The first heterogeneous carbonylative Stille coupling of organostannanes with aryl iodides catalyzed by MCM-41-supported bidentate phosphine palladium(0) complex

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The first heterogeneous carbonylative Stille coupling reaction of organostannanes with aryl iodides under an atmospheric pressure of carbon monoxide has been achieved in DMF at 80 °C in the presence of a catalytic amount of an MCM-41-supported bidentate phosphine palladium(0) complex [MCM-41-2P-Pd(0)], yielding a variety of unsymmetrical ketones in good to high yields. This polymeric palladium catalyst exhibited higher activity and selectivity than $PdCl_2(PPh_3)_2$ and can be recovered and recycled by a simple filtration of the reaction solution and used for at least 10 consecutive trials without any decrease in activity. Our system not only avoids the use of carbon monoxide under pressure, but also solves the basic problem of palladium catalyst recovery and reuse.

Introduction

Aryl ketones,[1] α,β-acetylenic ketones,[2] and α,β-vinylic ketones[3] are important building blocks for a large number of natural products and pharmaceutical compounds. One general approach for the synthesis of aryl ketones is the Friedel–Crafts acylation of substituted aromatic rings.[4] The crucial disadvantage of traditional Friedel–Crafts acylation is the use of more than a stoichiometric amount of aluminium trichloride, which is incompatible with many functional groups and generates a large amount of waste. A common route to α,β-acetylenic ketones involves the acylation of alkynyl organometallic reagents, such as silver,[5] copper,[6] lithium,[7] zinc,[8] silicon,[9] and tin[10] with acid chlorides. One of the most common methods for preparation of α,β-vinylic ketones is based on the Horner–Emmons reaction using β-oxophophonates and carbonyl compounds.[11] Generally, the preparation of unsymmetrical ketones by transition-metal-catalyzed cross-coupling reaction is severely limited, since the organometallic partners often react with the product ketone.

The palladium-catalyzed carbonylative cross-coupling of aryl and vinyl halides or triflates with organostannanes in the presence of carbon monoxide is an especially valuable synthetic procedure for the preparation of a variety of aryl, vinylic, and acetylenic ketones, since a wide variety of functionalities can be tolerated on either partner and the organotin reagents can be readily synthesized, purified, and stored.[12] However, the carbonylative Stille cross-coupling reaction generally proceeds in the presence of a homogeneous palladium catalyst such as $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, $PdCl_2$(dppf), $Pd(dba)_2/2PPh_3$, $PhPdI(PPh_3)_2$, and $PhCH_2PdCl(PPh_3)_2$, which makes the recovery of the metal tedious if not impossible and might result in unacceptable palladium contamination of the product. The high costs of the transition metal catalysts coupled with toxic effects associated with many transition metals has led to an increased interest in immobilizing catalysts onto a support. This class of supported reagents can facilitate both the isolation and recycling of the catalysts by simple filtration, thus providing an environmentally cleaner process.[13] So far, polymer-supported palladium catalysts have successfully been used for the Heck reaction,[14] the Suzuki reaction,[15] the Sonogashira reaction,[16] and the Stille reaction,[17] *etc.* However, to the best of our knowledge, there has been no general study of carbonylative Stille cross-coupling reaction catalyzed by a polymer-supported palladium complex described to date.

Recent developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilization of homogeneous catalysts.[18] MCM-41 has a regular pore diameter of *ca.* 5 nm and a specific surface area $> 700\ m^2\ g^{-1}$.[19] Its large pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to reach to the surface of the channel.[20] It is generally believed that high surface area of heterogeneous catalyst results in high catalytic activity. Considering the fact that MCM-41 support has an extremely high surface area and the catalytic palladium species is anchored on the inner surface of the mesopores of the MCM-41 support, we expect that MCM-41-supported palladium catalyst will exhibit high activity and good reusability. To date, a few palladium complexes on functionalized MCM-41 support have been prepared and successfully used in organic reactions.[21] Recently, we have reported the synthesis of the MCM-41-supported bidentate phosphine palladium(0) complex [abbreviated as MCM-41-2P-Pd(0)] and found that this complex is a highly active and recyclable catalyst for the Sonogashira reaction of aryl halides.[16e] In this paper, we wish to report that the carbonylative Stille coupling reaction of organostannanes with aryl iodides under an

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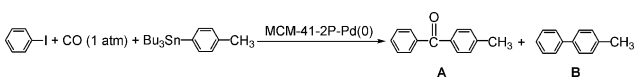
atmospheric pressure of carbon monoxide can be easily achieved in the presence of a catalytic amount of MCM-41-supported bidentate phosphine palladium(0) complex [MCM-41-2P-Pd(0)] to yield the corresponding aryl ketones, α,β-acetylenic ketones, and α,β-vinylic ketones in good to high yields. The developed methodology has important practical advantages deserving special note.

