delight, HCl worked well, resulting in higher yield of **2a** (57%, entry 11). Increasing the amount of HCl (3.0 and 4.0 equiv, entries 13 and 14) gave exclusive formation of **2a** in 75% yield (entry 14). Lowering the Pd catalyst loading to 5 mol % lowered the yield of **2a** (57%, entry 15). Lowering the CrO_3 concentration (1.0 and 0.5 equiv,

Table 1. Optimization of Reaction Conditions to Access α,β-Unsaturated Methyl Ketones[a]

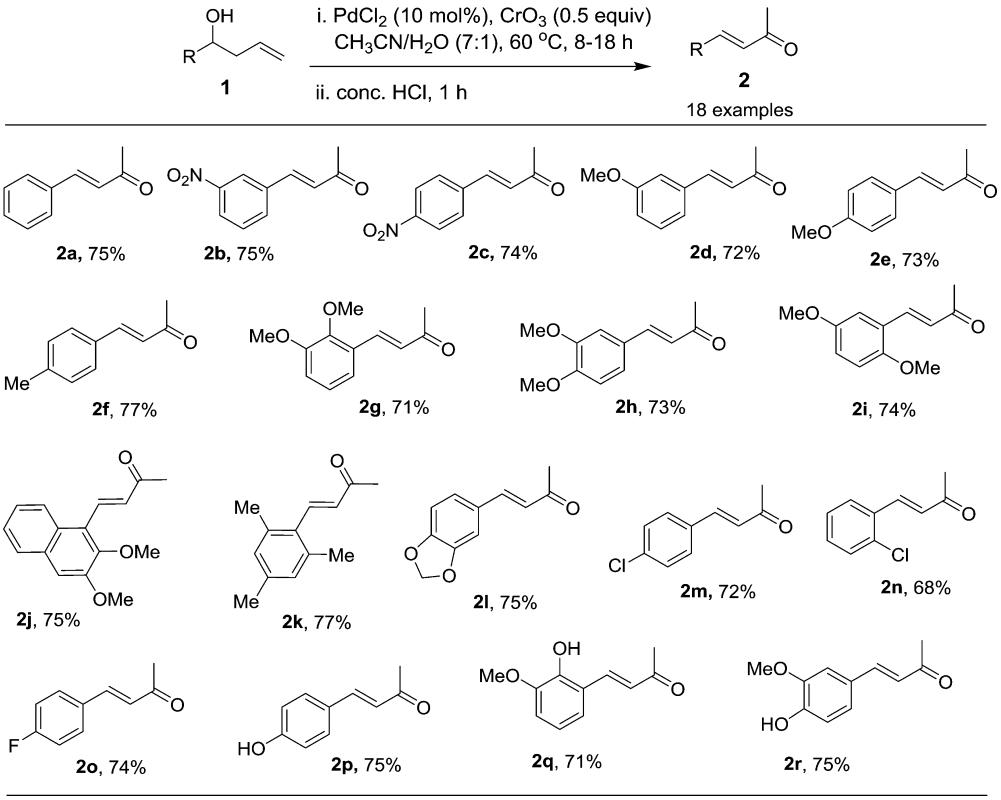


entry	Pd cat.(mol %)	CrO_3 (equiv)	acid (equiv)	time (h)	yield of **3** (%)	yield of **2a** (%)
1	$PdCl_2$ (10)	1.5		3	60	12
2		1.5		3		*b*
3	$PdCl_2$ (10)			3		
4	$PdCl_2$ (10)	0.5		6	71	
5	$PdCl_2$ (10)	3.0		3	58	22
6	$PdCl_2$ (10)	1.5		3	36	16[c]
7	$PdCl_2$ (10)	1.5	CH_3CO_2H (2)	15	27	30
8	$PdCl_2$ (10)	1.5	H_3PO_4 (2)	16	22	35
9	$PdCl_2$ (10)	1.5	HNO_3 (2)	16	15	36
10	$PdCl_2$ (10)	1.5	H_2SO_4 (2)	16	25	36
11	$PdCl_2$ (10)	1.5	HCl (2)	8	16	57
12	$PdCl_2$ (10)	1.5	oxalic acid (2)	16	14	44
13	$PdCl_2$ (10)	1.5	HCl (3)	6	6	67
14	$PdCl_2$ (10)	1.5	HCl (4)	4		75
15	$PdCl_2$ (5)	1.5	HCl (4)	6		57
16	$PdCl_2$ (10)	1	HCl (4)	16		74
17	$PdCl_2$ (10)	0.5	HCl (4)	18		72
18	$Pd(OAc)_2$ (10)	0.5	HCl (4)	16		58
19	$Pd(dba)_2$ (10)	0.5	HCl (4)	20		45
20	$Pd(Ph_3P)_4$ (10)	0.5	HCl (4)	21		48

[a]All reactions were performed with allyl alcohol **1a** (0.5 mmol), Pd-cat. (5–10 mol %), oxidant (0.5 to 1.5 equiv), and acid (2.0–4.0 equiv) at 60 °C in CH_3CN/H_2O (7:1). [b]1-Phenyl-3-buten-1-one (65%). [c]Reaction at 100 °C.

DOI: 10.1021/acs.joc.6b01899
J. Org. Chem. 2016, 81, 8577–8584

Scheme 2. One-Pot Conversion of Secondary Homoallyl Alcohols to *β*-Substituted *α,β*-Unsaturated Methyl Ketones

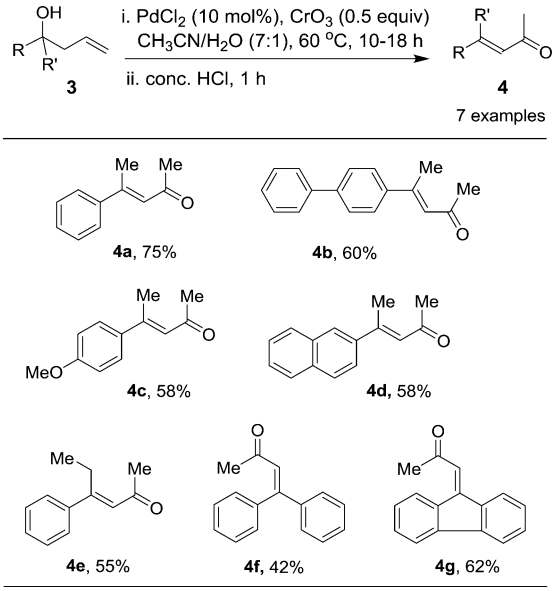


entries 16 and 17) also worked well, giving **2a** in 74 and 72% yields, respectively. A change in Pd catalyst to $Pd(OAc)_2$, $Pd(dba)_2$, or $Pd(PPh_3)_4$ did not improve the yield (entries 18–20). In all cases there was exclusive formation of the *E*-olefin bond.

