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Polymer-supported tertiaryphosphine (*JJ*−TPP) as a green and recyclable organocatalyst for α-addition of carbon nucleophiles to α,β-unsaturated compounds

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Abstract

***JJ*−TPP** has been demonstrated as an effective and reusable organocatalyst for α-addition of carbon nucleophiles to α,β-unsaturated compounds under very mild and environmentally friendly conditions. Under the optimized reaction conditions, the desired addition products were obtained as only *E* isomer with 18−90% isolated yields.

1. Introduction

The development of metal-free organocatalysts and their wide-ranging utilities for organic synthesis have received much attention and remarkable achievements have been made in this area recently.[1] Among this family of organocatalysts, phosphines as efficient nucleophilic catalysts have been widely used.[2] One of the most successful applications is the nucleophilic addition to the activated alkenes or alkynes, such as Michael-type addition, α- and γ-addition catalyzed by tertiaryphosphines.[3] However, in these previous addition reactions the employed phosphines are homogeneous, which makes the separation of products and recovery of catalysts rather difficult sometimes. Moreover, volatile toxic solvents such as toluene or benzene are required. To overcome these limitations, phosphines are immobilized on the polymers,[4,5] and these polymer-supported tertiaryphosphine reagents have been successfully applied in the isomerization of α,β-ynones,[6] Trost's γ-addition,[7] Aza-Baylis−Hillman reaction,[8] Morita−Baylis−Hillman reaction.[9] Despite significant advances in this area, how to explore these polymer-supported tertiaryphosphines as perfect catalysts for other organic reactions is still a challenge.

We have previously developed polymer-supported tertiaryphosphines **PS−TPP** and ***JJ*−TPP** as excellent catalysts for the isomerization of α,β-ynones to (*E*,*E*)-α,β-γ,δ-dienones in toluene, [6a] or under solvent-free condition.[6b] Encouraged by these results, we further investigated the utilization of polymer-supported tertiaryphosphines as catalysts for solvent-free organic reactions, and herein we wish to show that polymer-supported tertiaryphosphine ***JJ*−TPP** (Fig. 1) is an excellent organocatalyst for α-addition reaction of carbon nucleophiles

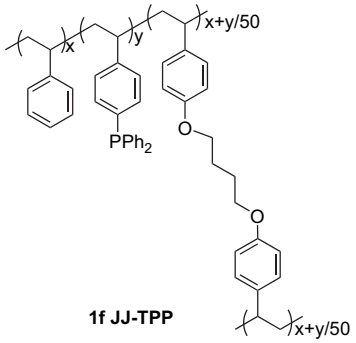

Figure 1.

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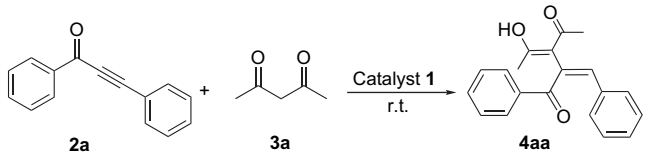
to α,β-unsaturated compounds under very mild and environmentally friendly conditions (solvent-free condition, room temperature, and ambient atmosphere).

2. Results and discussion

The catalysts screening protocol employed the α-addition reaction of **3a** to **2a**. Reactions were conducted with 0.25 mmol of **2a** and 1.2 equiv of **3a** using 20 mol % of different catalysts at room temperature for 12 h under solvent-free condition (unless otherwise mentioned). At first, we found the reaction could not proceed without any catalyst. Triphenylphosphine **1a**, previously used as the homogeneous catalyst for the Michael addition reaction, was found less effective. Then with the polymer-supported tertiaryphosphines in hand, we examined the efficiency of **1b–f** as catalysts for the α-addition reaction. As depicted in Table 1, using poly(ethylene glycol)-supported triphenylphosphine **1b** (**PEG–TPP**) and amphilic resin **1c** (**PS–PEG–DPP**), no addition product was detected (Table 1, entries 3 and 4). These results promoted us to test less polar immobilized tertiaryphosphines. As expected, catalyst polymer-supported diphenylphosphine **1d** (**PS–DPP**) and polymer-supported triphenylphosphine **1e** (**PS–TPP**) could give the desired product **4aa** in 75 and 95% GC yields, respectively (Table 1, entries 5 and 6). Loading level of the phosphorus has a close relationship with catalytic efficiency.[8a] P% of **1e** is higher than that of **1d**, which might be responsible for the difference in product yields. Gratifyingly, the use of triphenylphosphine supported on *JandaJel* resin **1f** (***JJ*–TPP**) resulted in **4aa** with 99% yield. The reason why the catalytic efficiency of homogeneous catalyst **1a** is lower than that of polymer-supported triphenylphosphine is not clear yet. Under solvent-free conditions, polymer's microenvironment might promote the reagents assemble and phosphine group attacked the substrates.

