The Alder–Rickert Reaction in a Synthesis of *m*-Chlorophenols and 4-Chloromycophenolic Acid[1]

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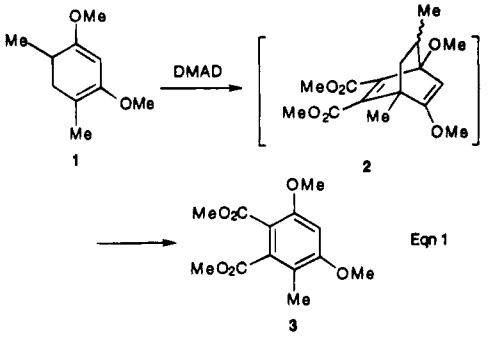
A new synthesis of highly substituted *m*-chlorophenols **12** using the Alder–Rickert reaction between 1-chloro-3-(trimethylsiloxy)-1,3-cyclohexadienes **10** and activated acetylenes has been devised. This sequence has been shown to be highly regioselective when methyl propiolate is the dienophile, and the methodology has been adapted to a facile preparation of 4-chloromycophenolic acid (**23**).

The Alder–Rickert reaction[2] is one of the most useful methods available in organic synthesis for constructing polysubstituted benzenes. A classic example is shown in eq 1 taken from the synthesis of mycophenolic acid by Birch and Wright.[3] This example illustrates an important feature of the Alder–Rickert reaction, namely the ability of the bicyclooctadiene intermediate **2** to retain functional groups that are labile to elimination during a thermal Diels–Alder reaction. In the aromatization of intermediate **2** by the thermal extrusion of propylene neither of the methoxy groups is at risk of being lost by elimination because one is on a bridgehead carbon and one is on an sp^2 carbon in a six-membered ring. This is in contrast to the situation in the more common monocyclic Diels–Alder reaction where substituents are readily lost. In fact, expendable substituents, which eliminate spontaneously after the cycloaddition reaction, are often incorporated by design into either the diene or dienophile, resulting in an *in situ* aromatization of the cycloadduct as illustrated by the example of eq 2 taken from the widely used siloxy diene variant of the Diels–Alder reaction by Danishefsky and Kitahara.[4] Although this aromatization by elimination is often very efficient, in many situations it limits the number and type of substituents in the final product. This report describes the use of certain chloro-1,3-cyclohexadienes in the Alder–Rickert reaction for the preparation of highly substituted *m*-chlorophenols and the application of this methodology to the synthesis of 4-chloromycophenolic acid (**23**).



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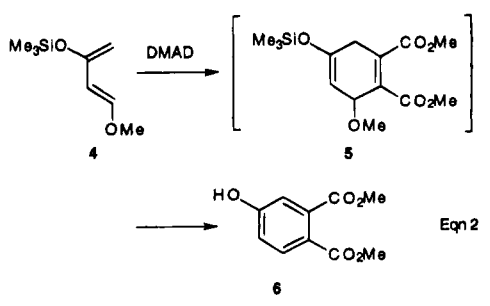
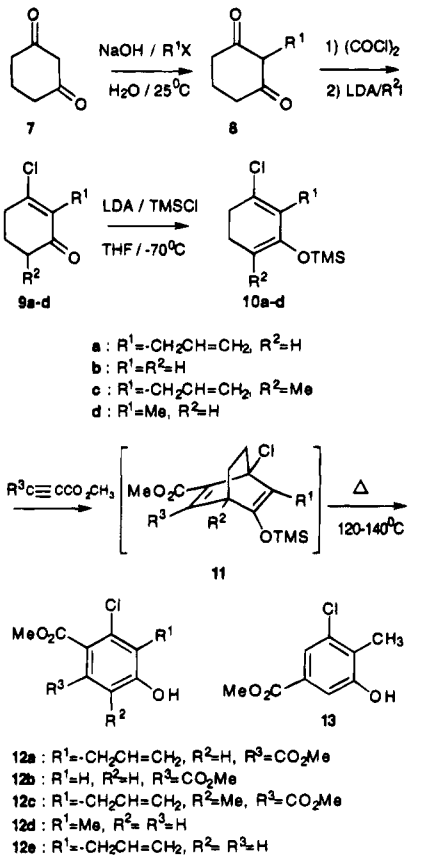