With the optimized conditions (Table 1, entry 17 with lower loading of CrO_3), the scope of the reaction was investigated by varying the aryl part of allyl alcohol (Scheme 2). Various aryl-substituted secondary homoallyl alcohols (**1a–r**), regardless of electron-donating or -withdrawing ability of substitutions on the aryl ring, reacted under the optimized conditions to afford the corresponding *β*-substituted, *α,β*-unsaturated methyl ketones in good yields (**2a–r**, Scheme 2). Thus, NO_2, OMe, Me, or OR groups containing compounds reacted well, giving **2b–l** under the optimized conditions. The halide-containing compounds **1m–o** were well-tolerated, providing **2m–o**, respectively, under $PdCl_2$ catalysis. Similarly, a free phenolic OH group did not pose any difficulty in the reaction, giving the products in good yields (**2p–r**) without the need of any OH group protection. The exclusive delivery of *E*-olefins is another notable feature in this transformation.

It is difficult to synthesize *β,β*-disubstituted, *α,β*-unsaturated methyl ketones via conventional methods as these suffer from lower reactivity of ketones, the generation of self- or cross-aldols, and/or Michael addition products. To demonstrate the generality of our protocol, we explored the scope of tertiary homoallyl alcohols to access *β,β*-disubstituted, *α,β*-unsaturated methyl ketones (Scheme 3). Tertiary homoallyl alcohols (**3a–e**) with alkyl or aryl groups were smoothly converted into the corresponding *β,β*-disubstituted, *α,β*-unsaturated methyl ketones (**4a–e**) in good yields (55–75%, Scheme 3). Homoallyl alcohol **3f** with both phenyl groups afforded **4f** in moderate

Scheme 3. One-Pot Conversion of Tertiary Homoallyl Alcohols to *β,β*-Disubstituted, *α,β*-Unsaturated Methyl Ketones

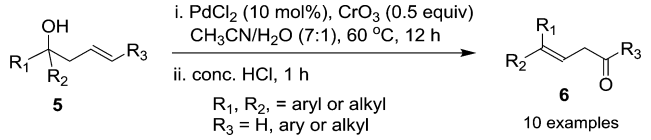


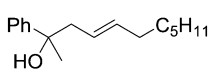
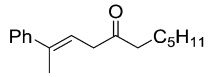
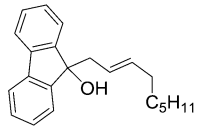
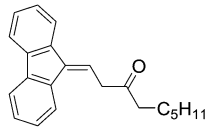
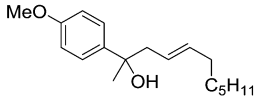
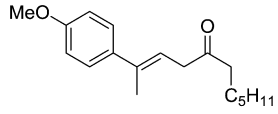
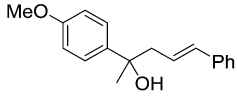
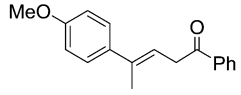
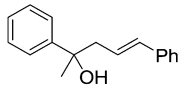
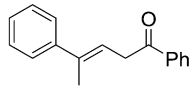
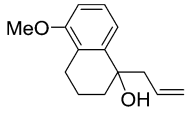
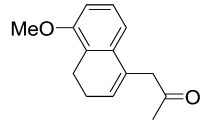
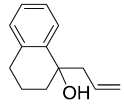
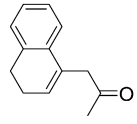
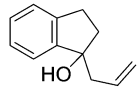
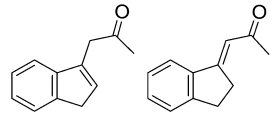
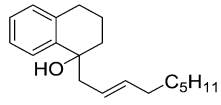
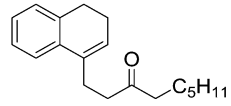
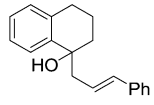
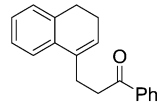
42% yield. Interestingly, fluorenyl homoallyl alcohol under this protocol gave **4g** in good yield of 62%.

To extend the scope of this reaction, we tested selected tertiary homoallyl alcohols under the standard conditions (Table 2). Thus, the reaction of internal olefin-based tertiary homoallyl alcohol **5a** delivered regioselectively *γ,γ*-disubstituted *β,γ*-unsaturated ketone **6a** in 63% yield (entry 1). We did not detect the other possible regioisomer or olefin isomerized

DOI: 10.1021/acs.joc.6b01899
J. Org. Chem. 2016, 81, 8577–8584

Table 2. One-Pot Access to *β,γ*-Unsaturated and Non-Conjugated Carbonyl Compounds from Selected Tertiary Homoallyl Alcohols[a]



Entry	Homoallylic alcohol		Product		Yield (%)
1		**5a**		**6a**	63
2		**5b**		**6b**	78
3		**5c**		**6c**	69
4		**5d**		**6d**	74
5		**5e**		**6e**	68
6		**5f**		**6f**	68
7		**5g**		**6g**	56
8		**5h**		**6h:6h'** 0.7:1	56
9		**5i**		**6i**	71
10		**5j**		**6j**	76

[a]All reactions were performed with **5** (0.5 mmol), $PdCl_2$ (10 mol %), CrO_3 (0.5 equiv), and concd HCl (4.0 equiv) at 60 °C in CH_3CN/H_2O (7:1).

product. The reaction displayed an excellent hydroxyl-directed regioselective Wacker oxidation, hydroxyl elimination, and remarkably no isomerization of the more substituted double bond. It is worth mentioning that the synthesis of such nonconjugated unsaturated carbonyl compounds would be quite a challenging task.[27] Similarly, the reaction of other representative internal olefin-based tertiary homoallyl alcohols **5b–e** delivered corresponding *β,γ*-unsaturated carbonyl compounds **6b–e** in good yields (entries 2–5). The cycloalkane-based terminal homoallylic alcohols **5f–h** also delivered the *β,γ*-

DOI: 10.1021/acs.joc.6b01899
J. Org. Chem. 2016, 81, 8577–8584

unsaturated methyl ketones **6f−h** in good yields (entries 6−8). The last case gave a mixture of β,γ- and α,β-unsaturated methyl ketones **6h** and **6h′** in a 0.7:1 ratio (entry 8). The internal olefin-based cyclohexane-derived tertiary homoallyl alcohols **5i** and **j** delivered corresponding γ,δ-unsaturated ketones **6i** and **j** in good yields (entries 9 and 10). The dehydration was found to preferentially deliver the endocyclic, internal, more substituted double bond over the exomethylene bond. A direct method to synthesize such compounds would be difficult.

