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**Research Article**

# Investigations into the *C*-deuteriation of silyl enol ethers derived from aryl alkyl ketones

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## Summary

Results are reported on the regioselective *C*-deuteriation of a series of silyl enol ethers derived from aryl alkyl ketones using deuterium ($D_2$) gas as the deuterium source and palladium-on-barium sulfate as the mediator. These results highlight the numerous reaction pathways and different product types available from simple deuteriation of substituted enol precursors. Copyright © 2006 John Wiley & Sons, Ltd.

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**Key Words:** alkyl aryl ketones; deuteriation; hydrogenation; palladium; reduction; silyl enol ethers and silyl ethers

## Introduction

The use of deuterium ($D_2$) gas as a *D*-source in the presence of a suitable metal catalyst has been shown to be a reliable method for selective deuterium incorporation.[1] By far, the most common approach has utilized reduction (through deuteriation) of carbon-carbon double bonds.[2] However, for π-activated enol equivalents, such as silyl enol ethers[3a] and enol esters,[3b] these processes are much less documented.

Within this area, Nakai has reported[4] the enantio- and regioselective protonation of silyl enol ether **1** using a combination of chiral catalyst {$PdCl_2$[(*R*)-BINAP] **3** and AgOTf, in the presence of molecular hydrogen to give enantiomerically enriched 2-methyl-tetralone (*R*)-**2** in 83% with 79%

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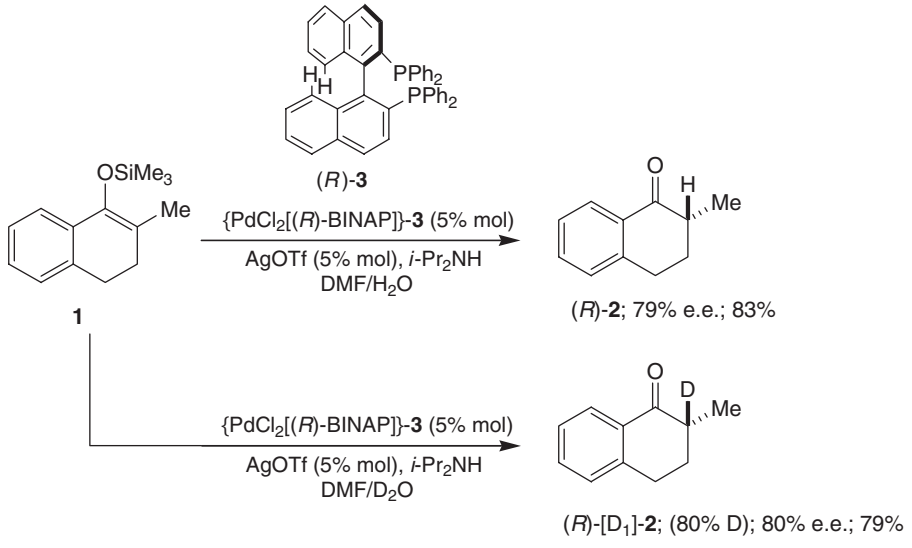
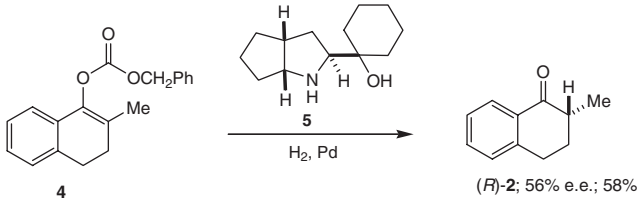



**Scheme 1.**




**Scheme 2.**

enantiomeric excess (Scheme 1).[4] By comparison, deuteriation of silyl enol ether **1** using $D_2O$ as the deuterium source gave the expected 2-deuterio-2-methyltetralone (*R*)-[$D_1$]-**2** in similar yield and enantiomeric excess, but with low deuterium incorporation (80%) (Scheme 1). This particular reaction pathway can also be achieved through hydrogenation of a related enol precursor, such as enol benzyl carbonate **4**, using palladium-on-charcoal in the presence of a chiral β-amino acid like **5**, to give the enantiomerically enriched 2-methyl-tetralone (*R*)-**2** in 58% yield with 56% enantiomeric excess (Scheme 2).[5]

We have recently become interested in these processes primarily as an indirect method for the resolution of α-substituted aryl alkyl ketones.[6,†] During our studies,[7] we have discovered that related enol acetates, like **6**, can be reduced (using $H_2$ and Pd-on-$BaSO_4$) to give acetate *syn*-**7**, with high levels of diastereoselectivity, and oxidized to give the related 2-methylnaphthoxy acetate **8** in 82 and 18% yields, respectively (Scheme 3).[7] Whereas, comparable

† For additional information see Eames *et al.*[8]



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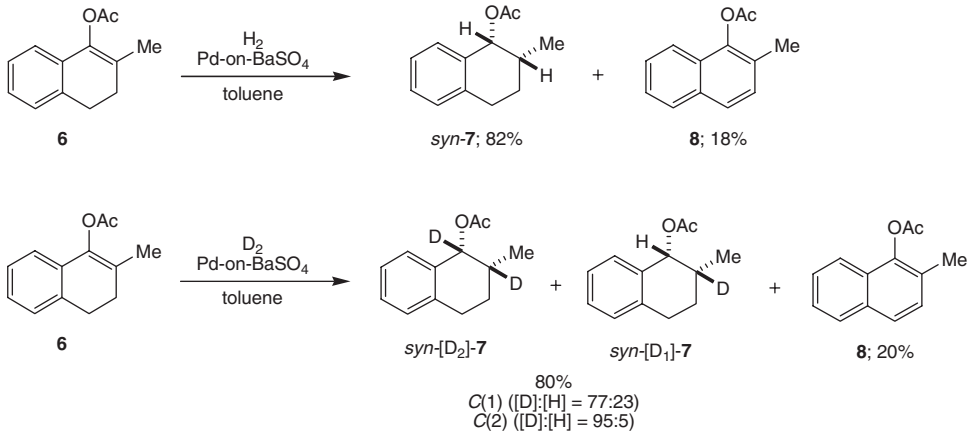


**Scheme 3.**

deuteriation of enol acetate **6** using $D_2$ in the presence of Pd-on-$BaSO_4$ gave the required *D*-labelled acetate *syn*-[$D_2$]-**7** with good levels of *D*-incorporation, and the unlabelled 2-methylnaphthoxy acetate **8** (Scheme 3).[7] These relative pathways appear to be uninfluenced by the presence of deuterium as both products *syn*-[$D_2$]-**7** and **8** were formed in similar amounts (Scheme 3). However, from this preliminary study it was evident that the structural nature of the enol derivative itself influenced the reaction pathway and product distribution.[7]

We now report our study into the regioselective *C*-deuteriation of silyl enol ethers derived from aryl alkyl ketones. We comment on factors that influence the product distribution and discuss the role these play for efficient regioselective *C*-deuteriation.

## Results and discussion

For this study, we were required to synthesize a series of structurally related silyl enol ethers **1**, **10**, **12**, **14**, **16** and **18** (Scheme 4). These silyl enol ethers were synthesised in good yield by treatment of the parent aryl alkyl ketones **2**, **9**, **11**, **13**, **15** and **17** with lithium diisopropylamide (LDA) in THF at $-78°C$, followed by the addition of trimethylsilyl chloride to the corresponding lithium enolate (Scheme 4).[8] With these compounds in hand, we first probed the hydrogenation of silyl enol ether **1** using palladium-on-barium sulphate as the mediator. Addition of silyl enol ether **1** to a stirred solution of palladium-on-barium sulphate in toluene under a hydrogen ($H_2$) atmosphere at room temperature, gave the diastereoisomerically pure[9,‡] *syn*-silyl ether **19** and 2-methyl tetralone **2** in 61 and 35% yields, respectively (Scheme 5). It is

‡The relative stereochemistry has been determined by a 400 MHz NOESY spectrum.



