

Reagents for Diverse Iodosilane-Mediated Transformations

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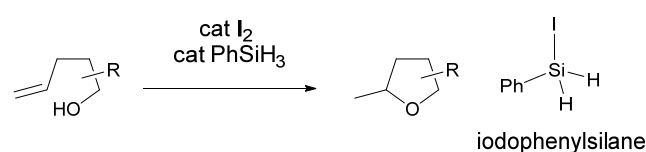
It was observed that a PhSiH₂I-mediated protocol using PhSiH₃ and cat. I₂ caused the deiodination of 2-iodomethyltetrahydrofuran. Stemming from the investigation of the mechanism, we found that the PhSiH₃-I₂ system selectively promotes diverse cascade transformations from cyclic ethers to acyclic alkyl iodides, and the PhSiH₃-N-iodosuccinimide (NIS) system also promotes cascade transformations from cyclic ethers to acyclic alcohols.

Introduction

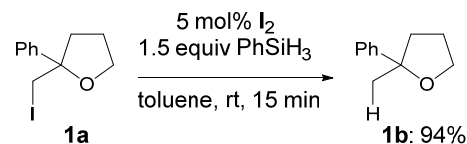
Organosilicon reagents enable various indispensable reaction in organic chemistry owing to their unique property.¹⁻³ Hydrosilanes such as Et₃SiH, Et₂SiH₂, and PhSiH₃ are used as a hydride source owing to the lower electronegativity of silicon (1.7) than that of hydrogen (2.1). These reagents cause the reduction of a carbonyl group, acetal, or benzylic ether in the presence of a Lewis acid or a Brønsted acid,⁴ and the hydrosilylation of unsaturated bonds catalyzed by a transition metal.⁵ (Me₃Si)₃SiH and PhSiH₃ are used as a hydrogen source in radical reactions.^{6,7} Recently, hydrosilanes have also been utilized in the catalytic functionalization of unactivated C-H bonds.^{8,9} On the other hand, silyl halides such as Me₃SiCl, Et₃SiCl, and *tert*-butyldimethylsilyl chloride (TBDMSCl) are used as silylation reagents for the protection of a hydroxy group and an amino group in the presence of a base.¹⁰ Although silyl halides also have the Lewis acidic property,¹¹ the typical silyl iodide, trimethylsilyl iodide (TMSI), has a particularly high reactivity owing to its Si-I bond consisting of a hard silicon atom and a soft iodine atom.¹² It is able to cleave inert C-O bonds of ethers, esters, and alcohols with the formation of a C-I bond and a Si-O bond.¹³ These properties of TMSI enable a variety of synthetically useful transformations, whereas the storage of TMSI requires special care owing to its lability. Recently, we have developed a silane-iodine catalytic system for the intramolecular hydroalkoxylation reaction of unactivated alkenes.¹⁴ The mechanistic study indicates that iodophenylsilane, PhSiH₂I, generated in situ from PhSiH₃ and I₂, acts as a possible actual catalytic species. Although the generation of silyl iodides from hydrosilanes such as polymethylhydrosiloxane (PHMS) and Et₃SiH by I₂ has been

reported, most of them are trialkylsilanes.¹⁵ Because PhSiH₂I has a distinctive structure possessing a hydrosilane (Si-H) moiety and a silyl iodide (Si-I) moiety in one molecule, we are interested in its reactivity. Although the preparation of PhSiH₂I has been reported, its reactivity remains unreported except in our report.^{14,16} During our continuing studies on the PhSiH₃-I₂ system, it was found that the deiodination of iodoether **1a** smoothly proceeds to provide cyclic ether **1b** (Scheme 1). To determine the reactivity of PhSiH₂I and explore the mechanism, different iodoethers were subjected to the deiodination reaction.¹⁷ Taking a cue from the mechanistic study, we found that a series of cascade reactions are caused by PhSiH₃-I₂ and PhSiH₃-NIS. Herein, we report these reactions together with our investigation of the deiodination reaction.

