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Trimethylamine catalyzed stereoselective reaction between dimethyl acetylenedicarboxylate and phenols

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Abstract Stereoselective reaction of various substituted phenols with dimethyl acetylenedicarboxylate in the presence of a catalytic amount of aqueous trimethylamine solution in dichloromethane leads to dimethyl 2-phenoxymaleates in good to excellent yields under mild condition.

Keywords Dimethyl phenoxymaleates; Acetylenic esters; Trialkylamines.

Introduction

Vinyl ethers of alcohols and phenols are well established monomers, building blocks, and auxiliaries in organic synthesis, steadily expanding their scope of application [1]. There are many studies on the reaction between acetylenic esters and phenols to produce these compounds [2–5]. In general, phenols react with acetylenic esters to give a mixture of phenoxymaleates and phenoxyfumarates, arising through a *cis* or *trans* – mode of addition [6–10]. Recently, silica-gel powder has been found [8] to catalyze the stereoselective conversion of phosphoranes obtained from the reaction of 2-nitrophenol and dialkyl acetylenedicarboxylates in the presence of triphenylphosphine to dialkyl 2-(2-nitro-phenoxy)-2-butenedioates under solvent-free conditions and under microwave and thermal conditions. In the above studies, usually the fumarate isomer is the major product. On the other hand, the addition of phenols to dimethyl acetylenedicarboxylate adsorbed onto alumina has been reported to be stereoselective, producing only maleate adducts, although only simple cresol and 4-bromophenol have been examined in that study [9]. *Stoermer* and *Fairlie* have described [10] the addition reaction of various phenols to dimethyl acetylenedicarboxylate in the presence of an excess amount of triethylamine in dry diethyl ether to produce a mixture of fumarate and maleate adducts. The time of the reactions was long and in some cases the yields of the products were poor. Also no considerable stereoselectivity was encountered in that study. In the current work we wish to report a facile synthesis of dimethyl 2-phenoxymaleates from the reaction of a wide range of functionalized phenols and dimethyl acetylenedicarboxylate in the presence of a catalytic amount of aqueous trimethylamine solution in dichloromethane.

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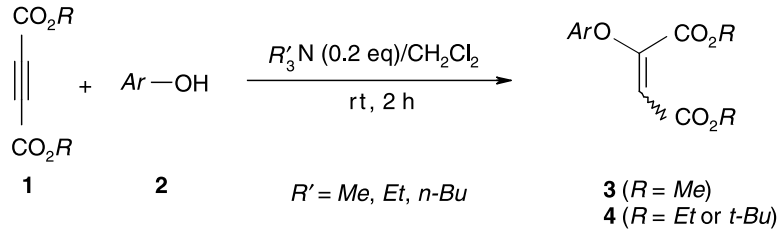
Results and discussion

Reaction of substituted phenols with dimethyl acetylenedicarboxylate (**1**, $R = Me$) in the presence of a catalytic amount of aqueous trimethylamine in dichloromethane at room temperature for 2 h, gives the maleate isomer of **3** in good to excellent yields (see Scheme 1 and Table 1). The ^{1}H and ^{13}C NMR spectra of the crude products clearly indicated the formation of compounds **3**. The ratio of fumarate:



Scheme 1

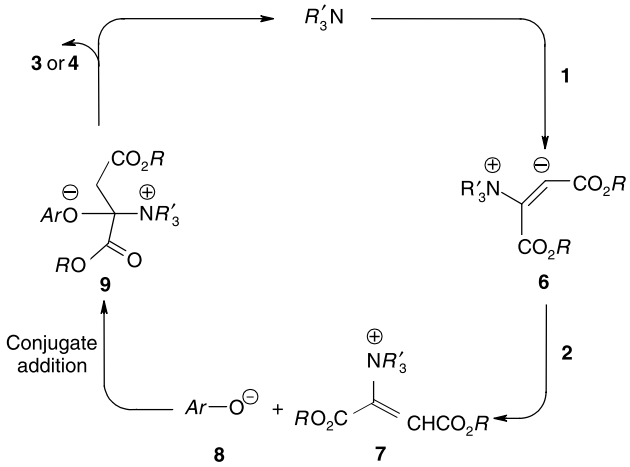
Table 1 Stereoselectivity in addition of phenols to dimethyl acetylenedicarboxylate in the presence of trimethylamine in CH_2Cl_2 at room temperature[a]