The reaction expectedly follows the hydroxyl-directed Wacker oxidation path, followed by acid-assisted hydroxyl elimination. It is less likely that the double bond would first isomerize to give allyl alcohol, followed by CrO_3 effecting the oxidation similar to that of tertiary allyl alcohols.[28] The formation of compound **3** as major product when no acid is employed supports the preceding claim. For compounds **6a−e**, the formation of more substituted double bond in conjugation with the aryl ring might prevent the isomerization to an α,β-unsaturated ketone system. Similarly, for products **6f−j**, the endocyclic double bond is preferred over the exocyclic, except for **6h′**.

CONCLUSIONS

In conclusion, we have demonstrated a new method for the one-pot synthesis of β-substituted and β,β-disubstituted α,β-unsaturated methyl ketones from homoallyl alcohols by sequential $PdCl_2/CrO_3$-promoted Wacker process followed by an acid-mediated dehydration reaction. We also explored internal homoallyl alcohols, which resulted in excellent regioselective formation of nonconjugated unsaturated carbonyl compounds under the optimized conditions. A new starting material-based synthesis of α,β-unsaturated and nonconjugated ketones is demonstrated.

EXPERIMENTAL SECTION

General Information. ^1H and ^{13}C NMR spectra were recorded with a spectrometer operating at 500 or 400 MHz and 125 or 100 MHz for proton and carbon nuclei, respectively. The chemical shifts are based on TMS peak at δ 0.00 pm for proton NMR and $CDCl_3$ peak at δ 77.00 ppm (t) in carbon NMR. IR spectra were obtained on an FT−IR spectrometer, and samples were prepared by evaporation from $CHCl_3$ on CsBr plates. High-resolution mass spectra (HRMS) were obtained using positive electrospray ionization by the TOF method.

General Procedure for One-Pot Synthesis of Unsaturated Carbonyl Compounds. To a stirred solution of homoallyl alcohol (**1**, **3**, or **5**; 0.5 mmol) in CH_3CN (3.5 mL) and H_2O (0.5 mL) were added $PdCl_2$ (7.2 mg, 0.05 mmol, 10 mol %) and CrO_3 (25.0 mg, 0.25 mmol, 0.5 equiv) at room temperature. The reaction mixture was warmed to 60 °C and stirred for 8−18 h. After completion of reaction (monitored by TLC), concd HCl (1.15 mL, 4.0 equiv) was added and stirred for another 1 h at the same temperature. The reaction mixture was then filtered through a small pad of silica gel and washed with EtOAc, and the filtrate was concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (85−95:15−5) as an eluent to afford the unsaturated carbonyl compounds **2a−r**, **4a−g**, and **6a−j**.

*(E)-4-Phenyl-3-buten-2-one (**2a**).*[15e,29a] Yield = 54.8 mg (75%); colorless oil; IR ($CHCl_3$) υ_{max} 3054, 3027, 2922, 1669, 1610, 1576, 1495, 1450, 1359, 1339, 1294, 1204, 1183, 1100, 1074, 977, 908, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 7.56−7.54 (m, 2H), 7.51 (d, J = 16.1 Hz, 1H), 7.42−7.39 (m, 3H), 6.72 (d, J = 16.2 Hz, 1H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.4, 143.4, 134.3, 130.5, 128.9, 128.2, 127.1, 27.5; HRMS (ESI-TOF) calcd for $[C_{10}H_{10}O + H]^+$ 147.0804, found 147.0811.

*(E)-4-(3-Nitrophenyl)-3-buten-2-one (**2b**).*[29b] Yield = 71.7 mg (75%); white solid; mp 98−99 °C; IR ($CHCl_3$) υ_{max} 3019, 1672, 1618, 1533, 1424, 1355, 1260, 1174, 1033, 975, 929, 770, 669 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$/TMS) δ 8.36 (d, J = 1.6 Hz, 1H), 8.21 (d, J = 0.6 Hz, 1H), 7.83 (d, J = 7.7 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.52 (d, J = 16.2 Hz, 1H), 6.81 (d, J = 16.2 Hz, 1H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 197.5, 148.6, 140.1, 136.2, 133.7, 130.0, 129.3, 124.6, 122.5, 27.9; HRMS (ESI-TOF) calcd for $[C_{10}H_9NO_3 + H]^+$ 192.0655, found 192.0657.

*(E)-4-(4-Nitrophenyl)-3-buten-2-one (**2c**).*[29a] Yield = 70.7 mg (74%); white solid; mp 116−118 °C; IR ($CHCl_3$) υ_{max} 3020, 1695, 1674, 1615, 1597, 1523, 1434, 1347, 1257, 1174, 1111, 1020, 977, 929, 828, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 8.26 (d, J = 8.8 Hz, 2H), 7.70 (d, J = 8.6 Hz, 2H), 7.54 (d, J = 16.3 Hz, 1H), 6.82 (d, J = 16.3 Hz, 1H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 197.6, 148.6, 140.6, 140.1, 130.3, 128.8, 124.2, 28.0; HRMS (ESI-TOF) calcd for $[C_{10}H_9NO_3 + H]^+$ 192.0655, found 192.0657.

