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Regioselective 1,4-conjugate aza-Michael addition of dienones with benzotriazole

DOI 10.1515/hc-2016-0182
Received November 28, 2016; accepted March 31, 2017; previously published online July 8, 2017

Abstract: The regioselective 1,4-conjugate aza-Michael addition of dienones with benzotriazole catalyzed by potassium acetate is described. A series of 3-(benzotriazol-1-yl)-1,5-diarylpent-4-en-1-ones were efficiently synthesized under mild conditions. This protocol has advantages of transition-metal free catalyst, high yield and high regioselectivity.

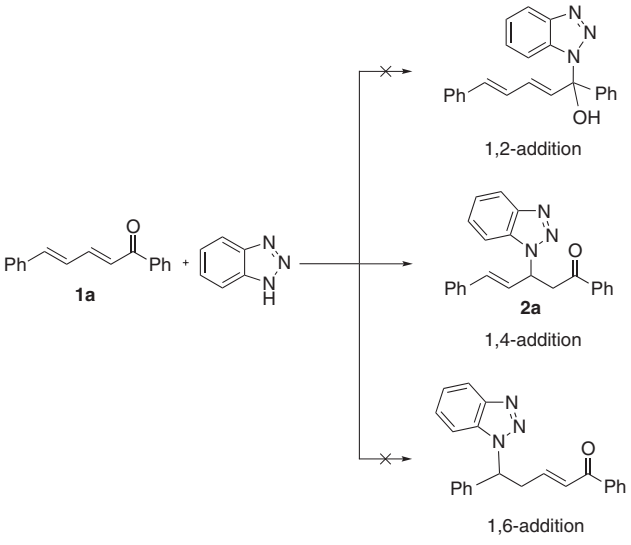
Keywords: aza-Michael addition; benzotriazole; dienone; regioselectivity; synthesis.

Introduction

The aza-Michael addition is an important reaction in synthetic organic chemistry, which has broad applications in pharmaceutical chemistry, biology, and material sciences [1]. The conjugate addition of *N*-heterocyclic agents, such as benzotriazole [2], indazole [3], pyrazole [4, 5], tetrazole [6] and piperazine [7], as nucleophiles to Michael acceptors are important reactions for construction of C-N bonds in organic chemistry. However, the reported Michael acceptors have mainly focused on one C=C bond substrates, such as α,β-unsaturated ketones [8–11], carboxylic acids [12], esters [13–15], amides [16], nitriles [17], and nitroalkenes [18–20]. Moreover, complex and expensive catalysts, such as transition metal complexes [21–24] and Brønsted, Lewis or heteropoly acids [25–27] are also required. Limited examples of the Michael acceptors with two C=C bonds, such as conjugated dienones, have been reported. Wang has reported a method for aza-Michael addition of benzotriazole to 6-arylhexa-3,5-dien-2-ones catalyzed by diethylamine in toluene [28]. Feng has reported one example of enantioselective direct Michael addition of benzotriazole to 1,5-diphenylpenta-2,4-dien-1-one in the presence of a complex catalyst in chloroform [29]. In fact, the aza-Michael addition of dienones poses problems of regioselective control, as the dienones can, in principle, undergo 1,2-, 1,4-, and 1,6-addition reactions. Herein, we report the regioselective 1,4-conjugate aza-Michael addition of benzotriazole to dienones under mild conditions by using potassium acetate as a catalyst.

Results and discussion

Initially, (*2E,4E*)-1,5-diphenylpenta-2,4-dien-1-one **(1a)** was selected as a substrate of aza-Michael addition with benzotriazole (Scheme 1). When the reaction was carried out in the presence of KF as a catalyst in acetonitrile, a sole product **2a** was isolated in 45% yield. This result indicates that the reaction of **1a** with benzotriazole proceeds by 1,4-conjugate addition. No 1,2- and 1,6- adducts were observed. The same product was also synthesized by Feng and co-workers in 45% yield in the presence of $Sc(OTf)_3$ as a catalyst [29]. In principle, the use of benzotriazole as a Michael donor can result in the formation of two additional products, *N1* and *N2* adducts, because of the tautomerism. However, in this reaction, the *N1* adduct is the sole product.



