DABCO-Catalyzed Reaction of Phenols or 1,2-Diphenols with Activated Alkynes Leading to the Formation of Alkenoic Acid Esters or 1,3-Dioxole Derivatives

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Received 20 January 2006; revised 27 February 2006

Abstract: The reaction of phenols or 1,2-diphenols with activated alkynes took place smoothly and rapidly in the presence of a catalytic amount of 1,4-diazabicyclo[2.2.2]octane (DABCO) at room temperature and resulted in the formation of various alkenoic acid esters or 1,3-dioxole derivatives in excellent yields. The scope and limitations, together with a plausible mechanism of the reaction are disclosed in this paper.

Key words: phenoles, 1,2-diphenoles, activated alkynes, alkenoic acid esters, 1,3-dioxoles

The facile reaction of nucleophiles with activated alkynes has received considerable interest in the past decades. In most cases, the reaction was viewed as starting from the initial formation of a zwitterionic intermediate derived from the addition of nucleophilic trigger to activated alkyne.[1] The vast majority of the previous investigations demonstrate that triphenyl phosphine,[2] pyridine,[3] isocyanides[4] and a wide range of tertiary amines[5] are excellent nucleophilic triggers for the above-mentioned reaction. On the basis of these observations and our interest in DABCO-catalyzed reaction,[6] we speculated that DABCO, a tertiary amine base with weak basicity and moderate hindrance, could lead to zwitterion formation and undergo further reaction with a number of nucleophiles. Herein, we wish to report our successful investigation on DABCO-catalyzed reaction of phenols or 1,2-diphenols with activated alkynes leading to the formation of alkenoic acid esters or 1,3-dioxole derivatives.

Although numerous reactions of phenols and 1,2-diphenols with activated alkynes have been reported, many of them suffer problems including low product yield,[7] long reaction time,[8] harsh reaction conditions[9] or lack of selectivity.[7b,8a] The present procedure has circumvented most of these problems to make it a useful reaction for the synthesis of a wide variety of molecules. With DABCO as a catalyst, the additions of phenols or 1,2-diphenols to activated alkynes proceed quickly (completed within a few minutes) under very mild conditions (at room temperature) for a wide range of functional groups on the phenols. Moreover, the yields are improved significantly (up to 99%).

In our initial experiment, the reaction of various phenols with dimethyl acetylenedicarboxylate (DMAD) in the presence of a catalytic amount of DABCO (10 mol%) was examined. In a typical procedure, DMAD (0.5 mmol), DABCO (0.05 mmol) and phenols (0.5 mmol) were stirred in dichloromethane for ten minutes at room temperature to give final products facilely by flash chromatography on silica column. The reaction appears to be general, with a number of phenols affording conjugate addition products in excellent yields (Table 1, entries 1–10). The structures of the products were characterized by spectroscopic analysis and further confirmed by X-ray diffraction of **3** as a representative example (Figure 1).[10] In some cases, the reaction gave alkenoic acid esters as a pair of inseparable *E*- and *Z*-isomers (Table 1, entries 1, 2, 6, 9, 10). The selectivity of this reaction increases moderately when the steric bulkiness of the aryl (Ar) substituents increases (Table 1, entry 7). The phenols with acetyl, nitro or formyl groups at 2-position generally led to almost quantitative *E*-isomers of the corresponding alkenoic acid esters (Table 1, entries 3–5). This selectivity may be attributed more to electronic factors than to steric factors as deduced with the reaction in entry 7. The same effect was also observed in entry 8.

We further investigated the reaction of other activated alkynes, such as benzyl propiolate and methyl propiolate

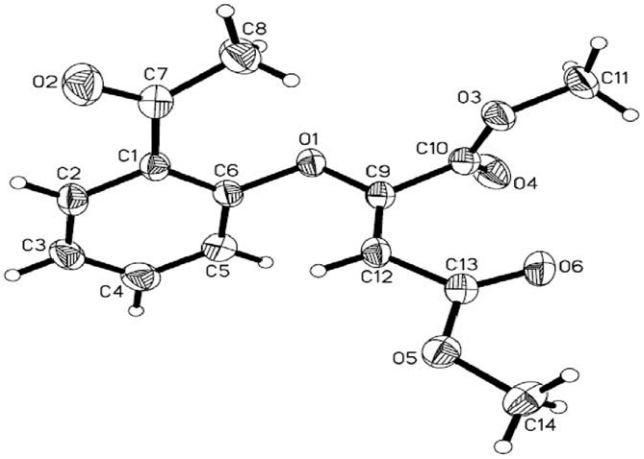
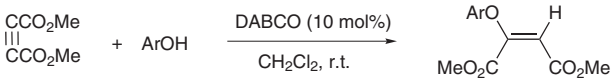
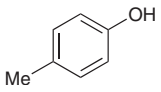
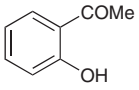
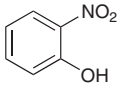
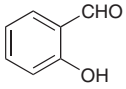
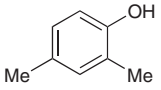
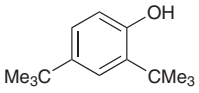
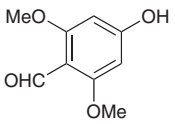
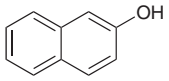
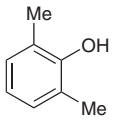