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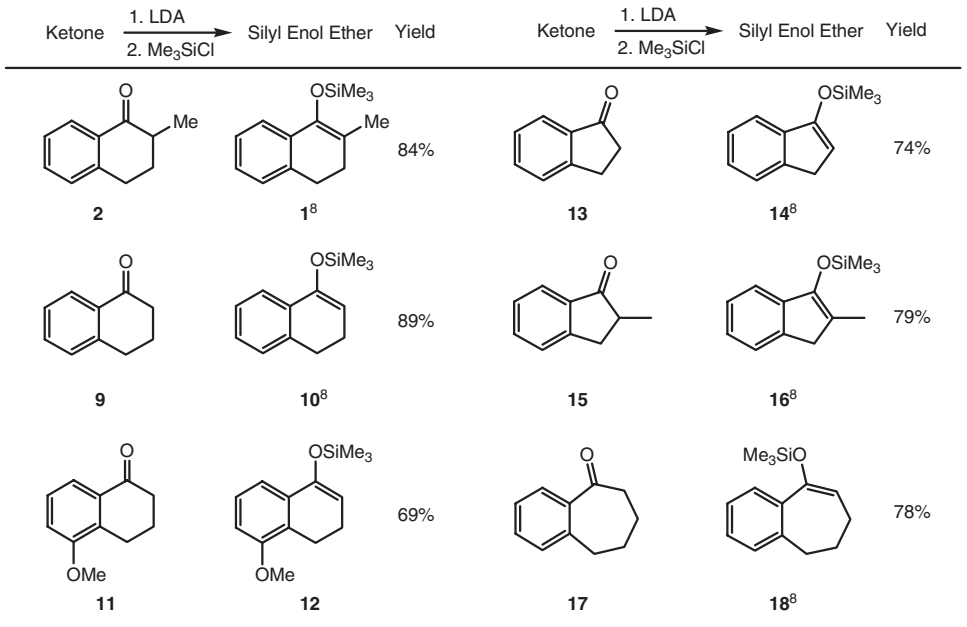
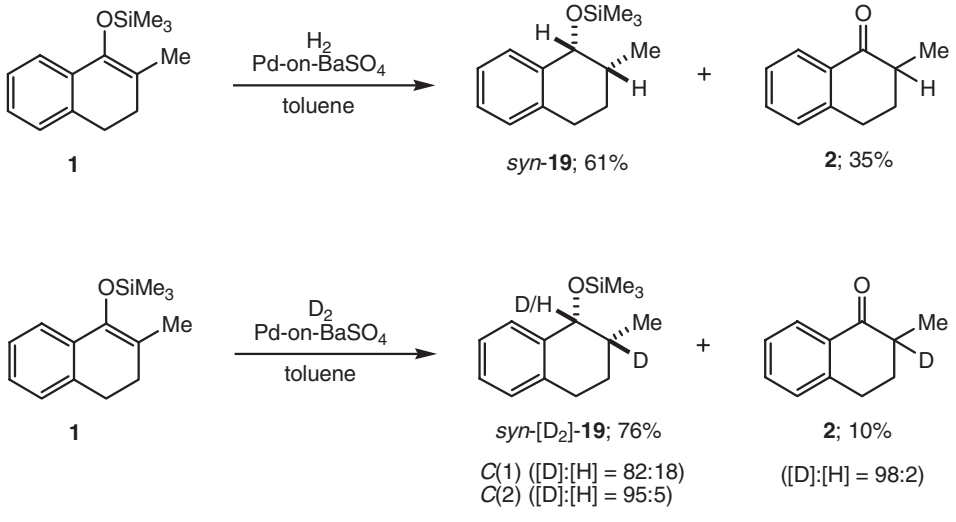



**Scheme 4.**




**Scheme 5.**

particularly interesting to note, dehydrogenation of silyl enol ether **1** (to give the corresponding 2-trimethylsilyl-2-methylnaphthyl ether) does not occur. However, reduction of its activated enol precursor (to give silyl ether *syn*-**19**) appears to be more efficient than the corresponding desilylation (to give



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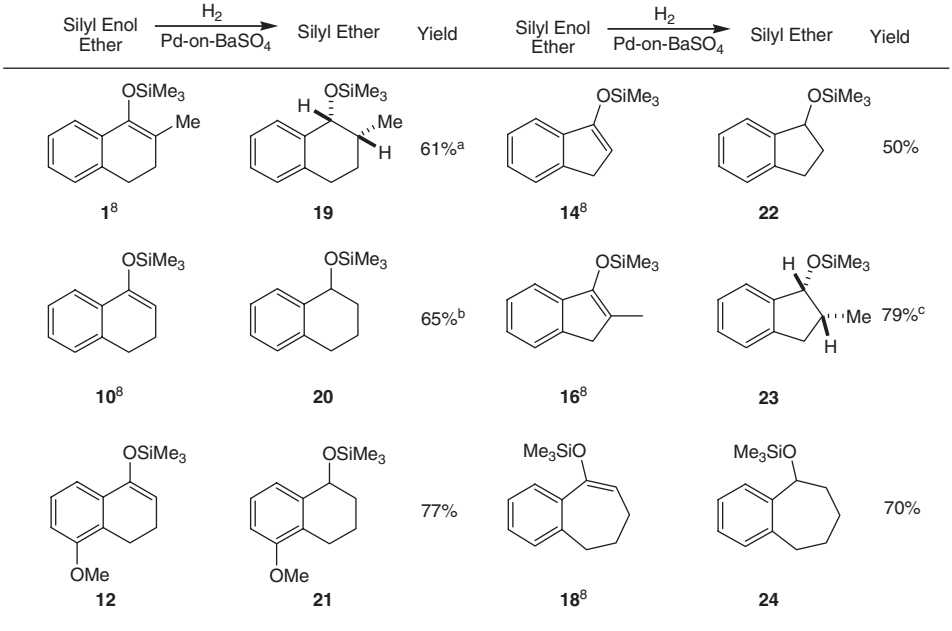
2-methyltetralone **2**) (Scheme 5). We next probed the deuteriation of silyl enol ether **1** under our standard conditions ($D_2$, Pd-on-$BaSO_4$), which gave the deuteriated *syn*-diastereoisomeric silyl ether [$D_2$]-**19** and 2-deuterio-2-methyl-tetralone [$D_1$]-**2** in 76% and 10% yields, respectively. From this study, it is apparent that near perfect isotopic incorporation had occured at the *C*(2) positions in both silyl ether *syn*-[$D_2$]-**19** and 2-deuterio-2-methyl-tetralone [$D_1$]-**2**, whereas, only moderate *D*-incorporation ([D]:[H] = 82:18) had occurred at the *C*(1) position for *syn*-[$D_2$]-**19** (Scheme 5). Under these conditions, competitive desilylation and deuteriation of **1** appears to be less favourable than analogous hydrogenation (Scheme 5).

