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Palladium-Catalyzed Desulfitative Conjugate Addition of Aryl Sulfinic Acids and Direct ESI-MS for Mechanistic Studies

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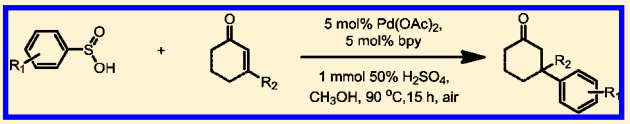
Supporting Information

ABSTRACT: A new and efficient method for palladium(II) catalytic desulfitative conjugate addition of arylsulfinic acids with α,β-unsaturated carbonyl compound has been developed. The key reacting intermediates including aryl Pd(II) sulfinic intermediate, aryl Pd(II), and C═O—Pd complexes were captured by ESI-MS/MS, which provide new experimental evidence for the understanding of addition mechanism.



Transition-metal-catalyzed conjugate addition of organometallic reagents to α,β-unsaturated carbonyl compound is one of the most useful methods for the construction of C−C bonds.[1] In these reactions, the generation of the desired organometallic nucleophile intermediates through transmetalation between transition metal (rhodium,[2] copper,[3] and palladium[4]) and organometallic reagents is important. Various organometallic reagents were used to adjust the reactivity, including organoboron,[5] organosilicon,[6] and aryltitanium reagents.[7] However, these organometallic reagents are generally expensive or unstable. The challenge to find alternatives to the conventional transmetalation method for the formation of organometallic intermediate still has a significant way to go.

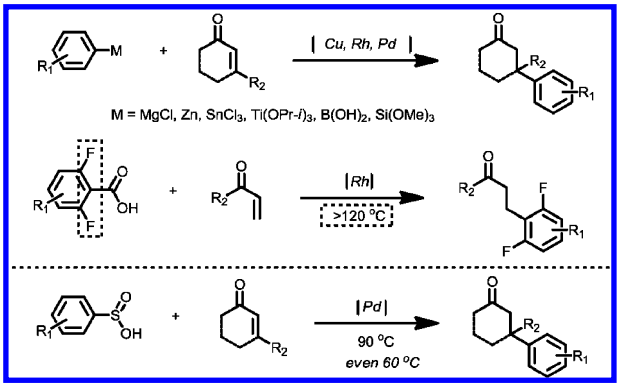
Benzoic acids, considered as ideal aryl sources,[8] were developed for conjugate addition reactions on the basis of decarboxylative generation of rhodium(I) aryl intermediates. However, an electron-withdrawing substituent at *ortho* position and a relatively high temperature (>120 °C) are necessary for the decarboxylative addition to occur successfully.[9]

Arenesulfonyl chlorides and aryl sulfinic acids have the potential to serve as complement aryl donators for C−C bond-forming reactions through the release of SO_2. These reactions may go back to Graves, who first investigated Pd-catalyzed desulfinative couplings, carbonylation, and vinylations reactions.[10] This methodology was then expanded to coupling reaction and 1,2-addition reactions.[11] Recently, O'Hair and coworkers studied the intrinsic reactivity orders for organocuprate formation via thermal extrusion of CO_2, SO_2, or SO_3 in metal complexes (Scheme 1).[12]

Herein, we report a new and efficient method for palladium(II) catalytic desulfitative conjugate addition of arylsulfinic acids with α,β-unsaturated carbonyl compounds and also provide some new experimental evidence for the understanding of addition mechanism by ESI-MS/MS.

