

Sequential and regioselective Friedel–Crafts reactions of *gem*-dihalogenocyclopropanecarbonyl chlorides with benzenes for the synthesis of 4-aryl-1-naphthol derivatives

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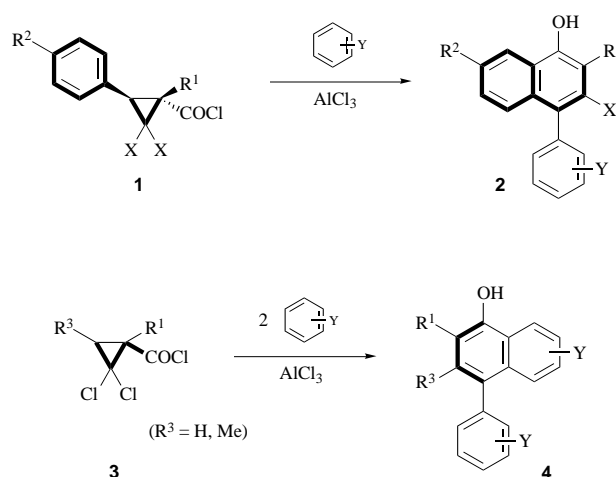
Novel, sequential and regioselective Friedel–Crafts type reactions of (*E*)-3-aryl-2,2-dihalogenocyclopropanecarbonyl chlorides **1** and 2,2-dichlorocyclopropanecarbonyl chlorides **3** with benzenes produce various 4-aryl-3-halogeno-1-naphthols **2** and 4-aryl-1-naphthols **4**, respectively. One of the benzannulations involves the intramolecular cyclization of acid chlorides **1**, followed by intermolecular coupling with substituted benzenes to give 4-aryl-3-halogeno-1-naphthols **2**. As a demonstration of this annulation, 4-aryl-3-bromo-1-naphthols **2i** and **2k** are successfully converted into new analogues of 1-aryl-3-hydroxymethyl-4-methoxy-2-naphthoic acid lactones **13**, a class of lignan lactones. The other benzannulation involves three series of reactions using acid chlorides **3a–c**: (1) the intermolecular Friedel–Crafts acylation of **3** with one benzene molecule giving the intermediary 2,2-dichlorocyclopropyl(phenyl)-methanones **14a–c**; (2) the intermolecular trapping of **14a–c** with another benzene molecule accompanied by regioselective ring opening; and (3) the final intramolecular cyclization giving 4-phenyl-1-naphthols **4a–c**. The use of *p*-xylene also gives the corresponding 4-(*p*-xylyl)-1-naphthol **4d**. The reactions of alternatively prepared ketones **14** with benzenes gives a variety of ‘unsymmetrically’ substituted 4-aryl-1-naphthols **4c,e–k** under identical conditions. However, the reaction using *p*-methoxyphenyl ketone analogues **14g** does not produce 4-aryl-1-naphthols, but gives 5-aryl-2-(*p*-methoxyphenyl)-3-methylfurans **16**. These annulations proceed straightforwardly (in a one-pot manner) and this variation is due to the highly regioselective cyclopropane ring-openings.

The characteristic features of cyclopropa(n)es has brought about a number of both unique and useful synthetic reactions.^{1a–c} This synthetic methodology has been continuously developed over the past two or three decades. The potentiality of these methods is largely ascribed to the nature of cyclopropa(n)es, *i.e.* relief of the inherent ring strain providing a variety of thermal, oxidative and reductive, and electrophilic and nucleophilic ring-opening reactions. Cyclopropa(n)ene ring expansions (annulation accompanying ring reconstructions) occupy a significant position in worthwhile synthetic methods.¹ Among them, benzannulation (construction of aromatic rings) utilizing cyclopropene intermediates has recently attracted attention in organic reactions,² wherein several naphthol analogues were produced by the reaction of carbene–metal complexes with cyclopropenes through rearrangement. Another notable benzannulation utilizing cyclobutene derivatives is also documented.³ These benzannulations are considered to be worthwhile synthetic methods in view of both their unique reaction mode and practicality in providing a variety of substituted aromatics.

Our attention has been focused on the chemistry of *gem*-dihalogenocyclopropane derivatives, because they possess the following noteworthy features: (a) ease of preparation by the addition of dihalogenocarbenes to olefins;⁴ (b) as the only precursor for halogenocyclopropanes when subjected to reductive dehalogenation using tributyltin hydride, metal hydrides and other reagents;⁵ (c) useful intermediates for Nazarov-type cyclopentannulation;⁶ (d) synthons of choice for cyclopropane derivatives by inter- and intra-molecular stereocontrolled C–C bond formation through both anionic⁷ and radical type methods;⁸ (e) other useful transformations;⁹ and (f) constituents of useful biologically active compounds.¹⁰ As part of our ongoing program for new and useful reactions and compounds utilizing *gem*-dihalogenocyclopropanes,^{8,11} we have previously reported a novel benzannulation using aryl(*gem*-dihalogeno-

cyclopropyl)methanols with acid catalysts for the synthesis of α - and β -halogenonaphthalenes, wherein two distinct types of highly regioselective acid-induced cyclopropane ring cleavages are involved.^{11a,d} These results prompted us to extend the more straightforward benzannulation aiming at the synthesis of the 4-aryl-1-naphthols.

This paper describes full details of the two types of novel, sequential and regioselective Friedel–Crafts (F–C) type benzannulations of *gem*-dihalogenocyclopropanecarbonyl chlorides **1** and **3** producing various 4-aryl-1-naphthols **2** and **4**, respectively (Scheme 1).^{11b} Since 4-arylnaphthalene derivatives are



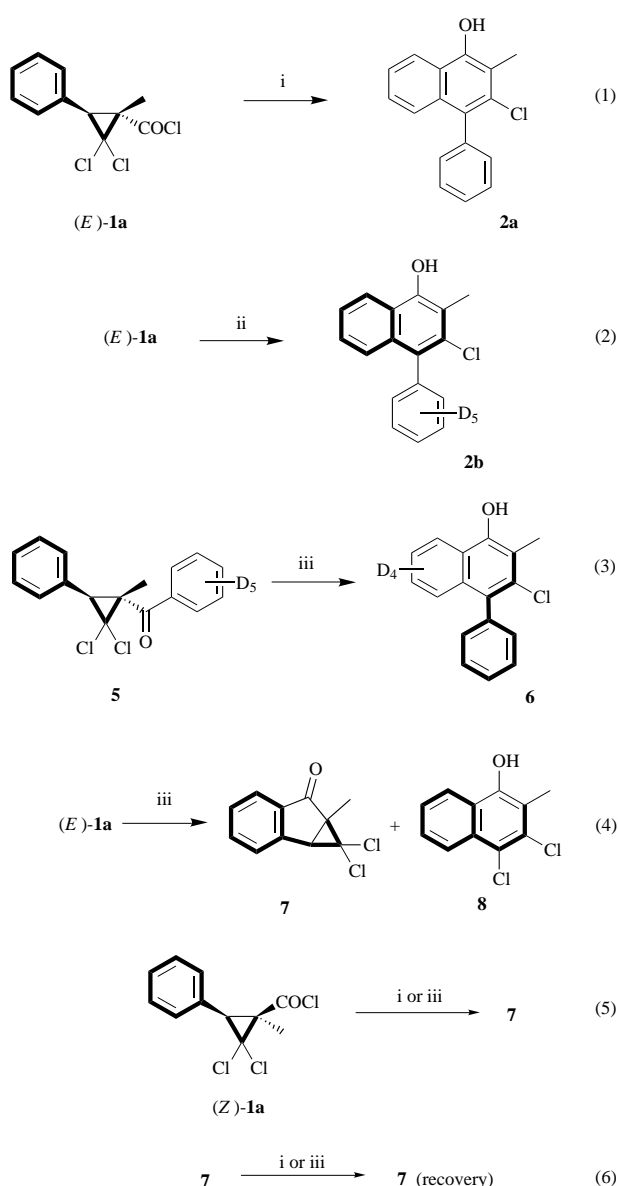
Scheme 1

attracting much attention as the basic skeleton of several biologically active lignan-type natural products and pharmaceuticals,¹² these compounds and their isosteres have been one

synthetic target of significance.¹³ Taking this background into account, we evaluated the application of 4-aryl-1-naphthols to the synthesis of new types of lignan lactones.

Results and discussion

One of the sequential F–C reactions involved the intramolecular cyclization of (*E*)-3-aryl-2,2-dihalogenocyclopropanecarbonyl chlorides **1**, followed by intermolecular coupling with substituted benzenes to give 4-aryl-3-halogeno-1-naphthols **2**. Initially, we allowed (*E*)-2,2-dichloro-1-methyl-3-phenylcyclopropanecarbonyl chloride (*E*)-**1a** to react with benzene in the presence of an acid such as AlCl₃, Et₂AlCl, TiCl₄, SnCl₄, ZnCl₂, BF₃·OEt₂ or CF₃CO₂H. After optimizing the conditions, the use of 1.1 equiv. of benzene and 2.2 equiv. of AlCl₃ at room temperature gave 3-chloro-2-methyl-4-phenyl-1-naphthol **2a** in 52% yield [Scheme 2, eqn. (1)]. To clarify this



Scheme 2 Reagents and conditions: i, benzene (1.2 equiv.), AlCl₃ (2.2 equiv.), 1,2-dichloroethane, room temp.; ii, [²H₆]benzene (1.2 equiv.), AlCl₃ (2.2 equiv.), 1,2-dichloroethane, room temp.; iii, AlCl₃ (2.2 equiv.), 1,2-dichloroethane, room temp.

reaction mechanism, we carried out the following five experiments [eqns. (2)–(6)]. (1) An identical reaction of (*E*)-**1a** using C₆D₆ in place of benzene gave the 4-C₆D₅-substituted naphthol **2b** [eqn. (2)]. (2) The C₆D₅-substituted ketone **5**, which was

prepared by an alternative method and is the postulated intermediate in the case where the intermolecular F–C acylation initially occurred, mainly afforded an isomeric naphthol **6** under identical conditions [eqn. (3)]. (3) The controlled reaction of (*E*)-**1a** without benzene gave the tricyclic ketone **7** and 3,4-dichloro-1-naphthol **8** as major products [eqn. (4)]. (4) The controlled reaction of (*Z*)-**1a** with or without benzene, on the other hand, gave the tricyclic ketone **7** as a major product in good yield [eqn. (5)]. (5) Treatment of **7** with or without benzene under identical conditions resulted only in the recovery of **7**.