Figure 1 X-ray crystal structure of **3**.

SYNTHESIS 2006, No. 14, pp 2286–2292
Advanced online publication: 26.06.2006
DOI: 10.1055/s-2006-942437; Art ID: F01306SS

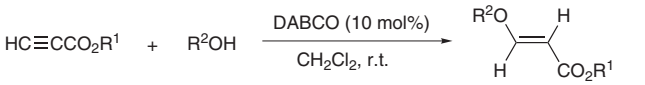
Table 1 Reaction of Phenols with DMAD[a]

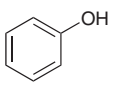
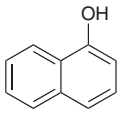
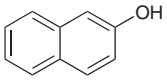
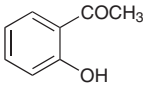


Entry	ArOH	Product	Yield (%)[b]	*E*/*Z*[c]
1		**1**	99	50:50
2		**2**	99	55:45
3		**3**	98	> 95:5
4		**4**	92	> 99:1
5		**5**	92	> 99:1
6		**6**	99	40:60
7		**7**	92	10:90
8		**8**	99	*E*
9		**9**	95	50:50
10		**10**	70	45:55

[a] All the reactions were performed at r.t. and went to completion within 10 min.
[b] Isolated yields.
[c] The *E*- and *Z*-isomers were determined by ^{1}H NMR (300 MHz) spectra.

Table 2 Reaction of Various Phenols with Activated Alkynes[a]



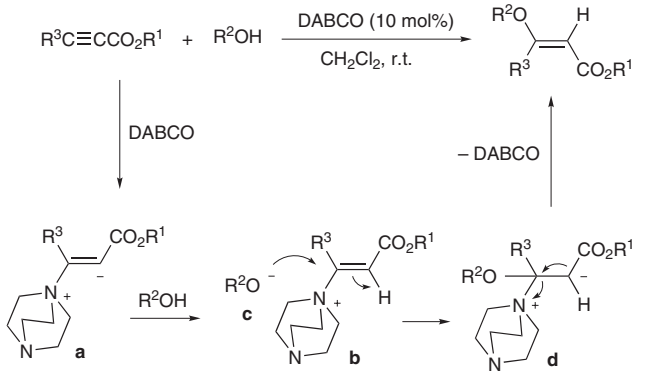
Entry	R^1	Nucleophile (R^2OH)	Product	Yield (%)[b]	*E*/*Z*[c]
1	Me		**11**	95	85:15
2	Me		**12**	97	> 95:5
3	Me		**13**	90	*E*
4	Bn		**14**	97	*E*

[a] All the reactions were performed at r.t. and went to completion within 10 min.
[b] Isolated yields.
[c] Determined by ^{1}H NMR (300 MHz) spectra.

with phenols. We were pleased to find that the results obtained were much better than expected under the same conditions (0.5 mmol of benzyl or methyl propiolate, 0.5 mmol of phenols, and 0.05 mmol of DABCO, CH_2Cl_2, at room temperature). The reaction proceeded smoothly and rapidly (within 10 min) to give the corresponding conjugate addition products in excellent yields with increased stereoselectivities (Table 2, entries 1–4).

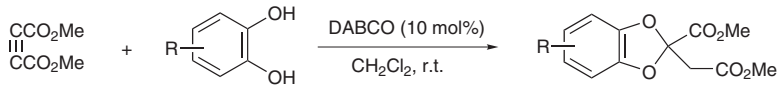
A proposed mechanism for this reaction is outlined in Scheme 1 based on the previous investigations of Nozaki et al.[11] Initially, DABCO reacts with the activated alkyne to generate the zwitterionic intermediate **a**, which deprotonates the nucleophile to give the corresponding intermediates **b** and **c**. Subsequent Michael addition of **b** to **c** forms intermediate **d**, which then eliminates DABCO to afford the final product.