Our previous study¹⁴



Initial observation: this study



Scheme 1 Intramolecular hydroalkoxylation and deiodination catalysed by silane-iodine system.

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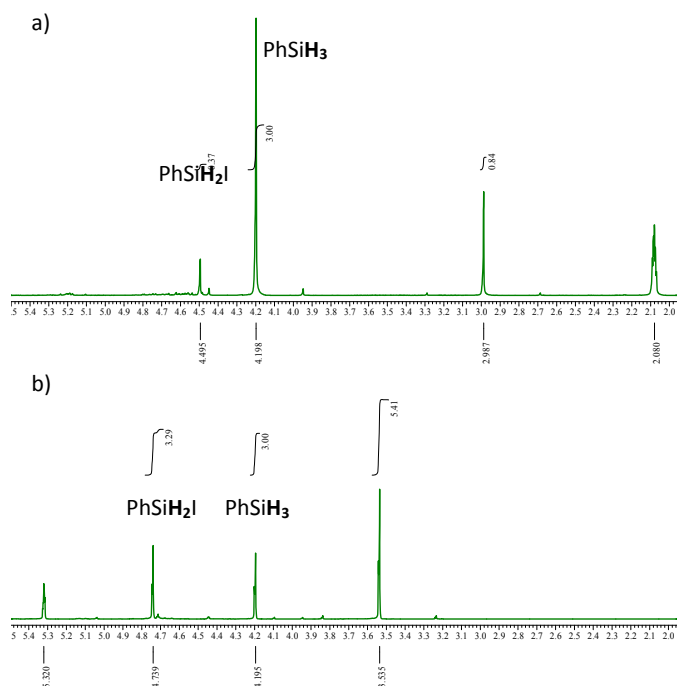
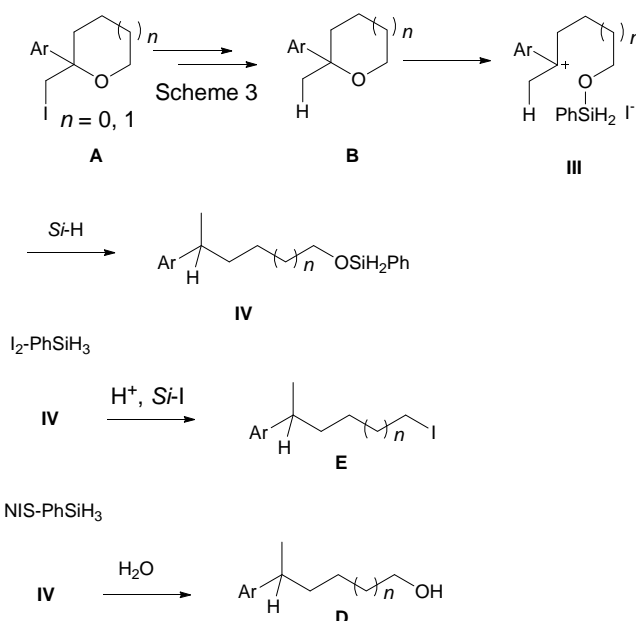


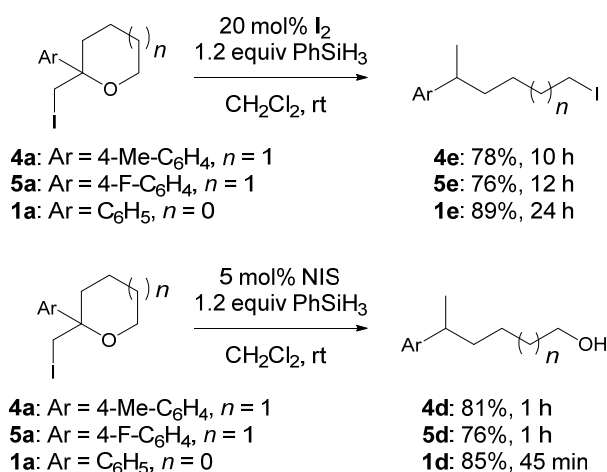
Figure 1 ^1H NMR spectra of the reaction mixture of PhSiH_3 and I_2 in toluene- d_6 (a) and that in CD_2Cl_2 (b), which were measured 30 min after mixing.