These results clearly indicate that during this sequential F–C reaction, intramolecular cyclization of the key ketene intermediate **9** precedes the intermolecular coupling with benzene (Scheme 3). The heavy lines in these structures indicate the backbones of the starting 2,2-dichloro-3-phenylcyclopropane moiety. Three important points should be noted: (1) bond-*a* cleavage proceeded with high regioselectivity to result in the selective synthesis of **2a**; ^{11a,d} (2) even 1.2 equiv. of benzene was sufficient for it to play its role as the intermolecular trapping agent; and (3) the *E*-configuration of acyl chloride **1a** was critical for this successful benzannulation. We have recently reported a new furan synthesis using **1a** and 5 equiv. of reactive benzenes such as toluene or anisole.^{11c} Accordingly, the reaction pathway involving **1** forks into two alternative branches, *i.e.*, 4-aryl-1-naphthol formation and diarylfuran formation, depending on the relative molar amounts of the benzenes used.

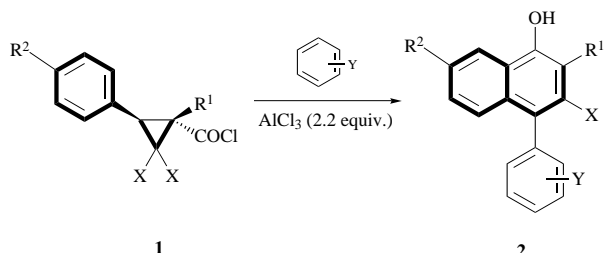
Table 1 lists the results of the synthesis of various 4-aryl-3-halogeno-1-naphthols **2** (Method A). As for the *para*-substituent (R²) in **1**, the MeO group led to a decreased product yield compared with the H or Cl. Whilst the use of toluene, chloro- bromo-benzenes as reactants gave the corresponding regioisomeric mixtures of 4-aryl-3-halogeno-1-naphthols **2**, 2,6-dichlorotoluene and 1,4-dichlorobenzene gave the corresponding single products **2f**, **g**, **k**, **m** and **o**.

The structures of the naphthols **2a** and **2f** were unambiguously determined by ¹H and ¹³C NMR spectroscopy,¹⁴ H–H and C–H COSY results, a DEPT spectrum and elemental analysis. The NOESY spectra of **2a**, **2b** and **2f** [interaction between the OH (5.32 ppm) and the Me (2.51–2.53 ppm)], and that of **2f** [interaction between OH (5.32 ppm) and 8-H (8.35 ppm)] also supported the assignment of a 4-aryl-2-naphthol skeleton to the compounds (see Fig. 1).

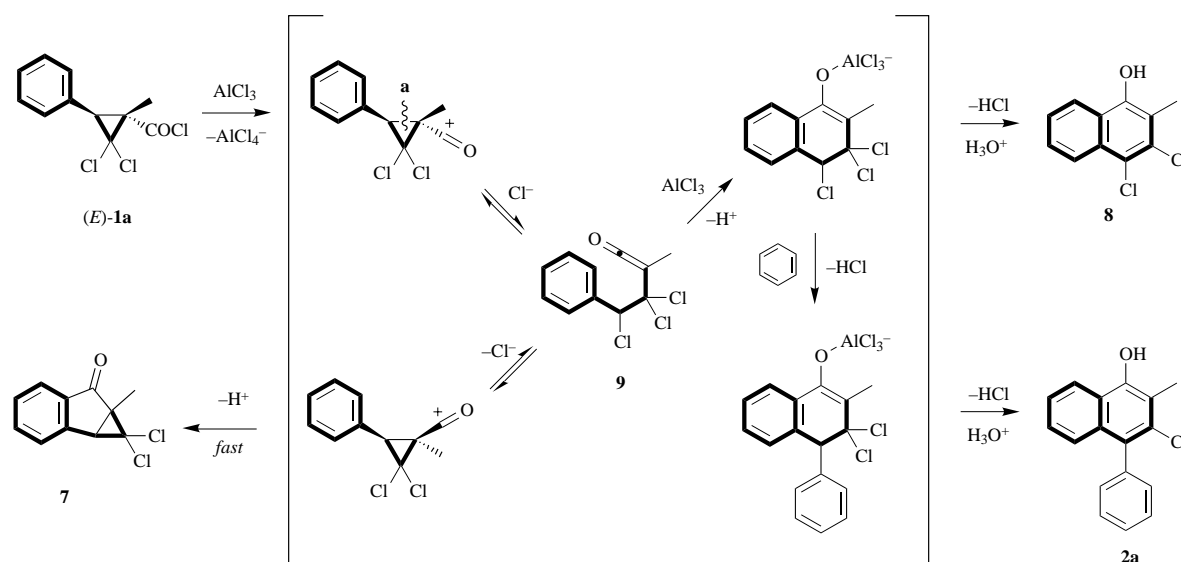
Murphy and Wattanasin reported the Lewis acid-promoted annulation of 2-arylcyclopropyl aryl ketones **10**, which were prepared by cyclopropanation of chalcones for the synthesis of tetralones.¹⁵ The modes of both this ring-expansion using **10** and the benzannulation using aryl(2,2-dihalogeno-3-phenylcyclopropyl)methanols **11**^{11a,d} are quite different from that of the present reaction, because those two methods involve the intramolecular F–C alkylation of the 3-position on the cyclopropane ring and no F–C intermolecular coupling (Scheme 4).

We next evaluated the utility of the 4-aryl-3-halogeno-1-naphthols **2**. Following our work utilizing **2**, we used the bromonaphthols **2i** and **2k** to prepare the two lignan lactones **13a** and **13b**, respectively (Scheme 5). Lithiation at the bromine position in **2i** and **2k**, followed by trapping with CO₂, gave the corresponding carboxylic acids, which were converted into the esters **12a** and **12b** by double methylation of the hydroxy and the carboxy groups with an excess of MeI. The desired lignans **13a** and **13b** were obtained by bromination of the *vicinal* methyl groups, followed by treatment with 1 M aqueous NaOH and acidic work-up. This sequence made good use of the bromine in the naphthalene for effective derivatization, compared with our earlier method for synthesizing natural lignan lactones utilizing the α -chloronaphthane intermediate,^{11a,d} wherein an extra dechlorination step was required.

The other sequential F–C reaction for benzannulation using 2,2-dichlorocyclopropanecarbonyl chlorides **3** involved the following reaction series: (1) the *intermolecular* F–C acylation

Table 1 Sequential Friedel–Crafts reaction of acyl chlorides **1** with benzenes (Method A)


Substrate	X	R ¹	R ²	Y-Benzene	Product	Yield (%)
1a	Cl	Me	H	Benzene	2a	52
				[² H ₆]Benzene	2b	50
				Toluene	2c	56 ^a
				Chlorobenzene	2d	81 ^b
				Bromobenzene	2e	64 ^c
				2,6-Dichlorotoluene	2f	60 ^d
				1,4-Dichlorobenzene	2g	47
1b	Cl	H	H	Chlorobenzene	2h	51 ^e
1c	Br	Me	H	Benzene	2i	47
				Chlorobenzene	2j	72 ^f
1d	Cl	Me	Cl	1,4-Dichlorobenzene	2k	48
				Benzene	2l	48
1e	Cl	Me	OMe	2,6-Dichlorotoluene	2m	44 ^d
				2,6-Dichlorotoluene	2n	23
					2o	44 ^d

^a Containing ca. 10% of 2-Me or 3-Me isomer. ^b Containing ca. 35% of 2-Cl isomer. ^c Containing ca. 20% of 2-Br isomer. ^d Exclusively single isomer.^e Containing ca. 30% of 2-Cl isomer. ^f Containing ca. 40% of 2-Cl isomer.**Scheme 3**

of 2,2-dichlorocyclopropanecarbonyl chlorides **3a–c** with one benzene molecule to give the ketones **14a–c**; (2) the *intermolecular* trapping of **14a–c** with another benzene molecule accompanied by cyclopropane ring-opening; and (3) the final *intramolecular* cyclization to give 4-aryl-1-naphthols **4a–c** (Scheme 6). It is also noteworthy that these reactions spontaneously took place in a one-pot manner with regioselective bond-**b** cleavage to give a selective synthesis of **4** (Table 2, Method B). Accordingly, the regioselective ring-cleavage position of **a** or **b** depends on the difference in substituents (3-position) on the cyclopropane ring. When *p*-xylene was used as the solvent, the desired reaction also proceeded to give **4d**. However, the reactions using monosubstituted benzenes such as toluene and *p*-methoxybenzene proved to very sluggish.

To confirm this reaction mechanism, we examined the benz-

annulation using the intermediary ketones **14c–f** which were prepared in an alternative way by the coupling of ArMgBr (1.0 equiv.) with the acyl chlorides **3** in 52–61% yields. As expected, these ketones gave the corresponding 4-aryl-1-naphthols **4c, e–k** under identical conditions. This improved method provided access to a variety of compounds **4** bearing ‘unsymmetrical’ substituents, by using variously substituted benzenes which could be incorporated stepwise (Table 3, Method C). A representative structure, that of 4-phenyl-1-naphthol **4c**, was also unambiguously determined (¹H and ¹³C NMR, H–H and C–H COSYs, and NOESY spectral evidence).