Results and discussion

The MCM-41-supported bidentate phosphine palladium(0) complex [MCM-41-2P-Pd(0)] was prepared by our previous procedure.[16e] The phosphine and palladium content was 1.15 and 0.52 mmol g^{-1}, respectively. Tanaka reported that carbonylative coupling reactions of aryl iodides with organostannanes catalyzed by $PhPdI(PPh_3)_2$ in HMPA required high temperature (120 °C) and high pressure of carbon monoxide (30 atm).[22] In our initial screening experiments, the realization of a carbonylative Stille coupling reaction catalyzed by the MCM-41-2P-Pd(0) under an atmospheric pressure of carbon monoxide was our goal. When we searched for a carbonylative coupling protocol for use with iodobenzene and (4-methylphenyl)tributylstannane, we observed that iodobenzene could react with (4-methylphenyl)tributylstannane in the presence of 1 mol% of the MCM-41-2P-Pd(0) in DMF under an atmospheric pressure of carbon monoxide at 60 °C to afford the desired carbonylative coupling product in 62% yield. Encouraged by this result, we continued our search to improve the yield of the product by optimization of the reaction conditions (Table 1).

We tested several different temperatures for the carbonylative coupling reaction catalyzed by MCM-41-2P-Pd(0) in DMF. 80 °C was found to be the most effective. Other temperatures such as 60 and 100 °C were substantially less effective, and no carbonylative coupling reaction occurred at 25 °C (entry 1). We then turned our attention to investigate the effect of solvents on the carbonylative coupling reaction. The solvents affected the selectivity of the reaction. When the reactions were conducted in DMF, NMP and HMPA, high yields of carbonylative coupling products **A** were isolated. Use of THF, CH_3CN and toluene as solvents led to slower reactions and the direct coupling products **B** were formed in 19–23% yields (entries 7–9). Increasing the amount of palladium catalyst could shorten the reaction time, but did not increase the yield of carbonylative coupling product **A** (entry 10). The low palladium concentration usually led to a long period of reaction, which was consistent with our experimental result (entry 11). Thus, the optimized reaction conditions for this carbonylative coupling reaction are the MCM-41-2P-Pd(0) (1 mol%) in DMF at 80 °C under atmospheric pressure of carbon monoxide for 6 h.

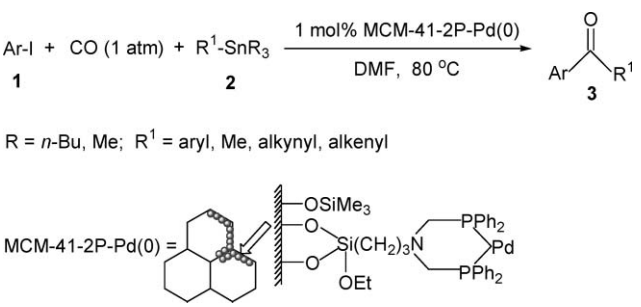
Table 1 Carbonylative Stille cross-coupling of (4-methylphenyl)-tributylstannane with iodobenzene under different conditions[a]



Entry	Solvent	Catalyst amount	Temp./°C	Time/h	Yield (%)[b] A	Yield (%)[b] B
1	DMF	1 mol%	25	24	0	17
2	DMF	1 mol%	60	24	62	13
3	DMF	1 mol%	80	6	86	4
4	DMF	1 mol%	100	4	84	7
5	NMP	1 mol%	80	6	85	6
6	HMPA	1 mol%	80	6	83	7
7	THF	1 mol%	60	24	43	19
8	Toluene	1 mol%	80	24	51	23
9	CH_3CN	1 mol%	80	24	42	20
10	DMF	2 mol%	80	4	86	5
11	DMF	0.5 mol%	80	14	85	4

[a] Iodobenzene (1.00 mmol), (4-methylphenyl)tributylstannane (1.10 mmol), CO (1 atm), and solvent (3 mL). [b] Isolated yields.