With this information in hand, we next probed the structural nature (ring size and substitution pattern) of the tetralone framework (in **1**) by studying the hydrogenation and deuteriation of silyl enol ethers **10**, **12**, **14**, **16** and **18** to determine which components were necessary for efficient deuteriation (Schemes 6 and 7). Under our standard conditions, these silyl enol ethers **10**, **12**, **14**, **16** and **18** behaved similarly to the original silyl enol ether **1** (derived from tetralone **2**) leading to unlabelled silyl ethers **19-24** and deuteriated silyl ethers [$D_2$]-**19–24** in good yields, respectively (Schemes 6 and 7). The stereochemical outcome for these deuteriations (and related hydrogenations) appear to be *syn*-stereoselective leading to the formation of single diastereoisomeric adducts by $^1$H NMR spectroscopy (Scheme 7). The levels of




[a]**2**; 35%; [b]**9**; 11%; [c]**15**; 12%

**Scheme 6.**



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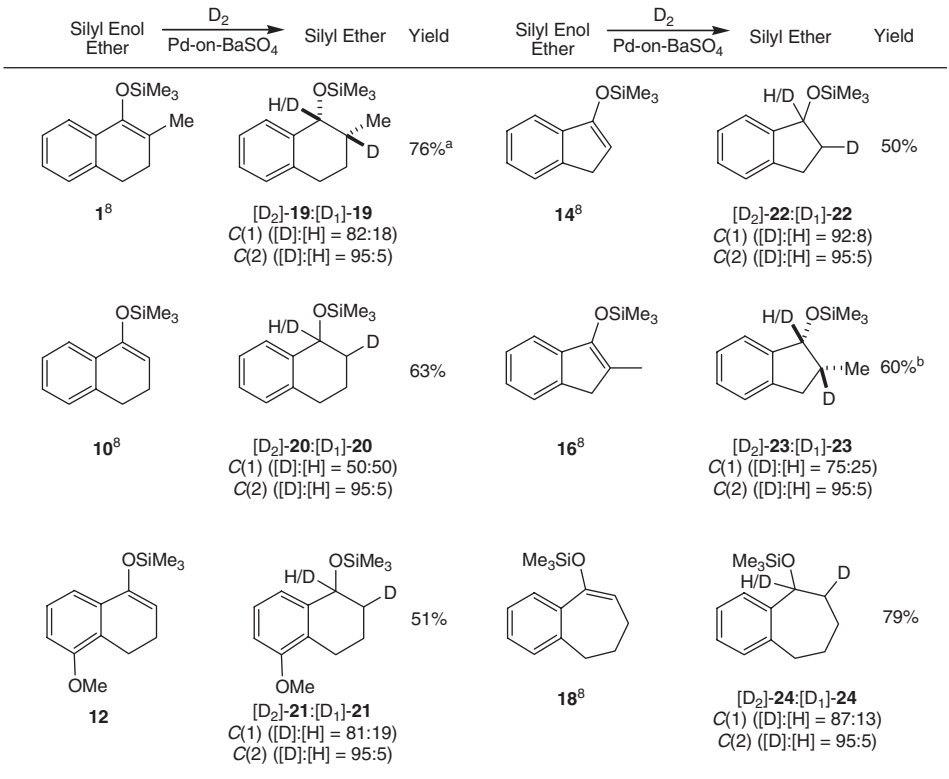


[a][D1]-**2**; 10% [(D):(H)] = 98:2; [b][D1]-**15**; 25% [(D):(H)] = 75:25

**Scheme 7.**

deuterium incorporation were characteristically higher in the *C*(2) position than the neighbouring *C*(1) position (Scheme 7). From this study, it is evident that the indenyl skeleton in **14** promoted efficient deuteriation at both *C*(1) and *C*(2) positions {[D]:[H] = 92:8 at *C*(1) and 95:5 at *C*(2), respectively} (Scheme 7). By comparison, the homologues tetralenyl and benzocycloheptenyl skeletons (in **10** and **18**) gave lower levels of deuteriation at their *C*(1) positions ([D]:[H] = 50:50 for **20** and 87:13 for **24**, respectively). Through probing the substitution pattern of these silyl enol ethers, we have found that the more substituted indenyl skeleton (in **16**) lowered the level of regioselective *C*(1) deuteriation ([D]:[H] = 75:25). For the analogous tetralenyl skeleton, increased substitution at *C*(2) appears to promote more regioselective *C*(1) deuteriation {[D]:[H] = 82:18 at *C*(1) for [$D_2$]-**19** and 50:50 at *C*(1) for [$D_2$]-**20**, respectively}. Whereas, by increasing the nucleophilicity of the aryl ring of the silyl enol ether through the use of a methyoxytetralenyl skeleton (in **12**) increased the levels of deuteriation to 81:19 ([D]:[H]) for [$D_2$]-**21**.



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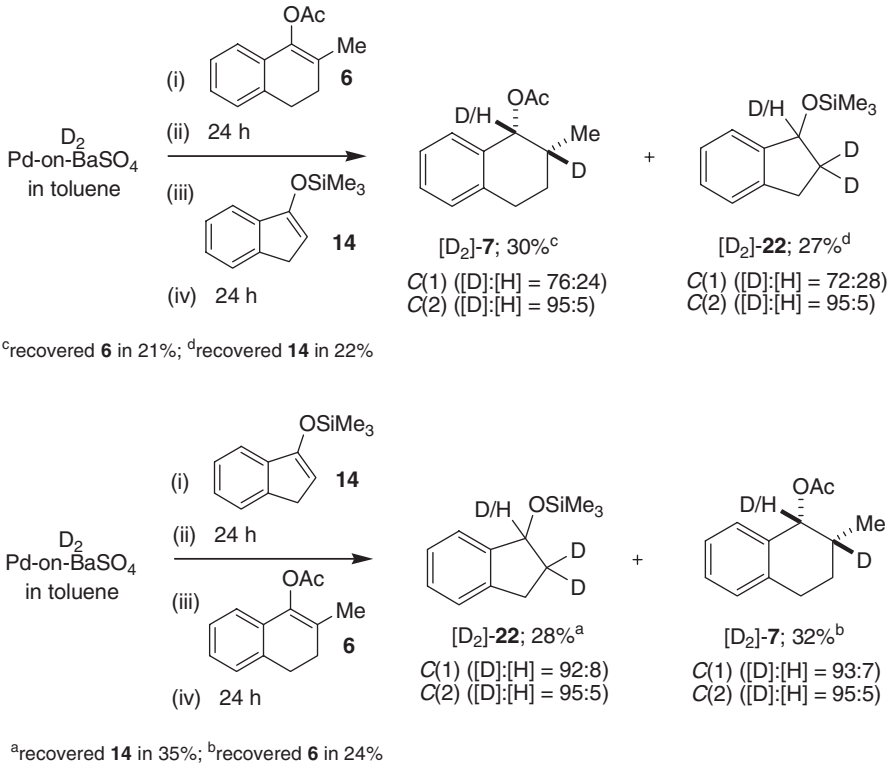


**Scheme 8.**

However, the role of the palladium catalyst was found to be important for the outcome of these deuteriations (Scheme 8). Attempts at pre-activating the palladium catalyst by pre-reduction of the enol acetate **6** (using palladium-on-barium sulphate) to give [$D_2$]-**7**; [D]:[H] = 76:24 (30% yield), followed by sequential deuteriation of silyl enol ether **14** gave the required silyl ether [$D_2$]-**22** with reduced deuterium incorporation at its *C*(2)-position {[D]:[H] = 72:28 (27% yield)}. By comparison, using silyl enol ether **14** as the suicide alkene, followed by deuteriation of enol acetate **6**, gave the silyl ether [$D_2$]-**22** {*C*(2) position [D]:[H] = 92:8 (28% yield)} and acetate [$D_2$]-**7** {*C*(2) position [D]:[H] = 93:7 (32% yield)} with much better levels of deuterium incorporation (Scheme 8). For the silyl enol ether **14**, the levels of deuterium incorporation were unsurprising due to the propensity of enol acetate **6** to oxidize (thought the loss of hydrogen) to form the unlabelled 2-methylnaphthoxy acetate **8** under these reaction conditions (as shown in Scheme 3). By comparison, the levels of deuterium incorporation for acetate [$D_2$]-**7** increased from [D]:[H] = 77:23 to 93:7 through using the silyl enol ether **14** as a suicide alkene (Scheme 8). Clearly, the structural nature of the 'active'-catalyst appears to be very important on the outcome and the levels of deuterium incorporation.



