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Rhodium-catalyzed conjugate addition of aryl- and alkenyl-stannanes to α,β-unsaturated carbonyl compounds

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Abstract—The addition of aryl- or alkenyl-trimethylstannanes to α,β-unsaturated carbonyl compounds in the presence of a catalytic amount of a cationic rhodium complex ([Rh(cod)(MeCN)$_2$]BF$_4$) and water to afford the conjugate addition products in good yields was examined. It was observed that addition of water was necessary for the reaction to proceed smoothly. The aryl- or alkenyl-rhodium complex, which is generated by the transmetalation from the organotin compound, is considered to be the active catalytic species. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

The conjugate addition of organometallic compounds to α,β-unsaturated carbonyl compounds, which involves the carbon–carbon bond formation at the β-position of the carbonyl compounds, is an important and useful method of synthesizing β-substituted saturated carbonyl compounds. Such reactions are typically carried out using organocopper reagents, which are generated from the reaction between copper salts and the corresponding organolithium or Grignard reagents.[1] Conjugate additions of organoaluminum[2] and organoboron[3] compounds, without a catalyst, have also been reported. Furthermore, transition metal-catalyzed conjugate addition reactions of main group organometallic reagents are potentially useful in terms of chemo-, regio-, and stereoselectivities, with a possible extension into asymmetric systems using a combination of appropriate catalysts. For example, nickel-catalyzed conjugate addition of organoaluminum,[4] organozinc,[5] and organozirconium[6] compounds, palladium-catalyzed conjugate addition of arylmercury,[7] arylantimony,[8] and aryltin compounds,[7,9] and rhodium-catalyzed conjugate addition of aryl- or alkenyl-boronic acids[10] have been reported. Previously, we have demonstrated that arylstannanes, in the presence of a cationic rhodium complex as the catalyst, can add to aldehydes[11] or to aldimines[12] to afford the corresponding arylated carbinols or amines, respectively. In these reactions, the arylrhodium species, which was generated by the transmetalation with the arylstannanes, were assumed to be the active species that actually adds to the aldehydes or aldimines. During our investigations on the utilization of this methodology, we realized that the conjugate addition of aryl- or alkenyl-stannanes occurred in the cases where the α,β-unsaturated carbonyl compounds were the substrates.[13] Herein, we wish to report scope and limitation of the rhodium-catalyzed conjugate addition reaction of organotin compounds to α,β-unsaturated carbonyl compounds. The reaction can be carried out under mild and neutral conditions, and furthermore, not only α,β-unsaturated ketones, but α,β-unsaturated esters and aldehydes were also shown to undergo similar conjugate additions.

2. Results and discussion

To optimize the reaction conditions, the reaction of 4-phenylbut-3-en-2-one (**1a**) with trimethylphenylstannane (**2a**) was examined under various settings (Table 1). Reactions were carried out in THF or CH$_2$Cl$_2$ as the solvent, in the presence of 2 mol% cationic rhodium complex, [Rh(cod)(MeCN)$_2$]BF$_4$, at room temperature for 20 h to afford 4,4-diphenylbutan-2-one (**3aa**) in approximately 50% yields (entries 1 and 2). However, using toluene as the solvent resulted in a lower yield of 41%, while using acetonitrile as the solvent gave only 6% yield (entries 3 and 4). When the reaction was carried out at 60°C in THF, a higher yield of **3aa** (86%) was observed for the reaction time of 2 h (entry 5). The neutral chlorine-bridged dimer complex, [RhCl(cod)]$_2$, did not show good activity as the cationic one affording the product in lower yield of 53% under similar conditions of 60°C in THF for 2 h (entry 6). The addition of phosphine ligands such as PPh$_3$

Keywords: conjugate addition; α,β-unsaturated carbonyl compound; organotin compounds; thodium catalyst.

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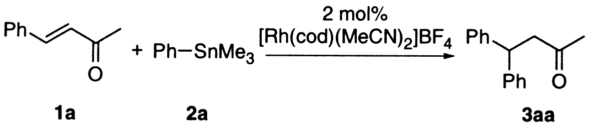
Table 1. Rhodium-catalyzed conjugate addition of **2a** to **1a** under various reaction conditions



Entry	Solvent	Ligand	Temperature (°C)/time (h)	Yield (%)[a]
1	THF	None	Rt/20	51
2	CH_2Cl_2	None	Rt/20	50
3	Toluene	None	Rt/20	41
4	CH_3CN	None	Rt/20	6
5	THF	None	60/2	86
6[b]	THF	None	60/2	53
7	THF	PPh_3[c]	60/2	63
8	THF	PPh_3[d]	60/2	15
9	THF	dppp[c,e]	60/2	48

Common reaction conditions: **1a** (1.0 mmol), **2a** (1.2 mmol), $[Rh(cod)(MeCN)_2]BF_4$ (0.02 mmol), solvent (1 mL), N_2 atmosphere.

[a] Isolated yield.