Scheme 1 Regioselective addition of dienone **1a** with benzotriazole.

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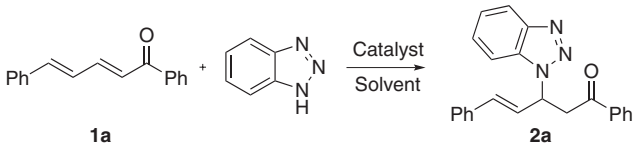
Table 1 Optimization of the reaction conditions[a].



1a **2a**

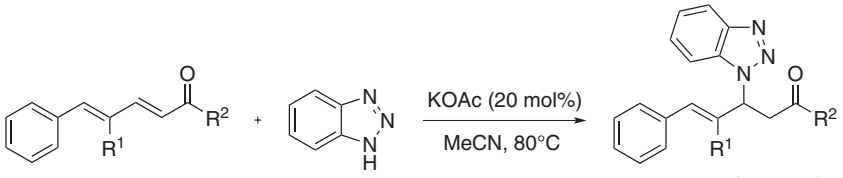
Entry	Catalyst (mmol%)	Solvent	Temperature (°C)	Yield (%)[b]
1	None	MeCN	80	0
2	LiCl (20)	MeCN	80	0
3	Na_2CO_3 (20)	MeCN	80	0
4	K_2CO_3 (20)	MeCN	80	0
5	KF (20)	MeCN	80	45
6	CsF (20)	MeCN	80	47
7	K_3PO_4 (20)	MeCN	80	51
8	Cs_2CO_3 (20)	MeCN	80	53
9	NaOH (20)	MeCN	80	46
10	DBU (20)	MeCN	80	62
11	Et_3N (20)	MeCN	80	49
12	Et_2NH (20)	MeCN	80	33
13	KOAc (20)	MeCN	80	85
14	KOAc (20)	DMF	150	48
15	KOAc (20)	DMSO	150	39
16	KOAc (20)	MeOH	60	28
17	KOAc (20)	EtOH	80	37
18	KOAc (20)	CH_2Cl_2	40	34
19	KOAc (20)	THF	60	26
20	KOAc (20)	1,4-dioxane	100	23
21	KOAc (20)	PhMe	110	21
22	KOAc (20)	MeCN	60	74
23	KOAc (20)	MeCN	40	62
24	KOAc (100)	MeCN	80	80
25	KOAc (50)	MeCN	80	83
26	KOAc (10)	MeCN	80	58
27	KOAc (5)	MeCN	80	26

[a]**1a** (0.5 mmol), benzotriazole (0.7 mmol), solvent (5 mL), 20 h.
[b]Isolated yield.

Subsequently, the reaction conditions were optimized. It was found that in the absence of catalyst the desired product **2a** was not formed (Table 1, entry 1). Some catalysts, such as LiCl, Na_2CO_3 and K_2CO_3, had no effect on the reaction (entries 2–4). However, inorganic bases, such as KF, CsF, K_3PO_4, Cs_2CO_3 and NaOH, and organic bases, such as DBU, Et_3N and Et_2NH, catalyze the reaction to give **2a** in moderate yield (entries 5–12). The highest yield of **2a** was obtained in the presence of KOAc (entry 13). These results suggest that the yield is related to basicity of catalyst. The moderate basicity of catalyst is advantageous for the reaction.

Solvent also plays a significant role. It was found that the reaction conducted in MeCN furnishes the desired product **2a** in highest yield (entry 13). Other tested solvents gave rise to **2a** in low yields (entries 14–21). In addition, 80°C is the optimal temperature as a decrease in the reaction temperature results in lower yield (entries 22–23). The increase of catalyst loading from 20 mmol% to 100 mmol% does not significantly improve the yield (entries 24–25). Inversely, the decrease of catalyst loading from 20 mmol% to 5 mmol% leads to decrease in the yield (entries 26–27).