Table 1
Optimization of the α-addition reaction[a]



Entry	Catalyst	Amount (%)	Reaction time (h)	Yield[b] (%)
1	None	—	12	0
2[c]	**TPP (1a)**	20	12	44
3	**PEG–TPP (1b)**	20	12	0
4	**PS–PEG–TPP (1c)**	20	12	0
5	**PS–DPP (1d)**	20	12	75
6	**PS–TPP (1e)**	20	12	95
7	***JJ*–TPP (1f)**	20	12	99
8	***JJ*–TPP**	10	12	99
9	***JJ*–TPP**	10	6	99
10	***JJ*–TPP**	10	3	89
11	***JJ*–TPP**	5	12	90

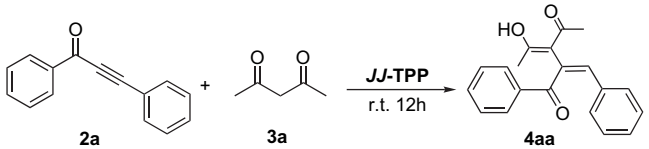
[a] Reaction condition: **2a** (0.25 mmol) and **3a** (1.2 equiv) were added.
[b] Determined by **GC**.
[c] CH_2Cl_2 (2 mL) was added.

At the next step, we optimized reaction conditions by varying the amount of catalyst ***JJ*–TPP** and reaction time. Reducing the amount of catalyst from 20 mol % to 10 mol % and reaction time from 12 h to 6 h, the yields of **4aa** was also 99%. Using 5 mol % of ***JJ*–TPP** resulted in only 90% of the desired product (Table 1, entry 11). The reaction time could affect the reaction to some extent. The proper time is beyond 6 h (Table 1, entries 9 and 10). The results in Table 1 revealed that the reaction was conducted smoothly with 10 mol % of ***JJ*–TPP** at room temperature for 6 h under solvent-free condition (Table 1, entry 9). It may be worth noting that the product **4aa** was isolated as only *E* isomer in stable enolic form. Intramolecular hydrogen bond and conjugation could stabilize the enolic form.[10] When the reaction scale was increased to 3 mmol, the reaction also proceeded smoothly and the product was obtained in 96% yield based on GC analysis.

Subsequently, we investigated the reusability of the catalyst. ***JJ*–TPP** could be recovered and reused through simple filtration and vacuum drying. As shown in Table 2, the reused catalyst gave the corresponding product **4aa** in greater than 93% GC yield after multiple trials. As we all know, one drawback to the use of tertiaryphosphines is their inherent air-sensitivity, which limits the reusability of catalysts. Whereas, the α-addition reaction was carried out under ambient atmosphere and the reused ***JJ*–TPP** still retained its catalytic activity after the third use. We suspect that the bone of ***JandaJel*** resin-supported triphenylphosphine is more air-stable. And proper reaction temperature and reaction system might slow down the oxidation of triphenylphosphine.

Under the given optimized reaction conditions, a variety of ynones and 1,3-dicarbonyl compounds were applied for the α-addition reaction using ***JJ*–TPP** as catalyst at room temperature. The desired products were obtained as *E* isomer in enolic form (except entries 10 and 11) with 18–90% isolated yields as shown in Table 3. Representative ynones with different substituents on the R^1 and R^2 position could react with acetylacetone (**3a**) to generate the corresponding products with high conversions and isolated yields (Table 3, entries 1–8). Subsequently, ethyl acetoacetate (**3b**) could undergo α-addition reaction smoothly (entries 9 and 12–14). The use of diethyl

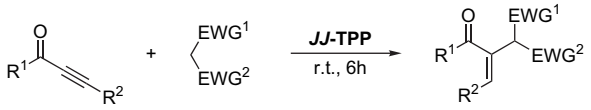
Table 2
Recycle of ***JJ*–TPP**[a]



	Conversion[b] (%)	Yield[b] (%)
Fresh	99	99
1	99	99
2	98	93
3	97	93

[a] Reaction condition: **2a** (0.25 mmol), **3a** (1.2 equiv), and ***JJ*–TPP** (10 mol %) stand still for 12 h.
[b] Determined by GC.