Finally, we describe a new furan synthesis using 2,2-dichloro-1-methylcyclopropyl(*p*-methoxyphenyl)methanone **14g** (Scheme 7). Treatment of the *p*-methoxyphenyl substituted ketone **14g** with benzene, toluene and chlorobenzene, respec-

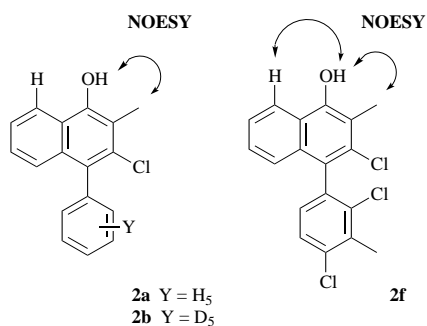
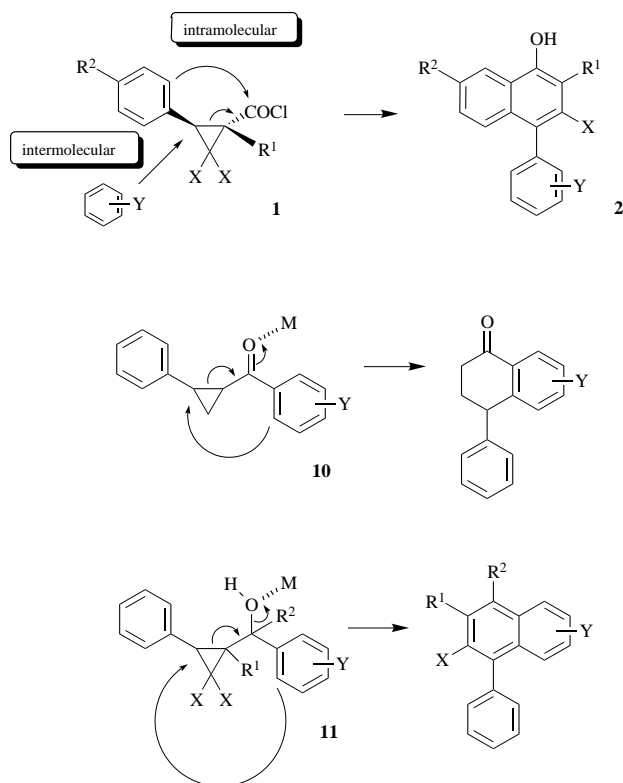


Fig. 1



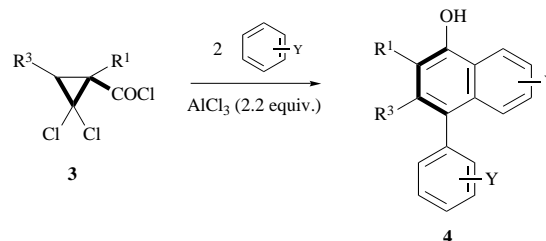
Scheme 4

tively, in the presence of AlCl₃, gave the corresponding 5-aryl-2-(*p*-methoxyphenyl)-3-methylfurans **16** in moderate yields; none of the expected 4-aryl-1-naphthols were produced. This unexpected result may be explained as follows; the *p*-methoxyphenyl group participates in stabilizing the intermediary benzyl cation **15** to such a degree that during the cyclopropane ring-opening, attack by the carbonyl oxygen at the 2-position of the cyclopropane ring occurs. This is followed by intermolecular trapping with benzenes as is described for the aforementioned benzannulations. Such a speculative mechanism could explain the reported furan formation when (*E*)-3-aryl-2,2-dihalogenocyclopropanecarbonyl chlorides (*E*)-**1** reacts with anisole (*p*-methoxybenzene).^{11c}

gem-Dihalogenocyclopropanecarbonyl chlorides **1** and **3** used as substrates throughout this study were readily prepared by a reported procedure (Scheme 8).

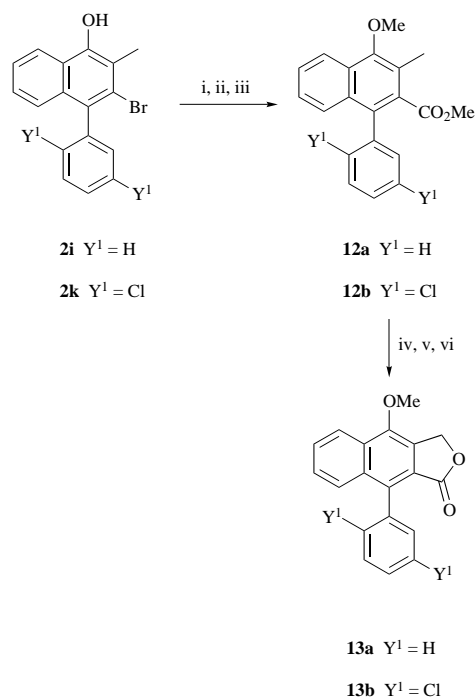
In conclusion, we have investigated two distinct types of sequential F–C reactions for new benzannulations using *gem*-dihalogenocyclopropanecarbonyl chlorides, in which various types of 4-aryl-1-naphthols were prepared. These reactions proceed in a more straightforward, one-pot manner, than the related annulations and *via* significantly different mechanisms. The variation in these annulations is unequivocally due to the high degree of site-selectivity in the ring-openings (bonds-**a** and -**b**); this behaviour is characteristic of *gem*-dihalogeno-

Table 2 Sequential Friedel–Crafts reactions of acyl chlorides **3** with benzene or *p*-xylene (Method B)



Substrate	R ¹	R ³	Y-Benzene	Product	Yield (%)
3a	H	H	Benzene	4a	38
3b	Me	Me	Benzene	4b	40
3c	Me	H	Benzene	4c	58 ^a
3c	Me	H	<i>p</i> -Xylene	4d	44

^a 3.0 Equiv. of AlCl₃ were used.



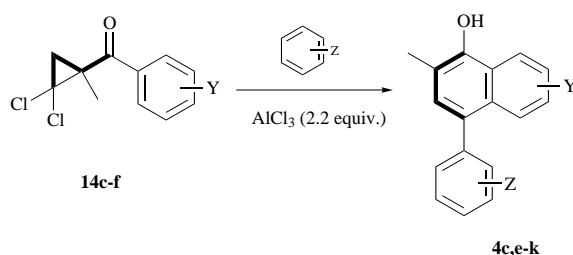
Scheme 5 Reagents and conditions: i, Bu^tLi (2.5 equiv.), THF, –60 °C; ii, CO₂; iii, K₂CO₃ (2.4 equiv.), MeI (2.4 equiv.), DMF, room temp.; iv, NBS (1.1 equiv.), cat. AIBN, CCl₄, reflux; v, 10% aq. NaOH–dioxane, 70 °C; vi, 4 M aq. HCl, room temp.

cyclopropanes. Further work on the use of *gem*-dihalogeno- or halogeno-cyclopropanes for new types of benzannulations is now underway.

Experimental

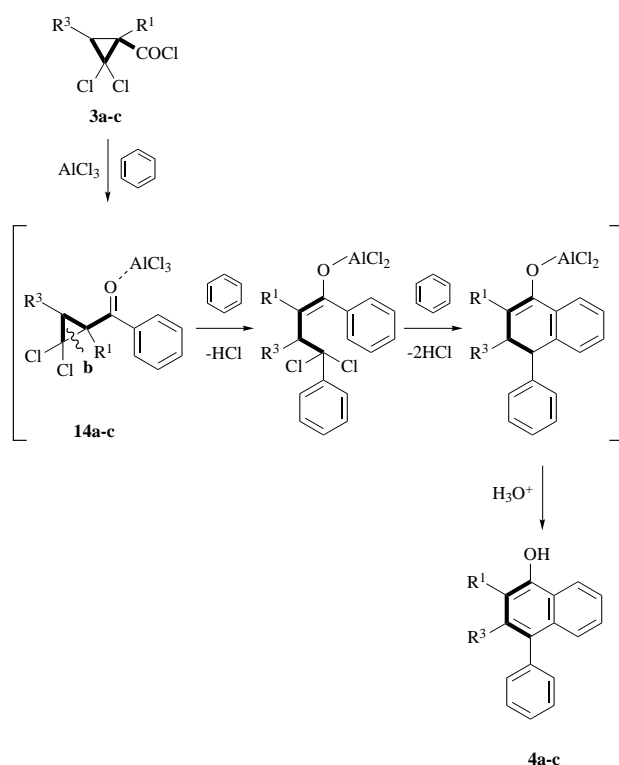
Melting points were determined on a hot-stage microscope apparatus (Yanagimoto) and are uncorrected. ¹H NMR Spectra were recorded on a JEOL EX-90 (90 MHz) and/or JEOL α (400 MHz) spectrometer in CDCl₃ using TMS as internal standard. ¹³C NMR Spectra were recorded on a JEOL α (100 MHz) spectrometer in CDCl₃ using TMS as internal standard. IR Spectra were recorded on a JASCO FT/IR-8000 spectrophotometer. Mass spectra and HRMS were recorded on JMS-AutoMass 50 KTR-3 and JMS-AX505H machines, respectively. Silica gel column chromatography was performed on a Merck Art. 7734 and/or 9385.

(1*R**,3*S**)-2,2-Dichloro-1-methyl-3-phenylcyclopropanecarbonyl chloride (*E*)-**1a**, (1*R**,3*S**)-2,2-dichloro-3-phenyl-

Table 3 Stepwise Friedel–Crafts reaction of the ketones **14** with benzenes (Method C)

Ketone	Y	Z-Benzene	Product	Yield (%)
14c	H	Benzene	4c	38
14c	H	2,6-Dichlorotoluene	4e	48 ^a
14d	4-Cl	Benzene	4f	52
14d	4-Cl	2,6-Dichlorotoluene	4g	23 ^a
14e	4-Me	Benzene	4h	32
14e	4-Me	2,6-Dichlorotoluene	4i	23 ^a
14f	3-Me	Benzene	4j	55 ^b
14f	3-Me	2,6-Dichlorotoluene	4k	43 ^{a,b}

^a Exclusively single isomer. ^b Exclusively 7-methyl isomer.