Based on the above promising findings, additional dienones were examined for the 1,4-conjugate addition in MeCN at 80°C using KOAc as a catalyst (Scheme 2). It was found that reactions of dienones bearing an electron-donating group on an aromatic ring R^2 furnish the corresponding products in high yields (**2b**,**c**). By contrast, the reactions of dienones bearing an electron-withdrawing group on the aromatic ring give slightly lower yields (**2d–g**). When R^2 is a heterocyclic group, such as 2-thienyl, the reaction takes place smoothly to give the corresponding product in high yield (**2h**, **2m**). However, for R^2 = alkyl, such as Me or Et, the reactions were not successful and



1a–m **2a–m** (78–87%)

2a: R^1 = H; R^2 = Ph
2b: R^1 = H; R^2 = 4-MeC_6H_4
2c: R^1 = H; R^2 = 4-$MeOC_6H_4$
2d: R^1 = H; R^2 = 4-FC_6H_4
2e: R^1 = H; R^2 = 4-ClC_6H_4
2f: R^1 = H; R^2 = 4-BrC_6H_4
2g: R^1 = H; R^2 = 3-BrC_6H_4
2h: R^1 = H; R^2 = 2-thienyl
2i: R^1 = Me; R^2 = Ph
2j: R^1 = Me; R^2 = 4-MeC_6H_4
2k: R^1 = Me; R^2 = 4-ClC_6H_4
2l: R^1 = Me; R^2 = 4-BrC_6H_4
2m: R^1 = Me; R^2 = 2-thienyl

Scheme 2 Regioselective aza-Michael addition of dienones with benzotriazole.

no desired adducts were isolated. However, a successful addition was reported by using diethylamine as a catalyst and toluene as solvent [28].

Conclusion

An efficient protocol was developed for high-yield regioselective 1,4-conjugate aza-Michael addition of dienones with benzotriazole using potassium acetate as a catalyst.

Experimental

^{1}H NMR and ^{13}C NMR spectra were recorded on a Mercury-400BB or Mercury-600BB instrument using $CDCl_3$ as solvent and Me_4Si as internal standard. Melting points were observed on an electrothermal melting point apparatus. IR spectra were obtained using KBr pellets. Dienones were prepared according to literature procedure [30].

General procedure for the 1,4-conjugate aza-Michael addition of dienone with benzotriazole

Dienone (0.5 mmol), benzotriazole (0.7 mmol), potassium acetate (0.1 mmol), and acetonitrile (5 mL) were sequentially charged into a dry Schlenk tube and the mixture was stirred at 80°C for 20 h. After the reaction was completed (monitored by TLC), the mixture was cooled to room temperature, diluted with ethyl acetate (5 mL) and washed with brine (3×5 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was subjected to silica gel column chromatography using petroleum ether and ethyl acetate (v/v 10:1) as eluent to give pure product.

(*E*)-3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-1,5-diphenylpent-4-en-1-one (2a) Yellow solid; mp 50–52°C; yield 85%; IR (cm^{-1}): 1683 (C=O); ^{1}H NMR (400 MHz): δ 8.05 (d, *J* = 8.3 Hz, 1H, ArH), 7.97 (d, *J* = 7.5 Hz, 2H, ArH), 7.72 (d, *J* = 8.3 Hz, 1H, ArH), 7.55 (t, *J* = 7.3 Hz, 1H, ArH), 7.48 (dd, *J* = 13.2, 5.0 Hz, 1H, ArH), 7.44 (t, *J* = 7.1 Hz, 2H, ArH), 7.36 (t, *J* = 7.3 Hz, 1H, ArH), 7.30 (t, *J* = 6.1 Hz, 3H, ArH), 7.19–7.26 (m, 2H, ArH), 6.55–6.56 (m, 2H, CH), 6.20–6.21 (m, 1H, CH), 4.45 (dd, *J* = 17.8, 7.8 Hz, 1H, CH), 3.86 (dd, *J* = 17.8, 5.4 Hz, 1H, CH); ^{13}C NMR (100 MHz): δ 195.8, 145.9, 136.1, 135.4, 133.6, 132.9, 128.6, 128.5, 128.3, 128.1, 127.3, 126.6, 126.4, 124.0, 119.8, 109.9, 56.5, 43.1. Anal. Calcd for $C_{23}H_{19}N_3O$: C, 78.16; H, 5.42; N, 11.89. Found: C, 78.08; H, 5.44; N, 11.92.