Table 3
Addition of carbon nucleophiles to ynones catalyzed by ***JJ*–TPP**[a]



Entry	2	3	4	Yield[b] (%)
1	**2a** (R^1=Ph; R^2=Ph)	**3a** (EWG^1=EWG^2=CH_3CO)	**4aa**	88
2	**2b** (R^1=Ph; R^2=4-$CH_3C_6H_4$)	**3a**	**4ba**	66
3	**2c** (R^1=4-$O_2NC_6H_4$; R^2=Ph)	**3a**	**4ca**	60
4[c]	**2d** (R^1=4-$CH_3C_6H_4$; R^2=Ph)	**3a**	**4da**	80
5	**2e** (R^1=furan; R^2=Ph)	**3a**	**4ea**	82
6	**2f** (R^1=thiophene; R^2=Ph)	**3a**	**4fa**	76
7[c]	**2g** (R^1=R^2=4-$CH_3C_6H_4$	**3a**	**4ga**	90
8[c]	**2h** (R^1=thiophene; R^2=4-$CH_3C_6H_4$)	**3a**	**4ha**	75
9	**2a**	**3b** (EWG^1=CH_3CO; EWG^2=COOEt)	**4ab**	78
10[d]	**2a**	**3c** (EWG^1=EWG^2=COOEt)	**4ac**	47
11[d,e]	**2a**	**3d** (EWG^1=EWG^2=C_6H_5CO)	**4ad**	18[f]
12[c]	**2d**	**3b**	**4db**	66
13	**2e**	**3b**	**4eb**	54
14	**2f**	**3b**	**4fb**	62

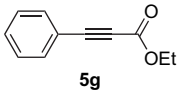
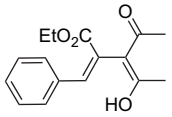
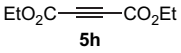
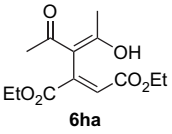
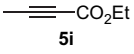
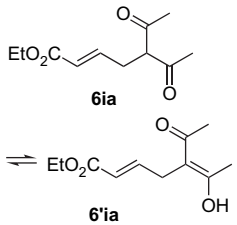
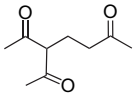
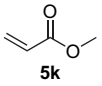
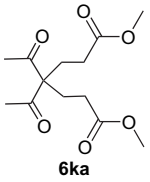
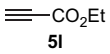
[a] Reaction condition: **2** (0.25 mmol), **3** (1.2 equiv), and ***JJ*–TPP** (10 mol %) for 6 h.
[b] Isolated yield.
[c] CH_2Cl_2 (0.5 g) was added.
[d] 18 h.
[e] Tetrahydrofuran (0.2 g) was added.
[f] Molar ratio of keto and enolic form was about 1:1.

malonate (**3c**) as nucleophile led to the relatively low yield (47%) of **4ac** (entry 10). Dibenzoylmethane (**3d**) afforded the product **4ad** as a mixture of keto and enolic form in only 18% isolated yield (entry 11).

These results prompted us to extend this process to other types of electron-deficient alkynes and alkenes (Table 4). Using ethyl 3-phenyl-2-propiolate (**5g**) and acetylacetone (**3a**) as reactants, the desired α-addition product **6ga** was obtained in 63% isolated yield. Interestingly, **3a** could undergo smoothly addition to diethyl acetylenedicarboxylate (**5h**) in the absence of catalyst and solvent, and the reaction gave product **6ha** with 80% yield. The reaction of ethyl 2-butynoate (**5i**) with **3a** gave γ-addition product **6ia** in 62% isolated yield.[11] There existed the tautomerism of keto–enol form and molar ratio of **6ia/6′ia**=1:1. The reaction conducted with acrylic compounds afforded Michael adducts. If molar ratio of **3a/5j**=1.2:1, mono Michael adduct **6ja** was obtained in 60% yield and keto form was the major product. Double Michael adduct **6ka** was obtained in 75% yield if molar ratio of **5k/3a**=2.5:1. However, a complex mixture was obtained when using ethyl propiolate (**5l**).

In the course of this study, we conducted ^{31}P NMR spectroscopy to obtain the evidence for the nucleophilic addition of triphenylphosphine to α,β-unsaturated alkynes or alkenes.

Table 4
Addition of acetylacetone to other types of electron-deficient alkynes and alkenes catalyzed by ***JJ*–TPP**[a]

Entry	Electrophile	Product	Yield[b] (%)
1	 **5g**	 **6ga**	63
2	 **5h**	 **6ha**	80
3[c]	 **5i**	 **6ia** **6'ia**	62[d]
4	 **5j**	 **6ja**	60
5[e]	 **5k**	 **6ka**	75
6	 **5l**	Complex	—

[a] Reaction condition: **5** (0.5 mmol), **3a** (1.2 equiv), and ***JJ*–TPP** (8 mol %) stand still for 6 h.
[b] Isolated yield.
[c] 12 h.
[d] Molar ratio of **6ia/6′ia**=1:1 and determined by ^1H NMR.
[e] Molar ratio of **5k/3a**=2.5:1.