4 5 6

Scheme 1



7 8 9a-d 10a-d 11 12 13

Scheme 1 illustrates the conversion of cyclohexane-1,3-dione **7** into a variety of substituted *m*-chlorophenols **12**. Thus, alkyl-substituted 3-chloro-2-cyclohexenones **9** can be transformed by deprotonation with LDA in the presence[5] of TMSCl into cyclohexadienes **10** which undergo cycloaddition with DMAD (dimethyl acetylenedicarboxylate). The resultant bicyclic intermediates **11** are not isolated but undergo thermal elimination of ethylene to

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Table 1. Alder–Rickert Synthesis of *m*-Chlorophenols

entry	dienophile	diene	product(s)	yield,[a] %
1	DMAD	**10a**: $R^1 = CH_2CH{=}CH_2$, $R^2 = H$	**12a**: $R^1 = CH_2CH{=}CH_2$, $R^2 = H$, $R^3 = CO_2Me$	37
2	DMAD	**10b**: $R^1 = R^2 = H$	**12b**: $R^1 = R^2 = H$, $R^3 = CO_2Me$	12
3	DMAD	**10c**: $R^1 = CH_2CH{=}CH_2$, $R^2 = Me$	**12c**: $R^1 = CH_2CH{=}CH_2$, $R^2 = Me$, $R^3 = CO_2Me$	53
4	$HCCCO_2Me$	**10d**: $R^1 = Me$, $R^2 = H$	**12d**: $R^1 = Me$, $R^2 = R^3 = H$	61
			and **13**	2
5	$HCCCO_2Me$	**10a**: $R^1 = CH_2CH{=}CH_2$, $R^2 = H$	**12e**: $R^1 = CH_2CH{=}CH_2$, $R^2 = H$, $R^3 = H$	29

[a] The yields reported are for the overall process for the conversion of the chlorocyclohexenone **9** to the diene **10** followed by the Alder–Rickert sequence to give the *m*-chlorophenol **12**.

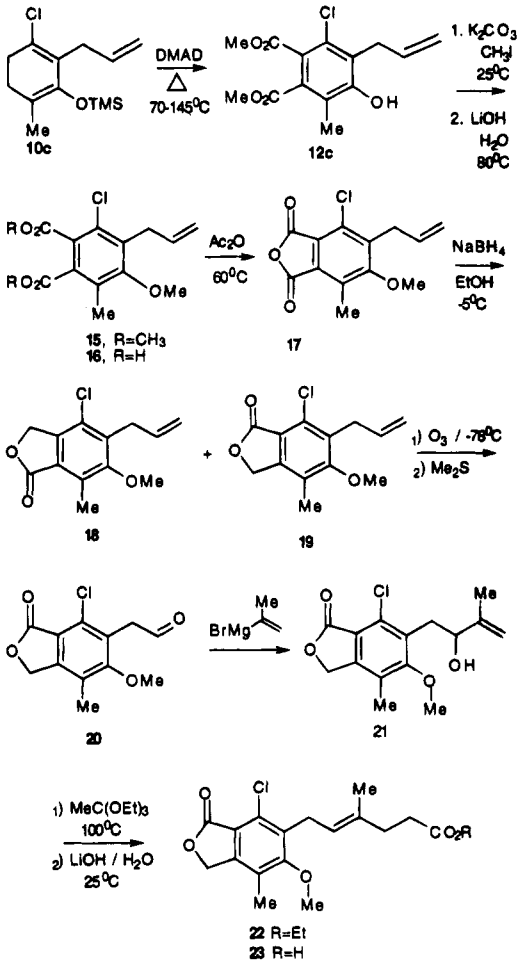
give *m*-chlorophenols **12**. The broad utility of this method derives from the availability of a wide variety of substituted 3-chloro-2-cyclohexenones. These cyclohexenones can be prepared by direct chlorination of symmetrically substituted 1,3-cyclohexanediones[6] or by the regiospecific alkylation[7] of 3-chloro-2-cyclohexenones at C-6. The critical feature of this synthesis is that the chloro and (trimethylsilyl)oxy groups are protected from elimination during the aromatization of the bicyclic intermediate **11**. The products **12** obtained by this Alder–Rickert approach complement those derived from traditional electrophilic aromatic substitution for the introduction of chlorine into phenols which provides ortho and/or para isomers. Furthermore, methyl propiolate may be substituted for DMAD, allowing the preparation of benzoic acids in addition to phthalic acids (Scheme 1, $R^3 = H$).