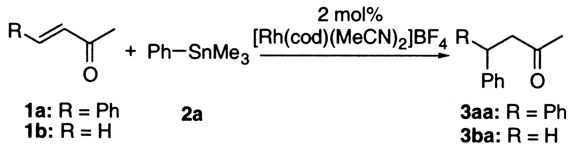
[b] $[RhCl(cod)]_2$ (0.01 mmol) was used as the catalyst.

[c] L/Rh=1.

[d] L/Rh=2.

[e] 1,3-Bis (diphenylphosphino)propane.

Table 2. Effect of additive in conjugate addition of **2a** to **1a** or **1b**



Entry	Enone **1**	Additive	yield (%)[a]
1	**1b**	None	18
2	**1b**	MeOH	63
3	**1b**	AcOH	0
4	**1b**	H_2O	80
5	**1a**	None	86
6	**1a**	H_2O	98

Reaction conditions: **1** (1.0 mmol), **2a** (1.2 mmol), additive (1.0 mmol), $[Rh(cod)(MeCN)_2]BF_4$ (0.02 mmol), THF (1 mL), 60°C, 5 h (for **1b**), 2 h (for **1a**), N_2 atmosphere.

[a] Isolated yield.

or 1,3-bis(diphenylphosphino)propane (dppp) to the cationic complex also resulted in lower yields (entries 7–9).

Based on the high yield, as shown in Table 1 (entry 5), similar conditions were employed for the reaction of methyl vinyl ketone (**1b**) with **2a**. However, despite the complete consumption of the enone **1b**, the conjugate adduct **3ba** was obtained in only an 18% yield (Table 2, entry 1), which can be explained by the further reactions of the product stannyl enol ether (vide infra) with the starting substrate enone **1b**. Thus, to immediately decompose the stannyl enol ether to ketone **3ba**, addition of protic species to the reaction was examined. As shown in Table 2 (entries 2 and 4), the addition of methanol or water was found to increase the yields; optimally, the addition of an equimolar amount of water afforded the desired product **3ba** in a yield of 80%. However, the addition of acetic acid did not show similar enhancements (entry 3). In the case of **1a**, the addition of water similarly increased the yield from 86 to 98% (entries 5 and 6).

Results of the conjugate addition between aryl- or alkenylstannanes **2a**–**f** and various α,β-unsaturated ketones (enones **1a**–**l**) are summarized in Table 3. Reactions between trimethylphenylstannane (**2a**) and enones, including cyclic enones, having mono- or di-substituted olefinic moieties (**1a**–**j**) proceeded smoothly to afford the corresponding β-phenylated ketones **3aa**–**ja** in good yields (entries 1–10). Unsaturated products of the Heck type were not observed for this series of reactions. In contrast, the reactions involving hindered enones, such as 3-methylpent-3-en-2-on (**1k**) and isophorone (**1l**) were sluggish; the former afforded the product **3ka** in a moderate yield of 37%, even under a longer reaction time of 24 h (entry 11), and the latter did not react under similar reaction conditions (entry 12).

Continuing with different stannanes, the reaction of **1a** with phenyltributylstannane (**2b**) resulted in a somewhat lower yield of 70% (entry 13), while the reaction with tetraphenylstannane (**2c**) resulted in a yield of only 11% (entry 14), which can be attributable to the steric hindrance of the phenylstannanes. Arylstannanes bearing an electron-withdrawing or -donating group, such as *p*-fluorophenyltrimethylstannane (**2d**) and *p*-methoxyphenyltrimethyl-

Table 3. Rhodium-catalyzed conjugate addition of organotin compounds **2** to α,β-unsaturated ketones **1**

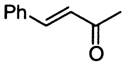
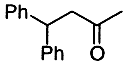
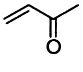
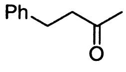
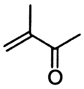
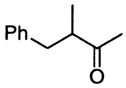
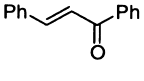
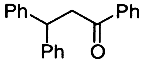
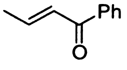
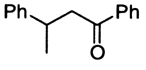
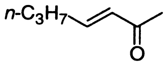
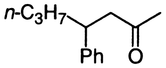
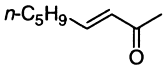
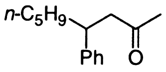
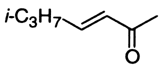
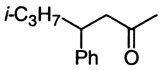
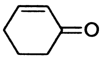
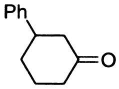
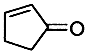
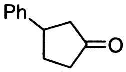
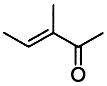
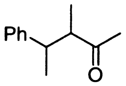
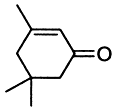
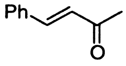
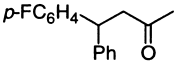
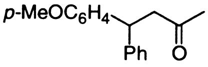
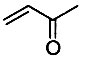
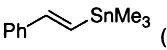
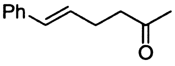
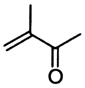
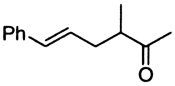
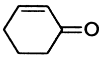
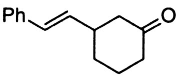
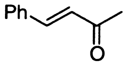
Entry	Enone **1**	Stannane **2**	Time (h)	Product	Yield (%)[a]
1	 **(1a)**	Ph-$SnMe_3$ (**2a**)	2	 **(3aa)**	98
2	 **(1b)**	**2a**	5	 **(3ba)**	80
3	 **(1c)**	**2a**	5	 **(3ca)**	88
4	 **(1d)**	**2a**	2	 **(3da)**	94