The reaction of triphenylphosphine (**1a**) was carried out with ethyl 3-phenyl-2-propiolate (**5g**) in aqueous THF (THF/H_2O=5:1, v/v) for 12 h. ^{31}P NMR chemical shift for Ph_3P is −3.76 in $CDCl_3$. Whereas, a new species was obtained after the reaction of **1a** and **5g**, which changed the chemical shift of ^{31}P to 26.36 suggesting the existence of phosphonium salt **7ag** (Fig. 2). The formation of **7ag** confirmed that the nucleophilic Michael addition of phosphine to ethyl 3-phenyl-2-

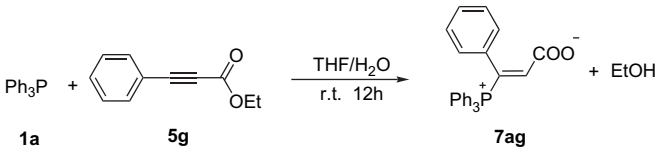


Figure 2.

propiolate generates zwitterions. Analogous zwitterions of DABCO or PTA (1,3,5-triaza-7-phosphaadamantane) with acrylic compounds were reported.[12,13]

3. Conclusion

In summary, ***JJ*−TPP** as an effective organocatalyst for α-addition of carbon nucleophiles to α,β-unsaturated compounds has been demonstrated under the solvent-free condition at room temperature under ambient atmosphere. ***JJ*−TPP** is easy to be recovered and reusable with high catalytic capability. More remarkably, this protocol is compatible to various substrates.

4. Experimental

4.1. General

Ynones were prepared according to the reference.[14] **PEG−TPP** (mp=44−46 °C, 0.4 mmol P/g) and **PS−DPP** (200−400 mesh, 2%DVB, 2.5 mmol P/g) were purchased from Fluka. **PS−TPP** (200−400 mesh, 2%DVB, 3.0 mmol P/g) and ***JJ*−TPP** (70−90 mesh, 2%DVB, 2−3 mmol P/g) were purchased from Aldrich chemical company. **PS−PEG−TPP** (0.6 mmol P/g) was prepared according to the patent.[15] All reactions were performed in a pear bottom flask without N_2 protection. Reagents were purchased from commercial suppliers and used without further purification. NMR spectra (^{1}H, ^{13}C, and ^{31}P) were recorded with Bruker Avance 400 MHz spectrometer using TMS as the internal standard (^{1}H and ^{13}C) and 85% phosphoric acid as external standard (^{31}P). IR spectra were obtained as potassium bromide pellets or as liquid films with a Brucker Vector 22 spectrometer. GC and Mass Spectra were run on a Finnigan Trace DSQ spectrometer. TLC (thin layer chromatography) was performed by using commercially available 100−400 mesh silica gel plates (GF 254), and visualization was effected at 254 nm. Elemental analysis was performed on a Vario EL elemental analyzer.

4.2. Typical procedure for the preparation of *4*

To a pear-shaped flask ***JJ*−TPP** (10 mol %), ynones **2** (0.25 mmol), and **3** (1.2 equiv) were added and stood still at room temperature for 6 h. Then 5 mL ethyl ether was added and stirred for 1 h. After the catalyst was separated by filtration, the residue was isolated by preparative TLC to obtain pure products **4**. The reused catalyst was washed several times with ethyl ether and stored under vacuum for next use.

4.2.1. 2-Benzylidene-3-(1-hydroxy-ethylidene)-1-phenyl-pentane-1,4-dione (***4aa***)[3i]

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.94 (s, 6H), 7.34−7.59 (m, 9H), 7.80 (t, J=4 Hz, 2H), 16.77 (s, 1H); MS (70 eV) *m/z* (%): 306 ($M^{\bullet+}$), 263, 245, 221, 201, 159, 115, 105 (100), 77, 43; IR (KBr) ν: 3058, 1645, 1605, 1493, 1399, 1253, 1016, 932, 863 cm^{-1}.