	Ar	Isomer/%	
		Fumarate	Maleate
3a	Phenyl	16	84
3b	4-Chlorophenyl	6	94
3c	2,4-Dichlorophenyl	3	97
3d	2-Acetylphenyl	6	94
3e	2-Formylphenyl	4	96
3f	2-Methoxyphenyl	3	97
3g	2-Methoxy-4-formylphenyl	3	97
3h	1-Naphthyl	8	92
3i	2-Naphthyl	7	93
3j	2-Nitrophenyl	4	96
3k	3-Nitrophenyl	13	87
3l	4-Nitrophenyl	9	91

[a] All of the reactions have quantitative yields except for **3i** which is about 85%

maleate isomers were detected by ^{1}H NMR spectroscopy. The vinylic proton positions for maleate isomers of **3** at $\delta = 5.00$–5.78 ppm compare favorably with the reported values for the proton positions in dimethyl 2-phenoxymaleates [6, 10]. Table 1 shows that this addition reaction tolerates a wide range of functional groups on the phenol including alkoxyls, ketones, aldehydes, halides, and nitro groups.

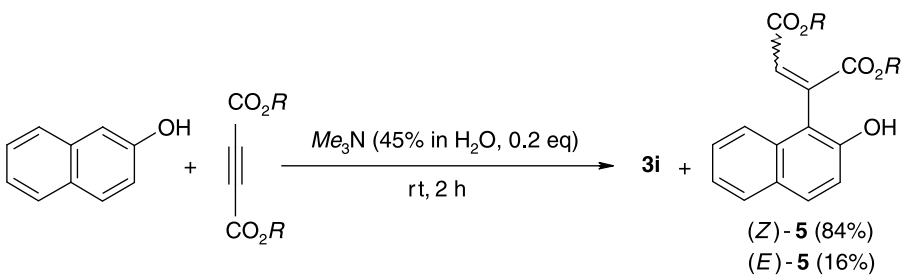
Although the mechanistic details of the above reaction are unknown, a proposed mechanism for this



Scheme 2

reaction is outlined in Scheme 2 based on the previous reports [11–16]. Initially, trialkylamine reacts with the electron-deficient acetylenic esters to generate the zwitterionic intermediate **6**, which deprotonates the nucleophile to give the corresponding intermediates **7** and **8**. Subsequent *Michael* addition of **8** to **7** forms the 1,3-dipolar ion **9**, which then eliminates trialkylamine to afford the final product [13, 17].

From the reaction of 2-naphthol with dimethyl acetylenedicarboxylate in the presence of trimethylamine, in addition to the derivative **3i**, addition products **5** (15%) were isolated (Scheme 3).



Scheme 3

Table 2 Stereoselectivity in addition of phenols to dialkyl acetylenedicarboxylates in the presence of trialkylamines in CH_2Cl_2 at room temperature

Ar	*R*	*R′*	Yield/%[a] of **3** or **4**	Isomer/%	
				Fumarate	Maleate
2-Acetylphenyl	*Me*	*Et*	**3d** (>98)	64	36
4-Chlorophenyl	*Me*	*Et*	**3b** (>98)	57	43
4-Chlorophenyl	*Me*	*n-Bu*	**3b** (>98)	52	48
4-Chlorophenyl	*Et*	*Me*	**4a** (>98)	13	87
4-Chlorophenyl	*t-Bu*	*Me*	**4b** (>98)	42	58
2-*t*-Butylphenyl	*Me*	*Me*	**3m** (47)	82	18
2,6-Dimethylphenyl	*Me*	*Me*	**3n** (87)	59	41
2,6-Dimethylphenyl	*t-Bu*	*n-Bu*	**4c** (>98)	71	29