We have investigated the reactions using a variety of organostannanes and a wide range of aryl iodides as the substrates under the optimized reaction conditions (Scheme 1) and the results are outlined in Table 2. As shown in Table 2, the carbonylative Stille coupling reaction of arylstannanes with a variety of aryl iodides proceeded smoothly under mild conditions to give the corresponding carbonylative coupling products **3a–f** in good to high yields (entries 1–6). The presence of a strong electron-withdrawing substituent such as NO_2 is known to promote the direct coupling reaction to produce biaryl. For example, the carbonylative coupling reaction of triphenylalane with 4-iodonitrobenzene was reported to provide a 41% yield of 4-nitrobenzophenone and a 55% yield of 4-nitrobiphenyl,[23] and an analogous reaction with tributyltin hydride resulted in only a 9% yield of 4-nitrobenzaldehyde with an accompanying 84% yield of nitrobenzene.[24] This polymeric palladium catalyst exhibits higher activity and selectivity than $PdCl_2(PPh_3)_2$. For example, the carbonylative coupling reaction of 4-iodonitrobenzene with (4-methylphenyl)tributylstannane in the presence of 1 mol% of MCM-41-2P-Pd(0) in DMF at 80 °C for 6 h gave a 90% yield of the carbonylative coupling product **3b** along with only 2% yield of 4-methyl-4′-nitrobiphenyl (entry 2), the same reaction in the presence of 1 mol% of $PdCl_2(PPh_3)_2$ in DMF at 80 °C for 6 h gave **3b** in 79% yield and 4-methyl-4′-nitrobiphenyl in 12% yield. The carbonylative coupling reaction of the sterically hindered 1-iodonaphthalene with (4-chlorophenyl)tributylstannane also proceeded to afford the corresponding carbonylative coupling product **3f** in good yield (entry 6). The reactions of tetramethylstannane with aryl iodides at 70 °C gave the corresponding methyl aryl ketones **3g** and **3h** in high yields (entries 7 and 8). The carbonylative coupling reaction of heteroaryl iodides such as 2-iodothiophene with tetramethylstannane at 70 °C afforded the corresponding methyl heteroaryl ketone **3i** in 75% yield (entry 9).



Scheme 1 Synthesis of unsymmetrical ketones.

Table 2 Synthesis of unsymmetrical ketones[a]

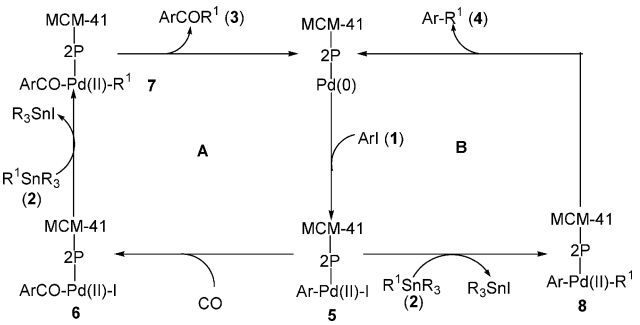
Entry	Ar	R	R^1	Product	Yield (%)[b]
1	Ph	*n*-Bu	4-$CH_3C_6H_4$	**3a**	86
2	4-$O_2NC_6H_4$	*n*-Bu	4-$CH_3C_6H_4$	**3b**	90
3	4-$CH_3OC_6H_4$	*n*-Bu	4-$CH_3C_6H_4$	**3c**	88
4	4-BrC_6H_4	*n*-Bu	4-ClC_6H_4	**3d**	85
5	4-$H_2NC_6H_4$	*n*-Bu	4-ClC_6H_4	**3e**	87
6	1-naphthyl	*n*-Bu	4-ClC_6H_4	**3f**	80
7	4-$O_2NC_6H_4$	Me	Me	**3g**	84[c]
8	4-$CH_3OC_6H_4$	Me	Me	**3h**	86[c]
9	2-thienyl	Me	Me	**3i**	75[c]
10	4-$O_2NC_6H_4$	*n*-Bu	$C_4H_9C{\equiv}C$	**3j**	81
11	4-$CH_3C_6H_4$	*n*-Bu	$C_4H_9C{\equiv}C$	**3k**	86
12	4-$CH_3OC_6H_4$	*n*-Bu	$C_4H_9C{\equiv}C$	**3l**	83
13	Ph	*n*-Bu	$PhC{\equiv}C$	**3m**	80
14	4-BrC_6H_4	*n*-Bu	$PhC{\equiv}C$	**3n**	84
15	4-$CH_3OC_6H_4$	*n*-Bu	$PhC{\equiv}C$	**3o**	85
16	4-$O_2NC_6H_4$	*n*-Bu	(*Z*)-$C_4H_9CH{=}CH$	**3p**	79[d]
17	4-$O_2NC_6H_4$	*n*-Bu	(*Z*)-$PhCH{=}CH$	**3q**	85[d]
18	4-$O_2NC_6H_4$	*n*-Bu	(*E*)-$C_4H_9CH{=}CH$	**3p**	84
19	2-$CH_3OC_6H_4$	*n*-Bu	(*E*)-$C_4H_9CH{=}CH$	**3r**	78
20	2-thienyl	*n*-Bu	(*E*)-$C_4H_9CH{=}CH$	**3s**	82
21	4-ClC_6H_4	*n*-Bu	(*E*)-$PhCH{=}CH$	**3t**	88
22	4-$CH_3OC_6H_4$	*n*-Bu	(*E*)-$PhCH{=}CH$	**3u**	86
23	2-$CF_3C_6H_4$	*n*-Bu	(*E*)-$PhCH{=}CH$	**3v**	72
24	Ph	*n*-Bu	$CH_2{=}CH$	**3w**	89
25	3-$O_2NC_6H_4$	*n*-Bu	$CH_2{=}CH$	**3x**	85
26	4-$CH_3C_6H_4$	*n*-Bu	$CH_2{=}CH$	**3y**	90
27	1-naphthyl	*n*-Bu	$CH_2{=}CH$	**3z**	84