(*E*)-3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-5-phenyl-1-(4-tolyl)pent-4-en-1-one (2b) White solid; mp 58–60°C; yield 82%; IR (cm^{-1}): 1685 (C=O); ^{1}H NMR (600 MHz): δ 8.05 (d, *J* = 8.3 Hz, 1H, ArH), 7.88 (d, *J* = 7.6 Hz, 2H, ArH), 7.72 (d, *J* = 8.1 Hz, 1H, ArH), 7.50 (t, *J* = 7.6 Hz, 1H, ArH), 7.37 (t, *J* = 7.5 Hz, 1H, ArH), 7.32 (d, *J* = 7.3 Hz, 2H, ArH), 7.28 (d, *J* = 7.0 Hz, 2H, ArH), 7.21–7.26 (m, 3H, ArH), 6.53–6.59 (m, 2H, CH), 6.21–6.22 (m, 1H, CH), 4.42 (dd, *J* = 17.7, 7.6 Hz, 1H, CH), 3.85 (dd, *J* = 17.6, 4.5 Hz, 1H, CH), 2.40 (s, 3H, CH_3); ^{13}C NMR (150 MHz): δ 195.4, 145.9, 144.5, 135.4, 133.7, 132.9, 132.8, 129.3, 128.5, 128.2, 127.3, 126.5, 123.9, 119.8, 109.9, 56.5, 43.00, 21.6. Anal. Calcd for $C_{24}H_{21}N_3O$: C, 78.45; H, 5.76; N, 11.44. Found: C, 78.56; H, 5.75; N, 11.40.

(*E*)-3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-1-(4-methoxyphenyl)-5-phenylpent-4-en-1-one (2c) White solid; mp 69–71°C; yield 78%; IR (cm^{-1}): 1674 (C=O); ^{1}H NMR (400 MHz): δ 8.05 (d, *J* = 8.4 Hz, 1H, ArH), 7.96 (d, *J* = 8.9 Hz, 2H, ArH), 7.73 (d, *J* = 8.4 Hz, 1H, ArH), 7.51 (dd, *J* = 8.1, 7.2 Hz, 1H, ArH), 7.34–7.40 (m, 1H, ArH), 7.30 (dd, *J* = 12.3, 7.5 Hz, 4H, ArH), 7.23–7.25 (m, 1H, ArH), 6.93 (d, *J* = 8.9 Hz, 2H, ArH), 6.55–6.57 (m, 2H, CH), 6.19–6.24 (m, 1H, CH), 4.40 (dd, *J* = 17.5, 7.8 Hz, 1H, CH), 3.86 (s, 3H, OCH_3), 3.81 (dd, *J* = 17.4, 6.5 Hz, 1H, CH); ^{13}C NMR (100 MHz): δ 194.4, 163.9, 145.9, 135.5, 132.9, 130.5, 129.3, 128.6, 128.3, 127.4, 126.7, 126.6, 124.1, 119.9, 113.9, 110.0, 109.9, 56.7, 55.5, 42.9. Anal. Calcd for $C_{24}H_{21}N_3O_2$: C, 75.18; H, 5.52; N, 10.96. Found: C, 75.13; H, 5.50; N, 10.99.