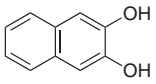
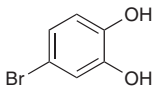
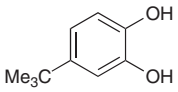
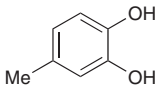
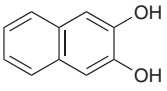
Further scope exploration of this process revealed that 1,2-diphenol was another class of suitable nucleophiles for this reaction. Interestingly, diphenols on treatment with DMAD in the presence of a catalytic amount of DABCO (10 mol%) in dichloromethane at room temperature afforded 1,3-dioxole derivatives in good to excellent yields (Table 3, entries 1–5). The structure of the product was revealed by ^{1}H and ^{13}C NMR analysis. In addition, the NMR-based structure was confirmed by X-ray crystallographic analysis of **15** (Figure 2).[12] Mechanistically, the reaction may also involve the initial generation of a zwitterionic intermediate **a** by reaction between DABCO and DMAD (Scheme 2), which is readily protonated by one of the two protons of 1,2-diphenol to yield intermediates **b** and **c**. Subsequent Michael addition of **b** to **c** forms **e**.



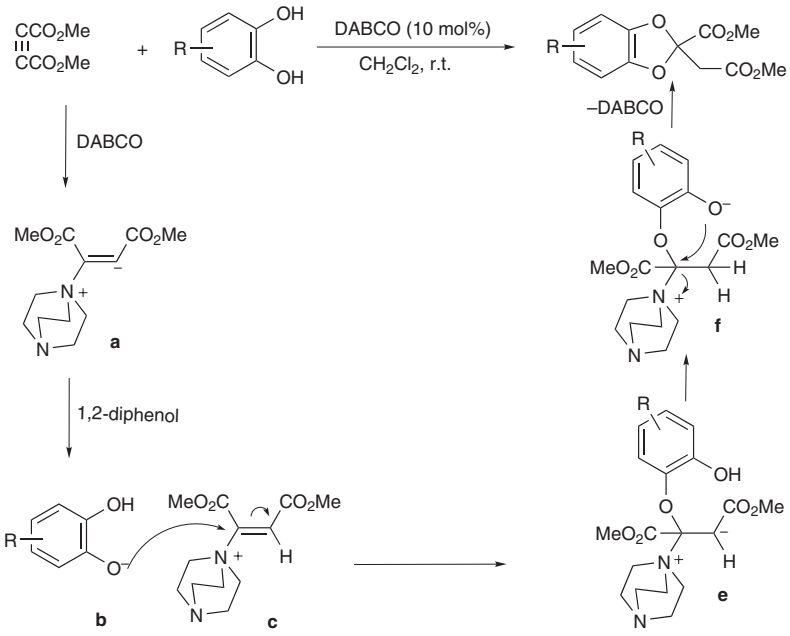
Scheme 1 Plausible mechanism for the reaction of various phenols with activated alkynes.

Table 3 Reaction of 1,2-Diols with DMAD[a]



Entry	Nucleophile	Product	Yield (%)[b]
1		**15**	95
2		**16**	71
3		**17**	91
4		**18**	80
5		**19**	97

[a] All the reactions were performed at r.t. and went to completion within 10 min.
[b] Isolated yields.



Scheme 2 Plausible mechanism for the reaction of 1,2-diphenols with DMAD.

It deprotonates the second phenolic group immediately to form intermediate **f**, which then undergoes cyclization to deliver 1,3-dioxole derivative and DABCO to be recycled.

It should be noted that when ethane-1,2-diol, ethane-1,2-diamine or 2-aminoethanol was used in this reaction, different results were obtained under the same conditions as those described above. The new synthetic procedure was found to be an effective method for the synthesis of other classes of heterocycles, such as 1,4-dioxane, piperazinone and morpholine derivatives (Scheme 3).