These results indicate that increasing the amount of PhSiH_2I enhanced the reaction and a high yield of acyclic iodide **2e** was consequently provided in CH_2Cl_2 . Acyclic iodide **2e** is presumably produced via reductive ring opening (**B** to **IV**) and subsequent iodination reaction (**IV** to **E**) after deiodination (**A** to **B**), as shown in Scheme 5.^{12,13d,18} Cyclic ether **2b** and acyclic alcohol **2d** as intermediates are detectable by TLC analysis. Although Panek *et al.* reported the reductive ring opening of aryl pyranosides using $\text{Sc}(\text{OTf})_3$ and Et_3SiH ,²⁰ it is interesting that similar reductive ring opening of the cyclic ethers efficiently occurs under PhSiH_2I -mediated conditions. Also note that it is not a stoichiometric amount but only a catalytic amount of I_2 that is required for the transformation from iodoether **2a** to acyclic iodide **2e**, which means that the iodine atom of **2e** originates from not only I_2 but also iodoether **2a**. 1 equiv of I_2 is released on the process of deiodinative ring opening of iodoether **2a** and PhSiH_2I is generated from the I_2 and PhSiH_3 (Scheme 3). As the results, the iodine atom of **2a** is reintroduced into acyclic iodide **2e**. Next, we treated iodoether **2a** with PhSiH_3 and NIS in CH_2Cl_2 (Scheme 4). Our previous study suggested that the reaction of PhSiH_3 and NIS also produces PhSiH_2I together with succinimide.¹⁴

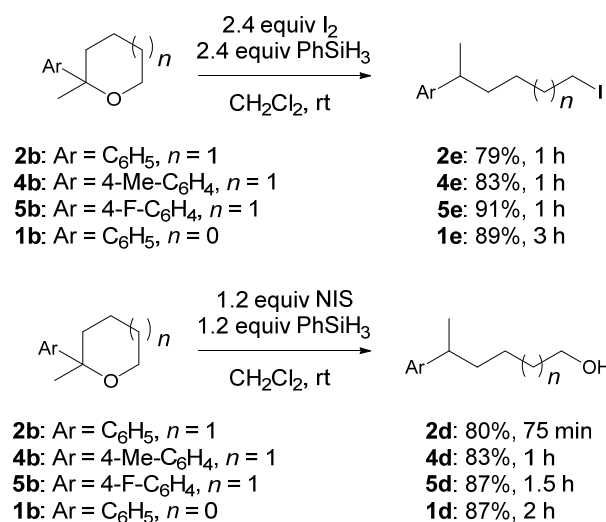


Scheme 5 Plausible reaction mechanism of the transformation from iodoether **A**.

A prolonged reaction time only resulted in the production of a small amount of acyclic iodide **2e**. While the PhSiH_3 - I_2 protocol provides acyclic iodide **2e**, the PhSiH_3 -NIS protocol gives acyclic alcohol **2d** from iodoether **2a**. The difference may originate from the existence of HI generated from the reaction of PhSiH_3 with I_2 , which could promote the iodination of acyclic alcohol **2d**. 4-Me- and 4-F-phenyl-substituted iodoethers **4a** and **5a** and 5-membered iodoether **1a** were treated with 20 mol% I_2 and 1.2 equiv PhSiH_3 and with 5 mol% NIS and 1.2 equiv PhSiH_3 (Scheme 6). All of the iodoethers afforded the corresponding acyclic iodides in high yields by the PhSiH_3 - I_2 protocol and afforded the corresponding acyclic alcohols by the PhSiH_3 -NIS protocol. The