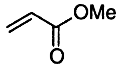
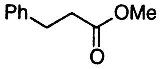
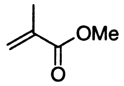
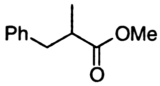
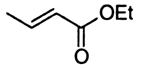
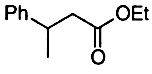
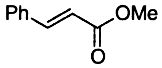
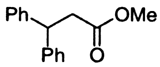
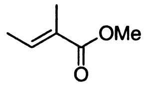
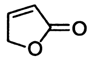
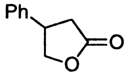
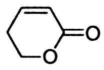
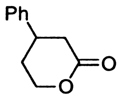
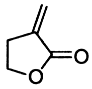
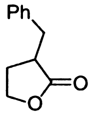
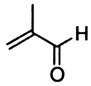
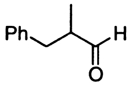
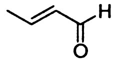
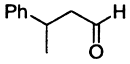
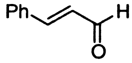
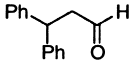
Table 3. (*continued*)

Entry	Enone **1**	Stannane **2**	Time (h)	Product	Yield (%)[a]
5	 **(1e)**	**2a**	2	 **(3ea)**	60
6	 **(1f)**	**2a**	2	 **(3fa)**	85
7	 **(1g)**	**2a**	2	 **(3ga)**	85
8	 **(1h)**	**2a**	15	 **(3ha)**	79
9	 **(1i)**	**2a**	2	 **(3ia)**	93
10	 **(1j)**	**2a**	5	 **(3ja)**	91
11	 **(1k)**	**2a**	24	 **(3ka)**	37
12	 **(1l)**	**2a**	24	–	0
13	 **(1a)**	Ph-SnBu$_3$ (**2b**)	2	**3aa**	70
14	**1a**	Ph$_4$Sn (**2c**)	2	**3aa**	11
15	**1a**	p-FC$_6$H$_4$-SnMe$_3$ (**2d**)	2	 **(3ad)**	68
16	**1a**	p-MeOC$_6$H$_4$-SnMe$_3$ (**2e**)	2	 **(3ae)**	74
17	 **(1b)**	 **(2f)**	20	 **(3bf)**	70
18	 **(1c)**	**2f**	20	 **(3cf)**	45
19	 **(1i)**	**2f**	20	 **(3if)**	23
20	 **(1a)**	**2f**	20	–	0

Reaction conditions: **1** (1.0 mmol), **2** (1.2 mmol), water (18 μL, 1.0 mmol), [Rh(cod)(MeCN)$_2$]BF$_4$ (0.02 mmol), THF (1 mL), 60°C, N$_2$ atmosphere.
[a] Isolated yield.

stannane (**2e**), reacted smoothly with **1a** to afford the corresponding conjugate adducts **3ad** and **3ae** in good yields of 68 and 74%, respectively (entries 15 and 16). Comparatively, the reactivities of alkenylstannanes appeared to be lower than those of arylstannanes. The addition of styryltrimethylstannane (**2f**) to methyl vinyl ketone (**1b**) afforded product **3bf** in a good yield of 70% (entry 17), whereas the additions to 3-methylbut-3-en-2-one (**1c**) and cyclohexenone (**1i**) afforded products **3cf** and **3if** in moderate yields of 45 and 23%, respectively (entries 18 and 19).

Table 4. Rhodium-catalyzed conjugate addition of **2a** to α,β-unsaturated esters **4** or aldehydes **6**

Entry	Ester **4** or aldehyde **6**	Product	Yield (%)[a]
1	 **(4a)**	 **(5aa)**	66
2	 **(4b)**	 **(5ba)**	75
3	 **(4c)**	 **(5ca)**	71
4	 **(4d)**	 **(5da)**	90
5	 **(4e)**	–	0
6	 **(4f)**	 **(5fa)**	68
7	 **(4g)**	 **(5ga)**	54
8	 **(4h)**	 **(5ha)**	57
9	 **(6a)**	 **(7aa)**	52
10	 **(6b)**	 **(7ba)**	47
11	 **(6c)**	 **(7ca)**	43

Reaction conditions: **4** or **6** (1.0 mmol), **2a** (1.2 mmol), water (18 μL, 1.0 mmol), [Rh(cod)(MeCN)$_2$]BF$_4$ (0.02 mmol), THF (1 mL), 60°C, N$_2$ atmosphere.

[a] Isolated yield.

Unfortunately, the addition reaction between **1a** and **2f** was not observed (entry 20).