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From this study it is apparent that the reaction pathway for hydrogenation (or deuteriation) of a seemingly simple enol equivalent is non-trivial. We have shown that hydrogenation of silyl enol ether **1** and enol acetate **6**[7] under our standard conditions (Pd-on-$BaSO_4$) can lead to the corresponding reduced silyl ether *syn*-**19** and acetate *syn*-**7**,[7] respectively (Schemes 3 and 5). Preferential formation of the parent ketone, tetralone **2**, although enantiomerically enriched can be achieved by analogous hydrogenation of related carbonate **4** (via the intermediate enol(ate) **25** through palladium mediated hydrogenation in the presence of **5)**,[5] and by protonation of the silyl enol ether **1** (using (*R*)-**3**, Pd(II)$Cl_2$, AgOTf in DMF and $H_2O$)[4] (Schemes 1 and 2).

In conclusion, we have shown that regioselective *C*-deuteriation of a silyl enol ether (e.g. **14**) can occur efficiently to give the corresponding dideuteriated silyl ether (e.g. [$D_2$]-**22**) in good yield. The overall levels of deuterium incorporation were found to be highly dependent on the structural and electronic nature of the parent silyl enol ether used; an indenyl skeleton gave higher levels of incorporation than larger tetralenyl and benzocycloheptenyl homologues. For all cases so far studied, the levels of *D*-incorporation were characteristically near perfect at the *C*(2) position but moderate at the neighbouring *C*(1) position. We are currently investigating the mechanistic outcome of these reactions and this study will be reported in due course.

## Experimental

### *General*

All solvents were distilled before use. Tetrahydrofuran (THF) was freshly distilled from sodium and triphenylmethane was used as the indicator. All reactions were carried out under nitrogen using oven-dried glassware. Flash column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh). Thin layer chromatography (TLC) was carried out on commercially available pre-coated plates (Merck Kieselgel 60$F_{254}$ silica). Proton and carbon NMR spectra were recorded on a JEOL EX 270, and Bruker AM 250, AMX 400 and AM 600 Fourier transform spectrometers (using an internal deuterium lock). Chemical shifts are quoted in parts per million downfield from tetramethylsilane. Carbon NMR spectra were recorded with broad proton decoupling. Infrared spectra were recorded on a Shimadzu 8300 FTIR spectrometer and mass spectra were recorded on a Kratos 50MSTC spectrometer using a DS503 data system for high-resolution analysis. Deuterium gas (99.8% atom D)(ISOTEC INC) was purchased from Aldrich Chemical Company (cat no. 36,186-0).



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*1-Trimethylsilyloxy-5-methoxy-tetral-1-ene* **12**

Using the same method as the silyl enol ether **1**, 5-methoxy-tetralone **11** (1.0 g, 5.7 mmol), LDA (formed by addition of *n*-BuLi (2.48 ml, 2.5 M in hexane, 6.2 mmol) to diisopropylamine (0.58 g, 0.79 ml, 5.7 mmol)] in THF (10 ml) and trimethylsilyl chloride (0.62 g, 0.72 ml, 5.7 mmol) gave, after column chromatography on silica gel eluting with light petroleum (b.p. 40-60 °C)-diethyl ether (9:1) 1-trimethylsilyloxy-5-methoxy-tetral-1-ene **12** (0.97 g, 69%) as a colourless oil; $R_F$ [light petroleum (b.p. 40-60°C)-diethyl ether (9:1)] 0.75; $\nu_{max}$(film)/$cm^{-1}$ 1640 (C = C); $\delta_H$(270 MHz, $CDCl_3$) 7.17−7.06 (2 H, m, 2 × CH; Ar), 6.79 (1 H, dd, *J* 7.9 and 1.2, CH; Ar), 5.17 (1 H, t, *J* 4.7, $CH_2$), 3.81 (3 H, s, $CH_3$), 2.75 (2 H, t, *J* 7.9, $CH_2$), 2.31-2.27 (2 H, m, $CH_2$) and 0.20 (9 H, s, 3 × $CH_3$; $Si(CH_3)_3$); $\delta_C$(100 MHz, $CDCl_3$) 155.5 ($COCH_3$; Ar), 147.6 (O*C* = C), 140.4 (*i*-C; Ar), 134.4 (*i*-C; Ar), 126.0, 114.6 and 109.8 (3 × CH; Ar), 105.3 (O*C* = C), 55.3 ($OCH_3$), 21.4 and 19.9 (2 × $CH_2$), and 0.2 (3 × $CH_3$; $(CH_3)_3Si$); *m*/*z* 176.1 (100%, $MH^+$—$SiMe_3$).

*1-Trimethylsilyloxy-2-methyl-tetralane Syn-19 and 2-methyl-tetralone* **2**

Hydrogen gas (500 ml) was gradually added to a stirred solution of 1-trimethylsilyloxy-2-methyl-tetral-1-ene **1**[8] (0.2 g, 0.86 mmol) and Pd-on-$BaSO_4$ (40 mg, 5% on $BaSO_4$ unreduced) in toluene (3 ml). The resulting solution was stirred for 48 h. A solution of ethyl acetate (5 ml) was added, and the mixture was filtered and evaporated under reduced pressure. The residue was purified by flush column chromatography on silica gel eluting with light petroleum (b.p. 40–60°C)-diethyl ether (9:1) to give diastereoisomerically pure [see footnote ‡] 1-trimethylsilyloxy-2-methyl-tetralane *syn*-**19** (0.12 g, 61%) as a colourless oil; $R_F$ [light petroleum (b.p. 40–60°C)-diethyl ether (19:1)] 0.5; $\nu_{max}$(film)/$cm^{-1}$ 1600 (Ar) and 1034 (C–O); $\delta_H$ (270 MHz, $CDCl_3$) 7.29-7.25 (1 H, m, CH; Ar), 7.16–7.13 (3 H, m, 3 × CH; Ar), 4.68 (1 H, d, *J* 3.5, CHO), 2.90–2.82 (1 H, m, $CH_AH_B$), 2.76–2.71 (1 H, m, $CH_AH_B$), 1.90–1.80 (1 H, m, $CHCH_3$), 1.71–1.67 (2 H, m, $CH_2$), 0.99 (3 H, d, *J* 6.5, $CH_3$) and 0.15 (9 H, s, 3 × $CH_3$; $(CH_3)_3Si$); $\delta_C$ (100 MHz, $CDCl_3$) 141.2 (*i*−C; Ar), 135.7 (*i*−C; Ar), 128.7, 128.1, 126.3 and 125.4 (4 × CH; Ar), 71.8 (CHOSi), 33.6 ($CHCH_3$), 27.5 and 26.4 (2 × $CH_2$), 16.6 ($CH_3$) and 0.2 (3 × $CH_3$; $(CH_3)_3Si$); *m*/*z* 235.1 (100%, $MH^+$); and 2-methyl-tetralone **2** (48 mg, 35%) as a colourless oil; $R_F$ [(light petroleum (b.p. 40–60°C)-diethyl ether) (19:1)] 0.25; $\nu_{max}$(NaCl)/$cm^{-1}$ 1683 (C = O); $\delta_H$(270 MHz, $CDCl_3$) 8.05 (1 H, d, *J* 7.3 Hz, CH; Ar), 7.45 (1 H, t, *J* 7.3 Hz, CH; Ar), 7.29 (1 H, t, *J* 7.3 Hz, CH; Ar), 7.20 (1 H, d, *J* 7.3 Hz, CH; Ar), 2.98 (2 H, d quintet, *J* 7.0 and 5.5, $CH_2$), 2.57 (1 H, m, CH), 2.12 (1 H, m, CH), 1.87 (1 H, d quintet, *J* 7.0 and 4.4, CH) and 1.26 (3 H, d, *J* 6.8, $CH_3$); $\delta_C$(100 MHz, $CDCl_3$) 201.0 (C = O), 144.4 and 133.2 (2 × *i*−C; Ar), 132.5,