[a] Isolated yields

The maleate:fumarate isomer ratio (84:16) obtained from the reaction of 4-chlorophenol with dimethyl acetylenedicarboxylate in chloroform at room temperature was approximately similar to the ratio obtained from its reaction in dichloromethane. When this reaction was carried out in refluxing chloroform, the isomer ratio of maleate:fumarate is changed to 61:39. This result clearly shows that the reaction is under kinetic control at room temperature. Also, when the reactions were carried out in the presence of bulky trialkylamines, bulky acetylenic esters, or with phenols containing bulky groups on *ortho* position, the stereoselectivity of the reaction was reduced or even inverted (see Table 2). In these cases, the reactions give products as a pair of inseparable (*E*)- and (*Z*)-isomers. It may be assumed that steric effects play a significant role in the stereoselectivity of these reactions. Maleate isomers are the major products when the alkyl groups on the ester moieties, amines, and on the *ortho* position of aryl groups are small.

In conclusion, the stereoselective reaction between dimethyl acetylenedicarboxylate and phenols in the presence of a catalytic amount of trimethylamine provides a simple entry to the synthesis of dimethyl 2-phenoxymaleates in good to excellent yields. This procedure has advantages of high yields, mild reaction conditions, and simple experimental and easy work-up conditions.

Experimental

Acetylenic esters, phenols, and trialkylamines were obtained from Fluka (Buchs, Switzerland) and were used without further purification. Melting points were measured with an Electrothermal 9100 apparatus. Elemental analyses (C, H, and N) were performed using a Heraeus CHN-O-Rapid analyzer. These results agreed favorably with the calculated values. IR spectra were measured with a Shimadzu IR-460 spectrometer. NMR spectra were recorded with a Bruker DRX-250 AVANCE instrument (250.1 MHz for ^{1}H and 62.9 MHz for ^{13}C) with $CDCl_3$ as solvent. Chemical shifts are given in ppm (δ) relative to internal *TMS*, and coupling constant (*J*) are reported in Hertz (Hz).

General procedure for the preparation of ***3***

To a stirred solution of 0.28 g dimethyl acetylenedicarboxylate (2 mmol) and 0.05 g trimethylamine solution (0.05 g, 45% in water, 0.4 mmol) in 8 cm^3 CH_2Cl_2 was added dropwise a mixture of 0.19 g phenol (2 mmol) in 4 cm^3 CH_2Cl_2 at 0°C over 5 min. The reaction mixture was then allowed to warm to room temperature and stirred for 2 h. The mixture was washed with dilute HCl and then cold H_2O. The organic phase was dried (Na_2SO_4) and the solvent was removed under reduced pressure to give **3a** as pale yellow oil. It should be noted that in some cases (**3i**, **3m**, and **3n**), the mixture of (*E*)- and (*Z*)-isomers were separated and purified by flash chromatography on a silica gel (Merck 230–400 mesh) column using *n*-hexane/*Et*OAc mixture as eluent. Compounds **3a** and **3b** [10], **3e** [6], and **3f**, **3g**, and **3l** [10] are known compounds.

Dimethyl 2-(2,4-dichlorophenyl)-2-butenedioate
(**3c**, $C_{12}H_{10}Cl_2O_5$)

Pale yellow oil; IR (KBr): $\bar{\nu} = 1748, 1717, 1637\,cm^{-1}$; Major isomer (*E*)-**3c**: 97%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 3.69$, 3.94 (2s, $2OCH_3$), 5.04 (s, =CH), 7.14 (d, $^3J_{HH} = 8.8$ Hz, H–*Ar*), 7.30 (dd, $^3J_{HH} = 8.8$, $^4J_{HH} = 2.5$ Hz, H–*Ar*), 7.49 (d, $^4J_{HH} = 2.5$ Hz, H–*Ar*) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 51.9$, 53.3 (2O*Me*), 99.6 (C=*C*H), 123.7 (CH), 127.7 (CCl), 128.7, 130.1 (CH), 132.6, (CCl), 147.2, 158.7 (2C), 162.5, 165.3 (2C=O, ester) ppm.