Initially, we studied the conjugate addition reaction of benzenesulfinic acid to 2-cyclohexenone with 5 mol % of $Pd(OAc)_2$ in CH_3OH aqueous at 90 °C in a closed vessel. Various ligands, solvents, and additives were investigated (Table 1). The initial result indicated that pyridine-type ligands such as bpy, phen, and dmphen (2,9-dimethyl-1,10-phenanthroline) were more efficient, while other screened ligands, TMEDA, PPh_3, and DPPE, were not very efficient. To our pleasure, the bidentate chelating "N,O" ligand L-proline showed similar activity with the pyridine-type ligands, which indicated potential applications in the asymmetric conjugate reactions. Solvents such as MeOH, EtOH, *i*-PrOH, and dioxane were equally efficient, while polar aprotic DMF and DMSO were improper. Further experiments showed that the reactivity was related with the acidity of additives (Table 1, entries 13−15). H_2SO_4 was supposed to be an effective additive on the basis of the fact that CF_3SO_2H could be hydrolyzed into H_2SO_4 in the aqueous solution. As expected, when 50% H_2SO_4 was used, **2a** was obtained in 99% GC yield. Thus, further experiments were conducted under this condition. However, another strong inorganic acid HCl was an improper additive and completely prohibited the reaction (Table 1, entry 17).

Scheme 1. Transition-Metal-Catalyzed Conjugate Addition of Organometallic Reagents to α,β-Unsaturated Carbonyl Compound



To investigate the reaction scope, various aryl-sulfinic acids as nucleophiles for this process were explored. As shown in Table 2, substrates with various substituents including methyl,

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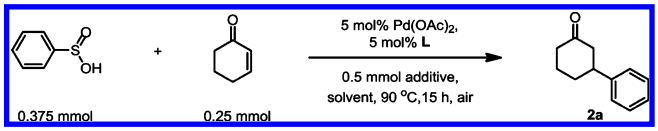
Table 1. Effect of Different Ligands, Acids, and Solvents[a]



entry 1	ligand	additive	solvent	GC yield (%)
1	bpy	HBF_4	CH_3OH	99
2	phen	HBF_4	CH_3OH	99
3	dmbpy	HBF_4	CH_3OH	99
4	TMEDA	HBF_4	CH_3OH	80
5	L-proline	HBF_4	CH_3OH	98
6	PPh_3	HBF_4	CH_3OH	53
7	DPPE	HBF_4	CH_3OH	65
8	bpy	HBF_4	CH_3OH	99
8	bpy	HBF_4	EtOH	99
9	bpy	HBF_4	*i*-PrOH	98
10	bpy	HBF_4	dioxane	98
11	bpy	HBF_4	DMF	58
12	bpy	HBF_4	DMSO	50
13	bpy	CF_3SO_3H	CH_3OH	99
14	bpy	CF_3CO_2H	CH_3OH	66
15	bpy	AcOH	CH_3OH	5
16	bpy	50% H_2SO_4	CH_3OH	99 (94[b])
17	bpy	37% HCl	CH_3OH	0

[a]Reaction conditions: 2-cyclohexenone (0.25 mmol), benzenesulfinic acid (0.375 mmol), $Pd(OAc)_2$ (0.0125 mmol), L (0.0125 mmol), solvent (2.0 mL), and additive (50% aqueous solution, 0.5 mmol) in a sealed tube stirred at 90 °C for 15 h under air. [b]Isolated yield.