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128.9, 127.5 and 126.7 (4 × CH; Ar), 42.8, 31.5 and 29.0 (3 × $CH_2$) and 15.5 ($CH_3$) (Found $M^+$ 160.0882, $C_{11}H_{12}O$ requires $M^+$ 160.0882).

*1-Trimethylsilyloxy tetralane 20 and tetral-1-one* **9**

Using the same method as the silyl ether *syn*-**19**, 1-trimethylsilyloxy-tetral-1-ene **10**[8] (0.78 g, 3.59 mmol), Pd-on-$BaSO_4$ (40 mg, 5% on $BaSO_4$ unreduced), hydrogen gas (500 ml) in toluene (10 ml) gave, after column chromatography on silica gel eluting with light petroleum (b.p. 40-60°C)-ether (9:1) 1-trimethylsilyloxy tetralane **20** (0.46 g, 65%) as a colourless oil; $R_F$ [light petroleum (b.p. 40–60°C)-ether (19:1)] 0.50; $\nu_{max}$(film)/$cm^{-1}$ 1174 (CO); $\delta_H$ (270 MHz, $CDCl_3$) 7.42–7.40 (1 H, m, CH; Ar), 7.24–7.18 (2 H, m, 2 × CH; Ar), 7.17–7.05 (1 H, m, CH; Ar), 4.67 (1 H, br s, CHO), 2.85–2.71 (2 H, m, $CH_2$), 2.01–1.93 (2 H, m, $CH_2$), 1.89–1.78 (2 H, m, $CH_2$) and 0.12 (9 H, s, 3 × $CH_3$; $(CH_3)_3Si$); $\delta_C$ (100 MHz, $CDCl_3$) 139.0 (*i*−C; Ar), 136.4 (*i*−C; Ar), 128.2, 127.5, 126.5 and 125.4 (4 × CH; Ar), 68.6 (CHO), 32.5, 28.7 and 19.2 (3 × $CH_2$) and 0.0 (3 × $CH_3$; $(CH_3)_3Si$); *m*/*z* 251.1 (100%, $MH^+$); and tetral-1-one **9** (58 mg, 11%). as a colourless oil; $R_F$ [light petroleum (b.p. 40–60°C)-ether (9:1)] 0.25; $\nu_{max}$(film)/$cm^{-1}$ 1714 (C = O); $\delta_H$ (270 MHz, $CDCl_3$) 8.01 (1 H, d, *J* 7.5, CH; Ar), 7.45 (1 H, t, *J* 7.3, CH; Ar), 7.30–7.24 (2 H, m, 2 × CH; Ar), 2.95 (2 H, t, *J* 6.8, $CH_2$), 2.65 (2 H, t, *J* 6.8, $CH_2$) and 2.13 (2 H, quintet, *J* 6.8, $CH_2$); $\delta_C$ (100 MHz, $CDCl_3$) 197.8 (C = O), 144.4 (*i*−C; Ar), 133.2 (*i*−C; Ar), 132.6, 128.7, 127.0 and 126.5 (4 × CH; Ar), 39.1, 29.6 and 23.0 (3 × $CH_2$).

*1-Trimethylsilyloxy-2-methyl-indanane 23 and 2-methyl-indan-1-one* **15**

Using the same method as the silyl ether *syn*-**19**, 1-trimethylsilyloxy-2-methyl-inden-1-ene **16**[8] (0.19 g, 0.86 mmol), Pd-on-$BaSO_4$ (40 mg, 5% on $BaSO_4$ unreduced), hydrogen gas (500 ml) in toluene (2 ml) gave, after column chromatography on silica gel eluting with light petroleum (b.p, 40-60°C)-diethyl ether (19:1) the 1-trimethylsilyloxy-2-methyl-indanane **23** (0.15 g. 79%) as a colourless oil; $R_F$ [light petroleum (b.p. 40–60°C)-diethyl ether (19:1)] 0.77; $\delta_H$ (270 MHz, $CDCl_3$) 7.29–7.19 (4 H, m, 4 × CH; Ar), 5.05 (1 H, d, *J* 6.2, CHO), 2.89 (1 H dd, *J* 15.3 and 6.9, C$H_A$$H_B$), 2.66 (1 H, dd, *J* 15.3 and 5.4, $CH_A$$H_B$), 2.50–2.56 (1 H, m, C*H*$CH_3$), 0.99 (3 H, d, *J* 6.9, CHC$H_3$) and 0.18 (9 H, s, 3 × $CH_3$; $(CH_3)_3Si$); $\delta_C$ (100 MHz, $CDCl_3$) 142.4 (*i*−C; Ar), 140.5 (*i*−C; Ar), 127.3, 126.0, 124.6 and 124.1 (4 × CH; Ar), 77.0 (CHO), 38.1 (*C*$HCH_3$), 37.6 and 13.7 (2 × $CH_2$) and 0.7 (3 × $CH_3$; $(CH_3)_3Si$); *m*/*z* 221.1 (100%, $MH^+$) and 2-methyl-indan-1-one **15** (16 mg, 12%) as a colourless oil; $R_F$ [light petroleum (b.p. 40–60°C)-diethyl ether (19:1)] 0.44; $\delta_H$ (270 MHz, $CDCl_3$) 7.74 (1 H, d, *J* 7.6, CH; Ar), 7.54 (1 H, t, *J* 7.6, CH; Ar), 7.43 (1 H, d, *J* 6.6, CH; Ar), 7.34 (1 H, t, *J* 7.6, CH; Ar), 3.37 (1 H, q, *J* 7.6, $CH_A$$H_B$), 2.75–2.68 (1 H, m, $CH_A$$H_B$), 2.69–2.63 (1 H, m, C*H*$CH_3$) and 1.24 (3 H, d,



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*J* 7.2, $CHCH_3$); $\delta_C$ (100 MHz, $CDCl_3$) 209.6 (C = O), 153.4 (*i*–C; Ar), 136.3 (*i*–C; Ar), 134.6, 127.3, 126.5 and 123.9 (4 × CH; Ar), 41.9 ($CHCH_3$), 34.9 ($CH_2$) and 16.2 ($CHCH_3$); *m*/*z* 133 (100%, $MH^+$—$CH_2$).