These two approaches to variation of substituents on the *m*-chlorophenol nucleus are illustrated by the examples in Table 1. It should be emphasized that this Alder–Rickert approach to *m*-chlorophenols is highly regioselective. In one case, using methyl propiolate as an unsymmetrical acetylene (Table 1, entry 5), examination of the reaction mixture by NMR showed no isomeric products. A second example with methyl propiolate (Table 1, entry 4) gave only 2% of the isomeric phenol **13** derived from the reverse orientation of the dienophile in the cycloaddition step of the Alder–Rickert sequence.

The Synthesis of 4-Chloromycophenolic Acid

Mycophenolic acid is an immunosuppressant and is effective in the treatment of psoriasis.[8] Mycophenolate Mofetil,[9] a prodrug of mycophenolic acid, is effective in rheumatoid arthritis[10] and for the treatment of kidney and heart transplant rejection.[11] Mycophenolic acid has been the subject of many syntheses,[12] including a recent one[13] from these laboratories using an Alder–Rickert reaction as the key step in generating a pentasubstituted benzene as a precursor to the phthalide moiety of mycophenolic acid. Because chlorine can function as a hydrogen-bond acceptor, it has been used as a replacement for hydroxyl groups in medicinal agents. As part of an investigation of the structure–activity relationships of mycophenolic acid analogs, the synthesis of 4-chloromycophenolic acid (**23**) was undertaken.

Scheme 2



Adaptation of the general methodology described above for the synthesis of *m*-chlorophenols to the preparation of this mycophenolic acid analog requires the cyclohexadiene **10c**. This diene in turn is readily available from the known[7] chlorocyclohexenone **9c** by enolization and trapping with TMSCl. The Alder–Rickert reaction with cyclohexadiene **10c** and DMAD afforded the *m*-chlorophenol **12c** (Scheme 2). This phenol was alkylated to give the methyl ether **15** which hydrolyzed to the diacid **16**. Reaction of **16** with acetic anhydride gave anhydride **17**. The reduction of phthalic anhydride **17** deserves comment. As shown in the original synthesis of mycophenolic acid by Birch and Wright,[3] reduction of 3-hydroxyphthalic anhydrides with zinc and HCl reduces the carbonyl distal to the hydroxyl group. However, in the case of the chloro anhydride **17**, zinc reduction gave a

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2:1 mixture of products which were separated by column chromatography. The major product was determined to have structure **19** on the basis of NMR spectroscopy. In particular, irradiation of the aromatic methyl group at C7 of isomer **19** caused NOE enhancement of the signal for the lactone methylene hydrogens. This assignment is also in agreement with the chemical shifts of the aromatic methyls (2.24 ppm for **19** and 2.61 ppm for **18**). Reduction of **17** with $NaBH_4$ in ethanol gave a virtually identical product ratio. A low degree of regioselectivity in the reduction of 3-chlorophthalic anhydride itself has been previously reported.[14] To complete the synthesis, the allyl moiety of **19** was converted[15] into the required (*E*)-4-methyl-4-hexenoic acid side chain by ozonolysis, Grignard reaction with 2-propenylmagnesium bromide, and Claisen ortho ester rearrangement to give, following hydrolysis of the ethyl ester, 4-chloromycophenolic acid (**23**).