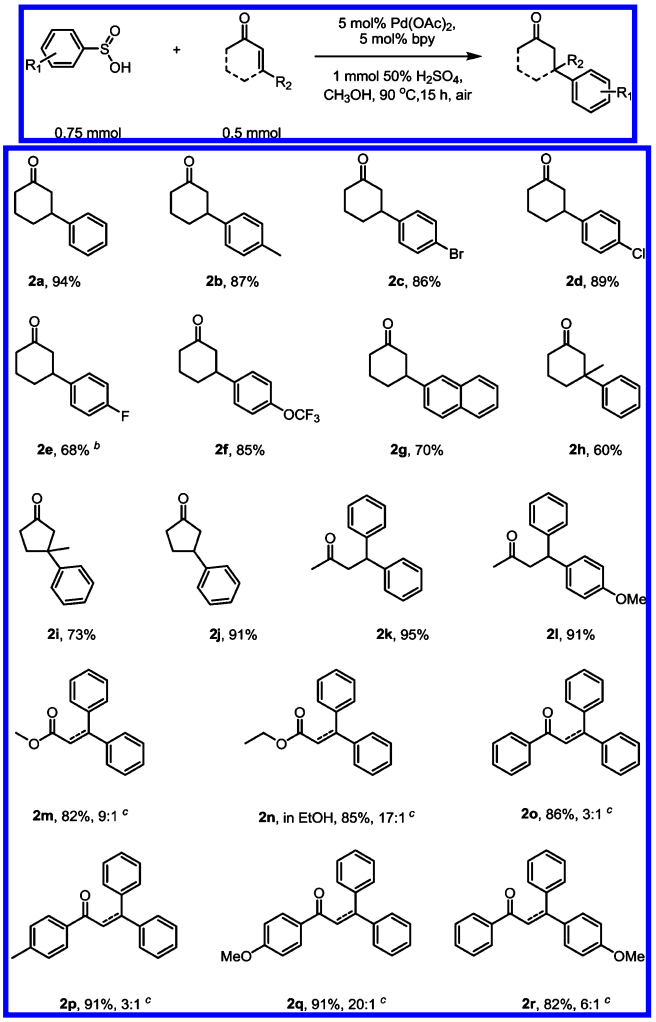
chloro, bromo, fluoro, and trifluoromethoxyl groups underwent the conjugate addition to form the corresponding products **2a**–**g** in good yields without detecting Mizoroki–Heck coupling byproduct. We also found that the steric hindrance at β-carbon of enones affects the reactivity obviously (**2h** and **2i**).

The reactions with acyclic α,β-unsaturated esters or ketones as substrates proceed smoothly with high conversion under the optimized reaction conditions (**2m**–**r**). However, GC and ^{1}H NMR revealed that these enones tend to yield the β-hydride elimination products. To reduce the coupling byproduct, the reaction was carried out under argon; however, the amount of addition products was decreased as well. We proposed that the key step is the protonolysis on the basis of the observation of importance of acidity (Table 1). It was also noted that the conjugate addition of ethyl cinnamate was carried out in EtOH in consideration of the hydrolyzation and esterfication side-reaction in MeOH (**2n**).

Mechanism of desulfitative conjugate addition of arylsulfinic acids is similar to that of palladium-catalyzed conjugate addition of aryl boronic acids.[13] As shown in Scheme 2, in place of transmetalation, first aryl palladium(II) nucleophile **B** would be generated from the palladium(II) sulfinic intermediate **A** by release of SO_2. Subsequently, olefin coordination by carbonyl oxygen forms the C═O—Pd enolate **C**; migratory insertion for the C═C unit of the C═O—Pd enolate into the Ar–Pd bond would form the desired C–C bond at β-position, that is, C–Pd intermediate **D**. Next, isomerization of the C–Pd intermediate **D** to its enol tautomer, i.e., O–Pd enolate **E**, followed by protonolysis would produce the product of conjugate addition last and then regenerate the palladium catalyst (Scheme 2).

Electrospray ionization mass spectrometry (ESI-MS)[14,15] makes possible the detailed observations for the transmetalation

Table 2. Palladium-Catalyzed Desulfitative Reaction of Arylsulfinic Acids with Enones[a]



[a]Reaction Conditions: enone (0.5 mmol), arylsulfinic acid (0.75 mmol), $Pd(OAc)_2$ (0.025 mmol), bpy (0.025 mmol), H_2SO_4 (50% aqueous solution, 1.0 mmol), and solvent (2.0 mL) in a sealed tube stirred at 90 °C for 15 h under air. [b]With 4-fluorobenzene sulfinic sodium. [c]Ratio (conjugate addition/Heck coupling) was calculated by ^{1}H NMR, total yield.

of transition-metal complexes with organometallic reagents, the insertion steps of enones into the aryl palladium intermediates forming C–Pd intermediates and O-bound enolates, which are hardly observed by crystal isolation and X-ray characterization.[7,9,13,16]