*1-Trimethylsilyloxy-5-methoxytetralane* **21**

Using the same method as the silyl ether *syn*-**19**, 1-trimethylsilyloxy-5-methoxy-tetral-1-ene **12** (0.28 g, 1.12 mmol), Pd-on-$BaSO_4$ (40 mg, 5% on $BaSO_4$ unreduced), hydrogen gas (500 ml) in toluene (2 ml) gave, after column chromatography on silica gel eluting with light petroleum (b.p. 40–60°C)-diethyl ether (9:1) the 1-trimethylsilyloxy-5-methoxytetralane **21** (0.22 g, 77%) as a colourless oil; $R_F$ [light petroleum (b.p. 40–60°C)-diethyl ether (9:1)] 0.9; $\nu_{max}$(film)/$cm^{-1}$ 1212 (C–O); $\delta_H$ (270 MHz, $CDCl_3$) 7.14 (1 H, t, *J* 7.7, CH; Ar), 6.95 (1 H, d, *J* 7.7, CH; Ar), 6.68 (1 H, d, *J* 7.7, CH; Ar), 4.77 (1 H, t, *J* 4.5, COH), 3.76 (3 H, s, $COCH_3$), 2.66–2.59 (2 H, m, $CH_2$), 1.96–1.92 (2 H, m, $CH_2$), 1.79–1.72 (2 H, m, $CH_2$) and 0.19 (9 H, s, 3 × $CH_3$; $Si(CH_3)_3$); $\delta_C$ (100 MHz, $CDCl_3$) 156.5 (*i*–CO; Ar), 140.1 and 125.4 (2 × *i*–C; Ar), 125.1, 120.0 and 108.0 (3 × CH; Ar), 68.6 (CHO), 54.8 ($COCH_3$), 31.8 (CH), 22.3 and 18.5 (2 × $CH_2$) and 0.84 (3 × $CH_3$; $(CH_3)_3Si$); *m*/z 251.1 (100%, $MH^+$).

*1-Trimethylsilyloxy-indanane* **22**

Using the same method as the silyl ether *syn*-**19**, 1-trimethylsilyloxy-indanane **14**[8] (0.2 g, 0.97 mmol) , Pd-on-$BaSO_4$ (40 mg, 5% on $BaSO_4$ unreduced), hydrogen gas (500 ml) in toluene (2 ml) gave, after column chromatography on silica gel eluting with light petroleum (b.p. 40–60°C)-diethyl ether (9:1) the 1-trimethylsilyloxy-indanane **22** (0.10 g. 50%) as a colourless oil; $R_F$ [light petroleum (b.p. 40–60°C)-diethyl ether (9:1)] 0.86; $\nu_{max}$(film)/$cm^{-1}$ 1108 (C–O); $\delta_H$ (270 MHz, $CDCl_3$) 7.23–7.19 (4 H, m, 4 × CH; Ar), 5.23 (1 H, t, *J* 6.7, CHO), 2.98–2.95 (1 H, m, $CH_AH_B$), 2.79–2.73 (1 H, m, $CH_AH_B$), 2.40–2.36 (1 H, m, $CH_AH_B$), 1.95–1.88 (1 H, m, $CH_AH_B$) and 0.20 (9 H, s, 3 × $CH_3$; $(CH_3)_3Si$); $\delta_C$ (100 MHz, $CDCl_3$) 144.9 (*i*–C; Ar), 142.3 (*i*–C; Ar), 127.4, 126.2, 124.4 and 123.8 (4 × CH; Ar), 75.9 (CHO), 35.9 and 30.6 ($CH_2$) and 0.2 (3 × $CH_3$; $(CH_3)_3Si$); *m*/*z* 207.1 (100%, $MH^+$).

*1-Trimethylsilyloxybenzosuberane* **24**

Using the same method as the silyl ether *syn*-**19**, 1-trimethylsilyloxy-benzosuber-1-ene **18**[8] (0.19 g, 0.8 mmol), Pd-on-$BaSO_4$ (40 mg, 5% on $BaSO_4$ unreduced), hydrogen gas (500 ml) in toluene (2 ml) gave, after column chromatography on silica gel eluting with light petroleum (b.p. 40–60°C)-diethyl ether (19:1) the 1-trimethylsilyloxybenzosuberane **24** (0.13 g, 70%) as a colourless oil; $R_F$ [light petroleum (b.p. 40–60°C)-diethyl ether (19:1)] 0.9; $\nu_{max}$(film)/$cm^{-1}$ 2927 (C–H) and 1110 (C–O); $\delta_H$ (270 MHz, $CDCl_3$) 7.40 (1 H,



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d, *J* 7.1, CH; Ar), 7.13–7.06 (3 H, m, 3 × CH; Ar), 4.84 (1 H, d, *J* 6.7, CHO), 2.91–2.86 (1 H, m, $CH_AH_B$), 2.72–2.68 (1 H, m, $CH_AH_B$), 2.08–1.96 (1 H, m, $CH_CH_D$), 1.89–1.66 (4 H, m, 2 × $CH_2$), 1.48–1.41 (1 H, m, $CH_CH_D$) and 0.08 (9 H, s, 3 × $CH_3$; $Si(CH_3)_3$); $\delta_C$ (100 MHz, $CDCl_3$) 144.8 (*i*–C; Ar), 140.5 (*i*–C; Ar), 129.1, 126.4, 125.8 and 125.2 (4 × CH; Ar), 74.2 (CHO), 37.8, 35.8, 27.9 and 27.7 (4 × $CH_2$) and 0.3 (3 × $CH_3$; $(CH_3)_3Si$); *m*/*z* 235.1 (100%, $MH^+$).

*1-Trimethylsilyloxy-1,2-dideuterio-2-methyl-tetralane [$D_2$]-syn-19 and 2-methyl-2-deuterio-tetralone [$D_1$]-***2***