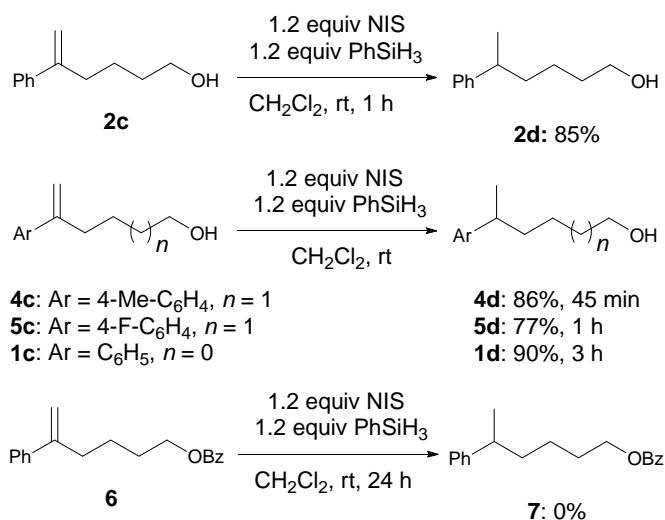
Scheme 6 Reductive ring opening of iodoethers **4a**, **5a**, and **1a**.

**Scheme 7** Reductive ring opening of cyclic ethers.

substituents on the benzene ring and the ring size of the cyclic ethers did not have a significant effect on the reaction times and yields.

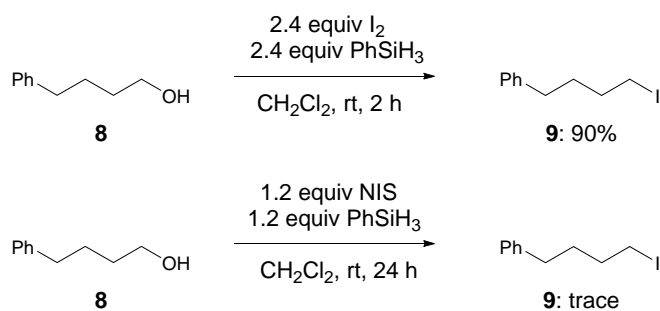
Because cyclic ether **B** is considered as an intermediate in the above cascade reactions, the reductive ring opening from cyclic ether **B** to acyclic alcohol **D** and acyclic iodide **E** is assumed to proceed according to the reaction pathway in Scheme 5. Although the combination of a catalytic amount of I₂ and a stoichiometric amount of PhSiH₃ resulted in no reaction, 2.4 equiv of I₂ and 2.4 equiv PhSiH₃ effectively caused the cascade reductive ring opening/iodination reaction of **2b** to provide the corresponding acyclic iodide **2e** in high yield (Scheme 7). Similarly, 1.2 equiv of NIS and 1.2 equiv of PhSiH₃ caused the reductive ring opening to selectively yield the corresponding acyclic alcohol **2d**. Cyclic ethers **4b**, **5b**, and **1b** also afforded the corresponding acyclic iodides by the treatment of I₂ and PhSiH₃ in high yields as well as the corresponding alcohols by the treatment of NIS and PhSiH₃.