**Scheme 6**

cyclopropanecarbonyl chloride **1b** and (1*R**,3*S**)-2,2-dibromo-1-methyl-3-phenylcyclopropanecarbonyl chloride **1c** were prepared from the alcohols **17a**, **17b** and **17c**, respectively, by the reported method.^{11c}

(1*R**,3*R**)-2,2-Dichloro-1-methyl-3-phenylcyclopropanecarbonyl chloride (**Z**)-**1a**

Jones reagent (5 cm³) was added to a stirred solution of (1*R**,3*R**)-2,2-dichloro-1-methyl-3-phenylcyclopropylmethanol^{11f} (1.20 g, 5.0 mmol) in acetone (10 cm³) at 0–5 °C, and the mixture was stirred at room temp. for 24 h. Acetone was evaporated from the mixture and water was added to the residue. The mixture was then extracted with ethyl acetate (20 cm³ × 2) and the combined extracts were washed with water and brine, dried (Na₂SO₄) and concentrated to give (1*R**,3*R**)-2,2-dichloro-1-methyl-3-phenylcyclopropanecarboxylic acid (1.20 g, 98%) as

colourless crystals, mp 142–144 °C (Found: C, 54.0; H, 4.0. C₁₁H₁₀Cl₂O₂ requires C, 53.90; H, 4.11%); ν_{\max} (KBr)/cm^{−1} 3600–2400, 1714 and 1249; δ_{H} (90 MHz) 1.83 (3 H, s), 2.90 (1 H, s) and 7.30–7.60 (5 H, m). A mixture of the carboxylic acid (1.08 g, 4.4 mmol), thionyl chloride (0.63 g, 5.3 mmol) and a drop of DMF in benzene (10 cm³) was refluxed for 16 h. The mixture was then concentrated under reduced pressure and distilled by bulb-to-bulb distillation [bp 130–145 °C (oven temp.)/0.2 mmHg] to give the title product (**Z**)-**1a** (1.16 g, 95%) as colourless crystals, mp 82 °C (decomp.); δ_{H} (90 MHz) 2.01 (3 H, s), 3.05 (1 H, s) and 7.25–7.65 (5 H, m); ν_{\max} (KBr)/cm^{−1} 2984, 1807 and 1448.

(1*R**,3*S**)-3-(4-Chlorophenyl)-2,2-dichloro-1-methylcyclopropanecarbonyl chloride **1d**

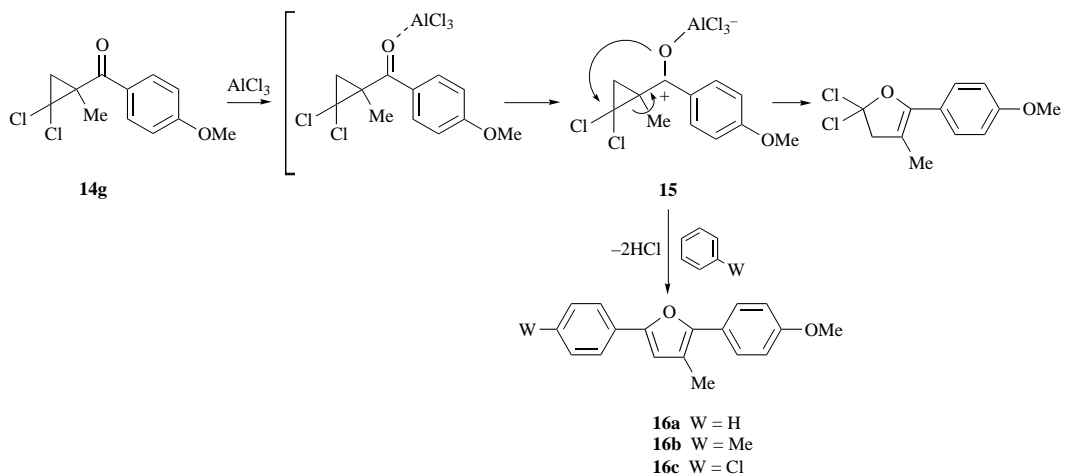
Following the procedure for preparing the acid chloride (**Z**)-**1a** described above, using the alcohol **17d**, (1*R**,3*S**)-3-(4-chlorophenyl)-2,2-dichloro-1-methylcyclopropanecarboxylic acid (87%) was obtained as colourless crystals, mp 153–154 °C (Found: C, 47.0; H, 3.1. C₁₁H₉Cl₃O₂ requires C, 47.26; H, 3.25%); δ_{H} (400 MHz) 1.42 (3 H, s), 3.59 (1 H, s), 7.22 (2 H, d, *J* 8.1) and 7.36 (2 H, d, *J* 8.1); δ_{C} 14.4, 39.1, 39.2, 65.6, 128.8, 129.8, 131.4, 133.9 and 174.9; ν_{\max} (KBr)/cm^{−1} 2993, 2880, 1705 and 1300. The acid was converted into the product **1d** (76%) by bulb-to-bulb distillation [bp 180–185 °C (oven temp.)/0.2 mmHg] as colourless crystals, mp 63–66 °C; δ_{H} (400 MHz), 1.52 (3 H, s), 3.58 (1 H, s), 7.20 (2 H, d, *J* 7.3) and 7.36 (2 H, d, *J* 7.3); ν_{\max} (KBr)/cm^{−1} 2999, 1772 and 1493.

(1*R**,3*S**)-2,2-Dichloro-3-(4-methoxyphenyl)-1-methylcyclopropanecarbonyl chloride **1e**

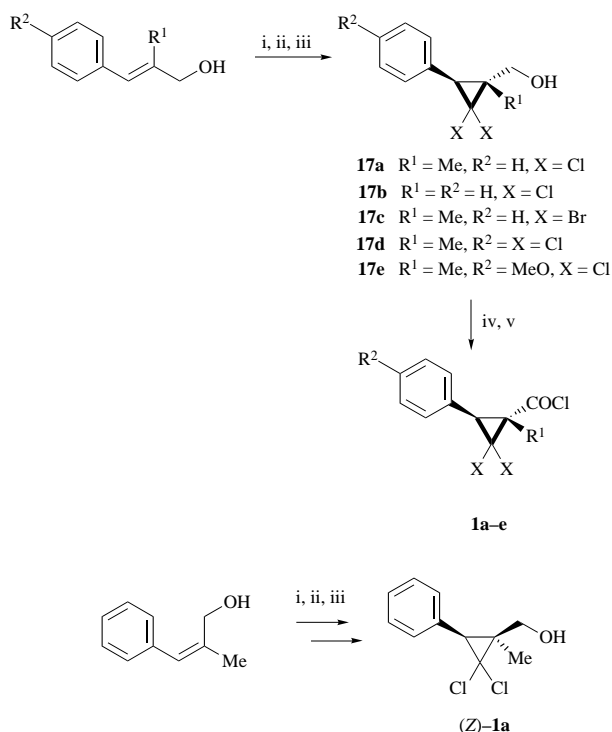
Following the procedure for preparing the acid chloride (**Z**)-**1a** described above, using the alcohol **17e**, (1*R**,3*S**)-2,2-dichloro-3-(4-methoxyphenyl)-1-methylcyclopropanecarboxylic acid (98%) was obtained as colourless crystals, mp 151–152 °C (Found: C, 52.0; H, 4.1. C₁₂H₁₂Cl₂O₃ requires C, 52.39; H, 4.40%); δ_{H} (90 MHz) 1.42 (3 H, s), 3.58 (1 H, s), 3.81 (3 H, s), 6.90 (2 H, d, *J* 8.7), 7.21 (2 H, d, *J* 8.7) and 8.50–9.70 (1 H, br, OH); ν_{\max} (KBr)/cm^{−1} 3459, 1705 and 1514. The acid was converted into the product **1e** (60%) by bulb-to-bulb distillation [bp 170–175 °C (oven temp.)/0.2 mmHg] as purple crystals, mp 68–73 °C; δ_{H} (90 MHz) 1.55 (3 H, s), 3.59 (1 H, s), 3.82 (3 H, s), 6.91 (2 H, d, *J* 8.6) and 7.20 (2 H, d, *J* 8.6); ν_{\max} (KBr)/cm^{−1} 1780, 1514 and 1250.

3-Chloro-2-methyl-4-phenyl-1-naphthol **2a** [eqn. (1)]

Method A: typical procedure. AlCl₃ (147 mg, 1.1 mmol) was



Scheme 7



Scheme 8 Reagents: i, 3,4-dihydro-2H-pyran; ii, CHX₃, 50% aq. NaOH; iii, H⁺; iv, Jones oxidation; v, SOCl₂, cat. DMF

added portion-by-portion to a stirred solution of cyclopropanecarbonyl chloride (*E*)-**1a** (132 mg, 0.50 mmol) and benzene (47 mg, 0.60 mmol) in 1,2-dichloroethane (2.5 cm³) at 0–5 °C, and the mixture was stirred at room temp. for 10 h. 1 M Aqueous HCl solution (*ca.* 5 cm³) and diethyl ether (*ca.* 5 cm³) were added to the cooled mixture, which was then stirred at room temp. for several min. The separated organic phase was washed with water and brine, dried (Na₂SO₄) and concentrated to give a crude oil. This was purified by silica gel column chromatography (hexane–diethyl ether, 8 : 1) to give the *product 2a* (70 mg, 52%) as colourless crystals, mp 85–88 °C (Found: C, 75.6; H, 4.5. C₁₇H₁₃ClO requires C, 75.98; H, 4.88%); δ_H(400 MHz) 2.52 (3 H, s), 5.32 (1 H, br s, OH), 7.22–7.38 (4 H, m), 7.40–7.55 (4 H, m) and 8.14 (1 H, d, *J* 7.4); δ_C 13.5, 115.6, 121.0, 122.9, 125.1, 125.3, 126.7, 127.4, 127.9, 128.3, 128.6, 130.7, 130.9, 132.3, 133.5, 138.6 and 148.8; ν_{max}(KBr)/cm^{−1} 3532, 3484, 1576, 1520 and 1506. Molar amounts of AlCl₃ were optimized as follows: 1.1 equiv. [*vs.* (*E*)-**1a**, 43%; 3.3 equiv.; 52%]. Under the identical conditions Et₂AlCl, SnCl₄, ZnCl₂, BF₃·OEt₂ or CF₃CO₂H failed to react. The reaction with TiCl₄ was very sluggish.