This report demonstrates the application of the Alder–Rickert reaction to chloro-1,3-cyclohexadienes to produce highly functionalized *m*-chlorophenols such as 4-chloromycophenolic acid. The synthesis of halobenzenes by cycloaddition processes is rare in the literature,[16] but the brevity of this approach has much to offer.

Experimental Section

Dimethyl 3-Chloro-5-hydroxy-6-methyl-4-(2-propenyl)phthalate (12c). A solution of LDA was prepared by addition of *n*-butyllithium (40.6 mL, 1.6 N in hexane) to diisopropylamine (9.1 mL, 65 mmol) in THF (110 mL) at −40 °C. The reaction mixture was cooled to −70 °C, and TMSCl (12 mL) was added over 10 min. A solution of 3-chloro-6-methyl-2-(2-propenyl)cyclohex-2-enone[7] (**9c**, 11.00 g, 59 mmol) in THF (5 mL) was added over 5 min, and the reaction mixture was stirred for 30 min at −70 °C. Triethylamine (20 mL) was added, and the reaction mixture was poured into ice water and hexane. The organic layer was washed with brine, dried over K_2CO_3, evaporated, and distilled (Kugelrohr) to give 1-chloro-4-methyl-2-(2-propenyl)-3-((trimethylsilyl)oxy)-1,3-cyclohexadiene (**10c**) (12.02 g, 79%): bp 80 °C/0.2 mm.

The siloxy diene **10c** (12.00 g, 47 mmol) in xylene (45 mL) was treated with DMAD (9.0 mL, 73 mmol) and heated at 70 °C for 2 h and then at 145 °C for 4 h. The xylene was removed *in vacuo*, and the residue was dissolved in ethyl acetate and stirred for 10 min with 1% aqueous HCl. The organic layer was separated, washed with $NaHCO_3$ and then brine, and dried over $MgSO_4$ and evaporated. The resulting residue was chromatographed on silica gel, eluting with ethyl acetate/hexane mixtures to give **12c** (9.48 g, 53% overall from **9c**) as an oil: IR (neat) 2954, 1739, 1717, 1296, 1206 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.9–5.7 (m, 1H), 5.1–5.0 (m, 2H), 3.79 (s, 3H), 3.77 (s, 3H), 3.54 (br d, J = 6.0 Hz, 2H), 2.16 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 167.0, 154.7, 133.3, 132.1, 130.0, 125.9, 124.0, 122.4, 117.2, 52.6, 52.5, 32.0, 12.9. Anal. Calcd for $C_{14}H_{15}ClO_5$: C, 56.29; H, 5.06. Found: C, 56.52; H, 5.33.

Dimethyl 3-Chloro-5-hydroxy-4-(2-propenyl)phthalate (12a). In a reaction sequence identical to that used to prepare chlorophenol **12c**, 3-chloro-2-(2-propenyl)cyclohex-2-enone[17] (**9a**, R^1 = 2-propenyl, R^2 = H) was deprotonated with LDA in the presence of TMSCl to give the (trimethylsilyl)oxy diene **10a** which upon heating with DMAD gave phthalate **12a** (37%): IR (neat) 1728, 1707, 1320, 1281, 1244 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 (s, 1H), 5.95–5.82 (m, 1H), 5.11–5.00 (m, 2H), 3.96 (s, 3H), 3.86 (s, 3H), 3.60 (d, J = 6.2 Hz, 2H). Anal. Calcd for $C_{13}H_{13}ClO_5$: C, 54.85; H, 4.60. Found: C, 55.08; H, 4.95.