[a] Reaction was carried out with organostannane (1.10 mmol), aryl iodide (1.00 mmol), CO (1 atm), and 1 mol% palladium catalyst in DMF (3 mL) at 80 °C for 6 h. [b] Isolated yields. [c] At 70 °C for 10 h. [d] Only (*E*)-isomer was obtained.

The carbonylative Stille cross-coupling of alkynylstannanes and vinylstannanes with a variety of aryl iodides also proceeded smoothly under the same conditions to give the corresponding α,β-acetylenic ketones **3j–3o** (entries 10–15) and α,β-vinylic ketones **3p–3z** (entries 16–27) in good to high yields, respectively. It was found that the (*E*)-configuration of the double bond in vinylstannanes was retained in the products (entries 18–23); however, the (*Z*)-configuration of the double bond in vinylstannanes was lost completely under the reaction conditions and only the (*E*)-isomer of the product was obtained (entries 16 and 17). A similar observation has been made by Stille *et al.* in carbonylative cross-coupling of vinyl iodides and vinylstannanes.[12b] The method provides a quite general route for synthesis of a variety of unsymmetrical ketones having various functionalities such as alkynyl, vinyl, halogen, NO_2, CH_3O, NH_2, CH_3, *etc.* The results above prompted us to investigate the reaction of aryl bromides, but the carbonylative coupling reaction was very slow under the conditions optimized for the iodides. Even though the carbonylative coupling reactions of aryl bromides were carried out in DMF at 100 or 120 °C, only traces of carbonylative coupling products were formed. On the other hand, the carbonylative coupling reaction of 4-bromoiodobenzene selectively occurred at the C–I bond, no diketones was formed (entries 4 and 14).

In order to determine whether the catalysis was due to the MCM-41-2P-Pd(0) complex or to a homogeneous palladium complex that comes off the support during the reaction and then returns to the support at the end, we performed the hot filtration test.[25] We focused on the carbonylative coupling reaction of iodobenzene with (4-methylphenyl)tributylstannane. We filtered off the MCM-41-2P-Pd(0) complex after a reaction time of 1 h and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (80 °C) in order to avoid possible recoordination or precipitation of soluble palladium upon cooling. We found that, after this hot filtration, no further reaction was observed. This result suggests that the palladium catalyst remains on the support at elevated temperatures during the reaction.

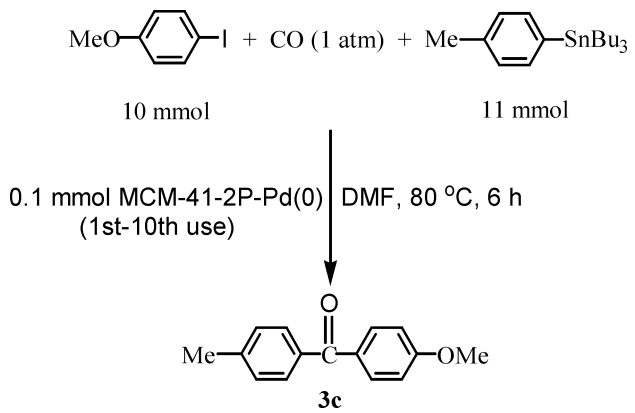
The heterogeneous carbonylative Stille cross-coupling of organostannanes with aryl iodide may proceed through a catalytic cycle analogous to that proposed for homogeneous palladium catalysts (cycle A in Scheme 2).[12b,22] Oxidative addition of ArI (**1**) to the MCM-41-2P-Pd(0) complex provides MCM-41-bound arylpalladium(II) complex (**5**), which is followed by migratory insertion of carbon monoxide giving MCM-41-bound acylpalladium(II) complex (**6**). Subsequent transmetalation between **6** and organostannanes (**2**) and reductive elimination of unsymmetrical ketone **3** from the intermediate (**7**) regenerate the MCM-41-2P-Pd(0) complex. Since **5** is a common intermediate for the carbonylation (cycle A) and the direct coupling giving biaryls (cycle B), a large amount of biaryl (**4**) is often formed when the insertion reaction of carbon monoxide into the intermediate (**5**) is slower than the transmetalation between **5** and organostannanes (**2**).



Scheme 2 Catalytic cycle.