Dimethyl 2-(2-acetylphenoxy)-2-butenedioate
(**3d**, $C_{14}H_{14}O_6$)

Yellow oil; IR (KBr): $\bar{\nu} = 1746, 1715, 1693, 1632\,cm^{-1}$; Major isomer (*E*)-**3d**: 94%; ^{1}H NMR (250.1 MHz, $CDCl_3$):

$\delta = 2.58$ (s, CH_3), 3.65, 3.90 (2s, $2OCH_3$), 5.14 (s, =CH), 7.12 (d, $^3J_{HH} = 8.0$ Hz, H–*Ar*), 7.31 (t, $^3J_{HH} = 8.0$ Hz, H–*Ar*), 7.53 (t, $^3J_{HH} = 8.0$ Hz, H–*Ar*), 7.84 (d, $^3J_{HH} = 8.0$ Hz, H–*Ar*) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 30.8$ (CH_3), 51.9, 53.3 ($2OCH_3$), 100.4 (C=*C*H), 121.9, 126.7, 131.0 (3CH), 131.2 (C), 134.0 (CH), 151.6, 159.7 (2C), 162.8, 165.4 (2C=O, ester), 197.3 (C=O) ppm.

Minor isomer (*Z*)-**3d**: 6%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 2.67$ (s, CH_3), 3.67, 3.72 (2s, $2OCH_3$), 6.65 (s, =CH), 7.10–7.84 (m, H–*Ar*) ppm.

Dimethyl 2-(1-naphthyloxy)-2-butenedioate (**3h**, $C_{16}H_{14}O_5$)
Yellow oil, IR (KBr): $\bar{\nu} = 1745$, 1716, 1634 cm^{-1}; Major isomer (*E*)-**3h**: 92%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 3.63$, 4.00 (2s, $2OCH_3$), 5.00 (s, =CH), 7.26–8.22 (m, H–*Ar*) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta =$ 52.0, 53.3 ($2OCH_3$), 101.8 (C=*C*H), 117.5, 119.3, 121.6, 126.9, 127.7, 129.3, 130.7 (7CH), 130.8, 136.1, 155.1, 159.7 (4C), 162.6, 165.2 (2C=O, ester) ppm.

Minor isomer (*Z*)-**3h**: 8%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 3.66$, 3.69 (2s, $2OCH_3$), 6.68 (s, =CH), 7.10–7.84 (m, H–*Ar*) ppm.

Dimethyl 2-(2-naphthyloxy)-2-butenedioate (**3i**, $C_{16}H_{14}O_5$)
Yellow oil; IR (KBr): $\bar{\nu} = 1747$, 1716, 1633 cm^{-1}; Major isomer (*E*)-**3i**: 93%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 3.67$, 3.95 (2s, $2OCH_3$), 5.19 (s, =CH), 7.19–7.92 (m, H–*Ar*) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 51.8$, 53.2 ($2OCH_3$), 99.3 (C=*C*H), 117.9, 120.0, 126.2, 127.0, 127.6, 127.9, 130.5 (7CH), 131.5, 134.0, 150.5, 160.9 (4C), 162.0, 165.9 (2C=O, ester) ppm.

Minor isomer (*Z*)-**3i**: 7%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 3.71$, 3.72 (2s, $2OCH_3$), 6.69 (s, =CH), 7.19–7.92 (m, H–*Ar*) ppm.