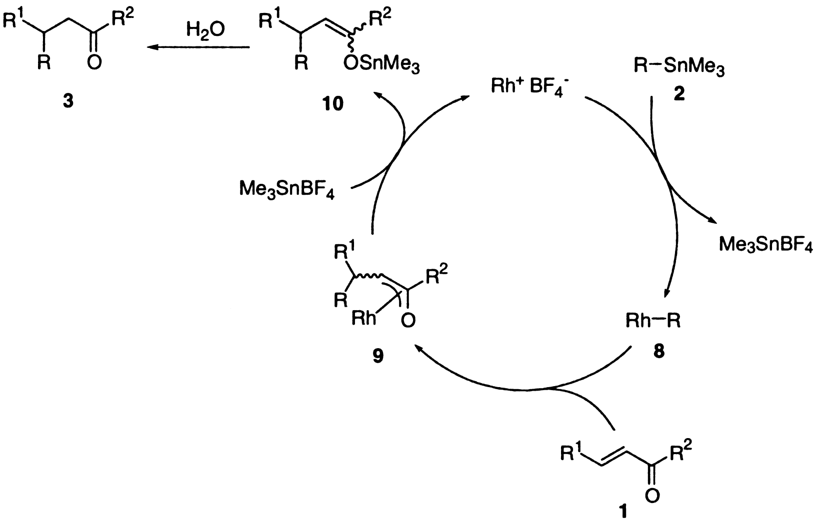
As summarized in Table 4, the conjugate addition of phenyltrimethylstannane (**2a**) to various α,β-unsaturated esters and aldehydes were also examined. The conjugate addition of **2a** to α,β-unsaturated esters having mono- or di-substituted olefinic moieties (**4a–d**) proceeded smoothly with good yields (entries 1–4). However, due to the steric hindrance of the substituents, the reaction between the α,β-unsaturated ester having trisubstituted olefinic moiety **4e** and **2a** was not observed (entry 5). Reactions involving *endo*- and *exo*-enlactones **4f–h** as the substrate resulted in acceptable yields (entries 6–8). For the cases involving α,β-unsaturated aldehydes as the substrate, the reactions of methacrolein (**6a**), crotonaldehyde (**6b**), and cinnamaldehyde (**6c**) with **2a** resulted in the conjugate adducts **7aa–ca** with yields of 52, 47, and 43%, respectively (entries 9–11). As a note, in the cases of the aldehydes, conjugate addition was predominantly observed, and the competing reaction of 1,2-addition was not detected.

In the presented reactions, an organorhodium species is assumed to be the active intermediate, which is generated by the transmetalation between the organotin compound and the rhodium complex. The presumed reaction pathway is shown in Scheme 1 (for simplification, ligands of the rhodium complexes not involved with the reaction are omitted). As the initial step, the transmetalation of the cationic rhodium complex (Rh$^+$BF$_4$$^-$) with organotin **2** produces the organorhodium intermediate **8** and Me$_3$SnBF$_4$. Addition of **8** to the α,β-unsaturated carbonyl compound **1** leads to the η^3-oxa-π-allylrhodium complex **9**, which then reacts with Me$_3$SnBF$_4$ to afford stannyl enol ether **10** and to regenerate the cationic rhodium complex. NMR studies of the reaction mixture, in the absence of water, indicated the formation of the corresponding stannyl enol ether **10**; furthermore, NOE experiments of **10** showed the preferential formation of the *Z*-isomer. The stannyl enol ether **10** was easily hydrolyzed to afford product **3**.[13a]

To gain information on the reaction mechanism, the reactivity of [Rh(cod)(CH$_3$CN)$_2$]BF$_4$ toward trimethylphenylstannane (**2a**) was studied. When 0.1 mmol of [Rh(cod)(CH$_3$CN)$_2$]BF$_4$ was treated with equimolar amount of **2a** and D$_2$O in THF at 25°C for 20 h, the stannane **2a** was completely consumed and deuterized benzene (44% yield, 78%-*d*) was formed. A control experiment confirmed that the stannane **2a** was inert to water. The result indicates the generation of a water-labile species from [Rh(cod)(CH$_3$CN)$_2$]BF$_4$ and the stannane **2a**, which we attribute to an unstable phenylrhodium species that should decompose rapidly to give benzene. Interestingly, the present conjugate addition reaction was carried out in the presence of water and that indicate that the unstable phenylrhodium species reacted with α,β-unsaturated carbonyl compounds faster than with water. Unfortunately, we tried in vain to detect a peak corresponding to the phenylrhodium species by ^{1}H and ^{13}C NMR measurements of the reaction without water in THF-d_8, which would be caused by the instability of the species. A similar reaction mechanism, which involves the generation of the organorhodium intermediate, has been proposed by Miyaura et al. in their studies of the rhodium-catalyzed conjugate addition of arylboronic acid to α,β-unsaturated carbonyl compounds.[10c]

3. Conclusion

A highly efficient rhodium-catalyzed conjugate addition of organotin compounds to α,β-unsaturated carbonyl compounds was examined. It was shown that the presence of water improved the reaction. An aryl- or alkenyl-rhodium complex, which was generated by the transmetalation from the organotin compound, is considered to be the active catalytic species. Since the organotin compounds are inert to many organic compounds, and the reaction can be



Scheme 1. Presumed reaction mechanism.

carried out under mild and neutral conditions, we believe that the present reaction can be a useful methodology in the synthesis of complicated compounds such as natural products.