Further comparative studies demonstrated that DABCO was the optimal catalyst for the addition of phenols and cyclization of 1,2-diols. Triphenylphosphine, which is commonly employed in the traditional conjugate addition reaction, was ineffective in promoting reactions of phenols and 1,2-diols (Table 4, entries 3 and 5). Although other amine catalysts such as triethylamine, 1,8-diazabi-

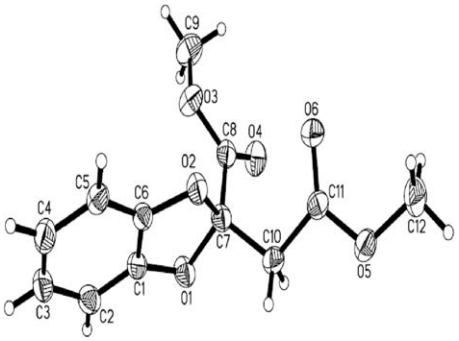
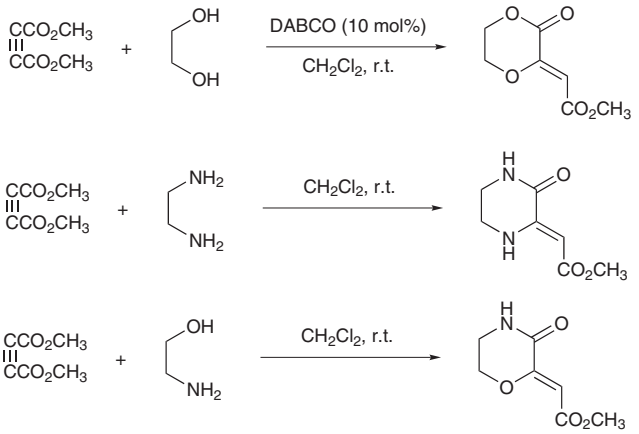


Figure 2 X-ray crystal structure of **15**.

cyclo[5.4.0]undec-7-ene (DBU) and 4-methylmorpholine provided the same catalytic abilities, the yields were reduced owing to the formation of many by-products (Table 4, entries 1, 2, 4, 6–9).

In conclusion, we have developed an efficient, DABCO-catalyzed reaction of diphenols or 1,2-diphenols with activated alkynes, which provides an easy access to the corresponding alkenoic acid esters or 1,3-dioxole derivatives in good to excellent yields under very mild conditions. Additional work aimed at obtaining further extension of this reaction is in progress.

All reagents were used directly as obtained commercially unless otherwise noted. Melting points were determined on a microscopic apparatus and are uncorrected. Column chromatography was carried out on silica gel (200–300 mesh, Qingdao Haiyang Chemical Co., Ltd.). ^{1}H NMR spectra were recorded at 300 MHz in $CDCl_3$ and ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$ using TMS as internal standard on a Varian Mercury Plus 300BB MHz NMR spectrometer. Mass spectra were recorded by the EI method on a HP5998 MS spectrometer. IR spectra were obtained on a Nicolet AVATAR 360 FT-IR spectrometer. Microanalyses were performed on a VarioEL instrument.

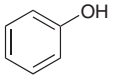
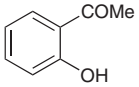
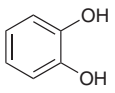
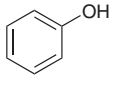


Scheme 3 Reaction of ethane-1,2-diol, ethane-1,2-diamine or 2-aminoethanol with DMAD.

Reaction of Various Phenols with Activated Alkynes; General Procedure

DMAD (0.5 mmol), DABCO (0.05 mmol) and phenols (0.5 mmol) were stirred in CH_2Cl_2 (4 mL) at r.t. for 10 min. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica column to give the final products.

Table 4 Reaction of Nucleophiles with Activated Alkynes Catalyzed by Various Catalysts[a]

Entry	Nucleophile	Activated alkynes	Catalyst	Time (h)	Product	Yield (%)[b]	*E*/*Z*[c]
1		DMAD	DBU	1	**1**	80	30:70
2		DMAD	Et_3N	21	**1**	78	35:65
3		DMAD	Ph_3P	24	**3**	No reaction	–
4		DMAD	Et_3N	24	**3**	60	40:60
5		DMAD	Ph_3P	24	**15**	0	–
6		DMAD	DBU	4	**15**	74	–
7		DMAD	Et_3N	4	**15**	81	–
8		DMAD	4-Methylmorpholine	4	**15**	81	–
9		Methyl propiolate	Et_3N	17	**11**	73	99:1

[a] All the reactions were performed at r.t. in the presence of 10 mol% base.
[b] Isolated yields.
[c] Determined by ^{1}H NMR (300 MHz) spectra.

Reactions of Ethane-1,2-diol, Ethane-1,2-diamine or 2-Aminoethanol with DMAD; Ethane-1,2-diol as an Example; Typical Procedure

DMAD (0.5 mmol), DABCO (0.05 mmol) and ethane-1,2-diol (3 mmol for 1,2-diol, 0.5 mmol for other nucleophiles) were stirred in CH_2Cl_2 (4 mL) at r.t. for 10 min. For the reaction of 2-aminoethanol, the reaction time needed to be extended to 10 h. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica column to give the final products.