Dimethyl 2-(2-nitrophenoxy)-2-butenedioate
(**3j**, $C_{12}H_{11}NO_7$)
Yellow oil; IR (KBr): $\bar{\nu} = 1746$, 1714, 1634 cm^{-1}; Major isomer (*E*)-**3j**: 96%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 3.70$, 3.93 (2s, $2OCH_3$), 5.24 (s, =CH), 7.32 (dd, $^3J_{HH} = 8.3$, $^4J_{HH} = 1.0$ Hz, H–*Ar*), 7.44 (m, H–*Ar*), 7.69 (m, H–*Ar*), 8.08 (dd, $^3J_{HH} = 8.3$, $^4J_{HH} = 1.5$ Hz, H–*Ar*) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 52.2$, 53.4 ($2OCH_3$), 102.2 (C=*C*H), 123.9, 126.5, 127.3, 135.3 (4CH), 141.8, 146.1, 158.4 (3C), 162.4, 165.2 (2C=O, ester) ppm.

Minor isomer (*Z*)-**3j**: 4%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 3.85$, 3.89 (2s, $2OCH_3$), 6.72 (s, =CH), 7.30–8.10 (m, H–*Ar*) ppm.

Dimethyl 2-(3-nitrophenoxy)-2-butenedioate
(**3k**, $C_{12}H_{11}NO_7$)
Pale yellow oil; IR (KBr): $\bar{\nu} = 1744$, 1718, 1633 cm^{-1}; Major isomer (*E*)-**3k**: 87%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 3.71$, 3.90 (2s, $2OCH_3$), 5.33 (s, =CH), 7.43 (d, $^3J_{HH} = 8.3$ Hz, H–*Ar*), 7.61 (t, $^3J_{HH} = 8.3$ Hz, H–*Ar*), 7.89 (s, H–*Ar*), 8.12 (d, $^3J_{HH} = 8.3$ Hz, H–*Ar*) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 52.0$, 53.2 ($2OCH_3$), 102.6 (C=*C*H), 115.8, 121.0, 126.6, 131.1 (4CH), 149.2, 153.7, 158.2 (3C), 162.4, 165.0 (2C=O, ester) ppm.

Minor isomer (*Z*)-**3k**: 13%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 3.77$, 3.79 (2s, $2OCH_3$), 6.73 (s, =CH), 7.24 (d, $^3J_{HH} =$ 8.3 Hz, H–*Ar*), 7.73 (t, $^3J_{HH} = 8.3$ Hz, H–*Ar*), 7.82 (s, H–*Ar*), 8.12 (d, $^3J_{HH} = 8.3$ Hz, H–*Ar*) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 52.2$, 53.3 ($2OCH_3$), 111.0 (C=*C*H), 118.2, 122.4, 126.6, 130.4 (4CH), 148.4, 153.7, 157.0 (3C), 161.8, 163.2 (2C=O, ester) ppm.

Dimethyl 2-(2-(tert-butyl)phenoxy)-2-butenedioate
(**3m**, $C_{16}H_{20}O_5$)
Pale yellow oil; IR (KBr): $\bar{\nu} = 1732$, 1706, 1647 cm^{-1}; Major isomer (*Z*)-**3m**: 82%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 1.53$ (s, C*Me*$_3$), 3.73, 3.75 (2s, $2OCH_3$), 6.61 (s, =CH), 6.63–7.45 (m, H–*Ar*) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 29.5$ (C*Me*$_3$), 34.8 (*C*Me$_3$), 51.9, 52.9 ($2OCH_3$), 114.1 (C=*C*H), 116.5, 120.5, 123.2, 127.0 (4CH), 138.1, 149.5, 154.2 (3C), 162.8, 164.2 (2C=O, ester) ppm.