4. Experimental

4.1. General information

All reactions were carried out in Schlenk tubes under N_2. THF was dried over sodium/benzophenone ketyl, and distilled before use. NMR spectra were recorded using $CDCl_3$ as the solvent. Elemental analyses were performed by the Microanalytical Laboratory of the Institute for Chemical Reaction Science, Tohoku University. Spherical silica gel (40–100 μm, Kanto Chemical) was used for flash chromatography. The cationic rhodium complex, $[Rh(cod)(MeCN)_2]BF_4$, was prepared as described.[14] The organotin compounds (**2d–f**) were prepared from the corresponding Grignard reagents and trimethylstannyl chloride.[15]

4.1.1. Catalytic conjugate addition of organotin compounds. To a mixture of 4-phenylbut-3-en-2-on (**1a**, 146 mg, 1.0 mmol) and $[Rh(cod)(MeCN)_2]BF_4$ (7.4 mg, 0.02 mmol) in THF (1 mL) were added trimethylphenylstannane (**2a**, 289 mg, 1.2 mmol) and water (18 μL, 1.0 mmol), and stirred at 60°C for 2 h. Et_2O (20 mL) was added to the reaction mixture and the resulting precipitate was removed by filtration. The solvent was removed in vacuo and the residue was purified by flash chromatography (hexane/AcOEt=10:1) to yield 4,4-diphenylbutan-2-one (**3aa**, 220 mg, 98%).[8] Mp 58–60°C. IR (KBr) 3022, 1720, 1602, 1499, 1455, 1360, 1161, 755, 700 cm^{-1}. ^{1}H NMR (250 MHz) δ 7.28–7.10 (m, 10H), 4.57 (t, *J*=7.5 Hz, 1H), 3.14 (d, *J*=7.5 Hz, 2H), 2.02 (s, 3H). ^{13}C NMR (62.5 MHz) δ 206.7, 143.7, 128.5, 127.6, 126.3, 49.5, 45.9, 30.5.

4.1.2. 4-Phenylbutan-2-one (3ba).[9] IR (neat) 3020, 2930, 1720, 1602, 1500, 1459, 1360, 1162, 750, 699 cm^{-1}. ^{1}H NMR (250 MHz) δ 7.31–7.16 (m, 5H), 2.89 (t, *J*=6.8 Hz, 2H), 2.77 (t, *J*=6.8 Hz, 2H), 2.13 (s, 3H). ^{13}C NMR (62.5 MHz) δ 207.4, 140.4, 128.0, 127.7, 125.6, 44.6, 29.5, 29.2.

4.1.3. 3-Methyl-4-phenylbutan-2-one (3ca).[16] IR (neat) 2970, 2930, 1713, 1456, 1360, 1162, 740, 700 cm^{-1}. ^{1}H NMR (250 MHz) δ 7.40–7.13 (m, 5H), 2.99 (dd, *J*=13.3, 6.7 Hz, 1H), 2.83 (ddq, *J*=7.5, 6.8, 6.7 Hz, 1H), 2.55 (dd, *J*=13.3, 7.5 Hz, 1H), 2.08 (s, 3H), 1.08 (d, *J*=6.8 Hz, 3H). ^{13}C NMR (62.5 MHz) δ 212.0, 139.6, 128.9, 128.3, 126.2, 48.7, 38.8, 28.8, 16.2.

4.1.4. 1,3,3-Triphenylpropan-1-one (3da).[9] IR (KBr) 3040, 1680, 1600, 1500, 1380, 1265, 1219, 754, 700 cm^{-1}. ^{1}H NMR (250 MHz) δ 7.93 (d, *J*=7.0 Hz, 2H), 7.58–7.41 (m, 3H), 7.38–7.15 (m, 10H), 4.83 (t, *J*=7.3 Hz, 1H), 3.74 (d, *J*=7.3 Hz, 2H). ^{13}C NMR (62.5 MHz) δ 210.2, 144.1, 137.1, 133.1, 128.6, 128.5, 128.1, 127.8, 126.4, 45.9, 44.7.

4.1.5. 1,3-Diphenylbutan-1-one (3ea). Mp 50–52°C. IR (KBr) 2961, 1680, 1598, 1497, 1444, 1204, 982, 759, 700, 690 cm^{-1}. ^{1}H NMR (250 MHz) δ 7.92 (d, *J*=7.1 Hz, 2H), 7.56–7.39 (m, 3H), 7.33–7.17 (m, 5H), 3.51 (ddq, *J*=8.3, 7.0, 5.9 Hz, 1H), 3.29 (dd, *J*=16.3, 5.9 Hz, 1H), 3.17 (dd, *J*=16.3, 8.3 Hz, 1H), 1.34 (d, *J*=7.0 Hz, 3H). ^{13}C NMR (62.5 MHz) δ 199.0, 146.5, 132.9, 128.5, 128.4, 128.0, 126.8, 126.2, 47.0, 35.5, 21.8. Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.60; H, 7.25.