1

Mixture of *Z*- and *E*-isomers; known compounds.[13]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.94–7.43 (m, 10 H), 6.54 (s, 1 H), 5.12 (s, 1 H), 3.90 (s, 3 H), 3.72 (s, 3 H), 3.69 (s, 3 H), 3.66 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.7, 163.7, 163.2, 162.5, 160.8, 156.4, 152.8, 149.7, 130.1, 129.5, 126.2, 123.2, 120.6, 115.9, 114.8, 98.7, 98.6, 52.9, 51.7, 51.5.

MS (EI, 70 eV): *m*/*z* (%) = 236 (5.67) [M$^+$], 205 (9.69), 177 (100), 77 (32.72).

2

Mixture of *Z*- and *E*-isomers.

IR (KBr): 2956, 2852, 1743, 1717, 1663, 1260, 1133, 767 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.83–7.20 (m, 8 H), 6.54 (s, 1 H), 5.12 (s, 1 H), 3.90 (s, 3 H), 3.71 (s, 3 H), 3.68 (s, 3 H), 3.65 (s, 3 H), 2.33 (s, 3 H), 2.28 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.8, 163.8, 163.2, 162.5, 161.2, 154.3, 150.5, 149.9, 136.0, 132.7, 130.5, 129.9, 120.3, 115.8, 114.9, 114.3, 98.1, 98.0, 52.8, 51.6, 51.4, 20.6, 20.4.

MS (EI, 70 eV): *m*/*z* (%) = 250 (12.42) [M$^+$], 219 (11.23), 191 (100), 107 (25.73), 91 (33.62).

Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.46; H, 5.52.

3

IR (KBr): 2961, 2852, 1749, 1722, 1683, 1637, 1281, 1210, 1133, 787 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.15–7.88 (m, 4 H), 5.18 (s, 1 H), 3.94 (s, 3 H), 3.69 (s, 3 H), 2.63 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.2, 165.3, 162.8, 159.6, 151.5, 133.9, 131.2, 130.9, 126.6, 121.8, 100.4, 53.2, 51.8, 30.8.

MS (EI, 70 eV): *m*/*z* (%) = 278 (0.71) [M$^+$], 247 (1.96), 219 (94.31), 177 (100).

Anal. Calcd for $C_{14}H_{14}O_6$: C, 60.43; H, 5.07. Found: C, 60.38; H, 5.17.

4

IR (KBr): 2958, 2853, 1745, 1717, 1643, 1531, 1368, 1223, 1134, 789 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32–8.09 (m, 4 H), 5.27 (s, 1 H), 3.92 (s, 3 H), 3.71 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.2, 162.4, 158.4, 146.1, 141.8, 135.3, 127.3, 126.5, 123.9, 102.2, 53.4, 52.2.

MS (EI, 70 eV): *m*/*z* (%) = 281 (0.81) [M$^+$], 250 (2.64), 222 (48.25), 122 (100).

Anal. Calcd for $C_{12}H_{11}NO_7$: C, 51.25; H, 3.94; N, 4.98. Found: C, 51.19; H, 3.52; N, 4.83.

5

IR (KBr): 2956, 2853, 1750, 1719, 1693, 1639, 1214, 1132, 788 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.29 (s, 1 H), 7.21–8.00 (m, 4 H), 5.25 (s, 1 H), 3.94 (s, 3 H), 3.71 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.6, 165.1, 162.5, 159.8, 155.0, 136.0, 129.1, 127.6, 126.8, 121.5, 101.5, 53.2, 51.9.

MS (EI, 70 eV): *m*/*z* (%) = 264 (0.19) [M$^+$], 233 (1.94), 205 (86.57), 173 (100).

Anal. Calcd for $C_{13}H_{12}O_6$: C, 59.09; H, 4.58. Found: C, 59.32; H, 4.34.

6

Mixture of *Z*- and *E*-isomers.

IR (KBr): 2954, 2844, 1726, 1637, 1269, 1132, 817 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.60–7.09 (m, 5 H), 6.53 (s, 1 H), 4.99 (s, 1 H), 3.96 (s, 3 H), 3.74 (s, 3 H), 3.71 (s, 3 H), 3.68 (s, 3 H), 2.36 (s, 3 H), 2.34 (s, 3 H), 2.28 (s, 3 H), 2.22 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.8, 163.8, 163.3, 162.5, 161.1, 152.7, 150.6, 148.6, 136.1, 132.7, 132.3, 131.8, 129.5, 127.9, 127.3, 126.8, 120.6, 114.1, 113.3, 96.7, 96.6, 52.7, 52.6, 51.5, 51.3, 20.5, 20.4, 15.8, 15.2.