Under the same conditions as the silyl ether *syn*-**19**, 1-trimethylsilyloxy-2-methyl-tetral-1-ene **1**[8] (0.2 g, 0.86 mmol), Pd-on-$BaSO_4$ (40 mg, 5% on $BaSO_4$ unreduced), deuterium gas (500 ml) in toluene (2 ml) gave, after column chromatography on silica gel eluting with light petroleum (b.p. 40–60°C)-diethyl ether (9:1), 2-deuterio-2-methyl-tetralone [$D_1$]-**2** (14 mg, 10%) ([D]:[H] = 98:2) as a colourless oil; $R_F$ [light petroleum (b.p. 40–60°C)-diethyl ether (19:1)] 0.33; $\nu_{max}$(film)/$cm^{-1}$ 2106 (C–D) and 1683 (CO); $\delta_H$(250 MHz, $CDCl_3$) 8.00 (1 H, d, *J* 7.7, CH; Ar), 7.47 (1 H, dd, *J* 7.7 and 7.6, CH; Ar), 7.25 (1 H, t *J* 7.7, CH; Ar), 7.22 (1 H, d, *J* 7.6, CH; Ar), 3.00 (2 H, m, $CH_2CH{=}C$), 2.20 (1 H, dt, *J* 13.2 and 4.4, $CH_AH_B$), 1.87 (1 H, m, $CH_AH_B$) and 1.28 (3 H, s, $CH_3CD$); $\delta_C$(67.5 MHz, $CDCl_3$) 200.8 (C=O), 144.2 (*i*–C; Ar), 133.1 (*i*–C; Ar), 132.4, 128.7, 127.4 and 126.6 (4 × CH; Ar), 42.0 (1 C, t [1:1:1], *J* 19.0, CDMe), 31.3 and 28.8 (2 × $CH_2$) and 15.3 ($CH_3$) (Found $MH^+$, 162.1034. $C_{11}H_{12}DO$ requires MH, 162.1029); *m*/*z* 162 (100%, $M^+$); the isotopic shift at 42.0 ppm was 75.4. Hz (0.74 ppm at 100.6 MHz); and diastereoisomerically pure (see foonote ‡) 1-trimethylsilyloxy-1,2-dideuterio-2-methyl-tetralane [$D_2$]-*syn*-**19** (0.15 g, 76%) as a colourless oil; $R_F$ [light petroleum (b.p. 40–60°C)-diethyl ether (19:1)] 0.7; $\nu_{max}$(film)/$cm^{-1}$ 2175 (C–D) and 1058 (C–O); $\delta_H$ (270 MHz, $CDCl_3$) 7.29–7.26 (2 H, m, 2 × CH; Ar), 7.16–7.13 (2 H, m, 2 × CH; Ar), 2.90–2.81 (1 H, m, $CH_AH_B$), 2.73–2.70 (1 H, m, $CH_AH_B$), 1.82–1.77 (1 H, m, $CH_CH_D$), 1.69–1.64 (1 H, m, $CH_CH_D$), 0.99 (3 H, s $CH_3$) and 0.15 (9 H, s, 3 × $CH_3$; $(CH_3)_3Si$); $\delta_C$ (100 MHz, $CDCl_3$) 141.1 (*i*–C; Ar), 135.9 (*i*–C; Ar), 128.5, 128.0, 126.4 and 125.3 (4 × CH; Ar), 71.7 (1 C, t [1:1:1], $^1J_{C,D}$ 21.2, CDO), 33.6 (1 C, t [1:1:1], $^1J_{C,D}$ 21.2, CD), 27.3 ($CH_2$), 26.4 ($CH_2$), 16.7 ($CH_3$) and 0.2 (3 × $CH_3$; $(CH_3)_3Si$); *m*/*z* 222.1 (100%, $MH^+$).

*1-Trimethylsilyloxy-1,2-dideuteriotetralane [$D_2$]-***20**

Using the same method as the silyl ether *syn*-**19**, 1-trimethylsilyloxy-tetral-1-ene **10**[8] (0.78 g, 3.6 mmol), Pd-on-$BaSO_4$ (40 mg, 5% on $BaSO_4$ unreduced), deuterium gas (250 ml) in toluene (2 ml) gave, after column chromatography on silica gel eluting with light petroleum (b.p. 40–60°C)-diethyl ether (9:1)



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1-trimethylsilyloxy-1,2-dideuteriotetralane [$D_2$]-**20** (0.50 g, 63%) as a colourless oil; $R_F$ [light petroleum (b.p. 40–60°C)-diethyl ether (9:1)] 0.6; $\delta_H$ (270 MHz, $CDCl_3$) 7.38 (1 H, d, *J* 6.9, CH; Ar), 7.16–7.10 (3 H, m, 3 × CH; Ar), 2.75 (2 H, t, *J* 7.6, $CH_2$), 1.99–1.95 (1 H, m, CDH), 1.80–1.73 (2 H, m, $CH_2$) and 0.22 (9 H, s, 3 × $CH_3$; $Si(CH_3)_3$); $\delta_C$ (100 MHz, $CDCl_3$) 138.4 (*i*−C; Ar), 135.2 (*i*−C; Ar), 128.1, 127.9, 126.9 and 125.3 (4 × CH; Ar), 68.3 (1 C, t [1:1:1], $^1J_{C,D}$ 22.1, CDO), 32.2 (1 C, t [1:1:1], $^1J_{C,D}$ 19 Hz, CD), 26.4 and 25.5 (2 × $CH_2$) and 0.1 (3 × $CH_3$; $(CH_3)_3Si$); *m*/*z* 222.1 (100%, $M^+$). The isotopic shift at *C*(1) (68.3 ppm) was 34.2 Hz (0.34 ppm at 100.6 MHz) and at *C*(1) was 38.2 Hz (0.38 ppm at 100.6 MHz).

### *1-Trimethylsilyloxy-1,2-dideuterio-5-methoxytetralane [$D_2$]-***21**

Using the same method as the silyl ether *syn*-**19**, 1-trimethylsilyloxy-5-methoxy-tetral-1-ene **12** (0.2 g, 0.8 mmol), Pd-on-$BaSO_4$ (40 mg, 5% on $BaSO_4$ unreduced), deuterium gas (250 ml) in toluene (2 ml) gave, after column chromatography on silica gel eluting with light petroleum (b.p. 40–60°C)-diethyl ether (9:1) the 1-trimethylsilyloxy-1,2-dideuterio-5-methoxytetralane [$D_2$]-**21** (0.10 g, 51%) as a colourless oil; $R_F$ [light petroleum (b.p. 40–60°C)-diethyl ether (9:1)] 0.8; $\nu_{max}$(film)/$cm^{-1}$ 2102 (C–D); $\delta_H$(270 MHz, $CDCl_3$) 7.17 (1 H, t, *J* 7.9, CH; Ar), 6.95 (1 H, d, *J* 7.9, CH; Ar), 6.70 (1 H, d, *J* 7.9, CH; Ar), 3.78 (3 H, s, $OCH_3$), 2.66–2.54 (2 H, m, $CH_2$), 2.00–1.93 (1 H, m, CH), 1.76–1.68 (2 H, m, $CH_2$) and 0.16 (9 H, s, 3 × $CH_3$; $Si(CH_3)_3$); $\delta_C$(100 MHz, $CDCl_3$) 156.4 (*i*−CO; Ar), 140.0 and 125.3 (2 × *i*−C; Ar), 125.4, 120.0 and 108.0 (3 × CH; Ar), 68.3 (1 C, t [1:1:1], $^1J_{C,D}$ 21.0, CDO), 55.2 ($CO\mathit{C}H_3$), 31.5 (1 C, t [1:1:1], $^1J_{C,D}$ 19.0, CD), 22.5 and 18.3 (2 × $CH_2$) and 0.4 (3 × $CH_3$; $Si(CH_3)_3$); *m*/*z* 253.1 (100%, $MH^+$). The isotopic shift at *C*(1) (68.3 ppm) was 31.2 Hz (0.31 ppm at 100.6 MHz) and at *C*(2) (31.5 ppm) was 49.3 Hz (0.49 ppm at 100.6 MHz).