*(E)-4-(3-Methoxyphenyl)-3-buten-2-one (**2d**).*[15e,29a] Yield = 63.4 mg (72%); colorless oil; IR ($CHCl_3$) υ_{max} 3011, 2961, 2837, 1668, 1610, 1582, 1488, 1455, 1434, 1360, 1160, 1083, 1047, 1006, 978, 950, 933, 870, 836, 686, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 7.48 (d, J = 16.2 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.11 (d, J = 7.5 Hz, 1H), 7.04 (s, 1H), 6.93 (dd, J = 8.2, 1.0 Hz, 1H), 6.68 (d, J = 16.2 Hz, 1H), 3.81 (s, 3H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.3, 159.9, 143.3, 135.7, 129.9, 127.3, 120.9, 116.3, 113.0, 55.2, 27.4; HRMS (ESI-TOF) calcd for $[C_{11}H_{12}O_2 + Na]^+$ 199.0730, found 199.0737.

*(E)-4-(4-Methoxyphenyl)-3-buten-2-one (**2e**).*[15e,29a] Yield = 64.3 mg (73%); yellow solid; mp 69−71 °C; IR ($CHCl_3$) υ_{max} 3014, 2959, 2938, 2846, 1683, 1664, 1625, 1602, 1573, 1511, 1464, 1423, 1360, 1331, 1301, 1173, 1109, 1022, 989, 854, 819, 667 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$/TMS) δ 7.48 (d, J = 8.6 Hz, 2H), 7.46 (d, J = 15.8 Hz, 1H), 6.90 (d, J = 8.8 Hz, 2H), 6.59 (d, J = 16.2 Hz, 1H), 3.83 (s, 3H), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 198.4, 161.6, 143.2, 129.9, 127.0, 125.0, 114.4, 55.3, 27.3; HRMS (ESI-TOF) calcd for $[C_{11}H_{12}O_2 + Na]^+$ 199.0730, found 199.0723.

*(E)-4-p-Tolyl-3-buten-2-one (**2f**).*[15e,29a] Yield = 61.7 mg (77%); colorless oil; IR ($CHCl_3$) υ_{max} 3026, 2921, 1664, 1618, 1569, 1512, 1413, 1357, 1326, 1293, 1180, 1109, 983, 909, 861, 804, 765, 709, 602 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$/TMS) δ 7.46 (d, J = 16.3 Hz, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 6.68 (d, J = 16.3 Hz, 1H), 2.38 (s, 3H), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 198.5, 143.5, 141.0, 131.6, 129.7, 128.2, 126.2, 27.4, 21.5; HRMS (ESI-TOF) calcd for $[C_{11}H_{12}O + H]^+$ 161.0961, found 161.0964.

*(E)-4-(2,3-Dimethoxyphenyl)-3-buten-2-one (**2g**).*[29b] Yield = 73.2 mg (71%); colorless oil; IR ($CHCl_3$) υ_{max} 3013, 2937, 1690, 1671, 1644, 1607, 1579, 1479, 1428, 1361, 1223, 1172, 1090, 1072, 1005, 924, 782, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 7.85 (d, J = 16.5 Hz, 1H), 7.16 (d, J = 7.9 Hz, 1H), 7.05 (t, J = 8.0 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.71 (d, J = 16.5 Hz, 1H), 3.86 (s, 6H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.8, 153.0, 148.4, 138.0, 128.5, 128.4, 124.2, 118.8, 114.1, 61.3, 55.8, 27.2; HRMS (ESI-TOF) calcd for $[C_{12}H_{14}O_3 + Na]^+$ 229.0835, found 229.0835.

*(E)-4-(3,4-Dimethoxyphenyl)-3-buten-2-one (**2h**).*[29c] Yield = 75.3 mg (73%); yellow solid; mp 65−66 °C; IR ($CHCl_3$) υ_{max} 3019, 2963, 2937, 2840, 1683, 1666, 1639, 1622, 1597, 1582, 1515, 1465, 1441, 1421, 1360, 1338, 1307, 1296, 1160, 1140, 1024, 974, 803, 666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 7.43 (d, J = 16.2 Hz, 1H), 7.10 (d, J = 8.3 Hz, 1H), 7.04 (s, 1H), 6.84 (d, J = 8.3 Hz, 1H), 6.57 (d, J = 16.2 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 2.34 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.4, 151.2, 149.2, 143.5, 127.3, 125.2, 123.0, 111.0, 109.5, 55.9, 55.8, 27.3; HRMS (ESI-TOF) calcd for $[C_{12}H_{14}O_3 + Na]^+$ 229.0835, found 229.0838.

*(E)-4-(2,5-Dimethoxyphenyl)-3-buten-2-one (**2i**).*[30a] Yield = 76.3 mg (74%); white solid; mp 49−51 °C; IR ($CHCl_3$) υ_{max} 3004, 2945, 2836, 1667, 1645, 1620, 1603, 1578, 1497, 1465, 1428, 1360, 1321, 1287, 1254, 1179, 1047, 1024, 982, 841, 807, 717 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 7.86 (d, J = 16.5 Hz, 1H), 7.07 (d, J = 3.0 Hz, 1H), 6.93 (dd, J = 9.0, 3.0 Hz, 1H), 6.86 (d, J = 9.0 Hz, 1H), 6.71 (d, J = 16.5 Hz, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 2.39 (s, 3H); $^{13}C\{^1H\}$

DOI: 10.1021/acs.joc.6b01899
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NMR (100 MHz, $CDCl_3$) δ 199.1, 153.6, 152.8, 138.5, 127.9, 123.9, 117.6, 112.6, 112.5, 56.1, 55.8, 27.1; HRMS (ESI-TOF) calcd for $[C_{12}H_{14}O_3 + Na]^+$ 229.0835, found 229.0835.

(E)-4-(2,3-Dimethoxynaphthalen-1-yl)-3-buten-2-one (**2j**). Yield = 96.1 mg (75%); yellow oil; IR ($CHCl_3$) υ_{max} 3018, 2929, 2847, 1666, 1601, 1465, 1422, 1361, 1339, 1177, 1153, 1119, 1042, 1020, 927, 835, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 8.07 (d, J = 16.6 Hz, 1H), 8.02 (dd, J = 7.6, 2.5 Hz, 1H), 7.73 (dd, J = 8.2, 1.7 Hz, 1H), 7.45−7.38 (m, 2H), 7.21 (s, 1H), 6.94 (d, J = 16.6 Hz, 1H), 4.00 (s, 3H), 3.88 (s, 3H), 2.47 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.9, 151.7, 148.6, 136.8, 133.7, 131.4, 127.2, 127.1, 125.7, 124.8, 124.2, 123.9, 109.0, 60.9, 55.7, 27.8; HRMS (ESI-TOF) calcd for $[C_{16}H_{16}O_3 + Na]^+$ 279.0992, found 279.0991.