In order to capture the ESI-MS signals of aryl Pd(II) intermediate **B** generated from Pd(II) sulfinic intermediate **A**,[11j] benzenesulfinic acid in the presence of 10 mol % $Pd(OAc)_2$ and 10 mol % bpy in aqueous methanol was heated at 60 °C for 1 h, and then an aliquot was withdrawn, filtered, and directly analyzed by ESI-MS(+). Several groups of peaks with m/z signals characterized for the isotopic pattern of single charged monopalladium and dipalladium intermediates were trapped (see the Supporting Information). On the basis of the m/z signals and MS/MS interpretation, structures of the intermediates **A** and **B** were assigned corresponding to different plausible roles in the desulfitative step. The cluster ions at m/z 401.1 and 403.1 were identified as Pd(II) sulfinic intermediate **A** according to the isotope distributions. The cluster ions at $m/$

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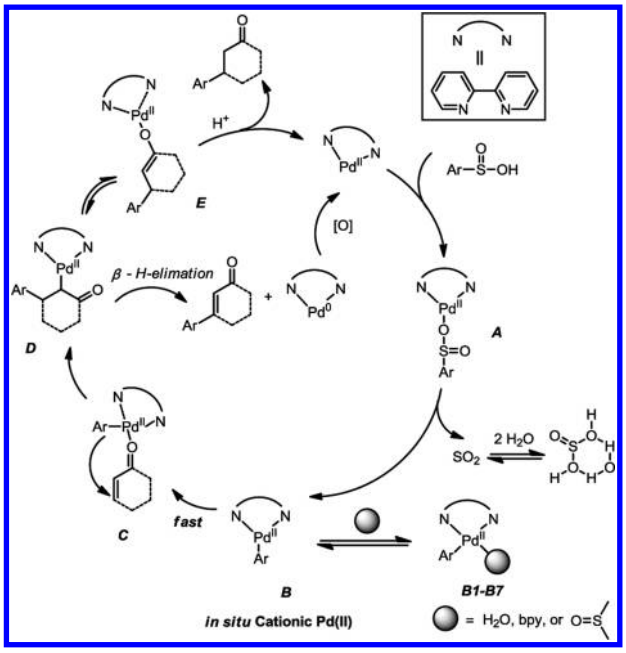
Scheme 2. Proposed Reaction Mechanism for Palladium-Catalyzed Reaction of Aryl Sulfinic Acids with Enones



z = 339.1 and 341.1 were interpreted as cationic aryl Pd(II) intermediate **B**. Besides, more abundant four-coordinated cationic aryl Pd(II) complexes (**B1**−**B7**) were detected, which were closely related to aryl Pd(II) intermediate **B** and involved in H_2O (**B1**, **B5**, and **B6**), S═O (**B2**, **B3** and **B7**), or bpy (**B4**) adduct ions. These in situ generated cationic intermediates, containing vacancies and weakly coordinating ligands in the Pd(II) center, cause dramatic rate enhancement toward alkene insertion over those of neutral complexes, as has been demonstrated in the cationic Pd^{II}-catalyzed addition reaction.[5d,17] The observation of Ar−Pd intermediates also indicated that the desulfitation even occurred at 60 °C under the catalytic condition, which is much lower than that of decarboxylation (130 °C).

For the alkene insertion into the aryl Pd intermediate **B**, two transition structures, i.e., (C═C)—Pd(II) and C═O—Pd(II), are possible. On the basis of the observation of Pd(II) intermediates (**B1**−**B7**), we speculated that it was in the form of C═O—Pd(II) transition structure. To confirm the existence of C═O—Pd(II) intermediate **C**, a controlled experiment by addition of chelating solvent DMSO was further evaluated. As expected, coordination of DMSO to aryl Pd(II) appeared and was identified by the cluster ions at m/z = 417.0 and 419.0 (see the Supporting Information).