4.2.2. 3-(1-Hydroxy-ethylidene)-2-(4-methyl-benzylidene)-1-phenyl-pentane-1,4-dione (***4ba***)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.94 (t, J=8 Hz, 6H), 2.34 (s, 3H), 7.15 (d, J=8 Hz, 2H), 7.31−7.57 (m, 6H), 7.77 (t, J=8 Hz, 2H), 16.75 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 197.6, 191.0, 146.1, 140.8, 138.3, 133.9, 132.0, 131.8, 130.0, 129.8, 129.4, 128.5, 108.9, 23.5, 21.4; MS (70 eV) *m/z* (%): 320 ($M^{\bullet+}$), 302, 277, 259, 245, 235, 215, 185, 173, 143, 129, 105 (100), 91, 77, 43; IR (KBr) ν: 3028, 2923, 1645, 1603, 1511, 1395, 1253, 1050, 990, 868 cm^{-1}. Anal. Calcd for $C_{21}H_{20}O_3$: C 78.73, H 6.29. Found: C 78.66, H 6.32.

4.2.3. 3-(1-Hydroxy-ethylidene)-2-(4-nitro-benzylidene)-1-phenyl-pentane-1,4-dione (***4ca***)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.94 (s, 6H), 7.33−7.44 (m, 6H), 7.90 (t, J=4 Hz, 2H), 8.35 (t, J=4 Hz, 2H), 16.80 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 195.9, 191.0, 149.7, 147.5, 143.9, 134.7, 134.0, 131.0, 130.2, 130.1, 129.3, 123.8, 108.0, 23.5; MS (70 eV) *m/z* (%): 351, 333, 308, 290, 266, 231, 215, 201, 183, 159, 150, 134, 104, 92, 76, 63, 43; IR (KBr) ν: 3064, 2985, 1743, 1653, 1457, 1371, 1102, 1035 cm^{-1}. Anal. Calcd for $C_{20}H_{17}NO_5$: C 68.37, H 4.88, N 3.99. Found: C 68.66, H 4.82, N 4.10.

4.2.4. 2-Benzylidene-3-(1-hydroxy-ethylidene)-1-p-tolyl-pentane-1,4-dione (***4da***)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.94 (s, 6H), 2.44 (s, 3H), 7.28−7.43 (m, 8H), 7.73 (d, J=8 Hz, 2H), 16.76 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 197.2, 191.0, 145.0, 143.1, 135.2, 134.9, 134.7, 130.0, 129.9, 129.8, 129.2, 129.0, 109.1, 23.5, 21.6; MS (70 eV) *m/z* (%): 320 ($M^{\bullet+}$), 302, 277, 259, 245, 235, 217, 201, 185, 159, 143, 119 (100), 105, 91, 65, 43; IR (KBr) ν: 3030, 2924, 1645, 1606, 1494, 1401, 1254, 1043, 920, 867 cm^{-1}. Anal. Calcd for $C_{21}H_{20}O_3S$: C 78.73, H 6.29. Found: C 78.59, H 6.52.

4.2.5. 2-Benzylidene-1-furan-2-yl-3-(1-hydroxy-ethylidene)-pentane-1,4-dione (***4ea***)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.92 (s, 6H), 6.56 (t, J=4 Hz, 1H), 7.18 (d, J=4 Hz, 1H), 7.35−7.70 (m, 7H), 16.74 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 191.4, 183.0, 152.2, 147.0, 143.1, 134.8, 133.9, 130.1, 129.1, 119.5, 112.2, 108.9, 23.6; MS (70 eV) *m/z* (%): 296 ($M^{\bullet+}$, 100), 267, 253, 235, 228, 185, 158, 151, 115, 95 (100), 77, 43; IR (KBr) ν: 3059, 2925, 1637, 1461, 1392, 1273, 1018, 925, 888 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_4$: C 72.96, H 5.44. Found: C 72.85, H 5.60.

4.2.6. 2-Benzylidene-3-(1-hydroxy-ethylidene)-1-thiophen-2-yl-pentane-1,4-dione (***4fa***)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.93 (s, 6H), 7.15 (t, J=4 Hz, 1H), 7.35−7.80 (m, 8H), 16.81 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 191.5, 187.6, 143.1, 142.6, 134.8, 134.4, 134.3, 134.0, 130.1, 130.0, 129.1, 128.0, 23.7; MS (70 eV) *m/z* (%): 312 ($M^{\bullet+}$), 294, 269, 251, 228, 201, 185, 171, 158, 151, 115, 111 (100), 105, 83, 63, 43; IR (KBr) ν: 3092, 2924, 1627, 1508, 1411, 1204, 1001, 920, 855 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_3S$: C 69.21, H 5.16. Found: C 69.10, H 5.30.