(E)-4-Mesityl-3-buten-2-one (**2k**).[30a] Yield = 72.5 mg (77%); colorless oil; IR ($CHCl_3$) υ_{max} 3012, 2962, 2862, 1670, 1609, 1567, 1458, 1359, 1304, 1254, 1174, 1150, 1031, 985, 898, 857, 721, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 7.68 (d, J = 16.6 Hz, 1H), 6.90 (s, 2H), 6.34 (d, J = 16.6 Hz, 1H), 2.39 (s, 3H), 2.33 (s, 6H), 2.29 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.5, 142.0, 138.5, 136.7, 132.3, 130.8, 129.2, 27.4, 21.04, 21.0; HRMS (ESI-TOF) calcd for $[C_{13}H_{16}O + H]^+$ 189.1274, found 189.1274.

(E)-4-(Piperonyl)-3-buten-2-one (**2l**).[30b] Yield = 71.3 mg (75%); white solid; mp 65−66 °C; IR ($CHCl_3$) υ_{max} 3019, 2897, 1666, 1625, 1601, 1505, 1491, 1449, 1359, 1257, 1179, 1104, 1041, 973, 932, 865, 669 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$/TMS) δ 7.42 (d, J = 16.1 Hz, 1H), 7.04 (s, 1H), 7.02 (d, J = 8.0 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.55 (d, J = 16.1 Hz, 1H), 6.01 (s, 2H), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 198.3, 149.8, 148.4, 143.2, 128.8, 125.3, 124.8, 108.6, 106.5, 101.6, 27.5; HRMS (ESI-TOF) calcd for $[C_{11}H_{10}O_3 + Na]^+$ 213.0522, found 213.0524.

(E)-4-(4-Chlorophenyl)-3-buten-2-one (**2m**).[17,29a] Yield = 65.0 mg (72%); yellow solid; mp 47−48 °C; IR ($CHCl_3$) υ_{max} 3016, 2921, 2850, 1686, 1660, 1610, 1590, 1491, 1406, 1361, 1317, 1092, 1013, 978, 866, 809, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 7.46 (dd, J = 8.7, 1.0 Hz, 2H), 7.45 (d, J = 16.2 Hz, 1H), 7.36 (dd, J = 8.7, 2.2 Hz, 2H), 6.67 (d, J = 16.2 Hz, 1H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.2, 141.9, 136.4, 132.9, 129.4, 129.2, 127.4, 27.6; HRMS (ESI-TOF) calcd for $[C_{10}H_9OCl + H]^+$ 181.0415, found 181.0413.

(E)-4-(2-Chlorophenyl)but-3-en-2-one (**2n**).[30c] Yield = 61.4 mg (68%); colorless oil; IR ($CHCl_3$) υ_{max} 3063, 2924, 1693, 1672, 1618, 1610, 1591, 1471, 1442, 1360, 1315, 1285, 1258, 1178, 1126, 1100, 1052, 1038, 975, 910, 695 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$/TMS) δ 7.92 (d, J = 16.3 Hz, 1H), 7.62 (d, J = 7.4 Hz, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.33−7.26 (m, 2H), 6.66 (d, J = 16.3 Hz, 1H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 198.3, 139.2, 135.1, 132.6, 131.2, 130.1, 129.6, 127.5, 127.2, 27.2; HRMS (ESI-TOF) calcd for $[C_{10}H_9OCl + H]^+$ 181.0415, found 181.0416.

(E)-4-(4-Fluorophenyl)-3-buten-2-one (**2o**).[15e,29a] Yield = 60.7 mg (74%); colorless oil; IR ($CHCl_3$) υ_{max} 3072, 3050, 2921, 2857, 1668, 1624, 1599, 1509, 1415, 1360, 1325, 1297, 1233, 1178, 1160, 1098, 978, 858, 819, 779, 733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 7.55−7.52 (m, 2H), 7.47 (d, J = 16.2 Hz, 1H), 7.08 (t, J = 8.6 Hz, 2H), 6.64 (d, J = 16.2 Hz, 1H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.1, 164.0 (d, $^1J_{C-F}$ = 250 Hz), 142.0, 130.6, 130.2, 126.8, 116.1 (d, $^2J_{C-F}$ = 22 Hz), 27.6; HRMS (ESI-TOF) calcd for $[C_{10}H_9OF + H]^+$ 165.0710, found 165.0712.

(E)-4-(4-Hydroxyphenyl)but-3-en-2-one (**2p**).[31a] Yield = 60.8 mg (75%); white solid; mp 111−112 °C; IR ($CHCl_3$) υ_{max} 3325, 3019, 1664, 1636, 1602, 1513, 1439, 1362, 1331, 1170, 1105, 1045, 975, 928, 823, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 7.51 (d, J = 16.2 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H), 6.91 (d, J = 8.4 Hz, 2H), 6.61 (d, J = 16.2 Hz, 1H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.1, 159.0, 144.8, 130.4, 126.4, 124.3, 116.2, 27.2; HRMS (ESI-TOF) calcd for $[C_{10}H_{10}O_2 + Na]^+$ 185.0573, found 185.0570.

(E)-4-(2-Hydroxy-3-methoxyphenyl)-3-buten-2-one (**2q**).[31b] Yield = 68.2 mg (71%); colorless oil; IR ($CHCl_3$) υ_{max} 3398, 3014, 2940, 2842, 1666, 1639, 1620, 1604, 1588, 1481, 1442, 1362, 1257, 1185, 1072, 982, 922, 833, 667 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$/TMS) δ 7.84 (d, J = 16.5 Hz, 1H), 7.11 (dd, J = 7.4, 2.0 Hz, 1H), 6.89−6.83 (m, 2H), 6.80 (d, J = 16.5 Hz, 1H), 6.23 (s, OH), 3.91 (s, 3H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 199.2, 146.8, 145.3, 138.2, 128.1, 120.8, 120.2, 119.8, 112.0, 56.2, 27.1; HRMS (ESI-TOF) calcd for $[C_{11}H_{12}O_3 + Na]^+$ 215.0679, found 215.0679.