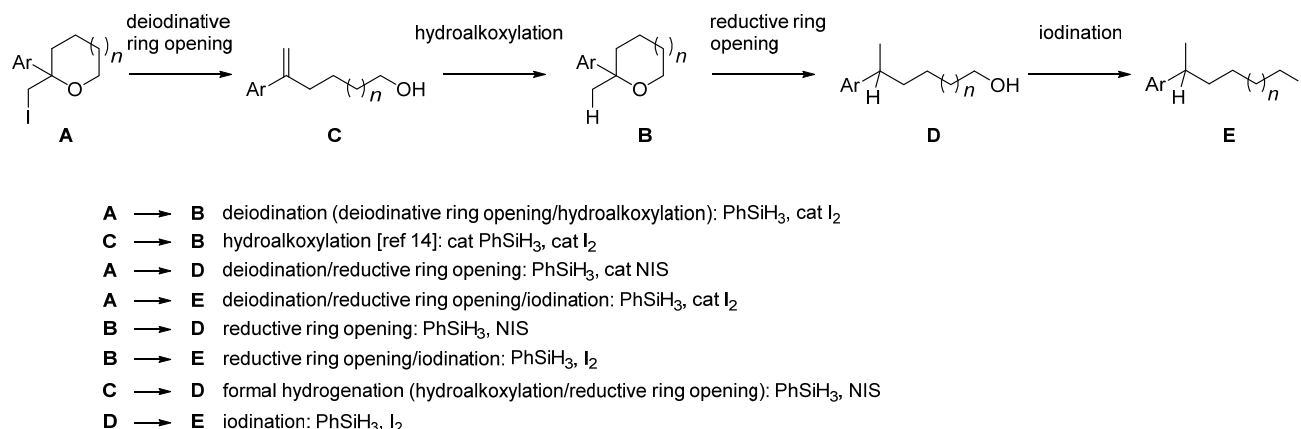
Hydroxy alkene **C** is also a putative intermediate of the cascade reaction from iodoether **A** to acyclic alcohol **D** (see Scheme 3 and 5). It is assumed that the cascade intramolecular hydroalkoxylation/reductive ring opening reaction of γ -hydroxy alkene **2c** occurred to provide saturated alcohol **2d**, which is a formal hydrogenation without hydrogen gas. On the basis of this assumption, γ -hydroxy alkene **2c** was treated with 1.2 equiv of NIS and 1.2 equiv of PhSiH₃ (Scheme 8). Thus, the saturated alcohol **2d** was obtained in high yield. 4-Me- and 4-F-phenyl-substituted alkenes **4c** and **5c** and alkene shorter by one carbon **1c** were smoothly reduced to the corresponding saturated alcohols, whereas benzoyl ester **6** did not afford the saturated alcohol **7** under the same conditions within 24 h.

**Scheme 8** Formal hydrogenation of phenyl-substituted olefins.

Finally, we examined the iodination of alcohol **8** employing the PhSiH₃-I₂ and PhSiH₃-NIS protocols (Scheme 9).^{13e,21} As expected from the results so far obtained, the iodination of **8** was efficiently caused by PhSiH₃ and I₂ to provide iodide **9** in high yield, while PhSiH₃ and NIS afforded a trace amount of iodide **9** even after 24 h.

As summarized in Scheme 10, PhSiH₃-I₂ and PhSiH₃-NIS generate highly reactive PhSiH₂I, which is able to mediate our previously reported intramolecular hydroalkoxylation as well as diverse transformations such as the deiodination of iodoethers, the reductive ring opening of iodoethers and cyclic ethers, and the formal hydrogenation of a γ -hydroxy phenyl-substituted alkene. The PhSiH₃-I₂ protocol causes the iodination of alcohols.

**Scheme 9** Reaction of alcohol **8** with PhSiH₃-I₂ and PhSiH₃-NIS.



Scheme 10. Summary of PhSiH₂I-mediated transformation.

Conclusions

The deiodination of iodoether **A** was rationalized by the deiodinative ring opening/intramolecular hydroalkoxylation mechanism mediated by PhSiH₂I. Stemming from the mechanistic study, we also found a series of PhSiH₂I-mediated reactions under PhSiH₃-I₂ and PhSiH₃-NIS protocols. Iodoether **A** and cyclic ether **B** as well as alcohol **D** are converted to acyclic iodide **E** under PhSiH₃-I₂ protocols, whereas iodoether **A**, cyclic ether **B**, hydroxy alkene **C** are converted to acyclic alcohol **D** under PhSiH₃-NIS protocols. These results indicate that PhSiH₂I acts as silyl iodide species having the properties of a Lewis acid and an iodide donor and as a hydrosilane species having the property of a hydride donor in these reactions. Further studies on the silane-iodine system are ongoing in our laboratory.

Experimental

General considerations

All reagents were obtained from commercial source and used without further purification. Reactions were carried out in a glass flask with a plastic cap. Column chromatography was performed on silica gel (Cica silica gel 60N). ¹H and ¹³C NMR were obtained for samples in CDCl₃ on a JEOL 400 MHz spectrometer at room temperature. ¹H NMR chemical shifts are reported in terms of chemical shift (δ, ppm) relative to the singlet at 7.26 ppm for chloroform. ¹³C NMR chemical shifts were fully decoupled and are reported in terms of chemical shift (δ, ppm) relative to the triplet at 77.0 ppm for CDCl₃.