*4.2.7. 3-(1-Hydroxy-ethylidene)-2-(4-methyl-benzylidene)-1-p-tolyl-pentane-1,4-dione (**4ga**)*

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.93 (d, J=4 Hz, 6H), 2.34 (s, 3H), 2.43 (s, 3H), 7.15 (d, J=8 Hz, 2H), 7.27–7.33 (m, 5H), 7.71 (d, J=8 Hz, 2H), 16.74 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 197.3, 191.0, 145.3, 142.9, 140.7, 135.4, 134.0, 131.9, 130.0, 129.8, 129.7, 129.2, 109.1, 23.5, 21.6, 21.4; MS (70 eV) *m/z* (%): 334 ($M^{\bullet+}$), 316, 301, 273, 249, 215, 200, 173, 157, 129, 119 (100), 115, 91, 65, 43; IR (KBr) ν: 3029, 2923, 1643, 1605, 1510, 1398, 1255, 1021, 921, 872 cm^{-1}. Anal. Calcd for $C_{22}H_{22}O_3$: C 79.02, H 6.63. Found: C 78.78, H 6.84.

*4.2.8. 3-(1-Hydroxy-ethylidene)-2-(4-methyl-benzylidene)-1-thiophen-2-yl-pentane-1,4-dione (**4ha**)*

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.93 (s, 6H), 2.35 (s, 3H), 7.13–7.18 (m, 3H), 7.36 (d, J=8 Hz, 2H), 7.66–7.79 (m, 3H), 16.81 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 191.6, 187.5, 143.3, 142.7, 140.7, 134.1, 133.9, 133.3, 132.0, 130.1, 129.8, 127.9, 109.4, 23.6, 21.4; MS (70 eV) *m/z* (%): 326 ($M^{\bullet+}$), 308, 283, 265, 251, 242, 227, 199, 185, 172, 128, 111 (100), 91, 83, 57, 43; IR (KBr) ν: 3025, 2923, 1628, 1510, 1411, 1257, 1053, 922, 861 cm^{-1}. Anal. Calcd for $C_{19}H_{18}O_3S$: C 69.91, H 5.56. Found: C 69.78, H 5.86.

*4.2.9. 2-(1-Benzoyl-2-phenyl-vinyl)-3-hydroxy-but-2-enoic acid ethyl ester (**4ab**)*

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.05 (t, J=8 Hz, 3H), 1.71 (s, 3H), 4.11 (q, J=8 Hz, 2H), 7.10 (s, 1H), 7.31–7.54 (m, 8H), 7.83 (t, J=4 Hz, 2H), 12.98 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 198.2, 174.9, 171.9, 142.7, 138.4, 135.3, 134.3, 132.0, 129.7, 129.4, 129.3, 128.7, 128.2, 98.8, 60.8, 19.4, 19.3; MS (70 eV) *m/z* (%): 290 (M−46), 275 (100), 261, 247, 218, 213, 199, 189, 171, 143, 127, 105, 77, 51; IR (KBr) ν: 3062, 2978, 1650, 1446, 1247, 1067, 959, 861 cm^{-1}. Anal. Calcd for $C_{21}H_{20}O_4$: C 74.98, H 5.99. Found: C 74.88, H 5.90.

*4.2.10. 2-(1-Benzoyl-2-phenyl-vinyl)-malonic acid diethyl ester (**4ac**)*

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.21–1.26 (m, 6H), 4.15–4.26 (m, 4H), 4.86 (s, 1H), 7.37–7.55 (m, 9H), 7.82–7.84 (m, 2H); ^{13}C NMR ($CDCl_3$) δ: 196.7, 167.7, 144.1, 137.5, 134.4, 134.3, 132.2, 129.9, 129.8, 129.2, 128.8, 128.3, 127.9, 62.0, 61.9, 51.5, 13.9; MS (70 eV) *m/z* (%): 366 ($M^{\bullet+}$), 348, 321, 293, 275, 264, 247, 207, 191, 160, 143, 115, 105 (100), 77, 51, 29; IR (KBr) ν: 3061, 2984, 1735, 1657, 1591, 1451, 1246, 1035, 979, 869 cm^{-1}. Anal. Calcd for $C_{22}H_{22}O_5$: C 72.12, H 6.05. Found: C 72.30, H 6.32.