Dimethyl 3-Chloro-5-hydroxyphthalate (12b). Similarly, 3-chlorocyclohex-2-enone[6] (**9b**, R^1 = R^2 = H) was converted to silyl enol ether **10b** and reacted with DMAD to give chlorophenol **12b** (12%): mp 109.5–114.0 °C (*t*-BuOMe/hexane); IR (KBr) 1715, 1439, 1332, 1256 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, J = 2.5Hz, 1H), 7.03 (d, J = 2.5 Hz, 1H), 3.95 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 157.3, 136.1, 132.6, 130.4, 126.7, 120.6, 116.0, 53.2, 52.9. Anal. Calcd for $C_{10}H_9ClO_5$: C, 49.09; H, 3.71. Found: C, 49.48; H, 3.74.

Methyl 2-Chloro-4-hydroxy-3-(2-propenyl)benzoate (12e). Similarly, heating the (trimethylsilyl)oxy diene **10a** with methyl propiolate gave the chlorophenol **12e** (29%): mp 120.3–122.3 °C (*t*-BuOMe/hexane); IR (KBr) 1694, 1586, 1267, 1202 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, J = 8.5 Hz, 1H), 6.80 (d, J = 8.5 Hz, 1H), 6.00–5.87 (m, 1H), 5.07–5.00 (m, 2H), 3.87 (s, 3H), 3.61 (d, J = 6.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 159.5, 135.6, 135.0, 131.0, 126.8, 122.1, 115.9, 113.7, 52.5, 31.7. Anal. Calcd for $C_{11}H_{11}ClO_3$: C, 58.29; H, 4.89. Found: C, 58.22; H, 4.84.

Methyl 2-Chloro-4-hydroxy-3-methylbenzoate (12d) and Methyl 3-Chloro-5-hydroxy-4-methylbenzoate (13). Similarly, 3-chloro-2-methylcyclohex-2-enone[6] (**9d**, R^1 = Me, R^2 = H) was reacted with LDA and TMSCl to give enol ether **10d**, which on heating with methyl propiolate gave two products which were separated by chromatography on silica gel, eluting with EtOAc/hexane mixtures to give **13** (2% from **9d**): mp 154.5–156.0 °C (*t*-BuOMe/hexane); IR (KBr) 1690, 1581, 1321, 1288, 1250 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J = 1.6 Hz, 1H), 7.42 (d, J = 1.6 Hz, 1H), 3.87 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 156.2, 135.2, 128.9, 128.6, 121.3, 114.1, 52.1, 13.1. Anal. Calcd for $C_9H_9ClO_3$: C, 53.88; H, 4.52. Found: C, 54.07; H, 4.55.

Further elution gave **12d** (61% from **9d**): mp 200.0–202.0 °C (MeOH); IR (KBr) 1694, 1588, 1288, 1271 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, J = 8.6 Hz, 1H), 6.79 (d, J = 8.6 Hz, 1H), 3.86 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 159.1, 134.9, 129.5, 124.7, 120.8, 112.5, 51.7, 12.7. Anal. Calcd for $C_9H_9ClO_3$: C, 53.88; H, 4.52. Found: C, 54.14; H, 4.42.

Dimethyl 3-Chloro-5-methoxy-6-methyl-4-(2-propenyl)phthalate (15). A mixture of phenol **12c** (9.46 g, 31.7 mmol) in DMF (20 mL) and K_2CO_3 (6.90 g, 50 mmol) and methyl iodide (3.11 mL, 50 mmol) was stirred at 25 °C for 2.5 h. The reaction mixture was poured into ice water and extracted with ethyl acetate. The extracts were washed with water and then brine, dried over $MgSO_4$, and evaporated to give **15** (8.82 g, 89%) as an oil: IR (neat) 2952, 1739, 1717, 1438, 1220 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.9–6.0 (m, 1H), 5.07 (d, J = 11.7 Hz, 1H), 5.00 (d, J = 17.1 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.73 (s, 3H), 3.59 (br d, J = 5.9 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 166.8, 159.0, 135.0, 134.3, 132.0, 130.3, 129.9, 129.2, 116.4, 61.3, 52.7, 52.6, 32.1, 13.5. Anal. Calcd for $C_{15}H_{17}ClO_5$: C, 57.60; H, 5.48. Found: C, 57.68; H, 5.56.