(E)-4-(4-Hydroxy-3-methoxyphenyl)-3-buten-2-one (**2r**).[31b] Yield = 72.1 mg (75%); white solid; mp 87−88 °C; IR ($CHCl_3$) υ_{max} 3531, 3019, 2972, 2847, 1664, 1635, 1603, 1591, 1513, 1465, 1430, 1361, 1257, 1184, 1123, 1034, 973, 929, 812, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 7.43 (d, J = 16.2 Hz, 1H), 7.10−7.03 (m, 2H), 6.91 (d, J = 8.1 Hz, 1H), 6.57 (d, J = 16.2 Hz, 1H), 6.27 (brs, 1H, *OH*), 3.90 (s, 3H), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.6, 148.3, 146.9, 143.9, 126.8, 124.8, 123.4, 114.9, 109.4, 55.9, 27.2; HRMS (ESI-TOF) calcd for $[C_{11}H_{12}O_3 + Na]^+$ 215.0679, found 215.0679.

(E)-4-Phenyl-3-penten-2-one (**4a**).[32a] Yield = 60.1 mg (75%); colorless oil; IR ($CHCl_3$) υ_{max} 3018, 2925, 2855, 1678, 1600, 1576, 1446, 1376, 1357, 1271, 1184, 1028, 963, 928, 854, 771, 696, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 7.48−7.47 (m, 2H), 7.39−7.37 (m, 3H), 6.51 (s, 1H), 2.54 (s, 3H), 2.29 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.9, 153.9, 142.5, 129.1, 128.5, 126.5, 124.5, 32.2, 18.3; HRMS (ESI-TOF) calcd for $[C_{11}H_{12}O + Na]^+$ 183.0780, found 183.0785.

(E)-4-(Biphenyl-4-yl)-3-penten-2-one (**4b**). Yield = 70.9 mg (60%); white solid; mp 120−121 °C; IR ($CHCl_3$) υ_{max} 3019, 1677, 1597, 1554, 1488, 1426, 1354, 1047, 1029, 963, 929, 832, 669 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$/TMS) δ 7.65−7.59 (m, 6H), 7.48 (t, J = 7.8 Hz, 2H), 7.41−7.38 (m, 1H), 6.61 (s, 1H), 2.60 (s, 3H), 2.34 (s, 3H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 198.9, 153.3, 142.0, 141.2, 140.2, 128.7, 127.7, 127.2, 127.0, 126.9, 124.3, 32.3, 18.2; HRMS (ESI-TOF) calcd for $[C_{17}H_{16}O + Na]^+$ 259.1093, found 259.1091.

(E)-4-(4-Methoxyphenyl)-3-penten-2-one (**4c**).[32b] Yield = 55.2 mg (58%); white solid; mp 67−68 °C; IR ($CHCl_3$) υ_{max} 3017, 2960, 2936, 2839, 1674, 1592, 1570, 1512, 1463, 1440, 1419, 1377, 1358, 1291, 1179, 1033, 963, 827, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 7.47 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 6.50 (s, 1H), 3.83 (s, 3H), 2.52 (s, 3H), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.8, 160.5, 153.4, 134.5, 127.9, 122.9, 113.9, 55.3, 32.3, 18.0; HRMS (ESI-TOF) calcd for $[C_{12}H_{14}O_2 + Na]^+$ 213.0886, found 213.0889.

(E)-4-(Naphthalen-2-yl)-3-penten-2-one (**4d**). Yield = 61.0 mg (58%); yellow oil; IR ($CHCl_3$) υ_{max} 3058, 3006, 2925, 2850, 1680, 1627, 1597, 1503, 1468, 1434, 1361, 1281, 1229, 1193, 1129, 1018, 962, 896, 861, 819, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 9.67 (s, 1H), 7.89−7.83 (m, 3H), 7.61 (dd, J = 8.6, 2.0 Hz, 1H), 7.54−7.49 (m, 2H), 6.67 (d, J = 1.1 Hz, 1H), 2.66 (d, J = 1.2 Hz, 3H), 2.34 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 198.9, 153.6, 139.6, 133.5, 133.1, 128.5, 128.2, 127.6, 126.7, 126.5, 126.2, 124.8, 124.0, 32.3, 18.3; HRMS (ESI-TOF) calcd for $[C_{15}H_{14}O + Na]^+$ 233.0937, found 233.0931.

(E)-4-Phenyl-3-hexen-2-one (**4e**).[33a] Yield = 47.9 mg (55%); colorless oil; IR ($CHCl_3$) υ_{max} 2969, 2933, 1679, 1597, 1572, 1357, 1180, 1099, 1020, 916, 736, 696, 650 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 7.45−7.43 (m, 2H), 7.39−7.37 (m, 3H), 6.40 (s, 1H), 3.05 (q, J = 7.5 Hz, 2H), 2.28 (s, 3H), 1.05 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.5, 160.4, 141.3, 132.3, 128.9, 128.5, 126.8, 124.2, 32.3, 24.4, 13.5; HRMS (ESI-TOF) calcd for $[C_{12}H_{14}O + Na]^+$ 197.0937, found 197.0933.

4,4-Diphenyl-3-buten-2-one (**4f**).[33b] Yield = 46.7 mg (42%); yellow oil; IR ($CHCl_3$) υ_{max} 3057, 3027, 2928, 1684, 1664, 1591, 1569, 1491, 1445, 1354, 1178, 1075, 1022, 858, 699, 666 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$/TMS) δ 7.51−7.49 (m, 3H), 7.45−7.32 (m, 5H), 7.28−7.24 (m, 2H), 6.61 (s, 1H), 1.91 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 200.2, 153.9, 140.7, 138.9, 129.5, 129.4, 128.7, 128.35, 128.3, 127.6, 30.3; HRMS (ESI-TOF) calcd for $[C_{16}H_{14}O + Na]^+$ 245.0937, found 245.0935.