(*E*)-3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-1-(4-fluorophenyl)-5-phenylpent-4-en-1-one (2d) Yellow solid; mp 84–86°C; yield: 80%; IR (KBr, cm^{-1}): 1690 (C=O); ^{1}H NMR (600 MHz): δ 8.06 (d, *J* = 8.5 Hz, 1H, ArH), 8.01 (dd, *J* = 8.7, 5.4 Hz, 2H, ArH), 7.72 (d, *J* = 8.5 Hz, 1H, ArH), 7.49–7.54 (m, 1H, ArH), 7.36–7.40 (m, 1H, ArH), 7.32 (d, *J* = 7.3 Hz, 2H, ArH), 7.29 (t, *J* = 7.5 Hz, 2H, ArH), 7.23–7.25 (m, 1H, ArH), 7.13 (t, *J* = 8.5 Hz, 2H, ArH), 6.55–6.56 (m, 2H, CH), 6.18–6.21 (m, 1H, CH), 4.46 (dd, *J* = 17.6, 8.0 Hz, 1H, CH), 3.81 (dd, *J* = 17.7, 5.4 Hz, 1H, CH). ^{13}C NMR (150 MHz): δ 194.4, 166.9, 165.2, 145.9, 135.4, 133.2, 133.0, 132.7, 130.9, 130.8, 128.6, 128.4, 127.5, 126.7, 126.4, 124.2, 119.9, 116.0, 115.8, 110.0, 109.9, 56.6, 43.1. Anal. Calcd for $C_{23}H_{18}FN_3O$: C, 74.38; H, 4.89; N, 11.31. Found: C, 74.26; H, 4.87; N, 11.29.

(*E*)-3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-1-(4-chlorophenyl)-5-phenylpent-4-en-1-one (2e) Yellow solid; mp 52–54°C; yield 82%; IR (cm^{-1}): 1690 (C=O); ^{1}H NMR (600 MHz): δ 8.05 (d, *J* = 8.4 Hz, 1H, ArH), 7.92 (d, *J* = 8.2 Hz, 2H, ArH), 7.71 (d, *J* = 8.3 Hz, 1H, ArH), 7.51 (t, *J* = 7.5 Hz, 1H, ArH), 7.43 (d, *J* = 8.0 Hz, 2H, ArH), 7.35–7.39 (m, 1H, ArH), 7.32 (d, *J* = 7.5 Hz, 2H, ArH), 7.28 (t, *J* = 7.5 Hz, 2H, ArH), 7.22–7.26 (m, 1H, ArH), 6.54–6.56 (m, 2H, CH), 6.16–6.20 (m, 1H, CH), 4.46 (dd, *J* = 17.7, 8.0 Hz, 1H, CH), 3.80 (dd, *J* = 17.7, 5.4 Hz, 1H, CH); ^{13}C NMR (150 MHz): δ 194.8, 146.0, 140.2, 135.4, 134.5, 133.2, 133.0, 129.6, 129.1, 128.7, 128.4, 127.5, 126.7, 126.3, 124.1, 119.9, 110.0, 109.9, 56.6, 43.1. Anal. Calcd for $C_{23}H_{18}ClN_3O$: C, 71.22; H, 4.68; N, 10.83. Found: C, 71.15; H, 4.67; N, 10.87.

(*E*)-3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-1-(4-bromophenyl)-5-phenylpent-4-en-1-one (2f) White solid; mp 67–69°C; yield 81%; IR (cm^{-1}): 1678 (C=O); ^{1}H NMR (400 MHz): δ 8.06 (d, *J* = 7.6 Hz, 1H, ArH), 7.80–7.88 (m, 2H, ArH), 7.71 (d, *J* = 7.6 Hz, 1H, ArH), 7.57–7.64 (m, 2H, ArH), 7.48–7.54 (m, 1H, ArH), 7.35–7.41 (m, 1H, ArH), 7.24–7.34 (m, 5H, ArH), 6.54–6.56 (m, 2H, CH), 6.16–6.20 (m, 1H, CH), 4.46 (dd, *J* = 17.8, 8.0 Hz, 1H, CH), 3.80 (dd, *J* = 17.7, 5.4 Hz, 1H, CH). ^{13}C NMR (100 MHz): δ 195.0, 146.0, 135.4, 134.9, 133.2, 133.0, 132.1, 129.7, 129.0, 128.7, 128.4, 127.5, 126.7, 126.3, 124.2, 119.9, 109.9, 56.6, 43.1. Anal. Calcd for $C_{23}H_{18}BrN_3O$: C, 63.90; H, 4.20; N, 9.72. Found: C, 63.97; H, 4.21; N, 9.69.