4.1.6. 4-Phenylheptan-2-one (3fa). IR (neat) 2978, 1730, 1604, 1501, 1460, 1362, 1170, 768, 707 cm^{-1}. ^{1}H NMR (250 MHz) δ 7.31–7.15 (m, 5H), 3.13 (quint, *J*=7.2 Hz, 1H), 2.71 (d, *J*=7.2 Hz, 2H), 2.00 (s, 3H), 1.65–1.51 (m, 2H), 1.21–1.08 (m, 2H), 0.84 (t, *J*=7.1 Hz, 3H). ^{13}C NMR (62.5 MHz) δ 208.0, 144.5, 128.4, 127.4, 126.3, 50.9, 41.0, 38.7, 30.6, 20.5, 13.9. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.66; H, 9.69.

4.1.7. 4-Phenylnonan-2-one (3ga).[8] IR (neat) 2930, 1720, 1455, 1360, 1160, 759, 701 cm^{-1}. ^{1}H NMR (250 MHz) δ 7.30–7.15 (m, 5H), 3.10 (quint, *J*=7.9 Hz, 1H), 2.70 (d, *J*=6.8 Hz, 2H), 2.00 (s, 3H), 1.57 (brs, 2H), 1.20 (brs, 6H), 0.82 (t, J=5.7 Hz, 3H). ^{13}C NMR (62.5 MHz) δ 207.9, 144.5, 128.3, 127.4, 126.2, 50.8, 41.2, 36.3, 31.6, 30.6, 27.0, 22.4, 13.9.

4.1.8. 5-Methyl-4-phenylhexan-2-one (3ha). IR (neat) 2960, 1715, 1457, 1359, 1160, 700 cm^{-1}. ^{1}H NMR (250 MHz) δ 7.30–7.12 (m, 5H), 2.96–2.87 (m, 1H), 2.80–2.77 (m, 2H), 1.96 (s, 3H), 1.89–1.76 (m, 1H), 0.93 (d, J=6.8 Hz, 3H), 0.74 (d, J=6.8 Hz, 3H). ^{13}C NMR (62.5 MHz) δ 209.0, 143.2, 128.2, 128.1, 126.2, 48.0, 47.5, 33.2, 30.5, 20.6, 20.2. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.80; H, 9.38.

4.1.9. 3-Phenylcyclohexan-1-one (3ia).[8] IR (neat) 2930, 1703, 1601, 1499, 1452, 1201, 756, 699 cm^{-1}. ^{1}H NMR (250 MHz) δ 7.42–7.20 (m, 5H), 3.02–2.96 (m, 1H), 2.96–2.36 (m, 4H), 2.18–2.05 (m, 2H), 1.88–1.73 (m, 2H). ^{13}C NMR (62.5 MHz) δ 211.0, 144.3, 128.7, 126.9, 126.6, 48.8, 44.7, 41.1, 32.7, 25.4.

4.1.10. 3-Phenylcyclopentan-1-one (3ja).[9] IR (neat) 3029, 2962, 2893, 1746, 1603, 1495, 1454, 1402, 1282, 1136, 763, 700 cm^{-1}. ^{1}H NMR (500 MHz) δ 7.36–7.32 (m, 2H), 7.26–7.23 (m, 3H), 3.45–3.38 (m, 1H), 2.67 (dd, J=18.2, 7.5 Hz, 1H), 2.49–2.41 (m, 2H), 2.37–2.26 (m, 2H), 2.04–1.94 (m, 1H). ^{13}C NMR (125 MHz) δ 218.2, 143.1, 128.7, 126.7, 45.7, 42.2, 38.8, 31.1.

4.1.11. 3-Methyl-4-phenylpentan-2-one (3ka). IR (neat) 2965, 1710, 1495, 1452, 1359, 700 cm^{-1}. ^{1}H NMR (250 MHz) δ 7.33–7.15 (m, 5H), 3.05–2.85 (m, 1H), 2.81–2.65 (m, 1H), 2.19 (s, 3H), 1.21 (d, J=6.8 Hz, 3H), 0.85 (d, J=6.8 Hz, 3H). ^{13}C NMR (62.5 MHz) δ 213.0, 144.6, 128.4, 127.3, 126.3, 54.0, 42.7, 29.2, 20.6, 16.0. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.65; H, 9.34.

4.1.12. 4-(4-Fluorophenyl)-4-phenylbutan-2-one (3ad). IR (neat) 3035, 1715, 1601, 1509, 1360, 1222, 1160, 840, 700 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.29–7.14 (m, 7H), 6.92 (t, J=6.5 Hz, 2H), 4.57 (t, J=7.5 Hz, 1H), 3.14 (d, J=7.5 Hz, 2H), 2.05 (s, 3H). ^{13}C NMR (62.5 MHz) δ 206.4, 161.3(d, J=972.8 Hz), 143.6, 139.6, 129.1, 129.0, 128.6, 127.5, 126.5, 115.4, 115.1, 49.6, 45.1, 30.5. Anal. Calcd for $C_{16}H_{15}O_2F$: C, 79.32; H, 6.14. Found: C, 79.48; H, 6.36.