The MCM-41-2P-Pd(0) complex catalyst can be easily recovered by simple filtration. We also investigated the possibility to reuse the catalyst by using the carbonylative coupling reaction of 4-iodoanisole with (4-methylphenyl)tributylstannane and the results are given in Table 3. In general, the continuous recycling of resin-supported palladium catalysts is difficult owing to leaching of the palladium species from the polymer supports, which often reduces their activity within five recycles. However, when the reaction of 4-iodoanisole with (4-methylphenyl)tributylstannane was performed even with 1 mol% of MCM-41-2P-Pd(0), the catalyst could be recycled 10 times without any loss of activity. The reaction promoted by the 10th recycled catalyst gave **3c** in 86% yield (entry 2). The average yield of **3c** in consecutive reactions promoted by the 1st through the 10th recycled catalyst was 87% (entry 3). The high stability and excellent reusability of the catalyst result from the chelating action of the bidentate phosphine ligand on palladium and the mesoporous structure of the MCM-41 support. The result is important from a practical point of view. The high catalytic activity, excellent reusability and the easy accessibility of the MCM-41-2P-Pd(0) complex

Table 3 Carbonylative Stille cross-coupling reaction of 4-iodoanisole with (4-methylphenyl)tributylstannane catalyzed by recycled catalyst



3c

Entry	Catalyst cycle	Isolated yield (%)	TON
1	1st	88	88
2	10th	86	86
3	1st to 10th consecutive	av. 87	total of 870

make them a highly attractive supported palladium catalyst for the parallel solution phase synthesis of diverse libraries of compounds.

Experimental

Aryl iodides, tetramethyltin, and ethenyltributylstannane were reagent grade and used as purchased. Arylstannanes, alkynylstannanes, and vinylstannanes were prepared according to the literature method.[12e] All the solvents were dried and distilled before use. The products were purified by flash chromatography on silica gel. A mixture of EtOAc and hexane was generally used as eluent. All carbonylative coupling products were characterized by comparison of their spectra and physical data with authentic samples. IR spectra were determined on a Perkin-Elmer 683 instrument. ^{1}H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. ^{13}C NMR spectra were recorded on a Bruker AC-P400 (100 MHz) spectrometer in $CDCl_3$ as solvent. Mass spectra (EI, 70 eV) were determined on a Finnigan 8230 mass spectrometer. Melting points are uncorrected. Microanalyses were measured by using a Yanaco MT-3 CHN microelemental analyzer.

Typical procedure for the carbonylative Stille cross-coupling reaction

A 50 mL round-bottomed flask equipped with a gas inlet tube, a reflux condenser, and a magnetic stirring bar was charged with MCM-41-2P-Pd(0) (20 mg, 0.01 mmol Pd), aryl iodide (1.0 mmol), and organostannanes (1.1 mmol). The flask was flushed with carbon monoxide, and DMF (3 mL) was then added. After stirring at 80 °C for 6 h under CO (1 atm), the reaction mixture was cooled to room temperature, diluted with diethyl ether (30 mL). The mixture was vacuum filtered using a sintered glass funnel and washed with diethyl ether (2 × 5 mL). The ether solution was washed with water (3 × 10 mL) and dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane–ethyl acetate = 10 : 1).

The recyclability of the MCM-41-2P-Pd(0)

After carrying out the reaction, the mixture was vacuum filtered using a sintered glass funnel and the residue was washed with diethyl ether (2 × 5 mL), DMF (2 × 5 mL), ethanol (2 × 5 mL), and diethyl ether (2 × 5 mL), respectively. After being dried in an oven, the catalyst can be reused directly without further purification.

4-Methylbenzophenone 3a. White solid, m.p. 56–57 °C, lit.[26] m.p. 57–58 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (m, 2 H), 7.72 (d, J = 8.0 Hz, 2 H), 7.56 (m, 1 H), 7.46 (m, 2 H), 7.26 (m, 2 H), 2.43 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 143.3, 138.0, 134.9, 132.2, 130.3, 130.0, 129.0, 128.2, 21.7. IR (KBr) ν (cm^{-1}) 1657, 1606, 1578, 1277, 700.

4-Methyl-4′-nitrobenzophenone 3b. Yellow solid, m.p. 120–122 °C, lit.[27] m.p. 120–121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (m, 2 H), 7.92 (m, 2 H), 7.71 (d, J = 8.4 Hz, 2 H), 7.32 (d, J = 8.0 Hz, 2 H), 2.47 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 149.7, 144.6, 143.3, 133.6, 130.6, 130.3, 129.4, 123.5, 21.8. IR (KBr) ν (cm^{-1}) 1652, 1600, 1520, 1353, 1315, 732.