In order to have a better insight of alkene insertion into the aryl Pd intermediate **B** to form the desired Pd(II) enolate **E**, an experiment of the addition of methyl cinnamate into the mixture of the first-step was further carried out. The peaks of aryl Pd intermediates (**B** and **B1**−**B7**) disappeared immediately; meanwhile, new cluster ions of Pd intermediate(**M**) at m/z 501.1 and 503.0 were formed (see the Supporting Information). This observation indicated that the process of methyl cinnamate coordinating with cationic Pd(II) intermediates (**B** and **B1**−**B7**) by ligand exchange is very fast. Our ESI-MS experiments and C═O—Pd(II) intermediate characterization were in agreement with Houk's DFT calculations,[13] which proposed that the formation of C═O—Pd complexes was favored both kinetically and thermodynamically in the palladium(II)-catalyzed conjugate additions of arylboronic acids to enones.

Intermediate **M** was further mass-selected for the tandem mass spectrometry (MS/MS) experiments (see the Supporting Information). On the basis of the MS/MS interpretation, we speculated the intermediate **M** is partly in the form of C═O—Pd(II) and partly in the form of C−Pd intermediate **D** or O−Pd enolate **E**. However, it is hard to determine the accurate coordinating site for the C−Pd intermediate **D** and enol tautomer O−Pd enolate **E** since they showed the same m/z signals at ESI-MS.

In conclusion, a new and efficient method for Pd(II) catalytic desulfitative conjugate addition of arylsulfinic acids with α,β-unsaturated carbonyl compounds in good to excellent yields has been developed. In addition, the key reacting intermediates including aryl Pd(II) sulfinic intermediate and aryl Pd(II) intermediate are captured by ESI-MS/MS. The experimental observations of C═O—Pd complexes are also demonstrated. Desulfitation could take place even at 60 °C under the Pd(II) catalytic condition.

EXPERIMENTAL SECTION

Representative Experimental Procedure of 3-Phenylcyclohexanone[5c] (2a). A reaction vessel (20 mL) was charged with a mixture of $Pd(OAc)_2$ (5.6 mg, 0.01 mmol), bipyridine (3.9 mg, 0.025 mmol), benzenesulfinic acid (107 mg, 0.75 mmol), 2-cyclohexenone (48.2 mg, 0.5 mmol), methanol (2 mL), and 50% H_2SO_4 (196 mg, 1.0 mmol) in order. The reaction vessel was closed, and the resulting solution was stirred at 90 °C for 15 h. After cooling to room temperature, the resulting mixture was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and then concentrated under a vacuum, and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 10:1) to give **2a** as a colorless oil: yield 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.16 (m, 5H), 3.07−2.90 (m, 1H), 2.65−2.28 (m, 4H), 2.21−1.98 (m, 2H), 1.92−1.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.1, 144.5, 128.9, 126.9, 126.8, 49.1, 44.9, 41.4, 32.9, 25.7; GC−MS (EI) m/z 174 $(M)^+$.

3-(*p*-Tolyl)cyclohexanone[5c] (2b). Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/5) giving a colorless oil: yield 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17−7.06 (m, 4H), 3.05−2.86 (m, 1H), 2.61−2.34 (m, 4H), 2.31 (s, 3H), 2.19−1.99 (m, 2H), 1.90−1.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.1, 141.5, 136.2, 129.4, 126.5, 49.1, 44.4, 41.2, 32.9, 25.6, 21.0; GC−MS (EI) m/z 188 $(M)^+$.

3-(4-Bromophenyl)cyclohexanone[6c] (2c). Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/5) giving a colorless oil: yield 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 3.06−2.87 (m, 1H), 2.60−2.30 (m, 4H), 2.20−1.98 (m, 2H), 1.87−1.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.4, 143.3, 131.8, 128.4, 120.4, 48.7, 44.1, 41.1, 32.6, 25.4; GC−MS (EI) m/z 252 $(M + 2)^+$, 250 $(M)^+$.

3-(4-Chlorophenyl)cyclohexanone[5c] (2d). Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/4) giving a colorless oil: yield 89%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 3.07−2.89 (m, 1H), 2.63−2.28 (m, 4H), 2.21−1.93 (m, 2H), 1.91−1.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.5, 142.8, 132.3, 128.8, 128.0, 77.5, 77.2, 76.9, 48.8, 44.1, 41.1, 32.7, 25.4; GC−MS (EI) m/z 206 $(M)^+$.