4.1.13. 4-(4-Methoxyphenyl)-4-phenylbutan-2-one (3ae).[9] IR (neat) 2960, 2940, 1720, 1605, 1506, 1250, 838, 700 cm^{-1}. ^{1}H NMR (250 MHz) δ 7.29–7.11 (m, 7H), 6.95 (d, J=6.6 Hz, 2H), 4.53 (t, J=7.6 Hz, 1H), 3.73 (s, 3H), 3.13 (d, J=7.6 Hz, 2H), 2.04 (s, 3H). ^{13}C NMR (62.5 MHz) δ 206.8, 158.0, 144.2, 135.9, 128.6, 128.5, 127.5, 126.3, 113.9, 55.1, 49.8, 45.2, 38.7, 30.5.

4.1.14. *trans*-6-Phenylhex-5-en-2-one (3bf).[17] IR (neat) 3026, 1715, 1598, 1492, 1439, 1364, 1160, 1070, 967, 749, 694 cm^{-1}. ^{1}H NMR (400 MHz) δ 7.34–7.18 (m, 6H), 6.41 (d, J=15.8 Hz, 1H), 6.19 (dt, J=15.8, 6.9 Hz, 1H), 2.61 (t, J=7.15 Hz, 2H), 2.48 (td, J=7.15, 6.9 Hz, 2H), 2.17 (S, 3H). ^{13}C NMR (100 MHz) δ 182.0, 137.5, 130.8, 128.9, 128.5, 127.1, 126.1, 43.2, 30.1, 27.2.

4.1.15. *trans*-3-Methyl-6-phenylhex-5-en-2-one (3cf). IR (neat) 2971, 1712, 1494, 1450, 1360, 1241, 1166, 967, 742, 693 cm^{-1}. ^{1}H NMR (500 MHz) δ 7.37–7.17 (m, 5H), 6.40 (d, J=15.8 Hz, 1H), 6.12 (dt, J=15.8, 7.2 Hz, 1H), 2.68–2.57 (m, 1H), 2.57–2.52 (m, 1H), 2.28–2.22 (m, 1H), 2.16 (s, 3H), 1.14 (d, J=7.0 Hz, 3H). ^{13}C NMR (125 MHz) δ 211.8, 137.3, 132.1, 128.5, 127.3, 127.2, 126.1, 47.1, 36.2, 28.4, 16.1. Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.53; H, 8.57.

4.1.16. 3-(*trans*-2-Phenylethenyl)cyclohexan-1-one (3if).[18] IR (neat) 3025, 2935, 1710, 1448, 966, 747, 694 cm^{-1}. ^{1}H NMR (400 MHz) δ 7.36–7.17 (m, 5H), 6.39 (d, J=16.0 Hz, 1H), 6.15 (dd, J=16.0, 6.8 Hz,1H), 2.72–2.62 (m, 1H), 2.55–2.50 (m, 1H), 2.43–2.37 (m, 1H), 2.35–2.27 (m, 2H), 2.14–2.06 (m, 1H), 2.04–1.97 (m, 1H), 1.80–1.69 (m, 1H), 1.66–1.56 (m, 1H). ^{13}C NMR (100 MHz) δ 210.1,137.1, 132.9, 129.1, 128.5, 127.3, 126.1, 47.3, 41.9, 41.2, 31.6, 25.0.

4.1.17. 3-Phenylpropanoic acid methyl ester (5aa).[19] IR (neat) 3027, 2951, 1738, 1495, 1453, 1436, 1365, 1257, 1196, 1162, 749, 700 cm^{-1}. ^{1}H NMR (250 MHz) δ 7.28–7.18 (m, 5H), 3.68 (S, 3H), 2.95 (t, J=8.1 Hz, 2H), 2.63 (t, J=7.7 Hz, 2H). ^{13}C NMR (62.5 MHz) δ 173.3, 143.5, 128.6, 127.6, 126.5, 51.7, 35.7, 30.9.

4.1.18. 2-Methyl-3-phenylpropanoic acid methyl ester (5ba). IR (neat) 3028, 2951, 1737, 1496, 1454, 1362, 1254, 1166, 745, 701 cm^{-1}. ^{1}H NMR (250 MHz) δ 7.34–7.13 (m, 5H), 3.58 (s, 3H), 3.02 (q, J=6.2 Hz, 1H),2.80–2.59 (m, 2H), 1.15 (s, 3H). ^{13}C NMR (62.5 MHz) δ 176.5, 139.3, 128.9, 128.3, 126.3, 51.5, 41.4, 39.6, 16.7. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.81; H, 7.56.