Representative procedure

Deiodination of iodoether A. I₂ (1.4 mg, 5.6 μmol) and PhSiH₃ (34 μl, 0.28 mmol) were added to a solution of **2a** (56 mg, 0.19 mmol) in toluene (2 ml) at room temperature. After stirring for 30 min, the reaction mixture was quenched with sat. Na₂S₂O₃ and extracted with Et₂O (three times). The combined organic layer was washed with brine, dried over MgSO₄ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane/Et₂O = 100:1) to afford **2b** (27 mg, 82%) as colorless oil. Analytical data of **1b** and **2b** were consistent with reported data.¹²

2-Methyl-2-(4-methylphenyl)tetrahydrofuran (4b). Colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.29 (d, 2H, *J* = 8.0 Hz), 7.17 (d, 2H, *J* = 8.0 Hz), 3.74-3.67 (m, 1H), 3.47 (td, 1H, *J* = 11.6, 4.8 Hz), 2.35 (s, 3H), 2.28 (dt, 1H, *J* = 13.6, 3.2 Hz), 1.76-1.36 (m, 5H), 1.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 142.2, 136.0, 129.1, 126.0, 75.9, 62.7, 34.6, 32.9, 26.0, 21.0, 20.1; IR (neat, cm⁻¹): 2937; HRMS (ESI, *m/z*) Calcd. for C₁₃H₁₈NaO [M+Na]⁺: 213.1255, found 213.1259.

2-Methyl-2-(4-fluorophenyl)tetrahydrofuran (5b). Colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.40-7.34 (m, 2H), 7.06-7.01 (m, 2H), 3.75-3.69 (m, 1H), 3.45 (ddd, 1H, *J* = 11.6, 10.6, 3.2 Hz), 2.28-2.21 (m, 1H), 1.78-1.41 (m, 5H), 1.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 161.6 (d, *J* = 244.4 Hz), 141.1 (d, *J* = 2.8 Hz), 127.5 (d, *J* = 7.6 Hz), 115.0 (d, *J* = 21.0 Hz), 75.5, 62.6, 34.6, 32.5, 25.9, 20.0; IR (neat, cm⁻¹): 2939; HRMS (DART, *m/z*) Calcd. for C₁₂H₁₉FNO [M+NH₄]⁺: 212.1451, found 212.1476.

Tandem deiodination/reductive ring opening/iodination reaction from iodoether A to acyclic iodide E. I₂ (8.4 mg, 0.033 mmol) and PhSiH₃ (24 μl, 0.19 mmol) were added to a solution of **2a** (50 mg, 0.17 mmol) in CH₂Cl₂ (0.5 ml) at room temperature. After stirring 12 h, the reaction mixture was quenched with H₂O and extracted with Et₂O (three times). The combined organic layer was washed with brine, dried over MgSO₄ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane/Et₂O = 100:1) to afford **2e** (39 mg, 82%) as colorless oil.

(6-Iodohexan-2-yl)benzene (2e). Yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.31-7.27 (m, 2H), 7.20-7.16 (m, 3H), 3.13 (td, 2H, $J = 6.8, 2.0$ Hz), 2.67 (sext, 1H, $J = 6.8$ Hz), 1.84-1.76 (m, 2H), 1.61-1.53 (m, 2H), 1.43-1.24 (m, 2H), 1.24 (d, 2H, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 147.3, 128.3, 127.0, 126.0, 39.8, 37.2, 33.6, 28.6, 22.3, 6.9; IR (neat, cm^{-1}): 2957, 2929; HRMS (DART, m/z) Calcd. for $\text{C}_{12}\text{H}_{21}\text{IN}$ $[\text{M}+\text{NH}_4]^+$: 306.0719, found 306.0716.