MS (EI, 70 eV): *m*/*z* (%) = 264 (21.14) [M$^+$], 233 (15.90), 205 (100).

Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.31; H, 5.76.

7

Z-Isomer.

IR (KBr): 2958, 2871, 1731, 1650, 1263, 1200, 818 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.04–7.37 (m, 3 H), 6.49 (s, 1 H), 3.71 (s, 3 H), 3.69 (s, 3 H), 1.46 (s, 9 H), 1.29 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.3, 162.9, 152.8, 149.8, 145.4, 137.0, 124.5, 123.4, 113.6, 52.9, 51.8, 34.9, 34.4, 31.6, 31.5, 29.8, 29.6.

MS (EI, 70 eV): *m*/*z* (%) = 348 (40.11) [M$^+$], 333 (100), 115 (85.37), 91 (99.42).

Anal. Calcd for $C_{20}H_{28}O_5$: C, 68.94; H, 8.10. Found: C, 68.90; H, 7.98.

E-Isomer.

IR (KBr): 2957, 2871, 1756, 1724, 1635, 1211, 1132, 826 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.92–7.41 (m, 3 H), 5.16 (s, 1 H), 3.96 (s, 3 H), 3.67 (s, 3 H), 1.35 (s, 9 H), 1.32 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.2, 163.7, 161.6, 149.2, 148.8, 140.8, 124.7, 124.3, 121.5, 97.9, 53.1, 51.6, 34.8, 34.7, 31.4, 30.3, 29.7.

MS (EI, 70 eV): *m*/*z* (%) = 348 (16.59) [M$^+$], 333 (94.79), 115 (26.15), 91 (27.85), 57 (100).

Anal. Calcd for $C_{20}H_{28}O_5$: C, 68.94; H, 8.10. Found: C, 68.98; H, 8.01.

8

IR (KBr): 2952, 2886, 2851, 2790, 1751, 1722, 1689, 1647, 1590, 1226, 1137, 826 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.40 (s, 1 H), 6.33 (s, 2 H), 5.52 (s, 1 H), 3.92 (s, 3 H), 3.91 (s, 3 H), 3.89 (s, 3 H), 3.74 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.7, 165.1, 163.6, 162.4, 159.3, 157.2, 111.9, 103.4, 95.9, 56.2, 53.5, 51.9.

MS (EI, 70 eV): *m*/*z* (%) = 324 (20.5) [M$^+$], 293 (9.4), 265 (99.3), 233 (90.3), 69 (100).

Anal. Calcd for $C_{15}H_{16}O_8$: C, 55.56; H, 4.97. Found: C, 55.76; H, 5.26.

9
Solid; mp 52–54 °C. Mixture of *Z*- and *E*-isomers.

IR (KBr): 2953, 2849, 1751, 1726, 1640, 1210, 1132 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.19–7.92 (m, 14 H), 6.70 (s, 1 H), 5.19 (s, 1 H), 3.96 (s, 3 H), 3.73 (s, 3 H), 3.72 (s, 3 H), 3.68 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.9, 163.9, 162.7, 160.9, 154.4, 150.4, 149.8, 133.9, 133.8, 131.5, 130.5, 130.2, 130.0, 127.8, 127.7, 127.6, 127.1, 127.0, 126.6, 126.3, 126.2, 124.7, 119.9, 117.9, 115.5, 115.4, 110.7, 99.1, 53.2, 53.1, 52.1, 51.8.

MS (EI, 70 eV): *m*/*z* (%) = 286 (23.1) [M^+], 255 (11.0), 227 (91.4), 115 (100).

Anal. Calcd for $C_{16}H_{14}O_5$: C, 67.13; H, 4.93. Found: C, 67.31; H, 4.59.

10
Mixture of *Z*- and *E*-isomers.

IR (KBr): 2954, 2851, 1749, 1726, 1637, 1267, 1173, 1133, 780 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.94–7.06 (m, 6 H), 6.09 (s, 1 H), 4.81 (s, 1 H), 3.95 (s, 3 H), 3.71 (s, 3 H), 3.63 (s, 3 H), 3.51 (s, 3 H), 2.24 (s, 6 H), 2.20 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.0, 164.3, 163.4, 162.4, 160.1, 152.0, 150.7, 148.9, 130.1, 129.7, 129.2, 128.7, 126.4, 125.0, 105.1, 95.3, 53.0, 52.8, 51.5, 16.4, 15.5.