### *1-Trimethylsilyloxy-1,2-dideuterioindanane [$D_2$]-***22**

Using the same method as the silyl ether *syn*-**19**, 1-trimethylsilyloxy-indan-1-ene **14**[8] (0.2 g, 0.98 mmol), Pd-on-$BaSO_4$ (40 mg, 5% on $BaSO_4$ unreduced), deuterium gas (250 ml) in toluene (2 ml) gave, after column chromatography on silica gel eluting with light petroleum (b.p. 40–60°C)-diethyl ether (9:1) the 1-trimethylsilyloxy-1,2-dideuterioindanane [$D_2$]-**22** (0.1 g 50%) as a colourless oil; $R_F$ [light petroleum (b.p. 40–60°C)-diethyl ether (9:1)] 0.86; $\nu_{max}$(film)/$cm^{-1}$ 2074 (C–D); $\delta_H$(270 MHz, $CDCl_3$) 7.28–7.19 (4 H, m, 4 × CH; Ar), 2.98 (1 H, dd, *J* 15.8 and 8.7, $CH_AH_B$), 2.77 (1 H, dd, *J* 15.8 and 7.9, $CH_A\mathit{H}_B$), 1.90 (1 H, dd, 8.7 and 7.9, C*H*D) and 0.18 (3 H, s, 3 × $CH_3$; $(CH_3)_3Si$); $\delta_C$(100 MHz, $CDCl_3$) 144.9 (*i*−C; Ar), 142.4 (*i*-C; Ar), 127.4, 126.2, 124.4 and 123.8 (4 × CH; Ar), 75.5 (1 C, t [1:1:1], $^1J_{C,D}$ 22.0, CDO), 35.7 (1 C, t [1:1:1],



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$^{1}J_{C,D}$ 20.0, CHD), 29.3 ($CH_2$) and 0.2 ($3 \times CH_3$; $Si(CH_3)_3$); *m/z* 209.1 (100%, $MH^+$). The isotopic shift at *C*(1) (75.5 ppm) was 37.2 Hz (0.37 ppm at 100.6 MHz) and at *C*(2) was 35.7 Hz (35.5 ppm at 100.6 MHz).

*1-Trimethylsilyloxy-1,2-dideuterio-2-methylindanane [$D_2$]-23 and 2-deuterio-2-methyl-indan-1-one [$D_1$]-***15**

Using the same method as the silyl ether *syn*-**19**, 1-trimethylsilyloxy-2-methyl-inden-1-ene **16**[8] (0.21 g, 0.98 mmol), Pd-on-$BaSO_4$ (40 mg, 5% on $BaSO_4$ unreduced), deuterium gas (250 ml) in toluene (2 ml) gave, after column chromatography on silica gel eluting with light petroleum (b.p. 40–60°C)-diethyl ether (9:1) the 1-trimethylsilyloxy-1,2-dideuterio-2-methylindanane [$D_2$]-**23** (0.13 g, 60%) as a colourless oil; $R_F$ [light petroleum (b.p. 40–60°C)-diethyl ether (9:1)] 0.77; $\nu_{max}$(film)/$cm^{-1}$ 2074 (CD); $\delta_H$ (270 MHz, $CDCl_3$) 7.24–7.18 (4 H, m, $4 \times CH$), 2.90 (1 H, d, *J* 9.3, $CH_AH_B$), 2.65 (1 H, d, *J* 9.3, $CH_AH_B$), 1.01 (3 H, s, $CH_3$) and 0.22 (9 H, s, $3 \times CH_3$; $(CH_3)_3Si$); $\delta_C$ (100 MHz, $CDCl_3$) 147.2 (*i*–C; Ar), 142.4 (*i*–C; Ar), 127.3, 126.0, 125.6 and 124.1 ($4 \times CH_2$), 77.0 (1 C, t, $^{1}J_{C,D}$ 22.1, CDO), 39.2 (1 C, t, $^{1}J_{C,D}$ 20.0, CD), 37.5 ($CH_2$), 13.6 ($CH_3$) and 0.41 ($3 \times CH_3$; $(CH_3)_3Si$); (*m/z*) 132.1 (50, [$D_2$]-M—$Me_3SiOD$ + H) and 131.1 (100, [$D_1$]-M—$Me_3SiOD$ + H); the isotopic shift at *C*(2) (39.2 ppm) was 20.1 Hz (0.20 ppm at 100.6 MHz), whereas, the isotopic shift at *C*(1) (77.0 ppm) could not be measured accurately due to overlap with $CDCl_3$; and 2-deuterio-2-methyl-indan-1-one [$D_1$]-**15** (36 mg, 25%) ([D]:[H] = 75:25); $R_F$ [light petroleum (b.p. 40–60°C)-diethyl ether (9:1)] 0.40; $\nu_{max}$(film)/$cm^{-1}$ 1716 (CO); $\delta_H$ (250 MHz, $CDCl_3$) 7.76 (1 H, d, *J* 7.6, CH, Ar), 7.58 (1 H, t, *J* 7.6, CH, Ar), 7.45 (1 H, d, *J* 7.6, CH, Ar), 7.35 (1 H, t, *J* 7.6, CH, Ar), 3.39 (1 H, d, *J* 17.1, $CH_AH_B$), 2.72 (1 H, d, *J* 17.1, $CH_AH_B$) and 1.30 (3 H, s, Me); $\delta_C$(67 MHz, $CDCl_3$) 209.5 (C = O), 153.5 (*i*–C; Ar), 136.4 (*i*–C; Ar), 134.6, 127.3, 126.6 and 124.0 ($4 \times CH$; Ar), 41.5 (1 C, t [1:1:1], $^{1}J_{C,D}$ 20.1, CDMe), 34.9 ($CH_2$) and 16.2 ($CH_3$); *m/z* 147.1 (42%, [$D_0$]-$M^+$) and 33 (100, [$D_0$]-$MH^+$—$CH_2$); the isotopic shift at *C*(2) (41.5 ppm) was 42.3 Hz (0.42 ppm at 100.6 MHz).

*1-Trimethylsilyloxy-1,2-dideuteriobenzosuberane [$D_2$]-***24**

Using the same method as the silyl ether *syn*-**19**, 1-trimethylsilyloxy-benzosuber-1-ene **18**[8] (0.19 g, 0.8 mmol), Pd-on-$BaSO_4$ (40 mg, 5% on $BaSO_4$ unreduced), deuterium gas (250 ml) in toluene (2 ml) gave, after column chromatography on silica gel eluting with light petroleum (b.p. 40–60°C)-diethyl ether (9:1) the 1-trimethylsilyloxy-1,2-dideuteriobenzosuberane [$D_2$]-**24** (0.15 g, 79%) as a colourless oil; $R_F$ [light petroleum (b.p. 40–60°C)-diethyl ether (9:1)] 0.9; $\nu_{max}$(film)/$cm^{-1}$ 2097 (C–D) and 1194 (C–O); $\delta_H$ (270 MHz, $CDCl_3$) 7.39 (1 H, d, *J* 7.6, CH; Ar), 7.18–7.03 (3 H, m, $3 \times CH_3$), 2.95–2.87



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(1 H, m, $CH_AH_B$), 2.72–2.63 (1 H, m, $CH_AH_B$), 2.02–1.98 (1 H, m, $CH_CH_D$), 1.76–1.68 (3 H, m, $CH_2$ and CHD), 1.52–1.40 (1 H, m, $CH_CH_D$) and 0.08 (9 H, s, $3 \times CH_3$; $Si(CH_3)_3$); $\delta_C$ (100 MHz, $CDCl_3$) 144.7 (*i*−C; Ar), 140.6 (*i*−C; Ar), 126.1, 126.5, 125.8 and 125.2 ($4 \times$ CH; Ar), 74.8 (1 C, t [1:1:1], $^1J_{C,D}$ 21.0, CDO), 37.2 (1 C, t [1:1:1], $^1J_{C,D}$ 20.0, CDH), 35.8, 27.8 and 27.6 ($3 \times CH_2$) and 0.3 ($3 \times CH_3$; $Si(CH_3)_3$); *m*/*z* 146.1 (100%, $[D_2]$-M—$Me_3SiOD$ + H) and 145.1. (50, $[D_1]$-M—$Me_3SiOD$ + $H^+$); *m*/*z* 235.1 (100%, $MH^+$). The isotopic shift at *C*(1) (74.8 ppm) was 35.2 Hz (0.35 ppm at 100.6 MHz).

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