4-Methoxy-4′-methylbenzophenone 3c. White solid, m.p. 88–89 °C, lit.[28] m.p. 85–87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (m, 2 H), 7.69 (d, J = 8.0 Hz, 2 H), 7.28 (d, J = 8.4 Hz, 2 H), 6.97 (m, 2 H), 3.90 (s, 3 H), 2.45 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 163.0, 142.6, 135.5, 132.5, 130.5, 130.0, 128.9, 113.5, 55.5, 21.6. IR (KBr) ν (cm^{-1}) 1646, 1598, 1505, 1262, 1170, 849, 761.

4-Bromo-4′-chlorobenzophenone 3d. White solid, m.p. 146–148 °C, lit.[29] m.p. 147–148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2 H), 7.64 (s, 4 H), 7.47 (d, J = 8.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 139.2, 136.0, 135.5, 131.8, 131.4, 131.3, 128.8, 127.8. IR (KBr) ν (cm^{-1}) 1646, 1586, 1289, 855, 753.

4-Amino-4′-chlorobenzophenone 3e. White solid, m.p. 183–184 °C, lit.[30] m.p. 182–184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.66 (m, 4 H), 7.44 (m, 2 H), 6.68 (m, 2 H), 4.18 (br, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 151.1, 137.7, 137.1, 132.9, 131.0, 128.4, 127.1, 113.7. IR (KBr) ν (cm^{-1}) 3342, 3228, 1639, 1630, 1587, 1320, 928, 836, 766.

1-(4-Chlorobenzoyl)naphthalene 3f[28]. Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12–7.91 (m, 3 H), 7.81 (m, 2 H), 7.57–7.41 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 139.7, 136.7, 135.9, 133.8, 131.8, 131.6, 130.9, 128.8, 128.5, 127.8, 127.5, 126.6, 125.6, 124.4. IR (neat) ν (cm^{-1}) 1661, 1586, 1508, 1284, 1251, 800, 778.

4-Acetylnitrobenzene 3g. Yellow solid, m.p. 76–78 °C, lit.[31] m.p. 78–80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (m, 2 H), 8.12 (m, 2 H), 2.69 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 150.4, 141.4, 129.3, 123.9, 27.0. IR (KBr) ν (cm^{-1}) 1694, 1608, 1527, 1346, 857, 750.

4-Acetylanisole 3h[31]. Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (m, 2 H), 6.93 (m, 2 H), 3.87 (s, 3 H), 2.56 (s, 3 H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 196.8, 163.5, 130.6, 130.4, 113.7, 55.5, 26.3. IR (neat) ν (cm^{-1}) 1668, 1606, 1577, 1509, 1261, 1179, 837.

2-Acetylthiophene 3i[32]. Oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (m, 1 H), 7.64 (m, 1 H), 7.13 (m, 1 H), 2.57 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 144.6, 133.8, 132.4, 128.1, 26.9. IR (neat) ν (cm^{-1}) 1652, 1518, 1416, 1275, 858, 726.

1-(4-Nitrophenyl)hept-2-yn-1-one 3j[33]. Oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 9.2 Hz, 2 H), 8.29 (d, J = 9.2 Hz, 2 H), 2.56 (t, J = 7.2 Hz, 2 H), 1.70 (m, 2 H), 1.52 (m, 2 H), 0.98 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 150.8, 141.1, 130.4, 123.7, 99.4, 79.4, 29.7, 22.1, 19.0, 13.5. IR (neat) ν (cm^{-1}) 2953, 2872, 2205, 1643, 1603, 1527, 1343, 1268, 865, 707.

1-(4-Methylphenyl)hept-2-yn-1-one 3k[33]. Oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 2 H), 7.27 (d, J = 8.4 Hz, 2 H), 2.50 (t, J = 7.2 Hz, 2 H), 2.42 (s, 3 H), 1.66 (m, 2 H), 1.50 (m, 2 H), 0.96 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 144.9, 134.7, 129.7, 129.2, 96.3, 79.7, 29.9, 22.1, 21.8, 18.9, 13.5. IR (neat) ν (cm^{-1}) 3031, 2959, 2873, 2200, 1642, 1605, 1268, 911, 742.

1-(4-Methoxyphenyl)hept-2-yn-1-one 3l[33]. Oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 9.2 Hz, 2 H), 6.94 (d, J = 9.2 Hz, 2 H), 3.88 (s, 3 H), 2.49 (t, J = 7.2 Hz, 2 H), 1.66 (m, 2 H), 1.50 (m, 2 H), 0.96 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 164.3, 131.9, 130.4, 113.7, 95.9, 79.7, 55.5, 29.9, 22.1, 18.9, 13.5. IR (neat) ν (cm^{-1}) 3075, 2959, 2873, 2201, 1639, 1598, 1257, 1166, 845, 759.