3-Chloro-2-methyl-4-(pentadeuteriophenyl)-1-naphthol **2b** [eqn. (2)]

Following the procedure of Method A described above, with [²H₆]benzene in place of benzene, the product **2b** (50%) was obtained as colourless crystals, mp 85–88 °C; δ_H(400 MHz) 2.51 (3 H, s), 5.32 (1 H, br s, OH), 7.24–7.54 (3 H, m) and 8.12 (1 H, d, *J* 7.4); ν_{max}(Nujol)/cm^{−1} 3532, 3492, 1578 and 1502.

(1*R,3*R**)-2,2-Dichloro-1-methyl-3-phenylcyclopropyl(pentadeuteriophenyl)methanone **5**.** According to the reported procedure^{11c} using C₆D₅MgBr in place of PhMgBr, the product **5** (65%) was obtained as colourless oil; δ_H(90 MHz) 1.44 (3 H, s), 3.58 (1 H, s) and 7.27–7.48 (5 H, m); ν_{max}(neat)/cm^{−1} 1686, 1244 and 1157.

3-Chloro-2-methyl-4-phenyl-5,6,7,8-tetradeuterio-1-naphthol **6 [eqn. (3)].** AlCl₃ (248 mg, 1.86 mmol) was slowly added portion-by-portion to a stirred solution of (1*R**,3*S**)-2,2-dichloro-1-methyl-3-phenylcyclopropyl(pentadeuteriophenyl)methanone (262 mg, 0.85 mmol) in 1,2-dichloroethane (4 cm³) at 0–5 °C, and the mixture was stirred at room temp. for 10 h. Work-up similar to that of Method A gave the product **6** (65 mg, 28%) together with 3-chloro-4-methyl-5-(pentadeuteriophenyl)-2-phenylfuran (93 mg, 40%).^{11c} Compound **6**: colourless crystals, mp 110–112 °C; δ_H(400 MHz) 2.51 (3 H, s), 5.32 (1 H, br s, OH), 7.20–7.35 (2 H, m) and 7.40–7.55 (3 H, m); ν_{max}(KBr)/cm^{−1} 3532, 3492, 1558 and 1462. 3-Chloro-4-methyl-5-(pentadeuteriophenyl)-2-phenylfuran: colourless crystals, mp 70–76 °C; δ_H(400 MHz) 2.29 (3 H, s), 7.28–7.35 (1 H, m), 7.42–7.48 (2 H, m) and 8.01 (2 H, d, *J* 8.3); ν_{max}(KBr)/cm^{−1} 2926, 2276 and 1564.

Controlled reaction using acyl chloride (*E*)-1a** in the absence of benzene [eqn. (4)].** AlCl₃ (293 mg, 2.2 mmol) was added portion-by-portion to a stirred solution of the carbonyl chloride (*E*)-**1a** (263 mg, 1.00 mmol) in 1,2-dichloroethane (5 cm³) at 0–5 °C, and the mixture was stirred at room temp. for 10 h. Following the work-up procedure of Method A, a crude oil was obtained which was purified by silica gel column chromatography (hexane–diethyl ether, 5 : 1) to afford 8,8-dichloro-2-methylcyclopropa[*b*]indan-1-one **7** (48 mg, 21%) and 3,4-dichloro-2-methyl-1-naphthol **8** (50 mg, 22%). Compound **7**: colourless crystals, mp 65–67 °C; δ_H(400 MHz) 1.72 (3 H, s), 3.20 (1 H, s), 7.40–7.45 (1 H, m), 7.54–7.62 (2 H, m) and 7.70 (1 H, d, *J* 7.7); δ_C 11.8, 42.1, 44.4, 75.9, 124.5, 126.4, 128.8, 134.5, 136.0, 148.6 and 198.1; ν_{max}(KBr)/cm^{−1} 1725, 1620 and 1303; *m/z* (EI) 226 (M⁺), 193 and 191 (M⁺ – Cl). Compound **8**: colourless crystals; mp 118–120 °C; δ_H(400 MHz) 2.50 (3 H, s), 5.27 (1 H, br s, OH), 7.50–7.62 (2 H, m), 8.10 (1 H, d, *J* 8.5) and 8.21 (1 H, d, *J* 8.5); δ_C 13.9, 116.6, 121.5, 122.0, 123.7, 124.7, 126.2, 127.5, 130.2, 131.7 and 148.1; ν_{max}(KBr)/cm^{−1} 3374, 1586 and 1263; *m/z* (EI) 226 (M⁺), 193 and 191 (M⁺ – Cl).

Controlled reaction using the acyl chloride (*Z*)-1a** in the pres-**

ence or absence of benzene [eqn. (5)]. Following the procedure of the controlled reaction using (*E*)-**1a** described above, reaction using the acyl chloride (*Z*)-**1a** gave the tricyclic product **7** (64% with benzene; 70% without benzene), wherein neither of the naphthols **2a** and **8** was detected.

Controlled reaction using the tricyclic ketone **7 in the presence or absence of benzene [eqn. (6)].** Following the procedure of the controlled reaction described above, a reaction using the tricyclic product **7** was carried out. It resulted in quantitative recovery of starting material both *with* and *without* benzene.

3-Chloro-2-methyl-4-(*p*-tolyl)-1-naphthol **2c (Method A).** The crude product which was roughly purified with silica gel column chromatography contained *ca.* 10% of the *o*-tolyl or *m*-tolyl regioisomer. This mixture was further purified chromatographically to give the pure product **2c** as colourless crystals, mp 138–143 °C; δ_{H} (90 MHz) 2.31 (3 H, s), 2.49 (3 H, s), 5.20 (1 H, br s, OH), 7.00–7.70 (7 H, m) and 8.00 (1 H, d, *J* 7.4); ν_{max} (KBr)/cm⁻¹ 3573, 1597, 1196 and 704; *m/z* (EI) 282.0808 (M⁺. C₁₈H₁₅ClO requires 282.0813).

3-Chloro-4-(4-chlorophenyl)-2-methyl-1-naphthol **2d (Method A).** The product **2d** containing *ca.* 35% of the 2-chlorophenyl regioisomer was obtained as an amorphous solid; δ_{H} (90 MHz) 2.53 (3 H \times 4/11, s, 2-Cl-compound), 2.55 (3 H \times 7/11, s), 5.52 (1 H, br s, OH), 7.02–7.90 (7 H, m) and 8.17 (1 H, d, *J* 8.4); ν_{max} (KBr)/cm⁻¹ 3564, 1574 and 760; *m/z* (EI) 302.0224 (M⁺. C₁₇H₁₂Cl₂O requires 302.0266).

3-Chloro-4-(4-bromophenyl)-2-methyl-1-naphthol **2e (Method A).** The product **2e** containing *ca.* 20% of the 2-bromophenyl regioisomer was obtained as an amorphous solid; δ_{H} (90 MHz) 2.52 (3 H \times 1/5, s, 2-Br-compound), 2.54 (3 H \times 4/5, s), 5.45 (1 H, br s, OH), 7.05–7.90 (7 H, m) and 8.08–8.30 (1 H, m); ν_{max} (KBr)/cm⁻¹ 3565 and 1573; *m/z* (EI) 345.9759 (M⁺. C₁₇H₁₂BrClO requires 345.9761).

3-Chloro-4-(2,4-dichloro-3-methylphenyl)-2-methyl-1-naphthol **2f (Method A).** Light brown crystals, mp 171–173 °C (Found: C, 61.1; H, 3.8. C₁₈H₁₃Cl₃O requires C, 61.48; H, 3.73%); δ_{H} (400 MHz) 2.53 (3 H, s), 2.58 (3 H, s), 5.32 (1 H, br s, OH), 7.04 (1 H, d, *J* 8.3), 7.16 (1 H, d, *J* 8.5), 7.36 (1 H, dd, *J* 8.5, 7.7), 7.42 (1 H, d, *J* 8.3), 7.48 (1 H, dd, *J* 8.3, 7.7) and 8.35 (1 H, d, *J* 8.3); δ_{C} 149.3, 136.3, 136.1, 135.1, 134.8, 132.7, 131.5, 129.8, 128.1, 127.6, 126.8, 125.5, 125.4, 122.8, 121.3, 115.5, 18.1 and 13.4; ν_{max} (KBr)/cm⁻¹ 3572, 3500, 1576, 1504 and 1368.

3-Chloro-4-(2,5-dichlorophenyl)-2-methyl-1-naphthol **2g (Method A).** Colourless crystals, mp 151–152 °C (Found: C, 60.1; H, 3.5. C₁₇H₁₁Cl₃O requires C, 60.48; H, 3.28%); δ_{H} (400 MHz) 2.53 (3 H, s), 5.45–5.50 (1 H, br, OH), 7.18 (1 H, d, *J* 8.4), 7.28 (1 H, d, *J* 2.1), 7.36–7.44 (2 H, m), 7.46–7.52 (2 H, m) and 8.16 (1 H, *J* 8.5); ν_{max} (KBr)/cm⁻¹ 3568, 1578, 1092 and 762.