4.1.19. 3-Phenylbutanoic acid ethyl ester (5ca). IR (neat) 2965, 1733, 1263, 1175, 1020, 700 cm^{-1}. ^{1}H NMR (250 MHz) δ 7.46–7.16 (m, 5H), 4.07 (q, J=7.1 Hz, 2H), 3.28 (ddq, J=8.0, 7.1, 7.0 Hz, 1H), 2.60 (dd, J=15.0, 7.0 Hz, 1H), 2.53 (dd, J=15.0, 8.0 Hz, 1H), 1.30 (d, J=7.1 Hz, 3H), 1.17 (t, J=7.1 Hz, 3H). ^{13}C NMR (62.5 MHz) δ 172.3, 145.7, 128.4, 126.3, 126.2, 60.2, 43.0, 36.5, 21.8, 14.1. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.87; H, 8.30.

4.1.20. 3,3-Diphenylpropanoic acid methyl ester (5da). IR (neat) 3030, 2959, 1740, 1497, 1451, 1260, 1160, 740, 700 cm^{-1}. ^{1}H NMR (250 MHz) δ 7.31–7.14 (m, 10H), 4.55 (t, J=8.0 Hz, 1H), 3.57 (s, 3H), 3.06 (d, J=8.0 Hz, 2H). ^{13}C NMR (62.5 MHz) δ 172.2, 143.4, 128.5, 127.6, 126.5, 51.6, 46.9, 40.5. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.95; H, 6.71. Found: C, 79.96; H, 6.95.

4.1.21. 4-Phenyltetrahydrofuran-2-one (5fa). IR (neat) 2911, 1775, 1604, 1496, 1169, 1019, 700 cm^{-1}. ^{1}H NMR (250 MHz) δ 7.41–7.22 (m, 5H), 4.70–4.23 (m, 2H), 3.79 (qui, J=8.4 Hz, 1H), 2.99–2.62 (m, 2H). ^{13}C NMR (62.5 MHz) δ 176.47, 139.47, 129.20, 127.78, 126.77, 74.10, 41.15, 35.76. Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 74.02; H, 6.22.

4.1.22. 4-Phenyltetrahydropyran-2-one (5ga). IR (neat)

2933, 1730, 1495, 1456, 1260, 1157, 1074, 762, 701 cm^{-1}. ^1H NMR (250 MHz) δ 7.37–7.20 (m, 5H), 4.58–4.34 (m, 2H), 3.32–3.19 (m, 1H), 3.01–2.60 (m, 2H), 2.30–1.97 (m, 2H). ^{13}C NMR (62.5 MHz) δ 170.6, 142.8, 129.0, 127.3, 126.4, 68.6, 37.5, 37.4, 30.3. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.69; H, 7.04.

4.1.23. 3-Phenylmethyltetrahydrofuran-2-one (5ha). IR (neat) 2915, 1769, 1497, 1454, 1374, 1148, 1023, 957, 751, 702 cm^{-1}. ^1H NMR (250 MHz) δ 7.35–7.19 (m, 5H), 4.26–4.08 (m, 2H), 2.88–2.71 (m, 2H), 2.28–2.17 (m, 1H), 2.07–1.91 (m, 2H). ^{13}C NMR (62.5 MHz) δ 178.7, 138.4, 128.9, 128.7, 126.7, 66.5, 41.1, 36.1, 28.0. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.80; H, 6.91.

4.1.24. 2-Methyl-3-phenylpropanal (7aa).[8] IR (neat) 3028, 2970, 2931, 2873, 2813, 2714, 1725, 1496, 1454, 1374, 1164, 927, 742, 701 cm^{-1}. ^1H NMR (250 MHz) δ 9.77 (d, J=1.5 Hz, 1H), 7.31–7.10 (m, 5H), 3.09 (dd, J=13.6, 5.8 Hz, 1H), 2.69–2.65 (m, 1H), 2.60 (dd, J=13.6, 8.3 Hz, 1H), 1.08 (d, J=6.9 Hz, 3H). ^{13}C NMR (62.5 MHz) δ 204.4, 138.9, 129.1, 128.6, 126.5, 48.1, 36.7, 13.3.

4.1.25. 3-Phenylbutanal (7ba).[8] IR (neat) 2960, 2720, 1725, 1601, 1498, 1455, 749, 680 cm^{-1}. ^1H NMR (250 MHz) δ 9.70 (dd, J=2.2, 1.7 Hz, 1H), 7.33–7.19 (m, 5H), 3.36 (ddq, J=7.7, 7.0, 6.8 Hz, 1H), 2.75 (ddd, J=16.6, 6.8, 1.7 Hz, 1H), 2.65 (ddd, J=16.6, 7.7, 2.2 Hz, 1H), 1.32 (d, J=7.0 Hz, 3H). ^{13}C NMR (62.5 MHz) δ 201.9, 145.4, 128.7, 126.8, 126.5, 51.7, 34.3, 22.2.

4.1.26. 3,3-Diphenylpropanal (7ca).[9] IR (neat) 2960, 2750, 1730, 1605, 1502, 1459, 759, 705 cm^{-1}. ^1H NMR (250 MHz) δ 9.74 (t, J=1.9 Hz, 1H), 7.63–7.10 (m, 10H), 4.62 (t, J=7.8 Hz, 1H), 3.19 (dd, J=7.8, 1.9 Hz, 2H). ^{13}C NMR (62.5 MHz) δ 200.0, 143.2, 128.7, 127.7, 126.7, 49.4, 45.0.

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