*4.2.11. 2-Benzylidene-3-(hydroxyl-phenyl-methlene)-1,4-diphenyl-1,4-dione (**4ad**)*

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.15–7.91 (m, 43H), 17.48 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 196.4, 195.6, 195.0, 194.8, 180.8, 154.4, 150.8, 145.2, 142.5, 139.8, 136.9, 133.0, 130.3, 129.9, 128.5, 128.2, 128.1, 128.0, 127.8, 127.6, 124.3, 60.6; MS (70 eV) *m/z* (%): 430 ($M^{\bullet+}$), 325, 297, 247, 223, 191, 165, 147, 129, 115, 105, 77, 69, 51, 32; IR (KBr) ν: 2960, 1646, 1490, 1447, 1386, 1317, 1260, 1025 cm^{-1}.

*4.2.12. 3-Hydroxy-2-[1-(4-methyl-benzoyl)-2-phenyl-vinyl]-but-2-enoic acid ethyl ester (**4db**)*

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.04 (t, J=8 Hz, 3H), 1.71 (s, 3H), 2.41 (s, 3H), 4.10 (d, J=8 Hz, 2H), 7.08 (s, 1H), 7.25–7.7.39 (m, 7H), 7.75 (d, J=8 Hz, 2H), 12.96 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 197.9, 175.0, 171.9, 142.7, 142.0, 135.6, 135.4, 134.4, 130.0, 129.3, 129.2, 128.9, 128.7, 99.0. 60.8, 21.6, 19.5, 13.9; MS (70 eV) *m/z* (%): 304 (M−46), 289 (100), 261, 213, 199, 189, 171, 128, 119, 91, 65, 43; IR (KBr) ν: 2982, 1651, 1608, 1380, 1247, 1069, 963, 867 cm^{-1}. Anal. Calcd for $C_{22}H_{22}O_4$: C 75.41, H 6.33. Found: C 75.15, H 6.55.

*4.2.13. 2-[1-(Furan-2-carbonyl)-2-phenyl-vinyl]-but-2-enoic acid ethyl ester (**4eb**)*

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.97 (t, J=4 Hz, 3H), 1.72 (s, 3H), 4.04–4.10 (m, 2H), 6.51 (t, J=4 Hz, 1H), 7.12 (d, J=4 Hz, 1H), 7.30–7.63 (m, 7H), 13.03 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 183.5, 175.0, 171.9, 152.3, 146.7, 141.0, 135.5, 133.1, 129.5, 129.3, 128.7, 119.2, 111.9, 98.9, 60.8, 19.5, 13.8; MS (70 eV) *m/z* (%): 280 (M−46, 100), 265, 252, 234, 209, 199, 181, 152, 128, 95, 89, 43; IR (KBr) ν: 3132, 2984, 1646, 1567, 1463, 1389, 1245, 1059, 934, 856 cm^{-1}. Anal. Calcd for $C_{19}H_{18}O_5$: C 69.93, H 5.56. Found: C 69.75, H 5.25.

*4.2.14. 3-Hydroxy-2-[2-phenyl-1-(thiophene-2-carbonyl)-vinyl]-but-2-enoic acid ethyl ester (**4fb**)*

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.96 (t, J=8 Hz, 3H), 1.73 (s, 3H), 4.07 (q, J=8 Hz, 2H), 7.11 (t, J=4 Hz, 1H), 7.32–7.77 (m, 8H), 13.05 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 188.5, 175.4, 171.9, 143.2, 140.7, 135.5, 133.8, 133.5, 129.4, 129.2, 128.7, 127.7, 99.2, 60.9, 19.6, 13.7; MS (70 eV) *m/z* (%): 341 (M−1), 312, 296 (M−46), 281, 263, 250, 221, 212, 199, 171, 155, 128, 111, 83, 39; IR (KBr) ν: 3093, 2925, 1639, 1508, 1410, 1249, 1062, 962, 855 cm^{-1}. Anal. Calcd for $C_{19}H_{18}O_4S$: C 66.65, H 5.30. Found: C 66.50, H 5.17.

*4.3. Typical procedure for the preparation of **6***

To a pear-shaped flask ***JJ*–TPP** (8 mol %), **5** (0.5 mmol), and **3a** (1.2 equiv) were added and stood still at room temperature for 6 h. Then 5 mL ethyl ether was added and stirred for 1 h. After the catalyst was separated by filtration, the residue was isolated by preparative TLC to obtain pure products **6**.

*4.3.1. 3-Acetyl-2-benzylidene-4-hydroxy-pent-3-enoic acid ethyl ester (**6ga**)*[3i]

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.31 (t, J=8 Hz, 3H), 1.90 (s, 6H), 4.27 (q, J=8 Hz, 2H), 7.33–7.35 (m, 3H), 7.43–7.45 (m, 2H), 7.85 (s, 1H), 16.65 (s, 1H); MS (70 eV) *m/z* (%): 274 ($M^{\bullet+}$), 256, 228, 213, 185, 158, 129, 115, 105, 77, 43; IR (KBr) ν: 3061, 2983, 1709, 1622, 1395, 1242, 1120, 1100, 1030 cm^{-1}.