1-(6-Iodohexan-2-yl)-4-methylbenzene (4e). yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.11-7.05 (m, 4H), 3.12 (td, 2H, $J = 7.2, 2.0$ Hz), 2.64 (sext, 1H, $J = 6.8$ Hz), 2.32 (s, 3H), 1.83-1.80 (m, 2H), 1.60-1.51 (m, 2H), 1.40-1.25 (m, 2H), 1.21 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 144.3, 135.3, 129.0, 126.8, 39.3, 37.2, 33.7, 28.7, 22.4, 21.0, 6.9; IR (neat, cm^{-1}): 2927; HRMS (DART, m/z) Calcd. for $\text{C}_{13}\text{H}_{23}\text{IN}$ $[\text{M}+\text{NH}_4]^+$: 320.0875, found 320.0873.

1-Fluoro-4-(6-iodohexane-2-yl)benzene (5e). Yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.14-7.10 (m, 2H), 6.99-6.95 (m, 2H), 3.13 (t, 2H, $J = 7.4$ Hz), 2.66 (sext, 1H, $J = 6.8$ Hz), 1.83-1.75 (m, 2H), 1.58-1.53 (m, 2H), 1.38-1.25 (m, 2H), 1.22 (d, 3H, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 161.2 (d, $J = 243.4$ Hz), 142.8 (d, $J = 2.8$ Hz), 128.1 (d, $J = 7.6$ Hz), 115.2 (d, $J = 21.0$), 39.1, 37.3, 33.5, 28.5, 22.4, 6.8; IR (neat, cm^{-1}): 2958; HRMS (DART, m/z) Calcd. for $\text{C}_{12}\text{H}_{20}\text{FIN}$ $[\text{M}+\text{NH}_4]^+$: 324.0624, found 324.0612.

(5-Iodopentan-2-yl)benzene (2e). Yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.32-7.28 (m, 2H), 7.21-7.17 (m, 3H), 3.13 (t, 2H, $J = 6.8$ Hz), 2.71 (sext, 1H, $J = 6.8$ Hz), 1.76-1.68 (m, 4H), 1.26 (d, 3H, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 146.8, 128.4, 126.9, 126.1, 39.2, 39.0, 31.6, 22.4, 7.1; IR (neat, cm^{-1}): 2958; HRMS (DART, m/z) Calcd. for $\text{C}_{11}\text{H}_{19}\text{IN}$ $[\text{M}+\text{NH}_4]^+$: 292.0562, found 292.0554.

Tandem deiodination/reductive ring opening reaction from iodoether A to acyclic alcohol D. After a solution of NIS (1.5 mg, 8.4 μmol) and PhSiH_3 (32 μl , 0.26 mmol) in CH_2Cl_2 (1.0 ml) was stirred for 30 min, a solution of **2a** (51 mg, 0.17 mmol) in CH_2Cl_2 (0.68 ml) was added at room temperature. The reaction mixture was stirred for 75 min, and then was quenched with H_2O and extracted with Et_2O (three times). The combined organic layer was washed with brine, dried over MgSO_4 and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane/ $\text{Et}_2\text{O} = 5:1$) to afford **2d** (27 mg, 92%) as colorless oil.

5-Phenylhexane-1-ol (2d). colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.31-7.26 (m, 2H), 7.19-7.16 (m, 3H), 3.59 (t, 2H, $J = 6.4$ Hz), 2.68 (sext, 1H, $J = 7.2$ Hz), 1.64-1.50 (m, 4H), 1.24 (s, 3H), 1.37-1.18 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 147.5, 128.3, 126.9, 125.8, 62.8, 39.9, 38.1, 32.8, 23.8, 22.3; IR (neat, cm^{-1}): 3333; HRMS (ESI, m/z) Calcd. for $\text{C}_{12}\text{H}_{18}\text{NaO}$: 201.1255 ($[\text{M}+\text{Na}]^+$), found 201.1263 ($[\text{M}+\text{Na}]^+$).