MS (EI, 70 eV): *m*/*z* (%) = 264 (11.4) [M^+], 232 (54.4), 205 (100).

Anal. Calcd for $C_{14}H_{16}O_5$: C, 79.37; H, 8.88. Found: C, 79.56; H, 8.68.

11
IR (KBr): 2951, 2844, 1716, 1650, 1592, 1226, 1123, 760, 692 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.79–7.84 (d, *J* = 12.3 Hz, 1 H), 7.05–7.40 (m, 5 H), 5.55–5.59 (d, *J* = 12.3 Hz, 1 H), 3.72 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.6, 159.1, 155.7, 129.9, 124.9, 117.9, 101.7, 51.3.

MS (EI, 70 eV): *m*/*z* (%) = 178 (62.5) [M^+], 147 (100), 77 (56.3).

Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.56; H, 5.59.

12
Solid; mp 34–36 °C.

IR (KBr): 2955, 1705, 1651, 1234, 1129, 795, 772 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.10–8.10 (m, 8 H), 5.62–5.66 (d, *J* = 12.3 Hz, 1 H), 3.73 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.6, 159.7, 151.7, 134.6, 127.8, 126.9, 126.4, 125.6, 125.5, 125.0, 121.3, 112.8, 102.0, 51.3.

MS (EI, 70 eV): *m*/*z* (%) = 228 (62.5) [M^+], 197 (19.3), 115 (100).

Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.43; H, 5.13.

13
Solid; mp 62–64 °C.

IR (KBr): 2950, 1724, 1653, 1254, 1168, 1128, 846, 755 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.92–7.96 (d, *J* = 12.3 Hz, 1 H), 7.22–7.85 (m, 7 H), 5.63–5.67 (d, *J* = 12.3 Hz, 1 H), 3.75 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.6, 158.9, 153.5, 133.8, 130.8, 130.2, 127.7, 127.3, 126.9, 125.4, 118.5, 113.4, 102.1, 51.4.

MS (EI, 70 eV): *m*/*z* (%) = 228 (72.8) [M^+], 197 (25.4), 115 (100).

Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.51; H, 5.24.

14
IR (KBr): 1714, 1684, 1648, 1222, 1128, 950, 763, 699 cm^{-1}.

^1H NMR (300M Hz, $CDCl_3$): δ = 7.05–7.82 (m, 10 H), 5.63–5.67 (d, *J* = 12.3 Hz, 1 H), 5.17 (s, 2 H), 2.56 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.2, 166.1, 158.4, 154.2, 135.7, 133.7, 130.4, 129.7, 128.3, 128.0, 125.1, 118.7, 102.9, 65.8, 31.1.

MS (EI, 70 eV): *m*/*z* (%) = 296 (0.05) [M^+], 190 (2.81), 161 (29.88), 145 (36.07), 91 (100).

Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.92; H, 5.46.

15
Solid; mp 58–60 °C.

IR (KBr): 2959, 2854, 1751, 1483, 1224, 1154, 1069, 755 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.87 (s, 4 H), 3.85 (s, 3 H), 3.72 (s, 3 H), 3.35 (s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.0, 166.0, 146.3, 122.2, 109.6, 109.0, 53.3, 52.2, 40.7.

MS (EI, 70 eV): *m*/*z* (%) = 252 (9.20) [M^+], 193 (76.05), 151 (100).

Anal. Calcd for $C_{12}H_{12}O_6$: C, 57.14; H, 4.80. Found: C, 57.19; H, 4.85.

16
IR (KBr): 2956, 2851, 1746, 1482, 1223, 1156, 1076 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.72–7.11 (m, 3 H), 3.85 (s, 3 H), 3.72 (s, 3 H), 3.35 (s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.6, 165.4, 147.3, 146.2, 145.9, 124.9, 122.2, 113.6, 108.9, 53.4, 52.2, 40.3.

MS (EI, 70 eV): *m*/*z* (%) = 330 (4.59) [M^+], 332 (4.14), 229 (51.13), 193 (100).

Anal. Calcd for $C_{12}H_{11}BrO_6$: C, 43.53; H, 3.35. Found: C, 43.47; H, 3.28.