(*E*)-3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-1-(3-bromophenyl)-5-phenylpent-4-en-1-one (2g) Yellow solid; mp 70–72°C; yield 83%; IR (cm^{-1}): 1676 (C=O); ^{1}H NMR (600 MHz): δ 8.10 (s, 1H, ArH), 8.05 (d, *J* = 8.4 Hz, 1H, ArH), 7.91 (d, *J* = 7.3 Hz, 1H, ArH), 7.68–7.73 (m, 2H, ArH), 7.51 (t, *J* = 7.6 Hz, 1H, ArH), 7.23–7.39 (m, 7H, ArH), 6.51–6.59 (m, 2H, CH), 6.16–6.20 (m, 1H, CH), 4.47 (dd, *J* = 17.8, 8.0 Hz, 1H, CH), 3.81 (dd, *J* = 17.8, 5.4 Hz, 1H, CH); ^{13}C NMR (150 MHz): δ 194.7, 146.0, 137.9, 136.5, 135.3, 133.3, 133.0, 131.3, 130.3, 128.7, 128.4, 127.5, 126.7, 126.6, 126.2,

124.1, 123.1, 120.0, 109.9, 56.5, 43.2. Anal. Calcd for $C_{23}H_{18}BrN_3O$: C, 63.90; H, 4.20; N, 9.72. Found: C, 63.84; H, 4.19; N, 9.75.

(*E*)-3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-5-phenyl-1-(thiophen-2-yl) pent-4-en-1-one (2h) White solid; mp 45–47°C; yield 84%; IR (cm^{-1}): 1667 (C=O); ^1H NMR (400 MHz): δ 8.05 (d, *J* = 8.4 Hz, 1H, ArH and ThH), 7.82 (d, *J* = 3.8 Hz, 1H, ArH and ThH), 7.70 (d, *J* = 8.4 Hz, 1H, ArH and ThH), 7.65 (d, *J* = 4.9 Hz, 1H, ArH and ThH), 7.50 (t, *J* = 7.6 Hz, 1H, ArH and ThH), 7.24–7.39 (m, 6H, ArH and ThH), 7.14 (t, *J* = 4.3 Hz, 1H, ArH and ThH), 6.52–6.60 (m, 2H, CH), 6.17–6.18 (m, 1H, CH), 4.37 (dd, *J* = 17.1, 7.9 Hz, 1H, CH), 3.82 (dd, *J* = 17.1, 5.7 Hz, 1H, CH). ^{13}C NMR (100 MHz): δ 188.7, 145.9, 143.3, 135.4, 134.5, 133.2, 133.0, 132.7, 128.6, 128.4, 128.3, 127.5, 126.7, 126.2, 124.1, 119.9, 109.9, 56.6, 43.8. Anal. Calcd for $C_{21}H_{17}N_3OS$: C, 70.17; H, 4.77; N, 11.69. Found: C, 70.29; H, 4.76; N, 11.69.