3-(4-Fluorophenyl)cyclohexanone[5c] (2e). Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/3) giving a colorless oil: yield 68%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.09 (m, 2H), 7.07−6.92 (m, 2H), 3.14−2.87 (m, 1H), 2.66−2.28 (m, 4H), 2.23−1.98 (m, 2H), 1.93−1.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.8, 161.7 (d, J

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= 244 Hz, 1C), 140.2, 128.1 (d, J = 7.8 Hz, 1C), 115.6 (d, J = 21 Hz, 1C), 49.2, 44.1, 41.2, 33.0, 25.5; GC−MS (EI) m/z 192 $(M)^+$.

3-(4-(Trifluoromethoxy)phenyl)cyclohexanone (2f). Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/4) giving a colorless oil: yield 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 3.11−2.93 (m, 1H), 2.63−2.29 (m, 4H), 2.22−2.00 (m, 2H), 1.91−1.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.5, 147.9, 143.1, 128.0, 121.3, 48.9, 44.1, 41.1, 32.8, 25.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −58.4; HR-ESI-MS $[M + Na]^+$ m/z calcd for $C_{13}H_{13}F_3NaO_2$ 281.0765, found 281.0764; GC−MS (EI) m/z 258 $(M)^+$.

3-(Naphthalen-2-yl)cyclohexanone[5c] (2g). Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/5) giving a colorless oil: yield 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.72 (m, 3H), 7.61 (s, 1H), 7.49−7.38 (m, 3H), 7.34 (d, J = 9.2 Hz, 1H), 3.19−3.06 (m, 1H), 2.72−2.29 (m, 4H), 2.21−2.04 (m, 2H), 1.97−1.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.1, 141.8, 133.6, 132.4, 128.4, 127.7, 127.7, 126.3, 125.7, 125.4, 124.8, 48.9, 44.8, 41.3, 32.7, 25.6; GC−MS (EI) m/z 224 $(M)^+$.

3-Methyl-3-phenylcyclohexanone[5d] (2h). Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/5) giving a colorless oil: yield 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.27 (m, 4H), 7.24−7.17 (m, 1H), 2.89 (d, J = 14.4 Hz, 1H), 2.44 (d, J = 14.4 Hz, 1H), 2.36−2.26 (m, 2H), 2.24−2.14 (m, 1H), 1.97−1.81 (m, 2H), 1.74−1.81 (m, 2H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.6, 147.6, 128.7, 126.4, 125.7, 53.3, 43.0, 41.0, 38.1, 30.0, 22.2; GC−MS (EI) m/z 188 $(M)^+$.

3-Methyl-3-phenylcyclopentanone[5d] (2i). Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/5) giving a colorless oil: yield 73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.26 (m, 4H), 7.26−7.19 (m, 1H), 2.64 (d, J = 17.6 Hz, 1H), 2.47 (d, J = 17.6 Hz, 1H), 2.43−2.21 (m, 4H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.5, 148.6, 128.6, 126.4, 125.5, 52.3, 43.9, 36.8, 35.9, 29.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −63.0 Hz; GC−MS (EI) m/z 174 $(M)^+$.

3-Phenylcyclopentanone[5c] (2j). Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/5) giving a colorless oil: yield 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.28 (m, 2H), 7.28−7.19 (m, 3H), 3.46−3.33 (m, 1H), 2.71−2.59 (m, 1H), 2.55−2.36 (m, 2H), 2.36−2.21 (m, 2H), 2.05−1.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.3, 143.1, 128.7, 126.8, 45.8, 42.2, 38.9, 31.2; GC−MS (EI) m/z 160 $(M)^+$.