3-Chloro-5-methoxy-6-methyl-4-(2-propenyl)phthalic Anhydride (17). The dimethyl phthalate **15** (8.82 g, 28.2 mmol) was heated at 80 °C for 5 h in a solution of LiOH (4.73 g, 113 mmol) in water (40 mL) and MeOH (40 mL). The reaction mixture was cooled, diluted with water, and washed with ether. The aqueous phase was cooled on ice, acidfied to pH 2 with aqueous HCl, and extracted with ethyl acetate. The extracts were washed with brine, dried over $MgSO_4$, and evaporated to give the phthalic acid **16**. This acid was then heated with acetic anhydride (5 mL) at 60 °C for 1.5 h. The excess acetic anhydride was evaporated and the residue was recrystallized from *t*-BuOMe/hexane to give anhydride **17** (6.52 g, 87%): mp 80–82 °C; IR (KBr) 1849, 1774, 1458, 1281 cm^{-1};^1H NMR (300 MHz, $CDCl_3$) δ 6.0–5.85 (m, 1H), 5.13 (d, J = 10.0 Hz, 1H), 5.03 (d, J = 18.0 Hz, 1H), 3.87 (s, 3H), 3.69 (d, J = 9.1 Hz, 2H), 2.64 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ

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164.6, 161.8, 160.0, 141.6, 133.3, 132.5, 132.0, 129.6, 123.4, 117.2, 61.9, 31.9, 11.7. Anal. Calcd for $C_{13}H_{11}ClO_4$: C, 58.55; H, 4.16. Found: C, 58.20; H, 4.14.

1,3-Dihydro-4-chloro-6-methoxy-7-methyl-3-oxo-5-(2-propenyl)isobenzofuran (19) and 1,3-Dihydro-4-chloro-6-methoxy-7-methyl-1-oxo-5-(2-propenyl)isobenzofuran (18). A solution of the phthalic anhydride **17** (3.065 g, 11.5 mmol) in EtOH (50 mL) was cooled to −5 °C and treated with $NaBH_4$ (0.60 g) in several portions over 2.5 h. The reaction was quenched by dropwise addition of HOAc, and the reaction mixture was then poured into water and extracted with ethyl acetate. The extracts were washed with brine, dried over $MgSO_4$, and evaporated. The resulting residue was chromatographed on silica gel, eluting with ethyl acetate/hexane mixtures to give phthalide **18** (1.042 g, 32%): mp 79–80 °C (*t*-BuOMe/hexane); IR (KBr) 1771, 1635, 1248, 1033 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.0–5.9 (m, 1H), 5.17 (s, 2H), 5.11 (d, J = 9.2 Hz,1H), 5.03 (d, J = 17.1 Hz, 1H), 3.79 (s, 3H), 3.64 (d, J = 5.1 Hz, 2H), 2.61 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 158.7, 140.9, 138.1, 134.2, 131.3, 124.1, 116.6, 67.7, 61.5, 31.9, 10.7. Anal. Calcd for $C_{13}H_{13}ClO_3$: C, 61.79; H, 5.18. Found: C, 61.37; H, 5.21.

Further elution gave the desired phthalide **19** (1.722 g, 59%): mp 67–70 °C (*t*-BuOMe/hexane); IR (KBr) 1769, 1638, 1118, 1031 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.0–5.9 (m, 1H), 5.14 (s, 2H), 5.08 (d, J = 8.4 Hz,1H), 5.00 (d, J = 17.2 Hz, 1H), 3.92 (s, 3H), 3.83 (d, J = 5.9 Hz, 2H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 162.4, 147.4, 144.6, 134.0, 131.6, 123.8, 118.1, 116.2, 67.4, 61.5, 31.3, 11.8. Anal. Calcd for $C_{13}H_{13}ClO_3$: C, 61.79; H, 5.18. Found: C, 61.52; H, 5.19.