Minor isomer (*E*)-**3m**: 18%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 1.42$ (s, C*Me*$_3$), 3.97, 3.99 (2s, $2OCH_3$), 5.23 (s, =CH), 6.63–7.45 (m, H–*Ar*); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 29.8$ (C*Me*$_3$), 34.5(*C*Me$_3$), 51.9, 53.5 ($2OCH_3$), 98.1 (C=*C*H), 116.5, 120.5, 123.2, 127.4 (4CH), 136.1, 149.5, 155.2 (3C), 162.8, 165.2 (2C=O, ester) ppm.

Dimethyl 2-(2,6-dimethylphenoxy)-2-butenedioate
(**3n**, $C_{14}H_{16}O_5$)
Pale yellow oil; IR (KBr): $\bar{\nu} = 1738$, 1707, 1646 cm^{-1}; Major isomer (*Z*)-**3n**: 59%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 2.24$ (s, $2CH_3$), 3.52, 3.72 (2s, $2OCH_3$), 6.10 (s, =CH), 6.90–7.01 (m, H–*Ar*) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 15.6$ ($2CH_3$), 53.0, 53.5 ($2OCH_3$), 105.2 (C=*C*H), 125.1 (CH), 128.8 (2CH), 129.9 (2C), 149.0, 150.8 (2C), 162.6, 165.1 (2C=O, ester) ppm.

Minor isomer (*E*)-**3n**: 41%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 2.21$ (s, $2CH_3$), 3.65, 3.97 (2s, $2OCH_3$), 4.82 (s, =CH), 7.02–7.07 (m, H–*Ar*) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 16.5$ ($2CH_3$), 51.6, 53.1 ($2OCH_3$), 95.4 (C=*C*H), 126.5 (CH), 129.3 (2CH), 130.2 (2C), 152.1, 160.2 (2C), 164.5, 166.1 (2C=O, ester) ppm.

Diethyl 2-(4-chlorophenoxy)-2-butenedioate
(**4a**, $C_{14}H_{15}ClO_5$)
Yellow oil; IR (KBr): $\bar{\nu} = 1741$, 1716, 1633 cm^{-1}; Major isomer (*E*)-**4a**: 87%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 1.16$, 1.28 (2t, $^3J_{HH} = 7.0$ Hz, $2OCH_2CH_3$), 4.09, 4.29 (2q, $^3J_{HH} =$ 7.0 Hz, $2OCH_2CH_3$), 5.09 (s, =CH), 7.01 (d, $^3J_{HH} = 8.7$ Hz, H–*Ar*), 7.31 (d, $^3J_{HH} = 8.7$ Hz, H–*Ar*) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 13.8$, 14.0 ($2OCH_2CH_3$), 60.6, 62.4 ($2OCH_2CH_3$), 99.9 (C=*C*H), 122.2, 130.2 (4CH), 131.6 (CCl), 151.5, 160.2 (2C), 162.5, 165.0 (2C=O, ester) ppm.

Minor isomer (*Z*)-**4a**: 13%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 1.16$, 1.28 (2t, $^3J_{HH} = 7.0$ Hz, $2OCH_2CH_3$), 4.09, 4.29 (2q, $^3J_{HH} = 7.0$ Hz, $2OCH_2CH_3$), 6.55 (s, =CH), 6.85 (d, $^3J_{HH} = 8.7$ Hz, H–*Ar*), 7.19 (d, $^3J_{HH} = 8.7$ Hz, H–*Ar*) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 13.8$, 14.0 ($2OCH_2CH_3$), 61.0, 62.3 ($2OCH_2CH_3$), 115.9 (C=*C*H), 117.4 (2CH), 128.3

(CCl), 129.5 (2CH), 149.4, 155.3 (2C), 161.7, 163.2 (2C=O, ester) ppm.