1-(9H-Fluoren-9-ylidene)propan-2-one (**4g**).[34a] Yield = 68.3 mg (62%); yellow solid; mp 97−98 °C; IR ($CHCl_3$) υ_{max} 3065, 2955, 2925, 2853, 1682, 1617, 1590, 1476, 1450, 1354, 1299, 1177, 1163, 1020, 980, 941, 846, 784, 728 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$/TMS) δ 8.79 (d, J = 7.8 Hz, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.64 (dd, J

DOI: 10.1021/acs.joc.6b01899
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= 7.5, 2.1 Hz, 2H), 7.43 (dq, J = 7.5, 1.0 Hz, 1H), 7.33−7.27 (m, 3H), 7.09 (s, 1H), 2.52 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 198.6, 145.9, 142.4, 141.3, 138.9, 135.3, 131.2, 130.7, 128.5, 128.2, 127.4, 121.1, 120.8, 119.9, 119.6, 32.4; HRMS (ESI-TOF) calcd for $[C_{16}H_{12}O + Na]^+$ 243.0780, found 243.0782.

*(E)-2-Phenyl-2-undecen-5-one (**6a**).* Yield = 77.0 mg (63%); yellow oil; IR ($CHCl_3$) υ_{max} 3063, 3020, 3000, 2957, 2931, 2858, 1754, 1625, 1601, 1495, 1448, 1407, 1376, 1261, 1178, 1102, 1072, 1028, 961, 920, 876, 821, 700, 667 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$/TMS) δ 7.99 (d, J = 7.3 Hz, 2H), 7.51−7.27 (m, 3H), 5.95 (td, J = 7.2, 1.1 Hz, 1H), 3.34 (d, J = 7.2 Hz, 2H), 2.50 (t, J = 7.5 Hz, 2H), 2.08 (s, 3H), 1.59−1.45 (m, 2H), 1.34−1.28 (m, 6H), 0.92 (t, J = 7.5 Hz, 3H); ^{13}C $\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 209.0, 143.2, 138.2, 128.2, 127.1, 125.8, 119.5, 43.2, 42.6, 31.6, 28.9, 23.8, 22.5, 16.3, 14.0; HRMS (ESI-TOF) calcd for $[C_{17}H_{24}O + H]^+$ 245.1900, found 245.1894.

*1-(9H-Fluoren-9-ylidene)nonan-3-one (**6b**).* Yield = 118.7 mg (78%); yellow oil; IR ($CHCl_3$) υ_{max} 2955, 2930, 2856, 1714, 1608, 1512, 1464, 1414, 1376, 1290, 1248, 1180, 1035, 911, 830, 734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 7.78−7.68 (m, 4H), 7.41−7.28 (m, 4H), 7.03 (t, J = 7.0 Hz, 1H), 3.93 (d, J = 7.0 Hz, 2H), 2.59 (t, J = 7.3 Hz, 2H), 1.69−1.62 (m, 2H), 1.33−126 (m, 6H), 0.94−0.87 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 207.3, 141.2, 139.0, 138.8, 137.3, 137.0, 128.3, 127.9, 127.1, 127.0, 124.6, 120.23, 120.16, 120.0, 119.5, 43.0, 42.6, 31.6, 28.8, 23.8, 22.5, 14.0; HRMS (ESI-TOF) calcd for $[C_{22}H_{24}O + Na]^+$ 327.1719, found 327.1722.

*(E)-2-(4-Methoxyphenyl)-2-undecen-5-one (**6c**).* Yield = 94.7 mg (69%); colorless oil; IR ($CHCl_3$) υ_{max} 2956, 2931, 2857, 1709, 1669, 1609, 1512, 1464, 1376, 1290, 1247, 1179, 1034, 909, 830, 733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 7.34 (d, J = 8.9 Hz, 2H), 6.86 (d, J = 8.9 Hz, 2H), 5.87 (td, J = 6.0, 1.2 Hz, 1H), 3.80 (s, 3H), 3.30 (d, J = 7.2 Hz, 2H), 2.47 (t, J = 7.5 Hz, 2H), 2.02 (s, 3H), 1.30−1.25 (m, 8H), 0.88−0.86 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 209.2, 158.8, 137.5, 135.7, 126.8, 117.8, 113.6, 55.3, 43.2, 42.5, 31.6, 28.9, 23.8, 22, 5, 16.3, 14.0; HRMS (ESI-TOF) calcd for $[C_{18}H_{26}O_2 + Na]^+$ 297.1825, found 297.1816.

*(E)-4-(4-Methoxyphenyl)-1-phenyl-3-penten-1-one (**6d**).* Yield = 98.5 mg (74%); colorless oil; IR ($CHCl_3$) υ_{max} 3155, 2959, 2930, 2840, 1682, 1607, 1512, 1465, 1449, 1380, 1324, 1290, 1247, 1180, 1096, 1034, 898, 832, 676 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 8.01 (dd, J = 7.7, 1.5 Hz, 2H), 7.60−7.41 (m, 3H), 7.36 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 6.03 (tq, J = 6.9, 1.3 Hz, 1H), 3.90 (dd, J = 6.9, 0.8 Hz, 2H), 3.81 (s, 3H), 2.15 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 198.0, 158.8, 137.4, 136.8, 135.7, 133.1, 128.3, 126.8, 118.1, 113.5, 55.3, 39.0, 16.4; HRMS (ESI-TOF) calcd for $[C_{18}H_{18}O_2 + Na]^+$ 289.1199, found 289.1193.

*(E)-1,4-Diphenyl-3-penten-1-one (**6e**).*[34b] Yield = 80.3 mg (68%); colorless oil; IR ($CHCl_3$) υ_{max} 3085, 3058, 3034, 2872, 2924, 2861, 1684, 1617, 1598, 1581, 1493, 1447, 1380, 1323, 1180, 1158, 1072, 1001, 910, 736, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$/TMS) δ 8.02 (dd, J = 8.3, 1.7 Hz, 2H), 7.60−7.57 (m, 1H), 7.50−7.47 (m, 2H), 7.42 (dd, J = 7.8, 1.0 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.25−7.23 (m, 1H), 6.12 (td, J = 6.8, 1.3 Hz, 1H), 3.91 (d, J = 6.8 Hz, 2H), 2.13 (d, J = 1.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 197.9, 143.2, 138.1, 136.8, 133.1, 128.6, 128.3, 128.2, 127.0, 125.8, 119.7, 39.0, 16.5; HRMS (ESI-TOF) calcd for $[C_{17}H_{16}O + Na]^+$ 259.1093, found 259.1092.