3-Chloro-4-(4-chlorophenyl)-1-naphthol **2h (Method A).** The product **2h** containing *ca.* 30% of the 2-chlorophenyl regioisomer was obtained as an amorphous solid; δ_{H} (90 MHz) 5.69 (1 H, br s, OH), 6.95 (1 H \times 1/3, s, 2-Cl-compound), 6.98 (1 H \times 2/3, s), 7.05–7.70 (7 H, m) and 8.10–8.40 (1 H, m); ν_{max} (KBr)/cm⁻¹ 3540, 3069, 2978, 1588, 1343 and 766; *m/z* (EI) 288.0118 (M⁺. C₁₆H₁₀Cl₂O requires 288.0110).

3-Bromo-2-methyl-4-phenyl-1-naphthol **2i (Method A).** Amorphous solid (Found: C, 64.8; H, 3.8. C₁₇H₁₃BrO requires C, 65.20; H, 4.18%); δ_{H} (90 MHz) 2.56 (3 H, s), 5.32 (1 H, br s, OH), 7.20–7.60 (8 H, m) and 8.14 (1 H, d, *J* 7.4); ν_{max} (KBr)/cm⁻¹ 3567 and 1573.

3-Bromo-4-(4-chlorophenyl)-2-methyl-1-naphthol **2j (Method A).** The product **2j** containing *ca.* 40% of the 2-chlorophenyl regioisomer was obtained as an amorphous solid; δ_{H} (90 MHz) 2.58 (3 H \times 2/5, s, 2-Cl-compound), 2.60 (3 H \times 3/5, s), 5.40 (1 H, br s, OH), 7.10–7.90 (7 H, m) and 8.04–8.28 (1 H, m); ν_{max} (KBr)/cm⁻¹ 3568 and 1574; *m/z* (EI) 345.9759 (M⁺. C₁₇H₁₂BrClO requires 345.9761).

3-Bromo-4-(2,5-dichlorophenyl)-2-methyl-1-naphthol **2k (Method A).** Yellow crystals, mp 148–151 °C (Found: C, 53.1; H, 2.6. C₁₇H₁₁BrCl₂O requires C, 53.44; H, 2.90%); δ_{H} (90 MHz)

2.59 (3 H, s), 5.39 (1 H, br s, OH), 7.17 (1 H, d, *J* 8.5), 7.25 (1 H, s), 7.34–7.45 (2 H, m), 7.46–7.58 (2 H, m) and 8.16 (1 H, d, *J* 8.5); ν_{max} (KBr)/cm⁻¹ 3565, 1572 and 762.

3,7-Dichloro-2-methyl-4-phenyl-1-naphthol **2l (Method A).** Orange crystals, mp 113–116 °C (Found: C, 67.0; H, 3.8. C₁₇H₁₂Cl₂O requires C, 67.35; H, 3.99%); δ_{H} (400 MHz) 2.52 (3 H, s), 5.40 (1 H, br s, OH), 7.20–7.40 (4 H, m), 7.45–7.55 (3 H, m) and 8.17 (1 H, s); ν_{max} (KBr)/cm⁻¹ 3492, 1660, 1586 and 1496.

3,7-Dichloro-4-(2,4-dichloro-3-methylphenyl)-2-methyl-1-naphthol **2m (Method A).** Light yellow crystals, mp 178–179 °C (Found: C, 55.8; H, 3.3. C₁₈H₁₂Cl₄O requires C, 55.99; H, 3.13%); δ_{H} (400 MHz) 2.53 (3 H, s), 2.60 (3 H, s), 5.20–5.40 (1 H, br s, OH), 7.02 (1 H, d, *J* 8.3), 7.10 (1 H, d, *J* 9.0), 7.29 (1 H, d, *J* 9.0), 7.43 (1 H, *J* 8.3) and 8.18 (1 H, s); ν_{max} (KBr)/cm⁻¹ 3564, 1580, 1496 and 1344.

3-Chloro-7-methoxy-2-methyl-4-phenyl-1-naphthol **2n (Method A).** Amorphous solid; δ_{H} (400 MHz) 2.54 (3 H, s), 3.96 (3 H, s), 5.38 (1 H, br s, OH), 7.02–7.05 (1 H, d, *J* 9.2), 7.23–7.40 (3 H, m) and 7.45–7.55 (4 H, m); ν_{max} (KBr)/cm⁻¹ 3447, 2361 and 1034; *m/z* (EI) 268.0754 (M⁺. C₁₈H₁₅ClO₂ requires 268.0762).

3-Chloro-4-(2,4-dichloro-3-methylphenyl)-7-methoxy-2-methyl-1-naphthol **2o (Method A).** Brown crystals, mp 170–173 °C; δ_{H} (400 MHz) 2.52 (3 H, s), 2.58 (3 H, s), 5.60–5.75 (1 H, br, OH), 7.00–7.10 (3 H, m), 7.40 (1 H, d, *J* 8.1) and 7.38 (1 H, d, *J* 2.4); ν_{max} (KBr)/cm⁻¹ 3552, 2932, 1624, 1508 and 1228; *m/z* (EI) 379.0072 (M⁺ – H. C₁₉H₁₄Cl₃O requires 379.0061).

2-Methyl-4-phenyl-1-naphthol **4c**

Method B: typical procedure. AlCl₃ (440 mg, 3.3 mmol) was added portion-by-portion to a stirred solution of 2,2-dichloro-1-methylcyclopropanecarbonyl chloride **3c** (200 mg, 1.1 mmol) in benzene (5 cm³) at room temp., and the mixture was stirred for 10 h. Work-up was similar to that described in Method A gave a crude oil, purification of which by silica gel column chromatography (hexane–diethyl ether, 8:1) gave the product **4c** (145 mg, 58%) and 2-methyl-3-phenyl-1-naphthol (60 mg, 24%). Compound **4c**: colourless crystals, mp 73–75 °C; δ_{H} (400 MHz) 2.17 (3 H, s), 5.46 (1 H, br s, OH), 6.77 (1 H, s), 7.24–7.54 (8 H, m) and 8.15 (1 H, d, *J* 11.6); δ_{C} 20.8, 111.1, 121.3, 122.7, 124.1, 126.1, 126.3, 126.8, 128.3, 130.7, 131.2, 133.4, 134.1, 139.7 and 150.4; ν_{max} (KBr)/cm⁻¹ 3389 and 1595; *m/z* (EI) 234.1065 (M⁺. C₁₇H₁₄O requires 234.1045), 219, 202 and 189. 2-Methyl-3-phenyl-1-naphthol: yellow oil; δ_{H} (400 MHz) 2.28 (3 H, s), 5.33 (1 H, br s, OH), 7.30–7.55 (8 H, m), 7.76 (1 H, d, *J* 7.6) and 8.13 (1 H, d, *J* 7.6); *m/z* (EI) 234 (M⁺. C₁₇H₁₄O requires 234), 219, 202 and 189. ¹H NMR data for the methyl ether of 2-methyl-3-phenyl-1-naphthol were identical with reported values.²

4-Phenyl-1-naphthol **4a (Method B).** Colourless crystals, mp 133–135 °C (lit.,¹⁶ 137 °C); δ_{H} (90 MHz) 5.46 (1 H, br s, OH), 7.00–8.00 (10 H, m) and 8.02–8.30 (1 H, m).

2,3-Dimethyl-4-phenyl-1-naphthol **4b (Method B).** Amorphous solid; δ_{H} (90 MHz) 2.16 (3 H, s), 2.39 (3 H, s), 5.40 (1 H, br s, OH), 7.00–7.80 (7 H, m) and 8.02–8.20 (1 H, m); ν_{max} (neat)/cm⁻¹ 3442 and 1699; *m/z* (EI) 248.1185 (M⁺. C₁₈H₁₆O requires 248.1202).

2,2-Dichloro-1-methylcyclopropyl(phenyl)methanone **14c.** A solution of 2,2-dichloro-1-methylcyclopropanecarbonyl chloride **3c** (500 mg, 2.7 mmol) in THF (2 cm³) was added to a Grignard reagent [generated from Mg (71 mg, 3.0 mmol) and bromobenzene (466 mg, 3.0 mmol) in THF (4 cm³)] at 0–5 °C, and the mixture was stirred at 0–5 °C for 30 min. The mixture was allowed to warm to room temp. during a period of 30 min, after which it was stirred for an additional 1 h at this temperature. The mixture was poured into an ice and aqueous sat. NH₄Cl mixture, which was then extracted twice with diethyl ether. The combined extracts were washed with water and brine, dried (Na₂SO₄) and concentrated to give a crude oil. This was purified by silica-gel column chromatography (hexane–diethyl

ether, 50:1) to give the *product* **14c** (401 mg, 65%) as a colourless oil (Found: C, 57.4; H, 4.2. $C_{11}H_{10}Cl_2O$ requires C, 57.67; H, 4.40%); δ_H (90 MHz) 1.49 (1 H, d, J 6.3), 1.63 (3 H, s), 2.31 (1 H, d, J 6.3), 7.40–7.79 (3 H, m) and 7.79–7.88 (2 H, m); ν_{max} (neat)/ cm^{-1} 1688, 1453 and 1262.

2,2-Dichloro-1-methylcyclopropyl(4-chlorophenyl)methanone 14d. Following the procedure for preparing the ketone **14c** described above, but using bromochlorobenzene in the place of bromobenzene, the *product* **14d** (64%) was obtained as a colourless oil (Found: C, 49.9; H, 3.3. $C_{11}H_9Cl_3O$ requires C, 50.13; H, 3.44%); δ_H (90 MHz) 1.50 (1 H, d, J 6.4), 1.64 (3 H, s), 2.29 (1 H, d, J 6.4), 7.52 (2 H, d, J 8.1) and 7.89 (2 H, d, J 8.1); ν_{max} (neat)/ cm^{-1} 1688, 1589 and 1262.