Di(tert-butyl)-2-(4-chlorophenoxy)-2-butenedioate (**4b**, $C_{18}H_{23}ClO_5$)

Yellow oil; IR (KBr): $\bar{\nu} = 1715, 1714, 1632\,cm^{-1}$; Major isomer (*E*)-**4b**: 58%; ^1H NMR (250.1 MHz, $CDCl_3$): $\delta = 1.43$, 1.49 (2s, 2C*Me*$_3$), 5.13 (s, =CH), 7.03 (d, $^3J_{HH} = 9.0$ Hz, H–*Ar*), 7.32 (d, $^3J_{HH} = 9.0$ Hz, H–*Ar*) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 27.8$, 28.1 (2C*Me*$_3$), 81.0, 83.7 (2*C*Me$_3$), 102.6 (C=*C*H), 122.0, 130.0 (4CH), 131.0 (CCl), 152.2, 155.5 (2C), 160.9, 164.3 (2C=O, ester) ppm.

Minor isomer (*Z*)-**4b**: 42%; ^1H NMR (250.1 MHz, $CDCl_3$): $\delta = 1.34$, 1.39 (2s, 2C*Me*$_3$), 6.44 (s, =CH), 6.88 (d, $^3J_{HH} =$ 9.0 Hz, H–*Ar*), 7.24 (d, $^3J_{HH} = 9.0$ Hz, H–*Ar*) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 27.7$, 28.0 (2C*Me*$_3$), 81.9, 83.5 (2*C*Me$_3$), 117.0 (C=*C*H), 117.4 (2CH), 128.0 (CCl), 129.4 (2CH), 149.5, 159.11 (2C), 161.4, 162.9 (2C=O, ester) ppm.

Di(tert-butyl)-2-(2,6-dimethylphenoxy)-2-butenedioate (**4c**, $C_{20}H_{28}O_5$)

Yellow oil; IR (KBr): $\bar{\nu} = 1728, 1713, 1633\,cm^{-1}$; Major isomer (*Z*)-**4c**: 71%; ^1H NMR (250.1 MHz, $CDCl_3$): $\delta = 1.20$, 1.45 (2s, 2C*Me*$_3$), 2.25 (s, 2CH$_3$), 5.81 (s, =CH), 6.90–7.00 (m, H–*Ar*) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 15.8$ (2CH$_3$), 27.4, 28.1 (2C*Me*$_3$), 80.9, 83.3 (2*C*Me$_3$), 105.9 (C=*C*H), 124.6 (CH), 128.8 (2CH), 129.7 (2C), 153.0, 154.3 (2C), 161.8, 163.7 (2C=O, ester) ppm.

Minor isomer (*E*)-**4c**: 29%; ^1H NMR (250.1 MHz, $CDCl_3$): $\delta = 1.41$, 1.56 (2s, 2C*Me*$_3$), 2.21 (s, 2CH$_3$), 4.71 (s, =CH), 7.02–7.06 (m, H–*Ar*) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 16.7$ (2CH$_3$), 27.4, 27.8 (2C*Me*$_3$), 80.5, 83.3 (2*C*Me$_3$), 97.0 (C=*C*H), 126.0 (CH), 129.0 (2CH), 130.6 (2C), 149.5, 159.8 (2C), 162.1, 164.9 (2C=O, ester) ppm.

Dimethyl 2-(2-hydroxy-1-naphthyl)-2-butenedioate (**5**, $C_{16}H_{14}O_5$)

Pale yellow oil; IR (KBr): $\bar{\nu} = 3420, 1747, 1716, 1633\,cm^{-1}$; Major isomer (*Z*)-**5**: 84%; ^1H NMR (250.1 MHz, $CDCl_3$): $\delta = 3.71$, 3.99 (2s, 2OCH$_3$), 5.26 (s, =CH), 6.23 (bs, OH), 7.11–7.92 (m, H–*Ar*) ppm.

Minor isomer (*E*)-**5**: 16%; ^1H NMR (250.1 MHz, $CDCl_3$): $\delta = 3.73$, 3.75 (2s, 2OCH$_3$), 6.23 (bs, OH), 6.74 (s, =CH), 7.11–7.92 (m, H–*Ar*) ppm.

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