1,3-Diphenylprop-2-yn-1-one 3m. White solid, m.p. 45–46 °C, lit.[34] m.p. 46–47 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.0 Hz, 2 H), 7.69 (d, J = 7.6 Hz, 2 H), 7.64 (t, J = 7.2 Hz, 1 H), 7.54–7.41 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 136.9, 134.1, 133.1, 130.8, 129.6, 128.7, 128.6, 120.2, 93.1, 86.9. IR (KBr) ν (cm^{-1}) 3056, 2201, 1641, 1587, 760.

1-(4-Bromophenyl)-3-phenylprop-2-yn-1-one 3n. White solid, m.p. 109–110 °C, lit.[34] m.p. 106–107 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (m, 2 H), 7.70–7.66 (m, 4 H), 7.53–7.42 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 135.7, 133.1, 132.0, 131.0, 130.9, 129.6, 128.8, 119.9, 93.7, 86.6. IR (KBr) ν (cm^{-1}) 3058, 2199, 1651, 1585, 751, 682.

1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-one 3o. White solid, m.p. 100–101 °C, lit.[34] m.p. 97–98 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 8.8 Hz, 2 H), 7.67 (d, J = 7.6 Hz, 2 H), 7.49–7.39 (m, 3 H), 6.99 (d, J = 8.4 Hz, 2 H), 3.90 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 164.5, 133.0, 132.0, 130.6, 130.4, 128.7, 120.4, 113.9, 92.3, 87.0, 55.6. IR (KBr) ν (cm^{-1}) 2201, 1631, 1603, 1160, 761.

(*E*)-1-(4-Nitrophenyl)hept-2-en-1-one 3p. Oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (m, 2 H), 8.04 (m, 2 H), 7.12 (dt, J = 15.6, 7.2 Hz, 1 H), 6.84 (d, J = 15.6 Hz, 1 H), 2.36 (m, 2 H), 1.53 (m, 2 H), 1.40 (m, 2 H), 0.95 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 152.5, 150.0, 142.9, 129.4, 125.6, 123.7, 32.7, 30.2, 22.3, 13.8. IR (neat) ν (cm^{-1}) 2931, 2861, 1674, 1621, 1602, 1524, 1346, 983. MS (EI), m/z (%): 233 (M^+, 73), 231 (61), 204 (93), 202 (97), 150 (100). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48. Found: C, 66.69; H, 6.30.

(*E*)-1-(4-Nitrophenyl)-3-phenylprop-2-en-1-one 3q. Yellow solid, m.p. 145–146 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 8.0 Hz, 2 H), 8.15 (d, J = 8.0 Hz, 2 H), 7.85 (d, J = 15.6 Hz, 1 H), 7.67 (m, 2 H), 7.51–7.45 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.1, 150.1, 146.9, 143.1, 134.3, 131.3, 129.4, 129.2, 128.7, 123.9, 121.3. IR (KBr) ν (cm^{-1}) 3053, 1663, 1591, 1516, 1335, 1208, 853, 742. MS (EI), m/z (%): 253 (M^+, 74), 252 (100), 103 (42), 77 (31). Anal. Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38. Found: C, 70.87; H, 4.19.

(*E*)-1-(2-Methoxyphenyl)hept-2-en-1-one 3r. Oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (m, 1 H), 7.42 (m, 1 H), 7.01–6.94 (m, 2 H), 6.82 (dt, J = 15.6, 6.8 Hz, 1 H), 6.66 (d, J = 15.6 Hz, 1 H), 3.85 (s, 3 H), 2.26 (m, 2 H), 1.47 (m, 2 H), 1.36 (m, 2 H), 0.92 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 157.8, 149.0, 132.3, 130.7, 130.0, 129.4, 120.6, 111.6, 55.6, 32.2, 30.2, 22.2, 13.8. IR (neat) ν (cm^{-1}) 2931, 2872, 1663, 1618, 1465, 1245, 1024, 981. MS (EI), m/z (%): 218 (M^+, 51), 161 (99), 135 (100), 121 (58), 77 (61). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.75; H, 8.12.

(*E*)-1-(2-Thienyl)hept-2-en-1-one 3s. Oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (m, 1 H), 7.64 (m, 1 H), 7.15–7.09 (m, 2 H), 6.79 (d, J = 15.6 Hz, 1 H), 2.31 (m, 2 H), 1.50 (m, 2 H), 1.38 (m, 2 H), 0.93 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.4, 149.3, 145.2, 133.5, 131.7, 128.1, 125.4, 32.4, 30.3, 22.3, 13.8. IR (neat) ν (cm^{-1}) 2957, 2930, 1659, 1615, 1516, 1416, 1235, 979, 721. MS (EI), m/z (%): 194 (M^+, 54), 165 (36), 111 (100). Anal. Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26. Found: C, 67.71; H, 7.38.