*4.3.2. 2-(1-Acetyl-2-hydroxy-propenyl)-but-enedioic acid diethyl ester (**6ha**)*

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.23 (t, J=8 Hz, 3H), 1.30 (t, J=8 Hz, 3H), 1.94 (s, 6H), 4.17 (q, J=8 Hz, 2H), 4.27 (q, J=8 Hz, 2H), 7.05 (s, 1H), 16.50 (s, 1H); MS (70 eV) *m/z*

(%): 270 ($M^{\bullet+}$), 255, 227, 209, 197, 181, 151 (100), 126, 109, 93, 82, 53, 43; ^{13}C NMR ($CDCl_3$) δ: 189.9, 166.2, 164.8, 139.5, 132.4, 107.2, 62.2, 61.2, 23.5, 14.1, 14.0; IR (KBr) ν: 2985, 2938, 1720, 1638, 1394, 1240, 1030 cm^{-1}. Anal. Calcd for $C_{13}H_{18}O_6$: C 57.77, H 6.71. Found: C 57.92, H 6.50.

4.3.3. 5-Acetyl-6-hydroxy-hepta-2,5-dienoic acid ethyl ester (**6ia**)[7]

^1H NMR ($CDCl_3$, 400 MHz) (molar ratio of **6ia/6′ia**=1:1) δ: 1.26 (q, J=8 Hz, 3H), 2.07 (s, 3H), 2.18 (s, 3H), 2.68–2.72 (m, 1H), 3.13 (dt, J_1=8 Hz, J_2=4 Hz, 1H), 3.76 (m, 0.5H, CH), 4.12–4.19 (m, 2H), 3.13 (dt, J_1=16 Hz, J_2=8 Hz, 1H), 6.75–6.98 (m, 1H), 16.74 (s, 0.5H, OH); MS (70 eV) *m/z* (%): 212 ($M^{\bullet+}$), 194, 170, 141, 125 (100), 99, 81, 53, 43; IR (KBr) ν: 2985, 2933, 1714, 1652, 1423, 1365, 1272, 1215, 1095 cm^{-1}.

4.3.4. 3-Acetyl-heptane-2,6-dione (**6ja**)[16]

^1H NMR ($CDCl_3$, 400 MHz) δ: 2.01–2.18 (m, 11H), 2.41 (t, J=8 Hz, 2H), 3.61 (t, J=8 Hz, 1H); MS (70 eV) *m/z* (%): 170 ($M^{\bullet+}$), 152, 128 (100), 110, 95, 85, 71, 58, 43; IR (KBr) ν: 1709, 1618, 1421, 1361 cm^{-1}.

4.3.5. 4,4-Diacetyl-heptanedioic acid dimethyl ester (**6ka**)[16]

^1H NMR ($CDCl_3$, 400 MHz) δ: 2.08–2.21 (m, 14H), 3.67 (s, 6H); MS (70 eV) *m/z* (%): 273 (M+1), 254, 230, 212, 198, 170, 167, 157, 138, 125, 110, 97, 81, 55, 43; IR (KBr) ν: 2961, 2875, 1734, 1459, 1362, 1184, 1073 cm^{-1}.

4.4. Typical procedure for the preparation of **7ag**

To a 25 mL round bottom flask, **TPP 1a** (0.5 mmol), ethyl 3-phenyl-2-propiolate **5g** (0.6 mmol) and 3 mL of aqueous THF (THF:H_2O=5:1, v/v) were added and stirred for 12 h at room temperature. Then the solvent was evaporated under reduced pressure. To the residue was added 10 mL Et_2O and a lot of white solid was produced. After filtration **7ag** was obtained.

4.4.1. Phosphonium salt **7ag**

^1H NMR ($CDCl_3$, 400 MHz) δ: 6.90–7.74 (m, 21H); ^{31}P NMR (D_2O) δ: 26.36; ^{13}C NMR (D_2O) δ: 173.8, 173.6, 153.4, 137.9, 137.5, 137.4, 136.6, 136.5, 134.5, 134.4, 134.3, 132.6, 132.5, 132.2, 132.1, 131.7, 131.6, 131.4, 131.0, 127.1, 126.4, 119.7, 118.8; IR (KBr) ν: 3058, 3024, 1642, 1611, 1484, 1439, 1368, 1316, 1164, 1104 cm^{-1}.

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