(*E*)-3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-4-methyl-1,5-diphenylpent-4-en-1-one (2i) White solid; mp 60–62°C; yield 87%; IR (cm^{-1}): 1688 (C=O); ^1H NMR (600 MHz): δ 8.04 (d, *J* = 8.4 Hz, 1H, ArH), 7.93 (d, *J* = 8.0 Hz, 2H, ArH), 7.71 (d, *J* = 8.4 Hz, 1H, ArH), 7.49 (t, *J* = 7.6 Hz, 1H, ArH), 7.34–7.38 (m, 1H, ArH), 7.31 (t, *J* = 7.6 Hz, 2H, ArH), 7.22–7.28 (m, 5H, ArH), 6.75 (s, 1H, CH), 6.14–6.16 (m, 1H, CH), 4.71 (dd, *J* = 17.5, 8.8 Hz, 1H, CH), 3.75 (dd, *J* = 17.4, 4.6 Hz, 1H, CH), 1.81 (s, 3H, CH_3); ^{13}C NMR (150 MHz): δ 195.7, 144.5, 136.4, 134.8, 134.0, 133.2, 130.2, 129.4, 129.3, 128.9, 128.4, 128.2, 127.3, 127.1, 124.1, 119.9, 110.2, 62.4, 40.6, 14.1. Anal. Calcd for $C_{24}H_{21}N_3O$: C, 78.45; H, 5.76; N, 11.44. Found: C, 78.37; H, 5.74; N, 11.41.

(*E*)-3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-4-methyl-5-phenyl-1-(4-tolyl)pent-4-en-1-one (2j) Yellow solid; mp 70–72°C; yield 85%; IR (cm^{-1}): 1690 (C=O); ^1H NMR (600 MHz): δ 8.04 (d, *J* = 8.4 Hz, 1H, ArH), 7.93 (d, *J* = 8.0 Hz, 2H, ArH), 7.71 (d, *J* = 8.4 Hz, 1H, ArH), 7.49 (t, *J* = 7.6 Hz, 1H, ArH), 7.34 – 7.38 (m, 1H, ArH), 7.31 (t, *J* = 7.6 Hz, 2H, ArH), 7.27 (d, *J* = 7.9 Hz, 2H, ArH), 7.22 (d, *J* = 8.0 Hz, 3H, ArH), 6.75 (s, 1H, CH), 6.13–6.14 (m, 1H, CH), 4.71 (dd, *J* = 17.5, 8.8 Hz, 1H, CH), 3.75 (dd, *J* = 17.4, 4.6 Hz, 1H, CH), 2.41 (s, 3H, CH_3), 1.81 (s, 3H, CH_3); ^{13}C NMR (150 MHz): δ 195.7, 144.5, 136.4, 134.8, 130.2, 129.4, 129.3, 129.1, 128.9, 128.4, 128.2, 127.3, 127.1, 124.1, 119.9, 110.2, 62.4, 40.6, 21.7, 14.1. Anal. Calcd for $C_{25}H_{23}N_3O$: C, 78.71; H, 6.08; N, 11.02. Found: C, 78.86; H, 6.10; N, 10.99.

(*E*)-3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-1-(4-chlorophenyl)-4-methyl-5-phenylpent-4-en-1-one (2k) White solid; mp 84–86°C; yield 83%; IR (cm^{-1}): 1691 (C=O); ^1H NMR (600 MHz): δ 8.04 (d, *J* = 8.4 Hz, 1H, ArH), 7.97 (d, *J* = 8.4 Hz, 2H, ArH), 7.69 (d, *J* = 8.4 Hz, 1H, ArH), 7.49 (t, *J* = 7.6 Hz, 1H, ArH), 7.45 (d, *J* = 8.4 Hz, 2H, ArH), 7.35–7.40 (m, 1H, ArH), 7.32 (t, *J* = 7.6 Hz, 2H, ArH), 7.23 (t, *J* = 7.9 Hz, 3H, ArH), 6.75 (s, 1H, CH), 6.10–6.12 (m, 1H, CH), 4.75 (dd, *J* = 17.5, 9.1 Hz, 1H, CH), 3.68 (dd, *J* = 17.5, 4.4 Hz, 1H, CH), 1.80 (s, 3H, CH_3); ^{13}C NMR (150 MHz): δ 195.0, 146.3, 140.1, 136.2, 134.8, 134.6, 129.7, 129.6, 129.4, 129.0, 128.9, 128.3, 127.4, 127.2, 124.1, 119.9, 110.1, 62.3, 40.7, 14.0. Anal. Calcd for $C_{24}H_{20}ClN_3O$: C, 71.73; H, 5.02; N, 10.46. Found: C, 71.80; H, 5.00; N, 10.49.