(*E*)-1-(4-Chlorophenyl)-3-phenylprop-2-en-1-one 3t. White solid, m.p. 92–94 °C, lit.[35] m.p. 91–92 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (m, 2 H), 7.82 (d, J = 15.6 Hz, 1 H), 7.65 (m, 2 H), 7.51–7.42 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 145.4, 139.2, 136.5, 134.7, 130.8, 129.9, 129.0, 128.5, 121.6. IR (KBr) ν (cm^{-1}) 3053, 1662, 1606, 1336, 983, 829, 764.

(*E*)-1-(4-Methoxyphenyl)-3-phenylprop-2-en-1-one 3u. White solid, m.p. 102–103 °C, lit.[12e] m.p. 105–106 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (m, 2 H), 7.80 (d, J = 15.6 Hz, 1 H), 7.65 (m, 2 H), 7.55 (d, J = 15.6 Hz, 1 H), 7.43–7.39 (m, 3 H), 6.98 (m, 2 H), 3.89 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 163.5, 144.0, 135.1, 131.1, 130.8, 130.3, 128.9, 128.4, 121.9, 113.9, 55.5. IR (KBr) ν (cm^{-1}) 1655, 1607, 1574, 1338, 974, 830, 763.

(*E*)-1-(2-Trifluoromethylphenyl)-3-phenylprop-2-en-1-one 3v[36]. Oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 1 H), 7.61 (m, 2 H), 7.53–7.45 (m, 3 H), 7.41–7.36 (m, 3 H), 7.30 (d, J = 16.0 Hz, 1 H), 7.04 (d, J = 16.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 147.8, 138.9, 134.1, 131.6, 131.1, 129.9, 129.0, 128.6, 128.1, 126.8, 126.7 (q), 125.0, 122.3. IR (neat) ν (cm^{-1}) 1651, 1606, 1576, 1449, 1315, 1172, 979, 830, 769.

1-Phenylprop-2-en-1-one 3w[37]. Oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (m, 2 H), 7.58 (m, 1 H), 7.48 (m, 2 H), 7.16 (m, 1 H), 6.43 (m, 1 H), 5.93 (m, 1 H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 191.1, 137.3, 133.0, 132.4, 130.2, 128.7, 128.6. IR (neat) ν (cm^{-1}) 1674, 1609, 1580, 1233, 728, 690.

1-(3-Nitrophenyl)prop-2-en-1-one 3x. Yellow solid, m.p. 104–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.45 (m, 1 H), 8.28 (m, 1 H), 7.71 (t, J = 8.0 Hz, 1 H), 7.18 (m, 1 H), 6.53 (m, 1 H), 6.08 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7, 148.5, 138.6, 134.2, 132.1, 131.5, 130.0, 127.3, 123.5. IR (KBr) ν (cm^{-1}) 1666, 1601, 1537, 1351, 1237, 727. MS (EI), m/z (%): 177 (M^+, 24), 150 (97), 104 (74), 76 (100), 55 (68). Anal. Calcd for $C_9H_7NO_3$: C, 61.02; H, 3.98. Found: C, 60.74; H, 3.73.

1-(4-Methylphenyl)prop-2-en-1-one 3y[38]. Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (m, 2 H), 7.28 (d, J = 8.0 Hz, 2 H), 7.16 (m, 1 H), 6.43 (m, 1 H), 5.90 (m, 1 H), 2.42 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 143.9, 134.8, 132.4, 129.7, 129.3, 128.9, 21.7. IR (neat) ν (cm^{-1}) 1673, 1608, 1579, 1234, 742.

1-(1-Naphthyl)prop-2-en-1-one 3z[12e]. Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 8.0 Hz, 1 H), 7.98 (d, J = 8.0 Hz, 1 H), 7.89 (m, 1 H), 7.72 (m, 1 H), 7.58–7.48 (m, 3 H), 6.95 (m, 1 H), 6.26 (m, 1 H), 6.04 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 137.0, 135.8, 133.9, 132.0, 131.3, 130.6, 128.4, 127.8, 127.5, 126.5, 125.6, 124.3. IR (neat) ν (cm^{-1}) 3049, 1667, 1603, 1508, 1102, 785.

Conclusions

In summary, we have developed a novel, efficient, practical and green catalyst system for the carbonylative Stille coupling reaction of organostannanes with aryl iodides by using the MCM-41-supported bidentate phosphine palladium(0) complex as catalyst in DMF under an atmospheric pressure of carbon monoxide. The carbonylative coupling reaction of organostannanes with aryl iodides generates a variety of unsymmetrical ketones having various functionalities in good to high yields under the present reaction conditions. Our system not only avoids the use of carbon monoxide under pressure, but also solves the basic problem of palladium catalyst recovery and reuse.

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