17
IR (KBr): 2959, 2870, 1749, 1222, 1158, 1078 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.73& ndash;6.92 (m, 3 H), 3.82 (s, 3 H), 3.70 (s, 3 H), 3.31 (s, 2 H), 1.26 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.2, 166.4, 146.5, 146.2, 144.2, 118.8, 110.0, 108.2, 106.9, 106.8, 53.5, 52.3, 41.0, 34.9, 31.7.

MS (EI, 70 eV): *m*/*z* (%) = 308 (10.41) [M^+], 249 (85.94), 207 (49.38), 59 (100).

Anal. Calcd for $C_{16}H_{20}O_6$: C, 62.33; H, 6.54. Found: C, 62.22; H, 6.33.

18
Solid; mp 52–53 °C.

IR (KBr): 2923, 2854, 1746, 1221, 1162, 1075 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.64–6.75 (m, 3 H), 3.84 (s, 3 H), 3.72 (s, 3 H), 3.33 (s, 2 H), 2.27 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.0, 166.1, 146.3, 144.2, 132.1, 122.1, 109.7, 109.6, 108.3, 53.3, 52.2, 40.6, 21.1.

MS (EI, 70 eV): *m*/*z* (%) = 266 (10.25) [M^+], 207 (55.87), 165 (100), 59 (65.10).

Anal. Calcd for $C_{13}H_{14}O_6$: C, 58.64; H, 5.30. Found: C, 58.60; H, 5.53.

19
Solid; mp 55–57 °C.

IR (KBr): 2955, 1741, 1234, 1166, 1074 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.66–7.69 (m, 2 H), 7.33–7.36 (m, 2 H), 7.17 (s, 2 H), 3.85 (s, 3 H), 3.74 (s, 3 H), 3.42 (s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.9, 165.9, 146.5, 130.4, 127.2, 124.7, 109.8, 104.4, 53.5, 52.3, 40.5.

MS (EI, 70 eV): *m/z* (%) = 302 (7.0) [M^+], 243 (56.6), 201 (100), 114 (59.1).

Anal. Calcd for $C_{16}H_{14}O_6$: C, 63.57; H, 4.67. Found: C, 63.56; H, 4.48.

Acknowledgment

We thank the NSF-20021001, NSF-20572038 and the 'Hundred Scientist Program' from the Chinese Academy of Sciences for financial support of this work.

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(10) Crystal data of **3** have been deposited in CCDC as deposition number 295601: $C_{14}H_{14}O_6$, MW = 278.25, *T* = 296 (2) K, λ = 0.71073 Å, Monoclinic space group *P*2(1)/*c*, *a* = 10.046 (2) Å, *b* = 18.482 (4) Å, *c* = 7.566 (1) Å, α = 90.00°, β = 95.32 (2)°, γ = 90.00°, *V* = 1398.7 (5) $Å^3$, *Z* = 4, D_c = 1.321 mg/m^3, μ = 0.104 mm^{-1}, *F*(000) = 584, Crystal size 0.58 × 0.52 × 0.50 mm, Independent reflections 2600 [*R*(int) = 0.0103], Reflections collected 3009, Refinement method, full-matrix least-squares on F^2, Goodness-of-fit on F^2 1.083, Final *R* indices [I > 2σ(I)] *R*1 = 0.0387, *wR*2 = 0.1116, R indices (all data) *R*1 = 0.0627, *wR*2 = 0.1197, Extinction coefficient 0.119 (6), Largest diff. peak and hole 0.233 and –0.166 $eÅ^{-3}$.
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(12) Crystal data of **15** have been deposited in CCDC as deposition number 295602: $C_{12}H_{12}O_6$, MW = 252.22, *T* = 296 (2) K, λ = 0.71073 Å, Orthorhombic space group *Pbca*, *a* = 7.314 (1) Å, *b* = 17.931 (4) Å, *c* = 18.351 (5) Å, α = 90.00°, β = 90.00°, γ = 90.00°, *V* = 2406.52 (67) $Å^3$, *Z* = 8, D_c = 1.392 mg/m^3, μ = 0.113 mm^{-1}, F(000) = 1056, Crystal size 0.60 × 0.34 × 0.34 mm, Independent reflections 2769 [*R*(int) = 0.0385], Reflections collected 3481, Refinement method, full-matrix least-squares on F^2, Goodness-of-fit on F^2 0.902, Final *R* indices [I > 2σ(I)] *R*1 = 0.0827, *wR*2 = 0.0975, *R* indices (all data) *R*1 = 0.0393, *wR*2 = 0.0879, Extinction coefficient 0.0098 (7), Largest diff. peak and hole 0.169 and –0.161 $eÅ^{-3}$.
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