5-(4-Fluorophenyl)hexane-1-ol (5 d). Colorless oil; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.14$ -7.09 (m, 2H), 6.99-6.93 (m, 2H), 3.57 (t, 2H, $J = 6.4$ Hz), 2.67 (sext, 1H, $J = 6.8$ Hz), 1.59-1.46 (m, 4H), 1.34-1.16 (m, 2H), 1.21 (d, 3H, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 161.1$ (d, $J = 243.4$ Hz), 143.0 (d, $J = 2.8$ Hz), 128.1 (d, $J = 7.6$ Hz), 114.9 (d, $J = 21.0$), 62.8, 39.2, 38.2, 32.7, 23.7, 22.4; IR (neat, cm^{-1}): 3335; HRMS (DART, m/z) Calcd. for $\text{C}_{12}\text{H}_{21}\text{FNO}$ $[\text{M}+\text{NH}_4]^+$: 214.1608, found 214.1631.

4-Phenylpentan-1-ol (1d). colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.31-7.26 (m, 2H), 7.20-7.16 (m, 3H), 3.58 (t, 2H, $J = 6.4$

Hz), 2.70 (sext, 1H, $J = 7.2$ Hz), 1.68-1.62 (m, 2H), 1.58-1.37 (m, 2H), 1.26 (d, 3H, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 147.3, 128.3, 127.0, 126.0, 63.0, 39.8, 34.4, 31.0, 22.4; IR (neat, cm^{-1}): 3348; HRMS (ESI, m/z) Calcd. for $\text{C}_{11}\text{H}_{16}\text{NaO}$ $[\text{M}+\text{Na}]^+$: 187.1099, found 187.1111.

Reductive ring opening/iodination reaction from cyclic ether B to acyclic iodide E. I_2 (136 mg, 0.54 mmol) and PhSiH_3 (66 μl , 0.54 mmol) were added to a solution of **2b** (39 mg, 0.22 mmol) in CH_2Cl_2 (0.75 ml) at room temperature. After stirring for 1 h, the reaction mixture was quenched with H_2O and extracted with Et_2O (three times). The combined organic layer was washed with brine, dried over MgSO_4 and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane/ $\text{Et}_2\text{O} = 100:1$) to afford **2e** (51 mg, 78%) as colorless oil.

Tandem deiodination/reductive ring opening reaction from cyclic ether B to acyclic alcohol D. After a solution of NIS (46 mg, 0.26 mmol) and PhSiH_3 (32 μl , 0.26 mmol) in CH_2Cl_2 (0.5 ml) was stirred for 30 min, a solution of **2b** (38 mg, 0.22 mmol) in CH_2Cl_2 (0.22 ml) was added at room temperature. The reaction mixture was stirred for 75 min, and then was quenched with H_2O and extracted with Et_2O (three times). The combined organic layer was washed with brine, dried over MgSO_4 and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane/ $\text{Et}_2\text{O} = 5:1$) to afford **2d** (31 mg, 80%) as colorless oil.

Formal hydrogenation from hydroxy alkene C to acyclic alcohols D. After a solution of NIS (51 mg, 0.30 mmol) and PhSiH_3 (37 μl , 0.30 mmol) in CH_2Cl_2 (0.5 ml) was stirred for 30 min, a solution of **2c** (44 mg, 0.25 mmol) in CH_2Cl_2 (0.22 ml) was added at room temperature. The reaction mixture was stirred for 1 h, and then was quenched with H_2O and extracted with Et_2O (three times). The combined organic layer was washed with brine, dried over MgSO_4 and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane/ $\text{Et}_2\text{O} = 5:1$) to afford **2d** (38 mg, 85%) as colorless oil.

Iodination of 4-phenyl-1-butanol. A solution of I_2 (238 mg, 0.94 mmol) and PhSiH_3 (115 μl , 0.94 mmol) was stirred for 1.5 h, and **8** (59 mg, 0.39 mmol) was added to the mixture at room temperature. After stirring for 2 h, the reaction mixture was quenched with sat. NaHCO_3 and extracted with Et_2O (three times). The combined organic layer was washed with brine, dried over MgSO_4 and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane/ $\text{Et}_2\text{O} = 100:1$) to afford **9** (92 mg, 90%) as colorless oil.

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