(*E*)-3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-1-(4-bromophenyl)-4-methyl-5-phenylpent-4-en-1-one (2l) White solid; mp 90–92°C; yield 80%; IR (cm^{-1}): 1689 (C=O). ^1H NMR (600 MHz): δ 8.04 (d, *J* = 8.3 Hz, 1H, ArH), 7.89 (d, *J* = 8.5 Hz, 2H, ArH), 7.86 (d, *J* = 8.4 Hz, 1H, ArH), 7.69 (d, *J* = 8.3 Hz, 1H, ArH), 7.63 (d, *J* = 8.5 Hz, 2H, ArH), 7.49 (t, *J* = 7.6 Hz, 1H, ArH), 7.39 (t, *J* = 7.6 Hz, 2H, ArH), 7.32 (d, *J* = 7.5 Hz, 1H, ArH), 7.23 (d, *J* = 8.1 Hz, 2H, CH), 6.74 (s, 1H, CH), 6.09–6.11 (m, 1H, CH), 4.74 (dd, *J* = 17.5, 9.1 Hz, 1H, CH), 3.67 (dd, *J* = 17.5, 4.4 Hz, 1H, CH), 1.80 (s, 3H, CH_3). ^{13}C NMR (150 MHz): δ 195.2, 150.8, 141.0, 132.0, 131.8, 129.9, 129.7, 129.6, 129.4, 128.9, 128.4, 128.3, 127.4, 127.2, 124.1, 120.0, 110.1, 62.3, 40.7, 14.0. Anal. Calcd for $C_{24}H_{20}BrN_3O$: C, 64.58; H, 4.52; N, 9.41. Found: C, 64.65; H, 4.51; N, 9.38.

(*E*)-3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-4-methyl-5-phenyl-1-(thiophen-2-yl)pent-4-en-1-one (2m) White solid; mp 78–80°C; yield 80%; IR (cm^{-1}): 1665 (C=O); ^1H NMR (600 MHz): δ 8.02–8.06 (m, 1H, ArH and ThH), 7.88–7.91 (m, 1H, ArH and ThH), 7.68 (d, *J* = 9.0 Hz, 1H, ArH and ThH), 7.66 (d, *J* = 4.9 Hz, 1H, ArH and ThH), 7.49 (dd, *J* = 8.0, 7.3 Hz, 1H, ArH and ThH), 7.37 (dd, *J* = 8.0, 7.3 Hz, 1H, ArH and ThH), 7.31 (t, *J* = 7.6 Hz, 2H, ArH and ThH), 7.23 (t, *J* = 8.5 Hz, 3H, ArH and ThH), 7.16 (t, *J* = 4.1 Hz, 1H, ArH and ThH), 6.75 (s, 1H, CH), 6.09–6.11 (m, 1H, CH), 4.62 (dd, *J* = 17.0, 9.0 Hz, 1H, CH), 3.75 (dd, *J* = 17.0, 4.9 Hz, 1H, CH), 1.80 (s, 3H, CH_3). ^{13}C NMR (150 MHz): δ 188.8, 146.2, 143.5, 136.3, 134.5, 134.4, 133.1, 132.7, 129.5, 128.9, 128.3, 128.2, 127.4, 127.2, 124.1, 119.9, 110.1, 62.3, 41.4, 14.0. Anal. Calcd for $C_{22}H_{19}N_3OS$: C, 70.75; H, 5.13; N, 11.25. Found: C, 70.61; H, 5.15; N, 11.29.

Online supplementary data

^1H and ^{13}C NMR spectra of the products.

Acknowledgment: The authors thank the National Natural Science Foundation of China (21462038, 21362034) and Key Laboratory of Eco-Environment-Related Polymer Materials for Ministry of Education for the financial support of this work.

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Supplemental Material: The online version of this article (DOI: 10.1515/hc-2016-0182) offers supplementary material.