2,2-Dichloro-1-methylcyclopropyl(*p*-tolyl)methanone 14e. Following the procedure for preparing the ketone **14c** described above, but using *p*-bromotoluene in the place of bromobenzene, the *product* **14e** (52%) was obtained as a colourless oil (Found: C, 59.0; H, 4.8. $C_{12}H_{12}Cl_2O$ requires C, 59.28; H, 4.97%); δ_H (90 MHz) 1.46 (1 H, d, J 6.3), 1.63 (3 H, s), 2.29 (1 H, d, J 6.3), 2.47 (3 H, s), 7.32 (2 H, d, J 8.1) and 7.88 (2 H, d, J 8.1); ν_{max} (neat)/ cm^{-1} 1684, 1607 and 1264.

2,2-Dichloro-1-methylcyclopropyl(*m*-tolyl)methanone 14f. Following the procedure for preparing the ketone **14c** described above, but using *m*-bromotoluene in the place of bromobenzene, the *product* **14f** (56%) was obtained as a colourless oil (Found: C, 59.0; H, 4.7. $C_{12}H_{12}Cl_2O$ requires C, 59.28; H, 4.97%); δ_H (90 MHz) 1.48 (1 H, d, J 6.4), 1.65 (3 H, s), 2.30 (1 H, d, J 6.4), 2.46 (3 H, s), 7.30–7.54 (2 H, m) and 7.66–7.90 (2 H, m); ν_{max} (neat)/ cm^{-1} 1686, 1314 and 1269.

2,2-Dichloro-1-methylcyclopropyl(4-methoxyphenyl)methanone 14g. Following the procedure for preparing the ketone **14c** described above, but using *p*-bromoanisole in the place of bromobenzene, the *product* **14g** (60%) was obtained as a colourless oil (Found: C, 55.3; H, 4.7. $C_{12}H_{12}Cl_2O_2$: C, 55.65; H, 4.97%); δ_H (90 MHz) 1.45 (1 H, d, J 7.1), 1.65 (3 H, s), 2.24 (1 H, d, J 7.1), 3.91 (3 H, s), 7.01 (2 H, d, J 9.1) and 7.94 (2 H, d, J 9.1); ν_{max} (neat)/ cm^{-1} 2936, 1678 and 1601.

Method C: typical procedure

$AlCl_3$ (147 mg, 1.1 mmol) was added portion-by-portion to a stirred solution of the ketone **14c** (115 mg, 0.50 mmol) in benzene (2.5 cm^3) at 0–5 °C, and the mixture was stirred at room temperature for 10 h. Work-up similar to that for Method A gave the naphthol **4c** (66 mg, 56%).

4-(2,5-Dimethylphenyl)-2,5,8-trimethyl-1-naphthol 4d (Method C). Amorphous solid; δ_H (400 MHz) 1.84 (3 H, s), 1.95 (3 H, s), 1.96 (3 H, s), 2.34 (3 H, s), 2.98 (3 H, s), 5.23 (1 H, br s, OH), 6.68 (1 H, s), 6.92 (1 H, s) and 7.00–7.20 (4 H, m); ν_{max} (neat)/ cm^{-1} 3526, 2967, 2932 and 1439; m/z (EI) 290.1679 (M^+ . $C_{21}H_{22}O$ requires 290.1672).

2-Methyl-4-(2,4-dichloro-3-methylphenyl)-1-naphthol 4e (Method C). Light yellow crystals, mp 126–127 °C; δ_H (400 MHz) 2.14 (3 H, s), 2.60 (3 H, s), 5.57 (1 H, br s, OH), 6.79 (1 H, s), 7.04 (1 H, d, J 8.1), 7.20 (1 H, d, J 8.0), 7.34–7.44 (2 H, m), 7.41 (1 H, d, J 8.1) and 8.21 (1 H, d, J 8.3); δ_C 18.1, 20.3, 110.9, 121.6, 122.8, 124.3, 125.1, 126.7, 127.5, 128.2, 130.0, 133.3, 133.9, 134.2, 134.9, 136.2, 137.4 and 151.1; ν_{max} (neat)/ cm^{-1} 3422, 2361 and 1655; m/z (EI) 316.0430 (M^+ . $C_{18}H_{14}Cl_2O$ requires 316.0423).

6-Chloro-2-methyl-4-phenyl-1-naphthol 4f (Method C). Amorphous solid; δ_H (400 MHz) 2.17 (3 H, s), 5.57 (1 H, br s, OH), 6.76 (1 H, s), 7.10–7.50 (7 H, m) and 8.20 (1 H, d, J 8.4); δ_C 20.8, 111.3, 121.4, 122.8, 124.2, 125.7, 126.5, 128.6, 129.8, 132.1, 132.8, 133.5, 133.9, 138.2 and 150.7; ν_{max} (Nujol)/ cm^{-1} 3540, 1580 and 1462; m/z (EI) 268.0666 (M^+ . $C_{17}H_{13}ClO$ requires 268.0656).

6-Chloro-4-(2,4-dichloro-3-methylphenyl)-2-methyl-1-naphthol 4g (Method C). Amorphous solid; δ_H (400 MHz) 2.12 (3 H, s), 2.58 (3 H, s), 5.30–5.80 (1 H, br s, OH), 6.79 (1 H, s), 7.00 (1 H, d, J 8.1), 7.10 (1 H, d, J 9.0), 7.28 (1 H, dd, J 9.0, J

2.2), 7.41 (1 H, d, J 8.1) and 8.39 (1 H, J 2.2); ν_{max} (Nujol)/ cm^{-1} 3280, 1600 and 1390; m/z (EI) 350.0026 (M^+ . $C_{18}H_{13}Cl_3O$ requires 350.0034).

2,6-Dimethyl-4-phenyl-1-naphthol 4h (Method C). Amorphous solid; δ_H (400 MHz) 2.16 (3 H, s), 2.50 (3 H, s), 5.28 (1 H, br s, OH), 6.75 (1 H, s), 7.18 (1 H, dd, J 8.5, 1.5), 7.21–7.31 (3 H, m), 7.36–7.51 (3 H, m) and 7.95 (1 H, s); ν_{max} (KBr)/ cm^{-1} 3540, 1580 and 1462; m/z (EI) 248.1199 (M^+ . $C_{18}H_{16}O$ requires 248.1202).

2,6-Dimethyl-4-(2,4-dichloro-3-methylphenyl)-1-naphthol 4i (Method C). Amorphous solid; δ_H (400 MHz) 2.10 (3 H, s), 2.52 (3 H, s), 2.61 (3 H, s), 5.39 (1 H, br s, OH), 6.75 (1 H, s), 6.90–7.50 (4 H, m) and 7.95 (1 H, s); ν_{max} (KBr)/ cm^{-1} 3422, 2361 and 1655; m/z (EI) 331.0662 ($M + H^+$. $C_{19}H_{17}Cl_2O$ requires 331.0658).

2,7-Dimethyl-4-phenyl-1-naphthol 4j (Method C). Amorphous solid; δ_H (400 MHz) 2.16 (3 H, s), 2.36 (3 H, s), 5.27 (1 H, br s, OH), 6.72 (1 H, s), 7.11 (1 H, s), 7.21–7.26 (3 H, m), 7.37–7.51 (3 H, m) and 8.06 (1 H, d, J 8.5); ν_{max} (KBr)/ cm^{-1} 3424, 2361 and 1717; m/z (EI) 248.1193 (M^+ . $C_{18}H_{16}O$ requires 248.1202).

2,7-Dimethyl-4-(2,4-dichloro-3-methylphenyl)-1-naphthol 4k (Method C). Amorphous solid; δ_H (400 MHz) 2.08 (3 H, s), 2.36 (3 H, s), 2.38 (1 H, br s, OH), 2.59 (3 H, s), 6.68 (1 H, s), 6.91 (1 H, s), 7.00 (1 H, d, J 8.3), 7.25 (1 H, d, J 8.5), 7.39 (1 H, d, J 8.3) and 8.07 (1 H, d, J 8.5); ν_{max} (KBr)/ cm^{-1} 3432, 1577 and 1455; m/z (EI) 330.0592 (M^+ . $C_{19}H_{16}Cl_2O$ requires 330.0580).

Methyl 1-(2,5-dichlorophenyl)-4-methoxy-3-methylnaphthalene-2-carboxylate 12b

Bu^+Li (1.0 M cyclohexane solution; 0.65 cm^3 , 0.65 mmol) was added to a stirred solution of 3-bromo-4-(2,5-dichlorophenyl)-2-methyl-1-naphthol **2k** (100 mg, 0.26 mmol) in THF (1 cm^3) at –60 °C, and the mixture was stirred for 1 h at the same temp. Several blocks of solid CO_2 (ca. 5 g) were added to the mixture, which was then stirred for 2 h at the same temp. The mixture was allowed to warm to room temp. during a period of 30 min after which it was stirred for an additional 30 min. Ice-aqueous 1 M HCl was added to the mixture, which was then extracted twice with diethyl ether. The combined extracts were washed with water and brine, dried (Na_2SO_4) and concentrated to give the crude 1-(2,5-dichlorophenyl)-4-hydroxy-3-methylnaphthalene-2-carboxylic acid (110 mg). K_2CO_3 (180 mg, 1.3 mmol) was added to a stirred solution of the crude naphthoic acid (110 mg) and MeI (185 mg, 1.3 mmol) in DMF (2 cm^3) at room temp. after which the mixture was stirred for 1.5 h. It was then poured into ice-water and extracted twice with diethyl ether. The combined extracts were washed with brine, dried (Na_2SO_4), concentrated and purified by silica gel column chromatography (hexane-diethyl ether, 15:1) to give the *product* **12b** (59 mg, 61%) as colourless crystals, mp 153–157 °C (Found: C, 63.7; H, 4.0. $C_{20}H_{16}Cl_2O_3$ requires C, 64.02; H, 4.30%); δ_H (400 MHz) 2.45 (3 H, s), 3.60 (3 H, s), 3.96 (3 H, s), 7.25–7.60 (6 H, m) and 8.05–8.27 (1 H, d, J 9.0); ν_{max} (KBr)/ cm^{-1} 2363, 1730 and 1583.