2-(1,3-Dihydro-4-chloro-6-methoxy-7-methyl-3-oxo-5-isobenzofuranyl)acetaldehyde (20). A solution of olefin **19** (0.52 g, 2.06 mmol) in CH_2Cl_2 (20 mL), MeOH (20 mL), and pyridine (0.5 mL) was cooled to −70 °C and treated with ozonized oxygen until a blue color persisted. The resulting ozonide was reduced by addition of Me_2S (1 mL), and the reaction mixture was stirred at 25 °C for 1 h. The reaction mixture was diluted with CH_2Cl_2, washed with cold 2% HCl and brine, dried over $MgSO_4$, and evaporated. The residue was recrystallized from *t*-BuOMe/EtOAc to give **20** (0.346 g, 66%): mp 113–116 °C; IR (KBr) 1769, 1719, 1116, 1043 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.81 (s, 1H), 5.17 (s, 2H), 4.04 (s, 2H), 3.77 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 167.9, 162.5, 148.7, 131.5, 128.0, 124.0, 118.3, 67.5, 61.3, 42.3, 11.9. Anal. Calcd for $C_{12}H_{11}ClO_4$: C, 56.59; H, 4.35. Found: C, 56.07; H, 4.43.

(*E*)-6-(1,3-Dihydro-4-chloro-6-methoxy-7-methyl-3-oxo-5-isobenzofuranyl)-4-methyl-4-hexenoic Acid (23). A solution of aldehyde **20** (0.31 g, 1.22 mmol) in THF (40 mL) was coooled to −70 °C and treated over 30 min with 2-propenylmagnesium bromide (2.0 mL of a solution prepared by addition of 2-bromopropene (6.0 mL, 67 mmol) to magnesium turnings (2.0 g, 82 mmol) in THF (60 mL)). The reaction mixture was poured into aqueous NH_4Cl and extracted with EtOAc. The extracts were washed with brine, dried over $MgSO_4$, and evaporated to give allylic alcohol **21** (0.321 g, 89%).

The allylic alcohol **21** in triethyl orthoacetate (30 mL) was treated with propionic acid (0.07 mL) and heated at 100 °C for 2 h. The excess ortho ester was evaporated, and the residue was chromatographed on silica gel, eluting with CH_2Cl_2/hexane/acetone mixtures to give the ethyl ester of 4-chloromycophenolic acid (**22**) (0.092 g, 21%) and unreacted allylic alcohol **21** (0.102 g, 32%).

The ethyl ester **22** (0.082 g, 0.22 mmol) in MeOH (4 mL) and water (2 mL) was treated with LiOH (0.040 g, 0.95 mmol). After stirring for 4 h at 25 °C, the reaction mixture was diluted with water and washed with ether. The resulting aqueous solution was cooled on ice, acidified to pH 2, and extracted with EtOAc. The extracts were washed with brine, dried over $MgSO_4$, and evaporated to give 4-chloromycophenolic acid (**23**, 0.057 g, 75%): mp 159–162 °C (*t*-BuOMe/EtOAc); IR (KBr) 1759, 1707, 1118, 1033 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.16 (t, J = 5.5 Hz, 1H), 5.12 (s, 2H), 3.78 (s, 3H), 3.57 (d, J = 7.5 Hz, 2H), 2.43 (m, 2H), 2.31 (m, 2H), 2.22 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.8, 168.4, 162.2, 147.1, 135.5, 134.8, 131.3, 123.8, 121.9, 118.0, , 67.4, 61.2, 34.2, 32.6, 26.4, 16.4, 11.8. Anal. Calcd for $C_{17}H_{19}ClO_5$: C, 60.27; H, 5.65. Found: C, 60.10; H, 5.63.

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