*1-(5-Methoxy-3,4-dihydronaphthalen-1-yl)propan-2-one (**6f**).* Yield = 73.5 mg (68%); yellow oil; IR ($CHCl_3$) υ_{max} 3016, 2937, 2837, 1709, 1573, 1473, 1461, 1439, 1408, 1356, 1347, 1299, 1262, 1193, 1161, 1140, 1050, 931, 910, 853, 825, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 7.13 (t, J = 8.0 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H); 6.01 (t, J = 4.5 Hz, 1H), 3.83 (s, 3H), 3.46 (s, 2H), 2.80 (t, J = 8.2 Hz, 2H), 2.36−2.28 (m, 2H), 2.12 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 208.2, 156.1, 135.1, 130.9, 129.9, 126.6, 124.1, 115.8, 110.0, 55.5, 49.6, 28.5, 22.7, 19.7; HRMS (ESI-TOF) calcd for $[C_{14}H_{16}O_2 + Na]^+$ 239.1043, found 239.1045.

*1-(3,4-Dihydronaphthalen-1-yl)propan-2-one (**6g**).* Yield = 52.1 mg (56%); yellow oil; IR ($CHCl_3$) υ_{max} 3059, 3020, 2934, 2885, 2831, 1710, 1675, 1579, 1488, 1449, 1427, 1355, 1325, 1225, 1159, 1039, 1022, 912, 790, 735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$/TMS) δ 7.19−7.08 (m, 4H), 6.01 (t, J = 4.5 Hz, 1H), 3.48 (s, 2H), 2.81 (t, J = 8.0 Hz, 2H), 2.37−2.32 (m, 2H), 2.15 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 207.9, 136.2, 134.1, 130.9, 129.6, 127.7, 127.2, 126.5, 122.8, 49.1, 28.5, 28.0, 23.2; HRMS (ESI-TOF) calcd for $[C_{13}H_{14}O + Na]^+$ 209.0937, found 209.0935.

*1-(1H-Inden-3-yl)propan-2-one (**6h**)*[35a] *and (E)-1-(2,3-Dihydro-1H-inden-1-ylidene)propan-2-one (**6h′**).*[35b] Mixture (0.7:1); yield = 48.2 mg (56%); colorless oil; IR ($CHCl_3$) υ_{max} 3068, 3041, 3019, 2922, 2855, 1712, 1676, 1646, 1594, 1473, 1461, 1438, 1394, 1361, 1322, 1278, 1256, 1223, 1188, 1170, 1106, 1039, 1017, 982, 962, 845 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) of the mixture δ 7.64 (d, J = 7.7 Hz, 1H), 7.48 (d, J = 2.6 Hz, 1H), 7.47 (d, J = 1.6 Hz, 2H), 7.40−7.21 (m, 4H), 6.75 (t, J = 2.5 Hz, 1H), 6.41 (t, J = 1.0 Hz, 1H), 3.66 (d, J = 1.2 Hz, 2H), 3.41 (d, J = 1.2 Hz, 2H), 3.32−3.28 (m, 2H), 3.08−3.06 (m, 2H), 2.32 (s, 3H), 2.20 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 206.2, 198.2, 161.9, 150.2, 144.0, 139.9, 137.2, 132.1, 131.1, 126.7, 126.2, 125.7, 124.9, 123.8, 121.5, 119.1, 115.1, 43.5, 38.0, 31.9, 31.6, 30.7, 29.1; HRMS (ESI-TOF) calcd for $[C_{12}H_{12}O + H]^+$ 173.0961, found 173.0955.

*1-(3,4-Dihydronaphthalen-1-yl)nonan-3-one (**6i**).* Yield = 96.0 mg (71%); yellow oil; IR ($CHCl_3$) υ_{max} 3057, 3018, 2931, 2858, 1713, 1487, 1450, 1412, 1370, 1278, 1234, 1160, 1127, 1081, 1038, 1022, 938, 868, 817, 790, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 7.22−7.19 (m, 2H), 7.18−7.14 (m, 2H), 5.86 (t, J = 4.5 Hz, 1H), 2.75−2.70 (m, 4H), 2.65−2.61 (m, 2H), 2.39 (t, J = 7.5 Hz, 2H), 2.26−2.21 (m, 2H), 1.64−1.51 (m, 2H), 1.34−1.19 (m, 6H), 0.88 (t, J = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 210.9, 136.7, 135.3, 134.3, 127.7, 126.7, 126.4, 125.3, 122.4, 43.1, 41.6, 31.6, 28.9, 28.3, 26.6, 23.8, 23.0, 22.5, 14.0; HRMS (ESI-TOF) calcd for $[C_{19}H_{26}O + Na]^+$ 293.1876, found 293.1867.

*3-(3,4-Dihydronaphthalen-1-yl)-1-phenylpropan-1-one (**6j**).* Yield = 99.7 mg (76%); yellow oil; IR ($CHCl_3$) υ_{max} 3061, 3033, 2931, 2888, 2833, 1685, 1488, 1448, 1359, 1291, 1236, 1204, 1178, 975, 911, 765, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 7.97 (dd, J = 8.2, 2.2 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.49−7.45 (m, 2H), 7.31−7.16 (m, 4H), 5.96 (t, J = 4.5 Hz, 1H), 3.23 (t, J = 7.7 Hz, 2H), 2.93 (t, J = 7.5 Hz, 2H), 2.75 (t, J = 8.0 Hz, 2H), 2.29−2.25 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.8, 136.9, 136.8, 135.4, 134.3, 132.9, 128.5, 128.0, 127.7, 126.7, 126.4, 125.5, 122.4, 37.7, 28.2, 27.1, 23.0; HRMS (ESI-TOF) calcd for $[C_{19}H_{18}O + Na]^+$ 285.1250, found 285.1238.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01899.

Copies of ^1H and ^{13}C NMR spectra for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This activity was supported by the Council of Scientific and Industrial Research (CSIR) New Delhi [Grant No. 02 (0158)/13/EMR-II], India. Financial support received from CSIR-India as a fellowship to V.B. is gratefully acknowledged.

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DOI: 10.1021/acs.joc.6b01899
J. Org. Chem. 2016, 81, 8577−8584