4,4-Diphenylbutan-2-one[18] (2k). Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/10) giving a colorless oil: yield 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.10 (m, 10H), 4.57 (t, J = 7.6 Hz, 1H), 3.13 (d, J = 7.6 Hz, 2H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.8, 143.9, 128.6, 127.7, 126.5, 49.6, 46.1, 30.6; GC−MS (EI) m/z 224 $(M)^+$.

4-(4-Methoxyphenyl)-4-phenylbutan-2-one[19] (2l). Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/10) giving a white solid: yield 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.07 (m, 7H), 6.78 (d, J = 8.0 Hz, 2H), 4.52 (t, J = 7.6 Hz, 1H), 3.70 (s, 3H), 3.11 (d, J = 7.6 Hz, 2H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 158.1, 144.3, 136.0, 128.7, 128.6, 127.6, 126.4, 114.0, 55.2, 49.8, 45.3, 30.6; GC−MS (EI) m/z 254 $(M)^+$.

Methyl 3,3-Diphenylpropanoate[20] (2m). Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/10) giving a colorless oil (mixture): yield 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.08 (m, 10H), 4.56 (t, J = 7.6 Hz, 1H), 3.55 (s, 3H), 3.05 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 143.6, 128.7, 127.7, 126.6, 51.7, 47.1, 40.7; GC−MS (EI) m/z 224 $(M)^+$.

Ethyl 3,3-Diphenylpropanoate[5c] (2n). Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/10) giving a colorless oil (mixture): yield 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.31 (m, 8H), 7.31−7.22 (m, 2H), 4.67 (t, J = 7.6 Hz, 1H), 4.12 (q, J = 7.2 Hz, 2H), 3.15 (d, J = 7.6 Hz, 1H), 1.19 (s, 3H),; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 143.5, 128.6, 127.7, 126.6, 60.5, 47.1, 40.9; GC−MS (EI) m/z 254 $(M)^+$.

1,3,3-Triphenylpropan-1-one (2o). Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/10) giving a white solid (mixture): yield 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.0 Hz, 2H), 7.52−7.02 (m, 15H), 4.82 (t, J = 7.6 Hz, 2H), 3.70 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 144.2, 137.1, 133.1, 128.6, 128.6, 128.1, 127.9, 126.4, 46.0, 44.8; GC−MS (EI) m/z 286 $(M)^+$.

3,3-Diphenyl-1-(*p*-tolyl)propan-1-one[21] (2p). Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/10) giving a white solid (mixture): yield 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0 Hz, 2H), 7.33−7.03 (m, 14H), 4.81 (t, J = 7.6 Hz, 2H), 3.67 (d, J = 7.6 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 144.3, 143.9, 134.6, 129.3, 128.6, 128.2, 127.9, 126.4, 46.0, 44.6, 21.7; GC−MS (EI) m/z 300 $(M)^+$.

1-(4-Methoxyphenyl)-3,3-diphenylpropan-1-one[21] (2q). Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/10) giving a white solid (mixture): yield 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.8 Hz, 2H), 7.92−7.80 (m, 10H), 6.83 (d, J = 8.8 Hz, 2H), 6.83 (t, J = 7.6 Hz, 1H), 3.71 (s, 3H), 3.63 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 163.4, 144.3, 130.3, 130.1, 128.5, 127.9, 126.3, 113.7, 55.4, 46.1, 44.3; GC−MS (EI) m/z 316 $(M)^+$.

3-(4-Methoxyphenyl)-1,3-diphenylpropan-1-one[18] (2r). Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/10) giving a white solid (mixture): yield 82%; ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.0 Hz, 2H), 7.53−7.08 (m, 10H), 6.78 (d, J = 8.8 Hz, 2H), 4.77 (t, J = 7.6 Hz, 1H), 3.68 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 158.1, 144.6, 137.1, 136.3, 133.1, 128.8, 128.6, 128.6, 128.1, 127.8, 126.3, 114.0, 55.2, 45.2, 44.9; GC−MS (EI) m/z 316 $(M)^+$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR and ^{13}C NMR spectra for all the compounds reported. ESI-MS/MS for the reaction mechanism. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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