Methyl 4-methoxy-3-methyl-1-phenylnaphthalene-2-carboxylate 12a. Following the procedure for preparing the ester **12b** described above, with **2i** in the place of **2k**, the *product* **12a** was obtained (65%) as colourless crystals, mp 113–116 °C (Found: C, 78.3; H, 5.6. $C_{20}H_{18}O_3$ requires C, 78.41; H, 5.92%); δ_H (90 MHz) 2.45 (3 H, s), 3.50 (3 H, s), 3.96 (3 H, s), 7.20–7.70 (8 H, m) and 8.05–8.27 (1 H, m); ν_{max} (KBr)/ cm^{-1} 2946, 1732 and 1223. Note: The yield was improved by optimization after our communication.^{11b}

1-(2,5-Dichlorophenyl)-3-(hydroxymethyl)-4-methoxy-2-naphthoic acid lactone 13b

A mixture of the methyl ester **12b** (40 mg, 107 μ mol), *N*-bromosuccinimide (21 mg, 118 μ mol) and azoisobutyronitrile (1 mg, 6 μ mol) in CCl_4 (0.5 cm^3) was heated under reflux for 2 h. After this the mixture was allowed to cool to room temp., when it was diluted with water (ca. 5 cm^3) and extracted twice with

diethyl ether. The combined extracts were washed with brine, dried (Na_2SO_4) and concentrated to give the crude bromide (60 mg). 4 M Aqueous NaOH (2 cm^3) was slowly added to a stirred solution of the crude bromide (60 mg) in dioxane (2 cm^3) at 70 °C. After the mixture had been stirred at the same temp. for 2 h it was allowed to cool to room temp. and diluted with diethyl ether (ca. 5 cm^3) and 4 M aqueous HCl (adjusted to pH 1). The separated organic phase was washed with water and brine, dried (Na_2SO_4) and concentrated to give a crude oil. This was purified by silica gel column chromatography (hexane–ethyl acetate, 4:1) to give the **product 13b** (36 mg, 95%) as colourless crystals, mp 235–240 °C (Found: C, 63.15; H, 2.97. $\text{C}_{19}\text{H}_{12}\text{Cl}_2\text{O}_3$ requires C, 63.53; H, 3.37%; δ_{H} (400 MHz) 4.21 (3 H, s), 5.64 (1 H, d, J_{gem} 14.2), 5.69 (1 H, d, J_{gem} 14.2), 7.27 (1 H, d, J 3.0), 7.41–7.45 (1 H, m), 7.50 (1 H, d, J 8.8), 7.53–7.57 (2 H, m), 7.60–7.71 (1 H, m) and 8.36 (1 H, d, J 8.8); ν_{max} (KBr)/ cm^{-1} 2365, 1750 and 1589.

1-Phenyl-3-(hydroxymethyl)-4-methoxy-2-naphthoic acid lactone 13a. Following the procedure for preparing the ester **13b** described above, with **12a** in the place of **12b**, the **product 13a** (98%) was obtained as colourless crystals, mp 181–184 °C (Found: C, 78.4; H, 4.6. $\text{C}_{19}\text{H}_{14}\text{O}_3$ requires C, 78.61; H, 4.86%; δ_{H} (400 MHz) 4.19 (3 H, s), 5.31 (2 H, s), 7.33–7.40 (2 H, m), 7.45–7.54 (4 H, m), 7.60–7.71 (1 H, m), 7.75 (1 H, d, J 8.05) and 8.35 (1 H, d, J 8.31); ν_{max} (KBr)/ cm^{-1} 2922, 1760 and 1361. Note: The yield was improved by optimization after our communication.^{11b}

2-(4-Methoxyphenyl)-3-methyl-5-phenylfuran 16a

Furan synthesis: typical procedure. AlCl_3 (138 mg, 1.03 mmol) was added portion-by-portion to a stirred solution of the ketone **14g** (123 mg, 0.47 mmol) in benzene (2.2 cm^3) at room temp. and the mixture was stirred for 20 h. Work-up similar to that described in method A gave the **product 16a** (55 mg, 44%) as colourless crystals, mp 91–92 °C (Found: C, 81.5; H, 5.9. $\text{C}_{18}\text{H}_{16}\text{O}_2$ requires C, 81.79; H, 6.10%; δ_{H} (90 MHz) 2.28 (3 H, s), 3.86 (3 H, s), 6.60 (1 H, s), 6.97 (2 H, d, J 8.6) and 7.19–7.82 (7 H, m); ν_{max} (KBr)/ cm^{-1} 2365, 1607 and 1507.

2-(4-Methoxyphenyl)-3-methyl-5-(p-tolyl)furan 16b. Following the procedure for preparing the furan **16a** described above, using toluene in the place of benzene the **product 16b** (65%) was obtained as colourless crystals, mp 105–107 °C (Found: C, 80.2; H, 6.3. $\text{C}_{19}\text{H}_{18}\text{O}_2$ requires C, 81.99; H, 6.52%; δ_{H} (90 MHz) 2.28 (3 H, s), 2.36 (3 H, s), 3.82 (3 H, s), 6.51 (1 H, s), 6.96 (2 H, d, J 9.1), 7.18 (2 H, d, J 8.6), 7.60 (2 H, d, J 8.6) and 7.61 (2 H, d, J 9.1); ν_{max} (KBr)/ cm^{-1} 2920, 1601 and 1510.

5-(4-Chlorophenyl)-2-(4-methoxyphenyl)-3-methylfuran 16c. Following the procedure for preparing the furan **16a** described above, with chlorobenzene in the place of benzene, the **product 16c** (37%) was obtained as colourless crystals, mp 85–86 °C (Found: C, 72.1; H, 4.9. $\text{C}_{18}\text{H}_{15}\text{ClO}_2$ requires C, 72.36; H, 5.06%; δ_{H} (90 MHz) 2.28 (3 H, s), 3.84 (3 H, s), 6.57 (1 H, s), 6.99 (2 H, d, J 8.6), 7.33 (2 H, d, J 8.6), 7.62 (2 H, d, J 8.6) and 7.62 (2 H, d, J 8.6); ν_{max} (KBr)/ cm^{-1} 2930, 1605 and 1507.

(1*R**,3*S**)-3-(4-Chlorophenyl)-2,2-dichloro-1-methylcyclopropylmethanol 17d

A mixture of (*E*)-3-(4-chlorophenyl)-2-methylprop-2-en-1-ol (5.40 g, 40 mmol), 3,4-dihydro-2*H*-pyran (5.00 g, 59 mmol) and a little (+)-camphorsulfonic acid in diethyl ether (40 cm^3) was stored at room temp. for 10 h. Saturated aqueous NaHCO_3 was added to the mixture, which was then extracted with diethyl ether (100 $\text{cm}^3 \times 2$). The combined extracts were washed with water and brine, dried (Na_2SO_4) and concentrated to give the crude tetrahydropyranol (THP) ether (8.31 g). 50% Aqueous NaOH (32.0 g) was added to a vigorously stirred mixture of the THP ether, benzyl(triethyl)ammonium chloride (456 mg, 2.0 mmol) and chloroform (47.8 g, 0.40 mol) at 35–40 °C. After being stirred for 16 h at the same temp., the mixture was diluted with water and extracted with CH_2Cl_2 (100 $\text{cm}^3 \times 2$). The

combined extracts were washed with water and brine, dried (Na_2SO_4) and concentrated. MeOH (50 cm^3) and a little toluene-*p*-sulfonic acid were added to the residue and the mixture was stored overnight. Saturated aqueous NaHCO_3 was added to the mixture which was then evaporated to give a residue; this was extracted with diethyl ether. The extract was washed with water and brine, dried (Na_2SO_4), and concentrated. Recrystallization of the residue from hexane–diethyl ether (5:1) gave the **product 17d** (5.17 g, 63%) as colourless crystals, mp 127–128 °C (Found: C, 49.6; H, 4.4. $\text{C}_{11}\text{H}_{11}\text{Cl}_3\text{O}$ requires C, 49.75; H, 4.17%; δ_{H} (400 MHz) 1.28 (3 H, s), 2.65 (1 H), 3.86 (1 H, d, J_{gem} 11.7), 4.01 (1 H, d, J_{gem} 11.7), 7.18–7.23 (2 H, m) and 7.30–7.35 (2 H, m); δ_{C} 15.0, 36.4, 39.1, 69.0, 69.2, 128.6, 131.2, 131.6 and 133.4; ν_{max} (KBr)/ cm^{-1} 3225, 1491 and 1042.

(1*R,3*S**)-3-(4-Methoxyphenyl)-2,2-dichloro-1-methylcyclopropylmethanol 17e.** Following the procedure for preparing the alcohol **17d** described above, with (*E*)-3-(4-methoxyphenyl)-2-methylprop-2-en-1-ol, the **product 17e** (77%) was obtained as colourless crystals, mp 93–94 °C (Found: C, 58.6; H, 5.4. $\text{C}_{12}\text{H}_{14}\text{Cl}_2\text{O}$ requires C, 58.79; H, 5.76%; δ_{H} (400 MHz) 1.20 (3 H, s), 1.50–1.90 (1 H, s, OH), 2.56 (1 H, s), 3.74 (3 H, s), 3.78 (1 H, d, J_{gem} 11.7), 3.96 (1 H, d, J_{gem} 11.7), 6.72–6.95 (2 H, m) and 7.01–7.28 (2 H, m); ν_{max} (KBr)/ cm^{-1} 3362, 1514 and 1246.

Acknowledgements

We thank Dr Yukihiko Hashimoto, Dr Minoru Hayashi and Mr Atsushi Sudoh of Tokyo University for HRMS measurements. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (Japan).

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Paper 6/05030A

Received 18th July 1996

Accepted 24th October 1996